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DIPOLE MOMENT EFFECT ON PHOTOCYCLOADDITION
OF DOUBLE BONDS TO TRIPLET BENZENE RINGS

presented by

Jong-Ill Lee

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Major professor

Date Dec. 13, 2001

DIPOLE

DIPOLE MOMENT EFFECT ON PHOTOCYCLOADDITION OF DOUBLE BONDS TO TRIPLET BENZENE RINGS

by

Jong-Ill Lee

A DISSERTATION

Submitted to
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In partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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Abstract

DIPOLE MOMENT EFFECT ON PHOTOCYCLOADDITION OF DOUBLE BONDS TO TRIPLET BENZENE RINGS

By

Jong-Ill Lee

The regioselectivity of the intramolecular [2+2] photocycloaddition of ortho-substituted *para*-butenoxy benzaldehydes, benzonitriles and cyclic phenyl ketones was investigated. This investigation probed the effect of dipole moment on the regioselectivity of cycloaddition.

Ortho substituted p-butenoxybenzaldehydes with electron-withdrawing groups and a weak electron-donating group (**Al-F**, **Al-CF3** and **Al-CH3**) generate syn-addition isomers, double bonds added toward substituents, while one with a strong electron-donating group (**Al-OCH3**) generates an anti-addition isomer, with the double bonds adding away from the substituents. Results show the interactions between the molecular dipole and transition dipole on the exciplex state to be the major factor in determining regioselectivity. The relatively low regioselectivity observed for **Al-F** is attributed to the direction of the molecular dipole moment, which aligns close to the molecular axis.

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p-Butenoxy tetralone (**TT**) and chromanone (**CR**), that are analogues of ortho methyl (**Al-CH3**) and methoxy (**Al-OCH3**) substituted p-butenoxybenzaldehydes with anti-conformation, form anti-addition products. Opposite regioselectivity of **TT**, compared to its analog **Al-CH3**, is attributed to its opposite direction of molecular dipole moment.

Ortho substituted p-butenoxybenzonitriles produced both regioisomers with varying ratios depending on the light source. Upon irradiation with 254 nm, all nitriles generate the anti-addition products as major isomers, with only **CN-CH3** and **CN-OCH3** affording, minor syn-addition products in 16.7 and 18.2% respectively. Changing the light source to 313 nm degrades the regioselectivity for all cases and a complete loss of selectivity is observed for **CN-CF3**.

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1.1. Brief H

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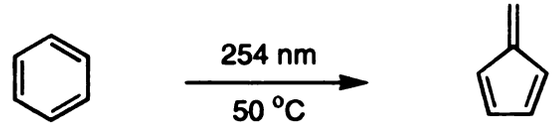
Part 1. Introduction

It is well documented that the benzene ring has a strong tendency to maintain its aromaticity during the thermal chemistry of benzene, while benzene loses its aromaticity during photoinduced chemical reactions.

1.1. Brief History

Fritzsche reported the first photodimerization of an aromatic compound in 1866 exploring anthracene photodimer.[1]

Bryce-Smith made the landmark discovery of photoisomerization of benzene to fulvene in 1957,[2] and reported the first photocycloaddition of excited benzene to alkenes in 1959.[3]



Since the initial discovery, a variety of mechanism studies have been carried out and synthetic applications were also extensively searched. [4, 5, 6, 7]

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1.2.1. Mode

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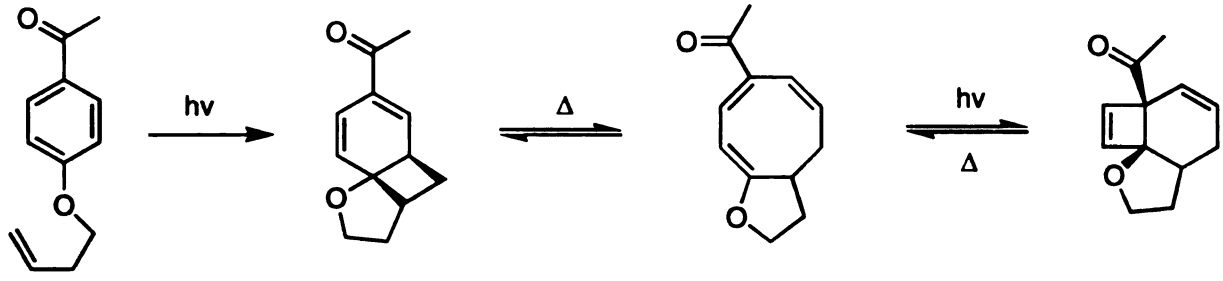
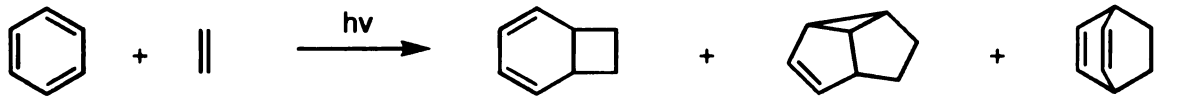
In 1987 Wagner and Nahm discovered a new [2+2] photocycloaddition. They found that phenyl ketones with the lowest $\pi\pi^*$ triplet states undergo intramolecular cycloaddition to double bonds to produce bicyclo[4,2,0]octa-2,4-dienes as initial photoproducts. The initial photoproducts then undergo thermal rearrangement followed by secondary photoreaction to produce a cyclobutene.[8, 9, 10]



1.2. Photocycloaddition of Benzene

1.2.1. Modes of Photocycloaddition

Irradiation of benzene at 254 nm in the presence of an alkene can lead to formation of 1,2-(*ortho*), 1,3-(*meta*), and 1,4-(*para*) cycloadducts depending on the substitution pattern of the arene and alkene.



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For all modes of cycloaddition, the stereochemistry of the alkene is preserved in the products.[11] Generally, both *ortho*[10] and *meta*[12] photocycloadditions are facile and occur with various substituents on the aromatic rings and double bonds. In contrast, *para* cycloaddition is very inefficient and rarely observed.

Wilzbach and Kaplan[13] and Bryce-Smith, Gilbert, and Orger[14] discovered the *meta* photocycloaddition of benzene to alkenes independently and simultaneously in 1966.

Wilzbach and Kaplan reported that irradiation of benzene with a 10% solution of cyclopentene produced a 1:1 ratio of adducts through the *meta* cyclization mode. Bryce-Smith, Gilbert, and Orger reported that irradiation of cis-cyclooctene in benzene gave a *meta* photocycloaddition adduct.

Regioselectivity was demonstrated for benzene with bearing either electron-donor group or electron-withdrawing groups. Srinivasan and Subrahmanyam observed intermolecular *meta* photocycloaddition of the double bond generally occurs at the 2- and 6- positions of the benzene ring, relative to the electron donor group.[15] However, as the size of donor groups increases, the double bond adds to the 3- and 5-position relative to the ring substituent. Cornelisse observed regioselectivity with electron-withdrawing groups on the benzene has a strong preference for position 2 and 4 without adduct at position 1.[16]

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Regioselectivity for intramolecular photocycloaddition has also been studied. Addition reactions of 5-phenylpent-1-ene and its derivatives shows two principal modes: 1,3-addition and 2,6-addition, Gilbert and Taylor[17] observed that 5-phenylpent-1-ene undergoes 2,6 as well as 1,3 addition in a ratio of 72:28.

Compared to other cycloaddition modes, para cycloaddition has drawn little attention to investigate the mechanistic nature of this pathway. Generally, para cycloaddition shows low efficiency and became the major pathway in only a few cases, such as addition of dienes and allenes to benzene.[18] When benzene was irradiated in the presence of isoprene, the para cycloadduct was produced as the major adduct with the *meta* cycloadduct as the minor product in the ratio of 4:1 respectively. Similarly, irradiation of cyclonona-1, 2-diene in benzene produced the para cycloadduct as the major product.[19,20]

1.2.2. Empirical Rule for Photocycloaddition Modes Prediction

Some empirical rules to formulate factors that affect the regioselectivity of this photocycloaddition were proposed by several researchers.

Bryce-Smith postulated that differences in ionization potentials (ΔIP) between the benzene ring and the alkene could be used to predict the mode of the cyclization.[21] *Ortho* cycloaddition is preferred with a strong donor and acceptor alkenes (9.6 eV < IP < 8.65

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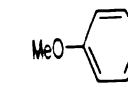
eV) while *meta* cycloaddition is preferred in the reactions between benzene (IP=9.24eV) and alkenes having IP's ranging from 9.6 eV to 8.65 eV.

Houk derived the same conclusion as Bryce-Smith and Gilbert but on the basis of orbital interactions. They also found that the ortho cycloaddition is favored when the alkene is either a better donor or a better acceptor than benzene.[22]

Mattay[23,24] has also presented an empirical correlation between the modes of cycloaddition and the free enthalpies of electron transfer based on the exciplex mechanism and the Weller equation. According to Mattay's rule, the Gibbs free energy (ΔG) of electron transfer can be accurately calculated from redox potentials of starting materials, excitation energy of the excited species, and coulombic interaction energy. In general, the mode of cycloaddition changes from meta to ortho when ΔG is 1.4-1.6 eV and electron transfer predominates when $\Delta G \leq 0$.

Gilbert demonstrated this empirical rule in photoreactions of benzenes with both electron releasing and electron withdrawing substituents. Photocycloaddition between 4-methoxybenzonitrile and cis-cyclooctene produces the endo meta cycloadduct while photocycloaddition between electron rich ethyl vinyl ether and 4-methoxybenzonitrile gives a 2:1 mixture of ortho cycloaddition products, 1-cyano-8-ethoxy-4-methoxy[4.2.$0^{1,6}$]octa-2,4-diene and 4-cyano-7-ethoxy-1-methoxy[4.2.0]octa-2,4-diene respectively.[25]



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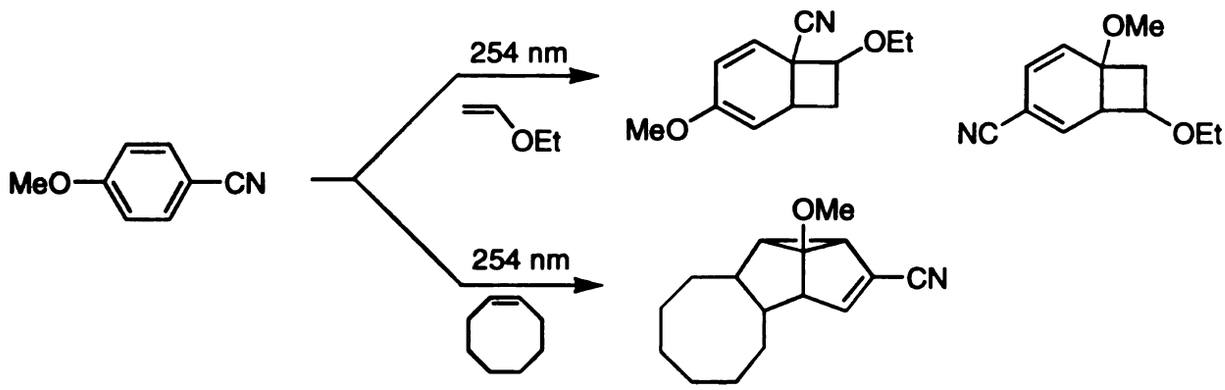

1.3. Photocycloaddition of Triplet benzene to Double Bonds

1.3.1. Nature of the Excited State of Substituted Benzene

Since its frontier orbitals are degenerate the actual frontier orbital of benzene cannot be described with a single frontier orbital but rather combinations of four frontier orbitals. The lowest excited triplet (T_1) and second lowest excited singlet (S_2) is represented as $\Psi_3\Psi_4 + \Psi_2\Psi_5$ (B_{1u}) and the lowest excited singlet (S_1) is represented as $\Psi_3\Psi_5 - \Psi_2\Psi_4$ (B_{2u}). [26] Substitution on the benzene ring with an electron-withdrawing group like cyano or acyl group simplifies the description of the excited states of substituted benzenes by removing the degeneracy of the frontier orbitals. If an electron-withdrawing group stabilizes Ψ_4 and destabilizes Ψ_3 then the lowest excited triplet, $^3B_{1u}$, (T_1) would be mostly a $\Psi_3\Psi_4$ component. Carbons 1 and 4, top and bottom carbons on the ring would possess high electron density.

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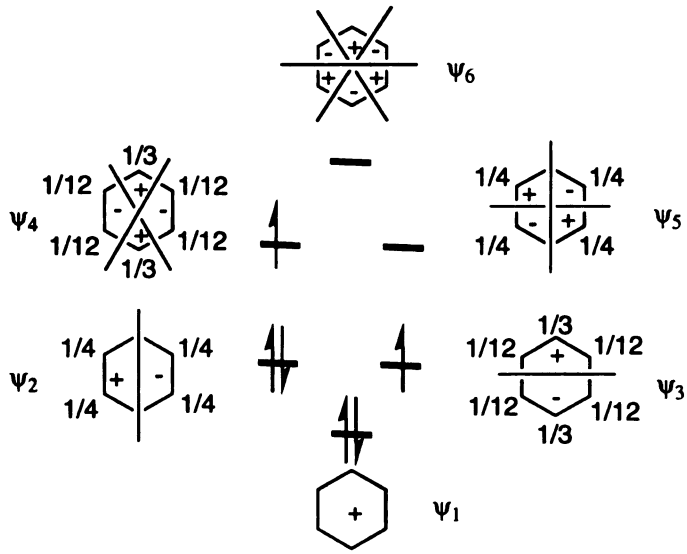
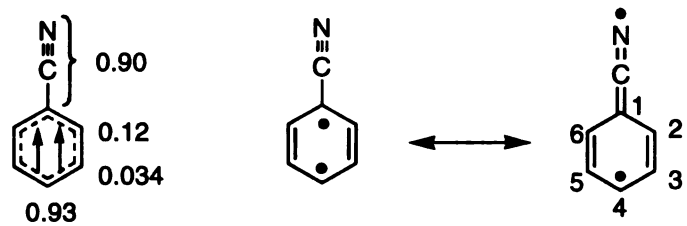


Generally, it is very difficult to know the exact electronic charge and spin density distribution of excited states. However, it can be predicted from reaction products, kinetics, some spectroscopic analysis, and quantum mechanical calculations. Wagner[27, 28] and Hirota[29] independently found that ortho and para to the nitrile group has the highest spin density in triplet benzonitriles.



Wagner pointed out that triplet benzonitrile is essentially a 1,4 diradical on the basis of analysis of the EPR spectra of triplet fluorobenzonitriles. The study showed that spin density on the carbon (C4) para to the cyano group is close to unity as shown above.

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This strongly suggested that a quinoidal structure is the most dominant valence bond structure for the benzonitrile triplet state.

Paquette and co-workers[30] reported several examples of regiospecificity in the di-π-methane rearrangements of benzonorboradienes substituted by electron donating or electron withdrawing groups. They have shown that cyano and acetyl substituents direct the rearrangement such that the double bond bridges to the benzene ring ortho or para but not meta. This suggests that the excited state is a 1,4 diradical.

1.3.2. Triplet Phenyl Ketone

Phenyl ketones are known to reach their triplet states with fast efficient intersystem crossing rate ($k_{isc} \sim 10^{11} sec^{-1}$, $\Phi isc=1$) via the n,π* lowest singlet state.[31, 32] The lowest triplet of phenyl ketones could be either n,π* or π,π* depending on the patterns of ring substituents. The n,π* transition is a result of excitation of a non-bonding electron of oxygen to the π* orbital of the carbonyl group and produces an alkoxy radical-like excited state.[33,34] On the other hand, π,π* transition is made by the excitation of an π electron to π* of whole π bond system of the molecule and π,π* triplets show little radical-like reactivity. This is because of charge-transfer components and a lack of strong spin localization on the carbonyl oxygen.[35,36]

Generally, unsubstituted alkyl phenyl ketones have n,π* lowest triplets about 3 kcal per mole lower in energy than their π,π* triplets. However electron-donating substituents at any ring position lower π,π* and raise n,π* transition energies to generate

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a π,π^* lowest triplet state.[16] On the other hand, inductively electron-withdrawing substituents lower n,π^* transition energies relative to π,π^* energies.[16,37,38] Para electron-withdrawing substituents like carbonyl and nitrile groups lower π,π^* triplet energies and π,π^* triplet becomes the lowest triplet. Meta substituents do not stabilize π,π^* triplets enough to invert triplet levels.[39]

1.3.3. Biradical character of π,π^* triplet state of acylbenzene

Wagner and Nahm discovered the first intramolecular 1,2-photocyclization of a triplet benzene to an olefin during their study of the intramolecular quenching of π,π^* triplets of ketones with remote unsaturated tethers.[8, 9] They found that double bonds add intramolecularly to the benzene moiety of phenyl ketones with the lowest π,π^* triplet states while phenyl ketone with the lowest n,π^* triplet states did not show any modes of cycloaddition reactivity. The difference in reactivity for the two types of triplets is attributed to their different spin densities at the para position to the carbonyl group. The n,π^* triplet has only partial radical character at the para position while the π,π^* triplet has almost full radical character at the para carbon. Valence bond representations of two triplet states for an aryl ketone are shown below.[27]

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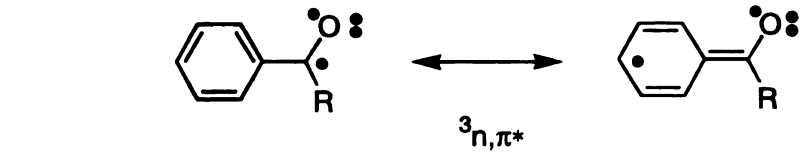

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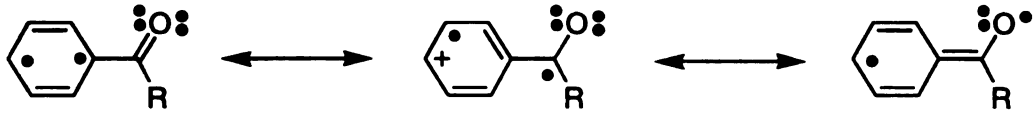

$^3\pi,\pi^*$

Both ortho and para-substituted ketones with the π,π^* triplet state undergoes intramolecular ortho cycloaddition, but meta-substituted ketones do not show any reactivity. This is attributed to the amount of unpaired electron density at those three position in the π,π^* triplet; unlike ortho and para positions, the meta position has very little spin density.[28]

Wagner and Sakamoto[40] demonstrated the effect of spin density on the reactivity of photocycloaddition reaction by irradiation of both 1-butenoxy-2-acetonaphthone and 2-butenoxy-1-acetonaphthone. Two acetonaphthone promoted ortho photocycloaddition from their π,π^* triplet states. Due to the different spin density, two isomer **a** and **b** showed the large kinetic differences. A faster reaction rate for isomer **a** than isomer **b** is attributed to the higher unpaired electron density on the α positions versus the β positions of naphthalene ring in triplet states.

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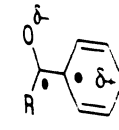

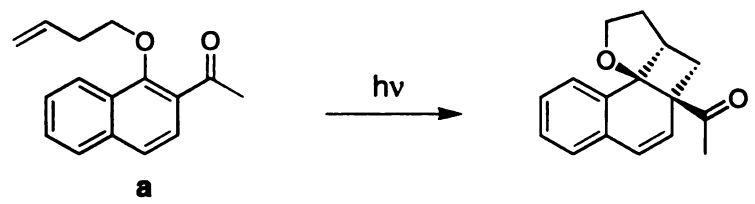

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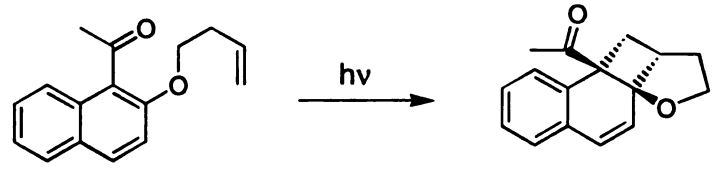

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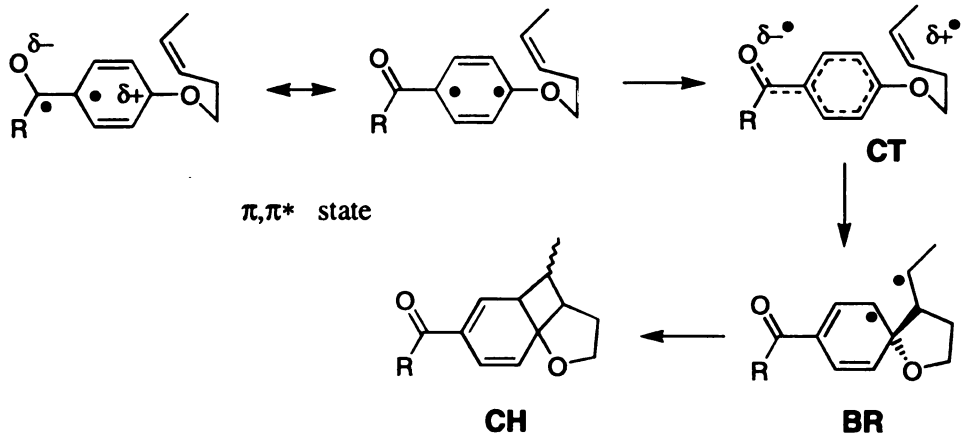
Wagner proposed that the π,π* triplet behaves like a biradical, one radical site adding to the remote double bond the way a 5-hexenyl radical would cyclize, generating the 1,4-biradical (**BR**) that cyclizes to form **CH** as shown below.



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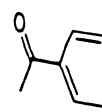

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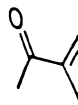
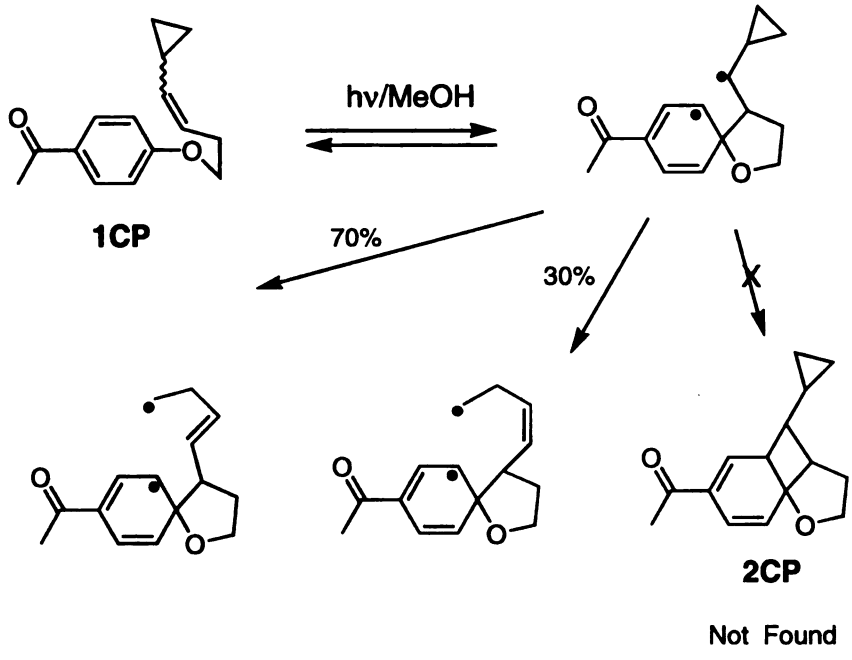


1.3.4. Biradical Intermediate

Upon irradiation of phenyl ketone, a charge transfer complex (CT) is formed, which is followed by the cycloaddition of the radical center para to the acyl group to the remote double bond. The addition generates a 1,4 biradical which will either close to the initial photoproduct or cleave to give starting material. During decay to the starting material cis-trans isomerization was observed supporting the presence of a biradical intermediate during the course of reaction.[8]

The photochemistry of **1CP** which, has a cyclopropyl group at the double bond, was carried out to support the idea of a 1,4 biradical intermediacy.[41] No cyclopropyl ring was observed intact after irradiation of **1CP**. The opening of the cyclopropyl ring strongly suggests the existence of a biradical intermediate as shown below.



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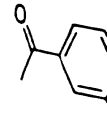
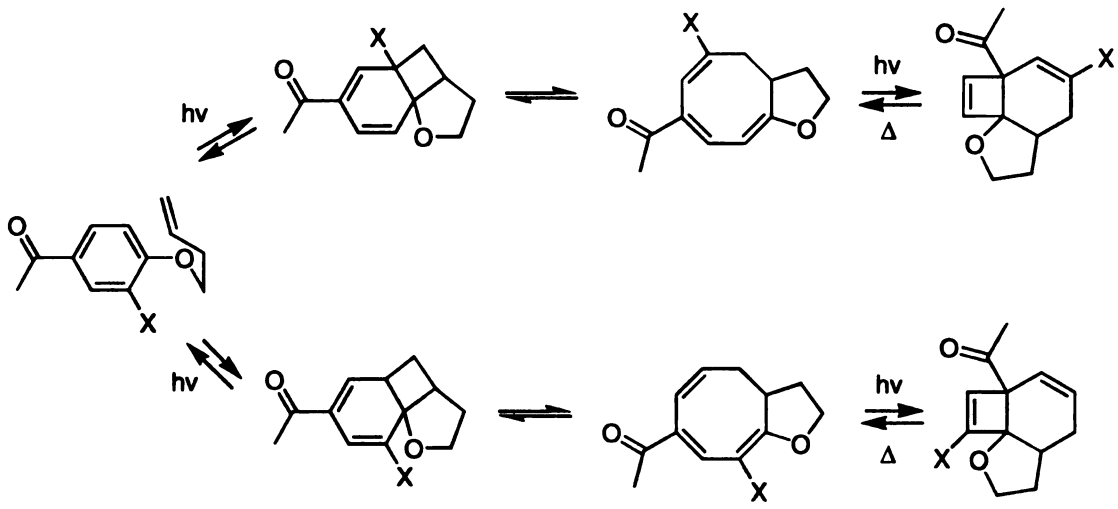


1.3.5. Regioselectivity

Introduction of a third substituent on the benzene ring of the p-alkenoxy ketones creates two possible directions of cycloaddition, one added toward and one added away from the third substituent.

Electron withdrawing and alkyl groups ortho to the alkenoxy group cause the alkene moiety to add toward the third substituent. Strong electron donating groups force the remote double bond to add away from the third group. Wagner, Sakamoto and Madkour[42] suggested that this regioselectivity reflects inductive effects of the third substituent both on the nature of initial triplet state cycloaddition and the competing thermal and photochemical reactions of the resultant photoproducts.



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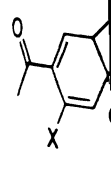

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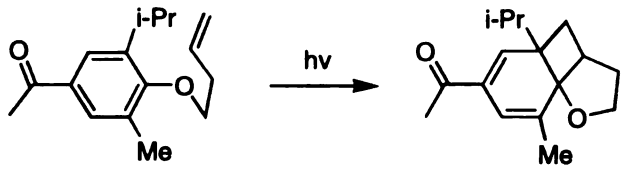
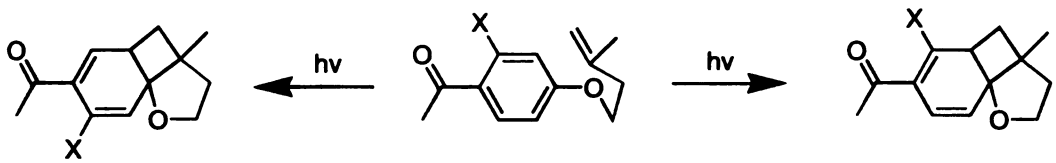
Wagner pointed out that the preference for addition toward isopropyl rather than methyl is a steric effect.[10]



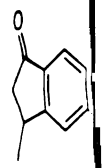
Wagner and Smart observed a higher degree of regioselectivity in a system with little steric interaction between the third group and the alkene tether.[43] Regardless of the electronic nature of the third substituents ortho to the acetyl group, photocycloaddition occurs toward them. Only fluorine was found to give 9% of the other isomer.



X=F (9%)

X=Me, OMe, CF_3 and F (91%)

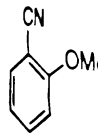
Wagner suggested that the direction of the carbonyl induced the regioselectivity based on the fact that fluorine, the smallest substituent studied, is the only one that showed both regioisomers. Wagner and Smart[43] also observed that indanone, whose carbonyl is pointing away from the alkyl group, generated only regioisomers with the double bonds adding away from the substituents.



1.3.6. Benz

Gilb

photocycloa

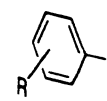


2` a

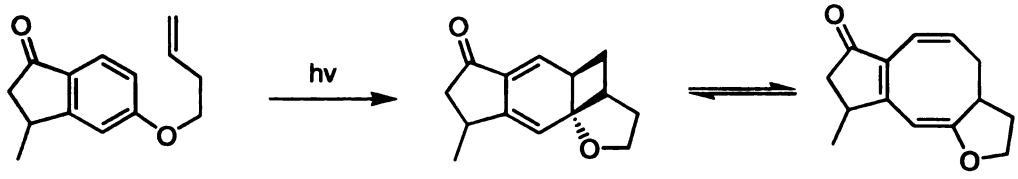
intramolecu

Gilbert[45] a

by 1,3 dien

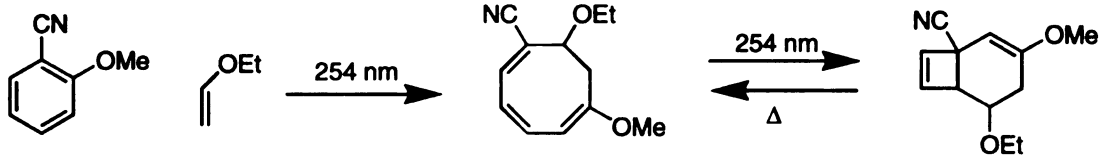


R=2' C
4' C

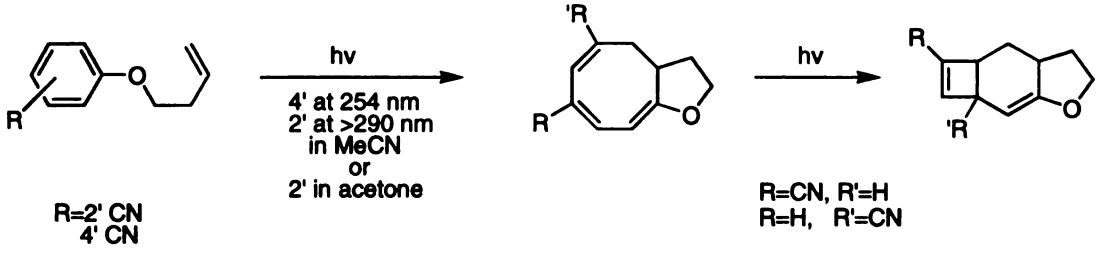


1.3.6. Benzonitrile System

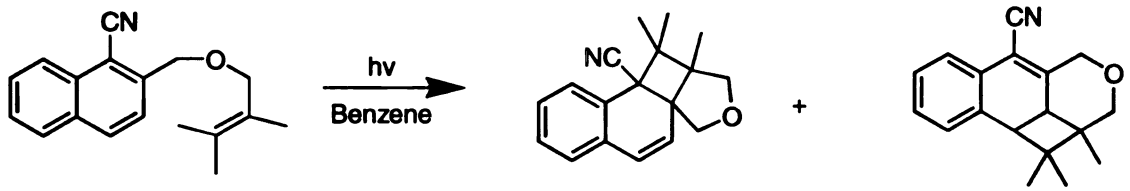
Gilbert reported that 2-methoxybenzonitriles undergoes efficient intermolecular photocycloaddition with electron rich alkenes.[44]



2' and 4' cyano substituted 4-phenoxybut-1-ene were shown to undergo intramolecular ortho cycloaddition upon both direct irradiation and triplet sensitization by Gilbert[45] and Wagner[46], respectively. The formation of the cyclooctatriene was quenched by 1,3 dienes whereas its intramolecular cyclization to cyclobutene was not quenched.



McCullough[47] observed that naphthonitrile systems show the same type of cycloaddition. When 2,3-dimethyl-2-butenyl(1-cyano-2-naphthyl) methyl ether in benzene was irradiated, a 20:1 mixture of two ortho cycloaddition products, **c** and **d**, respectively were detected as shown below. During the reaction no ring opening to cyclooctatriene was observed. Prolonged irradiation removed the initially formed major product and produced only one cycloadduct, **d** that was initially formed as the minor isomer.



c **d**

1.4. ^{1}H NM

In th

^{1}H NMR d

understand

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products th

Wagner re

chemical sh

1.4. ^{1}H NMR Data For Some Photoproducts

In the process of characterizing photoproducts so as to differentiate regioisomers, ^{1}H NMR data analysis played a crucial role throughout this research. Therefore, thorough understanding of the ^{1}H NMR spectra for many similar skeletal structures is necessary. The following tables are a collection of key ^{1}H NMR data of some ortho cycloaddition products that are **CH**, **CO**, **CB** and **LCB**, previously reported by other members of the Wagner research group. Product assignments depended heavily on comparison of NMR chemical shifts and coupling constants.

Table 1.

oabicyclo[

Chemical S
6.27(12.5) 2.38 O $CDCl_3$
6.02(11.3 6.36(11.3) O $CDCl_3$
5.92(br s) O C_6D_6
7.13(6.2) 5.75(13, 6.2 6.0 $CDCl_3$

Table 1. Selected chemical shifts and coupling constants of some 4-acetyl-11-oabicyclo[6.3.0]undeca-1,3,5-triene (**COT**) derivatives

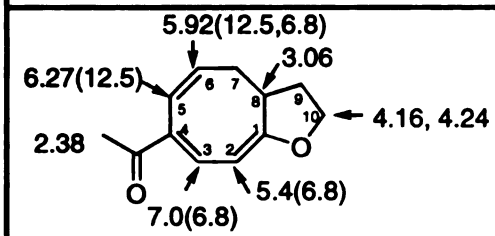
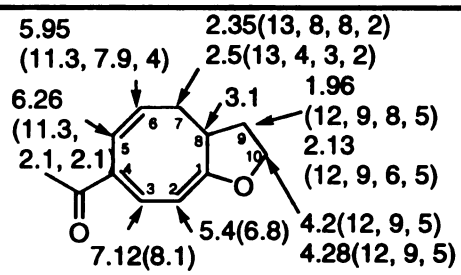
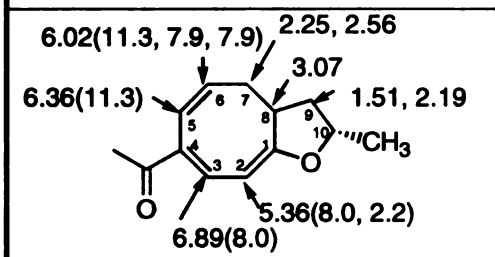
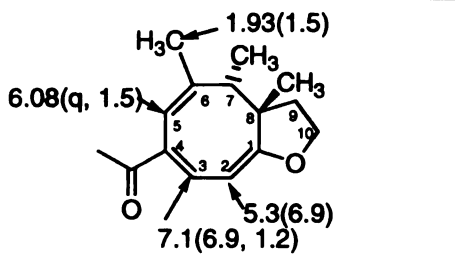
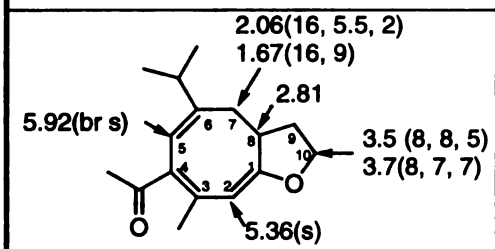
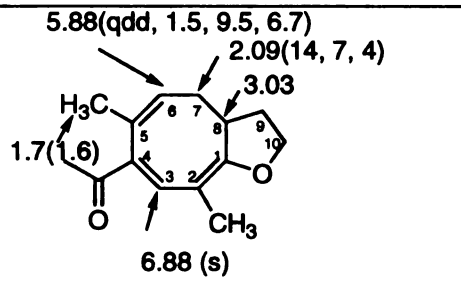
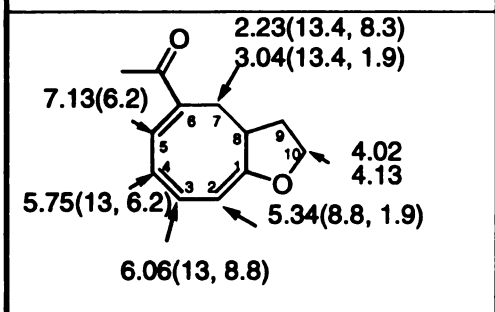
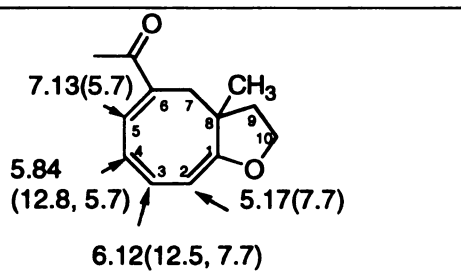
Chemical Shifts (coupling constants)	Ref.	Chemical Shifts (coupling constants)	Ref.
 $CDCl_3$	9	 CD_3OD	48
 $CDCl_3$	48	 CD_3OD	48
 C_6D_6	49	 $CDCl_3$	49
 $CDCl_3$	50	 $CDCl_3$	50

Table 1. (C

7.05(6.1) 5.73 (13.2, 6.1) 6.0 $CDCl_3$	
5.24(9.3,7. H_3CO O 7.19(5.3 $CDCl_3$	
6.8(9.2,6.5 F_3C O 7.2(4.8) $CDCl_3$	

Table 1. (Cont'd)

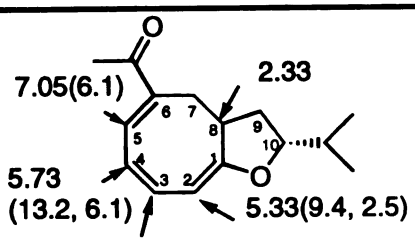
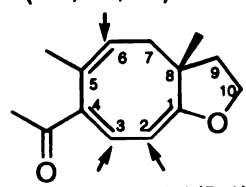
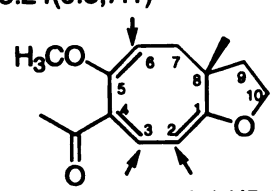
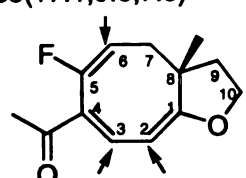
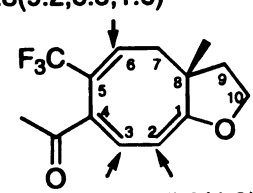
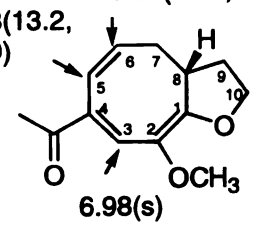
 $CDCl_3$	48	5.92(9.5,6.3,1.6)  $CDCl_3$	49
5.24(9.3,7.1)  $CDCl_3$	49	5.85(17.1,9.6,7.5)  $CDCl_3$	49
6.8(9.2,6.5,1.6)  $CDCl_3$	49	5.94(13.1,5.94) 6.28(13.2, 2.19)  $CDCl_3$	51

Table 2.

oxatricycl

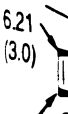
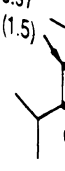
Chemical
5.85(2.7)
6.06(2.7
C_6D_6
6.43(2.9)
6.5(2.9)
CD_3OD
6.21 (3.0)  6.33 (3.0)
CD_3OD
5.97 (1.5)  3.62(3.72(
C_6D_6

Table 2. Selected chemical shifts and coupling constants of some 4-acetyl-11-oxatricyclo[6.3.0.0^{1,4}]undeca-2,5-diene (**CB**) derivatives

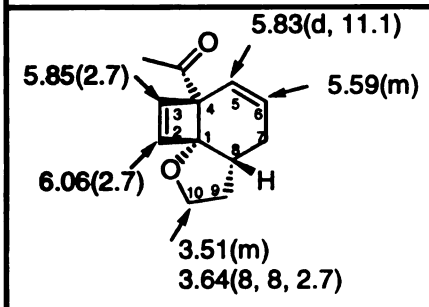
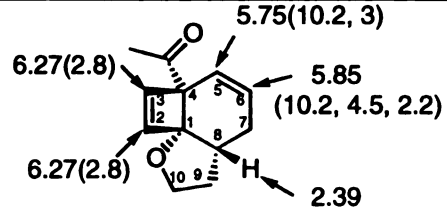
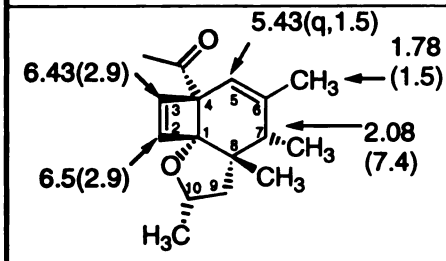
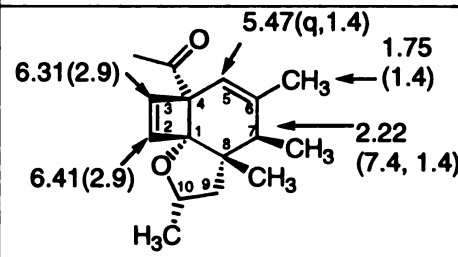
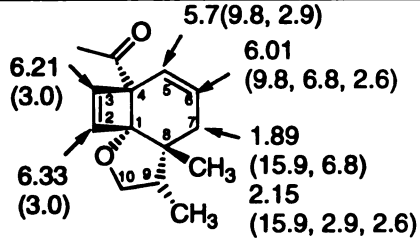
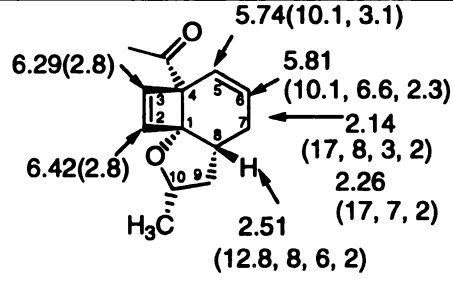
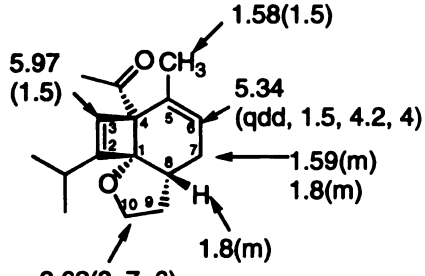
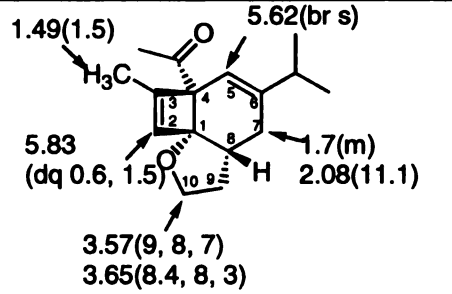
Chemical Shifts (coupling constants)	Ref.	Chemical Shifts (coupling constants)	Ref.
 C_6D_6	50	 CD_3OD	48
 CD_3OD	48	 CD_3OD	48
 CD_3OD	48	 CD_3OD	48
 C_6D_6	49	 C_6D_6	49

Table 2. (

6.28(3.03	
6.50(3.03	
CD_3OD	
6.35(2.9)	
6.5(2.94)	
CD_3OD	

Table 2. (Cont'd)

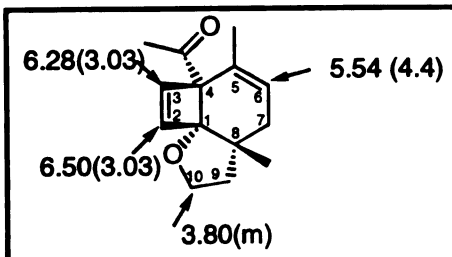
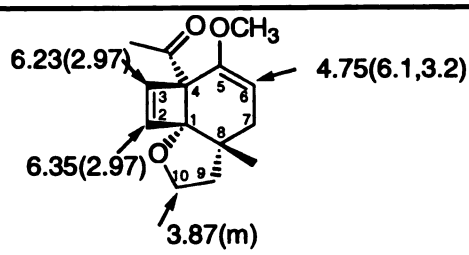
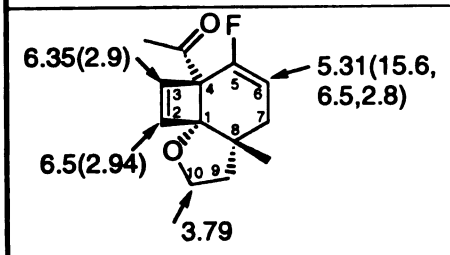
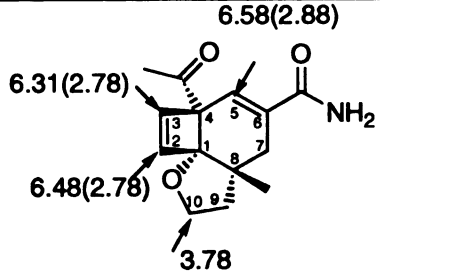
 CD_3OD	49	 CD_3OD	49
 CD_3OD	49	 CD_3OD	51

Table 3

oxatricyc

Chemical
5.81(2.8
6.04(2.8,
3
(
C_6D_6
6.11(2.8)
6.15(2.8)
3.42
(6.6
CD_3OD
6.24(2.8)
6.36
(2.8, 0.9)
3.49
(6.6,
C_6D_6

Table 3. Selected chemical shifts and coupling constants of some 4-acetyl-11-oxatricyclo[6.3.0.$0^{3,6}$]undeca-1,4-diene (**LCB**) derivatives

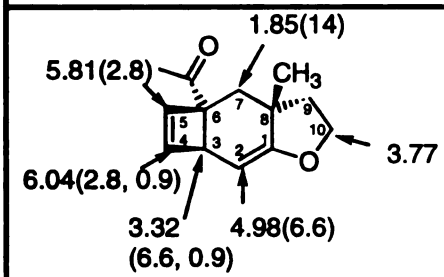
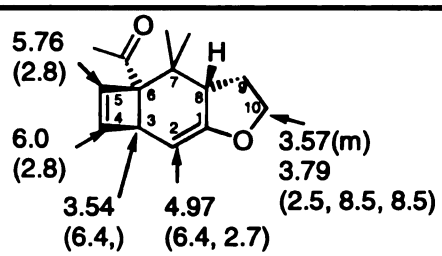
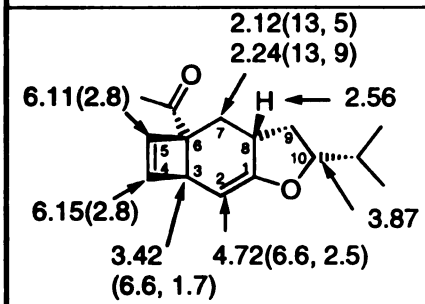
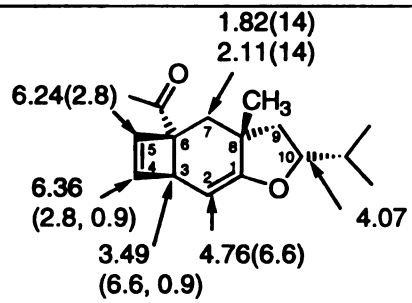
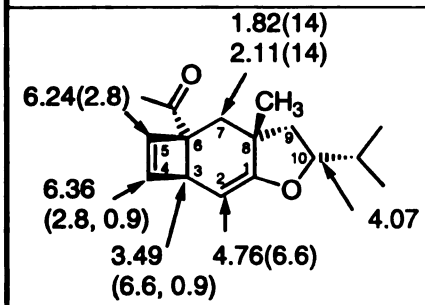
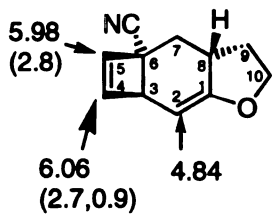
Chemical Shifts (coupling constants)	Ref.	Chemical Shifts (coupling constants)	Ref.
 C_6D_6	9	 C_6D_6	50
 CD_3OD	49	 CD_3OD	48
 C_6D_6	51	 $CDCl_3$	51

Table 4

oxatricyc

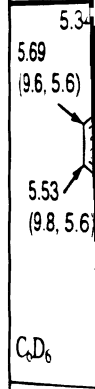
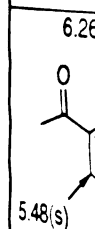
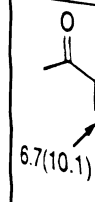
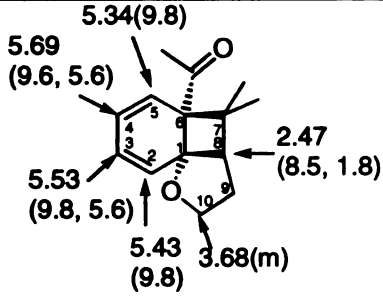
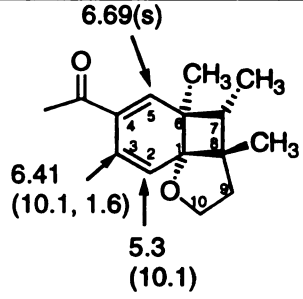
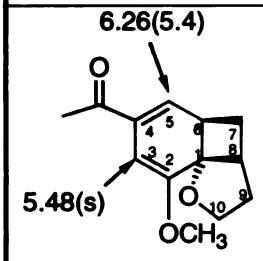
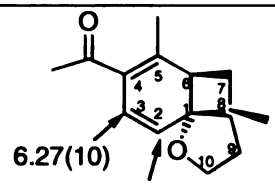
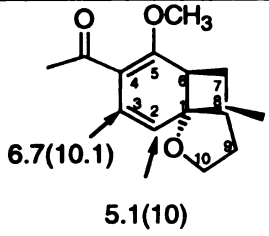
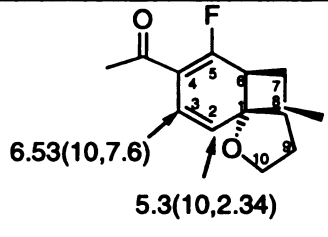
Chemical
 C_6D_6
 $CDCl_3$
 CD_3OD

Table 4. Selected chemical shifts and coupling constants of some 4-acetyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene (**CH**) derivatives

Chemical Shifts (coupling constants)	Ref.	Chemical Shifts (coupling constants)	Ref.
 C_6D_6	8	 CD_3OD	49
 $CDCl_3$	52	 $CDCl_3$	49
 CD_3OD	49	 $CDCl_3$	49

1.5. Goal

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1.5. Goals of Research

The goal of this research is to understand the mechanism of photochemical cycloadditions of excited triplet benzene to alkenes. The main focus of this study is:

a. To determine the regioselectivity of the initial ortho photocyclization onto bezene rings with substituents ortho to carbonyl and cyano groups.

b. To study the effect of the dipole moment of electron withdrawing groups such as acyl and nitrile on the corresponding regioselectivity.

2.1. Ring

Table 5. T

Ring S
W=aldehy
W=aldehy
W=aldehy
W=aldehy
W=CN, F
W=CN, F
W=CN, F
W=CN, F
W, R=CO
W, R=CO

Part 2. Results

2.1. Ring Substitution

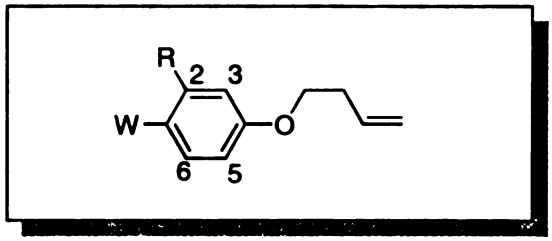

Figure 1. Structure of photoreactants

Table 5. Thesis notation of photoreactants

Ring Substituents	Name	Thesis Notation
W=aldehyde, R=CH_3	4-(3-Buten-1-oxy)-2-methylbenzaldehyde	Al-CH3
W=aldehyde, R=OCH_3	4-(3-Buten-1-oxy)-2-methoxybenzaldehyde	Al-OCH3
W=aldehyde, R=F	4-(3-Buten-1-oxy)-2-fluorobenzaldehyde	Al-F
W=aldehyde, R=CF_3	4-(3-Buten-1-oxy)-2-trifluoromethylbenzaldehyde	Al-CF3
W=CN, R=CH_3	4-(3-Buten-1-oxy)-2-methylbenzonitrile	CN-CH3
W=CN, R=OCH_3	4-(3-Buten-1-oxy)-2-methoxybenzonitrile	CN-OCH3
W=CN, R=F	4-(3-Buten-1-oxy)-2-fluorobenzonitrile	CN-F
W=CN, R=CF_3	4-(3-Buten-1-oxy)-2-trifluoromethylbenzonitrile	CN-CF3
W, R=$COCH_2CH_2CH_2$	6-(3-Buten-1-oxy)-1-tetralone	TT
W, R=$COCH_2CH_2O$	2,3-Dihydro-7-(3-buten-1-oxy)-4H-benzopyran-4-one	CR

2.2. Prep

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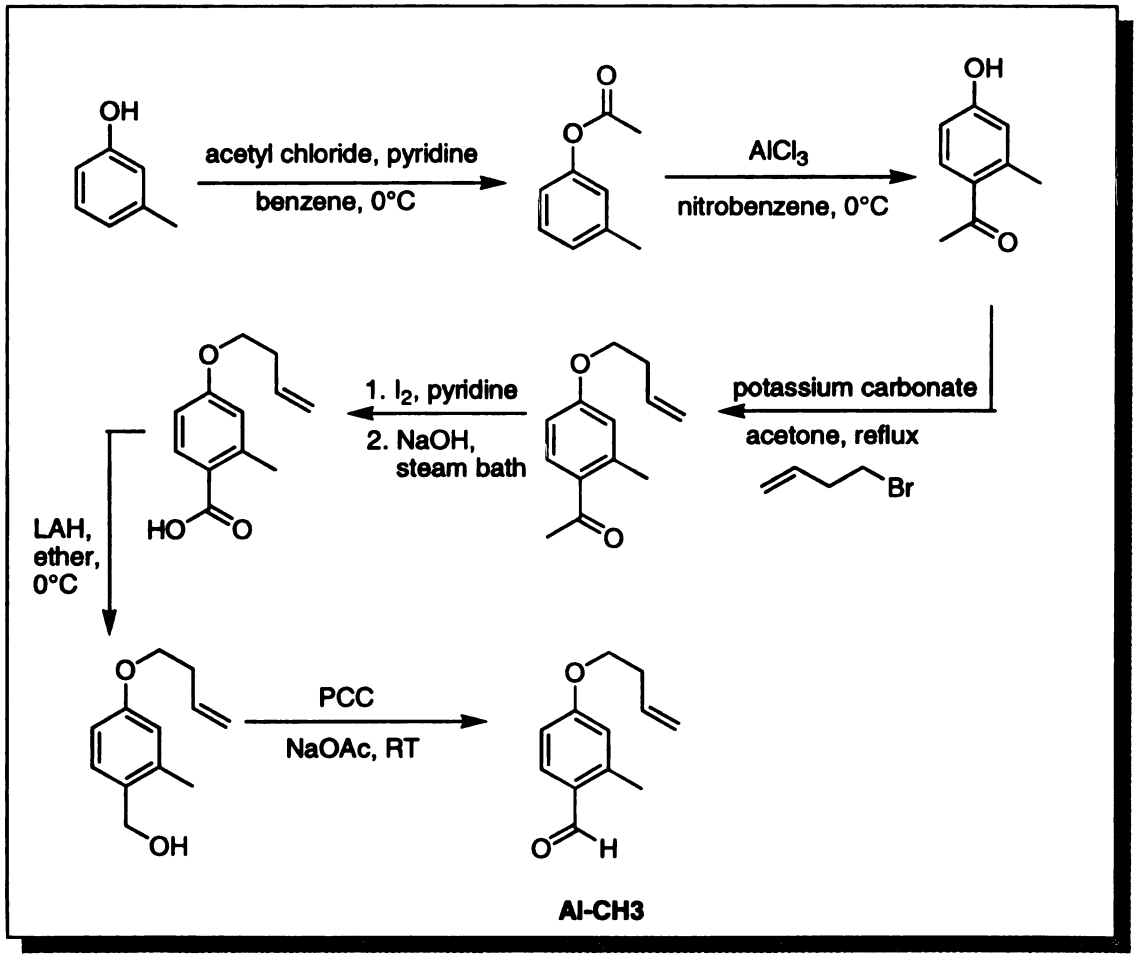
2.2. Preparation of Reactants

4-(3-Buten-1-oxy)-2-methylbenzaldehyde (**Al-CH3**) was prepared by esterification of cresol with acetyl chloride in pyridine and benzene at 0°C followed by Fries rearrangement[49] with aluminum chloride in nitrobenzene at 0°C. The resulting phenol was alkylated using 4-bromobutene with potassium carbonate in refluxing acetone followed by oxidation of the acetyl group with iodine. The carboxylic acid was reduced by lithium aluminium hydride (LAH) to the alcohol which was then oxidized to 4-(3-buten-1-oxy)-2-methylbenzaldehyde by pyridinium chlorochromate (PCC).



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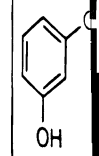

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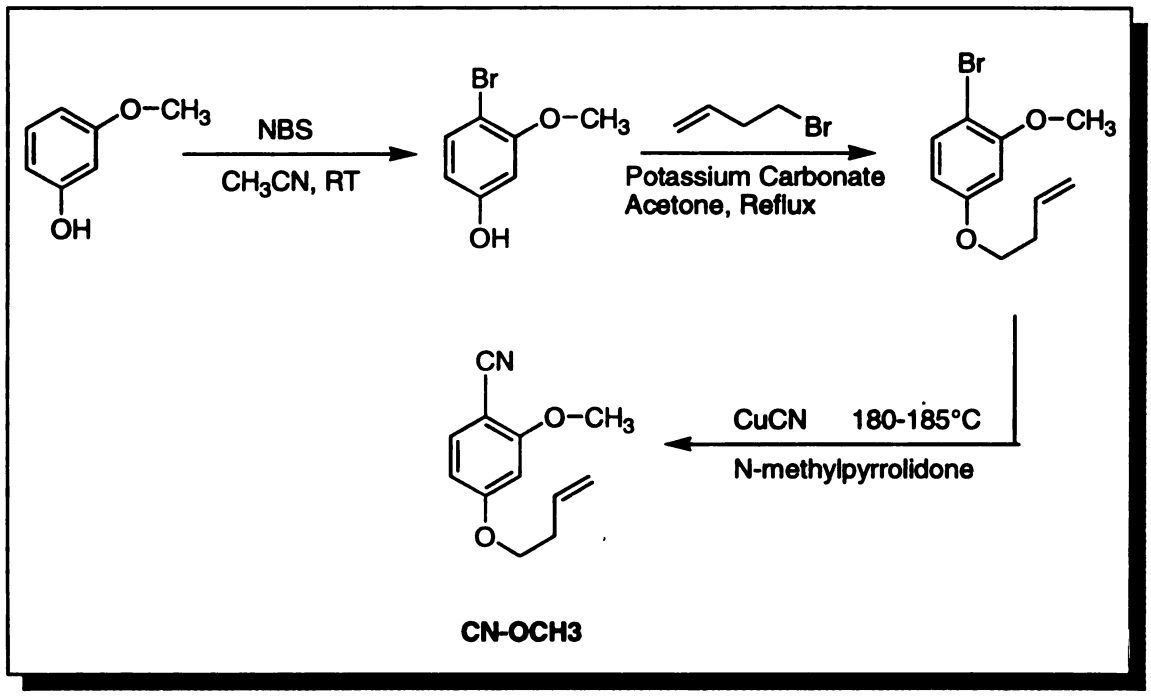
4-(3-Buten-1-oxy)-2-methoxybenzonitrile (**CN-OCH3**) was prepared by bromination[53] of 3-methoxyphenol in acetonitrile followed by alkylation using 4-bromobutene with potassium carbonate in refluxing acetone. The resulting product was treated by copper cyanide in N-methylpyrrolidone[54] at 180-185 °C to produce 4-(3-buten-1-oxy)-2-methoxybenzonitrile.



CN-OCH3

4-(3-Buten-1-oxy)-2-methoxybenzaldehyde (**Al-OCH3**) was prepared by reduction[55] of the cyano group of 4-(3-buten-1-oxy)-2-methoxybenzonitrile using diisobutylaluminium hydride (DIBAH) in hexane at –78 °C.

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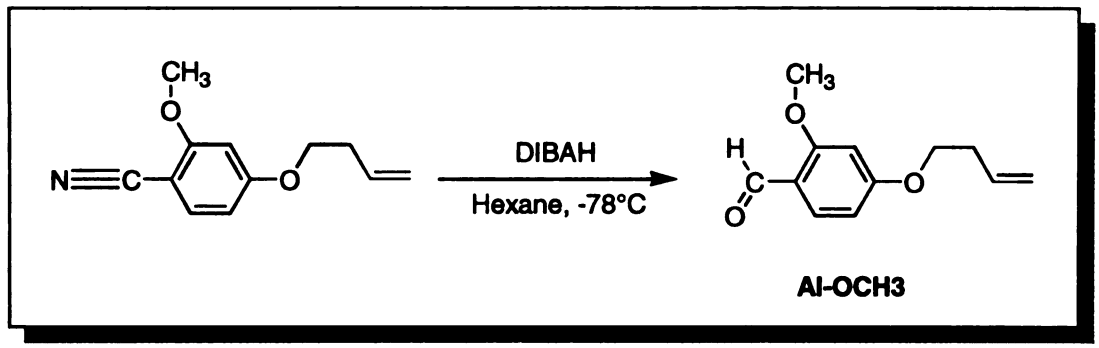
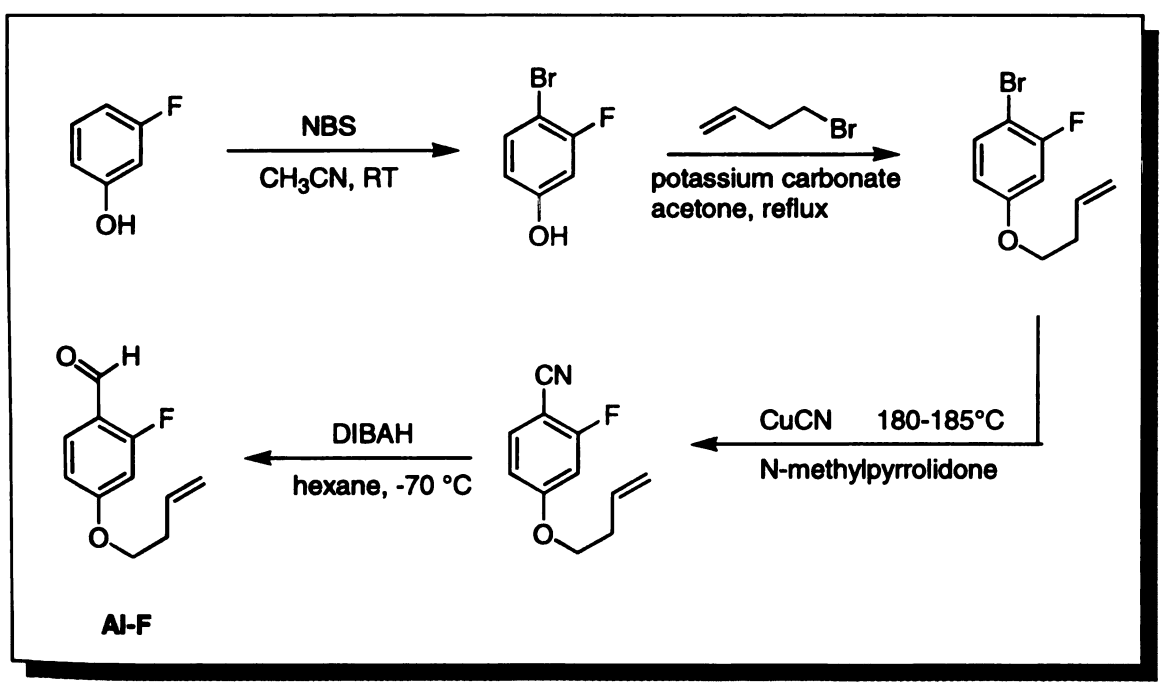
(DIBAH)

Al-F



4-(3-Buten-1-oxy)-2-fluorobenzaldehyde (**Al-F**) was prepared by bromination of 3-methoxyphenol in acetonitrile followed by alkylation using 4-bromobutene with potassium carbonate in acetone while refluxing. The resulting product, 1-bromo-4-(3-buten-1-oxy)-2-fluorobenzene, was treated by copper cyanide in N-methylpyrrolidone at 180-185 °C to replace the bromine atom with a cyano group. The resulting product, 4-(3-buten-1-oxy)-2-fluorobenzonitrile, was reduced with diisobutylaluminium hydride (DIBAH) in hexane at –70 °C to afford Al-F.



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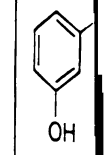

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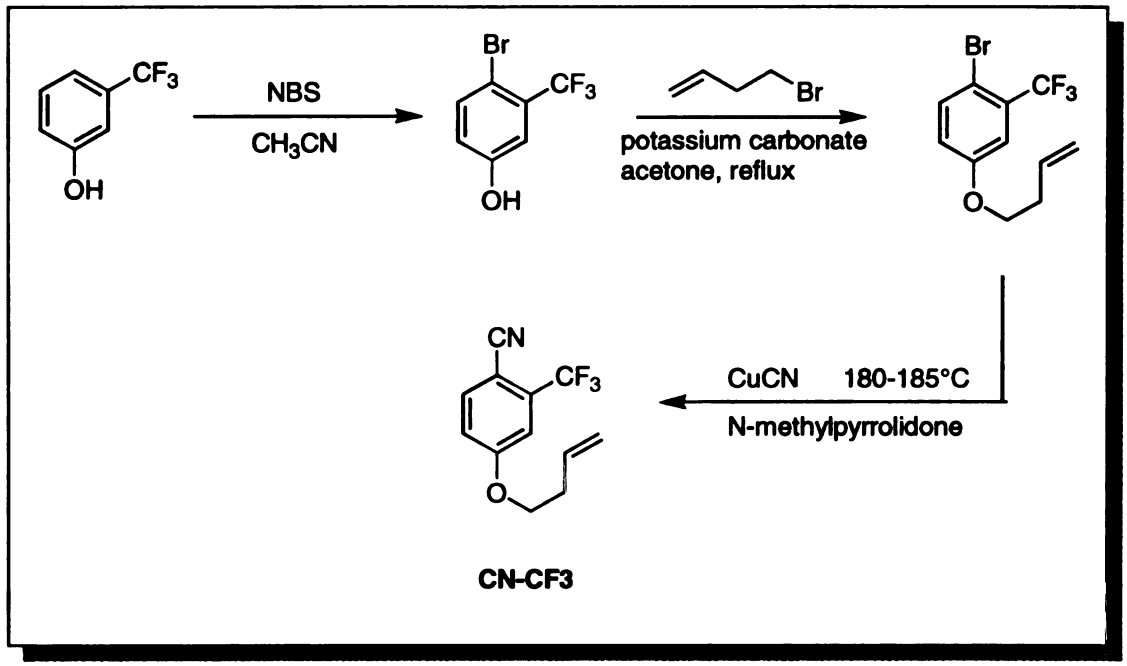
4-(3-Buten-1-oxy)-2-trifluoromethylbenzonitrile (**CN-CF3**) was prepared by bromination[56] of 3-trifluoromethylphenol in acetonitrile followed by alkylation using 4-bromobutene with potassium carbonate in acetone while refluxing. The resulting product, 1-bromo-4-(3-buten-1-oxy)-2-trifluoromethylbenzene, was treated by copper cyanide in N-methylpyrrolidone at 180-185 °C to give **CN-CF3**.



CN-CF3

4-(3-Buten-1-oxy)-2-trifluoromethylbenzaldehyde (**Al-CF3**) was prepared by reduction of cyano group of **CN-CF3** using diisobutylaluminium hydride (DIBAH) in hexane at –78 °C.

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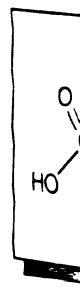

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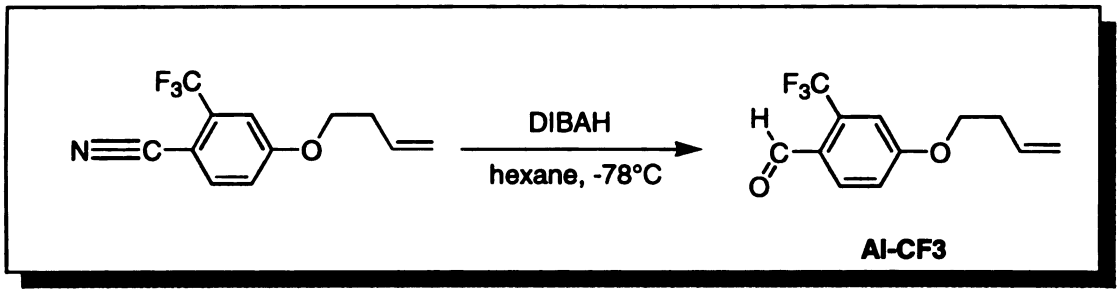
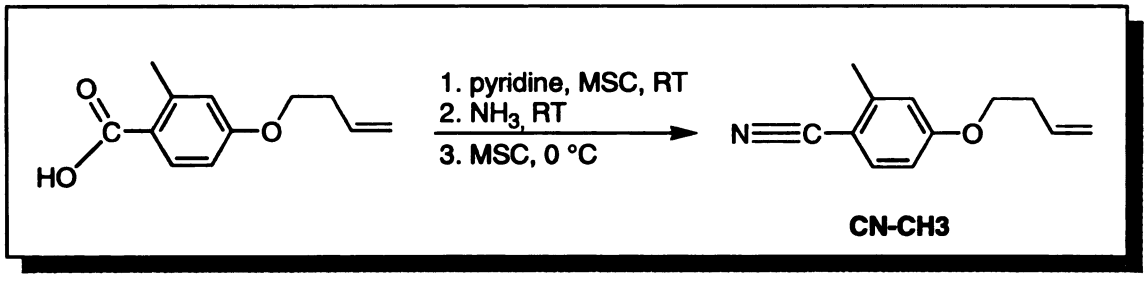
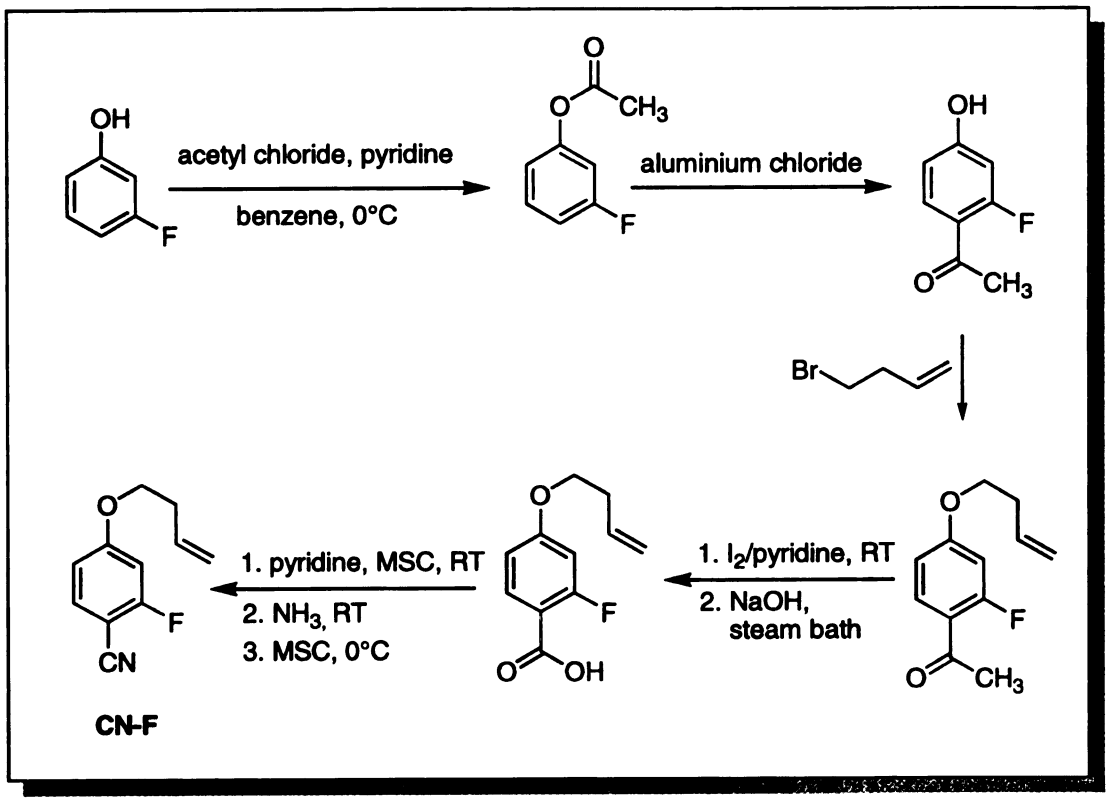


4-(3-Buten-1-oxy)-2-methylbenzonitrile (**CN-CH3**) was prepared by sulfonylation of carboxylic acid of 4-buten-1'-oxy-2-methylbenzoic acid with methylsulfonyl chloride (MSC) in pyridine followed by saturation with ammonia gas and then treatment again with methylsulfonyl chloride (MSC) to give **CN-CH3**.



4-(3-Buten-1-oxy)-2-trifluoromethylbenzonitrile (**CN-F**) was prepared by esterification of 3-fluorophenol with acetyl chloride in pyridine and benzene at 0°C followed by Fries rearrangement with aluminium chloride in nitrobenzene at 0°C. The resulting phenol was alkylated using 4-bromobutene with potassium carbonate inrefluxing acetone followed by oxidation of the acetyl group with iodine. The carboxylic acid, 4-buten-1'-oxy-2-methylbenzoic acid, was sulfonated with MSC in pyridine followed by saturation with ammonia gas and then treating again with methyl sulfonyl chloride (MSC) again to give **CN-F**.


OH
F
acetyl chloride, pyridine
benzene, 0°C
O
O
CH3
F
aluminium chloride
OH
F
O
CH3
Br
O
F
O
CH3
1. I2/pyridine, RT
2. NaOH,
steam bath
O
F
O
OH
1. pyridine, MSC, RT
2. NH3, RT
3. MSC, 0°C
O
F
CN
CN-F

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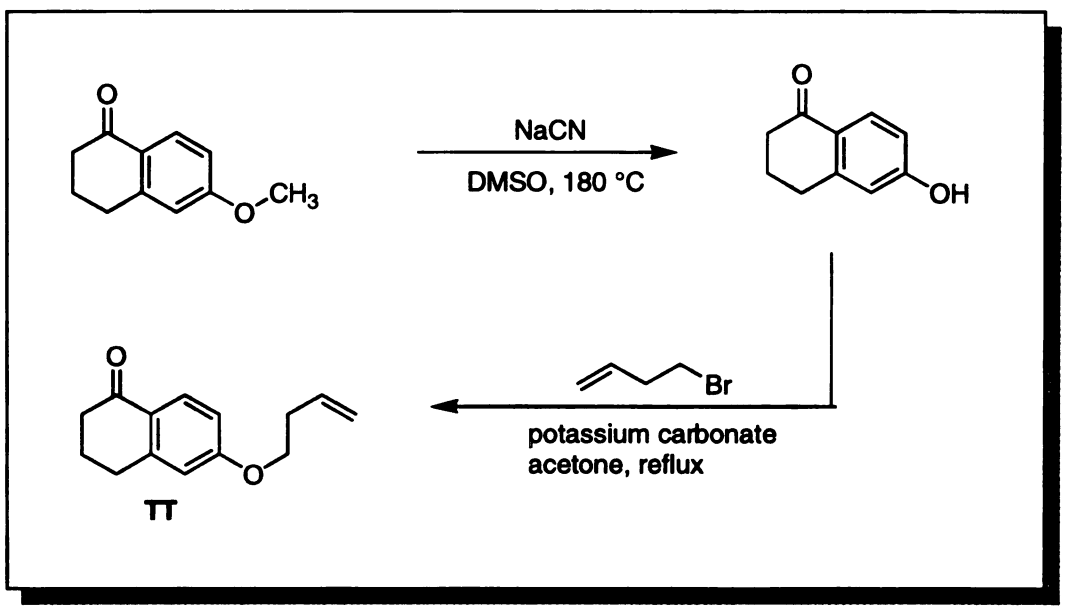
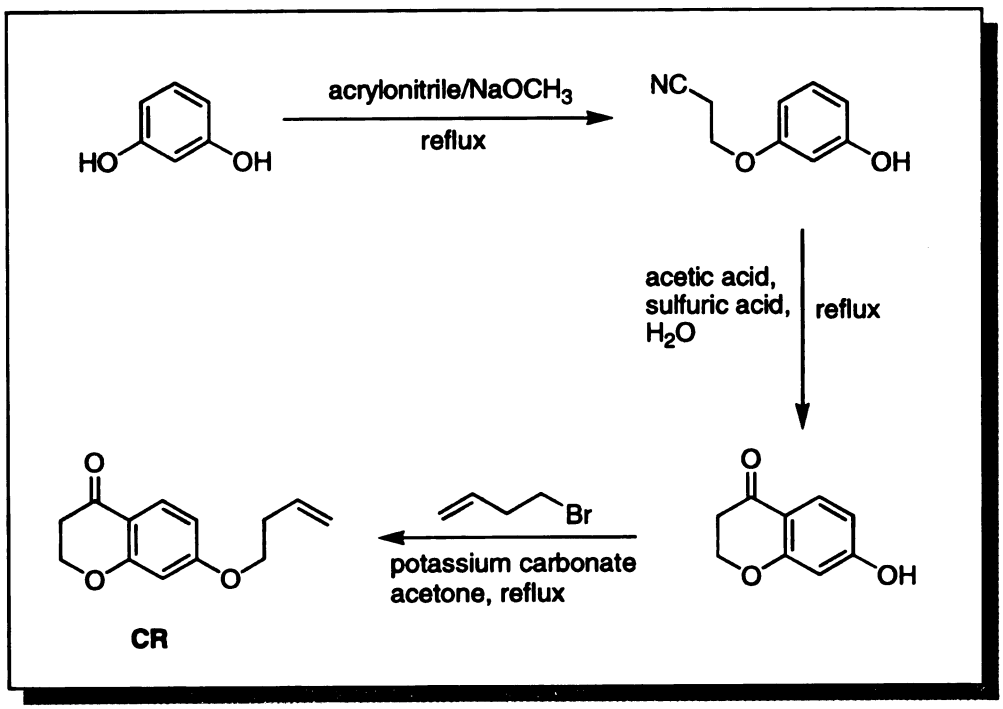
6-(3-Buten-1-oxy)-1-tetralone (**TT**) was prepared by demethylation of methoxytetralone using sodium cyanide in dimethyl sulfoxide (DMSO) at 180 °C followed by alkylation using 4-bromobutene with potassium carbonate in refluxing acetone.

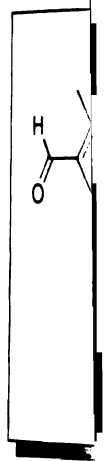


2,3-Dihydro-7-(3-buten-1-oxy)-4H-benzopyran-4-one (**CR**) was prepared by monoalkylation[57] of resorcinol using a refluxing mixture of acrylonitrile and sodium methoxide. Cyclization[58] was then done using an acetic acid-sulfuric acid-water mixture. The resulting product, 2,3-dihydro-7-hydroxy-4H-benzopyran-4-one, was alkylated using 4-bromobutene with potassium carbonate in refluxing acetone to give **CR**.


acrylonitrile/NaOCH3
reflux
HO
OH
NC
O
OH
acetic acid,
sulfuric acid,
H2O
reflux
O
OH
Br
potassium carbonate
acetone, reflux
O
O
O

CR

2.3. Ph



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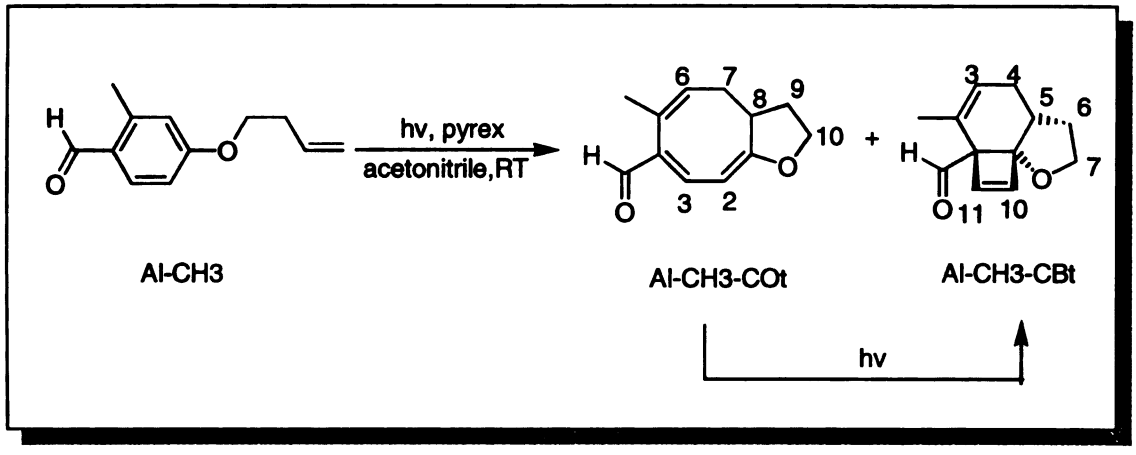
2.3. Photochemistry of 4-(3-buten-1-oxy)-2-methylbenzaldehyde (Al-CH3)



A solution of **Al-CH3** (1.9 mg) in deuterated acetonitrile (0.75 mL, 1.3 x 10^{-2} M) in NMR tube was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. One peak (a doublet around 6.42 ppm) was observed after 30 minutes but disappeared on prolonged irradiation. After three hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts. Preparatory scale photolysis was carried out to isolate the photoproducts. **Al-CH3** (150 mg) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium pressure mercury arc lamp through a Pyrex filter. After 7 hours of irradiation, ^{1}H NMR showed the presence of the starting aldehyde and its products. The reaction mixture was concentrated at reduced pressure immediately. The reaction mixtures were isolated and purified by preparative TLC followed by HPLC.

The photoproduct collected from HPLC at 3.5 minutes was identified as 4-formyl-5-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**Al-CH3-COt**) by its characteristic ^{1}H

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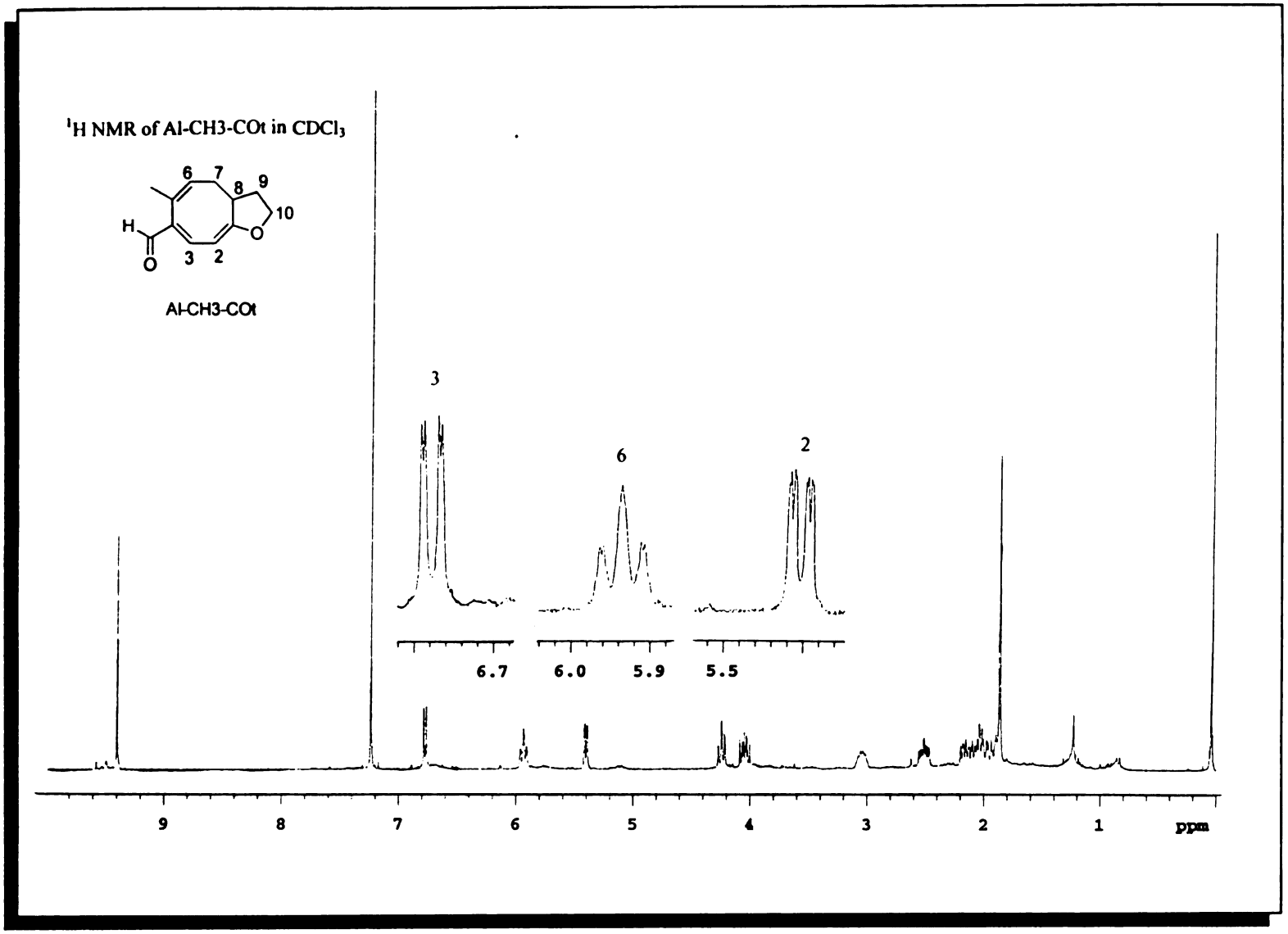
NMR. It showed peaks corresponding to three vinyl protons: a doublet of doublets at 6.77 ppm(H-3), a quartet of doublets of doublets at 5.93 ppm(H-6) and a doublet of doublets at 5.40(H-2). Peaks at 6.77 and 5.40 ppm are coupled to one another with 6.6 Hz coupling constant and both are also coupled to H-8 with 1.1 and 2.2 coupling constants, respectively. The peak at 5.93 ppm is assigned to H-6 coupled to two vicinal allylic protons H-7α and H-7β with 8.2 and 7.5 Hz coupling constants and to the methyl with 1.6 Hz coupling constant.

A thermally unstable photoproduct in the mixture was identified as 1-formyl-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,10-diene (**Al-CH3-CBt**) by its characteristic ^{1}H NMR in the mixture. It showed peaks corresponding to three vinyl protons: a doublet at 6.42 ppm(H-11), a doublet at 6.37 ppm(H-10) and multiplet at 5.62(H-3). Peaks at 6.42 and 6.37 ppm are coupled to one another with 3 Hz coupling. This AB quartet pattern uniquely identifies angular cyclobutenes arising from cyclization toward the ring substituent. The peak at 5.62 ppm is assigned to H-10 next to the methyl group. That proton (H-10) coupled to two vicinal allylic protons H-4α, H-4β and the methyl group.

Al-CH3-COt turned into **Al-CH3-CBt** upon prolonged irradiation but **Al-CH3-CBt** could not be isolated due to its thermal instability.


^{1}H NMR of Al-CH3-COt in $CDCl_3$
6 7 8 9 10
H
O
3 2
O
Al-CH3-COt
3
6
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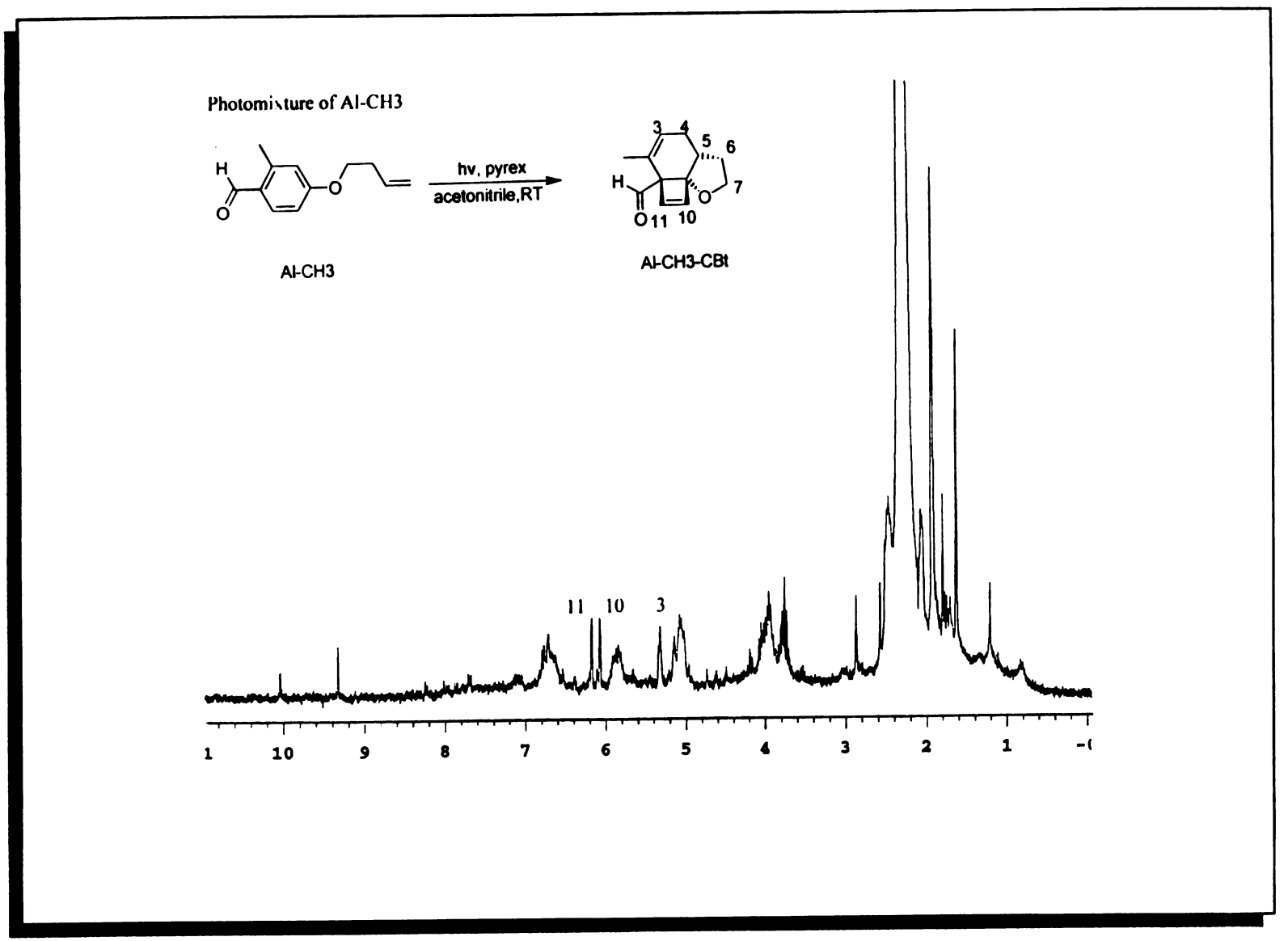
Photomixture of Al-CH3
hv, pyrex
acetonitrile,RT
Al-CH3
Al-CH3-CBt
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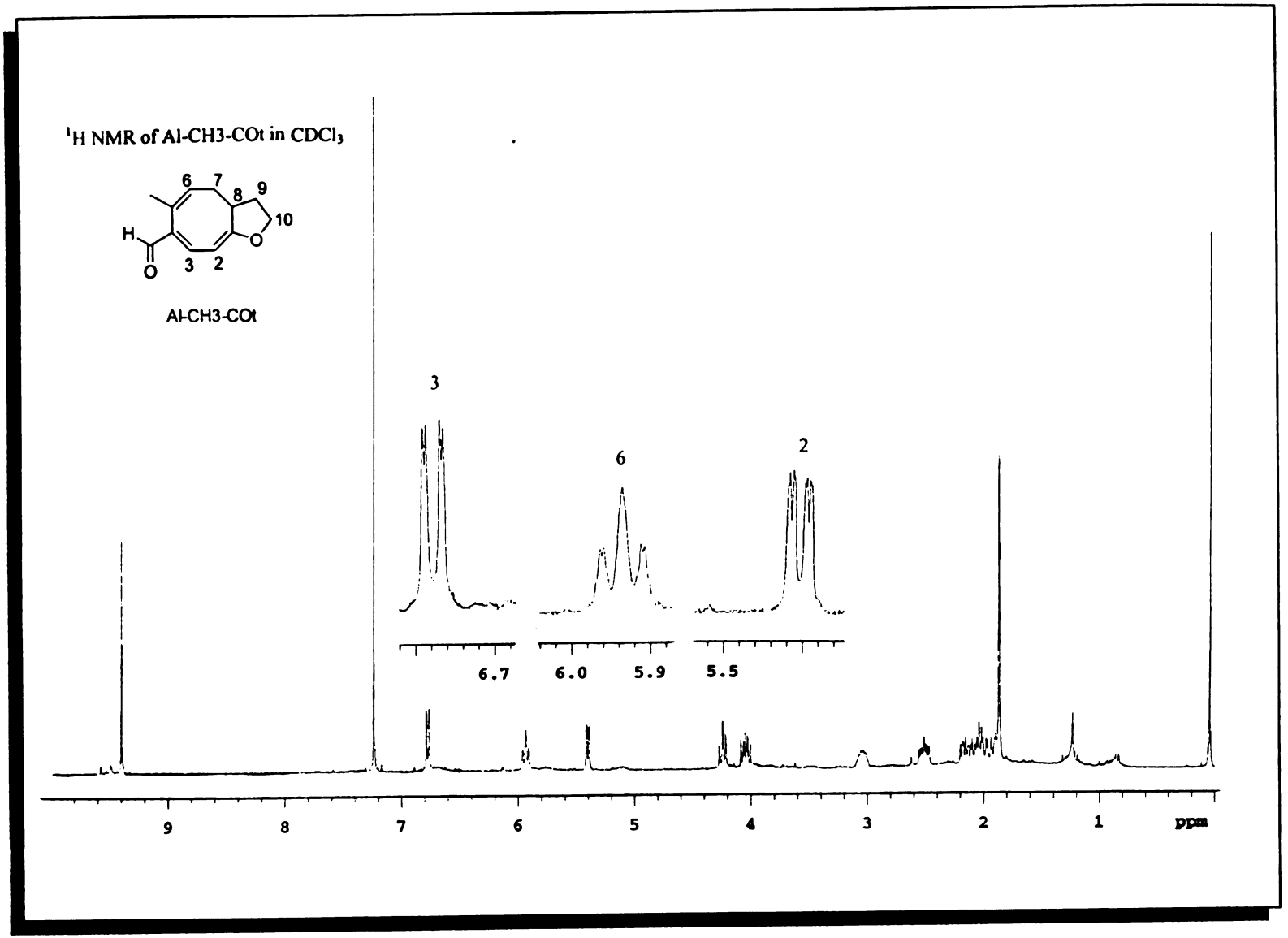
^{1}H NMR of Al-CH3-COt in $CDCl_3$
6
7
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H
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O
Al-CH3-COt
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6.0
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5.5
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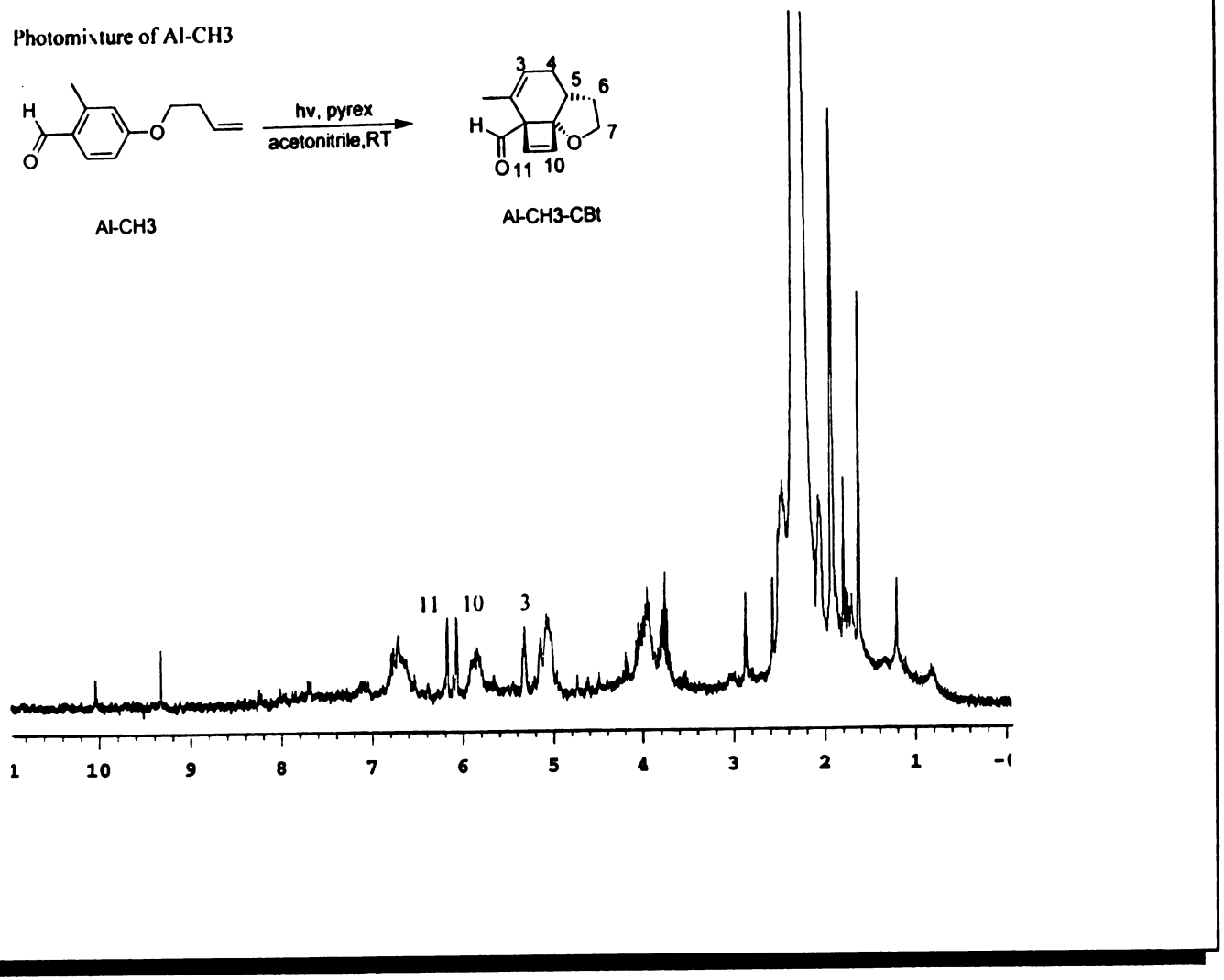
Photomixture of Al-CH3
hv, pyrex
acetonitrile,RT
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Al-CH3-CBt
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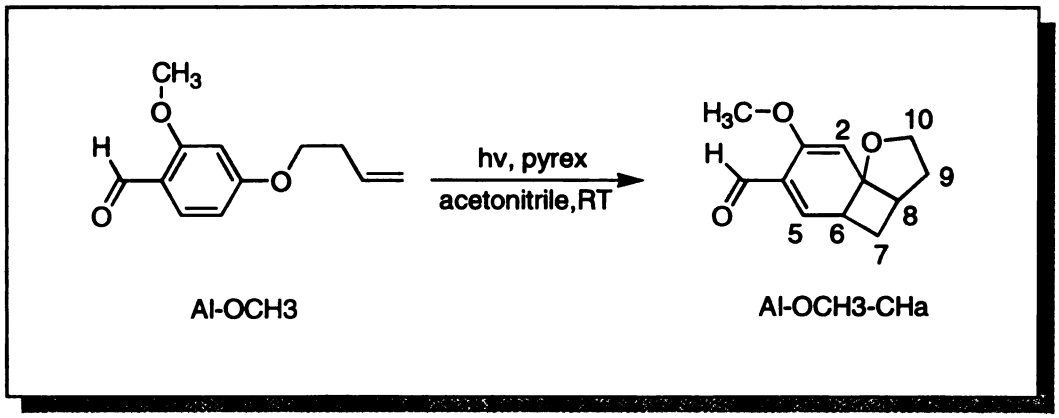
2.4. Photochemistry of 4-(3-buten-1-oxy)-2-methoxybenzaldehyde (Al-OCH3)



Al-OCH3 Al-OCH3-CHa

A solution of **Al-OCH3** (2.2 mg) in deuterated acetonitrile (0.75 mL, 1.41 x 10^{-2} M) in an NMR tube was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After four hours of irradiation, several photoproducts were observed by ^{1}H NMR. Preparatory scale photolysis was carried out to isolate the photoproducts. 4-(3-Buten-1-oxy)-2-methoxybenzaldehyde (135 mg) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium pressure mercury arc lamp through a Pyrex filter. After 8 hours of irradiation, the reaction mixture was concentrated at reduced pressure. ^{1}H NMR showed the single product. The reaction mixtures were isolated and purified by silica gel chromatography followed by HPLC.

The photoproduct was identified as 3-formyl-4-methoxy-11-oxatricyclo[6.3.0.$0^{1,6}$] undeca-2,4-diene (**Al-CH3O-CHa**) by its characteristic ^{1}H NMR in the mixture. It showed peaks corresponding to two vinyl protons: a doublet of doublets at 6.78 ppm(H-5) and a broad singlet at 4.66 ppm(H-2). The peak at 4.66 ppm is assigned to a proton on

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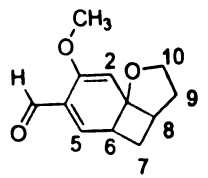
pro

enol ether based on its upfield shift. The peak at 6.78 was coupled to bridgehead proton(H-6) with 5.37 Hz; a typical coupling constant value for this system.

^{1}H NMR of Al-OCH3-CHa in $CDCl_3$



Al-OCH3-CHa

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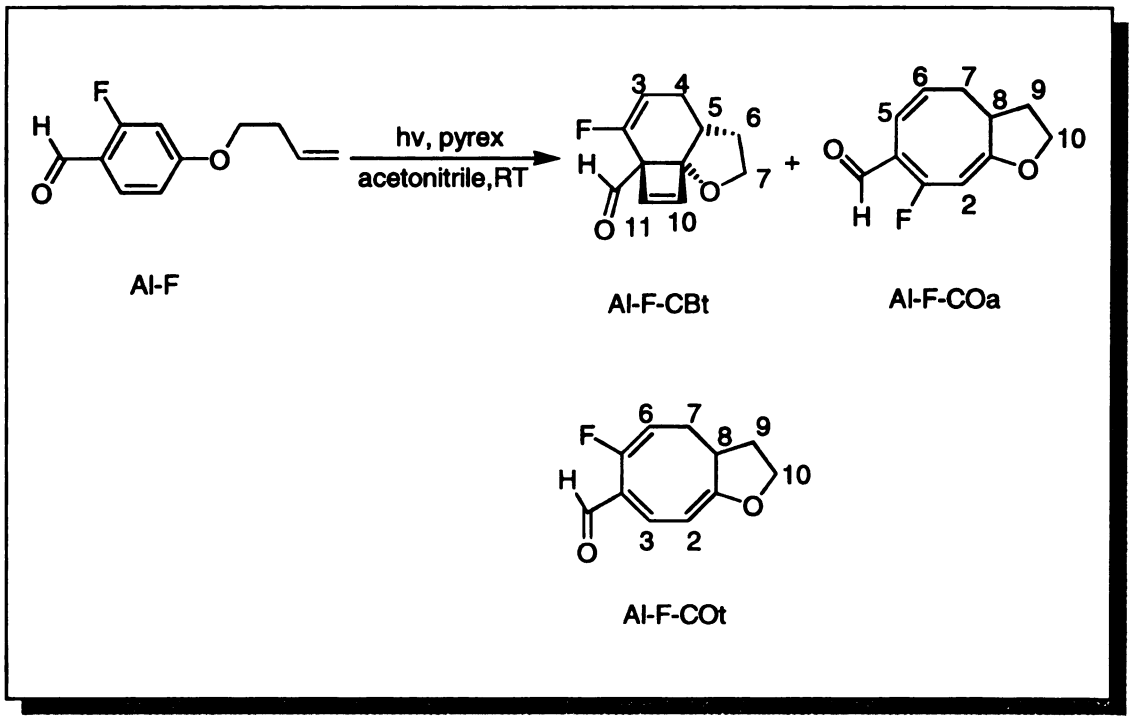
2.5. Photochemistry of 4-(3-buten-1-oxy)-2-fluorobenzaldehyde (Al-F)



A solution of **Al-F** (2.1 mg) in deuterated acetonitrile (0.75 mL, 1.44 x 10^{-2} M) in NMR tube was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 30 minutes of irradiation, NMR analysis of the reaction mixture was showed the presence of two major photoproducts. After 2 hours of irradiation, only one remained with several minor products. Preparatory scale photolysis was carried out to isolate the photoproducts. **Al-F** (160 mg) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium pressure mercury arc lamp through a Pyrex filter. After 1 hour of irradiation, the reaction mixture was concentrated at reduced pressure. ^{1}H NMR showed the presence of the starting aldehyde and its products. The reaction mixture was isolated and purified by preparative TLC followed by HPLC.

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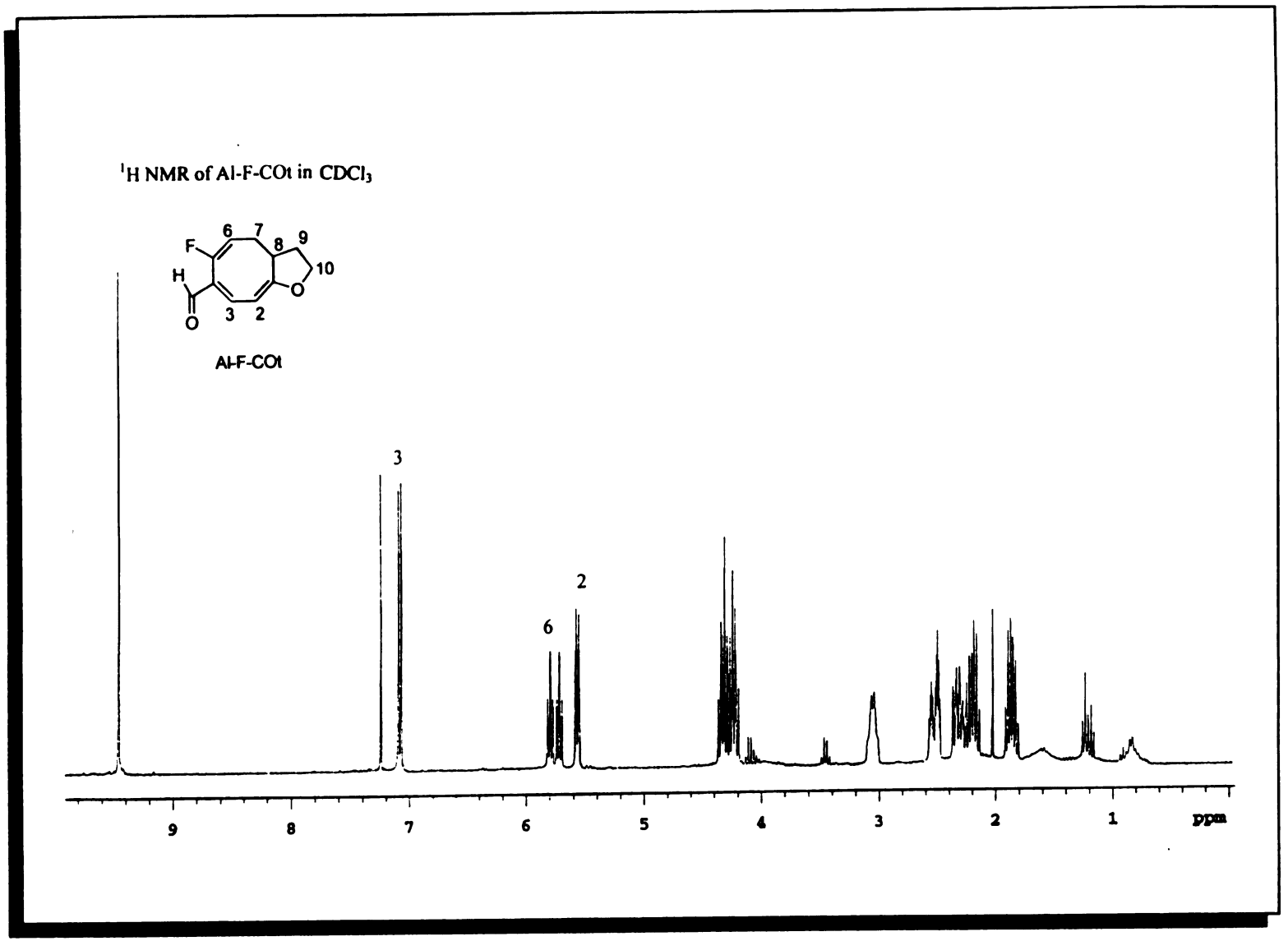
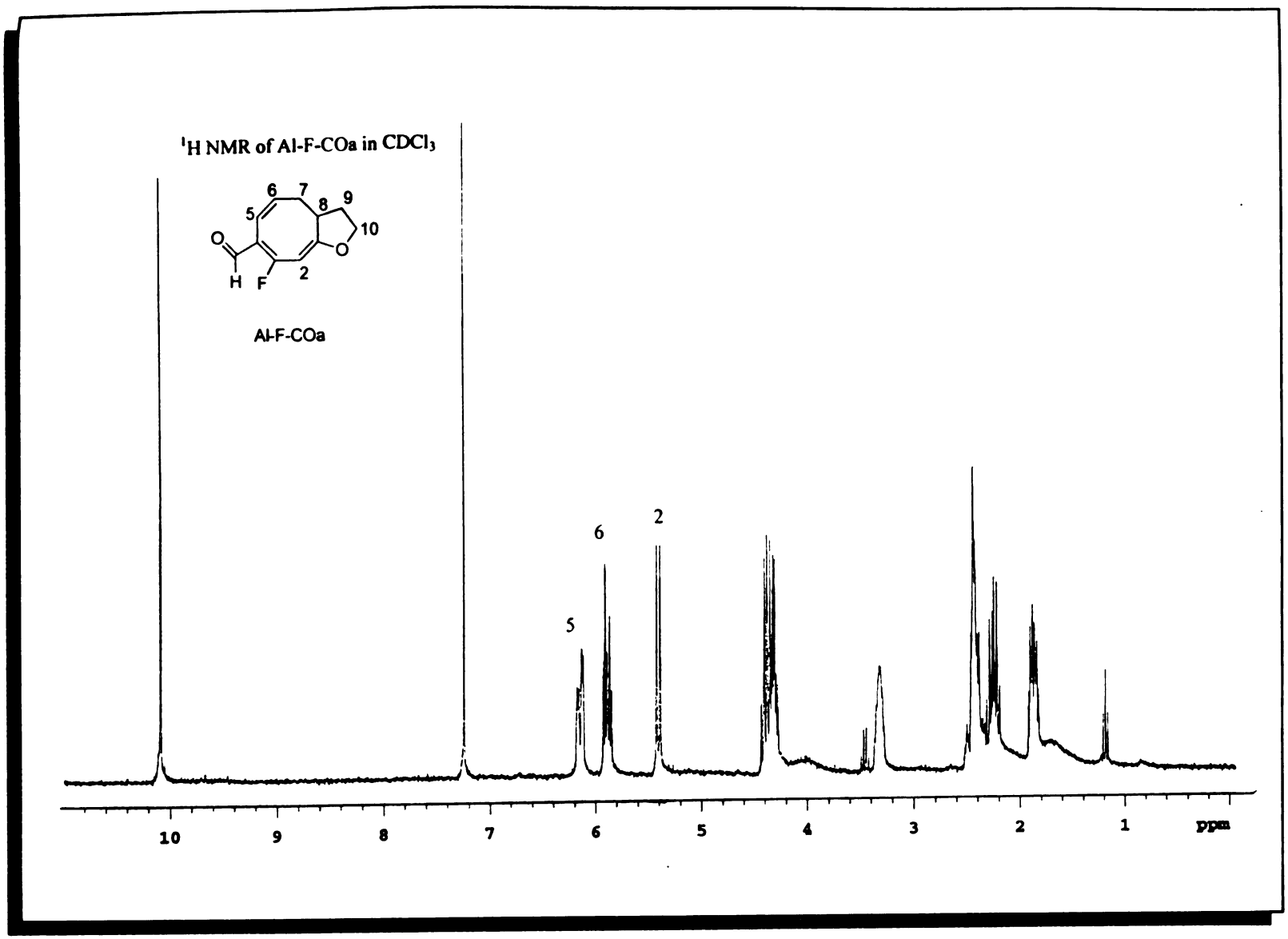
One photoproduct collected at 9.5 minutes from HPLC was identified as 4-formyl-3-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**Al-F-COa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet of doublets at 6.15 ppm(H-5), a doublet of triplets at 5.89 ppm(H-6) and a doublet at 5.40(H-2). Peaks at 6.15 and 5.89 ppm are coupled to one another with a 12.6 Hz coupling constant and the peak at 6.15 ppm(H-5) is coupled to fluorine with a 4.4 Hz coupling constant. The peak at 5.89 ppm coupled to the two vicinal allylic protons H-7 with a 5.49 Hz coupling constant. The peak at 5.4 ppm (H-2) coupled to fluorine with a 10.44 Hz coupling constant.

Another photoproduct collected at 6.5 minutes from HPLC was identified as 4-formyl-2-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**Al-F-COt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 7.08 ppm(H-3), a doublet of triplets at 5.76 ppm(H-6) and multiplet at 5.57 ppm(H-2). Peaks at 7.08 and 5.57 ppm are coupled to one another with ~7 Hz coupling. The peak at 5.76 ppm (H-10) is coupled to the two vicinal allylic protons (H-4) with 6.59 Hz coupling constant and the fluorine atom with a 23.07 coupling constant.


^{1}H NMR of Al-F-COt in $CDCl_3$
F
H
O
6
7
8
9
10
3
2
O
Al-F-COt
3
6
2
9
8
7
6
5
4
3
2
1
ppm


^{1}H NMR of Al-F-COa in $CDCl_3$
6
7
8
9
5
10
O
O
H
F
2
Al-F-COa
5
6
2
10
9
8
7
6
5
4
3
2
1
ppm

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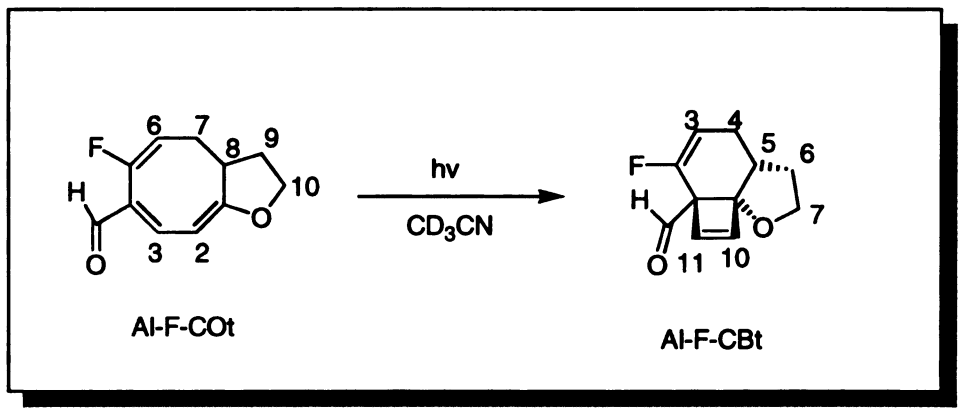
2.5.1. **Irradiation of 4-formyl-2-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-F-COt).**



Al-F-COt

Al-F-CBt

A solution of **Al-F-COt** (2.0 mg) in deuterated acetonitrile (0.75 mL) was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 30 minutes of irradiation, NMR analysis of the reaction mixture showed the presence of one photoproduct. The product was not isolated due to thermal instability and was one of the products in NMR scale reaction.

The thermally unstable photoproduct was identified as 1-formyl-2-fluoro-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,10-diene (**Al-F-CBt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a triplet at 6.45 ppm(H-11), a doublet at 6.39 ppm(H-10) and a doublet of doublet of doublets at 5.44(H-3). Peaks at 6.45 and 6.39 ppm are coupled to one another with a 2.75 Hz coupling constant and the peak at 6.45 ppm (H-5) is coupled to fluorine with ~2.75 Hz coupling constant. The peak

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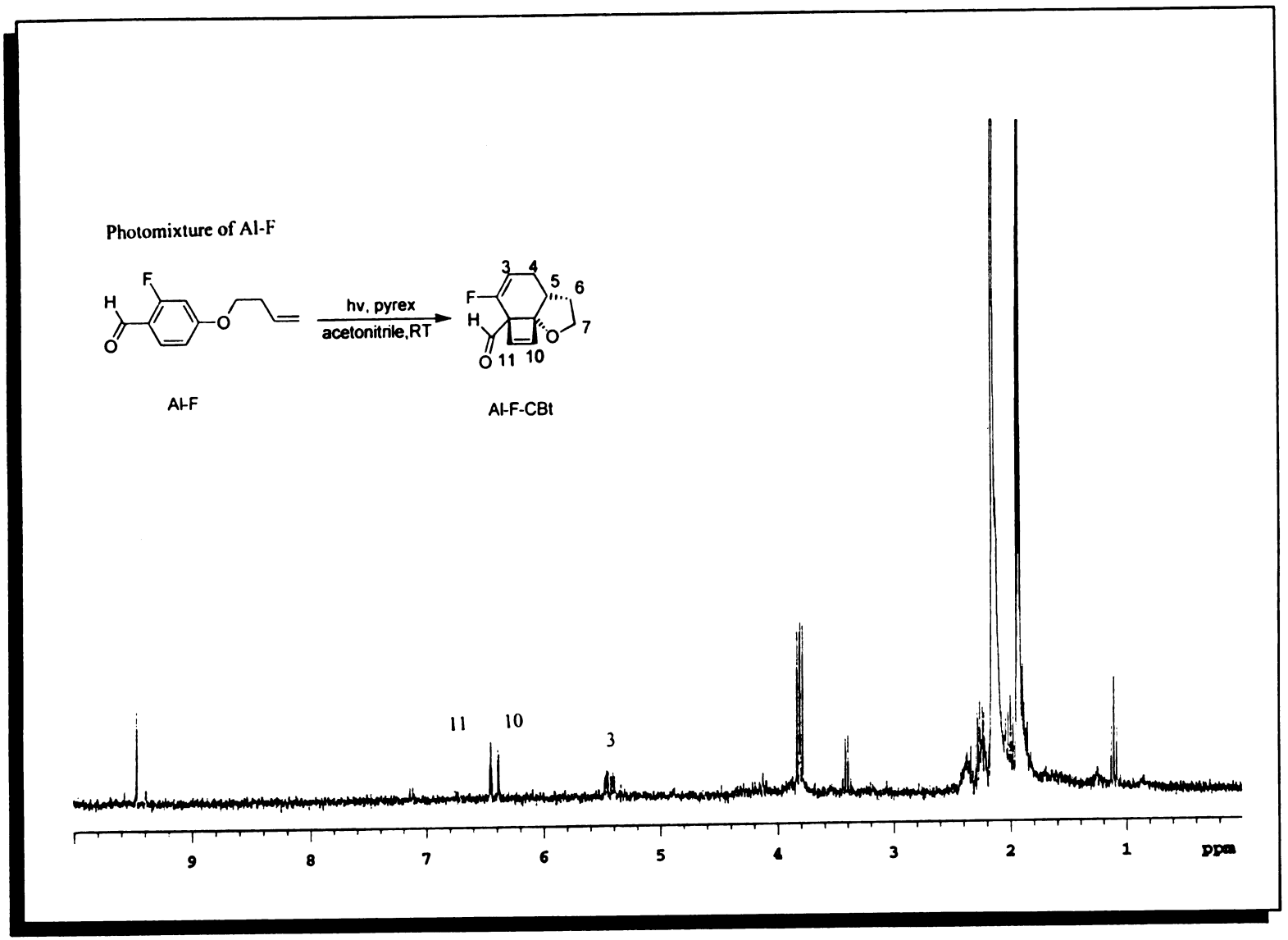
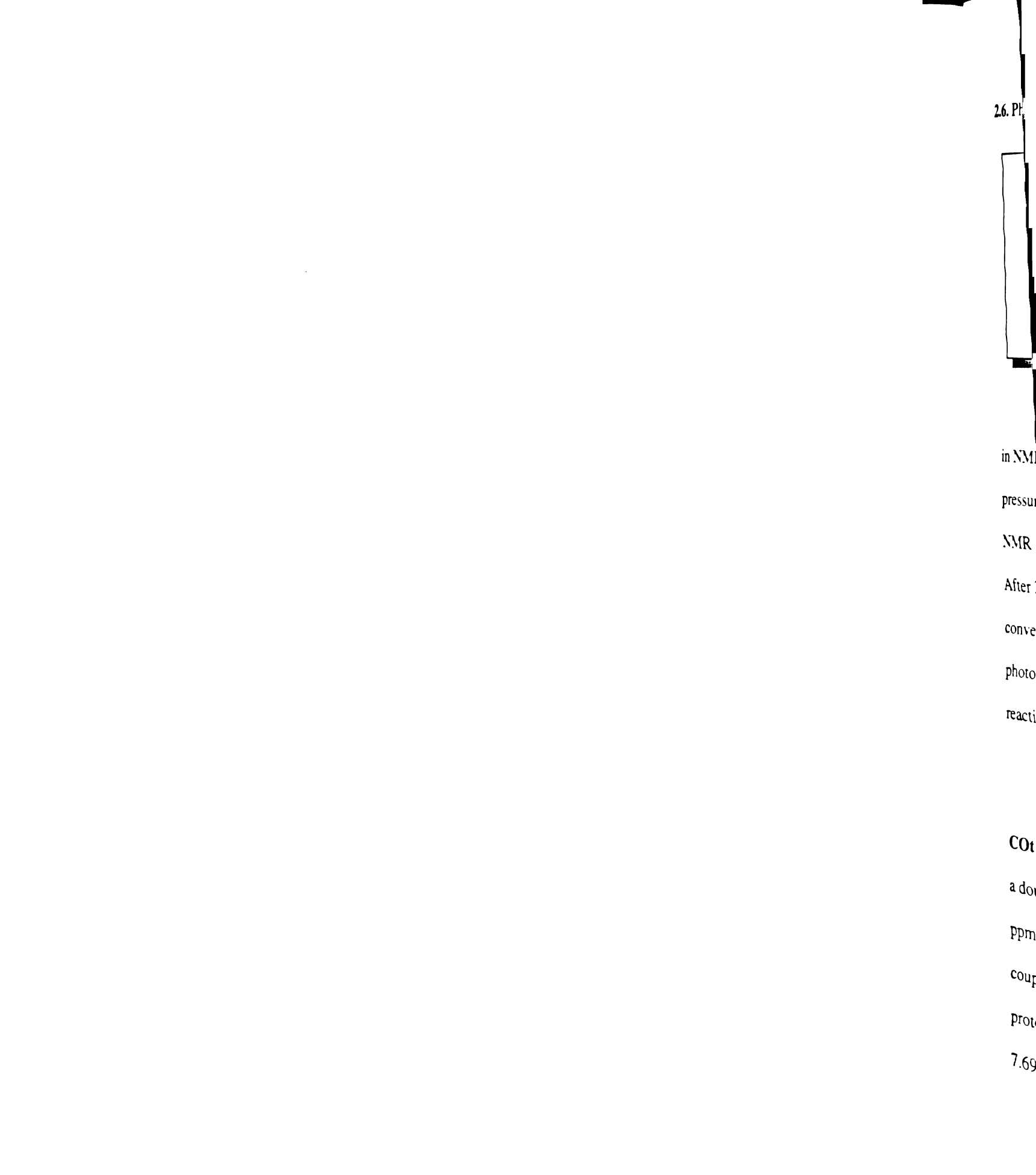
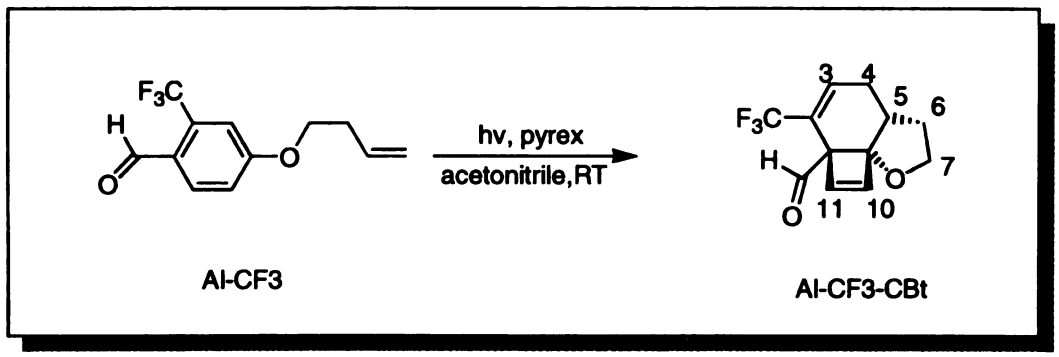
at 5.44 ppm is coupled to two vicinal allylic protons H-4α, H-4β with 6.04 and 3.85 Hz coupling constants, respectively and fluorine with a 15.93 Hz coupling constant.

In an NMR scale reaction, **Al-F-CBt** and **Al-F-COt** were formed in 2:1 ratio and **Al-F-COa** and **Al-F-COt** were formed in a 1:2.68 ratio in a preparatory scale reaction.


Photomixture of Al-F
F
H
O
O
hv, pyrex
acetonitrile,RT
3
4
5
6
F
H
O
7
O
11
10
Al-F
Al-F-CBt
11
10
3
9
8
7
6
5
4
3
2
1
ppm

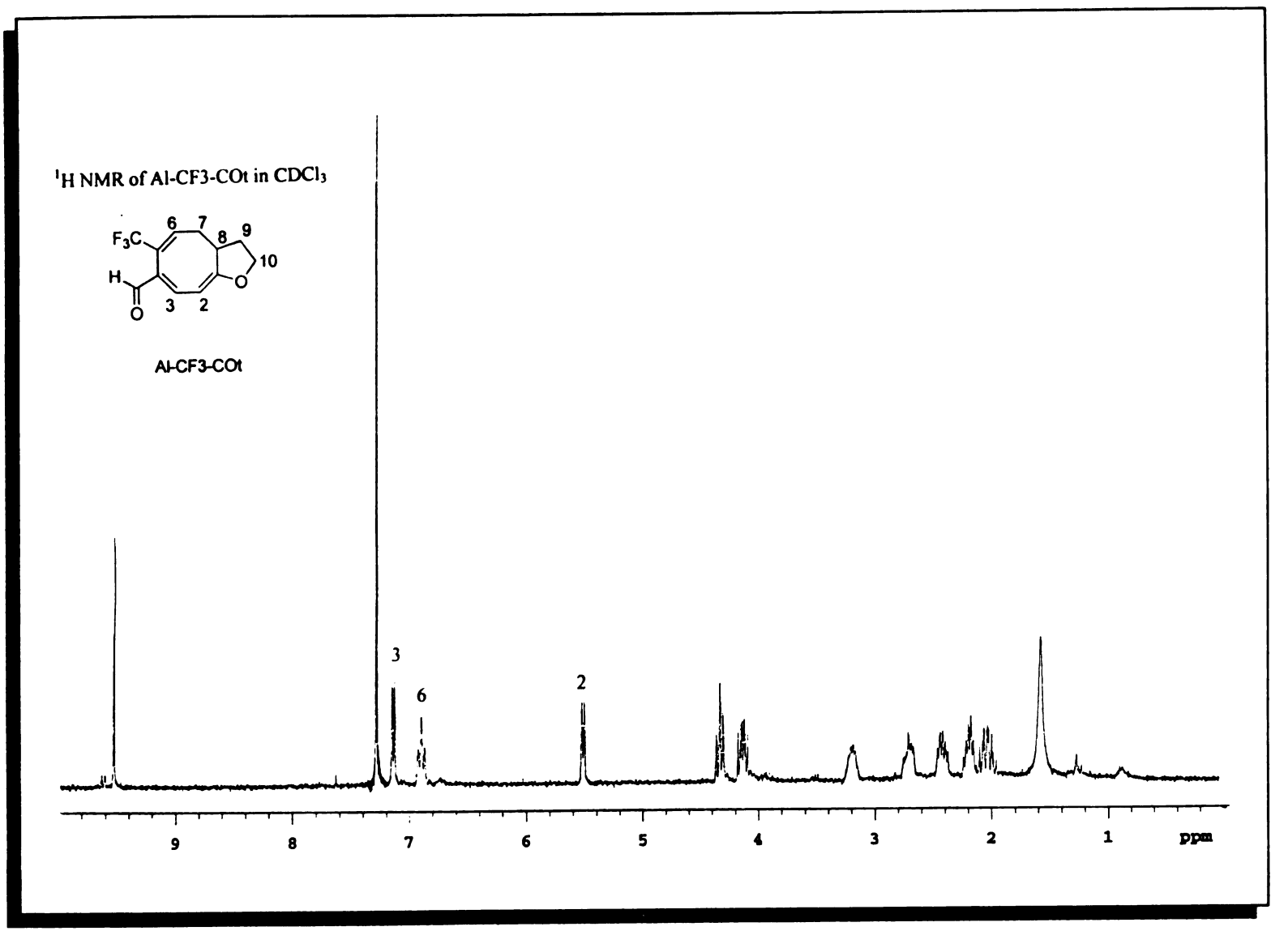


2.6. Photochemistry of 4-(3-buten-1-oxy)-2-trifluoromethylbenzaldehyde (Al-CF_3)

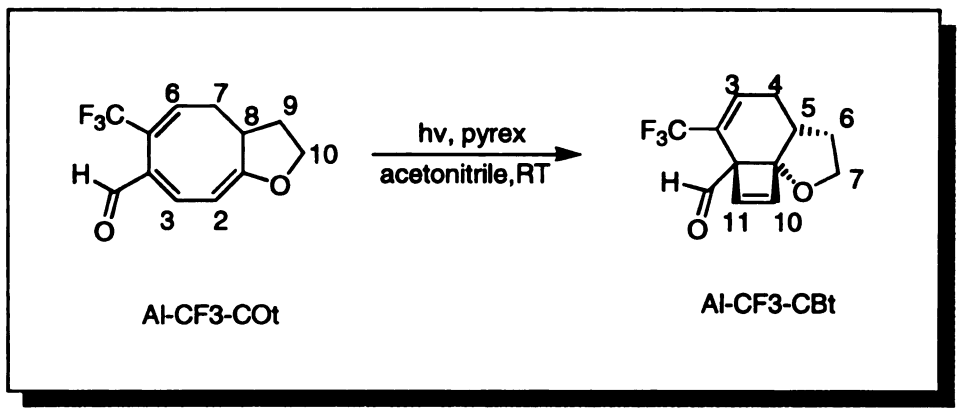


A solution of **Al-CF3** (2.0 mg) in deuterated acetonitrile (0.75 mL, 1.1 x 10^{-2} M) in NMR tube was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 30 minutes of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts. After 2 hours the reaction was complete. The major product was thermally unstable and converted to another product, which obsorbes UV light at 317 nm. Preparatory scale photolysis was carried out to isolate the photoproducts with 50 mg of **Al-CF3**. The reaction mixture was isolated and purified by preparative TLC followed by HPLC.

The photoproduct collected at 13 minutes from HPLC was identified as **Al-CF3-COt** by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 5.52 ppm(H-2), a doublet of doublets at 6.90 ppm(H-6) and a doublet at 7.14 ppm(H-3). The peaks at 7.14 and 5.52 ppm are coupled to one another with a 6.3 Hz coupling constant and the large upfield shift of proton H-2 is indicative of an enol ether proton. The peak at 7.14 ppm(H-3) is coupled to the two vicinal allylic protons(H-7) with 7.69 and 7.14 Hz coupling constatnts.

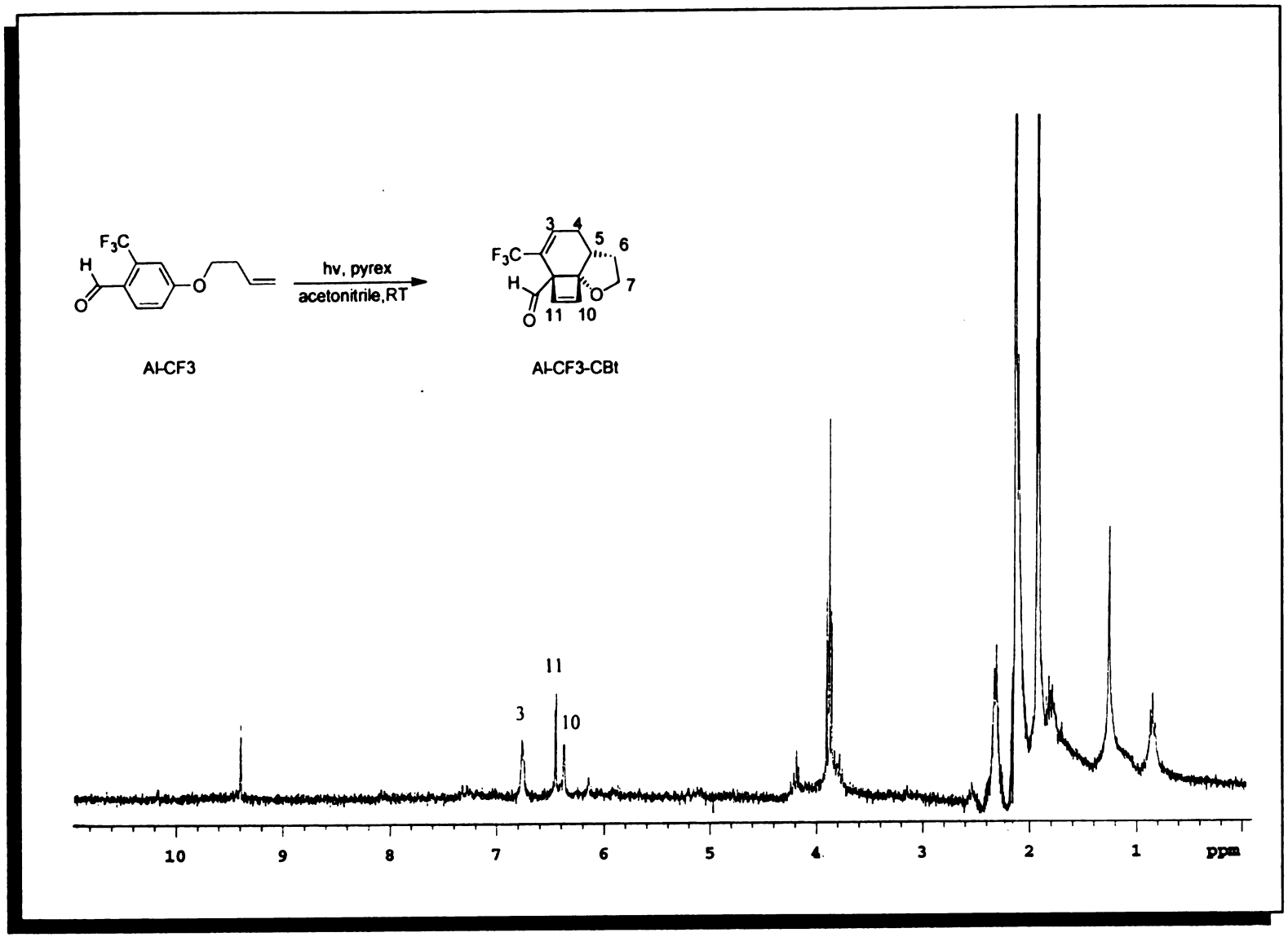

^{1}H NMR of Al-CF3-COt in $CDCl_3$
F_3C
H
O
6
7
8
9
10
3
2
Al-CF3-COt
3
6
2
9
8
7
6
5
4
3
2
1
ppm

2.6.1. **Irradiation of 4-formyl-2-trifluoromethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-CF3-COt).**

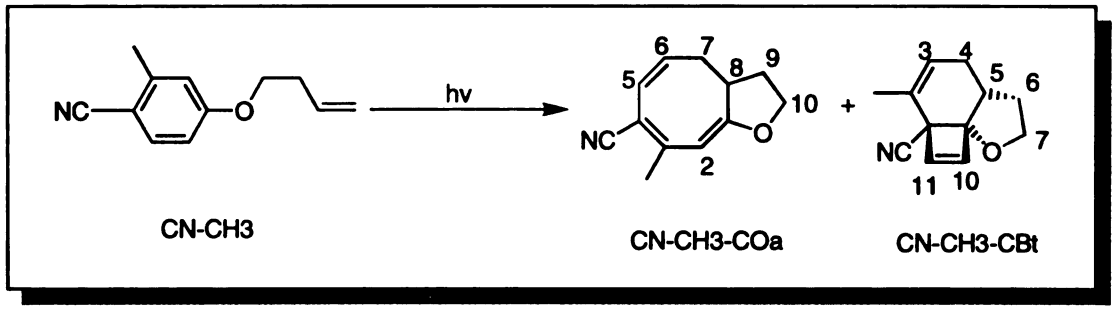


A solution of **Al-CF3-COt** (2.0 mg) in deuterated acetonitrile (0.75 mL) was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 1 hour of irradiation, NMR analysis of the reaction mixture showed the presence of a photoproduct and starting material **Al-CF3-COt**.

The thermally unstable photoproduct in the mixture was identified as 1-formyl-2-trifluoromethyl-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,10-diene (**Al-CF3-CBt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 6.43 ppm(H-11), a doublet at 6.51 ppm(H-10) and a multiplet at 6.82 ppm(H-3). The peaks at 6.43 and 6.51 ppm are coupled to one another with a 2.75 Hz coupling constant and the peak 6.82 ppm(H-3) is coupled to three fluorine atoms and two vicinal allylic protons H-4.


F3C
H
O
O
hv, pyrex
acetonitrile,RT
3
4
5
6
F3C
H
O
7
O
11
10
Al-CF3
Al-CF3-CBt
11
3
10
10
9
8
7
6
5
4
3
2
1
ppm

2.7. Photochemistry of 4-(3-buten-1-oxy)-2-methylbenzonitrile (CN-CH3)



A solution of **CN-CH3** (2.0 mg) in deuterated acetonitrile (0.75 mL, 1.43 x 10^{-2} M) in an NMR tube was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 14 days of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts with very low conversion.

A quartz test tube containing a solution of **CN-CH3** (8.0 mg) in deuterated acetonitrile (3.0 mL, 1.43 x 10^{-2} M) was purged with argon for 20 minutes and then irradiated in a Rayonet reactor with 254 nm lamps. After 18 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts.

Another solution of **CN-CH3** (2.0 mg) in deuterated acetone (0.75 mL, 1.43 x 10^{-2} M) in an NMR tube was purged with argon for 15 minutes and then irradiated through a 313 nm filter solution. After 24 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts. Preparatory scale photolysis was carried out to isolate the photoproducts. **CN-CH3** (183 mg) was dissolved in freshly distilled acetone (50 mL) and irradiated through a 313 nm filter solution. After 16 hours

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of irradiation, the reaction mixture was concentrated at reduced pressure. ^{1}H NMR showed the presence of the starting nitrile and its products. The reaction mixture was isolated and purified by silica gel chromatography followed by HPLC.

One photoproduct collected at 8 minutes from HPLC was identified as 4-cyano-3-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-CH3-COa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a singlet at 5.25 ppm(H-2), a broad doublet at 5.77 ppm(H-5) and a doublet of triplets at 6.77 ppm(H-6). The peaks at 5.77 and 6.77 ppm are coupled to one another with a 13 Hz coupling constant and the peak 6.77 ppm(H-6) is coupled to two vicinal allylic protons H-7 with a 4.4 Hz coupling constatnt. The large upfield shift of proton H-2 at 5.25 ppm is indicative of an enol ether proton.

Another photoproduct collected at 3 minutes from HPLC was identified as 1-cyano-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-CH3-CBt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 6.77 ppm(H-10), a doublet at 6.17 ppm(H-11) and a quartet of triplets at 5.48 ppm(H-3). The peaks at 6.77 and 6.17 ppm are coupled to one another with a 2.8 Hz coupling constants. The peak at 5.48 ppm(H-3) is coupled to two vicinal allylic protons H-4 with a 6.04 Hz coupling constant and the methyl group with a 1.65 Hz coupling constant.

The **CN-CH3-COa/ CN-CH3-CBt** ratios were measured by NMR analysis to be 1:2, 5:1 and 3:1 with the light sources of >300 nm, 254 nm and 313 nm, respectively.

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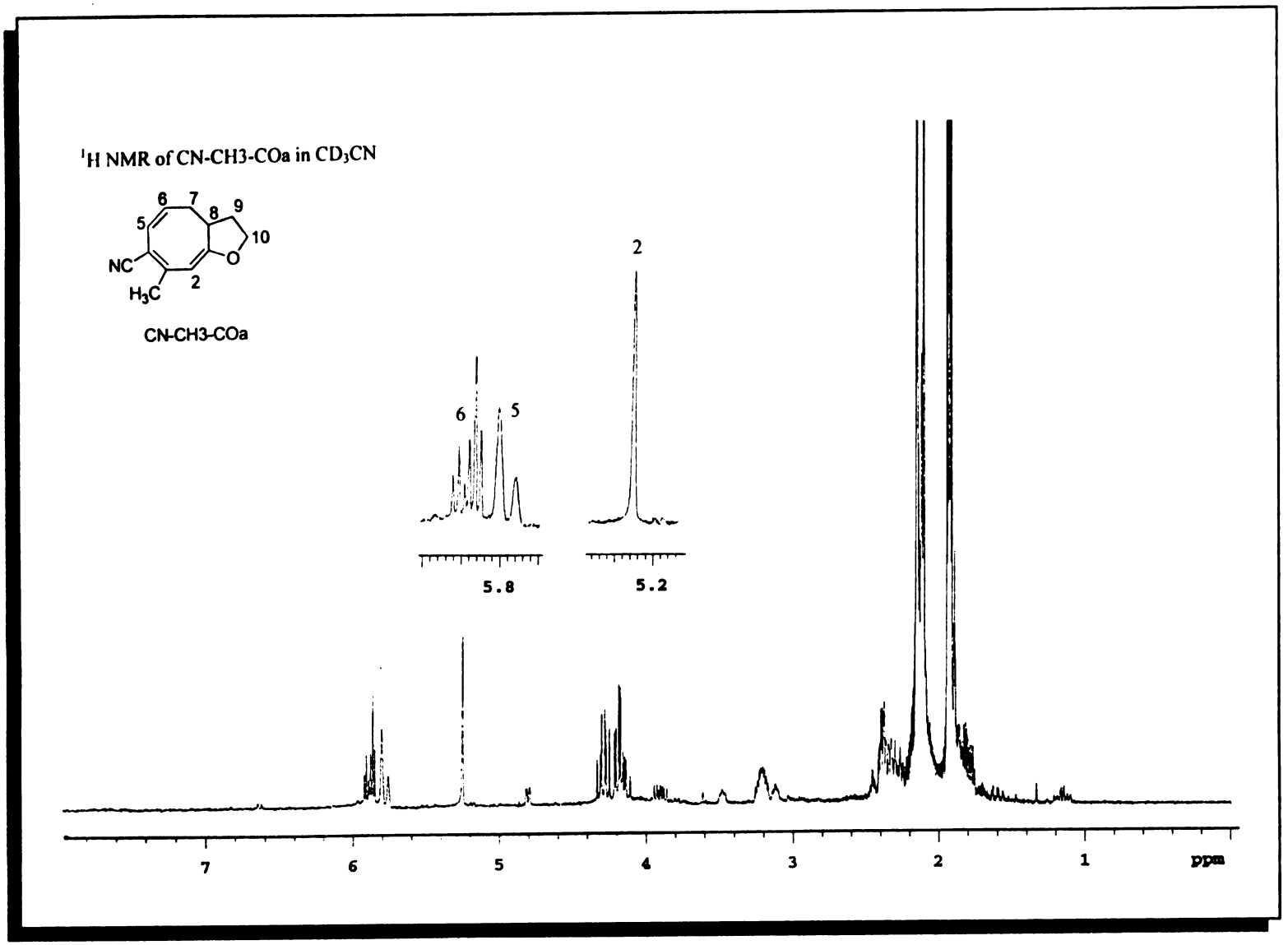
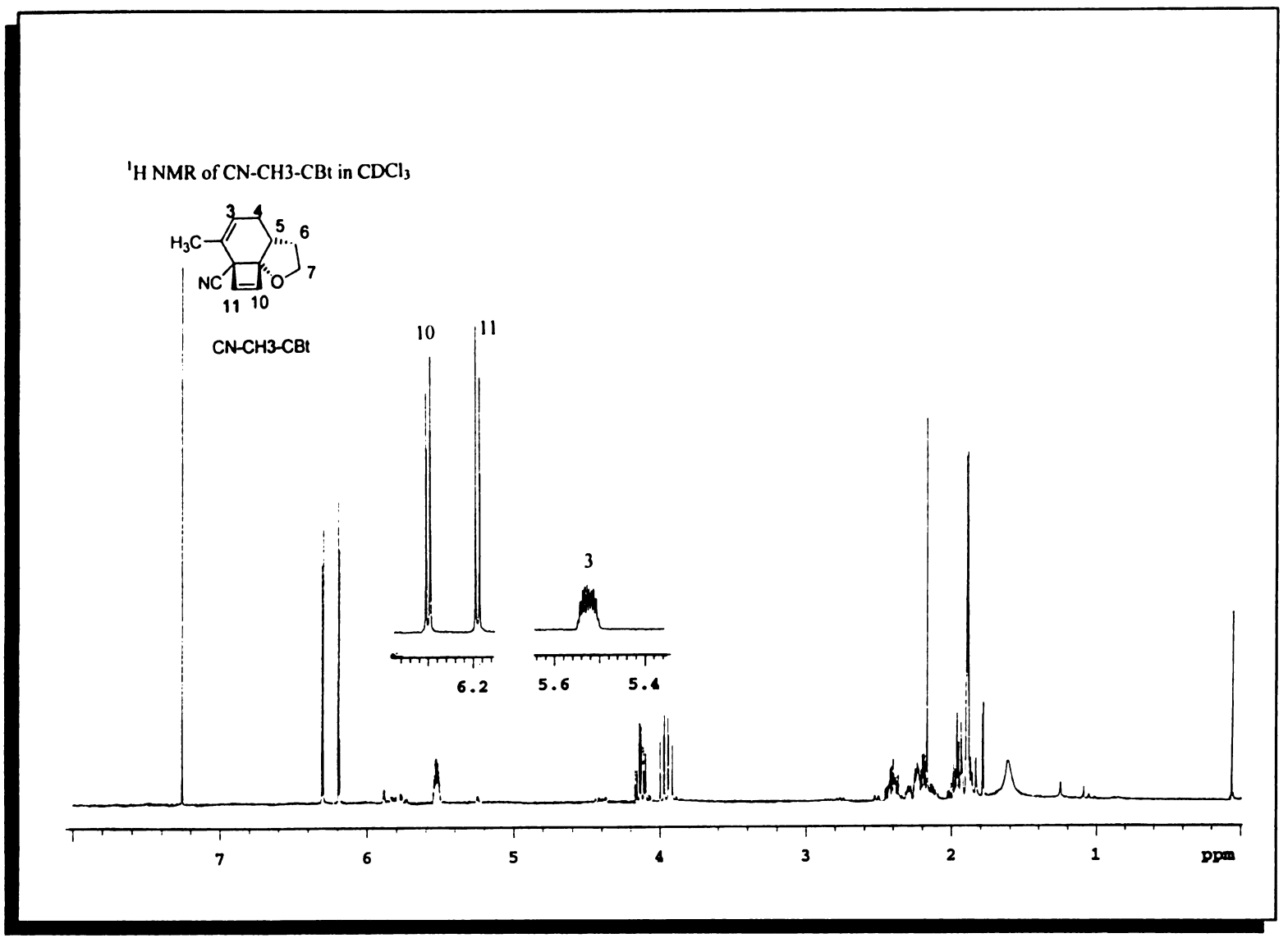
Dimerization between the double bond of the butenyl tether and acetone was observed along with dimerzation between acetones by ^{1}H NMR, ^{13}C NMR, DEPT, IR and MS.


^{1}H NMR of CN-CH3-COa in CD_3CN
6
7
8
9
5
10
NC
O
2
H_3C
CN-CH3-COa
2
6
5
5.8
5.2
7
6
5
4
3
2
1
ppm


^{1}H NMR of CN-CH3-CBt in CDCl$_3$
3 4 5 6
H_3C
NC
O
7
11 10
CN-CH3-CBt
10
11
3
6.2
5.6
5.4
7
6
5
4
3
2
1
ppm

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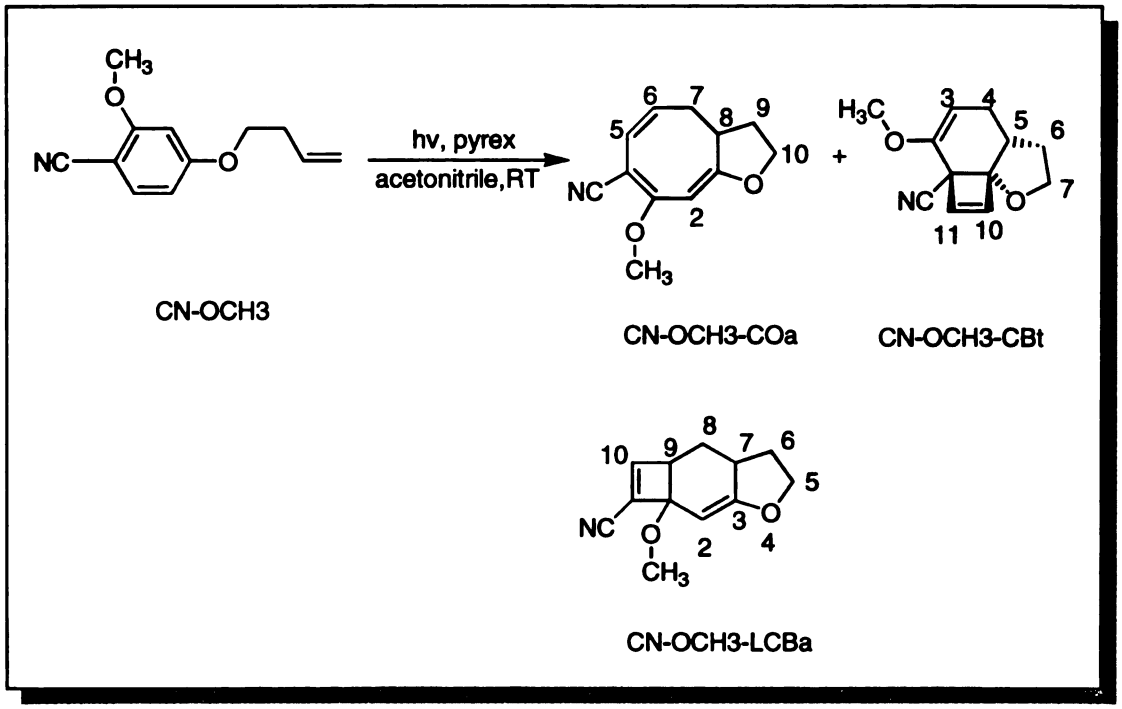
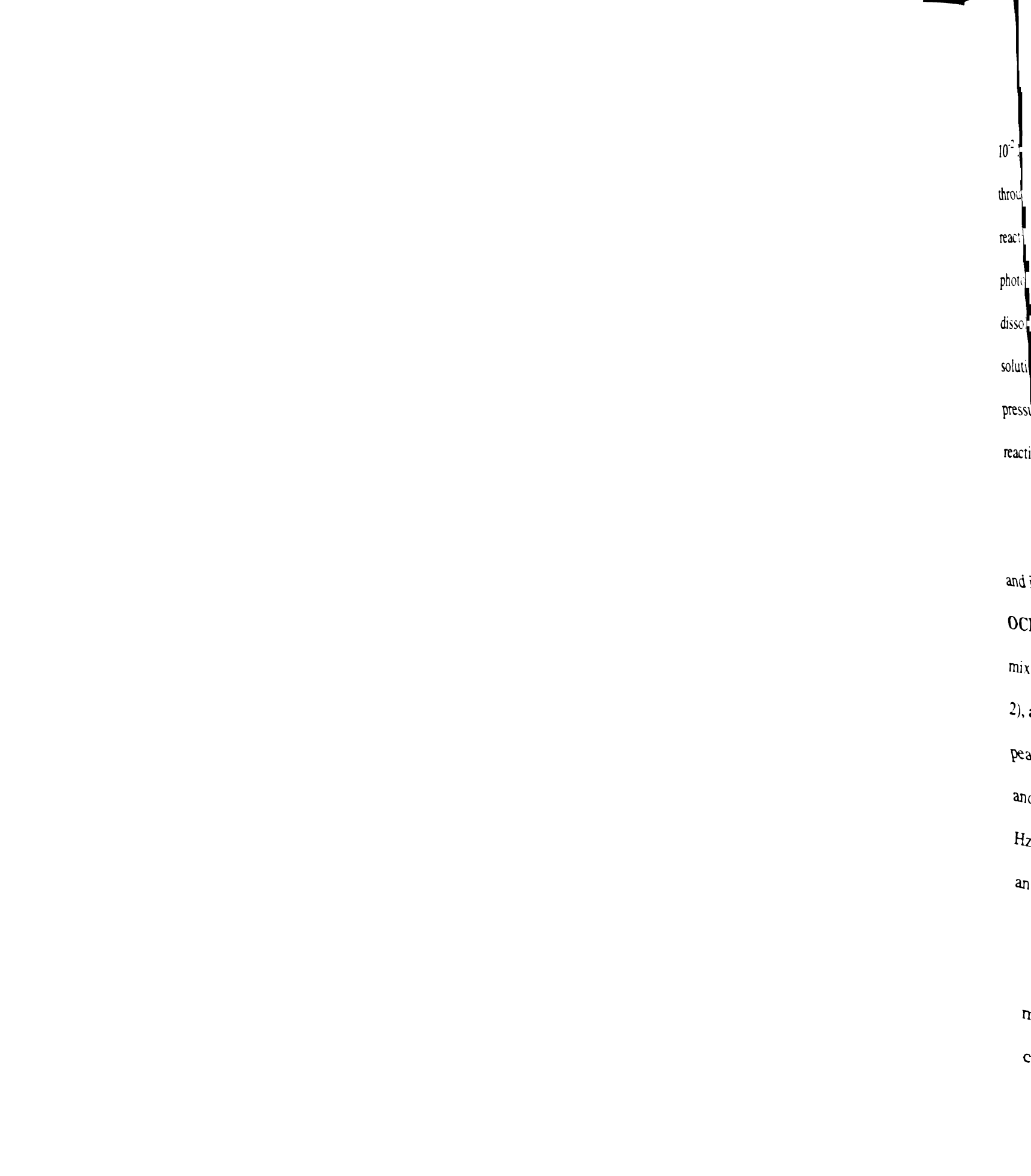
2.8. Photochemistry of 4-(3-buten-1-oxy)-2-methoxybenzonitrile (CN-OCH3)



A solution of **CN-OCH3** (2.7 mg) in deuterated acetonitrile (0.75 mL, 1.8 x 10^{-2} M) in an NMR tube was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 20 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts with very low conversion.

Another solution of **CN-OCH3** (10.8 mg) in deuterated acetonitrile (3.0 mL, 1.8 x 10^{-2} M) in a quartz test tube was purged with argon for 20 minutes and then irradiated in a Rayonet reactor with 254 nm lamps. After 18 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts.



Another solution of **CN-OCH3** (2.7 mg) in deuterated acetone (0.75 mL, 1.8 x 10^{-2} M) in an NMR tube was purged with argon for 15 minutes and then irradiated through a 313 nm filter solution. After 30 hours of irradiation, NMR analysis of the reaction mixture showed the presence of three photoproducts. Preparatory scale photolysis was carried out to isolate the photoproducts. **CN-OCH3** (177 mg) was dissolved in freshly distilled acetone (50 mL) and irradiated through a 313 nm filter solution. After 28 hours of irradiation, the reaction mixture was concentrated at reduced pressure. ^{1}H NMR showed the presence of the starting nitrile and its products. The reaction mixture was isolated and purified by preparative TLC followed by HPLC.

Two products eluted after at 9 minutes of HPLC. one photoproduct was isolated and identified as 4-cyano-3-methoxy-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-OCH3-COa**) by its characteristic ^{1}H NMR while the other product was identified in the mixture. It showed peaks corresponding to three vinyl protons: a singlet at 5.32 ppm(H-2), a doublet of triplets at 5.75 ppm(H-6) and a doublet of triplets at 5.83 ppm(H-5). The peaks at 5.75 and 5.83 ppm are coupled to one another with ~12 Hz coupling constant and the peak at 5.75 ppm(H-6) is coupled to the two vicinal allylic protons H-7 with 4.4 Hz coupling constatnt. The large upfield shift of proton H-2 at 5.32 ppm is indicative of an enol ether proton.

The other photoproduct to elute after 9 minutes was identified as 11-cyano-1-methoxy-4-oxatricyclo[7.2.0.$0^{3,7}$]undeca-2,10-diene (**CN-OCH3-LCBa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to two vinyl protons: a singlet at

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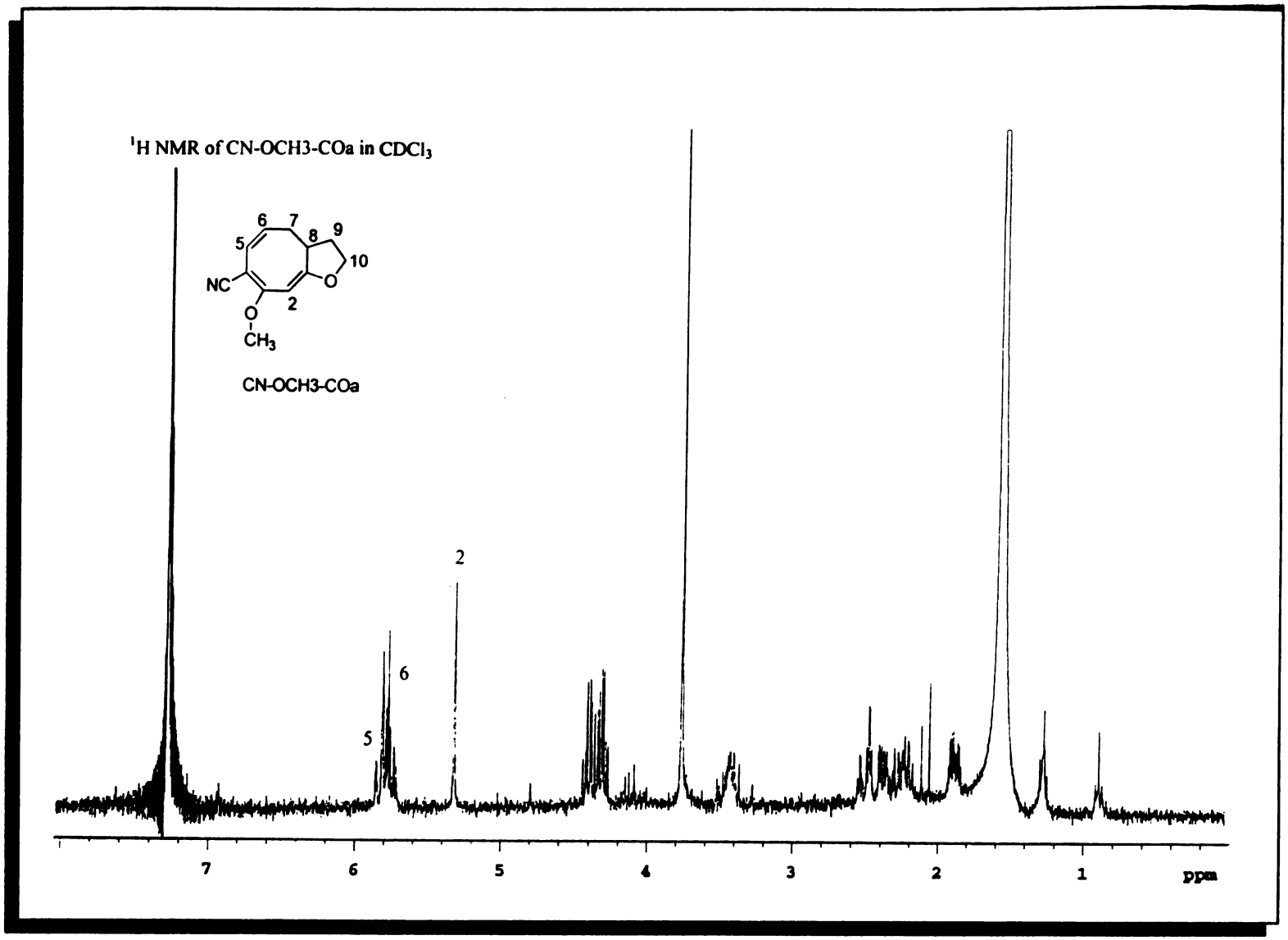
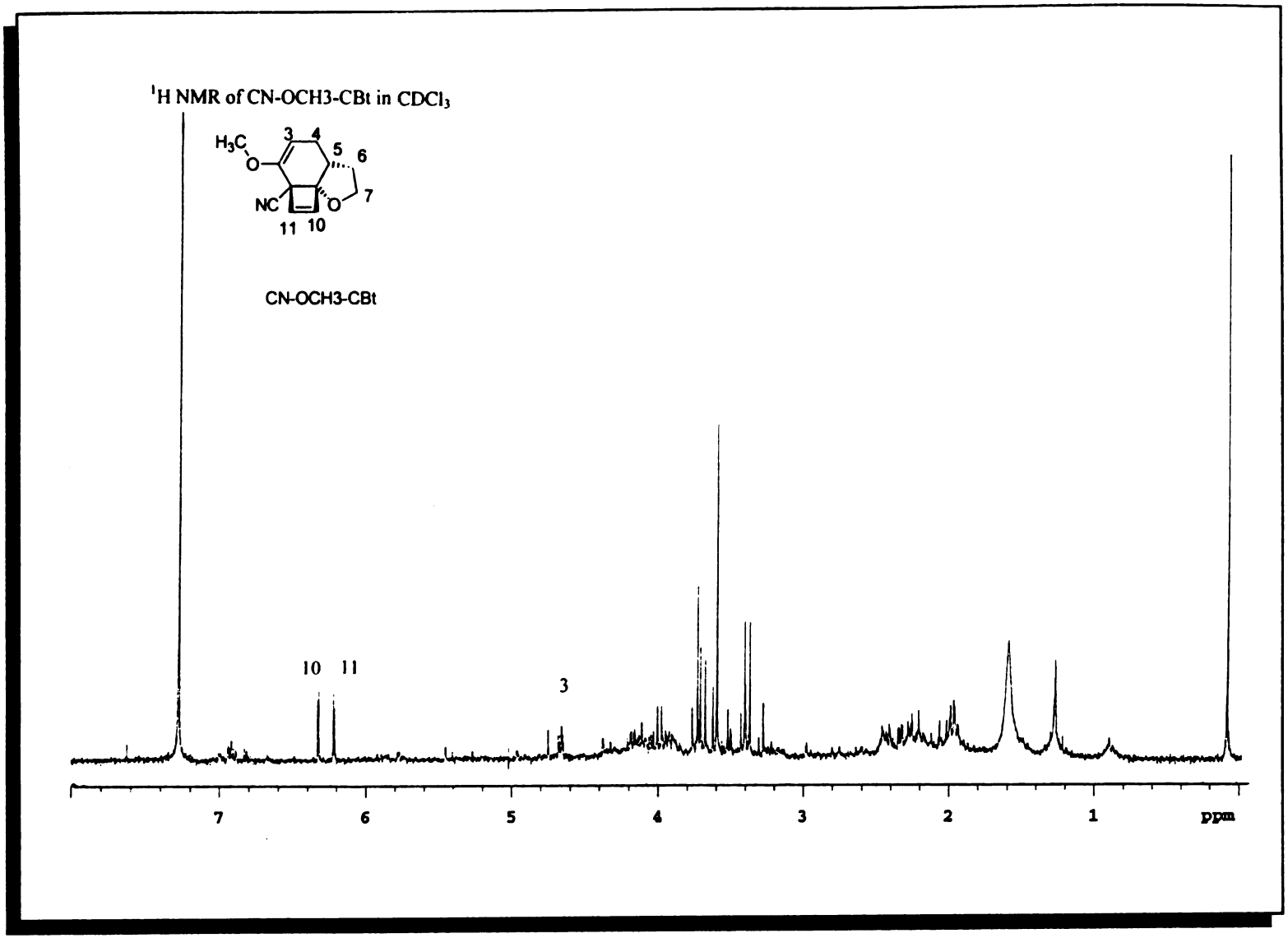
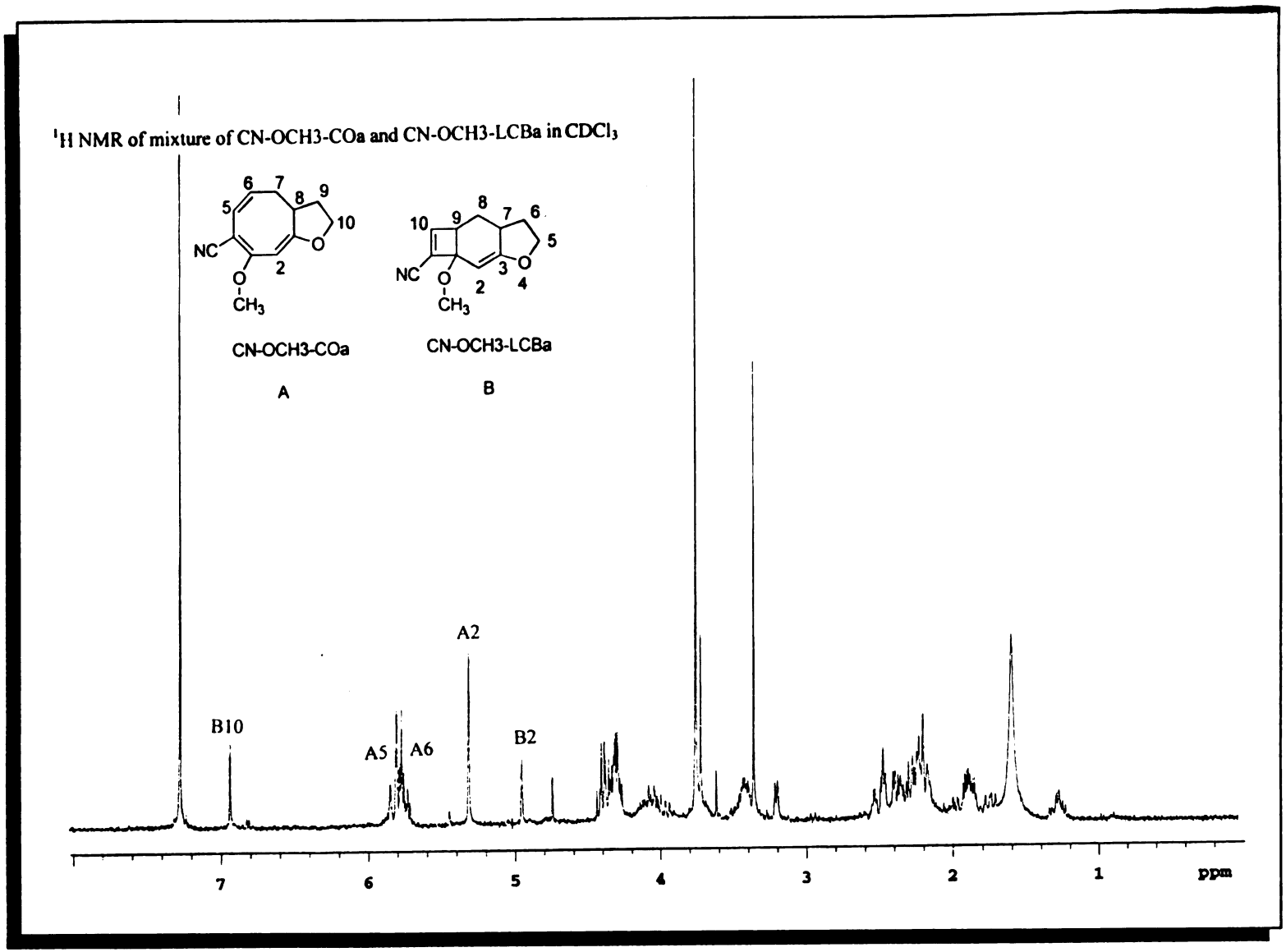
4.92 ppm(H-2) and a doublet at 6.9 ppm(H-10). The large upfield shift of proton H-2 at 4.92 ppm is indicative of an enol ether proton. The proton H-10 at 6.9 ppm coupled to the allylic proton H-9 with a 1 Hz coupling constant that is typical value for this structure.

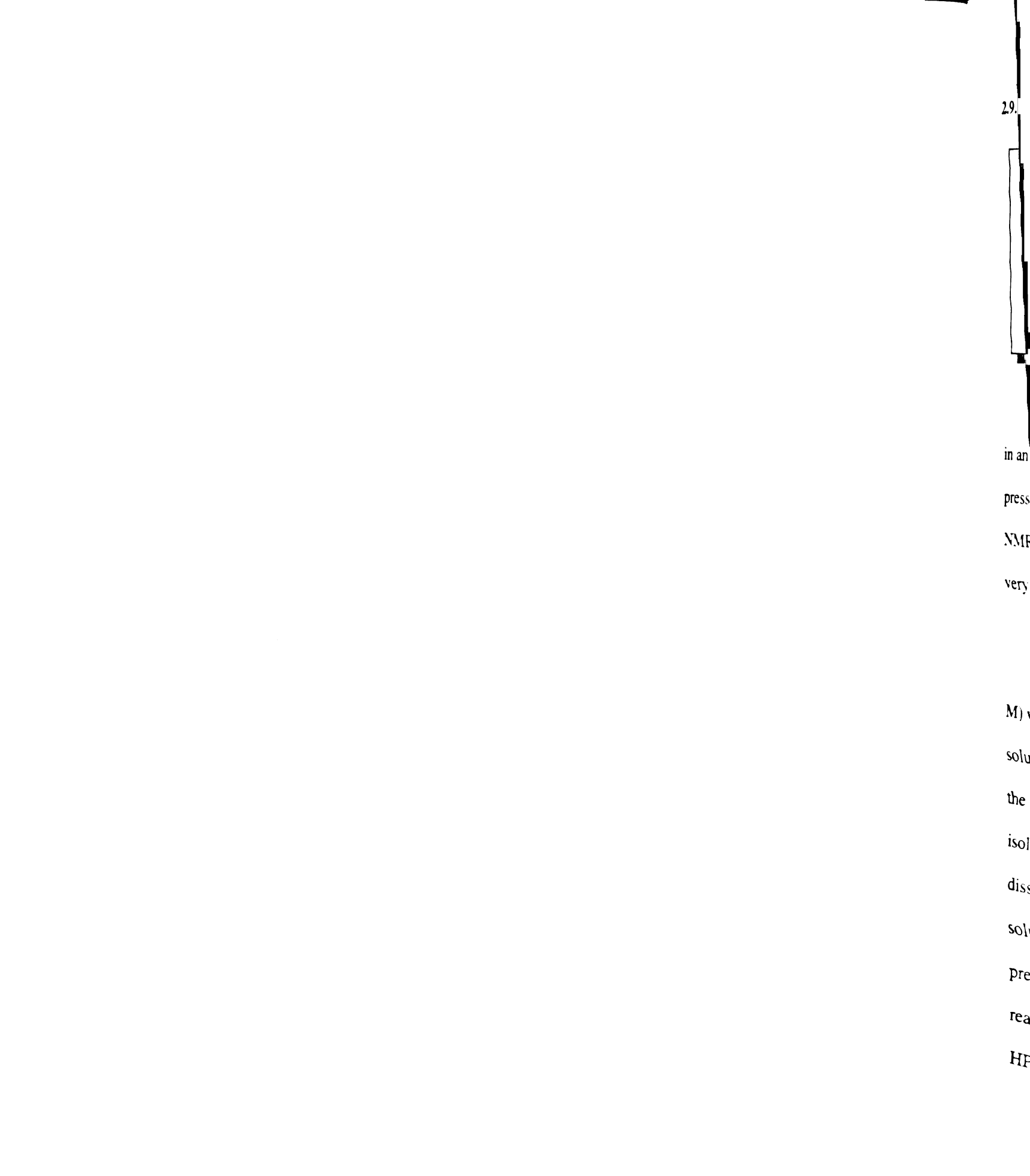
Another photoproduct collected at 6 minutes was not stable thermally and identified as 1-cyano-2-methoxy-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,10-diene (**CN-OCH3-CBt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 6.29 ppm(H-10), a doublet at 6.18 ppm(H-11) and a doublet of doublets at 4.65 ppm(H-3). The peaks at 6.29 and 6.18 ppm are coupled to one another with a 2.75 Hz coupling. The peak at 4.65 ppm(H-3) coupled to the two vicinal allylic protons H-4α and H-4β with 6.59 and 2.8 Hz coupling constants and its lager upfield shift is indicative of an enol ether proton.

The ratios of **CN-OCH3-COa**: **CN-OCH3-CBt**: **CN-OCH3-LCBa** were measured by NMR analysis to be 8: 2: 1 and 10:1:1 with the light sources of 254 nm and 313 nm, respectively.

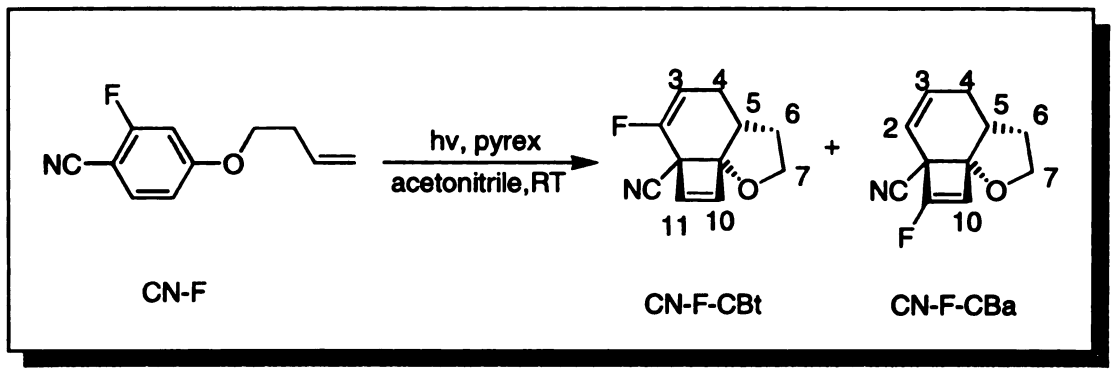

^{1}H NMR of CN-OCH3-COa in $CDCl_3$
6
7
8
9
5
10
NC
O
2
O
CH_3
CN-OCH3-COa
2
6
5
7
6
5
4
3
2
1
ppm


^{1}H NMR of CN-OCH3-CBt in $CDCl_3$
H_3C
O
3
4
5
6
NC
O
7
11
10
CN-OCH3-CBt
10
11
3
7
6
5
4
3
2
1
ppm


^{1}H NMR of mixture of CN-OCH3-COa and CN-OCH3-LCBa in $CDCl_3$
CN-OCH3-COa
A
CN-OCH3-LCBa
B
B10
A5
A6
A2
B2
7
6
5
4
3
2
1
ppm



2.9. Photochemistry of 4-(3-buten-1-oxy)-2-fluorobenzonitrile (CN-F)



CN-F CN-F-CBt CN-F-CBa

A solution of **CN-F** (2.0 mg) in deuterated acetonitrile (0.75 mL, 1.39 x 10^{-2} M) in an NMR tube was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 14 days of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts with very low conversion.

Another solution of **CN-F** (2.0 mg) in deuterated acetone (0.75 mL, 1.39 x 10^{-2} M) was purged with argon for 15 minutes and then irradiated through a 313 nm filter solution. After 24 hours of irradiation, NMR analysis of the reaction mixture was showed the presence of several photoproducts. Preparatory scale photolysis was carried out to isolate the photoproducts. 4-(3-Buten-1-oxy)-2-fluorobenzonitrile (166 mg) was dissolved in freshly distilled acetone (50 mL) and irradiated through a 313 nm filter solution. After 48 hours of irradiation, the reaction mixture was concentrated at reduced pressure. ^{1}H NMR showed the presence of the starting nitrile and its products. The reaction mixture was isolated and purified by silica gel chromatography followed by HPLC.

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9.89

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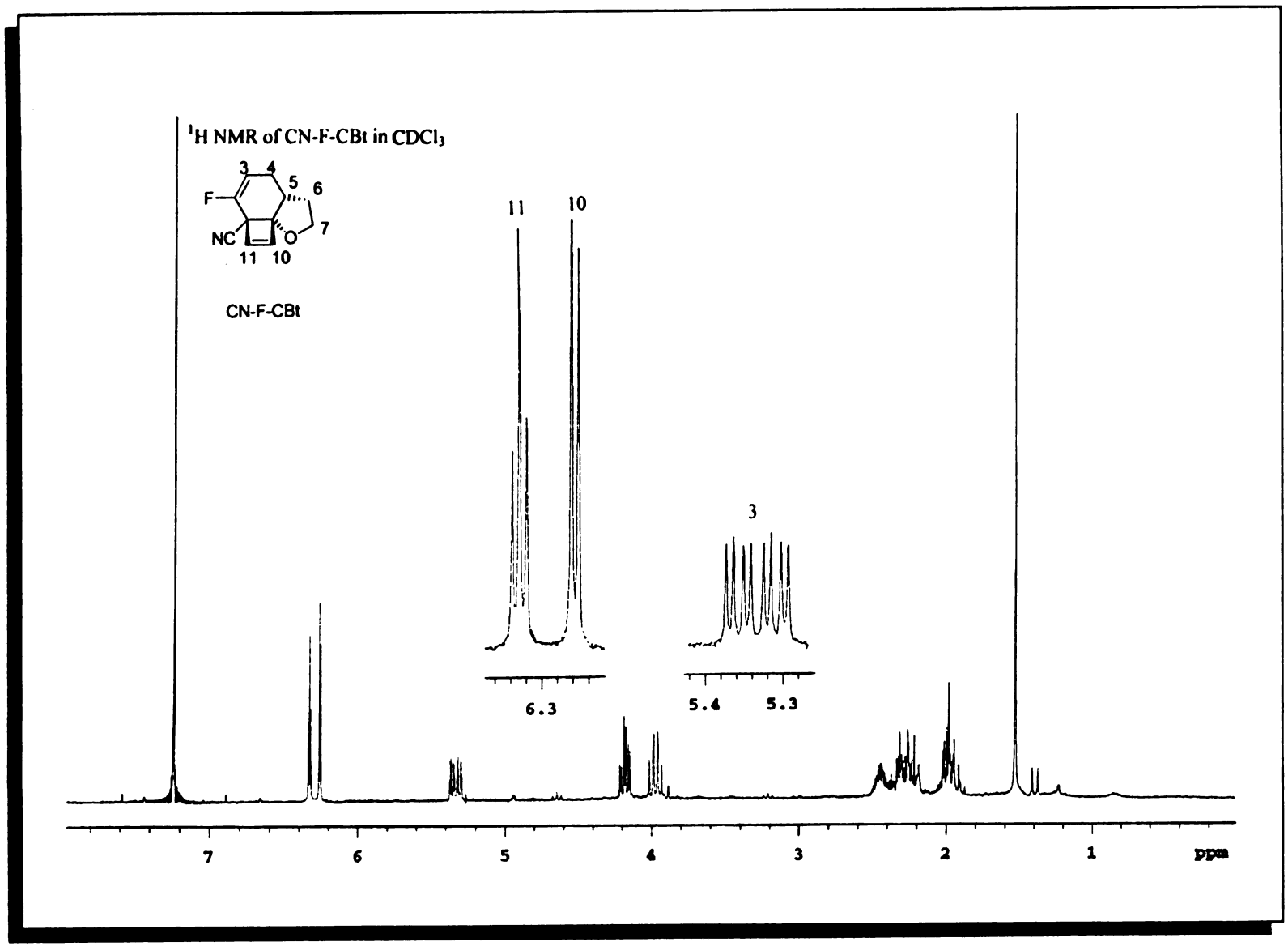
con

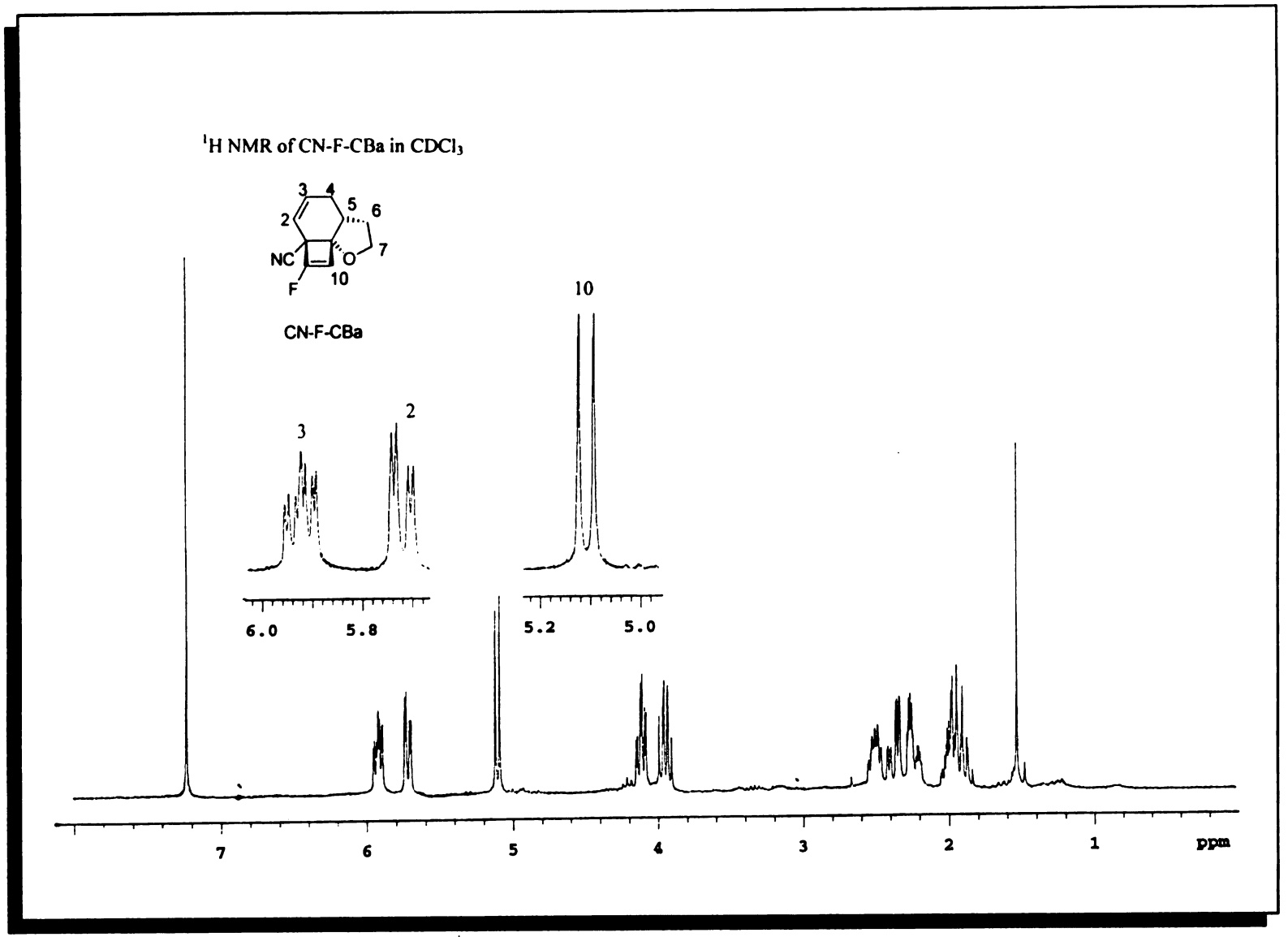
1 a

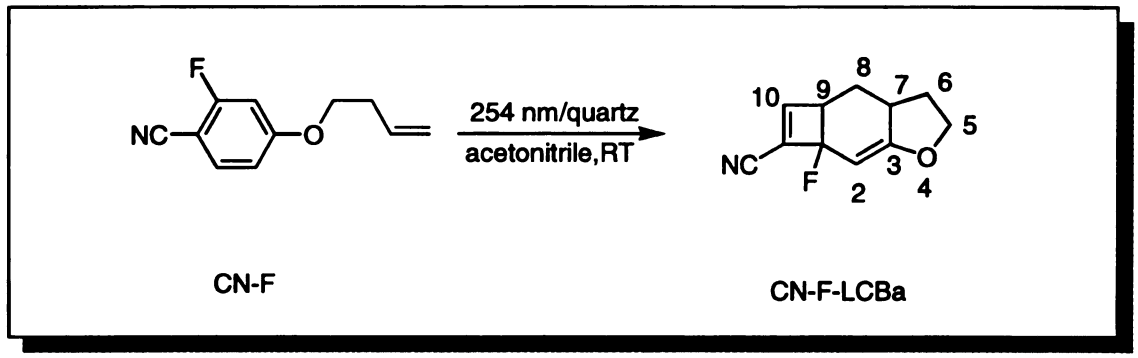
The photoproduct collected off the HPLC at 9.5 minutes was identified as 1-cyano-2-fluoro-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,10-diene (**CN-F-CBt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 6.25 ppm(H-11), a doublet at 6.33 ppm(H-10) and a doublet of doublets of doublets at 5.33 ppm(H-3). The peaks at 6.25 and 6.33 ppm are coupled to one another with a 2.75 Hz coupling and the peak at 6.33 ppm is coupled to the fluorine atom with ~3 Hz coupling constant. The peak 5.33 ppm(H-3) is coupled to the two vicinal allylic protons H-4α and H-4β with 8.24 and 3.3 Hz coupling constants and also coupled to fluorine with a 15.38 Hz coupling constant.

Another photoproduct collected off the HPLC at 5.5 minutes was identified as 1-cyano11-fluoro-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,10-diene (**CN-F-CBa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 5.11 ppm(H-10), a doublet of doublets at 5.72 ppm(H-2) and a doublet of doublet of doublets at 5.93 ppm(H-3). Peaks at 5.72 and 5.93 ppm are coupled to one another with a 9.89 Hz coupling. The peak at 5.72 ppm(H-2) is coupled to the vicinal allylic proton H-4α and the peak at 5.93 ppm is coupled to the two vicinal allylic protons H-4α and H-4β. The peak at 5.11 ppm(H-10) is coupled to a fluorine atom with a 8.79 Hz coupling constant .

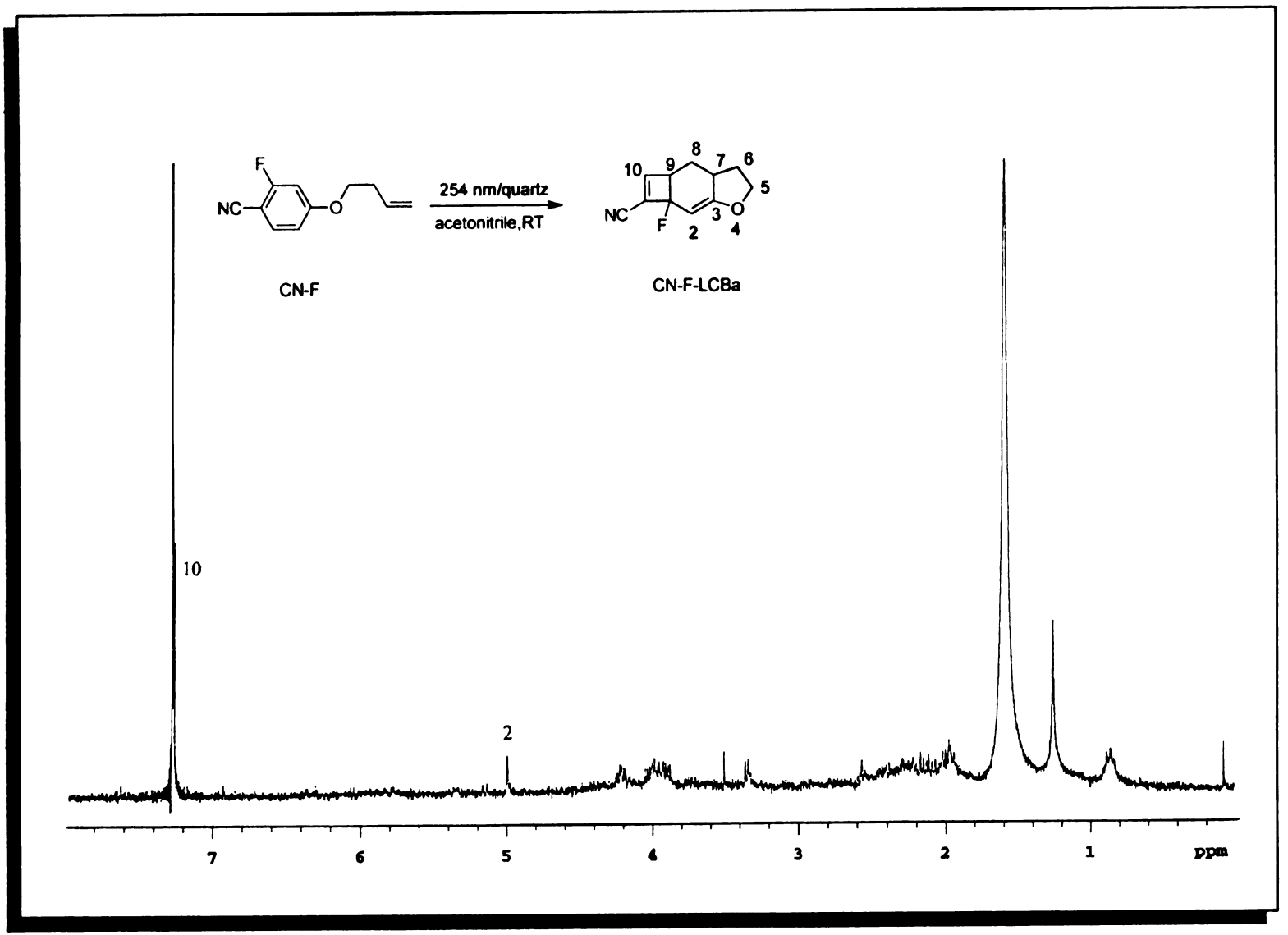
The ratios of **CN-F-CBt**: **CN-F-CBa** were measured by NMR analysis to be 1.6: 1 and 1: 1.8 ratio with the light sources of >300 nm and 313 nm, respectively.


^{1}H NMR of CN-F-CBt in $CDCl_3$
3
4
5
6
F
7
NC
O
11
10
CN-F-CBt
11
10
3
6.3
5.4
5.3
7
6
5
4
3
2
1
ppm

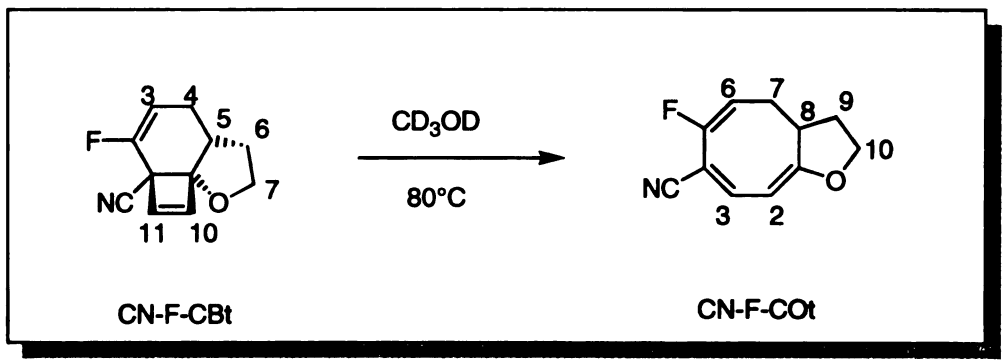

^{1}H NMR of CN-F-CBa in $CDCl_3$
3
4
5
6
2
7
NC
O
F
10
CN-F-CBa
10
3
2
6.0
5.8
5.2
5.0
7
6
5
4
3
2
1
ppm



A quartz test tube containing another solution of 4-(3-buten-1-oxy)-2-fluorobenzonitrile (8.0 mg) in deuterated acetonitrile (3.0 mL, 1.39 x 10^{-2} M) was purged with argon for 15 minutes and then irradiated in a Rayonet reactor with 254 nm lamps. After 30 hours of irradiation, NMR analysis of the reaction mixture was showed the presence of several photoproducts. After 60 hours of irradiation, one of the products in the mixture was assigned as 11-cyano-1-fluoro-4-oxatricyclo[7.2.0.$0^{3,7}$]undeca-2,10-diene (**CN-F-LCBa**) based on the characteristic two vinylic peaks at 4.96 ppm (H-2) and 7.23 ppm (H-10).


F
NC
O
254 nm/quartz
acetonitrile,RT
CN-F
10
9
8
7
6
5
NC
F
2
3
O
4
CN-F-LCBa
10
2
7
6
5
4
3
2
1
ppm

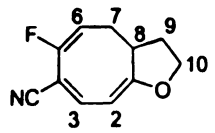
2.9.1. **Thermal chemistry of 1-cyano-2-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (CN-F-CBt)**



A solution of **CN-F-CBt** (1.1 mg) in deuterated methanol (1 mL) was purged with argon and heated in a constant temperature bath at 80 °C. The reaction progress was monitored by HPLC and ^{1}H NMR. After 12 hours of heating, a single product was formed.

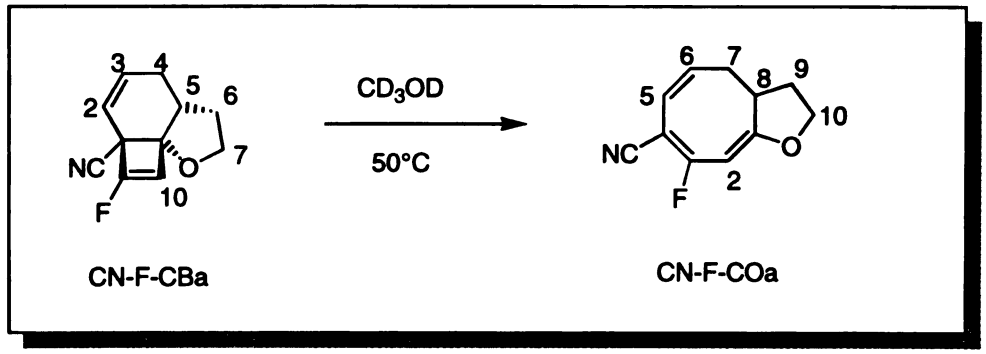
The product was identified as 4-cyano-5-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-F-COt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 5.40 ppm(H-2), a doublet of triplets at 5.70 ppm(H-6) and a doublet at 6.86 ppm(H-3). The peaks at 5.40 and 6.86 ppm are coupled to one another with a 7.32 Hz coupling. The peak at 5.70 ppm(H-6) is coupled to two vicinal allylic protons H-7 with a 5.86 Hz coupling constant and coupled to fluorine with a 23.93 Hz coupling constant.

^{1}H NMR of CN-F-COt in CD_3OD



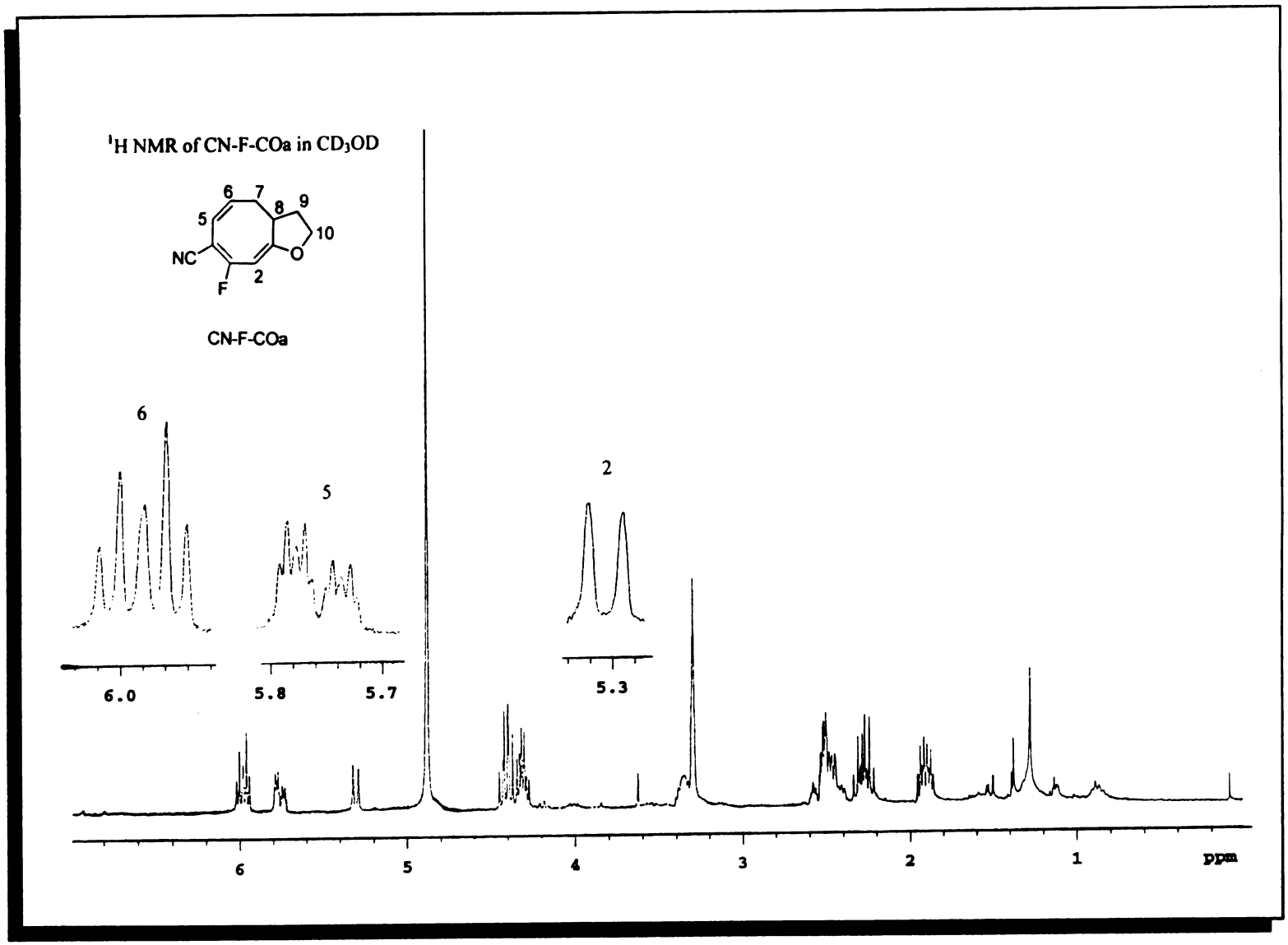
CN-F-COt

2.9.2. **Thermal chemistry of 1-cyano-11-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (CN-F-CBa)**

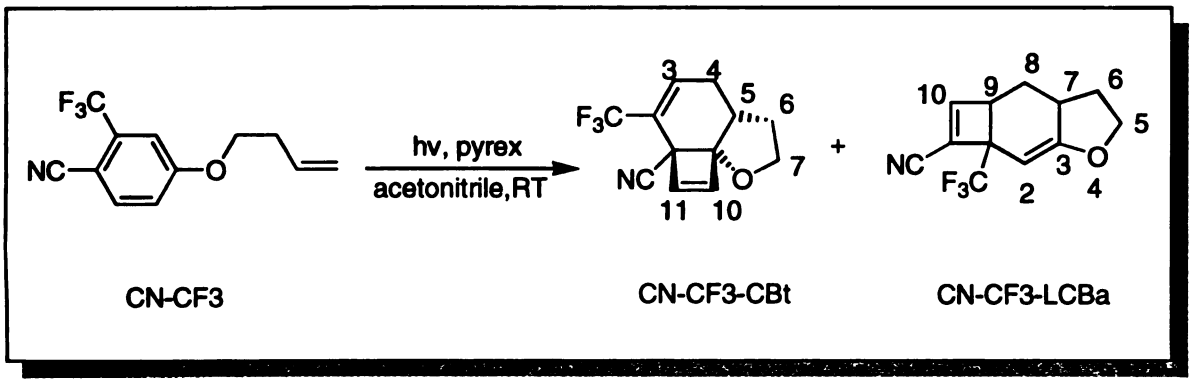


A solution of **CN-F-CBa** (2.2 mg) in deuterated methanol (1 mL) was purged with argon and heated in a constant temperature bath at 50 °C. The reaction progress was monitored by HPLC and ^{1}H NMR. After 24 hours of heating, a single product was produced. Same result was observed after heating at 80 °C for 6 hours.

The photoproduct was identified as 4-cyano-3-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-F-COa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 5.31 ppm(H-2), a doublet of doublets at 5.76 ppm(H-5) and a doublet of triplets at 5.98 ppm(H-6). Peaks at 5.76(H-5) and 5.98(H-6) ppm were coupled to one another with a 12.64 Hz coupling. The peak at 5.76(H-5) is coupled to fluorine atom with a 4.94 Hz coupling constant and the peak at 5.98(H-6) ppm is coupled to the two vicinal allylic proton H-7 with a 5.49 Hz coupling. The peak at 5.31 ppm(H-2) coupled to fluorine with a 9.34 Hz coupling constant and its large upfield shift is indicative of an enol ether proton. Irradiation of **CN-F-COt** and **CN-F-COa** gave only trace of corresponding **CB**.


^{1}H NMR of CN-F-COa in CD_3OD
6
7
8
9
5
10
NC
O
F
2
CN-F-COa
6
5
2
6.0
5.8
5.7
5.3
6
5
4
3
2
1
ppm

2.10. Photochemistry of 4-(3-buten-1-oxy)-2-trifluorofluoromethylbenzonitrile (CN-CF_3)



A solution of **CN-CF3** (2.1 mg) in deuterated acetonitrile (0.75 mL, 1.16 x 10^{-2} M) was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 36 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several products on the complete depletion of the reactant.

A quartz test tube contains another solution of **CN-CF3** (8.4 mg) in deuterated acetonitrile (3.0 mL, 1.16 x 10^{-2} M) was purged with argon for 15 minutes and then irradiated in a Rayonet reactor with 254 nm lamps. After 12 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts on the complete depletion of the reactant. The major product was identical to one of the products observed with irradiation of >300 nm.

Another solution of **CN-CF3** (2.0 mg) in deuterated acetone (0.75 mL, 1.5 x 10^{-2} M) was purged with argon for 15 minutes and then irradiated through a 313 nm filter

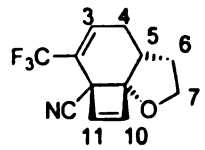
solution. After 22 hours of irradiation, NMR analysis of the reaction mixture showed the presence of two photoproducts. Preparatory scale photolysis was carried out to isolate the photoproducts. **CN-CF3** (148 mg) was dissolved in freshly distilled acetone (50 mL) and irradiated through a 313 nm filter solution. After 24 hours of irradiation, the reaction mixture was concentrated at reduced pressure. ^{1}H NMR showed the presence of the starting nitrile and its products. The reaction mixture was isolated and purified by preparative TLC followed by HPLC.

One photoproduct collected off the HPLC at 11 minutes was identified as 1-cyano-2-trifluoromethyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-CF3-CBt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 6.22 ppm(H-11), a doublet at 6.31 ppm(H-10) and a multiplet at 6.51 ppm(H-3). Peaks at 6.22 and 6.31 ppm are coupled to one another with a 2.75 Hz coupling constant. The peak a 6.51 ppm(H-3) coupled to two vicinal allylic protons H-4 and three fluorine atoms.

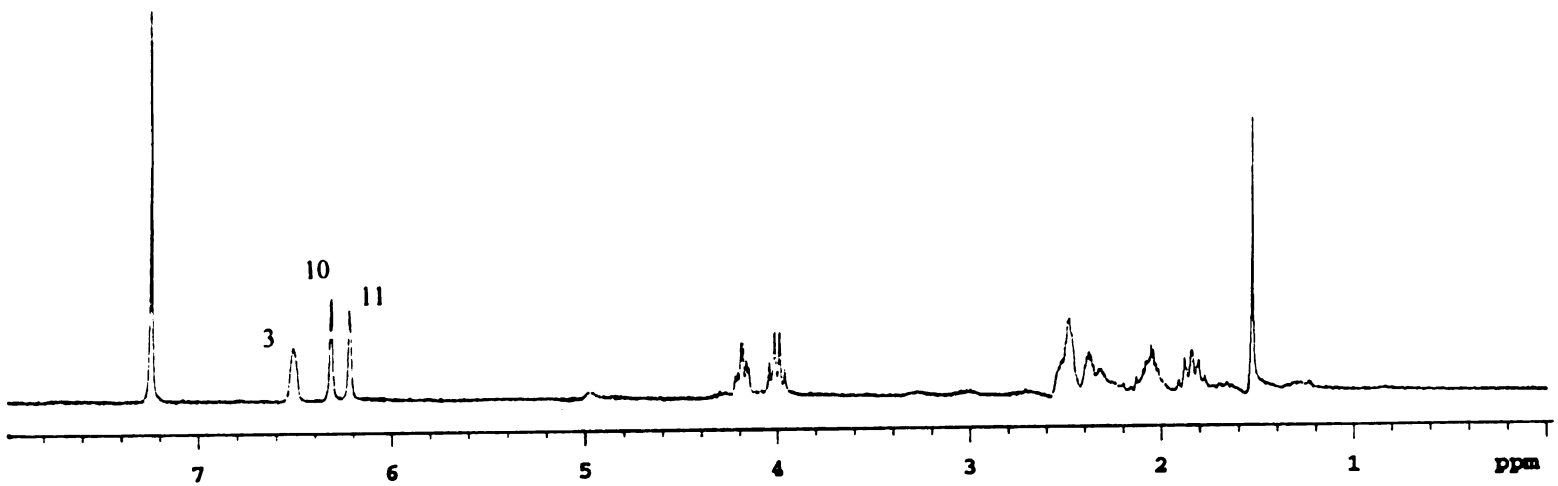
The other photoproduct collected off the HPLC at 7 minutes was identified as 11-cyano-1-trifluoromethyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (**CN-CF3-LCBa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to two vinyl protons: a singlet at 4.93 ppm(H-2) and a singlet at 6.94 ppm(H-10). The large upfield shift of the proton at 4.93 ppm(H-2) is indicative of an enol ether proton of linear cyclobutene structure.

The ratios of **CN-CF3-CBt**: **CN-CF3-LCBa** were measured by NMR analysis to be 1:10, 1:10 and 1:1 ratio with the light sources of >300 nm, 254 nm and 313 nm, respectively.

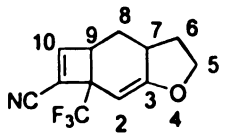
^{1}H NMR of CN-CF3-CBt in $CDCl_3$



CN-CF3-CBt

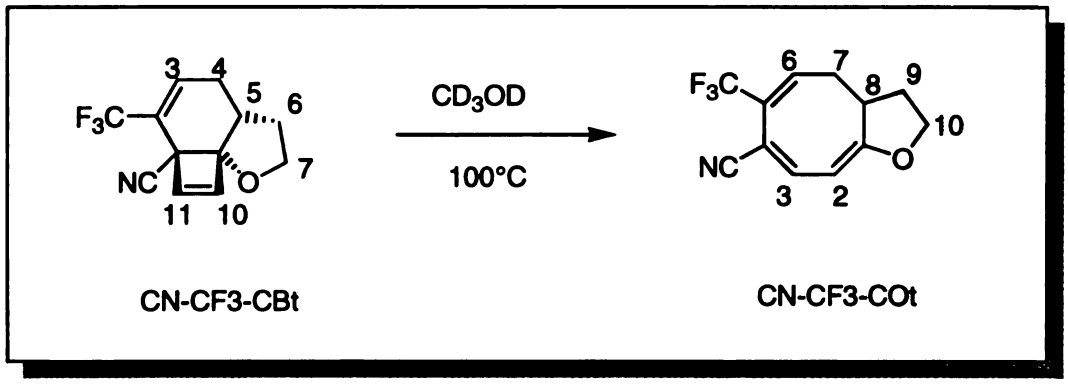


^{1}H NMR of CN-CF3-LCBa in $CDCl_3$



CN-CF3-LCBa

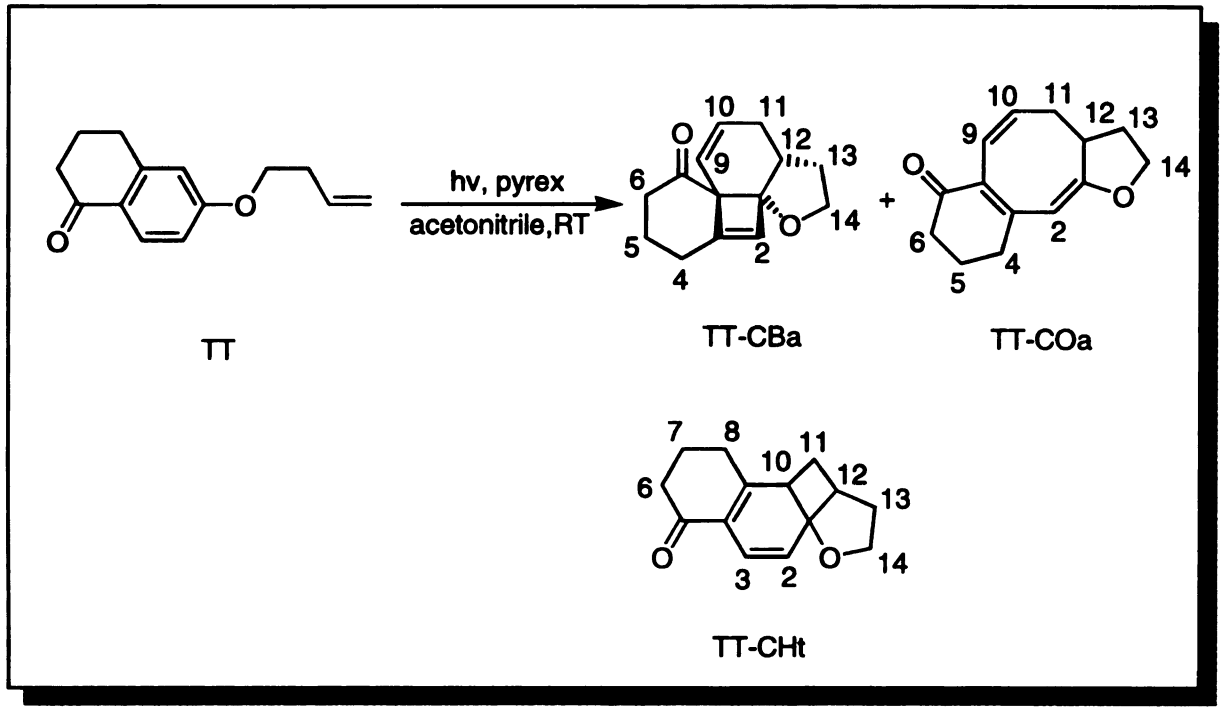
2.10.1. **Thermal chemistry of 1-cyano-2-trifluoromethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene (CN-CF3-CBt)**



A solution of **CN-CF3-CBt** (2.4 mg) in deuterated methanol (1 mL) was purged with argon and heated in a constant temperature bath at 100 °C. The reaction progress was monitored by HPLC and ^{1}H NMR. After 24 hours of heating, the mixture showed a compound absorbing UV around 320 nm and decomposed products.

The photoproduct was identified as 4-cyano-5-trifluoromethyl-11-oxabicyclo [6.3.0]undeca-1,3,5-triene (**CN-CF3-COt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 5.16 ppm(H-2), a triplet at 6.41 ppm(H-6) and a doublet at 6.54 ppm(H-3). Peaks at 5.16 and 6.54 ppm are coupled to one another with a 6.59 Hz coupling. The peak at 6.41 ppm(H-6) coupled to the two vicinal allylic protons H-7 with a 7.69 Hz coupling.

2.11. Photochemistry of 6-(3-Buten-1-oxy)-1-tetralone (TT)



A solution of **TT** (2.1 mg) in deuterated acetonitrile (0.75 mL, 1.29 x 10^{-2} M) was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 8 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts. Preparatory scale photolysis was carried out to isolate the photoproducts. **TT** (182 mg) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 8 hours of irradiation, the reaction mixture was concentrated at reduced pressure. ^{1}H NMR showed the presence of the starting ketone and its products. The reaction mixture was isolated and purified by preparative TLC followed by HPLC.

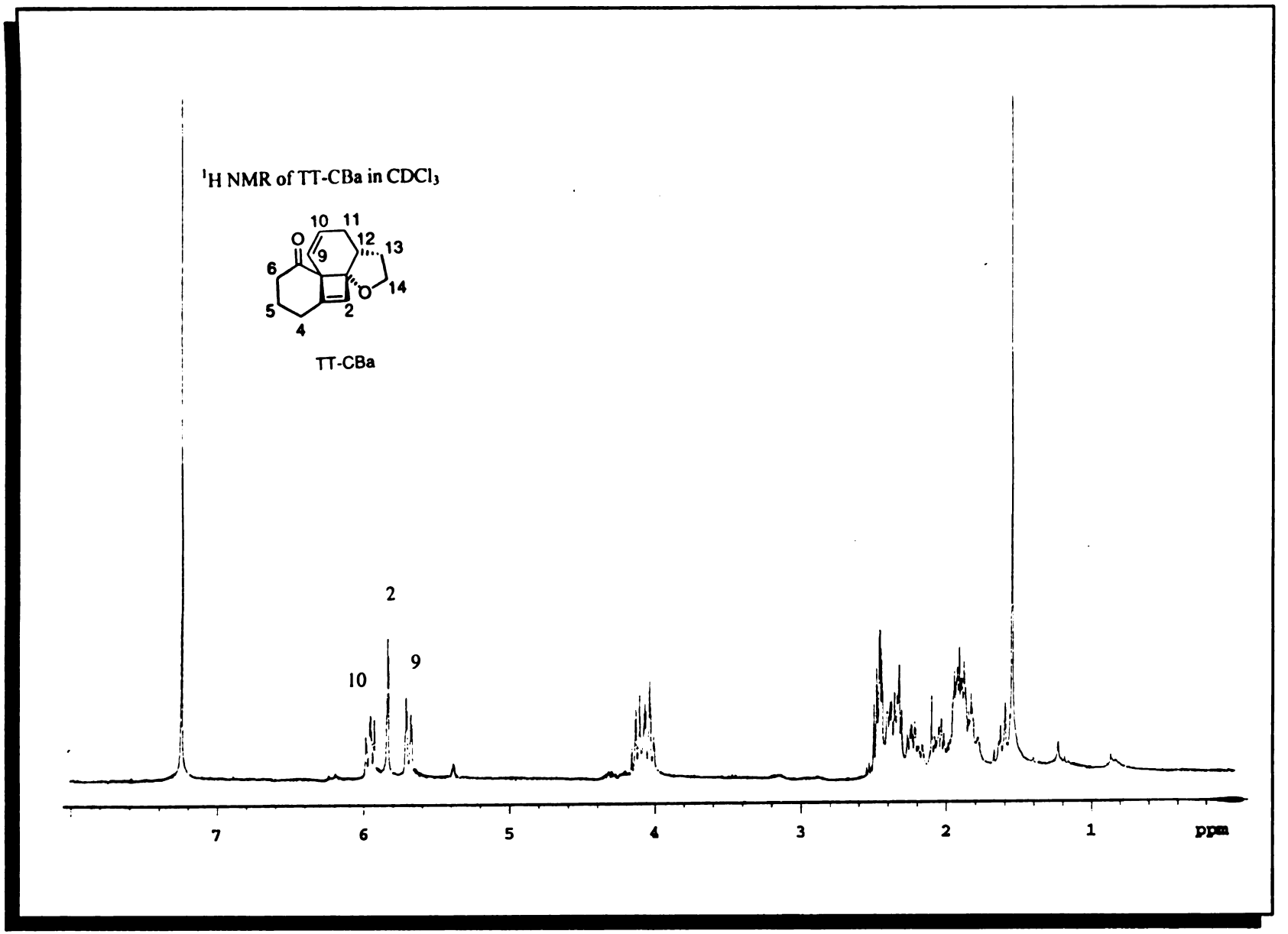
One photoproduct collected off the HPLC at 13 minutes was identified as 15-oxa-tetracyclo[10, 3, 0, $0^{1,8}$, $0^{3,8}$]pentadeca-2,9-diene-7-one (**TT-CBa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet of doublets at 5.69 ppm(H-9), a doublet at 5.83 ppm(H-2) and a doublet of doublet of doublets at 5.96 ppm(H-10). Peaks at 5.69(H-9) and 5.96 ppm(H-10) are coupled to one another with a 9.9 Hz coupling constant and the peak at 5.96 ppm(H-10) is coupled to two vicinal allylic protons H-11 with a coupling constant of 6.9 Hz and 1.8 Hz. The peak at 5.83 ppm(H-2) is coupled to allylic proton H-4α with a 2.1 Hz coupling constant.

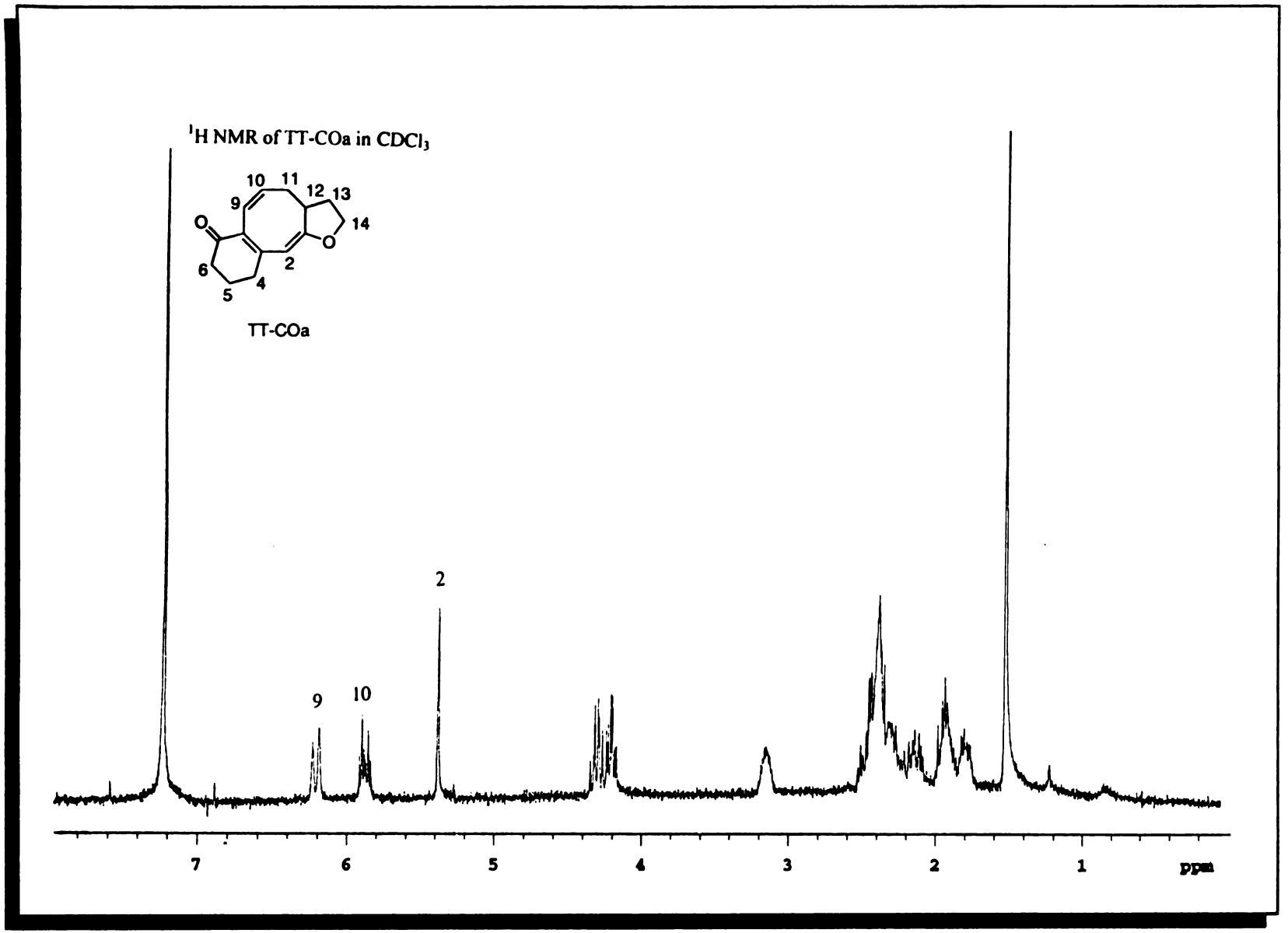
Another photoproduct collected off the HPLC at 10 minutes was identified as 15-oxa-tricyclo[10, 3, 0, $0^{3,8}$]pentadeca-1, 3, 9-triene-7-one (**TT-COa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a doublet at 6.21 ppm(H-9), a doublet of triplets at 5.86 ppm(H-10) and a singlet at 5.38 ppm(H-2). Peaks at 6.21 and 5.86 ppm are coupled to one another with ~12 Hz coupling constant and the peak at 5.86 ppm(H-10) is coupled to the two vicinal allylic protons H-11 with a coupling constant of 4.5 Hz. The large upfield shift of the proton at 5.38 ppm(H-2, singlet) is indicative of an enol ether.

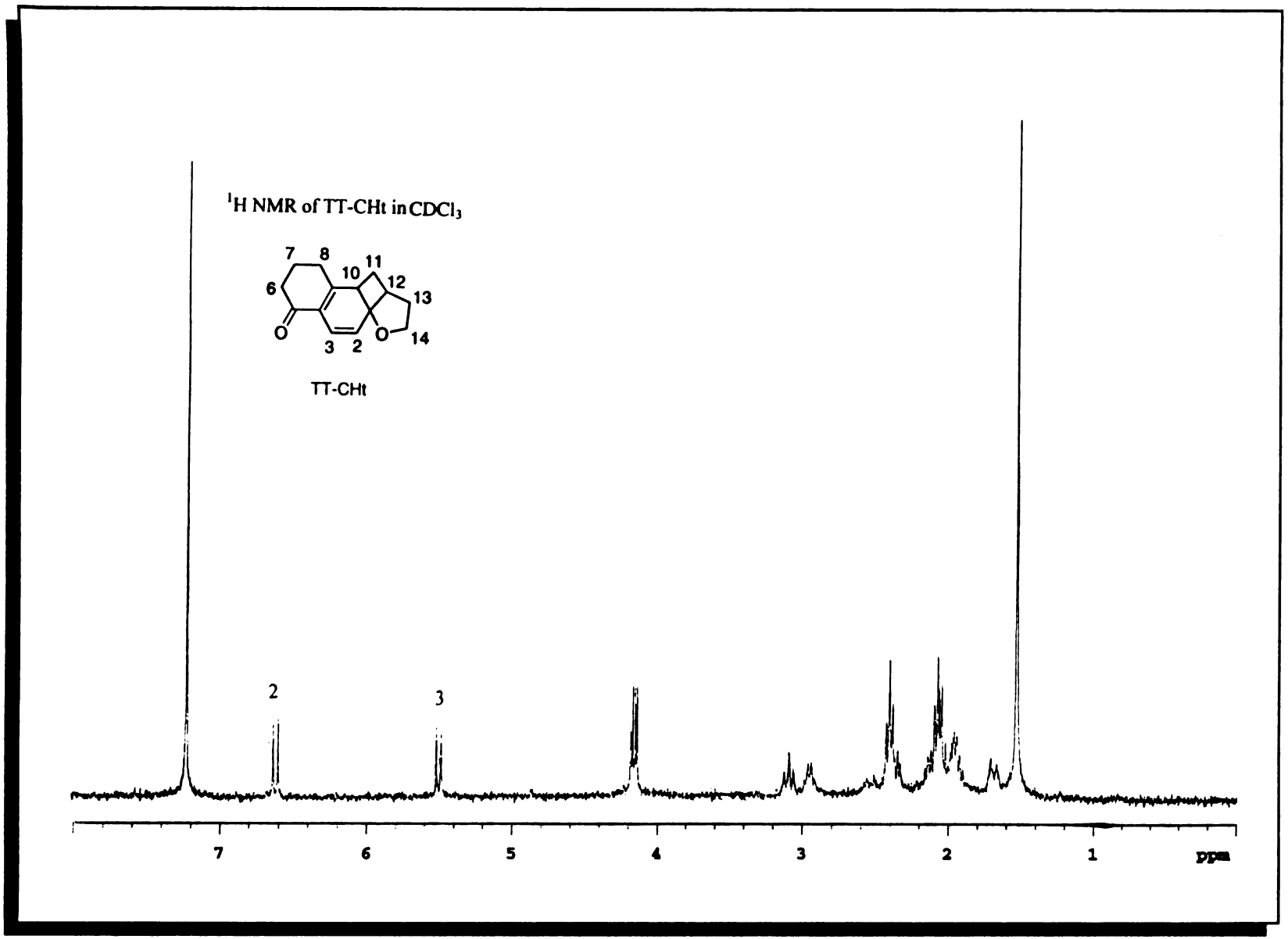
The other photoproduct collected off the HPLC at 9 minutes was identified as 15-oxa-tetracyclo[10, 3, 0, $0^{1,10}$, $0^{4,9}$]pentadeca-2, 4-diene-5-one (**TT-CHt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to two vinyl protons: a doublet at

5.5 ppm(H-2) and a doublet at 6.6 ppm(H-3). Two peaks were coupled to one another with a 10 Hz coupling constant that is a typical value for this structure.

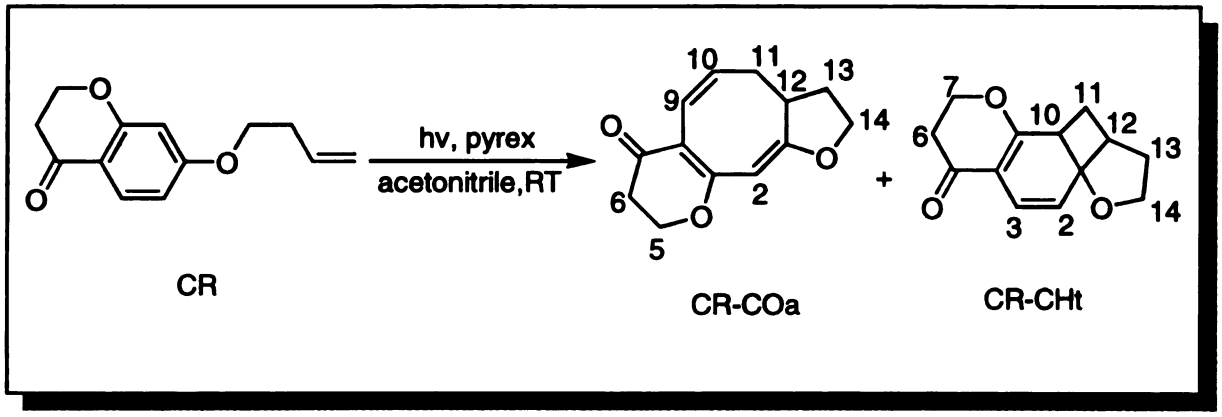
TT-CBa, **TT-COa** and **TT-CHt** were observed in 10:2:1 ratio.


^{1}H NMR of TT-CBa in $CDCl_3$
10
11
12
13
14
O
9
6
5
4
2
O
TT-CBa
2
10
9
7
6
5
4
3
2
1
ppm


^{1}H NMR of TT-COa in $CDCl_3$
10
11
12
13
9
14
O
O
6
2
5
4
TT-COa
2
9
10
7
6
5
4
3
2
1
ppm


^{1}H NMR of TT-CHt in $CDCl_3$
7
8
10
11
12
13
6
O
O
14
3
2
TT-CHt
2
3
7
6
5
4
3
2
1
ppm

2.12. Photochemistry of 6-(3-buten-1-oxy)-1-Chromonone (CR)



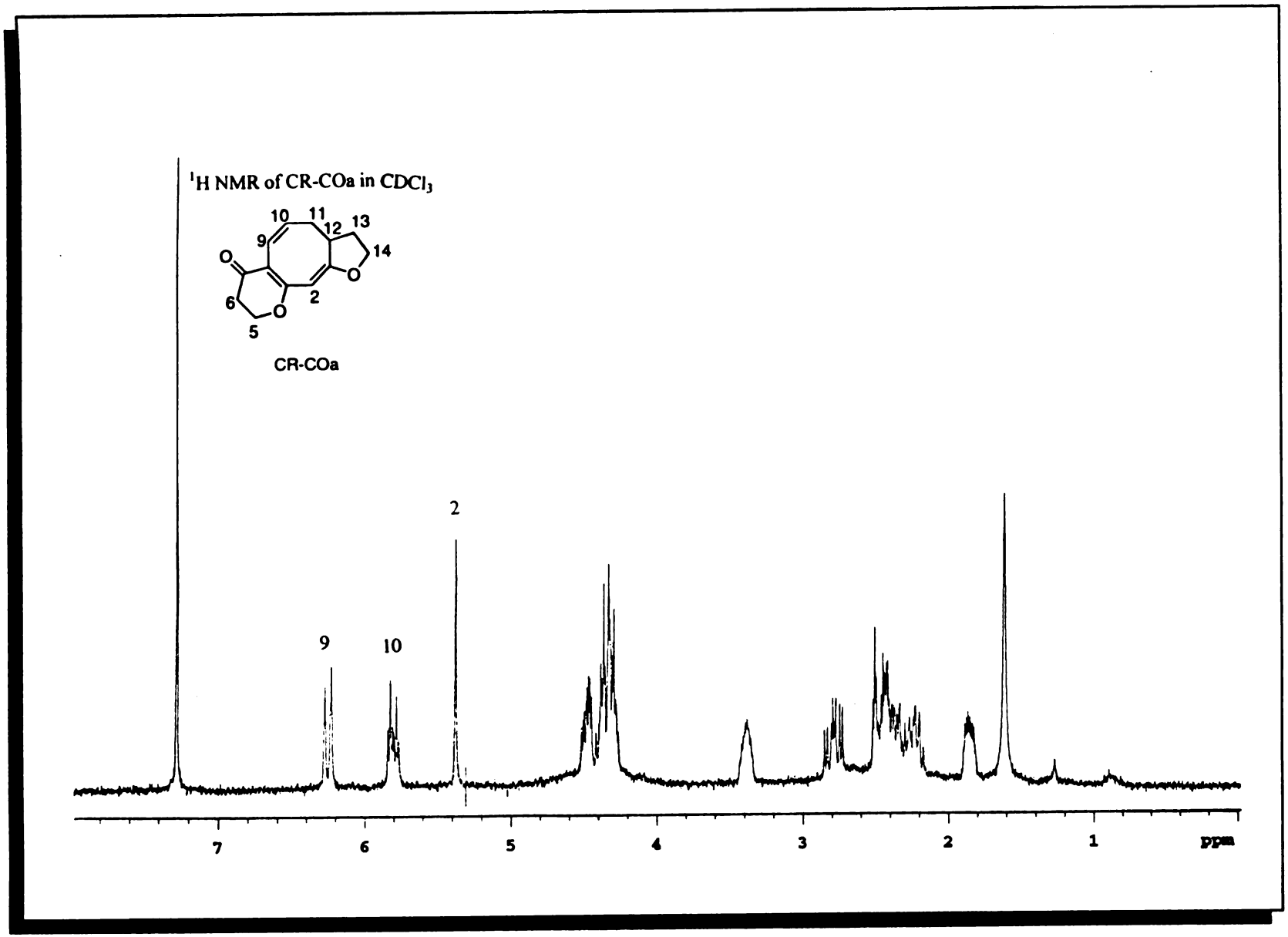
A solution of **CR** (2.1 mg) in deuterated acetonitrile (0.75 mL, 1.28 x 10^{-2} M) was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. After 2 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts. Preparatory scale photolysis was carried out to isolate the photoproducts. **CR** (170 mg) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated through a Pyrex filter sleeve. After 8 hours of irradiation, the reaction mixture was concentrated at reduced pressure. ^{1}H NMR showed the presence of the starting ketone and its products. The reaction mixture was isolated and purified by silica gel chromatography followed by HPLC.

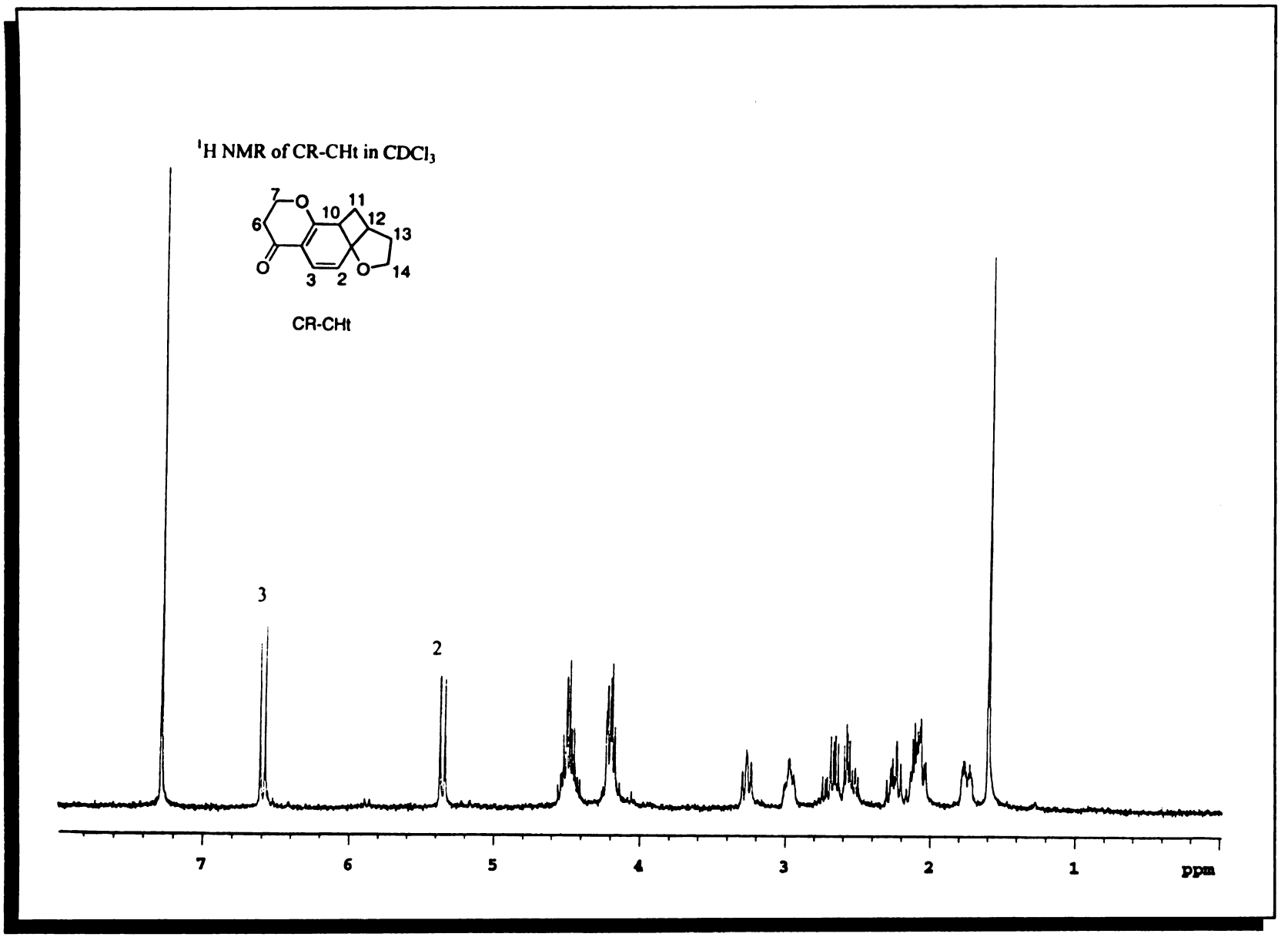
One photoproduct collected off the HPLC at 22 minutes was identified as 4,15-dioxa-tricyclo[10, 3, 0,$0^{3,8}$]pentadeca-1, 3, 9-triene-7-one (**CR-COa**) by its characteristic ^{1}H NMR. It showed peaks corresponding to three vinyl protons: a singlet at 5.3 ppm(H-2), a doublet of triplets at 5.8 ppm(H-10) and a doublet at 6.2 ppm(H-9). Peaks at 6.2 and

5.8 ppm are coupled to one another with a 12.5 Hz coupling constant and the peak at 5.8 ppm(H-10) is coupled to the two vicinal allylic protons H-7 with a coupling constant of 4.5 Hz. The large upfield shift of the proton at 5.38 ppm(H-2, singlet) is indicative of an enol ether.

The other photoproduct collected off the HPLC at 12 minutes was identified as 8,15-dioxa-tetracyclo[10, 3, 0, $0^{1,10}$, $0^{4,9}$]pentadeca-2, 4-diene-5-one (**CR-CHt**) by its characteristic ^{1}H NMR. It showed peaks corresponding to two vinyl protons: a doublet at 5.3 ppm(H-2) and a doublet at 6.5 ppm(H-3). Two peaks were coupled to one another with a 10 Hz coupling constant that is a typical value for the **CHt** structure.

Two products were identified as **CR-COa** and **CR-CHt** in 10 > 1 ratio.


^{1}H NMR of CR-COa in $CDCl_3$
10
11
12
13
9
14
O
O
6
2
O
5
CR-COa
2
9
10
7
6
5
4
3
2
1
ppm


^{1}H NMR of CR-CHt in $CDCl_3$
7
O
11
10
12
6
13
O
3
2
O
14
CR-CHt
3
2
7
6
5
4
3
2
1
ppm

Singlet and triplet energy of reactants were measured on a fluorescence spectrophotometer and UV-VIS spectrometer as shown in Table 6.

Table 6. Singlet and triplet energy of reactants.

	S_1(kcal/mol)	T_1(kcal/mol)		S_1(kcal/mol)	T_1(kcal/mol)
Al-CH3	96.3	67.6	CN-CH3	96.3	78.3
Al-OCH3	94.7	67.3	CN-OCH3	96.9	78.3
Al-F	97.6	69.9	CN-F	101.4	77.0
Al-CF3	98.6	66.5	CN-CF3	98.6	78.1

2.13. Computational Studies

Ab initio calculation of excited and ground states using the (U)HF/6-31G** method were carried out to provide additional insight into the factors that control the regioselectivity associated with the ortho [2+2] photocycloaddition.

Geometry optimization and energy calculations of ground states of **Al-CH3**, **Al-OCH3**, **Al-F** and **Al-CF3** were carried out for both conformers.

Table 7. Ground state energy of ortho substituted p-butenoxybenzaldehyde (**Al-X**)

	E_{anti}(kcal/mol)	E_{syn}(kcal/mol)
Al-CH3	-384204.040	-384204.675
Al-OCH3	-431171.3178	-431166.181
Al-F	-421739.154	-421735.948
Al-CF3	-570311.278	-570308.198

Geometry optimization, energies and dipole moment of excited triplet states of **Al-CH3**, **Al-OCH3**, **Al-F**, and **Al-CF3** were carried out for both conformers.

Table 8. Dipole moments and energy of anti/syn conformer of ortho substituted p-butenoxybenzaldehyde(**Al-X**).

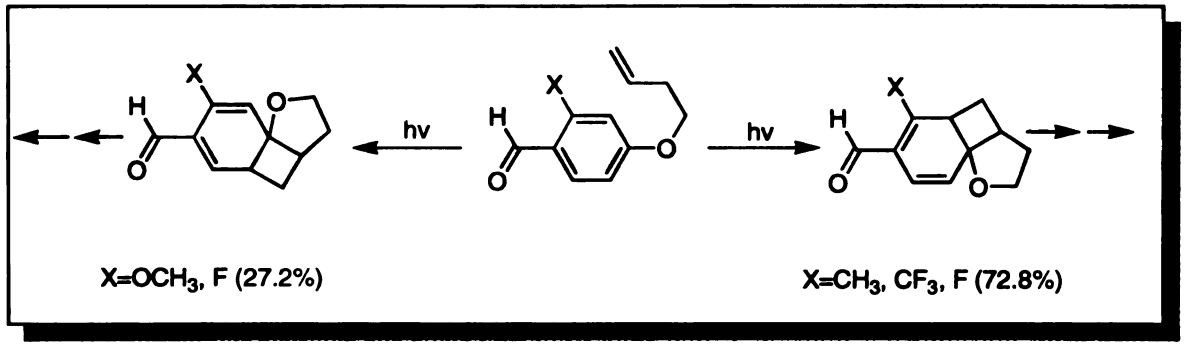
	Anti conformer		Syn conformer	
	E_{anti}(kcal/mol)	Dipole (Debye)	E_{syn}(kcal/mol)	Dipole(Debye)
Al-CH3	-384148.112	3.489	-384147.790	4.469
Al-OCH3	-431114.499	4.962	-431108.415	4.924
Al-F	-421683.555	4.397	-421677.992	6.381
Al-CF3	-570256.652	4.846	-570254.585	7.264

Geometry optimization and energies of **BR**, **CH**, **CO**, and **CB** of **Al-CH3**, **Al-OCH3**, **Al-F**, and **Al-CF3** were carried out for both conformers and both regioisomers.

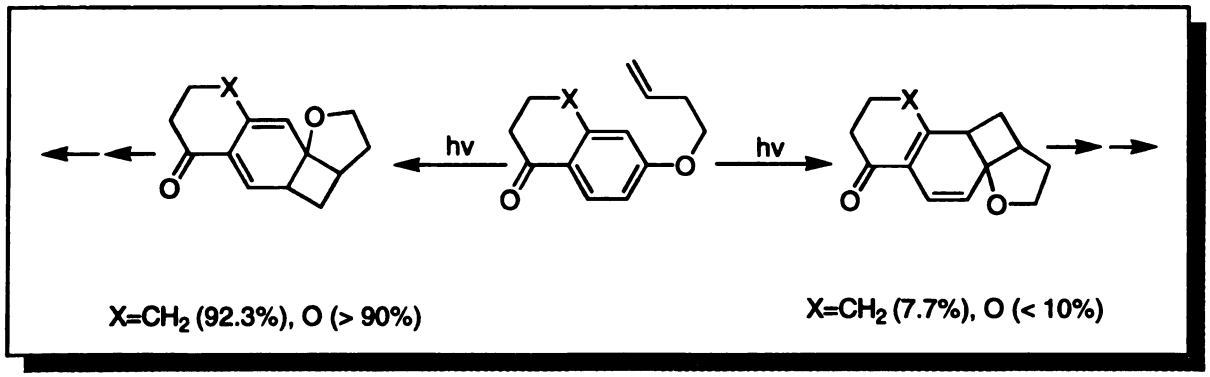
Part 3. Discussion

3.1. Regioselectivity

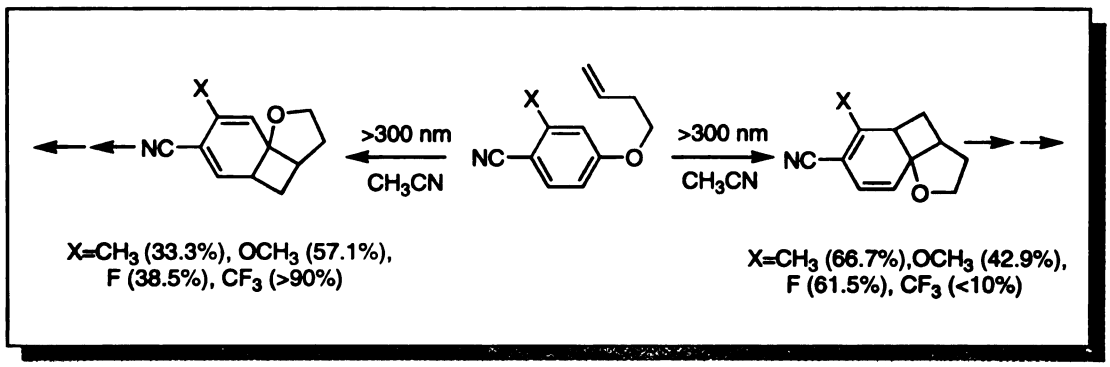
A high degree of regioselectivity was observed in photocycloaddition of ortho substituted p-butenoxybenzaldehydes and cyclic analogues while ortho substituted p-butenoxybenzonitrile showed relatively low degree of regioselectivity.



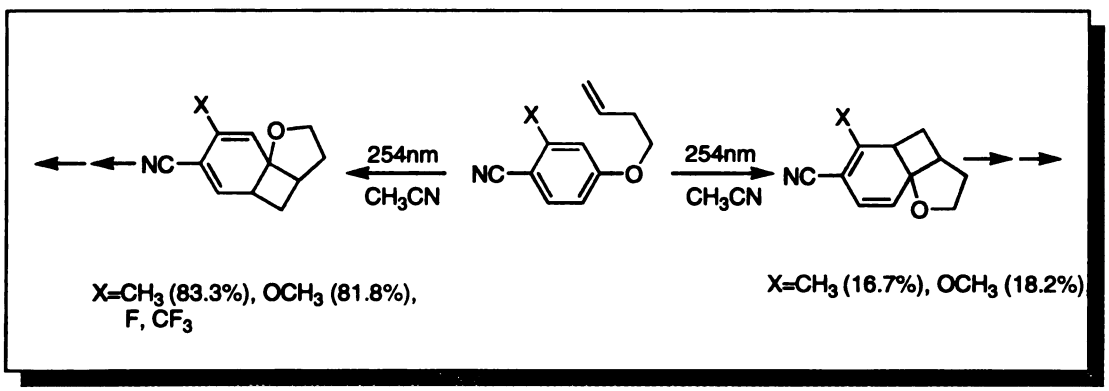
Generally, in case of the benzaldehyde system, electron-withdrawing groups direct the addition of the double bonds towards these substituents (syn-addition) while strong electron-donating groups drives the double bond away from the substituent (anti-addition).



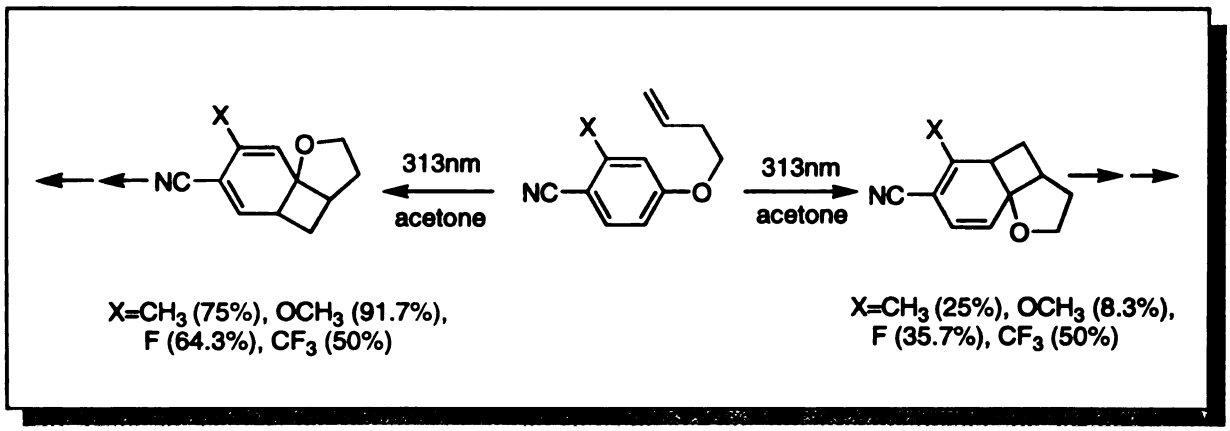
In case of cyclic phenylketone systems, p-butenoxy tetralone (**TT**) and chromanone (**CR**), which are analogues of ortho methyl (**Al-CH3**) and methoxy (**Al-OCH3**) substituted p-butenoxybenzaldehydes with anti-conformation, form regioisomers with the double bonds adding away from the substituents (anti-addition).



Regioselectivity of ortho substituted p-butenoxybenzonitrile showed a dependancy on the light source. In case of the light source over 300 nm, only CF_3 group showed a high degree of anti regioselectivity.



In case of direct irradiation with 254 nm, the initial [2+2] ortho cycloaddition of the double bond is anti to all ortho ring substituents with over 80% selectivity.

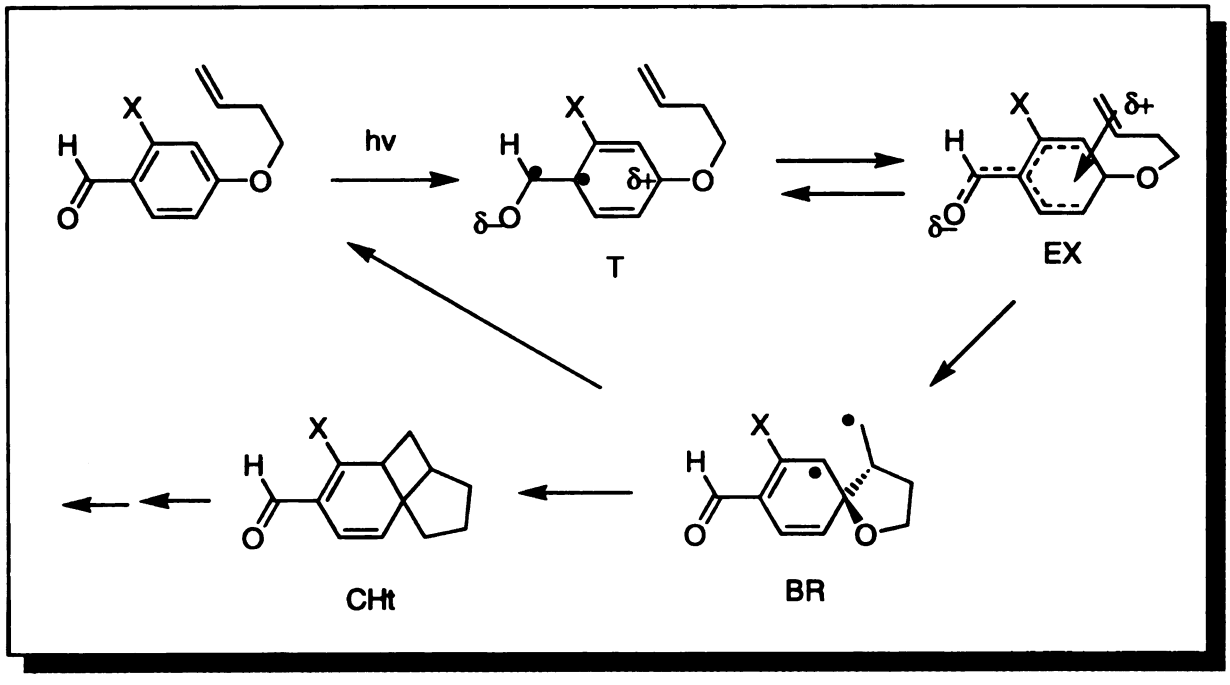


In case of sensitization by acetone with 313nm light source, stronger electron-donating groups showed higher degree of regioselectivity.

A high degree of regioselectivity was observed in the photocycloaddition of ortho substituted p-butenoxyacetophenone. In nearly all cases studied, electron-donating and electron-withdrawing groups direct the remote double bond syn. The difference between the two systems implies the presence of another major factor that determines regioselectivity. In order to understand the reason for this regioselectivity, each step of the reaction mechanism must be analyzed.

3.2. Overall Mechanism

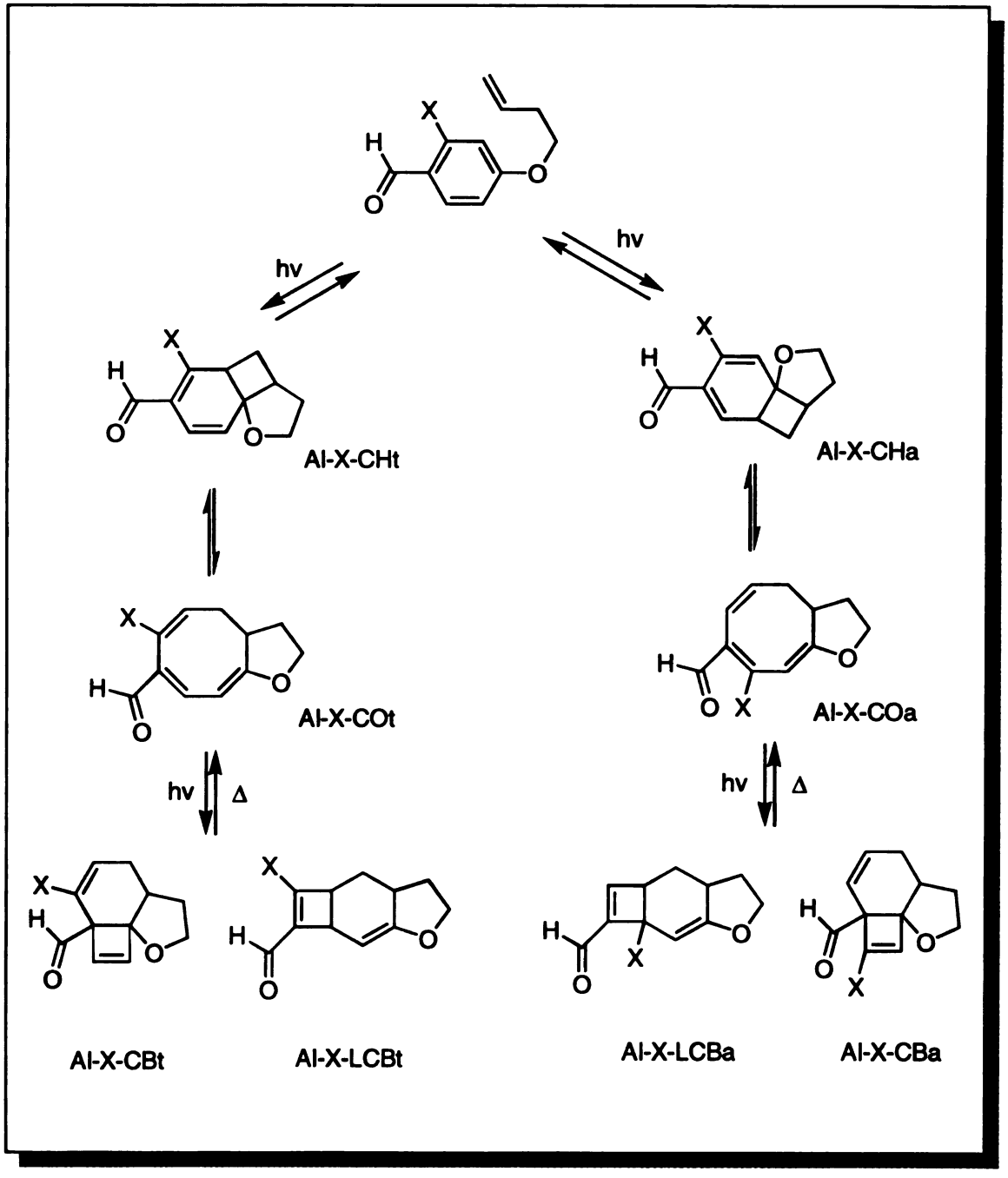
Irradiation of p-butenoxybenzaldehyde derivatives generates a charge transfer complex (exciplex; **EX**) that subsequently collapses to a biradical (**BR**). Then, the biradical (**BR**) can either convert to starting material or cyclize to form cyclohexadiene (**CH**).



Subtle electronic or steric effects at any step of initial cyclization mechanism could have profound effect on the regioselectivity. The significance of these factors on each step of the reactions scheme will be discussed.

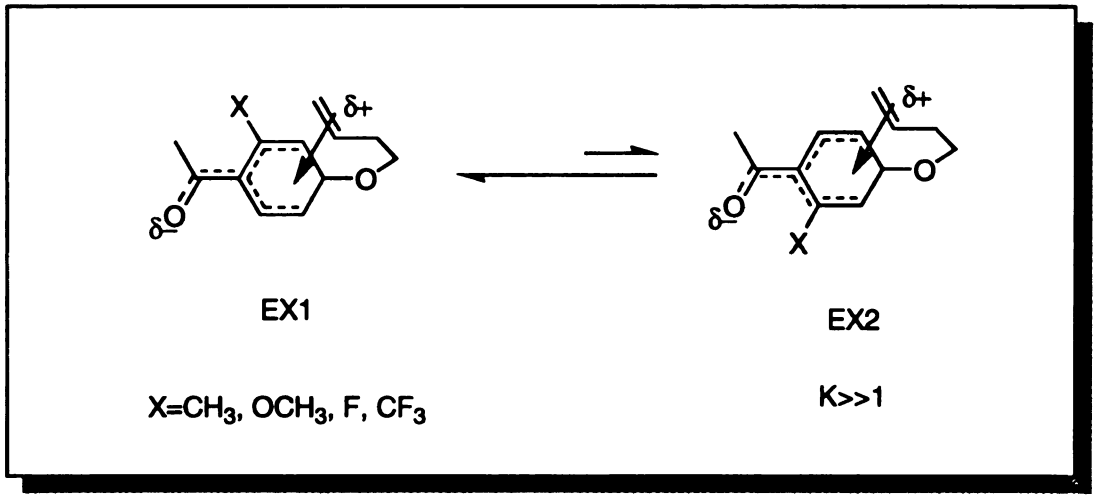
Cyclohexadiene (**CH**) thermally opens to cyclooctatriene (**CO**) which can photochemically cyclizes to either linear (**LCB**) or angular cyclobutene (**CB**). There are

two different modes of addition for each conformer of the two possible carbonyl rotomers.



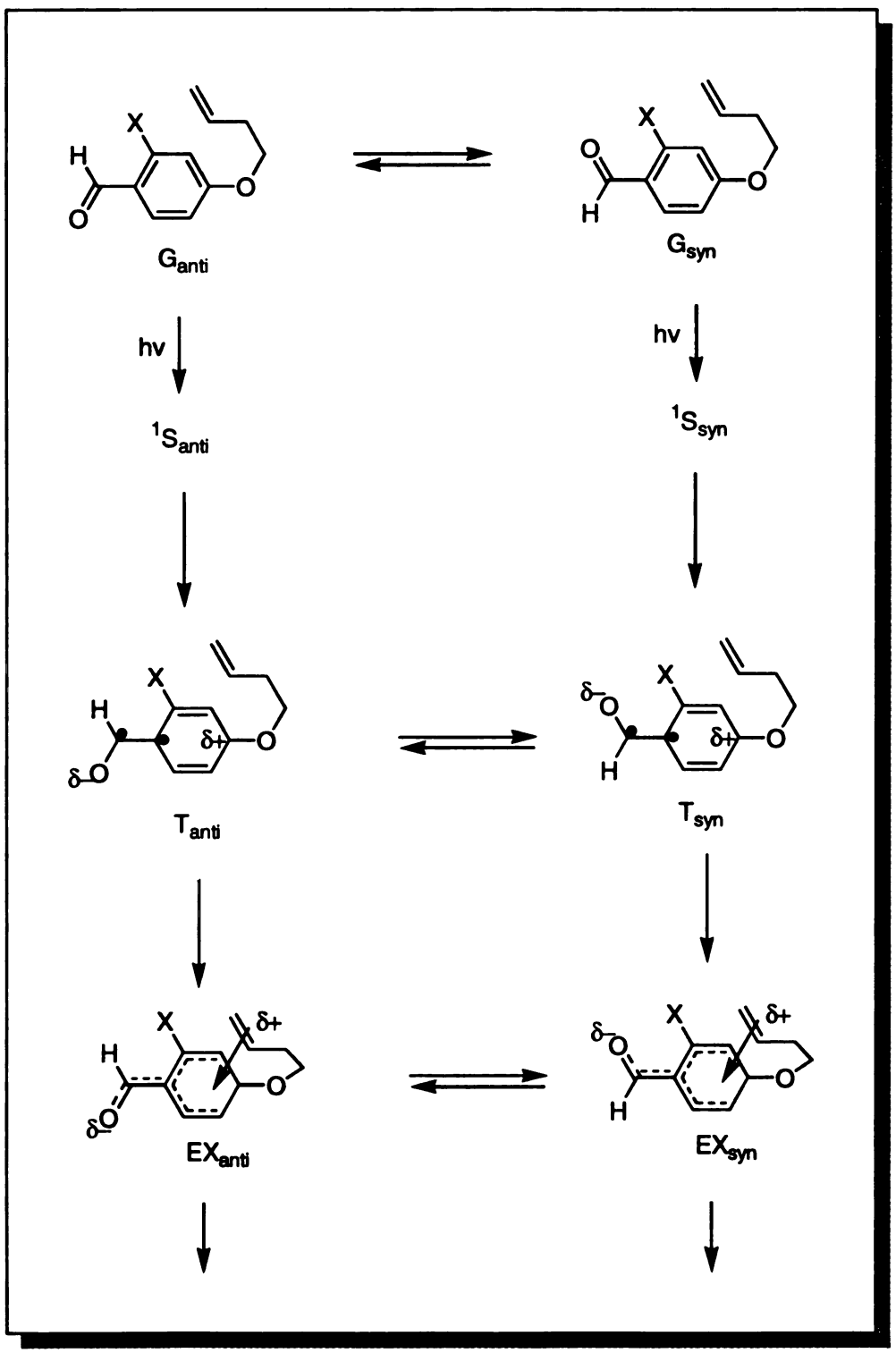
3.2.1. Formation of Exciplex

The conformational structure of the exciplex has been shown to affect regioselectivity in the ortho photocycloaddition of 2-substituted 4-butenoxyacetophenone. It is believed that charge transfer interactions will be stronger with a more positive carbon center. Since there is no strong steric interaction, after considering inductive and resonance effects of substituents to the acetyl group, it was concluded that all studied electron-donating and electron-withdrawing groups facilitate a syn orientation of the remote double bonds toward themselves.



Considering little difference in the structures between acetophenone and benzaldehyde derivatives, varying regioselectivity suggests that electronic effect is not solely responsible for the regioselectivity. It was suggested that the regioselectivity is associated with a differentiating effect by dipole-dipole interactions on exciplex

formation.[46] The following scheme shows the overall mechanism when the double bond adds toward the substituents (syn addition).



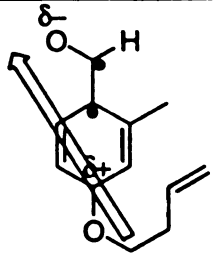
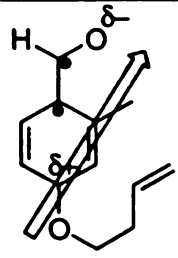
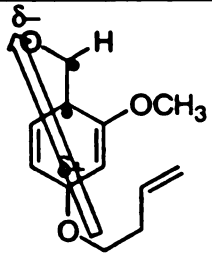
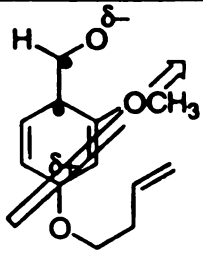
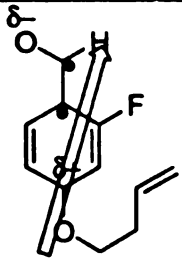
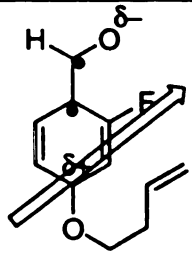
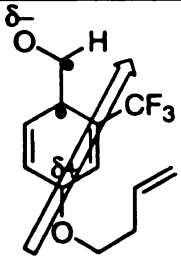
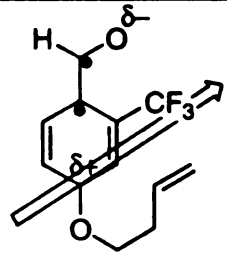
The rate of the triplet state anti→syn rotation was measured to be ~10^7 in photokinetic study of o-alkyl phenyl ketone by Wagner and Chen.[59]

Ab initio calculations on the ground states and excited triplet states of ortho substituted p-butenoxybenzaldehydes were carried out. The calculation suggests that anti conformers are more stable for the derivatives with all substituted butenoxybenzaldehydes in the ground state as well as excited triplet state. An exception was the mild electron-donating methyl group for which compound, syn conformer is more stable in the ground state while syn and anti conformer are similar in energy at excited triplet state.

Table 9. Ground state energy of ortho substituted p-butenoxybenzaldehyde (**Al-X**)

	$\Delta E=E_{anti}- E_{syn}$ (kcal/mol)	Calculated Ratio(anti/syn)
Al-CH3	-0.635	25.50 : 74.50
Al-OCH3	5.137	99.98 : 0.02
Al-F	3.206	99.56 : 0.44
Al-CF3	3.080	99.45 : 0.55

Table 10. Triplet excited state energy and direction of diploe moment of ortho substituted p-butenoxybenzaldehyde (**Al-X**)

	Dipole (Debye), μ of anti-conformer	Dipole (Debye), μ of syn-conformer	ΔE(kcal/mol)	Calculated Ratio (anti/syn)
Al-CH3	 3.489	 4.469	0.322	50.014 : 49.986
Al-OCH3	 4.962	 4.924	6.084	99.996 : 0.004
Al-F	 4.397	 6.381	5.563	99.992 : 0.008
Al-CF3	 4.846	 7.264	2.067	97.037 : 2.963

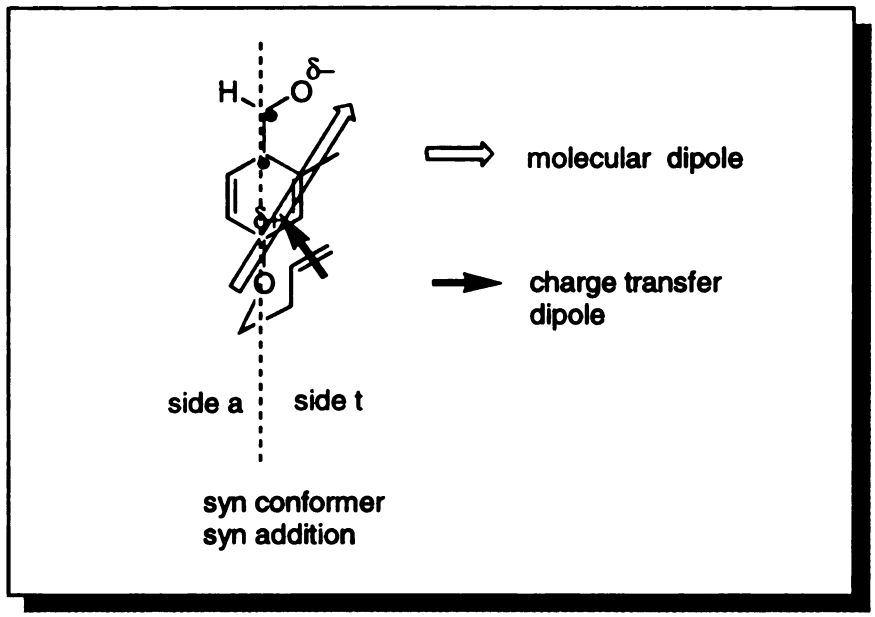


Figure 2. Dipole interaction of ortho substituted p-butenoxybenzaldehyde (**Al-X**) with syn conformer for syn addition.

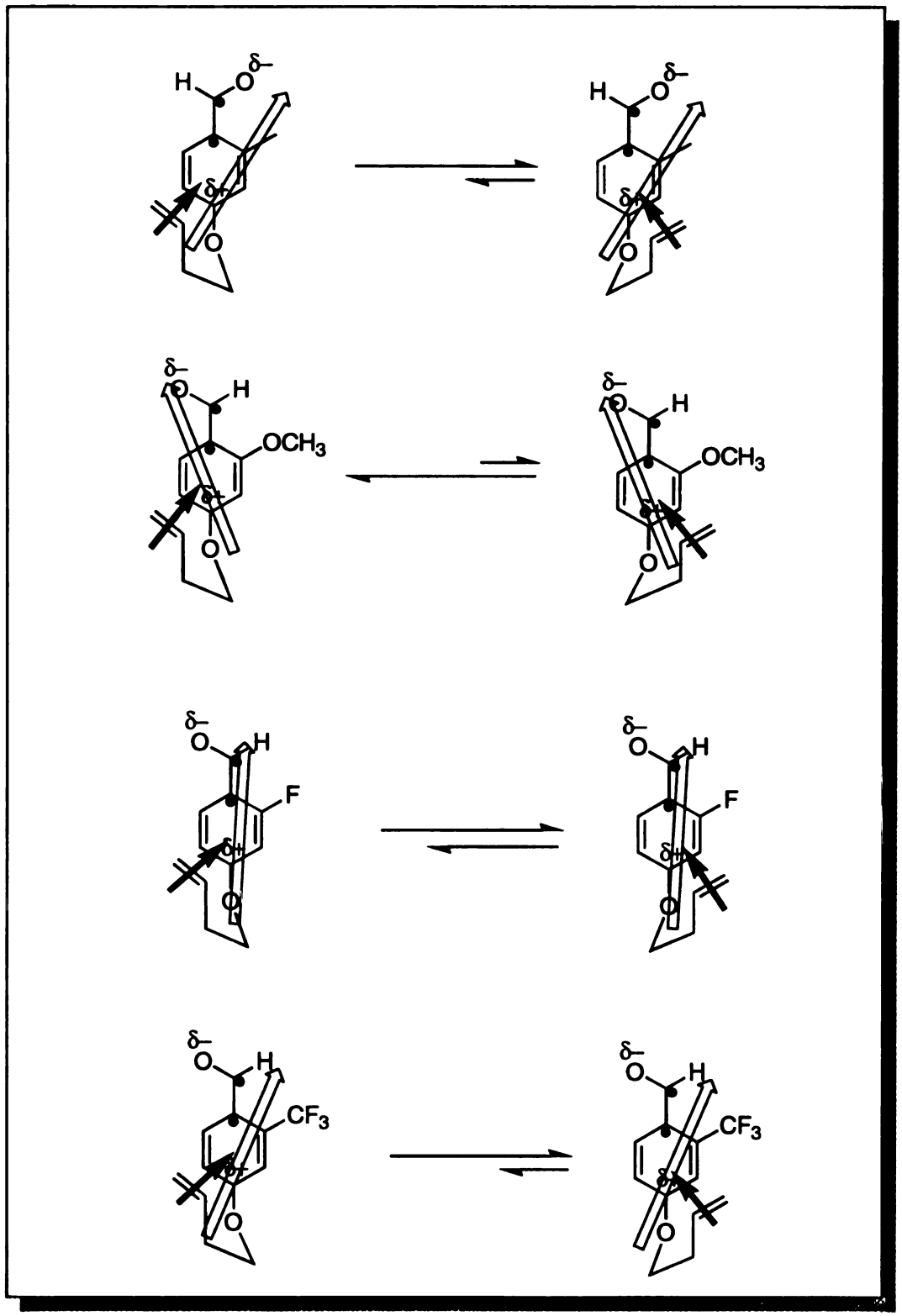


Figure 3. Equilibria between two addition modes of ortho substituted p-butenoxybenzaldehyde (**Al-X**) on exciplex state.

Consideration of interactions between the molecular dipole of the excited triplet state and the charge transfer dipole can provide insight into the interactions between two dipoles at the exciplex state. When the exciplex is formed, the induced additional dipole will change direction and size of the dipole moment vector from those of calculated triplet states. In case of the syn conformer, the molecular dipole will rotate clockwise after formation of exciplex, while that of anti conformer rotate anticlockwise.

The equilibria between exciplexes from the two different modes of cycloadditions with major conformers can be considered in explaning the observed regioselectivity. The dipole associated with charge transfer likely prefers to align itself perpendicular and not parallel to the molecular dipole. In case of **Al-CH3**, it was believed that the rate of rotation after excitation is slower than subsequent reaction rates. The major ground state conformation (syn), remains the same throughout the reaction and gives the syn cyclization product.

TT and **CR** were synthesized to demonstrate the same dipole moment effect on regioselectivity. The fused ring systems prevent bond rotation and thus allow only one molecular dipole moment. Irradiation of **TT** shows opposite regioselectivity from **Al-CH3** because it has opposite molecular dipole moment. The Scheme below illustrates that the anti addition imparts a perpendicular interaction between the two dipoles.

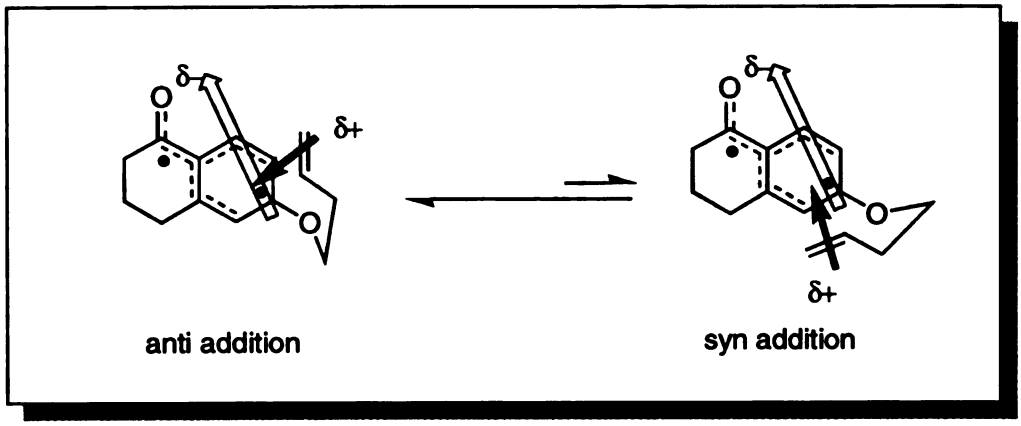
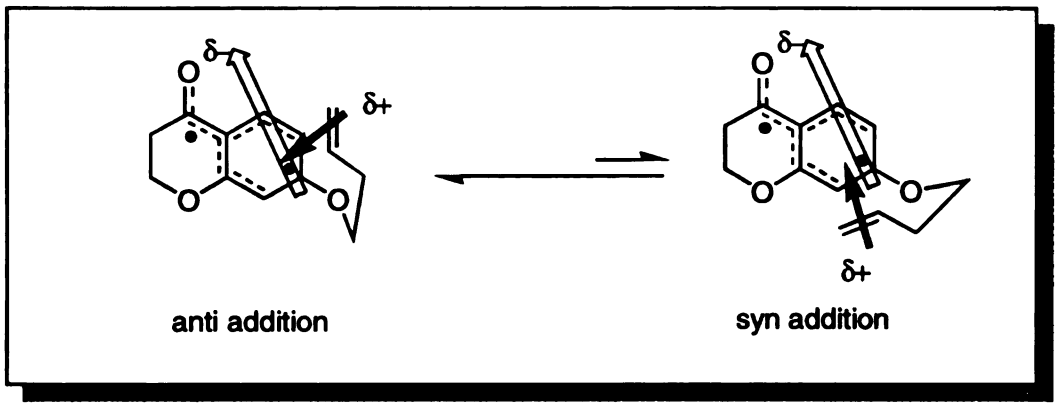


Figure 4 Equilibria between two addition modes of butenoxytetralone (**TT**) on exciplex state.

The same result was observed in the photochemistry of **CR**. The structure and direction of the molecular dipole moment of **CR** is a analogous to the favored anti conformation of **Al-OCH3**.



A similar explanation can be offered for the regioselectivity of acetophenones. Fluorine substituted acetophenones can proceed through both possible cyclization modes because fluorine is small size can allow to exist on both sides of the carbonyls.

3.2.2. Biradical

Two noninterconverting biradicals (**BR**) formed from the exciplex (**EX**) can subsequently couple to form either syn or anti addition products or decay to the ground state.

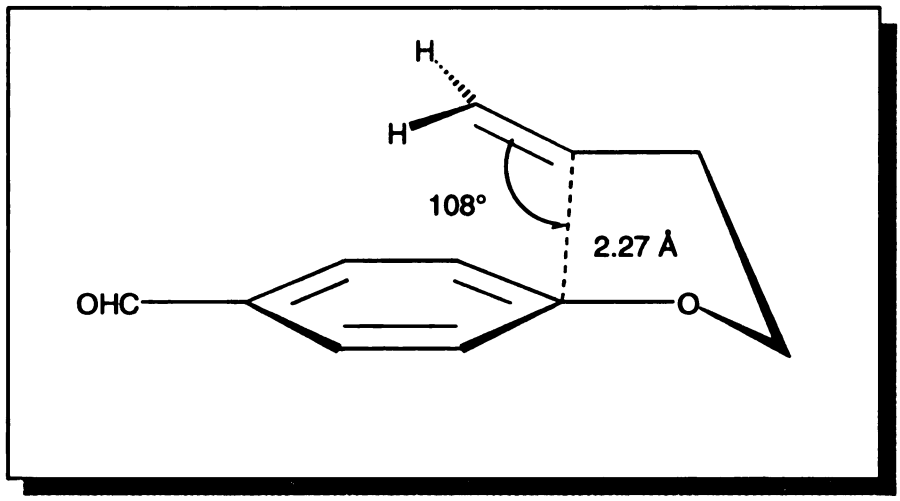
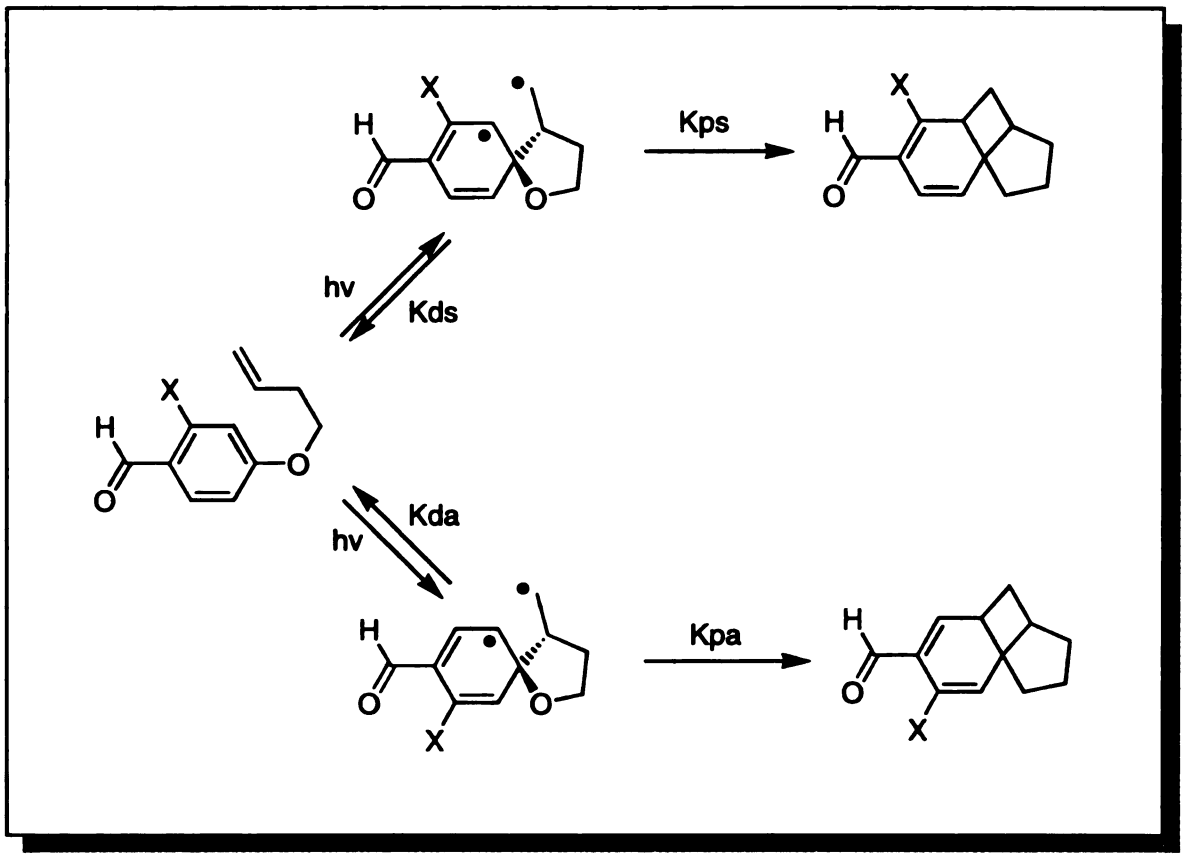


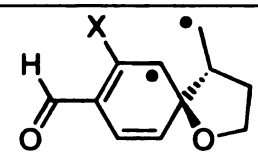
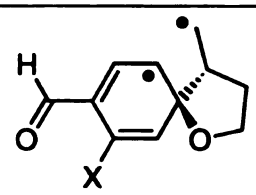
Figure 5. Calculated geometry of p-butenoxybenzaldehyde.

It was calculated that the C-C bond being formed has a bond distance of about 2.27 Å and the angle between the double bond and the incipient bond of about 108 °.[60] Since our system is analogous to the exo cyclization of a hexenyl radical,[61] these results can be applied to our system. It was believed that the transition state for the radical addition reaction is similar in structure to the exciplex with small differences; the distance between the ring carbon and the internal double bond carbon becomes about 2.27 Å and the external double bond carbon moves away vertically from the plane of the benzene ring to reach the 108° proposed angle of addition.



It is possible that $k_{ps} \neq k_{pa}$, but in order for the differential biradical partitioning to be totally responsible for the observed regioselectivity kps and kpa must show a large difference depending on the substituents, since there can be little difference between the rate of the syn and anti biradical decay to the ground state of the starting material ($k_{ds}=k_{da}$).

Table 11. Energy (in Kcal/mol) of biradicals (BR) of ortho substituted p-butenoxybenzaldehyde

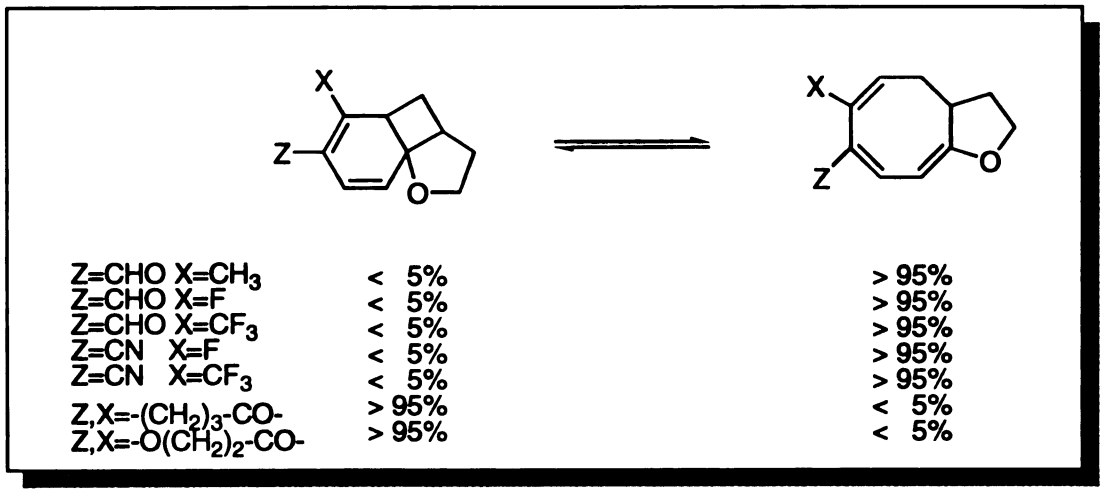
		
$X=CH_3$	-384168.5252	-384168.1224
$X=OCH_3$	-431129.1497	-431128.9966
X=F	-421699.31099	-421699.0888
$X=CF_3$	-570274.0517	-570273.9174

Ab initio calculation was carried out to estimate the stability of both biradicals. The result shows that two biradicals are similar in energy with a difference less than 1 Kcal/mol. The position of ring substituent X did not affect the stability of biradicals.

In order to form the cyclobutane ring of **CH**, the triplet biradical must undergo intersystem crossing to generate a singlet biradical. Both singlet and triplet surfaces of biradicals rise in energy along the reaction coordinate. The singlet surface is soon stabilized during bond formation while the triplet surface continuously rises. This causes surface crossing at a point and the ISC at this point benefits from large spin-orbital coupling (SOC). Michl's calculations[62] suggest that SOC will be strong in those geometries in which there is a significant covalent interaction between the two radical centers. Geometric difference by a slight puckering of the benzene ring at the ortho carbon to the tether might change the ISC rate.

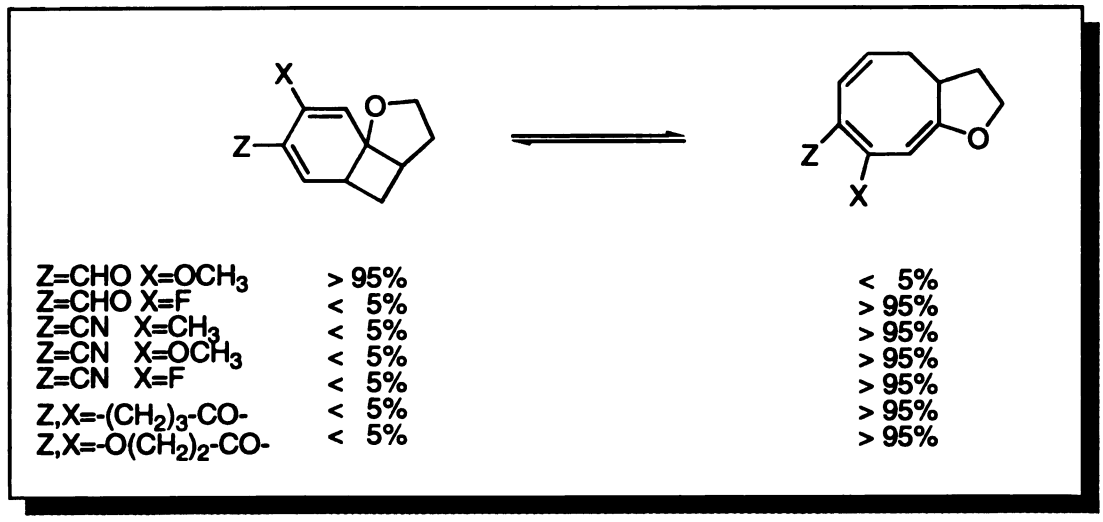
3.2.3. CH-CO Equilibrium

It is known from this study and other studies that substituents change the cyclohexadiene (**CH**) – cyclooctatriene (**CO**) equilibrium.



Z=CHO X=CH_3	< 5%	> 95%
Z=CHO X=F	< 5%	> 95%
Z=CHO X=CF_3	< 5%	> 95%
Z=CN X=F	< 5%	> 95%
Z=CN X=CF_3	< 5%	> 95%
Z,X=-$(CH_2)_3$-CO-	> 95%	< 5%
Z,X=-O$(CH_2)_2$-CO-	> 95%	< 5%

When syn cycloaddition occurs, aldehydes with CH_3, F and CF_3 and nitriles with F and CF_3 substituents were found to shift the equilibrium towards the cyclooctatriene (**CO**). For all those cases, no cyclohexadiene was detected by NMR during irradiation of the starting aldehydes.



Z=CHO X=OCH_3	> 95%	< 5%
Z=CHO X=F	< 5%	> 95%
Z=CN X=CH_3	< 5%	> 95%
Z=CN X=OCH_3	< 5%	> 95%
Z=CN X=F	< 5%	> 95%
Z,X=-$(CH_2)_3$-CO-	< 5%	> 95%
Z,X=-O$(CH_2)_2$-CO-	< 5%	> 95%

For anti cycloaddition, equilibria lie toward **CO**. The table below shows the result of ab initio calculations.

Table 12. Calculated energy of CH and CO of ortho substituted p-butenoxybenzaldehyde.

(in Kcal/mol)	CH		CO	
	Anti addition	Syn addition	Anti addition	Syn addition
Al-CH3	-384180.16	-384180.64	-384180.62	-384185.28
Al-OCH3	-431148.05	-431143.83	-431149.86	-431149.49
Al-F	-421715.39	-421713.74	-421720.24	-421717.97
Al-CF3	-570289.42	-570283.16	-570289.93	-570292.65

Results show that all substituents on the nitrile system have two regioisomers and the equilibriums shifted to **CO** when the cycloaddition is either in the syn and anti modes. Those results indicate that it is unlikely that this thermal process is responsible for the observed regioselectivity.

3.3. Photochemistry of Benzonitrile Derivatives

Photolysis of benzonitrile derivatives produced both regioisomers in most of the cases as compared to the results of the butenoxybenzaldehyde system, in which only fluorine substituted benzaldehyde showed regioselectivity in both directions.

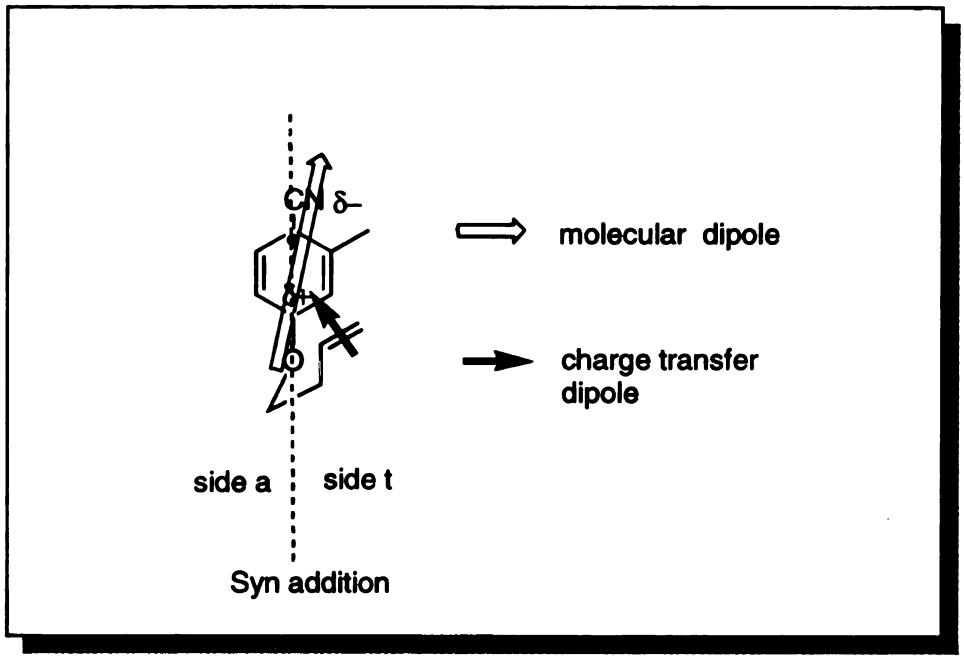
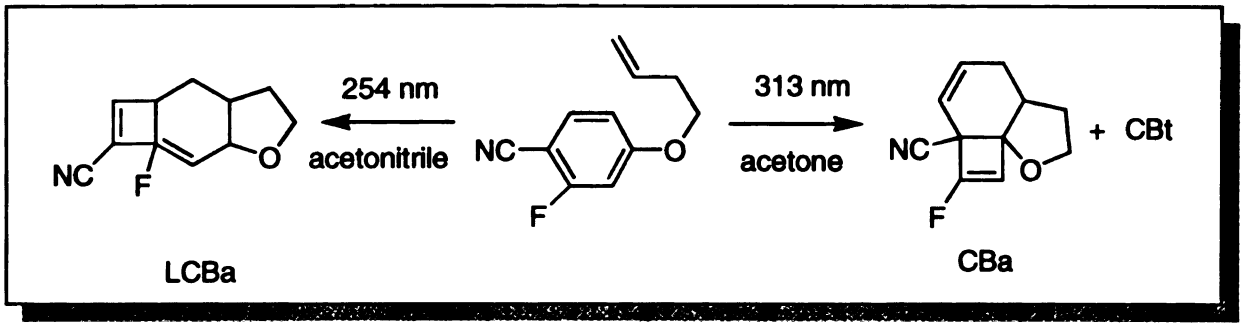


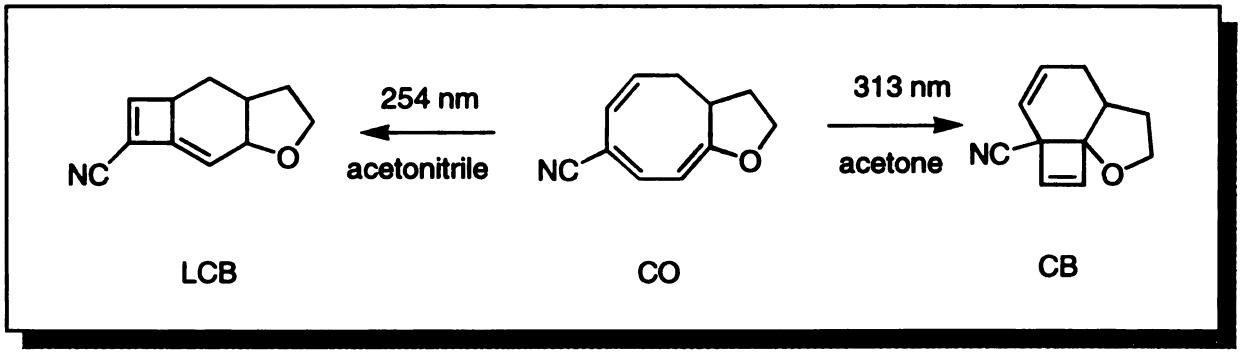
Figure 6. Dipole interaction of ortho substituted p-butenoxybenzonitrile (**CN-X**) for syn addition.

For the nitrile system, the direction of molecular dipole moments on the exciplex will align close to the middle axis going through cyano group and tether. Therefore, the interaction between the two dipoles will be smaller than that of the benzaldehyde system. The result suggests that the differentiating effect of the dipole moment is weak in nitrile derivatives. Generally, triplet sensitized reaction conditions give more syn addition products relative to direct irradiation.

It was found that different cyclobutene photoproducts were formed when irradiation conditions were changed in the case of fluorine substituted benzonitrile derivative (**CN-F**).



In the case of **CN-CF3**, the ratio of **LCBa** was increased from 50% to over 90% when the reaction condition was changed from acetone sensitization to direct irradiation. A similar tendency was observed for unsubstituted p-butenoxybenzonitrile.



Those observations raise many questions. It is possible that the singlet and triplet electronic states of the nitrile system is different and undergoes a different reaction pathway to generate different photoproducts. Gilbert performed a quenching study to show the presence of a reaction pathway from the singlet state.[45]

Part 4. Experimental

4.1. Instrumentation

This section describes the instrumentation used to characterize all substrates presented in this research.

^{1}H and ^{13}C :	Varian Gemini 300, Varian VXR-300, and Varian VXR-500
FT-IR :	Nicolet 42/Infrared Spectrophotometer with a 0.025 mm Z12308-0 Aldrich IR cell
MS :	Joel JMS-HX110 Mass Spectrometer and VG Trio-1 Benchtop GC-MS with a Hewlett Packard 5890 Gas Chromatography
UV :	Shimadzu UV-160 Recording UV-VIS
HPLC :	Rainin Dynamax HPLC interfaced with a dual wavelengh programmable detector and fraction collector
GC :	Varian 1400 and 3400 Gas Chromatography with Hewlett Packard HP3393A, HP3392A, and HP3395 Integrators
FS :	Perkin-Elmer MPF-44A Fluorescence Spectrophotometer
MP :	Thomas Hoover Capillary Melting Point Apparatus Melting Points are not corrected.

4.2. Chemicals

This section describes the preparation, purification, and identification of all chemicals used in this research. All substrates used in the preparation of the photoprecursors were the highest purity commercially available. The purity of such compounds was checked by gas chromatography or ^1H NMR prior to use.

4.2.1. Solvents

a. Acetonitrile[63]

Reagent-grade acetonitrile (2L) was refluxed over P_2O_5 (2g) for four hours, then distilled through a one foot column packed with glass helices. The solvent was then refluxed over CaH_2 for 24 hours and then fractionally distilled through a half meter column packed with glass helices. The middle fraction (80%) which boiled at 81-82°C was saved and stored over type 4Å Linde molecular sieves.

b. Acetone[62]

Capillary GC/GC-MS grade acetone (2L) was treated successively with small amounts of $KMnO_4$ (0.5 gram portions) until a violet color persists. Anhydrous K_2CO_3 (8 gram) was added and the mixture was refluxed for 12 hours. The solvent was then fractionally distilled through a one foot column packed with glass helices. The middle

fraction (90%) which distilled between 56-57 °C was saved and stored over type 4Å Linde molecular sieves.

c. Methanol[64]

Reagent-grade absolute methanol was refluxed over Mg metal (2.5 g/1200ml) overnight, then distilled through a half meter column packed with glass helices. The middle fraction (80%) which distilled between 64-65 °C was saved.

d. Benzene[62]

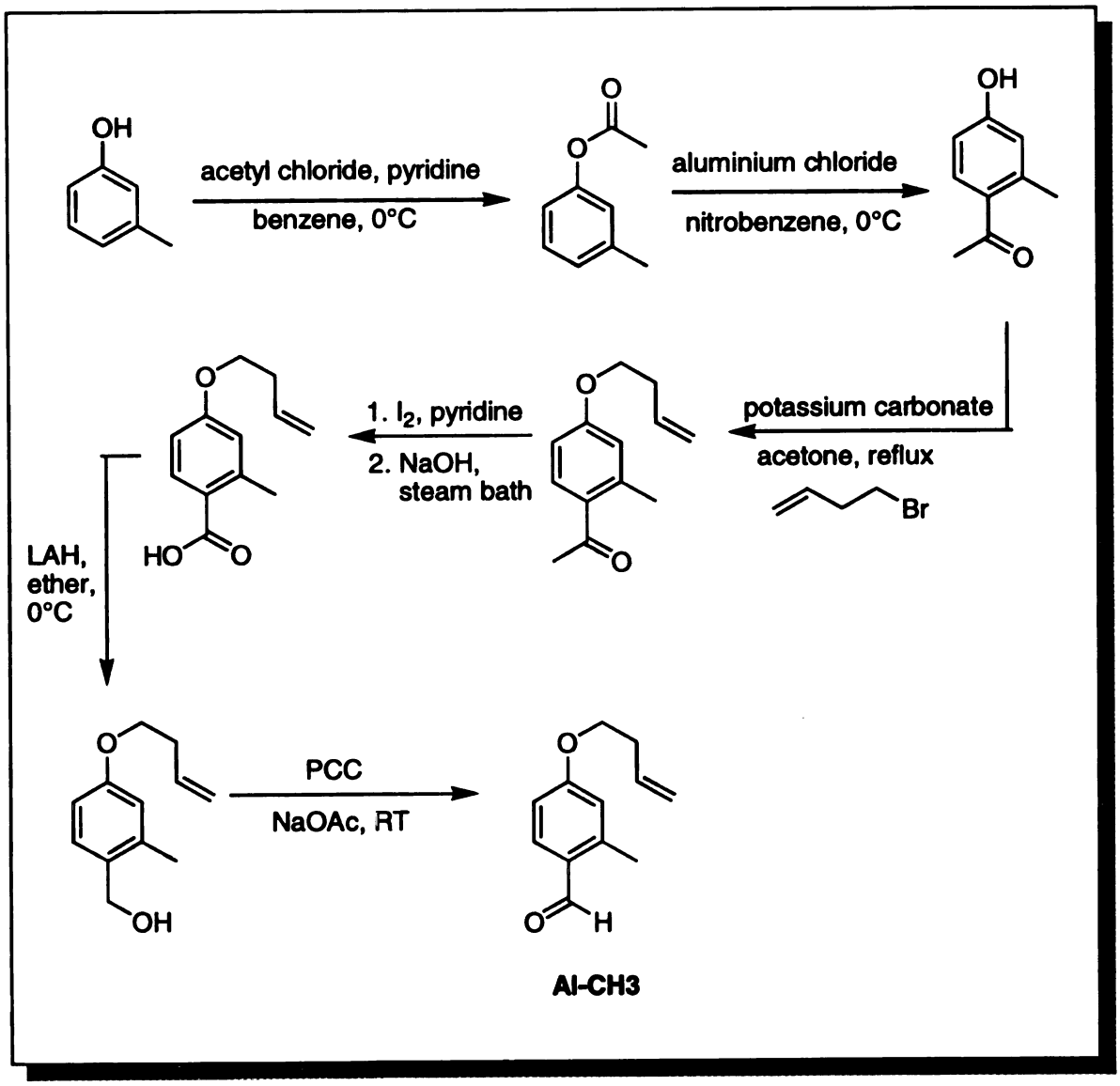
Reagent-grade benzene (3.5L) was stirred over conc. H_2SO_4 (0.5L) until the acid washing remained colorless (usually three portion of conc. H_2SO_4). The benzene layer was subsequently separated, washed with distilled water (3 x 150 mL), saturated $NaHCO_3$ (3 x 200 ml), saturated NaCl (2 x 100 ml), and then dried over $MgSO_4$. The filtered benzene was then refluxed for 24 hours over P_2O_5 (150 gram). After the stated period, the benzene was distilled through a meter column packed with stainless steel helices. The first and last 10 % were discarded. The middle fraction distilled between at 78-80 °C.

4.2.2. Chromatography Material

The majority of the photoreactants were purified by silica gel chromatography and photoproducts were purified by HPLC. Preparative thin layer chromatography (Analtech Uniplate silica gel plates of 20 x 20 cm, 1000 micron) was utilized for samples up to 150 miligrams. Flash chromatography (Aldrich [cat#22,719-6] silica gel, Merck, grade 60, 230-400 mesh, 60A.) was used for larger samples.

4.3. Preparations of Reactants

4.3.1. 4-(3-Buten-1-oxy)-2-methylbenzaldehyde



a. 3-methylphenyl acetate

Acetyl chloride (9.74 g, 0.124 mol) was added dropwise to a mixture of m-cresol (13.4 g, 0.124 mol) and pyridine (9.78 g, 0.124 mol) in 20 mL of dry benzene at 0°C. The mixture was stirred under nitrogen at room temperature for 24 hours. The mixture was hydrolyzed with 5% HCl (25 mL) and organic layer was separated. The organic layer was extracted four times with 10 mL portions of 2 N NaOH and dried over magnesium sulfate. The extract was concentrated in vacuo to give a crude yellow oil. Purification of the crude product by vacuum distillation gave 3-methylphenyl acetate as a colorless liquid (18.25 g, 98%), bp (218 °C).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.28 (s, 3H), 2.36 (s, 3H), 6.92 (m, 2H), 7.02 (broad d, J = 7.8 Hz, 1H), 7.24 (dd, J = 8.4 and 7.2 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 20.90, 21.10, 118.35, 122.01, 126.46, 128.98, 139.42, 150.48 and 169.42.

FT-IR (CCl_4, cm^{-1}): 1209.5, 1369.6, 1489.2, 1589.6, 1614.6, 1768.95, 2924 and 3036 cm^{-1}

GC-MS (m/z): 43.0, 77.0, 107.1, 108.1(Base), 150.1($M^{+\bullet}$).

b. 4-hydroxy-2-methylacetophenone

A solution of 3-methylphenyl acetate (15.0 g, 0.1 mol) in nitrobenzene (50 mL) was added dropwise to a solution of aluminium chloride (26.67 g, 0.2 mol) in nitrobenzene (200 mL) at 0°C under argon. The reaction mixture was warmed to room temperature and stirred for 96 hours. The mixture was then hydrolyzed with 5% HCl (200 mL). The nitrobenzene layer was diluted with ether (200 mL) and extracted with 50 mL portions of 2N NaOH. The combined aqueous washings were acidified with HCl to a pH of 3-5 and extracted with ether (6 x 100 mL). The organic extracts were dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by vacuum distillation gave 4-hydroxy-2-methylacetophenone as a white solid (7.5 g, 50%), m.p (129-131 °C).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.53(s, 3H), 2.54(s, 3H), 6.70(s, 1H), 6.71(d, J = 9 Hz, 1H) and 7.71(d, J = 9 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 22.54, 29.03, 112.37, 118.96, 129.50, 133.04, 142.82, 158.77 and 200.17.

FT-IR (CCl_4, cm^{-1}): 1240.4, 1363.9, 1647.4 and 3182.9 cm^{-1}.

GC-MS (m/z): 51.1, 77.0, 107.0, 135.0 (Base) and 150.0 ($M^{+\bullet}$).

c. 4-(3-Buten-1-oxy)-2-methylacetophenone

4-hydroxy-2-methylacetophenone (4.0 g, 0.0266 mol), 4-bromo-1-butene (4.60 g, 0.019 mol) and anhydrous potassium carbonate (11.03 g, 0.078 mol) in dry acetone (50 mL) were refluxed under argon for 40 hours. The cooled mixture was gravity filtered to remove the salt formed during the reaction and concentrated in vacuo. The resulting yellow oil was diluted with ether (50 mL) and extracted with 2N NaOH (4 x 25 mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 4-buten-1'-oxy-2-methylacetophenone in 68% yield as pale yellow liquid (3.69 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.51 (s, 3H), 2.53 (s, 3H), 2.53 (m, 2H), 4.02 (t, J = 6.6 Hz, 2H), 5.07-5.18 (m, 2H), 5.87 (ddt, J = 18, 10.5, and 6.6 Hz, 1H), 6.71 (m, 2H) and 7.72 (d, J = 9.6 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 22.58, 29.01, 33.42, 67.09, 110.92, 117.23, 117.96, 129.75, 132.51, 134.01, 142.15, 161.22 and 199.39.

FT-IR (CCl_4, cm^{-1}): 1246.2, 1317.6, 1450.7, 1566.4, 1603.1, 1674.4, 2928.3 and 3050 cm^{-1}.

GC-MS (m/z): 43.2, 55.1, 77.0, 107.2, 135.2 (Base) 150.3, 189.2 and 204.2 ($M^{+\bullet}$).

d. 4-(3-Buten-1-oxy)-2-methylbenzoic acid

Iodine (2.54 g, 0.01 mol) was added to the solution of 4-(3-buten-1-oxy)-2-methylacetophenone (2.04 g, 0.01mol) in pyridine (5 mL). The reaction mixture was heated on the steam bath for 30 min then stirred over night at room temperature. Excess pyridine was removed by vacuum distillation and the residue was washed with water. Sodium hydroxide (3g) was added to the suspension in the water (50 mL). The mixture was heated on the steam bath for 1 hour and acidified with concentrated hydrochloric acid. The precipitate was filtered and extracted with saturated sodium carbonate solution. The aqueous layer was acidified with concentrated hydrochloric acid and filtered. Purification of the crude product by column chromatography on silica gel (chloroform:acetone, 3:1) gave 4-buten-1'-oxy-2-methylbenzoic acid as solid (m.p. 130-132 °C) in 49% yield (1.0 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.53 (q, J = 6.6, 2H), 2.61 (s, 3H), 4.02 (t, J = 6.6 Hz, 2H), 5.09-5.20 (m, 2H), 5.88 (ddt, J = 17.1, 10.5, and 6.6 Hz, 1H), 6.77 (m, 2H) and 8.05 (d, J = 9.6 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 22.69, 33.45, 67.18, 111.43, 117.32, 117.69, 120.45, 134.07, 134.09, 144.26, 162.39 and 172.79.

FT-IR (CCl_4, cm^{-1}) : 1244.2, 1603.1, 1680.2, 2000-3350 cm^{-1}.

GC-MS (m/z) : 55.3(Base), 76.7, 105.0, 134.6, 152.0, 166.1, 178.0 and 206.1 ($M^{+\bullet}$).

e. 4-(3-Buten-1-oxy)-2-methylbenzyl alcohol

A suspension of lithium aluminium hydride (0.42 g, 0.011 mol) in anhydrous ether (10 mL) was cooled in an ice bath. A solution of 4-(3-buten-1-oxy)-2-methylbenzoic acid (1.5 g, 9 mmol) in tetrahydrofurane (25 ml) was added over 30 min period. The mixture was stirred at RT for 3 hrs and then cooled in an ice bath while water (25 mL) was added. The mixture was stirred overnight at RT. Magnesium sulfate was added and stirring continued for 3 hrs. The salt was removed by filteration and washed well with hot tetrahydrofuran and ether. Solvent was removed by vacuum distillation and the solid was recrystalized from benzene. The aqueous layer was acidified with concentrated hydrochloric acid and filtered. Purification of the crude product by column chromatography on silica gel (chloroform:acetone, 3:1) gave 4-buten-1'-oxy-2-methylbenzoic acid as pale yellow liquid in 49% yield (0.84 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.32 (s, 3H), 2.53 (q, J=6.6 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 4.58 (s, 2H), 5.07-5.19 (m, 2H), 5.87 (ddt, J = 17.1, 10.5, and 6.6 Hz, 1H), 6.71 (m, 2H) and 7.72 (d, J = 8.4 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 18.86, 33.57, 63.11, 67.04, 111.28, 116.82, 116.94, 129.40, 131.07, 134.39, 137.99 and 158.45.

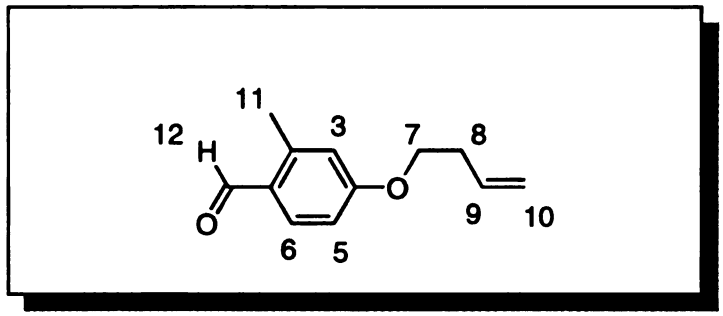
FT-IR (CCl_4, cm^{-1}): 752.3, 898.9, 991.5, 1253.9, 1383.1, 1502.7, 1608.8, 2928.3 3078.8, 3383.6 and 3609.3 cm^{-1}.

GC-MS (m/z): 39.0, 55.1(Base), 77.0, 91.1, 109.0, 120.0, 38.2, 151.1, 177.2 and 192.2($M^{+\bullet}$).

f. 4-(3-Buten-1-oxy)-2-methylbenzaldehyde

Pyridinium chlorochromate (1.8 g, 8.35 mmol) and sodium acetate (0.14 g, 1.65 mmol) were suspended in dichloromethane (12.5 mL). The mixture was stirred vigorously by using an overhead stirrer. A solution of the 4-(3-Buten-1-oxy)-2-methylbenzyl alcohol (0.8 g, 4 mmol) in dichloromethane (2 mL) was added and was stirred overnight. After 15 hours, it was diluted with ether (80 mL) and filtered through a short pad of silica gel. The ether layer was dried over magnesium sulfate, gravity filtered, and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product

by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-(3-buten-1-oxy)-2-methylbenzaldehyde as colorless liquid in 68% yield (0.52 g).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.52 (q, J = 6.6 Hz, $2H_8$), 2.60 (s, $3H_{11}$), 4.05 (t, J = 6.6 Hz, $2H_7$), 5.08-5.19 (m, $2H_{10}$), 5.86 (ddt, J = 17.1, 10.5, and 6.6 Hz, $1H_9$), 6.70 (d, J = 2.4 Hz, $1H_3$), 6.8 (dd, J = 8.4 Hz, 2.4 Hz, $1H_5$), 7.71 (d, J = 8.4 Hz, $1H_6$) and 10.07 (s, $1H_{12}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 19.85, 33.35, 67.26, 111.81, 117.37, 117.43, 127.78, 133.88, 134.70, 143.21, 162.92 and 191.15.

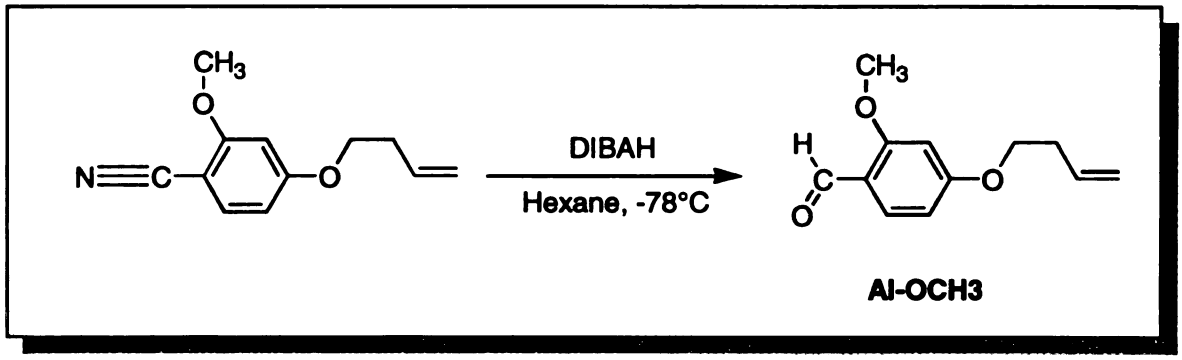
FT-IR (CCl_4, cm^{-1}): 733.0, 912.4, 1122.7, 1250.1, 1325.3, 1498.8, 1588.4, 1601.1, 1687.9, 2720, 2930.2 and 3110 cm^{-1}.

GC-MS (m/z): 38.9, 55.0(Base), 77.0, 91.0, 107.1, 124.1, 135.0, 162.1, 178.1 and 190.0($M^{+\bullet}$).

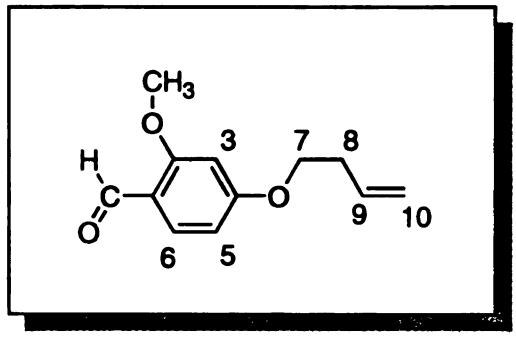
UV: 220.6, 269.2(max) and 297.

Anal: Calcd: C(%), 75.76; H(%), 7.42. Found: C(%), 75.16; H(%), 7.56.

4.3.2. 4-(3-Buten-1-oxy)-2-methoxylbenzaldehyde



4-(3-Buten-1-oxy)-2-methoxylbenzonitrile (**CN-OCH3**) (0.49 g, 2.4 mmol) was dissolved in 3 mL of dry hexane under argon atmosphere. The solution was cooled to –78 °C, and 0.04 mL of a 1 M hexane solution of diidobutylaluminum hydride was added. After 1 hr, ether (10 mL) and silica (1.5 g) were added, and the mixture was kept stirring at 4 °C for 15 hrs. Water was added, and the mixture was extracted twice with ether. The ether layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-(3-buten-1-oxy)-2-methoxylbenzaldehyde as colorless liquid in 85% yield (0.42 g).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.59 (q, J = 6.6 Hz, $2H_8$), 3.85 (s, $3H_{11}$), 4.08 (t, J = 6.6 Hz, $2H_7$), 5.10-5.20 (m, $2H_{10}$), 5.87 (ddt, J=17.1, 10.5, and 6.6 Hz, $1H_9$), 6.41 (d, J = 2.1 Hz, $1H_3$), 6.52 (dd, J = 8.7 Hz, 1.5 Hz, $1H_5$), 7.8 (d, J = 8.7 Hz, $1H_6$) and 10.30(s, $1H_{12}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.42, 55.59, 67.64, 98.64, 105.89, 117.59, 119.18, 130.27, 133.88, 163.04, 166.07 and 188.37.

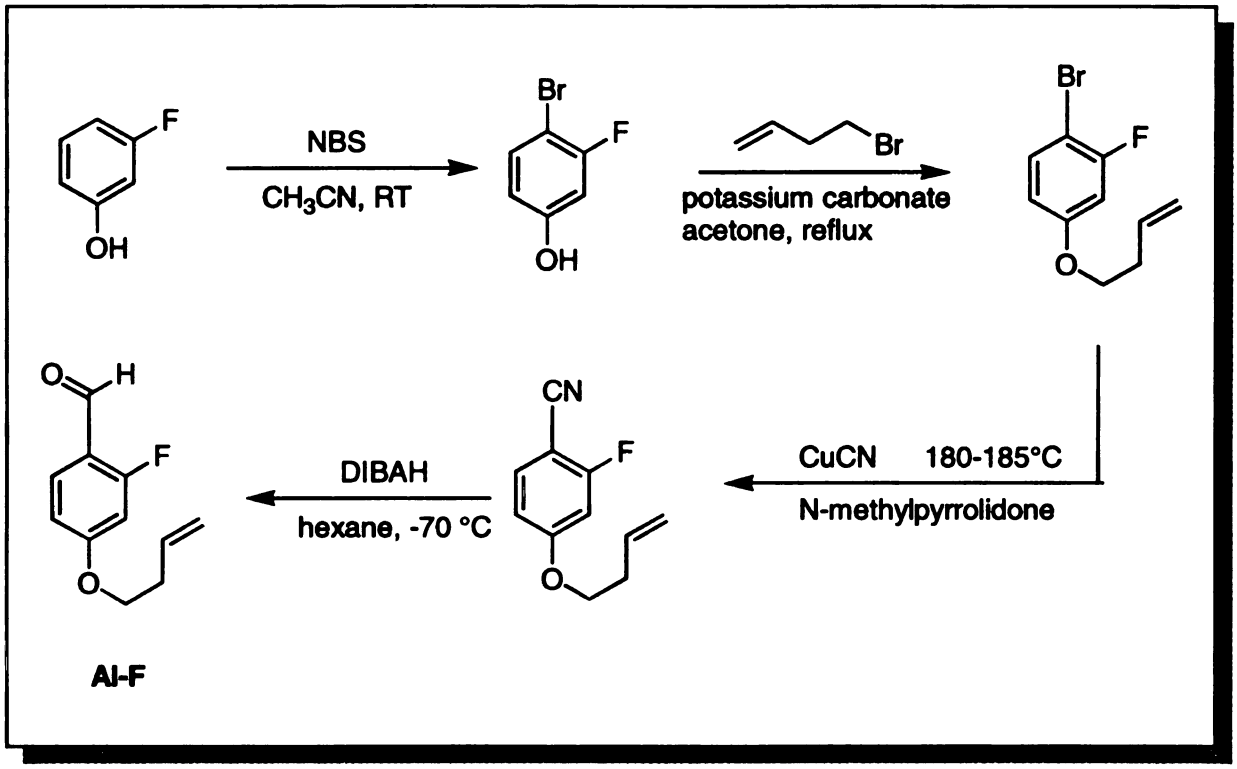
FT-IR (CCl_4, cm^{-1}): 733.0, 912.4, 1122.7, 1250.1, 1325.3, 1498.8, 1588.4, 1601.1, 1687.9, 2720, 2930.2 and 3110 cm^{-1}.

GC-MS (m/z): 39.0, 55.1, 63.1, 77.1, 92.0, 108.0, 124.0, 135.0, 151.0 (Base), 165.1, 177.1 and 206.1 ($M^{+\bullet}$).

UV: 228.6, 268.0(max) and 302.

Anal: Calcd: C(%), 69.89; H(%), 6.84. Found: C(%), 69.81; H(%), 6.79.

4.3.3. 4-(3-Buten-1-oxy)-2-fluorobenzaldehyde



Al-F

a. 4-Bromo-3-fluorophenol

NBS(17.8 g, 0.1 mol) was added to 3-fluorophenol (11.2 g, 0.1 mol) in DMSO (9 g, 0.11 mol) and CH_3CN (200 mL). The mixture was stirred at room temperature for 1 hr, the solvent evaporated and the residue treated with 100 mL of ethyl ether and water (3 x 50 mL). The ethereal layer was dried over $MgSO_4$, filtered and evaporated, and the crude product was obtained and purified by fractional distillation at reduced pressure (b.p. 60-

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65 at 3.5-4 mmHg) followed by flash chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-Bromo-3-fluorophenol as white solid (m.p. 72-73 °C) in 24 % yield (4.5 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 5.19 (s, 1H), 6.53 (ddd, J = 8.7, 2.7 and 1.2 Hz, 1H), 6.64(dd, J = 9.6 and 3 Hz, 1H) and 7.34(t, J = 8.4 Hz, 1H).

FT-IR (CCl_4, cm^{-1}): 734.97, 843.00, 964.53, 1097.64, 1151.05, 1305.97, 1448.72, 1468.02, 1498.34, 1599.19, 2980.40 and 3206.10 cm^{-1}.

GC-MS (m/z): 57.1, 83.0(Base), 95.0, 111.0, 134.8, 160.8 and 191.8($M^{+\bullet}$).

b. 1-Bromo-4-(3-buten-1-oxy)-2-fluorobenzene

4-Bromo-3-fluorophenol (4.0 g, 0.020 mol), 4-bromo-1-butene (3.3 g, 0.024 mol) and anhydrous potassium carbonate (7 g, 0.05 mol) in dry acetone (250 mL) were refluxed under argon for 40 hours. The cooled mixture was gravity filtered to removed the salt formed during the reaction and concentrated in vacuo. The resulting yellow oil was diluted with ether (100 mL) and extracted with 2N NaOH (4 x 50 mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography

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on silica gel (hexane:ethyl acetate, 95:5) gave 1-bromo-4-(3-buten-1-oxy)-2-fluorobenzene as colorless liquid in 40.6 % yield (2.1 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.51 (q, J = 5.4, 2H), 3.95 (t, J = 6.6, 2H), 5.12 (m, 2H), 5.85 (ddt, J = 17.1, 10.5, and 6.6 Hz, $1H_9$), 6.57 (ddd, J = 8.7, 2.7 and 1.2 Hz, 1H), 6.68 (dd, J = 9.6 and 3 Hz, 1H) and 7.37 (t, J=8.4 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.44, 67.73, 103.37(d), 111.85(d), 117.36, 117.38, 133.24, 133.58(d), 158.91(d) and 159.95(d).

FT-IR (CCl_4, cm^{-1}): 617.30, 833.35, 1022.40, 1167.08, 1290.54, 1321.41, 1468.02, 1489.24, 1663.76, 1694.98, 2985 and 3070 cm^{-1}.

GC-MS (m/z): 55.1 (Base), 81.0, 93.1, 161.0, 190.0, 216.1 and 245.1 ($M^{+\bullet}$).

c. 4-(3-Buten-1-oxy)-2-fluorobenzonitrile

A solution of 1-bromo-4-(3-buten-1-oxy)-2-fluorobenzene (2.1 g, 8.5 mmol) and cuprous cyanide (13.6 g) in 100 mL of N-methylpyrrolidone was heated at 180-185 °C for 21 h. It was then poured into 400 mL of a 1:1 mixture of water and concentrated aqueous ammonium hydroxide. After the resulting mixture had been stirred with cooling for 3 h, the mixture was extracted with ether. The ethereal layer was extracted by

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saturated potassium carbonate and NaOH (2N). The ether layer was dried over $MgSO_4$, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-(3-uten-1-oxy)-2-fluorobenzonitrile as colorless liquid in 17.2% yield (0.27 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.56 (br q, J = 5.4, 2H), 4.04 (t, J = 6.6 Hz, 2H), 5.12-5.21 (m, 2H), 5.86 (ddt, J = 17.1, 10.5, and 6.6 Hz, $1H_9$), 6.69 (dd, J = 11.1 and 2.1 Hz, 1H), 6.75 (dd, J = 8.7 and 2.7 Hz, 1H) and 7.50 (t, J = 8.7 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.13, 68.09, 100.30, 102.71(d), 111.64(d), 114.42, 117.76, 133.76(d), 134.20, 158.91(d) and 159.95(d).

FT-IR (CCl_4, cm^{-1}): 617.50, 834.10, 1024.33, 1101.49, 1172.07, 1253.89, 1302.18, 1336.84, 1498.94, 1500.02, 1574.11, 1622.34, 2231.92, 2856.94 and 2926.39cm^{-1}.

GC-MS (m/z): 54.8(Base), 83.8, 100.0, 120.0, 137.0, 150.0, 163.1, 191.2($M^{+\bullet}$).

Anal: Calcd: C(%), 69.10; H(%), 5.27; N(%), 7.33. Found: C(%), 69.02; H(%), 5.20; N(%), 7.32.

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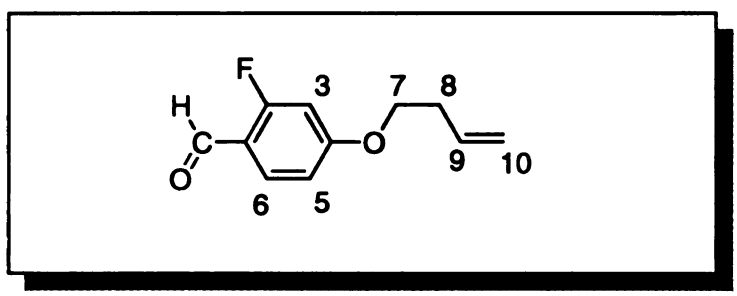
d. 4-(3-Buten-1-oxy)-2-fluorobenzaldehyde

4-(3-Buten-1-oxy)-2-fluorobenzonitrile (0.2 g, 1.05 mmol) was dissolved in 3 mL of dry hexane under argon atmosphere. The solution was cooled to –78 °C, and 0.04 mL of a 1 M hexane solution of diidobutylaluminum hydride was added. After 1 hr, ether (10 mL) and silica (1.5g) were added, and the mixture was kept stirring at 4 °C for 15 hrs. Water was added, and the mixture was extracted twice with ether. The ether layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-(3-buten-1-oxy)-2-fluorobenzaldehyde as colorless liquid in 58.9% yield (0.12 g).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.57 (br q, J = 5.1, $2H_8$), 4.07 (t, J = 6.6 Hz, $2H_7$), 5.12-5.19 (m, $2H_{10}$), 5.87 (ddt, J = 16.8, 10.2, and 6.5 Hz, $1H_9$), 6.62 (dd, J = 12.3 and 2.4 Hz, $1H_3$), 6.76 (dd, J = 8.7 and 2.4 Hz, $1H_5$), 7.80 (t, J = 8.7 Hz, $1H_6$) and 10.18 (s, $1H_{aldehyde}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.12, 67.92, 101.8(d), 111.52(d), 117.61, 117.64, 130.00(d), 133.47, 165.5(d), 166.15(d), and 185.81(d).

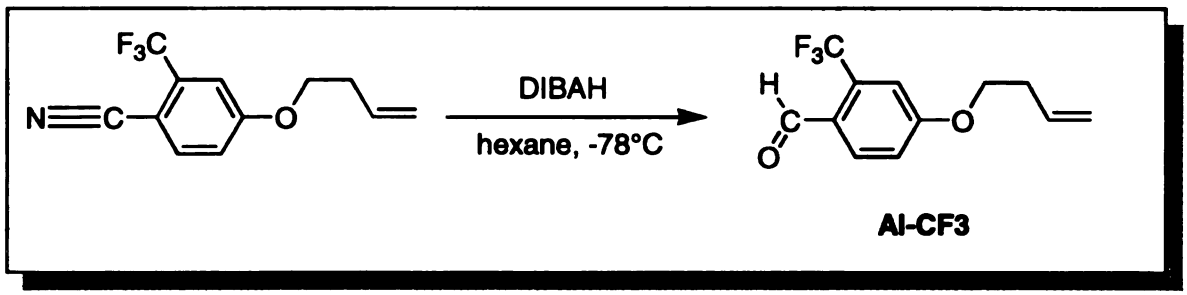
FT-IR (CCl_4, cm^{-1}): 650.09, 733.04, 910.52, 1095.71, 1129.21, 1253.89, 1437.15, 1504.67, 1577.97, 1820.41, 1689.86, 2862, and 2933 cm^{-1}.

GC-MS (m/z): 55.1(Base), 75.0, 83.0, 95.0, 122.9, 138.9, 153.0, 166.0 and 194.0 ($M^{+\bullet}$).

UV : 216.6, 264.6(max), 283 and 292.8.

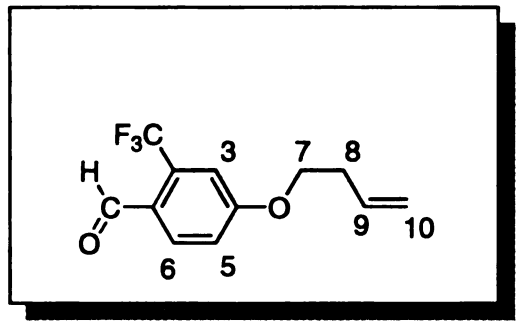
Anal: Calcd: C(%), 68.03; H(%), 5.71. Found: C(%), 67.69; H(%), 5.79.

4.3.4. 4-(3-Buten-1-oxy)-2-trifluoromethylbenzaldehyde



4-(3-Buten-1-oxy)-2-trifluoromethylbenzonitrile (**CN-CF3**) (0.2 g, 0.83 mmol) was dissolved in 3 mL of dry hexane under argon atmosphere. The solution was cooled to –78 °C, and 0.04 mL of a 1 M hexane solution of diidobutylaluminum hydride was added. After 1 hr, ether (10 mL) and silica (1.5g) were added, and the mixture was kept

stirring at 4 °C for 14 hrs. Water was added, and the mixture was extracted twice with ether. The ether layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-(3-buten-1-oxy)-2-trifluoromethylbenzaldehyde as colorless liquid in 54 % yield (0.11 g).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.57 (br q, J = 6.6, $2H_8$), 4.11 (t, J = 6.6 Hz, $2H_7$), 5.11-5.22 (m, $2H_{10}$), 5.87 (ddt, J = 17.0, 10.2, and 6.6 Hz, $1H_9$), 7.11 (dd, J = 8.8 and 2.2 Hz, $1H_3$), 7.22 (d, J = 2.2 Hz, $1H_5$), 8.09 (d, J = 8.3 Hz, $1H_6$) and 10.23 (br s, $1H_{aldehyde}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.23, 67.96, 112.85(q), 116.88, 117.79, 121.57, 125.21, 126.52, 131.67, 133.48, 162.95 and 187.76.

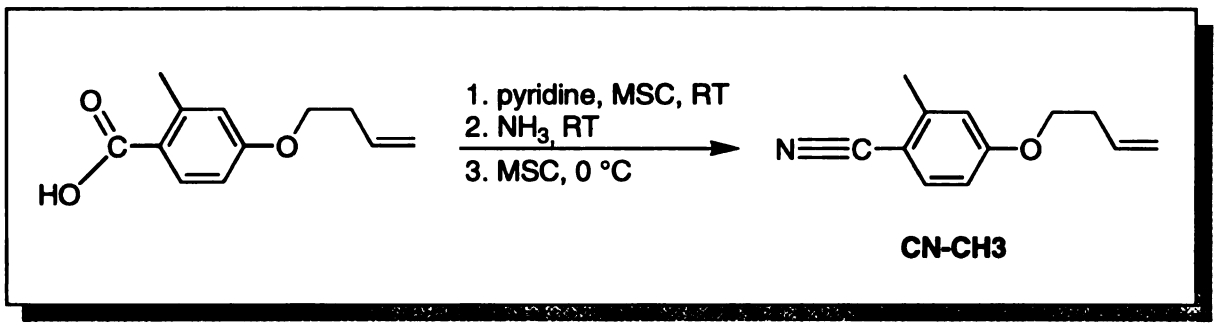
FT-IR (CCl_4, cm^{-1}): 650.09, 734.0, 911.3, 1095.71, 1127.44, 1460.15, 1579.32, 1820.41, 1697.8, 2780.2, 2930.2 and 3130 cm^{-1}.

GC-MS (m/z): 55.4(Base), 63.3, 75.3, 95.2, 113.2, 125.2, 145.3, 173.3, 189.3, 216.4 and 244.2 ($M^{+\bullet}$).

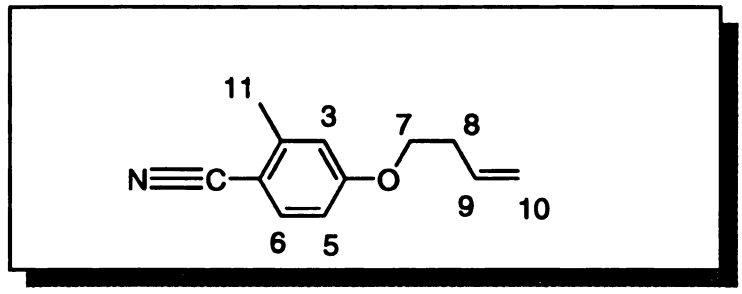
UV: 217.6, 269.8(max) and 290.

Anal: Calcd: C(%), 59.02; H(%), 4.54. Found: C(%), 60.38; H(%), 5.22.

4.3.5. 4-(3-Buten-1-oxy)-2-methylbenzonitrile



4-(3-Buten-1-oxy)-2-methylbenzoic acid (2.55 g, 12.4 mmol) and dry pyridine (85 mL) were stirred at RT. Then methyl sulfonyl chloride (MSC, 1.92 g) was added dropwise into the reaction flask. After 1 hour dry ammonia gas was passed for 2 min. The mixture was cooled to 0°C and additional methyl sulfonyl chloride (16 g) was added and stirred at RT for 24 hours. The mixture was poured into diluted acid and pH was adjusted to 7. The mixture was extracted with ethyl acetate (2X100 mL) and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 4-(3-buten-1-oxy)-2-methylbenzonitrile as colorless liquid (1.8 g, 77.6 %).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.46 (s, $3H_{11}$), 2.52 (qt, J = 6.6 and 1.6 Hz, $2H_8$), 4.01 (t, J = 6.6 Hz, $2H_7$), 5.07-5.19 (m, $2H_{10}$), 5.85 (ddt, J = 17.0, 10.4, and 6.6 Hz, $1H_9$), 6.71 (d, J = 2.2 Hz, $1H_3$), 6.75 (dd, J = 8.2, and 2.2 Hz, $1H_5$) and 7.47 (d, J = 8.2 Hz, $1H_6$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 20.61, 33.26, 67.30, 104.32, 112.40, 116.11, 117.40, 118.54, 133.76, 134.10, 143.96, and 161.95.

FT-IR (CCl_4, cm^{-1}): 721.5, 1248.1, 1377.3, 1458.4, 1498.9, 1606.9, 2224.2, 2855.0, and 2924.5 cm^{-1}.

GC-MS (m/z): 39.2, 55.2(Base), 77.1, 89.0, 104.0, 116.0, 133.0, 159.1 and 187.1($M^{+\bullet}$).

UV: 211, 246.8(max), 275.0 and 285.

Anal: Calcd: C(%), 76.98; H(%), 7.00; N(%), 7.48. Found: C(%), 75.69; H(%), 7.13; N(%), 7.16.

4.

a.

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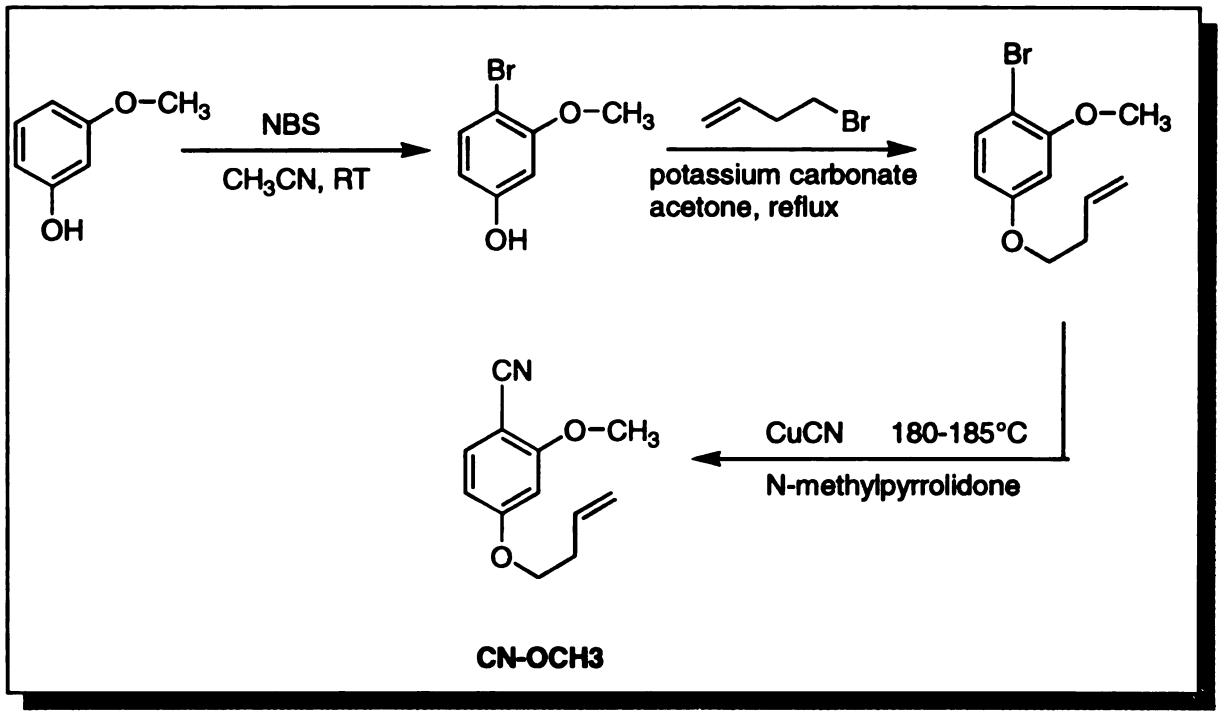
4.3.6. 4-(3-Buten-1-oxy)-2-methoxybenzonitrile



CN-OCH3

a. 4-Bromo-3-methoxy-phenol

NBS (17.8 g, 0.1 mol) was added to 3-methoxy phenol (12.4 g, 0.1 mol) in DMSO (9 g, 0.11 mol) and CH_3CN (200 mL). The mixture was stirred at room temperature for 1 hr, the solvent evaporated and the residue treated with 100 mL of ethyl ether and water (3 x 50 mL). The ethereal layer was dried over $MgSO_4$, filtered and evaporated, and the crude product was obtained and purified by fractional distillation at reduced pressure (b.p. 72-73 °C at 3.5-4 mmHg) followed by flash chromatography on

silica gel (hexane:ethyl acetate, 90:10) gave 4-bromo-3-methoxyphenol as white solid (m.p. 82-83 °C) in 10.8% yield (2.2 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 3.86 (s, 3H), 4.9 (s, 1H), 6.33 (dd, J = 8.4 and 2.7 Hz, 1H), 6.46 (d, J = 2.7 Hz, 1H) and 7.35 (d, J=8.4 Hz, 1H).

GC-MS (m/z): 51.1, 65.1, 93.1, 108.1, 131.0, 159.0, 187.0, 204.0 (Base, $M^{+\bullet}$).

b. 1-Bromo-4-(3-Buten-1-oxy)-2-methoxybenzene

4-Bromo-3-methoxy-phenol (2.0 g, 9.9 mmol), 4-bromo-1-butene (1.62 g, 12.1 mol) and anhydrous potassium carbonate (3.44 g, 0.024 mol) in dry acetone (50 mL) were refluxed under argon for 50 hours. The cooled mixture was gravity filtered to remove the salt formed during the reaction and concentrated in vacuo. The resulting yellow oil was diluted with ether (50 mL) and extracted with 2N NaOH (4 x 25 mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 1-bromo-4-(3-buten-1-oxy)-2-methoxybenzene as colorless liquid in 18.1% yield (0.46 g).

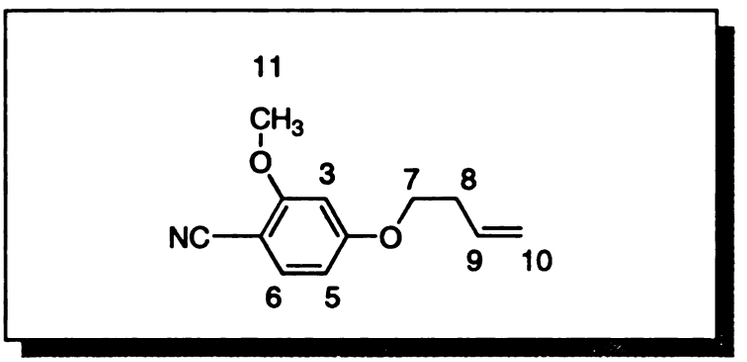
1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.54 (q, J = 6.59 Hz, 2H), 3.86 (s, 3H), 3.99 (t, J = 6.59Hz, 2H), 5.16 (m, 2H), 5.90 (ddt, J = 17.0, 10.4, and 6.59 Hz, 1H), 6.38 (dd, J = 8.79 and 2.75 Hz, 1H), 6.50 (d, J = 2.75 Hz, 1H) and 7.39 (d, J = 8.79 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.44, 55.95, 67.33, 100.32, 102.21, 106.33, 117.08, 132.95, 134.10, 156.32, and 159.35.

GC-MS (m/z): 55.1 (Base), 63.1, 79.1, 93.1, 128.8, 159.0, 203.9, 257.1 ($M^{+\bullet}$).

c. 4-(3-Buten-1-oxy)-2-methoxybenzonitrile

A solution of 1-bromo-4-(3-buten-1-oxy)-2-methoxybenzene (0.4 g, 1.95 mmol) and cuprous cyanide (3.1 g) in 23.5 mL of N-methylpyrrolidone was heated at 180-185 °C for 21 h. It was then poured into 400 mL of a 1:1 mixture of water and concentrated aqueous ammonium hydroxide. After the resulting mixture had been stirred with cooling for 3 h, the mixture was extracted with ether. The ethereal layer was extracted by saturated potassium carbonate and NaOH (2N). The ether layer was dried over $MgSO_4$, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel from dichloromethane gave 4-(3-buten-1-oxy)-2-methoxybenzonitrile as pale yellow liquid in 27.8% yield (0.11 g).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.52 (q, J = 6.59 Hz, 2H), 3.85 (s, 3H), 4.02 (t, J = 6.59Hz, 2H), 5.12 (m, 2H), 5.85 (ddt, J = 17.0, 10.4, and 6.59 Hz, 1H), 6.42 (d, J = 2.2 Hz, 1H), 6.47 (dd, J = 8.79 and 2.2 Hz, 1H), and 7.41 (d, J = 8.79 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.26, 55.91, 67.59, 98.88, 106.1, 116.94, 117.48, 133.72, 134.78, 162.73, 163.89 and 180.03.

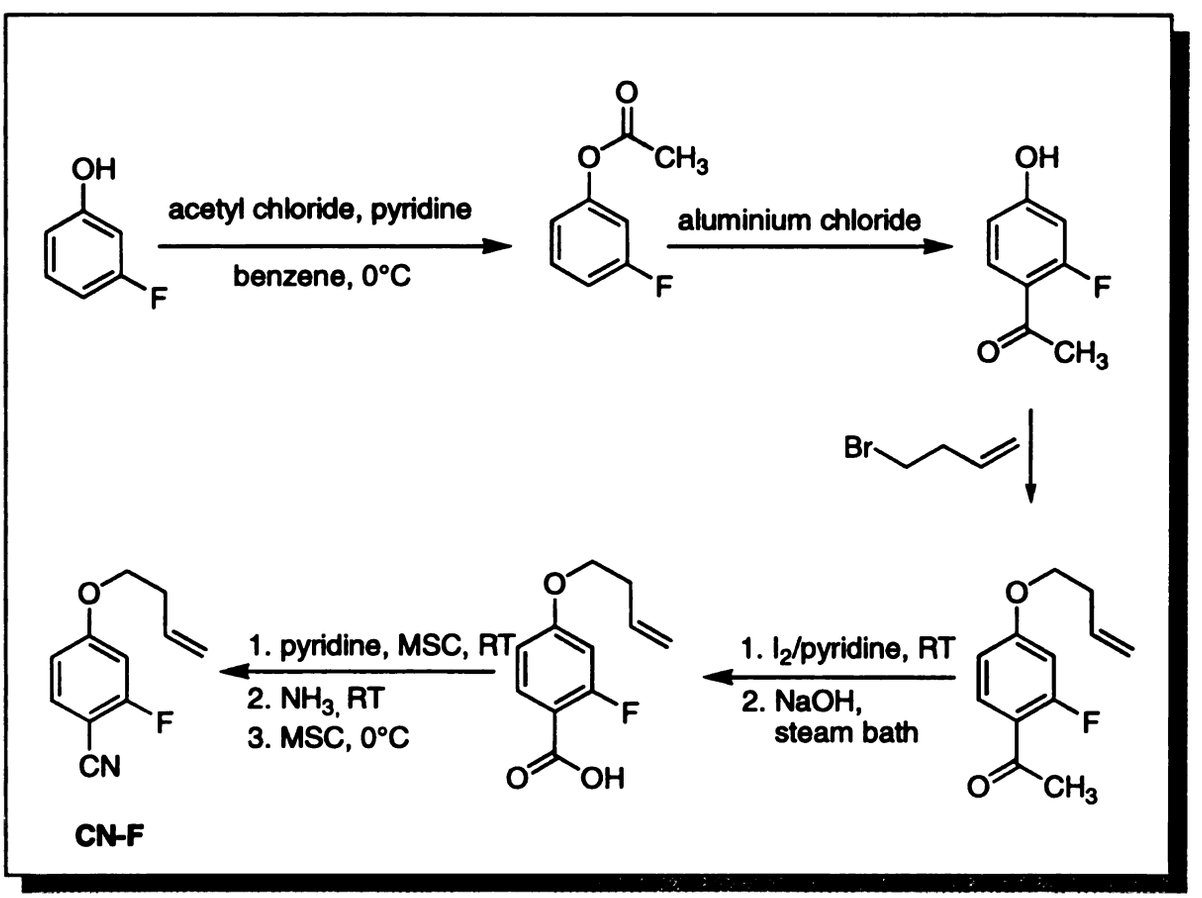
FT-IR (CCl_4, cm^{-1}): 724.7, 1115.30, 1250.1, 1451.5, 1496.3, 1612.8, 2223.7, 2877.0, and 2930.2, 3014.2 cm^{-1}.

GC-MS (m/z): 55.2 (Base), 77.2, 89.2, 120.2, 132.2, 149.2, 162.3, 175.1 and 203.3 ($M^{+\bullet}$).

UV: 215.6(max), 247.6, 287.0 and 293.2.

Anal: Calcd: C(%), 70.92; H(%), 6.45; N(%), 6.89. Found: C(%), 70.95; H(%), 6.60; N(%), 6.75.

4.3.7. 4-(3-Buten-1-oxy)-2-fluorobenzonitrile



a. 3-fluorophenyl acetate

Acetyl chloride (9.74 g, 0.124 mol) was added dropwise to the mixture of 3-fluorophenol (13.7 g, 0.124 mol) and pyridine (9.78 g, 0.124 mol) in 20 mL of dry

benzene at 0°C. The mixture was stirred under nitrogen at room temperature for 24 hours. The mixture was hydrolyzed with 5% HCl (25 mL) and organic layer was separated. The organic layer was extracted four times with 10 mL portions of 2 N NaOH and dried over magnesium sulfate. The extract was concentrated in vacuo to give a crude yellow oil. Purification of the crude product by vacuum distillation gave 3-fluorophenyl acetate as colorless liquid (18.5 g, 97%).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.25 (s, 3H), 6.85 (dd, J = 2.5 and 2.3 Hz, 1H), 6.93 (ddd, J = 8.5, 2.5 and 0.9 Hz, 1H) and 7.30 (m, 2H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 20.73, 109.5(d), 112.6(d), 117.25(d), 130(d), 151.4(d), 162.66(d) and 168.80.

FT-IR (CCl_4, cm^{-1}): 733.04, 910.52, 1122.71, 1209.52, 1371.56, 1487.31, 1601.12, and 1768.95 cm^{-1}.

GC-MS (m/z): 43.1, 57.0, 64.1, 83.0, 112.0(Base) and 154.0($M^{+\bullet}$).

b. 4-hydroxy-2-fluoroacetophenone

A solution of 3-fluorophenyl acetate (15.4 g, 0.1 mol) in nitrobenzene (50 mL) was added dropwise to a solution of aluminium chloride (26.67 g, 0.2 mol) in

nitrobenzene (200 mL) at 0°C under argon. The reaction mixture was warmed to room temperature and stirred for 96 hours. After stirring, the mixture was hydrolyzed with 5% HCl (200 mL). The nitrobenzene layer was diluted with ether (200 mL) and extracted with 50 mL portions of 2N NaOH. The combined aqueous washings were acidified with HCl to pH 3-5 and extracted with ether (6 x 100 mL). The organic extracts were dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by vacuum distillation (b.p. 139-140 °C at 3.5-4 mmHg) gave 4-hydroxy-2-fluoroacetophenone as a white solid (6.16 g, 40 %), m.p (115-117 °C).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.61 (d, J = 5.2, 3H), 6.63 (dd, J = 12.6 and 2.4 Hz, 1H) 6.71 (dd, J = 8.8 and 2.4 Hz, 1H), 6.85 (s, 1H), and 7.85 (t, J = 8.8 Hz, 1H).
13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 31.16(d), 103.56(d), 112.13, 117.20, 132.44(d), 162.17(d), 163(d), 195.80.

FT-IR (CCl_4, cm^{-1}): 854.57, 1247.17, 1278.97, 1338.77, 1367.70, 1570.26, 1651.28 and 3115.43 cm^{-1}.

GC-MS (m/z): 43.2, 57.1, 63.1, 77.0, 83.0, 95.0, 111.0, 139.1 (Base) and 154.1 ($M^{+\bullet}$).

c. 4-(3-Buten-1-oxy)-2-fluorolacetophenone

4-hydroxy-2-fluorolacetophenone (4.0 g, 0.0266 mol), 4-bromo-1-butene (4.60 g, 0.019 mol) and anhydrous potassium carbonate (11.03 g, 0.078 mol) in dry acetone (50 mL) were refluxed under argon for 40 hours. The cooled mixture was gravity filtered to removed the salt formed during the reaction and concentrated in vacuo. The resulting yellow oil was diluted with ether (50 mL) and extracted with 2N NaOH (4 x 25 mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-buten-1'-oxy-2-fluoroacetophenone as colorless liquid in 55% yield (3.04 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.51 (s, 3H), 2.53 (s, 3H), 2.53 (m, 2H), 4.02 (t, J = 6.6 Hz, 2H), 5.07-5.18 (m, 2H), 5.87 (ddt, J=18, 10.5, and 6.6 Hz, 1H), 6.71 (m, 2H) and 7.72 (d, J=9.6 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 22.58, 29.01, 33.42, 67.09, 110.92, 117.23, 117.96, 129.75, 132.51, 134.01, 142.15, 161.22 and 199.39.

FT-IR (CCl_4, cm^{-1}): 839.14, 968.39, 1130.43, 1165.15, 1259.68, 1361.92, 1435.22, 1574.11, 1618.48, 1680.21, 2945.66 and 3077.4 cm^{-1}.

GC-MS (m/z): 42.9, 54.9 (Base), 63.0, 82.9, 93.6, 109.9, 138.8, 153.8, 179.9, 192.9 and 207.9 ($M^{+\bullet}$).

d. 4-(3-Buten-1-oxy)-2-fluorobenzoic acid

Iodine (4.3 g, 0.017 mol) was added to the solution of 4-(3-buten-1-oxy)-2-fluoroacetophenone (3.5 g, 0.017 mol) in pyridine (10 mL). The reaction mixture was heated on the steam bath for 30 min then stirred over night at room temperature. Excess pyridine was removed by vacuum distillation and the residue was washed with water. Sodium hydroxide (5 g) was added to the suspension in the water (50 ml). The mixture was heated on the steam bath for 1 hour and acidified with concentrated hydrochloric acid. Precipitation was filtered and extracted with saturated sodium carbonate solution. The aqueous layer was acidified with concentrated hydrochloric acid and filtered. Purification of the crude product by column chromatography on silica gel (chloroform: acetone, 3:1) gave 4-buten-1'-oxy-2-fluorobenzoic acid as yellowish solid (m.p. 143-145 °C) in 49% yield (1.75 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.55 (qt, J = 6.6 and 1.0 Hz, 2H), 4.04 (t, J = 6.6 Hz, 2H), 5.08-5.20 (m, 2H), 5.86 (ddt, J = 17, 10.4, and 6.6 Hz, 1H), 6.63 (dd, J = 12.6 and 2.2 Hz, 1H) 6.72 (dd, J = 8.8 and 2.2 Hz, 1H) and 7.95 (t, J = 8.8 Hz, 1H).

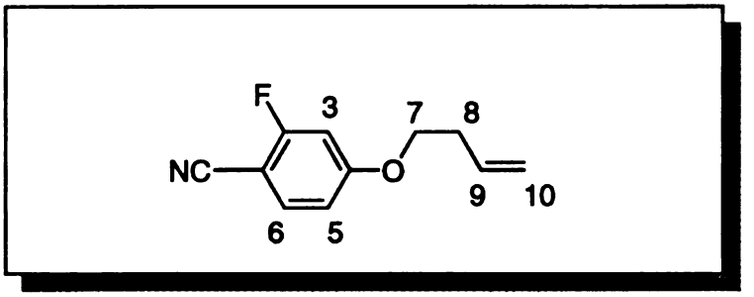
13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.23, 67.85, 102.7(d), 110.78(d), 117.63, 133.4, 133.62, 134.06, 164.1(d), 164.5(d) and 169.16.

FT-IR (CCl_4, cm^{-1}): 642.38, 846.86, 933.87, 1020.47, 1178.66, 1244.24, 1300.19, 1452.58, 1620.41, 1692.14 and 2953 cm^{-1}.

GC-MS (m/z): 55.3 (Base), 83.1, 94.1, 121.0, 138.9, 155.9, 169.0, 182.0 and 210.1 ($M^{+\bullet}$).

e. 4-(3-Buten-1-oxy)-2-fluorobenzonitrile

4-(3-Buten-1-oxy)-2-fluorobenzoic acid (1.5 g, 7.14 mmol) and dry pyridine (85 mL) were stirred at RT. Then methyl sulfonyl chloride (MSC, 1.13 g) was added dropwise into the reaction flask. After 1 hour, dry ammonia gas was passed for 2 min. The mixture was cooled to 0°C and additional methyl sulfonyl chloride (9.44 g) was added and stirred at RT for 20 hours. The mixture was poured into diluted acid and pH was adjusted to 7. The mixture was extracted with ethyl acetate (2X100 mL) and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 4-(3-buten-1-oxy)-2-fluorobenzonitrile as colorless liquid (0.97 g, 71%).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.54 (qt, J = 6.6 and 1.6 Hz, $2H_8$), 4.03 (t, J = 6.6 Hz, $2H_7$), 5.09-5.20 (m, $2H_{10}$), 5.84 (ddt, J = 17.0, 10.4, and 6.6 Hz, $1H_9$), 6.68 (dd, J = 11 and 2.2 Hz, $1H_3$), 6.73 (dd, J = 8.8 Hz and 1.6 Hz, $1H_5$) and 7.49 (d, J = 8.8 Hz, $1H_6$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.06, 68.06, 92.74, 102.7(d), 111.6(d), 114.38, 117.72, 133.36, 134.1, 164.1(d) and 164.5(d).

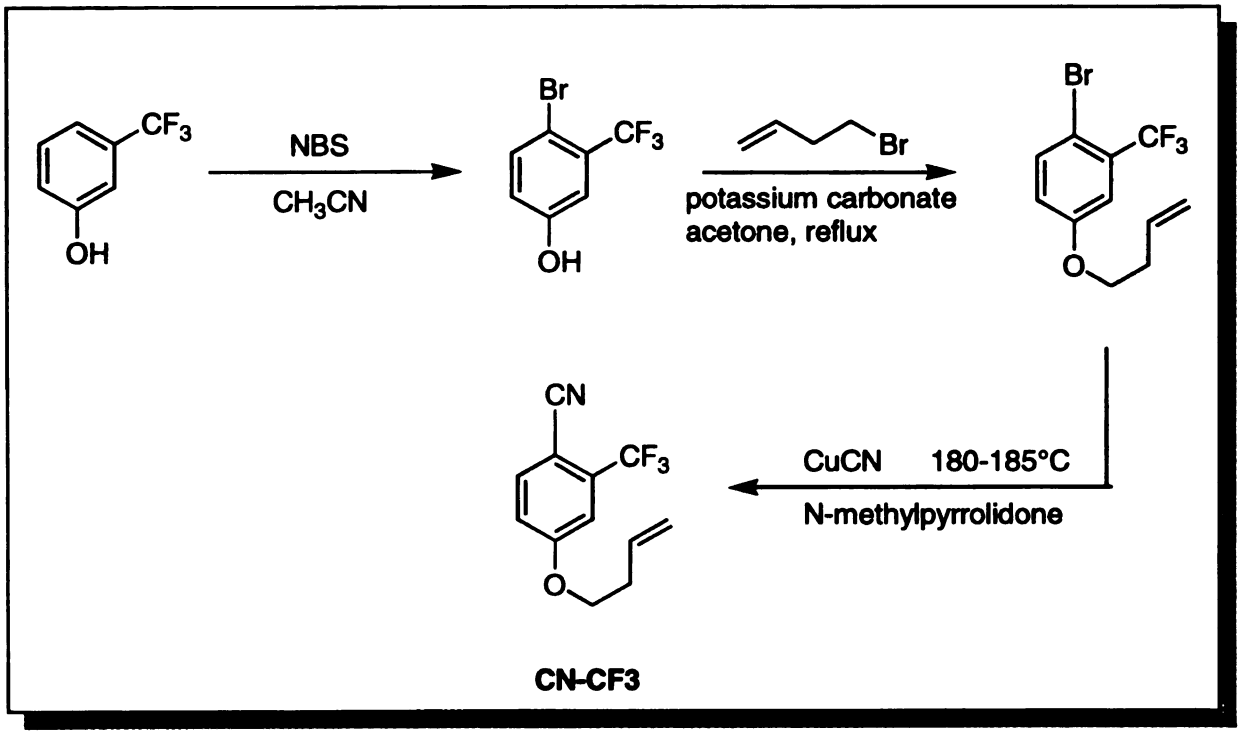
FT-IR (CCl_4, cm^{-1}): 634.66, 839.14, 920.16, 989.61, 1022.40, 1115.00, 1172.87, 1300.19, 1506.60, 1572.18, 1622.34, 2231.92, 2936.03 and 3060 cm^{-1}.

GC-MS (m/z): 39, 55 (Base), 63, 82, 93, 100, 108, 120, 137, 150, 163 and 191 ($M^{+\bullet}$).

UV: 207.0, 243.6(max), 276.8 and 283.2.

Anal: Calcd: C(%), 69.10; H(%), 5.27; N(%), 7.33. Found: C(%), 69.02; H(%), 5.20; N(%), 7.32.

4.3.8. 4-(3-Buten-1-oxy)-2-trifluoromethylbenzonitrile



a. 4-Bromo-3-trifluoromethyl-phenol

NBS (17.8 g, 0.1 mol) was added to 3-trifluoromethylphenol (16.2 g, 0.1 mol) in DMSO (9 g, 0.11 mol) and CH_3CN (200 mL). The mixture was stirred at room temperature for 1 hr, the solvent evaporated and the residue treated with 100 mL of ethyl ether and water (3 x 50 mL). The ethereal layer was dried over $MgSO_4$, filtered and evaporated, and the crude product was obtained and purified by fractional distillation at reduced pressure (b.p. 75-76 °C at 3.5-4 mmHg) followed by flash chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-bromo-3-methoxyphenol as white solid (m.p. 77 – 79 °C) in 21.6% yield (5.2 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 5.60 (s, 1H), 6.84 (dd, J = 8.8 and 2.7 Hz, 1H), 7.15 (d, J = 2.7 Hz, 1H) and 7.50 (d, J = 8.8, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 110.05, 115.24(q), 119.94, 122.37(q), 131.02, 135.96 and 154.60.

GC-MS (m/z): 40.1 (Base), 71.1, 83.1, 113.1, 132.1, 161.1, 192.0, 221.0, 241.0 ($M^{+\bullet}$).

b. 1-Bromo-4-(3-buten-1-oxy)-2-trifluoromethylbenzene

4-Bromo-3-trifluoromethylphenol (3.0 g, 12.5 mmol), 4-bromo-1-butene (2.03 g, 15 mmol) and anhydrous potassium carbonate (6.0 g, 43.4 mmol) in dry acetone (250 mL) were refluxed under argon for 51 hours. The cooled mixture was gravity filtered to removed the salt formed during the reaction and concentrated in vacuo. The resulting yellow oil was diluted with ether (200 mL) and extracted with 2N NaOH (4 x 100 mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 1-bromo-4-(3-buten-1-oxy)-2-trifluoromethylbenzene as pale yellow liquid in 42.5% yield (1.57 g).

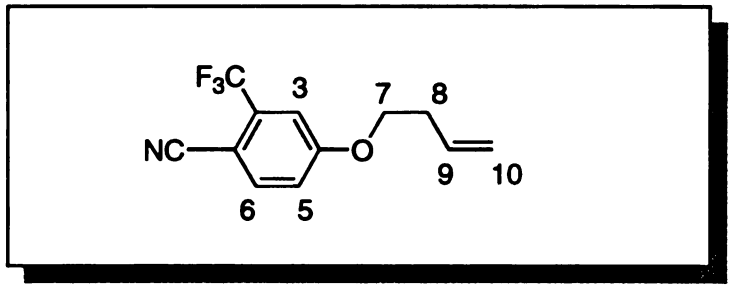
1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.54 (br q, J = 6.6 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 5.10-5.20 (m, 2H), 5.87 (ddt, J = 17.03, 10.44, and 6.60 Hz, 1H), 6.88 (dd, J = 8.8 and 2.75 Hz, 1H), 7.20 (d, J = 2.75 Hz, 1H) and 7.54 (d, J = 8.8, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 34.18, 68.53,110.20, 115.03(q), 117.91, 119.16, 122.86(q), 130.21, 134.27, 136.15 and 158.1.

GC-MS (m/z): 55.2 (Base), 149.1, 175.1, 217.2, 253.0, 295.1 ($M^{+\bullet}$).

c. 4-(3-Buten-1-oxy)-2-trifluoromethylbenzonitrile

A solution of 1-bromo-4-(3-buten-1-oxy)-2-trifluoromethylbenzene (1.3 g, 4.4 mmol) and cuprous cyanide (7.9 g, mol) in 100 mL of N-methylpyrrolidone was heated at 180-185 °C for 21 h. It was then poured into 500 mL of a 1:1 mixture of water and concentrated aqueous ammonium hydroxide. After the resulting mixture had been stirred with cooling for 3 h, the mixture was extracted with ether. The ethereal layer was extracted by saturated potassium carbonate and NaOH (2N). The ether layer was dried over $MgSO_4$, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-(3-buten-1-oxy)-2-trifluoromethylbenzonitrile as colorless liquid in 65.2% yield (0.69 g).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.57 (br q, J = 6.6 Hz, 2H), 4.10 (t, J = 6.6 Hz, 2H), 5.11-5.21 (m, 2H), 5.85 (ddt, J = 17.03, 9.9, and 6.60 Hz, 1H), 7.08 (dd, J = 8.2 and 2.2 Hz, 1H), 7.24 (d, J = 2.2 Hz, 1H) and 7.73 (d, J = 8.2, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.24, 68.87, 102, 115.03(q), 116.30, 117.58, 118.37, 122.5(q), 130.21, 133.69, 137.04, 162.4.

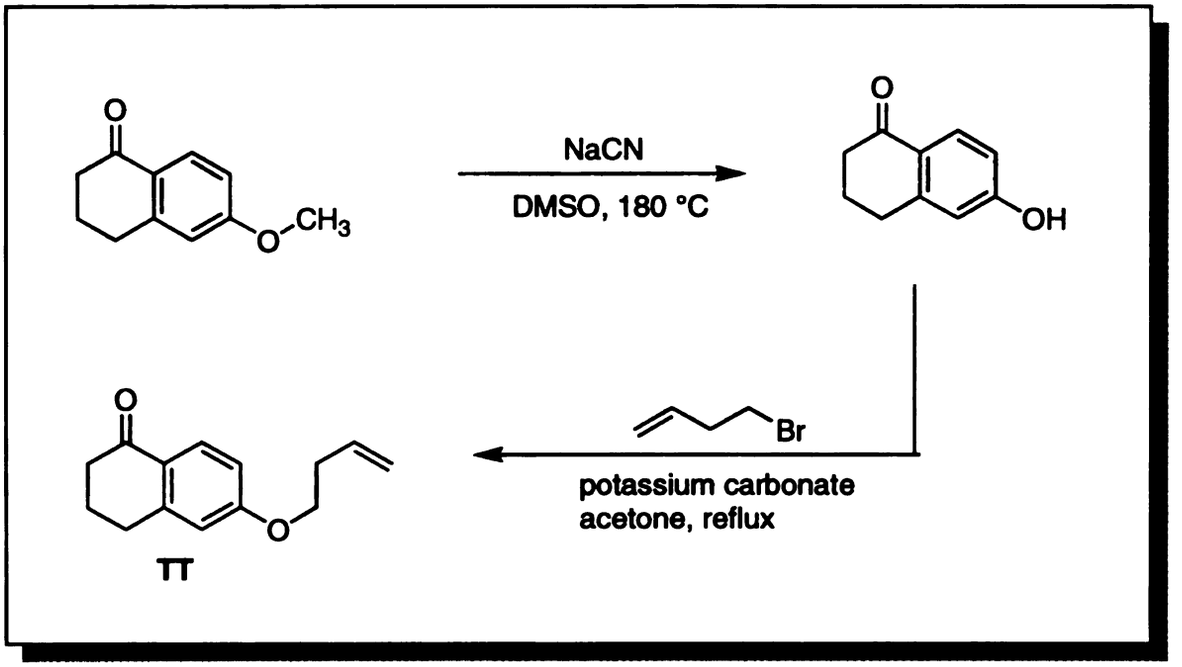
FT-IR (CCl4, cm^{-1}): 841.2, 920.16, 989.61, 1022.40, 1115.00, 1172.87, 1300.19, 1506.60, 1572.18, 1622.34, 2227.3, 2947.3 and 3021.0 cm^{-1}.

GC-MS (m/z): 55.2(Base), 69.1, 108.2, 120.1, 139.2, 151.0, 170.2, 187.2, 200.2, 213.2 and 241.2 ($M^{+\bullet}$).

UV: 208.8, 248.6(max), 277 and 290.

Anal: Calcd: C(%), 59.75; H(%), 4.18; N(%), 5.81. Found: C(%), 60.76; H(%), 4.53; N(%), 5.46.

4.3.9. 6-(3-Buten-1-oxy)-1-tetralone



a. 6-Hydroxy-1-tetralone

Methoxytetralone (5.29g, 30 mmol) and sodium cyanide (7.5g, 150 mmol) are added to DMSO (40 mL). The reaction mixture was heated at 180 °C for 5 h under nitrogen. The mixture was poured into ice-water and acidified with 6N HCl. The resulting precipitation is collected by filteration, washed with water, and dried. Recrystalization from benzene gives 6-hydroxy-1-tetralone as pale yellow crystals (2.5 g, 51%), m.p. 154-157 °C.

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.08 (q, J = 6.3 Hz, 2H), 2.61 (t, J = 6.3 Hz, 2H), 2.87 (t, J =6 .3 Hz, 2H), 6.70 (d, J = 1.8 Hz, 1H), 6.79 (dd, J = 8.7 and 1.8 Hz, 1H) 7.6 (br s, 1H) and 7.96 (d, J = 8.7 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 23.24, 29.89, 38.77, 114.62, 114.64, 125.66, 130.18, 147.83, 161.34 and 198.76.

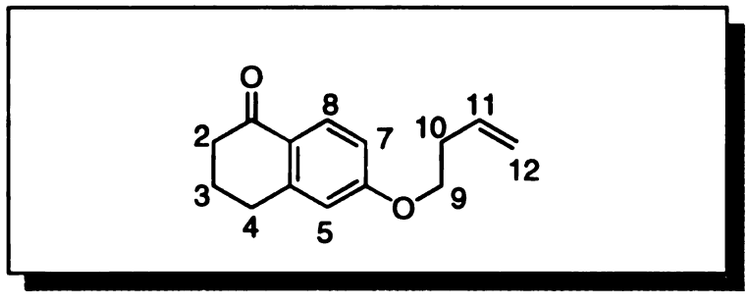
FT-IR (CCl_4, cm^{-1}): 455.20, 538.26, 652.02, 835.28, 895, 1110.98, 1288.61, 1348.41, 1560.61, 1652.5, 2708.4, 2948.5, 3078.2, 2500-3500 cm^{-1}.

GC-MS (m/z): 51.0, 66.0, 77.0, 91.1, 106.1, 134.0(Base), 147.1 and 162.1($M^{+\bullet}$).

b. 6-(3-Buten-1-oxy)-1-tetralone

6-Hydroxy-1-tetralone (1.62 g, 0.01 mol), 4-bromo-1-butene (2.7 g, 0.02 mol) and anhydrous potassium carbonate (5.5 g, 0.04 mol) in dry acetone (150 mL) were refluxed under argon for 42 hours. The cooled mixture was gravity filtered to removed the salt formed during the reaction and concentrated in vacuo. The resulting yellow oil was diluted with ether (50 mL) and extracted with 2N NaOH (4 x 30 mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on

silica gel (hexane : ethyl acetate, 90:10) gave 6-(3-buten-1-oxy)-1-tetralone as pale yellow liquid in 46.8% yield (1.01 g).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.09 (q, J = 6.6 Hz, $2H_3$), 2.53 (q, J = 6.6 Hz, $2H_{10}$), 2.58 (t, J = 6.6 Hz, $2H_4$), 2.90 (t, J = 6.6 Hz, $2H_2$), 4.05 (t, J = 6.6 Hz, $2H_9$), 5.10-5.21 (m, $2H_{12}$), 5.86 (ddt, J = 17.03, 9.9, and 6.60 Hz, $1H_{11}$), 6.69 (d, J = 2.4 Hz, $1H_5$), 6.80 (dd, J = 9 and 2.4 Hz, $1H_7$) and 7.98 (d, J = 9 Hz, $1H_8$).

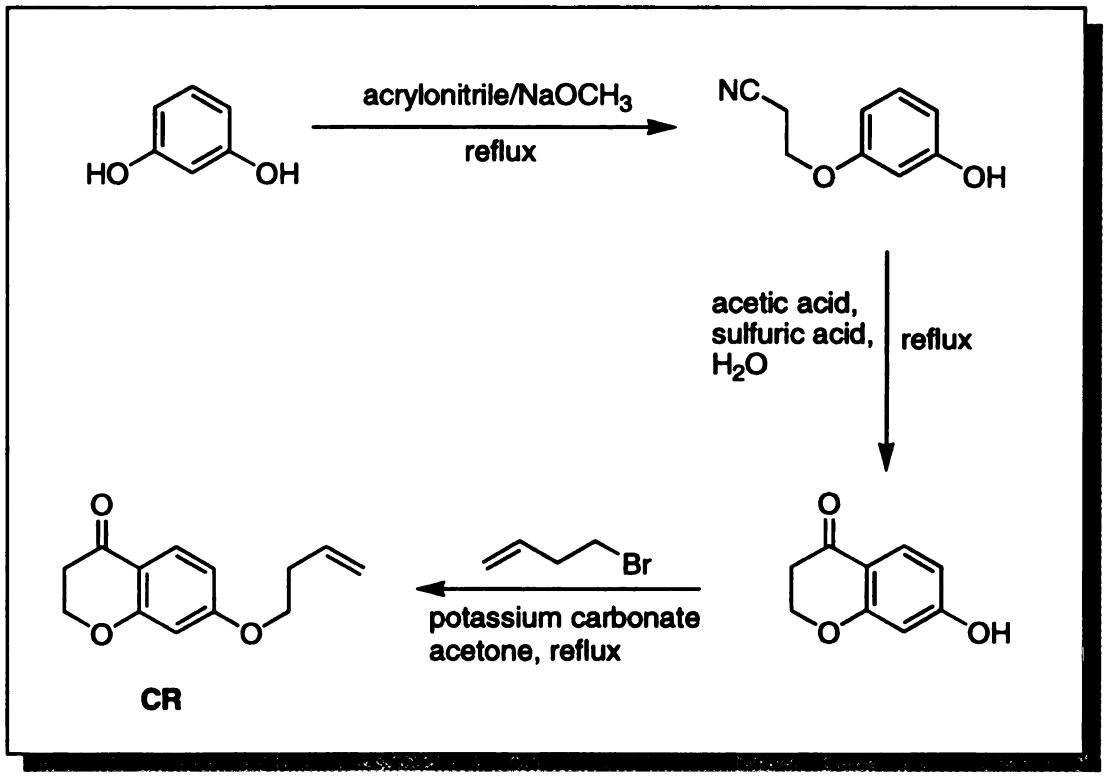
13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 23.29, 30.04, 33.36, 38.80, 67.19, 113.07, 113.33, 117.26, 126.15, 129.49, 133.94, 146.87, 162.79 and 197.11.

FT-IR (CCl_4, cm^{-1}): 650.09, 731.11, 906.66, 1035.91, 1126.57, 1258.03, 1350.34, 1495.02, 1599.19, 1670.57 and 2947.61cm^{-1}.

GC-MS (m/z): 55.0, 76.9, 89.0, 106.1, 134.0(Base), 147.0, 162.0, 204.1 and 216.1($M^{+\bullet}$).

Anal: Calcd: C(%), 77.75; H(%), 7.46. Found: C(%), 76.88; H(%), 7.54.

4.3.10. 6-(3-Buten-1-oxy)-1-chromonone



a. 3-(3-Hydroxyphenoxy) propanenitrile

A mixture of resorcinol (11g, 0.1 mol), acrylonitrile (10 mL) and sodium methoxide (1.08 g, 0.02 mol) was refluxed for 7 h. Excess of acrylonitrile was distilled off and the residue was extracted with $CHCl_3$. The organic layer was washed, dried with $CaCl_2$ and concentrated. The residue was repeatedly extracted with ether and the layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on

silica gel (hexane:ethyl acetate, 90:10) gave 3-(3-hydroxyphenoxy) propanenitrile as white solid (m.p. 85-86, lit. 87-88[55]) in 23.6% yield (3.85 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.79(t, J=6.3 Hz, 2H), 4.13(t, J=6.6 Hz, 2H), 5.57(s, 1H), 6.39(d, J=2.3 Hz, 1H), 6.46(m, 2H) and 7.12(t, J=8.2 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 18.52, 62.48, 102.41, 106.66, 109.01, 120.35, 130.32, 156.97 and 158.88.

FT-IR (CCl_4, cm^{-1}): 979.4, 1054.5, 1154.6, 1179.7, 1242.2, 1292.4, 1342.5, 1486.4, 1611.6, 2268.87, 2944.9, 3032.6 and 3351.8 cm^{-1}.

GC-MS (m/z): 39.0, 53.0, 65.0, 82.1, 93.0, 110.0 (Base), 123.1 and 163.1 ($M^{+\bullet}$).

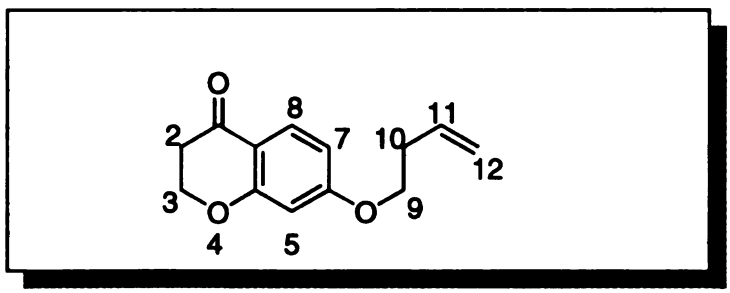
b. 2,3-Dihydro-7-hydroxy-4H-benzopyran-4-one

3-(3-Hydroxyphenoxy) propanenitrile (3.0 g, 18.4 mmol) in concentrated sulphuric acid-glacial acetic acid-water (1:1:1 15 mL) was refluxed for 5h. The deep red mixture was taken up in ether, washed with saturated. Sodium bicarbonate and water, dried over sodium sulfate and evaporated. Purification of the crude product by column chromatography on silica gel ($CHCl_3$:MeOH, 9:1) gave 2,3-dihydro-7-hydroxy-4H-benzopyran-4-one as white solid (m.p. 146-148, lit. 147-148[55]) in 10% yield (0.3 g).

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.77 (t, J = 6.4 Hz, 2H), 4.50 (t, J = 6.4 Hz, 2H), 6.40 (d, J = 2.3 Hz, 1H), 6.55 (dd, J = 8.6 and 2.3 Hz, 1H) 7.0 (s, 1H) and 7.81 (d, J = 8.6 Hz, 1H).

c. 2,3-Dihydro-7-(3-buten-1-oxy)-4H-benzopyran-4-one

2,3-Dihydro-7-hydroxy-4H-benzopyran-4-one (0.25 g, 1.5 mmol), 4-bromo-1-butene (0.41 g, 3 mmol) and anhydrous potassium carbonate (0.82 g, 5.9 mmol) in dry acetone (25 mL) were refluxed under argon for 40 hours. The cooled mixture was gravity filtered to removed the salt formed during the reaction and concentrated in vacuo. The resulting yellow oil was diluted with ether (25 mL) and extracted with 2N NaOH (4 x 10 mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated in vacuo to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 2,3-dihydro-7-(3-buten-1-oxy)-4H-benzopyran-4-one in 48.8% yield (0.16 g).



1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.50 (q, J = 6.6 Hz, 2H), 2.70 (t, J = 6.9 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 4.46 (t, J = 6.9 Hz, 2H), 5.06-5.16 (m, $2H_{12}$), 5.83 (ddt, J = 17.03, 9.9, and 6.60 Hz, $1H_{11}$), 6.35 (d, J = 2.1 Hz, 1H), 6.52 (dd, J = 8.7 and 2.1 Hz, 1H) and 7.77 (t, J = 8.7 Hz, 1H).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 33.22, 37.31, 67.256, 67.42, 101.18, 110.12, 115.12, 117.34, 128.74, 133.76, 163.66, 165.162 and 190.39.

FT-IR (CCl4, cm^{-1}): 778.2, 981.6, 1049.7, 1166.8, 11.87.4, 1190.6, 1238.8, 1294.1, 1344.6, 1487.9, 1566.2, 1613.0, 2976.1, and 3027.5 cm^{-1}.

GC-MS (m/z): 55.1(Base), 63.0, 80.0, 91.0, 108.0, 119.0, 136.0, 147.0, 164.0, 177.0, 190.1 and 218.1 ($M^{+\bullet}$).

Anal: Calcd: C(%), 71.54; H(%), 6.47. Found: C(%), 70.96; H(%), 6.40.

4.4 General Procedures

Small Scale irradiations were carried out using about 0.2 mg of reactant in 0.75 mL of deuterated acetonitrile or acetone in an NMR tube. The NMR tubes were sealed by a rubber stopper with Teflon tape over it. A long needle was inserted through the stopper for inflowing gas and a short needle for a vent. The sample solutions were degassed by bubbling with argon gas for 20 min. The irradiation sources included a medium pressure mercury arc lamp and a Rayonet reactor. The light from the source was filtered through a Pyrex or 313 nm filter solution. Samples for irradiation with 254 nm were placed in 5 mL quartz tubes.

Large scale irradiation were done using 0.1-0.2 g of reactants in degassed solvent such as acetonitrile and acetone in a 13 x 100 mm Pyrex culture tubes. The samples were degassed by argon-bubbling for 30 min. The photoreactions were monitored by HPLC and NMR. The ratios of isomers were measured by NMR analysis. The photoproducts were isolated by preparative TLC or HPLC. HPLC was operated with a Rainin column (Si-80-125-C5) at the flow rate of 0.8 ml/min.

Thermal chemistry of photoproducts (**CB**) was examined using 0.1-0.2 mg of photoproducts in 0.75 mL of deuterated methanol.

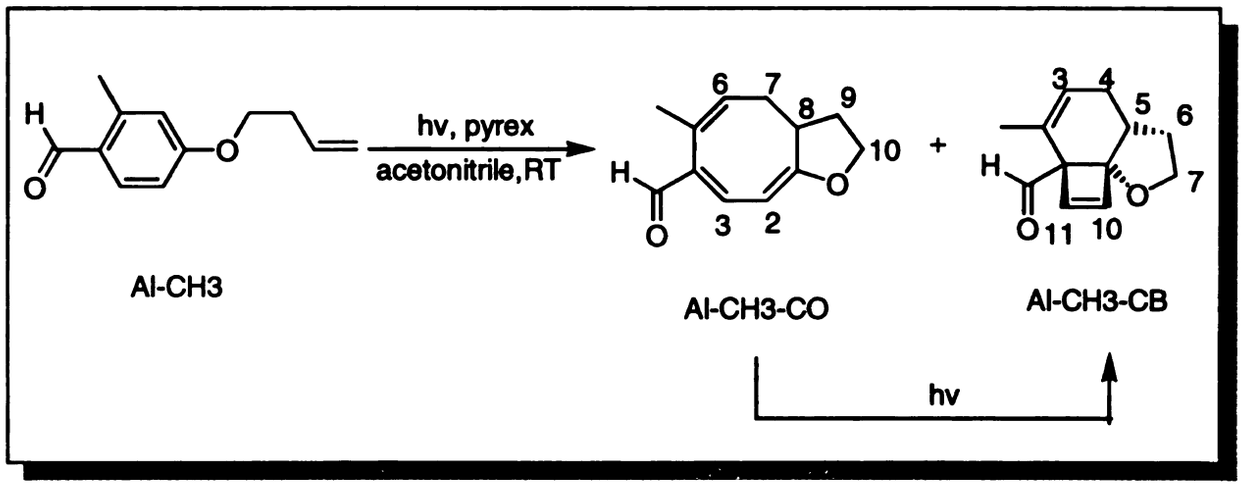
Cyclooctatrienes (**CO**) were irradiated to confirm the formation of corresponding photoproducts (**CB**).

4.5. Identification of Photoproducts

4.5.1. Photolysis of 4-(3-buten-1-oxy)-2-methylbenzaldehyde

In an NMR tube, 4-(3-buten-1-oxy)-2-methylbenzaldehyde (1.9 mg, 0.01 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.3 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^{1}H NMR and HPLC. After three hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts.

Large scale photolysis was carried out to isolate the photoproducts. 4-(3-Buten-1-oxy)-2-methylbenzaldehyde (150 mg, 0.79 mmol) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium pressure mercury arc lamp through a Pyrex filter. The reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20) followed by HPLC isolation (hexane:ethyl acetate, 80:20). **Al-CH3-COt** (11 mg, 7.3% yield) was collected at 3.5 minutes but **Al-CH3-CBt** could not be isolated due to its thermal instability.



a. 4-Formyl-5-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-CH3-COt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.87 (s, 3H), 1.88-2.08 (m, $2H_9$), 2.153 (ddd, J = 13.2, 7.5 and 6 Hz, $1H_7$), 2.51 (ddd, J = 13.2, 8.2 and 4.4 Hz, $1H_7$), 3.05 (m, $1H_8$), 4.04 (ddd, J = 11, 8.8 and 6 Hz, $1H_{10}$), 4.24 (m, $1H_{10}$), 5.40 (dd, J = 6.6 and 2.2 Hz, $1H_2$), 5.93 (qdd, J = 8.2, 7.5 and 1.6 Hz, $1H_6$), 6.77 (dd, J = 6.6 and 1.1 Hz, $1H_3$), 9.39 (s, $1H_{aldehyde}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 22.2, 27.8, 32.0, 44.1, 69.7, 95.8, 130.1, 134.7, 139.9, 149.0, 169.5 and 194.4.

GC-MS (m/z): 55.0(Base), 64.9, 77.0, 91.0, 104.9, 121.0, 134.9, 148.9, 162.1, 175.0 and 190.1($M^{+\bullet}$).

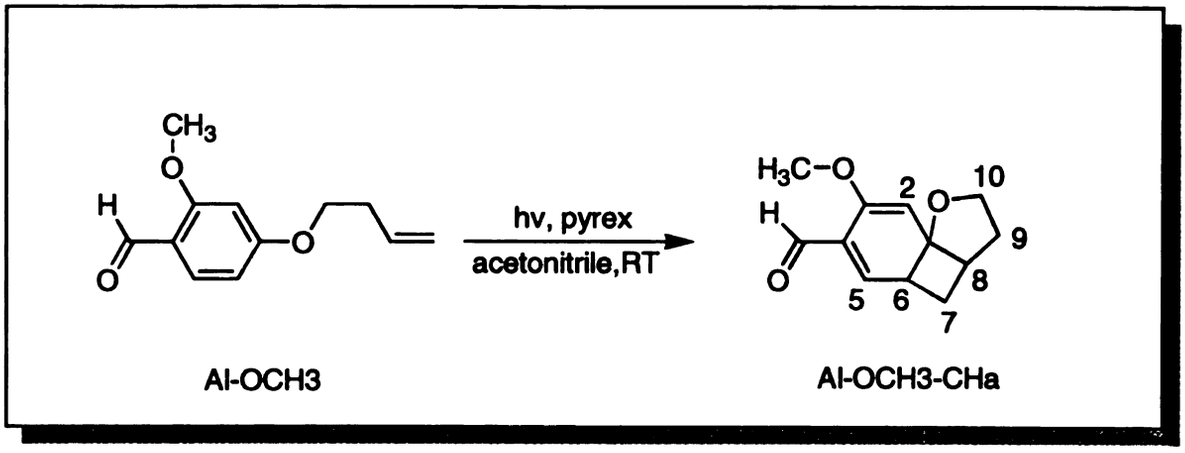
b. 1-Formyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (Al-CH3-CBt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): selected signals: 5.62 (m, $1H_3$), 6.37 (d, J = 3Hz, $1H_{11}$), 6.42 (d, J = 3Hz, $1H_{10}$), 9.40 (s, $1H_{aldehyde}$).

4.5.2. Photolysis of 4-(3-buten-1-oxy)-2-methoxybenzaldehyde

In an NMR tube, 4-(3-buten-1-oxy)-2-methoxybenzaldehyde (2.2 mg, 0.011 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.41 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^1H NMR and HPLC. After four hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts.

Large scale photolysis was carried out to isolate the photoproducts. 4-(3-buten-1-oxy)-2-methoxybenzaldehyde (135 mg, 0.66 mmol) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium pressure mercury arc lamp through a Pyrex filter. The reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20). One major product was identified by NMR analysis as 3-formyl-4-methoxy-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene **(Al-CH3O-CHa)** (15 mg, 11.1% yield).

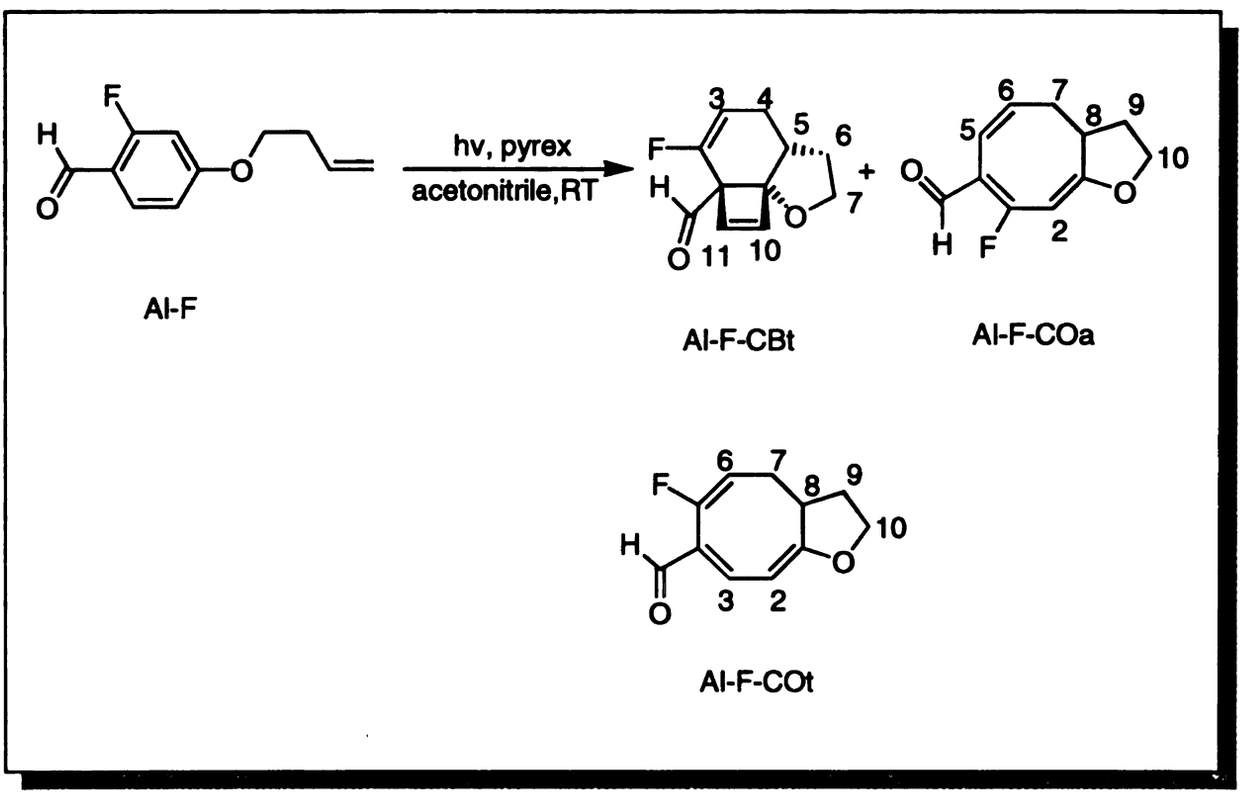


3-Formyl-4-methoxy-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene (Al-CH3O-CHa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.96 (tdd, J = 16.11, 7.81 and 7.32 Hz, $2H_9$), 2.17 (dddd, J = 17.09, 5.37, 2.44, and 1.95 Hz, $1H_7$), 2.42 (m, $1H_8$), 2.70 (dd, J = 17.09 and 2.44 Hz, $1H_{7'}$), 3.37 (br d, J = 4.9, $1H_6$), 3.64 (s, $3H_{Me}$), 3.82 (m, $2H_{10}$), 4.66 (s, $1H_2$), 6.78 (dd, J = 5.37 and 2.93 Hz, $1H_5$) and 9.47 (s, $1H_{aldehyde}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 21.27, 28.96, 36.92, 52.02, 56.96, 65.48, 82.40, 96.81, 139.65, 147.63, 156.41, 193.49.

4.5.3. Photolysis of 4-(3-buten-1-oxy)-2-fluorobenzaldehyde



In a NMR tube, 4-(3-buten-1-oxy)-2-fluorobenzaldehyde (2.1 mg, 0.011 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.44 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of two major photoproducts among several products in 2:1 ratio and one of them was thermally unstable.

Large scale photolysis was carried out to isolate the photoproducts. 4-(3-buten-1-oxy)-2-fluorobenzaldehyde (160 mg, 0.82 mmol) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium pressure mercury

arc lamp through a Pyrex filter. The reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20) followed by HPLC (hexane:ethyl acetate, 80:20). Two major products were identified by NMR analysis as 4-formyl-3-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**Al-F-COa**) (4 mg, 2.5% yield) and 4-formyl-2-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**Al-F-COt**) (10.7 mg, 6.7% yield) in 1:2.68. **Al-F-COt** was collected at 6.5 minutes and **Al-F-COa** was collected at 9.5 minutes from HPLC. One of the products in NMR scale reaction turned out to be **Al-F-COt**.

a. 4-Formyl-3-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-F-COa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.87 (dddd, J = 12.08, 10.99, 7.69 and 6.59 Hz, $1H_9$), 2.25 (dddd, J = 12.08, 11.54, 8.24 and 7.69 Hz, $1H_{9'}$), 2.43 (dd, J = 11.74 and 5.49 Hz, $2H_7$), 3.32 (m, $1H_8$), 4.35 (ddd, J = 8.79, 8.24 and 7.69 Hz, $2H_{10}$), 5.40 (d, J = 10.44 Hz, $1H_2$), 5.89 (dt, J = 12.64 and 5.49 Hz, $1H_6$) and 6.15 (dd, J=12.64 and 4.4 Hz, $1H_5$) and 10.09 (s, $1H_{aldehyde}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 19.40, 33.65, 67.09, 73.27, 112.05, 116.5(d), 127.89, 134.45, 137.70, 160.50(d), 206.60.

GC-MS (m/z): 55.1(Base), 77.0, 83.0, 97.0, 109.0, 115.0, 138.0 165.1, 179.0 and 194.1 ($M^{+\bullet}$).

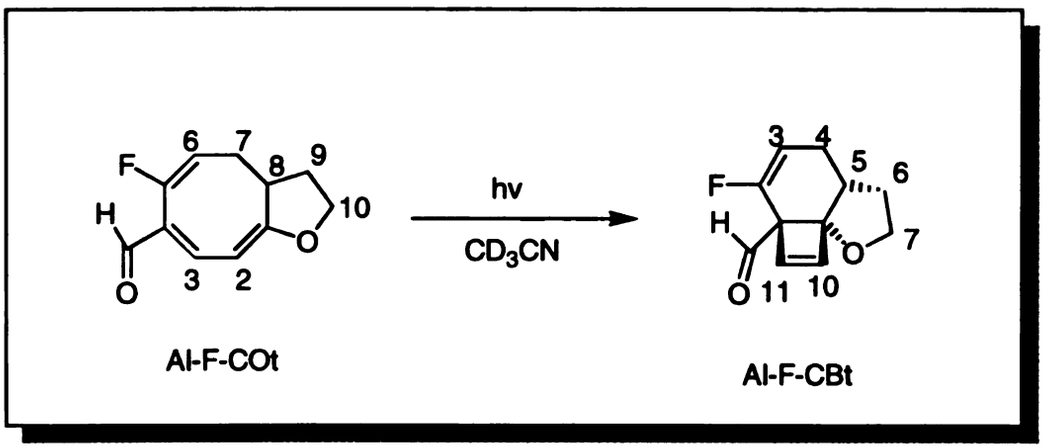
b. 4-Formyl-2-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-F-COt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.86 (d quartet, J = 13.19 and 6.59 Hz, $1H_9$), 2.20 (d quartet, J = 14.28 and 7.14 Hz, $1H_{9'}$), 2.31 (dtd, J = 15.93, 9.34 and 7.14 Hz, $1H_7$), 2.53 (d quartet, J = 15.9 and 3.3 Hz, $1H_7$), 3.05 (m, $1H_8$), 4.23 (dt, J = 8.79 and 7.14 Hz, $1H_{10}$), 4.33 (dt, J = 8.79 and 6.59 Hz, $1H_{10'}$), 5.57 (d, J = 6.59 Hz, $1H_2$), 5.76 (dt, J = 23.07 and 6.59 Hz, $1H_6$) and 7.08 (d, J = 7.14 Hz, $1H_3$) and 9.46 (s, $1H_{aldehyde}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 27.99(d), 31.23, 41.38, 70.02, 96.37, 111.36(d), 128.35(d), 148.63(d), 154.99, 173.19 and 191.23.

GC-MS (m/z): 55.1(Base), 77.0, 83.0, 97.0, 109.0, 115.0, 138.0, 151.0, 166.0 and 194.1 ($M^{+\bullet}$).

4.5.3.1. Irradiation of 4-formyl-2-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-F-COt).

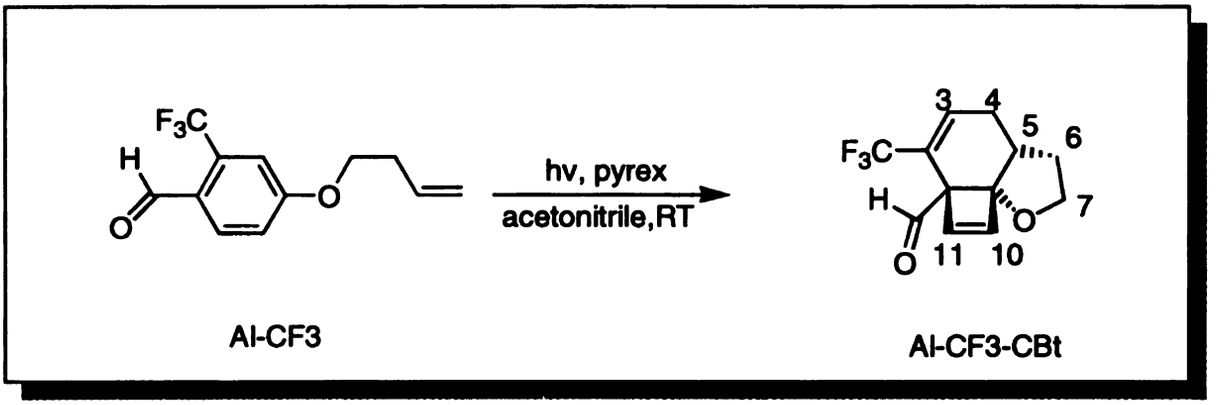


In an NMR tube, 4-formyl-2-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-F-COt) (2.0 mg, 0.01 mmol) was dissolved in deuterated acetonitrile (0.75 mL). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^1H NMR and HPLC. NMR analysis of the reaction mixture showed the presence 1-formyl-2-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**Al-F-CBt**).

1-Formyl-2-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (Al-F-CBt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.89 (H_6), 2.01 (H_4), 2.15 (H_6), 2.25 (H_5), 2.38 (H_4), 3.81 (t, J = 5.49, $2H_7$), 5.44 (ddd, J = 15.93, 6.04 and 3.85 Hz, $1H_3$), 6.39 (d, J = 2.75 Hz, $1H_{11}$), 6.45 (t, J = 2.75 Hz, $1H_{10}$).

4.5.4. Photolysis of 4-(3-Buten-1-oxy)-2-trifluoromethylbenzaldehyde



In an NMR tube, 4-(3-buten-1-oxy)-2-trifluoromethylbenzaldehyde (2.0 mg, 0.0082 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.1 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of one major photoproduct among several products after 2 hours of irradiation. After overnight at room temperature, the initial product converted to another product, which absorbs UV light at 317 nm.

Large scale photolysis was carried out to isolated the photoproducts. 4-(3-Buten-1-oxy)-2-trifluoromethylbenzaldehyde (50 mg, 0.20 mmol) was dissolved in freshly distilled acetonitrile (15 mL) and irradiated in an immersion well with a medium pressure

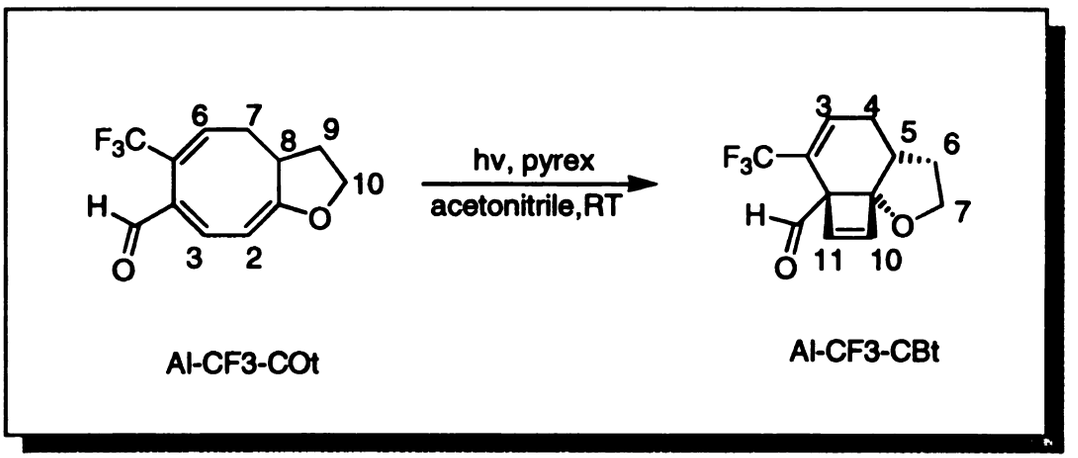
mercury arc lamp through a Pyrex filter. The reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20) followed by HPLC (hexane:ethyl acetate, 80:20). The products were collected at 13 minute from HPLC and identified by NMR analysis as 4-formyl-2-trifluoromethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene **(Al-CF3-COt)** (4 mg, 8% yield).

4-Formyl-2-trifluoromethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-CF3-COt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.04 (qd, J = 10.44 and 8.24 Hz, $1H_9$), 2.19 (ddd, J = 7.14, 6.49 and 6.04 Hz, $1H_{7'}$), 2.42 (ddd, J = 7.14, 6.59 and 6.04 Hz, $1H_7$), 2.69 (m, $1H_{9'}$), 3.15 (m, $1H_8$), 4.13 (ddd, J = 8.79, 5.49 and 4.94 Hz, $1H_{10}$), 4.34 (ddd, J = 8.79, 8.24 and 1.65 Hz, $1H_{10'}$), 5.52 (d, J = 6.3 Hz, $1H_2$), 6.90 (dd, J=7.14 and 7.69 Hz, $1H_6$), 7.14 (d, J = 6.3 Hz, $1H_3$) and 9.53 (s, $1H_{aldehyde}$).

UV: 317 nm.

4.5.4.1. Photochemistry of 4-formyl-2-trifluoromethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (Al-CF3-COt)



Al-CF3-COt

Al-CF3-CBt

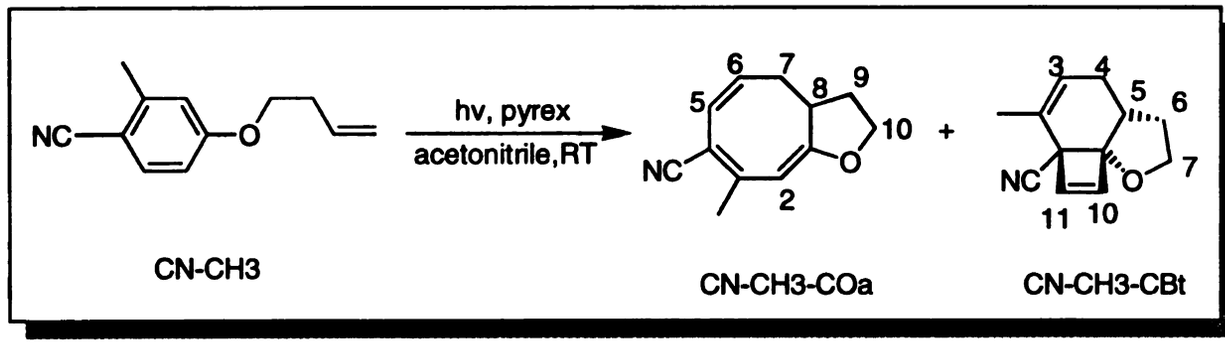
In an NMR tube, Al-CF3-COt (2.0 mg, 0.0082 mmol) was dissolved in deuterated acetonitrile (0.75 mL). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of 1-formyl-2-trifluoromethyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**Al-CF3-CBt**). The thermally unstable photoproduct in the NMR scale reaction of **Al-CF3** was found to be **Al-CF3-CBt**.

1-Formyl-2-trifluoromethyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (Al-CF3-CBt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): selected signals: 4.24 (t, J = 6.59 Hz, $2H_7$), 6.43 (d, J = 2.75 Hz, $1H_{11}$), 6.51 (d, J = 2.75 Hz, $1H_{10}$), 6.82 (m, $1H_3$) and 9.45 (s, $1H_{aldehyde}$).

4.5.5. Photolysis of 4-(3-buten-1-oxy)-2-methylbenzonitrile

In an NMR tube, 4-(3-buten-1-oxy)-2-methylbenzonitrile (2.0 mg) was dissolved in deuterated acetonitrile (0.75 mL, 1.43 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts after 14 days of irradiation.



4-(3-Buten-1-oxy)-2-methylbenzonitrile (2.0 mg, 0.0053 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.43 x 10^{-2} M) inside a quartz test tube. The sample was purged with argon for 20 minutes and then irradiated using a Rayonet reactor with 254 nm light bulbs. Reaction progress was monitored by time resolved ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts on the complete depletion of reactant after 18 hours of irradiation.

In an NMR tube, 4-(3-buten-1-oxy)-2-methylbenzonitrile (2.0 mg, 0.0053 mmol) was dissolved in deuterated acetone (0.75 mL, 1.43 x 10^{-2} M). The sample was purged

with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a 313 nm filter solution. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts after 24 hours of irradiation. Large scale photolysis was carried out to isolate the photoproducts. 4-(3-Buten-1-oxy)-2-methylbenzonitrile (183 mg) was dissolved in freshly distilled acetone (50 mL) and irradiated with a medium pressure mercury arc lamp through a 313 nm filter solution. The reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using HPLC (hexane:ethyl acetate, 80:20). Two major products were collected at 8 minutes and 3 minutes from HPLC and identified by NMR analysis as 4-cyano-3-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-CH3-COa**) (9 mg, 5% yield) and 1-cyano-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-CH3-CBt**) (2 mg, 1% yield), respectively. The **CN-CH3-COa/CN-CH3-CBt** ratios were measured by NMR analysis to be 1:2, 5:1 and 3:1 with the light source of >300 nm, 254nm, and 313 nm, respectively.

a. 4-Cyano-3-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (CN-CH3-COa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.80 (dddd, J = 12.09, 9.34, 6.59 and 6.04 Hz, $1H_9$), 2.17 (s, 3H), 2.33 (dddd, J = 12.09, 11.54, 10.44 and 8.24 Hz, $1H_9$), 2.39 (dddd, J = 9.89, 9.34, 4.4 and 1.65 Hz, $1H_7$), 2.45 (dddd, J = 9.34, 9.0, 4.4 and 1.65 Hz, $1H_7$), 3.20 (m, $1H_8$), 4.18 (ddd, J = 8.79, 8.24 and 3.3 Hz, $1H_{10'}$), 4.29 (ddd, J = 8.79, 6.59 and 6.04 Hz, $1H_{10}$), 5.25 (s, $1H_2$), 5.77 (br d, J=13 Hz, $1H_5$), 6.77 (dt, J=13 and 4.4 Hz, $1H_6$).

UV: 310 nm.

b. 1-Cyano-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (CN-CH3-CBt)

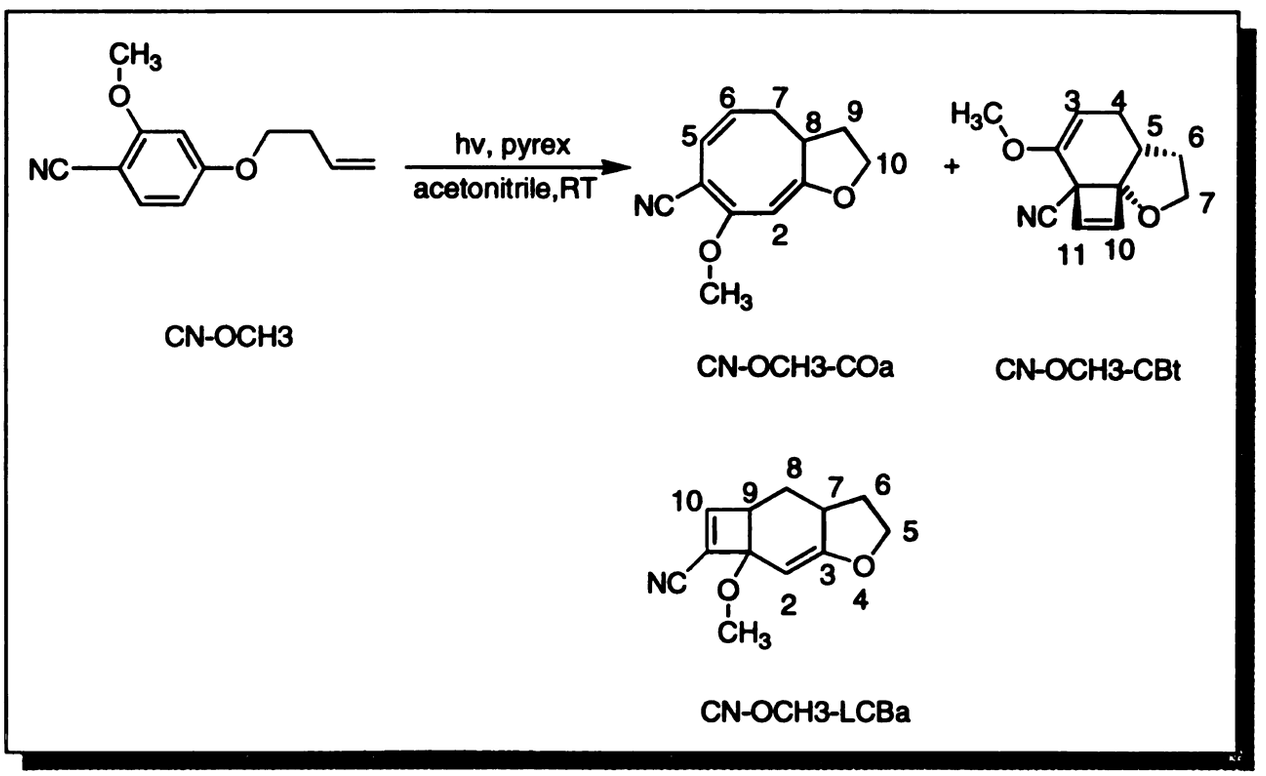
1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.89 (dtd, J = 12.64, 6.04 and 1.65 Hz, $1H_6$), 1.95 (d, J = 1.65 Hz, $3H_{methyl}$), 2.09 (ddd, J = 15.9, 5.1, and 4.3 Hz, $1H_4$), 2.16 (dddd, J = 12.64, 7.69, 6.04 and 1.65 Hz, $1H_6$), 2.21 (m, $1H_5$), 2.30 (m, $1H_4$), 3.81 (ddd, J = 8.24 Hz, 7.14 Hz, $1H_7$), 3.93 (ddd, J = 8.24 Hz, 3.29 Hz, $1H_7$), 5.48 (t quartet, J = 6.04 Hz and 1.65 Hz, $1H_3$), 6.17 (d, J = 2.8Hz, $1H_{11}$), 6.77 (d, J = 2.8 Hz, $1H_{10}$).

4.5.6. Photolysis of 4-(3-buten-1-oxy)-2-methoxylbenzonitrile

4-(3-Buten-1-oxy)-2-methoxybenzonitrile (2.7 mg, 0.013 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.8 x 10^{-2} M). The sample in a quartz test tube was purged with argon for 20 minutes and then irradiated using a Rayonet reactor with 254 nm lamps. Reaction progress was monitored by ^1H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts on the complete depletion of reactant after 18 hours of irradiation.

In an NMR tube, 4-(3-buten-1-oxy)-2-methoxybenzonitrile (2.7 mg, 0.013 mmol) was dissolved in deuterated acetone (0.75 mL, 1.8 x 10^{-2} M). The sample was purged

with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a 313 nm filter solution. Reaction progress was monitored by time resolved ^1H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts after 30 hours of irradiation.



In an NMR tube, 4-(3-buten-1-oxy)-2-methoxybenzonitrile (2.7 mg) was dissolved in deuterated acetonitrile (0.75 mL, 1.8 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^1H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts after 20 hours of irradiation. Large scale photolysis was carried out to isolate the photoproducts. 4-(3-Buten-1-oxy)-2-methoxybenzonitrile (177 mg) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium

pressure mercury arc lamp through Pyrex filter sleeve. After 28 hours, the reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20) and HPLC (hexane:ethyl acetate, 80:20). The reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20) and HPLC (hexane:ethyl acetate, 80:20). Two products came out at 9 minutes from HPLC. One photoproduct was isolated and identified as 4-cyano-3-methoxy-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-OCH3-COa**) (9 mg, 5%) while the other photoproduct at 9 minutes in the mixture with **CN-OCH3-COa** was identified as 11-cyano-1-methoxy-4-oxatricyclo[7.2.0.$0^{3,7}$]undeca-2,10-diene (**CN-OCH3-LCBa**). Another photoproduct collected at 6 minutes from HPLC was not stable thermally and identified as 1-cyano-2-methoxy-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,10-diene (**CN-OCH3-CBt**). The ratios of **CN-OCH3-COa**: **CN-OCH3-CBt**: **CN-OCH3-LCBa** were measured by NMR analysis to be 8:2:1 and 10:1:1 with the light source of 254 nm and 313 nm, respectively.

a. 4-Cyano-3-methoxy-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (CN-OCH3-COa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.88 (ddt, J = 12.64, 6.59 and 6.04 Hz, $1H_9$), 2.24 (m, $1H_9$), 2.38 (dddd, J = 10.44, 5.49, 4.94, and 4.40 Hz, $1H_7$), 2.51 (dtd, J=17.58, 4.4 and 1.65 Hz, $1H_7$), 3.43 (m, $1H_8$), 3.77 (s, $3H_{Me}$), 4.31 (ddd, J=8.79, 8.24 and 3.85 Hz,

$1H_{10}$), 4.39 (ddd, J=9.34, 8.79 and 6.04 Hz, $1H_{10}$), 5.32 (s, $1H_2$), 5.75 (dt, J=12.09 and 4.40 Hz, $1H_6$), 5.83 (br d, J=12.64, $1H_5$).

UV: 297 nm

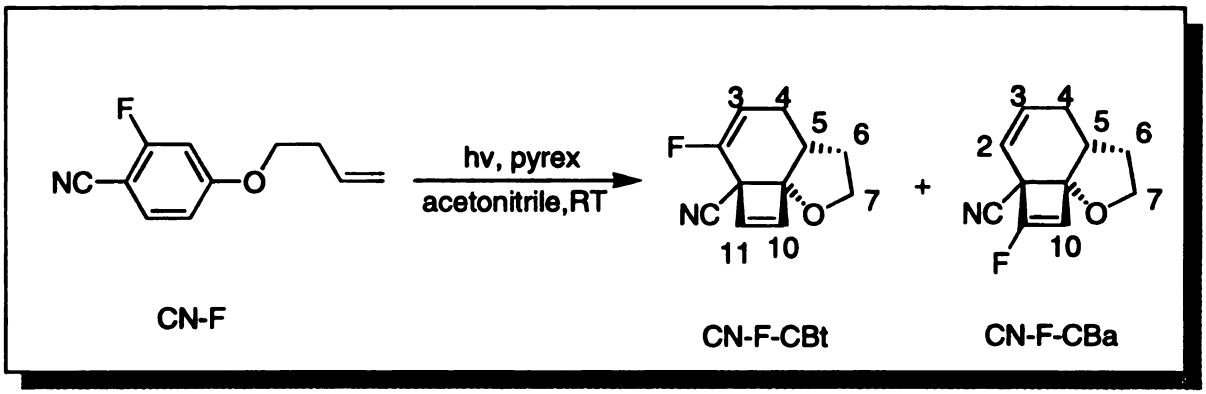
b. 1-Cyano-2-methoxy-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (CN-OCH3-CBt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): selected signals: 3.60 (s, $3H_{methyl}$), 3.98 (ddd, $1H_7$), 4.15 (ddd, $1H_{7'}$), 4.65 (dd, J = 6.59 and 2.75 Hz, $1H_3$), 6.18 (d, J = 2.75 Hz, $1H_{11}$), 6.29 (d, J = 2.75 Hz, $1H_{10}$).

c. 11-Cyano-1-methoxy-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (CN-OCH3-LCBa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): selected signals: 4.92 (s, $1H_2$) and 6.9 (d, J=1.0, $1H_{10}$).

4.5.7. Photolysis of 4-(3-buten-1-oxy)-2-fluorobenzonitrile



In an NMR tube, 4-(3-buten-1-oxy)-2-fluorobenzonitrile (2.0 mg, 0.01 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.39 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts after 14 days of irradiation.

In an NMR tube, 4-(3-buten-1-oxy)-2-fluorobenzonitrile (2.0 mg, 0.01 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.39 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a 313 nm filter solution. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts after 24 hours of irradiation. Large scale photolysis was carried out to isolate the photoproducts. 4-(3-Buten-1-oxy)-2-fluorobenzonitrile (166 mg, 0.87 mmol)

was dissolved in freshly distilled acetone (50 mL) and irradiated with a medium pressure mercury arc lamp through a 313 nm filter solution. The reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20) and HPLC (hexane:ethyl acetate, 80:20) after 48 hours of irradiation. One photoproduct was collected at 9.5 minute using HPLC and identified as 1-cyano-2-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-F-CBt**) (25.1 mg, 15%). Another photoproduct was collected at 5.5 minutes from HPLC and identified as 1-cyano-11-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-F-CBa**) (14.2 mg, 8.6%).

The ratios of **CN-F-CBt**: **CN-F-CBa** were measured by NMR analysis to be 1.6:1 and 1:1.8 ratio with the light sources of >300 nm and 313 nm, respectively.

a. 1-Cyano-2-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (CN-F-CBt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.96 (ddd, J = 11.54, 8.24 and 3.85 Hz, $2H_6$), 2.22 (dddd, J = 15.38, 9.89, 6.04 and 3.30 Hz, $1H_4$), 2.28 (dddd, J = 15.38, 8.79, 6.04 and 3.85 Hz, $1H_4$), 2.44 (m, $1H_5$), 3.97 (ddd, J = 9.34, 8.24 and 7.69 Hz, $1H_7$), 4.18 (ddd, J = 9.34, 8.24 and 3.30 Hz, $1H_7$), 5.33 (ddd, J=14.28, 7.14 and 2.75 Hz, $1H_3$), 6.25 (d, J = 2.75 Hz, $1H_{11}$) and 6.33 (t, J = 2.75 Hz, $1H_{10}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 22.10(d), 28.39, 38.65, 51.68, 61.24, 67.66, 102.28(d), 107.5, 135.17, 141.39 and 148.08.

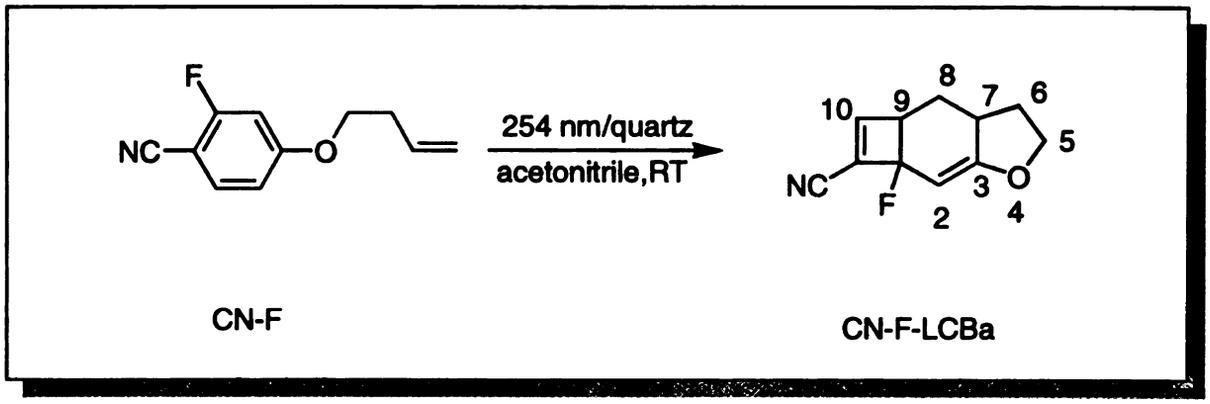
GC-MS (m/z): 39, 41, 51, 55(Base), 63, 69, 75, 83, 89, 95, 107, 115, 122, 135, 140, 162, 172 and 191($M^{+\bullet}$).

b. 1-Cyano-11-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (CN-F-CBa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.93 (ddd, J = 12.09, 9.34 and 2.20 Hz, $1H_6$), 2.00 (ddd, J = 12.09, 4.40 and 3.85 Hz, $1H_6$), 2.24 (ddd, J = 18.13, 6.04 and 2.75 Hz, $1H_4$), 2.38 (ddd, J = 18.13, 6.59 and 2.20 Hz, $1H_4$), 2.51 (m, $1H_5$), 3.95 (ddd, J = 8.79, 8.24 and 7.14 Hz, $1H_7$), 4.18 (ddd, J = 9.34, 8.24 and 3.30 Hz, $1H_7$), 5.11 (d, J = 8.79 Hz, $1H_{10}$), 5.72 (dd, J = 9.89 Hz and 2.75Hz, $1H_2$) and 5.93 (ddd, J = 9.89, 6.59 and 2.2 Hz, $1H_3$).

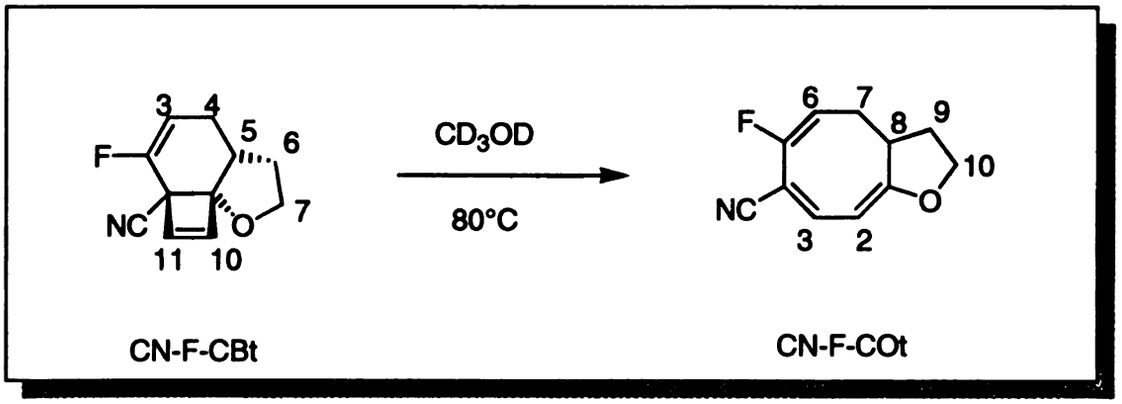
13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 24.18, 27.97, 37.28, 37.39, 66.76, 77.13, 107.46, 107.54, 120.13(d), 129.20 and 150.59(d).

GC-MS (m/z): 39.1, 55.1(Base), 63.0, 75.0, 83, 95.0, 109.0, 122.0, 135.0, 148.0, 164.0, 172.0 and 191($M^{+\bullet}$).



4-(3-Buten-1-oxy)-2-fluorobenzonitrile (8.0 mg, 0.042 mmol) was dissolved in deuterated acetonitrile (3.0 mL, 1.39 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated by a Rayonet reactor with 254 nm lamps. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts on the complete depletion of reactant after 30 hours of irradiation. One product in the mixture was identified as 11-cyano-1-fluoro-4-oxatricyclo[7.2.0.$0^{3,7}$]undeca-2,10-diene (**CN-F-LCBa**).

4.5.7.1. Thermal chemistry of 1-cyano-2-fluoro-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,10-diene (CN-F-CBt)



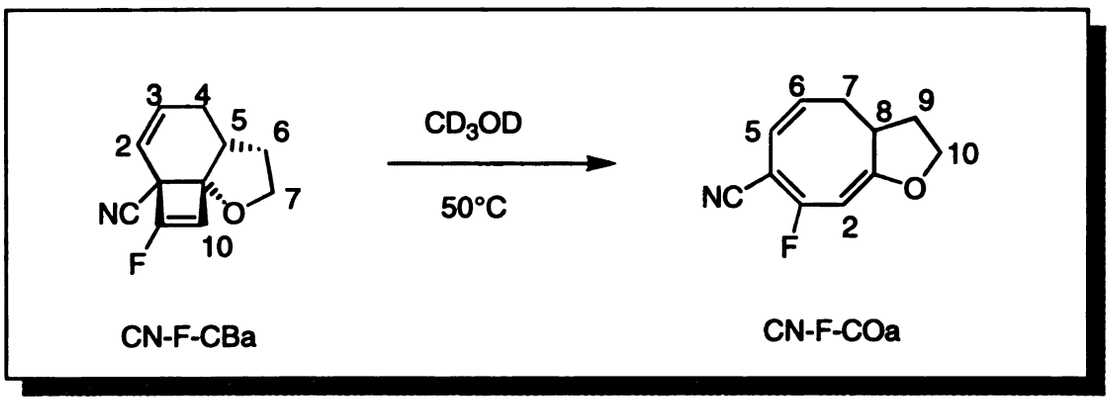
1-Cyano-2-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-F-CBt**) (1.1 mg, 0.0058 mmol) in deuterated methanol (1 mL) was heated at 50 °C in the silicone oil bath for 12 hours. The reaction was monitored by NMR and HPLC. The ring opening product was identified as 4-cyano-5-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-F-COt**).

4-Cyano-5-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (CN-F-COt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.85 (dddd, J = 19.04, 7.32, 6.84 and 5.37 Hz, $1H_9$), 2.23(dtd, J = 20.02, 7.81 and 4.40 Hz, $1H_9$), 2.43 (ddd, J = 16.6, 10.74, 5.86 and 2.93 Hz, $1H_7$), 2.55 (dddd, J = 16.6, 6.35, 5.86 and 2.93 Hz, $1H_7$), 3.07 (m, $1H_8$), 4.26 (ddd, J = 8.79, 7.81 and 4.88 Hz, $1H_{10}$), 4.30 (ddd, J = 8.79, 7.81 and 6.86 Hz, $1H_{10}$), 5.40 (d, J = 7.32 Hz, $1H_2$), 5.70 (dt, J = 23.93 and 5.86 Hz, $1H_6$), 6.86 (d, J = 7.32 Hz, $1H_3$).

UV: 320 nm.

4.5.7.2. Thermal chemistry of 1-cyano-11-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (CN-F-CBa)



1-Cyano-11-fluoro-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-F-CBa**) (2.2 mg, 0.012 mmol) in deuterated methanol (1 mL) was heated at 50 °C in the silicone oil bath for 24 hours. The reaction was monitored by NMR and HPLC. The ring opening product was identified as 4-cyano-3-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-F-COa**).

4-Cyano-3-fluoro-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (CN-F-COa)

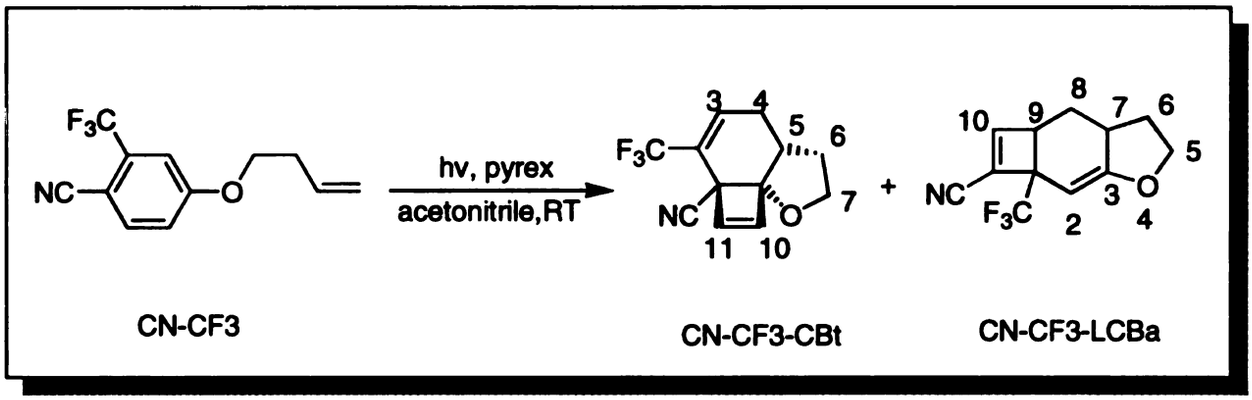
1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.91 (dddd, J = 12.09, 12.64, 4.94 and 4.39 Hz, $1H_9$), 2.28 (dddd, J = 12.09, 8.24, 7.69 and 4.39 Hz, $1H_9$), 2.47 (ddt, J = 10.44, 6.04 and 1.65 Hz, $1H_7$), 2.55 (dtd, J = 15.93, 3.86 and 1.65 Hz, $1H_7$), 3.35 (m, $1H_8$), 4.32 (ddd, J =

8.79, 7.69 and 4.39 Hz, $1H_{10}$), 4.41 (td, J = 8.79 and 6.59 Hz, $1H_{10'}$), 5.31 (d, J = 9.34 Hz, $1H_2$), 5.76 (dd, J = 12.64 and 4.94 Hz, $1H_5$) and 5.98 (dt, J = 12.64 and 5.49 Hz, $1H_6$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 30.88, 31.12, 40.08, 70.59, 89.61, 90.11, 103.92, 120.45 and 132.07.

UV: 298 nm

4.5.8. Photolysis of 4-(3-buten-1-oxy)-2-trifluoromethylbenzonitrile



In an NMR tube, 4-(3-buten-1-oxy)-2-trifluorofluoromethylbenzonitrile (2.1 mg, 0.0087 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.16×10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^1H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts after 36 hours of irradiation.

4-(3-Buten-1-oxy)-2-trifluoromethylbenzonitrile (8.4 mg, 0.035 mmol) was dissolved in deuterated acetonitrile (3.0 mL, 1.16 x 10^{-2} M). The sample was purged with argon for 15 min and then irradiated by a Rayonet reactor with 254 nm lamps. Reaction progress was monitored by ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts on the complete depletion of reactant after 12 hours of irradiation.

In an NMR tube, 4-(3-buten-1-oxy)-2-trifluoromethylbenzonitrile (2.0 mg, 0.0083 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.5 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated through a 313 nm filter solution. Reaction progress was monitored by time resolved ^{1}H NMR and HPLC. NMR analysis of the reaction mixture showed the presence of several photoproducts after 22 hours of irradiation.

Large scale photolysis was carried out to isolate the photoproducts. 4-(3-buten-1-oxy)-2-trifluoromethylbenzonitrile (148 mg, 0.61 mmol) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated through a 313 nm filter solution. The reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using preparative TLC HPLC (hexane:ethyl acetate, 80:20) and HPLC (hexane:ethyl acetate, 80:20) after 24 hours of irradiation.

One photoproduct was collected at 11 minutes using HPLC and identified as 1-cyano-2-trifluoromethyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-CF3-CBt**) (8 mg, 5.4%). Another photoproduct was collected at 7 minutes from HPLC and identified as 11-cyano-1-trifluoromethyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (**CN-CF3-LCBa**) (6 mg, 4%).

The ratios of **CN-CF3-CBt**: **CN-CF3-LCBa** were measured by NMR analysis to be 1:10, 1:10 and 1:1 ratio with the light sources of >300 nm, 254 nm and 313 nm, respectively.

a. 1-Cyano-2-trifluoromethyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (CN-CF3-CBt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.85 (ddd, J = 9.89, 9.34 and 7.14 Hz, $1H_6$), 2.06 (ddd, J = 14.28, 7.14, and 3.85 Hz, $1H_4$), 2.34 (ddd, J = 9.89, 6.59 and 3.30 Hz, $1H_6$), 2.49 (m, $1H_5$), 2.53 (ddd, J = 15.38, 8.79, and 3.85 Hz, $1H_4$), 4.02 (ddd, J = 8.79 and 3.85 Hz, $1H_7$), 4.19 (ddd, J = 8.79, 8.24 and 7.69 Hz, $1H_7$), 6.22 (d, J = 2.75 Hz, $1H_{11}$), 6.31 (d, J = 2.75 Hz, $1H_{10}$) and 6.51 (m, $1H_3$).

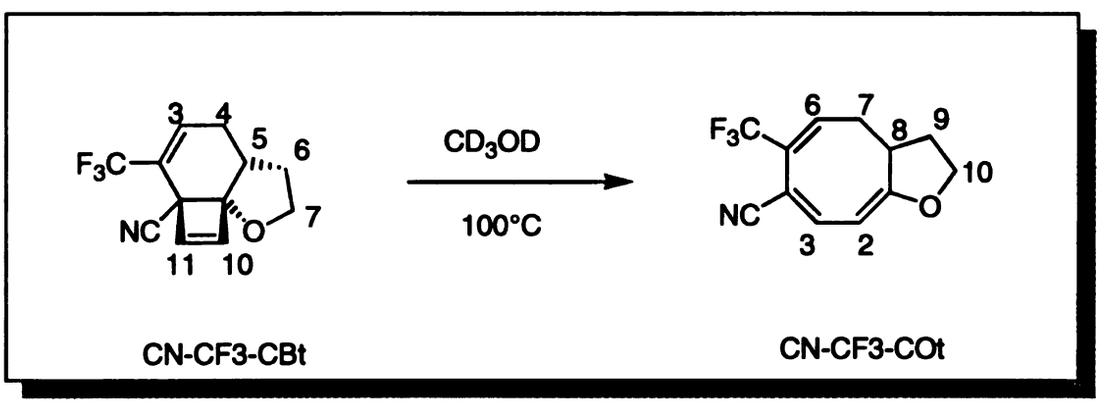
13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 24.57, 28.33, 37.64, 67.11, 89.59, 131.55(q), 136.35 and 140.54.

b. 11-Cyano-1-trifluoromethyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (CN-CF3-LCBa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.32 (m, J = 11.54 and 7.69 Hz, $1H_6$), 1.73 (dddd, J = 11.54, 8.79, 7.69 and 2.2 Hz, $1H_6$), 2.22 (ddd, J = 15.93, 6.59, and 1.65 Hz, $1H_8$), 2.27 (ddd, J = 15.93, 7.14 and 1.65 Hz, $1H_8$), 2.33 (m, H_7), 3.35 (dd, J = 5.49 and 1.65 Hz, $1H_9$), 4.03 (ddd, J = 8.79, 8.24 and 7.14 Hz, $1H_5$), 4.30 (ddd, J = 8.79 and 8.24 Hz, $1H_5$), 4.93 (d, H = 3 Hz, $1H_2$) and 6.94 (br s, $1H_{10}$).

UV: 267.

4.5.8.1. Thermal chemistry of 1-cyano-2-trifluoromethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene (CN-CF3-CBt)

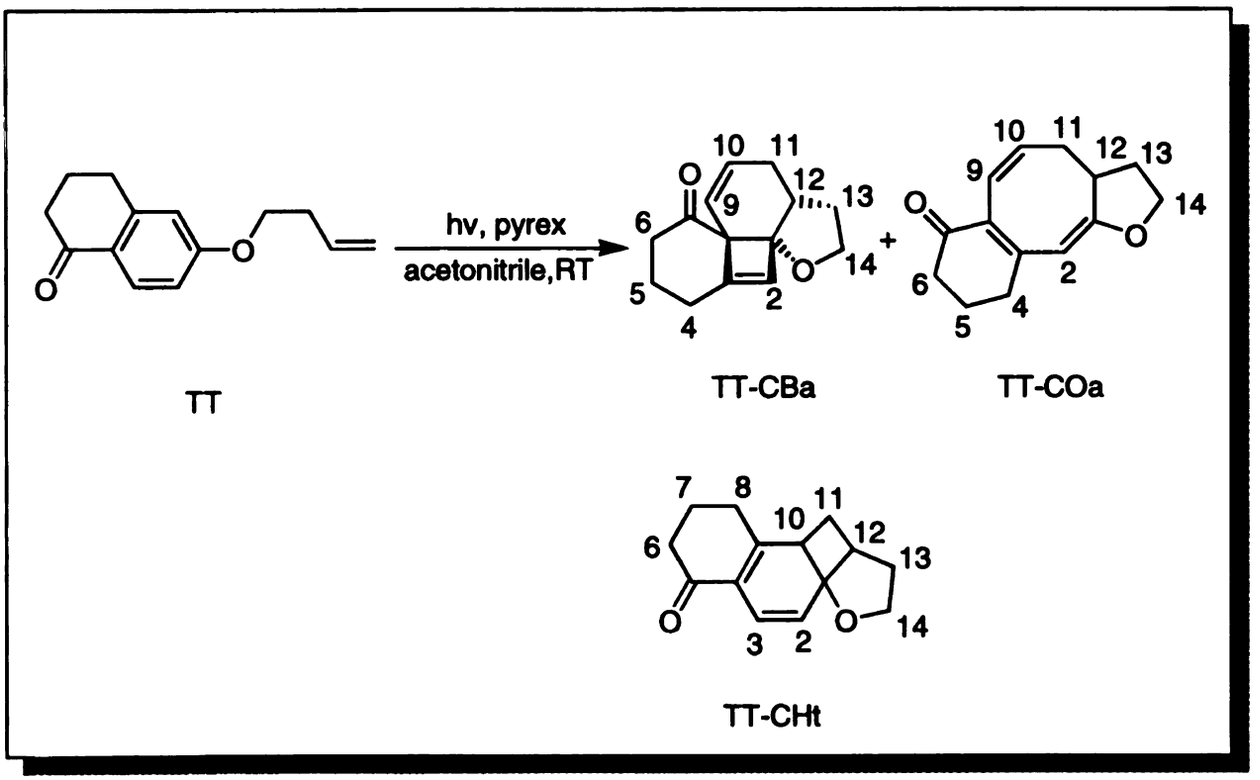


1-Cyano-2-trifluoromethyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,10-diene (**CN-CF3-CBt**) (2.4 mg, 0.01 mmol) in deuterated methanol (1 mL) was heated at 100 °C in the silicone oil bath for 24 hours. The reaction was monitored by NMR and HPLC. The ring opening product was identified as 4-cyano-5-trifluoromethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**CN-F-COa**).

4-Cyano-5-trifluoromethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (CN-CF3-COt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): seleted signals: 5.16 (d, J = 6.59 Hz, $1H_2$), 6.41 (t, J = 7.69 Hz, $1H_6$) and 6.54 (d, J = 6.59 Hz, $1H_3$).

4.5.9. 6-(3-Buten-1-oxy)-1-tetralone



In an NMR tube, 6-(3-Buten-1-oxy)-1-tetralone (2.1 mg, 0.01 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.29 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitered by time resolved ^{1}H NMR and HPLC. After 8 hours of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts.

Large scale photolysis was carried out to isolate the photoproducts. 6-(3-Buten-1-oxy)-1-tetralone (182 mg, 0.84 mmol) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium pressure mercury arc lamp through a Pyrex filter. The reaction progress was monitored by HPLC. The reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20) followed by HPLC (hexane:ethyl acetate, 80:20), after 8 hours of irradiation.

One photoproduct collected at 13 minutes from HPLC was identified as 15-oxa-tetracyclo[10, 3, 0, $0^{1,8}$, $0^{3,8}$]pentadeca-2,9-diene-7-one (**TT-CBa**) (13 mg, 7.1%). Another photoproduct collected at 10 minutes from HPLC was identified as 15-oxa-tricyclo[10, 3, 0, $0^{3,8}$]pentadeca-1, 3, 9-triene-7-one (**TT-COa**) (2 mg, 1.1%). The other photoproduct collected at 9 minutes from HPLC was identified as 15-oxa-tetracyclo[10, 3, 0, $0^{1,10}$, $0^{4,9}$]pentadeca-2, 4-diene-5-one (**TT-CHt**) (~1 mg).

Three products were identified as **TT-CBa, TT-COa, TT-CHt** in 10:2:1 ratio.

a. 15-Oxa-tetracyclo[10, 3, 0, $0^{1,8}$, $0^{3,8}$]pentadeca-2,9-diene-7-one (TT-CBa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.60 (dddd, J = 13.18, 9.77, 9.27 and 8.79 Hz, $1H_{13}$), 1.81 (m, J = 5.85 Hz, $2H_5$), 1.91 (dddd, J = 13.18, 9.77 and 8.79 Hz, $1H_{13}$), 1.92 (m, $1H_{12}$), 2.17 (ddd, J = 8.79, 6.35 and 5.86 Hz, $1H_4$), 2.23 (dddd, J = 8.79, 6.35, 5.86 and 2.1 Hz, $1H_4$), 2.36 (m, J = 6.9 and 1.8 Hz, $2H_{11}$), 2.48 (t, J = 5.86 Hz, $2H_6$), 4.04 (ddd, J = 15.63, 9.77 and 1.95 Hz, $1H_{14}$), 4.12 (ddd, J = 15.63, 8.79 and 1.95 Hz, $1H_{14'}$), 5.69 (dd, J = 9.9 and 2.4 Hz, $1H_9$), 5.83 (d, J = 2.1 Hz, $1H_2$) and 5.96 (ddd, J = 9.9, 6.9 and 1.8, $1H_{10}$).

13C-NMR ($CDCl_3$, 75 MHz, δ ppm): 23.80, 24.14, 26.16, 26.45, 33.07, 38.88, 39.78, 42.25, 68.04, 125.16, 127.39, 131.29, 155.45 and 208.01.

b. 15-Oxa-tricyclo[10, 3, 0, $0^{3,8}$]pentadeca-1, 3, 9-triene-7-one (TT-COa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.80 (J = 15.93, 9.89, 6.04 and 3.3 Hz, $1H_{13}$), 1.91 (J = 15.93 and 6.59 Hz, $1H_{13}$), 1.95 (J = 9.89, 8.79, 6.59 and 4.94 Hz, $1H_{11}$), 2.15 (J = 9.89, 7.69 and 3.85 Hz, $1H_{11}$), 2.24 (m, J = 5.49 and 1.65 Hz, $1H_4$), 2.31 (m, $1H_4$), 2.40 (quintet, J = 5.49 Hz, $2H_5$), 2.49 (dd, J = 5.49 and 4.94 Hz, $2H_6$), 3.1 (m, $1H_{12}$), 4.21 (td, J

= 8.24 and 3.30 Hz, $1H_{14}$), 4.31 (td, J = 8.79 and 6.59 Hz, $1H_{14}$), 5.38 (s, $1H_2$), 5.86 (dt, J = 12.6 and 4.5 Hz, $1H_{10}$) and 6.21 (br d, J = 12 Hz, $1H_9$).

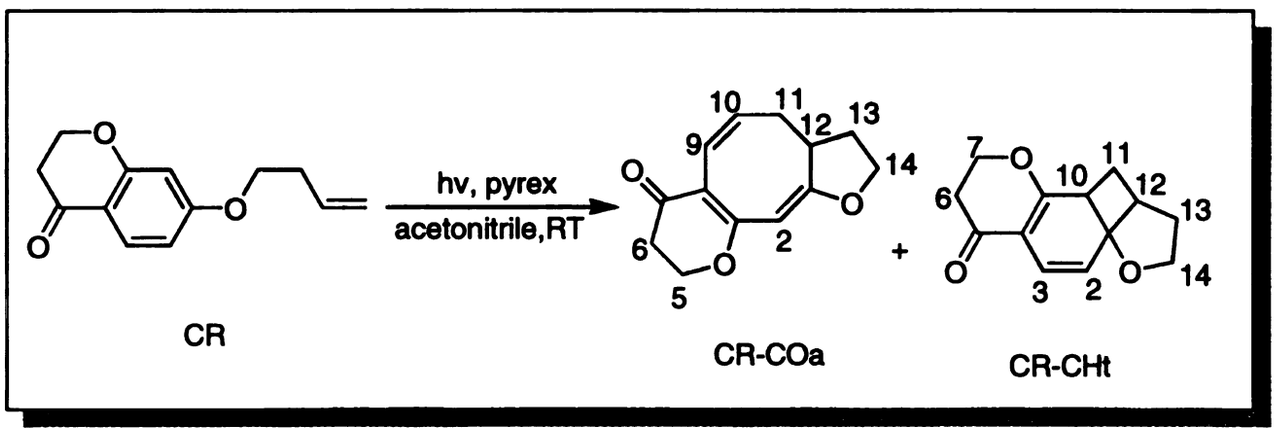
UV: 309.

c. 15-Oxa-tetracyclo[10, 3, 0, $0^{1,10}$, $0^{4,9}$]pentadeca-2, 4-diene-5-one (TT-CHt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.69 (dddd, $1H_{13}$), 1.96 (dddd, $1H_{13}$), 1.98 (tt, $2H_7$), 2.05 (t, $2H_8$), 2.09 (t, $2H_{11}$), 2.42 (t, $2H_6$), 2.94 (tt, $1H_{12}$), 3.11 (br t, $1H_{10}$), 4.17 (dt, $2H_{14}$), 5.53 (d, J = 10 Hz, $1H_2$) and 6.62 (d, J = 10 Hz, $1H_3$).

UV: 261

4.5.10. 6-(3-Buten-1-oxy)-1-chromonone



In an NMR tube, 6-(3-buten-1-oxy)-1-chromonone (2.1 mg, 0.01 mmol) was dissolved in deuterated acetonitrile (0.75 mL, 1.28 x 10^{-2} M). The sample was purged with argon for 15 minutes and then irradiated with a medium pressure mercury arc lamp through a Pyrex filter sleeve. Reaction progress was monitored by ^{1}H NMR and HPLC. After 2 hour of irradiation, NMR analysis of the reaction mixture showed the presence of several photoproducts.

Large scale photolysis was carried out to isolate the photoproducts. 6-(3-buten-1-oxy)-1-chromonone (170 mg, 0.78 mmol) was dissolved in freshly distilled acetonitrile (50 mL) and irradiated in an immersion well with a medium pressure mercury arc lamp through a Pyrex filter. The reaction progress was monitored by HPLC. After 8 hours of irradiation, the reaction mixture was concentrated at reduced pressure and separated using preparative TLC (hexane:ethyl acetate, 80:20) and HPLC (hexane:ethyl acetate, 80:20).

One photoproduct collected at 22 minutes from HPLC was identified as 4,15-dioxa-tricyclo[10, 3, 0,$0^{3,8}$]pentadeca-1, 3, 9-triene-7-one (**CR-COa**) (10 mg, 5.3%). The other photoproduct collected at 12 minutes from HPLC was identified as 8,15-dioxa-tetracyclo[10, 3, 0, $0^{1,10}$, $0^{4,9}$]pentadeca-2, 4-diene-5-one (**CR-CHt**) (~1 mg). The ratio of two product (**CR-COa/ CR-CHt**) was 10:1.

a. 4,15-Dioxa-tricyclo[10, 3, 0,$0^{3,8}$]pentadeca-1, 3, 9-triene-7-one (CR-COa)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.84 (ddt, J = 12.40, 6.26 and 5.95 Hz, $1H_{13}$), 2.24 (dddd, J = 12.40, 6.59, 6.22 and 4.3 Hz, $1H_{13}$), 2.38 (dtd, J = 10.44, 6.51 and 4.42 Hz, $1H_{11}$), 2.42 (td, J = 15.31 and 3.85 Hz, $1H_6$), 2.51 (m, J = 10.44, $1H_{11}$), 2.77 (td, J = 15.31 Hz and 3.2 Hz, $1H_6$), 3.37 (m, $1H_{12}$), 4.35 (t, J = 7.8 Hz, $2H_5$), 4.38 (td, J = 8.54 and 3.30 Hz, $1H_{14}$), 4.47 (td, J = 8.54 and 6.59 Hz, $1H_{14}$), 5.39 (s, $1H_2$), 5.83 (dt, J = 12.5 and 4.5 Hz, $1H_{10}$) and 6.22 (br d, J = 12.5 Hz, $1H_9$).

UV: 297

b. 8,15-Dioxa-tetracyclo[10, 3, 0, $0^{1,10}$, $0^{4,9}$]pentadeca-2, 4-diene-5-one (CR-CHt)

1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.77 (dddd, $1H_{13}$), 2.04 (dddd, $1H_{13}$), 2.23 (dt, $2H_6$), 2.54 (dt, $1H_{11}$), 2.64 (dt, $1H_{11}$), 2.97 (tt, $1H_{12}$), 3.24 (br t, $1H_{10}$), 4.18 (dt, $2H_{14}$), 4.46 (m, $2H_7$), 5.38 (d, J = 10 Hz, $1H_2$) and 6.59 (d, J = 10 Hz, $1H_3$).

4.6. Computational Analysis

The ground state and excited triplet state geometry and energy of the photoreactants, intermediates and photoproducts were obtained using Spartan. Directions of dipole moment for photoreactants in the ground state and excited triplet state were calculated. The ab initio calculations were carried out in the level of (U)HF/6-31G** using Spartan (version 5.0) on Silicone Graphics computers of SGI Indigo workstations.

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