SUPPORTING INFORMATION

PART A:
IRIDIUM CATALYZED C-H BORYLATION OF ARENES; ENGINEERING SELECTIVITY BY LIGAND DESIGN.
PART B:
Z-SELECTIVE PALLADIUM CATALYZED CROSS COUPLING OF E-VINYL GERMANES.

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A DISSERTATION

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SUPPORTING INFORMATION FOR CHAPTER 2

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I. General Methods Chapter 3:

Pinacol Borane (HBpin) (97% stabilized with 1% triethylamine) and Bispinacolatodiboron (B_2pin_2) were purchased commercially and used as received without further purification. The iridium catalyst, bis(1,5-cyclooctadiene)-di-μ-methoxy-diiridium(I), $[Ir(OMe)COD]_2$, was prepared by a literature procedure.[1] This catalyst complex is now widely commercially available.

The ligands were obtained from commercial sources and used as received except as follows: Di-(pyridin-2-yl)methane, (also known as dipyridyl methane and abbreviated **dpm**) was synthesized by a literature procedure.[2] Substituted bipyridine (bpy) ligands from Table 1, $N^4,N^4,N^{4'},N^{4'}$-tetramethyl-[2,2'-bipyridine]-4,4'-diamine[3] and 4,4'-bis(trifluoromethyl)-2,2'-bipyridine[4] were also synthesized by literature procedures. These ligands have also become commercially available recently, and several newer literature preps have been published since these were made.

The ligand, 2,2'-methylenebis (*N*,*N*-dimethyl pyridin-4-amine) (also known as dimethyl amino dipyridyl methane, abbreviated **dmadpm** in this paper) was synthesized according to modified literature procedures as detailed in the experimental section.[5,6]

The substrates featured in Tables 2 and 3 were obtained commercially. Liquid substrates were purified by distillation and solid substrates were purified by sublimation, except as noted. 5-Bromo-2-cyanothiophene was prepared by a literature procedure.[7] 2-Chloro-3-fluoropyridine and 5-methylfuranonitrile were purchased in small quantities, so they were passed through a short plug of activated alumina in the glove box in lieu of distillation. 2-Chloro-6-fluoropyridine was used as received without further purification. To aid transfer, the low melting solid was stored in the freezer and weighed cold into the reactions.

All reactions were carried out at ambient temperature in 20 mL vials equipped with stir bars in a glove box under a nitrogen atmosphere. All solvents were obtained from wet stills refluxing over sodium and benzophenone.

Reactions were monitored by gas chromatography (GC) equipped with a 10 m x 180 μm fused silica column. The GC method employed an initial temperature 50°C constant over 1 minute, ramp 50°C/minute over 9 minutes, 270°C constant over 5 minutes (total time 15 min at flow rate = 1 mL/min).

NMR spectra were recorded on a Varian 500 MHz DD2 Spectrometer equipped with a 1H-19F/15N-31P 5mm Pulsed Field Gradient (PFG) Probe. Spectra were taken in $CDCl_3$ referenced to 7.24 ppm in ^{1}H NMR and 77.0 ppm in ^{13}C NMR. Spectra were processed for display by iNMR software.

Single crystal analyses were performed by Michigan State University Center for Crystallographic Research on a Charge Coupled Device (CCD diffractometer).

High-resolution mass spectra were obtained at the Michigan State University Mass Spectrometry Core using quadrapole Time Of Flight instruments (q/TOF).

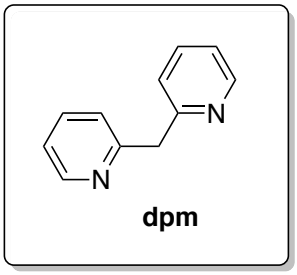
CHN analyses were performed on a CHNS/O analyzer at Michigan State University by analytical department staff.

Silica used for purification of crude material was standard laboratory grade 230 - 400 mesh designed for flash chromatography applications. Purification of crude materials on a 1 mmol scale was achieved by standard flash chromatography methods employing 2-3 g silica plugs in small chromatography columns of dimension approximately 2 x 30 cm. Larger scale reactions of 2.5 - 5 mmol were purified in a similar manner, using 10 - 20g silica. Concentrated crude material was dissolved in a minimum amount of solvent, applied to the silica with a Pasteur pipette and eluted

into test tubes. Compounds that eluted were visualized by spotting on TLC plates and irradiating with 254 nm UV light. Borylated compounds were additionally visualized by staining with alizarin stain in accordance with a literature procedure.[8] The stained compounds containing boron charred orange and fluoresced brightly under long wave UV light of 366 nm.

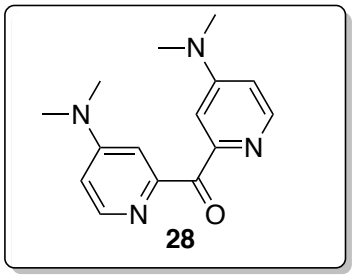
II. Experimental:

Preparation of the ligands:



Dpm was prepared by a literature procedure[1], and purified by distillation at 1 torr 100°C. This substrate can also be purified by Kugelrohr distillation.

Dpm Step 1: Preparation of the dipyridyl ketone:



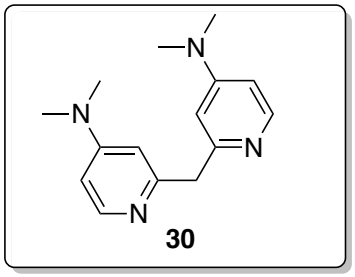
The ketone was synthesized starting from a literature prep of 2-bromo-*N*,*N*-dimethylpyridin-4-amine (2-bromo-DMAP).[5] A literature prep for an analogous dipyridyl ketone, referred to as compound **19** in the paper, was followed using 2-bromo-DMAP made by the procedure in reference 5 as starting material.[6] The ketone was isolated by column chromatography employing 25 g silica packed in 100% ethylacetate. The crude material was loaded onto the column dissolved in a minimum amount dichloromethane. Ethyl acetate was added until unreacted starting

material and bi-products had eluted. The fractions were analyzed by TLC in 100% methanol. 2-bromo-DMAP was seen as a spot with $r_f = 0.9$, and byproducts were seen as faint spots ranging in r_f from 0.4 – 0.7. The product was seen as a spot that did not move off the baseline. A gradient of 10% - 30% methanol in ethyl acetate was applied and the ketone eluted with 30% methanol. On a 5 mmol scale, 330 mg pale yellow crystalline solid was isolated (49% yield, m.p. = 175 – 178 °C). ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.30 (d, *J* = 5.9 Hz, 1H), 7.22 (d, *J* = 2.7 Hz, 1H), 6.56 (dd, *J* = 5.9, 2.7 Hz, 1H), 3.05 (s, 6H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 195.9, 155.3, 154.7, 149.2, 108.3, 108.0, 39.2. HRMS (ESI+) (*m/z*) calcd for $C_{15}H_{19}N_4O$ $[M+H]^+$ 271.1559, found 271.1566.

The ketone was recrystallized from dichloromethane and toluene to produce crystals suitable for x-ray diffraction, which yielded a crystal structure that confirmed the identity of the product. The CIF file is available for download from the Cambridge Crystallographic Data Centre (CCDC) and may be referenced by CCDC deposition # 1436384.

Step 2: Reduction of the dipyridyl ketone:

(note this is not a good way to make the hydrazone for use as a ligand. The synthesis of the hydrazone as a product is presented later)



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The ketone was reduced by a modified Wolf-Kishner procedure as follows:

Fine powdered potassium tert-butoxide, KO*t*Bu (1.0 g, 28.5 mmol, present in excess, ~8 equiv) was transferred into a 150 mL round bottom flask equipped with a stir bar. Hydrazine monohydrate solution (35 mL of a 65% solution, 469 mmol, present in excess, 127 equivalents) was added into the flask. (The precise number of hydrazine equivalents need not be calculated, as the 65%

hydrazine monohydrate solution is used as a solvent for the reaction, so a volume appropriate for the size of the flask was used.)

Dimethylamino dypyidyl ketone (1.0 g, 3.7 mmol, 1.0 equiv) was added into the reaction flask as a uniform dry powder that was free of clumps. A reflux condenser was attached to the flask and the mixture was refluxed vigorously (150 °C oil bath) for 6 hours. At the beginning, the ketone is an insoluble solid and floats on the top, but as the reaction progresses, the solid becomes an oil that floats on the top of the hydrazine. The reaction was allowed to cool to ambient temperature, after which, the reaction was extracted with 3 x 50 mL ethyl acetate. The combined organic layer was washed with brine and dried over sodium sulfate. The drying agent was removed by filtration and the filtrate was concentrated to a yellow solid. The crude material was dried under high vacuum overnight to yield 680 mg yellow product. The ligand was purified by chromatography on a silica gel column packed in ethyl acetate. The crude material was loaded dissolved in a minimum amount of CH_2Cl_2. Ethylacetate (200 mL) was eluted through the silica column. The column was then washed with 100% methanol to yield 596 mg (63% yield) of the product as a pale yellow solid.

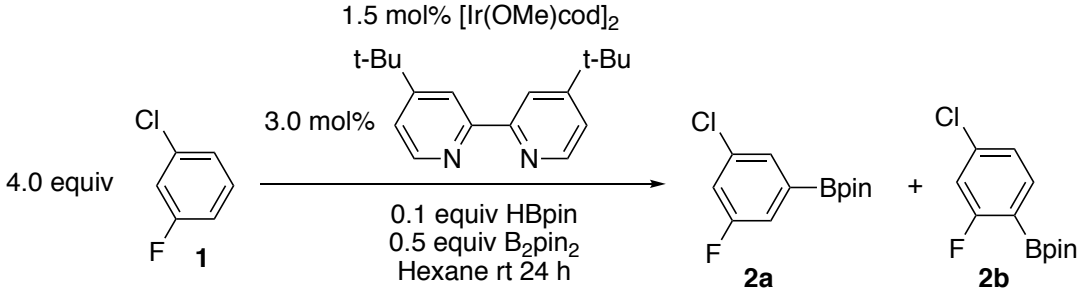
The product was then sublimed at 90°C under reduced pressure of 1 torr to furnish the pure ligand dmadpm as a white powder, m.p. = 99 – 103 °C. ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.14 (d, *J* = 6.0 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.33 (dd, *J* = 6.0, 2.6 Hz, 1H), 4.07 (s, 1H), 2.94 (s, 6H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 159.8, 154.9, 149.2, 106.1, 104.7, 48.1, 39.1. HRMS (ESI+) (*m/z*) calcd $[M+H]^+$ for $C_{15}H_{21}N_4$ 257.1766; found, 257.1773. The sublimed ligand was recrystallized from ethyl acetate and hexane to produce crystals that were suitable for X-ray diffraction, which yielded a crystal structure consistent with the product. The CIF file is available for download from the CCDC, and may be referenced by CCDC deposition # 143727.

Earlier procedures using KOH as the reductant did not reduce the hydrazone intermediate completely, but KO*t*Bu gave complete reduction, usually within 6 hours. Dmadpm does not go through a GC-FID well, but reactions were judged complete when the ketone peak was gone. Samples for GC analysis in hydrazine were removed from the reaction and put into a vial in the hood. Water (1mL) and CH_2Cl_2 (1mL) were added, and the sample was shaken in a vial or micro sep funnel. The water layer was removed and the CH_2Cl_2 layer was dried with sodium sulfate briefly before injection of the sample into the GC-FID.

III. Data:

Table 2.1 Electronic Effects on Borylation Regioselectivities

Table 2.1, Entry 1: Selectivity of 4-tBu substituted bpy ligand.



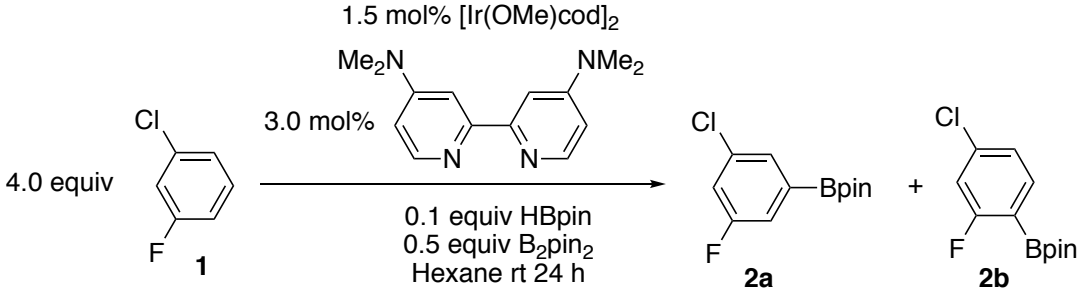
1.0 mmol based on B equivalents
(0.5 mmol B_2pin_2 = 1.0 mmol B equivalents)

ratio of crude material by GC1.8:1

A solution containing HBpin (15.5 mg, 17 μL, 0.12 equiv) in 1.0 mL hexane was transferred into a test tube containing $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). This mixture was transferred into a test tube containing the ligand 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (8 mg, 0.03 mmol 3 mol%) followed by a 1.0 mL hexane rinse. This solution was transferred to a 20 mL vial. B_2pin_2 (127 mg, 0.5 mmol, 0.5 equiv = 1.0 mmol boron equivalents) was added to the vial followed by a 1.0 mL hexane rinse. A stir bar was added and the solution was stirred for 15 minutes. 1-Chloro-3-fluorobenzene (522 mg, 428 μL, 4.0 mmol, 4.0 equiv) was

then added by pipettor into the reaction vial. The reaction was allowed to stir at ambient temperature in the glove box for 24 hours. After 24 hours, the GC sample of the reaction was taken, and a ratio of 1.8:1 of **2a**:**2b** was observed.

Table 2.1, Entry 2: Selectivity of 4-NMe_2 substituted bpy ligand.

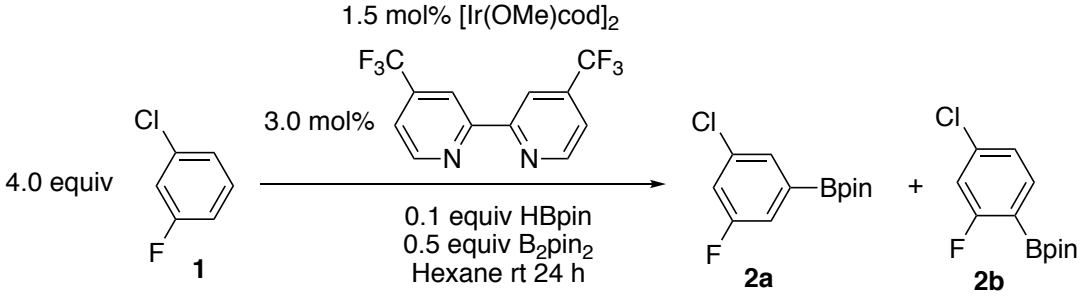


1.0 mmol based on B equivalents
(0.5 mmol B_2pin_2 = 1.0 mmol B equivalents)

ratio of crude material by GC 2.2:1

A solution containing HBpin (15.5 mg, 17 μL, 0.12 equiv) in 1.0 mL hexane was transferred into a test tube containing $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). This mixture was transferred into a test tube containing the ligand $N^4,N^4,N^{4'},N^{4'}$-tetramethyl-[2,2'-bipyridine]-4,4'-diamine (7.3 mg, 0.03 mmol, 3 mol%) followed by a 1.0 mL hexane rinse. This solution was transferred to a 20 mL vial. B_2Pin_2 (127 mg, 0.5 mmol, 0.5 equiv = 1.0 mmol boron equivalents) was added to the vial followed by a 1.0 mL hexane rinse. A stir bar was added and the solution was stirred for 15 minutes. 1-chloro-3-fluorobenzene (522 mg, 428 μL, 4.0 mmol, 4.0 equiv) was then added into the reaction vial. The reaction was allowed to stir at ambient temperature in the glove box for 24 hours. After 24 hours, a GC sample was taken and a ratio of 2.2:1 **2a**:**2b** was observed.

Table 2.1, Entry 3: Selectivity of 4-CF_3 substituted bpy ligand.



1.0 mmol B equivalents
0.5 mmol B_2pin_2 = 1.0 mmol B equivalents

ratio of crude material by GC 1:1.6

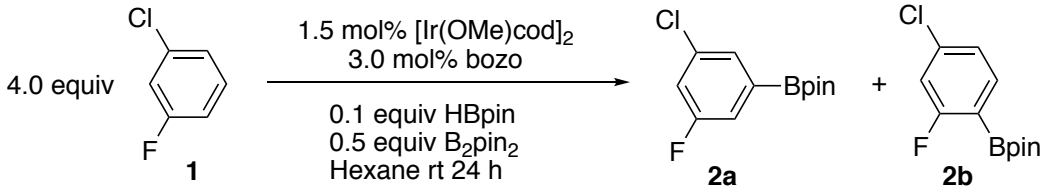
A solution containing HBpin (15.4 mg, 17 μL, 0.12 equiv) in 1.0 mL hexane was transferred into a test tube containing $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). This mixture was transferred into a test tube containing the ligand 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (8.8 mg, 0.03 mmol, 3 mol%) followed by a 1.0 mL hexane rinse. This solution was transferred to a 20 mL vial. B_2pin_2 (127 mg, 0.5 mmol, 0.5 equiv = 1.0 mmol boron equivalents) was added to the vial followed by a 1.0 mL hexane rinse. A stir bar was added and the solution was stirred for 15 minutes. 1-Chloro-3-fluorobenzene (522 mg, 428 μL, 4.0 mmol, 4.0 equiv) was then added into the reaction vial. The reaction was allowed to stir at ambient temperature in the glove box for 24 hours. After 24 hours, the GC ratio was taken.

Table 2.3: Borylation of 3-Fluorochlorobenzene Selectivity Comparison

Conversion was assessed by integration of ^{19}F NMR spectra. The theoretical yield for complete conversion corresponds to 1.0 mmol of borylated products, thus, for reactions with a 4-fold excess of substrate, 25% of the total ^{19}F resonances. The sum of the % borylated isomers divided by 25% was used to calculate the conversion. ^{11}B NMR spectra were also taken to confirm the presence or absence of HBpin (a doublet at 27 ppm). The presence of HBpin indicated

incomplete conversion of boron equivalents into borylated products; and the absence of HBpin confirmed complete conversion of boron equivalents.

Table 2.3, Entry 1: Selectivity of bozo ligand.



1.0 mmol B equivalents
(0.5 mmol B_2pin_2 = 1.0 mmol B equivalents)

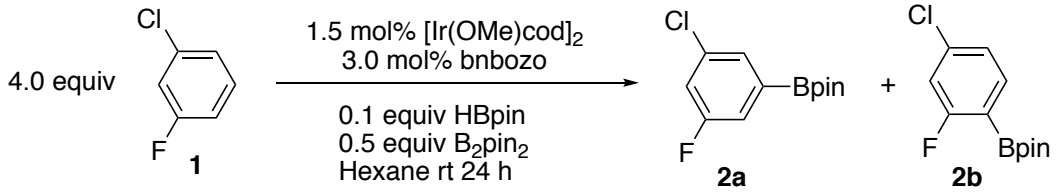
ratio of crude material by GC1:3.3
isolated yield 65% (1:3.6)

$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. 1.0 mL hexane was added to the vial, resulting in a clear, light yellow solution. HBpin (15.4 mg, 17 μL, 0.12 mmol) was added into the vial, and the solution turned a deep gold color. The ligand 2,2'-Bis(2-oxazoline) (bozo) (4.2 mg, 0.03 mmol, 3.0 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL hexane and the rinse was added to the reaction vial. The solution turned a cherry red color. B_2pin_2 (127 mg, 0.5 equiv 0.5 mmol = 1.0 mmol boron equivalents) was weighed into a test tube and added into the reaction mixture as a solid. The test tube was rinsed twice with 1.0 mL hexane and the rinses were added into the reaction vial. The mixture was stirred for 5 minutes until most solids were dissolved. Excess substrate (0.428 mL, 522.2 mg, 4.0 mmol, 4.0 equiv) was added. No initial gas evolution was observed. The sides of the vial were rinsed down with an additional 1.0 mL of hexane for a total volume of 5.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 1:3.7 borylated

isomers was observed by ^{19}F NMR and 74% conversion was calculated. The ^{11}B NMR showed unreacted HBpin present in the reaction mixture. A GC of the reaction showed a ratio of 1:3.3. The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2 g silica plug eluting with CH_2Cl_2 to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 166 mg, (65% isolated yield), of clear oil that was determined by ^{19}F NMR to be a 1:3.6 ratio of **2a**:2**b**.

Table 2.3, Entry 2: Selectivity of bnbozo ligand.



1.0 mmol B equivalents
(0.5 mmol B_2pin_2 = 1.0 mmol B equivalents)

ratio of crude material by GC 1:2.4
isolated yield 65% (1:2.5)

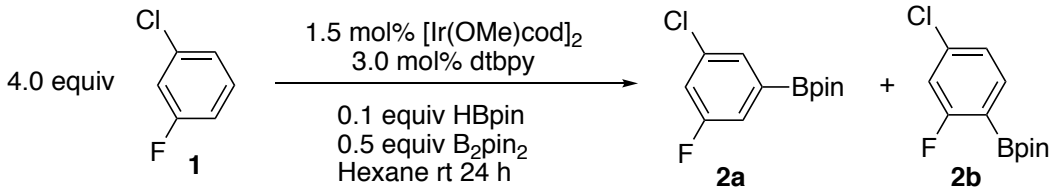
$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. Hexane (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (15.4 mg, 17 µL, 0.12 mmol, 0.12 equiv) was added into the vial, and the solution turned a deep gold color. The ligand 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) (10 mg, 0.03 mmol, 3.0 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL hexane and the rinse was added to the reaction vial. The solution turned a cherry red color. B_2pin_2 (127 mg, 0.5 equiv, 0.5 mmol = 1.0 mmol boron equivalents) was weighed into a test tube and added into the reaction mixture as a solid. The test tube was rinsed twice with 1.0 mL hexane and the rinses were added into the reaction vial. The mixture was stirred for 5 minutes until most solids were dissolved. Excess substrate (428 µL, 522 mg, 4.0 mmol, 4.0 equiv) was added. No initial gas evolution was observed. The sides of the vial were rinsed down with an

additional 1.0 mL of hexane for a total volume of 5.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 1:2.5 borylated isomers **2a**:**2b** was observed by ^{19}F NMR and 79% conversion was calculated. The ^{11}B NMR showed unreacted HBpin present in the reaction mixture. A GC of the reaction showed a ratio of 1:2.4 borylated isomers **2a**:**2b**.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2 g silica plug eluting with CH_2Cl_2 to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 152 mg (60% isolated yield), of clear oil that was determined by ^{19}F NMR to be a 1:2.5 mixture of **2a**:**2b**.

Table 2.3, Entry 3: Selectivity of dtbpy ligand.



1.0 mmol B equivalents
(0.5 mmol B_2pin_2 = 1.0 mmol B equivalents)

ratio of crude material by GC 1.8:1
isolated yield 99% (1.8:1)

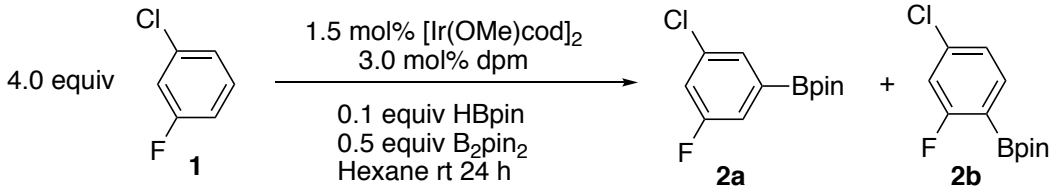
$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. Hexane (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (15.4 mg, 17 µL, 0.12 mmol, 0.12 equiv) was added into the vial, and the solution turned a deep gold color. The ligand 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (5 mg, 0.03 mmol, 3 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was

rinsed with 1.0 mL hexane and the rinse was added to the reaction vial. The solution turned dark red color. B_2pin_2 (127 mg, 0.5 equiv, 0.5 mmol = 1 mmol boron equivalents) was weighed into a test tube and added into the reaction mixture as a solid. The test tube was rinsed twice with 1.0 mL hexane and the rinses were added into the reaction vial. The mixture was stirred for 2 minutes and all solids were dissolved. Excess substrate (428 μL, 522.2 mg, 4.0 mmol, 4.0 equiv) was added. The sides of the vial were rinsed down with an additional 1.0 mL of hexane for a total volume of 5.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 1.7:1 **2a**:**2b** borylated isomers was observed by ^{19}F NMR and > 99% conversion was calculated. The ^{11}B NMR showed no HBpin present in the reaction mixture. A GC of the reaction showed a ratio of 1.8:1 **2a**:**2b** borylated isomers.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2 g silica plug eluting with CH_2Cl_2 to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 255 mg, (99% isolated yield), of clear oil that was determined by ^{19}F NMR to be a 1.8:1 ratio of **2a**:**2b** borylated isomers.

Table 2.3, Entry 4: Selectivity of dpm ligand.



1.0 mmol B equivalents
(0.5 mmol B_2pin_2 = 1.0 mmol B equivalents)

ratio of crude material by GC 2.4:1
isolated yield 75% 2.4:1

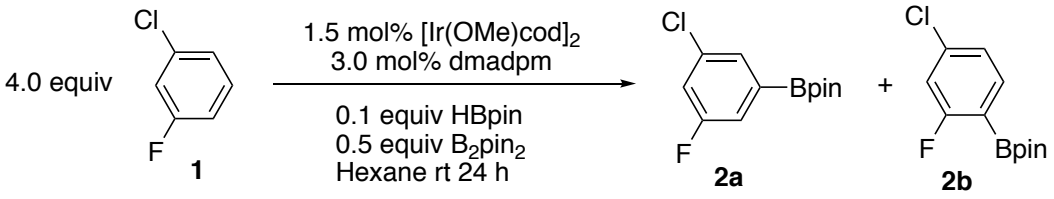
$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. Hexane (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (15.4 mg, 17 µL, 0.12 mmol, 0.12 equiv) was added into the vial, and the solution turned a deep gold color. The ligand dipyridyl methane, (dpm) (5 mg, 0.03 mmol, 3 mol%) was weighed into a test tube dissolved in 1.0 mL hexane. The solution was transferred in to the reaction vial. The test tube was rinsed with 1.0 mL hexane and the rinse was added to the reaction vial. The solution turned orange color. B_2pin_2 (127 mg, 0.5 equiv, 0.5 mmol = 1.0 mmol boron equivalents) was weighed into a test tube and added into the reaction mixture as a solid. The test tube was rinsed twice with 1.0 mL hexane and the rinses were added into the reaction vial. The mixture was stirred for 2 minutes and all solids were dissolved. Excess substrate (428 µL, 522.2 mg, 4.0 mmol, 4.0 equiv) was added. No initial gas evolution was observed. The sides of the vial were rinsed down with an additional 1.0 mL of hexane for a total volume of 5.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 2.3:1 **2a**:**2b** borylated isomers was observed by ^{19}F NMR and 89% conversion was calculated. The ^{11}B NMR

showed a small amount of HBpin present in the reaction mixture. A GC of the reaction showed a mixture of borylated isomers in a 2.4:1 ratio of **2a**:**2b**.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2 g silica plug eluting with CH_2Cl_2 to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 191 mg, (75% isolated yield), of clear oil that was determined by ^{19}F NMR to be a mixture of borylated isomers in a 2.2:1 ratio of **2a**:**2b**.

Table 2.3, Entry 5: Selectivity of dmadpm ligand.



1.0 mmol B equivalents
(0.5 mmol B_2pin_2 = 1.0 mmol B equivalents)

ratio of crude material by GC 2.9:1
isolated yield 76% (2.8:1)

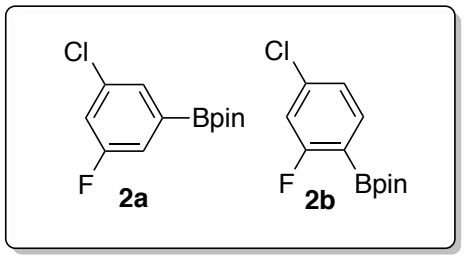
$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. Hexane (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. 0.12 equiv HBpin (15.4 mg, 17 μL, 0.12 mmol) was added into the vial, and the solution turned a deep gold color. The ligand, dimethylamino dipyridyl methane, (dmadpm) (8mg, 0.03 mmol, 3 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL hexane and the rinse was added to the reaction vial. The solution turned yellow-orange color. B_2Pin_2 (127 mg, 0.5 equiv, 0.5 mmol = 1.0 mmol boron equivalents) was weighed into a test tube and added into the reaction mixture as a solid. The test tube was rinsed twice with 1.0 mL hexane and the rinses were added into the reaction vial. The mixture was stirred for 2 minutes and all solids were dissolved. Excess substrate (0.428 mL, 522.2 mg, 4.0 mmol, 4.0 equiv) was added. No initial gas evolution was observed. The sides of the vial were rinsed down

with additional hexane (1.0 mL) for a total volume of 5.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 2.9:1 borylated isomers was observed complete conversion was calculated. The ^{11}B NMR showed a small amount of HBpin present in the reaction mixture. A GC of the reaction showed a ratio of borylated isomers. The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2 g silica plug eluting with CH_2Cl_2 to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 177 mg, (69% isolated yield), of clear oil that was determined by ^{19}F NMR to be a 2.8:1 ratio **2a**:**2b**.

Table 2.4: 6-Membered Arenes and Heterocycles

Table 2.4, Entry 1

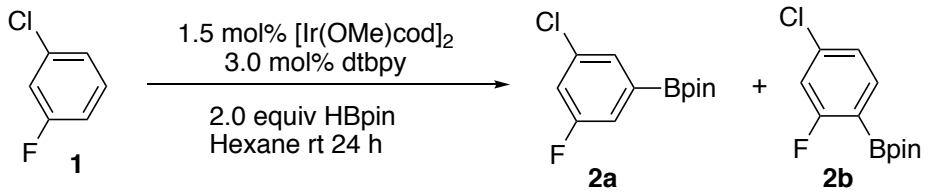


Characterization of 2a and 2b

Steric isomer 2a: ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.54 (d, *J* = 1.9 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.14 (dt, *J* = 8.7, 2.2 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 162.3 (d, J = 250.3 Hz), 134.7 (d, *J* = 9.0 Hz), 130.3 (d, *J* = 2.9 Hz), 119.3 (d, *J* = 19.8 Hz), 118.8 (d, *J* = 24.8 Hz), 84.4, 24.8. C5 adjacent to Boron is not visible due to quadrupolar relaxation. ^{11}B NMR (160 MHz; $CDCl_3$) δ 30.2. ^{19}F NMR (470 MHz $CDCl_3$) δ -111.9. **10a** was isolated as a clear oil.

Electronic isomer 2b: ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.65 (dd, *J* = 7.9, 6.7 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.04 (dd, *J* = 9.1, 1.8 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 167.1 (d, J = 254.6), 138.4 (d, 11.1 Hz), 137.6 (d, J = 9.3 Hz), 124.2 (d, J = 3.0 Hz), 116.1 (d, J = 27.7 Hz), 84.1, 24.8. C4 adjacent to Boron is not visible due to quadrupolar relaxation. ^{19}F NMR (470 MHz; $CDCl_3$): δ -100.5 (t, *J* = 7.5 Hz). ^{11}B NMR (160 MHz; $CDCl_3$): δ 29.9. **10b** was isolated as a white crystalline solid, mp 71 -72 °C. Spectra for **2b** matches previously reported data for this compound.[9]

Table 2.4, Entry 1: Selectivity of dtbpy ligand.



1.0 mmol

ratio of crude material by GC 1.8:1
isolated yield 99% (1.8:1)

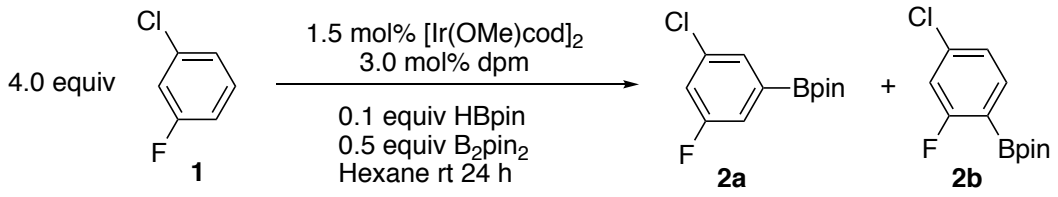
$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. Hexane (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (254 mg, 190µL, 2.0 mmol, 2.0 equiv) was added into the vial, and the solution turned a deep gold color. The ligand 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (8 mg, 0.03 mmol, 3 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL hexane and the rinse was added to the reaction vial. The solution turned dark red color. The mixture was allowed to stir for 2 minutes and all solids were dissolved. Substrate (107 µL, 131 mg, 1.0 mmol, 1.0 equiv) was added. The sides of the vial were rinsed down with an additional 1.0 mL of hexane for a total volume of 3.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 1.8:1 **2a**:**2b** borylated isomers was observed by ^{19}F NMR and > 99% conversion was observed. The ^{11}B NMR showed no HBpin present in the reaction mixture. A GC of the reaction showed a ratio of 1.8:1 **2a**:**2b** borylated isomers.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2g silica plug eluting

with CH_2Cl_2 to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 255 mg, (99% isolated yield), of clear oil that was determined by ^{19}F NMR to be a 1.8:1 ratio of **2a**:**2b** borylated isomers.

Table 2.4, Entry 1: Selectivity of dpm ligand.



1.0 mmol

ratio of crude material by GC 2.4:1
isolated yield 75% 2.4:1

Note: the ratio of **2a**:**2b** varied depending on the conditions. Typical ratios in hexane without excess substrate is 1.8:1, in THF 2:1. Using these conditions with 4-fold excess of starting substrate in hexane with B_2pin_2 produced the best ratio, 2.4:1.

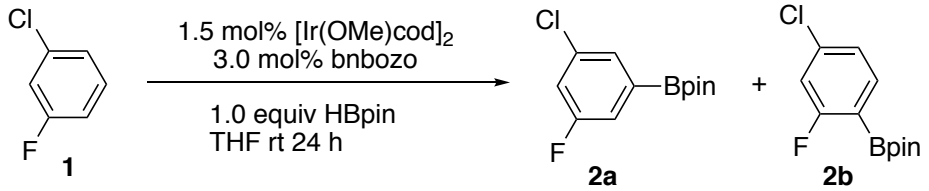
$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. Hexane (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (15.4 mg, 17 μL, 0.12 mmol, 0.12 equiv) was added into the vial, and the solution turned a deep gold color. The ligand dipyridyl methane, (dpm) (5 mg, 0.03 mmol, 3 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL hexane and the rinse was added to the reaction vial. The solution turned orange color. B_2pin_2 (127 mg, 0.5 equiv, 0.5 mmol = 1.0 mmol boron equivalents) was weighed into a test tube and added into the reaction mixture as a solid. The test tube was rinsed twice with 1.0 mL hexane and the rinses were added into the reaction vial. The mixture was allowed to stir for 2 minutes and all solids were dissolved. Excess substrate (428 μL, 522.2 mg, 4.0 mmol, 4.0 equiv) was added. No initial gas evolution was observed. The sides of the vial were rinsed down with an additional 1.0

mL of hexane for a total volume of 5.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 2.3:1 **2a**:**2b** borylated isomers was observed by ^{19}F NMR and 89% conversion was calculated. The ^{11}B NMR showed a small amount of HBpin present in the reaction mixture. A GC of the reaction showed a mixture of borylated isomers in a 2.4:1 ratio of **2a**:**2b**.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2g silica plug eluting with CH_2C_{l2} to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 191 mg, (75% isolated yield), of clear oil that was determined by ^{19}F NMR to be a mixture of borylated isomers in a 2.2:1 ratio of **2a**:**2b**. This mixture was dissolved in hexane and applied to a 5g silica plug eluting in hexane. The fractions were analyzed by TLC using 10% diethyl ether in hexane as eluent, then the TLC plates were treated with alizarin stain. Most fractions gave rise to only one spot, pure **2a** (r_f = 0.6), while the last 10 fractions showed traces of **2b** as a second spot (r_f = 0.52). The fractions containing only one spot were combined and concentrated to yield 73 mg of a clear, colorless oil that was pure **2a** by GC and ^{19}F NMR.

Table 2.4, Entry 1: Selectivity of bnbozo ligand.



1.0 mmol

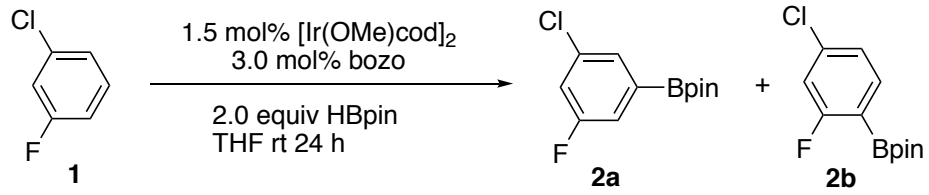
ratio of crude material by GC 1:2.4
isolated yield 65% (1:2.5)

$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. THF (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin 127 mg, 145 μL, 1.0mmol, 1.0 equiv) was added into the vial, and the solution turned a deep gold color. The ligand 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) (10 mg, 0.03 mmol, 3.0 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL THF and the rinse was added to the reaction vial. The solution turned a cherry red color. The mixture was stirred for 5 minutes until most solids were dissolved. Substrate (107 μL, 131 mg, 1.0 mmol, 1.0 equiv) was added. No initial gas evolution was observed. The sides of the vial were rinsed down with an additional 1.0 mL of THF for a total volume of 3.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 1:2.5 borylated isomers **2a**:**2b** was observed by ^{19}F NMR and 79% conversion was observed. The ^{11}B NMR showed unreacted HBpin present in the reaction mixture. A GC of the reaction showed a ratio of 1:2.4 borylated isomers **2**:**2b**.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2g silica plug eluting with CH_2Cl_2 to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 152 mg (60% isolated yield), of clear oil that was determined by ^{19}F NMR to be a 1:2.5 mixture of **2a**:**2b**.

Table 2.4, Entry 1: Selectivity of bozo ligand.



1.0 mmol

ratio of crude material by GC1:3.3
isolated yield isomer mixture 65% (1:3.6)
isolated crystals 40.1 mg **2b**, 16%

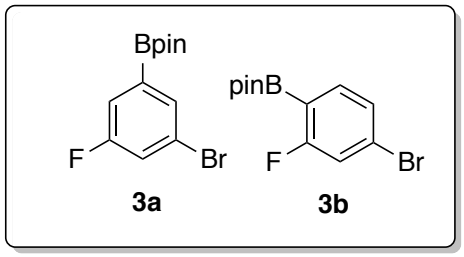
$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. 1.0 mL THF was added to the vial, resulting in a clear, light yellow solution. HBpin (127 mg, 145 µL, 1.0 mmol) was added into the vial, and the solution turned a deep gold color. The ligand 2,2'-Bis (2-oxazoline) (bozo) (4.2 mg, 0.03 mmol, 3.0 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL THF and the rinse was added to the reaction vial. The solution turned a cherry red color. The mixture was allowed to stir for 5 minutes until most solids were dissolved. Substrate (107 µL, 131 mg, 1.0 mmol, 1.0 equiv) was added. No initial gas evolution was observed. 1 mL THF was added for a total volume of 3.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. The sample

was subjected to ^{19}F NMR and ^{11}B NMR to assess reaction conversion. A ratio of 1:3.7 borylated isomers was observed by ^{19}F NMR and 74% conversion was obseved. The ^{11}B NMR showed unreacted HBpin present in the reaction mixture. A GC of the reaction showed a ratio of 1:3.3.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of CH_2Cl_2, and applied to a 2g silica plug eluting with CH_2Cl_2 to afford a mixture of borylated isomers and excess starting material. The starting material was removed by high vacuum to leave 166 mg, (65% isolated yield), of clear oil that was determined by ^{19}F NMR to be a 1:3.6 ratio of **2a**:**2b**. 1.0 mL hexane was added to the mixture and the solution was put in the -30 °C freezer for two days. Large, square white crystals formed in clumps. The supernatant was decanted and the crystals were washed twice in in ice cold hexane. The crystals were dried and 40.1 mg crystals were collected after drying. The crystals were shown to be single isomer **10b** by NMR.

Table 2.4, Entry 2

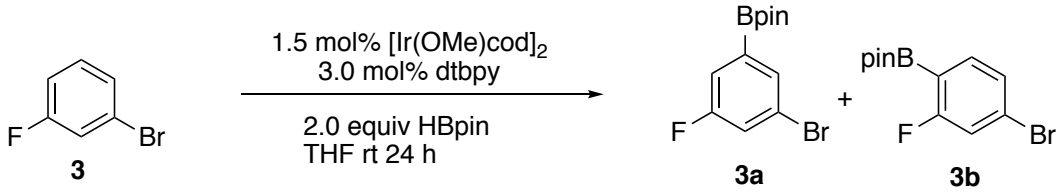


Characterization of 3a and 3b

Major isomer 3a: ^1H NMR (500 MHz; $CDCl_3$): δ 7.72 (d, J = 1.1 Hz, 1H), 7.42 (dd, J = 8.5, 2.2 Hz, 1H), 7.33 (dt, J = 8.3, 2.1 Hz, 1H), 1.35 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$), δ 162.5 (d, J = 251.8), 133.4 (d, J = 3.4 Hz), 122.5 (d, J = 8.4 Hz), 121.8 (d, 24.7 Hz), 119.9 (J= 19.2 Hz), 84.6, 25.0. (B-C not observed due to quadrupolar relaxation). ^{19}F NMR (470 MHz $CDCl_3$) δ -111.6. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.0. Spectra matches reported data for isomer **3a**.[10]

Minor isomer 3b: ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.61 (dd, *J* = 7.9, 6.6 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.24 (dd, *J* = 8.8, 1.6 Hz, 1H), 1.36 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$) δ 166.8 (d, J = 255.7 Hz), 137.8 (d, J = 9.4 Hz), 127.1 (d, J = 3.0 Hz) 126.4 (d, J = 10.3 Hz), 119.0 (d, J = 27.1 Hz), 84.1, 24.8. . (B-C not observed due to quadrupolar relaxation) ^{19}F NMR (470 MHz CDC_3) δ -100.3. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.0. Spectra matches reported data for isomer **3b**.[9]

Table 2.4, Entry 2: Selectivity of dtbpy Ligand



1.0 mmol

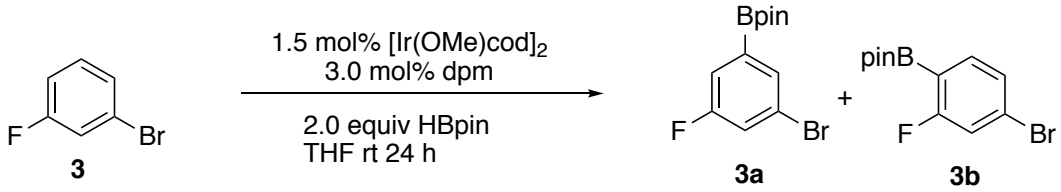
ratio of crude material by GC 7:1
isolated yield 82 % (3:1)

$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. THF (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (254 mg, 290 µL, 2.0 mmol, 2.0 equiv) was added into the vial, and the solution turned a deep gold color. The ligand 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (8 mg, 0.03 mmol, 3 mol%) was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL THF and the rinse was added to the reaction vial. The solution turned dark red color. The mixture was allowed to stir for 2 minutes and all solids were dissolved. Substrate (112 µL, 175 mg, 1.0 mmol, 1.0 equiv) was added. The sides of the vial were rinsed down with an additional 1.0 mL of THF for a total volume of 3.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, a ratio of 3:1 **3a**:**3b** borylated isomers and 90% conversion was observed was observed by ^{19}F NMR aand GC-FID.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of 1:1 dcm:hexane and applied to a 3g silica plug eluting with 1:1 dcm:hexane to afford a mixture of borylated isomers and residual starting material. Residual starting material was removed by high vacuum to leave 245 mg, (82% isolated yield), of clear oil that was determined by ^{19}F NMR to be a 3:1 ratio of **3a**:**3b** borylated isomers.

Table 2.4, Entry 2: Selectivity of dpm Ligand



1.0 mmol

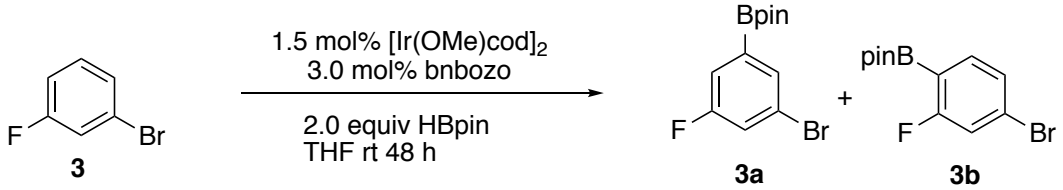
ratio of crude material by GC 7:1
isolated yield 60 % (7.2:1)

$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. THF (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (254 mg, 290 μL, 2 mmol, 2 equiv) was added into the vial, and the solution turned a deep gold color. The ligand dipyridyl methane, (dpm) (5 mg, 0.03 mmol, 3 mol%) was weighed into a gc vial and dissolved in 1.0 mL THF. The solution was transferred into the reaction vial with a Pasteur pipette. The gc vial was rinsed with 1.0 mL THF and the rinse was added to the reaction vial. The solution turned orange. The substrate (112 μL, 175 mg, 1 mmol, 1 equiv) was taken up by pipettor and added into the reaction vial. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h.

After 24 hours, the vial was opened in the glove box and an aliquot of the reaction was removed with a pipette. The aliquot was mixed with $CDCl_3$ and put into an NMR tube. 89% conversion and a ratio of 3:1 **3a**:**3b** borylated isomers was observed by ^{19}F NMR and GC-FID.

The reaction was concentrated by rotary evaporation to leave a brown oil. The crude material was dissolved in a minimum amount of 1:1 dcm:hexane and applied to a 3g silica plug eluting with 1:1 dcm:hexane to afford a mixture of borylated isomers and residual starting material. The starting material was removed by high vacuum to leave 180 mg, (60% isolated yield), of clear oil that was determined by ^{19}F NMR to be a mixture of borylated isomers in a 7.2:1 ratio of **3a**:**3b**.

Table 2.4, Entry 2: Selectivity of bnbozo Ligand



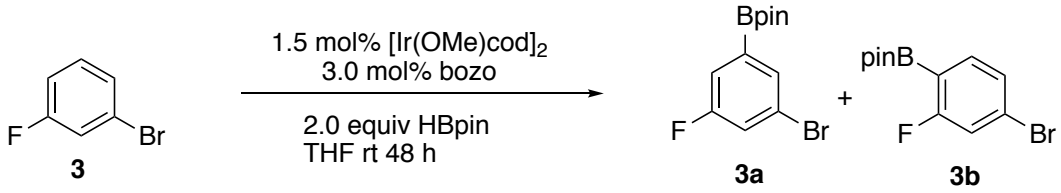
1.0 mmol

ratio of crude material by GC 1:1.6
51% conversion

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-fluorobromobenzene (0.175 g, 112 μL, 1.0 mmol, 1.0 equiv) was taken up by pipettor and added into the stirring mixture in the vial. Additional THF (1.0 mL) was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. After 48 h, 51% conversion

was seen by GC-FID and ^{19}F NMR. A ratio of 1:1.6 **3a**:**3b** was seen by ^{19}F NMR. Due to low conversion, the products were not isolated.

Table 2.4, Entry 2: Selectivity of bozo Ligand

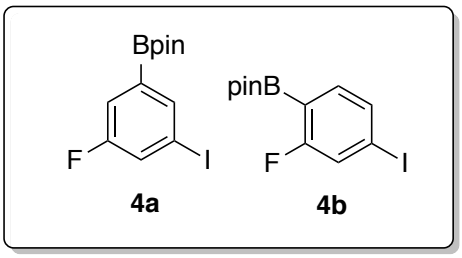


1.0 mmol

ratio of crude material by GC 1:1.8
41% conversion

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stirring bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. 2,2'-Bis(2-oxazoline) (box) was weighed into a test tube (5 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-fluorobromobenzene (0.175 g, 112 μL, 1.0 mmol, 1.0 equiv) was taken up by pipettor and added into the stirring reaction vial. Additional THF (1.0 mL) was added for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. After 48 h, 41% conversion was seen by GC-FID and ^{19}F NMR. A ratio of 1:1.8 **3a**:**3b** was seen by ^{19}F NMR. Due to low conversion, the products were not isolated.

Table 2.4, Entry 3

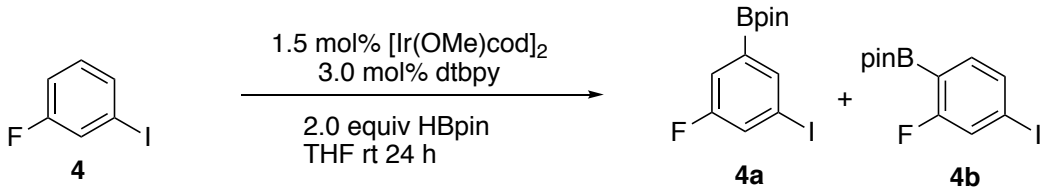


Characterization of 4a and 4b

Major isomer 4a: ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.89 (s, 1H), 7.49 (ddd, *J* = 8.1, 2.5, 1.6 Hz, 1H), 7.42 (dd, *J* = 8.6, 2.3 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 161.9 (d, J = 252.6 Hz), 139.2 (d, J = 3.5 Hz), 127.3 (d, J = 23.2 Hz), 120.4 (d, J = 19.2 Hz), 93.6 (d, J = 6.9 Hz), 84.4, 24.8. (B-C not observed due to quadrupolar relaxation). ^{19}F NMR (240 MHz, $CDCl_3$) δ -111.5. ^{11}B NMR (160 MHz, $CDCl_3$) 29.9.

Minor isomer 4b: Minor isomer **4b** was seen in NMRs in minor amounts that matched the reported data for **4b** which is known literature compound.[11]

Table 2.4, Entry 3: Selectivity of dtbpy Ligand



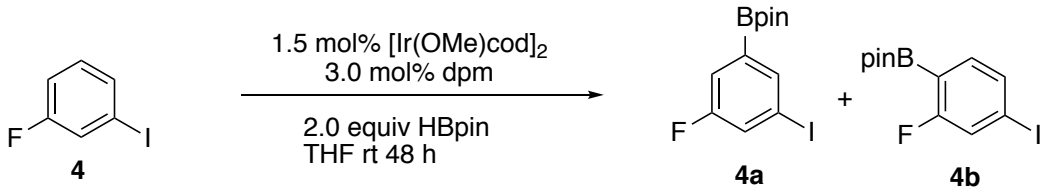
1.0 mmol

ratio of crude material by GC 2.8:1
isolated yield 87 % (3:1)

$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. THF (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (254 mg, 290 µL, 2.0 mmol, 2.0 equiv) was added into the vial, and the solution turned a deep gold color. The ligand 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (8 mg, 0.03 mmol, 3 mol%)

was weighed into a test tube and transferred as a solid into the reaction vial. The test tube was rinsed with 1.0 mL THF and the rinse was added to the reaction vial. The solution turned dark red color. The mixture was allowed to stir for 2 minutes and all solids were dissolved. Substrate (117 μL, 222 mg, 1.0 mmol, 1.0 equiv) was added. The sides of the vial were rinsed down with an additional 1.0 mL of THF for a total volume of 3.0 mL. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h. After 24 h, GC-FID and 19F NMR showed 88% conversion with ratio 2.8:1. The reaction was concentrated by rotary evaporation and the crude residue was dissolved in 1:1 dcm:hexane and subjected to a 3g silica column eluting with 1:1 dcm:hexane. A clear oil that was 3:1 mixture of borylated isomers **4a**:**4b** and residual starting material was obtained. The residual stating material was removed under high vacuum to leave 306 mg clear oil (87% isolated yield).

Table 2.4, Entry 3: Selectivity of dpm Ligand



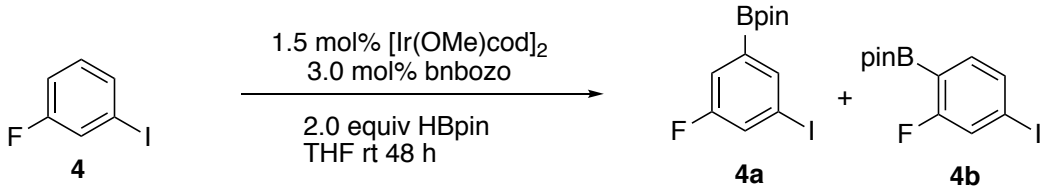
1.0 mmol

ratio of crude material by GC 6.8:1
isolated yield 60 % (6.8:1)

$[Ir(OMe)cod]_2$ (10 mg, 0.015 mol, 3.0 mol% Ir) was charged into a 20 mL vial equipped with a stir bar. THF (1.0 mL) was added to the vial, resulting in a clear, light yellow solution. HBpin (254 mg, 290 μL, 2 mmol, 2 equiv) was added into the vial, and the solution turned a deep gold color. The ligand dipyridyl methane, (dpm) (5 mg, 0.03 mmol, 3 mol%) was weighed into a gc vial and dissolved in 1.0 mL THF. The solution was transferred into the reaction vial with a Pasteur pipette. The gc vial was rinsed with 1.0 mL THF and the rinse was added to the reaction vial. The solution turned orange. The substrate (117 μL, 222 mg, 1 mmol, 1 equiv) was taken up

by pipettor and added into the reaction vial. The reaction was closed with a screw cap and allowed to stir in the glove box at ambient temperature for 24 h. After 24 h, 90% conversion and a ratio of 6.8:1 **4a**:**4b** was observed by a GC-FID and ^{19}F NMR. The reaction was concentrated by rotary evaporation. The crude material was dissolved in 1:1 dcm:hexane and passed through a silica plug eluting in 1:1 dcm:hexane. The residual starting material was removed by high vacuum leaving 209 mg clear oil (60% yield) that was 6.8:1 **4a**:**4b** by ^{19}F NMR.

Table 2.4, Entry 3: Selectivity of bnbozo Ligand

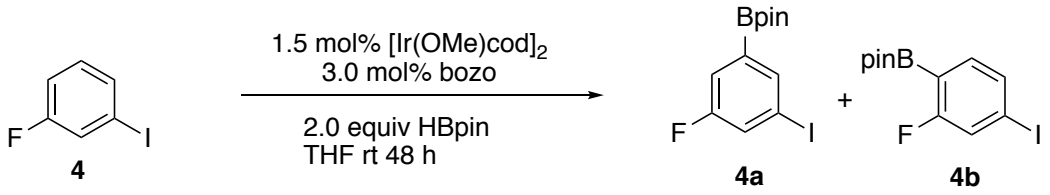


1.0 mmol

ratio of crude material by GC 1:1.3
2% conversion

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-fluorobromobenzene (0.222 g, 117 μL, 1.0 mmol, 1.0 equiv) was taken up by pipettor and added into the stirring mixture in the vial. Additional THF (1.0 mL) was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. After 48 h, only 2% conversion was seen by GC-FID and ^{19}F NMR. A ratio of 1:1.3 **4a**:**4b** was seen by ^{19}F NMR. Due to low conversion product was not isolated.

Table 2.4, Entry 3: Selectivity of bozo Ligand

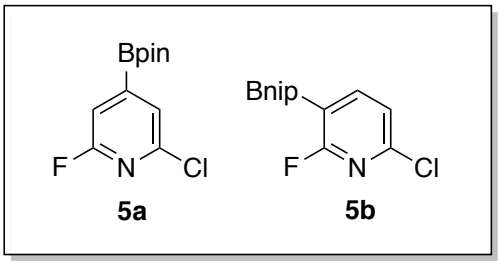


1.0 mmol

ratio of crude material by GC 1:2.6
30 % conversion

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stirring bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. 2,2'-Bis(2-oxazoline) (box) was weighed into a test tube (5 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-fluoroiodobenzene (0.222 g, 117 μL, 1.0 mmol, 1.0 equiv) was taken up by pipettor and added into the stirring reaction vial. Additional THF (1.0 mL) was added for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. After 48 h, 30% conversion was seen by GC-FID and ^{19}F NMR. A ratio of 1: 2.6 **4a**:**4b** was seen by ^{19}F NMR. Due to low conversion, the products were not isolated.

Table 2.4, Entry 4

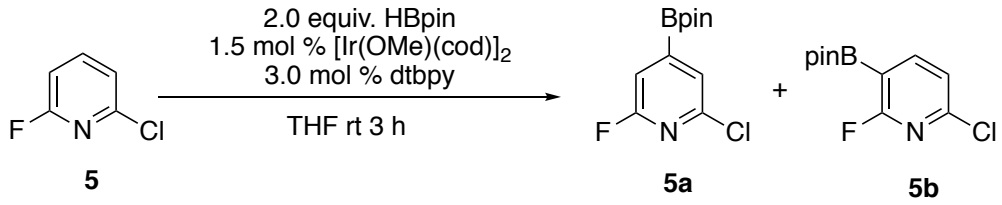


Characterization of 5a and 5b.

Steric isomer 5a: ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.54 (d, *J* = 1.7 Hz, 1H), 7.18 (d, *J* = 2.6 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 162.2 (d, J = 247.6), 148.5 (d, *J* = 12.3 Hz), 126.4 (d, *J* = 4.5 Hz), 112.7 (d, *J* = 33.2 Hz), 85.2, 24.8. C4 adjacent to Boron is not visible due to quadrupolar relaxation. ^{19}F NMR (470 MHz; $CDCl_3$): δ -67.4. ^{11}B NMR (160 MHz; $CDCl_3$): δ 29.6. **Electronic isomer 5b**: ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.09 (t, *J* = 7.9 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.7 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 165.8 (d, J = 251.6), 157.4 (d, J = 7.6 Hz), 151.9 (d, J = 14.8 Hz), 121.3 (d, J = 4.8 Hz), 84.6, 24.8. C5 adjacent to Boron is not visible due to quadrupolar relaxation. ^{19}F NMR (470 MHz; $CDCl_3$): δ -56.0 (d, J = 7.8 Hz). ^{11}B NMR (160 MHz; $CDCl_3$): δ 29.7. The assigned structures of **5a** and **5b** are also consistent with H-F coupling constants in ^{1}H spectra and chemical shifts in ^{19}F NMR spectra. For detailed information regarding H-F coupling constants in substituted fluoro-pyridines, see the following reference.[12]

CHN anal. calcd C, 51.31; H, 5.48; N, 5.44; found C, 51.49; H, 5.89; N, 5.44. HRMS (ESI+) (*m/z*) calcd for $C_{11}H_{15}BClFNO_2$ [M+H]+ 258.0868, found 258.0872. The structure of steric isomer 5**a** was confirmed by single crystal X-Ray diffraction. The CIF file is available for download from the CCDC and may be referenced by CCDC deposition # 1434792.

Table 2.4: Entry 4: Borylation with dtbpy as ligand.

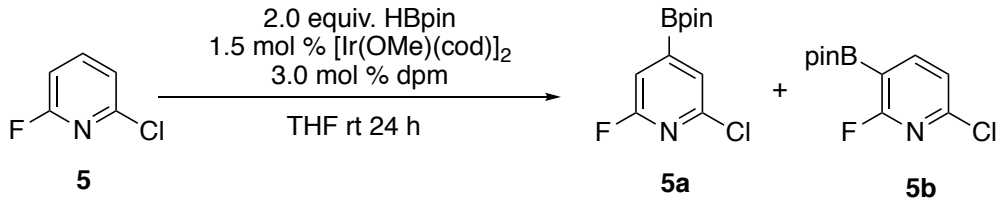


1.0 mmol

ratio of crude material by GC 6.5:1
isolated yield 71% (8:1)

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). THF (1.0 mL) was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added. 4,4'-di-t-butyl-2,2'-bipyridine (dtbpy) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol %), and the ligand was added to the vial as a solid. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 2-chloro-6-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box. The reaction was monitored by GC and judged complete after 3 hours. The volatiles were removed by rotary evaporation to yield brown oil. The crude ratio of borylated isomers was determined by GC and ^{19}F NMR to be 6.5:1 **5a**:**5b**. The crude material was dissolved in hexane and passed through a 3g silica plug eluting with hexanes, yielding 183 mg of white solid that was determined to be an 8:1 mixture of **5a**:**5b** by ^{19}F NMR. (71% yield)

Table 2.4: Entry 4: Borylation with dpm ligand.

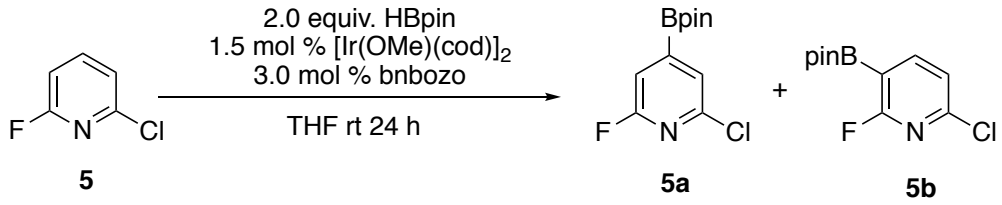


1 mmol

crude ratio 23 : 1
isolated yield: 91% 22:1 mixture

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred into the vial with a Pasteur pipette. The vial was rinsed with 0.5 mL THF and the rinse was added to the vial. 2-chloro-6-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 3 g silica plug to afford 231 mg of the corresponding borylated product as a white solid determined by ^{19}F NMR to be a 22:1 mixture. (91% yield of mixture).

Table 2.4: Entry 4 Borylation with bnbozo as ligand:

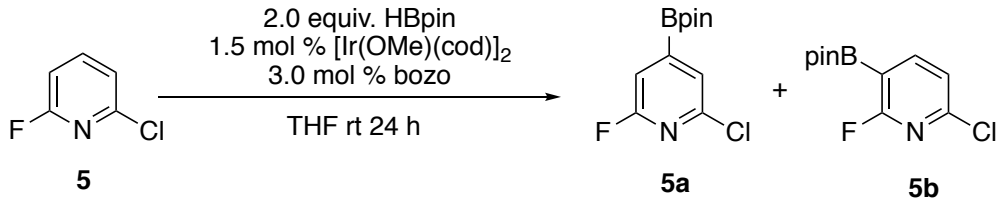


1.0 mmol

crude ratio 4.5 : 1
76% isolated yield 5:1 mixture

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 2-chloro-6-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After completion of the reaction, the volatile materials were removed on a rotary evaporator. The crude material was dissolved in CH_2Cl_2 and passed through a short plug of silica to afford 183 mg of the corresponding borylated product as a white solid determined by ^{19}F NMR to be a 5:1 mixture.

Table 2.4: Entry 4 Borylation with bozo as ligand:

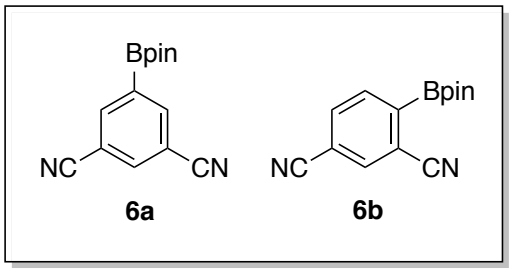


1.0 mmol

crude ratio 1.8: 1
isolated yield 77% 1.9 : 1 mixture

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stirring bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring. HBpin (290 μL, 254 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. 2,2'-Bis(2-oxazoline) (box) was weighed into a test tube (5 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 2-chloro-6-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a short plug of silica to afford 198 mg of a colorless oil determined by ^{19}F NMR to be a mixture of 1.9:1 borylated products and 10% starting material. (77% isolated yield of products when corrected for mass of recovered starting material).

Table 2.4, Entry 5:

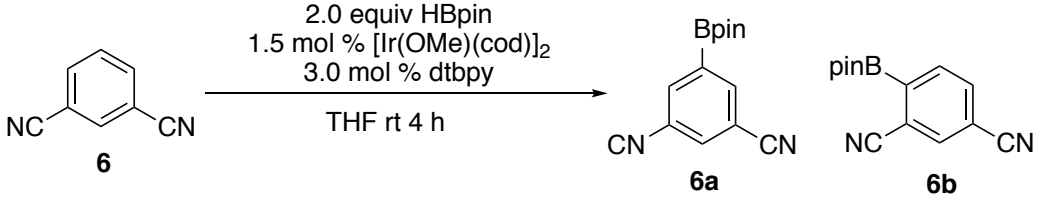


Characterization of 6a and 6b.

Steric Isomer 6a: ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.25 (d, *J* = 1.6 Hz, 2H), 7.96 (t, *J* = 1.6 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 141.8, 137.1, 116.7, 113.6, 85.2, 24.8. Carbon adjacent to Boron is not visible due to quadrupolar relaxation. ^{11}B (160 MHz; $CDCl_3$): δ 29.8. **6a** was isolated as a white solid, mp 105 – 107 °C.

Electronic isomer 6b: ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 0.8 Hz, 1H), 7.81 (dd, *J* = 7.8, 1.5 Hz, 1H), 1.37 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 136.6, 136.1, 134.4, 118.6, 116.8, 116.7, 115.3, 85.5, 24.7. Carbon adjacent to Boron is not visible due to quadrupolar relaxation.^{11}B (160 MHz; $CDCl_3$): δ 30.0.

Table 2.4, Entry 5: Borylation with dtbpy as ligand



0.1 mmol
well plate reaction

ratio of crude material by ^{1}H NMR 4.5:1

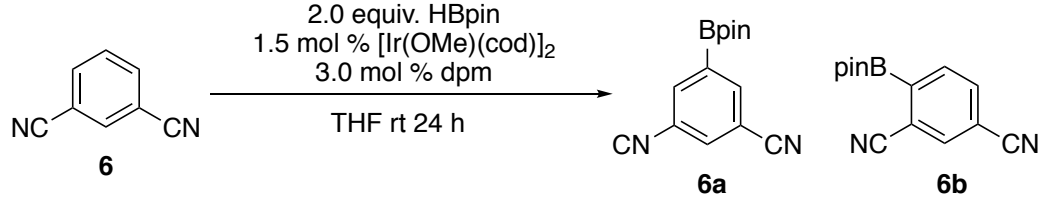
The ratio under the standard conditions of Table 3 was determined in well plate screening tests and is an average of 4 runs. A photoredox / catalysis 96 well plate was filled with 96 glass shell vials (750 μL 8 x 30 mm). Vials in wells were equipped with micro stir bars. Reagents were

made as stock solutions in 5 or 10 mL volumetric flasks as indicated. A 0.03 M stock solution of $[Ir(OMe)cod]_2$ was made by dissolving 0.100 g of the catalyst in 5.0 mL THF. A 0.06 M stock solution of dtbpy was made by dissolving 0.081 g of the ligand in 5.0 mL THF. A 0.5 M stock solution of 1,3-dicyanobenzene was made by dissolving 0.64 g of the substrate in 10.0 mL THF.

In the glove box, while stirring on a stir plate, 50 μL 0.03M $[Ir(OMe)cod]_2$ stock solution (1.5 μmol, 1.5 mol %) was added into selected wells by pipettor. 30 μL HBpin (0.2 mmol, 2 equiv.) was added into the same wells by pipettor. 50 μL of dtbpy solution was added by pipettor into the same wells as the previous reagents. The mixtures were stirred 5 minutes, then 200 μL of a 0.5 M stock solution of the substrate, 1,3-dicyanobenzene, (0.1 mmol, 1.0 equiv) was added into the same wells. 50 μL THF was then added to each well in order to make the volume up to 0.35 mL. A plastic liner was placed over the vials and the top of the plate was screwed shut. The reactions were stirred for 24 h, then analyzed by GC and NMR.

The contents of each well were removed and concentrated separately. Each well's crude material was weighed then dissolved in $CDCl_3$ for NMR analysis. Crude ^1H NMR ratios were determined to be 4.5:1 as an average of 2 duplicates over 2 different well plate trials. The spectroscopic data of **6a** and **6b** were consistent with literature values previously reported by the authors.[13]

Table 2.4, Entry 5: Borylation with dpm as ligand.



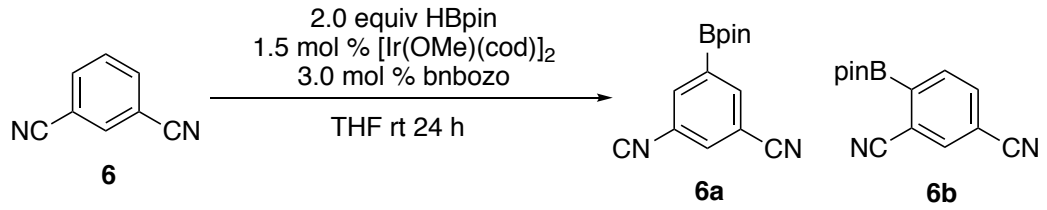
1.0 mmol

ratio of crude material ^1H NMR 12:1
isolated yield 74% **6a**

Just prior to the reaction, the substrate was freshly sublimed and dpm ligand was passed through a short plug of activated alumina. In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF was added (1.0 mL) with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added into the light-yellow solution, which deepened to a clear gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol%) and dissolved in 0.5 mL THF. The solution was transferred into the vial with a Pasteur pipette. The vial was rinsed with 0.5 mL THF and the rinse was added to the vial. 1,3-dicyanobenzene (0.128 g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After completion of the reaction, the volatile materials were removed by rotary evaporation. The conversion was determined by crude ^{1}H NMR to be 94% with a ratio of 12:1. The crude material was dissolved in CH_2Cl_2 and passed through a 2 g plug of silica to afford the corresponding borylated product as a white solid determined by ^{1}H NMR to be a 12:1 mixture of borylated isomers **6a**:**6b**, containing 6% starting material. The mixture was subjected to kugelrhor distillation under reduced pressure of 1 torr and heating to 50°C. One bulb was positioned inside the oven and another bulb was cooled with dry ice outside the oven. Starting material, all of the minor isomer and a small amount of major isomer were removed to the outer bulb, to leave 189 mg (74% isolated yield, m.p. 105-107°C) of a white solid in the distillation pot that was determined to be pure **6a** by ^{1}H NMR.

Table 2.4, Entry 5: Borylation with bnbozo as ligand.



0.1 mmol
well plate reaction

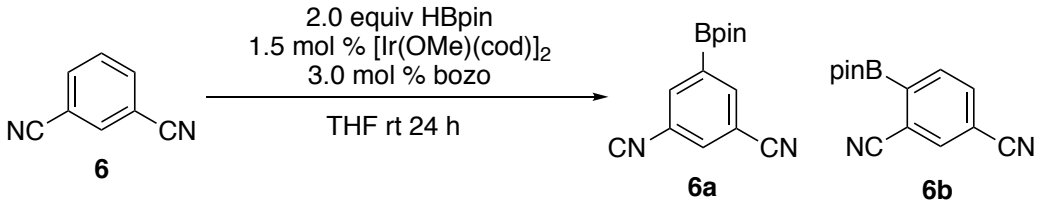
ratio of crude material by ^{1}H NMR 3:1
5% conversion

The ratio under the standard conditions of Table 3 was determined in well plate screening tests and is an average of 4 runs. A photoredox / catalysis 96 well plate was filled with 96 glass shell vials (750 μL 8 x 30 mm). Vials in wells were equipped with micro stir bars. Reagents were made as stock solutions in 5 or 10 mL volumetric flasks as indicated. A 0.03 M stock solution of $[Ir(OMe)cod]_2$ was made by dissolving 0.100 g of the catalyst in 5.0 mL THF. A 0.06 M stock solution of bnbozo was made by dissolving 0.096 g of the ligand in 5.0 mL THF. A 0.5 M stock solution of 1,3-dicyanobenzene was made by dissolving 0.64g of the substrate in 10.0 mL THF.

In the glove box, while stirring on a stir plate, 50 μL 0.03M $[Ir(OMe)cod]_2$ stock solution (1.5 μmol, 3.0 mol% Ir) was added into selected wells by micro-syringe. 30 μL HBpin (0.2 mmol, 2 equiv) was added into the same wells by micro-syringe. 50 μL of bnbozo solution was added with a micro-syringe into the same wells as the previous reagents. The mixtures were allowed to stir 5 minutes, then 200 μL of a 0.5 M stock solution of the substrate, 1,3-dicyanobenzene, (0.1 mmol, 1.0 equiv) was added into the same wells. 50 μL THF was then added to each well in order to make the volume up to 0.35 mL. A plastic liner was placed over the vials and the top of the plate was screwed shut. The reactions were stirred for 24 h, then analyzed by GC and NMR.

The contents of each well were removed and concentrated separately. Each well's crude material was weighed then dissolved in $CDCl_3$ for NMR analysis. Crude ^1H NMR ratios were determined to be 3:1 **6a**:**6b** as an average of 2 duplicates over 2 different well plate trials. Very low conversion was observed in all cases, and it was determined that bnbozo is not an active enough ligand to be of practical use for the borylation of this substrate.

Table 2.4, Entry 5: Borylation with bozo as ligand.



0.1 mmol
well plate reaction

ratio of crude material by ^1H NMR 1.5:1
5% conversion

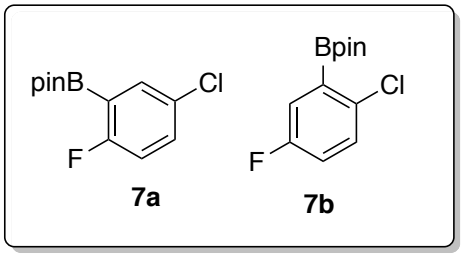
The ratio under the standard conditions of Table 3 was determined in well plate screening tests and is an average of 4 runs. A photoredox / catalysis 96 well plate was filled with 96 glass shell vials (750 μL 8 x 30 mm). Vials in wells were equipped with micro stir bars. Reagents were made as stock solutions in 5 or 10 mL volumetric flasks as indicated. A 0.03 M stock solution of $[Ir(OMe)cod]_2$ was made by dissolving 0.100 g of the catalyst in 5.0 mL THF. A 0.03 M stock solution of was made by dissolving 0.042 g of the ligand bozo in 10.0 mL THF. A 0.5 M stock solution of 1,3-dicyanobenzene was made by dissolving 0.64g of the substrate in 10.0 mL THF.

In the glove box, while stirring on a stir plate, 50 μL 0.03M $[Ir(OMe)cod]_2$ stock solution (1.5 μmol, 3 mol% Ir) was added into selected wells by micro-syringe. 30 μL HBpin (0.2 mmol, 2 equiv) was added into the same wells by micro-syringe. 100 μL of bozo solution was added with a micro-syringe into the same wells as the previous reagents. The mixtures stirred 5 minutes, then 200 μL of a 0.5 M stock solution of the substrate, 1,3-dicyanobenzene, (0.1 mmol, 1.0 equiv) was

added into the same wells. Total volume of THF in each well was 350 μL. A plastic liner was placed over the vials and the top of the plate was screwed shut. The reactions were stirred for 24 h, then analyzed by GC and NMR.

The contents of each well were removed and concentrated separately. Each well's crude material was weighed then dissolved in $CDCl_3$ for NMR analysis. Crude ^1H NMR ratios were determined to be 1.5:1 **6a**: **6b** as an average of 2 duplicates over 2 different well plate trials. Very low conversion was observed in all cases, and it was determined that bozo is not an active enough ligand to be of practical use for the efficient borylation of this substrate.

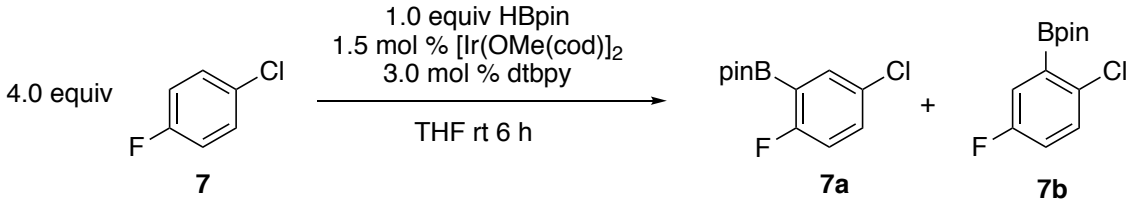
Table 2.4, Entry 6



Characterization of 7a

^1H NMR ($CDCl_3$ 500 MHz) δ 7.66 (dd, J = 4.9, 2.9 Hz, 1H); 7.32-7.36 (m, 1H); 6.96 (t, J = 8.3 Hz, 1H) 1.33 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.5 136.2, 133.0, 128.9, 116.8, 84.2, 24.8. ^{11}B NMR (96 MHz) δ 29.6. **7a** was isolated as a white solid, mp 75 – 76 °C.

Table 2.4, Entry 6: Selectivity of dtbpy ligand.



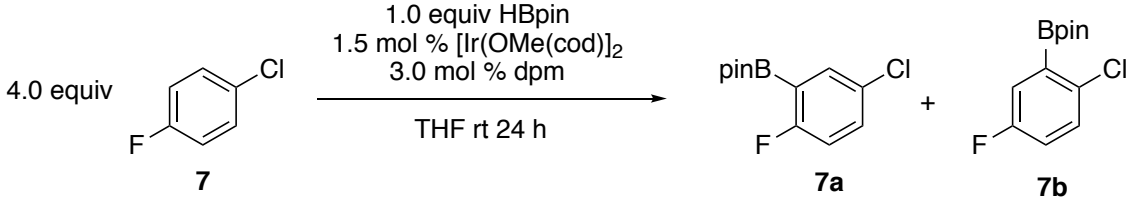
1.0 mmol

ratio of crude material by GC 32:1
isolated yield 68% **7a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (145 μL, 128 mg, 1.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 4,4'-Di-t-butyl-2,2'-bipyridine (dtbpy) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. p-Fluorochlorobenzene, **7**, (522 mg, 426 μL, 4.0 mmol, 4.0 equiv) was added last into the stirring mixture by automatic pippetor. THF (1.0 mL) was added to the reaction vial for a total volume of 3.0 mL solvent. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 6 hours.

After 6 h, complete conversion to products was determined by ^{19}F NMR (75% **7** is equivalent to complete conversion at a 4-fold excess of substrate) and ^{11}B NMR by absence of HBpin. GC-FID ratio of products was 32:1. The volatile materials were removed by rotary evaporation, and the reaction was pumped down under high vac to remove excess starting material. The crude material was dissolved in CH_2Cl_2 and passed through a 5 g silica plug to afford 163 mg of single isomer **7a**, as a whilte solid, mp 75 – 76 °C.

Table 2.4, Entry 6: Borylation with dpm as ligand



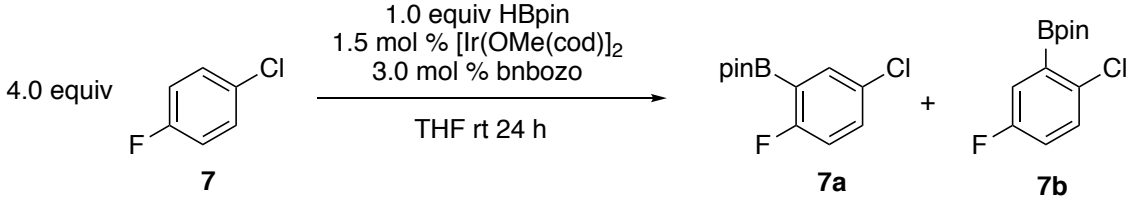
1.0 mmol

ratio of crude material by GC 38:1
isolated yield 64% **7a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (145 μL, 128 mg, 1.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. Dipyridyl methane (dpm) was weighed into a gc vial (5 mg, 0.03 mmol, 3 mol %), and dissolved in 05. mL THF. The mixture was transferred into the reaction vial by Pasteur pipette. The vial was rinsed with 0.5mL THF, and the rise was added to the reaction vial. The mixture turned bright orange. p-Fluorochlorobenzene, **7**, (522 mg, 426 μL, 4.0 mmol, 4.0 equiv) was added last into the stirring mixture by automatic pipettor. THF (1.0 mL) was added to the reaction vial for a total volume of 3.0 mL solvent. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 6 h, 90% conversion to products was determined by ^{19}F NMR (77.5% **7** is equivalent to 90% conversion at a 4-fold excess of substrate). ^{11}B NMR showed a trace of HBpin. GC-FID ratio of products was 38:1. The volatile materials were removed by rotary evaporation, and the reaction was pumped down under high vac to remove excess starting material. The crude material was dissolved in CH_2Cl_2 and passed through a 5 g silica plug to afford 175 mg of single isomer **7a** as a white solid, mp -75-77 °C. (64% yield).

Table 2.4, Entry 6: Selectivity of bnbozo ligand.



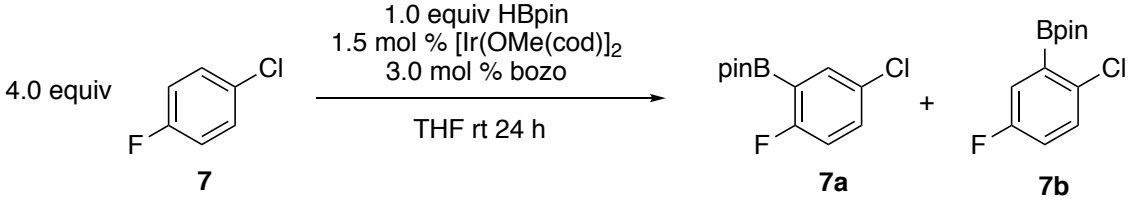
1.0 mmol

ratio of crude material by GC >99:1
isolated yield 89% **7a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (145 μL, 128 mg, 1.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %), and the ligand was added to the vial as a solid. The mixture turned cherry red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. p-Fluorochlorobenzene, **7**, (522 mg, 426 μL, 4.0 mmol, 4.0 equiv) was added last into the stirring mixture by automatic pipettor. THF (1.0 mL) was added to the reaction vial for a total volume of 3.0 mL solvent. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 6 h, complete conversion to products was determined by ^{19}F NMR (75% **7** is equivalent to complete conversion at a 4-fold excess of substrate) and ^{11}B NMR by absence of HBpin. GC-FID ratio of products was >99:1. The minor isomer was below integration threshold and was not seen in the NMR. The volatile materials were removed by rotary evaporation, and the reaction was pumped down under high vac to remove excess starting material. The crude material was dissolved in CH_2Cl_2 and passed through a 5 g silica plug to afford 229 mg of single isomer **7a** as a white solid, mp 75-76°C. (89% yield).

Table 2.4, Entry 6: Selectivity of bozo ligand.



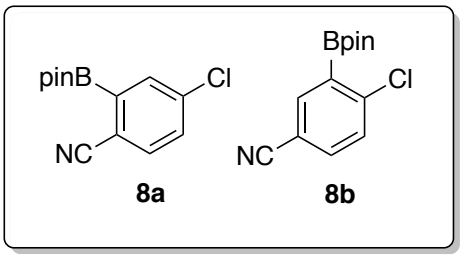
1.0 mmol

ratio of crude material by GC 27:1
isolated yield 70% **7a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (145 μL, 128 mg, 1.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2′-Bis -2-oxazoline (bozo) was weighed into a test tube (4 mg, 0.03 mmol, 3 mol %), and the ligand was added to the vial as a solid. The mixture turned cherry red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. p-Fluorochlorobenzene, **7**, (522 mg, 426 μL, 4.0 mmol, 4.0 equiv) was added last into the stirring mixture by automatic pipettor. THF (1.0 mL) was added to the reaction vial for a total volume of 3.0 mL solvent. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 6 h, 92% conversion to products was determined by ^{19}F NMR (78% **7** is equivalent to complete conversion at a 4-fold excess of substrate) and ^{11}B NMR showed a trace of HBpin. GC-FID ratio of products was 27:1. The volatile materials were removed by rotary evaporation, and the reaction was pumped down under high vac to remove excess starting material. The crude material was dissolved in CH_2Cl_2 and passed through a 5 g silica plug to afford 180 mg of single isomer **7a** as a white solid, mp 75-76°C. (70% yield)

Table 2.4, Entry 7

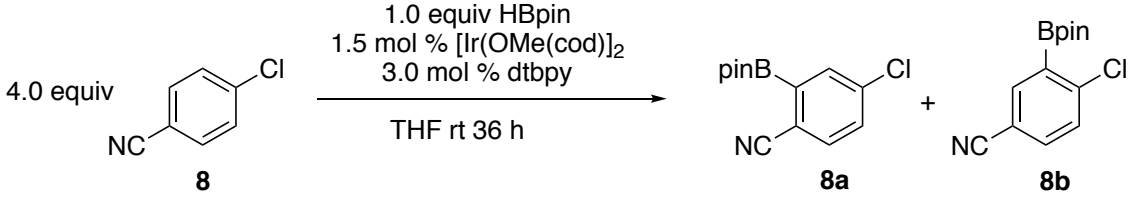


Characterization of 8a and 8b

Steric isomer 8a: ^{1}H NMR ($CDCl_3$ 300 MHz) δ 7.80 (d, J = 2 .2 Hz, 1H); 7.57 (d, J = 8.3 Hz, 1H); 7.57 (dd, J = 8.3 Hz, 1H) 1.33 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.5, 135.8, 134.5, 131.2, 118.0, 115.3, 85.0, 24.0. Carbon adjacent to Boron is not visible due to quadrupolar relaxation. ^{11}B NMR (96 MHz) δ 26.9.

Electronic isomer 8b: ^{1}H NMR ($CDCl_3$ 300 MHz) δ 7.94(d, J = 2 .2 Hz, 1H); 7.56 (d, J = 8.3 Hz, 1H); 7.41 (dd, J = 8.3 Hz, 1H) 1.32 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ144.5, 140.1, 134.6, 130.2, 117.8, 110.2, 84.7, 24.6. Carbon adjacent to Boron is not visible due to quadrupolar relaxation.^{11}B NMR (96 MHz) δ26.9.

Table 2.4, Entry 7: Borylation with dtbpy as ligand.

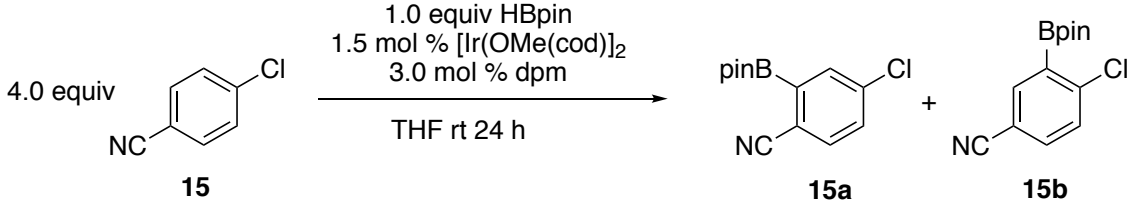


1.0 mmol

ratio of crude material by GC 4:1
isolated yield 76% (4:1)

The borylation of p-chlorobenzonitrile using dtbpy as the ligand was previously reported by the authors,[13] and is included here for comparison. The spectroscopic data was consistent with reported literature values from the reference above.

Table 2.4, Entry 7: Borylation with dpm as ligand.



1.0 mmol

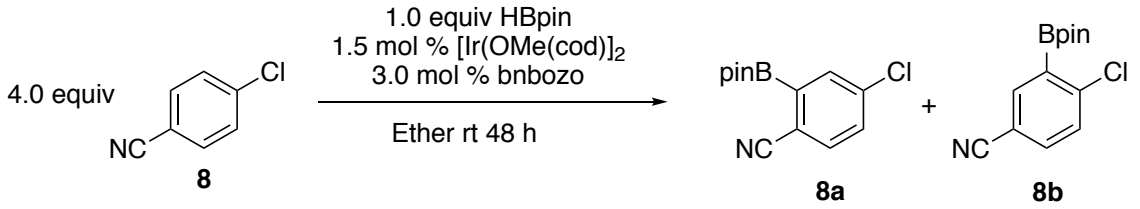
ratio of crude material by GC 5.6:1
calculated 10% isolated products (5.6:1)

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (145 μL, 128 mg, 1.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred into the vial with a Pasteur pipette, and the reaction mixture turned a bright orange color. The vial was rinsed with 0.5 mL THF and the rinse was added to the vial. p-Chlorobenzonitrile (550.3 mg, 4.0 mmol, 4.0 equiv) was weighed into a vial and added last as a solid into the stirring mixture in the reaction vial. The weighing vial was rinsed with 1.0 mL of THF and the rinse was added to the reaction vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, 60% conversion to products was determined by GC. The volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 5 g silica plug to afford 501 mg of a mixture of the corresponding borylated products and excess starting material as a white solid. Attempts to separate the starting material and borylated products by column chromatography failed. The ratio of starting material to borylated products in the

isolated material was determined by ^{1}H NMR to be 10%, thus the mass of borylated product calculated by mol fraction was 28 mg, which corresponds to a 10% isolated yield of products. The ratio of isomers was confirmed through repeated experiments, however moderate to poor conversions hampered attempts to isolate pure product mixtures from the large excess of starting material. Dpm was determined to be unsuitable for the efficient borylation of this substrate.

Table 2.4, Entry 7: Borylation with bnbozo as ligand.



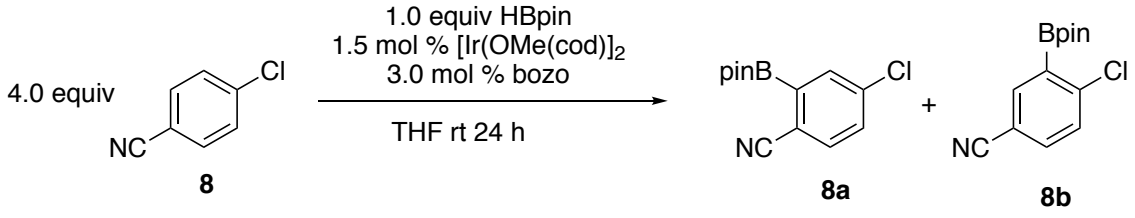
1.0 mmol

ratio of crude material by GC 13:1
60% isolated yield 13:1

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). Diethyl ether (1.0 mL) was added with stirring and a clear yellow solution resulted. HBpin (145 μL, 128 mg, 1.0 mmol, 1.0 equiv) was added by micro syringe into the light yellow solution, which deepened to a clear gold color. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture, and the mixture turned a cherry red color. The vial was rinsed with 1.0 mL diethyl ether and the rinse was added to the vial. p-Chlorobenzonitrile (550 mg, 4.0 mmol, 4.0 equiv) was weighed into vial and added last as a solid into the stirring mixture in the reaction vial. The weighing vial was rinsed with 1.0 mL of diethyl ether and the rinse was added to the reaction vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After completion of the reaction, the volatile materials were removed on a rotary evaporator. The crude material was dissolved in CH_2Cl_2 and passed through a 10g plug of silica to afford a mixture of the corresponding borylated product and starting material as a white solid. The starting material was removed by kugelrohr distillation under reduced pressure of 1 torr and heating to 50°C to leave 158 mg of a white powder that was determined by ^{1}H NMR to be a 13:1 mixture of borylated isomers (60% yield, m.p. 95 – 98 °C). Spectroscopic data were consistent with reported literature values.[13]

Table 2.4, Entry 7: Borylation with bozo as ligand.



1.0 mmol ratio of crude material by GC 4.5:1

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF (1.0 mL) was added with stirring and a clear yellow solution resulted. HBpin (145 μL, 128 mg, 1.0 mmol, 1.0 equiv) was added by micro syringe into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis(2-oxazoline) (bozo) was weighed into a test tube (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred into the vial with a Pasteur pipette, and the reaction mixture turned a cherry red color. The vial was rinsed with 0.5 mL THF and the rinse was added to the vial. p-Chlorobenzonitrile (550.3 mg, 4.0 mmol, 4.0 equiv) was weighed into a vial and added last as a solid into the stirring mixture in the reaction vial. The weighing vial was rinsed with 1.0 mL of THF and the rinse was added to the reaction vial for a total volume of 3.0 mL THF.

The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, conversion to products was determined by GC to be 54%. The volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 5 g silica plug to afford a mixture of the corresponding borylated product and excess starting material as a white solid. Attempts to separate the starting material and borylated products by column chromatography failed. The ratio of isomers was confirmed through repeated experiments, however moderate to poor conversions hampered attempts to isolate pure product mixtures from the large excess of starting material. Bozo was determined to be unsuitable for efficient borylation of this substrate.

Table 2.4, Entry 8

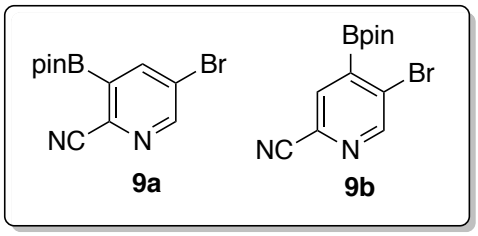
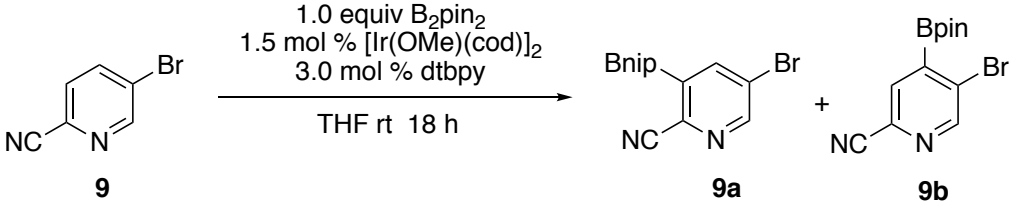


Table 2.4, Entry 8: Borylation with dtbpy as ligand.

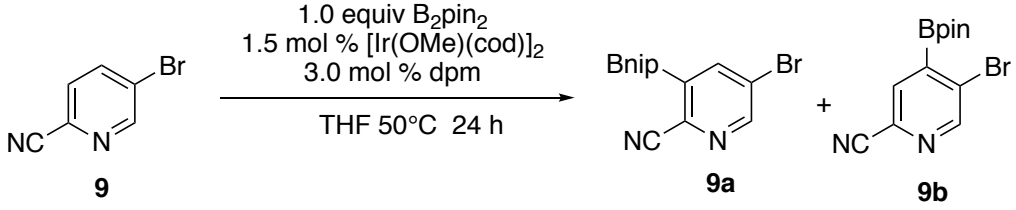


1.0 mmol

ratio of crude material by GC 2:1
isolated yield 81% (2:1)

The borylation of 5-bromopicolinonitrile using dtbpy as the ligand was previously reported by the authors,[13] and is included here for comparison. Spectral values of **9a** and **9b** were consistent with reported literature values from the above reference.

Table 2.4, Entry 8: Borylation with dpm as ligand.



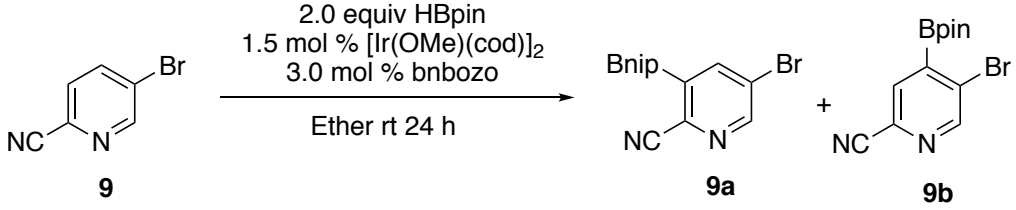
1.0 mmol

ratio of crude material 1:1
isolated yield 24% (1:1)

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF (1.0 mL) was added to the vial resulting in a clear yellow solution. HBPin (15 μL, 0.1 mmol, 1.0 equiv) was added to the yellow solution, which then deepened to a gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred by Pasteur pipette into the reaction vial. The GC vial was rinsed with 0.5 mL THF and the rinse was added to the reaction. B_2Pin_2 (256 mg, 1.0 mmol, 1.0 equiv) was weighed into a vial and added into the stirring reaction mixture as a solid. The weighing vial was rinsed with 1.0 mL THF and the rinse was added into the reaction. The resulting mixture was stirred until most solids dissolved. 5-bromopicolinonitrile (182 mg, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the reaction vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the reaction vial for a total volume of 3.0 mL solvent. The vial was closed with a screw cap and removed from the glove box. The reaction was allowed to stir with heating in a 50°Coil bath for 24 hours.

After 24 h, the reaction was stopped and the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 2 g silica plug to afford a mixture of the corresponding borylated product, starting material and unreacted B_2pin_2 as a white solid. Attempts to separate the starting material and borylated products by column chromatography, then crystallization failed. 200 mg of a mixture of borylated isomers and starting material remained. The borylated products in the isolated material were determined by ^1H NMR to be 50% of the mixture, thus the mass of borylated products calculated by mol fraction was 74 mg, which corresponds to a 24% isolated yield of products. The ratio of isomers was confirmed through repeated experiments, however incomplete conversion hampered the separation of residual starting material. Dpm was determined to be unsuitable for efficient borylation of this substrate.

Table 2.4, Entry 8: Borylation with bnbozo as ligand.



9 **9a** **9b**

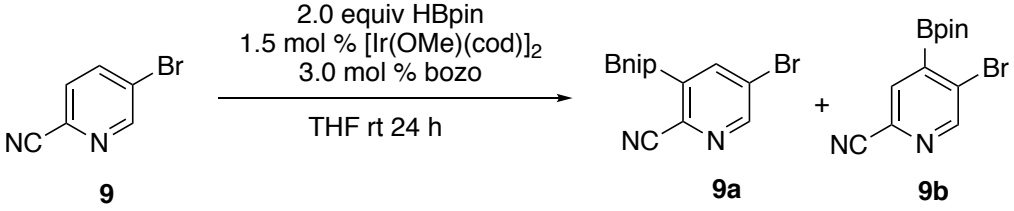
1.0 mmol

ratio of crude material by GC 13:1
isolated yield 74% (16:1)

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). Diethyl ether (1.0 mL) was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added into the light-yellow solution, which deepened to a clear gold color. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The reaction turned a cherry red color.

The vial was rinsed with 1.0 mL diethyl ether and the rinse was added to the vial. 5-Bromopicolinonitrile (0.182g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of diethyl ether and the rinse was added to the vial for a total volume of 3.0 mL solvent. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 2 g plug of silica to afford 266 mg of the corresponding borylated product mixed with starting material. The isolated material was subjected to kugelrohr distillation at reduced pressure of 1 torr heating to 50°C, which removed starting material and some minor isomer to leave 227 mg white solid that was 16:1 **9a**:**9b** by ^{1}H NMR (74% yield, m.p. = 125 – 130 °C). Spectral data was consistent with the reported literature values for **9a** and **9b**[13].

Table 2.4, Entry 8: Borylation with bozo as ligand.



1.0 mmol

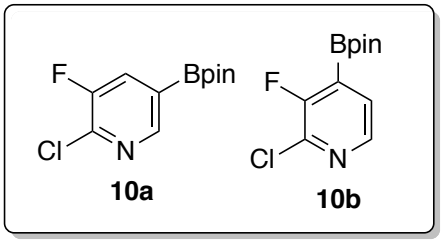
ratio of crude material by GC 2.8:1
isolated yield 77% (2.8:1)

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF was added (1.0 mL) with stirring and a clear yellow solution resulted. HBPin (15 µL, 0.1 mmol, 0.1 equiv) was added to the yellow solution, which then deepened to a gold color. 2,2'-Bis(2-oxazoline) (**bozo**) was weighed into a test tube (5 mg, 0.03 mmol, 3 mol %) and added as a solid into the mixture. The test tube

was rinsed with 1.0 mL THF and the rinse was added to the reaction. The reaction turned a cherry red color. B_2Pin_2 (256 mg, 1.0 mmol, 1.0 equiv) was weighed into a vial and added into the stirring reaction mixture as a solid. The weighing vial was rinsed with 1.0 mL THF and the rinse was added into the reaction. The reaction was allowed to stir about 5 minutes until most solids were dissolved. 5-Bromopicolinonitrile (183 mg, 1.0 mmol, 1.0 equiv) was weighed into a vial and added last as a solid into the stirring mixture in the reaction vial. The weighing vial was rinsed with 1.0 mL of THF and the rinse was added to the reaction vial for a total volume of 3.0 mL solvent. The vial was closed with a screw cap and brought out of the glove box. The reaction was allowed to stir closed in a 50°C oil bath for 24 hours. After 24 h, complete conversion to products was observed by GC.

After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 2g plug of silica to afford 230 mg of a white solid determined by ^{1}H NMR to be a 2.8:1 mixture of the borylated isomers **9a**:**9b** (77% yield, m.p. = 109 – 116 °C).

Table 2.4, Entry 9



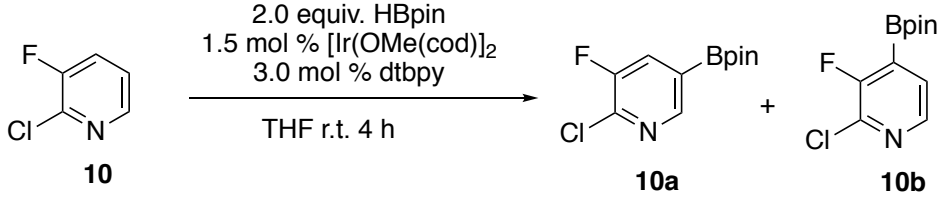
Characterization of 10a and 10b:

Steric isomer 10a: ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.49 (t, *J* = 1.2 Hz, 1H), 7.77 (dd, *J* = 8.4, 1.5 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 154.5 (d, J = 261.4 Hz); 150.4 (d, *J* = 6.2 Hz), 141.7 (d, J = 19.3 Hz); 129.7 (d, *J* = 17.1 Hz), 84.8, 24.8. C5 adjacent to Boron is not

visible due to quadrupolar relaxation. ^{19}F NMR (470 MHz; $CDCl_3$): δ -120.3 (d, J = 8.4 Hz). ^{11}B NMR (160 MHz; $CDCl_3$): δ 30.1. Identity of **10a** was confirmed by CHN analysis, HMRS and crystal structure of purified isomer material. The CIF file of **10a** is available for download from the CCDC, and may be referenced by the CCDC deposition # 1434794.

Electronic isomer 10b: Spectroscopic data were consistent with reported literature values, which were obtained from the synthesis of **10b** from corresponding commercial boronic acid and pinacol.[14] ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.18 (dd, J = 4.6, 0.9 Hz, 1H), 7.50 (dd, J = 4.5, 3.9 Hz, 1H), 1.35 (s, 12H). ^{13}C NMR (126 MHz $CDCl_3$): δ 158.0 (d, J = 265.1 Hz); 144.1 (d, J = 6.4 Hz), 139.3 (d, J = 21.9 Hz); 128.9 (d, J = 3.0 Hz), 85.0, 24.8. C4 adjacent to Boron is not visible due to quadrupolar relaxation. ^{19}F NMR (470 MHz; $CDCl_3$): δ -109.4 (d, J = 3.2 Hz). ^{11}B NMR (160 MHz; $CDCl_3$): δ 29.4. The identity of **10b** was confirmed by CHN analysis, HMRS and a crystal structure of the purified isolated isomer. CHN anal. calcd. C, 51.31; H, 5.48; N, 5.44; found: C, 51.29; H, 5.66, N, 5.38. HRMS (ESI+) (*m/z*) calcd for $C_{11}H_{15}BClFNO_2$ [M+H]+ 258.0868, found 258.0883. The CIF file of **10b** is available for download from the CCDC, and may be referenced by the CCDC deposition # 1434793.

Table 2.4, Entry 9: Borylation with dtbpy as ligand



10 **10a** **10b**

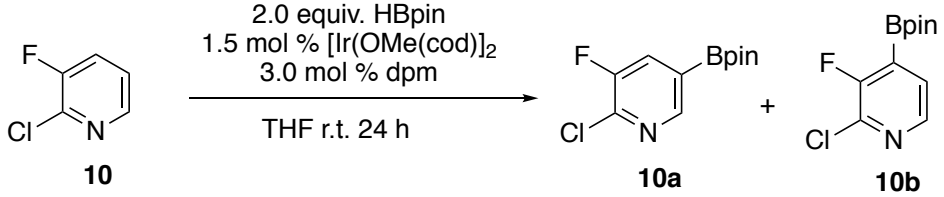
1.0 mmol

ratio of crude material by GC 1:1.6
isolated yield 77% (1:1.6)

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). THF was added (1.0 mL) with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was

added by into the light-yellow solution, which deepened to a clear gold color. 4,4'-Di-t-butyl-2,2'-bipyridine (dtbpy) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 2-Chloro-3-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the vial. Additional THF (1.0 mL) was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box. The reaction was monitored by GC and judged complete after 3 hours. The volatiles were removed by rotary evaporation to yield a brown oil. The crude ratio was determined by GC and ^{19}F NMR to be 1:1.6 **10a**:**10b**. The crude material was dissolved in CH_2Cl_2 and passed through a 2g silica plug, yielding 199 mg of white solid that was determined to be an 1:1.6 mixture **10a**:**10b** by GC and ^{19}F NMR. (77% isolated yield of mixture, m.p. = 85 – 87°C).

Table 2.4, Entry 9: Borylation with dpm as ligand



10 1.0 mmol

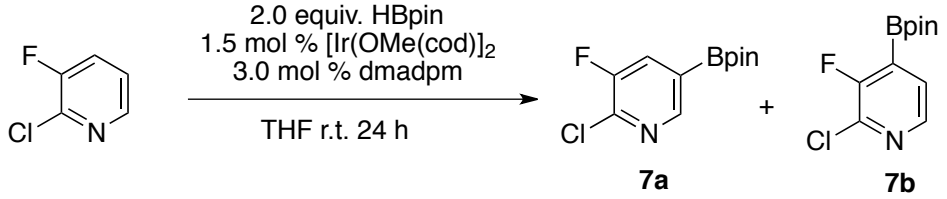
10a **10b** crude ratio 1.5:1
isolated yield 30% 3:1

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (190 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by micro syringe into the light-yellow solution, which deepened to a clear gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred into the vial with a Pasteur pipette, and the

reaction mixture turned a bright orange color. The vial was rinsed with 0.5 mL THF and the rinse was added to the vial. 2-Chloro-3-fluoropyridine (131 mg, 1.0 mmol, 1.0 equiv) was weighed into a vial and added last as a solid into the stirring mixture in the reaction vial. The weighing vial was rinsed with 1.0 mL of THF and the rinse was added to the reaction vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, conversion to products was determined by ^{19}F NMR to be 68%. The volatile materials were removed by rotary evaporation. The crude material was dissolved in hexanes and applied to a 3 g silica plug. Starting material was eluted off with hexanes then the solvent was changed to 1:1 CH_2Cl_2 / hexanes. The mix of borylated isomers then eluted to yield 78 mg of a white solid that was determined by ^{19}FNMR to be a 3:1 mixture of isomers. (30% yield, mp 85 – 87°C).

Table 2.4, Entry 9: Borylation with bnbozo as ligand



1.0 mmol

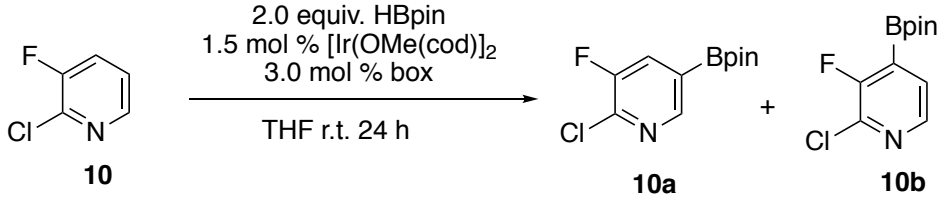
crude ratio 1:4.5
isolated yield 45% 1:5

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF

and the rinse was added to the vial. 2-Chloro-3-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. Conversion to products after 24 hours was determined by ^{19}F NMR to be 58%

After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 3 g silica plug to yield a pale yellow oil that was a mixture of isomers and starting material. The starting material was removed by high vacuum to leave 115 mg white solid that was determined by ^{19}FNMR to be a 1:5 mixture of isomers. (45% yield, mp 85-90°C).

Table 2.4, Entry 9: Borylation with bozo as ligand.



10 1.0 mmol

10a **10b** crude ratio 1:8.5
isolated yield 66% 1:9

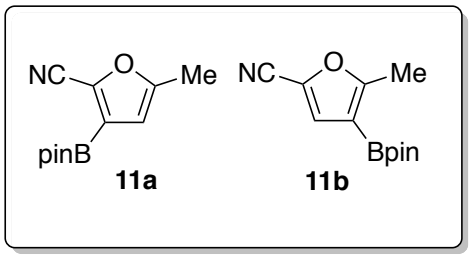
In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stirring bar was charged with [Ir(OMe)(COD)]$_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis(2-oxazoline) (bozo) was weighed into a test tube (5 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 2-Chloro-3-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0

mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After 24 hours, 85% conversion to products was observed by ^{19}F NMR.

After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a short plug of silica to afford 170 mg of a white crystalline solid determined by ^{19}F NMR to be a 1:9 mixture of borylated isomers (66% yield). The isolated material was recrystallized twice from hexanes to furnish material suitable for single crystal x-ray diffraction of **7b**.

Table 2.5: 5-Membered Heterocycles with F and CN Substituents

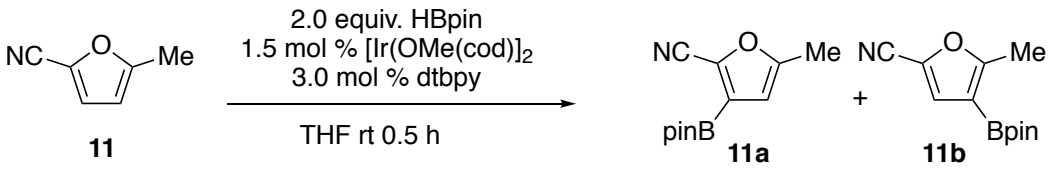
Table 2.5: Entry 1



Characterization of 11a and 11b

Major isomer 11a: ^{1}H NMR (500 MHz; $CDCl_3$): δ 6.26 (d, *J* = 0.9 Hz, 1H), 2.32 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 157.7, 130.5, 111.5, 84.5, 24.7, 13.5. ^{11}B NMR (160 MHz; $CDCl_3$): δ 28.8. **19a** was isolated as a white crystalline solid, mp 89 – 90 °C. **Minor isomer 11b**: ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.14 (s, 1H), 2.47 (s, 3H), 1.27 (s, 12H). ^{13}C NMR (126 MHz; CDCl3): δ 167.1, 127.4, 112.0, 83.8, 24.8, 14.3. ^{11}B NMR (160 MHz; $CDCl_3$): δ 28.8.

Table 2.5, Entry 1: Borylation with dtbpy as the ligand

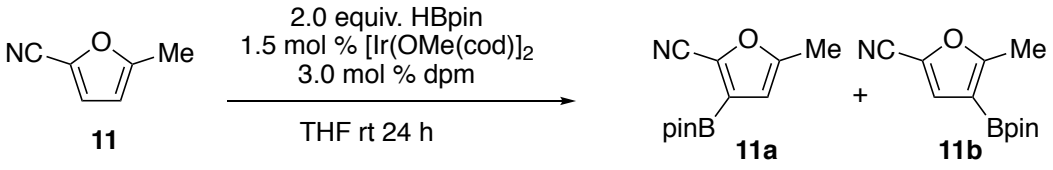


1.0 mmol

crude ratio 5.7:1
isolated yield 97% 5.7:1 mixture

The borylation of 5-methylfuran-2-carbonitrile using dtbpy as the ligand was previously reported by the authors,[13] and is included here for comparison.

Table 2.5, Entry 1: Borylation with dpm as the ligand



1.0 mmol

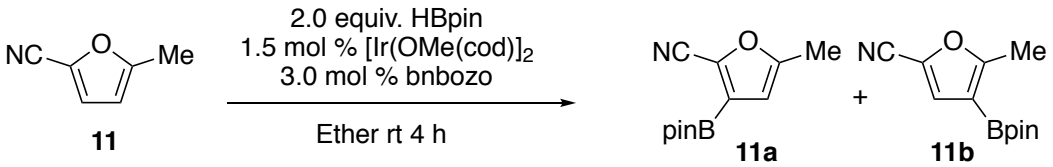
crude ratio 4.8:1
isolated yield 90% 5:1 mixture

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor into the light yellow solution, which deepened to a clear gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred into the vial with a Pasteur pipette, and the reaction mixture turned a bright orange color. The vial was rinsed with 0.5 mL THF and the rinse was added to the vial. 5-methylfuran-2-carbonitrile (107 mg, 105 μL, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. 1.0 mL additional THF was added to the vial for a total volume of 3.0 mL. The vial was closed with a screw cap and allowed

to stir at ambient temperature in the glove box for 24 hours. After 24 hours, complete conversion was observed by GC.

The volatiles were removed by rotary evaporation and the crude material was dissolved in CH_2Cl_2 and passed through a 2g silica plug to afford 232 mg of the borylated material as a white crystalline solid. (90% yield, m.p. = 78 – 84°C)

Table 2.5, Entry 1: Borylation with bnbozo as the ligand



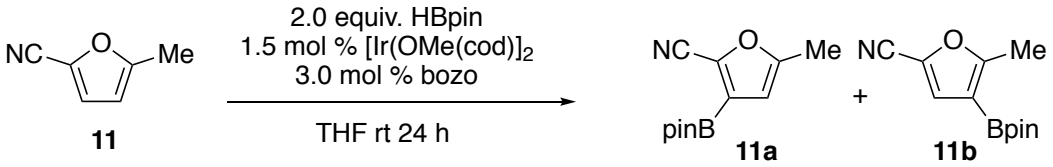
1.0 mmol

crude ratio >99:1
isolated yield 96% **11a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL diethyl ether was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor into the light -ellow solution, which deepened to a clear gold color. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbox) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL diethyl ether and the rinse was added to the vial. 5-methylfuran-2-carbonitrile (107mg, 105 μL, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. 1.0 mL additional diethyl ether was added to the vial for a total volume of 3.0 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 4 hours. After 4 hours, complete conversion to products was observed by GC.

After completion of the reaction, the volatiles were removed by rotary evaporation, and the crude material was dissolved in CH_2Cl_2 and passed through a 2g silica plug to afford 230mg of the borylated material as a white crystalline solid. (96%, m.p. = 89 – 90 °C)

Table 2.5, Entry 1: Borylation with bozo as ligand



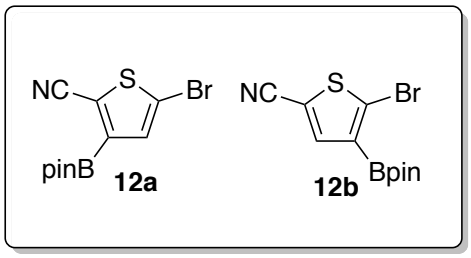
1.0 mmol

crude ratio 17:1
isolated yield 90% 17:1

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stirring bar was charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis(2-oxazoline) (**box**) was weighed into a test tube (5 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 5-methylfuran-2-carbonitrile (107mg, 105 μL, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. 1.0 mL additional THF was added to the vial for a total volume of 3.0 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After 24 hours, complete conversion to products was observed by GC.

After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a short plug of silica to afford 210 mg of a white crystalline solid (90% yield, m.p. = 87 – 90°C)

Table 2.5, Entry 2

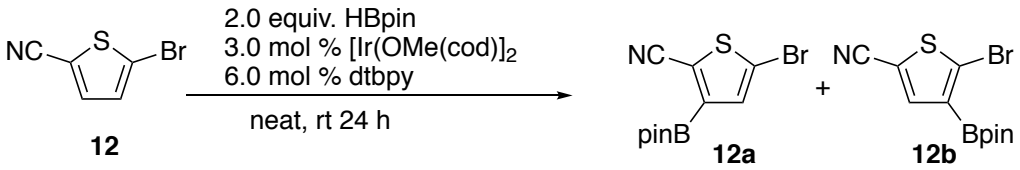


Characterization of 12a:

Major isomer 12a: ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.32 (s, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 136.0, 113.3, 84.5, 24.8. 11B NMR (160 MHz; CDCl3): δ 28.0. **12a** was isolated as an off-white solid, mp 89 – 90 °C.

The mixture was recrystallized from hexane to give pure **12a**. GC-MS (EI) *m/z* (% relative intensity) M+ 315 (100), 313 (97), 314 (59), 300 (32), 298 (30), 272 (85), 257 (47), 255 (48), 229 (22), 192 (76). CHN anal. calcd for $C_{11}H_{13}BBrNO_2S$: C, 42.07; H, 4.17; N, 4.46. Found: C, 42.32; H, 4.11; N, 4.50.

Table 2.5, Entry 2: Borylation with dtbpy as ligand



0.5 mmol

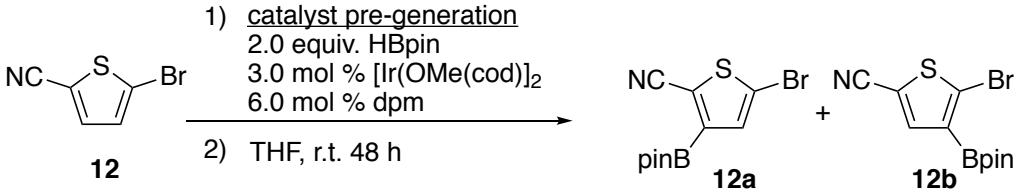
crude ratio 4.6:1
6% conversion

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). HBpin (190 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve solid. 4'-Di-t-butyl-2,2'-bipyridine (dtbpy) was weighed by difference directly into the vial, (8mg, 0.015 mmol, 6 mol %).

The mixture turned dark red. No solvent was added. 5-bromothiophene-2-carbonitrile (59 mg, 55 μL, 0.5 mmol, 1.0 equiv.) was added directly to the stirring mixture by pipettor. The already dark red mixture turned darker, red-black and gas was evolved. The mixture stirred 5 minutes, then the vial was closed with a screw cap and allowed to stir at ambient temperature for 24 h in the glove box. Only 6% conversion was observed by GC, and the product integrated to 6% in the crude ^{1}H NMR spectrum. The crude NMR sample was then analyzed by GC-MS, and peaks that had masses consistent with the desired borylated products were observed. After stopping the reaction, the volatiles were removed by rotary evaporation to yield a brown oil. The oil was dissolved in CH_2Cl_2 and passed through a 2g plug of silica to recover starting material and traces of the borylated products.

The experiment was repeated under different loadings and conditions, and gave results consistent with stoichiometric borylation with HBpin. No borylation occurred with B_2pin_2 under any circumstance. Although stoichiometric borylation was observed and traces of borylated products were isolated verified by mass spectrometry, dtbpy gives no conversion under any typical catalytic borylation reaction conditions, and thus cannot be used for any practical borylation of this substrate.

Table 2.5, Entry 2: Borylation with dpm as ligand



1 mmol

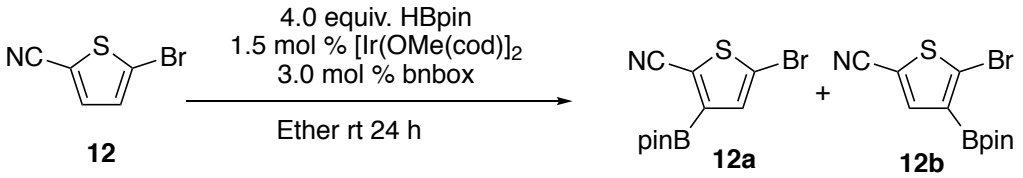
crude ratio 4.9:1
10% isolated yield 4.9:1

Under normal borylation conditions, no reaction was observed with dpm. However, higher Ir loading and pre-generation of the active catalyst in neat HBpin allowed partial conversion, as follows.

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with Di-(pyridin-2-yl)methane (dpm) (10 mg, 0.06 mmol, 6 mol %) and $[Ir(OMe)(COD)]_2$ (20 mg, 0.03 mmol, 6 mol % Ir). HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor into the reaction vial, and the mixture was stirred about 5 minutes to make a thick orange-brown solution. 5-bromothiophene-2-carbonitrile (188 mg, 110 μL, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. The reaction immediately turned very dark black-red and gas evolution was observed. When the gas evolution stopped, 3 mL THF was added to the reaction. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. After 48 hours, 42% conversion was observed by GC.

After the reaction was stopped the volatiles were removed by rotary evaporation and the crude material was dissolved in CH_2Cl_2 and passed through a 2g silica plug to afford a sticky tar-like substance contaminated with a significant quantity of borates. The material was re-dissolved in CH_2Cl_2 and passed through a fresh 3g column to yield 140 mg of an orange gel determined to be a mixture of 4.9:1 borylated products and starting material. Using the ratio of starting material to products from the ^1H NMR to calculate the mol fraction, the mass of borylated products present in the isolated material is 32 mg. (10% isolated yield). Although some borylation was observed at higher loadings with pre-generation, dpm gives no conversion under typical borylation reaction conditions, and thus is not practical for borylation of this substrate.

Table 2.5, Entry 2: Borylation with bnbox as ligand

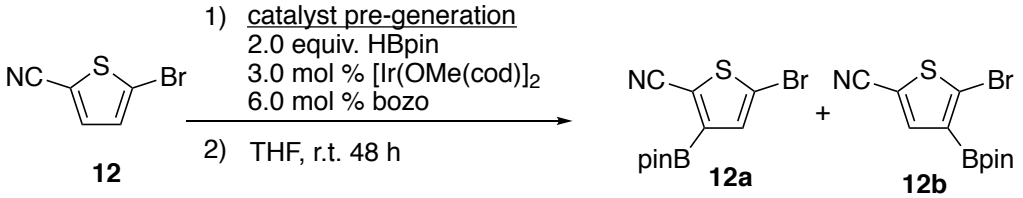


In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (5 mg, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 4.0 equiv.) was added into the light yellow solution, which deepened to a clear gold color. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (**bnbozo**) was weighed into a test tube (5 mg, 3 mol %) and added as a solid into the stirring reaction mixture. The mixture turned cherry red color. The vial was rinsed with 1.0 mL THF and the rinse was added to the vial. 5- bromothiophene-2-carbonitrile (94 mg, 55 μL, 0.5 mmol, 1.0 equiv) was added into the reaction vial. Upon addition of the substrate, the reaction turned a very dark red-black color, and moderate gas evolution was observed. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. After 48 hours, 90% conversion was observed by GC.

After the reaction was stopped, the volatile materials were removed on a rotary evaporator. The crude material was dissolved in CH_2Cl_2 and passed through a 2g silica plug to yield an orange sticky solid that was a mixture of borates, starting material and borylated products by ^{1}H NMR and 11B NMR. The semi-solid was re-dissolved in CH_2Cl_2 and applied to a fresh 2g silica column to yield a pale waxy solid that was determined to be a mixture of 55:1 borylated products and a trace of starting material by ^{1}H NMR. The material was pumped down under high vacuum until it became a dry, pale off-white solid with mass of 127 mg. (81% yield, m.p. = 89 – 90°C).

The regiochemistry of major isomer **12a** was confirmed by de-bromination of the pure material according to a literature procedure.[15] The reaction resulted in the disappearance of the pure starting material with the subsequent appearance of 3-Bpin-2-cyanothiophene, which matched reported NMR and mass spec data.[16] The de-bromination product of minor isomer **12b**, 4-Bpin-2-cyanothiophene, also a known compound[17] was not detected in the reaction mixture.

Table 2.5, Entry 2: Borylation with bozo as ligand



1 mmol

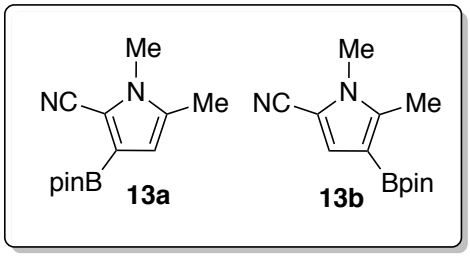
crude ratio 6:1
29% isolated yield 6:1

Under normal borylation conditions, no reaction was observed with bozo. However, higher Ir loading and pre-generation of the active catalyst in neat HBpin allowed partial conversion, as follows.

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with 2,2'-bis-2-oxazoline, (10 mg, 0.06 mmol, 6 mol %) and $[Ir(OMe)(COD)]_2$ (20 mg, 0.03 mmol, 6 mol % Ir). HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor into the reaction vial, and the mixture stirred about 5 minutes to make a thick orange-brown solution. 5-bromothiophene-2-carbonitrile (188 mg, 110 μL, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. The reaction immediately turned very dark black-red and moderate gas evolution was observed. When the gas evolution stopped, 3 mL THF was added to the reaction. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. After 48 hours, 50% conversion was observed by GC.

After the reaction was stopped, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 3g silica plug to yield an orange sticky solid that was a mixture of borates, starting material and borylated products by ^1H NMR and ^{11}B NMR. The semi-solid was re-dissolved in CH_2Cl_2 and applied to a fresh 3g silica column to yield a waxy orange solid that was determined to be a mixture of 6:1 borylated products and a starting material by ^1H NMR. The material was pumped down under high vacuum until it became a dry, pale orange solid with mass of 90 mg. (29% yield, m.p. = 84 - 88 °C).

Table 2.5: Entry 3

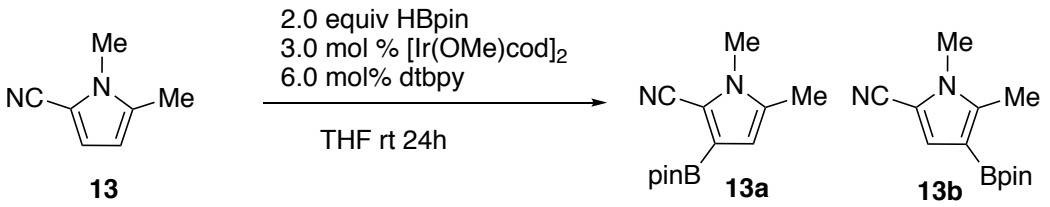


Characterization of 13a and 13b:

Steric isomer 13a: ^1H NMR ($CDCl_3$ 300 MHz) δ 6.22 (d, J = 0.7 Hz, 1H); 3.62 (s, 3H); 2.21 (d, J = 0.71 Hz, 3H); 1.29 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.6, 114.5, 114.3, 110.3 83.6, 32.4, 28.4, 12.2 ^{11}B NMR (96 MHz) δ 32.7. 20a was isolated as a waxy white solid, mp 62-63°C.

Electronic isomer 13b: ^1H NMR ($CDCl_3$ 300 MHz) δ 7.03 (s, 1H); 3.62 (s, 3H); 2.11 (d, s, 3H); 1.27 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.9, 125.2, 113.7, 103.8 82.6, 31.8, 24.4, 11.9 ^{11}B NMR (96 MHz) δ 32.7.

Table 2.5, Entry 3: Borylation with dtbpy as the ligand



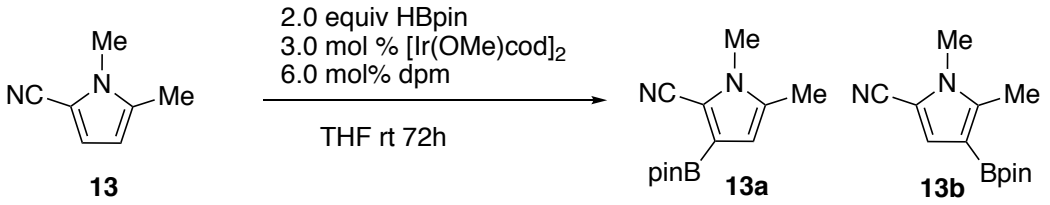
1.0 mmol

crude ratio 5.7:1
isolated yield 66% 5.7:1

This substrate is not very reactive towards borylation, so the catalyst was pre-generated in neat HBpin, the substrate was added and the solvent was added last.

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (20 mg, 0.015 mmol, 6 mol% Ir). HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve solid. 4,4'-di-t-butyl-2,2'-bipyridine (dtbpy) was weighed into a test tube (16 mg, 0.06 mmol, 6 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 1,5-Dimethyl-2-pyrrolcarbonitrile (0.107 g, 0.105 mL, 1.0 mmol) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The mixture was stirred 5 minutes and gas was evolved. All test tubes were rinsed with 3 x 1 mL THF for a total volume of THF = 3.0 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box. The reaction was monitored by GC and judged complete after 3 hours. The volatiles were removed by rotary evaporation to yield brown oil. The crude ratio of borylated isomers was determined by GC and ^{19}F NMR to be 5.7:1 **13a**:**13b**. The crude material was dissolved in hexane and passed through a 3g silica plug eluting with hexanes, yielding 154 mg of white solid that was determined to be 5.7:1 mixture of **13a**:**13b** by GC-FID (66% yield).

Table 2.5, Entry 3: Borylation with dpm as the ligand

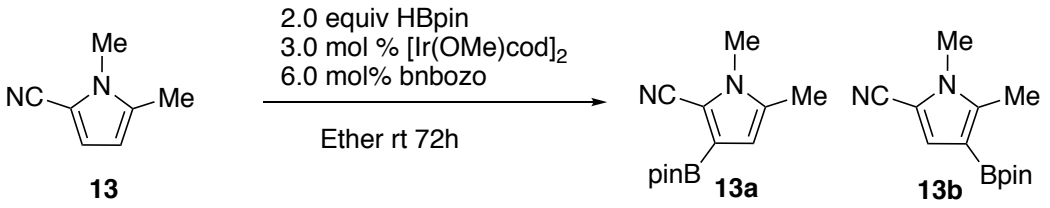


1.0 mmol

crude ratio 2.3:1 **13a**:**13b**
32% conversion – not isolated

In a glove box under nitrogen atmosphere, a test tube equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (20 mg, 0.015 mmol, 6 mol% Ir). HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve solid. Dipyridyl methane, (dpm) was weighed into a 20 mL reaction vial equipped with a stirbar (8 mg, 0.06 mmol, 6 mol %). The cztalyst HBpin solution was taken up by Pasteur pipette and added onto the ligand and mixed well. A thick orange solution formed. The mixture turned dark red. 1,5-dimethyl-2-pyrrolcarbonitrile (0.107 g, 0.105 mL, 1.0 mmol) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The mixture was stirred 5 minutes and gas was evolved. All test tubes were rinsed with 3 x 1 mL THF for a total volume of THF = 3.0 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 h. A GC-FID sample was taken 24 h later, and indicated only 32% conversion occurred. The reaction was stopped and the volatiles were removed by rotary evaporation to yield brown oil. The crude ratio of borylated isomers was determined by GC and ^{19}F NMR to be 5.7:1 **13a**:**13b**. The crude material was dissolved in hexane and passed through a 3g silica plug eluting with hexanes, yielding a mixture of starting material, product and borates. The product isomers 20a and 20b were present in a ratio of 2.3:1 mixture of **13a**:**13b** by GC-FID. The product was not purified or further isolated so no yield was obtained.

Table 2.5, Entry 3: Borylation with bnbozo as the ligand



13 **13a** **13b**

1.0 mmol

crude ratio 32:1 **13a**:**13b**
66% yield **13a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (20 mg, 0.015 mmol, 6 mol% Ir). HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve solid. 2,2′-Bis[(4*S*)-4-benzyl--2-oxazoline] (bnbozo) was weighed into a test tube (20 mg, 0.06 mmol, 6 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. 1,5-Dimethyl-2-pyrrolcarbonitrile (0.107 g, 0.105 mL, 1.0 mmol) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The mixture was stirred 5 minutes and gas was evolved. All test tubes were rinsed with 3 x 1 mL Ether for a total volume of Ether = 3.0 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 72 h. A GC-FID sample was taken 24 h later, and indicated about 90% conversion occurred. The reaction was stopped and the volatiles were removed by rotary evaporation to yield brown oil. The crude ratio of borylated isomers was determined by GC and ^{19}F NMR to be 5.7:1 **13a**:**13b**. The crude material was dissolved in CH_2Cl_2 and passed through a 3g silica plug eluting with 1:1 CH_2Cl_2 : hexanes, yielding a 155 mg of a white solid that was shown by GC-FID to be single isomer **13a** (66% yield)

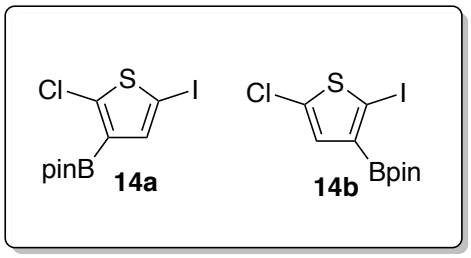
Table 2.5, Entry 3: Borylation with bozo as the ligand

1.0 mmol

crude ratio 13:1 **13a**:**13b**
61% yield **13a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (20 mg, 0.015 mmol, 6 mol% Ir). HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve solid. 2,2′-Bis-2-oxazoline (**bozo**) was weighed into a test tube (20 mg, 0.06 mmol, 6 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. 1,5-Dimethyl-2-pyrrolcarbonitrile (0.107 g, 0.105 mL, 1.0 mmol) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The mixture was stirred 5 minutes and gas was evolved. All test tubes were rinsed with 3 x 1 mL THF for a total volume of THF = 3.0 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 72 h. A GC-FID sample was taken 24 h later, and indicated about 80% conversion occurred. The reaction was stopped and the volatiles were removed by rotary evaporation to yield brown oil. The crude ratio of borylated isomers was determined by GC and ^{19}F NMR to be 13.3:1 **13a**:**13b**. The crude material was dissolved in CH_2Cl_2 and passed through a 3g silica plug eluting in 1:1 solvent mix of hexane : CH_2Cl_2. A white solid, 142 mg, was isolated and shown to be single isomer **13a**.

Table 2.5, Entry 4

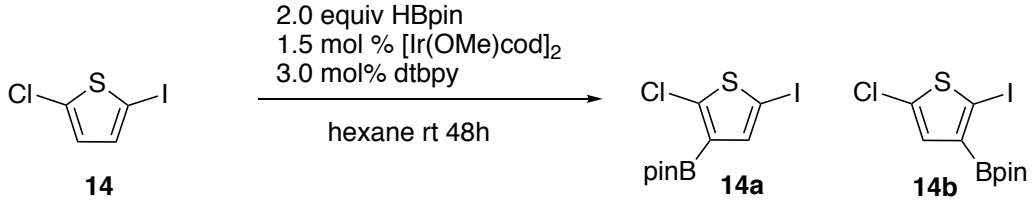


Characterization of 14a and 14b:

Steric isomer, 14a ^{1}H NMR ($CDCl_3$ 500 MHz) δ 7.32 (s, 1H); 1.30 (s, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.4, 142.3, 84.0, 69.3, 24.8 ^{11}B NMR (160 MHz) δ 28.3. Characterization of **14b** was determined from the spectra of concentrated crude reaction mixtures.

Electronic isomer, 14b ^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.87 (s, 1H); 1.31 (s, 12H) ^{13}C NMR ($CDCl_3$, 125 MHz) 132.8, 84.2, 81.1, 24.8. ^{11}B NMR (96 MHz) δ 28.3

Table 2.5, Entry 4: Borylation with dtbpy as the ligand



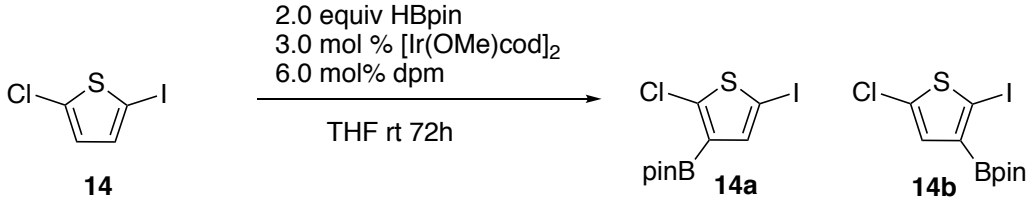
0.5 mmol

crude ratio 5.7:1 **14a**:**14b**
89% yield 5.7:1 **14**:**14b**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). HBpin (145 μL, 128 mg, 1.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve solid. 4,4'-di-t-butyl-2,2'-bipyridine (dtbpy) was weighed into a test tube (8 mg, 0.06 mmol, 6 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 2-Chloro-5-iodothiophene (0.122 g, 0.5 mmol) was

weighed into a test tube, dissolved in 1.0 mL THF and transferred into the reaction vial by Pasteur pipette. The test tubes were rinsed with 2 x 1 mL THF for a total volume of THF = 3.0 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box. The reaction was monitored by GC and stopped after 48 hours. The volatiles were removed by rotary evaporation to yield brown oil. The crude ratio of borylated isomers was determined by GC and ^{19}F NMR to be 5.7:1 **14a**:**14b**. The crude material was dissolved in hexane and passed through a 3g silica plug eluting with hexanes, yielding 154 mg of white solid that was determined to be 5.7:1 mixture of **14a**:**14b** by GC-FID (89% yield of mixture).

Table 2.5, Entry 4: Borylation with dpm as the ligand



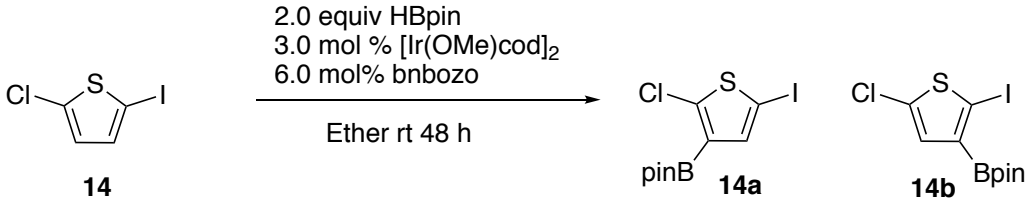
14 0.5 mmol

14a **14b** crude ratio 5.7:1 **14a**:**14b**
59% yield 3.2:1 **14a**:**14b**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 6 mol% Ir). HBpin (145 μL, 128 mg, 1.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve the yellow solid. Dipyridyl methane (dpm) was weighed into a GC vial (4 mg, 0.03 mmol, 6 mol %), and the ligand was dissolved in 145μL HBpin (128 mg, 1.0 mmol, 2 equiv). The mixture was transferred into the reaction vial, and the mixture turned very dark color. 2-Chloro-5-iodo thiophene (0.122 g, 0.5 mmol) was added to the vial, and gas was evolved. The gc vial was rinsed with 3 x 0.5 mL THF and added to the vial. The cap was put on the vial and the reaction was stirred at ambient temperature for 48 h. A GC-FID sample was taken 78% conversion occurred. The reaction was stopped and the volatiles were removed by rotary evaporation to yield brown oil. The crude ratio

of borylated isomers was determined by GC-FID to be 3.2:1 **14a**:**14b**. The crude material was dissolved in hexane and passed through a 2g silica plug eluting with hexanes, yielding a waxy semi-solid mixture of starting material, product and borates. The mixture was pumped down under high vacuum until a solid formed. Most starting material and borates were pumped off over two days to leave 110 mg of a waxy rose colored solid containing a ratio of 5.7:1 mixture of **14a**:**14b** by GC-FID. (59% yield)

Table 2.5, Entry 3: Borylation with bnbozo as the ligand



14 **14a** **14b**

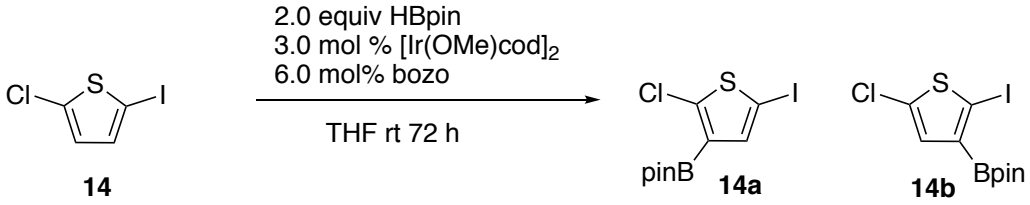
0.5 mmol

crude ratio 5.7:1 **14a**:**14b**
59% yield 3.2:1 **14a**:**14b**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 6 mol% Ir). HBpin (145 μL, 128 mg, 1.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve solid. 2,2′-Bis[(4*S*)-4-benzyl--2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 6 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. 2-Chloro-5-iodo thiophene (0.122 g, 0.5 mmol) was weighed into a test tube, dissolved in 1.0 mL diethyl ether and added last as a solid into the stirring mixture in the vial by Pasteur pipette. The test tubes were rinsed with 2 x 0.5 mL diethyl ether for a total volume of 1.5 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 h. A GC-FID sample was taken later, and indicated full conversion occurred. The reaction was stopped and the volatiles were removed by rotary evaporation to yield brown oil. The crude ratio of borylated isomers was determined by GC-

FID to be 12:1 **21a**:**21b**. The crude material was dissolved in CH_2Cl_2 and passed through a 3g silica plug eluting with 1:1 CH_2Cl_2 : hexanes, yielding an off white, faint rose colored solid was shown by GC-FID to be mostly **14a** product with traces of starting material and borates. The material was pumped down under high vacuum for 2 days until the GC-FID did not show starting material and borates. The material was a waxy pink solid **14a** with a trace of **14b** beneath the integration threshold of the GC-FID, and not visible in the ^{1}H NMR.

Table 2.5, Entry 4: Borylation with bozo as the ligand



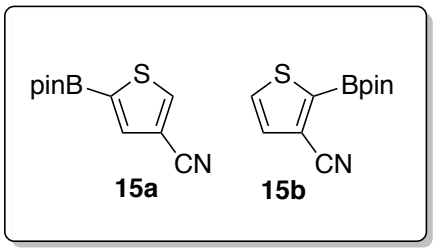
0.5 mmol

crude ratio 5.7:1 **14a**:**14b**
60% yield 6:1 **14a**:**14b**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 6 mol% Ir). HBpin (145 μL, 128 mg, 1.0 mmol, 2.0 equiv) was added and the mixture was stirred to dissolve solid. 2,2′-Bis-2-oxazoline (bozo) was weighed into a test tube (5 mg, 0.03 mmol, 6 mol %), and the ligand was added to the vial as a solid. The mixture turned dark. 2-chloro-5-iodothiophene (0.122 g, 0.5 mmol) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The mixture was stirred 5 minutes and gas was evolved. All test tubes were rinsed with 3 x 0.5 mL THF for a total volume of THF = 1.5 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 h. A GC-FID sample was taken later, and indicated full conversion occurred. The reaction was stopped and the volatiles were removed by rotary evaporation to yield brown oil. The crude ratio of borylated isomers was determined by GC-FID

to be 6:1 **14a**:**14b**. The crude material was dissolved in CH_2Cl_2 and passed through a 3g silica plug eluting with 1:1 CH_2Cl_2 : hexanes, yielding an off white, faint rose colored solid was shown by GC-FID to be6:1 **14a**:**14b** product with traces of starting material and borates. The material was pumped down under high vacuum for 2 days until the GC-FID did not show starting material and borates. The material was 112 mg of waxy pink solid of ratio 6:1 **14a**:**14b**. (60% yield)

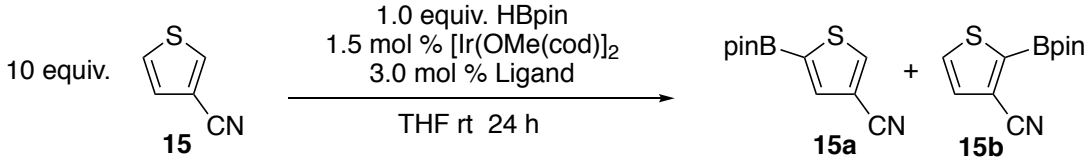
Table 2.5, Entry 5:



Characterization of 15a and 15b:

Steric isomer 15a: ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.13 (d, J = 1.0 Hz, 1H), 7.75 (d, J = 1.0 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 141.1, 138.2, 115.0, 111.8, 84.9, 24.7. ^{11}B NMR (160 MHz; CDCl3): δ 28.4. **Electronic isomer 15b**: ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.63 (d, J = 4.9 Hz, 1H), 7.38 (d, J = 4.9 Hz, 1H), 1.35 (s, 12H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 132.8, 131.4, 118.1, 115.4, 85.1, 24.7. 11B NMR (160 MHz; $CDCl_3$): δ 28.2.

Table 2.5, Entry 5: Borylation with 10-fold excess starting material.

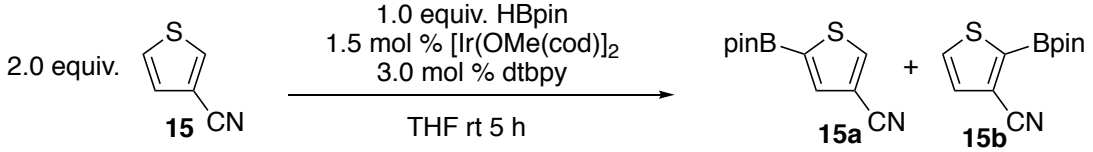


1 mmol

ratios of crude material by GC
dtbpy: 1:1.1
dpm: 2.3:1
bozo: 1:3.2
bnbozo: 1:1

The following general procedure was followed for each ligand: [Ir(OMe)cod]2 (10mg, 0.015 mmol, 3 mol% Ir) was weighed into a test tube equipped with a small magnetic stir bar. THF was added (1.0 mL) and the Ir precatalyst was dissolved. HBpin (145 μL, 1.0 mmol, 1.0 equiv) was added by syringe into the test tube and the mixture was stirred, resulting in a clear gold solution. The ligand (**dtbpy** = 8 mg; **dpm** = 4 mg; **bozo** = 4 mg; or **bnbozo** = 10 mg) was weighed into another test tube, and the HBPin-Ir solution was added onto the ligand with a Pasteur pipette. A stirbar was added and the mixture was stirred until a homogenous solution resulted. The first test tube was rinsed with 1.0 mL THF and the rinse was added into the second test tube. This mixture was stirred for 2 minutes. While the catalyst solution stirred, the substrate (908 μL, 10.0 mmol, 10.0 equiv) was transferred into a 20 mL vial equipped with a stir bar. The catalyst solution was removed from the test tube by Pasteur pipette and transferred into the reaction vial of excess substrate. The test tube was rinsed with 1.0 mL THF and the THF was added into the reaction. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After 24 hours, the ratio of isomers was determined by GC. The reaction was concentrated by rotary evaporation, and crude NMRs were taken. The crude material was dissolved in dcm and passed through a 2g silica plug eluting with dcm. The residual starting material was pumped off under high vacuum to leave the mixture of borylated isomers.

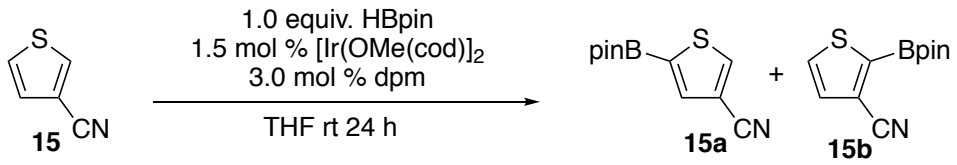
Table 2.5, Entry 5: Borylation with dtbpy as ligand



1 mmol crude ratio 1:1.1

The borylation of 3-cyanothiophene using dtbpy as the ligand was previously reported by the authors,[18] and is included here for comparison.

Table 2.5, Entry 5: Borylation with dpm as the ligand



5 mmol

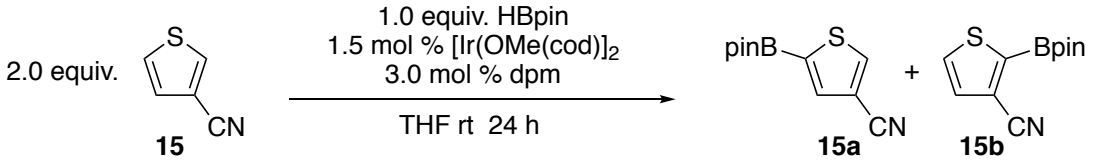
crude ratio 5.5:1 (15% diborylation)
74% isolated yield 5.5:1
recrystallized 43% **15a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (50 mg, 0.075 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (725 μL, 640 mg, 5.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a test tube (26 mg, 0.15 mmol, 3 mol %) and dissolved in 1.0 mL THF. The solution was transferred into the vial with a Pasteur pipette, and the reaction mixture turned a bright orange color. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-cyanothiophene (0.545 g, 455 μL, 5.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. Vigorous bubbling was observed. When the gas evolution subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, GC analysis indicated 10% starting material remaining with 15% diborylated substrate present. The diborylation of **15b** enhanced the ratio of **15a**:**15b** to 5.5:1. After the reaction was stopped, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and applied to a 10g silica plug eluting with 1:1 CH_2Cl_2 / hexanes to prevent diborylated material from passing through the plug. A mix of borylated isomers and residual starting material eluted as a clear, colorless oil. The starting material was removed under high vacuum to yield 860 mg of a white solid that was determined by GC and ^1H NMR to be a 3:1

mixture of isomers. (74% yield, mp 83-85°C) The mixture was dissolved in warm hexane and put in the-30°C freezer. Two crops of crystals were collected for 505 mg white crystalline solid, that was white and free flowing and granular in appearance, like table sugar. (43% yield, mp = 96 – 97°C)

Table 2.5, Entry 5: Borylation with dpm as the ligand, 2:1 substrate : HBpin



5 mmol

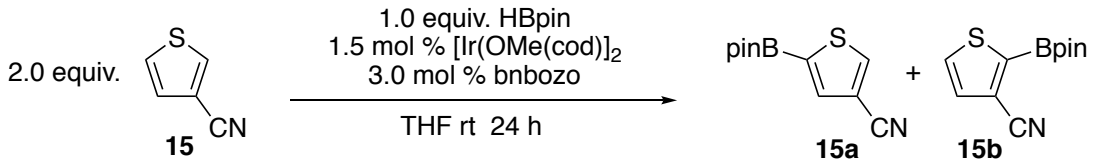
crude ratio 4.5:1 (3% diborylation)
74% isolated yield 4.5:1
recrystallized 36% **15a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (50 mg, 0.075 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (725 μL, 640 mg, 5.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a test tube (26 mg, 0.15 mmol, 3 mol %) and dissolved in 1.0 mL THF. The solution was transferred into the vial with a Pasteur pipette, and the reaction mixture turned a bright orange color. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-cyanothiophene (01.90 g, 910 μL, 10 mmol, 2.0 equiv.) was added last by pipettor into the stirring mixture in the reaction vial. Moderate bubbling was observed. When the gas evolution subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, GC analysis showed 55% starting material remaining, which translates to 90% conversion based on HBpin. 3% diborylated substrate present, and the ratio of **1a**:**1b** was observed to be 4.5:1. After the reaction was stopped, the volatile materials were removed by rotary

evaporation. The crude material was dissolved in CH_2Cl_2 and applied to a 10g silica plug eluting with 1:1 CH_2Cl_2 / hexanes to prevent diborylated material from passing through the plug. A mix of borylated isomers and residual starting material eluted as a clear, colorless oil. The starting material was removed under high vacuum to yield 745 mg of a white solid that was determined by GC and ^{1}H NMR to be a 3:1 mixture of isomers. (63% yield, mp 83-85°C). The mixture was dissolved in warm hexane and the flask was put in the -30°C freezer. Two crops of crystals were collected for a total of 423 mg. The crystals were shown to be pure **15a** by ^{1}H NMR. (36% yield, mp = 96 – 97°C) Crystals were white and granular like table sugar.

Table 2.5, Entry 5: Borylation with bnbozo as the ligand; 2:1 substrate : HBpin



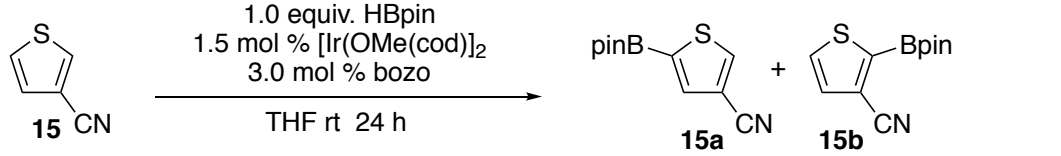
2.5 mmol

crude ratio 1:1.4 (12% diborylation)
61% isolated yield 1:1.3

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (25 mg, 0.0377 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (363 μL, 320 mg, 2.5 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) was weighed into a test tube (25 mg, 0.078 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-cyanothiophene (0.545 g, 455 μL, 5.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. Vigorous bubbling was observed. When the gas evolution subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, GC analysis indicated 59% starting material remaining (for a 2-fold excess of starting material where 50% starting material indicates complete conversion, this translates to 82% conversion) with 12% diborylated substrate present. The ratio of **15a**:**15b** was to 1:1.3. After the reaction was stopped, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and applied to a 10g silica plug eluting with 1:1 CH_2Cl_2 / hexanes to prevent diborylated material from passing through the plug. A mix of borylated isomers and residual starting material eluted as a clear, colorless oil. The starting material was removed under high vacuum to yield 360 mg of a white solid that was determined by GC and ^{1}H NMR to be a 1:1.3 mixture of isomers. (61% yield, mp 82-85°C).

Table 2.5, Entry 5: Borylation with bozo as the ligand 1:1 substrate : HBpin



5 mmol

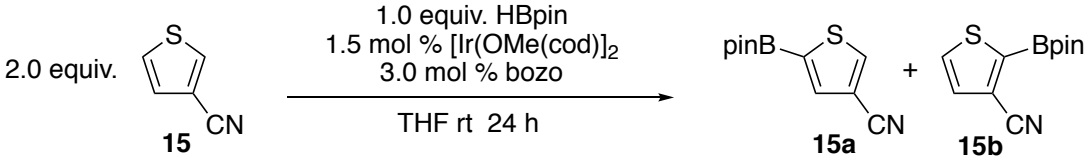
crude ratio 5.5:1 (19% diborylation)
69% isolated yield 1:4.5
recrystallized 36% **15b**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (50 mg, 0.075 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (725 μL, 640 mg, 5.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis(2-oxazoline) (bozo) was weighed into a test tube (25 mg, 0.078 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. and dissolved in 1.0 mL THF. The reaction turned a cherry red color. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-cyanothiophene (0.545 g, 455 μL, 5.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction

vial. Vigorous bubbling was observed. When the gas evolution subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, GC analysis indicated 16% starting material remaining with 19% diborylated substrate present. The diborylation of **15a** enhanced the ratio of **15a**:**15b** to 1:4.5. After the reaction was stopped, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and applied to a 10g silica plug eluting with 1:1 CH_2Cl_2 / hexanes to prevent diborylated material from passing through the plug. A mix of borylated isomers and residual starting material eluted as a clear, colorless oil. The starting material was removed under high vacuum to leave 810 mg of a white solid that was determined by GC and ^{1}H NMR to be a 1:5 mixture of isomers. (69% yield, mp 83-85°C). The white solid was dissolved in warm hexanes and allowed to sit open on the bench for about 3 hours until crystals were forming. The flask was closed with a septum and put in the 10°C refrigerator overnight. 2 crops of fine, fibrous needles that resembled glass wool were collected for a total of 470 mg of pure **15b**. (40% yield, m.p. = 103 – 105°C).

Table 2.5, Entry 5: Borylation with bozo as the ligand 2:1 substrate : HBpin



5 mmol

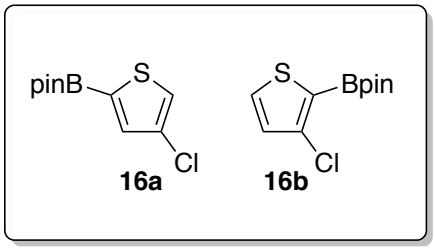
crude ratio 5.5:1 (5% diborylation)
69% isolated yield 1:4.5
recrystallized 36% **15b**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (50 mg, 0.075 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (725 μL, 640 mg, 5.0 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis(2-

oxazoline) (bozo) was weighed into a test tube (25 mg, 0.078 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. and dissolved in 1.0 mL THF. The reaction turned a cherry red color. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-cyanothiophene (1.09 g, 910 μL, 10 mmol, 2.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. Vigorous bubbling was observed. When the gas evolution subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, GC analysis indicated 50% starting material remaining, which corresponds to complete conversion. 5% diborylated substrate was present. The diborylation of **15a** enhanced the ratio of **15a**:**15b** to 1:3.3. After the reaction was stopped, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and applied to a 10g silica plug eluting with 1:1 CH_2Cl_2 / hexanes to prevent diborylated material from passing through the plug. A mix of borylated isomers and residual starting material eluted as a clear, colorless oil. The starting material was removed under high vacuum to leave 810 mg of a white solid that was determined by GC and ^{1}H NMR to be a 1:5 mixture of isomers. (69% yield, mp 83-85°C). The white solid was dissolved in warm hexanes and allowed to sit open on the bench for about 3 hours until crystals were forming. The flask was closed with a septum and put in the 10°C refrigerator overnight. 2 crops of fine, fibrous needles that resembled glass wool were collected for a total of 470 mg of pure **15b**. (40% yield, m.p. = 103 – 105°C).

Table 2.5, Entry 6

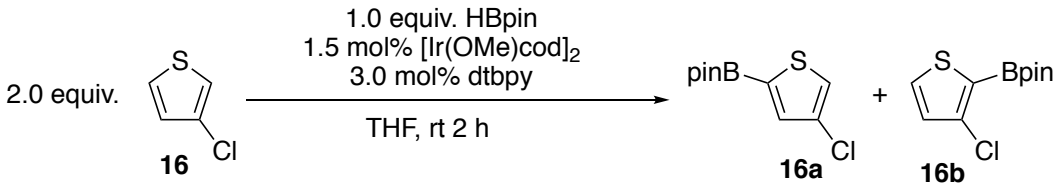


Characterization of 16a and 16b:

Steric isomer 16a: ^{1}H NMR (500 MHz; CDCl3): δ 7.43 (d, *J* = 1.2 Hz, 1H), 7.35 (d, *J* = 1.2 Hz, 1H), 1.32 (s, 12H). 13C NMR (126 MHz; $CDCl_3$): δ 136.9, 131.9, 126.8, 84.4, 24.7. 11B NMR (160 MHz; $CDCl_3$): δ 28.5. **Electronic isomer 16b**: ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.51 (d, *J* = 4.9 Hz, 1H), 7.01 (d, *J* = 4.9 Hz, 1H), 1.34 (s, 12H). 13C NMR (126 MHz; $CDCl_3$): δ 138.3, 129.7, 126.6, 84.2, 24.7. 11B NMR (160 MHz; $CDCl_3$): δ 28.5.

Borylation of 3-chlorothiophene with the ligand dtbpy in hexane with HBPin as the limiting reagent, was previously reported by the authors.[17] Under these conditions, a 3.5:1 ratio of **16a**:**16b** was obtained with an isolated yield of 66% of the isomer mixture. Spectral data were consistent with reported literature values from the reference above.

Table 2.5, Entry 6: Borylation with dtbpy as the ligand



2.5 mmol

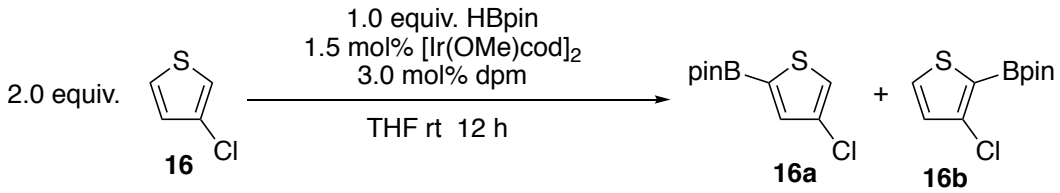
crude ratio 4:1 (5.5% diborylation)
60% isolated yield 4:1

Substrate **16** was previously reported by the authors as borylated with dtbpy in hexane.[17] The ratio obtained was 3.5:1. The borylation of **16** according to standard conditions for a ligand

screening was carried out in THF, whereby a different ratio was obtained. That synthesis is presented here.

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (25 mg, 0.038 mmol, 3 mol% Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (363 μL, 320 mg, 2.5 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 4,4'-Di-t-butyl-2,2'-bipyridine (dtbpy) was weighed into a test tube (20 mg, 0.075 mmol, 3 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-chlorothiophene (0.592g, 0.465 μL, 5.0 mmol, 2.0 equiv) was added by pipettor into the stirring mixture in the vial. Vigorous bubbling was observed. 1.0 additional mL of THF was added to the vial for a total volume of 3.0 mL THF. When gas evolution had subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box. The reaction was monitored by GC and judged complete based on HBpin after 2 hours. The volatiles were removed by rotary evaporation to yield a brown oil. The crude ratio was determined by GC and ^{1}H NMR to be 4:1 with 5.5% diborylated substrate present. The crude material was dissolved in CH_2Cl_2 and passed through a 10g silica plug eluting with CH_2Cl_2, yielding a mixture of borylated isomers and residual starting material. The starting material was removed under high vacuum to leave 450 mg of a clear oil determined by ^{1}H NMR to be a 4:1 mixture of borylated isomers (73% isolated yield).

Table 2.5, Entry 6: Borylation with dpm as the ligand



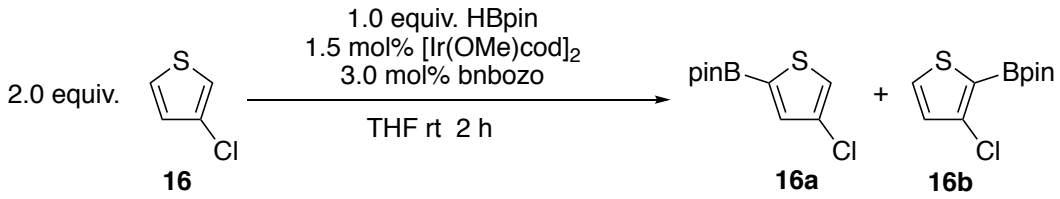
1 mmol

crude ratio 11.5:1 (5% diborylation)
94% isolated yield 11.5:1

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1mL THF was added into the vial to make a clear, light yellow solution. 1.0 equiv. HBPin (145 μL mg, 128 mg, 1.0 mmol) was added by pipettor to the yellow solution, which then deepened to a gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred by Pasteur Pipette into the reaction vial. The GC vial was rinsed with 0.5 mL THF and the rinse was added to the reaction. 3-chlorothihophene (237 mg, 183 μL, 2 mmol, 2.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. Vigorous gas evolution was observed. 1.0 mL of additional THF was added to the reaction vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 12 h. Full conversion based on HBpin was observed to by GC.

After the reaction was stopped, the volatile materials were removed by rotary evaporation. The ratio of 11a:11b was determined by ^{1}H NMR to be 11.5:1 with 5% diborylated substrate present. The crude material was dissolved in CH_2Cl_2 and passed through a 2 g silica plug eluting in 1:1 CH_2Cl_2 / hexanes to afford a mixture of the corresponding borylated product and starting material. The residual starting material was removed under high vacuum to afford 229 mg (94% yield) of a colorless oil that was determined by ^{1}H NMR to be an 11.5:1 mixture of the borylated isomers.

Table 2.5, Entry 6: Borylation with bnbozo as the ligand



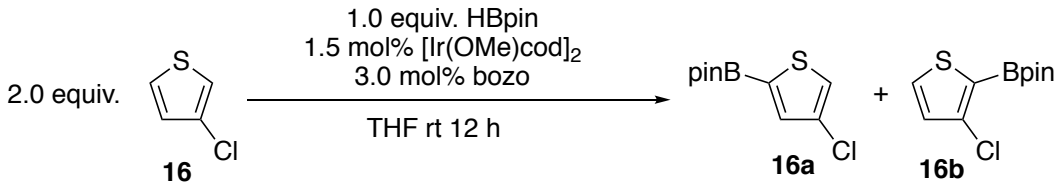
1 mmol

crude ratio 7:1 (5% diborylation)
84% isolated yield 8:1

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1mL THF was added into the vial to make a clear, light yellow solution. 1.0 equiv HBPin (145 μL mg, 128 mg, 1.0 mmol) was added by pipettor to the yellow solution, which then deepened to a gold color. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %) and transferred as a solid into the stirring reaction mixture. The solution turned bright orange. The vial was rinsed with 1.0 mL THF, and the rinse was added to the reaction mixture. 3-chlorothihophene (237 mg, 183 μL, 2 mmol, 2.0 equiv) was added last by pipettor into the reaction vial. Vigorous gas evolution was observed. 1.0 mL of additional THF was added to the reaction vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 2 h.

After 2 h, 90% conversion to products based on HBpin was observed by GC with 3% diborylated substrate present. The reaction was stopped and the volatile materials were removed by rotary evaporation. The ratio of 11a:11b was determined by ^{1}H NMR to be 8:1. The crude material was dissolved in CH_2Cl_2 and passed through a 3g silica plug eluting in 1:1 CH_2Cl_2 / hexanes to afford a clear oil that contained a mixture of the corresponding borylated isomers and residual starting material. The starting material was removed under high vacuum to yield 206 mg of a clear oil that was determined by ^{1}H NMR to be an 8:1 mixture of **16a** and **16b**.

Table 2.5, Entry 6: Borylation with bozo as the ligand



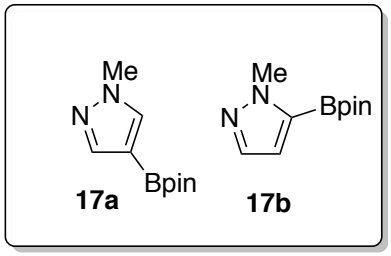
2.5 mmol

crude ratio 1:1 (4% diborylation)
49% isolated yield 1:1

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (25 mg, 0.038 mmol, 3 mol% Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (363 μL, 320 mg, 2.5 mmol, 1.0 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis(2-oxazoline) (**bozo**) was weighed into a test tube (25 mg, 0.078 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. and dissolved in 1.0 mL THF. The reaction turned a cherry red color. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-chlorothiophene (0.592 g, 465 μL, 5.0 mmol, 2.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. Vigorous bubbling was observed. When the gas evolution subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours.

After 24 h, GC analysis indicated full conversion based on HBpin, with 3% diborylated substrate present. After the reaction was stopped, the volatile materials were removed by rotary evaporation, and the ratio by ^{1}H NMR was found to be 1:1. The crude material was dissolved in CH_2Cl_2 and applied to a 10g silica plug eluting with 1:1 CH_2Cl_2 / hexanes to prevent diborylated material from passing through the plug. A mix of borylated isomers and residual starting material eluted as a clear, colorless oil. The starting material was removed under high vacuum to leave 300 mg (49% isolated yield) clear oil of a 1:1 ratio of **16a**:**16b**.

Table 2.5: Entry 7

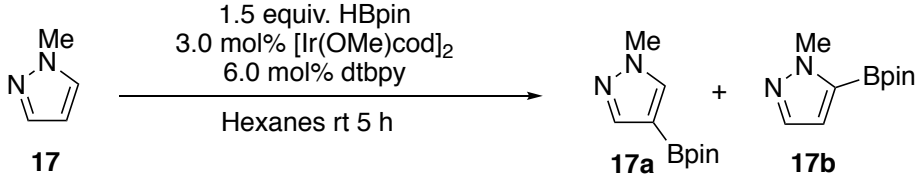


Characterization of 17b:

The steric product **17a** was isolated as a white, crystalline solid after elution in CH_2Cl_2 through a silica plug and subsequent crystallization from hexanes, mp 68 – 70°C. **17b** is difficult to separate from borate contamination by column chromatography, kugelrhor distillation or sublimation as **17b** co-elutes and co-sublimes with borates. On larger scales, it can be purified easily by crystallization, but yields are diminished on smaller scale preparations.

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.46 (d, J = 1.9 Hz, 1H), 6.69 (d, J = 1.9 Hz, 1H), 4.06 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (126 MHz; $CDCl3l_3$): δ 138.2, 115.7, 84.1, 39.3, 24.8. ^{11}B NMR (160 MHz; $CDCl_3$): δ 27.9. GC-MS (EI) *m/z* (% relative intensity): M^{+1} 209 (100), 193 (2), 165 (3), 122(6); HMRS (EI): *m/z* 209.1464 [(M^{+1}); Calcd for $C_{10}H_{18}BN_2O_2$].

Table 2.5, Entry 7: Borylation with dtbpy as the ligand



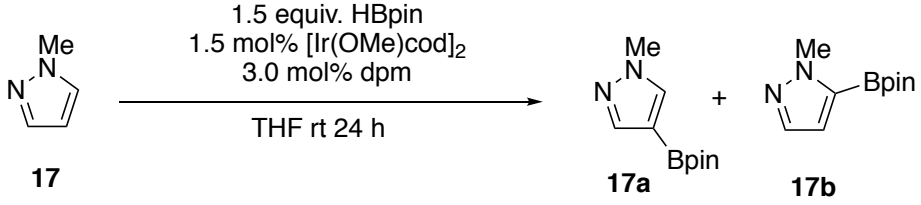
1.0 mmol

crude ratio 9:1
isolated yield 67% mixture 9:1

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(COD)]_2$ (20 mg, 0.03 mmol, 6 mol% Ir). 1.0 mL hexanes was added

with stirring and a clear yellow solution resulted. HBpin (218 μL, 192 mg, 1.5 mmol, 1.5 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 4,4'-Di-t-butyl-2,2'-bipyridine (dtbpy) was weighed into a test tube (16 mg, 0.06 mmol, 6 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. The test tube was rinsed with 1.0 mL hexanes and the rinse was added to the vial. N-methylpyrazine (0.82 g, 81 μL, 1.0 mmol, 1.0 equiv). The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box. The reaction was monitored by GC and judged complete after 5 hours. The volatiles were removed by rotary evaporation to yield a brown oil. The crude ratio was determined by GC to be 9:1. The crude material was dissolved in CH_2Cl_2 and passed through silica plug yielding 183 mg of white solid that was determined to be a 9:1 mixture by ^{1}H NMR. (67% isolated yield of mixture, m.p. = 62-62°C).

Table 2.5, Entry 7: Borylation with dpm as the ligand



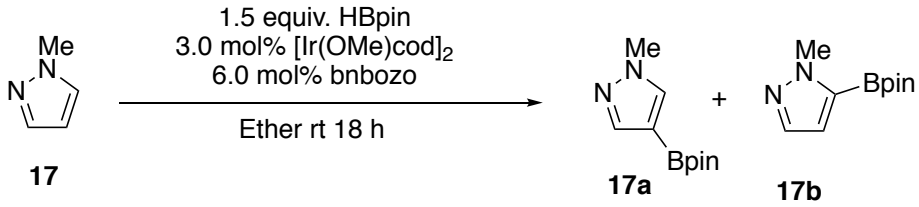
1.0 mmol crude ratio 1:9

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added into the vial to make a clear, light yellow solution. HBpin (218 μL mg, 192 mg, 1.5 mmol, 1.5 equiv) was added by pipettor to the yellow solution, which then deepened to a gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred by Pasteur Pipette into the reaction vial. The GC vial was rinsed with 0.5 mL THF and the rinse was added to the reaction. N-methylpyrazole (82 mg, 83

μL, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. 1.0 mL of additional THF was added to the reaction vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 h. Full conversion based on HBpin was observed to by GC.

After the reaction was stopped, the volatile materials were removed by rotary evaporation and ^{1}H NMR of the crude material confirmed the absence of starting material and indicated 9:1 ratio of **17a**:**17b**.

Table 2.5, Entry 7: Borylation with bnbozo as the ligand



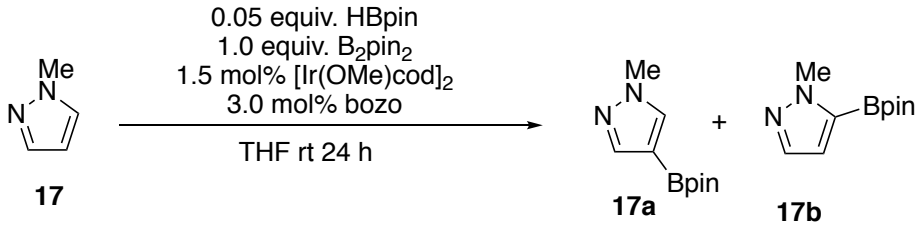
17 **17a** **17b**

1.0 mmol crude ratio 1:8

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (**bnbozo**) (20 mg, 0.03 mmol, 6 mol %). 1.0 mL diethyl ether was added to dissolve the ligand. $[Ir(OMe)(cod)]_2$ (20 mg, 0.03 mmol, 6 mol % Ir) was weighed into a test tube. HBpin (384 mg, 435μL, 3.0 mmol, 3 equiv) was added to the Ir pre-catalyst and mixed well with a Pasteur Pipette. The resulting golden solution was transferred into the reaction vial containing the ligand. The test tube was rinsed with 1.0 mL diethyl ether and the rinse was added to the reaction vial. N-methylpyrazole (82 mg, 83 μL, 1.0 mmol, 1.0 equiv) was added last by pipettor into the reaction vial. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 18 h. After the reaction was stopped, the volatiles were removed by rotary evaporation. Complete conversion was seen by ^{1}H NMR of the crude

reaction mixture and a ratio of 1:9 was observed.

Table 3.4, Entry 7: Borylation with bozo as the ligand



5.0 mmol

crude ratio 1:32
64% isolated yield **17b**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (50 mg, 0.075 mmol, 3 mol % Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin (40 μL, 35 mg, 0.28 mmol, 0.055 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis(2-oxazoline) (bozo) was weighed into a test tube (25 mg, 0.078 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The solution turned a cherry red color. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. B_2Pin_2 (1.27 g, 5.0 mmol, 1.0 equiv) was weighed into a vial and added into the stirring reaction mixture as a solid. The weighing vial was rinsed with 3 x 1 mL THF and the rinses were added into the reaction for a total volume of 5.0 mL. N-methylpyrazole (0.410 g, 415 μL, 5.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After the reaction was stopped, the volatiles were removed by rotary evaporation. Full conversion was seen by crude ^1H NMR and ratio of 1:32 was observed in the crude mixture. The crude material was dissolved in CH_2Cl_2 and passed through a 20 g silica plug with about 300 mL CH_2Cl_3. The eluent was concentrated to 1 g of a clear gel. A minimum amount of hexane was added with swirling of the flask until the mixture was

homogeneous and the gel appeared to be dissolved, resulting in a less viscous solution. The flask was closed with a septum and put in the -30°C freezer for 2 days. 0.66 g of a white crystalline solid were collected and combined from two crops. The isolated material was analytically pure **17b** by ^{1}H NMR (64% isolated yield, m.p. = 68 – 70°C).

Table 2.5, Entry 8

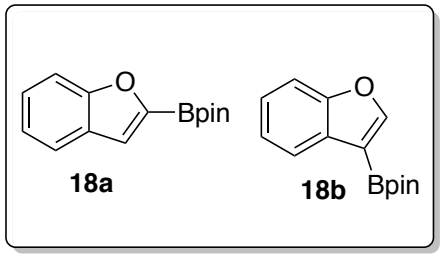
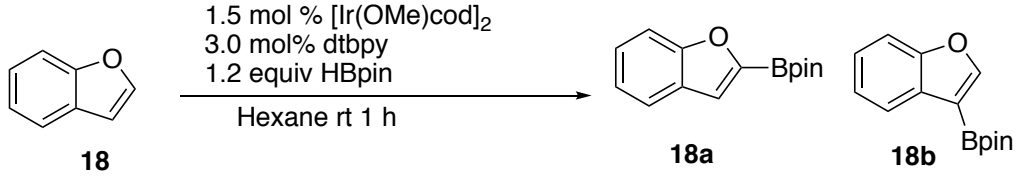


Table 2.5, Entry 8: Borylation with dtbpy as ligand



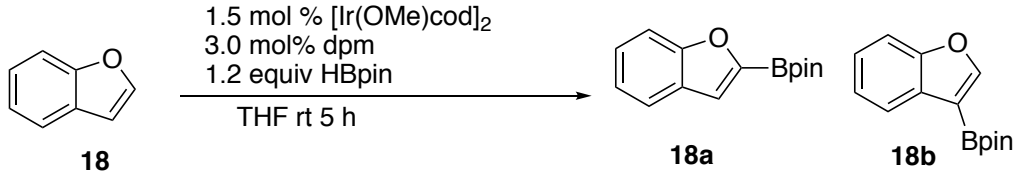
1mmol

ratio of crude material: 32:1
83% isolated yield **18a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin 175 μL, 1.2 mmol, 1.2 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 4,4'-Di-t-butyl-2,2'-bipyridine (dtbpy) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol %), and the ligand was added to the vial as a solid. The mixture turned dark red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. Benzofuran (0.118g, 110 μL, 1.0 mmol, 1.0 equiv) was added by pipettor into the stirring mixture in the vial. Vigorous bubbling was observed. 1.0 additional mL of THF was added to the vial for a total volume of 3.0 mL THF. When gas evolution

had subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 1 h, at which time the reaction was judged complete based by GC-FID. The volatiles were removed by rotary evaporation to yield a brown oil. The crude ratio was determined by GC and ^{1}H NMR to be 32:1. The crude material was dissolved in CH_2Cl_2 and passed through a 10g silica plug eluting with CH_2Cl_2, yielding isomer **18a** and borates. The material was recrystallized from hexane to afford 205 mg of the pure material, **18a**. (83% yield)

Table 2.5, Entry 8: Borylation with dpm as ligand



18 **18a** **18b**

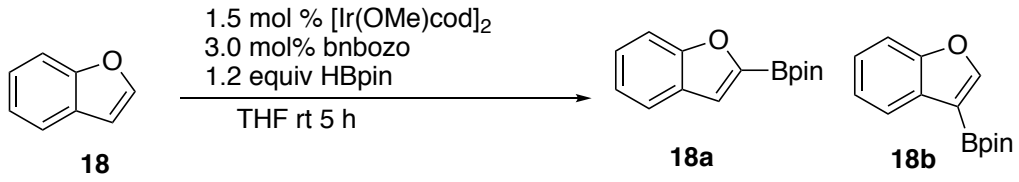
1mmol

ratio of crude material: 18:1
90% isolated yield **18a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). 1.0 mL THF was added into the vial to make a clear, light yellow solution. HBpin (175 µL mg, 1.2 mmol, 1.5 equiv) was added by pipettor to the yellow solution, which then deepened to a gold color. Di-(pyridin-2-yl)methane (dpm) was weighed into a GC vial (5 mg, 0.03 mmol, 3 mol %) and dissolved in 0.5 mL THF. The solution was transferred by Pasteur Pipette into the reaction vial. The GC vial was rinsed with 0.5 mL THF and the rinse was added to the reaction. Benzofuran (0.118 mg, 110 µL, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the reaction vial. 1.0 mL of additional THF was added to the reaction vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 h. Full conversion was observed to by GC-FID.

After the reaction was stopped, the volatile materials were removed by rotary evaporation and ^{1}H NMR of the crude material confirmed the absence of starting material and indicated 18:1 ratio of **18a**:**18b**. The crude material was dissolved in 1:1 dcm / hexane and applied to a 3g silica column eluting with 1:1 dcm / hexane. The fractions were concentrate and 221 mg of white solid was obtained that was pure **18a** by GC-FID and ^{1}H NMR. (90% isolated yield, mp 85°C sharp)

Table 2.5, Entry 8: Borylation with bnbozo as ligand



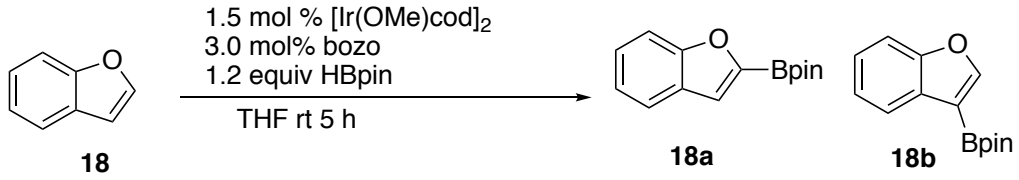
1 mmol

ratio of crude material: 99:1
95% isolated yield **18a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin 175 μL, 1.2 mmol, 1.2 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis[(4S-)4-benzyl)-2-oxazoline] (bnbozo) was weighed into a test tube (10 mg, 0.03 mmol, 3 mol %), and the ligand was added to the vial as a solid. The mixture turned cherry red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. Benzofuran (0.118g, 110 μL, 1.0 mmol, 1.0 equiv) was added by pipettor into the stirring mixture in the vial. Vigorous bubbling was observed. 1.0 additional mL of THF was added to the vial for a total volume of 3.0 mL THF. When gas evolution had subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 1 h, at which time the reaction was judged complete based by GC-FID. The volatiles were removed by rotary evaporation to yield a brown oil. The crude ratio was determined by GC and ^{1}H NMR to be >99:1. The crude material was dissolved in 1:1 dcm /

hexane and passed through a 3g silica plug eluting with 1:1 dcm / hexane. The fractions were combined to yield 222 mg of the pure material, **18a**. (95% isolated yield, 85°C sharp).

Table 2.5, Entry 8: Borylation with bozo as ligand



18 **18a** **18b**

1 mmol

ratio of crude material: 14:11
90% isolated yield 14:1 **18a:18b**

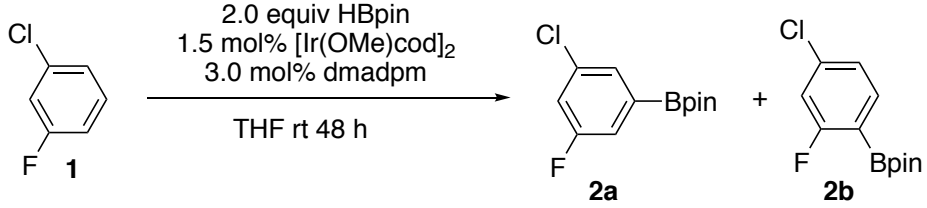
In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 0.015 mmol, 3 mol% Ir). 1.0 mL THF was added with stirring and a clear yellow solution resulted. HBpin 175 μL, 1.2 mmol, 1.2 equiv) was added by pipettor into the light-yellow solution, which deepened to a clear gold color. 2,2'-Bis-2-oxazoline (bozo) was weighed into a test tube (5 mg, 0.03 mmol, 3 mol %), and the ligand was added to the vial as a solid. The mixture turned cherry red. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. Benzofuran (0.118 g, 110 μL, 1.0 mmol, 1.0 equiv) was added by pipettor into the stirring mixture in the vial. Vigorous bubbling was observed. 1.0 additional mL of THF was added to the vial for a total volume of 3.0 mL THF. When gas evolution had subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 1 h, at which time the reaction was judged complete based by GC-FID. The volatiles were removed by rotary evaporation to yield a brown oil. The crude ratio was determined by GC and ^{1}H NMR to be 14:1. The crude material was dissolved in 1:1 dcm / hexane and passed through a 3g silica plug eluting with 1:1 dcm / hexane. The fractions were combined to yield 220 mg of a white solid 14:1 **18a:18b**. (90% isolated yield, mp 75 – 77°C).

Table 2.6: Comparison of dmadpm on selected substrates:

The ligands dtbpy, dpm, bnbozo, and bozo, were featured in table 3.3, and are included for comparison. For experimental procedures, see Tables 2.4 and 2.5.

Table 2.6, Entry 1: Borylation of 1 with dmadpm and 2 equiv HBpin

Isolation of single isomer 2a



1.0 mmol

ratio of crude material by GC 11:1
isolated yield 71% **2a**

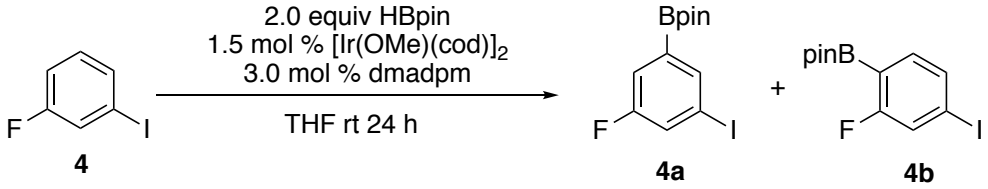
In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF (1.0 mL) was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added to the light-yellow solution, which deepened to a clear gold color. The ligand, dimethyl amino dipyridyl methane (dmadpm) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 1-Chloro-3-fluorobenzene (0.131 g, 107 μL, 1.0 mmol, 1.0 equiv) was added into the reaction vial. Additional THF (1.0 mL) was added into the reaction for a total volume of 3.0 mL. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. After 48 hours, 98% conversion to products was observed by CG and ^{19}F NMR with a ratio of 11:1 of the corresponding borylated isomers **2a**:**2b**.

After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in a minimum amount of CH_2Cl_2 and passed

through a 3 g plug of silica eluting with hexanes. The fractions were analyzed by TLC using 10% diethyl ether in hexane as eluent, then the TLC plates were treated with alizarin stain. Most fractions gave rise to only one spot, pure **2a** (r_f = 0.6), while the last 4 fractions showed traces of **2b** as a second spot (r_f = 0.52). The fractions containing only one spot were combined and concentrated to yield 181 mg of a clear, colorless oil that was pure **2a** by GC and ^{19}F NMR (71% yield) The last four fractions were combined and concentrated to yield 50 mg clear oil that was a 10:1 **2a**:**2b** isomeric ratio of borylated products by ^{19}F NMR. The combined mass of the two batches was 231 mg (90% yield).

Table 2.6, Entry 2: Borylation of 4 with dmadpm

The ligands dtbpy, dpm, bnbozo, and bozo, were featured in Tables 2.4 and 2.5, and are included in Table 2.6 for comparison. For experimental procedures, see Tables 2.4 and 2.5.



4 1.0 mmol

4a ratio of crude material by GC 14:1
isolated yield 82% **4a**

4b

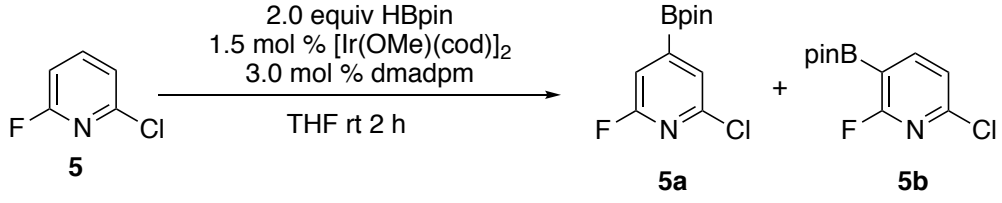
In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stirring bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF (1.0 mL) was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. The ligand, dimethyl amino dipyridyl methane, (dmadpm) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol%) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 3-Iodofluorobenzene (0.222 g, 118 μL, 1.0 mmol, 1.0 equiv) was dispensed into the stirring mixture in the vial by pipettor. Additional THF (1.0 mL) was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and

allowed to stir at ambient temperature in the glove box for 24 hours. ^{19}F NMR of a reaction aliquot showed 86% conversion with a ratio of 14:1. The reaction was stopped, and the volatile materials were removed by rotary evaporation. The crude material was dissolved in 1:1 dichloromethane : hexane and passed through a 3g plug of silica to afford the corresponding borylated product as 283 mg of clear oil, (82% isolated yield, 14:1 **4a**:**4b** by ^{19}F NMR.)

Table 2.6, Entry 3: Borylation of 5 with dmadpm

The ligands dtbpy, dpm, bnbozo, and bozo, were featured in Tables 2.4 and 2.5, and are included in Table 2.6 for comparison. For experimental procedures, see Tables 2.4 and 2.5.

Selectivity of dmadpm with 2 equiv HBpin - Isolation of single isomer 5a.



1.0 mmol

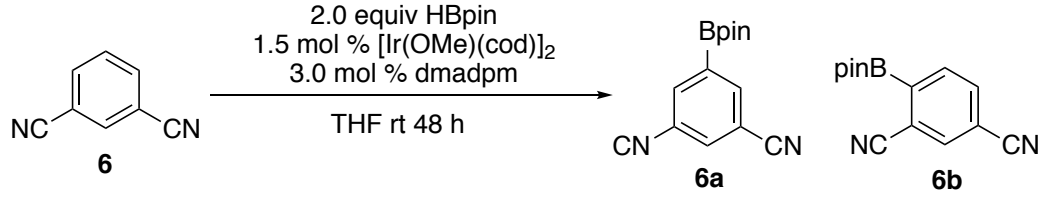
ratio of crude material by GC 38:1
isolated yield 91% **5a**

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stirring bar was charged with [Ir(OMe)cod]$_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF (1.0 mL) was added with stirring. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by pipettor. The ligand, dimethyl amino dipyridyl methane, (dmadpm) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol%) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial. 2-chloro-6-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After completion of the reaction, the volatile materials were removed

by rotary evaporation. The crude material was dissolved in hexane and passed through a 2g plug of silica to afford the corresponding borylated product as a white solid (234 mg, 91% isolated yield, m.p. = 72 – 76 °C) determined to be a single isomer **5a** by ^{19}F NMR.

Table 2.6, Entry 4: Borylation of 6 with dmadpm.

The ligands dtbpy, dpm, bnbozo, and bozo, were featured in Tables 2.4 and 2.5, and are included in Table 2.6 for comparison. For experimental procedures, see Tables 2.4 and 2.5.



1.0 mmol

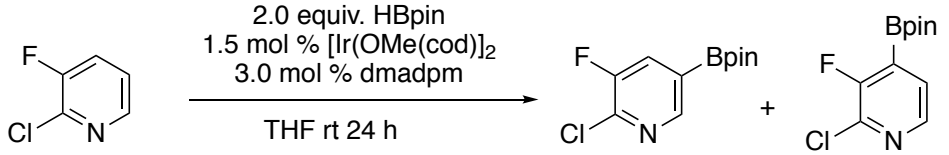
ratio of crude material by ^{1}H NMR 6:1
isolated yield 79% (7.5:1)
32% **14a** recrystallized from EtOH

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3.0 mol % Ir). THF (1.0 mL) was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added by syringe into the light-yellow solution, which deepened to a clear gold color. The ligand, dimethyl amino dipyridyl methane (dmadpm) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol%) and added as a solid into the stirring reaction mixture. The reaction turned a deep orange color. 1,3-Dicyanobenzene (0.128 g, 1.0 mmol, 1.0 equiv) was weighed into a test tube and added last as a solid into the stirring mixture in the vial. The test tube was rinsed with 1.0 mL of THF and the rinse was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 48 hours. 98% conversion was observed by GC.

After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 2g silica plug to yield 219 mg of a white solid that was determined to be a 7.5:1 mixture of isomers mixed and residual starting material (201 mg isomers corrected for mass of starting material, 79% isolated yield). The mixture was slurried in ethanol and warmed until all solids dissolved, then the flask was cooled slowly open to air for about 2 hours as crystals formed. The flask was closed with a septum and put in the 10°C refrigerator overnight. 82 mg (32% yield, m.p. = 118 – 120 °C) of clear, colorless crystals were collected by filtration, and were determined to be pure **6a** by GC and ^{1}H NMR.

Table 2.6, Entry 5: Borylation of 10 with dmadpm: Isolation of 10a

The ligands dtbpy, dpm, bnbozo, and bozo, were featured in Tables 2.4 and 2.5, and are included in Table 2.6 for comparison. For experimental procedures, see Tables 2.4 and 2.5.



10 **10a** **10b**

1.0 mmol

ratio of crude material by GC 2.3:1
isolated yield 60% (2.3:1)
recrystallized 38% (17:1)

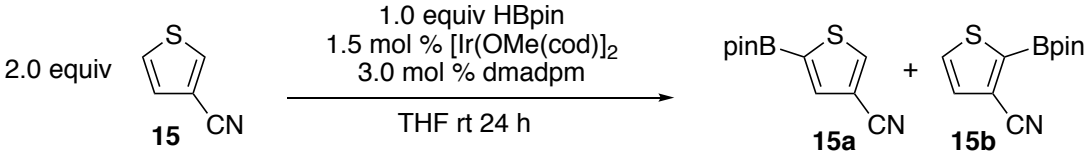
In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with [Ir(OMe)cod]$_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF (1.0 mL) was added with stirring and a clear yellow solution resulted. HBpin (290 μL, 256 mg, 2.0 mmol, 2.0 equiv) was added into the light-yellow solution, which deepened to a clear gold color. The ligand dimethylamino dipyridyl methane (dmadpm) was weighed into a test tube (8 mg, 0.03 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0

mL THF and the rinse was added to the vial. 2-Chloro-3-fluoropyridine (0.132g, 1.0 mmol, 1.0 equiv) was added last by pipettor into the stirring mixture in the vial. Additional solvent (1.0 mL) was added to the vial for a total volume of 3.0 mL THF. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 24 hours. After 24 hours, 70% conversion of starting material to products was observed by GC and ^{19}F NMR.

After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 2 g plug of silica to yield a clear oil that was a 2.3:1 mixture of borylated isomers **10a**:**10b** with residual starting material. The starting material was pumped off under high vacuum to afford 153 mg of a white crystalline solid of the same ratio. (60% yield) The isolated mixture was recrystallized from hexanes to yield 99 mg of a white crystalline solid that was determined by ^{19}F NMR to be a 17:1 mixture of borylated isomers. (38% yield) A second recrystallization furnished 41 mg pure **10a** (16% yield) suitable for single crystal x-ray diffraction, which resulted in a structure consistent with the steric isomer, **10a**.

Table 2.6, Entry 6: Borylation of 15 with dmadpm

The ligands dtbpy, dpm, bnbozo, and bozo, were featured in Tables 2.4 and 2.5, and are included in Table 2.6 for comparison. For experimental procedures, see Tables 2.4 and 2.5.



0.5 mmol HBpin

ratio of crude material 5.5:1 (4% diborylation)
80% isolated yield 10:1

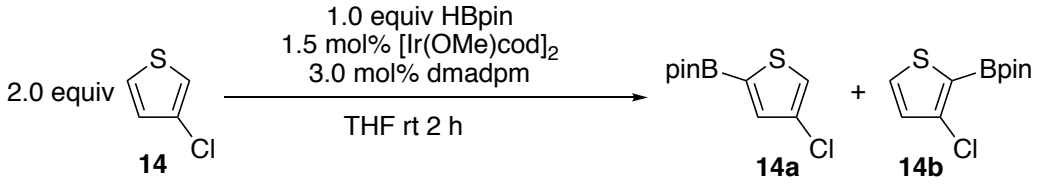
In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (5 mg, 0.0075 mmol, 3 mol % Ir). THF was added (0.5 mL) with

stirring and a clear yellow solution resulted. HBpin (73 μL, 64 mg, 0.5 mmol, 1.0 equiv) was added into the light-yellow solution, which deepened to a clear gold color. The ligand, dimethylamino dipyridyl methane (dmadpm) was weighed into a test tube (4 mg, 0.0015 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The test tube was rinsed with 1.0 mL THF and the rinse was added to the vial for a total volume of 1.5 mL of THF. 3-Cyanothiophene (0.109 g, 91 μL, 1.0 mmol, 2.0 equiv) was added into the stirring mixture in the vial by pipettor. The vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 4 hours. After 4 hours, complete conversion to products based on HBpin was observed by GC. 4% diborylated substrate was observed by ^{1}H NMR.

After completion of the reaction, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 2 g plug of silica and eluted with 1:1 CH_2Cl_2 / hexane to yield a clear oil that was a mixture of borylated isomers and residual starting material. The fractions were analyzed by GC, and the last two fractions contained higher ratios of minor isomer and thus were excluded when the fractions were combined. The starting material was pumped off under high vacuum to afford 94 mg of a white crystalline solid with a 10:1 ratio of **15a**:**15b**. (80% yield, m.p. = 93 – 94°C).

Table 2.6 Entry 7: Borylation of 14 with dmadpm

The ligands dtbpy, dpm, bnbozo, and bozo, were featured in Tables 2.4 and 2.5, and are included in Table 2.6 for comparison. For experimental procedures, see Tables 2.4 and 2.5.



1.0 mmol HBpin

ratio of crude material 9:1 (4% diborylation)
84% isolated yield (10:1)

In a glove box under nitrogen atmosphere, a 20 mL vial equipped with a magnetic stir bar was charged with $[Ir(OMe)cod]_2$ (10 mg, 0.015 mmol, 3 mol % Ir). THF was added (1.0 mL) with stirring and a clear yellow solution resulted. HBpin (145 μL, 128 mg, 1.0 mmol, 1.0 equiv) was added by pipettor into the light yellow solution, which deepened to a clear gold color. The ligand, dimethyl amino dipyridyl methane (dmadpm) was weighed into a test tube (8 mg, 0.0015 mmol, 3 mol %) and added as a solid into the stirring reaction mixture. The test tube was rinsed twice with 1.0 mL THF and the rinses were added to the vial for a total volume of 3.0 mL of solvent. 3-Chlorothiophene (236 mg, 186 μL, 2.0 mmol, 2.0 equiv) was added into the stirring mixture in the vial. Vigorous bubbling was observed. After the gas evolution subsided, the vial was closed with a screw cap and allowed to stir at ambient temperature in the glove box for 2 hours. After 2 hours, complete conversion to products based on HBpin was observed by GC. A ratio of 9:1 of the monoborylated isomers **14a**:**14b** and 4% diborylation was observed by ^{1}H NMR.

After the reaction was stopped, the volatile materials were removed by rotary evaporation. The crude material was dissolved in CH_2Cl_2 and passed through a 3 g plug of silica to yield a clear oil that was a mixture of borylated isomers and residual starting material. The starting material was pumped off under high vacuum to afford 206 mg of a clear, colorless oil containing a 10:1 ratio of corresponding borylated isomers **14a**:**14b** by GC and ^{1}H NMR (84% yield).

General Methods for Kinetics study:

NMR kinetics were performed on a variable temperature Varian Innova 300 MHz multi-channel NMR spectrometer in proteated solvents with a THF gradient shim map according to no-D techniques. Reactions were monitored by ^{19}F NMR as an automated array. Arrayed spectra were processed automatically with iNMR software. Reactions were referenced to hexafluorobenzene in ^{19}F NMR and cyclohexane in no-D ^{1}H NMR.

(coe)Ir(dtbpy)$Bpin_3$ was prepared according to a literature prep.[19] 3-Trifluoromethyltoluene was purchased commercially and passed through activated basic alumina before use. 3-Flourochlorobenzene was purchased commercially, refluxed over CaH_2 and distilled at atmospheric pressure before use. Cyclohexane and THF were dried over sodium and benzophenone, freshly collected from wet stills and brought into the glove box just prior to use. Reactions were made up in test tubes equipped with a small stir bar and mixed thoroughly before transferring into a screwcap NMR tube. A representative reaction is as follows:

Kineteics employing B_2pin_2 as the boron source:

All NMR tube reactions were made up in the glove box in a nitrogen atmosphere. The coe complex was weighed out in a test tube equipped with a stir bar. 0.6 mL cyclohexane was added with a gastight micro syringe. B_2pin_2 was weighed by difference into the test tube and stirred until dissolved. C_6F_6 was added as an internal standard with a gastight mocrosyringe. The contents were transferred into the srewcap NMR tube with a Pasteur pipette and the NMR tube was closed with the septum top cap. The substrate was put into an air tight gc vial to be added by syringe right before the arrayed experiment.

Kineteics employing HBpin as the boron source:

All NMR tube reactions were made up in the glove box in a nitrogen atmosphere. The coe complex was weighed out in a test tube equipped with a stir bar. 0.6 mL cyclohexane was added with a gastight micro syringe. HBpin was dispensed into the test tube by gastight micro syringe. The mixture was stirred about two minutes. C_6F_6 was added as an internal standard with a gastight micro syringe. The contents were transferred into the J-young tube with a Pasteur pipette and the NMR tube was closed with the septum top cap. The substrate was put into an air tight gc vial to be added by syringe right before the arrayed experiment.

Generation of the active catalyst from $[Ir(OMe)cod]_2$ and a ligand:

For experiments generating the active catalyst, $[Ir(OMe)cod]_2$ and ligands (dtbpy or dmadpm) were made into stock solutions in cyclohexane or THF depending on the solvent of the experiment. The concentrations were designed to add catalyst and ligand in volumes of 150µL each by gastight syringe. Catalyst stock solution (150µL) was added into the test tube by gas tight micro syringe, followed by ligand stock solution (150µL). B_2pin_2 or HBpin was added next, and 0.3 mL cyclohexane was added last. The reactions were stirred about two minutes and then were transferred into a screw cap tube NMR tube and the tube was closed with a screw cap. Like the general experiments, the substrate was stored in an air tight GC vial and added at the time of the experiment.

For Kinetics reactions that were heated, the reaction was brought to temperature within the spectrometer before adding the substrate by gas tight micro syringe.

The arrayed experiments acquired each spectrum as 4 scans with a 2 second delay between each scan. A time stamp was taken after 2 scans at the midpoint of each acquisition. Each spectrum had a 25 second acquisition time with 125 seconds between acquisitions. The log files were downloaded into Excel and processed automatically into time elapsed. The NMR peak areas were integrated automatically by iNMR and the integral values were pasted into Excel with the log file to generate the kinetics graphs. All graphs are included in the appendix.

General Methods for KIE studies:

Benzene was dried by reflux over CaH_2 and collected in a wet still just prior to use. NMR grade d_6-benzene was purchased commercially and used as received. All KIE reactions were made up in in a glove box with Nitrogen atmosphere in 20 mL vials equipped with stir bars. Reactions of 0.2 mmol scale were closed with cone-sealing screw caps and allowed to stir in the glove box.

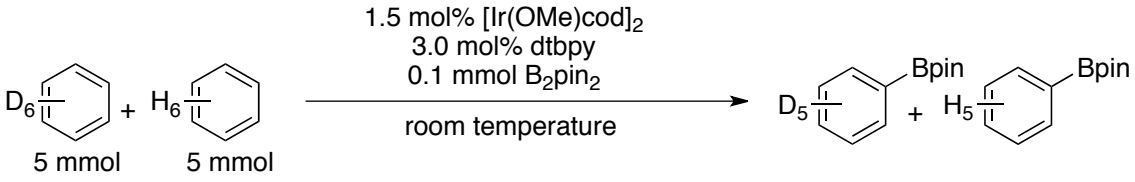
When reactions were monitored by GCMS, the screw cap was removed from the vial in the glove box, and accurate 100 μL aliquots were removed with gas tight micro syringes and dispensed into gc vials. The vials were brought out of the glove box and quenched with 1.0 mL anhydrous methanol from a 1.0 mL volumetric pipette. The volume of these samples was considered as 1.10 mL. Although 100μL samples are concentrated, the errors from sample removal are low and results are consistent and repeatable. Smaller sample size introduced greater error.

In order to judge % conversion of the boron source into phenyl Bpin, a dodecane internal standard was used. A calibration curve was constructed in the following manner: Phenyl Bpin standards of known concentration were prepared by a dilution series and the standards were spiked with a constant amount of dodecane, equal to one tenth the dodecane added to the experiments. Each standard was analyzed twice by GCMS to ensure reproducible auto-sampling. All the peak areas of the dodecane over all the standards were averaged and this area was set as a constant value for dodecane. The ratio of the average dodecane area to the known concentration of phenylBpin was plotted against the known molar concentrations of the phenyl Bpin standards. The area of the dodecane peak from the experimental sample was normalized to the average dodceane peak of the calibration curve. The slope of the calibration curve gives the molarity of phenyl Bpin in the experimental sample by setting the ratio of the areas of normalized dodecane to experimental phenyl Bpin as the X value in the equation of the calibration curve. The sample molarity is multiplied by 10 to calculate the molarity of the reaction. The moles of phenyl Bpin in the experimental sample were then determined and the % conversion was calculated from the theoretical moles of product. The method was tested by running trial samples of known concentrations of phenyl Bpin and the results were within 5% of the known concentrations.

In order to determine the H_5/D_5 ratio of the products, a quantitative GCMS program was used and calibration curves of d_5-phenyl Bpin and H_5-phenyl Bpin were made and saved in the program. A quantitative mass spec method with a slow ramp and long hold time was written in order to resolve the deuterated and protiated peaks. A scan rate of --- over a mass range of 190 – 220 amu was set in the method.

NMR tube reactions were made up in the glove box in vials equipped with stirbars, then transferred into J-Young NMR tubes with Pasteur pipettes and closed with septum topped screwcaps. Reactions in NMR tubes were monitored by ^{11}B NMR and did not contain deuterated NMR solvents. No-D ^{1}H NMR was run after the reaction was done. Conversion was determined by quenching with methanol and deconvolution of decoupled borate to Bpin peaks. When NMR reactions were monitored by GCMS, 100 μL samples were removed by gastight syringes through the syringe tops and dispensed into gc vials. To easily remove samples from NMR tubes, the tube was put under positive Ar pressure by inserting a thin stainless steel needle from the argon manifold into the septum cap. The needle was removed and the J young tube was inverted and the sample was removed by gas tight micro syringe. Samples were quenched with 1.0 mL anhydrous methanol from a 1.0 mL volumetric pipette. The GCMS delay was set to 3 minutes in order to allow benzene and methanol to pass the detector.

Experimental procedures for KIE experiments: dtbpy and B_2pin_2



In the glove box, B_2pin_2 (25 mg, 0.1 mmol B_2pin_2 = 0.2 mmol Boron) was weighed into a vial equipped with a stir bar. A stock solution of $[Ir(OMe)cod]_2$ was measured by gas tight micro

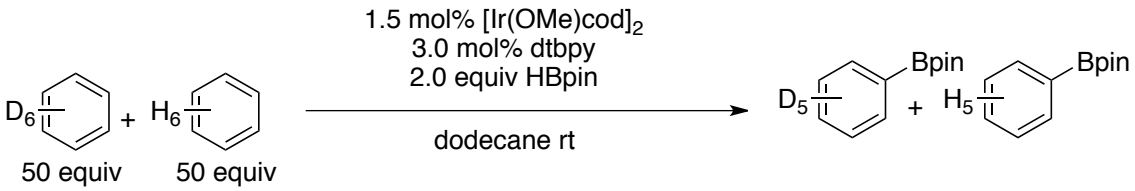
syringe and added into the vial (0.03 M cyclohexane solution, 100 μL, 1.5 x 10^{-6} mol, 1.5 mol% based on 0.2 mmol Boron). A stock solution of dtbpy was measured by gas tight micro syringe and added into the vial (0.06 M cyclohexane solution, 100 μL, 3.0 mol % based on 0.2 mmol boron). Benzene (5 mmol, 444 μL), and d_6-benzene (5 mmol, 443 μL) were accurately measured by gas tight syringe into a separate test tube and mixed well with a pasteur pipette. The mixture was taken up by Pasteur pipette and added into the reaction vial all at once. The vial was closed with a screw cap.

KIE studies of **dtbpy** and B_2Pin_2: The average K_H/K_D ratio obtained was 5.0 ± 0.4

entry	time (h)	vessel	*conversion	KIE
1	0.5	vial	*14%	5.0
2	1.0	vial-opened	*45%	5.4
3	2.0	vial-opened	* >50%	5.4
4	1.5	vial not opened	* >50%	5.2
5	1.0	NMR	21%	4.7
6	9	vial not opened	90%	4.8
7	9	NMR	60%	4.6

*Based on disappearance of B_2pin_2 in GCMS chromatograph. These trials were run before a reliable method to judge conversion with an internal standard was developed. Un-starred conversions were determined by dodecane internal standard after a suitable method was found.

KIE studies of **dtbpy** and HBpin:



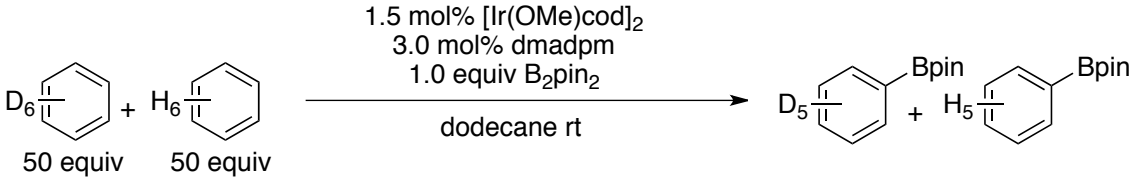
In the glove box, a stock solution of $[Ir(OMe)cod]_2$ was measured by gas tight micro syringe and added into the vial (0.03 M cyclohexane solution, 100 μL, 1.5 x 10^{-6} mol, 1.5 mol%

based on 0.2 mmol Boron). A stock solution of dtbpy was measured by gas tight micro syringe and added into the vial (0.06 M cyclohexane solution, 100 μL, 3.0 mol % ligand based on 0.2 mmol Boron). HBpin was added to the vial with gas tight micro syringe (29 μL, 0.2 mmol). Benzene (5 mmol, 444 μL), and d_6-benzene (5 mmol, 443 μL) were accurately measured by gas tight syringe into a separate test tube and mixed well with a pasteur pipette. The mixture was taken up by Pasteur pipette and added into the reaction vial all at once.

KIE studies of **dtbpy** and HBpin: The average K_H/K_D ratio obtained was 5.0 ± 0.4

entry	time (h)	vessel	conversion	KIE
1	0.5	vial	10%	5.0
2	2	vial-opened	45%	5.2
3	5	vial not opened	53%	5.2
4	5	NMR tube	14%	5.2
5	2	NMR tube	4%	5.2
6	9	vial not opened	82%	4.6

KIE studies of **dmadpm** and B_2pin_2:



In the glove box, B_2pin_2 (25 mg, 0.1 mmol B_2pin_2 = 0.2 mmol Boron) was weighed into a vial equipped with a stir bar. A stock solution of $[Ir(OMe)cod]_2$ was measured by gas tight micro syringe and added into the vial (0.03 M cyclohexane solution, 100 μL, 1.5 x 10^{-6} mol, 1.5 mol% based on 0.2 mmol boron). A stock solution of dmadpm was measured by gas tight micro syringe and added into the vial (0.02 M 2:1 cyclohexane : THF solution, 300 μL, 3.0 mol % based on 0.2 mmol boron). Benzene (5 mmol, 444 μL), and d_6-benzene (5 mmol, 443 μL) were accurately

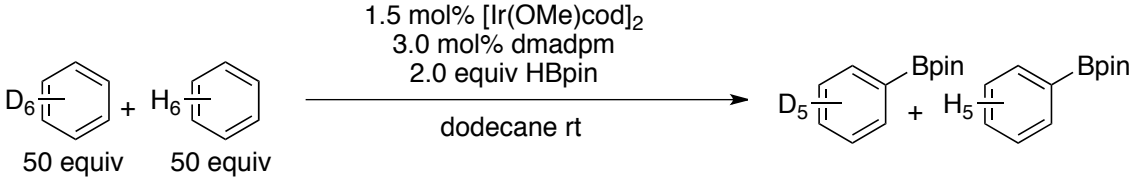
measured by gas tight syringe into a separate test tube and mixed well with a pasteur pipette. The mixture was taken up by Pasteur pipette and added into the reaction vial all at once. The vial was closed with a screw cap.

KIE studies of **dmadpm** and B_2pin_2: The average K_H/K_D ratio obtained was 3.8 ± 0.3

entry	time (h)	vessel	conversion	KIE
1	2	vial	9%	3.8
2	24	vial-opened	*> 50%	3.7
3	16	vial not opened	*44%	3.7
4	24	NMR tube	*> 50%	3.8

*Based on disappearance of B_2pin_2 in the GCMS chromatograph. These trials were run before a reliable method to judge conversion with an internal standard was developed. Un-starred conversions were determined by dodecane internal standard after a suitable method was found.

KIE studies of **dmadpm** and HBpin:



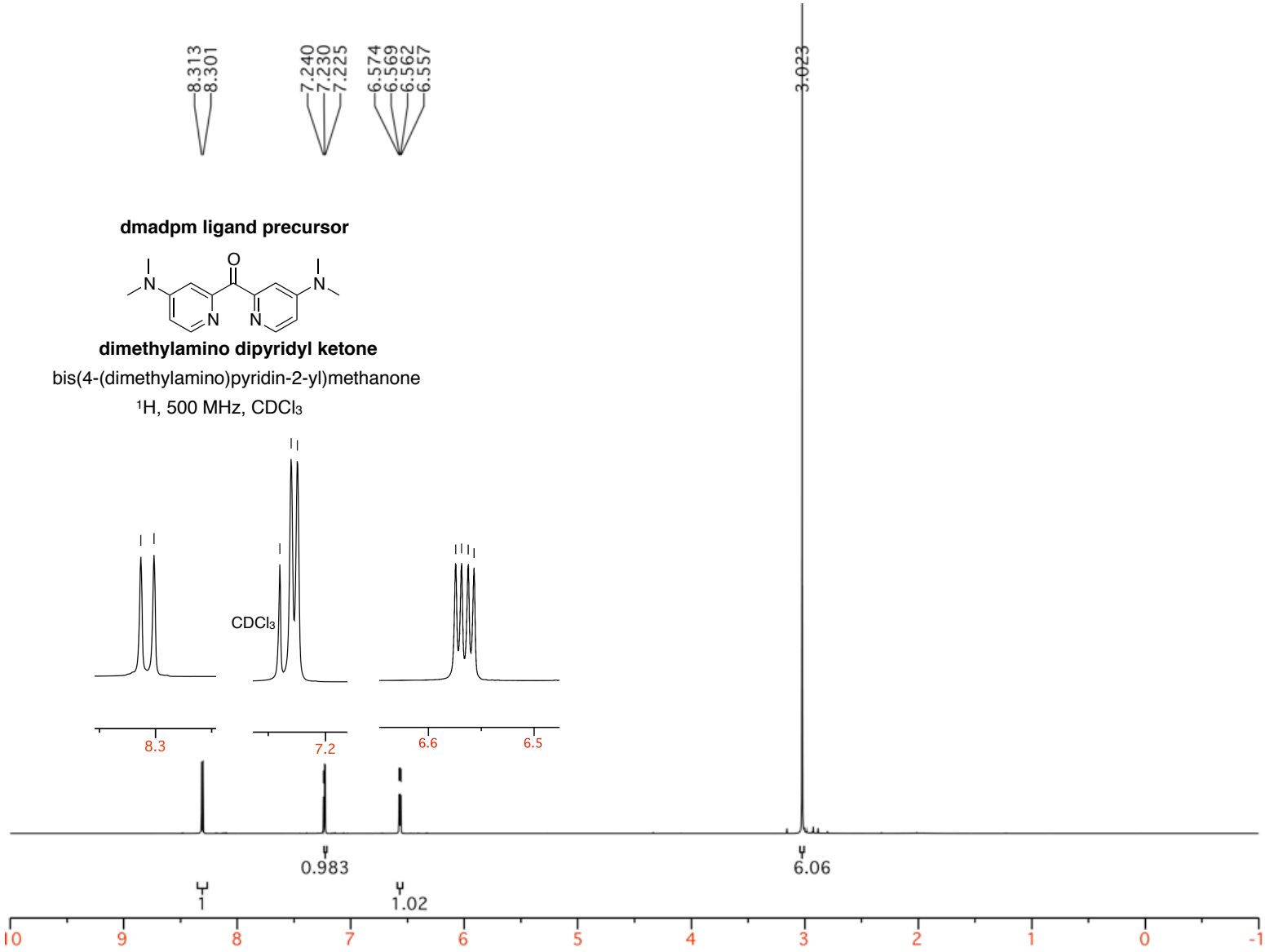
In the glove box, a stock solution of $[Ir(OMe)cod]_2$ was measured by gas tight micro syringe and added into the vial (0.03 M cyclohexane solution, 100 μL, 1.5 x 10^{-6} mol, 1.5 mol% based on 0.2 mmol Boron). A stock solution of dmadpm was measured by gas tight micro syringe and added into the vial (0.02 M 2:1 cyclohexane : THF solution, 300 μL, 3.0 mol % ligand based on 0.2 mmol Boron). HBpin was added to the vial with gas tight micro syringe (29 μL, 0.2 mmol). Benzene (5 mmol, 444 μL), and d_6-benzene (5 mmol, 443 μL) were accurately measured by gas

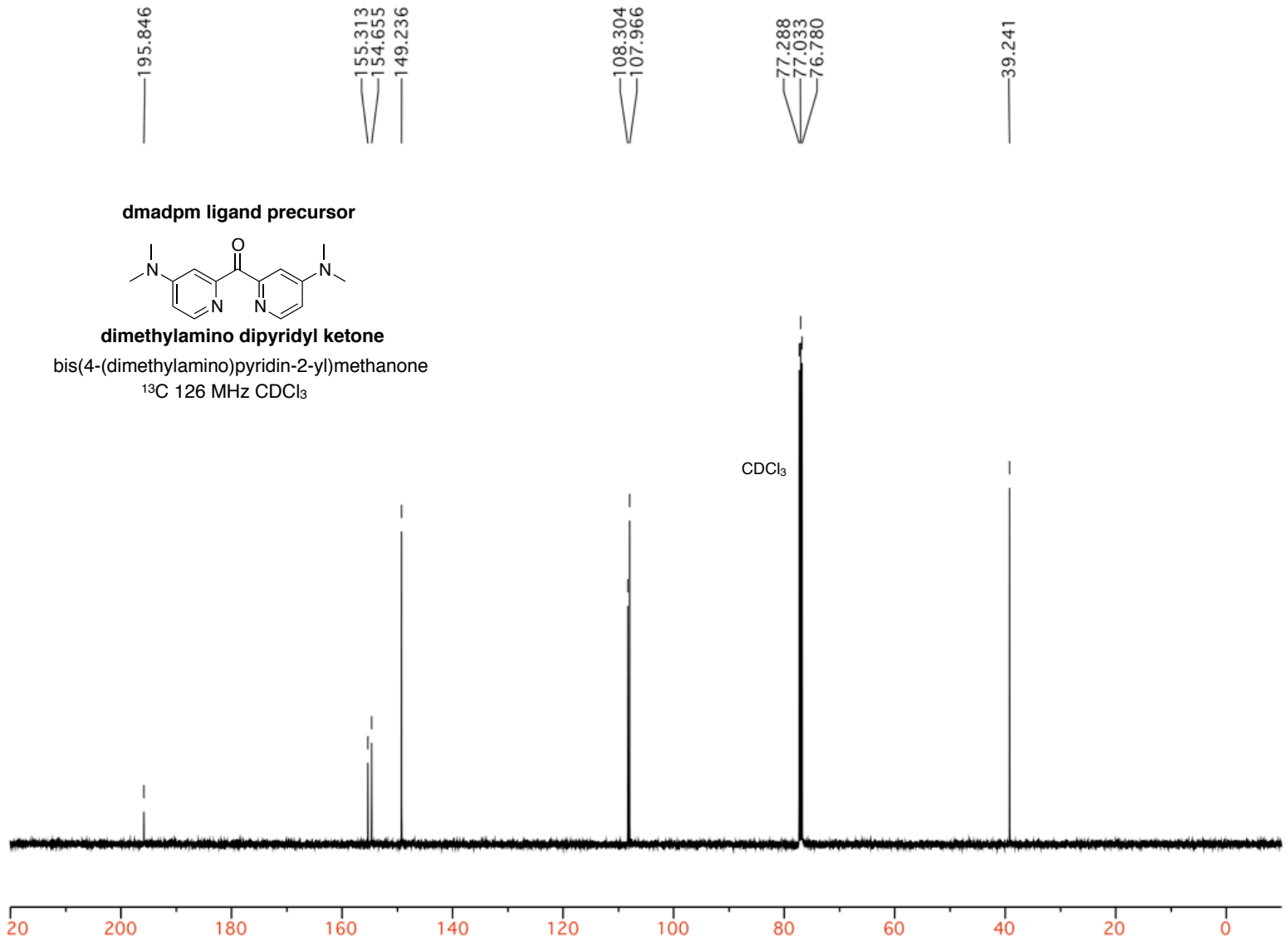
tight syringe into a separate test tube and mixed well with a pasteur pipette. The mixture was taken up by Pasteur pipette and added into the reaction vial all at once.

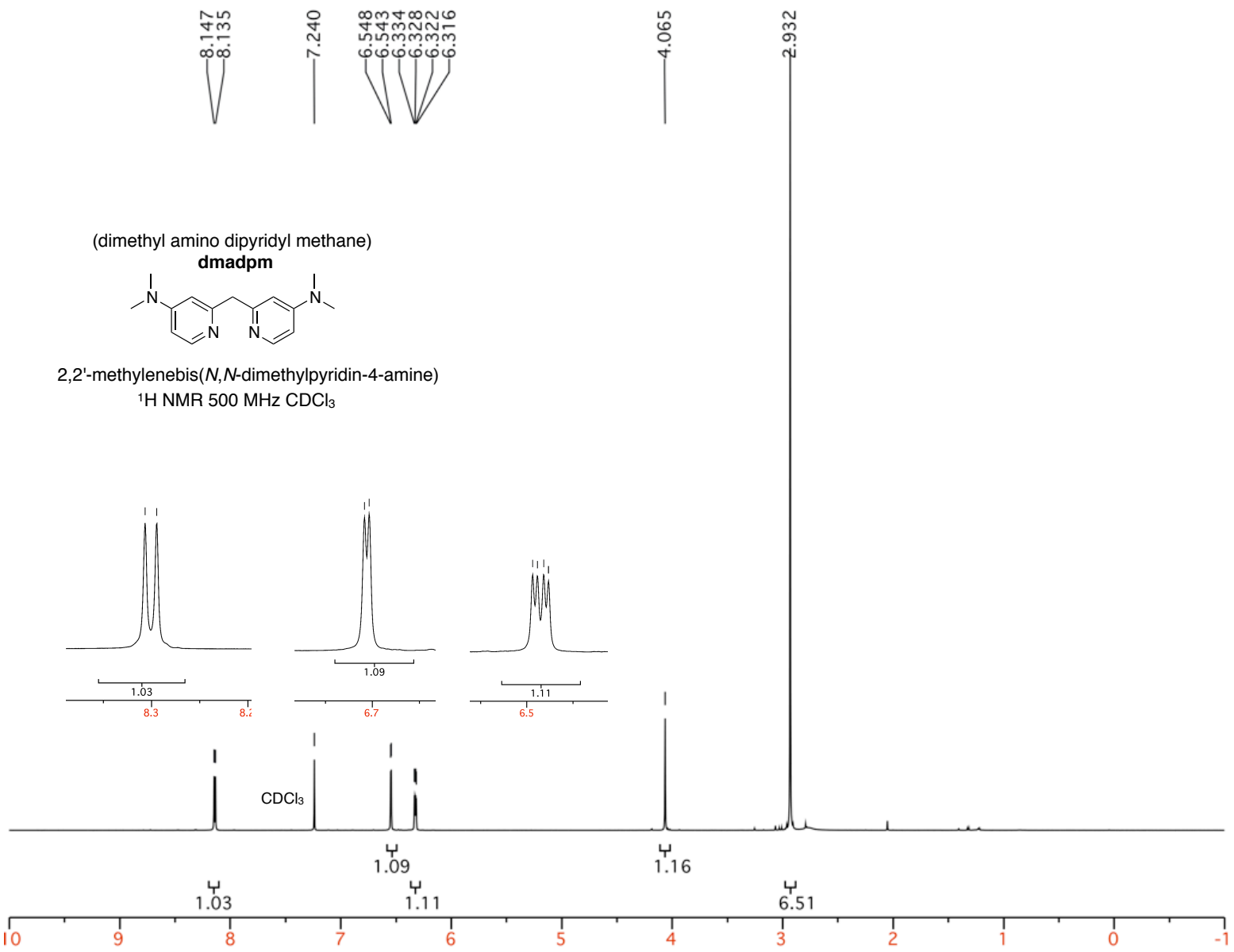
KIE studies of **dmadpm** and HBpin: The average K_H/K_D ratio obtained was 4.2 ± 0.

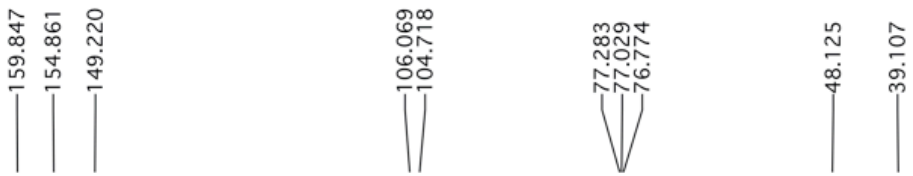
entry	time (h)	vessel	conversion	KIE
1	1	NMR tube	5%	4.1
2	5	NMR tube	10%	4.4
3	2	vial-unopened	10%	4.3
4	5	vial-unopened	40%	4.3
5	16	NMR tube	23%	4.1

NMR SPECTRA


8.313
8.301
7.240
7.230
7.225
6.574
6.569
6.562
6.557
3.023
dmadpm ligand precursor
dimethylamino dipyridyl ketone
bis(4-(dimethylamino)pyridin-2-yl)methanone
¹H, 500 MHz, CDCl₃
CDCl₃
8.3
7.2
6.6
6.5
0.983
6.06
1
1.02
10
9
8
7
6
5
4
3
2
1
0
-1

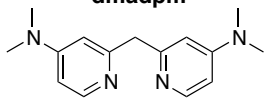

195.846
155.313
154.655
149.236
108.304
107.966
77.288
77.033
76.780
39.241
dmadpm ligand precursor
O
N
N
N
N
dimethylamino dipyridyl ketone
bis(4-(dimethylamino)pyridin-2-yl)methanone
13C 126 MHz CDCl3
CDCl3
20
200
180
160
140
120
100
80
60
40
20
0


8.147
8.135
7.240
6.548
6.543
6.334
6.328
6.322
6.316
4.065
2.932
(dimethyl amino dipyridyl methane)
dmadpm
2,2'-methylenebis(N,N-dimethylpyridin-4-amine)
1H NMR 500 MHz CDCl3
1.03
1.09
1.11
CDCl3
1.09
1.16
1.03
1.11
6.51



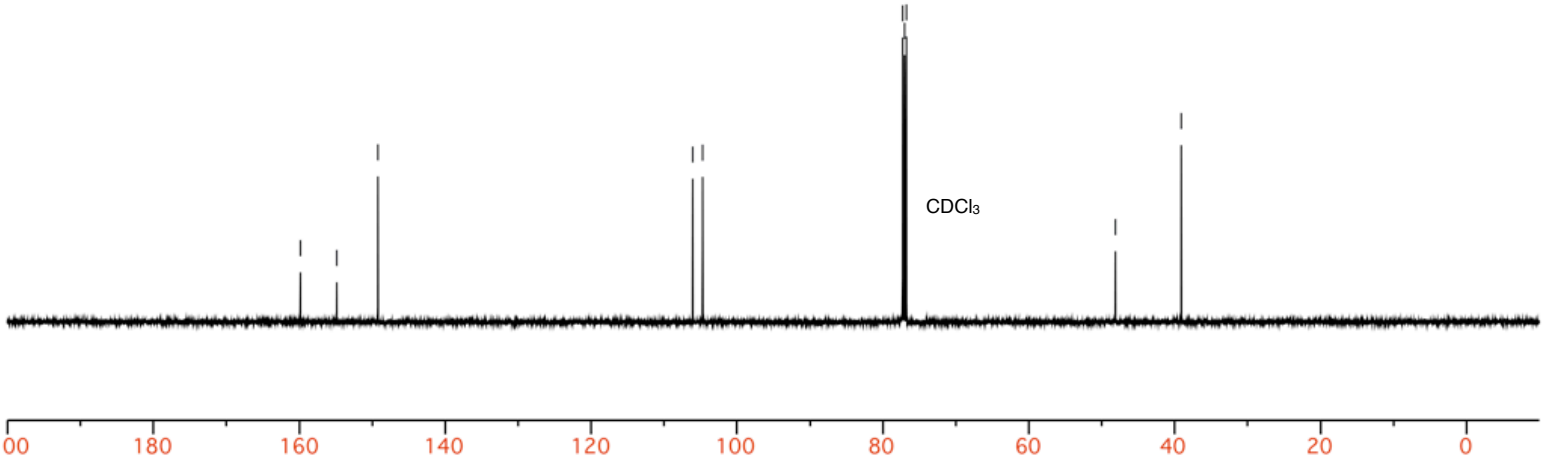
(dimethyl amino dipyridyl methane)

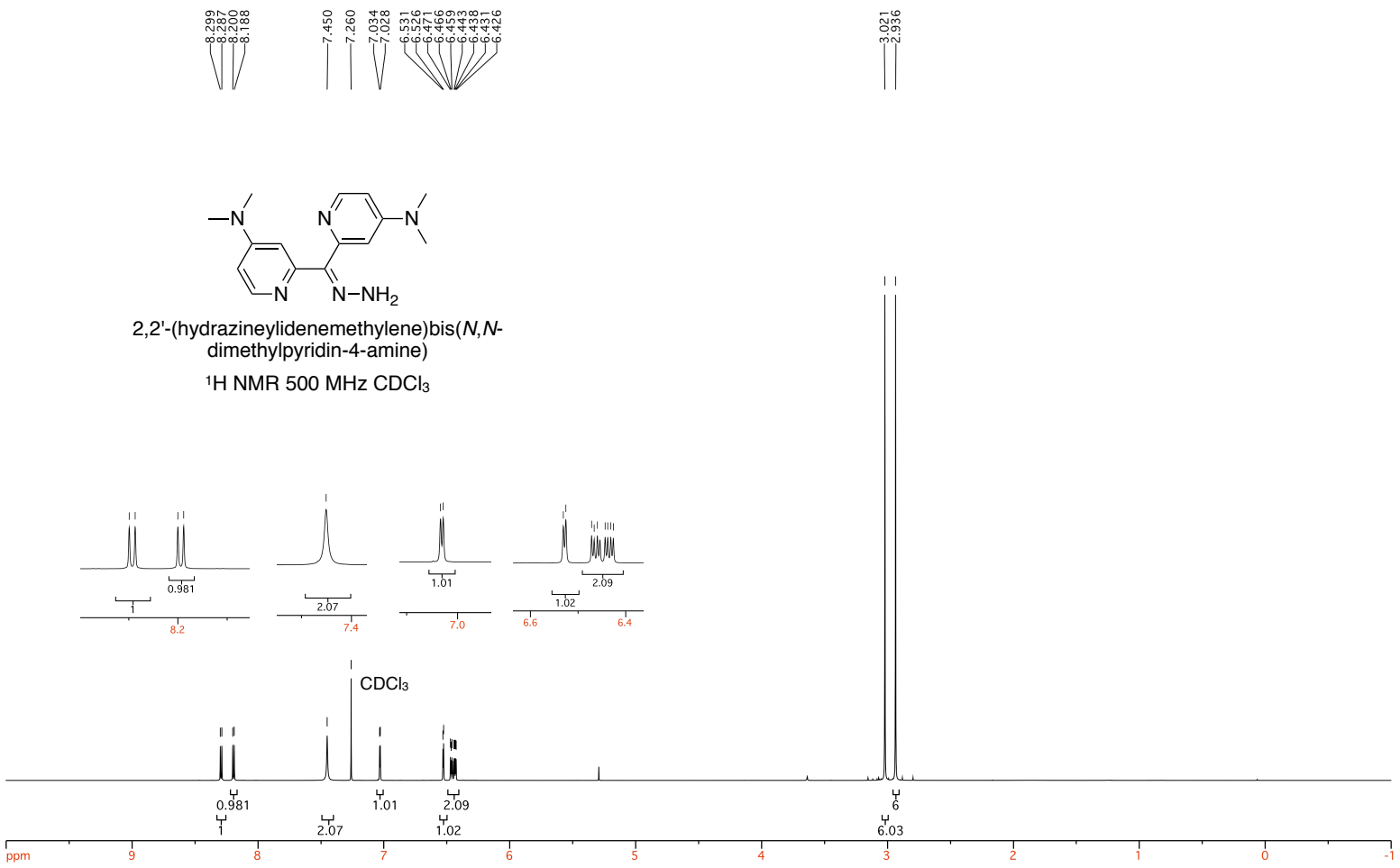
dmadpm

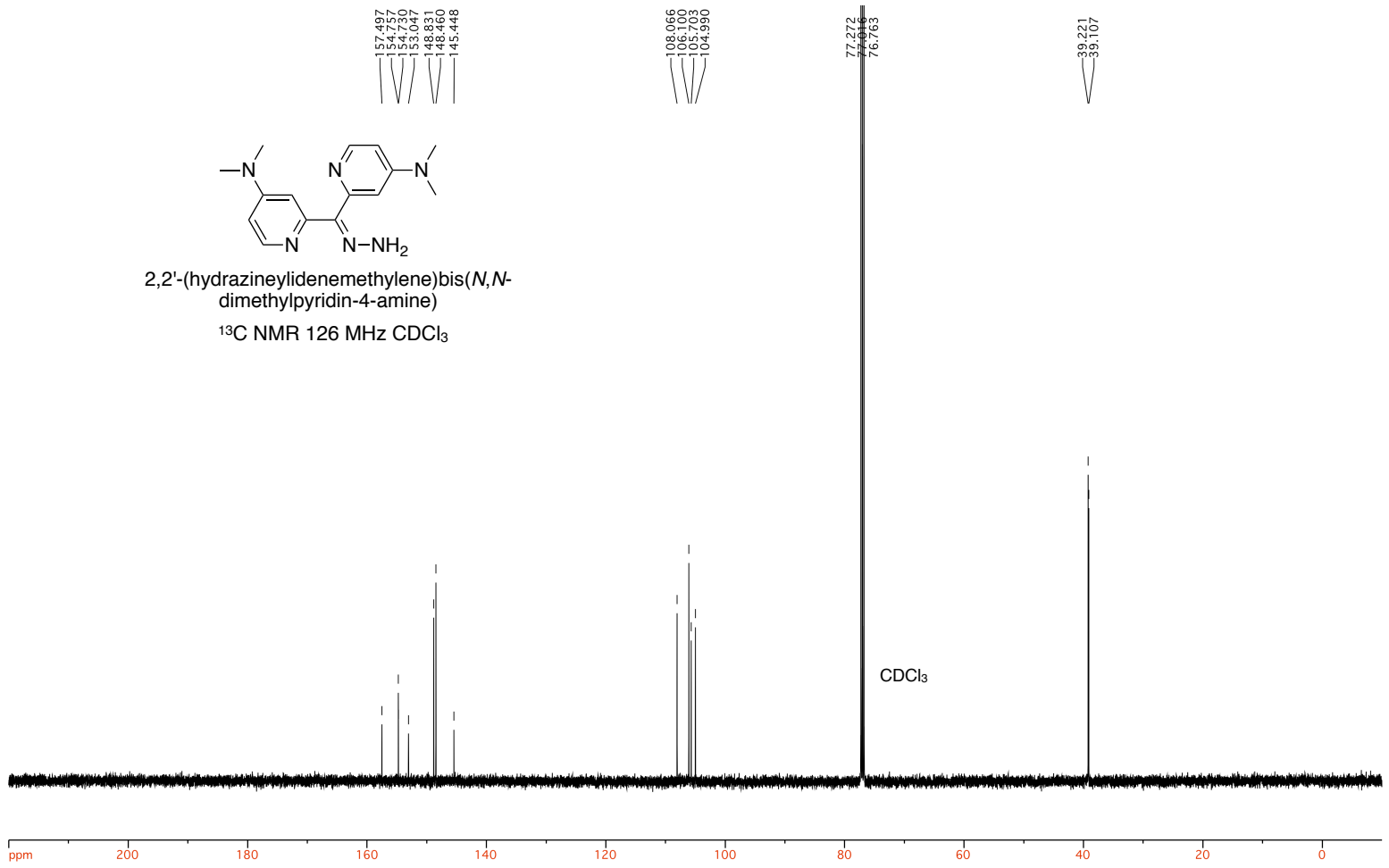


2,2'-methylenebis(*N*,*N*-dimethylpyridin-4-amine)

^{13}C NMR 126 MHz $CDCl_3$




8.299
8.287
8.200
8.188
7.450
7.260
7.034
7.028
6.531
6.526
6.471
6.466
6.459
6.443
6.438
6.431
6.426
3.021
2.936
2,2'-(hydrazineylidenemethylene)bis(N,N-dimethylpyridin-4-amine)
1H NMR 500 MHz CDCl3
CDCl3
0.981
2.07
1.01
2.09
6
1
2.07
1.02
6.03
ppm



2,2'-(hydrazineylidenemethylene)bis(*N*,*N*-dimethylpyridin-4-amine)

^{13}C NMR 126 MHz $CDCl_3$

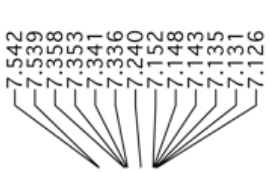
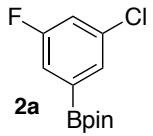


Table 2.4, Entry 1



2a

2-(3-chloro-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, 500 MHz, $CDCl_3$

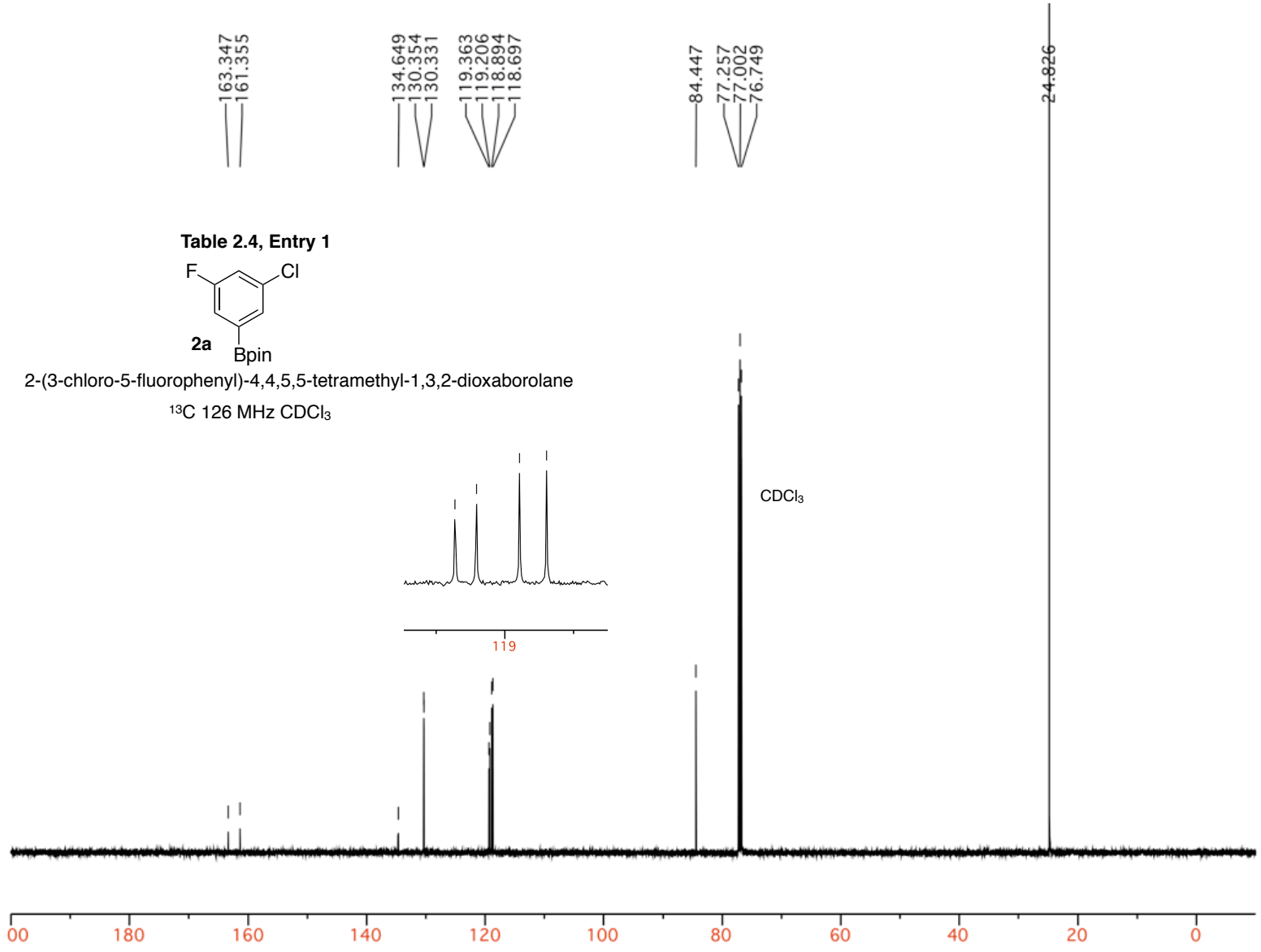
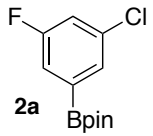

163.347
161.355
134.649
130.354
130.331
119.363
119.206
118.894
118.697
84.447
77.257
77.002
76.749
24.826
Table 2.4, Entry 1
F
Cl
2a
Bpin
2-(3-chloro-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
13C 126 MHz CDCl3
CDCl3
119
00
180
160
140
120
100
80
60
40
20
0

Table 2.4, Entry 1



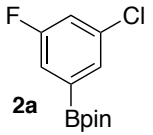
2a

2-(3-chloro-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{19}F 240 MHz, $CDCl_3$

30.176

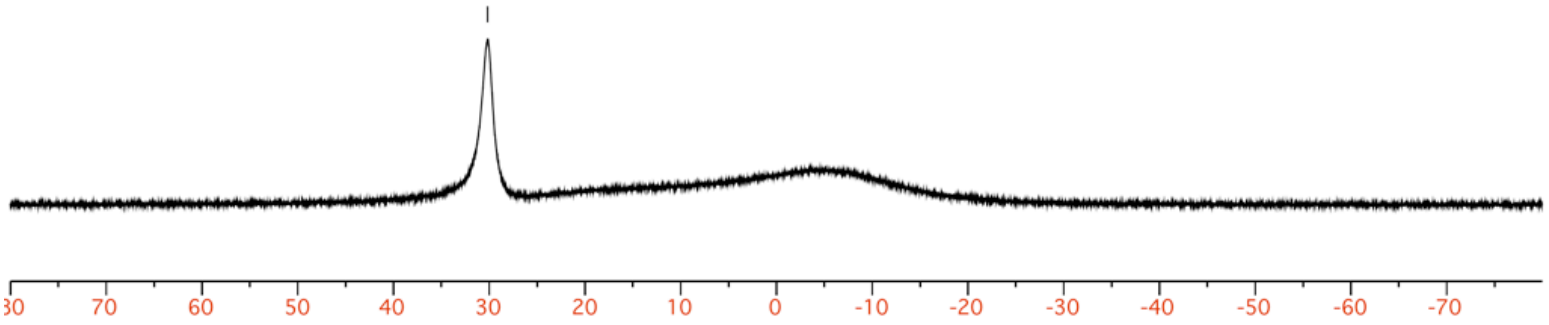
Table 2.4, Entry 1



2a

2-(3-chloro-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B 126 MHz $CDCl_3$



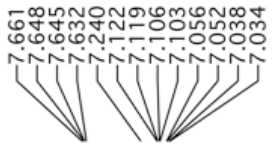
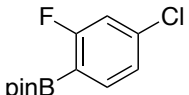


Table 2.4, Entry 1



2b

2-(4-chloro-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, 500 MHz, $CDCl_3$

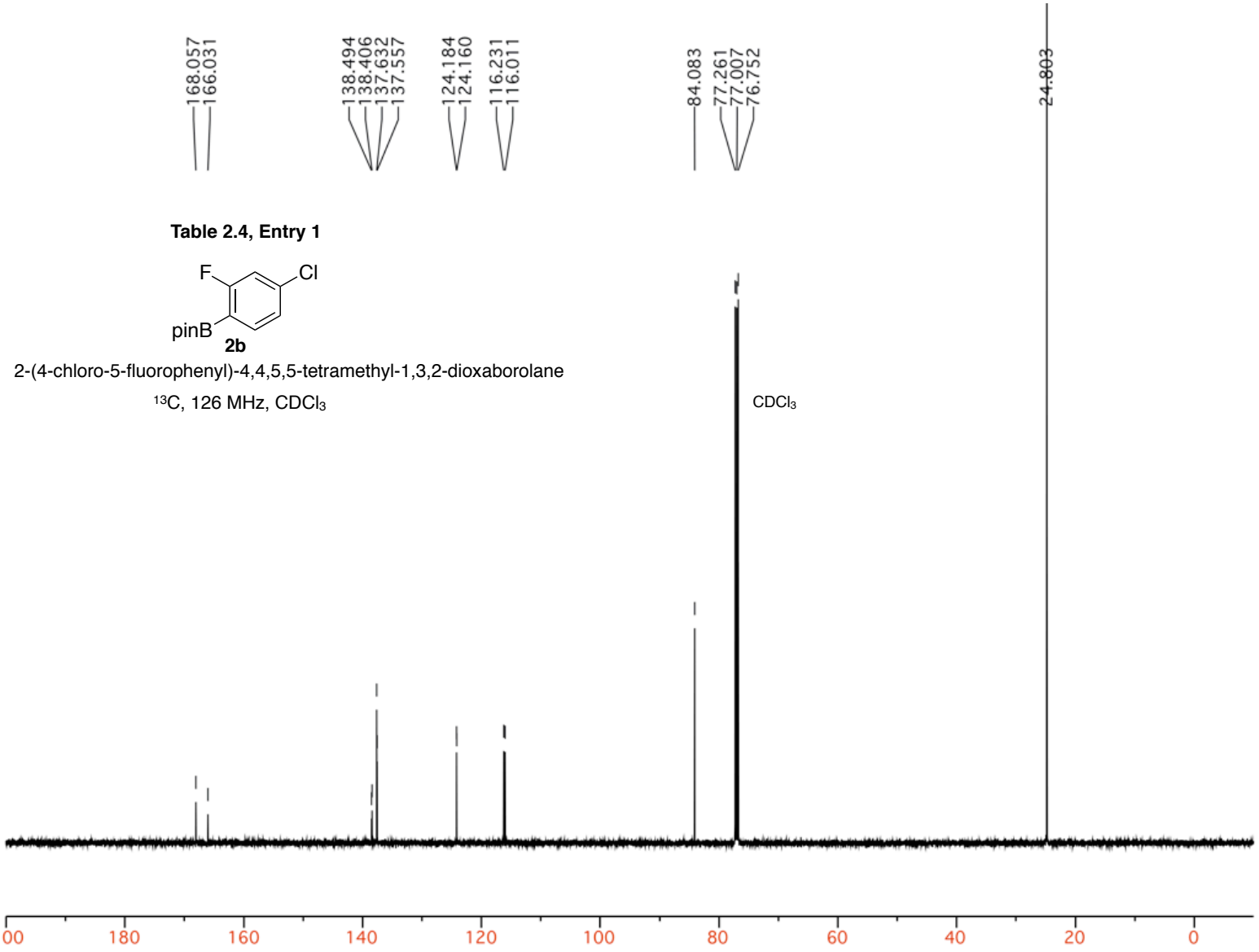


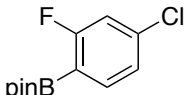
Table 2.4, Entry 1

2b

2-(4-chloro-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C, 126 MHz, $CDCl_3$

Table 2.4, Entry 1



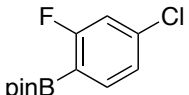
2b

2-(4-chloro-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{19}F, 240 MHz, $CDCl_3$

29.931

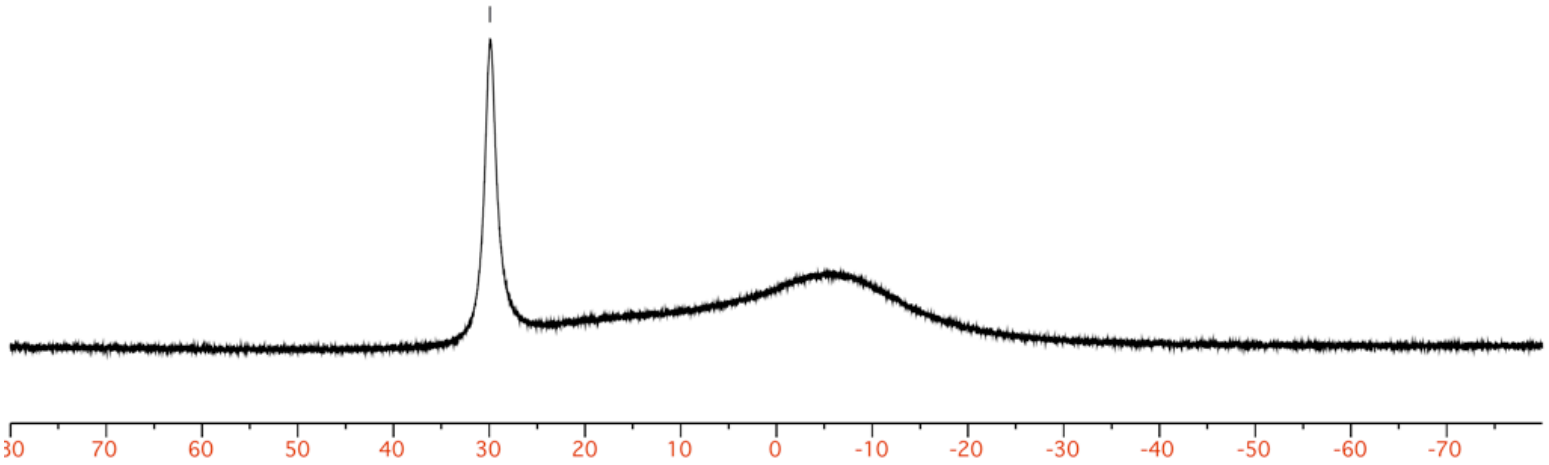
Table 2.4, Entry 1

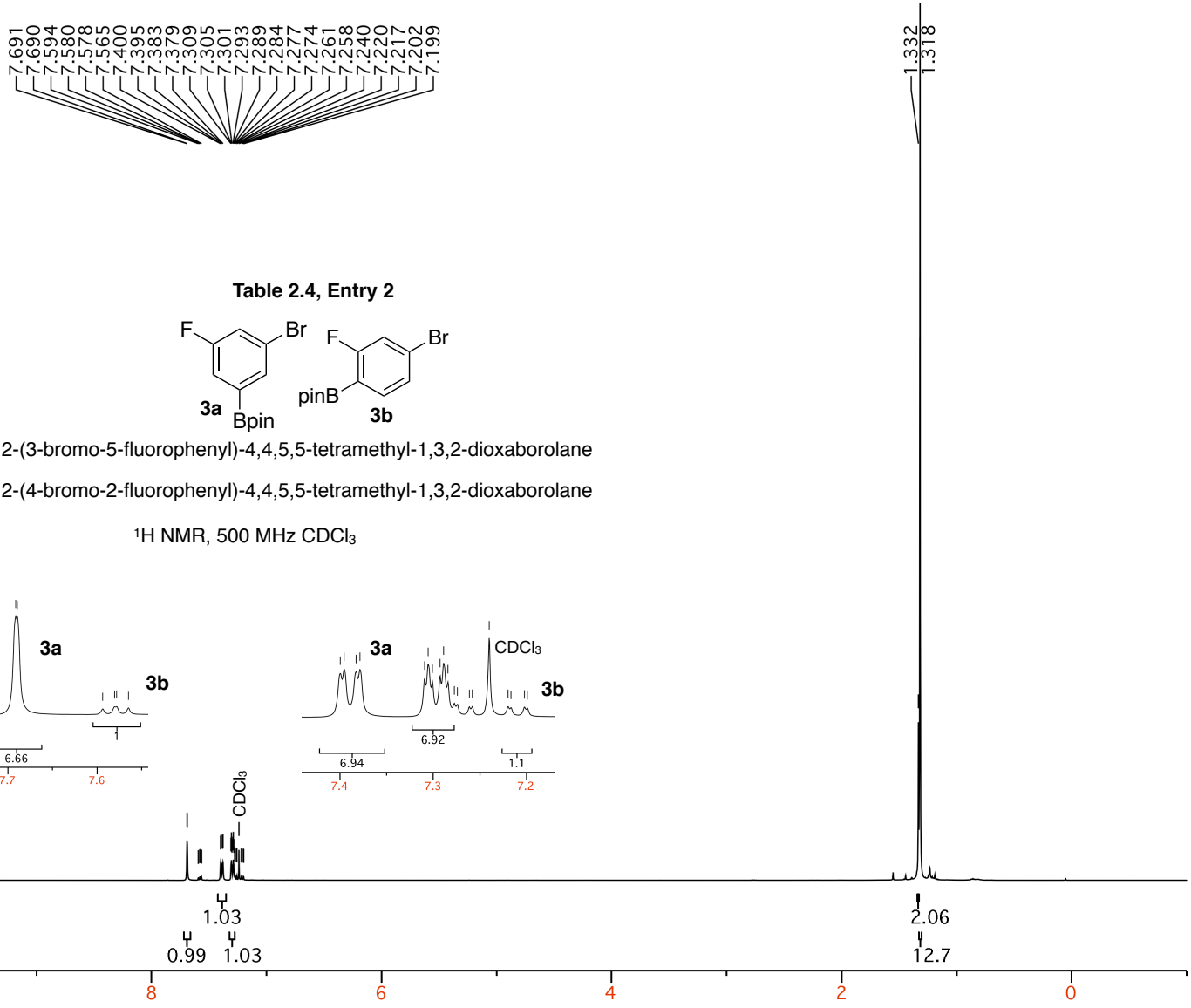


2b

2-(4-chloro-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B, 126 MHz, $CDCl_3$




7.691
7.690
7.594
7.580
7.578
7.565
7.400
7.395
7.383
7.379
7.309
7.305
7.301
7.293
7.289
7.284
7.277
7.274
7.261
7.258
7.240
7.220
7.217
7.202
7.199
1.332
1.318
Table 2.4, Entry 2
F
Br
3a
Bpin
F
Br
pinB
3b
2-(3-bromo-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
2-(4-bromo-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
1H NMR, 500 MHz CDCl3
3a
3b
6.66
1
7.7
7.6
3a
CDCl3
3b
6.92
6.94
1.1
7.4
7.3
7.2
CDCl3
1.03
0.99
1.03
2.06
12.7
ppm
8
6
4
2
0

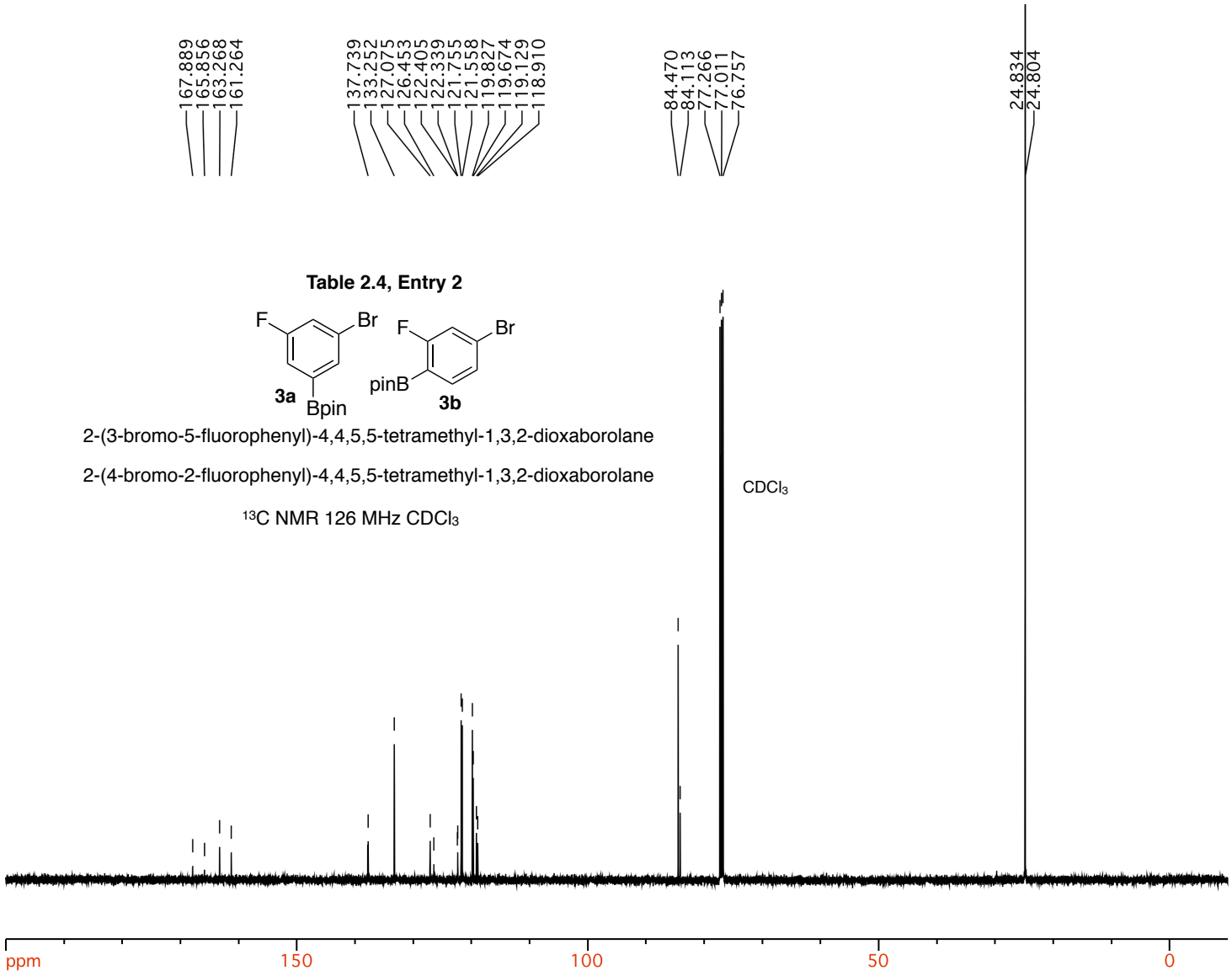
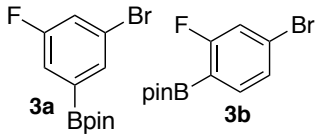

167.889
165.856
163.268
161.264
137.739
133.252
127.075
126.453
122.405
122.339
121.755
121.558
119.827
119.674
119.129
118.910
84.470
84.113
77.266
77.011
76.757
24.834
24.804
Table 2.4, Entry 2
F
Br
3a
Bpin
F
Br
pinB
3b
2-(3-bromo-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
2-(4-bromo-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
13C NMR 126 MHz CDCl3
CDCl3
ppm
150
100
50
0

Table 2.4, Entry 2



3a **3b**

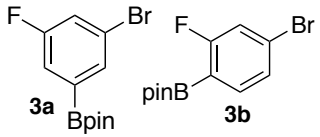
2-(3-bromo-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

2-(4-bromo-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{19}F NMR 240 MHz $CDCl_3$

29.966

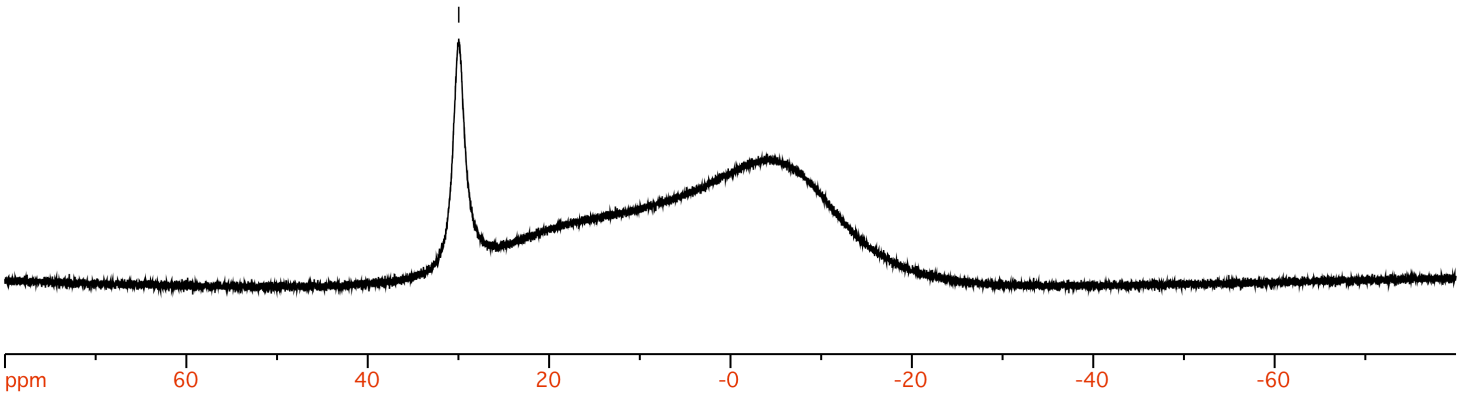
Table 2.4, Entry 2



2-(3-bromo-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

2-(4-bromo-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B NMR 160 MHz $CDCl_3$



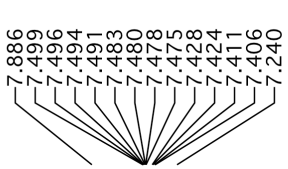
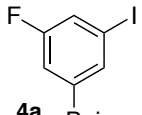


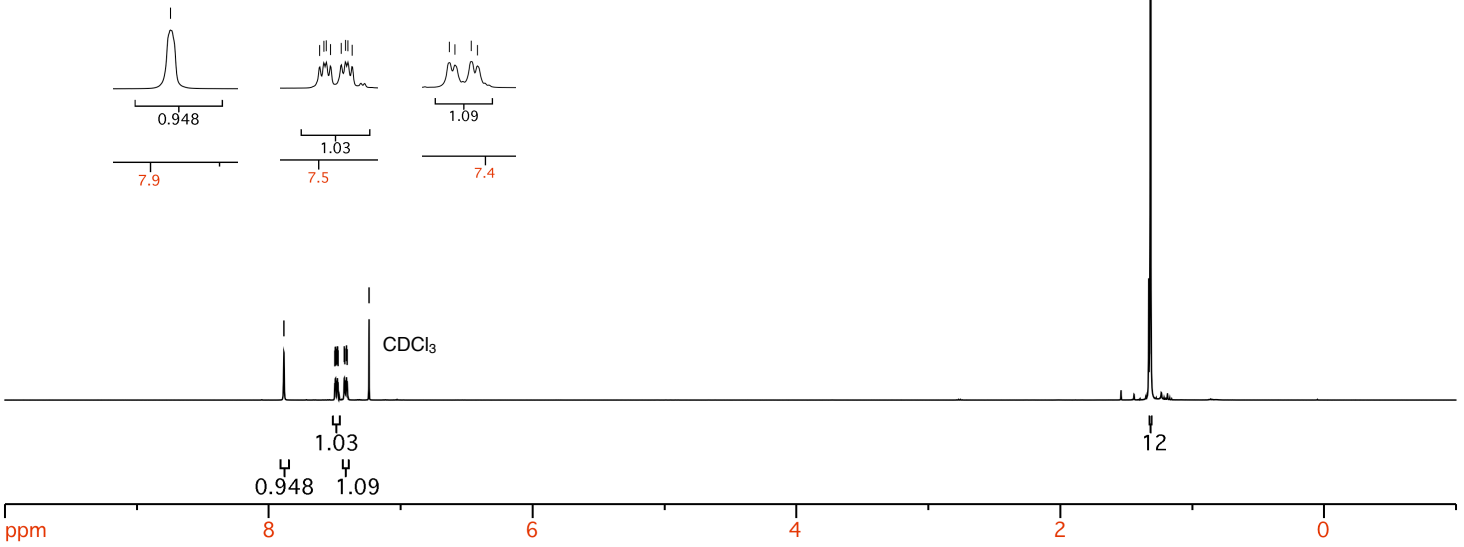
Table 2.4, Entry 3



4a

2-(3-fluoro-5-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H NMR, 500 MHz $CDCl_3$



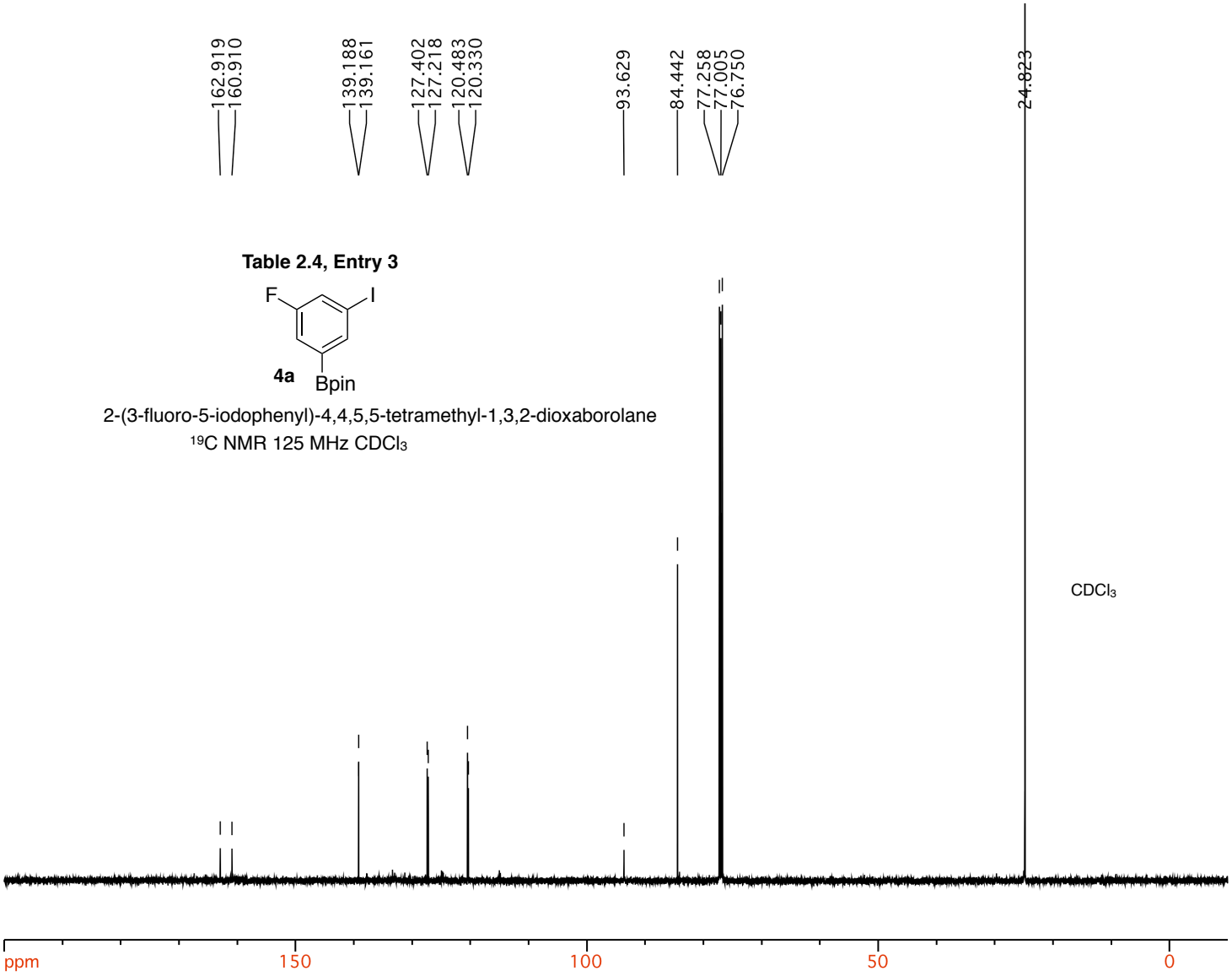
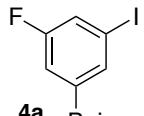

162.919
160.910
139.188
139.161
127.402
127.218
120.483
120.330
93.629
84.442
77.258
77.005
76.750
24.823
Table 2.4, Entry 3
F
I
4a
Bpin
2-(3-fluoro-5-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
19C NMR 125 MHz CDCl3
CDCl3
ppm
150
100
50
0

Table 2.4, Entry 3



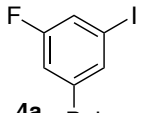
4a

2-(3-fluoro-5-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{19}F NMR 240 MHz $CDCl_3$

29.946

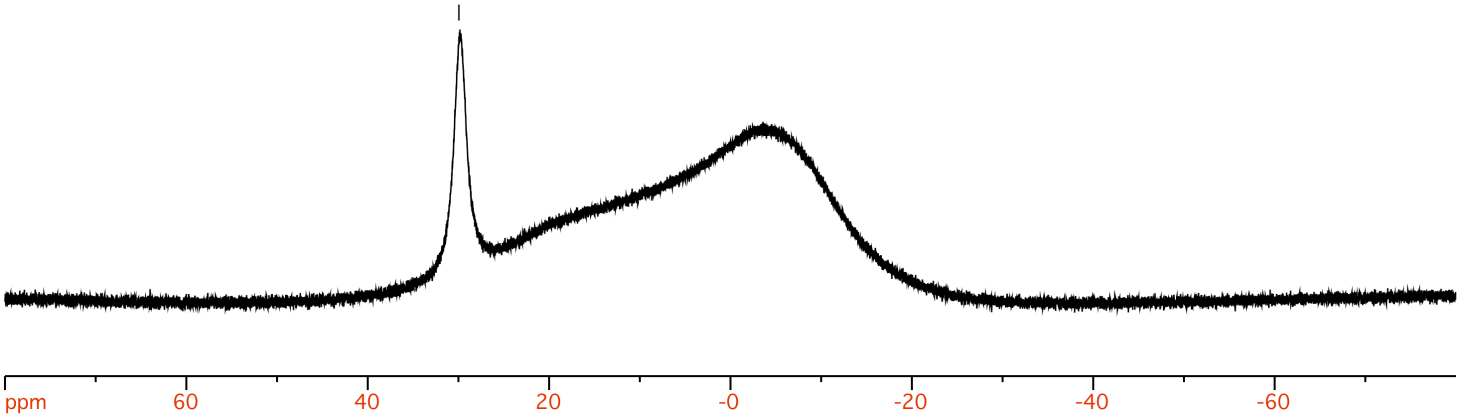
Table 2.4, Entry 3



4a

2-(3-bromo-5-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B NMR 160 MHz $CDCl_3$



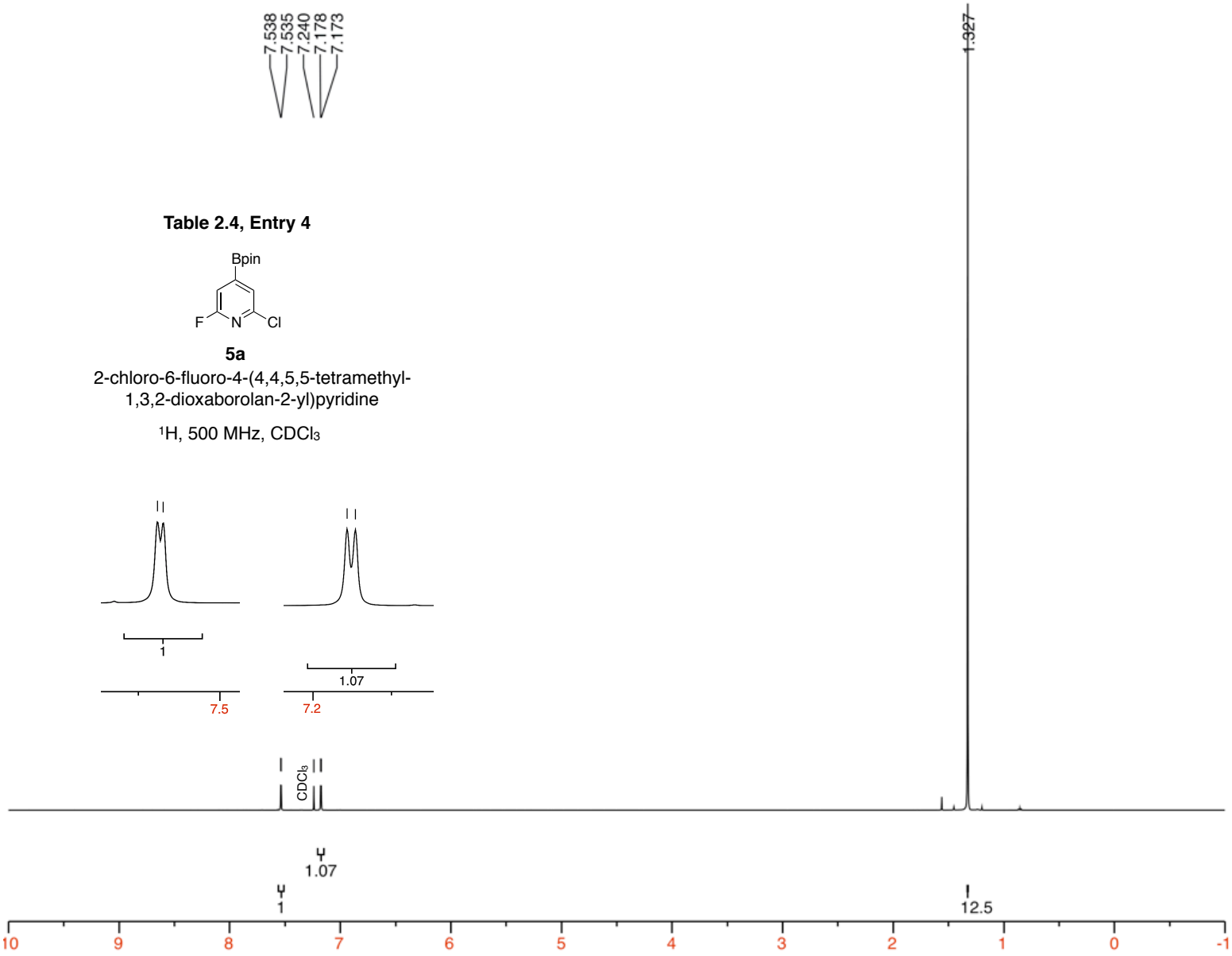
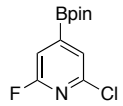

7.538
7.535
7.240
7.178
7.173
1.927
Table 2.4, Entry 4
Bpin
F
N
Cl
5a
2-chloro-6-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine
1H, 500 MHz, CDCl3
1
1.07
7.5
7.2
CDCl3
1.07
1
12.5
10
9
8
7
6
5
4
3
2
1
0
-1

Table 2.4, Entry 4

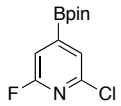


5a

2-chloro-6-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

^{13}C 126 MHz $CDCl_3$

Table 2.4, Entry 4



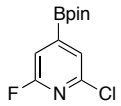
5a

2-chloro-6-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

^{19}F 240 MHz, $CDCl_3$

29.544

Table 2.4, Entry 4



5a

2-chloro-6-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

^{11}B 126 MHz $CDCl_3$

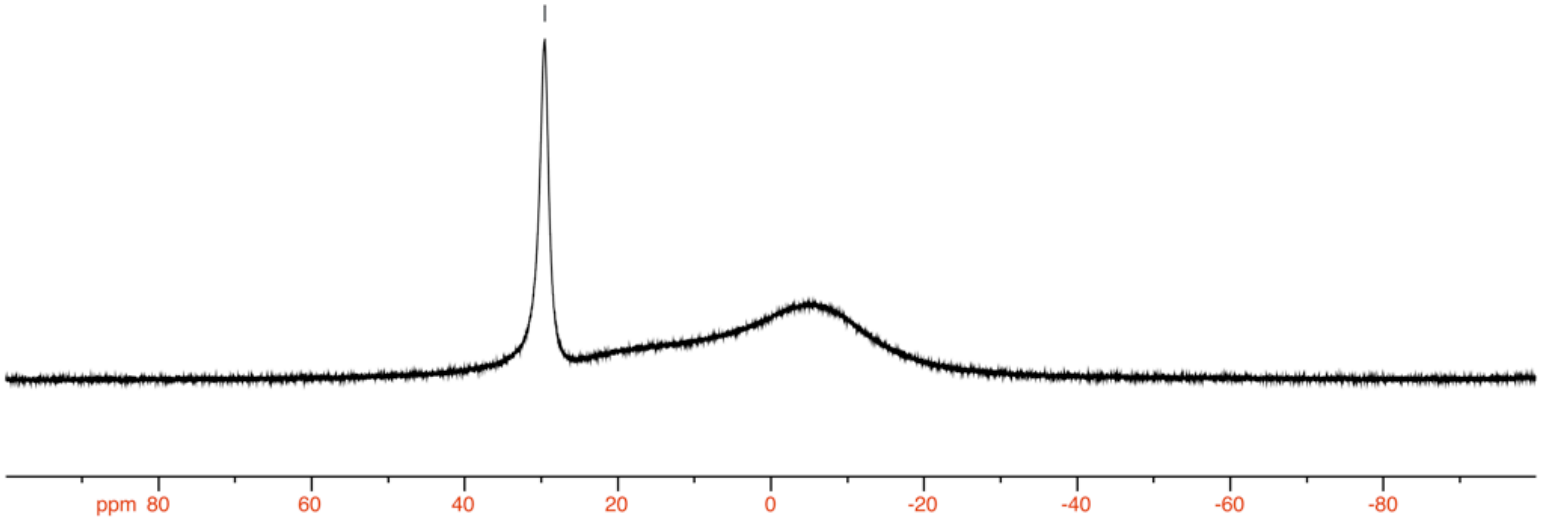
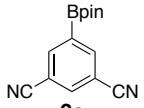


Table 2.4, Entry 5

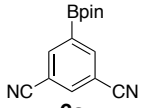


6a

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalonitrile

^{13}C 126 MHz $CDCl_3$

Table 2.4, Entry 5



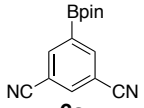
6a

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalonitrile

^{1}H 500 MHz, $CDCl_3$

29.800

Table 2.4, Entry 5



6a

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalonitrile

^{11}B 160 MHz $CDCl_3$

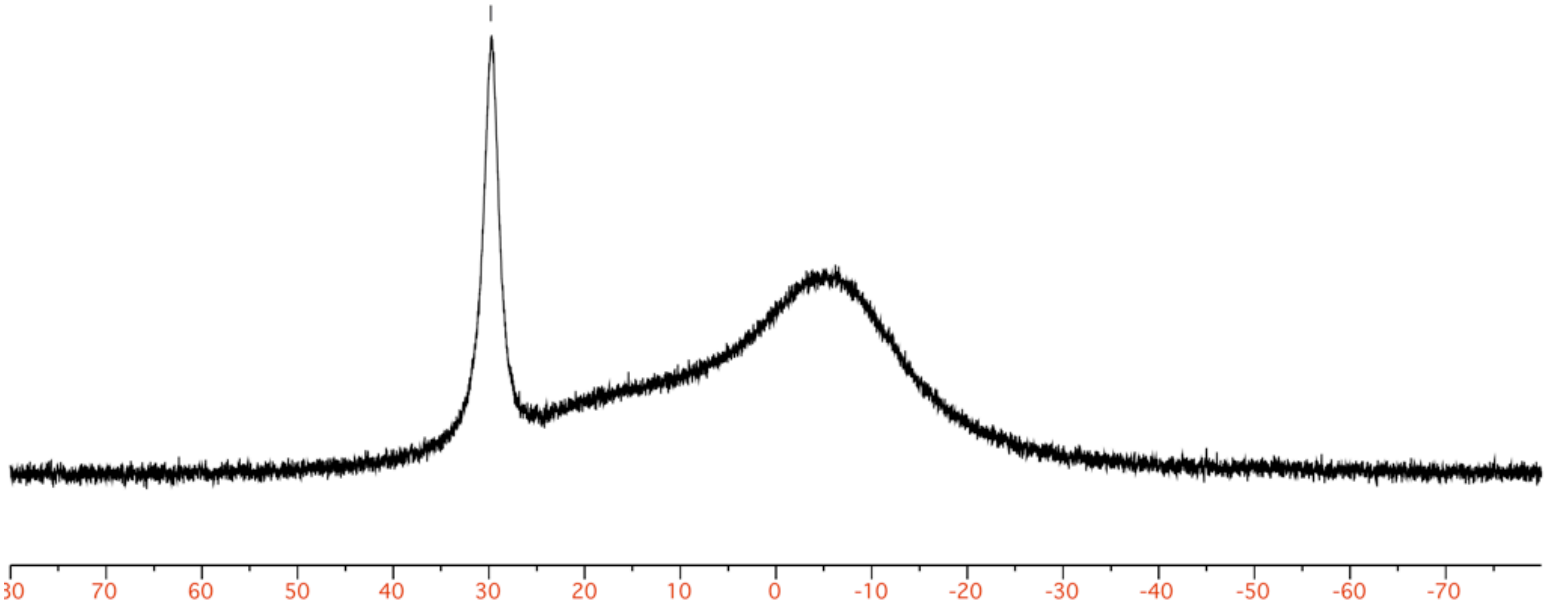
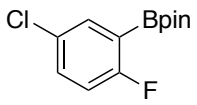


Table 2.4, Entry 6



7a

2-(5-chloro-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H 500 MHz $CDCl_3$

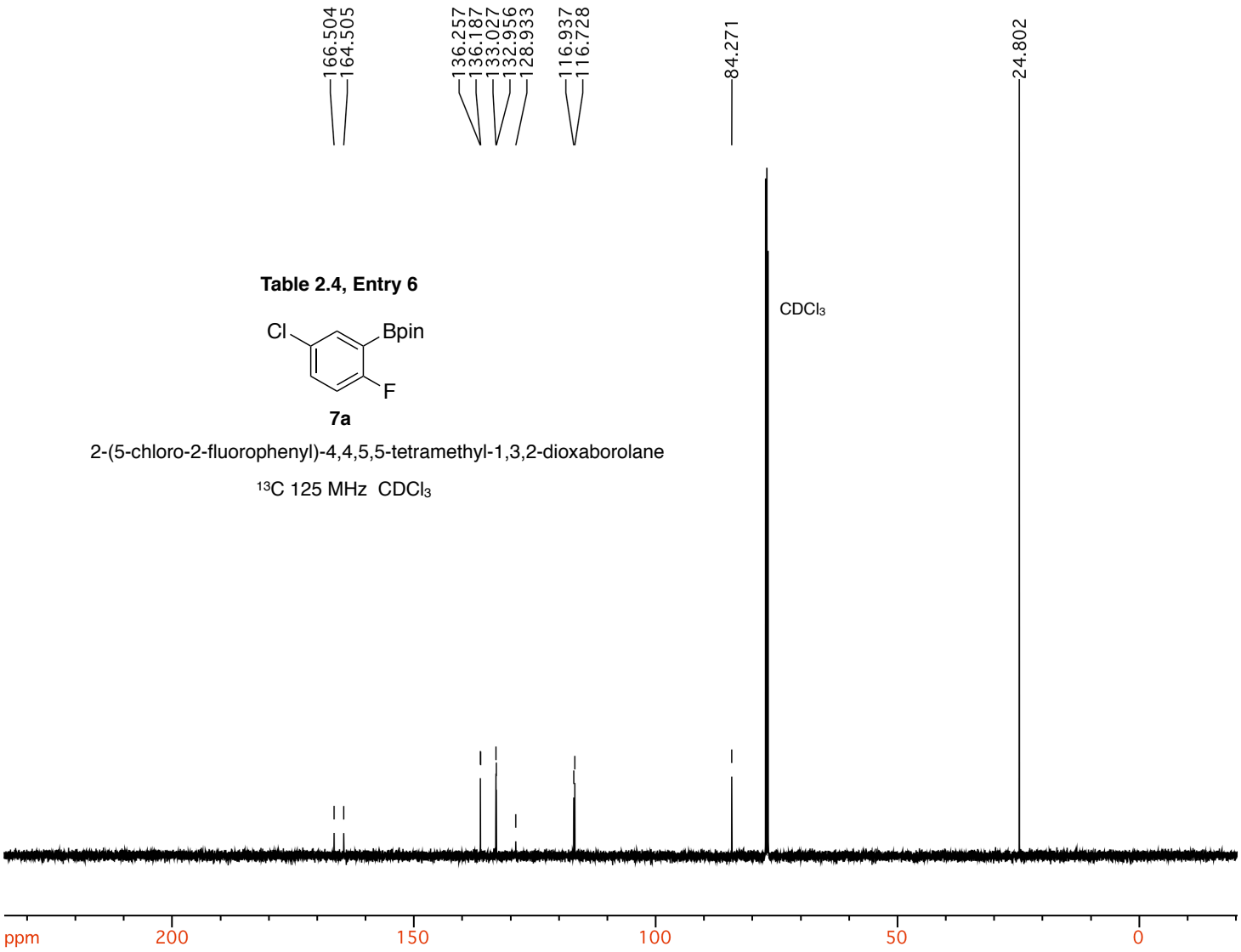
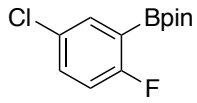

166.504
164.505
136.257
136.187
133.027
132.956
128.933
116.937
116.728
84.271
24.802
CDCl3
Table 2.4, Entry 6
Cl
Bpin
F
7a
2-(5-chloro-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
13C 125 MHz CDCl3
ppm
200
150
100
50
0

Table 2.4, Entry 6



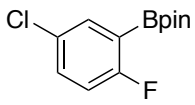
7a

2-(5-chloro-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{19}F 240 MHz $CDCl_3$

29.782

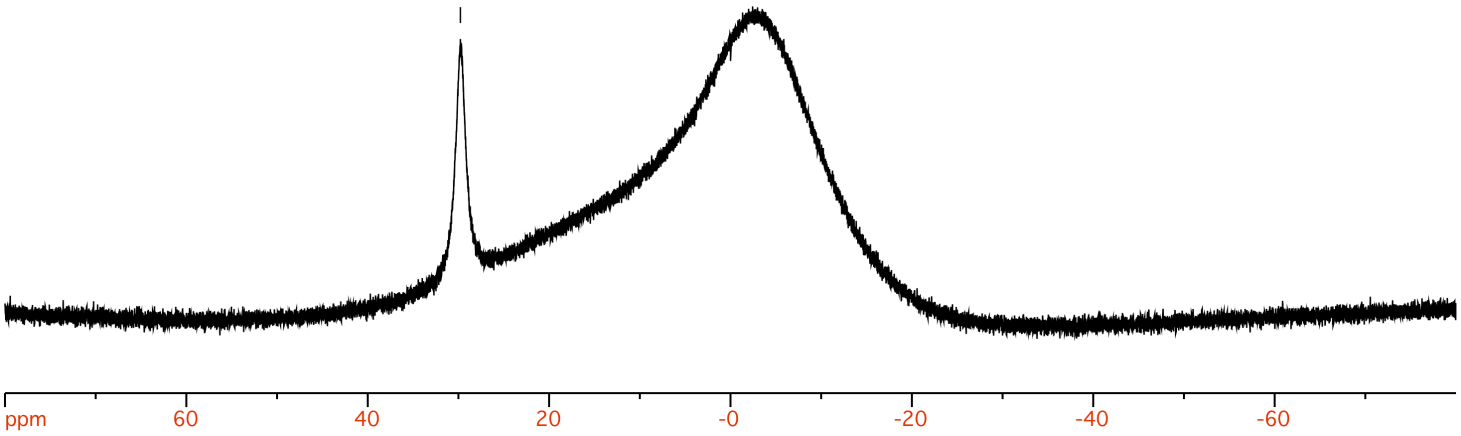
Table 2.4, Entry 6

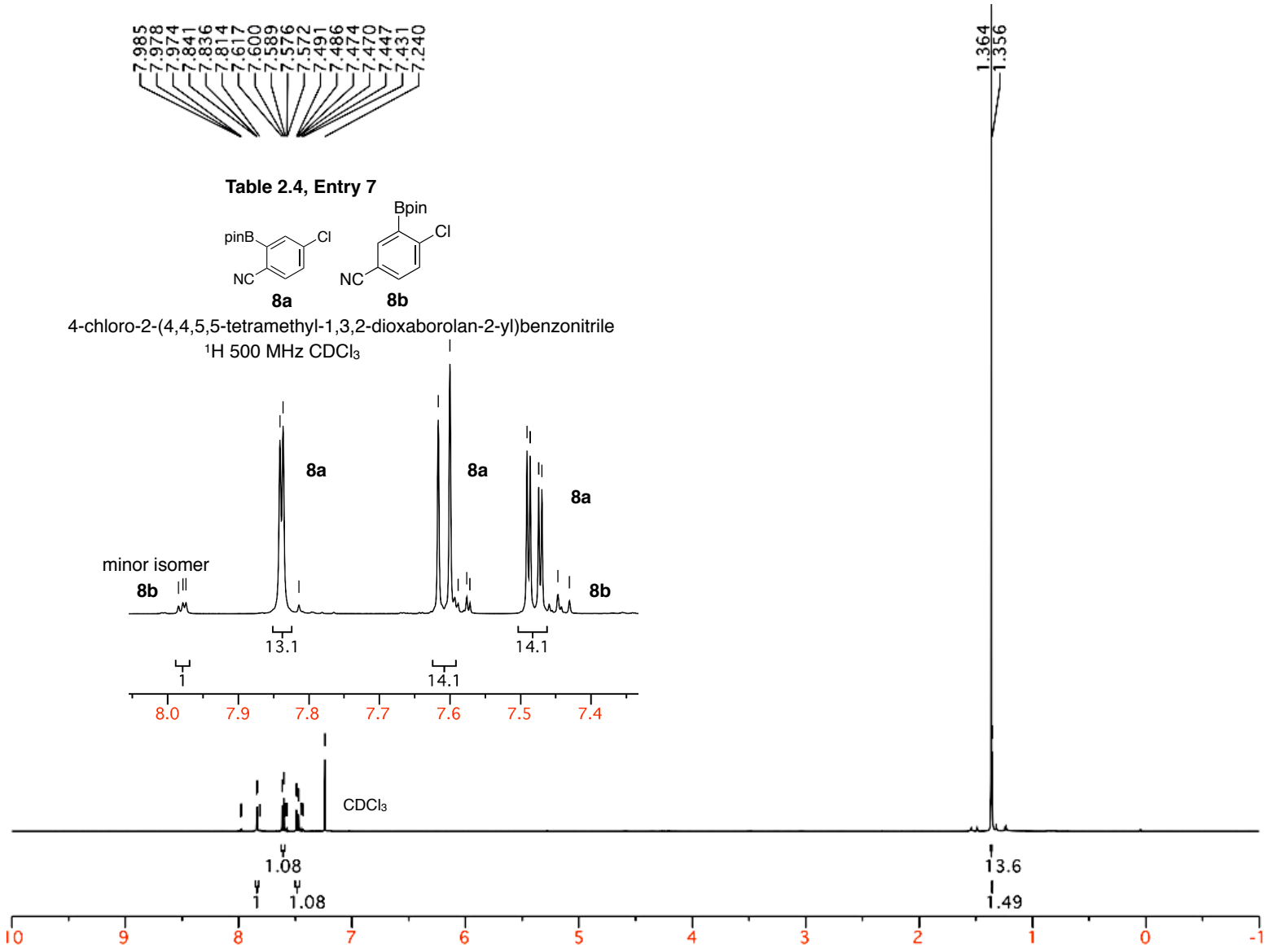


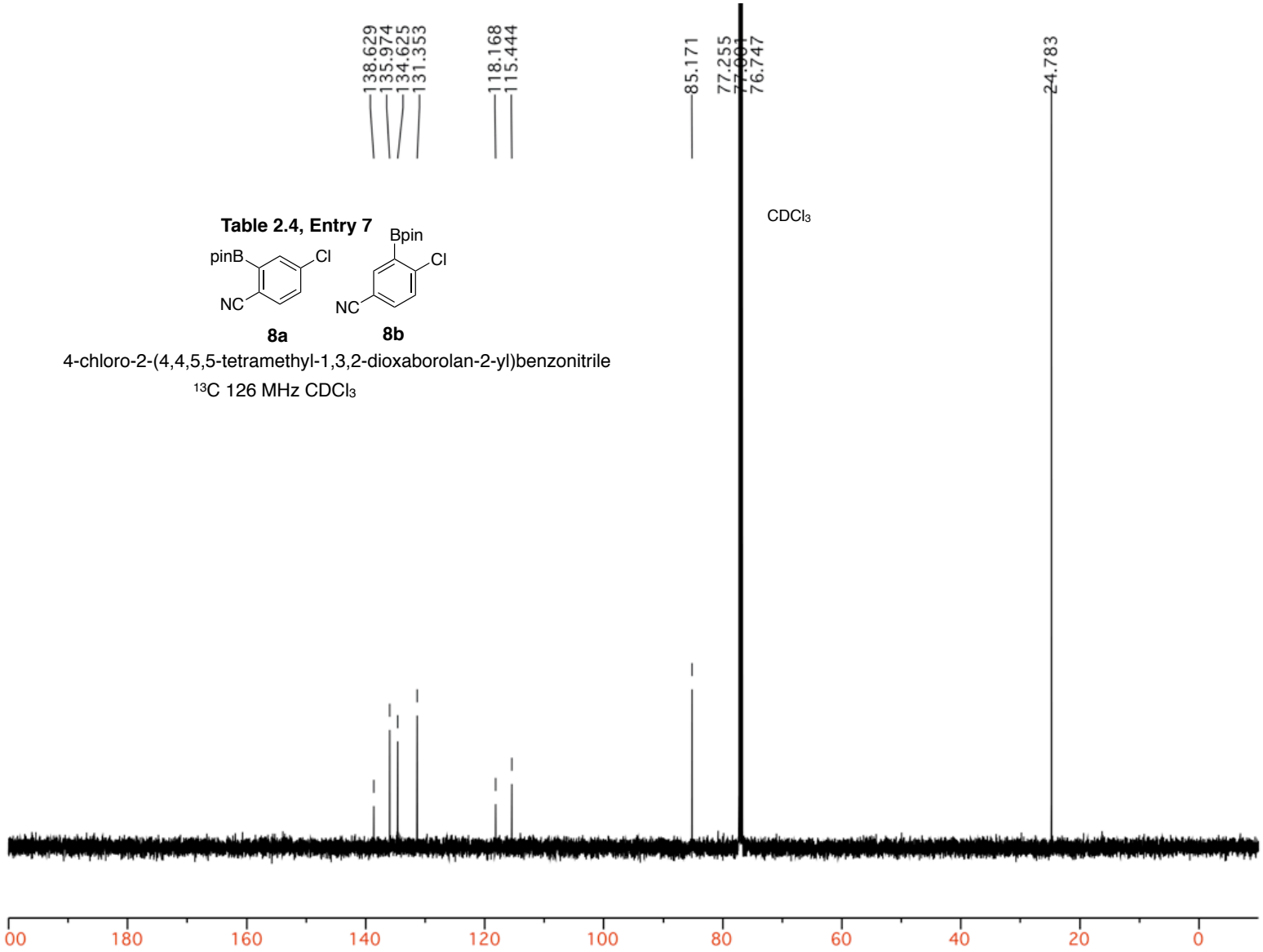
7a

2-(5-chloro-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B 125 MHz $CDCl_3$

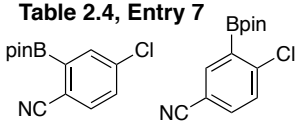



7.985
7.978
7.974
7.841
7.836
7.814
7.617
7.600
7.589
7.576
7.572
7.491
7.486
7.474
7.470
7.447
7.431
7.240
1.364
1.356
Table 2.4, Entry 7
pinB
Cl
NC
Bpin
Cl
NC
8a
8b
4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile
1H 500 MHz CDCl3
8a
8a
8a
minor isomer
8b
8b
13.1
14.1
1
14.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
CDCl3
1.08
1
1.08
13.6
1.49
10
9
8
7
6
5
4
3
2
1
0
-1


138.629
135.974
134.625
131.353
118.168
115.444
85.171
77.255
77.001
76.747
24.783
CDCl3
Table 2.4, Entry 7
pinB
Cl
NC
Bpin
Cl
NC
8a
8b
4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile
13C 126 MHz CDCl3
00
180
160
140
120
100
80
60
40
20
0

29.843

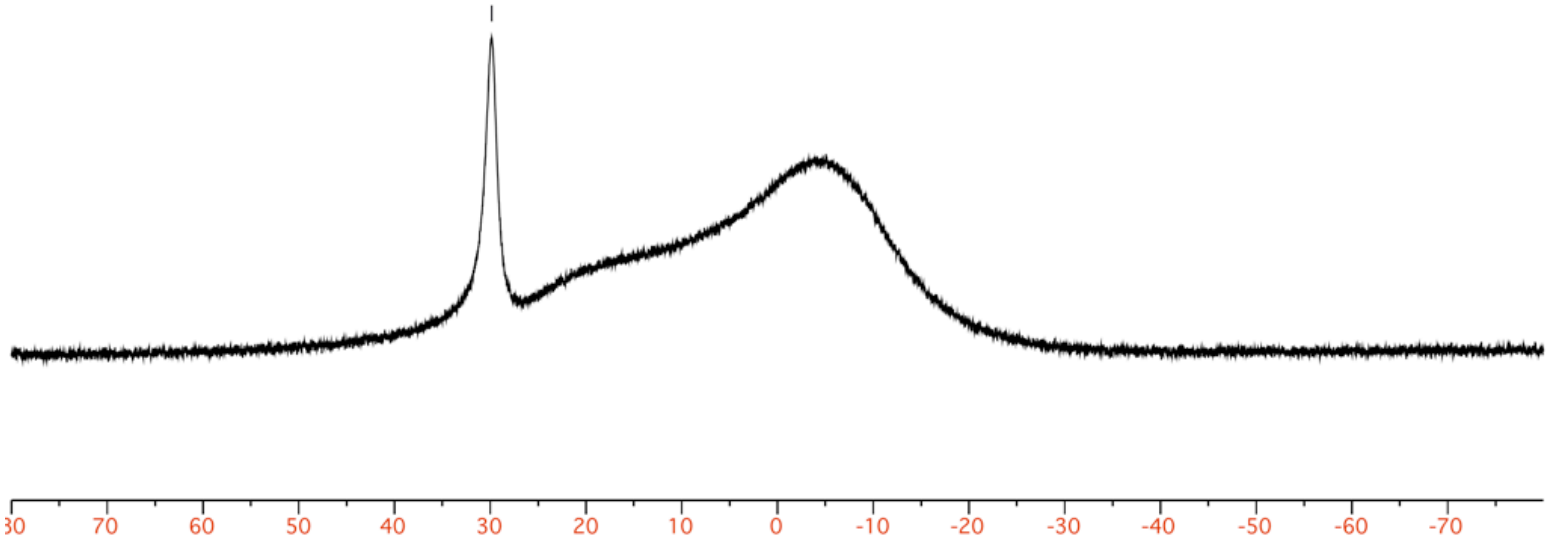
Table 2.4, Entry 7

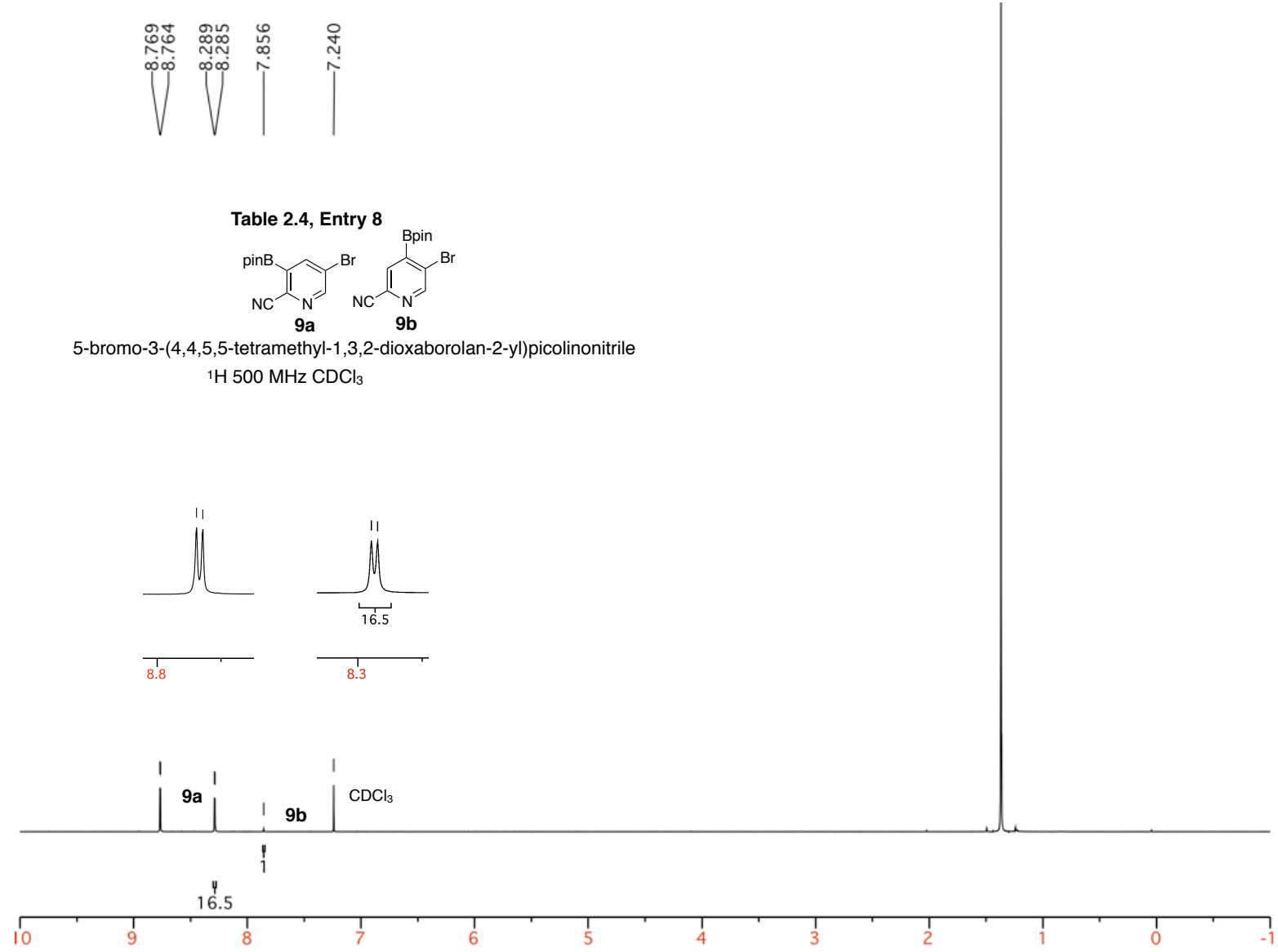


8a **8b**

4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile

^{11}B 160 MHz $CDCl_3$




8.769
8.764
8.289
8.285
7.856
7.240
Table 2.4, Entry 8
pinB
Br
NC
N
9a
Bpin
Br
NC
N
9b
5-bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)picolinonitrile
1H 500 MHz CDCl3
16.5
8.8
8.3
9a
9b
CDCl3
1
16.5
10
9
8
7
6
5
4
3
2
1
0
-1

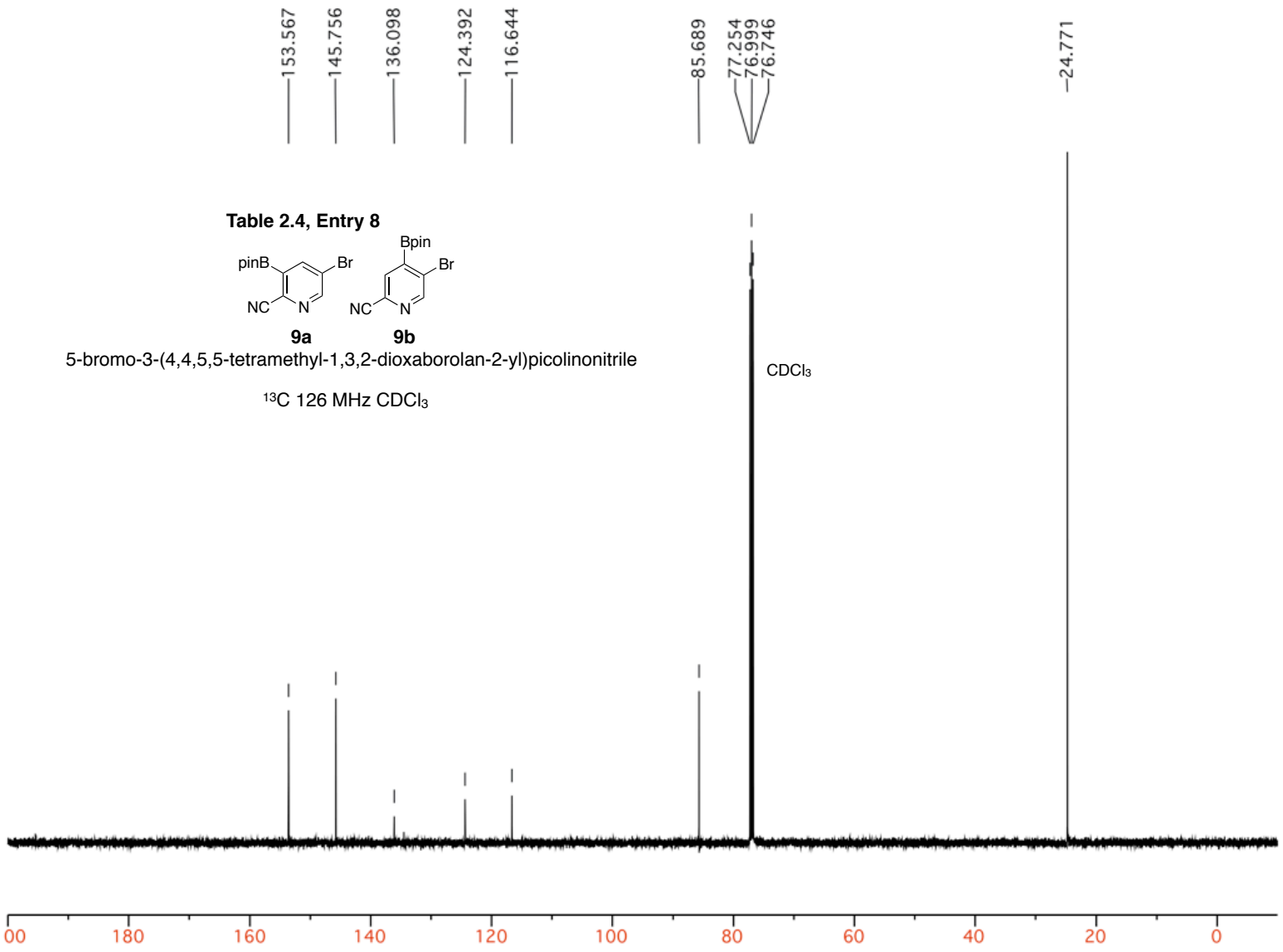


Table 2.4, Entry 8

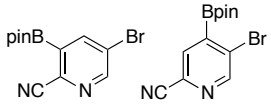
9a **9b**

5-bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)picolinonitrile

^{13}C 126 MHz $CDCl_3$

29.486

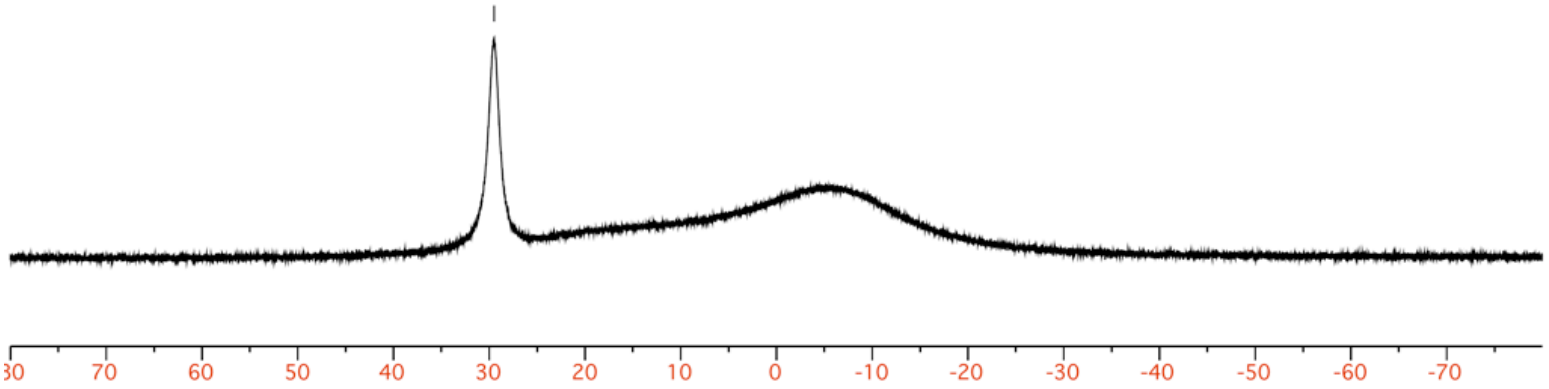
Table 2.4, Entry 8



9a **9b**

5-bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)picolinonitrile

^{11}B 160 MHz $CDCl_3$



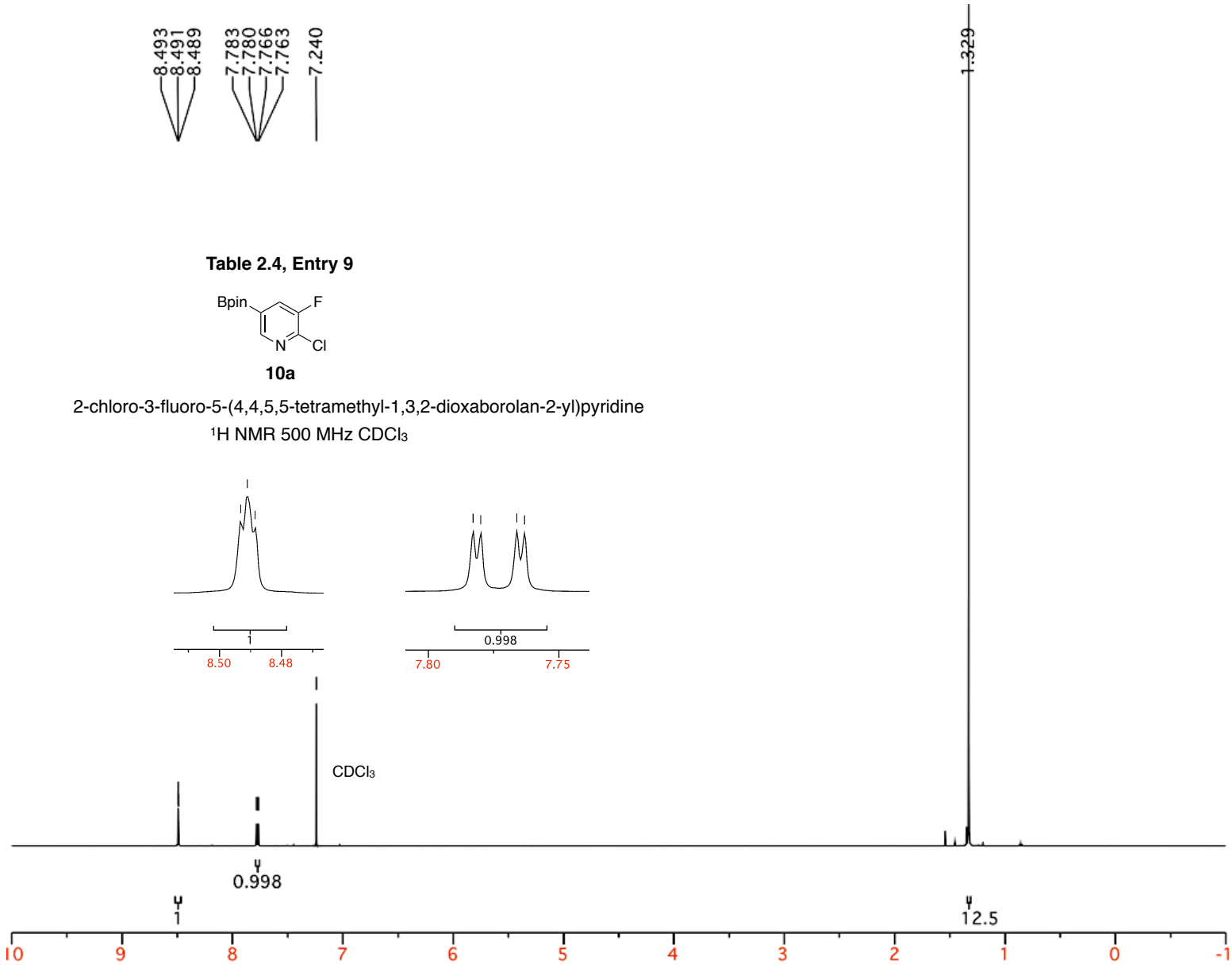


Table 2.4, Entry 9

10a

2-chloro-3-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

^{1}H NMR 500 MHz $CDCl_3$

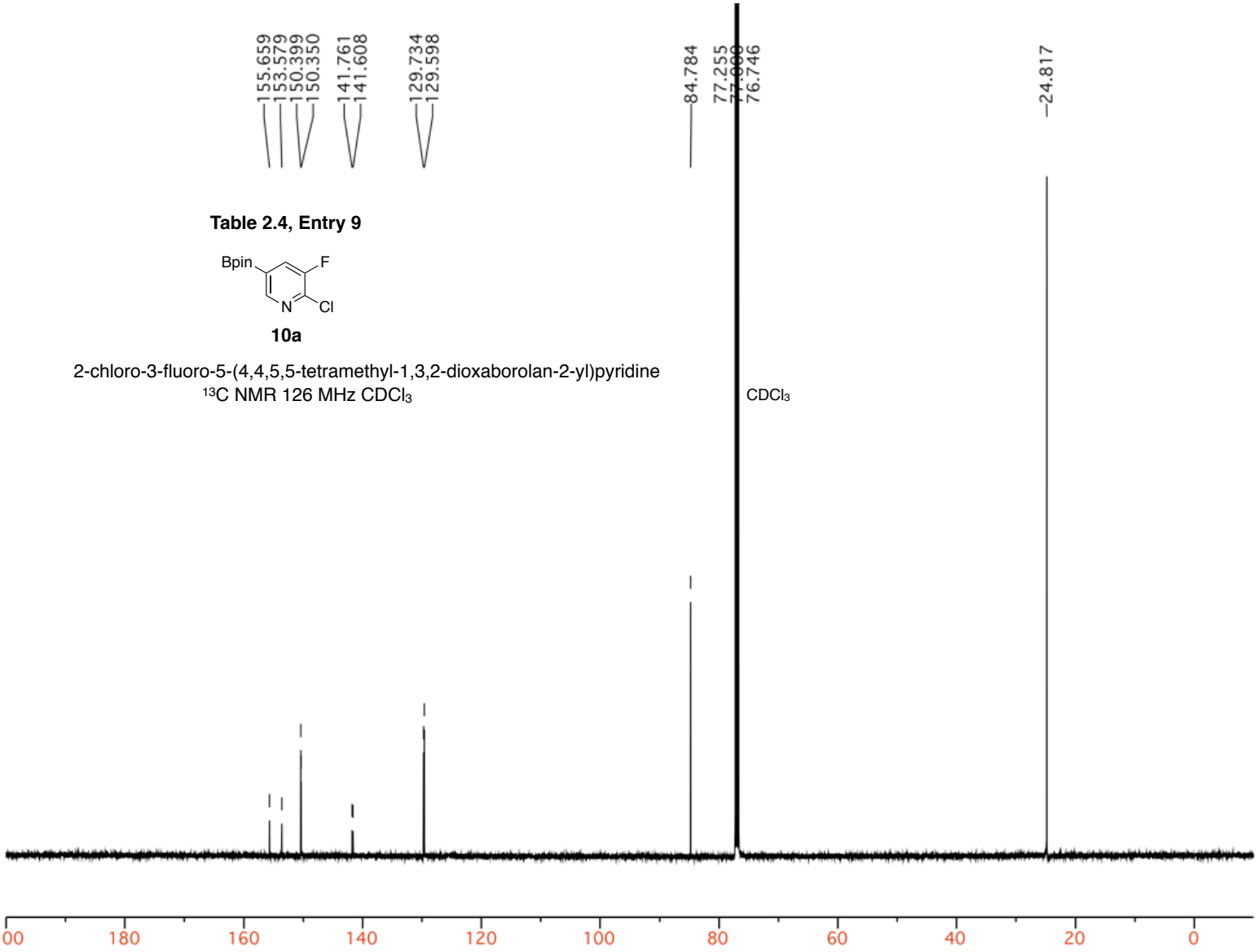
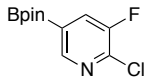


Table 2.4, Entry 9

10a

2-chloro-3-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine
^{13}C NMR 126 MHz $CDCl_3$

Table 2.4, Entry 9

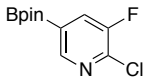


10a

2-chloro-3-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine
^{19}F NMR 470 MHz $CDCl_3$

30.106

Table 2.4, Entry 9



10a

2-chloro-3-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine
^{11}B NMR 160 MHz $CDCl_3$,

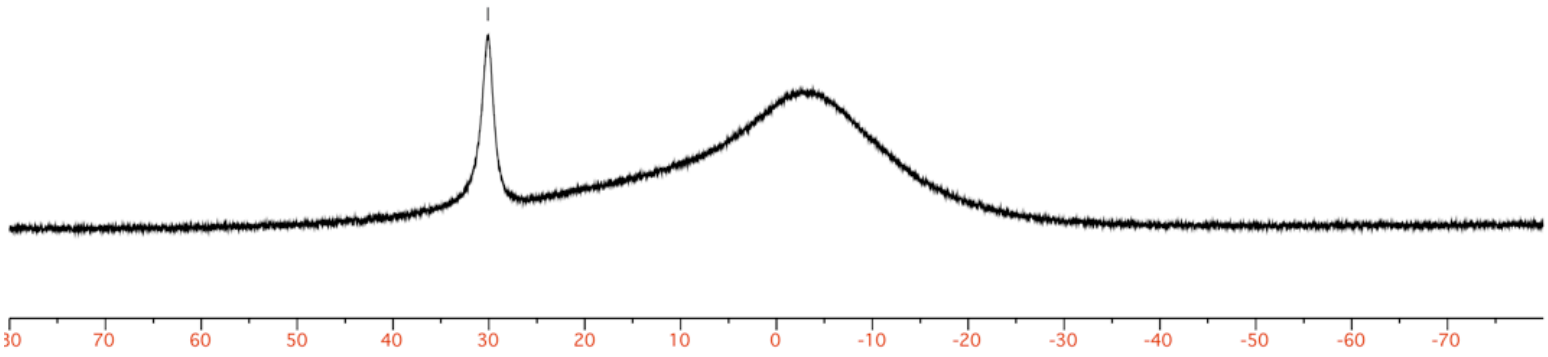
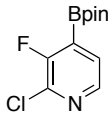


Table 2.4, Entry 9

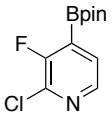


10b

2-chloro-3-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

^{1}H NMR 500 MHz $CDCl_3$

Table 2.4, Entry 9

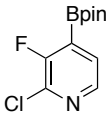


10b

2-chloro-3-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

^{13}C NMR 126 MHz $CDCl_3$

Table 2.4, Entry 9



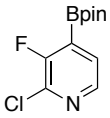
10b

2-chloro-3-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

^{19}F NMR 240 MHz $CDCl_3$

29.428

Table 2.4, Entry 9



10b

2-chloro-3-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

^{11}B NMR 160 MHz $CDCl_3$,

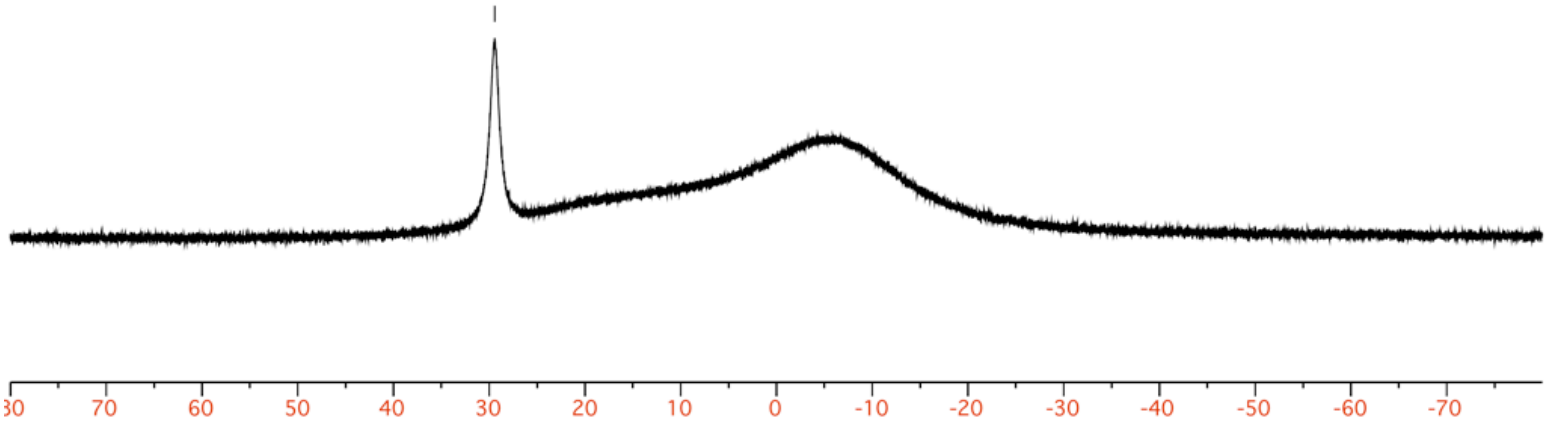
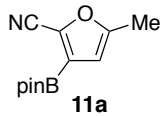


Table 2.5, Entry 1

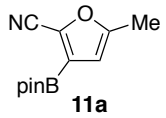


11a

5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-carbonitrile

^{1}H NMR 500 MHz $CDCl_3$

Table 2.5, Entry 1



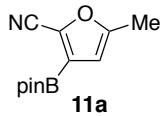
11a

5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-carbonitrile

^{13}C NMR 126 MHz $CDCl_3$

28.842

Table 2.5, Entry 1



11a

5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-carbonitrile

^{11}B NMR 160 MHz $CDCl_3$

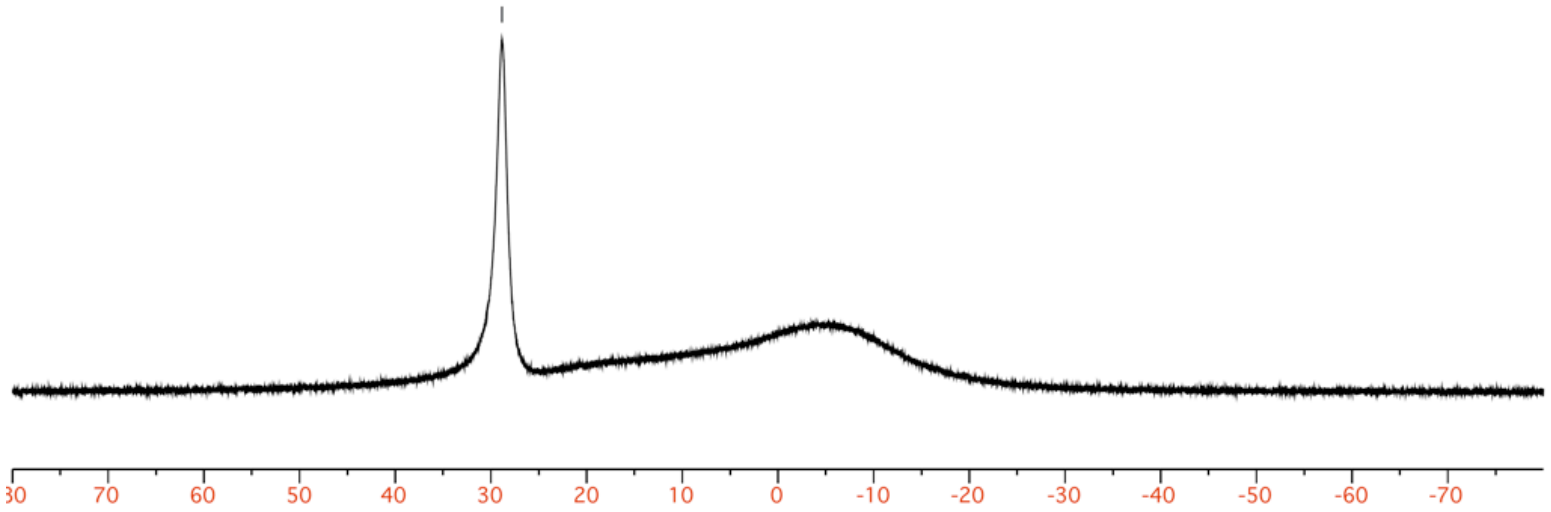
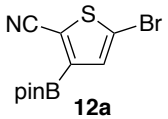


Table 2.5, Entry 2



12a

5-bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbonitrile

^{1}H NMR, 500 MHz $CDCl_3$

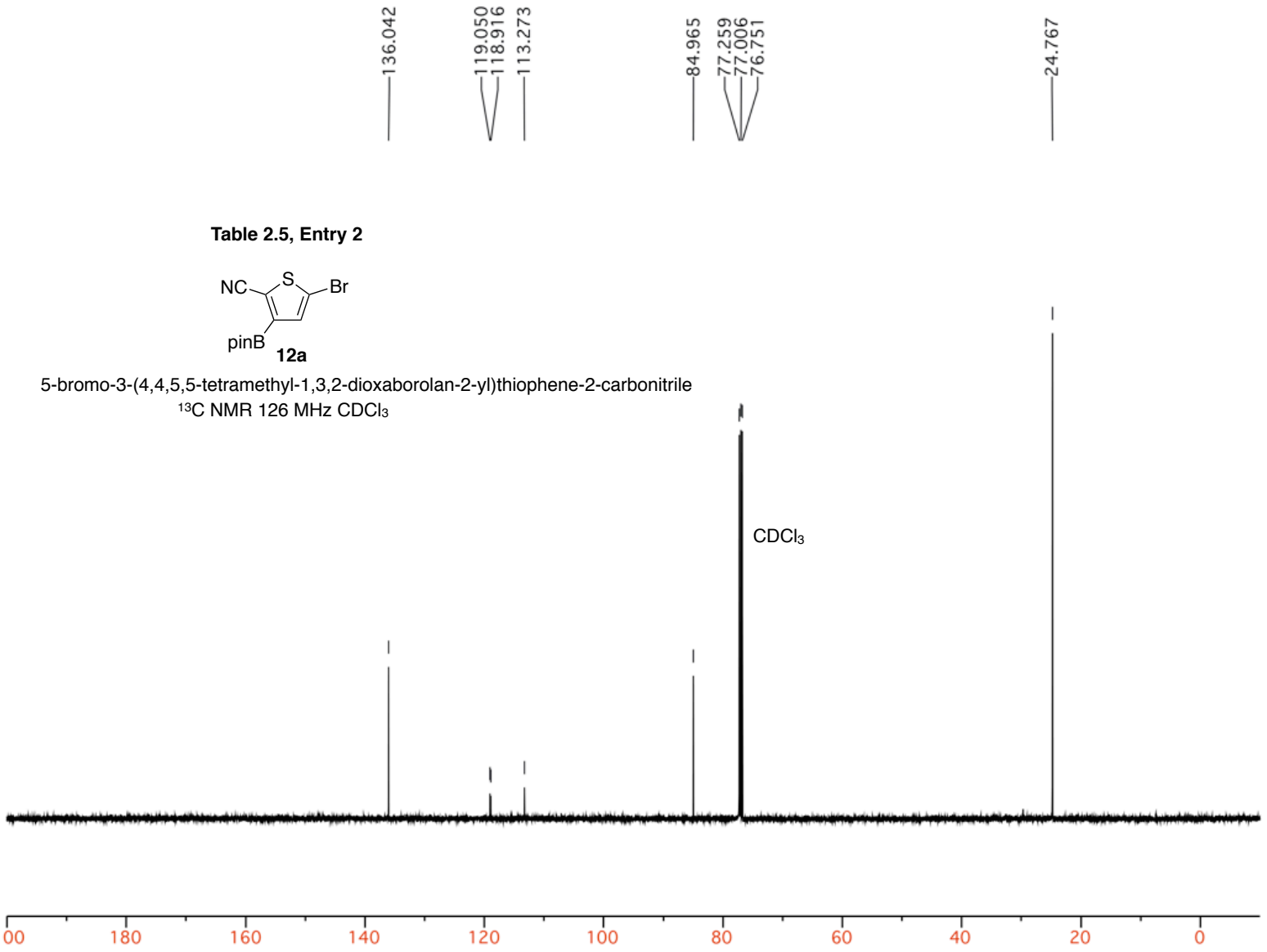


Table 2.5, Entry 2

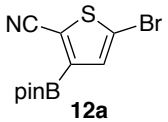
12a

5-bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbonitrile

^{13}C NMR 126 MHz $CDCl_3$

27.662

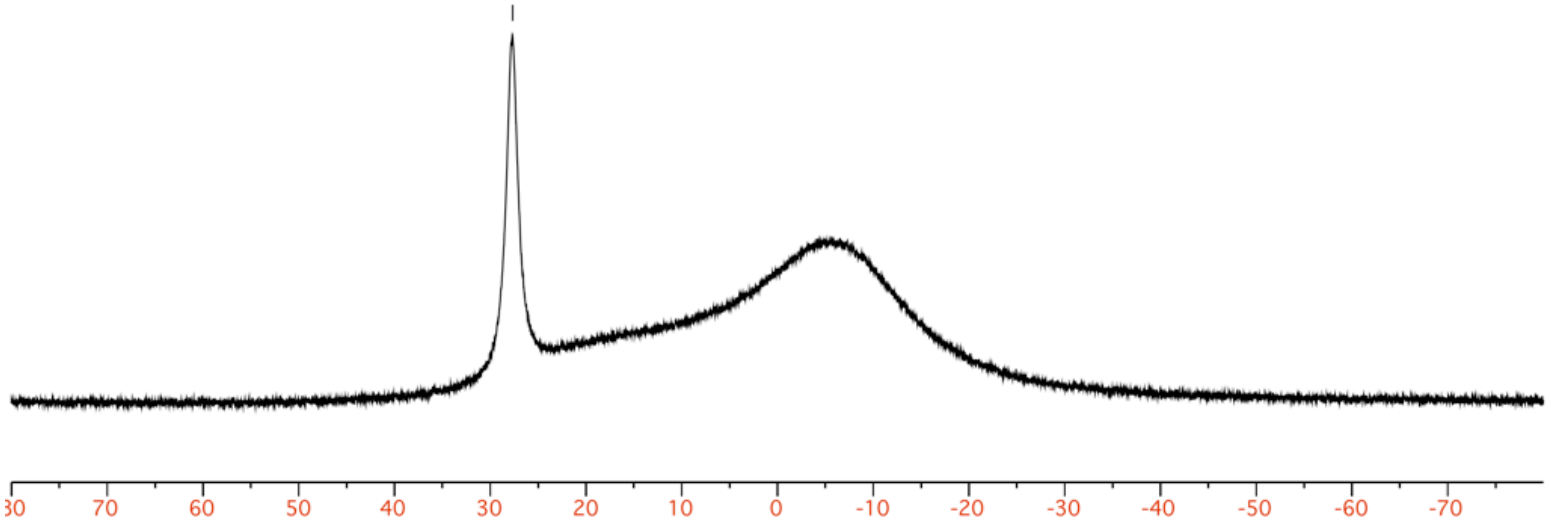
Table 2.5, Entry 2

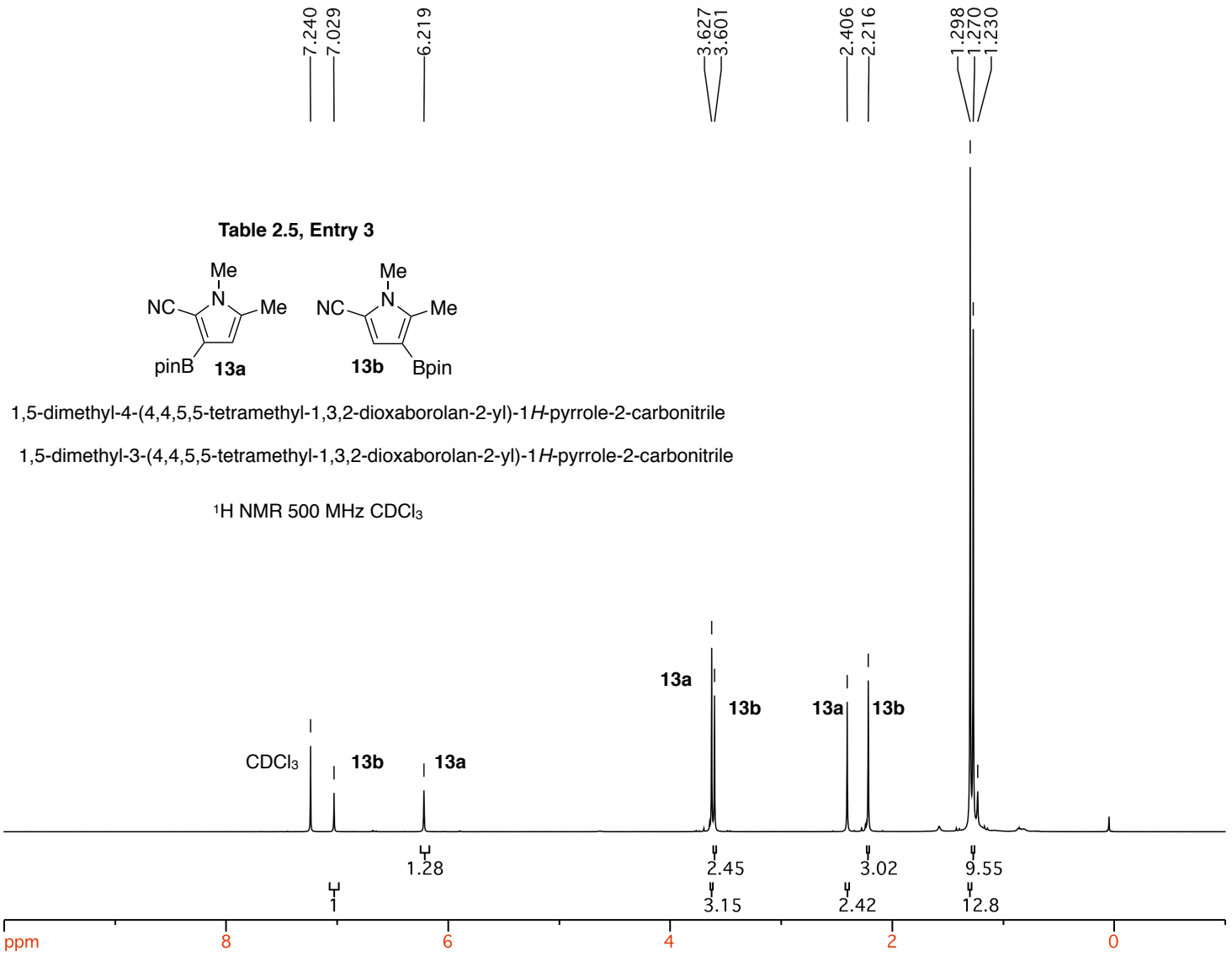


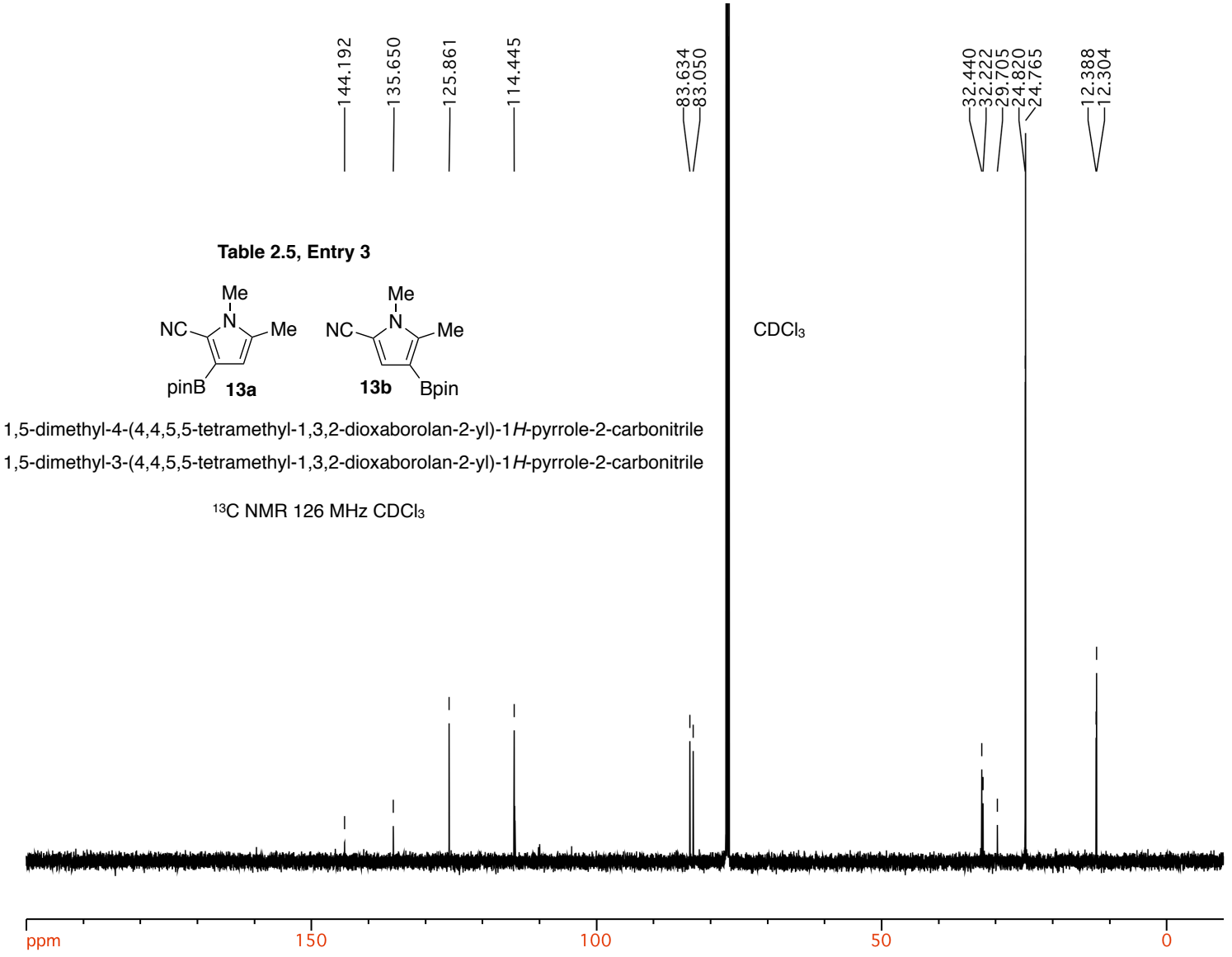
12a

5-bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbonitrile

^{11}B NMR 160 MHz $CDCl_3$

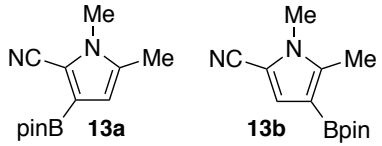



7.240
7.029
6.219
3.627
3.601
2.406
2.216
1.298
1.270
1.230
Table 2.5, Entry 3
Me
NC
N
Me
pinB
13a
Me
NC
N
Me
13b
Bpin
1,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole-2-carbonitrile
1,5-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole-2-carbonitrile
1H NMR 500 MHz CDCl3
CDCl3
13b
13a
13a
13b
13a
13b
1.28
2.45
3.02
9.55
1
3.15
2.42
12.8
ppm
8
6
4
2
0


144.192
135.650
125.861
114.445
83.634
83.050
32.440
32.222
29.705
24.820
24.765
12.388
12.304
CDCl3
Table 2.5, Entry 3
Me
N
NC
Me
pinB
13a
Me
N
NC
Me
13b
Bpin
1,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole-2-carbonitrile
1,5-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole-2-carbonitrile
13C NMR 126 MHz CDCl3
ppm
150
100
50
0

29.446

Table 2.5, Entry 3



1,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-2-carbonitrile

1,5-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-2-carbonitrile

^{11}B NMR 160 MHz $CDCl_3$

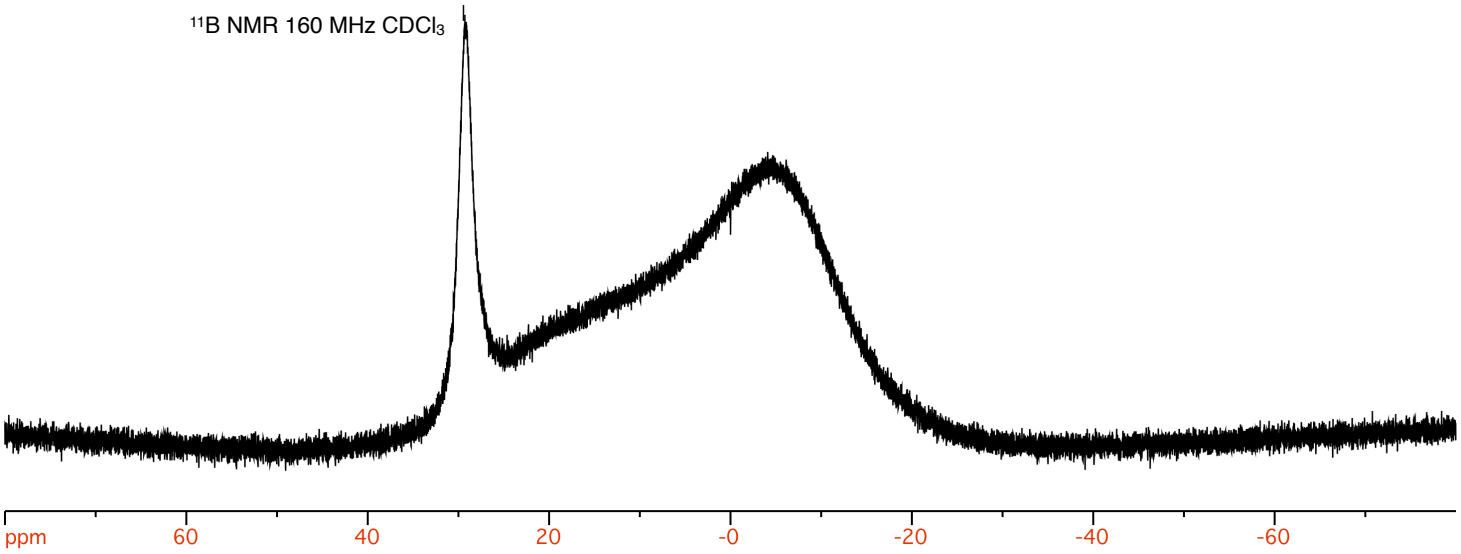
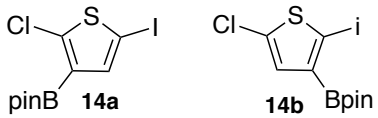


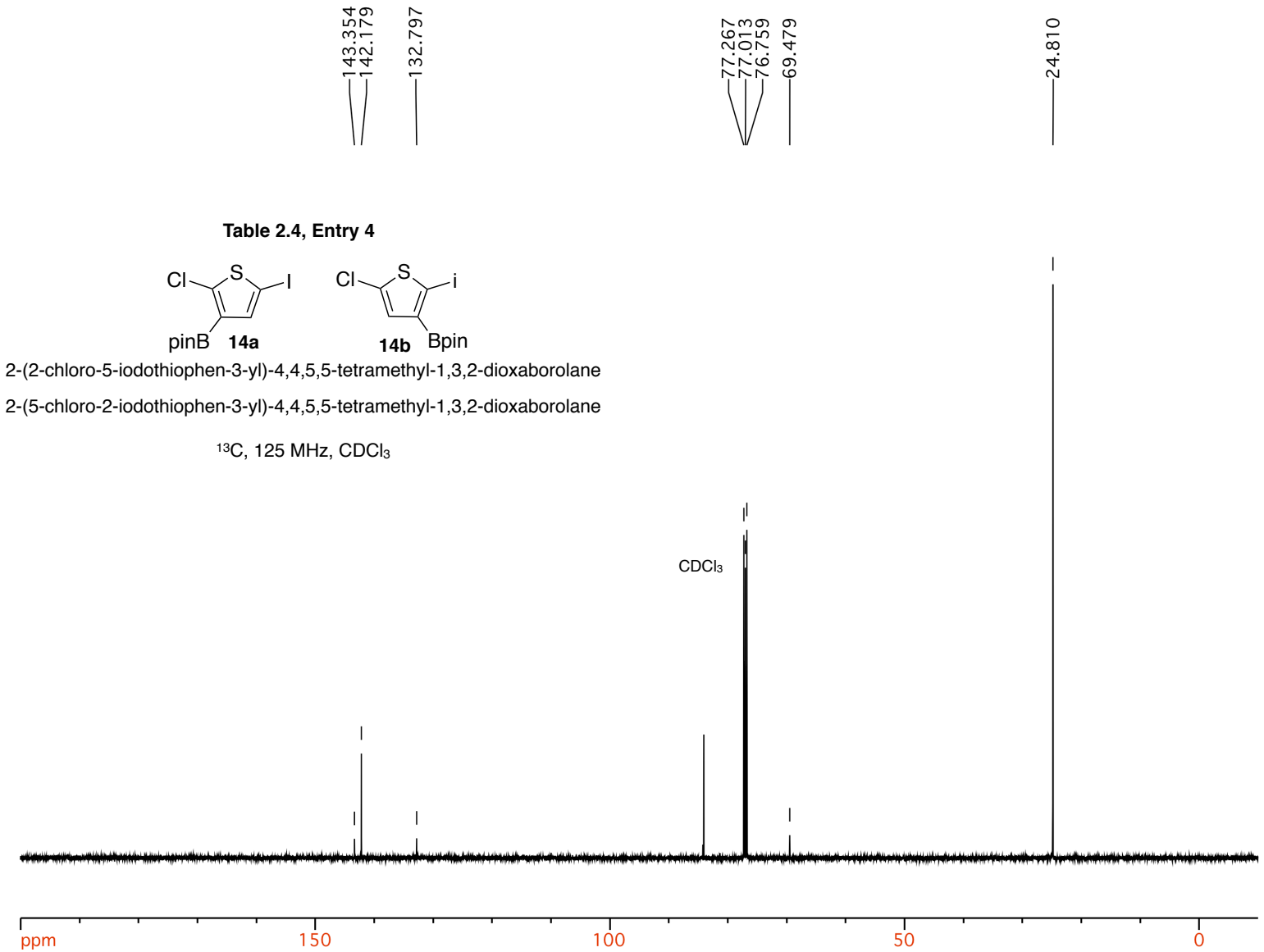
Table 2.4, Entry 4



2-(2-chloro-5-iodothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

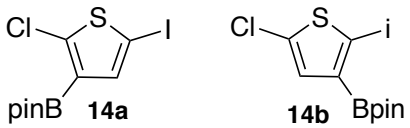
2-(5-chloro-2-iodothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, 500 MHz, $CDCl_3$


143.354
142.179
132.797
77.267
77.013
76.759
69.479
24.810
Table 2.4, Entry 4
Cl
S
I
pinB
14a
Cl
S
i
14b
Bpin
2-(2-chloro-5-iodothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
2-(5-chloro-2-iodothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
13C, 125 MHz, CDCl3
CDCl3
ppm
150
100
50
0

28.044

Table 2.4, Entry 4

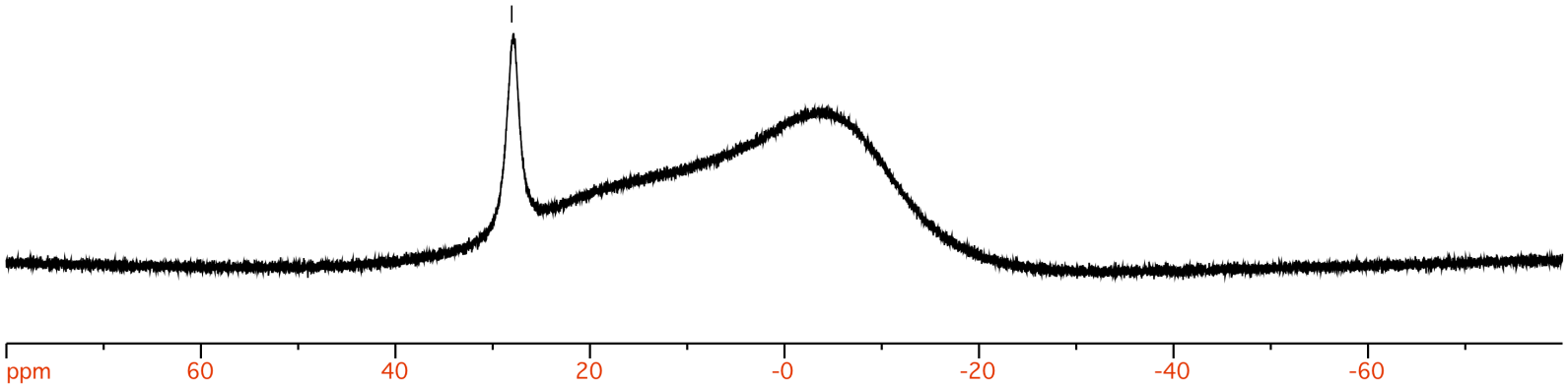


14a **14b**

2-(2-chloro-5-iodothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

2-(5-chloro-2-iodothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B, 126 MHz, $CDCl_3$



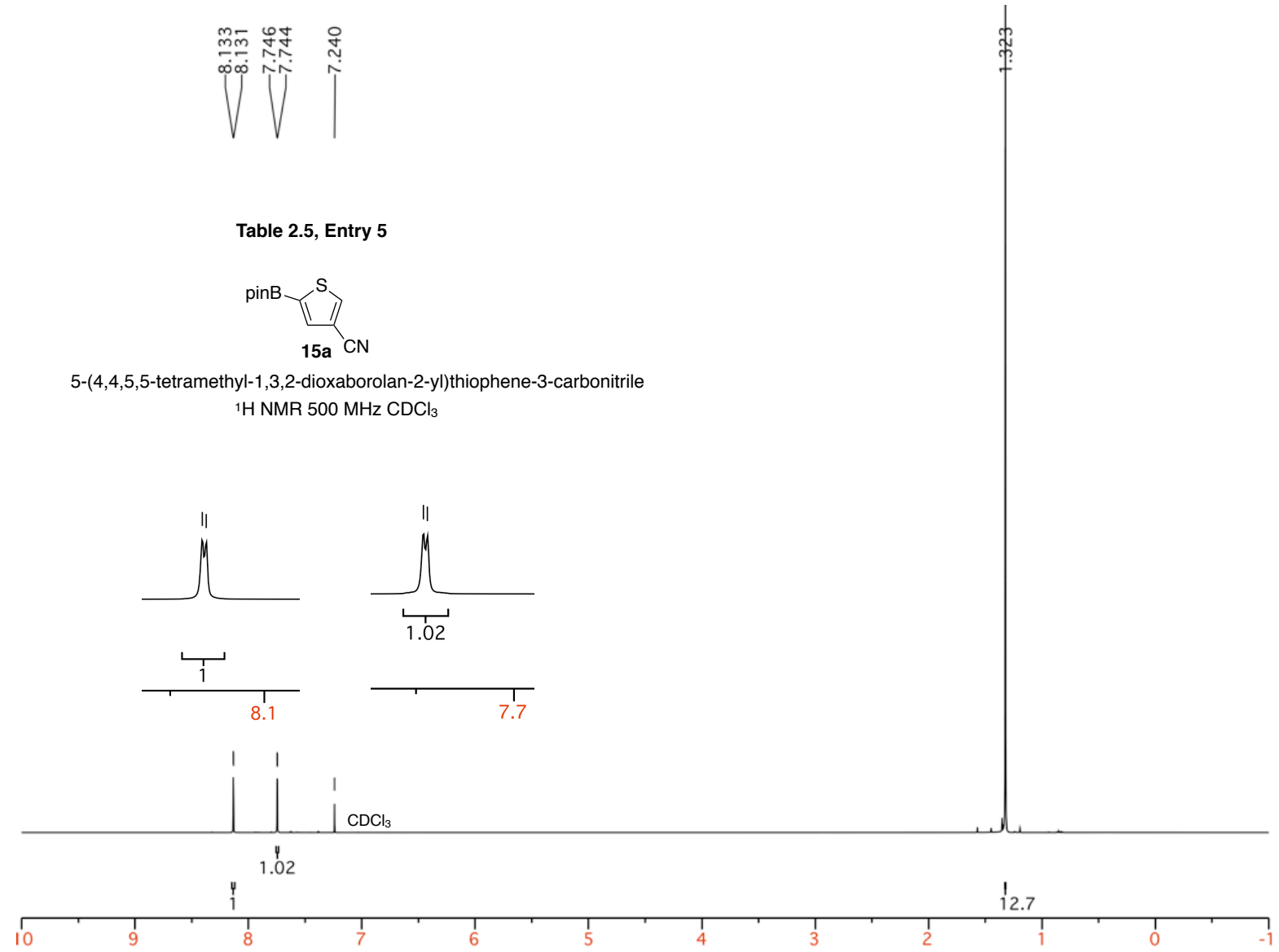


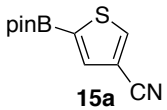
Table 2.5, Entry 5

15a

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-3-carbonitrile

^{1}H NMR 500 MHz $CDCl_3$

Table 2.5, Entry 5



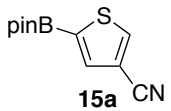
15a

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-3-carbonitrile

^{13}C NMR, 126 MHz $CDCl_3$,

28.386

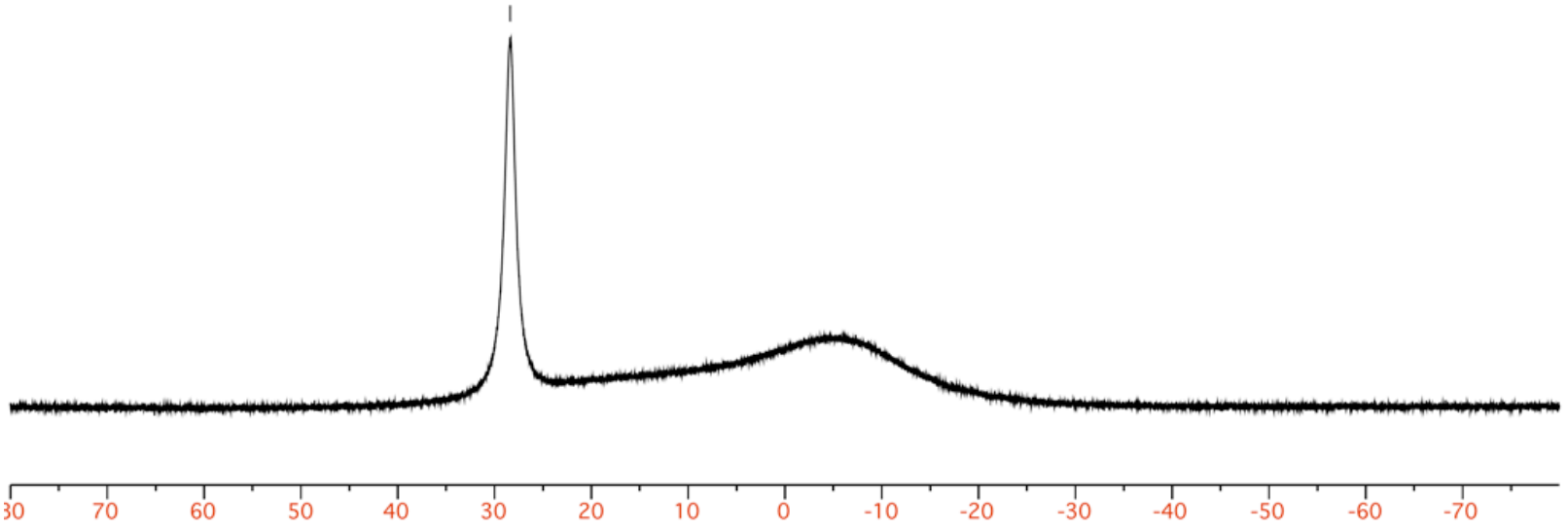
Table 2.5, Entry 5



15a

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-3-carbonitrile

^{11}B NMR 160 MHz $CDCl_3$



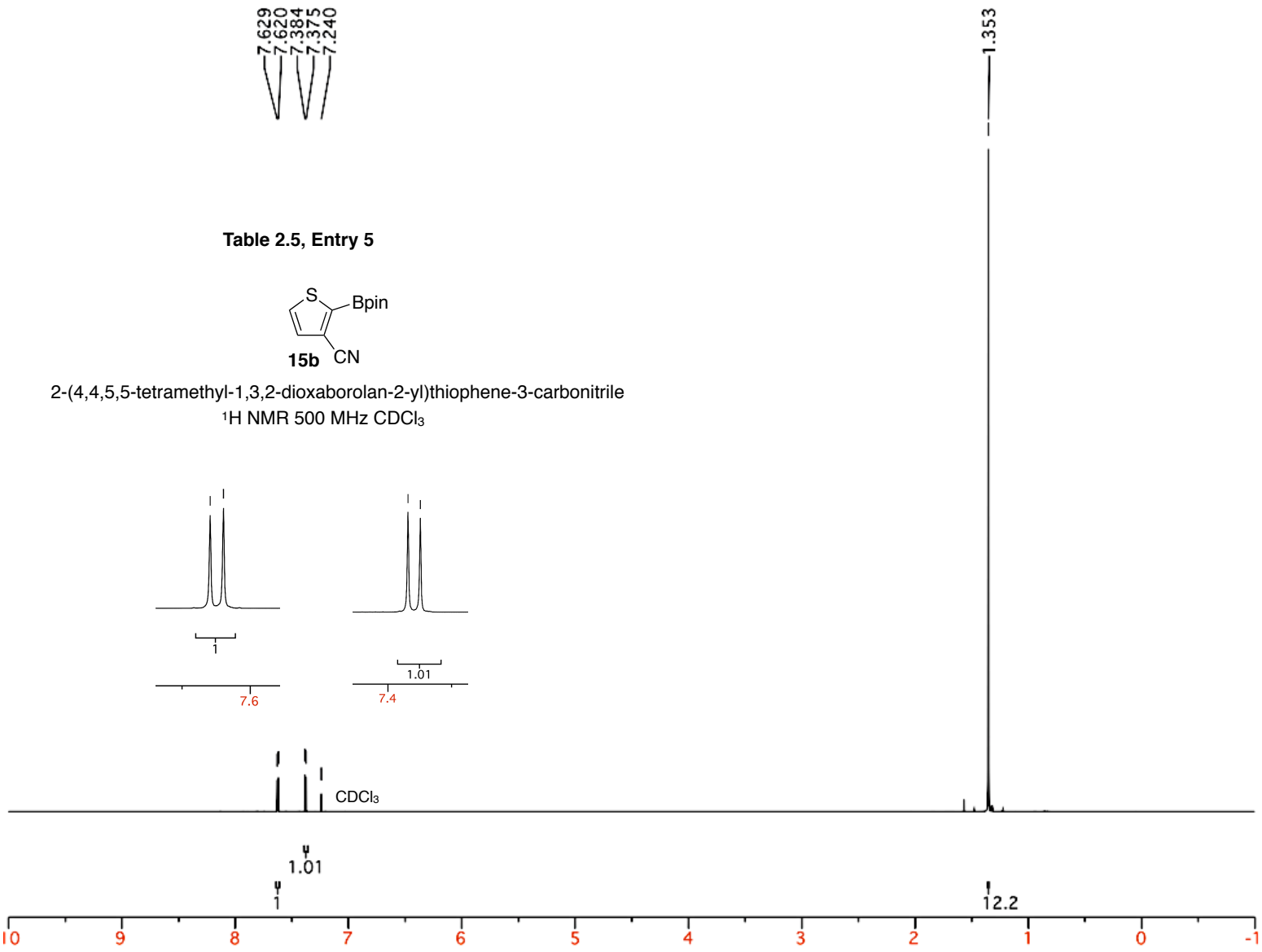
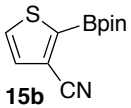

7.629
7.620
7.384
7.375
7.240
1.353
Table 2.5, Entry 5
S
Bpin
CN
15b
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-3-carbonitrile
1H NMR 500 MHz CDCl3
1
7.6
1.01
7.4
CDCl3
1.01
1
12.2
10
9
8
7
6
5
4
3
2
1
0
-1

Table 2.5, Entry 5



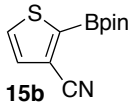
15b

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-3-carbonitrile

^{13}C NMR, 126 MHz $CDCl_3$,

28.169

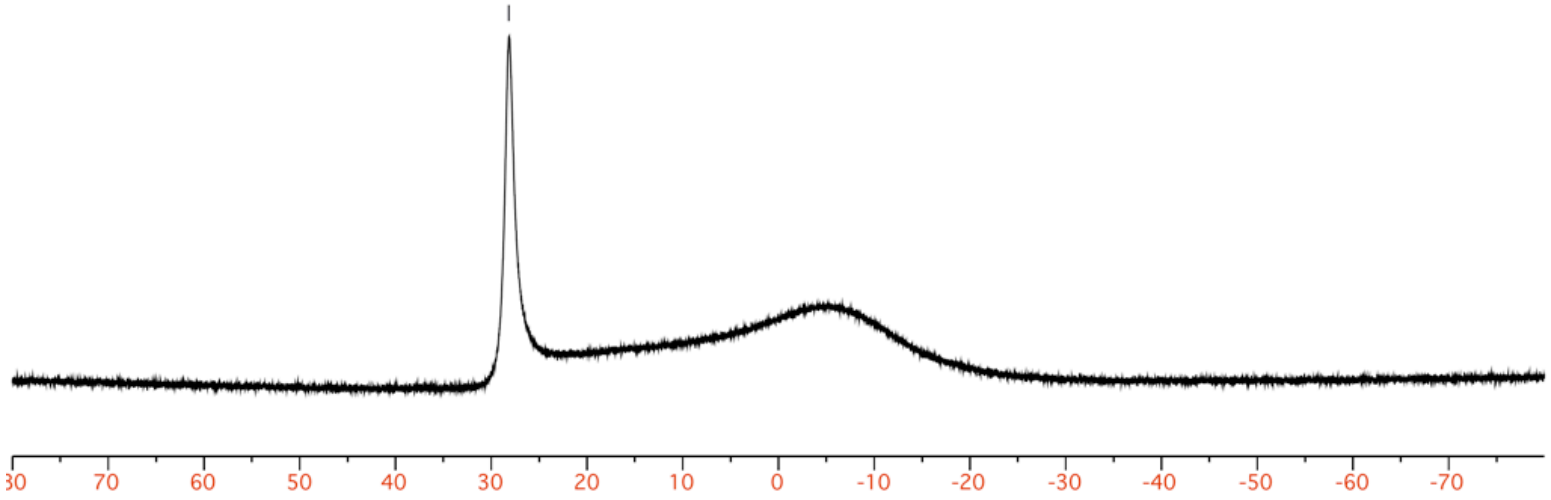
Table 2.5, Entry 5

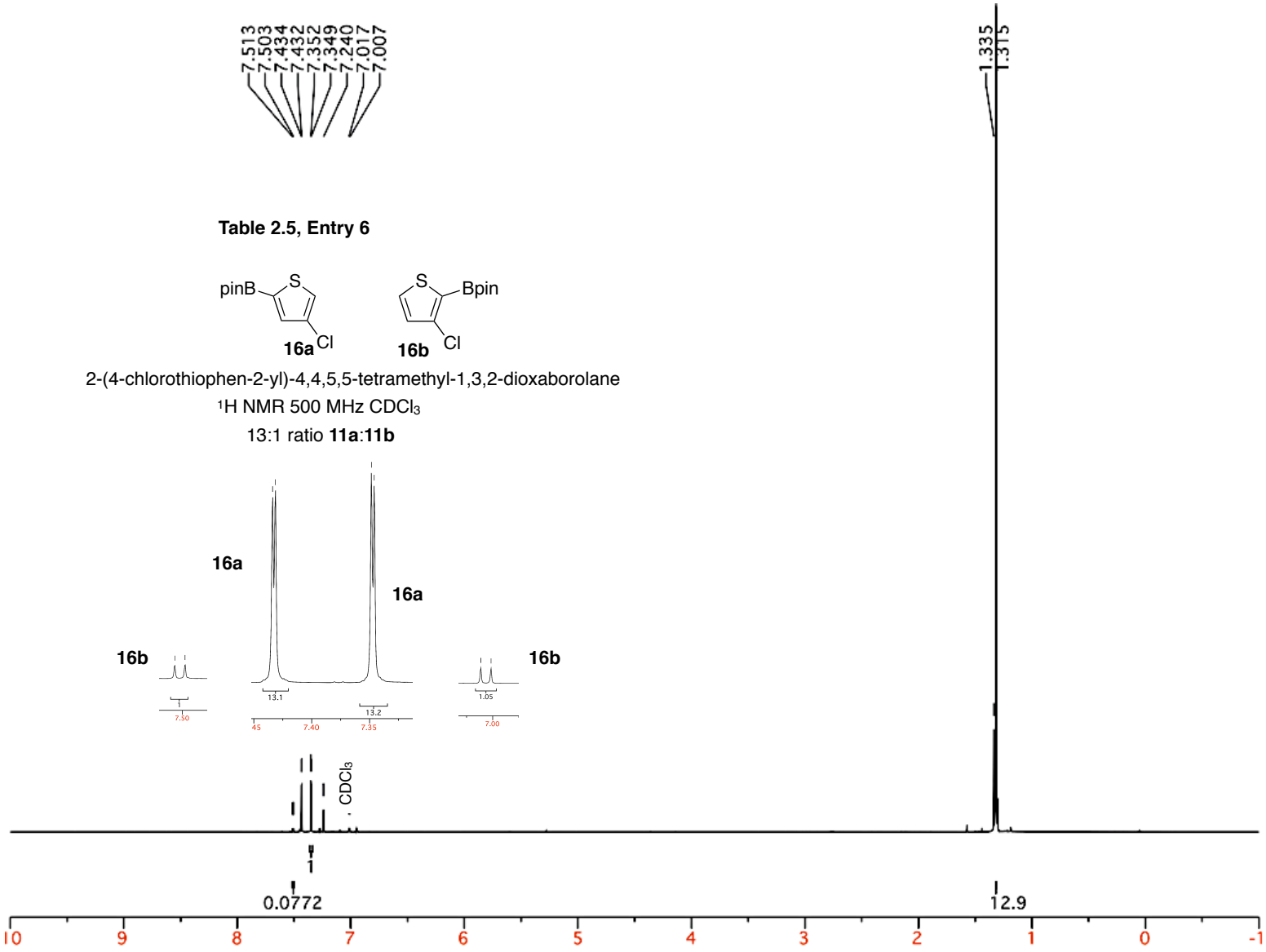


15b

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-3-carbonitrile

^{11}B NMR, 160 MHz $CDCl_3$,




7.513
7.503
7.434
7.432
7.352
7.349
7.240
7.017
7.007
1.335
1.315
Table 2.5, Entry 6
pinB
S
Cl
16a
S
Bpin
Cl
16b
2-(4-chlorothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
1H NMR 500 MHz CDCl3
13:1 ratio 11a:11b
16a
16a
16b
16b
13.1
13.2
1.05
7.50
7.40
7.35
7.00
CDCl3
1
0.0772
12.9
10
9
8
7
6
5
4
3
2
1
0
-1

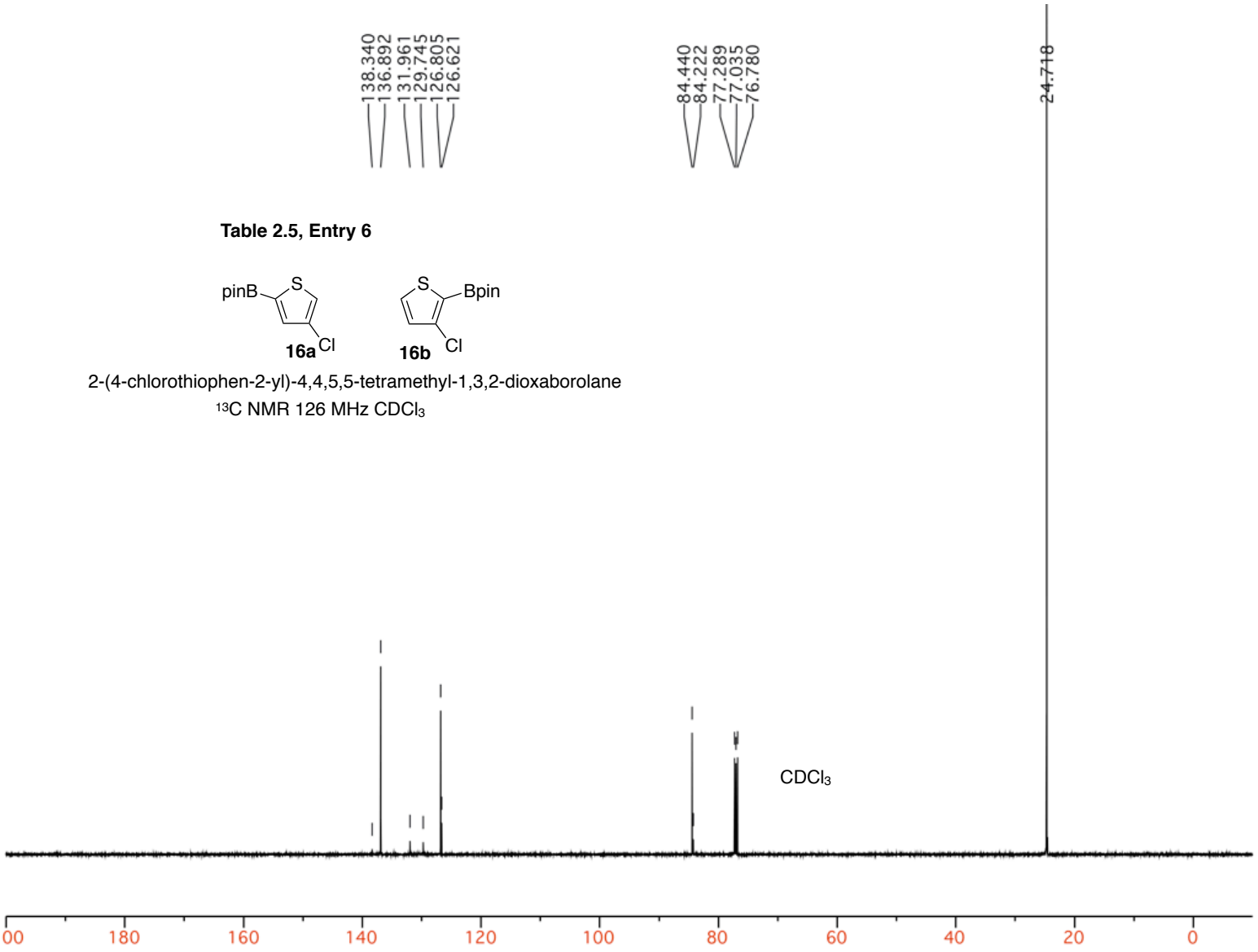


Table 2.5, Entry 6

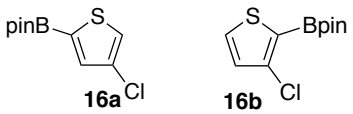
16a **16b**

2-(4-chlorothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C NMR 126 MHz $CDCl_3$

28.500

Table 2.5, Entry 6



16a

16b

2-(4-chlorothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B NMR 160 MHz $CDCl_3$

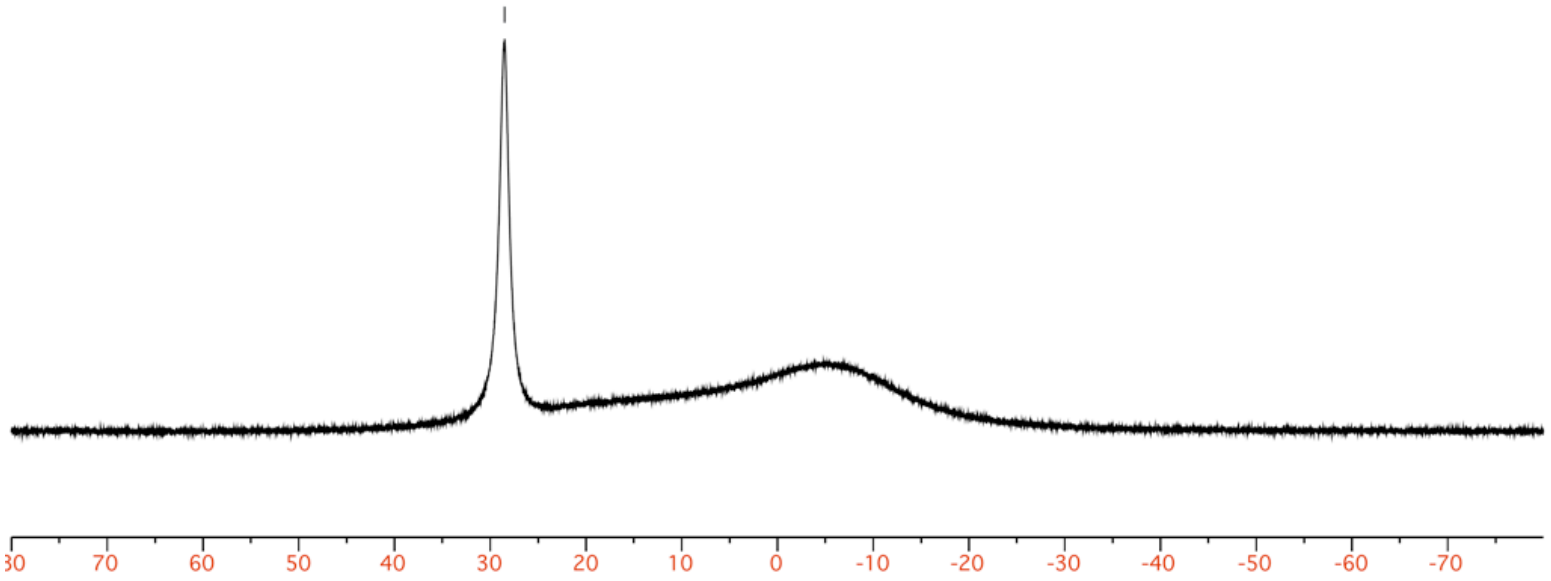
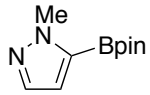


Table 2.5, Entry 7

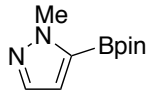


17b

1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole

^{1}H NMR 500 MHz $CDCl_3$

Table 2.5, Entry 7



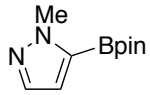
17b

1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole

^{13}C NMR 126 MHz $CDCl_3$

27.926

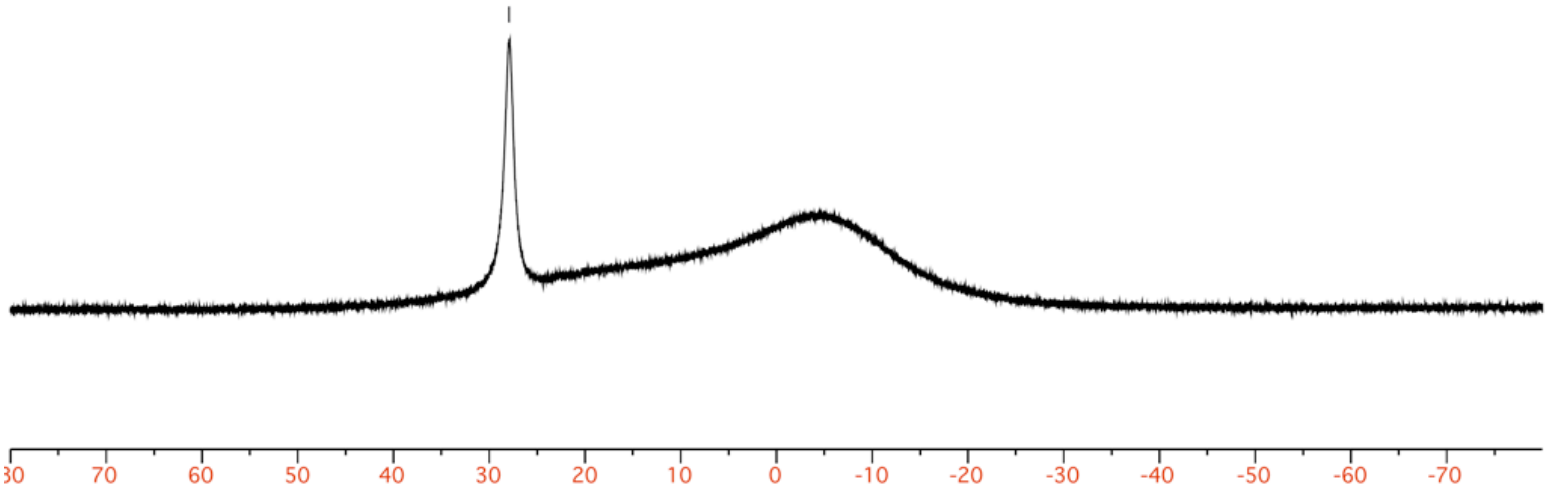
Table 2.5, Entry 7



17b

1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole

^{11}B NMR 160 MHz $CDCl_3$



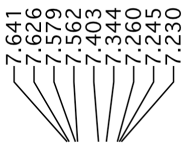
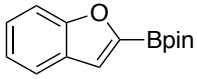


Table 2.5, Entry 8

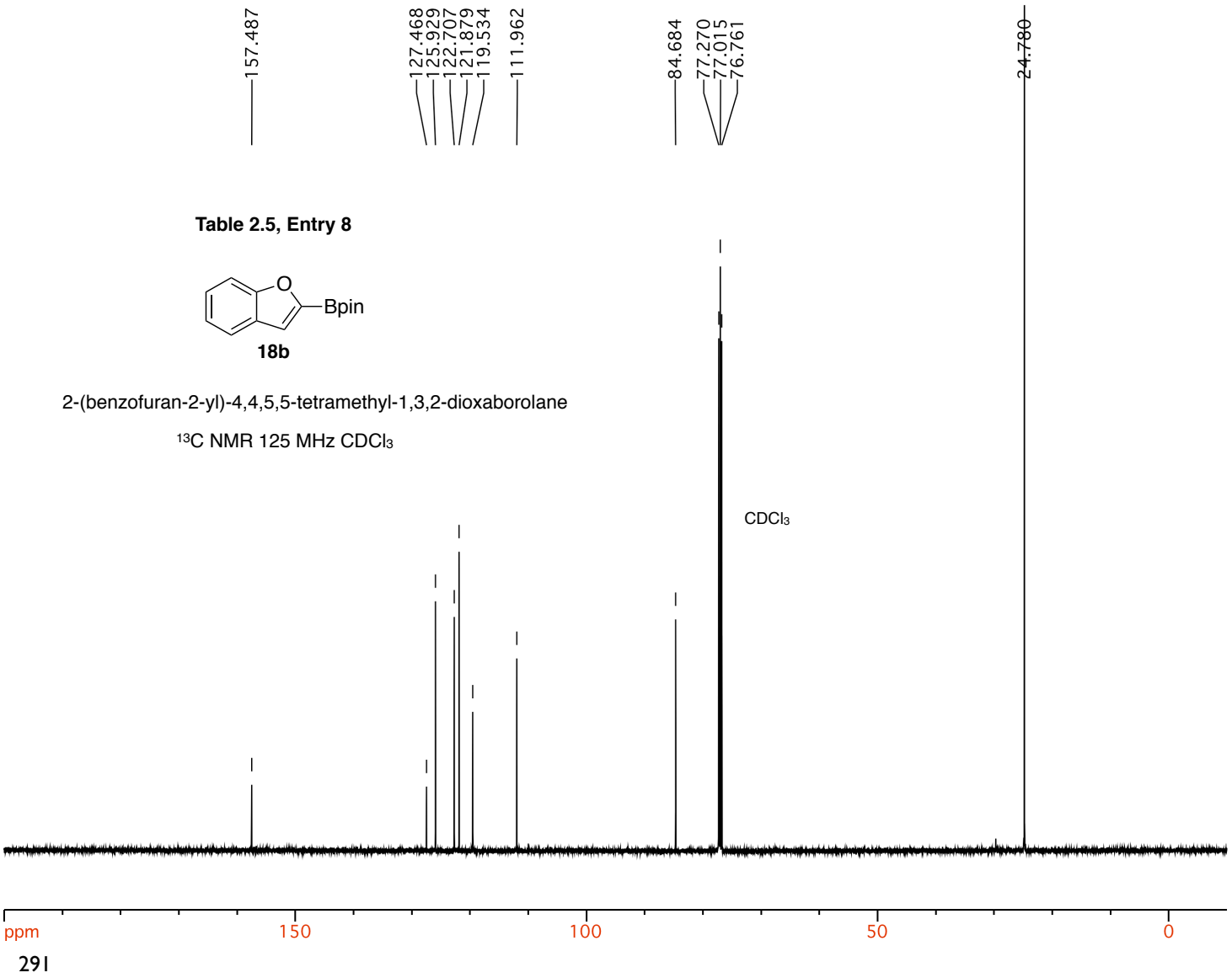


18b

2-(benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

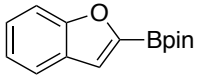
^{1}H NMR 500 MHz $CDCl_3$

290


157.487
127.468
125.929
122.707
121.879
119.534
111.962
84.684
77.270
77.015
76.761
24.780
Table 2.5, Entry 8
O
Bpin
18b
2-(benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
13C NMR 125 MHz CDCl3
CDCl3
ppm
150
100
50
0
291

27.787

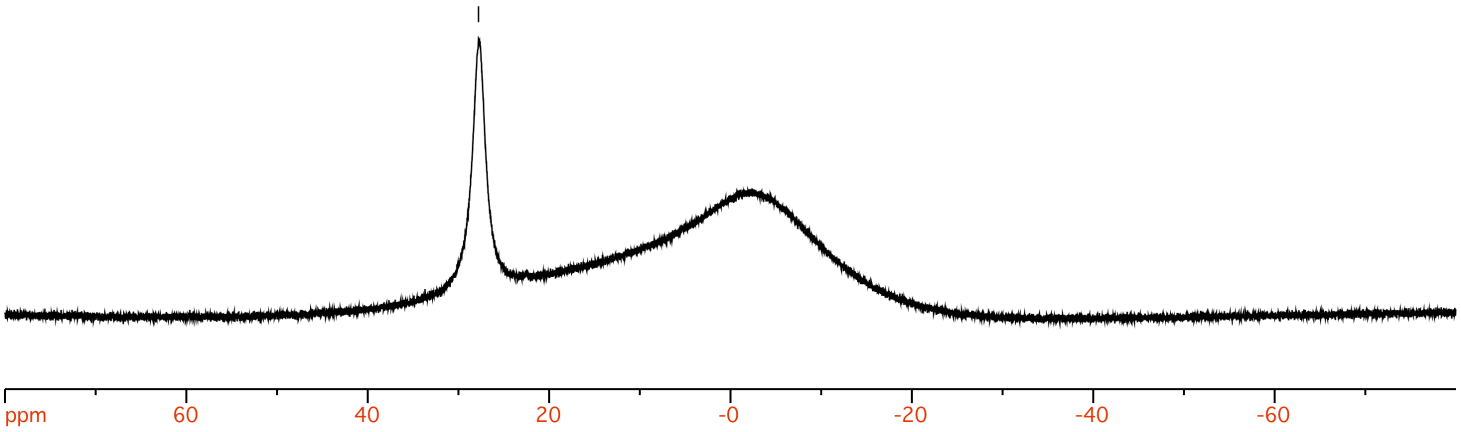
Table 2.5, Entry 8



18b

2-(benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B NMR 160 MHz $CDCl_3$



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CHAPTER 3 APPENDIX

I. General Methods:

Pinacol Borane (HBpin) (97% stabilized with 1% triethylamine) and Bispinacolatodiboron (B_2pin_2) were purchased commercially and used as received without further purification. The iridium catalyst, bis(η^4-1,5-cyclooctadiene)-di-μ-methoxy-diiridium (I), $[Ir(OMe)COD]_2$, was prepared by a literature procedure.[1]

The ligands were obtained from commercial sources and used as received except as follows: Di-(pyridin-2-yl)methane, (also known as dipyridyl methane and abbreviated **dpm**) was synthesized by a literature procedure.[2] Substituted bipyridine (bpy) ligands from Table 1, $N^4,N^4,N^{4'},N^{4'}$-tetramethyl-[2,2'-bipyridine]-4,4'-diamine[3] and 4,4'-bis(trifluoromethyl)-2,2'-bipyridine[4] were also synthesized by literature procedures.

The ligand, 2,2'-methylenebis (*N*,*N*-dimethyl pyridin-4-amine) (also known as dimethyl amino dipyridyl methane, abbreviated **dmadpm** in this paper) was synthesized according to modified literature procedures as detailed in the experimental section.[5,6]

The substrates featured in Tables 2 and 3 were obtained commercially. Liquid substrates were purified by distillation and solid substrates were purified by sublimation, except as noted. 5-Bromo-2-cyanothiophene was prepared by a literature procedure.[7] 2-Chloro-3-fluoropyridine and 5-methylfuranonitrile were purchased in small quantities, so they were passed through a short plug of activated alumina in the glove box in lieu of distillation. 2-Chloro-6-fluoropyridine was used as received without further purification. To aid transfer, the low melting solid was stored in the freezer and weighed cold into the reactions.

All reactions were carried out at ambient temperature in 20 mL vials equipped with stir bars in a glove box under a nitrogen atmosphere. All solvents were obtained from wet stills refluxing over sodium and benzophenone.

Reactions were monitored by gas chromatography (GC) equipped with a 10 m x 180 μm fused silica column. The GC method employed an initial temperature 50°C constant over 1 minute, ramp 50°C/minute over 9 minutes, 270°C constant over 5 minutes (total time 15 min at flow rate = 1 mL/min).

NMR spectra were recorded on a Varian 500 MHz DD2 Spectrometer equipped with a 1H-19F/15N-31P 5mm Pulsed Field Gradient (PFG) Probe. Spectra were taken in $CDCl_3$ referenced to 7.24 ppm in ^{1}H NMR and 77.0 ppm in ^{13}C NMR. Spectra were processed for display by iNMR software.

Single crystal analyses were performed by Michigan State University Center for Crystallographic Research on a Charge Coupled Device (CCD diffractometer).

High-resolution mass spectra were obtained at the Michigan State University Mass Spectrometry Core using quadrapole Time Of Flight instruments (q/TOF).

CHN analyses were performed on a CHNS/O analyzer at Michigan State University by analytical department staff.

Silica used for purification of crude material was standard laboratory grade 230 - 400 mesh designed for flash chromatography applications. Purification of crude materials on a 1 mmol scale was achieved by standard flash chromatography methods employing 2-3 g silica plugs in small chromatography columns of dimension approximately 2 x 30 cm. Larger scale reactions of 2.5 - 5 mmol were purified in a similar manner, using 10 - 20g silica. Concentrated crude material was dissolved in a minimum amount of solvent, applied to the silica with a Pasteur pipette and eluted into test tubes. Compounds that eluted were visualized by spotting on TLC plates and irradiating with 254 nm UV light. Borylated compounds were additionally visualized by staining with alizarin

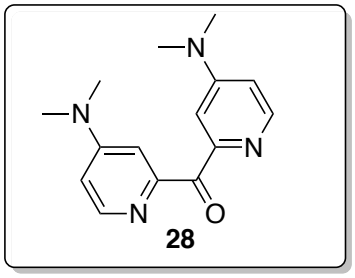
stain in accordance with a literature procedure.[8] The stained compounds containing boron charred orange and fluoresced brightly under long wave UV light of 366 nm.

II. Experimental:

Preparation of the ligands

Dpm was prepared by a literature procedure.[1] For preparation of dmadpm, see page 9 in the supporting information for chapter 2.

Step 1: Preparation of the dipyridyl ketone:



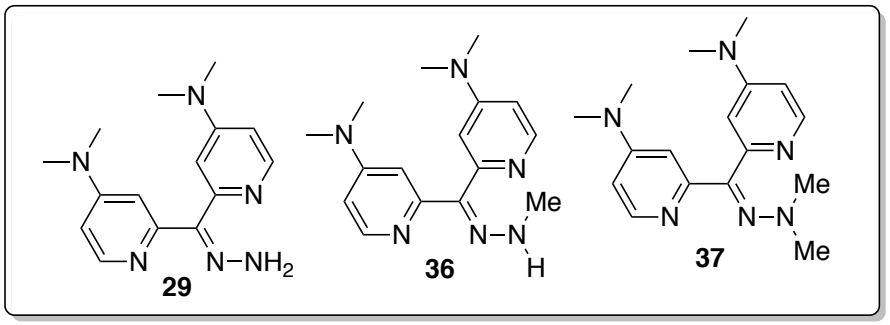
28

The ketone was synthesized starting from a literature prep of 2-bromo-*N*,*N*-dimethylpyridin-4-amine (2-bromo-DMAP).[5] A literature prep for an analogous dipyridyl ketone, referred to as compound **19** in the paper, was followed using 2-bromo-DMAP made by the procedure in reference 5 as starting material.[6] The ketone was isolated by column chromatography employing 25 g silica packed in 100% ethylacetate. The crude material was loaded onto the column dissolved in a minimum amount dichloromethane. Ethyl acetate was added until unreacted starting material and bi-products had eluted. The fractions were analyzed by TLC in 100% methanol. 2-bromo-DMAP was seen as a spot with $r_f = 0.9$, and byproducts were seen as faint spots ranging in r_f from 0.4 – 0.7. The product was seen as a spot that did not move off the baseline. A gradient of 10% - 30% methanol in ethyl acetate was applied and the ketone eluted with 30% methanol. On a 5 mmol scale, 330 mg pale yellow crystalline solid was isolated (49% yield, m.p. = 175 – 178 °C).

^{1}H NMR (500 MHz; $CDCl_3$): δ 8.30 (d, *J* = 5.9 Hz, 1H), 7.22 (d, *J* = 2.7 Hz, 1H), 6.56 (dd, *J* = 5.9, 2.7 Hz, 1H), 3.05 (s, 6H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 195.9, 155.3, 154.7, 149.2, 108.3, 108.0, 39.2. HRMS (ESI+) (*m/z*) calcd for $C_{15}H_{19}N_4O$ $[M+H]^+$ 271.1559, found 271.1566.

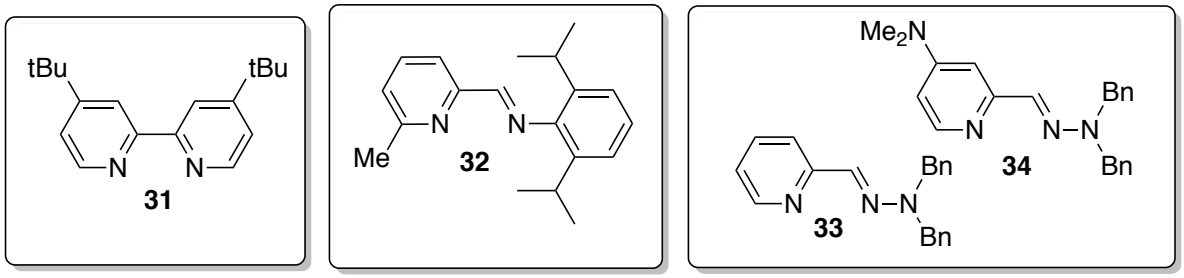
The ketone was recrystallized from dichloromethane and toluene to produce crystals suitable for x-ray diffraction, which yielded a crystal structure that confirmed the identity of the product. The CIF file is available for download from the Cambridge Crystallographic Data Centre (CCDC) and may be referenced by CCDC deposition # 1436384.

Step 2: Synthesis of the Dimethylamino dipyridyl hydrazones:



For 1 mmol of ketone **28**, 15 mL ethanol are put in a schlenk tube or side arm flask, and 1 mmol (1 equiv) glacial acetic acid was added to the ethanol. The ketone was weighed on a weigh paper and added into the ethanol-acid solution. 2 mmol (2 equiv) hydrazine monohydrate (or methylhydrazine or dimethylhydrazine, depending on which hydrazone is desired) was added by syringe and the mixture was allowed to stir under N_2 for 2 - 6 hours. When the ketone was gone by TLC or GC-FID, the flask was put under vacuum with stirring to pull off ethanol until a white solid precipitated. Three quarters of the volume of ethanol was pulled off, and the white solid was collected by filtration in glass fritted funnel in air, dried under vacuum and stored in a desiccator or a glove box.

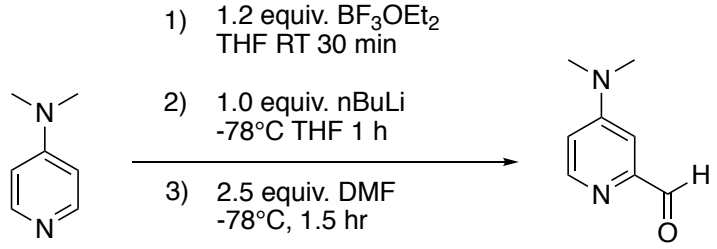
Other Ligands:



Ligand **31** is widely commercially available. Ligands **32**[20], **33**[21] and **34**[22] were synthesized by literature preparations.

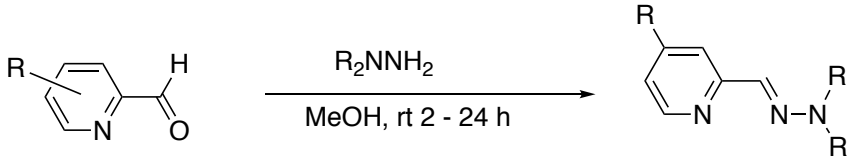
Preparation of Pyridyl–imine Ligands

Ligands **35**, **36** and **37** can be made starting from 4-dimethylamino pyridine (4-DMAP)



2-Pyridyl lithiation can also be achieved by use of dimethylamino ethanol (DMAE) as a metalation directing group.[3, 23]

To make ligand **38**, (methyl imine substituted) make a methyl pyridyl ketone instead of an aldehyde. Instead of DMF, add acetyl chloride in step 3.



35, R = 4-NMe_2, R' = H
36, R = 4-NMe_2, R' = H
37, R = 4-NMe_2, R' = H
38, R = H, R' = Me
39, R = H, R' = H
40, R = 4-Me, R' = H
41, R = 4-Br, R' = H
42, R = 3-Br, R' = H

For N substituent R_1 and/or $R_2 \neq H$, add 1 equiv glacial acetic acid

PART B: Supplemental Information for Germanium Coupling

Equipment and Procedures:

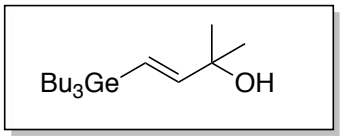
Reactions were monitored by GC-FID with WCOT fused silica 30 m x 0.25 mm ID coating CP-SIL 8CD. GC-FID method: 70°C 2min.; ramp 20 °C / min, 9 min; 250 °C hold 10 or 20 min. NMR were taken on 500 MHz spectrometer equipped with ^{1}H-$^{19}F/^{15}N$-^{31}P 5 mm Pulsed Field Gradient (PFG) probe, Z-axis PFG module, protune accessory for autotune and match; and autosampler. Spectra were taken in deuterated chloroform, $CDCl_3$, and referenced to 7.24 ppm residual proton in ^{1}H NMR and 77.0 ppm for ^{13}C NMR. NMR spectra were transformed for display from the original FID data files by iNMR software and no data or image files of spectra have been altered or edited in any way. All unprocessed FID files are available upon request.

Palladium acetate ($Pd(OAc)_2$), tetrakis(triphenylphosphine))palladium (0) ($Pd(PPh_3)_4$), bis(triphenylphosphine)palladium(II)dichloride, ($[Pd(PPh_3)_2Cl]_2$), triphenyl phosphine (TTP or PPh_3), and tetrabutylammonium bromide (TBAB or Bu_4NBr), Potassium carbonate (K_2CO_3), iodobenzene (PhI), 2-methylbut-3-yn-2-ol, 2-methyl-3-butyn-1-yl, tributyl germanium chloride (Bu_3GeCl), and tributyl germanium hydride (Bu_3GeH), were purchased from commercial sources and used as received. Acetonitrile (MeCN) and dichloromethane (DCM) were collected from a dry still of activated aluminum oxide, and tetrohydrofuran, (THF) was refluxed in a wet still over sodium and benzophenone and collected just prior to use.

Preparation of Vinyl Germanes:

A modified procedure was developed based on literature preparations of vinyl germanes.[24]

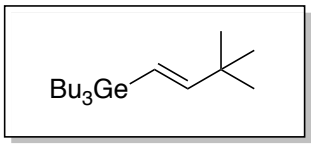
(E)-2-Methyl-4-(tributylgermyl)but-3-en-2-ol



Into a 50 mL oven-dried round bottom flask equipped with stir bar was weighed Bu_3GeH (1.025 g, 4 mmol, 1 equiv) and 2-methylbut-2-methyl-3-butyn-1-yl (0.325 g 4 mmol, 1.0 equiv), and the mixture was dissolved in 20 mL dry THF. Palladium caltalyst $[Pd((Ph_3)_2Cl]_2$ (44 mg, 1.5 mol%) was weighed on a weigh paper and addd as a solid into the stirring mixture. The clear, pale yellow reaction mixture was degassed by sparging Argon gas for 5 minutes. The flask was closed with a septum and stirred at ambient temperature under positive pressure of Ar for 2 h. After 15 minutes the reaction turned a root beer brown color. Complete conversion to product was seen by GC-FID after 2 h. The reaction was concentrated by rotary evaportation and isolated by 50 g silica column eluting in 5% ethyl acetate in hexane. The product was isolated as 1.03 g clear oil, 85% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.75 (m, 6 H, 3 x CH_2); 0.86 (m, 9 H, 3 x CH_3); 1.28 (s, 6 H, 2 x CH_3) overlapped with 1.3 (m, 12 H, 6 x CH_2); 1.44 (br. s, 1 H, OH); 5.85 (d, 1 H, J = 19 Hz); 6.01 (d, 1 H, J = 19 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 13.8, 26.4, 27.3, 29.5, 72.1, 122.8, 152.4. MS(EI) *m/z* 273 (M+ minus butyl radical ($C_4H_8^{\bullet}$), *i.e.* 329 - 56) (25); 255 (35); 217 (82); 199 (100); 157 (25); 143 (75); 115 (10), 89 (5), 69 (5).

(E)-Tributyl(3,3-dimethylbut-1-en-1-yl)germane



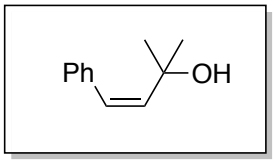
Into a 50 mL oven-dried round bottom flask equipped with stir bar was weighed Bu_3GeH (0.245 g, 1 mmol, 1 equiv) 2-methyl-3-butyn-1-yl (0.08 g 4 mmol, 1 equiv), and the mixture was dissolved in 10 mL dry THF. Palladium caltalyst $[Pd((Ph_3)_2Cl]_2$ (11 mg, 1.5 mol%) was weighed on a weigh paper and added as a solid into the stirring solution. The clear, pale yellow reaction mixture was degassed by sparging Argon gas for 5 minutes. The flask was closed with a septum and stirred at ambient temperature under positive pressure of Ar for 8 h. Complete conversion to product was seen by GC-FID. The reaction was concentrated by rotary evaporation and isolated by 10 g silica column eluting in hexane. The product was isolated as 0.185 g clear oil, 77 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.73 (m, 6 H, 3 x CH_2); 0.86 (m, 9 H, 3 x CH_3); 0.97 (s, 9 H, t-butyl) overlapped with 1.30 (m, 12 H, 3 x CH_3); 5.53 (d, 1 H, J = 18.5 Hz); 5.86 (d, 1 H, J = 18.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 13.8, 26.4, 27.3, 29.2, 35.2, 120.1, 156.5. MS(EI) *m/z* 271 (M+ minus butyl radical; ($C_4H_8^{\bullet}$), *i.e.* 327 – 56) (25); 255 (35); 217 (82); 199 (100); 157 (25); 143 (75); 115 (10), 89 (5), 69 (5).

Modified Heck Coupling of Aryl Halides with Tributylvinylgermanes:

A modified procedure was adapted from the published procedure of Torres, Lavis and Maleczka[25] which was based on conditions published by Jefferey.[26-27]

(Z)-2-methyl-4-phenylbut-3-en-2-ol



Into an oven dried 3 neck round bottom flask equipped with a stir bar was weighed (E)-tributyl (3,3-dimethylbut-1-en-1-yl) germane (0.125 mmol, 41 mg, 1 equiv). Solid reagents were weighed on weigh papers and added into the flask as follows; K_2CO_3 (0.32 mmol, 43 mg 2.5 equiv), TBAB (0.125 mmol, 40 mg, 1 equiv), PPh_3 (40 mol %, 13 mg, 0.05 mmol). The mixture was stirred in 1 mL water until most inorganic solids were dissolved, then 2 mL MeCN was added. The resulting mixture was two phases with most solids dissolved. PhI was measured by pipettor (0.25 mmol, 150 mg, 105 μL, 2 equiv) and added into the flask. This mixture was stirred for 5 – 10 minutes. $Pd(OAc)_2$ was weighed onto a weigh paper (20 mol%, 5.6 mg, 0.025 mmol), and added last. Additional MeCN was added to wash down the sides of the flask for a total of 4 mL of solvent that was a ratio of 3:1 MeCN:H_2O. A condenser with Ar inlet was attached and the flask was closed with septa. The assembly was put into a 70 °C oil bath and heated 24 h.

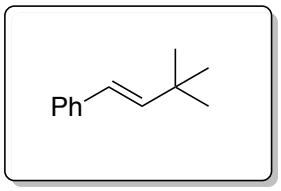
After 24 h, the reaction was stopped and conversion was assessed by GC-FID. The reaction was concentrated by rotary evaporation to remove MeCN. To the concentrated reaction, 2 mL saturated aqueous ammonium chloride and 10 mL diethyl ether was added. The layers were

separated and the organic layer was dried over sodium sulfate. The drying reagent was removed and the concentrated organic layer was subjected to a 10 g silica column eluting in DCM.

Crude NMR and GC-FID indicated 78% conversion with 22% starting material remaining. The ratio of products was 88:8:4 *Z*:*E*:*internal*. Products are known literature compounds and were verified by matching reported NMR and mass spec data.[28] TLC eluting in DCM showed starting material as a spot with rf = 0.6, and the *Z*-product with rf = 0.4 and the *E*-product rf = 0.35. The spots charred dark blue with phosphomolybdic acid (PMA) stain. The extracted material was applied to 10g silica column eluting in DCM. Fractions were analyzed by TLC and 10mg pure product was isolated for 56% yield of Z-isomer. Later fractions were combined and concentrated to 3 mg of a mix of E and Z isomers, for a total isolated yield of 65 %. 5mg starting material was recovered.

Modified Stille Coupling of Tributylvinylgermanes lacking an alcohol group at a tertiary allylic carbon.

(*E*)-(3,3-Dimethylbut-1-en-1-yl)benzene



Analogous hindered vinyl germanes lacking an allylic alcohol did not undergo coupling reactions with iodoarenes. A modified protocol based on literature procedure[29] was adapted to probe the function of the allylic alcohol in order to test whether inversion involved O atom participation or was induced by steric crowding.

The vinyl germane was weighed into a 3-neck 50 mL round bottom flask equipped with a stir bar and fitted with a reflux condenser. 3.0 mL toluene was added and Ar was bubbled through

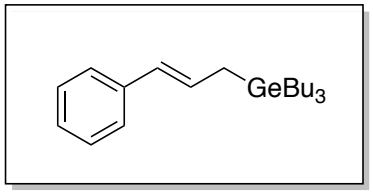
the solution. Tetrabutylammonimfluoride (TBAF) solution (1 mmol, 7 equiv, 1.0 mL 1M TBAF in THF) was taken up by syringe and added next. It formed a layer on the bottom that was not miscible with toluene. Phenyl iodide was weighed into a gc vial, dissolved in 0.5mL toluene, and the solution was added to the mixture of starting material and TBAF in the reaction flask while the sparging continued. Pd_2dba_3 (12 mg, 10 mol%) was weighed on a weigh paper and added last, and the sparge was continued for about 5 min.

The sparging was stopped and the flask was closed with septa, and an Ar inlet was added through the top of the condenser. The flask was put into a 100°C oil bath and heated with stirring overnight for 16 h. 20% conversion was seen by NMR and coupling product verified by mass spec. Only *(E)*-(3,3-Dimethylbut-1-en-1-yl)benzene coupling product was formed, and matched the NMR of the known compound.[30] No *Z* product was observed.

Preparation of Allylic Germanes by Grignard Reaction

by modified literature procedure.[31]

Tributyl(cinnamyl)germane

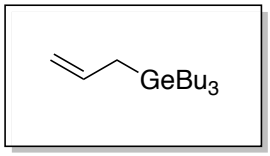


Mg turnings (0.25 g, 10 mmol, 2.3 equiv) were washed in dilute HCl and rinsed with water then acetone in a fritted funnel. The turnings were transferred into a 100 mL side arm Schlenk tube equipped with a stir bar and dried under vacuum with heating. The dried turnings were stirred vigorously under Ar overnight, resulting in fine gray powdered Mg with some larger pieces remaining.

Dry THF (10 mL) was added by syringe onto the dried, pulverized Mg turnings, and the mixture was stirred. Chlorotributylgermane (1.2 g, 4.4 mmol, 1 equiv) was weighed into an oven dried flask and dissolved in 10 mL dry THF. The mixture added by syringe into the stirring solution. (E)-3-bromoprop-1-ene-1-yl)benzene (0.88 g, 4.4 mmol, 1 equiv) was weighed as a frozen, low-melting solid into a beaker, and added into the flask as a solid under positive pressure of Ar. The beaker was rinsed with 10 mL dry THF. The reaction flask was degassed by 3 x vacuum -Ar purge. The reaction was heated gently with a heat gun on low setting to facilitate the start of the reaction. The mixture began to reflux and was allowed to react without further heating. The reaction stirred overnight open to the Ar manifold. The next day the reaction was transferred by filter cannula to a round bottom flask and 10 mL water was added. The mixture was poured into a sep funnel and the layers were separated. The aqueous layer was extracted with 2 x 10 mL DCM and the organic layers were combined and dried over sodium sulfate. The drying agent was removed by gravity filtration and the filtrate was concentrated. The extract was applied to a 20 g silica column eluting in pentane to yield 1.28g of a clear oil, for a 81% isolated yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.78 (9H, m, 3-butyl CH_3); 0.87 (18 H, m, 9 butyl CH_2); 1.83 (2H, d J = 7.5 Hz, alkyl CH_2); 6.21 – 6.30 (2H, m, 2 vinyl H overlapped) 7.13 – 7.24 (5H, m, aromatic). ^{13}C NMR ($CDCl_3$, 125 MHz,) δ 12.5, 13.6, 19.6, 26.5, 27.4, 125.9, 127.3, 127.7, 128.9, 136.6. MS(EI) *m/z* = 305 (M+ minus butyl radical, 361 – 56), 245 (32), 189 (100), 133 (72), 91 (17), 55 (10).

Allyltributylgermane



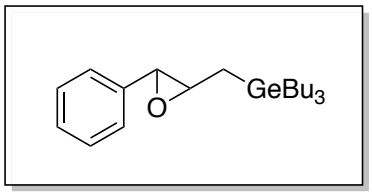
Mg turnings (0.18 g, 7 mmol, 2.5 equiv) were washed in dilute HCl and rinsed with water then acetone in a fritted funnel. The turnings were transferred into a 100 mL side arm Schlenk tube equipped with a stir bar and dried under vacuum with heating. The dried turnings were stirred vigorously under Ar overnight, resulting in fine gray powdered Mg with some larger pieces remaining.

Dry THF (10 mL) was added by syringe onto the dried, pulverized Mg turnings, and the mixture was stirred. Chlorotributylgermane (0.837g, 3 mmol, 1 equiv) was weighed into an oven dried flask and dissolved in 10 mL dry THF. The mixture added by syringe into the stirring solution. Allyl bromide (0.387 g, 3.6 mmol, 1.2 equiv) was weighed into an oven dried flask and dissolved in 10 mL dry THF. The mixture added by syringe into the stirring solution. The reaction flask was degassed by 3 x vacuum - Ar purge. The reaction was heated gently with a heat gun on low setting to facilitate the start of the reaction. The mixture began to reflux and was allowed to react without further heating. The reaction stirred overnight open to the Ar manifold. The next day the reaction was transferred by filter cannula to a round bottom flask and 10 mL water was added. The mixture was poured into a sep funnel and the layers were separated. The aqueous layer was extracted with 2 x 10 mL DCM and the organic layers were combined and dried over sodium sulfate. The drying agent was removed by gravity filtration and the filtrate was concentrated 0.692g clear oil. The NMR of the extract indicated pure allyltributylgermane for 81% yield.

Preparation of Allylic Germanium epoxides:

A modified procedure for acid sensitive epoxides was followed.[32-33]

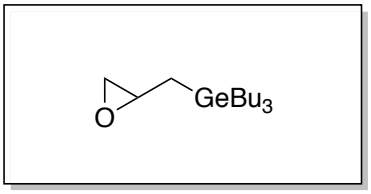
Tributyl((3-phenyloxiran-2-yl)methyl)germane



Allylic germane (0.09 g, 0.25 mmol, 1 equiv) was weighed into a 25 mL oven dried round bottom flask equipped with a stir bar, and dissolved in 3 mL dry DCM. Three mL 0.5 M aqueous $NaHCO_3$ was added by syringe and the biphasic mixture was stirred while bubbling Ar through it. Nerta-chloroperoxybenzoic acid (mCPBA) was weighed on a weigh paper (0.056 g, 0.32 mmol, 2.5 equiv) and added to the flask as a solid after stopping the sparge. The flask was closed and the mixture was allowed to stir 1 hour. TLC indicated the reaction was complete at 1 h. The reaction was poured into a sep funnel and the organic layer was separated. The aqueous layer was extracted with 2 x 3mL DCM. The organic phase was not dried, and was concentrated to 321 mg clear oil. The NMR contained residual benzoic acid and was wet showing a water peak.

^{1}H NMR ($CDCl_3$, 500 MHz); d 0.80 (6H, m, 3 CH_2); 0.87 (9H, m 3 CH_3); 1.33 (m, 12H, 6 CH_2); 1.40 (2H, dd, J_1 = 13.5 Hz, J_2 = 5 Hz, vinyl proton); 3.00 -3.03 (1H, m vinyl proton); 3.55 (1H, d, J = 2 Hz); 7.25 – 7.36 (5H, m, aromatic). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.3, 13.8, 20.1, 26.5, 27.3, 111.5, 136.6. MS(EI) *m/z* = 305 (10) (M+ minus butyl radical and O atom, 377 – [56+16]), 245 (37), 189 (100), 133 (75), 91 (20), 55 (10).

Tributyl(oxiran-2-ylmethyl)germane



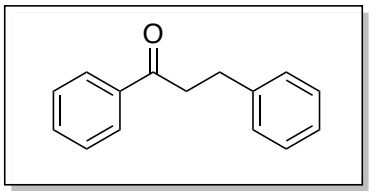
Allyltributylgermane (0.05 g, 0.175 mmol, 1 equiv) was weighed into a 25 mL oven dried round bottom flask equipped with a stir bar, and dissolved in 3 mL dry DCM. Three mL 0.5 M aqueous $NaHCO_3$ was added by syringe and the biphasic mixture was stirred while bubbling Ar through it. mCPBA was weighed on a weigh paper (0.045 g, 0.26 mmol, 1.5 equiv) and added to the flask as a solid after stopping the sparge. The flask was closed and the mixture was allowed to stir 1 hour. TLC indicated the reaction was complete at 1 h. The reaction was poured into a sep funnel and the organic layer was separated. The aqueous layer was extracted with 2 x 3mL DCM. The organic phase was not dried. Crude NMR was taken and the material contained residual benzoic acid and a water peak.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.74 – 0.77 (m, 6H, overlapped CH_2 butyl peaks), 1.86 (m, 9H, butyl end methyls), 1.13-1.16 (m, 12H, overlapped CH_2 butyl peaks), 3.69 (m, 1H), 3.80-3.83 (m, 1H), 5.33-5.35 (m, 1H). ^{13}C NMR ($CDCl_3$ 125 MHz) δ 13.7, 16.3, 25.9, 26.0, 26.1, 30, 66. Extra peaks are present in the aromatic region from residual benzoic acid from mCPBA. MS(EI) m/z = 245 (10) (M+ minus butyl radical, 301 - 56), 189 (100), 133 (75), 98 (20), 55 (10).

Addition of an Epoxide Probe to a Coupling Reaction in Progress:

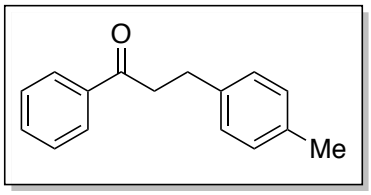
The Heck coupling reaction between vinyl germanes and aryl halides was carried out on a 0.12 mmol scale between (E)-2-methyl-(4-tributylgermyl)but-3-en-2-ol and iodoarene as previously described. The reaction was allowed to progress 4 hours. A GC sample was removed at 4 hours to ensure coupling product was being formed. The crude allylic germyl epoxide was synthesized and isolated as described above. The crude epoxide was dissolved in 1mL MeCN and added to the coupling reaction in progress by syringe. The reaction was allowed to progress for 16 more hours, (total time = 24 h). The reaction was worked up in the usual way, and the crude NMR

and mass were taken to look for a coupling side product or a free allylic alcohol in case of degermylation with out coupling. The crude reaction extract was passed through a silica plug in dichloromethane to isolate coupling products and side coupling products.



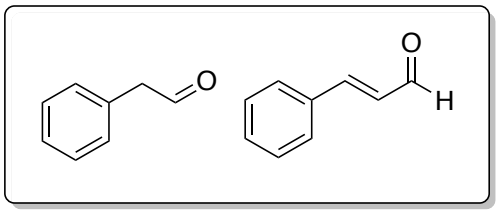
1,3-diphenylpropan-1-one

A coupling reaction of (E)-2-methyl-(4-tributylgermyl)but-3-en-2-ol and iodobenzene was started as described above. The epoxide tributyl((3-phenyloxiran-2-yl)methyl)germane was synthesized and the crude epoxide was dissolved in MeCN and added into the coupling reaction. The coupling product and 1,3-diphenyl propanone was found in the reaction mixture among residual epoxide, starting material and iodobenzene. The alcohol that would result from degermylation, 1-phenylprop-2-en-1-ol, was not seen in the NMR or mass spec. A TLC of the crude reaction eluting in dichloromethane showed iodobenzene traveling with solvent front, 1,3-diphenyl-propanone at r_f = 0.8, vinyl germane starting material at r_f = 0.5, and the expected coupling product with r_f = 0.3. The coupling side product was isolated by an extraction and subjecting the organic residue to silica gel chromatography eluting in dichloromethane. The spots charred dark blue with PMA stain. The side product is a known literature compound[34] and its identity was confirmed by and ^{1}H NMR and mass spec.



1-Phenyl-3-(*p*-tolyl)propan-1-one

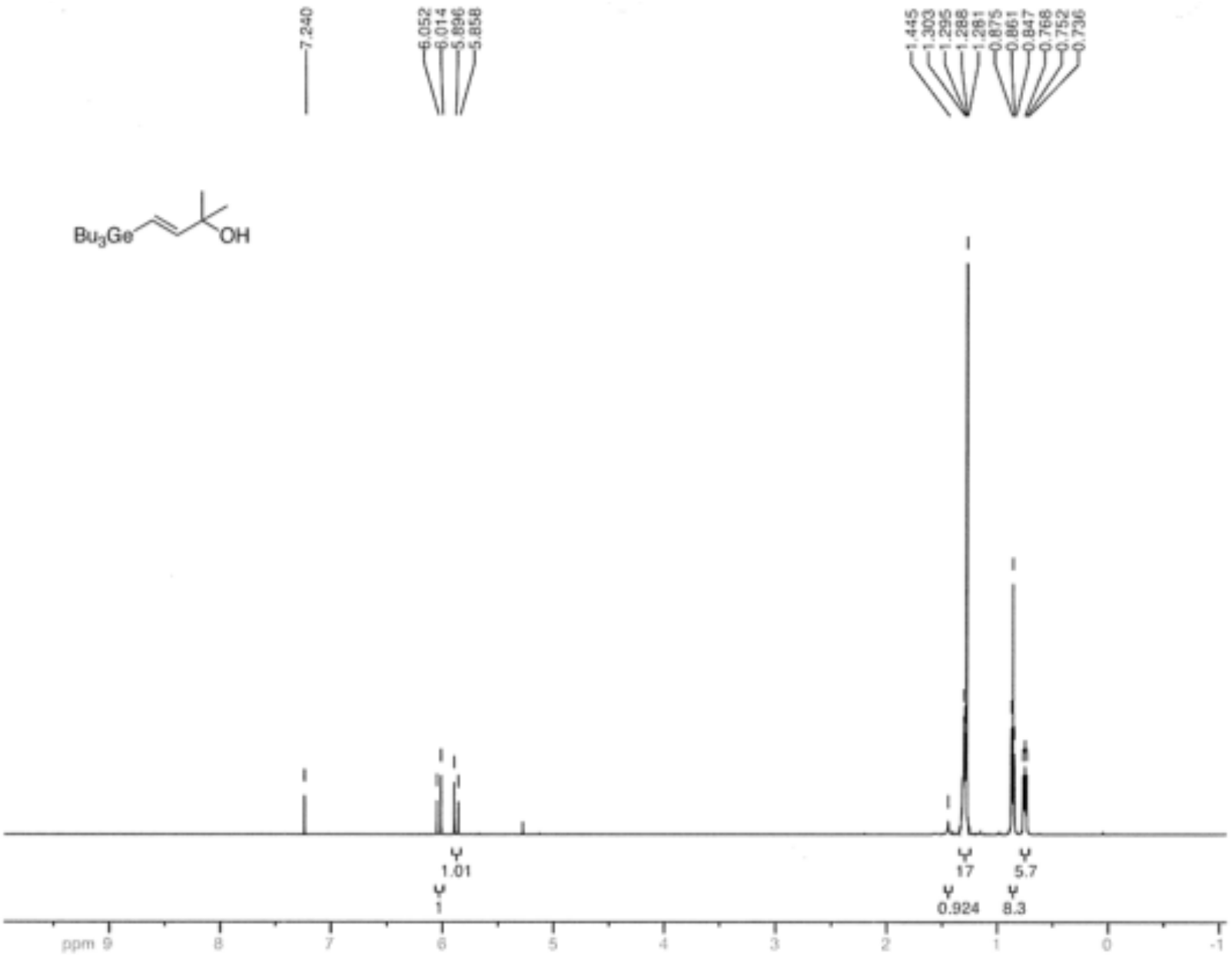
The above reaction was repeated with iodotoluene as the coupling partner in order to verify the coupling reaction between the epoxide and the iodoarene and also to rule out phenyl transfer from PPh_3. Iodotoluene is a slower coupling partner, so the epoxide was added after 8 hours instead of 4. The side product was seen in crude NMRs and mass spec. This product eluted with the residual germyl starting material. The side product is a known compound[35] and its identity was confirmed by NMR and mass spec.



3-Phenyl propanal and cinnamaldehyde

A coupling reaction of (E)-2-methyl-(4-tributylgermyl)but-3-en-2-ol and iodobenzene was started as described above. The unhindered epoxide, tributyl(oxiran-2-ylmethyl)germane was synthesized after 4 hours. The crude epoxide (2 equiv) was dissolved in MeCN and added into the coupling reaction. The reaction progressed a total of 24 h. The crude reaction smelled strongly of cinnamon. Phenylpropanal and trans Cinnamaldehyde were found in the reaction mixture, and their identities were confirmed by comparison to commercial samples in the lab.

NMR SPECTRA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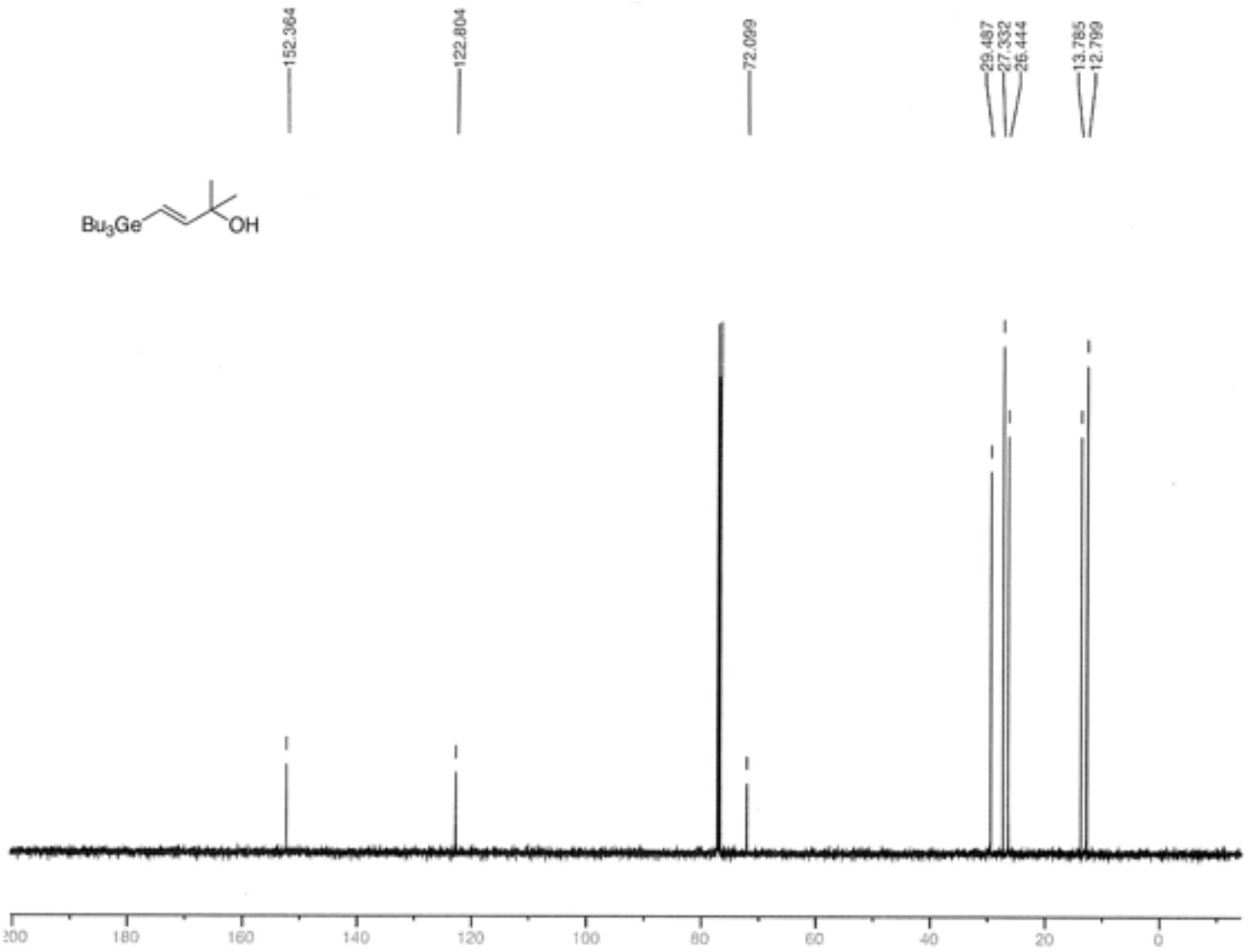
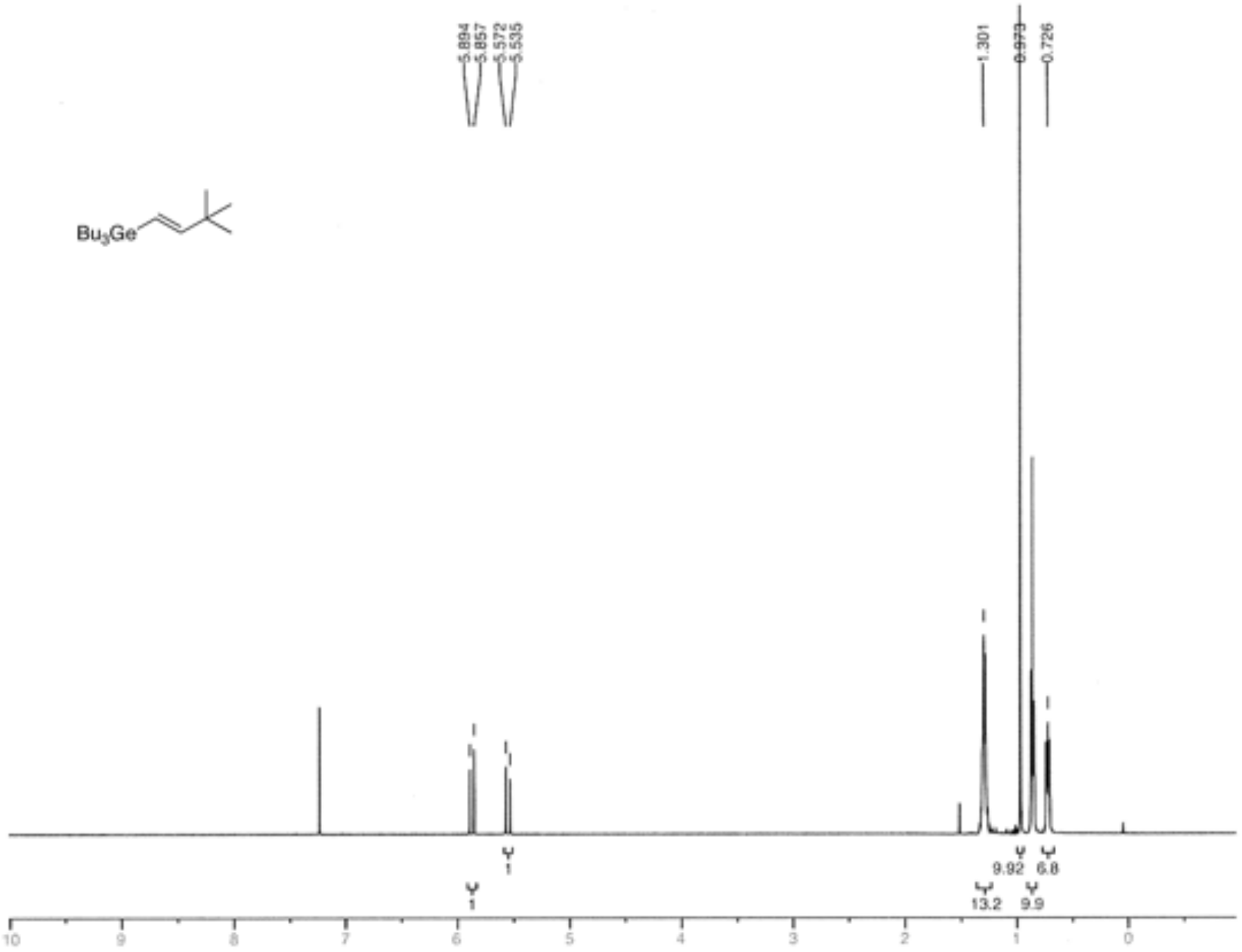
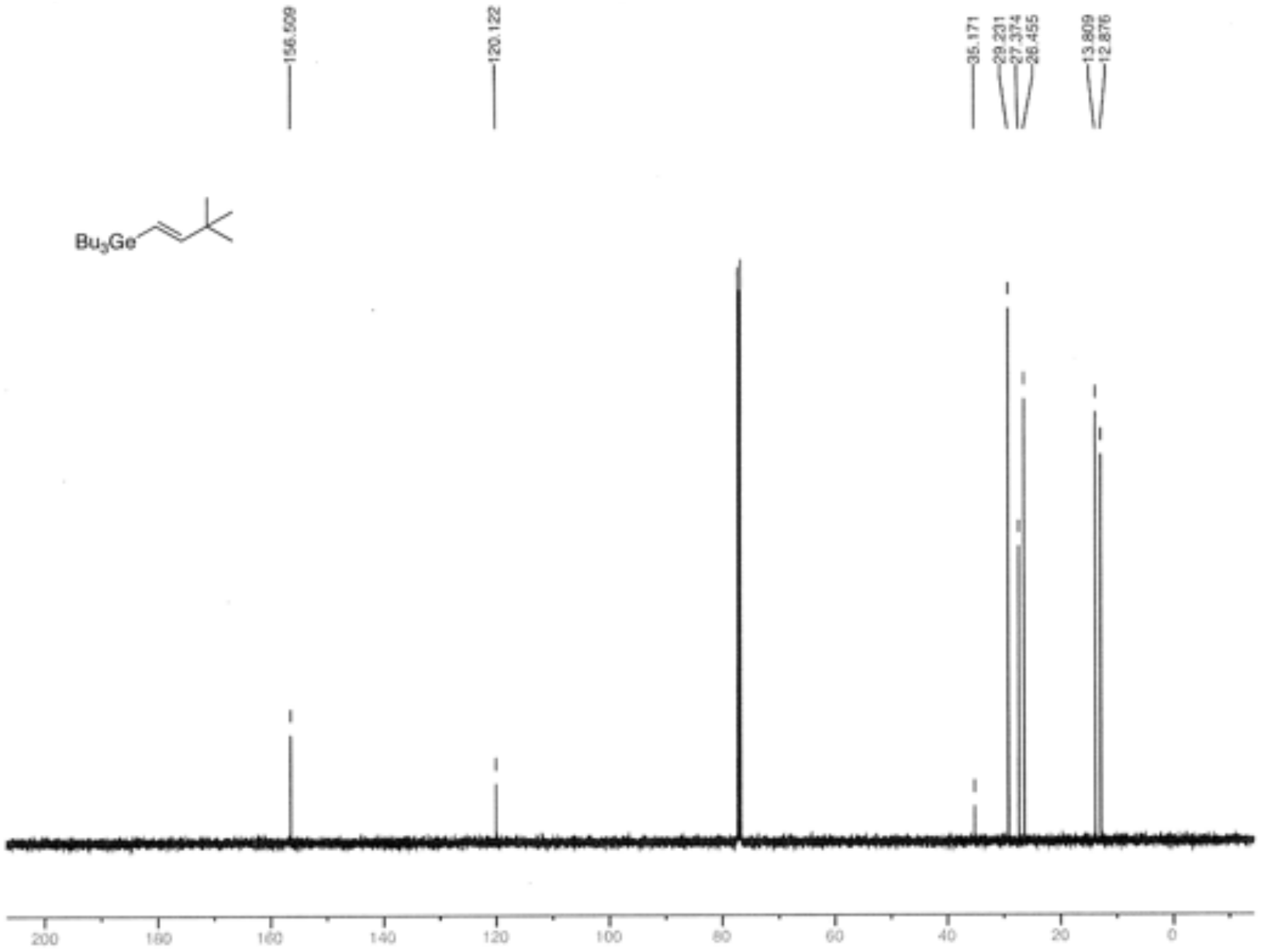
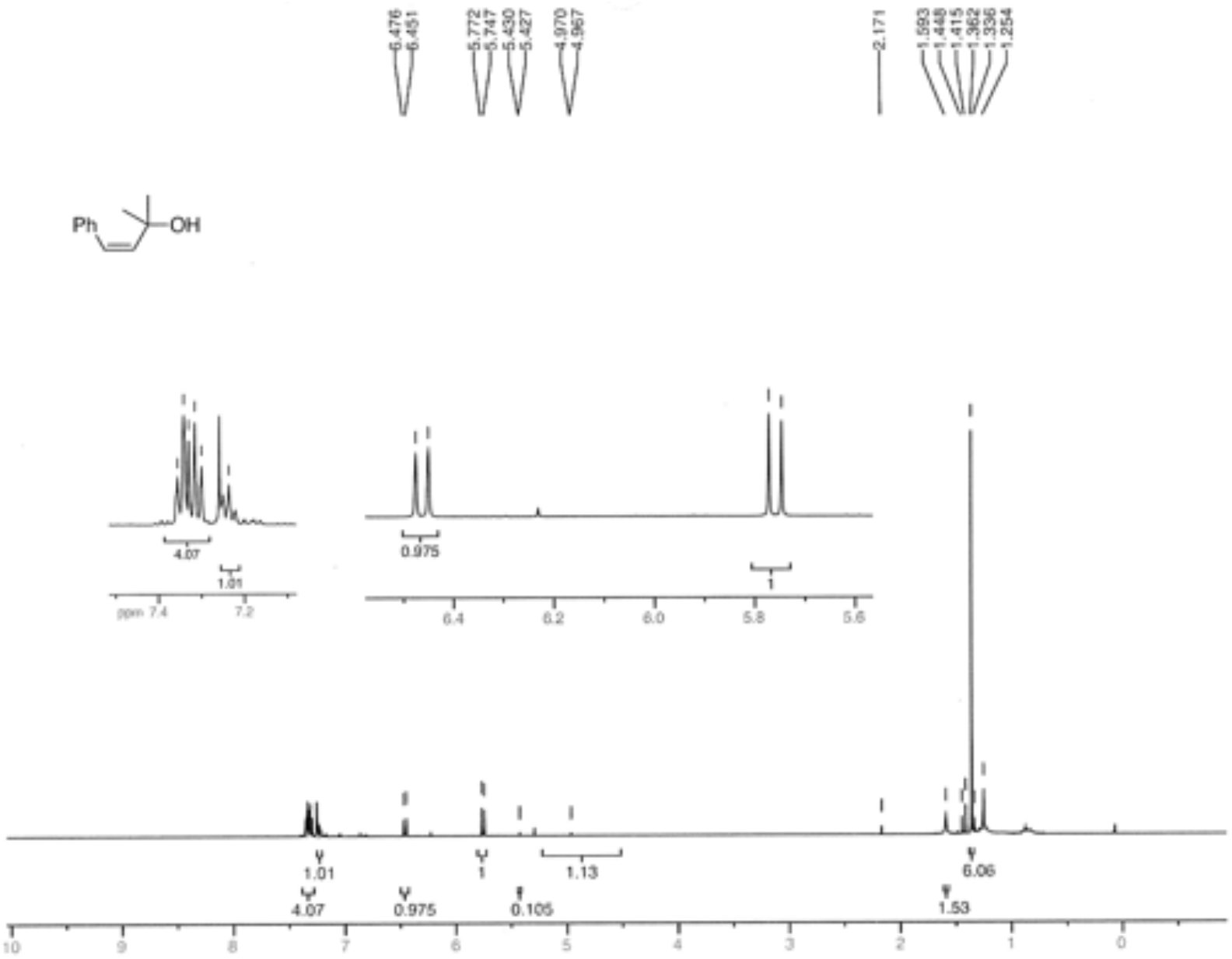
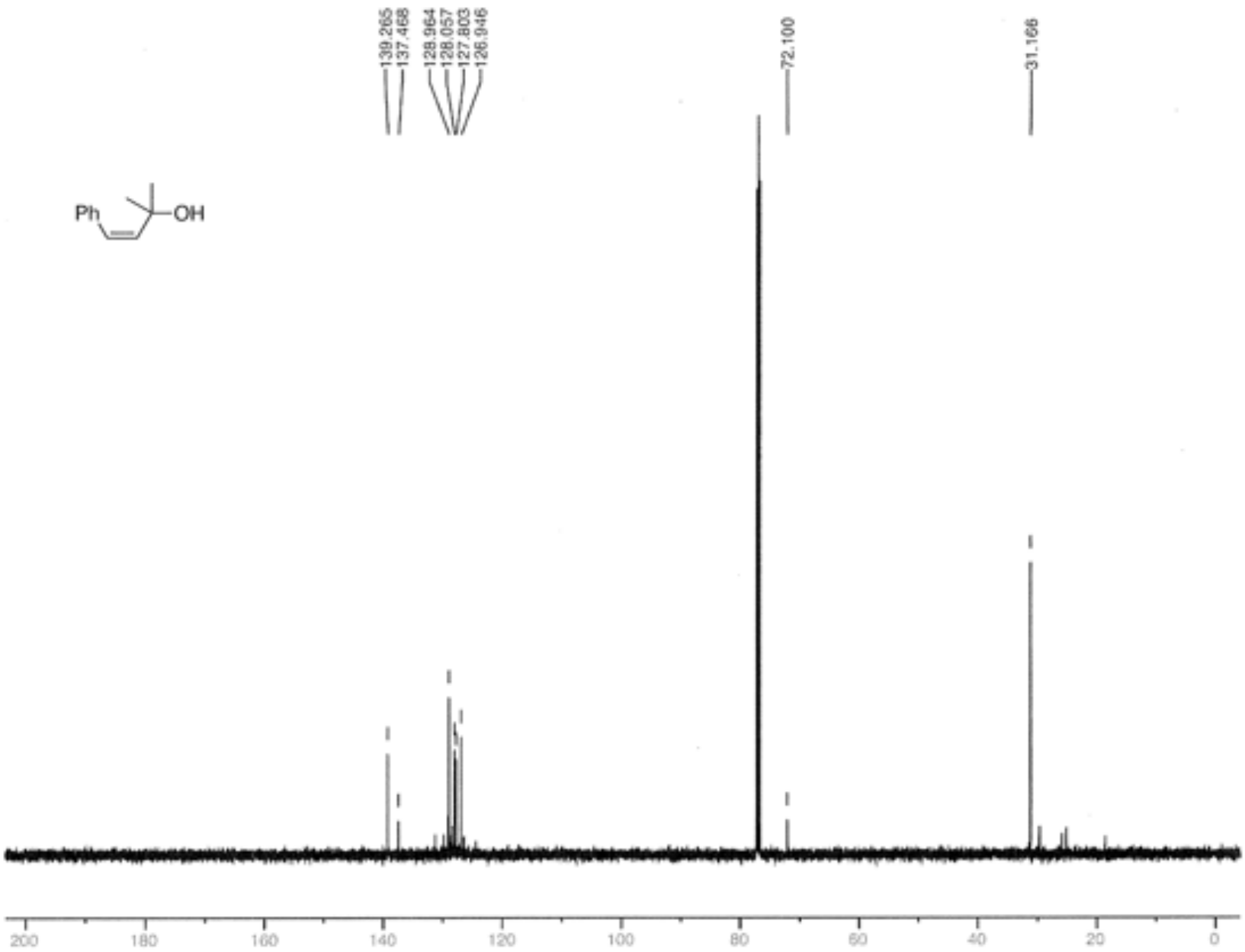
6.014
5.896
5.858
1.445
1.303
1.295
1.288
1.281
0.875
0.861
0.847
0.768
0.752
0.736
Bu3Ge
OH
1.01
1
17
0.924
5.7
8.3
ppm 9
8
7
6
5
4
3
2
1
0
-1

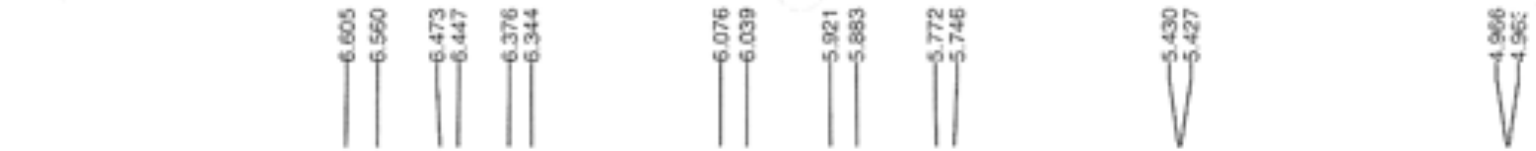

152.364
122.804
72.099
29.487
27.332
26.444
13.785
12.799
Bu3Ge
OH
200
180
160
140
120
100
80
60
40
20
0


5.894
5.857
5.572
5.535
1.301
0.973
0.726
Bu3Ge
1
1
9.92
6.8
13.2
9.9
10
9
8
7
6
5
4
3
2
1
0

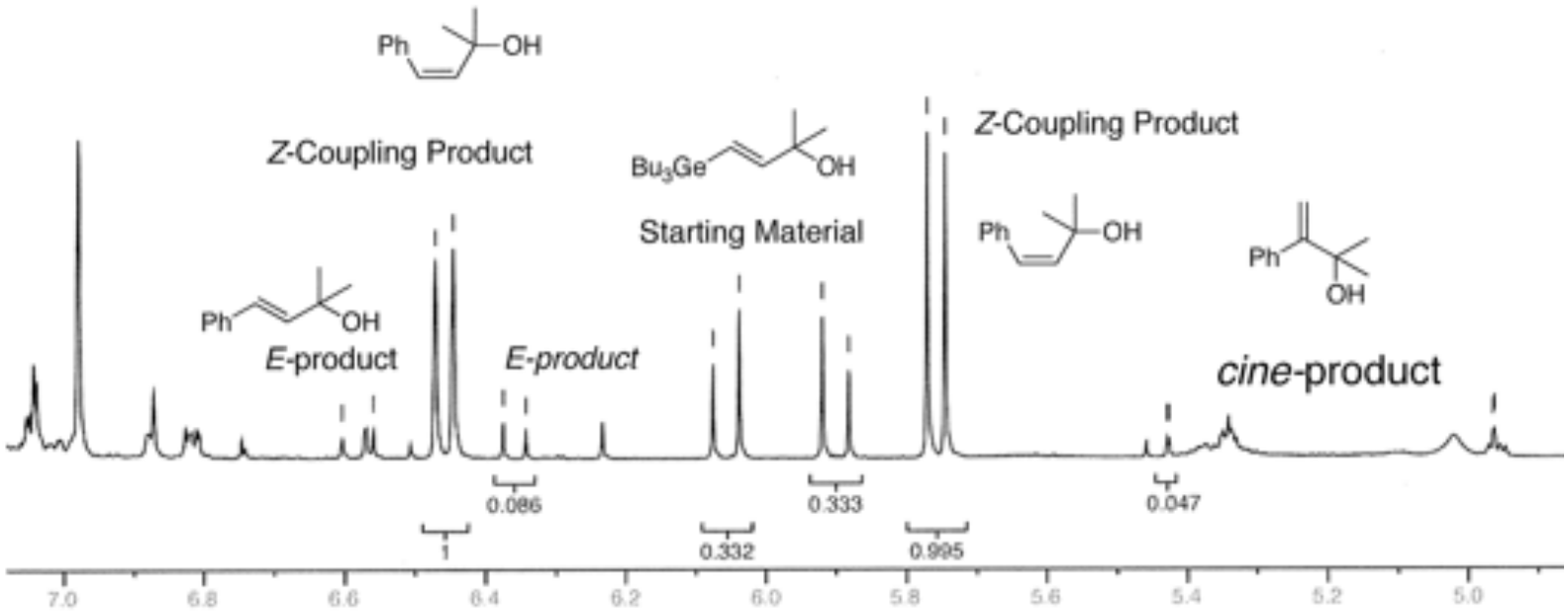

156.509
120.122
35.171
29.231
27.374
26.455
13.809
12.876
Bu3Ge
200
180
160
140
120
100
80
60
40
20
0


6.476
6.451
5.772
5.747
5.430
5.427
4.970
4.967
2.171
1.593
1.448
1.415
1.362
1.336
1.254
Ph
OH
4.07
1.01
0.975
1
1.01
1
1.13
6.06
4.07
0.975
0.105
1.53

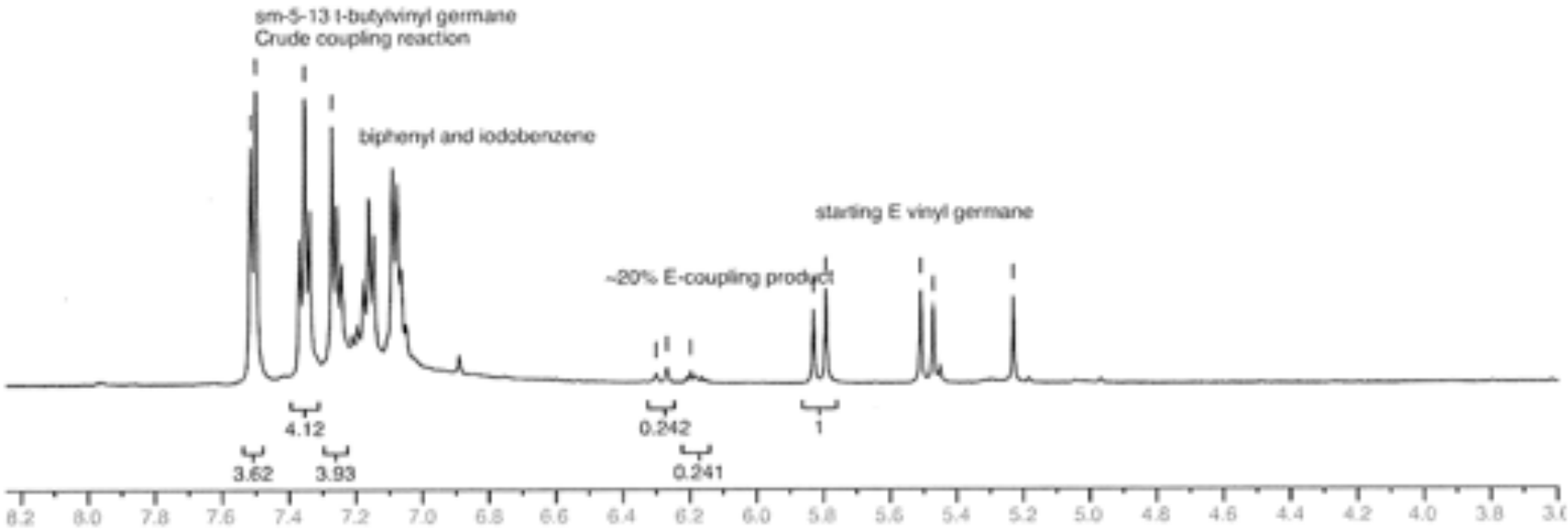

139.265
137.468
128.964
128.057
127.803
126.946
72.100
31.166
Ph
OH
200
180
160
140
120
100
80
60
40
20
0

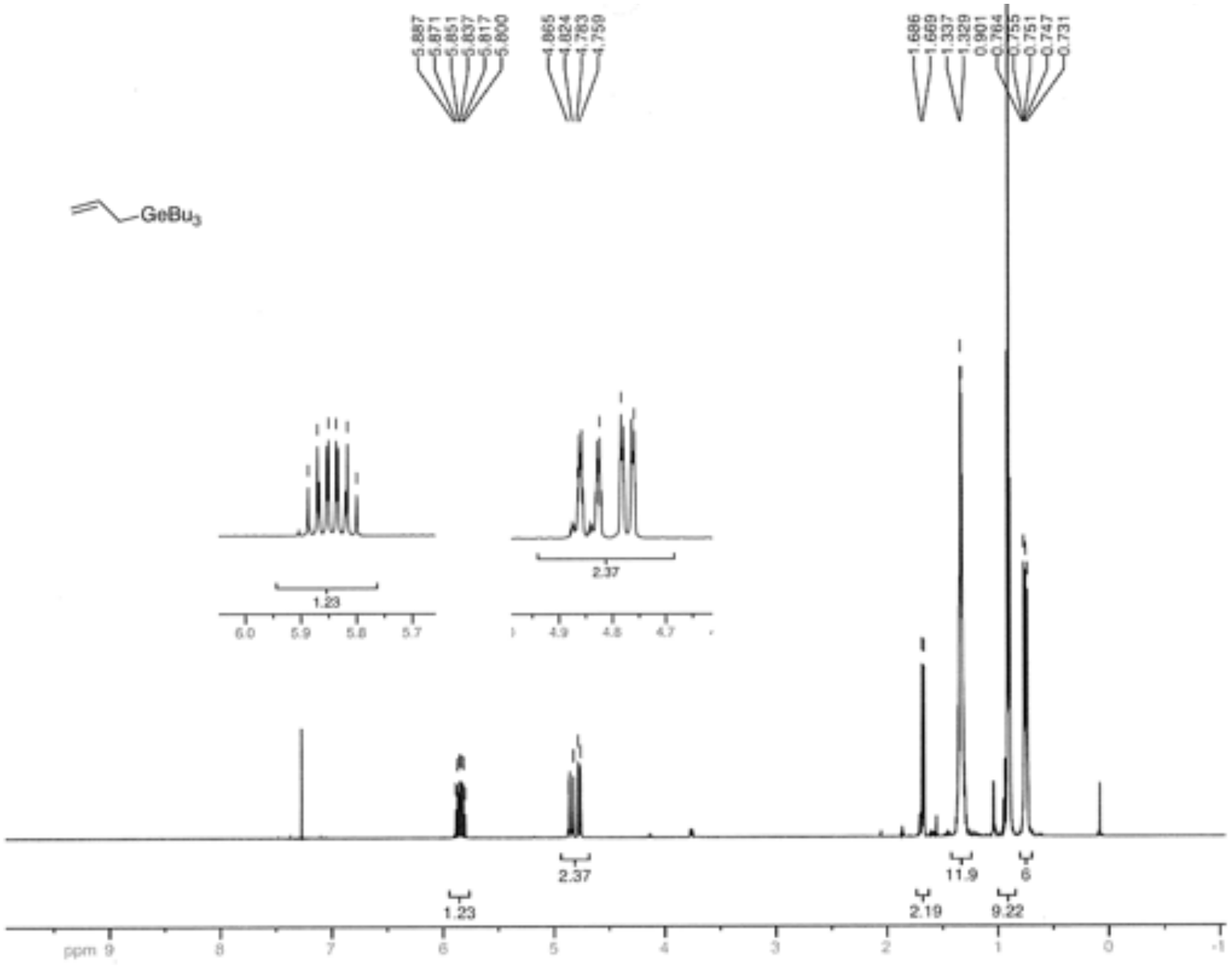


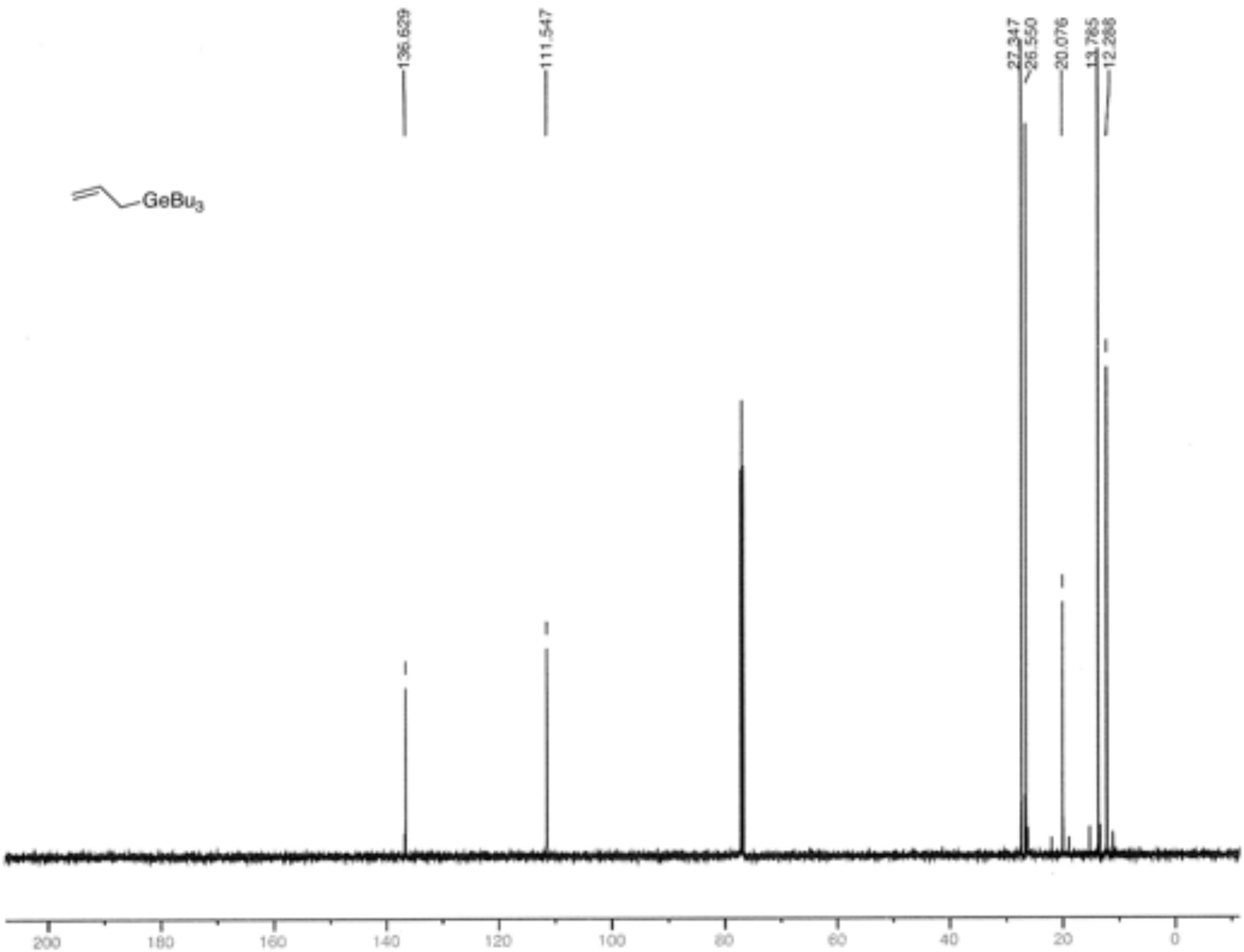
Crude Coupling Reaction

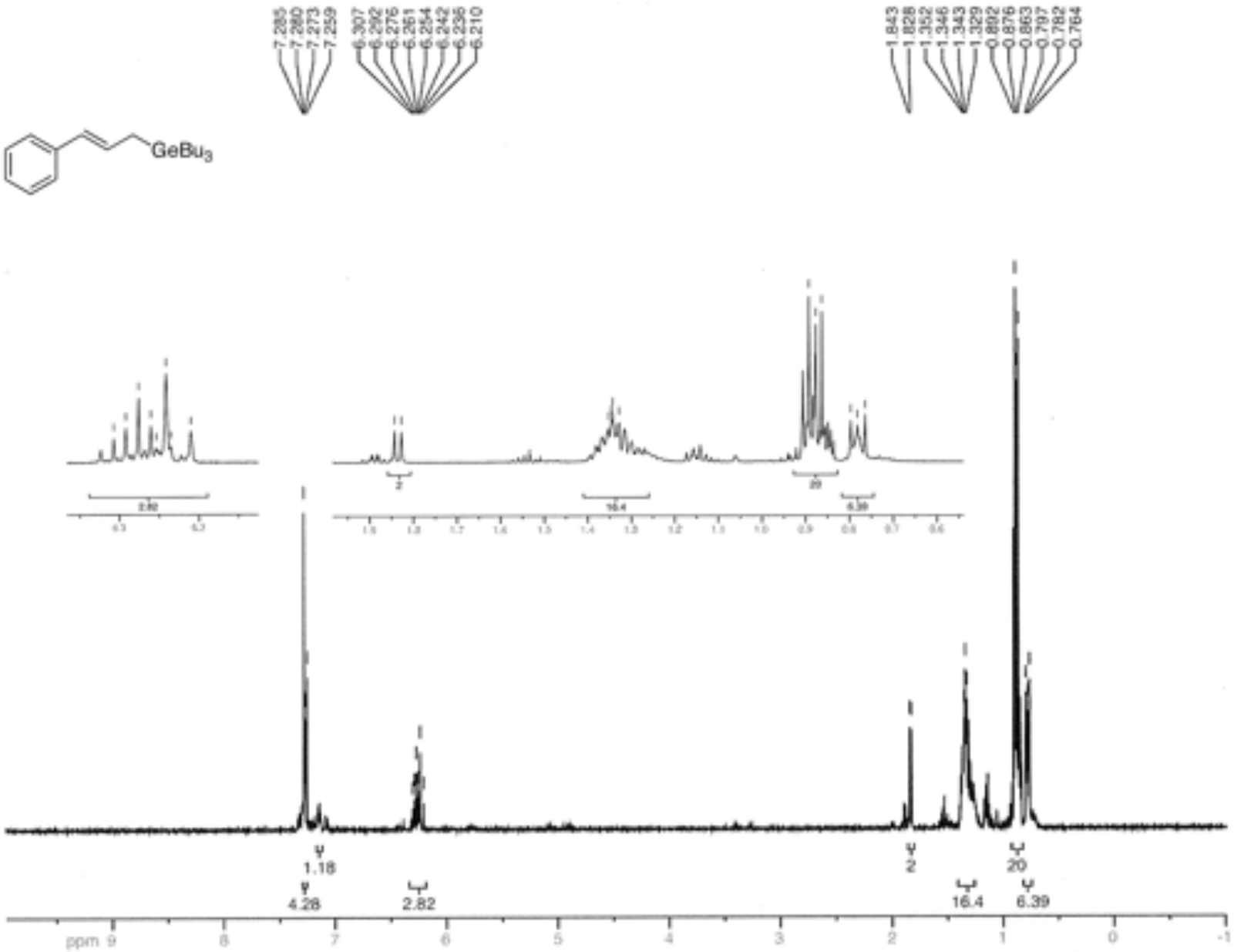


Only traces of *Z* coupling product were found.




5.887
5.871
5.851
5.837
5.817
5.800
4.865
4.824
4.783
4.759
1.686
1.669
1.337
1.329
0.901
0.764
0.755
0.751
0.747
0.731
GeBu3
1.23
2.37
1.23
2.37
11.9
6
2.19
9.22
ppm 9
8
7
6
5
4
3
2
1
0
-1


136.629
111.547
27.347
26.550
20.076
13.785
12.288
GeBu3
200
180
160
140
120
100
80
60
40
20
0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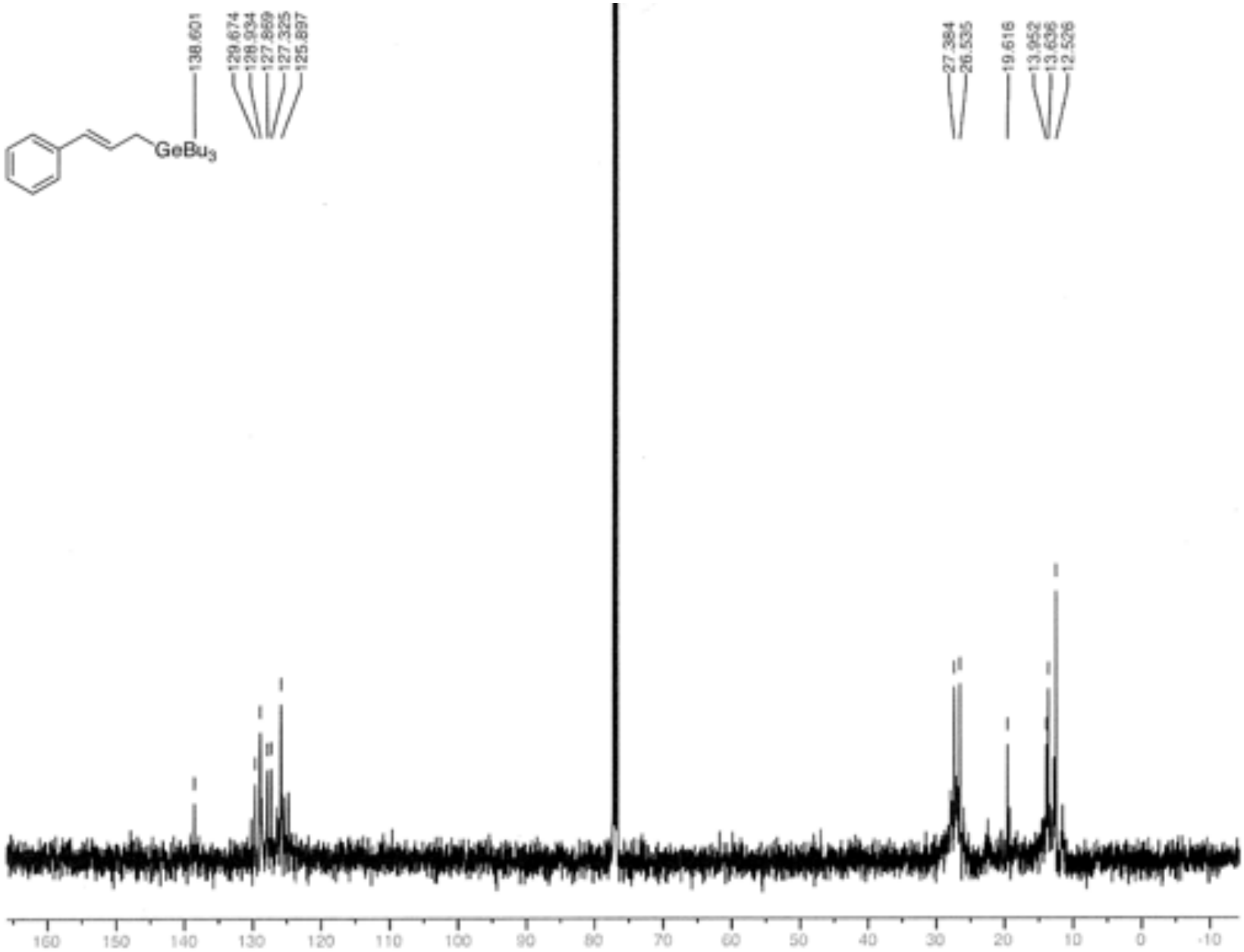
7.273
7.259
6.307
6.292
6.276
6.261
6.254
6.242
6.236
6.210
1.843
1.828
1.352
1.346
1.343
1.329
0.892
0.876
0.863
0.797
0.782
0.764
GeBu3
1.18
4.28
2.82
2
16.4
20
6.39
ppm 9
8
7
6
5
4
3
2
1
0
-1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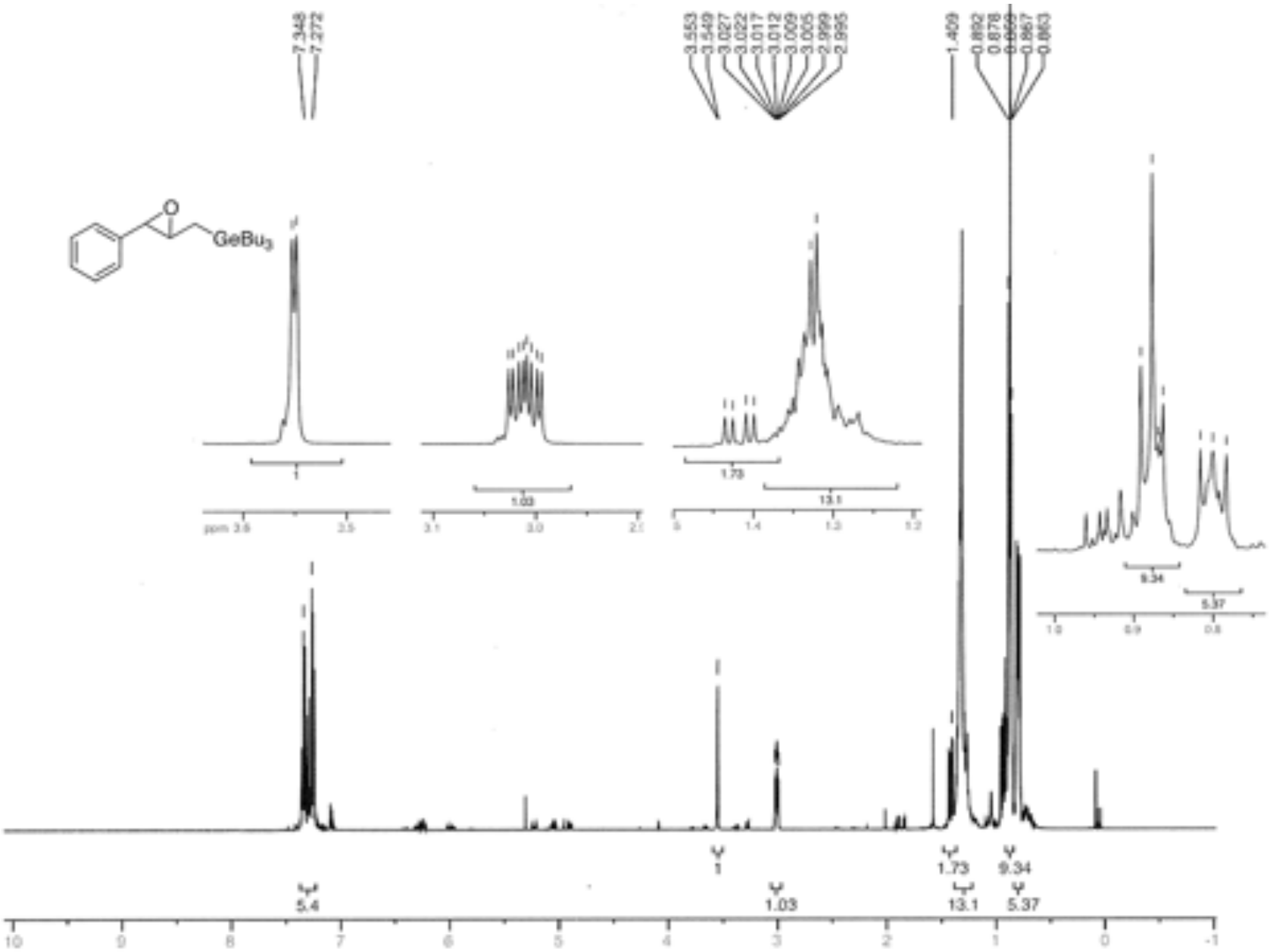
127.869
127.325
125.897
27.384
26.535
19.616
13.952
13.636
12.526
GeBu3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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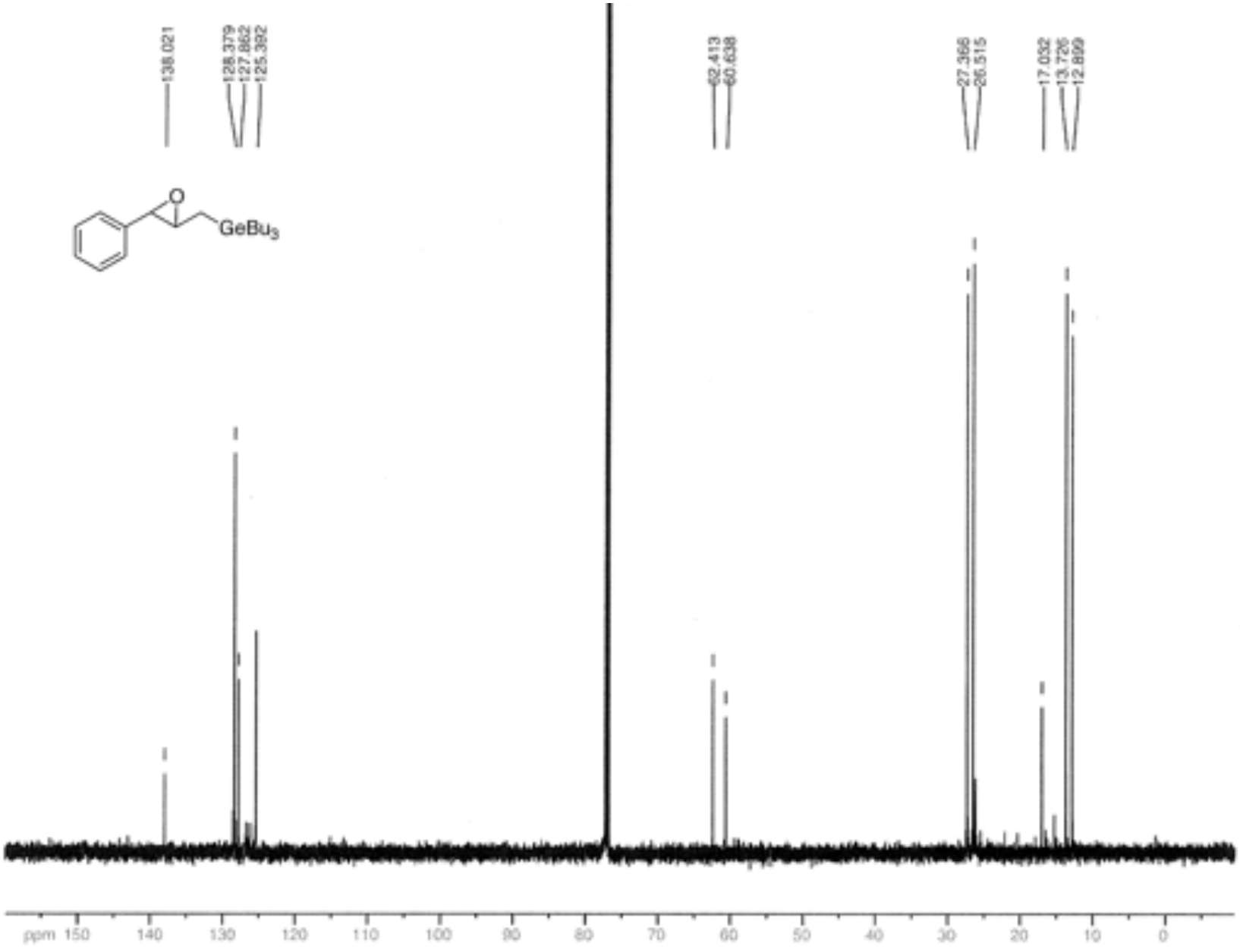
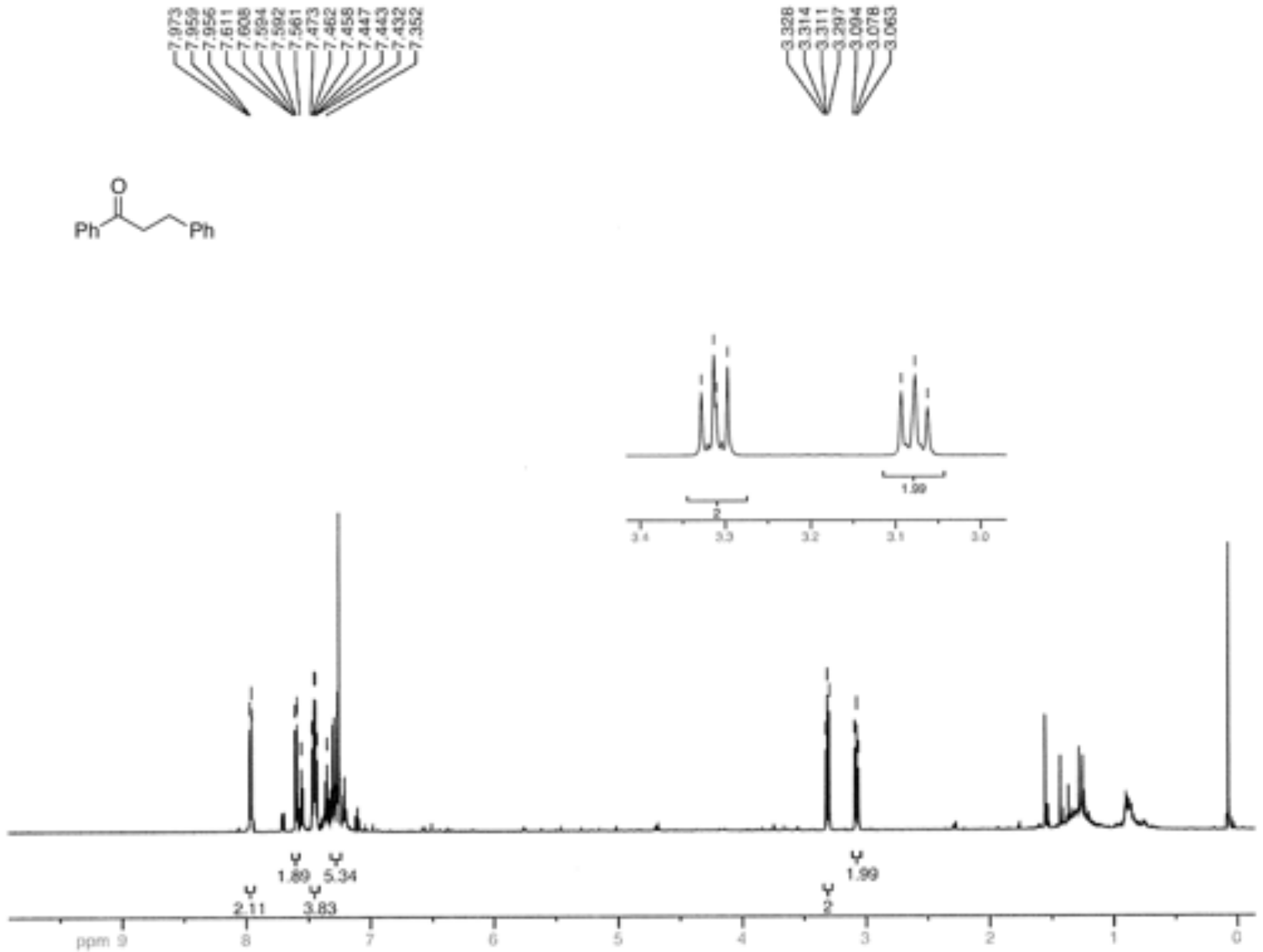
7.272
3.553
3.549
3.027
3.022
3.017
3.012
3.009
3.005
2.999
2.995
1.409
0.892
0.878
0.867
0.863
GeBu3
5.4
1
1.03
1.73
13.1
9.34
5.37


138.021
128.379
127.862
125.392
62.413
60.638
27.366
26.515
17.032
13.726
12.899
O
GeBu3
ppm 150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.956
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7.608
7.594
7.592
7.561
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7.462
7.458
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7.443
7.432
7.352
3.328
3.314
3.311
3.297
3.094
3.078
3.063
O
Ph
Ph
1.99
2
1.89
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7
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5
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3
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1
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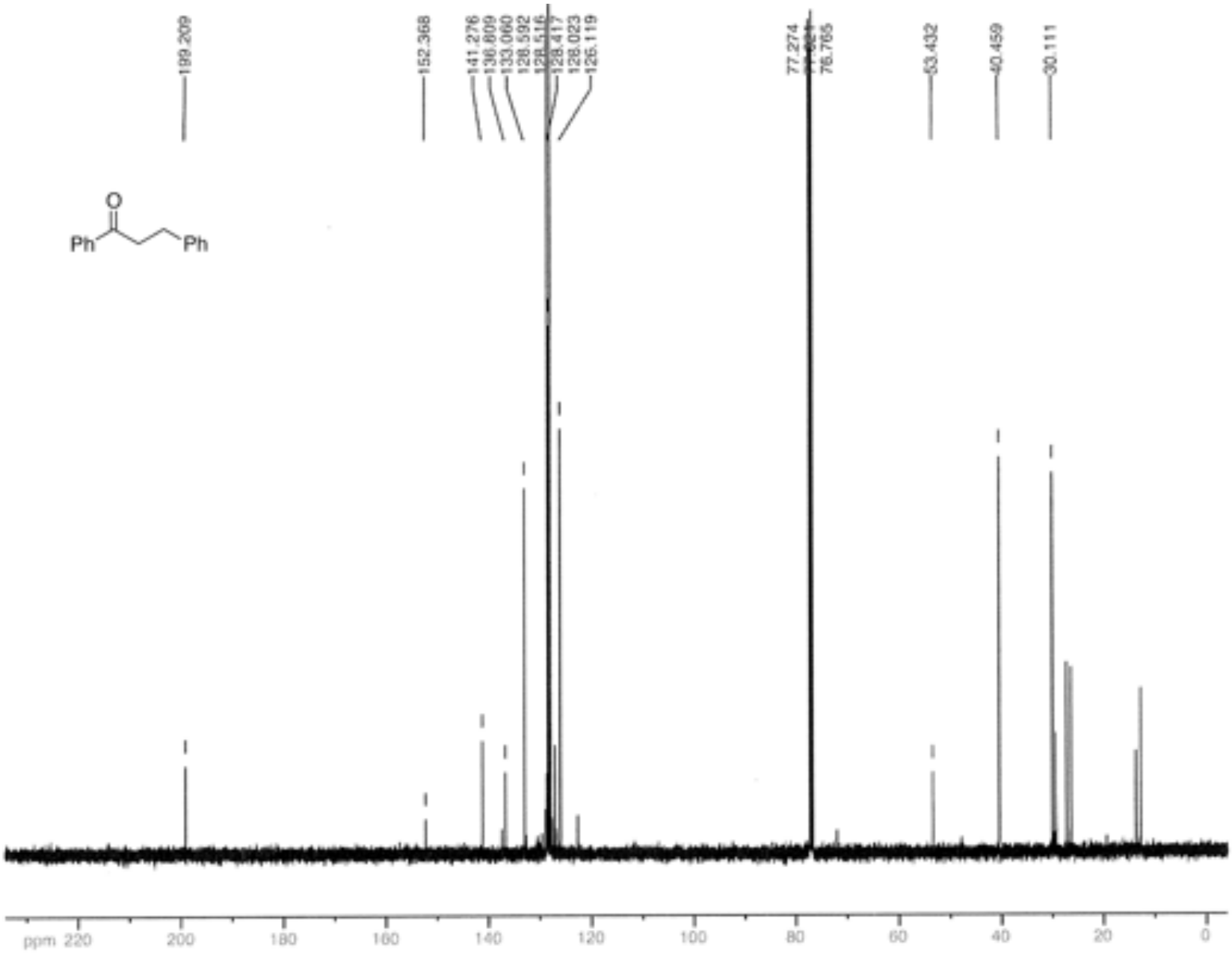
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O
Ph
Ph
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200
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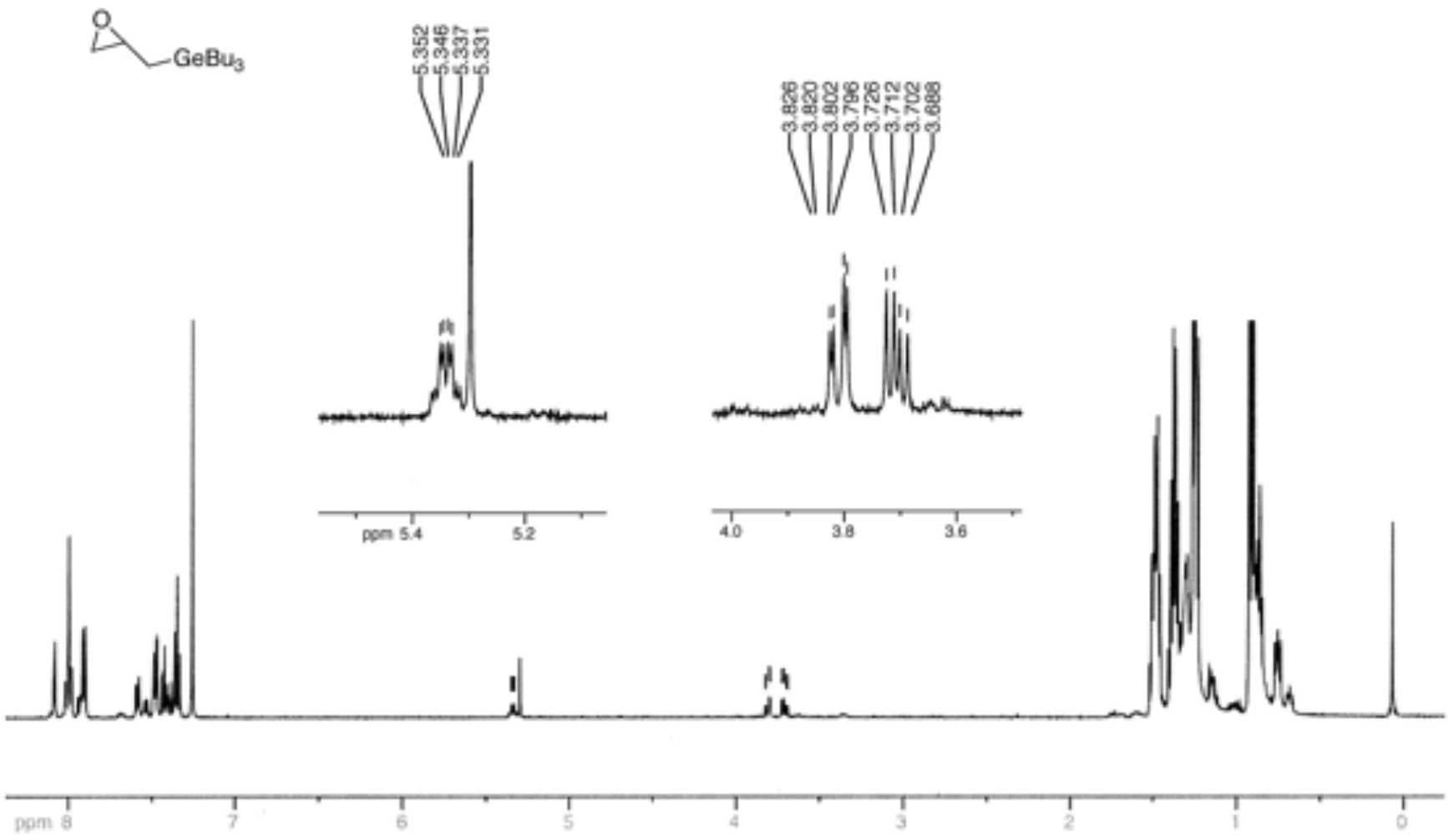
80
60
40
20
0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3.826
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3.802
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3.726
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3.702
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5.2
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3.8
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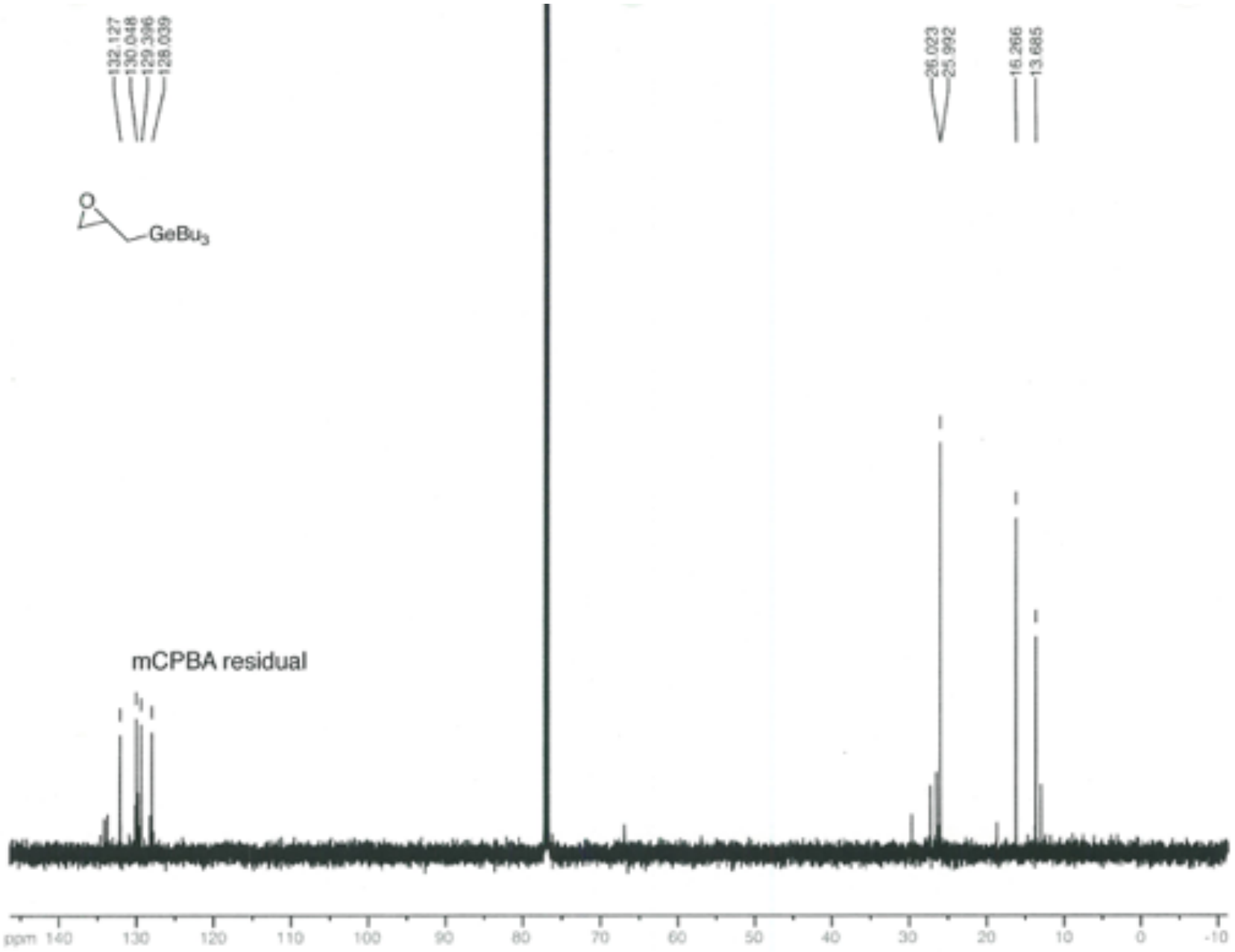
7
6
5
4
3
2
1
0


132.127
130.048
129.396
128.039
26.023
25.992
16.266
13.685
O
GeBu3
mCPBA residual
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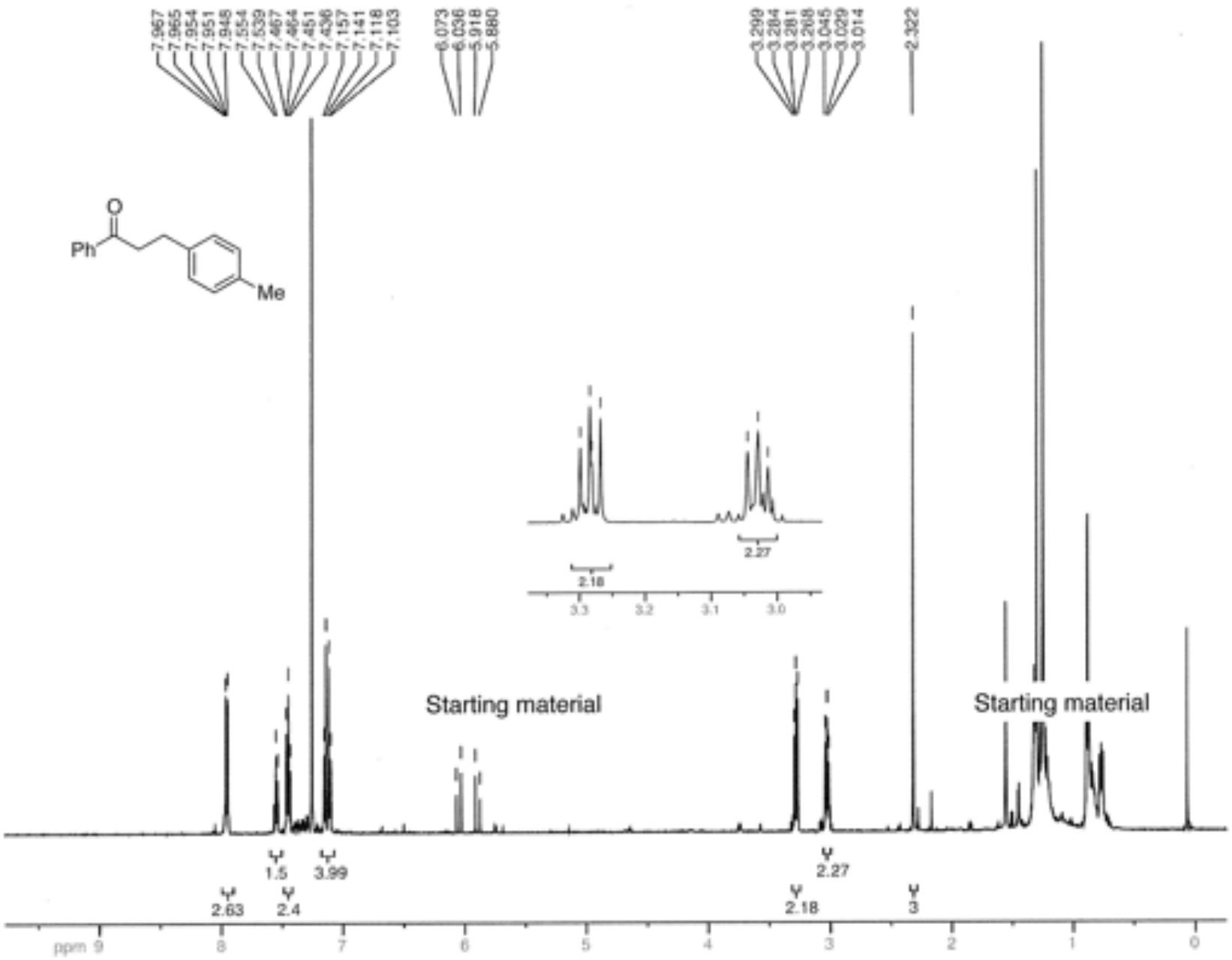
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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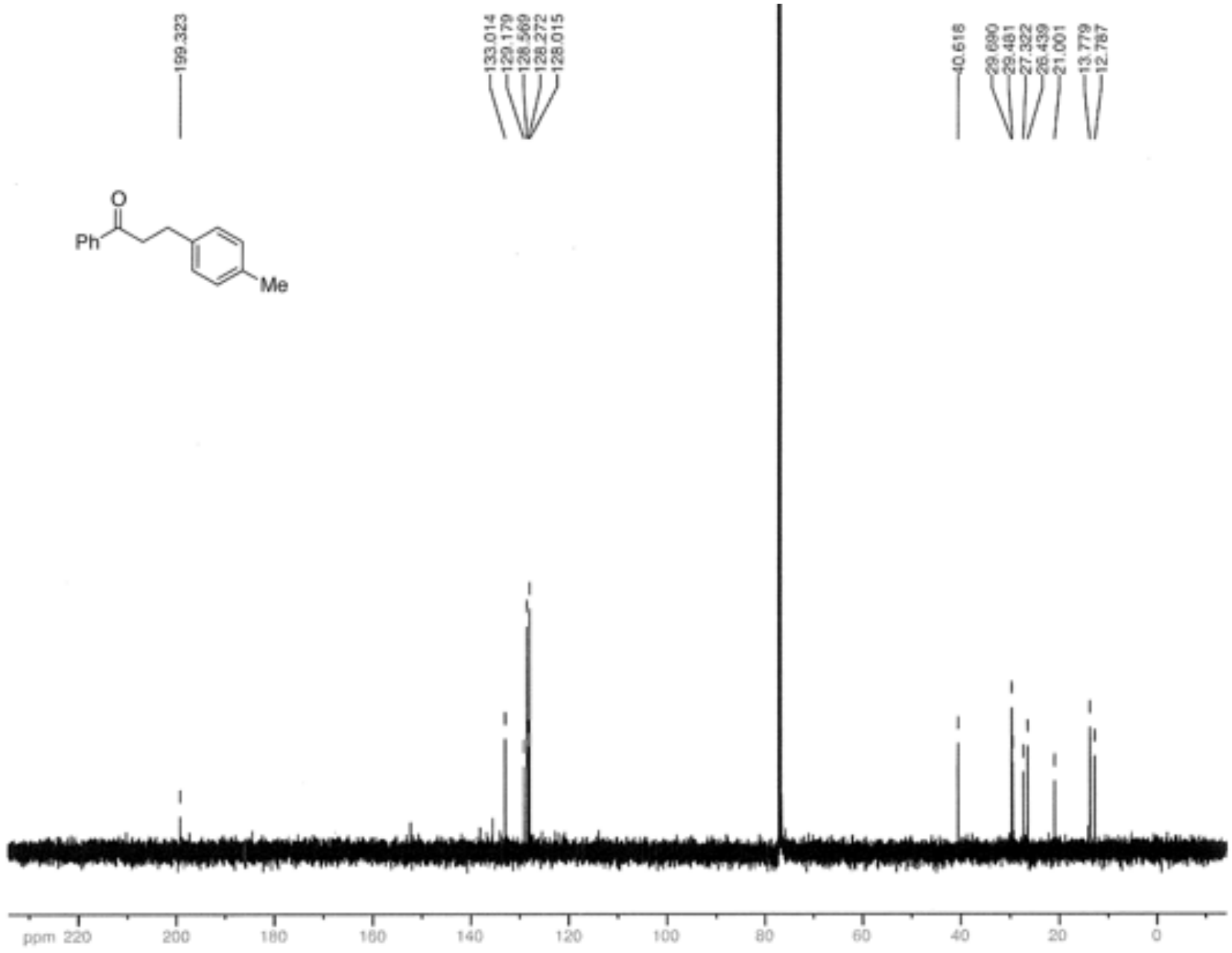
7.951
7.948
7.554
7.539
7.467
7.464
7.451
7.436
7.157
7.141
7.118
7.103
6.073
6.036
5.918
5.880
3.299
3.284
3.281
3.268
3.045
3.029
3.014
2.322
O
Ph
Me
2.27
2.18
3.3
3.2
3.1
3.0
Starting material
Starting material
1.5
3.99
2.27
2.63
2.4
2.18
3
ppm 9
8
7
6
5
4
3
2
1
0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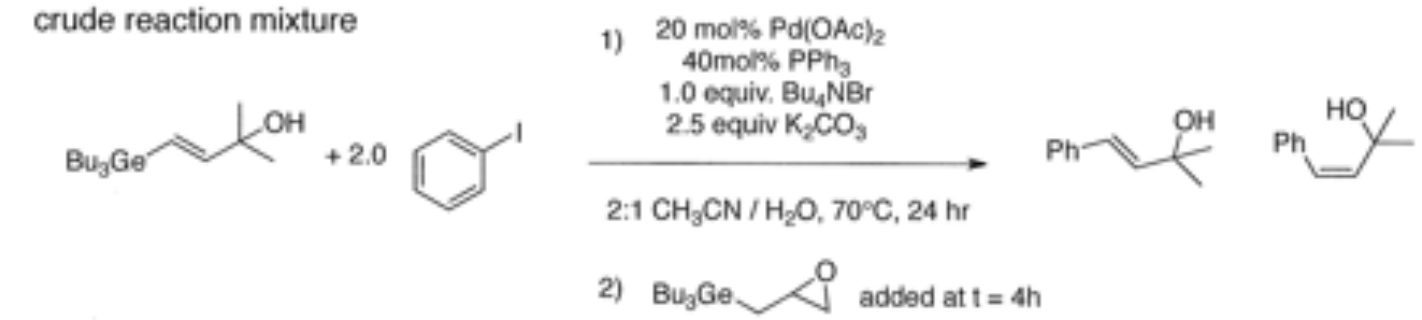
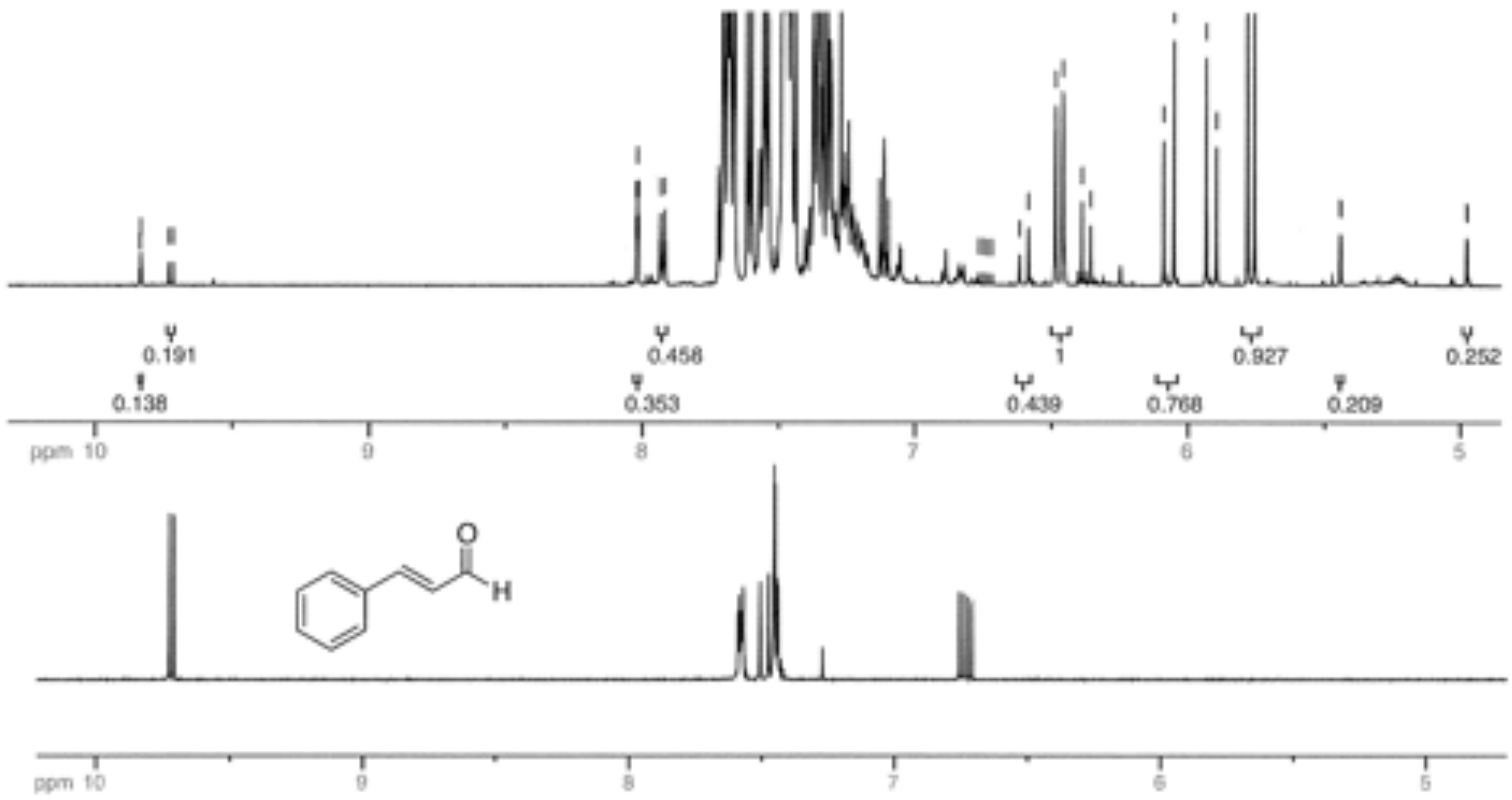
26.439
21.001
13.779
12.787
O
Ph
Me
ppm 220
200
180
160
140
120
100
80
60
40
20
0

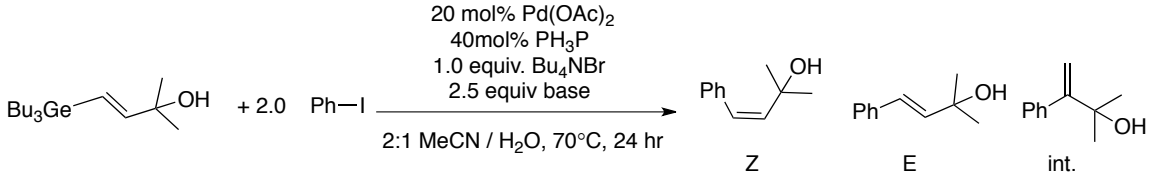
crude reaction mixture





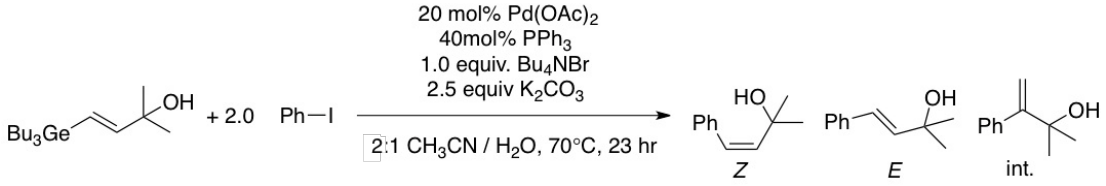
cinnamaldehyde purchased commercially

Optimization: Base



Entry	Base	NMR conversion	Z:E:internal
1	K_2CO_3	80 %	15:1:0.4
2	$KHCO_3$	36 %	12:1:1.5
3	*t*-BuOK	0 %	-
4	KOH	68 %	12:1:2
5	H_2PO_4/ HPO_4	0 %	-
6	Cs_2CO_3	25 %	36:1:5

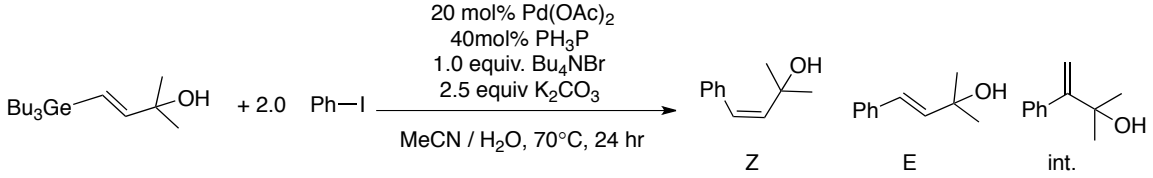
Optimization: Concentration



Entry	Volume of solvent (mL)	Concentration (mM)	NMR conversion	Z:E:internal
1	2.5	48	0 %	-
2	5	24	80 %	15:1:0.4
3	10	12	37 %	1.5:1:0.02

Optimization: MeCN/H_2O Solvent Ratio

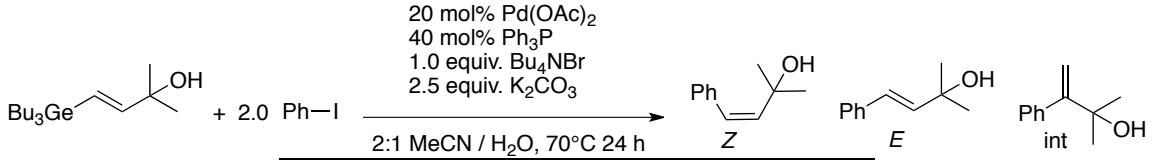
Table **III**. Conversion and selectivity of the cross coupling of *E*-2-methyl-4-(tributylgermyl)but-3-en-2-ol to iodobenzene under varied solvent ratios.



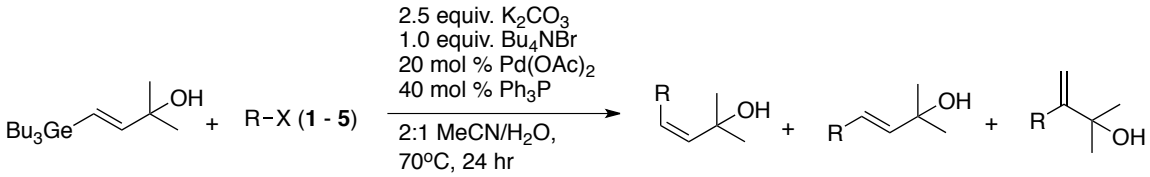
Entry	Solvent ratio MeCN:H_2O	NMR conversion	Z:E:internal
1	9:1	19 %	16:1:2
2	4:1	21 %	5:1:1
3	3:1	47 %	20:1:1
4	2:1	80 %	15:1:0.4
5	1:1	28 %	7:1:0.2

Repeat of Optimized Procedure

Table **IV**. Additional trials of the optimized cross coupling of E-2-methyl-4-(tributylgermyl)but-3-en-2-ol to iodobenzene did not consistently reproduce the conversion and selectivity.



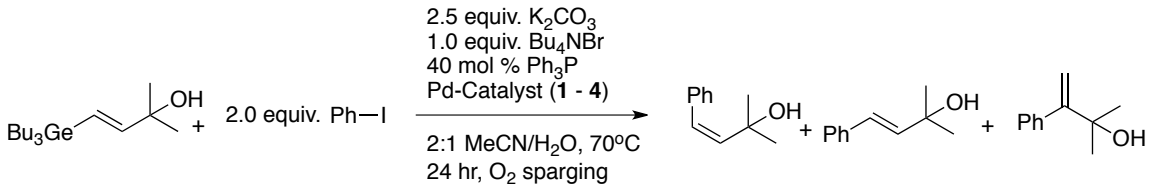
Trial	NMR conversion	*Z*:*E*:internal
1	80 %	15:1:0.4
2	40 %	-
3	60 %	9:1:1



Entry	Coupling Partner	NMR conversion	Yield	Tol:Ph Product
1	2.0 PhH	0 %	0 %	-
2	2.0 $C_{10}H_6ClSO_3Im$	0 %	0 %	-
3	2.0 Tol–I	>68 %	74 %	12:1
4	none	0 %	0 %	-
5	2.0 Ph_3P	3 %	0 %	-
6	2.0 Ph–I, 40 mol % Ph_3As, no Ph_3P	0 %	0 %	-

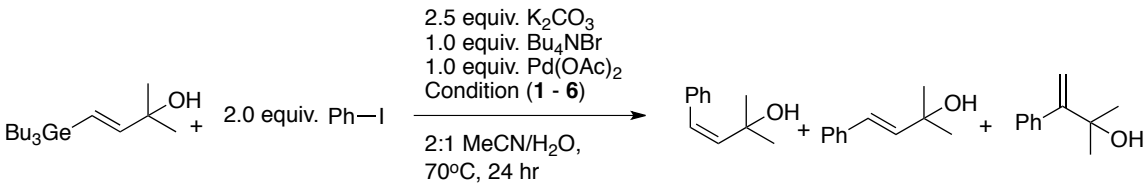
$C_{10}H_6ClSO_3Im$ = 4-chloronaphthalen-1-yl 1H-imidazole-1-sulfonate

Table **VIII**. Conversion and selectivity of the cross coupling of *E*-2-methyl-4-(tributylgermyl)but-3-en-2-ol to iodobenzene under varied Pd-catalyst.



Entry	Pd-Catalyst	NMR conversion	Yield	*Z*:*E*:internal
1	20 mol % $Pd(OAc)_2$	76 %	64 %	10:1:0.3
2	20 mol % $PdCl_2(PPh_3)_2$	3 %	-	-
3	20 mol % $Pd(PPh_3)_4$	69 %	60 %	4:1:0.06
4	20 mol % $Pd(dppf)Cl_2$	65 %	29 %	26:1:0.8

Table **VII**. Conversion and selectivity of the cross coupling of *E*-2-methyl-4-(tributylgermyl)but-3-en-2-ol to iodobenzene under stoichiometric $Pd(OAc)_2$ in varied conditions.



Entry	Condition	NMR conversion	Yield	*Z*:*E*:internal
1	O_2 atmosphere	95 %	-	1.8:1
2	O_2 atmosphere	95 %	-	5.7:1:0.5
3	O_2 atmosphere, 2 equiv. Ph_3P	80 %	-	17:1:2.5
4	O_2 atmosphere, 2 equiv. Ph_3P	48 %	-	23:1:3
5	N_2 sparging, 40 mol % Ph_3PO	>56 %	64 %	3:1:0.2
6	N_2 sparging, 40 mol % Ph_3P	29 %	18 %	33:1:3

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