Ir-Catalyzed ortho-Borylation of Phenols Directed by Substrate-Ligand Electrostatic Interactions: A Combined Experimental/*in Silico* Strategy for Optimizing Weak Interactions

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Supporting Information

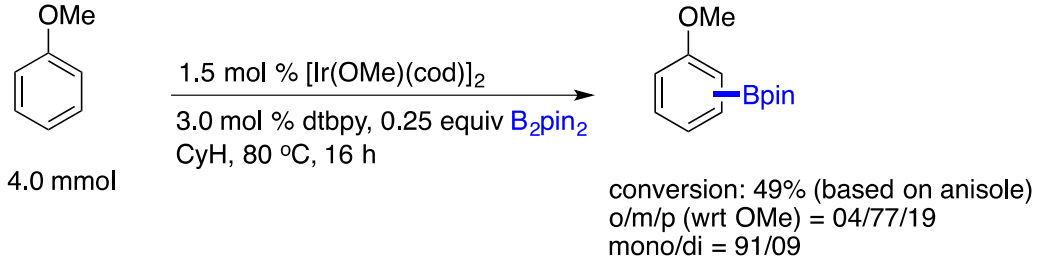
Experimental Section

General Information

All commercially available chemicals were used as received unless otherwise indicated. Bis(pinacolato)diboron (B_2pin_2) and tetrahydroxydiboron ($B_2(OH)_4$) were generously supplied by BoroPharm, Inc., and pinacolborane (HBpin) was purchased from Anderson Chemical Company. Bis(η^4-1,5-cyclooctadiene)-di-μ-methoxy-diiridium(I) $[Ir(OMe)(cod)]_2$ was prepared per literature procedure.[1] Cyclohexane (CyH) and tetrahydrofuran (THF) were refluxed over sodium/benzophenone ketyl, distilled and degassed. Column chromatography was performed on Silia P-Flash silica gel. Thin layer chromatography was performed on 0.25 mm thick aluminum-backed silica gel plates and visualized with ultraviolet light (λ = 254 nm) and iodine. Sublimations were conducted with a water-cooled cold finger.

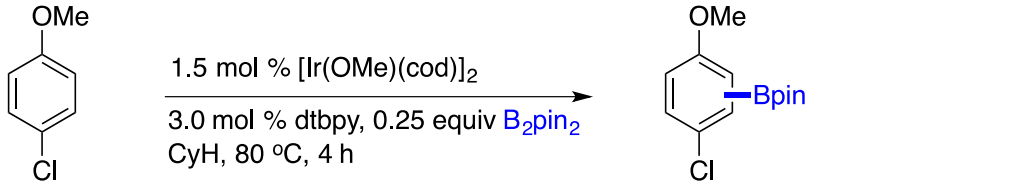
^1H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on 500 MHz NMR spectrometers. The boron bearing carbon atom was not observed due to quadrupolar relaxation. All coupling constants are apparent *J* values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, bs = broad singlet). High-resolution mass spectra (HRMS) were obtained at the Michigan State University Mass Spectrometry Service Center using electrospray ionization (ESI+ or ESI-).[2] Melting points were measured in a capillary melting point apparatus and are uncorrected.

Borylation of Anisole:



The reaction was conducted using a modified version of a previously reported[3] procedure. In a glovebox, a 5 mL conical vial was charged with anisole (435 µL, 4.0 mmol), $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3 mol %, 0.03 mmol), B_2Pin_2 (254 mg, 1.0 mmol, 0.25 equiv), and dry cyclohexane (3 mL). The vial was sealed and placed in a preheated aluminum block at 80°C for 16 h. The volatiles were then removed on the rotary evaporator, and the conversion and isomer ratios were determined by GC/FID. The results are shown in the scheme.

Borylation of 4-Chloroanisole with B_2pin_2 (2a):

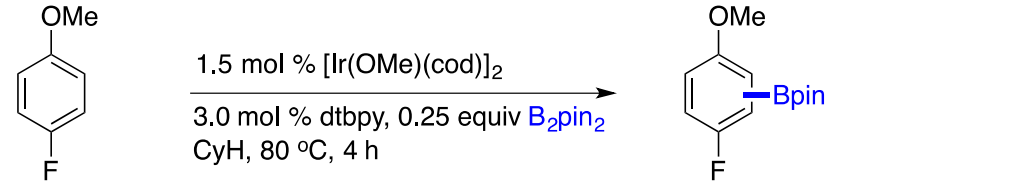


2.0 mmol

conversion: 47% (based on anisole)
o/m (wrt OMe) = 71/29
mono/di = 92/08

In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), and B_2pin_2 (127 mg, 0.25 equiv, 0.5 mmol). Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere and stirred for 5 min at room temperature. To this mixture, 4-chloroanisole (285 mg, 2.0 mmol) was added. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C and was stirred for 4 h. GC analysis showed that conversion of the starting material was 47% based on the consumption of the anisole and the borylation results[4] are as follows: mono/di = 92/08, ortho/meta (wrt OMe) = 71/29.

Borylation of 4-Fluoroanisole with B_2pin_2 (2c):

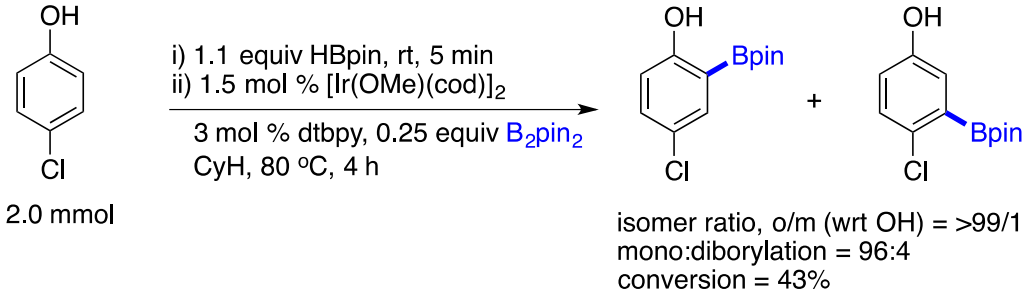


2.0 mmol

conversion: 49% (based on anisole)
o/m (wrt OMe) = 06/94
mono/di = 93/07

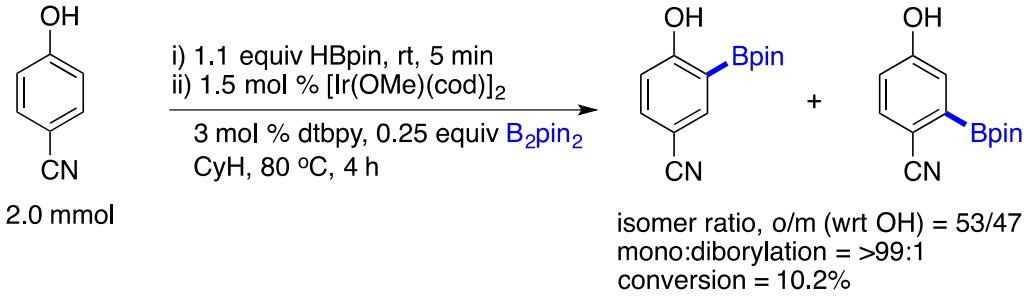
In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), and B_2pin_2 (127 mg, 0.25 equiv). Dry cyclohexane (3 mL) was added under an inert atmosphere and stirred for 5 min at room temperature. To this mixture, 4-fluoroanisole (252 mg, 2.0 mmol) was added. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C and was stirred for 4 h. GC analysis showed that conversion of the starting material was 49% based on the consumption of the anisole and the borylation results are as follows: mono/di = 93/07, ortho/meta (wrt OMe) = 06/94.

Borylation of 4-Chlorophenol with limiting B_2pin_2 (1a)



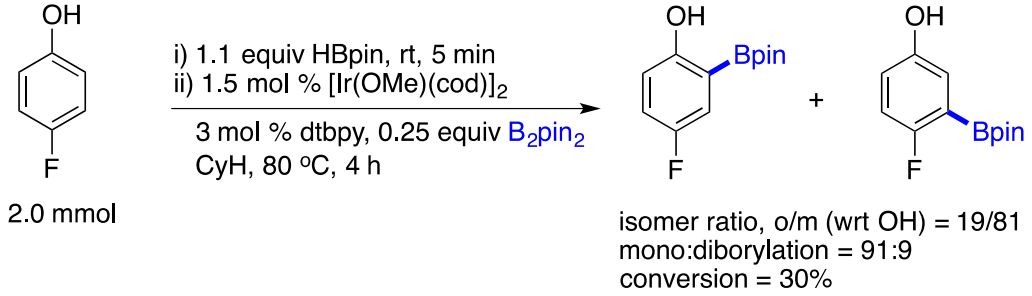
In a glovebox, a 5 mL conical vial was charged with 4-chlorophenol (257 mg, 2.0 mmol) and pinacolborane (319 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), and B_2pin_2 (127 mg, 0.25 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 4 h. The borylation results are shown in the scheme above and the results are based on GC and ^{1}H NMR data.

Borylation of 4-Cyanophenol with limiting B_2pin_2 (1b)



In a glovebox, a 5 mL conical vial was charged with 4-cyanophenol (238 mg, 2.0 mmol) and pinacolborane (319 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), and B_2pin_2 (127 mg, 0.25 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 4 h. The borylation results are shown in the scheme and the results are based on the crude ^{1}H NMR Data.

Borylation of 4-Fluorophenol with limiting B_2Pin_2 (1c)

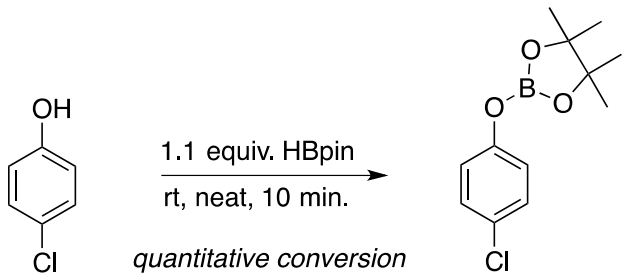


In a glovebox, a 5 mL conical vial was charged with 4-fluorophenol (224 mg, 2.0 mmol) and pinacolborane (319 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), and B_2pin_2 (127 mg, 0.25 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 4 h. The borylation results are shown in the scheme and the results are based on GC data.

General Procedure for the Synthesis of Pinacolborane (Bpin) Protected Phenols:

In a glovebox, under a N_2 atmosphere phenols (0.5 mmol) and HBpin (0.55 mmol) were charged in a 2 mL vial, and stirred at room temperature for 1-30 min until the reaction was complete (quantitative conversion). The product was characterized by ^{1}H, ^{13}C, and ^{11}B NMR in air-free, screw cap NMR tubes.

Preparation of 2-(4-chlorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



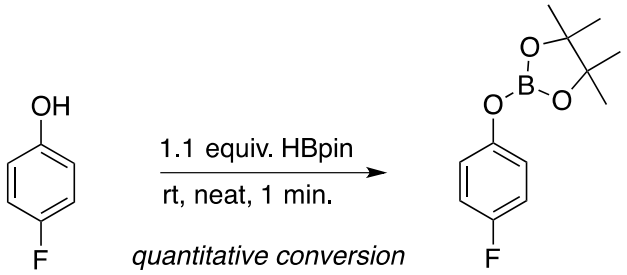
The Bpin protected 4-chlorophenol was prepared as described in the general procedure using 4-chlorophenol (0.5 mmol, 64 mg) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.22-7.19 (m, 2H), 7.03 – 6.99 (m, 2H), 1.30 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 152.0, 129.2, 128.1, 120.8, 83.7, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 2-(4-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



The Bpin protected 4-fluorophenol was prepared as described in the general procedure using 4-fluorophenol (56 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

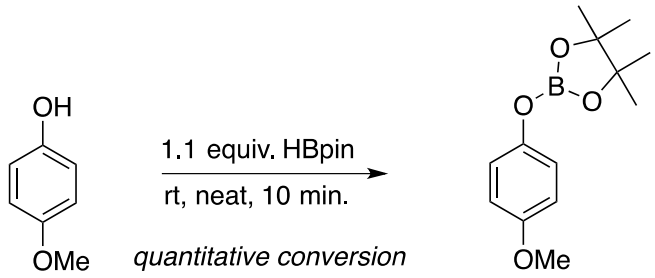
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.03-7.00 (m, 2H), 6.95 – 6.90 (m, 2H), 1.30 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 158.6 (d, $^{1}J_{C\text{-}F}$ = 241 Hz), 149.2 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 120.6 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 115.7 (d, $^{2}J_{C\text{-}F}$ = 23.4 Hz), 83.6, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

^{19}F NMR (470 MHz, $CDCl_3$): δ_F -121.1 (td, J = 13.3, 8.3, 4.9 Hz).

Preparation of 2-(4-methoxyphenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



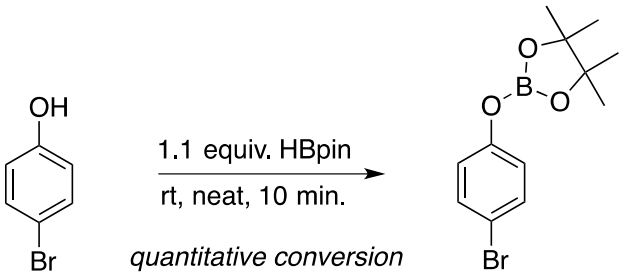
The Bpin protected 4-methoxyphenol was prepared as described in the general procedure using 4-methoxyphenol (54 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.01-6.97(m, 2H), 6.80 – 6.76 (m, 2H), 3.74 (s, 3H), 1.29 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 155.3, 147.3, 120.1, 114.3, 83.5, 55.6, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 2-(4-bromophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



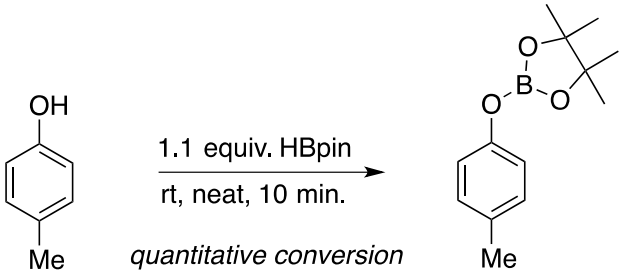
The Bpin protected 4-bromophenol was prepared as described in the general procedure using 4-bromophenol (87 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.37 – 7.33 (m, 2H), 6.97 – 6.95 (m, 2H), 1.29 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 152.6, 132.2, 121.4, 115.7, 83.8, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation 4,4,5,5-tetramethyl-2-(p-tolyloxy)-1,3,2-dioxaborolane:



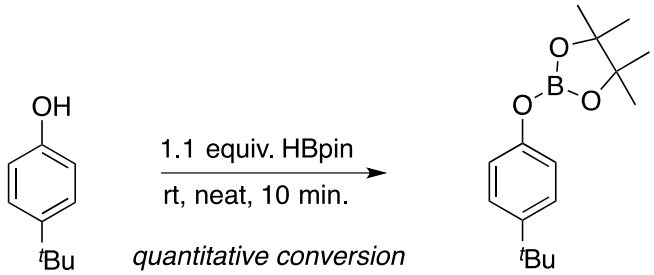
The Bpin protected *p*-cresol was prepared as described in the general procedure using the *p*-cresol (54 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.07-7.03(m, 2H), 6.97 – 6.93 (m, 2H), 2.27 (s, 3H) 1.29 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 151.2, 132.4, 129.8, 119.2, 83.5, 24.6, 20.7

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 2-(4-(tert-butyl)phenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



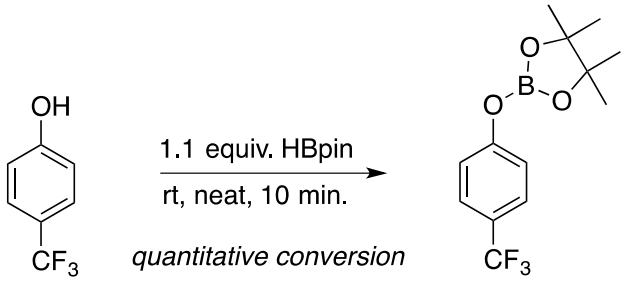
The Bpin protected 4-tert-butylphenol was prepared as described in the general procedure using 4-tert-butylphenol (75 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.28-7.25 (m, 2H), 7.01 – 6.98 (m, 2H), 1.30 (s, 12H), 1.30 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 151.0, 145.6, 126.1, 118.8, 83.5, 34.2, 31.5, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (br s).

Preparation of 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenoxy)-1,3,2-dioxaborolane:



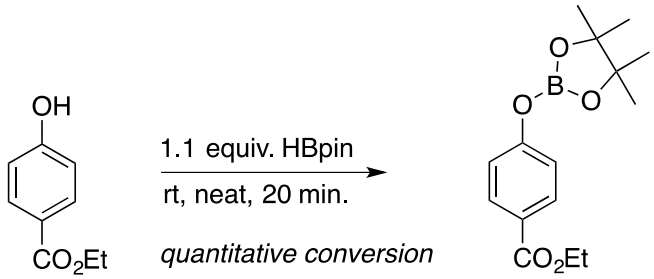
The Bpin protected 4-trifluorophenol was prepared as described in the general procedure using 4-trifluorophenol (81 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.55 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 1.34 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 156.0, 126.8 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 125.3 (q, $^{2}J_{C\text{-}F}$ = 32 Hz), 124.2, (q, $^{1}J_{C\text{-}F}$ = 271 Hz), 119.8, 83.9, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of ethyl 4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)benzoate:



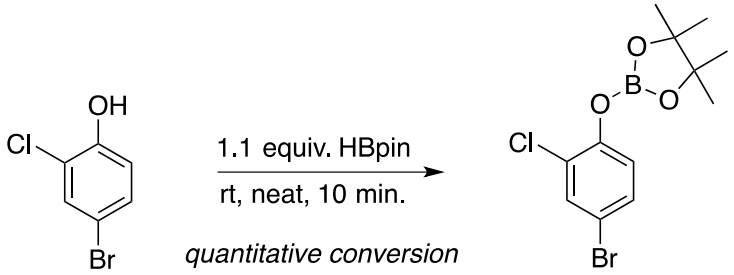
The Bpin protected ethyl 4-hydroxybenzoate was prepared as described in the general procedure using ethyl 4-hydroxybenzoate (83 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.98-7.94 (m, 2H), 7.14 – 7.10 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H), 1.30 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 166.2, 157.2, 131.3, 125.4, 119.4, 83.9, 60.7, 24.6, 14.3.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (br s).

Preparation of 2-(4-bromo-2-chlorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



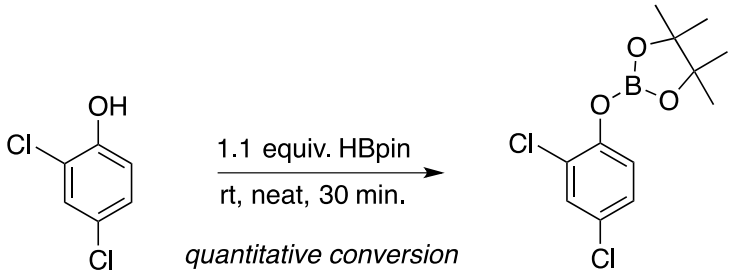
The Bpin protected 4-bromo-2-chlorophenol was prepared as described in the general procedure using 4-bromo-2-chlorophenol (104 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.52 (d, *J* = 2.4 Hz, 1H), 7.31 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.07 (d, J = 8.6 Hz, 1H), 1.29 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 148.9, 132.7, 130.7, 126.4, 122.6, 115.9, 84.2, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.6 (s).

Preparation of 2-(2,4-dichlorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



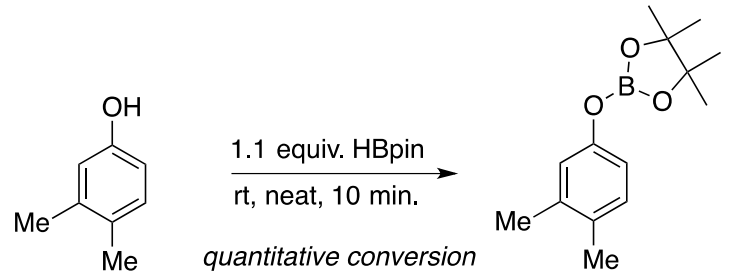
The Bpin protected 2,4-dichlorophenol was prepared as described in the general procedure using 2,4-dichlorophenol (82 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.35 (*J* = 2.4 Hz, 1H), 7.14 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 1.29 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 148.5, 129.8, 127.8, 126.0, 122.1, 117.1, 84.2, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.6 (s).

Preparation of 2-(3,4-dimethylphenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



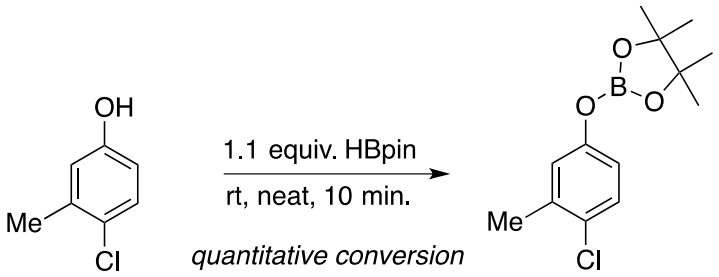
The Bpin protected 3,4-dimethylphenol was prepared as described in the general procedure using 3,4-dimethylphenol (61 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.03 (d, *J* = 8.3 Hz, 1H), 6.87 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 8.2, 2.6 Hz, 1H), 2.21 (s, 3H), 2.17 (s, 3H), 1.29 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 151.4, 137.6, 131.2, 130.2, 120.7, 116.6, 83.4, 24.6, 19.9, 19.0.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.8 (s).

Preparation of 2-(4-chloro-3-methylphenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



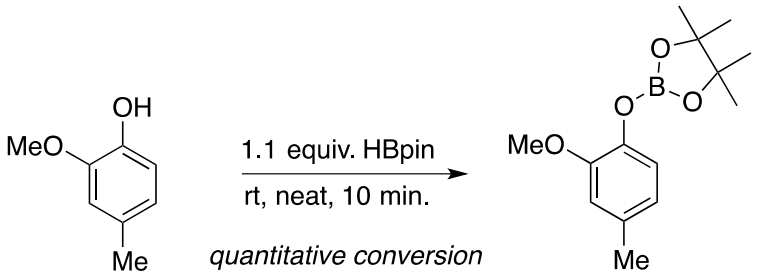
The Bpin protected 4-chloro-3-methylphenol was prepared as described in the general procedure using 4-chloro-3-methylphenol (71 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.19 (d, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 3.0 Hz, 1H), 6.85 (dd, *J* = 8.7, 3.1 Hz, 1H), 2.31 (s, 3H), 1.30 (s, 12H)

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 151.9, 136.9, 129.5, 128.4, 121.9, 118.3, 83.7, 24.6, 20.2

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 2-(2-methoxy-4-methylphenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



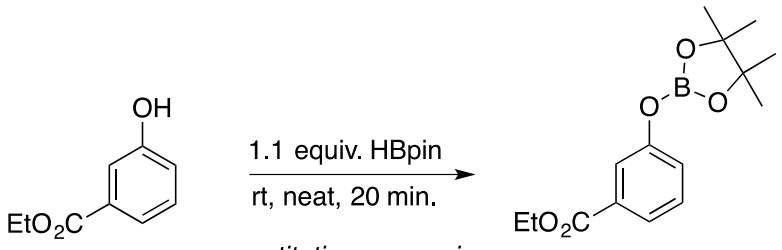
The Bpin protected 2-methoxy-4-methylphenol was prepared as described in the general procedure using 2-methoxy-4-methylphenol (69 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 6.95 (*J* = 8.1 Hz, 1H), 6.72 (s, 1H), 6.67 (d, 1H, *J* = 8.2 Hz), 3.83 (s, 3H), 2.31 (s, 3H), 1.30 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 149.7, 140.7, 133.5, 121.1, 120.1, 113.0, 83.4, 55.6, 24.5, 21.3.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.9 (s).

Preparation of ethyl 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)benzoate:



quantitative conversion

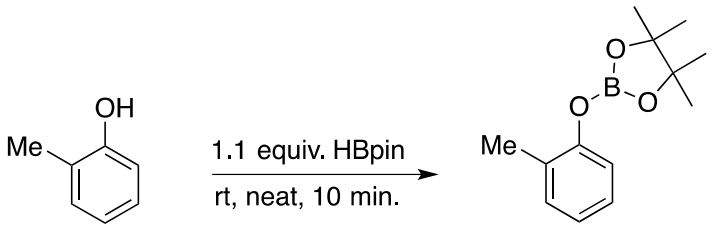
The Bpin protected ethyl 3-hydroxybenzoate was prepared as described in the general procedure using ethyl 3-hydroxybenzoate (83 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.77-7.74 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.30 – 7.27 (m, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.33 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 166.2, 153.4, 131.8, 129.2, 124.3, 124.1, 120.7, 83.8, 61.0, 24.6, 14.3.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 4,4,5,5-tetramethyl-2-(o-tolyloxy)-1,3,2-dioxaborolane:



quantitative conversion

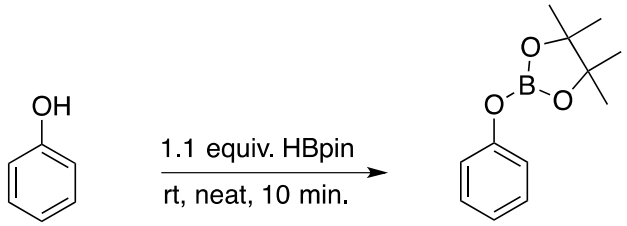
The Bpin protected *o*-cresol was prepared as described in the general procedure using *o*-cresol (54 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.18-7.12 (m, 2H), 7.09 – 7.08 (m, 1H), 6.99 (ddd, *J* = 7.3, 7.3, 1.2 Hz, 1H), 2.25 (s, 3H), 1.33 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 151.9, 130.9, 128.4, 126.7, 123.3, 119.4, 83.5, 24.6, 16.4

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaborolane:



quantitative conversion

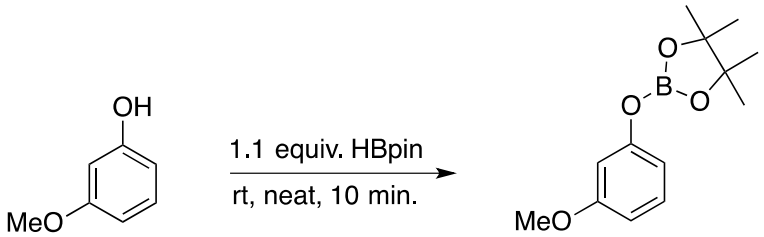
The Bpin protected phenol was prepared as described in the general procedure using phenol (47 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol) and stirring for ten minutes.

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.29(t, *J* = 7.7 Hz, 2H) , 7.11 (d, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.0 Hz, 1H), 1.33 (s, 12H)

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 153.4, 129.3, 123.1, 119.5, 83.5, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 2-(3-methoxyphenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



quantitative conversion

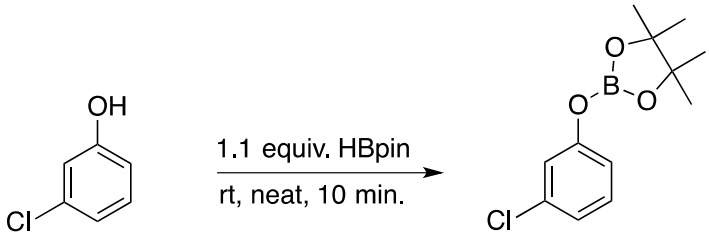
The Bpin protected 3-methoxyphenol was prepared as described in the general procedure using 3-methoxyphenol (62 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.15 (t, *J* = 8.2 Hz), 6.72 (ddd, *J* = 8.0, 2.3, 0.87 Hz, 1H), 6.68 (t, *J* = 2.3 Hz, 1H), 6.63 (ddd, *J* = 8.3, 2.4, 0.87 Hz, 1H), 3.76 (s, 3H), 1.30 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 160.5, 154.5, 129.7, 111.9, 108.6, 105.9, 83.6, 55.3, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 2-(3-chlorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



quantitative conversion

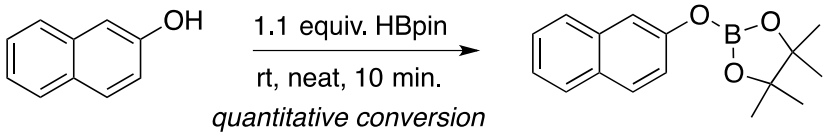
The Bpin protected 3-chlorophenol was prepared as described in the general procedure using 3-chlorophenol (64.3 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.17 (t, *J* = 8.2 Hz, 1H), 7.10 (t, *J* =2.4 Hz, 1H), 7.02 (ddd, *J* = 7.8, 3.0, 1.0 Hz, 1H), 6.97 (ddd, *J* = 8.3 Hz, 3.0 Hz, 1.0 Hz, 1H), 1.30 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 154.1, 134.4, 130.0, 123.4, 120.1, 117.9, 83.8, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.7 (s).

Preparation of 4,4,5,5-tetramethyl-2-(naphthalen-2-yloxy)-1,3,2-dioxaborolane:



The Bpin protected 2-naphthol was prepared as described in the general procedure using 2-naphthol (72 mg, 0.5 mmol) and HBpin (80 μL, 0.55 mmol).

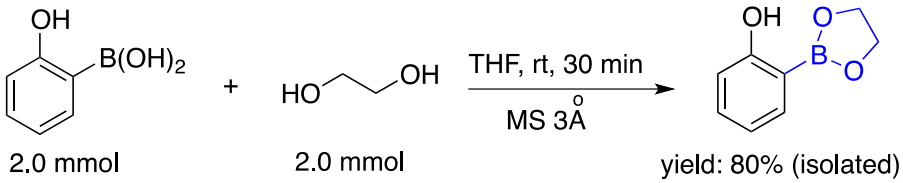
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.78 (m, 3H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.42 (ddd, *J* = 8.1, 5.9, 1.3 Hz, 1H), 7.36 (ddd, *J* = 8.2, 6.0, 1.4 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.5 Hz, 1H), 1.33 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 151.3, 134.2, 130.1, 129.3, 127.6, 127.2, 126.3, 124.5, 120.7, 115.2, 83.7, 24.6.

^{11}B NMR (176, MHz, $CDCl_3$): δ_B 21.9 (s).

Preparation of the Authentic Boronic Esters for Phenols:

2-(2-Hydroxyphenyl)1,3,2-dioxaborolane from 2-hydroxyphenylboronic acid and ethylene glycol:



A 5 mL conical vial was charged with 2-hydroxyphenylboronic acid (276 mg, 2.0 mmol), ethylene glycol (122 mg, 2.0 mmol) and molecular seives (3*Å*, 1.0 gm). Dry THF (3.0 mL) was added and the vial was capped with a teflon pressure cap and stirred at room temperature. After 30 min, the reaction mixture was filtered immediately through a short pad of celite under an inert atmosphere, which was then evaporated under reduced pressure to afford 265.0 mg of the boronic ester (80%) as oil. *The compound is highly air sensitive and decomposed rapidly.*

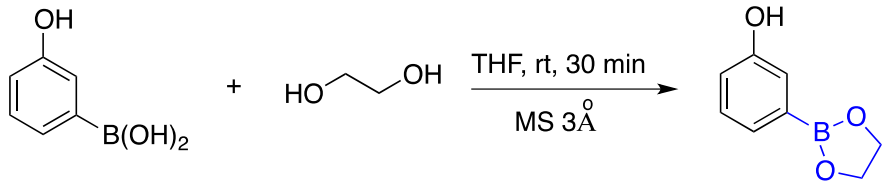
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.64 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.61 (s, 1H), 7.39 - 7.42 (m, 1H), 6.90 - 6.93 (m, 2H), 4.42 (s, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 163.4, 135.8, 134.1, 119.7, 115.6, 65.9.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 31.3 (br. s).

HRMS (ESI) *m/z* calcd for $C_8H_8BO_3$ $[M - H]^-$ 163.0568, found 163.0568.

2-(3-Hydroxyphenyl)1,3,2-dioxaborolane from 3-hydroxyphenylboronic acid and ethylene glycol:



2.0 mmol 2.0 mmol yield: 79% (isolated)

A 5 mL conical vial was charged with 3-hydroxyphenylboronic acid (276 mg, 2.0 mmol), ethylene glycol (122 mg, 2.0 mmol) and molecular seives (3*Å*, 1.0 gm). Dry THF (3.0 mL) was added and the vial was capped with a teflon pressure cap and stirred at room temperature. After 30 min, the reaction mixture was filtered immediately through a short pad of celite under an inert atmosphere, which was then evaporated under reduced pressure to afford 255 mg of the boronic ester (77%) as white solid (mp = 128-129 ^{o}C). *The compound is highly air sensitive and decomposed rapidly.*

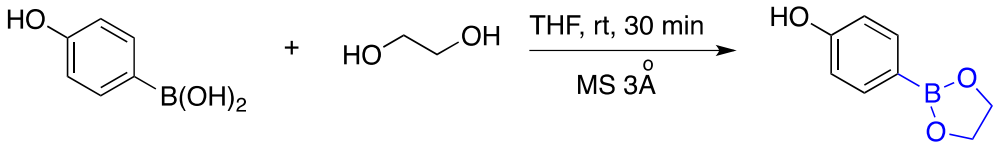
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.39 (d, *J* = 7.5 Hz, 1H), 7.20 - 7.34 (m, 2H), 6.98 (dd, *J* = 7.5, 2.0 Hz, 1H), 5.50 (br. s., 1H), 4.39 (s, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 155.2, 128.9, 126.6, 120.5, 119.2, 66.1.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 31.5 (br. s).

HRMS (ESI) *m/z* calcd for $C_8H_8BO_3$ $[M - H]^-$ 163.0568, found 163.0568.

2-(4-Hydroxyphenyl)1,3,2-dioxaborolane from 4-hydroxyphenylboronic acid and ethylene glycol:



2.0 mmol 2.0 mmol yield: 77% (isolated)

A 5 mL conical vial was charged with 3-hydroxyphenylboronic acid (276 mg, 2.0 mmol), ethylene glycol (122 mg, 2.0 mmol) and molecular seives (3*Å*, 1.0 gm). Dry THF (3.0 mL) was added and

the vial was capped with a teflon pressure cap and stirred at room temperature. After 30 min, the reaction mixture was filtered immediately through a short pad of celite under an inert atmosphere, which was then evaporated under reduced pressure to afford 260 mg of the boronic ester (79%) as white solid (mp = 131-132 ^{o}C). *The compound is highly air sensitive and decomposed rapidly.*

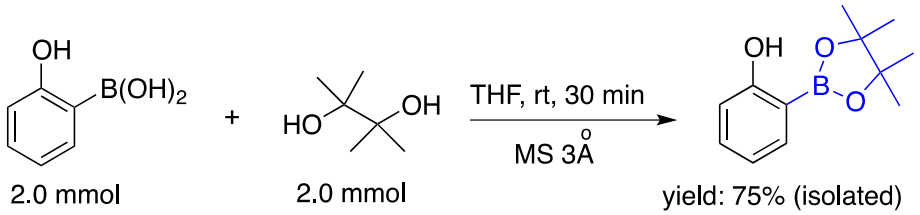
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.73 (d, *J* = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 5.35 (s, 1H), 4.37 (s, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 158.5, 136.9, 115.0, 66.0.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 31.5 (br. s).

HRMS (ESI) *m/z* calcd for $C_8H_8BO_3$ $[M - H]^-$ 163.0568, found 163.0568.

2-(2-Hydroxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane from 2-hydroxyphenylboronic acid and pinacol:

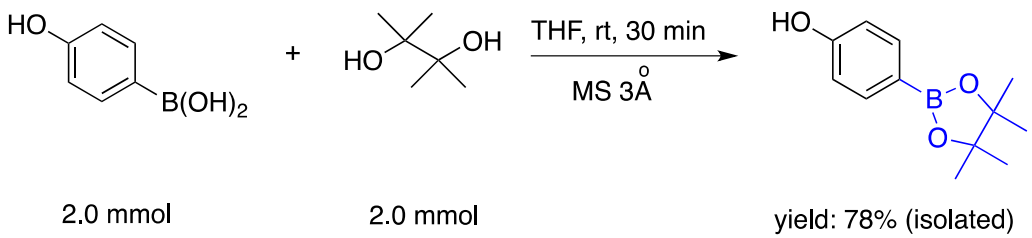


A 5 mL conical vial was charged with 2-hydroxyphenylboronic acid (276 mg, 2.0 mmol), pinacol (236 mg, 2.0 mmol) and molecular seives (3*Å*, 1.0 g). Dry THF (3.0 mL) was added and the vial was capped with a teflon pressure cap and stirred at room temperature. After 30 min, the reaction mixture was filtered immediately through a short pad of celite under inert atmosphere, which was then evaporated under reduced pressure to afford 330 mg of the boronic ester (80%) as colorless oil. The NMR data of this compound were in accordance with the literature reported compound.[5]

2-(3-Hydroxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

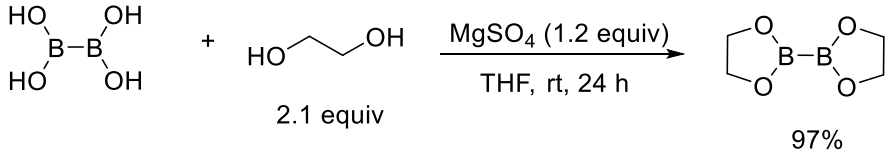
This compound is commercially available and was purchased from Sigma-Aldrich and used without any further purification.

2-(4-Hydroxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane from 4-hydroxyphenylboronic acid and pinacol:



A 5 mL conical vial was charged with 4-hydroxyphenylboronic acid (276 mg, 2.0 mmol), pinacol (236 mg, 2.0 mmol) and molecular seives (3*Å*, 1.0 g). Dry THF (3.0 mL) was added and the vial was capped with a teflon pressure cap and stirred at room temperature. After 30 min, the reaction mixture was filtered immediately through a short pad of celite under an inert atmosphere, which was then evaporated under reduced pressure to afford 341 mg of the boronic ester (78%) as white solid (mp = 102-105 ^{o}C). The NMR data of this compound were in accordance with the literature reported compound.[6]

Synthesis of 2,2'-bi(1,3,2-dioxaborolane) from Tetrahydroxydiboron:



This compound was synthesized by modifying the previously reported procedure.[7] A 100 mL round bottom flask was charged with tetrahydroxydiboron (1.0 g, 11.2 mmol, 1 equiv), dry $MgSO_4$ (1.61 g, 1.2 equiv) and dry THF (~20 mL) then sealed with a septa. To this solution was added freshly distilled ethylene glycol (1.31 mL, 23.4 mmol, 2.1 equiv). After stirring for 24 h at room temperature, the reaction mixture was filtered through a medium glass frit using approximately 30 mL THF to aid transfer and wash the $MgSO_4$. The THF solution was evaporated under reduced pressure to afford a white solid. The solid was dried under highvac to yield 1.53 g of pure B_2eg_2 (97%). It should be noted that if further purification is necessary B_2eg_2 sublimes at 0.01 mm Hg pressure and 65-70 ^{o}C. (mp = 159-160 ^{o}C).

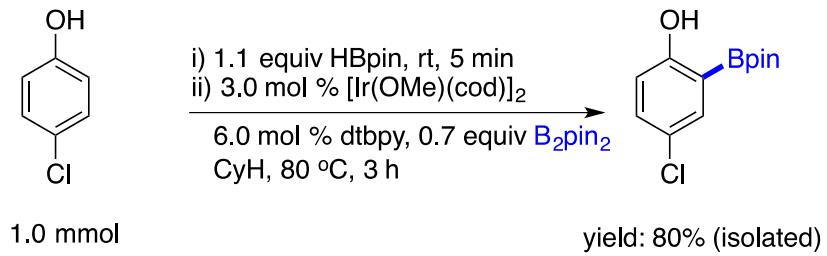
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.21 (s, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 65.3.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.9 (br. s).

HRMS (ESI) *m/z* calcd for $C_4H_9B_2O_4$ $[M + H]^+$ 143.0687, found 143.0685.

Borylation of 4-Chlorophenol with B_2pin_2 (1a):



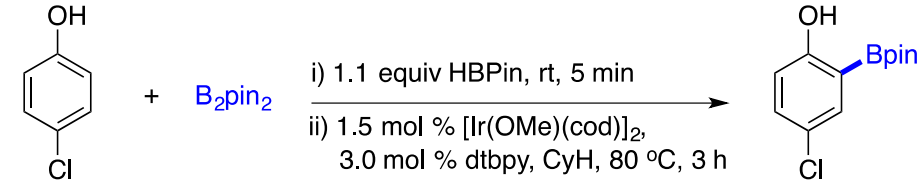
In a glovebox, a 5 mL conical vial was charged with 4-chlorophenol (129 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (254 mg, 1.0 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 3 h. After completion (judged by GC), the cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 203 mg of the ortho-borylated product (80%) as a white solid (mp = 59-60 °C). The NMR data was in accordance with the literature reported data.[5]

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.77 (s, 1H), 7.56 (d, J = 2.5 Hz, 1H), 7.31 (dd, J = 9.0, 2.5 Hz, 1H), 6.82 (d, J = 9.0 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 162.1, 134.8, 133.6, 124.5, 117.1, 84.9, 24.8.

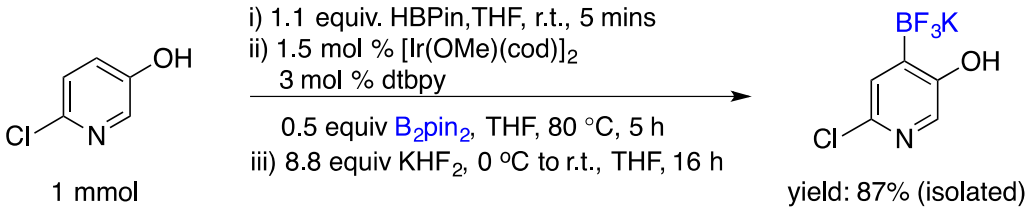
^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.7 (br. s).

Gram Scale Borylation of 4-Chlorophenol (1a):



In a glovebox, a 100 mL air free flask was charged with 4-chlorophenol (2.0 g, 15.5 mmol) and HBpin (2.18 g, 17.05 mmol). After stirring for 5 minutes, a solid had formed. Then, $[Ir(OMe)cod]_2$ (150 mg, 1.5 mol %, 0.226 mmol), dtbpy (125 mg, 3 mol %, 0.465 mmol), B_2Pin_2 (2.75 g, 10.85 mmol), and dry cyclohexane (25 mL) were added. The flask was sealed and heated at 80°C. After 3 h, the reaction was complete (judged by GC/FID), and the volatiles were removed under reduced pressure. Purification by column chromatography with chloroform as the eluent afforded 2.92 g of the analytically pure ortho-borylated product (74%) as a white solid.

Borylation of 2-Chloro-5-hydroxypyridine with B_2pin_2 (1b):



In a glovebox, a 5 mL conical vial was charged with 2-chloro-5-hydroxypyridine (129 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) in THF (1.5 mL) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), and B_2pin_2 (127 mg, 0.5 equiv) was charged. Additional THF (1.5 mL) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 5 hours. The reaction was then cooled to room temperature and transferred to a round bottom flask. It was washed in with additional THF (3 mL). The solution was cooled to 0 °C and degased with N_2 for 5 minutes. Then, KHF_2 (2.2 mL, 8.8 mmol, 4.0 M in H_2O) was added via syringe dropwise. The reaction was allowed to stir at 0 °C for 10 minutes, then the ice bath was removed and the reaction warmed to room temperature. After stirring at room temperature for 16 h, the reaction was filtered, and the recovered solid washed with THF to afford the organotrifluoroborate product (87%) as a white solid (mp = 226 – 230 °C dec).

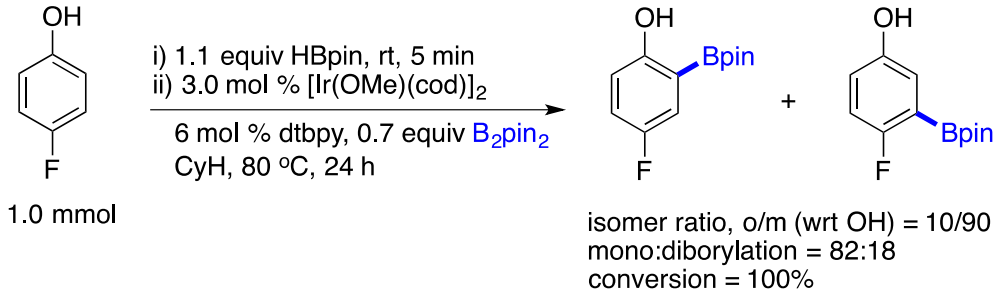
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ_H 7.65 (s, 1H), 7.47 (q, 1H, *J*=11.4 Hz), 7.15 (br, 1H)

^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 156.18, 140.18, 135.58, 127.59 (q, 1.88 Hz)

^{11}B NMR (160 MHz, $(CD_3)_2CO$): δ_B 2.65 (q, *J*= 51.5 Hz)

HRMS (ESI) *m/z* calcd for $C_5H_3BClF_3NO$ $[M\text{-}K]^-$ 195.9955, found 195.9948

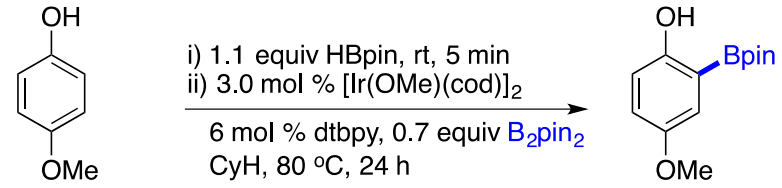
Borylation of 4-Fluorophenol with B_2pin_2 (1c):



In a glovebox, a 5 mL conical vial was charged with 4-fluorophenol (112 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. GC-FID showed 100% conversion of

the starting material. The ratio of products was 10:90 (ortho:meta wrt to OH), and 82:18 (monoborylation:diborylation).

Borylation of 4-methoxyphenol with B_2pin_2 (1d):



1.0 mmol

yield: 58% (isolated)

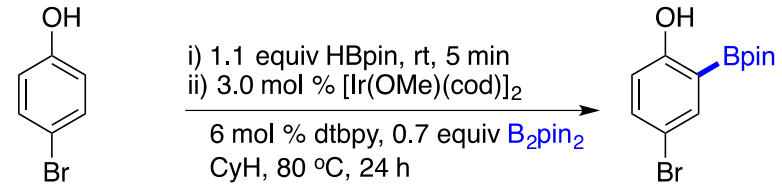
In a glovebox, a 5 mL conical vial was charged with 4-methoxyphenol (124 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC), the ratio of ortho/meta (wrt OH) borylated product was found to be 65/35. The cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 144.0 mg of the ortho-borylated product (58%) as a colorless oil. NMR data was in accordance with the literature reported data.[5]

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.52 (s, 1H), 7.10 (d, J = 3.0 Hz, 1H), 6.97 (dd, J = 9.5, 3.0 Hz, 1H), 6.83 (d, J = 9.5 Hz, 1H), 3.78 (s, 3H), 1.37 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 157.9, 152.6, 121.3, 118.0, 116.5, 84.5, 55.8, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 31.1 (br. s).

Borylation of 4-bromolphenol with B_2pin_2 (1e):



1.0 mmol

yield: 63% (isolated)

In a glovebox, a 5 mL conical vial was charged with 4-bromophenol (173 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2

(178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC), the cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 188 mg of the ortho-borylated product (63%) as a yellow solid (mp = 68-69 °C).

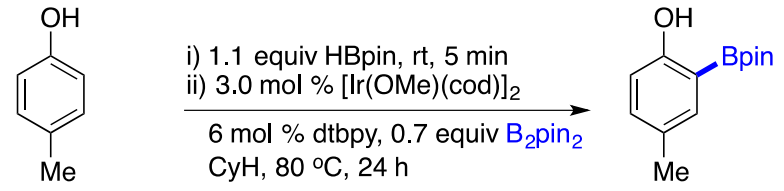
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.78 (s, 1H), 7.70 (d, *J* = 3.0 Hz, 1H), 7.44 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.78 (d, *J* = 9.0 Hz, 1H), 1.37 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 162.6, 137.8, 136.4, 117.6, 111.9, 84.9, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.6 (br. s).

HRMS (ESI) *m/z* calcd for $C_{12}H_{15}BBrO_3$ $[M - H]^-$ 297.0300, found 297.0299.

Borylation of 4-methylphenol with B_2pin_2 (1f):



1.0 mmol

yield: 85% (isolated)

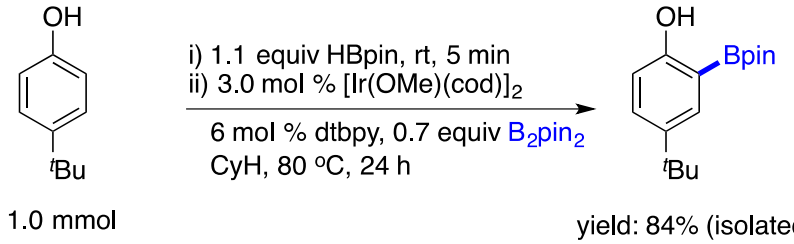
In a glovebox, a 5 mL conical vial was charged with 4-methylphenol (108 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 199 mg of the borylated product (85%) as a pale yellow solid (mp = 35-36 °C). The NMR data were in accordance with the literature reported data.[5]

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.66 (s, 1H), 7.42 (d, J = 1.5 Hz, 1H), 7.20 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 2.27 (s, 3H), 1.38 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 161.5, 135.6, 134.6, 128.5, 115.3, 84.4, 24.8, 20.3.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 31.0 (br. s).

Borylation of 4-tertbutylphenol with B_2pin_2 (1g):



1.0 mmol

yield: 84% (isolated)

In a glovebox, a 5 mL conical vial was charged with 4-tertbutylphenol (150 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 233 mg of the borylated product (84%) as a white solid (mp = 78-79 °C).

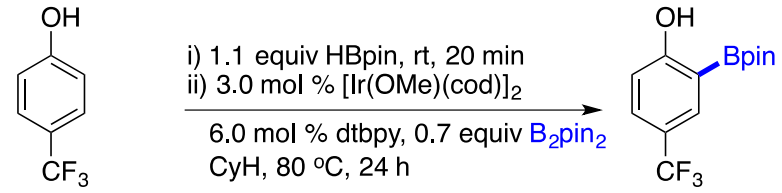
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.76 (s, 1H), 7.60 (d, J = 2.5 Hz, 1H), 7.42 (dd, J = 8.5, 2.5 Hz, 1H), 6.83 (d, J = 8.5 Hz, 1H), 1.37 (s, 12H), 1.31 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 161.5, 141.9, 131.9, 131.2, 115.0, 84.4, 34.0, 31.5, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.6 (br. s).

HRMS (ESI) *m/z* calcd for $C_{16}H_{24}BO_3$ $[M - H]^-$ 275.1822, found 275.1825.

Borylation of 4-trifluoromethylphenol with B_2pin_2 (1h):



1.0 mmol

yield: 65% (isolated)

In a glovebox, a 5 mL conical vial was charged with 4-trifluoromethylphenol (162 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 20 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum

block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 188 mg of the borylated product (63%) as a white solid (mp = 75-76 °C)

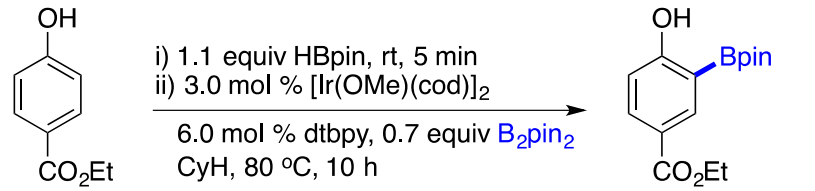
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.16 (s, 1H), 7.89 (d, *J* = 1.5 Hz, 1H), 7.61 (dd, *J* = 9.0, 1.5 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 1H), 1.39 (br. s., 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 166.1, 133.2 (q, *J* = 3.7 Hz), 130.7 (q, *J* = 3.1 Hz), 124.5 (q, *J* = 271.8 Hz), 121.9 (q, *J* = 33.0 Hz), 116.0, 85.1, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.6 (br. s).

HRMS (ESI) *m/z* calcd for $C_{13}H_{15}BF_3O_3$ $[M - H]^-$ 287.1069, found 287.1072.

Borylation of 4-carboethoxyphenol with B_2pin_2 (1i):



1.0 mmol

yield: 51% (isolated)

In a glovebox, a 5 mL conical vial was charged with 4-carboethoxyphenol (166 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 10 h. After completion (judged by GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 144 mg of the borylated product (51%) as a white solid (mp = 106-107 °C).

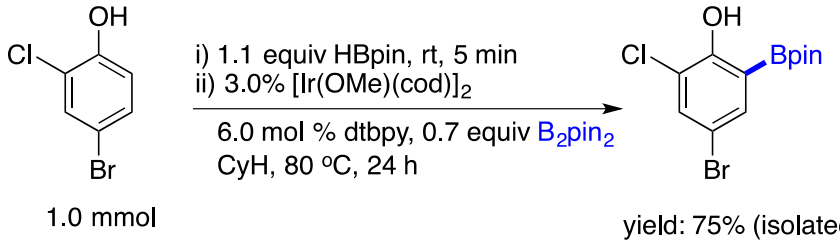
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.33 (d, *J* = 2.5 Hz, 1H), 8.25 (s, 1H), 8.0 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 4.35 (q, *J* = 7.3 Hz, 2H), 1.36 - 1.40 (m, Bpin 12H and ester 3H overlapped).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 167.3, 166.3, 138.1, 135.4, 122.1, 115.6, 84.9, 60.6, 24.8, 14.5;

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.8 (br. s).

HRMS (ESI) *m/z* calcd for $C_{15}H_{22}BO_5$ $[M + H]^+$ 293.1563, found 293.1565.

Borylation of 4-bromo-2-chlorophenol with B_2pin_2 (1j):



In a glovebox, a 5 mL conical vial was charged with 4-bromo-2-chlorophenol (207 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 250 mg of the borylated product (75%) as a brown solid (mp = 109-110 °C).

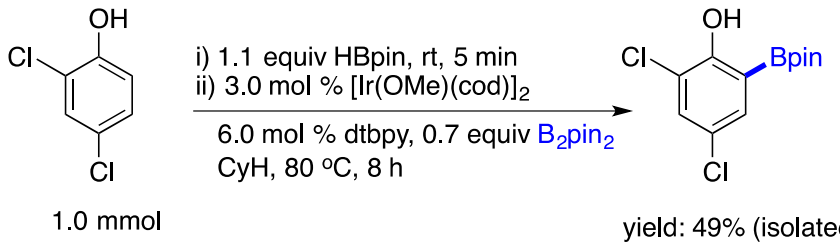
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.28 (s, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 157.9, 136.3, 136.1, 121.8, 111.5, 85.4, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.0

HRMS (ESI) *m/z* calcd for $C_{12}H_{14}BBrClO_3$ $[M - H]^-$ 330.9910, found 330.9910.

Borylation of 2,4-dichlorophenol with B_2pin_2 (1k):



In a glovebox, a 5 mL conical vial was charged with 2,4-dichlorophenol (163 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum

block at 80 °C. The reaction mixture was stirred for 8 h. After completion (judged by GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 141 mg of the borylated product (49%) as a yellow solid (mp = 108-109 °C).

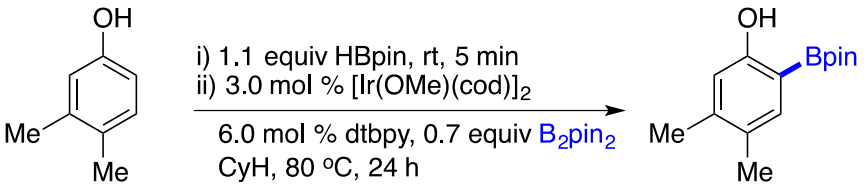
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.26 (s, 1H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 162.3, 157.4, 133.4, 124.7, 121.5, 85.3, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 31.1 (br. s).

HRMS (ESI) *m/z* calcd for $C_{12}H_{14}BCl_2O_3$ $[M - H]^-$ 287.0415, found 287.0418.

Borylation of 3,4-dimethylphenol with B_2pin_2 (1l):



1.0 mmol

yield: 68% (isolated)

In a glovebox, a 5 mL conical vial was charged with 3,4-dimethylphenol (122 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (chloroform as eluent) gave 169 mg of the borylated product (68%) as an oil.

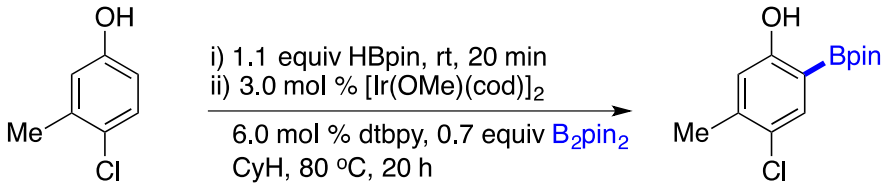
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.60 (s, 1H), 7.36 (s, 1H), 6.72 (s, 1H), 2.25 (s, 3H), 2.19 (s, 3H), 1.38 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 161.9, 143.2, 136.0, 127.5, 116.5, 84.2, 24.8, 20.3, 18.5.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.8 (br. s).

HRMS (ESI) *m/z* calcd for $C_{14}H_{20}BO_3$ $[M - H]^-$ 247.1508, found 247.1509.

Borylation of 4-chloro-3-methylphenol with B_2pin_2 (1m):



1.0 mmol

yield: 59% (isolated)

In a glovebox, a 5 mL conical vial was charged with 4-chloro-3-methylphenol (143 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 20 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 20 h. After completion (judged by GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (10% ethylacetate in hexane as eluent) gave 159 mg of the ortho-borylated product (59%) as a red liquid.

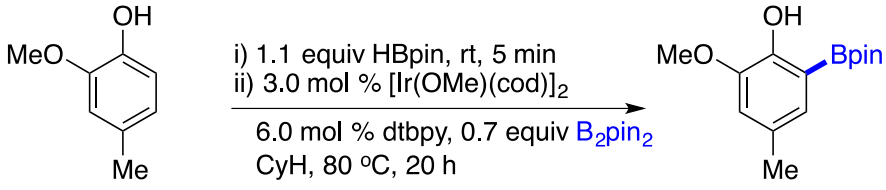
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.67 (s, 1H), 7.54 (s, 1H), 6.78 (s, 1H), 2.34 (s, 3H), 1.37 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 162.0, 142.0, 135.2, 125.1, 117.9, 84.7, 24.7, 20.6.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.5 (br. s).

HRMS (ESI) *m/z* calcd for $C_{13}H_{17}BClO_3$ $[M - H]^-$ 267.0962, found 267.0964.

Borylation of 2-methoxy-4-methylphenol with B_2pin_2 (1n):



1.0 mmol

yield: 66% (isolated)

In a glovebox, a 5 mL conical vial was charged with 2-methoxy-4-methylphenol (138 mg, 1.0 mmol) and pinacolborane (160 μL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 20 h. After completion (judged by

GC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (10% ethylacetate in hexane as eluent) gave 175 mg of the ortho-borylated product (66%) as a pale yellow oil.

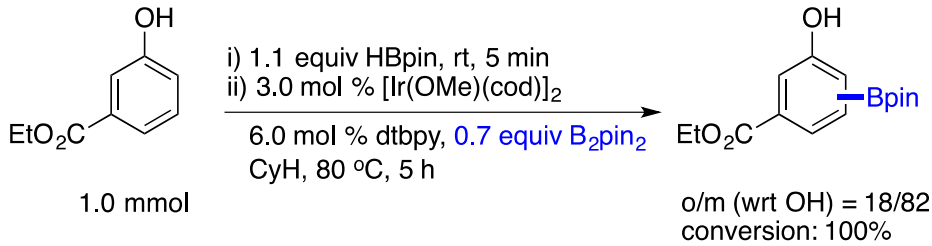
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.61 (s, 1H), 7.02 (d, J = 1.0 Hz, 1H), 6.82 (d, J = 1.5 Hz, 1H), 3.87 (s, 3H), 2.28 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 150.8, 147.1, 129.0, 126.6, 116.7, 84.4, 56.0, 24.8, 20.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.5 (br. s).

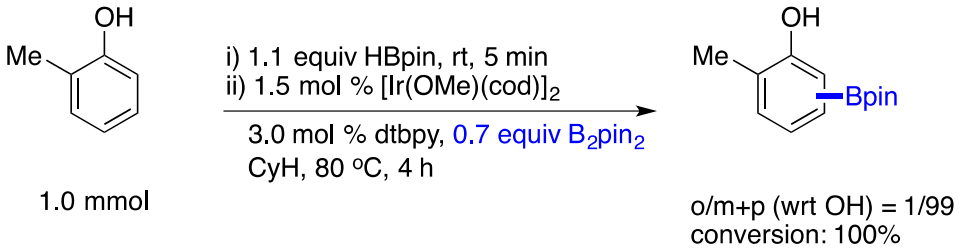
HRMS (ESI) *m/z* calcd for $C_{14}H_{22}BO_4$ $[M + H]^+$ 265.1614, found 265.1603.

Borylation of 3-carboethoxyphenol with B_2pin_2 (1o):



In a glovebox, a 5 mL conical vial was charged with 3-carboethoxyphenol (166 mg, 1.0 mmol) and pinacolborane (160 µL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 3.0 mol %, 0.03 mmol), dtbpy (16 mg, 6.0 mol %, 0.06 mmol), and B_2pin_2 (1.0 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 5 h. GC-FID showed a 100% conversion of the starting material. The ratio of products was 18:82 (ortho:meta wrt OH).

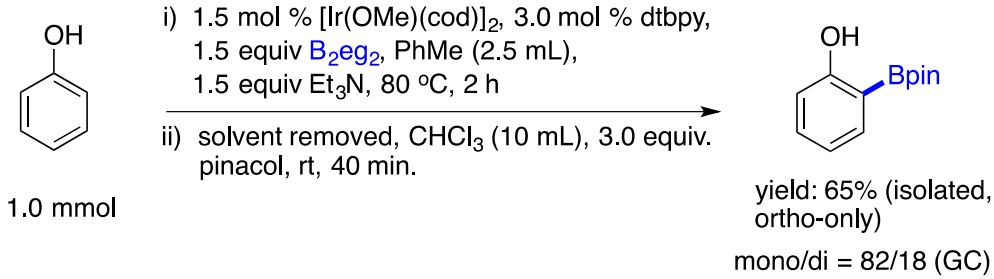
Borylation of ortho-cresol with B_2pin_2 (1p):



In a glovebox, a 5 mL conical vial was charged with ortho-cresol (108 mg, 1.0 mmol) and pinacolborane (160 µL, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), and B_2pin_2 (178 mg, 0.7 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert

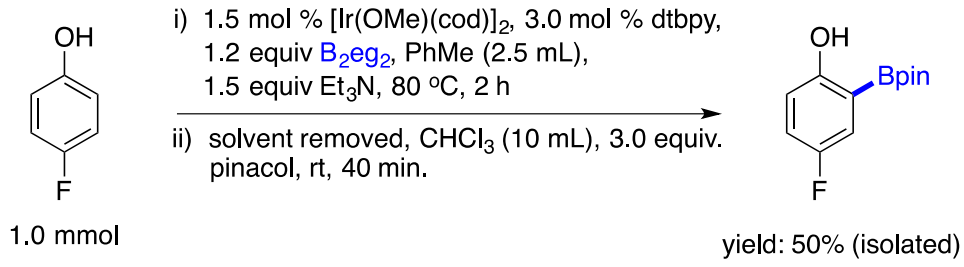
atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 4 h. GC-FID showed a 100% conversion of the starting material. The ratio of products was 1:99 (ortho:meta wrt OH).

Borylation of phenol with B_2eg_2 (1q):



In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (213 mg, 1.5 equiv, 1.5 mmol), phenol (94 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (209 µL, 1.5 equiv, 1.5 mmol). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 2 h. The solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min. Upon completion (judged by GC), the crude mixture was passed through a short pad of silica gel (chloroform as eluent) to afford the 142 mg of the ortho-borylated product (65%) as a colorless oil. The ratio of mono/*o*,*o*-di borylated product was found to be 82/18 by the GC-FID and the diborylated product was assigned by the crude NMR spectra, but was not isolated. The NMR data were in accordance with the literature reported data.[5]

Borylation of 4-Fluorophenol with B_2eg_2 (1r):



In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (170.07 mg, 1.2 equiv, 1.2 mmol), 4-fluorophenol (112 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (209 µL, 1.5 equiv, 1.5 mmol). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80

°C for 2 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min. Upon completion (judged by GC), the crude mixture was passed through a short pad of silica gel (chloroform as eluent) to afford the 118 mg of the ortho-borylated product (50%) as a brown oil. The ratio of mono/*o*,*o*-di borylated product was found to be 89/11 by the GC-FID and the di-borylated product was assigned by the crude NMR spectra, but not isolated. The NMR data of the isolated product were in accordance with the literature reported data.[5]

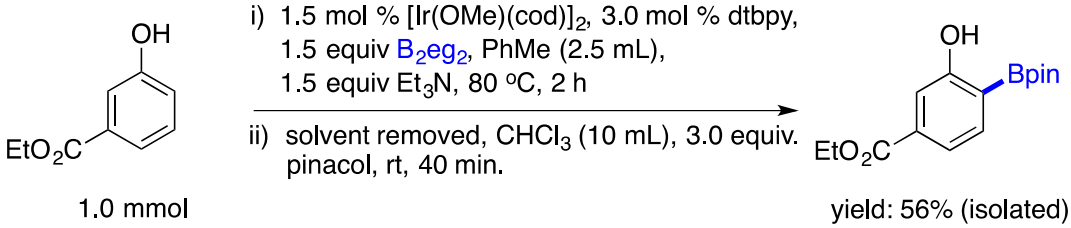
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.65 (s, 1H), 7.25 - 7.27 (m, OH and ArH overlapped, 2H), 7.06 (dt, J = 8.5, 3.5 Hz, 1H), 6.83 (dd, *J* = 8.5, 3.5 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 159.6 (d, *J* = 1.9 Hz), 156.3 (d, *J* = 237.6 Hz), 120.6 (d, *J* = 21.2 Hz), 120.4, 116.7 (d, *J* = 7.2 Hz), 84.8, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.4 (br. s).

^{19}F NMR (470 MHz, $CDCl_3$): δ_F -126.0 (td, *J* = 21.5, 13.3, 5.1 Hz).

Borylation of 3-carboethoxyphenol with B_2eg_2 (1s)



1.0 mmol

yield: 56% (isolated)

In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (213 mg, 1.5 equiv, 1.5 mmol), 3-carboethoxyphenol (166 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (209 μL, 1.5 equiv, 1.5 mmol). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 2 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min. Upon completion (judged by GC), the crude mixture was passed through a short pad of silica gel (chloroform as eluent) to afford the 163 mg of the ortho-borylated product (56%) as colorless oil. In this reaction, no di-borylation was observed.

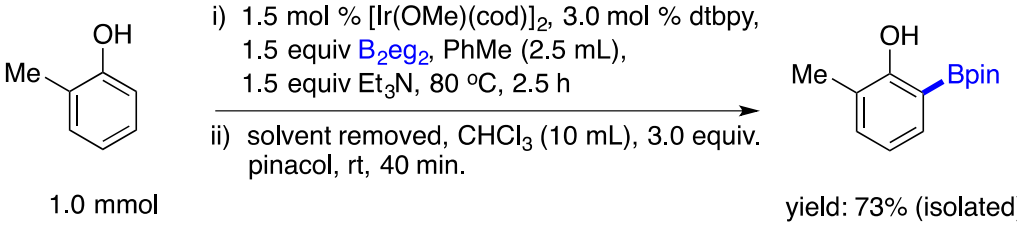
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.89 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.51 - 7.56 (m, 2H), 4.37 (q, *J* = 7.5 Hz, 2H), 1.38 - 1.41 (m, Bpin 12H and ester 3H overlapped, 15H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 166.3, 163.4, 135.7, 135.3, 120.2, 116.4, 84.9, 61.1, 24.8, 14.3.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.6 (br. s).

HRMS (ESI) *m/z* calcd for $C_{15}H_{20}BO_5$ [M - H]$^-$ 291.1407, found 291.1403.

Borylation of ortho-cresol with B_2eg_2 (1t):



1.0 mmol

yield: 73% (isolated)

In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (213 mg, 1.5 equiv, 1.5 mmol), o-cresol (108 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (209 μL, 1.5 equiv, 1.5 mmol). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 2.5 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min. Upon completion (judged by GC), the crude mixture was passed through a short plug of silica gel (chloroform as eluent) to afford the 172 mg of the ortho-borylated product (73%) as a solid (mp = 51-52 °C). No di-borylation was found in this reaction.

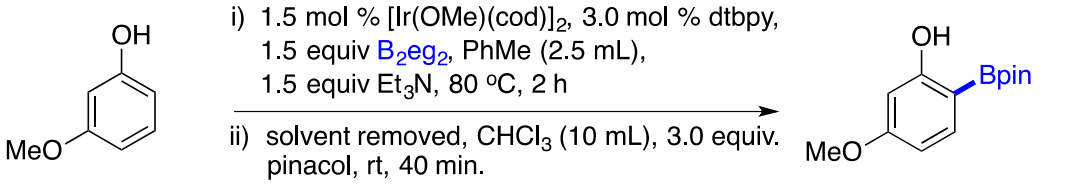
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.02 (s, 1H), 7.49 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 2.27 (s, 3H), 1.39 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 161.8, 134.9, 133.2, 124.4, 119.4, 84.4, 24.8, 16.0.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.9 (br. s).

HRMS (ESI) *m/z* calcd for $C_{13}H_{18}BO_3$ [M - H]$^-$ 233.1351, found 233.1354.

Borylation of 3-methoxyphenol with B_2eg_2 (1u):



1.0 mmol

yield: 80% (isolated, ortho-only)

mono/di = 81/19 (GC)

In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (213 mg, 1.5 equiv, 1.5 mmol), 3-methoxyphenol (124 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (209 μL, 1.5 equiv, 1.5 mmol).

The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 ^{o}C for 2 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min. Upon completion (judged by GC), the crude mixture was passed through a short pad of silica gel (chloroform as eluent) to afford 199 mg of the ortho-borylated product (80%) as a colorless oil. The ratio of mono/*o*,*o*-di borylated product was found to be 81/19 by the GC-FID and the di-borylated product was assigned by the crude NMR spectra, but it was not isolated.

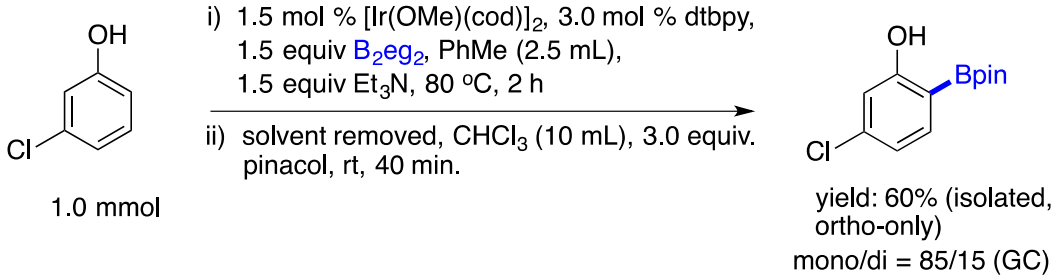
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.91 (s, 1H), 7.52 (d, J = 8.5 Hz, 1H), 6.48 (dd, J = 8.5, 2.5 Hz, 1H), 6.43 (d, J = 2.5 Hz, 1H), 3.81 (s, 3H), 1.37 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 165.5, 164.5, 136.8, 107.0, 100.1, 84.2, 55.2, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.8 (br. s).

HRMS (ESI) *m/z* calcd for $C_{13}H_{18}BO_4$ $[M - H]^-$ 249.1301, found 249.1303.

Borylation of 3-chlorophenol with B_2eg_2 (1v):



In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (213 mg, 1.5 equiv, 1.5 mmol), 3-chlorophenol (129 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (209 μL, 1.5 equiv, 1.5 mmol). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 ^{o}C for 2 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min. Upon completion (judged by GC), the crude mixture was passed through a short pad of silica gel (chloroform as eluent) to afford 199 mg of the ortho-borylated product (60%) as a white solid (mp = 62-63 ^{o}C). The ratio of mono/*o*,*o*-di borylated product was found to be 85/15 by the GC-FID and the di-borylated product was assigned by the crude NMR spectra, but was not isolated.

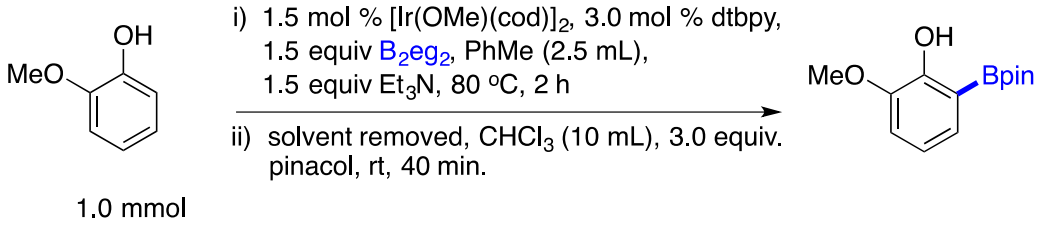
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.92 (s, 1H), 7.53 (d, J = 8.5 Hz, 1H), 6.91 (d, J = 1.5 Hz, 1H), 6.88 (dd, J = 8.5, 1.5 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 164.3, 139.4, 136.6, 120.1, 115.9, 84.7, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.6 (br. s).

HRMS (ESI) *m/z* calcd for $C_{12}H_{15}BClO_3$ $[M - H]^-$ 253.0805, found 253.0808.

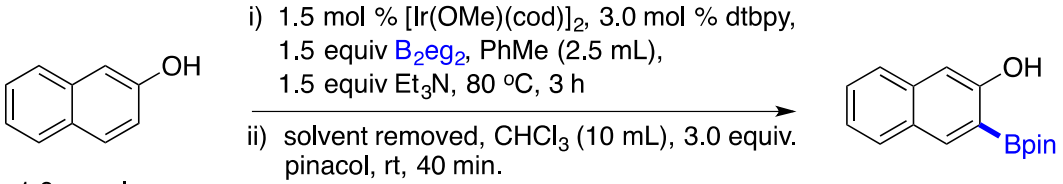
Borylation of 2-methoxyphenol with B_2eg_2 (1w):



1.0 mmol

In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (213 mg, 1.5 equiv, 1.5 mmol), 2-methoxyphenol (124 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (209 µL, 1.5 equiv, 1.5 mmol). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 2 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min. Upon completion (judged by GC), the crude mixture was purified by passing it through a short pad of silica gel (chloroform as eluent) followed by kugelrohr distillation (20 mm Hg/ 100 °C) to afford 183 mg of the ortho-borylated product (73%). NMR data of the isolated product were in accordance with the literature reported data.[8]

Borylation of 2-naphthol with B_2eg_2 (1x):



1.0 mmol

yield: 67% (isolated)

In a glovebox, a 5 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (213 mg, 1.5 equiv, 1.5 mmol), 2-naphthol (144 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (209 µL, 1.5 equiv, 1.5 mmol). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 3 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min. Upon completion (judged by GC), the crude mixture was passed through a short pad of silica gel

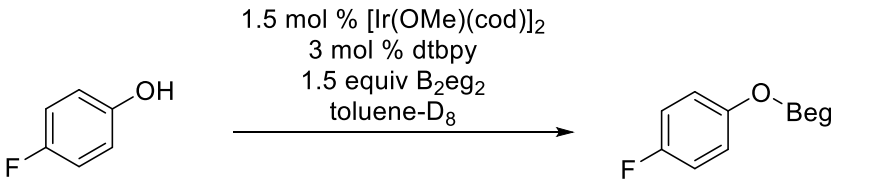
(chloroform as eluent) to afford the 181 mg of the ortho-borylated product (67%) as a colorless oil. The NMR data were in accordance with the literature reported data.[8]

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.27 (s, 1H) 7.79 - 7.81 (m, OH and ArH overlapped, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.46 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.30 (dt, *J* = 7.5, 1.0 Hz, 1H), 1.44 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 159.2, 138.2, 137.3, 128.6, 128.0, 127.8, 126.4, 123.2, 109.4, 84.8, 24.9.

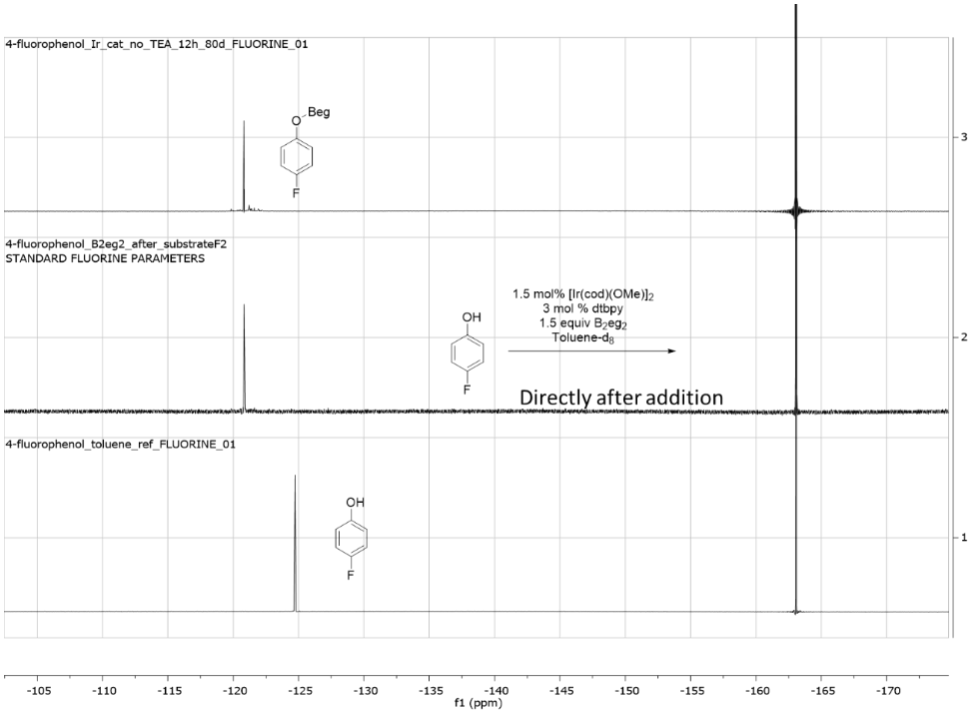
^{11}B NMR (160 MHz, $CDCl_3$): δ_B 30.7 (br. s).

Evidence for 2-(4-fluorophenoxy)-1,3,2-dioxaborolanephenols formation under the reaction conditions:

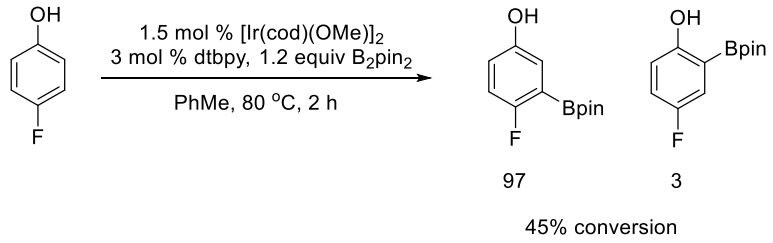


prior to any other product

Experimental: In a glove, $[Ir(OMe)(cod)]_2$ (0.001g, 1.5 mol %) was dissolved in 0.05 mL deuterated toluene, B_2eg_2 (0.021g, 0.15mmol, 1.5 equiv) was dissolved in 0.4 mL deuterated toluene, dtbpy (0.0008 g, 3 mol %) was dissolved in 0.05 mL, and 4-fluorophenol (0.0112 g, 0.1 mmol, 1 equiv) was dissolved in 0.2 mL deuterated toluene. The $[Ir(OMe)(cod)]_2$, B_2eg_2, and dtbpy solutions were transferred to a J-Young tube and C_6F_6 (3 µL) was added as a reference. The 4-fluorophenol was sealed in an air tight flask with a septa. The NMR tube was taken to a spectrometer and the 4-fluorophenol was injected into the NMR tube. The tube was inverted once for mixing and inserted into the spectrometer. ^{19}F NMR was collected. The time between addition of the phenol and the last scan for the ^{19}F NMR was ~2 minutes. The only observable product in ^{19}F NMR was the 2-(4-fluorophenoxy)-1,3,2-dioxaborolane which is shown below.

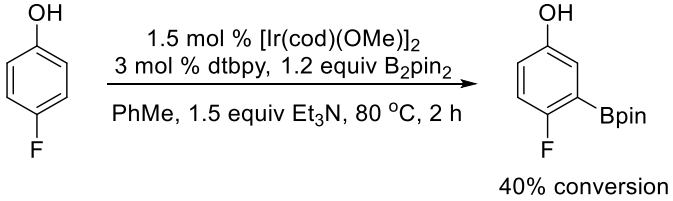


Control for effects of toluene on borylation selectivity:



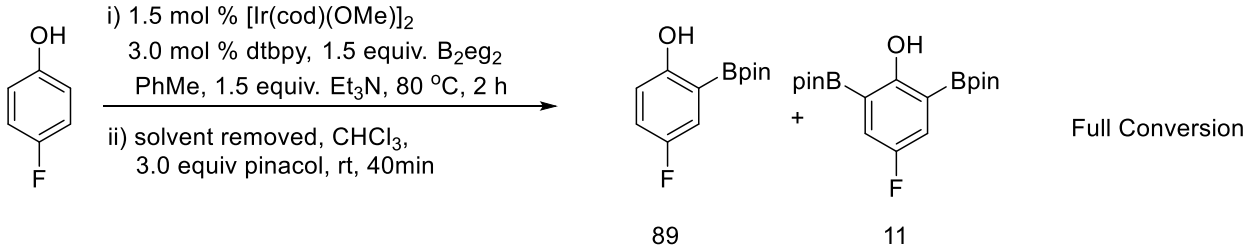
In a glovebox, a 3 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2pin_2 (304.7 mg, 1.2 equiv, 1.2 mmol), 4-fluorophenol (112 mg, 1.0 mmol), and dry PhMe (2.5 mL). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 2 h. Solvent was evaporated under reduced pressure and crude ^{19}F, ^{1}H, ^{11}B NMR were recorded. The ratio of products, 97:3 m:o (with respect to OH), and conversion, 45%, was judged based on integration of ^{19}F NMR.

Control for effects of toluene and triethylamine on borylation selectivity:

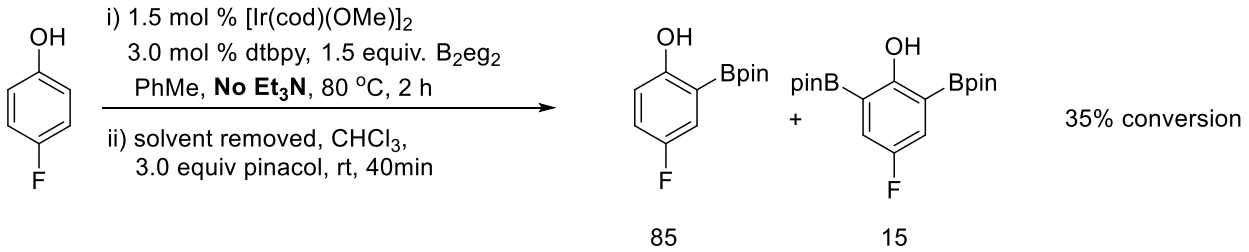


In a glovebox, a 3 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2pin_2 (304.7 mg, 1.2 equiv, 1.2 mmol), 4-fluorophenol (112 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (0.209 mL, 1.5 equiv, 1.5 mmol). The v ial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 2 h. Solvent was evaporated under reduced pressure and crude ^{19}F, ^{1}H, ^{11}B NMR were recorded. The conversion, 45%, was judged based on integration of ^{19}F NMR. It should be noted that no borylation ortho to OH was detected.

Example of effects of triethylamine on B_2eg_2 reaction:



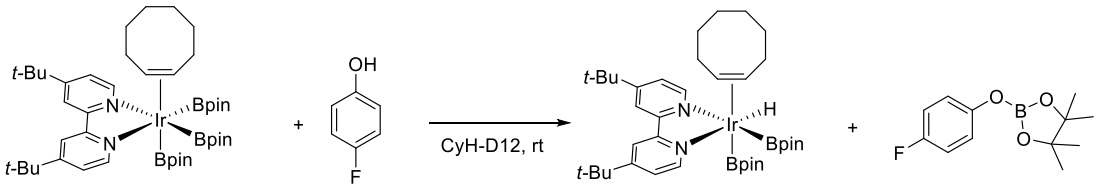
In a glovebox, a 3 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (212 mg, 1.5 equiv, 1.5 mmol), 4-fluorophenol (112 mg, 1.0 mmol), dry PhMe (2.5 mL) and Et_3N (0.209 mL, 1.5 equiv, 1.5 mmol). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 2 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture, pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min after which crude ^{19}F NMR was collected. The spectra showed full conversion and a 89:11 monoborylation:diborylation ratio.



In a glovebox, a 3 mL conical vial was charged with $[Ir(OMe)(cod)]_2$ (10 mg, 1.5 mol %, 0.015 mmol), dtbpy (8 mg, 3.0 mol %, 0.03 mmol), B_2eg_2 (212 mg, 1.5 equiv, 1.5 mmol), 4-fluorophenol (112 mg, 1.0 mmol) and dry PhMe (2.5 mL). The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C for 2 h. Solvent was evaporated under reduced pressure and dry chloroform (10 mL) was added. To this mixture,

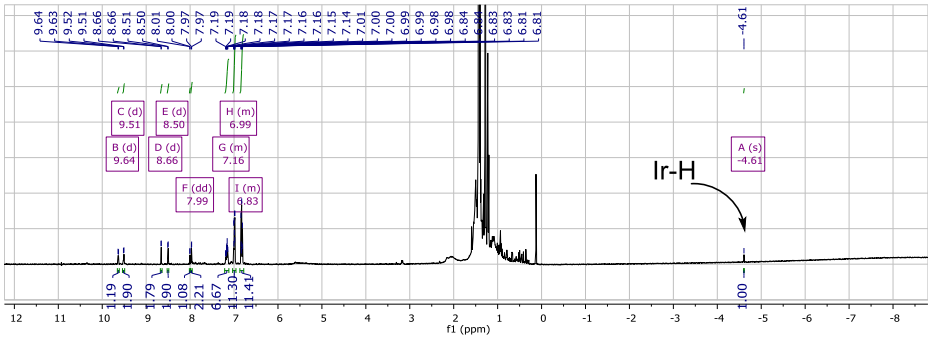
pinacol (354 mg, 3.0 equiv) was added and stirred at room temperature for 40 min after which crude ^{19}F NMR was collected. The spectra showed 35% conversion and a 85:15 monoborylation:diborylation ratio.

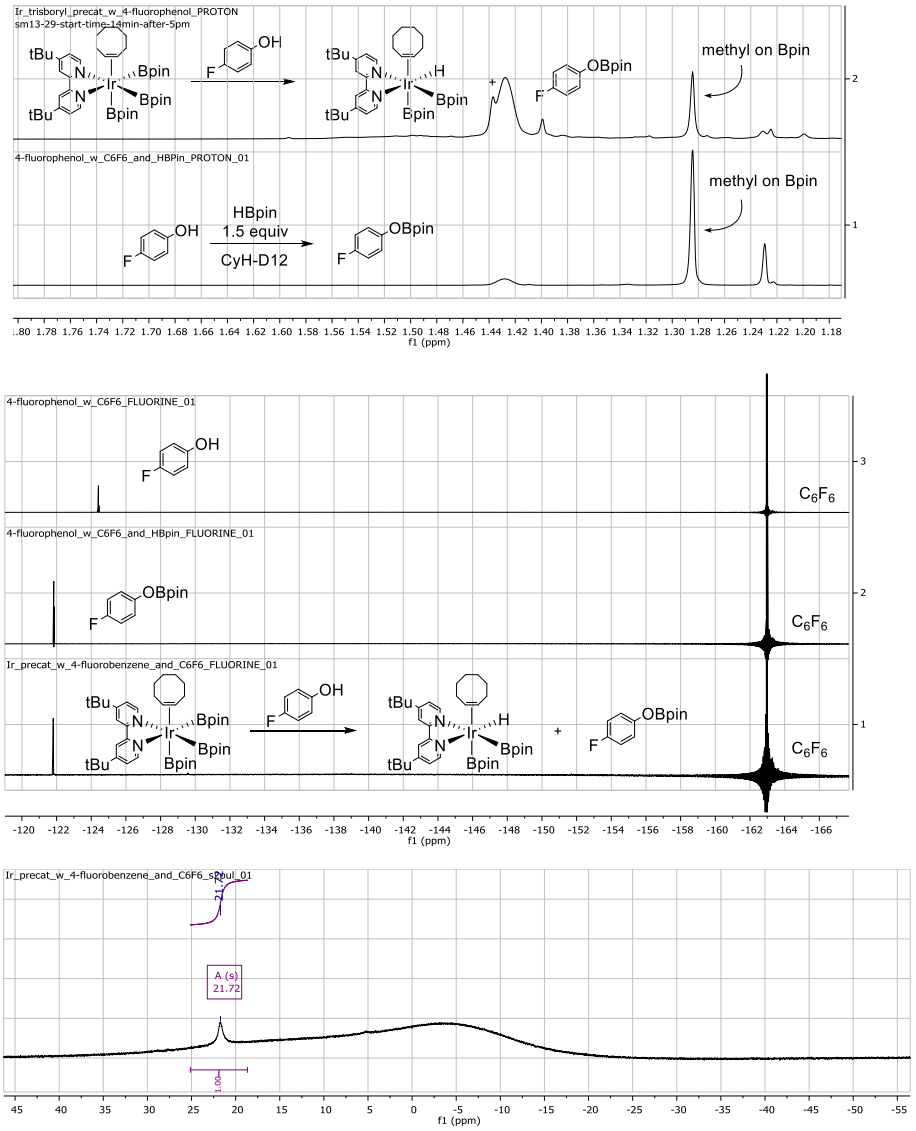
Synthesis of 2-(4-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane from 4-fluorophenol and the isolated trisboryl Ir catalyst:



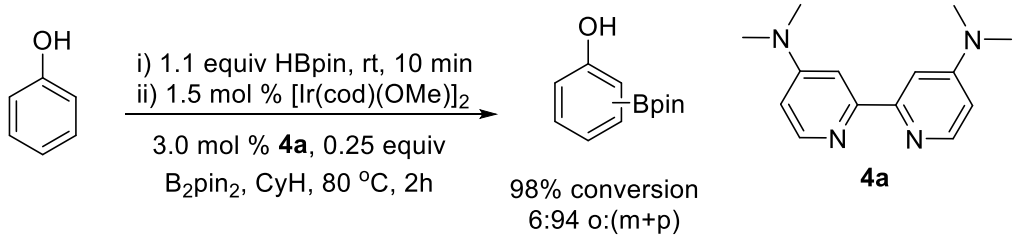
Experimental: In a glove, isolated trisboryl catalyst (0.0022g, 1 equiv) was dissolved in 0.4 mL deuterated cyclohexane and 4-fluorophenol (0.0003g, 1 equiv) was dissolved in 0.3 mL deuterated cyclohexane. The isolated trisboryl catalyst and 4-fluorophenol solutions were transferred into a J-Young tube and one drop of C_6F_6 was added as a reference. The tube was sealed with a J-Young valve and ^{19}F, ^{11}B, ^{1}H NMR were collected.

Analysis: Observed in the proton NMR, as shown below, is an iridium hydride species at -4.61 and the methyl groups on the Bpin of the phenol. The fluorine NMR shows the correct chemical shift at -121.8 ppm. Finally, the boron NMR showed the correct shift for the ArOBpin species at 21.7 ppm. Overall, this clearly demonstrates $ArOB(OR)_2$ species can form from the iridium trisboryl catalyst.





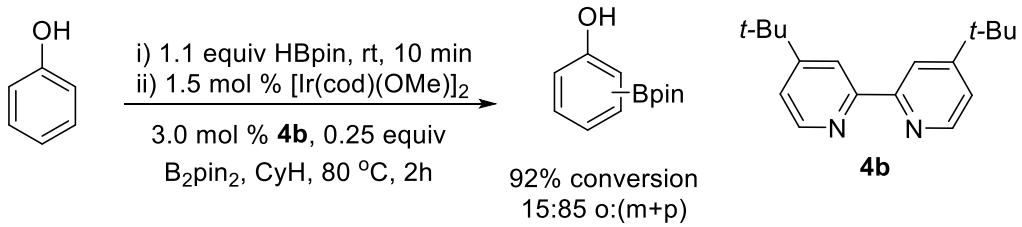
Borylation of phenol with Ligand 4a:



In a glovebox, a 5 mL conical vial was charged with phenol (188 mg, 2.0 mmol, 1.0 equiv) and pinacolborane (0.320 mL, 282 mg, 2.2 mmol, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 0.03 mmol, 1.5 mol %), 4,4'-Bis(N,N-dimethylamino)-2,2-bipyridine (**4a**) (14.5 mg, 0.06 mmol, 3.0 mol %), and B_2pin_2 (127 mg, 0.5 mmol, 0.25 equiv)

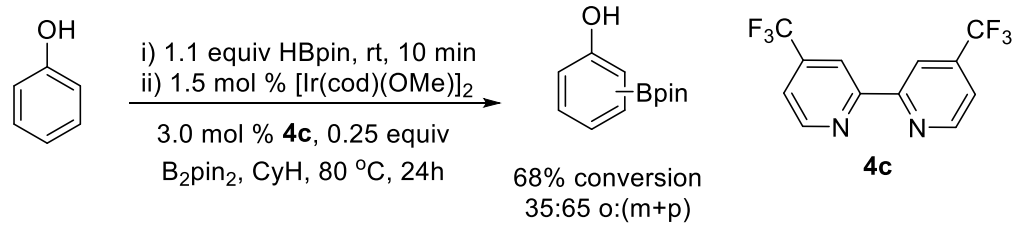
was charged. Dry cyclohexane (3 mL, 0.66 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 2 h. GC-FID showed 98% conversion (based on B_2pin_2). The ratio of products was 6:94 of o:(m+p) and 98:2 monoborylation:diborylation.

Borylation of phenol with Ligand 4b:



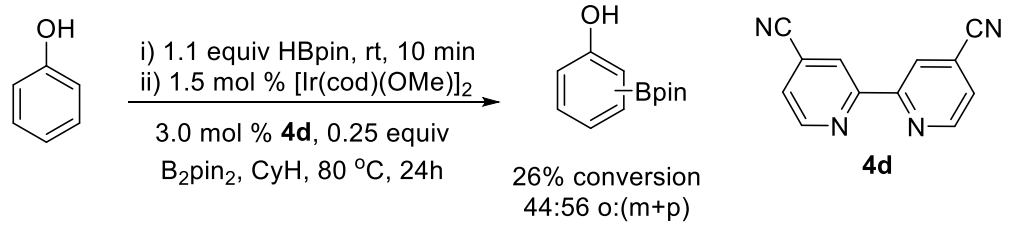
In a glovebox, a 5 mL conical vial was charged with phenol (188 mg, 2.0 mmol, 1.0 equiv) and pinacolborane (0.320 mL, 282 mg, 2.2 mmol, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 0.03 mmol, 1.5 mol %), dtbpy (**4b**) (16.1 mg, 0.06 mmol, 3.0 mol %), and B_2pin_2 (127 mg, 0.5 mmol, 0.25 equiv) was charged. Dry cyclohexane (3 mL, 0.66 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 2 h. GC-FID showed 92% conversion (based on B_2pin_2). The ratio of products was 15:85 of o:(m+p) and 98:2 monoborylation:diborylation.

Borylation of phenol with Ligand 4c:



In a glovebox, a 5 mL conical vial was charged with phenol (188 mg, 2.0 mmol, 1.0 equiv) and pinacolborane (0.320 mL, 282 mg, 2.2 mmol, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (20 mg, 0.03 mmol, 1.5 mol %), 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (**4c**) (17.5 mg, 0.06 mmol, 3.0 mol %), and B_2pin_2 (127 mg, 0.5 mmol, 0.25 equiv) was charged. Dry cyclohexane (3 mL, 0.66 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. GC-FID showed 68% conversion (based on B_2pin_2). The ratio of products was 35:65 of o:(m+p).

Borylation of phenol with Ligand 4d:



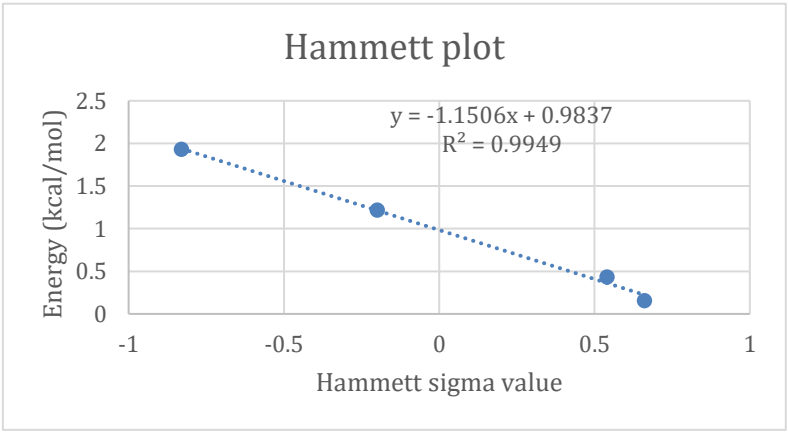
In a glovebox, a 5 mL conical vial was charged with phenol (94.1 mg, 1.0 mmol, 1.0 equiv) and pinacolborane (0.160 mL, 141 mg, 1.1 mmol, 1.1 equiv) and stirred for 5 min at room temperature. To this mixture, $[Ir(OMe)(cod)]_2$ (10 mg, 0.015 mmol, 1.5 mol %), [2,2'-bipyridine]-4,4'-dicarbonitrile (**4d**) (6.2 mg, 0.03 mmol, 3.0 mol %), and B_2pin_2 (63.5 mg, 0.25 mmol, 0.25 equiv) was charged. Dry cyclohexane (3 mL, 0.33 M) was added under an inert atmosphere. The vial was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 °C. The reaction mixture was stirred for 24 h. GC-FID showed 26% conversion (based on B_2pin_2). The ratio of products was 44:56 of o:(m+p).

Analysis:

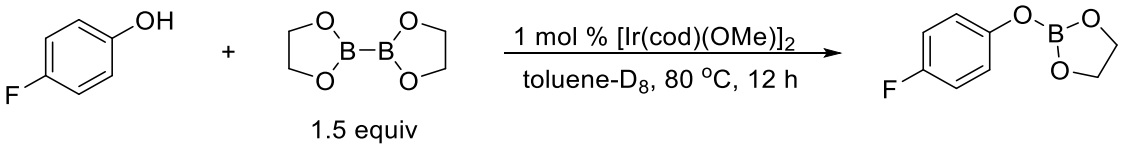
Below is a chart summing up the data and the equation used to calculate the energy. This data was graphed and a stong linear coorilation was observed.

R group	Hammett Value	ortho	meta+para	Energy at 80 (kcal/mol)
NMe2	-0.83	6	94	1.93086827
tBu	-0.2	15	85	1.217242651
CF3	0.54	35	65	0.434405897
CN	0.66	44	55	0.156589232

$$E = -RTln\left(\frac{o}{m+p}\right)$$



2-(4-fluorophenoxy)-1,3,2-dioxaborolane from 4-fluorophenol following Route B:



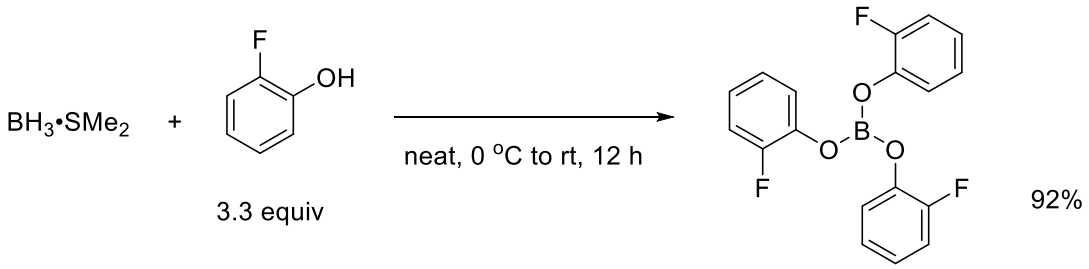
In a glove, $[Ir(OMe)(cod)]_2$ (0.0006g, 1 mol %) was dissolved in 0.05 mL deuterated toluene, 4-fluorophenol (0.0112g, 0.1 mmol, 1 equiv) was dissolved in 0.3 mL deuterated toluene, and B_2eg_2 (0.0141g, 0.1mmol, 1 equiv) was dissolved in 0.35 mL deuterated toluene then these three solutions were transferred to a J-Young tube and C_6F_6 (3 µL) was added as a reference. The tube was sealed with a J-Young valve the J-Young tube was then heated at 80 °C for 12 hours. After ~30 minutes the solution turned from a yellow to a black color and black sediment was observed. After heating ^{19}F, ^{11}B, ^{1}H NMR were collected. It should be noted that this compound was not isolated. Further evidence that this reaction produces the ArOBeg species can be found in the experiments with 2-fluorophenol.

^{1}H NMR (500 MHz, toluene-D_8): δ_H 6.79-6.84 (m, 2H), 6.57-6.63 (m, 2H), 3.83 (s)

^{11}B NMR (176 MHz, toluene-D_8): δ_B 22.6 (s).

^{19}F NMR (470 MHz, toluene-D_8): δ_F -120.80 (m)

2-(2-fluorophenoxy)-1,3,2-dioxaborolane from 2-fluorophenol Route A:



This procedure was adapted from a previous reported procedure[9]. To a flask under argon was added borane dimethylsulfide (1 mL, 10.5 mmol, 1 equiv). The flask was in an ice bath, connected to a bubbler, and 2-fluorophenol (3.1 mL, 34.7 mmol, 3.3 equiv) was added slowly. The reaction was allowed to warm to room temperature and stirred for 12 hours after which the dimethyl sulfide was distilled off via a short-path distillation head. After the distillation, the product was a solid that still contained 2-fluorophenol. To remove the excess 2-fluorophenol, the

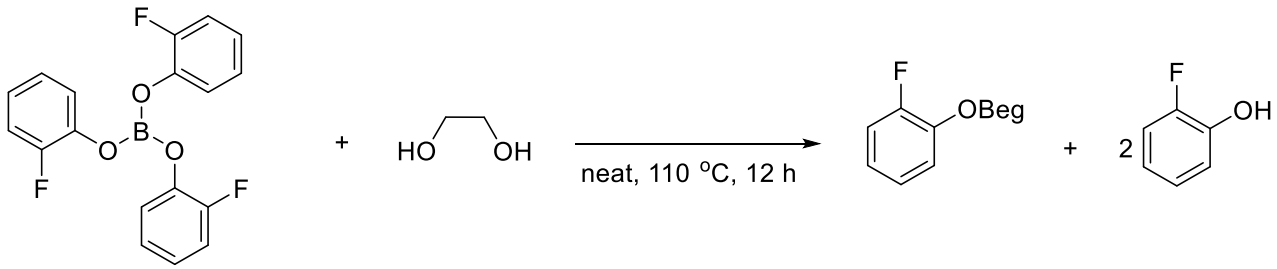
product was heated to 100 °C and exposed to vacuum (0.1 mBar). At this temperature, the product liquefies. After cooling, back to room temperature, the product was obtained in 92% yield (3.36 g).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.26-7.30 (m, 1H), 7.16-7.20 (m, 1H), 7.07-7.14 (m, 2H)

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 154.56, 152.60, 140.61, 140.52, 124.81 – 124.65 (m), 124.47 – 124.32 (m), 122.38, 116.53, 116.39

^{11}B NMR (176 MHz, $CDCl_3$): δ_B 16.47 (s).

^{19}F NMR (470 MHz, $CDCl_3$): δ_F -132.27 (m)



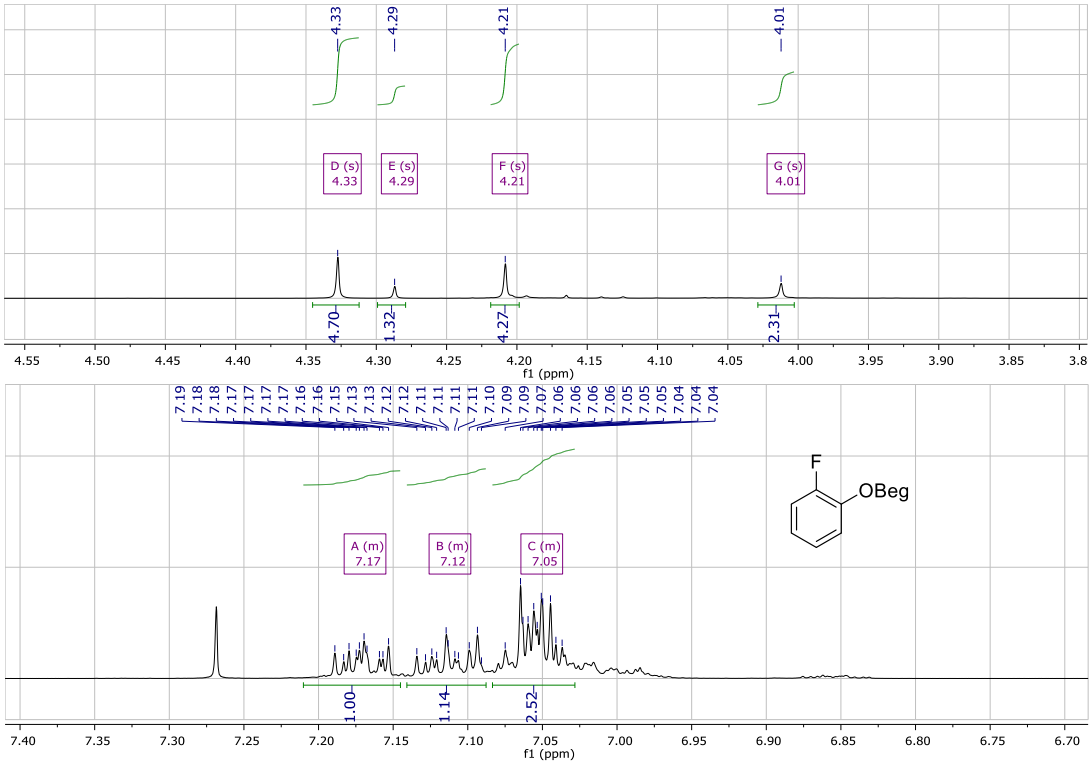
In a flask under argon was charged tris(2-fluorophenyl) borate (2.75 g, 8 mmol, 1 equiv) and ethylene glycol (0.497 g, 8 mmol, 1 equiv). The reaction mixture was heated to 110 °C in an oil bath and stirred under argon for 12 hours. The mixture was then distilled under vacuum to remove excess 2-fluorophenol. The resulting product was a yellow oil which was pure by ^{19}F NMR and ^{11}B NMR. However, the product contained extra glycol peaks in the ^{1}H NMR and could not be fully purified in our hands. The spectra are shown below.

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.15-7.19 (m, 1H), 7.09-7.13 (m, 1H), 7.04-7.07 (m, 2H), 4.33 (s, 4H)

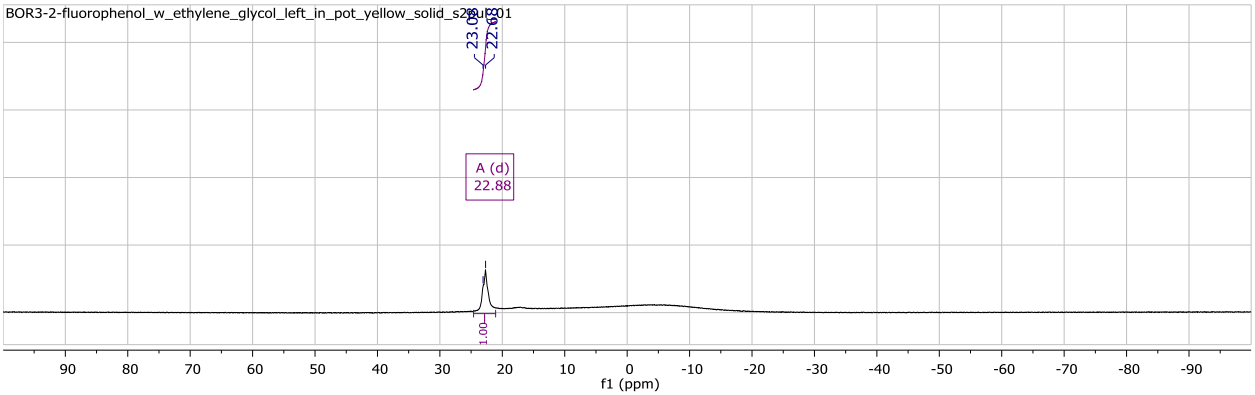
^{11}B NMR (176 MHz, $CDCl_3$): δ_B 22.88 (s).

^{19}F NMR (470 MHz, $CDCl_3$): δ_F -132.62 (m)

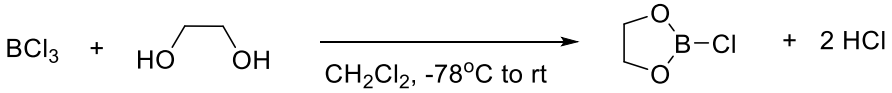
^{1}H NMR



^{11}B NMR

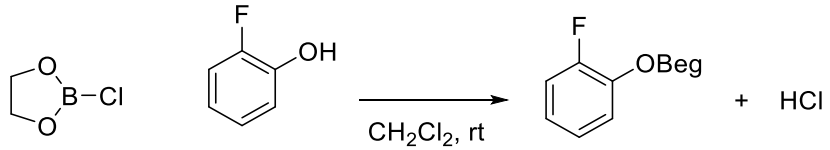


2-(2-fluorophenoxy)-1,3,2-dioxaborolane from 2-fluorophenol Route B:



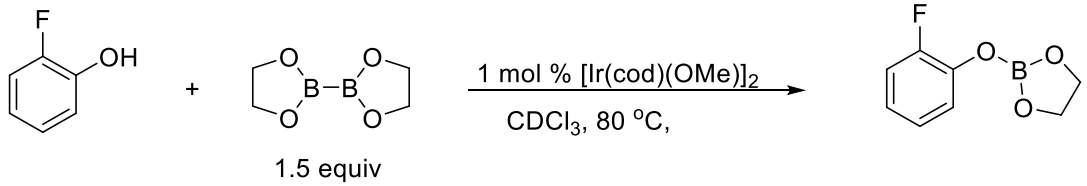
This route follows previously reported work[10]. In a flask under argon was BCl_3 (20 mL of 1 M solution in CH_2Cl_2, 20 mmol, 1 equiv) and ethylene glycol (1.24 g, 20 mmol, 1 equiv). The flask was connected to a bubbler and the ethylene glycol was added slowly at -78 ^{o}C. After addition, the reaction was allowed to stir until the bath had warmed to room temperature. The reaction mixture was then distilled under vacuum at room temperature, removing CH_2Cl_2. The resulting

product was distilled at 75 °C to give a viscus oil (0.424 g, 20%) that turned a reddish brown upon warming to room temperature. The low yield is likely due to the fact that the boron trichloride solution was no longer 1 M.



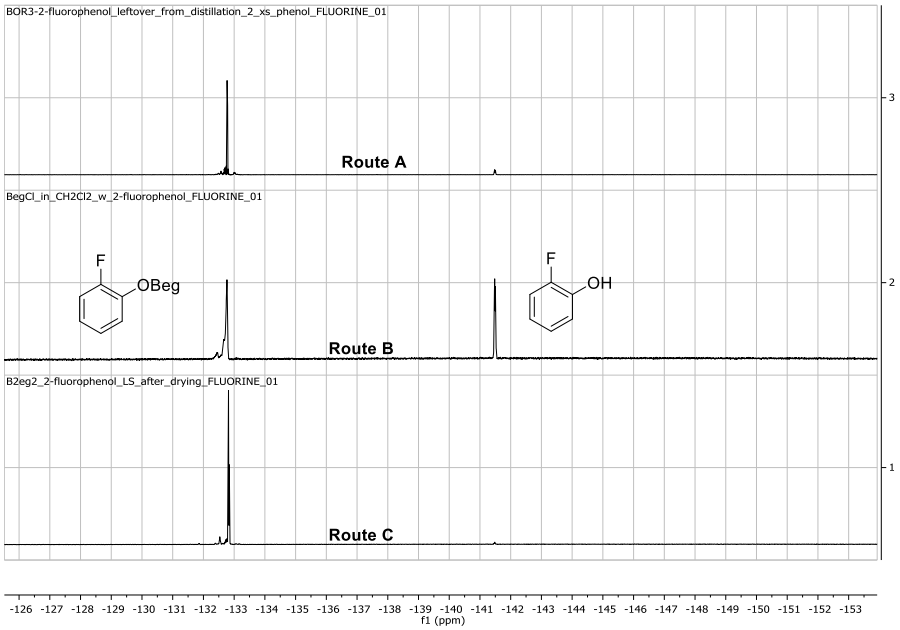
In a flask under argon was added 2-chloro-1,3,2-dioxaborolane (0.424g, 4 mmol, 1 equiv), CH_2Cl_2 (5 mL), and 2-fluorophenol (0.447g, 4mmol, 1 equiv) dropwise at room temperature. The reaction mixture was sampled for NMR without isolation. ^{19}F, ^{11}B, ^{1}H NMR were collected. It should be noted that this compound was not isolated.

2-(2-fluorophenoxy)-1,3,2-dioxaborolane from 2-fluorophenol Route C:



In a glove, $[Ir(OMe)(cod)]_2$ (0.0006g, 1 mol %) was dissolved in 0.05 mL deuterated chloroform, 2-fluorophenol (0.0112g, 0.1 mmol, 1 equiv) was dissolved in 0.3 mL deuterated chloroform, and B_2eg_2 (0.0141g, 0.1mmol, 1 equiv) was dissolved in 0.35 mL deuterated chloroform then these three solutions were transferred to a J-Young tube and C_6F_6 (3 µL) was added as a reference. The tube was sealed with a J-Young valve the J-Young tube was then heated at 80 °C for 12 hours. After ~30 minutes the solution turned from a yellow to a black color and black sediment was observed. After heating ^{19}F, ^{11}B, ^{1}H NMR were collected. It should be noted that this compound was not isolated.

Comparison between route A and B to 2-(2-fluorophenoxy)-1,3,2-dioxaborolane



Computational Procedures and Results

General

Calculations of structures, energies, and frequencies employed default procedures in Gaussian09[11,12,13] unless otherwise noted. Complete structures and energetics are provided in sections below. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol.

NPA charges were calculated with NBO 5.9.[14]

Guide to Structures, Structure Titles and Their Organization

The sections below are divided into reactants and transition structures, then divided into specific structures and given a descriptive title. The first line after the title for a structure is a file name for the original calculation file, so that this file can always be located even if the file title changes. The second line after the title shows the method and basis set. The basis sets "6-31G*" and "6-31+G**" were used as their 5D formulation. For "gen" basis sets, refer to the title description for BS1 versus BSsmall. "BS1" means that the iridium atom was given an SDD basis, while the remaining atoms were given a 6-31+G** basis set. "BSsmall" means that the iridium atom was given an SDD basis, while the remaining atoms were given a 6-31G* basis set.

Alternative conformations for important structures are given, along with a short explanation, with labels such as "Conf B". Alternative conformations for less important structures were obtained but are not included here.

It should be noted that in the case of the structures containing the Bpin' group, the lowest-energy structures were not modeled. Rather, structures were chosen that would include the steric interactions present with the full Bpin group.

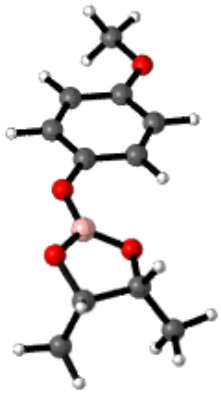
Calculated Structures, Energies, and Selected NPA Charges

Reactants:

4-MeO-C_6H_4OBpin' M06/6-31+G (3)**
MeOPhOBpinprimeM06PS
M06/6-31+G**
E(RM06) = -753.634700207

Zero-point correction= 0.253860 (Hartree/Particle)
Thermal correction to Energy= 0.267961
Thermal correction to Enthalpy= 0.268905
Thermal correction to Gibbs Free Energy= 0.212837
Sum of electronic and ZPE= -753.380840
Sum of electronic and thermal Energies= -753.366739
Sum of electronic and thermal Enthalpies= -753.365795
Sum of electronic and thermal Free Energies= -753.421863

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	168.148	55.651	118.005



C,0,0.8989574659,0.04675157,-1.2528236824
C,0,0.147143111,0.1420022159,-0.0894033793
C,0,0.7797232518,0.0740133624,1.153879395
C,0,2.1556642021,-0.0927360474,1.213870955
C,0,2.9156662173,-0.193500707,0.0462397102
C,0,2.281038254,-0.1233342107,-1.1944523496
B,0,-2.1972793913,0.1988215786,0.6560508735
O,0,-2.0720714699,-0.2448591683,1.9522671682
C,0,-3.3523459901,-0.0416729816,2.5702695706
C,0,-4.3226602953,0.0302616351,1.3737083774
O,0,-3.489971759,0.504499287,0.3100543971
C,0,-4.9448597992,-1.2858673487,0.9605237132
H,0,-5.1048369947,0.7791788472,1.5561270504
H,0,-3.321650894,0.9464845268,3.0576723802
C,0,-3.6125201939,-1.1063594599,3.6031111688
H,0,0.1954779439,0.1427025846,2.0661936029
H,0,2.6689036733,-0.1486676044,2.1708643992
O,0,4.2561818668,-0.3567643838,0.2184561241
H,0,2.8434880167,-0.1968272326,-2.1206776068
H,0,0.3867903425,0.1086675615,-2.2099337028
O,0,-1.2016976858,0.3322974235,-0.2511374308
H,0,-5.6471226071,-1.6570626456,1.7159535436
H,0,-5.4882734114,-1.1518053506,0.0201685962
H,0,-4.1717181058,-2.048116592,0.7988636411
H,0,-2.8542415077,-1.0586443948,4.3908437469
H,0,-4.596103354,-0.9638965788,4.0667167182
H,0,-3.576536222,-2.1061307352,3.1569519391
C,0,5.0548242612,-0.4767511146,-0.9330270354
H,0,6.0835984256,-0.5935424629,-0.5863129735
H,0,4.7730559866,-1.3575107137,-1.5287183578
H,0,4.9885746627,0.4204641401,-1.5658245525

4-MeO-C_6H_4OBpin' M06/6-31G* (3)
MeOPhOBpinprimeM06SB
M06/6-31G*
E(RM06) = -753.592046918

Zero-point correction= 0.255470 (Hartree/Particle)
Thermal correction to Energy= 0.270366
Thermal correction to Enthalpy= 0.271310
Thermal correction to Gibbs Free Energy= 0.211998
Sum of electronic and ZPE= -753.336577
Sum of electronic and thermal Energies= -753.321681
Sum of electronic and thermal Enthalpies= -753.320737
Sum of electronic and thermal Free Energies= -753.380049

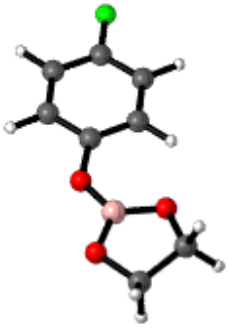
	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	169.657	57.193	124.831

C,0,0.8747774221,0.0088138081,-1.2385701465
C,0,0.1360719232,0.2037328314,-0.0798276431
C,0,0.7799555824,0.2171098778,1.1584454789
C,0,2.1508460814,0.026550814,1.2186764748
C,0,2.8980997939,-0.1747570698,0.0559974198
C,0,2.2524837197,-0.1819041538,-1.1797593432
B,0,-2.1973888152,0.2417507813,0.6676592578
O,0,-2.0575074242,-0.2500796355,1.9436105073
C,0,-3.3305541474,-0.0761560441,2.5764281788
C,0,-4.3101520839,0.039675822,1.3908261121
O,0,-3.4911801659,0.5576827718,0.3417832092
C,0,-4.9259073437,-1.2638635438,0.930457812
H,0,-5.0977650826,0.77466331,1.6091949449
H,0,-3.303383084,0.8915704284,3.1055886022
C,0,-3.5777815934,-1.1840022239,3.5673828847
H,0,0.2053203954,0.3660764677,2.0681642402
H,0,2.6750233928,0.0322175465,2.1724561333
O,0,4.2347796131,-0.3524414377,0.2310663836
H,0,2.8059058824,-0.3340357167,-2.1030769348
H,0,0.3532498384,0.0100333698,-2.1937112326
O,0,-1.2088109288,0.4156175841,-0.24063455
H,0,-5.6257335193,-1.6696018618,1.6719080663
H,0,-5.4701506443,-1.0993878456,-0.0060958567
H,0,-4.1457320846,-2.0140924012,0.7400413153
H,0,-2.8144828499,-1.1629141176,4.3533803059
H,0,-4.5608685196,-1.0710057412,4.0426703873
H,0,-3.5337808713,-2.1657759073,3.0813284388
C,0,5.02069274,-0.5296510024,-0.9173126076
H,0,6.0529677434,-0.640556183,-0.5744372205
H,0,4.7289689949,-1.4326876604,-1.4763973618
H,0,4.957234035,0.3395121331,-1.5907672566

4-F-C_6H_4OBeg M06/6-31+G**
pFPhOBegM06PS
M06/6-31+G**
E(RM06) = -659.807029462

Zero-point correction= 0.157604 (Hartree/Particle)
Thermal correction to Energy= 0.168384
Thermal correction to Enthalpy= 0.169328
Thermal correction to Gibbs Free Energy= 0.118827
Sum of electronic and ZPE= -659.649425
Sum of electronic and thermal Energies= -659.638646
Sum of electronic and thermal Enthalpies= -659.637701
Sum of electronic and thermal Free Energies= -659.688203

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	105.662	40.352	106.288



C,0,1.3598666814,1.714778561,-1.5472203797
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C,0,3.6953658017,1.4270035763,-1.0948937266
C,0,3.7082877172,2.5345330629,-0.2616070565
C,0,2.5253961893,3.2381074405,-0.0717265177
C,0,1.3547237096,2.8299793695,-0.7102211815
F,0,4.8384961115,0.7401591254,-1.2838816112
O,0,0.2454532531,3.5917500885,-0.45999687
B,0,-1.0352785675,3.4152682273,-0.8628633734
O,0,-1.5044358381,2.4174249292,-1.6851934107
C,0,-2.9251026767,2.5416394605,-1.7172129857
C,0,-3.2012820295,3.9382198488,-1.1423768757
O,0,-2.0106667214,4.2828297056,-0.4465640645
H,0,2.5799587486,0.1340445037,-2.3843164931
H,0,4.6321464033,2.8325842198,0.2257839224
H,0,2.488477073,4.1127612439,0.5722091666
H,0,-3.3819092294,4.6817385642,-1.9301593551
H,0,-4.0499155876,3.9547729178,-0.4508208509
H,0,-3.3612390382,1.7438185463,-1.1020972688
H,0,-3.2791635372,2.420687702,-2.7459258146
H,0,0.4485484214,1.400272523,-2.0446782849

4-F-C$_6$H$_4$OBeg M06/6-31G*
FPhOBeg
M06/6-31G* with ultrafine grid
E(RM06) = -659.770268208

Zero-point correction= 0.158255 (Hartree/Particle)
Thermal correction to Energy= 0.169057
Thermal correction to Enthalpy= 0.170001
Thermal correction to Gibbs Free Energy= 0.119105
Sum of electronic and ZPE= -659.612013
Sum of electronic and thermal Energies= -659.601211
Sum of electronic and thermal Enthalpies= -659.600267
Sum of electronic and thermal Free Energies= -659.651163

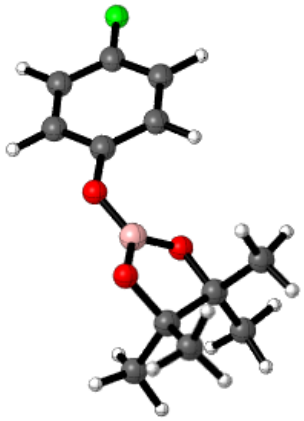
	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	106.085	40.185	107.120

C,0,1.3945375918,1.8285285449,-1.6838374867
C,0,2.5602509421,1.083825301,-1.8323626913
C,0,3.6758082436,1.4061660193,-1.0781647546
C,0,3.6630346293,2.4574856908,-0.1748389782
C,0,2.499043982,3.1991522201,-0.0267814409
C,0,1.3663216693,2.8848231647,-0.7750776405
F,0,4.7946780634,0.6862629708,-1.225562134
O,0,0.2756195208,3.6863790958,-0.575847866
B,0,-1.0161224662,3.4578297504,-0.9123534728
O,0,-1.50351012,2.3526009144,-1.5660111882
C,0,-2.9197117672,2.4735356294,-1.5817039763
C,0,-3.1898749047,3.9323152411,-1.1787985793
O,0,-1.9777872596,4.3789440505,-0.5960144407
H,0,2.6120833385,0.2529971319,-2.5321285674
H,0,4.5587104413,2.6831661559,0.3987963588
H,0,2.4469664161,4.0337696117,0.6688992634
H,0,-3.4260212191,4.5641690132,-2.0472601419
H,0,-4.0072242137,4.0295571739,-0.4542724168
H,0,-3.3451696107,1.7574616944,-0.8645276452
H,0,-3.2987062248,2.2252674576,-2.5800632646
H,0,0.5097649482,1.5855161683,-2.264872937

4-F-C$_6$H$_4$OBpin M06/6-31+G**
pFPhOBPINrM06PS
M06/6-31+G**
E(RM06) = -816.965258089

Zero-point correction= 0.268270 (Hartree/Particle)
Thermal correction to Energy= 0.284168
Thermal correction to Enthalpy= 0.285112
Thermal correction to Gibbs Free Energy= 0.224703
Sum of electronic and ZPE= -816.696988
Sum of electronic and thermal Energies= -816.681091
Sum of electronic and thermal Enthalpies= -816.680146
Sum of electronic and thermal Free Energies= -816.740555

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	178.318	63.299	127.141



C,0,1.3113529024,1.5205835616,-1.3280876739
C,0,2.552358047,1.0802699327,-1.7781183977
C,0,3.6974899786,1.6807852908,-1.2818861015
C,0,3.6474023102,2.7040274395,-0.3495372323

C,0,2.4042113473,3.1413886274,0.0951052399
C,0,1.240521335,2.5569666925,-0.3986096007
F,0,4.8979334084,1.2538992845,-1.7194793262
O,0,0.0511522748,3.0013935726,0.1137027324
B,0,-1.0944119708,3.1638832652,-0.6016402162
O,0,-1.1914423981,3.0808424051,-1.9672369749
C,0,-2.6059079235,3.0707301946,-2.2690089317
C,0,-3.2161996147,3.7881866977,-1.0218214946
O,0,-2.27956574,3.4434567612,0.0219482739
H,0,2.638985579,0.2778070797,-2.5053107756
H,0,4.5705224362,3.1436571265,0.0174802413
H,0,2.3183511341,3.9381313147,0.8293504742
C,0,-3.211696971,5.3049367752,-1.143444443
C,0,-4.5932744318,3.3009582781,-0.6219097537
C,0,-3.0180664446,1.6099515155,-2.3827735989
C,0,-2.8286985103,3.7797940689,-3.5878079683
H,0,0.3971202568,1.0709776017,-1.7070970401
H,0,-4.9390524394,3.859323641,0.2550411286
H,0,-5.3134077442,3.4639092458,-1.4341835954
H,0,-4.588804932,2.2381219799,-0.3629166898
H,0,-3.4560188455,5.7355388728,-0.1662657599
H,0,-2.2270923224,5.6826646057,-1.4430066066
H,0,-3.9545825991,5.6541697602,-1.8704326764
H,0,-3.9012523454,3.865702324,-3.8050882275
H,0,-2.3881214492,4.780935561,-3.5896750492
H,0,-2.363967761,3.2055045153,-4.3970114646
H,0,-4.0665444845,1.5060888859,-2.6860673184
H,0,-2.3926681988,1.1283287435,-3.1432772757
H,0,-2.8767248835,1.0739953792,-1.4361728976

4-F-C$_6$H$_4$OBpin M06/6-31G*

FPhOBpinrM06SB
M06/6-31G*
E(RM06) = -816.916040347

Zero-point correction= 0.269582 (Hartree/Particle)
Thermal correction to Energy= 0.285516
Thermal correction to Enthalpy= 0.286460
Thermal correction to Gibbs Free Energy= 0.224280
Sum of electronic and ZPE= -816.646458
Sum of electronic and thermal Energies= -816.630524
Sum of electronic and thermal Enthalpies= -816.629580
Sum of electronic and thermal Free Energies= -816.691760

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	179.164	63.046	130.869

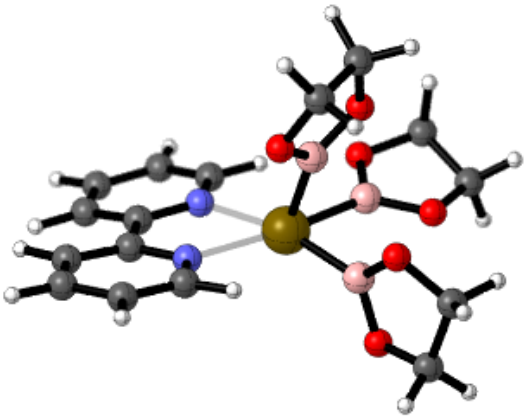
C,0,1.6140981727,2.4483414201,-1.8641145904
C,0,2.8761069565,1.9881362459,-2.2266412086
C,0,3.8192626177,1.7370023393,-1.2445935013
C,0,3.5389051341,1.9338492271,0.0986100565
C,0,2.2794417272,2.3920713703,0.4592034099
C,0,1.3168504358,2.6463994847,-0.5163395443
F,0,5.0318809535,1.2945954038,-1.6005193389
O,0,0.1155988205,3.1128149747,-0.0603945436
B,0,-1.0676078249,3.2060920498,-0.7193559525
O,0,-1.2940461351,2.8936638382,-2.0372066522
C,0,-2.7285532996,2.9127855006,-2.2111017857
C,0,-3.1848507742,3.8713703728,-1.0684078667
O,0,-2.1822332045,3.6485689138,-0.0598182958
H,0,3.1365371714,1.8232732036,-3.2696366342
H,0,4.304678786,1.7279823543,0.8426210985
H,0,2.018839622,2.562004695,1.5015909706
C,0,-3.105925745,5.3407509526,-1.4576127653
C,0,-4.5475563178,3.5609070577,-0.4856686777
C,0,-3.2144735786,1.483699401,-2.0209875512
C,0,-3.0468470646,3.3902961257,-3.6118528066
H,0,0.8617283092,2.6465760772,-2.6217546956
H,0,-4.783274219,4.2828472212,0.3059421694
H,0,-5.3263283609,3.6368600836,-1.2574457969
H,0,-4.5833847329,2.558060551,-0.0472935026
H,0,-3.2243072621,5.9507160191,-0.5539885622
H,0,-2.1338987109,5.5862056737,-1.9049931574
H,0,-3.896073604,5.6173525576,-2.1676284205
H,0,-4.1321264651,3.501516229,-3.7442563678
H,0,-2.5671374051,4.3493701612,-3.834069308
H,0,-2.690953561,2.6555355321,-4.3448356694
H,0,-4.2903431849,1.3917616907,-2.2179303947
H,0,-2.6792115307,0.8312758186,-2.7215134082
H,0,-3.0148967255,1.1242284542,-1.0032457066

(bpy)Ir(Beg)$_3$ M06/BS1

hartwigbpyIrBeg3
M06/gen
E(RM06) = -1361.09051610

Zero-point correction= 0.370807 (Hartree/Particle)
Thermal correction to Energy= 0.396820
Thermal correction to Enthalpy= 0.397764
Thermal correction to Gibbs Free Energy= 0.312274
Sum of electronic and ZPE= -1360.719709
Sum of electronic and thermal Energies= -1360.693696
Sum of electronic and thermal Enthalpies= -1360.692752
Sum of electronic and thermal Free Energies= -1360.778242

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	249.008	96.269	179.929



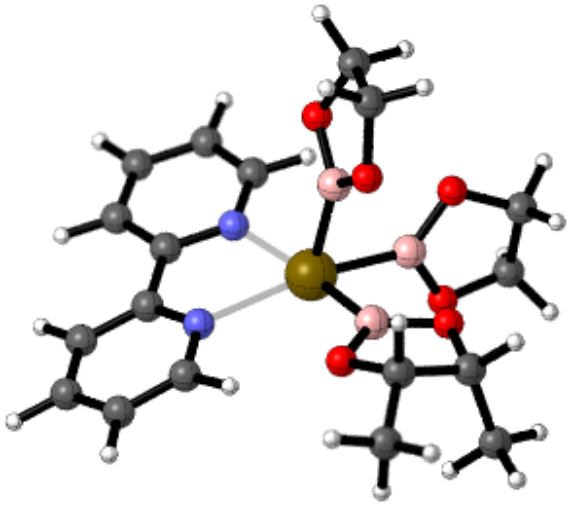
B,0,1.692786538,12.8875448334,5.6407656346
B,0,1.9813407921,11.0298443329,3.7297630086
B,0,2.5173353617,10.5405820385,6.2661351842
C,0,-0.313858819,11.4863345859,8.3591765148
H,0,0.7578461528,11.4258263238,8.536344993
C,0,-1.2139960623,11.7020569535,9.3945373931
H,0,-0.8554876842,11.8022225559,10.4145743272
C,0,-2.5663027972,11.7930745875,9.086367329
C,0,-2.9677323752,11.6680411218,7.7627857913

C,0,-2.0055334431,11.4458336439,6.7760237953
C,0,-2.3443384128,11.3246805757,5.3389888575
C,0,-3.6597886399,11.2669859103,4.877493239
H,0,-4.4937107382,11.2768093166,5.5730802863
C,0,-3.8982838978,11.1824670144,3.5117633314
C,0,-2.8193721186,11.1636806168,2.6362122535
H,0,-2.9611748436,11.1070408649,1.5610692923
C,0,-1.5341434789,11.2137389003,3.1644467089
H,0,-0.641687234,11.210616385,2.5372942534
C,0,2.8456097582,14.8196181405,5.3001008243
C,0,2.4661738637,14.6921788455,6.776041294
C,0,3.721511406,10.674745681,2.2824305398
C,0,2.6229038522,11.4663456143,1.5761223675
C,0,4.6495345825,10.4053582545,7.0468070627
C,0,3.9951349957,9.0272958918,7.1353288773
Ir,0,0.8049060841,11.1320867066,5.382676982
N,0,-0.6976375434,11.3548694517,7.0856429012
N,0,-1.303435399,11.28464317,4.4814613811
O,0,2.5223113011,13.5545856727,4.7468952648
O,0,1.5077292852,13.6453799433,6.7996429221
O,0,3.325246147,10.6691859361,3.6422147631
O,0,1.5055506585,11.3549988938,2.4456980143
O,0,3.564516933,11.2883921813,6.8107521722
O,0,2.7735711824,9.1765045249,6.4302732749
H,0,-4.0190809885,11.7588583445,7.5064017687
H,0,-4.9181772896,11.1331424297,3.1381252705
H,0,-3.3037344439,11.9669904327,9.8659669906
H,0,3.9106673422,15.0304681471,5.1475994242
H,0,2.0303885932,15.6086920765,7.1919229211
H,0,2.260272192,15.6002563754,4.7902101051
H,0,3.3297327658,14.4000872858,7.3923367112
H,0,5.1779455984,10.6965289354,7.9628417092
H,0,3.7842218503,8.7369388026,8.176870744
H,0,3.7832275041,9.6382493623,1.9159221903
H,0,2.3702681998,11.0699632013,0.5850799403
H,0,4.7122539856,11.1346044837,2.1837074623
H,0,2.8891374413,12.5289093149,1.4724844531
H,0,5.3505372492,10.4673992771,6.2006598375
H,0,4.5984865931,8.2362790618,6.6737666376

(bpy)Ir(Beg)$_2$(Bpin') M06/BSsmall
bypIRBeg2BpinprimeM06SB
M06/gen
E(RM06) = -1439.60530524

Zero-point correction= 0.428507 (Hartree/Particle)
Thermal correction to Energy= 0.457180
Thermal correction to Enthalpy= 0.458124
Thermal correction to Gibbs Free Energy= 0.366862
Sum of electronic and ZPE= -1439.176799
Sum of electronic and thermal Energies= -1439.148125
Sum of electronic and thermal Enthalpies= -1439.147181
Sum of electronic and thermal Free Energies= -1439.238443

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	286.885	106.972	192.077



B,0,1.7292028143,12.8794869661,5.6177213404
B,0,1.9828687113,10.9924072899,3.7534100062
B,0,2.5122670622,10.5715560996,6.2906498292
C,0,-0.3305631132,11.6179680635,8.355687241
H,0,0.7436274806,11.6093684422,8.5303988905
C,0,-1.2389279101,11.8494695936,9.3797482848
H,0,-0.8854428638,12.016097121,10.3939230327
C,0,-2.5925335339,11.8695331394,9.0698441354
C,0,-2.9884689129,11.6617175927,7.7559350467
C,0,-2.0188351467,11.4297620414,6.7804739034
C,0,-2.3511970005,11.2289204694,5.3513933961
C,0,-3.6607354299,11.0849074062,4.8953429955
H,0,-4.4942275743,11.0738360368,5.5930651128
C,0,-3.8945596561,10.9424631032,3.5344646341
C,0,-2.8178054615,10.9509761138,2.6579764591
H,0,-2.9580593013,10.8521707973,1.5845177477
C,0,-1.5368371807,11.081625397,3.1814531143
H,0,-0.6439271763,11.096868748,2.5544673045
C,0,2.9368193346,14.7661970532,5.2403861523
C,0,2.5725336914,14.6612756511,6.7221238379
C,0,3.7340146658,10.5719051112,2.3346689648
C,0,2.6458455262,11.370992553,1.6017745808
C,0,4.6431022825,10.4729840244,7.0706777069
C,0,4.0312684054,9.0708178518,7.1003115071
Ir,0,0.8007923544,11.1424236928,5.3968949342
N,0,-0.7086431741,11.4077630145,7.0918701411
N,0,-1.3100154545,11.2093924036,4.4938370398
O,0,2.5553779653,13.515655717,4.6991596892
O,0,1.5743866924,13.6586490375,6.7655348106
O,0,3.3393972124,10.6743683255,3.6956766643
O,0,1.5101761779,11.2356355253,2.451822982
O,0,3.5413645077,11.3332022032,6.8508888606
O,0,2.7931087498,9.2114191872,6.4319165246
H,0,-4.0431852962,11.7004848042,7.4961854645
H,0,-4.9117959329,10.8281887646,3.1648308369
H,0,-3.3373146639,12.0534705754,9.8416291827
H,0,4.0087171988,14.9339780609,5.0745207238
H,0,2.1871155889,15.5994957208,7.1421457453
H,0,2.3803246483,15.5710988427,4.7333789723
H,0,3.4346997897,14.3327553405,7.3240032786
H,0,5.1526754802,10.7435047002,8.005143512
H,0,3.858270685,8.7166020837,8.1298134033
C,0,3.833348728,9.1072463928,1.9579040043
C,0,2.3134767367,10.9422327345,0.1940812472

H,0,4.7154844886,11.0556528809,2.2151544149
H,0,2.9376962102,12.4364051772,1.6054447768
H,0,5.35868521,10.5848428477,6.2408518238
H,0,4.6518918045,8.3254143862,6.5853488015
H,0,4.5124978392,8.5998473597,2.6531595784
H,0,2.8508878793,8.6215801921,2.0397829585
H,0,4.2118201956,8.9671376682,0.9364224366
H,0,1.5208689929,11.57805572,-0.2185116115
H,0,3.1911316078,11.0251963796,-0.4611910083
H,0,1.9614770648,9.9030675958,0.172548588

(bpy)Ir(Beg)$_2$(Bpin') M06/BS1
bypIRBeg2BpinprimeM06PS
M06/gen
E(RM06) = -1439.66858895

Zero-point correction= 0.426348 (Hartree/Particle)
Thermal correction to Energy= 0.455049
Thermal correction to Enthalpy= 0.455994
Thermal correction to Gibbs Free Energy= 0.365325
Sum of electronic and ZPE= -1439.242241
Sum of electronic and thermal Energies= -1439.213540
Sum of electronic and thermal Enthalpies= -1439.212595
Sum of electronic and thermal Free Energies= -1439.303264

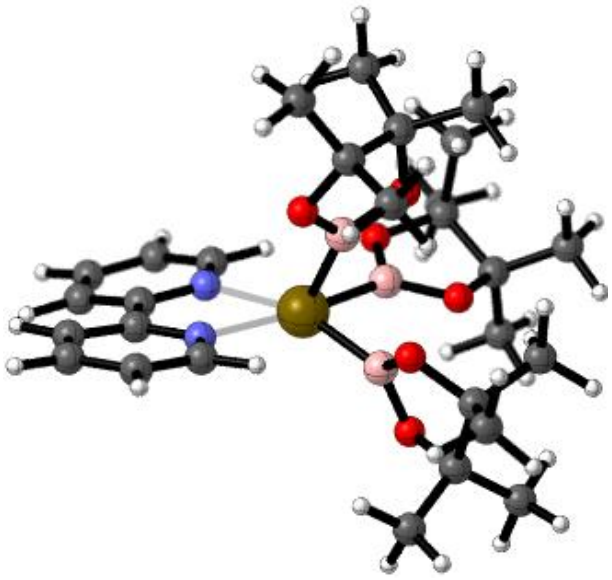
	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	285.548	107.503	190.828

B,0,1.708738587,12.8786923147,5.5963203156
B,0,1.9979558507,10.9676236296,3.7441294316
B,0,2.5402411653,10.5796465499,6.3047574858
C,0,-0.309034201,11.5540828632,8.3621601343
H,0,0.7634861549,11.533598095,8.5429954138
C,0,-1.2180972074,11.7718539863,9.3895387956
H,0,-0.8647947396,11.9188687031,10.405728112
C,0,-2.5724170684,11.8022456802,9.0785211538
C,0,-2.9671066281,11.6195614997,7.7597566827
C,0,-1.9958659297,11.4038583228,6.7804962777
C,0,-2.3295368768,11.2344050427,5.3469408724
C,0,-3.6432655882,11.1385087658,4.886333207
H,0,-4.4784146975,11.1493873821,5.5802298066
C,0,-3.8790019523,11.019857265,3.522621428
C,0,-2.7991379252,11.0055854627,2.6481937949
H,0,-2.9390311985,10.9248055455,1.574205832
C,0,-1.5156371391,11.0924345966,3.1759392147
H,0,-0.6237600248,11.0914764809,2.5484874113
C,0,2.8863053172,14.7888307001,5.2208878817
C,0,2.5172342471,14.6821731052,6.7011432925
C,0,3.7315498582,10.5201309369,2.3032168183
C,0,2.6625088531,11.3631259324,1.5912646839
C,0,4.6783358293,10.4908552201,7.0772321654
C,0,4.0221991776,9.1233943199,7.2611254179
Ir,0,0.8227334328,11.1152869642,5.3946822829
N,0,-0.6859146006,11.368942824,7.0931569567
N,0,-1.2874321809,11.1962767815,4.4910738173
O,0,2.5347283696,13.5238436442,4.6839911163
O,0,1.5315998965,13.6619129802,6.7398871134
O,0,3.343852731,10.6075666922,3.6707664483
O,0,1.5264094102,11.243458085,2.4470844897
O,0,3.5925416124,11.3588360288,6.7953661688
O,0,2.796179502,9.2282306014,6.5557157611
H,0,-4.0208411979,11.6619039697,7.5011493839
H,0,-4.8974211993,10.9424777113,3.1498108801
H,0,-3.316702665,11.9738197888,9.8521540254
H,0,3.9541464592,14.9770193448,5.058022682
H,0,2.1120912396,15.6129132841,7.1162027824
H,0,2.3120029162,15.575178999,4.7072222577
H,0,3.3784230346,14.364784555,7.3083049858
H,0,5.2161229811,10.838792212,7.9676151936
H,0,3.8171540573,8.9040087163,8.3210553778
C,0,3.7953878682,9.061729745,1.8954091239
C,0,2.3118186598,10.9733499011,0.1768795085
H,0,4.7232560748,10.9831246895,2.191895763
H,0,2.9823466173,12.4193686328,1.6155869238
H,0,5.3715508405,10.4964034238,6.2222453296
H,0,4.6201863425,8.3008845265,6.8503551477
H,0,4.4736541089,8.5267900018,2.5682619593
H,0,2.8057239849,8.5939678412,1.9782124116
H,0,4.158711119,8.9394506042,0.867377184
H,0,1.5402454091,11.6426056534,-0.2188301844
H,0,3.1898958463,11.0429836792,-0.4776165859
H,0,1.9282444662,9.9471597184,0.1354000661

(bpy)Ir(Bpin)$_3$ M06/BSsmall
bpyIrBPIN3M06SB
M06/gen
E(RM06) = -1832.47310358

Zero-point correction= 0.706376 (Hartree/Particle)
Thermal correction to Energy= 0.748008
Thermal correction to Enthalpy= 0.748952
Thermal correction to Gibbs Free Energy= 0.633777
Sum of electronic and ZPE= -1831.766728
Sum of electronic and thermal Energies= -1831.725095
Sum of electronic and thermal Enthalpies= -1831.724151
Sum of electronic and thermal Free Energies= -1831.839326

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	469.382	164.337	242.407



B,0,1.7486487866,12.8651667202,5.6436466567

B,0,1.9830539063,11.0359387379,3.6889461925
B,0,2.4691757191,10.5218527746,6.3058612124
C,0,-0.3090934882,11.5581839099,8.317279416
H,0,0.7663765691,11.5533320052,8.4936564246
C,0,-1.2197329071,11.7780809625,9.3419771424
H,0,-0.8670974295,11.9386371893,10.3575064553
C,0,-2.5738383881,11.7948757785,9.032022593
C,0,-2.967635046,11.5925422707,7.717088089
C,0,-1.9972237259,11.3678108224,6.7411714087
C,0,-2.3330730153,11.1610282988,5.3141766808
C,0,-3.6412129582,10.9778993967,4.8674179371
H,0,-4.4697768575,10.9437507891,5.5703521419
C,0,-3.8800639162,10.820265845,3.5089187739
C,0,-2.810120496,10.8518738952,2.6249348467
H,0,-2.9549574487,10.7387408195,1.5536150849
C,0,-1.5300746492,11.0221182427,3.1385853242
H,0,-0.6426709304,11.0560483323,2.5046108061
C,0,2.8592936883,14.8204745746,5.2573736617
C,0,2.2573215111,14.8343671816,6.6928686772
C,0,3.7103469338,10.6228821308,2.2256797264
C,0,2.6194991877,11.4795923125,1.5186102629
C,0,4.468574594,10.4341223494,7.4118931106
C,0,3.958479434,8.9880422786,7.1434015516
Ir,0,0.8114281091,11.1390028756,5.3472340106
N,0,-0.6864035418,11.3517132171,7.0519106765
N,0,-1.2979024999,11.167077682,4.4483156474
O,0,2.7882880966,13.4312718604,4.9117751009
O,0,1.3164152995,13.752221378,6.6314634745
O,0,3.3323097153,10.7142794212,3.5984330504
O,0,1.4963297866,11.325624533,2.4002587977
O,0,3.2786620142,11.2112615329,7.2161278646
O,0,2.9032053627,9.2018995114,6.2017991861
H,0,-4.0219707215,11.6284186225,7.4547501786
H,0,-4.8961933392,10.6728634839,3.1481702403
H,0,-3.3195010111,11.9711573564,9.8047404054
C,0,4.3011996185,15.2761294082,5.1561503735
C,0,1.5204003704,16.1062137773,7.0644196005
C,0,2.0045909609,15.5834015693,4.2508428038
C,0,3.2781847524,14.4949454043,7.7707570673
C,0,4.9957381147,10.6804260143,8.8118625933
C,0,3.3437245028,8.335298002,8.3753427187
C,0,3.6591790042,9.1501118408,1.837476744
C,0,2.2316303896,11.0060356438,0.1315361402
C,0,5.127580316,11.1449348016,2.0827970092
C,0,2.9623814377,12.9636189738,1.4818573151
C,0,5.4842553706,10.9122596447,6.3805577703
C,0,4.9850940687,8.0618873943,6.5212432503
H,0,5.3141459582,11.7271966489,8.90783357
H,0,4.2327562438,10.4904460043,9.5753323494
H,0,5.8680134,10.0443040222,9.0215763649
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H,0,4.1007457777,8.0673199805,9.1253450726
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H,0,4.5463634329,7.0660850967,6.3764024728
H,0,5.3061671309,8.4336117637,5.5413474194
H,0,5.8678022097,7.9555518446,7.1686752448
H,0,5.6538584824,11.9868402828,6.531393116
H,0,6.4495378338,10.397401646,6.4839307084
H,0,5.1037688008,10.7751158776,5.3591445441
H,0,4.2964231804,8.5843287431,2.5287176031
H,0,2.6398760124,8.7521155606,1.9249479304
H,0,4.0194350779,8.9797247591,0.8133840183
H,0,5.8186930988,10.4709903061,2.6074175704
H,0,5.4341122298,11.1916284465,1.0274955808
H,0,5.2311617403,12.1410891228,2.5293737038
H,0,1.4647954185,11.6721697319,-0.285882882
H,0,3.0964771166,11.0247005681,-0.5474871836
H,0,1.8234897436,9.9891549888,0.14687194
H,0,2.0714932386,13.5218564218,1.1636574521
H,0,3.2461807356,13.3192823624,2.4808613662
H,0,3.7746489623,13.1789215186,0.7739289255
H,0,2.7424580089,14.3109732033,8.7118770056
H,0,3.824142395,13.5777904346,7.5193668081
H,0,3.9888176626,15.3169516103,7.9337283593
H,0,1.1301202063,16.0184177182,8.0867361238
H,0,2.1950723884,16.9742011898,7.0349473062
H,0,0.673579444,16.2972147858,6.3962021507
H,0,4.6353765964,15.2082377245,4.1118467429
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H,0,4.9665958375,14.6511285636,5.7610002292
H,0,2.3678251583,15.3668739179,3.2381459409
H,0,0.9542709754,15.2679133089,4.3049840102
H,0,2.0554596951,16.669497519,4.4076320459

(bpy)Ir(Bpin)$_3$ M06/BS1

bpyIrBPIN3M06PS
M06/gen
E(RM06) = -1832.56850386

Zero-point correction= 0.702334 (Hartree/Particle)
Thermal correction to Energy= 0.744053
Thermal correction to Enthalpy= 0.744997
Thermal correction to Gibbs Free Energy= 0.629418
Sum of electronic and ZPE= -1831.866170
Sum of electronic and thermal Energies= -1831.824451
Sum of electronic and thermal Enthalpies= -1831.823507
Sum of electronic and thermal Free Energies= -1831.939086

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	466.900	165.113	243.258

B,0,1.702656396,12.81576038,5.629151248
B,0,1.9907846418,10.9705100756,3.6862387279
B,0,2.4847626304,10.462190892,6.3036486155
C,0,-0.2797684939,11.4783651155,8.3204529209
H,0,0.7935219563,11.4144638053,8.4971923378
C,0,-1.17585085,11.737269258,9.3494956722
H,0,-0.8134727557,11.8669502086,10.3649678841
C,0,-2.5287150892,11.8308863731,9.0421983669
C,0,-2.9338555516,11.668370084,7.7243553641
C,0,-1.9769049769,11.4047521575,6.7430354132
C,0,-2.3250061564,11.2477601425,5.3120507786
C,0,-3.6443790777,11.1742707873,4.8631043474
H,0,-4.4729318695,11.1946964594,5.5649242952
C,0,-3.8945517716,11.059560052,3.5016037415
C,0,-2.8233537973,11.0250241139,2.6171767633
H,0,-2.9748161052,10.9442087212,1.5448429533
C,0,-1.5336983374,11.0893122821,3.1330136711
H,0,-0.647293054,11.0715219421,2.497804681
C,0,2.7879195409,14.7905815698,5.2458118742
C,0,2.1898397111,14.790533439,6.6847297254
C,0,3.7408429711,10.6066965416,2.2271796147
C,0,2.6275176965,11.4316830506,1.5128539037

C,0,4.4916264785,10.4281721124,7.4111046142
C,0,4.0098240523,8.9676172461,7.1600557767
Ir,0,0.815336571,11.0605584375,5.3462184806
N,0,-0.6691764905,11.3070766058,7.0524494766
N,0,-1.2914755228,11.1920914615,4.4457559842
O,0,2.7247012316,13.401301857,4.8899910355
O,0,1.2629460459,13.6924269636,6.6228009483
O,0,3.3452521745,10.6730021654,3.5983100081
O,0,1.5048456201,11.255277218,2.3949971653
O,0,3.2858920839,11.1802142682,7.2011673693
O,0,2.942986086,9.1493790369,6.2205229793
H,0,-3.9841606241,11.7640484177,7.4653439874
H,0,-4.9176991845,10.9987453435,3.1388471727
H,0,-3.2621885236,12.0374643922,9.8176083211
C,0,4.2277381809,15.2534226683,5.1434098069
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H,0,6.4699442911,10.4100973302,6.4799693911
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H,0,3.1190631923,10.9827953234,-0.5484881727
H,0,1.8828993079,9.9081107759,0.1492641755
H,0,2.0303517729,13.4523639335,1.1234468252
H,0,3.1836398323,13.3007281214,2.4623793155
H,0,3.7485634406,13.1509281292,0.7691861659
H,0,2.6828016088,14.2697560742,8.7004775896
H,0,3.7807401799,13.5582654416,7.5133742074
H,0,3.9103185438,15.2993189599,7.9266783828
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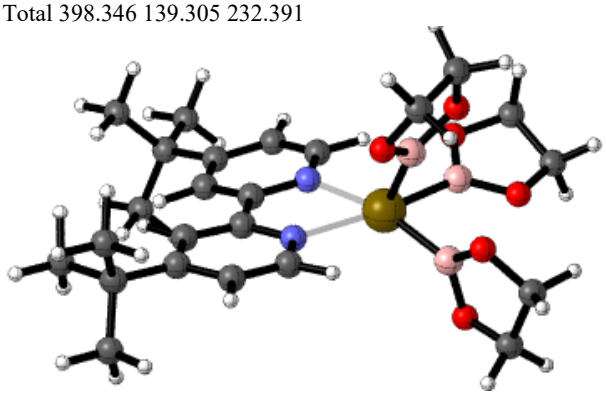
H,0,0.5792354242,16.2234878381,6.3986029941
H,0,4.5560626699,15.1959796065,4.0979175764
H,0,4.3315779317,16.2953859827,5.4755156275
H,0,4.8960373227,14.6246678035,5.7392864108
H,0,2.2927289862,15.3446274713,3.2329340955
H,0,0.8799086422,15.2236444643,4.2962921773
H,0,1.9654124076,16.6361421739,4.4083928807

(tbut-bpy)Ir(Beg)$_3$ M06/BSsmall
tbutbpyIrBeg3M06SB
M06/gen
E(RM06) = -1675.28804397

Zero-point correction= 0.597715 (Hartree/Particle)
Thermal correction to Energy= 0.634805
Thermal correction to Enthalpy= 0.635749
Thermal correction to Gibbs Free Energy= 0.525333
Sum of electronic and ZPE= -1674.690329
Sum of electronic and thermal Energies= -1674.653239
Sum of electronic and thermal Enthalpies= -1674.652295
Sum of electronic and thermal Free Energies= -1674.762711

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	398.346	139.305	232.391



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B,0,2.5769118175,10.5153153442,6.205558954
C,0,-0.230485539,11.5267347784,8.3526470903
H,0,0.8428043385,11.4808370377,8.5286450327
C,0,-1.1288038401,11.7258127962,9.3860733413
H,0,-0.7485607827,11.8213078145,10.4012932711
C,0,-2.4981126425,11.8125687762,9.1147827168
C,0,-2.8759010311,11.6889063559,7.7797567543
C,0,-1.9194847739,11.479579329,6.7851499193
C,0,-2.2702834828,11.3627659603,5.3494364881
C,0,-3.5815631783,11.2775600419,4.8961184422
H,0,-4.397595482,11.2572117423,5.6153180288
C,0,-3.8668065915,11.2008896939,3.5291719012
C,0,-2.7752183466,11.2218648796,2.6637387478
H,0,-2.9035099071,11.1764655877,1.5857396493
C,0,-1.4853687225,11.2933008609,3.1768419828
H,0,-0.604535897,11.3155949167,2.5327117508
C,0,3.0694090369,14.7792510066,5.3692670709
C,0,2.687304143,14.6369238496,6.8443760017
C,0,3.7510934595,10.7627584803,2.2265269518
C,0,2.6489873105,11.573901015,1.5451672412
C,0,4.7069973409,10.285172731,6.9559995413
C,0,4.0186841732,8.9208257244,6.9719258187
Ir,0,0.8779232505,11.1893665068,5.36274925
N,0,-0.610033675,11.3981132199,7.0771262403
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O,0,1.7122829426,13.6115595784,6.8584014928
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O,0,1.5477598772,11.4769141595,2.4292699432

O,0,3.6465916359,11.2057690087,6.7824103867
O,0,2.7985441092,9.1381933877,6.2910810334
H,0,-3.9234231621,11.7729938175,7.505174743
C,0,-5.309998858,11.0923003743,3.0522956035
C,0,-3.4940507871,12.0459710505,10.2429314898
H,0,4.1430911606,14.9525781326,5.2207398672
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H,0,5.4049559076,10.3754061576,6.1083095654
H,0,4.6011531906,8.1409026249,6.4642301004
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C,0,-3.3747884966,10.9064798347,11.261756251
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H,0,-2.1603479246,13.3985300714,11.3453597838
H,0,-3.2554272415,14.2158593719,10.2140119526
C,0,-5.4082207392,11.0447844925,1.529515461
C,0,-5.9279863572,9.8072974531,3.6161925863
C,0,-6.1033689365,12.3069578441,3.5477454649
H,0,-6.4621012123,10.9632065577,1.2323327367
H,0,-5.0036572267,11.9542093434,1.0644190934
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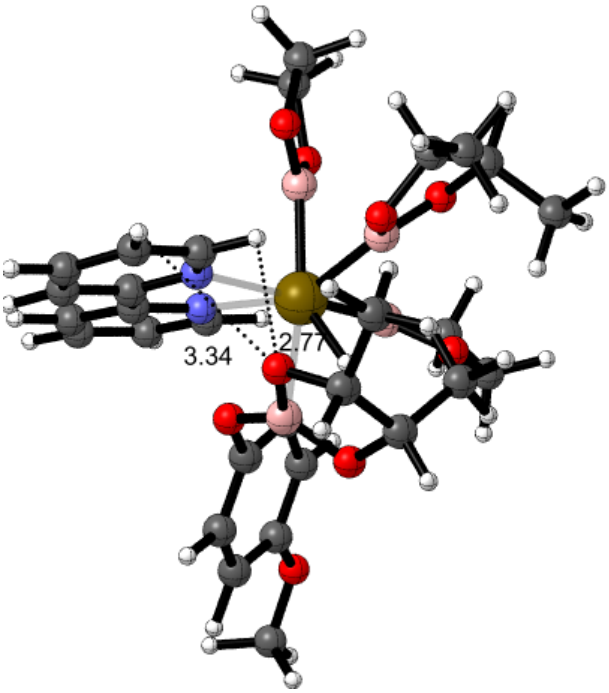
Transition Structures:

TS3-OBpin'$_{anti}$ M06/BSsmall

OBegleftantimetaOMeM06SB
M06/gen
E(RM06) = -2193.18937429

Zero-point correction= 0.682041 (Hartree/Particle)
Thermal correction to Energy= 0.725667
Thermal correction to Enthalpy= 0.726611
Thermal correction to Gibbs Free Energy= 0.606528
Sum of electronic and ZPE= -2192.507333
Sum of electronic and thermal Energies= -2192.463707
Sum of electronic and thermal Enthalpies= -2192.462763
Sum of electronic and thermal Free Energies= -2192.582846

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	455.363	167.968	252.736



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O,0,0.1284718577,-1.0325753194,-2.9860353036
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H,0,0.4260850614,-5.5461981336,0.9151738293
H,0,2.9240739484,-2.388137208,-3.8161155951
H,0,1.5892874738,-3.5236901721,-3.5001300643
H,0,1.4257541738,-0.6591151487,-4.5399500128
H,0,0.2771828525,-1.9930139444,-4.8101653761
H,0,-3.9639734093,4.4074743969,0.3136280686
H,0,-3.5494529819,3.9919680109,-1.9460222242
H,0,-5.8265425306,2.7641044999,-0.2223714833
H,0,-4.7774527469,1.4597888464,0.4008802046
H,0,-5.3327447793,2.7522039543,1.4857143879
H,0,-4.5179346576,1.7016025862,-2.216193131
H,0,-2.8618814582,1.7622991541,-2.8721315992
H,0,-3.1528474969,1.0161780839,-1.2853168724
H,0,-5.3883935402,-0.7344461457,0.82306409
H,0,-5.2187500462,-0.5700726755,-0.9401640523
H,0,-5.8664497944,-2.0721794215,-0.2412872894
H,0,-4.7560001344,-2.2638124763,-2.7306460373
H,0,-3.4491883916,-1.0438718442,-2.6623153015
H,0,-3.1306628636,-2.6399397457,-3.3567870067
C,0,4.6995672201,3.4500417737,-3.0827743924
H,0,5.4486848823,3.1023880944,-3.8001961523
H,0,4.1223670522,4.2706259896,-3.5380899383
H,0,5.2140022584,3.8367411961,-2.188206327

Atom No	Natural Charge
C 1	-0.24646
C 2	0.21581
N 3	-0.49138
C 4	0.07661
C 5	-0.27386
C 6	-0.19795
C 7	0.19519
N 8	-0.49548
C 9	0.08336
C 10	-0.24989
C 11	-0.20403
C 12	-0.24513
Ir 13	-0.02514
B 14	1.01502
O 15	-0.80561
C 16	-0.13951
C 17	-0.14019
O 18	-0.81237
C 19	-0.27611
C 20	-0.26647
C 21	0.31015
C 22	-0.34025
C 23	-0.24705
C 24	0.28632
O 25	-0.56346
O 26	-0.75724
B 27	1.36734
O 28	-0.77518
C 29	0.06467
C 30	-0.74261
B 31	0.93793
O 32	-0.77879
C 33	-0.14178
C 34	-0.14238
O 35	-0.78516
B 36	0.94922
O 37	-0.82952
C 38	0.06238
C 39	-0.72201
O 40	-0.80472
C 41	0.06468
C 42	-0.72889
O 43	-0.78107
C 44	0.06465
C 45	-0.72546
H 46	0.21114
H 47	0.27152
H 48	0.24550
H 49	0.26014
H 50	0.25431
H 51	0.24890
H 52	0.25604
H 53	0.26212
H 54	0.27939
H 55	0.22554
H 56	0.23221
H 57	0.24850
H 58	0.24898
H 59	0.24937
H 60	0.22786
H 61	0.21055
H 62	0.21174
H 63	0.22937
H 64	0.21083
H 65	0.22834
H 66	0.22748
H 67	0.21050
H 68	0.22483
H 69	0.23531
H 70	0.24705
H 71	0.25191
H 72	0.25572

H 73	0.23931
H 74	0.26683
H 75	0.25790
H 76	0.25045
H 77	0.24391
H 78	0.24995
H 79	0.23929
H 80	0.24840
H 81	0.25973
C 82	-0.33347
H 83	0.23551
H 84	0.21064
H 85	0.20817

TS3-OBpin'$_{anti}$ M06/BS1

OBegleftantimetaOMeM06PS
M06/gen
E(RM06) = -2193.29319812

Zero-point correction= 0.676815 (Hartree/Particle)
Thermal correction to Energy= 0.721187
Thermal correction to Enthalpy= 0.722131
Thermal correction to Gibbs Free Energy= 0.598260
Sum of electronic and ZPE= -2192.616383
Sum of electronic and thermal Energies= -2192.572011
Sum of electronic and thermal Enthalpies= -2192.571067
Sum of electronic and thermal Free Energies= -2192.694938

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	452.552	169.542	260.708

C	3.52785	-0.44173	2.98803
C	2.31424	-0.38682	2.29983
N	2.19639	-0.93317	1.07229
C	3.23827	-1.55786	0.51249
C	4.4707	-1.64999	1.1462
C	4.61621	-1.07307	2.4021
C	1.09118	0.21617	2.87585
N	-0.02488	0.10954	2.13372
C	-1.18575	0.55881	2.61249
C	-1.28906	1.17461	3.85324
C	-0.13791	1.32424	4.61529
C	1.06629	0.83342	4.12755
Ir	0.25694	-0.61537	-0.02621
B	0.67073	-1.32159	-1.88756
O	0.07846	-0.88065	-3.068
C	0.83486	-1.36114	-4.16591
C	1.69028	-2.48193	-3.57457
O	1.71963	-2.1953	-2.18324
C	1.17154	1.32868	-0.59632
C	2.24253	1.27269	-1.49391
C	3.14903	2.32385	-1.65122
C	2.9938	3.49589	-0.91401
C	1.90764	3.59094	-0.04559
C	1.01273	2.54125	0.09551
O	4.15532	2.105	-2.54807
O	-0.05743	2.72906	0.95705
B	-1.24405	3.1205	0.43125
O	-1.41391	3.54554	-0.86189
C	-2.82721	3.59367	-1.08884
C	-3.22778	2.35081	-1.8531
B	-0.24399	-2.56345	0.65302
O	0.43811	-3.72095	0.32577
C	-0.0918	-4.79059	1.09805
C	-1.42036	-4.24897	1.61904
O	-1.25678	-2.83821	1.57415
B	-1.68431	-1.12912	-0.5156
O	-2.82572	-0.52399	0.02681
C	-3.92229	-1.41329	-0.21589
C	-5.2332	-0.67313	-0.28525
O	-2.06603	-2.19124	-1.33442
C	-3.48399	-2.16655	-1.47639
C	-3.83635	-1.50577	-2.79367
O	-2.39983	3.1299	1.17394
C	-3.40465	3.72006	0.33899
C	-4.73389	3.05739	0.59075
H	-0.25968	0.67617	-0.91419
H	-2.04707	0.43299	1.95736
H	1.97214	0.93755	4.71738
H	-2.25093	1.54785	4.19174
H	-0.17278	1.81744	5.5838
H	3.62486	-0.00098	3.97536
H	5.56669	-1.11961	2.9283
H	5.293	-2.16298	0.65643
H	3.05388	-1.99014	-0.47138
H	-3.95035	-2.13111	0.62335
H	-3.8534	-3.2027	-1.45882
H	2.43068	0.38214	-2.09352
H	3.67933	4.33258	-1.01355
H	1.73501	4.50098	0.52605
H	-1.65543	-4.56742	2.64112
H	-2.25949	-4.52882	0.96116
H	0.60602	-5.02793	1.91507
H	-0.20319	-5.68081	0.4688
H	2.71203	-2.50256	-3.97234
H	1.23725	-3.47255	-3.72655
H	1.45184	-0.54074	-4.56521
H	0.1636	-1.70622	-4.96162
H	-3.46211	4.78947	0.60184
H	-3.04842	4.49609	-1.67502
H	-5.50214	3.44506	-0.08943
H	-4.6468	1.97405	0.44874
H	-5.06024	3.24381	1.6191
H	-4.28616	2.3753	-2.1433
H	-2.61978	2.27468	-2.76136
H	-3.04693	1.45199	-1.24629
H	-5.44348	-0.17857	0.66963
H	-5.22234	0.08719	-1.07502
H	-6.05427	-1.37132	-0.49194
H	-4.91735	-1.51373	-2.98098
H	-3.4775	-0.46798	-2.80923
H	-3.33714	-2.03763	-3.61022
C	5.09153	3.13364	-2.74241
H	5.80622	2.768	-3.4834
H	4.61608	4.04909	-3.12501
H	5.63051	3.37345	-1.81333

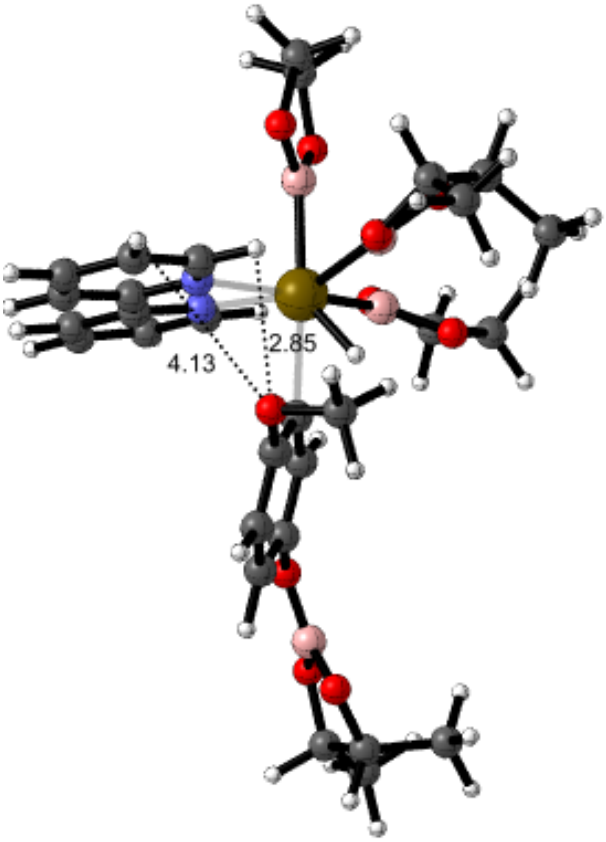
TS3-OMe$_{anti}$ M06/BSsmall

OMeleftmetaOBegM06SB
M06/gen
E(RM06) = -2193.18032628

Zero-point correction= 0.680323 (Hartree/Particle)

Thermal correction to Energy= 0.724912
Thermal correction to Enthalpy= 0.725856
Thermal correction to Gibbs Free Energy= 0.600324
Sum of electronic and ZPE= -2192.500003
Sum of electronic and thermal Energies= -2192.455414
Sum of electronic and thermal Enthalpies= -2192.454470
Sum of electronic and thermal Free Energies= -2192.580003

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	454.889	168.996	264.206



C,0,0.1350037065,3.9521785187,-2.0247472636
C,0,0.6320295662,2.8802586274,-1.2827690245
N,0,0.4322300422,1.6097705979,-1.6898525329
C,0,-0.2167112834,1.3745450672,-2.8364237057
C,0,-0.7278956633,2.3973701198,-3.6231808553
C,0,-0.5568388559,3.7085639664,-3.2013167176
C,0,1.4333112059,3.0649709536,-0.0537637292
N,0,1.8658400457,1.9434036159,0.5481338894
C,0,2.64605194,2.0341776383,1.6266508773
C,0,3.0305898306,3.2540291534,2.1666970173
C,0,2.5740000423,4.4191755886,1.5658906332
C,0,1.7680216624,4.3266351824,0.4415730055
Ir,0,1.078892252,-0.0530044932,-0.3156286583
B,0,0.3140025812,-1.6807475583,-1.2541496525
O,0,-0.0464597142,-2.8692332877,-0.6253082288
C,0,-0.5113503982,-3.7774861939,-1.6035363552
C,0,-0.8390913405,-2.8971161035,-2.8095025576
O,0,-0.0907894271,-1.7131786009,-2.5905479048
C,0,-0.8215318789,0.2674045179,0.7953206497
C,0,-2.0219202518,0.1005268496,0.0932900507
C,0,-3.2360726228,0.5462220175,0.6064807567
C,0,-3.2987837371,1.1590454337,1.8546762795
C,0,-2.1245706933,1.2965953812,2.5832732013
C,0,-0.9098295615,0.8530493656,2.0655274157
O,0,-4.3421767608,0.4040964488,-0.1976170765
B,0,-5.5872074828,0.0695228773,0.2111761407
O,0,-5.9730235708,-0.1958040418,1.5031451732
C,0,-7.3009799598,-0.7242696162,1.4242887782
C,0,-7.2338041952,-2.2307401879,1.5449405264
O,0,0.2210652035,1.0128089397,2.8416936486
B,0,2.8448463717,-0.2389572339,-1.4664358679
O,0,2.9335940172,-0.7042654419,-2.7652741989
C,0,4.2779268473,-0.5822217476,-3.1995318129
C,0,5.0702260667,-0.3505102956,-1.9138215624
O,0,4.1060015115,0.1319602474,-0.9933524976
B,0,2.4047735416,-1.3501694255,0.5713783075
O,0,2.9420456896,-1.1005451322,1.8358784424
C,0,3.9937802723,-2.0406194747,2.0487258864
C,0,4.118131785,-2.3540888167,3.5187949849
O,0,2.9295415639,-2.5302510423,0.0575206862
C,0,3.6166821266,-3.1969995956,1.1131426995
C,0,2.6909916319,-4.2363729841,1.7115861415
O,0,-6.6098837847,-0.0375074456,-0.6985747763
C,0,-7.8042552271,-0.1922237517,0.0669617718
C,0,-8.7974886007,-1.0453969996,-0.6801535762
H,0,0.344000105,-0.8195012334,0.9337408212
H,0,2.9608164328,1.0838237045,2.0566865733
H,0,1.4125894113,5.2315117575,-0.0437598576
H,0,3.6698734702,3.2811980633,3.0455563648
H,0,2.8457871161,5.395384526,1.9632407186
H,0,0.2863983012,4.9742452424,-1.6890986673
H,0,-0.9515889934,4.5379140638,-3.7851072367
H,0,-1.2522006801,2.1597436207,-4.5451233919
H,0,-0.3132125448,0.3237502923,-3.1104880616
H,0,4.9315213458,-1.5840077109,1.681417791
H,0,4.5151392243,-3.6783711857,0.6988151811
H,0,-2.0374393412,-0.3739165719,-0.8900103775
H,0,-4.2515888415,1.5011308176,2.251267877
H,0,-2.1324009476,1.7573017646,3.5711888268
H,0,5.8826254649,0.3784232789,-2.0260042425
H,0,5.4976668424,-1.2894002993,-1.5232043522
H,0,4.3608800984,0.2678343245,-3.8949110725
H,0,4.5800346113,-1.4912942691,-3.7339672073
H,0,-1.9116802338,-2.646556922,-2.8539975791
H,0,-0.5528905027,-3.3486109103,-3.767722346
H,0,-1.3819851713,-4.3264556382,-1.2225403351
H,0,0.2821170793,-4.5070075748,-1.8309156399
H,0,-7.8883502761,-0.3022085297,2.2519819066
H,0,-8.2319965403,0.8137742925,0.2230952868
H,0,4.3791434538,-1.4475300381,4.0782663665
H,0,3.1684327368,-2.7334010991,3.9169738372
H,0,4.8986285316,-3.104813098,3.7010400124
H,0,3.1907902319,-4.8424079188,2.4790052789
H,0,1.8091237787,-3.753899347,2.158086744
H,0,2.3318995812,-4.9003931953,0.9169367812
H,0,-8.2338969359,-2.6821327312,1.56204412
H,0,-6.6715546484,-2.6606247119,0.7044442225
H,0,-6.7141090425,-2.5020561992,2.4706185886
H,0,-9.7185576215,-1.1787422716,-0.097679456
H,0,-9.0587407209,-0.5662066795,-1.6302987924
H,0,-8.377981328,-2.0333085814,-0.9049672067
C,0,0.4556152675,-0.0696025032,3.7133749556

H,0,1.3800349812,0.1483616948,4.2607378143
H,0,-0.3745900026,-0.192873577,4.4286449396
H,0,0.5994438126,-1.0123082851,3.1600454055

Atom	No	Natural Charge
C	1	-0.24506
C	2	0.20934
N	3	-0.49068
C	4	0.07025
C	5	-0.27175
C	6	-0.19725
C	7	0.20317
N	8	-0.49267
C	9	0.08546
C	10	-0.27154
C	11	-0.20119
C	12	-0.24587
Ir	13	-0.01380
B	14	1.02034
O	15	-0.80426
C	16	-0.13931
C	17	-0.14001
O	18	-0.81375
C	19	-0.28572
C	20	-0.27053
C	21	0.31916
C	22	-0.30656
C	23	-0.26173
C	24	0.27756
O	25	-0.73960
B	26	1.36437
O	27	-0.78529
C	28	0.06148
C	29	-0.73800
O	30	-0.61056
B	31	0.91988
O	32	-0.77739
C	33	-0.14375
C	34	-0.14243
O	35	-0.78760
B	36	0.95018
O	37	-0.82101
C	38	0.06262
C	39	-0.72356
O	40	-0.79617
C	41	0.06315
C	42	-0.73021
O	43	-0.77113
C	44	0.05978
C	45	-0.72887
H	46	0.21838
H	47	0.26997
H	48	0.24609
H	49	0.25839
H	50	0.25445
H	51	0.24889
H	52	0.25633
H	53	0.26295
H	54	0.28001
H	55	0.22215
H	56	0.23251
H	57	0.24622
H	58	0.26164
H	59	0.25123
H	60	0.21309
H	61	0.22314
H	62	0.22567
H	63	0.21808
H	64	0.21130
H	65	0.22824
H	66	0.22580
H	67	0.21240
H	68	0.23867
H	69	0.22701
H	70	0.25390
H	71	0.24896
H	72	0.24544
H	73	0.23968
H	74	0.24997
H	75	0.26006
H	76	0.24859
H	77	0.24762
H	78	0.26491
H	79	0.24804
H	80	0.26317
H	81	0.25064
C	82	-0.30788
H	83	0.22626
H	84	0.19996
H	85	0.20860

TS3-OMe$_{anti}$ M06/BS1
OMeleftmetaOBegM06PS
M06/gen
E(RM06) = -2193.28495198

Zero-point correction= 0.676488 (Hartree/Particle)
Thermal correction to Energy= 0.721357
Thermal correction to Enthalpy= 0.722302
Thermal correction to Gibbs Free Energy= 0.595063
Sum of electronic and ZPE= -2192.608464
Sum of electronic and thermal Energies= -2192.563595
Sum of electronic and thermal Enthalpies= -2192.562650
Sum of electronic and thermal Free Energies= -2192.689889

	E KCal/Mol	CV Cal/Mol-K	S Cal/Mol-K
Total	452.659	169.934	267.795

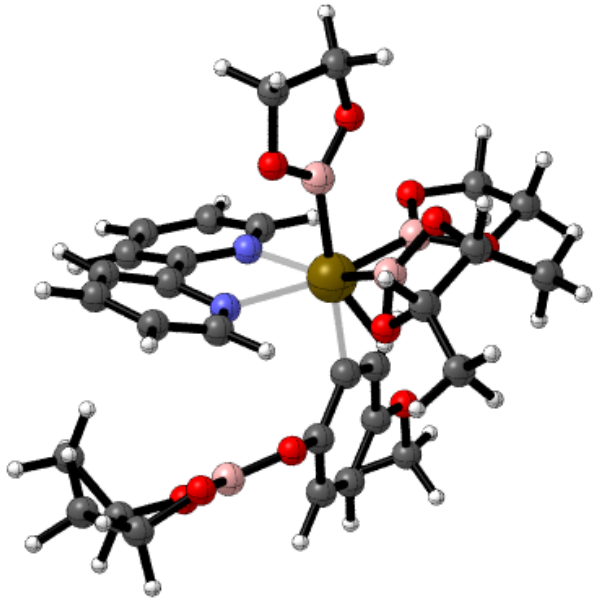
C	0.25942	4.36579	-0.88391
C	0.72454	3.12581	-0.44183
N	0.52873	2.01339	-1.17944
C	-0.08343	2.10286	-2.36705
C	-0.56373	3.30665	-2.86539
C	-0.39797	4.45573	-2.1024
C	1.48874	2.96302	0.81432
N	1.90429	1.71658	1.10061
C	2.65728	1.5062	2.18275
C	3.02719	2.53139	3.04377
C	2.58228	3.81934	2.77294
C	1.80569	4.04094	1.64475
Ir	1.11316	0.03486	-0.27628

B	0.35212	-1.27232	-1.63187
O	-0.04762	-2.57644	-1.35151
C	-0.46142	-3.19181	-2.55836
C	-0.75565	-2.01828	-3.49127
O	-0.00199	-0.94505	-2.94355
C	-0.80931	0.09313	0.84431
C	-1.99376	0.13772	0.09635
C	-3.2142	0.46517	0.6783
C	-3.30366	0.74089	2.04018
C	-2.1466	0.66259	2.80678
C	-0.92482	0.33592	2.22035
O	-4.29997	0.56037	-0.16225
B	-5.56119	0.15298	0.10524
O	-5.99624	-0.43244	1.27143
C	-7.32608	-0.90784	1.01513
C	-7.2725	-2.39546	0.74599
O	0.18672	0.26957	3.03801
B	2.91318	0.11262	-1.39505
O	3.03897	0.00184	-2.76797
C	4.40009	0.21413	-3.11763
C	5.15285	0.06461	-1.797
O	4.16464	0.31338	-0.80673
B	2.36737	-1.49497	0.28732
O	2.87741	-1.59375	1.58372
C	3.89616	-2.59584	1.57234
C	3.97466	-3.27471	2.91674
O	2.86814	-2.52759	-0.49683
C	3.51074	-3.46462	0.36687
C	2.54466	-4.59394	0.6628
O	-6.55454	0.29586	-0.834
C	-7.77881	-0.03285	-0.1712
C	-8.75547	-0.64366	-1.14257
H	0.32783	-1.00684	0.70101
H	2.96094	0.47397	2.3496
H	1.45735	5.04365	1.41744
H	3.64361	2.31442	3.91129
H	2.83957	4.64721	3.42931
H	0.40914	5.25784	-0.28405
H	-0.76885	5.41558	-2.45355
H	-1.0594	3.33133	-3.83125
H	-0.17718	1.16689	-2.91696
H	4.85443	-2.09259	1.34885
H	4.4065	-3.85011	-0.14141
H	-1.99259	-0.06951	-0.97448
H	-4.26045	0.99154	2.49004
H	-2.17426	0.8587	3.87771
H	5.98326	0.77119	-1.68382
H	5.54119	-0.95802	-1.66231
H	4.51137	1.22195	-3.54506
H	4.70575	-0.51722	-3.87454
H	-1.82363	-1.74924	-3.48637
H	-0.44737	-2.19749	-4.52785
H	-1.33601	-3.82686	-2.37417
H	0.35477	-3.82427	-2.93999
H	-7.93698	-0.70391	1.90463
H	-8.19903	0.90551	0.22882
H	4.25322	-2.55033	3.68995
H	3.00546	-3.70729	3.19182
H	4.72577	-4.07438	2.91137
H	3.01032	-5.38677	1.26109
H	1.66225	-4.21588	1.19744
H	2.19478	-5.02536	-0.28062
H	-8.27581	-2.81581	0.61053
H	-6.68126	-2.60683	-0.1541
H	-6.79554	-2.90316	1.59008
H	-9.69101	-0.91393	-0.63783
H	-8.9886	0.07389	-1.93532
H	-8.33655	-1.54098	-1.61094
C	0.38649	-1.00342	3.61846
H	1.29733	-0.94393	4.22374
H	-0.46359	-1.2852	4.25931
H	0.53656	-1.77637	2.8481

TS3-OBpin'$_{syn}$ M06/BSsmall
OBegleftsynmetaOMeM06SB
M06/gen
E(RM06) = -2193.18274050

Zero-point correction= 0.681553 (Hartree/Particle)
Thermal correction to Energy= 0.725715
Thermal correction to Enthalpy= 0.726659
Thermal correction to Gibbs Free Energy= 0.603579
Sum of electronic and ZPE= -2192.501187
Sum of electronic and thermal Energies= -2192.457026
Sum of electronic and thermal Enthalpies= -2192.456082
Sum of electronic and thermal Free Energies= -2192.579162

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	455.393	168.455	259.044



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C,0,-1.2119773504,0.2968032091,2.5300470881
N,0,-0.0883935347,0.8736659486,2.0559265617
C,0,0.3612136411,1.9975253131,2.6274752422
C,0,-0.301594063,2.6116420554,3.681843972
C,0,-1.4787613652,2.0458860699,4.1528286933
C,0,-1.6276103723,-0.9659717072,1.8924837321
N,0,-1.1157993623,-1.2095151257,0.6729906071
C,0,-1.4611233017,-2.3288340647,0.0340149622
C,0,-2.3131441678,-3.2743304099,0.5930320634
C,0,-2.8122320014,-3.0505881388,1.8688655437

C,0,-2.4695110899,-1.877388031,2.5288045272
Ir,0,0.8124757461,0.0086174257,0.179568634
B,0,2.5838263409,0.9790406313,0.0831000963
O,0,3.4415221986,1.016126597,-1.0075740401
C,0,4.5960686627,1.7485825844,-0.6467072554
C,0,4.1642980508,2.5508219931,0.5804325713
O,0,3.0409240454,1.8444606253,1.0814985735
C,0,-0.1841498541,1.6523320326,-0.9376682403
C,0,0.3333764476,2.9424011973,-0.7929805062
C,0,-0.3260227974,4.0736744263,-1.2786900702
C,0,-1.5260518635,3.9309102222,-1.9691110936
C,0,-2.0463486391,2.6522899503,-2.1501835511
C,0,-1.3936240373,1.5387812543,-1.6382335448
O,0,0.2873860503,5.2680629959,-1.0360262706
O,0,-1.903244475,0.2765711163,-1.8848967873
B,0,-3.1793487326,-0.057963546,-1.6004780935
O,0,-4.1247779914,0.7862698731,-1.0637589948
C,0,-5.2634595848,-0.0142370863,-0.7512977138
C,0,-5.2817347584,-0.2634165717,0.7407702707
B,0,1.8230448978,-1.3920154677,1.4055325636
O,0,3.0425529219,-1.1843471506,2.0259724891
C,0,3.4855578122,-2.4228737965,2.5512439007
C,0,2.2205035654,-3.277972363,2.625587469
O,0,1.3206320751,-2.6532621451,1.7227818675
B,0,1.6876812848,-1.4320011356,-1.0148368224
O,0,0.9618350786,-2.1001319625,-2.0000603721
C,0,1.779296857,-3.156192585,-2.5047391257
C,0,1.4879623103,-3.3910671048,-3.9656179124
O,0,2.9872696892,-1.917028597,-0.9695048359
C,0,3.2006462943,-2.7044951552,-2.138606313
C,0,3.900674683,-1.8478229356,-3.1733131751
O,0,-3.659489163,-1.3254483019,-1.8400872504
C,0,-5.0692445372,-1.2670124747,-1.6344517182
C,0,-5.57148449,-2.5767377317,-1.0806597072
H,0,0.7558533086,0.419258734,-1.4051236286
H,0,-1.0172469029,-2.4611109051,-0.9522726342
H,0,-2.8329222434,-1.6829554053,3.535426706
H,0,-2.5682317296,-4.1698038717,0.0310467167
H,0,-3.4621534303,-3.7801383659,2.3493665679
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H,0,-2.0364525814,2.5131545724,4.9621766649
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H,0,1.2929572042,2.3905318618,2.2204063494
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H,0,3.8293522269,-3.5666144302,-1.8703872932
H,0,1.282250609,3.1119764092,-0.2818224157
H,0,-2.0562535409,4.7872672803,-2.3782787989
H,0,-2.9774964054,2.5200703443,-2.6983469065
H,0,1.7796768877,-3.2799793104,3.6348586184
H,0,2.3864334871,-4.3204100613,2.3252178349
H,0,3.9625648402,-2.2690215425,3.5275607353
H,0,4.2308553369,-2.8548744361,1.8650521611
H,0,3.8575790538,3.5752626222,0.3112770187
H,0,4.9405754183,2.6161367726,1.3529288243
H,0,4.9155755781,2.3816458628,-1.4842010108
H,0,5.412476731,1.0473240441,-0.4124897729
H,0,-6.1662822349,0.536910931,-1.0524003971
H,0,-5.5416500565,-1.0822431801,-2.6151116991
H,0,-6.6583062759,-2.5498718597,-0.9275681687
H,0,-5.3439497456,-3.3880657605,-1.781940978
H,0,-5.0857575495,-2.8085857521,-0.1246074748
H,0,-6.1769324729,-0.8156282354,1.0548597412
H,0,-4.3926507112,-0.835144366,1.0429581461
H,0,-5.2606093688,0.6973153564,1.268877419
H,0,0.4416216598,-3.6891439974,-4.0995336164
H,0,1.6529572046,-2.4762673074,-4.5473623156
H,0,2.1271638283,-4.186231485,-4.3726777133
H,0,4.1573608262,-2.4190446696,-4.0753104454
H,0,3.2702762683,-0.9933029717,-3.4565740727
H,0,4.8215734075,-1.4409438762,-2.7392279068
C,0,-0.335204604,6.4220819448,-1.5280829899
H,0,0.2960202356,7.2674475373,-1.2389702513
H,0,-0.426075284,6.4019857507,-2.6258739611
H,0,-1.3394909132,6.5607488518,-1.095835761

TS3-OBpin'$_{syn}$ M06/BS1
OBegleftsynmetaOMeM06PS
M06/gen
E(RM06) = -2193.28699673

Zero-point correction= 0.677046 (Hartree/Particle)
Thermal correction to Energy= 0.721590
Thermal correction to Enthalpy= 0.722534
Thermal correction to Gibbs Free Energy= 0.598428
Sum of electronic and ZPE= -2192.609951
Sum of electronic and thermal Energies= -2192.565407
Sum of electronic and thermal Enthalpies= -2192.564463
Sum of electronic and thermal Free Energies= -2192.688569

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	452.805	169.793	261.203

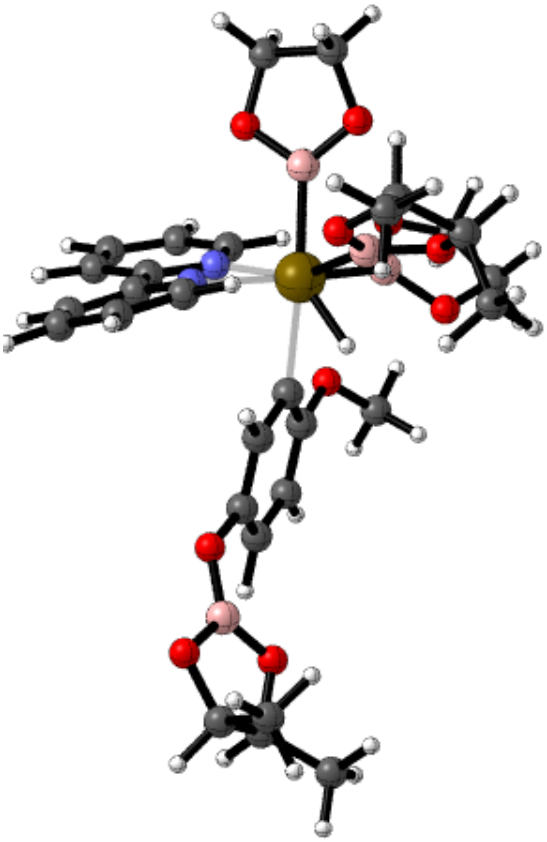
C,0,-2.1172927325,0.7460120366,3.4172143456
C,0,-1.3246651789,0.1933950911,2.4098566473
N,0,-0.2094535381,0.8191202329,1.9773583305
C,0,0.1535296281,1.9772375874,2.5433435662
C,0,-0.5847723294,2.5761900929,3.5555802059
C,0,-1.745973402,1.9518862936,3.9943535183
C,0,-1.6547714133,-1.0903744413,1.7616235462
N,0,-1.0655232311,-1.3208230571,0.5754699288
C,0,-1.314361967,-2.4665963584,-0.0633260952
C,0,-2.1417907932,-3.4509848111,0.4619274308
C,0,-2.730243614,-3.2345100863,1.7011388502
C,0,-2.4930614539,-2.0343216979,2.3586862898
Ir,0,0.8192535401,0.0024363882,0.1501779479
B,0,2.5715726953,1.0132177663,0.191071887
O,0,3.5451368904,1.0383046592,-0.7968148191
C,0,4.6729853198,1.7319915739,-0.2900702826
C,0,4.1105123231,2.5681664539,0.856988646
O,0,2.9198251097,1.8861516166,1.2275890352
C,0,-0.1757910802,1.6372202678,-0.9856158349
C,0,0.3815481602,2.9186054212,-0.9364485256
C,0,-0.2678874704,4.0422772941,-1.4520466385
C,0,-1.5026509474,3.9008371592,-2.0794800573
C,0,-2.0676873122,2.6288974406,-2.1628154967
C,0,-1.4226345359,1.5249563619,-1.6201810693
O,0,0.3911636303,5.230151736,-1.3053712077
O,0,-1.9861657002,0.2688121406,-1.7601221272
B,0,-3.2621991572,-0.0154182654,-1.4272603294
O,0,-4.1898993054,0.8805221026,-0.9403230377
C,0,-5.3401919909,0.1261201351,-0.5488871235
C,0,-5.3624876102,0.0183009315,0.9603324565

B,0,1.8647449685,-1.403166961,1.3557219845
O,0,3.1063455188,-1.2156810861,1.9413147014
C,0,3.5619577741,-2.468237009,2.4291602811
C,0,2.2949736854,-3.3179922141,2.5294021166
O,0,1.3702689954,-2.6710165792,1.6632977737
B,0,1.7433156374,-1.3725626693,-1.0904470655
O,0,1.0364390744,-2.007698484,-2.1117715144
C,0,1.8440434043,-3.0820759763,-2.5987173754
C,0,1.5797143147,-3.3164189795,-4.0645149425
O,0,3.0381411172,-1.8666001688,-1.033508143
C,0,3.2652807493,-2.6594627946,-2.1988681426
C,0,4.0149551163,-1.8263027718,-3.217991615
O,0,-3.7648026769,-1.2912534553,-1.5503249227
C,0,-5.1707073097,-1.2047515522,-1.3171202001
C,0,-5.6655411483,-2.4544564386,-0.6332984894
H,0,0.832791435,0.4295717951,-1.4171912137
H,0,-0.8179481379,-2.5814550589,-1.0258155926
H,0,-2.9291038092,-1.8478960901,3.3367359407
H,0,-2.3139555668,-4.3670905455,-0.0958435385
H,0,-3.3677999593,-3.9902976855,2.1549201417
H,0,-3.0297982585,0.2446344662,3.7289475472
H,0,-2.3597356967,2.3987530485,4.7727003114
H,0,-0.2501064561,3.5179560119,3.980225459
H,0,1.0777227467,2.4110968497,2.1668302918
H,0,1.575690863,-3.9863447497,-2.0219734448
H,0,3.8651384705,-3.5349160216,-1.910504156
H,0,1.3601863814,3.0874152496,-0.487162532
H,0,-2.0285831157,4.7476412992,-2.510787028
H,0,-3.028707722,2.4983012012,-2.6550921762
H,0,1.8833973937,-3.3341653548,3.5497888901
H,0,2.4437542836,-4.3541028318,2.2027628504
H,0,4.0692785292,-2.3313971916,3.3914250125
H,0,4.2806968373,-2.8890881522,1.7102028946
H,0,3.8555836172,3.5902383084,0.5343596253
H,0,4.7850457579,2.6325167861,1.7187200584
H,0,5.1285365747,2.3364775071,-1.0830261067
H,0,5.4142290925,0.9997132364,0.0650341501
H,0,-6.2337232035,0.6613782311,-0.8987487754
H,0,-5.6631191848,-1.1077916072,-2.299447601
H,0,-6.7476610588,-2.4055909234,-0.4614184865
H,0,-5.4565502093,-3.3274009021,-1.2606521738
H,0,-5.1603744036,-2.60081145,0.3292975376
H,0,-6.2691098571,-0.4836363411,1.3185622405
H,0,-4.4870623803,-0.5407313108,1.3182029628
H,0,-5.3254640483,1.0229900147,1.3944087361
H,0,0.5356630433,-3.6083330828,-4.2179588914
H,0,1.7620865807,-2.4041974787,-4.6432410366
H,0,2.2220369843,-4.115591864,-4.4552673018
H,0,4.2786324816,-2.4114333479,-4.1076498567
H,0,3.416538227,-0.959479839,-3.5268713487
H,0,4.9363242169,-1.4460503864,-2.7650772824
C,0,-0.2135205119,6.3793495933,-1.8400391351
H,0,0.4585380547,7.2140958935,-1.6274389191
H,0,-0.3497094413,6.2967796065,-2.9287303556
H,0,-1.1905591713,6.5778681921,-1.3737433707

TS3-OMe Conformer B M06/BSsmall
OMerightmetaOBegM06SBb
M06/gen
E(RM06) = -2193.17982496

Zero-point correction= 0.680847 (Hartree/Particle)
Thermal correction to Energy= 0.725458
Thermal correction to Enthalpy= 0.726402
Thermal correction to Gibbs Free Energy= 0.599436
Sum of electronic and ZPE= -2192.498978
Sum of electronic and thermal Energies= -2192.454367
Sum of electronic and thermal Enthalpies= -2192.453423
Sum of electronic and thermal Free Energies= -2192.580389

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	455.231	168.824	267.222



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N,0,1.6803437954,-2.074290212,-0.5730753639
C,0,2.3968575101,-2.9104771621,0.1839191809
C,0,2.6726185926,-4.2137299958,-0.2041456833
C,0,2.1914946387,-4.6583648925,-1.4282148817
C,0,0.4952806855,-1.4912460736,-2.5860458473
N,0,0.5388825524,-0.2183818887,-2.1524802498
C,0,-0.0342050774,0.7437631408,-2.8798007869
C,0,-0.7200986993,0.4809294424,-4.0591060312
C,0,-0.8129771685,-0.8353848172,-4.4900394311
C,0,-0.1906866504,-1.831828517,-3.7523905051
Ir,0,1.2211784857,0.0316035264,0.0498017853
B,0,1.9255026815,-0.0027853286,1.9504998608
O,0,1.3207906707,0.5471406554,3.0726342112
C,0,2.2224648665,0.4648513112,4.1554151917
C,0,3.2419592139,-0.5928447,3.725936671
O,0,3.1137534045,-0.6514867095,2.3168159728
C,0,-0.8282299371,-0.6697251799,0.5655027674
C,0,-1.018406071,-1.6345159693,1.5682215624

C,0,-2.271266562,-2.2036773946,1.7908735276
C,0,-3.3710224913,-1.8345101825,1.0232747885
C,0,-3.200787938,-0.8831299105,0.0265978867
C,0,-1.9495049075,-0.3143648618,-0.1891345025
O,0,0.0823366883,-2.0447875945,2.2818081871
O,0,-4.2208459298,-0.487079978,-0.8081058676
B,0,-5.5091838379,-0.2910512548,-0.4473803689
O,0,-6.0171930987,-0.3911984588,0.8256653865
C,0,-7.4356167864,-0.2677340932,0.699340252
C,0,-8.0110471685,0.4224576503,1.9094411497
B,0,3.2152708816,0.4783671023,-0.4908716524
O,0,3.9164243988,-0.3349597945,-1.3790450491
C,0,5.2549421724,0.1272984592,-1.4578324452
C,0,5.2067476807,1.5307454053,-0.8550992026
O,0,4.0133368445,1.5455556755,-0.0929100892
B,0,1.3952846998,2.0820081344,0.1197853234
O,0,1.3080993885,2.857651065,-1.042991114
C,0,1.771840966,4.1647094746,-0.7082643028
C,0,1.108443333,5.2021614518,-1.5792579916
O,0,1.5921194141,2.8930327749,1.221768336
C,0,1.5202210337,4.251418552,0.8050889683
C,0,0.1737447104,4.8187799675,1.2063738171
O,0,-6.4492308233,0.0564642923,-1.3862198462
C,0,-7.6197341443,0.4350680692,-0.6619513329
C,0,-7.6893846019,1.9461560035,-0.6026877407
H,0,-0.0295681847,0.704971807,0.8571658437
H,0,0.0739166575,1.7527222467,-2.4811153583
H,0,-0.2594102592,-2.8676354231,-4.0742932278
H,0,-1.1828369632,1.2941401155,-4.6124467258
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H,0,3.2620300893,-4.8579294581,0.4433312306
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H,0,2.8627840626,4.1808307192,-0.8801476609
H,0,2.3266572266,4.8119171182,1.3009336743
H,0,-2.3969882866,-2.9637398981,2.560700242
H,0,-4.3490534517,-2.2734060135,1.2049048694
H,0,-1.8732824727,0.4492402555,-0.9661089476
H,0,5.1490811151,2.3101274082,-1.6320372874
H,0,6.065640446,1.7553166046,-0.2102618112
H,0,5.5928668373,0.1168655621,-2.5018933915
H,0,5.9064445299,-0.546206183,-0.8798303783
H,0,3.0190357849,-1.5838244656,4.1582337313
H,0,4.2735236026,-0.3337045625,3.9972253965
H,0,1.6854465841,0.1939041655,5.0754278766
H,0,2.694068,1.4474693363,4.3127803095
H,0,1.3621672127,5.0295435197,-2.6321700413
H,0,0.0164494621,5.1580802966,-1.4827574978
H,0,1.4406658491,6.2140239826,-1.3108547738
H,0,0.0939124057,5.8898573994,0.977330705
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H,0,0.0273613881,4.6806273491,2.2836085877
H,0,-8.498190628,0.0365592427,-1.1894499876
H,0,-7.8510421724,-1.2877359574,0.6266703241
H,0,-9.099856889,0.5296501939,1.8179231366
H,0,-7.7982491429,-0.1627301461,2.8111301055
H,0,-7.5704925367,1.4177968071,2.0422442026
H,0,-8.6104429006,2.2937220366,-0.1177821116
H,0,-6.8302385726,2.3501392219,-0.0491270769
H,0,-7.6564212322,2.3536916544,-1.6192306398
C,0,-0.1082095948,-2.2775341258,3.6536086966
H,0,0.8878017252,-2.4096841992,4.0926365855
H,0,-0.6047087441,-1.4186799257,4.1308114198
H,0,-0.689146304,-3.1918400716,3.8521771502

TS3-OMe$_{syn}$ M06/BS1

OMerightmetaOBegM06PS
OMerightmetaOBeg
M06/gen
E(RM06) = -2193.28635803

Zero-point correction= 0.677703 (Hartree/Particle)
Thermal correction to Energy= 0.722240
Thermal correction to Enthalpy= 0.723185
Thermal correction to Gibbs Free Energy= 0.597612
Sum of electronic and ZPE= -2192.608655
Sum of electronic and thermal Energies= -2192.564118
Sum of electronic and thermal Enthalpies= -2192.563173
Sum of electronic and thermal Free Energies= -2192.688746

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	453.213	169.542	264.289

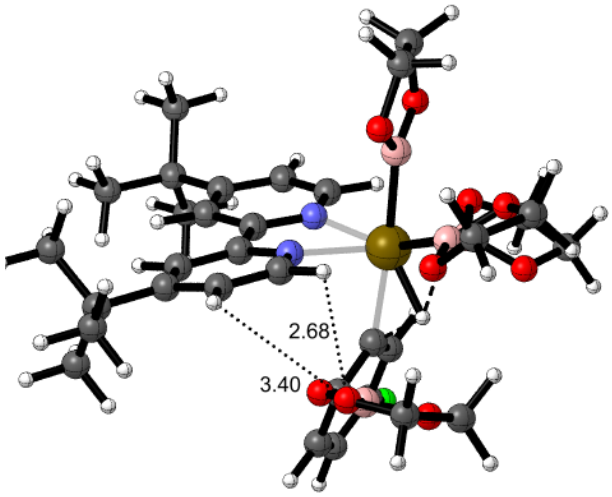
C,0.441931,-3.483352,-2.593041
C,0.569712,-2.219001,-2.012722
N,1.304915,-2.037812,-0.899794
C,1.941635,-3.078836,-0.351353
C,1.84752,-4.363455,-0.868896
C,1.078883,-4.567769,-2.008924
C,-0.053175,-1.014903,-2.602687
N,0.337962,0.168807,-2.094312
C,-0.144866,1.298631,-2.620387
C,-1.075795,1.305149,-3.653109
C,-1.523234,0.08748,-4.15011
C,-0.997864,-1.08649,-3.627976
Ir,1.342365,0.021732,0.008517
B,2.193419,-0.398287,1.805126
O,1.837814,0.151095,3.028325
C,2.406098,-0.638776,4.051962
C,3.548116,-1.383376,3.362119
O,3.180735,-1.380168,1.989194
C,-0.735637,-0.389684,0.697306
C,-0.979249,-1.51212,1.513585
C,-2.277024,-1.961409,1.749392
C,-3.375272,-1.302817,1.189936
C,-3.152812,-0.186258,0.397569
C,-1.850114,0.262629,0.175145
O,0.122805,-2.139778,2.026237
O,-4.149224,0.538924,-0.217417
B,-5.489138,0.409264,-0.121391
O,-6.180866,-0.464669,0.689051
C,-7.558306,-0.370193,0.302323
C,-8.455729,-0.600759,1.490228
B,3.348387,0.146697,-0.659894
O,3.938289,-0.899368,-1.371456
C,5.333954,-0.648709,-1.460511
C,5.460162,0.847328,-1.18977
O,4.276572,1.166993,-0.472849
B,1.830157,2.000624,0.306581
O,1.610522,2.951516,-0.69566
C,2.318562,4.133472,-0.31423

C,1.645084,5.361788,-0.873062
O,2.366915,2.602992,1.427057
C,2.400609,4.012018,1.215487
C,1.260451,4.652152,1.981354
O,-6.316684,1.204994,-0.8798
C,-7.645057,1.006008,-0.38792
C,-8.015064,2.163418,0.514379
H,0.34055,0.78813,1.027782
H,0.235093,2.217943,-2.17519
H,-1.340451,-2.046632,-4.002109
H,-1.45147,2.248361,-4.03898
H,-2.27283,0.048404,-4.936553
H,-0.134401,-3.617955,-3.502977
H,0.986126,-5.55789,-2.448891
H,2.378177,-5.179689,-0.387184
H,2.541751,-2.850707,0.528519
H,3.338413,4.047501,-0.725603
H,3.363719,4.395287,1.582659
H,-2.459995,-2.835051,2.37019
H,-4.383085,-1.657342,1.380934
H,-1.732546,1.162926,-0.429547
H,5.487619,1.43354,-2.120787
H,6.339636,1.108945,-0.590038
H,5.704836,-0.946715,-2.448235
H,5.854028,-1.24633,-0.69643
H,3.670846,-2.415391,3.716146
H,4.509468,-0.861601,3.479142
H,1.64316,-1.335191,4.439382
H,2.741868,-0.001809,4.879028
H,1.658593,5.3352,-1.968026
H,0.600631,5.421832,-0.545975
H,2.164108,6.272913,-0.549717
H,1.282566,5.746592,1.909367
H,0.294325,4.29322,1.602747
H,1.329972,4.370607,3.036847
H,-8.326673,0.964564,-1.248334
H,-7.737644,-1.15378,-0.452471
H,-9.510331,-0.517411,1.200892
H,-8.291409,-1.603734,1.896437
H,-8.252257,0.125398,2.284721
H,-9.052419,2.090659,0.861062
H,-7.355658,2.200247,1.391132
H,-7.899025,3.103607,-0.033637
C,-0.049692,-3.308671,2.779816
H,0.95543,-3.648934,3.05208
H,-0.626676,-3.12387,3.69914
H,-0.548411,-4.098811,2.196411

TS5-OBeg$_{anti}$ M06/BSsmall
OBegleftantimetaFM06SB
M06/gen
E(RM06) = -2335.05183674

Zero-point correction= 0.753989 (Hartree/Particle)
Thermal correction to Energy= 0.801889
Thermal correction to Enthalpy= 0.802833
Thermal correction to Gibbs Free Energy= 0.671652
Sum of electronic and ZPE= -2334.297848
Sum of electronic and thermal Energies= -2334.249948
Sum of electronic and thermal Enthalpies= -2334.249004
Sum of electronic and thermal Free Energies= -2334.380184

	E KCal/Mol	CV Cal/Mol-K	S Cal/Mol-K
Total	503.193	183.507	276.093



C,0,2.4882205871,-0.5833960495,3.4863387563
C,0,1.4708755934,-0.3563479925,2.5582308882
N,0,1.3957136511,-1.0726067019,1.4208943513
C,0,2.3074362671,-2.0269957264,1.196182081
C,0,3.3383897843,-2.2926083052,2.0802447458
C,0,3.4570395356,-1.5570623087,3.2633443447
C,0,0.3911427701,0.6285172553,2.7917434801
N,0,-0.6138104586,0.6198564805,1.8960914871
C,0,-1.6667182521,1.4031839916,2.1101608158
C,0,-1.754159566,2.2716554863,3.1906867295
C,0,-0.7048994109,2.3487073487,4.102176749
C,0,0.3748025125,1.4877315173,3.8850018556
Ir,0,-0.1721018927,-0.4986024731,-0.0855457346
B,0,0.3811955957,-1.6061521515,-1.6945357983
O,0,0.0884537048,-1.3084328389,-3.0190933483
C,0,0.622623656,-2.3274175773,-3.8414359374
C,0,1.6626278374,-3.0142108966,-2.9582184924
O,0,1.2639309046,-2.6886001185,-1.6365404019
C,0,1.2531379732,1.1032669029,-0.6748029831
C,0,2.4712558331,0.6843808376,-1.228024404
C,0,3.5417859115,1.5557477432,-1.341380413
C,0,3.4583732317,2.879394433,-0.9431927793
C,0,2.2486644328,3.3243125843,-0.4259690457
C,0,1.168942559,2.4535689913,-0.3081836698
F,0,4.6988791148,1.1007336913,-1.8495172386
O,0,0.0063091341,2.9785199392,0.2229007878
B,0,-1.0917892705,3.161943271,-0.5515425342
O,0,-1.1428436582,2.9393762256,-1.9014159059
C,0,-2.4819898175,3.1539342893,-2.3114020428
C,0,-3.1838421319,3.7678547142,-1.0819765917
O,0,-2.2605003395,3.6395966925,-0.0154753708
B,0,-1.3431552376,-2.1141975935,0.6145882779
O,0,-1.0015232475,-3.4521177744,0.5371327638
C,0,-1.9892152445,-4.212349028,1.2143141646
C,0,-3.1594179059,-3.244946594,1.3806708229
O,0,-2.5685886992,-1.9611708158,1.2685820277
B,0,-2.044482374,-0.4653113492,-0.9356636061
O,0,-2.9733625609,0.5506275604,-0.6666464361
C,0,-4.249840163,0.0675140727,-1.055787118
C,0,-3.9310853602,-1.0053069464,-2.0895858538

O,0,-2.6291055198,-1.4352654596,-1.7416517688
H,0,-0.1841402114,0.6611414192,-1.2586512465
H,0,-2.4560342563,1.3439715263,1.3625501668
H,0,1.2169709776,1.49920521,4.5737457204
H,0,-2.6355782388,2.9007899198,3.2780733345
C,0,-0.695239987,3.3043538078,5.2880397464
H,0,2.5100205595,0.003850669,4.3988382783
C,0,4.592409912,-1.8416685112,4.2376958392
H,0,4.0461883079,-3.0816740351,1.832901933
H,0,2.1823740213,-2.579943494,0.2652789656
H,0,-4.7556834312,-0.3556270203,-0.1735547965
H,0,-4.861051701,0.8894642073,-1.4539786841
H,0,-4.6271706137,-1.8534731594,-2.0635255781
H,0,-3.9203073119,-0.5987812477,-3.1141319854
H,0,2.6144859623,-0.3443831985,-1.5616203672
H,0,4.3169628933,3.5374590559,-1.0528137501
H,0,2.1198894112,4.359022886,-0.111883335
H,0,-3.674041999,-3.3413509055,2.3448015005
H,0,-3.9042641585,-3.3674197464,0.5761530417
H,0,-1.5894885265,-4.5493218754,2.1834794093
H,0,-2.2447057537,-5.1002968633,0.6231984157
H,0,2.6762926037,-2.6192314548,-3.1386573672
H,0,1.691965322,-4.1037553618,-3.0827710735
H,0,1.051839757,-1.8894220908,-4.7512912172
H,0,-0.18350589,-3.0167152763,-4.1373294383
H,0,-3.4218411188,4.8319992079,-1.2253112059
H,0,-4.1141161926,3.2440051563,-0.8255245903
H,0,-2.9204712864,2.1883192158,-2.5961524181
H,0,-2.4945078102,3.8180679411,-3.1847461149
C,0,-1.9626544506,4.1539035474,5.3486789716
C,0,-0.5910210445,2.5000714004,6.5888743531
C,0,0.5082350833,4.2459827012,5.1636289662
H,0,-1.9068230464,4.8353066171,6.2082061339
H,0,-2.086007687,4.7673509828,4.4457910887
H,0,-2.8637967675,3.5377638897,5.4740532458
H,0,-0.5970262496,3.1786435429,7.4535827491
H,0,-1.4382738246,1.8082981095,6.692881192
H,0,0.3328818462,1.908974143,6.6376058695
H,0,0.527314361,4.9457404368,6.0112086988
H,0,1.4620762771,3.7025989804,5.1587101333
H,0,0.4520994035,4.8323348126,4.2365512729
C,0,4.5473514094,-0.9351861337,5.4649033846
C,0,4.4950444631,-3.2978432964,4.7083944072
C,0,5.9299044542,-1.6214461123,3.5206350623
H,0,5.3087093303,-3.5213698007,5.4127640697
H,0,3.5407517481,-3.4841484668,5.2200042544
H,0,4.5725468917,-4.0070390822,3.8745500392
H,0,5.3863881298,-1.1759573483,6.1308784958
H,0,4.6355183399,0.1258779679,5.1929327349
H,0,3.620694648,-1.0714440052,6.039890967
H,0,6.7633097401,-1.8218558308,4.2086379745
H,0,6.0461840278,-2.2846190799,2.6539679146
H,0,6.0213821967,-0.5861062848,3.1651461832

TS5-OBeg$_{anti}$ M06/BS1
OBegleftantimetaFM06PS
M06/gen
E(RM06) = -2335.16879005

Zero-point correction= 0.749172 (Hartree/Particle)
Thermal correction to Energy= 0.797412
Thermal correction to Enthalpy= 0.798357
Thermal correction to Gibbs Free Energy= 0.666667
Sum of electronic and ZPE= -2334.419619
Sum of electronic and thermal Energies= -2334.371378
Sum of electronic and thermal Enthalpies= -2334.370433
Sum of electronic and thermal Free Energies= -2334.502123

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	500.384	184.801	277.165

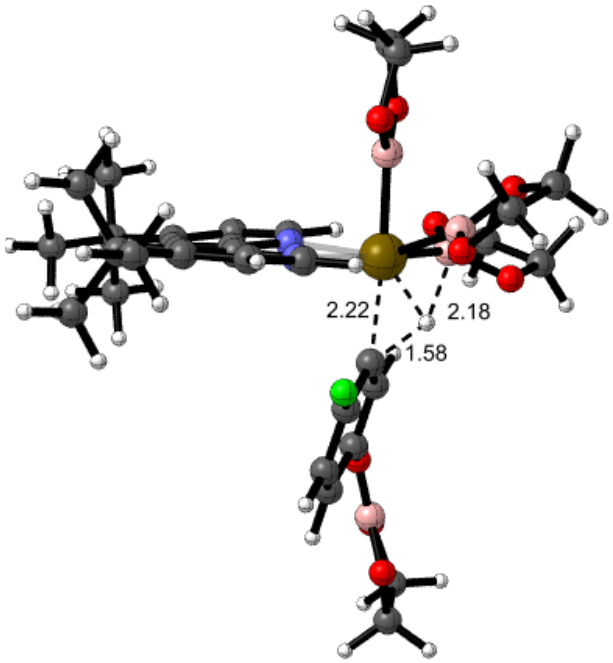
C,0,-3.4125366695,-0.4555369491,-0.575360218
C,0,-2.0575237021,-0.1564738736,-0.7230683852
N,0,-1.1420138504,-1.1319793852,-0.8637726401
C,0,-1.5536611731,-2.4019142591,-0.9546866483
C,0,-2.8857397604,-2.7586148628,-0.830717915
C,0,-3.8545968791,-1.777303304,-0.5947916647
C,0,-1.5374354563,1.2301498421,-0.7234656596
N,0,-0.1973510803,1.3566962693,-0.6745458498
C,0,0.3301458263,2.5767974172,-0.7355494895
C,0,-0.4420173349,3.730053872,-0.8110496071
C,0,-1.8314041488,3.634851158,-0.833111025
C,0,-2.3678054619,2.3431461803,-0.8012004549
Ir,0,0.9596025115,-0.6028140536,-0.2411062057
B,0,1.7611134847,-2.4502390584,0.0477288608
O,0,2.740303165,-2.7622322458,0.9838106552
C,0,3.0729560721,-4.1330085788,0.8500682453
C,0,1.8766472534,-4.7337649157,0.1146729853
O,0,1.2805674035,-3.6224428665,-0.541183528
C,0,0.046346605,-0.6390965672,1.7856535501
C,0,-0.4859443393,-1.8721307713,2.193626596
C,0,-1.4205678872,-1.9427302946,3.2114901833
C,0,-1.8449221079,-0.8245994102,3.909375472
C,0,-1.2889477263,0.4000026617,3.5563760016
C,0,-0.3537925641,0.4828615202,2.5262291823
F,0,-1.9406772423,-3.1494829649,3.5361142763
O,0,0.101315222,1.7481949549,2.2199167843
B,0,1.3982805596,2.1197489058,2.3568278964
O,0,2.3808844624,1.3564064041,2.9266849546
C,0,3.5852894114,2.1076469026,2.882069457
C,0,3.21788631,3.4248988856,2.1643108645
O,0,1.814068213,3.3641505268,1.9554371774
B,0,1.5683579628,-0.6515706496,-2.2713582251
O,0,1.487867336,-1.7497340072,-3.1068837129
C,0,1.8664747967,-1.35102013,-4.4178087949
C,0,2.5756967304,-0.0154730593,-4.2086307543
O,0,2.0664329002,0.4537990548,-2.9674958769
B,0,2.9054623267,0.0410951558,-0.4040581208
O,0,3.2791451151,1.3730046461,-0.1755632624
C,0,4.5565745024,1.5607057427,-0.7712873167
C,0,5.1462823762,0.1556949069,-0.8111993847
O,0,4.0063519541,-0.6858628237,-0.8444952851
H,0,1.5663632239,-0.4404959099,1.2723338139
H,0,1.4168584874,2.6286605767,-0.6926488657
H,0,-3.4452504547,2.2059775169,-0.8452854938
H,0,0.0657141612,4.6893134416,-0.8290849515
C,0,-2.7535223514,4.846288392,-0.8910708062
H,0,-4.1175900002,0.3519851349,-0.4085091583
C,0,-5.3006715341,-2.1723739764,-0.3308522262
H,0,-3.1494727876,-3.8121329468,-0.8816209482
H,0,-0.7640673073,-3.1401477729,-1.094380947
H,0,4.4183672555,1.9719687345,-1.7832489621
H,0,5.1512871177,2.2687658357,-0.178309358

H,0,5.771432979,-0.0266909677,-1.693206579
H,0,5.7397677558,-0.0687018138,0.08913323
H,0,-0.2077882124,-2.7999887562,1.6937368583
H,0,-2.5747774312,-0.9196146961,4.7084164214
H,0,-1.5716554848,1.3135050144,4.075072739
H,0,2.376686595,0.7179532442,-4.9985220828
H,0,3.6665535143,-0.1460639679,-4.1169034298
H,0,0.9651903496,-1.2475186915,-5.0400689282
H,0,2.5099735985,-2.1168264659,-4.8654064698
H,0,1.1471869451,-5.1749037099,0.8125583362
H,0,2.1549306408,-5.4952491929,-0.6229914881
H,0,3.2400254085,-4.5753635283,1.8392035704
H,0,4.0008927013,-4.2241843888,0.2657094553
H,0,3.4562257122,4.3133753824,2.7616143022
H,0,3.7132827755,3.511242477,1.1885993795
H,0,4.343789081,1.5339619364,2.3345081222
H,0,3.9411597256,2.2701089451,3.9072740326
C,0,-1.9729424945,6.1589413586,-0.9194326425
C,0,-3.6164373383,4.7692879796,-2.1569897374
C,0,-3.6552436452,4.8484550616,0.35040222
H,0,-2.6750705977,7.0004428453,-0.9658640217
H,0,-1.3601118822,6.2890222692,-0.018536688
H,0,-1.3178314814,6.2265182181,-1.7974897474
H,0,-4.277891239,5.6437714882,-2.2129247802
H,0,-2.9916756085,4.7559564544,-3.0592197583
H,0,-4.2493561457,3.8739102733,-2.1729919425
H,0,-4.3129182276,5.7274500207,0.3349021976
H,0,-4.2921895023,3.9571386004,0.4000753587
H,0,-3.0559130104,4.8842091521,1.2688365179
C,0,-6.21211543,-0.9597325729,-0.147800551
C,0,-5.8361684526,-3.001862509,-1.5039049794
C,0,-5.3365693323,-3.0049023179,0.9583381466
H,0,-6.8793168113,-3.2855439661,-1.3134688981
H,0,-5.8050674923,-2.4278131489,-2.4389779481
H,0,-5.2664655884,-3.9257337651,-1.656549293
H,0,-7.2387242629,-1.3008525317,0.0333302968
H,0,-5.9153134927,-0.3475717609,0.713633755
H,0,-6.2311324724,-0.3214868097,-1.0412511477
H,0,-6.3710673292,-3.2845098658,1.1969772299
H,0,-4.7497112709,-3.9265649975,0.8675925581
H,0,-4.9285574733,-2.435369299,1.8035451707

TS5-F M06/BSsmall
leftFmetaOBegM06SBa
leftFmetaOBeg
M06/gen
E(RM06) = -2335.04360634

Zero-point correction= 0.753465 (Hartree/Particle)
Thermal correction to Energy= 0.802253
Thermal correction to Enthalpy= 0.803197
Thermal correction to Gibbs Free Energy= 0.665879
Sum of electronic and ZPE= -2334.290142
Sum of electronic and thermal Energies= -2334.241353
Sum of electronic and thermal Enthalpies= -2334.240409
Sum of electronic and thermal Free Energies= -2334.377727

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	503.421	183.894	289.011



C,-0.845406,2.979139,1.338458
C,-0.965807,1.711894,0.765132
N,-0.246797,0.671115,1.225768
C,0.563816,0.85923,2.274973
C,0.711092,2.089906,2.88993
C,0.006442,3.200261,2.41651
C,-1.898403,1.427404,-0.34821
N,-1.844981,0.184525,-0.86121
C,-2.690102,-0.143243,-1.836638
C,-3.624369,0.745765,-2.352321
C,-3.703757,2.04142,-1.846456
C,-2.811804,2.365234,-0.82184
Ir,-0.322738,-1.269151,0.093399
B,1.013388,-2.395263,1.125825
O,1.731534,-3.465959,0.606282
C,2.543539,-4.010026,1.627367
C,2.598612,-2.913483,2.692442
O,1.477513,-2.093773,2.408837
C,2.562803,-0.220007,-0.608098
C,1.303115,-0.449642,-1.176614
C,1.103949,0.104125,-2.439541
C,2.047613,0.877443,-3.096319
C,3.27741,1.116539,-2.494535
C,3.528908,0.551302,-1.247905
F,-0.054254,-0.133665,-3.088518
O,4.705315,0.755887,-0.564903
B,5.93864,0.874615,-1.103894
O,6.251674,0.789462,-2.439064
C,7.635861,1.075057,-2.559038
C,8.175776,1.002372,-1.121253
O,7.027441,1.093996,-0.298072
B,-1.848609,-1.889095,1.419085
O,-1.705718,-2.114265,2.776283
C,-2.979367,-2.413344,3.322553
C,-3.845497,-2.72595,2.104266
O,-3.177482,-2.084675,1.031467
B,-1.130479,-3.056528,-0.537744

O,-1.798829,-3.167318,-1.757291
C,-2.532358,-4.380365,-1.74114
C,-1.847743,-5.213279,-0.65975
O,-1.206021,-4.254983,0.161173
H,0.56003,-1.843099,-1.173815
H,-2.598151,-1.163325,-2.209445
H,-2.843767,3.358682,-0.380219
H,-4.282107,0.405756,-3.147706
C,-4.700095,3.077412,-2.351682
H,-1.419053,3.803664,0.926975
C,0.181564,4.562684,3.073166
H,1.390189,2.17123,3.736417
H,1.097922,-0.027439,2.616867
H,-3.581311,-4.163178,-1.482124
H,-2.507513,-4.847311,-2.733558
H,-2.552366,-5.805925,-0.061764
H,-1.093714,-5.896956,-1.07935
H,1.813894,1.276797,-4.081458
H,4.036499,1.711186,-2.99522
H,-4.873307,-2.351131,2.18884
H,-3.886394,-3.809788,1.902371
H,-3.351508,-1.539475,3.88047
H,-2.89648,-3.25465,4.021657
H,3.519214,-2.311738,2.616122
H,2.527733,-3.300723,3.716701
H,3.531121,-4.267964,1.223888
H,2.078437,-4.930992,2.011883
H,8.106258,0.348221,-3.232064
H,7.75906,2.076465,-2.99681
H,8.870872,1.816942,-0.88305
H,8.686757,0.048891,-0.922198
C,-5.589536,2.522902,-3.462077
C,-5.600106,3.523939,-1.193729
C,-3.93506,4.284742,-2.905969
H,-6.333122,4.261457,-1.55015
H,-6.150591,2.671956,-0.772016
H,-5.029701,3.990794,-0.380337
H,-6.291365,3.29974,-3.793591
H,-5.004484,2.210888,-4.338182
H,-6.183771,1.664277,-3.120275
H,-4.641449,5.041013,-3.276615
H,-3.306347,4.762206,-2.143304
H,-3.284198,3.988843,-3.739974
C,-0.664564,5.643946,2.405399
C,-0.235104,4.464986,4.54571
C,1.654623,4.97805,2.981455
H,-0.116616,5.44137,5.036676
H,-1.287338,4.16286,4.63868
H,0.372736,3.738006,5.099537
H,1.797946,5.962745,3.448463
H,2.317249,4.268044,3.492341
H,1.980709,5.046048,1.934685
H,-0.49985,6.604359,2.911625
H,-0.397038,5.779585,1.348093
H,-1.738937,5.420639,2.466845
H,2.821056,-0.634925,0.367615

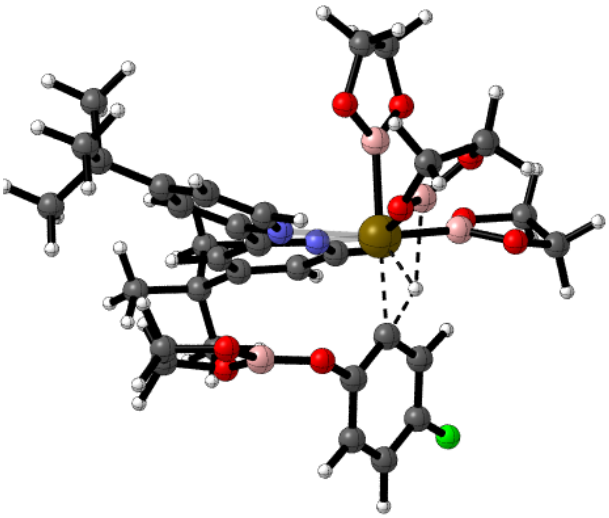
TS5-OBeg$_{syn}$ M06/BSsmall

This structure is the higher-energy *syn* conformer of TS5-OBeg$_{anti}$ given above and discussed in the main text.

OBegleftsynmetaFM06SB
OBegleftsynmetaF
M06/gen
E(RM06) = -2335.04787486

Zero-point correction= 0.753268 (Hartree/Particle)
Thermal correction to Energy= 0.801596
Thermal correction to Enthalpy= 0.802540
Thermal correction to Gibbs Free Energy= 0.670267
Sum of electronic and ZPE= -2334.294606
Sum of electronic and thermal Energies= -2334.246279
Sum of electronic and thermal Enthalpies= -2334.245335
Sum of electronic and thermal Free Energies= -2334.377608

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	503.009	183.823	278.393



C,2.223685,2.047328,-1.180309
C,1.335335,1.022238,-0.855648
N,0.004653,1.175812,-0.979581
C,-0.45803,2.327777,-1.483367
C,0.374624,3.373629,-1.840251
C,1.758321,3.263082,-1.673131
C,1.801767,-0.290493,-0.370643
N,0.898562,-1.02648,0.303854
C,1.270512,-2.227496,0.747492
C,2.537832,-2.756877,0.525793
C,3.480811,-2.030718,-0.19869
C,3.081292,-0.765285,-0.640756
Ir,-1.335654,-0.357138,-0.009288
B,-3.16104,0.266252,-0.617222
O,-4.373948,-0.060271,-0.030852
C,-5.374563,0.797334,-0.544512
C,-4.7452,1.409382,-1.795929
O,-3.350471,1.246479,-1.595488
C,-1.47155,1.050736,1.718001
C,-2.251592,2.206745,1.5538
C,-2.198406,3.243275,2.469484
C,-1.404308,3.185751,3.602045
C,-0.648714,2.038556,3.80063
C,-0.688967,0.997276,2.876769
F,-2.946632,4.338386,2.253879
O,0.036206,-0.142546,3.167339
B,1.383209,-0.131444,3.09499
O,2.137733,0.914396,2.614865

C,3.496542,0.529343,2.680285
C,3.493958,-0.884286,3.306371
O,2.134313,-1.195442,3.530101
B,-1.265917,-1.539255,-1.7666
O,-1.898844,-1.24402,-2.960733
C,-1.561983,-2.238317,-3.913374
C,-0.972618,-3.372913,-3.078065
O,-0.562519,-2.742371,-1.876305
B,-2.19167,-2.207306,0.311071
O,-1.650857,-3.102415,1.233941
C,-2.211075,-4.378581,0.973208
C,-3.496129,-4.065702,0.213325
O,-3.254181,-2.793802,-0.361401
H,-2.064466,-0.412089,1.462508
H,0.505452,-2.781538,1.291307
H,3.757002,-0.157028,-1.240147
H,2.759627,-3.744492,0.920772
C,4.866981,-2.563137,-0.544554
H,3.286091,1.890845,-1.011311
C,2.673656,4.429505,-2.017917
H,-0.074542,4.28324,-2.234411
H,-1.538994,2.385208,-1.604919
H,-1.507573,-4.960456,0.353979
H,-2.375541,-4.915961,1.915105
H,-3.720439,-4.796137,-0.57475
H,-4.367435,-4.002175,0.883011
H,-2.903713,2.33066,0.688996
H,-1.395339,4.013746,4.306578
H,-0.021993,1.933274,4.685523
H,-0.119408,-3.872048,-3.554777
H,-1.73093,-4.136981,-2.83838
H,-0.830392,-1.826792,-4.626499
H,-2.456518,-2.535232,-4.474471
H,-4.982784,2.473147,-1.925694
H,-5.041128,0.874198,-2.710825
H,-5.616773,1.563277,0.210292
H,-6.287469,0.226891,-0.75726
H,3.920044,0.533054,1.663284
H,4.055324,1.257417,3.283623
H,4.039955,-0.923824,4.258759
H,3.932256,-1.637242,2.631041
C,5.127463,-3.931208,0.080827
C,4.972817,-2.697449,-2.068964
C,5.943264,-1.592728,-0.044587
H,5.957917,-3.099517,-2.345378
H,4.203977,-3.379259,-2.457053
H,4.851564,-1.731236,-2.576301
H,6.139768,-4.268484,-0.178861
H,5.058811,-3.899717,1.17757
H,4.42219,-4.688925,-0.286584
H,6.940192,-1.96391,-0.320404
H,5.833958,-0.589381,-0.477133
H,5.915171,-1.493995,1.049851
C,4.143287,4.106543,-1.760743
C,2.507558,4.777761,-3.502025
C,2.286384,5.638724,-1.1586
H,3.167044,5.615869,-3.767747
H,2.769421,3.922567,-4.140128
H,1.479361,5.075221,-3.74465
H,2.936009,6.492785,-1.396765
H,1.248765,5.951808,-1.330967
H,2.395143,5.413685,-0.088979
H,4.761637,4.976818,-2.017581
H,4.330859,3.868409,-0.704362
H,4.490324,3.263057,-2.374261

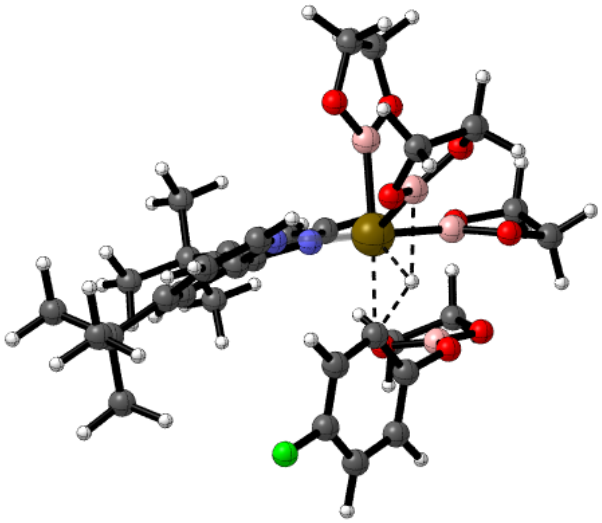
TS5-OBeg$_{syn}$ Conformer B M06/BSsmall

This structure is another higher-energy *syn* conformer of TS5-OBeg$_{syn}$ given above and discussed in the main text. In this conformer, the OBeg on the FPhOBeg is oriented for a Lewis acid/base interaction with a Beg on the Ir, but this does not lead to low-energy structure.

OBegrightsynmetaFM06SB
M06/gen
E(RM06) = -2335.05155106

Zero-point correction= 0.754817 (Hartree/Particle)
Thermal correction to Energy= 0.802154
Thermal correction to Enthalpy= 0.803098
Thermal correction to Gibbs Free Energy= 0.675357
Sum of electronic and ZPE= -2334.296734
Sum of electronic and thermal Energies= -2334.249397
Sum of electronic and thermal Enthalpies= -2334.248453
Sum of electronic and thermal Free Energies= -2334.376194

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	503.359	183.278	268.853



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C,0,-1.7751561363,-0.4188488598,-0.1205278109
N,0,-0.7278011301,-1.2598331506,-0.0324881026
C,0,-0.9696431732,-2.568092179,0.1193253236
C,0,-2.251940873,-3.0825325712,0.2029638739
C,0,-3.3593160156,-2.2316565957,0.1572604141
C,0,-1.4629196442,0.9949930509,-0.4223489037
N,0,-0.2189089636,1.2282362649,-0.8787356398
C,0,0.0961539186,2.4595982945,-1.2749737428
C,0,-0.7812610297,3.5327843266,-1.1619048192
C,0,-2.0392927132,3.3403714618,-0.5932036514
C,0,-2.3795485221,2.0269246573,-0.2562384969
Ir,0,1.3335567521,-0.3814666693,-0.1907953656
B,0,2.4655921684,-1.9431344833,0.4227613833
O,0,1.9419594721,-3.2329501551,0.6252920922
C,0,3.0419590493,-4.1043548702,0.8481725333
C,0,4.1473441436,-3.1704754821,1.3211088702

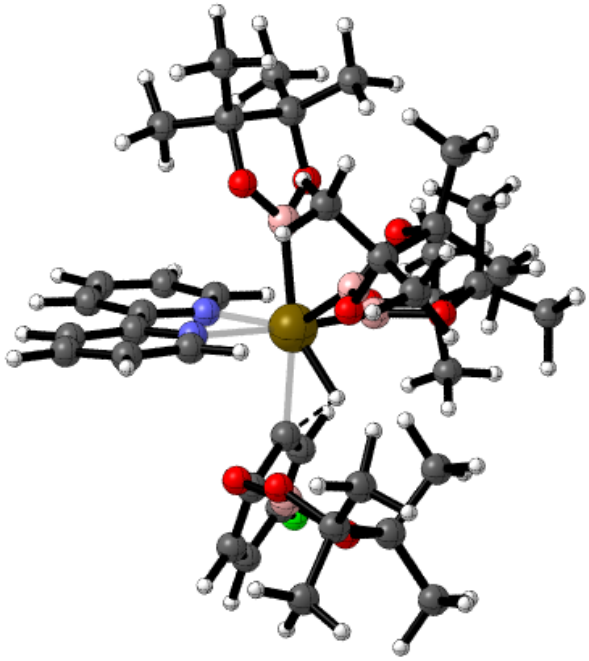
O,0,3.8111163998,-1.9222975293,0.743120183
C,0,1.1242521328,0.5377126924,1.8467228469
C,0,0.6759591045,1.8609445036,1.9775114842
C,0,0.2554854877,2.3664434695,3.1946643529
C,0,0.2918327676,1.6122931643,4.35406579
C,0,0.7828498061,0.316626401,4.2597929008
C,0,1.1997447008,-0.2001778822,3.0352566422
F,0,-0.1983925439,3.6341720834,3.2505595323
O,0,1.740632477,-1.471041084,3.0427818278
B,0,0.9595956734,-2.5683259311,3.1586959322
O,0,-0.4140076378,-2.5629983136,3.0553318542
C,0,-0.8493167967,-3.866672465,3.3952458672
C,0,0.4176127729,-4.7251365696,3.3015397537
O,0,1.4804255309,-3.8037050729,3.4660019422
B,0,1.4294712042,-1.2063280626,-2.1338447959
O,0,1.5558471019,-2.5477900741,-2.4514341212
C,0,1.5225226841,-2.685862855,-3.8626429597
C,0,1.7152619155,-1.2636970919,-4.387547107
O,0,1.3571357535,-0.4346840691,-3.2954826837
B,0,2.9806577025,0.3165388634,-1.2155690968
O,0,3.1139171511,1.6753117992,-1.5107335151
C,0,4.1328144311,1.8076428323,-2.4891742188
C,0,4.9277267512,0.5093412012,-2.3728400668
O,0,4.0181505532,-0.403298067,-1.7860752729
H,0,2.345747816,0.4542811917,0.7964108811
H,0,1.1151380348,2.5808487852,-1.645165392
H,0,-3.3504573774,1.8155127761,0.1874115489
H,0,-0.4481119737,4.517775631,-1.4775063696
C,0,-2.99793398,4.4799201078,-0.2805046626
H,0,-3.9025069416,-0.1636631851,-0.1092595839
C,0,-4.7702420857,-2.7939398732,0.2661543711
H,0,-2.3737543702,-4.1605085943,0.3009850008
H,0,-0.0852136361,-3.2027740788,0.1718501021
H,0,3.6668654612,1.9121562013,-3.4823830455
H,0,4.7302490624,2.7055249848,-2.2885132602
H,0,5.2699994696,0.1249088873,-3.3425216854
H,0,5.8052241171,0.6179972415,-1.717220622
H,0,0.6508940854,2.5327971597,1.1202999224
H,0,-0.0402869591,2.0379796747,5.2977337968
H,0,0.8570742293,-0.3123357603,5.1463922811
H,0,1.0903836718,-1.0316532553,-5.2591075041
H,0,2.7671017196,-1.0687313052,-4.6558727308
H,0,0.553318986,-3.1121512692,-4.1655501266
H,0,2.3131478187,-3.3740782438,-4.1863133354
H,0,5.1478375797,-3.4796570895,0.993428775
H,0,4.1446933885,-3.0771561006,2.418677772
H,0,3.2981549199,-4.6021376387,-0.10044476
H,0,2.7737036035,-4.8621762258,1.5940101107
H,0,0.4722891993,-5.5024669765,4.0733021811
H,0,0.5073524958,-5.2058918908,2.3131233199
H,0,-1.6400559708,-4.1860077505,2.7021334222
H,0,-1.2675077575,-3.8553354226,4.413169097
C,0,-2.4450241523,5.8322374732,-0.7241174343
C,0,-4.3363191549,4.2502527251,-0.9896957263
C,0,-3.2099446116,4.5157745894,1.2395286233
H,0,-3.1688335175,6.6216088874,-0.4819366274
H,0,-1.5052800226,6.0781836973,-0.2111476541
H,0,-2.2692800858,5.8672110558,-1.8084595025
H,0,-5.0319732256,5.0672823842,-0.7522532128
H,0,-4.2069295014,4.2206743663,-2.08044356
H,0,-4.8146033383,3.3112544101,-0.6821409067
H,0,-3.8342619885,5.3781740324,1.5128248783
H,0,-3.7142868568,3.6109521342,1.6038520998
H,0,-2.2520000543,4.5955356759,1.7717752197
C,0,-5.8339069088,-1.6987901046,0.2601604425
C,0,-5.0283080138,-3.7279135068,-0.9219019858
C,0,-4.8985045058,-3.5803273016,1.5763759472
H,0,-6.0415690229,-4.1491862256,-0.8581900138
H,0,-4.9436204446,-3.1859957123,-1.873753359
H,0,-4.3188195281,-4.5650384131,-0.9485278903
H,0,-6.8287376473,-2.1531388383,0.3585153198
H,0,-5.705068143,-0.9993462004,1.0979602734
H,0,-5.8282998721,-1.1244331902,-0.676667127
H,0,-5.9234757618,-3.9609988012,1.6873002652
H,0,-4.2215483289,-4.4441571053,1.6079805412
H,0,-4.6747605531,-2.9432833176,2.4434251365

TS for (bpy)IrBpin$_3$ + 4-FC$_6$H$_4$OBpin, meta to F, M06/BSsmall

BPINrOBPINMetaFM06SB
M06/gen
E(RM06) = -2649.38481910

Zero-point correction= 0.975237 (Hartree/Particle)
Thermal correction to Energy= 1.032493
Thermal correction to Enthalpy= 1.033437
Thermal correction to Gibbs Free Energy= 0.888855
Sum of electronic and ZPE= -2648.409582
Sum of electronic and thermal Energies= -2648.352326
Sum of electronic and thermal Enthalpies= -2648.351382
Sum of electronic and thermal Free Energies= -2648.495964

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	647.899	230.480	304.299



C,0,-3.6033436224,3.9399971904,0.7077285974
C,0,-2.2900682983,4.1052814719,0.3012719059
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C,0,-1.9165675995,1.7119045868,0.1743406612

C,0,-3.2573856145,1.5564868861,0.549338526
C,0,-4.0837960653,2.6417621285,0.822492881
Ir,0,-0.3239777333,0.1848843964,0.3195707614
N,0,-1.470751972,-0.8744721546,2.0202936829
C,0,-1.301436118,-0.3898713484,3.2623462567
C,0,-2.0069497914,-0.9189057537,4.3447019481
C,0,-2.8857299785,-1.9707011829,4.1307187749
C,0,-3.0336109236,-2.4774695053,2.8472192466
C,0,-2.3032198211,-1.8967578421,1.8187018246
C,0,-0.3208117291,0.7080076463,3.4107039592
N,0,0.2424871173,1.1791713471,2.2796224728
C,0,1.1633667904,2.148290703,2.3449555758
C,0,1.5699670366,2.7037164042,3.550195175
C,0,0.9976503953,2.2310610628,4.7243674006
C,0,0.0458839442,1.2253743241,4.654953224
B,0,1.4094695156,-0.9031262053,0.8468788904
O,0,1.4124047719,-2.0544906314,1.626065689
C,0,2.7257544851,-2.2037000539,2.1911272195
C,0,3.6124703113,-1.4130510709,1.1852628693
O,0,2.6979060869,-0.4218930078,0.6909075034
B,0,-0.1406998732,-1.4628961228,-0.9108293833
O,0,0.9961700995,-1.9075061292,-1.58175316
C,0,0.6206688074,-3.0074835871,-2.4177079553
C,0,-0.5875469452,-3.5900696555,-1.642526381
O,0,-1.1698275949,-2.4003274171,-1.0760405123
B,0,0.8517144824,1.1320489461,-1.0434472597
O,0,1.6699987975,2.2226678821,-0.7246481865
C,0,2.2270047321,2.7465969103,-1.9430594444
C,0,2.1201749169,1.520714557,-2.8926351829
O,0,0.943780961,0.8670036706,-2.4029212442
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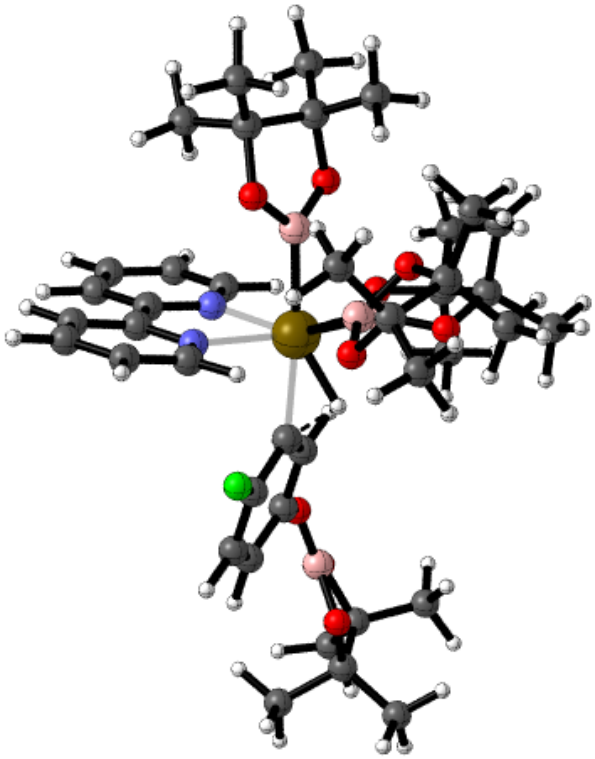
TS for (bpy)IrBpin$_3$ + 4-FC$_6$H$_4$OBpin, ortho to F, M06/BSsmall

BPINrOBPINOrthoFM06SB
M06/gen
E(RM06) = -2649.37950521

Zero-point correction= 0.973595 (Hartree/Particle)
Thermal correction to Energy= 1.031712
Thermal correction to Enthalpy= 1.032657
Thermal correction to Gibbs Free Energy= 0.883138

Sum of electronic and ZPE= -2648.405911
Sum of electronic and thermal Energies= -2648.347793
Sum of electronic and thermal Enthalpies= -2648.346849
Sum of electronic and thermal Free Energies= -2648.496367

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	647.409	231.471	314.688



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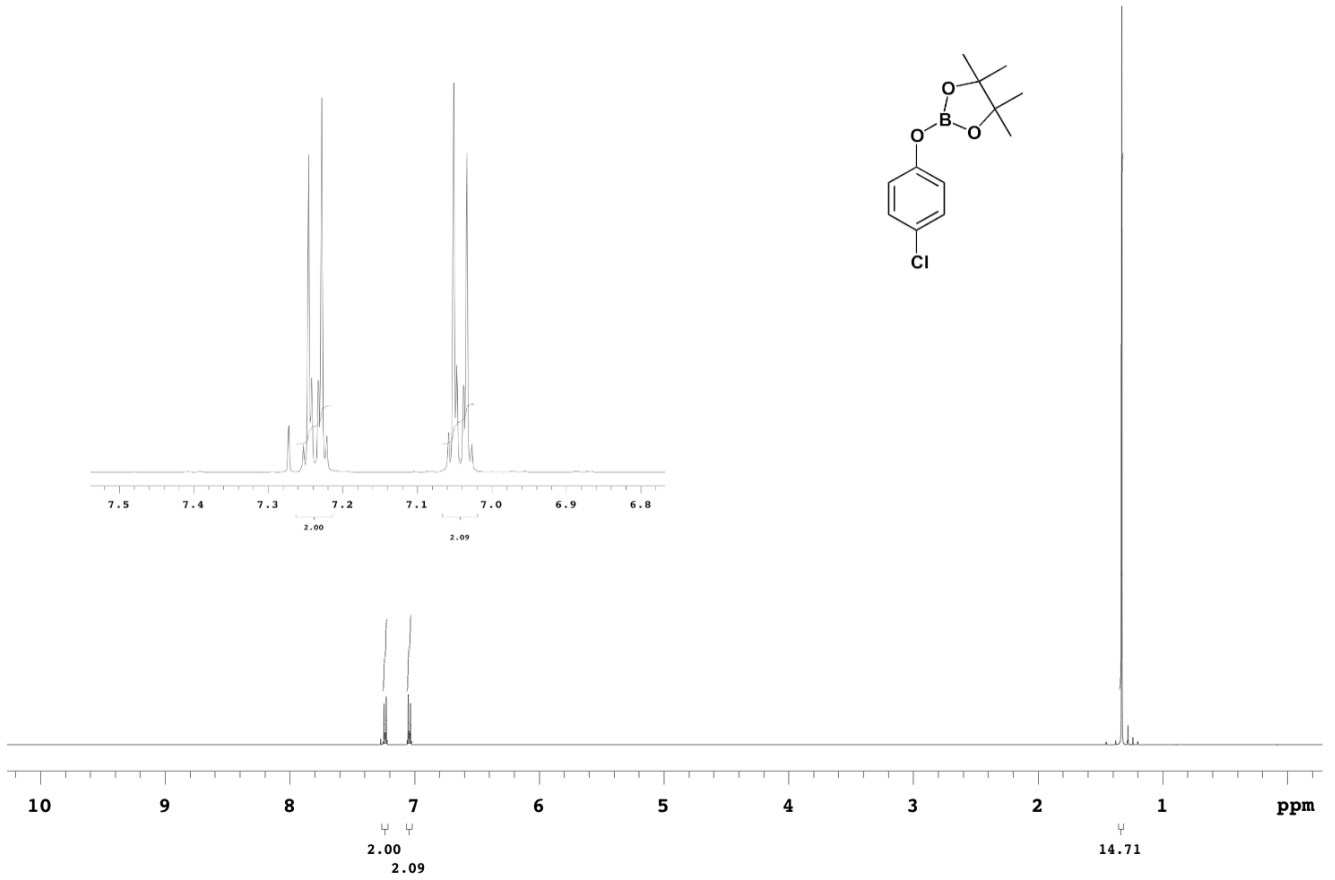
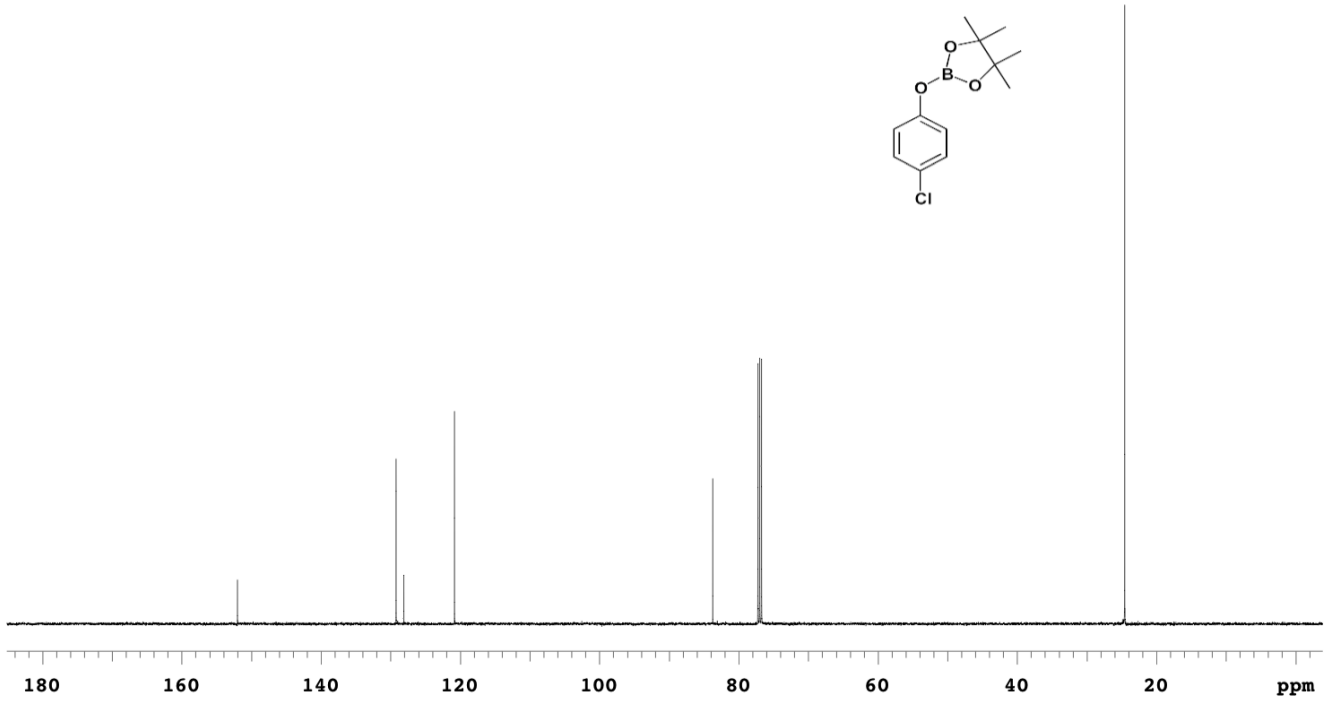
Spectral Copies



^{1}H-NMR (500 MHz, $CDCl_3$)



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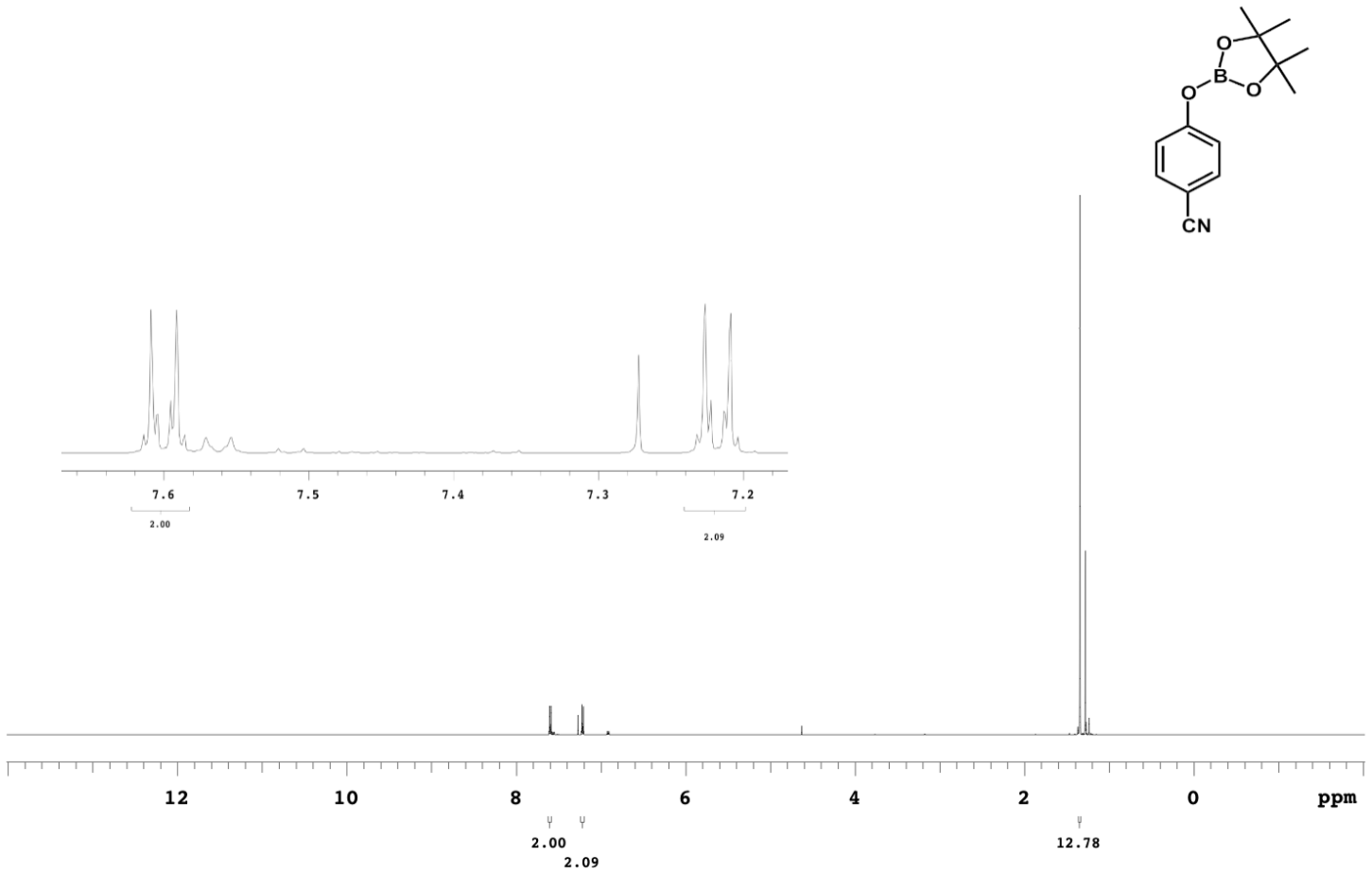
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2
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ppm
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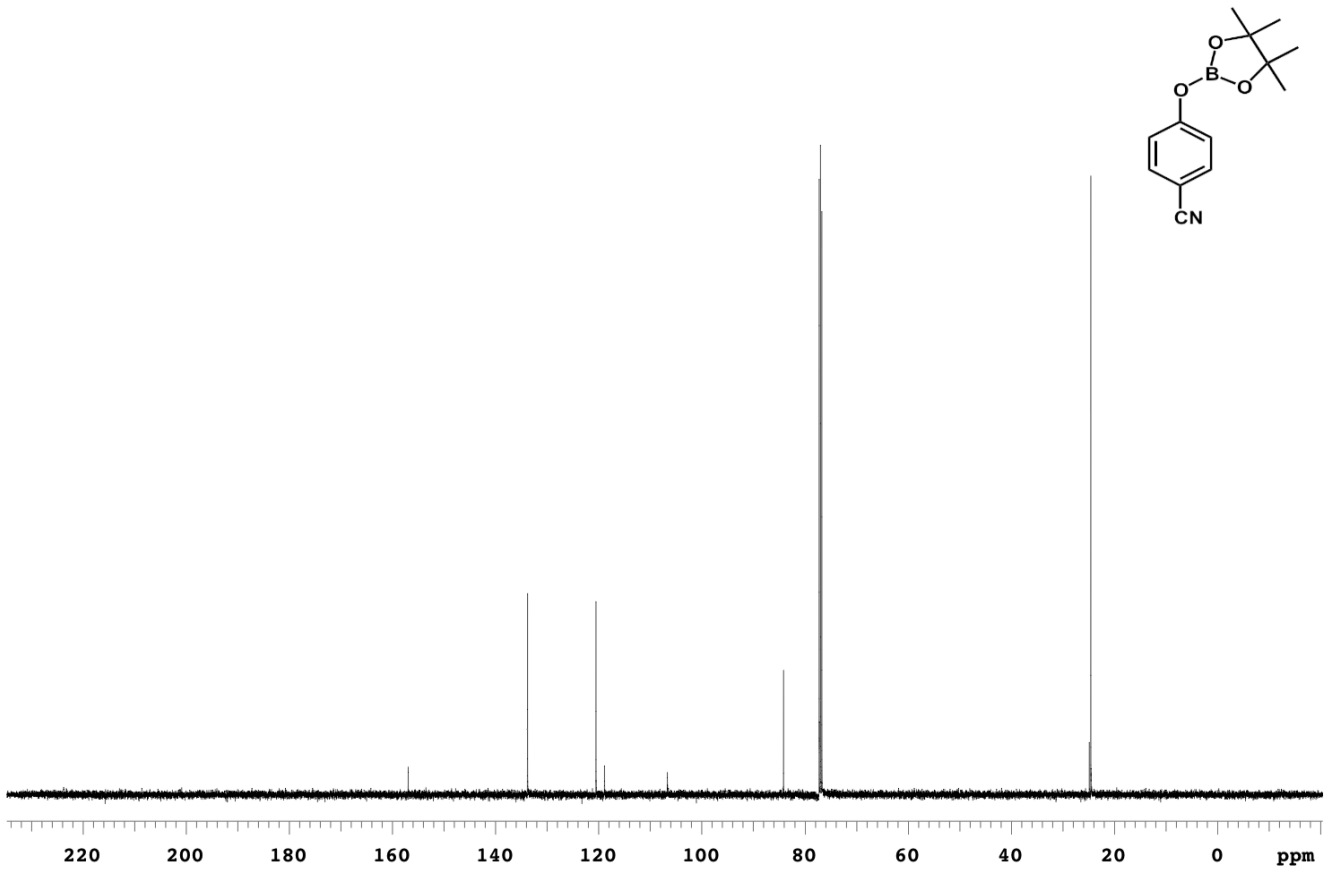
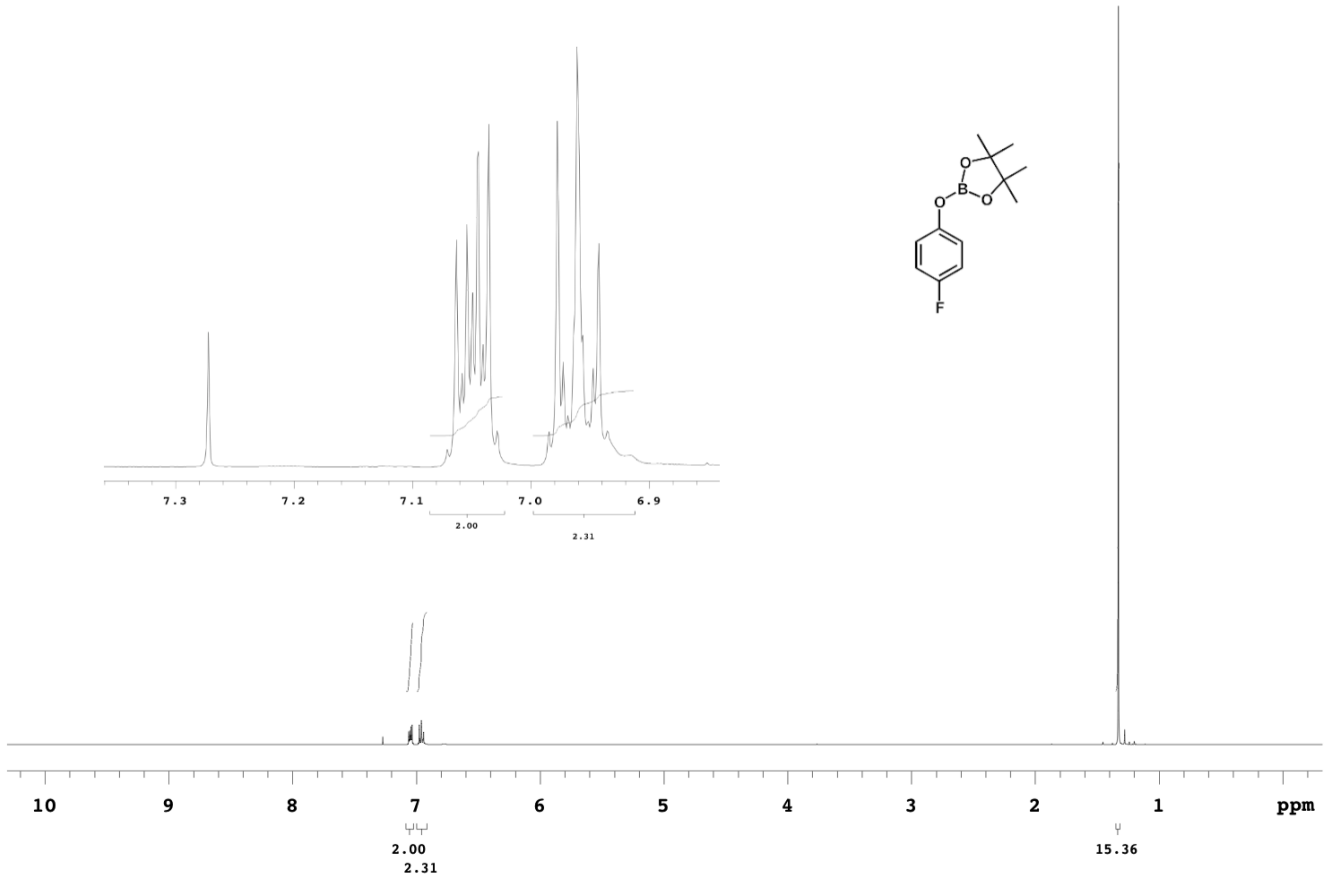


^{13}C NMR (125 MHz, $CDCl_3$)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6.9
2.00
2.31
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B
O
O
F
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9
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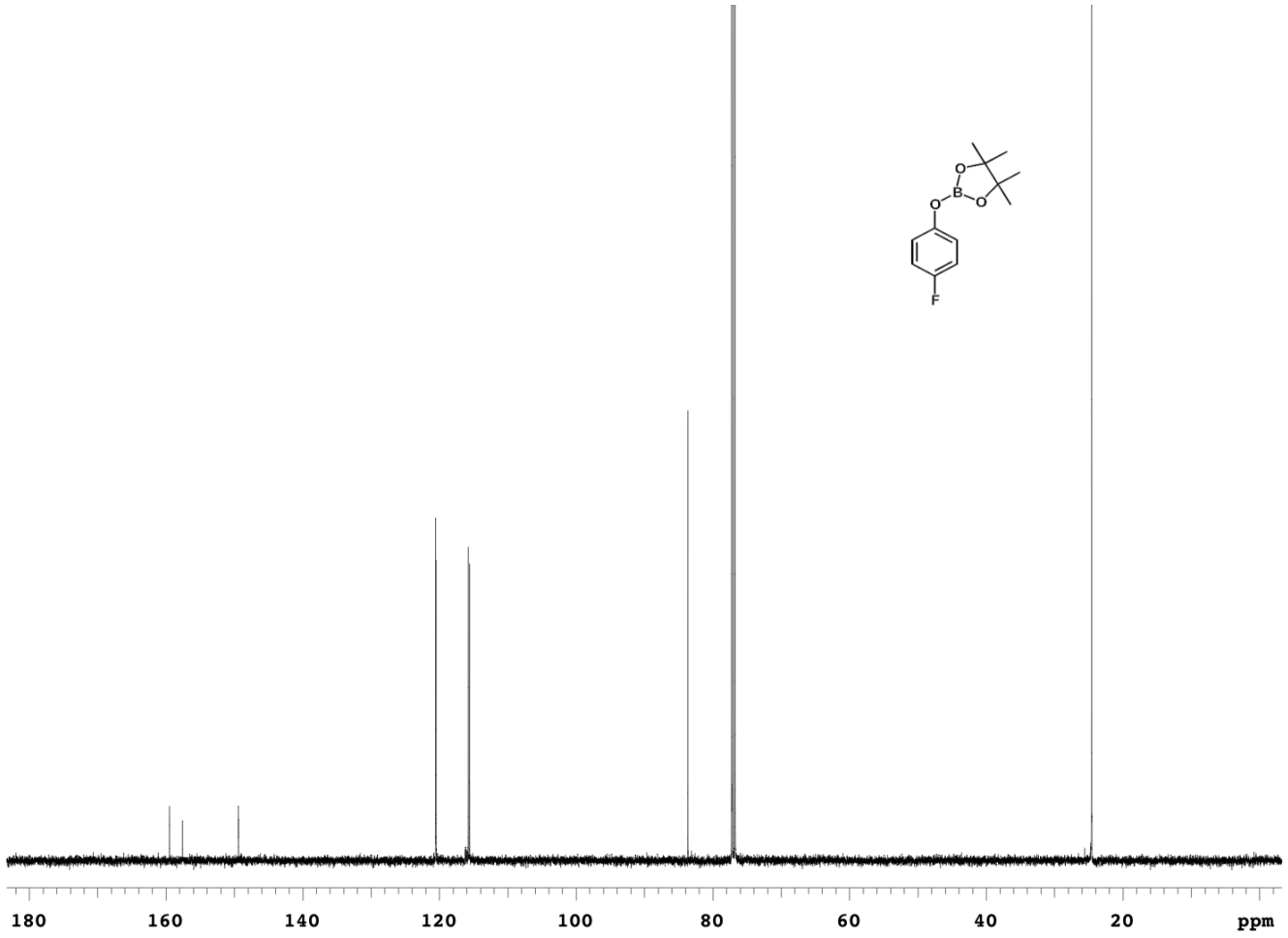
7
6
5
4
3
2
1
ppm
2.00
2.31
15.36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B
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O
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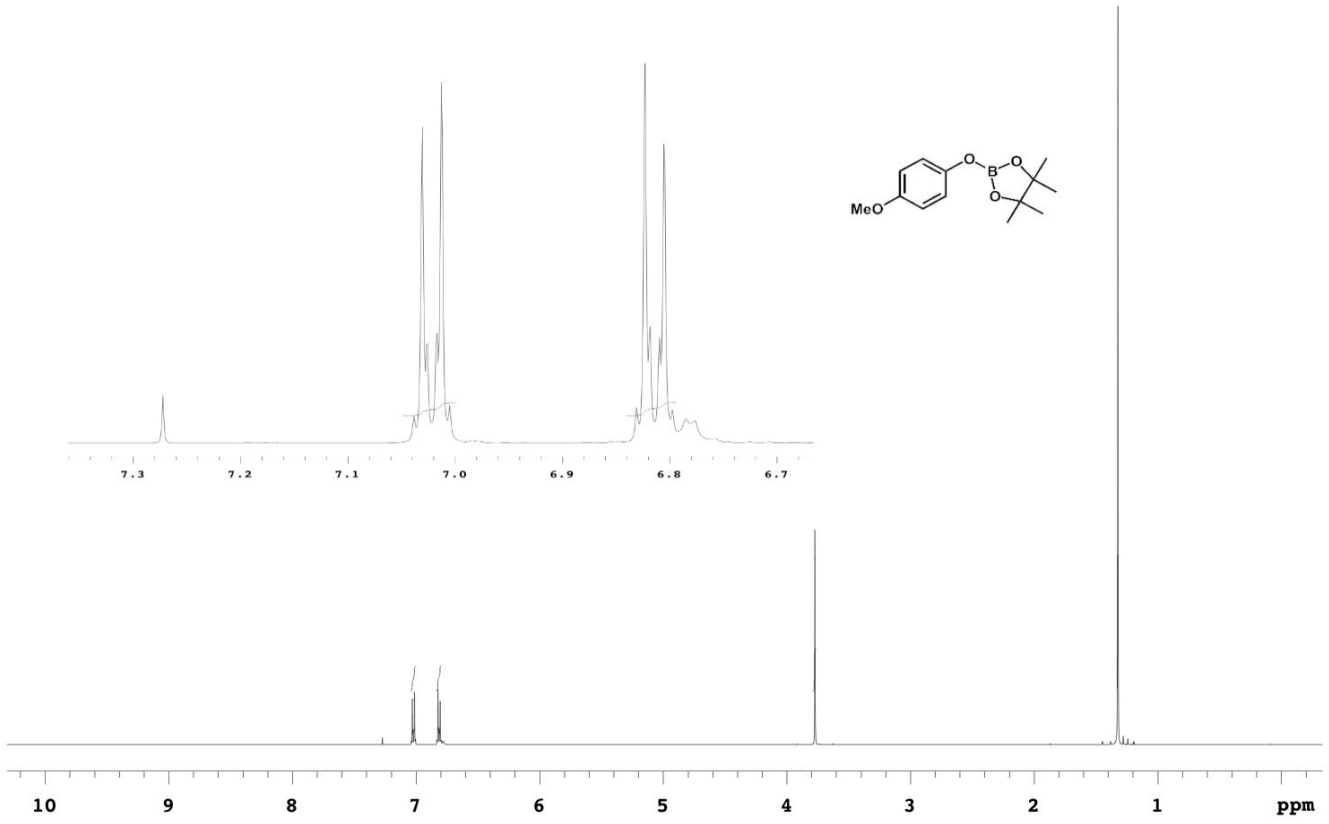
60
40
20
ppm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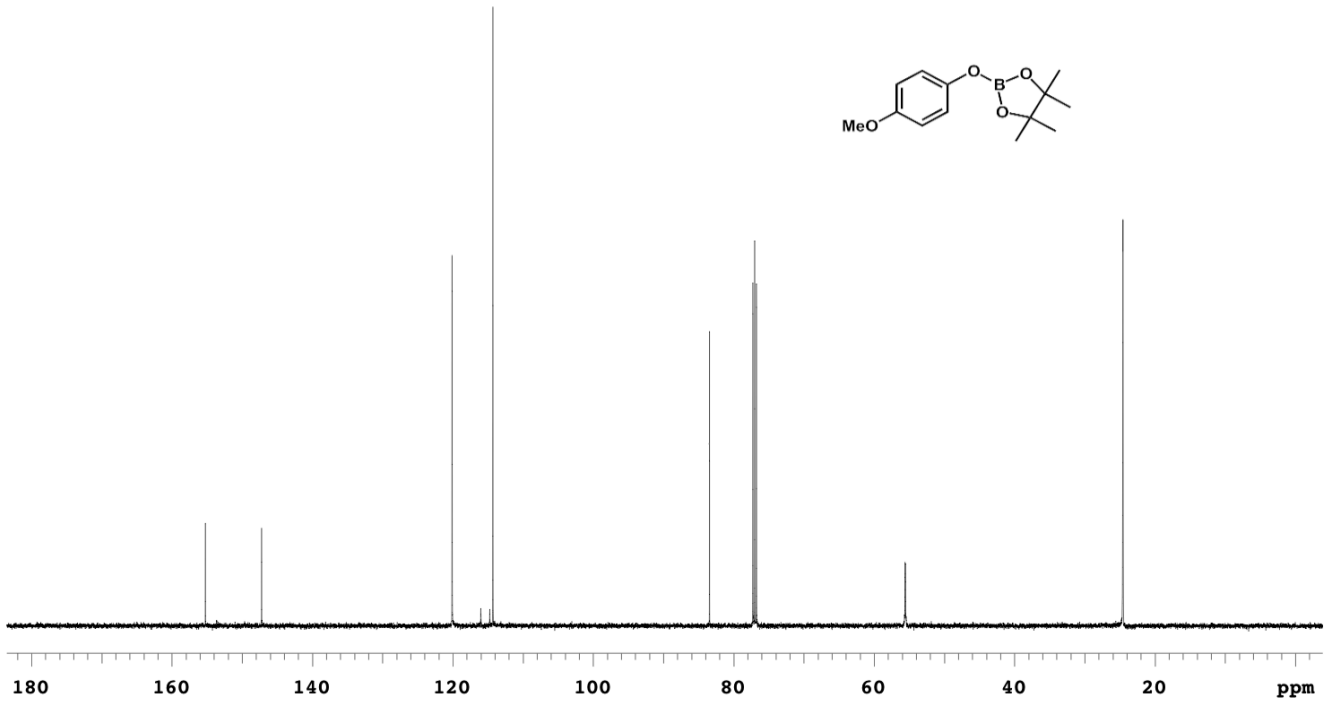
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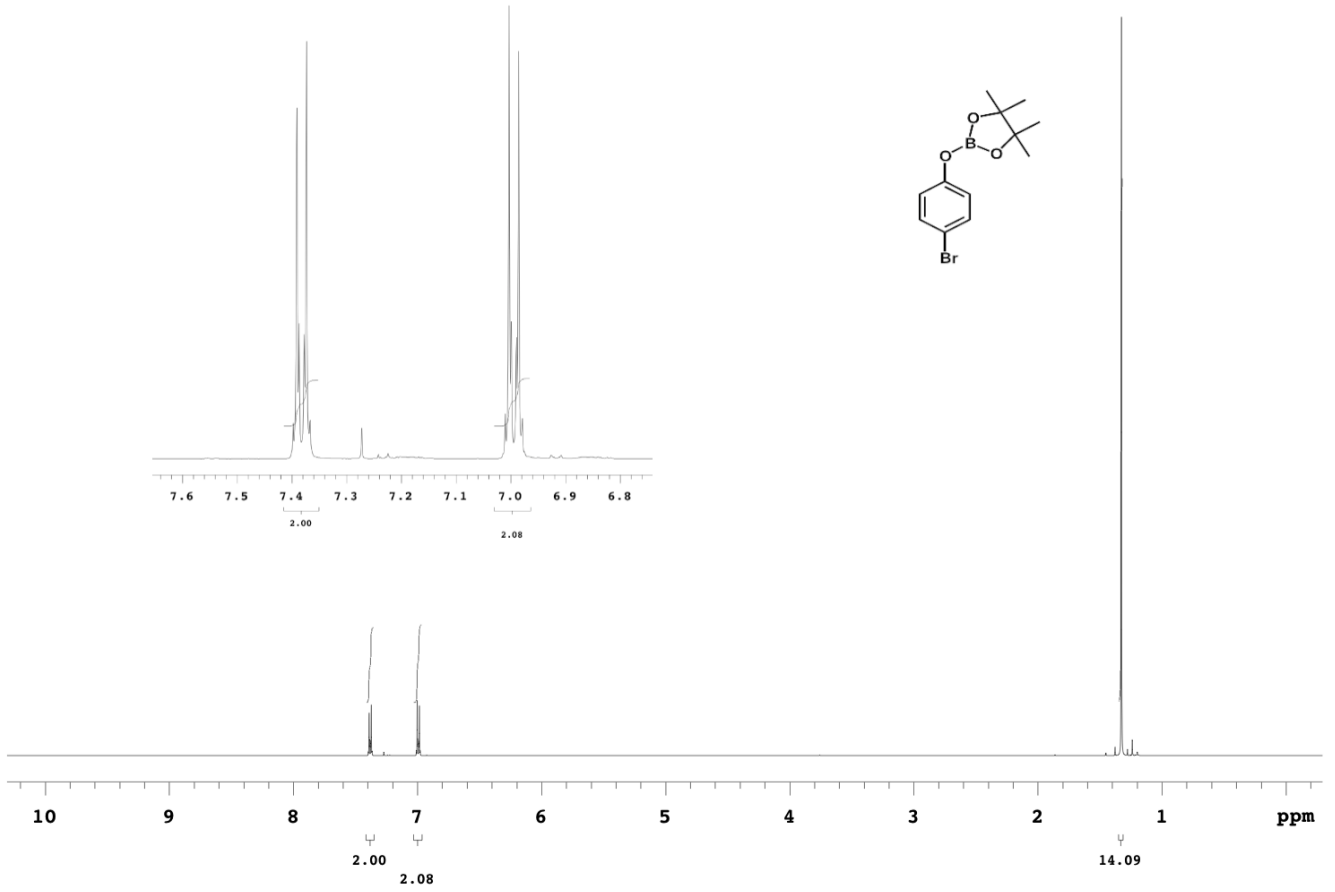
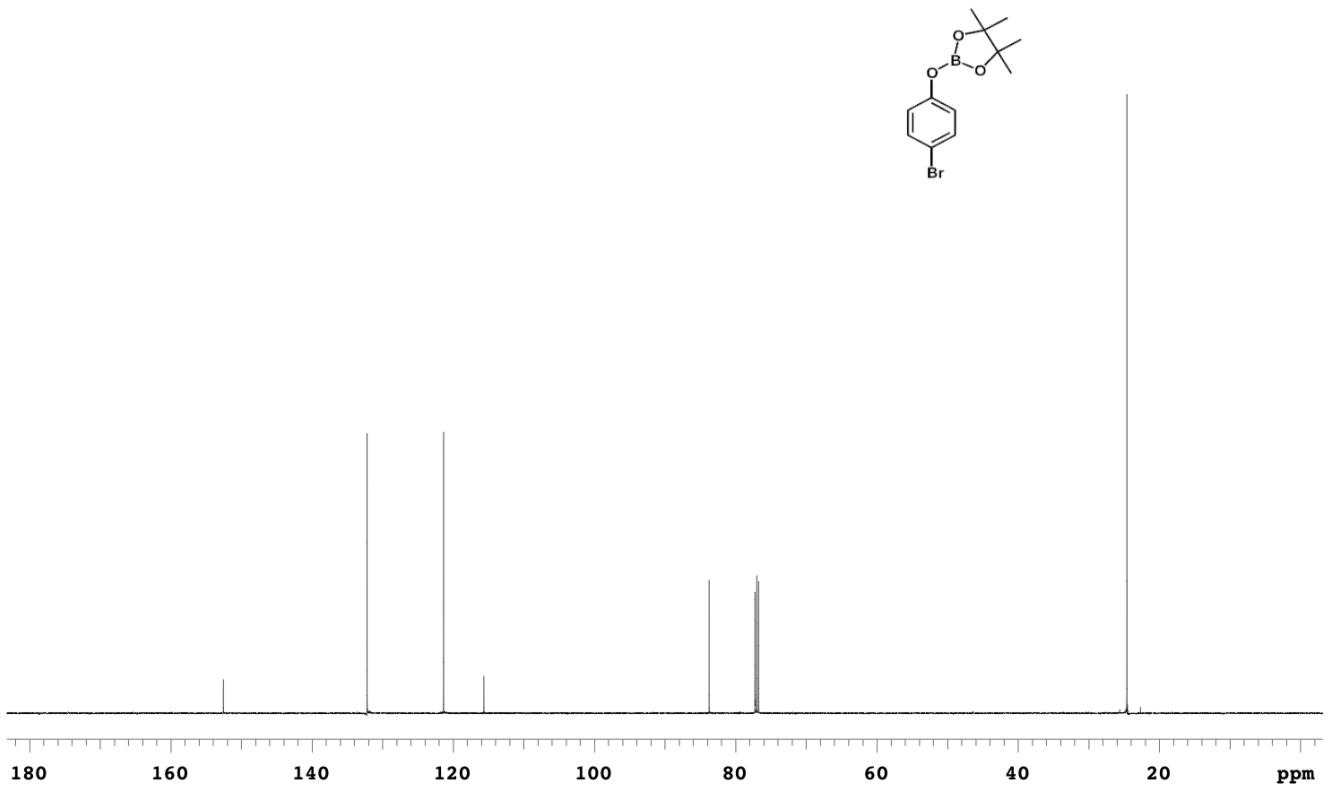
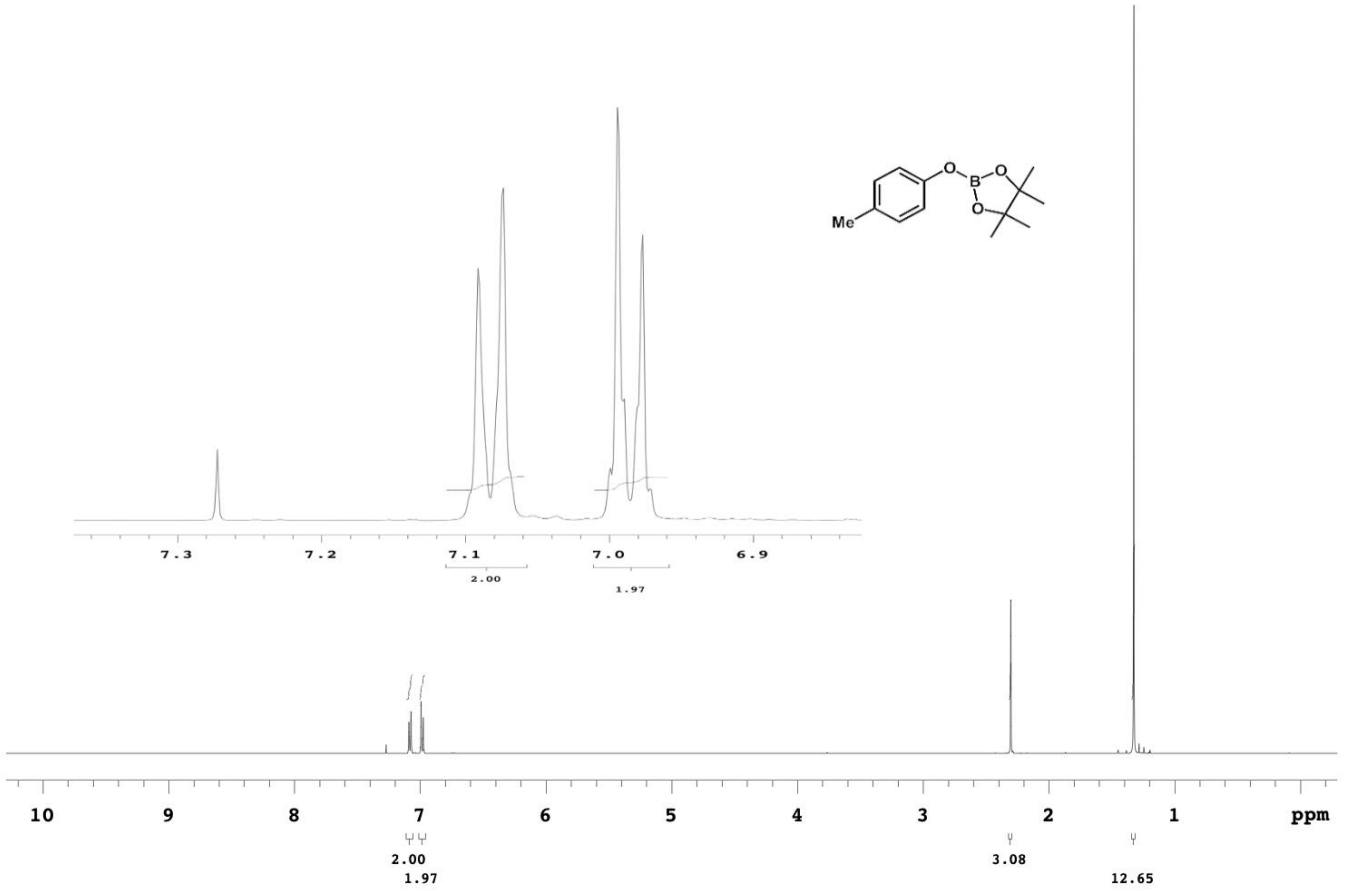


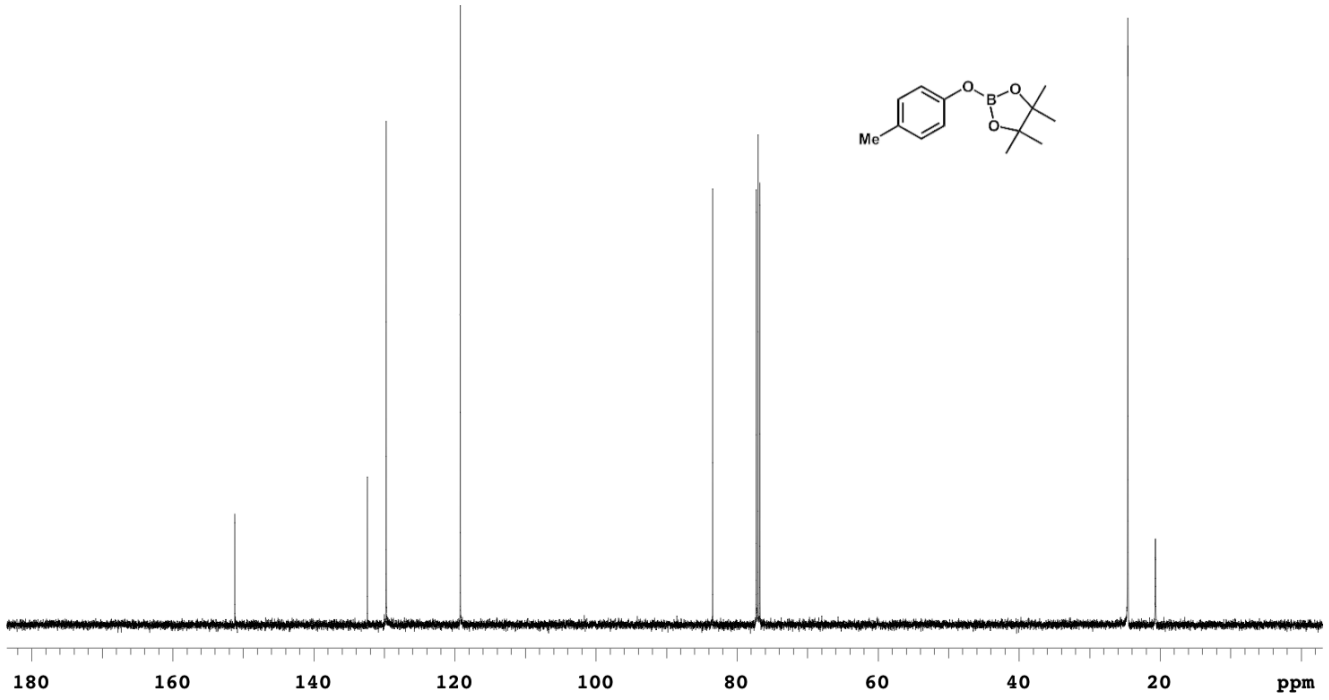
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)



^{1}H-NMR (500 MHz, $CDCl_3$)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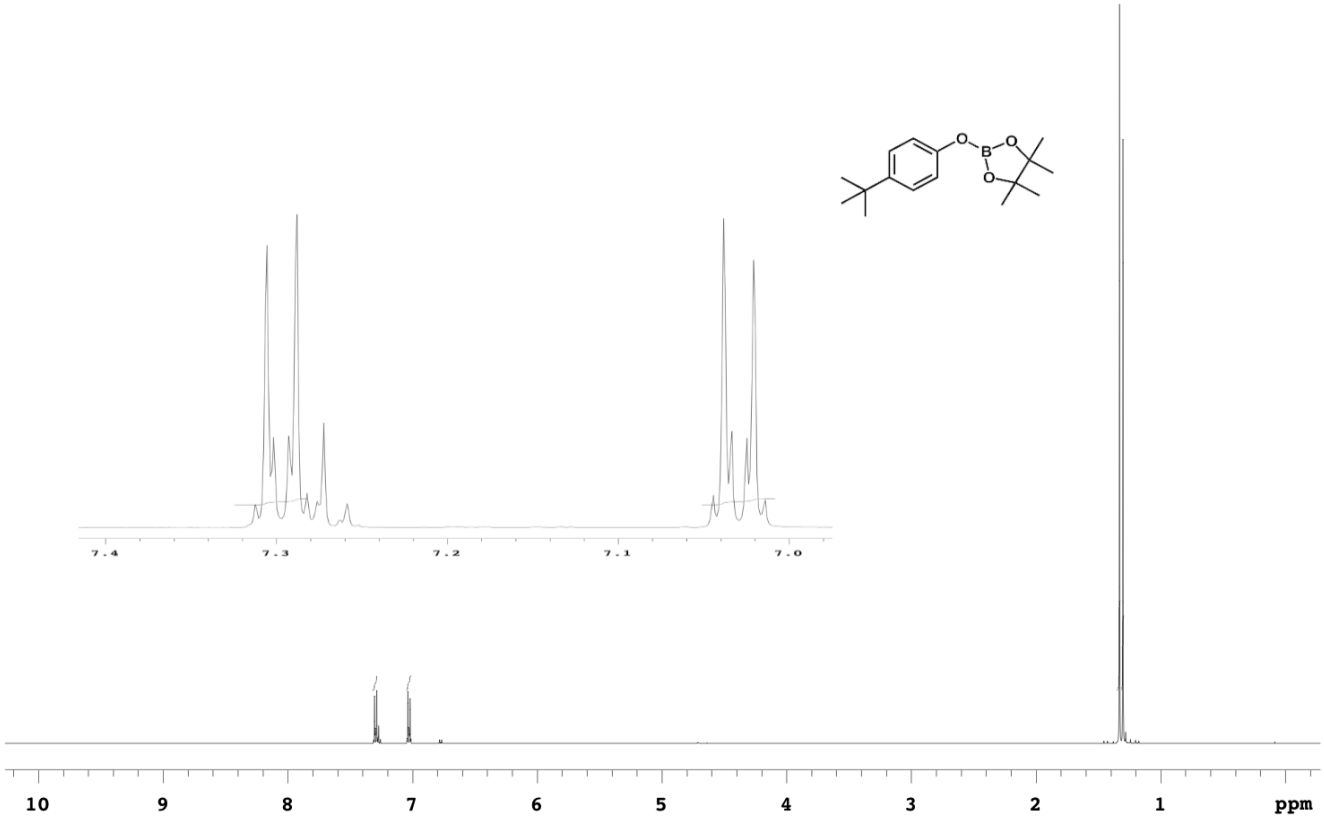
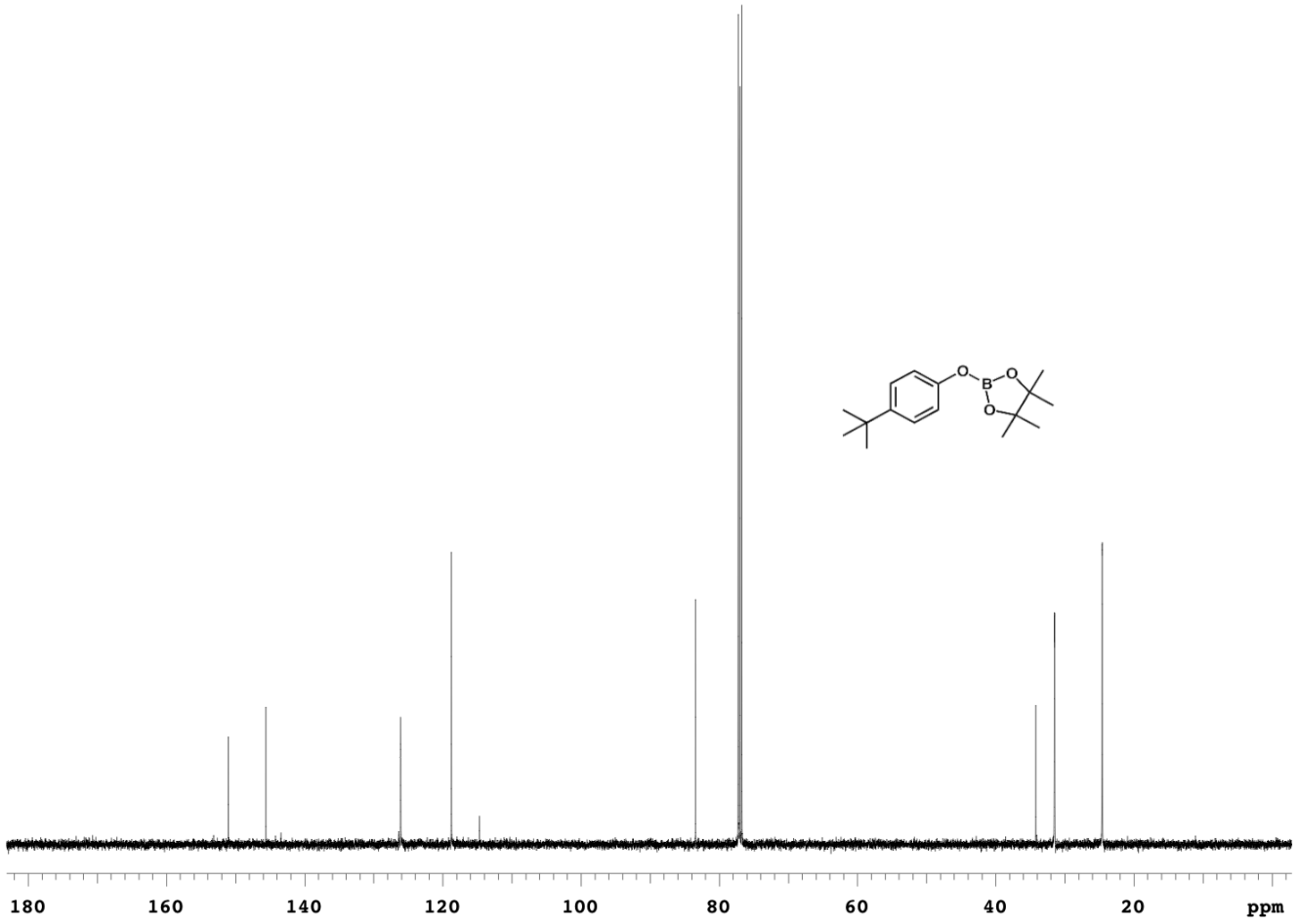
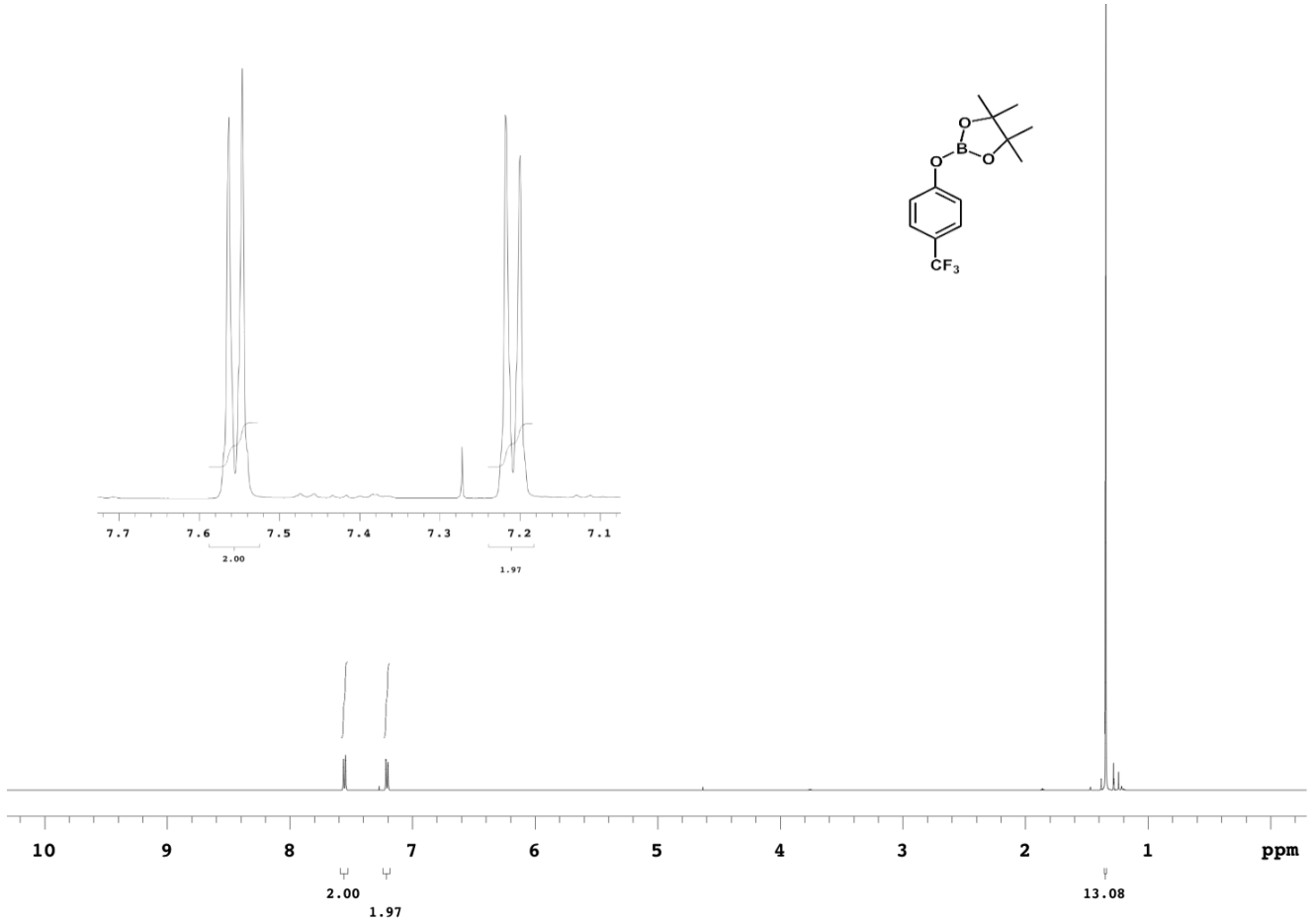


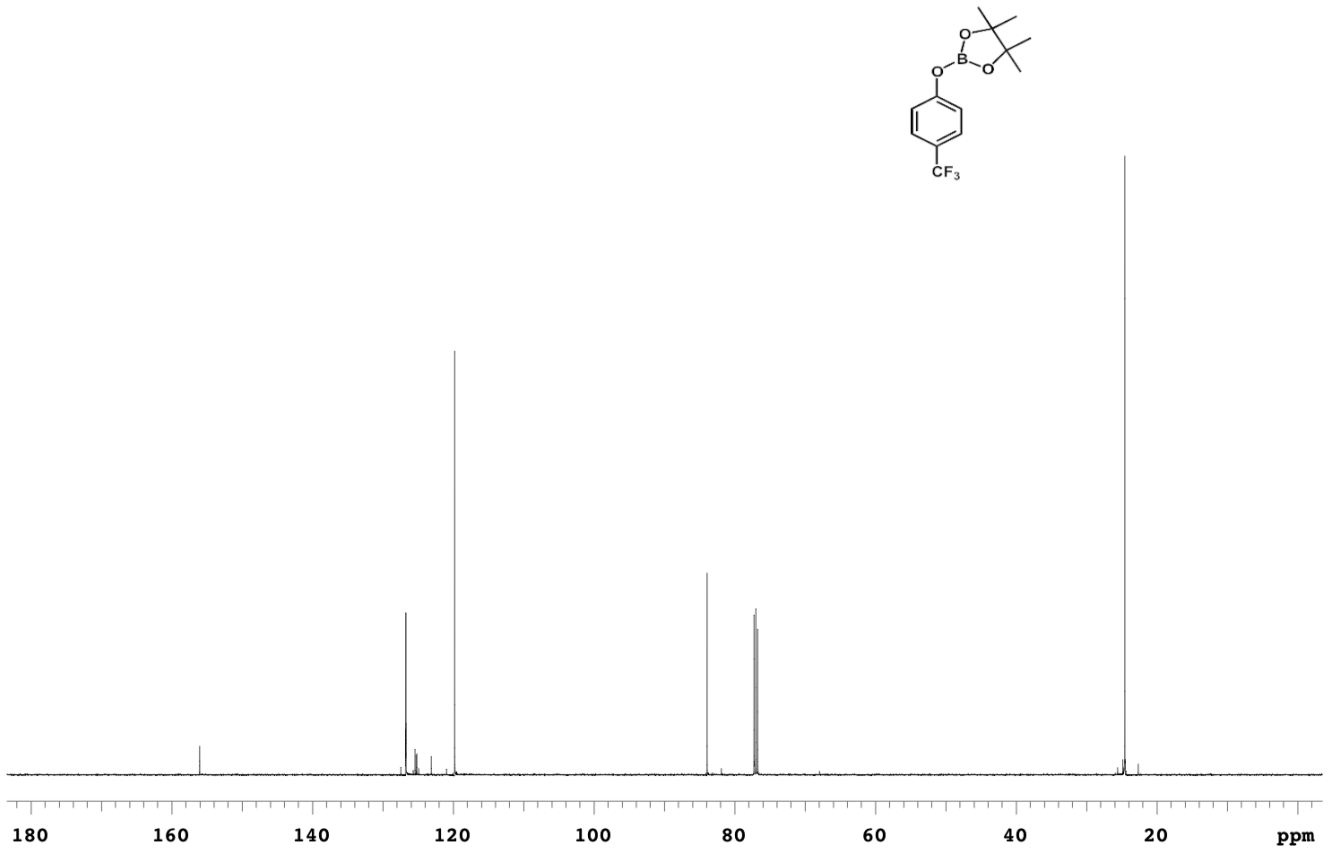
^{1}H-NMR (500 MHz, $CDCl_3$)

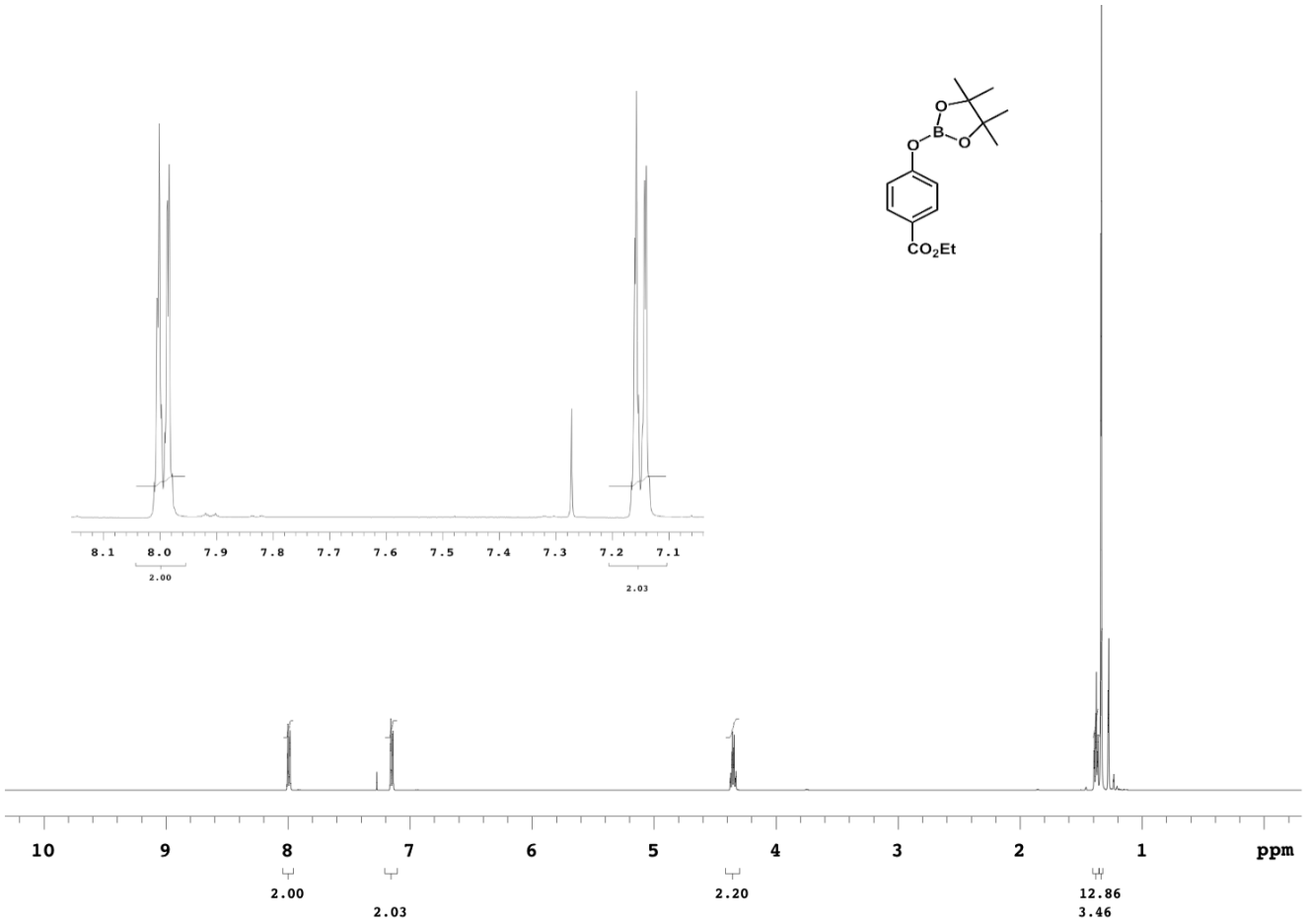


^{13}C-NMR (125 MHz, $CDCl_3$)

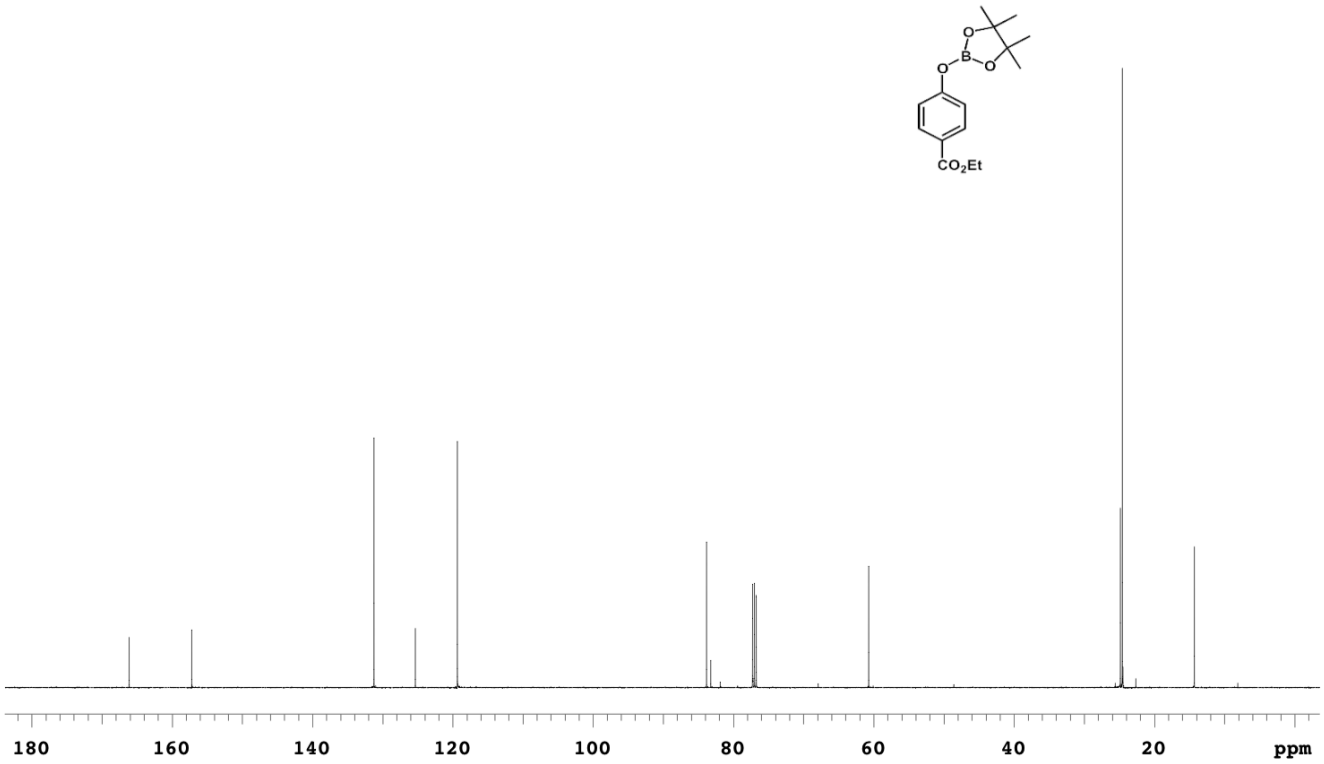


^{1}H-NMR (500 MHz, $CDCl_3$)

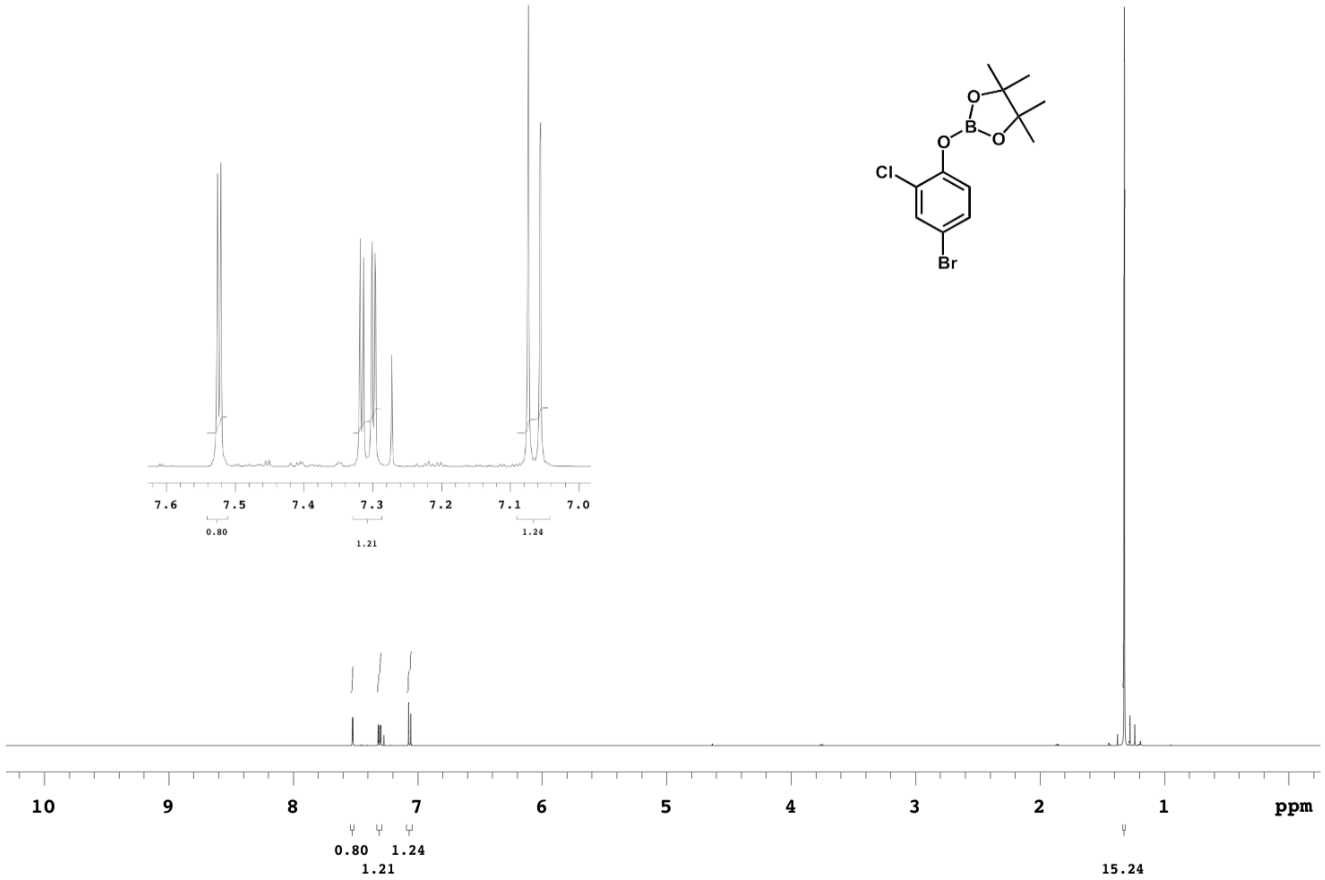

O
B
O
O
CF3
180
160
140
120
100
80
60
40
20
ppm



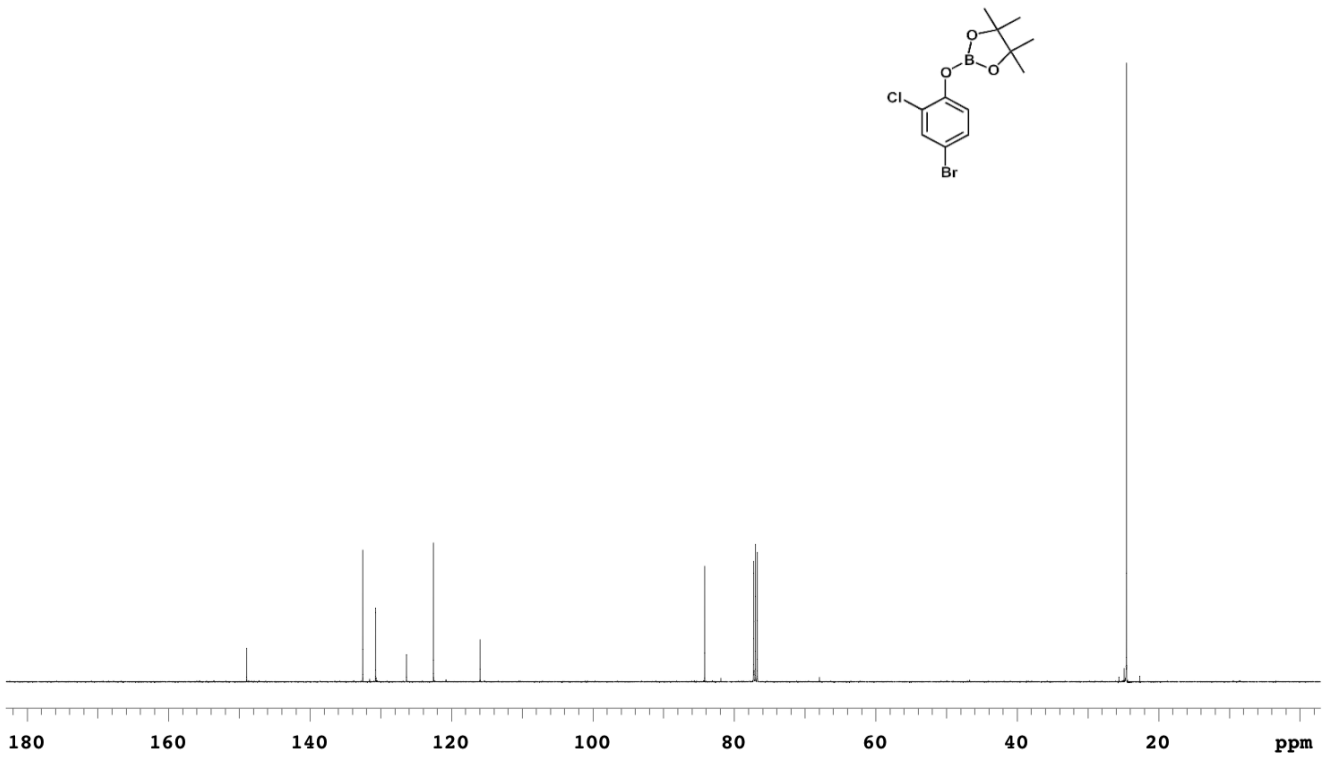
^{1}H-NMR (500 MHz, $CDCl_3$)



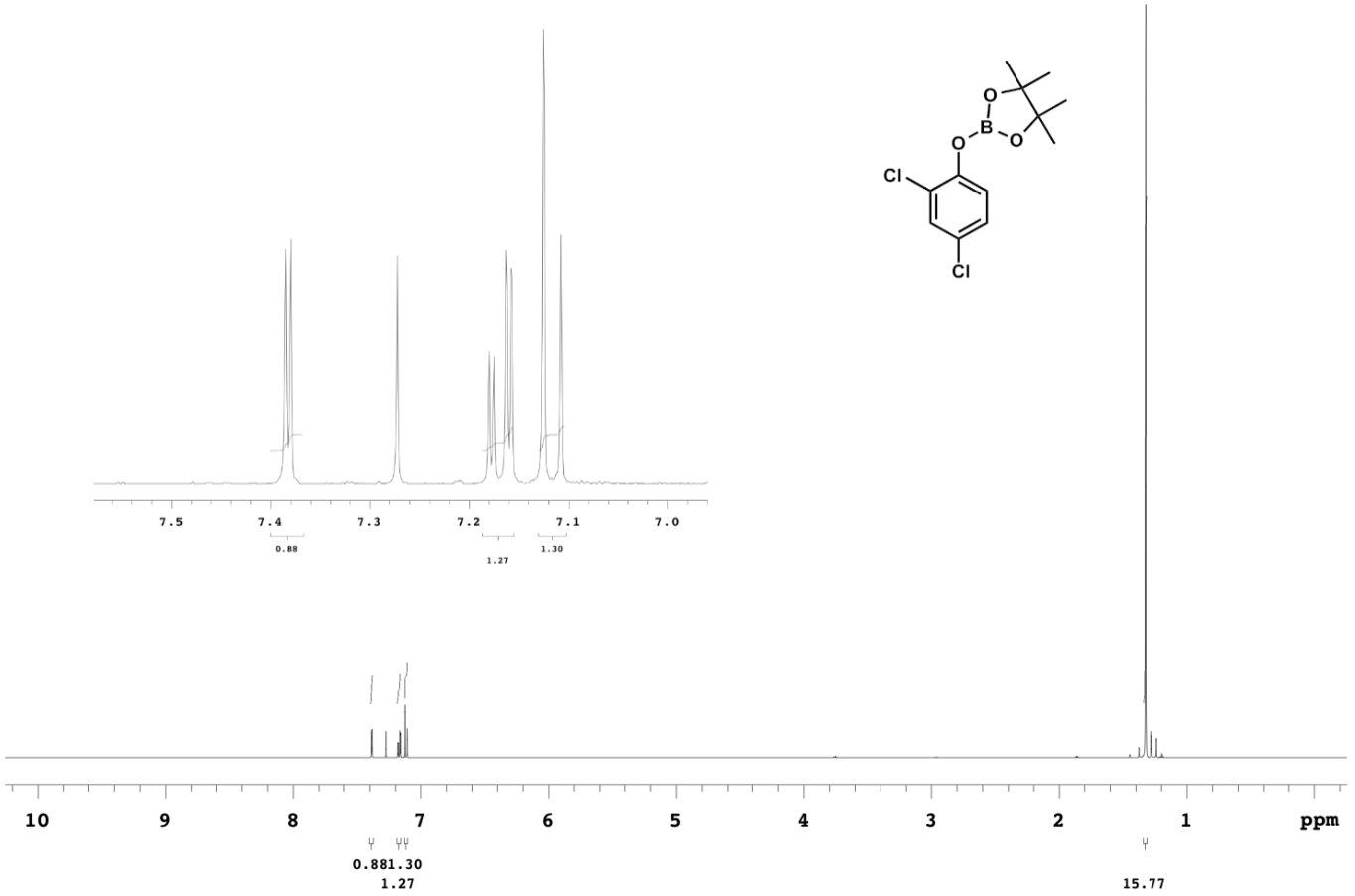
^{13}C-NMR (125 MHz, $CDCl_3$)



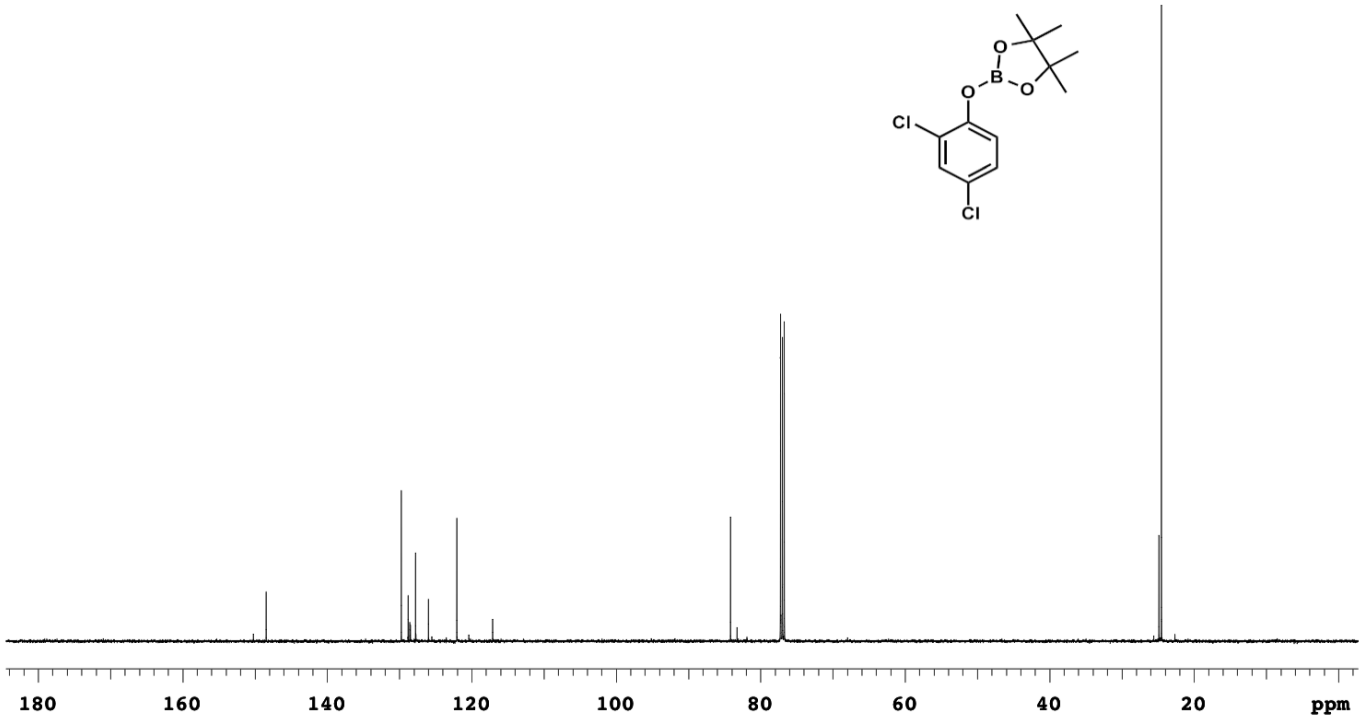
^{1}H-NMR (500 MHz, $CDCl_3$)



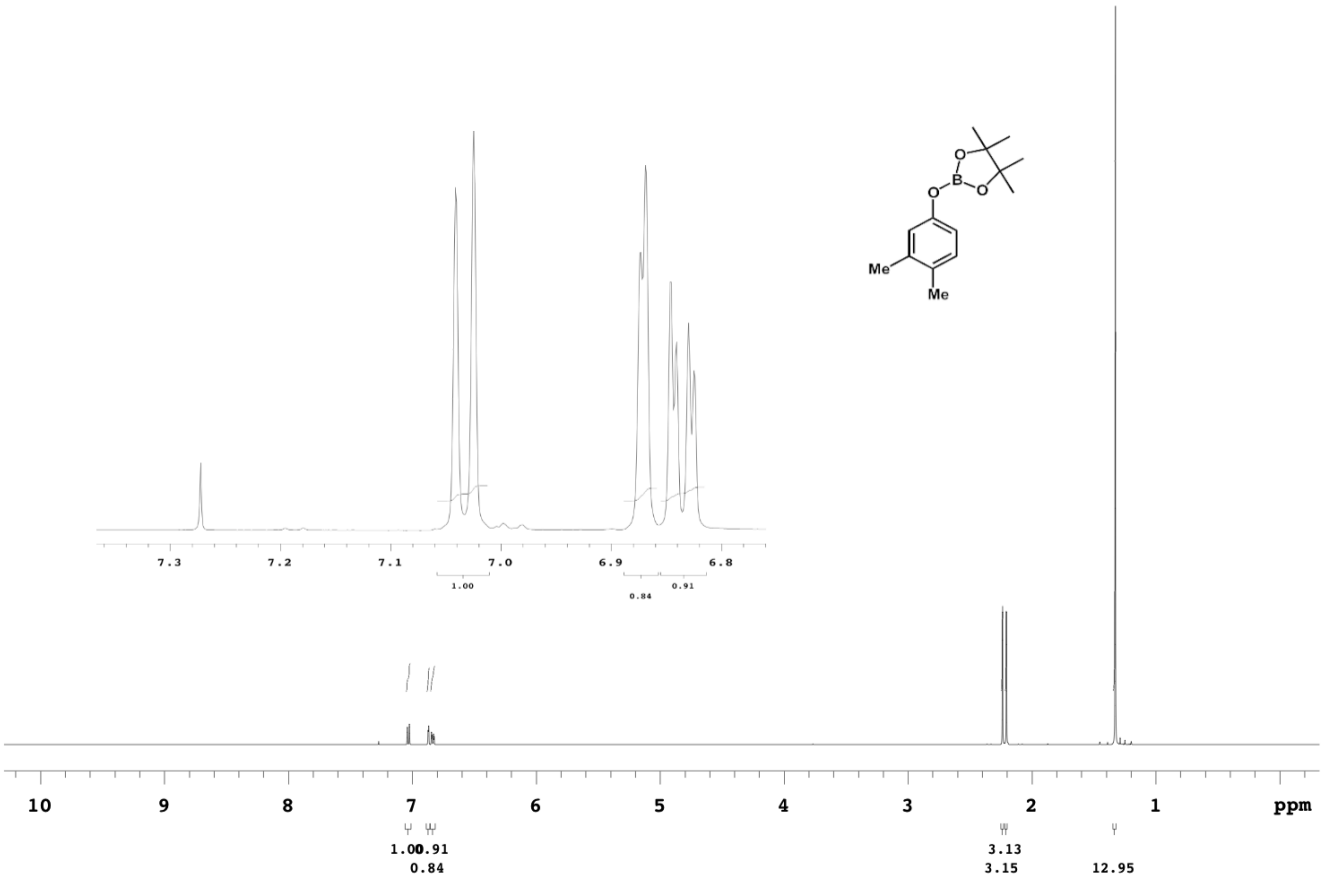
^{13}C-NMR (125 MHz, $CDCl_3$)



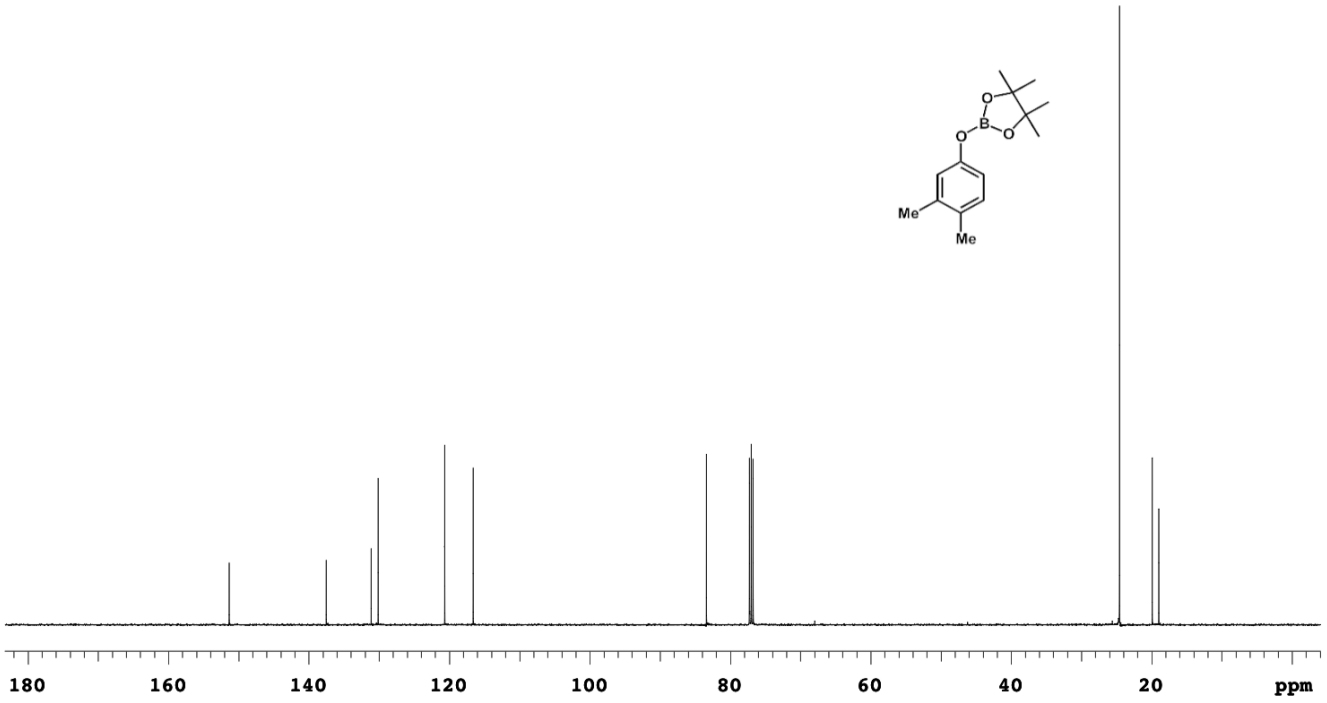
^{1}H-NMR (500 MHz, $CDCl_3$)



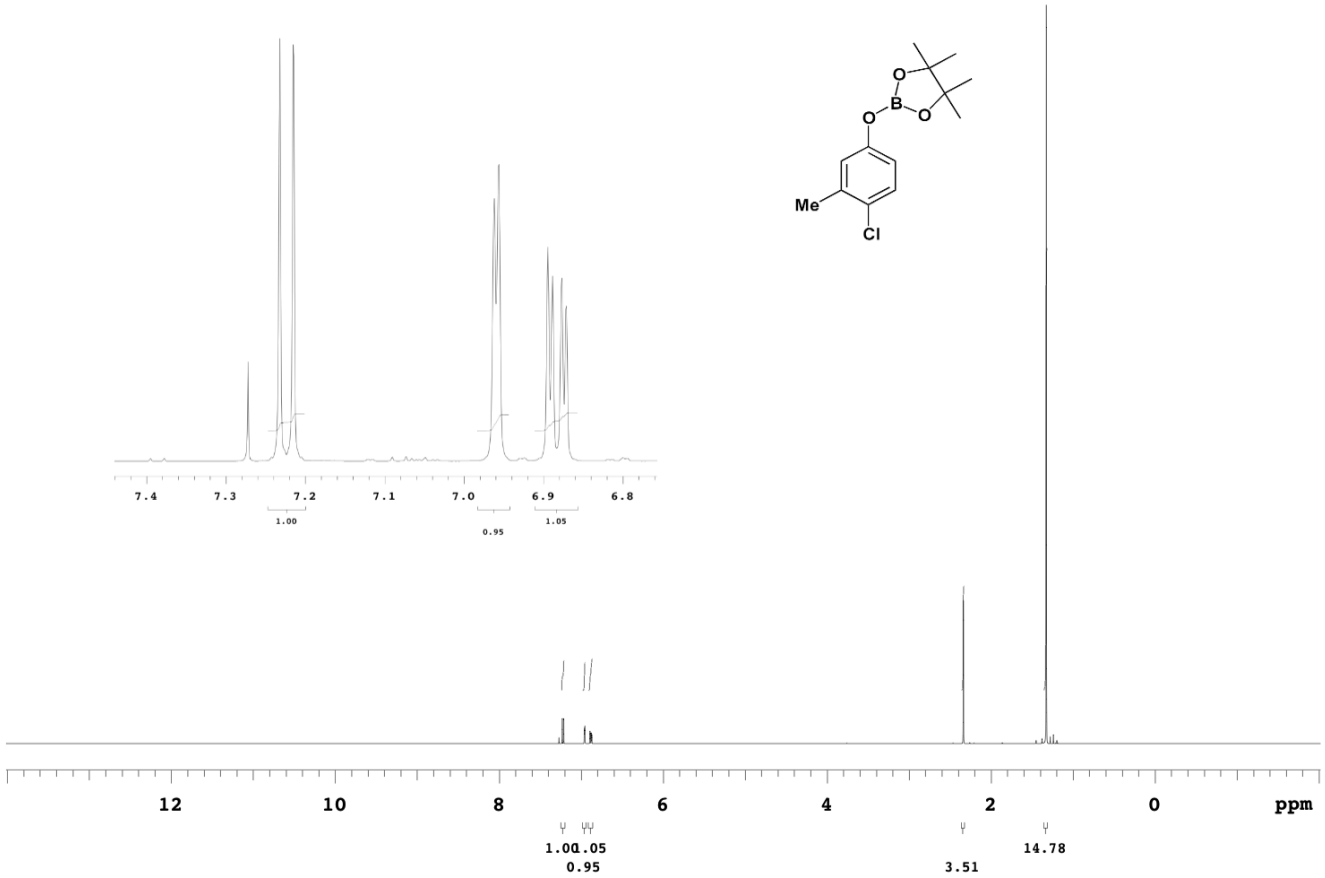
^{13}C NMR (125 MHz, $CDCl_3$)



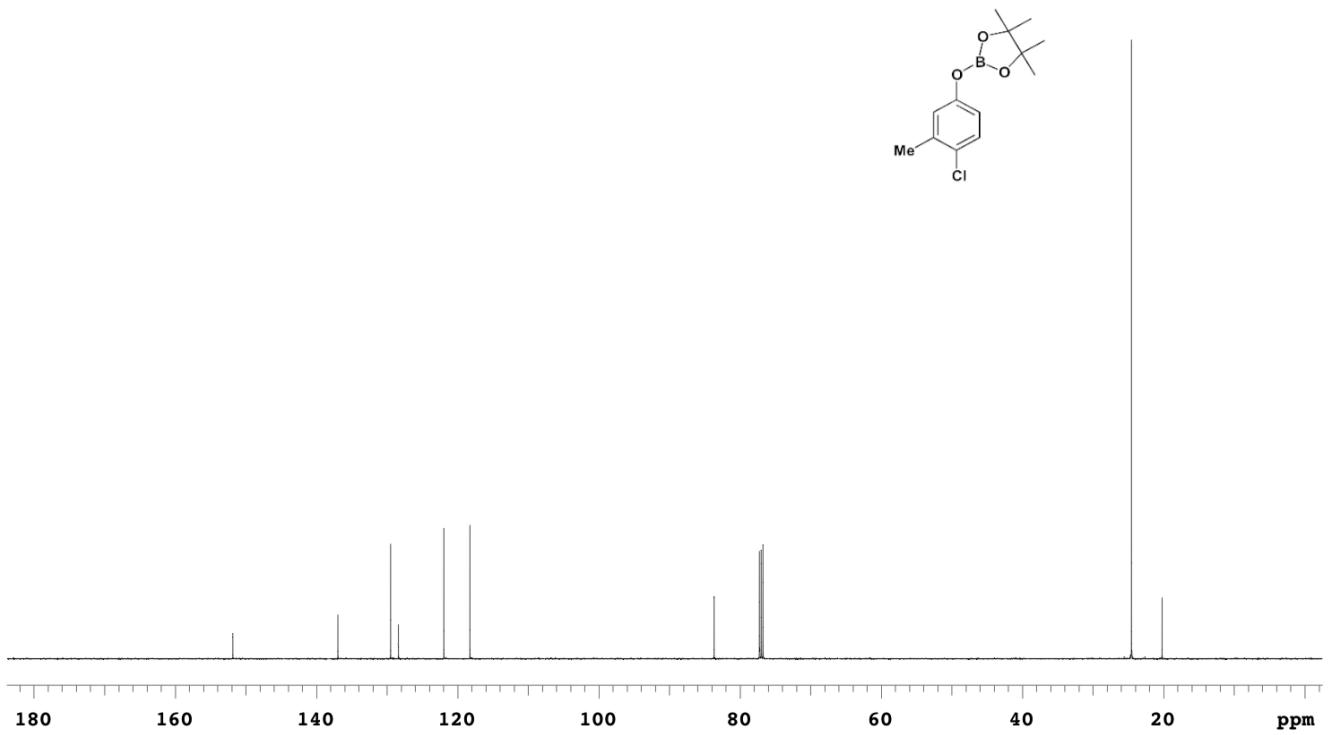
^{1}H-NMR (500 MHz, $CDCl_3$)



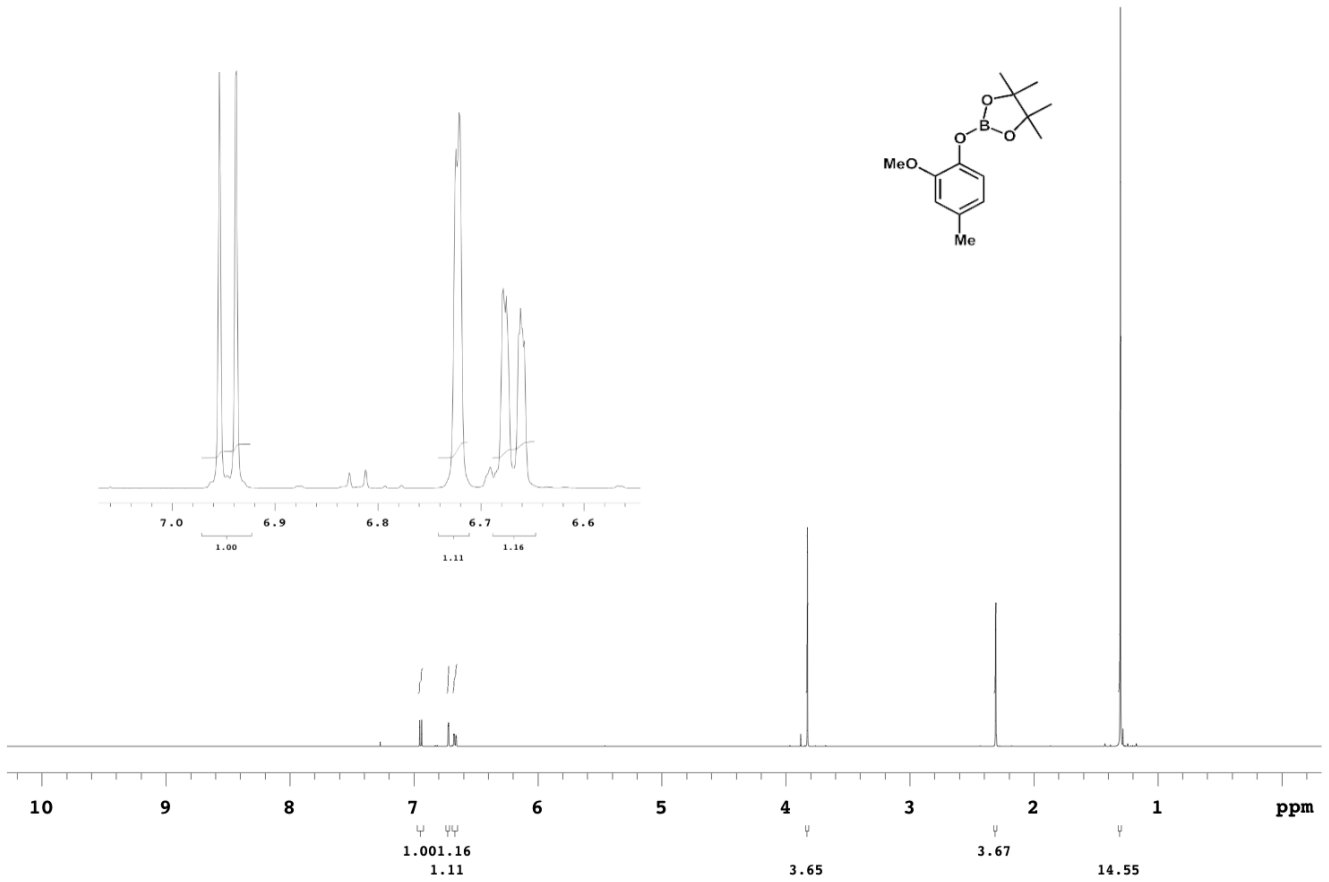
^{13}C-NMR (125 MHz, $CDCl_3$)



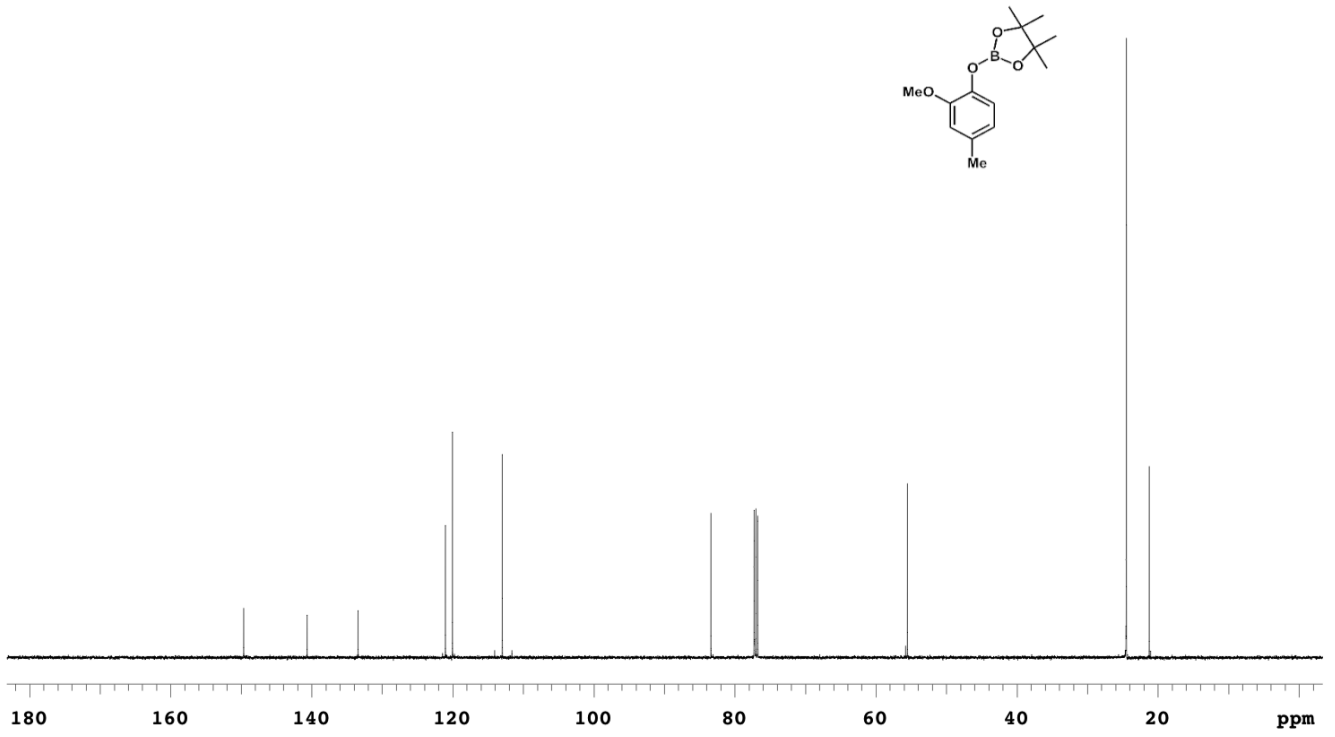
^{1}H-NMR (500 MHz, $CDCl_3$)



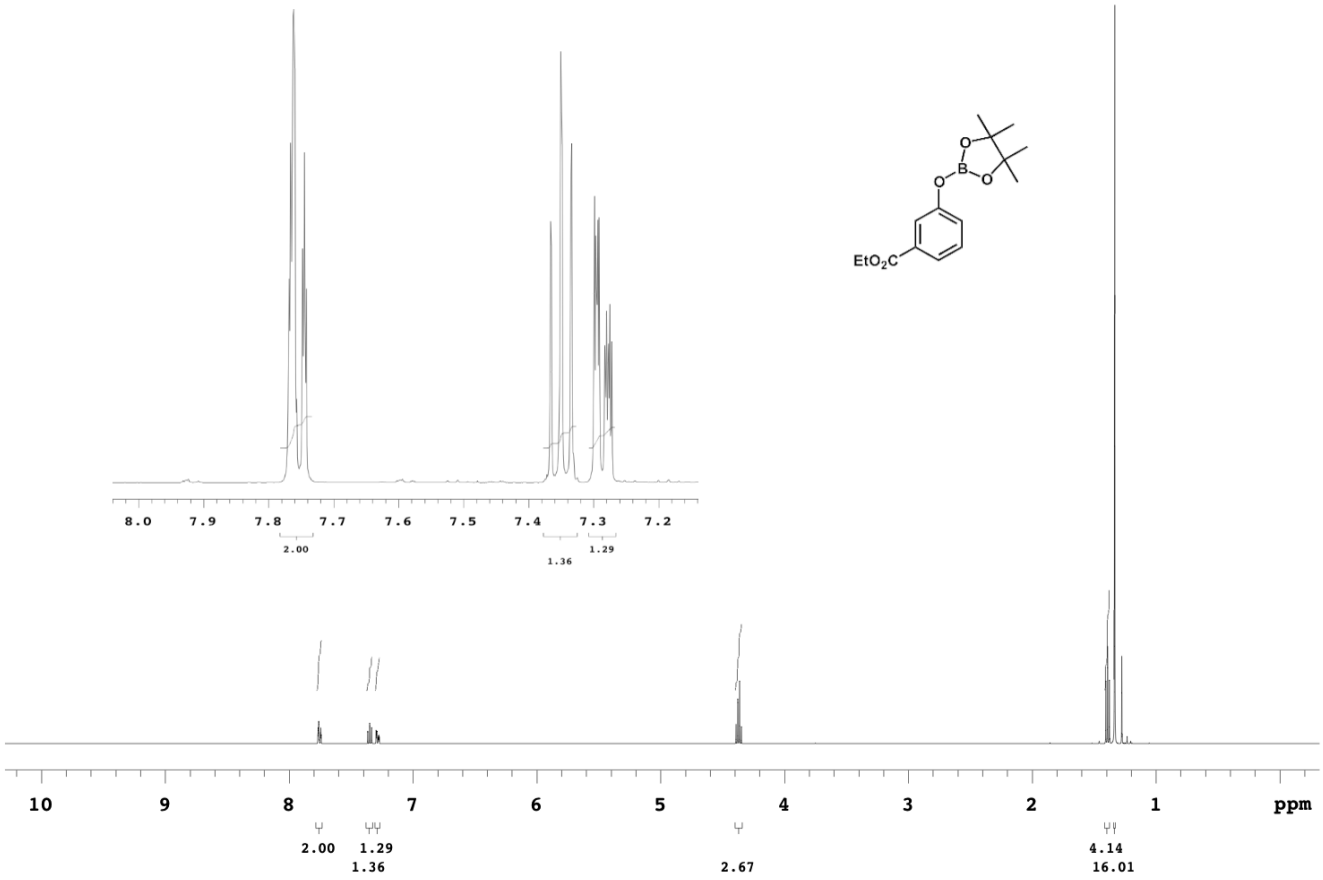
^{13}C-NMR (125 MHz, $CDCl_3$)



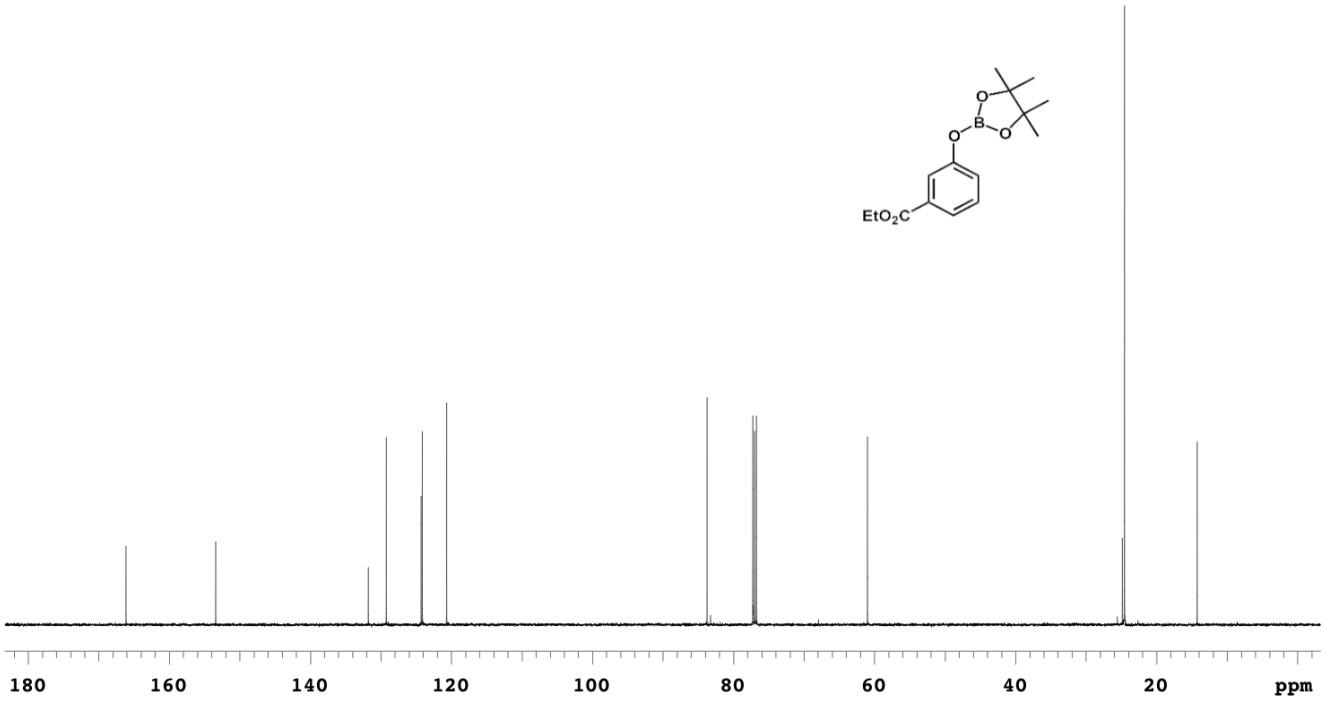
^{1}H-NMR (500 MHz, $CDCl_3$)



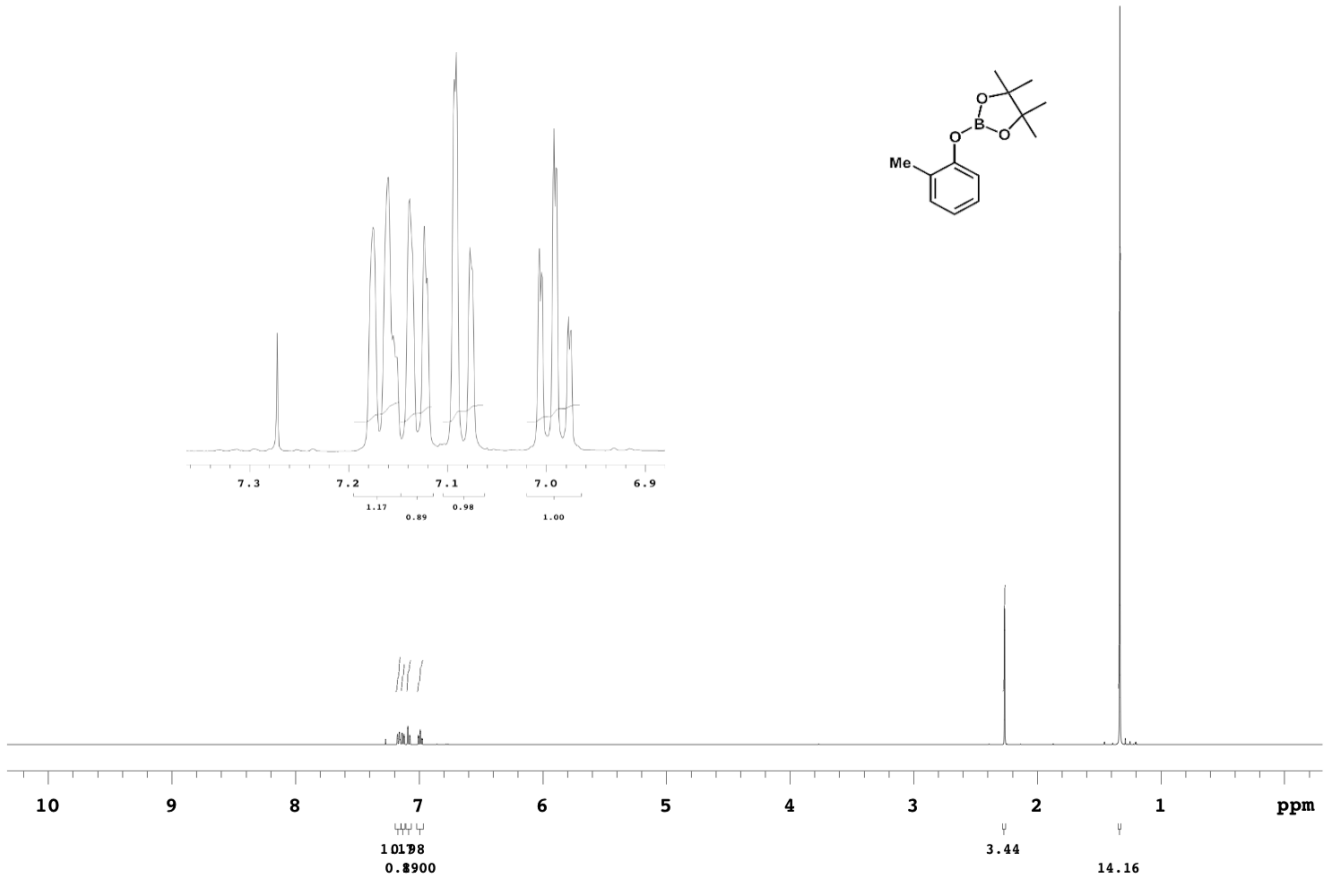
^{13}C-NMR (125 MHz, $CDCl_3$)

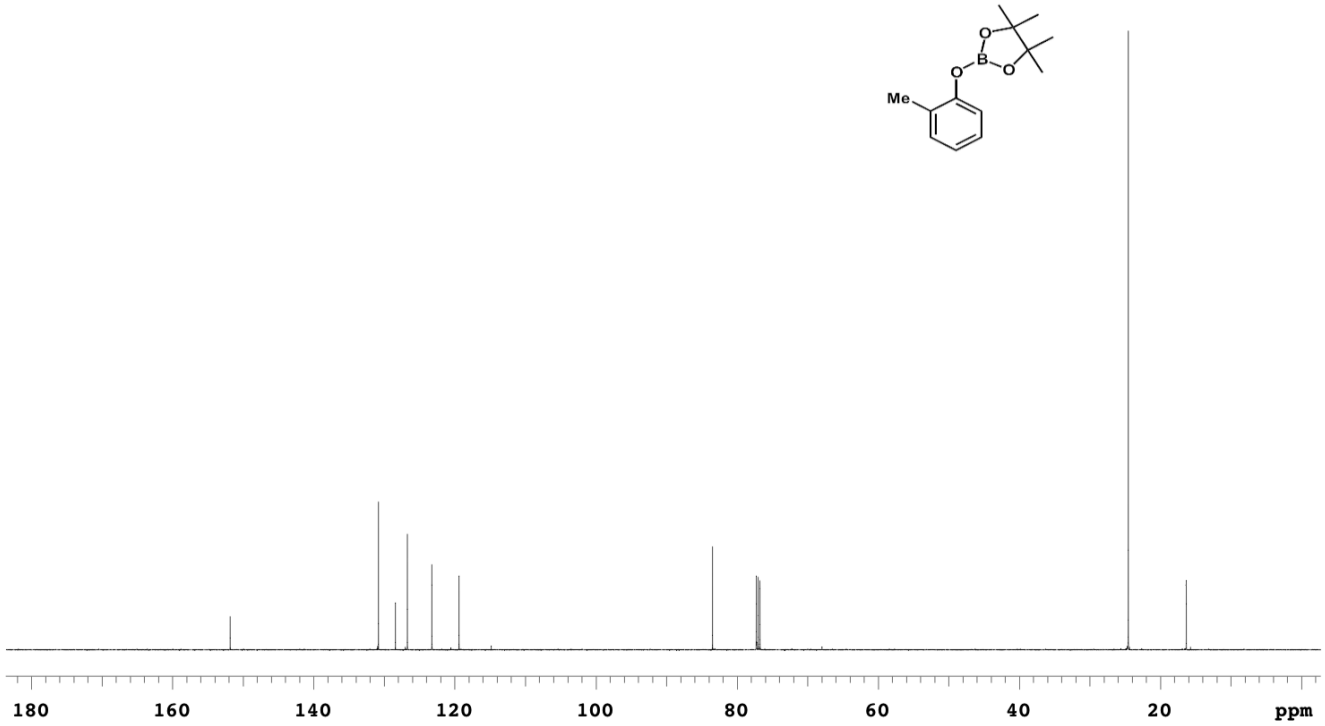


^{1}H-NMR (500 MHz, $CDCl_3$)

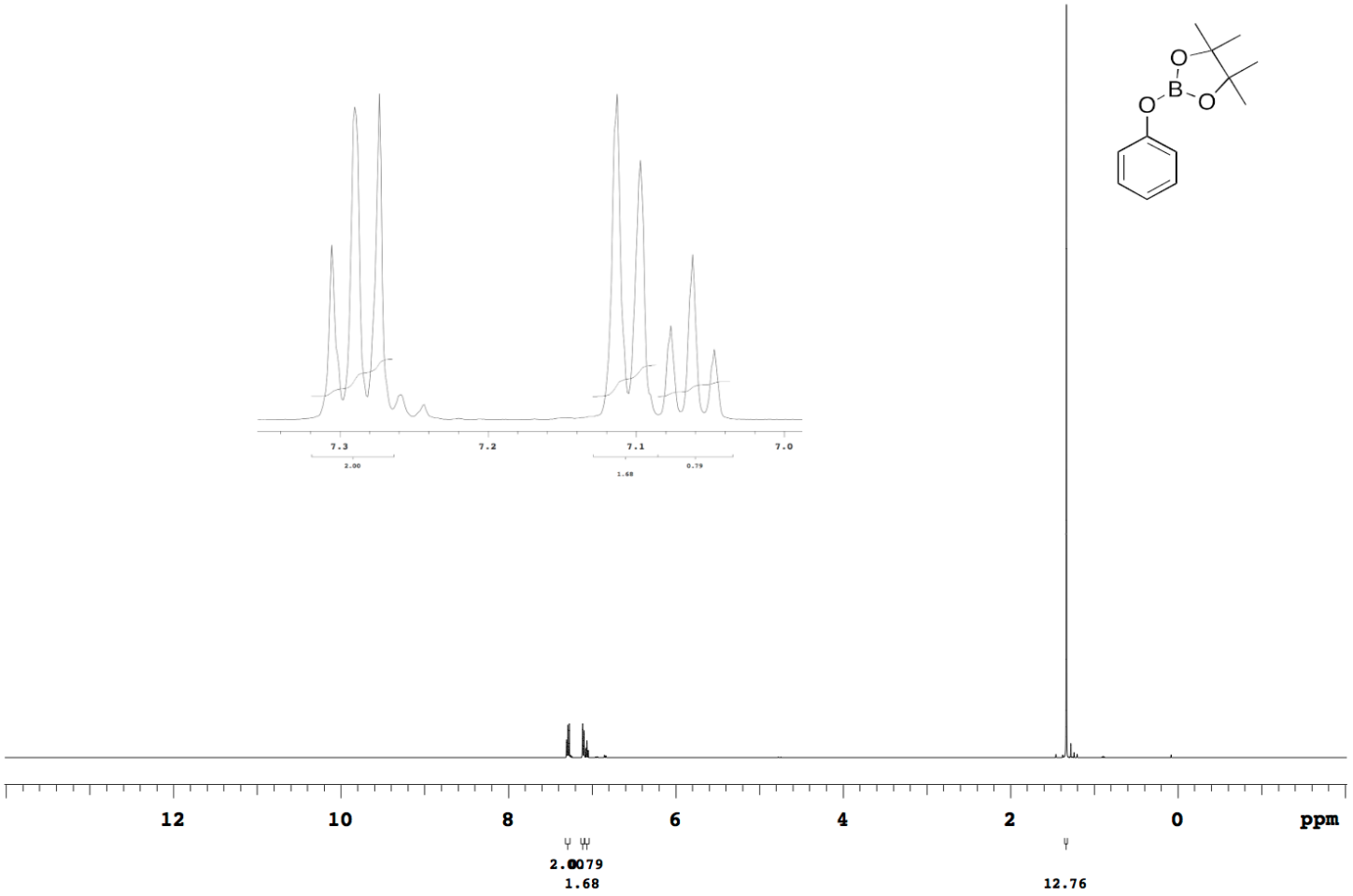


^{13}C-NMR (125 MHz, $CDCl_3$)

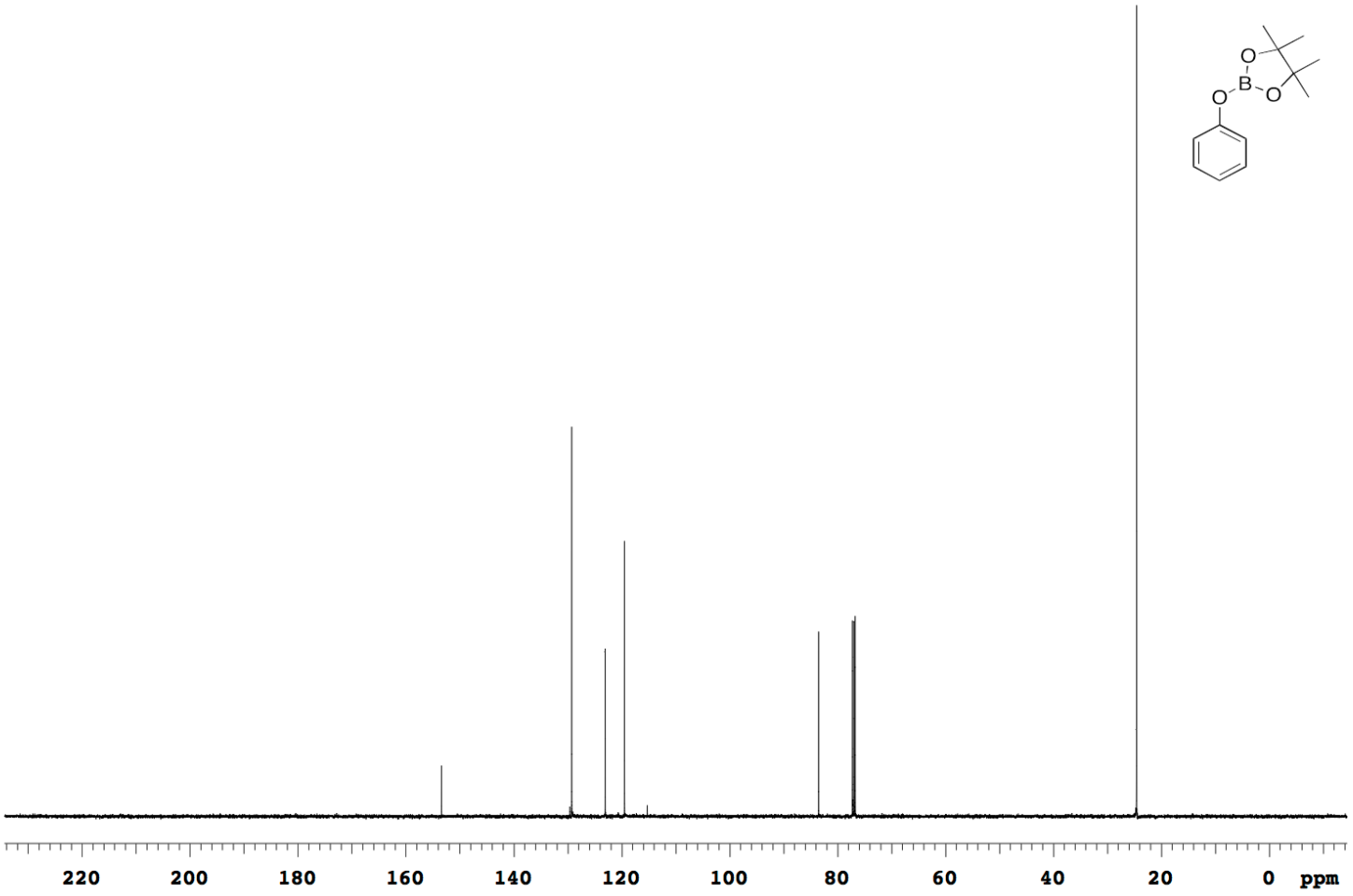

Me
O
B
O
O
7.3
7.2
7.1
7.0
6.9
1.17
0.89
0.98
1.00
10
9
8
7
6
5
4
3
2
1
ppm
3.44
14.16



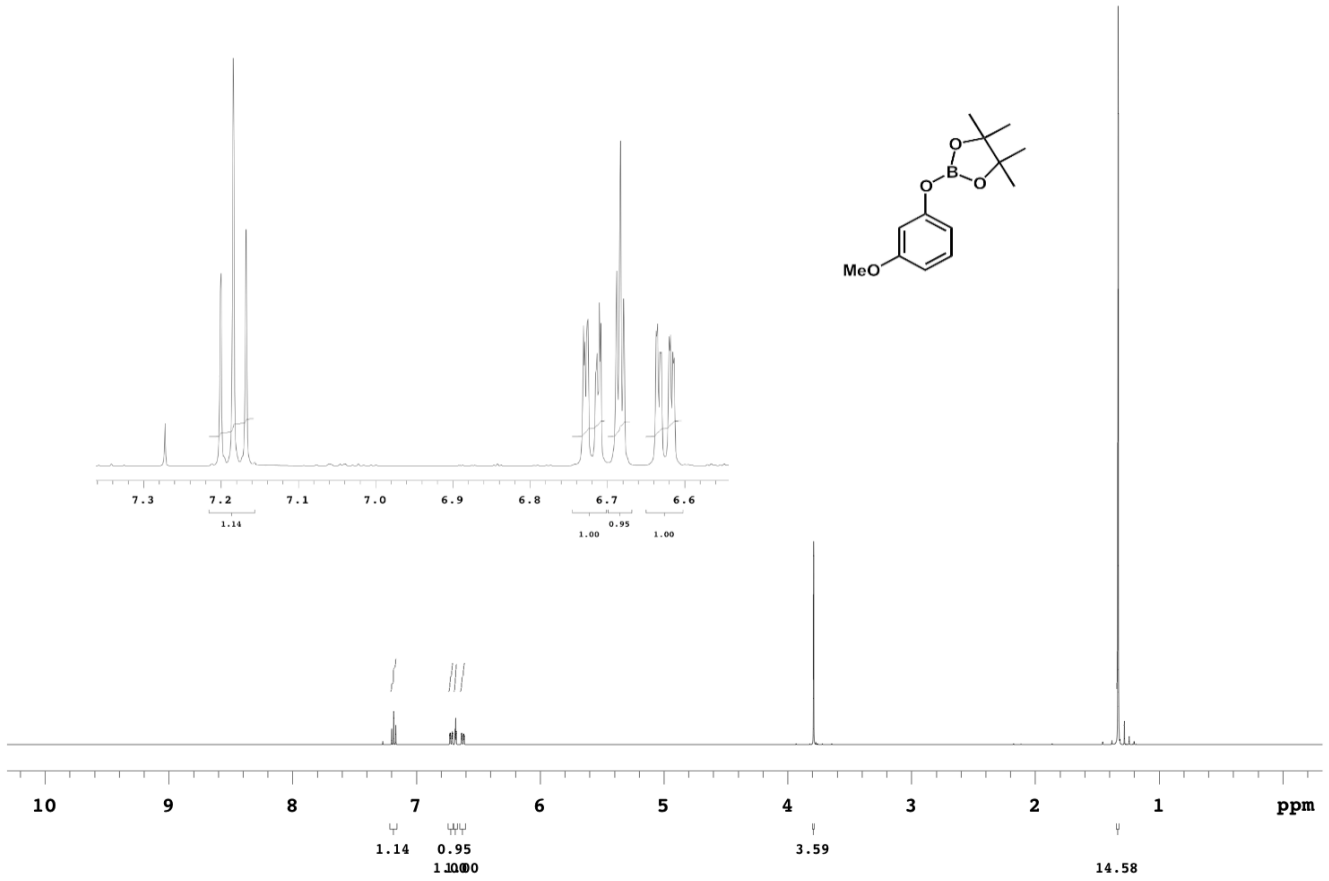
^{13}C-NMR (125 MHz, $CDCl_3$)



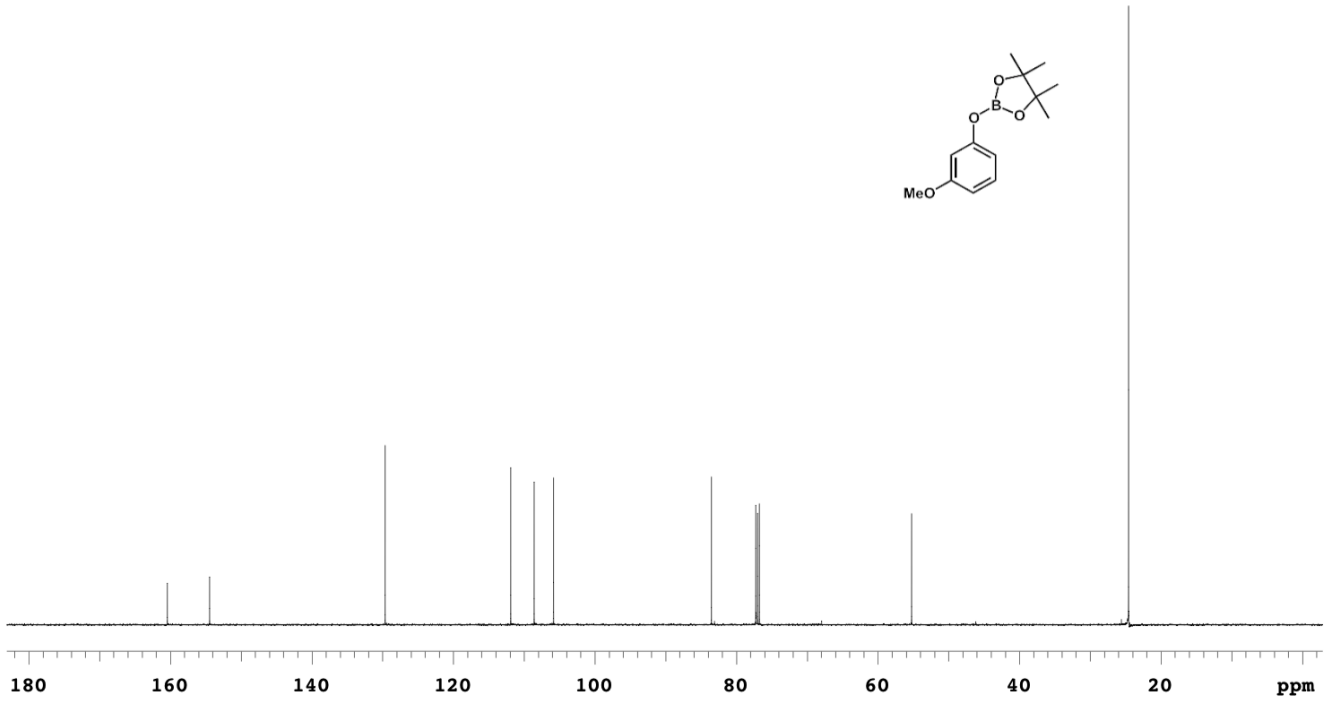
^{1}H-NMR (500 MHz, $CDCl_3$)



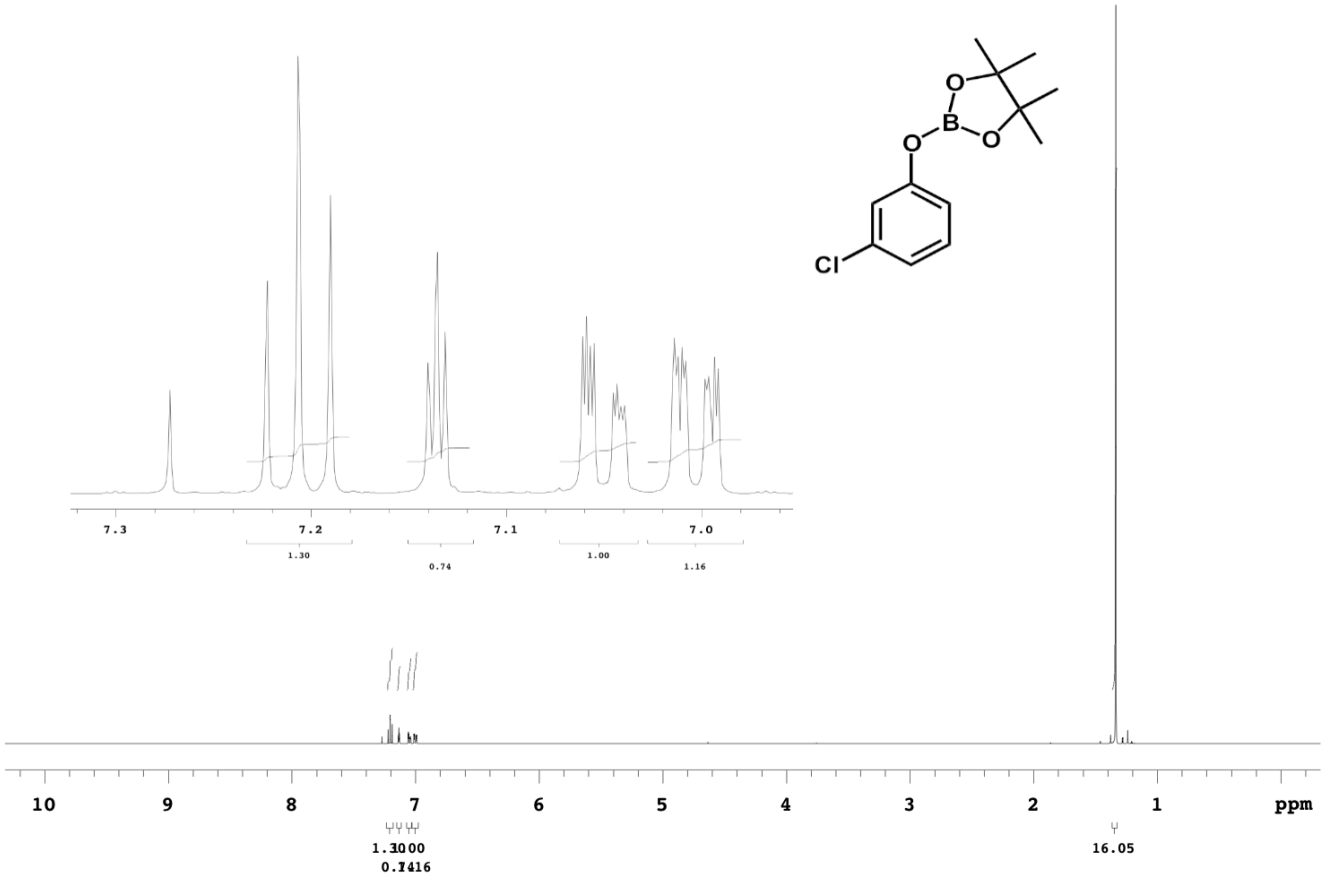
^{13}C-NMR (125 MHz, $CDCl_3$)



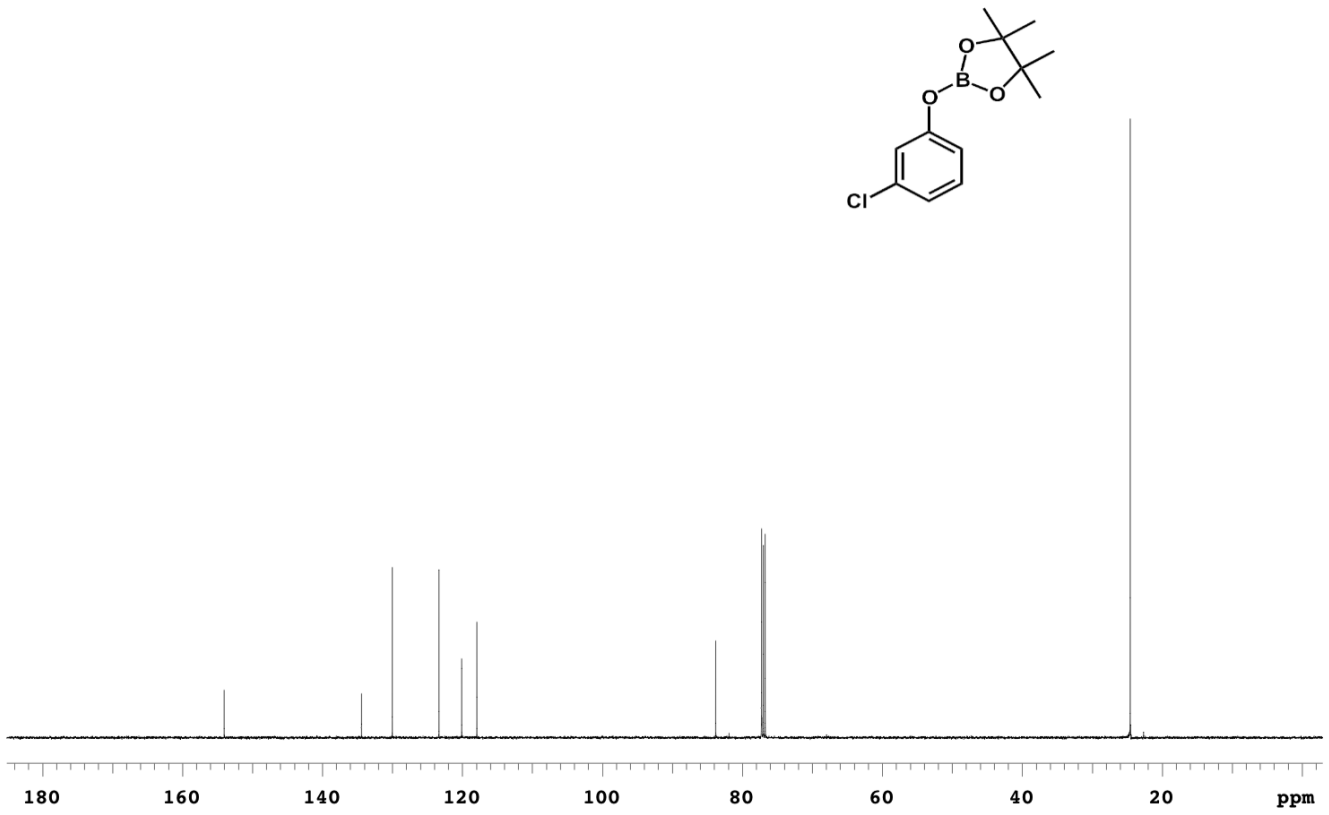
^{1}H-NMR (500 MHz, $CDCl_3$)



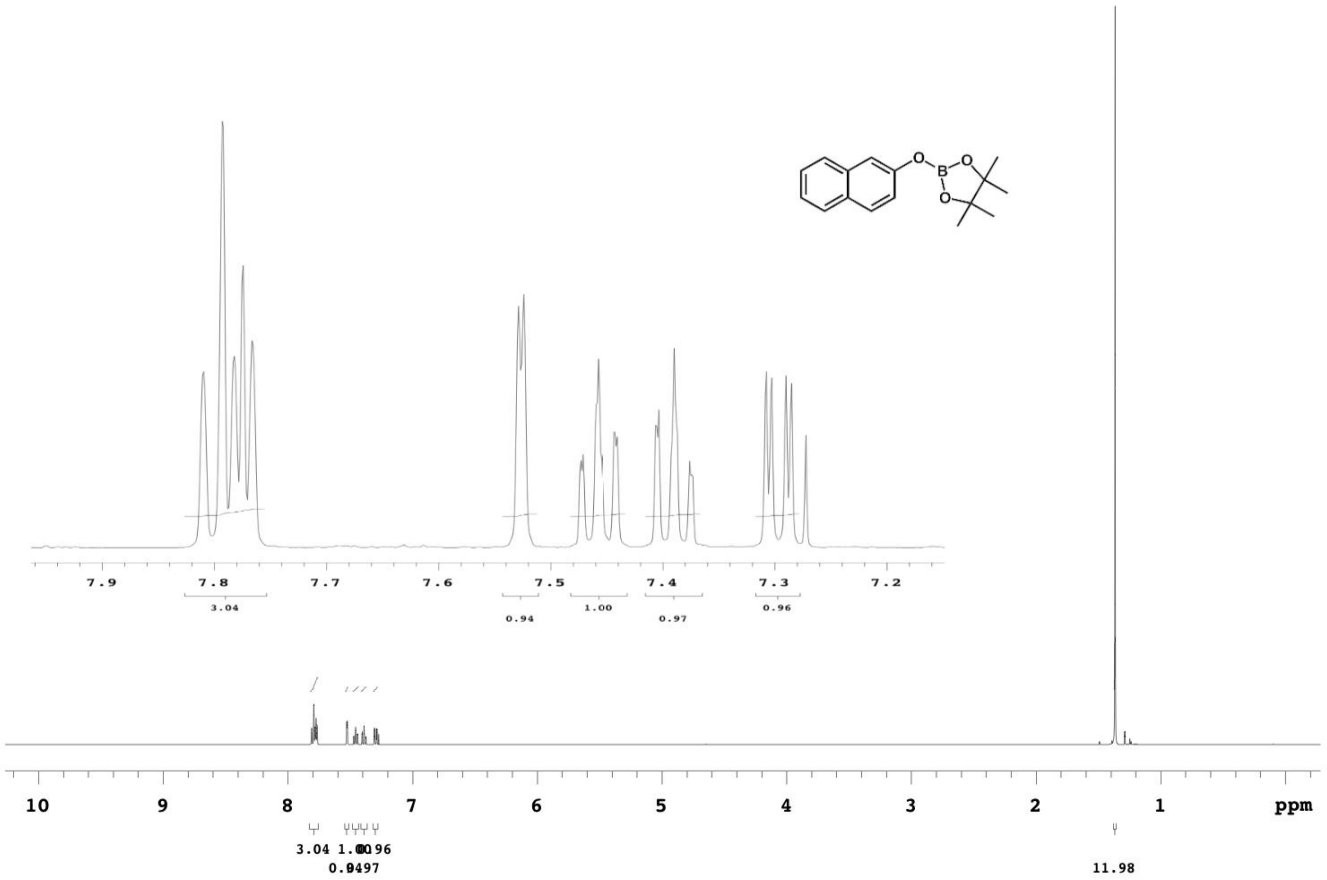
^{13}C-NMR (125 MHz, $CDCl_3$)

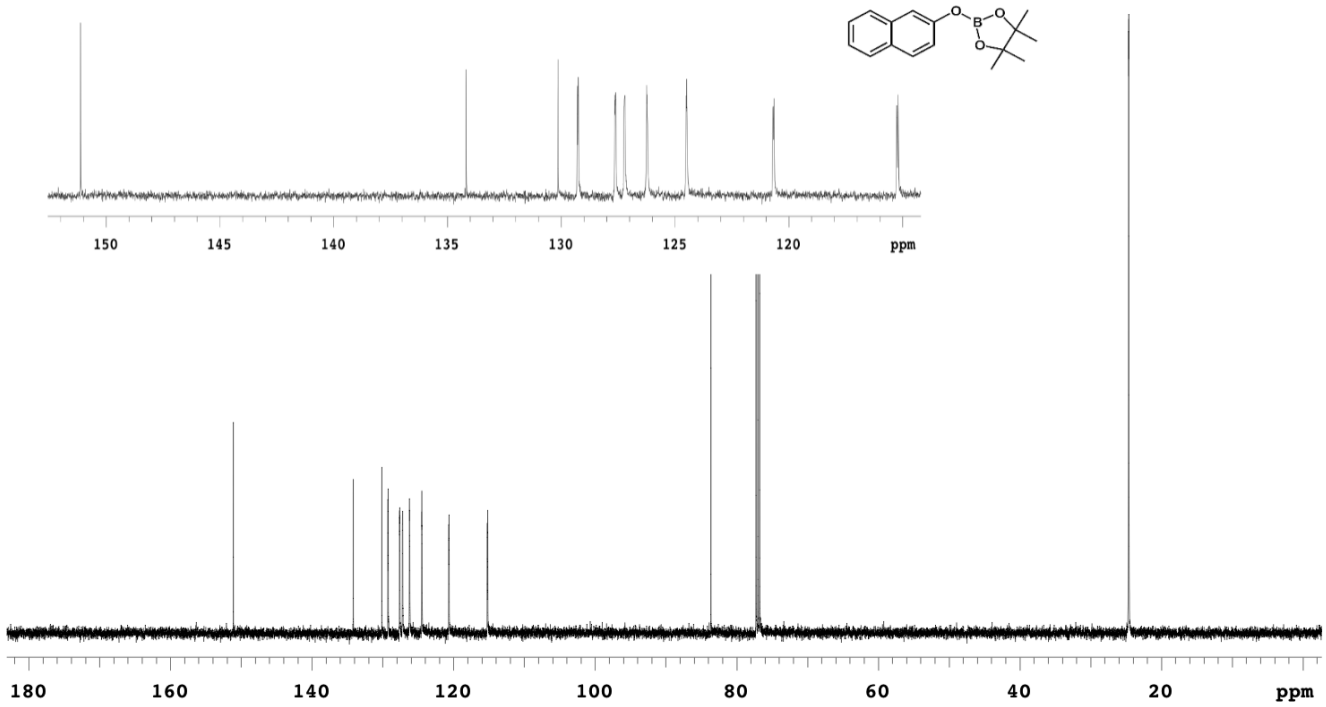

O
B
O
O
Cl
7.3
7.2
7.1
7.0
1.30
0.74
1.00
1.16
10
9
8
7
6
5
4
3
2
1
ppm
16.05

^{1}H-NMR (500 MHz, $CDCl_3$)

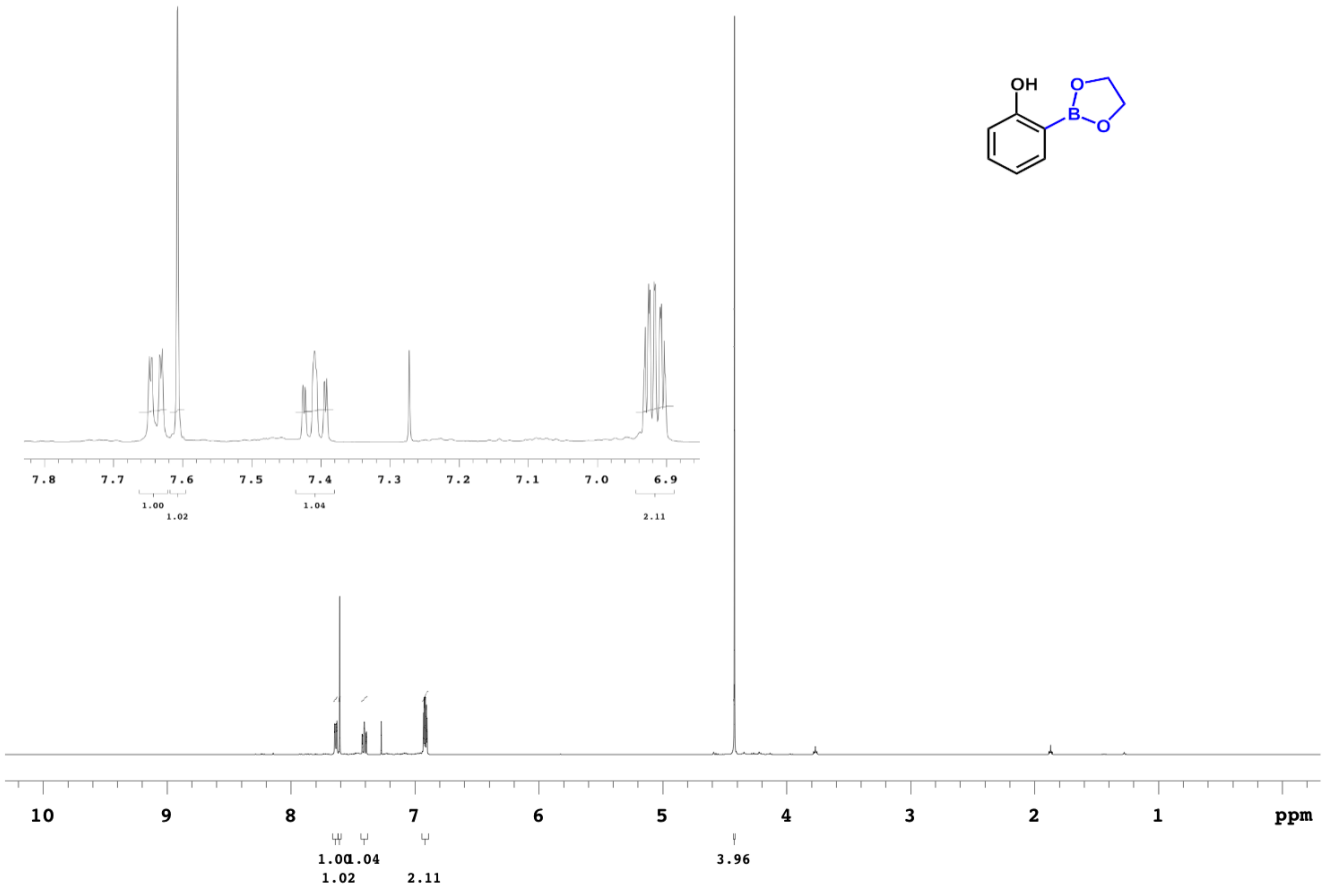


^{13}C NMR (125 MHz, $CDCl_3$)

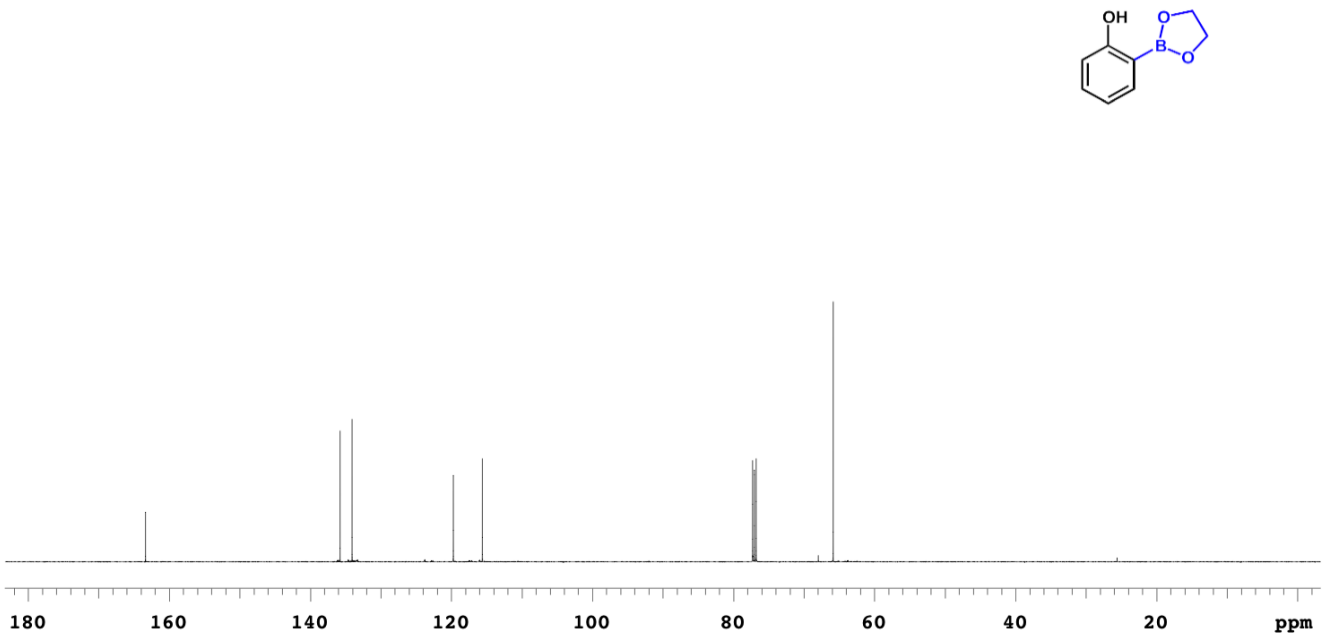

O
B
O
O
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
3.04
0.94
1.00
0.97
0.96
10
9
8
7
6
5
4
3
2
1
ppm
3.04
11.98



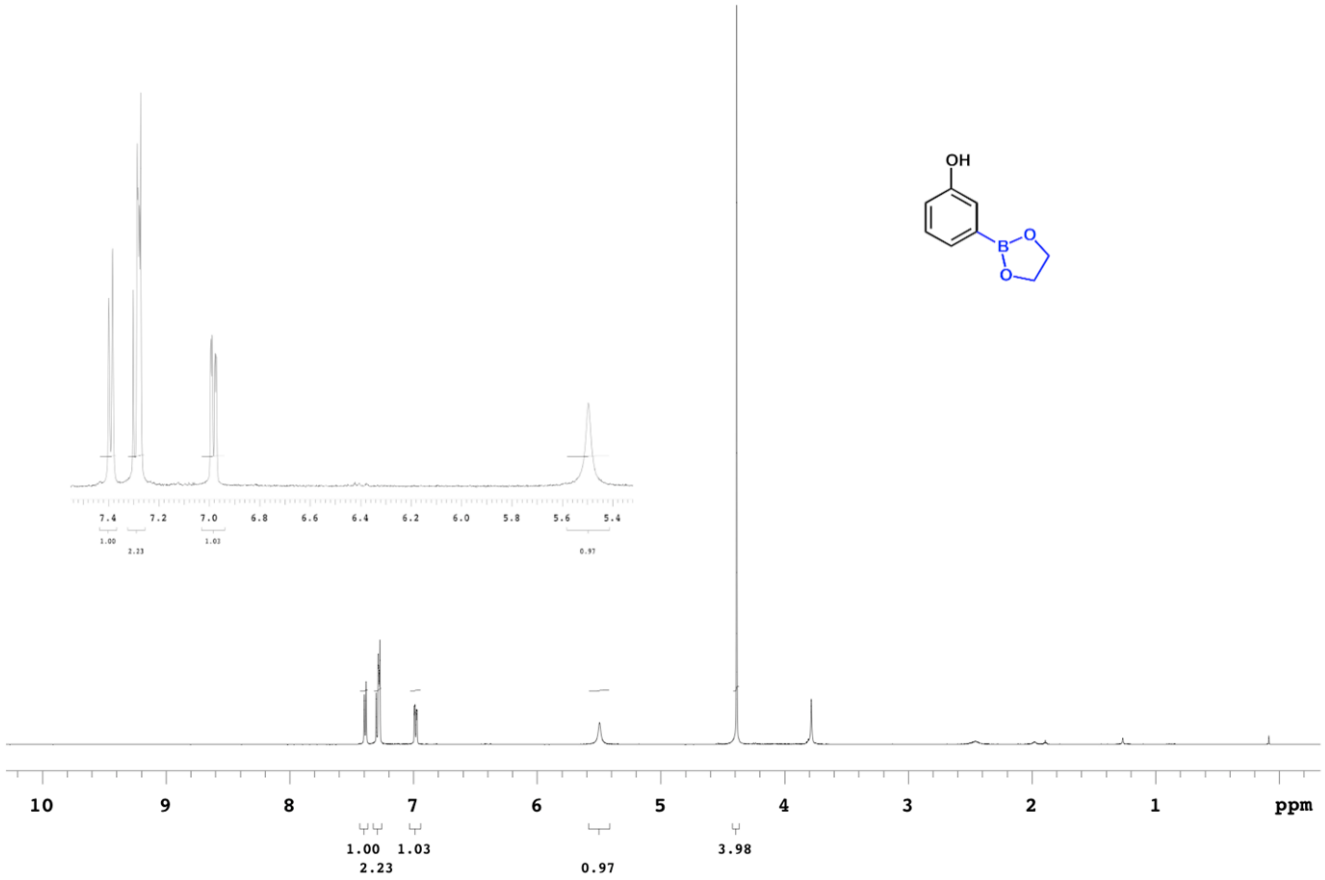
^{13}C-NMR (125 MHz, $CDCl_3$)

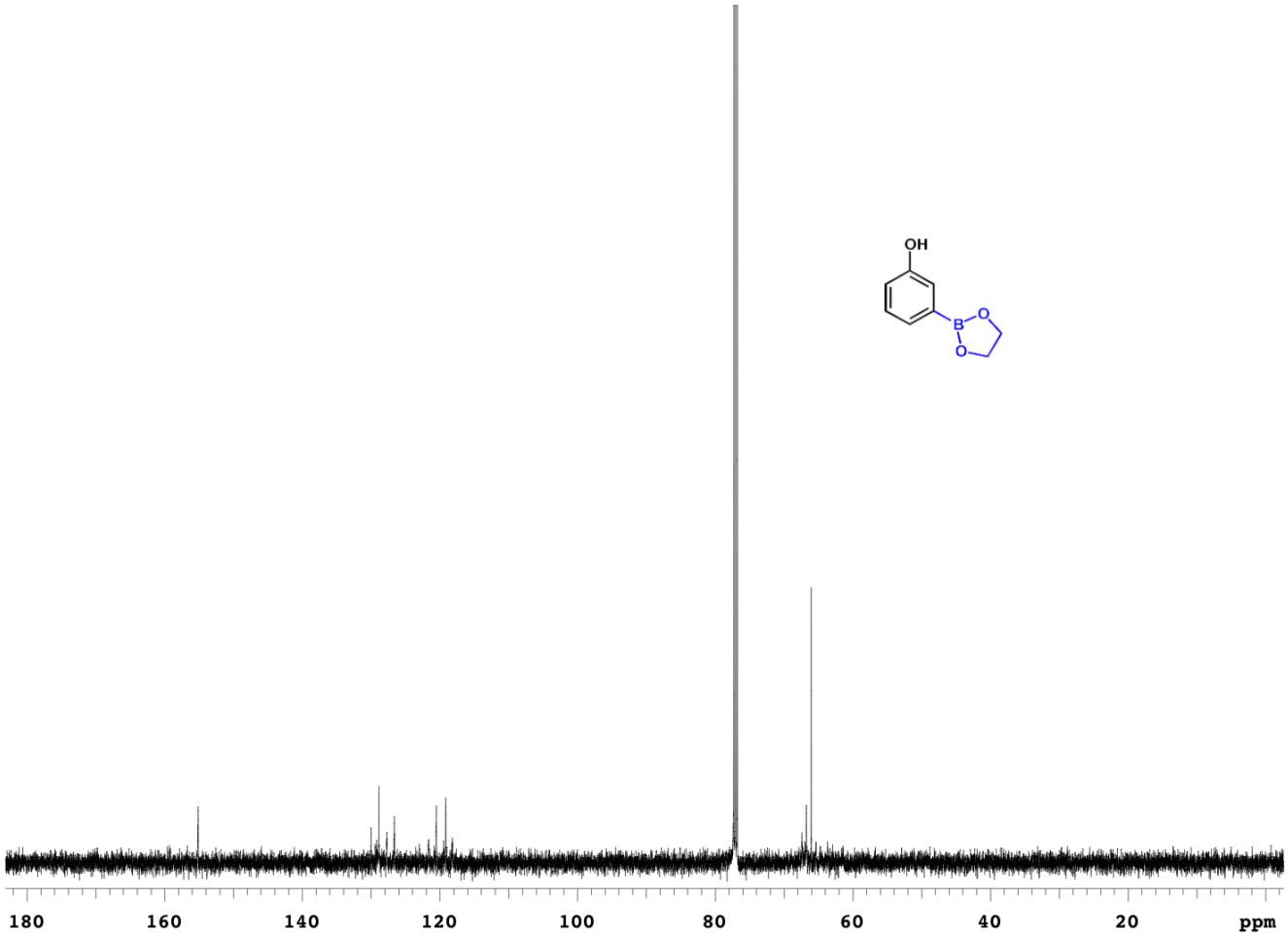


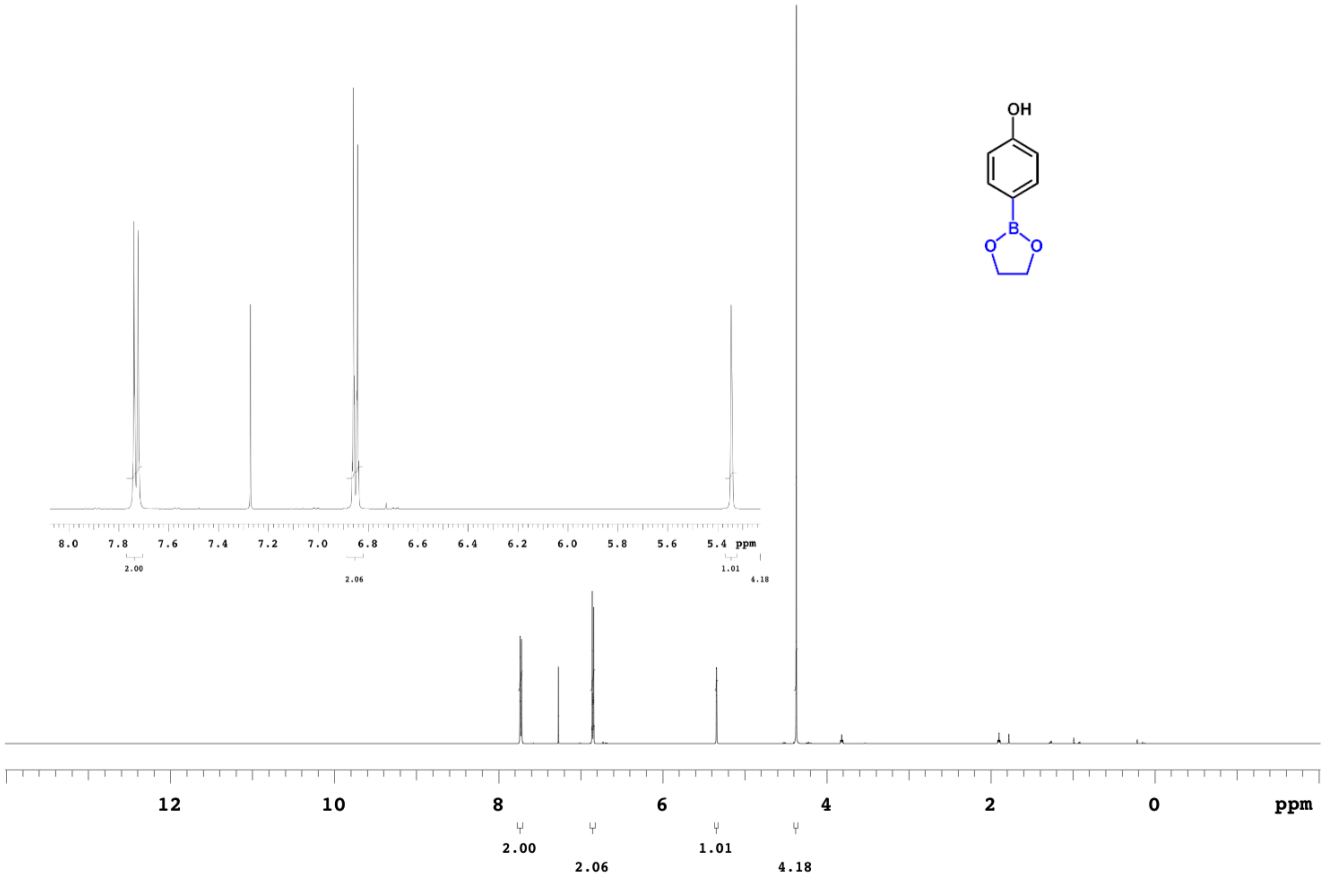
^{1}H-NMR (500 MHz, $CDCl_3$)



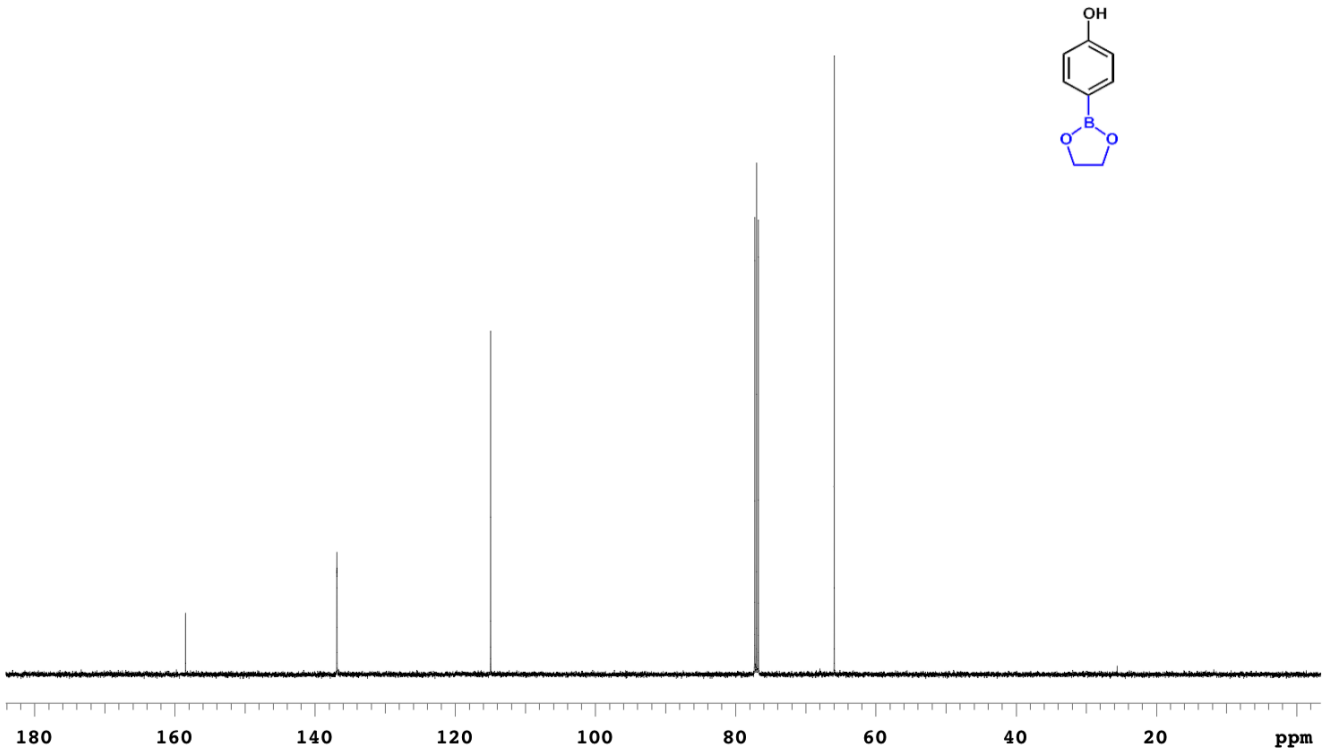
^{13}C NMR (125 MHz, $CDCl_3$)


OH
B
O
O
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
1.00
2.23
1.03
0.97
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
2.23
0.97
3.98

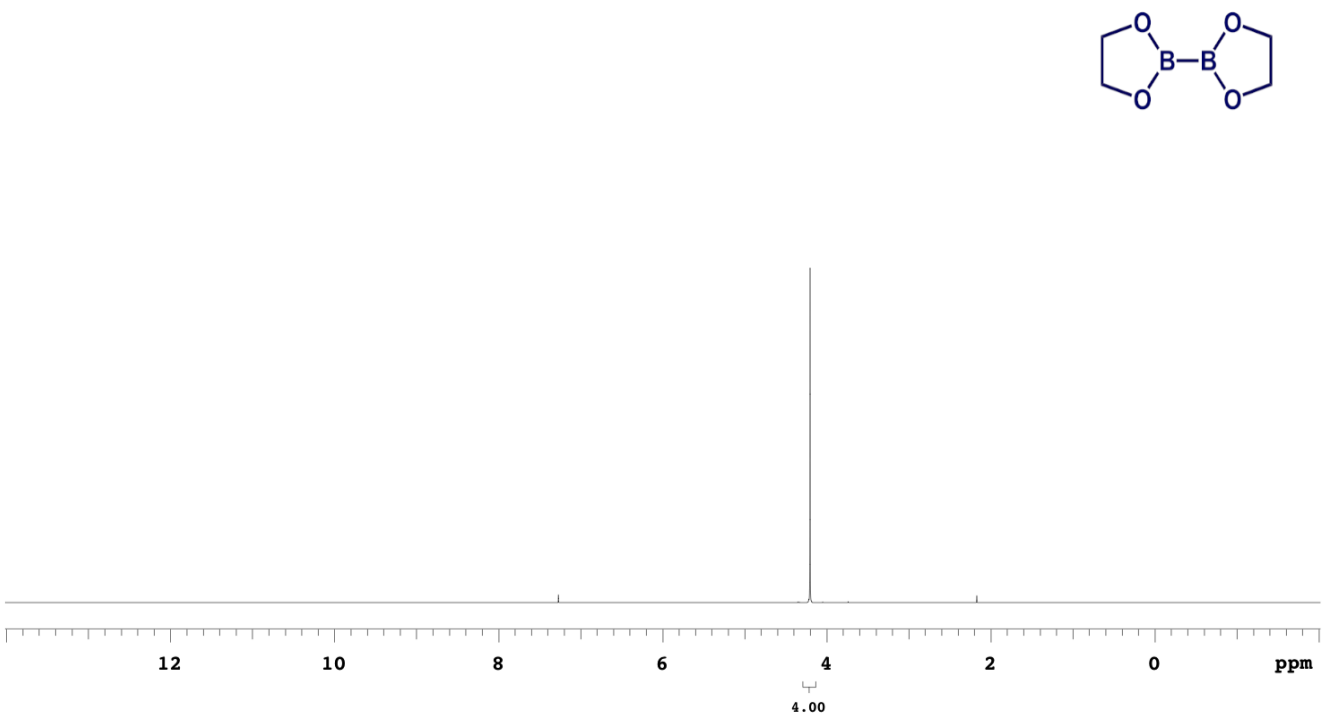

OH
B
O
O
180
160
140
120
100
80
60
40
20
ppm



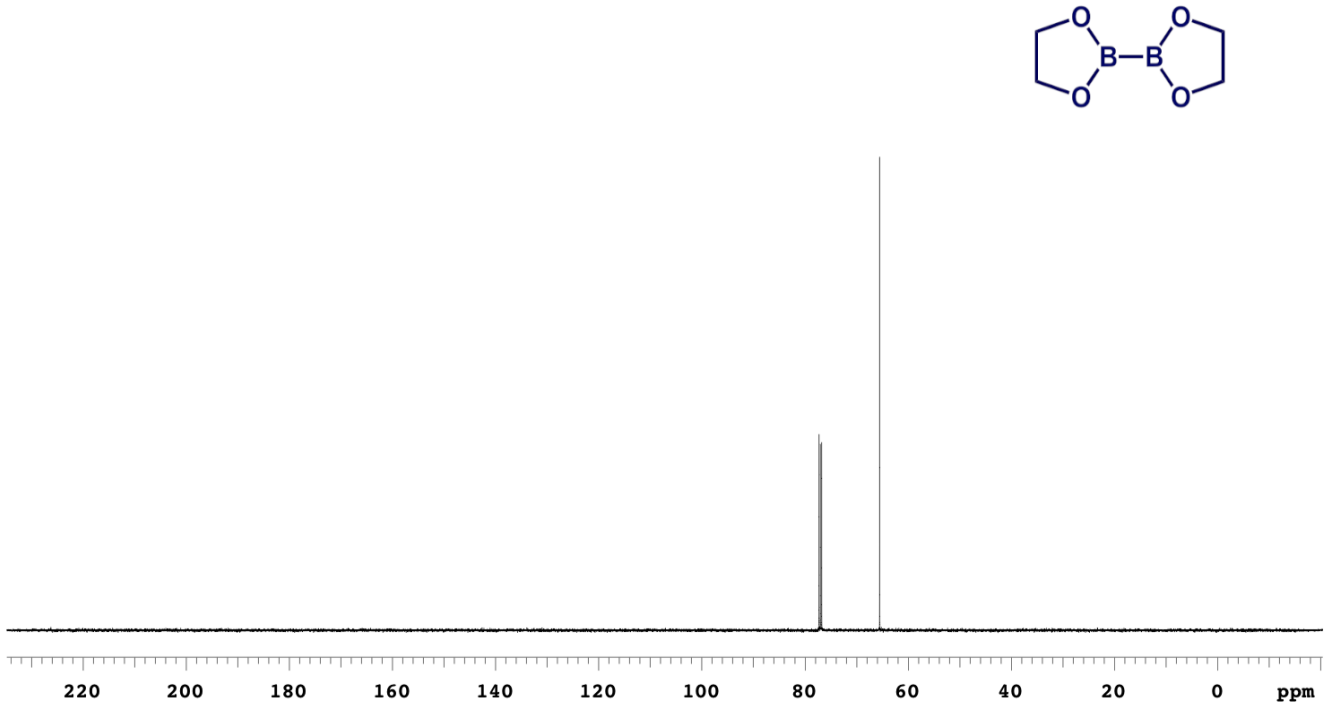
^{1}H-NMR (500 MHz, $CDCl_3$)



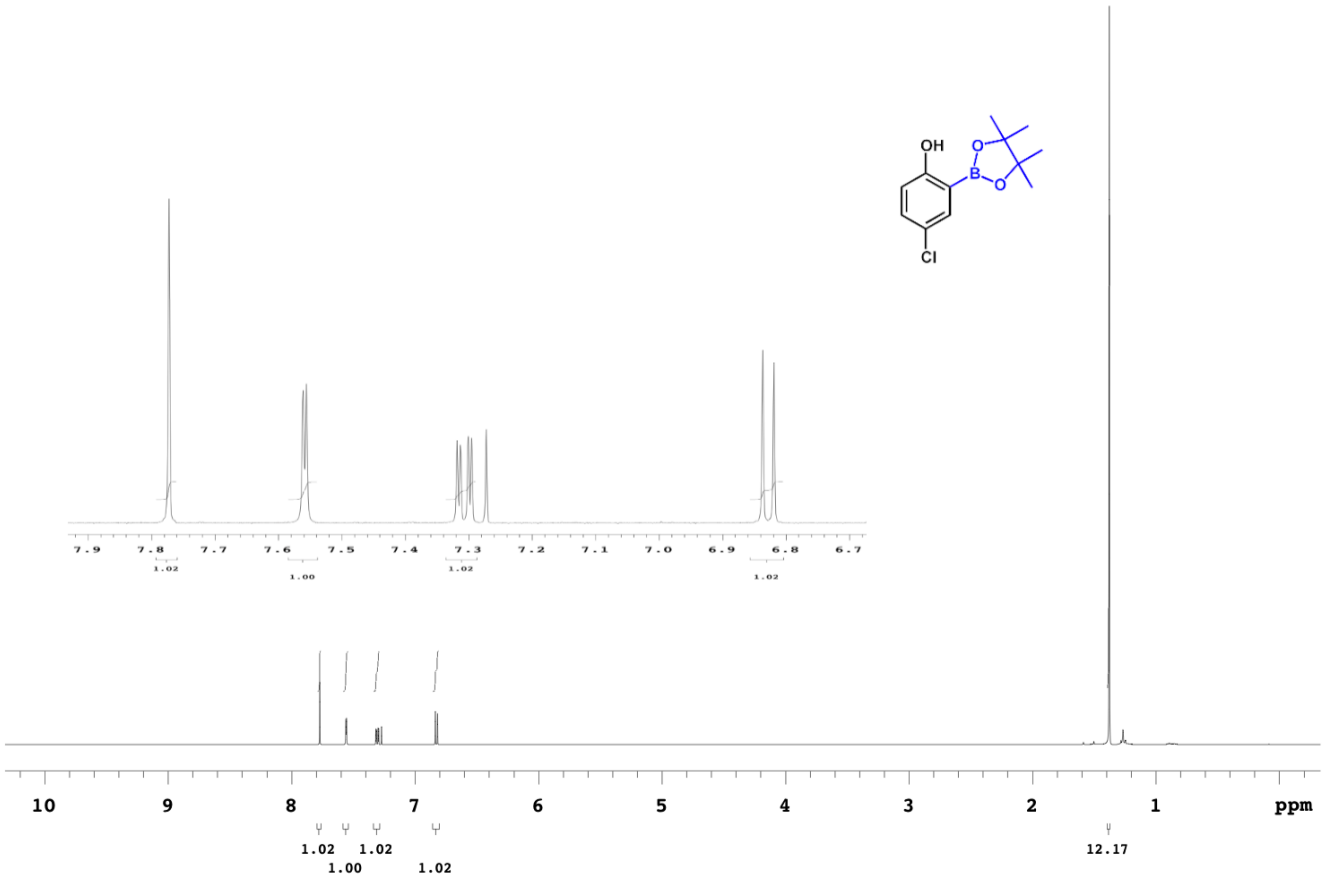
^{13}C-NMR (125 MHz, $CDCl_3$)



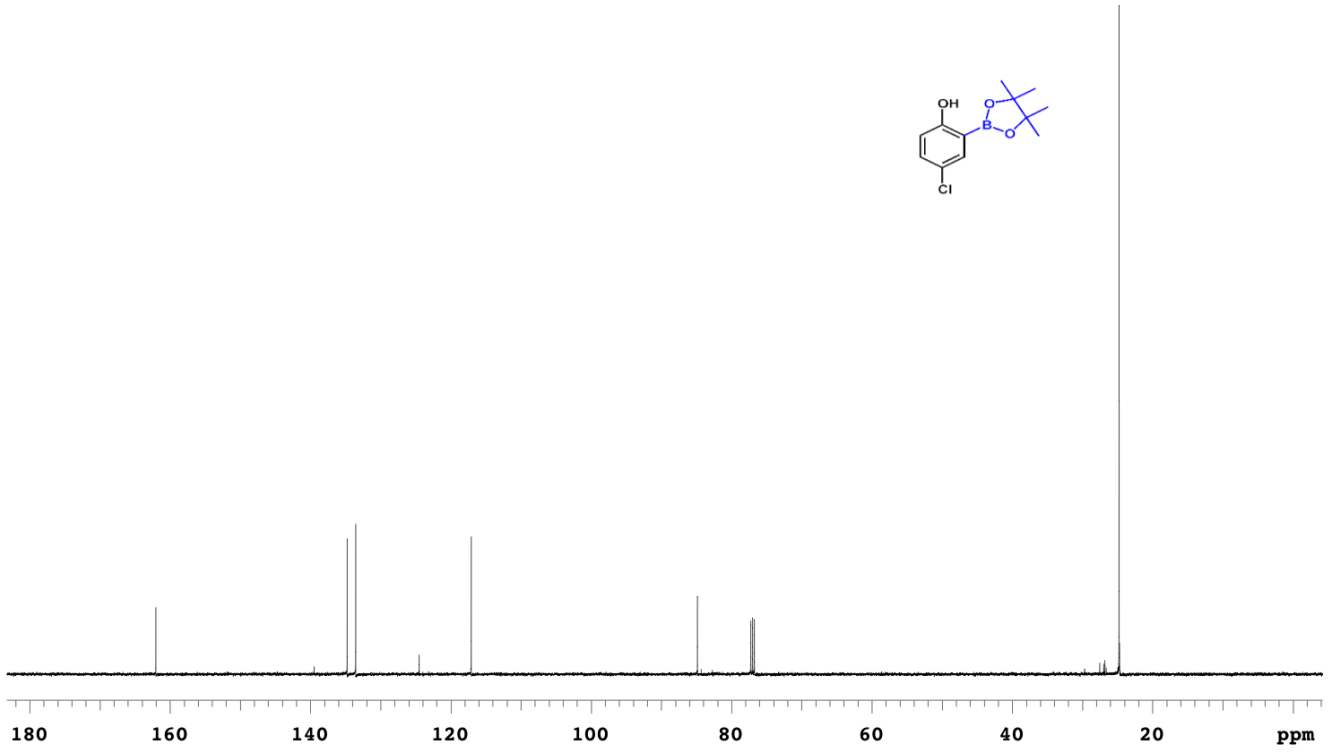
^{1}H-NMR (500 MHz, $CDCl_3$)


O
B
B
O
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

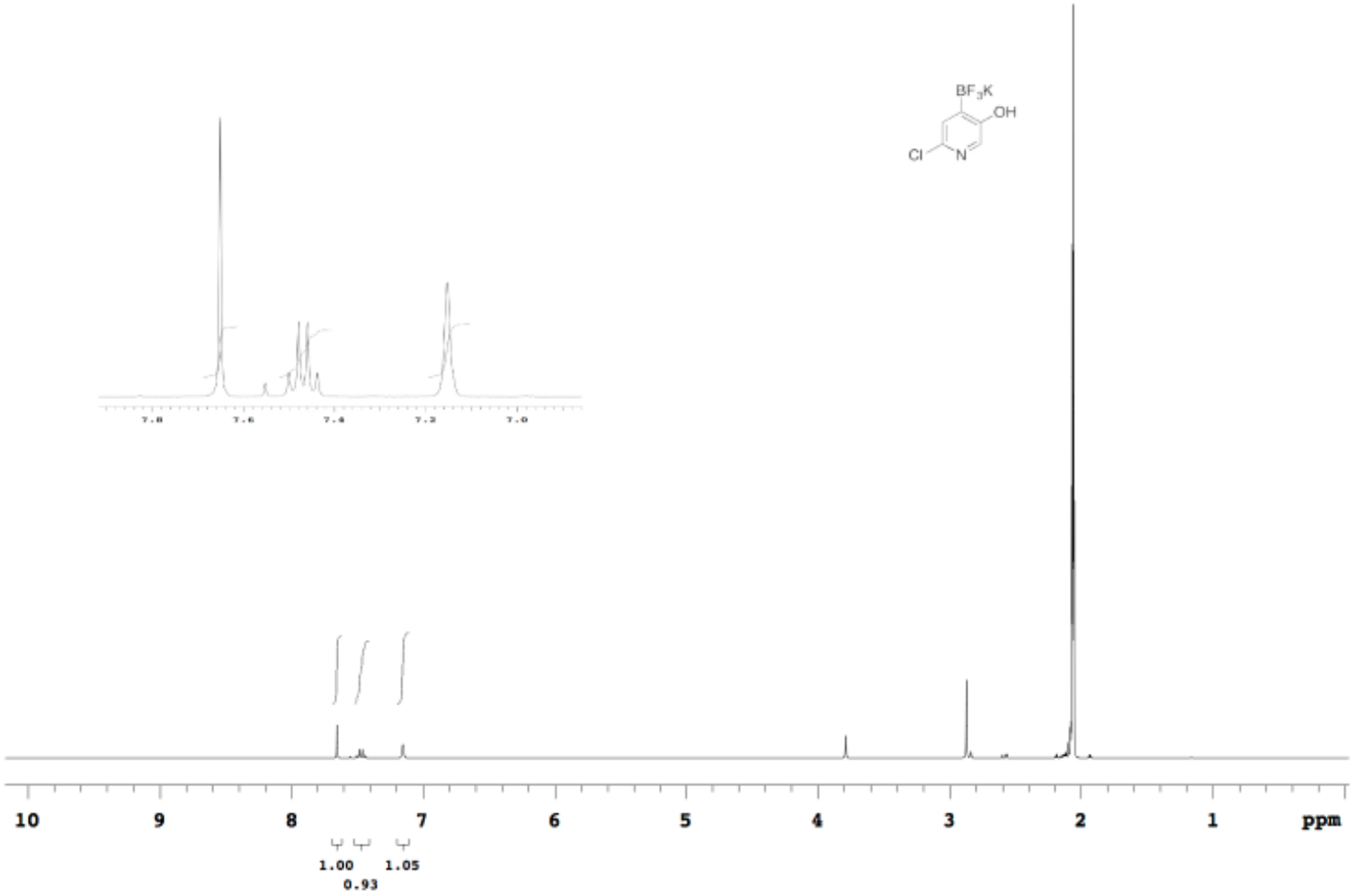
^{13}C NMR (125 MHz, $CDCl_3$)



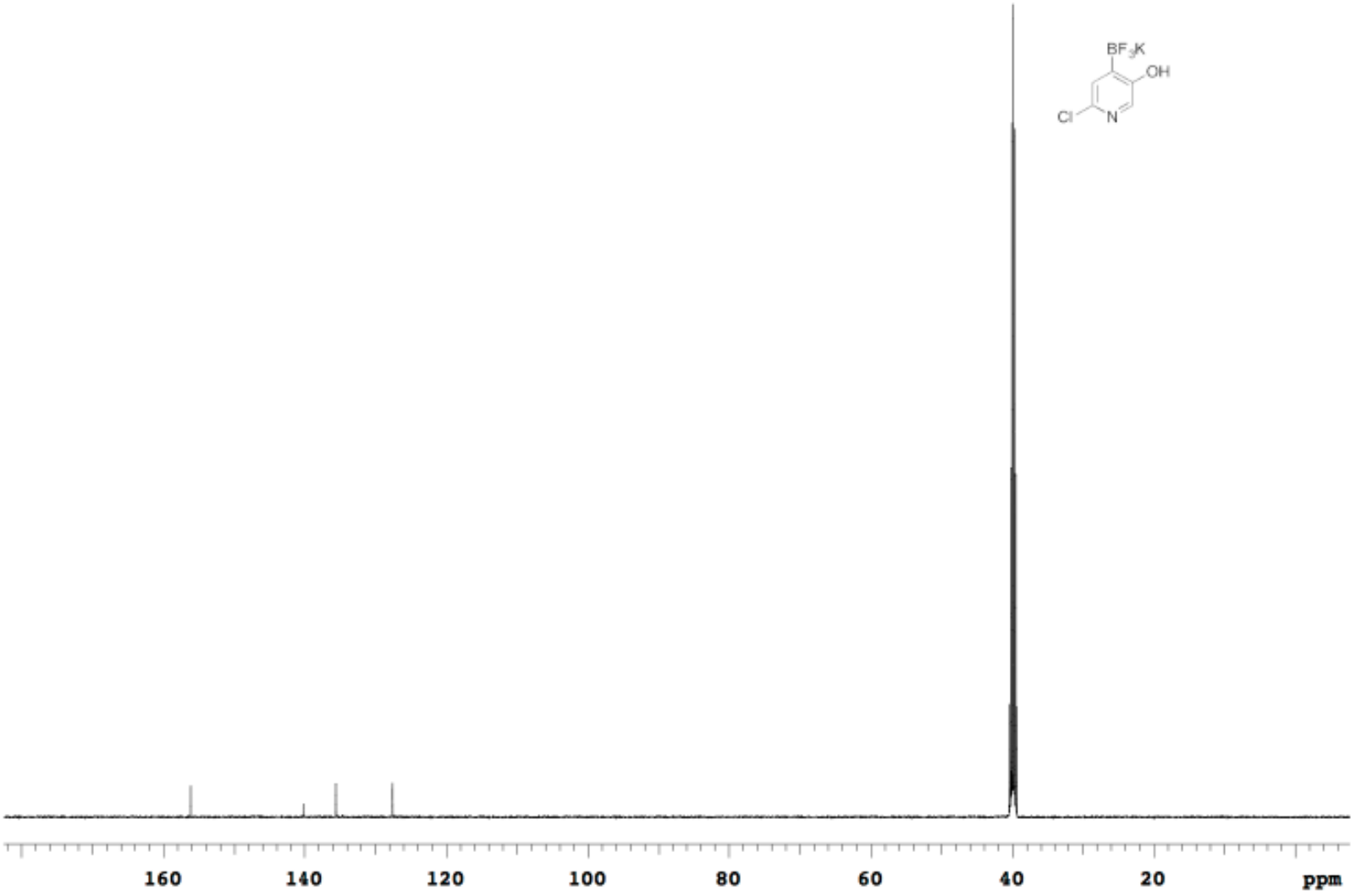
^{1}H-NMR (500 MHz, $CDCl_3$)



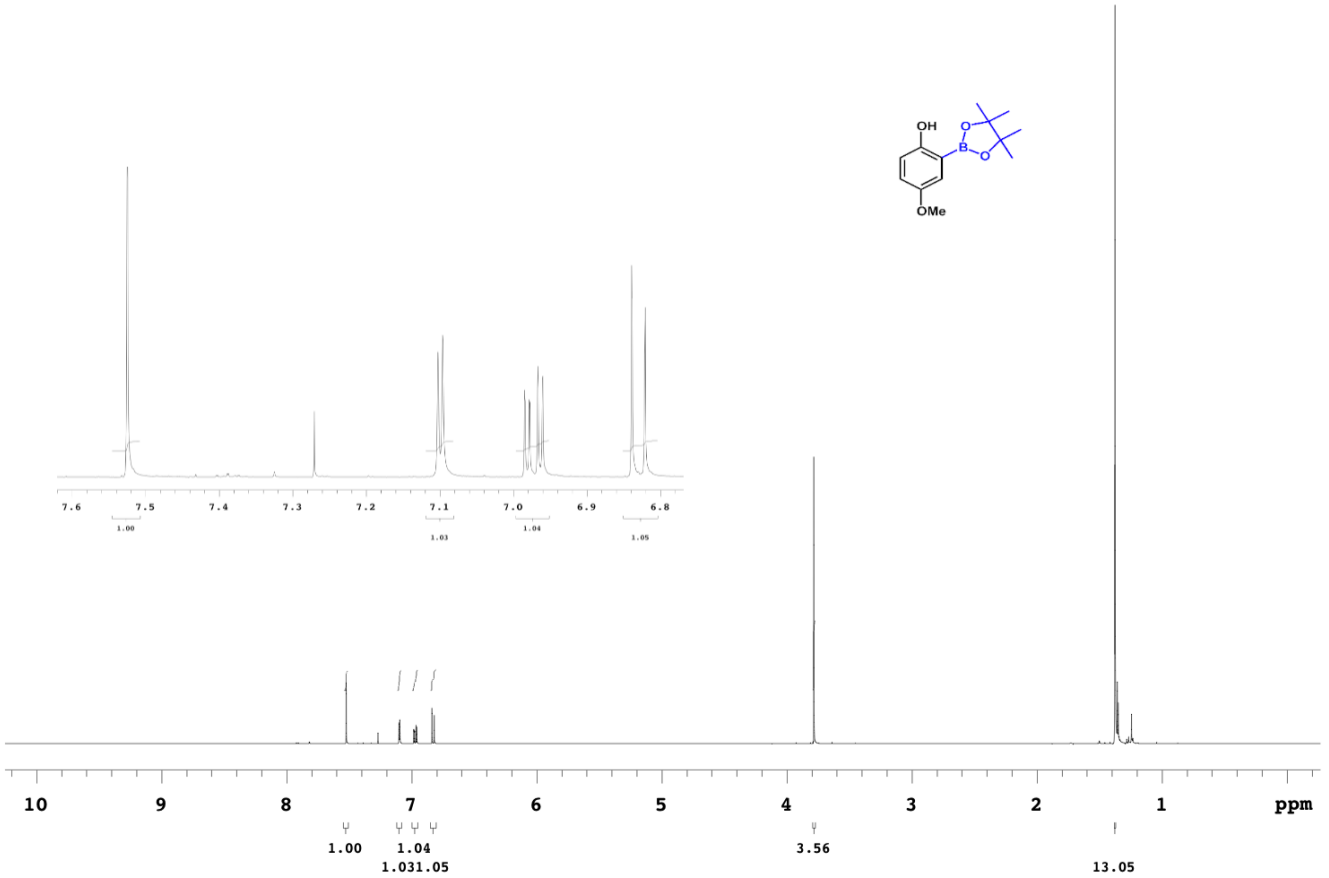
^{13}C-NMR (125 MHz, $CDCl_3$)



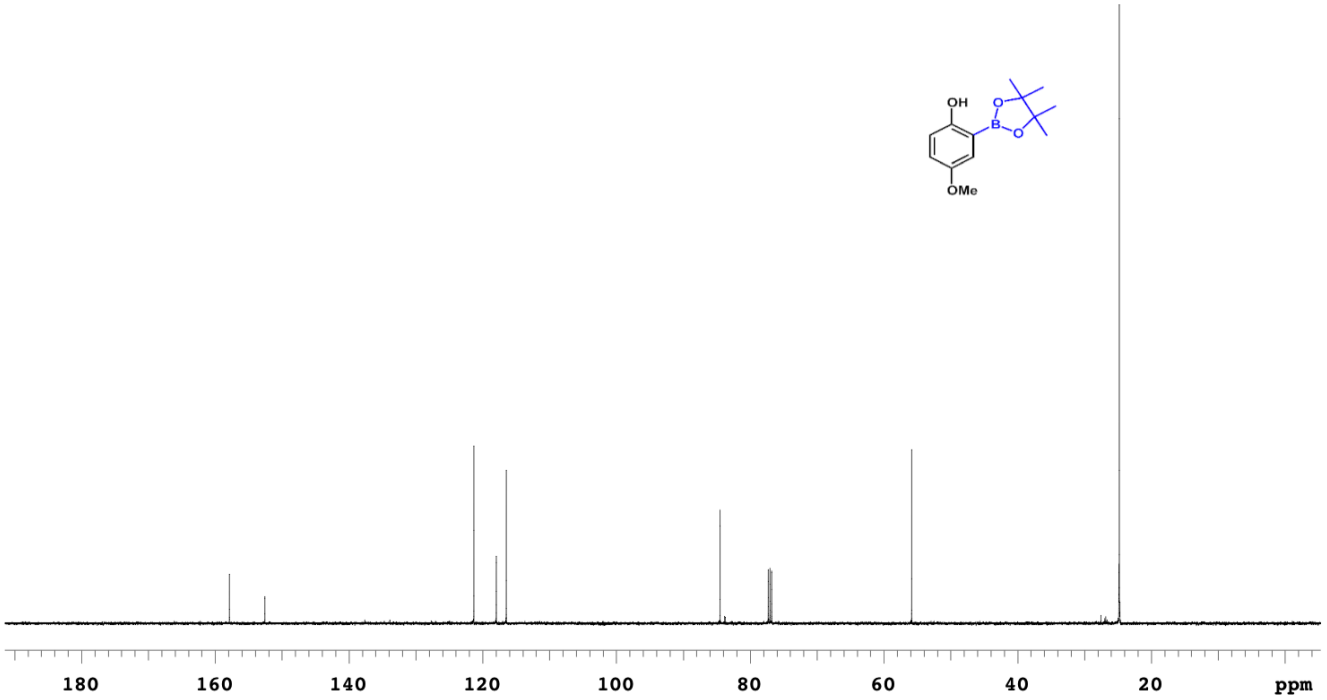
^{1}H-NMR (500 MHz, $(CD_3)_2CO$)



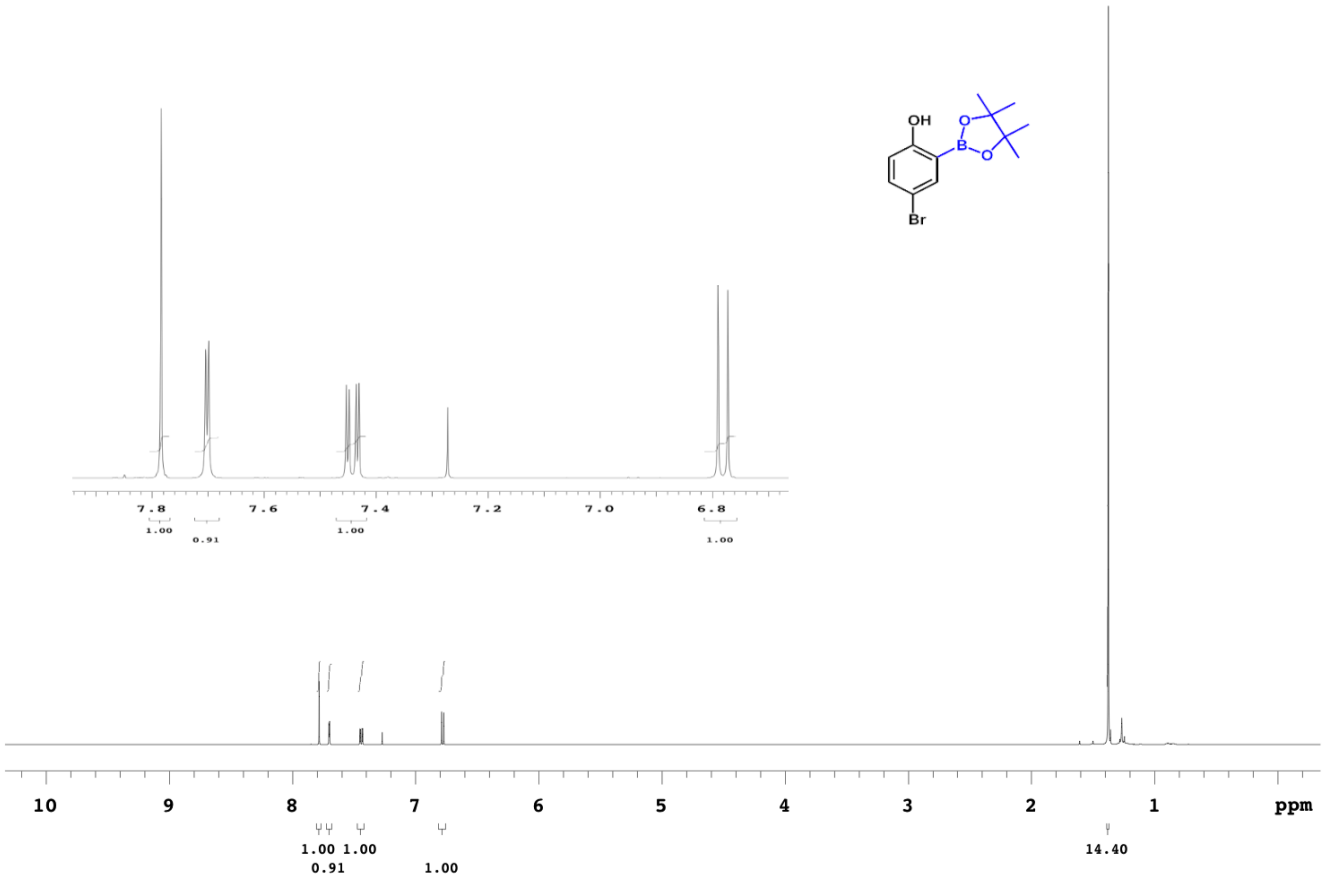
^{13}C-NMR (125 MHz, $(CD_3)_2SO$)



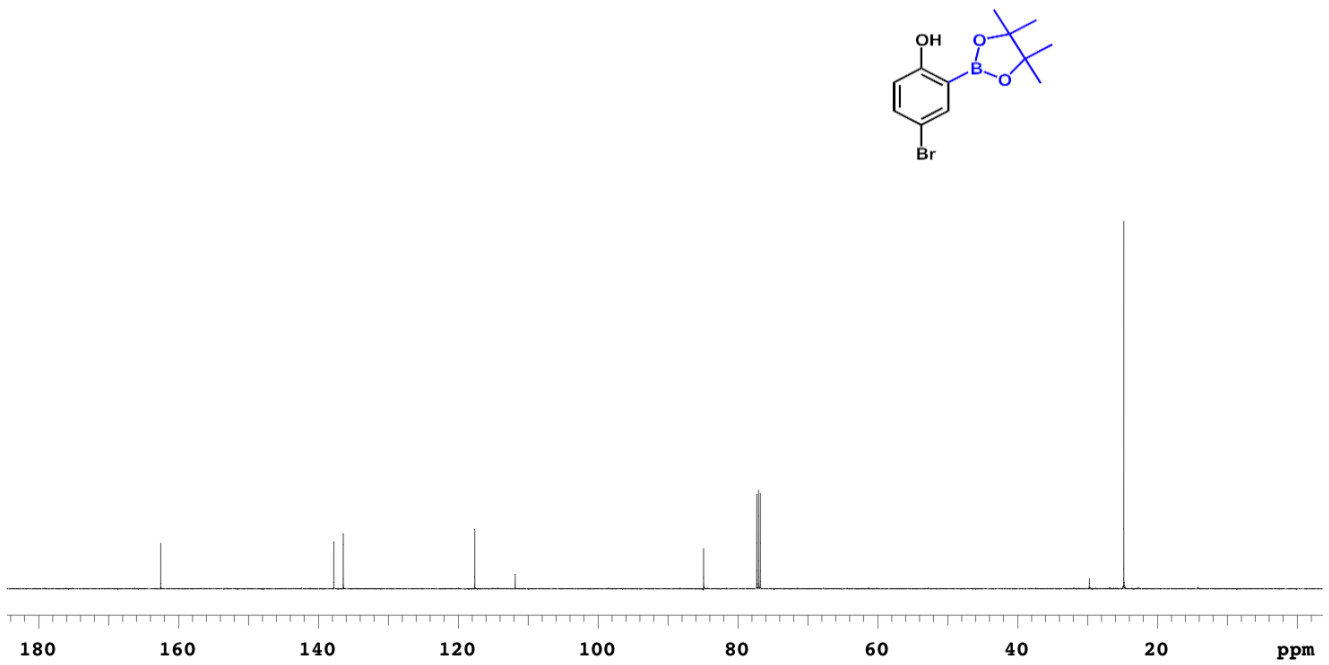
^{1}H-NMR (500 MHz, $CDCl_3$)



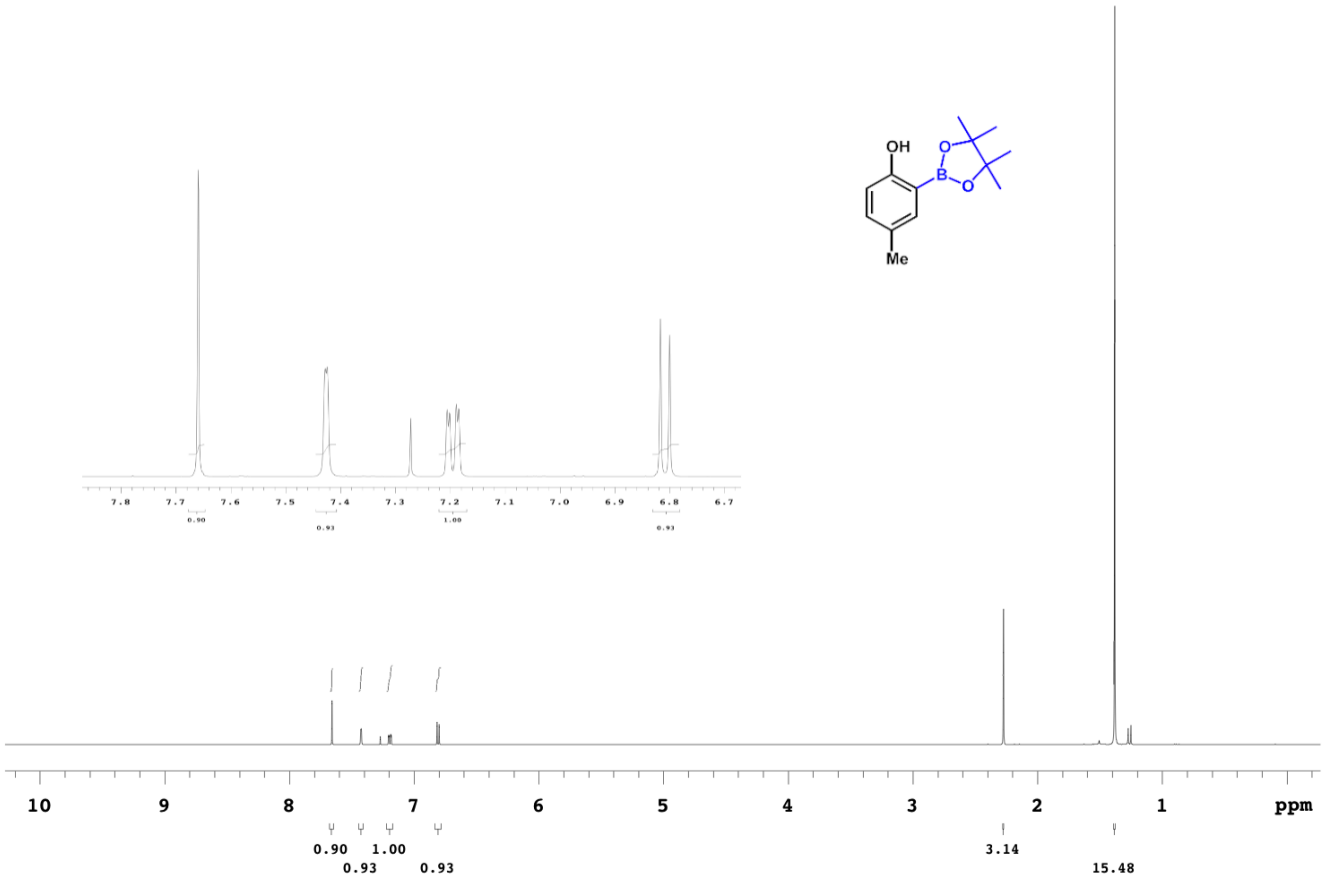
^{13}C-NMR (125 MHz, $CDCl_3$)


OH
O
B
O
Br
7.8
7.6
7.4
7.2
7.0
6.8
1.00
0.91
1.00
1.00
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
0.91
1.00
14.40

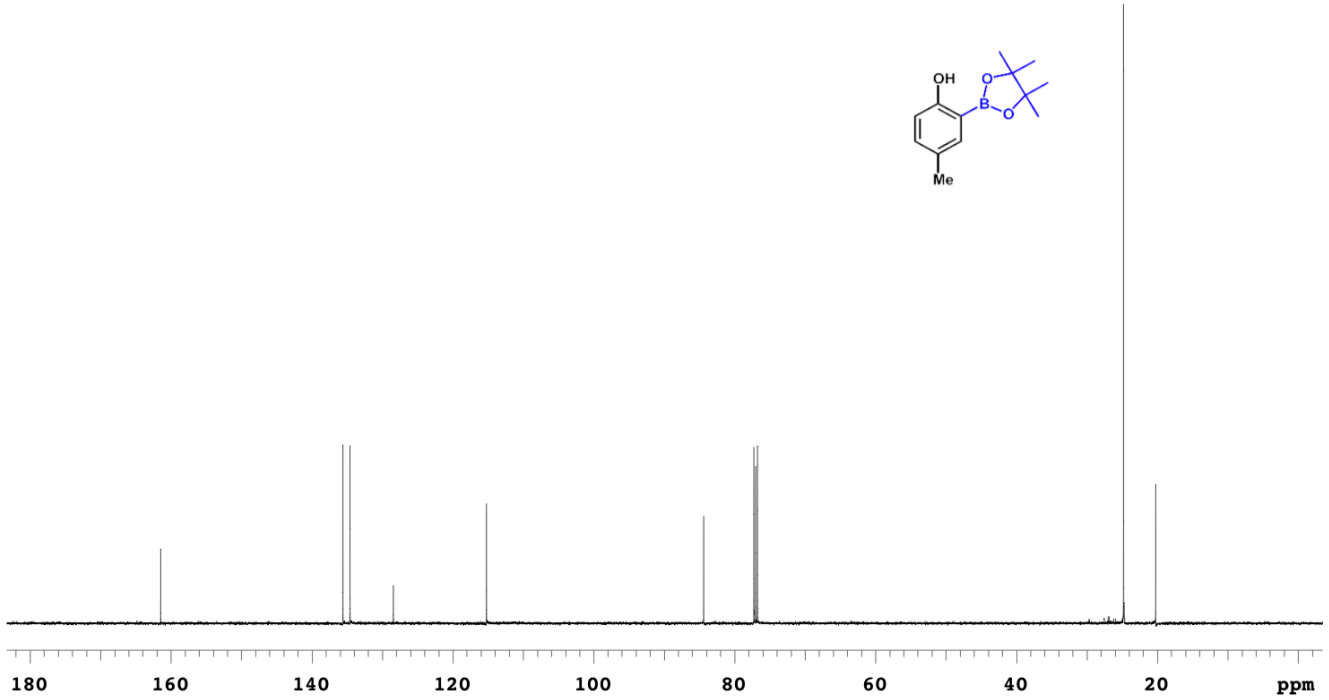
^{1}H-NMR (500 MHz, $CDCl_3$)



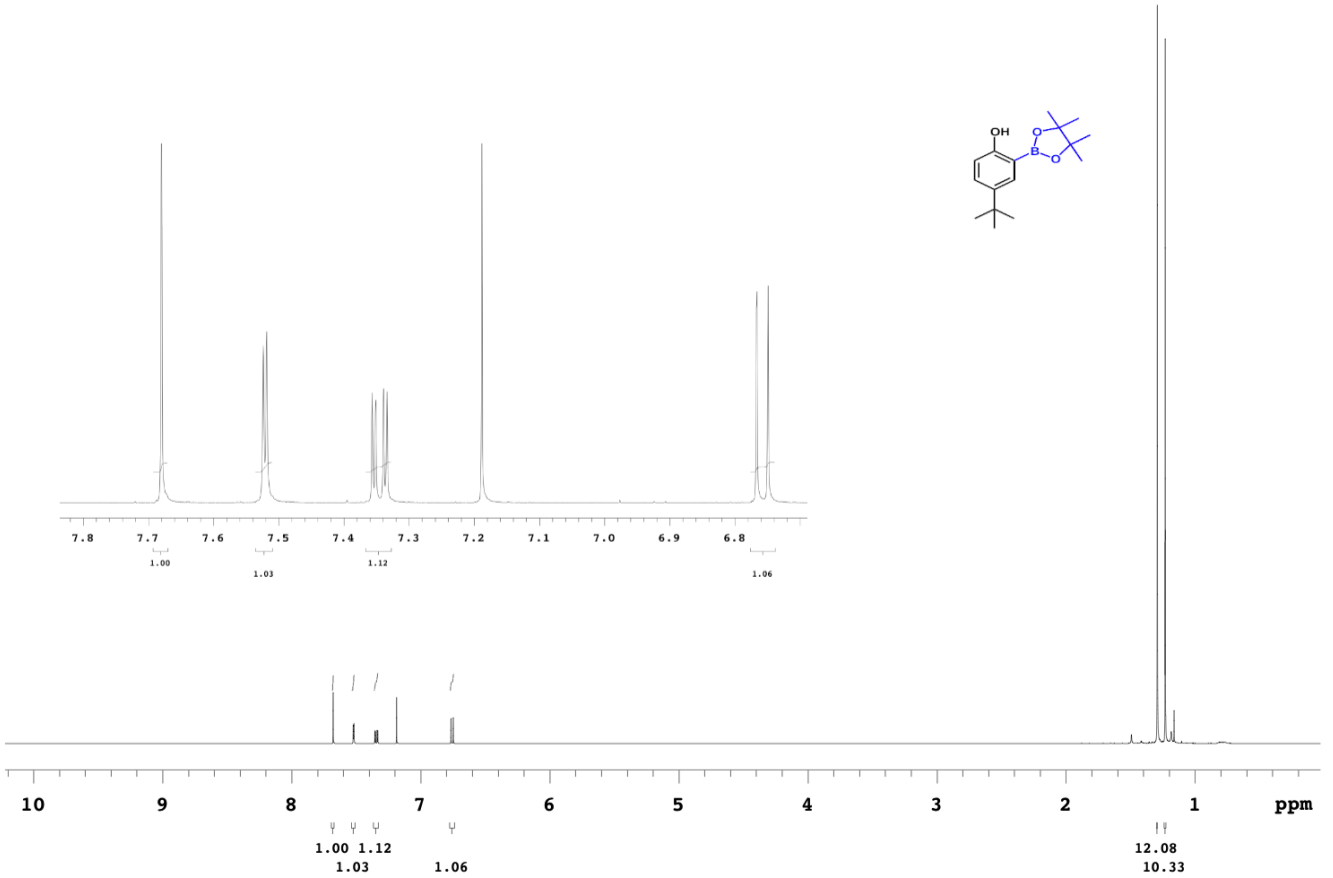
^{13}C-NMR (125 MHz, $CDCl_3$)



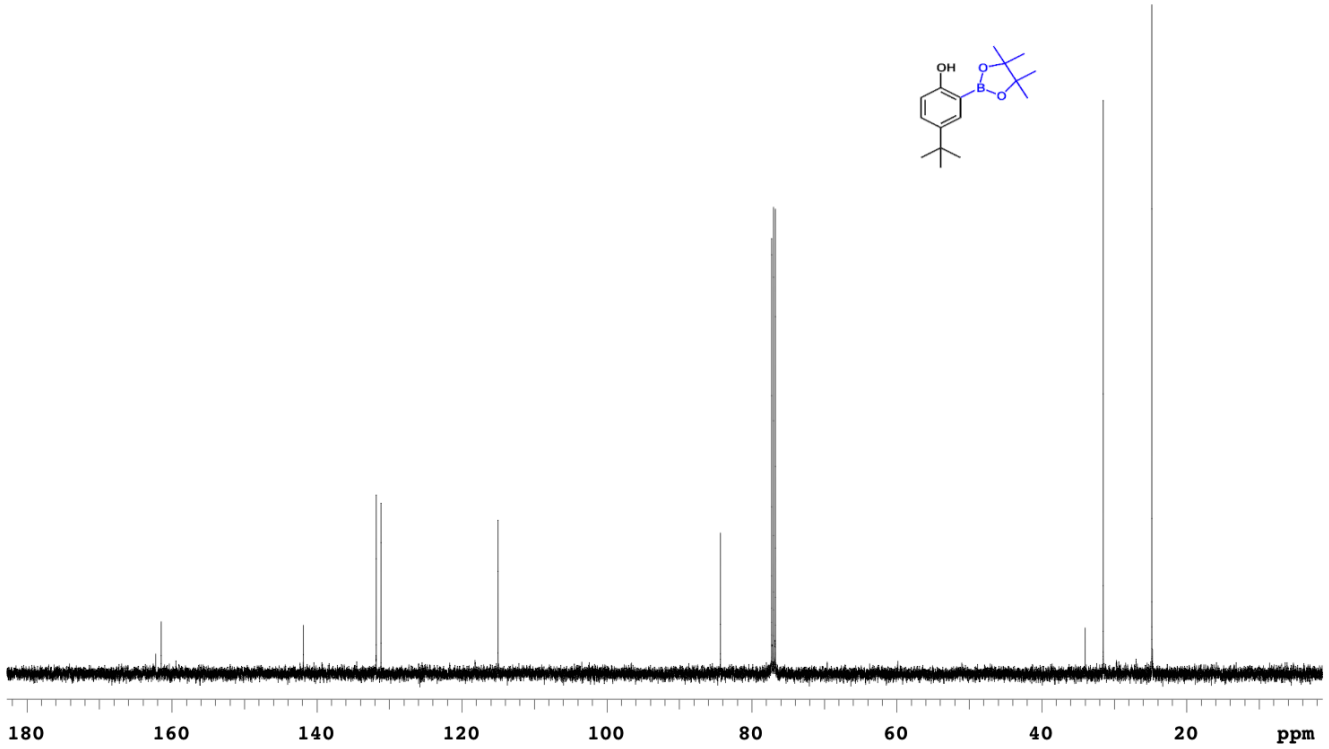
^{1}H-NMR (500 MHz, $CDCl_3$)


OH
O
B
O
Me
180
160
140
120
100
80
60
40
20
ppm

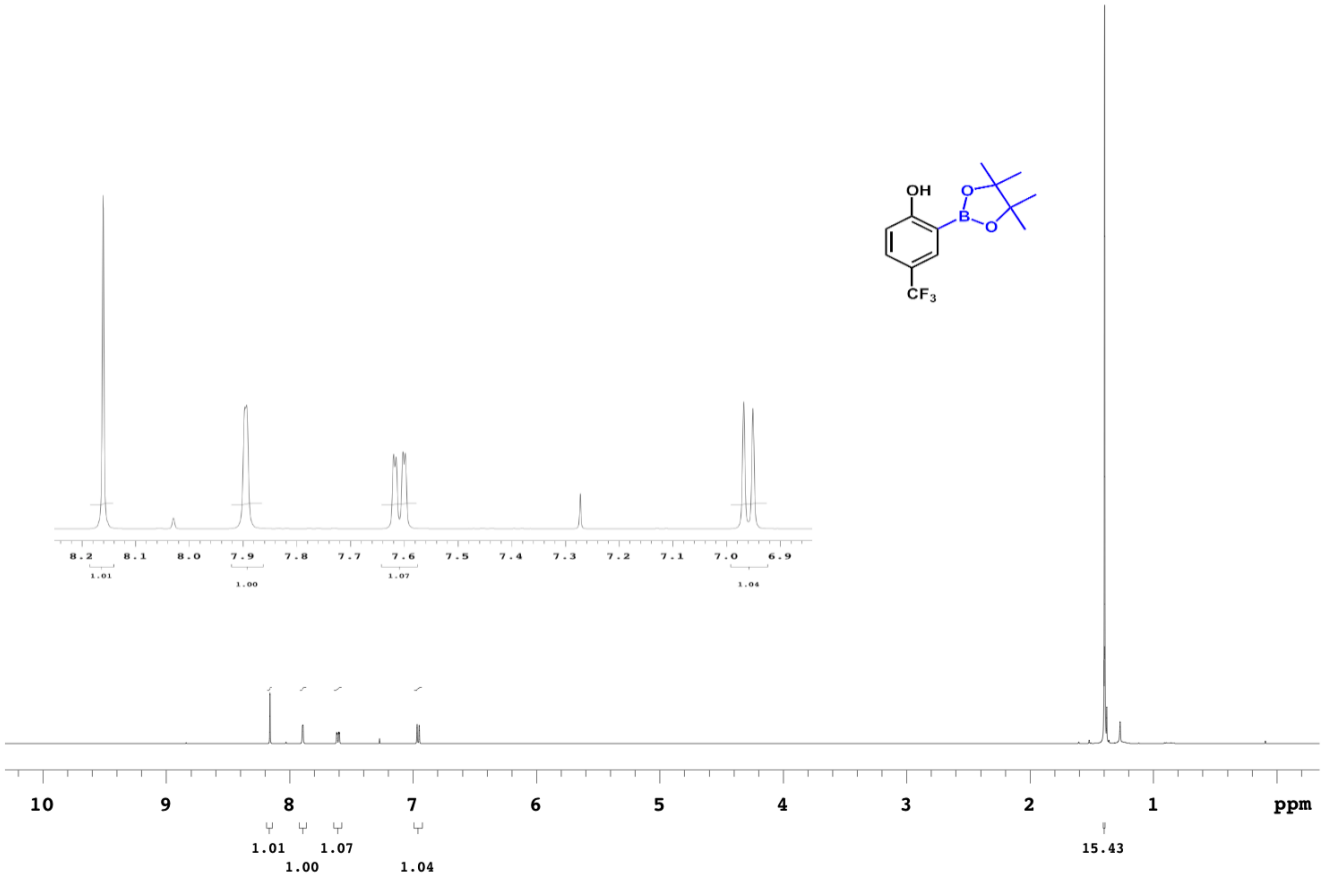
^{13}C-NMR (125 MHz, $CDCl_3$)



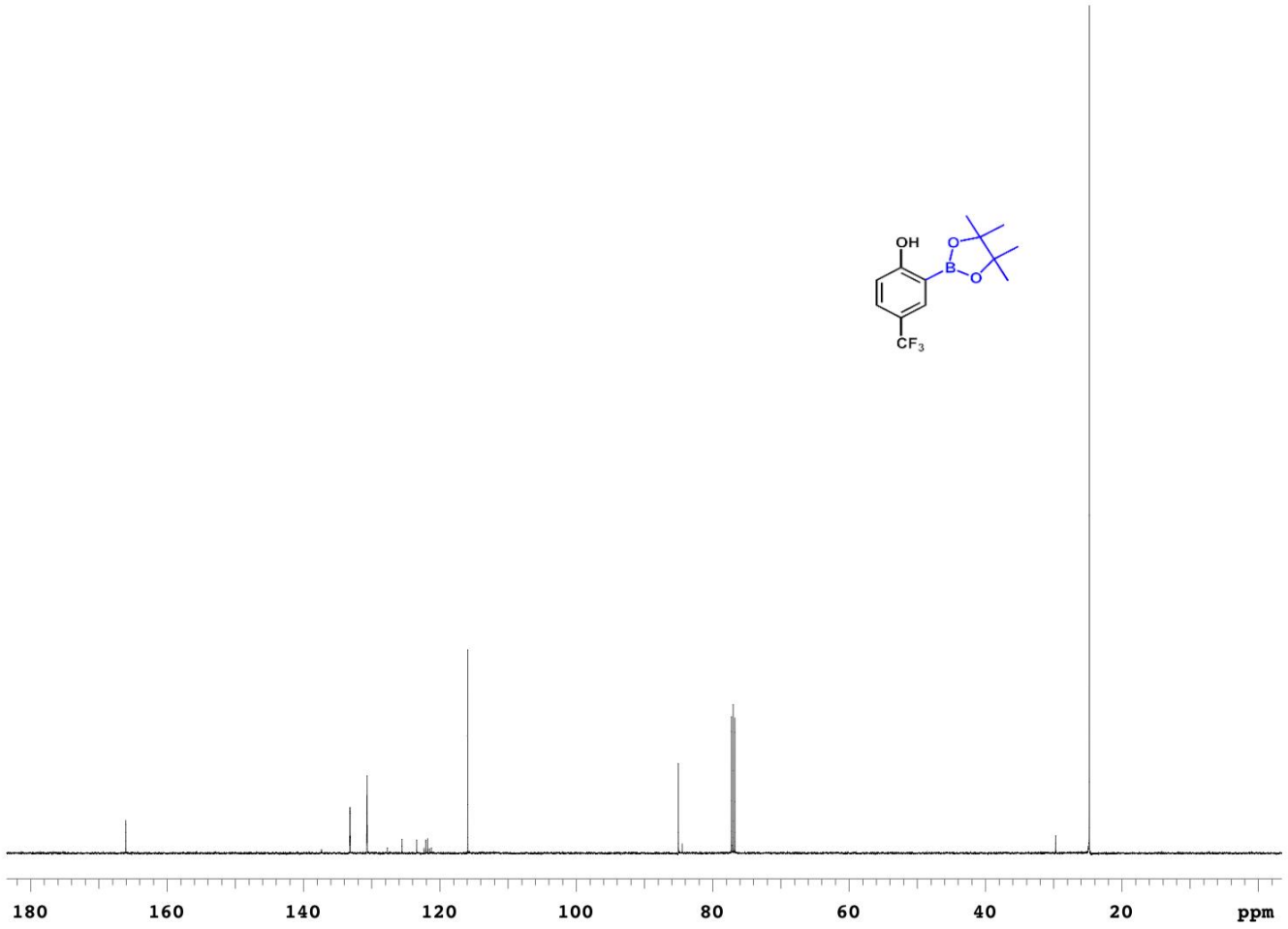
^{1}H-NMR (500 MHz, $CDCl_3$)



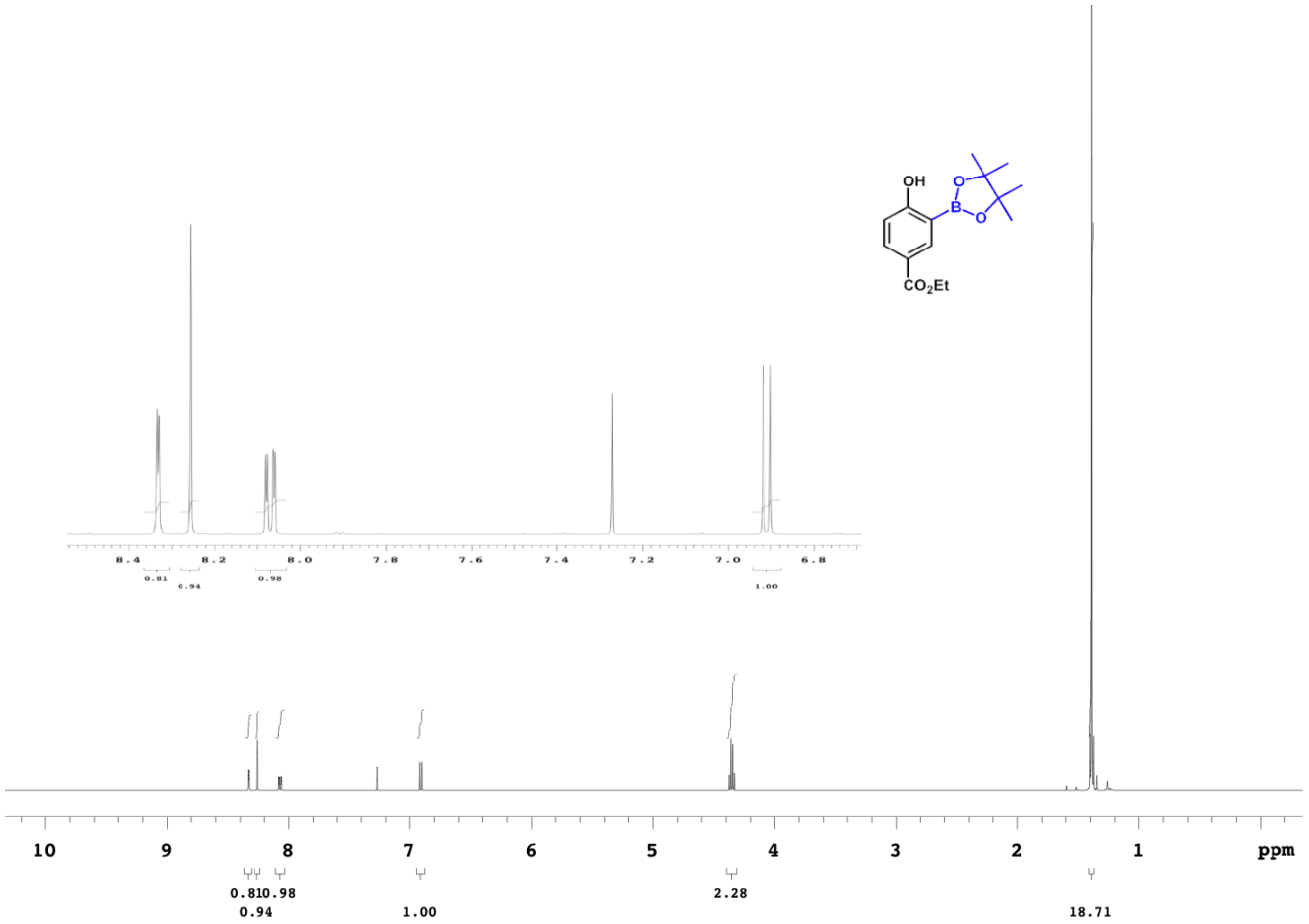
^{13}C-NMR (125 MHz, $CDCl_3$)



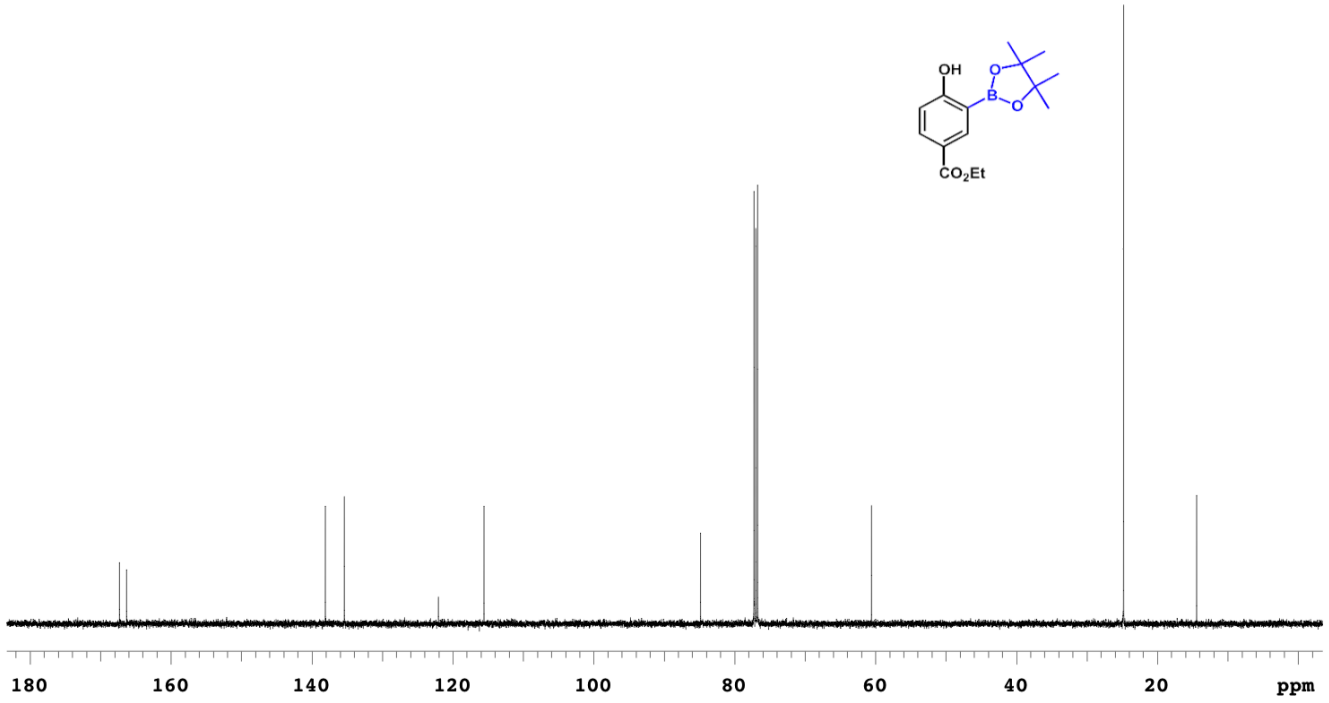
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)



^{1}H-NMR (500 MHz, $CDCl_3$)



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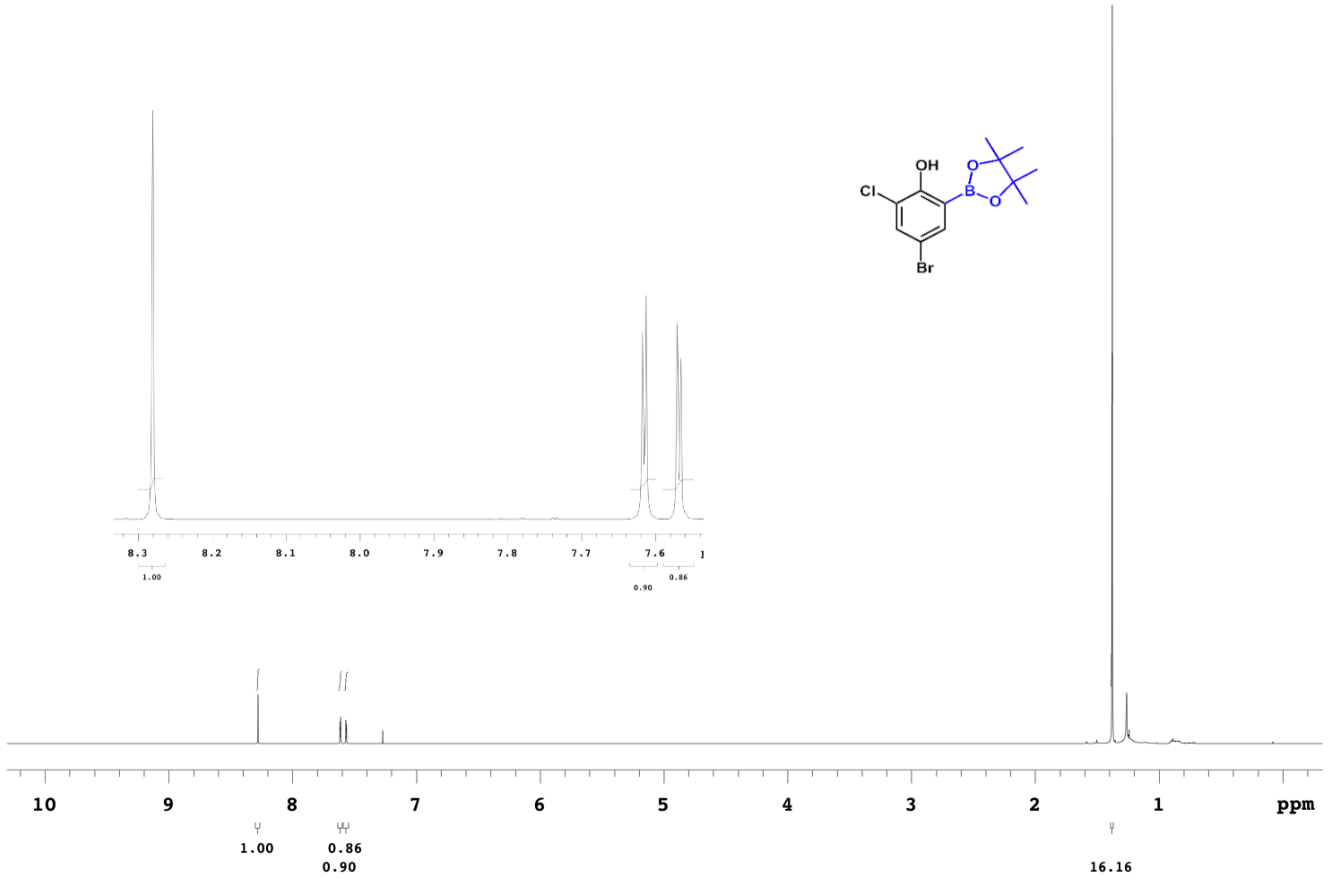

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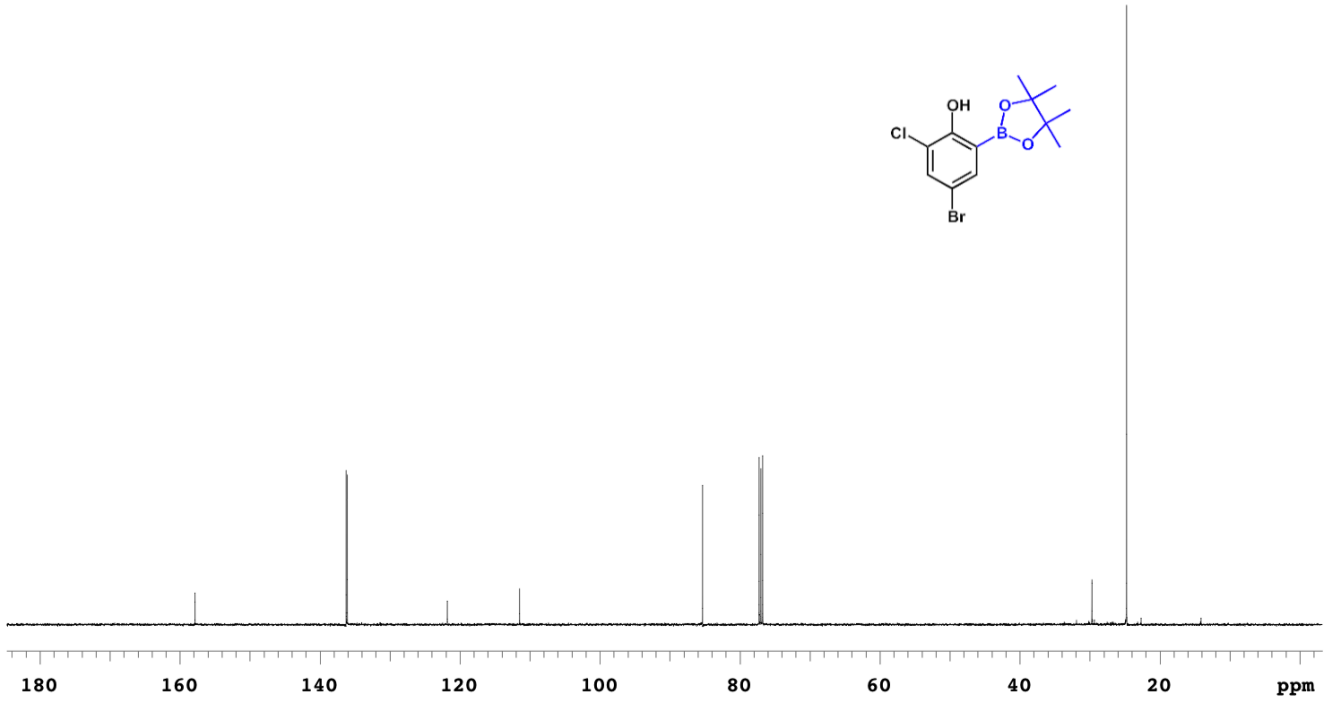

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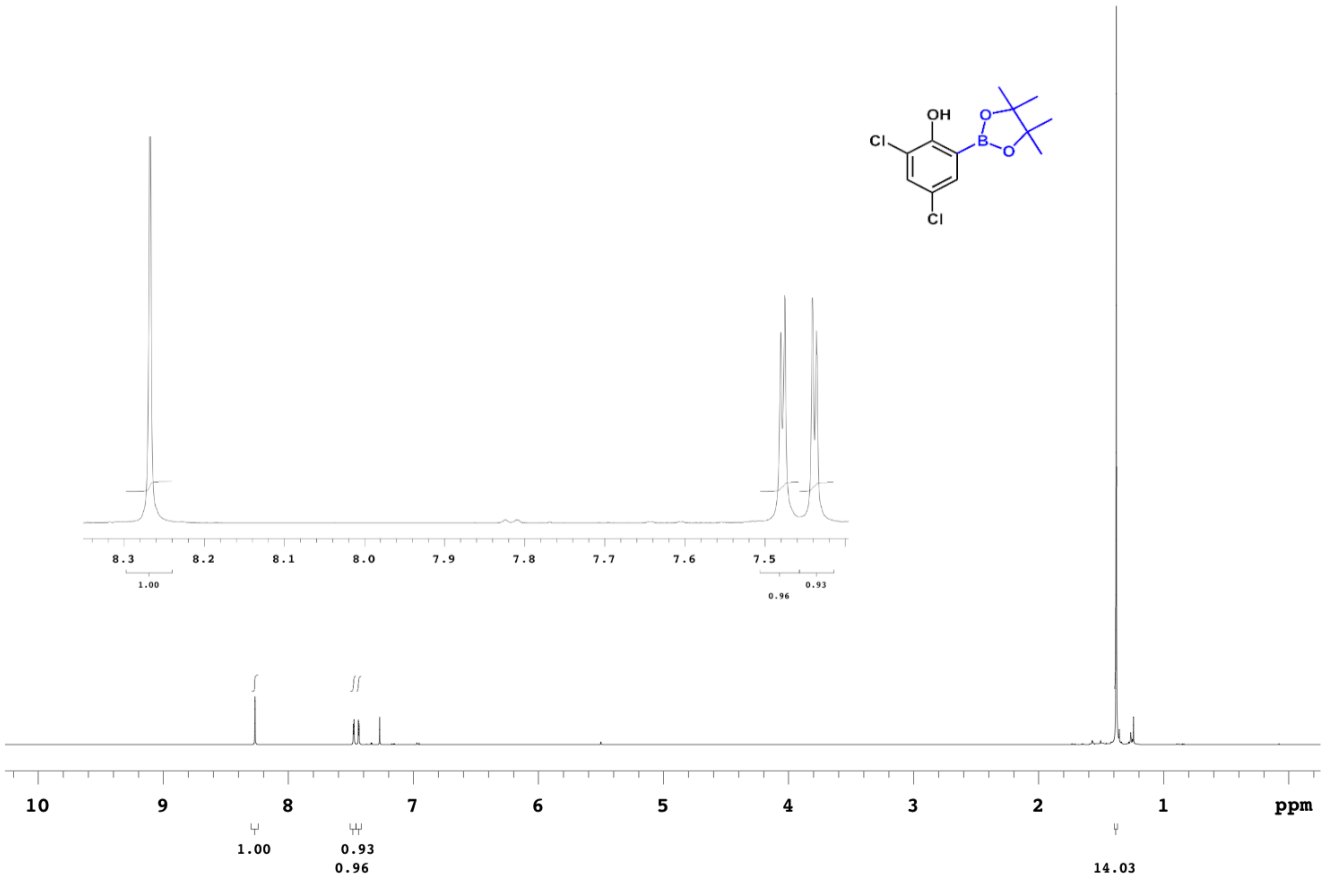

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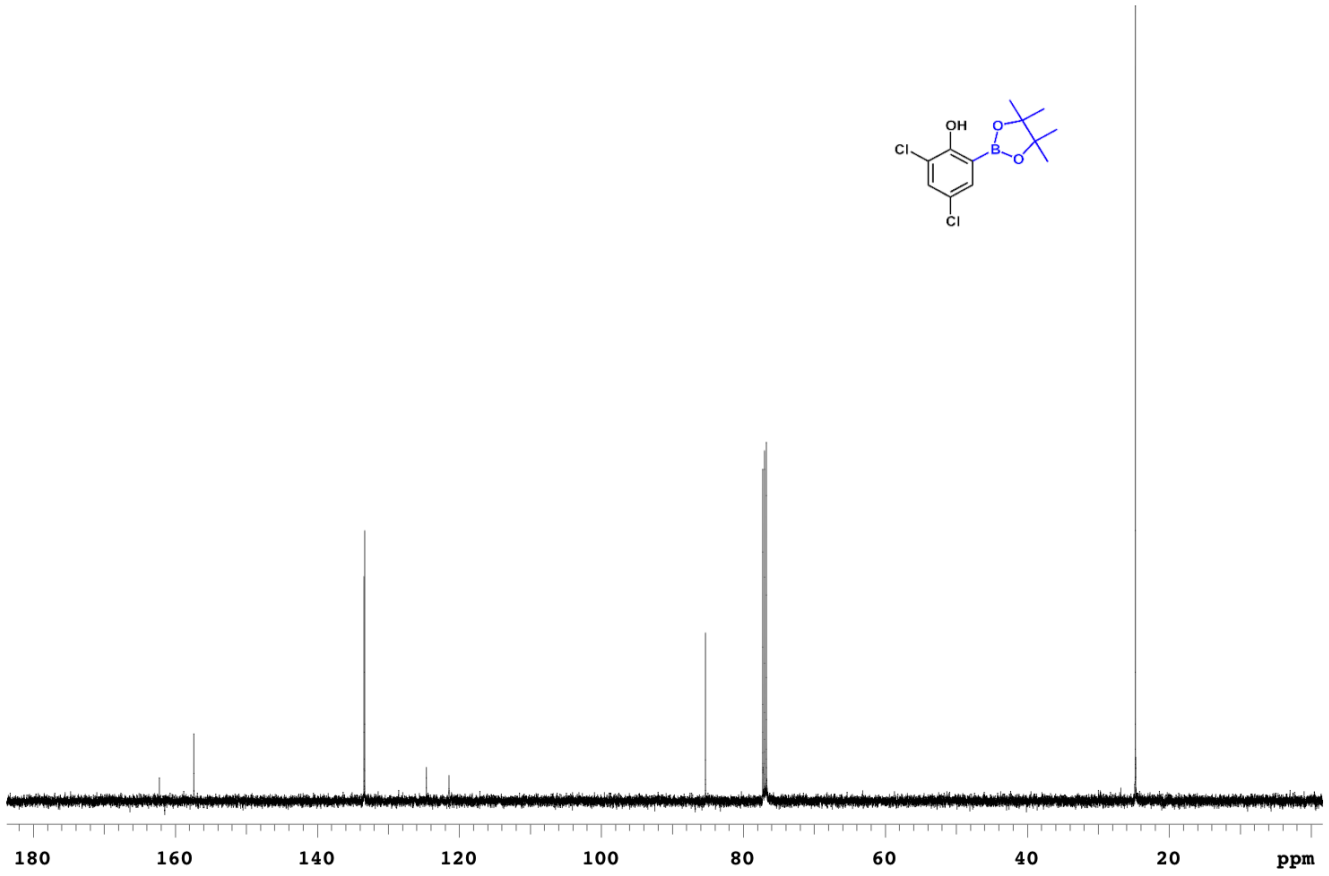

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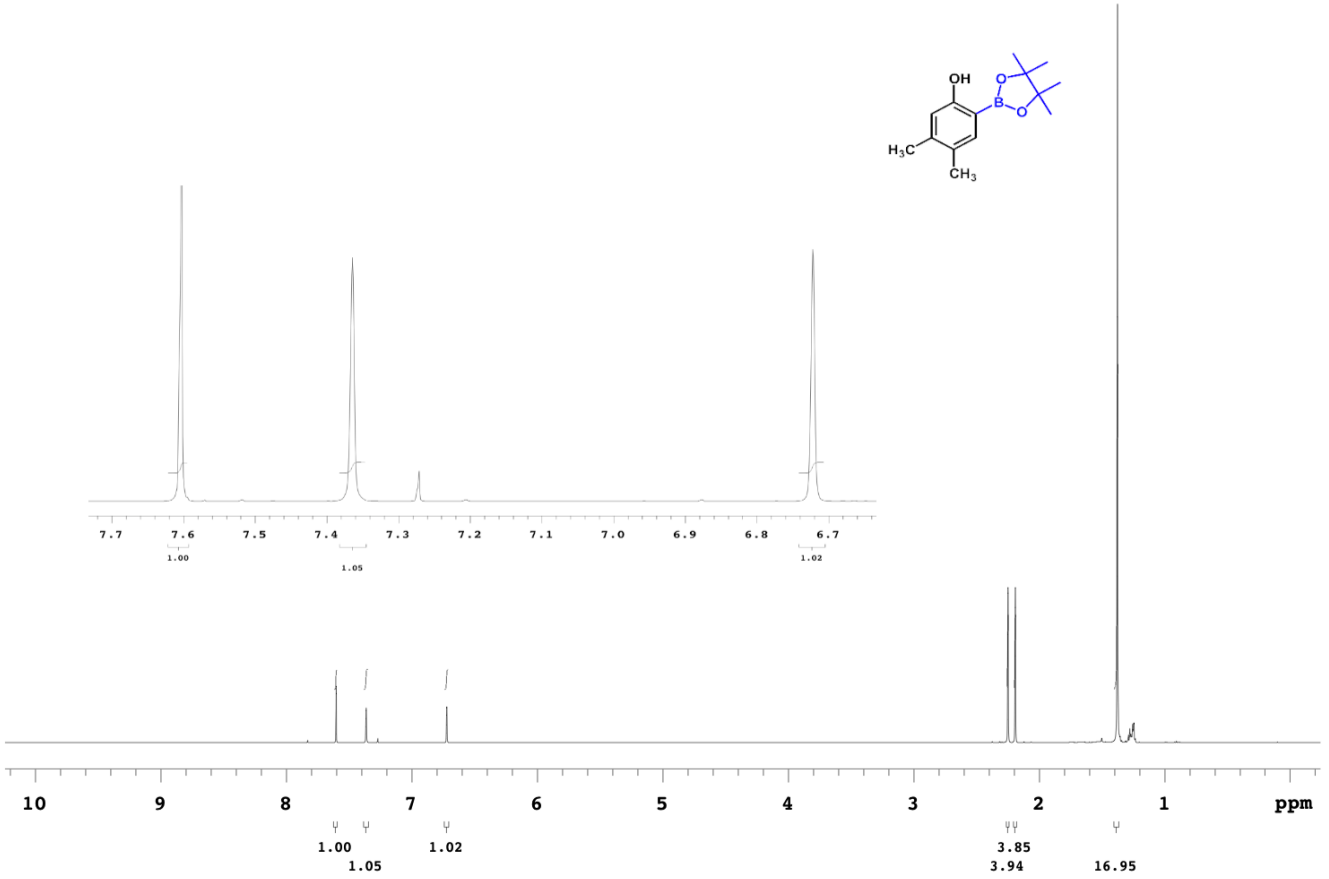

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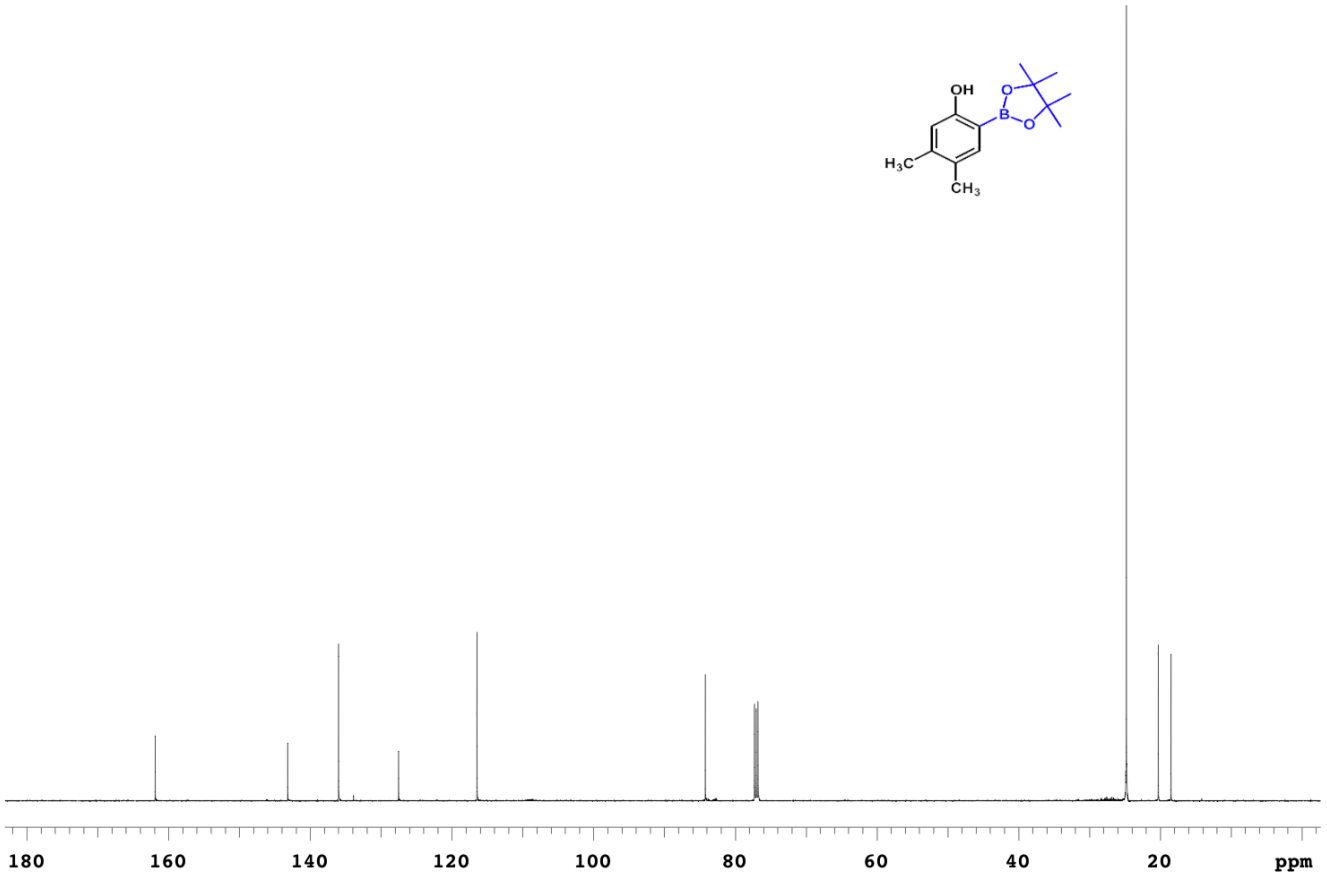

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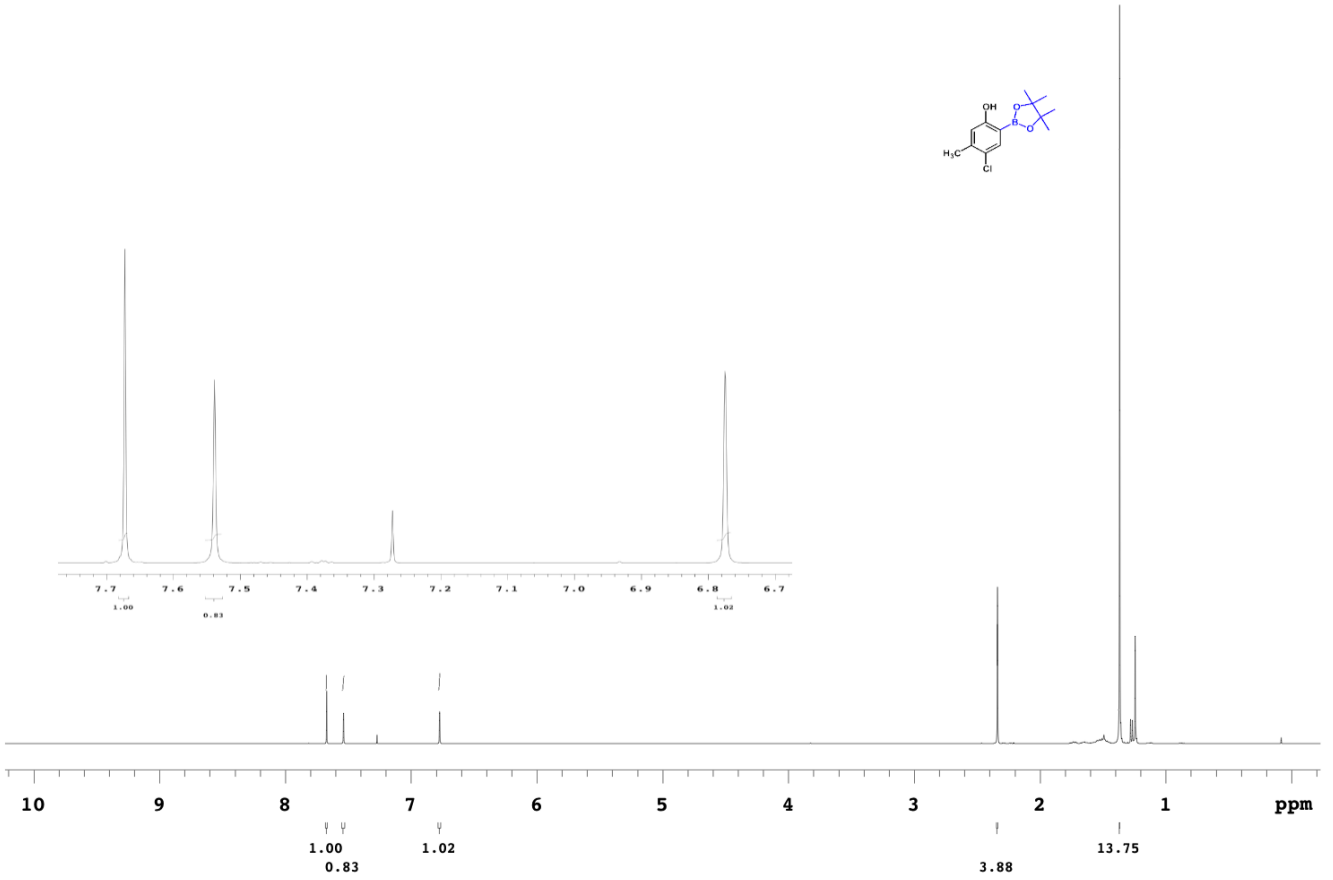

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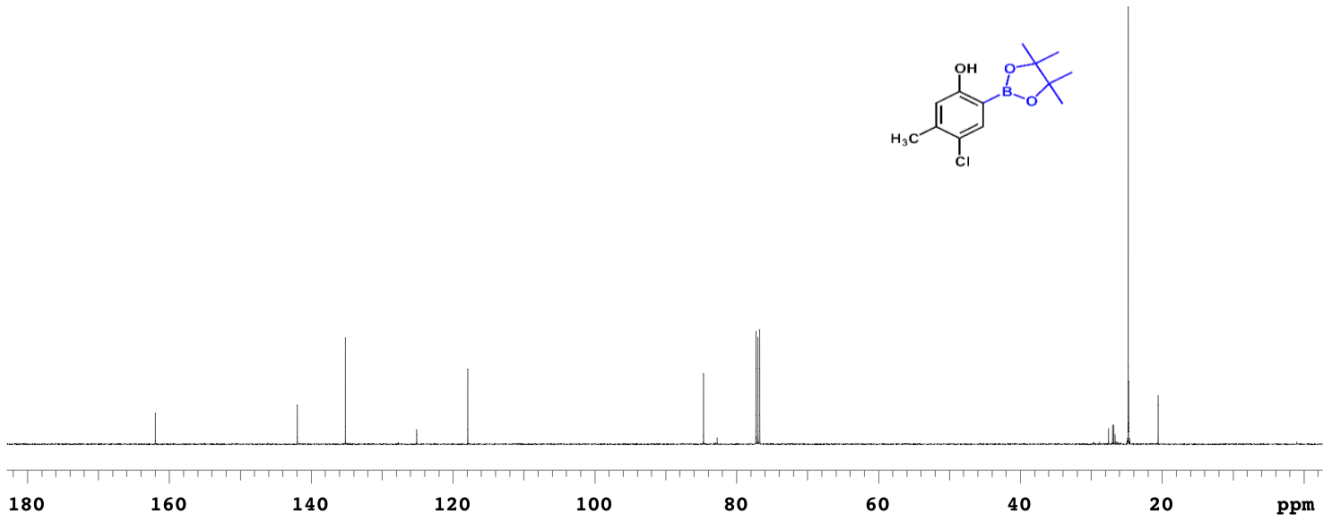

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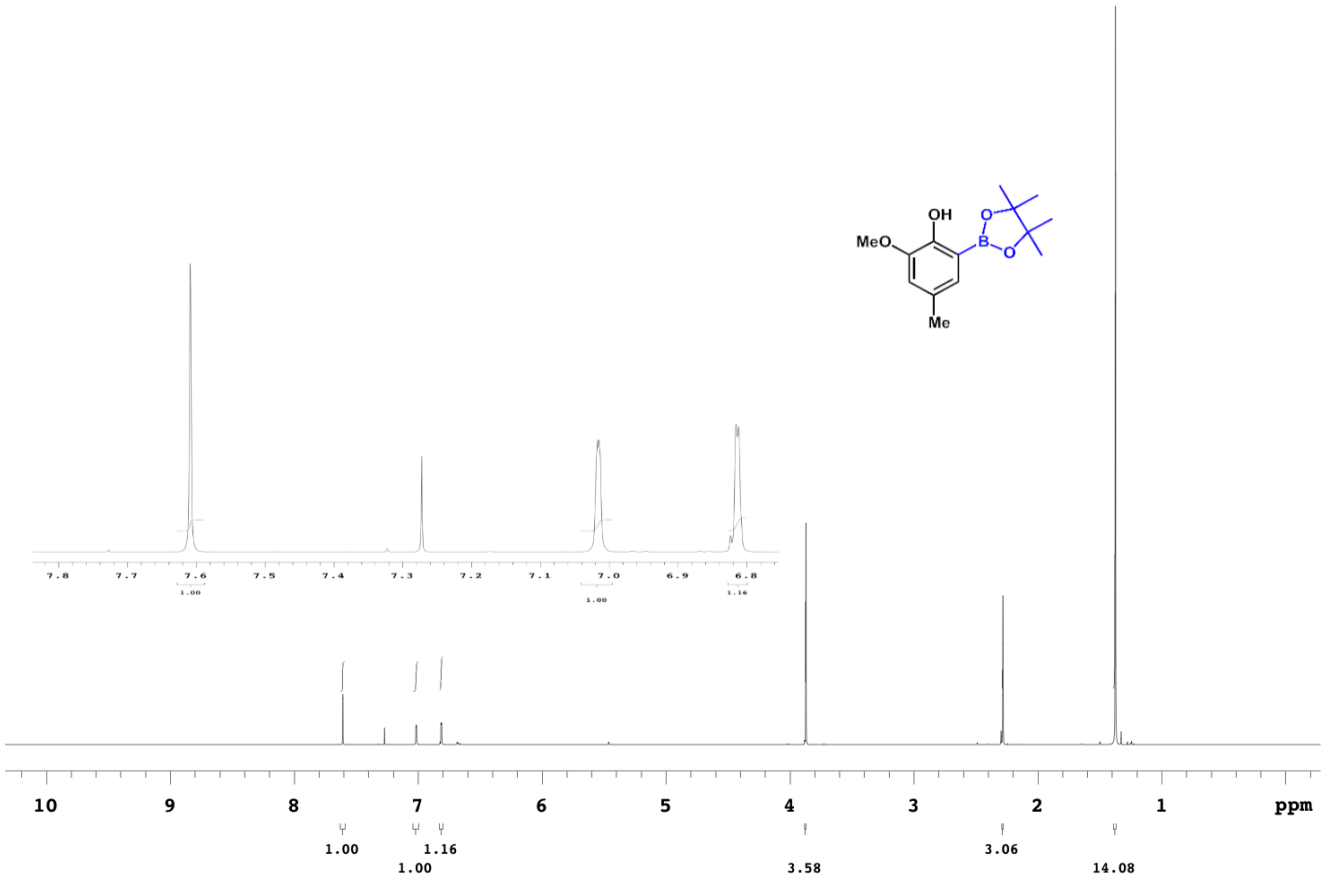

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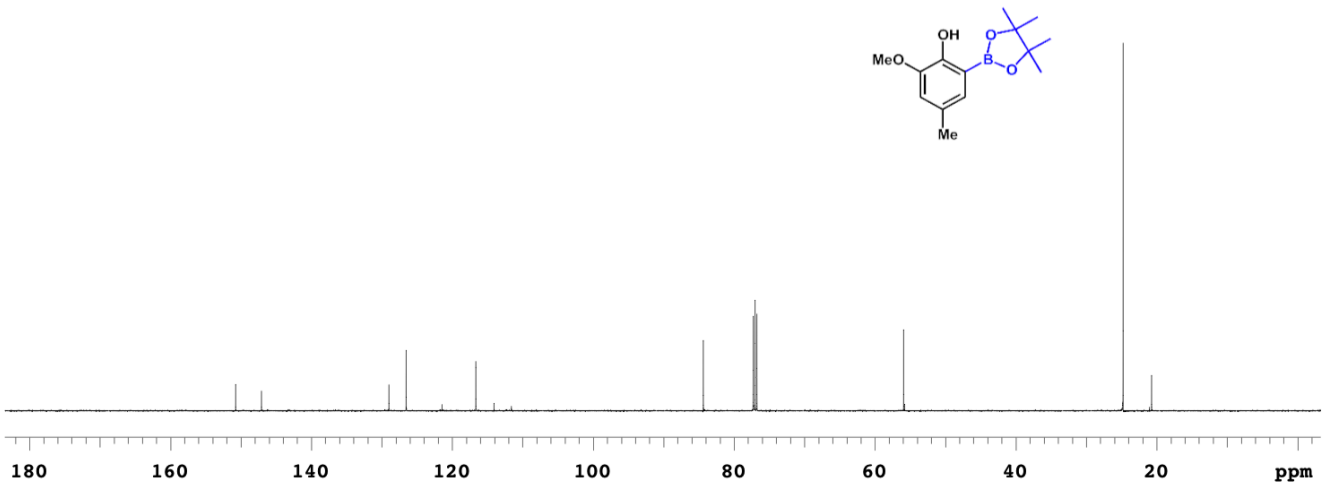

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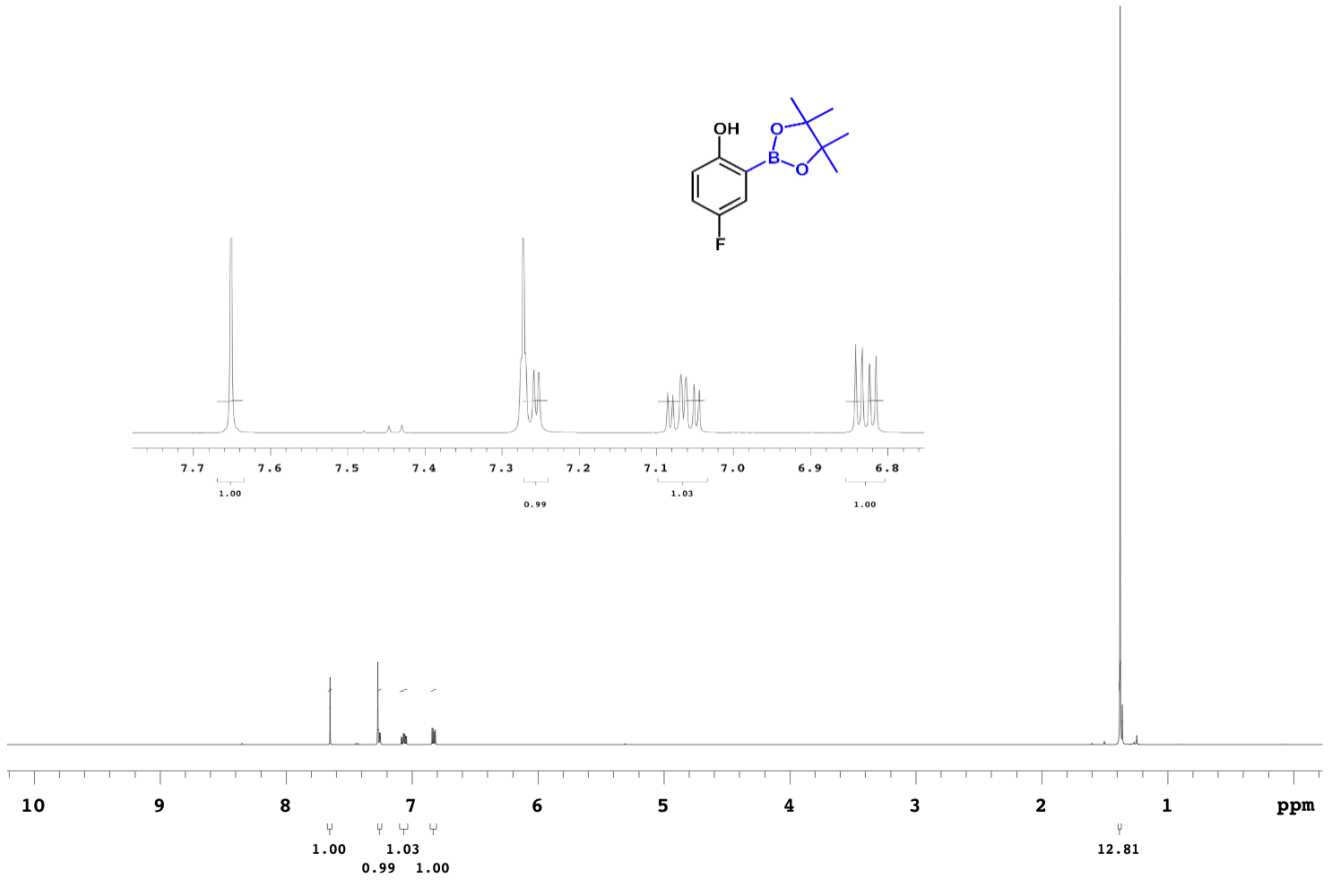
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1.00
0.99
1.03
1.00
10
9
8
7
6
5
4
3
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1
ppm
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1.03
0.99
1.00
12.81

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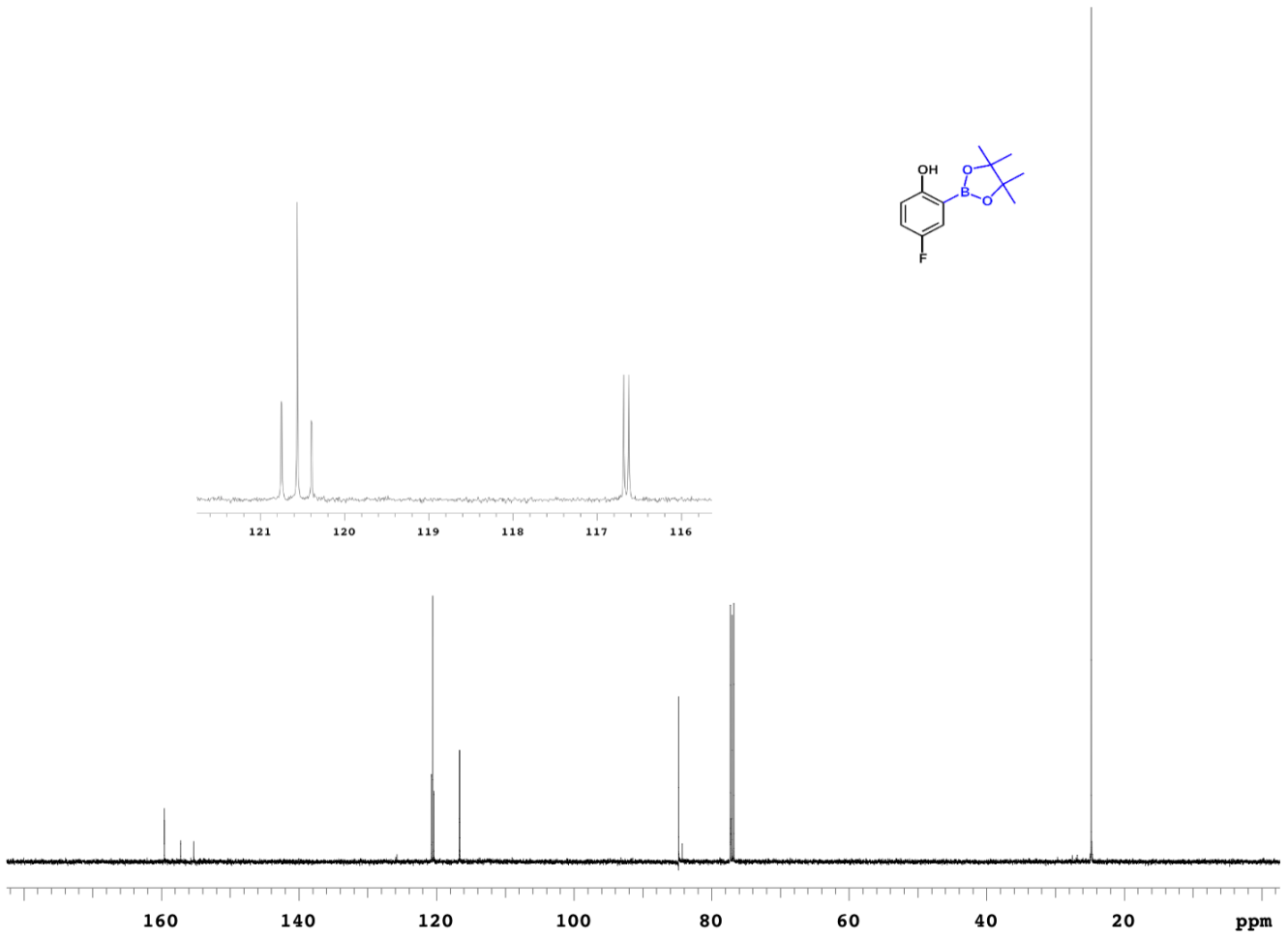

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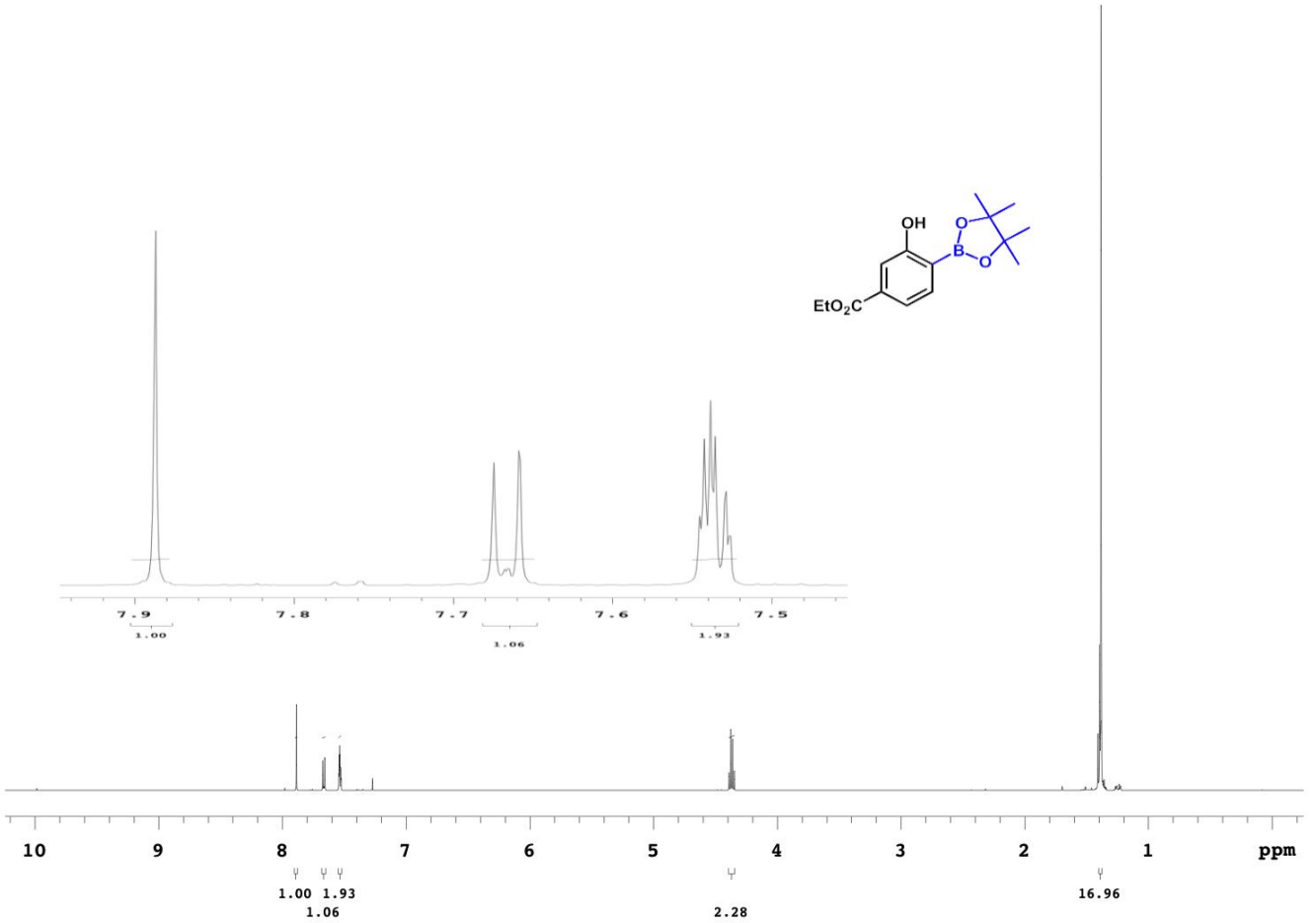

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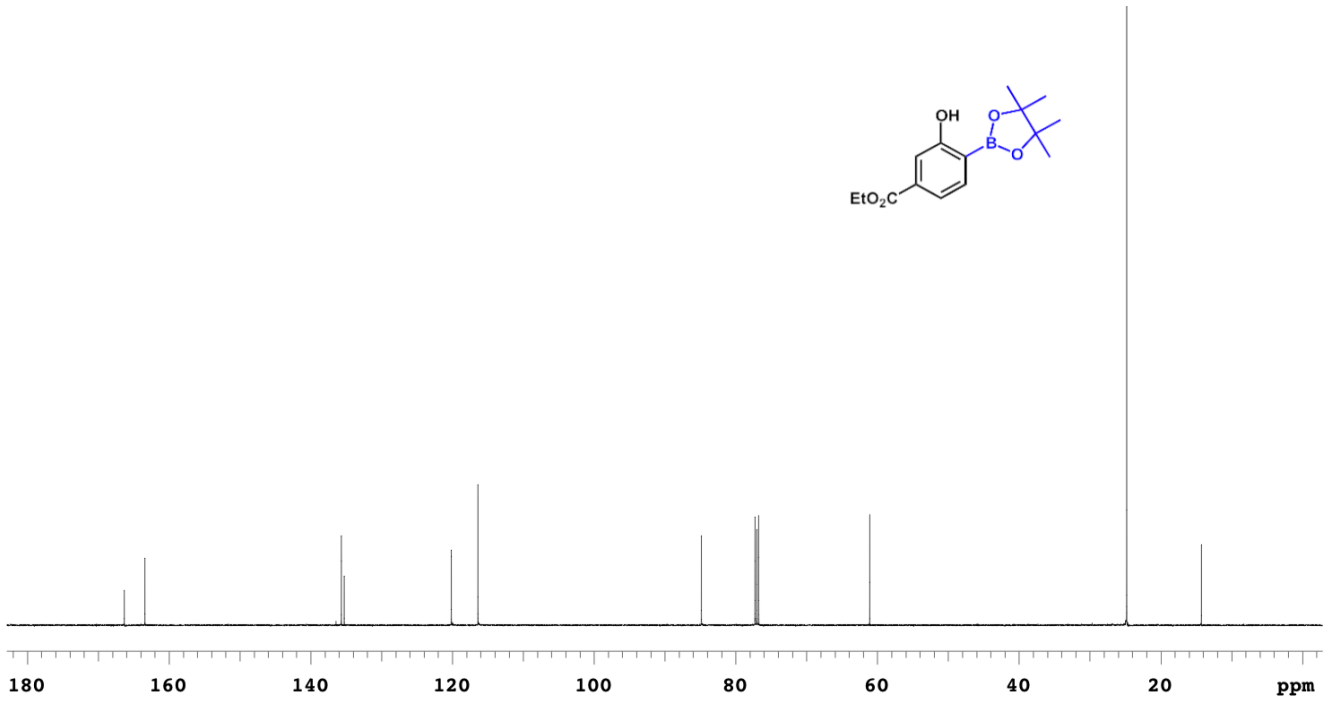

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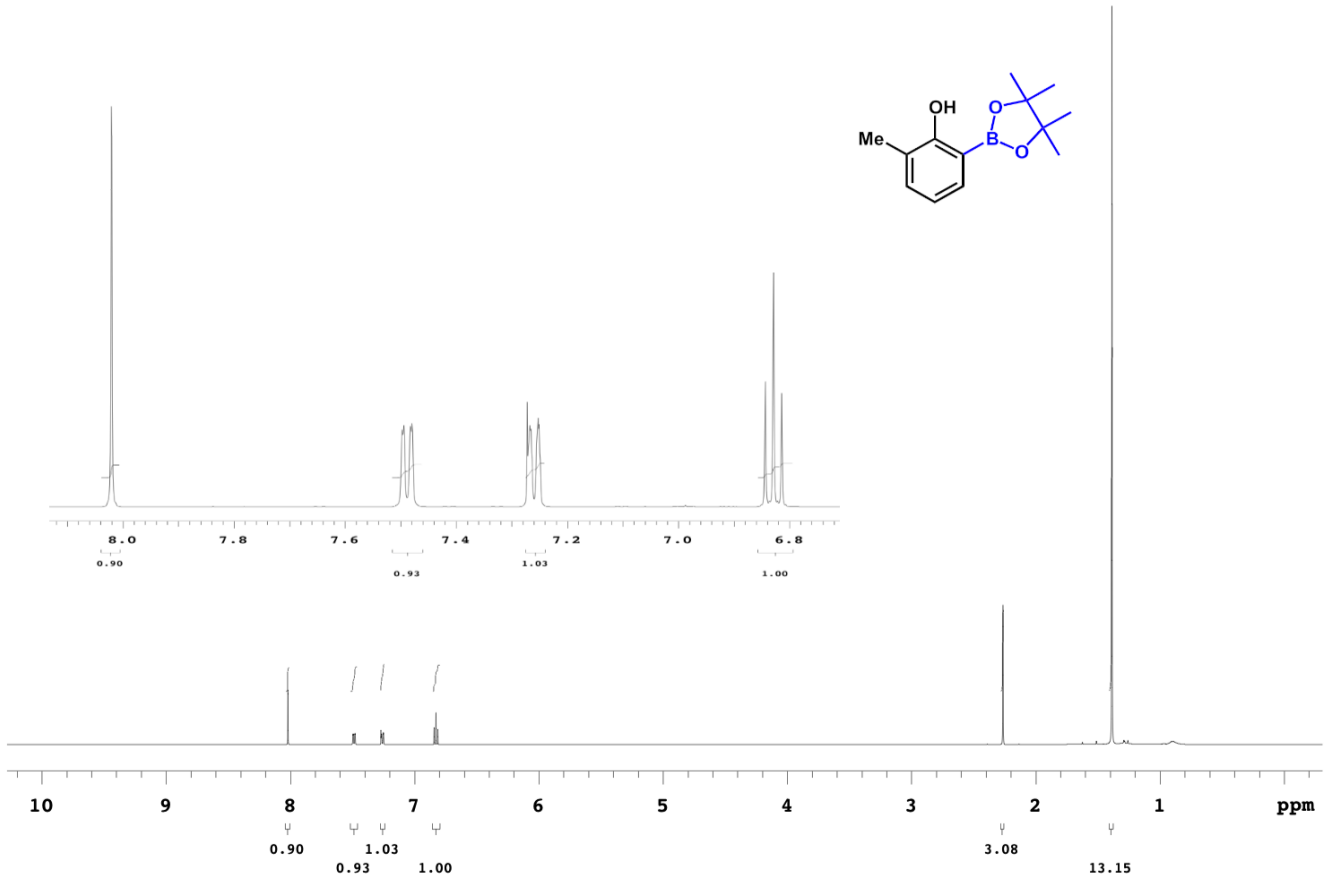
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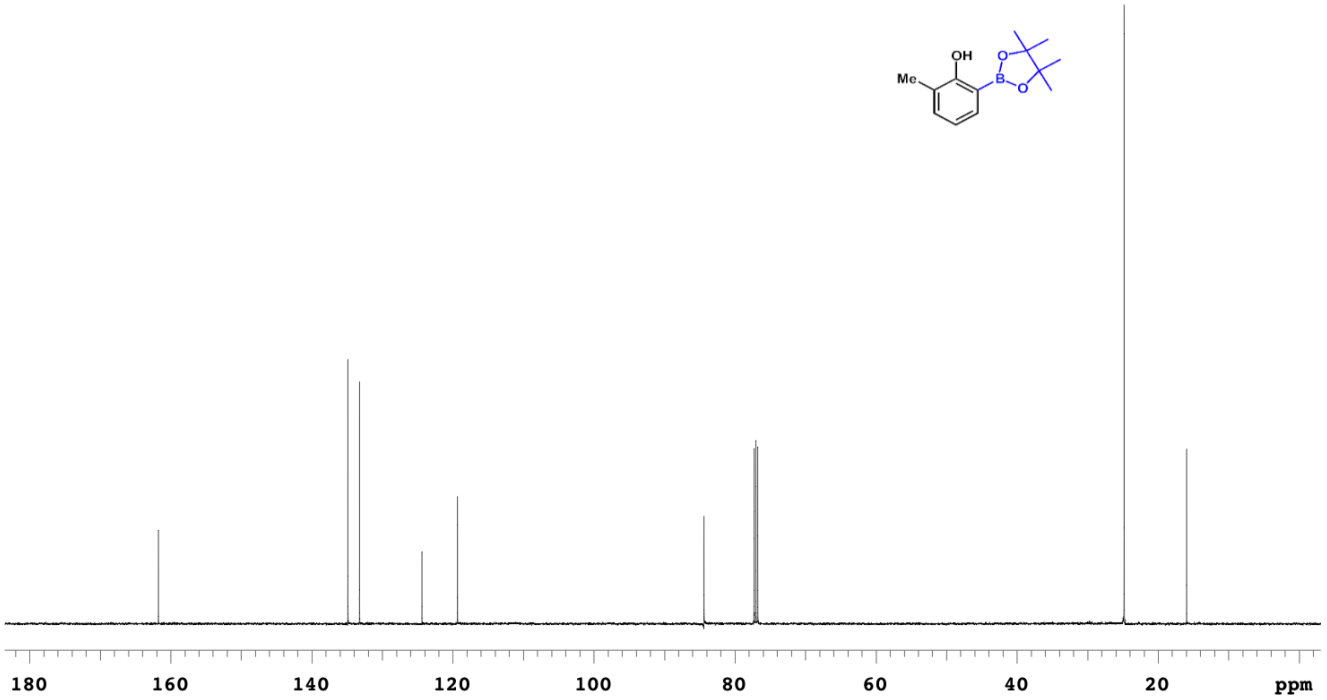
1.00
3.08
13.15



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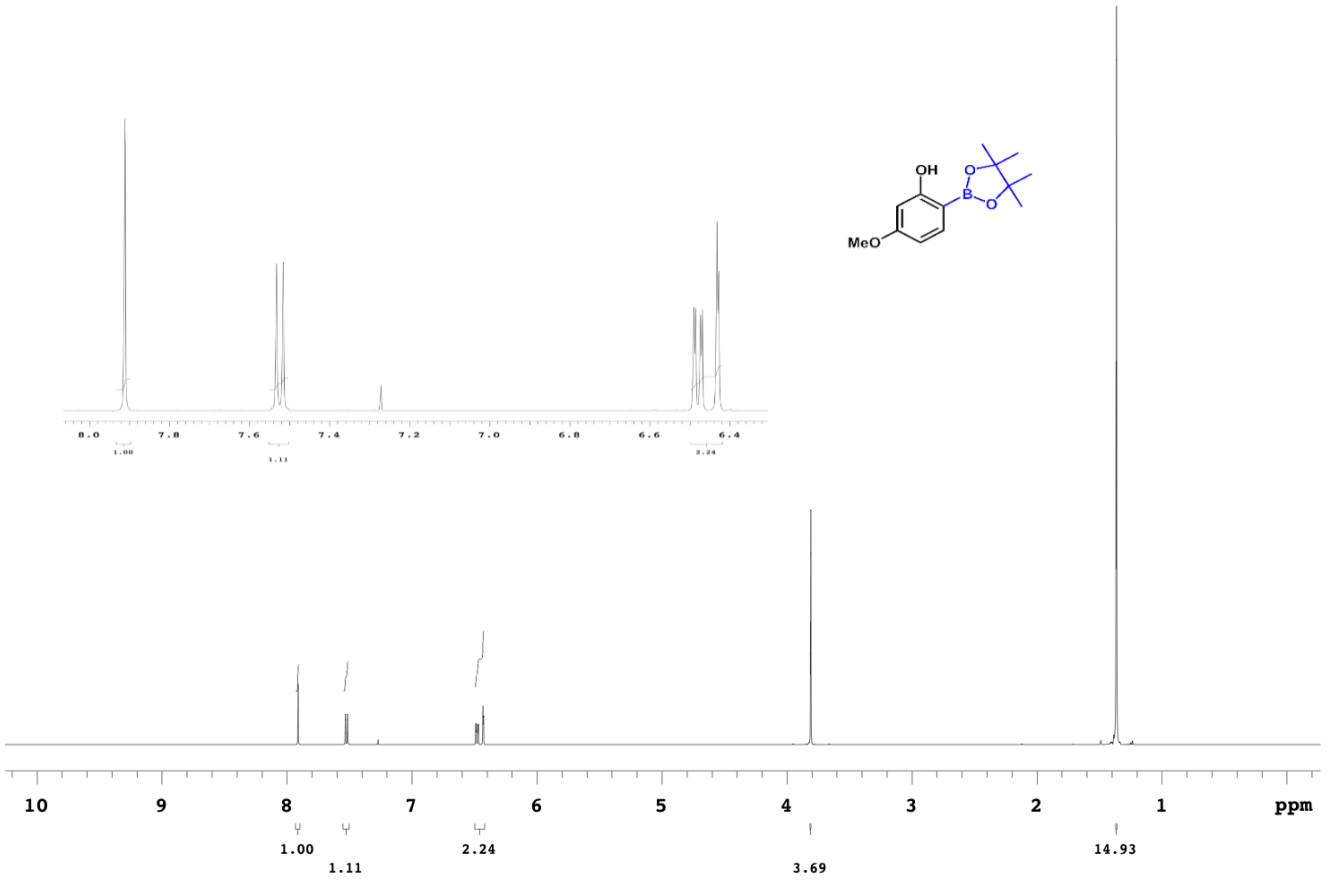

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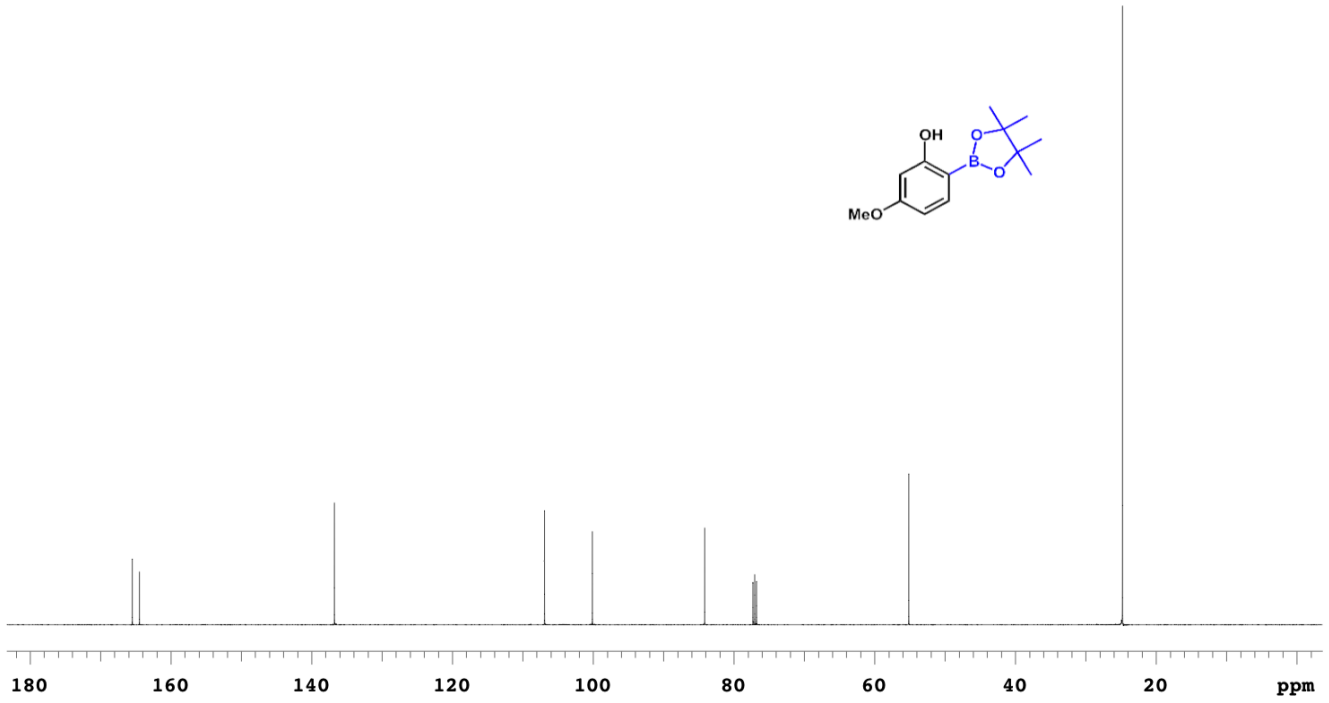

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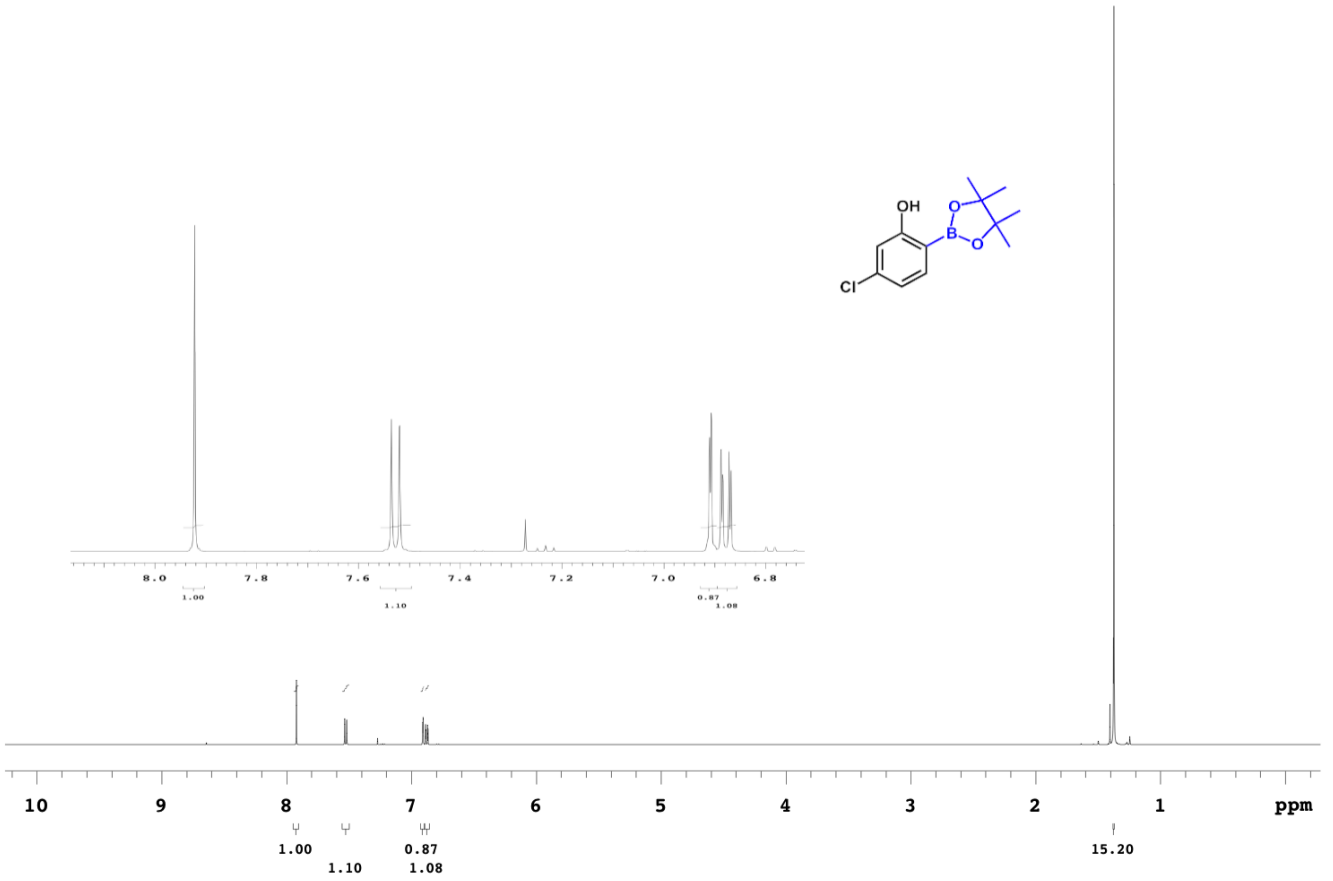
OH
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7.2
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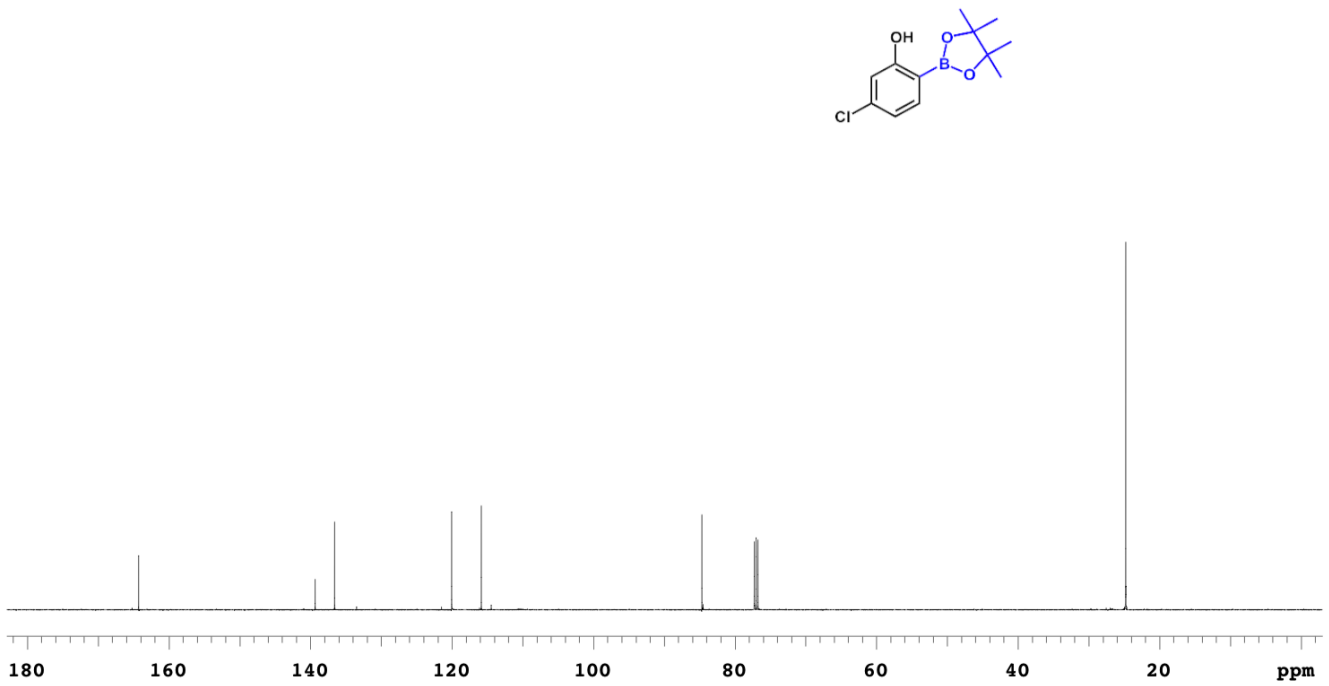
1.10
0.87
1.08
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.10
0.87
1.08
15.20

^{1}H-NMR (500 MHz, $CDCl_3$)



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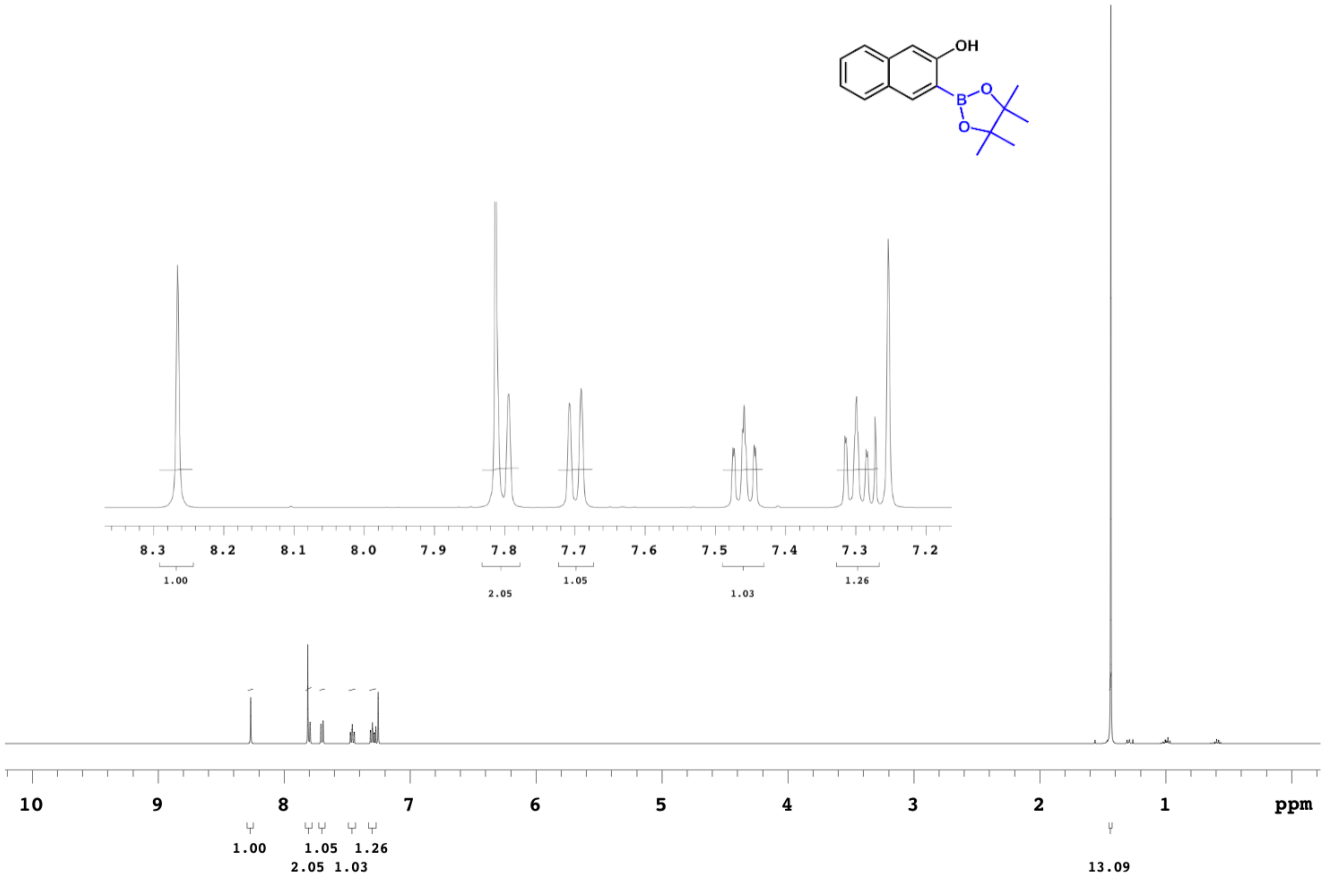

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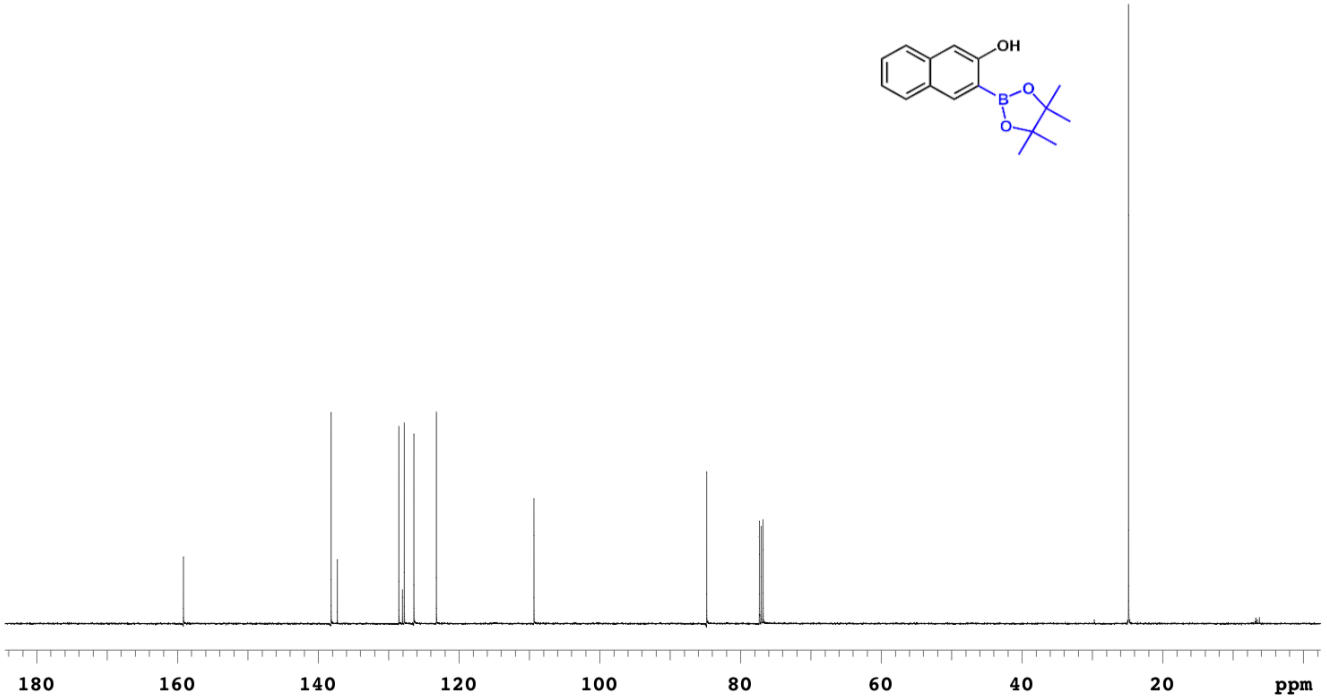

^{13}C-NMR (125 MHz, $CDCl_3$)

References

1) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126-130.

2) Ms. Yu-Ling Lien and the MSU Mass Spectrometry facility are thanked for obtaining ESI+ HRMS.

3) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390-391.

4) Cheng, C.; Hartwig, J. F. *Science* **2014**, *343*, 853-857.

5) Friedman, A. A.; Panteleev, J.; Tsoung, J.; Huynh, V.; Lautens, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 9755 –9758.

6) Huang, W.; Su, L.; Bo, Z. *J. Am. Chem. Soc.* **2009**, *82*, 870-878.

7) Welch, C. N.; Shore, S. G. *Inorg. Chem.* **1968**, *7*, 225-230.

8) Sumida, Y.; Kato, T.; Hosoya, T. *Org. Lett.* **2013**, *15*, 2806–2809.

9) a) Pineschi, M.; Bertolini, F.; Haak, R. M.; Crotti, P.; Macchia, F. *Chem. Commun.*, **2005**, 1426-1428. b) Laurent, J-P.; *Comptes Rendus Hebdomadaires des Seances de l'Academi des Sciences,* **1962**, *254*, 866-868.

10) Blau, J. A.; Gerrard, W.; Lappert, M. F.; *J. Chem. Soc.* **1957**, 4116-4119.

11) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

12) Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

13) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.;

Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

14) NBO 5.9. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2011); http://www.chem.wisc.edu/~nbo5