

Cobalt Catalyzed C-H Borylation

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Supporting Information

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Experimental Section

I. General Considerations. All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.¹ Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. The ligands 2,6-(CH₂P(ⁱPr)₂)₂C₅H₃N (ⁱPrPNP)² and 2,6-(NH₂P(ⁱPr)₂)₂C₅H₃N (ⁱPrPNNNP)³ were prepared according to literature procedures. (^tBuPDI)CoCl₂⁴ and (^{Cy}APDI)CoCH₃⁵ were prepared according to literature procedures.

¹H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to SiMe₄ using ¹H (residual) chemical shifts of the solvent as a secondary standard. ¹³C NMR spectra were recorded on a Bruker 500 spectrometer operating at 125.71 MHz. ¹³C chemical shifts are reported relative to SiMe₄ using chemical shifts of the solvent as a secondary standard where applicable. ¹¹B NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 299.763 MHz and were referenced to BF₃(OEt₂) as an external standard. ³¹P NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 299.763 MHz and were referenced to 85 % H₃PO₄ as an external standard. Infrared spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with molybdenum and copper X-ray tubes ($\lambda = 0.71073$ and 1.54184 Å respectively). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

II. Preparation of Cobalt Complexes

Preparation of (^tBuPDI)CoCH₃ (1). A 100 mL round bottom flask was charged with 0.250 g (0.450 mmol) of (^tBuPDI)CoCl₂ and 50 mL of toluene. The resulting solution was chilled in the cold well filled with liquid nitrogen. A 1.6 M solution of LiCH₃ in diethyl ether (0.530 mL, 0.848 mmol) was then added dropwise to the chilled solution of (^tBuPDI)CoCl₂. The dark pink solution was stirred for 2 hours at room temperature and was filtered through Celite. Concentration of the filtrate in vacuo yielded 0.201 g (89%) of a reddish brown powder. Anal Calcd for C₃₀H₃₈CoN₃: C, 72.13; H, 7.67; N, 8.41. Found: C, 71.95; H, 7.33; N, 8.24. ¹H NMR (benzene-*d*₆, 23 °C): δ -1.09 (bs, 6H, C(N)Me), 0.97 (bs, 8H, tBu Me), 7.23 (m, 2H, aryl CH), 7.34 (m, 2H, aryl CH), 7.65 (d, $\Delta\nu_{1/2} = 8.25$ Hz, 2H, aryl CH), 7.83 (d, $\Delta\nu_{1/2} = 7.45$ Hz, 2H, pyridine meta CH), 10.11 (t, $\Delta\nu_{1/2} = 7.45$ Hz, 2H, pyridine para CH). {¹H}¹³C NMR (benzene-*d*₆, 23 °C): δ 25.98 (C(N)Me), 31.87 (tBu Me), 37.03 (tBu C), 116.88 (pyridine para CH), 122.98 (pyridine meta CH), 124.69 (aryl CH), 125.84 (aryl CH), 126.00 (aryl CH), 128.73 (aryl CH), 140.90 (aryl ipso C), 156.00 (aryl ortho C), 158.66 (pyridine ortho C), 165.11 (C(N)Me).

Preparation of (ⁱPrPNP)CoCH₂SiMe₃ (3). A 20 mL scintillation vial was charged with 0.150 g (0.346 mmol) of (ⁱPrPNP)CoCl and 5 mL of diethyl ether. The purple solution was chilled in the freezer to -35 °C. A solution of 0.033 g (0.346 mmol) of LiCH₂SiMe₃ in 5 mL of diethyl ether was added to the warming solution and a color change from dark purple to brown was observed. The solution was stirred for 1 hour at room temperature before the volatiles were removed in vacuo and the residue extracted into 5 mL of toluene and filtered through Celite. Concentration of the filtrate in vacuo and recrystallization of the dark residue from diethyl ether at -35 °C for 18 hours yielded 0.150 g (88%) of analytically pure dark brown crystals suitable for X-ray diffraction. Anal Calcd for C₂₃H₄₆CoNP₂Si: C, 56.89; N, 9.55; N, 2.88. Found: C, 56.88; H, 9.07; N, 2.80. ¹H NMR (benzene-*d*₆, 23 °C): δ 0.22 (bs, Δ*v*_{1/2} = 19 Hz, 9H, CH₂SiMe₃), 1.00 (bs, Δ*v*_{1/2} = 36 Hz, 1H, aryl CH), 1.49 (bs, Δ*v*_{1/2} = 36 Hz, 12H, *i*Pr Me), 1.73 (bs, Δ*v*_{1/2} = 36 Hz, 12H, *i*Pr Me), 2.88 (bs, Δ*v*_{1/2} = 135 Hz, 2H, Co-CH₂ or aryl CH), 4.62 (bs, Δ*v*_{1/2} = 180 Hz, 4H, *i*Pr CH), 7.54 (bs, Δ*v*_{1/2} = 165 Hz, 4H, P-CH₂), 27.3 (bs, Δ*v*_{1/2} = 117 Hz, 2H, aryl CH). ¹H NMR (toluene-*d*₈, -75 °C): δ 1.17 (s, 2H, Co-CH₂), 1.09 (s, 12H, P-CHMe₂), 1.25 (s, 4H, P-CHMe₂), 1.37 (s, 12H, P-CHMe₂), 2.21 (s, 4H, P-CH₂), 5.58 (s, 2H, meta pyridine CH), 8.48 (s, 1H, para pyridine CH). {¹H}¹³C NMR (toluene-*d*₈, -70 °C): δ 0.4 (CH₂SiMe₃), 6.3 (CH₂SiMe₃), 18.6 (P-CHMe₂), 20.0 (P-CHMe₂), 23.2 (P-CHMe₂), 35.9 (P-CH₂), 111.0 (pyridine meta CH), 123.5 (pyridine para CH), 155.3 (pyridine ortho CH). {¹H}³¹P NMR (toluene-*d*₈, -70 °C): δ 46.8 (br s, P-CHMe₂).

Preparation of (ⁱPrPNP)CoH₂(BPin). A 20 mL scintillation vial was charged with 0.111 g (0.228 mmol) of (ⁱPrPNP)CoCH₂SiMe₃ and 1.5 mL of diethyl ether. A solution of 0.060 g (0.456 mmol) of pinacolborane in 0.5 mL of diethyl ether was added via pipette. A color

change to dark red-brown was immediately observed. Storing the solution at -35 °C overnight resulted in deposition of yellow-brown crystals. The crystals were washed with 2 x 1 mL of cold pentane and dried in vacuo and 0.080 g (67 % yield) of analytically pure material. Anal Calcd for $C_{25}H_{49}BCoNO_2P_2$: C, 56.94; H, 9.37; N, 2.66. Found: C, 56.63; H, 8.98; N, 2.47. 1H NMR (benzene- d_6 , 23 °C): δ -8.71 (br s, 2H, Co-*H*), 1.07 (pq, $^3J_{PH}$ = 6.1 Hz, 12H, P-CHMe $_2$), 1.15 (s, 12H, pinacol Me), 1.48 (pq, $^3J_{PH}$ = 7.1 Hz, 12H, P-CHMe $_2$), 2.41 (br m, 4H, P-CHMe $_2$), 2.86 (s, 4H, P-CH $_2$), 6.44 (d, $^3J_{HH}$ = 7.5 Hz, 2H, pyridine meta CH), 6.71 (t, $^3J_{HH}$ = 7.5 Hz, 1H, pyridine para CH). $\{^1H\}^{13}C$ NMR (benzene- d_6 , 23 °C): δ 17.8 (P-CHMe $_2$), 20.0 (P-CHMe $_2$), 24.7 (P-CHMe $_2$), 25.7 (pinacol Me), 38.3 (P-CH $_2$), 80.1 (pinacol C), 118.3 (pyridine meta CH), 130.6 (pyridine para CH), 161.5 (pyridine ortho CH). $\{^1H\}^{31}P$ NMR (benzene- d_6 , 23 °C): δ 103.5 (br s, P-CHMe $_2$). ^{11}B NMR (benzene- d_6 , 23 °C): δ 41.1 (br s, Co-BPin). IR (KBr): ν_{Co-H} = 1716 cm^{-1} .

Preparation of (iPr PNNNP)CoCl $_2$. A 100 mL round bottom flask was charged with a stirbar, 0.470 g (3.62 mmol) of cobalt dichloride and 40 mL of tetrahydrofuran. To this stirring suspension was added 1.293 g (3.65 mmol) of iPr PNNNP as a solid in one portion. The solution immediately turned red-brown and a red precipitate was observed. The solution was stirred at room temperature for 18 hours before the volatiles were removed in vacuo and the red solid collected on a sintered glass frit and washed with 50 mL of pentane (50 mL) and furnished 1.60 g (93%) of an analytically pure red solid identified as (iPr PNNNP)CoCl $_2$. Anal Calcd for $C_{17}H_{33}Cl_2CoN_3P_2$: C, 43.33; H, 7.06; N, 8.92. Found: C, 43.18; H, 6.80; N, 8.51. Magnetic Susceptibility (MSB): μ_{eff} = 1.84(2) μ_B .

Preparation of (iPr PNNNP)CoCH $_2$ SiMe $_3$ (4). A 50 mL round bottom flask was charged with 0.510 g (1.083 mmol) of (iPr PNNNP)CoCl $_2$ and 15 mL of toluene. A separate vial was

charged with 0.214 g (2.17 mmol) of $\text{LiCH}_2\text{SiMe}_3$ and 5 mL of toluene. The alkyl lithium solution was added dropwise via pipette to the stirring red cobalt suspension and an immediate color change from dark red to deep forest green was observed as the addition proceeded. The solution was stirred for 30 minutes before the solution was filtered through a pad of Celite to remove insoluble material. The volatiles were removed in vacuo and the resulting green material was recrystallized from concentrated toluene and furnished 0.280 g (53 %) of a microcrystalline green solid identified as $(^i\text{PrPNNNP})\text{CoCH}_2\text{SiMe}_3$. Anal Calcd for $\text{C}_{21}\text{H}_{44}\text{CoN}_3\text{P}_2\text{Si}$: C, 51.73; H, 9.10; N, 8.62. Found: C, 51.68; H, 8.74; N, 8.49. ^1H NMR (benzene- d_6 , 23 °C): δ -22.52 (bs, $\Delta\nu_{1/2}$ = 125 Hz, 2H, CH_2SiMe_3), -20.00 (bs, $\Delta\nu_{1/2}$ = 115 Hz, 9H, CH_2SiMe_3), 10.58 (bs, $\Delta\nu_{1/2}$ = 877 Hz, 12H, P- CHMe_2), 16.65 (bs, $\Delta\nu_{1/2}$ = 670 Hz, 14H, P- CHMe_2 and P-NH), 58.29 (bs, $\Delta\nu_{1/2}$ = 1893 Hz, 3H, meta and para pyridine CH). One signal not located. Magnetic Susceptibility (MSB): $\mu_{\text{eff}} = 2.6(1) \mu_{\text{B}}$.

II. General Procedures for Cobalt-Catalyzed Borylations.

A. 5-Membered Heterocycles with HBPIn. In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar and 0.004 g (0.008 mmol) of $(^i\text{PrPNP})\text{CoNs}$, 0.781 mmol of the desired 5-membered heterocycle, and 0.100 g (0.781 mmol) of HBPIn. The resulting mixture was stirred at 23 °C, 60 °C or 80 °C for 24 hours or until solid formed. The crude reaction mixture was dissolved in CDCl_3 , passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^1H and ^{13}C NMR spectroscopy without additional purification.

B. Substituted Pyridines with B_2Pin_2 . In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar and 0.008 g (0.016 mmol) of $(^i\text{PrPNP})\text{CoNs}$, 0.070 g

(0.276 mmol) (CONDITION A) or 0.140 g (0.552 mmol) (CONDITION B) of B_2Pin_2 , 0.552 mmol of the desired pyridine derivative and 1 mL of THF. The resulting mixture was stirred at 80 °C for 24 hours. The THF was removed by vacuum and the workup procedure is described for each individual example (see section III).

C. Arenes with B_2Pin_2 . In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.008 g (0.016 mmol) of (iPr PNP)CoNs, 0.070 g (0.276 mmol) of B_2Pin_2 , and 5.520 mmol of the corresponding arene. The resulting mixture was stirred at 80 °C for 24 hours. The reaction was quenched by exposing the mixture to air. The excess arene was removed via vacuum distillation and the crude product was dissolved in $CDCl_3$, passed through a plug of silica gel in a Pasteur pipette and then analyzed by 1H and ^{13}C NMR spectroscopy without additional purification.

D. Iridium Catalyzed Borylation of 2,4-lutidine. In the glovebox, a 20 mL scintillation vial was charged with a stir bar, 0.214 g (2 mmol) of 2,4-lutidine, 0.356 g (1.4 mmol) of B_2Pin_2 , 0.040 g (0.06 mmol) of $[(COD)Ir(OMe)]_2$ and 0.033 g (0.12 mmol) of 4,4'-di-tert-butyl-2,2'-bipyridine. To this vial was added 3.0 mL of tetrahydrofuran. The vial was tightly sealed with a screw cap before being heated to 80 °C for 16 h. The vial was cooled to room temperature and brought into the glovebox without being exposed to air. The volatile components were removed in vacuo and the dark residue dissolved in benzene- d_6 and analyzed by 1H NMR spectroscopy.

E. Deuterium Labeling Experiment. A scintillation vial was charged with a magnetic stir bar, 0.150 g (1.83 mmol) of 2-methylfuran, 0.236 g of DBPin (1.83 mmol) and with 0.009 g (0.018 mmol) of (iPr PNP)CoNs. After 1 hour, the mixture was transferred to a J-Young

tube and the volatiles (1:1 mixture of 2-methylfuran and DBPin) were separated from the borylation product via an air-free vacuum distillation. No deuterium incorporation (as judged by ^2H and quantitative ^{13}C NMR spectroscopies) was observed in the borylation product. Analysis of the volatiles by ^2H and quantitative ^{13}C NMR spectroscopies established no deuterium incorporation in the recovered 2-methylfuran. The volatiles (1:1 mixture of 2-methylfuran and DBPin) were then mixed with a stoichiometric amount of 1-octene and with 1 mol% of ($^{\text{Mes}}\text{PDI}$)CoCH₃ and analysis of 1-octyl pinacolboronate ester hydroboration product revealed a 16% reduction in deuterium content in the recovered DBPin.⁶

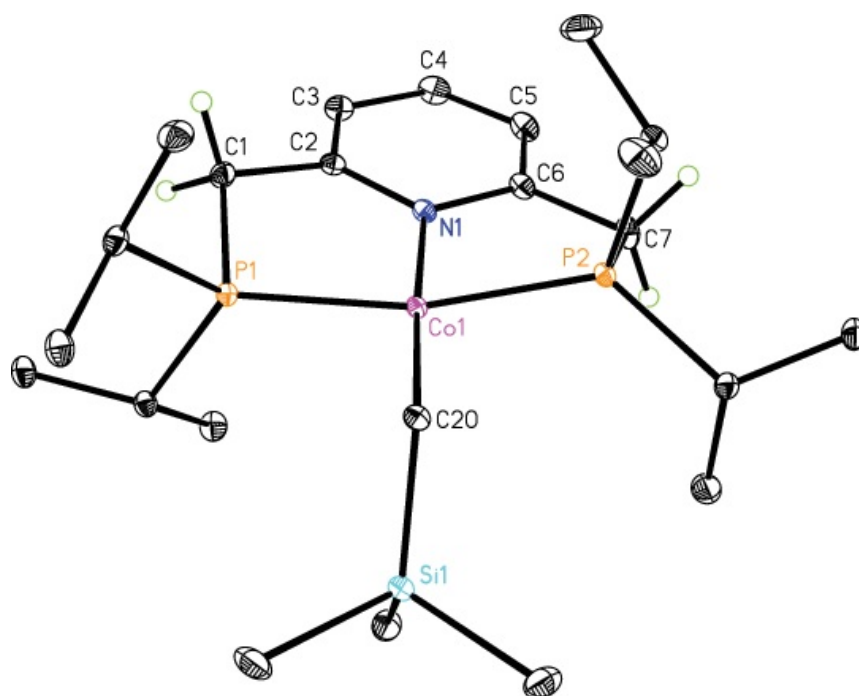


Figure S1. ORTEP plot ($i\text{PrPNP}$)Co(CH₂SiMe₃) at 30% probability ellipsoids. Hydrogen atoms, except those attached to benzylic positions, omitted for clarity.

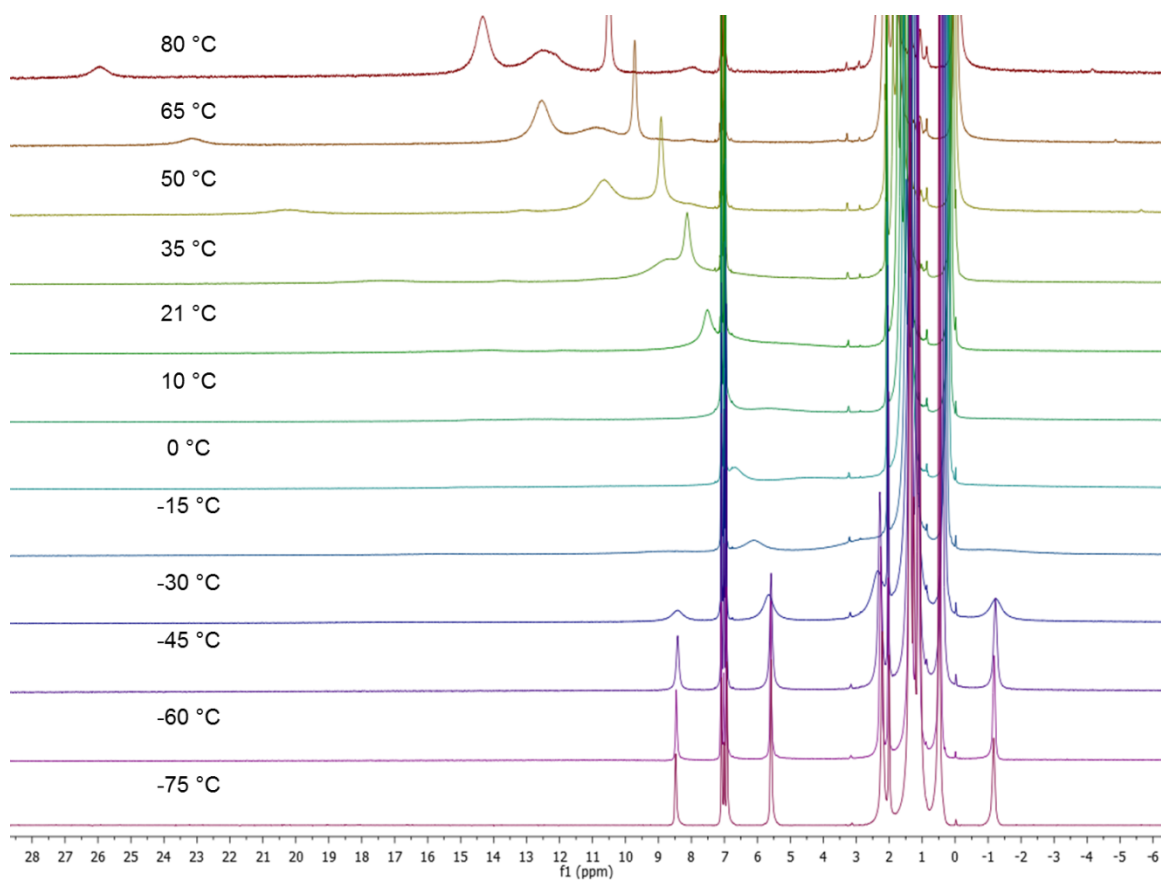


Figure S2. Variable temperature ^1H NMR spectra of $(i\text{PrPNP})\text{CoCH}_2\text{SiMe}_3$ recorded in toluene- d_8 .

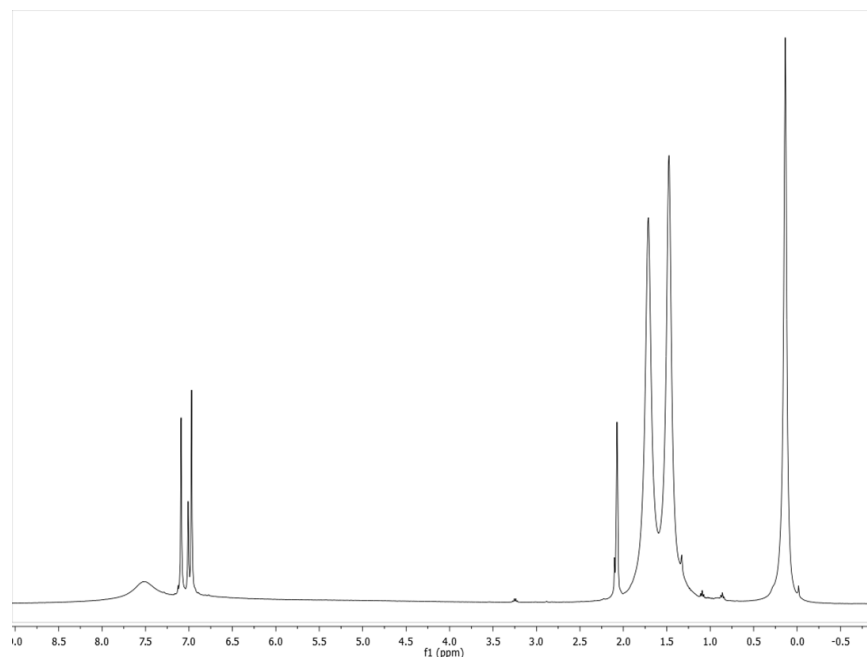


Figure S3. ^1H NMR spectrum of $(i\text{PrPNP})\text{CoCH}_2\text{SiMe}_3$ recorded at 21 °C in toluene- d_8 .

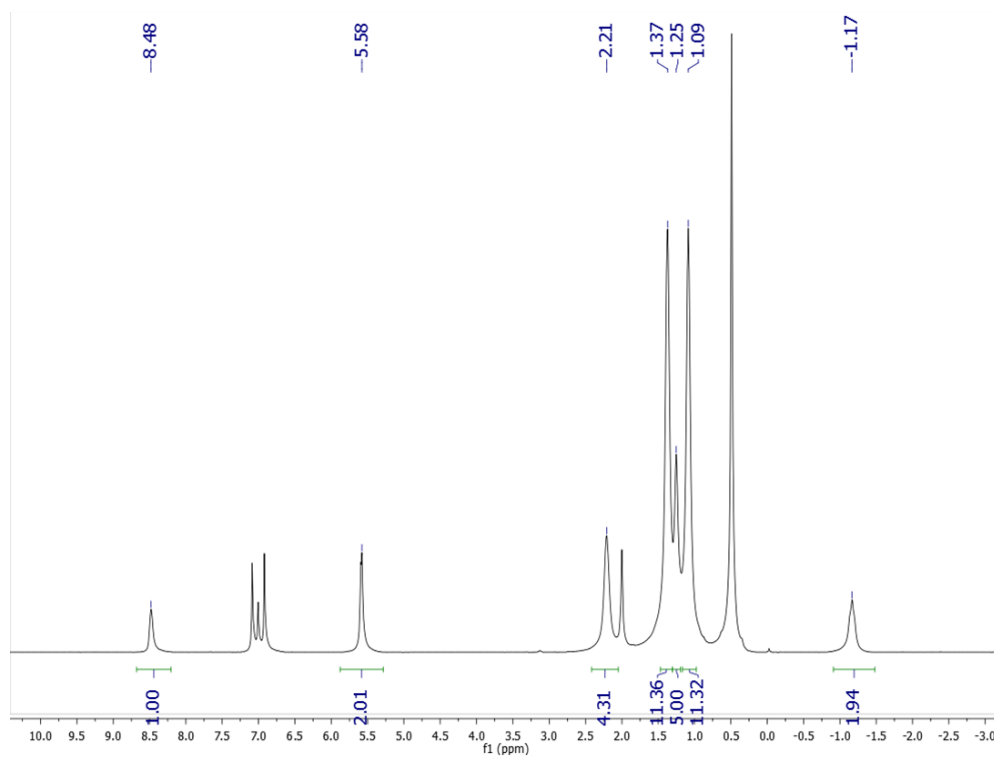


Figure S4. ^1H NMR spectrum of $(i\text{PrPNP})\text{CoCH}_2\text{SiMe}_3$ recorded at -75 °C in toluene- d_8 .

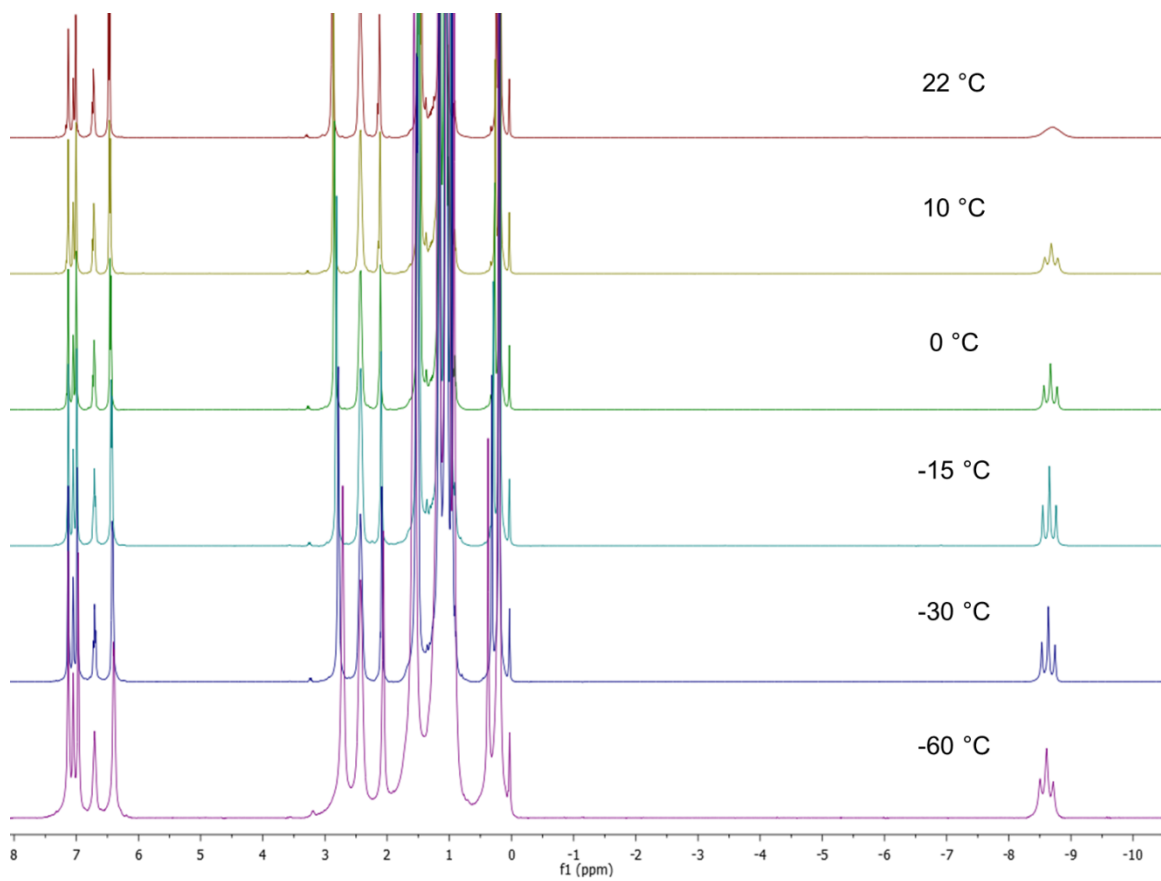


Figure S5. Variable temperature ^1H NMR spectra of $(i\text{PrPNP})\text{CoH}_2(\text{BPin})$ recorded in $\text{toluene-}d_8$.

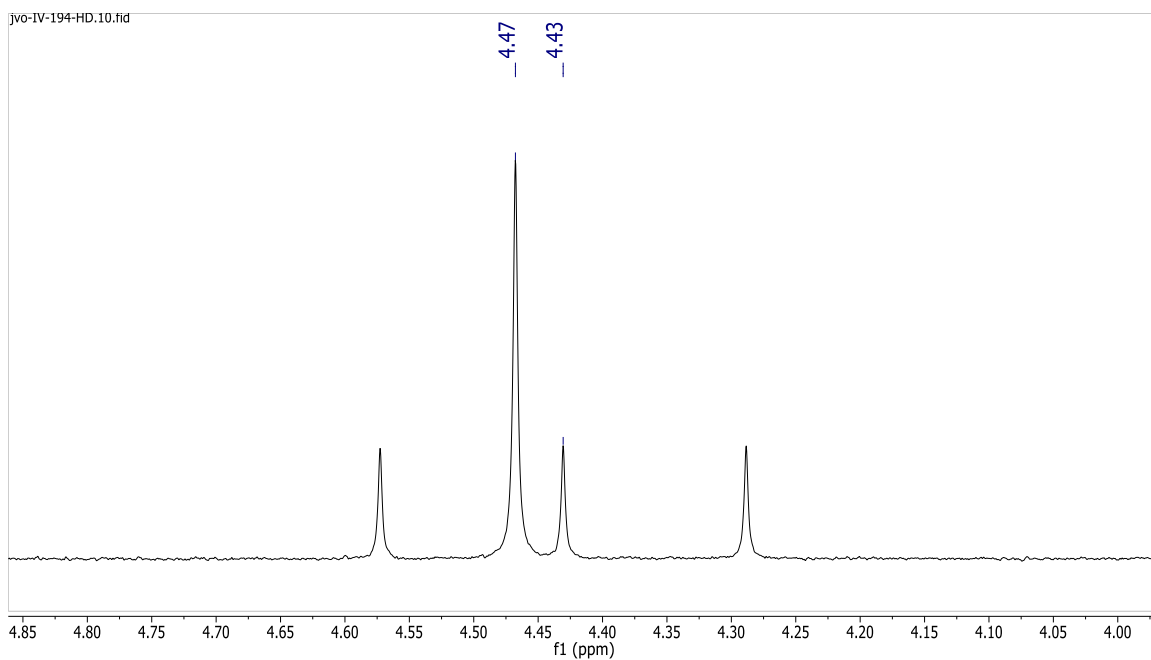


Figure S6. Detection of H_2 and HD gases by ^1H NMR spectroscopy following catalytic borylation of 2-methylfuran with DBPin in the presence of 1 mol% **3** (40% conversion).

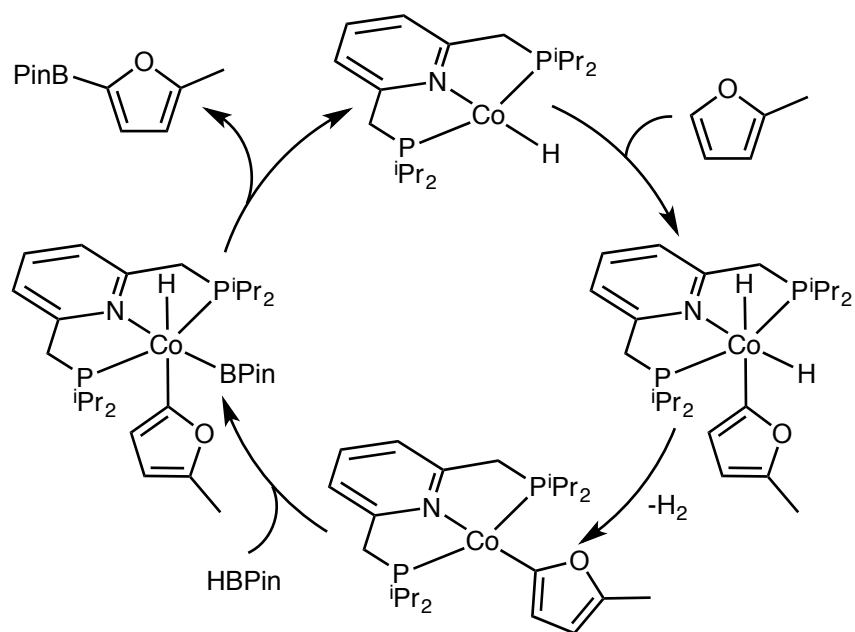
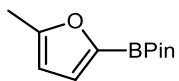
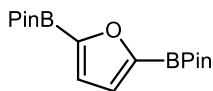


Figure S7. Alternative mechanism for cobalt-catalyzed borylation.

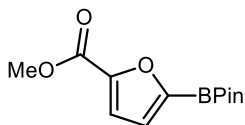
III. Characterization of Borylation Products.



(3a): In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar and 0.004 g (0.008 mmol) of (*i*^{Pr}PNP)CoNs, 0.064 g (0.781 mmol) of 2-methylfuran, and 0.100 g (0.781 mmol) of HBPIn. The resulting mixture was shaken in a vortex shaker at 23 °C for 72 hours. The crude reaction mixture was dissolved in hexane and the resulting solution was passed through a plug of silica gel in a Pasteur pipette to remove the catalyst. The title compound was isolated as a colorless oil (0.147 g, 91% yield) upon removal of solvent in vacuo. ¹H NMR (chloroform-*d*, 23 °C): δ 6.93 (d, Δ*v*_{1/2} = 3.07 Hz, 1H), 5.97 (d, Δ*v*_{1/2} = 3.07 Hz, 1H), 2.29 (s, 3H), 1.27 (s, 12H). {¹H}¹³C NMR (chloroform-*d*, 23 °C): δ 157.58, 124.80, 106.87, 83.90, 24.66, 13.83. GCMS *m/z* (% relative intensity, ion): 208.00 (68, M⁺), 193.00 (32, M⁺-15).

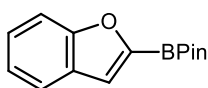


(3b): ¹H NMR (chloroform-*d*, 23 °C): δ 7.01 (s, 2H), 1.27 (s, 24H). {¹H}¹³C NMR (chloroform-*d*, 23 °C): δ 123.34, 84.22, 24.75. GCMS *m/z* (% relative intensity, ion): 320.20 (29, M⁺), 305.10 (23, M⁺-15), 277.10 (48, M⁺-43).



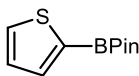
(3c): In a nitrogen-filled glovebox, a scintillation vial was charged with 0.006 g (0.012 mmol) of (*i*^{Pr}PNP)CoNs, 0.150 g (1.189 mmol) of methyl furan-2-carboxylate, and 0.152 g (0.189 mmol) of HBPIn. The resulting mixture was shaken in a vortex shaker at 23 °C until formation of a solid occurred. The crude reaction mixture was dissolved in pentane and the resulting solution was passed through a plug of silica gel in

a Pasteur pipette to remove the catalyst. The title compound was isolated as a white powder (0.300 g, >99% yield) upon removal of solvent in vacuo. ^1H NMR (chloroform-*d*, 23 °C): δ 7.18 (d, $\Delta v_{1/2}$ = 5.54 Hz, 1H), 7.06 (d, $\Delta v_{1/2}$ = 5.54 Hz, 1H), 3.89 (s, 3H), 1.34 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 159.22, 148.48, 124.19, 118.04, 84.87, 52.11, 24.86. GCMS *m/z* (% relative intensity, ion): 252.10 (16, M^+), 237.10 (25, $\text{M}^+ - 15$), 221.10 (12, $\text{M}^+ - 31$), 210.10 (47, $\text{M}^+ - 42$).

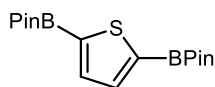


(3d): In a nitrogen-filled glovebox, a scintillation vial was charged with

0.006 g (0.012 mmol) of (i^{Pr} PNP)CoNs, 0.140 g (1.189 mmol) of benzofuran, and 0.152 g (0.189 mmol) of HBPIn. The resulting mixture was shaken in a vortex shaker at 23 °C until formation of a solid occurred. The crude reaction mixture was dissolved in pentane and the resulting solution was passed through a plug of silica gel in a Pasteur pipette to remove the catalyst. The title compound was isolated as a white powder (0.289 g, >99% yield) upon removal of solvent in vacuo. ^1H NMR (chloroform-*d*, 23 °C): δ 7.65 – 7.62 (m, 1H), 7.57 (dd, $\Delta v_{1/2}$ = 8.1, 1.1 Hz, 1H), 7.40 (s, 1H), 7.34 (ddd, $\Delta v_{1/2}$ = 8.4, 7.2, 1.3 Hz, 1H), 7.25 – 7.21 (m, 1H), 1.39 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 157.64, 127.62, 126.07, 122.85, 122.03, 119.68, 112.10, 84.83, 24.93. ^1H and ^{13}C NMR data agree with previously reported data.⁷

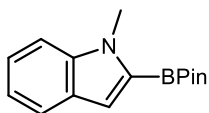


(3e): ^1H NMR (chloroform-*d*, 23 °C): δ 7.64 (d, $\Delta v_{1/2}$ = 3.23 Hz, 1H), 7.62 (d, $\Delta v_{1/2}$ = 4.87 Hz, 1H), 7.18 (m, 1H), 1.25 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 137.30, 132.51, 128.34, 84.27, 24.58. ^1H and ^{13}C NMR data agree with previously reported data.⁸



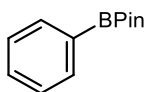
(3f): ^1H NMR (chloroform-*d*, 23 °C): δ 7.66 (s, 2H), 1.33 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$

NMR (chloroform-*d*, 23 °C): δ 137.82, 84.21, 24.82. ^1H and ^{13}C NMR data agree with previously reported data.⁹



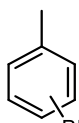
(3g): ^1H NMR (chloroform-*d*, 23 °C): δ 7.64 (d, $\Delta\nu_{1/2}$ = 8.05 Hz, 1H), 7.07

– 7.35 (m, 5H), 3.95 (s, 3H), 1.35 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 140.23, 127.94, 123.27, 121.67, 119.39, 114.36, 109.78, 83.77, 32.30, 24.91. ^1H and ^{13}C NMR data agree with previously reported data.¹⁰

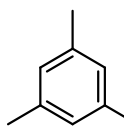


(3h): In a nitrogen-filled glovebox, a scintillation vial was charged with a

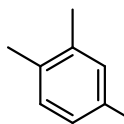
magnetic stir bar, 0.003 g (0.006 mmol) of (^iPr PNP)CoNs, 0.070 g (0.276 mmol) of B_2Pin_2 , and 0.431 g (5.520 mmol) of benzene. The resulting mixture was stirred at 80 °C for 24 hours. The HBPi formed and the excess benzene were removed via vacuum distillation and the crude product was dissolved in hexane and the resulting solution was passed through a plug of silica gel in a Pasteur pipette to remove the catalyst. The title compound was isolated as a white solid (0.049 g, 87% yield) upon removal of solvent in vacuo. ^1H NMR (chloroform-*d*, 23 °C): δ 7.83 (d, $\Delta\nu_{1/2}$ = 7.31 Hz, 2H), 7.50 – 7.34 (m, 3H), 1.35 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 134.87, 131.39, 127.85, 83.92, 25.01. ^1H and ^{13}C NMR data agree with previously reported data.¹¹



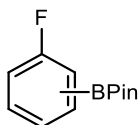
(3i): The ^1H NMR spectrum was not assigned because the proton resonances of the *meta* and *para* isomers overlap with each other. The *meta*: *para* ratio was determined to be 70:30 by integration of the characteristic peaks in the quantitative ^{13}C NMR spectrum. $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 137.27, 135.45, 132.19, 131.88, 127.83, 83.85, 24.97, 21.41 (*meta*); δ 141.55, 134.91, 128.65, 83.74, 24.97, 21.87 (*para*). ^{13}C NMR data agree with previously reported data.¹²



(3j): ^1H NMR (chloroform-*d*, 23 °C): δ 7.41 (s, 2H), 7.08 (s, 1H), 2.29 (s, 6H), 1.32 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 137.23, 133.07, 132.47, 83.80, 24.92, 21.22. ^1H and ^{13}C NMR data agree with previously reported data.¹³

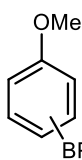


(3k): ^1H NMR (chloroform-*d*, 23 °C): δ 7.59 (s, 1H), 7.54 (d, $\Delta\nu_{1/2} = 7.38$ Hz, 1H), 7.15 (d, $\Delta\nu_{1/2} = 7.34$ Hz, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 1.34 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 140.25, 136.04, 135.97, 132.52, 129.26, 83.72, 24.93, 20.12, 19.58. ^1H and ^{13}C NMR data agree with previously reported data.¹⁴

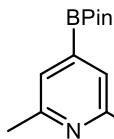


(3l): In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.003 g (0.006 mmol) of (^iPr PNP)CoNs, 0.070 g (0.276 mmol) of B_2Pin_2 , and 0.530 g (5.520 mmol) of fluorobenzene. The resulting mixture was stirred at 80 °C for

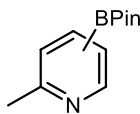
24 hours. The HBPin formed and the excess fluorobenzene were removed via vacuum distillation and the crude product was dissolved in hexane and the resulting solution was passed through a plug of silica gel in a Pasteur pipette to remove the catalyst. The title compound was isolated as a white solid (0.049 g, 95% yield) upon removal of solvent in vacuo. The ^1H NMR was not assigned since the proton resonances of the *meta* and *para* isomers overlap with each other. The *ortho: meta* ratio was determined to be 89:11 by integration of the characteristic peaks in the quantitative ^{13}C NMR spectrum. $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 168.29, 166.30, 136.97, 136.91, 133.43, 133.36, 123.72, 123.69, 115.46 115.27, 84.19, 24.94 (*ortho*).; δ 163.59, 161.63, 130.41, 130.38, 129.61, 129.56, 121.14, 120.99, 118.36, 118.20, 84.00, 24.97 (*meta*). ^{13}C NMR data agree with previously reported data.¹⁵



BPIn(**3m**): The ^1H NMR was not assigned since the proton resonances of the *meta*, *para* and *ortho* isomers overlap with each other. The *meta: para: ortho* ratio was determined to be 81:10:9 by integration of the characteristic peaks in the quantitative ^{13}C NMR spectrum. $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 159.04, 128.93, 127.15, 118.79, 117.75, 83.72, 54.89, 24.73 (*meta*).; δ 162.17, 136.54, 113.27, 83.43, 54.89, 24.70 (*para*). δ 164.19, 136.87, 132.54, 120.10, 110.27, 83.30, 55.42, 24.81 (*ortho*). ^{13}C NMR data agree with previously reported data.^{16,17,18}

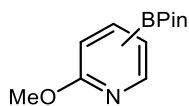


(3n): The crude reaction mixture was dissolved in CDCl_3 , passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^1H and ^{13}C NMR spectroscopy without additional purification. ^1H NMR (chloroform-*d*, 23 °C): δ 7.31 (s, 2H), 2.52 (s, 6H), 1.35 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 157.19, 125.38, 84.50, 24.99. ^1H and ^{13}C NMR data agree with previously reported data.¹³

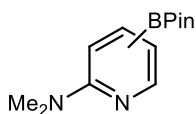


(3o): In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar and 0.008 g (0.016 mmol) of $(^i\text{Pr})\text{PNP})\text{CoNs}$, 0.140 g (0.551 mmol) of B_2Pin_2 , 0.051 g (0.551 mmol) of 2-picoline, and 1 mL of THF. The resulting mixture was stirred at 80 °C for 24 hours. The HBPIn and THF were removed by vacuum and the resulting mixture was dissolved in hexane and was passed through a plug of silica gel in a Pasteur pipette to remove the catalyst. The title compound was isolated as yellow crystals (0.111 g, 92% yield) upon removal of solvent in vacuo. The 4-:5-:6- isomer ratio was determined to be 79:12:9 by integration of the characteristic peaks in the ^1H NMR spectrum. ^1H NMR (chloroform-*d*, 23 °C): δ 8.51 (d, $\Delta\nu_{1/2}$ = 4.99 Hz, 1H), 7.52 (s, 1H), 7.44 (d, $\Delta\nu_{1/2}$ = 5.00 Hz, 1H), 2.56 (s, 3H), 1.34 (s, 12H) (4- isomer); δ 8.83 (s, 1H), 7.97 (dd, $\Delta\nu_{1/2}$ = 7.74 Hz, 1.66 Hz, 1H), 7.15 (d, $\Delta\nu_{1/2}$ = 7.71 Hz, 1H), 2.58 (s, 3H), 1.34 (s, 12H) (5- isomer); δ 7.36 (dd, $\Delta\nu_{1/2}$ = 9.15 Hz, 6.86 Hz, 1H), 6.41 (d, $\Delta\nu_{1/2}$ = 9.14 Hz, 1H), 6.04 (d, $\Delta\nu_{1/2}$ = 6.79 Hz, 1H), 2.32 (s, 3H), 1.34 (s, 12H) (6- isomer). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 157.53, 148.19, 128.80, 125.89, 84.64, 24.97, 24.00 (4-isomer); δ 160.81, 154.63, 143.10, 123.09, 84.64, 24.97, 24.23 (5-isomer); δ 145.08, 142.13,

117.09, 106.29, 84.64, 24.97, 19.47 (6-isomer). GCMS m/z (% relative intensity, ion): 219.10 (47, M⁺), 204.10 (53, M⁺-15).

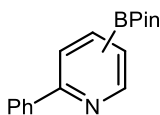


(3p): The crude reaction mixture was dissolved in CDCl₃, passed through a plug of silica gel in a Pasteur pipette and then analyzed by ¹H and ¹³C NMR spectroscopy without additional purification. The ¹H NMR was not assigned since the proton resonances of the 4- and 5- boronic ester isomers overlap with each other. The 4-:5- isomer ratio was determined to be 88:12 by integration of the characteristic peaks in the quantitative ¹³C NMR spectrum. {¹H}¹³C NMR (chloroform-*d*, 23 °C): δ 163.99, 146.37, 121.28, 116.62, 84.52, 53.49, 24.64 (4- isomer).; δ 166.16, 154.24, 144.60, 110.36, 83.94, 53.61, 25.00 (5- isomer). ¹³C NMR data agree with previously reported data.^{19,20}

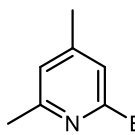


(3q): The crude reaction mixture was dissolved in CDCl₃, passed through a plug of silica gel in a Pasteur pipette and then analyzed by ¹H and ¹³C NMR spectroscopy without additional purification. The 4-:5-:6- isomer ratio was determined to be 83:12:5 by integration of the characteristic peaks in the ¹H NMR spectrum. ¹H NMR (chloroform-*d*, 23 °C): δ 8.17 (d, Δ*v*_{1/2} = 4.46 Hz, 1H), 6.90 (s, 1H), 6.86 (d, Δ*v*_{1/2} = 4.32 Hz, 1H), 3.07 (s, 6H), 1.33 (s, 12H) (4- isomer); δ 8.52 (s, 1H), 7.76 (d, Δ*v*_{1/2} = 8.73 Hz, 1H), 6.46 (d, Δ*v*_{1/2} = 8.71 Hz, 1H), 3.07 (s, 6H), 1.31 (s, 12H) (5- isomer); δ 7.86 (d, Δ*v*_{1/2} = 6.19 Hz, 1H), 7.57 (s, 1H), 6.71 (d, Δ*v*_{1/2} = 6.17 Hz, 1H), 3.07 (s, 6H), 1.33 (s, 12H) (6- isomer). {¹H}¹³C NMR (chloroform-*d*, 23 °C): δ 159.42, 147.30, 116.14, 111.52, 84.29, 38.27, 24.95 (4-isomer); δ 155.31, 143.20, 105.00, 82.89, 38.17, 24.69 (one signal not

located) (5-isomer); not observed (6-isomer). GCMS m/z (% relative intensity, ion): 248.10 (47, M^+), 233.10 (53, M^+-15).

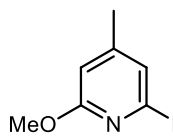


(3r): The crude reaction mixture was dissolved in $CDCl_3$, passed through a plug of silica gel in a Pasteur pipette and then analyzed by 1H and ^{13}C NMR spectroscopy without additional purification. The 4-:5- isomer ratio was determined to be 50:50 by integration of the pyridine protons at the 2-position of the product. 1H NMR analysis of isomer mixture (chloroform- d , 23 °C): δ 9.04 (dd, $\Delta v_{1/2}$ = 1.59 Hz, 0.97 Hz, 1H) (5-isomer), 8.73 (dd, $\Delta v_{1/2}$ = 4.76 Hz, 0.95 Hz, 1H) (4-isomer), 8.14 (dd, $\Delta v_{1/2}$ = 7.75 Hz, 1.71 Hz, 1H) (5-isomer), 8.11 (t, $\Delta v_{1/2}$ = 0.97 Hz, 1H) (4-isomer), 8.06-7.98 (m, 6H) (aryl CH), 7.72 (d, $\Delta v_{1/2}$ = 7.86 Hz, 1H) (5-isomer), 7.58 (dd, $\Delta v_{1/2}$ = 4.77 Hz, 0.97 Hz, 1H) (4-isomer), 7.50-7.40 (m, 4H) (aryl CH), 1.38 (s, 12H), 1.37 (s, 12H). $\{^1H\}^{13}C$ NMR of the isomer mixture (chloroform- d , 23 °C): δ 159.60 (5-isomer), 156.90 (4-isomer), 155.68 (5-isomer), 149.20 (4-isomer), 143.18 (5-isomer), 139.52 (4-isomer), 139.46 (5-isomer), 129.35, 128.94, 128.77, 127.28 (aryl CH), 127.24 (4-isomer), 127.11 (aryl CH), 120.70 (5-isomer), 119.94 (aryl CH), 84.65, 84.27, 25.00, 24.98. GCMS m/z (% relative intensity, ion): 281.10 (83, M^+), 266.10 (17, M^+-15).



(3s): The crude reaction mixture was dissolved in benzene- d_6 and was passed through a glass frit. The filtrate was placed in J-Young tube and was analyzed by 1H and ^{13}C NMR spectroscopies under air and moisture-free conditions. 1H NMR (benzene- d_6 , 23 °C): δ 7.64 (s, 1H), 6.58 (s, 1H), 2.47 (s, 3H), 1.88 (s, 3H), 1.13 (s, 12H).

{¹H}¹³C NMR (benzene-*d*₆, 23 °C): δ 158.56, 144.94, 129.47, 125.23, 83.91, 25.17, 25.05, 20.60. Combustion analysis was not successful.



The crude reaction mixture was dissolved in benzene-*d*₆ and was passed through a glass frit. The filtrate was placed in J-Young tube and was analyzed by ¹H and ¹³C NMR spectroscopies under air and moisture-free conditions. ¹H NMR (benzene-*d*₆, 23 °C): δ 7.47 (s, 1H), 6.54 (s, 1H), 3.89 (s, 3H), 1.84 (s, 3H), 1.14 (s, 12H).

{¹H}¹³C NMR (benzene-*d*₆, 23 °C): δ 164.92, 148.13, 127.15, 113.50, 83.97, 53.24, 25.06, 20.41. Combustion analysis was not successful.

IV. NMR Spectra of Borylation Products

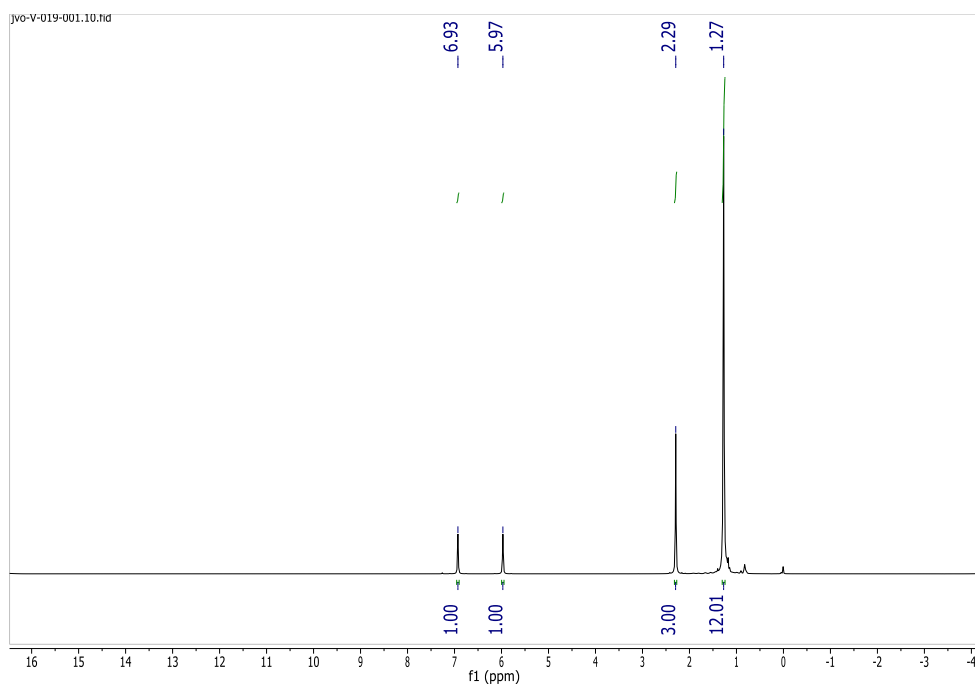


Figure S8. ¹H NMR spectrum of 3a.

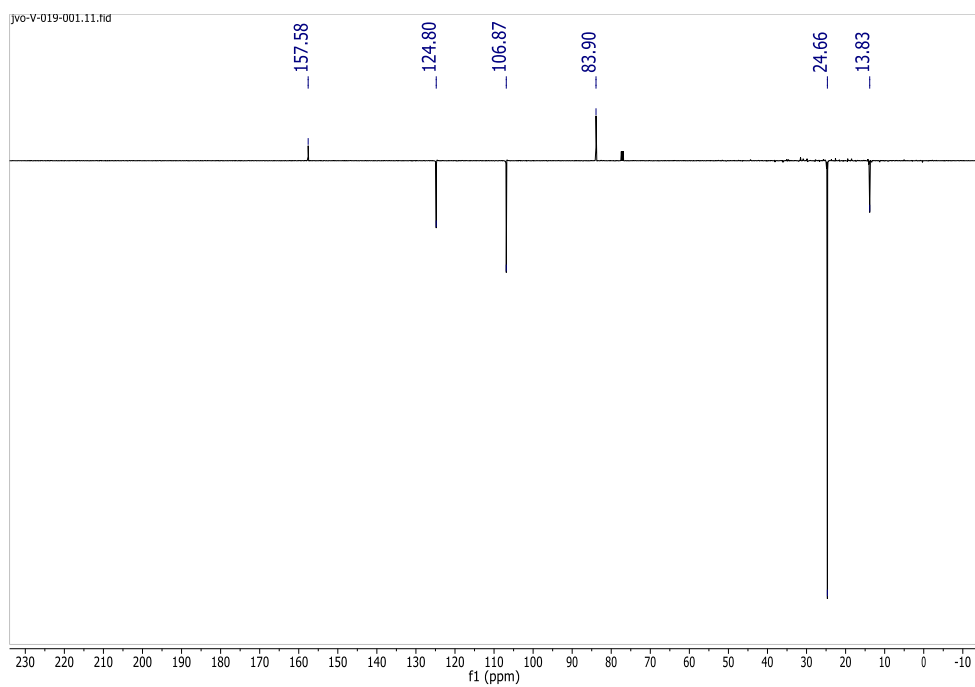


Figure S9. ¹³C NMR spectrum of 3a.

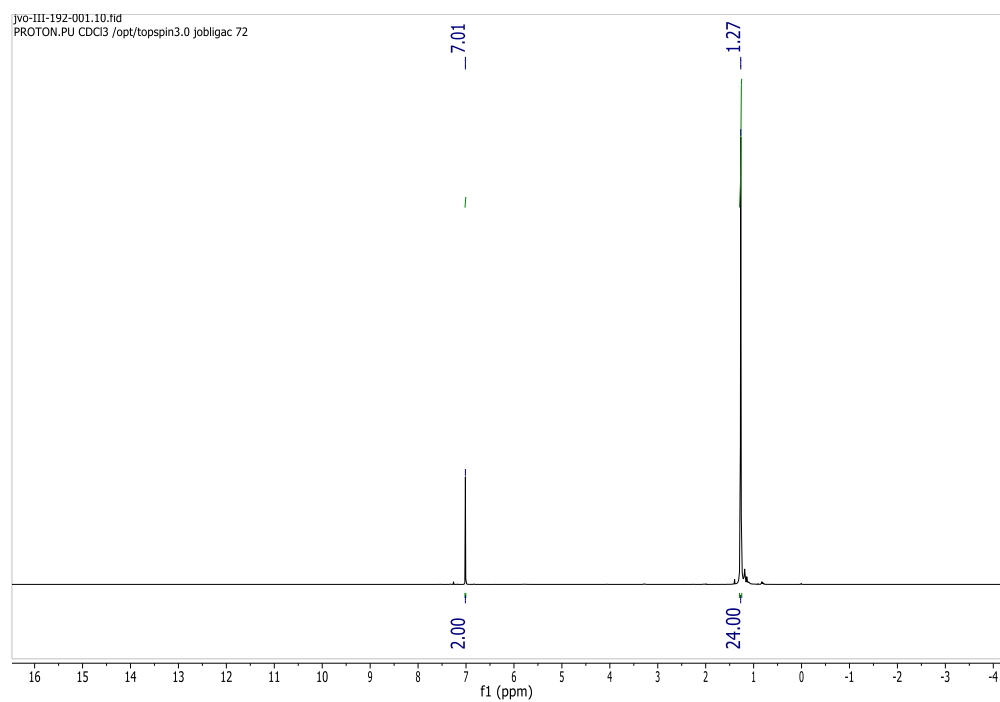


Figure S10. ¹H NMR spectrum of **3b**.

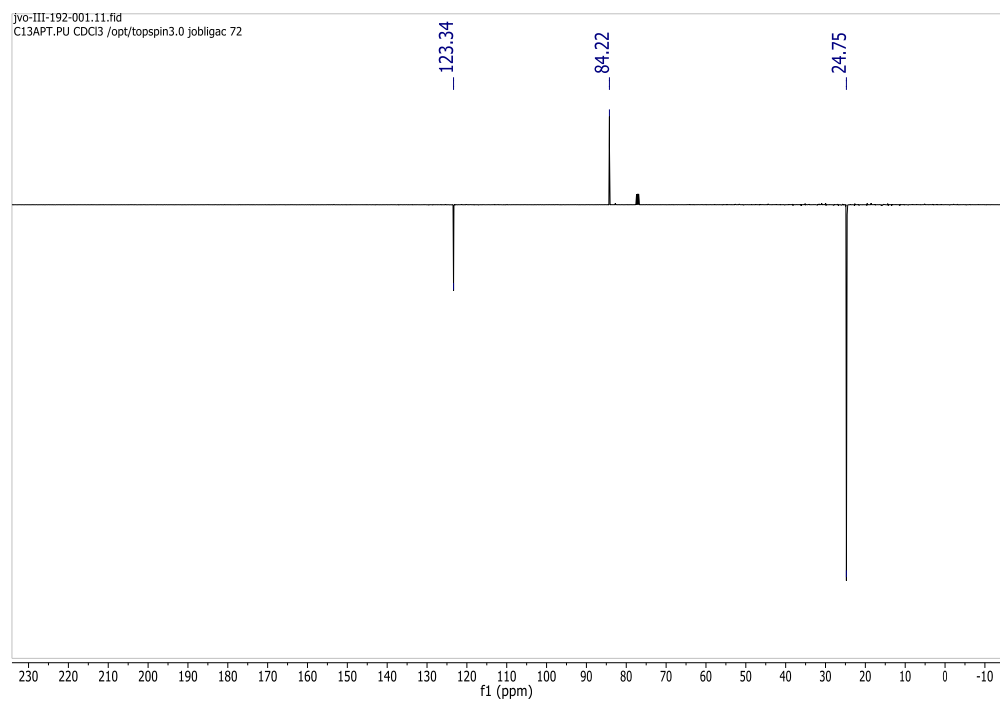


Figure S11. ¹³C NMR spectrum of **3b**.

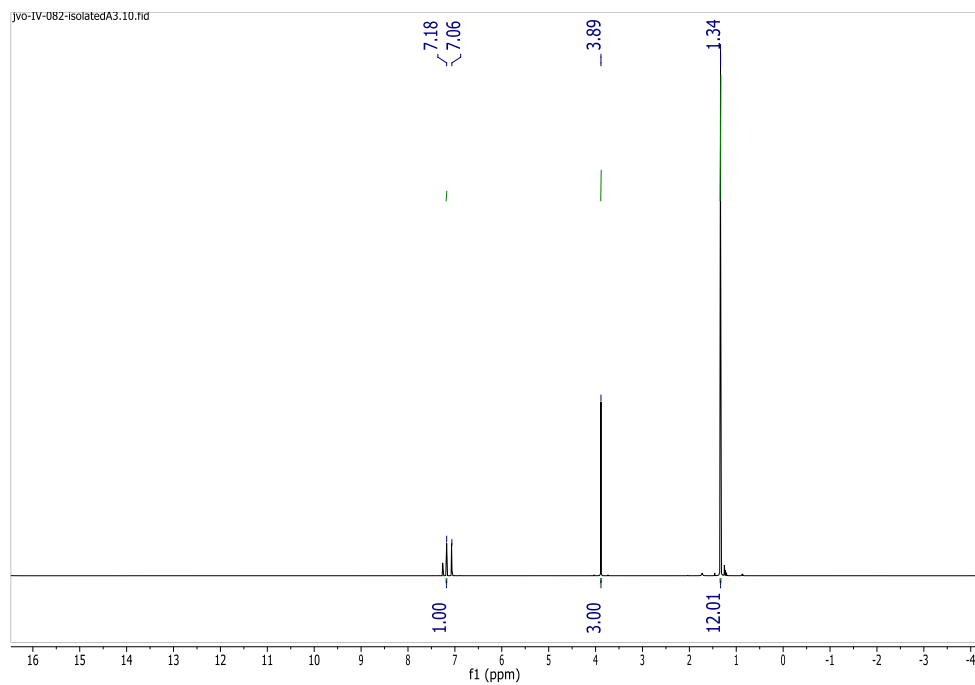


Figure S12. ^1H NMR spectrum of **3c**.

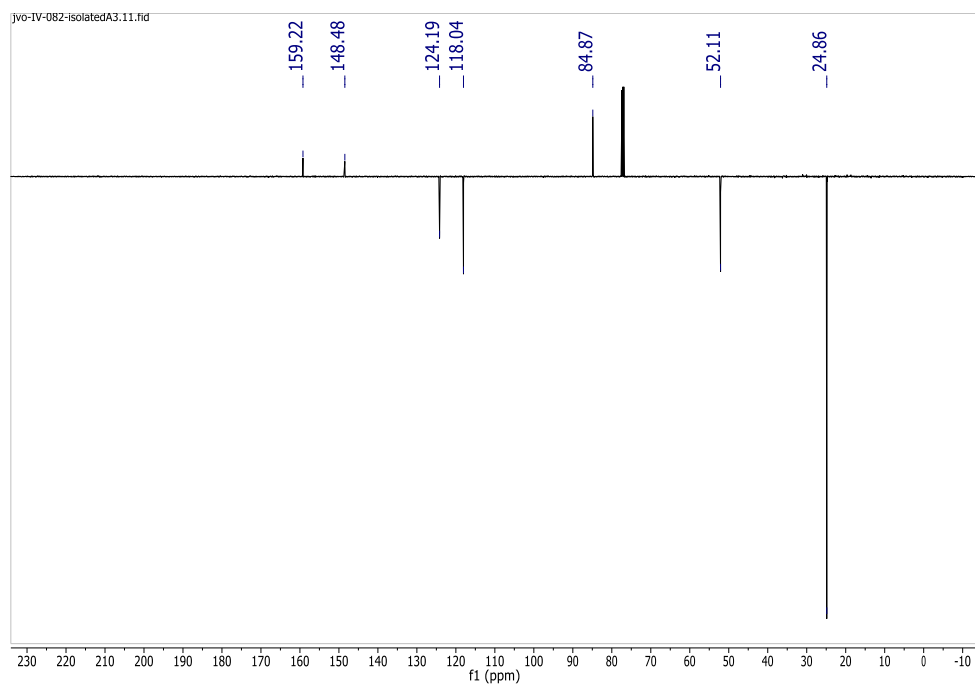


Figure S13. ^{13}C NMR spectrum of **3c**.

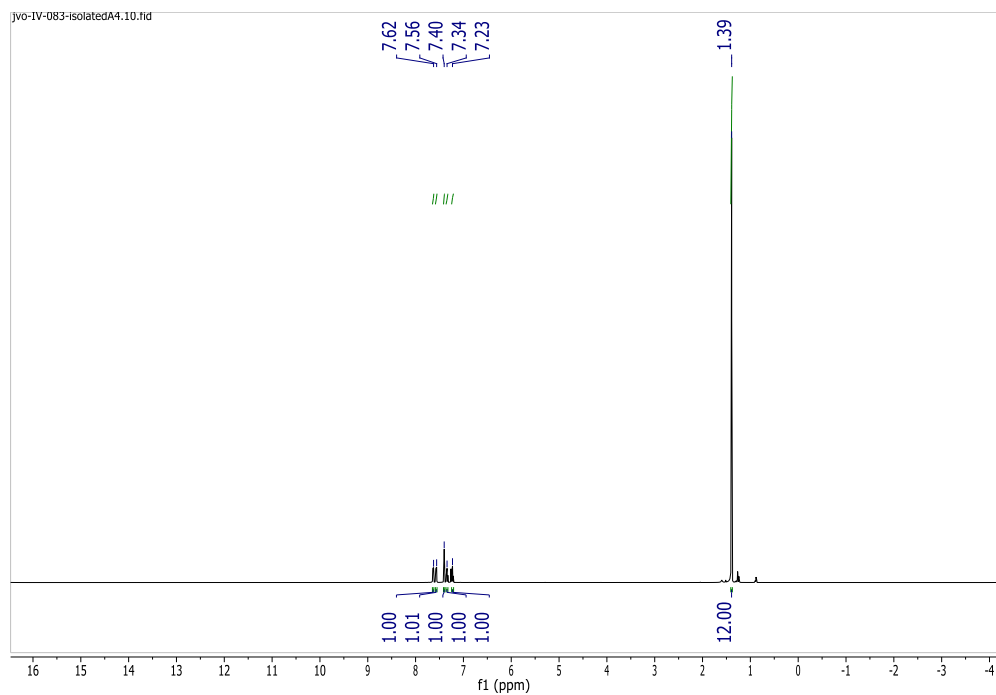


Figure S14. ^1H NMR spectrum of **3d**.

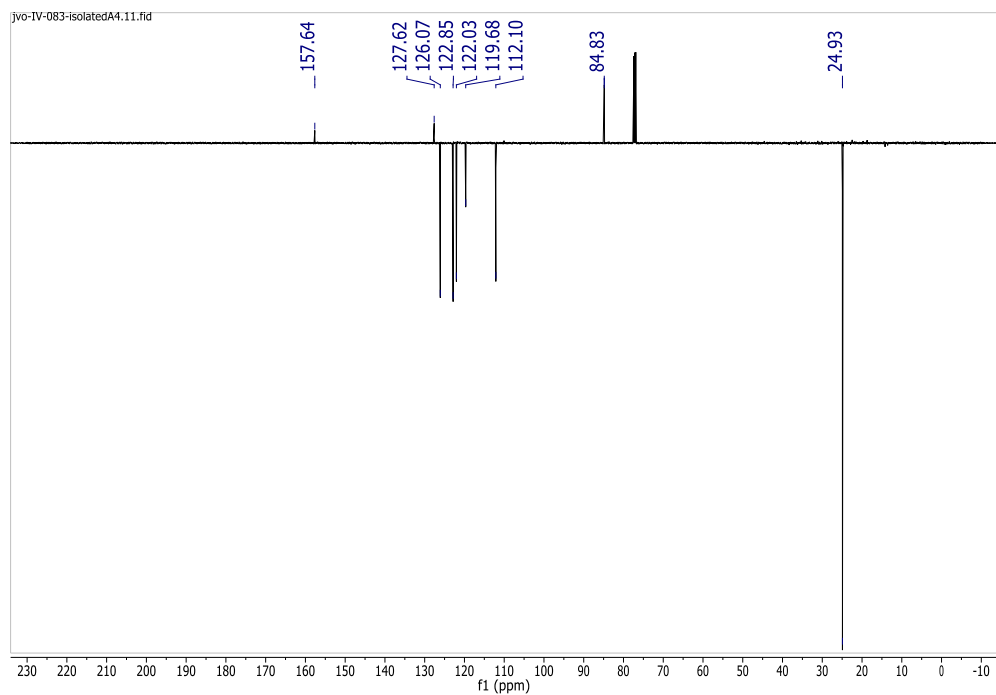


Figure S15. ^{13}C NMR spectrum of **3d**.

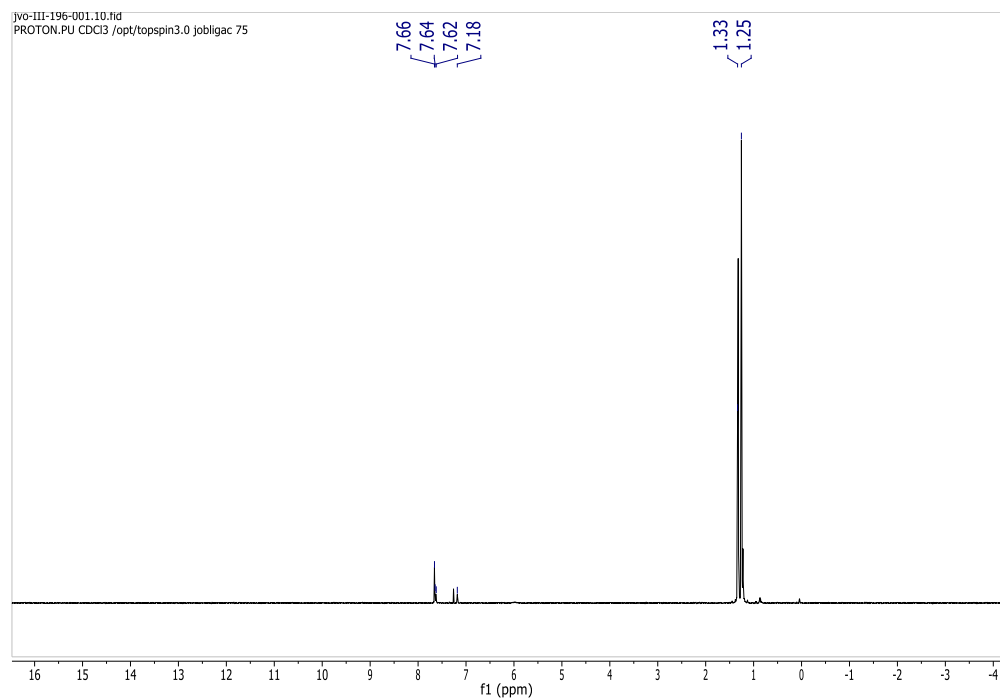


Figure S16. ^1H NMR spectrum of **3e** + **3f**.

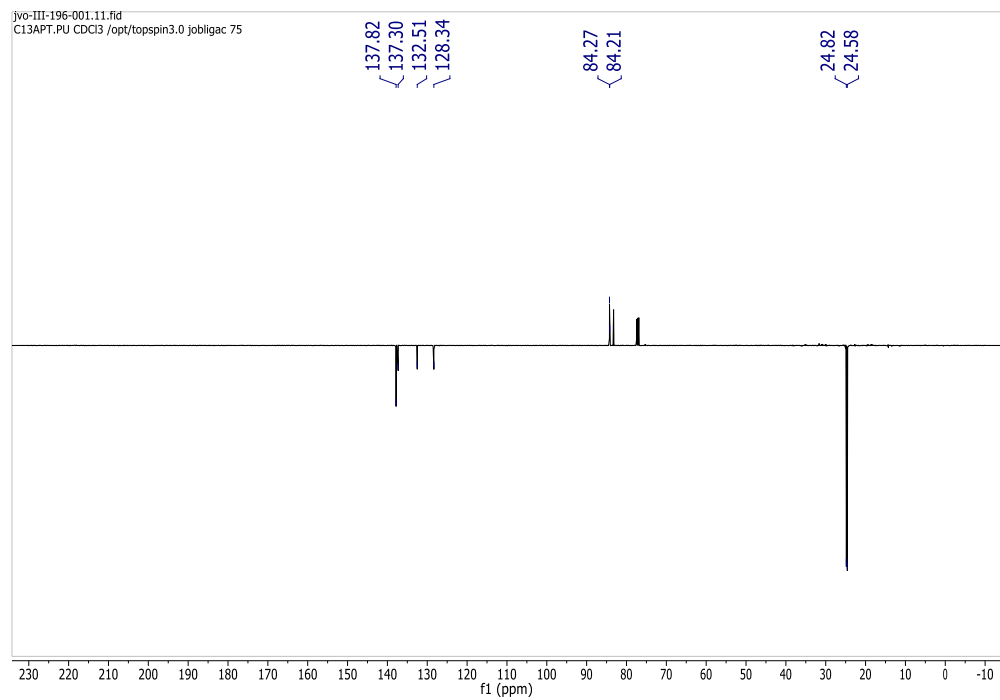


Figure S17. ^{13}C NMR spectrum of **3e** + **3f**.

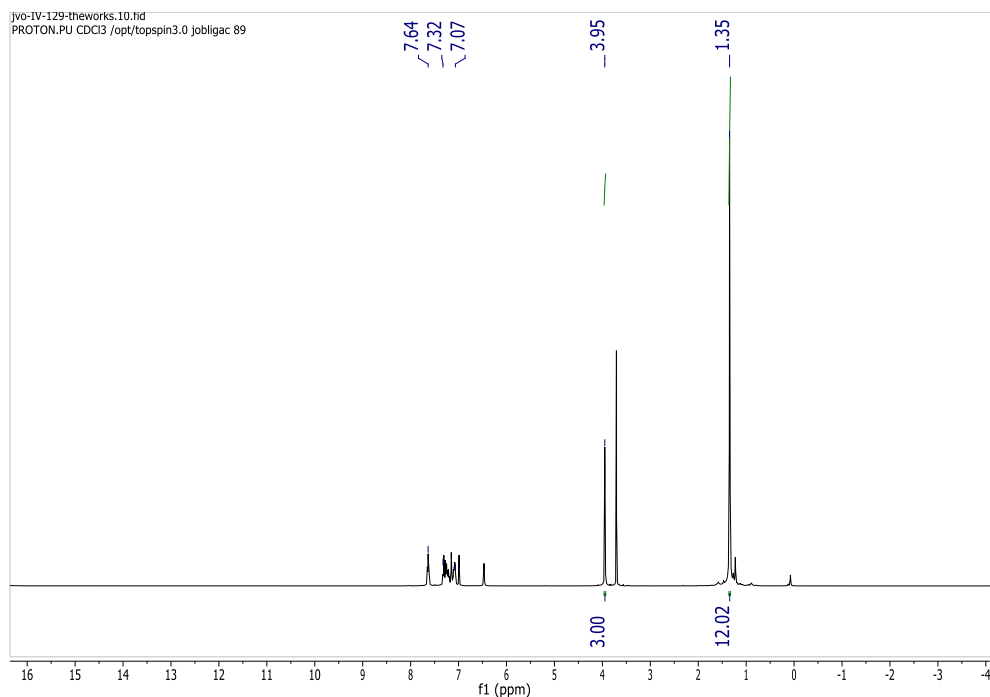


Figure S18. ^1H NMR spectrum of **3g**. The unlabeled peaks are that of the unreacted N-methyl indole.

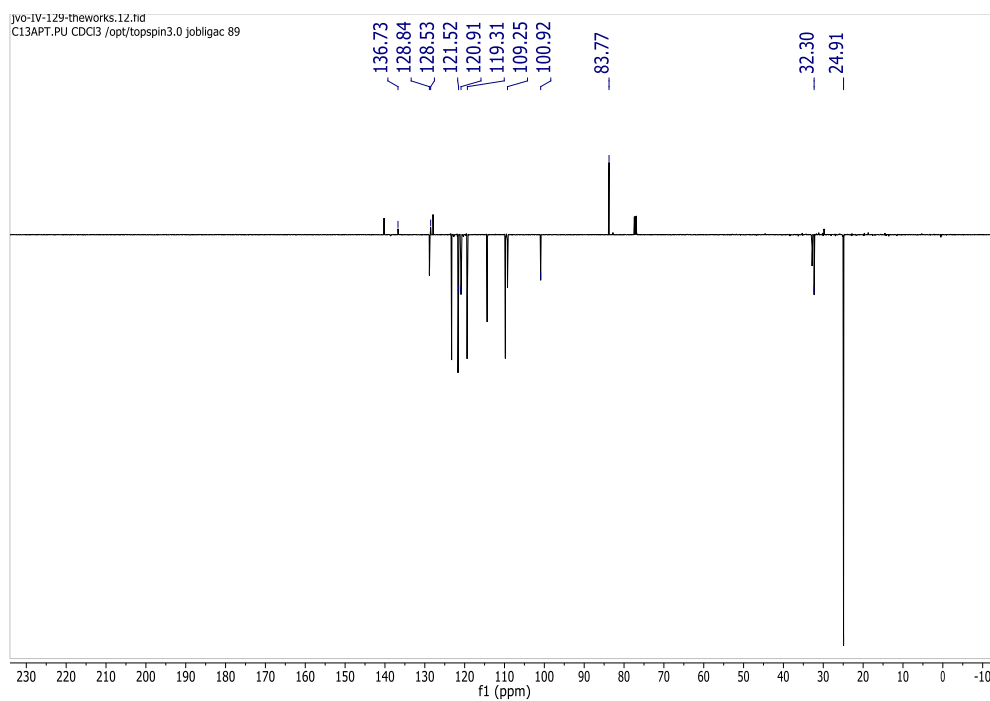


Figure S19. ^{13}C NMR spectrum of **3g**. The unlabeled peaks are that of the unreacted N-methyl indole.

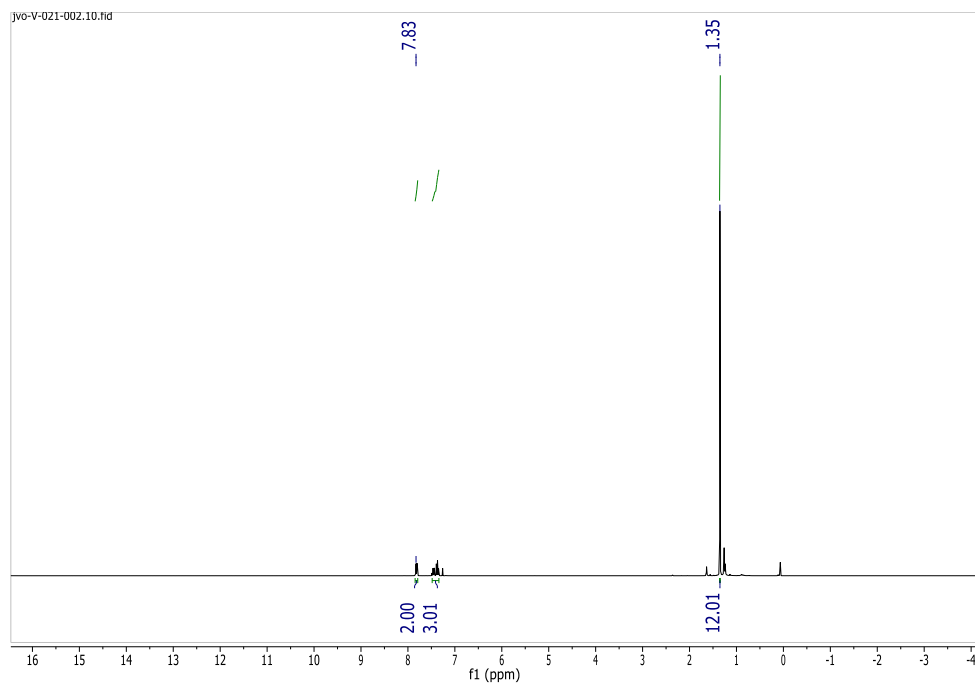


Figure S20. ^1H NMR spectrum of **3h**.

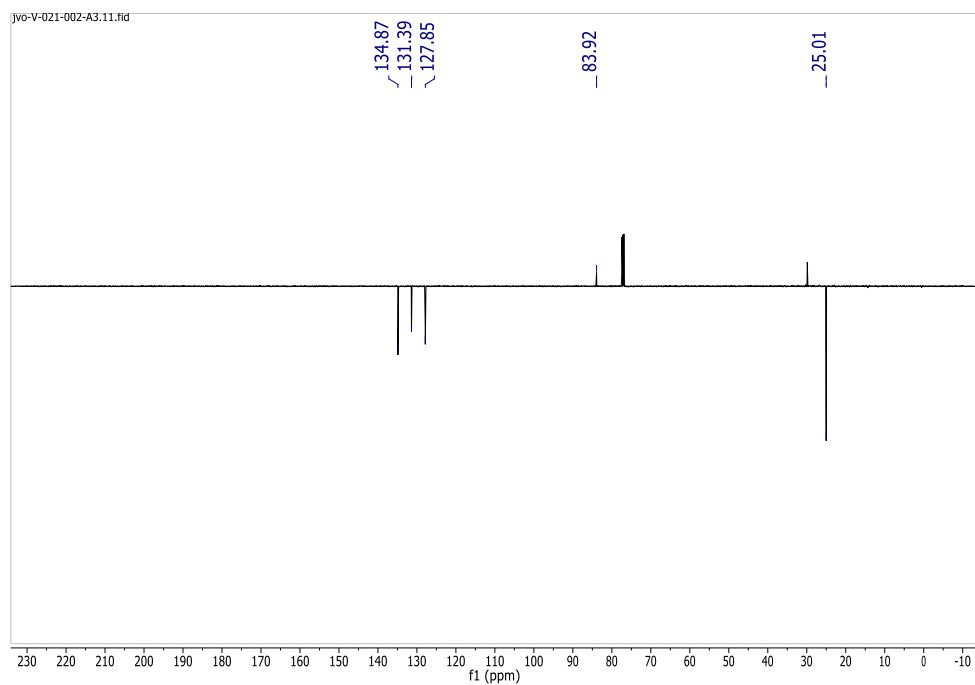


Figure S21. ^{13}C NMR spectrum of **3h**. The peak at $\delta = 29.86$ ppm is from H-grease.

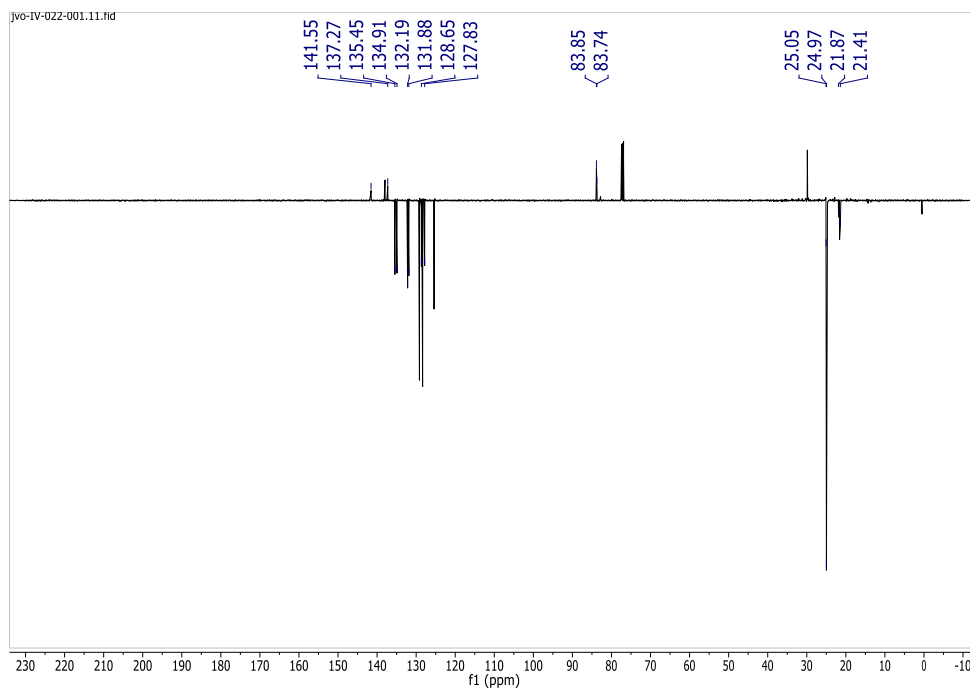


Figure S22. ^{13}C NMR spectrum of **3i**. The peaks at $\delta = 137.98$, 129.15 , 128.35 , and 21.61 ppm are from excess toluene in the reaction. The peak at $\delta = 29.86$ ppm is from H-grease.

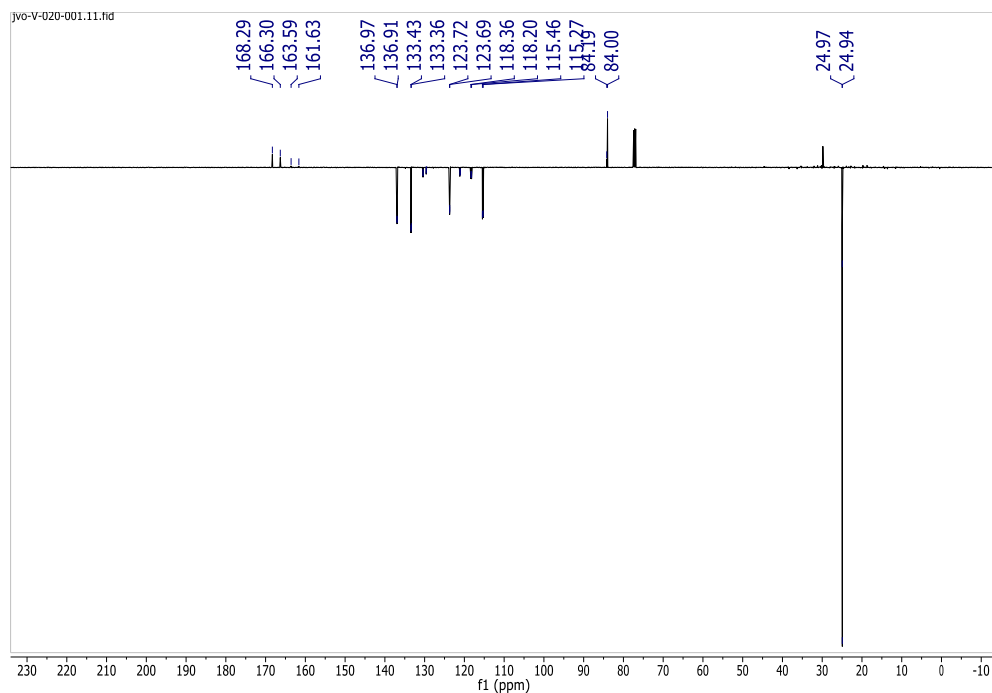


Figure S23. ^{13}C NMR spectrum of **3l**.

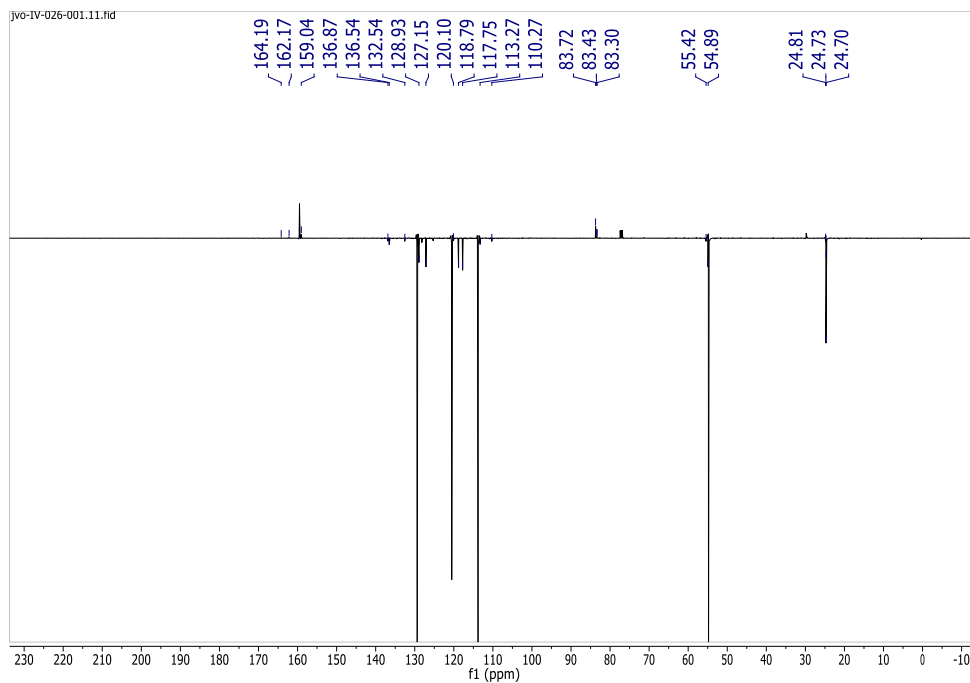


Figure S24. ^{13}C NMR spectrum of **3m**. The peaks at $\delta = 159.51$, 129.38, 120.53, 113.78, and 54.80 are from excess anisole in the reaction.

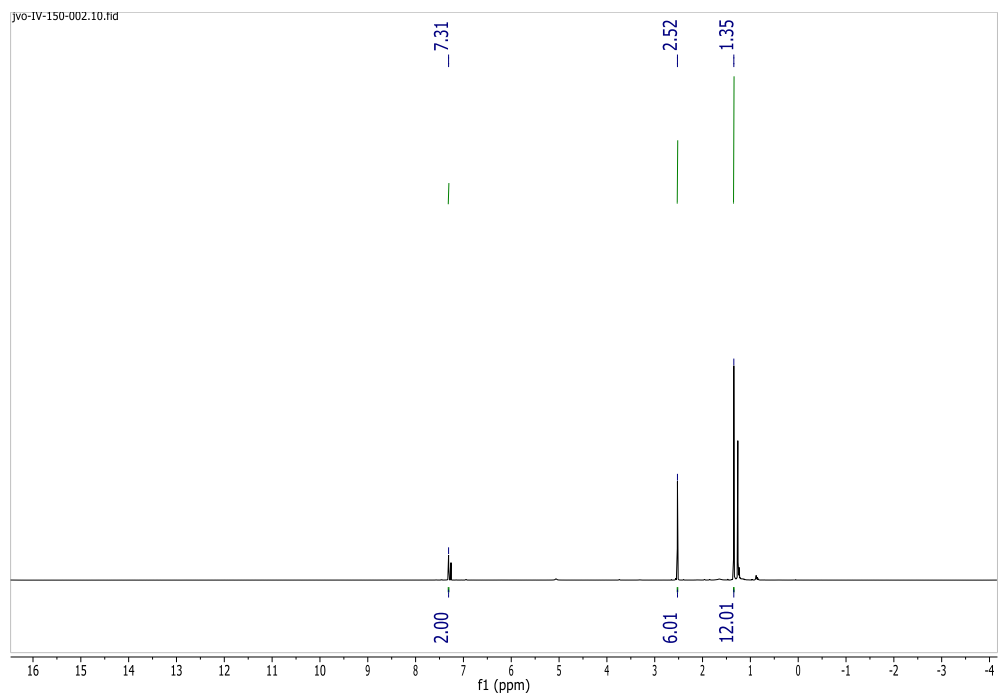


Figure S25. ^1H NMR spectrum of **3n**.

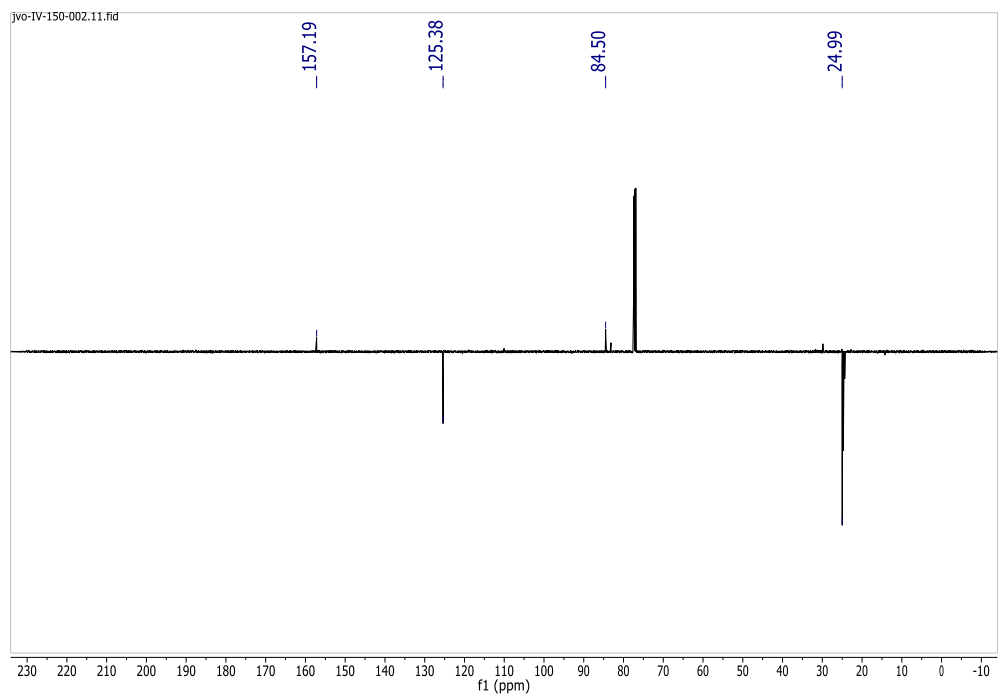


Figure S26. ^{13}C NMR spectrum of **3n**.

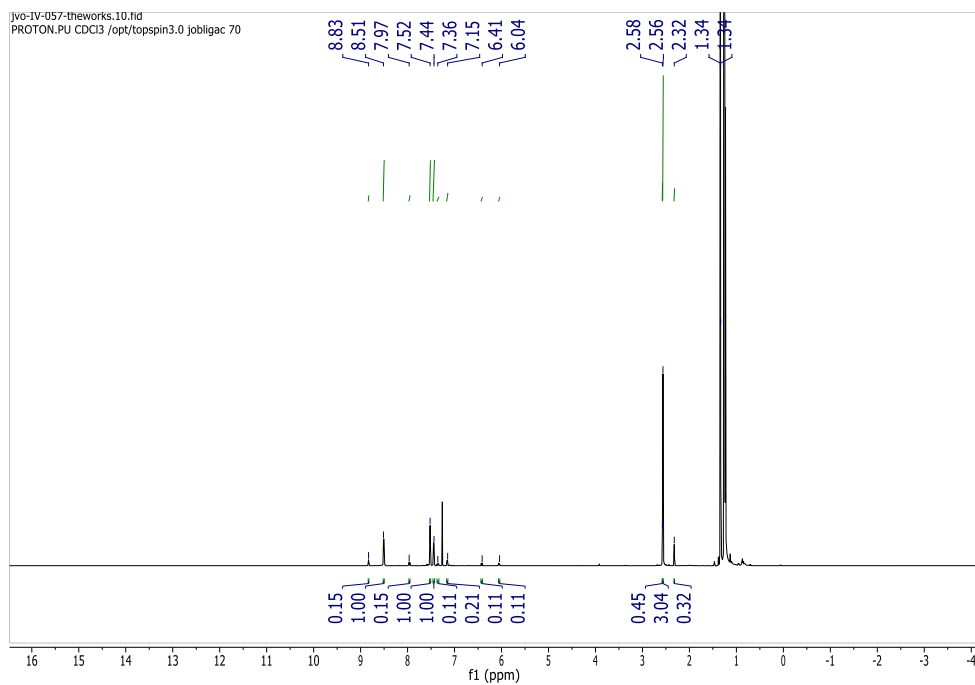


Figure S27. ^1H NMR spectrum of **3o**.

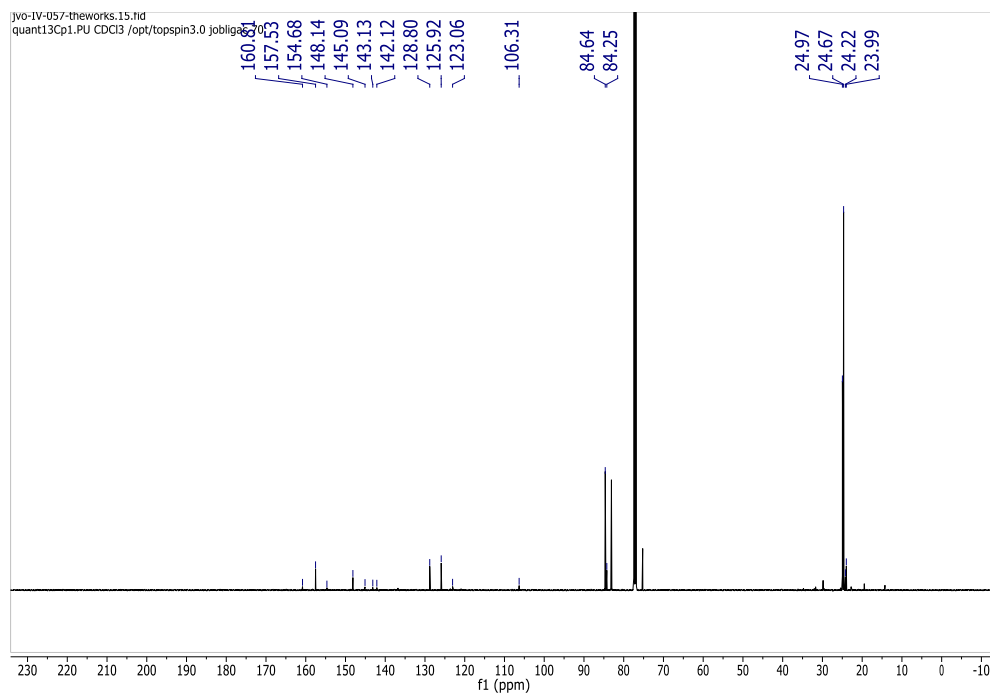


Figure S28. ^{13}C NMR spectrum of **3o**.

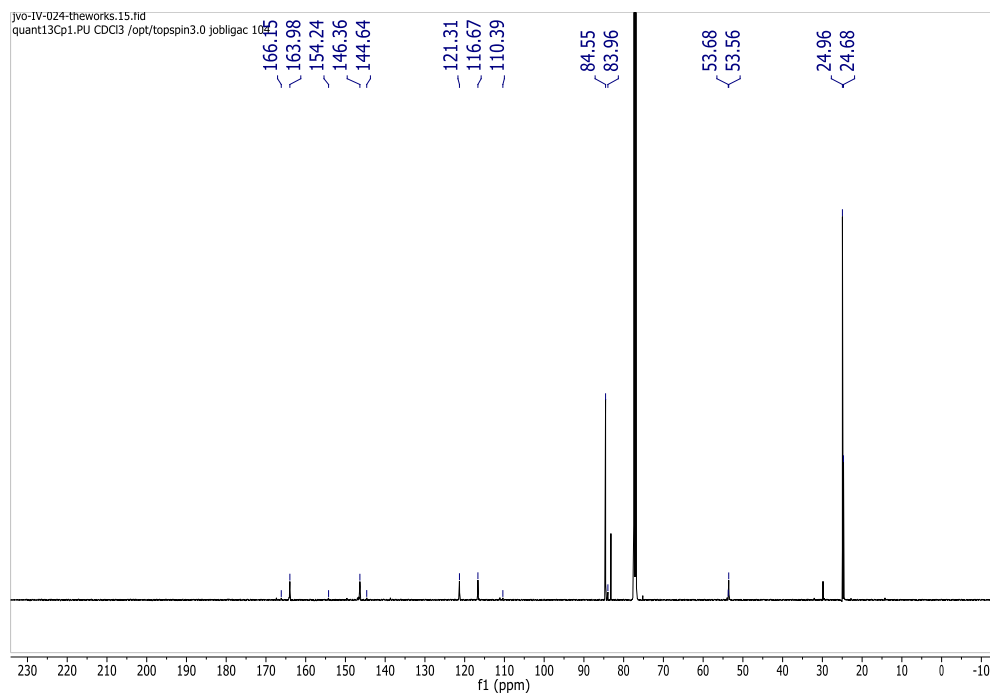


Figure S29. ^{13}C NMR spectrum of **3p**.

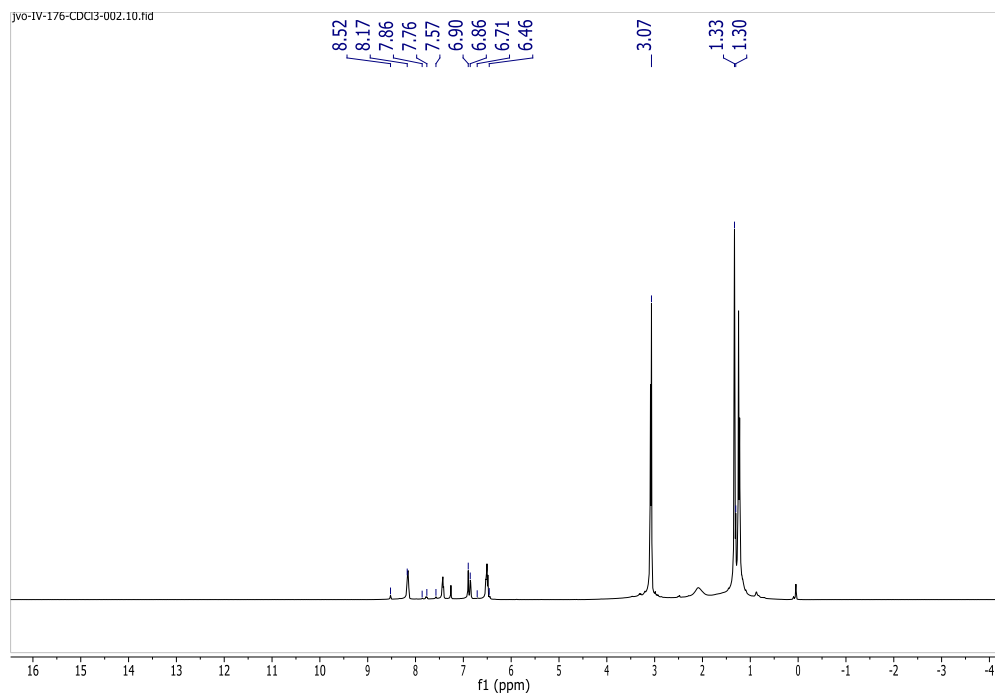


Figure S30. ^1H NMR spectrum of **3q**.

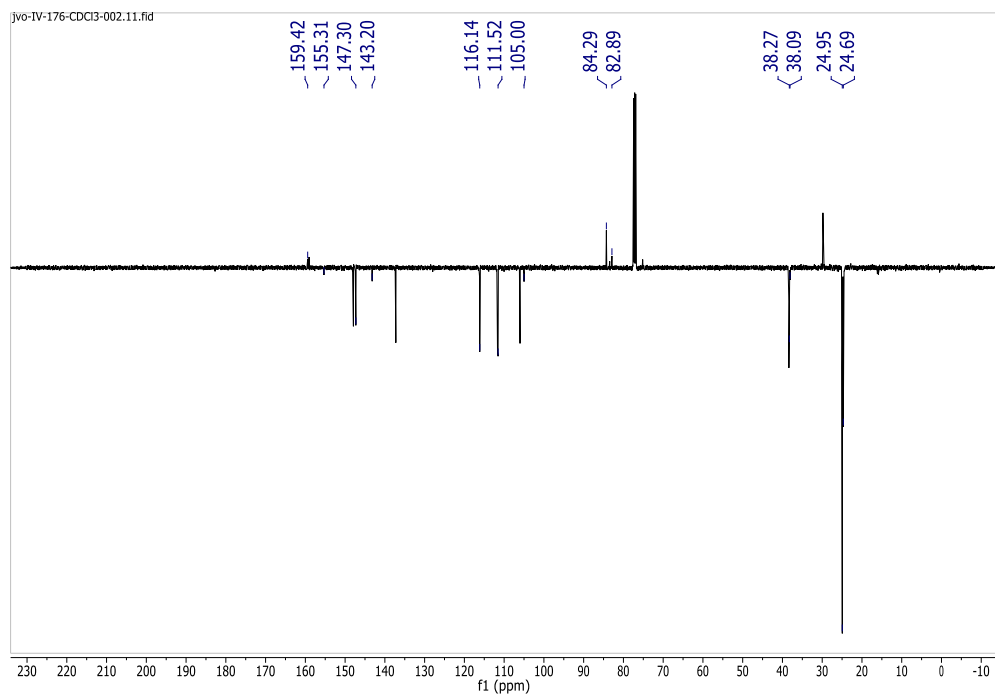


Figure S31. ^{13}C NMR spectrum of **3q**.

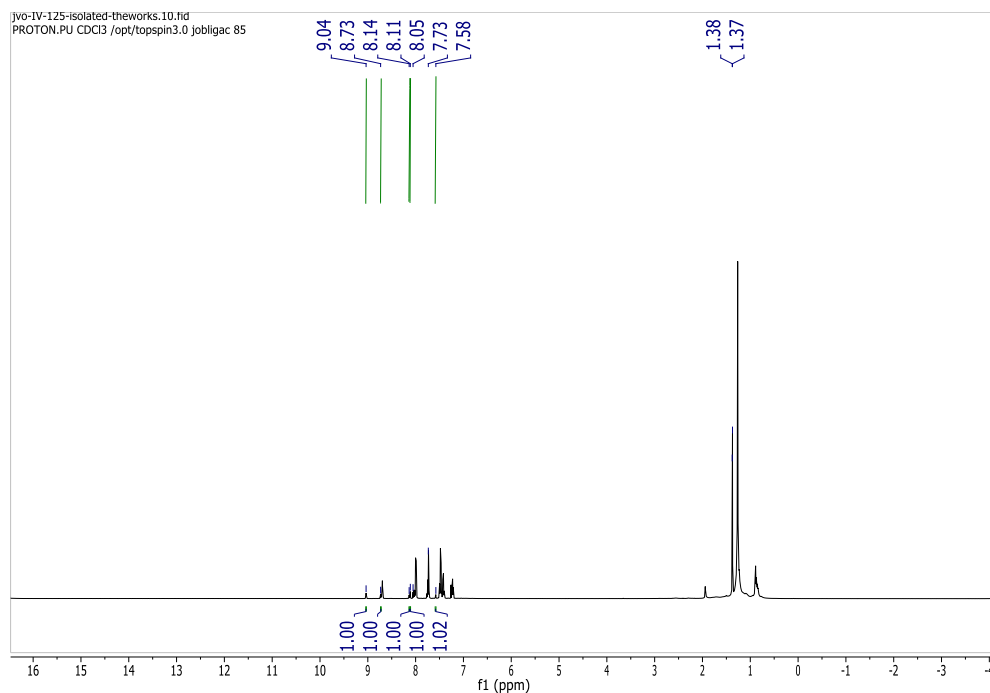


Figure S32. ^1H NMR spectrum of **3r**.

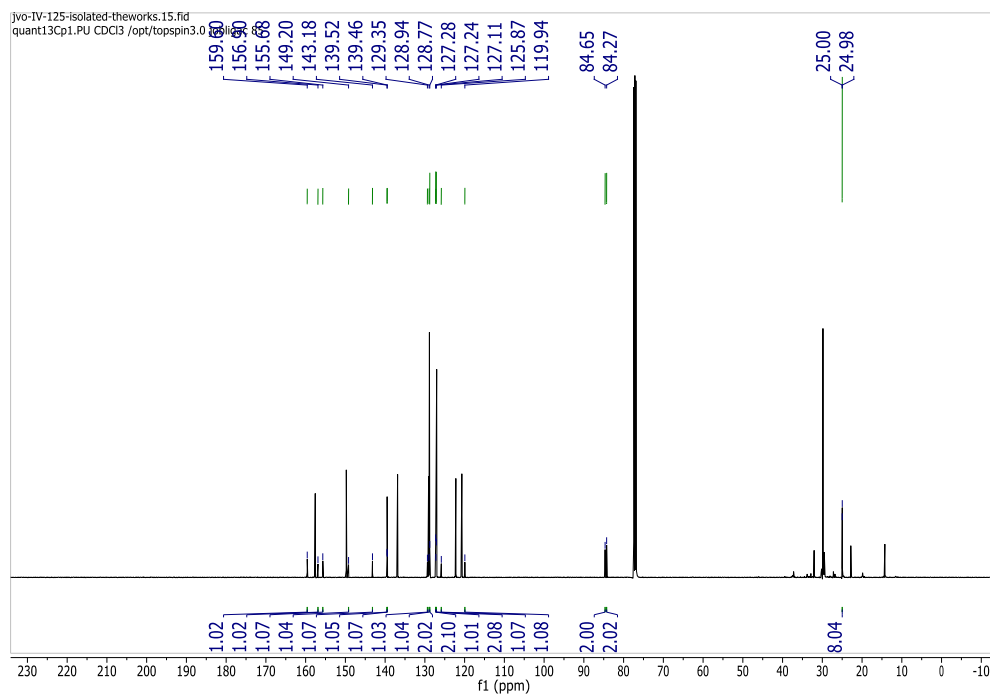


Figure S33. ^{13}C NMR spectrum of **3r**.

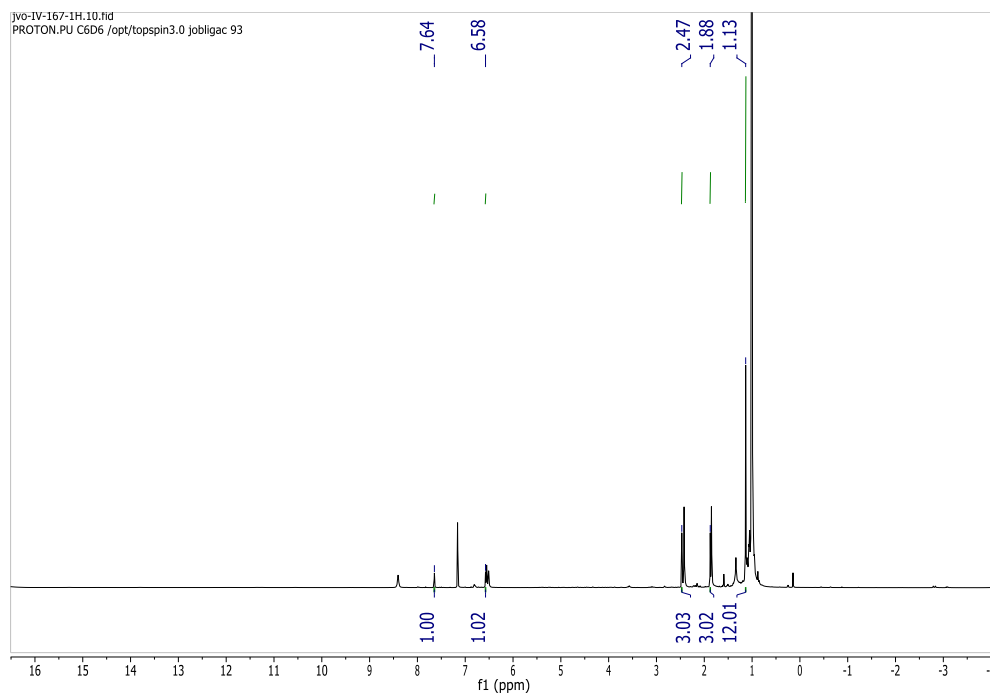


Figure S34. ^1H NMR spectrum of **3s**. The peaks at $\delta = 8.40$, 6.55, 6.51, 2.42, and 1.85 ppm are from unreacted 2,4-lutidine in the reaction. The peak at $\delta = 1.00$ is from unreacted B_2Pin_2 .

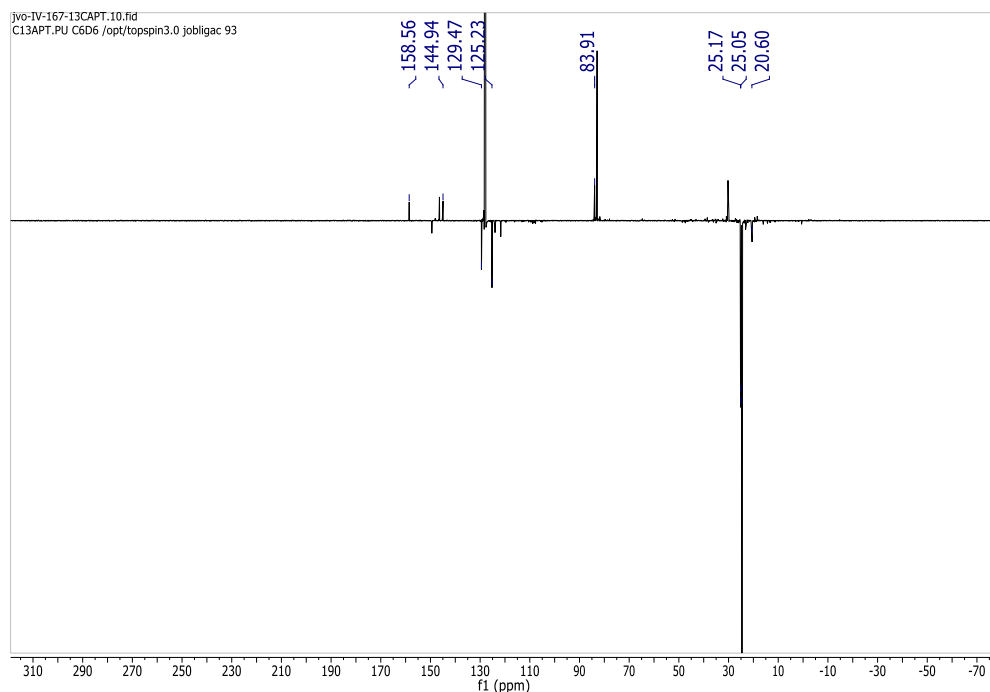


Figure S35. ^{13}C NMR spectrum of **3s**. The peaks at $\delta = 158.43$, 149.35, 146.55, 123.98, 121.72, 24.38, and 20.55 are from unreacted 2,4-lutidine in the reaction. The peak at $\delta = 24.67$ is from unreacted B_2Pin_2 .

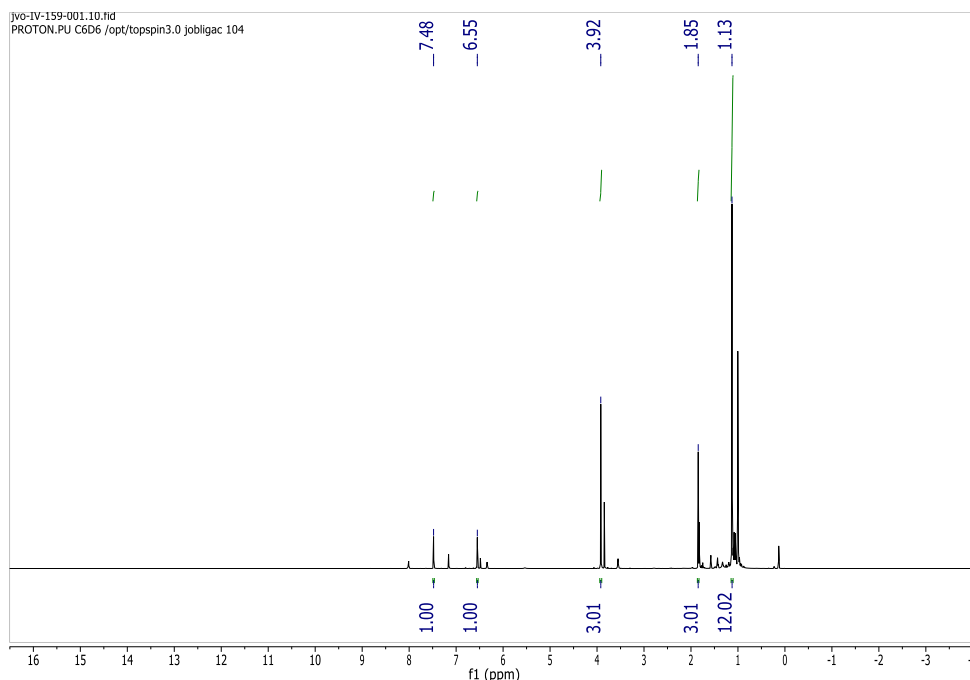


Figure S36. ^1H NMR spectrum of **3t**. The peaks at $\delta = 8.04$, 6.51 , 6.31 , 3.86 , and 1.78 ppm are from unreacted 2-methoxy-4-picoline in the reaction. The peaks at $\delta = 3.55$ and 1.44 are from THF. The peak at $\delta = 1.00$ is from unreacted B_2Pin_2 .

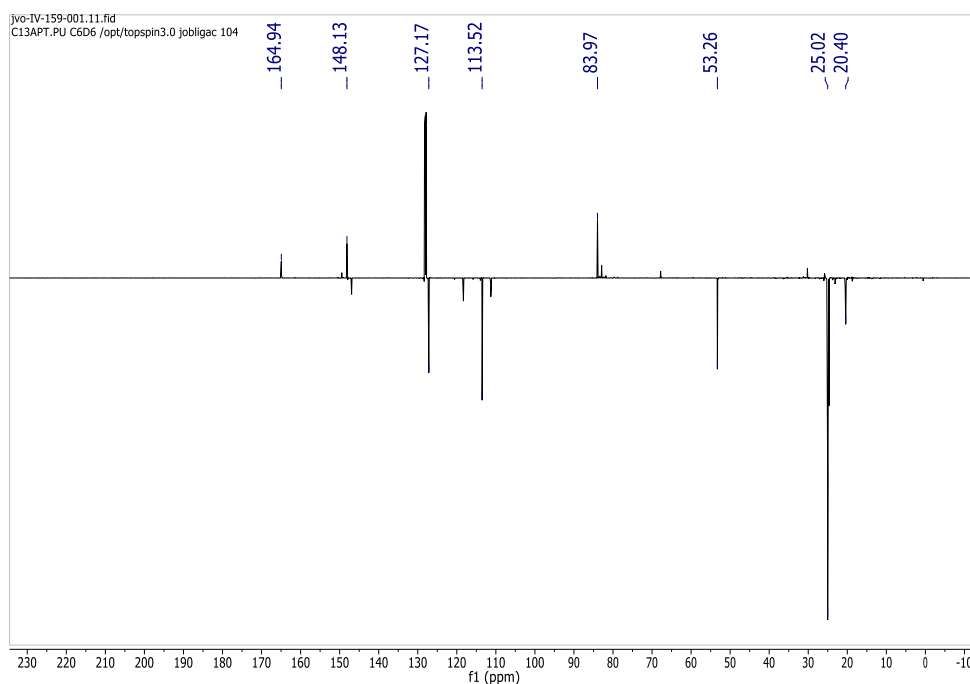


Figure S37. ^{13}C NMR spectrum of **3t**. The peaks at $\delta = 165.08$, 149.48 , 146.94 , 118.31 , 111.29 , 53.12 , and 20.55 are from unreacted 2-methoxy-4-picoline in the reaction. The peaks at $\delta = 67.80$ and 25.84 are from THF. The peak at $\delta = 24.66$ is from unreacted B_2Pin_2 .

IV. References.

- ¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
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