Electronic Ligand Modifications on Cobalt Complexes and their Application Towards the Semi-Hydrogenation of Alkynes and Para-hydrogenation of Alkenes

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Supporting Information

General Considerations. Unless otherwise stated all manipulations were carried out in an MBraun inert atmosphere drybox under an atmosphere of nitrogen or using standard Schlenk techniques. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using a Glass Contour System (SG Water USA, Nashua, NH) following literature procedure and stored over 4Å molecular sieves purchased from Strem prior to use. Celite 545 (J. T. Baker) was heated to 150°C under dynamic vacuum for 24h prior to use in the drybox. Deuterated NMR solvents were purchased from Cambridge Isotope Labs and were degassed and stored over 3 Å molecular sieves prior to use. 1,3-dibromo-5-(tert-butyl)benzene, 5-(trifluoromethyl)-1,3-phenylenediamine, triethyl orthoformate, DPEPhos, and ethyl acrylate were purchased from commercial sources and used as received. Trityl chloride and PPh_3 were purchased from commercial sources and recrystallized from THF under inert atmosphere before use. $LiNTMS_2$ was purchased from Sigma Aldrich and recrystallized from toluene under inert atmosphere before use. N-(2-bromophenyl)-2,4,6-trimethylaniline[1], $Pd(PPh_3)_4$[2], $Co(N(SiMe_3)_2)_2]_2$•THF[3,4], and KC_8[5] were prepared by literature procedures.

Characterization and Physical Methods. NMR spectra were recorded at ambient temperature or 37°C on a Varian spectrometer operating at either 500 MHz or 600 MHz (^{1}H NMR) and 126 MHz or 151 MHz (^{13}C NMR) and referenced to the peak of the residual solvent (δ in parts per million and *J* in Hz). Solid-state infrared spectra were measured using a PerkinElmer Frontier FT-IR spectrophotometer equipped with a KRS5 thallium bromide/iodide universal attenuated total reflectance accessory. Electrospray ionization mass spectrometry (ESI) was recorded on a Water Q-TOF Ultima ESI instrument at the University of Illinois at Urbana−Champaign School of Chemical Sciences Mass Spectrometry Laboratory in Urbana, IL.

Preparation of 5-(*tert*-butyl)benzene-1,3-diamine

A 150 mL Schlenk bomb was charged with 1,3-dibromo-5-(tert-butyl)benzene (0.530g, 1.821 mmol), $NiCl_2(PPh_3)_2$ (0.175g, 0.274 mmol) and lithium hexamethyldisilazide (0.914 g, 5.462 mmol) and diluted with ca. 75 mL of toluene and stirred at 100°C for 17 h. The reaction mixture was allowed to cool to ambient temperature and then filtered over a pad of Celite, eluting with 200 mL of DCM. The solution was concentrated to *ca*. 50 mL solvent and 50 mL of MeOH was added. The solution was transferred to a 250 mL separatory funnel and 15 mL of a 1 M HCl solution was added and shaken vigorously for ca. 5 minutes. The solution was then transfer to a 250 mL round bottom flask, where it was stirred vigorously for two hours. To the solution was added 100 mL of a 1 M KOH solution and 50 mL of DI H_2O. The MeOH was removed in vacuo and an organic extraction was performed with DCM (3 × 100 mL). The organic layer was collected and dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue adsorbed on 6g of dry silica. The silica was loaded onto a silica gel column and the product was separated with a stepwise gradient of 0-80% ethyl acetate/hexanes, yielding an off-white solid. The solid was taken into the glove box, dissolved in *ca*. 10 mL of benzene and stored over 4 Å molecular sieves for 18 h. The solution was filtered over a pad of Celite and solvent was removed under reduced pressure to yield a light brown solid (221 g, 1.346 mmol, 74%). The ^{1}H and ^{13}C NMR spectra matched those of the reported compound.[6]

Synthesis of N^1,$N^{1'}$-(5-(*tert*-butyl)-1,3-phenylene)bis(N^2-mesitylbenzene-1,2-diamine) (L2-^{t}Bu)

A 20 mL scintillation vial charged with $Pd(PPh_3)_4$ (0.257 g, 0.222 mmol) and DPEPhos (0.320 g, 0.594 mmol) was stirred at 80°C for 20 minutes in toluene (10 mL). The DPEPhos/$Pd(PPh_3)_4$ solution was then filtered through a pad of Celite into a 150 mL Schlenk bomb containing 5-(tert-butyl)benzene-1,3-diamine (0.208 g, 1.266 mmol), N-(2-bromophenyl)-2,4,6-trimethylaniline (0.850 g, 2.929 mmol), and sodium *tert*-pentoxide (0.810 g, 7.355 mmol). The mixture was then diluted with *ca*. 75 mL of toluene and stirred at 100°C for 24 h. The suspension was allowed to cool to ambient temperature and then filtered through a plug of silica, eluting with 400 mL of Et_2O. The solvent was removed under reduced pressure and the

residue was adsorbed on 5g of dry silica and loaded onto a silica gel column. The product was separated with a stepwise gradient of 0-10% ethyl acetate/hexanes, yielding a light brown solid after removal of the solvent (0.590 mg, 1.012 mmol, 85%). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 7.24 (d, *J* = 7.2, 2H), 6.93 – 6.91 (m, 6H), 6.74 (t, *J* = 7.3, 2H), 6.45 (d, *J* = 1.2, 2H), 6.26 – 6.24 (m, 3H), 5.50 (br s, 2H), 5.27 (br s, 2H), 2.31 (s, 6H), 2.14 (s, 12H), 1.29 (s, 9H). ^{13}C (125 MHz, $CDCl_3$, 25°C) δ 153.82, 146.46, 141.58, 136.01, 135.32, 135.07, 129.30, 129.08, 125.37, 124.23, 118.34, 112.77, 105.20, 100.77, 34.94, 31.45, 21.03, 18.36. HRMS (ESI) calc. for $C_{40}H_{46}N_4$ $(M - H)^+$: 583.38; found 583.38.

Synthesis of 1,1'-(5-(tert-butyl)-1,3-phenylene)bis(3-mesityl-1H-benzo[d]imidazol-3-ium) chloride $[H_3(^{Mes}CCC^{tBu})]Cl_2$

Compound **L2-^{t}Bu** (0.590 g, 1.012 mmol) was suspended in 70 mL of triethyl orthoformate and heated to reflux at 80°C. Concentrated hydrochloric acid (37% w/w, 0.8 mL, 9.7 mmol) was added dropwise and the color of the suspension turned purple. After stirring the mixture for 19 h, the suspension was allowed to cool to ambient temperature and 70 mL of Et_2O, followed by 210 mL of hexanes were added dropwise, resulting in the precipitation of a white solid. The solids were collected by filtration and washed with excess ether. The compound was then dissolved in *ca*. 20 mL of DCM and triturated with ca. 100 mL of hexanes. The suspension was filtered and the solid was taken into the dry box, stored over 4Å sieves in *ca*. 10mL of DCM. The solution was decanted, and solvent removed under reduced vacuum to yield an off white solid (0.540 g, 0.799 mmol, 79%). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 12.51 (s, 2H), 8.51 (d, *J* = 8.5, 2H), 8.47 (br s, 1H), 8.16 (d, *J* = 1.3, 2H), 7.88 (t, *J* = 7.8, 2H), 7.68 (t, *J* = 7.8, 2H), 7.32 (d, *J* = 8.5, 2H), 7.11 (s, 4H), 2.39 (s, 6H), 2.15 (s, 12H), 1.59 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C) δ 157.26, 144.18, 144.05, 141.83, 135.30, 134.31, 131.78, 131.12, 130.40, 129.25, 128.62, 128.03, 124.88, 120.99, 115.47, 113.46, 31.43, 21.34, 18.23. Analysis for $C_{42}H_{44}Cl_2N_4 \cdot 0.35(CH_2Cl_2) \cdot 0.8(C_6H_{14})$: Calcd. C, 73.13; H, 7.28; N, 7.23. Found: C, 73.24; H, 7.33; N, 7.34. HRMS (ESI) calc. for $C_{42}H_{44}ClN_4$ $(M - Cl)^+$: 639.33; found 639.33.

Synthesis of N^1,$N^{1'}$-(5-(trifluoromethyl)-1,3-phenylene)bis(N^2-mesitylbenzene-1,2-diamine) (L2-CF_3)

In the glovebox, a 20 mL scintillation vial was charged with $Pd(PPh_3)_4$ (0.924 g, 0.80 mmol, 0.20 eq) and DPEPhos (0.862 g, 1.60 mmol, 0.40 eq) and stirred at 80°C for 20 minutes in toluene (20 mL). The DPEPhos/$Pd(PPh_3)_4$ solution was then filtered through a pad of Celite into a 350 mL Schlenk bomb and N-(2-bromophenyl)-2,4,6-trimethylaniline (2.670 g, 9.2 mmol, 2.3 eq), 5-(Trifluoromethyl)-1,3-phenylenediamine (0.704 g, 4.0 mmol, 1.0 eq) and sodium *tert*-butoxide (1.922 g, 20 mmol, 5 eq) were added and the mixture was diluted with *ca.* 120 mL of toluene. After stirring the mixture at 100°C for 24 h, the suspension was allowed to cool to ambient temperature and then filtered through a plug of silica, eluting with 500 mL of Et_2O. The solvent was removed under reduced pressure and the residue adsorbed on 30 g of dry silica and loaded onto a silica gel column. The product is separated with a stepwise gradient of 2-5% ethyl acetate/hexanes, yielding an off-white powder (1.955 g, 3.3 mmol, 82%). The ^{1}H and ^{13}C NMR spectra matched those of the reported compound.[7]

Synthesis of 1,1'-(5-(trifluoromethyl)-1,3-phenylene)bis(3-mesityl-1H-benzo[d]imidazol-3-ium) chloride $[H_3(^{Mes}CCC^{CF3})]Cl_2$

L2-CF_3 (1.486 g, 2.5 mmol, 1 equiv) was suspended in 40 mL triethyl orthoformate and heated to reflux at 80°C under an N_2 atmosphere. Concentrated hydrochloric acid (37% w/w, 0.5 mL, 6 mmol) was added dropwise and the color of the suspension turned off-white. After stirring the mixture for 20 h, the suspension was allowed to cool to ambient temperature and 50 mL of Et_2O, followed by 150 mL of hexanes were added resulting in the precipitation of a white solid. After stirring for 20 min, the solid was collected by filtration and washed with excess ether and hexanes. The off-white solid was taken into the drybox,

dissolved in *ca.* 100 mL of DCM and stored under 4 Å molecular sieves for 24 h. The solution was decanted, and *ca.* 120 mL hexanes was added and a white solid was isolated by filtration (1.371 g, 1.99 mmol, 80%). The ^{1}H and ^{13}C NMR spectra match those of the reported compound.[7]

Synthesis of Metal Complexes

Synthesis of ($^{Mes}CCC^{tBu}$)$CoCl_2$py (1-^{t}Bu)

A solution of lithium hexamethyldisilazide (0.0266 g, 0.159 mmol) in *ca*. 2 mL of THF was added to a 20 mL scintillation vial charged with $[H_3(^{Mes}CCC^{tBu})]Cl_2$ (0.0980 g, 0.145 mmol) in *ca*. 10 mL of THF , and stirred at ambient temperature for 5 min. A THF solution (*ca*. 3 mL) of $[Co(N(SiMe_3)_2)_2]_2$•THF (0.0550 g, 0.145 mmol) and 5 drops of anhydrous pyridine was added dropwise, followed by the addition of a THF (*ca*. 3 mL) solution of trityl chloride (0.0526 g, 0.188 mmol). After stirring the mixture for 18 h, the volatiles were removed under reduced pressure and the green solid was washed with hexanes (2 × 10 mL), then with diethyl ether (2 × 10mL) and taken up in benzene (10 mL), filtered over a plug of Celite, frozen and dried (0.0334 g, 0.041 mmol, 28%). The rest of the product was dissolved in THF (5 mL), filtered over a plug of Celite. The solvent was removed under reduced pressure to yield a green solid (0.0332 g, 0.041 mmol, 28%). Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 9.20 (d, *J* = 5.3, 2H), 8.02 (d, *J* = 8.4, 2H), 7.85 (s, 2H), 7.06 (t, *J* = 7.5, 2H), 6.88 (t, *J* = 7.7, 2H), 6,74 (t, *J* = 7.2, 1H), 6.62 (d, *J* = 8.2, 2H), 6.32 (s, 4H), 6.13 (t, *J* = 7.0, 2H), 2.03 (s, 12H), 1.99 (s, 6H), 1.56 (s, 9H). ^{13}C NMR (125 MHz, THF-d_8): δ 200.57, 153.45, 153.28, 149.50, 148.78, 139.37, 137.54, 137.46, 134.20, 133.40, 133.10, 129.91, 124.38, 123.63, 112.57, 110.85, 107.67, 32.73, 26.43, 21.13, 18.33. Analysis for $C_{47}H_{46}Cl_2CoN_5 \cdot 1.1(H_2O) \cdot 1.35(C_6H_6)$: Calcd. C, 70.70; H, 6.06; N, 7.48. Found C, 70.64; H, 5.90; N, 7.32. HRMS (ESI), calc. for $C_{47}H_{46}N_5ClCo$ $(M - Cl)^+$: 774.2774; found 774.2786.

Synthesis of ($^{Mes}CCC^{CF3}$)$CoCl_2$py (1-CF_3)

A 20 mL scintillation vial was charged with $[H_3(^{Mes}CCC^{CF3})]Cl_2$ (137.5 mg, 0.20 mmol, 1.0 equiv) in ca. 5 mL of THF and a solution of lithium hexamethyldisilazide (33.5 mg, 0.20 mmol, 1 equiv) was added with ca. 3 mL of THF. The resulting suspension was stirred at ambient temperature for 5 min. A THF (ca. 4 mL) solution of $[Co(N(SiMe_3)_2)_2]$ 2•THF (90.4 mg, 0.20 mmol, 1.0 equiv) and 10 drops of anhydrous pyridine were added dropwise to the suspension. The resulting dark green suspension was stirred for 10 minutes, then a solution of trityl chloride (55.8 mg, 0.20 mmol, 1.0 equiv) in ca. 3 mL THF was added and then the reaction was stirred at ambient temperature for 18 h. The volatiles were then removed under reduced pressure and the green solid was washed with hexanes (3 × 10 mL), dissolved in DCM (10 mL), filtered over a plug of Celite and the solvent was removed under reduced pressure to give a green solid (145.9 mg, 0.18 mmol, 88%). Crystal suitable for X-ray diffraction were grown from slow evaporation of a $CDCl_3$ solution in an NMR tube. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 8.77 (d, *J* = 5.0 Hz, 2H), 8.26 (d, *J* = 8.2 Hz, 2H), 8.02 (s, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.20 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.58 – 6.54 (m, 2H), 6.53 (s, 4H), 2.20 (s, 6H), 1.82 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.55, 163.90, 151.96, 148.35, 138.58, 136.54, 136.32, 133.26, 132.11, 131.76, 128.89, 123.94, 123.34, 122.60, 111.71, 110.43, 106.33, 106.30, 20.76, 17.82. ^{19}F NMR (470 MHz, C_6D_6) δ -61.10. Analysis for $C_{44}H_{37}Cl_2CoF_3N_5 \cdot 0.15(H_2O) \cdot 0.35(CH_2Cl_2)$: Calcd. C, 62.30; H, 4.48; N, 8.19. Found C, 62.68; H, 4.66; N, 7.80. HRMS (ESI), calc. for $C_{44}H_{37}ClCoF_3N_5$ $(M - Cl)^+$: 786.2022; found 786.2015.

Synthesis of ($^{Mes}CCC^{tBu}$)Co-py (2-^{t}Bu)

A 20 mL scintillation vial was charged with **1-^{t}Bu** (0.0500 g, 0.061 mmol), which was dissolved in *ca*. 10 mL of THF. To the solution, a suspension of KC_8 (0.0200 g, 0.148 mmol) was added, resulting in an immediate color change from green to brown. After stirring for two hours at ambient temperature, the mixture was filtered over Celite and solvent was removed under reduced pressure to yield a brown solid.

The product was washed with hexanes (3 × 5 mL) and taken up in *ca*. 10 mL of benzene. The benzene wash was frozen solid and the solvent removed under reduced pressure to yield a brown powder (0.0398 g, 0.054 mmol, 88%). ^{1}H NMR (500 MHz, C_6D_6, 25°C) δ 8.27 (d, *J* = 8.27, 2H), 7.83 (s, 2H), 7.27 (t, *J* = 7.69, 2H), 7.00 (t, *J* = 7.69, 2H), 6.67 (d, *J* = 8.34, 2H), 6.33 (s, 4H), 1.96 (s, 6H), 1.86 (s, 12H), 1.70 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6, 25°C) δ 147.34, 144.43, 138.86, 136.10, 133.27, 131.67, 129.92, 129.05, 128.61, 126.56, 122.22, 122.11, 109.83, 108.49, 103.16, 32.30, 25.82, 20.89, 17.82. ^{19}F NMR (470 MHz, C_6D_6) δ -59.62.

Synthesis of (^{Mes}CCC^{CF3})Co-py (2-CF$_3$)

A 20 mL scintillation vial was charged with **1-CF$_3$** (0.0446 g, 0.054 mmol), which was dissolved in *ca*. 10 mL of THF. To the solution, a suspension of KC_8 (0.0180 g, 0.133 mmol) was added, resulting in an immediate color change from green to brown. After stirring for two hours at ambient temperature, the mixture was filtered over Celite and solvent was removed under reduced pressure to yield a brown solid. The product was washed with hexanes (3 × 5 mL) and taken up in *ca*. 15 mL of benzene. The benzene wash was frozen solid, and the solvent removed under reduced pressure to yield a brown powder (0.0240 g, 0.034 mmol, 63%). ^{1}H NMR (500 MHz, C_6D_6, 25°C) δ 8.04(s, 2H), 7.94 (d, *J* = 7.78, 2H), 7.37 (br s, 2H), 7.16 (m, 2H), 6.97 (t, *J* = 7.78, 2H), 6.61 (d, *J* = 8.11, 2H), 6.33 (br s, 1H), 6.27 (s, 4H), 5.75 (br s, 2H), 1.95 (s, 6H), 1.77 (s, 12H). ^{13}C NMR (125 MHz, C_6D_6, 25°C) 196.03, 148.71, 146.75, 138.42, 137.42, 135.95, 134.90, 132.72, 130.38, 129.10, 128.59, 128.35, 122.81, 122.68, 122.39, 110.47, 108.71, 102.04, 102.01, 30.23, 20.83, 17.73.

Synthesis of (^{Mes}CCC)Co(CO)$_2$ (3-H)

A 20 mL scintillation vial was charged with (^{Mes}CCC)Copy, prepared from previously reported literature procedures[4] (0.0250 g, 0.033 mmol) and stirred in THF (*ca*. 10 mL). To the solution was added a suspension of KC_8 (0.0090 g, 0.061 mmol) in THF (*ca*. 5 mL). After stirring for 1 h at ambient temperatures, the suspension was filtered over a pad of Celite into a 50 mL Schlenk flask. The flask was brought out of the glovebox, and the solution was subjected to two freeze-pump-thaw cycles followed by addition of 1 atm of CO at ambient temperature to yield an amber colored solution. The flask was brought back into the glove box and after stirring at room temperature for 1 h, the CO headspace was removed under reduced pressure. The solution was transferred to a 20 mL scintillation vial and the THF was removed under reduced pressure to yield a yellow-gold solid. The solid was washed with hexanes (10 mL), then taken up in benzene (15 mL), filtered over Celite, and concentrated to a yellow solid. The solid was triturated with hexanes (10 mL) and concentrated under vacuum to give a fine yellow power (0.021 g, 0.0316 mmol, 96%). Crystals suitable for X-ray diffraction were grown from slow evaporation from THF at -35°C. ^{1}H NMR (500 MHz, C_6D_6, 25°C) δ = 7.82 (d, *J* = 7.8, 2H), 7.74 (d, *J* = 7.8, 2H), 7.50 (t, *J* = 7.6, 1H), 7.07 (t, *J* = 7.8, 2H), 6.90 (t, *J* = 7.8, 2H), 6.65 (s, 4H), 6.56 (d, *J* = 6.6, 2H), 1.95 (s, 18H). ^{13}C NMR (125 MHz, THF-d_8, 25°C) δ = 207.4, 205.8, 170.9, 145.8, 139.9, 137.7, 134.0, 132.1, 130.3, 129.0, 123.6, 123.4, 121.3, 111.5, 110.2, 107.4, 21.3, 17.8. HRMS (ESI), calc. for $C_{38}H_{34}CoN_4$ $(M - CO - CO)^+$: 605.2115; found 605.2115. ATR-IR: 1918 and 1973 cm^{-1} (C≡O).

Synthesis of (^{Mes}CCC^{tBu})Co(CO)$_2$ (3-^{t}Bu)

A 20 mL scintillation vial was charged with **1-^{t}Bu** (0.0243 g, 0.030 mmol) and stirred in THF (*ca*. 10 mL). To the solution was added a suspension of KC_8 (0.0083 g, 0.061 mmol) in THF (*ca*. 2 mL). After stirring for 1 h at ambient temperatures, the suspension was filtered over a pad of Celite into a 50 mL Schlenk flask. The flask was brought out of the glovebox, and the solution was subjected to two freeze-pump-thaw cycles

followed by addition of 1 atm of CO at ambient temperatures to yield an amber colored solution. The flask was brought back into the glove box and after stirring at room temperature for 1 h, the CO headspace was removed under reduced pressure. The solution was transferred to a 20 mL scintillation vial and the THF was removed under reduced pressure to yield a yellow-gold solid. The solid was taken up in hexanes and filtered over Celite, and the solvent was removed under reduced pressure to yield a solid (16.3 mg, 0.023 mmol, 76%). The remaining solids were dissolved in THF and filtered over Celite to yield a solid (5.0 mg, 0.007 mmol, 23%). ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 8.05 (d, J = 8.1, 2H), 7.97 (s, 2H), 7.08 (t, J = 7.7 , 2H), 6.90 (t, J = 7.6, 2H), 6.68 (s, 4H), 6.58 (d, J = 7.9, 2H), 1.99 (s, 12H), 1.96 (s, 6H), 1.66 (s, 9H). ^{13}C NMR (125 MHz, THF-*d8*, 25°C): 208.0, 167.4, 145.9, 145.7, 140.0, 137.9, 137.6, 134.2, 132.2, 130.5, 129.2, 123.7, 123.5, 111.6, 110.4, 104.9, 36.1, 32.9, 21.5, 17.9. HRMS (ESI), calc. for $C_{43}H_{42}N_4OCo$ [M – CO + H]$^+$: 689.2691; found 689.2686. ATR-IR: 1939 and 1990 cm^{-1} (C≡O).

Synthesis of (^{Mes}CCC^{CF3})Co(CO)$_2$ (3-CF$_3$)

A 20 mL scintillation vial was charged with **1-CF$_3$** (24.7 mg, 0.030 mmol, 1.0 equiv) and stirred in THF (ca. 10 mL). To the solution was added a suspension of KC_8 (8.3 mg, 0.063 mmol, 2.1 equiv) in THF (ca. 2 mL). After stirring for 1 h at ambient temperatures, the suspension was filtered over a pad of Celite into a 50 mL Schlenk flask. The flask was brought out of the glovebox, and the solution was subjected to two freeze-pump-thaw cycles followed by addition of 1 atm of CO at ambient temperature to yield an amber colored solution. The flask was stirred for 1 h at room temperature and then brought back into the glove box. The CO headspace was removed under reduced pressure and the solution was then transferred to a 20 mL scintillation vial and the THF was removed under reduced pressure to yield a yellow-gold solid. The solid was taken up in hexanes and filtered over Celite, and the solvent was removed under reduced pressure to yield the desired product as a yellow-brown solid (13.6 mg, 0.019 mmol, 63%). The remaining powder on the Celite was eluted with ca. 2 mL THF and then volatiles were removed to isolate more of the desired product (6.5 mg, 0.009 mmol, 30%). ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 8.10 (s, 2H), 7.65 (d, J = 8.1 Hz, 2H), 6.97 (t, J = 7.3 Hz, 2H), 6.86 (t, J = 7.4 Hz, 2H), 6.64 (s, 4H), 6.50 (d, J = 7.9 Hz, 2H), 1.94 (s, 6H), 1.93 (s, 12H). ^{13}C NMR (125 MHz, C_6D_6): δ 206.97, 177.02, 147.32, 145.19, 139.31, 137.10, 136.63, 133.12, 131.27, 130.03, 128.59, 123.33, 123.13, 111.18, 109.78, 103.97, 103.93, 21.05, 17.62. ^{19}F NMR (470 MHz, C_6D_6): δ -59.03. HRMS (ESI), calc. for $C_{40}H_{33}CoF_3N_4O$ [M – CO + H]$^+$: 701.1938; found 701.1949. ATR-IR: 1951 and 2004 cm^{-1} (C≡O).

Synthesis of (^{Mes}CCC^{tBu})Co(N$_2$)PPh$_3$ (4-^{t}Bu)

A 20 mL scintillation vial was charged with **1-^{t}Bu** (0.0500 g, 0.062 mmol) and stirred in THF (*ca*. 10 mL). To the solution was added a suspension of KC_8 (0.0200 g, 0.148 mmol) in THF (*ca*. 2 mL). After stirring for 2 h at ambient temperatures, the suspension was filtered over a pad of Celite and solvent was removed under reduced pressure. The solid was wash with hexanes (2 × 5 mL), dissolved in benzene and solvent was removed under reduce pressure to yield a brown solid. The solid was dissolved in THF (*ca*. 6 mL) and a solution of triphenylphosphine (0.015 g, 0.057 mmol) in THF (*ca*. 4mL) was added, resulting in a color change of the mixture to dark red. After stirring for 1 h, the THF was removed under reduced pressure to yield a red solid which was triturated with hexanes (10 mL) and concentrated under vacuum to give a fine red power (0.047 g, 0.049 mmol, 79%). ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 8.02 (d, J = 7.8, 2H), 7.58 (s, 2H), 6.97 – 6.91 (m, 9H), 6.85 (t, J = 7.4, 4H), 6.78 – 6.74 (m, 10H), 6.57 (d, J = 7.9, 2H), 2.02 (s, 12H), 1.64 (s, 6H), 1.54 (s, 9H). ^{13}C NMR (125 MHz, THF-*d$_8$*, 25°C): δ 208.81, 143.04, 138.73, 138.37, 138.22, 136.68, 136.49, 134.10, 132.81, 131.94, 129.95, 129.08, 122.46, 122.24, 109.93, 108.74, 102.29, 31.96, 21.08, 18.09, 17.54. HRMS (ESI), calc. for $C_{42}H_{41}N_5PCo$ [M – N – (3 × C_6H_5)]$^+$: 705.2432; found 705.2444. ATR-IR: 2112 cm^{-1} (N_2)

Synthesis of (^{Mes}CCC^{CF3})Co(N_2)PPh_3 (4-CF_3)

A 20 mL scintillation vial was charged with **1-CF_3** (24.7 mg, 0.030 mmol, 1.0 equiv.) and THF (5 mL). After stirring for 10 min, KC_8 (9.3 mg, 0.069 mmol, 2.3 equiv.) was added to the green suspension with ca. 3 mL THF. Graphite was liberated immediately, and the resulting dark suspension was stirred for 3 h. The suspension was then filtered over Celite into a 20 mL scintillation vial containing triphenylphosphine (7.1 mg, 0.027 mmol, 0.90 equiv.) and a stir bar resulting in a color change of the mixture to dark red. After stirring the solution for 1 h, the THF was removed under reduced pressure. The product was then triturated with minimal cold hexanes, taken up in benzene (ca. 3 mL), filtered over Celite and concentrated to a red solid (24.3 mg, 0.025 mmol, 93%). Crystal suitable for X-ray diffraction were grown from a hexanes solution at -35 °C. ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 7.80 (s, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 7.3 Hz, 3H), 6.91 – 6.80 (m, 10H), 6.76 – 6.69 (m, 10H), 6.51 (d, J = 7.9 Hz, 2H), 2.01 (s, 6H), 1.98 (s, 6H), 1.57 (s, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 208.82, 171.51, 143.04, 138.74, 138.37, 138.21, 136.68, 136.49, 134.09, 132.80, 132.71, 131.94, 129.95, 129.08, 122.46, 122.24, 109.92, 108.74, 21.10, 18.11, 17.55. ^{19}F NMR (470 MHz, C_6D_6): δ -58.67. HRMS (ESI), calc. for $C_{39}H_{32}F_3N_5PCo$ $[M – N – (3 \times C_6H_5)]^+$: 717.1679; found 717.1691. ATR-IR: 2123 cm^{-1} (N_2)

Synthesis of (^{Mes}CCC^{tBu})Co(H_2)PPh_3 (5-^{t}Bu)

A solution of **4-^{t}Bu** (10 g, 0.010 mmol) in *ca*. ½ mL of benzene-d_6 was transferred to a J. Young tube and sealed. The sample was subjected to two freeze-pump-thaw cycles, exposed to 1 atm of H_2 at 77K, and allowed to warm to room temperature. Upon agitation, the solution went from red to red-orange. Upon exposure to N_2 atmosphere, the gradual formation was observed by ^{1}H NMR and the solution turned red. HRMS was not taken of the complex as exposure to N_2 would result in the dissociate of H_2 and the reformation of **4-^{t}Bu**. ^{1}H NMR NMR (500 MHz, C_6D_6, 25°C) δ 8.05 (d, J = 7.18 Hz, 2H), 7.69 (s, 2H), 6.89 – 6.98 (m, 9H), 6.74 - 6.87 (m, 12H), 6.66 (s, 2H), 6.54 (d, J = 7.05 Hz, 2H), 2.13 (s, 6H), 1.93 (s, 6H), 1.58 (s, 9H), 1.36 (s, 6H), -5.38 (br s, 2H).

Synthesis of (^{Mes}CCC^{CF3})Co(H_2)PPh_3 (5-CF_3)

A solution of **4-CF_3** (6.0 mg, 0.006 mmol) in *ca*. ½ mL of benzene-d_6 was transferred to a J. Young tube and sealed. The sample was subjected to two freeze-pump-thaw cycles, exposed to 1 atm of H_2 at 77K, and allowed to warm to room temperature. Upon agitation, the solution went from red to red-orange. Upon exposure to N_2 atmosphere, the gradual formation was observed by ^{1}H NMR and the solution turned red. HRMS was not taken of the complex as exposure to N_2 would result in the dissociate of H_2 and the reformation of **4-CF_3**. ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 7.91 (s, 2H), 7.70 (d, J = 7.64 Hz, 2H), 7.02 (t, J = 7.40 Hz, 4H), 6.82 – 6.88 (m, 9H), 6.78 (s, 2H), 6.71 – 6.74 (m, 6H), 6.64 (s, 2H), 6.49 (d, J = 8.09 Hz, 2H), 2.13 (s, 6H), 1.88 (s, 6H), 1.29 (s, 6H), -5.26 (br s, 2H).

Synthesis of (^{Mes}CCC^{tBu})Co(HD)PPh_3 (6-^{t}Bu)

A solution of **5-^{t}Bu** (0.0060 g, 0.006 mmol) in *ca.* ½ mL of benzene-d_6 was transferred to a J. Young tube and sealed. The sample was subjected to two freeze-pump-thaw cycles and exposed to a mixture of H_2 and D_2 (50:50) at 1 atm and 77K. The solution was warmed to room temperature and upon agitation, the solution went from red to red-orange. ^{1}H NMR spectroscopy revealed a J_{HD} coupling of 31 Hz.

Synthesis of (^{Mes}CCC^{CF3})Co(HD)PPh_3 (6-CF_3)

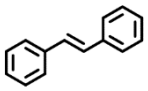
A solution of **5-CF_3** (0.0060 g, 0.006 mmol) in *ca.* ½ mL of benzene-d_6 was transferred to a J. Young tube and sealed. The sample was subjected to two freeze-pump-thaw cycles and exposed to a mixture of H_2 and

D_2 (50:50) at 1 atm and 77K. The solution was warmed to room temperature and upon agitation, the solution went from red to red-orange. ^{1}H NMR spectroscopy revealed a J_{HD} coupling of 33 Hz.

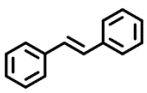
Semi-Hydrogenation of Alkynes

General Procedure for alkyne hydrogenation studies

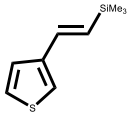
A 50 mL storage vessel charged with **4-^{t}Bu/4-CF_3**, alkyne, and 4 mL of THF was subjected to three freeze-pump-thaw cycles and placed under 1 atm of H_2 gas at 77K. The mixture was allowed warm to room temperature and was placed in a 30°C oil bath. After stirring for 17 h, the H_2 gas was vented and the reaction mixture was analyzed by GCMS to determine conversion. Alkene conversion is listed below accompanied by alkane in parentheses. The THF was removed under reduced pressure and the reaction mixture was filtered over a silica plug, eluting with hexanes. Selectivity was determined by GCMS and confirmed by NMR spectroscopy. 3-[(trimethylsilyl)ethynyl]thiophene was purchased from Alfa Aesar while the other two substrates were purchased from Sigma-Aldrich.



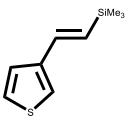
(E)-1,2-diphenylethene: (4-^{t}Bu) ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.52 (d, J = 7.7 Hz, 4H), 7.36 (t, J = 7.5 Hz, 4H), 7.24 – 7.30 (m, 2H), 7.11 (s, 2H). Conversion to alkene was 84% (16). Isolated Yield: (28.6 mg, 0.159 mmol, 71%) E:Z (>99). Catalyst (2.1 mg, 0.002 mmol) loading was 1% to substrate (40 mg, 0.224 mmol).



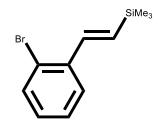
(E)-1,2-diphenylethene: (4-CF_3) ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.52 (d, J = 7.7 Hz, 4H), 7.36 (t, J = 7.5 Hz, 4H), 7.24 – 7.30 (m, 2H), 7.11 (s, 2H). Conversion to alkene was 95% (5). Isolated Yield: (34.3 mg, 0.190 mmol, 85%) E:Z (>99). Catalyst (2.2 mg, 0.002 mmol) loading was 1% to substrate (40 mg, 0.224 mmol).



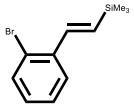
(E)-trimethyl(2-(thiophen-3-yl)vinyl)silane: (4-^{t}Bu) ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.26 – 7.21 (m, 2H), 7.17 (m, 1H), 6.85 (d, J = 19.1 Hz, 1H), 6.24 (d, J = 19.1 Hz, 1H), 0.14 (s, 9H). Conversion to alkene was 86% (13). Isolated Yield: (28.6 mg, 0.159 mmol, 71%) E:Z (>99). Catalyst (3.1 mg, 0.003 mmol) loading was 2% to substrate (30 mg, 0.166 mmol).



(E)-trimethyl(2-(thiophen-3-yl)vinyl)silane: (4-CF_3) ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.26 – 7.21 (m, 2H), 7.17 (m, 1H), 6.85 (d, J = 19.0 Hz, 1H), 6.24 (d, J = 19.0 Hz, 1H), 0.14 (s, 9H). Conversion to alkene was 88% (12). Isolated Yield: (26.2 mg, 0.143 mmol, 86%) E:Z (>99). Catalyst (3.2 mg, 0.003 mmol) loading was 2% to substrate (30 mg, 0.166 mmol).



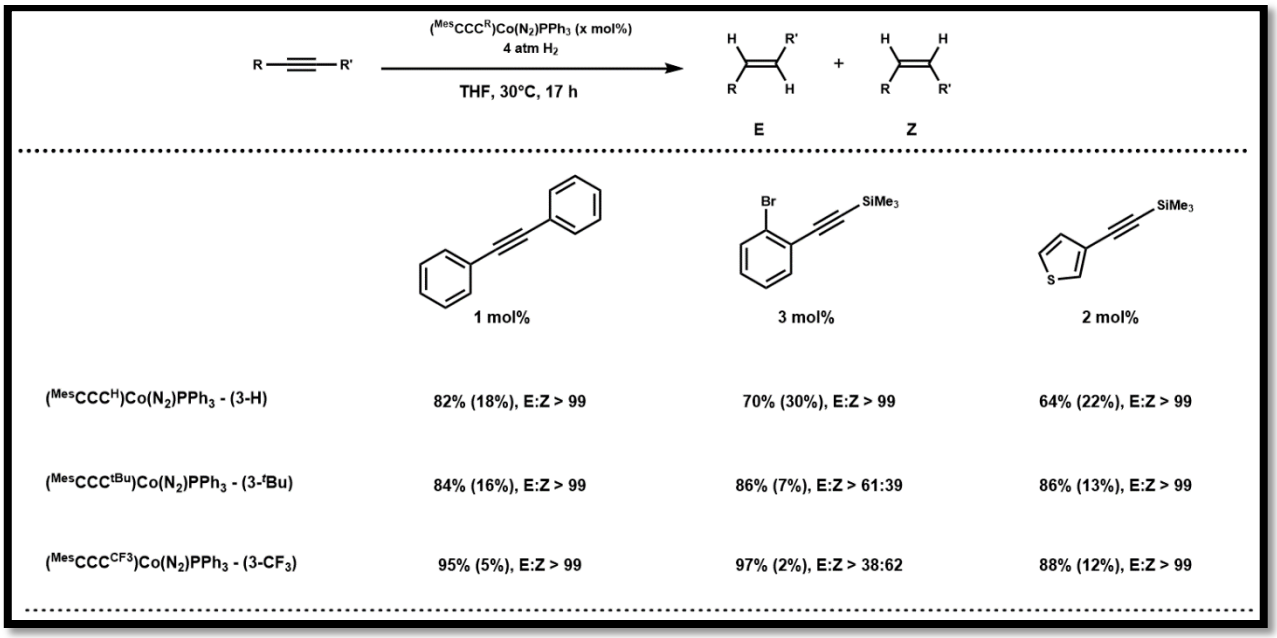
(E)-(2-bromostyryl)trimethylsilane: (4-^{t}Bu) ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.57 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H), 7.22 – 7.29 (m, 2H), 7.10 (t, J = 7.6 Hz, 1H), 6.46 (d, J = 18.9 Hz, 1H), 0.21 (s, 9H). Conversion to alkene was 86% (7). Isolated Yield: (28.6 mg, 0.159 mmol, 71%) E:Z (>99). Catalyst (3.3 mg, 0.003 mmol) loading was 3% to substrate (30 mg, 0.118 mmol).



(E)-(2-bromostyryl)trimethylsilane: (4-CF_3) ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.57 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H), 7.22 – 7.29 (m, 2H), 7.10 (t, J = 7.6 Hz, 1H), 6.46 (d, J = 18.9 Hz, 1H), 0.21 (s, 9H). Conversion to alkene was 95% (5). Isolated

Yield: (27.4 mg, 0.107 mmol, 91%) E:Z (38:62). Catalyst (3.4 mg, 0.003 mmol) loading was 3% to substrate (30 mg, 0.118 mmol).

Table S1: Semi-hydrogenation of alkynes with **4-^{t}Bu** and **4-CF$_3$** compared to that of **4-H**. Alkene yields are an average of duplicate runs and alkane yields are listed in parentheses.



Crystallographic Data

Table S2. Crystallographic parameters for **1-^{t}Bu**, **1-CF$_3$**, **3-H**, **4-CF$_3$**.

	(^{Mes}CCC^{tBu})CoCl2py (1-^{t}Bu)	(^{Mes}CCC^{CF3})CoCl2py (1-CF$_3$)	(^{Mes}CCC)Co(CO)$_2$ (3-H)	(^{Mes}CCC^{CF3})Co(N$_2$)PPh$_3$ (4-CF$_3$)
Empirical Formula	C47 H46 Cl2 Co N5	C91 H74 Cl13 Co2 D3 F6 N10	C40 H33 Co N4 O2	C60 H54 Co F3 N6 P
Formula Weight	810.72	2006.35	660.63	1005.99
Temperature	200.15	100.01	100	100(2)
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	Pnma	P 2$_1$/n	C 2/c	P -1
Unit Cell Dimensions	a = 15.6135(4) Å b = 17.6361(5) Å c = 17.3690(5) Å α = 90° β = 90° γ = 90°	a = 23.1102(9) Å b = 16.6078(6) Å c = 23.4753(9) Å α = 90° β = 97.1970(10)° γ = 90°	a = 23.7349(9) Å b = 14.5175(6) Å c = 9.3849(4) Å α = 90° β = 102.0336(14)° γ = 90°	a = 12.9132(6) Å b = 14.6537(7) Å c = 15.5103(7) Å α = 89.130(2)° β = 87.885(2)° γ = 74.406(2)°
Volume	4782.7(2) Å^3	8939.1(6) Å^3	3162.7(2) Å^3	2825.0(2) Å^3
Z	4	4	4	2
Reflections collected	36429	165171	61292	56082
Independent reflections	5089	16408	3497	10382

Goodness-of-Fit on F2	1.053	1.080	1.053	1.081
Final R indices [I>sigma(I)]	R1 = 0.0445 wR2 = 0.1315	R1 = 0.0683 wR2 = 0.1915	R1 = 0.0325 wR2 = 0.0823	R1 = 0.0427 wR2 = 0.1122

Table S3. Selected crystallographic parameters of the ($^{Mes}CCC^{R}$)$CoCl_2$py complexes, **1-^{t}Bu**, **1-H**, **1-CF_3**.

	1-^{t}Bu	**1-H**	**1-CF_3**
Bond distances (Å)			
Co-C_{NHC1}	1.9540(24)	1.961(4)	1.9601(54)
Co-C_{NHC2}	1.9540(24)	1.958(4)	1.9657(53)
Co-C_{Aryl}	1.8726(30)	1.871(4)	1.8672(53)
Co-Cl_1	2.2702(9)	2.2751(13)	2.2795(14)
Co-Cl_2	2.2605(9)	2.2651(12)	2.2503(14)
Co-N_{py}	2.0983(26)	2.090(3)	2.0939(48)
Bond Angles (°)			
Cl-Co-Cl	172.70(3)	173.28(5)	171.71(6)
C_{Aryl}-Co-N_{py}	179.63(12)	179.13(16)	179.51 (22)
Cl_1-Co-Cl_2	172.70(3)	173.28(5)	171.71(6)
C_{Aryl}-Co-C_{NHC1}	80.28(6)	80.29(18)	80.58(24)
C_{Aryl}-Co-C_{NHC2}	80.28(6)	80.44(18)	80.28(23)
C_{NHC}-Co-C_{NHC}	160.49(12)	160.73(17)	160.80(23)

Table S4. Selected crystallographic parameters of **3-H**, **4-H**, and **4-CF_3**.

	3-H	**4-H**	**4-CF_3**
Bond distances (Å)			
Co-C_{NHC1}	1.9119(15)	1.9147(13)	1.9122(21)
Co-C_{NHC2}	1.9119(15)	1.9001(13)	1.9057(21)
Co-C_{Aryl}	1.9102(22)	1.8750(13)	1.8677(21)
Co-P		2.2483(4)	2.2534(6)
Co-N_{N2}		1.8270(12)	1.8412(19)
N-N		1.1005(16)	1.0873(26)
Co-C_{CO}	1.7776(19)		
Bond Angles (°)			
C_{Aryl}-Co-N_{N2}		157.89(5)	160.08(9)
P-Co-N_{N2}		106.68(4)	104.81(6)
C_{Aryl}-Co-C_{NHC1}	172.70(3)	173.28(5)	171.71(6)
C_{NHC}-Co-C_{NHC}	156.27(10)	80.29(18)	80.58(24)
C_{CO}-Co-C_{CO}	112.93(14)		
C_{Aryl}-Co-C_{CO}	160.49(12)		

NMR Spectra of Ligand Precursors and Ligands

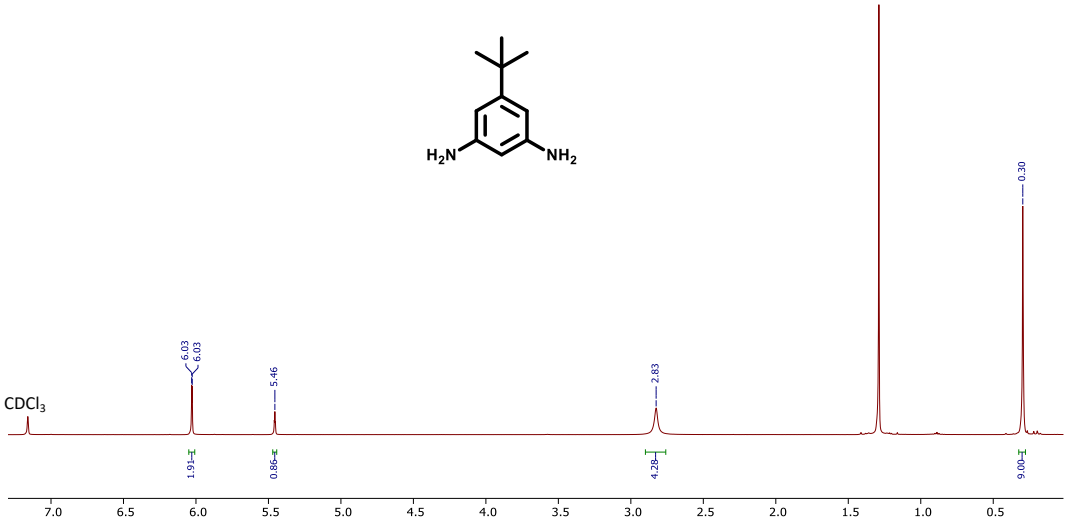


Figure S1. [1]H NMR spectrum of 5-(*tert*-butyl)benzene-1,3-diamine.

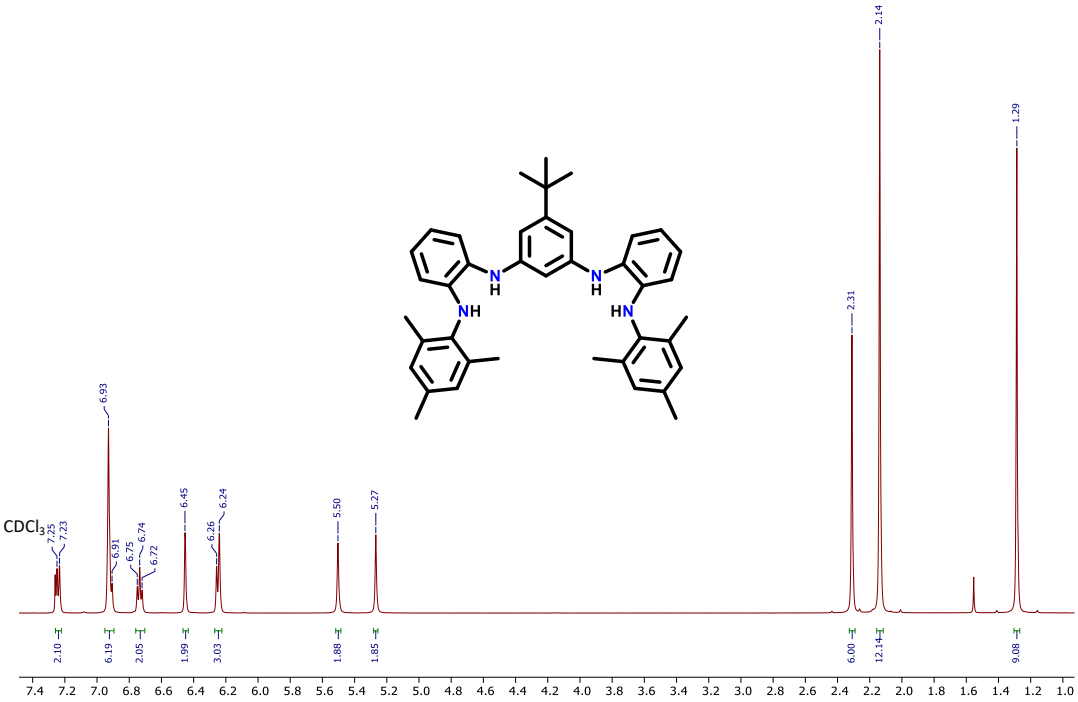


Figure S2. [1]H NMR spectrum of **L1a**

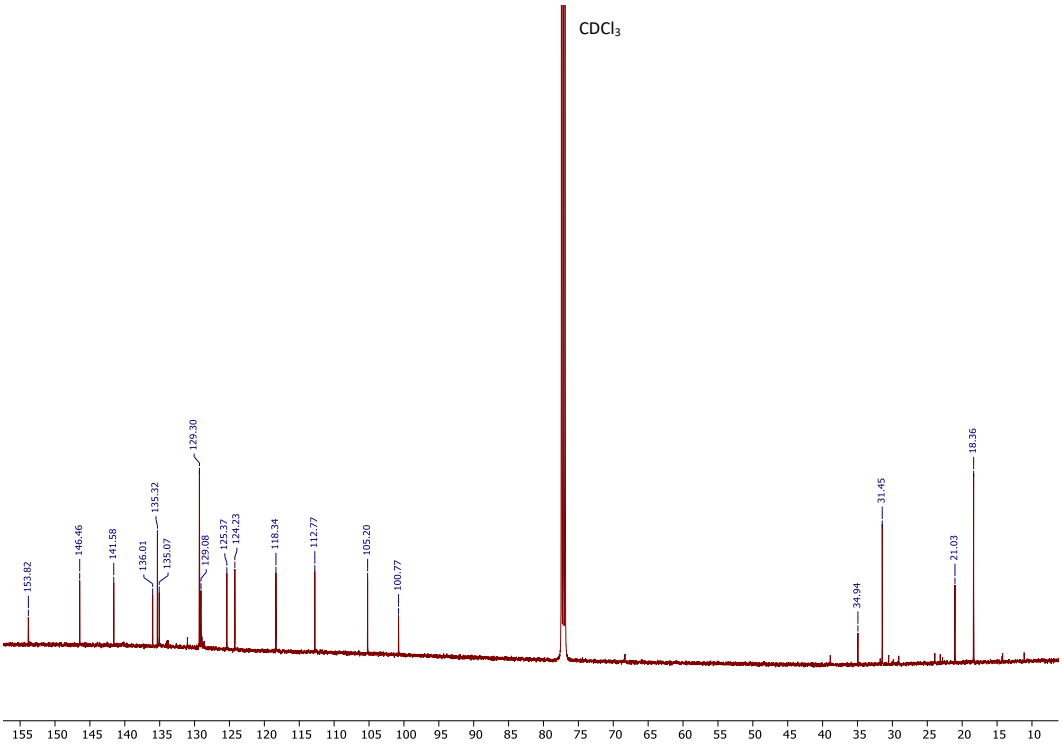


Figure S3. ^{13}C NMR spectrum of **L1a**

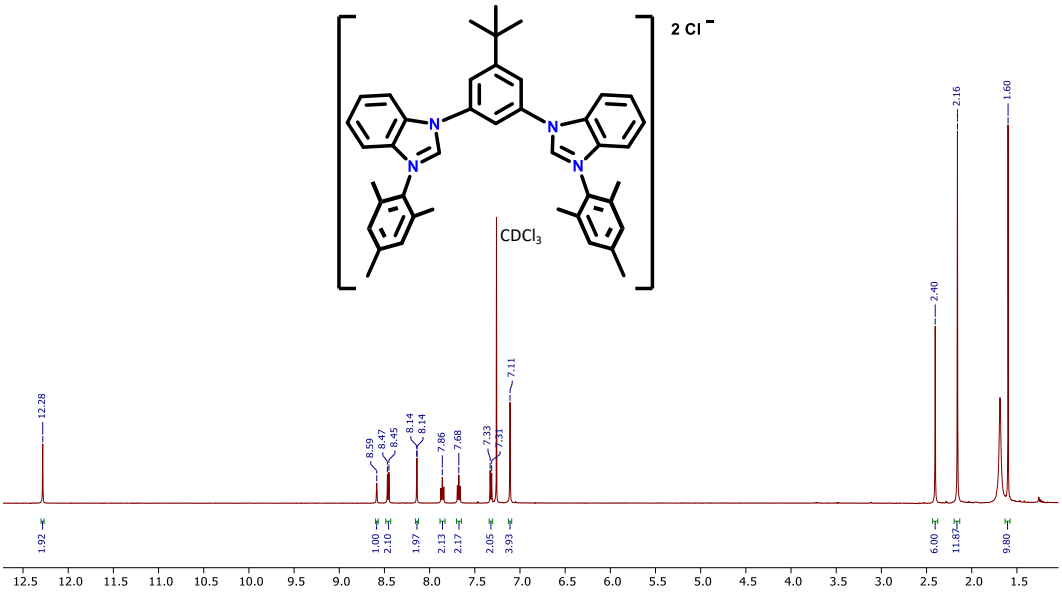


Figure S4. ^{1}H NMR spectrum of $[H_3(^{Mes}CCC^{tBu})]Cl_2$, .

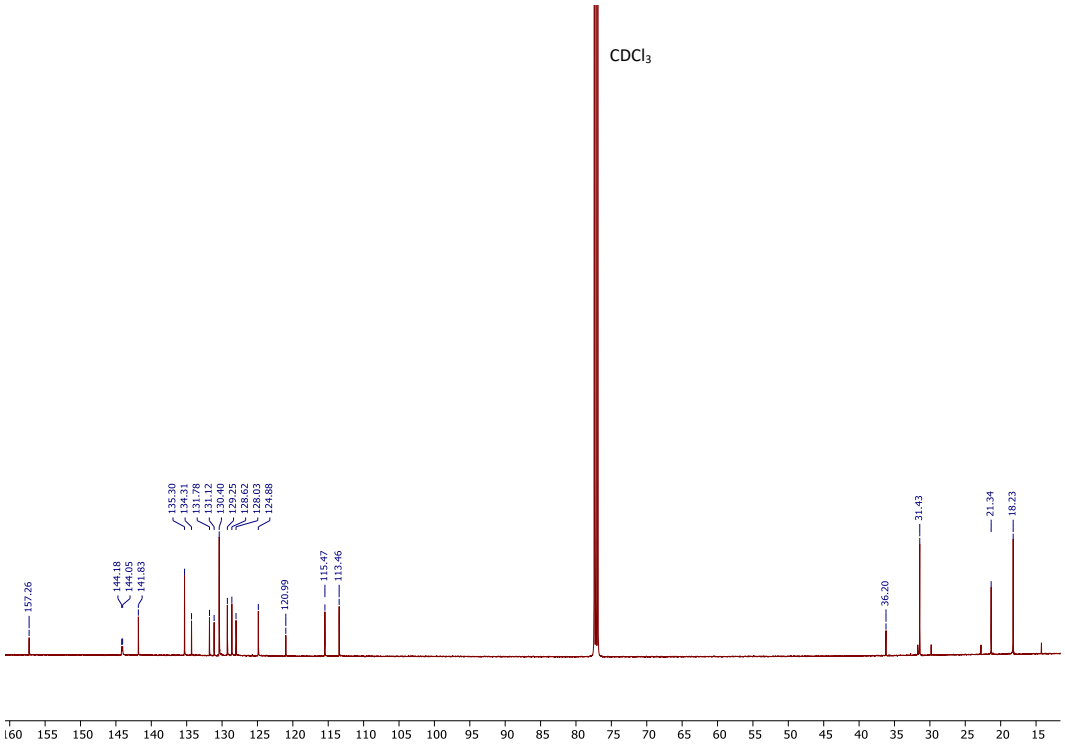


Figure S5. ^{13}C NMR spectrum of $[H_3(^{Mes}CCC^{tBu})]Cl_2$.

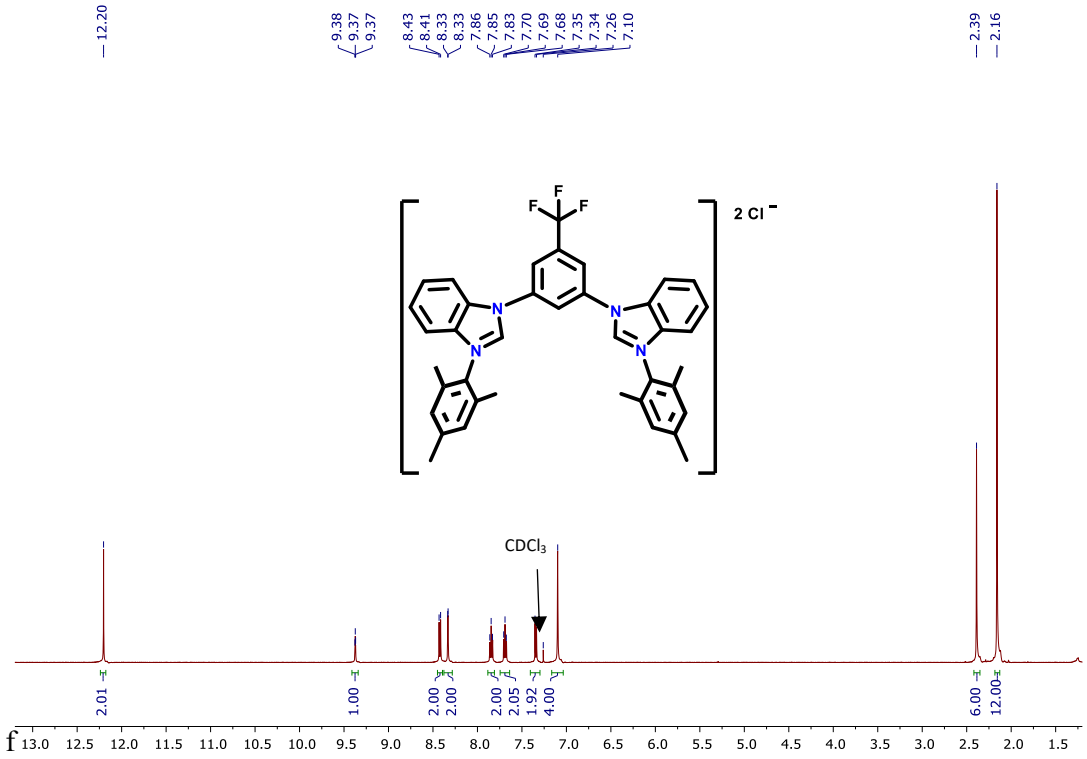


Figure S6. ^{1}H NMR spectrum of $[H_3(^{Mes}CCC^{CF3})]Cl_2$.

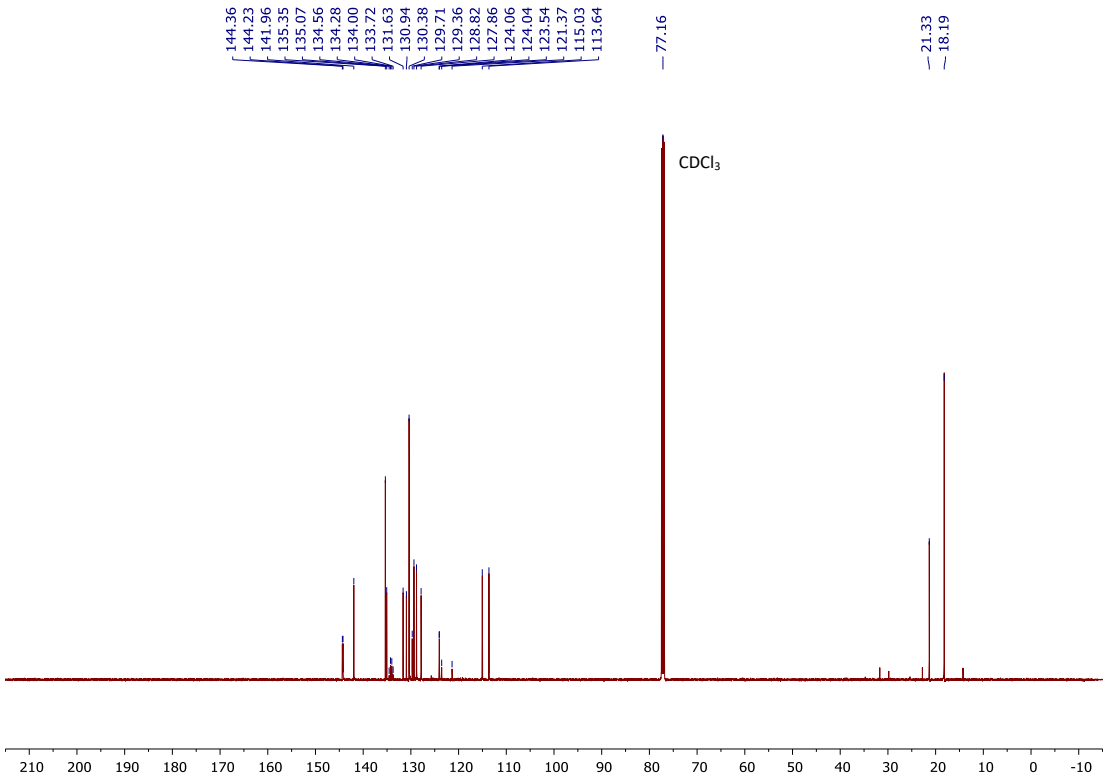


Figure S7. ^{13}C NMR spectrum of $[H_3(^{Mes}CCC^{CF3})]Cl_2$.

NMR and IR Spectra of Metal Complexes

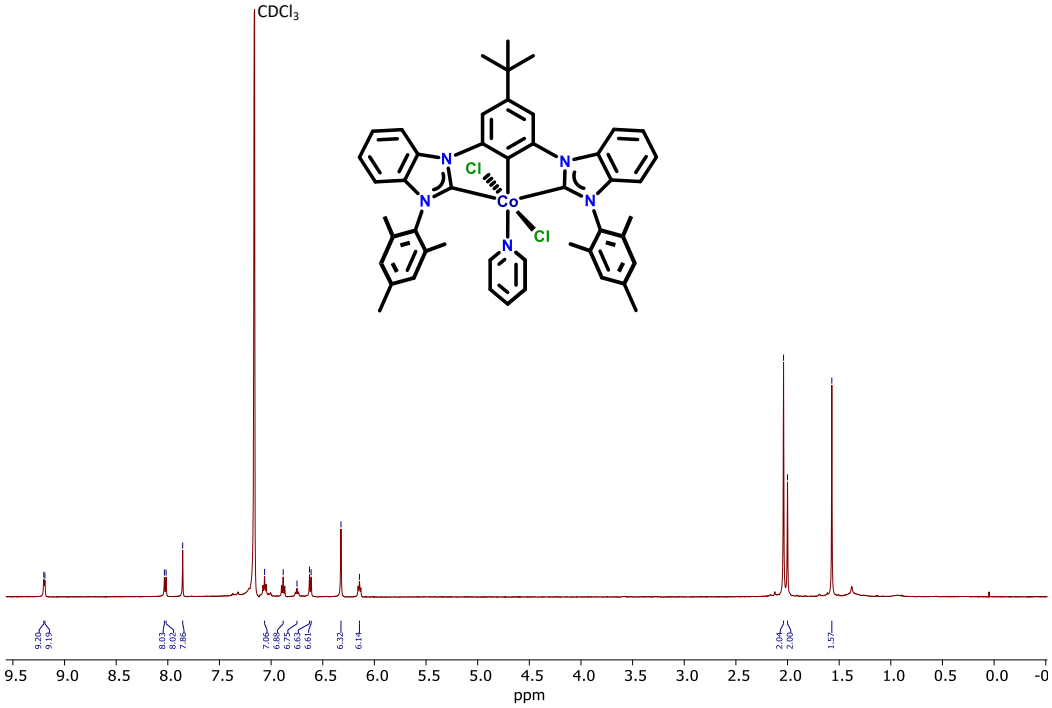


Figure S8. ^{1}H NMR spectrum of (^{Mes}CCC^{tBu})CoCl$_2$py, **1-^{t}Bu**.

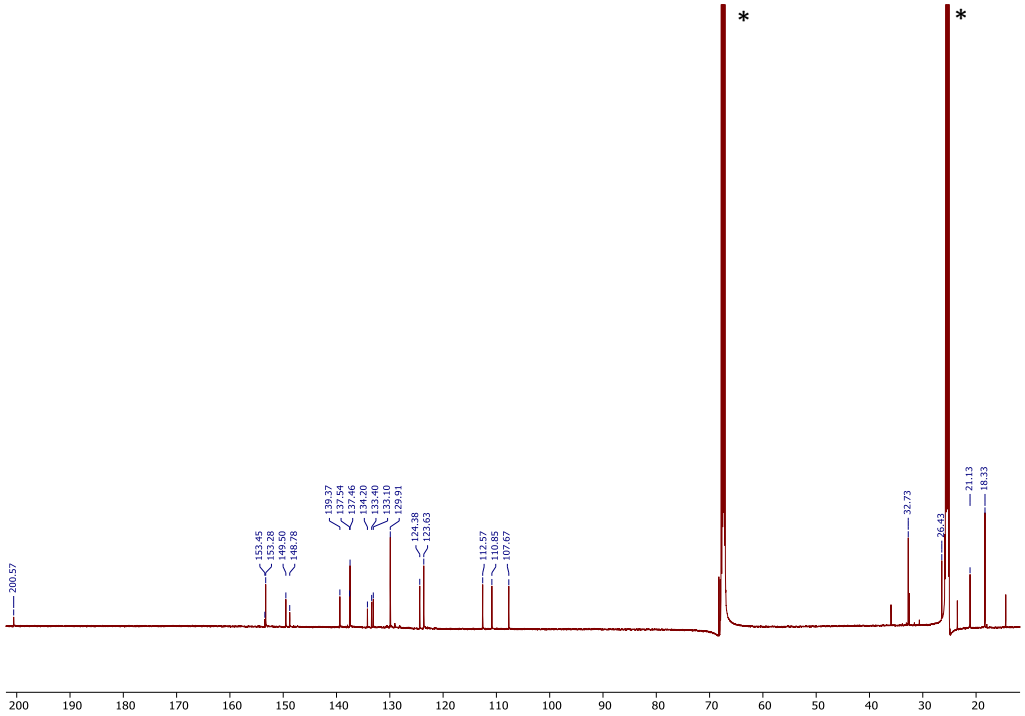


Figure S9. ^{13}C NMR spectrum of (^{Mes}CCC^{tBu})CoCl$_2$py, **1-^{t}Bu** (* = d_8-THF).

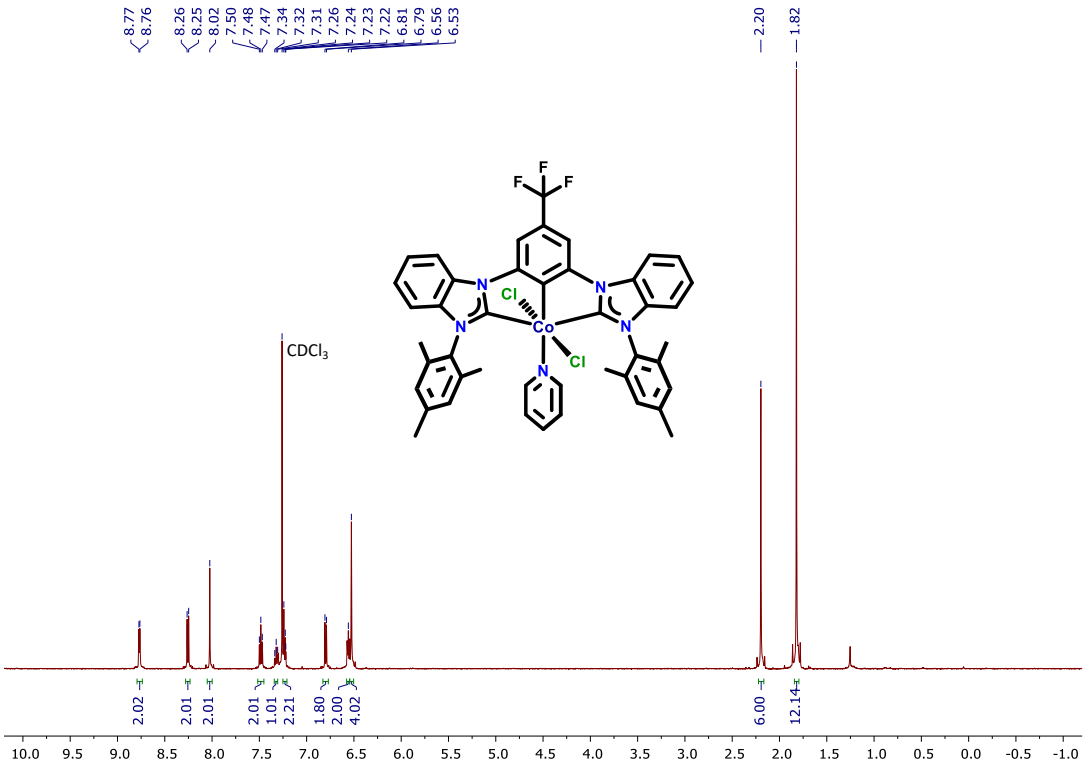


Figure S10. ^{1}H NMR spectrum of (^{Mes}CCC^{CF3})CoCl$_2$py, **1-CF$_3$**.

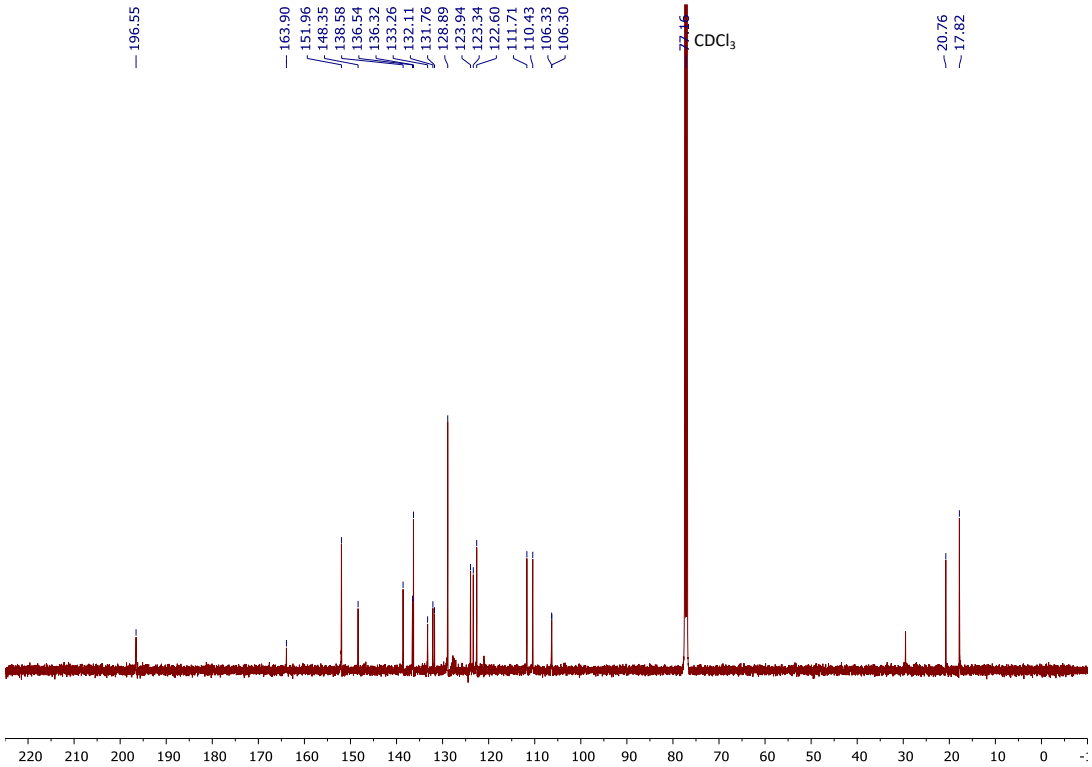


Figure S11. ^{13}C NMR spectrum of (^{Mes}CCC^{CF3})CoCl$_2$py, **1-CF$_3$**.

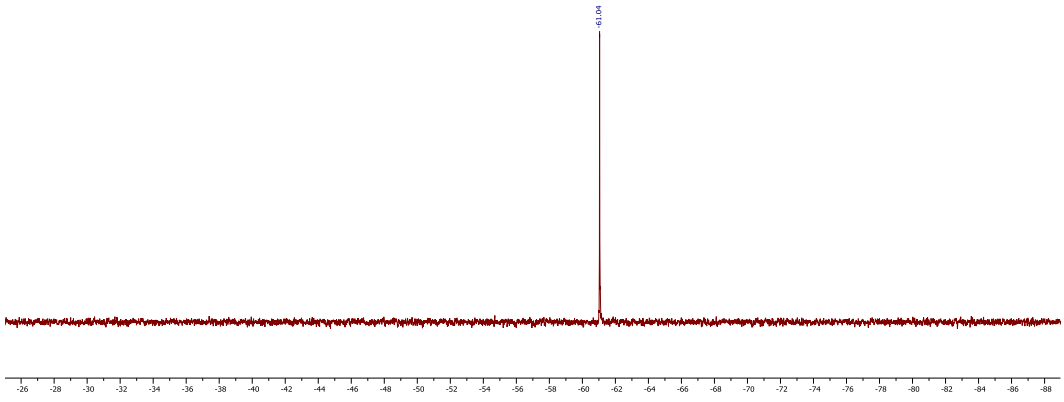


Figure S12. ^{19}F NMR spectrum of (^{Mes}CCC^{CF3})CoCl$_2$py, **1-CF$_3$**.

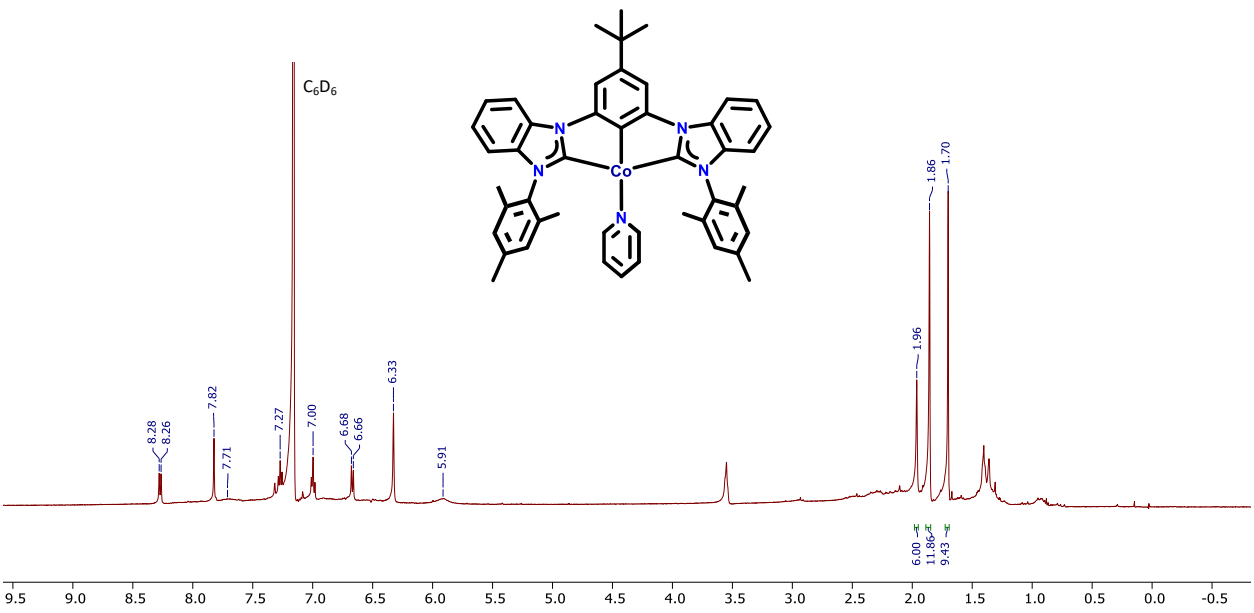


Figure S13. ^{1}H NMR spectrum of (^{Mes}CCC^{tBu})Co-py, **2-^{t}Bu**.

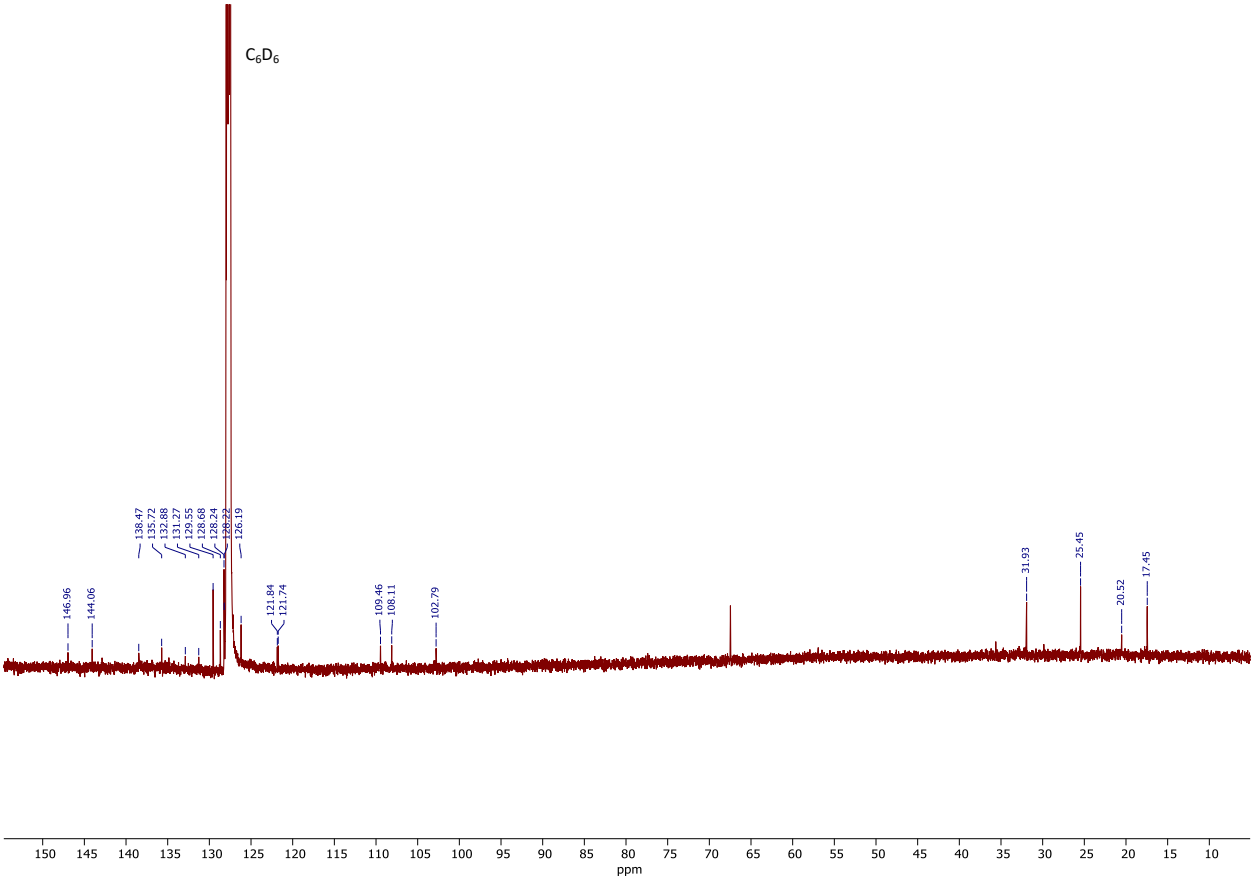


Figure S14. ^{13}C NMR spectrum of (^{Mes}CCC^{tBu})Co-py, **2-^{t}Bu**.

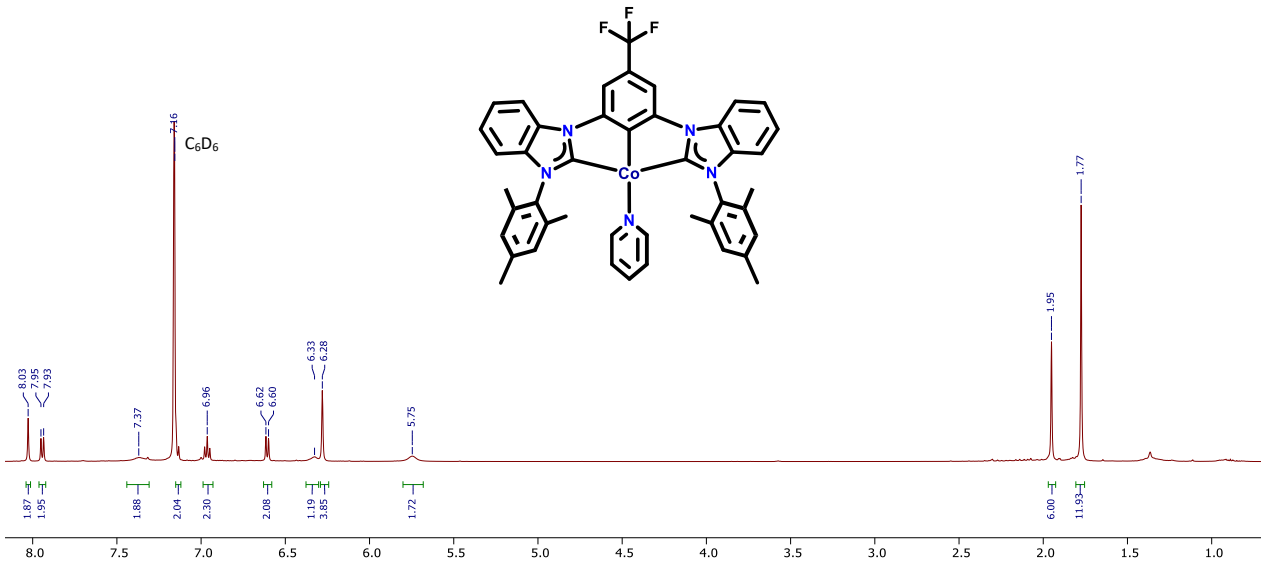


Figure S15. ^{1}H NMR spectrum of (^{Mes}CCC^{CF3})Co-py, **2-CF$_3$**.

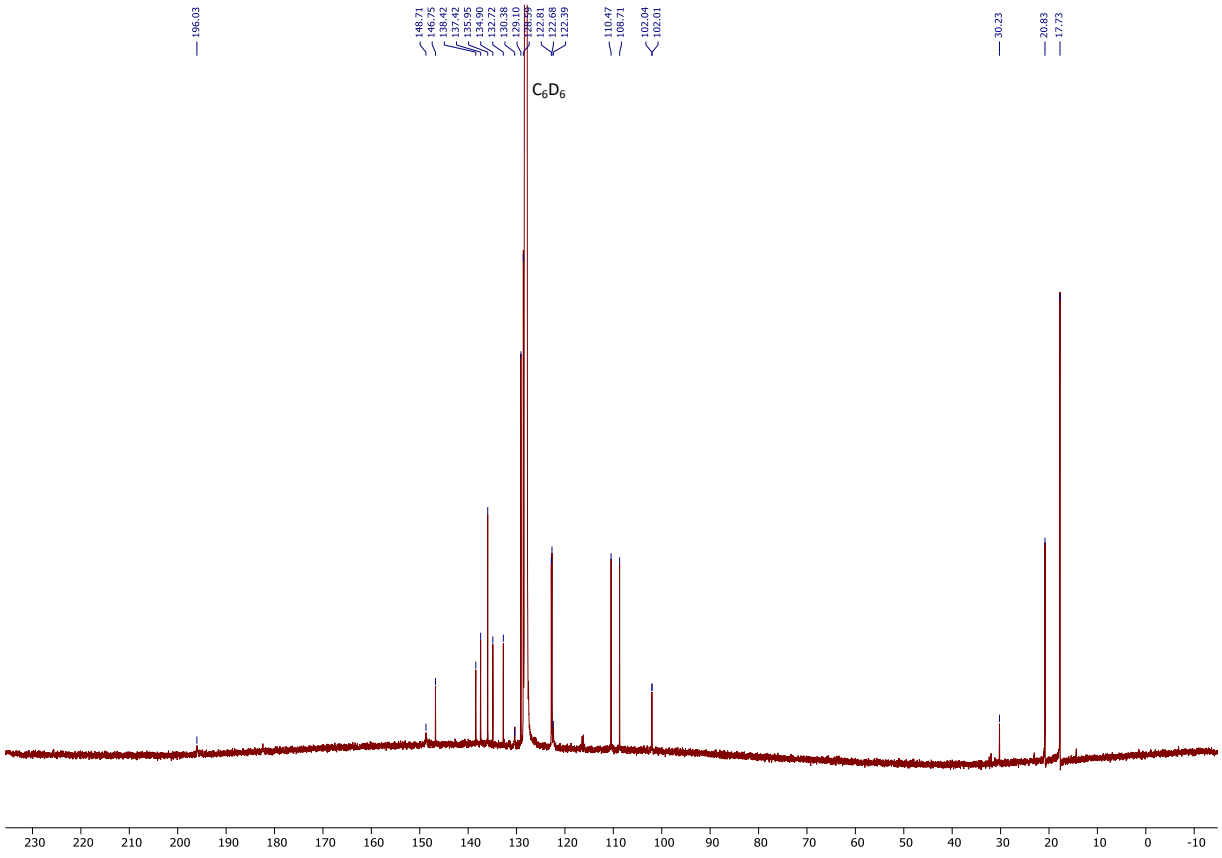


Figure S16. ^{13}C NMR spectrum of (^{Mes}CCC^{CF3})Co-py, **2-CF$_3$**.

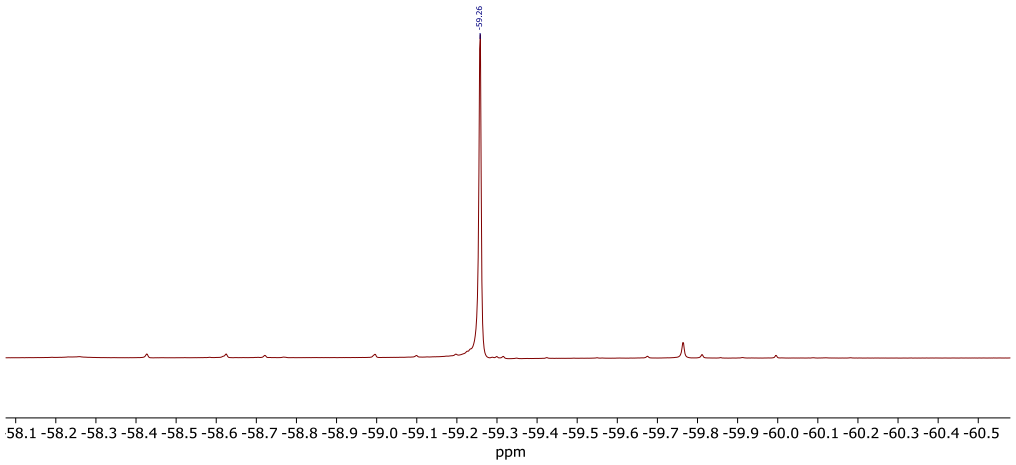


Figure S17. ^{19}F NMR spectrum of (^{Mes}CCC^{CF3})Co-py, **2-CF$_3$**.

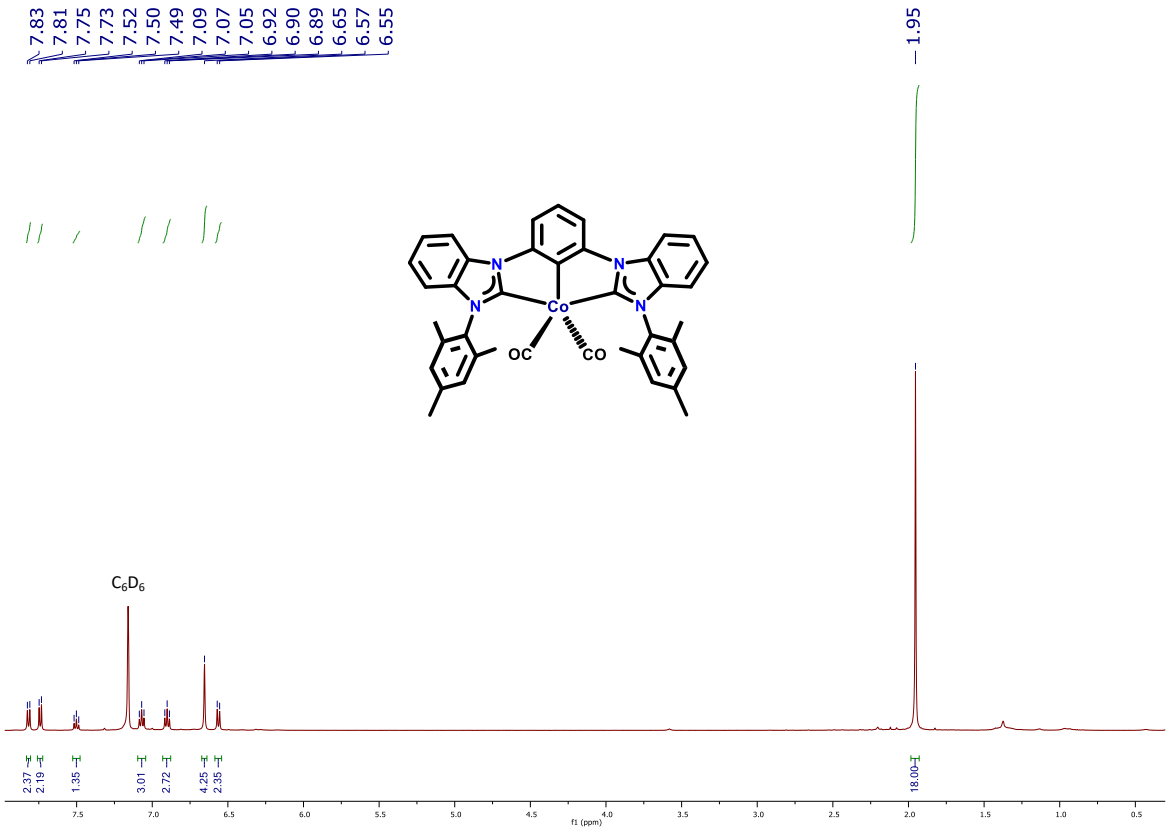


Figure S18. ^{1}H NMR spectrum of (^{Mes}CCC)Co(CO)$_2$, **3-H**.

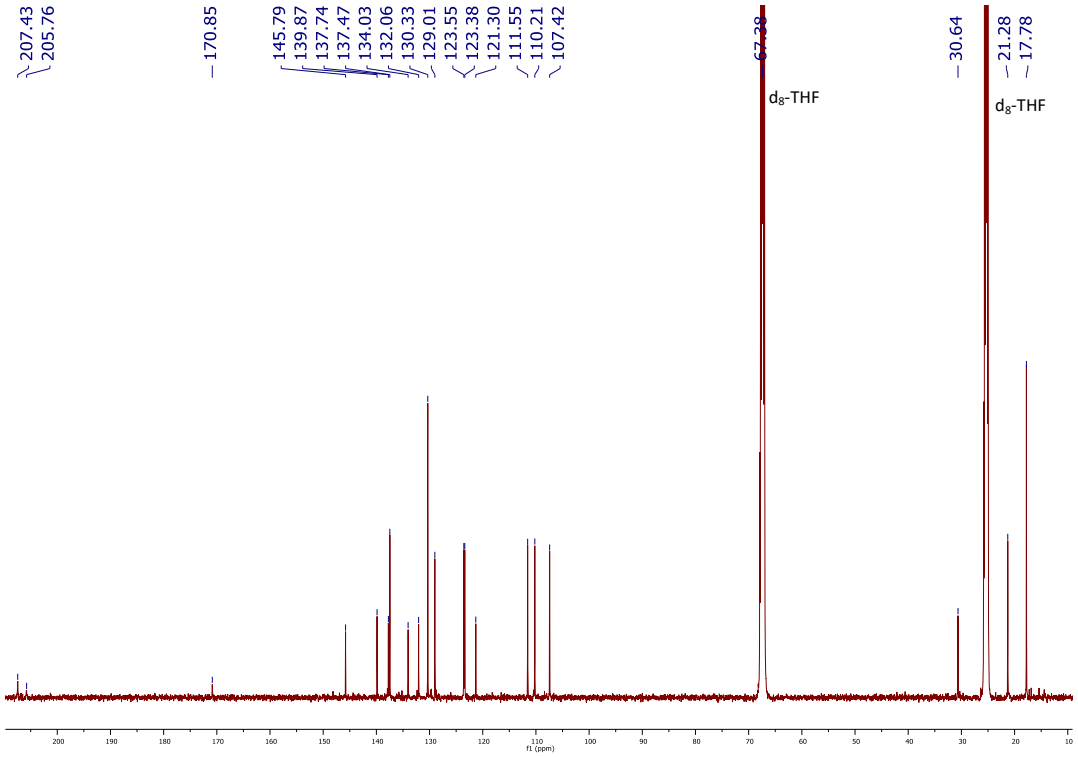


Figure S19. ^{13}C NMR spectrum of (^{Mes}CCC)Co(CO)$_2$, **3-H**.

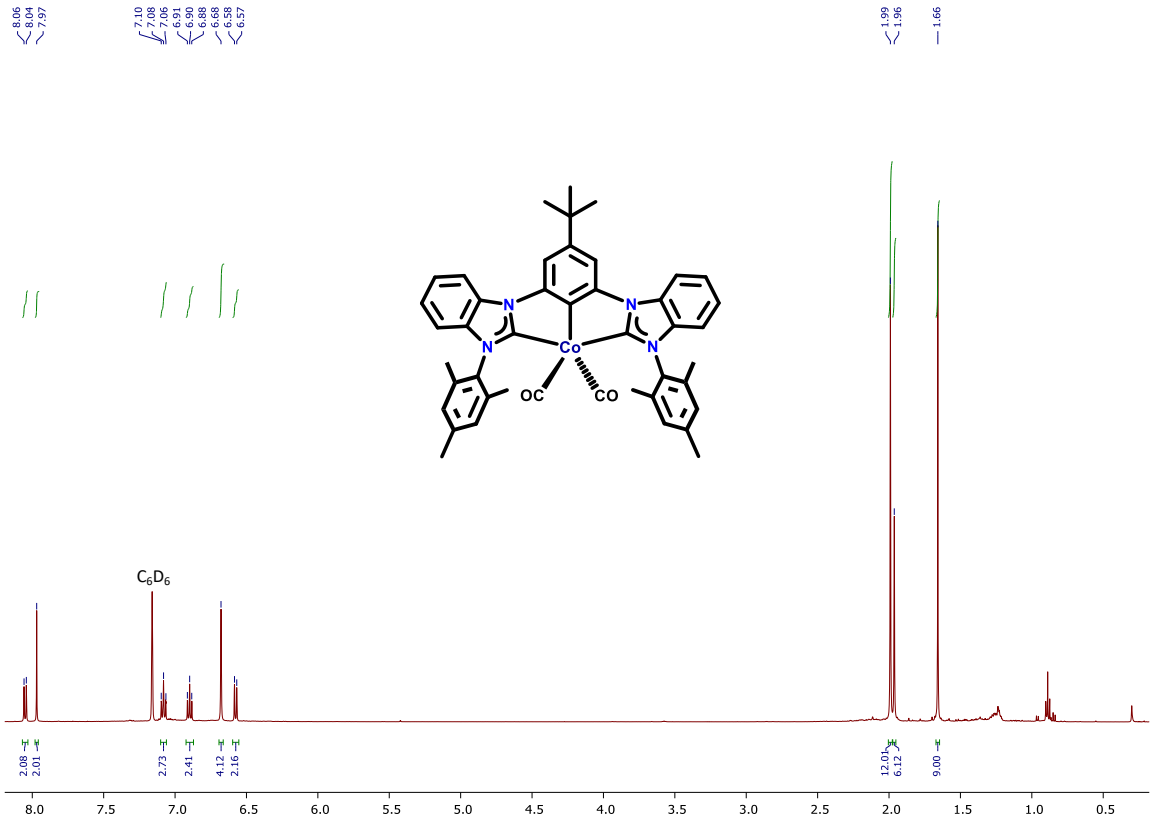


Figure S20. ^{1}H NMR spectrum of (^{Mes}CCC^{tBu})Co(CO)$_2$, **3-^{t}Bu**.

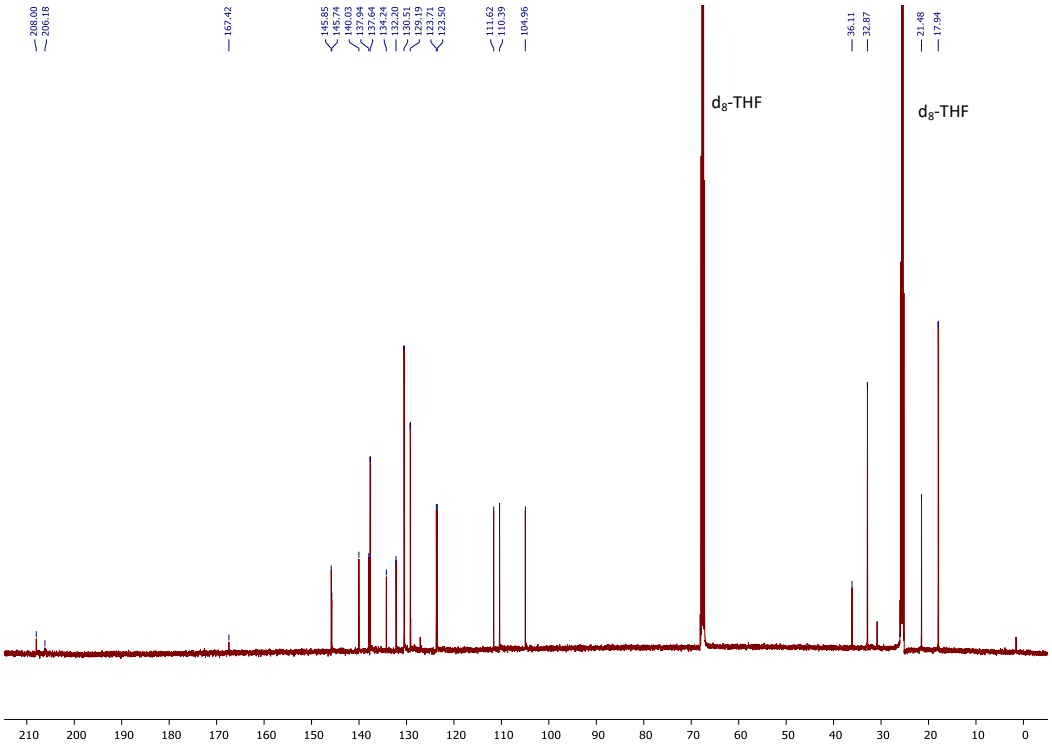


Figure S21. ^{13}C NMR spectrum of (^{Mes}CCC^{tBu})Co(CO)$_2$, **3-^{t}Bu**.

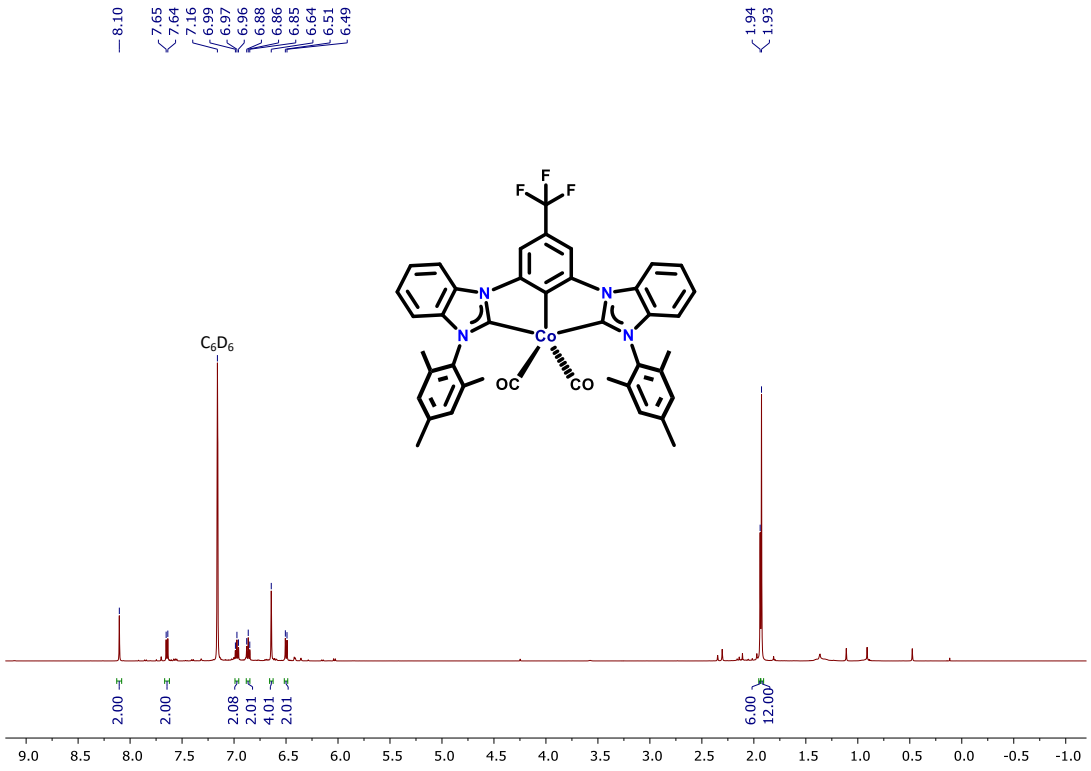


Figure S22. ^{1}H NMR spectrum of (^{Mes}CCC^{CF3})Co(CO)$_2$, **3-CF$_3$**.

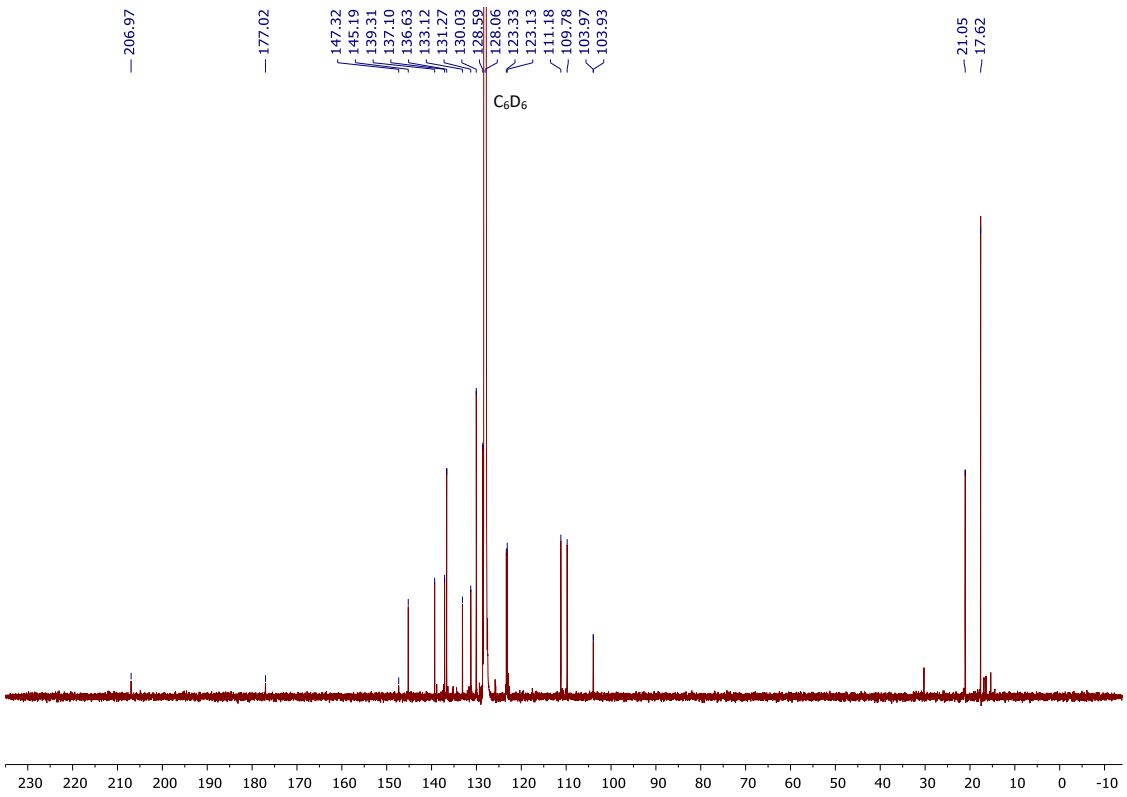


Figure S23. ^{13}C NMR spectrum of (^{Mes}CCC^{CF3})Co(CO)$_2$, **3-CF$_3$**.

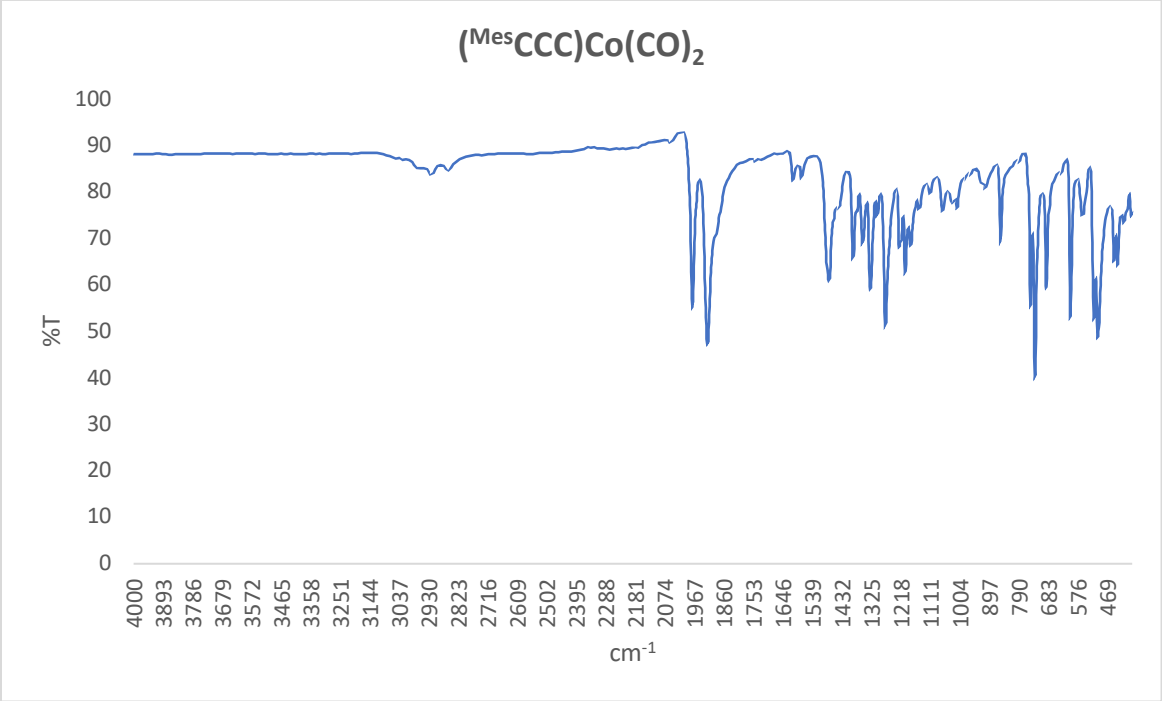


Figure S24. IR spectrum of (^{Mes}CCC)Co(CO)$_2$ $\nu_{C\equiv O}$ 1918 and 1973 cm^{-1}.

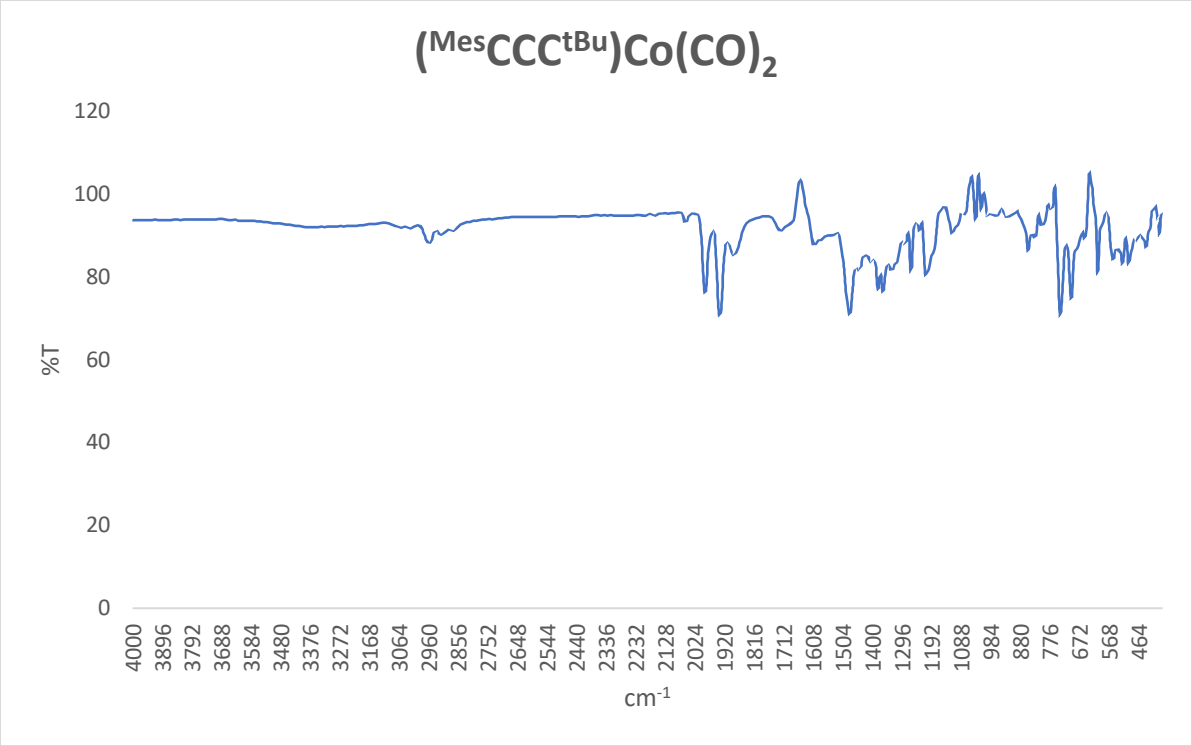


Figure S25. IR spectrum of (^{Mes}CCC^{tBu})Co(CO)$_2$ $\nu_{C\equiv O}$ 1939 and 1990 cm^{-1}.

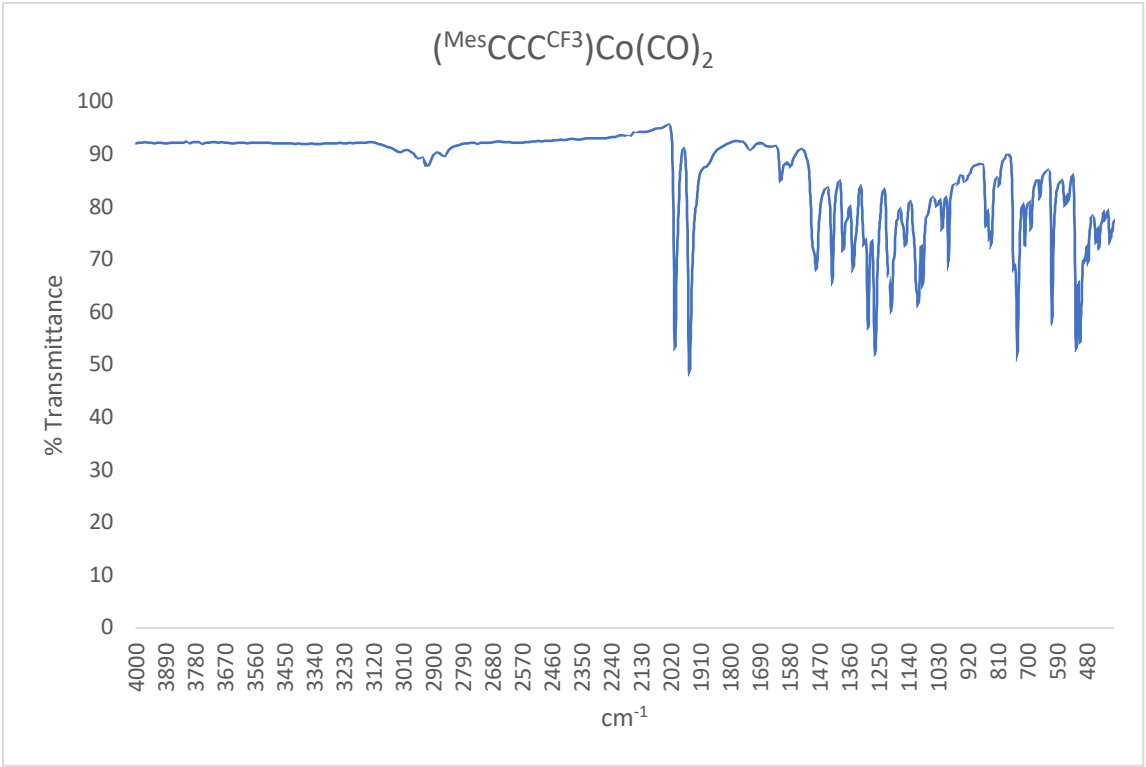


Figure S26. IR spectrum of (^{Mes}CCC^{CF3})Co(CO)$_2$ $\nu_{C\equiv O}$ 1951 and 2004 cm^{-1}.

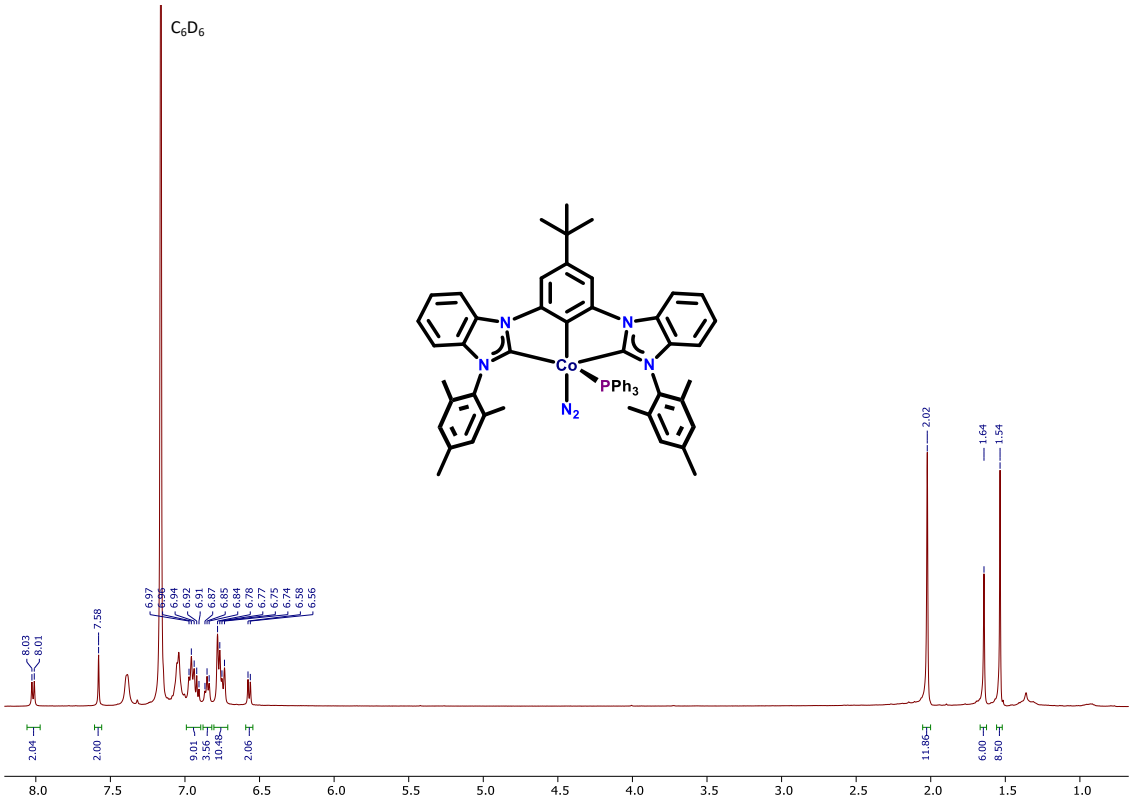


Figure S27. ^{1}H NMR spectrum of (^{Mes}CCC^{tBu})Co(N_2)PPh_3, **4-^{t}Bu**.

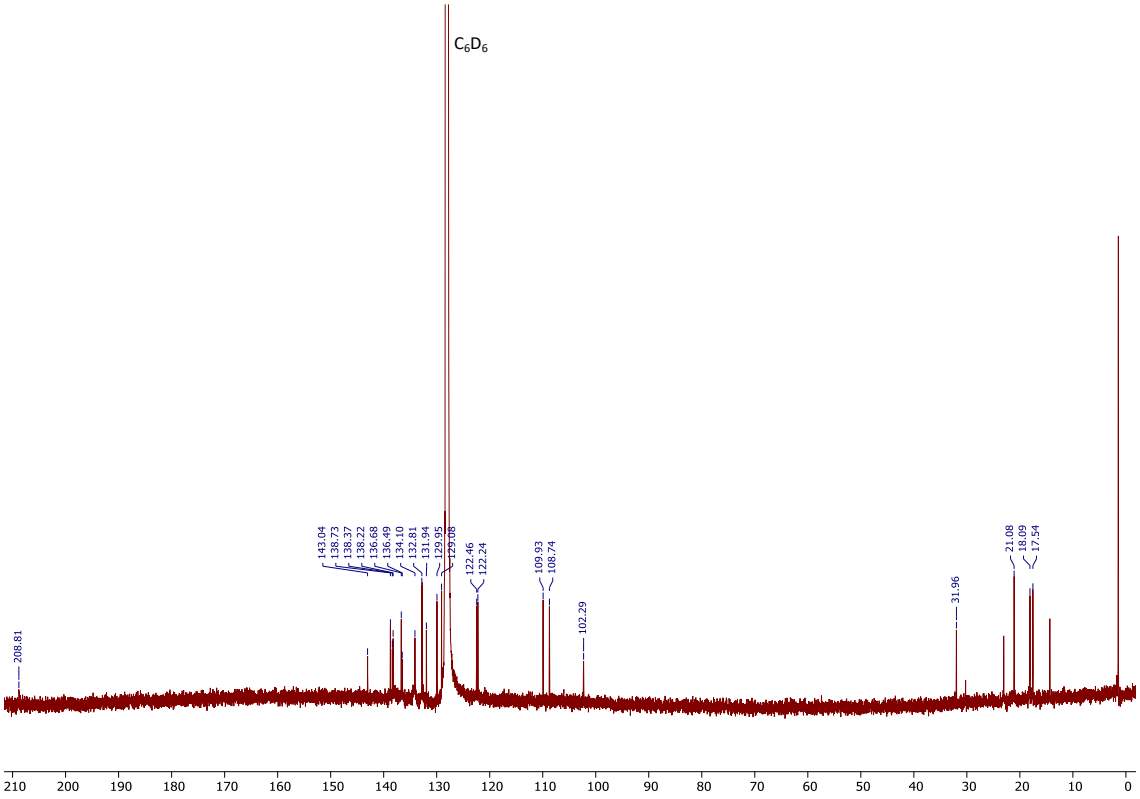


Figure S28. ^{13}C NMR spectrum of (^{Mes}CCC^{tBu})Co(N_2)PPh_3, **4-^{t}Bu**.

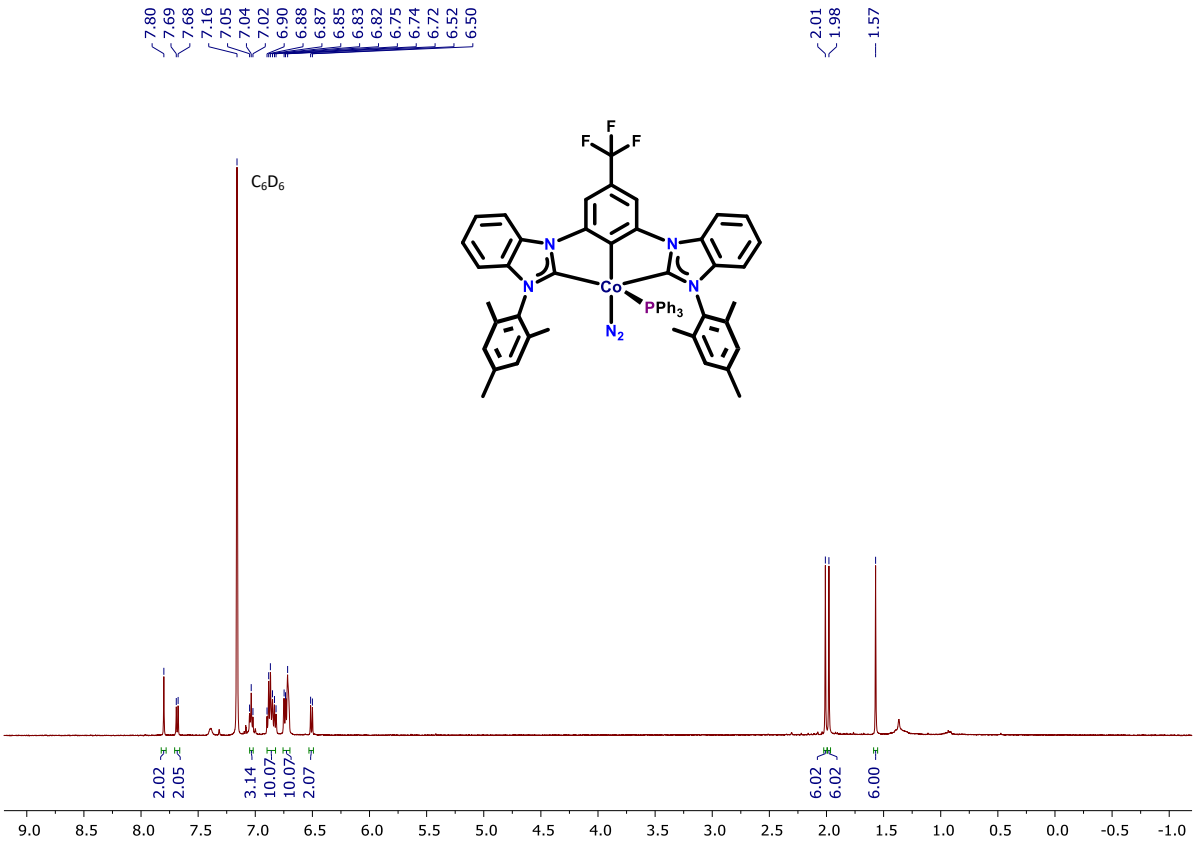


Figure S29. ^{1}H NMR spectrum of (^{Mes}CCC^{CF3})Co(N_2)PPh_3, **4-CF$_3$**.

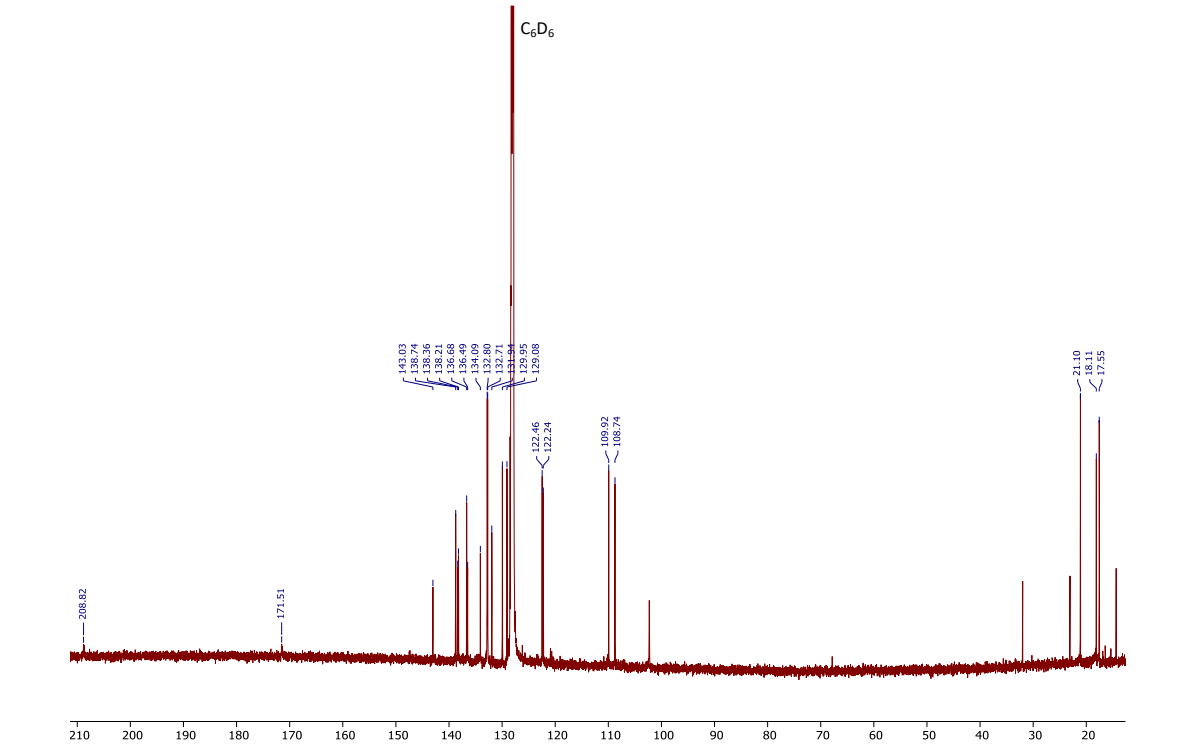


Figure S30. ^{13}C NMR spectrum of (^{Mes}CCC^{CF3})Co(N_2)PPh_3, **4-CF$_3$**.

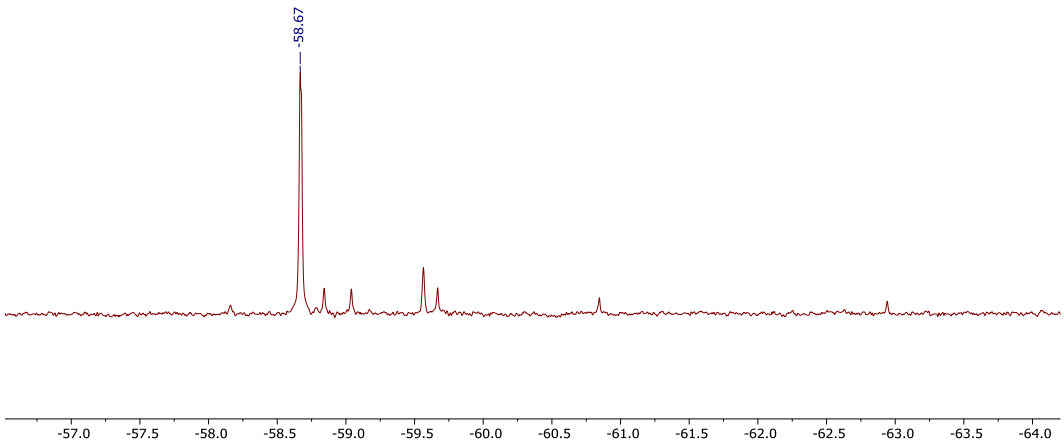


Figure S31. ^{19}F NMR spectrum of ($^{Mes}CCC^{CF3}$)Co(N_2)PPh_3, **4-CF_3**.

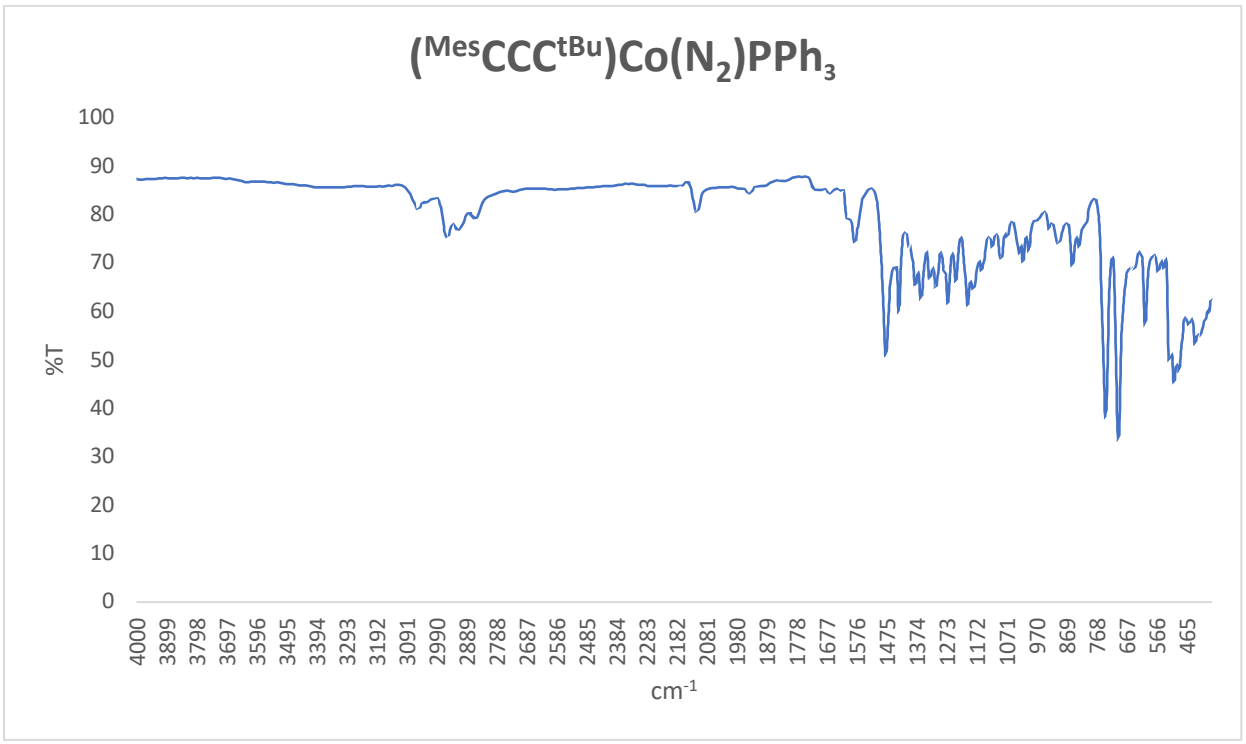


Figure S32. IR spectrum of (^{Mes}CCC^{tBu})Co(N_2)PPh_3 $\nu_{N=N}$ 2112 cm^{-1}.

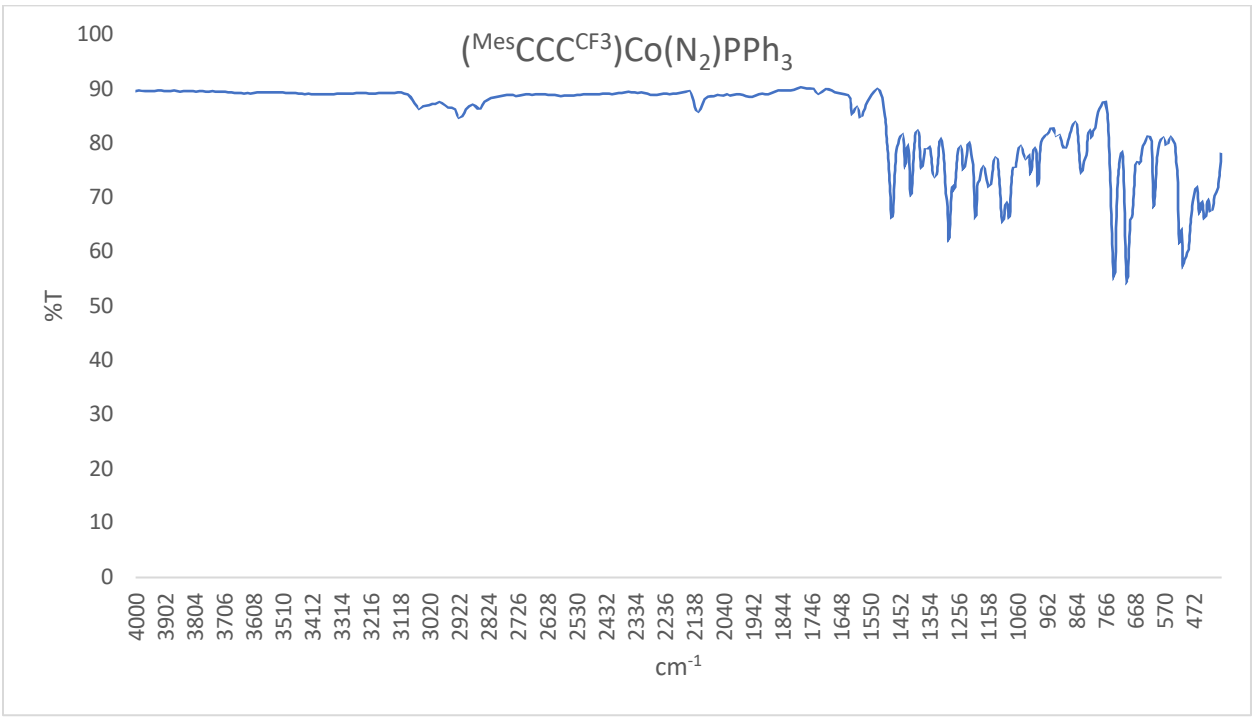


Figure S33. IR spectrum of (^{Mes}CCC^{CF3})Co(N_2)PPh_3 $\nu_{N=N}$ 2124 cm^{-1}.

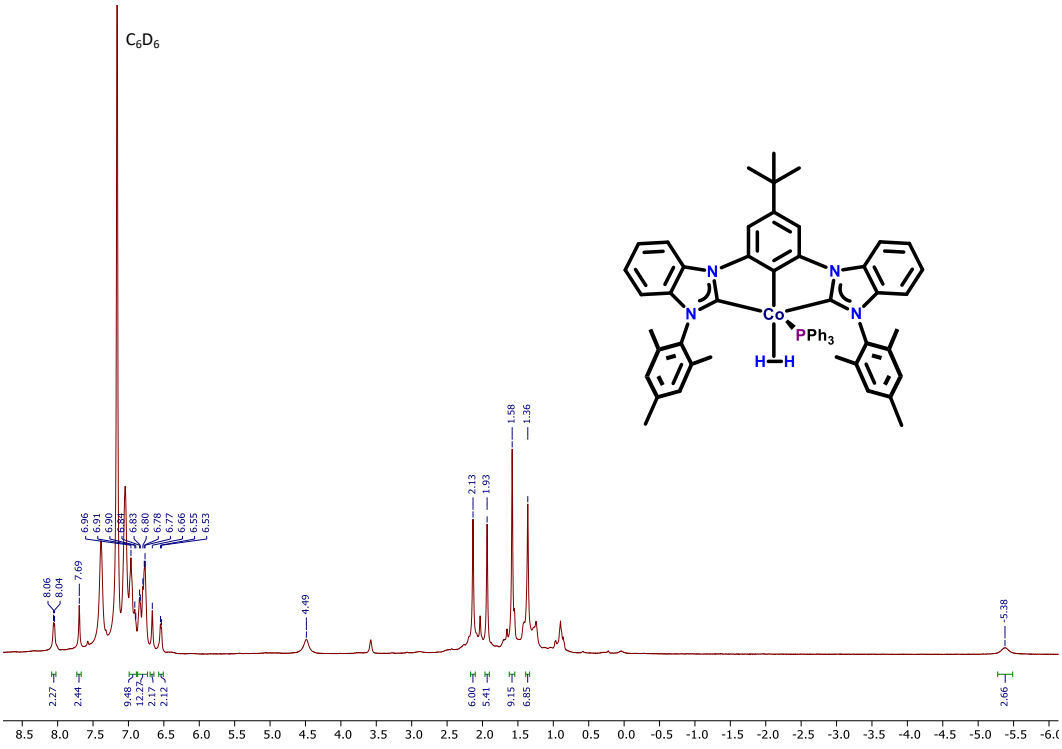


Figure S34. ^{1}H NMR spectrum of (^{Mes}CCC^{tBu})Co(H$_2$)PPh$_3$, **5-^{t}Bu**.

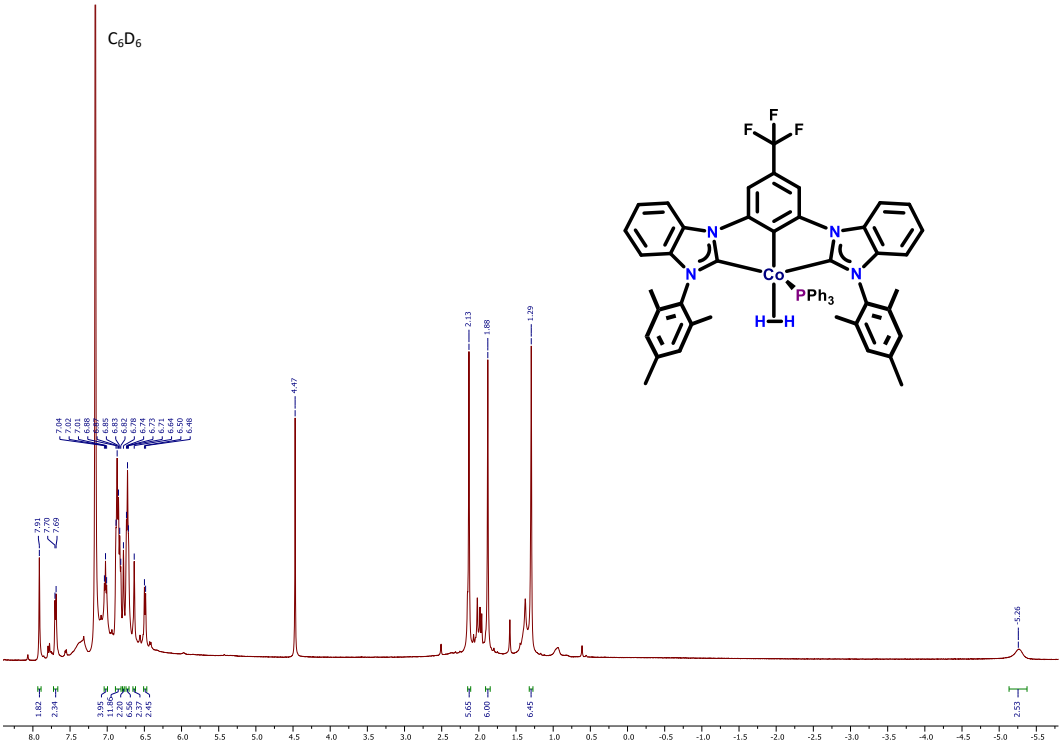


Figure S35. ^{1}H NMR spectrum of (^{Mes}CCC^{CF3})Co(H$_2$)PPh$_3$, **5-CF$_3$**.

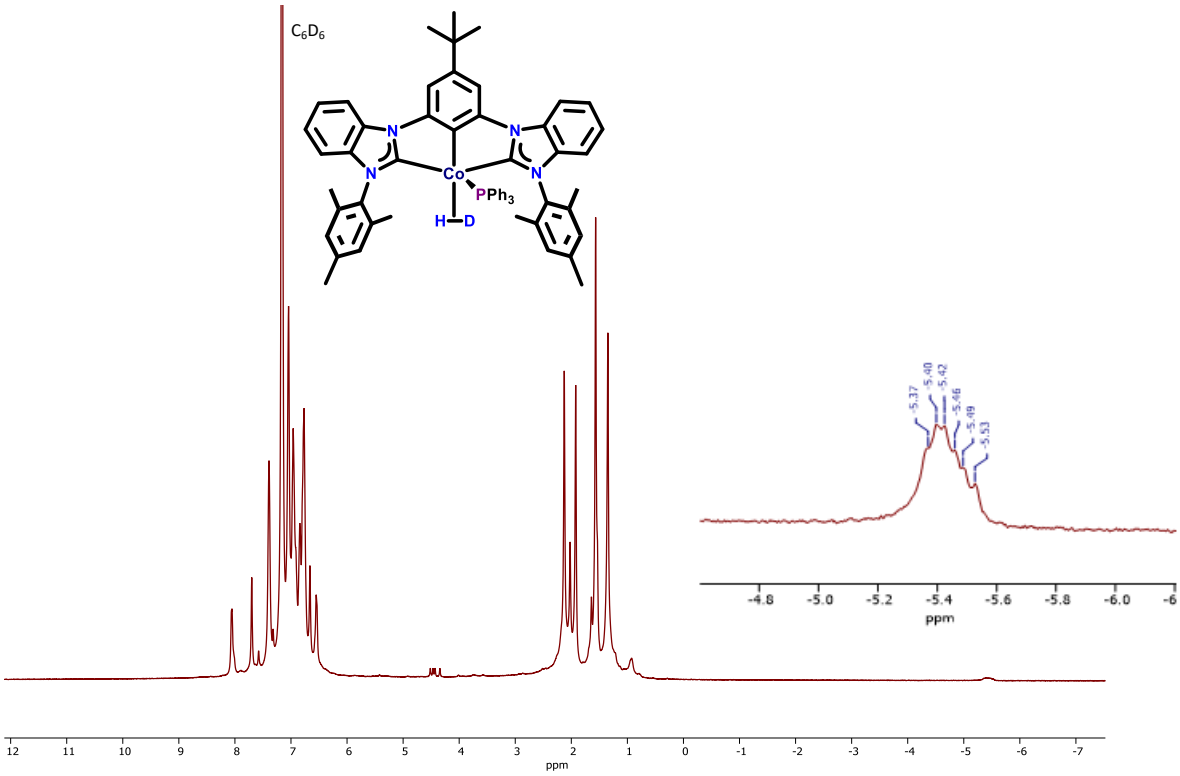


Figure S36. ^{1}H NMR spectrum of (^{Mes}CCC^{tBu})Co(HD)PPh$_3$, **6-^{t}Bu**.

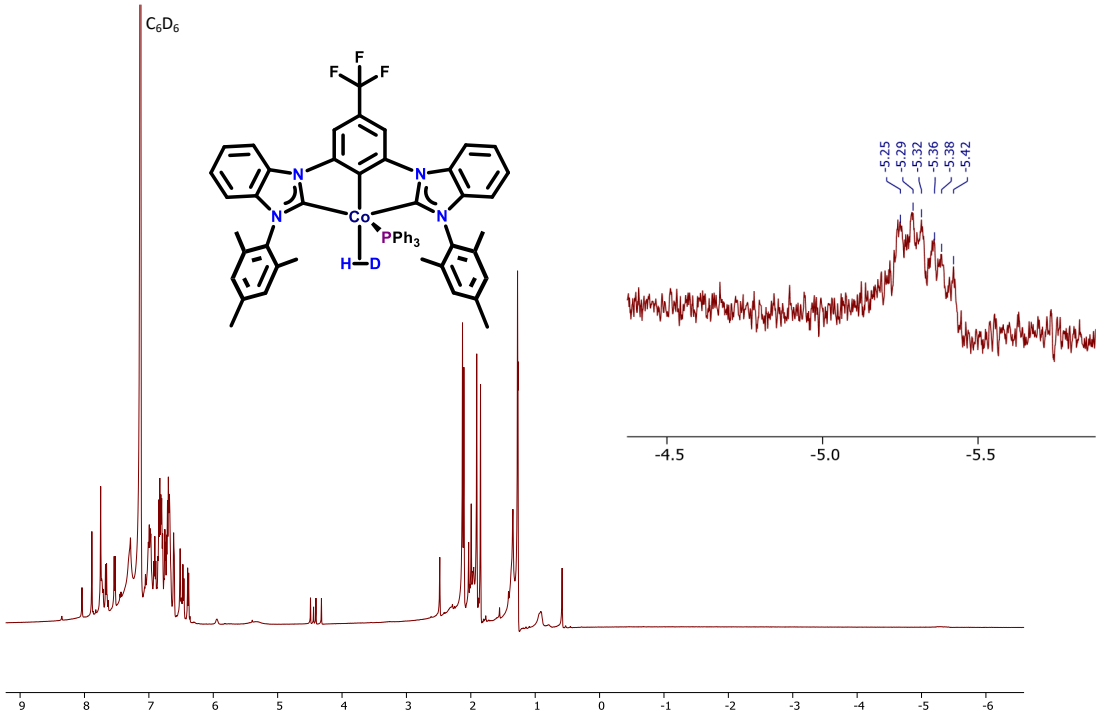


Figure S37. ^{1}H NMR spectrum of (^{Mes}CCC^{CF3})Co(HD)PPh$_3$, **6-CF$_3$**.

NMR Spectra of Semi-Hydrogenated Alkynes

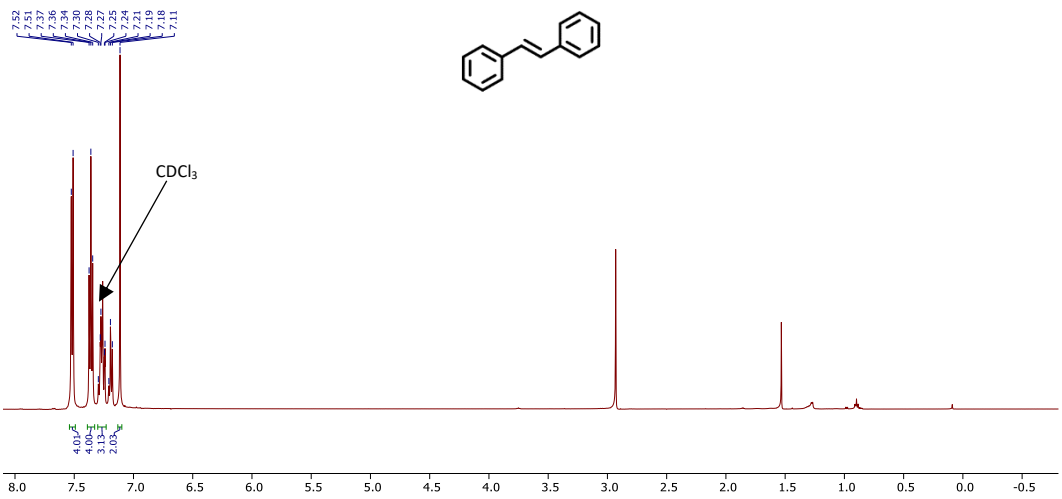


Figure S38. ^{1}H NMR of (E)-1,2-diphenylethene **- 4-^{t}Bu**.

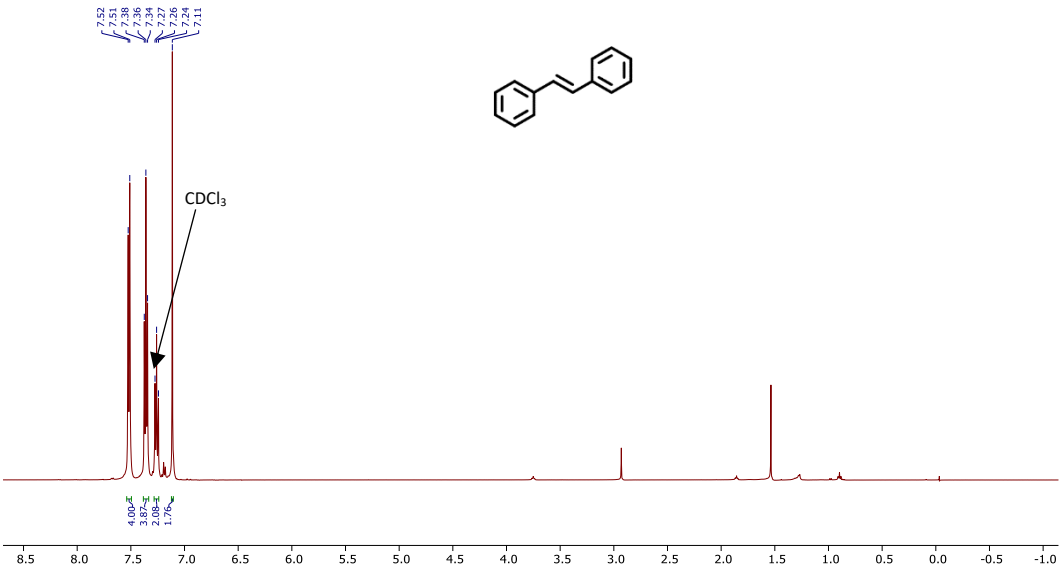


Figure S39. ^{1}H NMR of (E)-1,2-diphenylethene **- 4-CF$_3$**.

Figure S40. ^{1}H NMR of (E)-trimethyl(2-(thiophen-3-yl)vinyl)silane **- 4-^{t}Bu**.

Figure S41. ^{1}H NMR of (E)-trimethyl(2-(thiophen-3-yl)vinyl)silane **- 4-CF$_3$**.

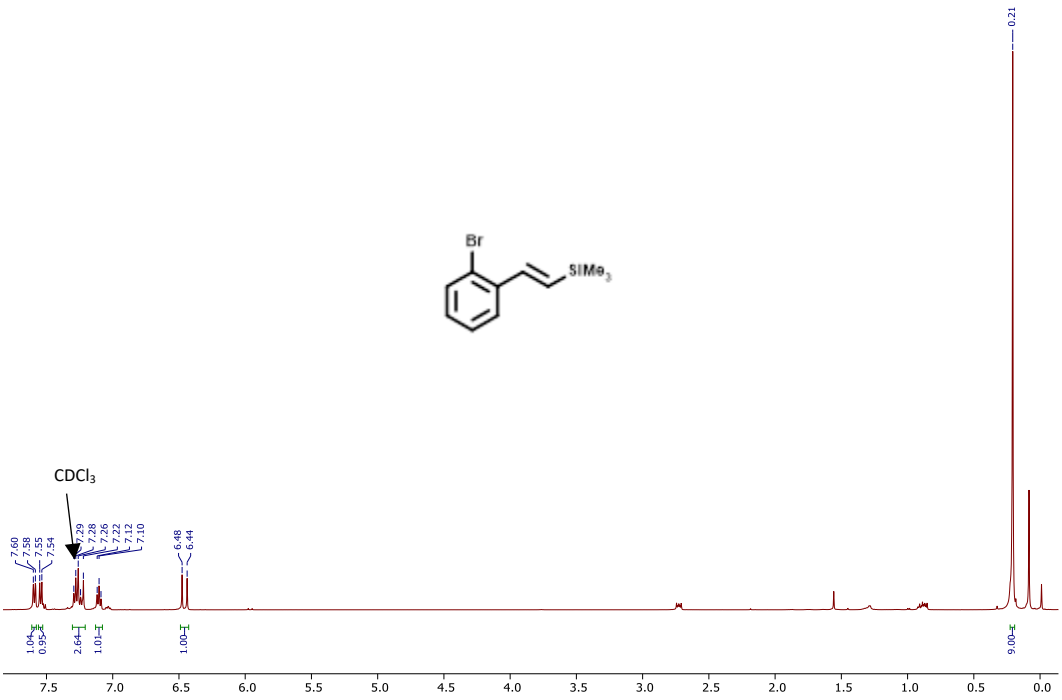


Figure S42. ^{1}H NMR of (E)-(2-bromostyryl)trimethylsilane **- 4-^{t}Bu**.

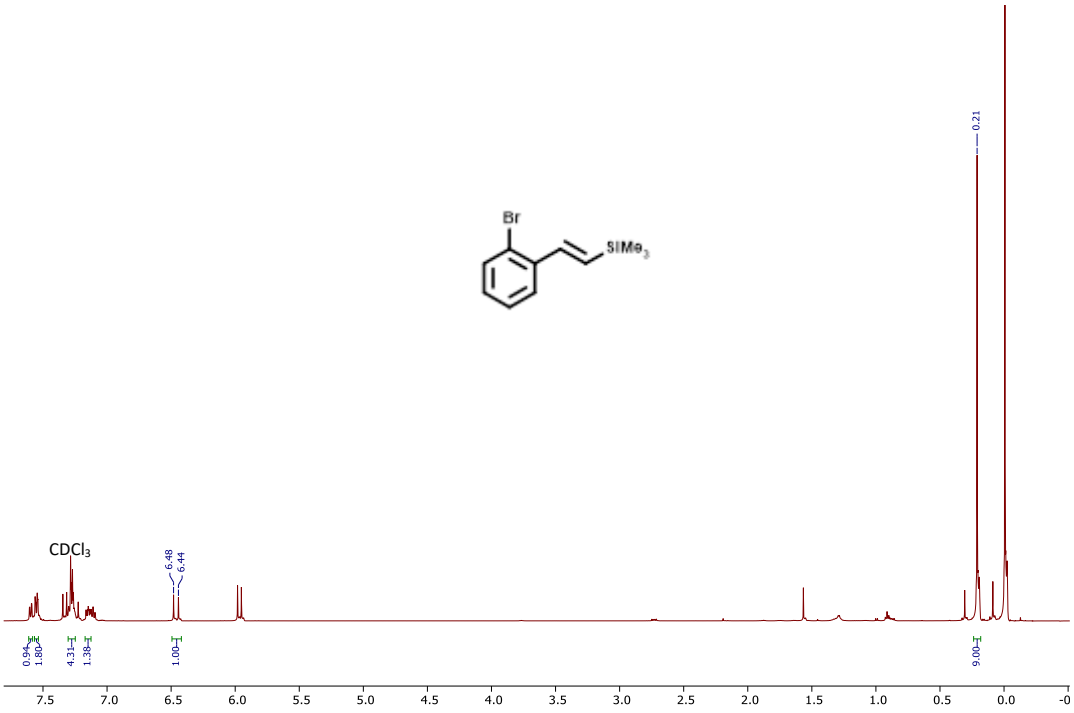


Figure S43. ^{1}H NMR spectrum of (E)-(2-bromostyryl)trimethylsilane **- 4-CF$_3$**.

***Para*hydrogen Induced Polarization Requirements[11,12]**

1. H atoms must end up on the same substrate – Must remained coupled
2. H atoms must end up in magnetically distinct positions
3. Reaction rate must be faster than the relaxation of the protons – Need a buildup of polarized product
4. Symmetry of parahydrogen must be broken upon addition to substrate

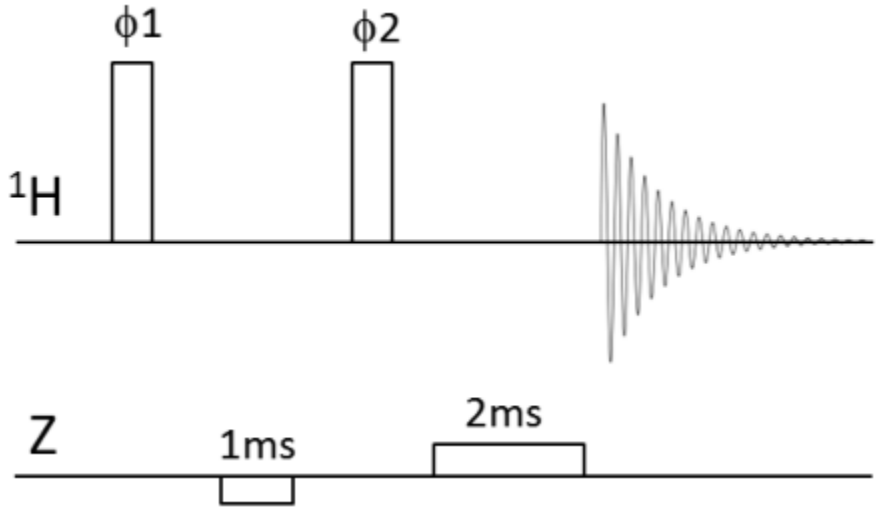
Mechanistic Studies

Sample Preparation

A standard J. Young NMR tube was charged with a solution of 3-[(trimethylsilyl)ethynyl]thiophene (0.010 g, 0.055 mmol) and catalyst (0.001 g, 0.001 mmol, 2 mol%) in *ca*. ½ mL of benzene-d_6. The sample was subjected to two freeze-pump-thaw cycles and 1 atm of *p*-H_2 gas was added at 77 K. The sample was kept frozen in liquid nitrogen and warmed to ambient temperature and shaken immediately before inserting into the NMR spectrometer. Because addition of the H_2 occurred outside of the magnet, the ALTADENA effect was observed. The spectra were collected at 30°C, and upon decay of the signal, the sample was ejected from the spectrometer, shaken, and reinserted to regain the signal.

NMR Spectrometer

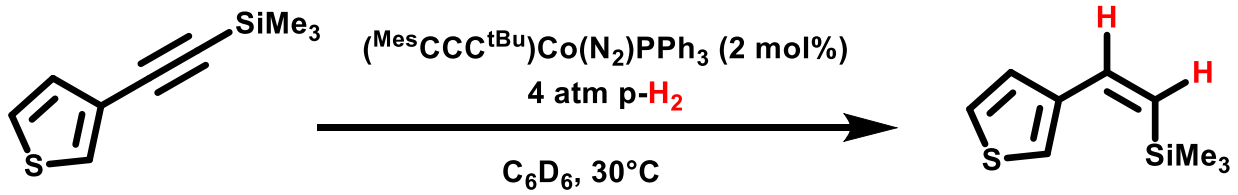
All PHIP NMR data were collected on a Varian UNITY INOVA 500 NB High-Resolution NMR Console with a 5mm Varian $^1H\{^{13}C/^{15}N\}$ PFG Z probe. All spectra were collected in benzene-d_6 and the residual solvent was referenced to 7.16 ppm. ^1H NMR spectra were collected using a 45° pulse angle. The spectral window of 15ppm was used in both proton and ^1H-OPSY experiments. ^1H-OPSY NMR data was collected via a double quantum coherence pathway using the pulse sequence below (**Scheme S1**). The OPSY spectra are anti-phase peaks and are displayed with absolute mode in the following spectra.[8,9]



Scheme S1. Double quantum OPSY pulse sequence (OPSY-d): the vertical bar at ^1H channel represents the π/2 pulse. Phase cycle: ϕ1: $(y)_4(x)_4$, ϕ2: $(x)_4(y)_4$, rec: $(x)_4(y)_4$. Z Gradient: 50 G/cm rectangular gradient was used. The first gradient was applied for 1 ms in the opposite direction of the second gradient, applied for 2 ms. 0.5 ms gradient recovery delays were used after each gradient. The acquisition time was 4 seconds and no delay between scans was used.

Generation of *para*hydrogen

A parahydrogen converter was used to generate the *para*-H_2 enriched hydrogen gas. This consisted of copper tubing filled with a hydrous ferric oxide catalyst that was cooled to 17 K using a closed-cycle ^{4}He cryostat. A detailed description of the converter can be found in Tom *et al*,[10] which was able to consistently convert naturally occurring hydrogen gas (3:1 *ortho:para*) to 99.99% *para*-H_2.



Scheme S2. *Para*hydrogenation of alkyne to show *cis*-hydrogenation with **4-^{t}Bu**.

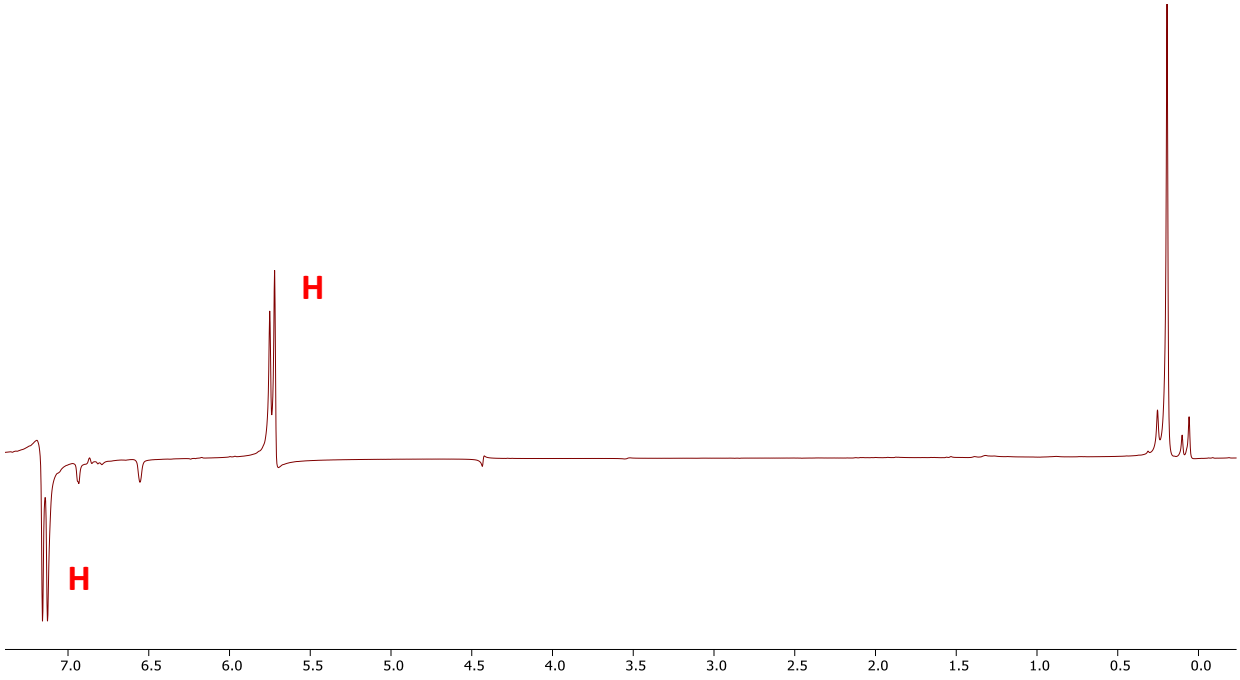


Figure S44. 45° pulse ^{1}H NMR spectrum of *cis*-hydrogenated product – **4-^{t}Bu**.

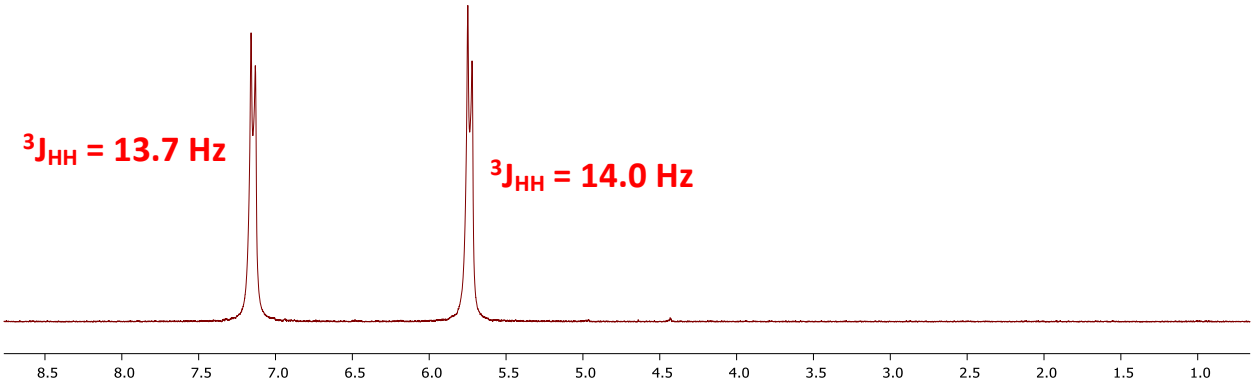
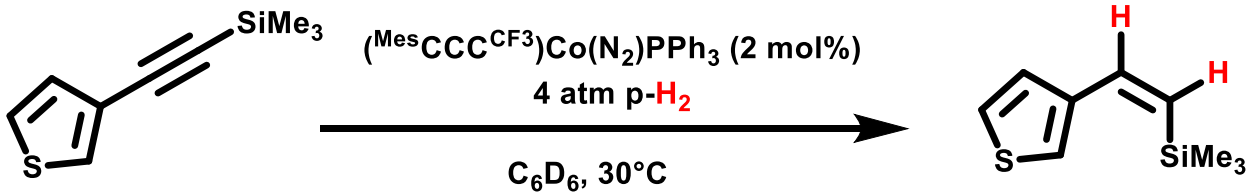


Figure S45. OPSY pulse ^{1}H NMR spectrum of *cis*-hydrogenated product – **4-^{t}Bu**.



Scheme S3. *Para*hydrogenation of alkyne to show *cis*-hydrogenation with **4-CF_3**.

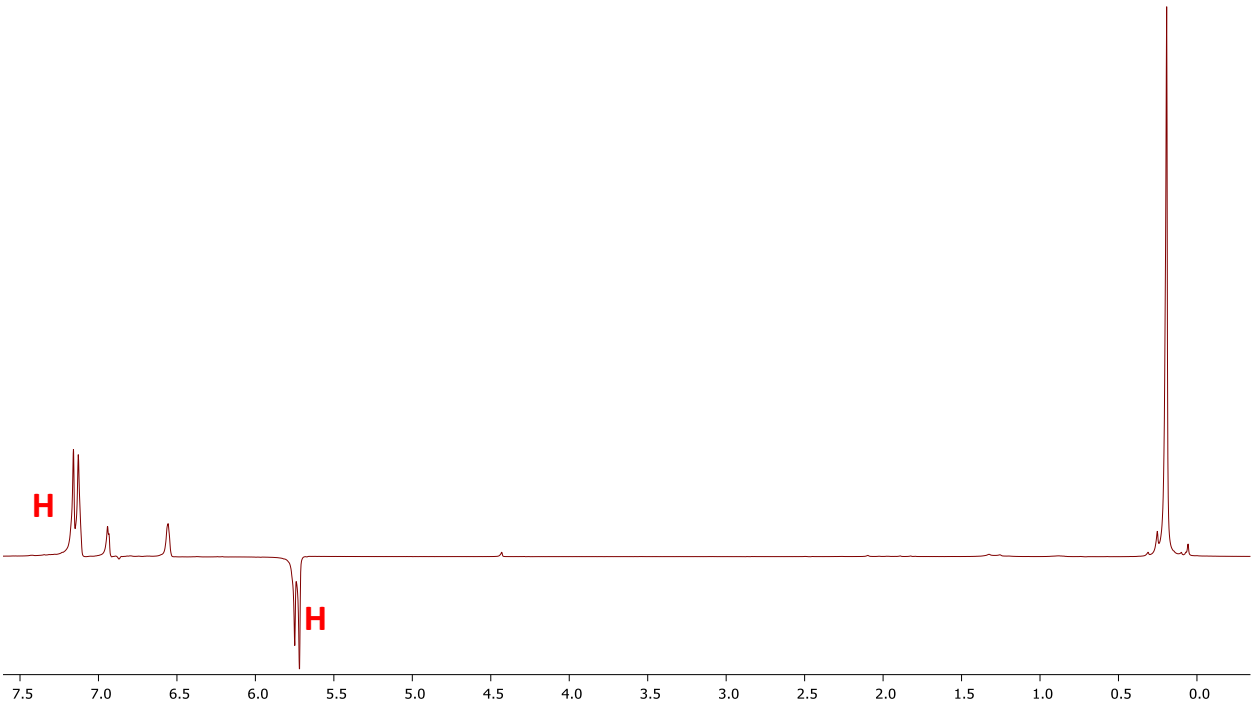


Figure S46. 45° pulse ^{1}H NMR spectrum of *cis*-hydrogenated product – **4-CF_3**.

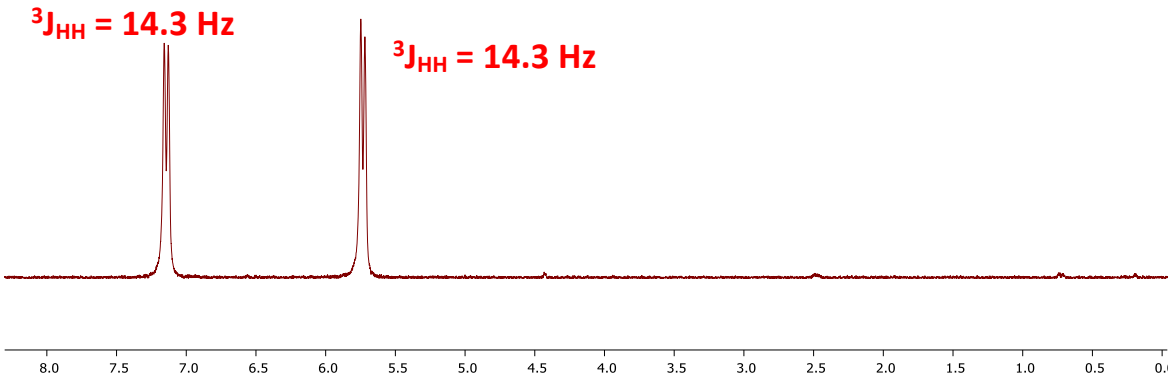
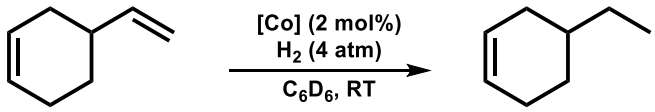


Figure S47. OPSY pulse ^{1}H NMR spectrum of *cis*-hydrogenated product – **4-CF$_3$**.



Scheme S4. Hydrogenation of 4-vinylcyclohexene with **4-H** and **4-CF$_3$**.

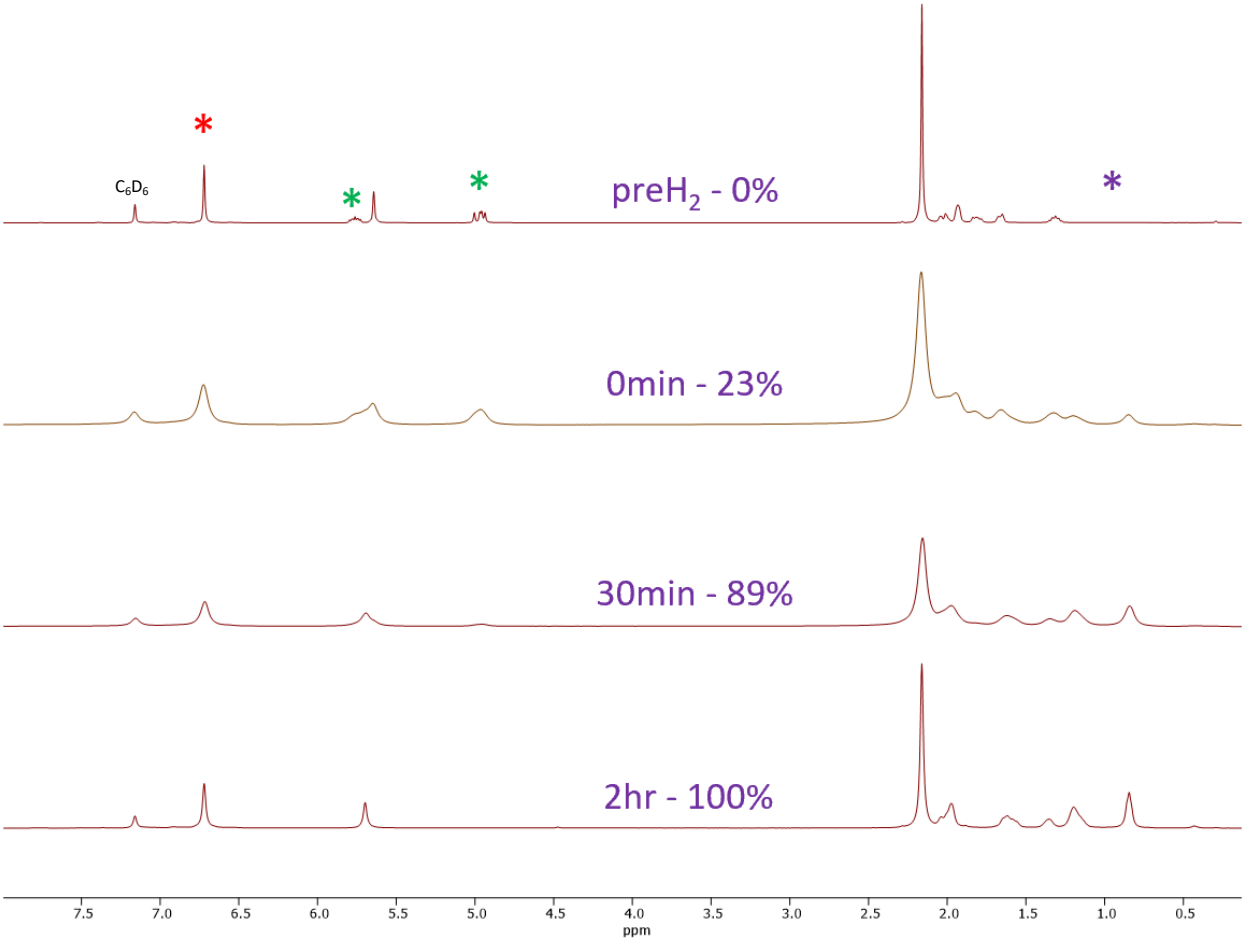


Figure S48. ^{1}H NMR spectra of the hydrogenation of 4-vinylcyclohexene by **4-H** monitored over time (* is mesitylene as an internal standard, * represents the starting olefin, and * represents the hydrogenated product).

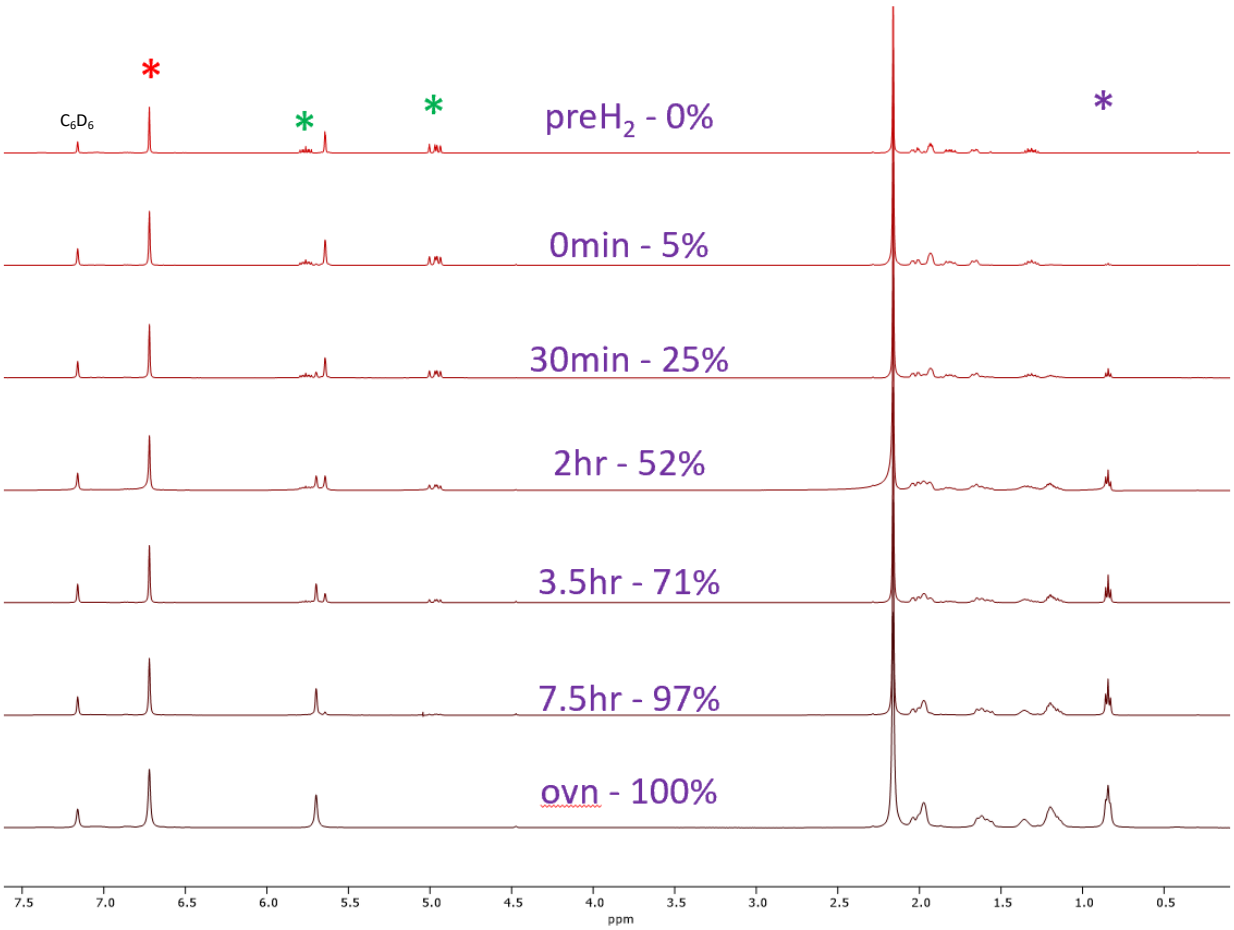


Figure S49. ^{1}H NMR spectra of the hydrogenation of 4-vinylcyclohexene by **4-CF$_3$** monitored over time (* is mesitylene as an internal standard, * represents the starting olefin, and * represents the hydrogenated product).

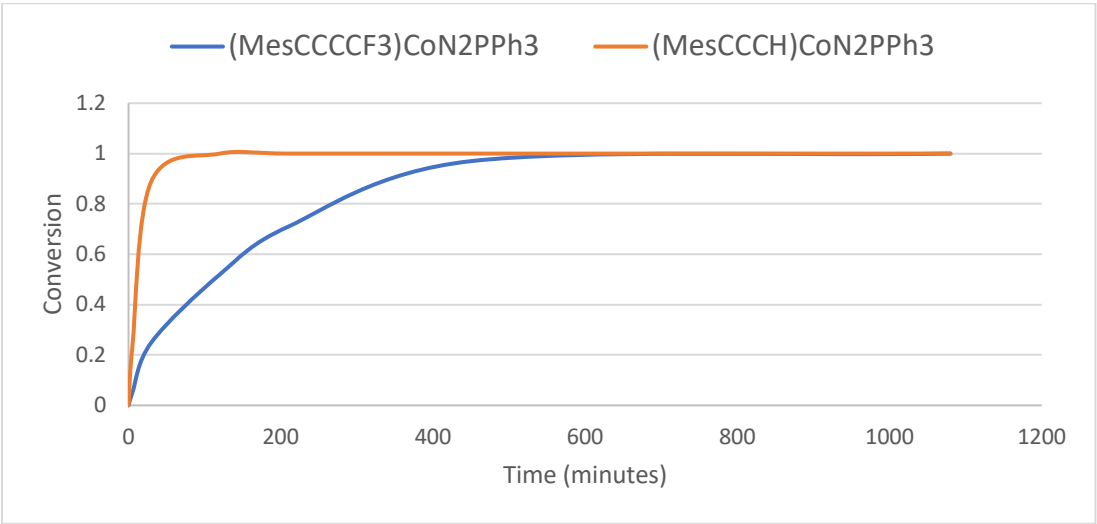
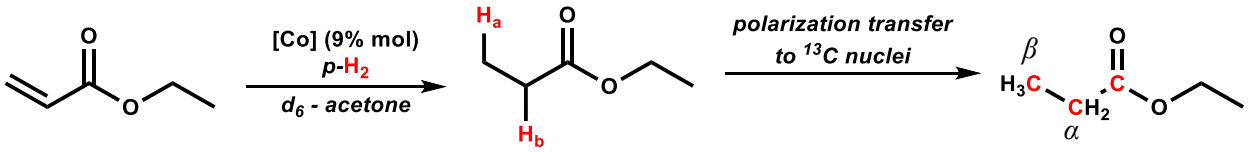


Figure S50. Graphical representation of the reaction time of the hydrogenation of 4-cvinylcyclohexene by **4-H** vs. **4-CF$_3$**.



Scheme S5. *Para*hydrogenation of ethyl acrylate with the Co^{I}-py catalyst, **2-^{t}Bu** and **2-CF_3**, and the spontaneous transfer to neighboring ^{13}C nuclei.

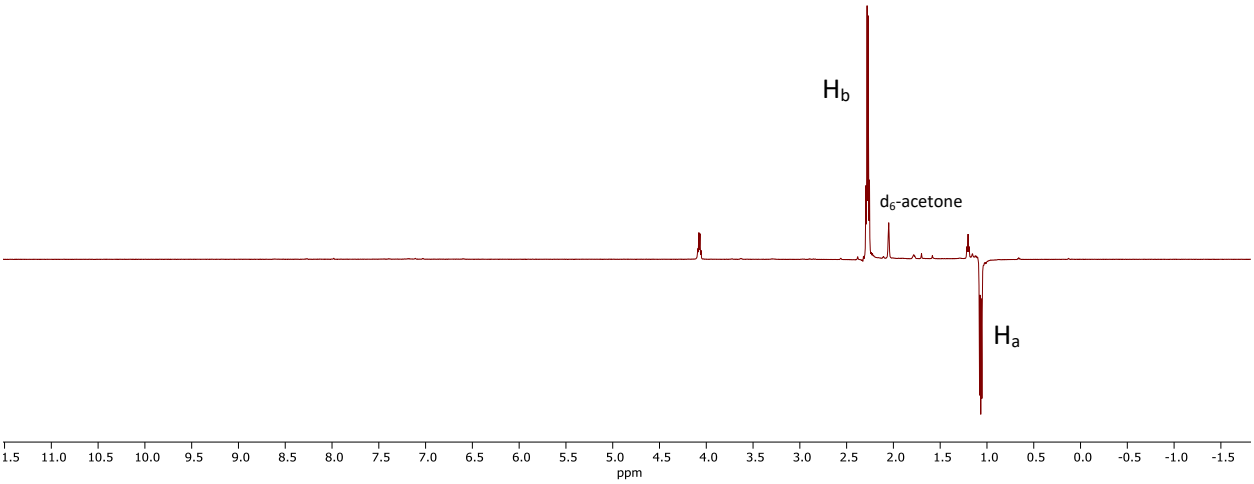


Figure S51. 45° pulse ^{1}H NMR spectrum of hyperpolarized ethyl propionate, catalyzed by **2-^{t}Bu**.

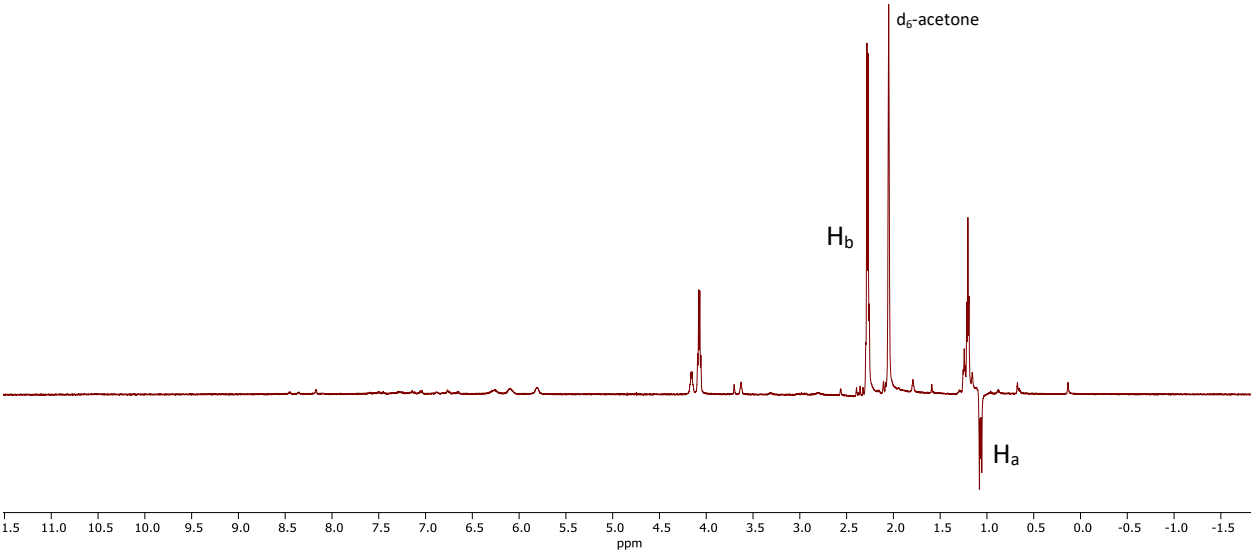


Figure S52. 45° pulse ^{1}H NMR spectrum of hyperpolarized ethyl propionate, catalyzed by **2-CF_3**.

Data Collection Procedure for PHIP on ^{13}C NMR

1. Sample is prepared and frozen before pH_2 addition.
2. Tube is thawed immediately before inserting into spectrometer
3. Tube is inserted and allowed to warm to temperature for 1 minute.
4. Sample is ejected and taken to an area at Earth's magnetic field
5. Sample is shaken at Earth's magnetic field for 5 seconds

6. Sample is ran back to spectrometer, inserted, and acquisition starts! (spectrum collected is designated as Shake 1)
7. After collection, repeat steps 4 – 6 (Shakes 2, 3, 4)

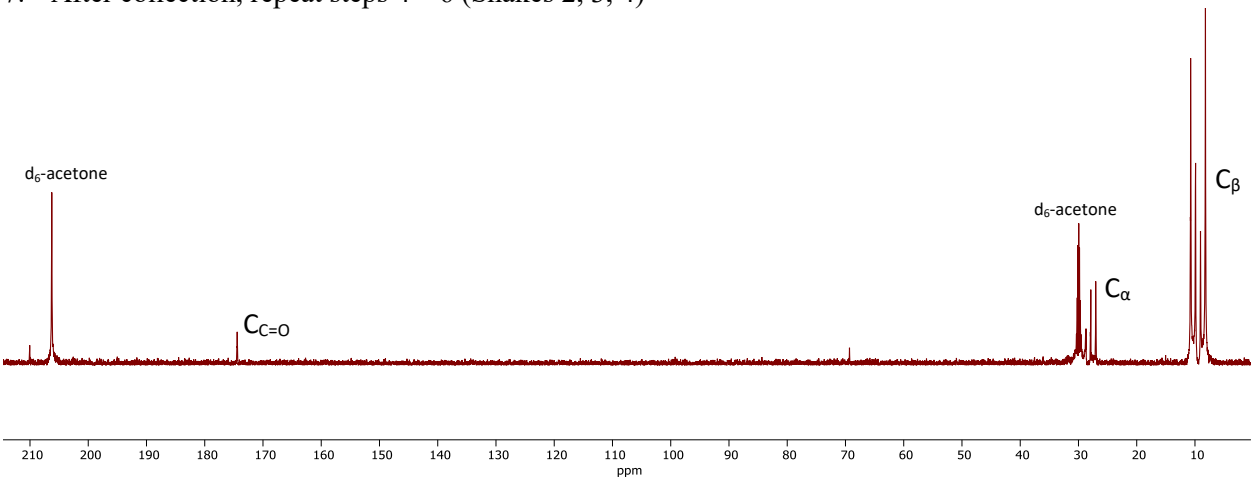


Figure S53. ^{13}C NMR spectrum of hyperpolarized ethyl propionate, catalyzed by **2-^{t}Bu**. Spectrum is shown in magnitude mode.

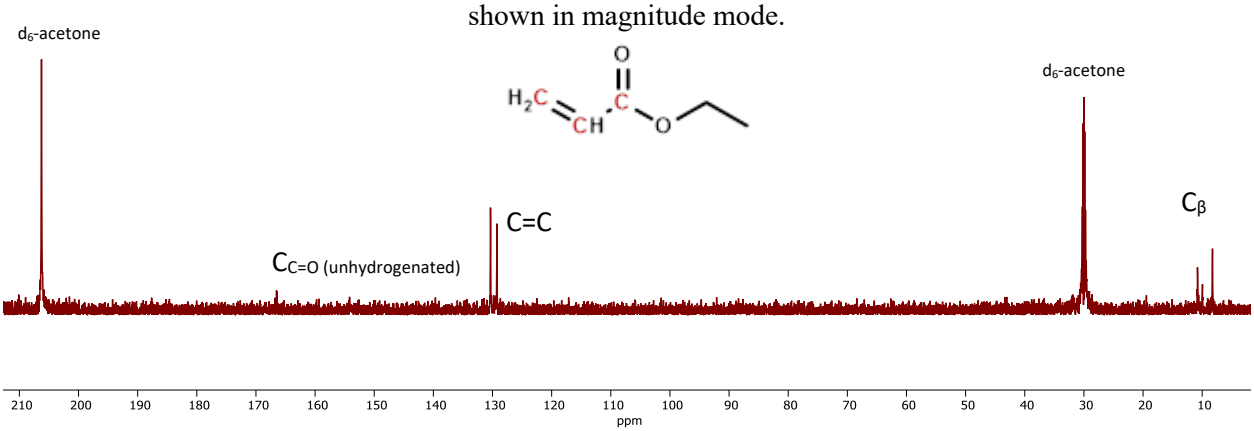


Figure S54. Shake 1 of ^{13}C NMR spectrum of hyperpolarized ethyl propionate, catalyzed by **2-CF$_3$**. Spectrum is shown in magnitude mode. This spectrum corresponds with the polarization of the unhydrogenated olefin, ethyl acrylate, as well as some of the hydrogenated product.

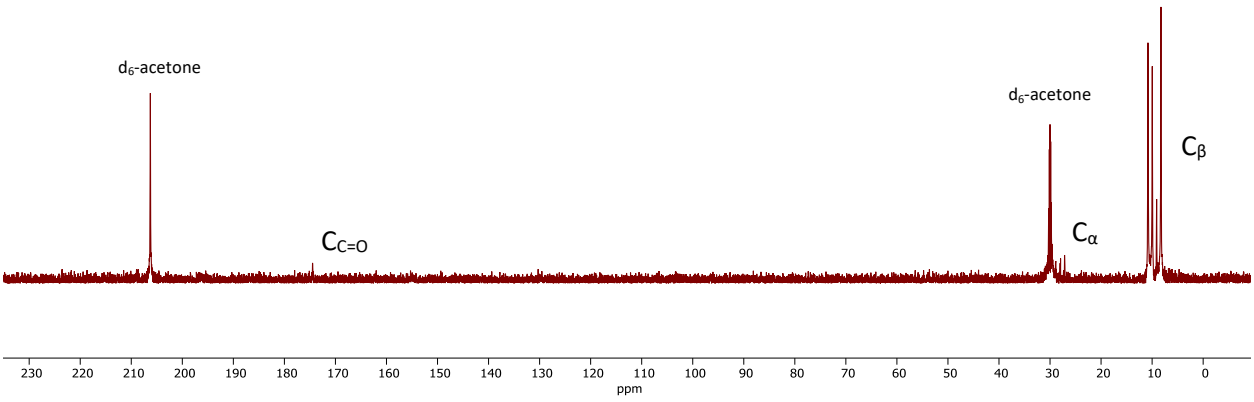


Figure S55. Shake 2 of ^{13}C NMR spectrum of hyperpolarized ethyl propionate, catalyzed by **2-CF$_3$**. Spectrum is shown in magnitude mode.

H_2 Exchange Studies

Method:

1. Determine the T1 relaxation time of the signal corresponding to free H_2 (~4.5ppm)
2. Conduct a spin saturation transfer experiment where you irradiate the Co-H_2 signal (~-5ppm) and see how the intensity of the free H_2 signal changes
3. Using MNova, conduct a max peak graph and plug in the T1 to the SST w/ baseline correction formula and 1/B is the relaxation rate. **Table S5.** Numerical value of experimental values from maximum peak graph of spin saturation transfer study on ($^{Mes}CCC^{H}$)Co(H_2)PPh_3, **4-H**.

Table S5. T1 relaxation times and exchanges rates of free H_2 from the ($^{Mes}CCC^{R}$)Co(H_2)PPh_3 complexes.

	T1 Bound H_2 (ms)	T1 Free H_2 (ms)	B = lifetime (s)	1/B = Exchange rate (s^{-1})
4-H	12	504	3.96	0.25
4-^{t}Bu	12	706	3.18	0.31
4-CF_3	12	288	3.31	0.30

Table S6. Table of comparative values.

	($^{Mes}CCC^{R}$)$CoCl_2$py			($^{Mes}CCC^{R}$)Co(CO)$_2$			($^{Mes}CCC^{R}$)Co(N_2)PPh_3			($^{Mes}CCC^{R}$)Co(H_2)PPh_3			($^{Mes}CCC^{R}$)Co(HD)PPh_3		
bond	1-H	1-^{t}Bu	1-CF_3	2-H	2-^{t}Bu	2-CF_3	4-H	4-^{t}Bu	4-CF_3	5-H	5-^{t}Bu	5-CF_3	6-H	6-^{t}Bu	6-CF_3
Co-C_{NHC1}	1.961(4)	1.9540(24)	1.9617(54)	1.9119(15)			1.9147(13)		1.9122(21)						
Co-C_{NHC2}	1.958(4)	1.9540(24)	1.9627(55)	1.9119(15)			1.9001(13)		1.9057(21)						
Co-C_{Ar}	1.871(4)	1.8726(30)	1.8744(52)	1.9102(22)			1.8750(13)		1.8677(21)						
Co-N_{py}	2.090(3)	2.0983(26)	2.0979(46)												
Co-Cl_1	2.2751(13)	2.2702(9)	2.2808(14)												
Co-Cl_2	2.2651(12)	2.2605(9)	2.2511(14)												
Co-C_{CO}				1.7776(19)											
Co-P							2.2483(4)		2.2534(6)						
Co-N_{N2}							1.8270(12)		1.8412(19)						
N-N							1.1005(16)		1.0873(26)						
C_{Ar}-Co-N_{py}	179.13(16)	179.63(12)	179.79(24)												
C_{Ar}-Co-Cl_1	86.75(12)	85.80(10)	85.56(17)												
C_{Ar}-Co-Cl_2	86.53(12)	86.90(10)	86.31(17)												
C_{CO}-Co-C_{CO}				112.93(14)											
C_{Ar}-Co-N_{N2}							157.89(5)		160.08(9)						
P-Co-N_{N2}							106.68(4)		104.81(6)						
ν_{C-O} (cm^{-1})				1918, 1973	1939, 1990	1951, 2004									
ν_{N-N} (cm^{-1})				2112	2112	2123									

H_2 exchange rate				0.25	0.31	0.30
$J_{H\text{-}D}$ (Hz)						
H-D bond distance (Å)						

H_2 exchange rate						
$J_{H\text{-}D}$ (Hz)	33	31	33			
H-D bond distance (Å)	0.87	0.90	0.87			

Figure S56. Modified proposed catalytic cycle for *cis*-hydrogenation of internal alkynes, followed by *trans*-isomerization using **4-H**.

References

1. Ibrahim, A. D., Tokmic, K., Brennan, M. R., Kim, D., Matson, E. M., Nilges, M. J., Bertke, J. A., and Fout, A. R. Monoanionic Bis(Carbene) Pincer Complexes Featuring Cobalt(I-III) Oxidation States. *Dalton Trans.*, **2016**, 45, 9805-9811.
2. Coulson, D. R.; Satek, L. C.; Grim, S. O. Tetrakis(triphenylphosphine)palladium(0). *Inorganic Syntheses*, **1972**, *13*, 121-123.
3. Eichhöfer, A.; Lan, Y.; Mereacre, V.; Bodenstein, T.; Weigend, F. Slow Magnetic Relaxation in Trigonal-Planar Mononuclear Fe(II) and Co(II) Bis(trimethylsilyl)amido Complexes—A Comparative Study. *Inorg. Chem.* **2014**, 53, 1962-1974.
4. Burger, H.; Wannagat, U. Silylamido-Derivate von Eisen und Kobalt. *Montash. Chem.* **1963**, *6*, 1007-1012.
5. Wietz, I. S.; Rabinovitz, M. The application of C_8K for organic synthesis: reduction of substituted naphthalenes. *J. Chem. Soc. Perkin Trans.* **1993**, *1*, 117-120.
6. Espinosa-Martinez, G., Nugent, J.W., Fout, A.R. Simple Nickel Salts for the Amination of (Hetero)Aryl Bromides and Iodides with Lithium Bis(Trimethylsilyl)Amide. *Organometallics* **2018**, 37, 2941-2944.
7. Chianese, A. R., Drance, M. Y., Jensen, K. H., McCollom, S. P., Yusufova, N., Shaner, S. E., Shopov, D. Y., Tendler, J. A. Acceptorless Alkane Dehydrogenation Catalyzed by Iridium CCC-Pincer Complexes. *Organometallics* **2014**, 33, 457-464.
8. Aguilar, J. A.; Adam, R. W.; Duckett, S. B.; Green, G. G. R.; Kandiah, R. Selective Detection of Hyperpolarized NMR Signals Derived from Para-Hydrogen Using the Only Para-Hydrogen SpectroscopY (OPSY) Approach. *J. Magn. Reson.* **2011**, *208*, 49-57.

9. Duckett, S. B.; Green, G. G. R.; Cowley, M. J. Pulse sequencing with hyperpolarisable nuclei. US Patent 20,110,274,626, November 10, 2011.
10. Tom, B. A.; Bhasker, S.; Miyamoto, Y.; Momose, T.; McCall, B. Producing and quantifying enriched para-H_2. *Rev. Sci. Instrum.* **2009**, *80*, 016108, 1-3.
11. Cavallari, E.; Carrera, C.; Reineri, F. ParaHydrogen Hyperpolarized Substrates for Molecular Imaging Studies. *Isr. J. Chem.* **2017**, *57* (9), 833–884.
12. Duckett, S. B.; Mewis, R. E. Application of Para Hydrogen Induced Polarization Techniques in NMR Spectroscopy and Imaging. *Acc. Chem. Res.* **2012**, *45* (8), 1247–1257.
13. Emondts, M.; Colell, J. F. P.; Blümich, B.; Schleker, P. P. M. Polarization Transfer Efficiency in PHIP Experiments. *Phys. Chem. Chem. Phys.* **2017**, *19* (33), 21933–21937.