Cobalt catalyzed sp3 C-H amination utilizing aryl azides

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Supporting Information

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I. General Information.

¹H and ¹³C NMR spectra were recorded at room temperature on a Varian Inova 600 spectrometer (600 MHz ¹H, 150 MHz ¹³C) and a Varian Inova 400 spectrometer (400 MHz ¹H, 100 MHz¹³C) in CDCl₃ (neutralized and dried with anhydrous K₂CO₃) with internal CHCl₃ as the reference (7.27 ppm for ¹H and 77.23 ppm for ¹³C). Chemical shifts (δ values) were reported in parts per million (ppm) and coupling constants (J values) in Hz. Multiplicity is indicated using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext =sextet, m = multiplet, b = broad signal.). Solution-state infrared (IR) spectra were recorded using Thermo Electron Corporation Nicolet 380 FT-IR spectrometer. Solid-state Infrared spectra were recorded as KBr pellets on a Varian Scimitar 800 Series FT-IR spectrophotometer. UV-Visible absorption spectra were recorded on a Cary50 spectrophotometer using 1.0 cm quartz cuvettes. High-resolution mass spectra were obtained using a Thermo Electron Corporation Finigan LTQFTMS (Mass Spectrometry Facility, Emory University). X-ray diffraction studies were carried out in the X-ray Crystallography Laboratory at Emory University on a Bruker Smart 1000 CCD diffractometer. We acknowledge the use of shared instrumentation provided by grants from the NIH and the NSF. Elemental analyses were preformed by either Atlanta Microlab, Inc. Norcross, GA or Midwest Microlab, LLC, Indianapolis, IN. Analytical thin layer chromatography (TLC) was performed on precoated glass backed EMD 0.25 mm silica gel 60 plates. Visualization was accomplished with UV light or ethanolic anisaldehyde, followed by heating. Flash column chromatography was carried out using Silicycle® silica gel 60 (40-63 μm).

All reactions were conducted with anhydrous solvents in oven-dried and nitrogencharged glassware or conducted in an MBraun Labmaster 130 drybox under a nitrogen atmosphere. Anhydrous solvents were purchased from Sigma-Aldrich and further purified by sparging with Ar gas followed by passage through activated alumina columns. Anhydrous solvents were stored inside an inert atmosphere dry box over freshly activated 4Å molecular sieves. Solvents for workup, extraction and column chromatography were used as received from commercial suppliers. All reagents used were purchased from commercial vendors and used as received unless otherwise noted.

II. Procedures and Characterization Data

a) Ligands



2,2'-Bis(*tert*-butylacetamido)diphenylamine (HN(*o*-PhNHC(O)'Bu)₂) [H₃L'^{Bu}]. A suspension of HN(*o*-PhNH₂)₂¹ (3.50 g, 17.6 mmol) in dichloromethane (DCM, 50 mL) was lowered to 0 °C under an atmosphere of N₂. Triethylamine (4.90 mL, 35.2 mmol) was then added, followed by the dropwise addition pivaloyl chloride (4.30 mL, 35.2 mmol) via a dropper funnel. The mixture was stirred at 0 °C for 1 h. The reaction mixture was slowly warmed to room temperature and stirred for an additional 24 h. The resulting pale brown-colored solution was extracted with saturated aqueous NaHCO₃ (3 x 30 mL) and brine (2 x 20 mL), and the organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude solid was recrystallized by slow diffusion of diethyl ether into a concentrated DCM solution of the product (5.20 g, 80 %). **IR** (KBr, cm⁻¹) $v(NH)_{Amine}$ 3343, $v(NH)_{Amide}$ 3428, v(CO) 1685; ¹H NMR (CDCl₃, 400 MHz) δ 7.66 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.64 (bs, 2H), 7.07-6.98 (m, 4H), 6.87 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.08 (bs, 1H), 1.19 (s, 18H); ¹³C NMR (CDCl₃, 100 MHz) δ 177.3, 135.7, 129.2, 126.0, 123.5, 123.0, 121.0, 39.6, 27.5; HRMS (+ESI) calculated for C₂₂H₃₀N₃O₂ 368.23380, found 368.23305 [M+H]⁺.



2,2'-Bis(diphenylacetamido)diphenylamine (HN(*o*-PhNHC(O)Ph)₂) [H₃L^{Ph}]. A suspension of HN(*o*-PhNH₂)₂¹ (6.31 g, 31.7 mmol) in dichloromethane (DCM, 50 mL) was lowered to 0 °C under an atmosphere of N₂. Triethylamine (9.75 mL, 63.4 mmol) was then added, followed by benzoyl chloride (8.10 mL, 63.4 mmol). The mixture was stirred at 0 °C for 1 h. The reaction mixture was slowly warmed to room temperature and stirred for an additional 20 h. The resulting pale brown solution was extracted with saturated aqueous NaHCO₃ (3 x 30 mL), and the organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude solid was recrystallized by layering hexanes over a concentrated DCM solution of the product (10.98 g, 85 %). **IR** (KBr, cm⁻¹) v(NH) 3386, 3292, v(CO) 1658; ¹H NMR (CDCl₃, 400 MHz) δ 8.35 (s, 2H), 7.73 - 7.80 (m, 6H), 7.49 (t, 2H, *J* = 4.4 Hz), 7.38 (m, 4H), 7.13 -7.01 (m, 6H), 6.12 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.4, 136.2, 134.2, 132.1, 129.1, 128.8, 127.6, 126.7, 124.5, 123.1, 121.0; **HRMS** (+ESI) calculated for C₂₆H₂₁N₃O₂407.1634, found 407.1626 [M]⁺.



2,2'-Bis(trifluoroacetamido)diphenylamine (HN(o-PhNHC(O)CF₃)₂) [H₃L^{CF3}]. A suspension of HN(o-PhNH₂)₂¹ (2.55 g, 12.8 mmol) in dichloromethane (DCM, 50 mL) was lowered to 0 °C under

an atmosphere of N₂. Triethylamine (3.60 mL, 25.8 mmol) was then added, followed by trifluoroacetic anhydride (3.60 mL, 14.5 mmol). The mixture was stirred at 0 °C for 1 h. The reaction mixture was slowly warmed to room temperature and stirred for an additional 20 h. The resulting pale brown solution was extracted with saturated aqueous NaHCO₃ (3 x 30 mL), and the organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude solid was recrystallized by layering hexanes over a concentrated DCM solution of the product (1.78 g, 80 %). **IR** (KBr, cm⁻¹) v(NH) 3298, v(CO) 1701; ¹**H NMR** (CDCl₃ 400 MHz) δ 8.33 (bs, 2H,), 7.67 (dd, 2H, *J* = 8.0, 1.6 Hz), 7.23 (td, 2H, *J* = 7.6, 1.6 Hz) 7.14 (td, 2H, *J* = 7.6, 1.2 Hz), 6.93 (dd, 2H, *J* = 8.0, 1.2 Hz), 5.49 (bs, 1H); ¹³C **NMR** (CDCl₃ 100 MHz) δ 131.9, 129.5, 127.7, 127.2, 125.3, 123.9, 1122.4, 110.7; **HRMS** (+ESI) calculated for C₁₆H₁₁F₆N₃O₂ 392.083, found 392.083 [M+H]⁺.

b) Co(II) Complexes

The cobalt complexes are all prepared by similar procedures. The cobalt complexes can be prepared as either dipotassium or bistetraethylammonium salts. The choice of counter cation does not impact the amination reactions.



K₂[**Co**₂(**L**^{*f*Bu})₂] (2). To a solution of [HN(*o*-PhNHC(O)'Bu)₂] (120 mg, 0.327 mmol) in dry dimethylformamide (DMF, 10 mL) was added potassium hydride (39.3 mg, 0.971 mmol) inside a nitrogen-filled atmosphere dry box. When gas evolution ceased, CoBr₂ (71 mg, 0.327 mmol) was added as a solid and the mixture stirred. After stirring for 3 h, DMF was removed under high vacuum and the resulting solid was dissolved in CH₃CN (15 mL), filtered through a medium porosity frit, and the filtrate was concentrated to dryness. Deep green X-ray diffraction quality crystals were obtained by slow diffusion of diethyl ether into a concentrated CH₃CN solution of K₂[Co₂(L^{*t*Bu})₂] (65 %, 179 mg). **IR** (KBr, cm⁻¹) v(CO) 1664; $\mu_{eff} = 4.67(6)$ μB (Evans Method, CD₂Cl₂, 298K); λ_{max} , nm (ε, M⁻¹cm⁻¹) (CH₃CN): 587 (764), 820 (245) sh. ¹**H NMR** (CDCl₃, 400 MHz) δ -65.65 (s), -48.87 (s), 14.20 (s), 18.214 (s), 28.21 (s), 59.39 (s); **HRMS** (+ESI) calculated for [Co₂(L^{*t*Bu})₂]¹⁻ 846.271, found 846.273; Anal. Calcd (found) for K₂[Co₂(L^{*t*Bu})₂]: C, 57.13 (56.63); H, 5.67 (5.49); N, 9.09 (9.44).



(Et₄N)₂[Co₂(L^{Ph})₂] (3). To a solution of [HN(*o*-PhNHC(O)Ph)₂] (150 mg, 0.368 mmol) in dry dimethylformamide (DMF, 10 mL) was added potassium hydride (44.3 mg, 1.10 mmol). When gas evolution ceased, CoBr₂ (81 mg, 0.368 mmol) was added as a solid and the mixture stirred for 1 h. Tetraethylammonium bromide (77.4 mg, 0.368 mmol) was then added to the deep green solution. After stirring for 3 h, DMF was removed under high vacuum and the resulting solid was dissolved in CH₃CN (15 mL), filtered through a medium porosity frit, and the filtrate was concentrated to dryness. Deep green X-ray diffraction quality crystals were obtained by slow diffusion of diethyl ether into a concentrated CH₃CN solution of (Et₄N)₂[Co₂(L^{Ph})₂] (75 %, 164 mg). **IR** (KBr, cm⁻¹) v(CO) 1655; μ_{eff} = 4.48(4) µB (Evans Method, CD₂Cl₂, 298K); λ_{max} , nm (ϵ , M⁻¹cm⁻¹) (CH₃CN): 597 (764), 936 (276); ¹H NMR (CDCl₃, 400 MHz) δ -106.72 (s), -9.521 (s), -3.736 (s), 6.87 (s), 25.93 (s), 28.78 (s), 61.89 (s); **HRMS** (+ESI) calculated for [Co₂(L^{Ph})₂]²⁻ 463.073, found 463.073; Anal. Calcd (found) for (Et₄N)₂[Co₂(L^{Ph})₂]•CH₃CN: C, 68.45 (68.62); H, 6.48 (6.18); N, 10.26 (10.36).



(Et₄N)₂[Co₂(L^{CF3})₂] (4). To a solution of HN(*o*-PhNHC(O)CF₃)₂ (140 mg, 0.358 mmol) in anhydrous dimethylformamide (DMF, 10 mL) was added potassium hydride (43 mg, 1.08 mmol). When gas evolution ceased, CoBr₂ (78 mg, 0.358 mmol) was added as a solid, and the mixture was stirred for 1 h. Tetraethylammonium bromide (75 mg, 0.358 mmol) was then added to the deep magenta-teal solution. After stirring for 3 h, DMF was removed under high vacuum and the resulting solid was dissolved in CH₃CN (15 mL), filtered through a medium porosity frit, and the filtrate was concentrated to dryness. Deep teal X-ray diffraction quality crystals were obtained by slow diffusion of diethyl ether into a concentrated CH₃CN solution of (Et₄N)₂[Co₂(L^{CF3})₂] (65%, 134 mg). IR (KBr, cm⁻¹) v(CO) 1637; μ_{eff} = 4.82(7) µB (Evans Method, CD₃CN, 298K); λ_{max} , nm (ϵ , M⁻¹cm⁻¹) (CH₃CN): 597 (360), 876 (31); ¹H NMR (CDCl₃, 400 MHz) δ) -1.372 (s), 38.753 (s), 44.278 (s), 54.962(s); ¹⁹F NMR (CD₃CN, 400 MHz) δ -57.139 (s); HRMS (-ESI) calculated for (Et₄N)[Co₂(L^{CF3})₂]⁻ 1024.1310, found1024.16936, calculated for[Co₂(L^{CF3})₂]²⁻ 446.986, found 446.99085; Anal. Calcd (found) for (Et₄N)₂[Co₂(L^{CF3})₂]: C, 49.92 (48.88); H, 4.82 (4.72); N, 9.70 (9.30).

c) Azides

General Procedure A. Procedure from the literature² was modified as follows: alkyne (1.2 equiv.) was added to a solution of 2-bromoaniline (1.0 equiv.), $PdCl_2(PPh_3)_3$ (5 mol %), and CuI (2 mol %) in THF at room temperature. N₂ was bubbled through the stirring mixture for 30 mins, after which a solution of ethanolamine in H₂O (3.0 M, 12 equiv.) was added slowly. The mixture was heated to reflux until thin layer chromatography indicated complete consumption of starting material. The reaction was cooled to room temperature and extracted with DCM. The combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash chromatography on silica gel as indicated afforded the desired product.

General Procedure B. Aniline (1.0 equiv.) and Pd/C (10 wt. %, 0.1 equiv.) in THF (0.12 M) were stirred at room temperature under a balloon of H₂. After thin layer chromatography indicated complete consumption of the starting material, the mixture was filtered through Celite and washed with Et_2O to afford crude product.

NaNO₂ (1.2 equiv.) was added to a stirring solution of crude aniline (1.0 equiv.) in a 1:1 mixture of AcOH and H₂O (0.8 M) at 0 °C. The mixture was stirred for two hours, and NaN₃ (1.4 equiv.) was added. The reaction was warmed to room temperature. After 30 minutes, H₂O and Et₂O were added. Na₂CO₃ was added slowly to neutralize the solution until pH 7 was reached. The phases were separated, and the aqueous phase was extracted with Et₂O. The combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash chromatography on silica gel as indicated afforded the azide.



2-(3-phenylprop-1-yn-1-yl)aniline. Prepared by general procedure A using PdCl₂(PPh₃)₃ (211 mg, 0.3 mmol), CuI (22 mg, 0.12 mmol), 2-bromoaniline (1.04 g, 6.0 mmol), 3-phenyl-1-propyne (0.9 mL, 7.2 mmol), and ethanolamine (4.4 mL, 72 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) afforded the title compound as an orange oil (988 mg, 79 %); $\mathbf{R_f}$ 0.28 (9:1 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3474, 3378, 3028, 1612, 1492, 1307, 906, 729; ¹H NMR (CDCl₃, 400 MHz) δ 7.43 (d, 2H, J = 8.2 Hz), 7.37-7.24 (m, 4H), 7.11 (t, 1H, J = 7.6 Hz) 6.71-6.67 (m, 2H), 4.14 (bs, 2H), 3.90 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 147.8, 136.8, 132.2, 129.1, 128.6, 127.9, 126.7, 117.8, 114.2, 108.4, 92.9, 79.2, 26.0; **HRMS** (+ESI) calculated for C₁₅H₁₄N 208.1121, found 208.1117 [M+H]⁺.



1-azido-2-(3-phenylpropyl)benzene. Prepared by general procedure B using 2-(3-phenylprop-1-yn-1-yl)aniline (947 mg, 4.6 mmol), Pd/C (450 mg, 10 wt. %), NaNO₂ (380 mg, 5.5 mmol), and NaN₃ (420 mg, 6.6 mmol). Purification by flash chromatography (hexanes → 97:3 hexanes/EtOAc) afforded the title compound as a light yellow oil (410 mg, 38 % over two steps); **R**_f 0.85 (95:5 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3025, 2990, 2858, 2116, 1581, 1488, 1450, 1282, 745; ¹**H NMR** (CDCl₃, 400 MHz) δ 7.29-7.22 (m, 3H), 7.21-7.10 (m, 5H), 7.04 (t, 1H, *J* = 7.4 Hz), 2.66-2.58 (m, 4H), 1.89 (quin, 2H, *J* = 7.8 Hz); ¹³**C NMR** (CDCl₃, 100 MHz) δ 142.2, 138.0, 133.8, 130.4, 128.5, 128.3, 127.3, 125.8, 124.7, 118.1, 35.7, 31.9, 31.0; **HRMS** (+ESI) calculated for C₁₅H₁₈N 212.1434, found 212.1431 [M-2N+3H]⁺.



2-(4-phenylbut-1-yn-1-yl)aniline. Prepared by general procedure A using PdCl₂(PPh₃)₃ (416 mg, 0.59 mmol), CuI (45 mg, 0.24 mmol), 2-bromoaniline (2.04 g, 11.9 mmol), 4-phenyl-1-butyne (2.0 mL, 14.2 mmol), and ethanolamine (8.6 mL, 142 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) afforded the title compound as an orange oil (820 mg,

31 %); **R**_f 0.28 (9:1 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3471, 3375, 3026, 2925, 1612, 1491, 1454, 1307, 905, 744; ¹**H NMR** (CDCl₃, 400 MHz) δ 7.32-7.27 (m, 4H), 7.24-7.19 (m, 2H), 7.05 (td, 1H, *J* = 7.7, 1.3 Hz) 6.63 (t, 2H, *J* = 7.5 Hz), 3.95 (bs, 2H), 2.93 (t, 2H, *J* = 7.5 Hz), 2.78 (t, 2H, *J* = 7.5 Hz); ¹³**C NMR** (CDCl₃, 100 MHz) δ 147.8, 140.6, 131.9, 128.9, 128.6, 128.4, 126.3, 117.7, 114.1, 108.5, 94.6, 77.9, 35.1, 21.7; **HRMS** (+ESI) calculated for C₁₆H₁₆N 222.1277, found 222.1273 [M+H]⁺.



1-azido-2-(4-phenylbutyl)benzene. Prepared by general procedure B using 2-(4-phenylbut-1yn-1-yl)aniline (820 mg, 3.7 mmol), Pd/C (370 mg, 10 wt. %), NaNO₂ (306 mg, 4.4 mmol), and NaN₃ (331 mg, 5.2 mmol). Purification by flash chromatography (hexanes → 97:3 hexanes/EtOAc) afforded the title compound as a light yellow oil (383 mg, 41 % over two steps); **R**_f 0.87 (95:5 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3024, 2929, 2857, 2113, 1581, 1488, 1451, 1283, 747; ¹**H NMR** (CDCl₃, 400 MHz) δ 7.29-7.10 (m, 8H), 7.03 (td, 1H, *J* = 7.0, 1.2 Hz), 2.65-2.56 (m, 4H), 1.69-1.55 (m, 4H); ¹³**C NMR** (CDCl₃, 100 MHz) δ 142.5, 137.9, 134.0, 130.4, 128.4, 128.2, 127.2, 125.6, 124.6, 118.0, 35.8, 31.2, 31.0, 29.9; **HRMS** (+ESI) calculated for C₁₆H₂₀N 226.1590, found 226.1586 [M-2N+3H]⁺.



2-(pyridin-3-ylethynyl)aniline. Prepared by general procedure A using PdCl₂(PPh₃)₃ (550 mg, 0.78 mmol), CuI (73 mg, 0.38 mmol), 2-bromoaniline (1.9 mL, 16.8 mmol), 3-ethynylpyridine (2.1 g, 20.4 mmol), and ethanolamine (12.3 mL, 204 mmol). Purification by flash chromatography (9:1 → 8:2 hexanes/EtOAc) afforded the title compound as an orange oil (1.78 g, 54 %); **R**_f 0.20 (7:3 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3456, 3324, 3192, 3030, 2211, 1615, 1493, 1407, 1314, 748; ¹**H NMR** (CDCl₃, 400 MHz) δ 8.75 (dd, 1H, J = 2.3, 0.8 Hz), 8.53 (dd, 1H, J = 4.9, 1.8 Hz), 7.78 (dt, 1H, J = 7.8, 2.0 Hz), 7.37 (dd, 1H, J = 8.0, 1.4 Hz), 7.27 (ddd, 1H, J = 8.4, 4.3, 1.0 Hz), 7.16 (ddd, 1H, J = 8.1, 7.1, 1.6 Hz), 6.74-6.70 (m, 2H), 4.31 (bs, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.03, 148.5, 147.9, 138.2, 132.2, 130.3, 123.0, 120.5, 118.0, 114.4, 107.1, 91.2, 89.3; **HRMS** (+ESI) calculated for C₁₃H₁₁N₂ 195.0917, found 195.0914 [M+H]⁺.



3-(2-azidophenethyl)pyridine. Prepared by general procedure B using 2-(pyridin-3-ylethynyl)aniline (1.5 g, 7.73 mmol), Pd/C (880 mg, 10 wt. %), NaNO₂ (640 mg, 9.28 mmol), and NaN₃ (700 mg, 10.94 mmol). Purification by flash chromatography (8:2 hexanes/EtOAc) afforded the title compound as a light yellow oil (1.32 g, 76 % over two steps); **R**_f 0.35 (7:3 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3027, 2928, 2118, 1709, 1579, 1489, 1284, 906, 712; ¹**H NMR** (CDCl₃ 400 MHz) δ 8.42 (tt, 2H, *J* = 5.1, 1.2 Hz), 7.47 (d, 1H, *J* = 7.9 Hz), 7.27-7.23

(m, 1H), 7.20 (dd, 1H, J = 7.8, 4.7 Hz), 7.13 (d, 1H, J = 7.9 Hz), 7.06-7.0 (m, 2H), 2.85 (s, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.7, 147.3, 137.9, 136.8, 136.1, 132.1, 130.5, 127.7, 124.7, 123.2, 118.1, 33.5, 32.9; HRMS (+ESI) calculated for C₁₃H₁₃N₄ 225.1135, found 225.1134 [M+H]⁺.



Phosphonium salt. Procedure from the literature³ was modified as follows: to a solution of 2nitrobenzylbromide (10.1 g, 46.9 mmol, 1 equiv.) in DMF (33 mL) was added triphenylphosphine (12.3, g, 46.9 mmol, 1 equiv.). The reaction mixture was stirred 26 h at room temperature, at which point it was diluted with toluene (1 M) and filtered. The filter was washed with DCM to dissolve the solid filtrate. The product solution was concentrated *in vacuo* and recrystallized out of DCM/Et₂O to yield pure phosphonium salt as a white solid (21.2 g, 94 %); **IR** (thin film, cm⁻¹) 3420, 3058, 2856, 2160, 1525, 1437, 1340, 1110, 722; ¹**H NMR** (CDCl₃, 400 MHz) δ 8.12 (dt, 1H, 7.5, 3.1 Hz), 7.91 (d, 1H, *J* = 8.3 Hz), 7.77 (td, 3H, *J* = 7.5, 0.9 Hz) 7.68 (dd, 6H, *J* = 12.7, 8.3 Hz), 7.63-7.59 (m, 7H), 7.46 (tt, 1H, *J* = 7.5, 2.2 Hz) 6.13 (d, 1H, *J* = 14.9 Hz); ¹³**C NMR** (CDCl₃, 100 MHz) δ 135.2, 134.3, 134.2, 130.3, 130.2, 125.7, 117.6, 117.0, 28.7; **HRMS** (+ESI) calculated for C₂₅H₂₁NO₂P 398.1310, found 398.1282 [M-Br]⁺.



3-(2-azidophenethyl)-1-(phenylsulfonyl)-1H-indole. Procedure from the literature³ was modified as follows: a solution of phosphonium salt (2.04 g, 4.3 mmol, 1.2 equiv.) in THF (0.2 M) was cooled to 0 °C, and KO'Bu (630 mg, 5.6 mmol, 1.6 equiv.) was added. The solution was stirred for 30 min at 0 °C, and 1-(phenylsulfonyl)-3-indolecarboxaldehyde (980 mg, 3.5 mmol, 1.0 equiv.) was added. The mixture was warmed to room temperature overnight and quenched with H₂O and EtOAc after 22 h. The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with brine, dried over MgSO₄, and concentrated in vacuo. The crude mixture was dissolved in EtOAc and passed through a plug of silica. The crude filtrate was concentrated in vacuo and carried on through general procedure B using Pd/C (300 mg, 10 wt. %), NaNO₂ (100 mg, 1.43 mmol), and NaN₃ (113 mg, 1.67 mmol). Purification by flash chromatography (8:2 \rightarrow 7:3 hexanes/EtOAc) afforded the title compound as an orange solid (320 mg, 44 % over three steps); \mathbf{R}_{f} 0.7 (7:3) hexanes/EtOAc); IR (thin film, cm⁻¹) 3065, 2928, 2119, 1446, 1365, 1280, 1173, 905, 725; ¹H **NMR** (CDCl₃ 400 MHz) δ 7.97 (dd, 1H, J = 8.2, 0.8 Hz), 7.81 (d, 2H, J = 8.6 Hz); 7.52 (t, 2H, J = 7.4 Hz, 7.41 (t, 2H, J = 7.4 Hz), 7.32-7.21 (m, 4H), 7.13 (d, 1H, J = 8.2), 7.05-6.97 (m, 2H), 2.91 (s, 4H); ¹³C NMR (CDCl₃ 100 MHz) δ 138.3, 138.0, 135.3, 133.6, 132.7, 131.0, 130.5, 129.2, 127.6, 126.7, 124.7, 123.1, 122.8, 122.7, 119.5, 118.1, 113.7, 31.0, 25.6; HRMS (+ESI) calculated for C₂₂H₂₁O₂N₂S 377.1318, found 377.1319 [M-2N+3H]⁺.



2-(3-phenylbut-1-yn-1-yl)aniline. Prepared by general procedure A using PdCl₂(PPh₃)₃ (211 mg, 0.3 mmol), CuI (23 mg, 0.12 mmol), 2-bromoaniline (1.04 g, 6.0 mmol), (1-methyl-2-propyn-1-yl)-benzene⁴ (940 mg, 7.2 mmol), and ethanolamine (4.4 mL, 72 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) afforded the title compound as an orange oil (498 mg, 37 %); **R**_f 0.31 (95:5 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3472, 3378, 3027, 2974, 1611, 1491, 1453, 1305, 747; ¹**H NMR** (CDCl₃, 400 MHz) δ 7.44 (d, 2H, *J* = 7.0 Hz), 7.33 (tt, 2H, *J* = 7.7, 1.76), 7.27-7.22 (m, 2H), 7.07 (td, 1H, *J* = 7.8, 1.5 Hz), 6.67-6.64 (m, 2H), 4.13 (bs, 2H), 4.03 (q, 1H, *J* = 7.0 Hz), 1.59 (d, 3H, *J* = 7.0 Hz); ¹³**C NMR** (CDCl₃, 100 MHz) δ 147.7, 143.4, 132.1, 129.1, 128.6, 126.9, 126.7, 117.8, 114.2, 108.5, 98.1, 78.9, 32.8, 24.8; **HRMS** (+ESI) calculated for C₁₆H₁₆N 222.1277, found 222.1279 [M+H]⁺.



1-azido-2-(3-phenylpropyl)benzene. Prepared by general procedure B using 2-(3-phenylbut-1yn-1-yl)aniline (438 mg, 2.0 mmol), Pd/C (200 mg, 10 wt. %), NaNO₂ (166 mg, 2.4 mmol), and NaN₃ (180 mg, 2.8 mmol). Purification by flash chromatography (hexanes → 97:3 hexanes/EtOAc) afforded the title compound as a light yellow oil (371 mg, 75 % over two steps); **R**_f 0.9 (95:5 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 2958, 2116, 1489, 1450, 1283, 905, 727; ¹**H NMR** (CDCl₃, 400 MHz) δ 7.32-7.28 (m, 2H), 7.22-7.18 (m, 4H), 7.08 (td, 2H, *J* = 8.0, 1.6 Hz), 7.01 (td, 1H, *J* = 7.4, 1.2 Hz), 2.71 (sxt, 1H, *J* = 7.1 Hz), 2.53-2.37 (m, 2H), 1.87-1.78 (m, 2H), 1.27 (d, 3H, *J* = 7.0 Hz); ¹³**C NMR** (CDCl₃, 100 MHz) δ 147.2, 137.9, 134.0, 130.3, 128.4, 127.2, 127.1, 126.0, 124.6, 118.0, 39.8, 38.6, 29.5, 22.6; **HRMS** (+ESI) calculated for C₁₅H₁₈N 212.1434, found 212.1431 [M-2N+3H]⁺.

d) Amination Reactions

General Procedure C. Inside a nitrogen-filled atmosphere dry box, a 20 mL scintillation vial was charged with a magnetic stir bar, aryl azide (1.0 equiv.), $(Et_4N)_2[Co_2(L^{iPr})_2]$ (1 mol%)¹, and a 4:1 mixture of toluene and DMF, respectively. To the reaction mixture was added freshly activated 4 Å molecular sieves. The reaction vial was sealed with a Teflon cap and the reaction mixture was heated to 110 °C for 24 h inside the dry box on a DynaBloc heating block. After 24 h, the reaction vial was removed from the heating block and allowed to stir at room temperature for 30 minutes. After reaction mixture cooled to room temperature, the molecular sieves were removed by filtration, and the solvent was removed under vacuum. Purification by flash chromatography on silica gel (7:1 hexanes/EtOAc) as indicated afforded the desired product.



2-phenylindoline (6).² Prepared by general procedure C using azide 5² (150 mg, 0.672 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (7.0 mg, 0.007 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (7:1 hexanes/EtOAc) afforded the title compound (105 mg, 80 %); ¹H NMR (400 MHz, CDCl₃) δ 7.44 - 7.28 (m, 5H), 7.12 - 7.04 (m,

2H), 6.76 (td, *J* = 1.0, 7.4 Hz, 1H), 6.69 (d, *J* = 7.3 Hz, 1H), 4.97 (t, *J* = 9.0 Hz, 1H), 4.17 (s, 1H), 3.47 (dd, *J* = 9.2, 15.7 Hz, 1H), 3.00 (dd, *J* = 8.8, 15.7 Hz, 1H).



2-(4-(trifluoromethyl)phenyl)indoline.² Prepared by general procedure C using 1-azido-2-(4-(trifluoromethyl)phenethyl)benzene² (150 mg, 0.515 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]$ (5.0 mg, 0.005 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (7:1 hexanes/EtOAc) afforded the title compound (113 mg, 83 % yield). ¹H NMR (400 MHz, CDCl₃) δ 7.63 - 7.50 (m, 4H), 7.08 (m, 2H), 6.74 (tdd, J = 7.4, 3.6, 1.1 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 5.01 (t, J = 9.3 Hz, 1H), 4.16 (s, 1H), 3.47 (dd, J = 15.6, 9.1 Hz, 1H), 2.93 (dd, J = 15.6, 9.1 Hz, 1H).



2-(4-methoxyphenyl)indoline.² Prepared by general procedure C using 1-azido-2-(4-methoxyphenethyl)benzene² (175 mg, 0.691 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (7.3 mg, 0.0069 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (7:1 hexanes/EtOAc) afforded the title compound (126 mg, 81 % yield). ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 8.4 Hz, 2H), 7.11 - 7.06 (m, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.76 - 6.73 (m, 1H), 6.67 (d, J = 8 Hz, 1H) 4.91 (t, J = 9.0 Hz, 1H), 4.11 (s, 1H), 3.81 (s, 3H), 3.41 (dd, J = 16.8, 6.4 Hz, 1H), 2.97 (dd, J = 17.6, 6.8 Hz, 1H).



2-phenyl-5-(trifluoromethyl)indoline.² Prepared by general procedure C using 1-azido-2-phenethyl-4-(trifluoromethyl)benzene² (170 mg, 0.584 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (6.1 mg, 0.0061 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (7:1 hexanes/EtOAc) afforded the title compound (110 mg, 72 % yield). ¹H NMR (400 MHz, CDCl₃) δ 7.50 - 7.59 (m, 7H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.04 (t, *J* = 9.0 Hz, 1H), 4.40 (s, 1H), 3.50 (dd, *J* = 15.6, 9.4 Hz, 1H), 3.00 (dd, *J* = 15.8, 8.4 Hz, 1H).



5-methoxy-2-phenyl-1H-indole. Prepared by general procedure C using 1-azido-4-methoxy-2-phenethylbenzene² (160 mg, 0.632 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (6.0 mg, 0.006 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Analysis of ¹H NMR before purification revealed indoline and indole were formed in a 2:1 ratio. Purification by flash chromatography (7:1 hexanes/EtOAc) resulted in recovery of 30 % 1-azido-4-methoxy-2-phenethylbenzene (48 mg), and exclusive formation of the oxidized indole⁵ product (85 mg, 60 % yield). ¹H NMR (400 MHz, CDCl₃) δ 8.22 (bs, 1H), 7.63 (dd, *J* = 10 Hz, 2H) 7.47 - 7.37

(m, 2H), 7.08 (d, J = 2.5 Hz, 1H), 6.85 (td, J = 8.8, 2.4 Hz, 1H), 6.75 (dt, J = 2.3, 1.2 Hz, 1H), 3.86 (s, 3H).



2-phenyl-1,2,3,4-tetrahydroquinoline. Prepared by general procedure C using 1-azido-2-(4-phenylbutyl)benzene (150 mg, 0.632 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (6.6 mg, 0.0063 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (7:1 hexanes/EtOAc) afforded the title compound (93 mg, 70 % yield).⁶ ¹H NMR (400 MHz, CDCl₃) δ 7.26-7.39 (m, 5H), 6.97-6.99 (m, 2H), 6.64 (td, J = 7.6, 0.8 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 4.41 (dd, J = 9.2, 3.2 Hz, 1H), 2.88-2.90 (m, 1H), 2.74 (dt, J = 16.4, 4.8 Hz, 1H), 2.08-2.10 (m, 1H), 1.96-2.02 (m, 1H).



2-phenyl-2,3,4,5-tetrahydro-1H-benzo[b]azepine. General procedure C was modified as follows: a mixture of 1-azido-2-(4-phenylbutyl)benzene (75 mg, 0.299 mmol) and 5 mol % $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (16 mg, 0.0076 mmol) was stirred in a 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (9:1 hexanes/EtOAc) afforded the title compound as a light orange oil (20 mg, 30 % yield). R_f (9:1 hexanes/EtOAc) 0.3; IR (thin film, cm⁻¹) 3840, 3648, 2924, 2702, 2356, 2157, 1935, 903, 721; ¹H NMR (CDCl₃ 400 MHz) δ 7.29-7.17 (m, 5H), 7.07-7.05 (m, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 3.89-3.84 (m, 2H), 3.14 (dd, *J* = 15.5, 8.5 Hz), 1H), 2.75-2.68 (m, 3H), 1.96-1.92 (m, 2H); ¹³C NMR (CDCl₃ 100 MHz) δ 141.7, 128.4, 128.3, 127.2, 125.9, 124.6, 118.5, 109.1, 59.5, 38.4, 36.1, 32.9, 14.2. HRMS (+ESI) calculated for C₁₆H₁₈N 224.14338, found 224.14303 [M+H]⁺.



2-(pyridin-3-yl)indoline. Prepared by general procedure C using 3-(2-azidophenethyl)pyridine (150 mg, 0.669 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (7.0 mg, 0.007 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (7:3 EtOAc/hexanes) afforded the title compound as a light yellow oil (105 mg, 80 % yield). **R**_f (7:3 EtOAc/hexanes) 0.25; **IR** (thin film, cm⁻¹) 3677, 2851, 2370, 2277, 2037, 1483, 1249, 901, 753; ¹**H NMR** (CDCl₃, 400 MHz) δ 8.63 (bs, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.27-7.24 (m, 1H), 7.07 (dd, *J* = 15.4, 13.6, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 4.97 (t, *J* = 9.2 Hz, 1H), 4.14 (bs, 1H), 3.46 (dd, *J* = 15.4, 9.2 Hz, 1H), 2.95 (dd, *J* = 15.8, 9.2 Hz, 1H); ¹³C **NMR** (CDCl₃, 100 MHz) δ 150.4, 148.0, 147.3, 134.9, 127.8, 127.4, 124.6, 123.9, 119.4, 109.2, 60.9, 39.5, 29.7; **HRMS** (+ESI) calculated for C₁₃H₁₃N₂ 197.1073, found 197.1074 [M+H]⁺.



3-(indolin-2-yl)-1-(phenylsulfonyl)-1H-indole. Prepared by general procedure C using 3-(2-azidophenethyl)-1-(phenylsulfonyl)-1H-indole (150 mg, 0.373 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (4.0 mg, 0.004 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (7:1 hexanes/EtOAc) afforded the title compound as a yellow oil (120 mg, 85 % yield). **R**_f 0.18 (7:1 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3369, 3030, 1608, 1484, 1246, 1033, 747; ¹**H NMR** (CDCl₃, 400 MHz) δ 8.01 (d, *J* = 8.4, 1.1 Hz, 1H), 7.91 - 7.84 (m, 2H), 7.57 (s, 1H), 7.55 - 7.48 (m, 2H), 7.47 - 7.38 (m, 2H), 7.36 - 7.27 (m, 1H), 7.26 - 7.17 (m, 1H), 7.16 - 7.03 (m, 2H), 6.76 (td, *J* = 7.4, 1.1 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 5.16 (tdd, *J* = 9.2, 3.3, 0.9 Hz, 1H), 4.12 (s, 1H), 3.48 (dd, *J* = 15.6, 9.3 Hz, 1H), 3.14-3.03 (m, 1H); ¹³C **NMR** (CDCl₃, 100 MHz) δ 150.5, 138.1, 135.8, 133.8, 129.3, 129.0, 128.1, 127.7, 126.8, 125.8, 124.9, 124.7, 123.2, 122.7, 120.2, 119.1, 113.9, 109.3, 56.0, 37.3; **HRMS** (+ESI) calculated for C₂₂H₁₉N₂O₂S 375.1167, found 375.1162 [M+H]⁺.



2-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline. Prepared by general procedure C using 1-azido-2-(3-phenylbutyl)benzene (150 mg, 0.597 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (6.3 mg, 0.006 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (9:1 hexanes/EtOAc) afforded the title compound as a yellow oil (120 mg, 85 % yield). **R**_f 0.8 (9:1 hexanes/EtOAc); **IR** (thin film, cm⁻¹) 3402, 3052, 3023, 2924, 2843, 2358, 2345; ¹H **NMR** (CDCl₃ 400 MHz) δ 7.38 (dd, J = 8.8, 1.2 Hz, 2H), 7.28 (t, J = 7.9 Hz, 2H), 7.19 (td, J = 7.6, 1.2 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.9 (d, J = 7.6 Hz, 1H), 6.61-6.58 (m, 2H), 4.11 (bs, 1H), 2.59 (dt, J = 16.4, 4.7 Hz, 1H), 2.31 (ddd, J = 16.2, 11.3, 5.3 Hz, 1H), 2.20 (dt, J = 12.9, 5.0 Hz, 1H) 1.9 (ddd, J = 12.9, 11.1, 4.7 Hz, 1H), 1.57 (s, 3H); ¹³C **NMR** (CDCl₃ 100 MHz) δ 148.2, 143.8, 129.2, 128.3, 126.9, 126.3, 125.4, 120.4, 116.6, 113.4, 55.5, 35.4, 30.6, 24.3; **HRMS** (+ESI) calculated for C₁₆H₁₈N 224.1434, found 224.1436 [M+H]⁺.



2-phenylindoline (6). General procedure C was modified as follows: to a mixture of azide 5^2 (170 mg, 0.761 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (8.0 mg, 0.0076 mmol) was added 0.06 mL of pyridine (0.761 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Purification by flash chromatography (7:1 hexanes/EtOAc) afforded the title compound (133 mg, 78 % yield).²

e) Control reactions. Several control reactions were conducted to ensure the cobalt catalysts were required for amination. Heating azide 5 at 110 °C for 48 hours in the presence of molecular sieves in a toluene:DMF (4:1) mixture did not lead to the formation of indoline 6; starting material was isolated in greater than 95% yield. Heating azide 5 at 110 °C for 48 hours in the presence of molecular sieves and $CoBr_2$ in a toluene:DMF (4:1) mixture did not lead to the formation of indoline 6; starting material was isolated in greater than 95% yield. Similarly, azide 5 does not react under similar conditions in the presence of free ligand.



f) Cyclized Ligand Byproduct: *N*-(2-(2-isopropyl-1H-benzo[d]imidazol-1-yl)phenyl)isobutyramide This cyclized ligand byproduct of catalyst 1 is observed when the amination reactions are run in wet organic solvents and/or in the absence of activated molecular sieves. Under these conditions, we see diminished indoline yields and observe and isolate this cyclized ligand product. This cyclized ligand species was isolated by column chromatography. ¹H NMR (CDCl₃, 400 MHz) δ 8.51 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.56 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.22, (t, *J* = 7.6 Hz, 1H), 6.95 (8, *J* = 7.6 Hz, 1H), 6.53 (bs, 1H), 2.93 (septet, *J* = 6.8 Hz 1H), 2.12 (septet, *J* = 6.8 Hz, 1H), 1.37 (d, *J* = 7.2, 3H), 1.27 (d, *J* = 7.2, 3H), 0.88 (d, *J* = 6.8, 3H), 0.87 (d, *J* = 6.8, 3H); HRMS (+ESI) calculated for C₂₀H₂₄N₃O 322.1919, found 322.1903 [M+H]⁺.



Figure S1. Thermal ellipsoid diagram of *N*-(2-(2-isopropyl-1H-benzo[d]imidazol-1-yl)phenyl)isobutyramide drawn at 50% probability. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å): O1–C17 1.220(3), N2–C13 1.320(3), N2–C8 1.396(3), N3–C6 1.415(3), N3–C17 1.360(3), N1–C1 1.430(3), N1–C7 1.386(3), N1–C13 1.383(3).

Table S1. X-ray crystallographic data for *N*-(2-(2-isopropyl-1H-benzo[d]imidazol-1-yl)phenyl)isobutyramide

Formula	$C_{40}H_{46}N_6O_2$	
Form. Wt. (g/mol)	642.83	
T (K)	173(2)	
Crystal system	monoclinic	
Space group	$P2_1/c$	
a (Å)	8.8762(18)	
<i>b</i> (Å)	13.892(3)	
<i>c</i> (Å)	14.471(3)	
α (°)	90	
β (°)	100.77(3)	
γ (°)	90	
V (Å ³)	1753.0(6)	
Z	2	
ρ, calcd (mg/mm ³)	1.218	
m/mm ⁻¹	0.077	
Crystal size (mm ³)	$0.188 \times 0.137 \times 0.064$	
Theta range	4.1 to 58.5°	
Refins. Collected	32111	
Unique reflns.	4760	
Data/rest./par.	4760/0/221	
GOF	0.970	
Final R indexes [I>2σ (I)]	$R_1 = 0.0606, wR_2 = 0.1179$	
All data	$R_1 = 0.1580, wR_2 = 0.1546$	

III. Kinetic Isotope Effect Experiment



Prepared by general procedure C azide 7^7 (150 mg, 0.666 mmol) and $(Et_4N)_2[Co_2(L^{iPr})_2]^1$ (7.0 mg, 0.0067 mmol) in 5.0 mL of a 4:1 mixture of toluene and DMF, respectively. Following filtration through Celite and removal of solvent *in vacuo*, ¹H NMR indicated formation of **8-D** and **8-H**. The mixture of indolines **8-D** and **8-H** were purified by flash chromatography. The kinetic isotope effect (KIE) was determined from the ratio of **8-D** and **8-H**, which were found identical in both the crude reaction mixture and purified product mixture.



Figure S-2. ¹H NMR spectra for **A**) deuterated azide **7**, **B**) indoline product **6**, **C**) aniline precursor to azide **7**,⁷ and **D**) reaction mixture of indoline products **8-D** and **8-H**.

Calculations used for the determination of KIE value from ¹H NMR analysis found in Figure S-2:

Before Reaction (H_b initial): 0.82 H_b

After Reaction (H_b final): 0.12 H_b

H_b consumed : (H_b initial) - (H_b final) = (0.82 - 0.12) = 0.70% of H_b consumed = $(0.70/0.82) \ge 100\% = 85\%$

Before Reaction (D_b initial): 2.0 - (H_b initial) = 2.0 - 0.82 = 1.18 D_b After Reaction (D_b final): 1 - (H_b initial) = 1.0 - 0.12 = 0.88

 D_b consumed : (D_b initial) - (D_b final) = (1.18 - 0.88) = 0.30 % of D_b consumed = (0.30 / 1.18) x 100% = 25%

$$KIE = K_H / K_D = 0.85 / 0.25 = 3.4$$

IV. ¹H and ¹³C NMR Spectra





2,2'-Bis(diphenylacetamido)diphenylamine



S20

2,2'-Bis(trifluoroacetamido)diphenylamine





1-azido-2-(3-phenylpropyl)benzene





1-azido-2-(4-phenylbutyl)benzene





3-(2-azidophenethyl)pyridine







3-(2-azidophenethyl)-1-(phenylsulfonyl)-1H-indole



S30

1-azido-2-(3-phenylpropyl)benzene





2-phenyl-2,3,4,5-tetrahydro-1H-benzo[b]azepine



3-(indolin-2-yl)-1-(phenylsulfonyl)-1H-indole



2-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline



V. X-ray Crystallographic Data for Cobalt Complexes



Figure S-3. Thermal ellipsoid diagram of **2** drawn at 40% probability. Hydrogen atoms and potassium counter cations have been removed for clarity. Selected bond distances (Å): Co1…Co1A 2.6586(7), Co1–N1 2.1123(16), Co–N1A 2.1123(16), Co–N2D 1.9639(14), Co1–N2 1.9639(14) and angles (°): N1–Co1–N1A 102.00(7), N1–Co–N2D 86.15(4), N1–Co1–N2 115.35(4), N2D–Co–N2 146.66(8).



Figure S-4. Thermal ellipsoid diagram of **3** drawn at 40% probability. Hydrogen atoms and tetraethylammonium counter cations have been removed for clarity. Selected bond distances (Å): Selected bond distances (Å): Co1-···Co1A 2.666(4), Co1-·N1 2.0407(10), Co-·N1A 2.048(10), Co-N2D 1.963(9), Co1-N2 1.963(9) and angles (°): N1-Co1-N1A 97.0(6), N1-Co-N2D 120.8(3), N1-Co1-N2 85.5(4), N2D-Co-N2 141.8(6).



Figure S-5. Thermal ellipsoid diagram of **4** drawn at 40% probability. Hydrogen atoms and tetraethylammonium counter cations have been removed for clarity. Selected bond distances (Å): Co1…Co1A 2.631(6), Co1–N1 2.043(3), Co–N1A 2.038(3), Co–N2D 1.982(3), Co1–N2 1.986(3) and angles (°): N1–Co1–N1A 100.12(11), N1–Co–N2D 118.08(11), N1–Co1–N2 86.82(11), N2D–Co–N2 141.55(2).

	2	3	4
Formula	$C_{44}H_{52}N_6O_4K_2Co_2$	$C_{70}H_{79}N_9O_4Co_2$	$C_{52}H_{66}Co_2F_{12}N_8O_5$
Form. Wt. (g/mol)	924.98	1228.28	1228.99
T (K)	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Trigonal	Monoclinic
Space group	Fddd	P3221	P21/n
a (Å)	10.8136(3)	14.064(2)	10.072(2)
b (Å)	27.5330(7)	14.064(2)	38.683(8)
c (Å)	29.5266(8)	27.143(5)	14.706(3)
α (°)	90	90	90
β (°)	90	90	98.28(3)
γ (°)	90	120	90
V (Å ³)	8791.0(4)	4649(2)	5670.2(19)
Z	8	3	4
ρ, calcd (g/cm ³)	1.398	1.316	1.4396
m/mm -1	7.994	0.59	0.677
Crystal size (mm ³)	$0.27\times0.13\times0.12$	$0.29 \times 0.15 \times 0.14$	$0.37 \times 0.13 \times 0.12$
Theta range	8.78 to 135.82	3.34 to 54.26°	3.5 to 57.4°
Reflns. Collected	15480	20628	101428
Unique reflns.	1971	4466	14606
Data/rest./par.	1971/0/133	4466 /444/487	14606/0/722
GOF	1.028	1.052	1.02
Final R indexes [I>2σ (I)]	R1 = 0.0288	R1 = 0.0814	R1 = 0.0609
All data	wR2 = 0.0811	wR2 = 0.1305	wR2 = 0.1705

Table S-2. Structural refinement data for dinuclear cobalt(II) complexes $K_2[Co_2(L^{tBu})_2]$ (2), $(Et_4N)_2[Co_2(L^{Ph})_2]$ (3) and $(Et_4N)_2[Co_2(L^{CF3})_2]$ (4).

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