FACTORS DETERMINING SELECTIVITIES IN THE [1,2]- AND [1,4]-WITTIG REARRANGEMENTS OF SILYL ALLYLIC ETHERS AND RELATED STUDIES

By

Luis M. Mori-Quiroz

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ABSTRACT

FACTORS DETERMINING SELECTIVITIES IN THE [1,2]- AND [1,4]-WITTIG REARRANGEMENTS OF SILYL ALLYLIC ETHERS AND RELATED STUDIES

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The [1,4]- and [1,2]-Wittig rearrangements of acyclic α-silyl and α,γ-disilyl allylic ethers have been studied. Structural and electronic modifications have been introduced to learn the effect that they produce in the [1,4]-/[1,2]-selectivity and diastereoselectivities in some cases. These acyclic substrates in general reacted sluggishly, and therefore most of these reactions show important limitations in term in efficiency and selectivities.

In a similar way, the [1,4]- and [1,2]-Wittig rearrangements of 2-silyl and 4-silyl 5,6-dihydropyrans have been explored, resulting in the discovery of an overall efficient isomerization to cyclopropylsilanes or silyl cyclopentenol structures. The [1,4]-/[1,2]-selectivity can be determined by proper structural and/or electronic modifications at the migrating group or at the allylic portion. The silyl group has been determinant in allowing clean isomerization, presumably due to an electronic contribution, but its steric demand also played a key role in determining the [1,4]-/[1,2]-selectivity and diastereoselectivities of these isomerizations.

The rearrangement of cyclic ethers has been expanded to more complex (bisallylic) substrates, with similar efficiency and selectivities, but larger or shorter rings showed lower reactivity, selectivity and overall efficiency. Comparison with non-silylated analogues provides a better picture of the contribution of silyl groups in these isomerizations.

To my family: Cristina, Luis and José

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LIST OF SYMBOLS AND ABBREVIATIONS

$[\alpha]$	specific rotation
Ac	acetate
AcOH	acetic acid
APCI	atmospheric-pressure chemical ionization
Ar	aromatic
BBN	borabicyclononane
$BF_3 \bullet OEt_2$	boron trifluoride diethyl ether
Bn	benzyl
Boc	*tert*-butoxycarbonyl
Bz	benzoyl
CI	chemical ionization
d	doublet
DBU	1,8-diazabicycloundec-7-ene
DCM	dichloromethane
DMAP	4-diaminopyridine
DMF	N,N-dimethylformamide
DMP	Dess-Martin periodinane
ee	enantiomeric excess
EI	electron ionization
ESI	electrospray ionization
EtOH	ethanol

Et_3N	triethylamine
Et_2O	diethyl ether
EtOAc	ethyl acetate
equiv	equivalents
g	gram(s)
h	hour(s)
HMPA	hexamethylphosphoramide
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectrometry
Hz	hertz
i-Pr	isopropyl
IR	infrared
J	NMR coupling constant
LDA	lithium diisopropylamide
LiHMDS	lithium bis(trimethylsilyl)amide
m	multiplet
m-CPBA	3-chloroperbenzoic acid
min	minute
mg	milligram
mL	milliliter
mp	melting point
MHz	megahertz

M	molar
Me	methyl
MeCN	acetonitrile
MeLi	methyllithium
MeO	methoxy
MS	mass spectrometry
m/z	mass to charge ratio
n-BuLi	*n*-butyllithium
n-Pr	*n*-propyl
NaOH	sodium hydroxide
Naph	naphtyl
NMR	Nuclear Magnetic Resonance
NOE	nuclear Overhauser effect
p-TSA	*para* toluene sulfonic acid
PCC	pyridinium chlorochromate
Ph	phenyl
PrLi	propyllithium
q	quartet
RCM	ring-closing metathesis
s	singlet
sat	saturated
sec-BuLi	*sec*-butyllithium
$SiEt_3$	triethylsilyl

$SiMe_2Ph$	phenyldimethylsilyl
$SiMePh_2$	diphenylmethylsilyl
S_N2	bimolecular nucleophilic substitution
$SiPh_3$	triphenylsilyl
rt	room temperature
t	triplet
t-BuLi	*tert*-butyllithium
t-BuOK	potassium *tert*-butoxide
TBAF	tetrabutylammonium fluoride
TBDPS	*tert*-butyldiphenylsilyl
TBS	*t*-butyldimethylsilyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography
TMEDA	tetramethylethylenediamine
TMS	trimethylsilyl
TMSLi	trimethylsilyllithium
TMSCl	trimethylsilylchloride
TMSOTf	trimethylsilyl trifluoromethane sulfonate
TS	transition state
μL	microliter

LIST OF SCHEMES

CHAPTER 1

INTRODUCTION

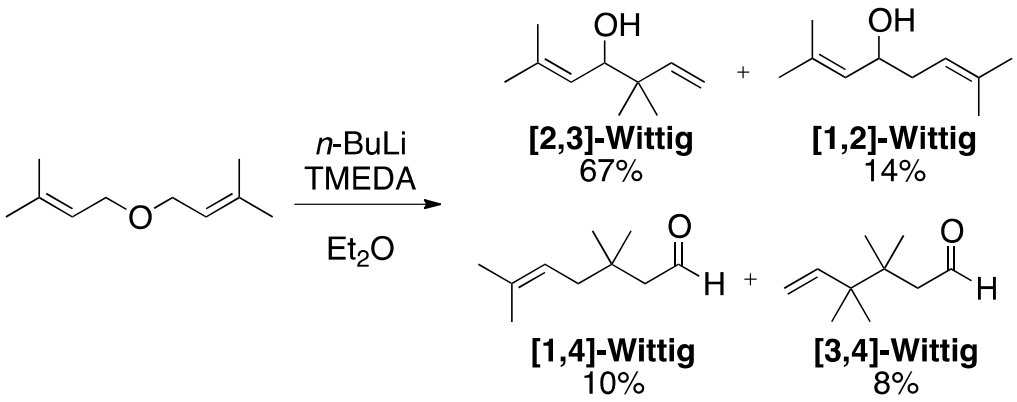
1.1 Background

Rearrangement reactions involve the reorganization of bonds within a molecule to produce structural isomers. These changes in atom connectivity are attractive processes because they can allow the predictable, selective and efficient formation of more complex *isomeric* molecules from simples ones. The migration of bonds can also change the oxidation state of some atoms, producing different functional groups. In addition, they are attractive from the standpoint of atom economy[1] because all the atoms from the reactant are present in the product. However, the use of catalysts, activators, or initiators can diminish the atom economy of a rearrangement, especially when they are used in stoichiometric or higher quantities.

Some of the most representative, well-studied and synthetically useful molecular isomerizations are classified as *sigmatropic rearrangements*.[2] The term *sigmatropic* was originally associated with concerted processes, but it is currently used in a more general sense to refer to the migration of a σ-bond from one part of the molecule to another. Depending on the extent of the σ-bond migration, sigmatropic rearrangements are described by an order term: [*i*,*j*], where *i* and *j* refer to number of bonds separating the newly bonded atoms with respect to the cleaved bond. Some important sigmatropic rearrangements available to organic chemists, are concerted [3,3]-shifts, such as the Claisen rearrangement[3] which isomerizes allylvinyl ethers and their

derivatives;[4] and the Cope rearrangement,[5] an isomerization of 1,5-dienes (and oxy-[6] or aza-Cope[7] variations as well).

Sigmatropic rearrangements of ethers, strictly speaking, the rearrangement of carbanionic ethers – Wittig rearrangements – are of particular interest in the sense that, depending on the nature and complexity of the reactant ether, multiple migrations are possible. In fact, the rearrangement of bis-(γ,γ-dimethyl)diallylether can follow up to four different pathways: [1,2]-, [2,3]-, [1,4]- and [3,4]-shifts (Scheme 1),[8] each of which leads to structurally different products.



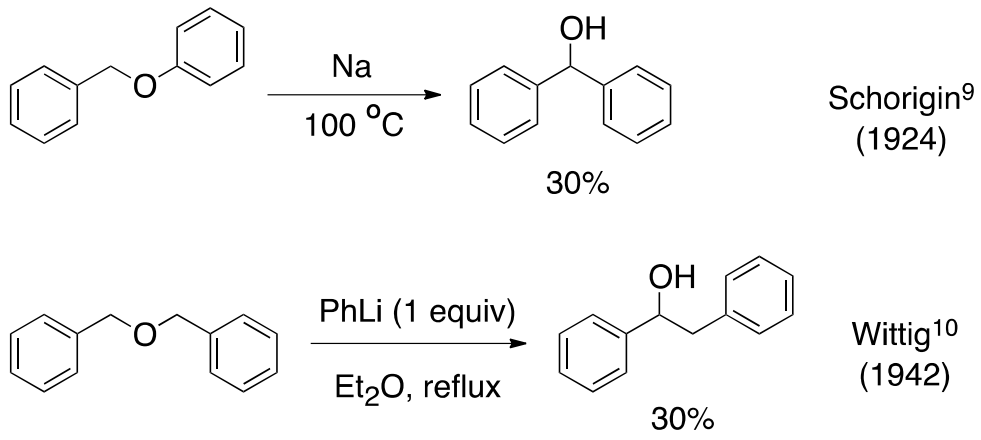
Scheme 1. All possible Wittig rearrangement pathways.

In the following paragraphs the main features of the [1,2]-, [2,3]- and [1,4]-Wittig rearrangement pathways will be described, with emphasis on the mechanistic aspects of these isomerizations. The utility of these reactions in building more complex molecules will also be highlighted.

1.2 The [1,2]-Wittig Rearrangement

1.2.1 Discovery

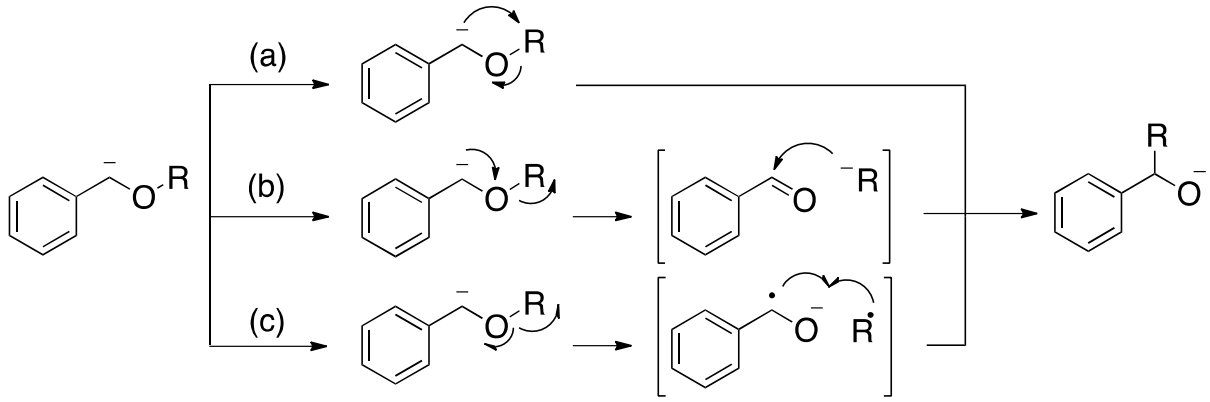
The earliest report describing the isomerization of ethers was disclosed by Paul Schorigin in 1924.[9] In his studies Schorigin described the rearrangement of benzyl aryl ethers to the corresponding carbinols in the presence of sodium metal. These examples represent formal [1,2]-aryl shifts (Scheme 2). Several years later Georg Wittig and Lisa Löhmann reported the isomerization of benzyl ethers to the corresponding carbinols (Scheme 2) which constitutes the first examples involving [1,2]-alkyl shifts.[10] Such a remarkable transformation, nowadays known as the [1,2]-Wittig rearrangement, involves the metalation at the benzylic position by sodium or phenyllithium; the resulting carbanion undergoes cleavage of a C-O bond and formation of a C-C bond. The driving force for the isomerization is the transfer of a negative formal charge from carbon to oxygen. This isomerization is related to the [1,2]-migrations of metalated ammonium salts, described by Stevens for the first time in 1928.[11]



Scheme 2. First examples of [1,2]-Wittig rearrangements.

1.2.2 Mechanistic studies of the [1,2]-Wittig rearrangement

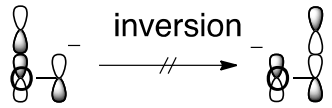
Three possible scenarios were proposed to account for the mechanism of the [1,2]-Wittig rearrangement of benzylic carbanion **I** (Scheme 3): 1) an intramolecular displacement in which the benzylic carbanion attacks the R group (pathway a) and directly produces alkoxide **II**,[12] 2) an elimination mechanism leading to benzaldehyde and ejection of carbanion $^{-}$R which attacks the newly formed carbonyl (pathway b),[13] and 3) homolytic cleavage of the C-O bond followed by recombination of the radical / radical-anion pair (pathway c).[14]



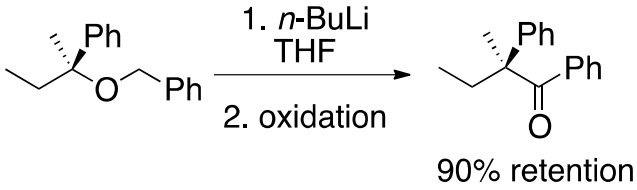
Scheme 3. Proposed mechanisms for the [1,2]-Wittig rearrangement (the positive counterion was omitted for clarity).

The development of Woodward and Hoffman's orbital symmetry rules[15] and Fukui's frontier orbital theory[16] provided a good basis to predict and better interpret experimental results relevant to the operating mechanism of the [1,2]-Wittig rearrangement. In that sense, orbital symmetry considerations argued against a concerted process (pathway a, Scheme 3), since such trajectory would imply a geometrically impossible [1,2]- *antarafacial* migration (Scheme 4),

with concomitant inversion of configuration at the migrating carbon. Schöllkopf showed that the rearrangement of optically active ethers underwent [1,2]-Wittig rearrangement with a high degree of retention of stereochemistry at the migrating center (Scheme 5),[13a, b, 17] thus ruling out a concerted process.



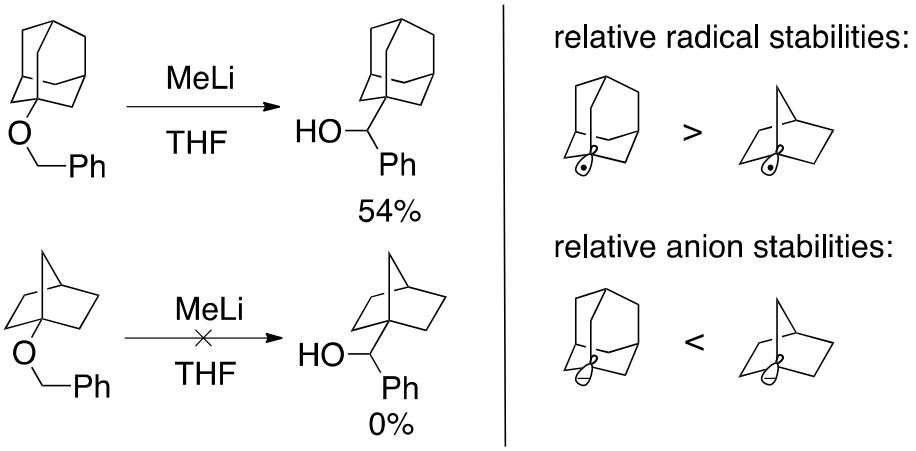
Scheme 4. Geometrically difficult, orbital symmetry-allowed [1,2]-migration.



Scheme 5. Retention of stereochemistry at the migrating carbon.

The observed retention of stereochemistry at the migrating carbon during [1,2]-Wittig migrations supported a stepwise mechanism, and initially this was interpreted as support for an elimination mechanism which involves heterolytic C-O cleavage (pathway b, Scheme 3).[13a, b] The isolation of *p*-nitrotoluene in the rearrangement of *p*-nitrobenzyl ethers was also regarded as evidence.[18] However, the higher migrating aptitude of tertiary alkyl groups with respect to secondary and primary alkyl was not in agreement with such mechanism.[14] Primary alkyl groups with vicinal hydrogen atoms with respect to the migrating carbon, and secondary alkyl to a lesser extent, underwent significant β-elimination.[10, 14, 19] The observed trend indirectly suggested the intermediacy of radicals as the migrating group species. In favor of a radical

mechanism (pathway c, Scheme 3) and against the formation of a migrating carbanion was the following observation: 1-adamantyl benzyl ether underwent [1,2]-Wittig rearrangement but 1-norbornyl benzyl ether did not (Scheme 6).[14, 20] Since the stability of 1-adamantyl radical is higher than that of the more strained 1-norbornyl radical,[21] and the corresponding lithium anions have inverse stability[22] therefore it is expected that a homolytic C-O cleavage takes place prior to recombination in the [1,2]-Wittig rearrangements.

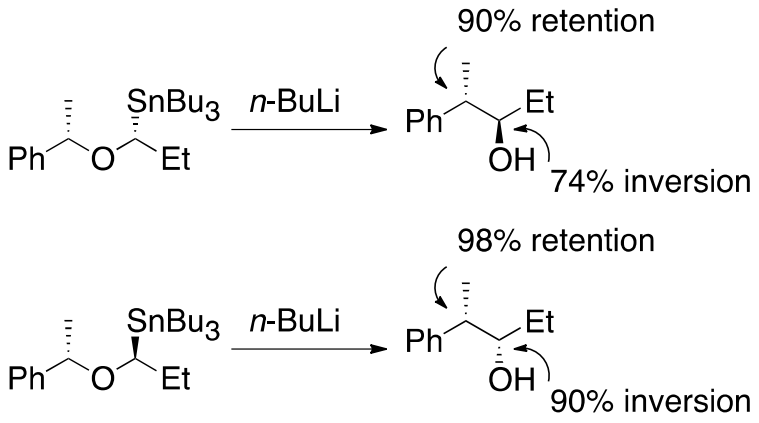


Scheme 6. Correspondence between radical vs anionic stability and ability to undergo rearrangement.

The high level of retention of stereochemistry at the migrating center implies that recombination of the radical pair is faster than planarization of the enantiomeric migrating radical. This has been rationalized as the cleavage and recombination taking place quickly within a "solvent cage". Evidence for a fleeting life of these radicals has been gathered by using a radical clock: The rearrangement of cyclopropylmethyl benzyl ether undergoes [1,2]-Wittig rearrangement without isomerization of the cyclopropylmethyl group.[13c] Since recombination of the radical /

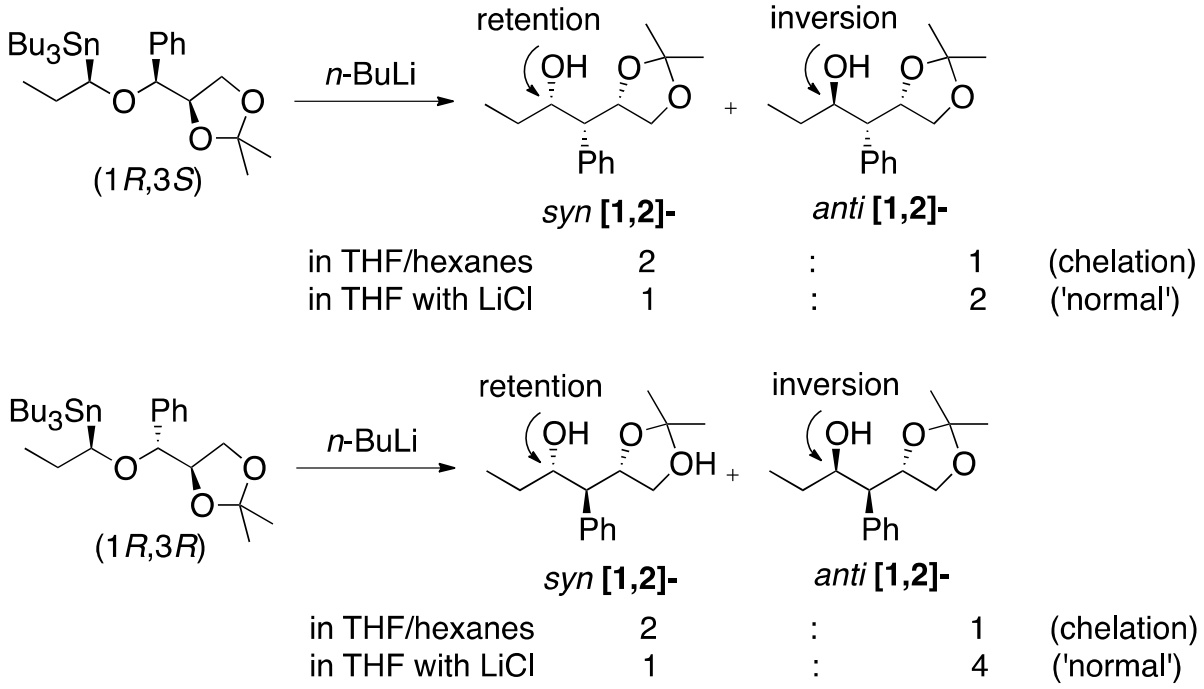
radical anion pair is faster than ring opening it can be inferred that rearrangement is faster than 9.4×10^7 s^{-1}.[23] Further support comes from experiments involving an inverse approach: The rearrangement of benzhydryl 5-hexenyl ether affords the expected [1,2]-Wittig product without isomerization of the 5-hexenyl portion,[24] which is consistent with a faster rate of rearrangement versus cyclization of the migrating 5-hexenyl radical. Importantly, recreation of the "intermolecular" portion of the [1,2]-Wittig, that is, the recombination of radicals that escaped the "solvent cage" after homolysis, has also been studied via reaction of benzophenone ketyl in presence of 5-hexenyl iodide.[24]

The stereochemical course at the lithium-bearing carbon in acyclic systems has also been studied by Nakai and coworkers,[25] and their results are in agreement with the observations made by the groups of Cohen[26] and Brückner[27] in cyclic systems. Optically active, diastereomeric α-alkoxy stannanes were independently metalated via tin-lithium exchange and underwent rearrangement to the corresponding carbinols. Analysis of these pairs of enantiomers revealed inversion of configuration at the lithium-bearing carbon. In both cases the level of retention of stereochemistry at the migrating carbon was higher than the level of inversion at the carbanion terminus. Interestingly, the level of retention/inversion was higher in one diastereomer, suggesting a significant degree of mutual recognition of the enantiomeric radicals during recombination.[25]



Scheme 7. Stereochemical course at the lithium-bearing carbon in the [1,2]-Wittig shift.

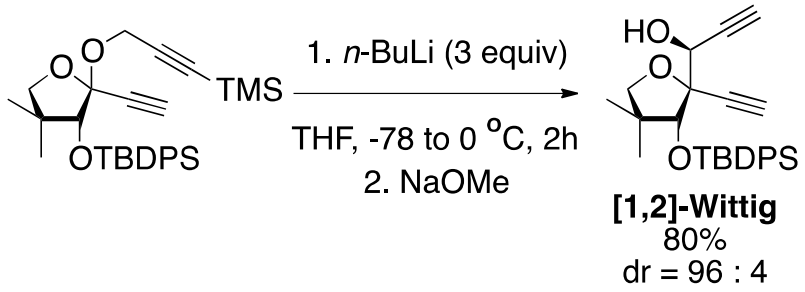
It is important to point out that the degree of inversion of stereochemistry at the lithium bearing carbon is susceptible to chelation by surrounding heteroatoms, [28] as demonstrated by Maleczka and Geng with diastereomeric stannyl ethers shown in Scheme 8.[29] Under conditions that maximize chelation, the expected inversion of configuration at the carbanionic center, generated via Sn/Li exchange, was reversed. Interestingly, and in agreement with observations of Nakai, [25] the relative stereochemistry of the migrating and lithium bearing carbon atoms in the starting ether showed different diastereoselectivity. [29] These studies show in some cases it is possible to manipulate the stereochemical outcome taking advantage of the properties of a reacting molecule.



Scheme 8. 'Chelation-controlled' and 'normal' stereochemical outcome in the [1,2]-Wittig rearrangement of stereodefined carbanions generated by Sn/Li exchange.

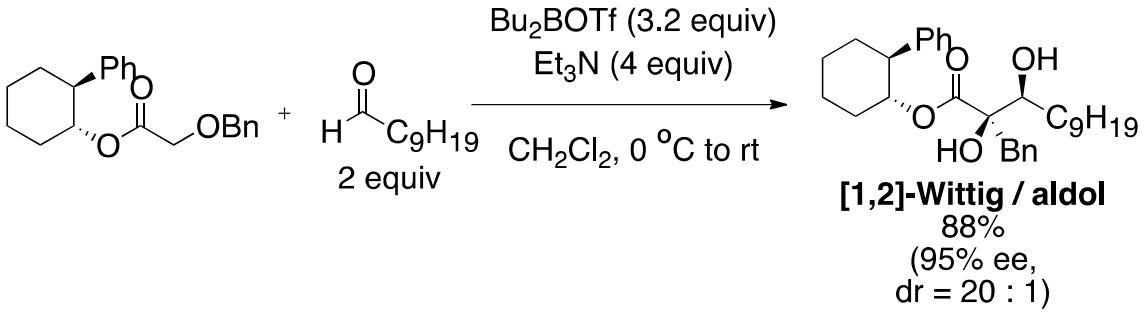
1.2.3 Representative examples of synthetically useful [1,2]-Wittig rearrangements

The substrate scope of the [1,2]-Wittig rearrangement is somewhat limited due to the requirement for radical stabilization of the migrating fragments. [25b] Another limitation is related to the method to generate an α-carbanionic ether, which does not always tolerate sensitive functionalities. However, there are several examples of highly efficient and stereoselective [1,2]-Wittig migrations. For example, Nakai *et al* took advantage of the inherent chirality of sugars and developed a highly stereocontrolled [1,2]-Wittig rearrangement of acetal systems (Scheme 9).[30] The utility of this technology[30b] has been highlighted in the total synthesis of zaragozic acid C. [30c]



Scheme 9. Stereocontrolloled [1,2]-Wittig rearrangement of glycosidic acetals.

The need for sufficiently acidic hydrogens can be met by using α-carbanion stabilizing groups, such as carbonyl groups.[31] Recently, Wolfe *et al.* employed esters[32] bearing a chiral auxiliary[32b, c] to promote a highly efficient sequence of [1,2]-Wittig rearrangement / aldol reaction (Scheme 10). Of special importance is the use of a Lewis acid to facilitate enolization with a mild base, triethylamine. Excellent diastereoselectivity and enantiocontrol was obtained with the optimum chiral auxiliary.



Scheme 10. Asymmetric, Lewis acid mediated [1,2]-Wittig rearrangement / aldol reaction.

1.3 The [2,3]-Wittig rearrangement

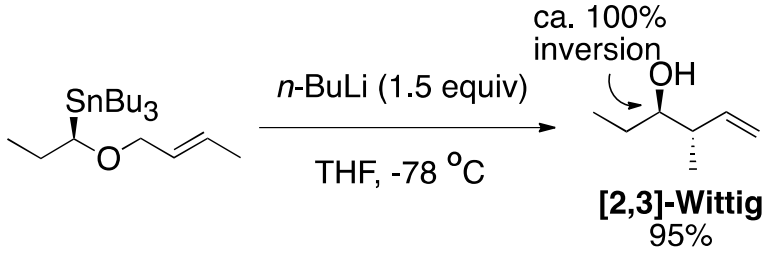
1.3.1 General characteristics

The [2,3]-Wittig rearrangement[19, 33] constitutes a migration pathway of allylic ethers metalated at the non-allylic position. Contrary to the [1,2]-pathway, the [2,3]-manifold is allowed by orbital symmetry according to the Woodward-Hoffmann rules,[16] and proceeds through a concerted mechanism involving a highly ordered 5-center, 6-electron transition state.[33] It constitutes the most developed and synthetically useful Wittig rearrangement pathway to date, and belongs to a greater family of concerted [2,3]-sigmatropic rearrangements that include the isomerization of allylic ylides such as *N*-oxides[34], ammonium salts,[35] and sulfonium salts,[36] and neutral species such as allylic sulfoxides.[37] Attractive characteristics of the [2,3]-Wittig rearrangement from a synthetic point of view include the ability to transfer chirality, create adjacent stereocenters with diastereo and/or enantiocontrol, and the formation of stereodefined olefins. In all ethers capable of [2,3]-Wittig rearrangement the [1,2]-shift is an inherently higher energy competitive pathway and therefore it is usually minimized at low temperatures. In some cases though the [1,2]-Wittig can effectively surpass the concerted [2,3]-pathway.

1.3.2 Stereochemical course at the lithium-bearing carbon

A common feature between the [1,2]- the [2,3]-Wittig rearrangements is the stereochemical course at the lithium-bearing carbon. Cohen,[38] Brückner[39] and Nakai[40] have studied the [2,3]-Wittig rearrangement of stereodefined lithiated ethers in detail and demonstrated that, like the [1,2]-pathway, the [2,3]-Wittig proceeds via inversion of configuration at the carbanion. In

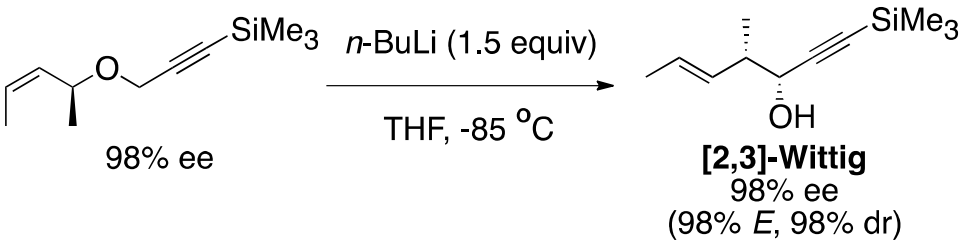
Nakai's approach, for example, an optically active α-allyloxy stannane underwent tin-lithium exchange with *n*-butyllithium followed by [2,3]-migration in excellent yield, complete diastereoselectivity and inversion of stereochemistry at the initially metalated carbon (Scheme 9).



Scheme 11. Stereochemical course at the carbanion terminus in the [2,3]-Wittig rearrangement.

1.3.3 Transfer of chirality

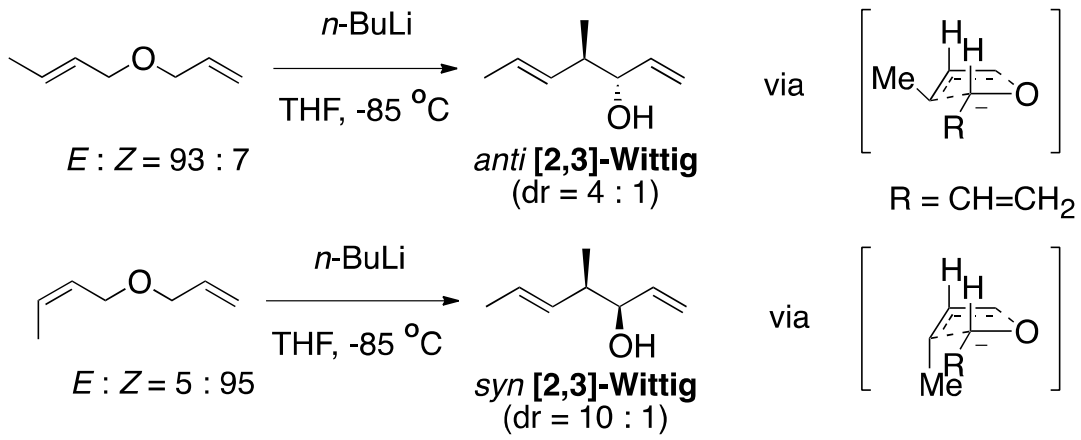
An important characteristic of the [2,3]-Wittig rearrangement is that the migration takes place across a conjugated system or, in other words, the migration occurs with transposition of the allylic portion. Were there a stereocenter at the α-allylic position, the chiral information is destroyed at this carbon atom due to the change in hybridization from sp^3 to sp^2, but at the same time it is transferred to a new chiral center in the product with high fidelity. In the example shown in Scheme 12, an optically active allylic propargylic alcohol (98% ee) rearranges via the [2,3]-sigmatropic shift to virtually form a single diastereomer with the same degree of enantiomeric purity (98% ee).[40b] This property has been coined by Nakai as 'asymmetric transmission'.



Scheme 12. Transfer of chirality in the [2,3]-Wittig rearrangement.

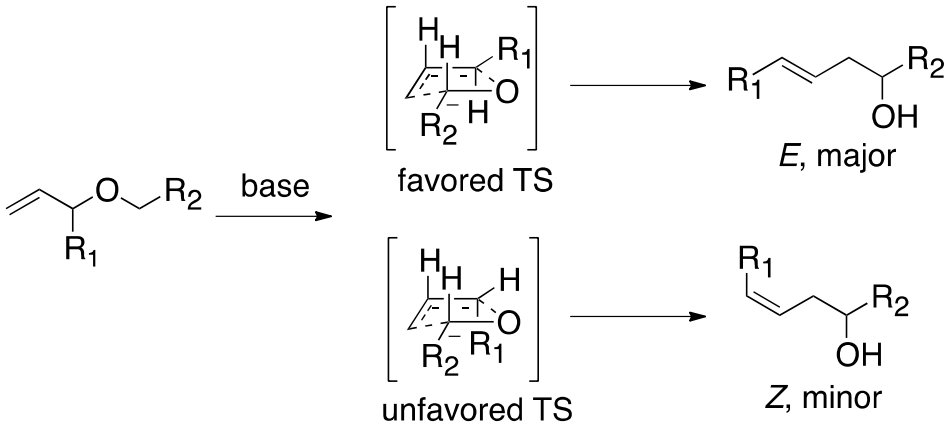
1.3.4 Stereoselectivity of the [2,3]-Wittig rearrangement

The creation of adjacent stereocenters is possible in the rearrangement of allylic ethers substituted at the terminal position. A good correspondence between the geometry of the initial olefin and the relative stereochemistry of the product is usually observed.[41] As shown in Scheme 13, *E*-crotyl allyl ether favors the *anti* [2,3]-Wittig whereas the isomeric *Z*-crotyl allyl ether predominantly gives the *syn* [2,3]-Wittig product. The diastereoselection, which is primarily determined by the geometry of the starting olefin, has been rationalized by transition state models based on 'folded envelope' conformations of a cyclopentane ring.[41b, 42] Although the degree of diastereoselectivity strongly depends on the nature of the R substituent (which is proposed to take a pseudo equatorial position, Scheme 11), these models allows the practitioner to predict the stereochemical outcome of the [2,3]-Wittig rearrangement.



Scheme 13. Correspondence between olefin geometry and diastereoselectivity of the [2,3]-Wittig rearrangement.

Another stereochemical feature of the [2,3]-Wittig rearrangement of ethers derived from secondary allylic alcohols (α-substituent at the allylic fragment) is the generation of internal olefins. In general, the [2,3]-Wittig pathway favors the formation of *E* olefins. Scheme 12 depicts two possible transition states for the rearrangement of an allylic ether substituted at the α-position.[42] The favored conformation, in which most substituents (R_1 and R_2) are positioned in pseudo equatorial orientations, clearly leads to the *E* olefin product. The *Z* olefin would be generated from the unfavored conformation in which R_1 takes a more hindered, pseudo axial orientation involving a 1,3-diaxial interaction. Once again it is important to emphasize the role of the R_2 substituent in determining the degree of geometrical diastereoselection.[33d]



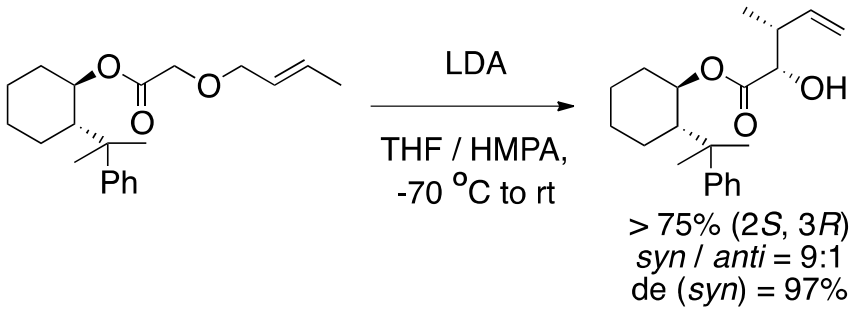
Scheme 14. Transition state models depicting the preference for *E*-geometry.

An important exception to the preference for *E* olefin formation is the 'Wittig-Still' modification[43] that involves the rearrangement of stannylmethyl ethers. In this particular case the highly unstable alkoxymethyl anion is generated via tin-lithium exchange and undergoes rearrangement to give predominantly the *Z* olefin product. However, it has been shown that in some cases this preference is solvent dependent.[44] On the other hand, experimental evidence indicates that the rearrangement of these methanides, generated via reduction of the corresponding sulfides, is independent of the metal cation.[45]

1.3.5 Other strategies for the stereoselective [2,3]-Wittig rearrangement of ethers

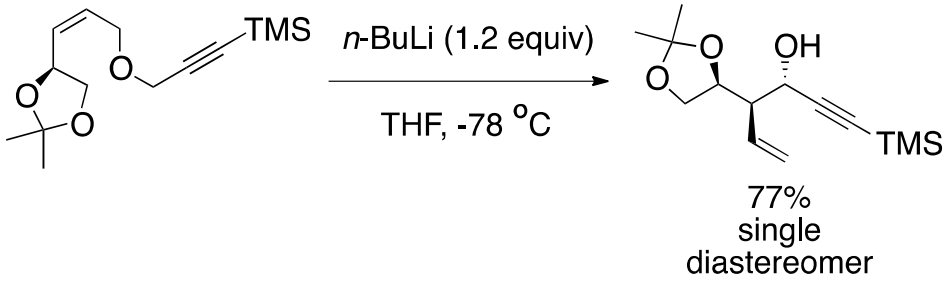
In complementary approaches to the transfer of chirality described above (Schemes 11 and 12), several workers have attempted to induce stereoselective [2,3]-migrations by introducing remote chirality, that is, a stereogenic center external to the sigmatropic framework. These stereocenters can be located near the latent carbanion center or proximal to the allylic fragment. For instance, Nakai and coworkers have studied the rearrangement of α-allyloxy esters of a chiral auxiliary

derived from (–)-menthol (Scheme 15).[46] In addition to the good diastereoselection (*syn* vs. *anti*), good enantioselectivity was observed. This case also exemplifies an exception to the correspondence between olefin geometry and diastereomeric preference of the product (Scheme 13). It has been consistently observed that α-allyloxy enolates follow an inverse trend[42, 47] whereas *E* olefins lead to *syn* diastereoselection.



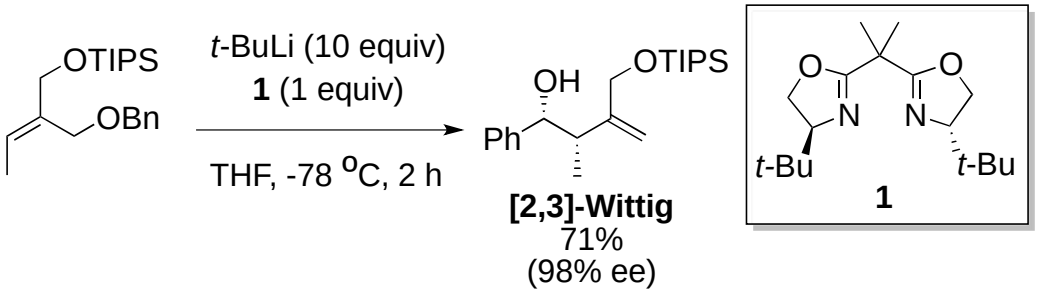
Scheme 15. Asymmetric induction by an intramolecular chiral auxiliary.

In another remarkable example, a chiral center proximal to the allylic framework and 5-bonds away from the carbanion center, directed the [2,3]-shift with complete diastereo and enantiocontrol to give a single product (Scheme 16).[48] The absence of [1,2]-Wittig products and the high diastereoselectivity observed might be consequence of coordination of the protected diol oxygen atoms to the lithium cation during rearrangement.



Scheme 16. Asymmetric induction by remote chirality.

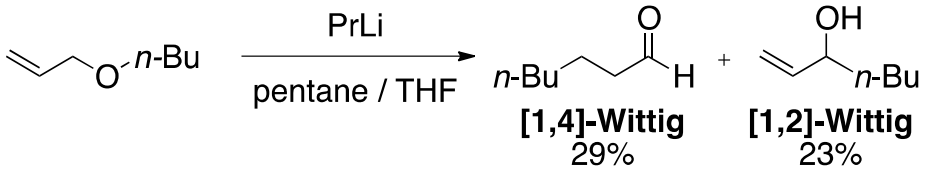
Perhaps the most attractive methodology for the enantioselective generation of adjacent chiral centers via [2,3]-Wittig rearrangements is that starting from racemic ethers which are deprotonated by chiral bases[49] or by achiral bases with a chiral ligand, [50] such as sparteine. For example, Maezaki *et al* employed a chiral bis-oxazoline ligand and excess *tert*-butyllithium for the enantioselective deprotonation of ethers (verified with deuterated substrates) followed by rearrangement to give homoallylic alcohols with excellent enantiomeric excess (Scheme 16).[51]



Scheme 17. Asymmetric induction by chiral ligand / achiral base.

1.4 The [1,4]-Wittig Rearrangement

The earliest report of a [1,4]-Wittig rearrangement dates back to 1969 when Felkin and Tambute reported the isomerization of unactivated alkyl allyl ethers (Scheme 18) to the corresponding aldehydes or ketones.[52] In addition to these carbonyl compounds, the [1,2]-Wittig products were also obtained, whose 'yields ranges from 7% to 33%'. [52] Although the authors provide limited information regarding yields and product ratios, it is clear that modest selectivity and low overall efficiency of the rearrangements are characteristics of these cases.

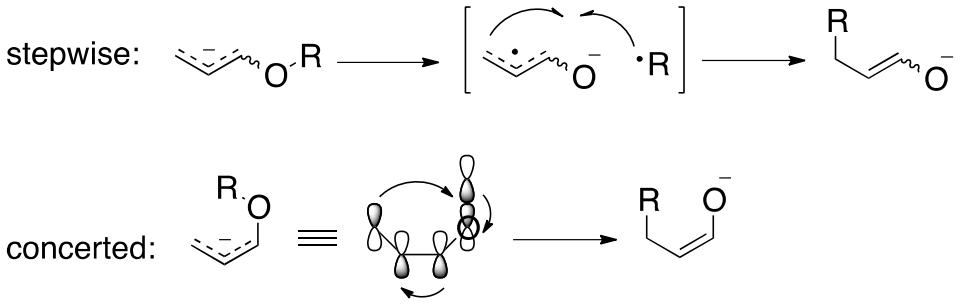


Scheme 18. One of the first [1,4]-Wittig rearrangements of ethers.

In contrast to the [2,3]-Wittig pathway, which also involves an allylic framework, the [1,4]-Wittig shift proceeds via an allylic anion that undergoes rearrangement to the corresponding enolate. Regular workup procedure affords the corresponding carbonyl compounds. Thus, the intermediacy of an enolate is a unique attribute of the [1,4]-Wittig pathway that has not been significantly exploited, even though it is a characteristic that clearly distinguished it from the alkoxide-forming [1,2]- and [2,3]-Wittig pathways.

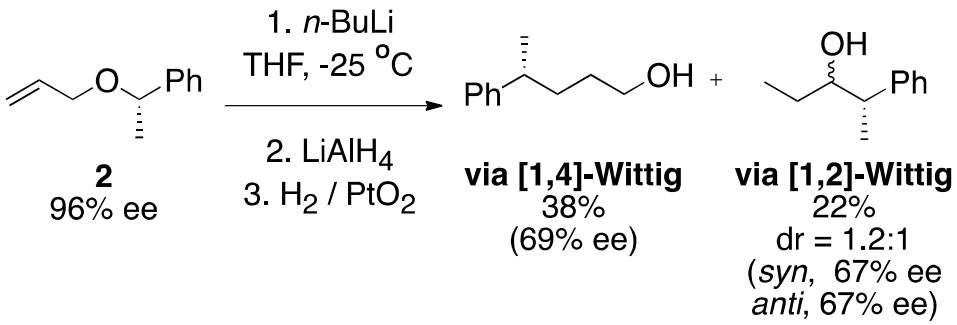
1.4.1 Mechanistic considerations of the [1,4]-Wittig pathway

The [1,4]-Wittig rearrangement can take place via two well-defined reaction pathways that resemble those of the [1,2]- and [2,3]-Wittig shifts. A first scenario involves a stepwise mechanism, similar to the inherently competitive [1,2]-shift, via the homolytic cleavage of the C-O bond, followed by recombination of the radical / radical anion fragments.[52] However, contrary to the [1,2]-shift, a concerted [1,4]-pathway is allowed by orbital symmetry,[33d, 53] according the Woodward-Hoffmann rules (Scheme 19).[15] It is important to point out that whereas both *cisoid* or *transoid* conformations are compatible with a stepwise process, a concerted mechanism very likely proceeds *only* via a *cisoid* conformation (Scheme 19).



Scheme 19. Possible mechanisms for the [1,4]-Wittig rearrangement.

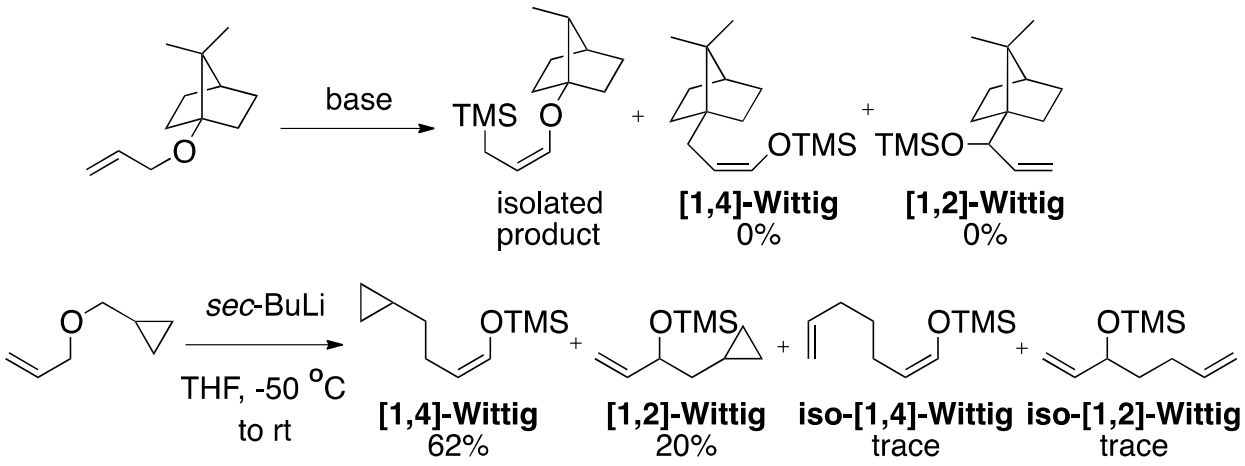
Early mechanistic studies showed that the [1,4]-Wittig product was obtained as a geometrically pure enolate.[54a] The stereochemical course of the [1,4]-shift has been studied: Rearrangement of optically pure ether **2** afforded the [1,4]- and [1,2]-Wittig products with retention of stereochemistry at the migrating carbon. A similar extent of racemization in both [1,4]- and [1,2]-pathways (~30%) was interpreted by the authors as a strong evidence in favor of an stepwise, radical / radical anion mechanism.[54b]



Scheme 20. Retention of stereochemistry at the migrating carbon in the [1,4]-Wittig migration.

More evidence favoring a non-concerted mechanism comes from the following observation: Apocamphylallyl ether underwent deprotonation but failed to rearrange either via [1,2]- or [1,4]-pathways (Scheme 21).[55] This result resembles previous studies on the [1,2]-Wittig

rearrangement with the related norbornyl ethers and, as discussed above (Scheme 6), is explained by the instability of the C1 norbornyl radical, due to the pyramidal geometry of this carbon.

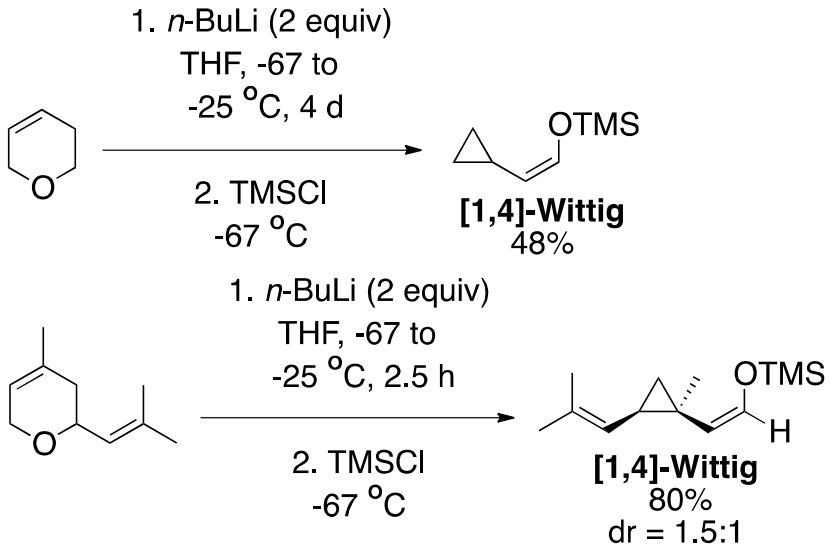


Scheme 21. Relevant experiments on the mechanism of the [1,4]-Wittig migration.

In addition, the rearrangement of cyclopropylmethyl allyl ether afforded the [1,4]- and [1,2]-Wittig products with virtually no ring opened isomeric products (Scheme 21).[55] This result parallels the isomerization of cyclopropylmethyl benzyl ether, which undergoes [1,2]-Wittig rearrangement without further isomerization (Section 1.2.2),[13c] and suggests that recombination of the radical pair is extremely fast (9.4×10^7 s^{-1} or higher).[23]

On the other hand, Rautenstrauch suggested that the [1,4]-Wittig rearrangement is a concerted process based in his studies of the rearrangements of 6-membered cyclic ethers.[56] Given its cyclic nature, the arrangement of the five atoms involved in the rearrangement are in a 'locked' *cisoid* conformation, which is the ideal arrangement for a concerted [1,4]-shift. For instance 5,6-

dihydropyran underwent exclusive [1,4]-Wittig rearrangement and was isolated as the corresponding trimethylsilyl enolate (Scheme 22). The rearrangement of nerol oxide also gave only the [1,4]-Wittig product with slight *cis* diastereoselectivity and no competing [1,2]-Wittig product was observed. Based on conformational analysis, Rautenstrauch suggested a concerted mechanism, leading predominantly to the *cis* product, was operative.[56]



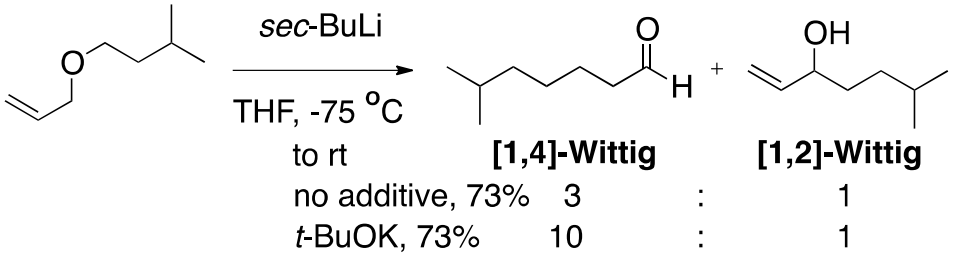
Scheme 22. [1,4]-Wittig rearrangement of dihydropyranyl systems.

1.4.2 The problem of regiocontrol between the [1,4]- vs [1,2]-Wittig pathways

The [1,2]-shift is an inherent competitive pathway of the [1,4]-Wittig rearrangement. Generally, the selectivity in favor of the [1,4]-pathway has been increased by running reactions at lower temperatures.[55] However, in most cases a significant amount of the [1,2]-Wittig product is formed, and is tipically the major product.[57] Furthermore, in the particular case of bisallylic ethers, compounds capable of at least four Wittig pathways ([1,2]-, [2,3]-, [1,4]- and [3,4]-, Scheme 1), the [2,3]-shift is predominant.[41a, 58] There are however some cases in which the

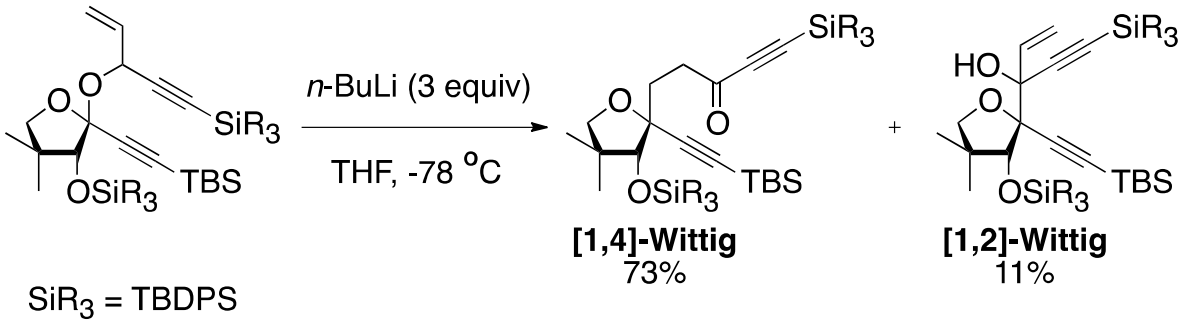
[1,4]-migration is predominant over the [1,2]-pathway[30b, 54b, 59] and in a very few cases, exclusive.[56] Some examples are given below.

Schlosser and Strunk reported the synthesis of aldehydes via the [1,4]-Wittig rearrangements of allyl alkyl ethers.[55] These studies revealed a slight dependence of the [1,4]-/[1,2]-selectivity on the base, and particularly on the base counter ion. For example, the rearrangement of (3-methyl)butyl allyl ether with *sec*-butyllithium led to a ~3:1 [1,4]-/[1,2]-selectivity, while addition of potassium *tert*-butoxide led to 10:1 selectivity at room temperature (Scheme 23). However, at lower temperatures the presence of potassium significantly retarded the rearrangement of ethers. Remarkably, these workers used this methodology to synthesize a pheromone from the coleopteran species *trogoderma inclusum* and *trogoderma variable*, which constitutes the only application of the [1,4]-Wittig rearrangement in total synthesis.



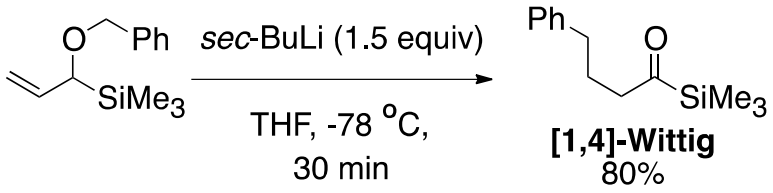
Scheme 23. Effect of the counterion in the [1,4]-/[1,2]-Wittig selectivity.

In a different system, Tomooka *et al* discovered that the proper choice of silyl group at a terminal alkyne allowed [1,4]-Wittig migration of the glycoside portion with good [1,4]-/[1,2]-selectivity (7:1) and good overall yield.[30b] Unfortunately, the origin of the observed selectivity was not discussed, however it seems such selectivity is substrate dependent.



Scheme 24. Selective [1,4]-Wittig shift of a glycoside system reported by Tomooka.

The most selective example towards the [1,4]-shift in acyclic ethers was reported by Onyeozili and Maleczka in 2006. Under optimized conditions α-benzyloxy allylsilane underwent exclusive [1,4]-Wittig rearrangement to the corresponding acylsilane in 80% yield (Scheme 25).[60] In addition, they trapped the obtained enolate with a series of electrophiles in good yields. The authors suggested the observed exclusive selectivity might be due to the operation of the concerted [1,4]-migration mechanism.

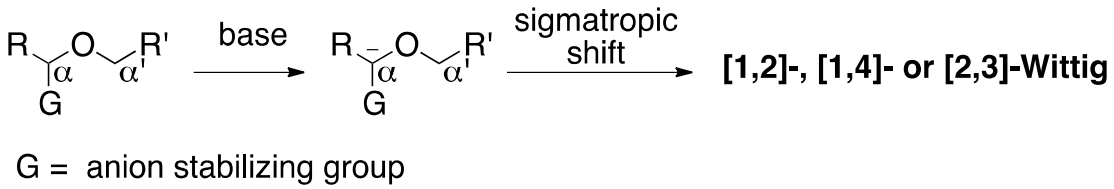


Scheme 25. Exclusive [1,4]-Wittig rearrangement of α-benzyloxy allylsilane.

1.5 Methods for the generation of carbanions capable of Wittig rearrangements

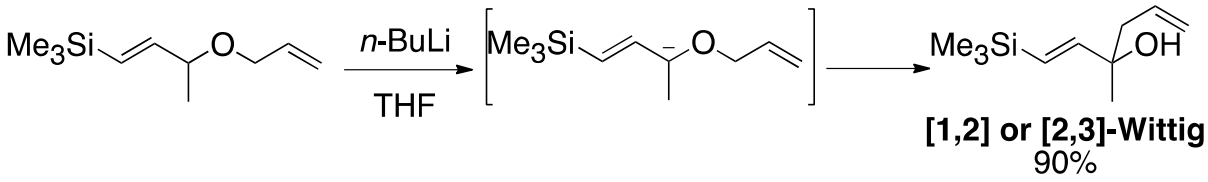
In general, compounds capable of Wittig rearrangements are limited by the accessibility of the required carbanion, the actual species that undergoes bond reorganization. The most common way to access such carbanions is by deprotonation with strong bases such as alkyllithiums. In the case of unsymmetrically substituted ethers regioselective metalation becomes an important

issue and the relative acidities of the α and α' protons will determine the site of deprotonation and therefore the possible Wittig shifts. To circumvent this problem an anion stabilizing group G is placed at the α (or α') position so that deprotonation is regioselective (Scheme 26). Groups such as alkynes, phenyl, carbonyl (ketones, amides, esters, aldehydes), cyano, sulfonyl and silyl can perform well as the G group. The latter is the most relevant to this thesis and will be described in some detail.



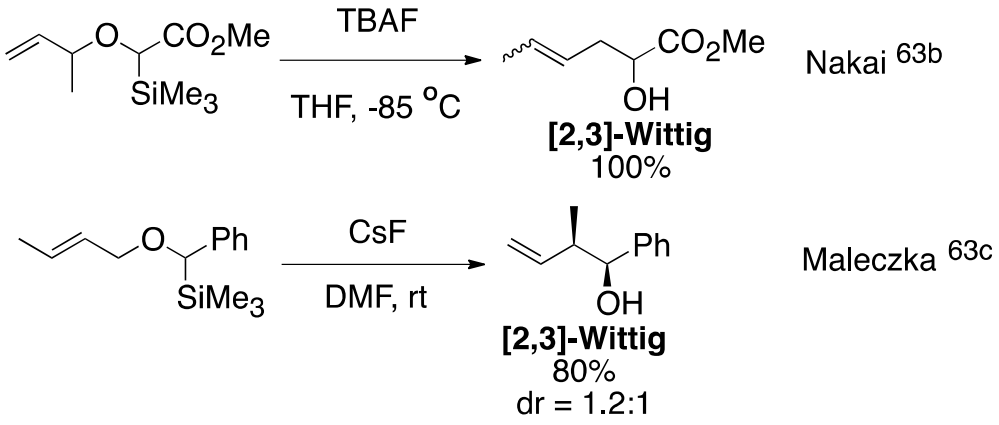
Scheme 26. Generation of carbanions via group G-directed deprotonation.

Silyl groups are capable of stabilizing an adjacent carbanion by delocalization the negative charge through silicon d orbitals,[61a,b] although others attribute this ability to hyperconjugation.[61c, d] The overall effect is the reduction in pKa of the conjugated acid. Also, silyl groups can be considered carbanion masks, which can be displaced to give a carbanion capable of Wittig rearrangements (or other reactions). Nakai *et al.* introduced the use of silyl groups in Wittig rearrangements. For example, silicon-free bisallylic ethers underwent selective deprotonation at the less substituted α position,[41a] but the presence of a silyl group at the γ position led to selective deprotonation at the most substituted α allylic position (Scheme 27).[62]



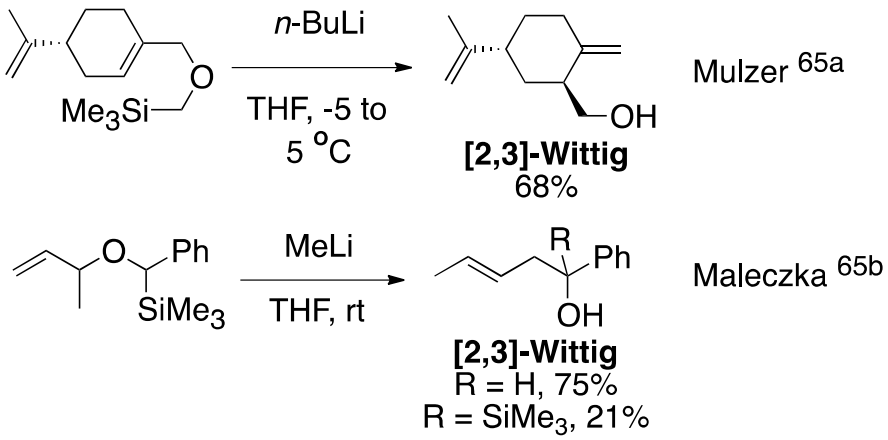
Scheme 27. Silicon-directed deprotonation of hindered allylic position.

The generation of carbanions by fluoride-promoted desilylation followed by Wittig rearrangements has been studied by Reetz[63a] and Nakai[63b] and Maleczka.[63c] This approach is very attractive because it avoids the use of strong bases, which are incompatible with many useful functional groups. Nakai reported a couple of examples in which α-allyloxy *C*-silylated esters underwent desilylation with tetrabutylammonium fluoride (TBAF) at low temperature in THF followed by [2,3]-Wittig rearrangement (Scheme 28).[63b] Maleczka and Geng reported the cesium fluoride promoted [1,2]- and [2,3]-Wittig rearrangement of α-alkoxysilanes in DMF, an unusual solvent in Wittig rearrangements (Seheme 28).[63c]



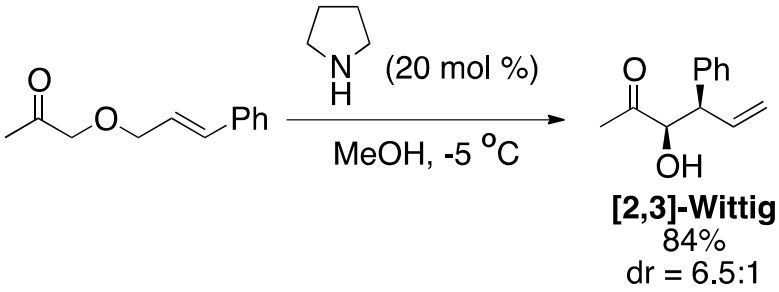
Scheme 28. Silicon-promoted Wittig rearrangements.

The Wittig-Still rearrangement[43] (section 1.3.4) is based on carbanion formation via tin-lithium exchange, a strategy that allows access to unstable carbanions that can then undergo Wittig rearrangements. Not surprisingly, this method is currently a common tool in natural product synthesis,[64] but the associated toxicity of tin has prompted a search for more benign approaches. Following two promising examples by Mulzer and List,[65a] Maleczka and Geng studied the silicon / lithium exchange / Wittig rearrangements of α-alkoxy silanes (Scheme 29).[65b] Interestingly, in Mulzer's examples the absence of anion stabilizing groups allowed selective Si/Li exchange with *n*-butyllithium followed by rearrangement, whereas in Maleczka's examples, Si/Li exchange was accompanied by competitive deprotonation / rearrangement due to the carbanion-stabilizing effect of the trimethylsilyl group along with the olefins and phenyl groups present in these molecules. Other methods for the generation of carbanions capable of Wittig rearrangements include the reductive lithiation of *O,S* acetals with lithium naphthalide,[26, 38] and the SmI_2 mediated reduction of diallyl acetals.[66]



Scheme 29. Examples involving Silicon-Lithium exchange / Wittig rearrangements.

It is important to mention that the formation of an actual carbanion can be avoided by generating synthetic equivalents. For example, α-allyloxy carbonyl compounds can be enolized with a Lewis acid and undergo Wittig rearrangement.[32] In a unique example by Gaunt *et al*, enamine formation with a catalytic amount of a secondary amine led to [2,3]-Wittig rearrangement of α-allyloxy ketones with excellent yields and modest diastereoselectivities (Scheme 30).[67]



Scheme 30. Organocatalytic enamine formation / [2,3]-Wittig rearrangement.

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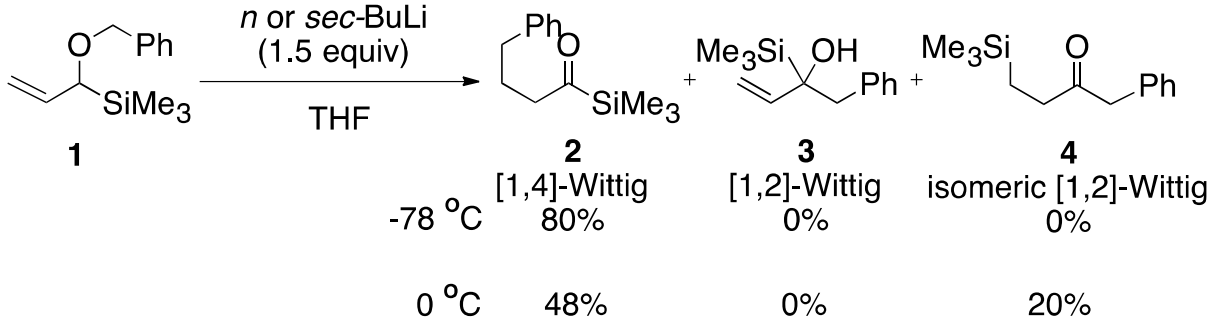
CHAPTER 2

STRUCTURAL AND ELECTRONIC PERTURBATIONS ON THE REACTIVITY AND SELECTIVITY IN [1,2]- vs [1,4]-WITTIG REARRANGEMENTS OF α-ALKOXYSILANES

2.1 Introduction

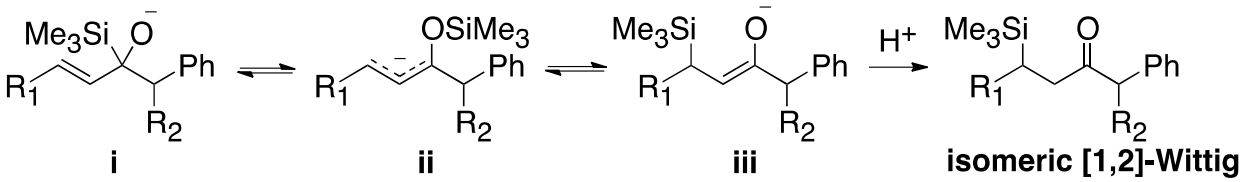
In an earlier study,[1] Maleczka and Onyeozili showed that unsubstituted α-alkoxysilane **1** rearranged exclusively via the [1,4]-pathway at low temperatures to give acylsilane **2** in 80% yield (Scheme 31). It was observed that the [1,2]-pathway became competitive with increasing temperature, leading to a gradual erosion in [1,4]-selectivity, resulting in mixtures of **2** and isomeric [1,2]-Wittig product **4**, with the [1,4]-/[1,2]-ratio reaching 2.5:1 at room temperature.[2] Following these results, we questioned whether a high [1,4]-/[1,2]-selectivity could be retained if we made structural changes to our model substrate **1** by either adding substituents at the olefin, at the migrating group, by changing the silyl group, or by introducing electronic modifications at the aromatic ring.



Scheme 31. [1,4]-/[1,2]-Wittig rearrangements of α-alkoxysilanes.

The formation of the isomeric [1,2]-Wittig product can be rationalized as shown in Scheme 32. Isomerization of the [1,2]-Wittig alkoxides (**i**) is likely to take place via Brook rearrangement to

homoenolate **ii** followed by a [1,4]-Retro-Brook migration to enolate **iii**. As pointed out elsewere,[3] such net carbon-to-carbon 1,3-silyl migrations are generally substrate-dependent, sensitive to steric and electronic factors, and favored at higher temperatures. We have evidence, however, that in our case this isomerization may, in part, also be an artifact of work-up and in certain cases can be minimized (vide infra).



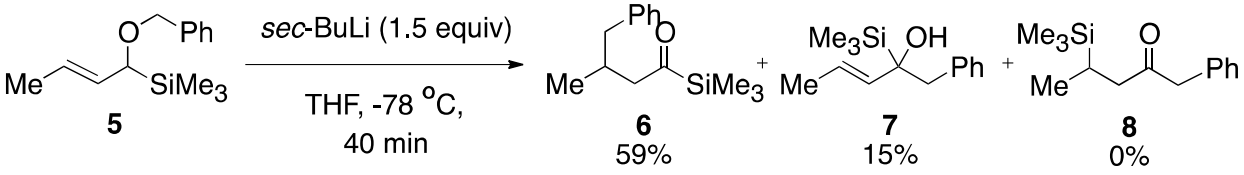
Scheme 32. Plausible mechanism for the isomerization of the [1,2]-Wittig alkoxide **i** to isomeric enolate **iii**.

2.2 Effect of alkyl substitution at the terminal allylic and benzylic positions

Nakai and co-workers have showed that the scope and limitations of the [1,2]-Wittig rearrangement are determined principally by the migratory aptitude of the alkyl group (primary < secondary < tertiary = allyl < benzyl) thus following increasing radical stability.[4] In cases of limited radical stability of the migrating group, carbanion-stabilizing groups similarly facilitate [1,2]-migrations.[3] In contrast, the yield of [1,4]-Wittig products has been reported to be relatively insensitive to substitution at the α- or γ-position of the allylic moiety,[5] although Schlosser observed that [1,4]-/[1,2]-selectivity is diminished with increasing alkyl substitution about the migrating carbon.[6] In the context of these previous findings, we set out to systematically investigate the introduction of alkyl substitution at the benzylic carbon and/or terminal allylic

carbon of α-alkoxyallylsilanes so as to gain insight into the steric and stereochemical factors that might control the course of Wittig rearrangements of α-alkoxyallylsilanes.

Dr. Onyeozili studied the effect of an alkyl substituent at the terminal sp^2 carbon of the allyl moiety (**5**, Scheme 33).[7] When subjected to our previously developed conditions (*sec*-BuLi, THF, –78 °C)[1] compound **5** afforded in 74% overall yield a 4:1 ratio of acylsilane **6** and alcohol **7** resulting from [1,4]- and [1,2]-Wittig rearrangements, respectively (Scheme 32). The effect such alkyl substitution on the rate of deprotonation / rearrangement was negligible, consistent with the fact that the site of deprotonation is at a relatively remote position with respect to the alkyl substituent. Notably, the erosion of the [1,4]-/[1,2]-selectivity with substitution at the terminal allylic position is in apparent contrast with literature reports.[5] Based on our earlier observations[1, 2] in which only the isomeric [1,2]-product was isolated (**4** instead of **3**, Scheme 31) we were surprised to find that the rearrangement of **5** gave the actual [1,2]-Wittig product (alcohol **7**, Scheme 33) but none of the isomeric product (ketone **8**).



Scheme 33. Effect of substitution at the terminal sp^2 carbon of the allylic moiety.

We continued our studies by analyzing the influence of substituents at the migrating (benzylic) carbon, a structural change that inherently led to diastereomeric substrates. Our simplest models,

α-(trimethylsilyl)allyl ethers *syn*–**9** and *anti*–**9** bearing a methyl group at the benzylic position, were not separable by silica gel column chromatography, thus a 1:1.4 mixture of *syn*–**9**/*anti*–**9** was employed (Scheme 34). Under our standard reaction conditions we found that the most reactive diastereomer (*syn*–**9**) was consumed within 8 hours whereas the 'less reactive' diastereomer *anti*–**9** was recovered in 43% (based on the *syn*–**9**/*anti*–**9** mixture). In other words, *anti*–**9** underwent only ~27% conversion, vs. 100% conversion of *syn*-**9**. The [1,4]- and isomeric [1,2]-products (**10** and **11**, respectively) were obtained in a ratio of 1.5:1 and in a combined 35% yield. It was observed that allowing the reaction to proceed overnight resulted in an increased overall yield of **10** and **11** (46%), with basically the same [1,4]-/[1,2]- ratio (1.7:1) with a corresponding decrease in the recovery of the 'less reactive' *anti*–**9** (26%). The near complete erosion of the [1,4]-/[1,2]- selectivity (>99:1 in compound **1**) is in agreement with the detrimental effect of increasing substituents at the migrating carbon in the [1,4]-/[1,2]-selectivity observed by Schlosser.[6] The marked difference in the reactivity of diastereomers *syn*–**9** and *anti*–**9** points to the determinant role of relative stereochemistry, and more specifically the steric environment around the allylic proton (α to silicon) in allowing the key deprotonation step to take place prior to rearrangement. We propose that the allylic C–H_a bond should be perpendicular to the olefin and therefore aligned with the π system. At the same time, antiperiplanar alignment of the allylic C-H_a bond to the cleaving C–O would allow weakening of the C–H_a bond. The phenyl group would take the less crowded and furthest position, maximizing conjugation by aligning with the C–O bond and thus leading to the pseudo-eclipsed conformers shown in Figure 1. These proposed conformational requirements pose a more severe steric interaction in *anti*–**9**, the less reactive diastereomer, in which the pseudo-eclipsing Methyl and

TMS groups collide. On the other hand, in *syn*–**9** the TMS group is pseudo-eclipsed with H_b and a less unfavorable steric interaction between the benzylic methyl and vinyl groups is possible. Alternatively, positioning the benzylic H_b proton in an "eclipsed" alignment with the TMS groups in both *anti*–**9** and *syn*–**9** would lead to an more unfavorable steric interaction in *anti*–**9** (Ph vs vinyl) than in *syn*–**9** (Me vs vinyl).

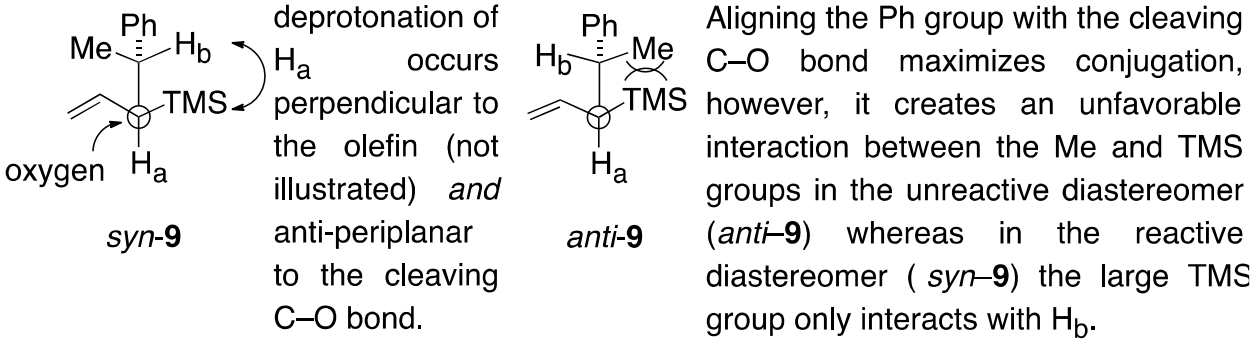
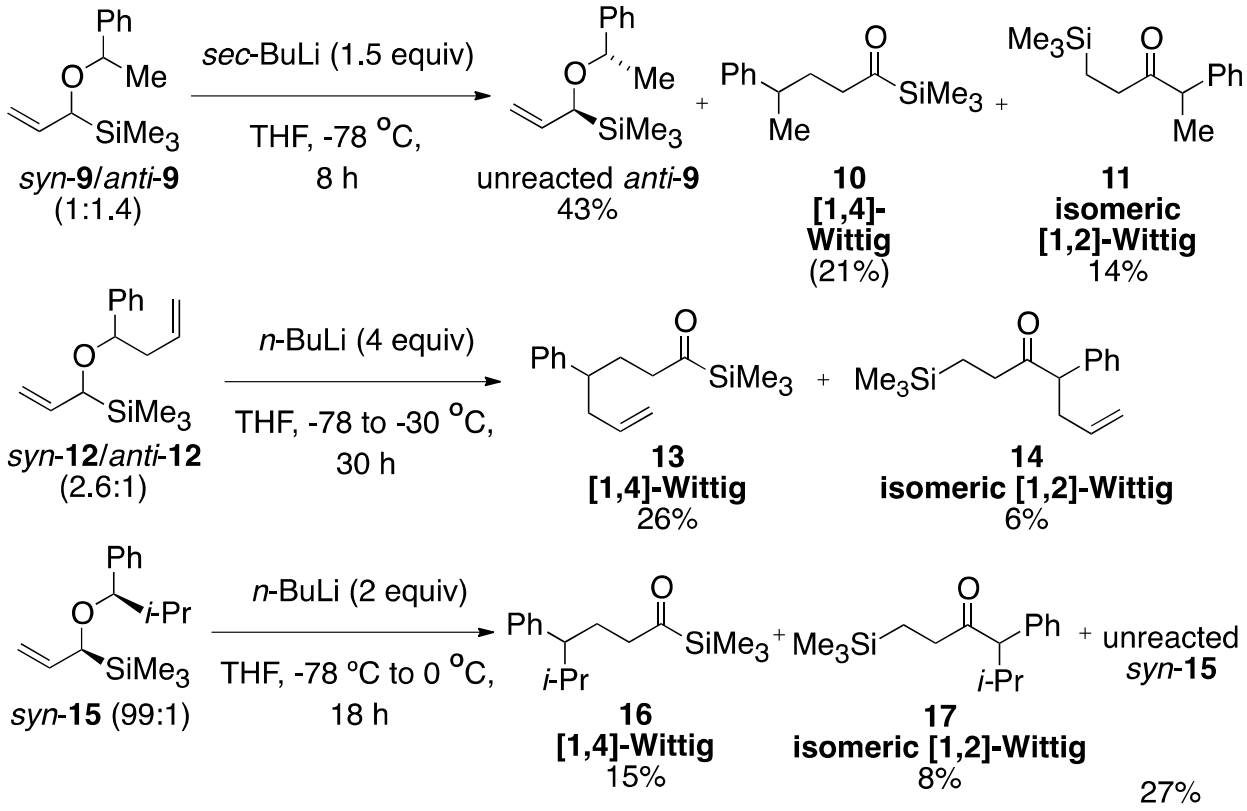


Figure 1. Proposed relevant conformers for the deprotonation of *syn*–**9** and *anti*–**9**.

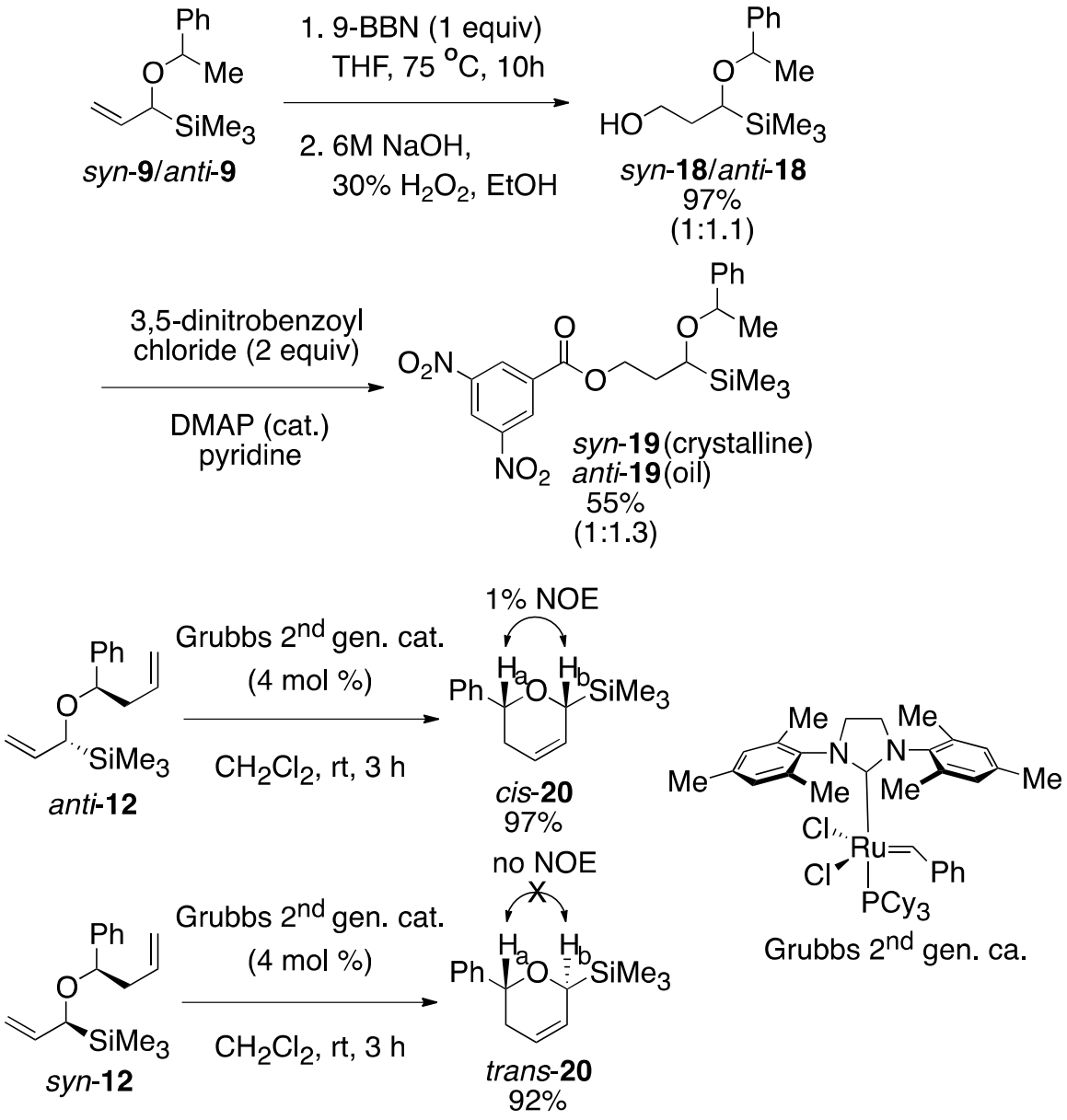


Scheme 34. Wittig rearrangements of α-alkoxysilanes **9**, **12**, and *syn*-**15** bearing a substituent (methyl, 2-propenyl and *iso*-propyl, respectively) at the benzylic carbon.

This is consistent with the observation that increasing the volume of the substituent at the benzylic position dramatically reduced deprotonation rate as the diastereomeric 2-propenyl (**12**) and the isopropyl (**15**) analogues were unreactive under standard reaction conditions (*sec*-BuLi, THF, -78 ^{o}C, 24 h). In these two cases the use of a less bulky base (*n*-BuLi) was necessary to effect a reaction. A mixture of *syn*-**12**/*anti*-**12** (2.6:1) required 30 h for complete reaction at –30 ^{o}C, yielding acylsilane **13** and ketone **14** in a 4.3:1 ratio. The seemingly higher [1,4]-/[1,2]-selectivity is clouded by the reaction also affording a complex mixture of alkylated and otherwise unidentified byproducts. A temperature of 0 ^{o}C was necessary for the isopropyl

substituted *syn*-**15** to undergo deprotonation and rearrangement to give the [1,4]- and isomeric [1,2]-products **16** and **17**, in 23% yield (1.8:1 ratio), along with 27% of unreacted *syn*-**15**.[7] Importantly, attempts to trap the initially formed allylic anion from *syn*–**9** and *anti*–**9** with D_2O were unsuccessful (< 5% D incorporation by ^1H NMR), suggesting that this allyllithium intermediate quickly rearranges.

It is important to mention that we have consistently observed that *syn* diastereomers are more reactive than the corresponding *anti* isomers in *all* cases (see below). The relative stereochemistry of *syn*–**9** was confirmed by X-ray crystallography of 3,5-dinitrophenyl ester *syn*-**19**, as shown in Scheme 35. Although crystalline *syn*-**19** was isolated from a diasteromeric mixture of *syn*-**19**/*anti*-**19**, independent derivatization of *anti*-**9** led to an ester spectroscopically identical to the non-crystalline *anti*-**19**. On the other hand, ring-closing metathesis of *syn*-**12** and *anti*-**12** followed by NOE studies of the corresponding products *trans*-**20** and *cis*-**20** led to the assignment of relative stereochemistry in *syn*-**12** and *anti*-**12** (Scheme 35).[7]

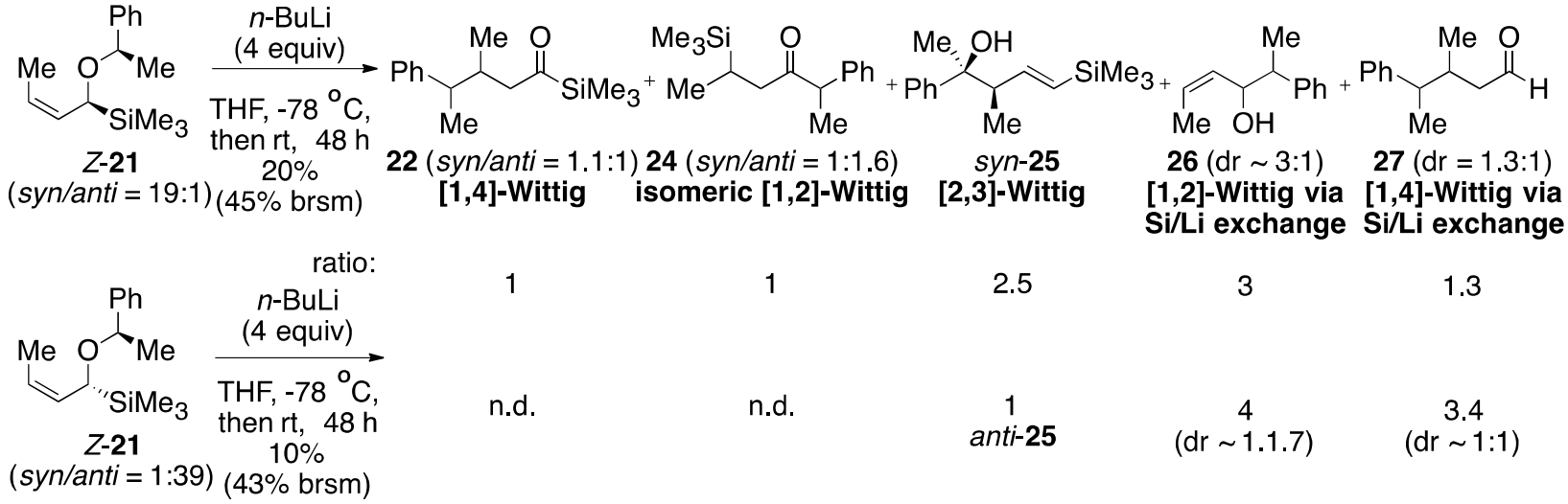


Scheme 35. Determination of relative stereochemistry of *syn*-**9**/*anti*-**9** and *syn*-**12**/*anti*-**12**.

The behaviors of substrates bearing substitution at both the migrating carbon and the terminal allylic carbon were also studied. These experiments gave us the opportunity to evaluate the effect of olefin geometry not only on the reactivity and selectivity of the rearrangements, but also on the stereochemistry of the bond reorganization.

Diastereomeric compounds **21** were synthesized as geometrically pure *Z* or *E* isomers. However, while the *Z* diastereomers (*syn Z*-**21** and *anti Z*-**21**) could be largely separated by column chromatography (dr >19:1), the *E* diastereomers proved very difficult to separate and therefore were used as a diastereomeric mixture (*E*-**21**).

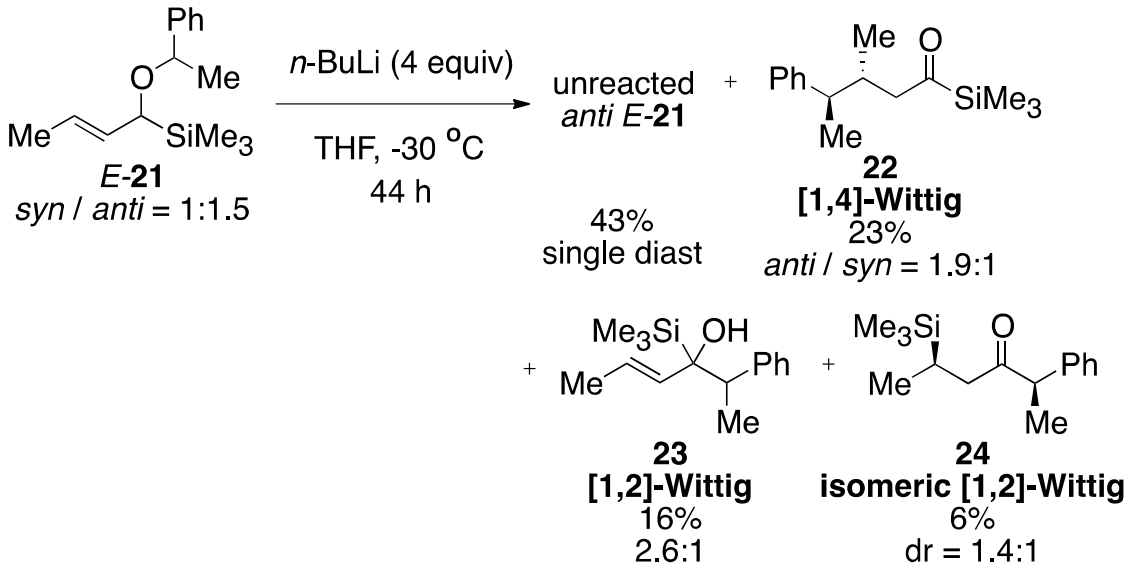
In theory, clean deprotonation of **21** (*E* or *Z*) followed by rearrangement should afford pairs of diastereomeric [1,4]- and [1,2]-products (**22** and **23** respectively). As described above, further isomerization of the [1,2]-products via silyl migration could also lead to another pair of diastereomeric ketones (**24**). In practice, *syn* and *anti Z*-**21** were very unreactive when treated with *n*-BuLi at low temperature, and even at room temperature these diastereomers reacted sluggishly. Reaction of *syn Z*-**21** (Scheme 36) with *n*-BuLi led to almost 50% conversion and ~20% yield of a complex mixture of products. Careful examination and separation of these mixtures revealed that compounds **23** and **24** were accompanied by [2,3]-Wittig (**25**), diastereomeric [1,2]- and [1,4]-Wittig products lacking the trimethylsilyl group (**26** and **27**, respectively) and alkylated products (not shown).



Scheme 36. Substitution at the migrating carbon and terminal sp^2 carbon, *Z* isomers. n.d.: not determined.

Although it was not possible to obtain exact ratios of products or diastereomers from either ^{1}H NMR or HPLC of crude reaction mixtures, the products could be partially purified allowing their approximate ratios to be determined. Approximate diastereomeric ratios from the crude reaction mixture were obtained by integration of the $SiMe_3$ or vinylic signals in the ^{1}H NMR, and were in accordance with the isolated diastereomeric ratios. The [2,3]-Wittig rearrangement of *syn Z*-**21** gave *syn*-**25** as a single diastereomer, whose stereochemistry was tentatively assigned by comparison with the known desilylated analogues.[8] Attempts to desilylate *syn*-**25** with TBAF or TFA were unsuccessful.

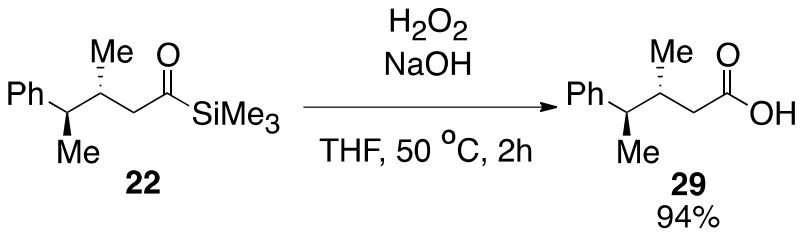
On the other, hand all other products from [1,4]- and [1,2]-migrations were obtained in low diastereomeric ratios (ranging from 1:1 to ~3:1). Isolation of the [2,3]-Wittig product is diagnostic of competitive deprotonation at the benzylic position, rather than α to silicon, perhaps as a consequence of the relatively elevated temperature required for the desired reaction to occur. As expected, *anti Z*-**21** was less reactive under the same reaction conditions. Here, the starting material was recovered in 77% and only a total ~10% yield of products **25**–**27** was obtained (Scheme 36). The absence of compounds **22**–**24** suggests that deprotonation α to silicon is inhibited due to severe steric crowding. [2,3]-Wittig rearrangement of *anti Z*-**21** was stereospecific[9] to giving only *anti*-**25**. Compounds **26** and **27** (Scheme 36), likely to be formed via a silicon/lithium exchange[2] followed by [1,2]- and [1,4]-Wittig rearrangement, respectively, were obtained again in low diastereomeric ratios. Interestingly, the [1,2]-product **26** showed an inverse diastereoselection in comparison to that observed in the rearrangement of *syn Z*-**21**.



Scheme 37. Substitution at the migrating carbon and terminal sp^2 carbon, *E* isomers.

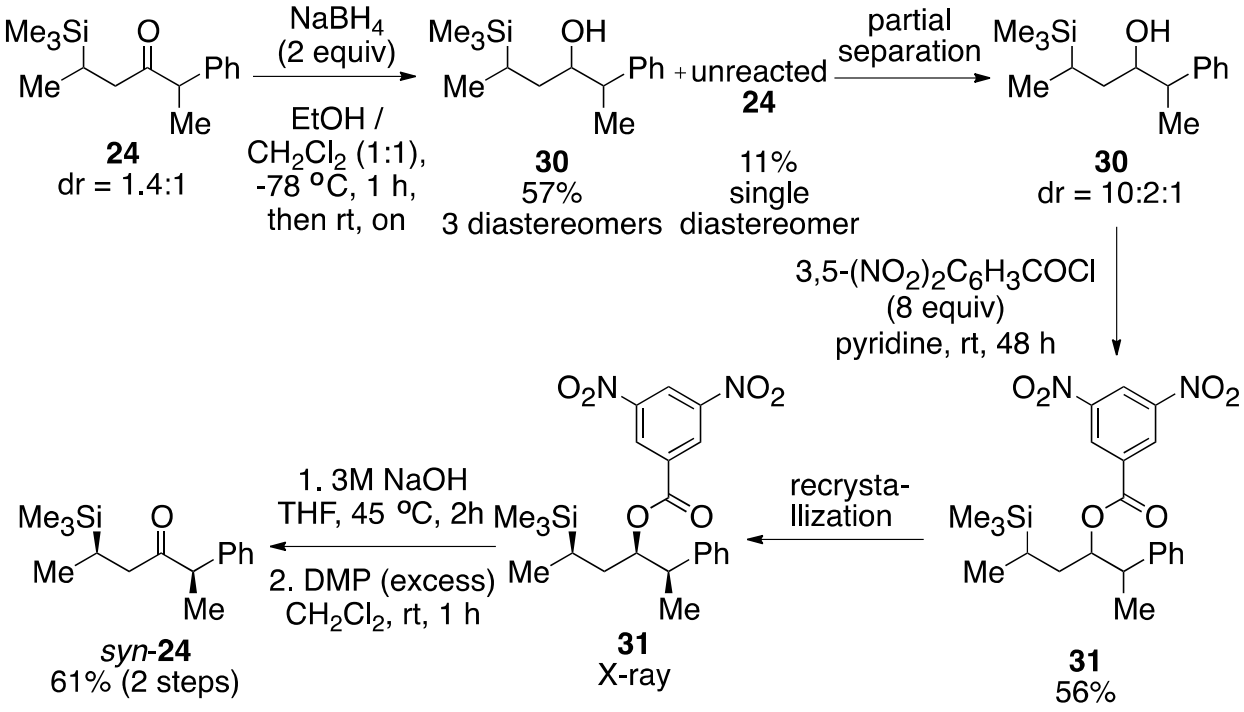
Changing the geometry of the olefin had a pronounced effect (Scheme 37).[7] In line with our previous discussion, the reactivity towards initial deprotonation was dominated by the relative configuration at the α and α' positions of the ethers, as illustrated by the rearrangement of *E*-**21** (*syn* / *anti* = 1:1.5). From this experiment, *syn E*-**21** was completely consumed by *n*-BuLi at low temperature, while its diastereomer *anti E*-**21** was mostly recovered (Scheme 37). Quenching the reaction at –30 ºC led to the isolation the [1,4]-Wittig product (**22**) in 23% yield and with low diastereoselectivity, accompanied by the isomeric [1,2]-product (**24**) also in low yield. Interestingly, quenching the reaction at lower temperature allowed the isolation of the direct [1,2]-Wittig product **23**, which in our previous room temperature experiments (Scheme 36) had undergone silicon migration and rearrangement to **24**. This was evidenced in an experiment run at 0 °C for 52 hours and quenched at –78 °C, which gave the [1,4]- and [1,2]-Wittig products **22** and **23** in 30% yield (1:1 ratio) with only traces of the isomeric [1,2]-product **24**. Thus, in certain

cases, quenching the reaction at low temperature significantly reduces silyl migration. The relative stereochemistry of the major diastereomer in **22** and **24** was determined as follows: **22** was oxidized to the known carboxylic acid **29** (Scheme 38).[10]



Scheme 38. Determination of relative stereochemistry of **22** by derivatization to **29**.

On the other hand, diastereomeric compound **24** (dr = 1.4:1) was reduced to the corresponding alcohol **30** as a mixture of only 3 diastereomers. Partial separation led to diastereomeric enrichment of **30** with a ratio of 10:2:1. Esterification with 3,5-dinitrobenzoylchloride gave **31** again as a mixture of diastereomers, recrystallization of the major component and X-ray crystallographic analysis provided the relative configuration of this isomer. The reverse transformations, that is, ester hydrolysis, and DMP oxidation afforded *syn*-**24**, which matched spectroscopically with the major diastereomer in the initial diastereomeric mixture of **24** (Scheme 39).

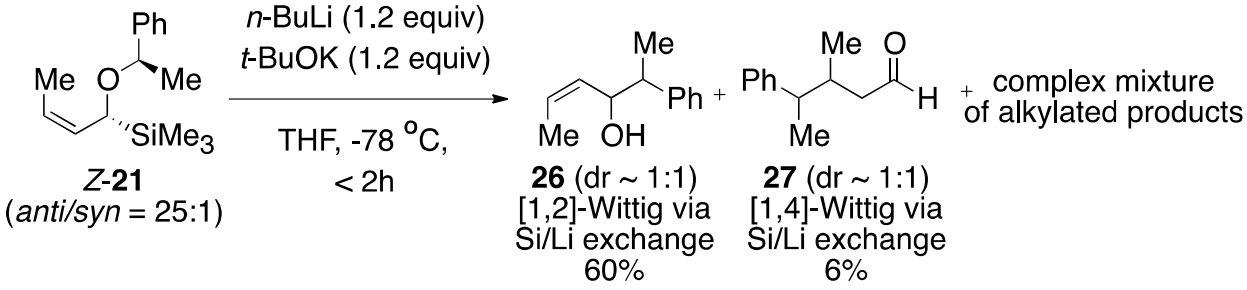


Scheme 39. Derivatization route for the determination of relative stereochemistry of **24**.

2.3 Discovery of an efficient silicon / lithium exchange / Wittig rearrangement protocol

In Chapter 1 (section 1.5) alternative methods for the generation of carbanions capable of Wittig rearrangements (other than by simple deprotonation) were described. Among those, the Wittig – Still approach, which is based on Sn/Li exchange of α-stannyl ethers to the corresponding α-carbanionic ethers, is a very useful and efficient method to initiate Wittig rearrangements. However, the innate toxicity of tin compounds[11] is an important limitation. For this reason safer alternatives have been sought, for example Mulzer[12] and Maleczka[2] have studied Si/Li exchange of α-silyl ethers with alkyllithiums followed by Wittig rearrangements (Scheme 29). This alternative desilylative process was inefficient for substrates in section 2.2, and only at higher temperatures the Si/Li exchange competed with the deprotonative pathway (Scheme 36).

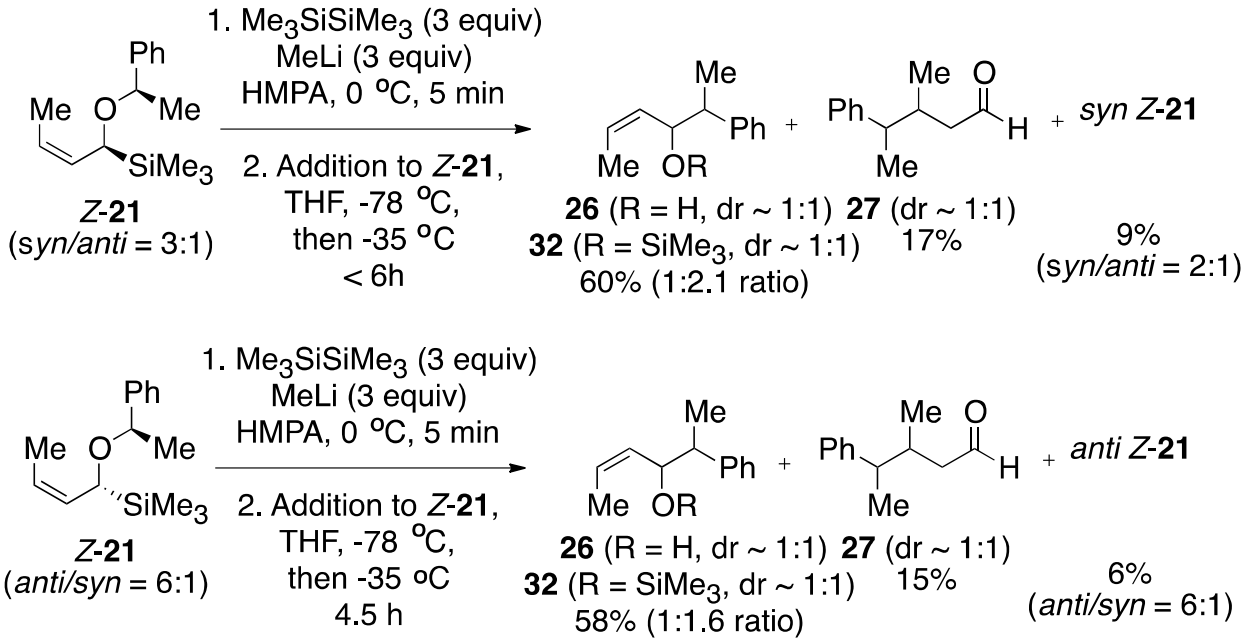
In the process of surveying alternative bases capable of allylic deprotonation in compounds substituted at the benzylic or olefinic positions it was found that Schlosser's superbase,[13] a combination of *n*-BuLi/KO*t*-Bu, effected transmetallation via Si/Li or Si/K exchange of the *anti* *Z*-**21** (*anti*/*syn* = 25:1) followed by [1,2]- and [1,4]-Wittig rearrangements in ~2.5 hours with good overall yield and modest [1,2]-/[1,4]-selectivity (Scheme 40). It is important to notice that *anti Z*-**21** was the most unreactive under conditions that were supposed to favor deprotonation (Scheme 36). Unfortunately, it was found that a significant amount of *anti Z*-**21** underwent alkylation, a known side-reaction of superbases (Scheme 40).[13]



Scheme 40. Wittig rearrangements of *anti Z*-**21** with *n*-BuLi/*t*-BuOK.

Later, it was found that trimethylsilyllithium (TMSLi), generated from hexamethyldisilane and methyllithium in HMPA, was an excellent reagent for the clean and selective Si/Li exchange. Treatment of *Z*-**21** (*anti*/*syn* = 3:1) with freshly prepared TMSLi led to almost complete desilylation followed by [1,2]- and [1,4]-Wittig rearrangements in good overall yield (Scheme 41). Due to the excess hexamethyldisilane (which is a byproduct of the Si/Li exchange process), part of the immediate [1,2]-Wittig alkoxide is trapped as the *O*-silyl ether. Both *syn Z*-**21** and *anti* *Z*-**21** had essentially the same reactivity, as observed from the reaction of a 6:1 *syn*/*anti* diastereomeric mixture of *Z*-**21** (Scheme 41).

It is important to point out that Schlosser obtained predominantly the [1,4]-Wittig product in the deprotonative rearrangement of unsubstituted allylic ethers bearing primary, secondary and tertiary alkyl allylic ethers.[6] In our results the [1,2]-Wittig product was the major product, presumably because there was an alkyl substituent at the terminal position. Another important difference is the effect of the counterion in the product distribution. Schlosser observed the use of the superbase *n*-BuLi/KO*t*-Bu provided higher [1,4]-/[1,2]-selectivity than the use of *n*-BuLi alone.[6] In our case, desilylation of *anti Z*-**21** in the presence of potassium counterion (*n*-BuLi/KO*t*-Bu, Scheme 40) led to an increase of the [1,2]-/[1,4]-product ratio relative to the product distribution when TMSLi was used. These differences should be independent of the method of metalation (deprotonation vs desilylation), and perhaps the use of HMPA in our studies was responsible for the switch in [1,2]-/[1,4]-selectivity and/or counterion effect.

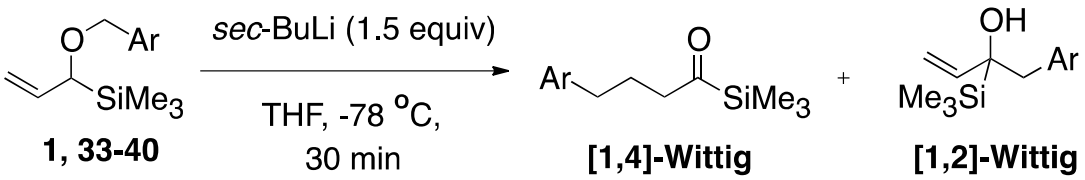


Scheme 41. Wittig rearrangements of *Z*-**21** via Si/Li exchange with TMSLi.

2.4 Electronic effects in the Wittig rearrangements of α-alkoxysilanes

The effect of electronic modifications at the aromatic ring, and therefore at the migrating benzylic carbon, was studied next. Several derivatives of **1** (scheme 31) bearing electron-donating and electron-withdrawing groups were synthesized – teamed with Mr. Kiyoto Tanemura[14] – and submitted to our optimized conditions (Table 1). Unfortunately our synthetic protocol (based on leaving-group activation at the benzylic position) was not suitable for the preparation of compounds bearing more representative electron-withdrawing groups, and moreover, our reaction conditions were incompatible with some of these groups (e.g. nitrile, carbonyl and nitro groups).

Table 1. Electronic effects in the [1,4]- and [1,2]-Wittig rearrangements of analogues of **1**.



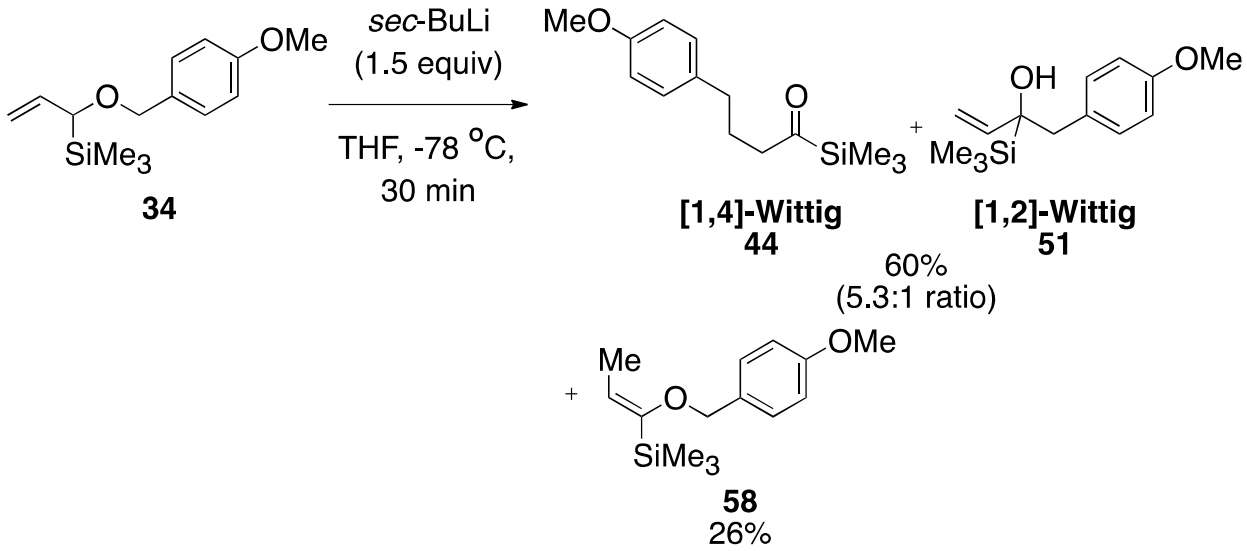
1, 33-40 **[1,4]-Wittig** **[1,2]-Wittig**

entry	substrate	Ar	yield **[1,4]-**[a]	yield **[1,2]-**[a]
1	**1**	Ph	(**2**) 80%	(**3**) -
2	**33**	4-MeC_6H_4	(**41**) 87%	(**50**) 3%
3[b]	**34**	4-MeOC_6H_4	(**42**) 51%	(**51**) 9%
4[c]	**35**	4-ClC_6H_4	(**43**) 57%	(**52**) 1%
5[d]	**36**	4-FC_6H_4	(**44**) 55%	(**53**) 2%
6	**37**	3-MeC_6H_4	(**45**) 76%	(**54**) 2%
7	**38**	3-MeOC_6H_4	(**46**) 73%	(**55**) 2%
8	**39**	2-MeOC_6H_4	(**47**) 80%	(**56**) 3%
9[e]	**40**	2-allylC_6H_4	(**48**) 64%	(**57**) n.d.

[a] In all cases the [1,4]- and [1,2]-Wittig products were isolated as a mixture from which yields were determined by ^{1}H NMR. [b] 26% isomeric enol ether **58**, [c] 1.1 equiv of *sec*-BuLi, 8% unreacted **34**. [d] 1.2 equiv *sec*-BuLi, 34% of mixture (4:1) of isomeric enol ether **59** and unreacted **35**. [e] 2.5 equiv of *n*-BuLi, 7% unreacted **39**. n.d. = not determined.

In all cases the [1,4]-Wittig products, acylsilanes **41**-**48**, were obtained after column chromatography as mixtures containing small quantities of the [1,2]- products (**50**-**57**). The

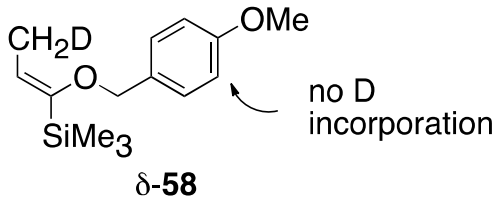
product ratios were determined by ^{1}H NMR and from them the corresponding yields were calculated (Table 1). Comparison of the reactivity of *p*-methyl, *p*-methoxy, *p*-chloro and *p*-fluoro benzyl ethers (entries 2-5) with that of **1** (entry 1) revealed a small effect on the product distribution, but in the case *p*-methoxy benzylether (**34**) the [1,4]-/[1,2]- selectivity was significantly lower (5:1). In addition, the reactivity of compounds **34**, **35**, and **36** was lower than that of unsubstituted (**1**) and *ortho* or *meta* substituted benzyl ethers (**37**-**40**). Although in the case of **35** the use of lower base equivalents (to avoid lithium-halogen exchange) might have led to incomplete conversion, the *p*-methoxy derivative (**34**) afforded isomeric enol ether **58**, whereas the *p*-fluoro substrate (**36**) gave isomeric enol ether **59**, both diagnostic of incomplete rearrangement of the allylic carbanion (Scheme 42).



Scheme 42. Incomplete rearrangement of **34** under optimized conditions.

The possibily of competitive *ortho* metalation of **34** in addition to allylic deprotonation suggested the intermediacy of a dianion that might be slower to rearrange. However, repetition of

the reaction shown in Scheme 42 and quenching with D_2O provided monodeuterated δ-**58** in which deuterium was incorporated only at the allylic position (Figure 2).



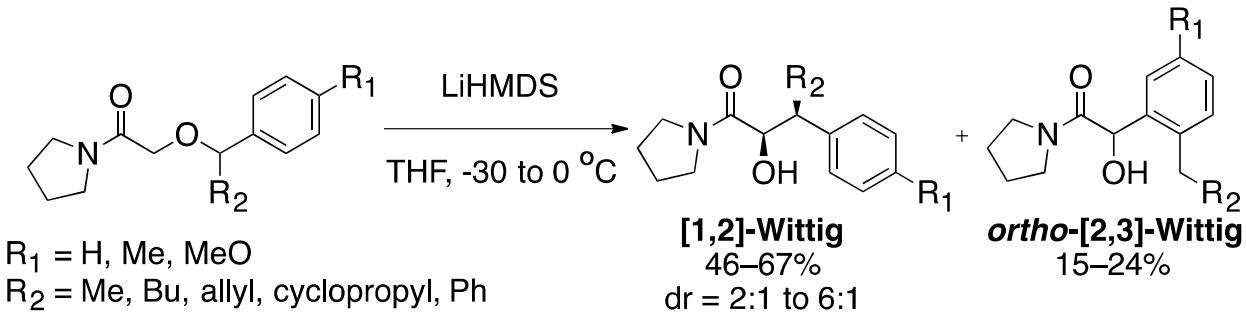
δ-**58**

Figure 2. Deuterium trapping experiment led to δ-**58**, suggesting competitive *ortho* metalation does not take place.

Substitution with other alkyl or methoxy groups at the *meta* or *ortho* positions (Table 1, entries 4-8) also led to the [1,4]-Wittig products with high selectivity and only traces of the [1,2]-alcohols were observed. In the case of 2-allylic substitution, competitive allylic deprotonation led to incomplete conversion under our standard conditions and thus an excess of a less reactive base (*n*-BuLi) was used (entry 8).

Examples of electronic effects in the Wittig rearrangements of *p*-substituted benzyl ethers are scarce and mostly limited to electron rich benzyl groups. For example, Cossy *et al.* studied the Wittig rearrangements of aryl substituted α-benzyloxy acetamides that proceeded predominantly via the [1,2]-shift (46-67% yield) and smaller amounts of the *ortho*-[2,3]-shift (15-24% yield).[15] Although the [1,4]-pathway was not possible in these cases, it is interesting that electron donating groups at the benzyl group had little effect in the yield of the [1,2]-Wittig product and its diastereoselectivity, although the authors did not specify the yield of the *ortho* [2,3]-Wittig products for each case, or mention any observation regarding enhancement or decrease of

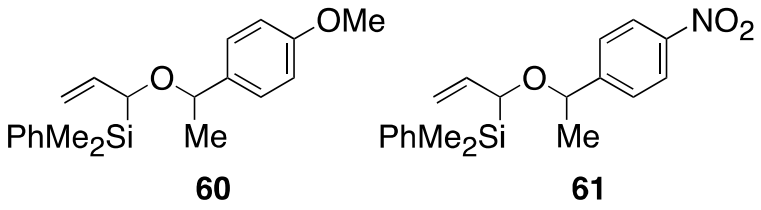
reactivity in these experiements. In a single example, the highly electron deficient *p*-nitro benzyl ether underwent extensive decomposition. It is worth noting that *p*-nitro benzyl ethers are also known to undergo elimination of *p*-nitrotoluene carbanion.[16]



Scheme 43. [1,2]- and ortho-[2,3]-Wittig rearrangements of α-benzyloxy acetamides.

Miyashita *et al.* also studied the [1,2]-Wittig migrations of aryl substituted α-benzyloxy imidazolium and benzimidazolium.[17] All *para*-substituents (Cl, Me, MeO) provided comparable yields (51–81%) without competition of other Wittig pathways and no differences in reactivity or others byproducts were reported. Based on their crossover experiments the authors suggested that an anionic mechanism was operative (Scheme 3, section 1.2.2), however a radical / radical anion mechanism is perfectly possible.

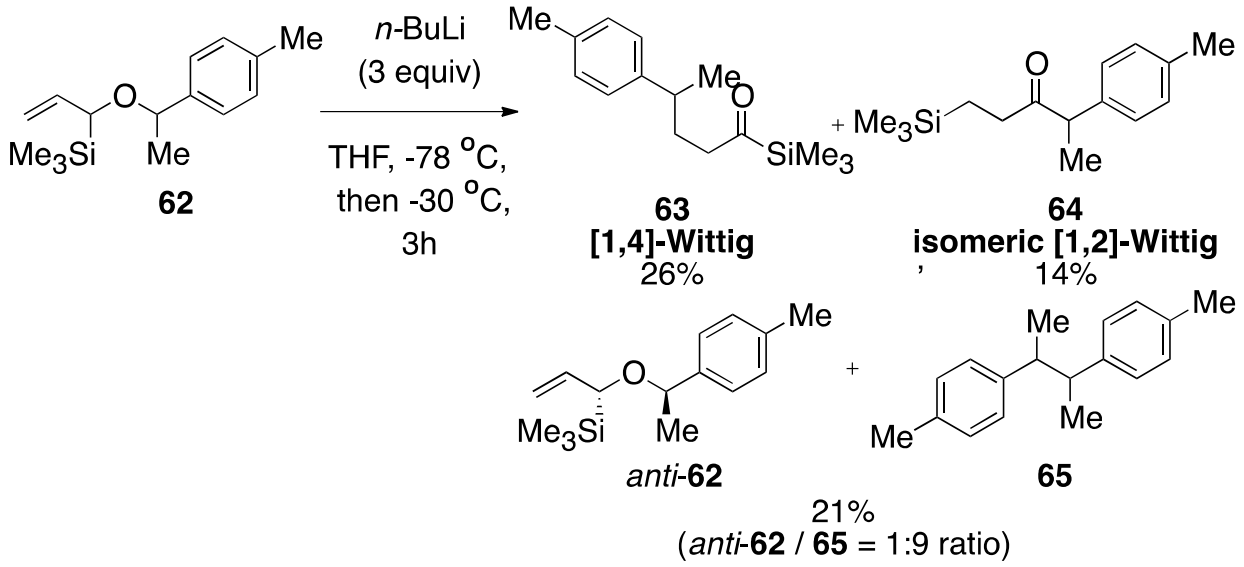
Dr. Onyeozili studied the rearrangement of diastereomeric *p*-methoxy and *p*-nitrobenzyl ethers **60** and **61** (Figure 3).[7] Although these examples contain additional modifications, such as an alkyl benzylic substitution and a different silyl group, it is significant that the former gave the [1,4]- and [1,2]- Wittig products in only 22% yield (1.8:1 ratio), while the latter underwent extensive decomposition.



60 **61**

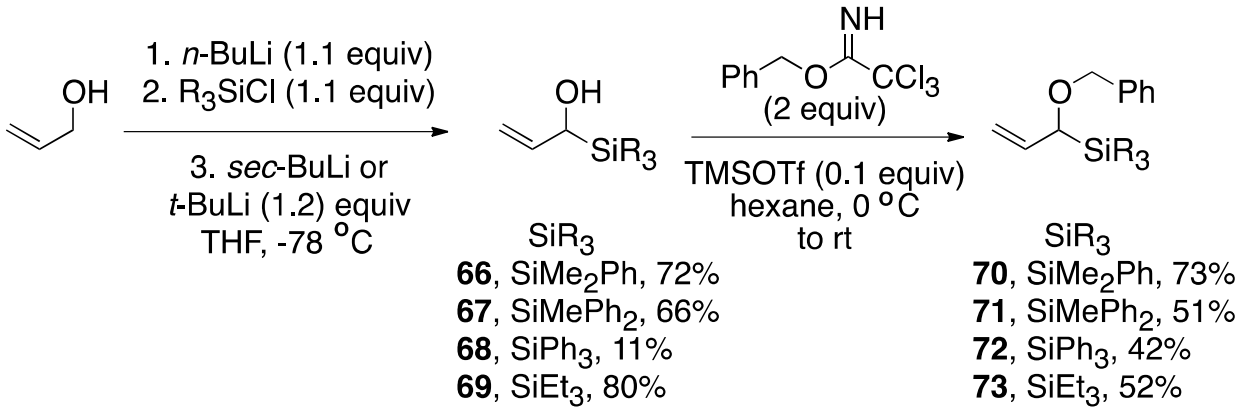
Figure 3. Substrates studied by Dr. Onyeozili.

In this study a similar result was obtained from the rearrangement of diastereomeric compounds **62**. Submission of a 1:1 (*anti/syn*) mixture of **62** to deprotonation with *n*-BuLi led to combined yield of 40% of the [1,4]- and [1,2]-Wittig products (**63** and **64**). A small amount of unreacted *anti*-**62** was recovered (<3%) accompanied by a compound that seems to be a dibenzyl dimer (**65**), which might have been formed by recombination of two benzyl radicals (Scheme 44). The product distribution (~2:1) resembles the rearrangement of unsubstituted compound **9** (Scheme 34), and also suggests that electronic effects play little role in determining the regioselectivity in the rearrangements of α-benzyloxy allylsilanes.



Scheme 44. Wittig rearrangements of diastereomeric **62**.

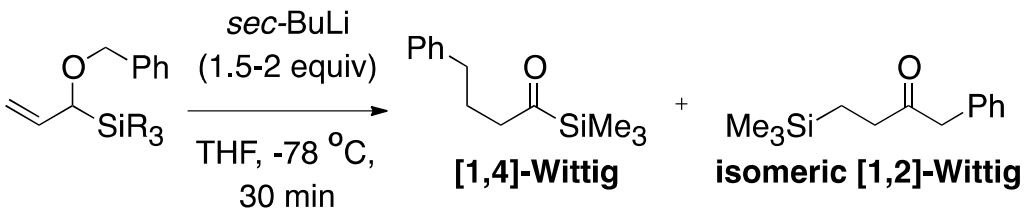
Finally, the effect of the silyl group in the [1,4]-/[1,2]-selectivity was studied. Derivatives of compound **1** (**70**-**73**) containing bulkier groups ($SiMe_2Ph$, $SiMePh_2$, $SiPh_3$ and $SiEt_3$) were synthesized via Lewis acid-catalyzed etherification of the corresponding α-silyl allylic alcohols with benzyltrichloroacetimidates. α-Silyl allylic alcohols (**66**-**69**) were obtained via retro-Brook rearrangement of the *in situ* generated *O*-silyl allylic alcohols (Scheme 45).

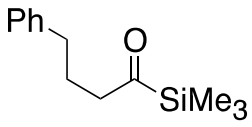
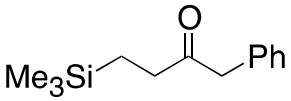
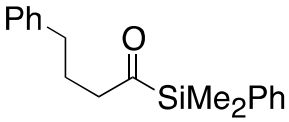
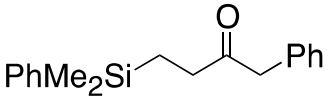
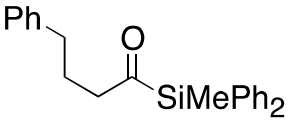
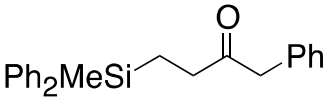
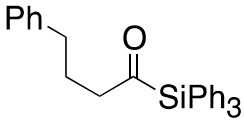
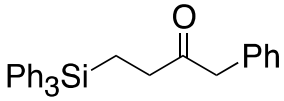
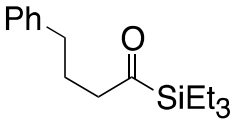
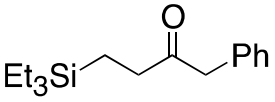


Scheme 45. Preparation of α-silyl allylic alcohols **56**-**59** and benzyl ethers **70**-**73**.

Showing similar selectivity as our model substrate **1** (table 2, entry 1), compound **70** bearing a single phenyl group at silicon selectively led to acylsilane **74** via the [1,4]-Wittig pathway, and only traces of the [1,2]- product (**78**) were observed (entry 2). On the other hand **71**, containing a $SiMePh_2$ group underwent rearrangement with a significantly low [1,4]-/[1,2]- selectivity (1.4:1) giving rise to acylsilane **75** in 48% and isomeric [1,2]-Wittig product **79** in 35% (entry 3). A $SiPh_3$ group (**72**) also led to low [1,4]-/[1,2]- selectivity (1.8:1) (entry 4) that is surprisingly similar to that of the $SiMePh_2$ example, whereas the bulky $SiEt_3$ group (**73**) provided almost exclusive [1,4]-Wittig product (entry 5).

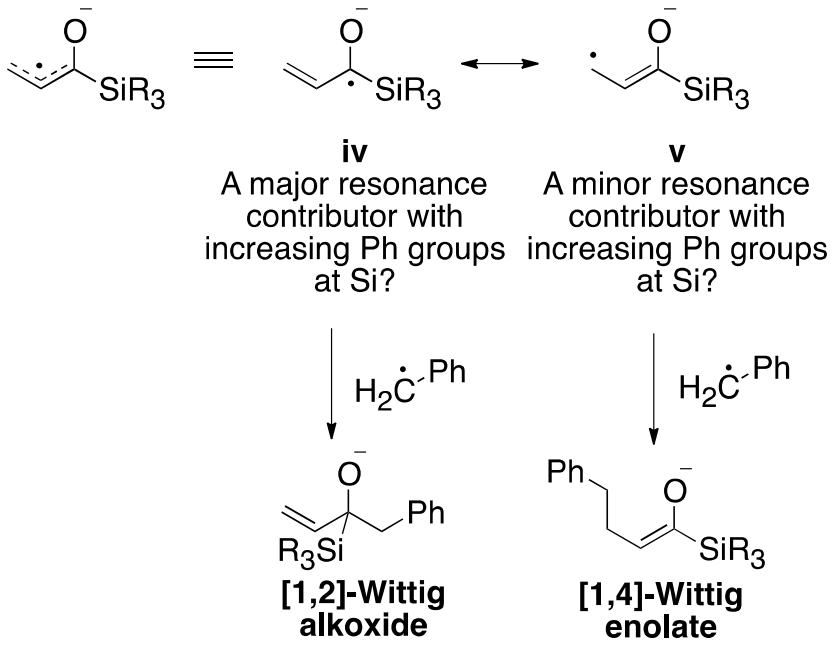
Table 2. Effect of the silyl group on the [1,4]-/[1,2]-selectivity.



entry	substrate	yield **[1,4]-** [a]	yield **[1,2]-** [a]
1	**1**	 **2** 80%	 **3** 0%
2	**60**	 **74** 67%	 **78** trace
3	**61**	 **75** 48%	 **79** 35%
4	**62**	 **76** 36%	 **80** 20%
5[b]	**63**	 **77** 67%	 **81** trace

[a] Isolated yields. [b] Reaction stopped after 2 hours.

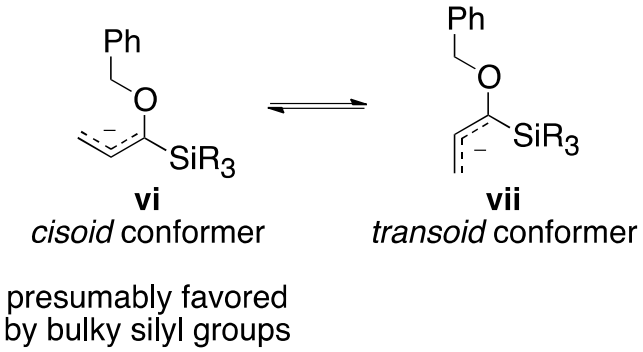
From the point of view of a stepwise mechanism involving a radical/radical anion pair. Silyl groups are known to stabilize α- and β-carboradicals by π(p-d) bonding and/or by hyperconjugation.[18] In the case of α-carboradicals, hyperconjugation does not play an important role and stabilization is primarily by π(p-d) bonding.[19] In addition, phenyl groups are likely to reinforce such π(p-d) interaction, increasing stabilization of the α-radical.[20] Considering the decrease of [1,4]-/[1,2]- selectivity shown in table 2 (entries 1-3), it is tempting to view the effect of increasing phenyl groups at silicon as increasing stabilization of the α-radical (**iv**, Scheme 46), leading to partial 'localization' of the radical α to silicon. A lower resonance contributor, the γ-radical resonance structure (**v**), would lead to the [1,4]-Wittig enolate, assuming this pathway proceeds via a stepwise mechanism. This is, of course, an over simplification, since the actual silyl intermediate is not only a radical anion, but also an allylic radical (Scheme 46). However, it is interesting that a $SiPh_3$ group led to a [1,4]-/[1,2]- selectivity similar to that of the $SiMePh_2$ analogue (entries 3 & 4), presumably because the higher steric demand of the $SiPh_3$ overcomes electronic stabilization and recombination at the α-position becomes prohibitive. On the other hand, increasing the steric demand from $SiMe_3$ to $SiEt_3$ did not affect the [1,4]-/[1,2]-selectivity.



Scheme 46. Radical-anion resonance contributors (**iv** and **v**) and recombination with benzyl radical to the corresponding Wittig anions.

In principle, a concerted mechanism for the [1,4]-Wittig pathway should be favored by an increase in the steric demand of the silyl group because this indirectly would favor the *cisoid* conformation (**vi**, Scheme 47) in which the olefinic π-system is in close proximity with the benzylic C-O bond (Scheme 47). In fact, it has been shown that 1-(trimethylsilyl)allyllithium,[21] as well as the related 1,3-bis(trimethylsilyl)allyllithium,[22] adopt a conformation in which the silyl groups are in the *exo* position. In addition, the steric bulk of the silyl groups plays an important role in determining the regioselectivity in the electrophile-trapping of 1-(trialkylsilyl)allyllithium.[23] The fact that the [1,2]-Wittig pathway is favored by bulkier silyl groups, and particularly those containing phenyl group at silicon, suggests that the electronic

factor exerts control in the [1,4]-/[1,2]- regioselectivity of the rearrangement in α-alkoxyallylsilanes.



Scheme 47. Two possible conformations of an ethereal allylic anion prior to rearrangement.

2.5 Conclusions

Substitution at the migrating carbon impacts the Wittig rearrangement of α-alkoxyallylsilanes, decreasing reactivity towards deprotonation and eroding the [1,4]-/[1,2]-selectivity. In addition, the reactivity in these diastereomeric substrates heavily depends on their relative stereochemistry, *syn* or *anti*, the former being more reactive in all cases. Similarly, substitutions at the terminal carbon of the allyl moiety alone or in combination with substitution at the migrating carbon also lowers the [1,4]-/[1,2]-selectivity, especially where substitution comes in the form of *Z*-olefins. The introduction of electronic modifications at the benzylic fragment appear not to have any impact on the [1,4]-/[1,2]-selectivity, although the reactivity of the carbanionic ethers to undergo rearrangement in certain cases is lowered.

The nature of the silyl groups affects the [1,4]-/[1,2]-selectivity, with inductively electron withdrawing groups (phenyl groups) on silicon favoring the [1,2]-Wittig pathway. Remarkably, this trend seems to be in conflict with the increasing steric demand of the silyl group, which is

expected to affect the [1,2]-pathway to a higher extent due to the proximity of the recombination carbon to the silyl group. Taken together these results show that the beneficial effect of silyl groups on reactivity (by lowering the pKa of allylic hydrogens) is countered by the steric congestion afforded upon substitution at the benzylic or allylic (or both) positions.

2.6 Experimental Section

*Preparation of α-alkoxysilanes – General procedure **A***. Trichloroacetimidate of the appropriate alcohol (prepared according to literature procedure)[24] (2.0 equiv) was added to a stirred solution of the requisite α-(trimethylsilyl)allyl alcohol[3d] (1.0 equiv) in cyclohexane or hexane (0.2 M) at room temperature. A solution of TMSOTf (0.055 equiv) in cyclohexane or hexane (usually 0.1 mL/1.0 mL cyclohexane) or, alternatively, BF_3•OEt_2 in dry diethyl ether, was then added dropwise. White precipitate formed upon addition of the Lewis acid. The reaction mixture was stirred at room temperature until completion as judged by ^{1}H NMR (typically overnight) and filtered through a plug of celite. The precipitate was then washed with pentane or hexane (precipitate is soluble in ether) and the filtrate diluted with ether. The diluted filtrate was subsequently washed with $NaHCO_{3(sat)}$ (twice), 1M HCl (twice), and lastly with brine (twice). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to furnish the crude product. Purification by column chromatography on silica gel (0–2% EtOAc in hexane gradient) afforded the pure product.

*Preparation of compound **5***

Applying the general procedure **A** to 6.75 g (46.86 mmol) of (*E*)-1-(trimethylsilyl)but-2-en-1-ol, 17.75 g (70.29 mmol) and the trichloroacetimidate of benzyl alcohol and BF_3•OEt_2 (0.65 mL, 5.15 mmol) in cyclohexane afforded 2.11 g (34%) of **5** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 5 H), 5.55–5.39 (m, 2 H), 4.69–4.65 (d, *J* = 12.4 Hz, 1 H), 4.37–4.28 (d, *J* = 12.4 Hz, 1 H), 3.52–3.50 (d, *J* = 7.1 Hz, 1 H), 1.74–1.72 (d, *J* = 4.7 Hz, 3 H), 0.01 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 129.7, 128.0 (2 C), 127.5 (2 C), 127.0, 125.1, 75.1, 71.3, 18.0, –3.7. HRMS (CI) *m/z* 252.1775 [$(M+NH_4)^+$; calcd for $C_{14}H_{22}OSi$, 252.1784].

*Preparation of compounds **9***

Applying general procedure **A** to 4.01 g (30.82 mmol) of □-hydroxysilane 1-(trimethylsilyl)-prop-2-en-1-ol, 17.25 g (58.57 mmol) of the trichloroacetimidate of 2-methyl-1-phenylpropan-1-ol, and 0.38 g (1.70 mmol) of TMSOTf, and stirring the reaction overnight afforded 5.7 g (79%) of **9** as a 1:1 mixture of diastereomers. *Compounds syn*-**9**/*anti*-**9b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.10 (m, 10 H), 5.83–5.68 (m, 2 H), 5.06–4.87 (m, 4 H), 4.56–4.46 (m, 2 H), 3.82–3.80 (dt, *J* = 6.9, 1.4 Hz, 1 H), 3.43–3.41 (dt, *J* = 6.9, 1.4 Hz, 1 H), 1.39 (d, *J* = 6.6 Hz, 3 H), 1.35 (d, *J* = 6.6 Hz, 3 H), 0.06 (s, 9 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 144.2, 137.6, 128.4, 128.0, 127.9, 127.1, 126.7, 126.6, 125.8, 112.1, 111.7, 76.0, 75.6, 74.1, 73.2, 24.8, 22.3, –3.7, –3.8. HRMS (EI) *m/z* 234.1434 [$(M)^+$; calcd for $C_{14}H_{22}OSi$, 234.1440]. *anti*-**9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.21 (m, 5 H), 5.82–5.70 (m, 1 H), 5.05–4.95 (m, 2 H), 4.56–4.49 (q,

J = 6.6, Hz, 1 H), 3.43–3.40 (dt, *J* = 7.1, 1.3 Hz, 1 H), 1.39 (d, *J* = 6.6 Hz, 3 H), 0.00 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 137.8, 128.2, 127.2, 126.8, 112.2, 75.7, 73.3, 24.6, –3.9. IR (neat) 2972, 2928, 2899, 1628, 1493, 1452, 1248 cm^{-1}. HRMS (EI) *m/z* 234.1428 [$(M)^+$; calcd for $C_{14}H_{22}OSi$, 234.1440].

*Preparation of compound **12***

12 was prepared following a procedure reported in literature.[25] Allyltrimethylsilane 1-(trimethylsilyl)prop-2-en-1-ol (1.26 g, 11.0 mmol, 1.75 mL), benzaldehyde (1.67 g, 11.0 mmol, 1.12 mL), and TMSOTf (0.36 mL, 2.0 mmol, 0.44 g) were successively added to a stirred cold (–78 ^{o}C) solution of α-(trimethylsilyl)allyl trimethysilyl ether (2.0 g, 10.0 mmol) in CH_2Cl_2 (100 mL). The reaction was stirred for 70 min and then quenched with $NaHCO_3$ (aq. sat.). The aqueous phase was extracted with CH_2Cl_2 (100 mL x 4), and the combined organic layers were washed with $NaHCO_3$ (100 mL x 2), brine (100 mL x 2), and then dried over $MgSO_4$. Filtration and concentration afforded the crude product as a 1:2.56 mixture of diastereomers. After silica gel chromatography 1.96 g (7.58 mmol) of the pure products were obtained in a combined yield of 77%. The pair of diastereomers is separable by column chromatography on silica gel (5% and 10% CH_2Cl_2 in hexanes). *Compound anti*-**12**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5 H), 5.88–5.69 (m, 2 H), 5.05–4.95 (m, 4 H), 4.46–4.42 (dd, *J* = 7.7, 5.8 Hz, 1 H), 3.44–3.42 (d, *J* = 7.4 Hz, 1 H), 2.59–2.49 (quint, *J* = 7.7 Hz, 1 H), 2.39–2.30 (quint, *J* = 6.86, 1 H), –0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 137.7, 135.4, 128.1 (2 C), 127.4 (3 C), 116.3, 112.9,

79.3, 73.0, 43.03, –4.0. HRMS (CI) *m/z* 261.1664 [$(M+H)^+$; calcd for $C_{16}H_{24}OSi$, 261.1675]. *Compound syn*-**12**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.30–7.20 (m, 5 H), 5.79–5.60 (m, 2 H), 5.01–4.80 (m, 4 H), 4.39–4.35 (t, *J* = 6.2 Hz, 1 H), 3.82–3.78 (dt, *J* = 7.1, 1.3 Hz, 1 H), 2.54–2.40 (m, 2 H), 0.05 (s, 9 H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.6, 137.9, 134.9, 127.8 (2 C), 126.9, 126.6 (2 C), 116.8, 111.9, 81.1, 75.8, 41.5, –3.7. HRMS (CI) *m/z* 261.1681 [$(M+H)^+$; calcd for $C_{16}H_{24}OSi$, 261.1675].

*Preparation of compound **15***

Applying general procedure **A** to 0.88 g of 1-(trimethylsilyl)-prop-2-en-1-ol (6.73 mmol), 3.96 g of the trichloroacetimidate of 1-phenylbutan-1-ol (13.45 mmol, 2 equiv) and 0.07 mL of TMSOTf (0.4 mmol, 0.055 equiv) overnight afforded 1.32 g of **15** (75%) as a 1:1 mixture of diastereomers after column chromatography (0–2% EtOAc gradient). IR (neat) 1628 cm^{-1}. *Compound anti*-**15**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.31–7.19 (m, 5 H), 5.77–5.70 (m, 1 H), 5.03–4.92 (dd, *J* = 10.6, 17.2 Hz, 2 H), 4.07–4.06 (d, *J* = 7.5 Hz, 1 H), 3.39–3.37 (d, *J* = 8.0 Hz, 1 H), 1.91–1.85 (m, 1 H), 1.01–1.00 (d, *J* = 6.6 Hz, 3 H), 0.72–0.70 (d, *J* = 7.1 Hz, 3 H), –0.01 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 138.0, 128.1 (2 C), 127.8, 127.1 (2 C), 113.1, 84.7, 72.6, 35.0, 19.2, 19.0, -4.0. HRMS (APCI) *m/z* 263.1821 [$(M+H)^+$; calcd for $C_{16}H_{27}OSi$, 263.1831]. *Compound syn*-**15**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.17 (m, 5 H), 5.64–5.53 (m, 1 H), 4.89–4.72 (dd, *J* = 10.7, 16.7 Hz, 2 H), 4.01–3.99 (d, *J* = 6.9 Hz, 1 H), 3.72–3.68 (d, *J* = 7.4 Hz, 1 H), 1.99–1.89 (m, 1 H), 0.93–0.91 (d, *J* = 6.9 Hz, 3 H), 0.77–0.74 (d, *J* = 6.9 Hz, 3 H),

0.05 (s, 9 H), 0.08 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 138.2, 127.4 (2 C), 127.3 (2 C), 126.5, 111.4, 87.5, 76.6, 34.5, 18.7 (2 C), –3.5. HRMS (APCI) *m/z* 263.1821 [$(M)^+$; calcd for $C_{16}H_{27}OSi$, 263.1831].

*Preparation of compound E-**21***

Applying general procedure **A** to 3.6 g of (*E*)-1-(trimethylsilyl)but-2-en-1-ol (24.98 mmol),[3d] 13.32 g of the trichloroacetimidate of phenethyl alcohol (49.5 mmol, 2 equiv) and 0.47 mL of BF_3•OEt_2 (3.74 mmol, 0.15 equiv) afforded 3.07 g of *E*-**21** (39%). *Compounds E*-**21** (mixture of diastereomers *anti/syn* 0.58:0.42): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.19 (m, 5 H), 5.42–5.31 (m, 2 H), 4.52 (q, *J* = 6.5 Hz, 0.58 H), 4.49 (q, *J* = 6.0 Hz, 0.42 H), 3.69 (d, *J* = 7.0 Hz, 0.42 H), 3.29 (d, *J* = 7.0 Hz, 0.58 H), 1.71 (d, *J* = 5.5 Hz, 1.74 H), 1.61 (d, *J* = 6.0 Hz, 1.26 H), 1.35 (d, *J* = 6.5 Hz, 1.74 H), 1.32 (d, *J* = 6.0 Hz, 1.26 H), 0.03 (s, 3.78 H), –0.05 (s, 5.22 H). ^{13}C NMR (125 MHz, $CDCl_3$) *anti E*-**21**: δ144.6, 130.2, 128.1 (2 C), 127.0, 126.8 (2 C), 124.6, 75.0, 72.4, 24.7, 17.9, –3.9. *syn E*-**21**: δ 145.8, 130.4, 127.9 (2 C), 126.6, 125.9 (2 C), 124.0, 75.2, 73.2, 22.0, 17.8, –3.8. HRMS (CI) *m/z* 248.1591 [$(M)^+$; calcd for $C_{15}H_{24}OSi$, 248.1596].

*Preparation of compound Z-**21***

Following the general procedure **A** to 3.49 g of 1-(trimethylsilyl)but-2-yn-1-ol (24.53 mmol) and 13.1 g of the trichloroacetimidate of *sec*-phenethyl alcohol (49.06 mmol, 2 equiv) in cyclohexane (140 mL) at 0 ^{o}C was added 0.46 mL of BF_3•OEt_2 (3.68 mmol, 0.15 equiv). After 1 hour the

reaction was stopped, worked up according to the general procedure **A** followed by column chromatography (8% DCM in hexanes) to afford 5 g (83%) of diastereomeric alkyne **28** as colorless oil (diastereomers partially separated). Alkyne reduction: To a solution of 1.435 g of **28** (5.82 mmol, dr = 1:1) in hexanes (210 mL) was added Et_3N (2.6 mL, 2.5 mL/mmol **28**) and Lindlar's catalyst (38.8 mg, 37.5 mg/mmol **28**). The flask was flushed with hydrogen and a hydrogen balloon attached. The mixture was vigorously stirred and the reaction monitored by NMR (about 4 h). The reaction mixture was partially concentrated, filtered through a plug of celite and fully concentrated. Column chromatography (10% DCM in hexanes) afforded 900 mg (62%) of *Z*-**21**. Note: Pure alkyne **28** decomposes relatively quickly after isolation and its decomposition products appear to poison the catalyst and hamper reduction thus requiring addition of more catalyst. Samples of **28** stored at –20 ^{o}C slowly decomposed turning yellow, such samples in hexanes were filtered through a short silica gel plug and rinsed with more hexanes. After concentration clean **28** was immediately submitted to the reduction reaction. Spectroscopic data for *anti*-**28**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.23 (m, 5 H), 4.79 (q, *J* = 6.5 Hz, 1 H), 3.43 (q, *J* = 2.5 Hz, 1 H), 1.88 (d, *J* = 2.5 Hz, 3 H), 1.40 (d, *J* = 7.0 Hz, 3 H), 0.06 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 128.3 (2 C), 127.3, 126.8 (2 C), 82.7, 77.6, 76.3, 60.5, 24.4, 3.9, –4.0. Spectroscopic data for *syn*-**28**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2 H), 7.30 (m, 2 H), 7.21 (tt, *J* = 1.5, 7.5 Hz, 1 H), 4.71 (q, *J* = 6.5 Hz, 1 H), 3.88 (q, *J* = 2.5 Hz, 1 H), 1.78 (d, *J* = 2.5 Hz, 3 H), 1.36 (d, *J* = 6.5 Hz, 3 H), 0.12 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 128.0 (2 C), 126.8, 126.1 (2 C), 83.1, 77.6, 76.1, 61.0, 21.4, 3.8, –3.8. IR

(neat) 2963, 2203, 1248, 1082, 843 cm^{-1}. HRMS (EI) *m/z* 246.1444 [$(M)^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

Spectroscopic data for *anti Z*-**21**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.0 Hz, 2 H), 7.23 (m, 3 H), 5.50 (ddq, *J* = 1.0, 7.0, 11.0 Hz, 1 H), 5.39 (ddq, *J* = 1.5, 10.5, 11.0 Hz, 1 H), 4.44 (q, *J* = 6.5 Hz, 1 H), 3.67 (d, *J* = 10.5 Hz, 1 H), 1.35 (ddd, *J* = 0.5, 2.0, 7.0 Hz, 3 H), 1.34 (d, *J* = 6.5 Hz, 3 H), –0.03 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 130.5, 128.1 (2 C), 127.1, 126.9 (2 C), 124.4, 75.6, 67.4, 24.6, 13.4, –3.9. HRMS (ESI) *m/z* 249.1663 [$(M+H)^+$; calcd for $C_{15}H_{25}OSi$, 249.1675]. Spectroscopic data for *syn Z*-**21** ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.26 (m, 4 H), 7.20 (m, 1 H), 5.43–5.32 (m, 2 H), 4.45 (q, *J* = 6.5 Hz, 1 H), 4.13 (d, *J* = 9.5 Hz, 1 H), 1.51 (m, 3 H), 1.34 (d, *J* = 6.5 Hz, 3 H), 0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 130.9, 127.9 (2 C), 126.7, 126.0 (2 C), 123.2, 75.8, 68.4, 22.0, 13.5, –3.8. HRMS (ESI) *m/z* 249.1675 [$(M+H)^+$; calcd for $C_{15}H_{25}OSi$, 249.1675].

Wittig rearrangements of α-alkoxysilanes – General procedure **B**. A solution of □-alkoxysilane (1.0 equiv) in freshly distilled THF (0.06–0.07 M) was cooled to the desired temperature under nitrogen. The required amount of *s*-BuLi (1.5–4.0 equiv, 1.3 M in cyclohexane) or *n*-BuLi (1.6 M in hexanes) was added dropwise via syringe. The reaction mixture was stirred at the reaction temperature for the desired length of time, then quenched with $NH_4Cl_{(sat)}$ and diluted with ether. Phases separated and the organic phase was washed with water and brine. The organic phase was

dried over anhydrous $MgSO_4$ and concentrated. Silica gel chromatography (0 to 2% EtOAc in hexane gradient) afforded the rearranged products usually as light oils.

*Wittig rearrangements of compound **5***

Applying the General procedure **B** to 141 mg (0.60 mmol) of **5** and 0.69 mL (0.90 mmol) of *sec*-BuLi (1.3 M in cyclohexane) at –78 °C for for 30 min, after purification by column chromatography on silica gel, afforded 106 mg (75%) of a 4:1 mixture of both [1,4]- and [1,2]-rearrangement products **6** (a light yellow oil) and **7** as a colorless oil. *Compound* **6**: ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.32–7.17 (m, 5 H), 2.61–2.50 (m, 2 H), 2.47–2.30 (m, 3 H), 0.84–0.81 (d, *J* = 6.6 Hz, 3 H), –0.13 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) □ 248.6, 140.6, 129.2 (2C), 128.2 (2C), 125.9, 54.9, 43.3, 29.6, 19.9, –3.3. IR (neat) 1709 cm^{-1}. HRMS (EI) *m/z* 233.1355 [(M–H)$^{+}$; calcd for $C_{14}H_{21}OSi$, 233.1362]. *Compound* **7**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.10 (m, 5 H), 5.60–5.56 (dq, *J* = 15.4, 1.6 Hz, 1 H), 5.19–5.12 (apparent dq, *J* = 15.4, 6.6 Hz, 1H), 2.86 (d, *J* = 7.7 Hz, 1 H), 2.81 (d, *J* = 7.7 Hz, 1 H), 1.64–1.62 (dd, *J* = 6.6, 1.6 Hz, 3 H), 0.05 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2, 135.4, 130.6 (2 C), 127.9 (2 C), 126.3, 121.62, 70.4, 43.1, 17.8, –4.2. IR (neat) 3432 cm^{-1}. HRMS (EI) *m/z* 234.1435 [(M)$^{+}$; calcd for $C_{14}H_{22}OSi$, 234.1440].

*Wittig rearrangements of compound **9***

Applying General procedure **B** to 360 mg (1.53 mmol) of **9** and 1.8 mL (2.30 mmol) of *s*-BuLi (1.3 M in cyclohexane) at –78 °C overnight, afforded 162 mg (46%) of a 1.68:1 mixture of **10** and **11** as a colorless oils. *Compound* **10**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.12 (m, 5 H), 2.67–2.57 (m, 1 H), 2.54–2.41 (m, 1 H), 1.89–1.67 (m, 2 H), 1.24–1.21 (d, *J* = 7.1 Hz, 3 H), 0.11 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 248.2, 146.6, 128.4, 127.0, 126.0, 46.4, 39.3, 30.2, 22.4, –3.2. IR (neat) 1643 cm^{-1}. HRMS (EI) *m/z* 233.1358 [$(M–H)^+$; calcd for $C_{14}H_{21}OSi$, 233.1362]. *Compound* **11**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.19 (m, 5 H), 3.82–3.75 (q, *J* = 6.9 Hz, 1 H), 2.34–2.28 (m, 2 H), 1.38 (d, *J* = 6.9 Hz, 3 H), 0.77–0.55 (m, 2 H), –0.11 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.8, 140.8, 128.8 (2 C), 127.8 (2 C), 127.0, 52.3, 35.6, 17.7, 10.3, –1.9. IR (neat) 1717, 1601 cm^{-1}. HRMS (CI) *m/z* 234.1466 [$(M)^+$; calcd for $C_{14}H_{22}OSi$, 234.1440].

*Wittig rearrangements of compound **12***

Applying General procedure **B** to 165 mg (0.638 mmol) of **12** and 1.6 mL of *n*-BuLi (2.55 mmol, 4 equiv, 1.6 M in hexanes) at –78 ^{o}C, allowing the reaction to warm to –30 ^{o}C and stirring at this temperature for about 48 h, after purification by column chromatography on silica gel afforded 45 mg (32%) of a 4.53:1 mixture of **13** and **14** as light yellow oils. Note: the reported yield is based on 2.64:1 diastereomeric ratio of *anti* / *syn* **12**. *Compound* **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.16 (m, 5 H), 5.78–5.60 (m, 1 H), 5.00–4.89 (m, 2 H), 2.58–2.52 (m, 1 H),

2.50–2.45 (m, 1 H), 2.39–2.31 (m, 3 H), 2.00–1.93 (m, 1 H), 1.72–1.64 (m, 1 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.1, 144.4, 136.8, 128.4 (2 C), 127.7 (2 C), 126.2, 116.0, 46.1, 45.1, 41.4, 27.9, –3.2. IR (neat) 1717, 1643 cm^{-1}. HRMS (EI) *m/z* 260.1595 [$(M)^+$; calcd for $C_{16}H_{24}OSi$, 260.1596].

Compound **14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.08 (m, 5 H), 5.68–5.60 (m, 1 H), 5.00–4.91 (m, 2 H), 3.72 (t, *J* = 7.4 Hz, 1 H), 2.81–2.75 (m, 1 H), 2.45–2.39 (m, 1 H), 2.31 (m, 2 H), 0.74–0.68 (m, 1 H), 0.62–0.56 (m, 1 H), –0.11 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 138.6, 135.9, 128.8 (2C), 128.2 (2C), 127.2, 116.6, 58.1, 36.7, 36.5, 10.1, –1.9. IR (neat) 1716, 1643 cm^{-1}. HRMS (EI) *m/z* 260.1593 [$(M)^+$; calcd for $C_{16}H_{24}OSi$, 260.1596].

*Wittig rearrangements of compound **15***

Applying General procedure **B** to 69.5 mg of *syn*-**15** (0.265 mmol) and 0.33 mL of *n*-BuLi (0.5296 mmol, 2 equiv) in THF (3.3 mL) at –78 ºC and then at 0 ^{o}C for 17 H afforded a mixture (15.8 mg) of **16** and **17** in a combined 23% yield as colorless oil along with 18.6 mg of unreacted *syn*-**15**. Column chromatography was performed with 3% EtOAc in hexanes. Spectroscopic data for **16**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.03 (m, 5 H), 2.39–2.35 (m, 1 H), 2.30–2.24 (m, 1 H), 2.20–2.15 (m, 1 H), 2.08–2.02 (m, 1 H), 1.80–1.73 (m, 1 H), 1.71–1.63 (m, 1 H), 0.94 (d, *J* = 6.8 Hz, 3 H), 0.68 (d, *J* = 6.8 Hz, 3 H), 0.06 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.6, 143.8, 128.4 (2 C), 128.1 (2 C), 126.0, 52.4, 33.7, 25.2, 20.9, 15.3, –3.3. IR (neat) 1719, 1643

cm^{-1}. HRMS (APCI) m/z 263.1840 $[(M+H)^+$; calcd for $C_{16}H_{27}OSi$, 263.1831]. Spectroscopic data for **17**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.29–7.20 (m, 5 H), 3.30 (d, *J* = 10.2 Hz, 1 H), 2.42–2.25 (m, 3 H), 0.94 (d, *J* = 6.3 Hz, 3 H), 0.74–0.67 (m, 1 H), 0.63 (d, *J* = 6.8 Hz, 3 H), 0.61–0.54 (m, 1 H), –0.11 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.7, 138.4, 128.7 (2C), 128.6 (2C), 127.0, 66.4, 37.8, 30.7, 21.7, 20.4, 9.9, –1.9. IR (neat) 1715 cm^{-1}. HRMS (CI) m/z 262.1755 $[(M)^+$; calcd for $C_{16}H_{26}OSi$, 262.1753].

*Wittig rearrangements of anti / syn E-**21***

Applying representative procedure **B** to 235 mg (0.946 mmol) of *E*-**21** (*anti*/*syn* = 1.5:1) and 2.36 mL of *n*-BuLi (3.78 mmol, 4 equiv, 1.6 M in hexanes) in THF (12 mL) at –30 ^oC for 44 h. After purification by column chromatography on silica gel (30% CH_2Cl_2 in hexanes) 101 mg of *anti E*-**21** (43%), 10.1 mg of **22** (16%) and 72 mg of a mixture of **23** (23%, *anti/syn* = 1.9:1) and **24** (6%, *anti/syn* = 1.44:1) were obtained. Analytical samples of **23** and **24** were obtained by subsequent column chromatography of the mixture (30% CH_2Cl_2 in hexanes). *Compound* **22**: (mixture of diastereomers *anti-**22**/syn*-**22**, 0.65:0.35 ratio): ^1H NMR (600 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2 H), 7.18–7.12 (m, 3 H), 2.64 (m, 0.65 H), 2.61 (m, 0.65 H), 2.52 (m, 0.35 H), 2.46 (m, 0.35 H), 2.38–2.26 (m, 2 H), 1.21 (d, *J* = 6.6 Hz, 1.05 H), 1.20 (d, *J* = 7.2 Hz, 1.95 H), 0.84 (d, *J* = 6.6 Hz, 1.05 H), 0.70 (d, *J* = 6.6 Hz, 1.95 H), 0.14 (s, 5.85 H), 0.08 (s, 3.15 H). ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer (*anti*-**22**): δ 248.6, 145.4, 128.1 (2 C), 127.9 (2 C), 126.0,

53.0, 44.6, 33.5, 18.2, 18.04, –3.16. Minor diastereomer (*syn*-**22**): δ 248.7, 146.3, 128.2 (2 C), 127.6 (2 C), 126.0, 54.0, 45.0, 33.8, 18.05, 17.4, –3.25. IR (neat) 1643 cm^{-1}. HRMS (ESI) *m/z* 249.1665 [$(M+H)^+$; calcd for $C_{15}H_{25}OSi$, 249.1675]. *Compound* **23** (mixture of diastereomers, 0.88:0.12 ratio, relative stereochemistry not assigned): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26–7.14 (m, 5 H), 5.72 (dd, *J* = 1.2, 15.6 Hz, 0.12 H), 5.59 (dd, *J* = 1.2, 15.6 Hz, 0.88 H), 5.28 (dq, *J* = 6.6, 15.6 Hz, 0.12 H), 5.12 (dq, *J* = 6.6, 15.6 Hz, 0.88 H), 3.04 (q, *J* = 7.2 Hz, 0.88 H), 3.00 (q, *J* = 7.2 Hz, 0.12 H), 1.71 (dd, *J* = 1.8, 6.6 Hz, 0.36 H), 1.61 (dd, *J* = 1.2, 6.6 Hz, 2.64 H), 1.32 (d, *J* = 7.2 Hz, 2.64 H), 1.27 (d, *J* = 7.2 Hz, 0.36 H), 1.03 (s, 0.12 H), 1.02 (s, 0.88 H), –0.03 (s, 7.92 H), –0.09 (s, 1.08 H). ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer: δ 142.8, 135.1, 128.9 (2 C), 127.8 (2 C), 126.3, 120.8, 73.6, 46.8, 17.8, 16.4, –2.5. Minor diastereomer: δ 143.0 133.5, 129.2 (2 C), 127.9 (2 C), 126.6, 122.0, 73.4, 46.9, 18.0, 16.5, –3.0. HRMS (CI) *m/z* 249.1666 [$(M+H)^+$; calcd for $C_{15}H_{24}OSi$, 249.1675]. *Compound* **24** (mixture of diastereomers, *anti*-***24***/*syn*-**24**, 0.55:0.45) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.24–7.20 (m, 3 H), 3.78 (q, *J* = 7.2 Hz, 0.55 H), 3.71 (q, *J* = 7.2 Hz, 0.45 H), 2.36 (m, 0.45 H), 2.33 (m, 0.55 H), 2.14 (dd, *J* = 10.2, 16.8 Hz, 0.45 H), 2.08 (dd, *J* = 10.8, 16.2 Hz, 0.55 H), 1.38 (d, *J* = 6.6 Hz, 1.35 H), 1.37 (d, *J* = 7.2 Hz, 1.65 H), 1.18 (m, 0.55 H), 1.13 (m, 0.45 H), 0.82 (d, *J* = 7.8 Hz, 1.35 H), 0.69 (d, *J* = 7.2 Hz, 1.65 H), –0.118 (s, 4.95 H), –0.160 (s, 4.05 H). ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer (*anti*-**24**): δ 210.8, 140.6, 128.8 (2 C), 127.91 (2 C), 127.05, 52.2, 43.3, 17.6, 15.3, 14.1, –3.55. Minor diastereomer (*syn*-**24**): δ 211.4, 128.7 (2 C), 127.89 (2 C), 127.03, 53.6, 43.5,

17.4, 15.5, 14.7, –3.54. IR (neat) 1718 cm^{-1}. HRMS (ESI) *m/z* 249.1667 [$(M+H)^+$; calcd for $C_{15}H_{25}OSi$, 249.1675].

*Wittig rearrangement of compound syn Z-**21***

Following the general procedure **B** to 253.8 mg of *syn Z*-**21** (1.02 mmol) in 10.5 mL of THF at –78 ^oC was added 2.56 mL of *n*-BuLi (4.086 mmol, 4 equiv, 1.6 M in hexanes), the cold bath was removed and the reaction stirred at room temperature for 48 h. After work up and column chromatography (gradient of 2–10% EtOAc in hexanes, then 50% EtOAc in hexanes) afforded 142.1 mg of *syn Z*-**21** (56%, dr = 18:1), 11.1 mg of a 1:1 mixture of **22** (*syn/anti* = 1.1:1) and **24** (*syn/anti* = 1:1.6), 15.6 mg of **25** (6%, single diastereomer), 13 mg of **26** (7%, dr = 3:1) and 5.4 mg of **27** (3%, *syn/anti* = 1.3:1). *Compound* **25**: (tentatively assigned as *syn*-**25**):[18] ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2 H), 7.31 (m, 2 H), 7.21 (tt, *J* = 1.5, 7.5 Hz, 1 H), 5.97 (dd, *J* = 8.0, 19.0 Hz, 1 H), 5.70 (dd, *J* = 1.0, 19.0 Hz, 1 H), 2.52 (m, 1 H), 1.85 (s, 1 H), 1.50 (s, 3 H), 0.84 (d, *J* = 6.5 Hz, 1 H), 0.04 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 147.0, 132.4, 127.8 (2C), 126.4, 125.2 (2C), 75.9, 51.4, 28.3, 14.5, –1.2. IR (neat) 3474 cm^{-1}. HRMS (ESI) *m/z* 249.1680 [$(M+H)^+$; calcd for $C_{15}H_{25}OSi$, 249.1675]. *Compound* **26**: (mixture of diastereomers, 0.63:0.37 ratio): ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 3 H), 7.19 (m, 2 H), 5.68 (m, 0.37 H), 5.49 (m, 0.63 H), 5.40 (m, 0.37 H), 5.31 (m, 0.63 H), 4.51 (m, 1 H), 1.66 (ddd, *J* = 0.5, 2.0, 7.0 Hz, 1.11 H), 1.53 (ddd, *J* = 0.5, 1.5, 6.5 Hz, 1.89 H), 1.43 (s, 1 H), 1.33 (dd, *J* = 0.5, 7.0 Hz, 1.89 H), 1.21 (dd, *J* = 0.5, 7.5 Hz, 1.11 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

143.28, 143.26, 131.33, 131.30, 128.6, 128.2, 128.1, 128.1, 127.7, 126.9, 126.7, 126.4, 71.7, 71.5, 46.6, 45.9, 17.5, 16.0, 13.5, 13.2. IR (neat) 3397 cm^{-1}. *Compound* **27**: (mixture of diastereomers 1:1 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (m, 1 H) 9.57 (m, 1 H), 7.28 (m, 4 H), 7.18 (m, 2 H), 7.14 (m, 4 H), 2.67 (m, 1 H), 2.56 (m, 1 H), 2.49 (ddd, *J* = 1.0, 4.5, 16.0 Hz, 1 H), 2.33–2.26 (m, 3 H), 2.17 (ddd, *J* = 3.0, 9.0, 16.0 Hz, 1 H), 2.07 (ddd, *J* = 2.5, 8.5, 16.0 Hz, 1 H), 1.26 (d, *J* = 2.5 Hz, 3 H), 1.25 (d, *J* = 2.5 Hz, 3 H), 0.99 (d, *J* = 6.5 Hz, 3 H), 0.85 (d, *J* = 6.5 Hz, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.8, 202.5, 145.7, 144.8, 128.4, 128.2, 127.8, 127.5, 126.3, 126.2, 49.5, 48.3, 45.1, 44.5, 34.6, 34.4, 18.4, 18.03, 17.98, 17.6. IR (neat) 1724 cm^{-1}. Diastereomers **27** are known compounds and have spectral data in accord with those previously reported.[10]

*Preparation of diastereomeric **18***

A 100 mL round-bottomed flask equipped with a magnetic stir bar and a nitrogen line was charged with 9-BBN (0.5 M solution in THF, 2.04 mL, 1.02 mmol) and substrate **9** (671 mg, 2.85 mmol) was then added as a THF solution (0.57 M). The reaction was refluxed at an oil bath temperature of 90 °C, for 10 h. The reaction mixture was cooled to 55 to 65 ºC and ethanol (2.0 mL), NaOH (6 M, 0.5 mL) and H_2O_2 (30% w/w, 1.0 mL) were added. The reaction was stirred at 55 to 65 °C for 1 h and cooled to room temperature. The aqueous phase was saturated with potassium carbonate, phases were separated, the organic phase was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by silica gel (EtOAc 0–10% in hexanes) gave 702 mg of pure *syn*-**18**/*anti*-**18** in 97% yield. IR (neat) 3370

cm^{-1}. Compound *anti*-**18**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.23 (m, 5 H), 4.56 (q, *J* = 6.5 Hz, 1 H), 3.86 (m, 1 H), 3.78 (m, 1 H), 3.23 (t, *J* = 5.0 Hz, 1 H), 2.75 (m, 1 H), 2.20–2.13 (m, 1 H), 1.63 (m, 1H), 1.42 (d, *J* = 6.5 Hz, 3 H), –0.06 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 128.2 (2 C), 127.5, 126.8 (2 C), 76.4, 70.1, 62.4, 31.7, 23.7, –2.8. HRMS (EI) *m/z* 253.1618 [$(M+H)^+$; calcd for $C_{14}H_{25}O_2Si$, 253.1624]. Compound *syn*-**18**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.29 (m, 1H), 4.36 (q, *J* = 6.5 Hz, 1 H), 3.54–3.45 (m, 2 H), 3.26 (dd, *J* = 4.5, 9.5 Hz, 1 H), 1.81 (m, 1 H), 1.67-1.60 (m, 2 H), 1.42 (d, *J* = 6.5 Hz, 3 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 128.5 (2 C), 127.8, 126.8 (2 C), 77.9, 69.1, 61.3, 33.8, 23.6, –2.5. HRMS (EI) *m/z* 253.1627 [$(M+H)^+$; calcd for $C_{14}H_{25}O_2Si$, 253.1624].

*Preparation of ester syn-**19***

A mixture of the substrate alcohol (obtained by 9-BBN oxidation of reactive *syn*-**18** (201 mg, 0.80 mmol), and 3,5-dinitrobenzoyl chloride (366 mg, 1.59 mmol) in pyridine as solvent, was heated to reflux for 52–55 h. Then the solvent was removed under reduced pressure and the crude product purified by chromatography on silica gel (hexanes/EtOAc (0–10%) to afford 194 mg, 55% of the expected ester *syn*-**19** as a solid. Recrystallization from a 1:1 EtOH/hexane mixed solvent afforded product as colorless crystals mp 74.5–75.5 ^{o}C. IR (neat) 1728, 1630 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (t, *J* = 2.2 Hz, 1 H), 8.88 (d, *J* = 2.2 Hz, 2 H), 7.29–6.99 (m, 5 H), 4.36–4.29 (m, 2 H), 4.18–4.10 (m, 1 H), 3.25–3.20 (dd, *J* = 8.0, 6.0 Hz, 1 H), 1.90–1.83 (m, 2 H), 1.41 (d, *J* = 6.3 Hz, 3 H), 0.15 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2,

148.4, 143.9, 134.0, 129.2, 128.2, 127.4, 126.7, 122.1, 78.1, 66.7, 64.4, 30.6, 23.6, –2.7. HRMS (ESI) *m/z* 447.1599 [$(M+H)^+$; calcd for $C_{21}H_{27}N_2O_7Si$, 447.1587].

*Preparation of cis-**20** and trans-**20***

To a solution of unreactive (*anti*) **12** (167 mg, 0.641 mmol) in CH_2Cl_2 (10 mL, ~0.7 M) was added second-generation Grubbs catalyst (4 mol%, 21.4 mg, 0.025 mmol) and the solution was stirred under nitrogen at room temperature for 3 h. The reaction mixture was concentrated and purified by column chromatography (10% CH_2Cl_2 in hexanes) to afford 144 mg 72 of *cis*-**20** (97%). *Compound cis*-**20**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.22 (m, 5 H), 5.82–5.78 (m, 2 H), 4.38 (dd, *J* = 3.5, 10 Hz, 1 H), 4.17–4.15 (m, 1 H), 2.26–2.12 (m, 2 H), 0.08 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 128.10 (2 C), 128.06, 126.9, 125.6 (2 C), 121.1, 75.3, 71.6, 34.2, –4.0. HRMS (CI) *m/z* 261.1681 [$(M+H)^+$; calcd for $C_{16}H_{24}OSi$, 261.1675]. The relative stereochemistry of *cis*-**20** was assigned based on positive NOESY signals between protons at 4.15 ppm and 2.26–2.12 ppm. Following the same procedure for *syn*-**12** (184 mg, 0.707 mmol) and Grubbs second-generation catalyst (4 mol%, 24 mg, 0.028 mmol) in CH_2Cl_2 for 3 h, followed by column chromatography (30% CH_2Cl_2 in hexanes) afforded 151 mg (92%) of *trans*-**20**. *Compound trans*-**20**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.24 (m, 5 H), 5.83-5.76 (m, 2 H), 4.72 (t, *J* = 5.5 Hz, 1 H), 4.01 (m, 1 H), 2.41–2.38 (m, 2 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 128.5 (2C), 128.4, 127.5, 126.9 (2C), 120.3, 72.6, 70.4, 30.4, –2.7. HRMS (CI)

m/z 261.1664 [$(M+H)^+$; calcd for $C_{16}H_{24}OSi$, 261.1675]. The relative stereochemistry of *trans*-**20** was confirmed based on negative NOESY signals between protons at 4.72 ppm and 4.01 ppm.

*Preparation of compound **29***

The [1,4]-Wittig product **23** from the Wittig rearrangement of □-alkoxysilane of *E*-**21** (217 mg, 0.87 mmol) was dissolved in THF (0.24 M, 3.6 mL), and 3M NaOH (0.83 mL/mmol starting material, 0.72 mL) added. The mixture was heated to 35–40 ^oC, and then oxidized by dropwise addition of 30% H_2O_2 (0.42 mL/mmol starting material, 0.36 mL), while maintaining the reaction temperature below 50 ºC for 2 h. The aqueous phase was cooled to 0 ^oC, and acidified to pH of 1–2 with 6 M HCl. The resulting aqueous material was extracted with ether (5 x 20 mL), and the ether solution dried with anhydrous $MgSO_4$. Filtration and concentration afforded 158 mg (94% yield) of diastereomeric **29** as a thick colorless oil. Purification by column chromatography on silica gel (hexane/EtOAc 0–10%) afforded **29** as a 2.8:1 mixture of diastereomers (ratio by ^1H NMR). IR (neat) 3100–2500 (br), 2967, 1707, 1495, 1452, 1412, 1290 cm^{-1}. *Compounds anti*-**29**/*syn*-**29** (2.8:1 ratio), *anti*-**29**: ^1H NMR (500 MHz, $CDCl_3$) δ 11.49 (s, 1 H), 7.31–7.18 (m, 5 H), 2.72–2.65 (quint, *J* = 7.1 Hz, 1 H), 2.53–2.48 (dd, *J* = 14.8, 4.4 Hz, 1 H), 2.28–2.18 (m, 1 H), 2.14–2.09 (dd, *J* = 15.1, 9.1 Hz, 1 H), 1.28–1.26 (d, *J* = 7.1 Hz, 3 H), 0.88 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.8, 144.8, 128.2, 127.6, 126.2, 44.4, 38.9, 36.2, 18.3, 17.5. *syn*-**29**: δ 11.49 (br s, 1 H), 7.33–7.18 (m, 5 H), 2.63–2.56 (quint, *J* = 7.1 Hz, 1 H), 2.35–2.31 (apparent dd, *J* = 15.4, 4.4 Hz, 1 H), 2.28–2.18 (m, 1 H), 2.04–1.99 (dd, *J* = 14.8, 9.3 Hz, 1 H), 1.27–1.24 (d, *J* = 7.1 Hz, 3 H), 1.04 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.8, 145.7, 128.2, 127.5, 126.1, 44.7, 39.8, 36.4, 18.3, 17.2. *anti*-**29** and *syn*-**29** are known compounds and have spectral data in accord with those previously reported.[10]

Assignment of relative stereochemistry for compound **24**

Preparation of compound **30**

To a cold (–78 ^{o}C) solution of **24** (50 mg, 0.20 mmol, dr = 1.4:1) in 1:1 CH_2Cl_2/EtOH (3 mL) was added a suspension of $NaBH_4$ (15.2 mg, 2 equiv) in EtOH (0.8 mL). After 1 hour the cold bath was removed and the reaction kept at room temperature overnight. The reaction mixture was then treated with water (2 mL) and diluted with diethyl ether. The aqueous phase was washed with diethyl ether (x 2). Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (5% EtOAc in hexanes) gave 28.5 mg (57%) of **30** in two fractions of different diastereomeric ratio along with 5.2 mg (11%) of unreacted **24**. *Compounds* **30** (major diastereomer): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (m, 2 H), 7.20 (m, 3 H), 3.80 (m, 1 H), 2.72 (quint, *J* = 6.6 Hz, 1 H), 1.42 (m, 1 H), 1.31 (d, *J* = 7.2 Hz, 3 H), 1.29 (d, *J* = 4.8 Hz, 1 H), 1.07 (m, 1 H), 0.84 (s, 3 H), 0.82 (m, 1 H), –0.10 (m, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.8, 128.4 (2 C), 127.7 (2 C), 126.3, 73.0, 46.4, 36.3, 15.9, 15.0, 13.1, –3.6. IR (neat) 3423, 2955, 1456, 1248, 839 cm^{-1}. HRMS (ESI) m/z 232.1651 [(M–OH)$^{+}$; calcd for $C_{15}H_{24}Si$, 232.1647].

Preparation of compound **31**:

One fraction of **30** (15.6 mg, 0.063 mmol, dr = 10:2:1) was dissolved in pyridine (1 mL) and 3,5-dinitrobenzoyl chloride (flakes were crushed prior to addition) was added in one portion. After 48 hours the mixture was diluted with diethyl ether (15 mL) and washed with 1M HCl (2 mL x 3), H_2O, brine, dried over $MgSO_4$ and concentrated. Partial separation of the diastereomers (2 fractions) by column chromatography (4% EtOAc in hexanes) gave 24.4 mg (56%) of **31** as a solid. Recrystallization of one fraction from CH_2Cl_2 / hexanes gave a single diastereomer of **31** whose relative stereochemistry was determined by x-ray crystallography. *Compound* **31** (major diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (t, *J* = 2.0 Hz, 1 H), 9.13 (d, *J* = 2.0 Hz, 2 H), 7.30 (t, *J* = 7.5 Hz, 2 H), 7.22 (m, 3 H), 5.86 (m, 1 H), 3.09 (m, 1 H), 1.75 (ddd, *J* = 2.5, 10.0, 13.0 Hz, 1 H), 1.32 (d, *J* = 7.0 Hz, 3 H), 1.26 (ddd, *J* = 2.5, 12.0, 14.5 Hz, 1 H), 0.87 (d, *J* = 7.5 Hz, 3 H), 0.47 (m, 1 H), –0.14 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 148.8 (2 C), 142.7, 134.3, 129.4 (2 C), 128.7 (2 C), 127.7 (2 C), 127.0, 122.3, 79.4, 44.5, 34.2, 17.7, 15.4, 13.5, –3.7. mp: 139–140 ^{o}C. IR (neat) 3107, 2957, 1726, 1545, 1348, 1278, 1170, cm^{-1}.

*Preparation of anti-**24** from recrystallized **31***

To a solution of **31** (4.4 mg, 0.010 mmol, dr > 95:5) in THF (1 mL) was added 3M NaOH (0.5 mL) and the mixture stirred for 2 hours in an oil bath at 45 ^{o}C. Then, the reaction mixture was diluted with diethyl ether (10 mL). The aqueous phase was washed with diethyl ether (2 mL x 2). Combined organic extracts were washed with water, brine, dried over $MgSO_4$ and concentrated. Pasteur pipette chromatography (5% EtOAc in hexanes) gave 1.5 mg (61%) of **30** as a single

diastereomer. This alcohol (1.5 mg) was dissolved in dry CH_2Cl_2 (0.5 mL) and DMP (0.3 M in CH_2Cl_2, 0.25 mL, excess) was added at room hexanes and filtered through a plug of silica to give ~1.5 mg (ca. 100%) of *anti*-**24**.

*Wittig rearrangements of Z-**21** via Silicon/Lithium exchange – General procedure **C**.*

To a solution of hexamethyldisilane (189 mg, 1.29 mmol, 3 equiv) in HMPA (4 mL) at 0 ^{o}C was added methyllithium (1.6 M in Et_2O, 0.81 mL, 3 equiv) dropwise to give a deep red solution. After 5 minutes this TMSLi solution was transferred via cannula to a solution of *Z*-**21** (107 mg, 0.43 mmol, 1 equiv) in THF (4.5 mL) at -78 ^{o}C. Then the temperature was raised to -35 ^{o}C. After ~6 hours the reaction was quenched by adding $NH_4Cl_{(sat)}$ (4 mL) and the mixture diluted with Et_2O (15 mL). The aqueous phase was extracted with Et_2O (3 × 10 mL). Combined organic extracts were washed with water (3 × 5 mL), brine and dried over $MgSO_4$. The solid was filtrated and the filtrate was concentrated. Silica gel column chromatography (5% and 15% EtOAc in hexanes) of the residue afforded 45 mg (28%) of a mixture of **32** and *Z*-**21** (6:1 ratio), 11.3 mg (15%) of **27** and 16.7 mg (22%) of **26** as clear oils.

Synthesis of trichloroacetimidate reagents

*Preparation of 4-methylbenzyl-2,2,2-trichloroacetimidate – General procedure **D***

To a suspension of sodium hydride (60% w/w oil dispersion, 147 mg, 3.68 mmol, 0.15 equiv) in Et_2O (10 mL) at 0 ºC was added a solution of 4-methylbenzyl alcohol (3 g, 24.6 mmol, 1 equiv)

in Et_2O (6 mL) dropwise. The mixture was stirred at room temperature for 30 minutes and cooled down in an ice bath. Trichloroacetonitrile (3.55 g, 24.6 mmol, 1 equiv) was added dropwise. After 3 hours dry methanol (79 mg) was added via syringe and after 5 minutes the mixture was concentrated. The residue was suspended in hexanes and filtered through a plug of celite. The filtrate was concentrated and used in the next step without further purification. Note: in some cases the trichloroacetimidates were purified by column chromatography (5% EtOAc in hexanes) using silica gel buffered with triethylamine. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 5.30 (s, 2 H), 2.36 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ162.6, 138.1, 132.4, 129.2 (2 C), 127.9 (2 C), 91.4, 70.7, 21.2. IR (film) 3341, 2924, 1662, 1304, 1078, 794 cm^{-1}.

Preparation of 4-methoxybenzyl-2,2,2-trichloroacetimidate

Applying general procedure **D** to 4-methoxybenzyl alcohol (3 g, 21.7 mmol, 1 equiv), sodium hydride (60% w/w oil dispersion, 87 mg, 0.1 equiv) and trichloroacetonitrile (3.13 g, 21.7 mmol, 1 equiv) in Et_2O (11 mL) provided 5.85 (95%) of the 4-methoxybenzyl-2,2,2-trichloroacetimidate as a yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (s, 1 H), 7.36 (m, 2 H), 6.89 (m, 2 H), 5.26 (s, 2 H), 3.80 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ162.6, 159.7, 129.7 (2 C), 127.5, 113.9 (2 C), 91.5, 70.7, 55.2. IR (film) 3339, 2957, 1662, 1516, 1304, 1250, 1078, 796 cm^{-1}.

Preparation of 4-chlorobenzyl-2,2,2-trichloroacetimidate

Applying general procedure **D** to 4-chlorobenzyl alcohol (2.95 g, 20.7 mmol, 1 equiv), sodium hydride (60% oil dispersion, 83 mg, 0.1 equiv) and trichloroacetonitrile (2.99 g, 20.7 mmol, 1 equiv) in Et_2O (11 mL) provided 5.5 (93%) of the 4-chlorobenzyl-2,2,2-trichloroacetimidate as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1 H), 7.36–7.32 (m, 4 H), 5.29 (s, 2 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 134.2, 133.9, 129.1 (2 C), 128.7 (2 C), 91.4, 69.8. IR (film) 3341, 2956, 1664, 1495, 1296, 1080, 794 cm^{-1}.

*Preparation of 4-fluorobenzyl-2,2,2-trichloroacetimidate – General procedure **E***

To a solution of 4-fluorobenzyl alcohol (2 g, 15.86 mmol, 1 equiv) and trichloroacetonitrile (3.4 g, 23.78 mmol, 1.5 equiv) in CH_2Cl_2 (80 mL) at 0 ^oC was added DBU (0.43 g, 2.85 mmol 0.18 equiv). The reaction was monitored by TLC using triethylamine pre-washed plates until completion (3-4 hours). The reaction mixture was concentrated to a small volune (~15 mL) and filtered trough a plug of silica buffered with ~1% triethylamine and rinsed with 5% EtOAc in hexanes. The filtrate was concentrated and the residue purified on a column (buffered with ~1% triethylamine) to give 3.22 (75%) of 4-fluorobenzyl-2,2,2-trichloroacetimidate as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1 H), 7.39 (m, 2 H), 7.05 (m, 2 H), 5.29 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7 (d, J = 248.0 Hz), 162.5, 131.2 (d, J = 3.6 Hz), 129.8 (d, J = 8.8 Hz, 2 C), 115.4 (d, J = 21.3 Hz, 2 C), 91.2, 70.0.

Preparation of 3-methylbenzyl-2,2,2-trichloroacetimidate

Applying general procedure **D** to 3-methylbenzyl alcohol (2 g, 16.37 mmol, 1 equiv), sodium hydride (60% oil dispersion, 98 mg, 0.15 equiv) and trichloroacetonitrile (2.36 g, 16.37 mmol, 1 equiv) in Et_2O (6 mL) provided, after column chromatography (5% EtOAc in hexanes) 3.43 g (74%) of 3-methylbenzyl-2,2,2-trichloroacetimidate as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1 H), 7.43 (dd, *J* = 1.0, 7.0 Hz, 1 H), 7.30 (dt, *J* = 1.5, 8.0 Hz, 1 H), 6.96 (dt, *J* = 0.5, 7.5 Hz, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 5.38 (s, 2 H), 3.83 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 138.2, 135.4, 129.0, 128.43, 128.42, 124.8, 91.4, 70.8, 21.4. IR (film) 3343, 3028, 2951, 1662, 1307, 1078, 796 cm^{-1}.

Preparation of 3-methoxybenzyl-2,2,2-trichloroacetimidate

Applying general procedure **D** to 3-methoxybenzyl alcohol (2.9 g, 21 mmol, 1 equiv), sodium hydride (60% oil dispersion, 84 mg, 2.1 mmol, 0.1 equiv) and trichloroacetonitrile (3.03 g, 21 mmol, 1 equiv) provided 5.79 g (97%) of 3-methoxybenzyl-2,2,2-trichloroacetimidate as a yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1 H), 7.28 (t, *J* = 7.8 Hz, 1 H), 6.99 (d, *J* = 7.8 Hz, 1 H), 6.97 (s, 1 H), 6.86 (dd, *J* = 2.0, 7.8 Hz, 1 H), 5.31 (s, 2 H), 3.80 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 159.7, 137.0, 129.6, 119.8, 113.7, 113.1, 91.4, 70.5, 55.2. IR (film) 3339, 2955, 2835, 1664, 1307, 1076, 798 cm^{-1}.

Preparation of 2-methoxybenzyl-2,2,2-trichloroacetimidate

Applying general procedure **D** to 2-methoxybenzyl alcohol (3 g, 21.71 mmol, 1 equiv), sodium hydride (60% oil dispersion, 130 mg, 0.15 equiv) and trichloroacetonitrile (3.13 g, 21.71 mmol, 1 equiv) in Et_2O (7.5 mL) provided, after column chromatography (5% EtOAc in hexanes), 5.0 g (77%) of 2-methoxybenzyl-2,2,2-trichloroacetimidate as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1 H), 7.42 (dd, *J* = 1.0, 7.0 Hz, 1 H), 7.30 (dt, *J* = 1.5, 8.0 Hz, 1 H), 6.96 (t, *J* = 7.5 Hz, 1 H), 6.88 (d, *J* = 7.0 Hz, 1 H), 5.37 (s, 2 H), 3.83 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 157.2, 129.4, 128.6, 123.9, 120.4, 110.3, 91.5, 66.5, 55.4. IR (film) 3341, 2941, 1662, 1300, 1248, 1080, 796 cm^{-1}.

Preparation of 2-(2-propen-3-yl)benzyl-2,2,2-trichloroacetimidate

Synthesis of 2-(2-propen-3-yl)-benzaldehyde

Following a known procedures,[26, 27] a round bottom flask was charged with 2-bromobenzadehyde ethylene acetal (12 g, 52.39 mmol, 1 equiv) and dissolved in Et_2O (360 mL). *n*-BuLi (1.6M in hexane, 32.7 mL, 52.39 mmol, 1 equiv) was added dropwise. After 1 hour $MgBr_2 \cdot Et_2O$ (13.5 g, 52.39 mmol, 1 equiv) was added in one portion. After 20 minutes the flask was transferred to an ice bath and kept at 0 ^oC for 30 minutes. Copper (I) iodide (10 g, 52.39 mmol, 1 equiv) was added in one portion to give a brown suspension. 20 minutes later a solution of allyl bromide (4.42 mL, 52.39 mmol, 1 equiv) in Et_2O (100 mL) was added via cannula to give a dark brown mixture. The reaction was left to reach room temperature and left overnight

(20 hours). The flask was then cooled down in an ice bath and quenched with 1M HCl (200 mL). The mixture was extracted with Et_2O (2 × 200 mL). Combined organic extracts were washed with $NaHCO_{3(sat)}$ (2 × 150 mL), brine (100 mL) and dried over $MgSO_4$. After filtration of the salt the filtrate was concentrated and the crude product was dissolved in CH_2Cl_2 (650 mL) and $FeCl_2 \cdot 6H_2O$ (43.2 g, 156 mmol, 3 equiv) as added and the suspension stirred at room temperature. The reaction was monitored by TLC (5 % EtOAc in hexanes). After ~3 hours the reaction was quenched with $NaHCO_3$ (200 mL). The aqueous phase was washed with CH_2Cl_2 (3 × 200 mL). Combined organic extracts were washed with brine (200 mL), dried over $MgSO_4$ and concentrated to give almost pure product 2-(2-propen-3-yl)-benzaldehyde as judged by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1 H), 7.83 (dd, *J* = 1.5, 8.0 Hz, 1 H), 7.51 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.27 (d, *J* = 7.5 Hz, 1 H), 6.022 (ddt, *J* = 6.5, 10.0, 16.5 Hz, 1 H), 5.07 (dq, *J* = 1.5, 10.0 Hz, 1 H), 4.96 (dq, *J* = 1.5, 17.0 Hz, 1 H), 3.80 (d, *J* = 6.5 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.3, 142.2, 136.9, 133.9, 133.8, 131.6, 131.0, 126.9, 116.4, 36.5.

Synthesis of 2-(2-propen-3-yl)-benzyl alcohol

To 2-(2-propen-1-yl)-benzaldehyde (1.86 g, 12.7 mmol, 1 equiv) in 30:1 THF/H_2O (38 mL) was added $NaBH_4$ (240 mg, 6.35 mmol) and the mixture stirred at room temperature. After 30 minutes the reaction was quenched with water (10 mL). The aqueous phase was extracted with

Et_2O (3× 20 mL) and combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated to 1.67 g (89%) of 2-(2-propen-1-yl)-benzyl alcohol.

*Preparation of compound **33***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (56% w/w in THF, 893 mg, 3.83 mmol, 1 equiv), 4-methylbenzyl-2,2,2-trichloroacetimidate (1.73 g, 6.14 mmol, 1.6 equiv) and TMSOTf (69 μL, 0.384 mmol, 0.1 equiv) in hexane (19 mL) afforded 356 mg (38%) of **33** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 5.81 (m, 1 H), 5.06 (m, 2 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.27 (d, *J* = 12.0 Hz, 1 H), 3.60 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.33 (s, 3 H), 0.00 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 136.9, 136.1, 128.8 (2 C), 127.8 (2 C), 112.5, 75.7, 71.7, 21.2, -4.0. IR (film) 2957, 2862, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 234.1432 [(M^+); calcd for $C_{14}H_{22}OSi$, 234.1440].

*Preparation of compound **34***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (600 mg, 4.61 mmol, 1 equiv), *4-methoxybenzyl-2,2,2-trichloroacetimidate* (1.95 g, 6.91 mmol, 1.5 equiv) and TMSOTf (trace) in hexane (25 mL) afforded 414 mg (36%) of **34** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 2 H), 6.85 (m, 2 H), 5.81 (ddd, *J* = 7.5, 11.0, 18.0 Hz, 1 H), 5.08–5.03 (m, 2 H), 4.62 (d, *J* = 11.5 Hz, 1 H), 4.24 (d, *J* = 11.5 Hz, 1 H), 3.79 (s, 3 H), 3.58 (dt, *J* = 1.5, 7.0 Hz, 1 H), -0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 137.4, 131.3, 129.2 (2 C), 113.6 (2 C),

112.5, 75.5, 71.5, 55.2, -4.0. IR (film) 3030, 2957, 2835, 1541, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 250.1398 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*Preparation of compound **35***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (56% w/w in THF, 893 mg, 3.83 mmol, 1 equiv), *4-chlorobenzyl-2,2,2-trichloroacetimidate* (1.86 g, 6.14 mmol, 1.6 equiv) and TMSOTf (<69 μL, 0.384 mmol, 0.1 equiv) in hexane (19 mL) afforded 473 mg (48%) of **35** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2 H), 7.23 (m, 2 H), 5.98 (m, 1 H), 5.05 (m, 2 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 4.27 (d, *J* = 12.0 Hz, 1 H), 3.58 (m, 1 H), 0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 137.1, 132.9, 129.0 (2 C), 128.3 (2 C), 112.8, 76.1, 71.1, -4.0. IR (film) 3081, 2959, 1491, 1248, 1089, 841 cm^{-1}. HRMS (EI) *m*/*z* 254.0893 [(M^+); calcd for $C_{13}H_{19}OSiCl$, 254.0894].

*Preparation of compound **36***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (86% w/w in THF, 585 mg, 3.84 mmol, 1 equiv), *4-fluorobenzyl-2,2,2-trichloroacetimidate* (1.56 g, 5.76 mmol, 1.5 equiv) and TMSOTf (35 μL, 0.192 mmol, 0.05 equiv) in hexane (20 mL) afforded 463 (51%) of **36** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 2 H), 7.00 (m, 2 H), 5.80 (m, 1 H), 5.07 (m, 1 H), 5.04 (m, 1 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 4.26 (d, *J* = 12.0 Hz, 1 H), 3.58 (m, 1 H), 0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.8 Hz), 137.2, 134.9, 129.3 (d, *J*

= 7.9 Hz, 2 C), 114.9 (d, *J* = 21.2 Hz, 2 C), 112.7, 76.0, 71.2, -4.0. IR (film) 3080, 2959, 1516, 1223, 843 cm^{-1}. HRMS (EI) *m*/*z* 238.1196 [(M^+); calcd for $C_{13}H_{19}OSiF$, 239.1189].

*Preparation of compound **37***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (56% w/w in THF, 893 mg, 3.83 mmol, 1 equiv), *3-methylbenzyl-2,2,2-trichloroacetimidate* (1.73 g, 6.14 mmol, 1.6 equiv) and TMSOTf (<69 μL, 0.384 mmol, 0.1 equiv) in hexane (19 mL) afforded 204 mg (29%) of **37** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 1 H), 7.09 (m, 3 H), 5.81(ddd, *J* = 6.9, 10.5, 17.7 Hz, 1 H), 5.10–5.02 (m, 2 H), 4.66 (d, *J* = 12.0 Hz, 1 H), 4.28 (d, *J* = 12.0 Hz, 1 H), 3.60 (dt, *J* = 1.2, 6.6 Hz, 1 H), 2.33 (s, 3 H), 0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 137.7, 137.4, 128.4, 128.1, 127.9, 124.7, 112.5, 75.9, 71.9, 21.4, -4.0. HRMS (EI) *m*/*z* 234.1430 [(M^+); calcd for $C_{14}H_{22}OSi$, 234.1440].

*Preparation of compound **38***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (54% w/w in THF, 1.1 g, 4.61 mmol, 1 equiv), *3-methoxybenzyl-2,2,2-trichloroacetimidate* (1.95 g, 6.91 mmol, 1.5 equiv) and TMSOTf (90 μL, 0.498, 0.11 equiv) in hexane (25 mL) afforded 297 mg (25%) of **38** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (*J* = 7.2 Hz, 1 H), 6.88 (m, 2 H), 6.79 (dd, *J* = 2.5, 8.4 Hz, 1 H), 5.81 (ddd, *J* = 7.2, 10.8, 17.8 Hz, 1 H), 5.09–5.05 (m, 2 H), 4.67 (d, *J* = 12.0 Hz, 1 H), 4.30 (d, *J* = 12.6 Hz, 1 H), 3.79 (s, 3 H), 3.62 (dt, *J* = 1.8, 7.2 Hz, 1 H), 0.02 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 141.0, 137.3, 129.1, 119.9, 112.88, 112.86, 112.7, 76.0,

71.7, 55.1, -4.0. IR (film) 3081, 2957, 1602, 1489, 1265, 1049, 841 cm^{-1}. HRMS (EI) *m*/*z* 250.1385 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*Preparation of compound **39***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (56% w/w in THF, 893 mg, 3.83 mmol, 1 equiv), *2-methoxybenzyl-2,2,2-trichloroacetimidate* (1.83 g, 6.14 mmol, 1.6 equiv) and TMSOTf (69 μL, 0.384, 0.1 equiv) in hexane (19 mL) afforded 191 mg (20%) of **39** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 1.0, 7.5 Hz, 1 H), 7.22 (dt, *J* = 2.0, 8.0 Hz, 1 H), 6.93 (dt, *J* = 1.0, 7.0 Hz, 1 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 5.83 (ddd, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.09 (dt, *J* = 2.0, 17.5 Hz, 1 H), 5.03 (dt, *J* = 1.5, 10.5 Hz, 1 H), 4.71 (d, *J* = 13 Hz, 1 H), 4.36 (d, *J* = 13 Hz, 1 H), 3.79 (s, 3 H), 3.66 (dt, *J* = 1.5, 6.5 Hz, 1 H), 0.02 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 137.5, 128.4, 128.0, 127,9, 120.2, 112.1, 109.9, 76.5, 67.2, 55.2, -4.0. IR (film) 3079, 2956, 1600, 1491, 1265, 1049, 841 cm^{-1}. HRMS (EI) *m*/*z* 250.1385 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*Preparation of compound **40***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (55% w/w in THF, 1.3 g, 5.47 mmol, 1 equiv), *2-allylbenzyl-2,2,2-trichloroacetimidate* (3.2 g, 10.9 mmol, 2.0 equiv) and TMSOTf (148 μL, 0.82, 0.15 equiv) in hexane (27 mL) afforded 669 mg (47%) of **40** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 1.5, 7 Hz, 1 H), 7.24-7.15 (m, 3 H),

5.94 (dddd, *J* = 6.5, 10, 13, 16.5 Hz, 1 H), 5.84 (ddd, *J* = 7.5, 10.5, 17.5 Hz, 1 H), 5.10-5.05 (m, 2 H), 5.03 (dq, *J* = 2, 10 Hz, 1 H), 4.98 (dq, *J* = 2, 17 Hz, 1 H), 4.69 (d, *J* = 12 Hz, 1 H), 4.30 (d, *J* = 12 Hz, 1 H), 3.62 (dt, *J* = 1.5, 7 Hz, 1 H), 3.43 (m, 2 H), 0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4, 137.5, 137.1, 136.9, 129.3, 129.0, 127.6, 126.1, 115.7, 112.7, 76.4, 70.0, 36.6, -3.9. IR (neat) 3078, 2959, 1637, 1454, 1248, 1049, 841 cm^{-1}. HRMS (EI) *m*/*z* 260.1590 [(M^+); calcd for $C_{16}H_{24}OSi$, 260.1596].

*Wittig rearrangement of compound **33***

Applying general procedure **B** to **33** (124 mg, 0.529 mmol, 1 equiv) in THF (6.6 mL) and *sec*-BuLi (1.4 M in cyclohexane, 0.6 mL, 1.5 equiv) afforded 111.2 mg (90%) of a mixture of **41** and **50** (29:1 ratio) as colorless oil. Spectroscopic data for **41**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.5 Hz, 2 H), 2.60 (t, *J* = 7.5 Hz, 2 H), 2.53 (t, *J* = 7.5 Hz, 2 H), 2.30 (s, 3 H), 1.81 (m, 2 H), 0.16 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.1, 138.8, 135.3, 129.0 (2 C), 128.3 (2 C), 47.6, 34.8, 23.8, 21.0, -3.2. IR (film) 2955, 1643, 1250, 844 cm^{-1}. HRMS (EI) *m*/*z* 234.1435 [(M^+); calcd for $C_{14}H_{22}OSi$, 234.1440].

*Wittig rearrangements of compound **34***

Applying general procedure **B** to **34** (87 mg, 0.347 mmol, 1 equiv) in THF (4.4 mL) and *sec*-BuLi (1.4 M in cyclohexane, 0.37 mL, 1.5 equiv) afforded 52.2 mg (90%) of a mixture of **42** and **51** (1:0.19 ratio) as colorless oil. Mixture of **42** and **51** (1:0.19 ratio) ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.05 (d, *J* = 9.0 Hz, 2 H), 7.03 (m, 0.38 H), 6.80 (m, 2.38 H), 5.98 (dd, *J* = 10.5, 17.0 Hz, 0.19 H), 4.94 (dd, *J* = 1.0, 10.5 Hz, 0.19 H), 4.79 (dd, *J* = 1.0, 17.0 Hz, 0.19 H), 3.77 (s, 3.57 H), 2.83 (m, 0.38 H), 2.58 (t, *J* = 7.0 Hz, 2 H), 2.51 (t, *J* = 7.5 Hz, 2 H), 1.80 (m, 2 H), 0.16 (s, 9 H), 0.08 (s, 1.71 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.2, 157.8, 133.9, 129.3 (2 C), 113.7 (2 C), 113.4, 55.2, 47.5, 34.3, 23.9, -3.2. IR (film) 2955, 1641, 1512, 1248, 843 cm^{-1}. HRMS (EI) *m*/*z* 250.1388 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*Wittig rearrangements of compound **35***

Applying general procedure **B** to **35** (95 mg, 0.373 mmol, 1 equiv) in THF (4.7 mL) and *sec*-BuLi (1.4 M in cyclohexane, 0.3 mL, 1.1 equiv) afforded, after column chromatography (0% and 4% EtOAc in hexanes), 54.6 mg (59%) of a mixture of **43** and **52** (57:1 ratio) as colorless oil, and 9.3 mg (8%) of unreacted **35**. Spectroscopic data for **43**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (m, 2 H), 7.06 (m, 2 H), 2.58 (t, *J* = 7.0 Hz, 2 H), 2.52 (t, *J* = 7.5 Hz, 2 H), 1.80 (m, 2 H), 0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ247.7, 140.3, 131.6, 129.7 (2 C), 128.4 (2 C), 47.3, 34.5, 23.5, -3.2. IR (film) 2955, 1645, 1493, 1250, 843 cm^{-1}. HRMS (EI) *m*/*z* 254.0890 [(M^+); calcd for $C_{13}H_{19}OSiCl$, 254.0894].

*Wittig rearrangements of compound **36***

Applying general procedure **B** to **36** (117 mg, 0.491 mmol, 1 equiv) in THF (6.2 mL) and *sec*-BuLi (1.4 M in cyclohexane, 0.53 mL, 1.5 equiv) afforded, after column chromatography (0% and 4% EtOAc in hexanes), 65.7 mg (57%) of a mixture of **41** and **53** (28:1 ratio) as colorless oil

and 6.7 mg (34%) of a mixture of isomeric enol ether **59** and **35** (4:1 ratio). Spectroscopic data for **44**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (m, 2 H), 6.93 (t, *J* = 8.5 Hz, 2 H), 2.58 (t, *J* = 7.0 Hz, 2 H), 2.53 (t, *J* = 7.5 Hz, 2 H), 1.80 (m, 2 H), 0.16 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.8, 161.3 (d, *J* = 244.1 Hz), 137.4 (d, *J* = 3.2 Hz), 129.7 (d, *J* = 7.8 Hz, 2 C), 115.0 (d, *J* = 21.3 Hz, 2 C), 47.3, 34.4, 23.7, -3.2. IR (film) 2955, 1643, 1516, 1250, 844 cm^{-1}. HRMS (EI) *m*/*z* 238.1192 [(M^+); calcd for $C_{13}H_{19}OSiF$, 239.1189].

*Wittig rearrangements of compound **37***

Applying general procedure **B** to **37** (100 mg, 0.427 mmol, 1 equiv) in THF (5.4 mL) and *sec*-BuLi (1.4 M in cyclohexane, 0.46 mL, 1.5 equiv) afforded 76 mg (78%) of a mixture of **45** and **54** (38:1 ratio) as colorless oil. Spectroscopic data for **45**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.5 Hz, 1 H), 6.99–6.92 (m, 3 H), 2.60 (t, *J* = 7.5 Hz, 2 H), 2.53 (t, *J* = 7.5 Hz, 2 H), 2.31 (s, 3 H), 1.83 (m, 2 H), 0.17 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.1, 141.8, 137.9, 129.3, 128.2, 126.6, 125.4, 47.6, 35.1, 23.7, 21.4, -3.2. IR (film) 3018, 2955, 1643, 1250, 844 cm^{-1}. HRMS (EI) *m*/*z* 234.1431 [($M)^+$; calcd for $C_{14}H_{22}OSi$, 234.1440].

*Wittig rearrangements of compound **38***

Applying general procedure **B** to **38** (30 mg, 0.120 mmol, 1 equiv) in THF (1.5 mL) and *sec*-BuLi (1.4 M in cyclohexane, 0.13 mL, 1.5 equiv) afforded 22 mg (73%) of **46** and **55** (35:1 ratio) as colorless oil. Spectroscopic data for **46**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.8 Hz, 1

H), 6.71 (m, 3 H), 3.77 (s, 3 H), 2.60 (t, *J* = 7.2 Hz, 2 H), 2.54 (t, *J* = 7.8 Hz, 2 H), 1.83 (quintet, *J* = 7.2 Hz, 2 H), 0.16 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 248.1, 159.6, 143.5, 129.3, 120.9, 114.1, 111.2, 55.1, 47.5, 35.2, 23.5, -3.2. IR (film) 3031, 2957, 1641, 1495, 1240, 844 cm^{-1}. HRMS (EI) *m*/*z* 250.1380 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*Wittig rearrangements of compound **39***

Following general procedure **B**, treatment of **39** (80 mg, 0.32 mmol, 1 equiv) in THF (4 mL) with *sec*-BuLi (1.4M in cyclohexane, 0.34 mL, 0.479 mmol, 1.5 equiv) afforded after column chromatography (5% EtOAc in hexanes) 66.1 mg of **47** (83%) containing traces of [1,2]-product **56** (3%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (dt, *J* = 1.5, 8.0 Hz, 1 H), 7.08 (dd, *J* = 1.5, 7.5 Hz, 1 H), 6.87 (dd, *J* = 1.0, 7.5 Hz, 1 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 3.79 (s, 3 H), 2.61 (t, *J* = 7.5 Hz, 2 H), 2.58 (t, *J* = 8.0 Hz, 2 H), 1.81 (quintet, *J* = 2.5 Hz, 2 H), 0.17 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.3, 157.4, 130.2, 129.9, 127.1, 120.3, 110.2, 55.1, 48.1, 29.7, 22.2, -3.2. IR (film) 2957, 1643, 1495, 1244, 844 cm^{-1}. HRMS (EI) *m*/*z* 250.1376 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*Wittig rearrangements of compound **40***

Following general procedure **B**, treatment of **40** (206 mg, 0.791 mmol, 1 equiv) in THF (8 mL) with *n*-BuLi (1.6 M in hexane, 1.24 mL, 0.479 mmol, 2.5 equiv) afforded, after column chromatography (5% EtOAc in hexanes), 128.2 mg of **48** (63%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (m, 4 H), 5.99 (m, 1 H), 5.07 (m, 1 H), 5.02 (dq, *J* = 1.5, 18.0 Hz, 1 H),

3.43 (dt, *J* = 1.5, 6.5 Hz, 2 H), 2.69 (t, *J* = 7.0 Hz, 2 H), 2.60 (m, 2 H), 1.83 (m, 2 H), 0.20 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.9, 140.0, 137.6, 137.3, 129.6, 129.3, 126.3, 126.2, 115.6, 47.9, 36.9, 32.1, 23.2, -3.2. IR (film) 3072, 2955, 1643, 1250, 844 cm^{-1}. HRMS (EI) *m*/*z* 260.1594 [(M^+); calcd for $C_{16}H_{24}OSi$, 260.1596].

*Preparation of compound **62***

Applying general procedure **A** to α-(trimethylsilyl)allyl alcohol[3d] (77.4% w/w in THF, 1.3 g, 7.68 mmol, 1 equiv), 1-(4-methylphenyl)ethyl 2,2,2-trichloroacetimidate (3 g, 10.75 mmol, 1.4 equiv) and TMSOTf (35 μL, 0.182 mmol, 0.025 equiv) in hexane (42 mL) afforded 1.7 g (95%) of **62** as a colorless oil (dr=1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.5 Hz, 2 H), 7.15–7.09 (m, 6 H), 5.73 (m, 2 H), 5.01–4.94 (m, 3 H), 4.88 (dt, *J* = 11.0 Hz, 1 H), 4.48 (q, *J* = 6.5 Hz, 1 H), 4.45 (d, *J* = 6.5 Hz, 1 H), 3.78 (dt, *J* = 1.5, 6.5 Hz, 1 H), 3.40 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.33 (s, 3 H), 2.31 (s, 3 H), 1.35 (d, *J* = 6.5 Hz, 3 H), 1.32 (d, *J* = 6.5 Hz, 3 H), 0.03 (s, 9 H), -0.05 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5, 141.3, 137.84, 137.81, 136.7, 136.3, 128.8 (2 C), 128.7 (2 C), 126.7 (2 C), 125.9 (2 C), 112.1, 111.6, 75.9, 75.4, 74.1, 73.1, 24.7, 22.2, 21.13, 21.09, -3.0, -4.0. IR (film) 3050, 2972, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 248.1597 [(M^+); calcd for $C_{15}H_{24}OSi$, 248.1596].

*Wittig rearrangement of compound **62***

Following general procedure **B**, treatment of **62** (66 mg, 0.281 mmol, 1 equiv) in THF (3.5 mL) with *n*-BuLi (1.6 M in hexane, 1.53 mL, 0.845 mmol, 3.0 equiv) afforded, after column

chromatography (3% EtOAc in hexanes), 16.3 mg (26%) of **63**, 10.2 mg (14%) of **64** as colorless oils, and 7.5 mg of a mixture of *anti*-**62** and **65** (1:9). An analytical sample of **65** was obtained by column chromatography eluting with hexanes. Spectroscopic data for **63**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.8 Hz, 2 H), 7.02 (d, *J* = 8.4 Hz, 2 H), 2.59 (m, 1 H), 2.51 (ddd, A of ABX system, *J* = 6.0, 9.0, 16.8 Hz, 1 H), 2.41 (ddd, B of ABX system, *J* = 6.0, 9.0, 17.4 Hz, 1 H), 2.30 (s, 3 H), 1.80 (m, 1 H), 1.72 (m, 1 H), 1.20 (d, *J* = 6.6 Hz, 3 H), 0.12 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 248.2, 143.6, 135.5, 129.1 (2 C), 126.9 (2 C), 46.5, 38.9, 30.3, 22.5, 21.0, -3.2. IR (film) 2959, 1643, 1250, 844 cm^{-1}. HRMS (EI) *m/z* 248.1595 [$(M)^+$; calcd for $C_{15}H_{24}OSi$, 248.1596]. Spectroscopic data for **64**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.0 Hz, 2 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 3.74 (q, *J* = 7.0 Hz, 1 H), 2.30 (m, 6 H), 1.35 (d, *J* = 7.0 Hz, 3 H), 0.71 (ddd, A of ABX system, *J* = 6.5, 10.0, 15.0 Hz, 1 H), 0.60 (ddd, B of ABX system, *J* = 6.5, 9.0, 14.0 Hz, 1 H), 0.11 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.0, 137.9, 136.7, 129.5 (2 C), 127.7 (2 C), 51.9, 35.5, 21.0, 17.7, 10.4, -1.9. IR (film) 2955, 1716, 1456, 1250, 837 cm^{-1}. HRMS (EI) *m/z* 233.1363 [$(M\text{-}CH_3)^+$; calcd for $C_{14}H_{21}OSi$, 233.1362]. Spectroscopic data for **65**: (1:0.7 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (m, 8 H), 6.97 (d, *J* = 8.0 Hz, 2.8 H), 6.91 (d, *J* = 8.5 Hz, 2.8 H), 2.90 (m, 1.4 H), 2.72 (m, 2 H), 2.32 (s, 6 H), 2.25 (s, 4.2 H), 1.20 (m, 4.2 H), 0.98 (m, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 142.8, 135.4, 135.0, 128.9, 128.5, 127.7, 127.5, 46.8, 45.8, 21.2, 21.0, 20.9, 17.8. IR (film) 3021, 2961, 1514, 1452, 817 cm^{-1}. HRMS (EI) *m/z* 238.1724 [$(M)^+$; calcd for $C_{18}H_{22}$, 238.1722].

*Preparation of compound **66**[28] – General procedure **F***

A solution of allyl alcohol (3 g, 51.65 mmol, 1 equiv) in THF (130 mL) at -78 ^{o}C was slowly added *n*-BuLi (1.6 M in hexanes, 35 mL, 55.78 mmol, 1.08 equiv). After 30 minutes phenyldimethylsilyl chloride, (9.52 g, 55.78 mmol, 1.08 equiv) was added and the mixture stirred at the same temperature for 1 hour. Then, *t*-BuLi (1.7 M in pentane, 36.5 mL, 62 mmol, 1.2 equiv) was added dropwise over ~50 minutes, and the yellow mixture was stirred at -78 ^{o}C for 2.5 hours. The reaction was quenched with $NH_4Cl_{(sat)}$ (60 mL, quick addition) and the mixture immediately diluted with Et_2O (100 mL). The aqueous phase was extracted with Et_2O (3 × 60 mL). Combined organic extracts were washed with water (3 × 60 mL), brine and dried over $MgSO_4$. Column chromatography afforded 7.15 g (72%) of **66** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 2 H), 7.36 (m, 3 H), 5.98 (ddd, *J* = 5.5, 11.0, 17.5 Hz, 1 H), 5.06 (dt, *J* = 1.5, 17.0 Hz, 1 H), 4.98 (dt, *J* = 1.5, 11.0 Hz, 1 H), 4.20 (m, 1 H), 0.33 (s, 3 H), 0.32 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.3, 136.0, 134.2 (2 C), 129.5, 127.9 (2 C), 110.1, 68.5, -5.8, -6.1. IR (film) 3426, 3071, 2959, 1427, 1250, 1115, 835 cm^{-1}.

*Preparation of compound **67***

Applying general procedure **F** to allyl alcohol (2 g, 34.48 mmol, 1 equiv) in THF (85 mL), *n*-BuLi (22 mL, 34.48 mmol, 1.0 equiv), methyldiphenylsilyl chloride (8.03 g, 34.48 mmol, 1.0 equiv) and *t*-BuLi (24 mL, 41.4 mmol, 1.2 equiv), afforded 5.77 g (66%) of **67** as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (m, 4 H), 7.43–7.35 (m, 6 H), 6.04 (ddd, *J* = 5.5, 11.0, 17.5 Hz, 1 H), 5.12 (dt, *J* = 2.0, 17.0 Hz, 1 H), 5.02 (dt, *J* = 2.0, 11.0 Hz, 1 H), 4.59 (m, 1 H), 1.43 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 135.1 (2 C), 135.0 (2 C), 134.4, 134.1, 129.7, 129.68, 127.93 (2 C), 129.1 (2 C), 110.8, 67.6, -7.1. IR (film) 3431, 3071, 3041, 3964, 1427, 1115, 904, 790 cm^{-1}.

*Preparation of compound **68***

Applying general procedure **F** to allyl alcohol (1 g, 17.22 mmol, 1 equiv) in THF (42 mL), *n*-BuLi (11 mL, 17.22 mmol, 1.0 equiv), triphenylsilyl chloride (5.1 g, 17.22 mmol, 1.0 equiv) and *t*-BuLi (22 mL, 35.6 mmol, 2.1 equiv), afforded 599 mg (11%) of **68** as a white solid. m.p. 55–57 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (m, 6 H), 7.44 (m, 3 H), 7.38 (m, 6 H), 6.15 (ddd, *J* = 5.0, 10.5, 17.0 Hz, 1 H), 5.16 (dq, *J* = 1.0, 17.5 Hz, 1 H), 5.06 (m, 1 H), 4.91 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9 (3 C), 136.2 (6 C), 132.4, 129.9 (3 C), 127.9 (6 C), 111.6, 67.5. IR (film) 3406, 3064, 1429, 1111 cm^{-1}.

*Preparation of compound **69*** [29]

Applying general procedure **F** to allyl alcohol (2 g, 34.5 mmol, 1 equiv) in THF (70 mL), *n*-BuLi (23.7 mL, 37.9 mmol, 1.1 equiv), triethylsilyl chloride (5.7 g, 37.9 mmol, 1.1 equiv) and *sec*-BuLi (30 mL, 41.4 mmol, 1.2 equiv), afforded 5.75 g (97%) of **69** as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05 (ddd, *J* = 5.0, 10.5, 16.0 Hz, 1 H), 5.07 (dd, *J* = 1.5, 17.0 Hz, 1 H), 4.96

(dd, *J* = 1.5, 10.5 Hz, 1 H), 4.16 (m, 1 H), 0.97 (t, *J* = 8.0 Hz, 9 H), 0.60 (q, *J* = 8.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 109.0, 67.4, 7.4, 1.6. IR (film) 3402, 2955, 1458, 1097 cm^{-1}.

*Preparation of compound **70***

Applying general procedure **A** to **66** (603 mg, 3.14 mmol, 1 equiv), benzyl-2,2,2-trichloroacetimidate (1.58 g, 6.27 mmol, 2.0 equiv) and TMSOTf (57 μL, 0.314 mmol, 0.1 equiv) in hexane (16 mL) afforded 509 (73%) of **70** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.37–7.26 (m, 5 H), 7.23 (m, 3 H), 5.79 (ddd, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.06 (m, 2 H), 4.68 (d, *J* = 12.5 Hz, 1 H), 4.30 (d, *J* = 12.0 Hz, 1 H), 3.83 (dt, *J* = 1.5, 6.5 Hz, 1 H), 0.32 (s, 3 H), 0.29 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.1, 136.9, 136.8, 134.3 (2 C), 129.2, 128.1 (2 C), 127.63 (2 C), 127.60 (2 C), 127.2, 113.1, 75.5, 72.0, -5.4, -5.7. IR (film) 3069, 2959, 1427, 1248, 1116, 833 cm^{-1}. HRMS (EI) *m*/*z* 282.1443 [(M^+); calcd for $C_{18}H_{22}OSi$, 282.1440].

*Preparation of compound **71***

Applying general procedure **A** to **67** (1 g, 3.93 mmol, 1 equiv), benzyl-2,2,2-trichloroacetimidate (1.99 g, 7.86 mmol, 2.0 equiv) and TMSOTf (107 μL, 0.590 mmol, 0.15 equiv) in cyclohexane (19 mL) afforded 690 (51%) of **67** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (m, 2 H), 7.54 (m, 2 H), 7.37 (m, 2 H), 7.32 (m, 4 H), 7.26 (m, 3 H), 7.20 (m, 2 H), 5.83 (ddd, *J* = 7.5, 11.0, 17.5 Hz, 1 H), 5.11 (dt, *J* = 1.5, 17.5 Hz, 1 H), 5.07 (dt, *J* = 2.0, 10.5 Hz, 1 H), 4.71 (d, *J* = 12.0 Hz, 1 H), 4.35 (d, *J* = 12.0 Hz, 1 H), 4.18 (dt, *J* = 1.5, 7.0 Hz, 1 H), 0.56 (s, 3 H). ^{13}C NMR

(151 MHz, $CDCl_3$) δ 138.8, 136.5, 135.3 (2 C), 135.1 (2 C), 135.0, 134,7, 129.39, 129.37, 128.1 (2 C), 127.8 (2 C), 127.7 (2 C), 127.6 (2 C), 127.2, 114.0, 74.9, 72.0, -6.7. IR (film) 3089, 2966, 1427, 1115, 733 cm^{-1}. HRMS (EI) *m*/*z* 344.1596 [(M^+); calcd for $C_{23}H_{24}OSi$, 344.1596].

*Preparation of compound **72***

Applying general procedure **A** to **68** (580 mg, 1.83 mmol, 1 equiv), benzyl-2,2,2-trichloroacetimidate (0.93 g, 3.67 mmol, 2.0 equiv) and TMSOTf (50 μL, 0.275 mmol, 0.15 equiv) in hexane (9.2 mL) afforded 316 (42%) of **72** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 6 H), 7.39 (m, 3 H), 7.32 (m, 6 H), 7.25 (m, 3 H), 7.18 (m, 2 H), 5.95 (m, 1 H), 5.13 (m, 1 H), 5.10 (m, 1 H), 4.75 (d, *J* = 11.5 Hz, 1 H), 4.47 (dt, *J* = 1.5, 7.0 Hz, 1 H), 4.40 (d, *J* = 12.0 Hz, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 136.4 (6 C), 136.1 (3 C), 133.1, 129.6 (3 C), 128.1 (2 C), 128.0 (2 C), 127.7 (6 C), 127.3, 115.3, 74.8, 72.0. IR (film) 3090, 2965, 1426, 1111, 732 cm^{-1}. HRMS (EI) *m*/*z* 406.1745 [(M^+); calcd for $C_{28}H_{26}OSi$, 406.1753].

*Preparation of compound **73***

Applying general procedure **A** to **69** (630 mg, 3.66 mmol, 1 equiv), benzyl-2,2,2-trichloroacetimidate (1.46 g, 5.48 mmol, 1.5 equiv) and TMSOTf (66 μL, 0.366 mmol, 0.1 equiv) in hexane (20 mL) afforded 500 (52%) of **69** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 4 H), 7.25 (m, 1 H), 5.86 (ddd, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.09 (dt, *J* = 2.0, 17.0 Hz, 1 H), 5.03 (dt, *J* = 1.5, 10.5 Hz, 1 H), 4.68 (d, *J* = 11.5 Hz, 1 H), 4.27 (d, *J* = 12.0 Hz, 1 H), 3.78 (dt, *J* = 1.0, 7.0 Hz, 1 H), 0.93 (t, *J* = 8.0 Hz, 9 H), 0.59 (dq, *J* = 2.5, 7.5 Hz, 6 H). ^{13}C

NMR (126 MHz, $CDCl_3$) δ 139.4, 137.7, 128.1 (2 C), 127.5 (2 C), 127.1, 112.2, 74.6, 72.0, 7.4, 1.7. IR (film) 3070, 2957, 1429, 1253, 1053, 698 cm^{-1}. HRMS (EI) *m*/*z* 262.1743 [(M^+); calcd for $C_{16}H_{24}OSi$, 262.1753].

*Wittig rearrangement of compound **70***

Following general procedure **B**, treatment of **70** (140 mg, 0.635 mmol, 1 equiv) in THF (7 mmol) with *sec*-BuLi (1.4 M in cyclohexane, 0.73 mL, 0.953 mmol, 1.5 equiv) afforded after column chromatography (5% EtOAc in hexanes) 93.8 mg (67%) of **74** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 2 H), 7.44–7.37 (m, 3 H), 7.25 (m, 2 H), 7.17 (m, 1 H), 7.07 (m, 2 H), 2.61 (t, *J* = 7.0 Hz, 2 H), 2.51 (t, *J* = 7.5 Hz, 2 H), 1.80 (m, 2 H), 0.49 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 245.9, 141.7, 134.4, 133.9 (2 C), 129.8, 128.3 (2 C), 128.2 (2 C), 128.1 (2 C), 125.7, 47.8, 35.0, 23.7, -4.8. IR (film) 3071, 2959, 1427, 1255, 1120, 831, 794 cm^{-1}. HRMS (EI) *m*/*z* 282.1426 [(M^+); calcd for $C_{18}H_{22}OSi$, 282.1440].

*Wittig rearrangements of compound **71***

Following general procedure **B**, treatment of **71** (108 mg, 0.313 mmol, 1 equiv) in THF (3.5 mL) with *sec*-BuLi (1.4 M in cyclohexane, 0.34 mL, 0.47 mmol, 1.5 equiv) afforded after column chromatography (4% EtOAc in hexanes) 51.8 mg (48%) of **75** and 37.5 mg (38%) of **79** as colorless oils. Spectroscopic data for **75**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 4 H), 7.44 (m, 3 H), 7.39 (m, 4 H), 7.23 (m, 2 H), 7.15 (m, 1 H), 7.04 (m, 2 H), 2.68 (t, *J* = 7.0 Hz, 2 H), 2.50 (t,

J = 7.5 Hz, 2 H), 1.81 (m, 2 H), 0.74 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 244.2, 141.7, 135.0 (4C), 132.7, 130.1 (2 C), 128.4 (2 C), 128.3 (2 C), 128.2 (4 C), 125.8, 48.8, 35.1, 23.8, -5.4. IR (film) 3024, 2930, 1641, 1429, 1113, 792 cm^{-1}. HRMS (EI) *m*/*z* 344.1590 [(M^+); calcd for $C_{23}H_{24}OSi$, 344.1596]. Spectroscopic data for **79**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 4 H), 7.43–7.36 (m, 6 H), 7.33 (m, 2 H), 7.28 (m, 1 H), 7.15 (m, 2 H), 3.65 (s, 2 H), 2.51 (m, 2 H), 1.35 (m, 2 H), 0.54 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.6, 136.3 (2 C), 134.4 (4 C), 134.3, 129.4 (2 C), 129.3 (2 C), 128.6 (2 C), 127.9 (4 C), 126.9, 49.4, 36.5, 7.7, -4.5. IR (film) 3069, 2924, 1716, 1427, 1113, 788 cm^{-1}. HRMS (EI) *m*/*z* 344.1588 [(M^+); calcd for $C_{23}H_{24}OSi$, 344.1596].

*Wittig rearrangements of compound **72***

Following general procedure **B**, treatment of **72** (310 mg, 0.762 mmol, 1 equiv) in THF (8 mL) with *sec*-BuLi (1.4 M in cyclohexane, 1.17 mL, 1.525 mmol, 2.0 equiv) afforded after column chromatography (4%, 6%, 8% and 10% EtOAc in hexanes) 111.3 mg (36%) of **75** and 61.2 mg (20%) of **80** as colorless oils. Spectroscopic data for **76**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (m, 6 H), 7.50 (m, 3 H), 7.43 (m, 6 H), 7.25 (m, 2 H), 7.18 (m, 1 H), 7.08 (m, 2 H), 2.81 (t, *J* = 7.0 Hz, 2 H), 2.54 (t, *J* = 8.0 Hz, 2 H), 1.88 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 242.8, 141.7, 136.1 (6 C), 131.3 (3 C), 130.2 (3 C), 128.4 (2 C), 128.2 (2 C), 128.1 (6 C), 125.7, 49.8, 35.0, 23.8. IR (film) 3069, 2928, 1643, 1429, 1111 cm^{-1}. HRMS (EI) *m*/*z* 406.1750 [(M^+); calcd for $C_{28}H_{26}OSi$, 406.1753]. Spectroscopic data for **80**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 6 H),

7.41 (m, 3 H), 7.36 (m, 6 H), 7.30 (m, 3 H), 7.12 (m, 2 H), 3.60 (s, 2 H), 2.57 (m, 2 H), 1.63 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.4, 136.1, 135.5 (6 C), 134.3 (3 C), 129.6 (3 C), 129.3 (2 C), 128.6 (2 C), 128.0 (6 C), 126.9, 49.5, 36.5, 6.6. IR (film) 3069, 2924, 1716, 1427, 1111 cm^{-1}. HRMS (EI) *m*/*z* 406.1740 [(M^+); calcd for $C_{28}H_{26}OSi$, 406.1753].

*Wittig rearrangement of compound **73***

Following general procedure **B**, treatment of **73** (95 mg, 0.362 mmol, 1 equiv) in THF (4.5 mL) with *sec*-BuLi (1.4 M in cyclohexane, 0.39 mL, 0.543 mmol, 1.5 equiv) afforded after column chromatography (25% CH_2Cl_2 in hexanes) 63.6 mg (67%) of **77** as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 2 H), 7.15 (m, 3 H), 2.57 (m, 4 H), 1.83 (quintet, *J* = 7.5 Hz, 2 H), 0.94 (t, *J* = 8.5 Hz, 9 H), 0.70 (q, *J* = 8.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.9, 141.9, 128.4 (2 C), 128.3 (2 C), 125.8, 49.2, 35.3, 23.5, 7.2, 2.1. IR (film) 3026, 2953, 1639, 1456, 1018 cm^{-1}. HRMS (EI) *m*/*z* 262.1750 [(M^+); calcd for $C_{16}H_{26}OSi$, 262.1753].

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CHAPTER 3

[1,2]- AND [1,4]-WITTIG REARRANGEMENTS OF γ-SILYL AND α,γ-DISILYL ALLYLIC ETHERS

3.1 Background

In Chapter 2 it was concluded that increasing structural complexity of α-silyl allylic ethers, in particular alkyl substitution at the migrating benzylic carbon or terminal allylic position, was detrimental to the reactivity and [1,4]-/[1,2]-selectivity. This was interpreted as the inability of the base to access the α allylic proton due to a steric clash with the silyl group itself, as well as with the substituents at the benzylic position. The marked difference in reactivity between the *syn* or *anti* diastereomeric ethers, partially supports this idea. It is possible that a specific conformation is required for facile allylic deprotonation, perhaps that in which the allylic C–H bond is properly aligned with the olefin π system and at the same time *anti* periplanar with the C–O bond of the benzylic fragment (Chapter 2, Figure 2). Such a conformation is optimal for delocalization of negative charge through the π system and to the antibonding orbital (σ*) of the C–O bond.

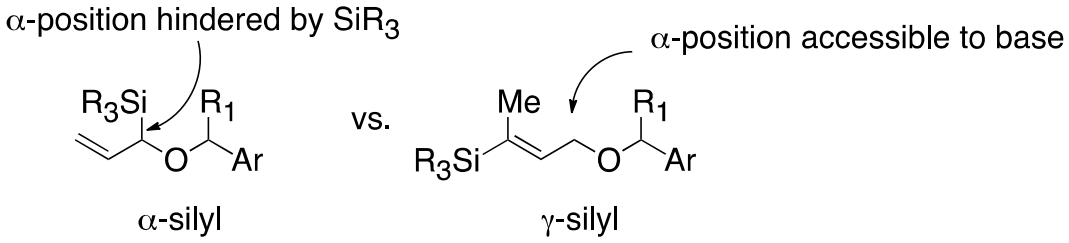
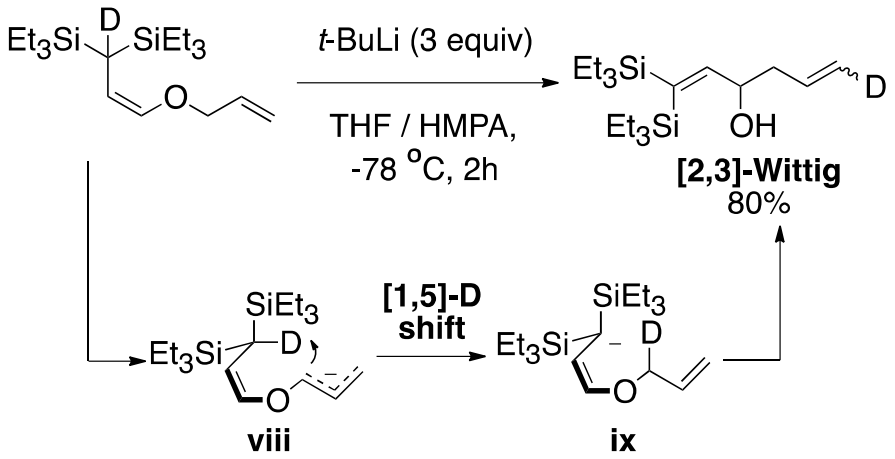


Figure 4. α- vs. γ-silyl ethers.

It was envisioned that a possible solution to this problem would be to move the silyl group to a remote position (γ) so that the allylic α position would be more accessible to the base. In addition

to this, having the silyl group at the γ position would ensure thast both C–O bond rotations were not limited by steric constraints, hence allowing any required conformation that would lead to easier deprotonation to be attainable (Figure 4).

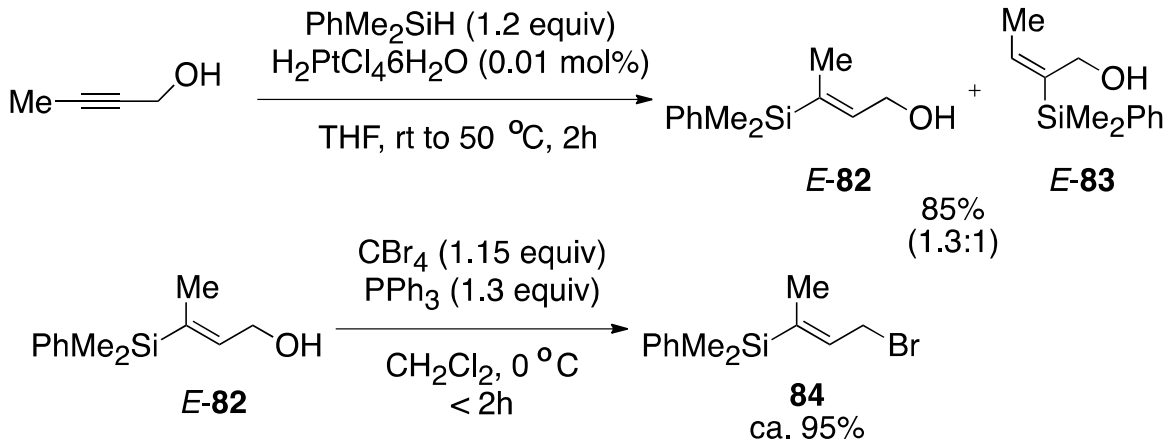
In studies regarding the [2,3]-Wittig rearrangements of bisallylic ethers, Nakai *et al.* demonstrated that a silyl group at the γ position of one of the allylic portions was effective in directing deprotonation to the corresponding α position (Chapter 1, Scheme 27).[1] Similar selectivity was observed by Mitchel *et al.* in the [2,3]-Wittig rearrangements of β-stannyl-γ-silyl allylic ethers.[2] Recently, Song and coworkers reported the [1,5]-anion relay / [2,3]-Wittig rearrangement of γ,γ-disilylpropenylallyl ethers (Scheme 48).[3] This isomerization is initiated by deprotonation on the unsubstituted allylic portion, followed by a [1,5]-proton (deuterium) abstraction to give the isomeric allylic carbanion (**viii** to **ix**) that then undergoes the [2,3]-sigmatropic rearrangement. These studies show that the steric demand of the silyl groups can prevent direct deprotonation by the base, even though the α proton (with respect to the silyl groups) is acidic. The steric demand of the silyl group has also been shown to determine the degree of regioselectivity in the electrophile-trapping of 1-(trimethylsilyl)allyllithium.[4]



Scheme 48. [1,5]-anion relay/[2,3]-Wittig rearrangement of bissilyl diallylic ethers.

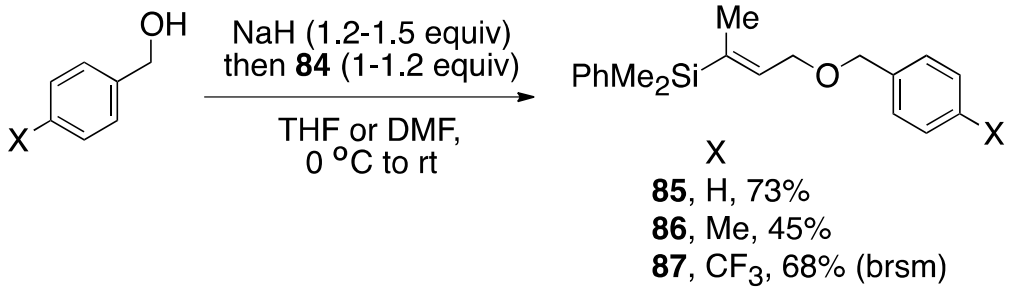
3.2 Synthesis of γ-silyl and α,γ-disilyl allylic ethers

The preparation of γ-silyl allylic ethers was much more convenient than that of α-silyl analogues because the introduction of the silyl group at the γ position could be achieved catalytically and under mild conditions, and therefore there was no need for using excess alkyllithiums as in the case of α-silyl alkoxy compounds. Thus, 2-butyn-1-ol underwent clean *syn* hydrosilylation with $PhMe_2SiH$ in the presence of a platinum catalyst to give alcohols *E*-**82** and *E*-**83**, which were easily separable by column chromatography (Scheme 49). Bromination of *E*-**82** with PPh_3 and CBr_4 afforded silane **84**.



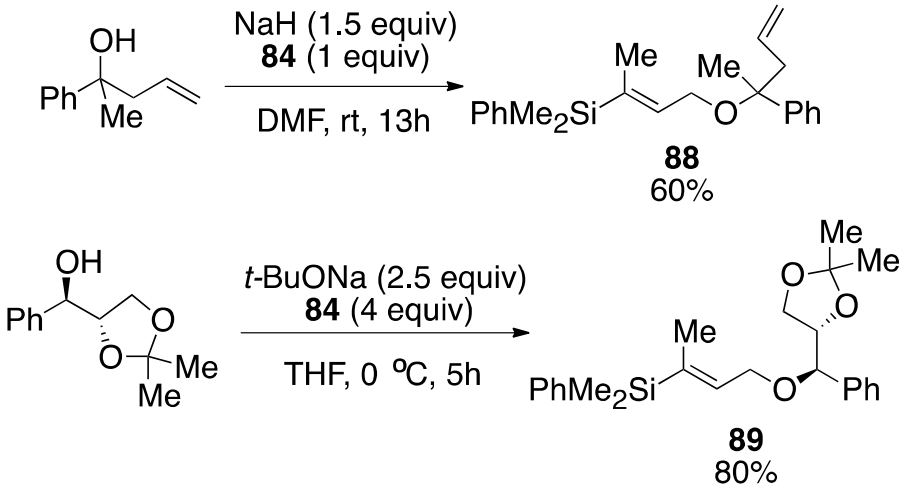
Scheme 49. Preparation of precursor **84** for the preparation of γ-silyl Wittig substrates.

Treatment of different benzylic alcohols with sodium hydride in THF or DMF followed by the addition of bromide **84** provided γ-silyl allylic ethers **85**-**87** (Scheme 50).



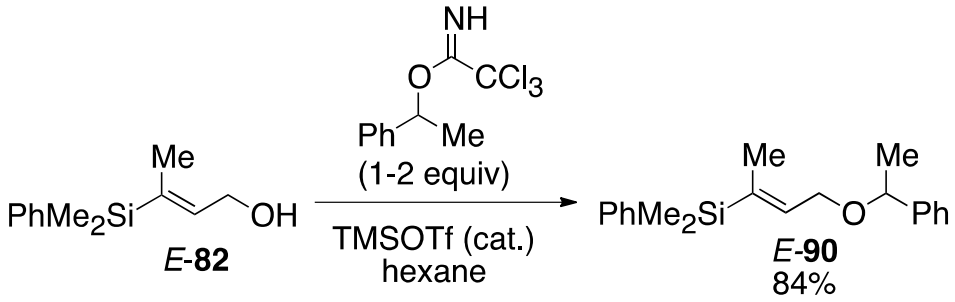
Scheme 50. Etherification of benzyl alcohols with bromide **84**.

The etherification of a tertiary benzylic alcohol or the protected triol shown below were also achieved by S_N2 displacement of bromide in **84** with the corresponding alcohols (Scheme 51). Both products were obtained reasonable yields.



Scheme 51. Synthesis of ethers **88** and **89** from allylic bromide **84**.

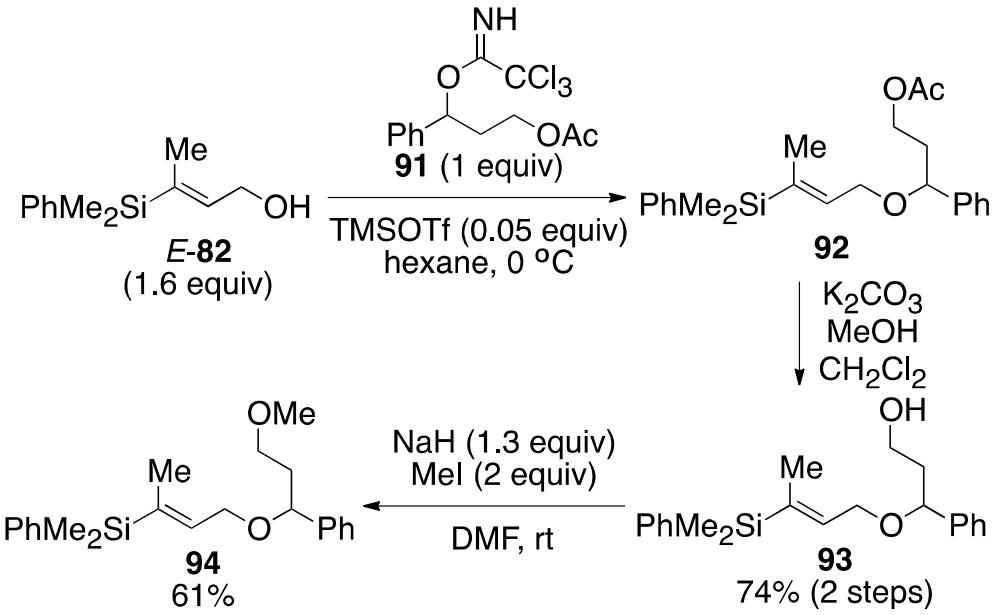
Alternatively, compound *E*-**82** could be alkylated with the corresponding benzylic trichloroacetimidates under acidic conditions (Scheme 52).[5] For example, treatment of *E*-**82** with the trichloroacetimidate from 1-phenylethanol provided *E*-**90** in good yield (Scheme 52).



Scheme 52. Preparation of **90** by etherification of *E*-**82** under with the corresponding trichloroacetimidate.

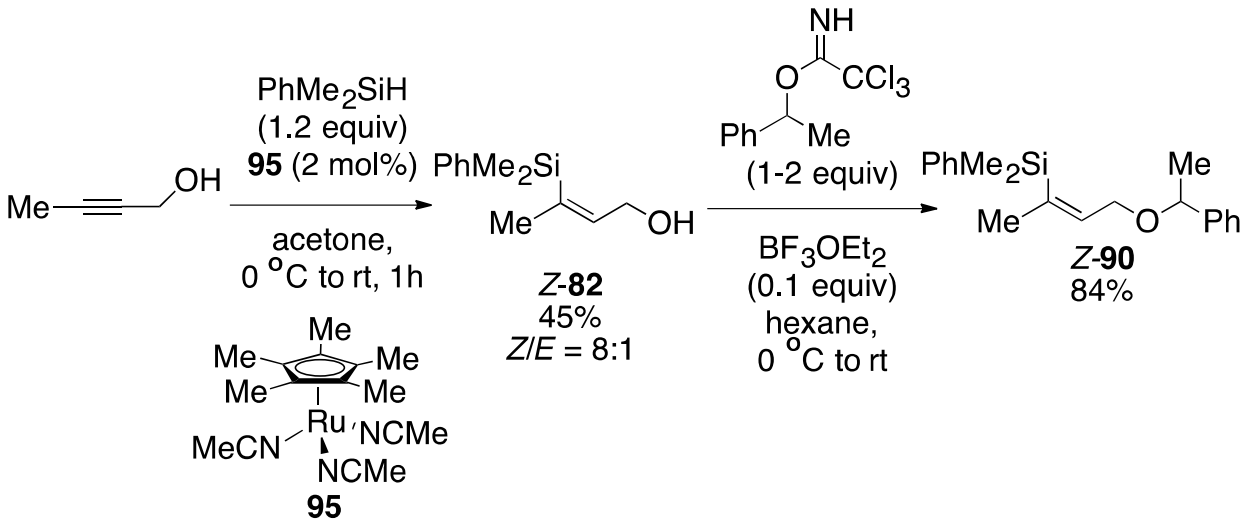
Compound *E*-**82** was also alkylated with functionalized trichloroacemidates like **91**, to give acetate **92**, which was submitted to *O*-deacetylation followed by methylation under basic

conditions to afford substrate **94**. Trichloroacetimidate **91** was prepared in 7 steps from benzaldehyde and details are provided in the experimental section.



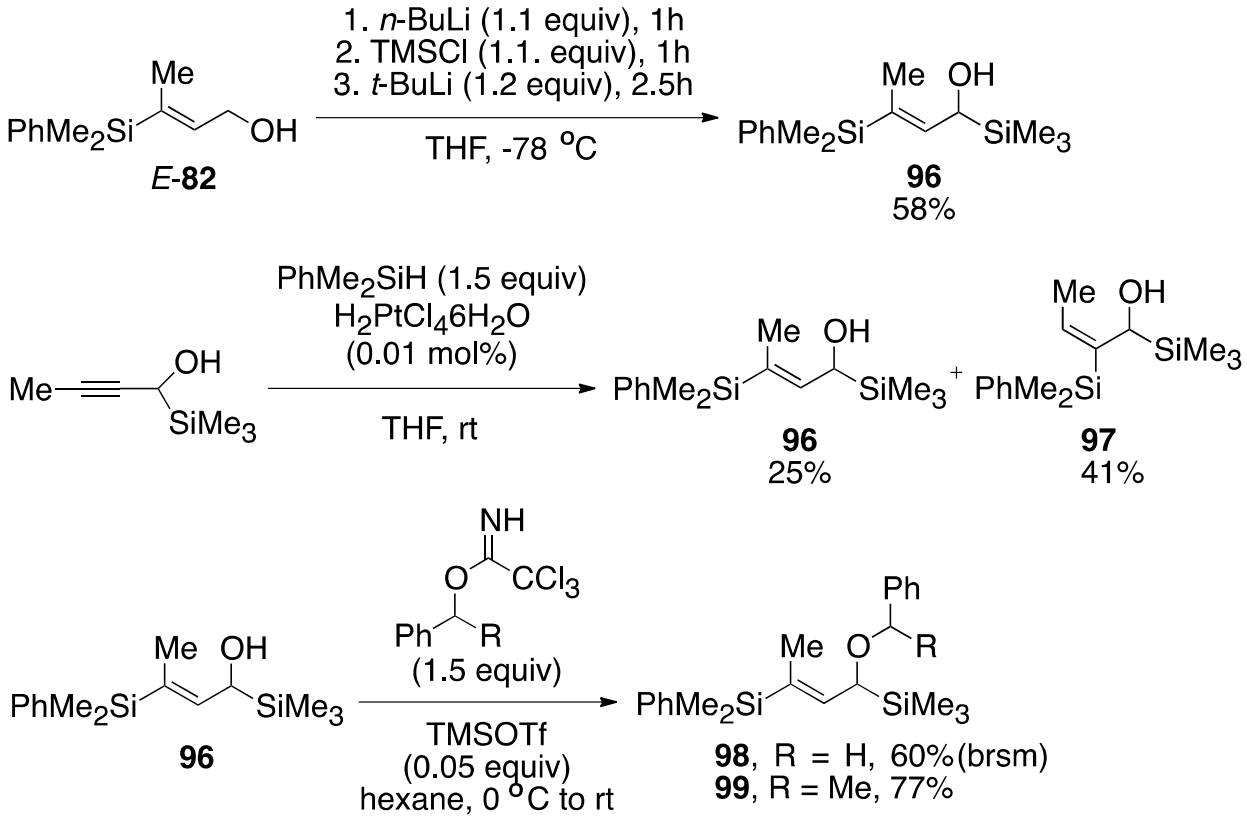
Scheme 53. Synthesis of **94** via alkylation of *E*-**82**, *O*-deacetylation and methylation.

In order to analyze the effect of olefin geometry, compound *Z*-**90** was prepared as shown in Scheme 54. *anti* Hydrosilylation using Trost catalyst (**95**) gave *Z*-**82** with good *E/Z* ratio (8:1).[6] Alkylation of *Z*-**82** with the corresponding trichloroacetimidate was done with $BF_3 \bullet OEt_2$ as the catalyst because geometrical isomerization does not take place to an observable extent, as was seen with TMSOTf.



Scheme 54. Synthesis of *E*-**90**, via *anti* hydrosilylation and trichloroacetimidate alkylation.

The synthesis of α,γ-disilyl allylic ethers **98** and **99**, with (R = H) or without (R = Me) substitution at the benzylic position, was based on the trichloroacetimidate alkylation of compound **96**, prepared by non-regioselective *syn* hydrosilylation of 1-trimethylsilyl-2-butyn-1-ol or in better yield by retro-Brook rearrangement of the *in situ* generated *O*-trimethylsilyl *E*-**82** (Scheme 55).



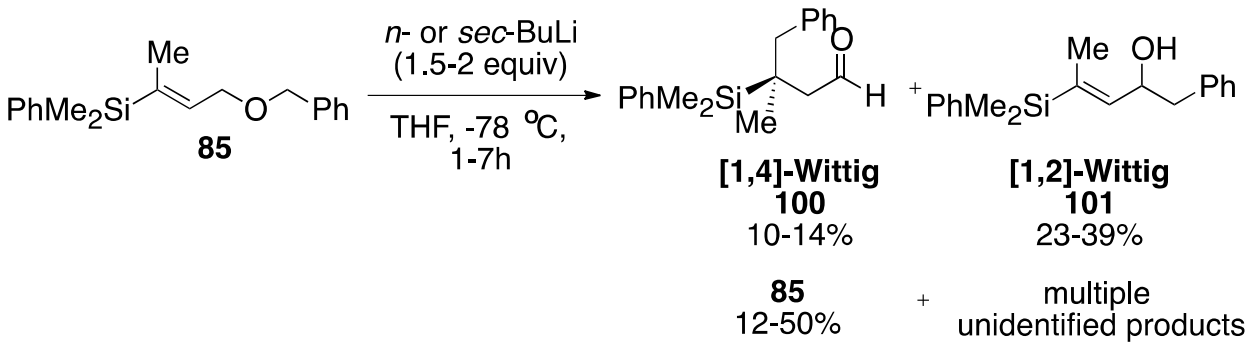
Scheme 55. Preparation of disilyl substrates **98** and **99**.

3.3 [1,4]- and [1,2]-Wittig rearrangements of γ-silyl allylic ethers

3.3.1 Reactivity of model substrate, γ-silyl allylic ether 85

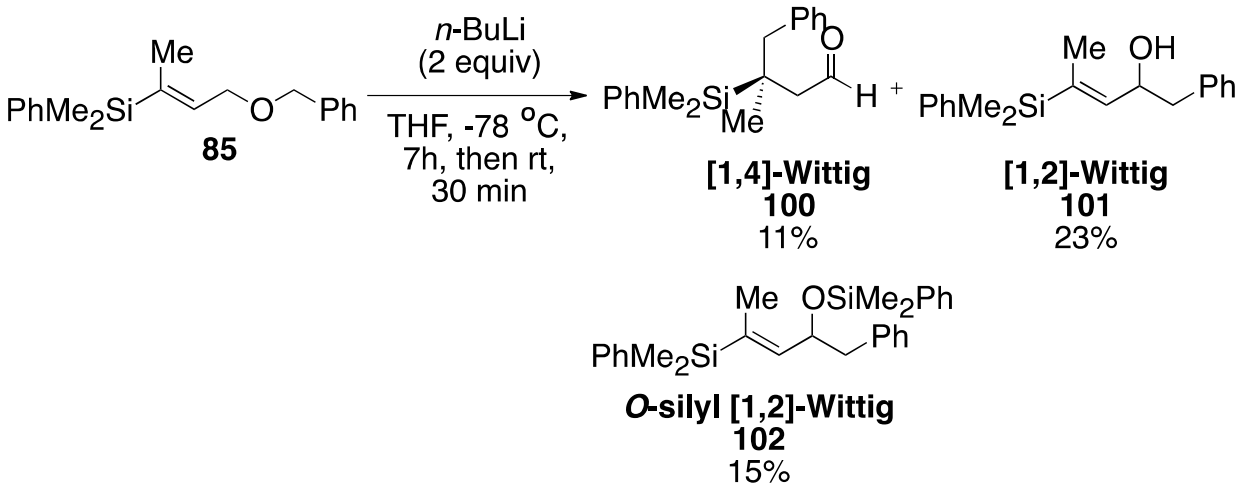
The study started with the rearrangement of geometrically pure (*E*) model substrate **85** under typical conditions used in the rearrangement of α-silyl allylic ethers (Chapter 2). Thus, treatment of compound **85** with *n*-BuLi, or *sec*-BuLi in THF afforded aldehyde **100** via [1,4]-shift and alcohol **101** via [1,2]-migration. Despite using excess base (1.5-2 equiv), the yields of both products were always in the same range: 10-14% for compound **100** and 23-39% for compound **101**. Additionally, incomplete conversion was usually observed at low temperature (-78 ºC) and unreacted **85** was recovered (Scheme 56). The crude reaction mixtures were relatively complex

by ^{1}H NMR spectroscopy and several, presumably aldehyde byproducts, were observed. Importantly, when the reaction was stopped early (1h), unreacted **85** was obtained unchanged, however, after longer reaction times (7h), a geometrical mixture of *E*/*Z*-**85** isomers was isolated.



Scheme 56. [1,4]- and [1,2]-Wittig rearrangements of compound **85**.

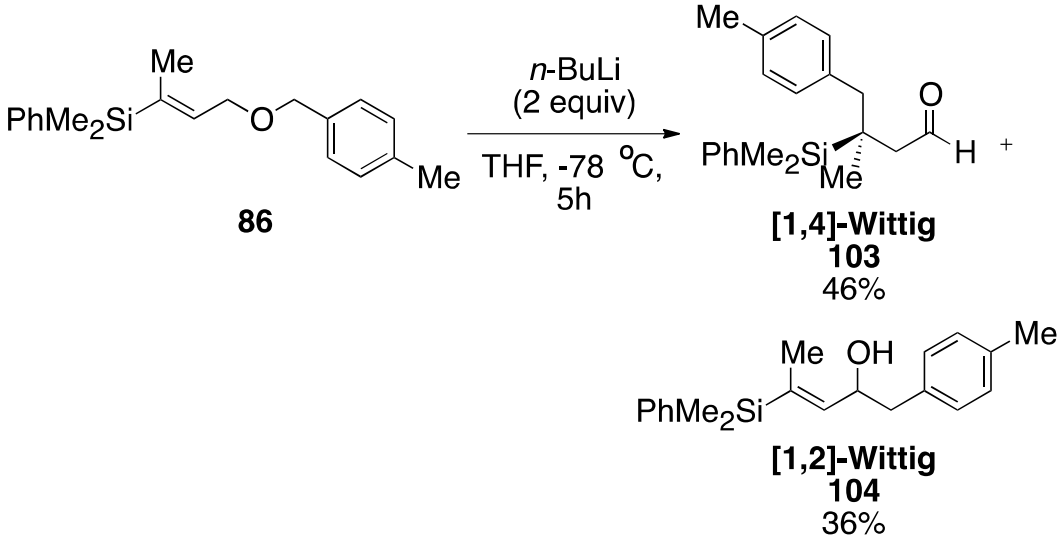
Another important observation is that when the reaction proceeded for 7 hours at -78 ^{o}C (partial conversion as indicated in Scheme 56) and at room temperature for 30 minutes, the expected products **100** and **101** were obtained in 11% and 23%, respectively, and were accompanied by *O*-silylated [1,2]- product **102** in 15% (Scheme 57). The formation of compound **102** suggests the [1,2]-Wittig alkoxide might have reacted with vinylsilane **85** at higher temperatures. Attack of such alkoxide on silicon, supported by the well-known ability of silicon to form pentacoordinated species,[7] might account for the observed geometrical isomerization of **85** at low temperatures. Deuterium trapping experiments might provide further information regarding the origin of the observed isomerization. The lack of deuterium incorporation in the unreacted, geometrically isomerized **85** would support the assumption that a pentacoordinated silicon species might be responsible for the *E* to *Z* isomerization.



Scheme 57. Effect of higher reaction temperature in the reaction of compound **85**.

3.3.2 Electronic effects in γ-silyl allylic ethers

Next, the effect of electronic modifications at the benzylic fragment was studied. The rearrangement of *p*-methyl substituted **86** afforded the corresponding [1,4]-Wittig and [1,2]-Wittig products **103** and **104** in good overall yield (Scheme 58). Although the [1,4]-/[1,2]-selectivity was low (1.3:1) it was surprising that in this case the [1,4]-product was major.



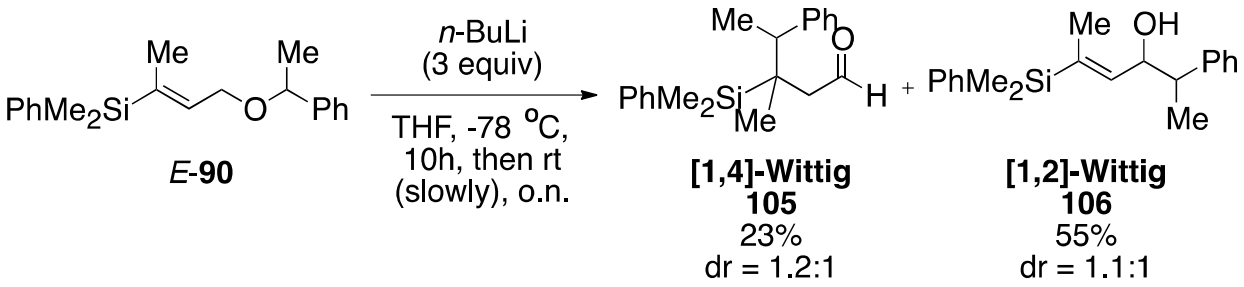
Scheme 58. Effect of electron-rich benzyl group in reactivity and product distribution.

It is not clear why the presence of a *para* methyl group on the aryl group (**86**) allows cleaner Wittig rearrangements, as compared to the unsubstituted analogue (**85**). The isolation of certain products from similar unsubstituted benzylic ethers (*vide infra*) suggest benzyl ethers bearing electron rich groups are less prone to other side reactions such as benzylic deprotonation, elimination of toluenyl anion or electron transfer reactions between radical and radical anion intermediates with alkyllithiums.

In contrast, reaction of of *p*-trifluoromethyl substituted compound **87** underwent complete decomposition when treated with *n*-BuLi at low temperatures. When the reaction was run at diluted concentration (0.008 M instead of 0.08 M), the reaction mixture also turned deep blue after the addition of *n*-BuLi, and complete decomposition of **87** took place. The ^{1}H NMR spectrum of the crude reaction mixture did not show any identifiable product. Presumably **87** undergoes competitive benzylic deprotonation, or alternatively, elimination of *p*-trifluoromethy benzylic anion, which is a serious side reaction in of *p*-nitrobenzyl ethers.[8]

3.3.3 Effect of alkyl substitution at the benzylic position

Compound *E*-**90**, bearing a methyl group at the benzylic position showed similar reactivity to the unsubstituted model **85** and underwent partial conversion at low temperature when treated with excess *n*-BuLi (3 equiv added in two portions). Increasing the temperature allowed complete consumption of *E*-**90** (Scheme 59).



Scheme 59. Alkyl substitution at the benzylic position: a secondary migrating group.

Compared to **85** (Scheme 57), *E*-**90** underwent a more efficient rearrangement and gave a 2.5:1 mixture of [1,2]- and [1,4]-Wittig products in 78% isolated yield (Scheme 59). The rearrangement of *E*-**90** also took place with the weaker base methyllithium at room temperature to give a [1,4]-/[1,2]-product ratio of 1.4:1 in 71% overall yield. Unfortunately both [1,4]- and [1,2]- migrations took place with low diastereoselectivity (Scheme 59). Attempts to improve the efficiency or diastereoselectivity using different bases (LDA, *sec*-BuLi) did not afford any improvement. Interestingly, when *sec*-BuLi was used as the base, a small amount of aldehyde **107** was isolated (figure 5). The known aldehyde **107**[9] might be formed from a radical anion fragment that did not undergo recombination with the benzylic radical.

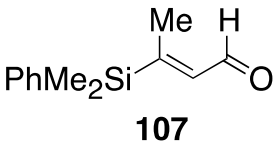
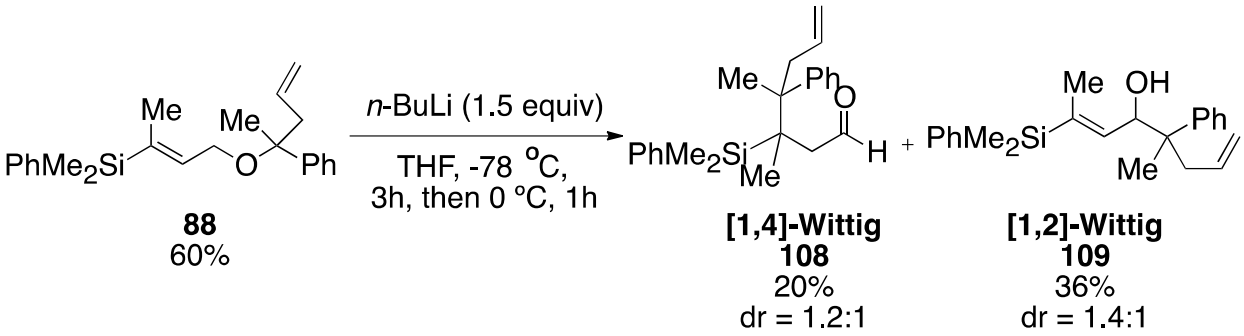


Figure 5. Fragmentation product from the reaction of *E*-**90**.

The rearrangement of compound **88**, featuring a tertiary migrating (benzylic) group underwent [1,4]- and [1,2]-Wittig rearrangements with modest regioselectivity (1.8:1) and with low diastereoselectivity in both shifts (Scheme 60), as observed with **90**. It is remarkable that the

[1,4]-Wittig product **108**, bearing two crowded adjacent quaternary centers, was formed in comparable yield to less sterically crowded [1,4]-products (e.g. **105**, Scheme 59). It is likely that the [1,4]-Wittig migration of **88** proceeds via a radical/radical anion mechanism, which is favored by migrating groups capable of sufficient radical stability (tertiary benzyl). This trend is a general characteristic of the [1,2]-Wittig rearrangements.[10] A stepwise mechanism is also expected based on steric grounds, since a concerted [1,4]-shift would require interaction between a quaternary carbon center and the disubstituted end of a π (allylic) system.



Scheme 60. Alkyl substitution at the benzylic position: a tertiary migrating group.

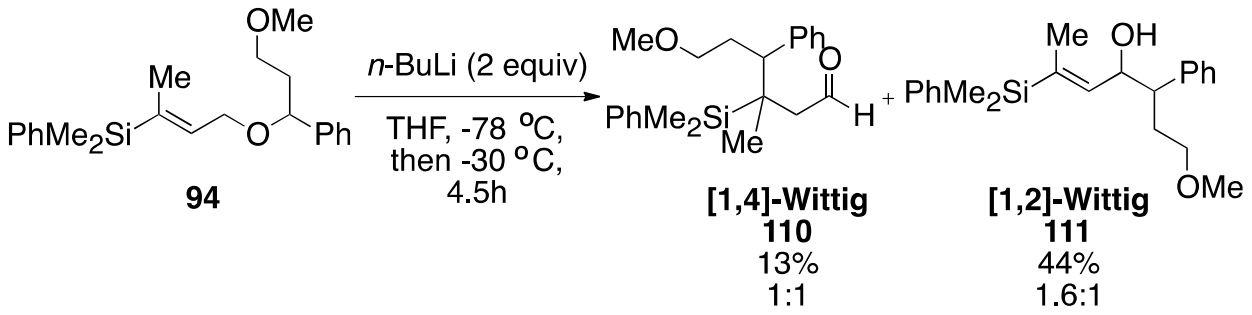
3.3.4 Effect of olefin geometry

Rearrangement of *Z*-**90** under same conditions of the geometrical isomer (*E*-**90**) provided a complex mixture of products, however, in the ^{1}H NMR spectrum of the crude reaction mixture signals attributable to the [1,4]- and [1,2]-products could be located and diastereomeric ratios of both products were approximately 1:1. Due to the complexity of the mixture, isolation of the products was not performed. The use of an internal standard was not a possible solution to heavy overlap of signals in the crude ^{1}H NMR spectrum.

3.3.5 Attempts to improve regio and diastereocontrol with an intramolecular coordinating group

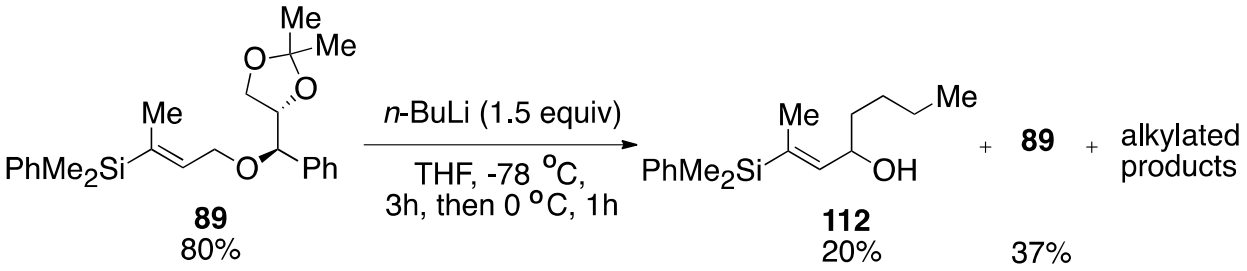
Schreiber and Goulet demonstrated that ether groups adjacent to the terminal allylic carbon (γ position) or proximal to the migrating center worked as directing groups by chelating the lithium cation in deprotonated allylic ethers, and provided good levels of diastereoselectivity in their [2,3]-Wittig rearrangement.[11] Maleczka and Geng, on the other hand, showed that such potentially coordinating groups are capable of reversing the 'normal' stereochemical course of the [1,2]-Wittig rearrangement of benzyl ethers by means of a chelation-controlled migration.[12] They also showed that the relative stereochemistry of the migrating center and the carbanion defined the degree of retention/inversion at the carbanion terminus.

In light of these precedents, and encouraged by the improved efficiency of migration of secondary benzylic groups, it was hypothesized that placing a coordinating group near the migrating carbon in our model system (**85**) would provide improved diastereoselectivity for the [1,4]- and/or [1,2]-shifts, and perhaps better 'regiocontrol' of the migrations. Thus, the rearrangement of compound **94** took place at -30 ^{o}C and afforded the [1,4]- and [1,2]-Wittig rearrangement products **110** and **111** in 13% and 44%, respectively (Scheme 61). Unfortunately, no changes in [1,4]-/[1,2]-selectivity or diastereoselectivity, relative to that of substrates lacking potentially coordinating groups, were observed. Attempts to promote the desired intramolecular coordination by using a non-polar solvent (hexane) at -35 ^{o}C led to 36% of alcohol **111** with low diastereoselectivity (1.2:1) and only traces of the [1,4]-product **110**.

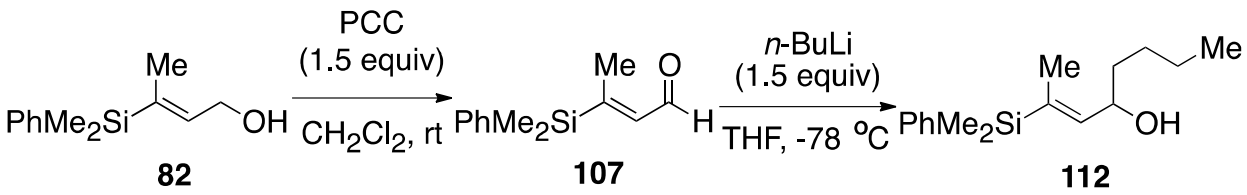


Scheme 61. Effect of a flexible coordinating motif near the migrating carbon.

A possible reason for the negligible effect of the proximal coordinating group (methoxy) present in **94** might be that its high degree of conformational flexibility increases the entropic cost of coordination to the lithium cation paired with the reacting allylic anion. Compound **89**, containing a rigid coordinating motif previously used in Wittig rearrangements,[11a, 12] underwent a sluggish reaction with *n*-BuLi at -78 °C. In the complex ^{1}H NMR spectrum there was no signal attributable to any aldehyde ([1,4]-product). In addition to mixtures of apparently alkylated compounds only alcohol **112** was isolated in 20%, together with unreacted **95** (37%). The formation of **112** is probably a consequence of the reaction between *n*-BuLi and allylic radical anion that did not undergo recombination. The identity of **112** was confirmed by independent synthesis: Treatment of **107**, prepared by PCC oxidation of **82** (*E/Z* = 2:1), with *n*-BuLi in THF at -78 °C gave alcohol **112** (Scheme 63).



Scheme 62. Reactivity of compound **89** bearing a rigid coordinating group.



Scheme 63. Independent synthesis of **112**.

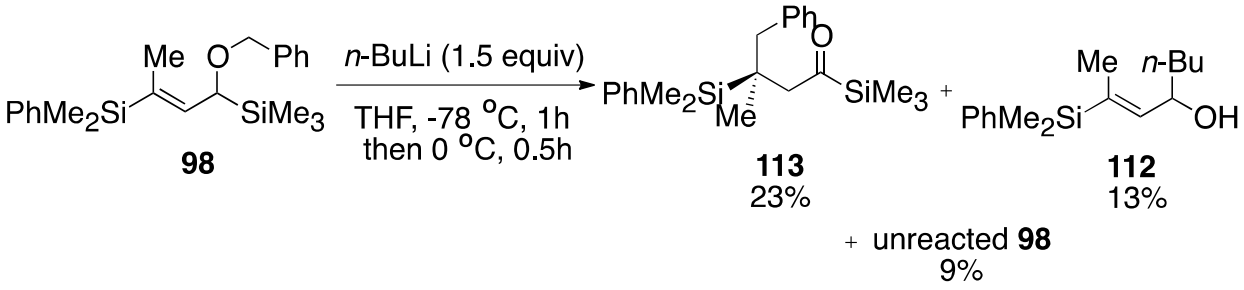
3.4 [1,4]- and [1,2]-Wittig rearrangements of α,γ-disilyl allylic ethers

Given that the [1,2]-Wittig product was the major product (albeit slightly) in the rearrangement of most γ-silyl substrates studied, it was thought that an additional silyl group at the α-position would prevent [1,2]- recombination and favor the [1,4]-migration. In addition, the rearrangement of α,γ-disilyl allylic ethers could be a method for the synthesis of β-silyl-α,β-unsaturated acylsilanes.

3.4.1 Reactivity of model substrate 98

Compound **98** underwent high conversion when treated with *n*-BuLi at -78 ^{o}C for 1.5 hours at 0 ^{o}C (Scheme 64). In addition to unreacted **98** (9%), the [1,4]-Wittig product was isolated in 23% yield, as well as the previously observed compound **112** in 13% yield. The mass recovery of the

reaction was less than 60%, and despite some signals in the ^{1}H NMR spectrum of the crude material suggesting the formation of the [1,2]-product, none of it was isolated, (we tentatively assigned the [1,4]-/[1,2]-ratio as 9:1). When the reaction was performed between -78 and -30 ^{o}C for 7 hours a similar yield of **113** was obtained (25%), together with unreacted **98** (15%).



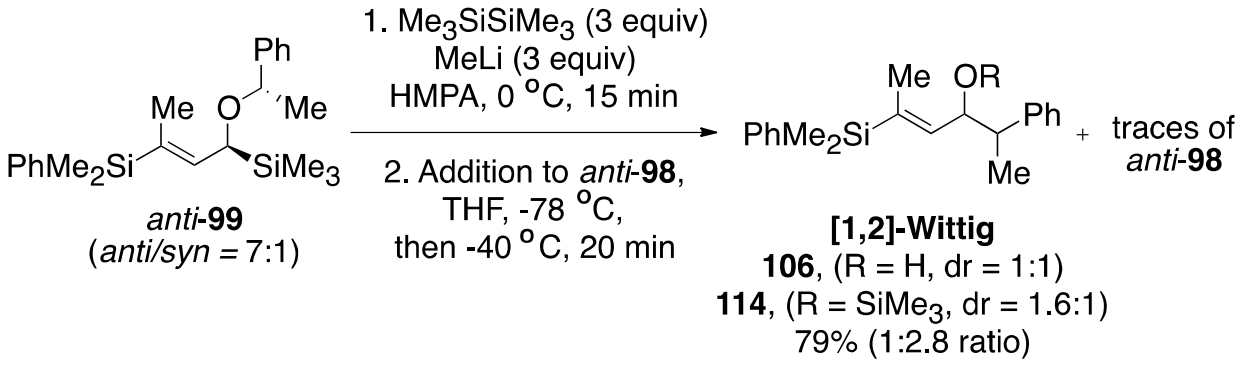
Scheme 64. Rearrangement of α,γ-disilyl allylic ether **98**.

3.4.2 Effect of substitution at the migrating carbon

Next, the behavior of diastereomeric α,γ-disilyl allylic ethers **99** containing a methyl group at the benzylic position was studied. As expected, a decrease in reactivity was observed, presumably because of high steric hindrance around the site of expected deprotonation. When treated with excess *n*-BuLi from -78 ^{o}C to room temperature, both *syn* and *anti*-**99** underwent little reaction, and were recovered mostly unchanged. Although diastereomerically enriched mixtures of **99** were used in these experiments (1.5:1 to 7:1), no significant change in dr of the recovered **99** was observed.

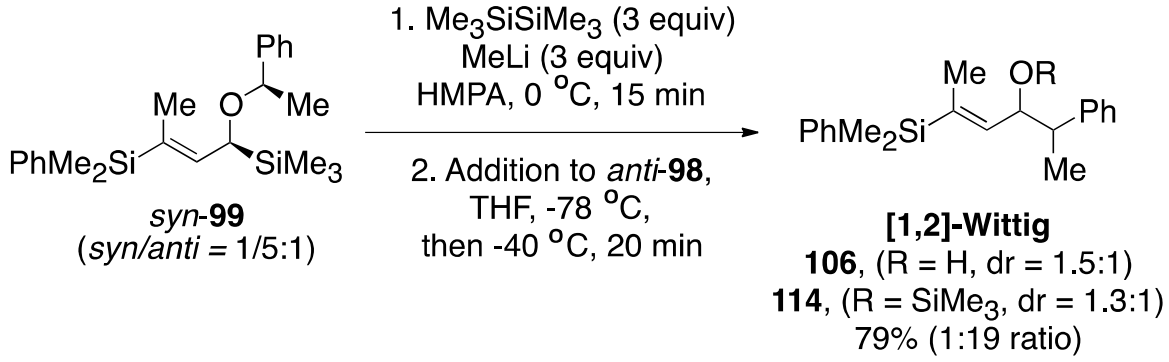
Given the low reactivity of these compounds, the rearrangement was initiated under conditions for Si/Li exchange (Chapter 2, Scheme 41). Treatment of *anti*-**99** (dr = 7:1) with *in situ* generated TMSLi at -78 ^{o}C and warming at -40 ^{o}C for 20 minutes allowed almost complete Si/Li exchange

followed by exclusive [1,2]-Wittig rearrangement. The [1,2]-Wittig products were obtained as the free alcohol (**106**) and *O*-silylated analogue (**114**) in excellent overall yield (79%).



Scheme 65. [1,2]-Wittig rearrangement of *anti*-**99** initiated by Si/Li exchange.

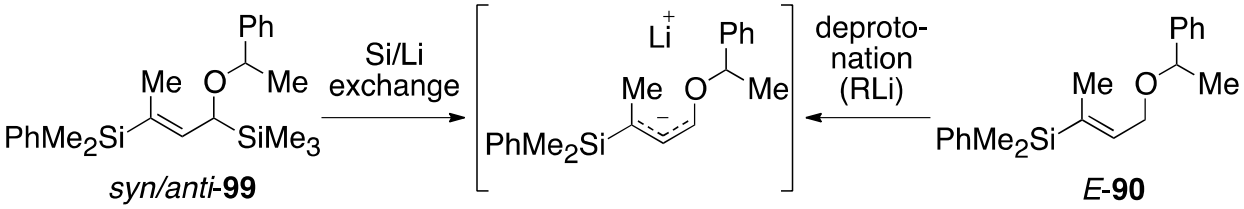
Diastereomerically enriched *syn*-**99** (dr = 1.5:1) equally underwent efficient Si/Li exchange followed by rearrangement to give **106** and **114** in 79% overall yield (1:19 ratio, Scheme 66).



Scheme 66. [1,2]-Wittig rearrangement of *syn*-**99** initiated by Si/Li exchange.

It is remarkable that under these conditions no [1,4]-migration takes place at all, as concluded from analysis of aldehyde region in the ^{1}H NMR spectrum of the crude material. The exclusive [1,2]-Wittig selectivity is remarkable, although no diastereoselectivity is observed. Also, it is interesting that the deprotonative rearrangement of *E*-**90** afforded a 2.5:1 ratio of [1,2]- and [1,4]-

products **106** and **105** (Scheme 59), whereas both diastereomers of **99** provided exclusive (>20:1) [1,2]-product **106**/**116** (Schemes 65 & 66) even though the same allylic anion undergoes bond reorganization (Scheme 67). This difference might be due to the proximity of the lithium cation in each case, and is consistent with the observed dependence of the product distribution on the base (or nucleophile) employed in the rearrangements.



Scheme 67. Allylic anion formation via Si/Li exchange or via deprotonation.

3.5 Conclusions

In conclusion, γ-silyl allylic ethers undergo [1,4]- and [1,2]-Wittig rearrangements with low efficiency and diastereoselectivity when treated with alkyllithiums. Minimal electronic effects were observed, although electron-withdrawing benzyl groups were incompatible with the reaction conditions. No improvement on the region- or diastereoselectivity was obtained by changing the olefin geometry or including flexible or rigid coordinating groups proximal to the migrating carbon.

Similarly, α,γ-disilyl allylic ethers undergo inefficient Wittig rearrangements when reacted with alkyllithiums (<30%), but importantly, the [1,4]-pathway is dominant. In addition, severe loss of reactivity towards allylic deprotonation is found when alkyl substitution at the migrating carbon is present. Importantly, clean and exclusive [1,2]-Wittig rearrangement of α,γ-disilyl allylic

ethers substituted at the benzylic position is achieved by carbanion generation via Si/Li exchange with TMSLi.

3.6 Experimental section

*Preparation of compounds E-**82** and E-**83***[13]

Following a literature procedure,[14] to a solution of 2-butyn-1-ol (1 g, 14.3 mmol) and $PhMe_2SiH$ (2.14 g, 15.7 mmol, 1.1 equiv) in THF (4 mL) was added a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in THF (14 μL, 0.0014 mmol, 0.0001 equiv) at room temperature. The solution was heated in an oil bath at 50 ^oC for 4h. The reaction mixture was concentrated and the mixture purified by column chromatography (10% and 25% EtOAc in hexanes) to give 1.6 g of *E*-**82** (54%) and 1.2 g of *E*-**83** (41%) as colorless oils. Spectroscopic data for *E*-**82**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.33 (m, 3 H), 5.94 (m, 1 H), 4.27 (t, *J* = 4.5 Hz, 2 H), 1.67 (m, 3 H), 1.53 (s, 1 H), 0.34 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 133.9 (2 C), 129.0, 127.8 (2 C), 59.8, 15.0, -3.7. Spectroscopic data for *E*-**83** ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.33 (m, 3 H), 6.02 (m, 1 H), 4.30 (d, *J* = 4.5 Hz, 2 H), 1.76 (m, 3 H), 1.54 (s, 1 H), 0.38 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 133.9 (2 C), 128.9, 127.8 (2 C), 60.7, 31.6, 14.7, -2.6. *E*-**82** *and E*-**83** are known compounds and their spectral data is identical to that in the literature.[13]

*Preparation of compound Z-**82***

Following a literature procedure,[6] to a solution of 2-butyn-1-ol (600 mg, 8.56 mmol, 1 equiv) and phenyldimethylsilane (1.4 g, 10.27 mmol, 1.2 equiv) in acetone (17 mL) at 0 ^{o}C was added $[Cp^*Ru(MeCN)_3]PF_6$ (4.7 mg, 0.009 mmol, 0.02 equiv) and the mixture stirred under nitrogen. After 1 hour the reaction was concentrated and the product purified by column chromatography (15% EtOAc in hexanes) affording 792 mg (45%) of *Z*-**82** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.33 (m, 3 H), 6.25 (m, 1 H), 3.94 (d, *J* = 7.0 Hz, 2 H), 1.86 (m, 3 H), 0.39 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 139.0, 138.0, 133.5 (2 C), 129.1, 128.0 (2 C), 62.0, 25.0, -1.4. IR (film) 3339, 3069, 2953, 1427, 1250, 1109, 815 cm^{-1}.

*Preparation of compound **84***

To a cold solution of *E*-**82** (380 mg, 1.84 mmol) in dichloromethane (4 mL) was added CBr_4 (702 mg, 1.15 equiv) followed by a solution of PPh_3 (628 mg, 1.3 equiv) in dichloromethane (4 mL). After 1 hour the reaction was judged complete by TLC. The reaction mixture was concentrated and the residue suspended in Et_2O. The insoluble material was filtrated and the filtrate concentrated. The residue was purified by column chromatography (10% CH_2Cl_2 in hexanes) to give 505 mg of **84** (ca. 100%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.34 (m, 3 H), 6.06 (m, 1 H), 4.01 (d, *J* = 7.8 Hz, 2 H), 1.75 (m, 3 H), 0.03 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.3, 137.3, 135.0, 134.0 (2 C), 129.2, 127.8 (2 C), 27.2, 14.4, -3.8.

*Preparation of compound **85***

To a suspension of NaH (60 % w/w, 71 mg, 1.76 mmol, 1 equiv) in THF (1 mL) was added slowly benzyl alcohol (191 mg, 1 equiv). After 5 minutes at room temperature a solution of bromide **84** (470 mg, 1 equiv) in THF (1.5 mL) was added, followed by a solution of TBAI (32 mg, <0.05 equiv) in THF (0.5 mL). The mixture was heated in an oil bath at 50 ^{o}C for 6 hours, then cooled down at room temperature. Water (3 mL) was added and the mixture extracted with Et_2O (3 × 5 mL). Combined organic extracts were washed with brine and dried over $MgSO_4$. After filtration of the salt, the filtrate was concentrated and the residue purified by column chromatography (4% EtOAc in hexanes) to afford 365 mg (73%) of **85** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 2 H), 7.32 (m, 7 H), 7.27 (m, 1 H), 5.97 (m, 1 H), 4.51 (s, 2 H), 4.14 (dd, *J* = 1.0, 5.5 Hz, 2 H), 1.63 (m, 3 H), 0.33 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 138.0, 137.9, 137.5, 133.9 (2 C), 128.9, 128.4 (2 C), 127.9 (2 C), 127.7 (2 C), 127.6, 72.6, 67.1, 15.2, -3.6. IR (film) 3030, 2923, 1246, 1111, 829 cm^{-1}. HRMS (EI) *m*/*z* 296.1590 [(M^{+}); calcd for $C_{19}H_{24}OSi$, 296.1596].

*Preparation of compound **86***

To a suspension of NaH (60 % w/w, 220 mg, 5.5 mmol, 1.5 equiv) in THF (3 mL) at room temperature was added slowly 4-methylbenzyl alcohol (672 mg, 5.5 mmol, 1.5 equiv). After 15

minutes at room temperature a solution of bromide **84** (987 mg, 3.67 mmol, 1 equiv) in THF (3 mL) was added. After 3 hours the reaction was quenched by adding water (3 mL). The mixture extracted with Et_2O (3 × 5 mL). Combined organic extracts were washed with brine and dried over $MgSO_4$. After filtration of the salt, the filtrate was concentrated and the residue purified by column chromatography (4% EtOAc in hexanes) to afford 571 mg (45%) of **86** as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.33 (m, 3 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 7.14 (d, *J* = 7.8 Hz, 2 H), 5.98 (m, 1 H), 4.48 (s, 2 H), 4.13 (dd, *J* = 1.0, 6.0 Hz, 2 H), 2.33 (s, 3 H), 1.64 (s, 3 H), 0.3 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 137.8, 137.6, 137.3, 135.2, 134.0 (2 C), 129.1 (2 C), 128.9, 128.0 (2 C), 127.7 (2 C), 72.4, 67.0, 21.2, 15.2, -3.6. IR (film) 3016, 2955, 1427, 1248, 1109, 833 cm^{-1}. HRMS (EI) *m/z* 310.1753 [(M^+); calcd for $C_{20}H_{26}OSi$, 310.1753].

*Preparation of compound **87***

To a solution of 4-(trifluoromethyl)benzyl alcohol (1 g, 5.68 mmol, 1 equiv) in DMF (6 mL) was added slowly NaH (60% w/w, 273 mg, 1.2 equiv), and the mixture was stirred at room temperature for 1 hour. The reaction was quenched by adding water (4 mL). The mixture extracted with Et_2O (3 × 10 mL). Combined organic extracts were washed with water (3 × 3 mL), brine and dried over $MgSO_4$. After filtration of the salt, the filtrate was concentrated and the residue purified by column chromatography (5% and 30% EtOAc in hexanes) to afford 298 mg (15%, 68% brsm) of **87** as a colorless oil and 780 mg (78%) of unreacted 4-(trifluoromethyl)benzyl alcohol.

*Preparation of compound **88***

Preparation of 2-phenyl-4-penten-1-ol: To a solution of benzophenone (2.5 g, 20.8 mmol, 1 equiv) in THF (50 mL) at 0 ^{o}C was added a solution of allylmagnesium chloride (2M in THF, 11.4 mL, 1.1 equiv) slowly. The temperature was slowly raisd. After 3 hours the reaction was quenched by adding $NH_4Cl_{(aq)}$ (~15 mL) and the mixture was acidified with 1M HCl. After extraction with ether (3 × 20 mL), combined organic extracts were washed with brine and dried over $MgSO_4$. The salts were filtrated, the filtrate was concentrated to give 3.47 g (ca. 100%) of crude product which was used in the next step without further purification. Spectral data are in accord with reported literature values.[15]

To a solution of of 2-phenyl-4-penten-1-ol (723 mg, 4.46 mmol, 1.2 equiv) in DMF (9.5 mL) was added NaH (60% w/w oil dispersion, 233 mg, 5.57 mmol, 1.5 equiv) and the mixture was stirred at room temperature until bubbling ceased. Then, bromide **84** (1 g, 3.71 mmol, 1 equiv) was added dropwise via syringe. After 13 hours the reaction was quenched by adding water and the mixture was extracted with Et_2O (3 × 15 mL). Combined organic extracts were washed with water (6 × 5 mL), brine and dried over $MgSO_4$. The solution was then concentrated and the residue purified by column chromatography (1.5% EtOAc in hexanes) to afford 245 mg (70%) of compound **88** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (m, 2 H), 7.37 (m, 2 H), 7.32 (m, 5 H), 7.23 (m, 1 H), 5.96 (m, 1 H), 5.64 (m, 1 H), 5.00 (m, 1 H), 4.98 (m, 1 H), 3.92 (ddd, A of ABX system, *J* = 0.5, 4.5, 10.5 Hz, 1 H), 3.78 (ddd, B of ABX system, *J* = 1.0, 5.0, 11.0 Hz, 1 H), 2.59 (dd, C of CDX system, *J* = 6.0, 11.5 Hz, 1 H), 2.53 (dd, D of CDX system, *J*

= 6.0, 11.5 Hz, 1 H), 1.54 (s, 3 H), 1.51 (m, 1 H), 0.33 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 138.7, 135.8, 134.2, 134.0 (2 C), 133.0, 128.9, 128.1 (2 C), 127.7 (2 C), 126.9, 126.3 (2 C), 117.6, 78.8, 60.4, 47.4, 23.5, 15.1, 0.8, -3.6. IR (film) 3030, 2954, 1426, 1248, 1111, 841 cm^{-1}. HRMS (EI) *m*/*z* 350.2056 [(M^+); calcd for $C_{23}H_{30}OSi$, 350.2066].

Preparation of compound **89**

To a solution of 1-phenyl-2-propen-1-ol[16] (2g, 14.9 mmol, 1 equiv), triethylamine (8.3 mL, 59.6 mmol, 4 equiv) at 0 ^oC was added acetic anhydride (2.28 g, 23.35 mmol, 1.5 equiv) and a few crystals of DMAP (catalyst). The mixture was stirred overnight and the temperature gradually increased (ice melting). Then the mixture was concentrated and the product purified by column chromatography (5% EtOAc in hexanes) to give 1.9 g (72%) of 1-phenylallyl acetate as a colorless oil. Spectral data is in accord with that reported in the literature.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.24 (m, 1 H), 6.25 (dt, *J* = 1.0, 5.5 Hz, 1 H), 6.00 (ddd, *J* = 6.0, 10.5, 17.0 Hz, 1 H), 5.29 (dt, *J* = 1.0, 17.0 Hz, 1 H), 5.24 (m, 1 H), 2.10 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 138.9, 136.3, 128.5 (2 C), 128.1, 127.1 (2 C), 116.9, 76.2, 21.2. IR (film) 3031, 2924, 1741, 1234, 1022 cm^{-1}.

To a solution of 1-phenylallyl acetate (566 mg, 3.21 mmol, 1 equiv) in acetone (26 mL) was added NMO (601 mg, 5.14 mmol, 1.6 equiv) and water (3 mL), followed by a 4% w/w aqueous solution of $K_2OsO_4 \cdot 2H_2O$ (23.6 mg, 0.064 mmol, 0.02 equiv). The reaction was monitored by

TLC (5% EtOAc in hexanes). After 7.5 hours 20% w/w aqueous solution of $Na_2S_2O_3$ (20 mL) was added and the mixture stirred for 2 hours. The aquous phase was extracted with EtOAc (3 × 25 mL) and combined organic extracts were washed with brine and dried over $MgSO_4$. The crude diol[17] was dissolved in acetone (32 mL) and 2,2-dimethoxypropane (3.9 mL, 32 mmol, 10 equiv) followed by *p*-TSA hydrate (304 mg, 1.6 mmol, 0.5 equiv) was added. The mixture was refluxed for 1 hour, cooled down and diluter with EtOAc (30 mL) and water (10 mL). The aqueous phase was extracted with EtOAc (3 × 25 mL), brine and dried over $MgSO_4$. Column chromatography (10% EtOAc in hexanes) afforded 616 mg (77%) of diastereomeric (2,2-dimethyl-1,3-dioxolan-4-yl)(phenyl)methyl acetate as a yellowish oil. Mixture of diastereomers (*syn/anti* = 1:0.6) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 8 H), 5.30 (d, *J* = 7.0 Hz, 0.6 H), 4.74 (d, *J* = 8.5 Hz, 1 H), 4.54 (m, 0.6 H), 4.32 (dd, A of ABX system, *J* = 3.0, 12.0 Hz, 1 H), 4.12 (dd, B of ABX system, *J* = 5.5, 12.0 Hz, 1 H), 4.00 (m, 1 H), 3.69 (dd, C of CDX system, *J* = 4.5, 12.0 Hz, 0.6 H), 3.60 (dd, D of CDX system, *J* = 8.0, 12.0 Hz, 0.6 H), 2.04 (s, 3 H), 1.90 (s, 1.8 H), 1.64 (s, 1.8 H), 1.57 (s, 3 H), 1.51 (s, 3 H), 1.47 (s, 1.8 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.5, 137.2, 137.0, 128.7, 128.5, 128.4, 128.3, 126.6, 126.4, 109.9, 109.2, 81.0, 79.9, 78.4, 76.2, 64.2, 63.0, 27.1, 27.0, 25.4, 25.0, 21.1, 20.7.

To a solution of (2,2-dimethyl-1,3-dioxolan-4-yl)(phenyl)methyl acetate (*anti/syn* > 20:1, 950 mg, 3.80 mmol, 1 equiv) in CH_2Cl_2 was added a mixture of 10:1 MeOH/water (79 mL) and K_2CO_3 (577 mg, 4.18 mmol, 1.1 equiv). The mixture was stirred at room temperature overnight, then it was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic extracts were dried

over $MgSO_4$. The solution was then concentrated and the residue purified by column chromatography (25 % EtOAc in hexanes) to afford 563 mg (71%) of (2,2-dimethyl-1,3-dioxolan-4-yl)(phenyl)methanol as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 4 H), 7.28 (m, 1 H), 5.30 (d, *J* = 7.0 Hz, 1 H), 4.45 (dt, *J* = 5.0, 7.5 Hz, 1 H), 3.21 (ddd, *J* = 5.0, 8.0, 12.0 Hz, 1 H), 3.09 (ddd, *J* = 4.5, 8.0, 12.0 Hz, 1 H), 1.62 (s, 3 H), 1.48 (s, 3 H), 1.35 (dd, *J* = 4.5, 8.5 Hz, 1 H).

To a vigorously stirred solution of (2,2-dimethyl-1,3-dioxolan-4-yl)(phenyl)methanol (*anti/syn* > 20:1, 90 mg, 0.432 mmol, 1 equiv) and **84** (233 mg, 0.864 mmol, 2 equiv) in THF (1 mL) at 0 ^{o}C was added *t*-BuONa (104 mg, 1.08 mmol, 2.5 equiv). After 5 hours the reaction was quenched by adding water (2 mL) and the mixture was diluted with Et_2O. The aqueous phase was extracted with Et_2O (3 × 3 mL). Combined organic extracts were washed with brine and dried over $MgSO_4$. The solution was concentrated and the residue purified by column chromatography (8% EtOAc in hexanes) to afford 137 mg (80%) of compound **89** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (m, 2 H), 7.26 (m, 8 H), 5.71 (m, 1 H), 5.20 (d, *J* = 7.0 Hz, 1 H), 4.52 (dt, *J* = 4.0, 7.5 Hz, 1 H), 3.87 (ddd, A of ABX system, *J* = 1.0, 5.5, 13.0 Hz, 1 H), 3.73 (ddd, B of ABX system, *J* = 1.0, 6.0, 8.0 Hz, 1 H), 3.02 (dd, C of CDX system, *J* = 8.0, 10.0 Hz, 1 H), 2.82 (dd, D of CDX system, *J* = 3.5, 10.0 Hz, 1 H), 1.61 (s, 3 H), 1.46 (m, 3 H), 1.42 (s, 3 H), 0.24 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 137.5, 137.2, 137.1, 133.9 (2 C), 128.9, 128.0 (2 C), 127.9, 127.7 (2 C), 126.7 (2 C), 108.9, 78.7, 77.5, 70.6, 68.1, 27.2, 24.7,

15.0, -3.67, -3.69. IR (film) 3030, 2972, 1246, 1110 cm^{-1}. HRMS (EI) *m*/*z* 396.2114 [(M^+); calcd for $C_{24}H_{32}O_3Si$, 396.2121].

Preparation of compound E-**90**

To a vigorously stirred solution of *E*-**82** (335 mg, 1.623 mmol, 1 equiv) and the trichloroacetimidate of 1-phenylethanol (606 mg, 2.27 mmol, 1.4 equiv) in hexane (8 mL) at 0 ^oC was added a solution of TMSOTf (21 μL, 0.114 mmol, 0.07 equiv) in hexane (1 mL). The reaction was followed by TLC (3% EtOAc in hexanes). After 3.5 hours the solids were filtrated and washed with hexanes (40 mL). The solution was extracted with $NaHCO_{3\ (sat)}$ (3 × 10 mL), water (3 × 10 mL), brine and dried over $MgSO_4$. The solution was concentrated and the residue purified by column chromatography (3% EtOAc in hexanes) to afford 512 mg (84%) of *E*-**90** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.34 (m, 7 H), 7.27 (m, 1 H), 5.98 (m, 1 H), 4.44 (q, *J* = 6.5 Hz, 1 H), 3.99 (dd, *J* = 0.5, 6.0 Hz, 1 H), 1.55 (m, 3 H), 1.47 (d, *J* = 6.5 Hz, 3 H), 0.34 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 138.1, 137.8, 137.2, 133.9 (2 C), 128.9, 128.4 (2 C), 127.7 (2 C), 127.4, 126.3 (2 C), 77.7, 65.8, 24.2, 15.1, -3.7. IR (film) 3064, 2972, 1248, 1101 cm^{-1}. HRMS (EI) *m*/*z* 310.1745 [(M^+); calcd for $C_{20}H_{26}OSi$, 310.1753].

Preparation of compound Z-**90**

To a vigorously stirred solution of *Z*-**82** containing minor (<10%) of the regioisomer *Z*-**83** (361 mg, 1.75 mmol, 1 equiv) and trichloroacetimidate of 1-phenylethanol (606 mg, 2.27 mmol, 1.3 equiv) in hexane (10 mL) at 0 ^oC was added $BF_3{\cdot}OEt_2$ (22 μL, 0.175 mmol, 0.1 equiv). The

reaction was kept at room temperature. When the reaction was judged complete by TLC (5% EtOAc) the solids were filtrated and washed with hexanes (40 mL). The solution was extracted with $NaHCO_{3\ (sat)}$ (3 × 10 mL), water (3 × 10 mL), brine and dried over $MgSO_4$. The solution was concentrated and the residue purified by column chromatography (5% EtOAc in hexanes) to afford 512 mg (84%) of *E*-**90** (containing ~10% of β regioisomer) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 2 H), 7.25 (m, 6 H), 7.20 (m, 2 H), 6.24 (m, 1 H) 4.18 (q, *J* = 6.5 Hz, 1 H), 3.67 (m, 2 H), 1.83 (s, 3 H), 1.36 (d, *J* = 6.5 Hz, 3 H), 0.29 (s, 3 H), 0.26 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 139.9, 138.8, 137.5, 133.6 (2 C), 128.9, 128.3 (2 C), 127.8 (2 C), 127.3, 126.2 (2 C), 77.6, 67.9, 25.1, 23.9, -1.5, -1.6. IR (film) 3060, 2971, 1248, 1110 cm^{-1}. HRMS (EI) *m*/*z* 310.1751 [(M^+); calcd for $C_{20}H_{26}OSi$, 310.1753].

Preparation of compound **91**

Compound **91** was prepared in 7 steps from benzaldehyde.

To a solution of benzaldehyde (3.86 g, 36.36 mmol, 1 equiv) in THF (80 mL) at 0 ^oC was added a solution of allylmagnesium chloride (2M in THF, 20 mL, 40 mmol, 1.1 equiv) slowly. The cold bath was removed and the mixture stirred at room temperature for 3h. The reaction was carefully quenched by addition $NH_4Cl_{\ (sat)}$ (25 mL) and diluted with Et_2O (50 mL). The mixture was acidified with 1 M HCl and extracted with Et_2O (3 × 30 mL), brine and dried over $MgSO_4$. The mixture was concentrated and the crude alcohol was dissolved in DMF (~60 mL), TBSCl (6 g, 40 mmol, 1.1 equiv) was added followed by solid imidazole (excess). The suspension was

stirred overnight. The next day the reaction was diluted with water (50 mL) and extracted with Et_2O (3 × 50 mL). Combined organic extracts were washed with water (5 × 20 mL), brine, dried over $MgSO_4$ and concentrated. The crude *O*-TBS alcohol was used in the next step without further purification. Spectral data are in accord with reported literature values.[18]

To a solution of the TBS ether of 1-phenyl-3-buten-1-ol (830 mg, 3.16 mmol, 1 equiv) in dioxane (2.5 mL) was added water (7.5 mL) and 2,6-lutidine (678 mg, 6.33 mmol, 2 equiv). The mixture was vigorously stirred at room temperature and a solution of $K_2OsO_4 \cdot 2H_2O$ (23.3 mg, 0.0632 mmol, 0.02 equiv) in water (~1 mL), followed by solid $NaIO_4$ (1.36 g, 12.65 mmol, 4 equiv). The reaction was followed by TLC (5% EtOAc in hexanes) until completion. The mixture was then extracted with a 10:1 mixture of hexanes / CH_2Cl_2, and the organic phase was washed with 1 M HCl, water, dried over $MgSO_4$ and concentrated. Purification by column chromatography (5% EtOAc in hexanes) afforded 702 (84%) of 3-(*tert*-butyldimethylsiloxy)-3-phenylpropanal. Spectral data are in accord with reported literature values.[18b] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (dd, *J* = 2.0, 2.5 Hz, 1 H), 7.42 (m, 4 H), 7.36 (m, 1 H), 5.30 (dd, *J* = 4.0, 8.0 Hz, 1 H), 2.95 (ddd, A of ABX system, *J* = 2.5, 8.0, 16.0 Hz, 1 H), 2.71 (ddd, B of ABX system, *J* = 2.0, 4.0, 16.0 Hz, 1 H), 0.95 (s, 9 H), 0.13 (s, 3 H), -0.05 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.9, 143.8, 128.4 (2 C), 127.6, 125.7 (2 C), 70.8, 54.0, 25.6 (3 C), 18.1, -4.6, -5.1.

3-(*tert*-butyldimethylsiloxy)-3-phenylpropanal (702 mg, 2.65 mmol, 1 equiv) was dissolved in wet THF (25 mL) and $NaBH_4$ (100 mg, 2.65 mmol, 1 equiv) was added. After 3 hours the reaction was carefully diluted with water (5 mL) and Et_2O (20 mL). The organic phase was washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (15% EtOAc in hexanes) afforded 608 mg, (86%) of 3-(*tert*-butyldimethylsiloxy)-3-phenylpropan-1-ol as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 4 H), 7.24 (m, 1 H), 4.94 (dd, *J* = 4.5, 7.0 Hz, 1 H), 3.69 (m, 2 H), 2.43 (s, 1 H), 1.90 (m, 2 H), 0.88 (s, 9 H), 0.04 (s, 3 H), -0.17 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 128.2 (2 C), 127.2, 125.8 (2 C), 74.5, 60.3, 42.2, 25.8 (3 C), 18.1, -4.7, -5.2. IR (film) 3372, 2955, 1471, 1257, 1093, 837 cm^{-1}. HRMS (EI) *m*/*z* 266.1706 [(M^+); calcd for $C_{15}H_{26}O_2Si$, 266.1702].

To a solution of 3-(*tert*-butyldimethylsiloxy)-3-phenylpropan-1-ol (546 mg, 2.05 mmol, 1 equiv) in CH_2Cl_2 (41 mL) was added triethylamine (1.29 mL, 9.23 mmol, 4.5 equiv) and acetic anhydride (0.29 mL, 3.08 mmol, 1.5 equiv). A couple of crystals of DMAP (catalyst) were added and the solution left to sit overnight. Then, the mixture was concentrated and the residue purified by column chromatography (5% EtOAc in hexanes) to afford 594 mg (94%) of 3-(*tert*-butyldimethylsiloxy)-3-phenylpropyl acetate as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 4 H), 7.21 (m, 1 H), 4.77 (dd, *J* = 4.0, 8.0 Hz, 1 H), 4.17 (m, 1 H), 4.08 (m, 1 H), 2.01 (s, 3 H), 1.95 (m, 2 H), 0.86 (s, 9 H), 0.00 (s, 3 H), -0.18 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 128.2 (2 C), 127.1, 125.7 (2 C), 71.7, 61.4, 39.6, 25.8 (2 C), 20.9, 18.1, -4.7, -5.2. IR

(film) 2957, 2856, 1743, 1242, 1097, 837 cm^{-1}. HRMS (EI) *m*/*z* 308.1804 [(M^{+}); calcd for $C_{17}H_{28}O_3Si$, 308.1808].

To a solution of 3-(*tert*-butyldimethylsiloxy)-3-phenylpropyl acetate (575.5 mg, 1.87 mmol, 1 equiv) in dry acetonitrile (2 mL) was added aqueous HF (5% w/w, 0.47 mL, excess). The mixture was stirred at room temperature and monitored by TLC (5% EtOAc hexanes). When the reaction was complete, the mixture was diluted with water (5 mL) and EtOAc (20 mL). The mixture was carefully extracted with $NaHCO_{3\ (sat)}$ (2 × 10 mL) and the aqueous phase extracted with with EtOAc (3 × 10 mL). Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (25% EtOAc in hexanes) afforded 260 mg (72%) of 3-hydroxy-3-phenylpropyl acetate as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.27 (m, 1 H), 4.78 (m, 1 H), 4.30 (ddd, *J* = 5.5, 7.5, 11.0 Hz, 1 H), 4.11 (m, 1 H), 2.19 (d, *J* = 3.5 Hz, 1 H), 2.04 (m, 2 H), 2.03 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 128.6 (2 C), 127.8, 125.7 (2 C), 71.3, 61.6, 37.9, 21.0. IR (film) 3426, 2959, 1734, 1244, 1041 cm^{-1}. HRMS (EI) *m*/*z* 176.0836 [$(M\text{-}H_2O)^{+}$; calcd for $C_{11}H_{12}O_2$, 176.0837].

To a solution of 3-hydroxy-3-phenylpropyl acetate (247 mg, 1.27 mmol, 1 equiv) in CH_2Cl_2 (8 mL) at 0 ^{o}C was added trichloroacetonitrile (275 mg, 1.91 mmol, 1.5 equiv) and DBU (35 mg, 0.229 mmol, 0.18 equiv). The reaction was monitored by TLC (5% EtOAc in hexanes) using silica plates pre-washed with triethylamine and dried. When the reaction was judged complete by

TLC, the mixture was concentrated and the residue subjected to column chromatography (column buffered with ~1% triethylamine) to afford 406 mg (95%) of the trichloacetimidate of 1-phenylpropyl-3-acetate (**91**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1 H), 7.38 (m, 2 H), 7.34 (m, 2 H), 7.28 (m, 1 H), 5.94 (dd, *J* = 5.0, 8.5 Hz, 1 H), 4.24 (m, 1 H), 4.12 (m, 1 H), 2.36 (m, 1 H), 2.34 (m, 1 H), 2.02 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 161.4, 139.4, 128.6 (2 C), 128.2, 126.0 (2 C), 91.5, 77.6, 60.7, 35.9, 20.9. IR (film) 3339, 2964, 1741, 1666, 1238, 1074, 796 cm^{-1}.

*Preparation of compound **92***

A solution of *E*-**82** (1.7 g, 8.2 mmol, 1.6 equiv) and trichloroacetimidate **91** (1.85 g, 5.43 mmol, 1 equiv) in hexane (24 mL) was cooled down in an ice bath and a solution of TMSOTf (49 μL, 0.272 mmol, 0.05 equiv) in hexane (1 mL) was added via syringe. After 2 hours the precipitate was filtered through a plug of celite and rinsed with hexanes. The filtrate was extracted with $NaHCO_{3\ (sat)}$ (3 × 10 mL), H_2O (2× 10 mL) and washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (7% EtOAc in hexanes) afforded 1.62 g (78%) of compound **92** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.35–7.24 (m, 7 H), 5.91 (m, 1 H), 4.36 (dd, *J* = 5.5, 8.5 Hz, 1 H), 4.18 (m, 1 H), 4.10 (m, 1 H), 3.98 (dd, A of ABX system, *J* = 5.5, 13.0 Hz, 1 H), 3.92 (dd, B of ABX system, *J* = 6.0, 13.0 Hz, 1 H), 2.12 (m, 1 H), 2.00 (s, 3 H), 1.94 (m, 1 H), 1.52 (s, 3 H), 0.32 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 141.9, 138.0, 137.7, 137.6, 133.9 (2 C), 128.9, 128.5 (2 C), 127.74, 127.72 (2 C), 126.6 (2

C), 78.6, 65.8, 61.6, 37.3, 20.9, 15.1, -3.6, -3.7. IR (film) 3070, 2957, 1740, 1244, 1041 cm^{-1}. HRMS (EI) *m*/*z* 382.1960 [(M^+); calcd for $C_{23}H_{30}O_3Si$, 382.1964].

*Preparation of compound **93***

To a solution of **92** in CH_2Cl_2 was added a mixture of 10:1 MeOH/water (100 mL) and K_2CO_3 (830 mg, 5.98 mmol, 1.1 equiv). The mixture was stirred at room temperature overnight, then it was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic extracts were dried over $MgSO_4$. The solution was then concentrated and the residue purified by column chromatography (25 % EtOAc in hexanes) to afford 1.373 g (95%) of compound **93** as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.35–7.26 (m, 8 H), 5.91 (m, 1 H), 4.52 (dd, *J* = 4.2, 9.6 Hz, 1 H), 4.01 (dd, A of ABX system, *J* = 5.4, 13.2 Hz, 1 H), 3.96 (dd, B of ABX system, *J* = 6.0, 12.6 Hz, 1 H), 3.77 (m, 2 H), 2.59 (t, *J* = 5.4 Hz, 1 H), 2.05 (m, 1 H), 1.86 (m, 1 H), 1.54 (s, 3 H), 0.33 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.8, 138.3, 137.9, 137.0, 133.9 (2 C), 129.0, 128.5 (2 C), 127.73 (2 C), 127.71, 126.5 (2 C), 81.7, 65.7, 61.2, 40.5, 15.1, -3.6, -3.7. IR (film) 3414, 3067, 2955, 1427, 1111, 830 cm^{-1}. HRMS (EI) *m*/*z* 340.1858 [(M^+); calcd for $C_{21}H_{28}O_2Si$, 340.1859].

*Preparation of compound **94***

To a solution of compound **93** (218 mg, 0.64 mmol, 1 equiv) in DMF (3 mL) was added sodium hydride (60% w/w oil dispersion, 34 mg, 0.832 mmol, 1.3 equiv) at room temperature. After 30

minutes methyl iodide (80 μL, 1.28 mmol, 2 equiv) was added. The reaction was monitored by TLC (10% EtOAc in hexanes). After 3 hours the reaction was quenched by adding water (6 mL). The aqueous phase was extracted with EtOAc (3 × 15 mL). Combined organic extracts were washed with water (3 × 15 mL), brine, dried over $MgSO_4$ and concentrated. Column chromatography (5% EtOAc in hexanes) 138 mg (61%) of **94** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.32 (m, 7 H), 7.25 (m, 1 H), 5.93 (m, 1 H), 4.42 (dd, *J* = 6.0, 8.4 Hz, 1 H), 3.97 (ddd, A of ABX system, *J* = 0.6, 5.4, 13.2 Hz, 1 H), 3.94 (dd, B of ABX system, *J* = 6.0, 12.6 Hz, 1 H), 3.40 (ddd, *J* = 5.4, 7.2, 9.6 Hz, 1 H), 3.30 (s, 3 H), 2.07 (ddt, *J* = 6.0, 8.4, 14.4 Hz, 1 H), 1.85 (m, 1 H), 1.53 (m, 3 H), 0.32 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 138.1, 137.8, 137.4, 134.0 (2 C), 128.9, 128.4 (2 C), 127.7 (2 C), 127.5, 126.7 (2 C), 78.5, 69.2, 65.8, 65.0, 58.6, 38.3, 15.1, -3.6, -3.7. IR (film) 3067, 2955, 1427, 1248, 1111, 833 cm^{-1}. HRMS (EI) *m*/*z* 354.2004 [(M^+); calcd for $C_{22}H_{30}O_2Si$, 354.2015].

*Preparation of compounds **96** and **97***

To a solution of 1-(trimethylsilyl)but-2-yn-1-ol (Chapter 2) (3 g, 21.1 mmol, 1 equiv), and $PhMe_2SiH$ (3.45 g, 25.3 mmol, 1.2 equiv) in THF (8 mL) was added a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in THF (21 μL, 0.0021 mmol, 0.0001 equiv) at room temperature. The solution was heated in an oil bath at 50 ^{o}C for 4h. The reaction mixture was concentrated and the mixture purified by column chromatography (4%, 10% and 13% EtOAc in hexanes) to give 1.46 g of **96** (25%) and 2.39 g of *E*-**97** (41%) as colorless oils. Spectroscopic data for **96**: ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.33 (m, 3 H), 5.88 (dq, *J* = 1.5, 9.5 Hz, 1 H), 4.43 (dd, *J* = 2.5, 9.5 Hz, 1 H), 1.62 (m, 3 H), 1.29 (d, *J* = 2.5 Hz, 1 H), 0.34 (s, 6 H), 0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 138.3, 133.9 (2 C), 132.9, 128.9, 127.7 (2 C), 65.3, 15.7, -3.4, -3.6, -4.0. IR (film) 3412, 2957, 1248, 1111, 837 cm^{-1}. HRMS (ESI) *m/z* 279.1603 [$(M+H)^+$; calcd for $C_{15}H_{27}OSi_2$, 279.1600]. Spectroscopic data for **97**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.31 (m, 3 H), 5.78 (dq, *J* = 1.8, 7.2 Hz, 1 H), 4.64 (s, 1 H), 1.65 (d, *J* = 7.2 Hz, 3 H), 0.43 (s, 3 H), 0.34 (s, 3 H), -0.01 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 140.4, 134.0 (2 C), 132.9, 128.7, 127.8 (2 C), 69.4, 16.8, -1.0, -1.3, -2.2. IR (film) 3427, 2955, 1248, 1109, 837 cm^{-1}.

*Preparation of compound **98***

To a vigorously stirred solution of **96** (700 mg, 2.55 mmol, 1 equiv) and trichloroacetimidate of benzyl alcohol (966 mg, 3.82 mmol, 1.5 equiv) in hexane (14 mL) at 0 ^oC was added a solution of TMSOTf (23 μL, 0.128 mmol, 0.05 equiv) in hexane via syringe. A white precipitate quickly formed. The cold bath was removed and the reaction stirred at room temperature. The reaction was monitored by TLC (5% EtOAc in hexanes). After 1 hour the precipitate was filtered through a plug of celite and rinsed with hexanes (60 mL). The filtrate was washed with $NaHCO_{3\ (sat)}$ (3 × 20 mL) and the organic phase was concentrated. The crude product was dissolved in THF (4 mL) and 2M NaOH was added. The mixture was heated in an oil bath at 50 ^oC for 2 hours. This basic treatment is to destroy an ester byproduct difficult to remove by regular column

chromatography. The mixture was diluted with Et_2O (30 mL) and the aqueous phase was washed with Et_2O (3 × 5 mL). Combined organic extracts were washed with brine and dried over $MgSO_4$. Filtration of the solid and concentration of the solution afforded cleaner product, which was purified by column chromatography (2-3% EtOAc in hexanes). 214 mg (24%) of compound **98** was obtained as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.33 (m, 3 H), 7.31–7.22 (m, 5 H), 5.88 (q, *J* = 1.5, 9.5 Hz, 1 H), 4.62 (d, *J* = 12.5 Hz, 1 H), 4.29 (d, *J* = 12.0 Hz, 1 H), 4.06 (d, *J* = 9.5 Hz, 1 H), 1.54 (d, *J* = 1.5 Hz, 3 H), 0.338 (s, 3 H), 0.331 (s, 3 H), 0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 139.3, 138.6, 135.0, 133.9 (2 C), 128.9, 128.1 (2 C), 127.8 (2 C), 127.7 (2 C), 127.2, 72.2, 71.5, 15.6, -3.3, -3.4, -3.7. IR (film) 3068, 2957, 2855, 1246, 1111, 835 cm^{-1}. HRMS (EI) *m*/*z* 368.1980 [(M^+); calcd for $C_{22}H_{32}OSi_2$, 368.1992].

*Preparation of compounds anti/syn-**99***

To a vigorously stirred solution of **96** (690 mg, 2.48 mmol, 1 equiv) and trichloroacetimidate of 1-phenylethanol (990 mg, 3.72 mmol, 1.5 equiv) in hexane (14 mL) at 0 ^{o}C was added a solution of TMSOTf (22 μL, 0.124 mmol, 0.05 equiv) in hexane (1 mL) via syringe. A white precipitate quickly formed. The cold bath was removed and the reaction stirred at room temperature for 1 hour. The reaction was monitored by TLC (5% EtOAc in hexanes). Then the precipitate was filtered through a plug of celite and rinsed with hexanes (60 mL). The filtrate was washed with $NaHCO_{3(sat)}$ (3 × 20 mL), water (2 × 20 mL), brine and dried over $MgSO_4$. The salts were filtrated and the solution was concentrated. The crude product was purified by column chromatography (10%, 15% and 20% CH_2Cl_2 in hexanes) to give 729 mg (77%) of **99** (dr =

1:1) as a colorless oil. Diastereomers *anti*-**99** and *syn*-**99** were partially separated under by column chromatography. Spectroscopic data for *anti*-**99** (dr = 6.7:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.35 (m, 3 H), 7.30 (t, *J* = 7.2 Hz, 3 H), 7.22 (m, 2 H), 5.86 (dq, *J* = 1.8, 10.2 Hz, 1 H), 4.42 (q, *J* = 6.0 Hz, 1 H), 3.84 (d, *J* = 10.2 Hz, 1 H), 1.36 (m, 6 H), 0.36 (s, 3 H), 0.35 (s, 3 H), -0.03 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 141.7, 138.7, 134.6, 133.9 (2 C), 128.8, 128.1 (2 C), 127.7 (2 C), 127.2, 126.9 (2 C), 76.2, 69.0, 24.6, 15.4, -3.3, -3.7. IR (film) 3418, 2957, 1248, 1082, 837 cm^{-1}. HRMS (EI) *m*/*z* 382.2162 [(M^+); calcd for $C_{23}H_{34}OSi_2$, 382.2148]. Spectroscopic data for *syn*-**99** (dr = 14:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 2 H), 7.32–7.25 (m, 7 H), 7.20 (m, 1 H), 5.72 (dq, *J* = 1.2, 9.6 Hz, 1 H), 4.36 (q, *J* = 6.6 Hz, 1 H), 4.21 (d, *J* = 9.6 Hz, 1 H), 1.48 (d, *J* = 1.8 Hz, 3 H), 1.36 (d, *J* = 6.6 Hz, 3 H), 0.19 (s, 3 H), 0.187 (s, 3 H), 0.03 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 142.2, 138.6, 133.9 (2 C), 132.2, 128.7, 128.0 (2 C), 127.6 (2 C), 126.8, 126.2 (2 C), 78.1, 71.3, 22.9, 15.3, -3.46, -3.55, -3.63. IR (film) 3068, 2957, 1246, 1111, 835 cm^{-1}. HRMS (EI) *m*/*z* 382.2144 [(M^+); calcd for $C_{23}H_{34}OSi_2$, 382.2148].

*Preparation of compounds **100** and **101** – General procedure A – Wittig rearrangement of ethers*

Compound **85** (58 mg, 0.196 mmol, 1 equiv) was dissolved in THF (2.5) and the resulting solution placed in an acetone/dry ice bath (-78 ^{o}C). *n*-Butyllithium (1.6 M in hexanes, 0.18 mL, 0.293 mmol, 1.5 equiv) was added dropwise to give a yellow solution. After 1 hour the reaction was quenched by adding $NH_4Cl_{(sat)}$ (~2 mL) and diluted with water (2 mL) and Et_2O (~7 mL).

The aqueous phase was extracted with Et_2O (3 × 50 mL). Combined organic extracts were washed with water, brine, dried over $MgSO_4$ and concentrated. Column chromatography (5% and 15% EtOAc in hexanes) afforded 7 mg (12%) of aldehyde **100**, 11 mg (19%) of alcohol **101** and 29.1 mg (50%) of unreacted **85**, all as colorless oils. Spectroscopic data for **100**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.44 (t, *J* = 3.0 Hz, 1 H), 7.52 (dd, *J* = 1.8, 7.2 Hz, 2 H), 7.37 (m, 3 H), 7.20 (m, 3 H), 7.02 (d, *J* = 7.2 Hz, 2 H), 2.82 (d, *J* = 13.2 Hz, 1 H), 2.67 (d, *J* = 13.8 Hz, 1 H), 2.19 (m, 2 H), 1.07 (s, 3 H), 0.38 (s, 3 H), 0.36 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.8, 137.2, 136.3, 134.7 (2 C), 130.9 (2 C), 129.4, 128.0 (2 C), 127.8 (2 C), 126.4, 49.9, 42.0, 24.6, 20.7, -5.1. IR (film) 2924, 1716, 1251, 1111, 815 cm^{-1}. HRMS (EI) *m*/*z* 296.1588 [(M^+); calcd for $C_{19}H_{24}OSi$, 296.1596]. Spectroscopic data for **101**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (m, 2 H), 7.33 (m, 3 H), 7.27 (t, *J* = 7.2 Hz, 2 H), 7.21(m, 3 H), 5.79 (dq, *J* = 1.8, 7.8 Hz, 1 H), 4.73 (q, *J* = 7.8 Hz, 1 H), 2.84 (dd, A of ABX system, *J* = 7.2, 13.2 Hz, 1 H), 2.77 (dd, B of ABX system, *J* = 6.0, 13.8 Hz, 1 H), 1.54 (s, 1 H), 1.53 (s, 3 H), 0.32 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 137.7, 137.67, 137.3, 133.9 (2 C), 129.6 (2 C), 129.0, 128.4 (2 C), 127.7 (2 C), 126.5, 69.3, 43.6, 15.1, -3.6, -3.8. IR (film) 3356, 3067, 2957, 1427, 1248, 1109, 814 cm^{-1}. HRMS (EI) *m*/*z* 278.1491 [$(M-H_2O)^+$; calcd for $C_{19}H_{22}Si$, 278.1491].

*Preparation of compound **102***

Applying general procedure A to **85** (170 mg, 0.573 mmol, 1 equiv) in THF (7 mL) and *n*-butyllithium (1.6 M in hexanes, 0.72 mL, 1.147 mmol, 2.0 equiv) for 7 hours at -78 ^{o}C and 0.5

hours at room temperature, afforded after column chromatography (5% and 20% EtOAc in hexanes) 37 mg (15%) of **102** as a colorless oil, along with 23.2 mg (11%) of **100** and 48 mg (23%) of **101**. Spectroscopic data for **102**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 2 H), 7.37 (m, 2 H), 7.33 (m, 5 H), 7.22 (m, 4 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 5.78 (dt, *J* = 1.5, 8.0 Hz, 1 H), 4.63 (q, *J* = 7.0 Hz, 1 H), 2.86 (dd, A of ABX system, *J* = 7.0, 13.0 Hz, 1 H), 2.67 (dd, B of ABX system, *J* = 6.5, 13.0 Hz, 1 H), 1.22 (s, 3 H), 0.27 (s, 3 H), 0.26 (s, 3 H), 0.25 (s, 3 H), 0.23 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) (two aromatic carbon atoms are likely overlapped) δ 143.3, 138.4, 138.0, 134.6, 133.9 (2 C), 133.5 (2 C), 129.9 (2 C), 129.4, 128.9, 128.0 (2 C), 127.7 (2 C), 127.6 (2 C), 126.0, 70.8, 44.4, 14.6, -1.1, -1.4, -3.6, -3.8.

*Preparation of **103** and **104** – Wittig rearrangements of **86***

Applying general procedure A to **86** (148 mg, 0.477 mmol, 1 equiv) in THF (6 mL) and *n*-butyllithium (1.6 M in hexanes, 0.6 mL, 0.953 mmol, 2.0 equiv) for 5 hours at -78 ^{o}C, afforded after column chromatography (5% and 20% EtOAc in hexanes) 68.3 mg (46%) of **103** and 52.7 mg (36%) of **104** as colorless oils. Spectroscopic data for **103**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.47 (t, *J* = 3.0 Hz, 1 H), 7.54 (m, 2 H), 7.38 (m, 3 H), 7.06 (d, *J* = 7.8 Hz, 2 H), 6.94 (d, *J* = 7.8 Hz, 2 H), 2.81 (d, *J* = 13.2 Hz, 1 H), 2.66 (d, *J* = 13.2 Hz, 1 H), 2.31 (s, 3 H), 2.21 (m, 2 H), 2.22 (dd, A of ABX system, *J* = 3.0, 15.6 Hz, 1 H), 2.19 (dd, B of ABX system, *J* = 3.0, 15.6 Hz, 1 H), 1.09 (s, 3 H), 0.40 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 136.3, 135.8, 134.7 (2 C), 133.9, 130.7 (2 C), 129.3, 128.6 (2 C), 127.8 (2 C), 49.9, 41.4, 24.5, 21.0, 20.6, -5.1, -5.2. IR (film) 3020, 2955, 1718, 1427, 1251, 1113, 817 cm^{-1}. HRMS (EI) *m*/*z*

310.1740 [(M^+); calcd for $C_{20}H_{26}OSi$, 310.1753]. Spectroscopic data for **104**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.35 (m, 3 H), 7.10 (s, 4 H), 5.82 (dq, *J* = 1.8, 7.8 Hz, 1 H), 4.72 (q, *J* = 7.8 Hz, 1 H), 2.80 (dd, A of ABX system, *J* = 7.8, 13.8 Hz, 1 H), 2.75 (dd, B of ABX system, *J* = 16.0, 3.8 Hz, 1 H), 2.33 (s, 3 H), 1.58 (d, *J* = 1.8 Hz, 3 H), 0.35 (s, 3 H), 0.34 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 137.8, 137.0, 134.5, 133.9 (2 C), 133.0, 129.5 (2 C), 129.1 (2 C), 128.9, 127.7 (2 C), 69.3, 43.2, 21.0, 15.1, -3.6, -3.8. IR (film) 3356, 3069, 2957, 1427, 1248, 1109, 814 cm^{-1}. HRMS (EI) *m*/*z* 292.1641 [($M-H_2O)^+$; calcd for $C_{20}H_{24}Si$, 292.1647].

*Preparation of **105** and **106** – Wittig rearrangements of E-**90***

Applying general procedure A to *E-**90*** (82 mg, 0.264 mmol, 1 equiv) in THF (3.3 mL) and *n*-butyllithium (1.6 M in hexanes, 0.25 mL, 0.792 mmol, 3.0 equiv) for 3 hours at -78 ^{o}C and slowly to room temperature overnight, afforded after column chromatography (5% and 20% EtOAc in hexanes) 18.6 mg (23%) of diastereomers **105** and 45 mg (55%) of diastereomeric **106** as colorless oils. Spectroscopic data for diastereomers **105** (partially separated, relative stereochemistry not assigned), first isomer: H NMR (500 MHz, $CDCl_3$) δ 9.27 (t, *J* = 1.5 Hz, 1 H), 7.49 (m, 2 H), 7.34 (m, 3 H), 7.23 (t, *J* = 8.0 Hz, 2 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 7.06 (d, *J* = 7.0 Hz, 2 H), 3.26 (q, *J* = 7.0 Hz, 1 H), 2.06 (dd, A of ABX system, *J* = 2.0, 18.0 Hz, 1 H), 1.93 (dd, B of ABX system, *J* = 1.0, 17.5 Hz, 1 H), 1.32 (d, *J* = 7.0 Hz, 3 H), 1.12 (s, 3 H), 0.47 (s, 3 H), 0.42 (s, 3 H). Second isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (t, *J* = 2.5 Hz, 1 H), 7.51 (m, 2 H), 7.36 (m, 3 H), 7.24 (m, 2 H), 7.20 (m, 1 H), 7.08 (d, *J* = 7.0 Hz, 2 H), 2.90 (q, *J* = 7.0

Hz, 1 H), 2.52 (dd, A of ABX system, *J* = 3.5, 15.0 Hz, 1 H), 2.33 (dd, B of ABX system, *J* = 2.5, 15.5 Hz, 1 H), 1.26 (d, *J* = 7.5 Hz, 3 H), 1.07 (s, 3 H), 0.40 (s, 3 H), 0.26 (s, 3 H). IR (film) 2964, 1716, 1253, 1109, 814 cm^{-1}. HRMS (EI) *m*/*z* 310.1753 [(M^+); calcd for $C_{20}H_{26}OSi$, 310.1753]. Spectroscopic data for diastereomers **106** (dr = 1:1): ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.36–7.17 (m, 18 H), 5.76 (dd, *J* = 1.5, 8.5 Hz, 1 H), 5.67 (dd, *J* = 2.0, 8.5 Hz, 1 H), 4.57 (m, 2 H), 2.88 (m, 1 H), 2.82 (m, 1 H), 1.69 (d, *J* = 2.0 Hz, 3 H), 1.53 (d, *J* = 1.5 Hz, 3 H), 1.37 (d, *J* = 7.0 Hz, 3 H), 1.23 (d, *J* = 7.0 Hz, 3 H), 0.37 (s, 6 H), 0.28 (s, 3 H), 0.26 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 143.0, 141.5, 141.1, 138.6, 137.8, 137.7, 137.4, 133.94 (2 C), 133.90 (2 C), 129.0, 128.9, 128.5 (2 C), 128.17 (2 C), 128.16 (2 C), 128.14 (2 C), 127.8 (2 C), 127.7 (2 C), 126.7, 126.4, 72.3, 72.1, 46.5, 46.0, 17.3, 16.1, 15.5, 15.2, -3.52, -3.54, -3.73, -3.84. IR (film) 3389, 3067, 2961, 1248, 1111, 815 cm^{-1}. HRMS (EI) *m*/*z* 292.1647 [($M-H_2O)^+$; calcd for $C_{20}H_{24}Si$, 292.1647].

*Preparation of compound **107***[19]

To a solution of *E*-**82** (611 mg, 2.96 mmol, 1 equiv) in CH_2Cl_2 (50 mL) at 0 ^oC was added PCC (766 mg, 3.55 mmol, 1.2 equiv) and the mixture was stirred overnight. The mixture was filtered through a plug of silica and rinsed with CH_2Cl_2. After concentration the residue was purified by column chromatography (10% EtOAc in hexanes) to afford 430 mg (72%) of **107** as a geometrical mixture *E*/*Z* = 1:0.15. ^1H NMR (500 MHz, $CDCl_3$) δ 10.1 (d, *J* = 8.0 Hz, 1 H), 7.47 (m, 2 H), 7.37 (m, 3 H), 6.24 (dq, *J* = 2.0, 8.0 Hz, 1 H), 2.20 (d, *J* = 2.0 Hz, 3 H), 0.43 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1, 163.8, 137.8, 135.4, 133.9 (2 C), 129.7, 128.1 (2 C), 15.9, -4.3. Spectral data is in accord with reported data in the literature.[19]

*Preparation of compounds **108** and **109** – Wittig rearrangements of compound **88***

Applying general procedure A to **88** (78 mg, 0.222 mmol, 1 equiv) in THF (3.0 mL) and *n*-butyllithium (1.6 M in hexanes, 0.21 mL, 0.333 mmol, 1.5 equiv) for 3 hours at -78 ^{o}C and 4 hours at 0 ^{o}C, after column chromatography (5% and 10% EtOAc in hexanes) afforded 9.2 mg and 6 mg of partially separated diastereomers **108** in combined 20%, and 27.9 mg (36%) of diastereomeric **109** (dr = 1:1), all these compounds as colorless oils. Spectroscopic data for diastereomer **108** (stereochemistry not assigned), first isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (m, 1 H), 7.27 (m, 2 H), 7.08–6.89 (m, 8 H), 5.07 (m, 1 H), 4.58 (m, 2 H), 2.74 (m, 1 H), 2.19 (m, 1 H), 2.09 (m, 1 H), 1.96 (dd, *J* = 9.6, 16.2 Hz, 1 H), 1.00 (s, 3 H), 0.93 (s, 3 H), 0.13 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.8, 142.7, 138.8, 135.2, 134.9 (2 C), 129.2 (2 C), 129.18, 127.9 (2 C), 127.8 (2 C), 126.4, 117.3, 48.8, 47.0, 42.3, 34.0, 23.5, 19.1, -1.0, -1.4. IR (film) 3068, 2957, 1711, 1255, 1111, 817 cm^{-1}. Second isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (t, *J* = 2.5 Hz, 1 H), 7.58 (m, 2 H), 7.36 (m, 3 H), 7.28 (m, 4 H), 7.19 (m, 1 H), 5.21 (m, 1 H), 4.76 (dt, *J* = 2.0, 10.0 Hz, 1 H), 4.70 (m, 1 H), 2.90 (dd, *J* = 4.5, 14.0 Hz, 1 H), 2.46 (dd, *J* = 3.0, 16.0 Hz, 1 H), 2.18 (dd, *J* = 2.5, 16.5 Hz, 1 H), 2.01 (dd, *J* = 9.0, 14.0 Hz, 1 H), 1.40 (s, 3 H), 1.35 (s, 3 H), 0.43 (s, 3 H), 0.35 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.3, 143.4, 128.7, 135.5, 134.9 (2 C), 129.2 (2 C), 128.9 (2 C), 128.0, 127.9 (2 C), 126.6,

117.0, 47.8, 46.5, 41.1, 34.6, 25.0, 18.0, -1.3, -1.4. IR (film) 3069, 2972, 1709, 1259, 1109, 819 cm^{-1}. HRMS (EI) *m*/*z* 350.2057 [(M^+); calcd for $C_{23}H_{30}OSi$, 350.2066]. Spectroscopic data for **109** (dr = 1.3:1) ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.39–7.27 (m, 18.4 H), 7.20 (m, 2.6 H), 5.61–5.46 (m, 2.3 H), 5.05–4.92 (m, 4.6 H), 4.52 (dd, *J* = 3.5, 8.5 Hz, 1 H), 4.48 (dd, *J* = 4.0, 9.0 Hz, 1.3 H), 2.81 (m, 2.3 H), 2.41 (dd, *J* = 8.5, 14.0 Hz, 1.3 H), 2.30 (dd, *J* = 8.5, 14.0 Hz, 1 H), 1.68 (m, 3 H), 1.52 (m, 3.9 H), 1.36 (s, 3.9 H), 1.28 (s, 3 H), 0.32 (s, 6 H), 0.27 (s, 3.9 H), 0.25 (s, 3.9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 143.3, 139.3, 139.2, 139.16, 138.8, 137.8, 137.7, 135.0, 134.8, 133.9, 129.0, 128.9, 128.1, 127.9, 127.75, 127.69, 127.67, 127.59, 126.3, 126.1, 117.4, 117.3, 74.4, 74.2, 46.4, 46.1, 42.3, 41.9, 19.5, 19.3, 15.7, 15.4, -3.5, -3.6, -3.7, -3.8. IR (film) 3447, 3068, 2959, 1248, 1111, 815 cm^{-1}. HRMS (EI) *m*/*z* 350.2065 [(M^+); calcd for $C_{23}H_{30}OSi$, 350.2066].

*Preparation of compounds **110** and **111** – Wittig rearrangements of **94***

Applying general procedure A to **94** (48 mg, 0.135 mmol, 1 equiv) in THF (1.7 mL) and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 0.271 mmol, 2.0 equiv) -78 ^oC and then at -30 ^oC for 4.5 hours, after column chromatography (8%, 15% and 20% EtOAc in hexanes) afforded 1.9 mg and 4.2 mg (combined 13%) of diastereomers **110**, and 13.3 mg and 7.8 mg (combined 44%) of diastereomers **111**, all of them as colorless oils. Spectroscopic data for **110**, first isomer: ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (t, *J* = 2.0 Hz, 1 H), 7.49 (m, 2 H), 7.33 (m, 3 H), 7.20 (m, 3 H), 7.05 (m, 2 H), 3.18 (m, 1 H), 3.17 (s, 3 H), 3.01 (m, 2 H), 2.07 (m, 1 H), 2.02 (dd, A of ABX system, *J* = 2.0, 18.0 Hz, 1 H), 1.97 (m, 1 H), 1.86 (dd, B of ABX system, *J* = 1.5, 18.0 Hz, 1 H),

1.15 (s, 3 H), 0.47 (s, 3 H), 0.45 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 141.2, 138.0, 134.6, 129.1, 128.2, 127.7, 126.8, 71.5, 58.6, 52.5, 45.7, 32.2, 28.8, 18.4, -2.3, -3.4. IR (film) 2953, 1722, 1427, 1253, 1115, 817 cm^{-1}. Second isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (t, *J* = 2.5 Hz, 1 H), 7.50 (m, 2 H), 7.33 (m, 3 H), 7.23 (m, 3 H), 7.06 (m, 2 H), 3.12 (s, 3 H), 2.96 (m, 1 H), 2.81 (m, 2 H), 2.56 (dd, *J* = 3.5, 15.5 Hz, 1 H), 2.37 (dd, *J* = 2.5, 15.5 Hz, 1 H), 2.02 (m, 1 H), 1.91 (m, 1 H), 1.69 (d, *J* = 1.5 Hz, 1 H), 0.99 (s, 3 H), 0.42 (s, 3 H), 0.24 (s, 3 H). IR (film) 2955, 1714, 1427, 1253, 1113, 817 cm^{-1}. HRMS (EI) *m/z* 354.2015 [(M^+); calcd for $C_{22}H_{30}O_2Si$, 354.2015]. Spectroscopic data for **111**, first isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 2 H), 7.32 (m, 3 H), 7.28 (d, *J* = 7.5 Hz, 2 H), 7.21 (m, 3 H), 5.67 (dq, *J* = 1.5, 8.5 Hz, 1 H), 4.65 (m, 1 H), 3.26 (m, 1 H), 3.23 (s, 3 H), 3.17 (m, 1 H), 2.82 (m, 1 H), 2.06 (m, 1 H), 1.82 (m, 1 H), 1.78 (m, 2 H), 1.62 (d, *J* = 1.5 Hz, 3 H), 0.31 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 140.8, 138.2, 137.8, 134.0, 129.0, 128.8, 128.5, 127.7, 126.8, 71.0, 70.8, 58.4, 49.2, 31.2, 15.4, -3.6, -3.7. IR (film) 3424, 2924, 1427, 1248, 1111, 815 cm^{-1}. HRMS (ESI) *m/z* 337.1924 [$(M+Na)^+$; calcd for $C_{22}H_{30}O_2NaSi$, 377.1913]. Second isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.22 (m, 8 H), 7.16 (m, 2 H), 5.66 (dq, *J* = 1.5, 8.5 Hz, 1 H), 4.64 (dt, *J* = 4.0, 8.5 Hz, 1 H), 3.38 (m, 1 H), 3.31 (s, 3 H), 3.28 (m, 1 H), 2.84 (m, 1 H), 2.31 (m, 2 H), 1.98 (m, 1 H), 1.59 (s, 1 H), 1.51 (d, *J* = 2.0 Hz, 3 H), 0.26 (s, 3 H), 0.23 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 131.68, 137.7, 137.3, 133.9, 128.8, 128.6, 128.4, 128.2 127.6, 126.5, 71.2, 71.1, 58.5, 49.9, 31.9, 15.2, -3.5, -3.9. IR (film) 3414, 2924, 1427, 1248, 1111, 815 cm^{-1}. HRMS (EI) *m/z* 336.1903 [$(M-H_2O)^+$; calcd for $C_{22}H_{28}OSi$, 336.1909].

*Preparation of compounds **112** and **113** – Wittig rearrangement of **98***

Applying general procedure A to **98** (73 mg, 0.198 mmol, 1 equiv) in THF (2.5 mL) and *n*-butyllithium (1.6 M in hexanes, 0.19 mL, 0.297 mmol, 1.5 equiv) -78 ^{o}C for 1 hour and then at 0 ^{o}C for 0.5 hours, after column chromatography (4% and 20% EtOAc in hexanes) afforded 16.8 (23%) of **113** and 7.4 mg (14%) of **112** as colorless oils. Spectroscopic data for **112**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.33 (m, 3 H), 5.75 (dq, *J* = 1.5, 8.5 Hz, 1 H), 4.51 (q, *J* = 7.0 Hz, 1 H), 1.69 (d, *J* = 1.5 Hz, 3 H), 1.57 (m, 1 H), 1.43 (m, 1 H), 1.38–1.24 (m, 4 H), 0.89 (t, *J* = 7.5 Hz, 3 H), 0.33 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 136.6, 133.9, 133.0, 129.0, 127.8, 68.1, 36.9, 27.5, 22.7, 15.2, 14.0, -3.5, -3.7. HRMS (EI) *m*/*z* 244.1643 [$(M\text{-}H_2O)^{+}$; calcd for $C_{16}H_{24}Si$, 244.1647]. Spectroscopic data for **113**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (m, 2 H), 7.34–7.24 (m, 8 H), 7.08 (m, 2 H), 3.48 (s, 2 H), 2.49 (d, *J* = 18.5 Hz, 1 H), 2.42 (d, *J* = 18.5 Hz, 1 H), 1.02 (s, 3 H), 0.34 (s, 3 H), 0.31 (s, 3 H), -0.06 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.9, 138.4, 134.8 (2 C), 134.4, 129.4 (2 C), 128.7, 128.6 (2 C), 127.4 (2 C), 126.9, 50.8, 48.9, 18.9, 9.9, -1.0, -2.1, -2.3. IR (film) 2957, 1645, 1253, 1100, 814 cm^{-1}. HRMS (EI) *m*/*z* 368.1990 [(M^{+}); calcd for $C_{22}H_{32}OSi_2$, 368.1992].

*Preparation of compounds **106** and **114** – Wittig rearrangement of **99** via Si/Li exchange*

To a solution of hexamethyldisilane (0.171 mL, 0.831 mmol, 3 equiv) in HMPA (2 mL) at 0 ^{o}C was added a *n*-butyllithium (1.6 M in hexanes, 0.52 mL, 0.831 mmol, 3 equiv) dropwise to give

a bright red solution. After 15 minutes the solution of freshly made TMSLi was transferred via cannula to a solution of *syn*-**99** (or *anti*-**99**) (106 mg, 0.277 mmol 1 equiv) in THF (2 mL) at -78 ^{o}C. Then, the reaction was transferred to a cold bath at –40 ^{o}C. The reaction was followed by TLC (3% EtOAc in hexane). The reaction was quenched by adding $NH_4Cl_{(sat)}$ (~2 mL) and diluted with water (2 mL) and Et_2O (~10 mL). The aqueous phase was extracted with Et_2O (3 × 50 mL). Combined organic extracts were washed with water, brine, dried over $MgSO_4$ and concentrated. Column chromatography (3% and 20% EtOAc in hexanes) afforded 78.9 mg (75%) of **114** and 3.1 mg (4%) of **106** as colorless oils. Spectroscopic data for **114** (dr ~ 1:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 4 H), 7.36–7.15 (m, 16 H), 5.74 (dq, *J* = 1.5, 8.5 Hz, 1 H), 5.69 (dq, *J* = 1.5, 8.5 Hz, 1 H), 4.51 (dd, *J* = 7.0, 8.5 Hz, 1 H), 4.46 (dd, *J* = 7.5, 8.5 Hz, 1 H), 2.81 (m, 1 H), 2.76 (m, 1 H), 1.55 (d, *J* = 2.0 Hz, 3 H), 1.35 (d, *J* = 7.5 Hz, 3 H), 1.34 (d, *J* = 2.0 Hz, 3 H), 1.22 (d, *J* = 7.0 Hz, 3 H), 0.05 (s, 9 H), -0.09 (s, 9 H).

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CHAPTER 4

STEREOCONVERGENT [1,2]- AND [1,4]-WITTIG REARRANGEMENTS OF 2-SILYL-5,6-DIHYDRO-(*2H*)-6-ARYL PYRANS

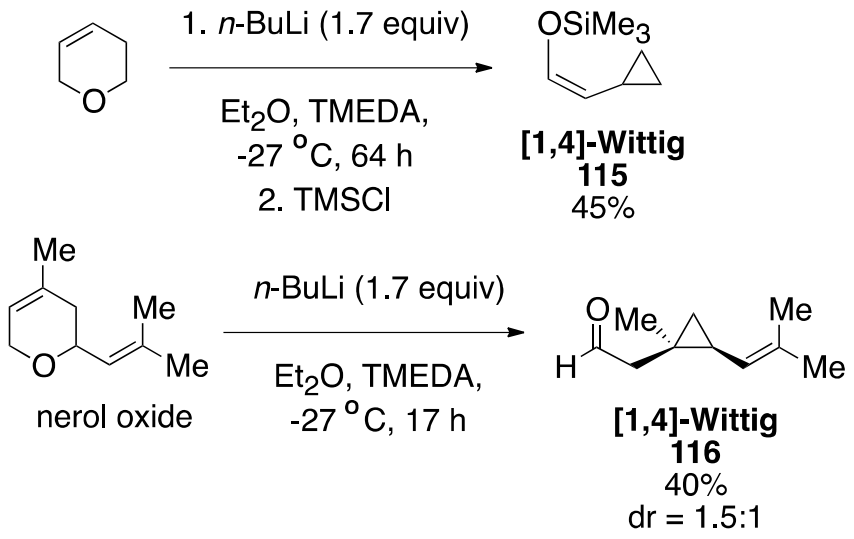
4.1 Introduction

Since its discovery 70 years ago,[1] the Wittig rearrangements have evolved into a powerful tool for the isomerization of α-metalated ethers into alkoxides via a concerted [2,3]-sigmatropic shift[2] or a stepwise [1,2]-migration involving a radical / radical-anion pair.[3] Arguably, the [2,3]-Wittig rearrangement pathway has enjoyed more attention from a mechanistic and synthetic perspective, resulting in an impressive display of remarkable features such as the stereoselective assembly of adjacent chiral centers, the transfer of chirality, and the formation of specific olefin geometries.[2] Although some of these features are also inherent characteristics of the [1,2]-Wittig rearrangement a narrower range of substrates are capable of efficient [1,2]-migration, perhaps a reflection of the required radical stabilizing groups for facile C-O bond homolysis. In addition, a 'problem' of regioselectivity arises in alkoxy allylmetal species, where the [1,4]-migration competes with the [1,2]-shift leading to mixtures of products.[4] Relative to the [2,3]- and [1,2]-shifts, the [1,4]-Wittig rearrangement is a unique and attractive pathway able to generate stereodefined enolates[5] (rather than alkyl alkoxides) in addition to the potentially stereoselective formation of adjacent chiral centers and the transfer of chirality. Unfortunately, little is known about the underlying factors that govern regiocontrol in favor of the [1,4]- or [1,2]-pathways. In general, the [1,4]-shift is favored at lower temperatures, while the nature of the base and base counterion have shown to affect the product distribution.[5c] However, the [1,4]-/[1,2]-selectivity

seems to be more substrated-dependent, and few systematic studies have addressed this aspect.[5c] Importantly, although some evidence supports a stepwise mechanism for [1,4]-pathway,[5c, 6] a concerted process is allowed by orbital symmetry and might be operative in some instances. In this Chapter we delineate structural and electronic characteristics that permit one to maneuver the rearrangement to favor either the [1,2]- or the [1,4]-Wittig pathways in the stereoconvergent ring contractions of diastereomeric 2-silyl-3,4-dihydro-(2*H*)-pyrans to the corresponding α-silyl cyclopentenol (via [1,2]-Wittig) and/or α-cyclopropyl acylsilanes (via [1,4]-Wittig), both of which proceed with excellent diastereoselectivities.

4.2 Ring contraction of ethers via Wittig rearrangements

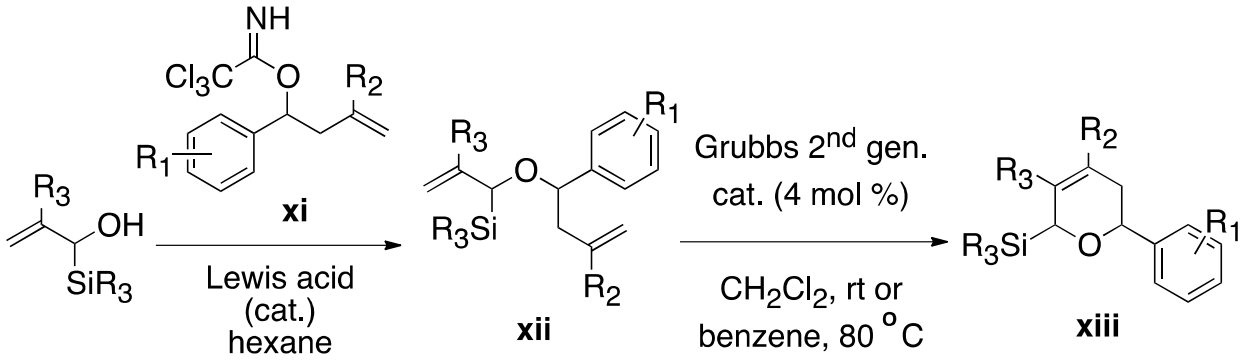
Although the ring contractions of macrocyclic ethers by means of Wittig rearrangements via [1,2]- and [2,3]-pathways have been documented by the work of Marshall[7] and Takahashi,[8, 9] the behavior of smaller cyclic ethers is limited to a few examples,[5b, 10] most of which are of mechanistic interest. We are aware of only two examples concerning the [1,4]-Wittig rearrangement of cyclic allylic ethers reported by Rautenstrauch: The isomerization of dihydropyran and nerol oxide to the corresponding α-cyclopropyl acetaldehydes (Scheme 68).[5b] Surprisingly, this unique strategy for the construction of the cyclopropane ring has received little attention,[11] despite its prospect as a complementary method to Simmons-Smith type reactions,[12] transition metal-catalyzed diazoalkyl decomposition / olefin insertion,[13] and intramolecular cyclizations,[14] cycloisomerizations[15] or stepwise cyclopropanation reactions.[16]



Scheme 68. Known Wittig Rearrangement of dihydropyrans in the literature.

4.3 Synthesis of reagents, precursors and cyclic ethers

The synthesis of the cyclic ethers (**xiii**) was primarily based on the previously described Lewis acid-catalyzed alkylation of α-silyl allylic alcohols with homoallylic trichloroacetimidate reagents (**xi**),[17] followed by ring closing metathesis of the α-benzyloxy allylsilane precursors (**xii**) with Grubbs 2nd generation catalyst (Scheme 69).[18]

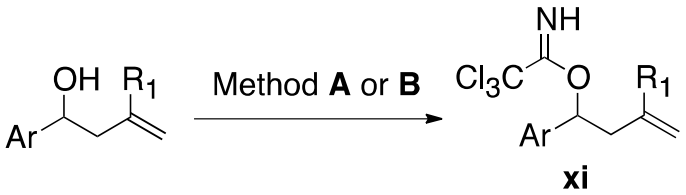


Scheme 69. Preparation of cyclic ethers **xiii** via alkylation of bisallylic precursors **xii**.

4.3.1 Synthesis of trichloroacetimidates xi

The alkylating agents **xi** were prepared via methods A and/or B. Table 3 shows trichloroacetimidates used in this Chapter. Given the acid-sensitive nature of these compounds, in some cases the crude trichloroacetimidates were used in the alkylating step without further purification.

Table 3. Preparation of trichloroacetimidate reagents.



xi

Method **A**: NaH (0.15 equiv), Cl_3CCN (1 equiv), Et_2O, 0 °C
Method **B**: Cl_3CCN (1.5 equiv), DBU (0.18 equiv), CH_2Cl_2

entry	Trichloro-acetimidate	Ar	R_1	method	yield (%)
1	**117**	2-$MeOC_6H_4$	H	A	78
2	**118**	3-$MeOC_6H_4$	H	A	85
3	**119**	4-$MeOC_6H_4$	H	A	65
4	**120**	2-MeC_6H_4	H	A	61
5	**121**	3-MeC_6H_4	H	A	80
6	**122**	4-MeC_6H_4	H	A	90
7	**123**	4-FC_6H_4	H	B	82
8	**124**	4-ClC_6H_4	H	A	76
9	**125**	4-BrC_6H_4	H	A	86

Table 3 (Cont'd)

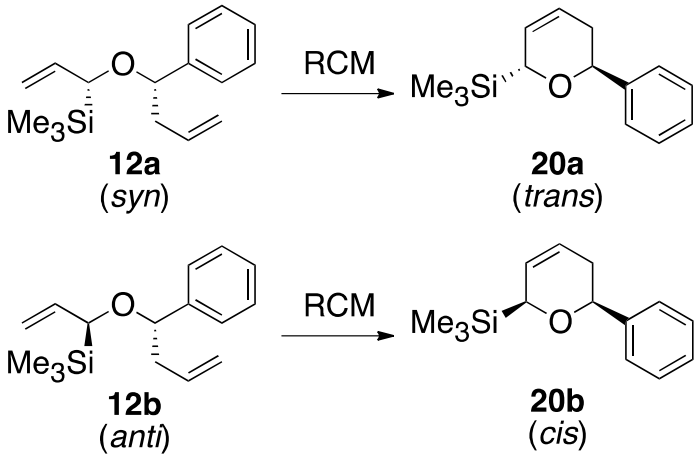
entry	Trichloro-acetimidate	Ar	R_1	method	yield (%)
10	**126**	2-naphtyl	H	B	95
11	**127**	2-PrC_6H_4	H	B	81
12	**128**	C_6H_5	Me	A	89
13	**129**	4-MeC_6H_4	Me	A	43
14	**130**	2-thiophenyl	H	B	95
15	**131**	2-furanyl	H	B	42
16	**132**	3-furanyl	H	B	87
17	**133**	3-indole	H	B	<30

4.3.2 Synthesis of α-benzyloxy allylsilanes xii

Trichloroacetimidate alkylation of α-silyl allylic alcohols proceeded in modest to excellent yields (Table 4) and α-benzyloxy allylsilanes **xii** were obtained as ~1:1 diastereomeric mixtures. In some instances these stereoisomers were separable by column chromatography. All ethers **xii** were obtained as colorless oils, with the exception of the indole-containing derivative **159** (white solid).

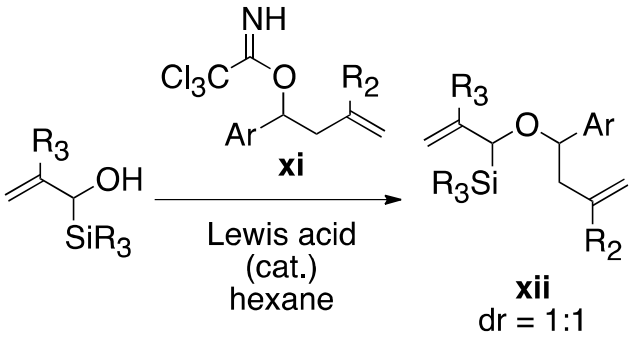
Throughout this work diastereomeric pairs **xii** were labeled by a number and their relative stereochemistry denoted by letters **a** (*syn*) or **b** (*anti*). The *syn* or *anti* relationship refers to the

pendant silyl and 2-propen-1-yl fragments (Scheme 70). Analogously, diastereomeric cyclic ethers were given a number and their relative stereochemistry denoted by **a** (*trans*) or **b** (*cis*).



Scheme 70. Relationship between relative stereochemistry and numbering.

Table 4. Preparation of α-benzyloxy allylsilanes **xii**.



entry	product **xii**	Ar	SiR_3	R_2	R_3	yield
1	**134**	2-$MeOC_6H_4$	$SiMe_3$	H	H	51%
2	**135**	3-$MeOC_6H_4$	$SiMe_3$	H	H	60%
3	**136**	4-$MeOC_6H_4$	$SiMe_3$	H	H	97%
4	**137**	2-MeC_6H_4	$SiMe_3$	H	H	73%
5	**138**	3-MeC_6H_4	$SiMe_3$	H	H	56%
6	**139**	4-MeC_6H_4	$SiMe_3$	H	H	75%
7	**140**	4-FC_6H_4	$SiMe_3$	H	H	39%
8	**141**	4-ClC_6H_4	$SiMe_3$	H	H	54%
9	**142**	4-BrC_6H_4	$SiMe_3$	H	H	37%
10	**143**	2-naphtyl	$SiMe_3$	H	H	48%
11	**144**	2-PrC_6H_4	$SiMe_3$	H	H	24%
12	**145**	C_6H_5	$SiMe_2Ph$	H	H	58%
13	**146**	C_6H_5	$SiMePh_2$	H	H	83%

Table 4 (Cont'd)

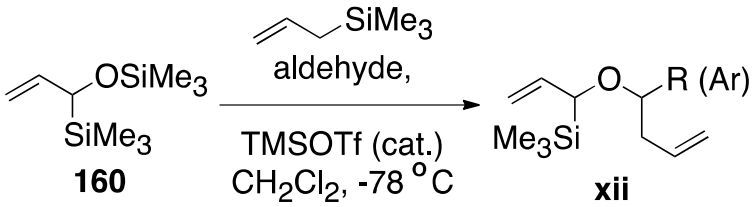
entry	product **xii**	Ar	SiR_3	R_2	R_3	yield
14	**147**	C_6H_5	$SiEt_3$	H	H	70%
15	**148**	3-$MeOC_6H_4$	$SiMe_2Ph$	H	H	71%
16	**149**	4-ClC_6H_4	$SiMe_2Ph$	H	H	91%
17	**150**	2-naphtyl	$SiEt_3$	H	H	45%
18	**151**	C_6H_5	$SiMe_3$	H	Me	44%
19	**152**	4-$MeOC_6H_4$	$SiMe_3$	H	Me	83%
20	**153**	4-MeC_6H_4	$SiMe_3$	H	Me	61%
21	**154**	C_6H_5	$SiMe_3$	Me	H	61%
22	**155**	4-MeC_6H_4	$SiMe_3$	Me	H	65%
23	**156**	2-thiophenyl	$SiMe_3$	H	H	60%
24	**157**	2-furyl	$SiMe_3$	H	H	49%
25	**158**	3-furyl	$SiMe_3$	H	H	60%
26[a]	**159**	3-indole	$SiMe_3$	H	H	52%

[a] dr = 3.5:1

Alternatively, some α-benzyloxy allylsilanes **xii** were prepared by a tricomponent condensation of α-silyl allylic alcohol **160** with alkyl or aryl aldehydes and allyltrimethylsilane, catalyzed by

TMSOTf (Table 5).[19] This route afforded **xii** with modest diastereoselectivity in favor of the *anti* isomer.

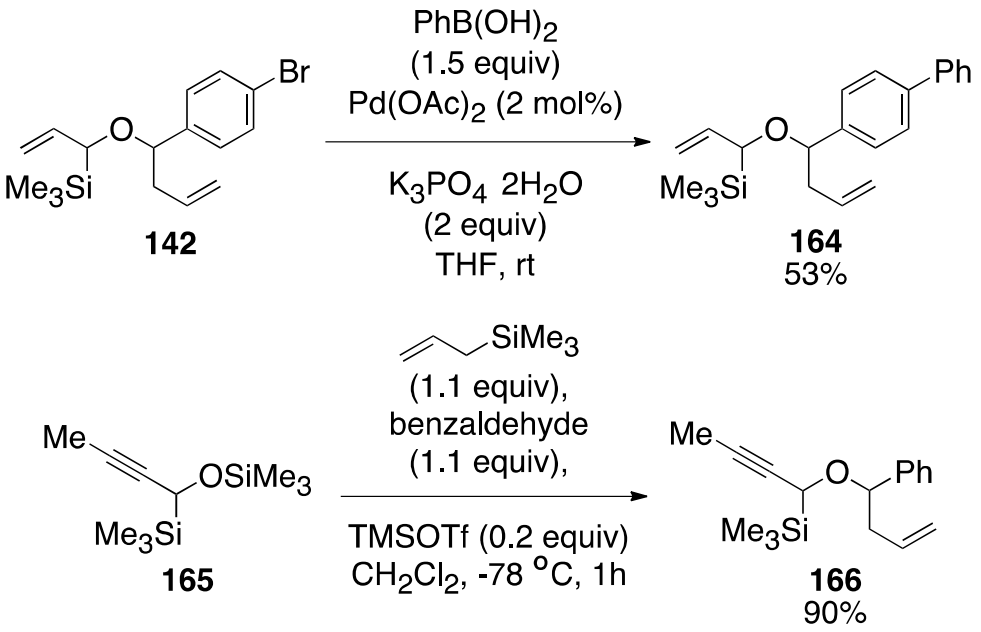
Table 5. Alternative protocol for the preparation of particular compounds **xii**.



160 **xii**

entry	α-benzyloxy allylsilanes **xii**	Ar	yield
1	**161**	4-$CF_3C_6H_4$	47%
2	**162**	4-$NO_2C_6H_4$	57%
3	**163**	cyclohexyl	31%

Other substrates were prepared as follows: Diastereomeric biphenyl ethers **164** were prepared by Suzuki cross-coupling[20] of bromide **142** with phenyl boronic acid. Enyne **166** was prepared by tricomponent condensation of **165** with allyltrimethylsilane and benzaldehyde (Scheme 71).[19]



Scheme 71. Syntheses of biphenyl α-benzyloxy allylsilane **164** and enyne **166**.

4.3.3 Synthesis of cyclic ethers xiii

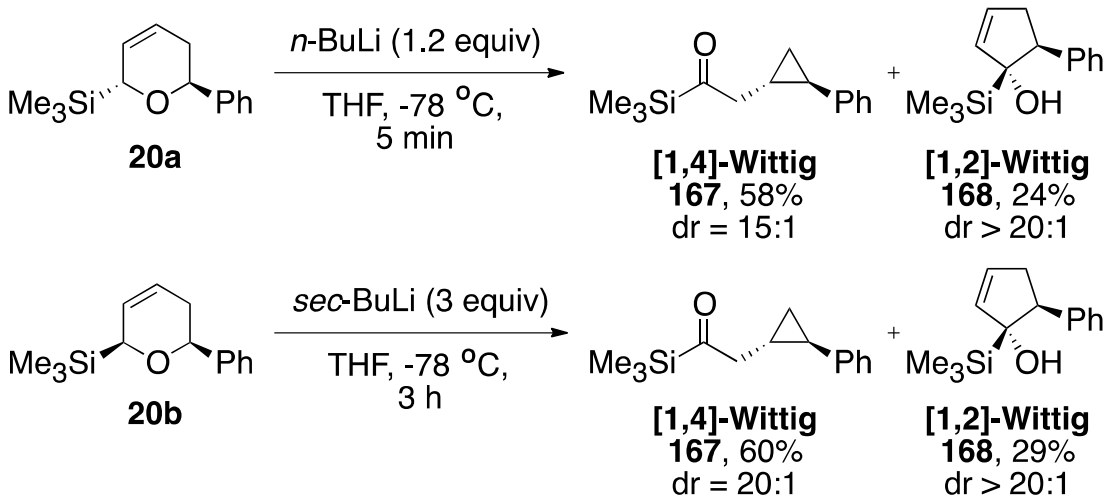
Cyclic ethers **xiii** (Scheme 69) were prepared as mixtures of *cis*/*trans* diastereomers (from diastereomeric **xii**) or as a single diasteromers (from either *syn* or *anti*-**xii**) via ring closing metathesis (Scheme 69).[18] In the former case, *cis*/*trans* cyclic ethers were *completely* separable by column chromatography, without exception. Because *syn/anti* ratios of starting **xii** were variable, yields of individual diastereomers also varied, but the overall yields were usually around 80% (see experimental section).

4.4 Wittig rearrangements of cyclic ethers

4.4.1 Behavior of model substrates

We recently reported the highly selective [1,4]-Wittig rearrangement of allyl benzyl ether bearing a trimethylsilyl group at the α-allylic position.[21] Given the ability of the silyl group to 1)

allow a selective deprotonation step and 2) suppress the competitive [1,2]-pathway, we envisioned that diastereomeric cyclic ethers **20a**/**20b** would be suitable model substrates (Scheme 1). Indeed, under optimized conditions the *trans* diastereomer **20a** underwent fast deprotonation with *n*-butyllithium and rearrangement within 5 minutes to give a mixture the *trans* [1,4]-Wittig (**167**) and *cis* [1,2]-Wittig (**168**) with good overall yield (82%), albeit with modest selectivity (~2.4:1) in favor of the [1,4]-product. Remarkably, the diastereoselectivity of both [1,4]- and [1,2]-pathways was excellent. *cis* Diastereomer **20b** was significantly less reactive and required excess *sec*-butyllithium for complete conversion in 3 hours. To our surprise, the same major diastereomer for the corresponding [1,4]-shift (**167**) and [1,2]-shift (**168**) were obtained in virtually the same [1,4]-/[1,2]- regioisomeric ratio (~2.1:1) and good overall yield.



Scheme 72. Rearrangement of model substrates under optimized conditions.

4.4.2 Electronic effects at the aromatic appendage

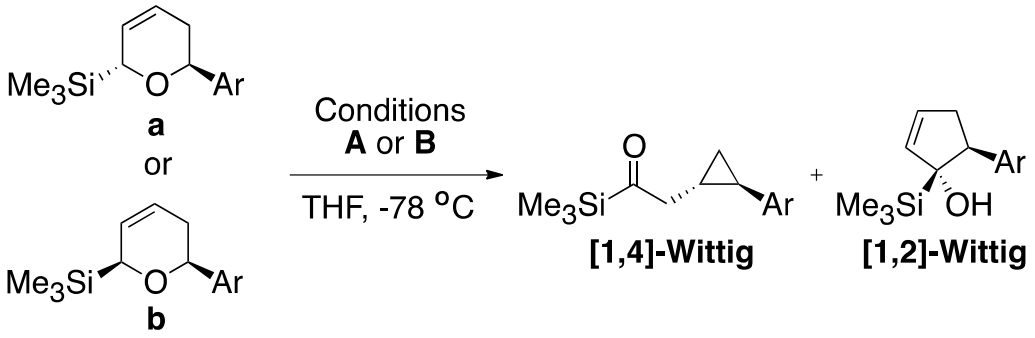
Our study continued with the evaluation of the electronically different substituents on the aromatic appendage (Table 6). In general, the same reactivity trend was observed in these

compounds: *trans* Diastereomers (substrates **a**, entries 1-11) underwent complete rearrangement within 10 minutes whereas *cis* diastereomers required at least 3 hours (substrates **b**, entries 12-22). A second trend was clearly observed from the *trans* diastereomers: Electron-donating groups located at the *ortho* and *para* positions increased the [1,4]-selectivity (entries 3, 4 & 6) with a *p*-methoxy group (**171a**) giving exclusive [1,4]-selectivity. *o*-Methoxy substrate **169a** (entry 1) is an exception, which might be attributed to coordination of oxygen lone pairs to the lithium cation during rearrangement leading to a slight decrease in [1,4]-/[1,2]-selectivity. Interestingly, electron-donating groups at the *meta* substitution (entries 2 & 5) resulted in a decreased [1,4]-/[1,2]-selectivity. This was most pronounced in the case of *m*-methoxy (**170a**) providing the [1,2]-Wittig product in slight excess over the [1,4]-product. The fine balance between resonance and inductive effects was even more evident in halogenated compounds **175a** and **176a** (entries 7 & 8): *p*-Fluoro substrate afforded a 6:1 [1,4]-/[1,2]-selectivity whereas *p*-chloro compound gave a reverse regioselection (1:1.5). On the other hand, a *p*-trifluoromethyl group led to exclusive formation of the [1,2]-Wittig product (entry 9), whereas substrates bearing weakly electron withdrawing groups, a *p*-biphenyl and 2-naphyl (entries 10 & 11), also afforded high selectivity in favor of the [1,2]-shift. In all pertinent cases the [1,2]-Wittig product was obtained as a single diastereomer whereas the [1,4]-product was formed with high diastereoselection (>15:1).

Evaluation of *cis* diastereomers (entries 12-22, Table 1) confirmed the stereoconvergence of the [1,4]- and [1,2]-Wittig rearrangements. Both pathways proceeded with similar diastereoselectivity as their *trans* counterparts, and the same electronic effects on the product distribution were observed in most cases. The sluggishness of *cis* diastereomers to undergo

deprotonation had a detrimental effect in the overall yield due to competitive reactions such as *ortho* metalation (entries 14 & 18), lithium-halogen exchange (entry 19) and presumably competitive benzylic deprotonation (entry 20).

Table 6. Electronic effects on the [1,4]-/[1,2]-product distribution.



entry	substrate	Ar	cond.	[1,4]- [a]	dr [1,4] [b]	[1,2] [a,c]
1	**169a**	2-$MeOC_6H_4$	**A**	(**180**) 56%	15:1	(**181**) 37%
2	**170a**	3-$MeOC_6H_4$	**A**	(**182**) 33%	17:1	(**183**) 44%
3	**171a**	4-$MeOC_6H_4$	**A**	(**184**) 65%	15:1	-
4	**172a**	2-MeC_6H_4	**A**	(**185**) 80%	20:1	(**186**) 15%
5	**173a**	3-MeC_6H_4	**A**	(**187**) 59%	20:1	(**188**) 30%
6	**174a**	4-MeC_6H_4	**A**	(**189**) 86%	20:1	(**190**) 7%
7	**175a**	4-FC_6H_4	**A**	(**191**) 66%	20:1	(**192**) 11%
8 [d]	**176a**	4-ClC_6H_4	**A**	(**193**) 28%	15:1	(**194**) 65%
9	**177a**	4-$CF_3C_6H_4$	**A**	Trace	-	(**195**) 90%
10	**178a**	4-PhC_6H_4	**A**	(**196**) 4%	nd	(**197**) 59%
11	**179a**	2-Naph	**A**	(**198**) 3%	nd	(**199**) 96%
12	**169b**	2-$MeOC_6H_4$	**B**	(**180**) 47%	15:1	(**181**) 39%
13	**170b**	3-$MeOC_6H_4$	**B**	(**182**) 33%	18:1	(**183**) 25%

Table 6 (Cont'd)

entry	substrate	Ar	cond.	[1,4]- [a]	dr [1,4] [b]	[1,2] [a,c]
14	**171b**	4-$MeOC_6H_4$	**B** [e]	(**184**) 52%	nd	-
15	**172b**	2-MeC_6H_4	**B**	(**185**) 69%	20:1	(**186**) 12%
16	**173b**	3-MeC_6H_4	**B**	(**187**) 51%	20:1	(**188**) 20%
17	**174b**	4-MeC_6H_4	**B**	(**189**) 73%	20:1	(**190**) 7%
18 [f]	**175b**	4-FC_6H_4	**B**	(**191**) 25%	10:1	(**192**) 3%
19 [g]	**176b**	4-ClC_6H_4	**B**	(**193**) nd	-	(**194**) nd
20 [g]	**177b**	4-$CF_3C_6H_4$	**B**	nd	-	(**195**) 12%
21	**178b**	4-PhC_6H_4	**B**	(**196**) 7%	7:1	(**197**) 75%
22	**179b**	2-Naph	**B** [h]	(**198**) <4%	nd	(**199**) 59%

Conditions **A**: *n*-BuLi (1.2 equiv), 10 min. Conditions **B**: *sec*BuLi (3 equiv), 3 h. [a] Isolated yields. [b] Determined by ^{1}H NMR of isolated material. [c] dr >> 20:1 in all cases. [d] 1.1 of *n*-BuLi. [e] -78 ^oC, 6h, then rt, 20h. [f] 58% recovered **175b** and isomeric enol. [g] Complex mixture. [h] Reaction time was 6h.

Data from the *para*-substituted *trans* substrates provided an opportunity to take advantage of the Hammet equation 1,[22]

$$\text{Log}\ (k_X/k_0) = \rho\ .\ \sigma_X \qquad \text{eq. 1}$$

where σ_X represents a substituent parameter and ρ a reaction constant, which depends only on the type of reaction. Although the original σ_X values (σ) were obtained from the ionization of substituted benzoic acids,[22] deviation of linearity due to different balance of resonance and polar

effects has led to the development of different σ_X substituent constant scales, typically classified as σ^-, σ^+ and $\sigma^\cdot$.[23]

The [1,2]-Wittig migration of our cyclic ether likely proceeds by a stepwise mechanism in which the intermediate (Figure 6), possessing a benzylic radical and a radical-anion segment, intramolecularly recombines in a [1,2]- fashion. On the other hand, although the [1,4]-shift can proceed through a concerted process, it is also likely that it also takes place via intramolecular [1,4]- recombination of a diradical anion species. Substituent effects are likely to stabilize, or desestabilize, such transient benzylic radicals, and for that reason it was thought that $\sigma^\cdot$ would be more relevant for analyzing the data on Table 6. However, attempts to fit this data (Log(k_X/k_0) in which k_X is the [1,2]-/[1,4]-ratio for *X*) with known $\sigma^\cdot$ scales[24] led to severe deviations from linearity. On the other hand, and quite surprisingly, good correlation ($R^2 > 0.96$) was found with σ and σ^+ parameters (Figure 7). These observations suggest that spin delocalization of a presumed benzylic radical is not as important as the polar effects induced by the different substituents *X* in the transition state. Notice that such early transition state in the rate-limiting step probably refers to the C-O bond cleavage, and not to the [1,2]- or [1,4]-intramolecular recombination of the diradical anion.

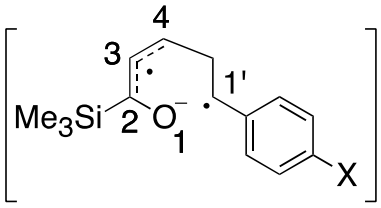


Figure 6. Presumed diradical anion intermediate.

It is also interesting to consider that both *para* electron-donating and *para* electron-withdrawing groups are expected to stabilize a benzylic radical by resonance or inductive means, relative to the unsubstituted benzylic radical, due to spin delocalization away from the benzylic carbon, [25] which is at least qualitatively indicated by $\sigma^{\cdot}$ scales.[24] This expectation is not clearly reflected in the obtained Hammett plots (Figure 7).

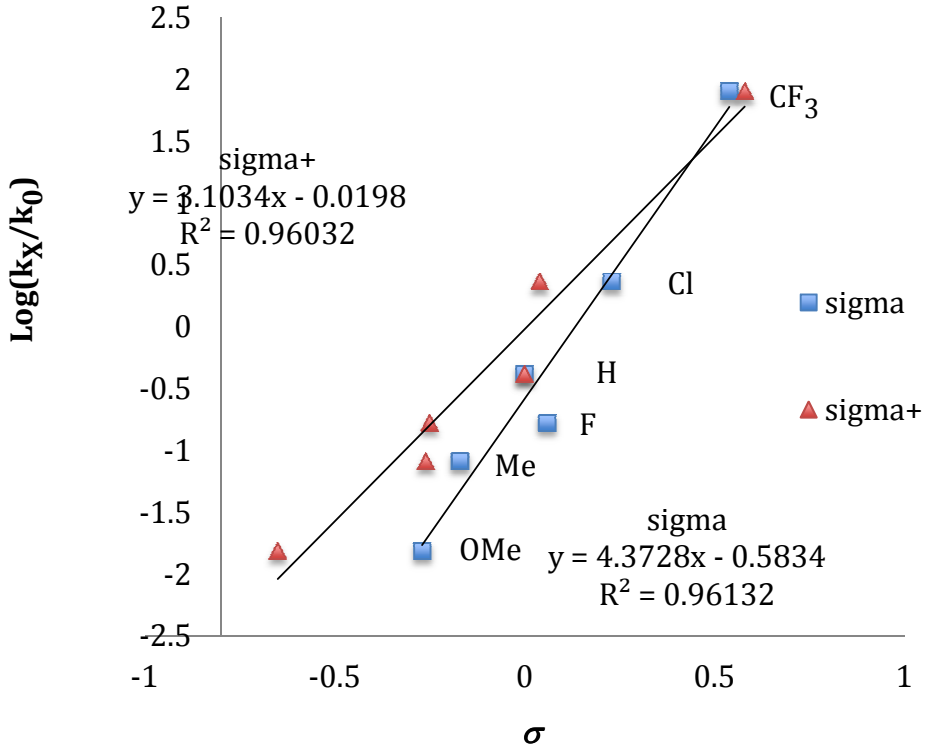


Figure 7. Plots of Log (k_X/k_0) vs σ and σ^+ parameters. "For the interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation"

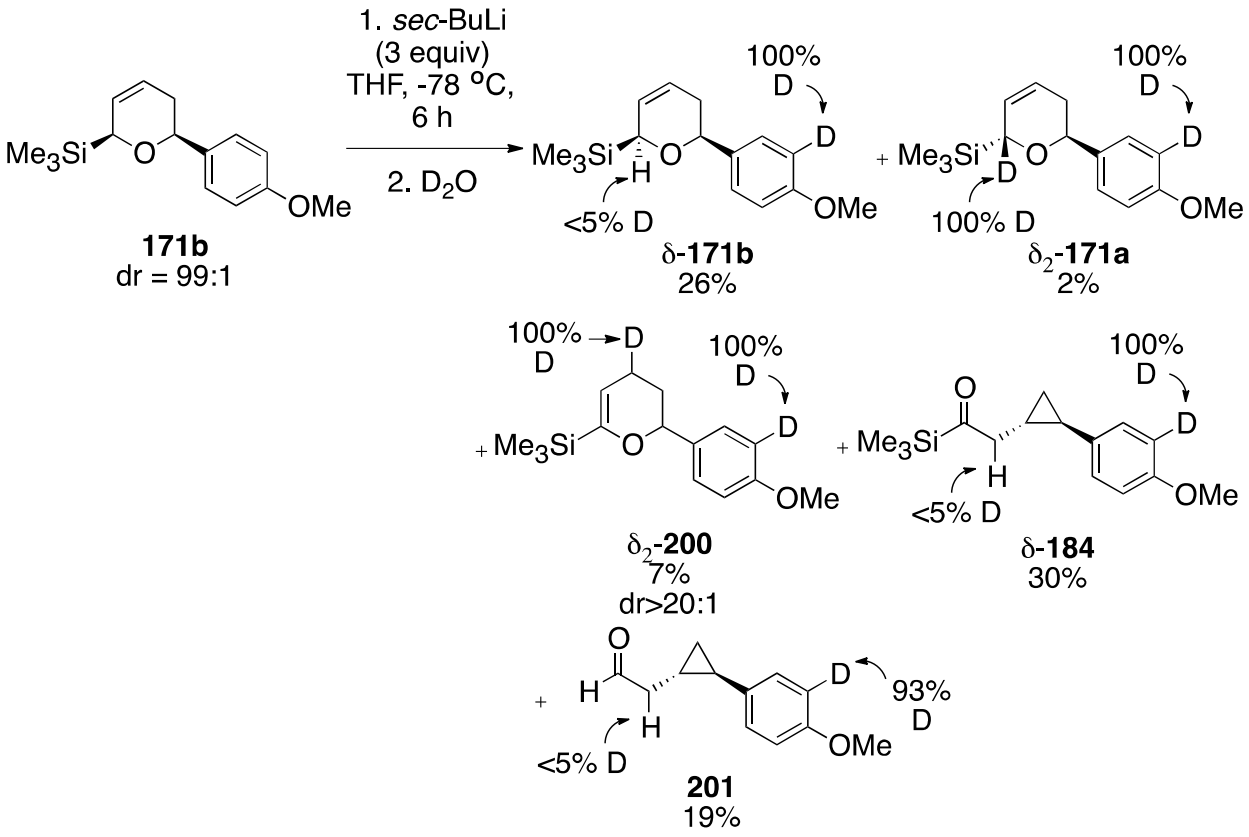
The large ρ values (3.10 from σ, 4.37 from σ^+) indicate a high sensitivity to the nature of the substituent *X*, and a balance between resonance and inductive effects seems to play an important

role in the [1,4]-/[1,2]-selectivity. That dependence is more consistent with a stepwise mechanism for the [1,4]-Wittig rearrangement. Following that assumption, it appears that the intrinsic electrophilic character of the unsubstituted benzylic radical changes in different directions, thus becoming a 'nucleophilic' benzylic radical[26] with highly electron-donating groups (e.g. methoxy) leading to the [1,4]-shift, or increasingly electrophilic radical[27] with electron-withdrawing groups (e.g. trifluoromethyl), favoring the [1,2]-shift (retarding [1,4]-recombination). These conjectures await some clarification by computational studies.

4.4.3 Deuterium trapping experiments

Evidence for *ortho* metalation was gathered from deuterium trapping experiments with **171b** (Scheme 73), moreover, other important additional information was also obtained. The first indication that competitive *ortho* metalation of **171b** was taking place came from the observed incomplete conversion at low temperature after prolonged reaction time, a situation that was solved by increasing the temperature (Table 6, entry14). When the reaction was quenched after 6 hours at –78 ^{o}C, 26% of unreacted δ-**171b**, in which deuterium was incorporated (100%) *ortho* to the methoxy group (Scheme 73). Although the allylic position of **171b** was not deuterated (<5% by ^{1}H NMR), the isomeric enol ether δ_2-**200** was obtained in 7% as a single diastereomer, in which deuterium was at both allylic and aryl positions. Importantly, trace amounts (2%) of epimeric δ_2-**171a**, also doubly deuterated, was isolated. The monodeuterated [1,4]-Wittig product **184** was obtained in 30% yield, along with desilylated [1,4]-Wittig aldehyde **201** in 19% yield. When the experiment was repeated and quenched after shorter reaction times (1.5-3 hours), monodeuterated δ-**171b** was isolated in greater amounts and was fully deuterated at the

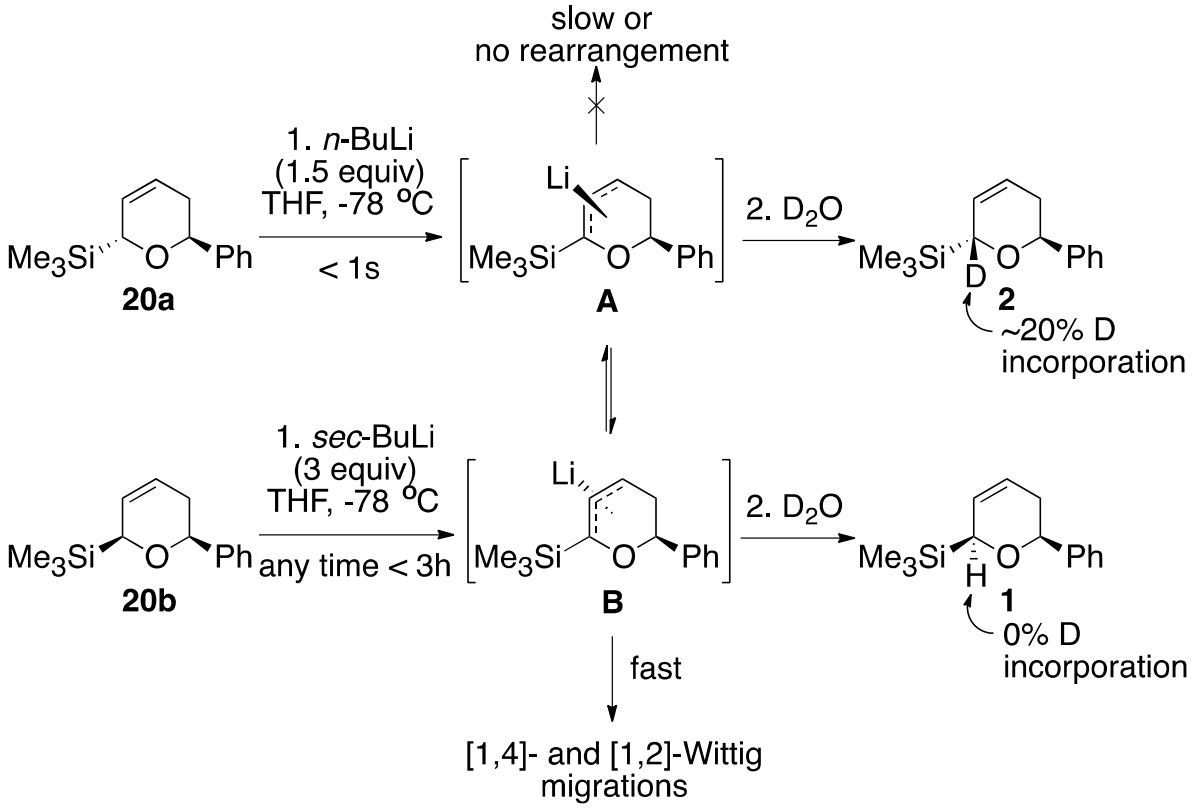
ortho position relative to the methoxy group. These results indicate that: 1) *ortho* Metalation of **171b** is faster than allylic deprotonation, 2) *ortho* metalated **171b** is sluggish to undergo rearrangement at low temperatures, but increasing the temperature allows selective [1,4]-Wittig rearrangement, presumably via a dianion species (allylic/aryl dilithium), and 3) such dianion species seems to be slow to rearrange, as evidenced by the epimerization at the allylic position (compound δ_2-**171a**).



Scheme 73. Deuterium trapping experiment with **171b**.

Point 3 is consistent with the fact that the reaction of **171a** (*trans*) underwent almost complete rearrangement, via the monoanion allylic species, in 15 minutes (no deuterium incorporation at the *ortho* position).

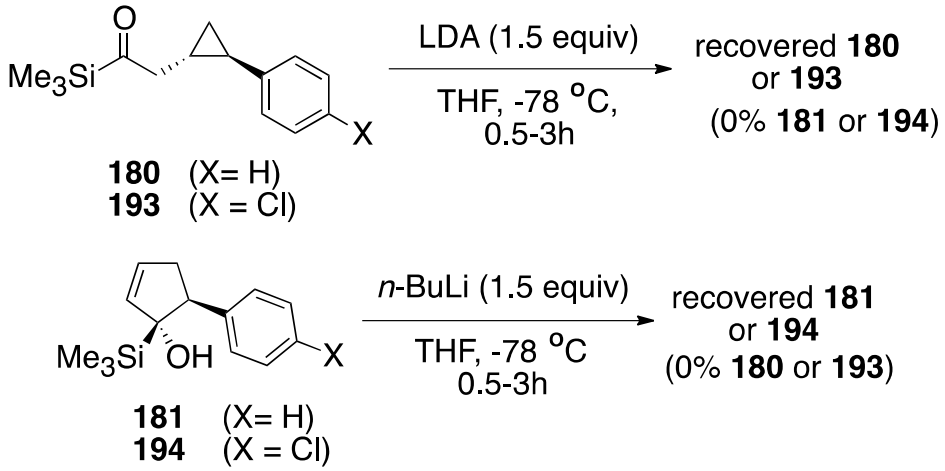
Trapping experiments with diastereomerically pure model compounds **20a** and **20b** were also instructive. Quenching the allylic anion derived from deprotonation of **20a** (**A**, Scheme 74) with D_2O immediately after *n*-BuLi addition (< 1s) led to deuterium incorporation *without epimerization* (dr >> 20:1 by ^1H NMR). On the other hand, attempts to trap the allylic anion derived from **20b** (**B**) with D_2O at different reaction times (1-3 hours) were unsuccessful, suggesting such species (**B**) undergoes immediate rearrangements as soon as it is formed (Scheme 74). This interpretation is in accord with the observed stereoconvergence of both rearrangements and is probably due to the isomerization of allylic anion **A** to the most reactive diastereomer **B**. Additional evidence supporting such allylic epimerization is presented below with optically active compounds **20a**/**20b**.



Scheme 74. Deuterium trapping experiments with **20a** and **20b**.

4.4.4 The possibility of epimerization or equilibration of the [1,4]-enolate and [1,2]-alkoxide

We were cognizant of the possibility that the [1,2]-Wittig alkoxide and [1,4]-Wittig enolate products might equilibrate prior to work up, giving a false 'electronic effect'. In fact, α-cyclopropyl ketones bearing anion-stabilizing groups on the ring are known to undergo ring expansion to the cyclopentenol isomers under basic conditions,[28] whereas some cyclopropyl thioenolates isomerize to the corresponding cyclopentenyl thiolates.[11e, f] However, generation of the anionic products under similar reaction conditions did not lead to any [1,2]-/[1,4]-interconversion (and visa versa). In line with this observation, the diastereoselectivity in both [1,4]- and [1,2]-ring contractions is defined during rearrangement, as little or no decrease of dr was observed in these control experiments (Scheme 75). Thus, we have established that the observed product ratios are a true consequence of electronic effects, and the possibility that the [1,4]-Wittig enolate isomerized to the [1,2]-Wittig alkoxide, or visa versa, has been discarded.



Scheme 75. Control experiments ruled out interconversion between [1,4]- and [1,2]-products under similar reaction conditions within reaction time scale.

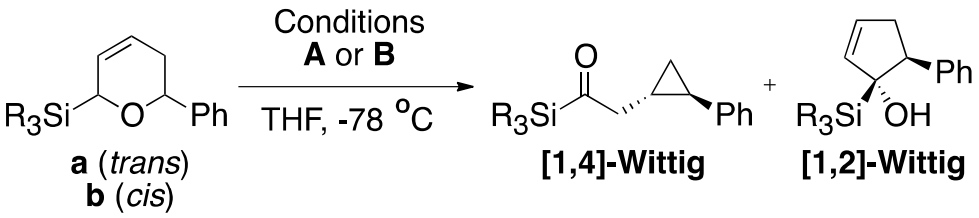
4.4.5 Effect of the silyl group on the [1,4]-/[1,2]-selectivity

We then proceeded to tackle the modest [1,4]-/[1,2]-selectivity obtained in most cases and the preference for [1,2]-Wittig migration in electron deficient substrates. Inspection of the [1,2]-Wittig product reveals two adjacent stereocenters in which the bulkier groups (Ph and $SiMe_3$) are in a *cis* relationship. Since the [1,2]-Wittig pathway proceeds via a radical/radical anion intermediate (Figure 6),[3] we rationalized that increasing the steric demand of the silyl group would inhibit recombination via the [1,2]-pathway, indirectly stimulating [1,4]-migration. Gratifyingly, our hypothesis proved right and a gradual increase of the steric demand of the silyl group consistently led to a greater [1,4]-/[1,2]-product ratio (Table 7). In the *trans* series changing a $SiMe_3$ group (**20a**) to a $SiMe_2Ph$ group (**202a**) increased the selectivity from 2.4:1 to 10:1 (entries 1 & 2), and further steric increase to a $SiMePh_2$ group (**203a**) allowed exclusive [1,4]-Wittig rearrangement to the cyclopropyl acylsilane in excellent yield (entry 3). We believe the observed improvement in regioselectivity is highly dominated by sterics with little, electronic effect of the silyl group. In fact, increasing the bulkiness of the silyl group only with alkyl substituents at silicon, that is, a $SiEt_3$ group (**204a**, entry 4), led to excellent [1,4]-/[1,2]-selectivity.

The corresponding *cis* diastereomers afforded virtually the same product ratio and with excellent diastereoselectivities (entries 5-8). However, in these cases increasing the steric demand of the silyl group was deleterious for the reactivity of certain substrates. Compound **203b** bearing $SiMePh_2$ group (entry 7) underwent incomplete conversion in 3 hours (standard reaction time),

whereas compound **204b** having a $SiEt_3$ group (entry 8) also underwent partial conversion even with more base equivalents and higher reaction temperature.

Table 7. Effect of silyl group in the [1,4]-/[1,2]-Wittig selectivity.

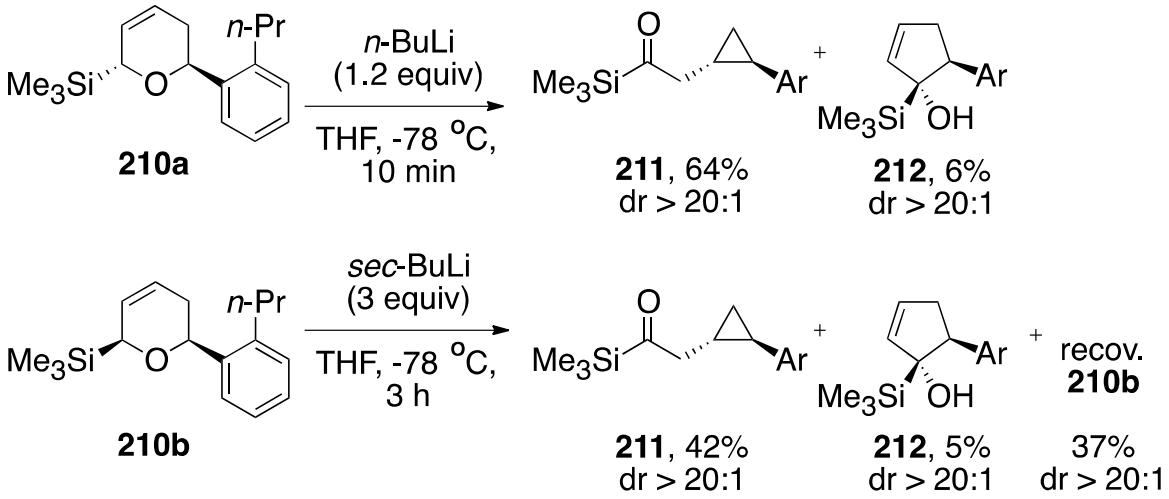


entry	substrate	SiR_3	[1,4]-Wittig[a]	[1,2]-Wittig[a]
1	**20a**	$SiMe_3$	(**167**) 58%	(**168**) 24%
2	**202a**	$SiMe_2Ph$	(**205**) 69%	(**206**) 7%
3	**203a**	$SiMePh_2$	(**207**) 79%	-
4	**204a**	$SiEt_3$	(**208**) 93%	(**209**) 5%
5	**20b**	$SiMe_3$	(**167**) 60%	(**168**) 29%
6	**202b**	$SiMe_2Ph$	(**205**) 74%	(**206**) 7%
7[b]	**203b**	$SiMePh_2$	(**207**) 51%	-
8[c]	**204b**	$SiEt_3$	(**208**) 60%	(**209**) 4%

Unless otherwise noticed, conditions **A**: *n*-BuLi (1.2 equiv), 10 min. Conditions **B**: *sec*-BuLi (3 equiv), 3 h. [a] Isolated yields. [b] 16% recovered **203b**. [c] 4 equiv *sec*-BuLi, -78 °C, 30 min then 0 °C, 3 h, 8% recovered **204b**.

Given that the reactivity of *trans* isomers was not affected, the loss of reactivity in *cis* diastereomers suggests bulkier silyl groups favor conformational equilibrium to the less reactive

ring conformer. Consistent with this hypothesis is the observation that a sterically demanding group (propyl) at the *ortho* position of the phenyl ring (**210a**/**210b**) led to a decrease in reactivity of the *cis* diastereomer (**210b**), whereas the reactivity of the corresponding *trans* (**210a**) isomer was unaffected (Scheme 76).



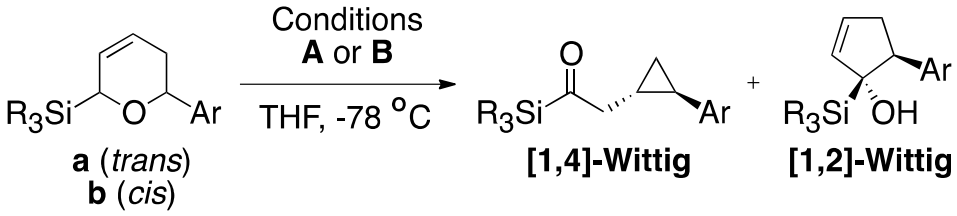
Scheme 76. Influence of steric demand at the *ortho* position of the aromatic ring.

4.4.6 Competition between electronic and steric effects

Competition between *opposite* steric and electronic effects was then evaluated. For instance, *trans* and *cis* diastereomers **213a** and **213b** bearing a *m*-methoxy group and bulky silyl group ($SiMe_2Ph$) underwent rearrangement with higher ~4:1 [1,4]-/[1,2]-selectivity (Table 8, entries 1 & 2) relative to the $SiMe_3$ counterpart (Table 6, entries 2 & 13). *Trans* substituted, *p*-chlorophenyl substrate (**214a**, entry 3) led to a 1:1 product ratio showing a modest increase of [1,4]-/[1,2]-selectivity from 1:2 in the $SiMe_3$ analogue (Table 6, entry 8). The opposite diastereomer (**214b**) was not evaluated because of complications due to competitive

halogen/lithium exchange. 2-Naphtyl diastereomers bearing a $SiEt_3$ group (**215a**/**215b**) deserve special comment due to the observed opposite [1,4]-/[1,2]-selectivity obtained from each diastereomer. Compound **215a** (*trans*) underwent smooth rearrangements under standard conditions used for *trans* diastereomers, providing ~1:5 [1,4]-/[1,2]-selectivity in 91% overall yield (entry 4). Comparison of this product ratio (1:5) with that from the *trans* and *cis* $SiMe_3$ substituted counterparts (~1:30, Table 6, entries 11 & 22) revealed a significant improvement in [1,4]-/[1,2]-ratio, although the [1,2]-Wittig product largely remained the major component. On the other hand, the opposite diastereomer **215b** was extremely unreactive (<<50% conversion at -50 ^{o}C, 4h) under standard conditions applied to most *cis* diastereomers, as expected due to the presence of two bulky groups. This limitation was solved by increasing the temperature to 0 ^{o}C, which surprisingly, led to opposite [1,4]-/[1,2]- selectivity (5:1). Usually the [1,4]-Wittig pathway is favored at lower temperatures[5c] and the [1,2]-shift becomes competitive as the temperature increases. This result seems to be a consequence of isomerization of the [1,2]-Wittig alkoxide to the [1,4]-Wittig enolate. It is interesting that the analogous model substrate **20b** (Scheme 72) underwent rearrangements within 1 hour without significant change in [1,4]-/[1,2]-selectivity when the temperature was raised from -78 ^{o}C to 0 ^{o}C.

Table 8. Competition between steric and electronic effects.



entry	substrate	SiR_3	Ar	[1,4]-Wittig[a]	[1,2]-Wittig[a]
1	**213a**	$SiMe_2Ph$	3-$MeOC_6H_4$	(**216**) 67%	(**217**) 17%
2[b]	**213b**	$SiMe_2Ph$	3-$MeOC_6H_4$	(**216**) 49%	(**217**) 14%
3[c]	**214a**	$SiMe_2Ph$	4-ClC_6H_4	(**218**) 47%	(**219**) 44%
4	**215a**	$SiEt_3$	2-Naph	(**220**) 16%[d]	(**221**) 75%
5[e]	**215b**	$SiEt_3$	2-Naph	(**220**) 45%[f]	(**221**) %9

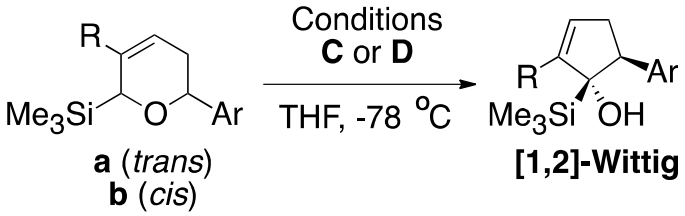
Unless otherwise noticed, conditions **A**: *n*-BuLi (1.2 equiv), 10-30 min. Conditions **B**: *sec*-BuLi (3 equiv), 3 h. [a] Isolated yields. [b] 6h, 20% recovered **213b** and isomeric enol ether. [c] 1.1 equiv *n*-BuLi. [d] dr = 6:1 [e] -78 °C to 0 °C, 6h. [f] dr = 3:1.

4.4.7 Impact of olefin substitution

4.4.7.1 Alkyl substitution proximal to the silyl group

The effect of substitution at the olefin was studied next. Alkyl or alkenyl substitution at the *proximal* position relative to the silyl group, surprisingly, led to exclusive [1,2]-Wittig rearrangement in good yields and excellent diastereoselectivities, from both *trans* and *cis* cyclic ethers (Table 9). Importantly, the observed [1,2]-selectivity was independent of electronic effects and no cyclopropane compounds were observed when *para* electron-donating groups were present at the aromatic appendage (entries 2, 3, 6 & 7).

Table 9. Effect of olefin substitution *proximal* to the silyl group on the [1,4]-/[1,2]-selectivity.

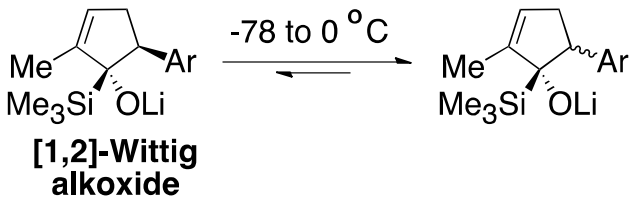


entry	substrate	R	Ar	time (h)	[1,2]-Wittig[a]
1	**222a**	Me	Ph	0.5	(**226**) 85%
2	**223a**	Me	4-$MeOC_6H_4$	0.5	(**227**) 72%
3	**224a**	Me	4-MeC_6H_4	0.5	(**228**) 91%
4[b]	**225a**	*iso*propenyl	Ph	1.5	(**229**) 75%
5	**222b**	Me	Ph	7	(**226**) 79%
6	**223b**	Me	4-$MeOC_6H_4$	7	(**227**) 26%
7	**224b**	Me	4-MeC_6H_4	6	(**228**) 75%
8[c]	**225b**	*iso*propenyl	Ph	20	(**229**) 12%

Conditions **A**: *n*-BuLi (1.2 equiv). Conditions **B**: *sec*BuLi (3 equiv). [a] Isolated yields. [b] 13% recovered **225a**. [c] 51% recovered **225b**.

A decrease in reactivity was observed in both *trans* and *cis* diastereomeric ethers and longer reaction times were required for complete conversion. The overwhelming steric effect suggests planarization of the allylic anion (prior to rearrangement), or of the putative allylic radical oxyanion intermediate (Figure 6) is prevented to a significant degree, which at this point, is difficult to interpret. We suspect, however, that this substitution inhibits the [1,4]-migration, rather than enhancing the [1,2]-shift.

Is is worth mentioning that following [1,2]-Wittig rearrangement of these compounds, increasing the reaction temperature (~24 ^{o}C, 12 hours) led to significant epimerization (dr ~ 1:1), however, no [1,4]-Wittig products were observed (Scheme 77). Although the overall yield remained high, no optimization or additional studies to achieve complete epimerization were attempted, nor it is known whether epimerization occurs only at the benzylic position, at the alkoxide-bearing carbon, or both.

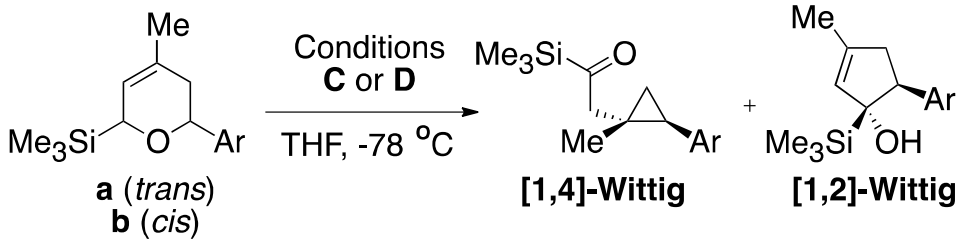


Scheme 77. Epimerization of [1,2]-Wittig alkoxide at higher temperatures.

4.4.7.2 Alkyl substitution distal to the silyl group

In contrast to the previous examples, alkyl (methyl) olefin substitution *distal* to the silyl group provided modest [1,4]-/[1,2]-product selectivity (Table 10, entries 1 & 2), even when a more electron rich aromatic group was present (entry 3 & 4). Although the diastereoselectivity in the [1,4]-products was lower than in our model substrates, it was remarkable an all-carbon quaternary center is formed in good yield.

Table 10. Effect of olefin substitution *distal* to the silyl group on the [1,4]-/[1,2]-selectivity.



a (*trans*)
b (*cis*)

[1,4]-Wittig **[1,2]-Wittig**

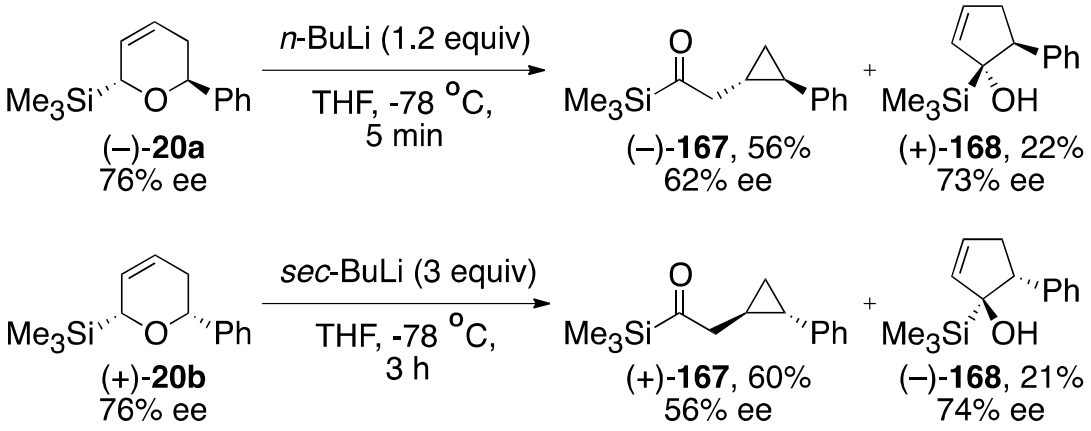
entry	substrate	Ar	[1,4]-Wittig[a]	dr	[1,2]-Wittig[a]	dr
1	**230a**	Ph	(**232**) 44%	7:1	(**233**) 38%	20:1
2	**230b**	Ph	(**232**) 42%	6:1	(**233**) 32%	12:1
3	**231a**	4-MeC_6H_4	(**234**) 44%	9:1	(**235**) 43%	20:1
4	**231b**	4-MeC_6H_4	(**234**) 45%	5:1	(**235**) 30%	20:1

[a] Isolated yields.

4.4.8 Origin of stereoconvergence

In order to ascertain the origin of stereoconvergence we first studied the rearrangement of enantiomerically enriched substrates (–)-**20a** and (+)-**20b**. Although the [1,2]-Wittig shift is known to occur with high retention of stereochemistry at the migrating carbon, in both acyclic[3] and cyclic ethers,[10d] the stereochemical course of the competing [1,4]-Wittig pathway has only been studied in one acyclic instance. As expected, [1,2]-Wittig rearrangement of (–)-**20a** and (+)-**20b** proceeds with retention of stereochemistry at a very high degree (96% and 97% retention, respectively). The [1,4]-Wittig shift of (–)-**20a** and (+)-**20b** also occurred with retention of stereochemistry, albeit to a lower degree (82% and 74% retention, respectively).

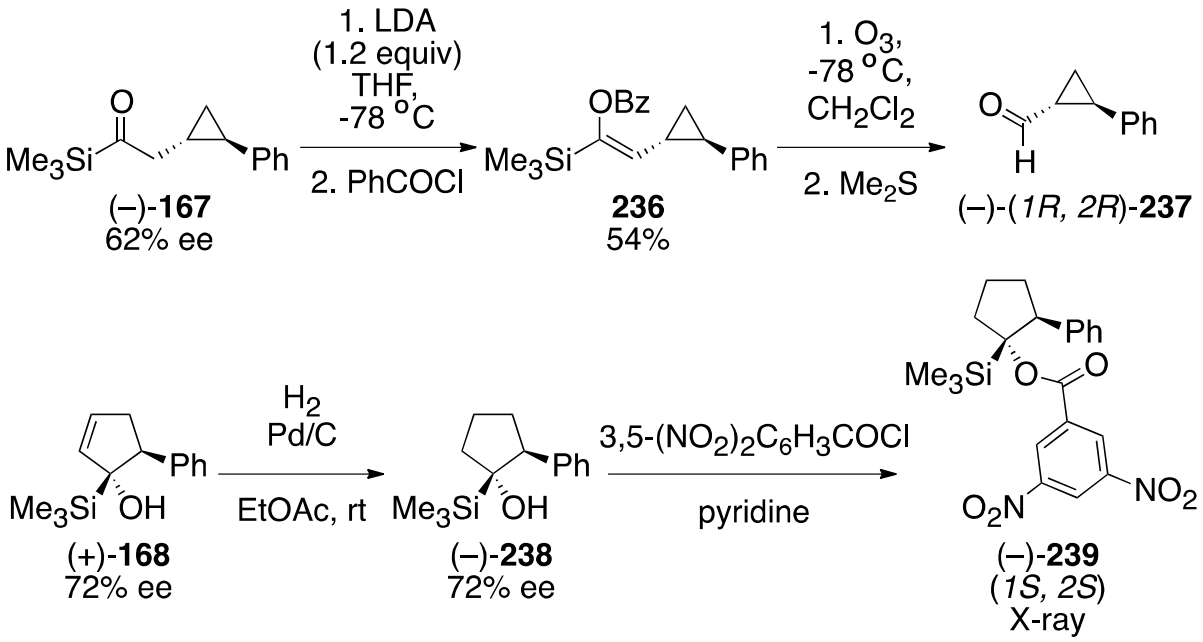
These results, together with deuterium trapping experiments previously discussed (Section 4.4.3) support the idea that diastereomeric allyllithium species generated from the deprotonation of **20a** and **20b** converge to the more reactive conformer (presumably that coming from **20b**) which quickly rearranges via [1,4]- and [1,2]-shifts. This is also consistent with the fact that the absolute stereochemistry of the products is exclusively determined by the configuration of the migrating carbon, while the chiral information at the allylic carbon before deprotonation is destroyed in the process.



Scheme 78. Stereochemical course of the [1,4]- and [1,2]-Wittig rearrangements of (–)-**20a** and (+)-**20b**.

The absolute stereochemistry of the products was determined as follows: Compound (–)-**167** was deprotonated with LDA and the enolate trapped as the benzoate enol **236**. Ozonolysis afforded the known aldehyde (–)-(*1R, 2R*)-**237** (Scheme 79).[29] Cyclopentenol (+)-**168** (72% ee) was reduced to cyclopentanol (–)-**238** without losss of chiral information (72% ee). This reduction was necessary due to instability of the allylic tertiary alcohol and because the presumed ester product likely undergoes S_N2' reactions. Thus, (–)-**238** was esterified with 3,5-dinitrobenzoyl

chloride to afford the crystalline ester (–)-**239** from which X-ray analysis confirmed the absolute stereochemistry as (*1S,2S*).



Scheme 79. Determination of the absolute stereochemistry of (–)-**167** and (+)-**168**.

4.4.9 Extension to heteroaromatic substrates

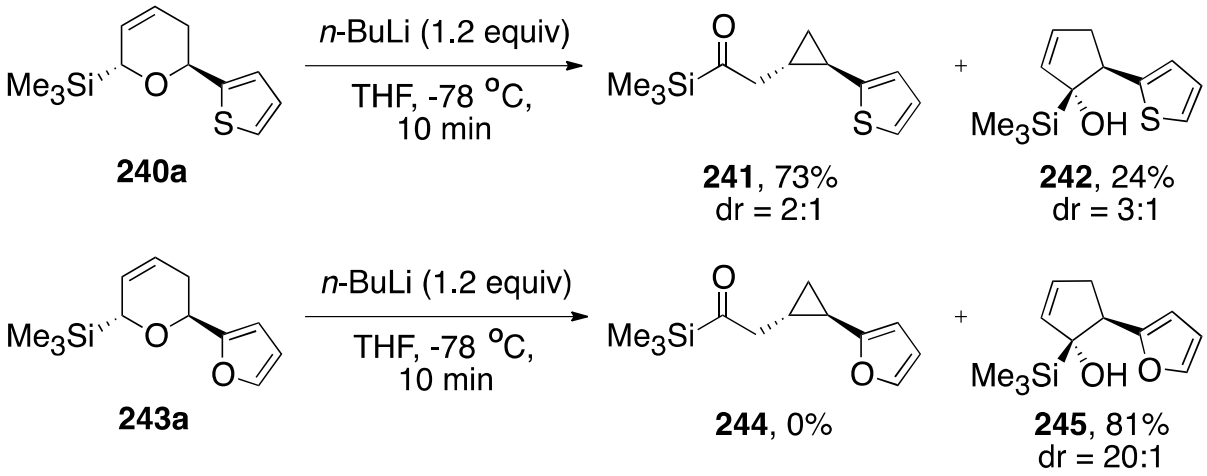
Wittig rearrangements of migrating centers stabilized by heteroaromatic substituents rather than substituted aryl groups have been studied by several groups over the years. Nakai *et al.* studied the [2,3]-Wittig rearrangemens of 2-, 3- and 4-pyridyl substituted ethers.[30] The authors concluded that a combination of both electronic and steric effects were responsible for the slight variations on diastereoselectivity. Honda *et al.* [9b, 31] and others[32] have studied the [2,3]-Wittig rearrangements of ethers bearing 2- and 3-furyl groups attached at the α-position, including the ring contraction of macrocyclic ethers. Other heteroaromatic sytems such as thiophenyl, isoxazolyl, benzothiazolyl and thiazolyl have also been studied in [1,2]- and [2,3]-Wittig

rearrangements.[33] The only report in which heteroaryl-substituted (2-furyl, 2-thiophenyl) migrating carbon underwent a [1,4]-Wittig shift was reported by Kanematsu.[32b] The yields were low (12-22%) and the [1,2]-Wittig product was major.

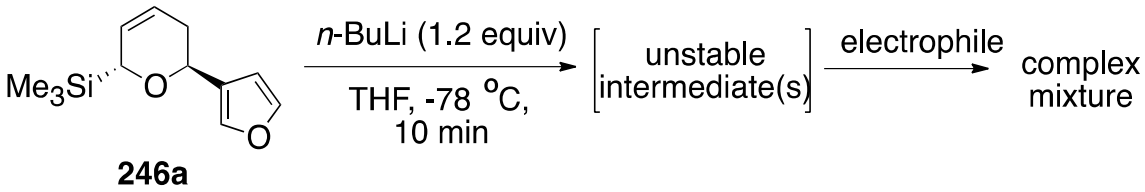
Thus, it was of interest to us to evaluate the behavior of 2-silyl dihydropyrans bearing heteroaromatic groups at the migrating carbon. The preparation of furyl, thiophenyl and indolyl compounds was possible via Lewis acid-catalyzed trichloroacetimidate alkylation of α-silyl allyl alcohol (Section 4.3.2, Table 4). Unfortunately, this protocol was not compatible with pyridyl analogues, and therefore these compounds were not studied.

The study was initiated with the *trans* diastereomers, which were expected to be more reactive towards the rate-limiting step (deprotonation). Thus, reaction of 2-thiophenyl ether **240a** with *n*-butyllithium afforded the [1,4]- and [1,2]-Wittig products **241** and **242** in excellent overall yield, favoring the [1,4]-product (Scheme 80). The diastereoselecty was low in both cases, but no evidence of epimerization or [1,4]-/[1,2]- interconversion was observed when the reaction mixture was left for longer time (3h) at low temperature (-78 ^{o}C). 2-Furyl ether **243a** also reacted completely within 10 minutes and afforded exclusively the [1,2]-Wittig product **245** with good yield and diastereoselectivity. No evidence of [1,4]-Wittig product **244** was observed. The surprising reversal of [1,4]-/[1,2]-selectivity in going from 2-thiophenyl to 2-furyl was accentuated when reaction of 3-furyl substrate **246a** led to a complex mixture of products following work up. Attempts to trap the presumed unstable product with PhCOCl, gave also a

mixture of products (Scheme 81). We speculate that this unstable product is a ring-opened species formed as a consequence of an aborted cyclization.



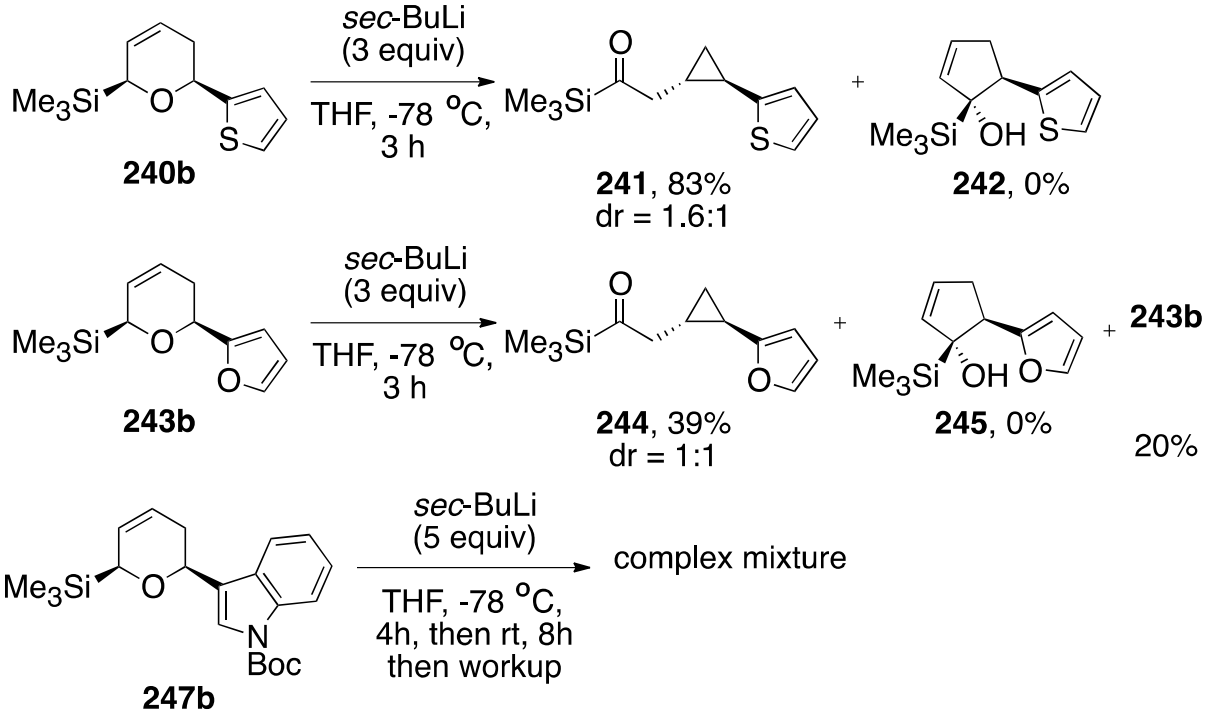
Scheme 80. Wittig rearrangements of *trans* 2-thiophenyl and 2-furyl cyclic ethers.



Scheme 81. Unsuccessful rearrangement of 3-furyl substituted **246a**.

On the other hand, and quite remarkably, *cis* counterparts **240b** and **243b** underwent exclusive [1,4]-Wittig rearrangement to cyclopropanes **241** and **244** in 83% and 39%, respectively (Scheme 82). Initially these results were cautiously received given the suspicion of further isomerization of a [1,2]-Wittig alkoxides to the [1,4]-Wittig enolates within the reaction time (3h). However, keeping the reaction mixtures of **240a** and **243a**, which had undergone complete rearrangement in 10 minutes (Scheme 80), for longer reaction time (3h) led to negligible

variation in product ratios. This observation led us to consider that the 'anomalous' behavior of *cis* counterparts (**240b** and **243b**) was due to the rearrangement of the corresponding dianion (Figure 8).



Scheme 82. Anomalous reactivity of *cis* 2-thiophenyl, 2-furyl and 3-indolyl compounds.

In fact, deuterium trapping experiments conducted with **240b** and **243b** revealed that dianion formation was faster than rearrangement, and 100% deuterium incorporation at the 5-position of the thiophene and furan moieties in unreacted **240b** and **243b**, respectively, was observed when the reaction was stopped at 1h.

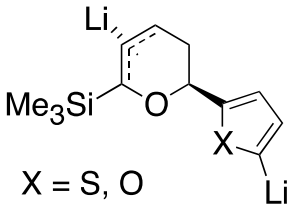
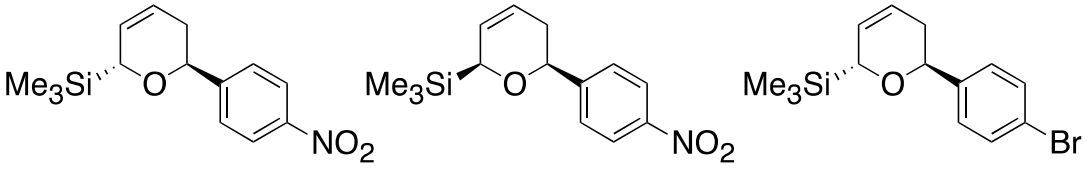


Figure 8. Dianions derived from **240b** and **243b** that undergo selective [1,4]-Wittig shift.

3-Indolyl substituted compound **247b** underwent Boc deprotection at low temperatures and no rearrangements were observed. Increasing the temperature led to almost complete conversion, however, only a complex mixture of product, resembling the observations previously made with 3-furyl substituted **246a**, were observed. We hypothesize that the workup procedure might be responsible for the observed extensive decomposition. Unusual color changes during the workup procedure, perhaps due to a drastic change in the pH of the mixture, suggest such an idea.

4.4.10 Other substrates incompatible with the reaction conditions

It was found that nitro substituted compounds **248a** and its diastereomer **248b** underwent complete decomposition when submitted to our standard conditions (Figure 9). It is likely that this is due to the competitive reaction between the nitro groups and the alkyllithiums. Organomagnesium reagents, for example, are known to attack aromatic nitro groups in the course of indole formation.[34] In addition, *p*-bromo substituted compound **249a** underwent complete halogen/lithium exchange and no rearrangement products were observed in the crude reaction mixture. However, the chemical events that took place are interesting and deserve further comment.

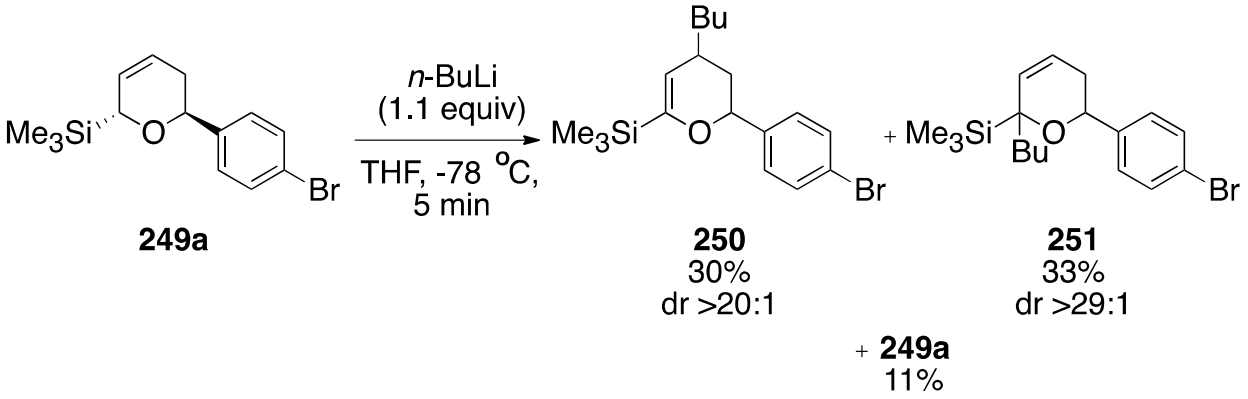


248a **248b** **249a**

Figure 9. Substrates incompatible with reaction conditions.

Reaction of **249a** with *n*-BuLi led to alkylated allylic ether **250** in 30% as a single diastereomer, together with cyclic enol ether **251** in 33% yield (dr ~ 9:1) and unreacted starting **249a**. The

formation of compounds **250** and **251** is a consequence of the reaction of 1-bromobutane (formed by Br/Li exchange between **249a** and *n*-BuLi) with allylic lithium intermediate at the 4- and 2-positions, respectively (Scheme 83).

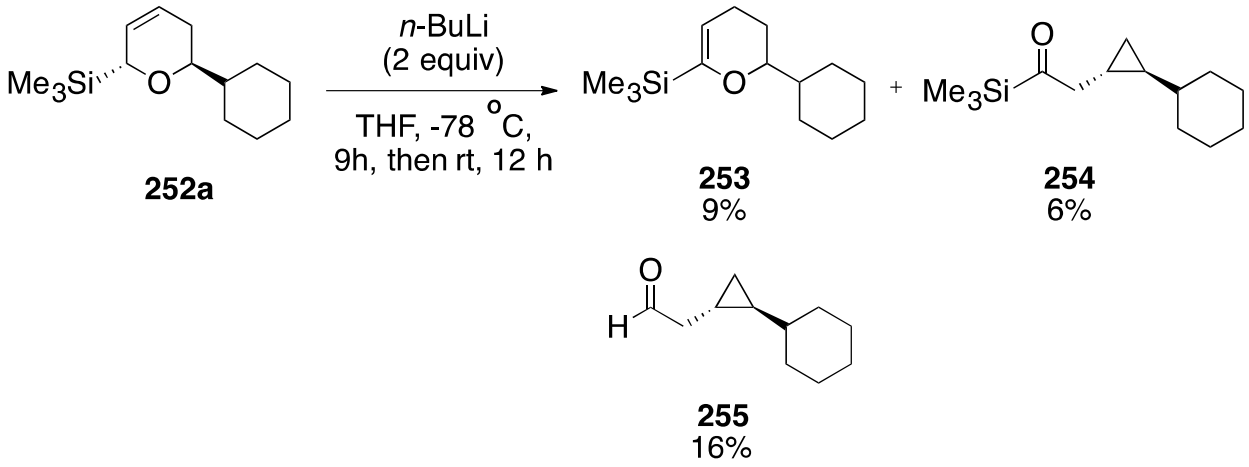


Scheme 83. Sequence Br/Li exchange / allylic deprotonation / alkylation.

4.4.11 Rearrangement of a substrate bearing an unactivated migrating center

In contrast to substrates bearing an aromatic or pseudoaromatic group at the migrating center, an analogous compound substituted with a simple alkyl group (cyclohexyl) was very sluggish to undergo rearrangement. At -78 ^{o}C, *trans* substituted compound **252a** did not undergo rearrangement after 9 hours, and it was necessary to increase the temperature to observe conversion. The major products of this reaction were enol ether **253**, [1,4]-Wittig product **254** and desilylated [1,4]-Wittig aldehyde **255**, all in low yields (Scheme 84). In a separate experiment, treatment of **252a** with *n*-butyllithium (2 equiv) at -78 ^{o}C and quenching with D_2O led to 32% of recovered **252a** (single diastereomer) with 92% deuterium incorporation at the allylic position and 23% of isomeric enol ether **253** (deuterium incorporation not determined). These experiments demonstrate that the allylic anion –the actual species that undergoes bond reorganization– is formed relatively quickly (< 2h) but it is very slow to rearrange at low

temperature. It is also interesting to note that raising the temperature led to predominantly [1,4]-Wittig products, although it is not possible to establish a high [1,4]-selectivity due to the low mass balance of the reaction. However, these results are promising in terms of the substrate scope. It is important to mention that the relative stereochemistry of products **254** and **255** could not be confirmed by NOE (inconclusive) but it has been tentatively assigned.

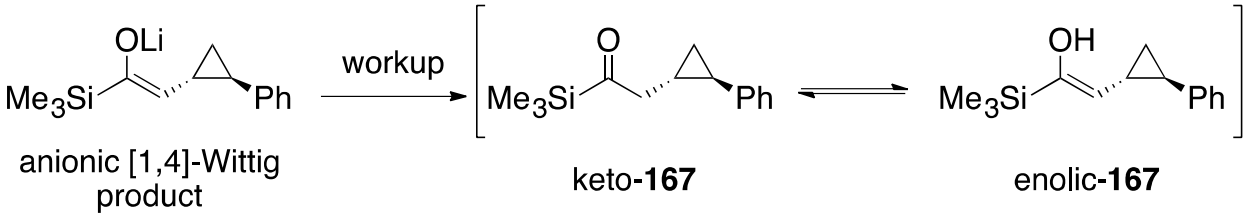


Scheme 84. Rearrangement of alkyl-substituted substrate **252a**.

4.4.12 Tautomeric behavior of α-(2-arylcyclopropyl)acylsilanes

In the earlier stages of this study the rearrangement of model compounds **20a** and **20b** were not reproducible in terms of yields. Although the reaction afforded only two major products: acylsilane **167** and alcohol **168**, analysis of the crude reaction mixture showed additional signals in the ^{1}H NMR spectrum. In particular, resonances attributable to a different cyclopropane compound –other than cyclopropane **167**– were observed, and their integrated areas were in connection with doublet at 4.51 ppm and a broad singlet at 4.39 ppm. Spiking of this sample with D_2O led to dissapareance of the singlet at 4.39 ppm on the ^{1}H NMR spectrum. The ^{13}C NMR of this mixture showed, in addition to the signals corresponding to compounds **167** and **168**,

additional peaks attributable to a cyclopropyl ring and two peaks at 158.2 and 117.2 ppm. These observations are in accord with the expected spectroscopic characteristics of the enolic form of compound **167**. That is, the keto and enolic forms of compound **167** are in equilibrium following workup. However, following column chromatography of the crude reaction mixture, only the keto form of compound **167** was isolated, accompanied by the [1,2]-Wittig product **168**.



Scheme 85. Tautomeric equilibration of cyclopropyl acylsilane **167** following workup of its enolate.

Attempts to control the relative ratio of these tautomers were met with failure. Different workup procedures were employed: dilute HCl, acetic acid, silica gel, water; and different drying agents ($MgSO_4$, Na_2SO_4, molecular sieves) were tested, and in all cases a mixture of the tautomeric forms of **167** were observed in the crude reaction mixture. Thus, it appeared that such tautomerizaion is responsible for the observed lack of reproducibility. However, it was found that following concentration of the reaction mixture, *immediate* submission to column chromatography in buffered silica gel (~1%) led to reproducible yields of both **167** and **168**, and this proved to be general for all other derivatives.

The facile propensity of compound **167** to exist in two tautomeric forms following protonation of the corresponding enolate is likely due to the presence of the silyl group. Given the olefin-like

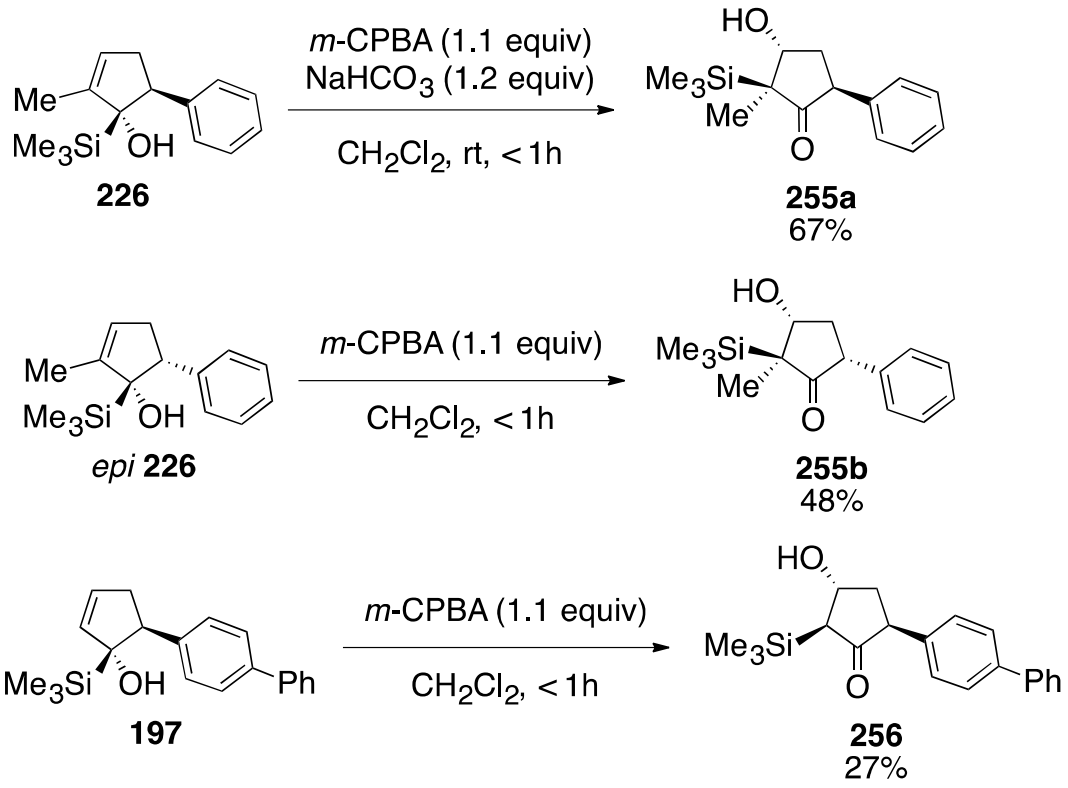
character of the cyclopropyl, a certain degree of "p" conjugation between the aryl group and the cyclopropane moiety exists, and it is reasonable to expect that this system engage in conjugation with silyl group through the enolic double bond.

Finally, additional evidence for the persistence of the enolic form of **167** comes from the following experiments. Deprotonation of acylsilane **167** with LDA followed by aqueous workup led to mixture of keto and enolic **167**, and the ^{1}H NMR and ^{13}C NMR spectra matches the species observed following workup of the rearrangement of compounds **20a** and **20b**. In addition, quenching of the rearrangement reaction of **20a** or **20b** with D_2O and following regular aqueous workup and column chromatography led to **167** with little deuterium incorporation at the α-position. Presumably, the initial deuterium incorporation at the α-position is lost via enolization in aqueous media or in silica gel.

4.5 Unexpected 1,2-silyl migrations in α-silyl cyclopentenol structures triggered by epoxidation

Experiments aimed at derivatizing [1,2]-Wittig products with the purpose of confirming their relative stereochemistry led to the discovery of an unexpected rearrangement involving a 1,2-silyl migration. Treatment of alcohol **226a** with *m*-CPBA in the presence of sodium bicarbonate led to ketone **255a** as a single diastereomer (Scheme 86). The relative stereochemistry of **255a** was confirmed by X-ray crystallographic analysis and remarkably features a silyl-substituted chiral quaternary center (Figure 10). Treatment of the diasteromer *epi*-**226** with *m*-CPBA in the absence of sodium bicarbonate provided ketone **225b** again as a single diastereomer. Although

these experiments involved racemic **226a** or *epi*-**226**, it seems the silyl group migrates in a *syn* fashion and without epimerization at the benzylic position.



Scheme 86. A 1,2-silyl migration triggered by epoxidation of α-silyl cyclipentenols.

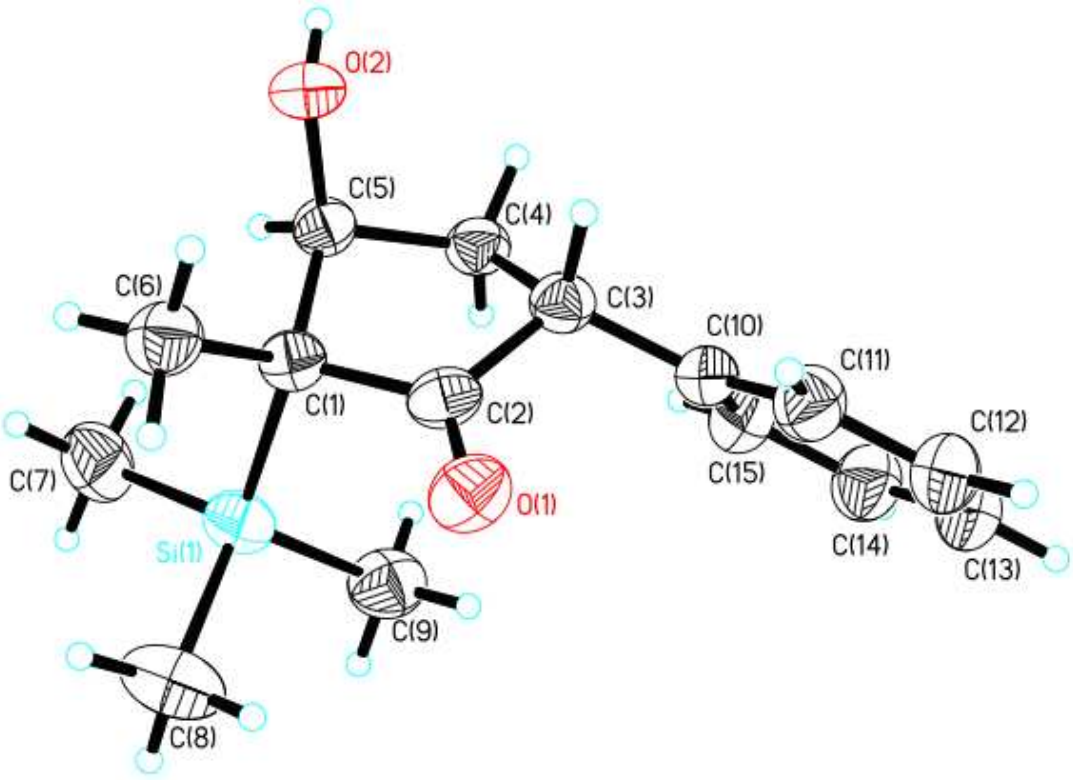


Figure 10. X-ray structure of compound **255a**.

It is likely that this transformation proceeds via a stereoselective epoxidation of the olefin by *m*-CPBA, guided by intermolecular hydrogen bonding interaction with the tertiary alcohol. Presumably, the epoxide product (Figure 11) is very prone to isomerization, perhaps due to increased ring strain in the cyclopentane framework due to the installation of the epoxide group. In addition, this migration might be driven by the release of unfavorable steric interactions between the bulky phenyl and trimethylsilyl groups and between the methyl and trimethylsily groups all of which are *syn* to one another. Whether this isomerization is a concerted process (epoxide ring opening/silyl migration) or stepwise (epoxide ring opening to give a tertiary carbocation, then silyl migration) it is not known at this point. However, a concerted mechanism

seems unlikely because it would involve an intramolecular S_N2 reaction at a quaternary center by a bulky silyl group. On the other hand, several reports that involve carbocation formation followed by 1,2-silyl migration exist in the literature, and are tipically triggered by protic acids.[35] In addition, related 1,2-silyl migrations in alkynyl silanes or silyl propagylic systems catalyzed by Lewis acids[36] and/or transition metals are well known.[37]

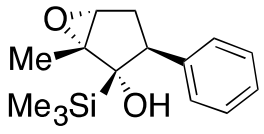


Figure 11. Presumed epoxide intermediate in the formation of ketone **255a**.

Preliminary results shown this isomerization is independent to the substitution at the aromatic group and more importantly, alkyl substitution at the olefin is not a requirement.

4.6 Conclusions

2-Silyl-5,6-dihydro-6-aryl dihydropyrans undergo stereoconvergent [1,4]- and [1,2]-Wittig rearrangements after deprotonation with alkyllithiums in THF at low temperatures to form cyclopropyl acylsilanes and silyl cyclopentenol structures, respectively, with excellent diastereoselectivities. The origin of the stereoconvergence is dictated by the configuration at the migrating carbon, which retains its chiral information during both [1,4]- and [1,2]-shifts, whereas that of the allylic carbon is lost.

The shift in selectivity in favor of the [1,4]-pathway is possible by electronic modifications of the aromatic appendage, specifically, electron-donating groups located at the *para* position relative

to the benzylic carbon lead to improved, if not exclusive, [1,4]- ring contraction to the corresponding cyclopropane products. In addition, increasing steric demand of the silyl group leads to better [1,4]-/[1,2]- selectivity, although electronic effects seem to dominate in this cases. That is, electron-withdrawing groups *para* to the benzylic carbon provide regioselectivity in favor of the [1,2]-shift, even when sterically bulky silyl groups are present on the rearranging molecule. The [1,2]-Wittig pathway becomes esclusive when alkyl or alkyls substitution *proximal* to the silyl is present at the olefin.

Finally, *trans* diastereomers are more reactive than their *cis* counterparts, presumably because an optimal conformation suitable for allylic deprotonation is easily attainable. This is supported by the observation that increasing bulkiness of the silyl or aromatic groups has little effect on the reactivity of *trans* diastereomers, whereas *cis* cyclic ethers become much less reactive.

4.7 Experimental Section

General Considerations

Unless otherwise noticed all reactions were run under a positive atmosphere of nitrogen in oven-dried (at least 4 hours) or flame-dried round bottom flasks or disposable drum vials capped with rubber septa. Solvents were removed by rotary evaporation at temperatures lower than 45 ^{o}C. Thin Layed Chromatography (TLC) was run in Column chromatography was run on Silicycle Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone ketyl; dichloromethane, benzene, diisopropylamine, triethylamine and trimethylsilyl chloride were distilled from calcium hydride. Hexane and was used as received. Triethylsilyl chloride, dimethylphenylsilyl chloride, diphenylmethylsilyl chloride were purchased from Gelest Inc. and

were used as received. Methyllithium (1.4 M in diethyl ether), *n*-butyllithum (1.6 M in hexanes), *sec*-butyllithium (1.4 M in cyclohexane) and *tert*-butyllithium (1.7 M in pentane) were purchased from Aldrich and (with the exception of *tert*-butyllithium) their concentration calculated by titration with diphenylacetic acid (average of three runs). All other chemicals were purchased from Aldrich and used as received.

^{1}H NMR spectra was collected in 500 MHz and 600 MHz Varian instruments using $CDCl_3$ as solvent, which was referenced at 7.24 ppm (residual chloroform proton) and ^{13}C NMR spectra was collected in $CDCl_3$ at 126 MHz or 151 MHz and referenced at 77 ppm. High-resolution mass spectrometric analysis was run in TOF instruments. Optical rotations were measured in chloroform.

Preparation of trichloroacetimidates (xi) – ***General Procedure A****:*

To a solution of the corresponding homoallylic alcohol (~110 mmol) in diethyl ether (12 mL) was added slowly sodium hydride (0.15 equiv, dispersion in mineral oil, 60% w/w). The mixture was stirred vigorously for 5 minutes and then cooled down in an ice bath. Trichloroacetonitrile (1 equiv) was then added dropwise, within five minutes approximately. The ice bath was removed after 15 minutes and the mixture stirred for about 1 hour at room temperature and then concentrated by rotary evaporation. A solution of dry methanol (0.15 equiv) in pentane (12 mL) was added to precipitate salts. The solids were filtered through a plug a celite and rinsed with pentane. The filtrate was concentrated by rotary evaporation and the crude product could be used without further purification in the next step. However, in all cases the crude product was partially

purified by silica gel column chromatography (typically 5% EtOAc in hexanes) buffered with ~1% triethylamine.

Preparation of trichloroacetimidates (xi) – ***General Procedure B****:*

To a solution of the corresponding homoallylic alcohol (16 mmol) in dichloromethane (80 mL) was added DBU (0.18 equiv). The solution was cooled down at 0 ^{o}C and trichloroacetonitrile (1.4 equiv) was added. The reaction was monitored by TLC (typically 5% EtOAc in hexanes) using triethylamine pre-washed plates. After completion of the reaction (typically 3-4 hours) the reaction was concentrated by rotary evaporation and the residue was partially purified by silica gel column chromatography (tipycally 5% EtOAc in hexanes) buffered with ~1% triethylamine.

Etherification of α-Hydroxysilanes (iii) to α-benzyloxy allylsilanes (xii) – ***General Procedure C****:*

To a solution of α-silyl allylic alcohol (4 mmol, 1 equiv) in hexane (22 mL) was added the desired trichloroacetimidate (1.5–1.9 equiv). The solution was cooled down at 0 ^{o}C and a solution of the Lewis acid (trace to 0.1 equiv, TMSOTf was added in ~1 ml of hexane; BF_3OEt_3 was added in ~1 mL of diethyl ether) was added dropwise. The cold bath was removed and the reaction was monitored by TLC. Typically, formation of a thick suspension indicated the end of the reaction. The solid was filtered through a plug of celite and rinsed with hexanes (~50 mL). The filtrate was extracted with $NaHCO_{3\ (sat)}$, (3 × 20 mL), water (2 × 20 mL), brine (20 mL) and dried over $MgSO_4$. After filtration and concentration the residue was purified by column chromatography.

*Alternative synthesis of α-benzyloxy allylsilanes (xii) – **General Procedure D**:*

To a solution of *O*-trimethylsilyl α-trimethylsilylallylic alcohol (10 mmol) in dichloromethane (50 mL) was added allyltrimethylsilane (1.1 equiv) and the desired benzaldehyde derivative (1.1 equiv). The solution was cooled down at -78 ^{o}C and TMSOTf (0.2 equiv) was added dropwise. The reaction was followed by TLC and usually required between 1-4 hours. The reaction was quenched by adding $NaHCO_{3\ (sat)}$ (20 mL). The aqueous phase was washed with dichloromethane (2 × 30 mL). Combined organic extracts were washed with $NaHCO_{3\ (sat)}$, (2 × 20 mL), water (20 mL), brine (20 mL) and dried over $MgSO_4$. After filtration and concentration the residue was purified by column chromatography.

*Synthesis of cyclic ethers (xiii) – **General Procedure E**:*

To a solution of α-benzyloxy allylsilane (**xii**, 0.96 mmol) in dichloromethane (10 mL) was added 2nd generation Grubbs catalyst and the mixture was stirred at room temperature under nitrogen. After 3 hours the solution was concentrated by rotary evaporation and the residue purified by column chromatography.

*Synthesis of cyclic ethers (xiii) – **General procedure F**:*

A round bottom flask was charged with α-benzyloxy allylsilane (**xii**, 0.96 mmol) and dissolved in benzene (0.05–0.07 M). 2nd generation Grubbs catalyst was added and a condenser attached to the flask. The system was flushed with nitrogen and then heated in an oil bath at 80 ^{o}C for 1

hour. The reaction mixture was then cooled down at room temperature, concentrated and the product purified by column chromatography.

Notes:

- All 2-silyl-6-aryl-5,6-dihydropyrans are air sensitive and upon isolation slowly undergo autooxidation, which is minimized when the compound is diluted (<0.05M). For this reason, freshly purified dihydropyrans were immediately submitted to the Wittig rearrangements upon purification.

- In some cases a diastereomeric mixture of α-benzyloxy allylsilanes **xii** was submitted to ring closing methatesis and, without exception, diastereomeric producs *trans* and *cis* were easily and completely separated by column chromatography.

Wittig Rearrangements of trans-2-silyl-6-aryl-5,6-dihydropyrans (xii) – ***General procedure G****:*

Freshly prepared and purified 2-silyl-dihydropyran was dissolved in THF under nitrogen (concentration = 0.08 M, unless otherwise noticed) and the solution cooled down at -78 ^{o}C (dry ice/acetone bath). *n*-Butyllithium (1.2 equiv, 1.6 M in hexanes) was added dropwise (1 drop/second) to give a colored solution. After the indicated time (5 to 30 minutes) the reaction was quenched by adding $NH_4Cl_{(sat)}$, diluted with water and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with $NH_4Cl_{(sat)}$, water, and brine. The solution was dried over $MgSO_4$, filtered, quickly concentrated in a rotavap at room temperature (or lower) and immediately loaded into a buffered column

(packed with ~1% triethylamine). Elution with 5% and 10% EtOAc in hexanes afforded the acylsilane and cyclopentenol products, respectively.

Wittig Rearrangements of cis-2-silyl-6-aryl-5,6-dihydropyrans (xii) – ***General procedure H****:*

Freshly prepared and purified 2-silyl-dihydropyran was dissolved in THF under nitrogen (concentration = 0.08 M, unless otherwise noticed) and the solution cooled down at -78 ^{o}C (dry ice/acetone bath). *sec*-Butyllithium (3.0 equiv, 1.4 M in cyclohexane) was added dropwise (1 drop/second) to give a colored solution. After the indicated time (at least 3 hours) the reaction was quenched by adding $NH_4Cl_{(sat)}$, diluted with water and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with $NH_4Cl_{(sat)}$, water and brine. The solution was dried over $MgSO_4$, filtered, quickly concentrated in a rotavap at room temperature (or lower) and immediately loaded into a buffered column (packed with ~1% triethylamine). Elution with 5% and 10% EtOAc in hexanes afforded the acylsilane and cyclopentenol products, respectively.

Synthesis of trichloroacetimidates

Preparation of compound ***117***

Applying general procedure A to 1-(2-methoxyphenyl)but-3-en-1-ol (13 g, 73.4 mmol, 1 equiv), sodium hydride (0.44 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (10.6, 73.4 mmol, 1 equiv) and diethyl ether (24 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 18.4 g (78%) of **117** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25, 7.42 (dd, *J* = 1.2, 7.8 Hz, 1 H), 7.24 (m, 1 H), 6.94 (t, *J* = 7.8 Hz, 1 H), 6.87 (d, *J*

= 7.8 Hz, 1 H), 6.28 (t, *J* = 6.6 Hz, 1 H), 5.84 (m, 1 H), 5.08 (dd, *J* = 1.8, 16.8 Hz, 1 H), 5.03 (d, *J* = 10.2 Hz, 1 H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 155.9, 133.6, 128.7, 128.4, 125.9, 120.6, 117.6, 110.4, 91.8, 75.0, 55.5, 39.6. IR (film) 3344, 3070, 2955, 1664, 1300, 1076, 794 cm^{-1}.

*Preparation of compound **118***

Applying the general procedure A to 1-(3-methoxyphenyl)but-3-en-1-ol (13 g, 72.9 mmol, 1 equiv), sodium hydride (0.29 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (10.5 g, 72.9 mmol, 1 equiv) and diethyl ether (24 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 19.88 g (85%) of **118** as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 7.27 (t, *J* = 8.0 Hz, 1 H), 6.97 (m, 2 H), 6.83 (dd, *J* = 2.5, 8.0 Hz, 1 H), 5.86 (m, 1 H), 5.81 (m, 1 H), 5.13 (m, 1 H), 5.08 (m, 1 H), 3.79 (s, 3 H), 2.78 (m, 1 H), 2.64 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 159.6, 141.3, 133.0, 129.4, 118.4, 118.1, 113.3, 111.6, 91.7, 79.9, 55.1, 41.0. IR (film) 3341, 3070, 2936, 1664, 1290, 1078, 796 cm^{-1}.

*Preparation of compound **119***

Applying the general procedure A to 1-(4-methoxyphenyl)but-3-en-1-ol (10.7 g, 60 mmol, 1 equiv), sodium hydride (0.36 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (8.7 g, 60 mmol, 1 equiv) and diethyl ether (20 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 12.6 g (65%) of **119** as a yellowish oil. ^{1}H NMR (500

MHz, $CDCl_3$) δ 8.26 (s, 1 H), 7.33 (m, 2 H), 6.87 (m, 2 H), 5.83 (m, 1 H), 5.77 (m, 1 H), 5.11 (m, 1 H), 5.06 (m, 1 H), 3.79 (s, 3 H), 2.79 (m, 1 H), 2.61 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 159.3, 133.2, 131.6, 127.7 (2 C), 118.1, 113.7 (2 C), 91.8, 79.9, 55.2, 40.9. IR (film) 3340, 3065, 2930, 1664, 1295, 1076, 796 cm^{-1}.

*Preparation of compound **120***

Applying the general procedure A to 1-(2-methylphenyl)but-3-en-1-ol (4.5 g, 27.74 mmol, 1 equiv), sodium hydride (0.166 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (4 g, 27.74 mmol, 1 equiv) and diethyl ether (10 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 7.29 g (61%) of **120** as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.25 (t, *J* = 8.0 Hz, 1 H), 7.21 (m, 2 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 5.86 (dd, *J* = 5.0, 7.5 Hz, 1 H), 5.83 (m, 1 H), 5.13 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.09 (m, 1 H), 2.78 (m, 1 H), 2.62 (m, 1 H), 2.36 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 139.6, 137.9, 133.2, 128.7, 128.3, 126.8, 123.1, 118.1, 91.7, 80.2, 41.1, 21.5. IR (film) 3418, 1653, 1305, 1085 cm^{-1}.

*Preparation of compound **121***

Applying the general procedure A to 1-(3-methylphenyl)but-3-en-1-ol (4.22 g, 26 mmol, 1 equiv), sodium hydride (0.156 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (3.75 g, 26 mmol, 1 equiv) and diethyl ether (15 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 6.37 g (80%) of **121** as a yellowish oil. ^{1}H NMR

(500 MHz, $CDCl_3$) δ 8.22 (s, 1 H), 7.44 (m, 1 H), 7.20–7.13 (m, 3 H), 6.04 (dd, *J* = 5.0, 8.0 Hz, 1 H), 5.82 (ddt, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.12 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.07 (m, 1 H), 2.74 (m, 1 H), 2.57 (m, 1 H), 2.42 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 138.2, 135.0, 133.3, 130.2, 127.8, 126.2, 125.5, 118.0, 91.7, 77.1, 40.3, 19.2. IR (film) 3344, 3078, 2980, 1662, 1311, 1078, 796 cm^{-1}.

*Preparation of compound **122***

Applying the general procedure A to 1-(4-methylphenyl)but-3-en-1-ol (6.5 g, 40.07 mmol, 1 equiv), sodium hydride (0.24 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (5.79 g, 40.1 mmol, 1 equiv) and diethyl ether (14 mL) afforded after column chromatography (4% EtOAc in hexanes, column buffered with Et_3N) 11.08 g (90%) of **122** as a semisolid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 5.84 (dd, *J* = 5.0, 7.5 Hz, 1 H), 5.80 (ddt, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.11 (dq, *J* = 1.5, 17.5 Hz, 1 H), 5.07 (m, 1 H), 2.77 (m, 1 H), 2.61 (m, 1 H), 2.33 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 137.7, 136.6, 133.2, 129.1 (2 C), 126.2 (2 C), 118.1, 91.7, 80.1, 41.0, 21.2. IR (film) 3335, 3060, 1662, 1310, 1060 cm^{-1}.

*Preparation of compound **123***

Applying the general procedure B to 1-(4-fluorophenyl)-3-en-1-ol (4.07 g, 24.49 mmol, 1 equiv), trichloroacetonitrile (5.3 g, 36.74 mmol, 1 equiv) and DBU (810 mg, 5.31 mmol, 0.18 equiv) in CH_2Cl_2 (150 mL) afforded after column chromatography (5% EtOAc in hexanes, column

buffered with Et_3N) 6.25 g (82%) of **123** as a yellowish oil. ^1H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.36 (m, 2 H), 7.02 (m, 2 H), 5.84 (dd, *J* = 5.4, 7.8 Hz, 1 H), 5.76 (ddt, *J* = 7.2, 10.2, 17.4, 1 H), 5.11–5.06 (m, 2 H), 2.76 (m, 1 H), 2.60 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4 (*J* = 246.4 Hz), 161.4, 135.3 (d, *J* = 3.2 Hz), 132.7, 128.1 (d, *J* = 8.5 Hz, 2 C), 118.4 (d, *J* = 3.2 Hz), 115.3 (d, *J* = 21.1 Hz, 2 C), 91.6, 79.4 (d, *J* = 1.7 Hz), 40.9. IR (film) 3343, 3083, 2982, 1664, 1512, 1230, 1076, 796 cm^{-1}.

*Preparation of compound **124***

Applying the general procedure A to 1-(4-chlorophenyl)but-3-en-1-ol (11 g, 60.22 mmol, 1 equiv), sodium hydride (0.36 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (8.7 g, 60.22 mmol, 1 equiv) and diethyl ether (21 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 14.97 g (76%) of **124** as a yellowish oil. ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.32 (s, 4 H), 5.83 (dd, *J* = 5.5, 7.5 Hz, 1 H), 5.77 (m, 1 H), 5.11–5.06 (m, 2 H), 2.75 (m, 1 H), 2.60 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 138.1, 133.8, 132.6, 128.6 (2 C), 127.7 (2 C), 118.6, 91.5, 79.4, 40.8. IR (film) 3343, 3081, 2928, 1664, 1294, 1078, 796 cm^{-1}.

*Preparation of compound **125***

Applying the general procedure A to 1-(4-bromophenyl)but-3-en-1-ol (9.54 g, 42 mmol, 1 equiv), sodium hydride (0.25 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (6.06 g, 42 mmol, 1 equiv) and diethyl ether (14 mL) afforded after column chromatography (5%

EtOAc in hexanes, column buffered with Et_3N) 13.4 g (86%) of **125** as a yellowish semisolid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 7.48 (m, 2 H), 7.27 (m, 2 H), 5.83 (dd, *J* = 5.5, 7.5 Hz, 1 H), 5.77 (ddt, *J* = 6.5, 10.0, 17.0 Hz, 1 H), 5.13–5.07 (m, 2 H), 2.76 (m, 1 H), 2.61 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 138.6, 132.5, 131.5 (2 C), 128.0 (2 C), 121.9, 118.6, 91.5, 79.3, 40.7. IR (film) 3343, 3081, 2934, 1664, 1294, 1072, 794 cm^{-1}. mp = 37–38 ^oC.

*Preparation of compound **126***

Applying the general procedure B to 1-(naphtalen-2-yl)-3-en-1-ol (4.63 g, 23.3 mmol, 1 equiv), trichloroacetonitrile (5.05 g, 34.95 mmol, 1 equiv) and DBU (640 mg, 4.19 mmol, 0.18 equiv) in CH_2Cl_2 (350 mL) afforded after column chromatography (8% EtOAc in hexanes, column buffered with Et_3N) 7.62 g (95%) of **126** as a cream-colored solid. ^1H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 7.83 (m, 4 H), 7.53 (dd, *J* = 1.8, 9.0 Hz, 1 H), 7.47 (m, 2 H), 6.05 (m, 1 H), 5.83 (m, 1 H), 5.13 (m, 1 H), 5.08 (m, 1 H), 2.88 (m, 1 H), 2.71 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 137.0, 133.1, 133.06, 133.01, 128.3, 128.1, 127.7, 126.2, 126.1, 125.5, 124.0, 118.3, 91.7, 80.3, 40.9. IR (film) 3341, 3059, 1664, 1304, 1076, 794 cm^{-1}. mp = 42–43 ^oC

*Preparation of compound **127***

Applying the general procedure B to 1-(2-propylphenyl)-3-en-1-ol (1.5 g, 7.88 mmol, 1 equiv), trichloroacetonitrile (1.7 g, 11.82 mmol, 1 equiv) and DBU (240 mg, 1.58 mmol, 0.2 equiv) in CH_2Cl_2 (40 mL) afforded after column chromatography (5% EtOAc in hexanes, column

buffered with Et_3N) 2.15 g (81%) of **127** as a yellowish oil. ^1H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1 H), 7.47 (m, 1 H), 7.21 (m, 2 H), 7.16 (m, 1 H), 6.10 (dd, *J* = 4.5, 9.0 Hz, 1 H), 5.87 (ddt, *J* = 7.5, 10.5, 17.5 Hz, 1 H), 5.14 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.08 (m, 1 H), 2.75 (m, 2 H), 2.67 (m, 1 H), 2.54 (m, 1 H), 1.77–1.62 (m, 2 H), 1.00 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 139.5, 137.8, 133.6, 129.3, 127.8, 126.1, 125.7, 117.9, 91.7, 76.9, 41.1, 34.6, 24.0, 14.2. IR (film) 3346, 3078, 2961, 1664, 1309, 1076, 794 cm^{-1}.

*Preparation of compound **128***

Compound **128** was prepared in 3 steps from indole-3-carboxaldehyde involving N-Boc protection, Grignard addition and trichloroacetimidate formation.

To a suspension of sodium hydroxide (1.64 g, 41.1 mmol, 2.75 equiv) and tetrabutylammonium bisulfate (0.1g, 0.3 mmol, 0.02 equiv) in CH_2Cl_2 (20 mL) at 0 ^oC was added indole-3-carboxaldehyde (2.18 g, 15 mmol, 1 equiv), followed by a solution of Boc_2O (3.6 g, 16.5 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL). After 20 minutes the mixture was diluted with CH_2Cl_2 (10 mL) and stirred for an additional 2 hours. The reaction mixture was diluted with CH_2Cl_2 (40 mL) and water (20 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. The crude 1-(*tert*-butoxycarbonyl)indole-3-carbaldehyde was clean by ^1H NMR and was used in the next step

withouth further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.08 (s, 1 H), 8.27 (m, 1 H), 8.21 (s, 1 H), 8.13 (d, *J* = 8.4 Hz, 1 H), 7.39 (m, 1 H), 7.35 (m, 1 H), 1.69 (s, 9 H).

To a solution of 1-(*tert*-butoxycarbonyl)indole-3-carbaldehyde (~15 mmol, 1 equiv) in THF (150 mL) at -78 ^{o}C was added a solution of allylmagnesium chloride (2 M in THF, 9.75 mL, 19.5 mmol, 1.3 equiv) dropwise. After 1 hour the reaction mixture was poured over saturated ammonium chloride (50 mL) and diluted with water (20 mL) and diethyl ether (50 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. The crude alcohol was used in the next step without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1 H), 7.64 (d, *J* = 7.8 Hz, 1 H), 7.53 (s, 1 H), 7.30 (m, 1 H), 7.22 (m, 1 H), 5.87 (m, 1 H), 5.19 (dq, *J* = 1.2, 17.4 Hz, 1 H), 5.15 (m, 1 H), 5.00 (dd, *J* = 5.6, 7.8 Hz, 1 H), 2.72 (m, 1 H), 2.66 (m, 1 H), 1.65 (s, 9 H).

Applying the general procedure B to 1-(*tert*-butoxycarbonyl)-3-(hydroxybut-3-en-1-yl)indole (~15 mmol, 1 equiv), trichloroacetonitrile (3.25 g, 22 mmol, 1.5 equiv) and DBU (0.6 g, 4 mmol, 0.27 equiv) in CH_2Cl_2 (100 mL) afforded 1.92 g (30%) of slightly impure trichloroacetimidate **128** that was immediately used in the next step. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (s, 1 H), 8.12 (s, 1 H), 7.70 (m, 1 H), 7.64 (s, 1 H), 7.31 (m, 1 H), 7.23 (m, 1 H), 6.22 (dd, *J* = 6.0, 6.6 Hz, 1 H), 5.84 (m, 1 H), 5.15 (m, 1 H), 5.08 (m, 1 H), 2.96 (m, 1 H), 2.83 (m, 1 H), 1.65 (s, 9 H).

*Preparation of compound **129***

Applying the general procedure A to 3-methyl-1-(*p*-tolyl)but-3-en-1-ol (4 g, 22.64 mmol, 1 equiv), sodium hydride (0.136 g, 60% w/w oil dispersion, 0.15 equiv), trichloroacetonitrile (3.27 g, 42 mmol, 1 equiv) and diethyl ether 8.5 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 31 g (43%) of **129** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 5.95 (dd, *J* = 5.0, 9.0 Hz, 1 H), 4.81 (m, 1 H), 4.76 (m, 1 H), 2.77 (dd, A of ABX system, *J* = 9.0, 14.5 Hz, 1 H), 2.48 (dd, B of ABX system, *J* = 5.0, 14.5 Hz, 2 H), 2.33 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 140.9, 137.7, 137.1, 129.1 (2 C), 126.2 (2 C), 113.7, 91.7, 79.2, 45.1, 22.8, 21.2. IR (film) 3343, 3070, 2924, 1660, 1304, 1080, 794 cm^{-1}. mp = 59–60 ^oC.

*Preparation of compound **130***

Applying the general procedure B to 1-(thiophen-2-yl)but-3-en-1-ol (2.5 g, 16.21 mmol, 1 equiv), trichloroacetonitrile (3.51 g, 24.31 mmol, 1 equiv) and DBU (0.44 g, 2.92 mmol, 0.18 equiv) in CH_2Cl_2 (100 mL) afforded after column chromatography (7% EtOAc in hexanes, column buffered with Et_3N) 4.1 g (95%) of **130** as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 7.26 (dd, *J* = 1.5, 5.5 Hz, 1 H), 7.10 (m, 1 H), 6.96 (dd, *J* = 3.5, 5.0 Hz, 1 H), 6.20 (dd, *J* = 6.0, 7.5 Hz, 1 H), 5.81 (ddt, *J* = 6.5, 10.0, 17.0 Hz, 1 H), 5.16 (dq, *J* = 1.5, 17.5 Hz, 1 H), 5.10 (m, 1 H), 2.88 (m, 1 H), 2.75 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 141.9, 132.6, 126.4, 126.0, 125.4, 118.6, 91.5, 75.6, 40.7. IR (film) 3341, 3078, 2943, 1662, 1290, 1072, 794 cm^{-1}.

*Preparation of compound **131***

Applying the general procedure B to 1-(furan-2-yl)but-3-en-1-ol (2.53 g, 18.31 mmol, 1 equiv), trichloroacetonitrile (3.97 g, 27.47 mmol, 1 equiv) and DBU (0.5 g, 3.3 mmol, 0.18 equiv) in CH_2Cl_2 (170 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 2.17 g (42%) of **131** as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 7.39 (dd, *J* = 1.0, 2.0 Hz, 1 H), 6.39 (d, *J* = 3.0 Hz, 1 H), 6.33 (dd, *J* = 2.0, 3.0 Hz, 1 H), 6.00 (t, *J* = 6.5 Hz, 1 H), 5.77 (ddt, *J* = 7.0, 10.5, 17.0 Hz, 1 H), 5.15 (dq, *J* = 1.5, 17.5 Hz, 1 H), 5.08 (m, 1 H), 2.90–2.78 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 151.5, 142.6, 132.5, 118.4, 110.2, 108.9, 91.5, 73.0, 36.9. IR (film) 3343, 3080, 2926, 1662, 1300, 1076, 796 cm^{-1}.

*Preparation of compound **132***

Applying the general procedure B to 1-(furan-3-yl)but-3-en-1-ol (3.6 g, 26.02 mmol, 1 equiv), trichloroacetonitrile (5.6 g, 39.1 mmol, 1 equiv) and DBU (0.71 g, 4.68 mmol, 0.18 equiv) in CH_2Cl_2 (250 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 6.3 g (87%) of **132** as a yellowish oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 7.46 (m, 1 H), 7.36 (m, 1 H), 6.43 (m, 1 H), 5.94 (t, *J* = 6.6 Hz, 1 H), 5.80 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.13 (m, 1 H), 5.08 (m, 1 H), 2.75 (m, 1 H), 2.66 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6, 143.1, 140.4, 132.8, 123.8, 118.3, 108.8, 91.7, 73.0, 39.2. IR (film) 3343, 3070, 2982, 1662, 1302, 1078, 794 cm^{-1}.

*Preparation of compounds **134a/134b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (2.78 g, 54.7% w/w in THF, 1 mmol), **117** (6.7 g, 20.73 mmol, 1.8 equiv) and TMSOTf (trace) in cyclohexane (64 mL) afforded after column chromatography (10 % CH_2Cl_2 in hexanes) 2.58 (77 %) of **134a**/**134b** (1:1) as a colorless oil. Mixture of diastereomers (**134a**/**134b** = 1:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 1.5, 8.0 Hz, 1 H), 7.34 (dd, *J* = 1.5, 7.5 Hz, 1 H), 7.18 (m, 2 H), 6.94 (t, *J* = 7.5 Hz, 1 H), 6.92 (t, *J* = 7.5 Hz, 1 H), 6.82 (dd, *J* = 1.0, 8.5 Hz, 1 H), 6.79 (dd, *J* = 1.0, 8.0 Hz, 1 H), 5.87 (ddt, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.77 (m, 2 H), 5.65 (ddd, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.01–4.87 (m, 8 H), 4.80 (m, 2 H), 3.79 (dt, *J* = 1.5, 7.5 Hz, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.44 (dt, *J* = 1.0, 7.5 Hz, 1 H), 2.47–2.35 (m, 4 H), 0.04 (s, 9 H), -0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 155.7, 138.02, 137.98, 135.9, 135.4, 132.3, 131.0, 127.8, 127.5, 127.4, 127.3, 120.4, 120.2, 116.2, 115.9, 112.7, 111.7, 110.3, 109.9, 75.6, 74.4, 73.2, 72.5, 55.4, 55.3, 41.9, 39.9, -3.7, -3.9. IR (film) 3076, 2957, 2835, 1489, 1244, 841 cm^{-1}. HRMS (EI) *m*/*z* 290.1700 [(M^+); calcd for $C_{17}H_{26}O_2Si$, 290.1702].

*Preparation of compounds **135a/135b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (1.83 g, 54.7% w/w in THF, 7.68 mmol), **118** (4.46 g, 13.8 mmol, 1.8 equiv) and TMSOTf (97 μL, 0.538 mmol, 0.07 equiv) in cyclohexane (43 mL) afforded after column chromatography (15 % CH_2Cl_2 in hexanes) 1.34 (60 %) of **135a**/**135b** (1:1) as a colorless oil. Mixture of diastereomers (**135a**/**135b** = 1:0.4) ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.0 Hz, 0.4 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 6.88 (m, 1 H), 6.85 (m, 1 H), 6.80 (m, 1.2 H), 6.75 (ddd, *J* = 1.0, 2.5, 8.0 Hz, 1 H), 5.80 (m, 0.4 H), 5.71 (m, 1.4 H), 5.67 (ddd, *J* = 2.0, 10.5, 17.0 Hz, 1 H), 5.03–4.95 (m, 3.6 H), 4.92 (dt, *J* = 1.5, 17.0 Hz, 1 H), 4.83 (dt, *J* = 1.5, 11.0 Hz, 1 H), 4.40 (dd, *J* = 6.0, 8.0 Hz, 0.4 H), 4.34 (t, *J* = 6.0 Hz, 1 H), 3.79 (s, 1.2 H), 3.78 (s, 3 H), 3.77 (dt, *J* = 1.5, 7.0 Hz, 1 H), 3.44 (dt, *J* = 1.5, 7.5 Hz, 0.4 H), 2.48 (m, 1.4 H), 2.41 (m, 1 H), 2.32 (m, 0.4 H), 0.04 (s, 9 H), -0.02 (s, 3.6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 159.3, 145.3, 144.3, 137.8, 137.5, 135.4, 134.8, 129.0, 128.8, 119.8, 119.0, 116.8, 116.4, 113.0, 112.9, 112.3 (2 C), 112.1, 111.9, 80.8, 79.1, 75.7, 72.9, 55.14, 55.12, 43.0, 41.6, -3.7, -3.9. IR (film) 3076, 2957, 1248, 1047, 841 cm^{-1}. HRMS (EI) *m*/*z* 290.1685 [(M^+); calcd for $C_{17}H_{26}O_2Si$, 290.1702].

*Preparation of compounds **136a/136b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (2 g, 15.35 mmol), **119** (9.9 g, 30.7 mmol, 2 equiv) and TMSOTf (194 μL, 1.07 mmol, 0.07 equiv) in cyclohexane (85 mL) afforded after column chromatography (15% CH_2Cl_2 in hexanes) 4.35 (60%) of **136a**/**136b** (1:1) as a colorless oil. Spectroscopic data for **136a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.5 Hz, 2 H), 6.82 (d, *J* = 8.5 Hz, 2 H), 5.74–5.62 (m, 2 H), 4.96 (m, 2 H), 4.92 (dt, *J* = 2.0, 17.0 Hz, 1 H), 4.82 (dt, *J* = 1.5, 10.0 Hz, 1 H), 4.30 (t, *J* = 6.0 Hz, 1 H), 3.78 (s, 3 H), 3.76 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.49 (m, 1 H), 2.39 (m, 1 H), 0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 138.0, 135.7, 135.0, 127.7 (2 C), 116.7, 113 (2 C), 111.6, 80.7, 75.5, 55.2, 41.5, -3.7. IR (film) 3076, 2957, 1514, 1248, 1039, 841 cm^{-1}. HRMS (EI) *m*/*z* 290.1688 [(M^+); calcd for

$C_{17}H_{26}O_2Si$, 290.1702]. Spectroscopic data for **136b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.5 Hz, 2 H), 6.84 (d, *J* = 8.0 Hz, 2 H), 5.82-5.68 (m, 2 H), 4.97 (m, 4 H), 4.36 (t, *J* = 7.0 Hz, 1 H), 3.79 (s, 3 H), 3.39 (dt, *J* = 1.0, 7.0 Hz, 1 H), 2.51 (m, 1 H), 2.31 (m, 1 H), -0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 137.7, 135.6, 134.5, 128.5, 116.2, 113.5, 112.7, 78.7, 72.5, 55.2, 43.0, -4.0. IR (film) 3076, 2957, 1514, 1258, 1039, 841 cm^{-1}. HRMS (EI) *m*/*z* 290.1695 [(M^+); calcd for $C_{17}H_{26}O_2Si$, 290.1702].

*Preparation of compounds **137a/137b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (1.17 g, 85.5% w/w in Et_2O, 8.98 mmol), **120** (3.85 g, 12.57 mmol, 1.4 equiv) and TMSOTf (40 μL, 0.225 mmol, 0.025 equiv) in cyclohexane (45 mL) afforded after column chromatography (hexanes) 1.81 (73%) of **137a**/**137b** (1:1) as a colorless oil. Mixture of diastereomers (**137a**/**137b** = 1.0:0.5) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 1.0, 7.5 Hz, 1 H), 7.38 (dd, *J* = 1.5, 7.5 Hz, 0.5 H), 7.23 (m, 4.5 H), 5.86 (ddt, *J* = 7.0, 10.0, 17.0 Hz, 0.5 H), 5.79 (m, 1.5 H), 5.63 (ddd, *J* = 7.5, 10.5, 18.0 Hz, 1 H), 5.06–4.96 (m, 4 H), 4.91 (ddd, *J* = 1.5, 2.0, 17.5 Hz, 1 H), 4.81 (ddd, *J* = 1.5, 2.0, 10.0 Hz, 1 H), 4.77 (dd, *J* = 5.0, 8.0 Hz, 0.5 H), 4.56 (dd, *J* = 5.5, 6.5 Hz, 1 H), 3.79 (dt, *J* = 1.0, 7.5 Hz, 1 H), 3.39 (dt, *J* = 1.5, 8.0 Hz, 0.5 H), 2.52–2.44 (m, 1.5 H), 2.41–2.29 (m, 1.5 H), 2.28 (s, 4.5 H), 0.07 (s, 9 H), 0.01 (s, 4.5 H). ^{13}C NMR (151 MHz, $CDCl_3$) **137a** (major): δ 142.1, 138.06, 135.1, 134.0, 129.8, 126.7, 126.57, 125.7, 116.7, 111.8, 78.2, 75.0, 41.1, 19.3, -3.7. **137b** (minor): δ 140.7, 138.1, 135.9, 135.6, 129.9, 126.8, 126.60, 125.9, 116.3, 113.1, 76.6, 73.0, 42.3,

19.1, -3.9. IR (film) 3077, 2957, 1247, 1060, 842 cm^{-1}. HRMS (EI) *m*/*z* 274.1753 [(M^+); calcd for $C_{17}H_{24}OSi$, 274.1753].

*Preparation of compounds **138a**/**138b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (1.17 g, 85.5% w/w in Et_2O, 8.98 mmol), **121** (3.85 g, 12.57 mmol, 1.4 equiv) and TMSOTf (162 μL, 0.898 mmol, 0.1 equiv) in cyclohexane (45 mL) afforded after column chromatography (hexanes) 1.38 (56%) of **138a**/**138b** (1:1) as a colorless oil. Spectroscopic data for **138a**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.0 Hz, 1 H), 7.08 (m, 2 H), 7.02 (d, *J* = 7.5 Hz, 1 H), 5.72 (ddt, *J* = 7.0, 10.0, 17.5 Hz, 1 H), 5.67 (ddd, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.01–4.93 (m, 2 H), 4.91 (dt, *J* = 2.0, 17 Hz, 1 H), 4.83 (ddd, *J* = 1.5, 2.0, 10.5 Hz, 1 H), 4.33 (t, *J* = 6.0 Hz, 1 H), 3.79 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.50 (m, 1 H), 2.40 (m, 1 H), 2.33 (s, 3 H), 0.05 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 137.9, 137.3, 135.0, 127.7, 127.6, 127.3, 123.7, 116.7, 111.8, 104.7, 81.0, 75.6, 41.6, 21.5, -3.7. IR (film) 3079, 2958, 1247, 910, 845 cm^{-1}. HRMS (EI) *m*/*z* 274.1750 [(M^+); calcd for $C_{17}H_{24}OSi$, 274.1753]. Spectroscopic data for **138b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.5 Hz, 1 H), 7.06 (m, 2 H), 7.02 (d, *J* = 8.0 Hz, 1 H), 5.81 (ddt *J* = 7.0, 10.0, 17.0 Hz, 1 H), 5.73 (ddd, *J* = 7, 10.5, 17.0 Hz, 1 H), 5.01 (m, 1 H), 4.97 (m, 1 H), 4.39 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.42 (dt, *J* = 1.0, 7.9 Hz, 1 H), 2.51 (m, 1H), 2.34 (s, 3 H), 2.31 (m 1 H), -0.02 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5, 137.63, 137.62, 135.6, 128.0, 127.96, 127.95, 124.4, 116.2,

112.7, 79.2, 72.8, 43.1, 21.4, -3.9. IR (film) 3079, 2959, 1247, 911, 842 cm^{-1}. HRMS (EI) *m*/*z* 274.1741 [(M^+); calcd for $C_{17}H_{24}OSi$, 274.1753].

*Preparation of compounds **139a**/**139b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (2.78 g, 54% w/w in Et_2O, 11.52 mmol, 1 equiv), **122** (6 g, 19.58 mmol, 1.7 equiv) and TMSOTf (trace, <0.02 equiv) in hexane (64 mL) afforded after column chromatography (hexanes) 2.38 (75%) of **139a**/**139b** (1:1) as a colorless oil. Spectroscopic data for **139a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.5 Hz, 2 H), 7.09 (d, *J* = 8.5 Hz, 2 H), 5.72 (m, 1 H), 5.67 (m, 1 H), 5.01–4.90 (m, 3 H), 4.83 (m, 1 H), 4.34 (t, *J* = 6.0 Hz, 1 H), 3.78 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.51 (m, 1 H), 2.41 (m, 1 H), 2.32 (s, 3 H), 0.05 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.5, 137.9, 136.4, 135.0, 128.6 (2C), 126.5 (2C), 116.7, 111.7, 80.8, 75.5, 41.5, 21.1, -3.7. IR (film) 3070, 2959, 1514, 1248, 1062, 910, 841 cm^{-1}. HRMS (EI) *m*/*z* 274.1749 [(M^+); calcd for $C_{17}H_{24}OSi$, 274.1753]. Spectroscopic data for **139a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (s, 4 H), 5.81 (m, 1 H), 5.74 (m, 1 H), 5.04–4.95 (m, 4 H), 4.40 (dd, *J* = 6.0, 7.5 Hz, 1 H), 3.43 (dt, *J* = 1.0, 7.5 Hz, 1 H), 2.53 (m, 1 H), 2.34 (s, 3 H), 2.33 (m, 1 H), -0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 137.7, 136.9, 135.6, 128.8 (2 C), 127.3 (2 C), 116.2, 112.8, 79.0, 72.7, 43.1, 21.2, -4.0. IR (film) 3076, 2957, 1514, 1248, 1057, 910, 841 cm^{-1}. HRMS (EI) *m*/*z* 274.1753 [(M^+); calcd for $C_{17}H_{24}OSi$, 274.1753].

*Preparation of compounds **140a/140b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (1.26 g, 69.9% w/w in THF, 6.73 mmol, 1 equiv), **123** (2.9 g, 9.43 mmol, 1.4 equiv) and TMSOTf (121 μL, 0.673 mmol, 0.1 equiv) in hexane (37 mL) afforded after column chromatography (hexanes) a total of 724 mg (39%) of **140a**/**140b** (1:1) as a colorless oil. Diastereomers were partially separated. Spectroscopic data for **140a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 6.0, 9.0 Hz, 2 H), 6.96 (t, *J* = 9.0 Hz, 2 H), 5.65 (m, 2 H), 4.96 (m, 2 H), 4.87 (dt, *J* = 1.5, 17.0 Hz, 1 H), 4.83 (dt, *J* = 1.5, 10.5 Hz, 1 H), 4.33 (t, *J* = 6.0 Hz, 1 H), 3.77 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.48 (m, 1 H), 2.38 (m, 1 H), 0.03 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.1 Hz), 139.2 (d, *J* = 3.2 Hz), 137.7, 134.5, 128.1 (d, *J* = 7.9 Hz, 2 C), 117.1, 114.6 (d, *J* = 21.7 Hz, 2 C), 111.9, 80.4, 75.8, 41.4, -3.8. IR (film) 3078, 2959, 1518, 1224, 839 cm^{-1}. HRMS (EI) *m*/*z* 278.1505 [(M^+); calcd for $C_{16}H_{23}OSiF$, 278.1502]. Spectroscopic data for **140b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 5.5, 8.0 Hz, 2 H), 6.99 (t, *J* = 8.5 Hz, 2 H), 5.73 (m, 2 H), 5.02–4.94 (m, 4 H), 4.39 (t, *J* = 6.5 Hz, 1 H), 3.36 (d, *J* = 7.5 Hz, 1 H), 2.50 (m, 1 H), 2.31 (m, 1 H), -0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.3 Hz), 138.1 (d, *J* = 3.2 Hz), 137.4, 135.1, 128.8 (d, *J* = 7.9 Hz, 2 C), 116.6, 114.9 (d, *J* = 21.3 Hz, 2 C), 113.0, 78.6, 73.0, 43.0, -4.0. IR (film) 3078, 2959, 1518, 1224, 835 cm^{-1}. HRMS (EI) *m*/*z* 278.1492 [(M^+); calcd for $C_{16}H_{23}OSiF$, 278.1502].

*Preparation of compounds **141a/141b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (5.5 g, solution 36.2% w/w in THF, 15.35 mmol, 1 equiv), **124** (10 g, 30.7 mmol, 2 equiv) and TMSOTf (190 μL, 1.07 mmol, 0.07 equiv) in cyclohexane (85 mL) afforded after column chromatography (hexanes) 1.425 g (54%) of **141a**/**141b** (1:1) as a colorless oil. Mixture of diastereomers (**141a**/**141b** = 0.7:1.0) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 3.4 H), 7.24 (m, 2 H), 7.18 (m, 1.4 H), 5.82–5.62 (m, 3.4 H), 5.04 (m, 0.7 H), 5.02–4.96 (m, 4.1 H), 4.90 (dt, *J* = 1.5, 17.0 Hz, 1 H), 4.85 (dt, *J* = 1.5, 11.0 Hz, 1 H), 4.42 (dd, *J* = 6.0, 7.0 Hz, 0.7 H), 4.36 (t, *J* = 6.0 Hz, 1 H), 3.80 (dt, *J* = 1.5, 7.0 Hz, 1 H), 3.39 (m, 0.7 H), 2.55–2.30 (m, 3.4 H), 0.06 (s, 9 H), -0.01 (s, 7.3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 140.9, 137.7, 137.3, 134.9, 134.7, 134.3, 133.0, 132.5, 128.7 (2 C), 128.3 (2 C), 128.2, 128.0 (2 C), 127.9 (2 C), 127.4, 117.2, 116.8, 113.1, 112.1, 80.3, 78.6, 75.9, 73.1, 42.9, 41.3, -3.8, -4.0. IR (film) 3078, 2957, 1491, 1248, 1089, 841 cm^{-1}. HRMS (EI) *m*/*z* 294.1218 [(M^+); calcd for $C_{16}H_{23}OSiCl$, 294.1207].

*Preparation of compounds **142a/142b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (2.3 g, solution 44% w/w in THF, 11.51 mmol, 1 equiv), **125** (6.8 g, 18.4 mmol, 1.6 equiv) and TMSOTf (208 μL, 1.151 mmol, 0.1 equiv) in hexane (64 mL) afforded after column chromatography (hexanes) 1.425 g (37%) of **142a**/**142b** (1:1) as a colorless oil. Mixture of diastereomers (**142a**/**142b** = 1:1) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (m, 2 H), 7.39 (m, 2 H), 7.14 (m, 2 H), 7.10 (m, 2 H), 5.76–5.59 (m, 4 H), 5.01–4.93 (m, 6 H), 4.87 (dt, *J* = 1.8, 16.8 Hz, 1 H), 4.83 (dt, *J* = 1.8, 10.8 Hz, 1 H),

4.38 (dd, *J* = 6.0, 7.8 Hz, 1 H), 4.32 (t, *J* = 6.0 Hz, 1 H), 3.77 (dt, *J* = 1.8, 7.2 Hz, 1 H), 3.35 (dt, *J* = 1.1, 7.8 Hz, 1 H), 2.49 (m, 2 H), 2.40 (m, 1 H), 2.35 (m, 1 H), 0.03 (s, 9 H), -0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 141.5, 137.6, 137.3, 134.8, 134.2, 131.3 (2 C), 131.0 (2 C), 129.1 (2 C), 128.3 (2 C), 121.1, 120.6, 117.3, 116.8, 113.1, 112.1, 80.3, 78.6, 76.0, 73.1, 42.8, 41.3, -3.8, -4.0. IR (film) 3078, 2957, 1487, 1246, 1070, 1010, 841 cm^{-1}. HRMS (EI) *m*/*z* 338.0712 [(M^+); calcd for $C_{16}H_{23}OSiBr$, 338.0702].

*Preparation of compounds **143a**/**143b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (1.07 g, 44% w/w in THF, 5.72 mmol, 1 equiv), **126** (2.74 g, 8 mmol, 1.4 equiv) and TMSOTf (47 μL, 0.259 mmol, 0.05 equiv) in hexane (32 mL) afforded after column chromatography (10% CH_2Cl_2 in hexanes) a total of 852 mg (48%) of **143a**/**143b** (1:1) as colorless oils. Compounds **143a**/**143b** were separable by column chromatography. Spectroscopic data for **143a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 2 H), 7.78 (dd, *J* = 1.5, 8.5 Hz, 1 H), 7.72 (s, 1 H), 7.45 (m, 3 H), 5.80–5.63 (m, 2 H), 5.02–4.96 (m, 2 H), 4.92 (dq, *J* = 2.0, 15.0 Hz, 1 H), 4.81 (dq, *J* = 1.5, 10.5 Hz, 1 H), 4.53 (m, 1 H), 3.59 (dq, *J* = 1.5, 7.0 Hz, 1 H), 2.61 (m, 1 H), 2.51 (m, 1 H), 0.08 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 137.9, 134.8, 133.1, 132.8, 127.9, 127.6, 127.5, 125.8, 125.4, 125.3, 125.0, 116.9, 111.9, 81.3, 75.9, 41.5, -3.7. IR (film) 3060, 2959, 2825, 1241, 860, 841 cm^{-1}. HRMS (EI) *m*/*z* 310.1753 [(M^+); calcd for $C_{20}H_{26}OSi$, 310.1753]. Spectroscopic data for **143b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 3 H), 7.65 (s, 1 H), 7.44 (m, 3 H), 5.86–5.72 (m, 2 H),

5.06–4.96 (m, 4 H), 4.59 (dd, *J* = 6.0, 7.5 Hz, 1 H), 3.44 (m, 1 H), 2.62 (m, 1 H), 2.43 (m, 1 H), -0.02 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 137.5, 135.3, 133.1, 133.0, 128.0, 127.8, 127.7, 126.5, 125.9, 125.6, 125.1, 116.5, 112.9, 79.3, 72.9, 42.8, -4.0. IR (film) 3057, 2959, 2831, 1246, 859, 841 cm^{-1}. HRMS (EI) *m*/*z* 310.1745 [(M^+); calcd for $C_{20}H_{26}OSi$, 310.1753].

*Preparation of compounds **144a**/**144b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (380 mg, 69.6% w/w in THF, 2.03 mmol, 1 equiv), **127** (679 mg, 2.03 mmol, 1 equiv) and TMSOTf (37 μL, 0.2 mmol, 0.1 equiv) in hexane (11 mL) afforded after column chromatography (hexanes) a total of 144.5 mg (24%) of **144a**/**144b** (1:1) as colorless oils. Compounds **144a**/**144b** were separable by column chromatography. Spectroscopic data for **144a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 1 H), 7.15 (m, 2 H), 7.07 (m, 1 H), 5.80 (ddt, *J* = 7.0, 10.0, 17.0 Hz, 1 H), 5.61 (ddd, *J* = 7.5, 10.5, 17.5 Hz, 1 H), 5.03–4.97 (m, 2 H), 4.87 (dt, *J* = 2.0, 17.5 Hz, 1 H), 4.79 (ddd, *J* = 1.5, 2.0, 10.5 Hz, 1 H), 4.58 (dd, *J* = 5.0, 7.5 Hz, 1 H), 3.78 (dt, *J* = 1.5, 7.5 Hz, 1 H), 2.53 (m, 2 H), 2.46 (m, 1 H), 2.36 (m, 1 H), 1.59 (m, 2 H), 0.96 (t, *J* = 7.5 Hz, 3 H), 0.05 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 138.5, 138.1, 135.4, 128.8, 126.9, 126.6, 125.6, 116.6, 111.8, 77.9, 76.6, 42.1, 34.5, 24.2, 14.2, -3.8. IR (film) 3074, 2959, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 302.2078 [(M^+); calcd for $C_{19}H_{30}OSi$, 302.2066]. Spectroscopic data for **144b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 1.5, 7.5 Hz, 1 H), 7.18 (m, 2 H), 7.10 (m, 1 H), 5.92 (m, 1 H), 5.76 (ddd, *J* = 7.5, 11.0, 17.5 Hz, 1 H), 5.06–4.96 (m, 4 H), 4.78 (dd, *J* = 4.5, 9.0 Hz, 1 H), 3.39 (dt, *J* = 1.0, 7.0 Hz, 1 H), 2.53 (m, 2 H), 2.47 (m, 1 H), 2.28 (m, 1 H), 1.55 (m, 2 H), 0.95 (t, *J* = 7.0 Hz, 3 H), 0.00

(s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 140.4, 138.1, 135.9, 129.1, 126.8, 126.7, 126.0, 116.1, 112.8, 74.4 72.8, 43.2, 34.5, 24.6, 14.2, -4.0. IR (film) 3076, 2959, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 302.2080 [(M^+); calcd for $C_{19}H_{30}OSi$, 302.2066].

*Preparation of compounds **145a**/**145b***

Applying general procedure C to **66** (256 mg, 1.331 mmol, 1 equiv), trichloroacetimidate of 1-phenylbut-3-en-1-ol (662 mg, 2.26 mmol, 1.7 equiv) and TMSOTf (24 μL, 0.133 mmol, 0.1 equiv) in hexane (7 mL) afforded after column chromatography (hexanes) a total of 250 mg (58%) of **145a**/**145b** (1:1) as a colorless oil. Compounds **145a**/**145b** were separable by column chromatography. Spectroscopic data for **145a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (m, 2 H), 7.35 (m, 3 H), 7.26 (m, 2 H), 7.21 (m, 3 H), 5.65–5.55 (m, 2 H), 4.91–4.87 (m, 3 H), 4.81 (m, 1 H), 4.28 (t, *J* = 6.0 Hz, 1 H), 3.98 (dt, *J* = 1.8, 7.2 Hz, 1 H) 2.45 (m, 1 H), 2.35 (m, 1 H), 0.36 (s, 3 H), 0.31 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 137.4, 137.0, 134.7, 134.3 (2 C), 129.2, 127.8 (2 C), 127.6 (2 C), 126.9, 126.6 (2 C), 81.1, 75.2, 41.5, -5.2, -5.5. IR (film) 3071, 2961, 1427, 1248, 1115, 837 cm^{-1}. HRMS (EI) *m*/*z* 322.1751 [(M^+); calcd for $C_{21}H_{26}OSi$, 322.1753]. Spectroscopic data for **145b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.36 (m, 1 H), 7.32 (m, 2 H), 7.21 (m, 3 H), 7.06 (m, 2 H), 5.78 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.69 (ddd, *J* = 7.2, 10.8, 17.4 Hz, 1 H), 5.02–4.93 (m, 4 H), 4.43 (dd, *J* = 5.4, 7.8 Hz, 1 H), 3.60 (d, *J* = 7.8 Hz, 1 H), 2.50 (quintet, A of ABX system, *J* = 7.2 Hz, 1 H), 2.32 (quintet, B of ABX system, *J* = 7.2 Hz, 1 H), 0.28 (s, 3 H), 0.25 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 137.1, 136.8, 135.4, 134.4 (2 C), 129.0, 128.0 (2 C), 127.4 (2 C), 127.30 (2 C), 127.26, 79.2,

72.5, 43.0, -5.3, -6.0. IR (film) 3071, 2961, 1427, 1248, 1115, 837 cm^{-1}. HRMS (EI) *m*/*z* 322.1753 [(M^+); calcd for $C_{21}H_{26}OSi$, 322.1753].

*Preparation of compounds **146a**/**146b***

Applying general procedure C to **67** (2.17 g, 8.53 mmol, 1 equiv), trichloroacetimidate of 1-phenylbut-3-en-1-ol (5 g, 17.07 mmol, 2 equiv) and TMSOTf (230 μL, 1.28 mmol, 0.15 equiv) in cyclohexane (41 mL) afforded after column chromatography (10% CH_2Cl_2 in hexanes) 2.7 g (83%) of **146a**/**146b** (1:1) as a colorless oil. Spectroscopic data for **146a**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 2 H), 7.59 (m, 2 H), 7.39–7.33 (m, 5 H), 7.27 (m, 3 H), 7.22 (m, 3 H), 5.67 (ddd, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.47 (m, 1 H), 4.93 (dt, *J* = 2.0, 17.5 Hz, 1 H), 4.85–4.81 (m, 3 H), 4.31 (dt, *J* = 1.5, 7.0 Hz, 1 H), 4.27 (t, *J* = 7.0 Hz, 1 H), 2.44 (m, 1 H), 2.31 (m, 1 H), 0.59 (m, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 137.1, 135.4 (2 C), 135.2 (2 C), 134.8, 134.6, 129.4, 129.3, 127.8 (2 C), 127.7 (2 C), 127.6 (2 C), 127.0, 126.7, 81.4, 74.7, 41.5, -6.5. IR (film) 3071, 2975, 1429, 1115, 734 cm^{-1}. HRMS (EI) *m*/*z* 384.1901 [(M^+); calcd for $C_{26}H_{28}OSi$, 384.1909]. Spectroscopic data for **146b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (m, 2 H), 7.49 (m, 2 H), 7.40 (m, 1 H), 7.37–7.29 (m, 5 H), 7.19 (m, 3 H), 6.97 (m, 2 H), 5.84–5.73 (m, 2 H), 5.05–4.97 (m, 4 H), 4.50 (dd, *J* = 5.5, 7.5 Hz, 1 H), 3.93 (dt, *J* = 1.5, 8.0 Hz, 1 H), 2.53 (m, 1 H), 2.35 (m, 1 H), 0.53 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 136.7, 135.5 (2 C), 135.4, 135.3 (2 C), 135.2, 129.4, 129.2, 128.0 (2 C), 127.54 (2 C), 127.52 (2 C), 127.46 (2 C), 127.3, 116.5,

114.8, 79.2, 72.1, 42.9, -6.6. IR (film) 3071, 3976, 1429, 1115, 724 cm^{-1}. HRMS (EI) *m*/*z* 384.1889 [(M^+); calcd for $C_{26}H_{28}OSi$, 384.1909].

*Preparation of compounds **147a**/**147b***

Applying general procedure C to **69** (583 mg, 3.38 mmol, 1 equiv), trichloroacetimidate of 1-phenylbut-3-en-1-ol (1.48 g, 5.07 mmol, 1.5 equiv) and TMSOTf (31 μL, 0.169 mmol, 0.05 equiv) in hexane (19 mL) afforded after column chromatography (hexanes) a total of 720 mg (70%) of **147a**/**147b** (1:1) as colorless oils. Compounds **147a**/**147b** were separable by column chromatography. Spectroscopic data for **147a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 4 H), 7.20 (m, 1 H), 5.68 (m, 2 H), 4.98–4.88 (m, 3 H), 4.80 (dd, *J* = 1.0, 10.0 Hz, 1 H), 4.35 (t, *J* = 6.0 Hz, 1 H), 3.98 (dd, *J* = 1.5, 7.5 Hz, 1 H), 2.52 (m, 1 H), 2.42 (m, 1 H), 0.98 (t, *J* = 8.0 Hz, 9 H), 0.62 (dq, *J* = 1.5, 7.5 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 138.3, 134.8, 127.8 (2 C), 126.8, 126.6 (2 C), 116.8, 111.8, 80.9, 74.3, 41.3, 7.5, 1.8. IR (film) 3078, 2953, 1454, 1014, 910 cm^{-1}. HRMS (EI) *m*/*z* 302.2063 [(M^+); calcd for $C_{19}H_{30}OSi$, 302.2066]. Spectroscopic data for **147b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.24 (m, 3 H), 5.78 (m, 2 H), 5.02–4.95 (m, 4 H), 4.41 (dd, *J* = 5.4, 7.8 Hz, 1 H), 3.55 (dt, *J* = 1.2, 7.8 Hz, 1 H), 2.52 (m, 1 H), 2.34 (m, 1 H), 0.88 (t, *J* = 7.8 Hz, 9 H), 0.54 (dq, *J* = 2.4, 7.8 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 138.0, 135.5, 128.1 (2 C), 127.43 (2 C), 127.37, 116.3, 112.8, 79.0, 71.5, 42.9, 7.3, 1.6. IR (film) 3064, 2953, 1450, 1011, 910 cm^{-1}. HRMS (EI) *m*/*z* 302.2065 [(M^+); calcd for $C_{19}H_{30}OSi$, 302.2066].

*Preparation of compounds **148a/148b***

Applying general procedure C to **66** (1 g, 5.2 mmol, 1 equiv), **118** (2.68 g, 8.32 mmol, 1.6 equiv) and TMSOTf (94 μL, 0.52 mmol, 0.1 equiv) in hexane (29 mL) afforded after column chromatography (15% CH_2Cl_2 in hexanes) a total of 1.298 g (71%) of **148a**/**148b** (1:1) that were partially separated and obtained as colorless oils. Spectroscopic data for **148a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (m, 2 H), 7.36 (m, 3 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 6.85 (d, *J* = 0.6 Hz, 1 H), 6.81 (dd, *J* = 0.6, 7.2 Hz, 1 H), 6.76 (ddd, *J* = 0.6, 2.4, 7.8 Hz, 1 H), 5.70–5.59 (m, 2 H), 4.94 (m, 3 H), 4.86 (dt, *J* = 10.8 Hz, 1 H), 4.29 (t, *J* = 6.0 Hz, 1 H), 4.00 (dt, *J* = 1.2, 7.8 Hz, 1 H), 3.78 (s, 3 H), 2.46 (m, 1 H), 2.37 (m, 1 H), 0.39 (s, 3 H), 0.35 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 145.0, 137.4, 136.9, 134.7, 134.3 (2 C), 129.2, 128.8, 127.6 (2 C), 119.0, 116.8, 112.5, 112.4, 111.9, 81.0, 75.2, 55.1, 41.6, -5.2, -5.6. IR (film) 3071, 2958, 1254, 1046, 837 cm^{-1}. HRMS (EI) *m*/*z* 352.1855 [(M^+); calcd for $C_{22}H_{28}O_2Si$, 352.1859]. Spectroscopic data for **148b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.33 (m, 3 H), 7.14 (t, *J* = 7.8 Hz, 1 H), 6.76 (ddd, *J* = 0.6, 2.4, 7.8 Hz, 1 H), 6.68 (m, 2 H), 5.80 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.69 (ddd, *J* = 7.2, 10.2, 18.0 Hz, 1 H), 5.03–4.94 (m, 4 H), 4.43 (dd, *J* = 5.4, 7.8 Hz, 1 H), 3.69 (s, 3 H), 3.66 (dt, *J* = 1.2, 7.2 Hz, 1 H), 2.51 (m, 1 H), 2.33 (m, 1 H), 0.29 (s, 3 H), 0.27 (s, 3 H).). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 143.8, 137.1, 136.8, 135.4, 134.4 (2 C), 129.04, 129.03, 127.4 (2 C), 119.8, 116.4, 113.7, 113.2, 112.2, 79.1, 72.5, 43.0, -5.3, -5.8. IR (film) 3071, 2958, 1254, 1046, 837 cm^{-1}. HRMS (EI) *m*/*z* 352.1859 [(M^+); calcd for $C_{22}H_{28}O_2Si$, 352.1859].

*Preparation of **149a**/**149b***

Applying general procedure C to **66** (1 g, 5.2 mmol, 1 equiv), **124** (2.72 g, 8.32 mmol, 1.6 equiv) and TMSOTf (94 μL, 0.52 mmol, 0.1 equiv) in hexane (29 mL) afforded after column chromatography (hexanes and 10% CH_2Cl_2 in hexanes) a total of 1.686 g (91%) of **149a**/**149b** (1:1) that were partially separated and obtained as colorless oils. Spectroscopic data for **149a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (m, 2 H), 7.40–7.36 (m, 3 H), 7.25 (m, 2 H), 7.18 (m, 2 H), 5.67–5.55 (m, 2 H), 4.95–4.85 (m, 4 H), 4.29 (t, *J* = 6.0 Hz, 1 H), 4.00 (dt, *J* = 1.2, 5.4 Hz, 1 H), 2.45 (m, 1 H), 2.35 (m, 1 H), 0.39 (s, 3 H), 0.35 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.8, 137.2, 136.7, 134.3 (2 C), 134.2, 132.5, 129.2, 128.0 (2 C), 127.9 (2 C), 127.6 (2 C), 117.2, 112.6, 80.4, 75.4, 41.3, -5.3, -5.7. IR (film) 3072, 2961, 1490, 1114, 913, 836 cm^{-1}. HRMS (EI) *m*/*z* 356.1352 [(M^+); calcd for $C_{21}H_{25}OSiCl$, 356.1363]. Spectroscopic data for **149b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.39 (tt, *J* = 1.8, 7.8 Hz, 1 H), 7.34 (t, *J* = 7.2 Hz, 2 H), 7.17 (m, 2 H), 6.95 (m, 2 H), 5.76 (m, 1 H), 5.71 (ddd, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.03 (dt, *J* = 1.8, 10.8 Hz, 1 H), 5.01–4.96 (m, 3 H), 4.42 (dd, *J* = 6.0, 7.8 Hz, 1 H), 3.56 (d, *J* = 7.8 Hz, 1 H), 2.48 (m, 1 H), 2.30 (m, 1 H), 0.31 (s, 3 H), 0.26 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 136.8, 136.6, 134.8, 134.4 (2 C), 132.9, 129.1, 128.6 (2 C), 128.2 (2 C), 127.5 (2 C), 116.8, 113.7, 78.5, 72.7, 42.9, 31.6, 22.7, 14.1, -5.3, -6.3. IR (film) 3076, 2961, 1489, 1093, 911, 830 cm^{-1}. HRMS (EI) *m*/*z* 356.1355 [(M^+); calcd for $C_{21}H_{25}OSiCl$, 356.1363].

*Preparation of **150a/150b***

Applying general procedure C to **69** (860 mg, 5 mmol, 1 equiv), **126** (2.4 g, 7 mmol, 1.4 equiv) and TMSOTf (22.5 μL, 0.125 mmol, 0.025 equiv) in hexane (28 mL) afforded after column chromatography (hexanes and 10% CH_2Cl_2 in hexanes) a total of 793 mg (45%) of **150a**/**150b** (1:1) that were partially separated and obtained as colorless oils. Spectroscopic data for **150a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (m, 2 H), 7.81 (d, *J* = 8.5 Hz, 1 H), 7.74 (s, 1 H), 7.47 (m, 3 H), 5.74 (m, 2 H), 5.04–4.95 (m, 3 H), 4.82 (m, 1 H), 4.55 (d, *J* = 6.0 Hz, 1 H), 4.08 (dt, *J* = 1.0, 7.0 Hz, 1 H), 2.65 (m, 1 H), 2.54 (m, 1 H), 1.05 (t, *J* = 8.0 Hz, 9 H), 0.69 (dq, *J* = 2.0, 8.0 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 138.3, 134.7, 133.1, 132.7, 127.9, 127.7, 127.5, 125.7, 125.4, 125.3, 125.0, 116.9, 111.9, 81.2, 74.6, 41.4, 7.5, 1.8. IR (film) 3057, 2953, 2878, 1414, 1018, 910, 817 cm^{-1}. HRMS (EI) *m*/*z* 352.2210 [(M^+); calcd for $C_{23}H_{32}OSi$, 352.2222]. Spectroscopic data for **150b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (m, 3 H), 7.63 (s, 1 H), 7.46–7.41 (m, 3 H), 5.79 (m, 2 H), 5.04–4.94 (m, 4 H), 4.59 (dd, *J* = 6.0, 8.0 Hz, 1 H), 3.58 (d, *J* = 8.0 Hz, 1 H), 2.60 (m, 1 H), 2.41 (m, 1 H), 0.88 (t, *J* = 8.0 Hz, 9 H), 0.55 (dq, *J* = 4.0, 8.0 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.7, 138.0, 135.4, 133.1, 133.09, 128.0, 127.8, 127.7, 126.6, 125.9, 125.6, 125.1, 116.5, 112.9, 79.1, 71.6, 42.9, 7.4, 1.6. IR (film) 3059, 2953, 2876, 1458, 1020, 910 cm^{-1}. HRMS (EI) *m*/*z* 352.2222 [(M^+); calcd for $C_{23}H_{32}OSi$, 352.2222].

*Preparation of compounds **151a/151b***

Applying general procedure C to 2-methyl-1- (trimethylsilyl)prop-2-en-1-ol (2.6 g, 76.9% w/w in THF, 13.86 mmol, 1 equiv), trichloroacetimidate of 1-phenylbut-3-en-1-ol (7.3 g, 24.95 mmol,

1.8 equiv) and TMSOTf (0.25 mL, 1.386 mmol, 0.1 equiv) in hexane (70 mL) afforded after column chromatography (hexanes) a total of 1.67 g (44%) of **151a**/**151b** (1:1) as a colorless oil. Mixture of diastereomers (**151a**/**151b** = 1:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.19 (m, 10 H), 5.81 (ddt, *J* = 7.0, 10.5, 17.0 Hz, 1 H), 5.67 (ddt, *J* = 7.0, 10.5, 17.0 Hz, 1 H), 5.00–4.93 (m, 3 H), 4.80 (m, 1 H), 4.66 (m, 2 H), 4.32 (t, *J* = 6.0 Hz, 1 H), 4.28 (dd, *J* = 6.0, 8.0 Hz, 1 H), 3.77 (s, 1 H), 3.31 (s, 1 H), 2.52 (m, 2 H), 2.48 (m, 1 H), 2.34 (m, 1 H), 1.63 (m, 3 H), 1.51 (m, 3 H), 0.07 (s, 9 H), -0.02 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 144.4, 143.4, 142.3, 135.5, 134.6, 128.1 (2 C), 127.8 (2 C), 127.5 (2 C), 127.4, 126.8, 126.6 (2 C), 116.9, 116.4, 109.9, 109.5, 80.0, 79.0, 77.8, 75.4, 43.0, 40.5, 20.4, 20.3, -3.0, -3.2. IR (film) 3072, 2959, 1248, 1060, 839 cm^{-1}. HRMS (EI) *m*/*z* 274.1753 [(M^{+}); calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compounds **152a/152b***

Applying general procedure C to 2-methyl-1- (trimethylsilyl)prop-2-en-1-ol (660 mg, 79% w/w in THF, 3.6 mmol, 1 equiv), **119** (1.86 g, 5.77 mmol, 1.6 equiv) and TMSOTf (0.32 μL, 0.18 mmol, 0.05 equiv) in hexane (20 mL) afforded after column chromatography (15% and 20% CH_2Cl_2 in hexanes) a total of 918 mg (83%) of **152a**/**152b** (1:1) as colorless oils. Compounds **152a**/**152b** were separable by column chromatography. Spectroscopic data for **152a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 2 H), 6.81 (m, 2 H), 5.66 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 4.98–4.93 (m, 2 H), 4.67 (m, 1 H), 4.65 (m, 1 H), 4.27 (t, *J* = 6.6 Hz, 1 H), 3.78 (s, 3 H), 3.75 (s, 1 H), 2.52 (m, 1 H), 2.43 (m, 1 H), 0.06 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 145.1, 135.5, 134.8, 127.7 (2 C), 116.8, 113.1 (2 C), 109.3, 79.8, 77.7, 55.1, 40.5, 20.3, -2.9. IR (film) 3033,

2950, 1238, 840 cm^{-1}. HRMS (EI) *m*/*z* 304.1853 [(M^+); calcd for $C_{18}H_{28}O_2Si$, 304.1859]. Spectroscopic data for **152b**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 2 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 5.78 (ddt, *J* = 6.6, 9.6, 16.8 Hz, 1 H), 4.99–4.94 (m, 2 H), 4.80 (s, 1 H), 4.66 (s, 1 H), 4.23 (t, *J* = 7.2 Hz, 1 H), 3.80 (s, 3 H), 3.30 (s, 1 H), 2.53 (m, 1 H), 2.33 (m, 1 H), -0.02 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 144.5, 135.6, 134.3, 128.7 (2 C), 116.3, 113.4 (2 C), 109.8, 78.5, 75.0, 55.1, 43.0, 20.4, -3.2. IR (film) 3074, 2955, 1247, 824 cm^{-1}. HRMS (EI) *m*/*z* 304.1859 [(M^+); calcd for $C_{18}H_{28}O_2Si$, 304.1859].

*Preparation of compounds **153a/153b***

Applying general procedure C to 2-methyl-1-(trimethylsilyl)prop-2-en-1-ol (380 mg, 79% w/w in THF, 2.083 mmol, 1 equiv), **122** (1.02 g, 3.33 mmol, 1.6 equiv) and TMSOTf (19 μL, 0.104 mmol, 0.05 equiv) in hexane (12 mL) afforded after column chromatography (2% CH_2Cl_2 in hexanes) a total of 390 mg (61%) of **153a**/**153b** (1:1) as a colorless oil. Mixture of diastereomers (**153a**/**153b** = 1.4:1.0) ^1H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2.8 H), 7.13 (s, 4 H), 7.09 (d, *J* = 7.8 Hz, 2.8 H), 5.81 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.68 (ddt, *J* = 6.6, 9.6, 16.8 Hz, 1.4 H), 5.01–4.94 (m, 4.8 H), 4.81 (m, 1 H), 4.69 (m, 1 H), 4.67 (m, 2.8 H), 4.31 (t, *J* = 5.4 Hz, 1.4 H), 4.27 (t, *J* = 6.6 Hz, 1 H), 3.78 (s, 1.4 H), 3.33 (s, 1 H), 2.53 (m, 2.4 H), 2.46 (m, 1.4 H), 2.35 (s, 3 H), 2.34 (heavily overlapped, m, 1 H), 2.33 (s, 4.2 H), 1.64 (d, *J* = 0.6 Hz, 3 H), 1.53 (d, *J* = 0.6 Hz, 4.2 H), 0.07 (s, 12.6 H), -0.08 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) **153a** (major): δ 145.0, 140.4, 136.2, 134.8, 128.5 (2C), 126.5 (2C), 116.8, 109.4, 79.8, 77.6, 40.5, 21.1, 20.3, -3.0. **153b** (minor): δ 144.4, 139.3, 136.9, 135.7, 128.8 (2 C), 127.5 (2 C), 116.3,

109.8, 78.8, 75.2, 43.1, 21.2, 20.4, -3.2. IR (film) 3075, 2957, 1247, 840 cm^{-1}. HRMS (EI) *m*/*z* 288.1895 [(M^+); calcd for $C_{18}H_{28}OSi$, 288.1909].

*Preparation of compounds **154a**/**154b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (1.5 g, 44% w/w in THF, 5.07 mmol, 1 equiv), **128** (2.49 g, 8.11 mmol, 1.6 equiv) and TMSOTf (47 μL, 0.5 mmol, 0.1 equiv) in hexane (28 mL) afforded after column chromatography (2% CH_2Cl_2 in hexanes) a total of 847 mg (61%) of **154a**/**154b** (1:1) as colorless oils. Compounds **154a**/**154b** were separable by column chromatography. Spectroscopic data for **154a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 4 H), 7.19 (m, 1 H), 5.62 (ddd, *J* = 7.0, 10.5, 17.0 Hz, 1 H), 4.88 (m, 1 H), 4.79 (m, 1 H), 4.70 (m, 1 H), 4.60 (m, 1 H), 4.41 (t, *J* = 6.5 Hz, 1 H), 3.76 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.52 (dd, A of ABX system, *J* = 7.0, 14.0 Hz, 1 H), 2.26 (dd, B of ABX system, *J* = 6.5, 14.0 Hz, 1 H), 1.67 (s, 3 H), 0.02 (s, 9 H). IR (film) 3065, 2957, 1245, 841 cm^{-1}. HRMS (EI) *m*/*z* 274.1741 [(M^+); calcd for $C_{17}H_{26}OSi$, 274.1753]. Spectroscopic data for **154b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 2 H), 7.28 (m, 3 H), 5.76 (ddd, *J* = 7.5, 10.5, 17.5 Hz, 1 H), 5.06 (dq, *J* = 1.0, 10.0 Hz, 1 H), 4.99 (dt, *J* = 1.5, 17.5 Hz, 1 H), 4.75 (m, 1 H), 4.67 (m, 1 H), 4.55 (dd, *J* = 6.0, 8.0 Hz, 1 H), 3.42 (dt, *J* = 1.0, 7.5 Hz, 1 H), 2.52 (dd, A of ABX system, *J* = 8.0, 13.5 Hz, 1 H), 2.29 (dd, B of ABX system, *J* = 5.0, 13.5 Hz, 1 H), 1.76 (s, 3 H), 0.00 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 142.8, 137.5, 128.0 (2 C), 127.3 (2 C), 127.27, 113.0, 112.6, 78.7, 72.8, 47.0, 23.3, -4.0. IR (film) 3076, 2959, 1247, 840 cm^{-1}. HRMS (EI) *m*/*z* 274.1745 [(M^+); calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compounds **155a/155b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (0.97 g, 85.5% w/w in THF, 6.35 mmol, 1 equiv), **129** (2.85 g, 8.89 mmol, 1.4 equiv) and TMSOTf (57 μL, 0.317 mmol, 0.05 equiv) in hexane (35 mL) afforded after column chromatography (5% and 30% CH_2Cl_2 in hexanes) a total of 1.2 g (65%) of **155a**/**155b** (1:1) as colorless oils. Compounds **155a**/**155b** were separable by column chromatography. Spectroscopic data for **155a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.0 Hz, 2 H), 7.07 (d, *J* = 7.5 Hz, 2 H), 5.64 (dddd, *J* = 1.0, 7.0, 10.5, 17.0 Hz, 1 H), 4.90 (dq, *J* = 1.5, 17.0 Hz, 1 H), 4. 80 (m, 1 H), 4.70 (m, 1 H), 4.61 (m, 1 H), 4.39 (t, *J* = 7.0 Hz, 1 H), 3.75 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.51 (dd, A of ABX system, *J* = 7.0, 14.0 Hz, 1 H), 2.31 (s, 3 H), 2.25 (dd, B of ABX system, *J* = 6.5, 13.5 Hz, 1 H), 1.67 (d, *J* = 1.0 Hz, 3 H), 0.02 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 141.0, 138.2, 136.4, 128.5 (2 C), 126.6 (2 C), 113.0, 111.6, 80.5, 76.0, 46.1, 23.1, 21.1, -3.7. IR (film) 3079, 2961, 1248, 1060, 841 cm^{-1}. HRMS (EI) *m*/*z* 288.1900 [(M^+); calcd for $C_{18}H_{28}OSi$, 288.1909]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (m, 4 H), 5.72 (ddd, *J* = 8.0, 11.0, 17.5 Hz, 1 H), 5.00 (ddd, *J* = 1.0, 2.0, 10.5 Hz, 1 H), 4.95 (ddd, *J* = 1.0, 2.0, 17.0 Hz, 1 H), 4.71 (m, 1 H), 4.64 (m, 1 H), 4.49 (dd, *J* = 5.0, 8.0 Hz, 1 H), 3.39 (dt, *J* = 1.0, 7.5 Hz, 1 H), 2.46 (dd, A of ABX system, *J* = 9.0, 13.5 Hz, 1 H), 2.33 (s, 3 H), 2.23 (dd, B of ABX system, *J* = 5.5, 14.0 Hz, 1 H), 1.72 (m, 3 H), -0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 139.7, 137.6, 136.8, 128.8 (2 C), 127.2 (2 C), 112.9, 112.5, 78.4, 72.6, 47.0,

23.3, 21.2, -4.0. IR (film) 3076, 2961, 1248, 1053, 841 cm^{-1}. HRMS (EI) *m*/*z* 288.1909 [(M^+); calcd for $C_{18}H_{28}OSi$, 288.1909].

*Preparation of compounds **156a**/**156b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (1.03 g, 77.4% w/w in THF, 6.14 mmol, 1 equiv), **130** (2.75 g, 9.21 mmol, 1.5 equiv) and TMSOTf (55.5 μL, 0.307 mmol, 0.05 equiv) in hexane (34 mL) afforded after column chromatography (hexanes) a total of 982 mg (60%) of **156a**/**156b** (1:1) as colorless oils. Compounds **156a**/**156b** were separable by column chromatography. Spectroscopic data for **156a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 1.0, 5.0 Hz, 1 H), 6.91 (dd, *J* = 3.0, 5.0 Hz, 1 H), 6.86 (m, 1 H), 5.80–5.70 (m, 2 H), 5.07–4.96 (m, 3 H), 4.89 (dt, *J* = 1.5, 10.5 Hz, 1 H), 4.64 (t, *J* = 6.0 Hz, 1 H), 3.83 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.63–2.50 (m, 2 H), 0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 137.5, 134.3, 126.1, 124.0, 123.6, 117.3, 112.3, 76.5, 75.7, 41.4, -3.86. IR (neat) 3076, 2957, 1248, 1062, 912, 841 cm^{-1}. HRMS (EI) *m*/*z* 266.1148 [(M^+); calcd for $C_{14}H_{22}OSiS$, 266.1161]. Spectroscopic data for **156b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (m, 1 H), 6.92 (dd, *J* = 3.5, 5.0 Hz, 1 H), 6.87 (m, 1 H), 5.79 (dddd, *J* = 7.0, 10.0, 14.0, 17.0 Hz, 1 H), 5.71 (ddd, *J* = 7.5, 10.5, 17.5 Hz, 1 H), 5.04 (m, 1 H), 5.01 (m 2 H), 4.98 (m, 1 H), 4.69 (t, *J* = 7.0 Hz, 1 H), 3.56 (dt, *J* = 1.5, 7.5 Hz, 1 H), 2.61 (m, 1 H), 2.45 (m, 1 H) -0.03 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 137.4, 134.9, 126.0, 125.5, 124.8, 116.8, 113.1, 74.7, 72.8, 43.4, -4.0. IR (neat) 3076, 2957, 1248, 914, 843 cm^{-1}. HRMS (EI) *m*/*z* 266.1153 [(M^+); calcd for $C_{14}H_{22}OSiS$, 266.1161].

*Preparation of compounds **157a/157b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (990 mg, 77.4% w/w in THF, 5.9 mmol, 1 equiv), **131** (2.17 g, 7.67 mmol, 1.3 equiv) and TMSOTf (27 μL, 0.147 mmol, 0.025 equiv) in hexane (33 mL) afforded after column chromatography (hexanes) a total of 720 mg (49%) of **157a**/**157b** (1:1) as colorless oils. Compounds **157a**/**157b** were separable by column chromatography. Spectroscopic data for **157a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 1H), 6.27 (ddd, *J* = 0.5, 2.0, 3.0 Hz, 1 H), 6.19 (m, 1 H), 5.75 (dddd, *J* = 7.0, 10.5, 14.0, 17.5 Hz, 1 H), 5.69 (ddd, *J* = 7.0, 10.5, 17.0 Hz, 1 H), 5.04 (ddt, *J* = 1.5, 2.0, 17.0 Hz, 1 H), 4.99 (m, 1 H), 4.92 (ddd, *J* = 1.5, 2.0, 17.5 Hz, 1 H), 4.83 (ddd, *J* = 1.0, 2.0, 11.0 Hz, 1 H), 4.33 (t, *J* = 6.5 Hz, 1 H), 3.73 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.64–2.52 (m, 2 H), 0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 141.4, 137.6, 134.5, 117.0, 111.4, 109.9, 107.2, 76.0, 75.1, 38.0, -3.89. IR (neat) 3078, 2959, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 250.1381 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389]. Spectroscopic data for **157b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 1 H), 6.29 (dd, *J* = 2.0, 3.0 Hz, 1 H), 6.17 (dd, *J* = 1.0, 3.5 Hz, 1 H), 5.75 (m, 2 H), 5.05–4.95 (m, 4 H), 4.40 (t, *J* = 7.0 Hz, 1 H), 3.51 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.60 (m, 1 H), 2.52 (m, 1 H), -0.07 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 141.9, 137.3, 134.7, 116.7, 112.4, 109.7, 108.0, 73.1, 72.7, 39.4, -4.21. IR (neat) 3078, 2957, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 250.1379 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*Preparation of compounds **158a/158b***

Applying general procedure C to α-(trimethylsilyl)allyl alcohol (990 mg, 77.4% w/w in THF, 5.9 mmol, 1 equiv), **131** (2 g, 7.08 mmol, 1.2 equiv) and TMSOTf (5 μL, 0.027 mmol, 0.005 equiv) in hexane (33 mL) afforded after column chromatography (5% and 8% CH_2Cl_2 in hexanes) a total of 884 mg (60%) of **158a**/**158b** (1:1) as colorless oils. Compounds **158a**/**158b** were separable by column chromatography. Spectroscopic data for **158a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 1.8 Hz, 1H), 7.29 (m, 1H), 6.32 (m, 1H), 5.77–5.70 (m, 2H), 5.03–4.96 (m, 3H), 4.90 (dt, *J* = 1.8, 4.8 Hz, 1H), 4.37 (t, *J* = 6.0 Hz, 1H), 3.78 (dt, *J* = 1.2, 7.2 Hz, 1H), 2.50–2.40 (m, 2H), -0.018 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.6, 139.5, 137.8, 134.6, 127.5, 117.0, 111.9, 109.2, 75.0, 73.4, 39.6, -3.87. IR (neat) 3078, 2959, 1248, 1028, 841 cm^{-1}. HRMS (EI) *m*/*z* 250.1389 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389]. Spectroscopic data for **158b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 1H), 7.26 (m, 1H), 6.31 (m, 1H), 5.78 (dddd, *J* = 6.6, 10.2, 14.4, 17.4 Hz, 1H), 5.72 (m, 1H), 5.02–4.96 (m, 4H), 4.38 (t, *J* = 6.6 Hz, 1H), 3.52 (dt, *J* = 1.8, 6.6 Hz, 1H), 2.52 (m, 1H), 2.35 (m, 1H), -0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 140.5, 137.6, 135.2, 125.9, 116.5, 112.5, 108.9, 72.3, 71.0, 41.6, -4.08. IR (neat) 3079, 2959, 1248, 1022, 841 cm^{-1}. HRMS (EI) *m*/*z* 250.1383 [(M^+); calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*Preparation of compounds **161b/161a***

Applying general procedure D to trimethyl((1-(trimethylsilyl)allyl)oxy)silane (1 g, 4.95 mmol, 1 equiv), 4-(trifluoromethyl)benzaldehyde (862 mg, 4.95 mmol, 1 equiv), allyltrimethylsilane (625

mg, 4.95 mmol, 1 equiv) amd TMSOTf (180 μL, 0.989 mmol, 0.2 equiv) in CH_2Cl_2 (50 mL) for 30 minutes at -78 ^oC, afforded after workup and column chromatography (10% CH_2Cl_2 in hexanes) 765 mg of a mixture of **161b**/**161a** (4:1) as a colorless oil. Mixture of diastereomers (**161b**/**161a** = 0.8:0.2) ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1.6 H), 7.56 (d, *J* = 7.8 Hz, 0.4 H), 7.42 (d, *J* = 8.4 Hz, 0.4 H), 7.37 (d, *J* = 7.8 Hz, 1.6 H), 5.83–5.73 (m, 1.6 H), 5.71–5.64 (m, 0.4 H), 5.07 (m, 0.8 H), 5.03–4.98 (m, 2.8 H), 4.92 (dt, *J* = 1.8, 17.4 Hz, 0.2 H), 4.86 (dt, *J* = 1.8, 10.8 Hz, 0.2 H), 4.53 (dd, *J* = 6.6, 7.8 Hz, 0.8 H), 4.47 (t, *J* = 6.0 Hz, 0.2 H), 3.84 (dt, *J* = 1.8, 7.2 Hz, 0.2 H), 3.40 (d, *J* = 7.8 Hz, 0.8 H), 2.53 (m, 1 H), 2.46 (m, 0.2 H), 2.36 (m, 0.8 H), 0.09 (s, 1.8 H), 0.02 (s, 7.2 H). ^{13}C NMR (151 MHz, $CDCl_3$) mixture of diastereomers (**161b**/**161a** = 0.8:0.2) *anti*: δ 146.7, 137.2, 134.6, 129.6 (q, *J* = 32.3 Hz), 127.6 (2C), 125.1 (q, *J* = 3.78 Hz, 2 C), 124.3 (q, *J* = 272.0 Hz), 117.0, 113.4, 78.7, 73.5, 42.9, -4.0. *syn*: δ 147.7, 137.5, 134.0, 129.1 (q, *J* = 32.1 Hz), 126.8 (2C), 124.9 (q, *J* = 3.6 Hz, 2 C), CF_3 carbon could not be located, 117.5, 112.4, 80.3, 76.2, 41.3, -3.8. IR (film) 3080, 2959, 1325, 1128, 841 cm^{-1}. HRMS (EI) *m*/*z* 328.1457 [(M^+); calcd for $C_{17}H_{23}OSiF_3$, 328.1470].

*Preparation of compounds **162a/162b***

Applying general procedure D to trimethyl((1-(trimethylsilyl)allyl)oxy)silane (1 g, 4.95 mmol, 1 equiv), 4-nitrobenzaldehyde (750 mg, 4.95 mmol, 1 equiv), allyltrimethylsilane (640 mg, 4.95 mmol, 1 equiv) amd TMSOTf (180 μL, 0.989 mmol, 0.2 equiv) in CH_2Cl_2 (50 mL) for 50 minutes at -78 ^oC, afforded after workup and column chromatography (30% CH_2Cl_2 in hexanes)

878 mg of a mixture of **162b**/**162a** (4.5:1) as a colorless oil. Mixture of diastereomers (**162b**/**162a** = 1.0:0.2) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 2 H), 8.14 (d, *J* = 9.0 Hz, 0.4 H), 7.43 (d, *J* = 8.5 Hz, 0.4 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 5.73 (m, 2 H), 5.63 (m, 0.4 H), 5.04 (d, *J* = 10.5 Hz, 1 H), 4.96 (m, 3.4 H), 4.92–4.82 (m, 0.4 H), 4.56 (t, *J* = 6.5 Hz, 1 H), 4.48 (t, *J* = 6.0 Hz, 0.2 H), 3.82 (d, *J* = 7.5 Hz, 0.4 H), 3.34 (d, *J* = 7.5 Hz, 1 H), 2.54–2.44 (m, 1.4 H), 2.34 (m, 1 H), 0.05 (s, 1.8 H), -0.02 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) **162b** (major): δ 150.1, 147.4, 136.9, 134.0, 127.9 (2 C), 123.4 (2 C), 117.4, 113.6, 78.5, 74.0, 42.7, -4.1. **162a** (minor): δ 151.2, 146.9, 137.2, 133.4, 127.2 (2 C), 123.2 (2 C), 117.8, 112.7, 79.9, 76.5, 41.0, -3.9. IR (film) 3060, 2959, 1528, 1348, 1074, 814 cm^{-1}. HRMS (EI) *m*/*z* 305.1441 [(M^{+}); calcd for $C_{16}H_{23}NO_3Si$, 305.1447].

*Preparation of compounds **163a/163b***

Applying general procedure D to trimethyl((1-(trimethylsilyl)allyl)oxy)silane (1 g, 4.95 mmol, 1 equiv), cyclohexane carboxaldehyde (611 mg, 5.445 mmol, 1.1 equiv), allyltrimethylsilane (622 mg, 5.445 mmol, 1.1 equiv) amd TMSOTf (180 μL, 0.989 mmol, 0.2 equiv) in CH_2Cl_2 (50 mL) for 2 hours at -78 ^{o}C, afforded after workup and column chromatography (hexanes) 1.32 g of a mixture of **163b**/**163a** (3.4:1) as a colorless oil. Compounds **163b**/**163a** were partially separated by column chromatography. Spectroscopic data for **163a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82-5.69 (m, 2 H), 5.03-4.95 (m, 4 H), 3.69 (dt, *J* = 1, 8.5 Hz, 1 H), 3.16 (dt, *J* = 4.5, 6 Hz, 1 H), 2.28-2.14 (m, 2 H), 1.85 (m, 1 H), 1.70 (m, 2 H), 1.63-1.56 (m, 3 H), 1.38 (m, 1 H), 1.20-0.98

(m, 4 H), -0.01 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 135.6, 116.1, 112.9, 80.0, 73.4, 40.7, 33.8, 29.5, 28.3, 26.8, 26.5, 26.4, -3.9. IR (film) 2959, 1325, 1128, 841 cm^{-1}. HRMS (EI) *m*/*z* 266.2062 [(M^+); calcd for $C_{16}H_{30}OSi$, 266.2066]. Spectroscopic data for **163b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86-5.74 (m, 2 H), 5.x00-4.92 (m, 4 H), 3.62 (dt, *J* = 1, 8.5 Hz, 1 H), 3.13 (dt, *J* = 4, 6 Hz, 1 H), 2.16 (tt, *J* = 1, 6.5 Hz, 1 H), 1.72 (m, 2 H), 1.63 (m, 3 H), 1.47 (m, 1 H), 1.26-0.97 (m, 5 H), -0.005 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 136.9, 115.6, 112.3, 82.4, 75.4, 40.4, 35.9, 28.7, 28.2, 26.9, 26.7, 26.6, -3.9. IR (film) 2955, 1128, 839 cm^{-1}. HRMS (EI) *m*/*z* 266.2058 [(M^+); calcd for $C_{16}H_{30}OSi$, 266.2066].

*Preparation of compounds **164a/164b***

To a solution of **164a**/**164b** (1:1, 342 mg, 1.01 mmol, 1 equiv) in THF (2.2 mL) was added *S*-Phos (4.2 mg, 0.02 mmol, 0.02 equiv), phenylboronic acid (184 mg, 1.512 mmol, 1.5 equiv) and $K_2PO_3{}^{\cdot}2H_2O$ (500 mg, 2.016 mmol, 2 equiv). The mixture was degassed with 3 freeze-pump-thaw cycles and then $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 0.01 equiv) was added at room temperature. The mixture was stirred at room temperature under nitrogen atmosphere and the reaction monitored by TLC (hexanes). After 9 hours the reaction was concentrated and the residue subjected to column chromatography (10% CH_2Cl_2 in hexanes) to afford a total of 327 mg (53%) of **164a**/**164b** (1:1) that were partially separated. Spectroscopic data for **164a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (m, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.43 (t, *J* = 7.2 Hz, 2 H), 7.37 (d, *J*

= 8.4 Hz, 2 H), 7.33 (tt, *J* = 1.2, 7.2 Hz, 1 H), 5.77 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.72 (ddd, *J* = 7.2. 10.8, 18.0 Hz, 1 H), 5.04–4.98 (m, 2 H), 4.96 (dt, *J* = 1.8, 16.8 Hz, 1 H), 4.87 (dt, *J* = 1.8, 10.8 Hz, 1 H), 4.45 (t, *J* = 6.0 Hz, 1 H), 3.85 (dt, *J* = 1.2, 7.2 Hz, 1 H), 2.57 (m, 1 H), 2.49 (m, 1 H), 0.09 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 141.1, 139.7, 137.9, 134.8, 128.7 (2 C), 127.04, 127.02 (2 C), 126.97 (2 C), 126.6 (2 C), 116.9, 112.0, 80.6, 75.7, 41.4, -3.7. IR (film) 3077, 2957, 1250, 840 cm^{-1}. HRMS (EI) *m*/*z* 336.1923 [(M^+); calcd for $C_{22}H_{28}OSi$, 336.1909]. Spectroscopic data for **164b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 2 H), 7.56 (d, *J* = 7.8 Hz, 2 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.33 (m, 3 H), 5.85 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.77 (ddd, *J* = 7.8, 10.8, 18.0 Hz, 1 H), 5.07–5.00 (m, 4 H), 4.50 (dd, *J* = 5.4, 7.8 Hz, 1 H), 3.49 (d, *J* = 7.2 Hz, 1 H), 2.58 (m, 1 H), 2.40 (m, 1 H), 0.01 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.6, 140.9, 140.2, 137.6, 135.4, 128.7 (2 C), 127.7 (2 C), 127.2, 127.0 (2 C), 126.8 (2 C), 116.5, 112.9, 78.9, 72.9, 43.1, -3.9. IR (film) 3077, 2957, 1247, 840 cm^{-1}. HRMS (EI) *m*/*z* 336.1920 [(M^+); calcd for $C_{22}H_{28}OSi$, 336.1909].

*Preparation of compound **165***

A solution of 2-butyn-1-ol (3 g, 42.8 mmol, 1 equiv) in THF (150 mL) at -78 °C was slowly added *n*-BuLi (1.6 M in hexanes, 31 mL, 46.2 mmol, 1.08 equiv). After 30 minutes trimethylsilyl chloride (5 g, 46.2 mmol, 1.08 equiv) was added and the mixture stirred at the same temperature for 1 hour. Then, *t*-BuLi (1.7 M in pentane, 31 mL, 51.3 mmol, 1.2 equiv) was added dropwise over ~1 hour, and the yellow mixture was stirred at -78 °C for 3 hours. Trimethylsilyl chloride (6.93 g, 64.2 mmol, 1.5 equiv) was added slowly (5 minutes) and the mixture stirred at -78 °C

for 1 hour and at room temperature for 1 hour. The reaction was cooled down at -78 ^{o}C and quenched with $NaHCO_{3\ (sat)}$ (50 mL) and the mixture immediately diluted with Et_2O (100 mL). The aqueous phase was extracted with Et_2O (3 × 50 mL). Combined organic extracts were washed with brine and dried over $MgSO_4$. Column chromatography (2% EtOAc in hexanes) afforded 6.4 g (70%) of **165** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (q, *J* = 2.5 Hz, 1 H), 1.83 (d, *J* = 2.5 Hz, 3 H), 0.11 (s, 9 H), 0.05 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 82.4, 79.4, 56.5, 3.9, 0.0, -4.2.

*Preparation of compounds **166a/166b***

Applying general procedure D to compound **165** (1 g, 4.66 mmol, 1 equiv), benzaldehyde (544 mg, 5.13 mmol, 1.1 equiv), allyltrimethylsilane (586 mg, 5.13 mmol, 1.1 equiv) amd TMSOTf (170 μL, 0.932 mmol, 0.2 equiv) in CH_2Cl_2 (47 mL) for 1 hour at -78 ^{o}C, afforded after workup and column chromatography (1% EtOAc in hexanes) 1.08 g (90%) of a mixture of **166b**/**166a** (1.6:1) as a yellowish oil. Compounds **166b**/**166a** were partially separated by column chromatography. Spectroscopic data for **166a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4 H), 7.21 (tt, *J* = 1.5, 7 Hz, 1 H), 5.72 (dddd, *J* = 7, 10, 14, 17 Hz, 1 H), 4.98 (m, 2 H), 4.56 (t, *J* = 6 Hz, 1 H), 3.86 (q, *J* = 2.5 Hz, 1 H), 2.57-2.44 (m, 2 H), 1.70 (d, *J* = 3 Hz, 3 H), 0.12 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 134.6, 127.8, 126.9, 126.7, 116.9, 83.4, 81.1, 77.6, 62.3, 40.7, 3.7, -3.7. IR (neat) 3072, 3030, 2959, 2363, 2335, 1641, 1452, 1248, 1057, 843 cm^{-1}. HRMS (EI) *m*/*z* 272.1594 [(M^{+}); calcd for $C_{17}H_{24}OSi$, 272.1596]. Spectroscopic data for **166b**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.25 (m, 3 H), 5.75 (dddd, *J* = 7, 10.5, 14, 17.5 Hz, 1 H), 5.01-4.93 (m, 2 H), 4.67 (t, *J* = 7 Hz, 1 H), 3.45 (q, *J* = 2.5 Hz, 1 H), 2.54 (m, 1 H), 2. 36 (m, 1 H), 1.87 (d, *J* = 2.5 Hz, 3 H), 0.05 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 135.2, 128.1, 127.4, 127.3, 116.2, 82.8, 79.8, 77.3, 60.3, 42.6, 3.9, -4. IR (neat) 3076, 2959, 2361, 2336, 1653, 1539, 1456, 1248, 844 cm^{-1}. HRMS (EI) *m/z* 272.1590 [(M^{+}); calcd for $C_{17}H_{24}OSi$, 272.1596].

*Preparation of compounds **167** and **168***

Applying general procedure H to **20b** (67.2 mg, 0.289 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 0.65 mL, 3 equiv) at -78 ^{o}C for 3 hours afforded, after workup and column chromatography (5% and 10% EtOAc in hexanes) 40.4 mg (60%) of **167** (dr > 20:1) and 19.2 mg (29%) of **168** (dr > 20:1) as colorless oils. Spectroscopic data for **167**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06-7.27 (m, 5 H), 2.68 (dd, *J* = 6.3, 16.8 Hz, 2 H), 1.65 (dt, *J* = 5.1, 9.3 Hz, 1 H), 1.31 (m, 1 H), 1 (m, 1 H), 0.76 (m, 1 H), 0.2 (s, 9 H). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 247.2, 142.8, 129.1, 128.2, 125.9, 125.5, 53.1, 22.7, 16.7, 15.7, -3.1. IR (film) 3028, 2959, 1711, 1643, 1604, 1496, 1250, 846 cm^{-1}. HRMS (ESI) *m/z* 233.1362 [$(M+H)^{+}$ calcd for $C_{14}H_{21}OSi$, 233.1362]. Spectroscopic data for **168**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.31 (m, 3 H), 7.38 (m, 2 H), 5.98 (dddd, *J* = 1.8, 2.7, 4.8, 5.7 Hz, 1 H), 5.76 (dddd, *J* = 1.5, 2.1, 3.6, 5.7 Hz, 1 H), 3.43 (dd, *J* = 8.4, 10.5 Hz, 1 H), 2.57-2.79 (m, 2 H), 1.48 (s, 1 H), -0.31 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 137.3, 130.6, 128.5, 128.17, 126.7, 84.4, 60, 35.4, -3.5. IR (neat) 3441,

3059, 2955, 2928, 2856, 1496, 1452, 1246 cm^{-1}. HRMS (ES) *m/z* 215.1244 [$(M\text{-}OH)^+$ calcd for $C_{14}H_{19}Si$, 215.1256].

*Preparation of compounds **169a**/**169b***

Applying general procedure E to **134a**/**134b** (2:1 ratio, 280 mg, 0.964 mmol, 1 equiv) and 2nd generation Grubbs catalyst (33 mg, 0.039 mmol, 0.04 equiv) in CH_2Cl_2 (10 mL) for 3 hours afforded after column chromatography (25% CH_2Cl_2 in hexanes and 7% EtOAc in hexanes) 153 mg (62%) of **169a** and 82 mg (31%) of **169b** as colorless oils. Spectroscopic data for **169a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 1.8, 7.8 Hz, 1 H), 7.23 (t, *J* = 8.4 Hz, 1 H), 6.95 (tt, *J* = 0.6, 7.2 Hz, 1 H), 6.85, (d, *J* = 8.4 Hz, 1 H), 5.82 (m, 2 H), 5.02 (dd, *J* = 4.2, 8.4 Hz, 1 H), 4.14 (m, 1 H), 3.81 (s, 3 H), 2.29 (m, 2 H), 0.09 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 131.0, 128.2, 127.8, 127.0, 120.9, 120.6, 110.3, 72.3, 67.0, 55.3, 30.7, -2.7. IR (film) 1493, 1248, 1049, 839 cm^{-1}. HRMS (EI) *m/z* 262.1388 [(M^+); calcd for $C_{15}H_{22}O_2Si$, 262.1389]. Spectroscopic data for **169b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 1.8, 7.8 Hz, 1 H), 7.21 (dt, *J* = 1.8, 7.8 Hz, 1 H), 6.98 (dt, *J* = 1.2, 7.8 Hz, 1 H), 6.83 (d, *J* = 1.2, 7.8 Hz, 1 H), 5.80 (m, 2 H), 4.72 (dd, *J* = 2.4, 10.2 Hz, 1 H), 4.16 (m, 1 H), 3.80 (s, 3 H), 2.35 (m, 1 H), 1.98 (m, 1 H), 0.10 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 132.7, 127.7, 127.6, 126.1, 121.7, 120.8, 109.9, 71.4, 70.0, 55.3, 32.9, -3.9. IR (film) 1493, 1248, 1049, 841 cm^{-1}. HRMS (EI) *m/z* 262.1382 [(M^+); calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*Preparation of compounds **170a***

Applying general procedure E to **135a** (95.9 mg, 0.33 mmol, 1 equiv) and 2nd generation Grubbs catalyst (9.8 mg, 0.012 mmol, 0.035 equiv) in CH_2Cl_2 (3.5 mL) for 3 hours afforded after column chromatography (35% CH_2Cl_2 in hexanes) 74 mg (86%) of **170a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (m, 1 H), 6.94 (m, 2 H), 6.79 (m, 1 H), 5.79 (m, 2 H), 4.69 (t, *J* = 5.5 Hz, 1 H), 4.03 (m, 1 H), 3.79 (s, 3 H), 2.39 (m, 2 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 143.9, 129.2, 128.1, 120.0, 118.9, 112.6, 112.3, 72.3, 70.2, 55.2, 30.3, -2.9. IR (film) 1248, 1051, 841 cm^{-1}. HRMS (EI) *m*/*z* 262.1400 [(M^+); calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*Preparation of compounds **170b***

Applying general procedure E to **135b** (109 mg, 0.375 mmol, 1 equiv) and 2nd generation Grubbs catalyst (17.7 mg, 0.021 mmol, 0.04 equiv) in CH_2Cl_2 (5.5 mL) for 3 hours afforded after column chromatography (30% CH_2Cl_2 in hexanes) 91 mg (92%) of **170b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.0 Hz, 1 H), 6.92 (m, 2 H), 6.78 (ddd, *J* = 0.5, 2.5, 8.0 Hz, 1 H), 5.79 (m, 2 H), 4.37 (dd, *J* = 3.0, 10.0 Hz, 1 H), 4.15 (m, 1 H), 3.79 (s, 3 H), 2.23 (m, 1 H), 2.15 (m, 1 H), 0.08 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 145.8, 129.1, 128.0, 121.1, 118.0, 112.2, 111.4, 75.2, 71.6, 55.1, 34.1, -4.0. IR (film) 1248, 1049, 841 cm^{-1}. HRMS (EI) *m*/*z* 262.1394 [(M^+); calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*Preparation of compounds **171a***

Applying general procedure E to **136a** (155 mg, 0.534 mmol, 1 equiv) and 2nd generation Grubbs catalyst (14 mg, 0.016 mmol, 0.03 equiv) in CH_2Cl_2 (6 mL) for 3 hours afforded after column chromatography (35% CH_2Cl_2 in hexanes) 126 mg (90%) of **171a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 9.0 Hz, 2 H), 6.87 (d, *J* = 9.0 Hz, 1 H), 5.80 (m, 2 H), 4.70 (t, *J* = 5.0 Hz, 1 H), 3.98 (m, 1 H), 3.79 (s, 3 H), 2.40 (m, 2 H), 0.10 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 134.2, 128.1, 127.9, 120.0, 113.6, 71.9, 69.6, 55.2, 30.0, -3.0. IR (film) 1513, 1248, 1038, 840 cm^{-1}. HRMS (EI) *m*/*z* 262.1403 [(M^+); calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*Preparation of compounds **171b***

Applying general procedure E to **136b** (149 mg, 0.513 mmol, 1 equiv) and 2nd generation Grubbs catalyst (17.4 mg, 0.021 mmol, 0.04 equiv) in CH_2Cl_2 (6 mL) for 3 hours afforded after column chromatography (25% CH_2Cl_2 in hexanes) 122 mg (91%) of **171b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2 H), 6.87 (m, 2 H), 5.79 (m, 2 H), 4.34 (dd, *J* = 4.0, 9.0 Hz, 1 H), 4.16 (m, 1 H), 3.79 (s, 3 H), 2.18 (m, 2 H), 0.08 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 136.3, 128.1, 126.9, 121.2, 113.5, 75.0, 71.7, 55.2, 34.1, -4.0. IR (film) 1248, 1072, 1039, 841 cm^{-1}. HRMS (EI) *m*/*z* 262.1390 [(M^+); calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*Preparation of compounds **172a/172b***

Applying general procedure E to **137a**/**137b** (2:1 ratio, 234 mg, 0.8526 mmol, 1 equiv) and 2nd generation Grubbs catalyst (29 mg, 0.034 mmol, 0.04 equiv) in CH_2Cl_2 (9 mL) for 3 hours afforded after column chromatography (15% CH_2Cl_2 in hexanes and 5% EtOAc in hexanes) 114 mg (62%) of **169a** and 79 mg (30%) of **169b** as colorless oils. Spectroscopic data for **169a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 1 H), 7.19 (m, 3 H), 5.90 (m, 1 H), 5.82 (dq, *J* = 2.0, 10.0 Hz, 1 H), 4.99 (t, *J* = 5.0 Hz, 1 H), 3.82 (quintet, *J* = 3.0 Hz, 1 H), 2.54–2.46 (m, 1 H), 2.42 (s, 3 H), 2.40–2.34 (m, 2 H), 0.11 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 136.3, 130.3, 128.2, 127.2, 126.6, 125.5, 120.4, 69.7 (d, *J* = 5.8 Hz), 68.5 (d, *J* = 3.2 Hz), 29.5, 19.4 (d, *J* = 1.4 Hz,), -3.3. IR (film) 3028, 2955, 1247, 1052, 840 cm^{-1}. HRMS (EI) *m*/*z* 246.1444 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **169b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 7.17 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.13 (d, *J* = 7.0 Hz, 1 H), 5.84 (m, 2 H), 4.56 (dd, *J* = 4.5, 8.5 Hz, 1 H), 4.20 (m, 1 H), 2.35 (s, 3 H), 2.22 (m, 2 H), 0.12 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 134.6, 130.0, 128.0, 126.8, 126.1, 125.6, 121.5, 73.1 (d, *J* = 3.9 Hz, 1 H), 71.8, 32.4, 19.2, -3.9. IR (film) 3027, 2957, 1247, 1072, 843 cm^{-1}. HRMS (EI) *m*/*z* 246.1436 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compounds **173a/173b***

Applying general procedure E to **138a**/**138b** (~2:1 ratio, 228 mg, 0.8307 mmol, 1 equiv) and 2nd generation Grubbs catalyst (24.8 mg, 0.029 mmol, 0.035 equiv) in CH_2Cl_2 (9 mL) for 3 hours afforded after column chromatography (15% CH_2Cl_2 in hexanes and 5% EtOAc in hexanes) 120 mg (59%) of **173a** and 60 mg (29%) of **173b** as colorless oils. Spectroscopic data for **173a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.8 Hz, 1 H), 7.19 (m, 2 H), 7.09 (d, *J* = 7.8 Hz, 1 H), 5.81 (m, 2 H), 4.69 (t, *J* = 6.0 Hz, 1 H), 4.07 (m, 1 H), 2.39 (m, 2 H), 2.36 (s, 3 H), 0.12 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 137.8, 128.09, 128.06, 128.0, 127.2, 123.6, 120.1, 72.5, 70.4, 30.5, 21.5, -2.9. IR (film) 3028, 2917, 1247, 1055, 840 cm^{-1}. HRMS (EI) *m*/*z* 246.1440 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **173b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.8 Hz, 1 H), 7.18 (m, 2 H), 7.06 (d, *J* = 7.8 Hz, 1 H), 5.83 (m, 2 H), 4.38 (dd, *J* = 3.0, 9.6 Hz, 1 H), 4.19 (m, 1 H), 2.37 (s, 3 H), 2.27–2.17 (m, 2 H), 0.12 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 128.1 (2 C), 127.7, 126.4, 122.7, 121.2, 75.5, 71.6, 34.1, 21.5, -3.9. IR (film) 3028, 2917, 1247, 1074, 873 cm^{-1}. HRMS (EI) *m*/*z* 246.1436 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compounds **174a/174b***

Applying general procedure E to **139a**/**139b** (~1.15:1 ratio, 228.8 mg, 0.834 mmol, 1 equiv) and 2nd generation Grubbs catalyst (28.3 mg, 0.033 mmol, 0.04 equiv) in CH_2Cl_2 (9 mL) for 3 hours afforded after column chromatography (10% CH_2Cl_2 in hexanes and 6% EtOAc in hexanes) 108

mg (53%) of **174a** and 88 mg (43%) of **174b** as colorless oils. Spectroscopic data for **174a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.5 Hz, 2 H), 7.14 (d, *J* = 8 Hz, 2 H), 5.83–5.76 (m, 2 H), 4.71 (t, *J* = 5.5 Hz, 1 H), 4.00 (m, 1 H), 2.39 (m, 2 H), 2.33 (s, 3 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 136.8, 128.9 (2 C), 128.1, 126.6 (2 C), 120.1, 72.2, 69.8, 30.1, 21.1, -2.9. IR (film) 3028, 2955, 1248, 1053, 841 cm^{-1}. HRMS (EI) *m*/*z* 246.1452 [(M^{+}); calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **174b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 5.82–5.77 (m, 2 H), 4.36 (dd, *J* = 4.0, 9.5 Hz, 1 H), 4.15 (m, 1 H), 2.33 (s, 3 H), 2.24–2.13 (m, 2 H), 0.08 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 136.5, 128.8 (2 C), 128.1, 125.6 (2 C), 121.2, 75.3, 71.6, 34.1, 21.1, -4.0. IR (film) 3028, 2957, 1248, 1072, 858, 841 cm^{-1}. HRMS (EI) *m*/*z* 246.1440 [(M^{+}); calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compounds **175a***

Applying general procedure E to **140a** (95 mg, 0.341 mmol, 1 equiv) and 2nd generation Grubbs catalyst (11.6 mg, 0.014 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) for 3 hours afforded after column chromatography (30% CH_2Cl_2 in hexanes) 75.2 mg (88%) of **175a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.5, 9.0 Hz, 2 H), 7.01 (t, *J* = 9.0 Hz, 2 H), 5.79 (m, 2 H), 4.70 (t, *J* = 5.5 Hz, 1 H), 3.98 (m, 1 H), 2.44–2.32 (m, 2 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 247.1 Hz), 137.7 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 8.0 Hz, 2 C), 128.2, 119.8,

114.9 (d, *J* = 21.2 Hz, 2 C), 71.6, 69.8, 30.1, -3.0. IR (film) 3030, 2957, 2899, 1510, 1248, 1055, 841 cm^{-1}. HRMS (EI) *m*/*z* 250.1177 [(M^+); calcd for $C_{14}H_{19}OSiF$, 250.1189].

*Preparation of compounds **175b***

Applying general procedure F to **140b** (93 mg, 0.334 mmol, 1 equiv) and 2nd generation Grubbs catalyst (11.3 mg, 0.013 mmol, 0.04 equiv) in benzene (4.2 mL) for 1 hour at 80 °C afforded after column chromatography (10% CH_2Cl_2 in hexanes) 77.5 mg (93%) of **175b** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.00 (m, 2 H), 5.80 (m, 2 H), 4.37 (dd, *J* = 3.5,10.0 Hz, 1 H), 4.17 (m, 1 H), 2.21 (m, 1 H), 2.13 (m, 1 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, *J* = 244.9 Hz), 139.8 (d, *J* = 3.5 Hz), 128.1, 127.2 (d, *J* = 7.9 Hz, 2 C), 121.0, 114.9 (d, *J* = 21.2 Hz, 2 C), 74.8, 71.7, 34.2, -4.0. IR (film) 3030, 2959, 2775, 1512, 1248, 839 cm^{-1}. HRMS (EI) *m*/*z* 250.1183 [(M^+); calcd for $C_{14}H_{19}OSiF$, 250.1189].

*Preparation of compounds **176a**/**176b***

Applying general procedure E to **141a**/**141b** (~1:1.4 ratio, 210 mg, 0.746 mmol, 1 equiv) and 2nd generation Grubbs catalyst (25.3 mg, 0.03 mmol, 0.04 equiv) in CH_2Cl_2 (8 mL) for 3 hours afforded after column chromatography (10% and 25% CH_2Cl_2 in hexanes) 75.5 mg (38%) of **176a** and 105.6 mg (53%) of **176b** as colorless oils. Spectroscopic data for **176a**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 4 H), 5.78 (m, 2 H), 4.71 (dd, *J* = 5.0, 10.0 Hz, 1 H), 3.97 (m, 1 H),

2.42 (m, 1 H), 2.34 (m, 1 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 132.9, 128.3 (2 C), 128.2, 128.0 (2 C), 119.7, 71.6, 69.7, 30.0, -3.0. IR (film) 3030, 2956, 1492, 1248, 1090, 1055, 1015, 841 cm^{-1}. HRMS (EI) *m*/*z* 266.0890 [(M^+); calcd for $C_{14}H_{19}OSiCl$, 266.0894]. Spectroscopic data for **176b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 4 H), 5.81 (m, 2 H), 4.37 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.17 (m, 1 H), 2.22 (m, 1 H), 2.12 (m, 1 H), 0.10 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 132.6, 128.2 (2 C), 128.1, 127.0 (2 C), 120.9, 74.7, 71.7, 34.0, -4.0. IR (film) 3030, 2957, 2896, 1490, 1248, 1088, 1073, 1014, 841 cm^{-1}. HRMS (EI) *m*/*z* 266.0883 [(M^+); calcd for $C_{14}H_{19}OSiCl$, 266.0894].

*Preparation of compounds **177a**/**177b***

Applying general procedure E to **166a**/**166b** (~1:4.1 ratio, 296 mg, 0.904 mmol, 1 equiv) and 2nd generation Grubbs catalyst (31 mg, 0.036 mmol, 0.04 equiv) in CH_2Cl_2 (9.5 mL) for 3 hours afforded after column chromatography (10% and 25% CH_2Cl_2 in hexanes) 50 mg (18%) of **177a** and 201 mg (74%) of **177b** as colorless oils. Spectroscopic data for **177a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 5.80 (m, 2 H), 4.77 (t, *J* = 5.0 Hz, 1 H), 4.01 (m, 1 H), 2.46 (m, 1 H), 2.36 (m, 1 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 129.4 (q, *J* = 32.1 Hz), 128.3, 126.8 (2 C), 125.1 (q, *J* = 3.9 Hz, 2 C), 124.3 (q, *J* = 270.8 Hz), 119.6, 71.7, 70.0, 30.1, -3.1. IR (neat) 1325, 1250, 1126, 1068, 839 cm^{-1}. HRMS (EI) *m*/*z* 300.1151 [(M^+); calcd for $C_{15}H_{19}OSiF_3$, 300.1157]. Spectroscopic data for **177b**: ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.0 Hz, 1 H), 5.87–5.79 (m, 2 H), 4.46 (dd, *J* = 3.0, 10.0 Hz, 1 H), 4.19 (m, 1 H), 2.27 (m, 1 H), 2.14 (m, 1 H), 0.12 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 129.2 (q, *J* = 38.4 Hz), 128.1, 125.9 (2 C), 125.1 (q, *J* = 4.7 Hz, 2 C), 124.3 (q, *J* = 324.3 Hz), 120.7, 74.9, 71.7, 34.0, -4.1. IR (neat) 1325, 1250, 1165, 1126, 1068, 841 cm^{-1}. HRMS (EI) *m*/*z* 300.1157 [(M^+); calcd for $C_{15}H_{19}OSiF_3$, 300.1157].

*Preparation of compounds **178a/178b***

Applying general procedure E to **164a**/**164b** (~2:1 ratio, 161 mg, 0.478 mmol, 1 equiv) and 2nd generation Grubbs catalyst (16.2 mg, 0.0191 mmol, 0.04 equiv) in CH_2Cl_2 (5 mL) for 3 hours afforded after column chromatography (15% and 35% CH_2Cl_2 in hexanes) 24.6 mg (17%) of **178a** and 67 mg (46%) of **178b** as colorless oils. Spectroscopic data for **178a**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 4 H), 7.44 (m, 4 H), 7.33 (m, 1 H), 5.83 (m, 2 H), 4.79 (t, *J* = 6.0 Hz, 1 H), 4.06 (m, 1 H), 2.45 (m, 2 H), 0.12 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 141.0, 140.1, 128.7 (2 C), 128.2, 127.1, 127.08 (2 C), 127.05 (2 C), 126.97 (2 C), 120.0, 72.1, 70.0, 30.2, -2.9. IR (film) 3028, 2955, 1248, 1070, 841 cm^{-1}. HRMS (EI) *m*/*z* 308.1584 [(M^+); calcd for $C_{20}H_{24}OSi$, 308.1596]. Spectroscopic data for **178b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (m, 4 H), 7.44 (m, 4 H), 7.43 (m, 1 H), 5.85 (m, 2 H), 4.47 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.22 (s, 1 H), 2.33–2.20 (m, 2 H), 0.12 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 141.1, 139.9, 128.7

(2 C), 128.1, 127.1 (3 C), 126.9 (2 C), 126.1 (2 C), 121.1, 75.2, 71.7, 34.1, -4.0. IR (film) 3030, 2957, 1246, 1070, 841 cm^{-1}. HRMS (EI) *m/z* 308.1594 [(M^+); calcd for $C_{20}H_{24}OSi$, 308.1596].

*Preparation of compounds **179a***

Applying general procedure F to **143a** (102 mg, 0.328 mmol, 1 equiv) and 2nd generation Grubbs catalyst (11.2 mg, 0.013 mmol, 0.04 equiv) in benzene (4.1 mL) for 1 hour at 80 °C afforded after column chromatography (40% CH_2Cl_2 in hexanes) 83.4 mg (90%) of **179a** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (m, 4 H), 7.54 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.45 (m, 2 H), 5.87 (m, 1 H), 5.81 (m, 1 H), 4.91 (t, *J* = 6.0 Hz, 1 H), 4.04 (quintet, *J* = 3.0 Hz, 1 H), 2.52 (m, 2 H), 0.12 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 133.2, 132.8, 128.2, 128.0, 127.9, 127.6, 125.9, 125.7, 125.2, 125.1, 120.0, 72.5, 69.9, 30.2, -3.0. IR (film) 3028, 2955, 2897, 1248, 841 cm^{-1}. HRMS (EI) *m/z* 282.1436 [(M^+); calcd for $C_{18}H_{22}OSi$, 282.1440].

*Preparation of compounds **179b***

Applying general procedure F to **143b** (110 mg, 0.3543 mmol, 1 equiv) and 2nd generation Grubbs catalyst (12 mg, 0.014 mmol, 0.04 equiv) in benzene (4.4 mL) for 1 hour at 80 °C afforded after column chromatography (10% CH_2Cl_2 in hexanes) 93 mg (93%) of **179b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 4 H), 7.48 (dd, *J* = 1.5, 8.5 Hz, 1 H), 7.44 (m, 2 H), 5.84 (m, 2 H), 4.56 (dd, *J* = 3.5, 9.5 Hz, 1 H), 4.23 (m, 1 H), 2.34–2.22 (m, 2 H), 0.12 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 133.3, 132.8, 128.1, 127.9, 127.8, 127.6, 125.8,

125.5, 124.3, 124.1, 121.1, 75.5, 71.7, 34.0, -4.0. IR (film) 3028, 2957, 2772, 1246, 1072, 841 cm^{-1}. HRMS (EI) *m/z* 267.1217 $[(M-CH_3)^+$; calcd for $C_{17}H_{19}OSi$, 267.1205].

*Preparation of compounds **180** and **181***

Applying general procedure H to **169b** (76 mg, 0.2896 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 0.62 mL, 3 equiv) at -78 ^oC for 3 hours afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 35.5 mg (47%) of **180** (dr = 18:1) as a colorless oil and 29.6 mg (39%) of **181** (dr > 20:1) as a white solid. Spectroscopic data for **180**: ^1H NMR (600 MHz, $CDCl_3$) δ 6.92 (ddd, *J* = 2.4, 7.2, 8.4 Hz, 1 H), 6.66 (m, 2 H), 6.62 (d, *J* = 8.4 Hz, 1 H), 2.84 (dd, A of ABX system, *J* = 6.0, 16.8 Hz, 1 H), 2.53 (dd, B of ABX system, *J* = 7.2, 16.8 Hz, 1 H), 1.91 (dt, *J* = 4.8, 8.4 Hz, 1 H), 1.30 (m, 1 H), 0.91 (dt, *J* = 5.4, 8.4 Hz, 1 H), 0.72 (dt, *J* = 5.4, 9.0 Hz, 1 H), 0.19 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.6, 158.0, 130.9, 126.4, 125.2, 120.5, 110.1, 55.4, 53.3, 16.7, 15.3, 14.7, -3.2. IR (film) 2955, 1645, 1248, 1047, 843 cm^{-1}. HRMS (ESI) 263.1464 $[(M+H)^+$ calcd for $C_{15}H_{23}O_2Si$, 263.1467]. Spectroscopic data for **181**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 1.8, 7.8 Hz, 1 H), 7.23 (m, 1 H), 6.97 (dt, *J* = 0.6, 7.8 Hz, 1 H), 6.88 (dd, *J* = 1.2, 8.4 Hz, 1 H), 5.90 (m, 1 H), 5.74 (m, 1 H), 3.87 (s, 1 H, OMe), 3.87 (m, 1 H, overlapped with OMe), 3.84 (s, 1 H), 2.83 (m, A of ABX system, 1 H), 2.54 (dddd, B of ABX system, *J* = 1.2, 3.0, 8.4, 15.6 Hz, 1 H), -0.31 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 136.9, 129.2, 128.7, 127.9, 127.7, 121.1, 110.6, 84.0, 55.6, 52.7, 35.3, -3.9. mp = 46–47 ^oC. HRMS (ESI) 245.1357 $[(M-OH)^+$ calcd for $C_{15}H_{21}OSi$, 245.1362].

*Preparation of compounds **182** and **183***

Applying general procedure G to **170a** (70.4 mg, 0.268 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.2 mL, 1.2 equiv) at -78 ^{o}C for 10 minutes afforded, after workup and column chromatography (5% and 10% EtOAc in hexanes) 22.9 mg (33%) of **182** (dr = 17:1) and 31.1 mg (44%) of **183** (dr > 20:1) as colorless oils. Spectroscopic data for **182**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 8.0 Hz, 1 H), 6.66 (m, 2 H), 6.60 (m, 1 H), 2.74 (dd, A of ABX system, *J* = 6.5, 17.0 Hz, 1 H), 2.57 (dd, B of ABX system, *J* = 7.0, 17.0 Hz, 1 H), 1.62 (dt, *J* = 5.0, 8.5 Hz, 1 H), 1.31 (m, 1 H), 0.97 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.74 (dt, *J* = 5.5, 9.0 Hz, 1 H), 0.19 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.1, 159.7, 144.6, 129.2, 118.4, 111.7, 110.9, 55.1, 53.1, 22.8, 16.8, 15.8, -3.2. IR (film) 2957, 1645, 1250, 1157, 1047, 844 cm^{-1}. HRMS (ESI) 263.1467 [$(M+H)^{+}$ calcd for $C_{15}H_{23}O_2Si$, 263.1467]. Spectroscopic data for **183**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.5 Hz, 1 H), 6.97 (m, 2 H), 6.77 (m, 1 H), 5.96 (m, 1 H), 5.76 (m, 1 H), 3.41 (dd, *J* = 8.0 10.0 Hz, 1 H), 2.70 (m, 1 H), 2.62 (m, 1 H), 1.24 (s, 1 H), -0.3 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 142.1, 137.2, 130.5, 129.1, 120.9, 114.4, 112.0, 84.3, 60.0, 55.2, 35.4, -3.4. IR (film) 3452, 3055, 2952, 1246, 839 cm^{-1}. HRMS (ESI) 245.1360 [$(M-OH)^{+}$ calcd for $C_{15}H_{21}OSi$, 245.1362].

*Preparation of compounds **184***

Applying general procedure G to **171a** (82 mg, 0.312 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.23 mL, 1.2 equiv) at -78 ^{o}C for 10 minutes afforded, after workup and column

chromatography (5% and EtOAc in hexanes) 53.2 mg (65%) of **184** (dr = 15:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.5 Hz, 2 H), 6.77 (d, *J* = 8.5 Hz, 2 H), 2.70 (dd, A of ABX system, *J* = 6.5, 17.0 Hz, 1 H), 2.60 (dd, B of ABX system, *J* = 7.0, 17.0 Hz, 1 H), 1.59 (dt, *J* = 4.5, 9.0 Hz, 1 H), 1.22 (m, 1 H), 0.89 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.68 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.18 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.7, 157.7, 134.8, 127.1 (2 C), 113.8 (2 C), 55.3, 53.2, 22.0, 16.1, 15.0, -3.1. IR (film) 2958, 1644, 843 cm^{-1}. HRMS (ESI) *m/z* 263.1466 [$(M+H)^+$ calcd for $C_{15}H_{23}O_2Si$, 263.1467]

*Preparation of compounds **185** and **186***

Applying general procedure G to **172a** (109 mg, 0.442 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.33 mL, 1.2 equiv) in THF (5.5 mL) at -78 ^{o}C for 10 minutes afforded, after workup and column chromatography (5% and 10% EtOAc in hexanes) 86.6 mg (80%) of **185** (dr > 20:1) and 16.3 mg (15%) of **186** (dr > 20:1) as colorless oils. Spectroscopic data for **185**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13–7.04 (m, 4 H), 2.84 (dd, A of ABX system, *J* = 6.0, 16.8 Hz, 1 H), 2.63 (dd, B of ABX system, *J* = 7.2, 16.8 Hz, 1 H), 2.37 (s, 3 H), 1.64 (dt, *J* = 5.4, 10.2 Hz, 1 H), 1.34 (m, 1 H), 0.92 (dt, *J* = 5.4, 9.0 Hz, 1 H), 0.74 (dt, *J* = 4.8, 8.4 Hz, 1 H), 0.22 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.3, 140.2, 137.5, 129.5, 125.8, 125.74, 125.73, 53.2, 20.9, 19.7, 14.5, 13.6, -3.2. IR (film) 3065, 2958, 1643, 1249, 847 cm^{-1}. HRMS (EI) *m/z* 246.1432 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **186**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 1 H), 7.16–7.09 (m, 3 H), 6.00 (ddd, *J* = 2.0, 2.5, 5.5 Hz, 1 H), 5.72 (ddd, *J* = 1.5, 2.5,

6.0 Hz, 1 H), 3.76 (t, *J* = 9.0 Hz, 1 H), 2.77 (ddt, A of ABX system, *J* = 2.5, 9.5, 16.5 Hz, 1 H), 2.71 (dddd, B of ABX system, *J* = 1.5, 2.5, 8.5, 16.5 Hz, 1 H), 2.49 (s, 3 H), 1.40 (s, 1 H), -0.28 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 138.2, 136.5, 131.3, 130.7, 127.2, 126.4, 125.4, 86.2, 55.0, 38.1, 21.0, -3.4. IR (film) 3440, 3060, 2958, 1247, 839 cm^{-1}. HRMS (ESI) 229.1411 $[(M\text{-}OH)^+$ calcd for $C_{15}H_{21}Si$, 229.1413].

*Preparation of compounds **187** and **188***

Applying general procedure G to **173a** (91.4 mg, 0.371 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.28 mL, 1.2 equiv) in THF (4.6 mL) at -78 ^{o}C for 10 minutes afforded, after workup and column chromatography (5% and 10% EtOAc in hexanes) 53.5 mg (50%) of **187** (dr > 20:1) and 27.6 mg (30%) of **188** (dr > 20:1) as colorless oils. Spectroscopic data for **187**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.2 Hz, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 6.88 (s, 1 H), 6.86 (d, *J* = 7.8 Hz, 1 H), 2.75 (dd, A of ABX system, *J* = 6.0, 16.8 Hz, 1 H), 2.58 (dd, B of ABX system, *J* = 7.2, 16.8 Hz, 1 H), 2.30 (s, 3 H), 1.61 (dt, *J* = 4.8, 9.0 Hz, 1 H), 1.30 (m, 1 H), 0.97 (dt, *J* = 5.4, 8.4 Hz, 1 H), 0.73 (dt, *J* = 5.4, 8.4 Hz, 1 H), 0.19 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.2, 142.7, 137.8, 128.1, 126.6, 126.3, 122.9, 53.1, 22.6, 21.4, 16.6, 15.7, -3.2. IR (film) 3066, 2958, 1643, 1249, 844 cm^{-1}. HRMS (EI) *m/z* 246.1434 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **188**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (m, 1 H), 7.17 (m, 2 H), 7.04 (m, 1 H), 5.98 (ddd, *J* = 1.8, 2.4, 5.4 Hz, 1 H), 5.75 (ddd, *J* = 1.8, 2.4, 6.0 Hz, 1 H), 3.40 (ddt, *J* = 7.8, 10.2 Hz, 1 H), 2.72 (ddt, A of ABX system, *J* = 2.4, 10.8, 16.2 Hz, 1 H), 2.62

(dddd, *J* = 1.8, 3.0, 8.4, 16.2 Hz, 1 H), 2.33 (s, 3 H), 1.48 (s, 1 H), -0.30 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 137.6, 137.2, 130.6, 129.4, 128.0, 127.4, 125.3, 84.4, 59.9, 35.4, 21.4, -3.5. IR (film) 3440, 2957, 1490, 1247, 838 cm^{-1}. HRMS (ESI) 229.1401 [$(M\text{-}OH)^+$ calcd for $C_{15}H_{21}Si$, 229.1413].

*Preparation of compounds **189** and **190***

Applying general procedure G to **174a** (70.6 mg, 0.2865 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.21 mL, 1.2 equiv) in THF (3.6 mL) at -78 ^{o}C for 10 minutes afforded, after workup and column chromatography (5% and 10% EtOAc in hexanes) 60.3 mg (86%) of **189** (dr > 20:1) and 4.9 mg (7%) of **190** (dr > 20:1) as colorless oils. Spectroscopic data for **189**: Mixture of tautomers (keto / enol = 1:0.06) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.5 Hz, 2.12 H), 6.97 (d, *J* = 8.0 Hz, 2.12 H), 4.52 (d, *J* = 7.0 Hz, 0.06 H), 4.40 (s, 0.06 H), 2.74 (dd, A of ABX system, *J* = 6.0, 16.0 Hz, 1 H), 2.58 (dd, B of ABX system, *J* = 7.0, 17.0 Hz, 1 H), 1.84 (m, 0.06 H), 1.68 (m, 0.06 H), 1.61 (dt, *J* = 5.0, 9.0 Hz, 1 H), 1.27 (m, 1 H), 1.19 (m, 0.06 H), 0.99 (m, 0.06 H), 0.93 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.72 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.19 (s, 9 H), 0.12 (s, 0.55 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.3, 139.7, 135.0, 128.9 (2C), 125.9 (2C), 53.2, 22.4, 20.9, 16.5, 15.4, -3.2. IR (film) 3060, 2958, 1643, 1248, 844 cm^{-1}. HRMS (EI) *m*/*z* 246.1442 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **190**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 7.5 Hz, 2 H), 5.97 (m, 1 H), 5.75 (ddd, *J* = 1.5, 2.0, 6.0 Hz, 1 H), 3.39 (dd, *J* = 8.0, 10.5 Hz, 1 H), 2.70 (m, 1 H), 2.59 (m, 1 H), 2.32 (s, 3 H), -

0.30 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.2, 136.2, 130.6, 128.8 (2 C), 128.3 (2 C), 84.4, 59.7, 35.5, 21.0, -3.4. IR (film) 3443, 2957, 1491, 1247, 839 cm^{-1}. HRMS (ESI) 229.1407 [$(M\text{-}OH)^+$ calcd for $C_{15}H_{21}Si$, 229.1413].

*Preparation of compounds **191** and **192***

Applying general procedure G to **175a** (60.3 mg, 0.24 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.18 mL, 1.2 equiv) in THF (3 mL) at -78 ^{o}C for 10 minutes afforded, after workup and column chromatography (5% EtOAc in hexanes) 39.5 mg (66%) of **191** (dr > 20:1) and 6.7 mg (11%) of **192** (dr > 20:1) as colorless oils. Spectroscopic data for **191**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (m, 2 H), 6.90 (m, 2 H), 2.67 (m, 2 H), 1.60 (dt, *J* = 4.5, 9.0 Hz, 1 H), 1.23 (m, 1 H), 0.90 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.72 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.18 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.1, 161.1 (d, *J* = 243.4 Hz), 138.3 (d, *J* = 3.2 Hz), 127.5 (d, *J* = 7.7 Hz, 2 C), 114.9 (d, *J* = 21.3 Hz, 2 C), 53.0, 22.1, 16.3, 15.2, -3.2. IR (film) 3071, 2959, 1645, 1512, 1250, 844 cm^{-1}. HRMS (EI) *m*/*z* 250.1181 [(M^+); calcd for $C_{14}H_{19}OSiF$, 250.1189]. Spectroscopic data for **192**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 2 H), 6.98 (m, 2 H), 5.97 (ddd, *J* = 2.0, 3.0, 5.5 Hz, 1 H), 5.75 (ddd, *J* = 1.5, 2.5, 6.0 Hz, 1 H), 3.40 (t, *J* = 8.5 Hz, 1 H), 2.70–2.59 (m, 2 H), -0.30 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, *J* = 245.7 Hz), 137.4, 136.2, 130.5, 129.8 (d, *J* = 7.8 Hz, 2 C), 114.8 (d, *J* = 20.8 Hz, 2 C), 84.2, 59.2, 35.6, -3.4. IR (film) 3431, 3059, 2922, 1510, 839 cm^{-1}. HRMS (EI) *m*/*z* 232.1085 [$(M\text{-}H_2O)^+$; calcd for $C_{14}H_{17}SiF$, 232.1084].

*Preparation of compounds **193** and **194***

Applying general procedure G to **176a** (93 mg, 0.349 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.24 mL, 1.1 equiv) in THF (4.4 mL) at -78 ^{o}C for 5 minutes afforded, after workup and column chromatography (5% and 10% EtOAc in hexanes) 26 mg (28%) of **193** (dr = 15:1) and 60.4 mg (65%) of **194** (dr > 20:1) as colorless oils. Spectroscopic data for **193**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 2 H), 6.99 (d, *J* = 9.0 Hz, 2 H), 2.66 (d, *J* = 7.0 Hz, 2 H), 1.59 (dt, *J* = 5.0, 9.0 Hz, 1 H), 1.25 (m, 1 H), 0.92 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.74 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.18 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.0, 141.4, 131.1, 128.3 (2 C), 127.4 (2 C), 53.0, 22.2, 16.7, 15.5, -3.2. IR (film) 3072, 2960, 1645, 1496, 1250, 846 cm^{-1}. HRMS (EI) *m*/*z* 266.0891 [(M^{+}); calcd for $C_{14}H_{19}SiOCl$, 266.0894]. Spectroscopic data for **194**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 2 H), 7.24 (m, 2 H), 5.96 (ddd, *J* = 2.0, 2.5, 5.5 Hz, 1 H), 5.74 (ddd, *J* = 1.0, 2.0, 5.5 Hz, 1 H), 3.38 (dd, *J* = 8.0, 10.0 Hz, 1 H), 2.66 (ddt, A of ABX system, *J* = 2.0, 10.0, 16.0 Hz, 1 H), 2.60 (dddd, B of ABX system, *J* = 1.5, 3.0, 8.0, 16.0 Hz, 1 H), 1.50 (s, 1 H), -0.30 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 137.4, 132.4, 130.4, 129.8 (2 C), 128.2 (2 C), 84.2, 59.3, 35.3, 3.4. IR (film) 3443, 3054, 2957, 1491, 1247, 838 cm^{-1}. HRMS (ESI) *m*/*z* 249.0867 [$(M\text{-}OH)^{+}$; calcd for $C_{14}H_{18}SiCl$, 249.0866].

*Preparation of compound **195***

Applying general procedure G to **177a** (42 mg, 0.1378 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.13 mL, 1.5 equiv) in THF 1.5 mL) at -78 ^{o}C for 30 minutes afforded, after workup

and column chromatography (10% and 15% EtOAc in hexanes) 38 mg (90%) of **195** (dr > 20:1) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (m, 4 H), 5.99 (ddd, *J* = 1.8, 3.0, 6.0 Hz, 1 H), 5.77 (ddd, *J* = 1.2, 2.4, 6.0 Hz, 1 H), 3.48 (dd, *J* = 7.8, 9.6 Hz, 1 H), 2.73 (ddt, A of ABX system, *J* = 2.4, 10.8, 16.2 Hz, 1 H), 2.65 (dddd, B of ABX system, *J* = 1.2, 3.0, 7.8, 15.6 Hz, 1 H), 1.53 (s, 1 H), -0.31 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7, 137.4, 130.3, 129.0 (q, *J* = 32.3 Hz), 128.8 (2 C), 124.9 (q, *J* = 3.8 Hz, 2 C), 124.3 (q, *J* = 272.6 Hz), 84.2, 59.7, 35.2, -3.5. IR (neat) 3441, 1327, 1248, 1165, 1126, 1070, 843 cm^{-1}. HRMS (ESI) *m/z* 283.1138 [(M-OH)$^{+}$ calcd for $C_{15}H_{18}SiF_3$, 283.1130].

*Preparation of compounds **196** and **197***

Applying general procedure H to **178b** (66.8 mg, 0.2165 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 0.46 mL, 3 equiv) in THF (2.4 mL) at -78 ^{o}C for 3 hours afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 3.5 mg (5%) of **196** (dr = 7:1) as colorless oil and 50.4 mg (75%) of **197** (dr > 20:1) as a white solid. Spectroscopic data for **196**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.46 (m, 2 H), 7.40 (m, 2 H), 7.30 (m, 1 H), 7.13 (m, 2 H), 2.76 (dd, A of ABX system, *J* = 6.0, 16.5 Hz, 1 H), 2.62 (dd, B of ABX system, *J* = 7.0, 17.0 Hz, 1 H), 1.68 (dt, *J* = 5.0, 9.0 Hz, 1 H), 1.35 (m, 1 H), 1.01 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.78 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.20 (s, 9 H). Spectroscopic data for **197**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (m, 2 H), 7.56 (m, 2 H), 7.48 (m, 2 H), 7.43 (m, 2 H), 7.33 (m, 1 H), 6.01 (ddd, *J* = 1.5, 2.5, 5.5 Hz, 1 H), 5.80 (ddd, *J* = 1.5, 2.5, 6.0 Hz, 1 H), 3.49 (dd, *J* = 8.0, 10.0 Hz, 1 H), 2.78 (ddt, A of ABX system, *J* = 2.0, 10.0, 16.0 Hz, 1 H), 2.68 (dddd, B of ABX system, *J* =

1.0, 3.0, 8.0, 16.0 Hz, 1 H), 1.56 (s, 1 H), -0.25 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 139.6, 137.3, 130.5, 128.9 (2 C), 128.7 (2 C), 127.1, 126.9 (2 C), 126.7 (2 C), 84.5, 59.7, 35.4, -3.4 (one aromatic carbon could not be located). IR (film) 3442, 3060, 2955, 1246, 839 cm^{-1}. HRMS (EI) *m*/*z* 290.1481 [$(M-H_2O)^+$; calcd for $C_{20}H_{22}Si$, 290.1491]. m.p. = 75–76 °C.

*Preparation of compounds **198** and **199***

Applying general procedure G to **179a** (83.4 mg, 0.295 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.22 mL, 1.2 equiv) in THF (3.7 mL) at -78 °C for 10 minutes afforded, after workup and column chromatography (5% and 10% EtOAc in hexanes) 2.6 mg (3%) of **198** (dr > 20:1) as a colorless oil and 79.9 mg (96%) of **199** (dr > 20:1) as a white solid. Spectroscopic data for **198**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (m, 3 H), 7.51 (s, 1 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 7.36 (t, *J* = 7.8 Hz, 1 H), 7.20 (d, *J* = 8.4 Hz, 1 H), 2.77 (dd, A of ABX system, *J* = 6.0, 17.0 Hz, 1 H), 2.67 (dd, B of ABX system, *J* = 6.6, 16.8 Hz, 1 H), 1.80 (m, 1 H), 1.42 (m, 1 H), 1.09 (dt, *J* = 4.8, 8.4 Hz, 1 H), 0.82 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.2, 140.3, 133.5, 131.9, 127.9, 127.6, 127.3, 125.9, 125.0, 124.9, 124.0, 53.2, 23.0, 16.8, 15.7, -3.1, -3.5. IR (film) 3053, 2957, 1645, 1250, 844 cm^{-1}. HRMS (EI) *m*/*z* 282.1429 [(M^+); calcd for $C_{18}H_{22}OSi$, 282.1440]. Spectroscopic data for **199**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (m, 3 H), 7.77 (d, *J* = 9.0 Hz, 1 H), 7.60 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.44 (m, 2 H), 6.04 (ddd, *J* = 2.4, 3.0, 6.0 Hz, 1 H), 5.82 (dq, *J* = 1.2, 6.0 Hz, 1 H), 3.61 (dd, *J* = 8.4, 10.8 Hz, 1 H), 2.89 (ddt, A of ABX system, *J* = 1.8, 10.8, 16.2 Hz, 1 H), 2.73 (dddd, B of ABX system, *J* = 1.2, 2.4, 7.8, 15.6 Hz, 1 H), 1.60 (s, 1 H), -0.31 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.2, 137.5, 133.3, 132.5, 130.5, 128.0, 127.7, 127.6,

127.5, 126.1, 125.9, 125.4, 84.4, 60.1, 35.5, -3.3. IR (film) 3437, 3055, 2957, 2855, 1246, 839 cm^{-1}. HRMS (EI) *m*/*z* 264.1326 [(M^+); calcd for $C_{18}H_{20}Si$, 264.1334]. mp = 58–60 ^oC.

*Deuterium trapping experiments – Preparation of compounds **200** and **201***

Applying general procedure H to **171b** (96 mg, 0.366 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in hexanes, 0.78 mL, 3 equiv) in THF (4 mL) at -78 ^oC for 6 hours afforded after workup and column chromatography (30% CH_2Cl_2 in hexanes, then 5% and 10% EtOAc in hexanes) 6.9 mg (7%) of δ_2-**200**, 13.2 mg (19%) of δ-**201** (dr > 20:1), 25.2 mg (26%) of δ-**171b**, 2.2 mg (2%) of δ_2-**171a** and 28 mg (30%) of δ-**184** as colorless oils. Spectroscopic data for δ_2-**200**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 2 H), 6.87 (m, 1 H), 5.02 (m, 1 H), 4.70 (dd, *J* = 2.5, 10.0 Hz, 1 H), 3.79 (s, 3 H), 2.18 (m, 1 H), 2.00 (dddd, *J* = 1.0, 2.5, 6.5, 13.5, Hz, 1 H), 1.80 (dt, *J* = 10.0, 13.0 Hz, 1 H), -0.10 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 135.5, 126.9 (2 C), 126.8 (2 C), 113.6, 109.7, 75.8, 55.3, 30.2, 20.9 (t, *J* = 20.2 Hz), -2.4. Spectroscopic data for δ-**201**: ^1H NMR (500 MHz, $CDCl_3$) δ 9.82 (t, *J* = 2.0 Hz, 1 H), 7.01 (m, 2 H), 6.79 (d, *J* = 9.0 Hz, ~1 H), 3.76 (s, 3 H), 2.50 (ddd, A of ABX system, *J* = 2.0, 7.0, 17.5 Hz, 1 H), 2.43 (ddd, B of ABX system, *J* = 2.0, 7.5, 17.5 Hz, 1 H), 1.71 (dt, *J* = 5.0, 9.0 Hz, 1 H), 1.23 (m, 1 H), 0.98 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.80 (dt, *J* = 5.0, 8.5 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.7, 157.8, 127.1, 127.0, 113.9, 55.3, 48.2, 21.9, 15.5, 14.6.

*Preparation of compounds **202a***

Applying general procedure E to **145a**/**145b** (~13:1 ratio, 99 mg, 0.307 mmol, 1 equiv) and 2nd generation Grubbs catalyst (10 mg, 0.0123 mmol, 0.04 equiv) in CH_2Cl_2 (3.5 mL) at room temperature afforded after column chromatography (10% and 30% CH_2Cl_2 in hexanes) 80.4 mg (89%) of **202a** and 2.5 mg (3%) of **202b** as colorless oils. Spectroscopic data for **202a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 2 H), 7.39-7.32 (m, 7 H), 7.26 (m, 1 H), 5.84-5.77 (m, 2 H), 4.65 (dd, *J* = 5.0, 6.5 Hz, 1 H), 4.29 (m, 1 H), 2.42-2.31 (m, 2 H) 0.43 (s, 3 H), 0.40 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 136.9, 134.1, 129.3, 128.2, 127.8, 127.2, 126.6, 120.5, 72.3, 69.8, 30.2, -4.4, -4.6. IR (film) 3071, 2960, 1113, 724 cm^{-1}. HRMS (EI) *m*/*z* 294.1436 [(M^+); calcd for $C_{19}H_{22}OSi$, 294.1440].

*Preparation of compounds **202b***

Applying general procedure E to **145b** (119.8 mg, 0.3714 mmol, 1 equiv) and 2nd generation Grubbs catalyst (12.6 mg, 0.0148 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) at room temperature afforded after column chromatography (20% CH_2Cl_2 in hexanes) 99 mg (91%) of **202b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 2 H), 7.43-7.38 (m, 7 H), 7.31 (t, *J* = 7 Hz, 1 H), 5.84 (m, 2 H), 4.48 (m, 2 H), 2.33-2.19 (m, 2 H), 0.47 (s, 3 H), 0.45 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 136.7, 134.2, 129.2, 128.1, 127.8, 127.7, 127.0, 125.6, 121.5, 75.5,

71.3, 34.0, -5.1, -5.9. IR (film) 3071, 2959, 1428, 1115, 724 cm^{-1}. HRMS (EI) *m*/*z* 294.1440 [(M^+); calcd for $C_{19}H_{22}OSi$, 294.1440].

*Preparation of compounds **203a**/**203b***

Applying general procedure F to **146a**/**146b** (~1:1.7 ratio, 312 mg, 0.811 mmol, 1 equiv) and 2nd generation Grubbs catalyst (27.5 mg, 0.032 mmol, 0.04 equiv) in benzene (11.6 mL) at room temperature afforded after column chromatography (20% and 30% CH_2Cl_2 in hexanes) 75 mg (26%) of **203a** and 101 mg (35%) of **203b** as colorless oils. Spectroscopic data for **203a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (m, 2 H), 7.59 (m, 2 H), 7.49–7.23 (m, 11 H), 5.87–5.80 (m 2 H), 4.63 (m, 2 H), 2.43–2.32 (m, 2 H), 0.66 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 135.3, 135.13 (2 C), 135.08 (2 C), 134.97, 129.5, 129.4, 128.1 (2 C), 127.9 (2 C), 127.8 (2 C), 127.7, 127.2, 126.7 (2 C), 121.1, 72.1, 68.5, 29.7, -5.5. IR (film) 3071, 2975, 1111, 724 cm^{-1}. HRMS (EI) *m*/*z* 356.1579 [(M^+); calcd for $C_{24}H_{24}OSi$, 356.1596]. Spectroscopic data for **203b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (m, 4 H), 7.41–7.30 (m, 10 H), 7.24 (m, 1 H), 5.80 (m, 2 H), 4.76 (m, 1 H), 4.49 (dd, *J* = 3.0, 10.0 Hz, 1 H), 2.26 (m, 1 H), 2.19 (m, 1 H), 0.64 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 135.22 (2 C), 135.16, 135.1 (2 C), 134.8, 129.5, 129.4, 128.1 (2 C), 127.8 (2 C), 127.7 (2 C), 127.6, 126.9, 125.6 (2 C), 122.1, 75.8, 70.9, 33.9, -6.4. IR (film) 3069, 2963, 1427, 788, 696 cm^{-1}. HRMS (EI) *m*/*z* 356.1587 [(M^+); calcd for $C_{24}H_{24}OSi$, 356.1596].

*Preparation of compounds **204a***

Applying general procedure E to **147a** (73.5 mg, 0.243 mmol, 1 equiv) and 2nd generation Grubbs catalyst (8.3 mg, 0.01 mmol, 0.04 equiv) in CH_2Cl_2 (3 mL) at room temperature afforded after column chromatography (25% CH_2Cl_2 in hexanes) 55.9 mg (84%) of **204a** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 2 H), 7.32 (t, *J* = 7.2 Hz, 2 H), 7.24 (m, 1 H), 5.76 (m, 2 H), 4.74 (t, *J* = 5.4 Hz, 1 H), 4.14 (m, 1 H), 2.44 (m, 1 H), 2.39 (m, 1 H), 0.97 (t, *J* = 7.8 Hz, 9 H), 0.64 (q, *J* = 7.8 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 128.9, 128.1 (2 C), 127.1, 126.6 (2 C), 119.4, 72.3, 67.7, 30.0, 7.5, 2.6. IR (film) 3030, 2955, 1454, 1072 cm^{-1}. HRMS (EI) *m*/*z* 274.1737 [(M^+); calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compounds **204b***

Applying general procedure E to **147b** (102 mg, 0.337 mmol, 1 equiv) and 2nd generation Grubbs catalyst (11.4 mg, 0.013 mmol, 0.04 equiv) in benzene (4.8 mL) at 80 ^{o}C for 1 hour afforded after column chromatography (10% CH_2Cl_2 in hexanes) 88 mg (95%) of **204b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 4 H), 7.24 (m, 1 H), 5.84 (m, 1 H), 5.76 (m, 1 H), 4.39 (dd, *J* = 3.5, 9.5 Hz, 1 H), 4.33 (m, 1 H), 2.28–2.16 (m, 2 H), 1.01 (t, *J* = 8.0 Hz, 9 H), 0.68 (q, *J* = 8.0 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.2, 128.7, 128.1 (2 C), 126.9, 125.6 (2 C), 120.7, 75.7, 70.2, 34.1, 7.5, 1.9. IR (film) 3028, 2953, 1454, 1072 cm^{-1}. HRMS (EI) *m*/*z* 274.1746 [(M^+); calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compounds **205** and **206***

Applying general procedure G to **202a** (80.4 mg, 0.273 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.26 mL, 1.5 equiv) in THF (2.9 mL) at -78 ^{o}C for 10 minutes afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 55 mg (69%) of **205** (dr > 20:1) as colorless oil and 6 mg (~6%) of **206** (dr > 20:1) contaminated with desilylated **205** as colorless oil. Spectroscopic data for **205**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.42–7.36 (m, 3 H), 7.21 (m, 2 H), 7.11 (m, 1 H), 7.00 (m, 2 H), 2.70 (dd, A of ABX system, *J* = 6.5, 17.0 Hz, 1 H), 2.57 (dd, B of ABX system, *J* = 7.0, 16.5 Hz, 1 H), 1.54 (dt, *J* = 4.5, 9.0 Hz, 1 H), 1.23 (m, 1 H), 0.87 (dt, *J* = 5.5, 9.0 Hz, 1 H), 0.64 (dt, *J* = 5.5, 9.0 Hz, 1 H), 0.49 (s, 3 H), 0.48 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 245.2, 142.7, 134.3, 134.0 (2 C), 129.9, 128.17 (2 C), 128.16 (2 C), 125.8 (2 C), 125.4, 53.3, 22.6, 16.7, 15.6, -4.79, -4.82. IR (film) 3089, 2987, 1642, 1423, 1113, 698 cm^{-1}. HRMS (EI) *m/z* 294.1440 [(M^{+}); calcd for $C_{19}H_{22}OSi$, 294.1440]. Spectroscopic data for a mixture of **206** and desilylated **205** (1:0.33): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (m, 0.33 H), 7.30 (m, 2.66 H), 7.26–7.20 (m, 8 H), 7.14 (m, 0.33 H), 7.07 (m, 0.66 H), 5.98 (m, 1 H), 5.70 (m, 1 H), 3.44 (t, *J* = 9.0 Hz, 1 H), 2.59–2.48 (m, 2.33 H), 2.43 (m, 0.33 H), 1.75 (m, 0.33 H), 1.55 (s, 1 H), 1.32 (m, 1 H), 1.06 (m, 0.33 H), 0.87 (m, 0.33 H), 0.00 (s, 3 H), -0.11 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 137.3, 134.5 (3 C), 131.0, 128.9, 128.7 (2 C), 128.0 (2 C), 127.3 (2 C), 126.8, 125.9, 84.2, 59.8, 35.4, -4.9, -5.4. HRMS (ESI) *m/z* 277.1402 [$(M\text{-}OH)^{+}$ calcd for $C_{19}H_{21}Si$, 277.1413].

*Preparation of compounds **207***

Applying general procedure G to **203a** (70 mg, 0.196 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.15 mL, 1.2 equiv) in THF (2.5 mL) at -78 ^{o}C for 10 minutes afforded after workup and column chromatography (5% EtOAc in hexanes) 48.6 mg (70%) of **207** (dr = 20:1) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 4 H), 7.43 (m, 2 H), 7.37 (m, 4 H), 7.20 (t, *J* = 7.5 Hz, 2 H), 7.11 (tt, *J* = 1.5, 7.5 Hz, 1 H), 6.98 (m, 2 H), 2.77 (dd, A of ABX system, *J* = 6.0, 17.5 Hz, 1 H), 2.66 (dd, B of ABX system, *J* = 7.0, 17.0 Hz, 1 H), 1.52 (m, 1 H), 1.26 (m, 1 H), 0.88 (m, 1 H), 0.74 (s, 3 H), 0.63 (dt, *J* = 5.5, 9.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 243.6, 142.8, 135.0 (4 C), 132.61, 132.59, 130.1 (2 C), 128.22 (4 C), 128.18 (2 C), 125.9 (2 C), 125.4, 54.1, 22.6, 16.7, 15.6, -5.3. IR (film) 3089, 2990, 1643, 1429, 1113, 698 cm^{-1}. HRMS (EI) *m*/*z* 356.1605 [(M^{+}); calcd for $C_{24}H_{24}OSi$, 356.1596].

*Preparation of compounds **208** and **209***

Applying general procedure G to **204a** (91.4 mg, 0.333 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.25 mL, 1.5 equiv) in THF (4.2 mL) at -78 ^{o}C for 10 minutes afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 85.2 mg (93%) of **208** (dr > 20:1) and 4 mg (~5%) of **209** (dr > 20:1) as colorless oils. Spectroscopic data for **208**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (m, 2 H), 7.12 (m, 1 H), 7.06 (m, 2 H), 2.73 (dd, A of ABX system, *J* = 6.6, 17.4 Hz, 1 H), 2.56 (dd, B of ABX system, *J* = 7.2, 16.8 Hz, 1 H), 1.62 (dt, *J* = 4.8, 9.0 Hz, 1 H), 1.33 (m, 1 H), 0.96 (m, heavily overlapped, 1 H), 0.96 (t, *J* = 7.8 Hz, 9 H), 0.73 (m, heavily overlapped, 1 H), 0.73 (q, *J* = 7.8 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

247.0, 142.9, 128.2 (2 C), 125.9 (2 C), 125.4, 54.8, 22.6, 16.5, 15.7, -7.2, -2.1. IR (film) 3033, 2952, 1644, 1011, 730 cm^{-1}. HRMS (EI) *m*/*z* 274.1753 [$(M)^+$; calcd for $C_{17}H_{26}OSi$, 274.1753]. Spectroscopic data for **209**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2 H), 7.28 (t, *J* = 7.8 Hz, 2 H), 7.23 (m, 1 H), 5.95 (m, 1 H), 5.83 (m, 1 H), 3.40 (t, *J* = 8.4 Hz, 1 H), 2.74 (m, 1 H), 2.64 (m, 1 H), 1.41 (s, 1 H), 0.81 (t, *J* = 7.8 Hz, 9 H), 0.27 (dq, *J* = 4.8, 7.8 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 138.1, 130.5, 128.5 (2 C), 128.1 (2 C), 126.8, 85.9, 60.6, 35.6, 7.8, 2.2. IR (film) 3465, 2951, 2878, 1012, 729 cm^{-1}. HRMS (EI) *m*/*z* 256.1641 [$(M\text{-}H_2O)^+$; calcd for $C_{17}H_{24}Si$, 256.1647].

*Preparation of compounds **210a***

Applying general procedure F to **144a** (36 mg, 0.119 mmol, 1 equiv) and 2nd generation Grubbs catalyst (4 mg, 0.0048 mmol, 0.04 equiv) in benzene (2.4 mL) at 80 °C for 1 hour afforded after column chromatography (25% CH_2Cl_2 in hexanes) 27.9 mg (85%) of **210a** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 1 H), 7.17 (m, 3 H), 5.86 (dq, *J* = 3.5, 10.0 Hz, 1 H), 5.81 (m, 1 H), 4.97 (t, *J* = 5.5 Hz, 1 H), 3.90 (quintet, *J* = 3.0 Hz, 1 H), 2.72–2.60 (m, 2 H), 2.42–2.31 (m, 2 H), 1.61 (m, 2 H), 0.98 (t, *J* = 7.0 Hz, 3 H), 0.07 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 139.3, 129.2, 128.1, 127.2, 126.9, 125.6, 120.5, 69.4, 69.1, 34.6, 30.7, 24.9, 14.3, -3.1. IR (film) 3028, 2959, 2872, 1248. 839 cm^{-1}. HRMS (EI) *m*/*z* 274.1755 [$(M^+$); calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compounds **210b***

Applying general procedure F to **144b** (57 mg, 0.188 mmol, 1 equiv) and 2nd generation Grubbs catalyst (6.4 mg, 0.0075 mmol, 0.04 equiv) in benzene (3.8 mL) at 80 ^{o}C for 1 hour afforded after column chromatography (12% CH_2Cl_2 in hexanes) 38.6 mg (75%) of **210b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 2.0, 7.0 Hz, 1 H), 7.20 (m, 2 H), 7.15 (m, 1 H), 5.83 (m, 2 H), 4.58 (dd, *J* = 3.0, 10.0 Hz, 1 H), 4.18 (m, 1 H), 2.62 (m, 2 H), 2.25 (m, 1 H), 2.17 (m, 1 H), 1.63 (m, 2 H), 0.99 (t, *J* = 7.0 Hz, 3 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 139.3, 128.9, 128.0, 126.9, 126.1, 126.0, 121.6, 72.7, 71.9, 34.5, 33.4, 24.6, 14.3, -3.9. IR (film) 3028, 2959, 2872, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 274.1740 [(M^{+}); calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compounds **211** and **212***

Applying general procedure G to **210a** (26.6 mg, 0.097 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 73 μL, 1.2 equiv) in THF (1.2 mL) at -78 ^{o}C for 10 minutes afforded after workup and column chromatography (5% EtOAc in hexanes) 15.4 mg (64%) of **211** (dr > 20:1) and 3 mg (6%) of **212** (dr > 20:1) as colorless oils. Spectroscopic data for **211**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (m, 3 H), 7.01 (m, 1 H), 2.86 (dd, A of ABX system, *J* = 5.5, 16.5 Hz, 1 H), 2.69 (m, 2 H), 2.57 (dd, B of ABX system, *J* = 7.5, 17.0 Hz, 1 H), 1.68 (dt, *J* = 5.0, 9.0 Hz, 1 H), 1.62 (m, 2 H), 1.34 (m, 1 H), 0.98 (t, *J* = 7.0 Hz, 3 H), 0.92 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.74 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.20 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.3, 141.7, 139.8, 128.7, 125.9,

125.7, 125.6, 53.3, 35.2, 23.8, 20.3, 14.9, 14.3, 14.2, -3.2. IR (film) 3064, 2959, 2872, 1645, 1250, 844 cm^{-1}. HRMS (EI) *m*/*z* 274.1739 [(M^+); calcd for $C_{17}H_{26}OSi$, 274.1753]. Spectroscopic data for **212**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 1 H), 7.16–7.10 (m, 3 H), 6.02 (dt, *J* = 2.5, 5.5 Hz, 1 H), 5.74 (dt, *J* = 2.0, 6.0 Hz, 1 H), 3.81 (t, *J* = 8.5 Hz, 1 H), 3.11 (ddd, *J* = 6.5, 8.5, 14.0 Hz, 1 H), 2.80–2.69 (m, 2 H), 2.54 (ddd, *J* = 7.0, 9.5, 14.0 Hz, 1 H), 1.58 (m, 2 H), 0.96 (t, *J* = 7.0 Hz, 3 H), -0.28 (s, 9 H). IR (film) 3444, 3058, 2957, 1490, 1246, 838 cm^{-1}. HRMS (EI) *m*/*z* 274.1739 [(M^+); calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compound **213a***

Applying general procedure E to **148a** (174 mg, 0.4936 mmol, 1 equiv) and 2^{nd} generation Grubbs catalyst (17 mg, 0.0197 mmol, 0.04 equiv) in CH_2Cl_2 (5 mL) at room temperature for 3 hours afforded after column chromatography (40% CH_2Cl_2 in hexanes) 137.4 mg (86%) of **213a** as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 (m, 2 H), 7.39–7.34 (m, 3 H), 7.24 (t, *J* = 8.4 Hz, 1 H), 6.89 (m, 2 H), 6.80 (m, 1 H), 5.83–5.77 (m, 2 H), 4.62 (t, *J* = 5.4 Hz, 1 H), 4.30 (m, 1 H), 3.79 (s, 3 H), 2.40–2.31 (m, 2 H), 0.42 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 143.7, 136.9, 134.1 (2 C), 129.3, 129.1, 127.8 (2 C), 127.7, 120.5, 118.9, 112.7, 112.2, 72.2, 69.9, 55.1, 30.2, -4.4, -4.6. IR (film) 3071, 2954, 1492, 1244, 814 cm^{-1}. HRMS (EI) *m*/*z* 324.1536 [(M^+); calcd for $C_{20}H_{24}O_2Si$, 324.1546].

*Preparation of compounds **213b***

Applying general procedure F to **148b** (95 mg, 0.269 mmol, 1 equiv) and 2nd generation Grubbs catalyst (9.2 mg, 0.011 mmol, 0.04 equiv) in benzene (3.8 mL) at 80 ^{o}C for 1 hour afforded after column chromatography (30% CH_2Cl_2 in hexanes) 75.4 mg (87%) of **213b** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (m, 2 H), 7.37 (m, 3 H), 7.26 (t, *J* = 7.8 Hz, 1 H), 6.96 (m, 1 H), 6.94 (dd, *J* = 0.6, 7.2 Hz, 1 H), 6.81 (ddd, *J* = 1.2, 3.0, 8.4 Hz, 1 H), 5.79 (m, 2 H), 4.42 (m, 2 H), 3.82 (s, 3 H), 2.25 (m, 1 H), 2.16 (m, 1 H), 0.41 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 145.6, 136.7, 134.2 (2 C), 129.2, 129.1, 127.7, 127.6 (2 C), 121.5, 118.0, 112.4, 111.2, 75.3, 71.3, 55.1, 33.9, -5.2, -5.9. IR (film) 3070, 2959, 1494, 1249, 815 cm^{-1}. HRMS (EI) *m*/*z* 324.1546 [(M^{+}); calcd for $C_{20}H_{24}O_2Si$, 324.1546].

*Preparation of compounds **214a***

Applying general procedure F to **149a** (128 mg, 0.359 mmol, 1 equiv) and 2nd generation Grubbs catalyst (12.2 mg, 0.014 mmol, 0.04 equiv) in benzene (5.1 mL) at 80 ^{o}C for 1 hour afforded after column chromatography (25% CH_2Cl_2 in hexanes) 109 mg (92%) of **214a** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.39–7.33 (m, 3 H), 7.27 (m, 2 H), 7.21 (m, 2 H), 5.80–5.75 (m, 2 H), 4.58 (t, *J* = 5.4 Hz, 1 H), 4.22 (m, 1 H), 2.35–2.27 (m, 2 H), 0.39 (s, 3 H), 0.37 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 136.7, 134.1 (2 C), 132.9, 129.3, 128.3 (2 C), 128.0 (2 C), 127.9, 127.8 (2 C), 120.3, 71.5, 69.6, 30.0, -4.4, -4.7. IR (film)

3068, 2957, 1490, 1249, 809 cm^{-1}. HRMS (EI) *m*/*z* 328.1035 [(M^+); calcd for $C_{19}H_{21}OSiCl$, 328.1050].

*Preparation of compounds **215a***

Applying general procedure F to **150a** (99.5 mg, 0.282 mmol, 1 equiv) and 2nd generation Grubbs catalyst (9.6 mg, 0.0113 mmol, 0.04 equiv) in benzene (4 mL) at 80 °C for 1 hour afforded after column chromatography (25% CH_2Cl_2 in hexanes) 85.7 mg (94%) of **215a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (m, 4 H), 7.57 (dd, *J* = 1.5, 8.5 Hz, 1 H), 7.49 (m, 2 H), 5.85 (m, 2 H), 4.96 (t, *J* = 5.0 Hz, 1 H), 4.20 (m, 1 H), 2.63–2.52 (m, 2 H), 1.03 (t, *J* = 8.0 Hz, 9 H), 0.70 (dq, *J* = 1.5, 8.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 133.2, 132.7, 129.0, 128.1, 127.8, 127.6, 125.8, 125.6, 125.3, 125.1, 119.4, 72.4, 67.6, 29.9, 7.5, 2.6. IR (film) 3055, 2953, 2874, 1458, 1018, 817, 719 cm^{-1}. HRMS (EI) *m*/*z* 324.1902 [(M^+); calcd for $C_{21}H_{28}OSi$, 324.1909].

*Preparation of compounds **215b***

Applying general procedure F to **150b** (102.2 mg, 0.29 mmol, 1 equiv) and 2nd generation Grubbs catalyst (9.8 mg, 0.0116 mmol, 0.04 equiv) in benzene (4.1 mL) at 80 °C for 1 hour afforded after column chromatography (10% CH_2Cl_2 in hexanes) 74.8 mg (79%) of **215b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 4 H), 7.49 (dd, *J* = 1.0, 8.0 Hz, 1 H), 7.44

(m, 2 H), 5.88 (m, 1 H), 5.81 (m, 1 H), 4.55 (dd, *J* = 4.5, 9.5 Hz, 1 H), 4.39 (m, 1 H), 2.31 (m, 2 H), 1.04 (t, *J* = 8.0 Hz, 9 H), 0.70 (dq, *J* = 1.5, 8.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 133.3, 132.7, 128.7, 128.0, 127.8, 127.6, 125.8, 125.5, 124.3, 124.1, 120.7, 75.9, 70.3, 34.0, 7.5, 1.9. IR (film) 3028, 2951, 2874, 1458, 1072, 815, 715 cm^{-1}. HRMS (EI) *m*/*z* 324.1894 [(M^+); calcd for $C_{21}H_{28}OSi$, 324.1909].

*Preparation of compounds **216** and **217***

Applying general procedure G to **213a** (75.4 mg, 0.232 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 1.2 equiv) at -78 ^{o}C for 10 minutes afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 41.3 mg (44%) of **216** (dr = 17:1) and 14.3 mg (20%) of **217** (dr > 20:1). Spectroscopic data for **216**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.42–7.34 (m, 3 H), 7.12 (t, *J* = 7.8 Hz, 1 H), 6.66 (dd, *J* = 3.0, 7.8 Hz, 1 H), 6.58 (d, *J* = 7.2 Hz, 1 H), 6.52 (t, *J* = 2.4 Hz, 1 H), 3.75 (s, 3 H), 2.69 (dd, A of ABX system, *J* = 6.0, 16.8 Hz, 1 H), 2.53 (dd, B of ABX system, *J* = 7.2, 17.4 Hz, 1 H), 1.51 (dt, *J* = 4.8, 9.0 Hz, 1 H), 1.22 (m, 1 H), 0.86 (dt, *J* = 5.4, 8.4 Hz, 1 H), 0.62 (dt, *J* = 5.4, 8.4 Hz, 1 H), 0.48 (s, 3 H), 0.47 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 245.2, 159.6, 144.5, 134.3, 134.0 (2 C), 129.9, 129.2, 128.2 (2 C), 118.3, 111.5, 110.9, 55.1, 53.2, 22.7, 16.8, 15.8, -4.80, -4.83. IR (film) 2957, 1645, 844 cm^{-1}. HRMS (EI) *m*/*z* 324.1546 [(M^+); calcd for $C_{20}H_{24}O_2Si$, 324.1546]. Spectroscopic data for **217**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 3 H), 7.23 (m, 2 H), 7.14 (t, *J* = 7.8 Hz, 1 H), 6.87 (m, 1 H), 6.79 (s, 1 H), 6.75 (dd, *J* = 2.4, 8.4 Hz, 1 H), 5.97 (m, 1 H), 5.71 (m, 1 H), 3.70 (s, 3 H), 3.42 (dd, *J* = 8.4, 10.2 Hz, 1 H), 2.58–2.48 (m, 2 H), 1.59 (s, 1 H), 0.05 (s, 3 H), -0.05 (s, 3

H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 141.6, 137.3, 137.0, 134.5 (2 C), 131.0, 128.92, 128.89, 127.3 (2 C), 121.0, 114.5, 112.3, 84.1, 59.7, 55.1, 35.4, -4.9, -5.2. IR (film) 3440, 3030, 2957, 1250, 819 cm^{-1}. HRMS (EI) *m*/*z* 306.1436 [$(M-H_2O)^+$; calcd for $C_{20}H_{22}OSi$, 306.1440].

*Preparation of compounds **218** and **219***

Applying general procedure G to **214a** (83 mg, 0.2524 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 1.1 equiv) at -78 ^oC for 5 minutes afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 38.4 mg (47%) of **218** (dr > 20:1) and 36.1 mg (44%) of **219** (dr > 20:1). Spectroscopic data for **218**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.41 (m, 1 H), 7.36 (m, 2 H), 7.15 (m, 2 H), 6.90 (m, 2 H), 2.61 (m, 2 H), 1.48 (dt, *J* = 4.8, 9.0 Hz, 1 H), 1.16 (m, 1 H), 0.82 (dt, *J* = 5.4, 9.0 Hz, 1 H), 0.63 (dt, *J* = 5.4, 9.0 Hz, 1 H), 0.48 (s, 3 H), 0.47 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 245.1, 141.3, 134.3, 134.0 (2C), 131.0, 129.9, 128.23 (2C), 128.20 (2 C), 127.3 (2 C), 53.1, 22.1, 16.8, 15.5, -4.8, -4.9. IR (film) 3030, 2958, 1641, 1490, 1012, 823, 734 cm^{-1}. HRMS (EI) *m*/*z* 328.1049 [$(M^+$); calcd for $C_{19}H_{21}OSiCl$, 328.1050]. Spectroscopic data for **219**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (m, 1 H), 7.27 (m, 2 H), 7.23 (m, 2 H), 7.15 (m, 4 H), 5.98 (ddd, *J* = 1.8, 3.0, 6.0 Hz, 1 H), 5.73 (ddd, *J* = 1.2, 2.4, 6.0 Hz, 1 H), 3.39 (dd, *J* = 7.2, 10.2 Hz, 1 H), 2.55 (dddd, A of ABX system, *J* = 1.2, 3.0, 7.8, 15.6 Hz, 1 H), 2.45 (ddt, B of ABX system, *J* = 2.4, 10.2, 18.0 Hz, 1 H), 1.56 (s, 1 H), 0.04 (s, 3 H), -0.03 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 137.4, 136.5, 134.3 (2 C), 132.4, 131.0, 129.9 (2 C), 129.0, 128.0 (2 C), 127.4 (2 C), 84.2, 59.0, 35.3, -4.8, -5.2. IR (film)

3440, 2950, 1246, 820 cm^{-1}. HRMS (EI) *m*/*z* 310.0946 [$(M\text{-}H_2O)^+$; calcd for $C_{19}H_{19}SiCl$, 310.0945].

*Preparation of compounds **220** and **221***

Applying general procedure H to **215b** (133.5 mg, 0.411 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 1.5 mL, 5 equiv) at -78 ^oC, and then at 0 ^oC for 6 hours, afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 58.8 mg (45%) of **220** (dr = 3.2:1) and 11.8 mg (9%) of **221** (dr > 20:1) as colorless oils. Spectroscopic data for **220**: Major diastereomer (*trans*): ^1H NMR (500 MHz, $CDCl_3$) δ 7.76–7.70 (m, 3 H), 7.51 (s, 1 H), 7.43–7.34 (m, 2 H), 7.20 (dd, *J* = 2.0, 8.5 Hz, 1 H), 2.77 (dd, A of ABX system, *J* = 6.0, 17.0 Hz, 1 H), 2.62 (dd, B of ABX system, *J* = 7.0, 17.4 Hz, 1 H), 1.79 (quintet, *J* = 4.5 Hz, 1 H), 1.44 (m, 1 H), 1.10 (m, 1 H, 0.96 (t, *J* = 7.5 Hz, 9 H), 0.81 (m, 1 H), 0.74 (q, *J* = 7.5 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.1, 140.4, 135.5, 131.9, 127.8, 127.5, 127.3, 125.9, 125.0, 124.9, 124.0, 54.8, 22.9, 16.5, 15.7, 7.3, 2.1. IR (film) 3055, 2955, 2876, 1639, 1018, 910, 740 cm^{-1}. HRMS (EI) *m*/*z* 324.1901 [$(M)^+$; calcd for $C_{21}H_{28}OSi$, 324.1909]. Spectroscopic data for **221**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (m, 3 H), 7.76 (d, *J* = 8.5 Hz, 1 H), 7.61 (dd, *J* = 1.0, 8.5 Hz, 1 H), 7.44 (m, 2 H), 6.00 (m, 1 H), 5.88 (m, 1 H), 3.57 (m, 1 H), 2.87 (m, 1 H), 2.73 (m, 1 H), 0.77 (t, *J* = 8.0 Hz, 9 H), 0.26 (dq, *J* = 1.5, 8.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 138.3, 133.3, 132.5, 130.5, 127.9, 127.7, 127.6, 127.4, 126.2, 125.8, 125.3, 85.9, 60.7, 35.8, 7.8, 2.3. IR

(film) 3053, 2951, 2876, 1458, 1012, 819, 727 cm^{-1}. HRMS (ESI) *m/z* 307.1869 [$(M\text{-}OH)^+$ calcd for $C_{21}H_{27}Si$, 307.1882].

*Preparation of compounds **222a**/**222b***

Applying general procedure E to **151a**/**151b** (~1:1 ratio, 309 mg, 1.126 mmol, 1 equiv) and 2nd generation Grubbs catalyst (38 mg, 0.045 mmol, 0.04 equiv) in benzene (13 mL) at room temperature for 3 hours afforded after column chromatography (10% and 25% CH_2Cl_2 in hexanes) 159 mg (57%) of **222a** and 100 mg of **222b** (36%) as colorless oils. Spectroscopic data for **222a**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 4 H), 7.24 (tt, *J* = 1.5, 6.5 Hz, 1 H), 5.47 (m, 1 H), 4.54 (dd, *J* = 5.0, 7.5 Hz, 1 H), 4.01 (d, *J* = 1.0 Hz, 1 H), 2.33-2.29 (m, 2, H), 1.68 (m, 3 H), 0.18 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 135.4, 128.2 (2 C), 127.1, 126.0 (2 C), 115.8, 75.0, 72.9, 32.1, 20.4, -1.4. IR (film) 3029, 2957, 1250, 839 cm^{-1}. HRMS (EI) *m/z* 246.1440 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **222b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 4 H), 7.22 (m, 1 H), 5.51 (m, 1 H), 4.29 (dd, *J* = 3.0, 8.5 Hz, 1 H), 4.05 (m, 1 H), 2.20 (m, 1 H), 2.10 (m, 1 H), 1.66 (m, 3 H), 0.13 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 135.3, 128.1 (2 C), 126.8, 125.6 (2 C), 117.0, 75.0, 74.4, 34.2, 20.0, -2.6. IR (film) 3030, 2957, 1248, 839 cm^{-1}. HRMS (EI) *m/z* 246.1432 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compounds **223a***

Applying general procedure E to **152a** (94.6 mg, 0.311 mmol, 1 equiv) and 2nd generation Grubbs catalyst (10.6 mg, 0.0124 mmol, 0.04 equiv) in CH_2Cl_2 (3.5 mL) at room temperature for 3 hours afforded after column chromatography (60% CH_2Cl_2 in hexanes) 61.5 mg (72%) of **223a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2 H), 6.87 (m, 2 H), 5.47 (m, 1 H), 4.49 (dd, *J* = 4.5, 9.0 Hz, 1 H), 3.99 (m, 1 H), 3.78 (s, 3 H), 2.37–2.24 (m, 2 H), 1.64 (m, 3 H), 0.15 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 135.3, 134.9, 127.3 (2 C), 115.9, 113.6 (2 C), 74.9, 72.5, 55.2, 32.0, 20.4, -1.4. IR (film) 2959, 1248, 838 cm^{-1}. HRMS (EI) *m*/*z* 276.1549 [(M^+); calcd for $C_{16}H_{24}O_2Si$, 276.1546].

*Preparation of compounds **223b***

Applying general procedure E to **152b** (116.9 mg, 0.3839 mmol, 1 equiv) and 2nd generation Grubbs catalyst (13 mg, 0.0154 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) at room temperature for 3 hours afforded after column chromatography (35% CH_2Cl_2 in hexanes) 91 mg (86%) of **223b** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (m, 2 H), 6.85 (m, 2 H), 5.49 (m, 1 H), 4.23 (dd, *J* = 3.0, 10.8 Hz, 1 H), 4.04 (m, 1 H), 3.78 (s, 3 H), 2.16 (m, 1 H), 2.07 (m, 1 H), 1.65 (d, *J* = 1.2 Hz, 3 H), 0.11 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 136.3, 135.3, 126.8 (2 C), 117.1, 113.5 (2 C), 74.6, 74.4, 55.2, 34.2, 20.0, -2.6. IR (film) 2964, 1248, 839 cm^{-1}. HRMS (EI) *m*/*z* 276.1551 [(M^+); calcd for $C_{16}H_{24}O_2Si$, 276.1546].

*Preparation of compounds **224a/224b***

Applying general procedure F to **153a**/**153b** (~1.5:1 ratio, 159 mg, 0.551 mmol, 1 equiv) and 2nd generation Grubbs catalyst (17.6 mg, 0.021 mmol, 0.04 equiv) in benzene (7 mL) 80 ^{o}C for 1 hour afforded after column chromatography (15% and 35% CH_2Cl_2 in hexanes) 86 mg (60%) of **224a** and 55 mg (38%) of **224b** as colorless oils. Spectroscopic data for **224a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 7.8 Hz, 2 H), 5.49 (m, 1 H), 4.52 (dd, *J* = 4.2, 9.0 Hz, 1 H), 4.02 m, 1 H), 2.34 (s, 3 H), 2.31 (m, 2 H), 1.65 (m, 3 H), 0.16 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 136.7, 135.3, 128.9 (2 C), 125.9 (2 C), 115.9, 74.9, 72.8, 32.2, 21.1, 20.4, -1.4. IR (film) 3026, 2959, 1250, 839 cm^{-1}. HRMS (EI) *m*/*z* 260.1583 [(M^{+}); calcd for $C_{16}H_{24}OSi$, 260.1596]. Spectroscopic data for **224b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.8 Hz, 2 H), 7.14 (d, *J* = 7.8 Hz, 2 H), 5.52 (m, 1 H), 4,28 (dd, *J* = 3.0, 4.2 Hz, 1 H), 4.07 (m, 1 H), 2.34 (s, 3 H), 2.21 (m, 1 H), 2.12 (m, 1 H), 1.68 (m, 3 H), 0.15 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 136.4, 135.3, 128.7 (2 C), 125.6 (2 C), 117.1, 74.8, 74.3, 34.2, 21.1, 20.0, -2.6. IR (film) 3028, 2963, 1248, 843 cm^{-1}. HRMS (EI) *m*/*z* 260.1590 [(M^{+}); calcd for $C_{16}H_{24}OSi$, 260.1596].

*Preparation of compounds **225a***

Applying general procedure E to **166a** (201 mg, 0.738 mmol, 1 equiv) and 2nd generation Grubbs catalyst (25 mg, 0.03 mmol, 0.04 equiv) in CH_2Cl_2 (8 mL) at room temperature for 12 hours afforded after column chromatography (4% EtOAc in hexanes) 125 mg (62%) of **225a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4 H), 7.25 (tt, *J* = 1.5, 7 Hz, 1 H), 5.83 (m, 1 H), 4.92 (s, 1 H), 4.82 (s, 1 H), 4.65 (q, *J* = 2.0 Hz, 1 H), 4.56 (dd, *J* = 6.0, 8.5 Hz, 1 H), 2.42 (m, 2 H), 1.89 (t, *J* = 0.5, Hz, 3 H), 0.10 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 141.5, 140.5, 128.3 (2 C), 127.3, 125.8 (2 C), 117.8, 112.3, 72.8, 71.8, 32.7, 21.4, -0.8. IR (neat) 3089, 3031, 2955, 2895, 1450, 1248, 1028, 839 cm^{-1}. HRMS (EI) *m*/*z* 272.1590 [(M^+); calcd for $C_{17}H_{24}OSi$, 272.1596].

*Preparation of compounds **225b***

Applying general procedure E to **166b** (291.7 mg, 1.07 mmol, 1 equiv) and 2nd generation Grubbs catalyst (74.4 mg added in two portions, 0.0154 mmol, 0.07 equiv) in CH_2Cl_2 (11 mL) at room temperature for 27 hours afforded after column chromatography (4% EtOAc in hexanes) 141.8 mg (49%) of **225b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.24 (tt, *J* = 1.5, 7.0 Hz, 1 H), 5.88 (dt, *J* = 1.5, 7.5 Hz, 1 H), 4.85 (s, 2 H), 4.63 (t, *J* = 2,0 Hz, 1 H), 4.28 (dd, *J* = 3.0, 10.0 Hz, 1 H), 2.32 (ddt, *J* = 3.0, 7.0, 17.0 Hz, 1 H), 2.19 (dddd, *J* = 2.5, 4.0, 12.5, 16.5 Hz, 1 H), 1.90 (s, 3 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 142.7, 140.7, 128.1 (2 C), 127.0, 125.7 (2 C), 118.5, 111.5, 74.3, 71.5, 34.7, 21.7, -2.3. IR (neat) 3088,

3030, 2953, 2895, 1452, 1246, 1028, 841 cm^{-1}. HRMS (EI) *m*/*z* 272.1586 [(M^+); calcd for $C_{17}H_{24}OSi$, 272.1596].

*Preparation of compound **226***

Applying general procedure H to **222a** (200 mg, 0.81 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 1.8 mL, 3 equiv) at -78 ^oC for 7 hours afforded after workup and column chromatography (10% EtOAc in hexanes) 157.7 mg (79%) of **226** (dr = 20:1) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (m, 2 H), 7.27 (m, 2 H), 7.22 (m, 1 H), 5.64 (m, 1 H), 3.41 (m, 1 H), 2.63 (m, 1 H), 2.43 (m,, 1 H), 1.76 (m, 3 H), 1.40 (s, 1 H), -0.30 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 140.9, 128.7 (2 C), 128.1 (2 C), 126.8, 124.8, 84.8, 61.8, 32.9, 14.6, -2.2. IR (film) 3440, 2957, 1243, 838 cm^{-1}. HRMS (ESI) *m*/*z* 229.1401 [($M-OH)^+$; calcd for $C_{15}H_{21}Si$, 229.1413].

*Preparation of compound **227***

Applying general procedure G to **223a** (61.5 mg, 0.2225 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 1.2 equiv) at -78 ^oC for 35 minutes afforded after workup and column chromatography (10% EtOAc in hexanes) 44 mg (72%) of **227** (dr = 20:1) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2 H), 6.82 (m, 2 H), 5.62 (m, 1 H), 3.78 (s, 3 H), 3.34 (dd, *J* = 7.5, 10.5 Hz, 1 H), 2.58 (m, 1 H), 2.41 (m, 1 H), 1.75 (dt, *J* = 1.5, 3.0 Hz, 3 H), 1.37 (s, 1 H), -0.29 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 145.6, 132.9, 129.5 (2 C), 124.8, 113.5 (2

C), 84.8, 61.0, 55.2, 33.1, 14.6, -2.1. IR (film) 3435, 2952, 1240, 838 cm^{-1}. HRMS (ESI) *m*/*z* 259.1507 $[(M\text{-}OH)^{+}$; calcd for $C_{16}H_{23}OSi$, 259.1518]. m.p. = 96–97 ^{o}C.

*Preparation of compound **228***

Applying general procedure G to **224a** (66.6 mg, 0.2557 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.19 mL, 1.2 equiv) at -78 ^{o}C for 15 minutes afforded after workup and column chromatography (10% EtOAc in hexanes) 60.2 mg (91%) of **228** (dr = 20:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 5.63 (quintet, *J* = 1.5 Hz, 1 H), 3.36 (dd, *J* = 8.0, 11.0 Hz, 1 H), 2.61 (m, 1 H), 2.41 (m, 1 H), 2.32 (s, 3 H), 1.76 (m, 3 H), 1.37 (s, 1 H), -0.30 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 137.7, 136.2, 128.8 (2 C), 128.5 (2 C), 124.8, 84.8, 61.4, 33.0, 21.0, 14.6, -2.2. IR (film) 3434, 2953, 1246, 830 cm^{-1}. HRMS (ESI) *m*/*z* 243.1568 $[(M\text{-}OH)^{+}$; calcd for $C_{16}H_{23}Si$, 243.1569].

*Preparation of compound **229***

Applying general procedure G to **225a** (120 mg, 0.445 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.56 mL, 2 equiv) at -78 ^{o}C for 1.5 hours afforded after workup and column chromatography (4% EtOAc in hexanes) 16.3 mg (13%) of unreacted **225a** and 90 mg (75%) of **2290** (dr = 20:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 2 H), 7.30 (m, 2 H), 7.24 (tt, *J* = 1.5, 7.0 Hz, 1 H), 5.96 (dd, *J* = 2.5, 3.5 Hz, 1 H), 5.63 (d, *J* = 1.0 Hz, 1 H), 4.98 (s, 1 H), 3.53 (dd, *J* = 8.0, 12.0 Hz, 1 H), 2.71 (dd, *J* = 11.5, 16.5 Hz, 1 H), 2.49 (ddd, *J* = 3.5, 7.5, 16.5 Hz, 1 H), 1.94 (s, 3 H), 1.67 (s, 1 H), 0.32 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5,

140.1, 139.0, 128.7 (2 C), 128.1 (2 C), 126.9, 115.1, 85.2, 62.2, 31.7, 23.1, -1.7. IR (film) 3443, 3029, 2956, 1242, 833 cm^{-1}. HRMS (ESI) *m/z* 255.1562 [$(M\text{-}OH)^{+}$; calcd for $C_{17}H_{23}Si$, 255.1569].

*Preparation of compound **230a***

Applying general procedure F to **154a** (102 mg, 0.3716 mmol, 1 equiv) and 2nd generation Grubbs catalyst (12.6 mg, 0.015 mmol, 0.04 equiv) in benzene (10 mL) at 80 °C for 1.5 hours afforded after column chromatography (30% CH_2Cl_2 in hexanes) 58 mg (63%) of **230a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4 H), 7.26 (tt, *J* = 2.0, 7.5 Hz, 1 H), 5.47 (m, 1 H), 4.73 (t, *J* = 5.5 Hz, 1 H), 3.95 (m, 1 H), 2.29 (m, 2 H), 1.78 (m, 3 H), 0.08 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 128.2, 127.5, 127.2, 126.6, 121.2, 72.5, 69.5, 34.8, 23.4, -2.9. IR (film) 3030, 2959, 1248, 1099, 841 cm^{-1}. HRMS (EI) *m/z* 246.1433 [$(M^{+}$); calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compound **230b***

Applying general procedure E to **154b** (104.2 mg, 0.3796 mmol, 1 equiv) and 2nd generation Grubbs catalyst (13 mg, 0.0152 mmol, 0.04 equiv) in CH_2Cl_2 (5.4 mL) at 80 °C for 2 hours afforded after column chromatography (10% CH_2Cl_2 in hexanes) 62 mg (67%) of **230b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2 H), 7.31 (t, *J* = 7.5 Hz, 2 H),

7.23 (tt, *J* = 1.5, 7.0 Hz, 1 H), 5.47 (d, *J* = 1.0 Hz, 1 H), 4.38 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.08 (m, 1 H), 2.15-2.02 (m, 2 H), 1.73 (s, 3 H), 0.06 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 128.8, 128.1, 126.9, 125.6, 121, 75.7, 71.2, 38.9, 23.2, -3.97. IR (film) 3035, 2958, 1248, 1099, 840 cm^{-1}. HRMS (EI) *m*/*z* 246.1430 [(M^+); calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compound **231a***

Applying general procedure F to **155a** (148.7 mg, 0.515 mmol, 1 equiv) and 2nd generation Grubbs catalyst (17.5 mg, 0.0206 mmol, 0.04 equiv) in benzene (10.5 mL) at 80 ^{o}C for 1.5 hours afforded after column chromatography (30% CH_2Cl_2 in hexanes) 110 mg (82%) of **231a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.5 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 5.44 (m, 1 H), 4.69 (t, *J* = 5.5 Hz, 1 H), 3.92 (quintet, *J* = 2.5 Hz, 1 H), 2.33 (s, 3 H), 2.27 (m, 2 H), 1.77 (m, 3 H), 0.06 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 136.8, 128.9 (2C), 127.6, 126.6 (2C), 121.2, 72.4, 69.3, 34.7, 23.5, 21.1, -3.0. IR (film) 3025, 2959, 2855, 1248, 841 cm^{-1}. HRMS (EI) *m*/*z* 260.1583 [(M^+); calcd for $C_{16}H_{24}OSi$, 260.1596].

*Preparation of compound **231b***

Applying general procedure F to **155b** (122 mg, 0.4229 mmol, 1 equiv) and 2nd generation Grubbs catalyst (14.4 mg, 0.0169 mmol, 0.04 equiv) in benzene (8.5 mL) at 80 ^{o}C for 1.5 hours afforded after column chromatography (10% CH_2Cl_2 in hexanes) 66 mg (60%) of **231b** as a

colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 5.46 (d, *J* = 1.8, Hz, 1 H), 4.34 (dd, *J* = 3.0, 10.2 Hz, 1 H), 4.07 (m, 1 H), 2.33 (s, 3 H), 2.11 (m, 1 H), 2.02 (dt, *J* = 3.0, 16.8 Hz, 1 H), 1.73 (m, 3 H), 0.06 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 136.5, 128.80, 128.78 (2C), 125.6 (2C), 121.0, 75.6, 71.2, 38.9, 23.2, 21.1, -3.9. IR (film) 3019, 2959, 2766, 1246, 1101, 841 cm^{-1}. HRMS (EI) *m*/*z* 260.1602 [(M^{+}); calcd for $C_{16}H_{24}OSi$, 260.1596].

*Preparation of compounds **232** and **233***

Applying general procedure G to **230a** (51.3 mg, 0.208 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.16 mL, 1.2 equiv) at -78 ^{o}C for 30 minutes afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 22.5 mg (44%) of **232** (dr = 7:1) and 19.6 mg (38%) of **233** (dr = 20:1) as colorless oils. Spectroscopic data for **232**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 4 H), 7.16 (m, 1 H), 2.91 (d, *J* = 17.5 Hz, 1 H), 2.52 (d, *J* = 17.5 Hz, 1 H), 1.89 (dd, *J* = 6.5, 8.5 Hz, 1 H), 0.81 (m, 2 H), 0.73 (s, 3 H), 0.20 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.9, 139.5, 129.4, 128.9, 127.9, 125.8, 58.6, 28.2, 18.8, 18.5, 17.1, -3.3. IR (film) 3061, 2959, 1647, 1250, 844 cm^{-1}. HRMS (EI) *m*/*z* 246.1436 [(M^{+}); calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **233**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 2 H), 7.28 (m, 2 H), 7.21 (m, 1 H), 5.38 (m, 1 H), 3.47 (dd, *J* = 8.0, 10.0 Hz, 1 H), 2.68 (m, 1 H), 2.51 (dd, *J* = 8.0, 15.5 Hz, 1 H), 1.84 (m, 3 H), 1.42 (s, 1 H), -0.33 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

141.2, 140.8, 130.7, 128.4 (2C), 128.1 (2C), 126.7, 84.4, 60.4, 39.6, 17.2, -3.3. IR (film) 3437, 3034, 2912, 1244, 837, 758 cm^{-1}. HRMS (ESI) *m/z* 229.1413 [$(M\text{-}OH)^+$ calcd for $C_{15}H_{21}Si$, 229.1412].

*Preparation of compounds **234** and **235***

Applying general procedure G to **231a** (50.3 mg, 0.193 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.145 mL, 1.2 equiv) at -78 ^oC for 15 minutes afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 21.8 mg (44%) of **234** (dr = 9:1) and 21.5 mg (43%) of **235** (dr = 20:1) as colorless oils. Spectroscopic data for **234**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.8 Hz, 2 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 2.88 (d, *J* = 17.4 Hz, 1 H), 2.52 (d, *J* = 16.8 Hz, 1 H), 2.30 (s, 3 H), 1.85 (t, *J* = 7.2 Hz, 1 H), 0.76 (m, 2 H), 0.72 (s, 3 H), 0.20 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.0, 136.3, 135.2, 129.3 (2C), 128.8, 128.6 (2C), 128.5, 58.7, 27.8, 21.0, 18.8, 18.3, 17.0, -3.2. IR (film) 3051, 2957, 2868, 1647, 1250, 844 cm^{-1}. HRMS (EI) *m/z* 260.1599 [(M^+); calcd for $C_{16}H_{24}OSi$, 260.1596]. Spectroscopic data for **235**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.8 Hz, 2 H), 7.08 (d, *J* = 7.8 Hz, 2 H), 5.37 (s, 1 H), 3.42 (t, *J* = 8.4 Hz, 1 H), 2.65 (dd, A of ABX system, *J* = 9.8, 15.0 Hz, 1 H), 2.49 (dd, B of ABX system, *J* = 7.2, 15.6 Hz, 1 H), 2.31 (s, 3 H), 1.83 (s, 3 H), 1.40 (s, 1 H), -0.32 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 137.7, 136.1, 130.6, 128.8 (2C), 128.3 (2C), 84.5, 60.0, 39.7, 21.0, 17.2, -3.3. IR (film) 3434, 3020, 2961, 2853, 1244, 837 cm^{-1}. HRMS (EI) *m/z* 242.1502 [(M^+); calcd for $C_{16}H_{22}Si$, 242.1491].

*Preparation of compound **237***

A solution of diisopropylamine (41 μL, 0.29 mmol, 1.3 equiv) in THF (1 mL) was cooled at -78 ^{o}C and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 1.2 equiv) was added dropwise via syringe. After 10 minutes the reaction was warmed to 0 ^{o}C for 15 minutes and cooled down to -78 ^{o}C. To this solution (–)-**167** (51.5 mg, 0.222 mmol, 1 equiv) in THF (2 mL) was added via syringe to give a yellow solution. After 1 hour, benzoyl chloride (52 μL, 0.444 mmol, 2 equiv) was added via syringe. After 30 minutes at -78 ^{o}C, the reaction was warmed to 0 ^{o}C for one hour. The reaction was quenched by adding $NaHCO_{3\ (sat)}$ (2 mL) and extracted with diethyl ether (3 × 5 mL). Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was dissolved in CH_2Cl_2 (1.5 mL), cooled at -78 ^{o}C and bubbled with O_3 until a slightly blue color persisted (~10 minutes), Then dimethylsulfide (~50 μL, excess) was added. After 15 minutes the cold bath was removed and the reaction left to reach room temperature. The solvent was evaporated and the crude product subjected to column chromatography to afford 15 mg (42%) of compound (*1R,2R*)-**237** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (d, *J* = 5.0 Hz, 1 H), 7.28 (m, 2 H), 7.21 (m, 1 H), 7.08 (m, 2 H), 2.61 (m, 1 H), 2.16 (m, 1 H), 1.17 (dt, *J* = 5.5, 10.0 Hz, 1 H), 1.52 (ddd, *J* = 5.0, 7.0, 8.5 Hz, 1 H). $[\alpha]_D$ = -183.4^{o} (c = 0.46, $CHCl_3$, Lit. -378, c = 0.374, $CHCl_3$).

*Preparation of compound **238***

To a solution of (+)-**168** (15 mg, 0.0646 mmol) in EtOAc (1 mL) was added 10% Pd/C (~3 mg). The system was closed with a septum and evacuated and filled with H_2. An H_2 balloon was attached and the mixture vigorously stirred for 30 minutes. Then, the reaction mixture was filtered though a short plug of silica and concentrated. Column chromatography afforded 15 mg mg (100%) of (–)-**238** as a colorless oil. $[\alpha]_D = -13.5^o$ (c = 1, $CHCl_3$)

*Preparation of compound **239***

To a solution of **238** (15 mg, 0.064 mmol, 1 equiv) in pyridine (2 mL) was added 3,5-dinitrobenzoyl chloride (74.5 mg, 0.323 mmol, 5 equiv) and the mixture vigorously stirred for ~36 hours. The reaction was quenched with water (2 mL) and diluted with diethyl ether. The aqueous phase was extracted with diethyl ether (3 × 3 mL). Combined organic extracts were washed with 0.1 M HCl (2 mL), brine, drived over $MgSO_4$ and concentrated. Column chromatography (4% EtOAc in hexanes) followed by recrystallization from hexanes/CH_2Cl_2 afforded 10.6 mg (39%) of **239** as white crystals suitable for X-ray analysis and 4.4 mg (29%) of unreacted **238**. M.p.= 137 ^{o}C (dec.) $[\alpha]_D = -87^o$ (c = 1.06, $CHCl_3$)

*Preparation of compounds **240a**/**240b***

Applying general procedure E to **156a**/**156b** (~2:1 ratio, 95 mg, 0.357 mmol, 1 equiv) and 2nd generation Grubbs catalyst (12 mg, 0.0143 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) at room temperature for 3 hours afforded after column chromatography (10% and 20% CH_2Cl_2 in

hexanes) 53 mg (62%) of **240a** and 27 mg (31%) of **240b** as colorless oils. Spectroscopic data for **240a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 1.8, 5.4 Hz, 1 H), 6.96 (m, 1 H), 6.95 (dd, *J* = 3.6, 5.4 Hz, 1 H), 5.77 (m, 2 H), 5.05 (t, *J* = 4.8 Hz, 1 H), 4.00 (m, 1 H), 2.58 (m, 1 H), 2.42 (m, 1 H), 0.08 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 128.3, 126.3, 124.7, 124.5, 119.3, 68.5, 68.1, 30.2, -3.3. IR (neat) 3031, 2957, 1248, 1051, 841 cm^{-1}. HRMS (EI) *m*/*z* 238.0840 [(M^+); calcd for $C_{12}H_{18}OSiS$, 232.0848]. Spectroscopic data for **240b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 1.8, 5.4 Hz, 1 H), 6.95 (dd, *J* = 3.6, 4.8 Hz, 1 H), 6.92 (m, 1 H), 5.81–5.74 (m, 2 H), 4.64 (t, *J* = 6.0 Hz, 1 H), 4.18 (m, 1 H), 2.33 (m, 2 H), 0.07 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 128.1, 126.2, 124.1, 122.4, 120.4, 71.96, 71.94, 33.9, -4.1. IR (neat) 3030, 2957, 1248, 1070, 843 cm^{-1}. HRMS (EI) *m*/*z* 238.0824 [(M^+); calcd for $C_{15}H_{14}OSi$, 238.0814].

*Preparation of compounds **241** and **242***

Applying general procedure G to **240a** (108 mg, 0.453 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.34 mL, 1.2 equiv) at -78 ^{o}C for 10 minutes afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 78.8 mg (73%) of **241** (dr = 2.1:1) and 25.9 mg (24%) of **242** (dr = 3.2:1) as colorless oils. Spectroscopic data for **241**: ^{1}H NMR (500 MHz, $CDCl_3$) mixture of diastereomers (1.0:0.6) δ 7.05 (dd, *J* = 1.0, 5.0 Hz, 0.6 H), 7.01 (dd, *J* = 1.0, 5.5 Hz, 1 H), 6.87 (dd, *J* = 3.0, 5.0 Hz, 0.6 H), 6.85 (dd, *J* = 3.5, 5.0 Hz, 1 H), 6.75 (m, 1 H), 6.67 (dt, *J* = 1.0, 3.5 Hz, 0.6 H), 2.71 (dd, A of ABX system, *J* = 6.0, 16.5 Hz, 1 H), 2.60 (dd, B

of ABX system, *J* = 7.0, 17.5 Hz, 1 H), 2.45 (dd, C of CDX system, *J* = 8.0, 18.5 Hz, 0.6 H), 2.39 (dd, D of CDX system, *J* = 6.0, 18.5 Hz, 0.6 H), 2.23 (m, 0.6 H), 1.81 (m, 1 H), 1.48 (m, 0.6 H), 1.33 (m, 1 H), 1.17 (dt, *J* = 5.5, 8.5 Hz, 0.6 H), 0.99 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.77 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.63 (q, *J* = 5.5 Hz, 0.6 H), 0.19 (s, 9 H), 0.04 (s, 5.4). ^{13}C NMR (126 MHz, $CDCl_3$) mixture of diastereomers (1.0:0.6), major diastereomer: δ 246.9, 147.2, 126.7, 122.8, 122.1, 52.7, 17.9, 17.5, 16.4, -3.2. Minor diastereomer: δ 247.5, 143.5, 126.6, 125.5, 123.4, 47.6, 14.9, 13.2, 11.9, -3.4. IR (film) 3071, 2959, 1645, 1250, 846 cm^{-1}. HRMS (ESI) *m*/*z* 239.0922 [$(M+H)^+$; calcd for $C_{12}H_{19}OSiS$, 239.0926]. Spectroscopic data for **242**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (dd, *J* = 2.0, 6.5 Hz, 1 H), 6.07 (m, 1 H), 5.83 (ddd, *J* = 3.5, 8.5, 12.0 Hz, 1 H), 5.66 (ddd, *J* = 1.0, 3.0, 6.5 Hz, 1 H), 5.42 (dd, *J* = 3.0, 7.0 Hz, 1 H), 4.40 (m, 1 H), 2.81 (m, 1 H), 2.46 (quintet, *J* = 3.5 Hz, 1 H), 1.59 (s, 1 H), 0.15 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 131.8, 129.1, 126.3, 123.1, 122.7, 67.8, 57.2, 26.4, -2.3. IR (film) 3418, 3017, 2955, 1246, 839 cm^{-1}. HRMS (ESI) *m*/*z* 221.0821 [$(M-OH)^+$; calcd for $C_{12}H_{19}OSiS$, 221.0820].

*Preparation of compounds **243a***

Applying general procedure E to **157a** (45.5 mg, 0.1817 mmol, 1 equiv) and 2nd generation Grubbs catalyst (6.1 mg, 0.007 mmol, 0.04 equiv) in CH_2Cl_2 (2 mL) at room temperature for 3 hours afforded after column chromatography (30% CH_2Cl_2 in hexanes) 33 mg (82%) of **243a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 1 H), 6.31 (dd, *J* = 2.0, 3.0 Hz, 1 H), 6.26 (m, 1 H), 5.76 (m, 2 H), 4.86 (t, *J* = 5.0 Hz, 1 H), 3.86 (m, 1 H), 2.49–2.37 (m, 2 H), 0.07 (s, 9

H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 141.9, 128.1, 119.2, 109.9, 107.1, 68.1, 66.4, 27.7, -3.4. IR (neat) 3030, 2955, 1248, 1057, 1012, 841 cm^{-1}. HRMS (EI) *m*/*z* 222.1081 [(M^+); calcd for $C_{12}H_{18}O_2Si$, 222.1076].

*Preparation of compounds **243b***

Applying general procedure F to **157b** (108 mg, 0.431 mmol, 1 equiv) and 2nd generation Grubbs catalyst (14.6 mg, 0.017 mmol, 0.04 equiv) in benzene (6 mL) at 80 ^{o}C for 1 hour afforded after column chromatography (20% CH_2Cl_2 in hexanes) 83 mg (87%) of **243b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 1 H), 6.32 (dd, *J* = 2.0, 3.0 Hz, 1 H), 6.23 (m, 1 H), 5.77 (m, 2 H), 4.42 (dd, *J* = 3.0, 5.5 Hz, 1 H), 4.14 (m, 1 H), 2.43 (m, 1 H), 2.21 (m, 1 H), 0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 141.7, 128.1, 120.6, 110.0, 105.8, 71.7, 69.6, 29.8, -4.1. IR (film) 3030, 2959, 2776, 1248, 843 cm^{-1}. HRMS (EI) *m*/*z* 222.1080 [(M^+); calcd for $C_{12}H_{18}O_2Si$, 222.1076].

*Preparation of compound **244***

Applying general procedure H to **243b** (56.6 mg, 0.255 mmol, 1 equiv) and *sec*-butyllithium (1.6 M in cyclohexane, 0.55 mL, 3 equiv) at -78 ^{o}C for 3.5 hours afforded after workup and column chromatography (5% EtOAc in hexanes) 21.2 mg (37%) of **244** (dr = 1:0.7) as a colorless oil and 12.9 (23%) of unreacted **243b** (single diastereomer). Mixture of diastereomers (1:0.7) ^{1}H NMR

(600 MHz, $CDCl_3$) δ 7.23 (m, 1 H), 7.20 (m, 0.7 H), 6.24 (m, 1 H), 6.22 (m, 0.7 H), 5.94 (m, 1 H), 5.92 (m, 1 0.7 H), 2.70 (dd, A of ABX system, *J* = 6.6, 17.4 Hz, 0.7 H), 2.54 (dd, B of ABX system, *J* = 7.2, 16.8 Hz, 0.7 H), 2.50 (dd, C of CDX system, *J* = 7.2, 18.0 Hz, 1 H), 2.39 (dd, D of CDX system, *J* = 6.0, 18.0 Hz, 1 H), 2.05 (dt, *J* = 6.0, 9.0 Hz, 1 H), 1.64 (dt, *J* = 4.8, 8.0 Hz, 0.7 H), 1.43 (m, 1 H), 1.38 (m, 0.7 H), 1.10 (dt, *J* = 4.8, 8.4 Hz, 1 H), 1.03 (dt, *J* = 4.8, 9.0 Hz, 0.7 H), 0.66 (m, 1.7 H), 0.18 (s, 6.3 H), 0.08 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) Major diastereomer: δ 247.3, 154.4, 141.0, 110.1, 106.5, 47.7, 13.3, 12.6, 10.1, -3.2. Minor diastereomer: δ 246.9, 156.2, 140.4, 110.2, 103.6, 52.5, 15.8, 14.5, 13.3, -3.1. IR (film) 2961, 1645, 1250, 844 cm^{-1}. HRMS (EI) *m/z* 222.1086 [(M^+); calcd for $C_{12}H_{18}O_2Si$, 222.1076].

*Preparation of compound **245***

Applying general procedure G to **243a** (93.8 mg, 0.422 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.29 mL, 1.2 equiv) at -78 ^oC for 10 minutes afforded after workup and column chromatography (10% EtOAc in hexanes) 76 mg (81%) of **245** (dr = 20:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (dd, *J* = 2.0, 3.0 Hz, 1 H), 5.84 (dddd, *J* = 0.5, 3.5, 7.5, 12.0 Hz, 1 H), 5.63 (ddd, *J* = 0.5, 3.0, 12.0 Hz, 1 H), 5.46 (m, 1 H), 5.15 (m, 1 H), 4.11 (m, 1 H), 2.82 (d of quintets, A of ABX system, *J* = 3.5, 20.0 Hz, 1 H), 2.50 (dt, B of ABX system, *J* = 7.5, 20.0 Hz, 1 H), 0.13 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 145.3, 132.1, 131.1, 103.8. 100.4, 64.9, 50.3, 24.5, -2.6. IR (film) 3499, 3013, 2955, 1246, 1151, 839 cm^{-1}. HRMS (EI) *m/z* 222.1068 [(M^+); calcd for $C_{12}H_{18}O_2Si$, 222.1076].

*Preparation of compounds **246a***

Applying general procedure E to **158a** (97 mg, 0.387 mmol, 1 equiv) and 2nd generation Grubbs catalyst (13.2 mg, 0.0155 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) at room temperature for 3 hours afforded after column chromatography (30% CH_2Cl_2 in hexanes) 77 mg (90%) of **246a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 2 H), 6.41 (m, 1 H), 5.74 (m, 2 H), 4.77 (t, *J* = 4.5 Hz, 1 H), 3.90 (m, 1 H), 2.46 (m, 1 H), 2.24 (m, 1 H), 0.07 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 139.9, 128.2, 126.0, 119.5 109.9, 67.8, 65.6, 29.4, -3.3. IR (neat) 3028, 2957, 1248, 1055, 1026, 841 cm^{-1}. HRMS (EI) *m*/*z* 222.1072 [(M^+); calcd for $C_{12}H_{18}O_2Si$, 222.1076].

*Preparation of compounds **247b***

Applying general procedure F to **159b** (96 mg, 0.24 mmol, 1 equiv) and 2nd generation Grubbs catalyst (8.2 mg, 0.0096 mmol, 0.04 equiv) in benzene (3 mL) at 80 ^{o}C for 1 hour afforded after column chromatography (30% CH_2Cl_2 in hexanes) 85 mg (95%) of **247b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.53 (s, 1 H), 7.33 (m, 1 H), 7.24 (m, 1 H), 5.88 (m, 2 H), 4.70 (m, 1 H), 4.25 (m, 1 H), 2.57–2.50 (m, 1 H), 2.40–2.33 (m, 1 H), 1.69 (s, 9 H), 0.12 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 135.7, 129.2, 128.1, 124.2, 123.1, 122.3, 122.0, 120.9, 120.4, 115.2, 83.4, 71.7, 70.3, 31.8, 28.2, -4.0. HRMS (EI) *m*/*z* 371.1910 [(M^+); calcd for $C_{21}H_{29}NO_3Si$, 371.1917].

*Preparation of compounds **248a/248b***

Applying general procedure E to **162a**/**162b** (~1:4.8 ratio, 313 mg, 1.025 mmol, 1 equiv) and 2nd generation Grubbs catalyst (35 mg, 0.041 mmol, 0.04 equiv) in CH_2Cl_2 (11 mL) at room temperature overnight afforded after column chromatography (35% and 50% CH_2Cl_2 in hexanes) 41.1 mg (14%) of **248a** and 225 mg (79%) of **248b** as colorless oils. Spectroscopic data for **248a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.0 Hz, 2 H), 7.52 (d, *J* = 9.0 Hz, 2 H), 5.78 (m, 2 H), 4.79 (dd, *J* = 4.2, 6.6 Hz, 1 H), 3.99 (m, 1 H), 2.47 (m, 1 H), 2.33 (m, 1 H), 0.08 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.6, 147.0, 128.3, 127.2 (2 C), 123.4 (2 C), 119.3, 71.4, 70.1, 30.1, -3.1. Spectroscopic data for **248b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.0 Hz, 2 H), 7.49 (d, *J* = 9.0 Hz, 2 H), 5.83 (m, 1 H), 5.78 (m, 1 H), 4.48 (dd, *J* = 3.0, 10.8 Hz, 1 H), 4.17 (m, 1 H), 2.27 (m, 1 H), 2.09 (m, 1 H), 0.09 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3, 147.0, 128.1, 126.3 (2 C), 123.4 (2 C), 120.4, 74.6, 71.7, 33.8, -4.1.

*Preparation of compounds **249a/249b***

Applying general procedure E to **142a**/**142b** (~1:1 ratio, 237 mg, 0.698 mmol, 1 equiv) and 2nd generation Grubbs catalyst (23.7 mg, 0.0279 mmol, 0.04 equiv) in CH_2Cl_2 (7 mL) at room temperature for 4 hours afforded after column chromatography (8% and 30% CH_2Cl_2 in hexanes) 98 mg (45%) of **249a** and 100 mg (47%) of **249b** as colorless oils. Spectroscopic data for **249a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 5.77 (m, 2 H), 4.67 (dd, *J* = 4.8, 6.0 Hz, 1 H), 3.95 (m, 1 H), 2.40 (m, 1 H), 2.33 (m, 1 H), 0.07 (s, 9

H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 131.3 (2 C), 128.4 (2 C), 128.2, 121.0, 119.7, 71.6, 69.7, 29.9, -3.1. HRMS (EI) *m*/*z* 310.0381 [(M^+); calcd for $C_{14}H_{19}OSiBr$, 310.0389]. Spectroscopic data for **249b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 5.79 (m, 2 H), 4.33 (dd, *J* = 3.0, 10.2 Hz, 1 H), 4.14 (m, 1 H), 2.19 (m, 1 H), 2.11 (m, 1 H), 0.07 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 131.2 (2 C), 128.1, 127.4 (2 C), 120.8, 120.7, 74.8, 71.7, 34.0, -4.0. HRMS (EI) *m*/*z* 310.0388 [(M^+); calcd for $C_{14}H_{19}OSiBr$, 310.0389].

*Preparation of compounds **250** and **251***

Applying general procedure G to **249a** (86 mg, 0.276 mmol, 1 equiv) and *n*-BuLi (solution in hexanes, 0.19 mL, 0.304 mmol, 1.1 equiv) in THF (3 mL) at -78 ^{o}C for 5 minutes afforded, after workup and column chromatography 24 mg (30%) of **250** and 26 mg (32%) of **251** as colorless oils, and 9 mg (11%) of unreacted **249a**. Spectroscopic data for **250**: Mixture of diastereomers (10:1 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.27 (m, 1 H), 4.91 (t, *J* = 1.5 Hz, 1 H), 4.76 (dd, *J* = 2.0, 11.5 Hz, 1 H), 2.38 (m, 1 H), 2.08 (m, 1 H), 1.44–1.31 (m, 7 H), 0.89 (t, *J* = 7.0 Hz, 3 H), 0.12 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 143.4, 128.2 (2 C), 127.2, 125.7 (2 C), 115.1, 76.9, 38.6, 35.9, 33.0, 29.0, 22.8, 14.1, -2.4. HRMS (EI) *m*/*z* 288.1900 [(M^+); calcd for $C_{18}H_{28}OSi$, 288.1909]. Spectroscopic data for **251**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.25 (m, 1 H), 5.87 (m, 1 H), 5.63 (dt, *J* = 2.0, 10.5 Hz, 1 H), 4.68 (dd, *J* = 5.0, 8.0 Hz, 1 H), 2.20 (m, 2 H), 1.75 (m, 1 H), 1.56 (m, 1 H), 1.46 (m, 1 H), 1.34–1.25 (m, 3 H), 0.91 (t,

J = 7.5 Hz, 3 H), 0.10 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 131.6, 128.2 (2 C), 127.1, 126.0 (2 C), 121.6, 76.3, 73.0, 36.4, 32.8, 25.2, 23.3, 14.3, -2.1. HRMS (EI) *m*/*z* 288.1895 [(M^+); calcd for $C_{18}H_{28}OSi$, 288.1909].

*Preparation of compound **255a** – General Procedure I*

To a solution of **222** (30.5 mg, 0.124 mmol, 1 equiv) in CH_2Cl_2 (0.5 mL) was added $NaHCO_3$ (12.5 mg, 0.149 mmol, 1.2 equiv) and *m*-CPBA (~77% w/w, 30.5 mg, 0.136 mmol, 1.1 equiv) and the mixture was stirred at room temperature without the exclusion of air. The reaction was monitored by TLC (10% EtOAc in hexanes). After 35 minutes the starting material was consumed. The reaction was diluted with CH_2Cl_2 (3 mL) and washed with $Na_2SO_{3\ (sat)}$ (2 mL) and $NaHCO_{3\ (sat)}$ (2 mL). The aqueous phase was extracted with CH_2Cl_2 (3 mL). Combined organic extracts were dried over $MgSO_4$ and concentrated. The crude product was clean as judged by ^{1}H NMR. Recrystallization from hexanes/ CH_2Cl_2 afforded crystals suitable for X-ray analysis. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.27 (m, 4 H), 7.21 (m, 1 H), 4.55 (m, 1 H), 3.76 (dd, *J* = 9.0, 12.6 Hz, 1 H), 2.49 (ddd, A of ABX system, *J* = 1.2, 8.4, 13.8 Hz, 1 H), 2.40 (dd, B of ABX system, *J* = 4.2, 12.6, 13.8 Hz, 1 H), 1.73 (s, 1 H), 1.28 (s, 3 H), -0.04 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.0, 137.0, 128.4 (2 C), 127.8 (2 C), 126.7, 72.5, 50.7, 50.1, 36.7, 13.8, -2.3.

*Preparation of compound **255b***

Applying general procedure I to the diastereomer of **222** (16.6 mg, 0.067 mmol, 1 equiv) and *m*-CPBA (77% w/w, 16.6 mg, 0.074 mmol, 1.1 equiv) in CH_2Cl_2 (2 mL) afforded after column chromatography (20% EtOAc in hexanes) 8.4 mg (48%) of **255b** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (m, 2 H), 7.21 (m, 3 H), 4.54 (m, 1 H), 3.37 (dd, *J* = 8.4, 9.6 Hz, 1 H), 2.74 (ddd, *J* = 5.4, 9.6, 13.8 Hz, 1 H), 2.18 (ddd, *J* = 4.8, 8.4, 13.8 Hz, 1 H), 1.65 (s, 1 H), 1.23 (s, 3 H), 0.12 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 218.1, 139.2, 128.6 (2 C), 128.5 (2 C), 126.7, 72.8, 53.9, 49.7, 38.6, 12.2, -3.6.

*Preparation of compound **256***

Applying general procedure I to **197** (49 mg, 0.1588 mmol, 1 equiv) and *m*-CPBA (77% w/w, 39 mg, 0.074 mmol, 1.1 equiv) in CH_2Cl_2 (2.5 mL) afforded after column chromatography (30% EtOAc in hexanes) 14 mg (27%) of **256** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (m, 4 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 7.31 (m 1 H), 7.27 (d, *J* = 8.4 Hz, 1 H), 4.71 (d, *J* = 4.2 Hz, 1 H), 3.86 (dd, *J* = 8.4, 12.6 Hz, 1 H), 2.53 (m, 1 H), 2.36 (dt, *J* = 4.2, 13.2 Hz, 1 H), 2.31 (m, 1 H), 1.72 (s, 1 H), 0.15 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 215.7, 140.9, 139.8, 136.3, 128.7 (2 C), 128.4 (2 C), 127.3 (2 C), 127.1, 127.0 (2 C), 70.5, 54.0, 51.0, 39.2, -1.5.

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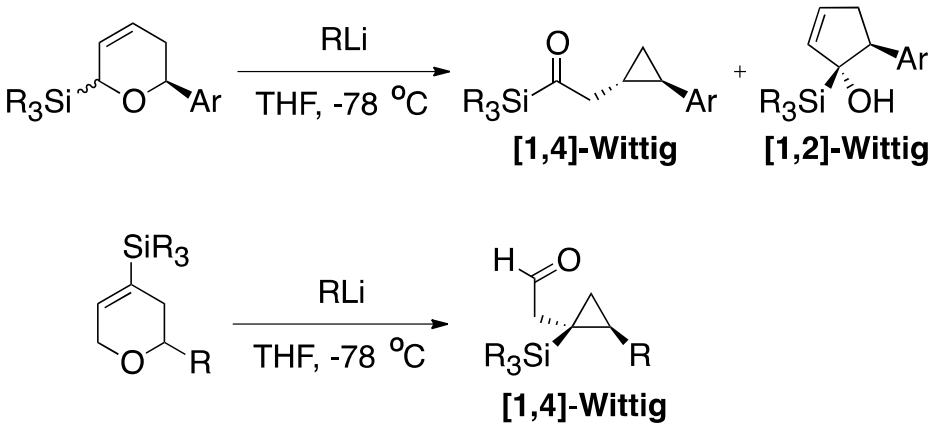
CHAPTER 5

SILYL CYCLOPROPANES VIA [1,4]-WITTIG REARRANGEMENTS OF 4-SILYL-5,6-DIHYDRO-(*2H*)-PYRANS

5.1 Introduction

The construction and functionalization of the cyclopropane ring,[1, 2] as well as the exploitation of its biochemical properties are of current interest among chemists.[3] Its unique olefin-like chemical behavior, as well as its ring strain, make it a versatile synthetic intermediate and therefore methods for the rapid access to adorned cyclopropane compounds are of current interest. Metalloid-substituted cyclopropanes, in particular those potentially able to undergo cross-coupling reactions,[4] are of great value because they can lead to a plethora of more complex derivatives. In general, the synthesis cyclopropyl compounds containing B, Si, Ge and Sn are based on carbene additions to olefins or [2+1]-cycloadditions,[5] addition of metal hydrides M-H (M=B, Ge, Sn) or bismetallic species to cyclopropenes,[6] and intramolecular 1,3-cyclizations.[7] Silyl cyclopropanes, in particular, are prepared from vinylsilanes and carbenes, from olefins and trialkylsilyl diazomethane reagents, by trapping cyclopropyl anions with silyl electrophiles, by addition of bismetallic silyl reagents to cyclopropenes and by intramolecular ring closures. The development of alternative methods to silyl cyclopropanes is desirable, especially if unique features like regio and stereoselectivity complement the outcome of existing synthetic approaches. In this chapter we describe the efficient ring contraction of easily accessible 4-silyl-5,6-dihydropyrans via [1,4]-Wittig rearrangement to the corresponding silyl cyclopropanes (Scheme 87). The rearrangements proceed with exceptional [1,4]-selectivity, and little or no [1,2]-Wittig products are observed in most cases. The diastereoselectivity, albeit modest, leads to

cyclopropane compounds in which different silyl groups are located at a quaternary carbon in the most hindered position. In addition, not only benzylic groups undergo intramolecular migration, but also simple, unactivated alkyl groups are competent in this transformation.



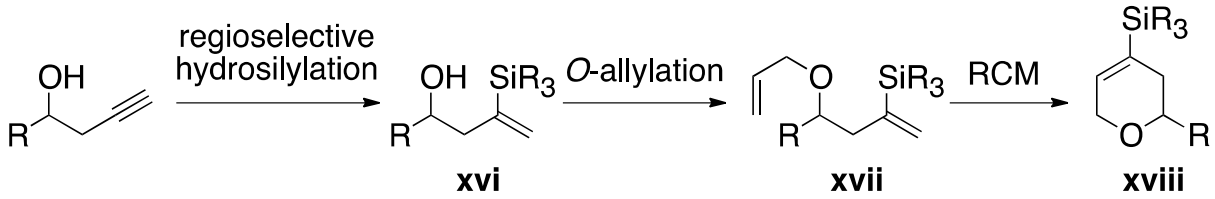
Scheme 87. Wittig rearrangements of silyl dihydropyrans.

As part of efforts to understand the factors that control the regioselection between [1,4]- vs. [1,2]-Wittig rearrangements of ethers, Chapter 4 described the stereoconvergent ring contraction of 2-silyl-5,6-dihydropyrans to the corresponding α-cyclopropyl acylsilanes (via [1,4]-Wittig) and α-silyl cyclopentenol derivatives (via [1,2]-Wittig), respectively (Scheme 87). The observation that *cis* diastereomers were less reactive that their *trans* counterparts led us to explore how the reactivity and [1,4]-/[1,2]-selectivity would be affected by transferring the silyl group to a remote position. We hypothesized that placing the silyl group at the 4-position would still favor deprotonation at the allylic position, rather than at the benzylic. In fact, Nakai and coworkers have shown unsymmetrical γ-silyl bisallylic ethers undergo selective deprotonation at the allylic moiety bearing silicon.[8] In addition, although we had previously observed that alkyl substitution at the 4-position led to low [1,4]-/[1,2]-selectivity, we envisioned the use of electron

rich aryl groups could be used to steer the regioselectivity in favor of the [1,4]-Wittig pathway, however, the steric demand of the silyl group does not decrease the [1,4]-/[1,2]-selectivity.

5.2 Synthesis of 4-silyl-5,6-dihydro-(*2H*)-pyrans

The construction of dihydropyran scaffolds and its derivatives is of current interest among synthetic organic chemists given its presence in biologically active natural products and pharmaceutical molecules.[9] Many of these approaches are flexible enough to allow the introduction of silyl groups at the 4-position and therefore we anticipate that shorter synthetic routes or asymmetric versions would provide easy access to cyclic ethers of general structure **xviii** (Scheme 88).

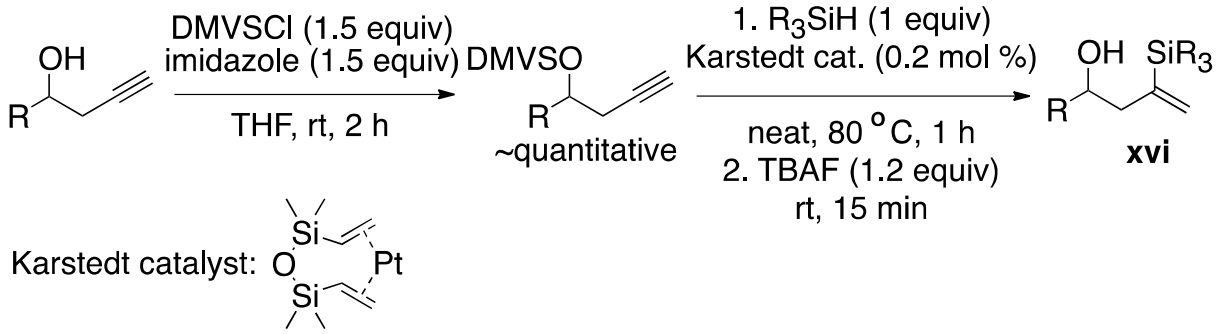


xvi **xvii** **xviii**

Scheme 88. General synthetic approach for the preparation of 4-silyl dihydropyrans **xviii**.

All 4-silyl-5,6-dihydro-(*2H*)-pyrans (**xviii**) involved in this study were prepared by ring-closing metathesis (RCM) of silylated diene precursors **xvii** which, in turn, were accessed by *O*-allylation of 3-silyl homoallylic alcohols **xvi** (Scheme 88). The synthesis of 3-silyl homoallylic alcohols was achieved by transition metal-catalyzed regioselective hydrosilylation of the corresponding homopropargylic alcohols with different silanes. As it will be shown later, the order of steps involving hydrosilylation and *O*-allylation were interchangeable, which makes the whole process accessible to the introduction of sensitive silanes.

Table 11. Synthesis of internal vinyl silanes **xvi** following Tomooka's strategy.

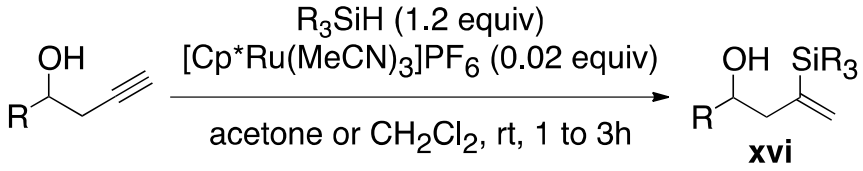


Entry	R	SiR_3	Yield **xvi** [a]
1	Ph	$SiMePh_2$	(**257**) 53%
2	Ph	$SiEt_3$	(**258**) 77%
3	4-MeC_6H_4	$SiMePh_2$	(**259**) 64%
4	4-ClC_6H_4	$SiMePh_2$	(**260**) 73%
5	2-pyridyl	$SiMePh_2$	(**261**) 22%
6	2-naphtyl	$SiMePh_2$	(**262**) 59%
7	Ferrocenyl	$SiMePh_2$	(**263**) 71%
8	cyclohexyl	$SiMePh_2$	(**264**) 67%
9	propyl	$SiMePh_2$	(**265**) 73%
10	cyclopropyl	$SiMePh_2$	(**266**) 51%
11	cyclopropyl	$SiEt_3$	(**267**) 60%

[a] Isolated yields of mixtures of regioisomers (>10:1).

Applying the strategy recently developed by Tomooka *et al.*[10] different aryl and alkyl homopropargylic alcohols were *O*-silylated with dimethylvinylsilyl chloride (DMVSCl) and the crude siloxane intermediate was regioselectively hydrosilylated with Karstedt catalyst to give the desired regioisomer with good selectivity (>10:1) after *O*-desilylation with TBAF (Table 11). Alternatively, the required internal vinylsilanes were prepared by regioselective hydrosilylation of homopropargylic alcohols with Trost catalyst[11] $[Cp^*Ru(MeCN)_3]PF_6$ (Table 12). This method was more compatible with volatile ($EtMe_2SiH$) and sensitive silanes ($BnMe_2SiH$), since no heating was required and no fluoride sources were needed.

Table 12. Regioselective hydrosilylation of homopropargylic alcohols with Trost catalyst.

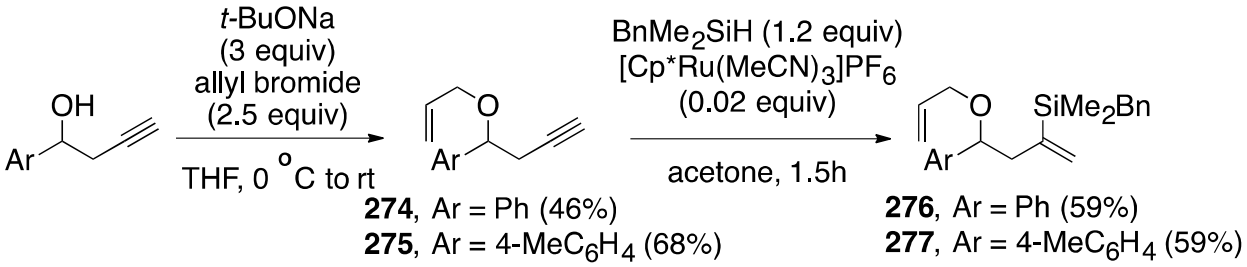


xvi

entry	R	SiR_3	Yield **xvi** [a]
1	Ph	$SiMe_2Et$	(**268**) 72%
2	Ph	$SiMe_2Bn$	(**269**) 57%
3	2-MeC_6H_4	$SiMe_2Et$	(**270**) 88%
4	3-ClC_6H_4	$SiMe_2Et$	(**271**) 81%
5	3-$MeOC_6H_4$	$SiMe_2Et$	(**272**) 73%
6	2-thiophenyl	$SiMe_2Et$	(**273**) 29%

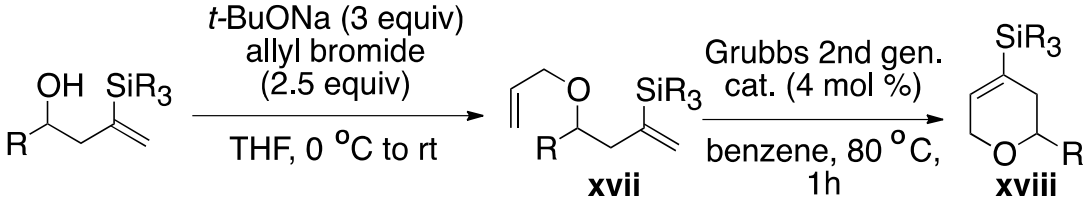
[a] Isolated yields of >>10:1 mixture of regioisomers.

With the 3-silyl homoallylic alcohols (**xvi**) in hand, the next steps involved etherification with allyl bromide under basic conditions to compounds **xvii**, and ring closing metathesis to obtain dihydropyrans **xviii**. Table 13 shows the *O*-allylation of some 3-silyl homoallylic alcohols (exceptions are entries 4 & 6) and the subsequent ring closing metathesis catalyzed by 2nd generation Grubbs catalyst, which proceeded smoothly at 80 ^{o}C to provide all the desired 4-silyl-5,6-dihydropyrans **xviii** in excellent yields. This route worked well for most substrates, however, substrates **xvi** bearing a dimethylbenzylsilane group (e.g. **269**) were susceptible to nucleophilic attack at silicon by the base (*t*-BuONa) and little or no desired products were obtained in these cases. For this reason the introduction of the dimethylbenzylsilyl group was done after alkylation of homopropargylic alcohols. Accordingly, homopropargylic alcohols were first etherified with benzyl bromide, and the resulting enynes (**274** & **275**) were regioselectively hydrosilylated using Trost catalyst (Scheme 89). Importantly, the use of acetone[11b] as the solvent was key to allow *anti*-Markovnikov hydrosilylation. The use of dichloromethane, a solvent that provides good regioselectivity for the hydrosilylation of most homopropargylic alcohols, was detrimental for the selectivity in the hydrosilylation of ethers. Although acetone and dichloromethane have been shown to give comparable regioselectivitity for the hydrosilylation of terminal alkynes bearing remote ester and alcohol groups, the behavior of terminal alkynes bearing only ethers has not been reported. The improvement of regioselection observed in the hydrosilylation of allylic homopropagyl ethers (**274** and **275**) in going from dichloromethane to acetone is an observation of practical importance.



Scheme 89. Switching steps: *O*-alkylation followed by regioselective hydrosilylation.

Table 13. Preparation of cyclic ethers **xviii** by etherification and ring-closing metathesis.



entry	R	SiR_3	Yield **xvii** [a]	Yield **xviii** [a]
1	Ph	$SiMe_2Ph$	(**278**) 90%	(**294**) 99%
2	Ph	$SiEt_3$	(**279**) 88%	(**295**) 97%
3	Ph	$SiMe_2Et$	(**280**) 78%	(**296**) 91%
4	Ph	$SiMe_2Bn$	(**276**) n.a.[b]	(**297**) 59%
5	4-MeC_6H_4	$SiMe_2Ph$	(**281**) 86%	(**298**) 96%
6	4-MeC_6H_4	$SiMe_2Bn$	(**277**) n.a.[b]	(**299**) 80%
7	2-MeC_6H_4	$SiMe_2Et$	(**282**) 92%	(**300**) 99%
8	3-$MeOC_6H_4$	$SiMe_2Et$	(**283**) 85%	(**301**) 86%
9	ferrocenyl	$SiMe_2Ph$	(**284**) 78%	(**302**) 70%
10	2-thiophenyl	$SiMe_2Et$	(**285**) 84%	(**303**) 60%

Table 13 (cont'd)

entry	R	SiR_3	Yield **xvii** [a]	Yield **xviii** [a]
11	4-ClC_6H_4	$SiMe_2Ph$	(**286**) 91%	(**304**) 97%
12	3-ClC_6H_4	$SiMe_2Et$	(**287**) 91%	(**305**) 84%
13	2-pyridyl	$SiMe_2Ph$	(**288**) 87%	(**306**) 98%
14	2-naphtyl	$SiMe_2Ph$	(**289**) 89%	(**307**) 86%
15	cyclohexyl	$SiMe_2Ph$	(**290**) 69%	(**308**) 96%
16	Propyl	$SiMe_2Ph$	(**291**) 90%	(**309**) 80%
17	cyclopropyl	$SiMe_2Ph$	(**292**) 80%	(**310**) 91%
18	cyclopropyl	$SiEt_3$	(**293**) 84%	(**311**) 86%

[a] Isolated yields of single regioisomer. [b] Not applicable, see Scheme 89.

5.3 [1,4]- and [1,2]-Wittig rearrangements of 4-silyl-5,6-dihydro-(*2H*)-pyrans

5.3.1 Influence of the silyl group on the [1,4]-/[1,2]-selectivity

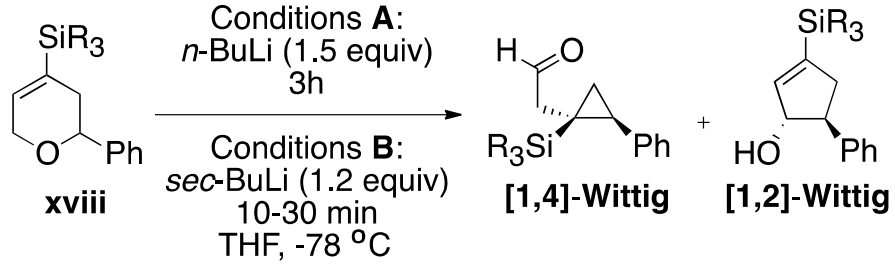
We commenced our study by submitting compound **294**, bearing a $SiMe_2Ph$ group, to similar conditions we used in our previous study (Table 14). Allylic deprotonation of **294** with *n*-butyllithium at -78 ^oC (conditions **A**) took place regioselectively, and followed exclusive [1,4]-Wittig rearrangement to give, after work up, silyl cyclopropane **312** in excellent yield and modest diastereoselectivity (entry 1). No [1,2]-Wittig products were observed in the ^1H NMR spectrum of the crude reaction mixture, but traces of another aldehyde were detected. The rearrangement did not reached completion after ~3 hours when 1.2 equivalents of *n*-butyllithium

was employed. The reaction time decreased to 1 hour when the temperature was raised to -45 ^{o}C after addition of 2 equivalents *n*-butyllithium at -78 ^{o}C, affording compound **312** in 93% yield, also with modest diastereoselectivity (2.2:1, data not shown in Table 14). When the reaction was quenched at -78 ^{o}C, 10 minutes after *n*-butyllithium addition, the product was obtained with similar diastereomeric ratio (3:1) to that observed after 3 hours, confirming that no epimerization of the [1,4]-enolate intermediate took place within the reaction period. The use of a stronger base, *sec*-butyllithium, reduced the reaction time to only 30 minutes (conditions **B**) and provided product **312** with a subtle increase in diastereomeric ratio (entry 2).

The effect of the silyl group on the product distribution and diastereoselectivity was studied next (Table 14). An analogous compound (**295**) having the bulkier $SiEt_3$ group gave the [1,4]-Wittig product (**313**) in good yield and improved diastereoselectivity under both reaction conditions, but also provided trace amounts of the competitive [1,2]-Wittig product **314** (entries 3 & 4). It is interesting that increasing the bulkiness of the silyl group (e.g. $SiEt_3$) had a little effect on the [1,4]-/[1,2]-selectivity. This is in contrast to the case of 2-silyl-5,6-dihydropyrans (Chapter 4) in which the increase of steric demand of the silyl group led to better [1,4]-/[1,2]-selectivity, presumably by preventing [1,2]- cyclization of the intermediate diradical anion. The smaller $SiMe_2Et$ group in compound **296** provided exclusive cyclopropylsilane product (**315**) with slightly improved diastereoselectivity (entries 5 & 6) relative to the $SiMe_2Ph$ analogue. It was gratifying that the $SiMe_2Bn$ group (compound **297**), which did not survive basic conditions at

room temperature (Section 5.2), remained untouched and clean [1,4]-Wittig rearrangement of **297** produced aldehyde **316** in excellent yield, albeit with modest diastereoselectivity (entry 7).

Table 14. Effect of silyl group in the Wittig rearrangements of 4-silyldihydropyrans.



entry	substrate	SiR_3	Conditions	Yield [1,4] [a]	dr [b]	Yield [1,2] [a]	dr [b]
1	**294**	$SiMe_2Ph$	**A** [c]	(**312**) 80%	3.3:1	-	-
2	**294**	$SiMe_2Ph$	**B**	(**312**) 91%	4.7:1	-	-
3 [d]	**295**	$SiEt_3$	**A**	(**313**) 78%	11:1	(**314**) trace	n.d.
4	**295**	$SiEt_3$	**B**	(**313**) 70%	11:1	(**314**) 2%	20:1
5 [e]	**296**	$SiMe_2Et$	**A**	(**315**) 66%	9:1	-	-
6	**296**	$SiMe_2Et$	**B**	(**315**) 85%	4:1	-	-
7	**297**	$SiMe_2Bn$	**B**	(**316**) 90%	3:1	-	-

[a] Isolated yields. [b] Determined by ^{1}H NMR. [c] 1.2 equiv of *n*-BuLi, 7% recovered **294**. [d] 13% recovered **295**. [e] 25% recovered **296**.

Thus, multiple silyl groups were compatible with our reaction conditions and reacted, in virtually all cases, exclusively via the [1,4]-Wittig pathway. The relative stereochemistry of the major diastereomer in **312** was assigned as *cis* based on NOE studies, and supported by the significant

non-equivalence of the silyl methyl protons in the ^{1}H NMR spectrum. In all cases shown in table 14 the major diastereomer of the cyclopropyl silanes was *cis* (with respect to the silyl and aryl groups) even when bulkier silyl groups (e.g. $SiEt_3$) were present.

5.3.2 Substrate scope

We then proceeded to study the scope of this reaction under conditions **B** (*sec*-BuLi, -78 ^{o}C, 10 minutes). Electron-donating groups at the aromatic appendage (**298** – **301**) also allowed exclusive rearrangement via the [1,4]-Wittig manifold to give silyl cyclopropanes **317 – 320** in excellent yields (Figure 12). Notably, an *ortho* methyl group at the aromatic ring was tolerated without leading to competitive [1,2]-shift, and product aldehyde **319** was obtained with good diastereoselectivity. It is interesting that a methoxy group located at the *meta* position in compound **320** (and therefore inductively electron-withdrawing with respect to the benzylic position) rearranged exclusively via the [1,4]-Wittig pathway, in stark contrast to the 2-silyl analogue (Chapter 4) which afforded a 2:1 mixture of [1,2]- and [1,4]-Wittig products. A ferrocenyl group (compound **302**) was tolerated and underwent selective [1,4]- migration to silyl cyclopropane **321**. 2-thiophenyl substituted compound **303**, also rearranged selectively to give silylcyclopropane **322** with low diastereomeric ratio (2:1).

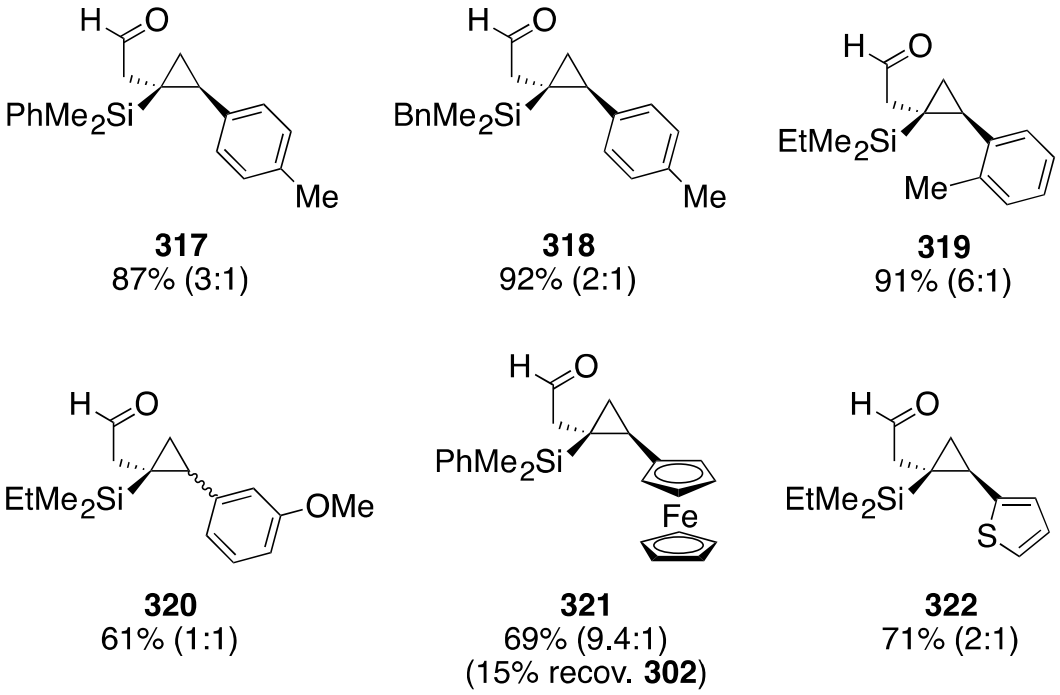
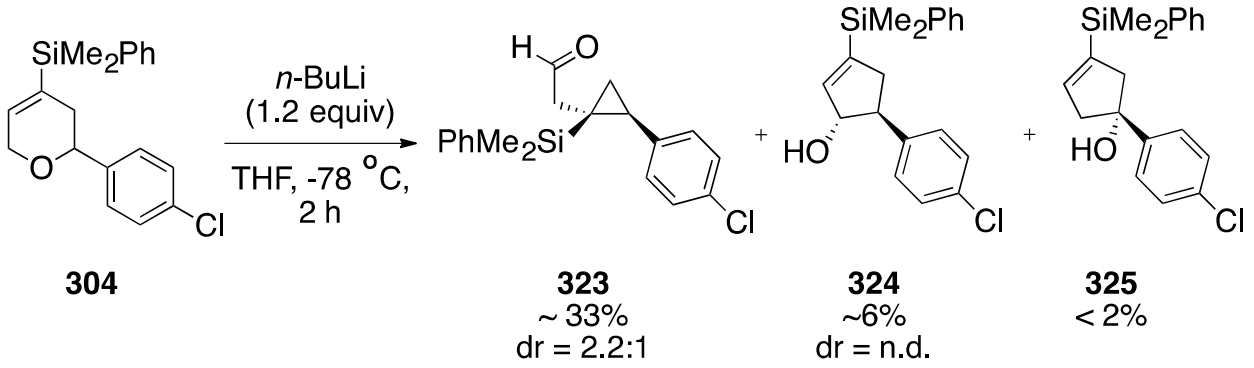


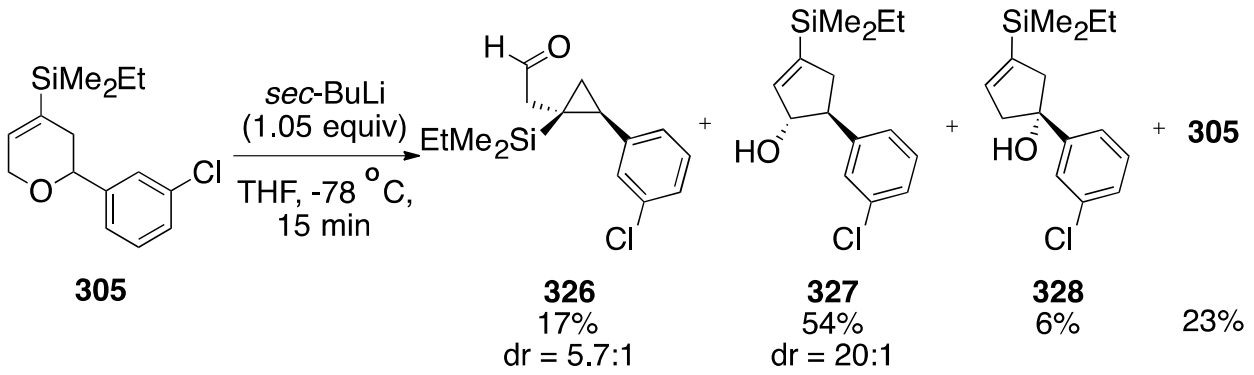
Figure 12. Silyl cyclopropanes with different aryl groups obtained by selective [1,4]-Wittig rearrangements (under conditions **B**).

On the contrary, electron-deficient aromatic group on the cyclic ethers facilitated competitive [1,2]-Wittig shift, leading to mixtures of products. For instance, *para*-chloro substitution at the phenyl ring (compound **304**) led to a mixture of [1,4]- and [1,2]-Wittig products **323** and **324** arising from allylic deprotonation / rearrangements in a ratio of 5.5:1. A minor amount of isomeric [1,2]-Wittig product **325**, formed by benzylic deprotonation followed by [1,2]-shift, was also isolated (Scheme 90).



Scheme 90. Behavior of electron-deficient substrate **304**.

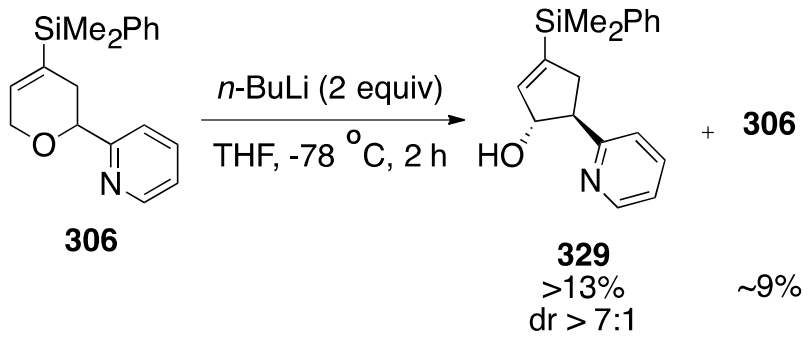
In a similar way, *meta*-chloro substituted compound **305** underwent competitive [1,2]-Wittig rearrangements from both allylic and benzylic deprotonation leading to alcohols **327** and **328** in a combined 60% (9:1 ratio). The [1,4]-pathway was minor and only 17% of silyl cyclopropane **326** was obtained (Scheme 91). These results are in line with previous discussed results (Section 4.4.2) in which electron-withdrawing groups at the aromatic group led to increased [1,2]-/[1,4]-ratio.



Scheme 91. Wittig rearrangements of electron-deficient substrate **305**.

Pyridyl substituted compound **306**, being intrinsically electron-deficient, underwent rearrangement to give a complex mixture of products, from which unreacted **306** was isolated

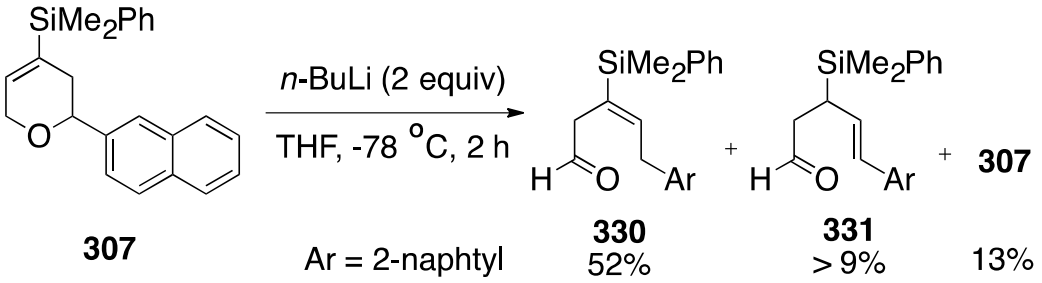
together with [1,2]-Wittig rearrangement **329** (Scheme 92). Importantly, ^{1}H NMR analysis of the crude reaction mixture did not show any hint of the expected [1,4]-Wittig products (no aldehyde signals). The relative stereochemistry of [1,2]-Wittig products **327** and **329** could not be confirmed by NOE studies due to ambiguous and inconclusive results, and thus has been tentatively assigned as *trans* according to the stereochemical outcome observed and discussed in Chapter 4.



Scheme 92. Wittig rearrangement of 2-pyridyl substrate **306**.

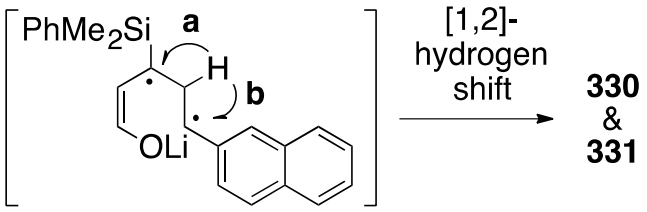
Another interesting result came from the behavior of 2-naphtyl substituted **307**. Deprotonation of **307** with *n*-BuLi led to a complex mixture of products from which unreacted starting material was recovered along with aldehydes **330** and **331** (Scheme 93). This constitutes the first case, to the best of my knowledge, in which ring-opened products have been identified in the Wittig rearrangements of small cyclic ethers. It can be argued that the steric demand of the silyl and 2-naphtyl groups prevent a [1,4]-shift due to steric clash, however, the analogous desilylated compound also afford ring-opened products (Chapter 6). In addition, this is is not consistent with the observation that the [1,2]-Wittig product is not formed even though there are no unfavorable steric interactions that might prevent it. It is important to mention that the analogous diastereomeric 2-silyl-6-(2'-napthtyl)dihydropyran **179a**/**179b** (table 6, entries 11 & 22) afford

predominantly the [1,2]-Wittig product without detection (by ^{1}H NMR) of ring-opened products similar to **330** and **331**.



Scheme 93. A possible case of interrupted Wittig rearrangements due to electronic or steric reasons.

The structures of **330** and **331** resemble that of a presumed intermediate diradical anion in which [1,2]- and [1,4]- recombination that did not take place perhaps due to electronic (in the case of [1,2]-shift), or steric (in the case of the [1,4]-shift) reasons. Instead, a [1,2]-hydrogen shift via pathways **a** or **b** would lead to the observed aldehyde products **330** and **331** (Scheme 94).

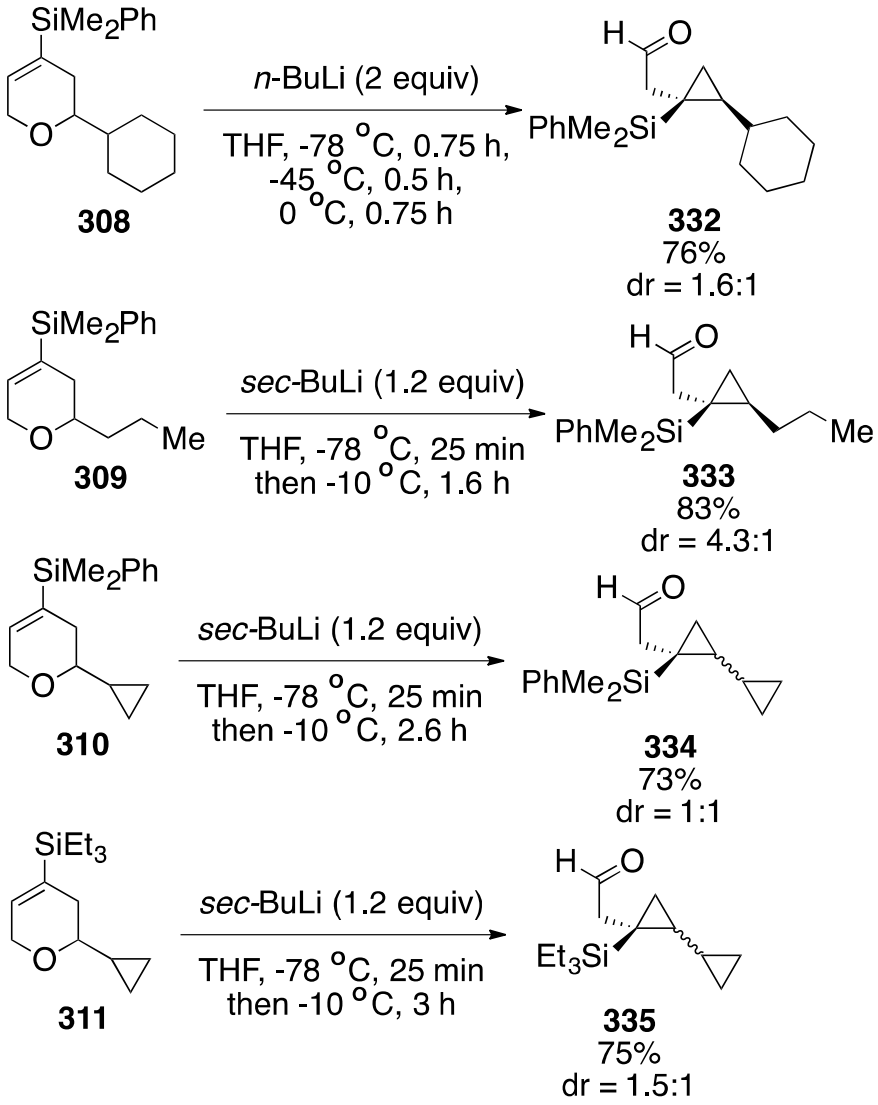


Scheme 94. Possible [1,2]-hydrogen shift of intermediate diradical anion to observed products.

The virtually complete [1,4]-Wittig selectivity in systems containing non-biased aryl substitution (Table 14) and electron-rich aryl or heteroaryl groups (Figure 12) at the migratin center suggests the silyl group is effectively favoring this pathway. The observation of an interrupted bond re-

organization (Scheme 93) supports a stepwise mechanism involving a diradical anion (Scheme 94) in which the silyl radical provides stabilization at the allyloxy radical-anion fragment. Although the stabilization of α-carboradicals by silyl groups is still a matter of debate,[12] several reports in the literature support this possibility. Such presumed stabilization seems to be overshadowed by the effect of electron deficient groups at the migrating carbon.[13]

Finally, we have found that cyclic allylic ethers bearing unactivated alkyl groups undergo selective [1,4]-Wittig rearrangement, also with modest diastereoselectivity (Scheme 95). Cyclohexyl (**308**), propyl (**309**) and cyclopropyl (**310** & **311**) groups attached to the migrating carbon of the cyclic ether allowed selective [1,4]-shift, albeit at higher temperatures. Interestingly, the cyclopropyl-substituted substrate did not afford any ring-opened products, as judged by ^{1}H NMR analysis of the crude reaction mixture. Cyclopropyl groups at the migrating carbon have been used as radical in mechanistic studies of the [1,2]- and [1,4]-Wittig rearrangements and therefore these experiments suggest that radical recombination occurs faster than ring opening.



Scheme 95. Selective [1,4]-Wittig rearrangements of unactivated alkyl-sustituted dihydropyrans.

5.4 Conclusions

In conclusion, 4-silyl-5,6-dihydro-(*2H*)-pyrans undergo selective [1,4]-Wittig rearrangement to the corresponding silyl cyclopropane products with modes diastereoselectivity. In all cases the major diastereomer has the silyl group at a quaternary carbon, oriented in the most hindered position of the cyclo propyl group. Different silyl groups have been evaluated and most of them

provide exclusively the [1,4]-product, being a triethylsilyl group the only exception that provides minor amounts of the [1,2]-product

Phenyl and electron-rich aromatic groups attached at the migrating carbon allow exclusive [1,4]-shift, whereas electron withdrawing aryl groups allow the [1,2]-pathway to become competitive, and in one case dominant. Also, such electron deficiency at the aromatic appendage allows benzylic deprotonation, leading to isomeric [1,2]- products.

Ring opened products, suggestive of a diradical anion intermediate, have been isolated in one case, which are proposed to arise from [1,2]-hydrogen shift in such intermediate. Further experiments in this regard are necessary to determine if this is indeed true.

Finally, simple alkyl groups at the migrating center also allow exclusive [1,4]-Wittig ring contraction in excellent yields and modest diastereoselectivities, albeit requiring higher reaction temperatures. This constitutes a significant expansion of the substrate scope for the [1,4]-Wittig rearrangements of (silyl) cyclic ethers that should be of significant practical interest to synthetic organic chemists.

5.5 Experimental section

*Preparation of aryl homopropargylic alcohols – **General Procedure A**:*

Following a reported procedure,[15] to a vigorously stirred suspension of Zinz dust (5.3 g, 81 mmol, 3 equiv) in THF (200 mL) at 0 ^{o}C was added propargyl bromide (80% w/w in toluene, 12 g, 81 mmol, 3 equiv) followed by $TiCl_4$ (1M in CH_2Cl_2, 1.35 mL, 1.35 mmol, 0.05 equiv). After

10 minutes, the desired aryl aldehyde (27 mmol, 1 equiv) in THF (60 mL) was adde via syringe slowly. The reaction was followed by TLC and was typically complete in 3-4 hours. The reaction was quenched by adding $NH_4Cl_{(sat)}$ (~150 mL) and slightly acidified with 1M HCl to remove the emulsion. The mixture was extracted with Et_2O (3 × 150 mL). Combined organic extracts were dried over $MgSO_4$ and concentrated. The product was purified by column chromatography.

Preparation of alkyl homopropargylic alcohols – ***General Procedure B****:*

Following a reported procedure slightly modified,[16] to a solution of 1,2-dibromoethane (0.15 mL, 1.783 mmol, 0.2 equiv) in THF (20 mL) was added Zn dust (1.17 g, 17.83 mmol, 2 equiv) with vigorous stirring. The mixture was heated at 65 ^oC for 10 minutes and then cooled down at room temperature. After 20 minutes trimethylsilyl chloride (23 μL, 0.178 mmol, 0.02 equiv) was added dropwise and 20 minutes later the reaction was cooled down at 0 ^oC. Propargyl bromide (80% w/w in toluene, 2.65 g, 17.83 mmol, 2 equiv) was added slowly with vigorous stirring. After 1 hour the mixture was cooled down at -78 ^oC and the desired alkyl aldehyde (8.915 mmol, 1 equiv) was slowly added as a solution in THF (10 mL). The temperature was slowly raised to 0 ^oC. The reaction was monitored by TLC until completion. The reaction was quenched by adding $NH_4Cl_{(sat)}$ (10 mL) and extracted with Et_2O (3 × 15 mL). Combined organic extracts were dried over $MgSO_4$ and concentrated. The product was purified by column chromatography.

Preparation of 3-silyl homoallylic alcohols (xvi) – ***General Procedure C****:*

Following a reported procedure,[17] to a solution of the desired homopropargylic alcohol (1.286 mmol, 1 equiv) and dimethylvinylsilyl chloride (1.929 mmol, 1.5 equiv) in THF (5.6 mL) at room temperature was added imidazole (1.929 mmol, 1.5 equiv) in one portion and the mixture was stirred for 2-12 hours under nitrogen. The reaction was monitored by TLC until completion. The mixture was then filtered through a plug of celite, rinsing with hexanes, and the filtrate was concentrated and suspended in hexanes. Filtration through a plug of celite and concentration afforded the crude dimethylvinylsiloxy that was used in the next step without further purification. In some cases it was necessary to repeat the treatment with hexanes to remove all insoluble material.

To a mixture of the above *O*-dimethylvinylsilyl-3-silyl homoallylic alcohol (1.813 mmol, 1 equiv) and the corresponding silane (1.813 mmol, 1 equiv) was added Karstedt catalyst as a solution in xylenes (2% w/w in xylenes, 80.7 μL, 0.002 equiv) and the mixture was heated under nitrogen at 80 ^{o}C for 1-1.5 hours. The reaction mixture was cooled down at room temperature and diluted with THF (18 mL) and TBAF (1M in THF, 2.18 mmol, 2.18 mL, 1.2 equiv) was added slowly. After 20 minutes the solution was concentrated and the residue subjected to column chromatography (EtAc/hexanes) to afford the desired 3-silyl homoallylic alcohol xvi.

Preparation of 3-silyl homoallylic alcohols (xvi) – ***General Procedure D****:*

Following a literature procedure,[11b] a solution of the desired homopropargylic alcohol (3.625 mmol, 1 equiv) and silane (4.35 mmol, 1.2 equiv) in freshly distilled acetone (11 mL, distilled from drierite) was cooled down at 0 ^{o}C and $[Cp^*Ru(MeCN)_3]PF_6$ (36.6 mg, 0.072 mmol, 0.02

equiv) was added quickly, the reaction was kept under nitrogen and the cold bath was removed. After about 1 hour the reaction mixture was concentrated and the product purified by column chromatography (EtOAc/hexanes).

Etherification of 3-silyl homoallylic alcohols (xvi) to RCM precursors (xvii) – ***General Procedure E****:*

To a solution of 3-silyl homoallylic alcohol **xvi** (0.918 mmol, 1 equiv) and allyl bromide (194 μL, 2.296 mmol, 2.5 equiv) in THF (2 mL) at 0 ^{o}C was added *t*-BuONa (265 mg, 2.75 mmol, 3 equiv) and the mixture was vigorously stirred at room temperature. After 4 hours the reaction was quenched with water (3 mL) and diluted with EtOAc (5 mL). The aqueous phase was extracted with EtOAc (3 × 5 mL). Combined organic extracts were washed with water (3 mL), brine, dried over $MgSO_4$ and concentrated. The product was purified by short column chromatography.

Preparation of 4-silyl dihydropyrans (xviii) via ring-closing metathesis of (xvii) – ***General Procedure F****:*

A round-bottom flask was charged with a magnetic stirred, the allylic ether **xvii** (100 mg, 0.31 mmol, 1 equiv) and benzene (6.2 mL), and then second-generation Grubbs catalyst (10.5 mg, 0.0124 mmol, 0.04 equiv) was added in one portion. A condenser was attached and the system flushed with nitrogen. The reaction was heated in an oil bath at 80 ^{o}C for 1-1.5 hours. The reaction was then cooled down at room temperature and concentrated. The residue was subjected

to column chromatography (CH_2Cl_2 in hexanes) to afford the desired product **xviii** as a colorless oil.

Wittig rearrangements of 4-silyl-6-aryl dihydropyrans (xviii) – ***General Procedure G****:*

Freshly prepared and purified **xvii** was dissolved in THF under nitrogen (concentration = 0.08 M, unless otherwise noticed) and the solution cooled down at -78 ^{o}C (dry ice/acetone bath). *n*-Butyllithium (1.2 equiv, 1.6 M in hexanes) or *sec*-butyllithium (1.2 equiv, 1.4 M in cyclohexane) was added dropwise (1 drop/second) to give a colored solution. After the indicated time (~3 hours or ~10 minutes, respectively) the reaction was quenched by adding $NH_4Cl_{(sat)}$, diluted with water and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with water, and brine. The solution was dried over $MgSO_4$, filtered, concentrated in a rotavap at room temperature (or lower) and the residue purified by column chromatography (5-10% EtOAc in hexanes) to afford the aldehyde and or alcohol as colorless oils.

Wittig rearrangements of 4-silyl-6-alkyl dihydropyrans (xviii) – ***General Procedure H****:*

Freshly prepared and purified **xvii** was dissolved in THF under nitrogen (concentration = 0.08 M, unless otherwise noticed) and the solution cooled down at -78 ^{o}C (dry ice/acetone bath). *n*-Butyllithium (1.2 equiv, 1.6 M in hexanes) or *sec*-butyllithium (1.2 equiv, 1.4 M in cyclohexane) was added dropwise (1 drop/second) with stirring to give a colored solution. After ~25 minutes the temperature was raised to –10 ^{o}C (unless otherwise indicated). After the indicated time (1.5-3

hours) the reaction was cooled down at -78 ^{o}C and quenched by adding $NH_4Cl_{(sat)}$, diluted with water and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with water, and brine. The solution was dried over $MgSO_4$, filtered, concentrated in a rotavap at room temperature (or lower) and the residue purified by column chromatography (4-5% EtOAc in hexanes) to afford the aldehyde as a colorless oil.

*Preparation of compound **257***[18]

Following general procedure C, the title compound was prepared in 53% yield. Compound **257** is a known compound and its spectral data are in accord with reported literature values.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.36 (m, 3 H), 7.28 (m, 2 H), 7.21 (m, 3 H), 5.84 (m, 1 H), 5.62 (m, 1 H), 4.53 (dt, *J* = 3.0, 9.5 Hz, 1 H), 2.58 (A of ABX system, m, 1 H), 2.43 (B of ABX system, dd, *J* = 10.0, 14.0 Hz, 1 H), 1.94 (d, *J* = 2.5 Hz, 1 H), 0.43 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 144.1, 137.6, 133.9 (2 C), 130.0, 129.3, 128.3 (2 C), 128.0 (2 C), 127.3, 125.7 (2 C), 72.2, 47.0, -2.90, -2.99. IR (neat) 3420, 3067, 2957, 1427, 1250, 1111, 833, 817 cm^{-1}.

*Preparation of compound **258***

Following general procedure C, the title compound was prepared in 77% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.32 (m, 4 H), 7.26 (m, 1 H), 5.82 (m, 1 H), 5.52 (d, *J* = 2.5 Hz, 1 H), 4.73

(dd, *J* = 2.5, 8.0 Hz, 1 H), 2.60 (m, 1 H), 2.40 (dd, *J* = 8.0, 11.5 Hz, 1 H), 2.13 (s, 1 H), 0.95 (t, *J* = 6.5 Hz, 9 H), 0.65 (dq, *J* = 1.5, 6.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 144.1, 129.5, 128.4 (2 C), 127.4, 125.8 (2 C), 72.0, 47.2, 7.3, 2.9. IR (film) 3406, 3032, 2953, 2876, 1456, 1008, 721 cm^{-1}. HRMS (EI) *m/z* 245.1712 [$(M\text{-}OH)^+$; calcd for $C_{16}H_{25}Si$, 245.1726].

*Preparation of compound **259***

Following general procedure C, the title compound (colorless oil) was prepared in 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.37 (m, 3 H), 7.11 (s, 4 H), 5.85 (m, 1 H), 5.62 (d, *J* = 2.5 Hz, 1 H), 4.53 (ddd, *J* = 2.5, 3.5, 9.5 Hz, 1 H), 2.57 (A of ABX system, m, 1 H), 2.44 (B of ABX system, dd, *J* = 10.0, 14.0 Hz, 1 H), 2.32 (s, 3 H), 1.92 (d, *J* = 2.0 Hz, 1 H), 0.438 (s, 3 H), 0.429 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 141.1, 137.7, 136.9, 133.9 (2 C), 129.8, 129.2, 128.9 (2 C), 127.9 (2 C), 125.6 (2 C), 72.0, 46.9, 21.1, -2.896, -2.977. IR (neat) 3422, 3047, 2955, 1427, 1248, 1111, 1047, 815 cm^{-1}. HRMS (EI) *m/z* 279.1568 [$(M\text{-}OH)^+$; calcd for $C_{19}H_{23}Si$, 279.1569].

*Preparation of compound **260***

Following general procedure C, the title compound (colorless oil) was prepared in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.36 (m, 3 H), 7.23 (d, *J* = 8.5 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 5.81 (m, 1 H), 5.63 (d, *J* = 3.0 Hz, 1 H), 4.47 (m, 1 H), 2.53 (A of ABX system, ddd, *J* = 1.0, 3.5, 14.0 Hz, 1 H), 2.36 (B of ABX system, dd, *J* = 10.0, 14.5 Hz, 1 H), 1.94 (d, *J* = 2.0 Hz, 1 H), 0.423 (s, 3 H), 0.411 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 142.5, 137.5,

133.9 (2 C), 132.9, 130.2, 129.4, 128.4 (2 C), 128.0 (2 C), 127.1 (2 C), 71.5, 47.1, -2.94, -3.0. IR (neat) 3420, 3052, 2955, 1491, 1427, 1250, 1111, 1012, 815 cm^{-1}. HRMS (EI) *m/z* 299.0955 $[(M\text{-}OH)^{+}$; calcd for $C_{18}H_{20}SiCl$, 299.1023].

*Preparation of compound **261***

Following general procedure C, the title compound (yellowish oil) was prepared in 22% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (ddd, *J* = 0.6, 1.2, 4.8 Hz, 1 H), 7.58 (dt, *J* = 1.8, 7.8 Hz, 1 H), 7.53 (m, 2 H), 7.33 (m, 3 H), 7.13 (dddd, *J* = 0.6, 1.2, 4.8, 7.2 Hz, 1 H), 7.05 (dd, *J* = 0.6, 7.8 Hz, 1 H), 5.83 (quintet, 1 H), 5.58 (d, *J* = 2.4 Hz, 1 H), 4.87 (quintet, 1 H), 3.64 (d, *J* = 5.4 Hz, 1 H), 2.63 (A of ABX system, m, 1 H), 2.42 (B of ABX system, dd, *J* = 9.0, 14.4 Hz, 1 H), 0.408 (s, 3 H), 0.399 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 148.4, 146.7, 137.9, 136.4, 134.0 (2 C), 129.6, 129.1, 127.9 (2 C), 122.2, 120.5, 71.9, 45.5, -2.9, -2.95. IR (neat) 3401, 3070, 2956, 1427, 1248, 1111, 817 cm^{-1}. HRMS (ESI) *m/z* 284.1468 $[(M+H)^{+}$; calcd for $C_{17}H_{22}NOSi$, 284.1471].

*Preparation of compound **262***

Following general procedure C, the title compound (colorless oil) was prepared in 59% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (m, 3 H), 7.62 (s, 1 H), 7.56 (m, 2 H), 7.44 (m, 2 H), 7.39 (m, 3 H), 7.31 (dd, *J* = 2.0, 9.0 Hz, 1 H), 5.89 (m, 1 H), 5.64 (d, *J* = 3.0 Hz, 1 H), 4.70 (dt, *J* = 3.0, 9.5 Hz, 1 H), 2.67 (A of ABX system, ddd, *J* = 1.0, 4.0, 14.5 Hz, 1 H), 2.51 (B of ABX system, dd, *J* = 9.5, 14.0 Hz, 1 H), 2.05 (d, *J* = 2.5 Hz, 1 H), 0.459 (s, 3 H), 0.433 (s, 3 H). ^{13}C NMR (126

MHz, $CDCl_3$) δ 147.4, 141.4, 137.6, 133.9 (2 C), 133.2, 132.8, 130.1, 129.3, 128.02, 128.0 (2 C), 127.9, 127.6, 126.0, 125.7, 124.3, 124.0, 72.3, 47.0, -2.88, -2.92. IR (neat) 3424, 3051, 2955, 1427, 1248, 1111, 815 cm^{-1}. HRMS (EI) *m/z* 315.1553 $[(M\text{-}OH)^+$; calcd for $C_{22}H_{23}Si$, 315.1569].

*Preparation of compound **263***

Following general procedure C, the title compound (orange oil) was prepared in 71% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.35 (m, 3 H), 5.79 (m, 1 H), 5.57 (d, *J* = 3.0 Hz, 1 H), 4.28 (dq, *J* = 4.0, 9.5 Hz, 1 H), 4.15 (q, *J* = 1.5 Hz, 1 H), 4.08 (t, *J* = 3.0 Hz, 2 H), 4.07 (s, 5 H), 4.01 (q, *J* = 3.0 Hz, 1 H), 2.51 (m, 1 H), 2.42 (dd, *J* = 9.0, 14.0 Hz, 1 H), 1.86 (d, *J* = 3.5 Hz, 1 H), 0.40 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 138.0, 134.0 (2 C), 129.2, 129.1, 127.9 (2 C), 93.3, 68.3 (5 C), 68.1, 67.7, 67.6, 66.8, 65.7, 45.1, -2.8, -2.9. IR (film) 3412, 3097, 2955, 1427, 1248, 1107, 817 cm^{-1}. HRMS (ESI) *m/z* 373.1069 $[(M\text{-}OH)^+$; calcd for $C_{22}H_{25}FeSi$, 373.1075].

*Preparation of compound **264***

Following general procedure C, the title compound (colorless oil) was prepared in 67% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.34 (m, 3 H), 5.79 (quintet, 1 H), 5.57 (d, *J* = 3.0 Hz, 1 H), 3.24 (m, 1 H), 2.45 (A of ABX system, m, 1 H), 2.07 (B of ABX system, dd, *J* = 10.0, 13.5 Hz, 1 H), 1.75–1.67 (m, 3 H), 1.61 (m, 1 H), 1.55 (m, 1 H), 1.30–1.23 (m, 2 H), 1.22–1.08 (m, 3

H), 0.94 (m, 2 H), 0.39 (s, 3 H), 0.38 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 137.8, 133.8 (2 C), 129.5, 129.1, 127.9 (2 C), 73.4, 43.3, 41.7, 28.9, 28.1, 26.5, 26.3, 26.1, -2.77, -2.86. IR (neat) 3472, 3049, 2926, 2853, 1427, 1250, 1113, 817 cm^{-1}. HRMS (EI) *m/z* 288.1894 [$(M)^+$; calcd for $C_{18}H_{28}OSi$, 288.1909].

*Preparation of compound **265***

Following general procedure C, the title compound (colorless oil) was prepared in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.34 (m, 3 H), 5.78 (m, 1 H), 5.57 (d, *J* = 3.0 Hz, 1 H), 3.48 (m, 1 H), 2.37 (m, 1 H), 2.13 (dd, *J* = 9.0, 13.5 Hz, 1 H), 1.50 (s, 1 H), 1.35 (m, 3 H), 1.23 (m, 1 H), 0.84 (t, *J* = 6.5 Hz, 3 H), 0.39 (s, 3 H), 0.38 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 137.8, 133.8 (2 C), 129.4, 129.2, 127.9 (2 C), 69.3, 45.0, 39.1, 18.8, 14.0, -2.87, -2.93. IR (film) 3379, 3049, 2957, 2872, 1427, 1250, 1111, 817 cm^{-1}. HRMS (EI) *m/z* 230.1503 [$(M\text{-}H_2O)^+$; calcd for $C_{15}H_{22}Si$, 230.1491].

*Preparation of compound **266***

Following general procedure C, the title compound (colorless oil) was prepared in 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.34 (m, 3 H), 5.81 (m, 1 H), 5.56 (dd, *J* = 1.0, 3.0 Hz, 1 H), 2.76 (dt, *J* = 3.0, 9.0 Hz, 1 H), 2.52 (m, 1 H), 2.29 (dd, *J* = 4.5, 13.5 Hz, 1 H), 1.58 (s, 1 H), 0.80 (m, 1 H), 0.50–0.36 (m, 2 H), 0.38 (s, 6 H), 0.21 (m, 1 H), 0.00 (m, 1 H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 147.5, 137.8, 133.8 (2 C), 129.3, 129.1, 127.9 (2 C), 74.5, 44.3, 17.3, 2.9, 2.2, -2.8, -2.9. IR (film) 3408, 3069, 2957, 2909, 1427, 1250, 1111, 817 cm^{-1}. HRMS (EI) *m/z* 228.1331 $[(M-H_2O)^+$; calcd for $C_{15}H_{20}Si$, 228.1334].

*Preparation of compound **267***

Following general procedure C, the title compound (colorless oil) was prepared in 60% yield. HRMS (EI) *m/z* 206.1484 $[(M-H_2O)^+$; calcd for $C_{13}H_{24}Si$, 206.1491].

*Preparation of compound **268***

Following general procedure D, the title compound (colorless oil) was prepared in 72% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 7.26 (m, 1 H), 5.76 (m, 1 H), 5.53 (dt, *J* = 0.5, 8.0, Hz, 1 H), 4.73 (ddd, *J* = 2.0, 3.5, 10.0 Hz, 1 H), 2.62 (dddd, *J* = 0.5, 1.5, 3.5, 14.0 Hz, 1 H), 2.43 (dd, *J* = 9.5, 14.5 Hz, 1 H), 2.10 (m, 1 H), 0.93 (t, *J* = 8.0 Hz, 3 H), 0.61 (q, *J* = 8.0 Hz, 2 H), 0.11 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 128.7, 128.4 (2 C), 127.4, 125.8 (2 C), 72.2, 47.1, 7.3, 6.9, -3.6, -3.7. IR (film) 3389, 3031, 2955, 1248, 1049, 833 cm^{-1}. HRMS (EI) *m/z* 217.1401 $[(M-HO)^+$; calcd for $C_{14}H_{21}Si$, 217.1413].

*Preparation of compound **269***

Following general procedure D, the title compound (colorless oil) was prepared in 57% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.27 (m, 1 H), 7.20 (m, 2 H), 7.07 (m, 1 H), 7.00 (m,

2 H), 5.79 (m, 1 H), 5.53 (d, *J* = 0.5, 2.5 Hz, 1 H), 4.68 (ddd, *J* = 2.5, 4.0, 10.0 Hz, 1 H), 2.58 (m, 1 H), 2.44 (ddd, *J* = 1.0, 10.0, 14.5 Hz, 1 H) 2.19 (s, 2 H), 2.01 (d, *J* = 2.5 Hz, 1 H), 0.11 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 144.1, 139.6, 129.3, 128.4 (2 C), 128.23 (2 C), 128.20 (2 C), 127.5, 125.8 (2 C), 124.2, 72.4, 46.7, 25.5, -3.2, -3.5. HRMS (EI) *m/z* 279.1561 [$(M\text{-}OH)^+$; calcd for $C_{19}H_{23}Si$, 279.1569].

*Preparation of compound **270***

Following general procedure D, the title compound (colorless oil) was prepared in 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 1.2, 7.2 Hz, 1 H), 7.23 (m, 1 H), 7.16 (dt, *J* = 1.8, 7.2 Hz, 1 H), 7.12 (dd, *J* = 0.6, 7.8 Hz, 1 H), 5.82 (m, 1 H), 5.58 (d, *J* = 3.0 Hz, 1 H), 4.96 (dd, *J* = 3.0, 9.6 Hz, 1 H), 2.59 (m, 1 H), 2.36 (dd, *J* = 10.2, 13.8 Hz, 1 H), 2.35 (s, 3 H), 2.05 (s, 1 H), 0.94 (t, *J* = 8.4 Hz, 3 H), 0.62 (q, *J* = 7.8 Hz, 2 H), 0.12 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 142.3, 134.2, 130.3, 128.8, 127.1, 126.3, 125.3, 68.4, 45.4, 19.2, 7.3, 6.9, -3.6, -3.7. IR (film) 3408, 3052, 2953, 1458, 1248, 1049, 819 cm^{-1}. HRMS (EI) *m/z* 231.1555 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{23}Si$, 231.1569].

*Preparation of compound **271***

Following general procedure D, the title compound (colorless oil) was prepared in 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2 H), 7.25–7.21 (m, 3 H), 5.76 (m, 1 H), 5.55 (dt, *J* = 1.0, 3.0 Hz, 1 H), 4.69 (dd, *J* = 3.5, 10.5 Hz, 1 H), 2.59 (m, 1 H), 2.36 (ddd, *J* = 0.5, 10.0, 14.0 Hz, 1

H), 2.14 (s, 1 H), 0.93 (t, *J* = 7.5 Hz, 3 H), 0.60 (q, *J* = 8.0 Hz, 2 H), 0.10 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 146.2, 134.3, 129.6, 129.1, 127.5, 126.0, 123.9, 71.5, 47.1, 7.3, 6.9, -3.6, -3.7. IR (film) 3402, 3051, 2955, 1431, 1248, 1055, 817 cm^{-1}. HRMS (EI) *m/z* 251.1014 $[(M\text{-}OH)^+$; calcd for $C_{14}H_{20}SiCl$, 251.1023].

*Preparation of compound **272***

Following general procedure D, the title compound (colorless oil) was prepared in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.0 Hz, 1 H), 6.93 (m, 2 H), 6.80 (m, 1 H), 5.76 (m, 1 H), 5.53 (d, *J* = 2.5 Hz, 1 H), 4.70 (dt, *J* = 3.0, 4.5 Hz, 1 H), 3.81 (s, 3 H), 2.62 (m, 1 H), 2.41 (dd, *J* = 10.0, 14.0 Hz, 1 H), 2.08 (d, *J* = 2.0 Hz, 1 H), 0.93 (t, *J* = 8.0 Hz, 3 H), 0.60 (q, *J* = 8.0 Hz, 2 H), 0.10 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 148.2, 145.9, 129.4, 128.7, 118.1, 112.8, 111.3, 72.1, 55.2, 47.0, 7.3, 6.9, -3.6, -3.7. IR (film) 3049, 2955, 1603, 1255, 1045, 777 cm^{-1}. HRMS (EI) *m/z* 246.1441 $[(M\text{-}H_2O)^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compound **273***

Following general procedure D, the title compound (colorless oil) was prepared in 29% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 1.5, 5.0 Hz, 1 H), 6.96 (m, 2 H), 5.75 (m, 1 H), 5.53 (d, *J* = 2.5 Hz, 1 H), 4.99 (dt, *J* = 3.0, 9.5 Hz, 1 H), 2.73 (m, 1 H), 2.58 (dd, *J* = 9.5, 14.5 Hz, 1 H), 2.17 (d, *J* = 3.0 Hz, 1 H), 0.93 (t, *J* = 8.0 Hz, 3 H), 0.59 (q, *J* = 8.0 Hz, 2 H), 0.09 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 147.6, 128.9 126.5, 124.4, 123.5, 68.5, 46.8, 7.3, 6.8, -3.7, -

3.8. IR (film) 3402, 2955, 1248, 1116, 833 cm^{-1}. HRMS (EI) *m/z* 223.0975 [$(M\text{-}OH)^+$; calcd for $C_{12}H_{19}SSi$, 223.0977].

*Preparation of compound **274***

Following general procedure E, the title compound (colorless oil) was prepared in 46% yield. HRMS (EI) *m/z* 186.1041 [$(M^+$); calcd for $C_{13}H_{14}O$, 186.1045].

*Preparation of compound **275***

Following general procedure E, the title compound (colorless oil) was prepared in 68% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.5 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 5.88 (m, 1 H), 5.24 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.14 (m, 1 H), 4.44 (t, *J* = 6.5 Hz, 1 H), 3.95 (ddt, A of ABX system, *J* = 1.0, 5.0, 12.5 Hz, 1 H), 3.80 (ddt, B of ABX system, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 2.69 (ddd, C of CDX system, *J* = 2.5, 6.5, 16.5 Hz, 1 H), 2.53 (ddd, D of CDX system, *J* = 2.5, 6.5, 16.5 Hz, 1 H), 2.34 (s, 3 H), 1.94 (t, *J* = 3.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 134.6, 129.1 (2 C), 126.7 (2 C), 126.5, 117.0, 81.0, 79.1, 69.9, 69.6, 28.1, 21.2. HRMS (EI) *m/z* 200.1202 [$(M^+$); calcd for $C_{14}H_{16}O$, 200.1201].

*Preparation of compound **276***

Following general procedure D, the title compound (colorless oil) was prepared in 59% yield from compound **274**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 2 H), 7.26 (m, 3 H), 7.17 (t, *J* = 7.5 Hz, 2 H), 7.04 (t, *J* = 7.5 Hz, 1 H), 6.96 (d, *J* = 7.0 Hz, 2 H), 5.87 (m, 1 H), 5.63 (m, 1 H),

5.38 (d, *J* = 3.0 Hz, 1 H), 5.21 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.11 (m, 1 H), 4.37 (dd, *J* = 5.0, 7.5 Hz, 1 H), 3.87 (ddt, A of ABX system, *J* = 1.5, 5.0, 12.5 Hz, 1 H), 3.73 (ddt, B of ABX system *J* = 1.5, 6.5, 13.0 Hz, 1 H), 2.65 (dd, C of CDX system, *J* = 8.0, 14.5 Hz, 1 H), 2.39 (dd, D of CDX system, *J* = 5.5, 15.0 Hz, 1 H), 2.13 (s, 2 H), 0.02 (s, 3 H), 0.00 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 142.4, 140.0, 135.0, 128.31, 128.30 (2 C), 128.29 (2 C), 128.1 (2 C), 127.5, 126.9 (2 C), 124.0, 116.7, 81.3, 69.5, 44.4, 25.4, -3.52, -3.53. IR (film) 3024, 2955, 1493, 1248, 1086, 925, 833 cm^{-1}. HRMS (EI) *m*/*z* 336.1908 [(M^+); calcd for $C_{22}H_{28}OSi$, 336.1909].

*Preparation of compound **277***

Following general procedure D, the title compound (colorless oil) was prepared in 59% yield from compound **275**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (m, 5 H), 7.05 (t, *J* = 7.0 Hz, 1 H), 6.96 (d, *J* = 7.5 Hz, 2 H), 5.86 (m, 1 H), 5.64 (s, 1 H), 5.38 (s, 1 H), 5.21 (d, *J* = 17.5 Hz, 1 H), 5.11 (d, *J* = 10.0 Hz, 1 H), 4.35 (m, 1 H), 3.86 (dd, A of ABX system, *J* = 4.5, 12.5 Hz, 1 H), 3.71 (dd, B of ABX system, *J* = 5.5, 12.5 Hz, 1 H), 2.65 (dd, C of CDX system, *J* = 8.0, 14.5 Hz, 1 H), 2.38 (dd, *J* = 5.0, 14.5 Hz, 1 H), 2.34 (s, 3 H), 2.13 (s, 2 H), 0.03 (s, 3 H), 0.01 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 140.0, 139.3, 137.1, 135.0, 129.0 (2 C), 128.3 (2 C), 128.2, 128.0 (2 C), 126.9 (2 C), 123.9, 116.6, 81.0, 69.4, 44.4, 25.4, 21.1, -3.5. IR (film) 3025, 2922, 1493, 1248, 1084, 815 cm^{-1}. HRMS (EI) *m*/*z* 350.2060 [(M^+); calcd for $C_{23}H_{30}OSi$, 350.2066].

*Preparation of compound **278***

Following general procedure E, the title compound (colorless oil) was prepared in 90% yield from compound **257**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.33 (m, 3 H), 7.27 (t, *J* = 6.5 Hz, 2 H), 7.22 (m, 1 H), 7.13 (m, 2H), 5.77(m, 1 H), 5.69 (m, 1 H), 5.47 (d, *J* = 2.5 Hz, 1 H), 5.14 (m, 1 H), 5.07 (m, 1 H), 4.19 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.74 (A of ABX system, ddt, *J* = 1.5, 5.5, 13.0 Hz, 1 H), 3.52 (B of ABX system, ddt, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 2.64 (A of ABX system, dd, *J* = 8.0, 14.5 Hz, 1 H), 2.39 (B of ABX system, dd, *J* = 5.5, 14.5 Hz, 1 H), 0.36 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 142.4, 138.3, 135.0, 134.0 (2 C), 129.2, 128.9, 128.2 (2 C), 127.7 (2 C), 127.4, 126.8 (2 C), 116.5, 80.7, 69.4, 44.7, -2.924, -2.917. IR (neat) 3067, 2955, 1427, 1248, 1111, 815 cm^{-1}. HRMS (EI) *m/z* 307.1504 [$(M\text{-}CH_3)^+$; calcd for $C_{20}H_{23}OSi$, 307.1518].

*Preparation of compound **279***

Following general procedure E, the title compound (colorless oil) was prepared in 88% yield from compound **258**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.23 (m, 5 H), 5.86 (m, 1 H), 5.64 (m, 1 H), 5.36 (d, *J* = 3.5 Hz, 1 H), 5.19 (dq, *J* = 2.0, 17.5 Hz, 1 H), 5.10 (m, 1 H), 4.37 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.85 (m, 1 H), 3.71 (m, 1 H), 2.62 (dd, A of ABX system, *J* = 8.0, 14.5 Hz, 1 H), 2.37 (dd, B of ABX system, *J* = 5.5, 14.5 Hz, 1 H), 0.90 (t, *J* = 8.0 Hz, 9 H), 0.58 (dq, *J* = 2.0, 8.0 Hz, 6 H). IR (film) 3030, 2953, 1454, 1086, 924, 700 cm^{-1}. HRMS (EI) *m/z* 302.2051 [$(M)^+$; calcd for $C_{19}H_{30}OSi$, 302.2066].

*Preparation of compound **280***

Following general procedure E, the title compound (colorless oil) was prepared in 78% yield from compound **268**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 2 H), 7.26 (m, 2 H), 7.24 (m, 1 H), 5.86 (m, 1 H), 5.58 (m, 1 H), 5.37 (dt, *J* = 0.5, 3.0 Hz, 1 H), 5.19 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.11 (m, 1 H), 4.36 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.85 (ddt, A of ABX system, *J* = 1.5, 5.0, 12.5, Hz, 1 H), 3.72 (ddt, B of ABX system, *J* = 1.5, 6.0, 12.5 Hz, 1 H), 2.64 (m, 1 H), 2.39 (m, 1 H), 0.89 (t, *J* = 8.0 Hz, 3 H), 0.54 (q, *J* = 8.0 Hz, 2 H), 0.04 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 142.5, 135.0, 128.3 (2 C), 127.6, 127.4, 126.9 (2 C), 116.6, 81.1, 69.5, 44.5, 7.4, 6.8, -3.7, -3.8. IR (film) 3030, 2955, 2874, 1248, 1087, 819 cm^{-1}. HRMS (EI) *m/z* 274.1748 [$(M)^{+}$; calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compound **281***

Following general procedure E, the title compound (colorless oil) was prepared in 86% yield from compound **259**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.34 (m, 3 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 5.78 (m, 1 H), 5.70 (m, 1 H), 5.47 (m, 1 H), 5.14 (m, 1 H), 5.07 (m, 1 H), 4.17 (dd, *J* = 5.0, 8.0 Hz, 1 H), 3.74 (A of ABX system, m, 1 H), 3.52 (B of ABX system, m, 1 H), 2.64(A of ABX system, ddd, *J* = 0.5, 8.0, 14.5 Hz, 1 H), 2.38 (B, of ABX system, ddd, *J* = 0.5, 5.0, 14.0 Hz, 1 H), 2.32 (s, 3 H), 0.364 (s, 3 H), 0.361 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 139.3, 138.3, 137.0, 135.1, 134.0 (2 C), 129.1, 128.9, 128.8 (2 C), 127.7 (2 C), 126.8 (2 C), 116.4, 80.4, 69.3, 44.7, 21.1, -2.89, -2.91. IR (neat) 3049, 2955, 2858,

1427, 1248, 1111, 815 cm^{-1}. HRMS (EI) *m/z* 321.1667 [$(M\text{-}CH_3)^+$; calcd for $C_{21}H_{25}OSi$, 321.1675].

*Preparation of compound **282***

Following general procedure E, the title compound (colorless oil) was prepared in 92% yield from compound **270**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 1.0, 7.5 Hz, 1 H), 7.20 (t, *J* = 7.5 Hz, 1 H), 7.15 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.10 (m, 1 H), 5.87 (m, 1 H), 5.67 (quintet, *J* = 1.5 Hz, 1 H), 5.41 (dt, *J* = 1.0, 3.0 Hz, 1 H), 5.19 (dq, *J* = 1.0, 17.5 Hz, 1 H), 5.11 (dq, *J* = 1.5, 10.5 Hz, 1 H), 4.64 (dd, *J* = 4.0, 9.0 Hz, 1 H), 3.85 (ddt, A of ABX system, *J* = 1.5, 5.0, 12.5 Hz, 1 H), 3.69 (ddt, B of ABX system, *J* =1.5, 6.0, 13.0 Hz, 1 H), 2.54 (m, 1 H), 2.34 (m, 1 H), 2.30 (s, 3 H), 0.90 (t, *J* = 8.0 Hz, 3 H), 0.56 (q, *J* = 8.0 Hz, 2 H), 0.05 (s, 3 H), 0.04 (s 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 140.8, 135.20, 135.18, 130.3, 127.1, 127.0, 126.22, 126.18, 116.5, 77.6, 69.4, 43.2, 19.3, 7.4, 6.8, -3.75, -3.78. IR (film) 3049, 2957, 1426, 1248, 1109, 815 cm^{-1}. HRMS (EI) *m/z* 230.1484 [$(M\text{-}OCH_2CHCH_2)^+$; calcd for $C_{15}H_{22}Si$, 230.1491].

*Preparation of compound **283***

Following general procedure E, the title compound (colorless oil) was prepared in 85% yield from compound **272**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.0 Hz, 1 H), 6.85 (m, 2 H), 6.79 (m, 1 H), 5.86 (m, 1 H), 5.60 (m, 1 H), 5.38 (d, *J* = 3.0 Hz, 1 H), 5.20 (dq, *J* = 1.5, 17.5 Hz, 1 H), 5.11 (dq, *J* = 1.5, 10.5 Hz, 1 H), 4.34 (dd, *J* = 5.0, 8.0 Hz, 1 H), 3.88 (ddt, A of ABX system, *J* = 1.5, 5.0, 12.5 Hz, 1 H), 3.80 (s, 3 H), 3.71 (ddt, B of ABX system, *J* = 1.5, 6.0, 12.5

Hz, 1 H), 2.62 (dd, C of CDX system, J = 8.0, 14.5 Hz, 1 H), 2.38 (dd, D of CDX system, J = 5.0, 14.5 Hz, 1 H), 0.89 (t, J = 8.0 Hz, 3 H), 0.54 (q, J = 8.0 Hz, 2 H), 0.04 (s, 3 H), 0.03 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 147.2, 144.3, 135.0, 129.2, 127.5, 119.4, 116.7, 112.9, 112.2, 81.0, 69.6, 55.2, 44.5, 7.4, 6.8, -3.71, -3.73. IR (film) 3049, 2953, 1601, 1257, 1045, 819, 779 cm^{-1}. HRMS (EI) *m*/*z* 246.1441 [$(M\text{-}C_3H_6O)^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compound **284***

Following general procedure E, the title compound (colorless oil) was prepared in 78% yield from compound **263**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 2 H), 7.36 (m, 3 H), 5.85 (m, 1 H), 5.78 (ddt, J = 5.5, 10.5, 17.5 Hz, 1 H), 5.56 (d, J = 2.5 Hz, 1 H), 5.18 (dq, J = 1.2, 17.0 Hz, 1 H), 5.06 (dq, J = 1.5, 10.5 Hz, 1 H), 4.12 (dd, J = 3.5, 9.0 Hz, 1 H), 4.08 (m, 4 H), 3.99 (s, 5 H), 3.89 (ddt, J = 1.5, 5.0, 12.5 Hz, 1 H), 3.69 (ddt, J = 1.5, 5.5, 12.5 Hz, 1 H), 2.72 (A of ABX system, m, 1 H), 2.65 (B of ABX system, dd, J = 4.5, 15.0 Hz, 1 H), 0.429 (s, 3 H), 0.421 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 138.3, 135.4, 134.0 (2 C), 129.1, 128.4, 127.8 (2 C), 89.3, 76.1, 69.2, 68.6 (5 C), 68.4, 67.8, 67.1, 66.1, 42.1, -2.69, -2.75. IR (neat) 3070, 2955, 1427, 1248, 1107, 815 cm^{-1}. HRMS (EI) *m*/*z* 430.1402 [$(M)^+$; calcd for $C_{25}H_{30}SiOFe$, 430.1415].

*Preparation of compound **285***

Following general procedure E, the title compound (colorless oil) was prepared in 84% yield from compound **273**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, J = 0.5, 5.0 Hz, 1 H), 6.92 (dd, J = 3.5, 5.0 Hz, 1 H), 6.89 (dd, J = 1.0, 3.0 Hz, 1 H), 5.86 (m, 1 H), 5.59 (dt, J = 1.5, 2.5 Hz, 1 H),

5.37 (d, *J* = 3.0 Hz, 1 H), 5.21 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.13 (dq, *J* = 1.5, 10.0 Hz, 1 H), 6.64 (t, *J* = 7.0 Hz, 1 H), 3.95 (ddt, A of ABX system, *J* = 1.5, 5.5, 12.5 Hz, 1 H), 3.79 (ddt, B of ABX system, *J* = 1.5, 6.5, 12.5 Hz, 1 H), 2.76 (m, 1 H), 2.51 (m, 1 H), 0.89 (t, *J* = 8.0 Hz, 3 H), 0.54 (q, *J* = 8.0 Hz, 2 H), 0.04 (s, 3 H), 0.03 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 146.4, 134.8, 127.7, 126.2, 125.3, 124.7, 117.0, 76.3, 69.4, 44.8, 7.3, 6.8, -3.7, -3.8. HRMS (EI) *m*/*z* 280.1310 [$(M)^+$; calcd for $C_{15}H_{24}SiOS$, 280.1317].

*Preparation of compound **286***

Following general procedure E, the title compound (colorless oil) was prepared in 91% yield from compound **260**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.33 (m, 3 H), 7.22 (d, *J* = 8.5 Hz, 2 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 5.75 (m, 1 H), 5.64 (m, 1 H), 5.47 (d, *J* = 3.0 Hz, 1 H), 5.13 (dq, *J* = 1.5, 17.5 Hz, 1 H), 5.07 (m, 1 H), 4.14 (dd, *J* = 5.5, 7.5 Hz, 1 H), 3.71 (A of ABX system, ddt, *J* = 1.5, 5.0, 12.5 Hz, 1 H), 3.50 (B of ABX system, ddt, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 2.62 (A of ABX system, dd, *J* = 7.5, 14.0 Hz, 1 H), 2.34 (B, of ABX system, dd, *J* = 5.5, 14.0 Hz, 1 H), 0.352 (s, 3 H), 0.349 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 140.8, 138.1, 134.7, 134.0 (2 C), 133.0, 129.4, 129.0, 128.3 (2 C), 128.2 (2 C), 127.8 (2 C), 116.7, 80.0, 69.4, 44.6, -2.97, -3.0. IR (neat) 3068, 2955, 1489, 1427, 1248, 1087, 815 cm^{-1}. HRMS (EI) *m/z* 356.1340 [$(M)^+$; calcd for $C_{21}H_{25}OSiCl$, 356.1363].

*Preparation of compound **287***

Following general procedure E, the title compound (colorless oil) was prepared in 91% yield from compound **271**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 1 H), 7.25–7.21 (m, 2 H), 7.15 (dt, *J* = 1.5, 6.5 Hz, 1 H), 5.85 (m, 1 H), 5.56 (m, 1 H), 5.38 (d, *J* = 2.5 Hz, 1 H), 5.20 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.13 (dq, *J* = 1.5. 10.5 Hz, 1 H), 4.33 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.86 (ddt, A of ABX system, *J* = 1.5, 5.5, 13.0 Hz, 1 H), 3.72 (ddt, B of ABX system, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 2.61 (dd, C of CDX system, *J* = 8.0, 14.5 Hz, 1 H), 2.35 (dd, D of CDX system, *J* = 5.5, 15.0 Hz, 1 H), 0.89 (t, *J* = 7.5 Hz, 3 H), 0.53 (q, *J* = 7.5 Hz, 2 H), 0.04 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 144.8, 134.7, 134.2, 129.6, 127.9, 127.6, 127.0, 125.1, 116.9, 80.5, 69.7, 44.4, 7.3, 6.8, -3.7, -3.8. IR (film) 3060, 2955, 1427, 1248, 1092, 815 cm^{-1}. HRMS (EI) *m*/*z* 308.1372 [(M^{+}); calcd for $C_{17}H_{25}OSiCl$, 308.1363].

*Preparation of compound **288***

Following general procedure E, the title compound (colorless oil) was prepared in 87% yield from compound **261**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (ddd, *J* = 0.5, 1.5, 4.5 Hz, 1 H), 7.60 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.50 (m, 2 H), 7.31(m, 3 H), 7.23 (m, 1 H), 7.12 (ddd, *J* = 1.0, 4.5, 7.5 Hz, 1 H), 5.79 (m, 1 H), 5.76 (m, 1 H), 5.47 (d, *J* = 3.0 Hz, 1 H), 5.15 (dq, *J* = 1.5, 17 Hz, 1 H), 5.07 (dq, *J* = 1.5, 10.5 Hz, 1 H), 4.46 (dd, *J* = 6.0, 7.5 Hz, 1 H), 3.79 (A of ABX system, ddt, *J* = 1.5, 5.0, 13.0 Hz, 1 H), 3.65 (B of ABX system, ddt, *J* = 1.5, 5.5, 12.5 Hz, 1 H), 2.58 (m, 2 H), 0.368 (s, 3 H), 0.355 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 149.1, 146.1, 138.3, 136.4, 134.8, 134.0 (2 C), 129.1, 128.9, 127.7 (2 C), 122.3, 120.9, 116.6, 82.0, 70.0, 42.8, -2.83, -2.92.

IR (neat) 3049, 2924, 2853, 1589, 1453, 1248, 1111, 1084, 817 cm^{-1}. HRMS (EI) *m/z* 324.1772 [$(M+H)^+$; calcd for $C_{20}H_{26}NOSi$, 324.1784]

*Preparation of compound **289***

Following general procedure E, the title compound (colorless oil) was prepared in 89% yield from compound **262**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.81–7.75 (m, 3 H), 7.53 (m, 2 H), 7.45 (m, 3 H), 7.38–7.33 (m, 4 H), 5.80 (m, 1 H), 5.70 (m, 1 H), 5.48 (d, *J* = 3.0 Hz, 1 H), 5.16 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.10 (m, 1 H), 4.36 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.77 (A of ABX system, ddt, *J* = 1.5, 5.0, 13.0 Hz, 1 H), 3.57 (B of ABX system, ddt, *J* = 1.5, 6.0, 12.5 Hz, 1 H), 2.75 (A of ABX system, dd, *J* = 7.5, 14.0 Hz, 1 H), 2.50 (B of ABX system, dd, *J* = 5.5, 14.5 Hz, 1 H), 0.39 (s, 3 H), 0.38 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 139.7, 138.3, 134.9, 134.0 (2 C), 133.1, 133.0, 129.3, 129.0, 128.1, 127.8, 127.8 (2 C), 127.7, 126.0, 125.9 125.7, 124.6, 116.6, 80.8, 69.4, 44.6, -2.87, -2.95. IR (neat) 3051, 2957, 2856, 1427, 1248, 1111, 1082, 817 cm^{-1}. HRMS (EI) *m/z* 372.1906 [$(M)^+$; calcd for $C_{25}H_{28}OSi$, 372.1909].

*Preparation of compound **290***

Following general procedure E, the title compound (colorless oil) was prepared in 69% yield from compound **264**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.33 (m, 3 H), 5.81 (m, 1 H), 5.77 (m, 1 H), 5.49 (d, *J* = 3.0 Hz, 1 H), 5.15 (dq, *J* = 2.0, 17.5 Hz, 1 H), 5.05 (dq, *J* = 1.5, 10.5 Hz, 1 H), 3.79 (A of ABX system, ddt, *J* = 1.5, 5.5, 12.5 Hz, 1 H), 3.74 (B of ABX system, ddt, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 3.02 (m, 1 H), 2.28 (d, *J* = 6.5 Hz, 1 H), 1.67 (m, 2 H), 1.59 (m, 2 H),

1.39–1.29 (m, 2 H), 1.15–1.01 (m, 4 H), 0.97 (m, 1 H), 0.39 (s, 3 H), 0.37 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 138.3, 135.7, 133.9 (2 C), 128.9, 128.8, 127.7 (2 C), 116.0, 82.3, 71.1, 40.8, 38.0, 29.2, 27.4, 26.6, 26.5, 26.4, -2.71, -2.86. IR (neat) 3069, 2926, 2853, 1450, 1248, 1111, 817 cm^{-1}. HRMS (EI) *m/z* 328.2233 [$(M)^+$; calcd for $C_{21}H_{32}OSi$, 328.2222].

*Preparation of compound **291***

Following general procedure E, the title compound (colorless oil) was prepared in 90% yield from compound **265**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.33 (m, 3 H), 5.81 (m, 1 H), 5.74 (m, 1 H), 5.49 (d, *J* = 3.0 Hz, 1 H), 5.16 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.08 (m, 1 H), 3.82 (ddt, A of ABX system, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 3.76 (ddt, B of ABX system, *J* = 1.5, 6.0, 12.5 Hz, 1 H), 3.22 (m, 1 H), 2.44 (ddt, C of CDX system, *J* = 1.0, 5.5, 14.0 Hz, 1 H), 2.15 (dd, D of CDX system, *J* = 7.5, 14.0 Hz, 1 H), 1.35–1.25 (m, 3 H), 1.13 (m, 1 H), 0.79 (t, *J* = 7.0 Hz, 3 H), 0.38 (s, 3 H), 0.37 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 138.1, 135.5, 133.9 (2 C), 129.0, 128.9, 127.7 (2 C), 116.3, 77.9, 69.9, 41.4, 36.0, 18.5, 14.1, -2.7, -2.9. IR (neat) 3062, 2924, 2851, 1248, 1111, 816 cm^{-1}. HRMS (EI) *m/z* 273.1660 [$(M\text{-}CH_3)^+$; calcd for $C_{17}H_{25}OSi$, 273.1675].

*Preparation of compound **292***

Following general procedure E, the title compound (colorless oil) was prepared in 80% yield from compound **266**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.32 (m, 3 H), 5.81 (m, 2 H), 5.48 (d, *J* = 2.5 Hz, 1 H), 5.18 (dq, *J* = 1.5, 14.5 Hz, 1 H), 5.07 (dq, *J* = 1.5, 9.0 Hz, 1 H), 4.04

(ddt, A of ABX system, *J* = 1.0, 4.5, 10.5 Hz, 1 H), 3.75 (ddt, B of ABX system, *J* = 1.5, 4.5, 10.5 Hz, 1 H), 2.60 (dt, *J* = 3.5, 6.5 Hz, 1 H), 2.45 (dd, C of CDX system, *J* = 6.5, 12.0 Hz, 1 H), 2.39 (dd, D of CDX system, *J* = 3.5, 12.0 Hz, 1 H), 0.73 (m, 1 H), 0.49 (m, 1 H), 0.36 (s, 6 H), 0.34 (m, 1 H), 0.25 (m, 1 H), -0.10 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0, 138.4, 135.7, 134.0 (2 C), 128.9, 128.8, 127.7 (2 C), 116.0, 82.2, 69.7, 42.0, 15.1, 4.4, 1.3, -2.7, -2.8. IR (film) 3069, 3005, 2957, 2858, 1427, 1111, 815 cm^{-1}. HRMS (EI) *m/z* 286.1741 [$(M)^+$; calcd for $C_{18}H_{26}OSi$, 286.1753].

*Preparation of compound **293***

Following general procedure E, the title compound (colorless oil) was prepared in 84% yield from compound **267**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88 (m, 1 H), 5.48 (dt, *J* = 1.8, 3.0 Hz, 1 H), 5.37 (d, *J* = 3.0 Hz, 1 H), 5.22 (dq, *J* = 1.8, 17.4 Hz, 1 H), 5.09 (dq, *J* = 1.8, 12.0 Hz, 1 H), 4.16 (ddt, A of ABX system, *J* = 1.8, 6.0, 13.2 Hz, 1 H), 3.93 (ddt, B of ABX system, *J* = 1.2, 5.4, 12.6 Hz, 1 H), 2.79 (dt, *J* = 4.8, 7.8 Hz, 1 H), 2.42 (dd, C of CDX system, *J* = 7.2, 14.4 Hz, 1 H), 2.35 (dd, D of CDX system, *J* = 4.8, 14.4 Hz, 1 H), 0.91 (t, *J* = 7.8 Hz, 9 H), 0.83 (m, 1 H), 0.59 (q, *J* = 7.8 Hz, 6 H), 0.55 (m, 1 H), 0.43 (m, 1 H), 0.36 (m, 1 H), 0.08 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 135.7, 128.0, 116.1, 82.3, 69.8, 41.9, 15.2, 7.4, 4.4, 3.0, 1.4. IR (film) 3070, 2957, 1427, 1113, 815 cm^{-1}. HRMS (EI) *m/z* 266.2062 [$(M)^+$; calcd for $C_{16}H_{30}OSi$, 266.2066].

*Preparation of compound **294***

Following general procedure F, the title compound (colorless oil) was prepared in 99% yield from compound **278**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.36–7.29 (m, 7 H), 7.25 (m, 1 H), 6.10 (m, 1 H), 4.47 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.40 (m, 2 H), 2.35–2.28 (m, 1 H), 2.26–2.21 (m, 1 H), 0.36 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 137.4, 136.1, 135.1, 134.0 (2 C), 129.1, 128.3 (2 C), 127.8 (2 C), 127.4, 125.8 (2 C), 75.6, 67.7, 34.5, -3.86, -3.98. IR (neat) 3067, 2955, 2901, 2818, 1427, 1248, 1115, 833, 819 cm^{-1}. HRMS (EI) *m/z* 294.1434 [$(M)^{+}$; calcd for $C_{19}H_{22}OSi$, 294.1440].

*Preparation of compound **295***

Following general procedure F, the title compound (colorless oil) was prepared in 97% yield from compound **279**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 7.26 (m, 1 H), 6.03 (m, 1 H), 4.47 (dd, *J* = 3.0, 10.0 Hz, 1 H), 4.40 (m, 2 H), 2.31 (m, 1 H), 2.22 (m, 1 H), 0.94 (t, *J* = 8.0 Hz, 9 H), 0.59 (q, *J* = 8.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 135.5, 133.9, 128.4 (2 C), 127.4, 125.9 (2 C), 75.7, 67.8, 35.3, 7.4, 2.3. IR (film) 3030, 2953, 2814, 1454, 1126, 1026, 698 cm^{-1}. HRMS (EI) *m/z* 274.1751 [$(M)^{+}$; calcd for $C_{17}H_{26}OSi$, 274.1753].

*Preparation of compound **296***

Following general procedure F, the title compound (colorless oil) was prepared in 91% yield from compound **280**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 7.26 (m, 1 H), 6.04 (m, 1 H), 4.48 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.39 (m, 2 H), 2.31 (m, 1 H), 2.24 (m, 1 H), 0.93 (t, *J* = 8.0 Hz,

3 H), 0.56 (q, *J* = 8.0 Hz, 2 H), 0.05 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 135.9, 134.6, 128.4 (2 C), 127.4, 125.8 (2 C), 75.7, 67.7, 34.8, 7.4, 6.1, -4.8. IR (film) 3032, 2953, 2816, 1246, 1124, 1026, 819 cm^{-1}. HRMS (EI) *m/z* 246.1426 [$(M)^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compound **297***

Following general procedure F, the title compound (colorless oil) was prepared in 59% yield from compound **276**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 7.28 (m, 1 H), 7.22 (m, 2 H), 7.08 (m, 1 H), 7.00 (m, 2 H), 6.03 (m, 1 H), 4.43 (dd, *J* = 3.5, 10.5 Hz, 1 H), 4.38 (m, 2 H), 2.26 (m, 1 H), 2.16 (s, 2 H), 2.11 (m, 1 H), 0.07 (s, 3 H), 0.05 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 139.8, 135.5, 135.1, 128.4 (2 C), 128.2 (4 C), 127.4, 125.8 (2 C), 124.1, 75.6, 67.7, 34.8, 25.0, -4.5, -4.7. IR (film) 3061, 2955, 2818, 1493, 1124, 1028, 833 cm^{-1}. HRMS (EI) *m/z* 308.1591 [$(M^+$); calcd for $C_{20}H_{24}OSi$, 308.1596].

*Preparation of compound **298***

Following general procedure F, the title compound (colorless oil) was prepared in 96% yield from compound **281**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.34 (m, 3 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.09 (m, 1 H), 4.44 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.39 (m, 2 H), 2.35–2.27 (m, 1 H), 2.31 (s, 3 H), 2.22 (m, 1 H), 0.35 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 137.5, 137.0, 136.1, 135.2, 134.0 (2 C), 129.1, 129.0 (2 C), 127.8 (2 C), 125.8 (2 C),

75.5, 67.7, 34.5, 21.1, -3.85, -3.98. IR (neat) 3013, 2920, 2814, 1427, 1248, 1115, 817 cm^{-1}. HRMS (EI) *m*/*z* 308.1596 [(M^+); calcd for $C_{20}H_{24}OSi$, 308.1596].

*Preparation of compound **299***

Following general procedure F, the title compound (colorless oil) was prepared in 80% yield from compound **277**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.23–7.18 (m, 4 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.98 (d, *J* = 7.5 Hz, 2 H), 6.01 (m, 1 H), 4.29 (dd, *J* = 3.5, 10.5 Hz, 1 H), 4.36 (m, 2 H), 2.33 (s, 3 H), 2.29–2.21 (m, 1 H), 2.14 (s, 2 H), 2.09 (m, 1 H), 0.05 (s, 3 H), 0.04 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 137.0, 135.5, 135.2, 129.0 (4 C), 128.2 (4 C), 125.7, 124.1, 75.5, 67.7, 34.9, 25.0, 21.1, -4.5, -4.6. IR (film) 3030, 2957, 1492, 1112, 833 cm^{-1}. HRMS (EI) *m*/*z* 322.1731 [(M^+); calcd for $C_{18}H_{22}OSi$, 322.1753].

*Preparation of compound **300***

Following general procedure F, the title compound (colorless oil) was prepared in 99% yield from compound **282**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 7.10 (m, 2 H), 5.99 (m, 1 H), 4.60 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.34 (m, 2 H), 2.29 (s, 3 H), 2.24 (m, 1 H), 2.17 (m, 1 H), 0.88 (t, *J* = 8.0 Hz, 3 H), 0.51 (q, *J* = 8.0 Hz, 2 H), 0.00 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 136.2, 134.55, 134.51, 130.2, 127.2, 126.3, 125.4, 72.7, 67.9, 33.2, 19.1, 7.4, 6.1, -4.7, -4.8. IR (film) 3370, 3009, 2953, 2814, 1460, 1246, 1124, 1032, 835 cm^{-1}. HRMS (EI) *m*/*z* 260.1582 [(M^+); calcd for $C_{16}H_{24}OSi$, 260.1596].

*Preparation of compound **301***

Following general procedure F, the title compound (colorless oil) was prepared in 86% yield from compound **283**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 1 H), 6.93 (m, 2 H), 6.80 (m, 1 H), 6.02 (m, 1 H), 4.45 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.38 (m, 2 H), 2.30 (m, 1 H), 2.23 (m, 1 H), 0.92 (t, *J* = 8.0 Hz, 3 H), 0.55 (q, *J* = 8.0 Hz, 2 H), 0.03 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 144.6, 135.9, 134.5, 129.4, 118.2, 113.1, 111.2, 75.6, 67.7, 55.2, 34.8, 7.4, 6.1, -4.8. IR (film) 3005, 2953, 1257, 1033, 775 cm^{-1}. HRMS (EI) *m/z* 276.1540 [$(M)^{+}$; calcd for $C_{16}H_{24}O_2Si$, 276.1546].

*Preparation of compound **302***

Following general procedure F, the title compound (orange oil) was prepared in 70% yield from compound **284**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.37 (m, 3 H), 6.07 (m, 1 H), 4.32 (dd, *J* = 4.0, 7.0 Hz, 1 H), 4.29 (m, 1 H), 4.25 (m, 1 H), 4.21 (m, 1 H), 4.11 (m, 2 H), 4.08 (m, 1 H), 4.06 (s, 5 H), 2.34 (m, 2 H), 0.40 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 136.1, 134.9, 133.9 (2 C), 129.1, 127.8 (2 C), 88.8, 71.7, 68.6 (5 C), 68.0, 67.6, 67.5, 66.8, 66.4, 32.4, -3.9, -4.0. IR (film) 3069, 2956, 1424, 1248, 1110, 815 cm^{-1}. HRMS (EI) *m/z* 402.1108 [$(M)^{+}$; calcd for $C_{23}H_{26}OSiFe$, 402.1102].

*Preparation of compound **303***

Following general procedure F, the title compound (colorless oil) was prepared in 60% yield from compound **285**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 1 H), 6.99 (m, 1 H), 6.96 (dd, *J* = 3.5, 5.0 Hz, 1 H), 6.00 (m, 1 H), 4.77 (dd, *J* = 3.5, 9.5 Hz, 1 H), 4.39 (m, 1 H), 4.33 (m, 1 H), 2.47 (m, 1 H), 2.37 (m, 1 H), 0.92 (t, *J* = 8.0 Hz, 3 H), 0.56 (q, *J* = 8.0 Hz, 2 H), 0.05 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 135.3, 134.4, 126.5, 124.6, 123.7, 71.4, 67.3, 34.4, 7.4, 6.0, -4.8. IR (film) 2953, 1246, 1120, 833 cm^{-1}. HRMS (EI) *m/z* 252.0992 [$(M)^{+}$; calcd for $C_{13}H_{20}OSiS$, 252.1004].

*Preparation of compound **304***

Following general procedure F, the title compound (colorless oil) was prepared in 97% yield from compound **286**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.35 (m, 3 H), 7.26 (m, 4 H), 6.10 (m, 1 H), 4.45 (dd, *J* = 5.0, 9.0 Hz, 1 H), 4.38 (m, 2 H), 2.23 (m, 2 H), 0.36 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 137.3, 136.0, 134.9, 133.9 (2 C), 133.0, 129.2, 128.4 (2 C), 127.9 (2 C), 127.2 (2 C), 74.8, 67.6, 34.4, -3.9, -4.0. IR (neat) 3069, 2955, 2820, 1493, 1248, 1115, 825 cm^{-1}. HRMS (EI) *m/z* 328.1067 [$(M)^{+}$; calcd for $C_{19}H_{21}OSiCl$, 328.1050].

*Preparation of compound **305***

Following general procedure F, the title compound (colorless oil) was prepared in 84% yield from compound **287**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 1.5 Hz, 1 H), 7.27–7.21 (m, 3

H), 6.01 (m, 1 H), 4.44 (dd, *J* = 5.5, 8.0 Hz, 1 H), 4.36 (q, *J* = 2.5 Hz, 2 H), 2.23 (m, 2 H), 0.91 (t, *J* = 8.0 Hz, 3 H), 0.54 (q, *J* = 8.0 Hz, 2 H), 0.03 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 135.6, 134.4, 134.3, 129.6, 127.4, 126.0, 123.9, 74.9, 67.6, 34.6, 7.4, 6.0, -4.8. IR (film) 3013, 2953, 2820, 1126, 835 cm^{-1}. HRMS (EI) *m/z* 280.1064 [(M^+); calcd for $C_{15}H_{21}OSiCl$, 280.1050]

*Preparation of compound **306***

Following general procedure F, the title compound (colorless oil) was prepared in 98% yield from compound **288**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (m, 1 H), 7.66 (dt, *J* = 1.5, 8.0 Hz, 1 H), 7.49 (m, 2 H), 7.42 (d, *J* = 7.5 Hz, 1 H), 7.33 (m, 3 H), 7.14 (m, 1 H), 6.09 (m, 1 H), 4.60 (dd, *J* = 3.5, 10.5 Hz, 1 H), 4.43 (m, 2 H), 2.45 (m, 1 H), 2.30 (m, 1 H), 0.35 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 148.9, 137.3, 136.7, 135.9, 135.0, 134.0 (2 C), 129.1, 127.8 (2 C), 122.3, 120.1, 76.3, 67.6, 33.0, -3.81, -3.93. IR (neat) 3067, 2955, 2822, 1591, 1465, 1248, 1128, 1032, 821 cm^{-1}. HRMS (ESI) *m/z* 296.1470 [$(M)^+$; calcd for $C_{18}H_{22}ONSi$, 296.1471].

*Preparation of compound **307***

Following general procedure F, the title compound (colorless oil) was prepared in 86% yield from compound **289**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (m, 4 H), 7.55 (m, 2 H), 7.48 (m, 3 H), 7.39 (m, 3 H), 6.17 (m, 1 H), 4.69 (dd, *J* = 3.5, 9.5 Hz, 1 H), 4.48 (m, 2 H), 2.46–2.34 (m, 2 H), 0.40 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 137.4, 136.1, 135.1, 134.0 (2 C), 133.3, 132.8, 129.1, 128.1, 128.0, 127.9 (2 C), 127.6, 126.0, 125.7, 124.4, 124.2, 75.6, 67.7, 34.5, -3.8, -

3.9. IR (neat) 3057, 2955, 2818, 1427, 1248, 1115, 815 cm^{-1}. HRMS (EI) *m/z* 344.1580 [$(M)^+$; calcd for $C_{23}H_{24}OSi$, 344.1596].

*Preparation of compound **308***

Following general procedure F, the title compound (colorless oil) was prepared in 96% yield from compound **290**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.35 (m, 3 H), 6.01 (m, 1 H), 4.25–4.15 (m, 2 H), 3.14 (ddd, *J* = 3.5, 5.5, 10.0 Hz, 1 H), 2.03 (m, 1 H), 1.99–1.92 (m, 2 H), 1.70 (m, 2 H), 1.62 (m, 2 H), 1.33 (m, 1 H), 1.25–1.11 (m, 3 H), 0.96 (m, 2 H), 0.32 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 136.5, 134.7, 134.0 (2 C), 129.0, 127.8 (2 C), 77.9, 67.5, 42.8, 29.4, 29.0, 28.5, 26.6, 26.2, 26.1, -3.8, -3.9. IR (neat) 2924, 2853, 1427, 1246, 1126, 835 cm^{-1}. HRMS (EI) *m/z* 300.1893 [$(M)^+$; calcd for $C_{19}H_{28}OSi$, 300.1909].

*Preparation of compound **309***

Following general procedure F, the title compound (colorless oil) was prepared in 80% yield from compound **291**. ^1H NMR (600 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.34 (m, 3 H), 6.02 (m, 1 H), 4.21 (m, 2 H), 3.41 (m, 1 H), 1.96 (m, 2 H), 1.50 (m, 1 H), 1.46 –1.32 (m, 3 H), 0.89 (t, *J* = 7.2 Hz, 3 H), 0.33 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.7, 136.2, 134.7, 134.0 (2 C), 129.0, 127.8 (2 C), 73.3, 67.1, 38.1, 32.4, 18.7, 14.1, -3.9, -4.0. IR (film) 3069, 2957, 2812, 1427, 1248, 1130, 833 cm^{-1}. HRMS (EI) *m/z* 260.1596 [$(M)^+$; calcd for $C_{16}H_{24}OSi$, 260.1596].

*Preparation of compound **310***

Following general procedure F, the title compound (colorless oil) was prepared in 91% yield from compound **292**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.34 (m, 3 H), 5.99 (m, 1 H), 4.26 (m, 1 H), 4.18 (m, 1 H), 2.75 (ddd, *J* = 3.0, 7.8, 9.6 Hz, 1 H), 2.17–2.11 (m, 1 H), 2.09–2.05 (m, 1 H), 0.87 (m, 1 H), 0.51 (m, 1 H), 0.45 (m, 1 H), 0.33 (s, 6 H), 0.33 (overlapped) 0.17 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 136.2, 134.6, 134.0 (2 C), 129.0, 127.8 (2 C), 77.9, 67.2, 31.9. 15.7, 2.8, 1.8, -3.8, -3.9. IR (neat) 3070, 3007, 2957, 1427, 1248, 1122, 817 cm^{-1}. HRMS (EI) *m/z* 258.1429 [$(M)^+$; calcd for $C_{16}H_{22}OSi$, 258.1440].

*Preparation of compound **311***

Following general procedure F, the title compound (colorless oil) was prepared in 86% yield from compound **293**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (m, 1 H), 4.25 (m, 1 H), 4.17 (m, 1 H), 2.74 (m, 1 H), 2.13 (m, 1 H), 2.04 (m, 1 H), 0.91 (t, *J* = 8.0 Hz, 9 H), 0.90 (m, heavily overlapped, 1 H), 0.57 (q, *J* = 8.0 Hz, 6 H), 0.53–0.48 (m, 2 H), 0.34 (m, 1 H), 0.20 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.4, 133.5, 78.0, 67.2, 32.6, 15.7, 7.4, 2.9, 2.3, 1.8. IR (film) 3082, 3007, 2953, 1124, 1018, 731 cm^{-1}. HRMS (EI) *m/z* 238.1763 [$(M)^+$; calcd for $C_{14}H_{26}OSi$, 238.1753].

*Preparation of compound **312***

Following general procedure G, the title compound (colorless oil) was prepared in 80% yield from compound **294**. ^{1}H NMR (500 MHz, $CDCl_3$) mixture of diastereomers (1.0:0.3 ratio) δ

9.67 (t, *J* = 2.0 Hz, 1 H), 9.33 (dd, *J* = 2.0, 2.5 Hz, 0.3 H), 7.55 (m, 0,6 H), 7.38 (m, 0,9 H), 7.33–7.17 (m, 10.9 H), 7.10 (m, 0.6 H), 2.66 (dd, *J* = 2.0, 17.0 Hz, 1 H), 2.25 (dd, *J* = 6.0, 8.0 Hz, 0.3 H), 2.22 (dd, *J* = 6.0, 8.0 Hz, 1 H), 2.18 (dd, *J* = 3.0, 17.5 Hz, 0.3 H), 2.01 (dd, *J* = 2.0, 17.0 Hz, 1 H), 1.79 (dd, *J* = 2.0, 17.5 Hz, 0.3 H), 1.39 (dd, *J* = 4.5, 6.0 Hz, 1 H), 1.16 (dd, *J* = 5.5, 8.0 Hz, 0.3 H), 1.09 (t, *J* = 5.0 Hz, 0.3 H), 0.93 (dd, *J* = 4.5, 8.5 Hz, 1 H), 0.36 (s, 0.9 H), 0.35 (s, 0.9 H), 0.08 (s, 3 H), -0.23 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer δ 202.7, 139.1, 137.9, 134.0, 129.9, 129.0, 128.0, 127.7, 126.5, 53.2, 29.4, 15.7, -2.8, -3.4. Minor diastereomer (a substituted aromatic carbon could not be located) δ 203.2, 137.8, 134.1 (2 C), 129.5, 129.3 (2 C), 128.2 (2 C), 127.9 (2 C), 126.4, 45.1, 24.9, 10.3, -4.35, -4.43. IR (neat) 3063, 2956, 1722, 1496. 1427, 1250, 1111, 816 cm^{-1}. HRMS (EI) *m/z* 294.1430 [$(M)^+$; calcd for $C_{19}H_{22}OSi$, 294.1440].

*Preparation of compound **313***

Following general procedure G, the title compound (colorless oil) was prepared in 78% yield from compound **295**. (dr > 20:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (dd, *J* = 2.5, 3.0 Hz, 1 H), 7.30 (m, 2 H), 7.24 (m, 2 H), 7.18 (m, 1 H), 2.72 (dd, A of ABX system, *J* = 2.5, 17.0 Hz, 1 H), 2.14 (dd, *J* = 6.0, 8.0 Hz, 1 H), 2.04 (dd, B of ABX system, *J* = 2.0, 17.0 Hz, 1 H), 1.32 (dd, *J* = 4.5, 5.5 Hz, 1 H), 0.91 (dd, *J* = 4.5, 8.0 Hz, 1 H), 0.78 (t, *J* = 8.0 Hz, 9 H), 0.30 (m, 3 H), 0.15 (m, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 139.4, 129.7 (2 C), 127.9 (2 C), 126.4, 53.6, 28.7, 15.7, 9.4, 7.5, 3.2. IR (film) 3060, 2956, 1725, 1450, 1250, 814 cm^{-1}. HRMS (EI) *m/z* 274.1747 [$(M)^+$; calcd for $C_{17}H_{26}OSi$, 274.1753].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2 H), 7.23 (m, 2 H), 7.20 (m, 1 H), 6.03 (m, 1 H), 4.88 (m, 1 H), 3.13 (m, 1 H), 2.96 (m, 1 H), .244 (m, 1 H), 1.67 (m, 1 H), 0.95 (t, *J* = 8.0 Hz, 9 H), 0.63 (q, *J* = 8.0 Hz, 6 H). HRMS (EI) *m/z* 257.1722 [$(M\text{-}OH)^{+}$; calcd for $C_{17}H_{25}Si$, 257.1726].

*Preparation of compound **315***

Following general procedure G, the title compound (colorless oil) was prepared in 85% yield from compound **296**. Mixture of diastereomers (1.0:0.3 ratio) ^{1}H NMR 600 MHz, $CDCl_3$) δ 9.90 (dd, *J* = 1.8, 6.0 Hz, 1 H), 9.50 (dd, *J* = 2.4, 6.0 Hz, 0.3 H), 7.29 (m, 2 H), 7.24 (m, 2.6 H), 7.17 (m, 1.9 H), 2.74 (dd, *J* = 6.0, 16.8 Hz, 1 H), 2.19 (m, 1.6 H), 2.01 (dd, *J* = 1.8, 16.8 Hz, 1 H), 1.80 (dd, *J* = 2.4, 17.4 Hz, 0.3 H), 1.24 (dd, *J* = 4.8, 6.0 Hz, 1 H), 1.13 (dd, *J* = 5.4, 7.8 Hz, 0.3 H), 1.07 (t, *J* = 5.4 Hz, 0.3 H), 0.97 (t, *J* = 7.8 Hz, 0.9 H), 0.86 (dd, *J* = 4.8, 8.4 Hz, 1.3 H), 0.76 (t, *J* = 7.8 Hz, 3 H), 0.56 (q, *J* = 7.8 Hz, 0.6 H), 0.26 (m, 2 H), 0.00 (s, 1.8 H), -0.32 (s, 3 H), -0.42 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) Major diastereomer: δ 202.9, 139.4, 129.9 (2 C), 127.9 (2 C), 126.4, 53.4, 29.4, 15.3, 9.9, 7.3, 6.6, -3.8, -4.0. Minor diastereomer: δ 203.4, 138.1, 129.4 (2 C), 128.2 (2 C), 126.4, 45.4, 24.7, 13.7, 9.1, 7.4, 5.8, -5.0, -5.1. IR (film) 3059, 2955, 1724, 1454, 1250, 814 cm^{-1}. HRMS (EI) *m/z* 246.1431 [$(M)^{+}$; calcd for $C_{15}H_{22}OSi$, 246.1440].

*Preparation of compound **316***

Following general procedure G, the title compound (colorless oil) was prepared in 90% yield from compound **297**. Mixture of diastereomers (15:1 ratio) ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.91

(s, 1 H), 7.35–7.20 (m, 5 H), 7.12 (t, *J* = 7.2 Hz, 2 H), 7.01 (m, 1 H), 6.78 (d, *J* = 7.2 Hz, 2 H), 2.82 (m, 0.8 H), 2.24 (m, 1 H), 2.06 (d, *J* = 16.8 Hz, 0.6 H), 1.86 (d, A of ABX system, *J* = 13.2 Hz, 1 H), 1.80 (d, B of ABX system, *J* = 13.8 Hz, 1 H), 1.26 (m, 1 H), 0.89 (m, 1 H), -0.33 (s, 3 H), -0.45 (s, 3 H). IR (film) 3030, 2957, 1720, 1491, 1250, 827 cm^{-1}. HRMS (EI) *m*/*z* 308.1594 [(M^+); calcd for $C_{20}H_{24}OSi$, 308.1596].

*Preparation of compound **317***

Following general procedure G, the title compound (colorless oil) was prepared in 87% yield from compound **298**. Mixture of diastereomers (1:0.4 ratio) ^1H NMR (500 MHz, $CDCl_3$) δ 9.67 (t, *J* = 2.0 Hz, 1 H), 9,34 (t, *J* = 2.0 Hz, 0.4 H), 7.55 (m, 0.8 H), 7.39–7.27 (m, 6.2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.05 (m, 2.8 H), 6.99 (d, *J* = 8.0 Hz, 0.8 H), 2.64 (dd, *J* = 2.0, 17.0 Hz, 1 H), 2.33 (s, 2 H), 2.30 (s, 0.8 H), 2.22–2.16 (m, 1.8 H), 1.99 (dd, *J* = 2.0, 17.5 Hz, 1 H), 1.81 (dd, *J* = 2.0, 17.5 Hz, 0.4 H), 1.38 (t, *J* = 4.5 Hz, 1 H), 1.14 (dd, *J* = 5.0, 8.0 Hz, 0.4 H), 1.07 (t, *J* = 5.5 Hz, 0.4 H), 0.92 (dd, *J* = 4.5, 8.0 Hz, 1 H), 0.36 (s, 1.2 H), 0.35 (s, 1.2 H), 0.10 (s, 3 H), -0.21 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) Major diastereomer: δ 202.6, 138.0, 135.97, 135.96, 134.1, 134.0 (2 C), 129.7 (2 C), 128.6 (2 C), 127.7 (2 C), 53.2, 29.0, 21.1, 15.7, 10.3, -2.7, -3.4. Minor diastereomer (one aromatic carbon could not be located): δ 203.2, 136.8, 135.94, 134.6, 129.4, 129.2 (2 C), 129.0 (2 C), 128.9 (2 C), 127.9 (2 C), 45.1, 24.5, 21.0, 13.9, 9.3, -4.2, -4.4. IR (film) 3033, 2954, 1719, 1490, 1250, 830 cm^{-1}. HRMS (EI) *m*/*z* 308.1591 [(M^+); calcd for $C_{20}H_{24}OSi$, 308.1596].

*Preparation of compound **318***

Following general procedure G, the title compound (colorless oil) was prepared in 92% yield from compound **299**. Mixture of diastereomers (1.0:0.24 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (dd, *J* = 2.0, 2.5 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.12 (t, *J* = 7.5 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 7.00 (t, *J* = 7.5 Hz, 1 H), 6.78 (m, 2 H), 2.79 (dd, A of ABX system, *J* = 3.0, 17.5 Hz, 1 H), 2.32 (s, 3 H), 2.18 (m, 1 H), 2.04 (dd, B of ABX system, *J* = 2.5, 17.5 Hz, 1 H), 1.86 (d, C of CDX system, *J* = 13.5 Hz, 1 H), 1.80 (dd, D of CDX system, *J* = 13.5 Hz, 1 H), 1.22 (t, *J* = 5.5 Hz, 1 H), 0.86 (dd, *J* = 5.0, 8.5 Hz, 1 H), -0.32 (s, 3 H), -0.45 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer δ 202.8, 139.7, 136.2, 136.1, 129.8 (2 C), 128.7 (2 C), 128.2 (2 C), 128.0 (2 C), 124.0, 53.4, 29.3, 24.8, 21.1, 15.5, 9.8, -3.3, -3.6. IR (film) 3024, 2957, 2720, 1722, 1493, 1250, 827 cm^{-1}. HRMS (EI) *m*/*z* 231.1197 $[(M-C_7H_7)^+$; calcd for $C_{14}H_{19}OSi$, 231.1205]. The minor diastereomer was also partially purified as the major component. (1.0:0.1 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (dd, *J* = 2.0, 3.0 Hz, 1 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.07 (m, 3 H), 7.02 (m, 2 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 2.32 (s, 3 H), 2.18 (m, 4 H), 1.87 (dd, *J* = 2.0, 17.5 Hz, 1 H), 1.12 (dd, *J* = 5.5, 8.0 Hz, 1 H), 1.05 (t, *J* = 5.5 Hz, 1 H), -0.01 (s, 3 H), -0.02 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.3, 139.5, 136.0, 134.6, 129.3 (2 C), 128.9 (2 C), 128.3 (4 C), 124.2, 45.4, 24.6, 24.2, 21.0, 13.9, 8.9, -4.5, -4.7. IR (film) 3025, 2956, 2720, 1722, 1493, 1251, 827 cm^{-1}. HRMS (EI) *m*/*z* 231.1209 $[(M-C_7H_7)^+$; calcd for $C_{14}H_{19}OSi$, 231.1205].

*Preparation of compound **319***

Following general procedure G, the title compound (colorless oil) was prepared in 91% yield from compound **300**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (t, *J* = 2.5 Hz, 1 H), 7.12–7.05 (m, 4 H), 2.56 (dd, *J* = 2.5, 16.5 Hz, 1 H), 2.37 (overlapped, dd, *J* = 3.0, 16.5 Hz, 1 H), 2.37 (s, 3 H), 1.95 (dd, *J* = 6.0, 8.0 Hz, 1 H), 1.37 (dd, *J* = 5.0, 6.0 Hz, 1 H), 0.97 (dd, *J* = 5.0, 8.5 Hz, 1 H), 0.76 (t, *J* = 8.0 Hz, 3 H), 0.26 (m, 2 H), -0.30 (s, 3 H), -0.39 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 138.8, 137.5, 129.7, 128.3, 126.6, 125.3, 53.5, 29.0, 20.1, 14.7, 10.3, 7.3, 6.8, -3.7, -3.9. IR (film) 3029, 2953, 1722, 1124, 830 cm^{-1}. HRMS (EI) *m*/*z* 260.1605 [(M^{+}); calcd for $C_{16}H_{24}OSi$, 260.1596].

*Preparation of compound **320***

Following general procedure G, the title compound (colorless oil) was prepared in 61% yield from compound **301**. Mixture of diastereomers (*cis*/*trans* 1.1:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (t, *J* = 2.5 Hz, 1.1 H), 9.51 (dd, *J* = 2.0, 3.0 Hz, 1 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 7.15 (t, *J* = 8.0 Hz, 1.1 H), 6.87 (m, 2.1 H), 6.71 (m, 4.2 H), 2.74 (dd, *J* = 3.0, 17.5 Hz, 1.1 H), 2.18 (m, 3.1 H), 1.22 (dd, *J* = 4.5, 5.5 Hz, 1.1 H), 1.12 (dd, *J* = 5.0, 8.0 Hz, 1 H), 1.05 (t, *J* = 5.5 Hz, 1 H), 0.97 (t, *J* = 8.0 Hz, 3 H), 0.86 (m, 1.1 H), 0.77 (t, *J* = 8.0 Hz, 3.3 H), 0.55 (q, *J* = 8.0 Hz, 2 H), 0.28 (m, 2.2 H), 0.00 (s, 6 H), -0.29 (s, 3.3 H), -0.39 (s, 3.3 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer δ 202.9, 159.3, 141.1, 128.9, 121.8, 115.5, 112.0, 29.5, 15.5, 9.9, 7.3, 6.7, -4.0, -5.0. Minor diastereomer δ 203.5, 159.5, 139.8, 129.2, 122.3, 115.5, 111.4, 24.8, 13.9, 9.1,

7.4, 5.8, -3.7, -5.2. IR (film) 2955, 1722, 1601, 1255, 1045, 835 cm^{-1}. HRMS (EI) *m*/*z* 276.1550 [$(M)^{+}$; calcd for $C_{16}H_{24}O_2Si$, 276.1546]

*Preparation of compound **321***

Following general procedure G, the title compound (colorless oil) was prepared in 69% yield from compound **302**. Mixture of diastereomers (1.0:0.12 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 9.53 (t, *J* = 7.0 Hz, 1 H), 7.31 (m, 2 H), 7.28 (m, 3 H), 4.30 (m, 1 H), 4.09 (m, 1 H), 4.08 (s, 5 H), 3.92 (m, 1 H), 3.76 (m, 1 H), 2.42 (dd, A of ABX system, *J* = 2.0, 17.0 Hz, 1 H), 1.97 (dd, B of ABX system, *J* = 2.0, 17.0 Hz, 1 H), 1.93 (dd, *J* = 6.5, 9.0 Hz, 1 H), 1.03 (d, *J* = 4.5, 6.0 Hz, 1 H), 0.87 (dd, *J* = 5.0, 8.5 Hz, 1 H), 0.06 (s, 3 H), -0.04 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 138.1, 134.2 (2 C), 129.0, 127.6 (2 C), 86.5, 70.1, 69.3, 68.7 (5 C), 68.2, 66.0, 53.3, 24.9, 16.8, 11.2, -2.5, -2.9. IR (film) 3091, 2988, 1722, 1427, 1250, 1107, 816 cm^{-1}. HRMS (EI) *m*/*z* 402.1093 [(M^{+}); calcd for $C_{23}H_{26}OSiFe$, 402.1102].

*Preparation of compound **322***

Following general procedure G, the title compound (colorless oil) was prepared in 71% yield from compound **303**. Mixture of diastereomers (*cis*/*trans* 0.5:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (dd, *J* = 2.0, 3.0 Hz, 0.5 H), 9.57 (dd, *J* = 2.0, 3.0 Hz, 1 H), 7.10 (m, 1.5 H), 6.90 (dd, *J* = 3.5, 5.0 Hz, 1.0 H), 0.87 (dd, *J* = 3.5, 5.0 Hz, 0.5 H), 6.81 (dt, *J* = 1.5, 3.5 Hz, 0.5 H), 6.73 (dt, *J* = 1.5, 3.5 Hz, 1 H), 2.65 (dd, A of ABX system, *J* = 3.0, 17.5 Hz, 0.5 H), 2.30 (dd, C of CDX system, *J* = 3.0, 17.5 Hz, 1 H), 2.24 (dd, *J* = 5.5, 7.0 Hz, 1 H), 2.14 (dd, *J* = 6.0, 7.5 Hz, 0.5 H),

2.02 (dd, B of ABX system, *J* = 2.0, 17.0 Hz, 0.5 H), 1.95 (dd, D of CDX system, *J* = 2.0, 17.5 Hz, 1 H), 1.25 (m, 1.5 H), 1.01 (t, *J* = 5.0 Hz, 1 H), 1.00 (m, 0.5 H), 0.97 (t, *J* = 8.0 Hz, 3 H), 0.81 (t, *J* = 8.0 Hz, 1.5 H), 0.54 (q, *J* = 8.0 Hz, 2 H), 0.40–0.28 (m, 1 H), -0.01 (s, 3 H), 0.02 (s, 3 H), -0.21 (s, 1.5 H), -0.32 (s, 1.5 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer: δ 203.2, 142.6, 126.9, 126.0, 124.1, 19.2, 16.4, 10.1, 7.4, 5.8, -5.0, -5.3. Minor diastereomer: δ 202.7, 144.1, 126.5, 126.2, 124.0, 23.3, 17.6, 11.2, 7.3, 6.4, -4.0, -4.3. IR (film) 2953, 1722, 1250, 833 cm^{-1}. HRMS (EI) *m/z* 252.1001 [$(M)^+$; calcd for $C_{13}H_{20}OSiS$, 252.1004].

*Preparation of compound **323***

Following general procedure G, the title compound (colorless oil) was prepared in 71% yield from compound **303**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (t, *J* = 2.0 Hz, 1 H), 7.31 (m, 1 H), 7.26 (m, 4 H), 7.16 (m, 2 H), 2.72 (dd, *J* = 2.0, 17.5 Hz, 1 H), 2.13 (dd, *J* = 6.0, 8.0 Hz, 1 H), 2.01 (dd, *J* = 1.5, 17.5 Hz, 1 H), 1.33 (dd, *J* = 4.5, 5.5 Hz, 1 H), 0.92 (dd, *J* = 5.0, 8.5 Hz, 1 H), 0.10 (s, 3 H), -0.17 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 137.7, 137.5, 133.9 (2 C), 132.1, 131.2 (2 C), 129.1, 128.0 (2 C), 127.7 (2 C), 53.3, 28.7, 15.8, 10.5, -2.7, -3.2. IR (film) 3060, 2956, 1721, 1427, 1243, 1111, 814 cm^{-1}. HRMS (EI) *m/z* 328.1048 [$(M)^+$; calcd for $C_{19}H_{21}OSiCl$, 328.1050].

*Preparation of compound **325***

Following general procedure G, the title compound (colorless oil) was obtained in 2% yield from compound **303**, in addition to **323** and **324**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.38

(d, *J* = 8.5 Hz, 2 H), 7.34 (m, 3 H), 7.26 (m, 2 H), 6.09 (m, 1 H), 2.97 (m, 1 H), 2.89–2.74 (m, 3 H), 2.0 (s, 1 H), 0.39 (s, 6 H).

*Preparation of compound **326***

Following general procedure G, the title compound (colorless oil) was prepared in 17% yield from compound **305**, in addition to compounds **327** and **328**. Mixture of diastereomers (*cis* / *trans* = 1:0.15 ratio) ^{1}H NMR (600 MHz, $CDCl_3$) major (*cis*) diastereomer: δ 9.87 (dd, *J* = 1.8, 3.0 Hz, 1 H), 7.28 (m, 1 H), 7.21 (m, 1 H), 7.19–7.15 (m, 2 H), 2.78 (dd, *J* = 2.4, 17.4 Hz, 1 H), 2.12 (dd, *J* = 6.6, 8.4 Hz, 1 H), 2.00 (dd, *J* = 1.8, 17.4 Hz, 1 H), 1.20 (dd, *J* = 5.4, 6.0 Hz, 1 H), 0.87 (dd, *J* = 5.4, 8.4 Hz, 1 H), 0.77 (t, *J* = 7.8 Hz, 3 H), 0.26 (m, 2 H), -0.31 (s, 3 H), -0.41 (s, 3 H). Minor (*trans*) diastereomer: δ 9.51 (dd, *J* = 1.8, 3.0 Hz, 0.15 H), 7.20–7.14 (m, heavily overlapped with major diastereomer, 0.45 H), 7.03 (m, 0.15 H), 2.17 (m, 0.30 H), 1.79 (dd, *J* = 1.8, 17.4 Hz, 0.15 H), 1.14 (dd, *J* = 5.4, 7.8 Hz, 0.15 H), 1.03 (t, *J* = 5.4 Hz, 0.15 H), 0.96 (t, *J* = 7.8 Hz, 0.45 H), 0.55 (q, *J* = 7.8 Hz, 0.30 H), 0.01 (s, 0.9 H). ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer δ 202.4, 141.8, 133.8, 129.9, 129.2, 128.2, 126.6, 53.3, 29.0, 15.5, 10.2, 7.3, 6.7, -3.7, -3.9. IR (film) 3422, 3061, 2955, 2876, 1724, 1250, 814 cm^{-1}. HRMS (EI) *m/z* 228.1042 [$(M)^{+}$; calcd for $C_{15}H_{21}OSiCl$, 280.1050].

*Preparation of compound **327***

Following general procedure G, the title compound (colorless oil) was prepared in 54% yield from compound **305** in addition to compounds **326** and **328**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 1.8 Hz, 1 H), 7.20 (d, *J* = 7.2 Hz, 1 H), 7.17 (m, 1 H), 7.11 (m, 1 H), 5.99 (q, *J* = 1.8 Hz, 1

H), 4.83 (m, 1 H), 3.12 (m, 1 H), 2.95 (ddt, *J* = 1.8. 8.4, 16.8 Hz, 1 H), 2.41 (ddt, *J* = 1.8, 6.6, 16.8 Hz, 1 H), 1.80 (s, 1 H), 0.95 (t, *J* = 7.8 Hz, 3 H), 0.60 (q, *J* = 7.8 Hz, 2 H), 0.09 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 146.3, 141.8, 134.3, 129.8, 127.3, 126.4, 125.4, 86.4, 54.9, 43.0, 7.4, 6.6, -4.2, -4.3. IR (film) 3352, 2955, 1458, 1250, 1089, 837 cm^{-1}. HRMS (EI) *m/z* 263.1019 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{20}SiCl$, 263.1023].

*Preparation of compound **328***

Following general procedure G, the title compound (colorless oil) was obtained in 6% yield from compound **305**, in addition to compounds **326** and **327** . ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (t, *J* = 1.8 Hz, 1 H), 7.34 (ddd, *J* = 1.2, 1.8, 7.8 Hz, 1 H), 7.24 (m, 1 H), 7.20 (ddd, *J* = 1.2, 2.4, 7.8 Hz, 1 H), 6.01 (m, 1 H), 2.97 (dq, *J* = 1.8, 18.0 Hz, 1 H), 2.87 (m, 1 H), 2.80–2.75 (m, 2 H), 2.04 (s, 1 H), 0.94 (t, *J* = 7.8 Hz, 3 H), 0.58 (q, *J* = 7.8 Hz, 2 H), 0.08 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.0, 142.3, 137.8, 134.1, 129.4, 126.8, 125.4, 123.1, 82.9, 53.9, 52.4, 7.4, 6.7, -4.11, -4.13. IR (film) 3397, 3031, 2955, 1253, 839 cm^{-1}. HRMS (EI) *m/z* 263.1009 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{20}SiCl$, 263.1023].

*Preparation of compound **329***

Following general procedure G, the title compound (colorless oil) was obtained in 6% yield from compound **306**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (m, 1 H), 7.57 (m, 1 H), 7.51 (m, 2 H), 7.34 (m, 3 H), 7.14 (d, *J* = 7.8 Hz, 1 H), 7.10 (dd, *J* = 4.8, 7.2 Hz, 1 H), 6.12 (m, 1 H), 5.14 (m, 1 H),

3.36 (q, *J* = 7.8 Hz, 1 H), 2.91 (dd, *J* = 4.2, 15.6 Hz, 1 H), 2.80 (s, 1 H), 2.58 (m, 1 H), 0.40 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 149.2, 144.6, 143.9, 137.5, 136.4, 133.8, 129.1, 127.8, 122.0, 121.4, 84.8, 57.3, 40.2, -3.4. IR (neat) 3402, 3062, 2955, 1599, 1460, 1248, 821 cm^{-1}.

*Preparation of compound **330***

Following general procedure G, the title compound (colorless oil) was obtained in 52% yield from compound **307**, in addition to compound **331**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (t, *J* = 2.5 Hz, 1 H), 7.79 (m, 3 H), 7.59 (s, 1 H), 7.51 (m, 2 H), 7.45 (m, 2 H), 7.37 (m, 3 H), 7.30 (dd, *J* = 2.0, 8.5 Hz, 1 H), 6.39 (t, *J* = 7.0 Hz, 1 H), 3.63 (d, *J* = 7.0 Hz, 2 H), 3.34 (m, 2 H), 0.39 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.1, 144.9, 137.2, 137.1, 134.0 (2 C), 133.6, 132.1, 130.8, 129.3, 128.2, 127.9 (2 C), 127.6, 127.4, 127.1, 126.5, 126.1, 125.4, 44.9, 35.7, -3.3. IR (film) HRMS (EI) *m/z* 344.1593 [$(M)^+$; calcd for $C_{23}H_{24}OSi$, 344.1596].

*Preparation of compound **331***

Following general procedure G, the title compound (colorless oil) was obtained in ~9% yield from compound **307**, as a mixture with isomeric **330** (1:0.6 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (m, 1 H), 7.81–7.28 (heavily overlapped, 12 H), 6.38 (m, 1 H), 6.23 (m, 1 H), 2.59–2.47 (m, 3 H), 0.38 (s, 6 H).

*Preparation of compound **332***

Following general procedure G, the title compound (colorless oil) was obtained in 76% yield from compound **308**. Mixture of diastereomer (~1:0.6 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (dd, *J* = 2.0, 3.0 Hz, 1 H), 9.47 (dd, *J* = 2.0, 3.0 Hz, 0.6 H), 7.49 (m, 3.2 H), 7.34 (m, 4.8 H), 2.54 (dd, *J* = 3.0, 17.0 Hz, 1 H), 2.50 (22, *J* = 3.5, 17.5 Hz, 0.6 H), 2.06 (dd, *J* = 2.0, 17.0 Hz, 0.6 H), 1.84 (m, 1 H), 1.75–1.56 (m, 8.80 H), 1.17–0.93 (m, 8.64 H), 0.89–0.80 (m, 2 H), 0.70 (m, 1 H), 0.63–0.52 (m, 3.2 H), 0.38 (s, 3 H), 0.31 (s, 3 H), -0.23 (d, 3.6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 203.7, 138.2, 137.1, 134.1, 134.0, 129.3, 129.1, 127.8, 127.7, 53.2, 44.5, 39.1, 37.6, 34.3, 33.43, 33.41, 33.38, 33.3, 26.6, 26.4, 26.33, 26.31, 26.30, 26.0, 25.9, 16.7, 14.1, 6.8, 5.3, -1.4, -2.2, -4.6, -4.7. HRMS (EI) *m/z* 300.1909 [$(M)^+$; calcd for $C_{19}H_{28}OSi$, 300.1909].

*Preparation of compound **333***

Following general procedure G, the title compound (colorless oil) was obtained in 83% yield from compound **309**. Mixture of diastereomers (*cis*/*trans* = 4.5:1 ratio). ^{1}H NMR (600 MHz, $CDCl_3$) major diastereomer (*cis*): δ 9.53 (t, *J* = 2.4 Hz, 1 H), 7.50 (m, 2 H), 7.34 (m, 3 H), 2.41 (dd, A of ABX system, *J* = 2.4, 16.8 Hz, 1 H), 1.80 (dd, B of ABX system, *J* = 2.4, 17.4 Hz, 1 H), 1.56 (m, 1 H), 1.38 (m, 2 H), 1.11 (m, 1 H), 0.88 (t, *J* = 7.2 Hz, 3 H), 0.81 (m, 1 H), 0,61 (dd, C of CDX system, *J* = 4.2, 8.4 Hz, 1 H), 0.56 (dd, D of CDX system, *J* = 4.2, 5.4 Hz, 1 H), 0.36 (s, 3 H), 0.32 (s, 3 H). Minor diastereomer (*trans*): δ 9.50 (t, *J* = 2.4 Hz, 1 H), 7.48 (m, 2 H), 2.38 (dd, A of ABX system, *J* = 3.0, 17.4 Hz, 1 H), 2.23 (dd, B of ABX system, *J* = 2.4, 17.4 Hz, 1 H), 0.24 (s, 6 H), all other protons are overlapped with major diastereomer, presumably at 7.34 (3 H), 1.38 (4 H), 0.92–079 (6 H). ^{13}C NMR (151 MHz, $CDCl_3$) mixture of diastereomers (*cis* /

trans = 4.5:1 ratio), Major (*cis*) diastereomer: δ 203.3, 138.4, 134.1 (2 C), 129.1, 127.8 (2 C), 53.4, 33.5, 26.0, 23.3, 17.9, 13.9, 6.4, -1.4, -2.1. IR (neat) 3070, 2957, 2872, 1725, 1427, 1251, 1111, 816 cm^{-1}. HRMS (EI) *m/z* 260.1590 $[(M)^+$; calcd for $C_{16}H_{24}OSi$, 260.1596].

*Preparation of compound **334***

Following general procedure G, the title compound (colorless oil) was obtained in 73% yield from compound **310**. Mixture of diastereomers (1:1 ratio) ^1H NMR (600 MHz, $CDCl_3$) δ 9.58 (t, *J* = 3.0 Hz, 1 H), 9.49 (t, *J* = 2.4 Hz, 1 H), 7.54 (m, 2 H), 7.47 (m, 2 H), 7.34 (m, 6 H), 2.49 (dd, A of ABX system, *J* = 2.4, 17.4 Hz, 1 H), 2.40 (dd, B of ABX system, *J* = 2.4, 18.0 Hz, 1 H), 2.36 (dd, C of CDX system, *J* = 2.4, 16.8 Hz, 1 H), 1.81 (dd, D of CDX system, *J* = 2.4, 16.8 Hz, 1 H), 0.78–0.72 (m, 2 H), 0.71 (t, *J* = 4.8 Hz, 1 H), 0.61–0.57 (m, 2 H), 0.54–0.43 (m, 6 H), 0.40 (s, 3 H), 0.37 (m, 3 H), 0.31 (t, *J* = 4.8 Hz, 1 H), 0.26 (m, 1 H), 0.23 (s, 3 H), 0.22 (s, 3 H), 0.21 (m, overlapped with Me singlet at 0.22, 1 H), 0.17–0.12 (m, 2 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.0, 203.1, 138.3, 137.1, 134.2 (2 C), 134.0 (2 C), 129.3, 129.1, 127.83 (2 C), 127.80 (2 C), 53.1, 45.5, 29.8, 23.2, 17.3, 14.7, 11.9, 9.5, 7.3, 6.7, 6.1, 6.0, 5.3, 4.5, -1.9, -2.2, -4.52, -4.55. IR (neat) 3071, 3000, 2959, 2816, 1722, 1427, 1250, 1113, 815 cm^{-1}. HRMS (EI) *m/z* 258.1440 $[(M)^+$; calcd for $C_{16}H_{22}OSi$, 258.1440].

*Preparation of compound **335***

Following general procedure G, the title compound (colorless oil) was obtained in 76% yield from compound **311**. Mixture of diastereomers (1:0.7 ratio) ^1H NMR (600 MHz, $CDCl_3$) (1:0.7

ratio) δ 9.79 (t, *J* = 2.5 Hz, 0.7 H), 9.68 (dd, *J* = 2.5, 3.5 Hz, 1 H), 2.49 (dd, A of ABX system, *J* = 2.5, 17.0 Hz, 0.7 H), 2.42 (dd, C of CDX system, *J* = 3.0, 16.5 Hz, 1 H), 2.40 (dd, B of ABX system, *J* = 2.5, 17.0 Hz, 0.7 H), 1.77 (dd, D of CDX system, *J* = 2.5, 17.0 Hz, 1 H), 0.97 (t, *J* = 8.0 Hz, 9 H), 0.92 (t, *J* = 8.0 Hz, 6.3 H), 0.74 (dd, *J* = 4.5, 8.0 Hz, 0.7 H), 0.69–0.60 (m, heavily overlapped with $SiCH_2$, not quantified), 0.60 (q, *J* = 8.0 Hz, 6 H), 0.52–0.47 (m, ~6 H), 0.46 (q, *J* = 8.0 Hz, 4.2 H), 0.37 (m, 1 H), 0.28–0.17 (m, ~4 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer: δ 203.9, 53.5, 29.2, 17.4, 12.2, 7.6, 6.0, 5.3, 4.5, 3.7. Minor diastereomer: δ 204.5, 46.2, 22.8, 14.5, 9.6, 7.4, 6.5, 5.6, 4.3, 2.2. IR (film) 3078, 2999, 2953, 1724, 1458, 1018, 733 cm^{-1}. HRMS (EI) *m*/*z* 238.1756 [$(M)^+$; calcd for $C_{14}H_{26}OSi$, 238.1753].

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CHAPTER 6

COMPARATIVE STUDIES ON THE [1,4]- AND [1,2]-WITTIG REARRANGEMENTS OF STRUCTURALLY DIVERSE SILYL DIHYDROPYRANS AND ANALOGUES

6.1 Introduction

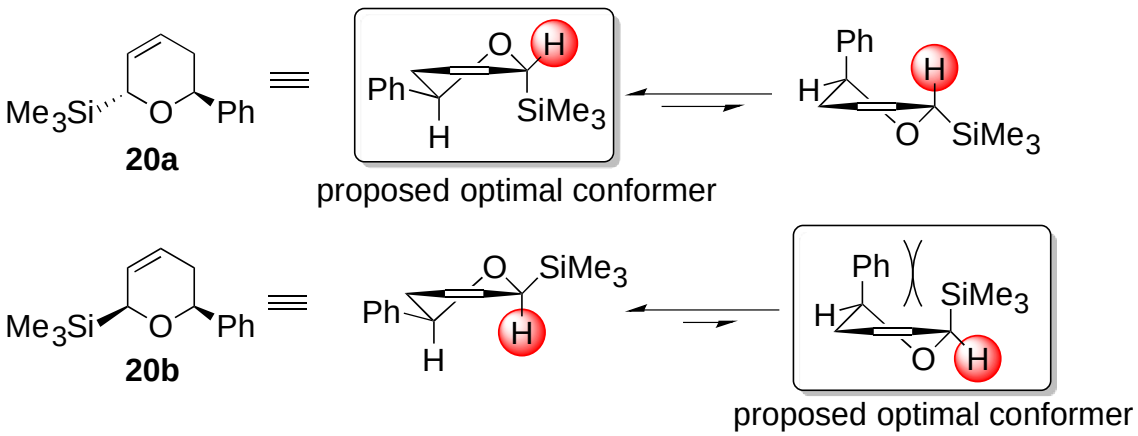
In Chapters 4 and 5 the [1,4]- and [1,2]-Wittig rearrangement of 5,6-dihydro-(*2H*)-pyrans bearing a silyl group at the 2- and 4- positions were studied. The effect of electronic modifications at the migrating carbon, typically benzylic, was evaluated, and some structural changes, such as substitution at the olefin or at silicon, along with mechanistic studies were described. However, many questions remained unanswered and new ones arised, and therefore it was of interest to approach them in order to better understand the factors that determine the reactivity of these cyclic ether and their selectivities in the rearrangements, and the possibility to expand the substrate scope to shorter or larger cyclic ethers or to ring expansions instead of ring contractions.

We have determined that 2-silyl dihydropyrans undergo a more facile and clean α-deprotonation in comparison to the 2-silyl tetrahydropyran analogues. Alternatively, a α-pendant olefin on a tetrahydropyran or tetrahydrofuran moiety allows also selective allylic deprotonation, but leads to exclusive ring contraction via [1,2]-Wittig shifts, and no [1,4]-ring expansion is observed. Seven-membered cyclic ethers also show exclusive [1,2]-regioselectivity. In addition, we have learned that bisallylic cyclic ethers, that is a 5,6-dihydro-(*2H*)-pyrans bearing a pendant olefin at the 2-position, undergo [1,4]- and [1,2]-Wittig ring contractions to the corresponding cyclopropyl enones of α-vinylcyclopentenol structures with excellent efficiency and diastereoselectivity. Electronic effects previously discussed in Chapters 4 and 5 seem to control

the regioselectivity in these transformations. Also, the role of the silyl group has been studied by comparing desilylated analogues in the context of the Wittig rearrangements of 2-silyl-5,6-dihydropyrans.

6.2 The role of the olefin in the reactivity of 5,6-dihydropyrans

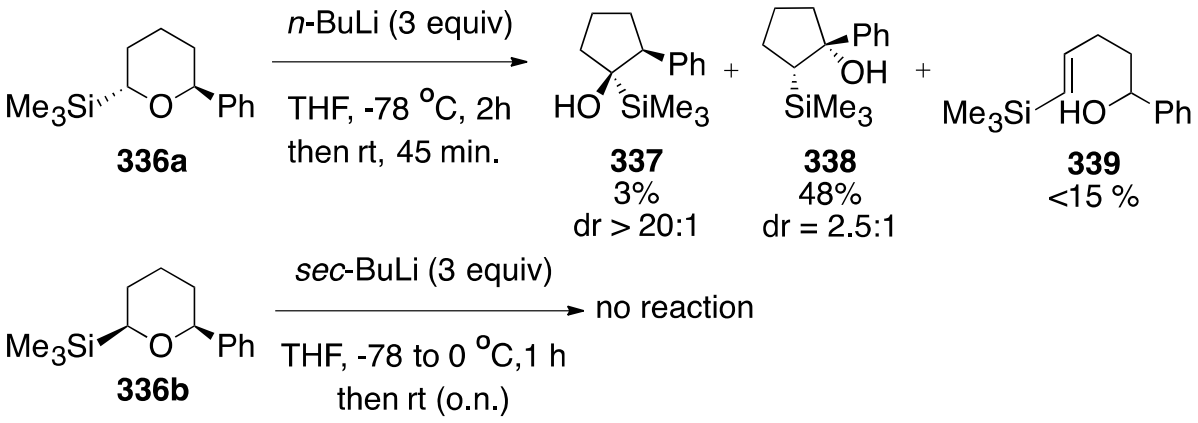
As described in Chapter 4, the observed [1,4]-/[1,2]-selectivity in the stereoconvergent Wittig rearrangements of model diastereomeric dihydropyrans **20a**/**20b** was ~2.5:1. In addition, the relative stereochemistry of these diastereomers, and their analogues, markedly defined their reactivity, with *trans* isomers being much more reactive than their *cis* counterparts. This was rationalized as the ability of **20a** to easily adopt an optimal conformation for the deprotonation step, in which the C-H bond is antiperiplanar to the C-O bond cleaving during rearrangement (Scheme 96). This is partially supported by the conformational A-values for phenyl and trimethylsilyl groups in cyclohexane, 2.9 and 2.5 respectively,[1] which should slightly favor a conformer of **20a** in which phenyl is at an pseudo equatorial orientation and the trimethylsilyl group at a pseudo axial orientation.



Scheme 96. Conformational analysis of **20a**/**20b** and proposed optimal conformers for allylic deprotonation.

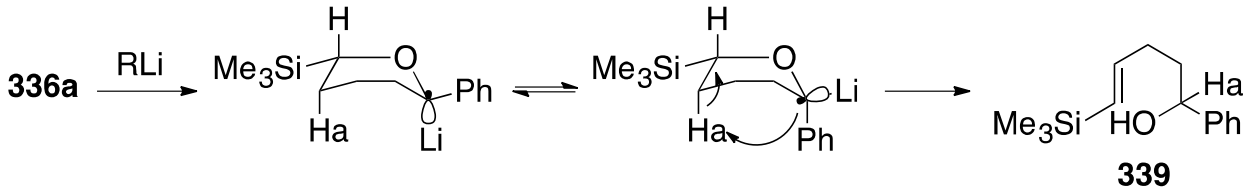
In the case of the *cis* diastereomer **20b** both substituents are "locked" in pseudo equatorial orientations, and therefore the presumably more reactive conformation is difficult to achieve. Experiments with cyclic ethers in which the aryl group was more sterically demanding have shown that the reactivity of *cis* substrates further diminished relative to model **20b**, whereas the reactivity of their *trans* counterparts remained unchanged (Chapter 4).

It was hypothesized that removing the olefin from dihydropyran models **20a**/**20b** should have a proportional effect (compounds **336a**/**336b**), decreasing their reactivity towards deprotonation but keeping the *trans* isomer more reactive than the *cis* one because their corresponding conformational preferences would resemble that of **20a**/**20b**. The absence of an olefin would also limit the rearrangement pathways to only the [1,2]-shift, which, in addition, should follow the "normal" stereochemical pathway of the [1,2]-Wittig rearrangement: Inversion of stereochemistry at the lithium-bearing carbon and retention at the migrating carbon.[2]



Scheme 97. Wittig rearrangements of α-silyl tetrahydropyrans **336a**/**336b**.

Accordingly, *trans* tetrahydropyran **336a** was less reactive at low temperature than its dihydropyran analogue **20a**, and required room temperature for complete conversion (Scheme 97). Surprisingly, the expected [1,2]-Wittig product, resulting from deprotonation α- to the silyl group, was isolated in only 3%, apparently featuring the expected stereochemical outcome of the [1,2]-Wittig rearrangement. The relative stereochemistry was confirmed by hydrogenation of the epimer of **168** (Chapter 4). The major product of the mixture was alcohol **338**, a [1,2]-Wittig product arising from benzylic deprotonation. Interestingly, its diastereoselectivity was low, presumably because the benzylic anion is not configurationally stable and undergoes epimerization before rearrangement.[3] The other product that could be isolated was the known vinylsilane **339**, which is likely formed by transannular hydrogen transfer in a benzylic anion species followed by intramolecular elimination (Scheme 98). In fact, in their studies of [1,2]- and [2,3]-Wittig rearrangements of cyclic ethers, Verner and Cohen demonstrated, via deuterated substrates that these β-eliminations, which are serious side reactions, are stereospecific.[4]

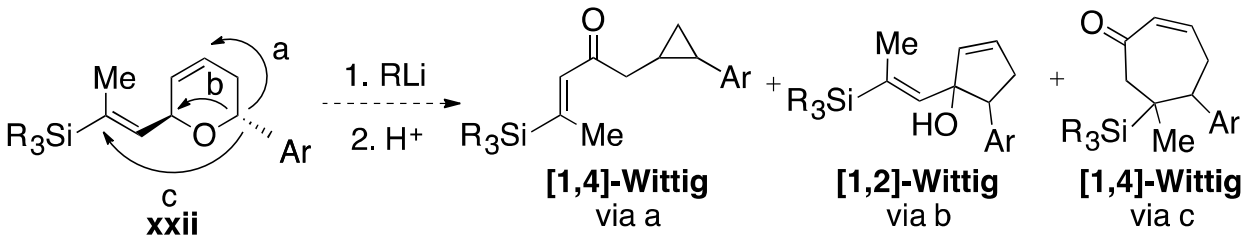


Scheme 98. Presumed transannular H-transfer / elimination leading to **339**.

cis Diastereomer **336b** was extremely unreactive and even at room temperature did not undergo deprotonation to a detectable extent (^{1}H NMR) and was recovered unchanged (Scheme 97). Thus these results are consistent with the hypothesis that the reactivity towards deprotonation of tetrahydropyrans **336a**/**336b** and dihydropyrans **20a**/**20b** is determined by the ability of these molecules to adopt an optimal conformation. In addition, it has been demonstrated that a trialkylsilyl group is not capable enough to significantly reduce the acidity of α-protons in the absence of an adjacent olefin.

6.3 Ring contraction vs ring expansion of bisallylic cyclic ethers via [1,4]- and [1,2]-Wittig rearrangements

We continued our studies by studying the effect of an additional olefin adjacent to the allylic carbon (Scheme 99). An obvious expectation of such structural and electronic modification was that the acidity of the bisallylic proton would remain comparable to that of 2-silyl dihydropyrans (Chapter 4) and higher than that of 4-silyl dihydropyrans (Chapter 5). In addition, we planned to place a silyl group at the exocyclic olefin in order to evaluate its effect in the Wittig rearrangements. Based on our studies described in Chapter 4, we targeted bisallylic ethers of the general structure **xxii** in which the relative stereochemistry of aryl and vinylsilane groups is *trans*.

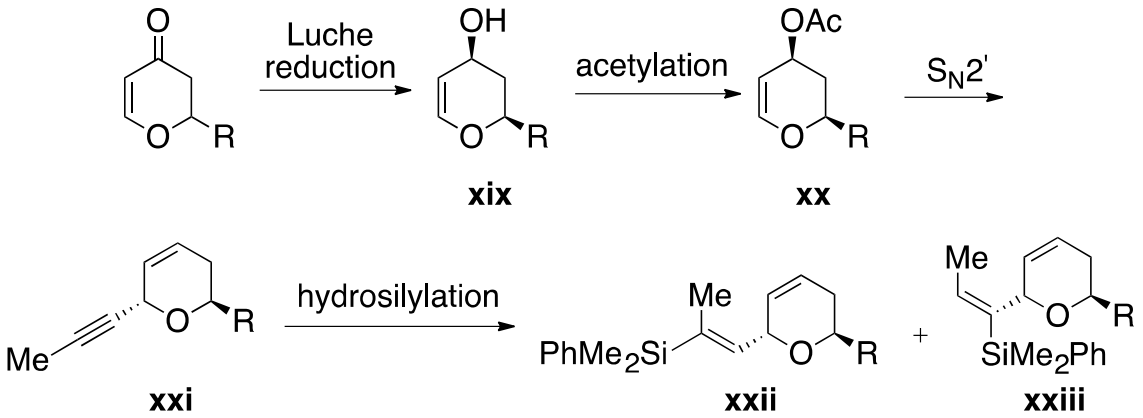


Scheme 99. Possible scenarios for the rearrangement of bisallylic ethers **xxii**.

In theory, selective deprotonation at the bisallylic position (C2 in **xxii**) would generate a lithium carbanion capable of [1,4]- (ring contraction, via a) and [1,2]- (ring contraction, via b) shifts, leading to a cyclopropyl enone and a cyclopentenol structure, respectively. In addition to these known Wittig ring contraction pathways, a ring-expansion via [1,4]-Wittig rearrangement involving the exocyclic olefin (via c) was an attractive possibility that would lead to cycloheptenones bearing two adjacent chiral centers.

6.3.1 Synthesis of bisallylic ethers xxii and xxiii

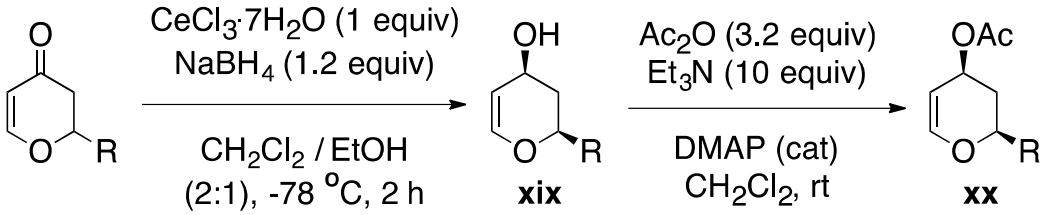
A stereoselective general route to the *trans* diastereomers **xxii** and **xxiii** is shown in Scheme 100. Dihydropyranones, easily prepared via 4+2 cycloaddition of Danishefsky's diene with aldehydes in the presence of a Lewis acid,[5] were stereo- and regioselectively reduced to allylic alcohols following Luche's conditions.[6] S_N2' displacement followed by hydrosilylation provided regioisomeric bisallylic ethers **xxii** and **xxiii**. This route allowed the preparation of not only aryl substituted (R = Ar) dihydropyrans, but also vinyl groups could be placed at that position (R = vinyl), and it is expected that a variety of alkyl groups can take that position as well.



Scheme 100. General route to bisallylic cyclic ethers **xxii** and **xxiii**.

Table 15 lists the yields obtained in the preparation of intermediates **xix** and **xx**. Luche reduction[6] of dihydropyranones proceeded with excellent diastereoselectivity (>20:1) and in some cases the crude alcohol was submitted for acetylation without further purification (entries 2, 4, 6-8).

Table 15. Synthesis of intermediates allylic alcohols **xix** and acetates **xx**.



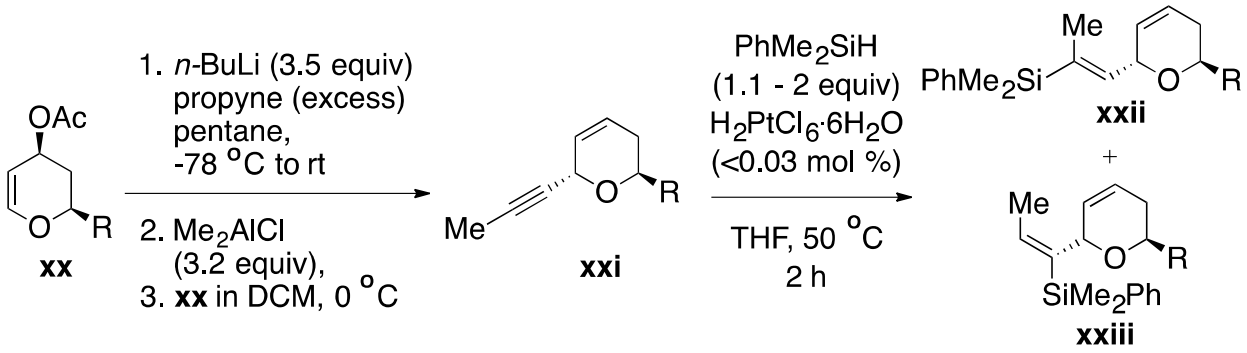
entry	R	Yield **xix** [a]	Yield **xx** [a]
1	Ph	(**340**) 97%	(**349**) 88%
2	4-$MeOC_6H_4$	(**341**) n.d.	(**350**) 83%[b]
3	4-MeC_6H_4	(**342**) 99%	(**351**) 88%
4	4-ClC_6H_4	(**343**) n.d.	(**352**) 85%[b]
5	4-$CF_3C_6H_4$	(**344**) 99%	(**353**) 89%
6	3-$CF_3C_6H_4$	(**345**) n.d.	(**354**) 85%[b]
7	3-$NO_2C_6H_4$	(**346**) n.d.	(**355**) 96%[b]
8	β-styryl	(**347**) n.d.	(**356**) 79%[b]
9	Cyclohexenyl	(**348**) 97%	(**357**) 99%

[a] Isolated yields. [b] Yield for two steps. n.d. = not determined.

As shown in Table 16, S_N2' displacement7 of the acetate groups in **xx** with *in situ* generated propynyldimethylaluminum reagent[8] provided enynes **xxi** in good yields, the minor impurity being the corresponding trans methylated pyran. Finally, hydrosilylation with dimethylphenyl silane in the presence of Speier's catalyst[9] (H_2PtCl_6•$6H_2O$) took place cleanly to afford a

mixture of regioisomers **xxii** and **xxiii**, which could be separated by column chromatography and studied separately. In some cases isomers **xxiii** were not studied nor characterized due to limited sample availability.

Table 16. Synthesis of enynes **xxii** and final products biallylic ethers **xxiii**.



entry	R	Yield **xxi** [a]	Yield **xxii** /**xxiii** [b]	ratio **xxii** /**xxiii**
1	Ph	(**358**) 72%	(**367**/**368**) 80%	3:1
2	4-$MeOC_6H_4$	(**359**) 80%	(**369**/**370**) 89%	7:1
3	4-MeC_6H_4	(**360**) 93%	(**371**/**372**) 75%	1.7:1
4	4-ClC_6H_4	(**361**) 84%	(**373**/**374**) 84%	7.5:1
5	4-$CF_3C_6H_4$	(**362**) 92%	(**375**/**376**) 90%	1.8:1
6	3-$CF_3C_6H_4$	(**363**) 86%	(**377**/**378**) 79%	5.4:1
7	3-$NO_2C_6H_4$	(**364**) 82%	(**379**/**380**) 94%	4:1
8	β-styryl	(**365**) 83%	(**381**/**382**) 92%	8:1
9	Cyclohexenyl	(**366**) 76%	(**383**/**384**) 81%	7:1

[a] Minor amounts of methylated impurity included. [b] Combined isolated yields.

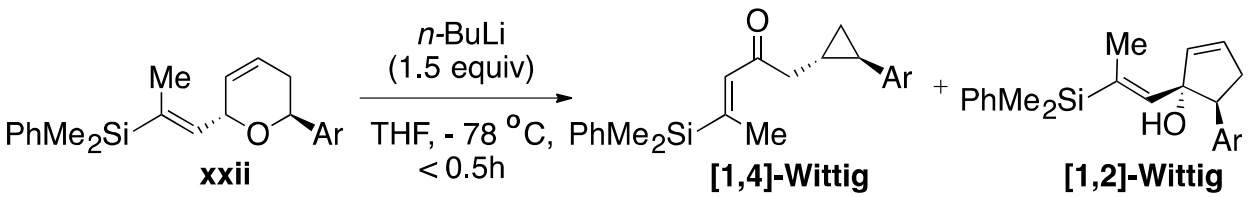
6.3.2 Wittig rearrangements of aryl bisallylic ethers xxii and xxiii

We first studied the Wittig rearrangements of bisallylic ethers of type **xxii** (Table 17) in which the silyl group is located *distal* to the bisallylic carbon. Treatment of these compounds with *n*-butyllithium afforded, within 30 minutes, cyclopropyl enones as the [1,4]-Wittig product, and/or cyclopentenol α-vinylsilane as the [1,2]-Wittig product. The exception being 4-methoxy substituted compound **369** that required 2.5 hours for complete conversion (*vide infra*). From our previous work, we expected that electron-donating groups at the aromatic ring should favor the [1,4]-pathway, and indeed this was the case. 4-Methoxy and 4-methyl substituted bisallylic ethers (**369** and **371**) afforded exclusively the [1,4]-Wittig products **387** and **389** in good yields (entries 2 and 3). Interestingly, the unsubstituted phenyl compound **367** also underwent exclusive [1,4]-shift (entry 1), in contrast to the modest [1,4]-/[1,2]-selectivity observed in 2-silyl dihydropyran analogues **20a**/**20b** (Chapter 4). The selectivity observed in **367** also resembles that of the 4-silyl dihydropyrans (**294**, **295**, **296** & **297**, Chapter 5).

The behavior of electron-deficient substrates was also interesting. As described in Chapters 4 and 5, a *para* chloro substituent at the aromatic ring led to preferential [1,2]-migration, and also competitive benzylic deprotonation in some cases. Chlorinated analogue bisallylic ether **373** underwent [1,4]-shift as the dominant pathway ([1,4]-/[1,2]-selectivity = 4.6:1). The more electron deficient *para* and *meta* trifluoromethyl substituted compounds **375** and **377** rearranged predominantly via the [1,2]-pathway, but significant amounts of [1,4]-Wittig products were isolated. In agreement with our previous observations, *meta* nitro substituted compound **379** underwent extensive decomposition under the reaction conditions, with only 1.1 equivalents of base, and no observable products could be identified in the crude reaction mixture by ^{1}H NMR

other than unreacted **379**. It is also notable that no ring-expanded products, via a potential [1,4]-pathway, were observed in these reactions. Also, for all [1,4]- and [1,2]- ring contracted products the geometry of the vinylsilane group remained intact, and no isomerization was observed.

Table 17. Wittig rearrangements of aryl bisallylic ethers **xxii**.

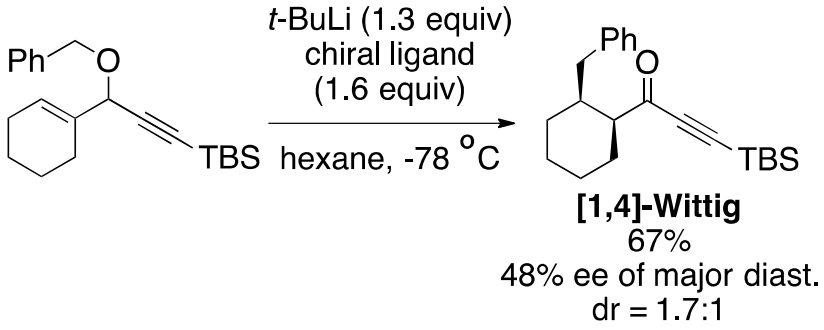


entry	substrate	R	Yield **xxi** [a]	dr [b]	Yield **xxii** /**xxiii** [a, c]
1	**367**	Ph	(**385**) 80%	10:1	(**386**) -
2 [d]	**369**	4-$MeOC_6H_4$	(**387**) 69%	7:1	(**388**) -
3	**371**	4-MeC_6H_4	(**389**) 59%	8:1	(**390**) -
4	**373**	4-ClC_6H_4	(**391**) 74%	18:1	(**392**) 12%
5	**375**	4-$CF_3C_6H_4$	(**393**) 10%	n.d.	(**394**) 40%
6	**377**	3-$CF_3C_6H_4$	(**395**) 20%	17:1	(**396**) 62%
7 [e]	**379**	3-$NO_2C_6H_4$	-		-

[a] Isolated yields. [b] Determined by ^{1}H NMR of isolated material. [c] dr > 20:1. [d] reaction time was 2.2 hours. [e] Complex mixture, 42% recovered **379**.

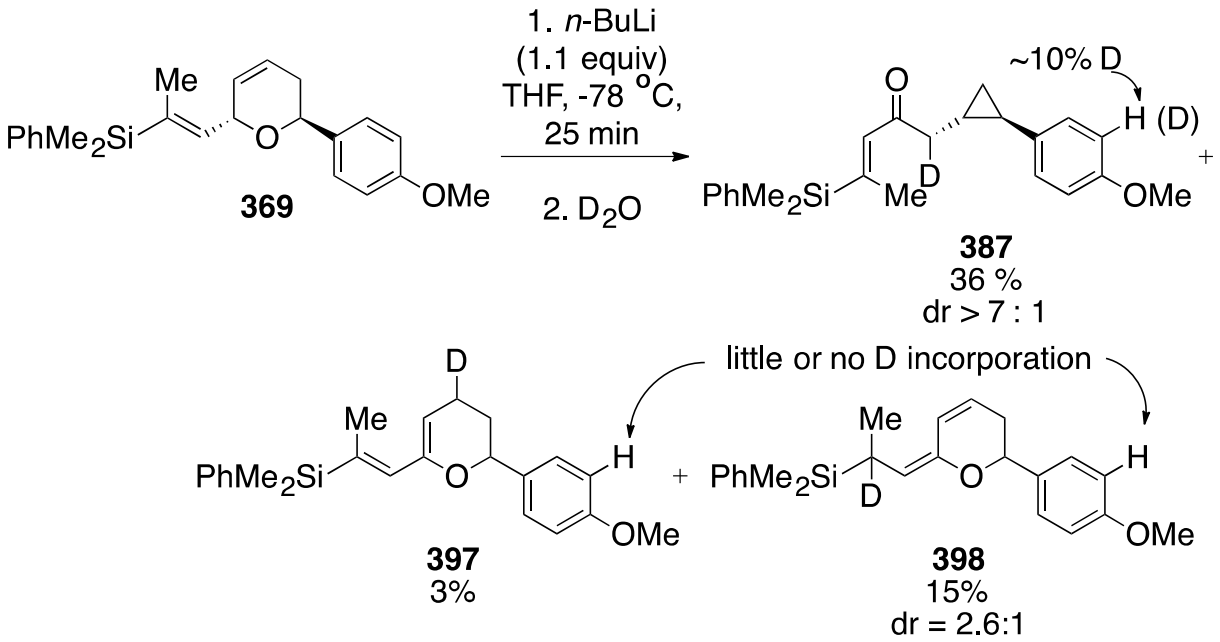
The observed general shift in preference towards the [1,4]-Wittig pathway in most substrates studied suggests that increasing stabilization of a presumed radical-anion fragment favors the [1,4]-shift, even when migrating centers that electronically favor the [1,2]-shift are present in the molecule (e.g. **373**). This resembles the exceptional cases in which the [1,4]-pathway is

dominant. For instance, Tomooka *et al.* has reported that allylic propargylic ethers, undergo preferential [1,4]-migrations (Schemes 24 and 101).[10]



Scheme 101. Enantio and regioselective [1,4]-Wittig rearrangement of allylic propargylic ether.

The reactivity of compound **369**, which possesses an electron-rich migrating carbon, deserved further comment. Complete conversion took more than 2 hours, as opposed to other substrates that were consumed within 30 minutes. In fact, trifluoromethyl substituted compounds **375** and **377** were consumed in less than 10 minutes. **369** afforded only 40% of [1,4]-Wittig product **387** when the reaction was stopped after 30 minutes, and unreacted material accounted for at least 17%. In the light of our previous studied (Scheme 73, Chapter 4), it was suspected that **369** underwent competitive *ortho* metalation, thus retarding rearrangement. A control experiment, involving only a slight excess of *n*-butyllithium and quenching the reaction early (25 minutes) demonstrated that such *ortho* metalation is not competitive (Scheme 102).

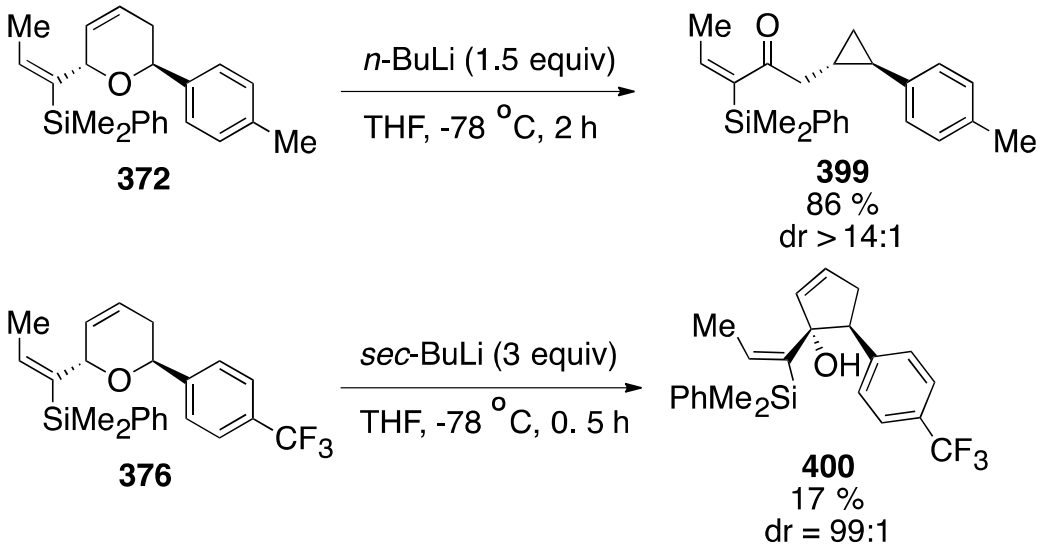


Scheme 102. Deuterium trapping experiment to discard competitive *ortho* metalation in **369**.

Expected deuterium incorporation was observed α to the carbonyl group in compound **387**, but little (<10%) was observed in the aromatic ring, *ortho* to the methoxy group. Also, although **369** was not recovered, isomeric starting material **397** and **398**, fully deuterated at the terminal allylic positions, were isolated. In these compounds no deuteration was detected in the aromatic ring, thus ruling out *ortho* metalation as a possible reason for the slow rearrangement of **369**.

The rearrangement of isomeric compounds **372** and **376**, in which the silyl group is located *proximal* to the bisallylic carbon, was also studied and reflected the electronic trends previously discussed (Scheme 103). A *para* methyl group at the phenyl ring led to exclusive [1,4]-shift providing cyclopropyl enone **399** in excellent yield. On the other hand a *para* trifluoromethyl group led to only 17% on the [1,2]-Wittig product **400**. It is likely that the low yield of **400** is due to the purification procedure involving intrinsically acidic silica gel, which leads to dehydration.

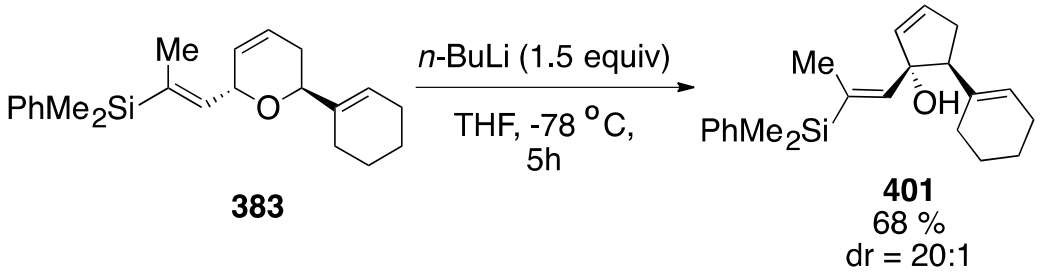
In fact, the fast dehydration of the isomeric alcohol **394** (Table 17) has been observed by ^{1}H NMR.



Scheme 103. Representative Wittig rearrangements of compounds **xxiii**.

6.3.3 Wittig rearrangements of trisallylic ether 383

The rearrangement of compound **383** bearing an alkenyl group instead of an aryl group was studied next. In this case, unselective deprotonation could lead, at least theoretically, to up to 9 Wittig rearrangement pathways involving ring expansion or contraction via [1,2]-, [1,4]-, [2,3]- and [3,4]- shifts. Remarkably, only the previously observed [1,2]-Wittig pathway, resulting from bisallylic deprotonation, is operative (Scheme 104), and afforded bisallylic alcohol **401** in excellent yield and diastereoselectivity. Moreover, the complete [1,2]-selectivity contrasts the exclusive [1,4]-shift of nerol oxide (also a vinylic dihydropyran as **383**), as reported by Rautenstrauch in 1972 (Scheme 68).[11]



383

401
68 %
dr = 20:1

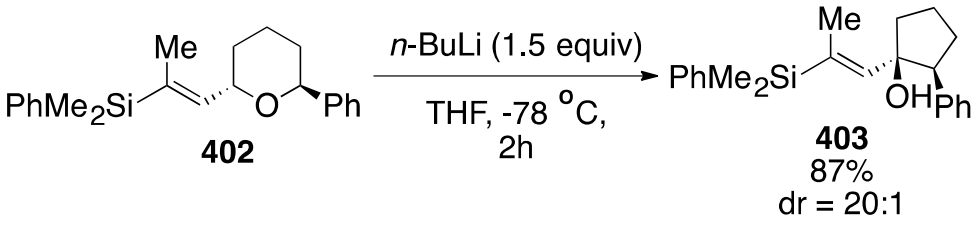
Scheme 104. Regio and stereoselective [1,2]-Wittig rearrangement of trisallylic ether **383**.

In his report, Rautenstrauch suggested that such [1,4]-shift proceeded in a concerted fashion, but no experimental evidence could support his claim.[11] It is interesting that the addition of an exocyclic vinyl group at the allylic position (e.g. **383**) led to such reversal of regioselectivity. It is reasonable to think that such modification significantly stabilized a diradical anion from **383**, whereas in the case of nerol oxide limited radical stabilization, making C-O homolysis difficult, allowed a concerted [1,4]-shift. Another explanation could be associated to the fact that cyclohexenyl fragment, possessing a trisubstituted olefin (doubly substituted proximal to the migrating center), is inhibiting the [1,4]-pathway from taking place. A similar capricious behavior, leading to exclusive [1,2]-shift, has been previously observed in cases where alkyl substitution was proximal at the silyl group in 2-silyl pyrans (Table 9, Chapter 4).

6.3.4 Wittig rearrangements of vinyl tetrahydropyran

Since ring expansion was not observed in any of the bisallylic ethers studied (*vide supra*), it was rationalized that removing the endocyclic olefin not only would shut off a [1,4]- ring contraction, but perhaps allow a [1,4]-ring expansion. Thus, tetrahydropyran **402** was prepared by stereoselective alkynylation of the corresponding 6-phenyl tetrahydropyranose followed by hydrosilylation of the alkyne applying conditions previously described (Table 16).

Regioselective allylic deprotonation of **402** followed by bond reorganization provided [1,2]-Wittig product **403** as the only observed product. Importantly, the stereochemistry of the major diastereomer of **403** was the opposite to that of **392**, **394**, **396**, **400** and **401**, thus showing a "normal" stereochemical course for a [1,2]-Wittig migration. These results are consistent with our observations in the rearrangement of 2-silyl tetrahydropyran **336a** (Scheme 97), which also undergo [1,2]-shift with apparent retention of stereochemistry at the migrating carbon and inversion at the lithium bearing carbon.



Scheme 105. Selective [1,2]-ring contraction of vinyl silane tetrahydropyran **402**.

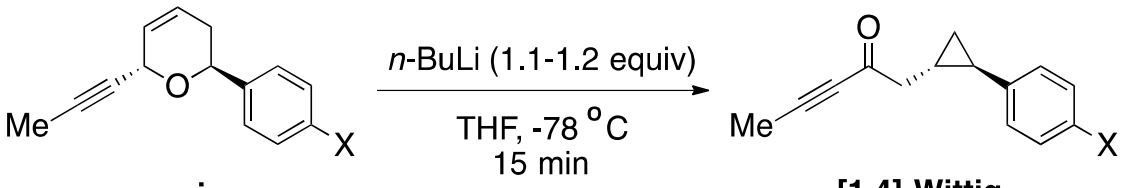
The results presented in this section appear to indicate that a ring expansion via [1,4]-Wittig shift is impossible due to the significant distance between the migrating carbon and the remote sp^2 carbon of the exocyclic vinylsilane. In addition, since the [1,2]-shift is a non-concerted process and is the only operative in this case, it can be inferred that one requirement for a stepwise [1,4]-migration is a close proximity between the migrating and remote allylic carbons.

6.3.5 Wittig rearrangements of silyl-free precursors xxi

Given the precedence of successful [1,4]-selectivity in 3-alkoxy-4-en-1-yne systems (Scheme 24 & 101),[10] it was decided to evaluate alkynes **xxi** (precursors of compounds **xxii**, Table 16), which, in contrast to these previous examples, lack silyl groups. Interestingly, all the enyne

systems studied, bearing representative electronic character at the benzylic carbon: Electron neutral (**258**), electron-rich (**259**) and electron-deficient (**261**) *para* substituents, afforded exclusively the [1,4]-Wittig product in good yields (Table 18), with the exception of **259**, presumably due to competitive *ortho* metalation. These results support the notion that the [1,4]-Wittig pathway is favored predominantly by increasing conjugation *proximal* to the allylic center to be deprotonated, and thus remote silyl substitution does not seem to be critical in determining [1,4]- vs. [1,2]- selectivity (compare Tables 17 & 18). Remarkably, the diastereoselectivity of these rearrangements is very good (>14:1).

Table 18. Selective [1,4]-Wittig rearrangement of enyne systems lacking silicon.



xxi **[1,4]-Wittig**

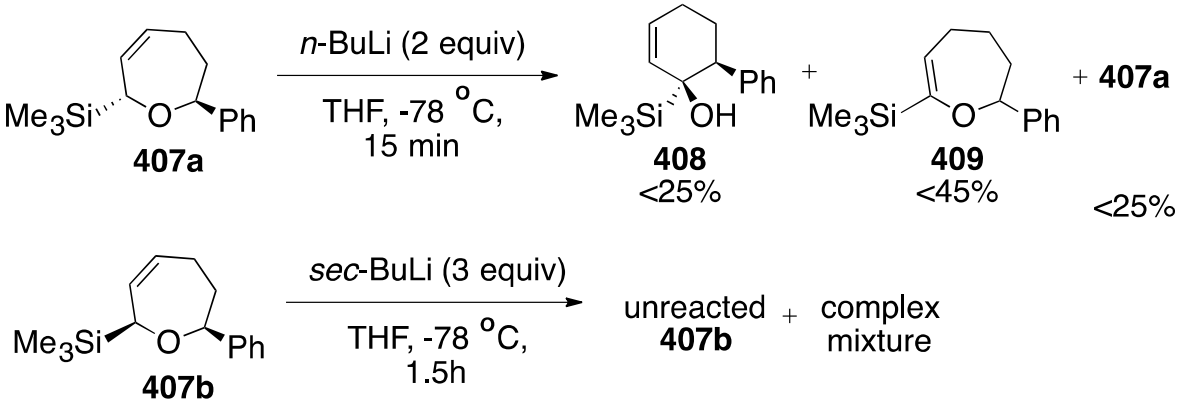
entry	substrate	X	Yield [1,4]-Wittig	dr
1	**258**	H	(**404**) 74%	20:1
2	**259**	MeO	(**405**) 21%	14:1
3	**261**	Cl	(**406**) 93%	20:1

6.4 Behavior of 7-membered and 5-membered cyclic ethers

It was of interest to know whether larger cyclic ethers would also undergo [1,2]- and [1,4]-Wittig rearrangements. No reports of [1,4]-Wittig rearrangements of cyclic ethers exist in the literature, other than that of dihydropyrans described in this document.

6.4.1 Ring contraction of 7-membered cyclic ethers 404a and 404b

7-Membered cyclic ethers showed similar reactivity as model diastereomeric dihydropyrans, *trans* cyclic ether **407a** was more reactive towards deprotonation than *cis* **407b**. In addition, the rearrangement of **407a** was quite slow relative to its dihydropyrans analogue (e.g. **20a**, Chapter 4). When the reaction of **407a** was stopped after 15 minutes, imcomplete conversion was observed (Scheme 106), and unreacted **407a** and isomeric product **409** were isolated, together with only the [1,2]-Wittig product **408**. Interestingly, the stereochemistry of cyclohexenol **408** was determined as *trans*, as opposed to the *cis* relative stereochemistry observed in all [1,2]-Wittig products of 2-silyldihydripyrans (Chapter 4). This assignment was based on NOE signals between the benzylic proton and the trimethylsilyl group. The absence of [1,4]-Wittig products (cyclobutyl acyl silanes), is probably due to the distance between the migrating carbon and remote allylic carbon.

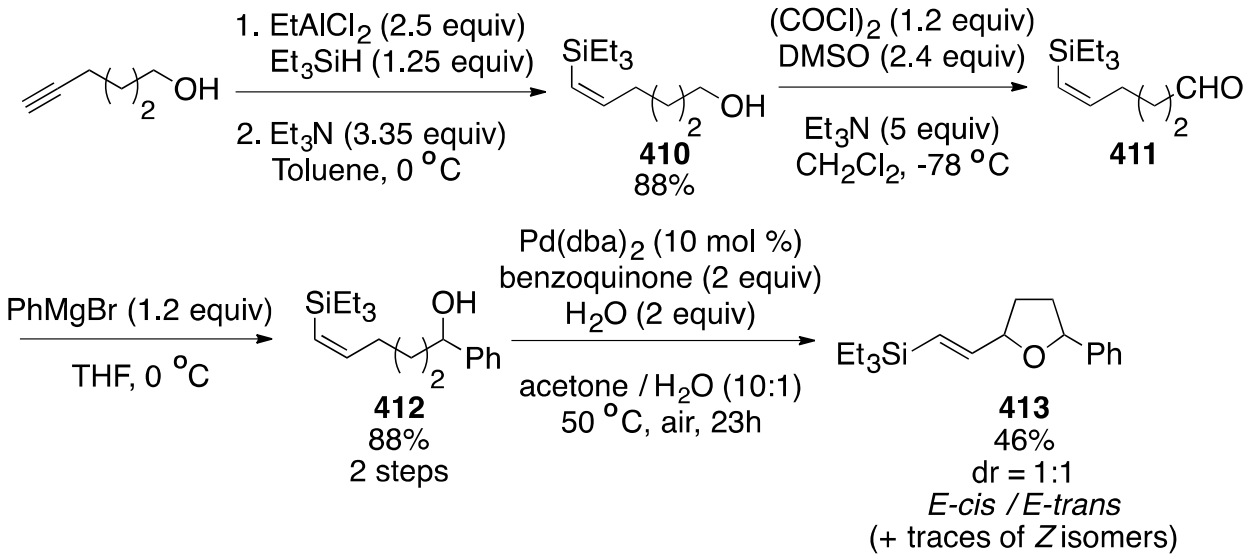


Scheme 106. Behavior of 7-membered cyclic ethers **407a** and **407b**.

6.4.2 Ring contraction of tetrahydrofurans 410a/410b

A model 5-phenyl tetrahydrofuran bearing a vinylsilane group at the 2-position was prepared as shown in Scheme 107. Regioselective *anti* hydrosilylation of 5-hexyn-1-ol gave *Z* vinylsilane

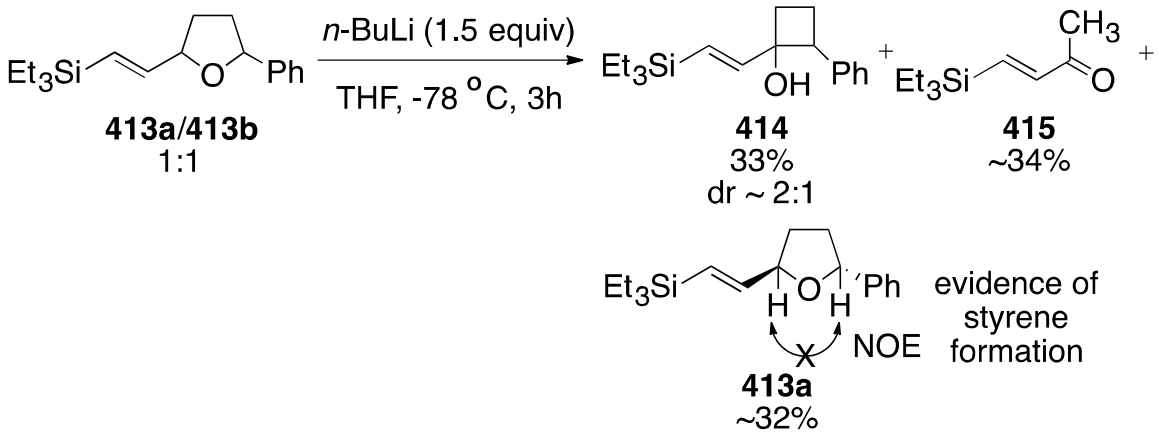
407 and followed Swern oxidation to aldehyde **408**. Grignard addition afforded alcohol **409** in good yield over two steps. Palladium-catalyzed oxidative cyclization employing Stambuli's conditions[12] afforded diastereomeric tetrahydrofuran **413** bearing a *E* vinylsilane, however traces of geometrical isomers were detected as minor impurities.



Scheme 107. Synthesis of diastereomeric tetrahydrofuryl vinyl silane **413**.

The diastereomeric mixture was studied, however, the relative stereochemistry in each **413a** and **413b** (*trans* and *cis*, respectively) was independently confirmed by NOE studies. Reaction of a 1:1 diastereomeric mixture of **413a** and **413b** with *n*-butyllithium (1.5 equiv) afforded, after 3 hours at -78 ºC, 30% of [1,2]-Wittig product **414** in low diastereomeric ratio (2:1), together with unreacted *trans* diastereomer **413a** in ~32% yield. Although the diastereomeric ratio is low, it suggests a certain degree of stereoconvergence towards the major [1,2]-product, whose relative stereochemistry has not been determined. Significant amounts of enone **415** were detected, along with styrene formation by ^{1}H NMR. These eliminations products are an expected consequence of a well-known side reaction typical of the related THF solvent with alkyllithiums. Importantly,

the less reactive diastereomer was the *trans*, which was recovered in about ~32%. Consistent with previous results (Section 6.2), no ring expansion via [1,4]-Wittig shift took place, presumably because of the vinylsilane group is oriented far from the migrating (benzylic) carbon.



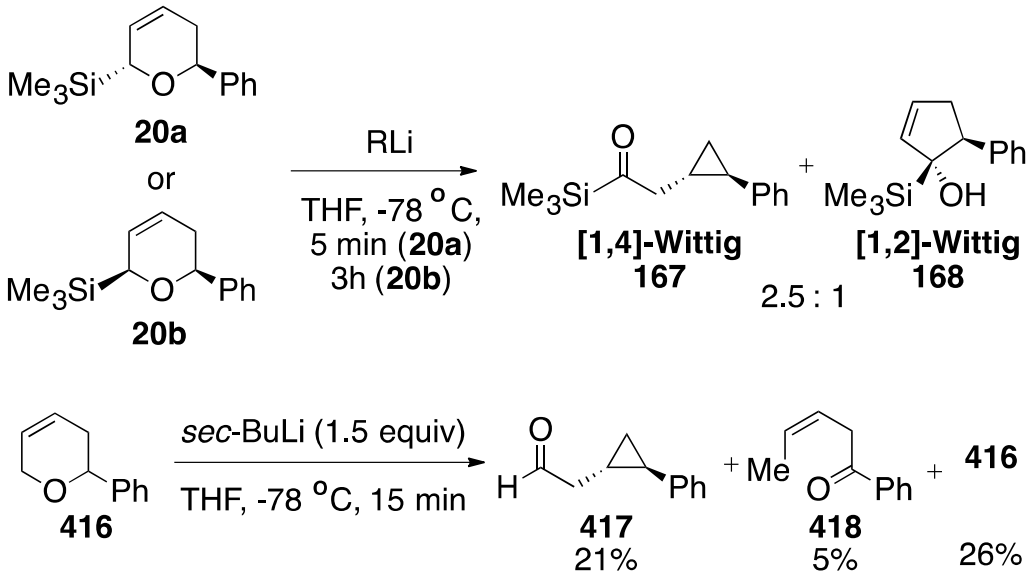
Scheme 108. [1,2]-Wittig rearrangement of tetrahydrofuran **413a**/**413b**.

6.5 Wittig rearrangements of carbon analogues

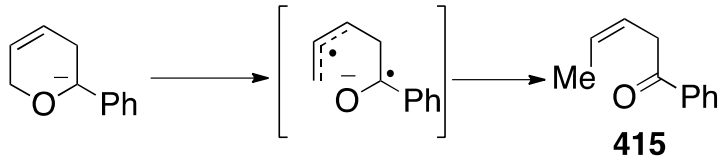
Up to this point only the Wittig rearrangements of silicon-containing cyclic ethers have been discussed. It was important to explore the reactivity of desilylated or carbon-substituted analogues to compare with our results and have a better understanding of the true effect of the silyl group in these rearrangements.

For example 6-phenyl-5,6-dihydropyran **416** afforded exclusively the [1,4]-Wittig product (**417**) accompanied by known ketone **418** as the minor identifiable product (Scheme 109). The low yields are presumably due to partial decomposition during purification in silica gel, and/or due to the expected volatility of these compounds. Ketone **418** could be formed by benzylic deprotonation followed by elimination, however the excess alkyllithium should have reacted

with the ketone. A more likely process is that the allylic anion from **416** undergoes C-O bond homolysis to a diradical anion species that fails to recombine intramolecularly (Scheme 110).



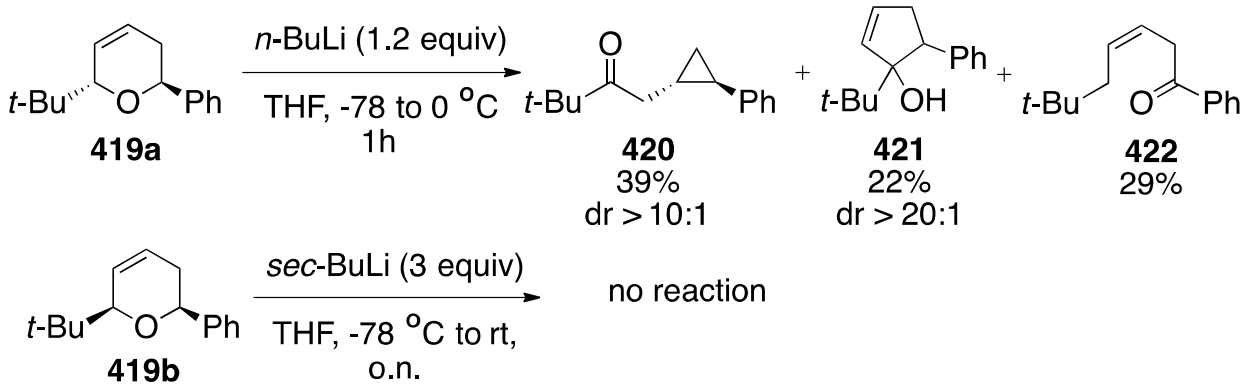
Scheme 109. Wittig rearrangement of **416**, desilylated analogue of **20a**/**20b** and **294**-**297**.



Scheme 110. Possible pathway giving rise to **418**.

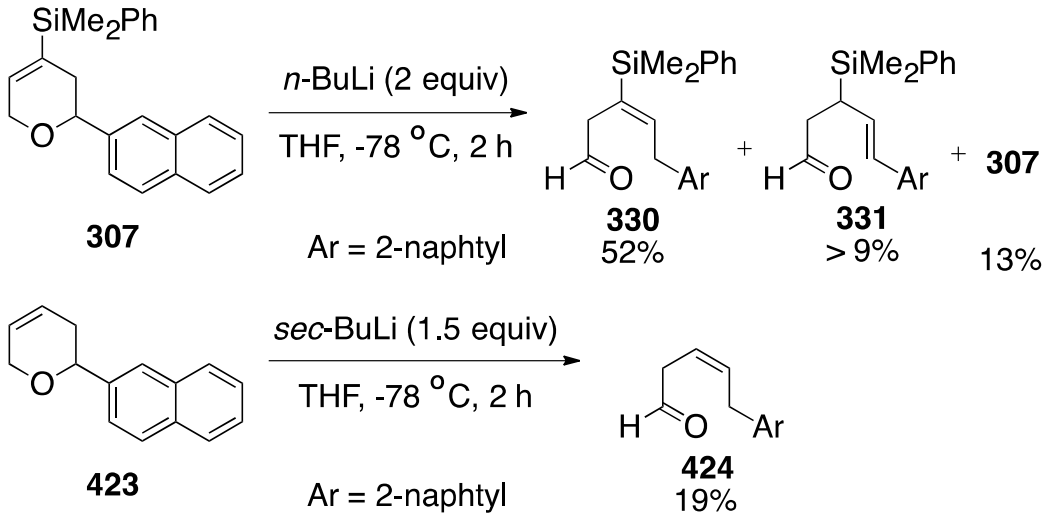
We also studied the rearrangement of carbon analogues of **20a**/**20b**, that is, diastereomeric 2-*t*-butyl substituted compound **419** (Scheme 111) The *trans* diastereomer **419a** was unreactive at -78 °C and it was necessary to increase the temperature to 0 °C. Interestingly, in this case the [1,4]- and [1,2]-Wittig products **420** and **421** were obtained in a 1.8:1 ratio (combined 61% yield) accompanied by ketone **422** in 29% yield. The relative stereochemistry of the [1,2]-product could not be determined, but the *Z* geometry of the olefin in **422** was confirmed by NOE.

The formation of **422** resembles that of **315** and is also diagnostic of a competitive elimination, which is absent in the case of **20a**/**20b** or **294**-**297**. Interestingly, the ratio of [1,4]- and [1,2]-Wittig products roughly matches that observed in the rearrangement of **20a**/**20b** (2.5:1) but not that of **416**. This suggests that the steric demand of the silyl group is actually detrimental for the [1,4]-/[1,2]-selectivity. However, the presence of silyl group increases the acidity of the allylic protons, relative to the unsubstituted (**416**) and carbon substituted analogue (**419a**/**419b**). Once again, it was demonstrated that the relative stereochemistry determines the reactivity. For example *cis* diastereomer **419b** was completely unreactive even at room temperature.



Scheme 111. Wittig rearrangements of *t*-butyl substituted dihydropyrans **419a**/**419b**.

In Chapter 5 it was observed that 2-naphtyl substituted 4-silyl dihydropyran **307** underwent ring opening to aldehydes **330** and **331** (Scheme 93). It was tempting to assume that the steric demand of the bulky silyl group and 2-naphtyl groups prevented [1,4]-recombination, but the absence of [1,2]-Wittig products did not support this idea. For this reason the desilylated analogue **423** was prepared and submitted to rearrangement conditions. Surprisingly, no Wittig rearrangement products could be isolated, and only aldehyde **424**, analogue of **330**, could be obtained (Scheme 112).



Scheme 112. Wittig rearrangements of 2-naphtyl substituted pyran **423**.

6.6 Conclusions

In conclusion, no stereoconvergence in the rearrangement of silyl tetrahydropyrans could be observed due to the lack of reactivity of the *cis* substrate. Whereas the *trans* isomer provided the 'normal' [1,2]-Wittig product in which inversion of stereochemistry at the lithium-bearing carbon and retention at the benzylic carbon took place. However, the lack of reactivity towards deprotonation α- to silicon, relative to their dihydropyran counterpars, leads to competitive benzylic deprotonation to a great extent. This serious problem in tetrahydropyrans can by alleviated by placing an exocyclic olefin at the α-position, allowing smooth allylic deprotonation. Unfortunately, no [1,4]-Wittig rearrangements via ring expansion, involving this exocyclic olefin, have been observed in any studied case.

Bisallylic cyclic ethers, that is, 5,6-dihydropyrans bearing a vinyl group at the 2-position, undergo preferential [1,4]-Wittig rearrangement, although the electronic effects previously observed determine the regioselectivity in most cases: Electron-rich migrating carbons prefer

[1,4]-migration whereas electron-deficient migrating centers migrate via a [1,2]-shift. A bisallylic cyclic ether bearing an alkenyl group at the migrating carbon undergo exclusive [1,2]-Wittig rearrangement. At this point, this selectivity is not well understood when compared with the rearrangement of aryl-substituted analogues, but it seems that the weakly electron-deficient nature of the alkenyl group leads to such selectivity.

Results from silylated and non-silylated analogues seem to indicate that the silicon group has an important electronic effect in these rearrangements by allowing 1) a clean and selective deprotonation step and 2) efficient rearrangements, minimizing other side reactions that are significantly competitive in non-silylated analogues. In addition, the [1,4]-/[1,2] selectivity appears to be influenced only by the sterics of the silyl group, and little or no electronic contribution has been clearly observed in this regard. Also, the outcome of the reactions is dominated by the electronic properties of the migrating carbon, and therefore, by the substituent at this position.

6.7 Experimental section

*Wittig rearrangements of **336a** – General Procedure A*

A solution of **336a** (48 mg, 0.205 mmol, 1 equiv) in THF (2.7 mL) was cooled down at –78 ^{o}C and *n*-butyllithium (1.6 M in hexanes, 0.38 mL, 0.614 mmol, 3 equiv) was added slowly via syringe. The reaction was kept at -78 ^{o}C (or indicated temperature). After 2.5 hours (or indicated reaction time) the reaction was quenched at -78 ^{o}C by adding $NH_4Cl_{(sat)}$ and diluted with Et_2O (~10 mL) and water (~2 mL). The aqueous phase was extracted with Et_2O (3 × 5 mL).

Combined Et_2O. Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (3%, 4% and 8% EtOAc in hexanes) afforded 1.6 mg (3%) of compound **337**, 23 mg (48%) of compound **338** and 7.2 mg of compound **339**, all as colorless oils. Spectroscopic data for **337**:

Spectroscopic data for **338**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.30 (m, 2 H), 7.19 (m, 1 H), 2.09 (m, 1 H), 2.04–1.83 (m, 6 H), 1.47 (t, *J* = 10.0 Hz, 1 H), 1.44 (s, 1 H), -0.16 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 127.8 (2 C), 126.1, 124.8 (2 C), 86.4, 47.6, 42.0, 27.7, 24.8, -1.1. Spectroscopic data for **339**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 4 H), 7.25 (m, 1 H), 6.02 (dt, *J* = 6.0, 18.5 Hz, 1 H), 5.67 (dt, *J* = 1.5, 18.5 Hz, 1 H), 4.67 (m, 1 H), 2.15 (m, 2 H), 1.92 (m, 1 H), 1.82 (m, 1 H), 0.02 (s, 9 H).

Preparation of Danishefsky's diene[13]

Following a reported procedure,[13b] a dry pre-weighted round-bottom flask was charged with $ZnCl_2$ and then flame-dried dried under nitrogen (120 mg of $ZnCl_2$, 0.87 mmol, 0.03 equiv). Triethylamine (8.9 mL, 63.7 mmol, 2.2 equiv) was added and the mixture was stirred for 2 hours at room temperature to give a white suspension. 4-methoxy-3-buten-2-one (2.9 g, 28.97 mmol, 1 equiv) was added as a solution in benzene (15 mL) and then freshly distilled TMSCl (7.35 mL, 57.93 mmol, 2 equiv) was added dropwise via syringe, over a period of 30 minutes. The mixture was heated in an oil bath at 40 ^{o}C for 24 hours. The reaction was cooled down at room temperature and Et_2O (150 mL) was added. The resulting mixture was filtered through a short

alumina plug. The filtrate was concentrated to give 5.4 g of the crude diene (87%) as a deep red oil which was used in the next step without further purification.

Preparation of dihydropyranones – General Procedure B

Following a reported procedure,[14] to a solution of Danishefsky diene (1 g, 5.8 mmol, 1 equiv) and benzaldehyde (0.65 mL, 6.38 mmol, 1.1 equiv) in CH_2Cl_2 (60 mL) at -78 ^oC was added BF_3•OEt_2 (0.73 mL, 5.8 mmol, 1 equiv) dropwise with stirring. The temperature was slowly raised to -40 ^oC (~2 hours) and then quenched with $NaHCO_{3\ (sat)}$ (10 mL). The mixture was left to reach room temperature and poured into a 3:1 mixture of CH_2Cl_2 / $NaHCO_{3\ (sat)}$ (300 mL). The aquous phase was extracted with CH_2Cl_2. Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated to ~100 mL. Trifluoroacetic acid (1.1 equiv) was added dropwise and the resulting solution stirred at room temperature for 1 hour. The reaction was quenched by adding $NaHCO_{3\ (sat)}$ (20 mL). The aquous phase was extracted with CH_2Cl_2. Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (Et_2O/hexanes 1:1) afforded 650 mg (64 %) of 2-phenyl-2,3-dihydro-*4H*-pyran-4-one as a colorless oil.

Preparation of 2-(p-methoxyphenyl)-2,3-dihydro-4H-pyran-4-one

Following the general procedure B, the title compound was prepared in 53% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 0.5, 6.0 Hz, 1 H), 7.31 (m, 2 H), 6.92 (m, 2 H), 5.48 (dd, *J* =

1.5, 6.0 Hz, 1 H), 5.35 (dd, *J* = 3.5, 14.5 Hz, 1 H), 3.81 (s, 3 H), 2.90 (dd, A of ABX system, *J* = 14.5, 16.0 Hz, 1 H), 2.60 (ddd, B of ABX system, *J* = 1.5, 3.5, 17.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.3, 163.2, 160.1, 129.8, 127.7 (2 C), 114.2 (2 C), 107.3, 80.9, 55.3, 43.2. IR (film) 3069, 2963, 1676, 1595, 1518, 1253 1035 cm^{-1}.

Preparation of 2-(p-methylphenyl)-2,3-dihydro-4H-pyran-4-one

Following the general procedure B, the title compound was prepared in 71% yield.

Preparation of 2-(p-chlorophenyl)-2,3-dihydro-4H-pyran-4-one

Following the general procedure B, the title compound was prepared in 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.0 Hz, 1 H), 7.37 (m, 2 H), 7.32 (m, 2 H), 5.51 (dd, *J* = 1.0, 6.0 Hz, 1 H), 5.38 (dd, *J* = 3.5, 14.0 Hz, 1 H), 2.83 (dd, A of ABX system, *J* = 14.0, 16.5 Hz, 1 H), 2.62 (ddd, B of ABX system, *J* = 1.5, 3.5, 16.5 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 162.9, 136.4, 134.8, 129.0 (2 C), 127.4 (2 C), 107.5, 80.3, 43.3. IR (film) 3068, 2913, 1684, 1595, 1271 cm^{-1}.

Preparation of 2-(p-trifluoromethylphenyl)-2,3-dihydro-4H-pyran-4-one

Following the general procedure B, the title compound was prepared in 64% yield.

Preparation of 2-(m-chlorophenyl)-2,3-dihydro-4H-pyran-4-one

Following the general procedure B, the title compound was prepared in 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1 H), 7.63 (m, 1 H), 7.54 (m, 2 H), 7.48 (d, *J* = 6.0 Hz, 1 H), 5.54 (d, *J* = 6.0 Hz, 1 H), 5.47 (dd, *J* = 3.5, 14.0 Hz, 1 H), 2.85 (dd, A of ABX system, *J* = 14.5, 16.5 Hz, 1 H), 2.67 (ddd, B of ABX system, *J* = 1.0, 3.5, 16.5 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 162.8, 139.0, 131.3 (q, *J* = 32.8 Hz), 129.4, 129.2 (d, *J* = 1.4 Hz), 125.6 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 273.2 Hz), 122.8 (q, *J* = 4.0 Hz), 107.7, 80.2, 43.4. IR (film) 3069, 2983, 1690, 1320 cm^{-1}.

Preparation of 2-(m-nitrophenyl)-2,3-dihydro-4H-pyran-4-one

Following the general procedure B, the title compound was prepared in 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (m, 1 H), 8.23 (m, 1 H), 7.70 (m, 1 H), 7.61 (t, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 6.0 Hz, 1 H), 5.56 (d, *J* = 6.0 Hz, 1 H), 5.52 (dd, *J* = 4.0, 14.5 Hz, 1 H), 2.86 (dd, A of ABX system, *J* = 14.0, 16.5 Hz, 1 H), 2.72 (dd, B of ABX system, *J* = 4.0, 17.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 162.5, 148.6, 140.1, 131.8, 130.0, 123.7, 121.1, 107.9, 79.6, 43.3. IR (film) 3090, 1676, 1597, 1529, 1348 1271 cm^{-1}.

Preparation of 2-(2'-styryl)-2,3-dihydro-4H-pyran-4-one

Following the general procedure B, the title compound was prepared in 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (m, 1 H), 7.38 (m, 2 H), 7.33 (m, 2 H), 7.27 (m, 1 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 6.28 (dd, *J* = 6.5, 16.0 Hz, 1 H), 5.45 (dd, *J* = 1.0, 6.5 Hz, 1 H), 5.05 (m, 1 H), 2.72

(dd, A of ABX system, *J* = 13.0, 16.5 Hz, 1 H), 2.60 (ddd, B of ABX system, *J* = 1.0, 4.0, 17.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 162.9, 135.5, 133.7, 128.7 (2 C), 128.5, 126.7 (2 C), 125.0, 107.3, 79.7, 41.9. IR (film) 3057, 2925, 1674, 1594, 1267 1037 cm^{-1}.

Preparation of 2-(1'-cyclohexenyl)-2,3-dihydro-4H-pyran-4-one

Following the general procedure B, the title compound was prepared in 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.0 Hz, 1 H), 5.81 (m, 1 H), 5.38 (dd, *J* = 1.0, 6.0 Hz, 1 H), 4.69 (dd, *J* = 3.5, 14.5 Hz, 1 H), 2.72 (dd, A of ABX system, *J* = 14.5, 17.0 Hz, 1 H), 2.38 (ddd, B of ABX system, *J* = 1.5, 3.5, 17.0 Hz, 1 H), 2.05 (m, 4 H), 1.73–1.59 (m, 3 H), 1.55 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 163.4, 145.5, 134.3, 127.1, 106.9, 83.4, 40.3, 24.9, 24.0, 22.2, 22.0. IR (film) 3060, 2930, 1676, 1595, 1269, 1221, 1037 cm^{-1}.

*Preparation of alcohols **xix** – General Procedure C*

To a solution of 6-phenyl dihydropyran-4-one (637 mg, 3.66 mmol, 1 equiv) in CH_2Cl_2/EtOH (2:1, 42 mL) was added $CeCl_3 7H_2O$ (1.36g, 3.66 mmol, 1 equiv) and the mixture was cooled at -78 ^oC. A solution of $NaBH_4$ (166 mg, 4.39 mmol, 1.2 equiv) in EtOH (14 mL) was added over a period of 40 minutes (syringe pump), and then the mixture was stirred at that temperature for an additional 1.6 hours. The temperature was raised to 0 ^oC and the reaction mixture poured into a mixture of EtOAc/Et_2O/$NaHCO_{3\,(sat)}$ (1:1:1, 300 mL). The aqueous phase was extracted with Et_2O. Combined organic extracts were washed with $NaHCO_3$, brine, dried over $MgSO_4$ and

concentrated. Column chromatography (EtOAc/hexanes 1:1) afforded 621 mg (97%) of the corresponding alcohol as a yellowish oil. Spectroscopic data for **340**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 7.30 (m, 1 H), 6.51 (dd, *J* = 0.6, 6.6 Hz, 1 H), 4.98 (dd, *J* = 2.4, 12.0 Hz, 1 H), 4.85 (dt, *J* = 1.8, 6.0 Hz, 1 H), 4.59 (m, 1 H), 2.37 (m, 1 H), 1.99 (ddd, *J* = 9.0, 11.4, 13.2 Hz, 1 H), 1.33 (d, *J* = 7.8 Hz, 1 H).

*Preparation of compound **341***

Following the general procedure C, the title compound was prepared in >83% crude yield and was used in the next step without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (m, 2 H), 6.88 (m, 2 H), 6.48 (d, *J* = 6.6 Hz, 1 H), 4.92 (dd, *J* = 1.8, 11.4 Hz, 1 H), 4.83 (dt, *J* = 1.8, 6.6 Hz, 1 H), 4.58 (m, 1 H), 3.79 (s, 3 H), 2.33 (m, A of ABX system, 1 H), 1.99 (ddd, B of ABX system, *J* = 9.6, 12.0, 13.2 Hz, 1 H), 1.38 (d, *J* = 7.8 Hz, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 145.5, 132.4, 127.4 (2 C), 114.0 (2 C), 105.6, 76.5, 63.3, 55.3, 39.8. IR (film) 3400, 3064, 2926, 1645, 1516, 1234, 1033 cm^{-1}.

*Preparation of compound **342***

Following the general procedure C, the title compound was prepared in 99% crude yield and was used in the next step without further purification. . ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 2 H), 7.16 (d, *J* = 7.8 Hz, 2 H), 6.49 (d, *J* = 6.0 Hz, 1 H), 4.94 (dd, *J* = 1.8, 11.4 Hz, 1 H), 4.83 (dt, *J* = 2.4, 6.6 Hz, 1 H), 4.58 (m, 1 H), 2.36 (m, 1 H), 2.33 (s, 3 H), 1.98 (m, 1 H), 1.37 (s, 1 H).

*Preparation of compound **343***

Following the general procedure C, the title compound was prepared in >85% crude yield and was used in the next step without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (m, 2 H), 7.28 (m, 2 H), 6.48 (dd, *J* = 0.6, 6.0 Hz, 1 H), 4.94 (dd, *J* = 1.8, 11.4 Hz, 1 H), 4.84 (dt, *J* = 1.8, 6.6 Hz, 1 H), 4.57 (m, 1 H), 2.33 (m, A of ABX system 1 H), 1.92 (ddd, B of ABX system, *J* = 9.6, 12.0, 13.2 Hz, 1 H), 1.52 (s, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.2, 138.8, 133.7, 128.7 (2 C), 127.3 (2 C), 105.9, 76.1, 63.3, 39.9. IR (film) 3366, 3063, 2924, 1645, 1495, 1234 cm^{-1}.

*Preparation of compound **344***

Following the general procedure C, the title compound was prepared in 99% crude yield and was used in the next step without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 6.51 (d, *J* = 6.6 Hz, 1 H), 5.03 (d, *J* = 11.4 Hz, 1 H), 4.88 (dt, *J* = 1.8, 6.0 Hz, 1 H), 4.60 (m, 1 H), 2.38 (m, 1 H), 1.94 (dd, *J* = 9.0, 11.4, 13.2 Hz, 1 H), 1.37 (d, *J* = 7.2 Hz, 1 H).

*Preparation of compound **345***

Following the general procedure C, the title compound was prepared in >85% crude yield and was used in the next step without further purification. ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 141.4, 130.9 (*J* = 32.3 Hz), 129.2, 129.0, 124.8 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.4 Hz), 122.8 (q, *J* = 3.8 Hz), 106.0, 76.1, 63.3, 40.0. IR (film) 3364, 3068, 2926, 1647, 1329, 1126 cm^{-1}.

*Preparation of compound **346***

Following the general procedure C, the title compound was prepared in >96% crude yield and was used in the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (m, 1 H), 8.16 (ddd, *J* = 1.0, 2.0, 8.0 Hz, 1 H), 7.68 (m, 1 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 6.52 (dd, *J* = 1.0, 6.5 Hz, 1 H), 5.08 (dd, *J* = 2.0, 12.0 Hz, 1 H), 4.90 (dt, *J* = 2.0, 6.0 Hz, 1 H), 4.63 (m, 1 H), 2.42 (m, A of ABX system, 1 H), 1.95 (ddd, B of ABX system, *J* = 4.0, 12.0, 13.5 Hz, 1 H), 1.38 (d, *J* = 7.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 144.9, 142.6, 131.9, 129.6, 123.0, 121.0, 106.2, 75.6, 63.1, 39.9. IR (film) 3391, 3101, 2924, 1647, 1533, 1340, 1238, 1041 cm^{-1}.

*Preparation of compound **347***

Following the general procedure C, the title compound was prepared in >83% crude yield and was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2 H), 7.31 (t, *J* = 7.5 Hz, 2 H), 7.24 (m, 1 H), 6.64 (d, *J* = 16.0 Hz, 1 H), 6.44 (d, *J* = 11.5 Hz, 1 H), 6.25 (dd, *J* = 6.0, 16.0 Hz, 1 H), 4.83 (m, 1 H), 4.64 (m, 1 H), 4.46 (m, A of ABX system, 1 H), 2.30 (m, B of ABX system, *J* = 8.0, 10.0, 14.0 Hz, 1 H), 1.51 (s, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 136.3, 131.4, 128.6 (2 C), 127.91, 127.89, 126.6 (2 C), 105.4, 74.9, 62.5, 38.1. IR (film) 3362, 3057, 2924, 1643, 1232 1028 cm^{-1}.

*Preparation of compound **348***

Following the general procedure C, the title compound was prepared in 97% yield and was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 (m, 1 H), 5.74 (m, 1 H), 4.73 (dt, *J* = 2.5, 6.5 Hz, 1 H), 4.44 (q, *J* = 7.5 Hz, 1 H), 4.26 (d, *J* = 11.5 Hz, 1 H), 2.11 (m, 1 H), 2.03 (m, 3 H), 1.95 (m, 1 H), 1.82 (ddd, *J* = 9.5, 11.5, 12.5 Hz, 1 H), 1.69–1.51 (m, 4 H), 1.48 (d, *J* = 7.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 136.3, 124.8, 105.2, 78.8, 63.5, 36.5, 24.9, 24.1, 22.5, 22.3. IR (film) 3375, 3058, 2928, 1645, 1228 1032 cm^{-1}.

*Preparation of acetates **xx** – General Procedure D*

*Preparation of acetate **349***

To a solution of alcohol **340** (618 mg, 3.51 mmol, 1 equiv) in CH_2Cl_2 (100 mL) was added triethyl amine (5.2 mL, 37.1 mmol, 10.6 equiv), acetic anhydride (1.06 g, 11.22 mmol 3.2 equiv) and a few crystals of DMAP (catalyst). The reaction was followed by TLC. After completion of the reaction the mixture was concentrated and the product purified by column chromatography (20% EtOAc in hexanes) to afford 723 mg (95%) of acetate **349** as a colorless oil. Spectroscopic data for **332**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.29 (m, 1 H), 6.58 (d, *J* = 6.0 Hz, 1 H), 5.55 (m, 1 H), 5.01 (dd, *J* = 2.4, 12.0 Hz, 1 H), 4.82 (dt, *J* = 1.8, 6.6 Hz, 1 H), 2.45 (ddt, *J* = 1.8, 6.6, 13.2 Hz, 1 H), 2.04 (ddd, *J* = 9.6, 12.0, 13.2 Hz, 1 H), 2.00 (s, 3 H).

*Preparation of compound **350***

Applying the general procedure D to crude alcohol **341**, the title compound was prepared in 83% yield (2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2 H), 6.88 (m, 2 H), 6.55 (d, *J* = 6.0 Hz,

1 H), 5.54 (m, 1 H), 4.94 (d, *J* = 1.5, 12.0 Hz, 1 H), 4.79 (dt, *J* = 2.0, 6.5 Hz, 1 H), 3.79 (s, 3 H), 2.41 (m, 1 H), 2.03 (m, 1 H), 2.02 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 159.5, 147.0, 132.1, 127.4 (2 C), 113.9 (2 C), 101.4, 76.4, 66.3, 55.3, 35.4, 21.2. IR (film) 3068, 2934, 1734, 1232, 1035 cm^{-1}. HRMS

*Preparation of compound **351***

Applying the general procedure D to alcohol **342**, the title compound was prepared in 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.8 Hz, 2 H), 7.16 (d, *J* = 7.8 Hz, 2 H), 6.57 (dd, *J* = 0.6, 6.0 Hz, 1 H), 5.55 (m, 1 H), 4.97 (dd, *J* = 2.4, 12.6 Hz, 1 H), 4.81 (dt, *J* = 1.8, 6.6 Hz, 1 H), 2.43 (m, 1 H), 2.34 (s, 3 H), 2.04 (m, 1 H), 2.01 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 146.9, 137.8, 137.0, 129.1 (2 C), 125.9 (2 C), 101.3, 76.5, 66.2, 35.4, 21.14, 21.09. IR (film) 3030, 2928, 1734, 1647, 1232, 1032 cm^{-1}.

*Preparation of compound **352***

Applying the general procedure D to crude alcohol **343**, the title compound was prepared in 85% yield (2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2 H), 7.27 (d, *J* = 8.5 Hz, 2 H), 6.56 (d, *J* = 6.0 Hz, 1 H), 5.52 (m, 1 H), 4.98 (dd, *J* = 1.5, 11.5 Hz, 1 H), 4.82 (dt, *J* = 1.5, 6.0 Hz, 1 H), 2.42 (m, 1 H), 2.00 (s, 3 H), 1.97 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 146.7, 138.6, 133.8, 128.7 (2C), 127.3 (2C), 101.6, 75.8, 65.8, 35.5, 21.1. IR (film) 3073, 2929, 1734, 1653, 1232, 1032 cm^{-1}.

*Preparation of compound **353***

Applying the general procedure D to alcohol **344**, the title compound was prepared in 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 6.58 (dd, *J* = 0.6, 6.0 Hz, 1 H), 5.52 (m, 1 H), 5.08 (dd, *J* = 2.4, 12.0 Hz, 1 H), 4.85 (dt, *J* = 1.8, 6.6 Hz, 1 H), 2.46 (ddt, *J* = 2.4, 6.6, 13.2 Hz, 1 H), 2.00 (ddd, *J* = 9.0, 11.4, 13.8 Hz, 1 H), 1.96 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 146.5, 144.1 (d, *J* = 1.4 Hz), 130.1 (q, *J* = 32.3 Hz), 126.1 (2 C), 125.4 (q, *J* = 3.8 Hz, 2 C), 124.0 (q, *J* = 272.4 Hz), 101.7, 75.6, 65.4, 35.4, 21.0. IR (film) 3072, 2936, 1734, 1647, 1327, 1236, 1127 cm^{-1}.

*Preparation of compound **354***

Applying the general procedure D to crude alcohol **345**, the title compound was prepared in 85% yield (2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1 H), 7.55 (d, *J* = 7.5 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 6.59 (dd, *J* = 0.5, 6.0 Hz, 1 H), 5.53 (m, 1 H), 5.08 (dd, *J* = 2.0, 11.5 Hz, 1 H), 4.86 (dt, *J* = 1.5, 6.0 Hz, 1 H), 2.48 (ddt, *J* = 2.0, 6.5, 13.5 Hz, 1 H), 2.02 (ddd, *J* = 9.0, 11.5, 13.5 Hz, 1 H), 1.98 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 146.6, 141.2, 131.0 (q, *J* = 32.3 Hz), 129.2 (d, *J* = 1.4 Hz), 129.0, 124.8 (q, *J* = 3.5 Hz), 124.0 (q, *J* = 272.8 Hz), 122.7 (q, *J* = 4.0 Hz), 101.8, 75.6, 65.5, 35.4, 21.1. IR (film) 3073, 2934, 1734, 1647, 1329, 1234, 1126 cm^{-1}.

*Preparation of compound **355***

Applying the general procedure D to crude alcohol **346**, the title compound was prepared in 96% yield (2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (m, 1 H), 8.15 (m, 1 H), 7.66 (m, 1 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 6.59 (d, *J* = 7.0 Hz, 1 H), 5.53 (m, 1 H), 5.13 (dd, *J* = 2.0, 11.5 Hz, 1 H), 4.88 (m, 1 H), 2.51 (m, 1 H), 2.02 (m, 1 H), 1.97 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 148.4, 146.3, 142.3, 131.9, 129.5, 122.9, 121.0, 101.9, 75.0, 65.2, 35.3, 21.1.

*Preparation of compound **356***

Applying the general procedure D to crude alcohol **347**, the title compound was prepared in 79% yield (2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 2 H), 7.31 (m, 2 H), 7.24 (m, 1 H), 6.63 (d, *J* = 16.0 Hz, 1 H), 6.51 (dd, *J* = 1.0, 6.0 Hz, 1 H), 6.28 (dd, *J* = 6.5, 16.0 Hz, 1 H), 5.43 (dddd, *J* = 1.0, 2.5, 6.0, 8.0 Hz, 1 H), 4.81 (ddd, *J* = 1.5, 2.5, 6.0 Hz, 1 H), 4.66 (m, 1 H), 2.38 (dddd, A of ABX system, *J* = 1.5, 2.5, 6.0, 13.0 Hz, 1 H), 2.03 (s, 3 H), 1.90 (ddd, B ox ABX system, *J* = 8.5, 10.5, 13.5 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 146.5, 136.4, 131.8, 128.6 (2 C), 127.9, 127.5, 126.6 (2 C), 101.0, 74.8, 65.0, 33.8, 21.2. IR (film) 3063, 2929, 1734, 1645, 1232, 1028 cm^{-1}.

*Preparation of compound **357***

Applying the general procedure D to alcohol **348**, the title compound was prepared in 99% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (d, *J* = 6.0 Hz, 1 H), 5.79 (s, 1 H), 5.46 (m, 1 H), 4.72 (dt, *J* = 2.0, 6.5 Hz, 1 H), 4.31 (d, *J* = 12.0 Hz, 1 H), 2.24 (m, A of ABX system, 1 H), 2.06 (s, 3 H),

2.22–1.96 (m, 4 H), 1.89 (dt, B of ABX system, J = 9.5, 12.5 Hz, 1 H), 1.70–1.53 (m, 4 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 146.9, 135.9, 125.3, 101.0, 78.8, 66.4, 32.2, 24.9, 23.9, 22.4, 22.3, 21.3. IR (film) 3068, 2832, 1734, 1645, 1230, 1032 cm^{-1}.

*Preparation of enynes **xxi** – General Procedure E*

*Preparation of compound **358***

n-Butyllithium (4.1 mL, 6.54 mmol, 4.3 equiv) was added to a round bottom flask containing dry pentane (5 mL) and the solution was cooled down at -78 ^{o}C. The solution was bubbled with propyne (excess) via a needle for about 3 minutes, and a white precipitate quickly formed. The cold bath was removed and the mixture left to reach room temperature. Under vigorous stirring, dimethylaluminum chloride (1M in hexane, 6.1 mL, 4 equiv) was added via syringe. After 2 hours at room temperature, the white suspension was cooled down at 0 ^{o}C and acetate **349** (332 mg, 2.35 mmol, 1 equiv) was added as a solution in CH_2Cl_2 (3 mL). The white suspension turned yellow immediately. The reaction was followed by TLC (5% EtOAc in hexanes). The reaction was then carefully quenched by adding water and diluted with CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2. Combined organic extracts were washed with brine and dried over $MgSO_4$. After concentration the residue was purified by column chromatography (40% CH_2Cl_2 in hexanes) afforded 189 mg (64%) of **358** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (m, 2 H), 7.36 (m, 2 H), 7.28 (m, 1 H), 5.94 (m, 1 H), 5.82 (m, 1 H), 5.06 (m, 1 H), 4.98 (dd, J = 3.6, 10.2, Hz, 1 H), 2.34 (m, 1 H), 2.28 (m, 1 H), 1.85 (d, J = 2.4 Hz, 3 H). ^{13}C

NMR (151 MHz, $CDCl_3$) δ 142.2, 128.3 (2 C), 127.4, 127.1, 126.0 (2 C), 124.8, 82.3, 77.3, 71.0, 64.7, 32.3, 3.7. IR (film) 3036, 2918, 2281, 2220, 1074, 1051 cm^{-1}.

*Preparation of compound **359***

Applying the general procedure E to acetate **350**, the title compound was prepared in 80% yield after column chromatography (7:3 CH_2Cl_2/hexanes). ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 5.90 (m, 1 H), 5.78 (m, 1 H), 5.00 (s, 1 H), 4.89 (dd, *J* =3.6, 10.8 Hz, 1 H), 3.78 (s, 3 H), 2.32 (m, 1 H), 2.21 (m, 1 H), 1.85 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 134.4, 127.4 (2 C), 127.1, 124.9, 113.7 (2 C), 82.2, 77.4, 70.7, 64.7, 55.3, 32.1, 3.7. IR (film) 3041, 2918, 1516, 1248, 1074 cm^{-1}. HRMS (ESI) *m*/*z* 229.1234 [$(M+H)^+$; calcd for $C_{15}H_{17}O_2$, 229.1229].

*Preparation of compound **360***

Applying the general procedure E to acetate **351**, the title compound was prepared in 93% yield after column chromatography (40% CH_2Cl_2 in hexanes). ^1H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.8 Hz, 2 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 5.91 (m, 1 H), 5.79 (m, 1 H), 5.02 (s, 1 H), 4.92 (dd, *J* = 3.6, 10.2 Hz, 1 H), 2.33 (s, 3 H), 2.31 (m, 1 H), 2.24 (m, 1 H), 1.85 (d, *J* = 2.4 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 137.1, 129.0 (2 C), 127.1, 126.0 (2 C), 124.9, 82.2, 77.4, 70.9, 64.7, 32.2, 21.1, 3.7. IR (film) 3030, 2970, 2922, 1124, 1060 cm^{-1}.

*Preparation of compound **361***

Applying the general procedure E to acetate **352**, the title compound was prepared in 84% yield after column chromatography (25% CH_2Cl_2 in hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 4 H), 5.89 (m, 1 H), 5.79 (m, 1 H), 5.02 (m, 1 H), 4.91 (dd, *J* = 6.0, 7.8 Hz, 1 H), 2.23 (m, 2 H), 1.85 (d, *J* = 2.4 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 133.1, 128.4 (2 C), 127.4 (2 C), 127.1, 124.5, 82.5, 77.1, 70.3, 64.7, 32.3, 3.7. IR (film) 3040, 2918, 2219, 1493, 1074 cm^{-1}.

*Preparation of compound **362***

Applying the general procedure E to acetate **353**, the title compound was prepared in 92% yield after column chromatography (40% CH_2Cl_2 in hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 5.91 (m, 1 H), 5.81 (m, 1 H), 5.05 (m, 1 H), 5.01 (dd, *J* = 4.2, 9.6 Hz, 1 H), 2.31–2.21 (m, 2 H), 1.85 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3 (d, *J* = 1.1 Hz), 129.6 (q, *J* = 32.3 Hz), 127.2, 126.2 (2C), 125.2 (q, *J* = 3.8 Hz, 2C), 124.4, 124.2 (q, *J* = 272.4 Hz), 82.7, 77.0, 70.3, 64.7, 32.4, 3.7. IR (film) 3045, 2922, 1327, 1123, 1086 cm^{-1}.

*Preparation of compound **363***

Applying the general procedure E to acetate **354**, the title compound was prepared in 86% yield after column chromatography (20% CH_2Cl_2 in hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (s, 1 H), 7.56 (d, *J* = 7.2 Hz, 1 H), 7.52 (d, *J* = 7.8 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 1 H), 5.91 (m, 1 H), 5.81 (m, 1 H), 5.05 (m, 1 H), 5.00 (dd, *J* = 4.2, 9.0 Hz, 1 H), 2.27 (m, 2 H), 1.86 (s, 3 H), 1.85 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 130.6 (q, *J* = 32.3 Hz), 129.3 (d, *J* = 1.7 Hz), 128.7,

127.2, 124.4, 124.2 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.4 Hz), 122.8 (q, *J* = 3.7 Hz), 82.7, 70.3, 64.7, 32.4, 3.7. IR (film) 3047, 2922, 2224, 1329, 1126, 1074 cm^{-1}.

*Preparation of compound **364***

Applying the general procedure E to acetate **355**, the title compound was prepared in 82% yield after column chromatography (50% CH_2Cl_2 in hexanes). ^1H NMR (600 MHz, $CDCl_3$) δ 8.25 (m, 1 H), 8.11 (m, 1 H), 7.72 (m, 1 H), 7.51 (t, *J* = 7.8 Hz, 1 H), 5.91 (m, 1 H), 5.81 (m, 1 H), 5.06 (m, 1 H), 5.04 (dd, *J* = 3.6, 10.2 Hz, 1 H), 2.32 (m, 1 H), 2.25 (m, 1 H), 1.85 (d, *J* = 1.2 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 144.5, 132.1, 129.3, 127.2, 124.1, 122.4, 121.1, 82.9, 69.9, 64.8, 32.3, 3.7. IR (film) 3041, 2924, 2283, 1529, 1348, 1074 cm^{-1}.

*Preparation of compound **365***

Applying the general procedure E to acetate **356**, the title compound was prepared in 83% yield after column chromatography (20% CH_2Cl_2 in hexanes). Mixture of diastereomers (10:1 ratio) ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 (m, 2 H), 7.29 (t, *J* = 7.8 Hz, 2 H), 7.21 (m, 1 H), 6.65 (d, *J* = 16.2 Hz, 1 H), 6.26 (dd, *J* = 5.4, 16.2 Hz, 1 H), 5.86 (m, 1 H), 5.75 (m, 1 H), 4.97 (s, 1 H), 4.60 (m, 1 H), 2.21 (m, 1 H), 2.13 (m, 1 H), 1.86 (d, *J* = 2.4 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.8, 130.6, 129.6, 128.5 (2 C), 127.6, 127.0, 126.5 (2 C), 124.3, 82.3, 77.3, 69.4, 64.0, 30.6, 3.8. IR (film) 3034, 2918, 2283, 1074 cm^{-1}. HRMS (ESI) *m/z* 225.1271 $[(M+H)^+$; calcd for $C_{16}H_{17}O$, 225.1279].

*Preparation of compound **366***

Applying the general procedure E to acetate **357**, the title compound was prepared in 76% yield after column chromatography (35% CH_2Cl_2 in hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84 (m, 1 H), 5.72 (m, 1 H), 5.69 (m, 1 H), 4.91 (m, 1 H), 4.23 (dd, *J* = 3.0, 10.8 Hz, 1 H), 2.19 (ddq, *J* = 2.4, 10.2, 17.4 Hz, 1 H), 2.02 (m, 4 H), 1.96 (m, 1 H), 1.84 (d, *J* = 2.4 Hz, 3 H), 1.63 (m, 2 H), 1.56 (m, 2 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 126.8, 125.0, 123.1, 82.0, 77.5, 72.6, 64.3, 28.9, 25.0, 24,7, 22.6, 22.5, 3.8. IR (film) 3038, 2924, 2837, 1076 cm^{-1}.

*Preparation of compounds **xxii** and **xxiii** – General Procedure F*

*Preparation of **367** and **368***

A round-bottom flask was charged with alkyne **358** (37.6 mg, 0.1896 mmol, 1 equiv) and phenyldimethylsilane (28.4 mg, 0.2086 mmol, 1.1 equiv). The flask was capped with a septum and THF (0.2 mL) was added under nitrogen via syringe. Then, a solution of $H_2PtCl_6 \cdot 6H_2O$ in THF (0.1 M in THF, ~0.2 μL, ~0.00019 mmol, 0.0001 equiv) was added at room temperature. The solution was heated in an oil bath at 50 ^{o}C for 2 hours. The reaction mixture was concentrated and the mixture purified by column chromatography (4% Et_2O in hexanes) to give 47.5 mg (60%) of **367** and 15.5 mg (20%) of **368** as colorless oils

*Preparation of compounds **369** and **370***

Applying the general procedure F to alkyne **359**, compounds **369** and **370** were prepared in 89% yield (7:1 ratio). Spectroscopic data for **369**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.32 (m, 3 H), 7.29 (d, *J* = 9.0 Hz, 1 H), 6.87 (d, *J* = 9.0 Hz, 1 H), 6.03 (dd, *J* = 1.8, 7.2 Hz, 1 H), 5.95

(m, 1 H), 5.72 (m, 1 H), 5.12 (m, 1 H), 4.74 (dd, *J* = 3.6, 9.0 Hz, 1 H), 3.79 (s, 3 H), 2.35 (m, 1 H), 2.26 (m, 1 H), 1.72 (d, *J* = 1.8 Hz, 3 H), 0.34 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 139.2, 138.0, 136.7, 134.5, 134.0 (2 C), 128.9, 128.4, 127.71 (2 C), 127.69 (2 C), 124.1, 113.7 (2 C), 70.5, 70.2, 55.3, 31.4, 15.3, -3.5, -3.6. IR (film) 3036, 2955, 1514, 1248, 814 cm^{-1}. HRMS (EI) *m/z* 364.1853 [$(M)^+$; calcd for $C_{23}H_{28}O_2Si$, 364.1859]. Spectroscopic data for **370**: ^{1}H NMR (600 MHz, $CDCl_3$) mixture of isomers (7:1 ratio) major isomer: δ 7.51 (m, 2 H), 7.30 (m, 3 H), 7.24 (m, 2 H), 6.83 (m, 2 H), 5.94 (m, 1 H), 5.81 (s, 1 H), 5.51 (dd, *J* = 1.2, 10.2 Hz, 1 H), 4.85 (m, 1 H), 4.76 (s, 1 H), 3.79 (s, 3 H), 2.39 (m, 1 H), 2.29 (m, 1 H), 1.67 (d, *J* = 6.6 Hz, 3 H), 0.39 (s, 3 H), 0.36 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 141.2, 140.0, 139.5, 134.2 (2C), 133.1, 130.2, 128.40 (2C), 128.39 (2C), 127.4, 123.1, 113.4 (2C), 70.9, 69.1, 55.2, 27.3, 15.6, -1.2, -1.5. IR (film) 3036, 2953, 1512, 1248, 829 cm^{-1}. HRMS (EI) *m/z* 364.1846 [$(M)^+$; calcd for $C_{23}H_{28}O_2Si$, 364.1859].

*Preparation of compounds **371** and **372***

Applying the general procedure F to alkyne **360**, compounds **371** and **372** were prepared in 75% yield (1.7:1 ratio). Compounds **371** and **372** were separated by column chromatography (25% CH_2Cl_2 in hexanes). Spectroscopic data for **371**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.36 (m, 3 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 6.09 (dq, *J* = 1.8, 7.2 Hz, 1 H), 5.99 (m, 1 H), 5.78 (m, 1 H), 5.20 (m, 1 H), 4.81 (dd, *J* = 3.6, 9.0 Hz, 1 H), 2.40 (m, 1 H), 2.38 (s, 3 H), 2.31 (m, 1 H), 1.78 (d, *J* = 1.8 Hz, 3 H), 0.39 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

139.4, 139.2, 137.9, 137.0, 136.7, 134.0 (2 C), 129.0 (2 C), 128.9, 128.3, 127.7 (2 C), 126.3 (2 C), 124.1, 70.5, 70.4, 31.5, 21.1, 15.3, -3.6, -3.7. IR (film) 3030, 2955, 1427, 1248, 1076, 814 cm^{-1}. Spectroscopic data for **372**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.32 (m, 3 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 5.97 (dq, *J* = 1.2, 6.6 Hz, 1 H), 5.82 (m, 1 H), 5.55 (dq, *J* = 1.8, 10.2 Hz, 1 H), 4.86 (t, *J* = 4.2 Hz, 1 H), 4.82 (s, 1 H), 2.39 (m, 1 H), 2.34 (s, 3 H), 2.32 (m, 1 H), 1.69 (d, *J* = 6.6 Hz, 3 H), 0.42 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 140.0, 139.6, 138.0, 136.7, 134.2 (2 C), 130.1, 128.8 (2 C), 128.4, 127.4 (2 C), 127.0 (2 C), 123.1, 71.1, 69.3, 27.4, 21.1, 15.7, -1.2, -1.5. IR (film) 3030, 2920, 1427, 1068, 816 cm^{-1}. HRMS (EI) *m*/*z* 348.1908 [$(M)^{+}$; calcd for $C_{23}H_{28}OSi$, 348.1909].

*Preparation of compounds **373** and **374***

Applying the general procedure F to alkyne **361**, compounds **373** and **374** were prepared in 84% yield (7.5:1 ratio). Spectroscopic data for **373**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (m, 2 H), 7.33 (m, 3 H), 7.31 (s, 4 H), 6.00 (dd, *J* = 1.2, 7.2 Hz, 1 H), 5.94 (m, 1 H), 5.73 (m, 1 H), 5.14 (m, 1 H), 4.75 (t, *J* = 6.6 Hz, 1 H), 2.27 (m, 2 H), 1.74 (d, *J* = 1.8 Hz, 3 H), 0.34 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.9, 138.8, 137.9, 137.3, 134.0 (2 C), 133.1, 129.0, 128.44 (2 C), 128.43, 127.7 (2 C), 127.6 (2 C), 123.7, 70.5, 69.9, 31.5, 15.3, -3.6, -3.7. IR (film) 3038, 2957, 1493, 1248, 1076, 814 cm^{-1}. Spectroscopic data for **374**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.33–7.28 (m, 3 H), 7.24 (m, 4 H), 5.97 (dq, *J* = 1.8, 6.6 Hz, 1 H), 5.78 (m, 1 H), 5.54 (dq, *J* = 1.8, 10.2 Hz, 1 H), 4.78 (m, 2 H), 2.34 (m, 1 H), 2.24 (m, 1 H), 1.68 (d, *J* = 6.6 Hz, 3 H), 0.38 (s, 3 H), 0.35 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.0, 139.8, 139.7, 139.6, 134.2 (2

C), 132.9, 130.2, 128.5, 128.4 (2 C), 128.2 (2 C), 127.4 (2 C), 122.8, 70.6, 69.6, 27.5, 15.7, -1.2, -1.5. IR (film) 3067, 2955, 1491, 1068, 827 cm^{-1}. HRMS (EI) *m*/*z* 368.1353 [$(M)^+$; calcd for $C_{22}H_{25}OSiCl$, 368.1363].

*Preparation of compounds **375** and **376***

Applying the general procedure F to alkyne **362**, compounds **375** and **376** were prepared in 90% yield (1.8:1 ratio). Compounds **375** and **376** were separated by column chromatography (40% CH_2Cl_2 in hexanes). Spectroscopic data for **375**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2 H), 7.49 (m, 4 H), 7.34 (m, 3 H), 6.02 (dq, *J* = 1.8, 7.2 Hz, 1 H), 5.96 (m, 1 H), 5.77 (m, 1 H), 5.20 (m, 1 H), 4.84 (dd, *J* = 4.2, 8.4 Hz, 1 H), 2.30 (m, 2 H), 1.77 (d, *J* = 1.8 Hz, 3 H), 0.36 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 138.6, 137.8,137.6, 134.0 (2 C), 129.5 (q, *J* = 32.3 Hz), 129.0, 128.5, 127.7 (2 C), 126.5 (2 C), 125.2 (q, *J* = 3.8 Hz, 2 C), 124.2 (q, *J* = 272.6 Hz), 123.6, 70.6, 69.9, 31.7, 15.3, -3.6, -3.7. IR (film) 3045, 2922, 1325, 1126, 1060, 833 cm^{-1}. Spectroscopic data for **376**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2 H), 7.52 (m, 2 H), 7.41 (d, *J* = 7.8 Hz, 2 H), 7.31 (m, 3 H), 6.03 (dq, *J* = 1.8, 7.2 Hz, 1 H), 5.83 (m, 1 H), 5.60 (dq, *J* = 1.8, 10.8 Hz, 1 H), 4.85 (d, *J* = 1.8 Hz, 1 H), 4.82 (t, *J* = 4.8 Hz, 1 H), 2.35 (m, 1 H), 2.27 (m, 1 H), 1.72 (d, *J* = 7.2 Hz, 3 H), 0.41 (s, 3 H), 0.38 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 140.9, 140.1, 139.8, 134.2 (2 C), 130.2, 129.4 (q, *J* = 32.3 Hz), 128.5, 127.4 (2 C), 127.1 (2 C), 125.0 (q, *J* = 3.6 Hz, 2 C), 124.2 (q, *J* = 272.4 Hz), 122.8, 70.6, 70.1, 27.8, 15.7, -1.2, -1.5. IR (film) 3045, 2920, 1325, 1126, 1066, 833 cm^{-1}.

*Preparation of compounds **377** and **378***

Applying the general procedure F to alkyne **363**, compounds **377** and **378** were prepared in 90% yield (5.4:1 ratio). Spectroscopic data for **377**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1 H), 7.55 (d, *J* = 7.8 Hz, 1 H), 7.52 (d, *J* = 7.8 Hz, 1 H), 7.47 (m, 2 H), 7.45 (t, *J* = 7.8 Hz, 1 H), 7.33 (m, 3 H), 6.00 (dq, *J* = 1.8, 7.2 Hz, 1 H), 5.95 (m, 1 H), 5.75 (m, 1 H), 5.18 (m, 1 H), 4.81 (dd, *J* = 5.4, 7.2 Hz, 1 H), 2.30 (m, 2 H), 1.75 (d, *J* = 1.8 Hz, 3 H), 0.34 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5, 138.6, 137.8, 137.5, 134.0 (2C), 130.6 (q, *J* = 31.8 Hz), 129.5 (d, *J* = 1.5 Hz), 129.0, 128.7, 128.4, 127.7 (2C), 124.2 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.4 Hz), 123.6, 123.0 (q, *J* = 3.7 Hz), 70.7, 69.9, 31.7, 15.3, -3.5, -3.7. IR (fillm) 3068, 2956, 1329, 1126 cm^{-1}. Spectroscopic data for **378**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 1 H), 7.48 (m, 4 H), 7.40 (t, *J* = 7.8 Hz, 1 H), 7.29 (m, 3 H), 6.03 (dq, *J* = 1.2, 6.6 Hz, 1 H), 5.81 (m, 1 H), 5.58 (dq, *J* = 1.8, 10.2 Hz, 1 H), 4.84 (d, *J* = 1.8 Hz, 1 H), 4.78 (t, *J* = 5.4 Hz, 1 H), 2.34 (m, 1 H), 2.26 (m, 1 H), 1.71 (d, *J* = 7.2 Hz, 3 H), 0.39 (s, 3 H), 0.36 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 140.8, 140.3, 139.7, 134.2, 130.5 (q, *J* = 32.3 Hz), 130.2 (2 C), 128.5 (2 C), 127.4 (2 C), 124.2 (q, *J* = 273.0 Hz), 124.0 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 3.8 Hz), 122.9, 70.6, 70.0, 28.0, 15.7, -1.2, -1.5. IR (film) 3069, 2955, 1329, 1128 1074 cm^{-1}.

*Preparation of compounds **379** and **380***

Applying the general procedure F to alkyne **364**, compounds **379** and **380** were prepared in 94% yield (4:1 ratio). Spectroscopic data for **379**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (t, *J* = 1.5 Hz, 1 H), 8.12 (ddd, *J* = 1.0, 2.5, 8.5 Hz, 1 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 7.50 (t, *J* = 8.0 Hz, 1 H), 7.47

(m, 2 H), 7.32 (m, 3 H), 5.98 (dq, *J* = 4.0, 7.0 Hz, 1 H), 5.95 (m, 1 H), 5.76 (m, 1 H), 5.19 (m, 1 H), 4.85 (dd, *J* = 4.0, 9.0 Hz, 1 H), 2.35 (m, 1 H), 2.28 (ddq, *J* = 5.0, 9.5, 17.5 Hz, 1 H), 1.76 (d, *J* = 1.5 Hz, 3 H), 0.34 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$)δ 148.4, 144.8, 138.4, 138.0, 137.8, 134.0 (2C), 132.3, 129.2, 129.0, 128.6, 127.8 (2C), 123.3, 122.4, 121.3, 70.7, 69.5, 31.7, 15.4, -3.5, -3.7. IR (film) 3067, 2957, 1529, 1348, 1074, 814 cm^{-1}. HRMS (ESI) *m/z* 380.1666 [$(M+H)^+$; calcd for $C_{22}H_{26}NO_3Si$, 380.1682].

*Preparation of compounds **381** and **382***

Applying the general procedure F to alkyne **365**, compounds **381** and **382** were prepared in 94% yield (8:1 ratio). Spectroscopic data for **381**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.38 (m, 2 H), 7.33 (m, 3 H), 7.30 (t, *J* = 7.2 Hz, 2 H), 7.22 (m, 1 H), 6.62 (d, *J* = 15.6 Hz, 1 H), 6.30 (dd, *J* = 6.0, 16.2 Hz, 1 H), 5.96 (m, 1 H), 5.88 (m, 1 H), 5.68 (m, 1 H), 5.15 (dd, *J* = 1.8, 4.8 Hz, 1 H), 4.47 (m, 1 H), 2.23 (m, 1 H), 2.17 (m, 1 H), 1.75 (d, *J* = 1.8 Hz, 3 H), 0.35 (s, 6 H). IR (film) 3030, 2957, 1427, 1248, 1072, 814 cm^{-1}.

*Preparation of compounds **383** and **384***

Applying the general procedure F to alkyne **366**, compounds **383** and **384** were prepared in 81% yield (7:1 ratio). Spectroscopic data for **383**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.32 (m, 3 H), 5.97 (dq, *J* = 1.8, 7.2 Hz, 1 H), 5.86 (m, 1 H), 5.68 (m, 1 H), 5.63 (m, 1 H), 5.06 (m, 1 H), 4.05 (dd, *J* = 3.0, 9.0 Hz, 1 H), 2.22 (ddq, *J* = 2.4, 9.6, 17.4 Hz, 1 H), 2.09–1.95 (m, 5 H), 1.72 (d, *J* = 1.8 Hz, 3 H), 1.62 (m, 2 H), 1.56 (m, 2 H), 0.33 (s, 6 H). ^{13}C NMR (151 MHz,

$CDCl_3$) δ 139.5, 138.1, 137.6, 136.2, 134.0 (2C), 128.9, 128.0, 127.7 (2C), 124.2, 123.2, 72.1, 70.3, 28.3, 25.1, 25.0, 22.7, 22.5, 15.2, -3.5, -3.7. IR (film) 3031, 2926, 1427, 1248, 1076, 814 cm^{-1}. Spectroscopic data for **384**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.29 (m, 3 H), 5.96 (q, *J* = 7.2 Hz, 1 H), 5.69 (m, 1 H), 5.56 (s, 1 H), 5.46 (dd, *J* = 1.2, 10.8 Hz, 1 H), 4.86 (s, 1 H), 4.08 (s, 1 H), 2.18 (m, 1 H), 2.11–1.98 (m, 4 H), 1.82 (m, 1 H), 1.77 (d, *J* = 6.6 Hz, 3 H), 1.64–1.50 (m, 4 H), 0.37 (s, 3 H), 0.35 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 140.0, 139.5, 135.9, 134.2 (2 C), 129.6, 128.4, 127.3 (2 C), 123.2, 122.7, 72.8, 69.0, 25.9, 25.8, 25.0, 22.9, 22.5, 15.7, -1.3, -1.6. IR (film) 3025, 2928, 2855, 1427, 1244, 1064, 833 cm^{-1}.

*Preparation of compounds **385***

Applying the general procedure A to silane **367**, compound **385** was obtained in 80% yield (dr = 10:1) as a colorless oil after column chromatography (5% EtOAc in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 2 H), 7.35 (m, 3 H), 7.23 (m, 2 H), 7.13 (m, 1 H), 7.06 (m, 2 H), 6.47 (q, *J* = 2.0 Hz, 1 H), 2.56 (dd, A of ABX system, *J* = 7.0, 16.0 Hz, 1 H), 2.47 (dd, B of ABX system, *J* = 7.0, 16.5 Hz, 1 H), 2.16 (d, *J* = 2.0 Hz, 3 H), 1.70 (dt, *J* = 5.0, 9.5 Hz, 1 H), 1.32 (m, 1 H), 0.99 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.81 (dt, *J* = 6.0, 8.5 Hz, 1 H), 0.37 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 158.1, 142.7, 136.2, 134.5, 134.0 (2C), 129.4, 128.3 (2C), 127.9 (2C), 125.9 (2C), 125.5, 48.8, 22.9, 18.3, 18.1, 15.7, -3.99, -4.01. IR (film) HRMS (ESI) *m*/*z* 335.1820 $[(M+H)^+$; calcd for $C_{22}H_{27}OSi$, 335.1831].

*Preparation of compounds **387***

Applying the general procedure A to silane **369** and *n*-butyllithium (1.6 M in hexanes, 1.1 equiv) for 2.5 hours at -78 ^{o}C, compound **387** was obtained in 69% yield (dr = 7.5:1) after column chromatography (5% EtOAc in hexanes). Mixture of diastereomers (11:1) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (m, 2 H), 7.35 (m, 3 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 6.47 (m, 1 H), 3.76 (s, 3 H), 2.52 (dd, A of ABX system, *J* = 6.6, 16.2 Hz, 1 H), 2.46 (dd, B of ABX system, *J* = 7.2, 16.2 Hz, 1 H), 2.15 (s, 3 H), 1.65 (dt, *J* = 4.8, 9.0 Hz, 1 H), 1.23 (m, 1 H), 0.90 (dt, *J* = 5.4, 9.0 Hz, 1 H), 0.73 (m, 1 H), 0.37 (s, 6 H).

*Preparation of compounds **389***

Applying the general procedure A to silane **367**, compounds **389** was obtained in 80% yield (dr = 8:1) after column chromatography (5% EtOAc in hexanes). Mixture of diastereomers (*trans* / *cis* = 8:1) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.40–7.34 (m, 3 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 6.96 (d, *J* = 7.8 Hz, 2 H), 6.48 (q, *J* = 1.8 Hz, 1 H), 2.56 (dd, A of ABX system, *J* = 6.6, 16.2 Hz, 1 H), 2.45 (dd, B of ABX system, *J* = 7.2, 16.2 Hz, 1 H), 2.30 (s, 3 H), 2.16 (d, *J* = 1.8 Hz, 3 H), 1.67 (dt, *J* = 4.8, 9.0 Hz, 1 H), 1.28 (m, 1 H), 0.96 (dt, *J* = 5.4, 9.0 Hz, 1 H), 0.78 (dt, *J* = 5.4, 8.4 Hz, 1 H), 0.38 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.3, 158.0, 139.6, 136.2, 135.0, 134.6, 134.0 (2C), 129.4, 129.0 (2C), 127.9 (2C), 125.9 (2C), 48.9, 25.6, 20.9, 18.1, 15.5, -3.98, -4.00. IR (film) 3060, 2957, 1684, 1113, 814 cm^{-1}. IR (film) HRMS (EI) *m*/*z* 348.1901 [$(M)^{+}$; calcd for $C_{23}H_{28}OSi$, 348.1909].

*Preparation of compounds **391** and **392***

Applying the general procedure A to silane **368**, compound **391** was obtained in 74% yield (dr = 18:1) along with compound **392** in 12% as colorless oils after column chromatography (5% and 10% EtOAc in hexanes). Spectroscopic data for **391**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (m, 2 H), 7.39–7.32 (m, 3 H), 7.18 (m, 2 H), 6.98 (m, 2 H), 6.44 (m, 1 H), 2.50 (d, *J* = 7.0 Hz, 2 H), 2.15 (m, 3 H), 1.65 (dt, *J* = 5.0, 9.5 Hz, 1 H), 1.27 (m, 1 H), 0.94 (m, 1 H), 0.80 (dt, *J* = 6.0, 9.0 Hz, 1 H), 0.38 (s, 3 H), 0.37 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.0, 158.4, 141.3, 136.2, 134.5, 134.0 (2C), 131.2, 129.5, 128.3 (2C), 128.0 (2C), 127.4 (2C), 48.7, 22.4, 18.3, 18.1, 15.6, -3.96, -3.98. IR (film) 3069, 2957, 1686, 1587, 1493, 1113, 814 cm^{-1}. HRMS (EI) *m*/*z* 368.1348 [$(M)^+$; calcd for $C_{22}H_{25}OSiCl$, 368.1363]. Spectroscopic data for **392**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (m, 1 H), 7.27 (m, 2 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 7.15 (m, 2 H), 7.10 (d, *J* = 9.0 Hz, 2 H), 6.02 (dt, *J* = 2.4, 6.0 Hz, 1 H), 5.95 (dt, *J* = 2.4, 6.0 Hz, 1 H), 5.48 (q, *J* = 1.8 Hz, 1 H), 3.48 (t, *J* = 7.2 Hz, 1 H), 2.86 (ddt, *J* = 1.8, 7.8, 16.8 Hz, 1 H), 2.54 (dt, *J* = 1.8, 6.0, 16.2 Hz, 1 H), 1.89 (s, 1 H), 1.69 (d, *J* = 1.8 Hz, 3 H), 0.12 (s, 3 H), 0.11 (s, 3 H). IR (film) 3387, 3060, 2955, 1487, 1427, 1093, 814 cm^{-1}. HRMS (EI) *m*/*z* 351.1322 [$(M\text{-}OH)^+$; calcd for $C_{22}H_{24}SiCl$, 351.1336].

*Preparation of compounds **393** and **394***

Applying the general procedure A to silane **375**, compound **393** was obtained in 10% yield (dr = 10:1) along with compound **394** (dr = 20:1) in 40% after column chromatography (15% EtOAc in hexanes). Spectroscopic data for **394**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 2 H), 7.27 (m,

5 H), 7.18 (m, 2 H), 6.05 (m, 1 H), 5.98 (m, 1 H), 5.46 (m, 1 H), 3.58 (t, *J* = 6.5 Hz, 1 H), 2.91 (m, 1 H), 2.60 (m, 1 H), 1.95 (s, 1 H), 1.70 (m, 3 H), 0.09 (s, 6 H).

*Preparation of compounds **395** and **396***

Applying the general procedure A to silane **377**, compound **395** was obtained in 20% yield (dr = 17:1) along with compound **396** (dr > 20:1) in 62% as colorless oils after column chromatography (15% EtOAc in hexanes). Spectroscopic data for **395**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (m, 2 H), 7.39–7.31 (m, 5 H), 7.29 (s, 1 H), 7.22 (m, 1 H), 6.43 (q, *J* = 2.0 Hz, 1 H), 2.53 (d, *J* = 6.5 Hz, 2 H), 2.15 (d, *J* = 2.0 Hz, 3 H), 1.73 (dt, *J* = 5.0, 9.5 Hz, 1 H), 1.35 (m, 1 H), 1.01 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.87 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.37 (s, 3 H), 0.36 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.8, 158.7, 143.8, 136.1, 134.3, 134.0 (2C), 130.6 (q, *J* = 31.9 Hz), 129.5, 129.3, 128.7, 128.0 (2C), 124.2 (q, *J* = 272.4 Hz), 122.6 (q, *J* = 3.8 Hz), 122.3 (q, *J* = 3.8 Hz), 48.6, 22.8, 18.6, 18.1, 15.9, -3.9, -4.0. IR (film) 3072, 2959, 1687, 1325, 1124, 814 cm^{-1}. HRMS (EI) *m*/*z* 402.1625 [$(M)^{+}$; calcd for $C_{22}H_{25}OSiF_3$, 402.1627]. Spectroscopic data for **396**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.37 (d, *J* = 7.8 Hz, 1 H), 7.32 (t, *J* = 7.8 Hz, 1 H), 7.29 (tt, *J* = 1.8, 7.8 Hz, 1 H), 7.23 (m, 2 H), 7.16 (m, 2 H), 6.05 (dt, *J* = 2.4, 6.0 Hz, 1 H), 5.97 (dt, *J* = 2.4, 6.0 Hz, 1 H), 5.47 (q, *J* = 1.8 Hz, 1 H), 3.58 (dd, *J* = 6.0, 7.8 Hz, 1 H), 2.93 (ddt, A of ABX system, *J* = 2.4, 7.8, 16.8 Hz, 1 H), 2.61 (ddt, B of ABX system, *J* = 1.8, 6.0, 16.8 Hz, 1 H), 1.95 (s, 1 H), 1.68 (d, *J* = 1.8 Hz, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 140.2, 138.8, 137.5, 137.1, 133.8 (2C), 132.3, 131.5 (d, *J* = 1.1 Hz),

130.2 (q, *J* = 31.7 Hz), 128.8, 128.3, 127.6 (2C), 124.7 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 273.0 Hz), 123.1 (q, *J* = 3.8 Hz), 89.3, 57.8, 37.5, 16.2, -3.8, -3.9. IR (film) 3381, 3069, 2957, 1327, 1128, 814 cm^{-1}. HRMS (EI) *m*/*z* 385.1588 $[(M-OH)^+$; calcd for $C_{22}H_{24}SiCl$, 385.1599].

*Preparation of compound **399***

Applying the general procedure A to silane **372**, compound **399** was obtained in 86% yield (dr = 14:1) as a colorless oil after column chromatography (6% EtOAc in hexanes). Spectroscopic data for **391**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.37 (m, 3 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.91 (d, *J* = 8.0 Hz, 2 H), 5.98 (q, *J* = 7.0 Hz, 1 H), 2.51 (dd, A of ABX system, *J* = 6.0, 17.0 Hz, 1 H), 2.29 (s, 3 H), 2.25 (dd, B of ABX system, *J* = 7.5, 17.0 Hz, 1 H), 1.74 (d, *J* = 7.0 Hz, 3 H), 1.48 (dt, *J* = 5.0, 9.5 Hz, 1 H), 1.23 (m, 1 H), 0.85 (dt, *J* = 5.5, 9.5 Hz, 1 H), 0.59 (dt, *J* = 5.5, 9.0 Hz, 1 H), 0.41 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.2, 147.9, 139.6, 139.2, 136.8, 134.9, 134.0 (2 C), 129.4, 128.9 (2 C), 127.9 (2 C), 125.8 (2 C), 49.1, 22.2, 20.9, 17.5, 17.1, 15.4, -2.7, -2.8. IR (film) 3070, 2920, 1684, 1653, 1109, 810 cm^{-1}. HRMS (ESI) *m*/*z* 349.1980 $[(M+H)^+$; calcd for $C_{23}H_{29}OSi$, 349.1988].

*Preparation of compound **400***

Applying the general procedure A to silane **376**, compound **400** was obtained in 17% yield (dr = 20:1) as a colorless oil after column chromatography (15% EtOAc in hexanes). Compound **400** underwent fast dehydration in $CDCl_3$ and the low yield is probably due to loss during the purification process in silica gel. ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 2 H), 7.37

(m, 2 H), 7.28 (m, 3 H), 7.20 (d, *J* = 7.8 Hz, 2 H), 6.09 (m, 1 H), 5.92 (m, 1 H), 5.66 (s, broad, 1 H), 3.59 (s, broad, 1 H), 3.06 (dd, *J* = 7.2, 16.8 Hz, 1 H), 2.61 (s, broad, 1 H), 1.75 (s, 1 H), 1.35 (s, broad, 3 H), 0.40 (s, broad, 3 H), 0.24 (s, 3 H).

*Preparation of compound **401***

Applying the general procedure A to silane **383**, compound **401** was obtained in 68% yield (dr = 20:1) as a colorless oil after column chromatography (15% EtOAc in hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (m, 2 H), 7.32 (m, 3 H), 6.20 (d, *J* = 1.2 Hz, 1 H), 5.76 (dd, *J* = 3.0, 11.4 Hz, 1 H), 5.60 (ddd, *J* = 3.0, 8.4, 11.4 Hz, 1 H), 5.39 (d, *J* = 7.2 Hz, 1 H), 2.85 (dd, *J* = 2.4, 18.6 Hz, 1 H), 2.42 (dt, *J* = 8.4, 19.2 Hz, 1 H), 2.36 (d, *J* = 9.6 Hz, 1 H), 2.16 (m, 1 H), 1.98 (m, 2 H), 1.82 (d, *J* = 1.8 Hz, 3 H), 1.80 (m, 1 H), 1.73 (m, 1 h), 1.52 (s, 1 H), 1.47–1.33 (m, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.1, 142.0, 138.7 (br), 138.2, 137.6, 133.9 (2C), 128.9, 127.7 (2C), 126.3, 118.0 (br), 52.2 (br), 38.4 (br), 28.3 (br), 27.5, 26.8, 25.4, 17.2, -3.37, -3.42.

*Preparation of compound **402***

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.39–7.32 (m, 7 H), 7.24 (m, 1 H), 6.11 (dq, *J* = 1.5, 7.0 Hz, 1 H), 4.83 (dd, *J* = 4.0, 7.5 Hz, 1 H), 4.70 (m, 1 H), 1.91 (m, 1 H), 1.80–1.71 (m, 3 H), 1.69 (d, *J* = 1.5 Hz, 3 H), 1.59 (m, 1 H), 0.36 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 142.5, 140.1, 138.4, 138.2, 134.0 (2C), 128.9, 128.3 (2C), 127.7 (2C), 127.0, 126.4 (2C), 72.7, 69.2, 30.7, 30.2, 19.3, 15.4, -3.49, -3.55. IR (film) 3067, 2936, 1427, 1248, 111, 1030, 812 cm^{-1}. HRMS (EI) *m*/*z* 336.1900 [$(M)^{+}$; calcd for $C_{22}H_{28}OSi$, 336.1909].

*Preparation of compound **403***

Applying the general procedure A to silane **402**, compound **403** was obtained in 87% yield (dr = 20:1) as a colorless oil after column chromatography (15% EtOAc in hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (m, 1 H), 7.35 (m, 2 H), 7.30 (m, 4 H), 7.22 (m, 1 H), 5.85 (dt, *J* = 1.8, 9.0 Hz, 1 H), 3.13 (q, *J* = 9.6 Hz, 1 H), 2.27 (m, 1 H), 2.04 (m, 3 H), 1.87 (m, 2 H), 1.68 (s, 1 H), 1.25 (d, *J* = 1.8 Hz, 3 H), 0.29 (s, 3 H), 0.28 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 139.2, 138.5, 137.8, 133.9 (2 C), 128.7, 127.9 (2 C), 127.6 (2 C), 126.5, 125.1 (2 C), 84.9, 50.5, 42.1, 30.7, 22.5, 15.2, -3.2, -3.6. IR (film) 3473, 3069, 2959, 1248, 1111, 814 cm^{-1}.

*Preparation of compound **404***

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 2 H), 7.14 (m, 1 H), 7.08 (m, 2 H), 2.57 (m, 2 H), 1.93 (s, 3 H), 1.77 (dt, *J* = 4.5, 9.0 Hz, 1 H), 1.39 (m, 1 H), 1.04 (dt, *J* = 5.0, 8.5 Hz, 1 H), 0.86 (dt, *J* = 5.5, 9.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.2, 142.5, 128.2 (2 C), 125.9 (2 C), 125.6, 91.2, 80.3, 49.6, 23.0, 18.0, 15.3, 4.0.

*Preparation of compound **405***

Applying general procedure A to compound **258**, afforded ynone **405** as a colorless oil in 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 9.0 Hz, 2 H), 6.79 (d, *J* = 9.0 Hz, 2 H), 3.76 (s, 3 H), 2.55 (d, *J* = 7.0 Hz, 2 H), 1.95 (m, 3 H), 1.72 (dt, *J* = 5.0, 9.0 Hz, 1 H), 1.30 (m, 1 H), 0.95 (m, 1 H), 0.79 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.4, 157.7, 134.4, 127.2 (2 C), 113.7 (2 C), 91.1, 80.4, 55.3, 49.7, 22.2, 17.4, 14.7, 4.1.

*Preparation of compound **406***

Applying general procedure A to compound **259**, afforded ynone **406** as a colorless oil in 21% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 8.0 Hz, 2 H), 2.59 (dd, A of ABX system, *J* = 6.5, 16.5 Hz, 1 H), 2.53 (dd, B of ABX system, *J* = 7.0, 16.5 Hz, 1 H), 1.94 (s, 3 H), 1.72 (dt, *J* = 5.0, 9.0 Hz, 1 H), 1.34 (m, 1 H), 0.99 (dt, *J* = 5.5, 8.5 Hz, 1 H), 0.86 (dt, *J* = 5.5, 9.0 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.0, 141.0, 131.2, 131.2 (2 C), 128.3 (2 C), 91.2, 80.3, 49.5, 22.4, 18.0, 15.3, 4.0.

*Preparation of compounds **407a/407b***

Applying general procedure A to compound **261**, afforded ynone **407** as a colorless oil in 93% yield. Acyclic precursor (*syn*): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 4.5 Hz, 4 H), 7.25 (m, 1 H), 5.82 (dddd, *J* = 6.5, 10.5, 13.0, 17.0 Hz, 1 H), 5.68 (ddd, *J* = 7.0, 10.5, 17.0 Hz, 1 H), 5.01 (dq, *J* = 1.5, 17.0 Hz, 1 H), 4.97-4.91 (m, 2 H), 4.84 (m, 1 H), 4.37 (t, *J* = 6.0 Hz, 1 H), 3.79 (dt, *J* = 1.5, 7.5 Hz, 1 H), 2.04 (m, 2 H), 1.88 (m, 1 H), 1.77 (m, 1 H), 0.09 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 138.7, 138.0, 127.9 (2 C), 126.8 (2 C), 126.6, 114.4, 111.7, 80.9, 75.8, 36.2, 29.3, -3.7. IR (neat) 3079, 2957, 1453, 1248, 1059, 909, 841 cm^{-1}. Acyclic precursor (*anti*): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5, 2 H), 7.24 (m, 3 H), 5.81 (dddd, *J* = 6.0, 10.0, 13.0, 16.5 Hz, 1 H), 5.74 (ddd, *J* = 7.5, 10.5, 17.0 Hz, 1 H), 5.03-4.91 (m, 4 H), 4.39 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.39 (d, *J* = 8.0 Hz, 1 H), 2.17 (m, 1 H), 2.05 (m, 1 H), 1.86 (m, 1 H), 1.65 (m, 1 H), -0.03 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 138.8, 137.8, 128.1, 127.3 (2 C), 127.2

(2 C), 114.3, 113.0, 78.9, 72.9, 37.7, 30.2, -4.0. IR (film) 3079, 2957, 1454, 1248, 1024, 841 cm^{-1}.

*Preparation of compounds **419a** and **419b***

To a solution of 4,4-dimethylpent-1-en-3-ol (650 mg, 5.69 mmol, 1 equiv) and the trichloroacetimidate of 1-phenylbut-3-en-1-ol (2.5 g, 8.54 mmol, 1.5 equiv) in hexane (28 mL) at 0 ^{o}C was added a solution of TMSOTf (126 mg, 0.569 mmol, 0.1 equiv) in hexane (1 mL) with vigorous stirring. After 2 hours the reaction mixture was filtered through a plug of celite and rinsed with hexanes. The filtrate was washed with $NaHCO_{3\ (sat)}$ (3 × 30 mL), water, brine, dried over $MgSO_4$ and concentrated. Column chromatography (hexanes) afforded 737 mg (53%) of acyclic ethers as colorless oils. Spectroscopic data for syn diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 4 H), 7.19 (m, 1 H), 5.73 (ddt, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.53 (ddd, *J* = 8.5, 10.5, 17.5 Hz, 1 H), 5.01–4.93 (m, 4 H), 4.35 (t, *J* = 6.0 Hz, 1 H), 3.45 (d, *J* = 8.5 Hz, 1 H), 2.53 (m, 1 H), 2.43 (m, 1 H), 0.93 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 136.9, 134.9, 127.8 (2 C), 126.8, 126.7 (2 C), 117.7, 116.8, 88.5, 79.2, 41.5, 34.9, 26.3. IR (film) Spectroscopic data for anti diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.24 (m, 3 H), 5.77 (ddt, *J* = 7.0, 10.5, 17.5 Hz, 1 H), 5.66 (ddd, *J* = 9.0, 10.5, 17.5 Hz, 1 H), 5.25 (m, 1 H), 5.00–4.93 (m, 3 H), 4.32 (dd, *J* = 6.0, 8.0 Hz, 1 H), 3.06 (d, *J* = 8.5 Hz, 1 H), 2.52 (m, 1 H), 2.32 (m, 1 H, 0.82 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 136.4, 135.5, 128.1 (2 C), 127.4 (2 C), 127.3, 119.0, 116.3, 85.1, 77.5, 42.9, 34.3, 26.2.

*Preparation of compound **410***

Following a literature procedure,[12] to a solution of ethylaluminum dichloride (1 M in hexane, 28 mL, 28 mmol, 2.5 equiv) in toluene (12 mL) at 0 ^{o}C was added triethylsilane (3.26 g, 14 mmol, 1.25 equiv) slowly. After 10 minutes, 5-hexyn-1-ol (1.1 g, 11.21 mmol, 1 equiv) was added slowly via syringe and the mixture was stirred at 0 ^{o}C for 1.5 hours. Triethylamine (5.3 mL, 37.56 mmol. 3.35 equiv) was added and the mixture stirred for 5 additional minutes. Then, $NaHCO_{3\ (sat)}$ (30 mL) was added and the mixture stirred for 10 minutes. The mixture was extracted with diethyl ether, dried over $MgSO_4$ and concentrated. Column chromatography (30% EtOAc in hexanes) afforded 2.11 g (88%) of **410** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.34 (dt, *J* = 7.2, 14.4 Hz, 1 H), 5.39 (dt, *J* = 1.2, 14.4 Hz, 1 H), 3.63 (t, *J* = 6.6 Hz, 2 H), 2.12 (dq, *J* = 1.2, 7.8 Hz, 2 H), 1.57 (m, 2 H), 1.44 (m, 2 H), 1.29 (s, 1 H), 0.92 (t, *J* = 7.8 Hz, 9 H), 0.58 (q, *J* = 7.8 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.6, 125.6, 62.9, 33.7, 32.4, 25.9, 7.5, 4.7. IR (film) 3335, 2953, 2874, 1458 cm^{-1}.

*Preparation of compound **411***

To a solution of oxalyl chloride (1.5 g, 11.83 mmol, 1.2 equiv) in CH_2Cl_2 (20 mL) at -78 ^{o}C was added DMSO (1.8 g, 23.7 mmol, 2.4 equiv) as a solution in CH_2Cl_2 (5 mL) over a period of 7 minutes. After 10 minutes, a solution of alcohol **410** (2.09 g, 9.86 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added over 10 minutes. The mixture was stirred at -78 ^{o}C for 1 hour and then

triethylamine (6.87 mL, 49.3 mmol, 5 equiv) was added over 5 minutes and stirred for 1 hour at room temperature. The reaction was quenched with water (mL) and extracted with CH_2Cl_2. Combined organic extracts were dried over $MgSO_4$ and concentrated. Column chromatography (30% EtOAc in hexanes) afforded 2.09 g (ca. 100%) of aldehyde **411** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75 (t, *J* = 1.2 Hz, 1 H), 6.30 (dt, *J* = 7.8, 14.4 Hz, 1 H), 5.44 (d, *J* = 13.8 Hz, 1 H), 2.43 (dt, *J* = 1.2, 7.8 Hz, 2 H), 2.13 (dq, *J* = 0.6, 7.2 Hz, 2 H), 1.71 (quintet, *J* = 7.8 Hz, 2 H), 0.92 (t, *J* = 7.8 Hz, 9 H), 0.58 (q, *J* = 7.8 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.3, 148.4, 126.8, 43.2, 33.1, 22.0, 7.5, 4.6. IR (film) 2955, 2874, 1728, 733 cm^{-1}.

*Preparation of compound **412***

To a solution of aldehyde **411** (1.844 g, 8.68 mmol, 1 equiv) in THF (100 mL) at 0 ^{o}C was added phenylmagnesium bromide (3 M in THF, 3.5 mmol, 1.2 equiv). After 3 hours the reaction was quenched by adding NH_4Cl (sat) and slightly acidified with 1 M HCl. The mixture was extracted with diethyl ether. Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (15% EtOAc in hexanes) afforded 2.22 g (88%) of alcohol **412** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (m, 4 H), 7.26 (m, 1 H), 6.33 (dt, *J* = 7.2, 14.4 Hz, 1 H), 5.39 (dt, *J* = 1.2, 13.8 Hz, 1 H), 4.65 (t, *J* = 6.6 Hz, 1 H), 2.11 (dq, *J* = 1.2, 7.2 Hz, 2 H), 1.88 (s, 1 H), 1.81 (m, 1 H), 1.73 (m, 1 H), 1.51 (m, 1 H), 1.35 (m, 1 H), 0.91 (t, *J* = 7.8 Hz, 9 H), 0.58 (q, *J* = 7.8 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.6, 144.7, 128.4 (2C), 127.5, 125.9 (2C), 125.6, 74.6, 38.6, 33.8, 25.9, 7.5, 4.7. IR (film) 3345, 3030, 2953,

1604, 1456, 1016, 731 cm^{-1}. HRMS (EI) *m/z* 261.1674 [$(M-C_2H_5)^+$; calcd for $C_{16}H_{25}OSi$, 261.1675].

*Preparation of compound **413a** and **413b***

Following a literature procedure,[12] to a solution of alcohol **412** (365 mg,, 1.256 mmol, 1 equiv) and benzoquinone (272 mg, 2.512 mmol, 2 equiv) in 10:1 acetone/HOAc (6.6 mL) was added water (4.5 mg, 2.51 mmol, 2 equiv) and $Pd(dba)_2$ (72 mg, 0.1256 mmol, 0.1 equiv). A condenser was attached to the flask and the mixture was heated in an oil bath at 50 ^oC for 24 hours. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and $NaHCO_{3\ (sat)}$ (10 mL). The aqueous phase was extracted with CH_2Cl_2. Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (7% EtOAc in hexanes) afforded 165.4 mg (46%) of alcohols **413a**/**413b** as a mixture (1.45:1 ratio) (colorless oil).

*Preparation of compound **414***

Applying general procedure A to **413a**/**413b** (1.45:1 ratio, 103 mg, 0.357 mmol, 1 equiv) and *n*-butyllithium (1.6 M in THF, 0.33 mL, 0.536 mmol, 1.5 equiv) in THF (4.5 mL) afforded, after column chromatography (5% and 10% EtOAc in hexanes) 34 mg (33%) of diastereomeric alcohols **414** (dr = 2:1) as a colorless oils. The relative stereochemistry of the products was not assigned.

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