Cobalt-Catalyzed Z-Selective Hydroboration of Terminal Alkynes and Elucidation of the Origin of Selectivity.

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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. Alkyne substrates were dried over CaH_2 and distilled under reduced pressure before use. Pinacolborane was used as received. (^{iPr}PDI)$CoCH_3$,[2] (^{Cy}APDI)$CoCH_3$,[3] DBPin[4], and PhCCBPin[5] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on a Varian Inova 400 or Bruker 300 AVANCE spectrophotometers operating at 400 MHz, and 300 MHz, respectively. All chemical shifts are reported relative to $SiMe_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. ^{13}C NMR spectra were recorded on a Bruker 500 spectrometer operating at 125 MHz. ^{13}C chemical shifts are reported relative to $SiMe_4$ using chemical shifts of the solvent as a secondary standard where applicable. All coupling constants are reported in Hertz (Hz). Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.

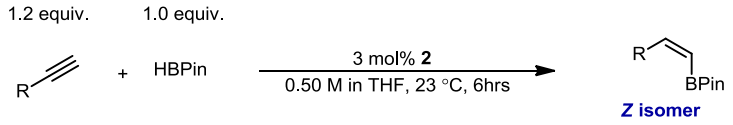
Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with molybdenum and copper X-ray tubes (λ = 0.71073 and 1.54184 Å respectively). 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 1-d_1-1-octyne. A thick-walled glass vessel was charged with a magnetic stir bar, 5.000 g (45.37 mmol) of 1-octyne and 18.603 g (181.49 mmol) of a 40 wt% solution of NaOD in D_2O. The resulting biphasic mixture was vigorously stirred at 95 °C for 7 days. The reaction was cooled to room temperature and the 1-d_1-1-octyne layer was collected using a pipette, washed with deionized water, and separated from residual water via vacuum distillation. A clear liquid identified as **1-d_1-1-octyne** (95% deuterium incorporation) was obtained in 76% yield (3.839 g). ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 0.88 (t, J = 6.94 Hz, 3H), 1.23 – 1.33 (m, 4H), 1.35 – 1.42 (m, 2H), 1.48 – 1.55 (m, 2H), 2.17 (t, J = 7.18 Hz, 2H). $\{^1H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C): δ 14.17, 18.51, 22.68, 28.59, 28.62, 31.47, 67.91 (t, J_{CD} = 37.9 Hz), 84.42 (t, J_{CD} = 7.47 Hz).

III. General Procedure for Cobalt-Catalyzed (*Z*)-Selective Hydroboration of Terminal Alkynes.

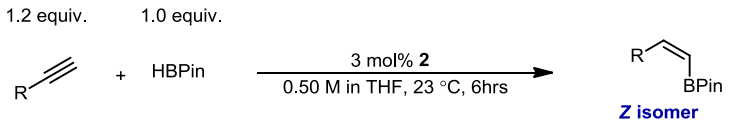
General Procedure A



In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.006 g (0.015 mmol) of (^{Cy}APDI)$CoCH_3$ (**2**) and 1 mL of THF. In a separate vial, 0.600 mmol of the corresponding alkyne and 0.064 g (0.500 mmol) of HBPin were mixed. The alkyne/HBPin mixture was added to the stirring solution of the catalyst at 23 °C and the resulting mixture was stirred for 6 hours. The reaction was then quenched by exposing the mixture to air, the solvent

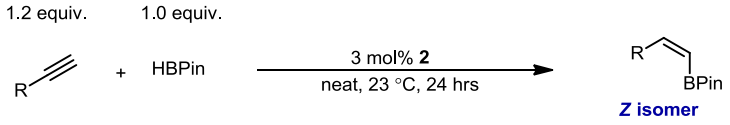
was evaporated in vacuo, and the product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes using hexanes/ether (100:1 then 20:1) as the eluent.

General Procedure B



In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar and 0.006 g (0.015 mmol) of (^{Cy}APDI)$CoCH_3$ (**2**). In a separate vial, 0.600 mmol of the corresponding alkyne, 0.064 g (0.500 mmol) of HBPin and 1 mL of THF were mixed. The THF solution of alkyne and HBPin was added to the solid catalyst at 23 °C and the resulting mixture was stirred for 6 hours. The reaction was then quenched by exposing the mixture to air, the solvent was evaporated in vacuo, and the product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes using hexanes/ether (100:1 then 20:1) as the eluent.

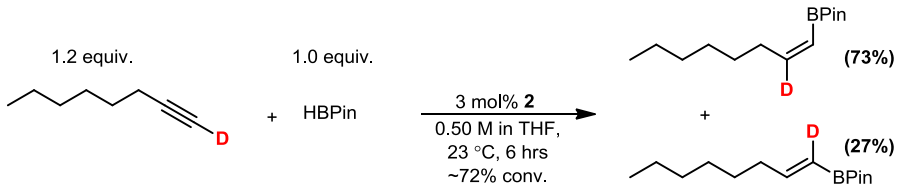
General Procedure C



In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar and 0.009 g (0.023 mmol) of (^{Cy}APDI)$CoCH_3$ (**2**). In a separate vial, 0.900 mmol of the corresponding alkyne and 0.096 g (0.750 mmol) of HBPin were mixed. The mixture of alkyne and HBPin was added to the catalyst at 23 °C and the resulting mixture was stirred for 24 hours. The reaction was then quenched by exposing the mixture to air and the product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes using hexanes/ether (100:1 then 20:1) as the eluent.

IV. Deuterium Labelling Experiments

A. Hydroboration of 1-d_1-1-octyne with HBPin Catalyzed by (^{Cy}APDI)$CoCH_3$ (2)



In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.006 g (0.015 mmol) of (^{Cy}APDI)$CoCH_3$ (**2**) and 1 mL of THF. In a separate vial, 0.067g (0.600 mmol) of 1-d_1-1-octyne and 0.064 g (0.500 mmol) of HBPin were mixed. The 1-d_1-1-octyne/HBPin mixture was added to the stirring solution of the catalyst at 23 °C and the resulting mixture was stirred for 6 hours. The reaction was then quenched by exposing the mixture to air and the volatiles were removed in vacuo. The resulting oil was dissolved in a 10:1 pentane: ether mixture and then passed through a plug of silica gel deactivated with 2% NEt_3 in pentane.. The filtrate was concentrated in vacuo and the resulting clear oil was analyzed by gas chromatography, ^{2}H NMR and quantitative ^{13}C NMR spectroscopies without further purification.

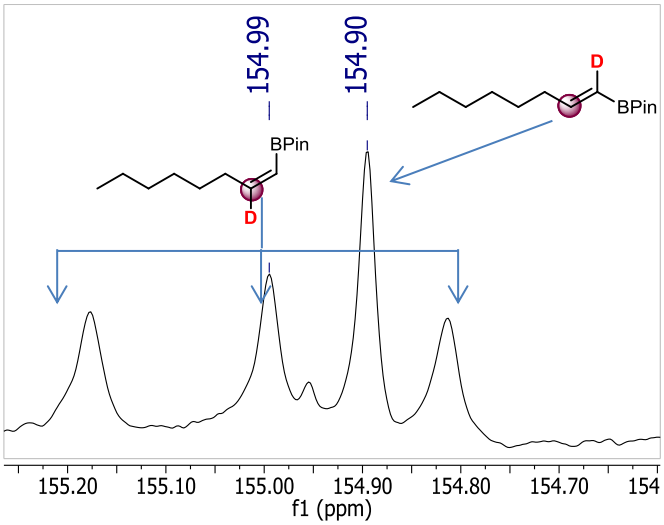
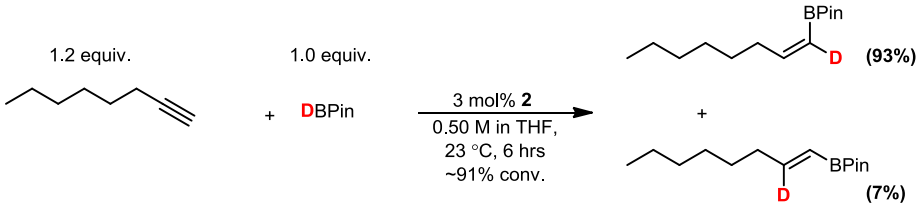


Figure S1. Quantitative ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of the reaction of 1-d_1-1-octyne with HBPin catalyzed by (^{Cy}APDI)$CoCH_3$ (**2**).

B. Deuterioboration of 1-octyne with DBPin Catalyzed by (^{Cy}APDI)$CoCH_3$ (2)



In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.006 g (0.015 mmol) of (^{Cy}APDI)$CoCH_3$ (**2**) and 1 mL of THF. In a separate vial, 0.066g (0.600 mmol) of 1-octyne and 0.065 g (0.500 mmol) of DBPin were mixed. The 1-octyne/DBPin mixture was added to the stirring solution of the catalyst at 23 °C and the resulting mixture was stirred for 6 hours. The reaction was quenched by exposing the mixture to air and the volatiles were removed in vacuo. The resulting oil was dissolved in a 10:1 pentane: ether mixture and then passed through a plug of silica gel deactivated with 2% NEt_3 in pentane. The filtrate was concentrated in vacuo and the resulting clear oil was analyzed by gas chromatography, ^{2}H NMR and quantitative ^{13}C NMR spectroscopies without further purification.

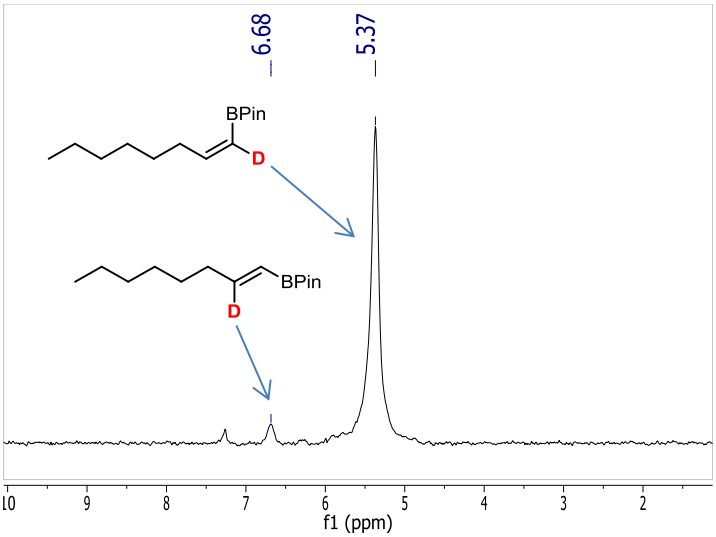
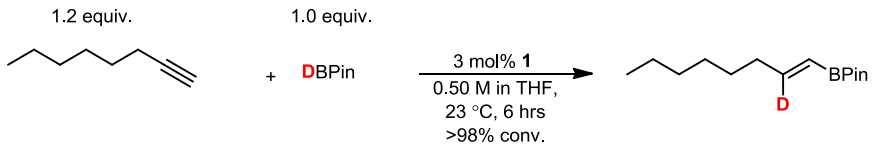


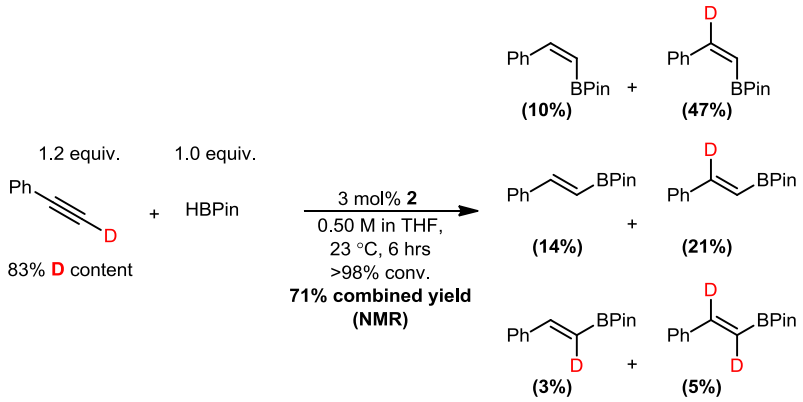
Figure S2. ^{2}H NMR (77 MHz, $CDCl_3$) spectrum of the reaction of 1-octyne with DBPin catalyzed by (^{Cy}APDI)$CoCH_3$ (**2**).

C. Deuterioboration of 1-octyne with DBPin Catalyzed by (^{iPr}PDI)$CoCH_3$ (1)



In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.008 g (0.015 mmol) of (^{iPr}PDI)$CoCH_3$ (**1**) and 1 mL of THF. In a separate vial, 0.066g (0.600 mmol) of 1-octyne and 0.065 g (0.500 mmol) of DBPin were mixed. The 1-octyne/DBPin mixture was added to the stirring solution of the catalyst at 23 °C and the resulting mixture was stirred for 6 hours. The reaction was then quenched by exposing the mixture to air and the volatiles were removed in vacuo. The resulting oil was dissolved in a 10:1 pentane: ether mixture and then passed through a plug of silica gel deactivated with 2% NEt_3 in pentane. The filtrate was concentrated in vacuo and the resulting clear oil was analyzed by gas chromatography, ^{2}H NMR and quantitative ^{13}C NMR spectroscopies without further purification.

D. Hydroboration of phenylacetylene-d_1 with HBPin Catalyzed by (^{Cy}APDI)$CoCH_3$ (2)



In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.006 g (0.015 mmol) of (^{Cy}APDI)$CoCH_3$ (**2**) and 1 mL of THF. In a separate vial, 0.067g (0.600 mmol) of phenylacetylene-d_1 and 0.064 g (0.500 mmol) of HBPin were mixed. The phenylacetylene-d_1/HBPin mixture was added to the stirring solution of the catalyst at 23 °C

and the resulting mixture was stirred for 6 hours. The reaction was then quenched by exposing the mixture to air and the volatiles were removed in vacuo. The resulting oil was dissolved in a 10:1 pentane: ether mixture and then passed through a plug of silica gel deactivated with 2% NEt_3. The filtrate was concentrated in vacuo and the resulting clear oil was analyzed by gas chromatography, ^{2}H NMR and quantitative ^{13}C NMR spectroscopies without further purification.

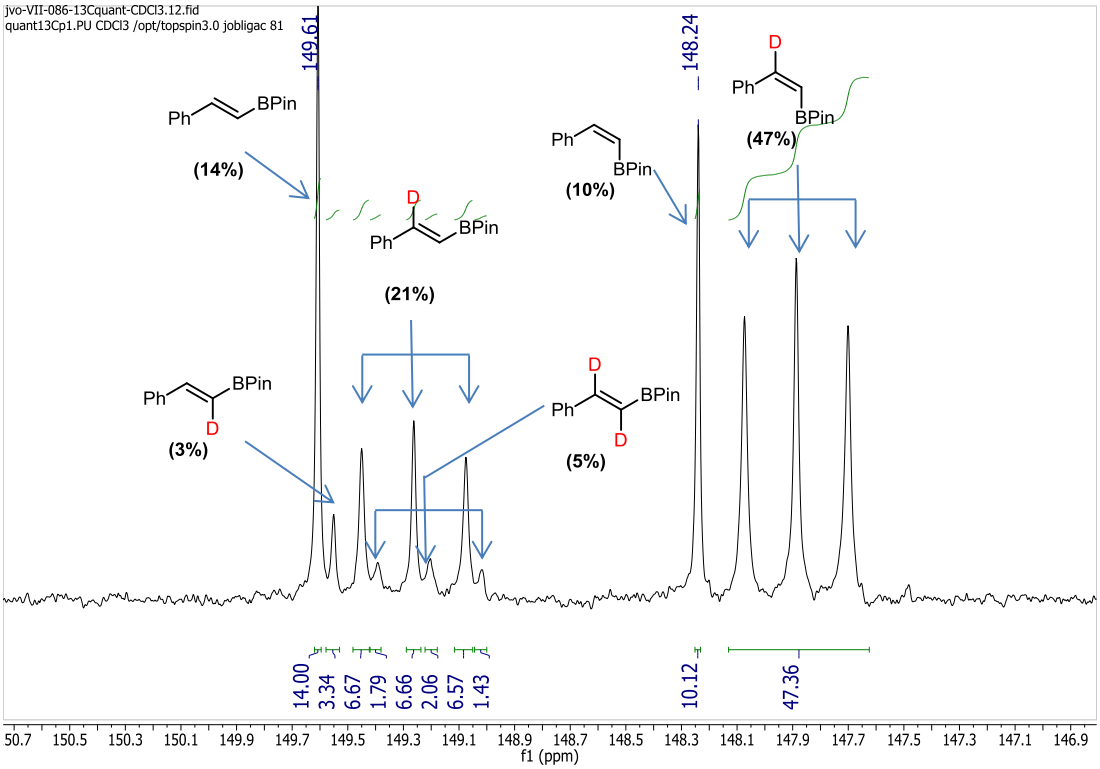


Figure S3. Quantitative ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of the reaction of phenylacetylene-d_1 with HBPin catalyzed by (^{Cy}APDI)$CoCH_3$ (**2**).

V. Isomerization Experiments

A. Hydroboration of 1-octyne with Excess (1.2 equiv.) HBPin Catalyzed by (^{Cy}APDI)$CoCH_3$ (2). In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.006 g (0.015 mmol) of (^{Cy}APDI)$CoCH_3$ (**2**) and 1 mL of THF. In a separate vial, 0.055 g (0.500 mmol) of 1-octyne and 0.077 g (0.600 mmol) of HBPin were mixed. The alkyne/HBPin mixture was added to the stirring solution of the catalyst at 23 °C and the resulting mixture was stirred at 23

°C. Aliquots were taken at different time points and the *Z*/*E* ratio as a function of time was determined using gas chromatography.

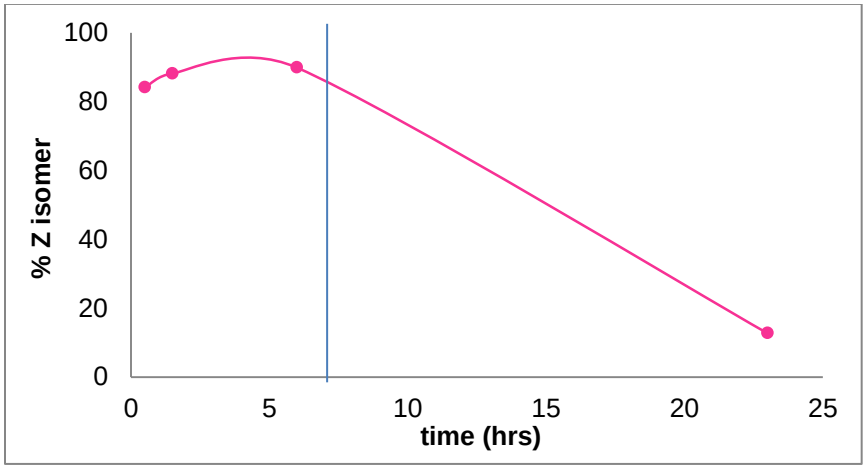


Figure S4. (*Z*)-selectivity as a function of time of the hydroboration of 1-octyne with 1.2 equiv. HBPin catalyzed by (^{Cy}APDI)$CoCH_3$ (**2**). The blue line represents the time at complete conversion of the alkyne.

B. Hydroboration of Phenylacetylene with Excess (1.2 equiv.) DBPin Catalyzed by (^{Cy}APDI)$CoCH_3$ (2). In a nitrogen-filled glovebox, a scintillation vial was charged with a magnetic stir bar, 0.006 g (0.015 mmol) of (^{Cy}APDI)$CoCH_3$ (**2**) and 1 mL of THF. In a separate vial, 0.051 g (0.500 mmol) of phenylacetylene and 0.077 g (0.600 mmol) of HBPin were mixed. The alkyne/HBPin mixture was added to the stirring solution of the catalyst at 23 °C and the resulting mixture was stirred at 23 °C. Aliquots were taken at different time points and the *Z*/*E* ratio as a function of time was analyzed using gas chromatography. After 4 hours, the reaction was quenched by exposing the mixture to air and the product was isolated by column chromatography over silica gel deactivated with 2% NEt_3.

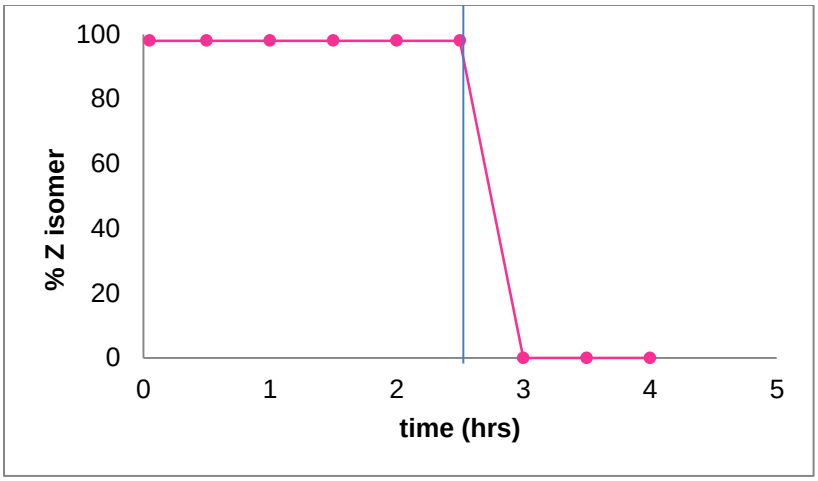


Figure S5. (*Z*)-selectivity as a function of time of the hydroboration of phenylacetylene with 1.2 equiv. DBPin catalyzed by (^{Cy}APDI)$CoCH_3$ (**2**). The blue line represents the time at complete conversion of the alkyne.

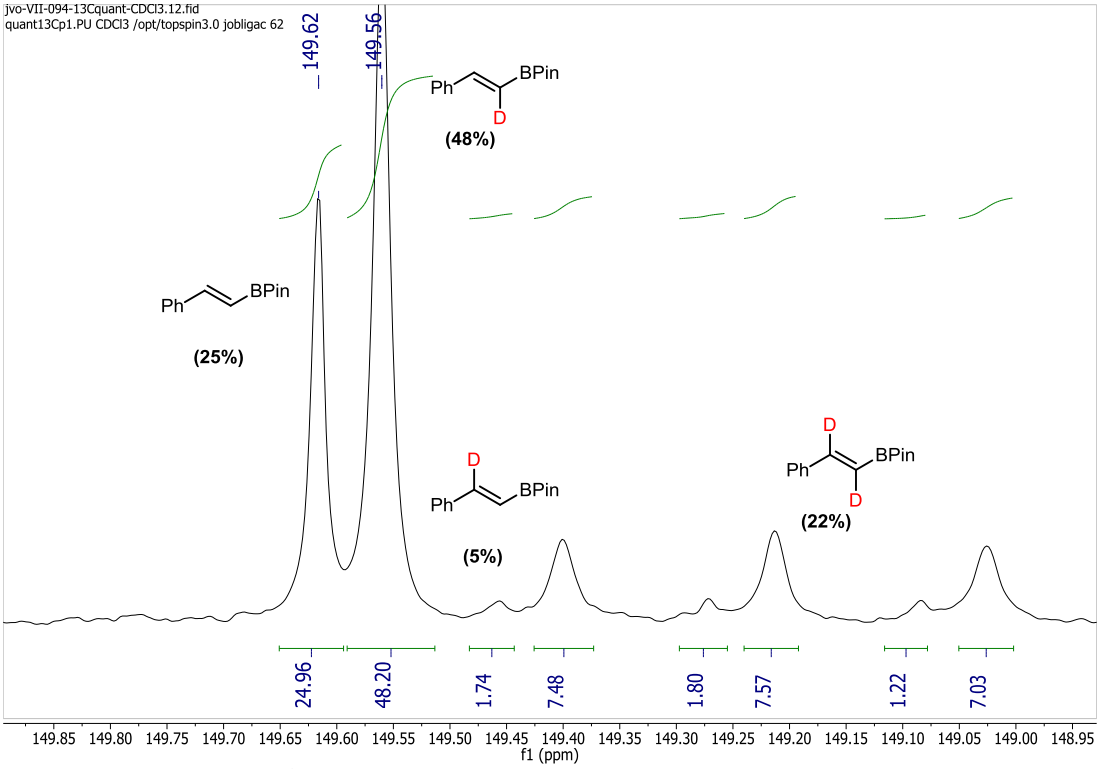


Figure S6. Quantitative ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of the hydroboration of phenylacetylene with 1.2 equiv. DBPin catalyzed by **2**.

V. Stoichiometric Experiments

A. Reaction of (^{Cy}APDI)CoCH$_3$ with HBPin. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.025 g (0.063 mmol) of (^{Cy}APDI)CoCH$_3$ and with 0.5 mL of benzene-d_6. To this solution, 0.008 g (0.063 mmol) of HBPin were added. The resulting brownish-black solution was then filtered through a glass frit and was transferred to a J Young tube and was analyzed by multinuclear spectroscopy.

B. Reaction of (^{Cy}APDI)CoCCPh with H$_2$. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.025 g (0.063 mmol) of (^{Cy}APDI)CoCH$_3$ and with 0.5 mL of benzene-d_6. The resulting solution was transferred to a J Young tube. The tube was degassed then before 1 atm of H$_2$ was admitted to to it. The resulting brown solution was then filtered through a glass frit and was transferred to a J Young tube and was analyzed by multinuclear spectroscopy.

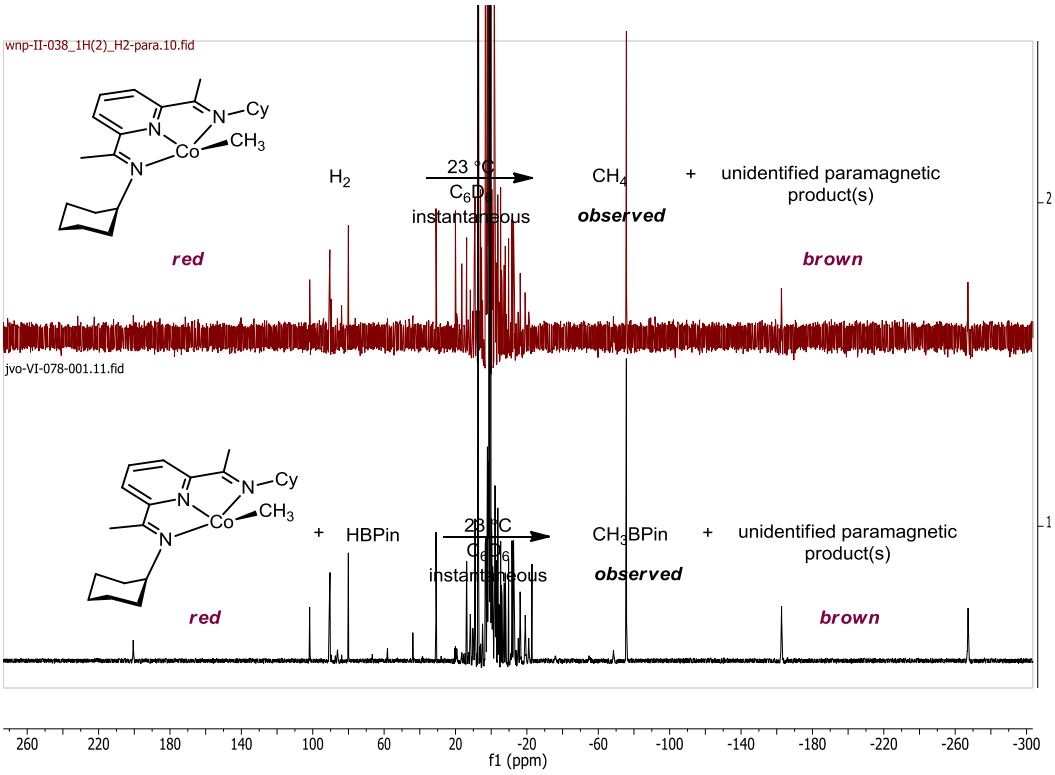


Figure S7. ^{1}H NMR (500 MHz, C$_6$D$_6$, 23 °C) spectrum of (^{Cy}APDI)CoCH$_3$ mixed with H$_2$ (top) and HBPin (bottom).

B. Reaction of (^{Cy}APDI)CoCH$_3$ with Phenyacetylene. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.020 g (0.050 mmol) of (^{Cy}APDI)CoCH$_3$ and with 0.5 mL of benzene-d_6. To this solution, 0.006 g (0.059 mmol) of phenylacetyene were added. Evolution of gas was observed upon addition of the alkyne. The resulting purple solution was then filtered through a glass frit and was transferred to a J Young tube and was analyzed by multinuclear spectroscopy.

Preparation of (^{Cy}APDI)CoCCPh (3). In a nitrogen-filled glovebox, a 50 mL round bottom flask was charged with 0.500 g (1.252 mmol) of (^{Cy}APDI)CoCH$_3$ and 40 mL of diethyl ether. In a separate vial, 0.128 g (1.253 mmol) of phenylacetylene was charged and diluted with 10 mL of diethyl ether. The diethyl ether solution of phenylacetylene was added dropwise to the stirring solution of (^{Cy}APDI)CoCH$_3$ and the solution changed color from red to purple upon addition of the alkyne. The reaction was stirred for 1 hour at 23 °C and the volatiles were removed under reduced pressure. The resulting bluish purple powder was identified as **(^{Cy}APDI)CoCCPh** (0.587 g, 97% yield). Anal Calcd for $C_{29}H_{36}CoN_3$: C, 71.74; H, 7.47; N, 8.65. Found: C, 71.58; H, 7.65; N, 8.56. ^{1}H NMR (500 MHz, C_6D_6, 23 °C): δ 0.41 (s, 6H, (CNC*H*$_3$)), 1.59 – 1.78 (m, 8H, cyclohexyl C*H*), 1.95 (d, *J* =12.05 Hz, 4H, cyclohexyl C*H*), 2.40 (d, *J* = 12.28 Hz, 4H, cyclohexyl C*H*), 3.65 – 3.81 (m, H, cyclohexyl C*H*), 4.69 – 4.81 (m, 2H, NC*H*), 6.69 (d, *J* =7.81 Hz, 2H, py *m-H*), 6.93 (t, *J* =7.41 Hz, 1H, Ph *p-H*), 7.23 (t, *J* = 7.66 Hz, 2H, Ph m-*H*), 7.61 (d, *J* = 7.86 Hz, 2H, Ph *o-H*), 9.25 (t, *J* = 7.61 Hz, 1H, py, *p-H*). {^{1}H}^{13}C NMR (126 MHz, C_6D_6, 23 °C): δ 18.46 ((CN)*C*H$_3$), 26.06 (cyclohexyl *C*), 26.11 (cyclohexyl *C*), 31.12 (cycohexyl *C*), 69.49 (N*C*H), 113.85 (py *p-C*), 124.44 (py, *m-C*), 125.22 (Ph, *p-C*), 128.38 (Ph, *m-C*), 130.81 (Ph, *o-C*), 147.97 (Ph, *i-C*), 148.74 (py, *o-C*), 162.59 ((*C*N)CH$_3$). 2 carbon resonances not located.

Reaction of (^{Cy}APDI)CoCH$_3$ with 1-octyne. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.025 g (0.063 mmol) of (^{Cy}APDI)CoCH$_3$ and with 0.5 mL of benzene-d_6. To this

solution, 0.007 g (0.064 mmol) of 1-octyne was added. Evolution of gas was observed upon addition of the alkyne. The resulting purple solution was then filtered through a glass frit and was transferred to a J Young tube and was analyzed by multinuclear spectroscopy.

Preparation of (^{Cy}APDI)CoCC^{n}Hex (4). In a nitrogen-filled glovebox, a scintillation vial was charged with 0.274 g (0.686 mmol) of (^{Cy}APDI)CoCH$_3$ and 10 mL of diethyl ether. In a separate vial, 0.076 g (0.689 mmol) of 1-octyne was charged and diluted with 5 mL of diethyl ether. The diethyl ether solution of 1-octyne was added dropwise to the stirring solution of (^{Cy}APDI)CoCH$_3$ and the solution changed color from red to purple upon addition of the alkyne. The reaction was stirred for 1 hour at 23 °C and the volatiles were removed under reduced pressure. The resulting purple powder was recrystallized in diethyl ether at -35 °C and was identified as **(^{Cy}APDI)CoCCn-hexyl (4)** (0.206 g, 67% yield). ^{1}H NMR (500 MHz, C_6D_6, 23 °C): δ 0.32 (s, 6H, (CN)C*H*$_3$), 0.88 (t, *J* = 3.34 Hz, 3H, acetylide C*H*$_3$), 1.29 – 1.35 (m, 2H, acetylide C*H*$_2$), 1.54 – 1.59 (m, 2H, acetylide C*H*$_2$), 1.67 – 1.95 (overlapping m, acetylide C*H*$_2$ and cyclohexyl C*H*), 2.01 – 2.09 (m, 4H, cyclohexyl C*H*), 2.38 – 2.45 (m, 4H, cyclohexyl C*H*), 3.43 (t, *J* = 7.34 Hz, 2H, CoCC-C*H*$_2$), 3.77 – 3.87 (m, 4H, cyclohexyl C*H*), 4.78 – 4.85 (m, 2H, NC*H*), 6.72 (d, *J* = 7.69 Hz, 2H, py *m-H*), 9.40 (t, J = 7.74 Hz, 1H, py *p-H*). {^{1}H}^{13}C NMR (126 MHz, C_6D_6, 23 °C): δ 14.44 (acetylide *C*H$_3$), 18.96 ((CN)*C*H$_3$), 23.00 (acetylide *C*H$_2$), 23.24 (CoCC-*C*H$_2$), 26.27 (cyclohexyl *C*), 29.52 (acetylide *C*H$_2$), 31.05 (cyclohexyl *C*), 32.29 (acetylide *C*H$_2$), 32.47 (acetylide *C*H$_2$), 69.86 (N*C*H), 113.05 (py *p-C*), 124.71 (py *m-C*), 149.09 (py *o-C*), 150.55 (CoC*C*-n-hexyl), 162.28 ((*C*N)CH$_3$). One carbon resonance not located.

Reaction of (^{Cy}APDI)CoCCPh with HBPin. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.070 g (0.144 mmol) of (^{Cy}APDI)CoCCPh and with 0.75 mL of C_6D_6. To this solution, 0.018 g (0.142 mmol) of HBPin was added. The resulting deep red solution was then

filtered through a glass frit and was transferred to a J Young tube and was analyzed by multinuclear spectroscopy.

Preparation of (^{Cy}APDI)CoCPhHBPin (5). In a nitrogen-filled glovebox, a 100 mL round bottom flask was charged with 0.250 g (0.515 mmol) of (^{Cy}APDI)CoCCPh and 20 mL of diethyl ether. In a separate vial, 0.066 g (0.515 mmol) of HBPin was charged and diluted with 5 mL of diethyl ether. The diethyl ether solution of HBPin was added dropwise to the stirring solution of (^{Cy}APDI)CoCCPh and the solution changed color from purple to red upon addition of HBPin. The reaction was stirred for 2 hours at 23 °C and the volatiles were removed under reduced pressure. The resulting red powder was recrystallized in a pentane/ trimethylsilane mixture at -35 °C and was identified as an 85:15 mixture of **5-pro-(*E*)** and **5-pro-(*Z*)** (for the reasoning behind the spectroscopic assignments, see section below) in (0.256 g, 81% yield).). Anal Calcd for $C_{35}H_{49}BCoN_3O_2$: C, 68.52; H, 8.05; N, 6.85. Found: C, 68.29; H, 8.29; N, 6.72. ^{1}H NMR (500 MHz, C_6D_6, 23 °C): δ -0.07 (s, 6H, (CN)C*H*$_3$, 5-pro-(*E*)), 0.60 (, 6H, (CN)C*H*$_3$, 5-pro-(*Z*)), 0.73 (s, 12H, pinacol C*H*$_3$, 5-pro-(*E*)), 1.04 (s, 12H, pinacol C*H*$_3$, 5-pro-(*Z*)), 1.18 – 1.77 (overlapping m, 22H, cyclohexyl C*H*, 5-pro-(*E*) and 5-pro-(*Z*)), 1.86 – 1.94 (overlapping m, 6H, cyclohexyl C*H*, 5-pro-(*E*) and 5-pro-(*Z*)), 2.36 – 2.43 (m, 4H, cyclohexyl C*H*, 5-pro-(*Z*)), 2.45 – 2.57 (m, 2H, cyclohexyl C*H*, 5-pro-(*E*)), 2.60 – 2.68 (m, 2H, cyclohexyl C*H*, 5-pro-(*E*)), 2.78 -2.91 (m, 2H, cyclohexyl C*H*, 5-pro-(*E*)), 2.97 – 3.04 (m, 2H, cyclohexyl C*H*, 5-pro-(*E*)), 4.50 – 4.57 (m, 2H, NC*H*, 5-pro-(*Z*)), 5.80 (s, 1H, vinyl C*H*, 5-pro-(*Z*)), 6.26 (d, *J* = 7.45 Hz, 2H, Ph *o-H*, 5-pro-(*E*)), 6.44 -6.52 (m, 2H, NC*H*, 5-pro-(*E*)), 6.55 (d, *J* = 7.50 Hz, 1H, Ph *p-H*, 5-pro-(*Z*)), 6.68 – 6.75 (overlapping m, 6H, Ph *m-H*, 5-pro-(*E*), Ph *o-H*, 5-pro-(*Z*) and Ph *m-H*, 5-pro-(*Z*)), 6.77 -6.83 (overlapping m, Ph *p-H* and vinyl C*H*, 5-pro-(*E*)), 6.89 (d, *J* = 7.49 Hz, 2H, py *m-H*, 5-pro-(*Z*)), 7.36 (d, *J* = 7.74 Hz, 2H, py m-*H*, 5-pro-(*E*)), 8.22 (t, *J* = 7.74 Hz, 1H, py *p-H*, 5-pro-(*Z*)), 9.84 (t, *J* = 7.64 Hz, 1H, py *p-H*, 5-pro-(*E*)). {^{1}H}^{13}C NMR (126 MHz, C_6D_6, 23 °C): δ 17.77 ((*C*N)CH$_3$, 5-pro-(*Z*)), 23.50 ((*C*N)CH$_3$, 5-pro-(*E*)), 24.81 (pinacol *C*H$_3$, 5-pro-(*E*)), 24.92 (pinacol *C*H$_3$, 5-pro-

(*Z*)), 25.89 (cyclohexyl *C*, 5-pro-(*Z*)), 26.59 (cyclohexyl *C*, 5-pro-(*E*)), 26.86 (cyclohexyl *C*, 5-pro-(*E*)), 27.31 (cyclohexyl *C*, 5-pro-(*E*)), 28.26 (cyclohexyl *C*, 5-pro-(*E*)), 30.29 (cyclohexyl *C*, 5-pro-(*E*)), 30.62 (cyclohexyl *C*, 5-pro-(*Z*)), 34.46 (cyclohexyl *C*, 5-pro-(*Z*)), 68.20 (N*C*H, 5-pro-(*Z*)), 72.33 (N*C*H, 5-pro-(*E*)), 81.58 (pinacol quat. *C*, 5-pro-(*Z*)), 82.41 (pinacol quat. *C*, 5-pro-(*E*)), 112.18 (py *p-C*, 5-pro-(*Z*)), 114.24 (py *p-C*, 5-pro-(*E*)), 118.22 (vinyl *C*H, 5-pro-(*E*)), 121.75 (Ph *m-C*, 5-pro-(*Z*)), 122.97 (py *m-C*, 5-pro-(*Z*)), 123.18 (py *m-C*, 5-pro-(*E*)), 123.53 (Ph *p-C*, 5-pro-(*Z*)), 125.91 (Ph *p-C*, 5-pro-(*E*)), 126.33 (Ph *o-C*, 5-pro-(*E*)), 126.55 (Ph *o-C*, 5-pro-(*Z*)), 127.23 (Ph *m-C*, 5-pro-(*E*)), 144.81 (py *o-C*, 5-pro-(*Z*)), 147.57 (Ph *i-C*, 5-pro-(*E*)), 148.92 (Ph *i-C*, 5-pro-(*Z*)), 152.75 (py *o-C*, 5-pro-(*E*)), 156.35 ((*C*N)CH_3, 5-pro-(*Z*)), 160.44 ((*C*N)CH_3, 5-pro-(*E*)).

Structural characterization of the isomers of (^{Cy}APDI)CoCPhHBPin (5) by HMBC. In the HMBC of the mixture of the 2 isomers of **5**, the vinyl proton of the minor isomer displayed a strong correlation peak to the *ipso* carbon of the phenyl ring indicating a ^3J *trans* coupling across the double bond. However, the vinyl proton of the major isomer displayed a very weak correlation peak to the *ipso* carbon of the phenyl ring indicating a ^3J *cis* coupling across the double bond. These disproportionate intensities of the ^{3}J through-olefinic-bond HMBC connectivities clearly establish that the major component (85%) is **5-Pro-(*E*)** and the minor component (15%) is **5-Pro-(*Z*)**.

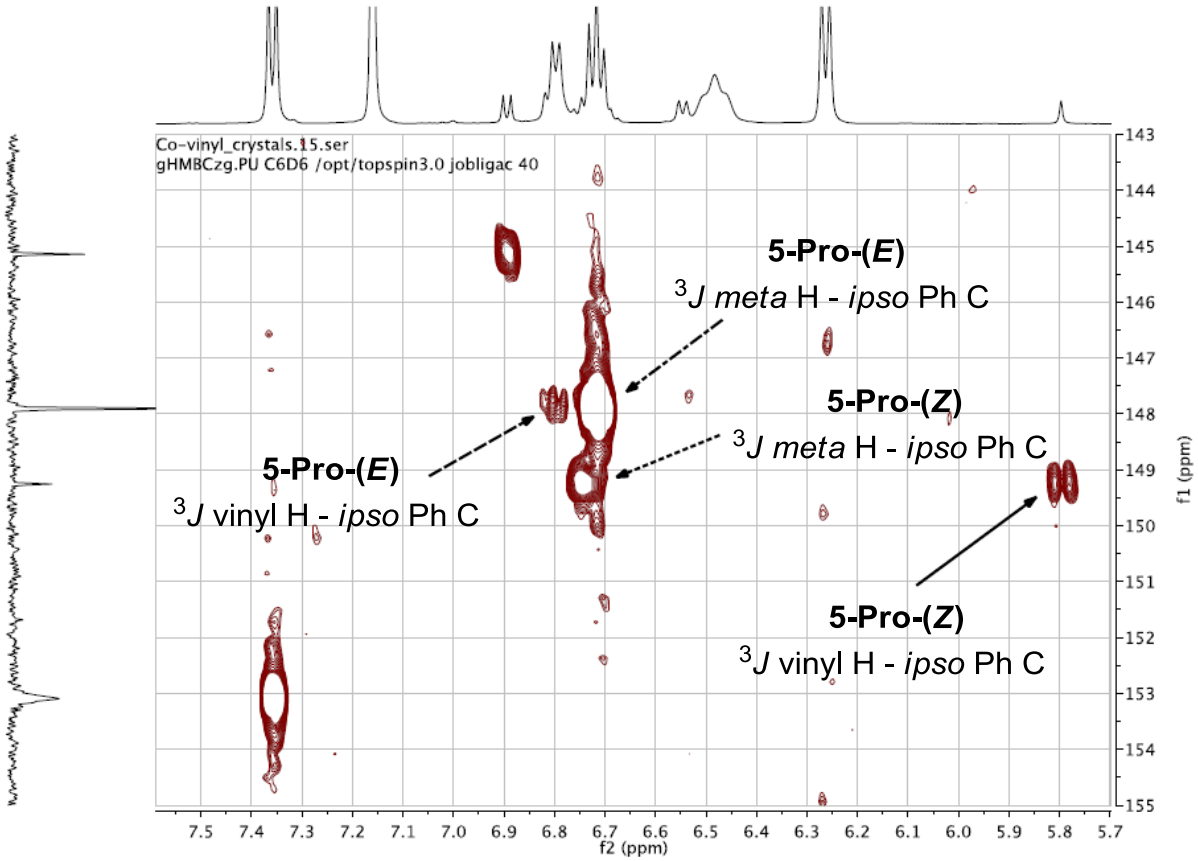


Figure S8. HMBC (C_6D_6, 23 °C) of 85:15 mixture of **5-pro-(*E*)** and **5-pro-(*Z*)**.

Reaction of an 85 : 15 mixture of 5-pro-(*E*) and 5-pro-(*Z*) with DCl. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.070 g (0.114 mmol) of (^{Cy}APDI)CoCPhHBPin (5) and with 0.75 mL of C_6D_6. The resulting solution was transferred to a J Young tube. Analysis by ^{1}H NMR revealed an 85:15 mixture of 5-pro-(*E*) and 5-pro-(*Z*). The tube was then degassed before excess DCl gas (1.0 M in diethyl ether) was admitted. Upon warming of the solution, immediate formation of a green precipitate, identified as (^{Cy}APDI)$CoCl_2$, was observed. The mixture was exposed to air and the contents of the J Young tube were transferred to a scintillation vial containing 10 mL of diethyl ether. The resulting suspension was filtered through a glass frit to remove (^{Cy}APDI)$CoCl_2$ and then the filtrate was collected. Analysis of an aliquot of the filtrate by GC revealed an 80 : 20 mixture of (*E*):(*Z*)-vinylboronates. The rest of the filtrate

was evaporated to dryness and was analyzed by ^{1}H, ^{2}H, and quantitative ^{13}C NMR spectroscopies.

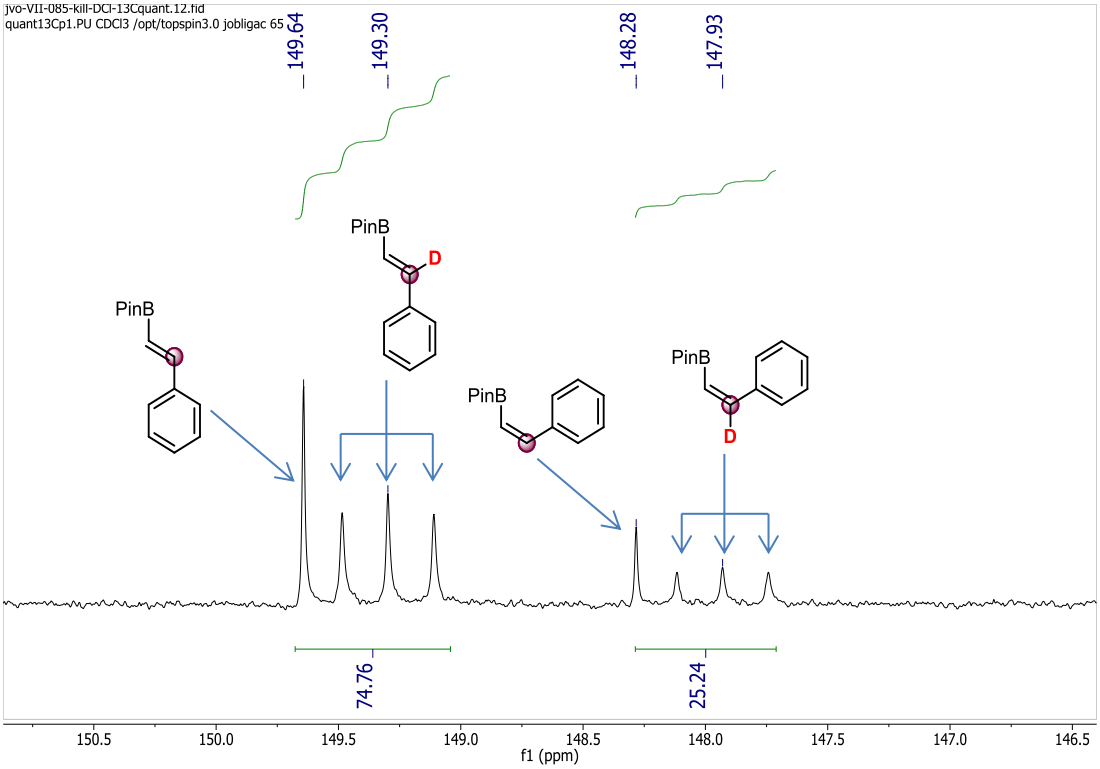


Figure S9. Quantitative ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of the reaction of an 85 : 15 mixture of 5-pro-(*E*) and 5-pro-(*Z*) with DCl.

Reaction of an 85 : 15 mixture of 5-pro-(*E*) and 5-pro-(*Z*) with 1 equiv. of Phenylacetylene. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.012 g (0.020 mmol) of (^{Cy}APDI)CoCPhHBPin (**5**) and with 0.75 mL of C_6D_6. The resulting solution was transferred to a J Young tube. Analysis by ^{1}H NMR revealed an 85:15 mixture of 5-pro-(*E*) and 5-pro-(*Z*). Phenylacetylene (0.002 g, 0.020 mmol) was added to the J Young tube and the color of the solution immediately changed from deep red to purple. The mixture was analyzed by ^{1}H NMR spectroscopy.

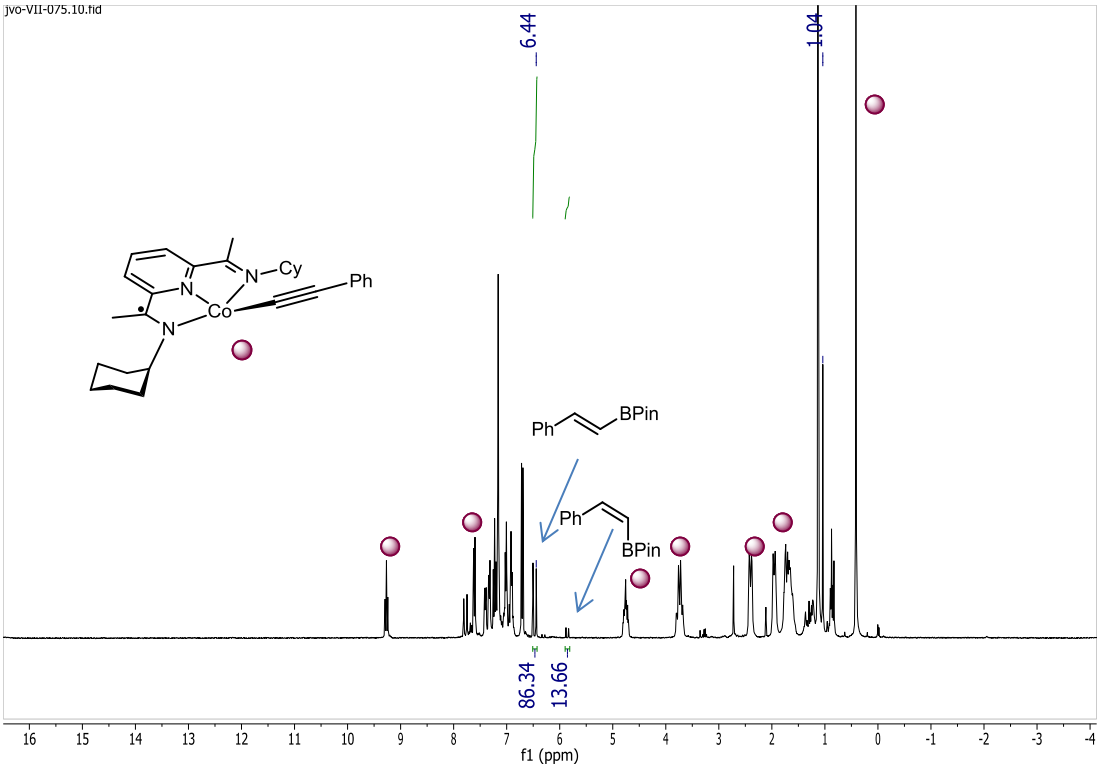


Figure S10. ^{1}H NMR (500 MHz, C_6D_6, 23 °C) spectrum of the reaction of an 85 : 15 mixture of 5-pro-(*E*) and 5-pro-(*Z*) with 1 equiv. of phenylacetylene.

Reaction of an 85 : 15 mixture of 5-pro-(*E*) and 5-pro-(*Z*) with 1 equiv. of 1-octyne. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.028 g (0.046 mmol) of (^{Cy}APDI)CoCPhHBPin (**5**) and with 0.75 mL of C_6D_6. The resulting solution was transferred to a J Young tube. Analysis by ^{1}H NMR revealed an 85:15 mixture of 5-pro-(*E*) and 5-pro-(*Z*). 1-octyne (0.005 g, 0.046 mmol) was added to the J Young tube and the tube was rotated using for 3 hours. The color of the solution gradually changed from deep red to purple. The mixture was analyzed by ^{1}H NMR spectroscopy.

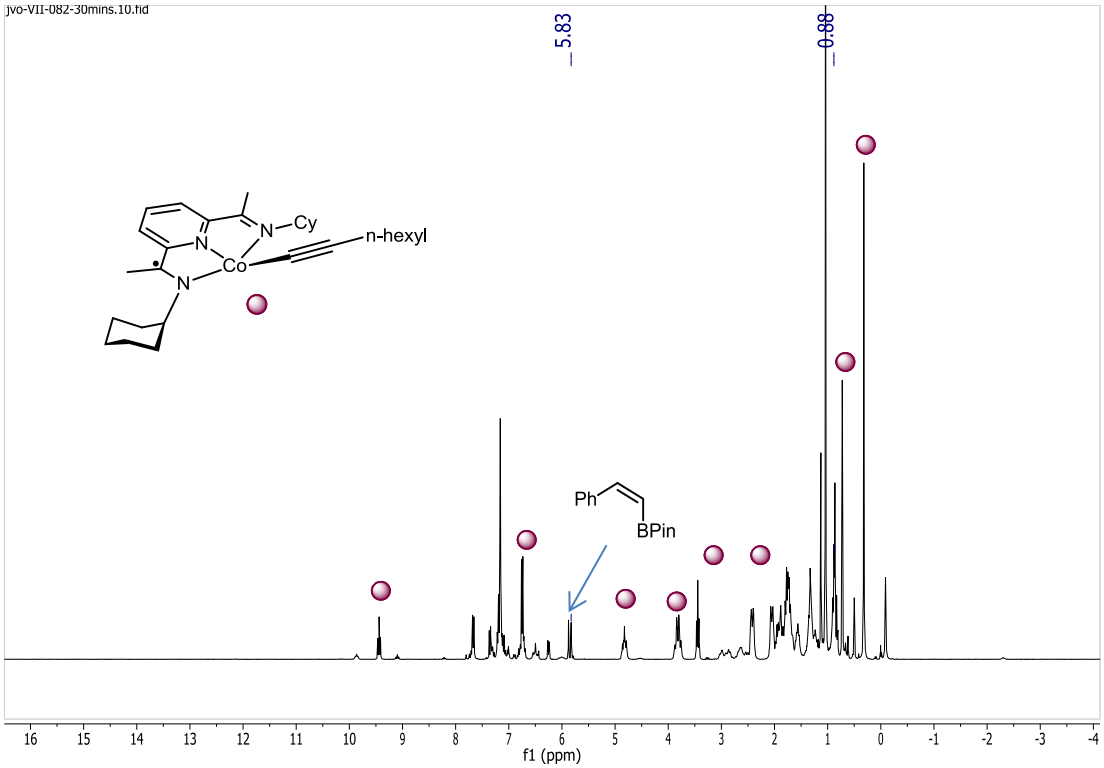


Figure S11. ^{1}H NMR (500 MHz, C_6D_6, 23 °C) spectrum of the reaction of an 85:15 mixture of 5-pro-(*E*) and 5-pro-(*Z*) with 1 equiv. of 1-octyne.

Reaction of an 85:15 mixture of 5-pro-(*E*) and 5-pro-(*Z*) with 0.5 equiv. of Phenylacetylene. In a nitrogen-filled glovebox, a scintillation vial was charged with 0.024 g (0.040 mmol) of (^{Cy}APDI)CoCPhHBPin (**5**) and with 0.75 mL of C_6D_6. The resulting solution was transferred to a J Young tube. Analysis by ^{1}H NMR revealed an 85 : 15 mixture of 5-pro-(*E*) and 5-pro-(*Z*). Phenylacetylene (0.002 g, 0.020 mmol) was added to the J Young tube and the color of the solution immediately changed from deep red to violet. The mixture was analyzed by ^{1}H NMR spectroscopy.

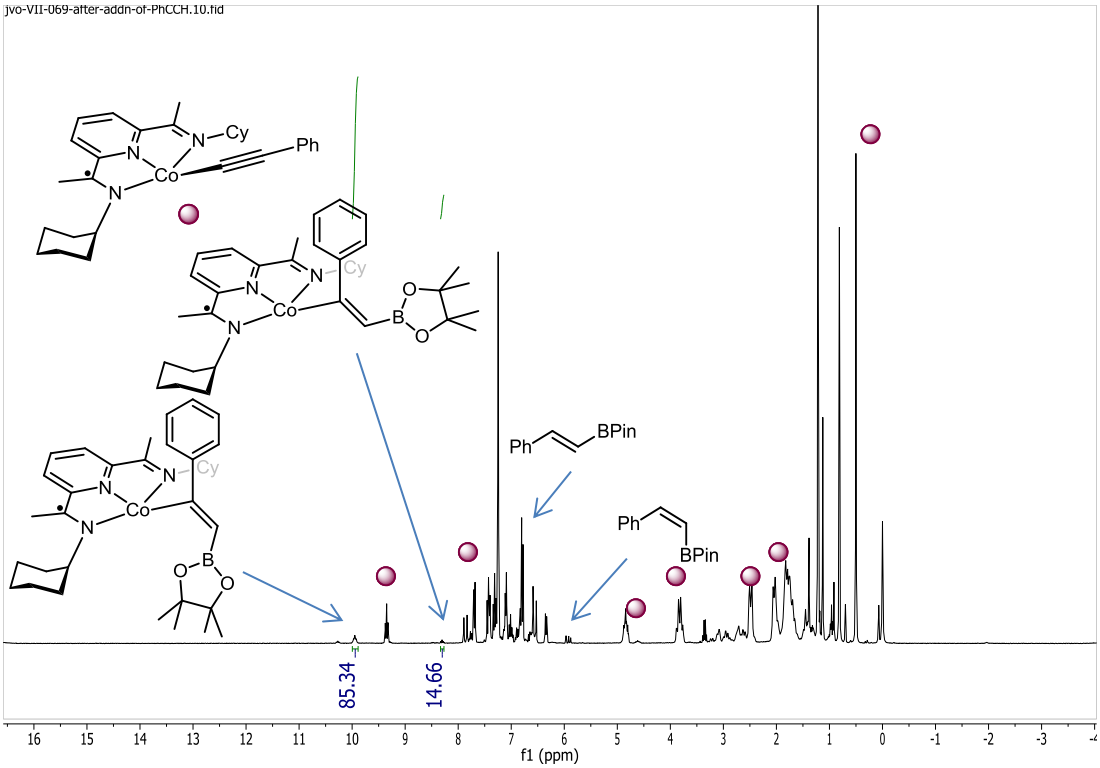


Figure S12. ^{1}H NMR (500 MHz, C_6D_6, 23 °C) spectrum of the reaction of an 85 : 15 mixture of 5-pro-(*E*) and 5-pro-(*Z*) with 0.5 equiv. of phenylacetylene.

Reaction of (^{Cy}APDI)CoCH$_3$ with PhCCBPin and HBPin.

In a nitrogen-filled glovebox, a scintillation vial was charged with 0.020 g (0.050 mmol) of (^{Cy}APDI)CoCH$_3$ (**2**) and 0.011 g (0.050 mmol) of PhCCBPin, In a separate vial, 0.006 g (0.050 mmol) of HBPin was mixed with 0.5 mL of C_6D_6. The C_6D_6 solution of HBPin was added to the vial containing the (^{Cy}APDI)CoCH$_3$ and PhCCBPin. The resulting red solution was transferred to a J Young tube. The mixture was analyzed by ^{1}H NMR spectroscopy.

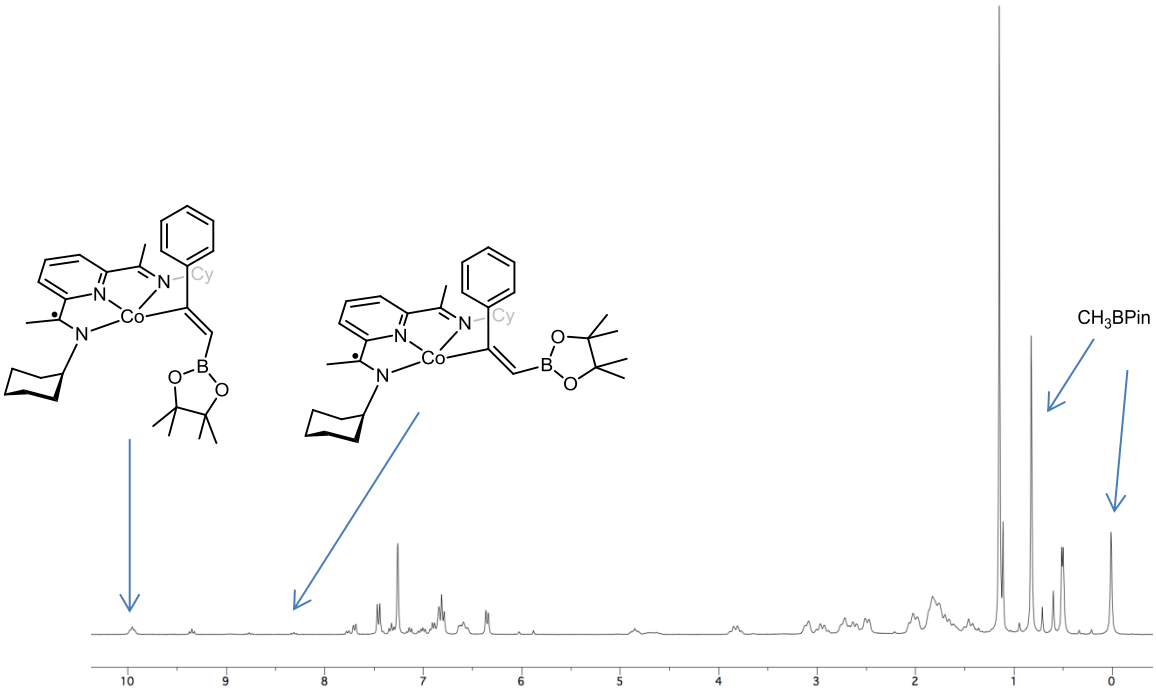
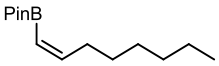
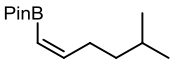


Figure S13. ^{1}H NMR (500 MHz, C_6D_6, 23 °C) of the reaction of (^{Cy}APDI)$CoCH_3$ with PHCCBPin and HBPin.

VI. Characterization of (Z)-Vinyl BPin Products

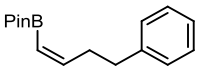


(**2a**): The title compound was isolated as a clear liquid (92% *Z* selectivity) in 67% yield (0.079 g) using **General Procedure A**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 0.86 (t, *J* = 6.61 Hz, 3H), 1.24 (s, 12H), 1.25 – 1.40 (m, 8H), 2.36 (q, *J* = 7.40 Hz, 2H), 5.30 (dt, *J* = 13.72, 1.21 Hz, 1H), 6.40 (dt, *J* = 13.71, 7.32 Hz, 1H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 14.22, 22.71, 24.92, 28.82, 29.50, 31.75, 32.27, 82.85, 155.36. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[6]

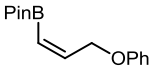


(**2b**): The title compound was isolated as a clear liquid (97% *Z* selectivity) in 79% yield (0.088 g) using **General Procedure A**.. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 0.87 (d, *J* = 6.68 Hz, 6H), 1.24 (s, 14H), 1.54 (septet, *J* = 6.76 Hz, 1H), 2.36 – 2.41 (m, 2H), 5.29 (dt, *J* = 13.50, 1.18 Hz, 1H), 6.41 (dt, *J* = 13.39, 7.63 Hz, 1H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ

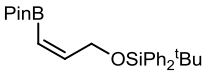
22.61, 24.95, 27.63, 30.35, 38.91, 82.85, 155.55. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[6]



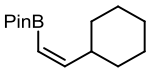
(**2c**): The title compound was isolated as a clear liquid (97% *Z* selectivity) in 91% yield (0.118 g) using **General Procedure A**.. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.27 (s, 12H), 2.69 – 2.78 (m, 4H), 5.40 (d, *J* = 13.46 Hz, 1H), 6.50 (dt, *J* = 13.48, 7.13 Hz, 1H), 7.16 – 7.32 (m, 5H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 24.93, 34.02, 36.12, 82.89, 125.77, 128.27, 128.61, 142.01, 153.90.



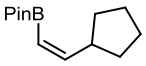
(**2d**): The title compound was isolated as a colorless oil (>98% *Z* selectivity) in 51% yield (0.066 g) using **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.29 (s, 12H), 4.90 (dd, *J* = 5.91, 1.76 Hz, 2H), 5.61 (dt, *J* = 13.97, 1.80 Hz, 1H), 6.62 (dt, *J* = 13.94, 5.89 Hz, 2H), 6.92 – 6.99 (m, 3H), 7.25 – 7.30 (m, 2H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 25.02, 67.66, 83.55, 114.96, 120.74, 129.51, 149.50, 158.78. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[6]



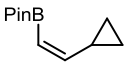
(**2e**): The title compound was isolated as a clear liquid (98% *Z* selectivity) in 72% yield (0.153 g) using **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.06 (s, 9H), 1.15 (s, 12H), 4.57 (dd, *J* = 6.0, 1.5 Hz, 2H), 5.39 (dt, *J* = 14.0, 1.5 Hz, 1H), 6.62 (dt, *J* = 14.0, 6.0 Hz, 1H), 7.36 – 7.42 (m, 6H), 7.69 – 7.71 (m, 4H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 153.7, 135.7, 134.1, 129.6, 127.7, 83.2, 64.3, 27.0, 24.9, 19.4.



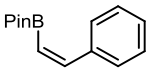
(**2g**): The title compound was isolated as a pale yellow liquid (92% *Z* selectivity) in 59% yield (0.104 g) using **General Procedure C**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.02 – 1.34 (m, 6H), 1.26 (s, 12H), 1.62 – 1.72 (m, 4H), 2.66 – 2.74 (m, 1H), 5.22 (dd, *J* = 13.5, 0.5 Hz, 1H), 6.25 (dd, *J* = 13.5, 9.5 Hz, 1H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 24.9, 25.9, 26.1, 33.5, 40.7, 82.9, 160.8. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[7]



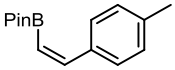
(**2h**): The title compound was isolated as a pale yellow liquid (84% *Z* selectivity) in 61% yield (0.102 g) using **General Procedure C**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.28 (s, 12H), 1.56 – 1.71 (m, 6H), 1.80 – 1.86 (m, 2H), 3.14 – 3.22 (m, 1H), 5.24 (dd, *J* = 13.5, 0.5 Hz, 1H), 6.33 (dd, *J* = 13.0, 9.5 Hz, 1H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 24.9, 25.9, 33.9, 42.7, 82.9, 160.3. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[6]



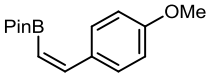
(**2i**): The title compound was isolated as a pale yellow liquid (56% *Z* selectivity) in 56% yield (0.082 g) using **General Procedure C**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 0.43 – 0.46 (m, 2H), 0.84 – 0.87 (m, 2H), 1.30 (s, 12H), 2.28 – 2.35 (m, 1H), 5.21 (d, *J* = 13.5 Hz, 1H), 5.69 (dd, *J* = 13.0, 11.0 Hz, 1H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 8.2, 14.6, 25.0, 82.9, 159.8. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[6]



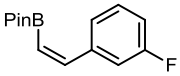
(**2j**): The title compound was isolated as a pale yellow oil (95% *Z* selectivity) in 83% yield (0.095 g) using **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.22 (s, 12H), 5.52 (d, *J* = 14.92 Hz, 1H), 7.12 – 7.29 (m, 4H), 7.46 (d, *J* = 7.48 Hz, 2H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 24.92, 83.61, 128.05, 128.13, 128.73, 138.57, 148.27. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[6]



(**2k**): The title compound was isolated as a pale yellow oil (95% *Z* selectivity) in 76% yield (0.093 g) using **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.30 (s, 12H), 2.35 (s, 3H), 5.53 (d, *J* = 14.79 Hz, 1H), 7.12 (d, *J* = 7.99 Hz, 2H), 7.18 (d, *J* = 14.26 Hz, 1H), 7.46 (d, *J* = 8.18 Hz, 2H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 21.44, 24.94, 83.55, 128.76, 135.76, 138.07, 148.32. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[8]



(**2l**): The title compound was isolated as a yellow liquid (87% *Z* selectivity) in 41% yield (0.053 g) using **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.30 (s, 12H), 3.82 (s, 3H), 5.46 (d, *J* = 15.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 25.0, 55.4, 83.5, 113.4, 131.4, 130.4, 148.2, 159.7. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[7]



(**2m**): The title compound was isolated as a pale yellow oil (>98% *Z* selectivity) in 69% yield (0.086 g) using **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 1.22 (s, 12H), 5.58 (d, *J* = 14.77 Hz, 1H), 6.86 – 6.90 (m, 1H), 7.09 (d, *J* = 14.83 Hz, 1H), 7.14 – 7.21 (m, 2H), 7.31 (dt, *J* = 10.55, 1.83 Hz, 1H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 24.91, 83.81, 114.85, 115.02, 115.05, 115.22, 124.80, 124.82, 129.44, 129.51, 140.74, 140.80, 146.88, 146.90, 161.80, 163.74.

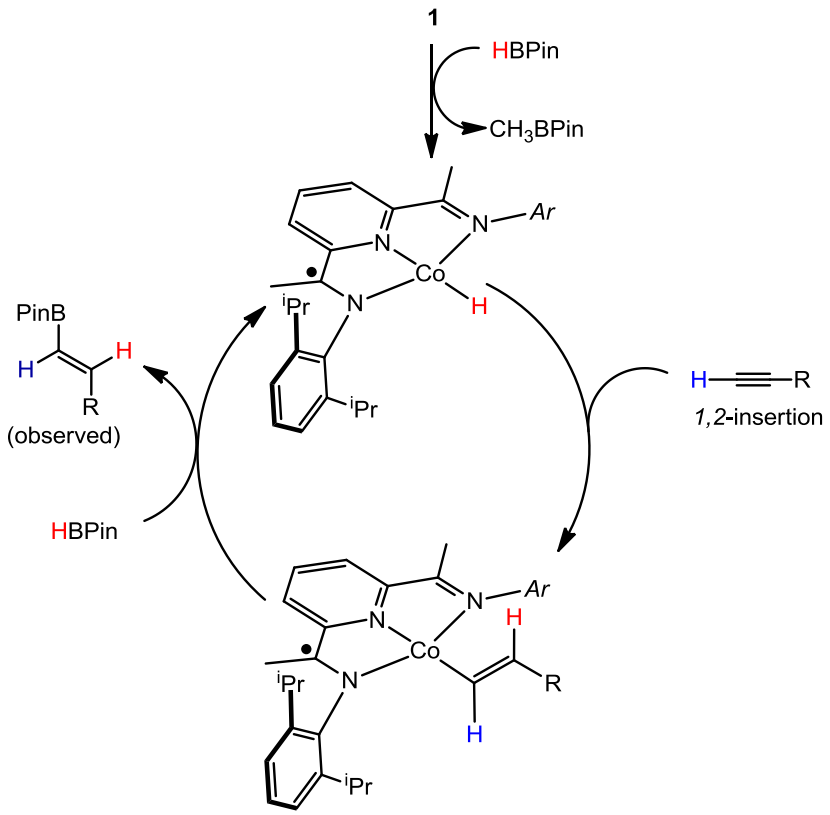


Figure S14. Proposed mechanism for (E)-selective terminal alkyne hydroboration with **1**.

VII. NMR Spectra of Hydroboration Products

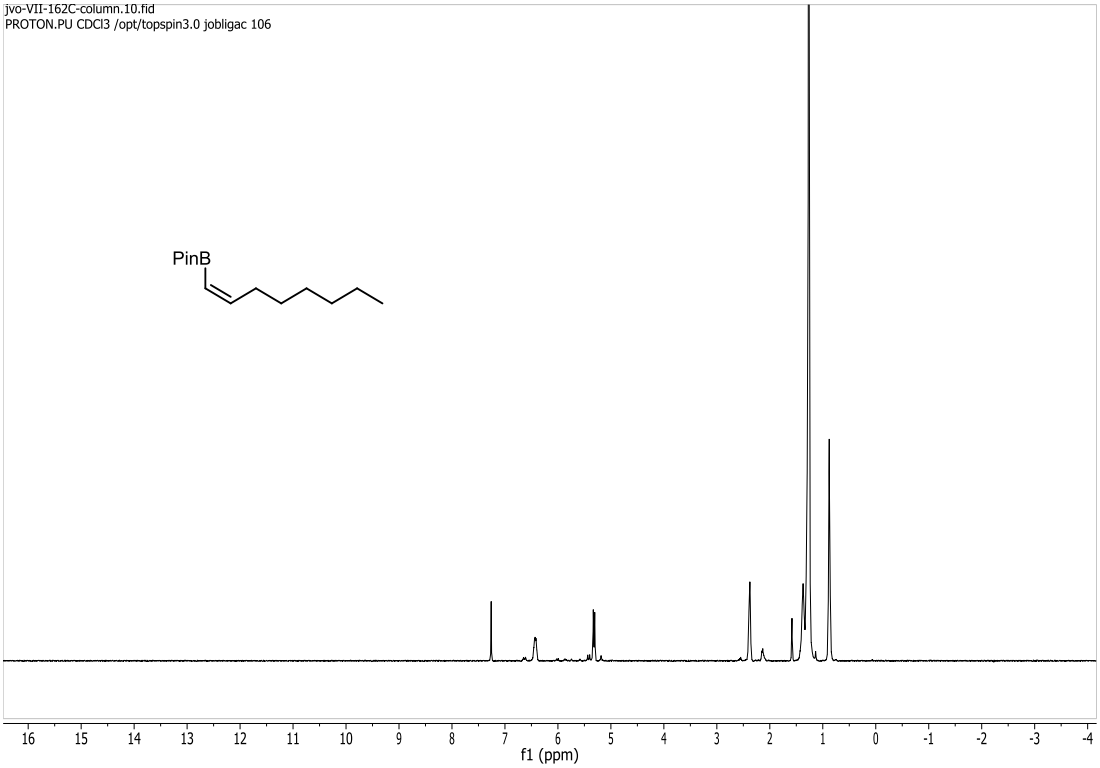


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2a**.

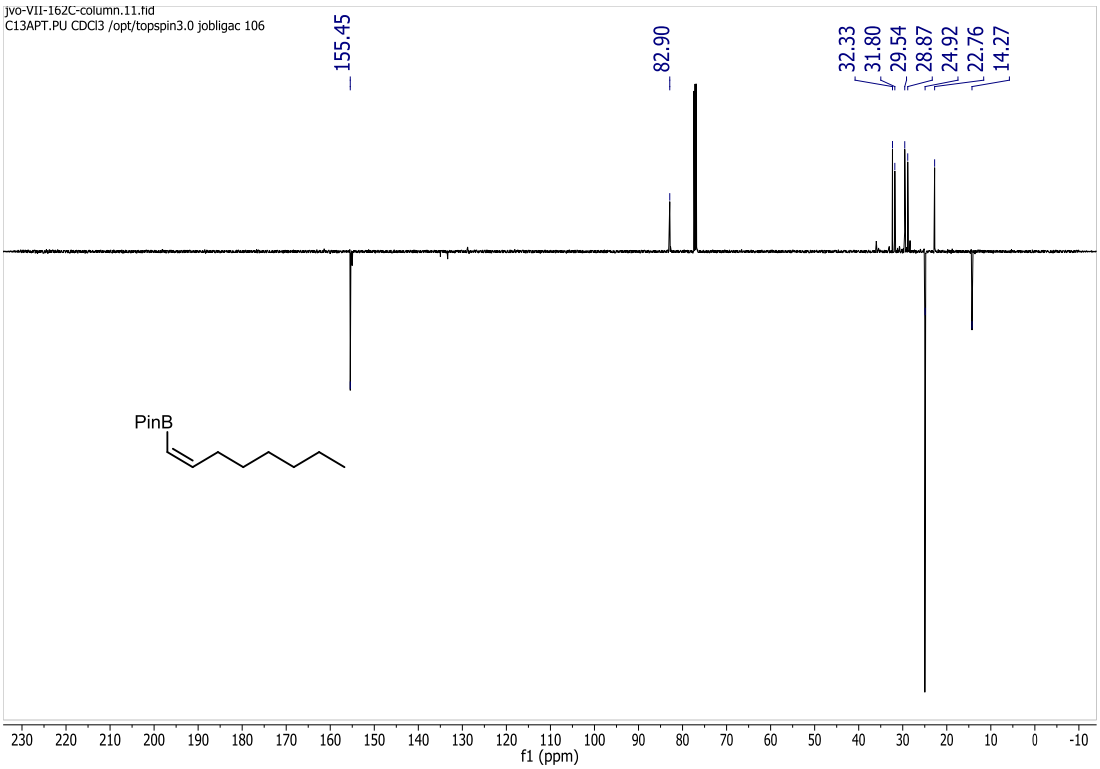


Figure S16. {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2a**.

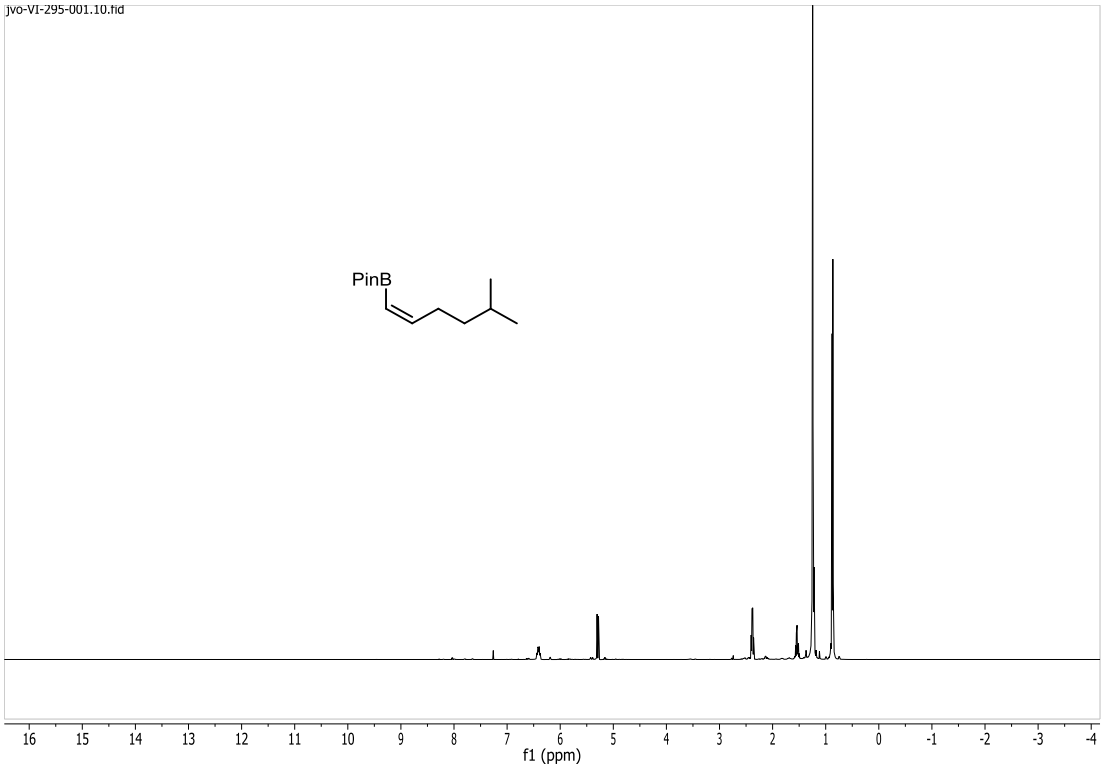


Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2b**.

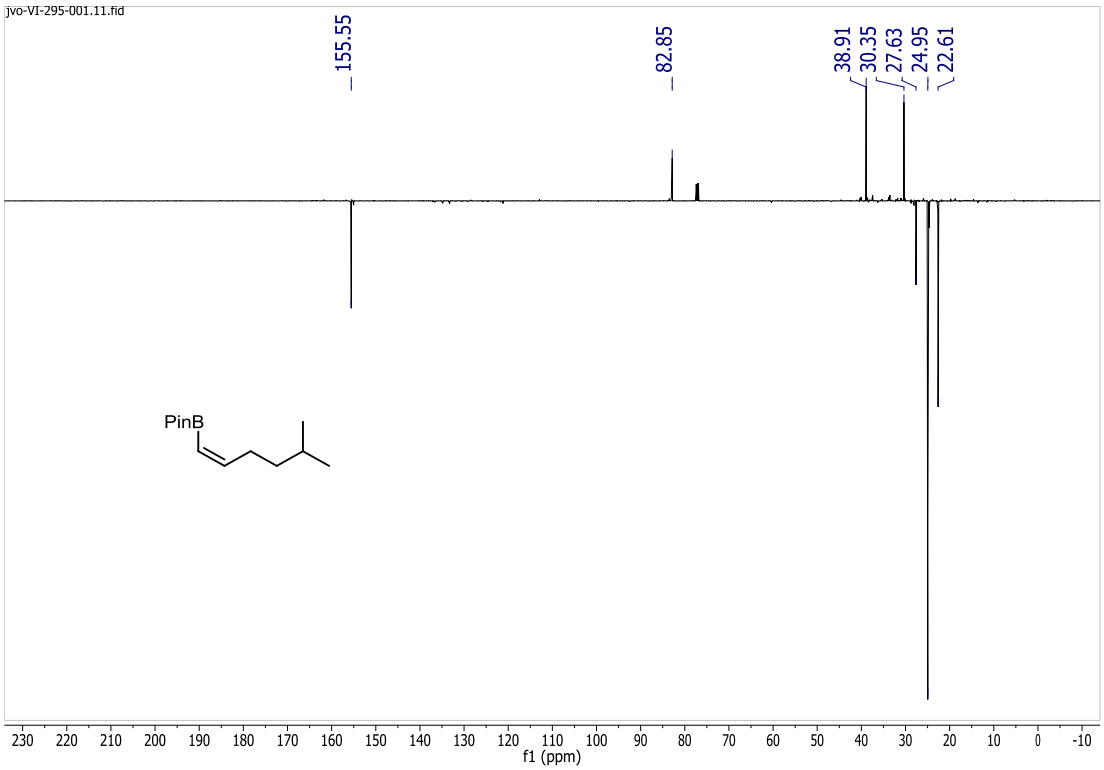


Figure S18. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2b**.

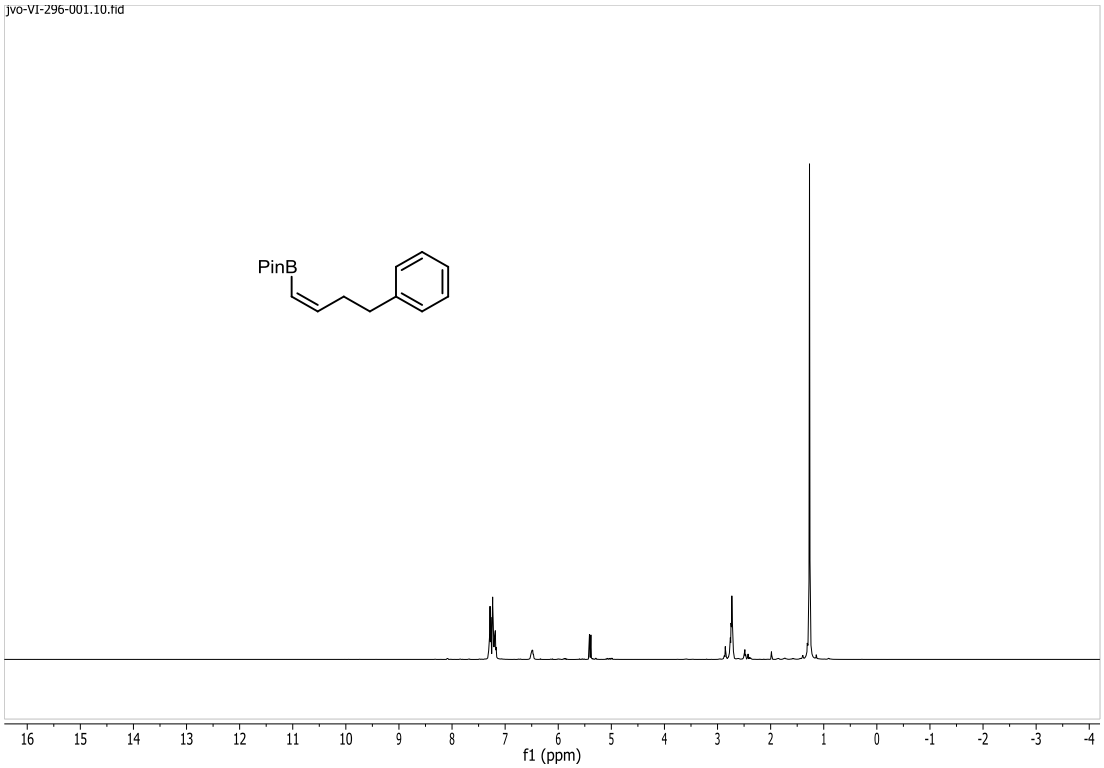


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2c**.

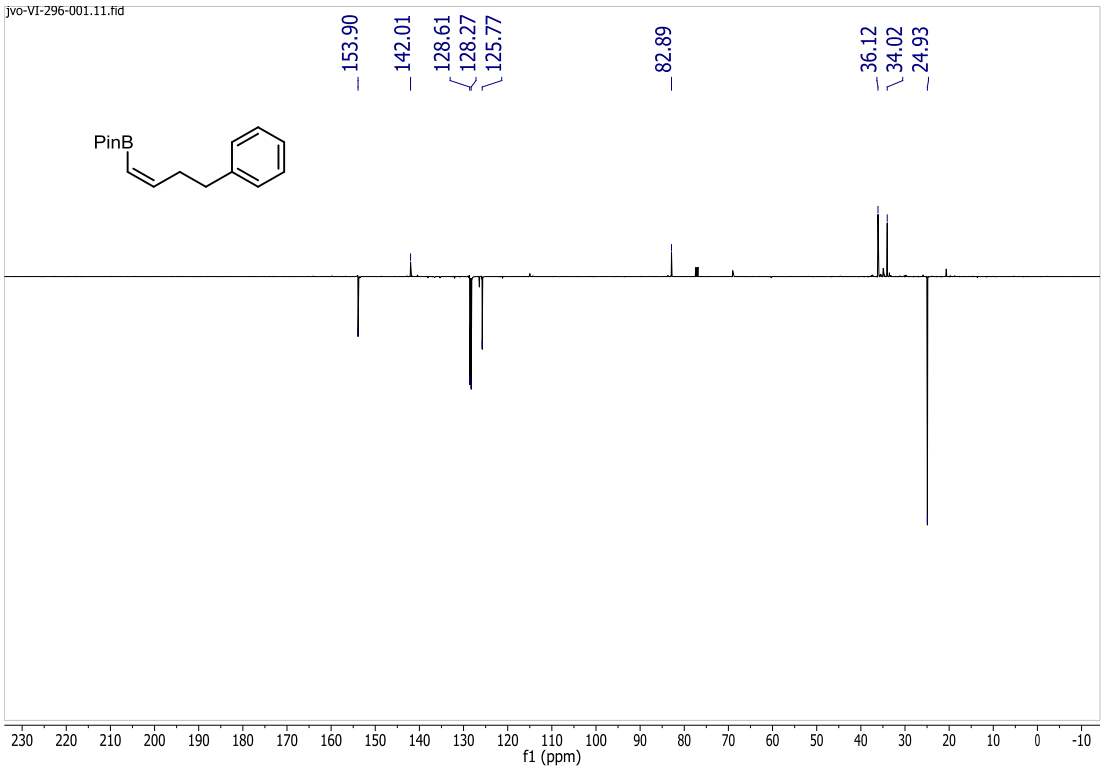


Figure S20. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2c**.

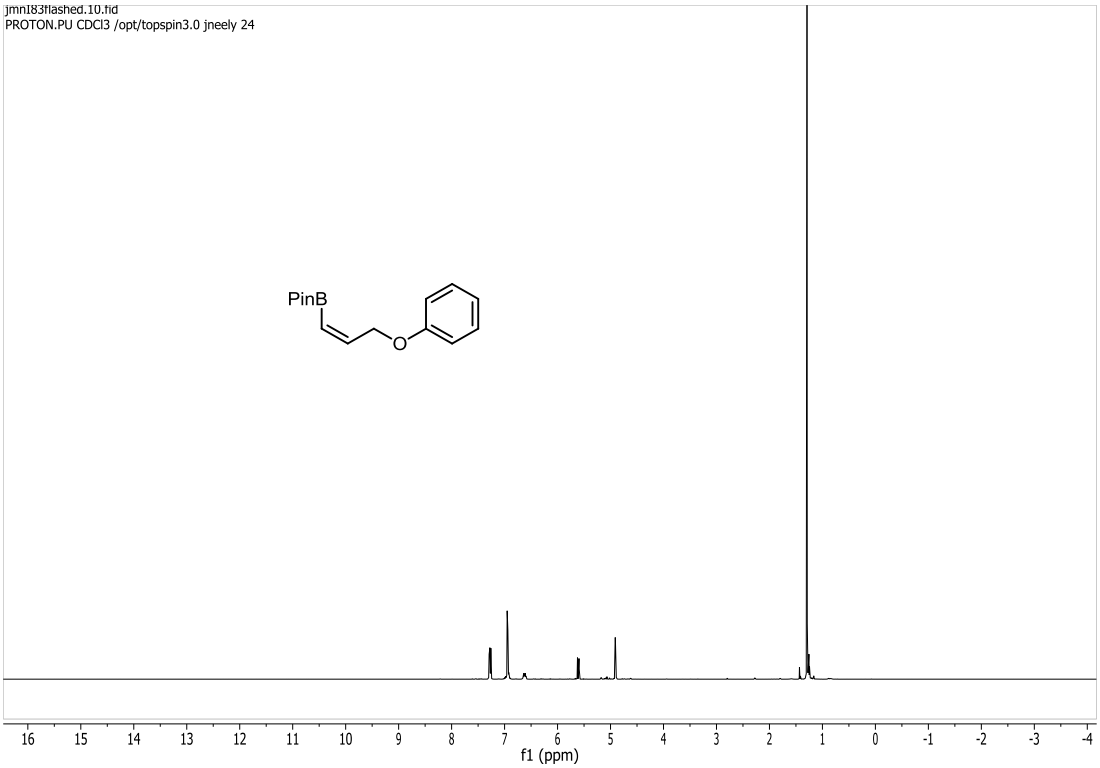


Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2d**.

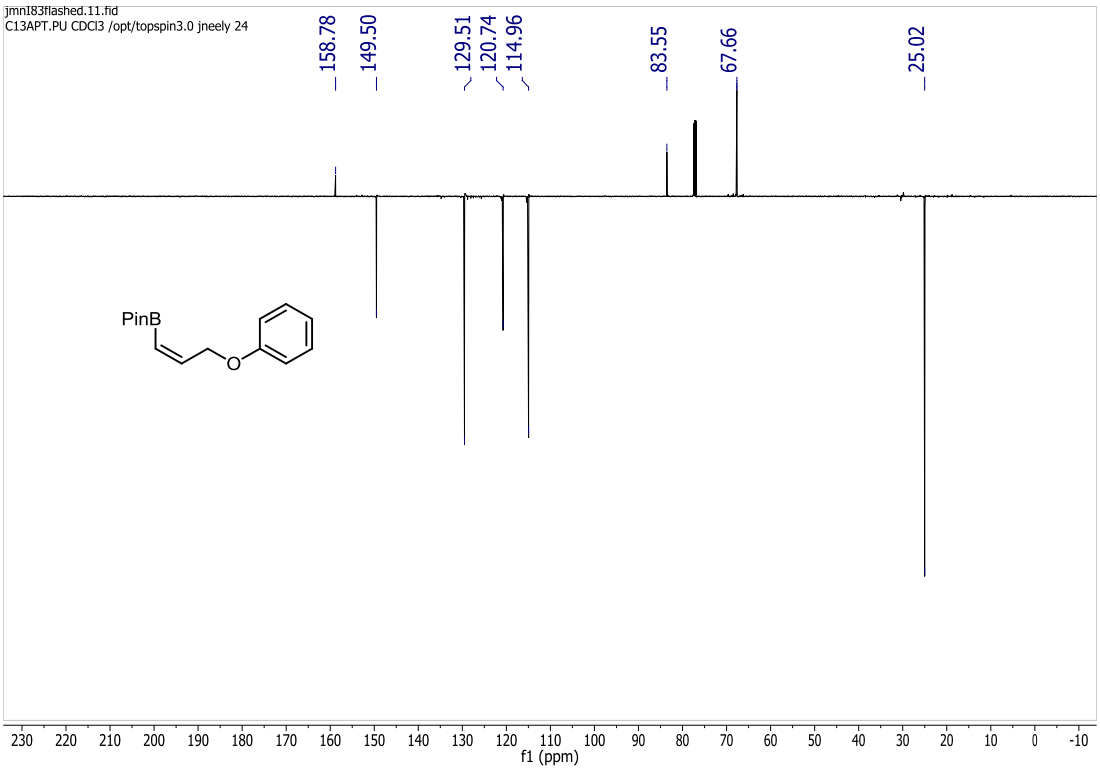


Figure S22. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2d**.

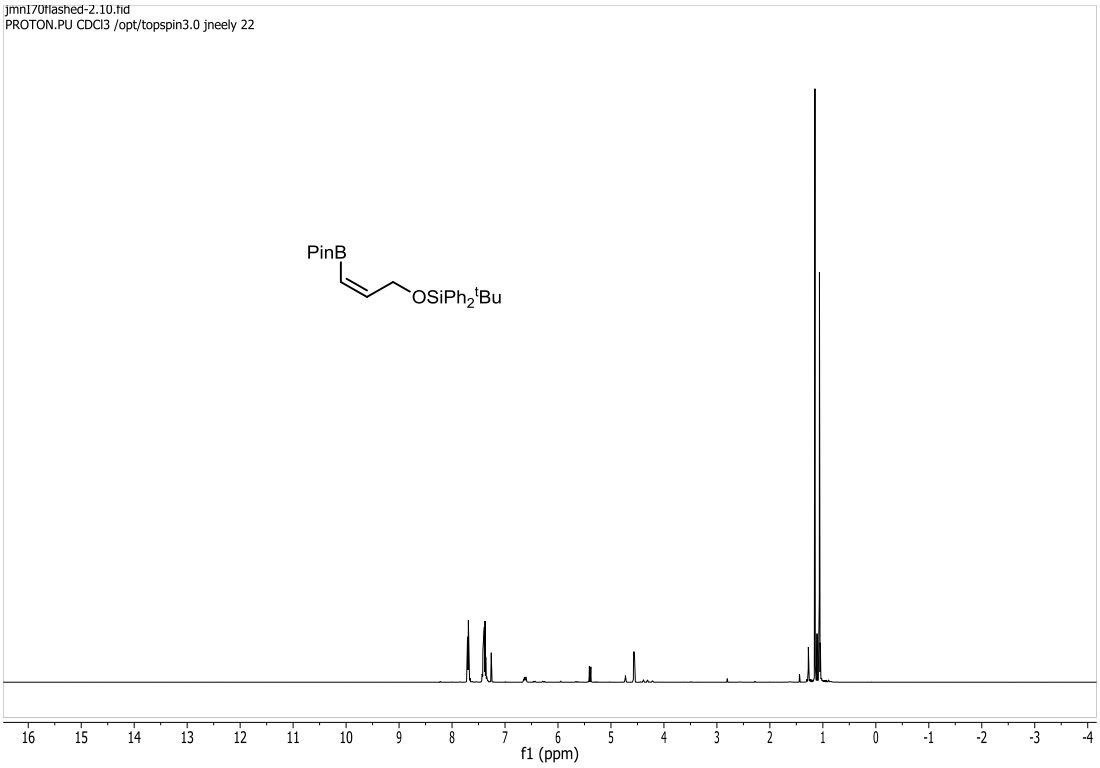


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2e**.

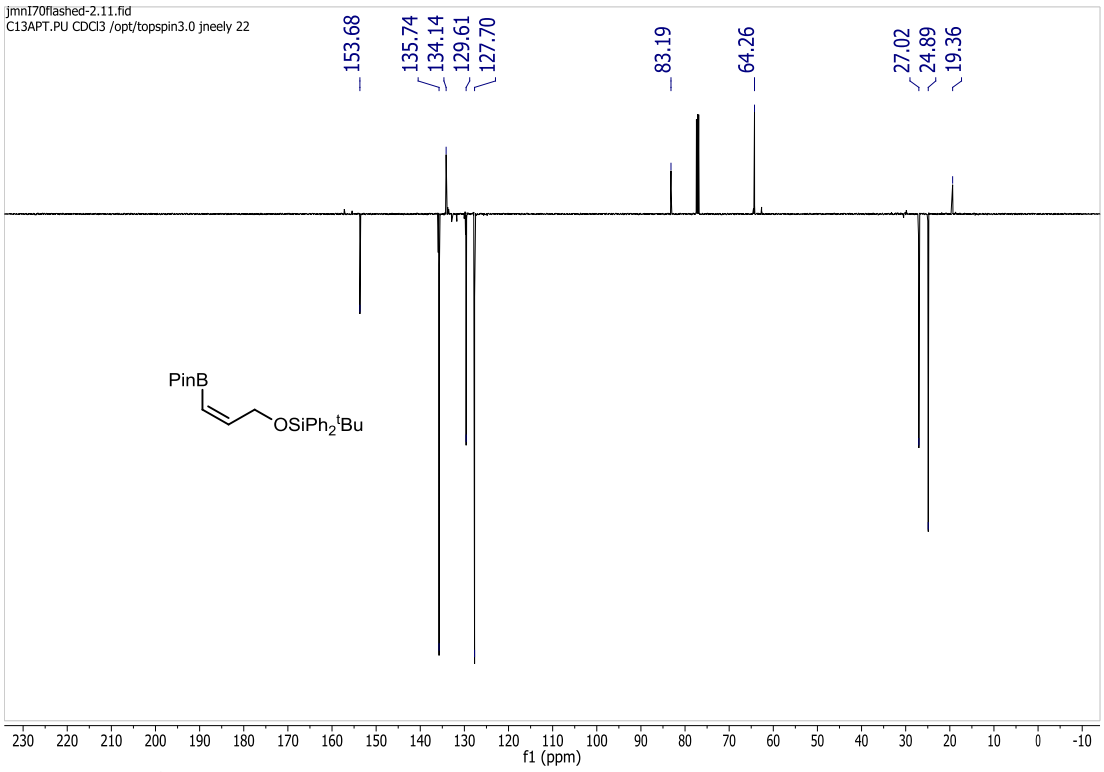


Figure S24. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2e**.

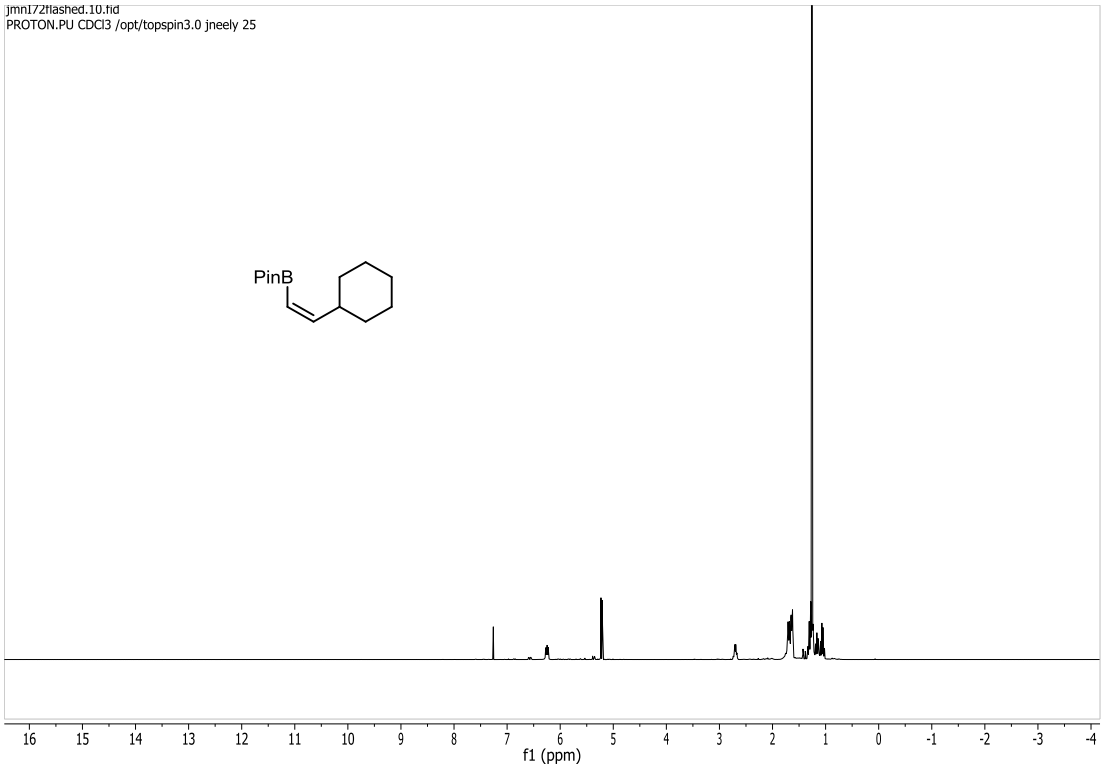


Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2g**.

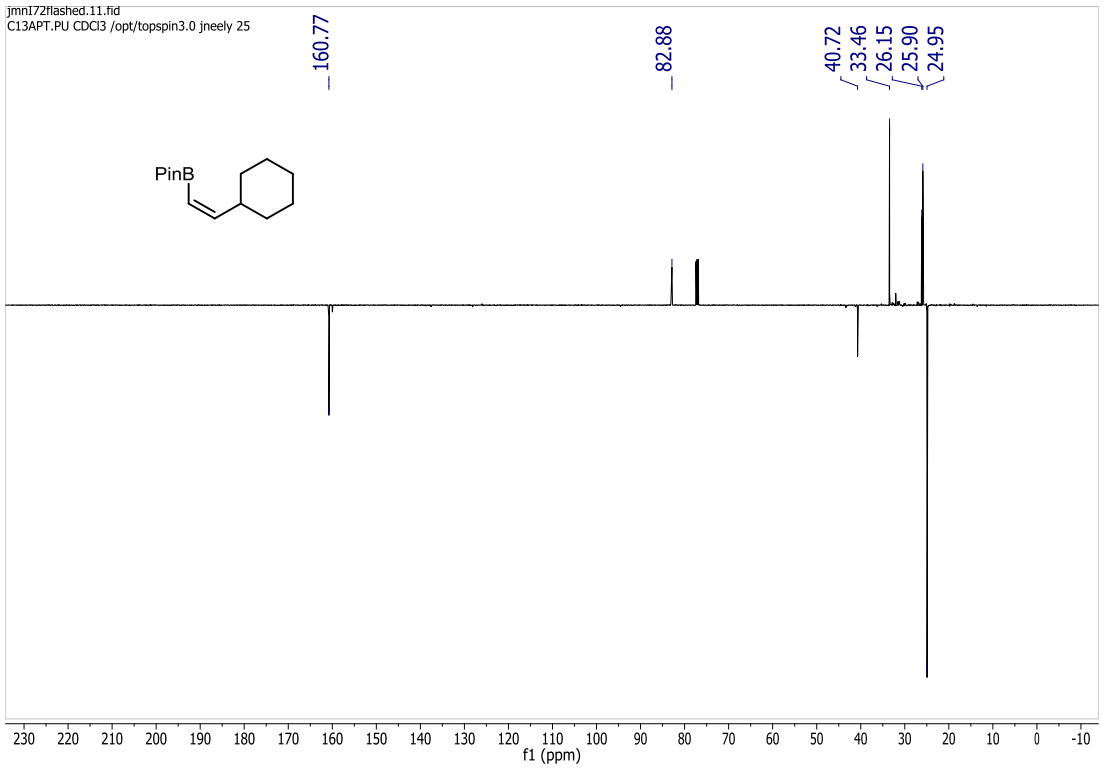


Figure S26. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2g**.

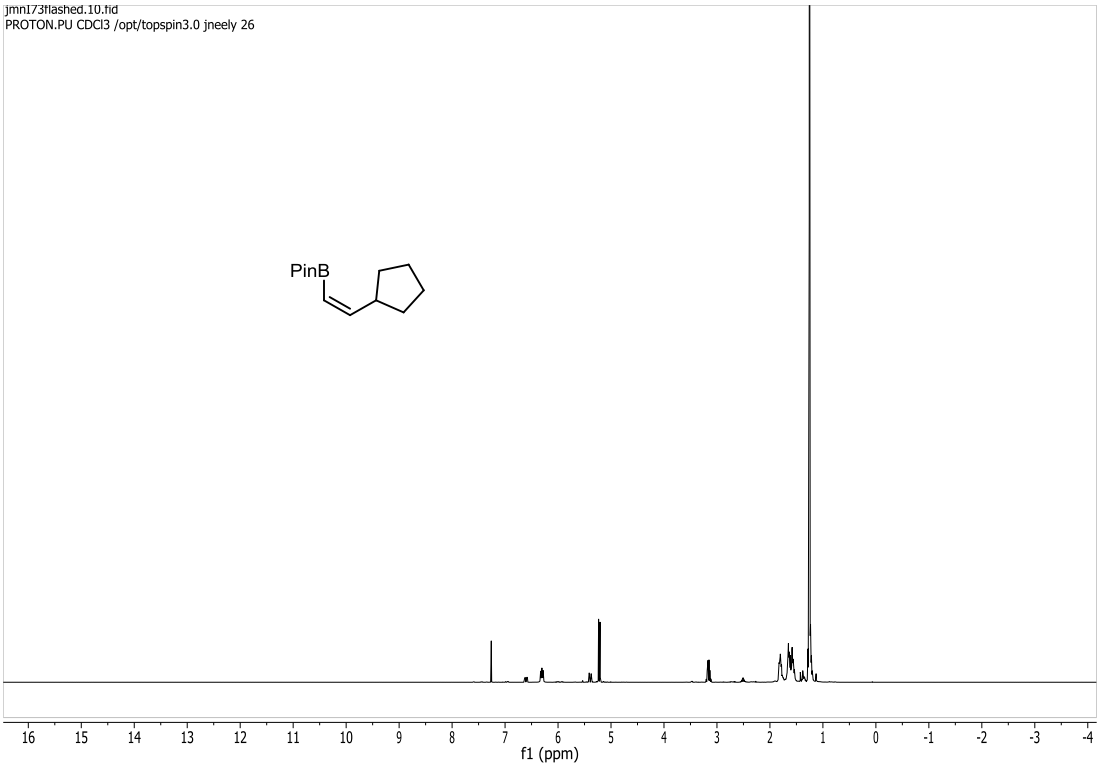


Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2h**.

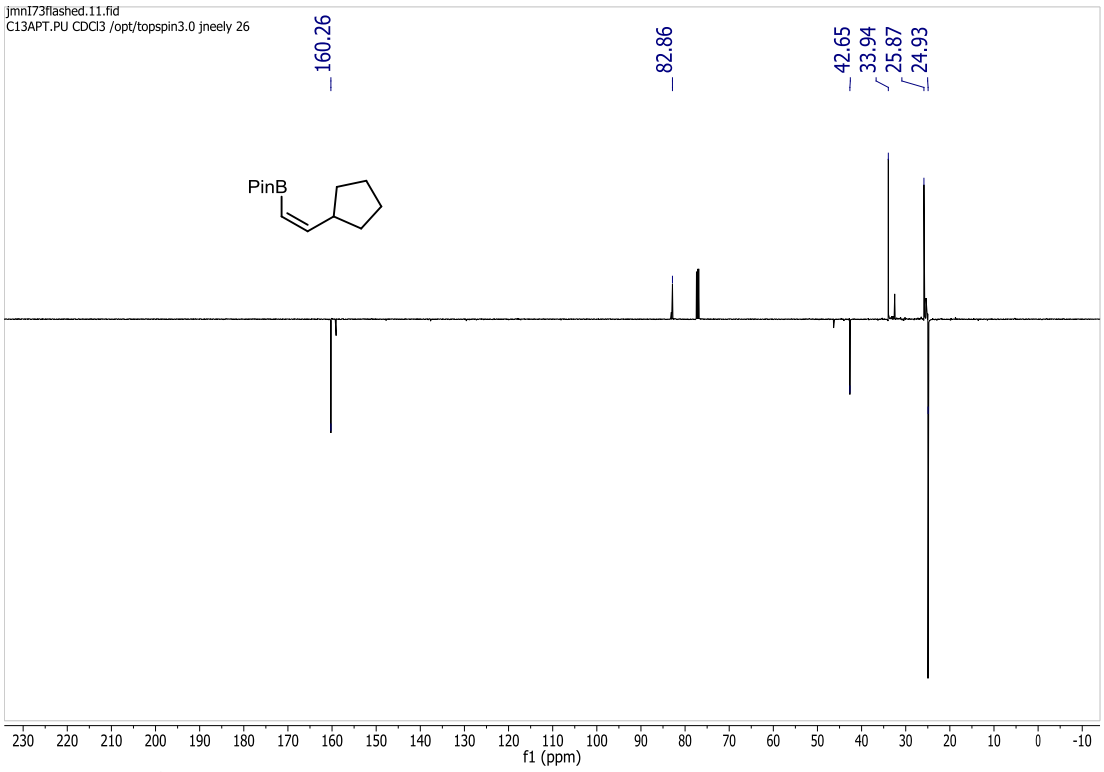


Figure S28. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2h**.

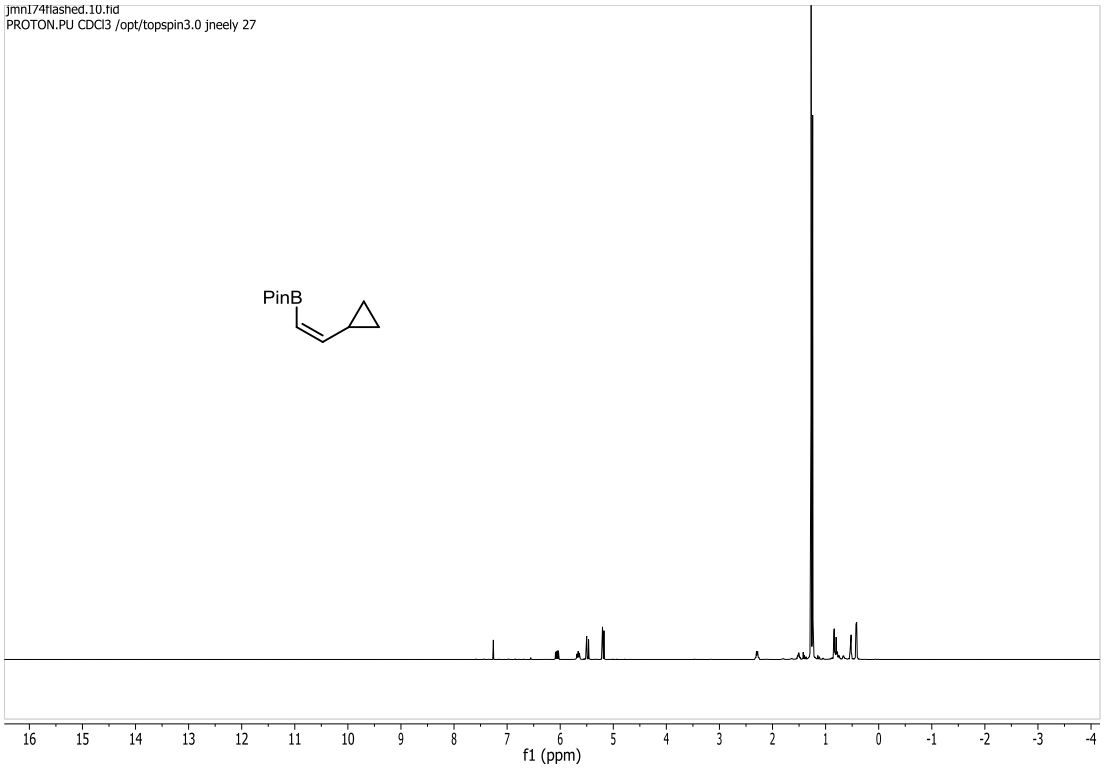


Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2i**.

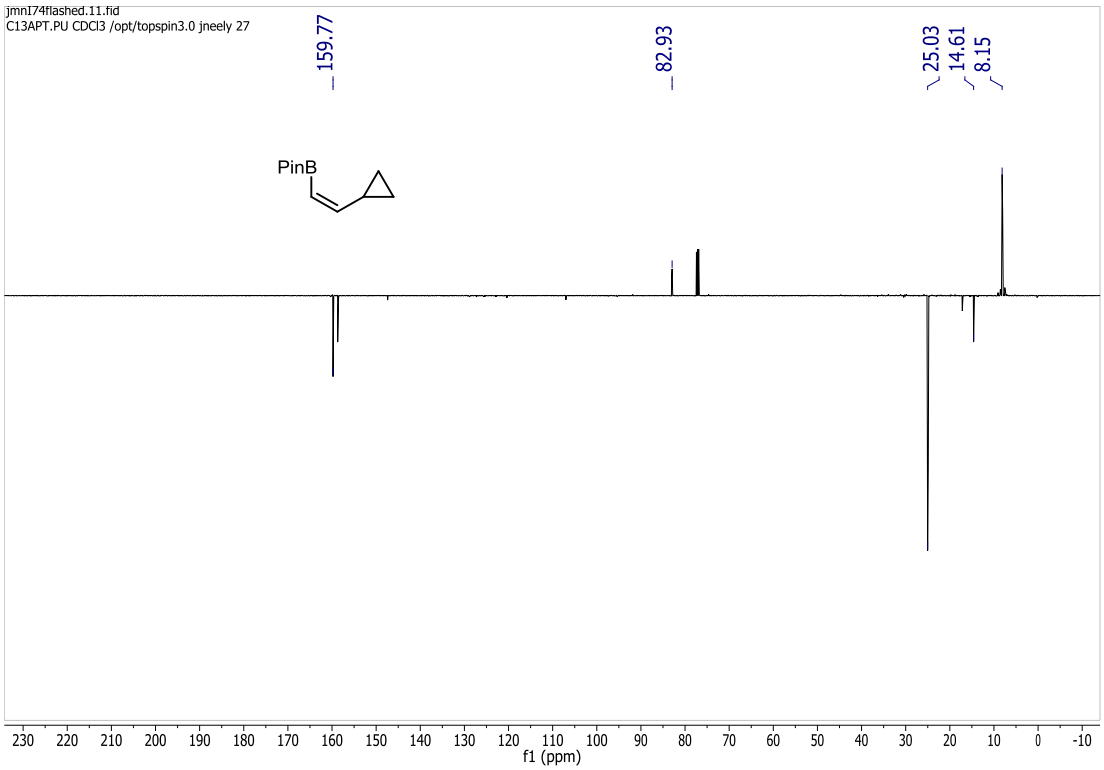


Figure S30. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2i**.

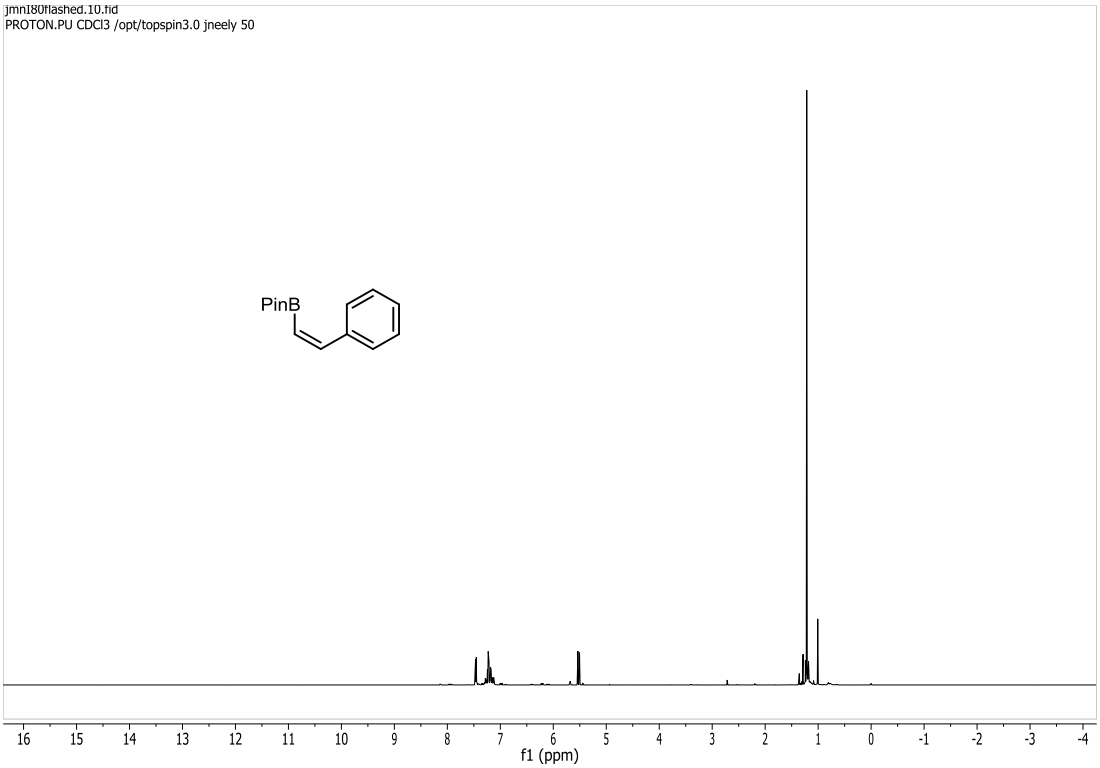


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2j**.

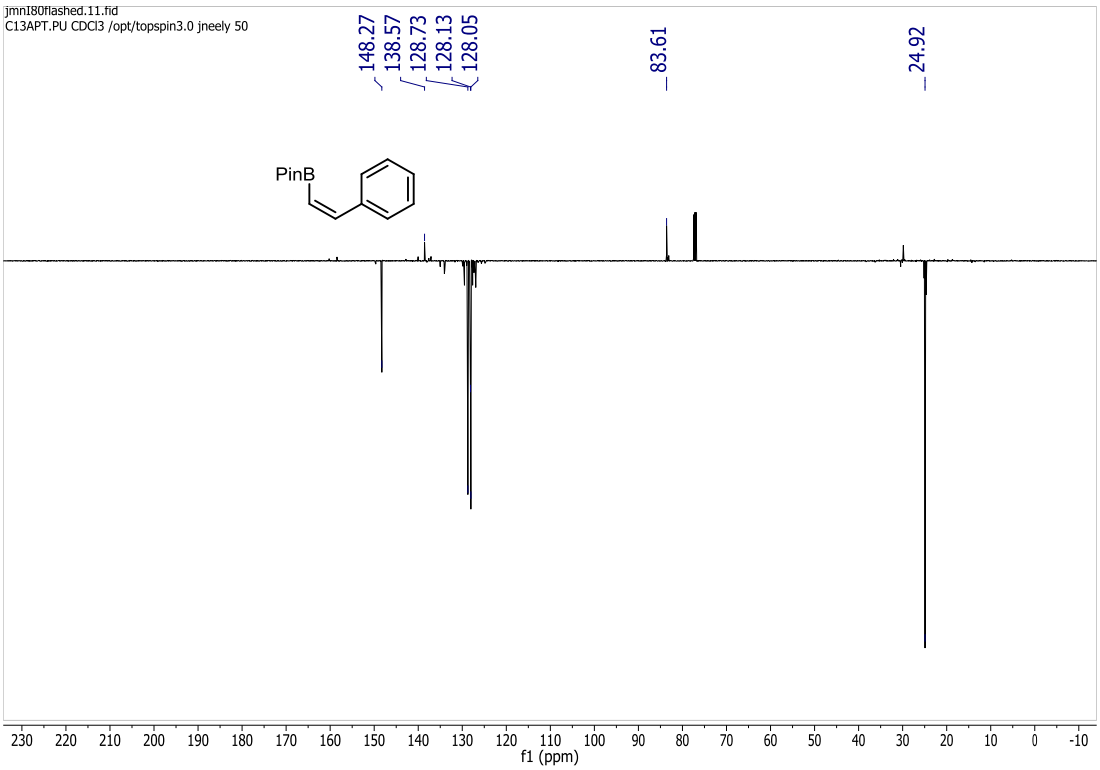


Figure S32. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2j**.

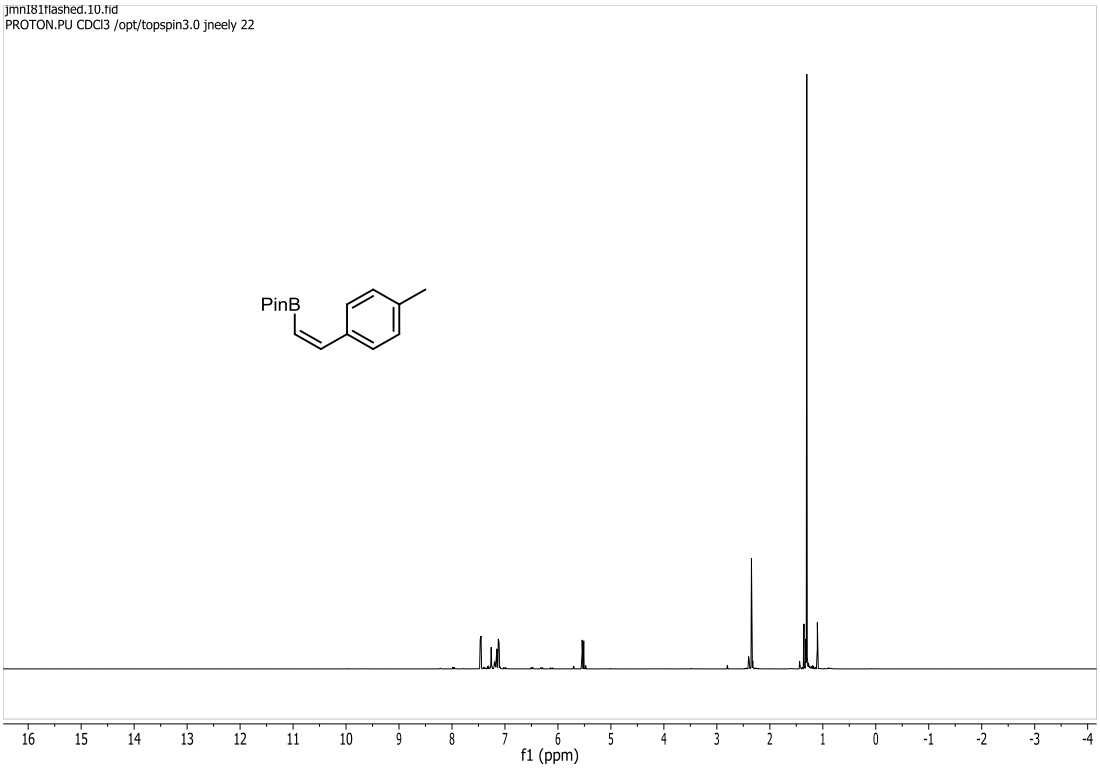


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2k**.

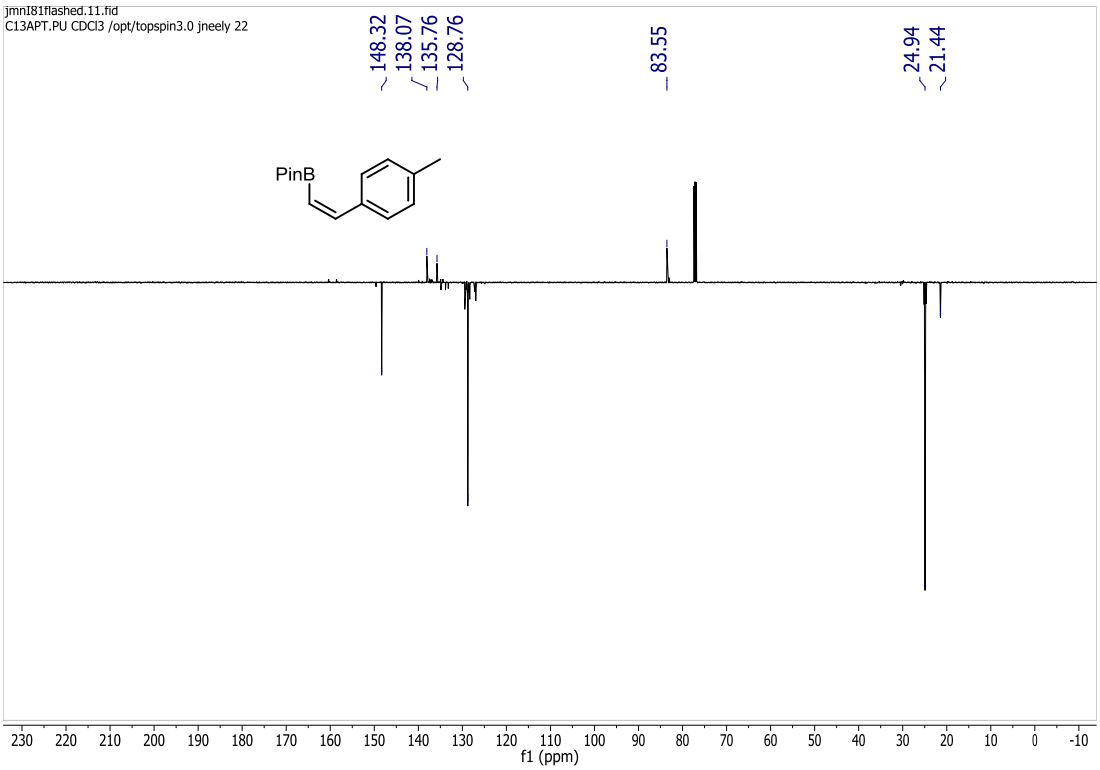


Figure S34. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2k**.

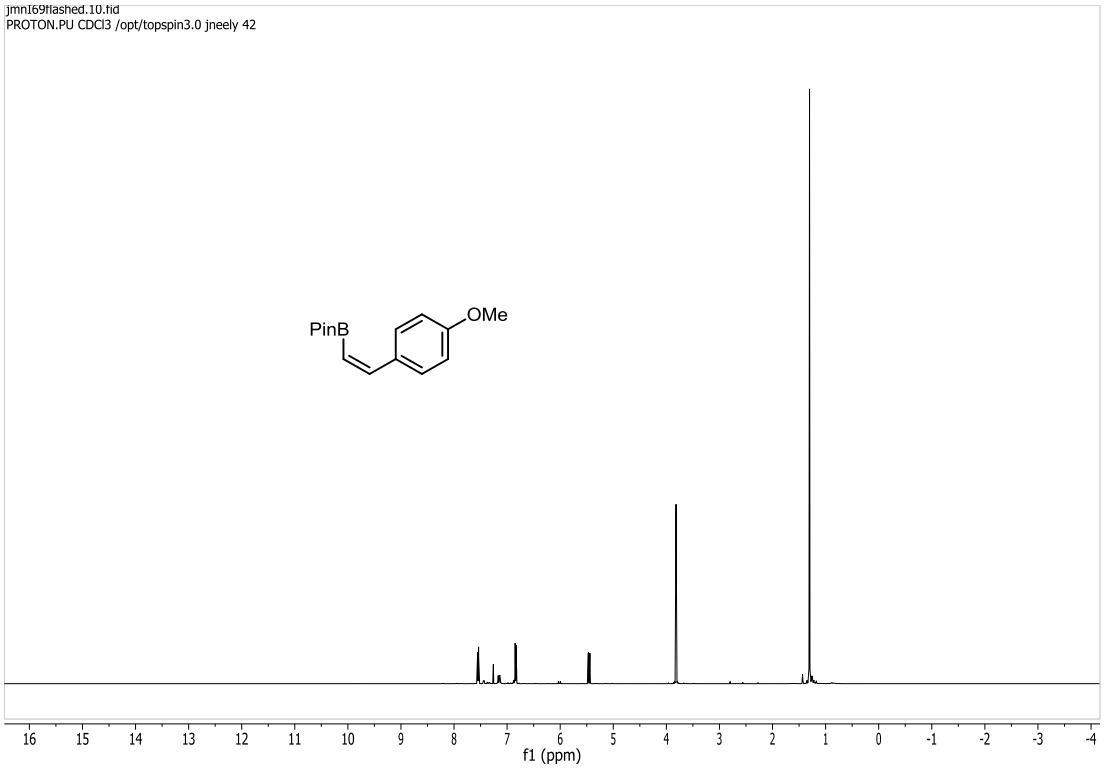


Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2l**.

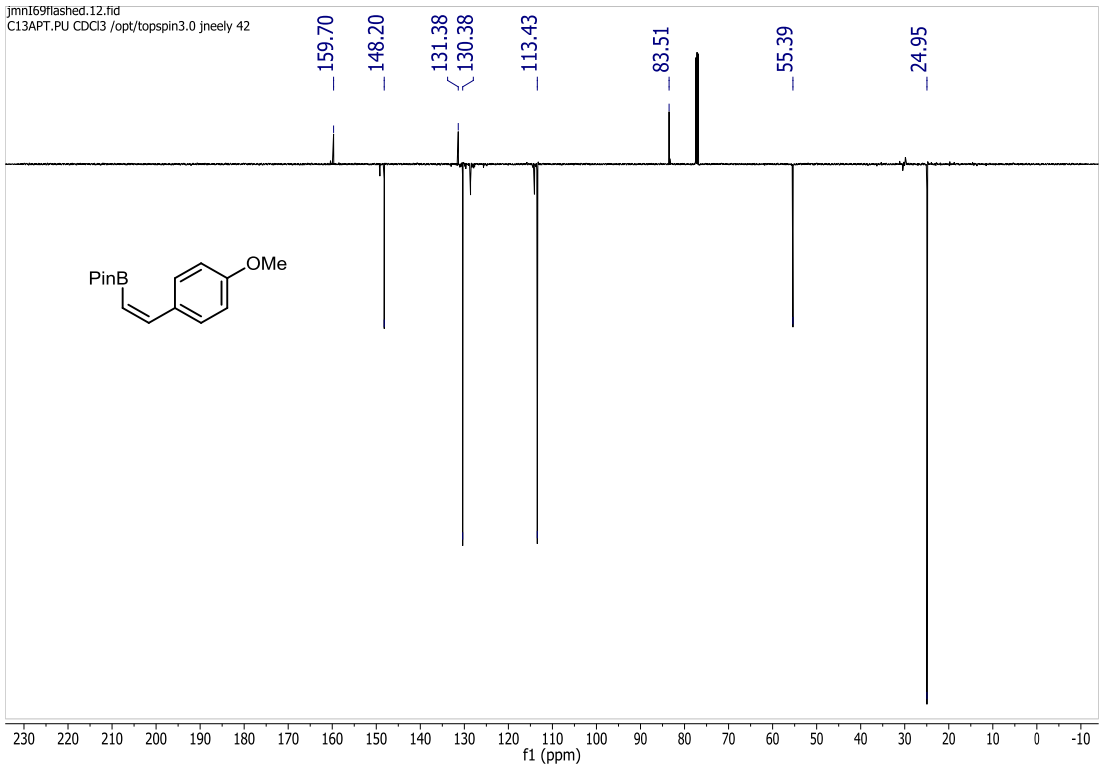


Figure S36. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2l**.

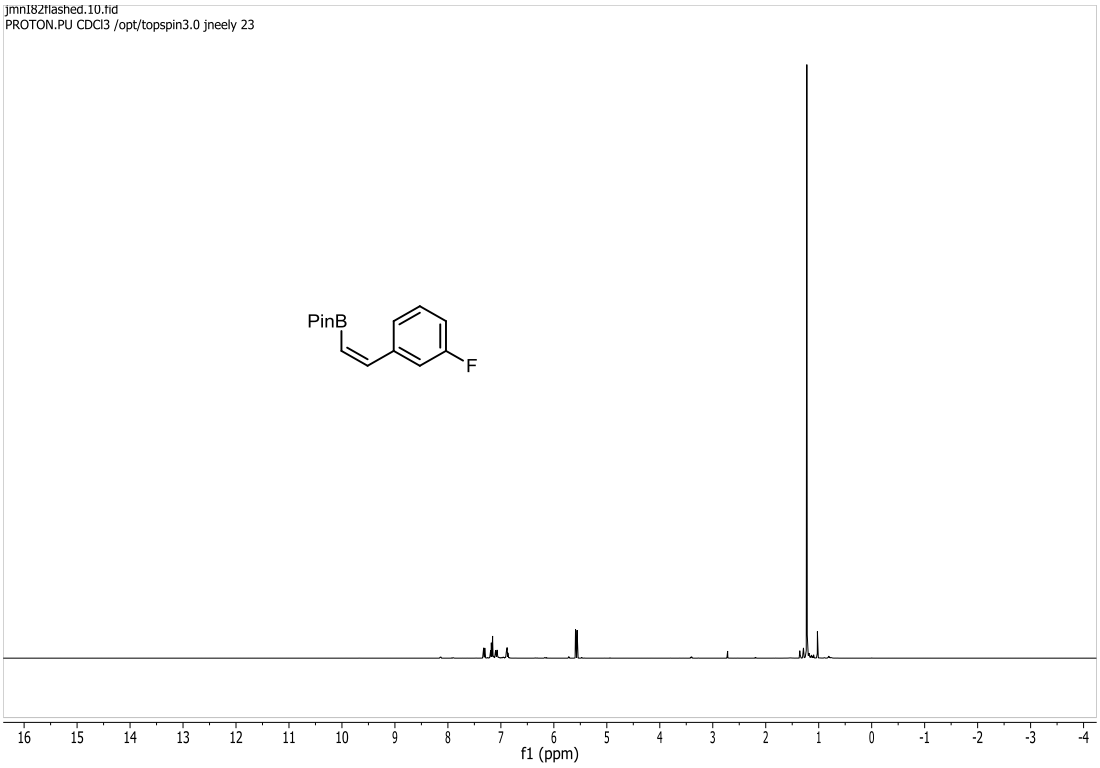


Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of **2m**.

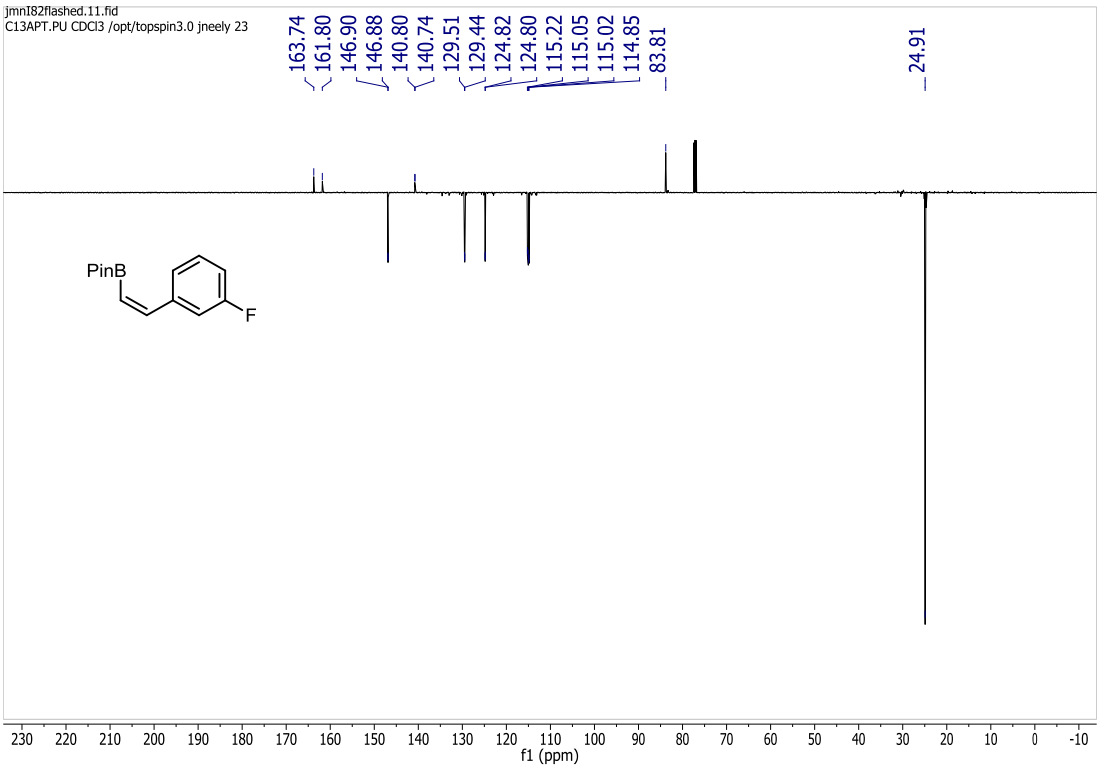


Figure S38. $\{^{1}H\}^{13}C$ NMR (126 MHz, $CDCl_3$, 23 °C) spectrum of **2m**.

VIII. NMR Spectra of Cobalt Compounds

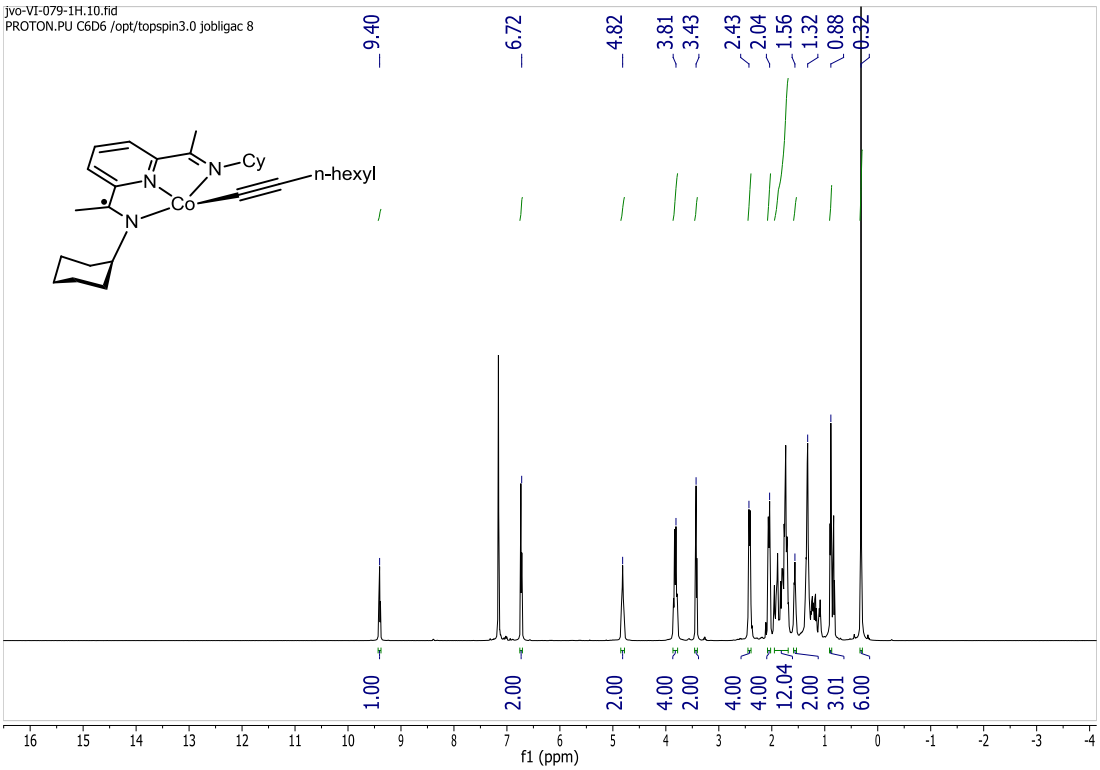


Figure S39. ^{1}H NMR (500 MHz, C_6D_6, 23 °C) spectrum of (^{Cy}APDI)CoCC-n-hexyl.

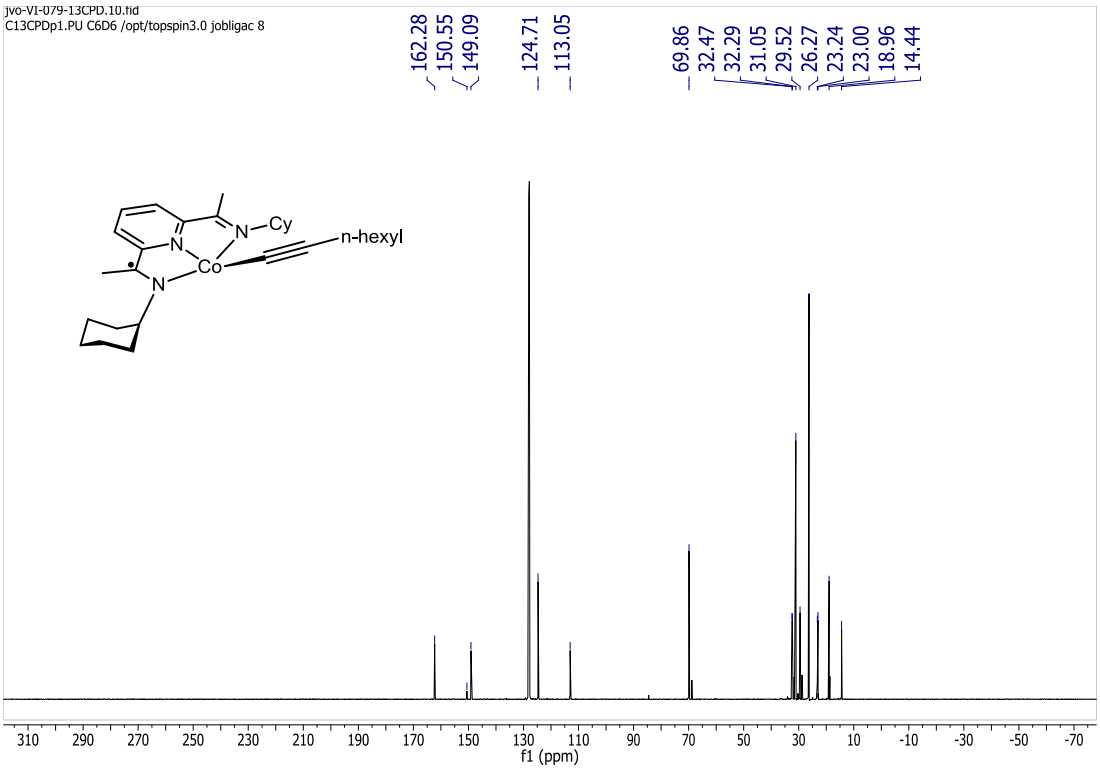


Figure S40. ^{13}C NMR (126 MHz, C_6D_6, 23 °C) spectrum of (^{Cy}APDI)CoCC-n-hexyl.

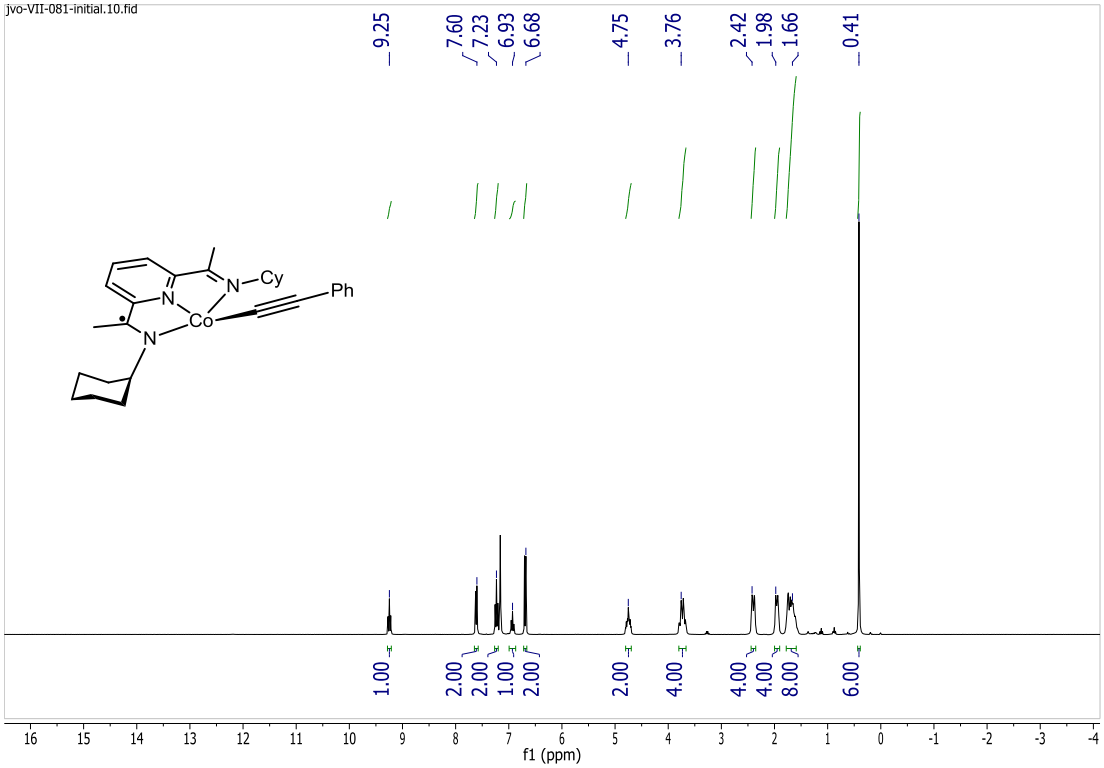


Figure S41. ^{1}H NMR (500 MHz, C_6D_6, 23 °C) spectrum of (^{Cy}APDI)CoCCPh.

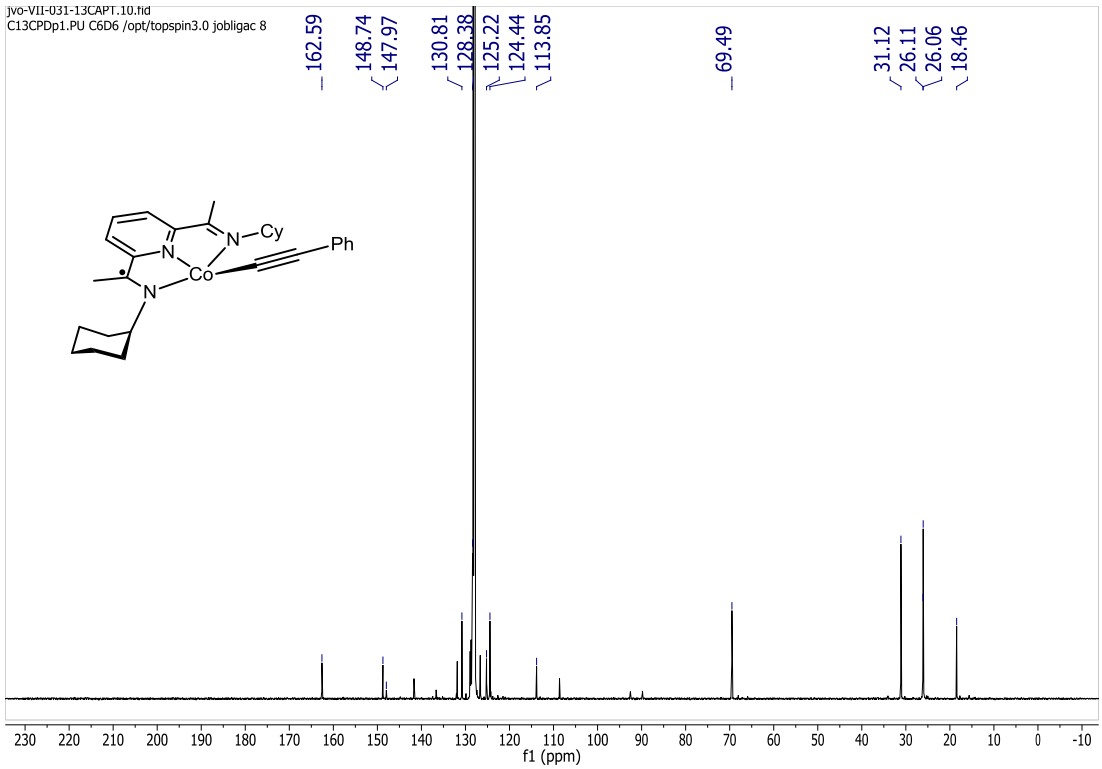


Figure S42. ^{13}C NMR (126 MHz, C_6D_6, 23 °C) spectrum of (^{Cy}APDI)CoCCPh.

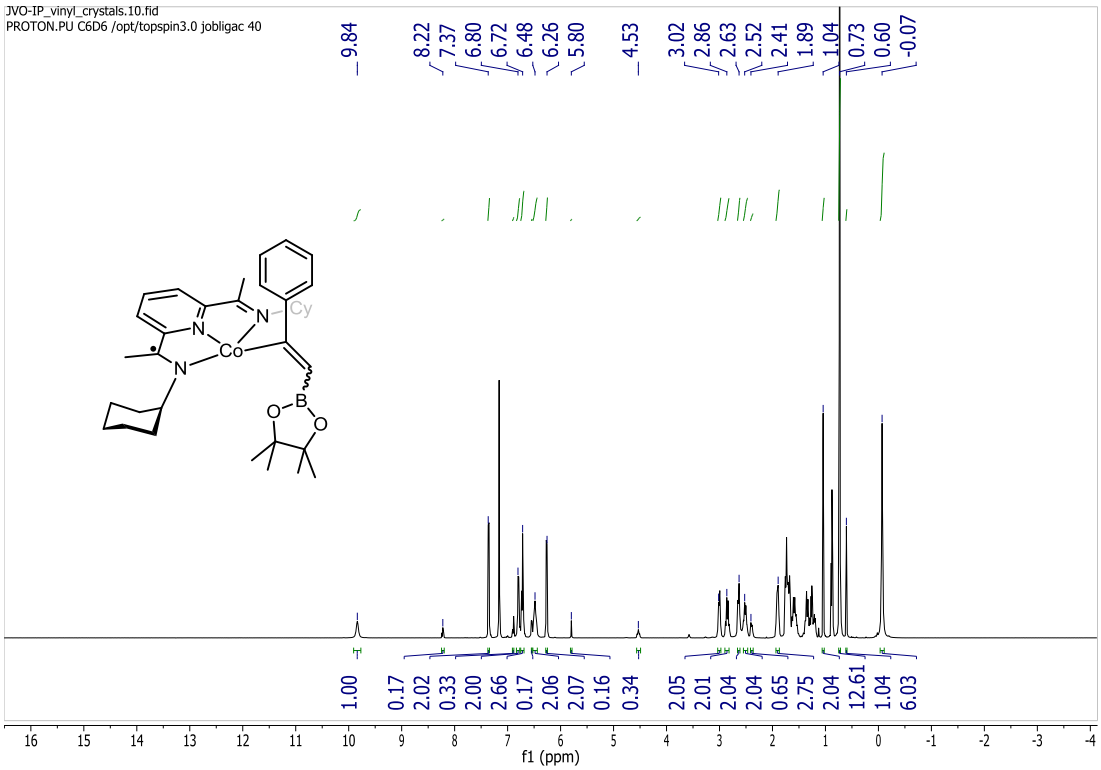


Figure S43. ^{1}H NMR (500 MHz, C_6D_6, 23 °C) spectrum of an 85 : 15 mixture of **5-pro-(*E*)** and **5-pro-(*Z*)**.

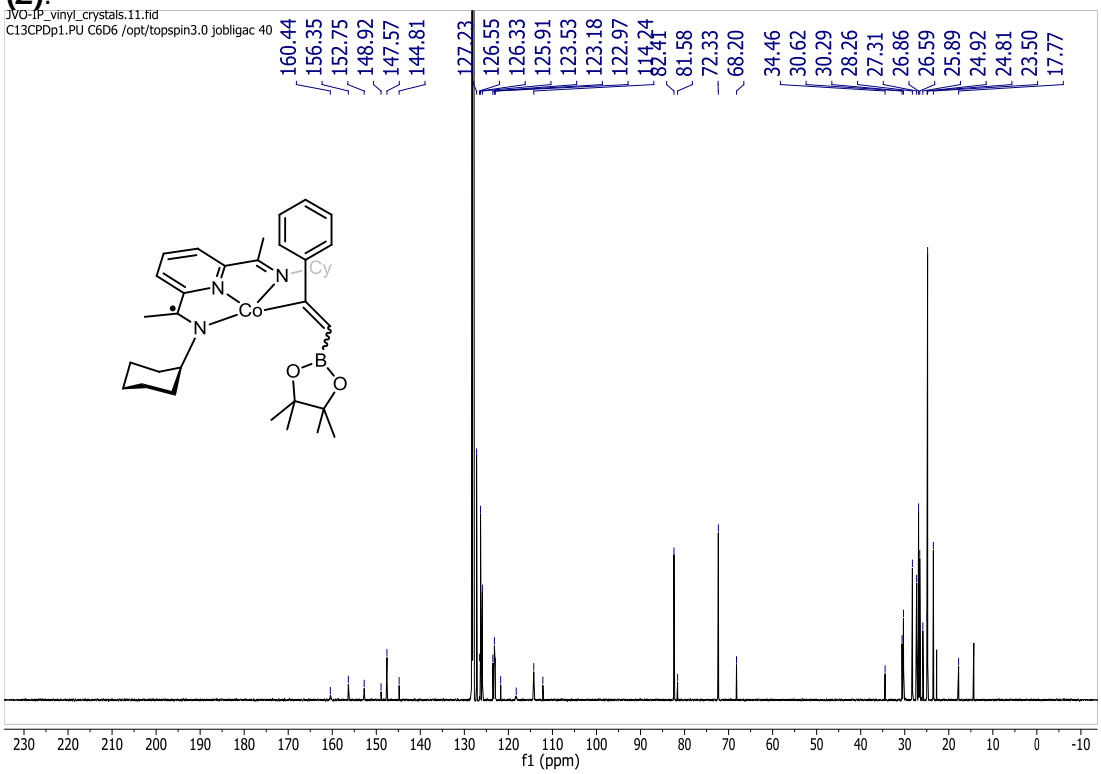


Figure S44. ^{13}C NMR (126 MHz, C_6D_6, 23 °C) spectrum of an 85 : 15 mixture of **5-pro-(*E*)** and **5-pro-(*Z*)**.

IX. References

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