Supporting Information

Insights into Base Metal Pre-catalyst Activation Relevant to C-H Functionalization

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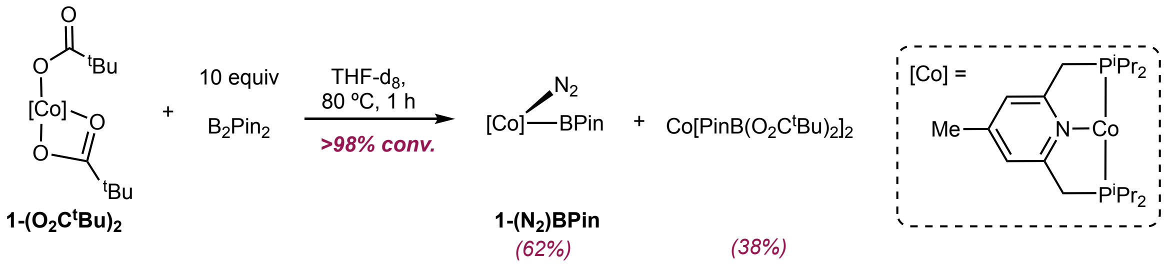
I. General Considerations. All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed 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. All other reagents were used as received.

^1H 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 ^1H (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. ^{31}P NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 300 MHz and were referenced to 85 % H_3PO_4 as an external standard. ^{11}B NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 299.763 MHz and were referenced to $BF_3(OEt_2)$ as an external standard. All coupling constants are reported in Hertz (Hz). Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.

II. Reaction of $\mathbf{1\text{-}(O_2C^tBu)_2}$ with $\mathbf{B_2Pin_2}$



In a nitrogen-filled glovebox, a scintillation vial was charged with B_2Pin_2 (0.070 g, 0.28 mmol), $\mathbf{1\text{-}(O_2C^tBu)_2}$[1] (0.017 g, 0.028 mmol), and 0.5 mL of THF-d_8. The vial was swirled until the mixture became homogeneous and the resulting solution was transferred to a J-Young tube. The tube was sealed, brought out of the glovebox and was heated in an oil bath at 80 °C for 1 hour. The reaction was cooled to room temperature and analyzed using ^1H and ^{31}P NMR spectroscopy.

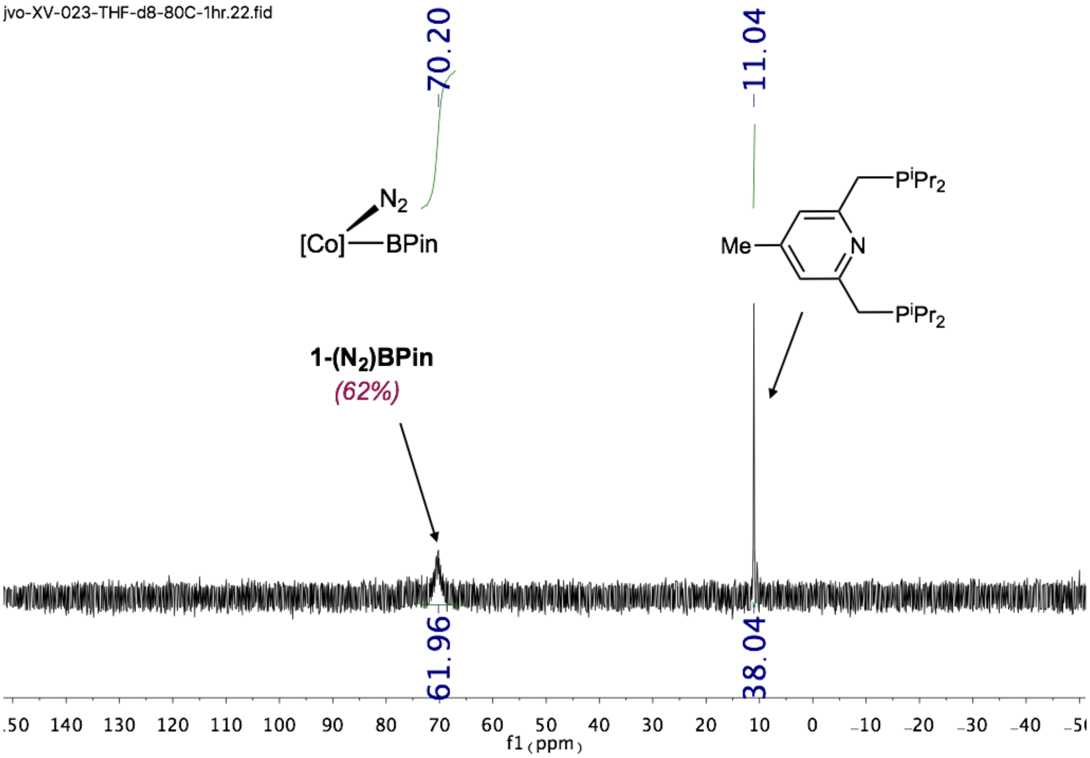
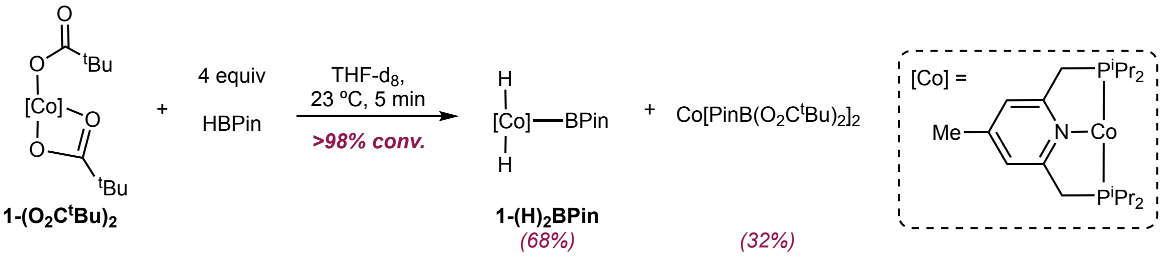


Figure S1. ^{31}P NMR spectrum (THF-d_8, 23 °C) of the reaction of $\mathbf{1\text{-}(O_2C^tBu)_2}$ with B_2Pin_2.

NMR Resonances of Co[PinB(O_2C^tBu)$_2$]$_2$

^{1}H NMR (THF-d_8, 23 °C): δ 14.20 (s, 12H, BPin *Me*), -3.05 (s, 36H, OPiv *Me*), -24.02 (s, 12H, BPin *Me*).

III. Reaction of 1-(O_2C^tBu)$_2$ with HBPin



In a nitrogen-filled glovebox, a scintillation vial was charged with HBPin (0.025 g, 0.20 mmol), **1-(O_2C^tBu)$_2$**[1] (0.030 g, 0.049 mmol), and 0.5 mL of THF-d_8. The vial was swirled until the mixture became homogeneous and the resulting solution was transferred to a J-Young tube. The tube was sealed, brought out of the glovebox and and analyzed using ^{1}H and ^{31}P NMR spectroscopy.

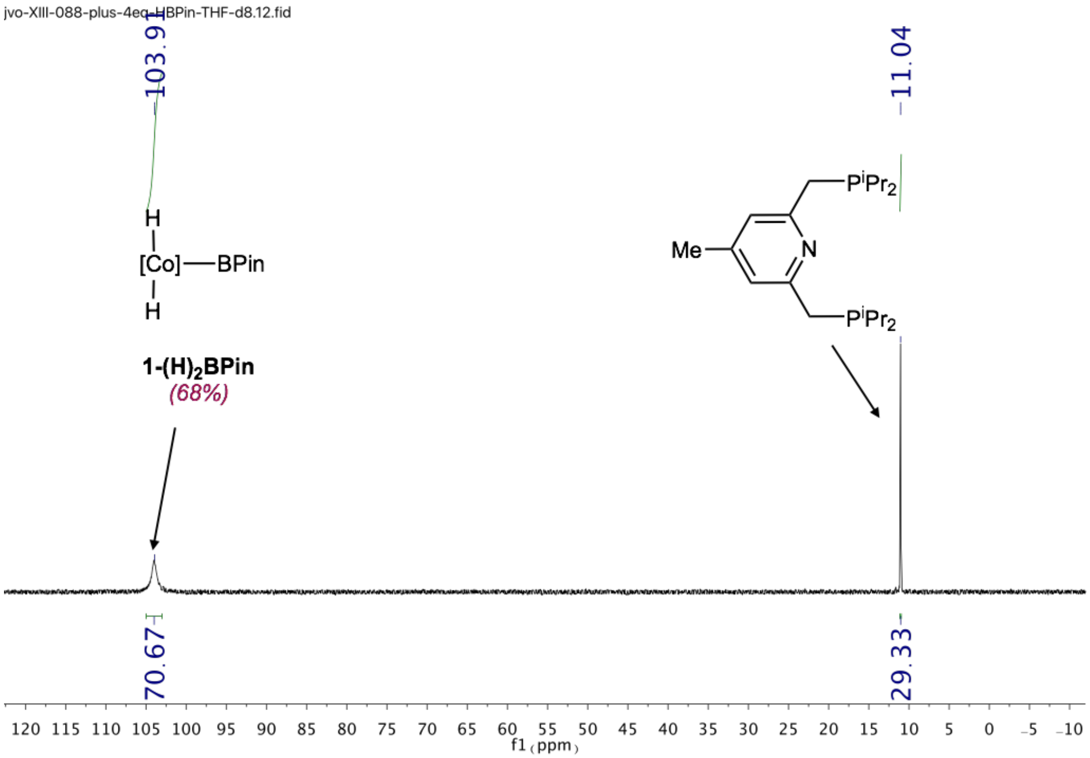


Figure S2. ^{31}P NMR spectrum (THF-d_8, 23 °C) of the reaction of **1-(O_2C^tBu)$_2$** with HBPin.

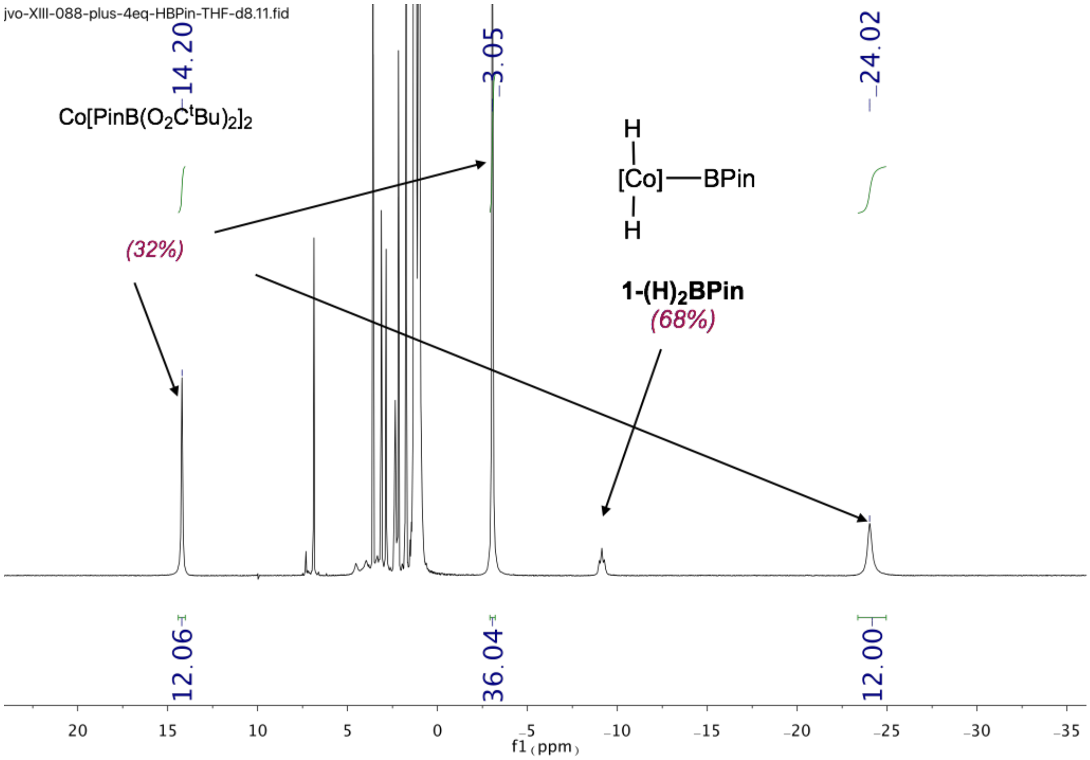
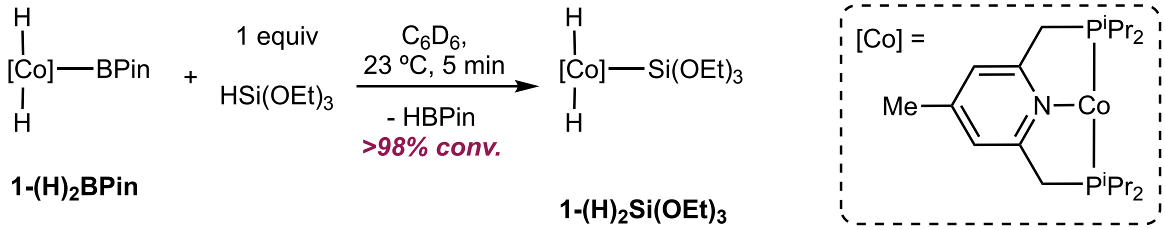


Figure S3. ^{1}H NMR spectrum (THF-d_8, 23 °C) of the reaction of **1-(O_2C^tBu)$_2$** with HBPin.

IV. Reaction of 1-$(H)_2$BPin with $HSi(OEt)_3$



In a nitrogen-filled glovebox, a scintillation vial was charged with $HSi(OEt)_3$ (0.009 g, 0.05 mmol), **1-$(H)_2$BPin**[2] (0.030 g, 0.055 mmol), and 0.5 mL of C_6D_6. The vial was swirled until the mixture became homogeneous and the resulting solution was transferred to a J-Young tube. The tube was sealed, brought out of the glovebox and the reaction was analyzed using ^1H and ^{31}P NMR spectroscopy. The resulting compound was identified as **1-$(H)_2Si(OEt)_3$**.

^1H NMR (benzene-d_6, 23 °C): δ 6.28 (s, 2H, meta py C*H*), 4.10 (q, *J* = 7.08 Hz, 6H, -OCH_2CH_3), 2.94 – 2.87 (m, 4H, -PCH_2), 2.51 – 2.36 (m, 4H, PC*H*Me_2), 1.74 (s, 3H, py *Me*), 1.55 – 1.45 (m, 12H, PCHMe_2), 1.38 (t, *J* = 7.13 Hz, 9H, -OCH_2CH_3), 1.11 – 1.03 (m, 12H, PCHMe_2), -9.02 (t, *J* = 43.5 Hz, 2H, Co-*H*).

{^1H}^{13}C NMR (benzene-d_6, 23 °C): δ 161.08 (*ortho* py *C*), 143.51 (*para* py *C*), 119.16 (*meta* py *C*H), 57.29 (-O*C*H_2CH_3), 38.83 (-P*C*H_2), 25.31 (P*C*HMe_2), 20.31 (py *Me*), 19.36 (PCHMe_2), 18.95 (-OCH_2*C*H_3), 17.82 (PCHMe_2).

^{31}P\{^1H\} NMR (benzene-d_6, 23 °C): δ 98.67 (br s, *P*-CHMe_2).

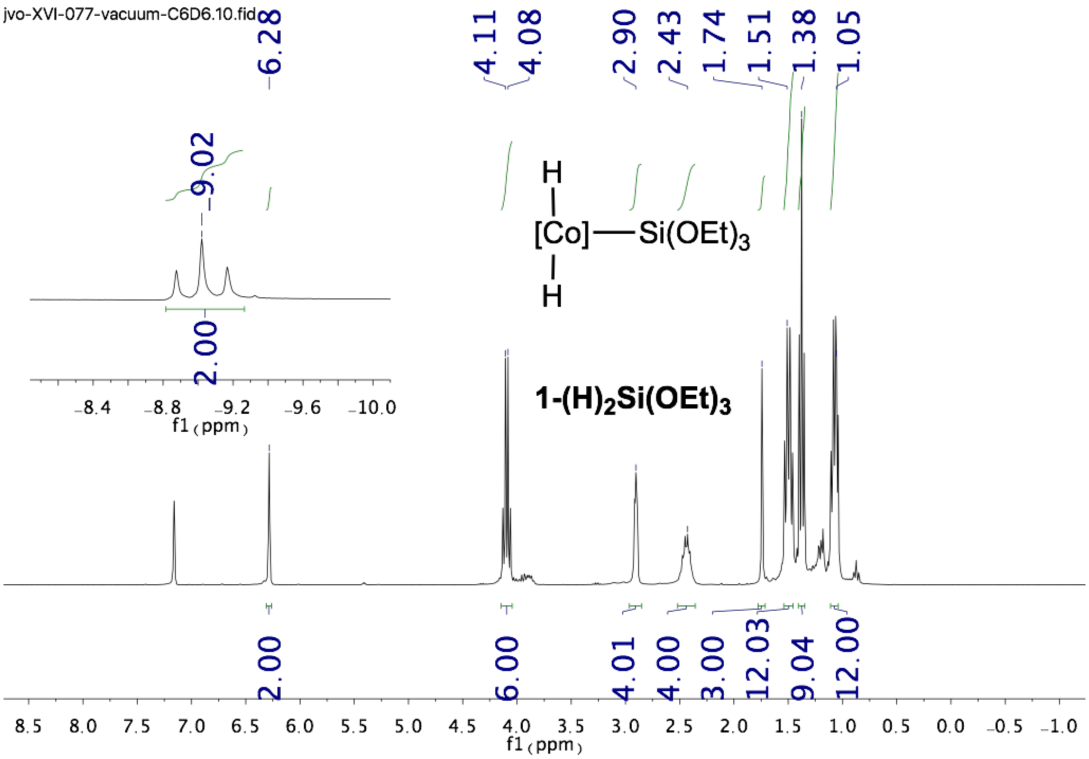


Figure S4. ^{1}H NMR spectrum (C_6D_6, 23 °C) of the reaction of **1-(H)$_2$BPin** with $HSi(OEt)_3$.

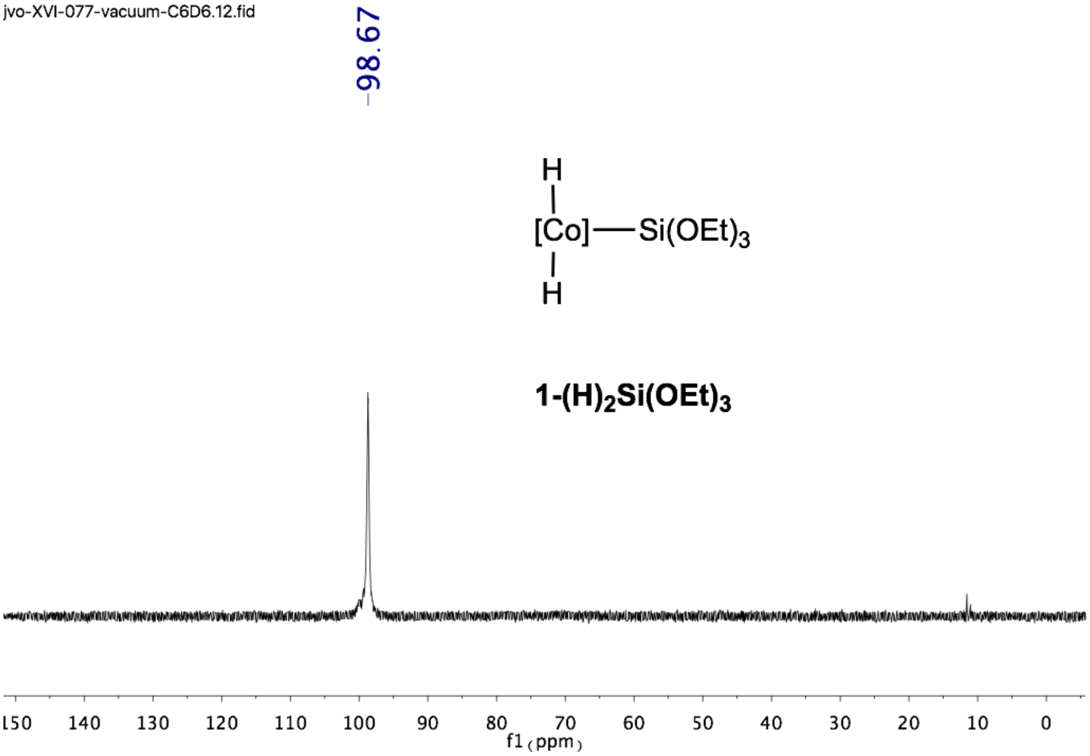
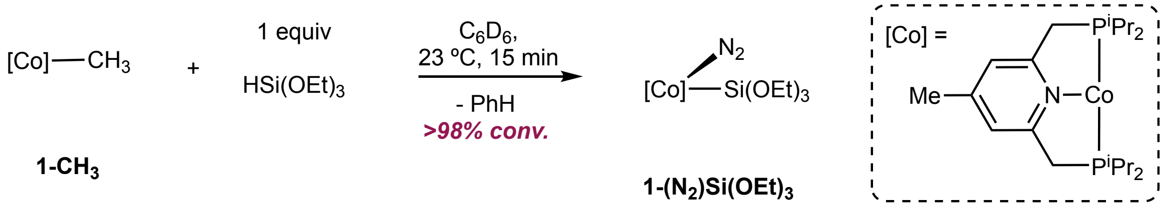


Figure S5. ^{31}P NMR spectrum (C_6D_6, 23 °C) of the reaction of **1-(H)$_2$BPin** with $HSi(OEt)_3$.

V. Reaction of 1-CH_3 with $HSi(OEt)_3$



In a nitrogen-filled glovebox, a scintillation vial was charged with $HSi(OEt)_3$ (0.006 g, 0.04 mmol), **1-CH_3**[2] (0.020 g, 0.04 mmol), and 0.5 mL of C_6D_6. The vial was swirled until the mixture became homogeneous and the resulting solution was transferred to a J-Young tube. The tube was sealed, brought out of the glovebox and the reaction was analyzed using ^1H and ^{31}P NMR spectroscopy. The resulting compound is tentatively assigned as **1-$(N_2)Si(OEt)_3$**.

^1H NMR (benzene-d_6, 23 °C): δ 6.33 (s, 2H, meta py C*H*), 3.94 (q, *J* = 7.07 Hz, 6H, -OCH_2CH_3), 3.44 – 3.05 (m, 4H, -PCH_2), 2.89 – 2.29 (m, 4H, $PCHMe_2$), 1.69 (s, 3H, py *Me*), 1.56 – 1.14 (overlapping m, 36H, $PCHMe_2$, -OCH_2CH_3).

$^{31}P\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 76.39 (br s, *P*-$CHMe_2$).

IR (benzene-d_6, 23 °C): νN_2 = 2053.71 cm^{-1}.

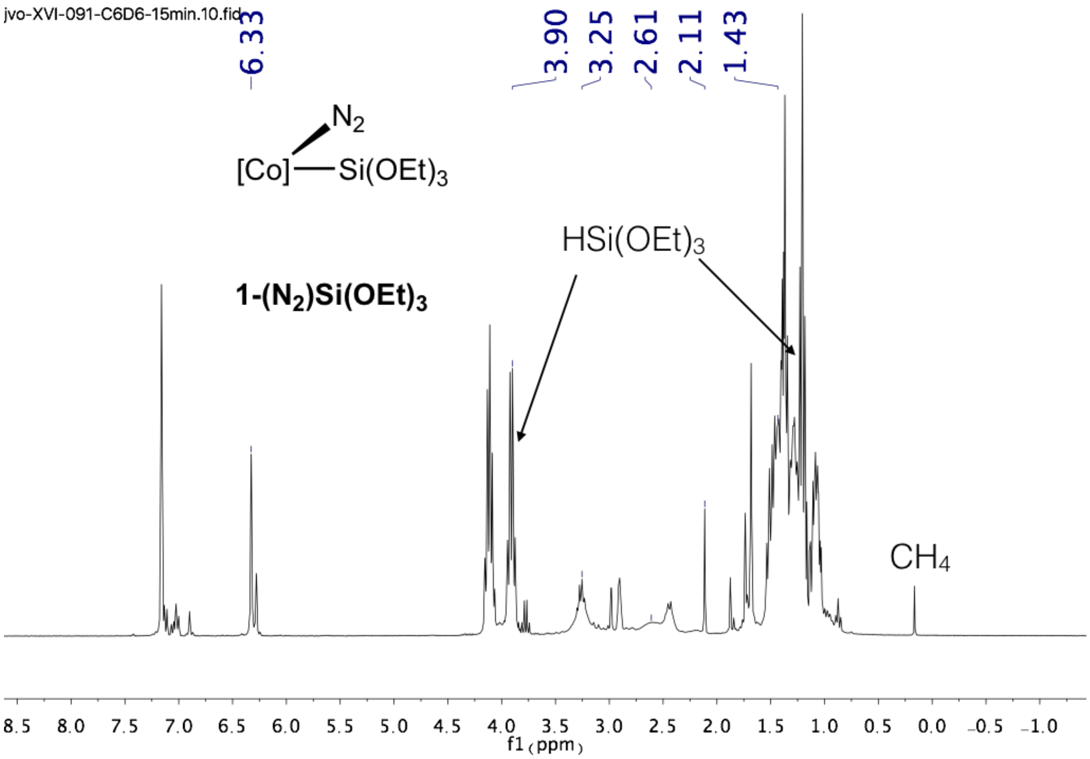


Figure S6. ^{1}H NMR spectrum (C_6D_6, 23 °C) of the reaction of **1-CH$_3$** with HSi(OEt)$_3$.

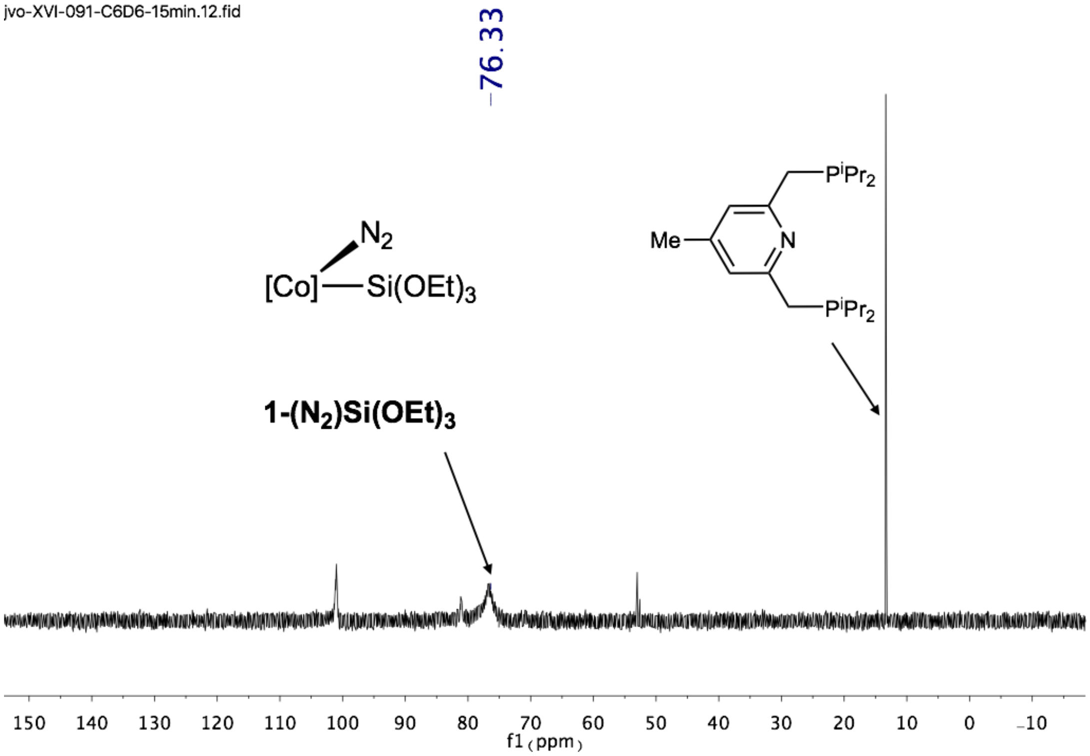
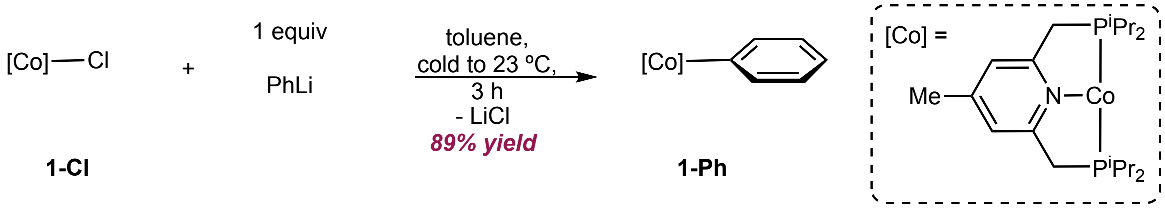


Figure S7. ^{31}P NMR spectrum (C_6D_6, 23 °C) of the reaction of **1-CH$_3$** with HSi(OEt)$_3$.

VI. Synthesis of 1-Ph



In a nitrogen-filled glovebox, a 100 mL round bottom flask was charged with **1-Cl**[2] (0.287 g, 0.640 mmol) and 30 mL of toluene. In a separate vial, PhLi (0.337 mL of a 1.9 M solution in dibutyl ether, 0.640 mmol) was diluted with 5 mL of toluene. The round bottom flask containing **1-Cl** and the vial containing PhLi were chilled in a cold well filled with liquid nitrogen for 20 mins. The cold solution of PhLi was then added dropwise to a cold, stirring solution of **1-Cl** in toluene. The reaction was allowed to cool to room temperature and was stirred for 3 hours. The solution was filtered through Celite and the volatiles were evaporated in vacuo to yield a red-brown solid identified as **1-Ph** (0.279 g, 89% yield).

^{1}H NMR (benzene-d$_6$, 23 °C): δ 7.32 (d, *J* = 8.03 Hz, 2H, Co-*Ph*), 7.03 (t, *J* = 8.03 Hz, 2H, Co-*Ph*), 6.79 (d, *J* = 7.64 Hz, 1H, Co-*Ph*), 5.77 (s, 2H, meta py C*H*), 2.25 – 2.10 (overlapping m, 8H, PC*H*Me$_2$ and -PC*H*$_2$), 1.28 – 1.16 (overlapping m, 24H, PCH*Me*$_2$), 0.63 (s, 3H, py *Me*).

{^{1}H}^{13}C NMR (benzene-d$_6$, 23 °C): δ 157.84 (*ortho* py *C*), 139.18 (Co-*Ph*), 124.43 (Co-*Ph*), 122.12 (Co-*Ph*), 118.26 (Co-*Ph*), 35.46 (-P*C*H$_2$), 23.13 (P*C*HMe$_2$), 22.69 (py *Me*), 18.95 (PCH*Me*$_2$), 17.97 (PCH*Me*$_2$).

^{31}P{^{1}H} NMR (benzene-d$_6$, 23 °C): δ 45.98 (br s, *P*-CHMe$_2$).

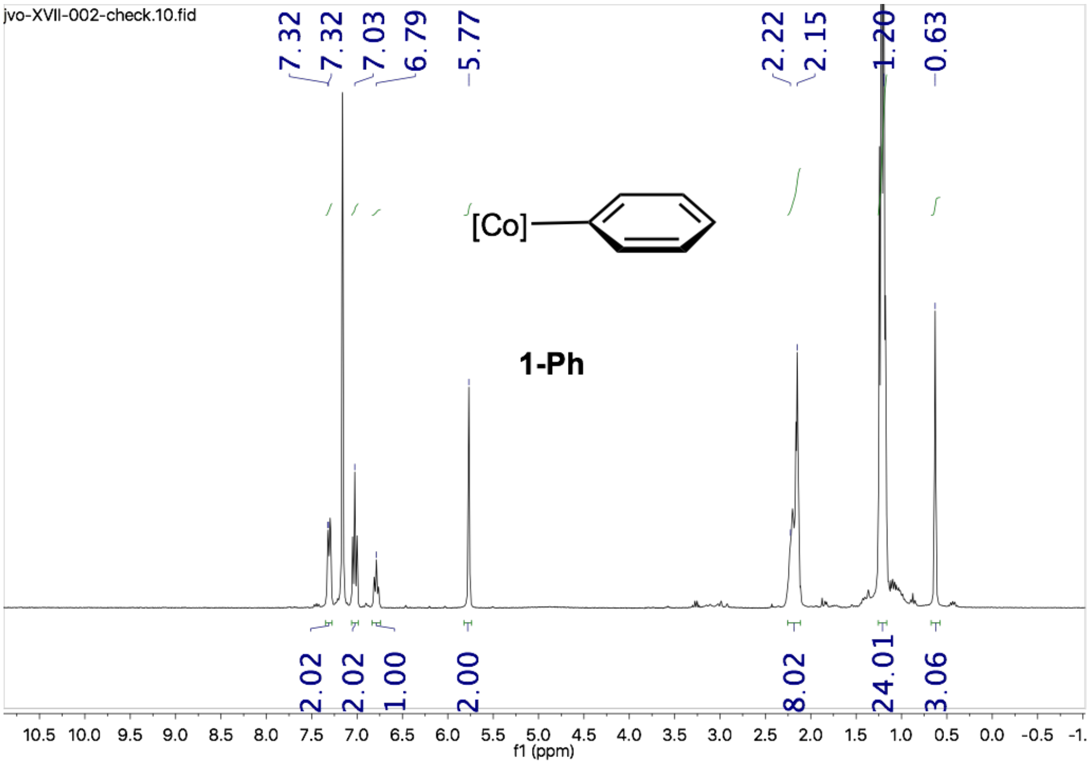


Figure S8. ^{1}H NMR spectrum (C_6D_6, 23 °C) of **1-Ph**.

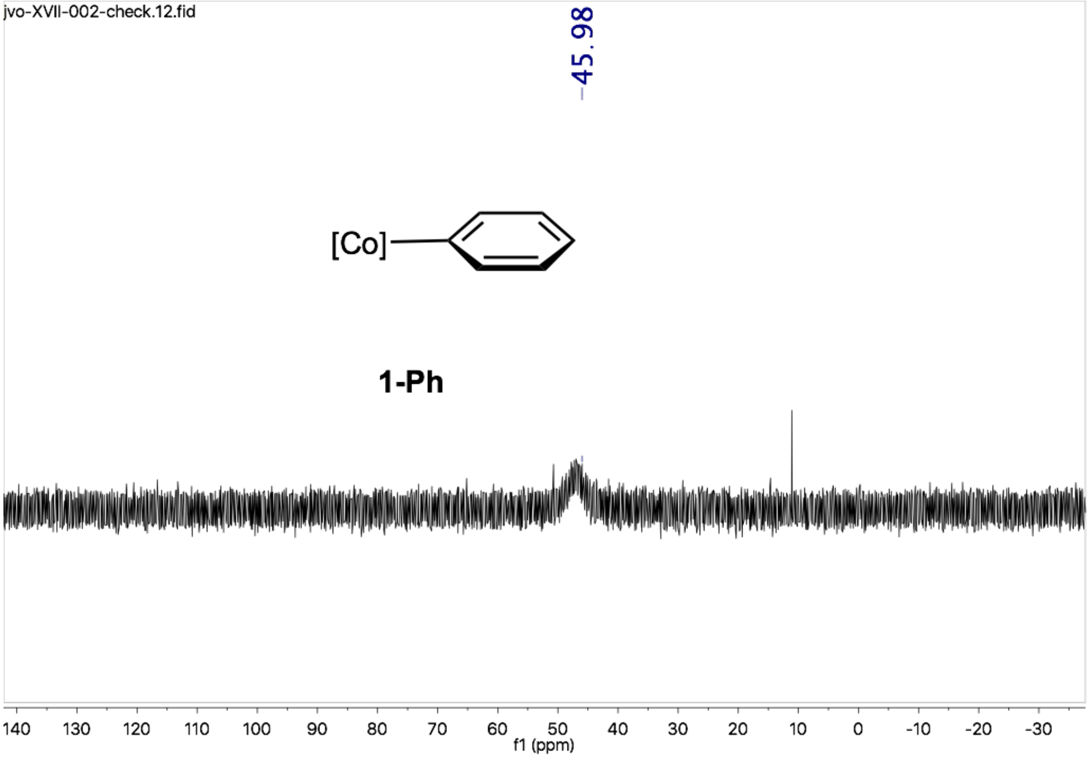
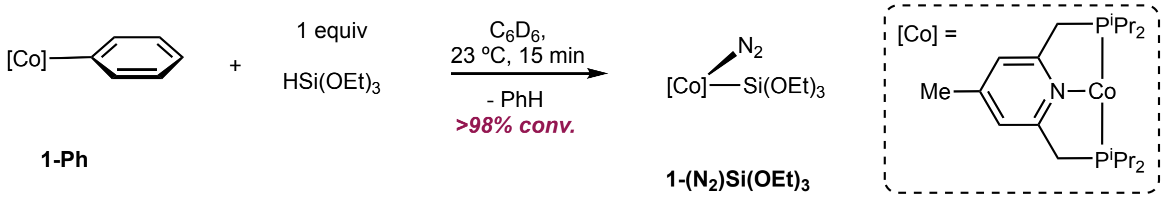


Figure S9. ^{31}P NMR spectrum (C_6D_6, 23 °C) of **1-Ph**.

VII. Reaction of 1-Ph with $HSi(OEt)_3$



1-Ph

1-(N_2)Si(OEt)$_3$

In a nitrogen-filled glovebox, a scintillation vial was charged with $HSi(OEt)_3$ (0.010 g, 0.06 mmol), **1-Ph** (0.030 g, 0.061 mmol), and 0.5 mL of C_6D_6. The vial was swirled until the mixture became homogeneous and the resulting solution was transferred to a J-Young tube. The tube was sealed, brought out of the glovebox and the reaction was analyzed using ^{1}H and ^{31}P NMR spectroscopy. The resulting compound is tentatively assigned as **1-(N_2)Si(OEt)$_3$**.

^{1}H NMR (benzene-d_6, 23 °C): δ 6.33 (s, 2H, meta py C*H*), 3.94 (q, *J* = 7.07 Hz, 6H, -OC*H*$_2$CH$_3$), 3.44 – 3.05 (m, 4H, -PC*H*$_2$), 2.89 – 2.29 (m, 4H, PC*H*Me$_2$), 1.69 (s, 3H, py *Me*), 1.56 – 1.14 (overlapping m, 36H, PCH*Me*$_2$, -OCH$_2$C*H*$_3$).

^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 76.39 (br s, *P*-CHMe$_2$).

IR (benzene-d_6, 23 °C): νN_2 = 2053.71 cm^{-1}.

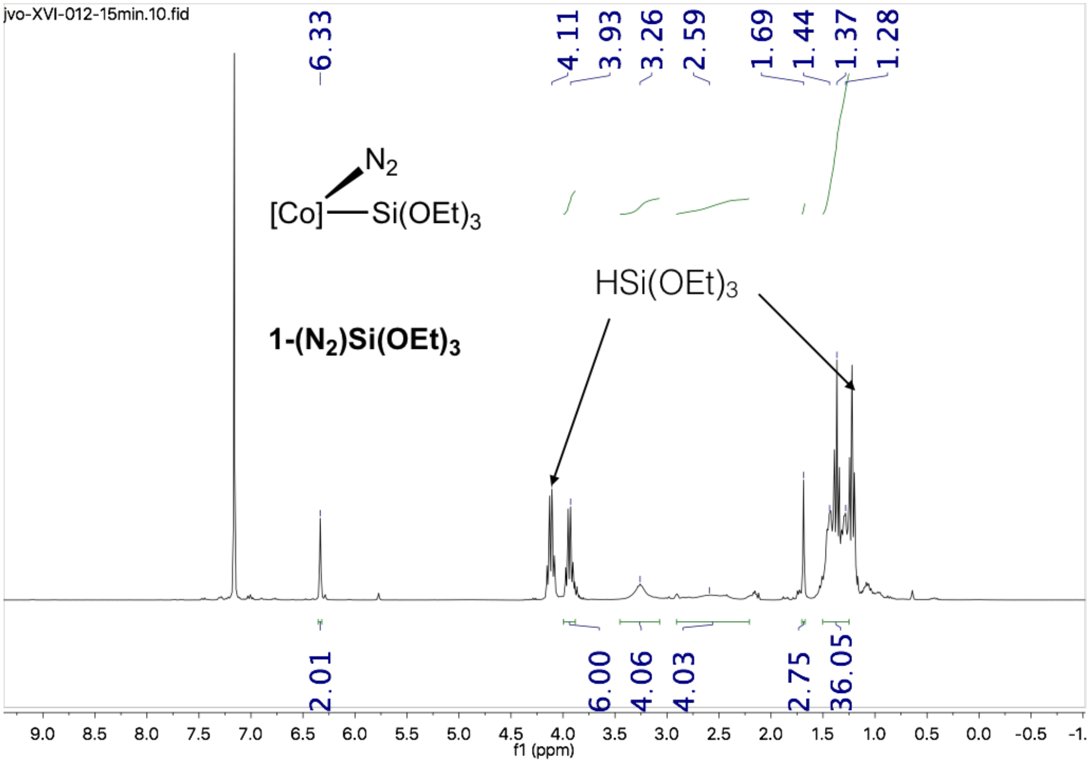


Figure S10. ^{1}H NMR spectrum (C_6D_6, 23 °C) of the reaction of **1-Ph** with HSi(OEt)$_3$.

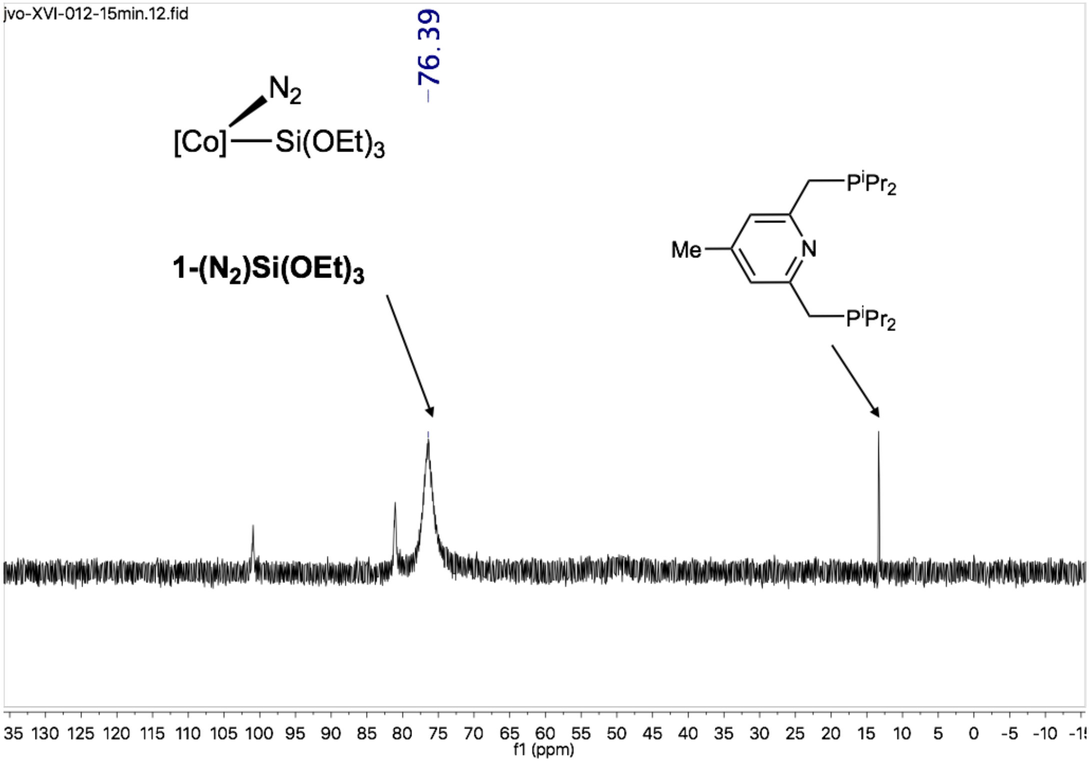
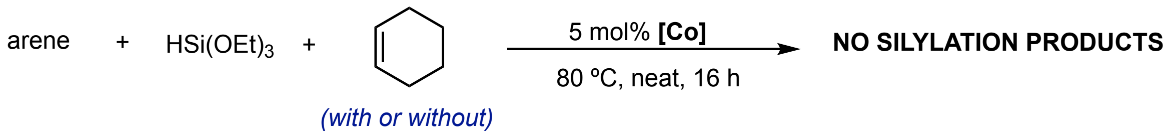
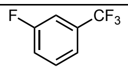
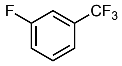
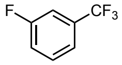
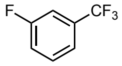
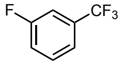
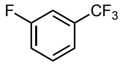
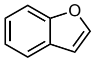


Figure S11. ^{31}P NMR spectrum (C_6D_6, 23 °C) of the reaction of **1-Ph** with HSi(OEt)$_3$.

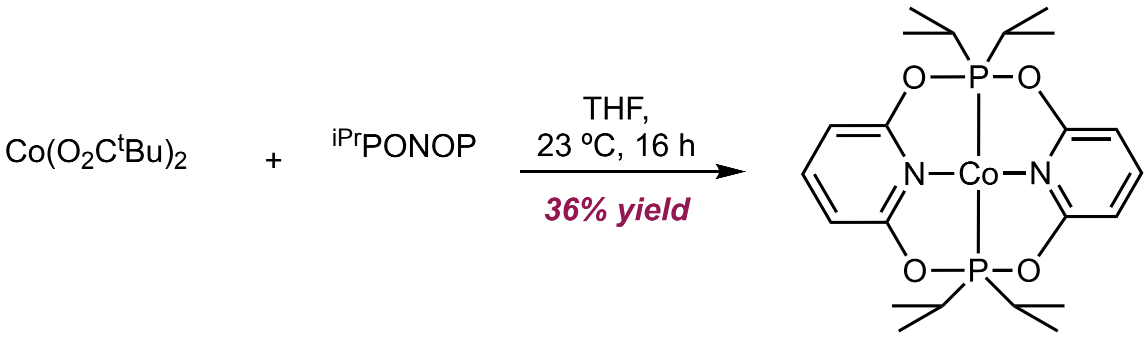
VIII. Evaluation of the Cobalt Pre-catalysts for C-H Silylation



In a nitrogen-filled glovebox, a scintillation vial was charged with arene (0.78 mmol), $HSi(OEt)_3$ (0.78 mmol), cyclohexene (0 mmol or 0.78 mmol) and cobalt pre-catalyst (5 mol%) (see table below). The vial was sealed at was heated to 80 °C for 16 hours. The reaction was quenched by exposure to air and an aliquot of the mixture was analyzed by gas chromatography. No silylation product(s) were observed under these conditions.

Entry	Arene	Acceptor?	Pre-catalyst
1		No	**1-$(H)_2$BPin**
2		No	**$(^{iPr}\text{PNP})\text{CoCH}_2\text{SiMe}_3$**[3]
3		Yes	**1-$(H)_2$BPin**
4		Yes	**$(^{iPr}\text{PNP})\text{CoCH}_2\text{SiMe}_3$**[3]
5		Yes	**1-$(O_2C^tBu)_2$**
6		No	**4-BPin-$(^{iPr}\text{PNP})\text{CoCH}_3$**[2]
7		No	**4-BPin-$(^{iPr}\text{PNP})\text{CoCH}_3$**[2]

IX. Synthesis of 2



2

In a nitrogen-filled glovebox, a scintillation vial was charged with anhydrous $Co(O_2C^tBu)_2$[4] (0.100 g, 0.384 mmol), ^{iPr}PONOP[5] (0.132 g, 0.384 mmol), and 10 mL of THF. The resulting solution was stirred at room temperature for 1 hour. The solution was filtered through Celite on a glass frit and the volatiles are removed in vacuo. The resulting residue was dissolved in Et_2O to form a saturated solution. Recrystallization at -35 °C overnight yielded orange crystals (0.083 g, 36 % yield). ^1H NMR (300 MHz, C_6D_6, 23 °C): δ -16.92 ($\Delta\nu_{½}$ = 72 Hz), δ -9.93 ($\Delta\nu_{½}$ = 144 Hz), δ 13.35 ($\Delta\nu_{½}$ = 596 Hz), δ 57.65 ($\Delta\nu_{½}$ = 726 Hz).

Anal Calcd for $C_{22}H_{34}CoN_2O_4P_2$: C, 51.67; H, 6.70; N, 5.48, Found: C, 51.76; H, 6.79; N, 5.40.

Effective magnetic moment (Evans Method, 23 °C): $\mu_{eff} = 1.8\ u_B$.

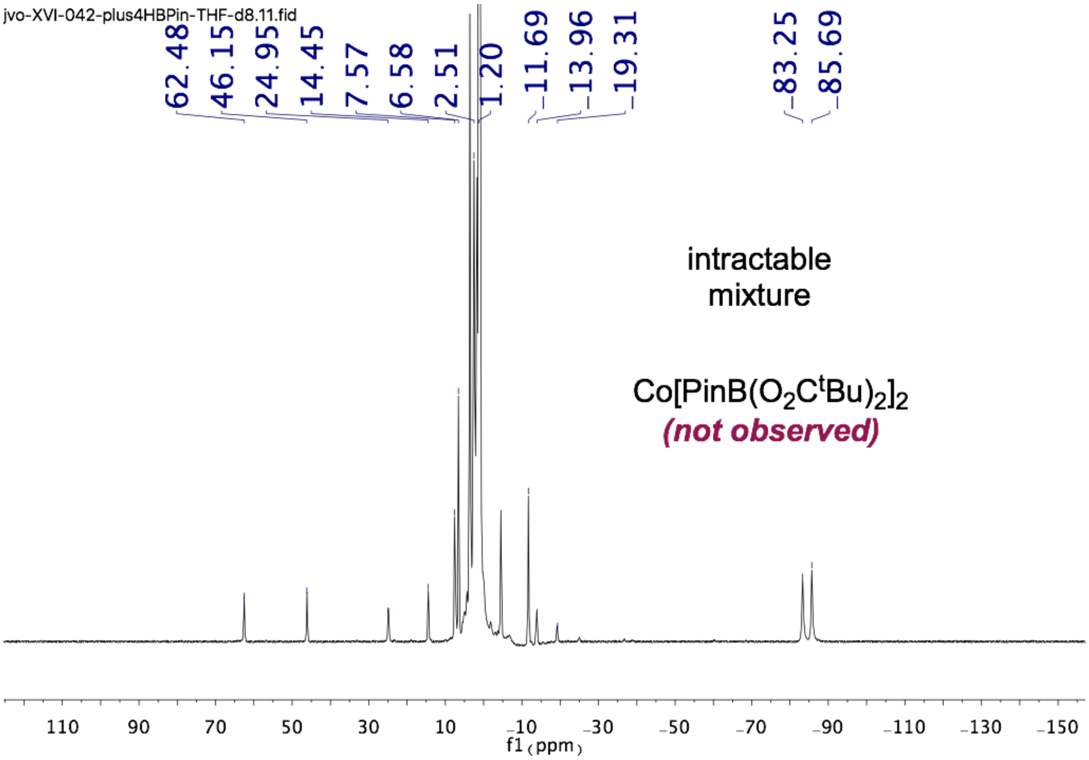
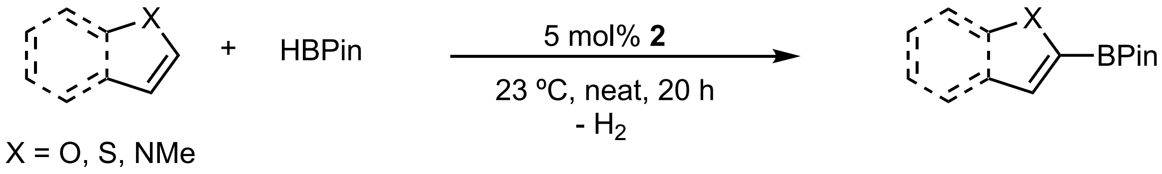


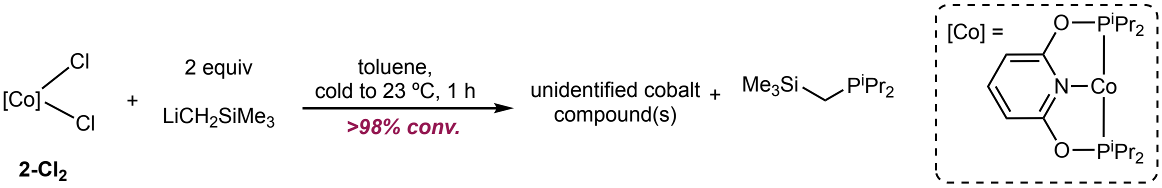
Figure S12. ^{1}H NMR spectrum (C_6D_6, 23 °C) of **2**.

X. Evaluation of 2 for C-H Borylation



In a nitrogen-filled glovebox, a scintillation vial was charged with heteroarene (0.55 mmol), HBPin (0.55 mmol), and **2** (5 mol%). The vial was sealed at was heated to 80 ºC for 20 hours. The reaction was quenched by exposure to air and an aliquot of the mixture was analyzed by gas chromatography.

XI. Reaction of 2-Cl$_2$ with LiCH$_2$SiMe$_3$



In a nitrogen-filled glovebox, a 100 mL round bottom flask was charged with **$2\text{-}Cl_2$**[6] (0.200 g, 0.423 mmol) and 30 mL of toluene. In a separate vial, $SiMe_3CH_2Li$ (0.080 g, 0.850 mmol) was diluted with 5 mL of toluene. The round bottom flask containing **$2\text{-}Cl_2$** and the vial containing $SiMe_3CH_2Li$ were chilled in a cold well filled with liquid nitrogen for 20 mins. The cold solution of $SiMe_3CH_2Li$ was then added dropwise to a cold, stirring solution of **$2\text{-}Cl_2$** in toluene. The reaction was allowed to cool to room temperature and was stirred for 3 hours. The crude reaction mixture was analyzed using ^1H and ^{31}P NMR spectroscopy. The volatile materials were then collected and analyzed using ^1H and ^{31}P NMR spectroscopy.

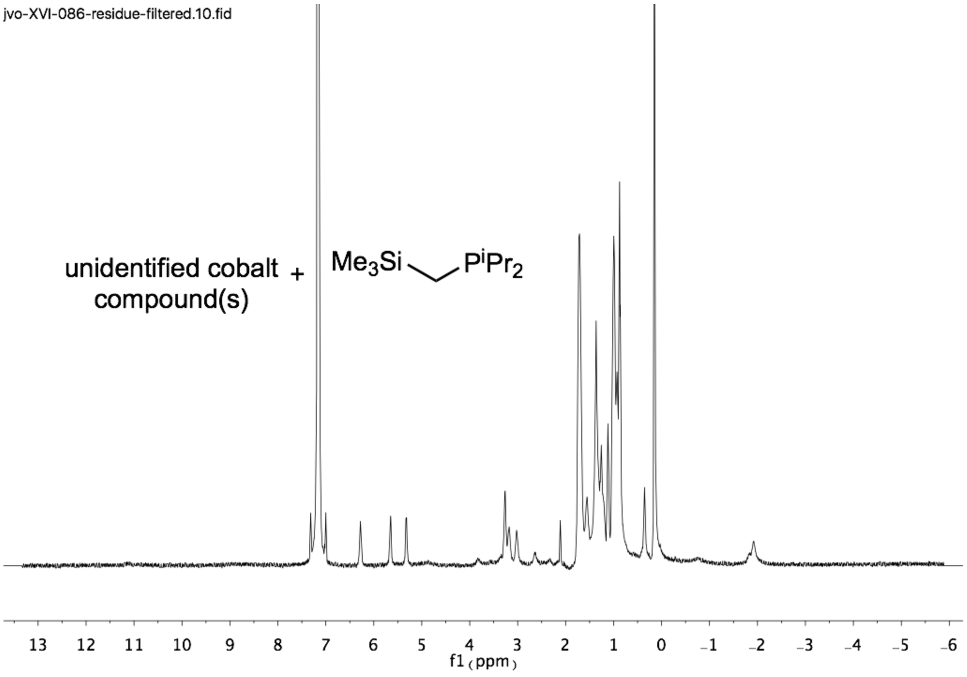


Figure S13. ^1H NMR spectrum (C_6D_6, 23 °C) of the reaction of **$2\text{-}Cl_2$** with $LiCH_2SiMe_3$ (unpurified reaction mixture).

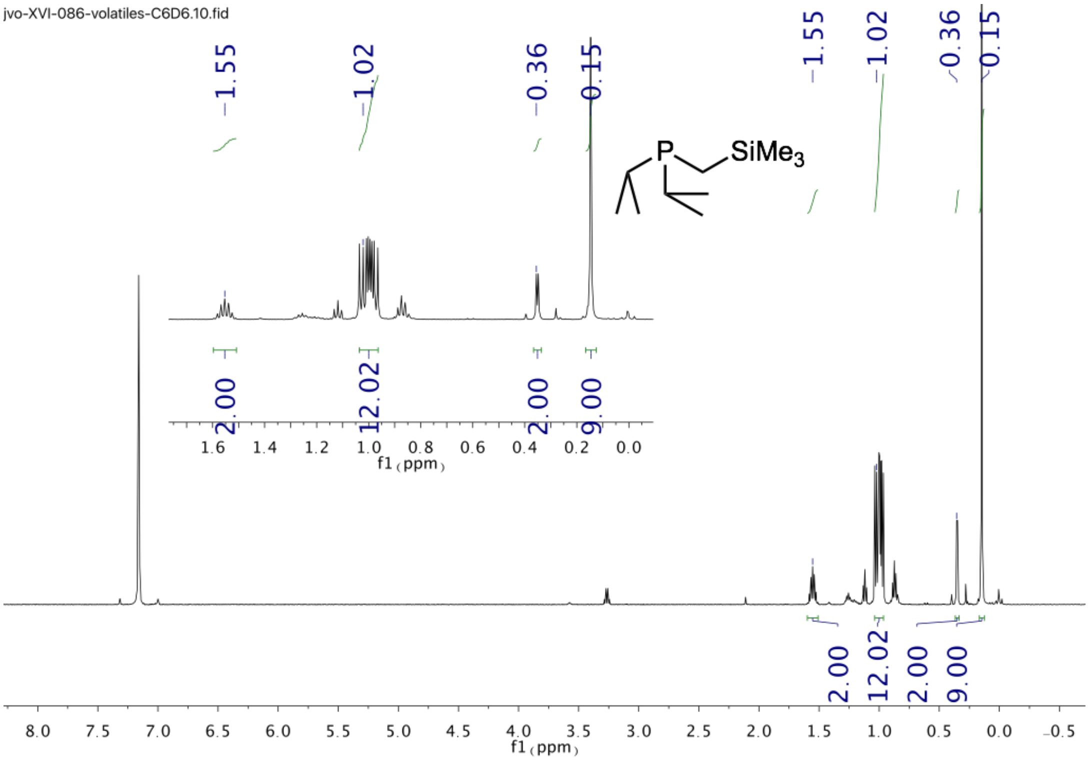


Figure S14. ^{1}H NMR spectrum (C_6D_6, 23 °C) of the reaction of **2-Cl₂** with $LiCH_2SiMe_3$ (volatiles).

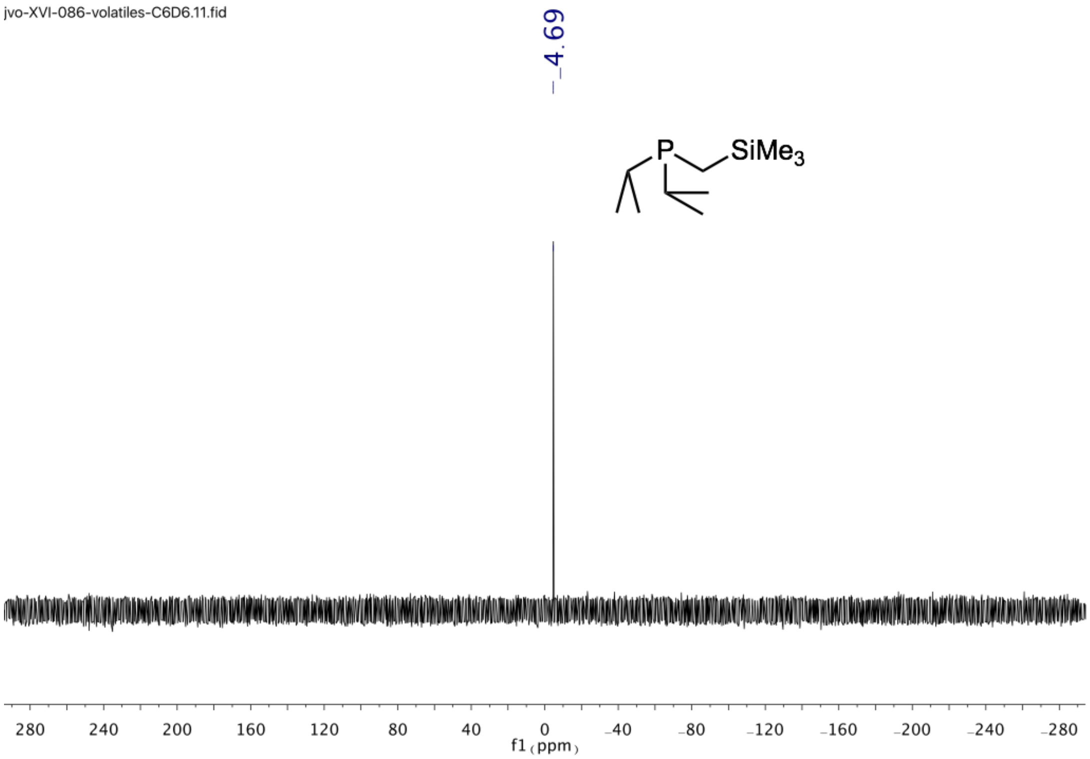
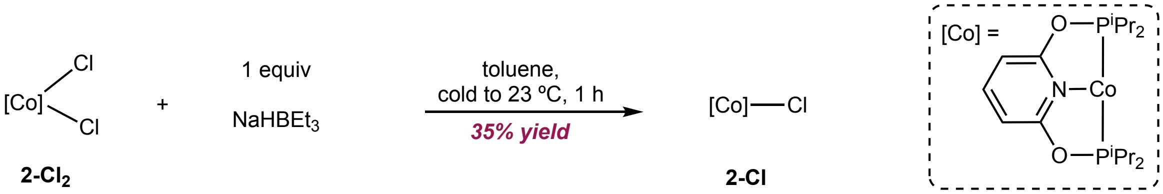


Figure S15. ^{31}P NMR spectrum (C_6D_6, 23 °C) of the reaction of **2-Cl$_2$** with $LiCH_2SiMe_3$ (volatiles).

XII. Synthesis of 2-Cl



In a nitrogen-filled glovebox, a 100 mL round bottom flask was charged with **2-Cl$_2$**[5] (0.500 g, 1.06 mmol) and 40 mL of toluene. In a separate vial, $NaHBEt_3$ (1.06 mL of a 1.0 M solution in toluene, 1.06 mmol) was diluted with 5 mL of toluene. The round bottom flask containing **2-Cl$_2$** and the vial containing $NaHBEt_3$ were chilled in a cold well filled with liquid nitrogen for 20 mins. The cold solution of $NaHBEt_3$ was then added dropwise to a cold, stirring solution of **1-Cl$_2$** in toluene. The reaction was allowed to cool to room temperature and was stirred for 3 hours. The solution was filtered through Celite and the volatiles were evaporated in vacuo to yield a blue residue that was recrystallized twice at -35 °C in toluene to yield blue crystals identified as **2-Cl** (0.164 g, 35% yield).

^{1}H NMR (benzene-d_6, 23 °C): δ 6.87 (t, *J* = 7.80 Hz, 1H, para py C*H*), 5.75 (d, *J* = 7.87 Hz, 2H, meta py C*H*), 2.52 – 2.35 (m, 4H, PC*H*Me$_2$), 1.65 – 1.50 (m, 12H, PCH*Me*$_2$), 1.44 – 1.33 (m, 12H, PCH*Me*$_2$).

{^{1}H}^{31}P NMR (benzene-d_6, 23 °C): δ 195.57 (br s, *P*-CHMe$_2$).

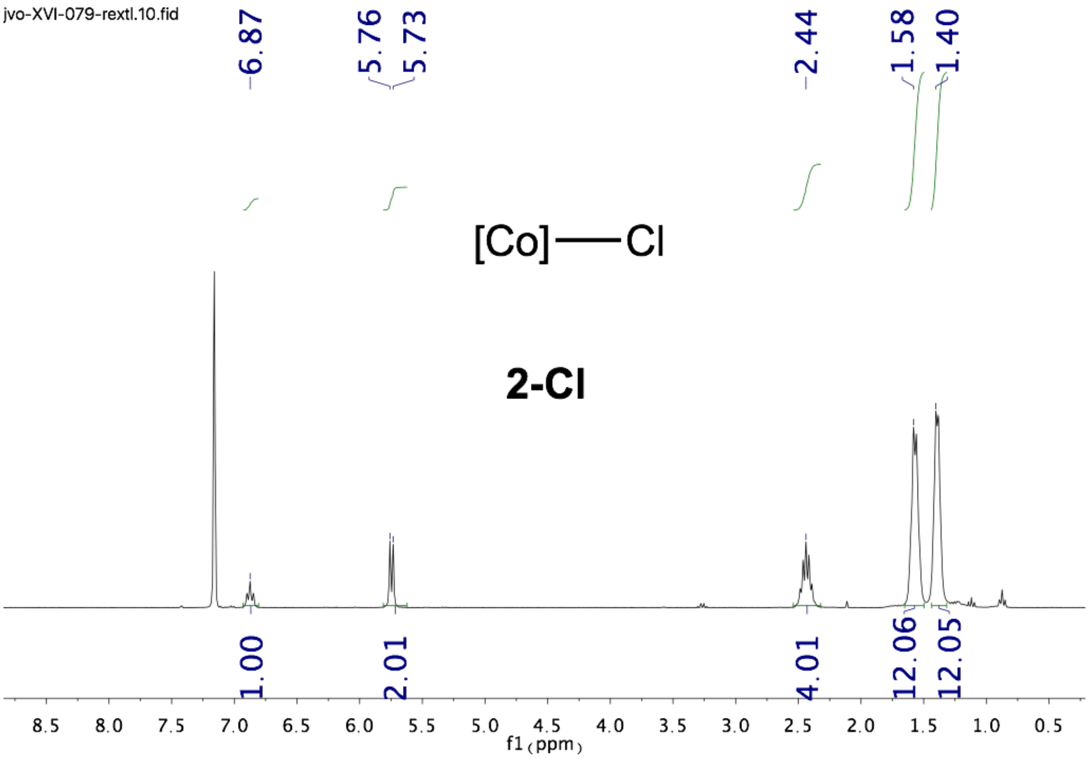


Figure S16. ^{1}H NMR spectrum (C_6D_6, 23 °C) of **2-Cl**.

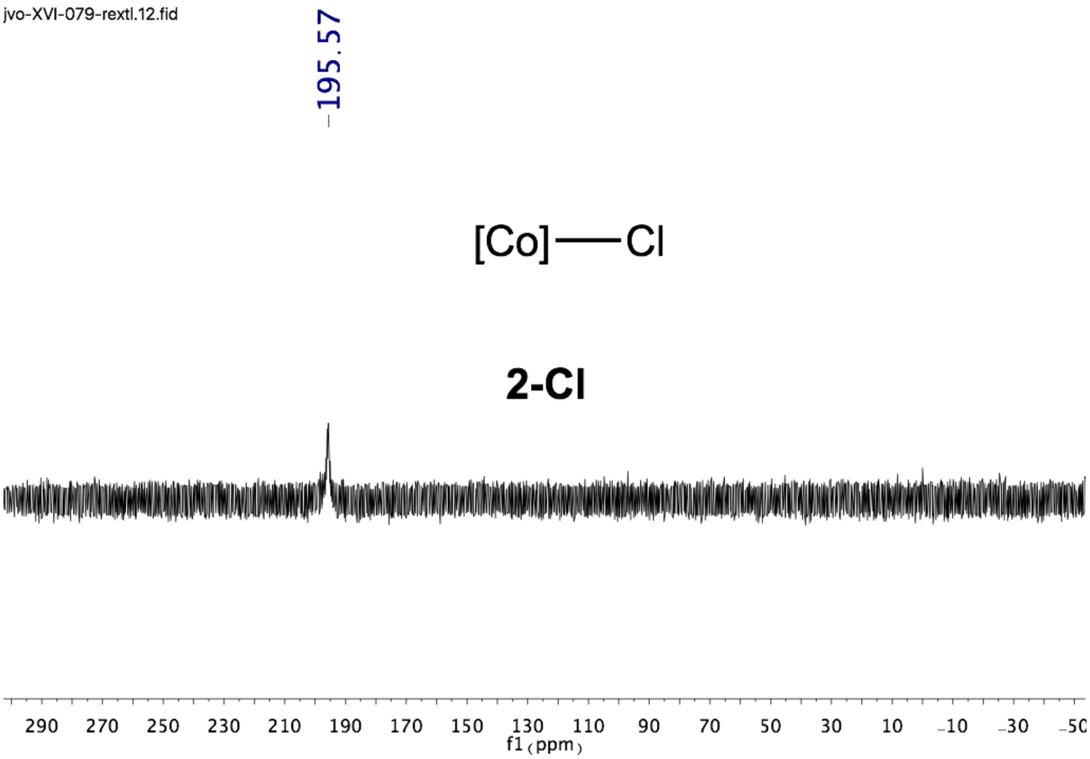
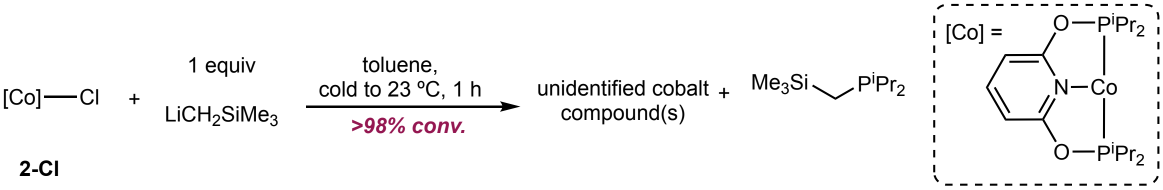


Figure S17. ^{31}P NMR spectrum (C_6D_6, 23 °C) of **2-Cl**.

XIII. Reaction of 2-Cl with $LiCH_2SiMe_3$



In a nitrogen-filled glovebox, a scintillation vial was charged with **2-Cl** (0.034 g, 0.078 mmol) and 5 mL of toluene. In a separate vial, $SiMe_3CH_2Li$ (0.007 g, 0.074 mmol) was diluted with 2 mL of toluene. The vial containing **2-Cl** and the vial containing $SiMe_3CH_2Li$ were chilled in a cold well filled with liquid nitrogen for 20 mins. The cold solution of $SiMe_3CH_2Li$ was then added dropwise to a cold, stirring solution of **2-Cl** in toluene. The reaction was allowed to cool to room temperature and was stirred for 1 hour. The crude reaction mixture was analyzed using ^{1}H NMR spectroscopy.

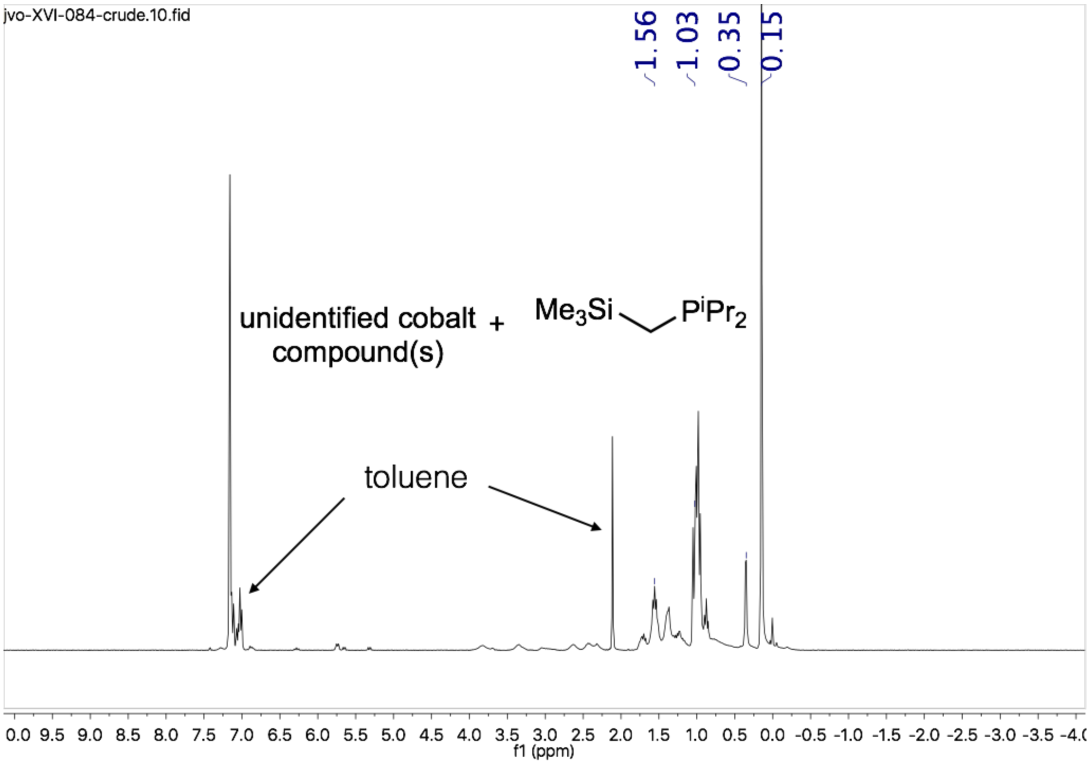


Figure S18. ^{1}H NMR spectrum (C_6D_6, 23 °C) of the reaction of **2-Cl** with $LiCH_2SiMe_3$ (crude reaction mixture).

XIV. References

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