

# Catalytic C–H Amination Mediated by Dipyrrin Cobalt Imidos

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## General Considerations.

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. Ligand and ligand precursors were synthesized as previously reported.<sup>1</sup> All glassware was oven dried for a minimum of 1 hour and cooled in an evacuated antechamber prior to use in the drybox. Benzene, *n*-hexane, toluene, and dichloromethane were dried over 4 Å molecular sieves (Strem) prior to use. Chloroform-*d* and deuterium oxide (D<sub>2</sub>O) were purchased from Cambridge Isotope Labs and used as received. Benzene-*d*<sub>6</sub> and pyridine-*d*<sub>5</sub> were purchased from Cambridge Isotope Labs and were degassed and stored over 4 Å molecular sieves prior to use. Methylmagnesium bromide solution (3.0 M in diethyl ether), isopropylmagnesium chloride lithium chloride complex solution (1.3 M in THF), azidotrimethylsilane, palladium on carbon (10 wt%), benzaldehyde, trimethylamine, thionyl chloride, sodium borodeuteride, chlorodiphenylphosphine, 4-iodobenzotrifluoride, methyl-3-butenolate, tri(*o*-tolyl)phosphine, 4-phenylbutanoic acid, 4-(*p*-tolyl)butanoic acid, 4-(4-methoxyphenyl)butanoic acid, and 2-methylhexan-2-ol were purchased from Aldrich and used as received. 2,5-dimethylhexan-2-ol and 3-methyl-3-trimethylsiloxy-1-butyne were purchased from Alfa Aesar and used as received. Boron trifluoride diethyl etherate, palladium(II) acetate, and cobalt(III) acetylacetonate were purchased from Strem and used as received. Methoxybenzoquinone (MBQ) was purchased from TCI-America and used as received. Pyridine, 4-*tert*-butylpyridine and 4-trifluoromethylpyridine were purchased from Aldrich, degassed and stored over 4 Å molecular sieves prior to use. 4-Dimethylaminopyridine was purchased from Aldrich and recrystallized from toluene prior to use. Anhydrous cobalt(II) bromide was purchased from Aldrich and used as received. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received.

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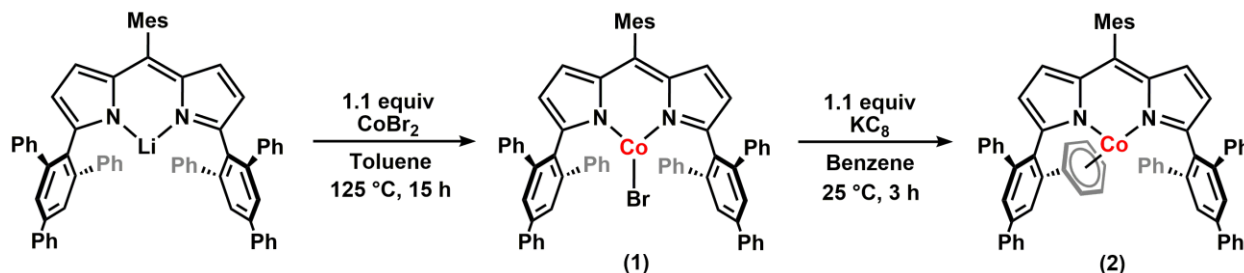
<sup>1</sup> King, E.R.; Hennessy, E.T.; Betley, T.A. *J. Am. Chem. Soc.* **2011**, *136*, 10940

### **Characterization and Physical Measurements.**

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian Unity/Inova 500 MHz- or Agilent DD2 600 MHz spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported relative to  $\text{SiMe}_4$  using the chemical shift of residual solvent peaks as reference. Gas chromatography/mass spectrometry (GC/MS) was performed on an Agilent GC/MS 5975 Turbo system. High-resolution mass spectrometry was performed on a Bruker microTOFII ESI LCMS. Elemental analyses (%CHN) were obtained on a PerkinElmer 2400 Series II CHNS/O Analyzer.

## Metal Complexes Syntheses.

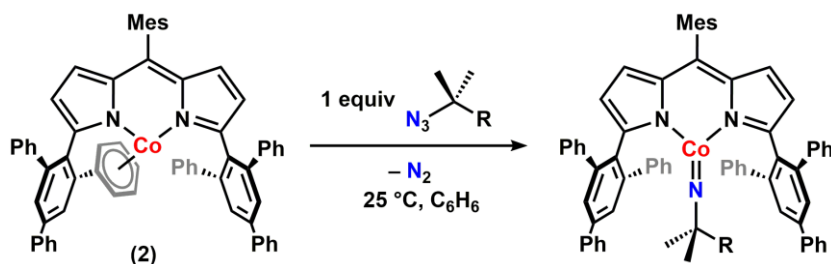
### A. Synthesis of cobalt synthons.



**( $^{\text{Ar}}\text{L}$ )CoBr, (1):** In an oven-dried 50 mL pressure vessel, ( $^{\text{Ar}}\text{L}$ )Li (0.5 g, 0.57 mmol) and  $\text{CoBr}_2$  (0.137 g, 0.627 mmol, 1.10 equiv) were dissolved in 20 mL toluene and stirred for 15 hours at  $125^\circ\text{C}$ . The dark maroon mixture was filtered through a coarse glass frit with Celite to remove lithium chloride and excess cobalt. The Celite was washed with an additional 20 mL benzene. The collected filtrate was frozen and benzene was removed by sublimation *in vacuo* to afford **1** as a maroon powder (0.52 g, 90%). Crystals suitable for X-ray diffraction were grown from a 2:1 *n*-hexane/benzene mixture at  $-35^\circ\text{C}$ .  $^1\text{H}$  NMR (600 MHz, 295 K,  $\text{C}_6\text{D}_6$ ):  $\delta$ /ppm 94.31, 91.62, 26.23, 24.02, 18.59, 13.83, 13.27, 12.64, 12.41, 2.12,  $-27.85$ ,  $-36.76$ ,  $-41.50$ . Anal. Calc. for  $\text{C}_{66}\text{H}_{49}\text{ClCoN}_2$ : C 82.19, H 5.12, N 2.90; Found: C 81.89, H 5.29, N 2.95.

**( $^{\text{Ar}}\text{L}$ )Co, (2):** In a 20 mL vial, **1** (0.5 g, 0.496 mmol) was dissolved in 10 mL of benzene and added to a frozen benzene solution of potassium graphite ( $\text{KC}_8$ , 0.074 g, 0.545 mmol, 1.1 equiv). The reaction mixture was slowly warmed up to room temperature and stirred for 3 hours at room temperature. The dark purple mixture was filtered through a coarse glass frit with Celite. The Celite was washed with an additional 20 mL benzene. The collected filtrate was frozen and benzene removed by sublimation *in vacuo* to afford **2** as a dark purple powder. (0.4 g, 87%). Crystals suitable for X-ray diffraction were grown from a 2:1 *n*-hexane/benzene mixture at  $-35^\circ\text{C}$ .  $^1\text{H}$  NMR (600 MHz, 295 K,  $\text{C}_6\text{D}_6$ ):  $\delta$ /ppm 45.11, 14.12, 13.68, 12.41, 8.16, 7.58, 5.13, 1.35,  $-1.55$ ,  $-16.71$ . Anal. Calc. for  $\text{C}_{66}\text{H}_{49}\text{CoN}_2$ : C 85.33, H 5.32, N 3.02; Found: C 84.96, H 5.50, N 3.07.

## B. Synthesis of cobalt imido species.



**General procedure:** A solution of azide (1.0 equiv) in benzene was added to a stirring solution of (<sup>Ar</sup>L)Co (**2**) (50 mg, 1.0 equiv) in benzene to observe an immediate color change from dark purple to grayish purple. After stirring for 10 minutes at room temperature, the reaction mixture was concentrated *in vacuo* to afford the corresponding cobalt imido complex.

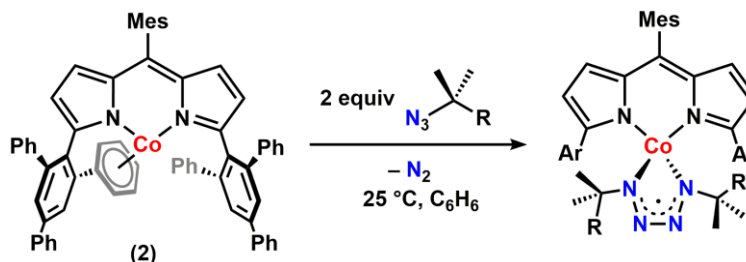
(<sup>Ar</sup>L)Co(NR'), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> (**3**): 52 mg, 92%. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ/ppm 24.82 (s), 20.97 (s), 11.21 (s), 11.14 (s), 11.00 (s), 10.37 (s), 8.01 (s), 7.82 (s), 7.67 (m), 5.20 (s), 4.88 (s), 3.95 (s), 3.37 (s), 0.89 (s), -9.32 (s). Anal. Calc. for C<sub>73</sub>H<sub>64</sub>CoN<sub>3</sub>: C 84.12, H 6.19, N 4.03; Found: C 84.20, H 6.09, N 4.36. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at -35 °C.

(<sup>Ar</sup>L)Co(NR'), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> (**4**): 51 mg, 90%. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ/ppm 25.26 (s), 20.92 (s), 11.34 (s), 11.14 (s), 10.62 (s), 8.02 (s), 8.01 (s), 7.84 (t), 7.68 (m), 5.12 (s), 4.96 (s), 3.87 (s), 3.27 (t), 2.56 (d), 1.02 (s), -9.91 (s). Anal. Calc. for C<sub>74</sub>H<sub>66</sub>CoN<sub>3</sub>: C 84.14, H 6.30, N 3.98; Found: C 84.03, H 6.35, N 4.30. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at -35 °C.

(<sup>Ar</sup>L)Co(NAd) (**10**): 50 mg, 87%. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ/ppm 19.88 (s), 15.01 (s), 11.97 (s), 11.84 (s), 11.54 (s), 11.29 (d), 8.75 (d), 8.11 (d), 7.93 (t), 7.78 (t), 5.26 (s), 4.91 (s), 3.71 (s), 2.85 (t), 0.34 (s), -11.64 (s). Anal. Calc. for C<sub>76</sub>H<sub>64</sub>CoN<sub>3</sub>: C 84.65, H 5.98, N 3.90; Found: C 84.95, H 5.99, N 3.76. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:toluene solution at -35 °C.



### C. Synthesis of cobalt tetrazenes species.



**General procedure:** A solution of azide (2.0 equiv) in benzene was added to a stirring solution of (<sup>Ar</sup>L)Co (**2**) (50 mg, 1.0 equiv) in benzene to observe an immediate color change from dark purple to reddish purple. After stirring for 6 hours at room temperature, the reaction mixture was concentrated *in vacuo* to afford the corresponding cobalt tetrazenes complex.

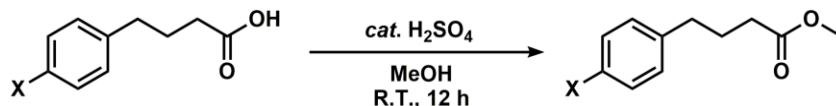
(<sup>Ar</sup>L)Co( $\kappa^2$ -N<sub>4</sub>R'<sub>2</sub>), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> (**5**): 56 mg, 88%. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ /ppm 31.13 (br. s), 24.61 (s), 20.78 (s), 16.30 (s), 13.05 (s), 12.02 (s), 10.30 (s), 7.74 (s), 5.37 (s), 2.26 (s), 0.35 (s), 0.33 (s), -3.45 (s), -5.55 (br. s), -6.17 (br. s), -6.89 (br. s), -7.13 (br. s), -9.16 (s), -10.60 (br. s), -34.98 (br. s), -42.87 (br. s). Anal. Calc. for C<sub>80</sub>H<sub>79</sub>CoN<sub>6</sub>: C 81.19, H 6.73, N 7.10; Found: C 80.89, H 6.57, N 6.98. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.

(<sup>Ar</sup>L)Co( $\kappa^2$ -N<sub>4</sub>R'<sub>2</sub>), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> (**6**): 61 mg, 93%. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ /ppm 30.57 (br. s), 20.98 (br. s), 16.14 (s), 11.94 (s), 9.43 (br. s), 5.71 (s), 5.52 (s), 3.89 (s), 0.09 (s), -3.95 (br. s), -4.45 (br. s), -6.18 (br. s), -7.54 (br. s), -9.83 (br. s), -14.00 (br. s), -65.09 (br. s). Anal. Calc. for C<sub>82</sub>H<sub>83</sub>CoN<sub>6</sub>: C 81.29, H 6.91, N 6.94; Found: C 81.05, H 6.54, N 6.58. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.

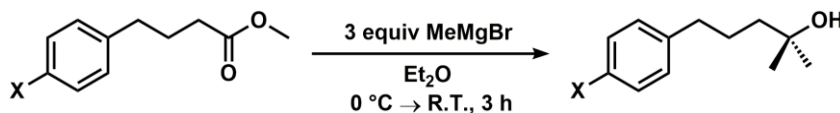
(<sup>Ar</sup>L)Co( $\kappa^2$ -N<sub>4</sub>Ad<sub>2</sub>) (**11**): 61 mg, 91%. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ /ppm 30.57 (br. s), 20.98 (br. s), 16.14 (s), 11.94 (s), 9.43 (br. s), 5.71 (s), 5.52 (s), 3.89 (s), 0.09 (s), -3.95 (br. s), -4.45 (br. s), -6.18 (br. s), -7.54 (br. s), -9.83 (br. s), -14.00 (br. s), -65.09 (br. s). Anal. Calc. for C<sub>86</sub>H<sub>79</sub>CoN<sub>6</sub>: C 82.27, H 6.34, N 6.69; Found: C 82.19, H 6.40, N 7.06. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.

## Organoazide Syntheses.

### General procedures for preparation of organoazides.



**Procedure A:** Catalytic amount of concentrated  $\text{H}_2\text{SO}_4$  was added to a solution of the corresponding 4-phenylbutanoic acid (1 equiv) in 50 mL methanol. The reaction mixture was stirred at 25 °C for 12 hours. Upon completion, the reaction mixture was concentrated and diluted in  $\text{Et}_2\text{O}$ . The aqueous phase was extracted three times with  $\text{Et}_2\text{O}$  and the combined organic phases were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated. The product was used without further purification.

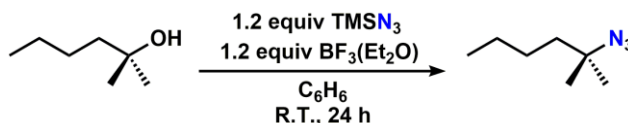


**Procedure B:** An oven-dried Schlenk flask was charged with 3 g of the corresponding methyl 4-phenylbutanoate in dry  $\text{Et}_2\text{O}$  and placed under  $\text{N}_2$ . The solution was cooled in an ice-bath and a diethyl ether solution of methylmagnesium bromide (3.0 M in diethyl ether) was added slowly at 0 °C. The reaction mixture was stirred at room temperature for 3 hours before it was quenched with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and diluted with water. The aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated. The product was used without further purification.



**Procedure C:** (adapted from literature procedure)<sup>2</sup>: An oven-dried Schlenk flask was charged with a tertiary alcohol (15 mmol, 1 equiv) and azidotrimethylsilane (1.2 equiv) in benzene (0.5 M) under N<sub>2</sub>. Boron trifluoride diethyl etherate (1.2 equiv) was added dropwise at 25 °C to the stirring solution. After 24 hours, the mixture was poured into water and extracted three times with Et<sub>2</sub>O. The combined organic phases were washed with brine and dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude products were purified via silica gel chromatography (100% hexanes as an eluent) and stored over molecular sieves for further use.

**A. 2-Methyl-2-azidohexane:** Synthesized following Procedure C. 67%



**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ/ppm 1.47–1.50 (m, 2 H), 1.31–1.34 (m, 4 H), 1.25 (s, 6 H), 0.90 (d, 6 H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (125 MHz, CDCl<sub>3</sub>): δ/ppm 61.9, 41.3, 26.6, 26.1, 23.2, 14.2. **HRMS** (ESI<sup>+</sup>) *m/z* Calc. 159.1604 [C<sub>7</sub>H<sub>15</sub>N<sub>3</sub>+NH<sub>4</sub>]<sup>+</sup>, Found 159.1604 [M+NH<sub>4</sub>]<sup>+</sup>.

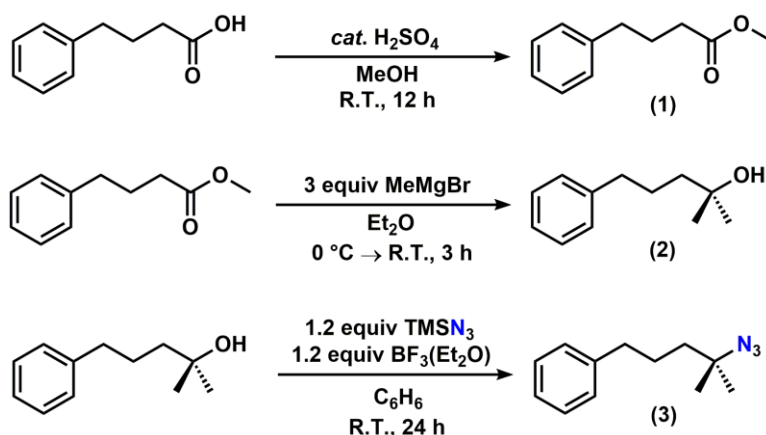
**B. 2,4-Dimethyl-2-azidohexane:** Synthesized following Procedure C. 73%



**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ/ppm 1.46–1.50 (m, 4 H), 1.25 (s, 6 H), 1.20–1.23 (m, 1 H), 0.81 (d, *J* = 6.6 Hz, 6 H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (125 MHz, CDCl<sub>3</sub>): δ/ppm 61.9, 39.3, 33.3, 28.5, 26.2, 22.7. **HRMS** (ESI<sup>+</sup>) *m/z* Calc. 173.1761 [C<sub>8</sub>H<sub>17</sub>N<sub>3</sub>+ NH<sub>4</sub>]<sup>+</sup>, Found 173.1760 [M+NH<sub>4</sub>]<sup>+</sup>.

<sup>2</sup> Hennessy, E.T.; Betley, T.A. *Science*. **2013**, 340, 591

### C. Synthesis of (4-azido-4-methylpentyl)benzene.



(1) **Methyl 4-phenylbutanoate:** Synthesized following Procedure A. Spectral data were consistent with previously reported characterization of the product.<sup>3</sup>

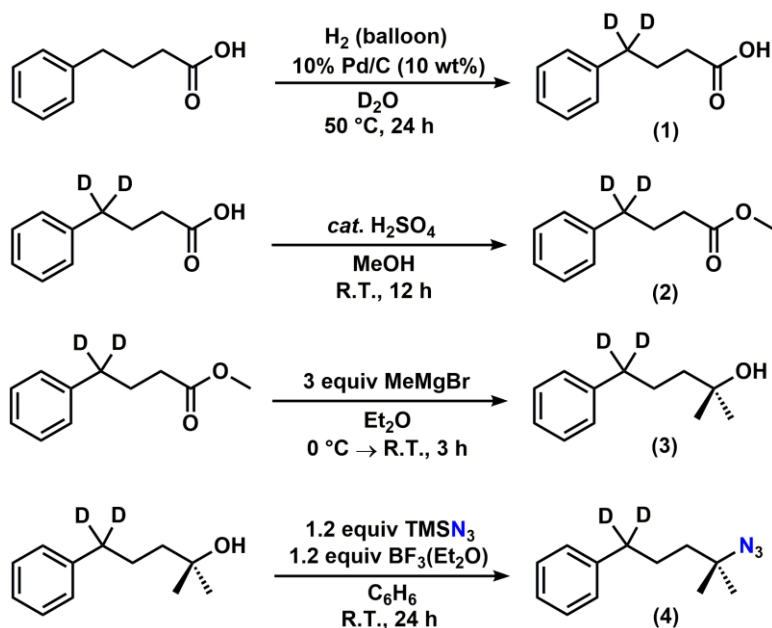
(2) **2-Methyl-5-phenylpentan-2-ol:** Synthesized following Procedure B. Spectral data were consistent with previously reported characterization of the product.<sup>4</sup>

(3) **(4-azido-4-methylpentyl)benzene:** Synthesized following Procedure C. 76% <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ/ppm 7.28–7.31 (m, 2 H), 7.18–7.21 (m, 3 H), 2.63 (t, 2 H), 1.67–1.73 (m, 2 H), 1.51–1.55 (m, 2 H), 1.25 (s, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ/ppm 142.2, 128.5, 126.0, 61.7, 41.2, 36.2, 26.3, 26.1. HRMS (ESI<sup>+</sup>) *m/z* Calc. 221.1761 [C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>+NH<sub>4</sub>]<sup>+</sup>, Found. 221.1763 [M+NH<sub>4</sub>]<sup>+</sup>.

<sup>3</sup> Faisal, S.; Zang, Q.; Maity, P. K.; Brandhofer, A.; Kearney, P. C.; Reiser, O.; Grass, R. N.; Stoianova, D.; Hanson, P. R. *Org. Lett.* **2017**, *19*, 2274

<sup>4</sup> Cui, L.-Q.; Liu, K.; Zhang, C. *Org. Biomol. Chem.* **2011**, *9*, 2258

#### D. Synthesis of (4-azido-4-methylpentyl-1,1-*d*<sub>2</sub>)benzene.



**(1) 4-phenylbutanoic-4,4-*d*<sub>2</sub> acid:** The procedure was modified from a previously reported preparation.<sup>5</sup> A 50 mL Schlenk flask was charged with 4-phenylbutanoic acid (3 g, 1.0 equiv) and 10 % Pd/C (0.3 g, 10 wt%) with 12 mL D<sub>2</sub>O. The reaction flask was fitted with a balloon full of H<sub>2</sub> and purged with H<sub>2</sub> three times. The resulted black suspension was heated at 50 °C for 24 hours. After 24 hours, the reaction mixture was filtered through Celite to remove Pd/C and washed with diethyl ether. The aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The product was used without further purification. The deuterium content (93%) was determined by <sup>1</sup>H NMR integration of methyl groups to the benzylic hydrogens. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>) δ/ppm: 12.1 (br, s, 1 H), 7.13 (t, 2 H), 7.06 (t, 1 H), 6.97 (d, 2 H), 2.01 (t, 2 H), 1.70 (t, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ/ppm: 179.9, 141.2, 128.6, 128.5, 126.2, 34.4 (quint, *J*<sub>C-D</sub> = 18.1 Hz), 33.3, 26.2. HRMS (ESI<sup>+</sup>) *m/z* Calc. 167.1036 [C<sub>10</sub>H<sub>10</sub>D<sub>2</sub>O<sub>2</sub>+H]<sup>+</sup>, Found. 167.1011 [M+H]<sup>+</sup>.

**(2) methyl-4-phenylbutanoate-4,4-*d*<sub>2</sub>:** Synthesized following Procedure A. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ/ppm: 7.27–7.30 (m, 2 H), 7.17–7.21 (m, 3 H), 3.67 (s, 3 H), 2.33 (m, 2 H), 1.95 (m, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ/ppm: 174.0, 141.4, 128.6, 128.5, 126.1, 51.6, 34.5 (quint,

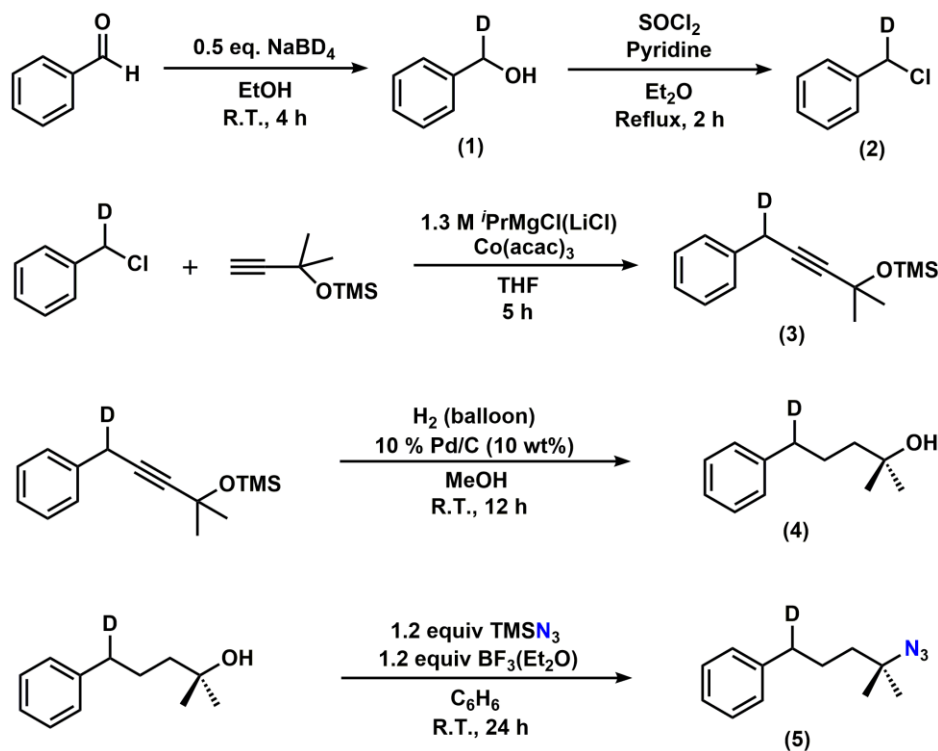
<sup>5</sup> Kurita, T.; Hattori, K.; Seki, S.; Mizumoto, T.; Aoki, F.; Yamada, Y.; Ikawa, K.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2008**, *14*, 664

$J_{C-D} = 19.3$  Hz), 33.4, 26.4. **HRMS** (ESI<sup>+</sup>)  $m/z$  Calc. 181.1192 [C<sub>11</sub>H<sub>12</sub>D<sub>2</sub>O<sub>2</sub>+H]<sup>+</sup>, Found. 182.1190 [M+H]<sup>+</sup>.

**(3) 2-methyl-5-phenylpentan-5,5-*d*<sub>2</sub>-2-ol**: Synthesized following Procedure B. **<sup>1</sup>H NMR** (600 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ /ppm: 7.18–7.20 (m, 2 H), 7.08–7.10 (m, 3 H), 1.55–1.58 (m, 2 H), 1.26–1.29 (m, 2 H), 0.98 (s, 6 H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 142.2, 128.2, 128.1, 125.5, 70.5, 43.2, 35.7 (quintet,  $J_{C-D} = 19.2$  Hz), 28.9, 26.0. **HRMS** (ESI<sup>+</sup>)  $m/z$  Calc. 181.1556 [C<sub>12</sub>H<sub>16</sub>D<sub>2</sub>O+H]<sup>+</sup>, Found. 181.1517 [M+H]<sup>+</sup>.

**(4) (4-azido-4-methylpentyl-1,1-*d*<sub>2</sub>)benzene**: Synthesized following Procedure C. 70% **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 7.29–7.31 (m, 2 H), 7.19–7.22 (m, 3 H), 1.68–1.71 (m, 2 H), 1.52–1.55 (m, 2 H), 1.26 (s, 6 H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 142.1, 128.5, 126.0, 61.7, 41.1, 35.4 (quintet,  $J_{C-D} = 19.4$  Hz), 26.1. **HRMS** (ESI<sup>+</sup>)  $m/z$  Calc. 223.1886 [C<sub>12</sub>H<sub>15</sub>D<sub>2</sub>N<sub>3</sub>+NH<sub>4</sub>]<sup>+</sup>, Found. 223.1883 [M+NH<sub>4</sub>]<sup>+</sup>.

#### E. Synthesis of (4-azido-4-methylpentyl-1-*d*)benzene.



**(1) phenylmethan-*d*-ol:** Synthesized following previously reported procedure.<sup>6</sup> Spectral data were consistent with previously reported characterization of the product.<sup>6</sup>

**(2) (chloromethyl-*d*)benzene:** Synthesized following previously reported procedure.<sup>7</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ/ppm: 7.32–7.41 (m, 5 H), 4.59 (d, 1 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ/ppm: 137.6, 128.9, 128.7, 128.5, 46.1 (t, *J*<sub>C-D</sub> = 23.1 Hz). GCMS (EI) *t*<sub>R</sub> = 4.95 min *m/z*: 130.03, 129.03, 128.03, 127.03, 126.02, 125.02.

**(3) trimethyl((2-methyl-5-phenylpent-3-yn-2-yl-5-*d*)oxy)silane:** Synthesized following previously reported procedure.<sup>8</sup> An oven-dried Schlenk flask was charged with 3-methyl-3-trimethylsiloxy-1-butyne (1.5 equiv) in dry THF. The solution was cooled to 0 °C and <sup>i</sup>PrMgCl(LiCl) (1.6 equiv) was added. The reaction mixture was stirred for 2 hours at room temperature. Then the reaction mixture was Cannula-transferred to a solution of (chloromethyl-*d*)benzene (1.0 equiv) and Co(acac)<sub>3</sub> (0.03 equiv) in THF at 0 °C. The reaction mixture was stirred for another 5 hours and quenched with a saturated aqueous solution of NH<sub>4</sub>Cl and diluted with water. The aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated. The product was purified by flash column chromatography on silica gel with hexanes as an eluent. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ/ppm: 7.32–7.41 (m, 5 H), 4.59 (d, 1 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ/ppm: 136.7, 128.6, 128.0, 126.7, 87.8, 80.7, 66.8, 33.4 24.9 (t, *J*<sub>C-D</sub> = 19.9 Hz ), 2.03. HRMS (ESI<sup>+</sup>) *m/z*: Calc. 248.1575 [C<sub>15</sub>H<sub>21</sub>DOSi+H]<sup>+</sup>, Found. 248.1572 [M+H]<sup>+</sup>.

**(4) 2-methyl-5-phenylpentan-5-*d*-2-ol:** Synthesized following previously reported procedure.<sup>9</sup> An oven-dried Schlenk flask was charged with trimethyl((2-methyl-5-phenylpent-3-yn-2-yl-5-*d*)oxy)silane in MeOH and the solution was purged with N<sub>2</sub> three times. 10% of Pd/C (10 wt%) was added and a balloon of H<sub>2</sub> was attached to the flask. The reaction mixture was stirred for 12 hours at room temperature, filtered through Celite, and washed with Et<sub>2</sub>O. The product was purified by flash column chromatography on silica gel with 10:1 (hexanes:ethyl acetate) as an

<sup>6</sup> Wang, L.; Shang, S.; Li, G.; Ren, L.; Lv, Y.; Gao, S. *J. Org. Chem.* **2016**, *81*, 2189

<sup>7</sup> Popoff, N.; Macqueron, B.; Sayhoun, W.; Espinas, J.; Pelletier, J.; Boyron, O.; Boisson, C.; Merle, N.; Szeto, K. C.; Gauvin, R. M.; De Mallmann, A.; Taoufik, M. *Eur. J. Inorg. Chem.* **2014**, *5*, 888

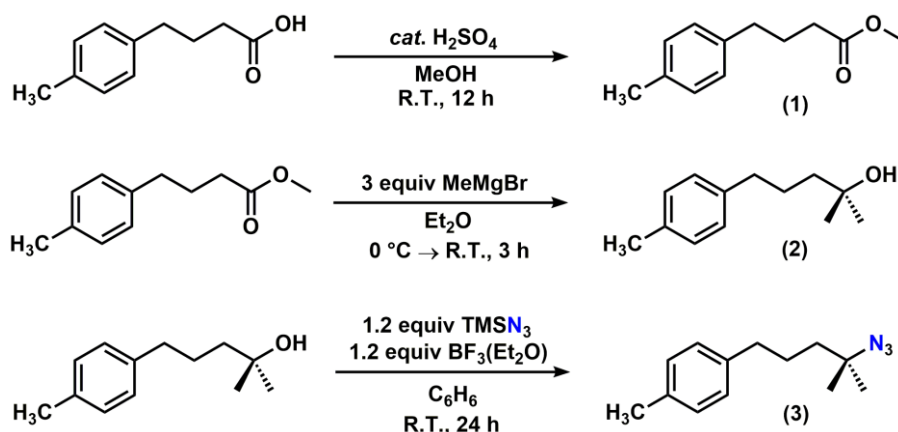
<sup>8</sup> Quinio, P.; François, C.; Escribano Cuesta, A.; Steib, A. K.; Achraier, F.; Zipse, H.; Karaghiosoff, K.; Knochel, P. *Org. Lett.* **2015**, *17*, 1010

<sup>9</sup> Nicolaou, K. C.; Reingruber, R.; Sarlah, D.; Bräse, S. *J. Am. Chem. Soc.* **2009**, *131*, 2086

eluent.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 7.32–7.41 (m, 5 H), 4.59 (d, 1 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 142.4, 128.3, 128.2, 125.6, 70.6, 43.4, 35.9 (t,  $J_{\text{C-D}} = 19.4$  Hz), 26.2. HRMS (ESI $^+$ )  $m/z$  Calc. 180.1493 [ $\text{C}_{12}\text{H}_{17}\text{DO}+\text{H}$ ] $^+$ , Found. 180.1478 [ $\text{M}+\text{H}$ ] $^+$ .

**(5) (4-azido-4-methylpentyl-1-*d*)benzene:** Synthesized following Procedure C. 53%  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 7.29–7.31 (m, 2 H), 7.19–7.22 (m, 3 H), 1.68–1.71 (m, 2 H), 1.52–1.55 (m, 2 H), 1.26 (s, 6 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 142.1, 128.5, 126.0, 61.7, 41.1, 35.8 (t,  $J_{\text{C-D}} = 19.5$  Hz), 26.1. HRMS (ESI $^+$ )  $m/z$  Calc. 222.1823 [ $\text{C}_{12}\text{H}_{16}\text{DN}_3+\text{NH}_4$ ] $^+$ , Found. 222.1823 [ $\text{M}+\text{NH}_4$ ] $^+$ .

#### F. Synthesis of 1-(4-azido-4-methylpentyl)-4-methylbenzene.



**(1) methyl 4-(*p*-tolyl)butanoate:** Synthesized following Procedure A. Spectral data were consistent with previously reported characterization of the product.<sup>10</sup>

**(2) 2-methyl-5-(*p*-tolyl)pentan-2-ol:** Synthesized following Procedure B. Spectral data were consistent with previously reported characterization of the product.<sup>11</sup>

**(3) 1-(4-azido-4-methylpentyl)-4-methylbenzene:** Synthesized following Procedure C. 56%  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ /ppm: 6.98–7.03 (m, 4 H), 2.39 (t, 2 H), 1.50–1.54 (m, 2 H), 1.23–1.26 (m, 2 H), 0.90 (s, 6 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 139.1, 135.4, 129.2, 128.4,

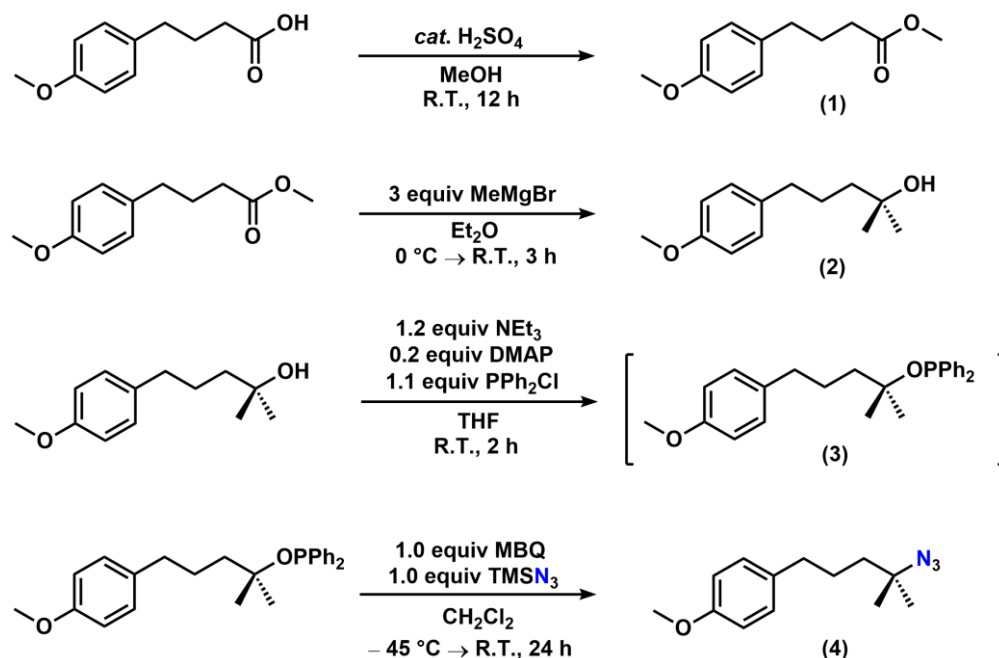
<sup>10</sup> Shimogaki, M.; Fujita, M.; Sugimura, T. *Angew. Chem. Int. Ed.* **2016**, *55*, 15797

<sup>11</sup> Benoit, Gerard; Gronemeyer, Hinrich; Lanotte, Michel; Gottardis, Marco. U.S. 6624154, **2003**



61.73, 41.21, 35.74, 26.37, 26.13, 21.15. **HRMS** (ESI<sup>+</sup>) *m/z* Calc. 235.1917 [C<sub>13</sub>H<sub>19</sub>N<sub>3</sub>+NH<sub>4</sub>]<sup>+</sup>, Found. 235.1914 [M+NH<sub>4</sub>]<sup>+</sup>.

### G. Synthesis of 1-(4-azido-4-methylpentyl)-4-methoxybenzene.



**(1) methyl 4-(4-methoxyphenyl)butanoate:** Synthesized following Procedure A. Spectral data were consistent with previously reported characterization of the product.<sup>12</sup>

**(2) 5-(4-methoxyphenyl)-2-methylpentan-2-ol:** Synthesized following Procedure B. Spectral data were consistent with previously reported characterization of the product.<sup>11</sup>

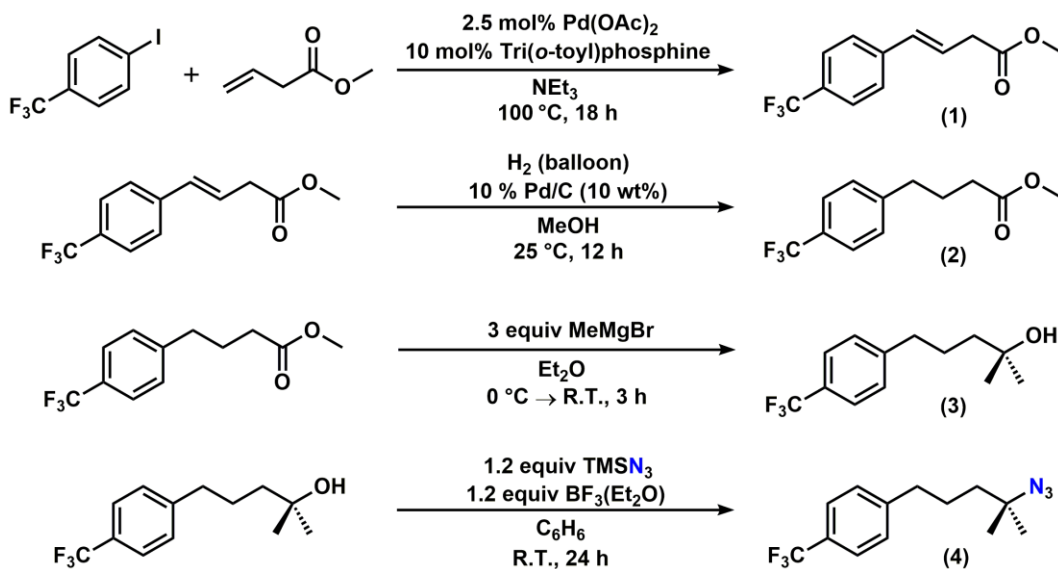
**(3) ((5-(4-methoxyphenyl)-2-methylpentan-2-yl)oxy)diphenylphosphane:** Adapted from previously reported procedure.<sup>13</sup> An oven-dried Schlenk flask was charged with 5-(4-methoxyphenyl)-2-methylpentan-2-ol (1.0 equiv) and DMAP (0.2 equiv) in THF. To the stirring solution were added NEt<sub>3</sub> (1.2 equiv) and PPh<sub>2</sub>Cl (1.1 equiv). The reaction mixture was stirred for 2 hours at room temperature, filtered through a pad of alumina, and concentrated. The isolated material was used for azidation without further purification.

<sup>12</sup> Bunce, R. A.; Cox, A. N. *Org. Prep. Proced. Intl.* **2010**, 42, 2010

<sup>13</sup> Kuroda, K.; Hayashi, Y.; Mukaiyama, T. *Tetrahedron.* **2007**, 63, 6358

**(4) 1-(4-azido-4-methylpentyl)-4-methoxybenzene:** Adapted from previously reported procedure.<sup>13</sup> An oven-dried Schlenk flask was charged with ((5-(4-methoxyphenyl)-2-methylpentan-2-yl)oxy)diphenylphosphane (1.0 equiv) in dry dichloromethane and the solution was cooled to  $-45\text{ }^{\circ}\text{C}$ . MBQ (1.0 equiv) and  $\text{TMSN}_3$  (1.0 equiv) were added to the stirring solution. The reaction mixture was slowly warmed up to room temperature and stirred for 24 hours. The product was purified by preparative TLC to afford the product.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 7.10–7.09 (d, 2 H), 6.84–6.83 (d, 2 H), 3.79 (s, 3 H), 2.56 (t, 2 H), 1.66 (m, 2 H), 1.52 (m, 2 H), 1.24 (s, 6 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 157.9, 134.3, 129.4, 113.9, 61.73, 55.40, 41.14, 35.26, 26.47, 26.14. HRMS (ESI<sup>+</sup>)  $m/z$  Calc. 251.1886 [ $\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}+\text{NH}_4$ ]<sup>+</sup>, Found. 251.1883 [ $\text{M}+\text{NH}_4$ ]<sup>+</sup>.

#### H. Synthesis of 1-(4-azido-4-methylpentyl)-4-(trifluoromethyl)benzene.



**(1) methyl (E)-4-(4-(trifluoromethyl)phenyl)but-3-enoate:** Synthesized following previously reported procedure.<sup>14</sup> Spectral data were consistent with previously reported characterization of the product.<sup>14</sup>

**(2) methyl 4-(4-(trifluoromethyl)phenyl)butanoate:** An oven-dried Schlenk flask was charged with methyl (E)-4-(4-(trifluoromethyl)phenyl)but-3-enoate in MeOH and the solution was purged

<sup>14</sup> Leach, Colin Andrew and Smith, Stephen Allan, WO 2003042206, 2003

with N<sub>2</sub> three times. 10% of Pd/C (10 wt%) was added and a balloon of H<sub>2</sub> was attached to the flask. The reaction mixture was stirred for 12 hours at room temperature after which it was filtered through Celite. The Celite was washed with Et<sub>2</sub>O and the combined filtrate was concentrated *in vacuo*. The concentrated material was used for the next step without further purification. Spectral data were consistent with previously reported characterization of the product.<sup>11</sup>

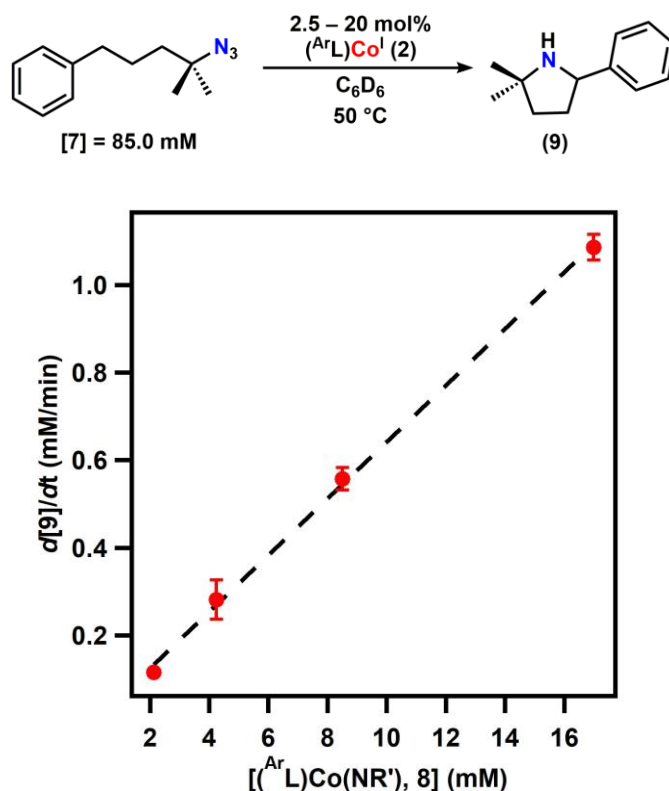
**(3) 2-methyl-5-(4-(trifluoromethyl)phenyl)pentan-2-ol:** Synthesized following Procedure B. Spectral data were consistent with previously reported characterization of the product.<sup>11</sup>

**(4) 1-(4-azido-4-methylpentyl)-4-(trifluoromethyl)benzene:** Synthesized following Procedure C. 62% <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ/ppm: 7.54–7.55 (d, 2 H), 7.29–7.30 (d, 2 H), 2.68 (t, 2 H), 1.68–1.74 (m, 2 H), 1.50–1.52 (m, 2 H), 1.25 (s, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ/ppm: 146.23, 128.79, 128.56 (q, *J*<sub>C-F</sub> = 32.4 Hz), 128.05 (q, *J*<sub>C-F</sub> = 3.78 Hz), 121.25 (q, *J*<sub>C-F</sub> = 271.7 Hz), 61.55, 41.09, 35.95, 26.12, 25.91. HRMS (ESI<sup>+</sup>) *m/z* Calc. 289.1635 [C<sub>13</sub>H<sub>16</sub>F<sub>3</sub>N<sub>3</sub>+NH<sub>4</sub>]<sup>+</sup>, Found. 290.1568 [M+NH<sub>4</sub>]<sup>+</sup>.

## Mechanistic Studies.

**General considerations for kinetic experiments.** All kinetic experiments were run in J Young nmr tubes at the noted temperature. Stock solutions of (<sup>Ar</sup>L)Co **2**, azide substrate **7**, and pyridine-*d*<sub>5</sub> were prepared in benzene-*d*<sub>6</sub> and were added separately with a micro-syringe to the J Young tube. The reaction mixture was frozen prior to NMR analysis. The frozen reaction mixture was thawed and placed into a thermally stabilized NMR instrument. Reactions were monitored to less than 10% of product (2,2-dimethyl-5-phenylpyrrolidine) **9** formation. <sup>1</sup>H NMR data collection was done by using the array command, collecting spectra every 15 or 30 seconds. The resulting data points were analyzed using the initial rate method assuming the concentration of the cobalt imido **8** is constant during early stages of catalytic reactions. Each experiment was conducted in triplicate and average rates are reported with error bars corresponding to standard errors of those three experiments. 1,3,5-trimethoxybenzene was used as internal standard for <sup>1</sup>H NMR integration.

**A. Order in imido.** The reaction order in imido **8** was determined using the initial rate method with four different **[2]** and constant **[7]** at 50 °C in benzene-*d*<sub>6</sub>. A plot of rate versus **[8]** gave a straight line ( $R^2 = 0.9988$ ), indicating first order dependence on **[8]**.

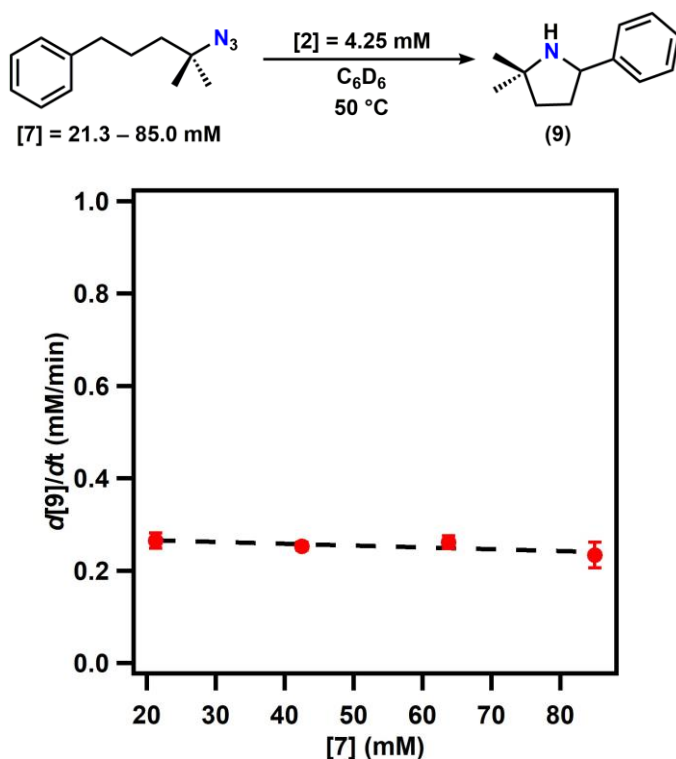


**Figure S-1.** Rate of formation of **9** (mM/min) versus concentrations of imido **8** (mM).

**Table S-1.** Averages and standard errors for the observed initial rates with varying concentrations of imido. The concentrations of imido **8** were calculated based on the initial amount of **2** assuming a quantitative conversion of **2** to **8**.

Entry	$(^{Ar}L)Co^I$ (mol%)	<b>[8]</b> (mM)	Rate (mM/min)
1	2.5	2.13	$1.15(4) \times 10^{-1}$
2	5.0	4.25	$2.81(45) \times 10^{-1}$
3	10	8.50	$5.57(25) \times 10^{-1}$
4	20	17.0	1.09(3)

**B. Order in azide substrate.** The order in the azide substrate, (4-azido-4-methylpentyl)benzene **7** was determined using the initial rate methods with four different [7] and constant [2] at 50 °C in benzene-*d*<sub>6</sub>.



**Figure S-2.** Rate of formation of **9** (mM/min) versus concentrations of azide **7** (mM).

**Table S-2.** Averages and standard errors of the observed initial rates with varying concentrations of azide. [2] and [7] are the initial concentrations of the catalyst and the azide, respectively.

Entry	[2] (mM)	[7] (mM)	Rate (mM/min)
1	4.25	21.3	2.65(17) × 10 <sup>-1</sup>
2	4.25	42.5	2.52(9) × 10 <sup>-1</sup>
3	4.25	63.8	2.61(14) × 10 <sup>-1</sup>
4	4.25	85.0	2.33(28) × 10 <sup>-1</sup>

C. Proposed catalytic cycle for intramolecular C–H amination in the absence of pyridine.

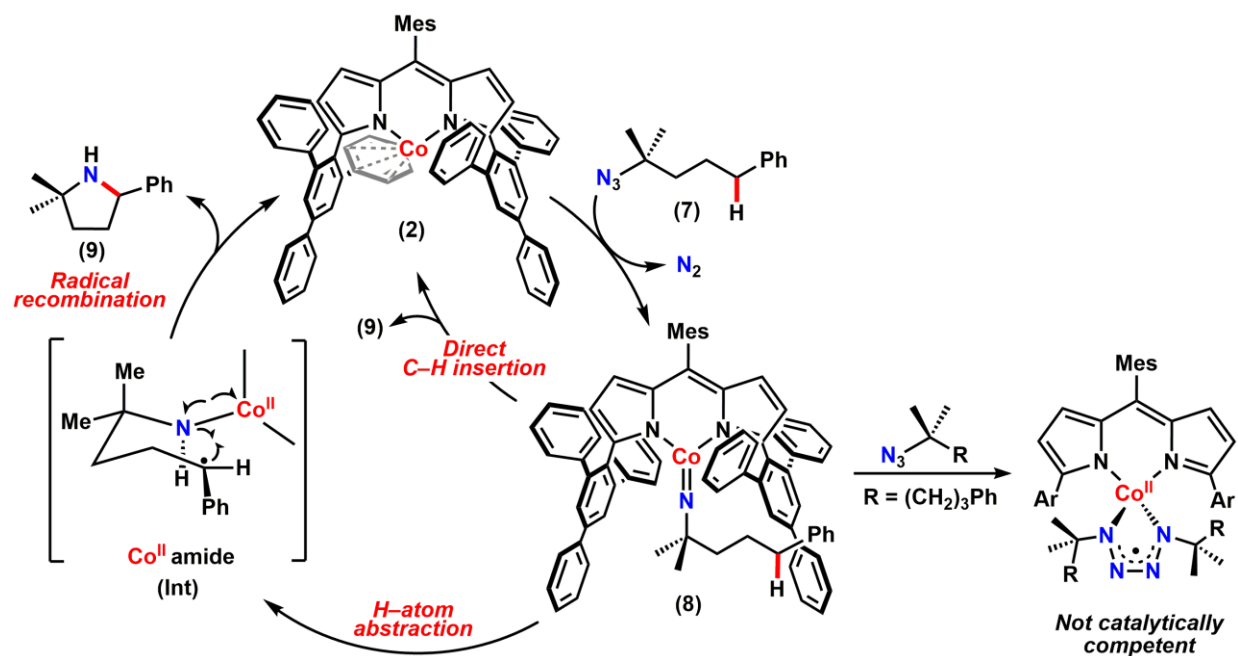
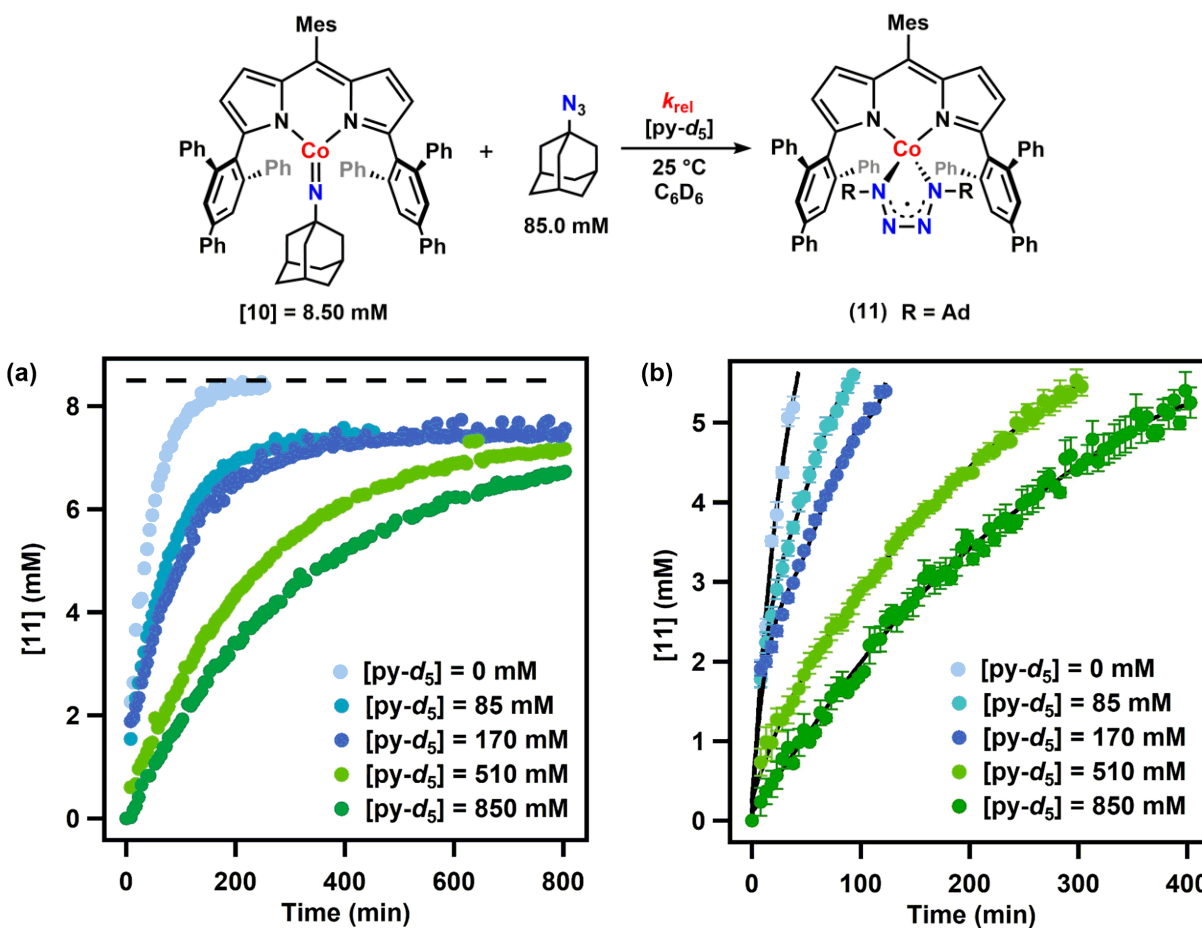


Figure S-3. Proposed catalytic cycle in the absence of pyridine.

**D. Formation of cobalt tetrazido complex as a function of [pyridine-*d*<sub>5</sub>].** The rate of formation of **11** as a function of [pyridine-*d*<sub>5</sub>] was measured at 25 °C in benzene-*d*<sub>6</sub> with [**10**] = 8.50 mM, [**N**<sub>3</sub>Ad] = 85.0 mM, and varying concentrations of pyridine-*d*<sub>5</sub>.



**Figure S-4.** Formation of cobalt tetrazido complex as a function of [pyridine-*d*<sub>5</sub>] (a) Each reaction was monitored up to >75% formation of **11**. Black dashed line represents the [11] at full conversion indicating an empirically determined constant infinity point. (b) Averages of triplicate results measured up to 60% formation of **11**. Error bars depict standard errors. Black lines represent fittings to a 6<sup>th</sup> polynomial, where  $c_0, c_1, c_2 \dots c_6$  are constants, to obtain the overall rates at 50% formation of **11**.<sup>15</sup>

$$[11] = f(t) = c_0 + c_1t + c_2t^2 + c_3t^3 + c_4t^4 + c_5t^5 + c_6t^6$$

<sup>15</sup> Kennedy, C. R.; Lehnher, D.; Rajapaksa, N. S.; Ford, D. D.; Park, Y.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2016**, *138*, 13525



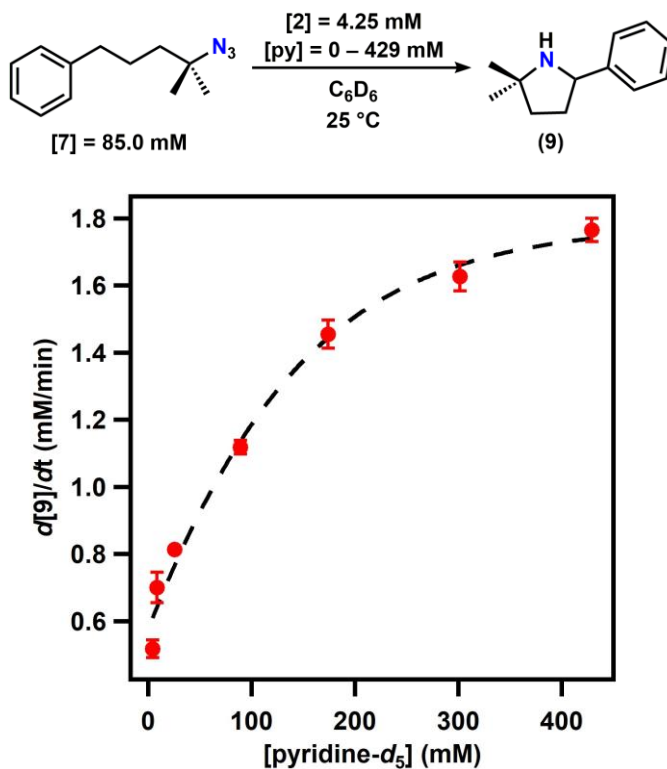
The rate of formation of **11** was obtained from the derivative of  $f(t)$  as following.

$$rate = \frac{d[\mathbf{11}]}{dt} = \frac{df(t)}{dt} = c_1 + 2c_2t + 3c_3t^2 + 4c_4t^3 + 5c_5t^4 + 6c_6t^5$$

**Table S-3.** Averages and standard errors of the rates at 50% formation of the cobalt tetrazido complex **11** as a function of [pyridine- $d_5$ ].

Entry	[pyridine- $d_5$ ] (mM)	Rate (mM/min)	Relative rates $k_{rel}$
1	0	$2.03(6) \times 10^{-1}$	1.00 (def.)
2	85	$1.33(6) \times 10^{-1}$	0.659(40)
3	170	$9.06(2) \times 10^{-2}$	0.447(17)
4	510	$3.12(1) \times 10^{-2}$	0.157(8)
5	850	$2.21(3) \times 10^{-2}$	0.109(4)

**E. Saturation kinetics in pyridine.** The rate of formation of **9** (< 10%) as a function of [pyridine-*d*<sub>5</sub>] was measured at 25 °C in benzene-*d*<sub>6</sub> with [2] = 4.25 mM and [7] = 85.0 mM.

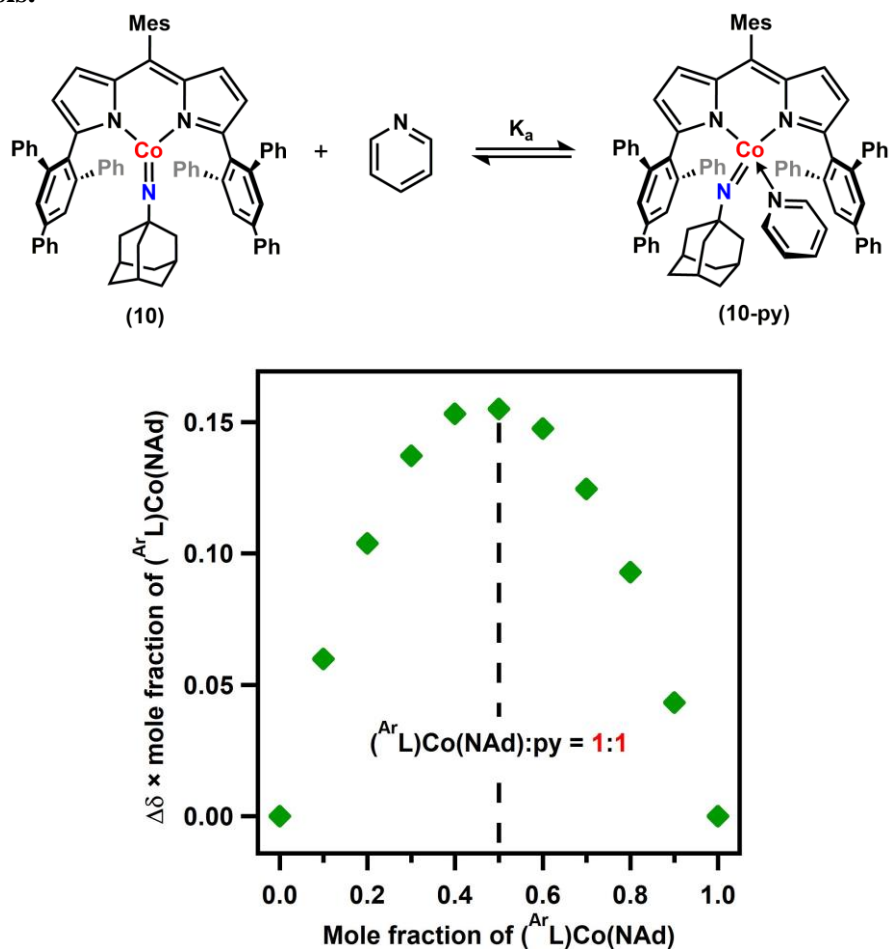


**Figure S-5.** Rate of formation of **9** (mM/min) versus [pyridine-*d*<sub>5</sub>] (mM).

**Table S-4.** Averages and standard errors of the observed initial rates of amination as a function of [pyridine-*d*<sub>5</sub>].

Entry	[pyridine- <i>d</i> <sub>5</sub> ] (mM)	Rate (mM/min)
1	0	N/A
2	4.25	$5.17(27) \times 10^{-1}$
3	8.50	$7.00(45) \times 10^{-1}$
4	25.5	$8.13(5) \times 10^{-1}$
5	89.3	1.12(2)
6	174	1.45(4)
7	302	1.63(4)
8	429	1.77(3)

## F. Job analysis.



**Figure S-6.** Job plot obtained at 25 °C in benzene- $d_6$  with **[10]** + [pyridine] = 4.25 mM.

**Table S-5.** Chemical shifts (ppm) of **10** as a function of [pyridine] at 25 °C in benzene- $d_6$ .

Entry	[10] (mM)	[pyridine] (mM)	Chemical shift (ppm)
1	4.250	0	19.88
2	3.825	0.425	19.83
3	3.400	0.850	19.77
4	2.975	1.275	19.70
5	2.550	1.700	19.64
6	2.125	2.125	19.57
7	1.700	2.550	19.50
8	1.275	2.975	19.43
9	0.850	3.400	19.36
10	0.425	3.825	19.28

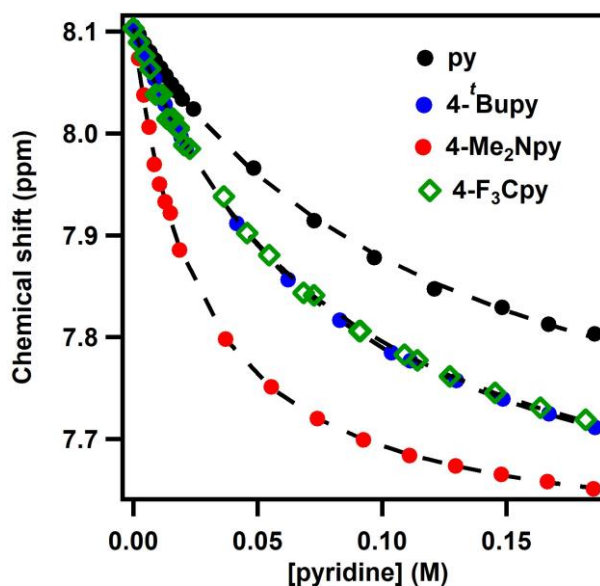
**G.  $^1\text{H}$  NMR titration experiments.** A solution of ( $^{\text{Ar}}\text{L}$ )Co(NAd) **10** was prepared in benzene- $d_6$  and its concentration was maintained constant throughout the titration with pyridines. The chemical shifts corresponding to **10** as a function of the concentration of pyridines were fitted with a 1:1 binding isotherm by solving the following equations: (1)–(4);  $[\text{M}]_0$  is the total concentration of **10** and the corresponding pyridine-bound imido **10-py**;  $[\text{L}]_0$  is the total concentration of pyridine;  $[\text{ML}]$  is the concentration of **10-py**;  $[\text{M}]$  is the concentration of **10**;  $[\text{L}]$  is the concentration of free pyridine.  $\delta_{\text{free}}$  is the chemical shift of **10**;  $\delta_{\text{bound}}$  is the chemical shift of **10-py**.  $\delta_{\text{bound}}$  is estimated and obtained by fitting the titration curve.<sup>16</sup>

$$K_{\text{eq}} = \frac{[\text{ML}]}{[\text{M}][\text{L}]}$$

$$[\text{ML}] = [\text{M}]_0 - [\text{M}]$$

$$[\text{ML}] = \frac{([\text{M}]_0 + [\text{L}]_0 + K_{\text{eq}}^{-1}) - \sqrt{([\text{M}]_0 + [\text{L}]_0 + K_{\text{eq}}^{-1})^2 - 4[\text{M}]_0[\text{L}]_0}}{2}$$

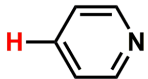
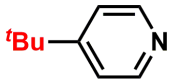
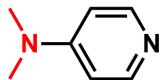
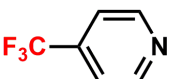
$$\delta_{\text{obs}} = \frac{[\text{ML}]}{[\text{M}]_0} \delta_{\text{bound}} + \frac{[\text{M}]}{[\text{M}]_0} \delta_{\text{free}}$$



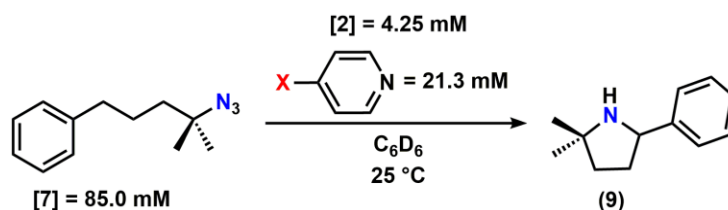
**Figure S-7.**  $^1\text{H}$  NMR titration curves of **10** with substituted pyridines. Chemical shifts (ppm) for **10** as a function of concentration of substituted pyridines at 25 °C in benzene- $d_6$ . Each black dashed line depicts a nonlinear regression fit to a 1:1 complexation model.

<sup>16</sup> Fielding, L. *Tetrahedron*. **2000**, 56, 6151

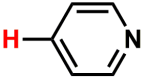
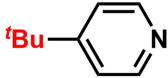
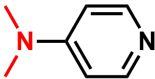
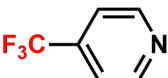
**Table S-6.** Calculated binding constants ( $K_a$ ) for 4-substituted pyridines using a nonlinear regression fit to a 1:1 complexation model.

Entry	Substituted pyridine	$K_a$ ( $M^{-1}$ )
1		8.04
2		12.9
3		41.8
4		12.5

**H. Initial rate kinetics with 4-substituted pyridines.** The rate of formation of **9** (< 10%) in the presence of 4-substituted pyridines was measured at 25 °C in benzene-*d*<sub>6</sub> with [2] = 4.25 mM and [7] = 85.0 mM.

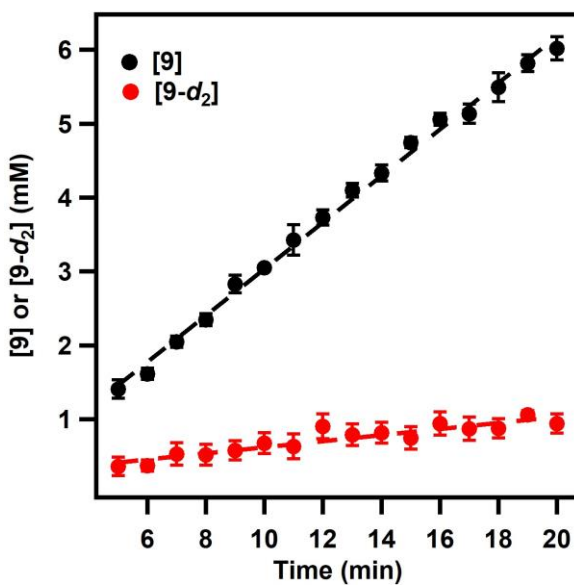
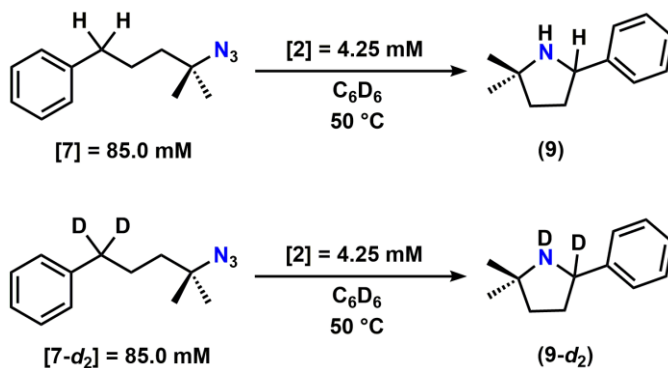


**Table S-7.** Averages and standard errors for the observed initial rates of C–H amination in the presence of substituted pyridines.

Entry	Substituted pyridine	Rate (mM/min)	Relative rate $k_X/k_H$	Final yield (%)
1		$7.59(8) \times 10^{-1}$	1.00 (def.)	36.4
2		1.26(3)	1.66(36)	89.4
3		2.36(2)	3.11(68)	90.8
4		$2.71(50) \times 10^{-1}$	0.357(16)	20.4

## I. Intermolecular kinetic isotope effect (KIE) study.

(A) The intermolecular KIE was determined by comparing the first order rate constants of the amination at 50 °C in benzene- $d_6$ .



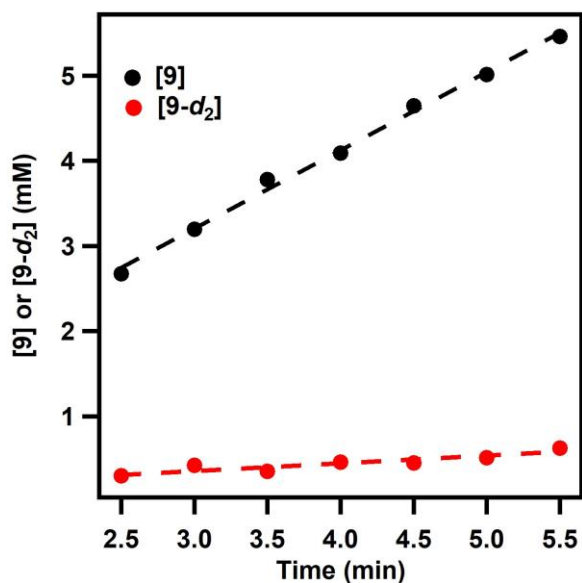
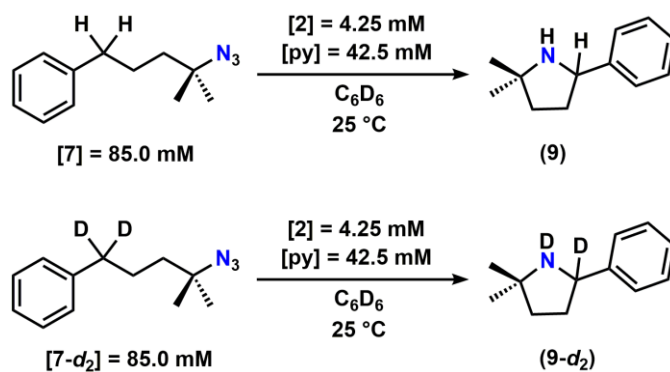
**Figure S-8.** Intermolecular KIE at 50 °C in benzene- $d_6$ .

$$k_H = 7.4(6) \times 10^{-2} \text{ (min}^{-1}\text{)}$$

$$k_D = 9.7(5) \times 10^{-3} \text{ (min}^{-1}\text{)}$$

$$\text{KIE} = k_H/k_D = 7.6(2)$$

(B) The intermolecular KIE in the presence of pyridine was determined by comparing the first order rate constants of the amination at 25 °C in benzene-*d*<sub>6</sub>.



**Figure S-9.** Intermolecular KIE at 25 °C in benzene-*d*<sub>6</sub> with [pyridine] = 42.5 mM.

$$k_{\text{H}} = 2.16(9) \times 10^{-2} \text{ (min}^{-1}\text{)}$$

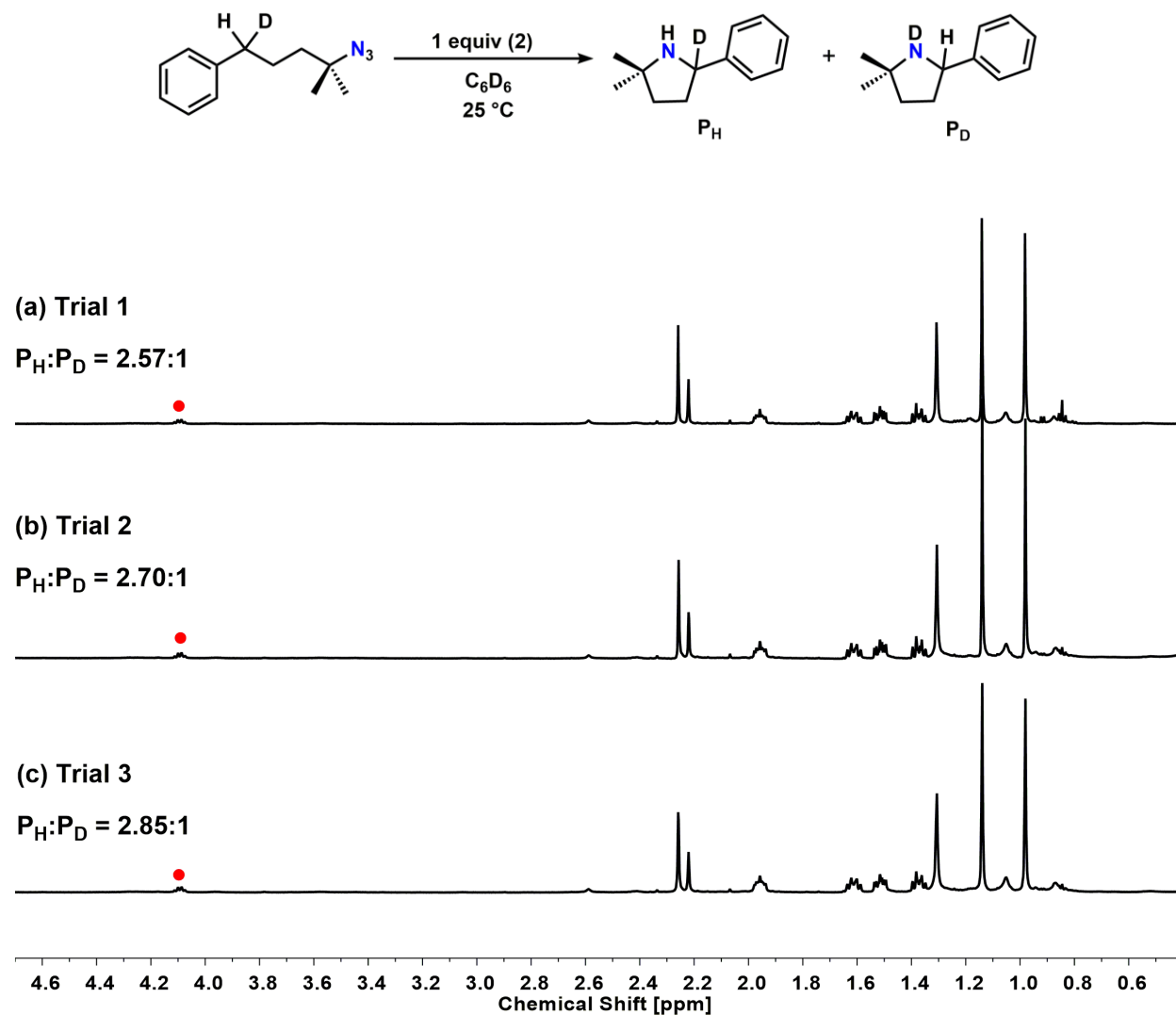
$$k_{\text{D}} = 2.1(8) \times 10^{-3} \text{ (min}^{-1}\text{)}$$

$$\text{KIE} = k_{\text{H}}/k_{\text{D}} = 10.2(9)$$



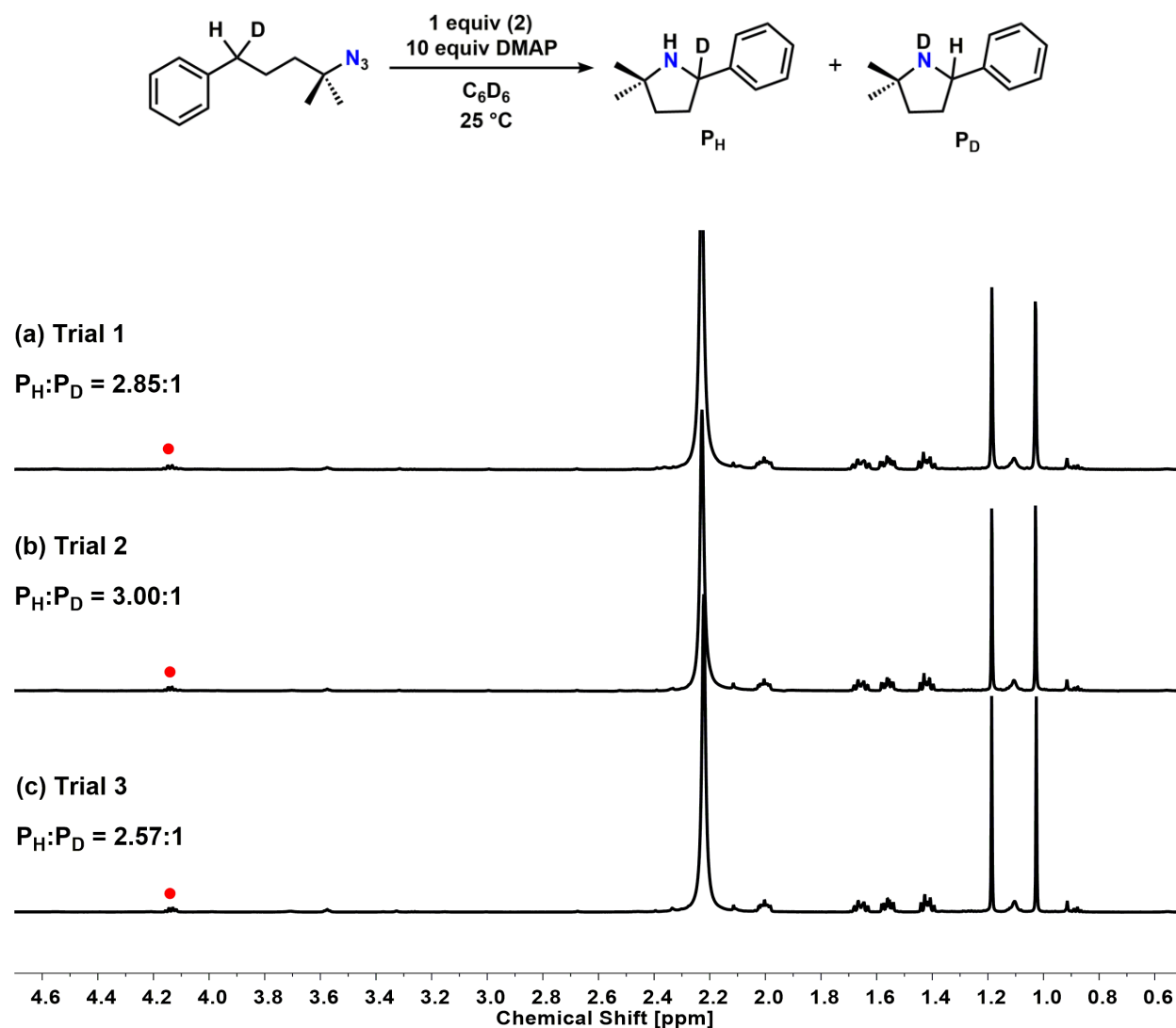
### J. Intramolecular kinetic isotope effect.

(A) The KIE obtained upon the intramolecular competition was determined by measuring the ratio between the  $P_H$  and  $P_D$  using  $^1H$  NMR integration. In order to completely exclude the off-cycle reaction (i.e., formation of the tetrazido complex) this experiment was performed using a stoichiometric amount of ( $^{Ar}L$ )Co **2**. A KIE value of 2.70(7) was found.



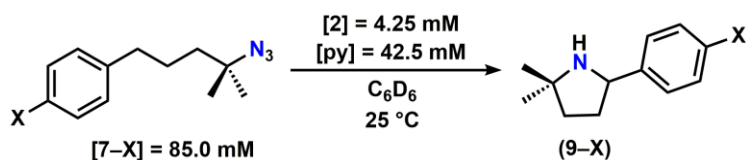
**Figure S-10.**  $^1H$  NMR spectra showing the distributions of  $P_H$  and  $P_D$ . The highlighted peak at 4.10 ppm corresponds to  $P_D$  and was used for the quantification of each of the products.

(B) The intramolecular competition KIE in the presence of 10 equivalents of DMAP was determined by measuring the ratio between the  $P_H$  and  $P_D$  using  $^1H$  NMR integration. In order to completely exclude the off-cycle reaction (i.e., formation of the tetrazido complex) this experiment was performed using a stoichiometric amount of ( $^{Ar}L$ )Co **2**. A KIE value of 2.87(6) was found.



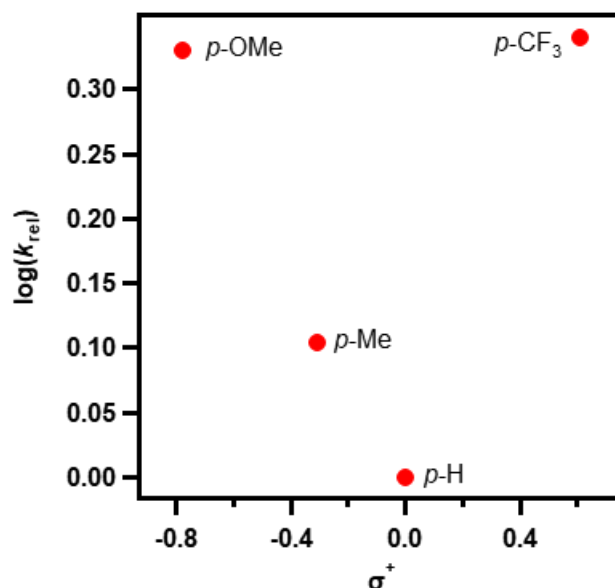
**Figure S-11.**  $^1H$  NMR spectra showing the distributions of  $P_H$  and  $P_D$ . The highlighted peak at 4.10 ppm corresponds to  $P_D$  and was used for the quantification of each of the products. The singlet at 2.23 ppm is from the  $-CH_3$  groups of DMAP.

**K. Initial rate kinetics with para-substituted azide substrates.** The initial rates of amination for *para*-substituted azide substrates (**7-X**) were measured at 25 °C in benzene-*d*<sub>6</sub> with **[2]** = 4.25 mM and [pyridine] = 42.5 mM.

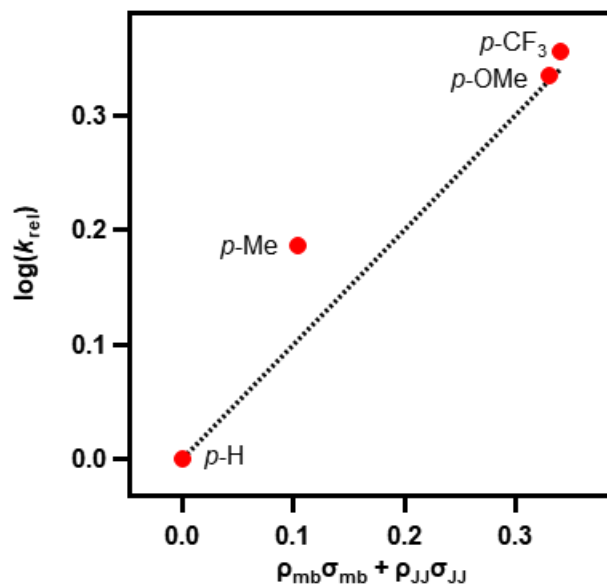


**Table S-8.** Averages and standard errors of the observed initial rates for *para*-substituted azide substrates.

Entry	<i>para</i> substituent (X)	Rate (mM/min)
1	H	$9.18(9) \times 10^{-1}$
2	<i>p</i> -CH <sub>3</sub>	1.02(3)
3	<i>p</i> -OCH <sub>3</sub>	1.28(2)
4	<i>p</i> -CF <sub>3</sub>	1.29(5)



**Figure S-12.** Free-energy correlation of  $\log(k_{rel})$  vs.  $\sigma^+$ .

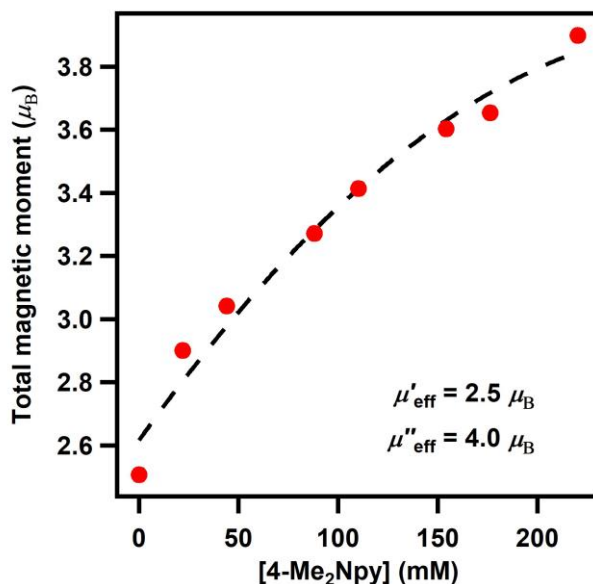
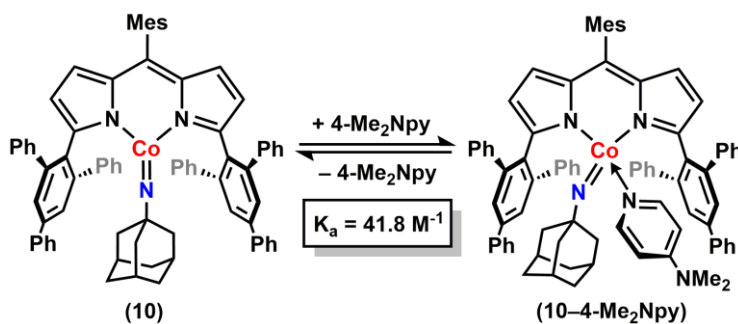


**Figure S-13.** Linear-free-energy correlation of  $\log(k_{rel})$  vs.  $(\sigma_{mb}$  and  $\sigma_{JJ})$ .  $\rho_{mb} = -0.25$  and  $\rho_{JJ}^* = 0.72$ .<sup>17</sup>

<sup>17</sup> Jiang, X.-K. *Acc. Chem. Res.*, **1997**, 30, 283

**L. Solution magnetic moment.** The magnetic moment of imido **10** was measured as a function of [4-Me<sub>2</sub>Npy] at 25 °C in benzene-*d*<sub>6</sub> using (trifluoromethyl)benzene as a reference for <sup>19</sup>F NMR. The individual magnetic moments,  $\mu'_{\text{eff}}$  and  $\mu''_{\text{eff}}$  resulting from **10** and **10-(4-Me<sub>2</sub>Npy)**, respectively were calculated based on the following equation using the binding constant ( $K_a$ ) of 4-Me<sub>2</sub>Npy at 25 °C.  $\chi_{10}$  and  $\chi_{10-(4\text{-Me}_2\text{Npy})}$  represent mole fractions of **10** and **10-(4-Me<sub>2</sub>Npy)**, respectively at certain concentrations of 4-Me<sub>2</sub>Npy.

$$\text{Total } \mu_{\text{eff}} = \mu'_{\text{eff}}(\chi_{10}) + \mu''_{\text{eff}}(\chi_{10-(4\text{-Me}_2\text{Npy})})$$

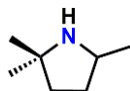


**Figure S-14.** Solution magnetic moments of a mixture of **10** and **10-(4-Me<sub>2</sub>Npy)** as a function of [4-Me<sub>2</sub>Npy] at 25 °C in benzene-*d*<sub>6</sub>.

## Characterization of Substituted Pyrrolidines.

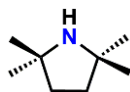
**Catalytic reactions.** Under N<sub>2</sub> atmosphere, (<sup>Ar</sup>L)Co (8.50 mM in benzene) and the desired 4-phenyl substituted azide (10 equiv, 85.0 mM in benzene) were added to an oven-dried pressure vessel. The reaction mixture was heated to 80 °C for 12 hours. The crude reaction mixture was concentrated via rotary evaporation and the desired substituted pyrrolidine was isolated via a flash silica chromatography using (EtOAc:MeOH:NH<sub>4</sub>OH = 10:1:0.1) as an eluent. Since the purpose of such catalytic runs was to characterize the desired pyrrolidines from the corresponding azide substrate which are used for the kinetic analysis, the reactions were not conducted under the optimized conditions (i.e., in the presence of pyridine).

### (1) 2,2,5-trimethylpyrrolidine



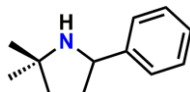
Spectral data were consistent with previously reported characterization of the product.<sup>18</sup>

### (2) 2,2,5,5-tetramethylpyrrolidine



Spectral data were consistent with previously reported characterization of the product.<sup>19</sup>

### (3) 2,2-dimethyl-5-phenylpyrrolidine



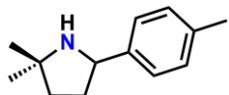
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ/ppm: 7.37 (m, 2 H), 7.31 (t, 2 H), 7.21 (t, 1 H), 4.31 (t, 1 H), 2.22–2.27 (m, 1 H), 1.79–1.85 (m, 1 H), 1.71–1.77 (m, 2 H), 1.29 (s, 3 H), 1.25 (s, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR

<sup>18</sup> Moffett, R. B.; White, J. L. *J. Org. Chem.* **1952**, *17*, 407

<sup>19</sup> Hodgson, D. M.; Bray, C. D.; Kindon, N. D.; Reynolds, N. J.; Coote, S. J.; Um, J. M.; Houk, K. N. *J. Org. Chem.* **2009**, *74*, 1019

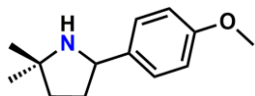
(125 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 145.37, 128.46, 126.84, 126.70, 62.23, 59.34, 40.36, 35.28, 30.77, 29.70. **HRMS** (ESI<sup>+</sup>)  $m/z$  Calc. 176.1434 [C<sub>12</sub>H<sub>17</sub>N+H]<sup>+</sup>, Found. 176.1433 [M+H]<sup>+</sup>.

**(4) 2,2-dimethyl-5-(*p*-tolyl)pyrrolidine**



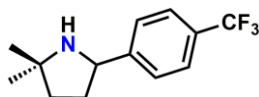
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 7.25 (d, 2 H), 7.13 (d, 2 H), 4.27 (t, 1 H), 2.32 (s, 3 H), 2.19–2.25 (m, 1 H), 1.77–1.83 (m, 1 H), 1.69–1.76 (m, 2 H), 1.28 (s, 3 H), 1.24 (s, 3 H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 142.28, 136.37, 129.13, 126.60, 62.01, 59.31, 40.41, 35.30, 30.77, 29.72, 21.18. **HRMS** (ESI<sup>+</sup>)  $m/z$  Calc. 190.1590 [C<sub>13</sub>H<sub>19</sub>N+H]<sup>+</sup>, Found. 190.1588 [M+H]<sup>+</sup>.

**(5) 5-(4-methoxyphenyl)-2,2-dimethylpyrrolidine**



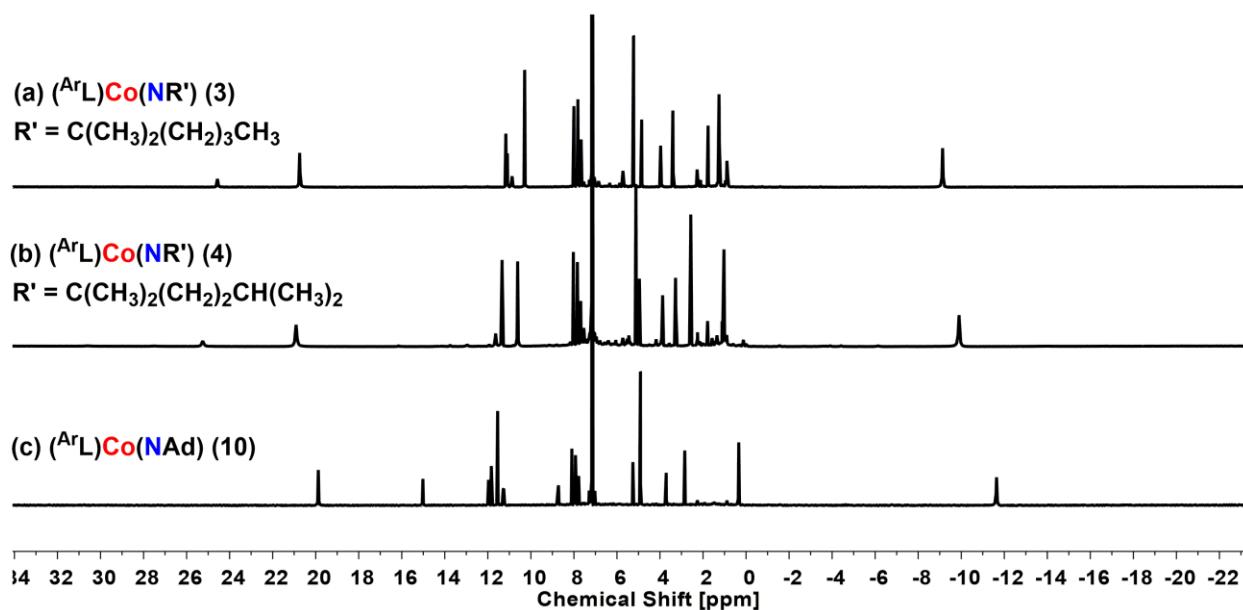
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 7.32 (d, 2 H), 6.86 (d, 2 H), 4.35 (t, 1 H), 3.79 (s, 3 H), 2.21–2.26 (m, 1 H), 1.87–1.94 (m, 1 H), 1.74–1.83 (m, 2 H), 1.30 (s, 3 H), 1.28 (s, 3 H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 142.28, 136.37, 129.13, 126.60, 62.01, 59.31, 40.41, 35.30, 30.77, 29.72, 21.18. **HRMS** (ESI<sup>+</sup>)  $m/z$  Calc. 206.1539 [C<sub>13</sub>H<sub>19</sub>NO+H]<sup>+</sup>, Found. 206.1537 [M+H]<sup>+</sup>.

**(6) 2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pyrrolidine**

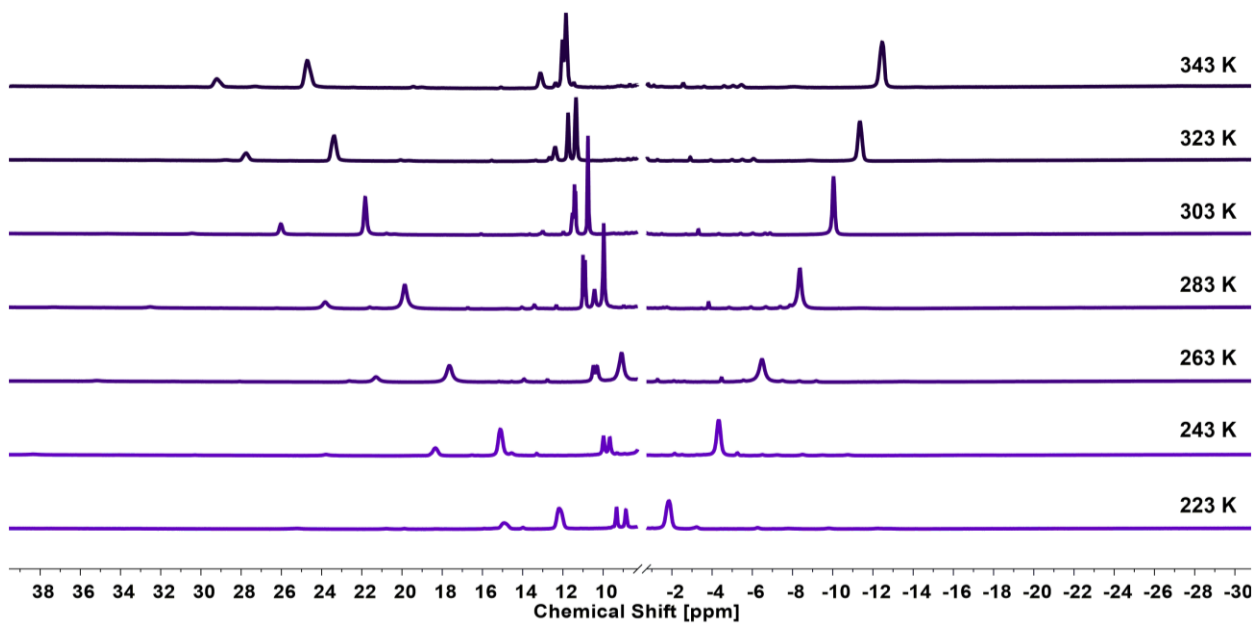


**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 7.49–7.56 (m, 4 H), 4.39 (t, 1 H), 2.26–2.30 (m, 1 H), 1.70–1.78 (m, 3 H), 1.28 (s, 3 H), 1.27 (s, 3 H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 150.06, 128.56 (q,  $J_{C-F}$  = 32.3 Hz), 126.92, 125.25 (q,  $J_{C-F}$  = 3.77 Hz), 121.21 (q,  $J_{C-F}$  = 271.8 Hz), 61.51, 59.36, 40.08, 35.34, 30.81, 29.67. **HRMS** (ESI<sup>+</sup>)  $m/z$  Calc. 244.1308 [C<sub>13</sub>H<sub>16</sub>F<sub>3</sub>N+H]<sup>+</sup>, Found. 244.1303 [M+H]<sup>+</sup>.

### <sup>1</sup>H NMR Spectra of Metal Compounds.



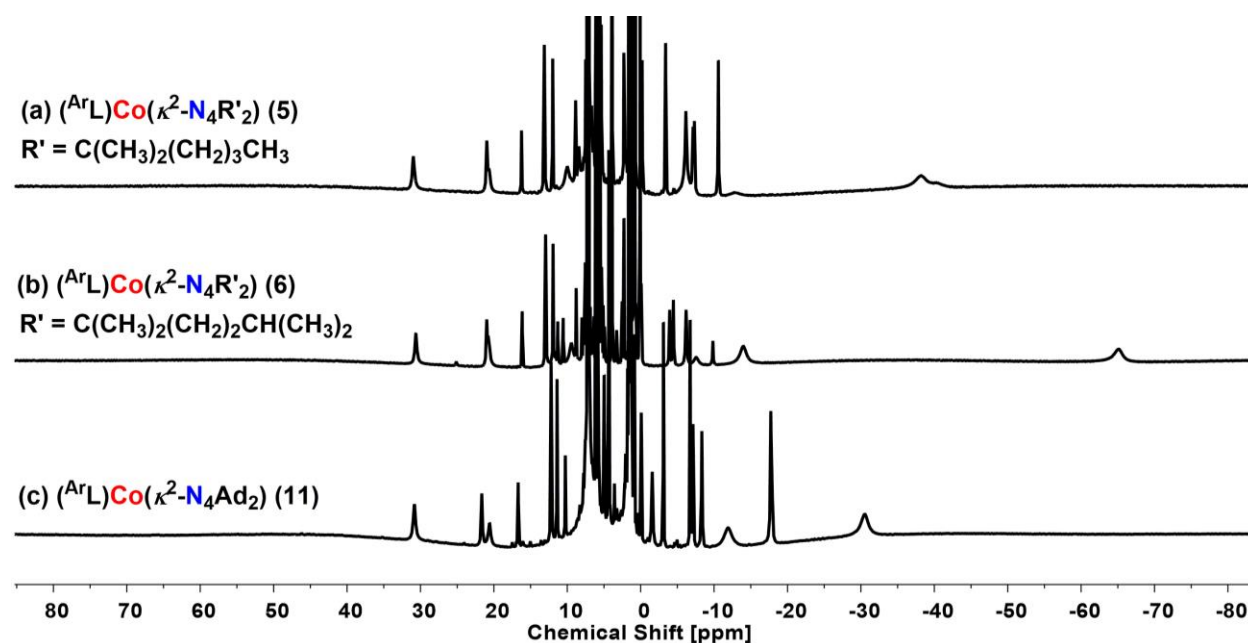
**Figure S-15.** <sup>1</sup>H NMR spectra of a series of cobalt alkyl imidos in benzene-*d*<sub>6</sub>.



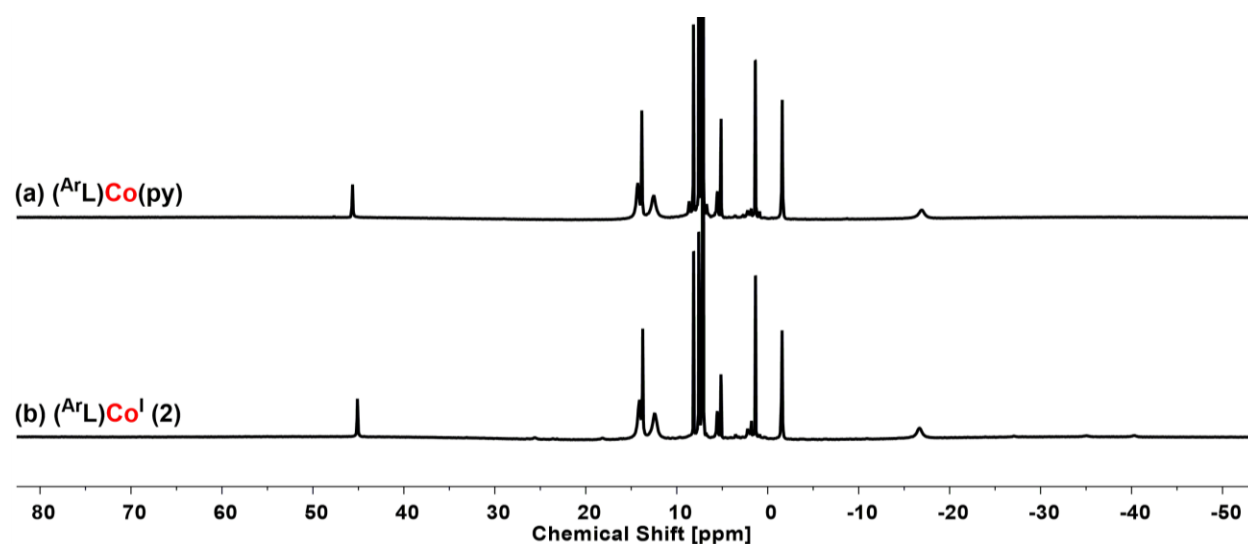
**Figure S-16.** Variable temperature <sup>1</sup>H NMR spectra of imido complex **3** in toluene-*d*<sub>8</sub> exhibiting a similar temperature dependent feature with the one observed from the previously reported Co<sup>III</sup> imido (<sup>Ar</sup>L)Co(N<sup>t</sup>Bu).<sup>20</sup>

<sup>20</sup> King, E.R.; Sazama, G.T.; Betley, T.A. *J. Am. Chem. Soc.* **2012**, *134*, 17858

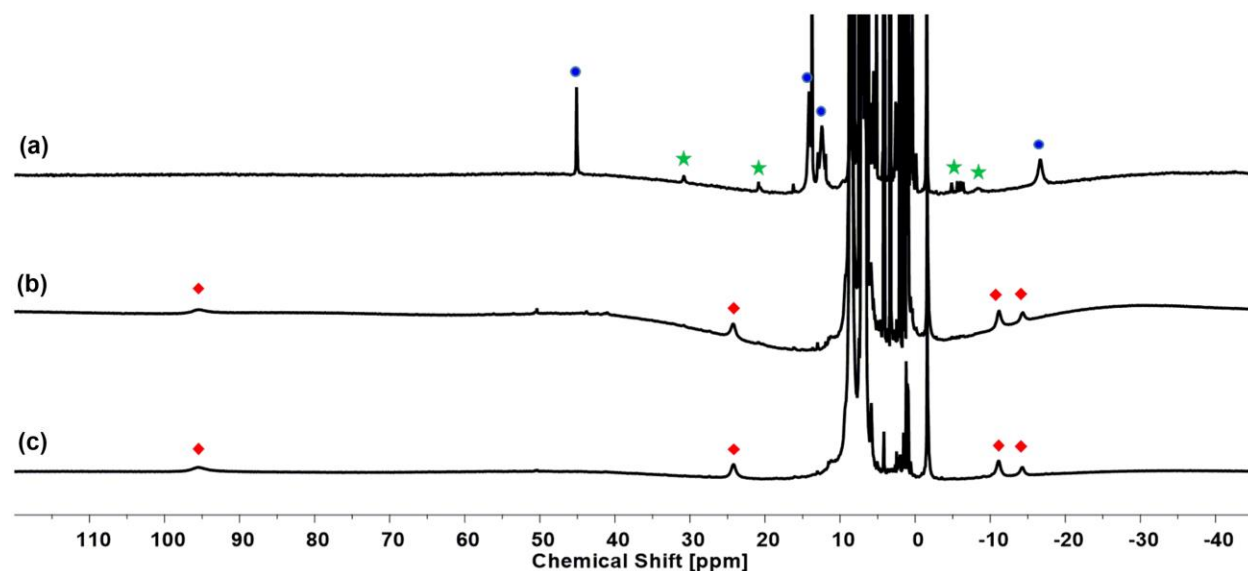




**Figure S-17.**  $^1\text{H}$  NMR spectra of a series of cobalt tetrazido complexes in benzene- $d_6$ .

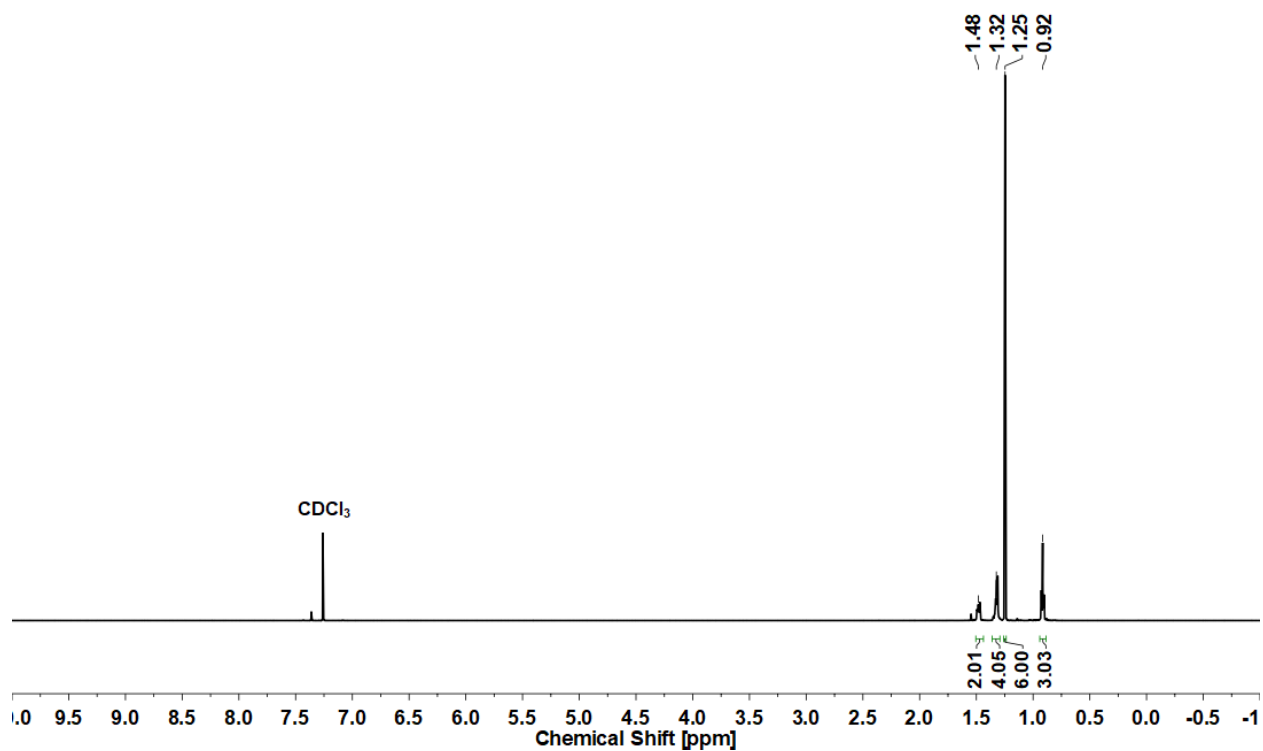


**Figure S-18.**  $^1\text{H}$  NMR spectra of  $(^{\text{Ar}}\text{L})\text{Co}(\text{py})$  and  $(^{\text{Ar}}\text{L})\text{Co}$  2 in benzene- $d_6$ .

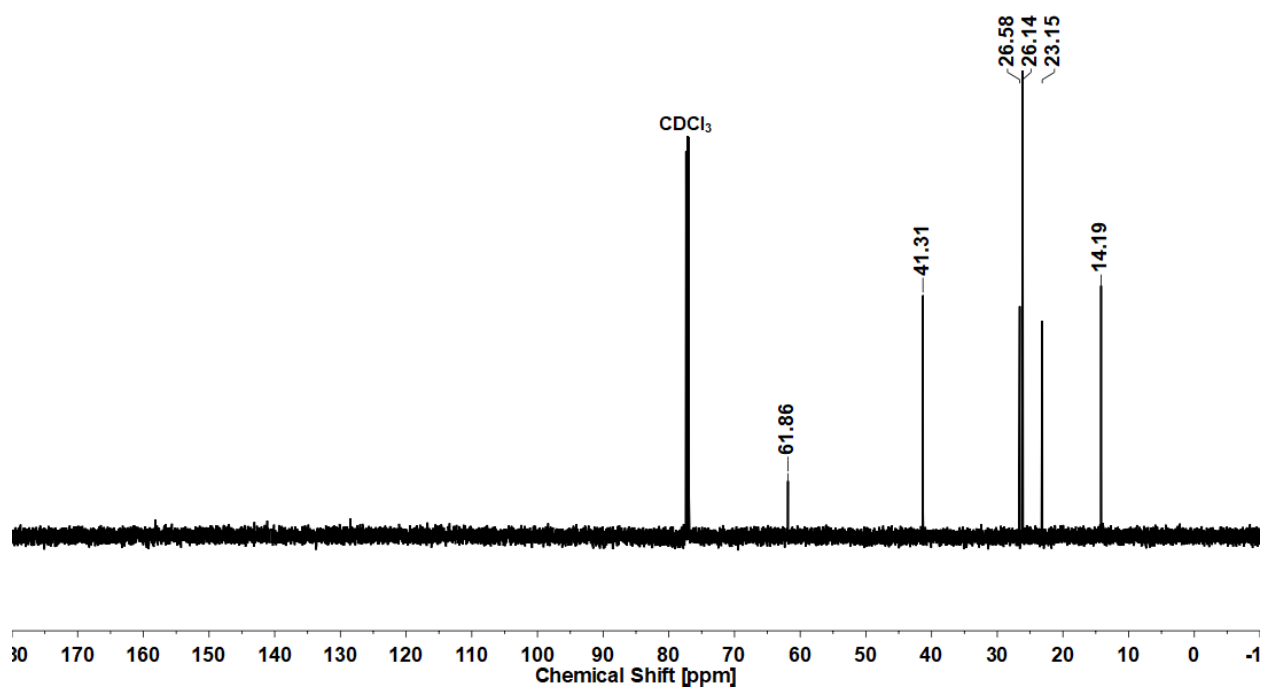


**Figure S-19.**  $^1\text{H}$  NMR spectra of  $(^{\text{Ar}}\text{L})\text{Co}(\text{py})$  and  $(^{\text{Ar}}\text{L})\text{Co}(\text{py})_2$ . (A)  $^1\text{H}$  NMR spectrum of a catalytic reaction (5 mol% of **2** at 80 °C) in benzene- $d_6$  after full consumption of **7** in the presence of 10 equiv of pyridine- $d_5$ . Blue markers indicate peaks from  $(^{\text{Ar}}\text{L})\text{Co}(\text{py})$  and green markers indicate peaks from the corresponding cobalt tetrazido complex  $(^{\text{Ar}}\text{L})\text{Co}(\kappa^2\text{-N}_4\text{R}_2)$ . (B)  $^1\text{H}$  NMR spectrum of a catalytic reaction (5 mol% of **2** at 80 °C) in benzene- $d_6$  after full consumption of **7** in the presence of 100 equiv of pyridine- $d_5$ . (C)  $^1\text{H}$  NMR spectrum of  $(^{\text{Ar}}\text{L})\text{Co}$  in the presence of 100 equiv of  $d_5$ -pyridine in benzene- $d_6$ . Red markers indicate peaks from  $(^{\text{Ar}}\text{L})\text{Co}(\text{py})_2$ .

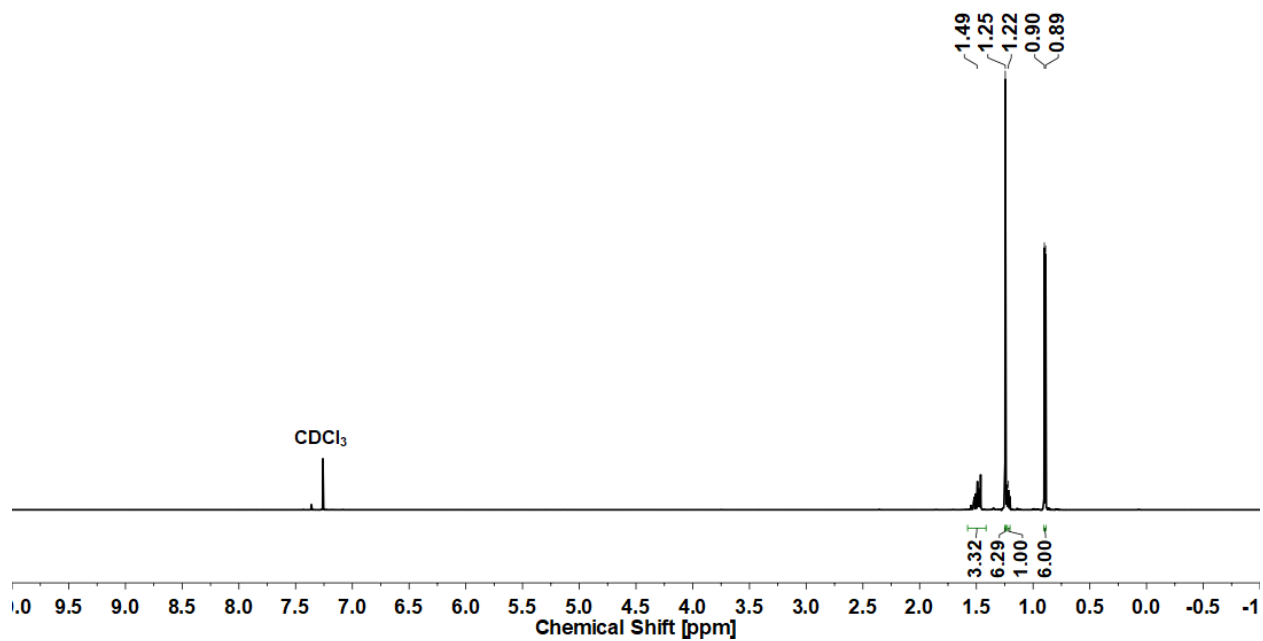
# NMR Spectra of Organoazides and Substituted Pyrrolidines.



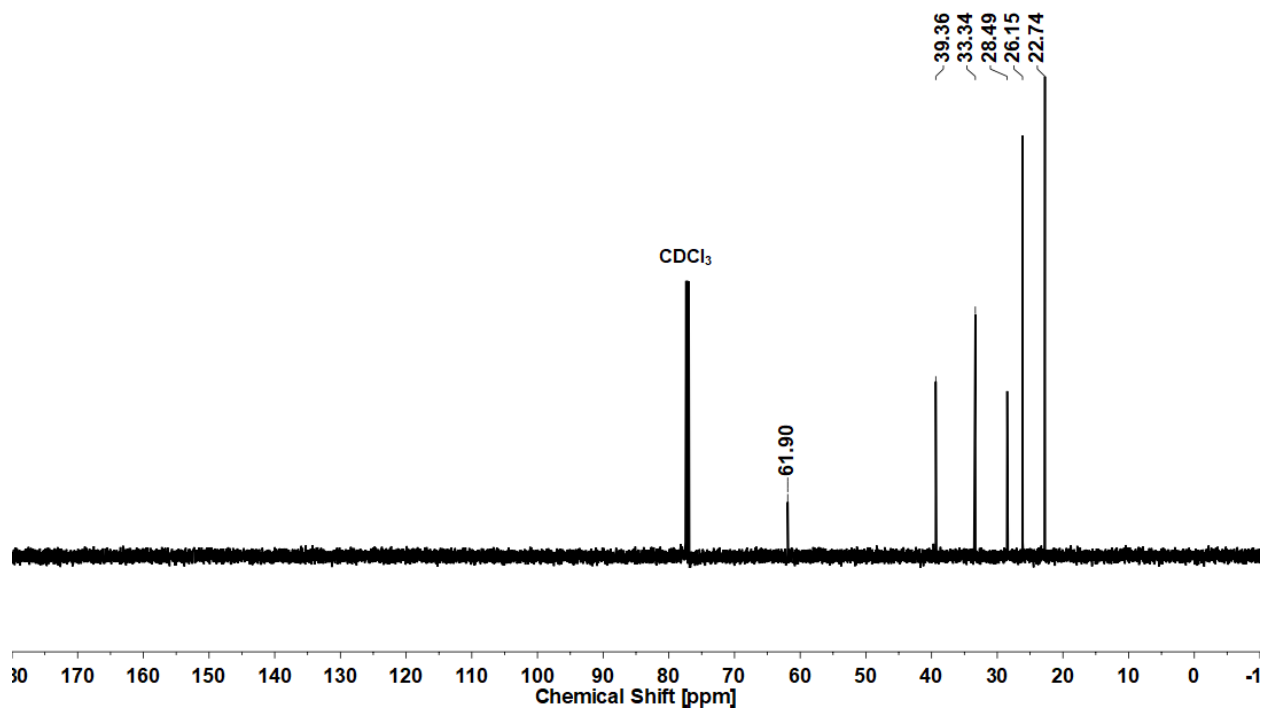
**Figure S-20.** <sup>1</sup>H NMR spectrum of 2-azido-2-methylhexane in chloroform-*d*.



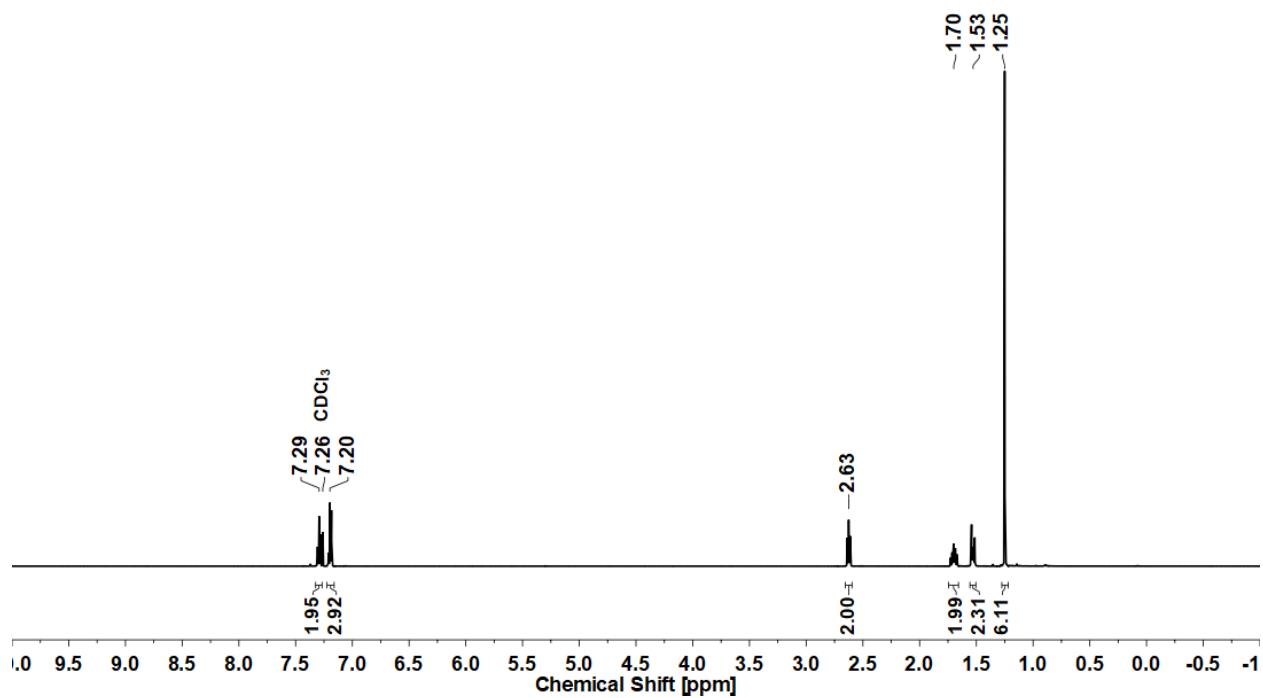
**Figure S-21.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2-azido-2-methylhexane in chloroform-*d*.



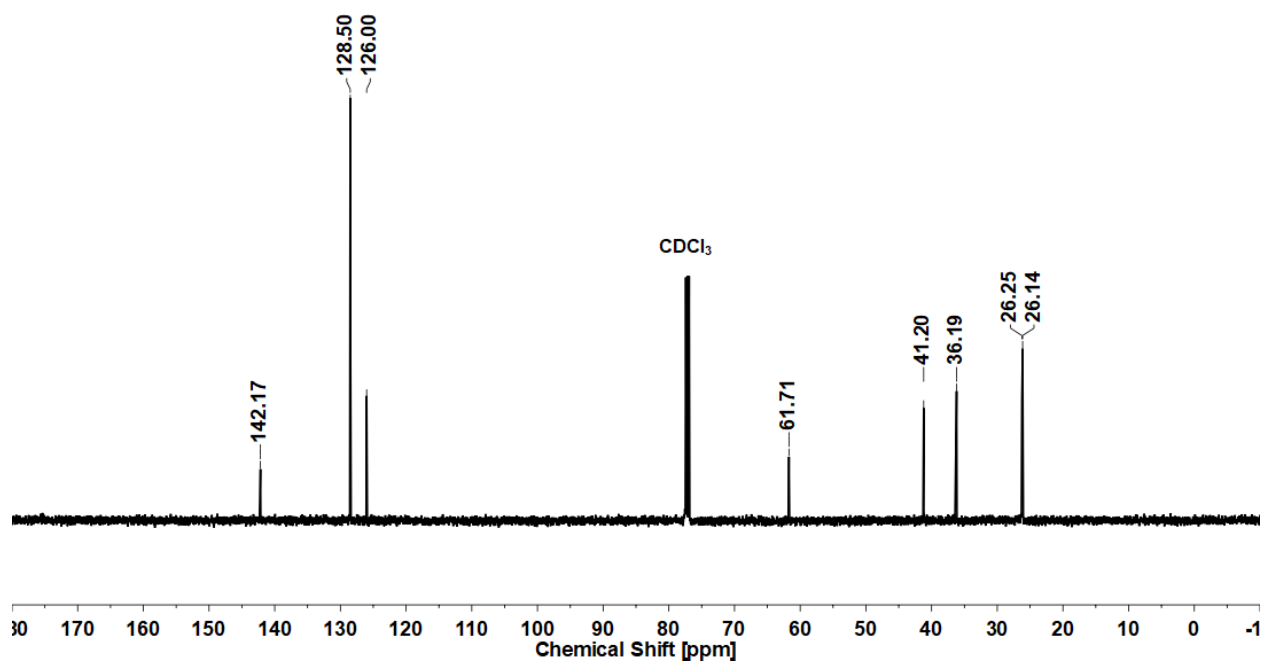
**Figure S-22.** <sup>1</sup>H NMR spectrum of 2-azido-2,5-dimethylhexane in chloroform-*d*.



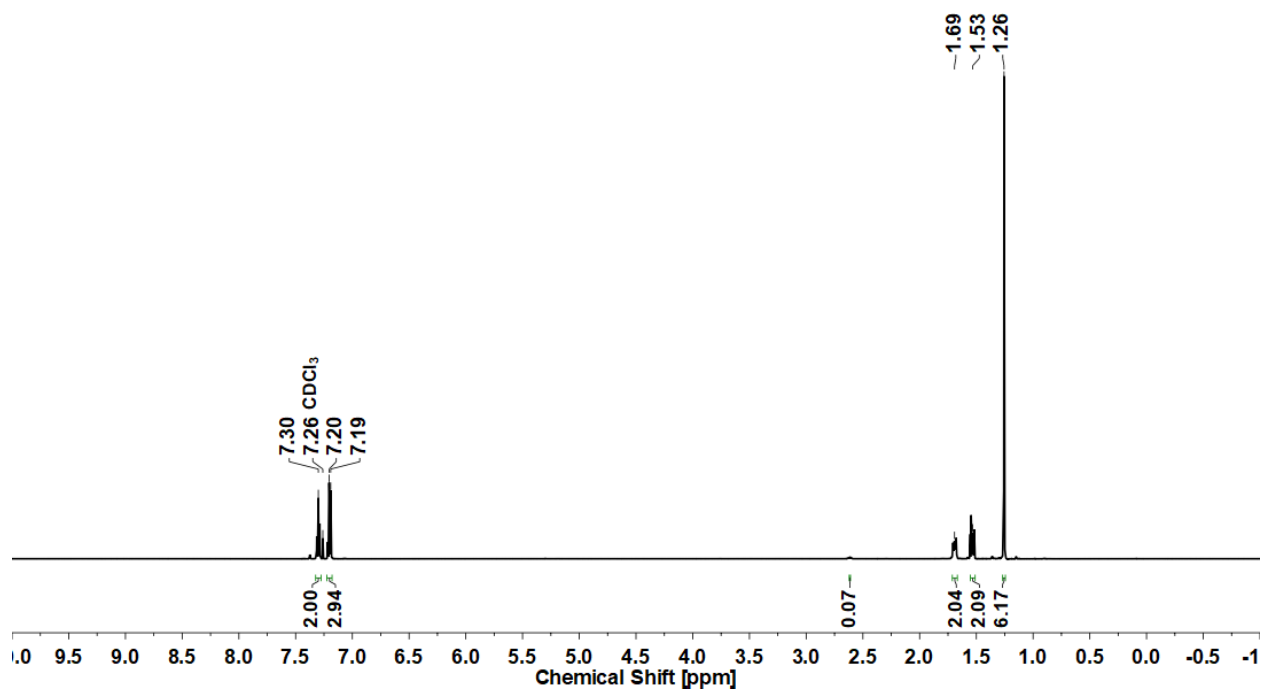
**Figure S-23.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2-azido-2,5-dimethylhexane in chloroform-*d*.



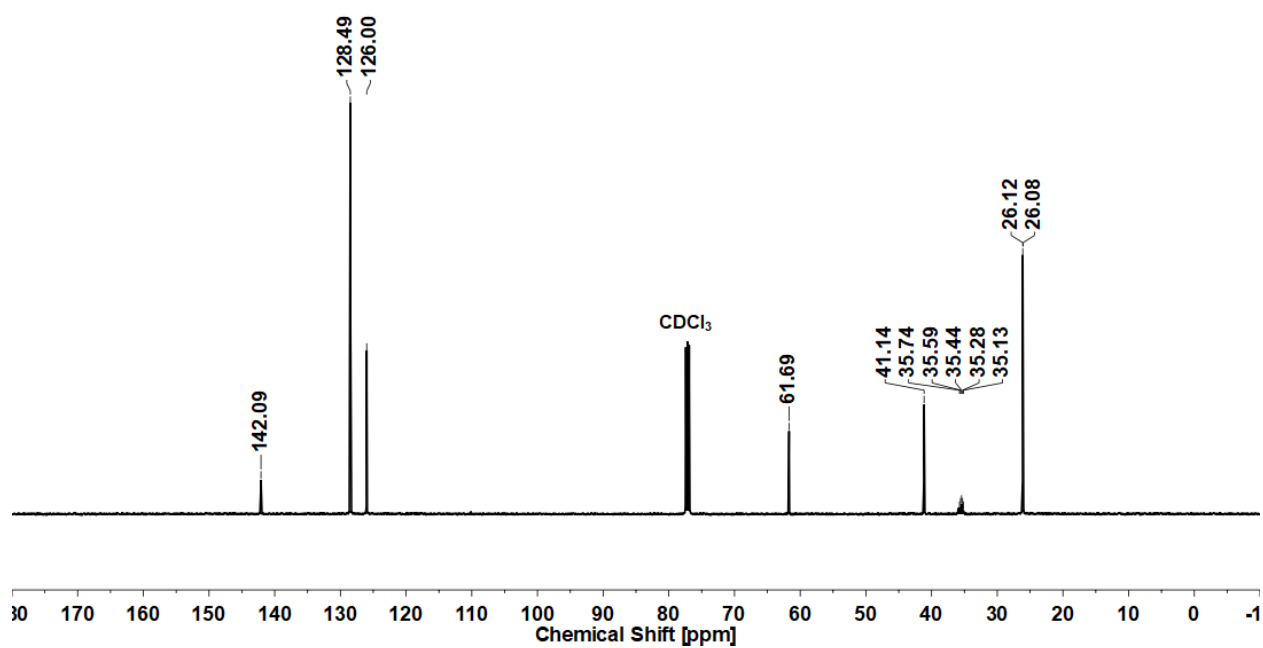
**Figure S-24.** <sup>1</sup>H NMR spectrum of (4-azido-4-methylpentyl)benzene in chloroform-*d*.



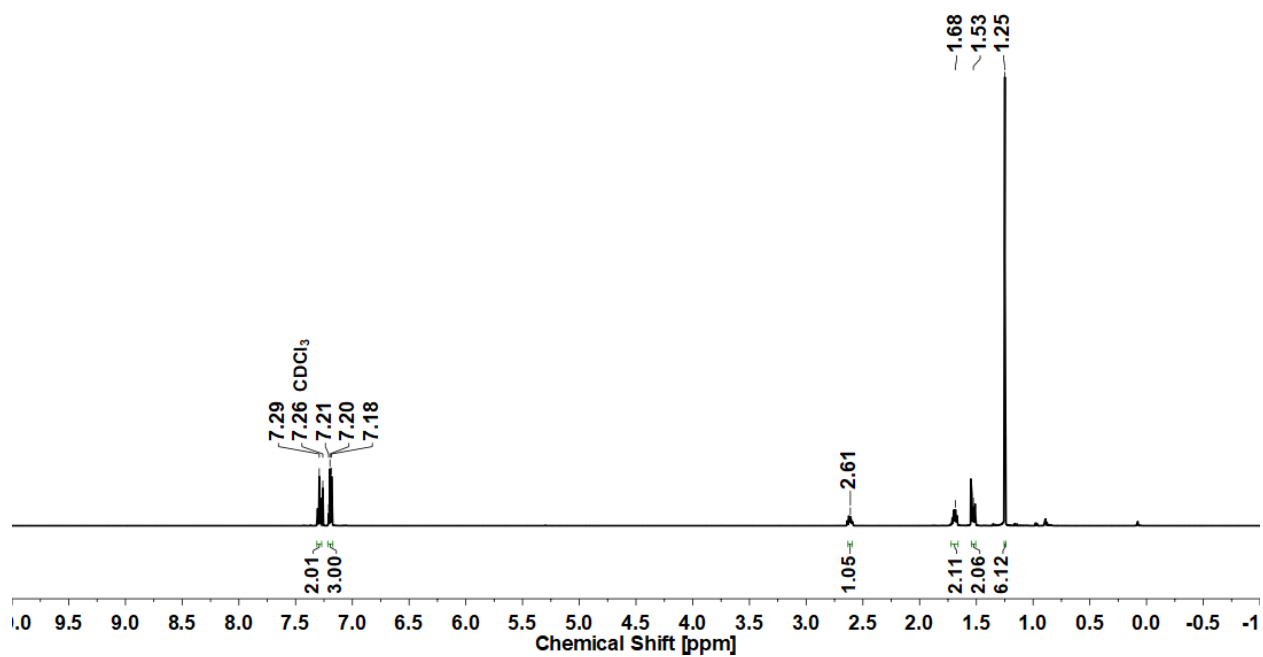
**Figure S-25.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of (4-azido-4-methylpentyl)benzene in chloroform-*d*.



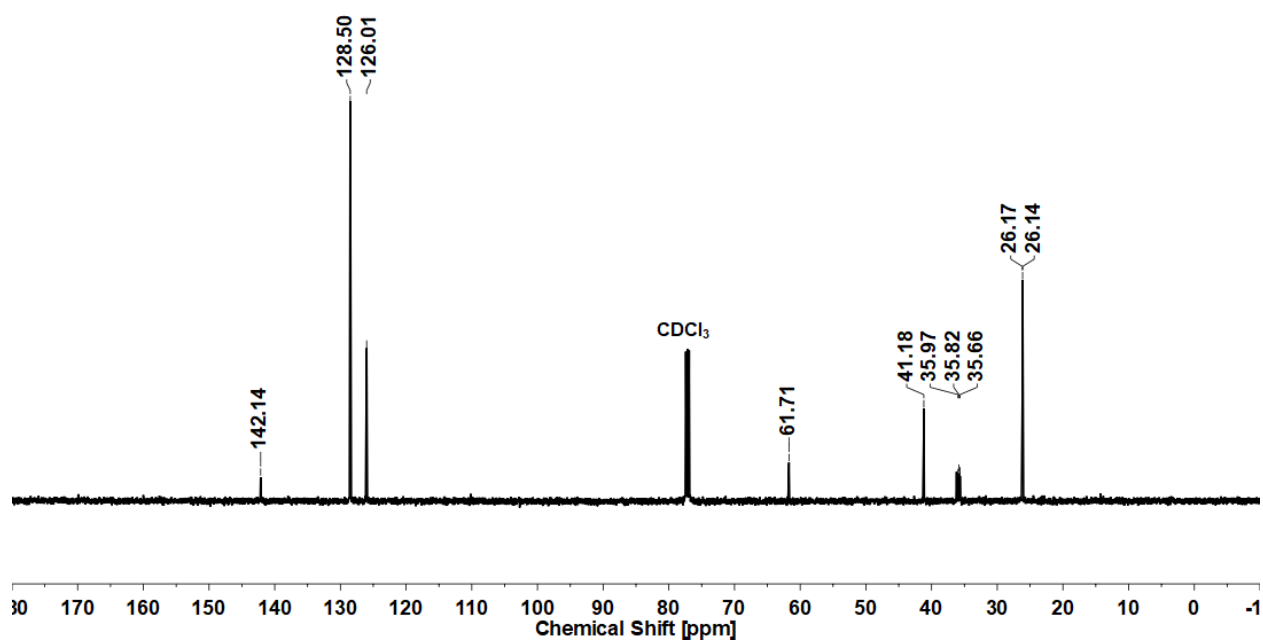
**Figure S-26.** <sup>1</sup>H NMR spectrum of (4-azido-4-methylpentyl-1,1-*d*<sub>2</sub>)benzene in chloroform-*d*.



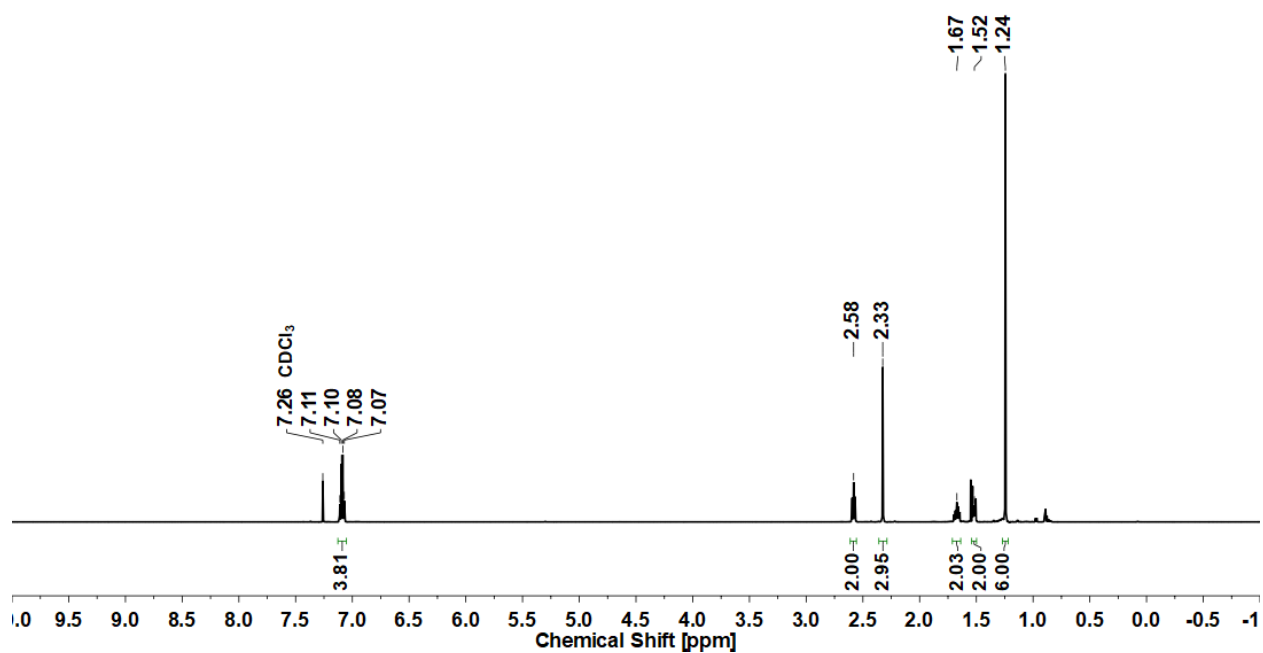
**Figure S-27.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of (4-azido-4-methylpentyl-1,1-*d*<sub>2</sub>)benzene in chloroform-*d*.



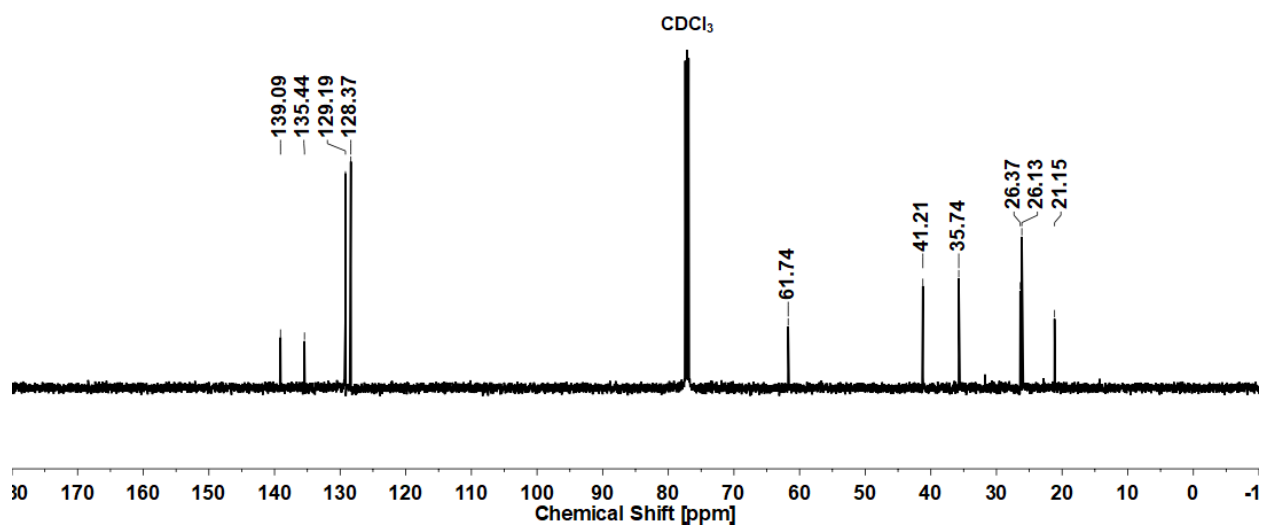
**Figure S-28.** <sup>1</sup>H NMR spectrum of (4-azido-4-methylpentyl-1-*d*)benzene in chloroform-*d*.



**Figure S-29.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of (4-azido-4-methylpentyl-1-*d*)benzene in chloroform-*d*.

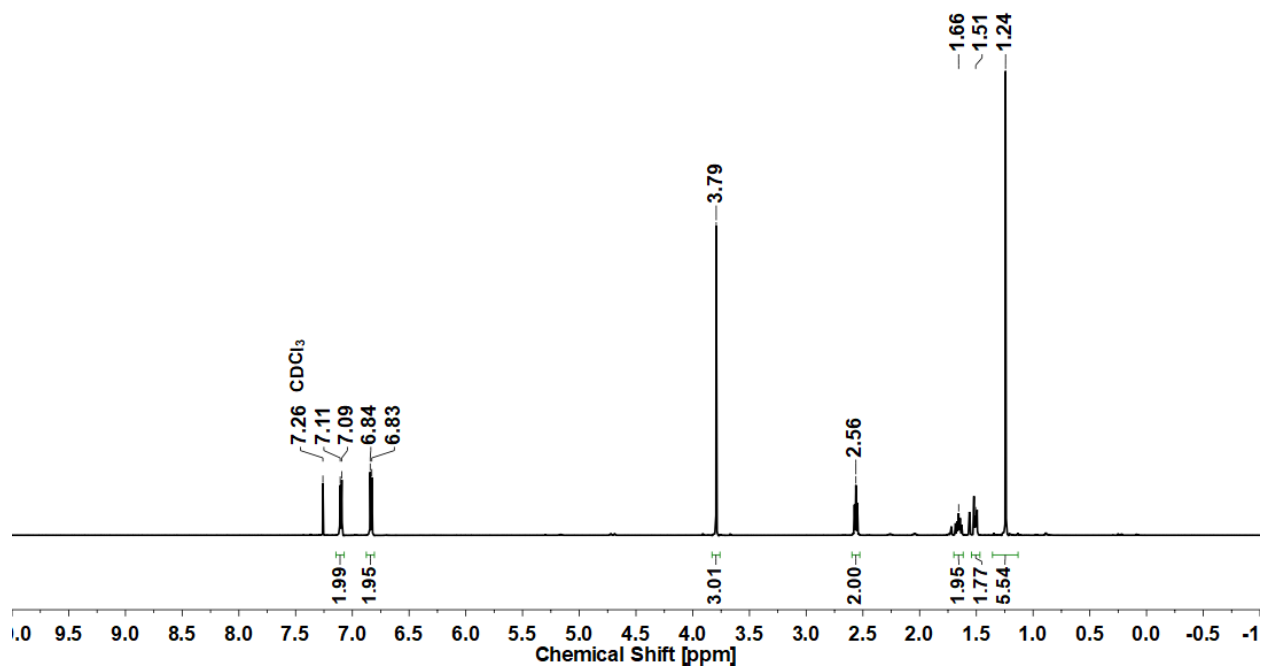


**Figure S-30.** <sup>1</sup>H NMR spectrum of 1-(4-azido-4-methylpentyl)-4-methylbenzene in chloroform-*d*.

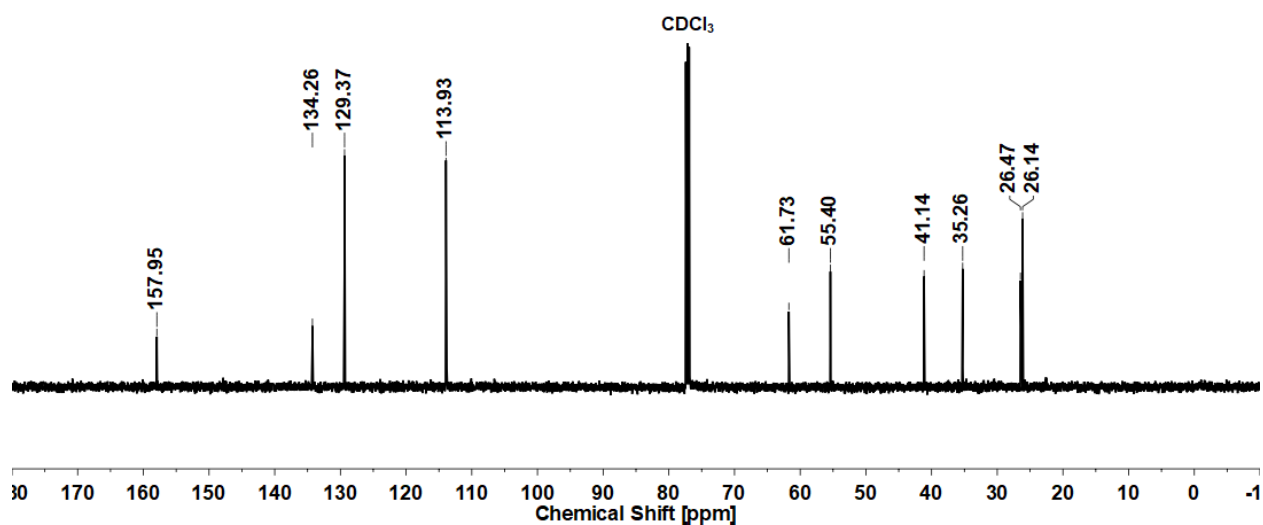


**Figure S-31.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 1-(4-azido-4-methylpentyl)-4-methylbenzene in chloroform-*d*.

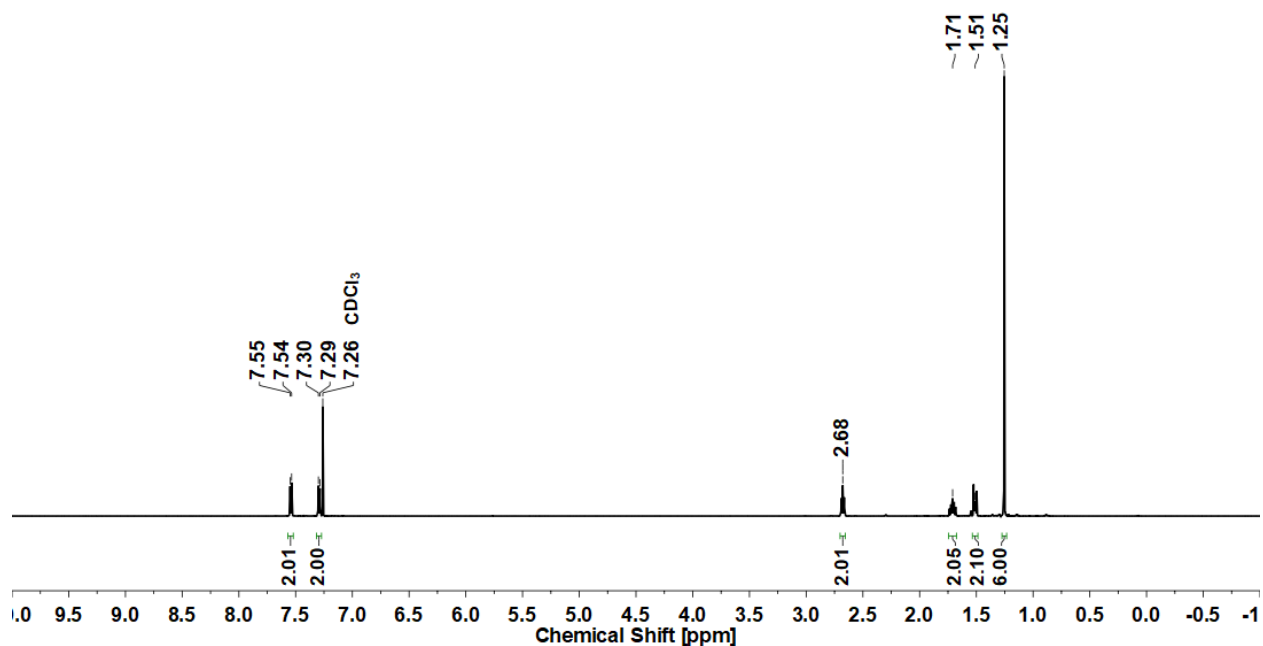




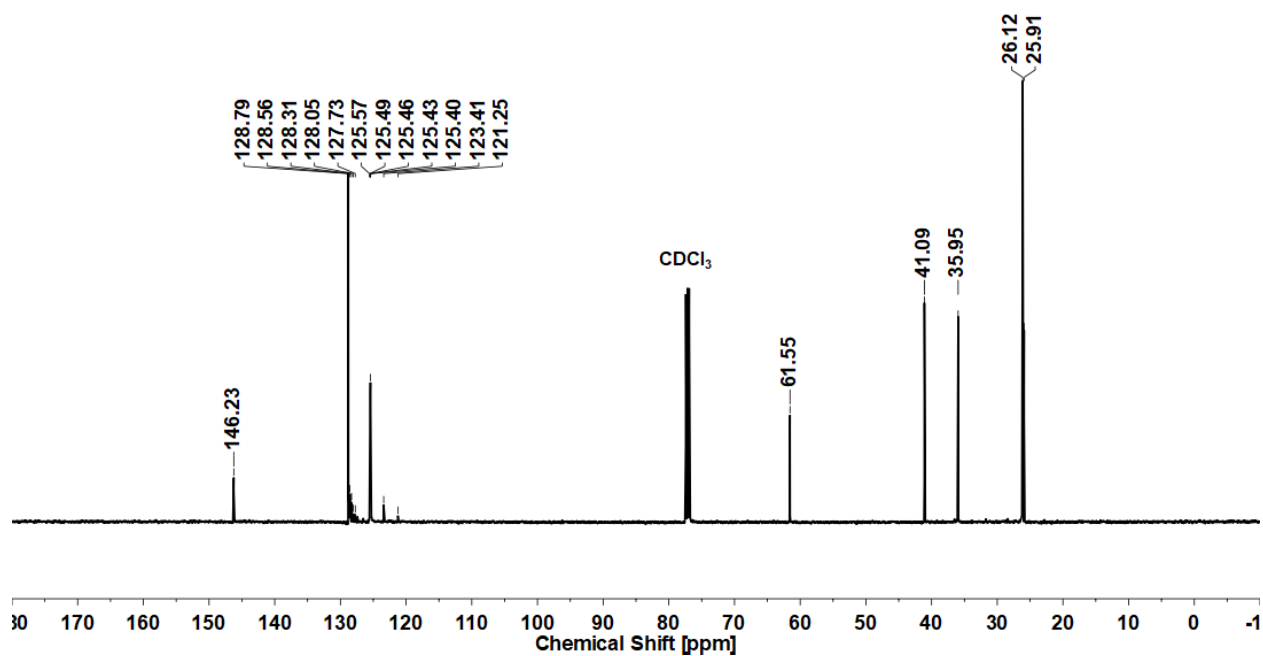
**Figure S-32.** <sup>1</sup>H NMR spectrum of 1-(4-azido-4-methylpentyl)-4-methoxybenzene in chloroform-*d*.



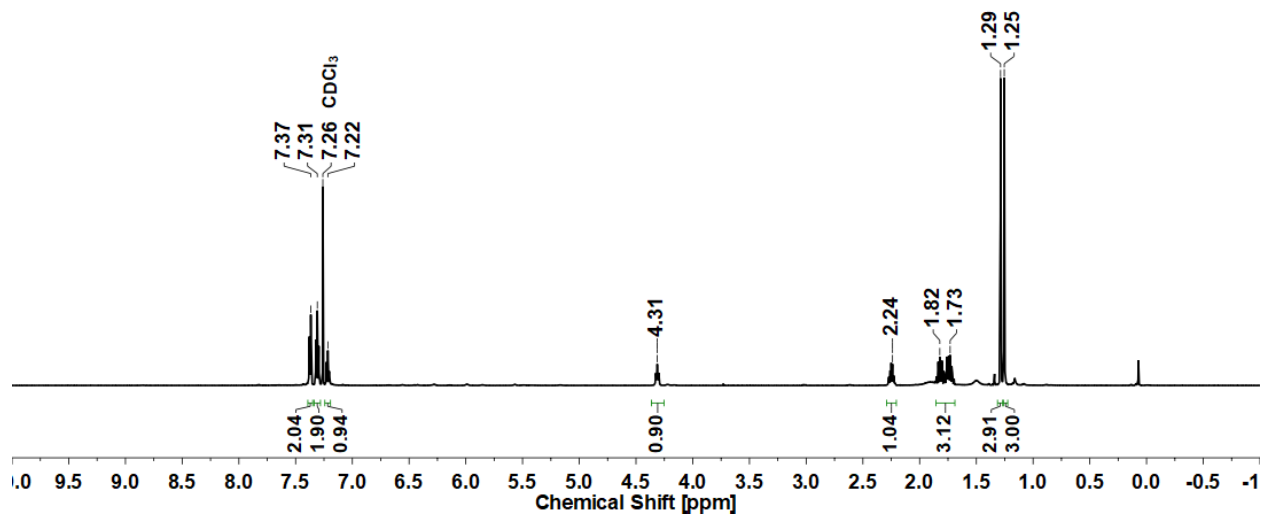
**Figure S-33.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 1-(4-azido-4-methylpentyl)-4-methoxybenzene in chloroform-*d*.



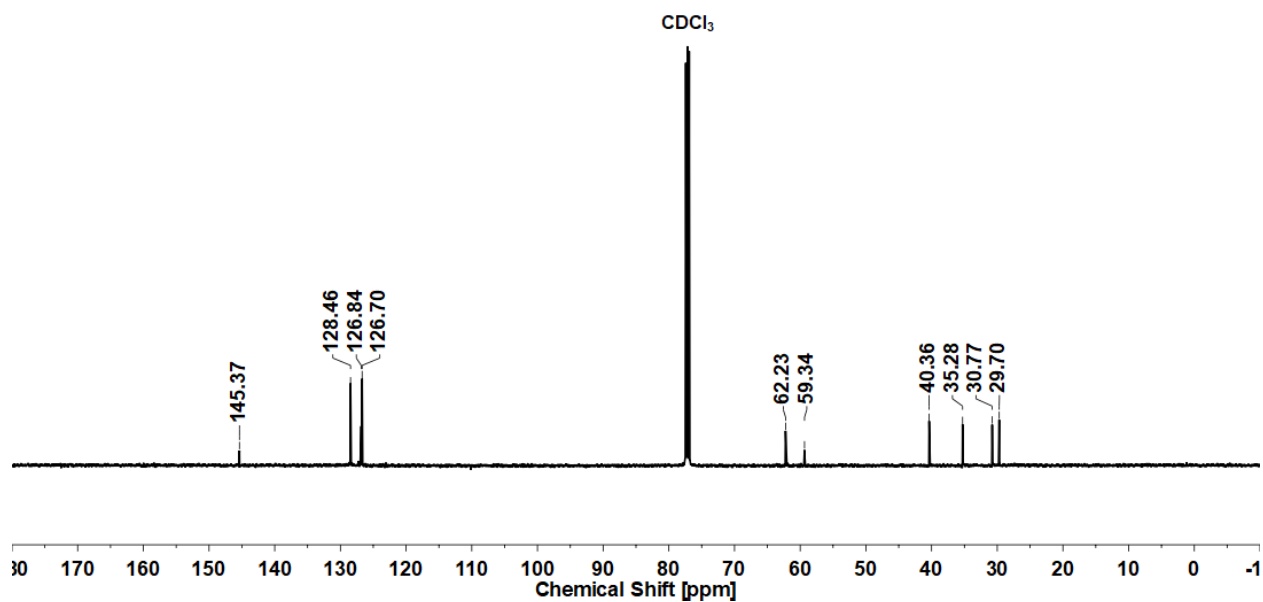
**Figure S-34.** <sup>1</sup>H NMR spectrum of 1-(4-azido-4-methylpentyl)-4-(trifluoromethyl)benzene in chloroform-*d*.



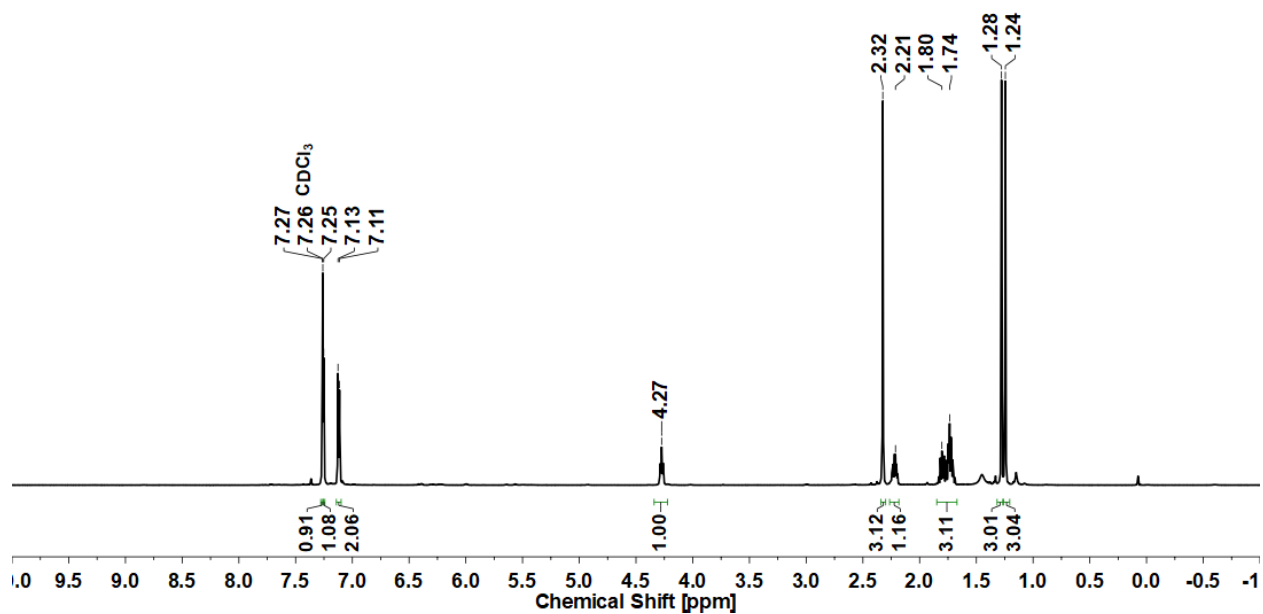
**Figure S-35.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 1-(4-azido-4-methylpentyl)-4-(trifluoromethyl)benzene in chloroform-*d*.



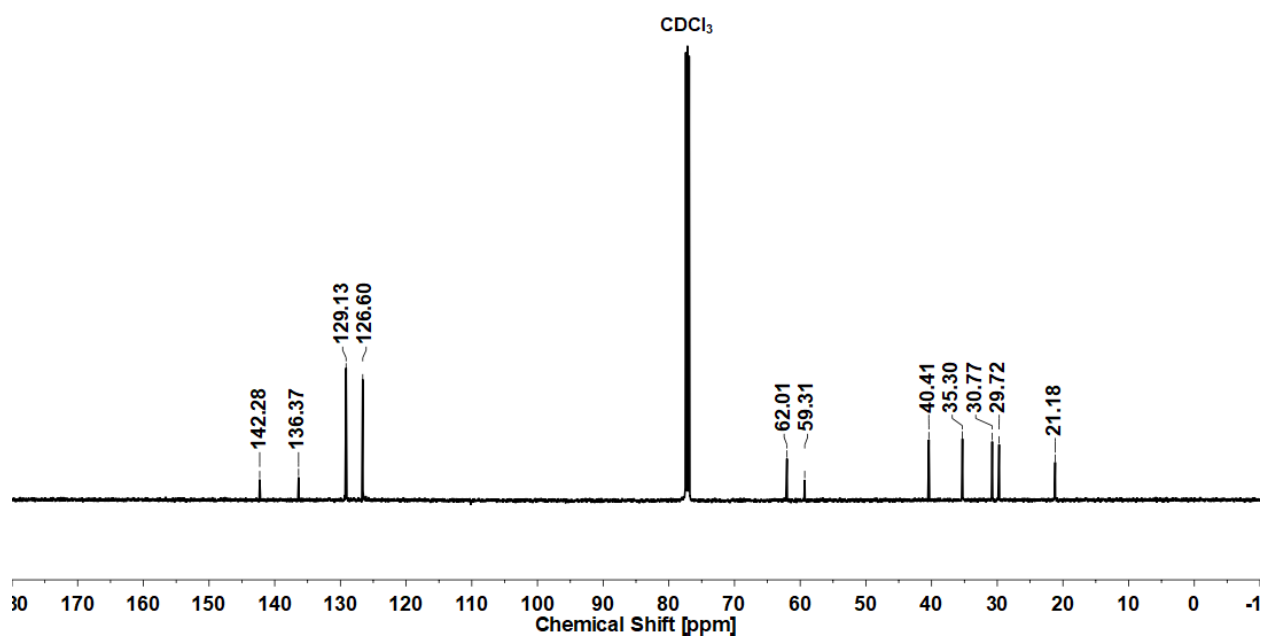
**Figure S-36.** <sup>1</sup>H NMR spectrum of 2,2-dimethyl-5-phenylpyrrolidine in chloroform-*d*.



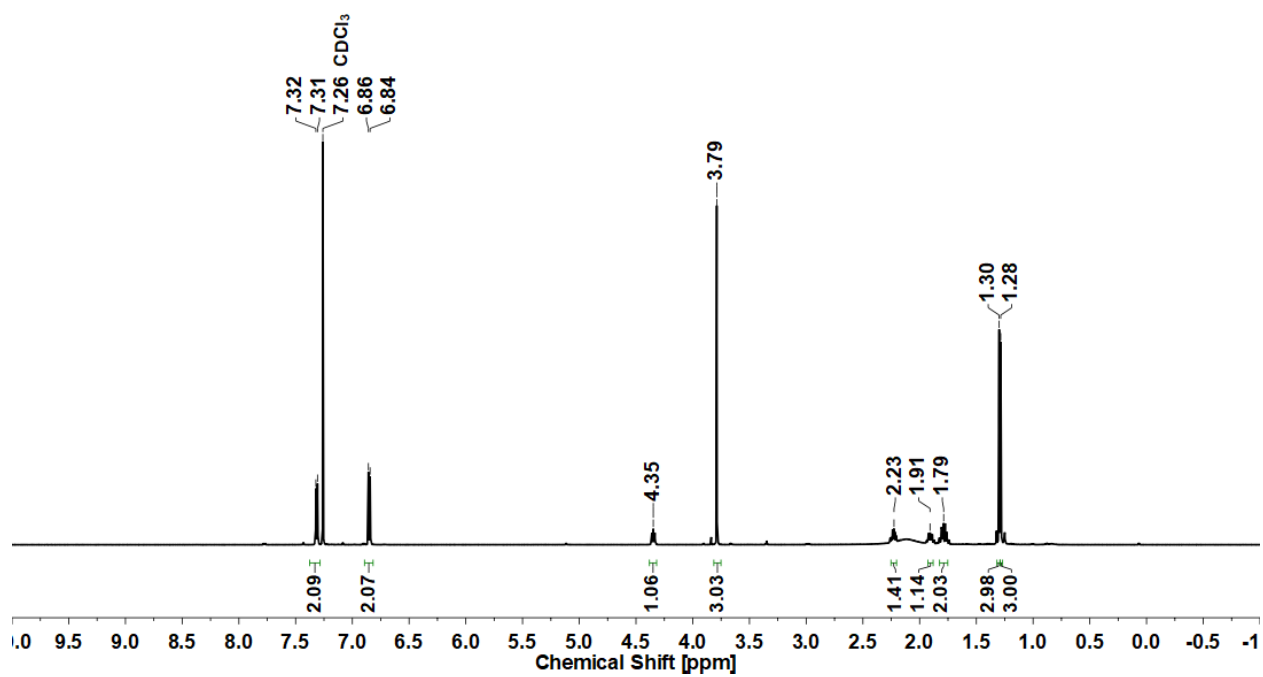
**Figure S-37.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2,2-dimethyl-5-phenylpyrrolidine in chloroform-*d*.



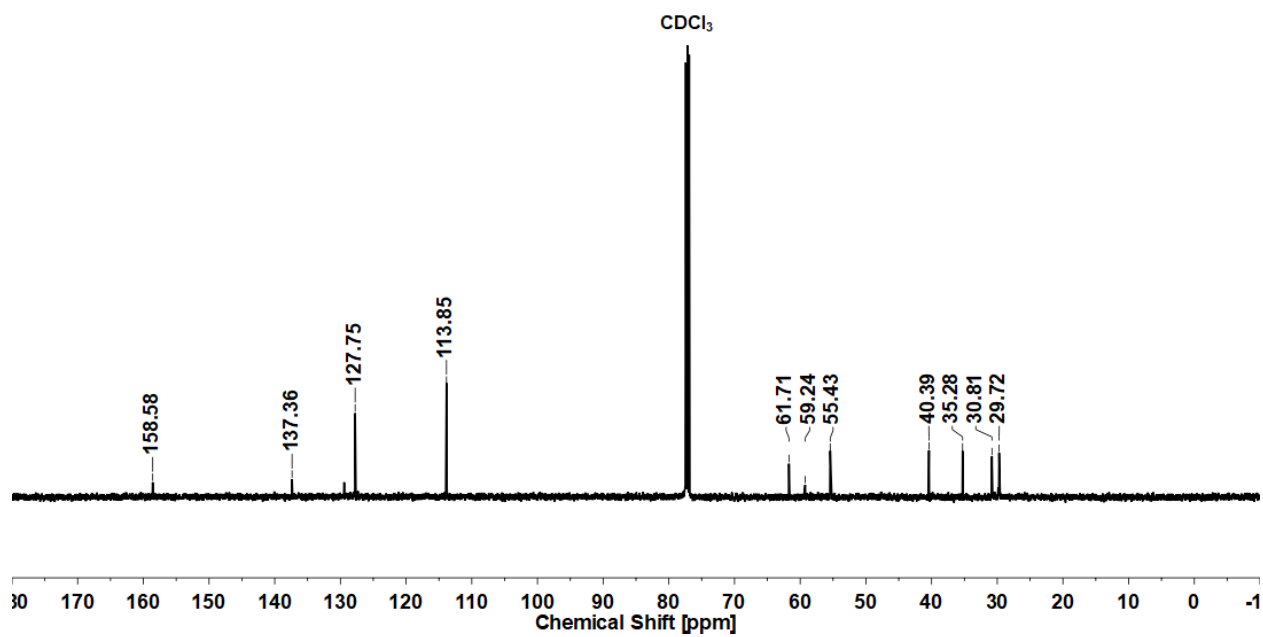
**Figure S-38.** <sup>1</sup>H NMR spectrum of 2,2-dimethyl-5-(*p*-tolyl)pyrrolidine in chloroform-*d*.



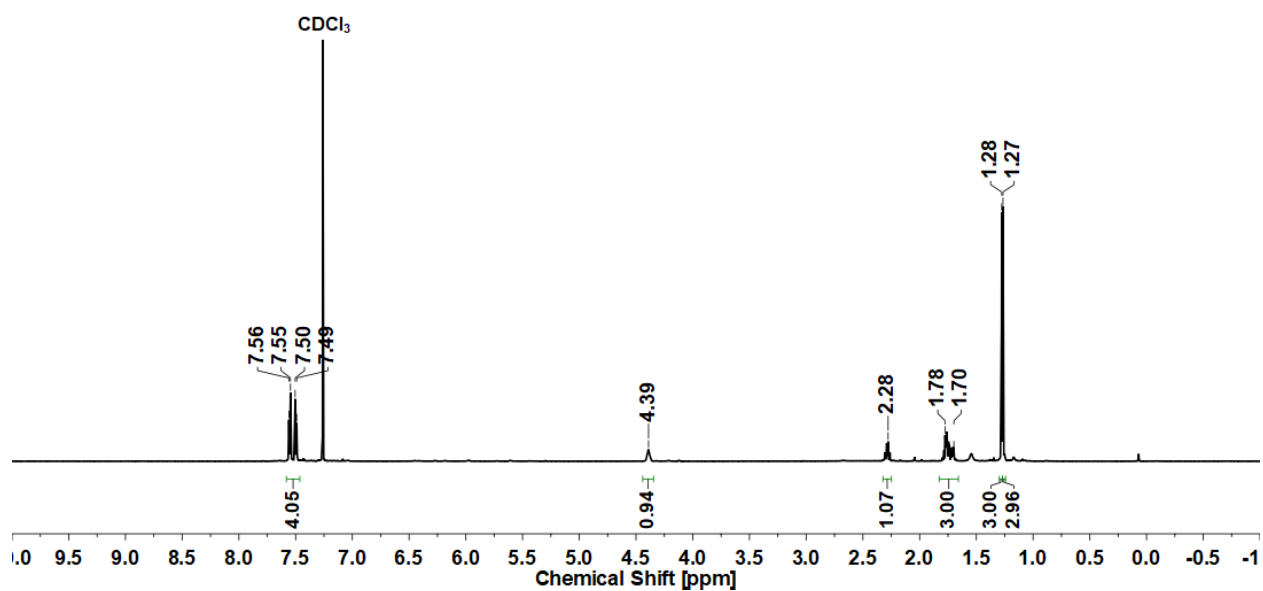
**Figure S-39.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2,2-dimethyl-5-(*p*-tolyl)pyrrolidine in chloroform-*d*.



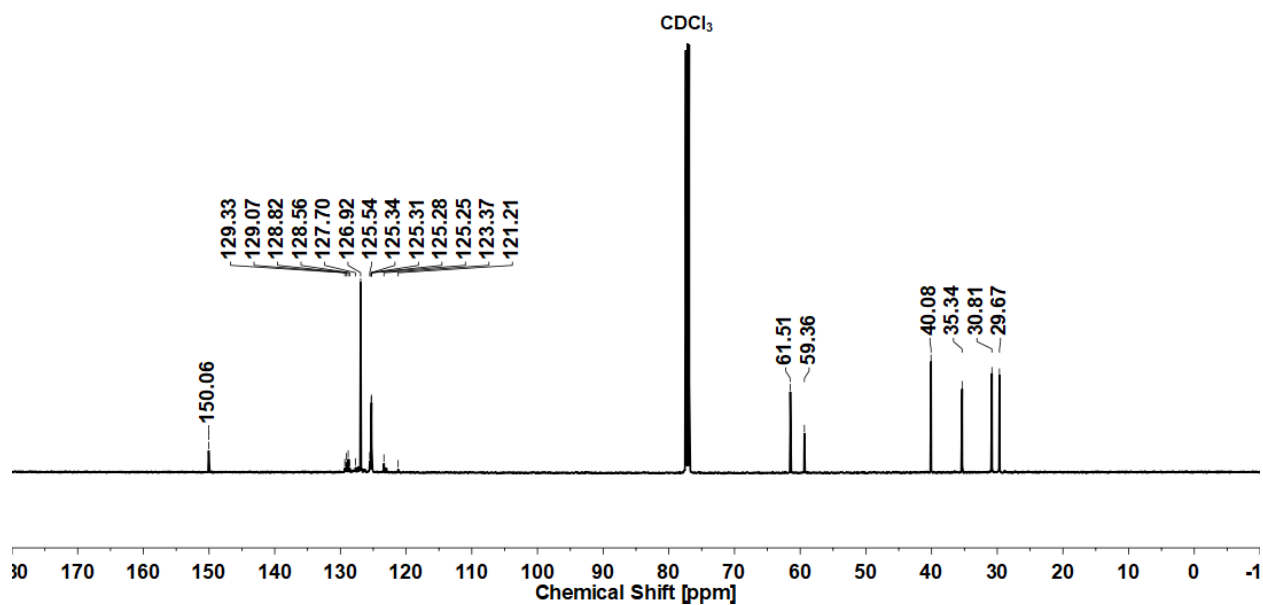
**Figure S-40.** <sup>1</sup>H NMR spectrum of 5-(4-methoxyphenyl)-2,2-dimethylpyrrolidine in chloroform-*d*.



**Figure S-41** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 5-(4-methoxyphenyl)-2,2-dimethylpyrrolidine in chloroform-*d*.



**Figure S-42.** <sup>1</sup>H NMR spectrum of 2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pyrrolidine in chloroform-*d*.



**Figure S-43.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pyrrolidine in chloroform-*d*.

## X-Ray Diffraction Techniques.

All structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo K $\alpha$  (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data was collected as a series of  $\phi$  and/or  $\omega$  scans. Data was integrated using SAINT<sup>21</sup> and scaled with either a numerical or multi-scan absorption correction using SADABS<sup>19</sup>. The structures were solved by direct methods or Patterson maps using SHELXS-97<sup>22</sup> and refined against  $F^2$  on all data by full matrix least squares with SHELXL-97<sup>20</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the atoms they are linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

**(<sup>Ar</sup>L)CoBr (1).** The structure was solved in the monoclinic space group  $C2/c$  with 8 molecules per unit cell. Benzene solvent molecules exhibited positional disorder and were modeled using similarity constraints.

**(<sup>Ar</sup>L)Co (2).** The structure was solved in the triclinic space group  $P\bar{1}$  with 2 molecules per unit cell. One of the phenyl rings in the molecule exhibited positional disorder and was refined using similarity constraints. One of the benzene solvent molecules exhibited positional disorder and was refined using similarity constraints.

**(<sup>Ar</sup>L)Co(NR'), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> (3).** The structure was solved in the triclinic space group  $P\bar{1}$  with 2 molecules per unit cell. One of alkyl groups in the molecule exhibited positional disorder and was refined using similarity constraints. Benzene solvent molecules exhibited positional disorder and were modeled using similarity constraints.

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<sup>21</sup> APEX2 Software Suite; Bruker AXS: Madison, WI, 2014.

<sup>22</sup> Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112-122

**(<sup>Ar</sup>L)Co(NR'), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> (4).** The structure was solved in the triclinic space group  $P\bar{1}$  with 2 molecules per unit cell.

**(<sup>Ar</sup>L)Co(NAd) (10).** The structure was solved in the triclinic space group  $P\bar{1}$  with 2 molecules per unit cell. One of the adamantyl substituents exhibited positional disorder and was refined using similarity constraints. One of the phenyl rings in the molecule exhibited positional disorder and was refined using similarity constraints.

**(<sup>Ar</sup>L)Co( $\kappa^2$ -N<sub>4</sub>R'<sub>2</sub>), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> (5).** The structure was solved in the monoclinic space group  $P2_1/c$  with 4 molecules per unit cell.

**(<sup>Ar</sup>L)Co( $\kappa^2$ -N<sub>4</sub>R'<sub>2</sub>), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> (6).** The structure was solved in the monoclinic space group  $P2_1/c$  with 4 molecules per unit cell. One of alkyl groups in the molecule exhibited positional disorder and was refined using similarity constraints.

**(<sup>Ar</sup>L)Co( $\kappa^2$ -N<sub>4</sub>Ad<sub>2</sub>) (11).** The structure was solved in the monoclinic space group  $C2/c$  with 8 molecules per unit cell.

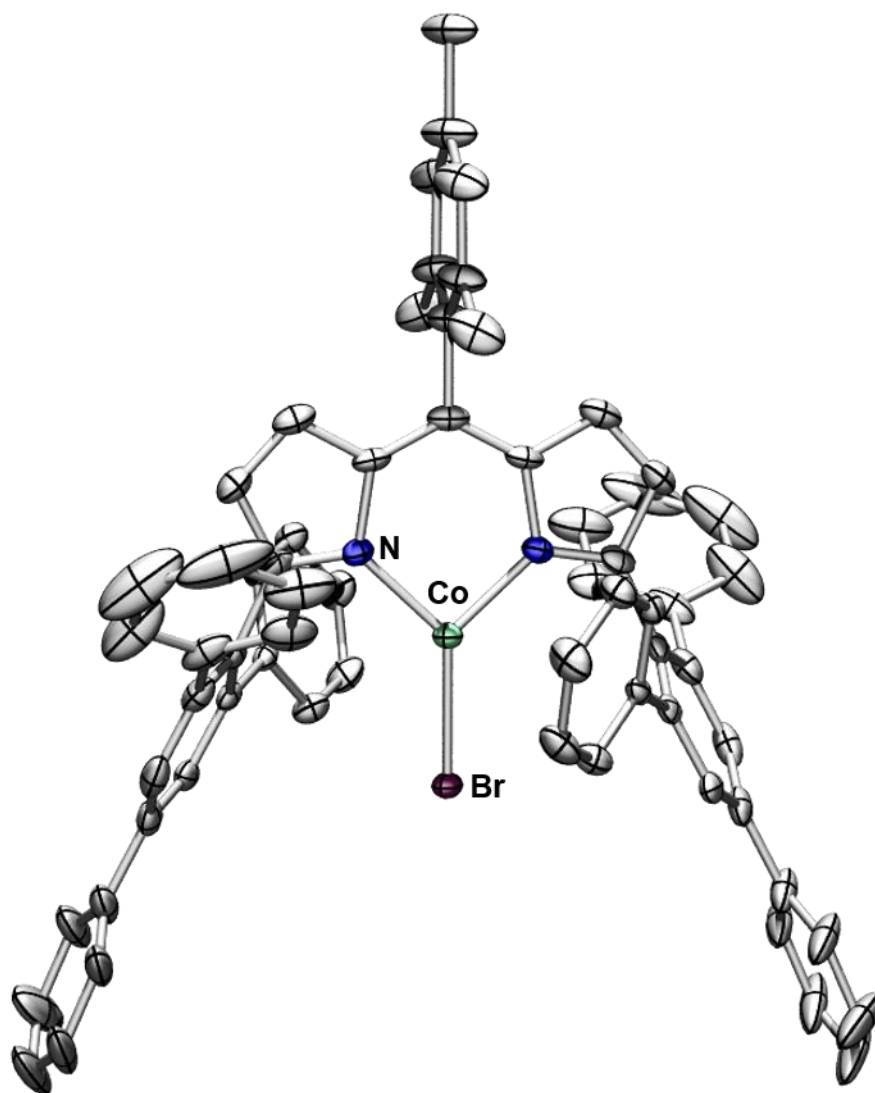


**Table S-9.** X-ray diffraction experimental details<sup>a,b</sup>

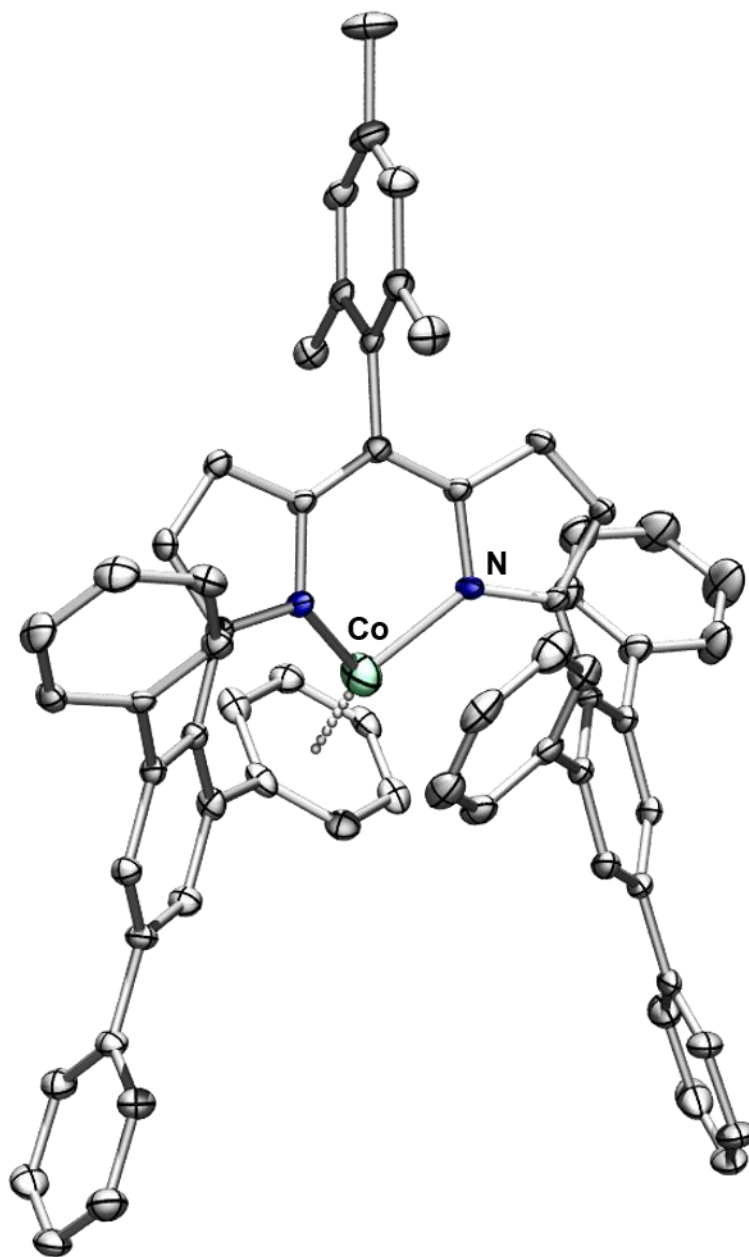
	( <sup>Ar</sup> L)CoBr (1)	( <sup>Ar</sup> L)Co (2)	( <sup>Ar</sup> L)Co(NR') R' = C(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> (3)	( <sup>Ar</sup> L)Co(NR') R' = C(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> (4)
<b>Moiety</b>	C <sub>66</sub> H <sub>49</sub> BrCoN <sub>2</sub> ;	C <sub>66</sub> H <sub>49</sub> CoN <sub>2</sub> ;	C <sub>73</sub> H <sub>64</sub> CoN <sub>3</sub> ;	C <sub>74</sub> H <sub>66</sub> CoN <sub>3</sub>
<b>Formula</b>	3×(C <sub>6</sub> H <sub>6</sub> )	3×(C <sub>6</sub> H <sub>6</sub> )	1×(C <sub>6</sub> H <sub>6</sub> )	
<b>FW</b>	1243.31	1163.40	1120.38	1056.30
<b>Crystal System</b>	monoclinic	triclinic	triclinic	triclinic
<b>Space Group</b>	<i>C</i> 2/ <i>c</i> (8)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)
<b>(Z)</b>				
<b>a (Å)</b>	15.9671(16)	12.594(9)	11.9404(10)	12.0205(16)
<b>b (Å)</b>	22.041(2)	14.092(10)	16.2194(13)	16.024(2)
<b>c (Å)</b>	18.9148(18)	20.413(16)	16.2288(14)	16.411(2)
<b>α (°)</b>	90	75.348(11)	87.845(2)	87.612(3)
<b>β (°)</b>	106.561(2)	84.047(10)	87.553(2)	72.643(3)
<b>γ (°)</b>	90	64.970(12)	72.424(2)	88.139(3)
<b>Volume (Å<sup>3</sup>)</b>	6380.6(11)	3176(4)	2992.5(4)	3013.8(7)
<b>Calc. ρ (mg/m<sup>3</sup>)</b>	1.294	1.217	1.243	1.166
<b>μ (mm<sup>-1</sup>)</b>	0.94	0.32	0.34	0.33
<b>Crystal Size (mm)</b>	0.20×0.15×0.09	0.18×0.16×0.15	0.15×0.10×0.07	0.25×0.12×0.07
<b>Reflections</b>	5707	11197	10583	10696
<b>Completeness</b>	98.7%	99.6%	99.5%	99.6%
<b>GOF on F<sup>2</sup></b>	1.11	1.04	1.02	0.96
<b>R1, wR2<sup>c</sup> [I&gt;2σ(I)]</b>	0.089, 0.219	0.085, 0.273	0.073, 0.163	0.090, 0.235

	<sup>(ArL)</sup> Co(NAd) (10)	<sup>(ArL)</sup> Co( $\kappa^2$ -N <sub>4</sub> R' <sub>2</sub> ) R' = C(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> (5)	<sup>(ArL)</sup> Co( $\kappa^2$ -N <sub>4</sub> R' <sub>2</sub> ) R' = C(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> (6)	<sup>(ArL)</sup> Co( $\kappa^2$ -N <sub>4</sub> Ad <sub>2</sub> ) (11)
<b>Moiety Formula</b>	C <sub>76</sub> H <sub>64</sub> CoN <sub>3</sub> ; 1×(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	C <sub>80</sub> H <sub>79</sub> CoN <sub>6</sub>	C <sub>82</sub> H <sub>83</sub> CoN <sub>6</sub> 1×(C <sub>6</sub> H <sub>14</sub> )	C <sub>86</sub> H <sub>79</sub> CoN <sub>6</sub>
<b>FW</b>	1170.44	1183.49	1297.72	1255.55
<b>Crystal System</b>	triclinic	monoclinic	monoclinic	monoclinic
<b>Space Group</b>	<i>P</i> $\bar{1}$ (2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (4)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (4)	<i>C</i> 2/ <i>c</i> (8)
<b>(Z)</b>				
<b>a (Å)</b>	16.068(1)	12.7287(7)	13.4875(7)	47.858(10)
<b>b (Å)</b>	16.5966(10)	16.2170(9)	16.1414(8)	18.405(4)
<b>c (Å)</b>	24.9849(15)	33.8667(19)	33.4198(17)	18.553 (4)
<b><math>\alpha</math> (°)</b>	74.791(2)	90	90	90
<b><math>\beta</math> (°)</b>	73.522(2)	95.843(2)	98.765(2)	103.82(3)
<b><math>\gamma</math> (°)</b>	85.350(2)	90	90	90
<b>Volume (Å<sup>3</sup>)</b>	6165.2(7)	6954.5(7)	7190.8(6)	15869(6)
<b>Calc. <math>\rho</math> (mg/m<sup>3</sup>)</b>	1.261	1.130	1.199	1.051
<b><math>\mu</math> (mm<sup>-1</sup>)</b>	0.33	0.29	0.29	0.26
<b>Crystal Size (mm)</b>	0.15×0.06×0.04	0.40×0.20×0.07	0.40×0.19×0.06	0.25×0.10×0.09
<b>Reflections</b>	21790	12335	12739	14112
<b>Completeness</b>	99.5%	99.5%	99.7%	99.7%
<b>GOF on F<sup>2</sup></b>	1.01	1.06	1.07	1.05
<b>R1, wR2<sup>c</sup> [I&gt;2<math>\sigma</math>(I)]</b>	0.111, 0.227	0.049, 0.117	0.073, 0.168	0.044, 0.105

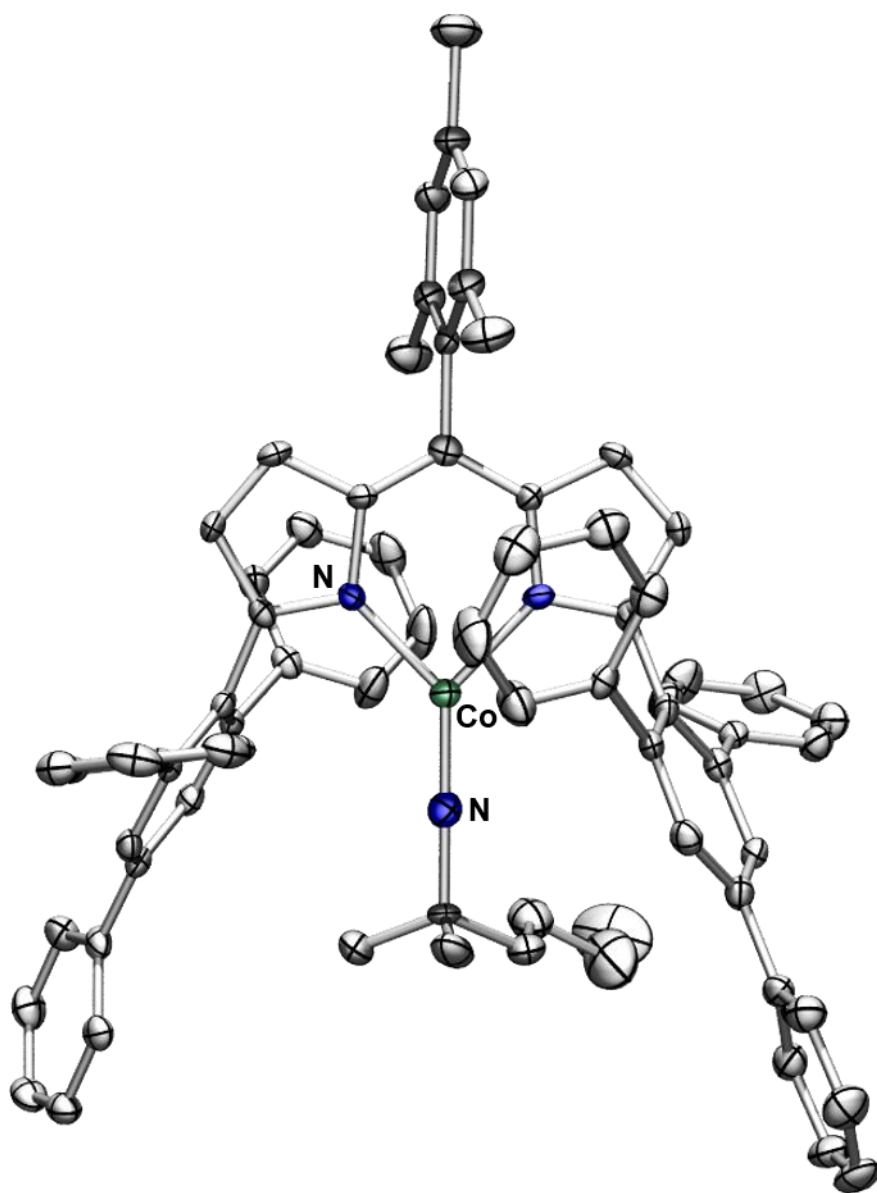
<sup>a</sup>  $\lambda$  = 0.71073 Å; <sup>b</sup> T = 100(2) K; <sup>c</sup> R1 =  $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$ , wR2 =  $\{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$



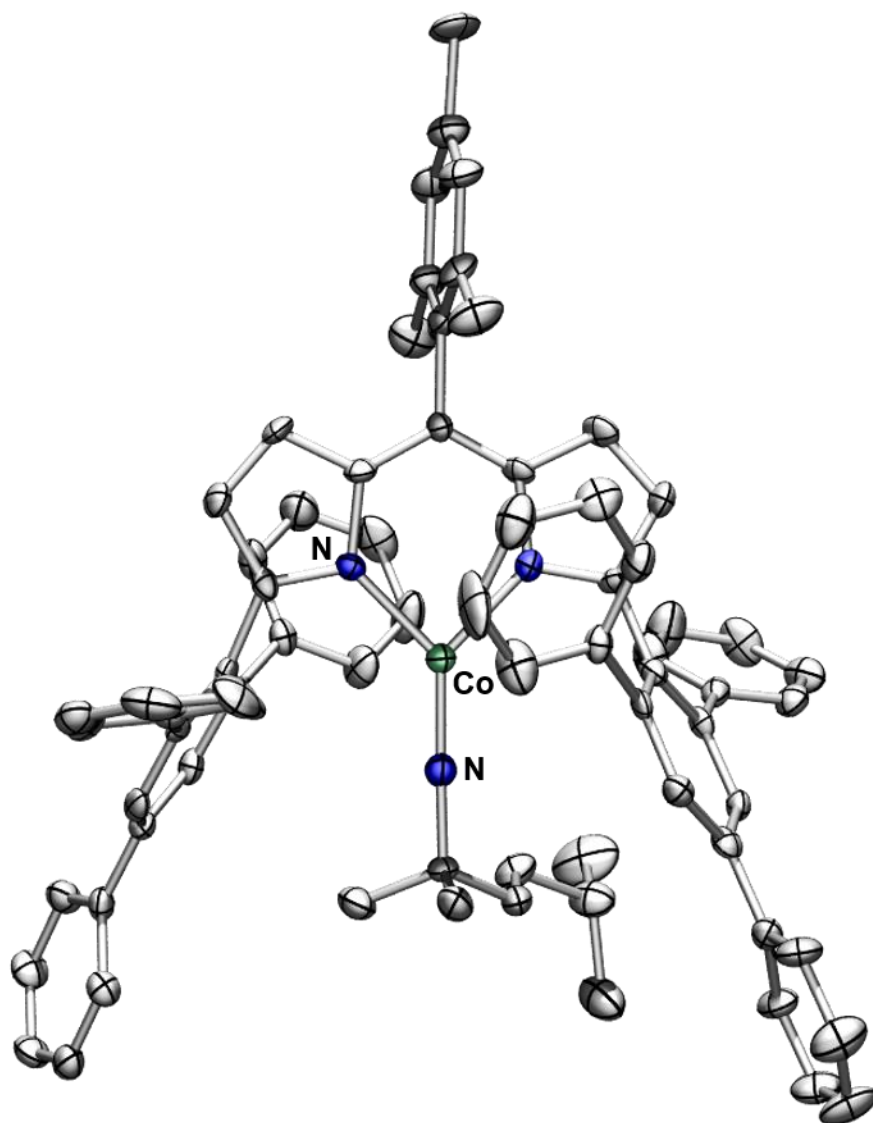
**Figure S-44.** Solid-state molecular structure for ( $^{\text{Ar}}\text{L}$ )CoBr (**1**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.



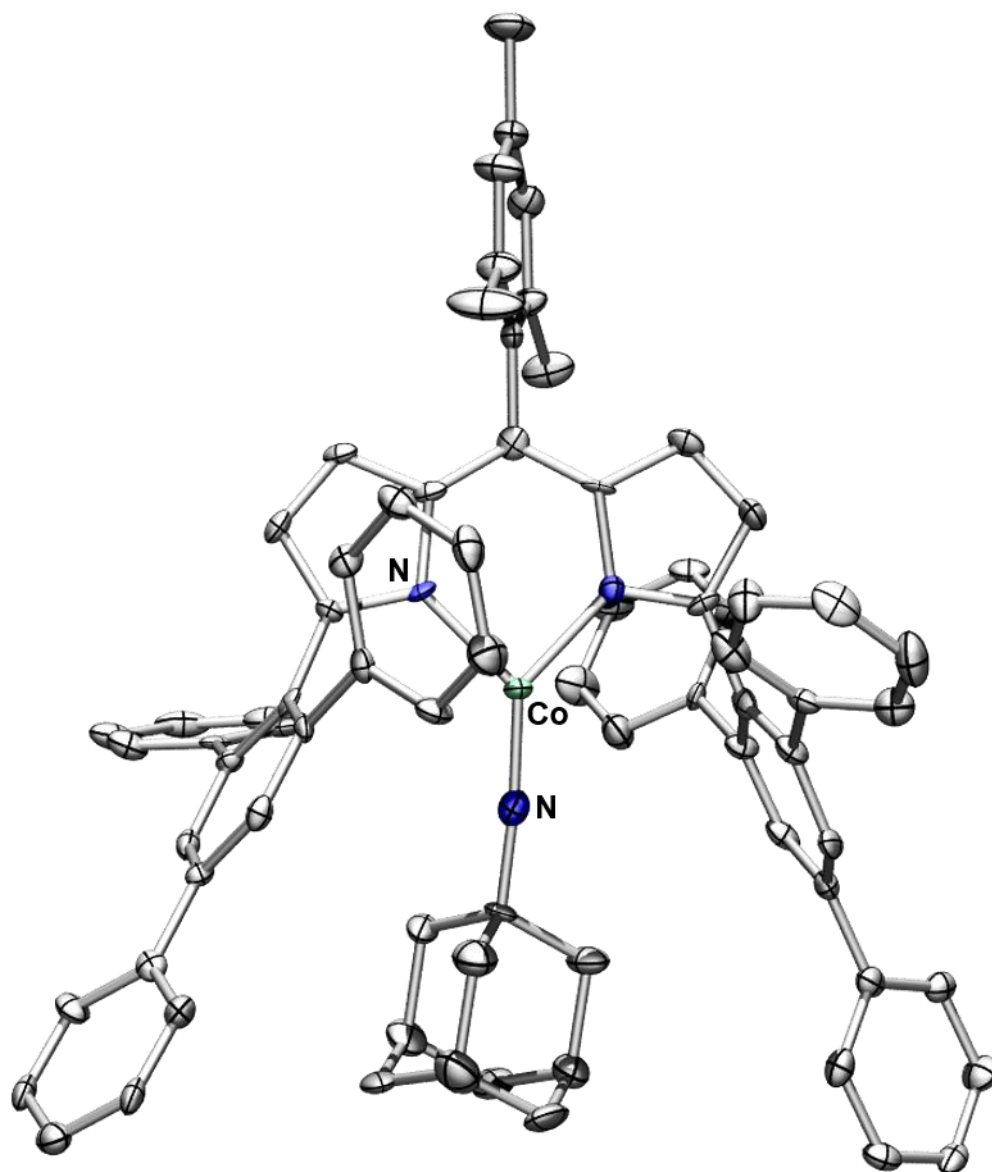
**Figure S-45.** Solid-state molecular structure for (<sup>Ar</sup>L)Co (**2**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.



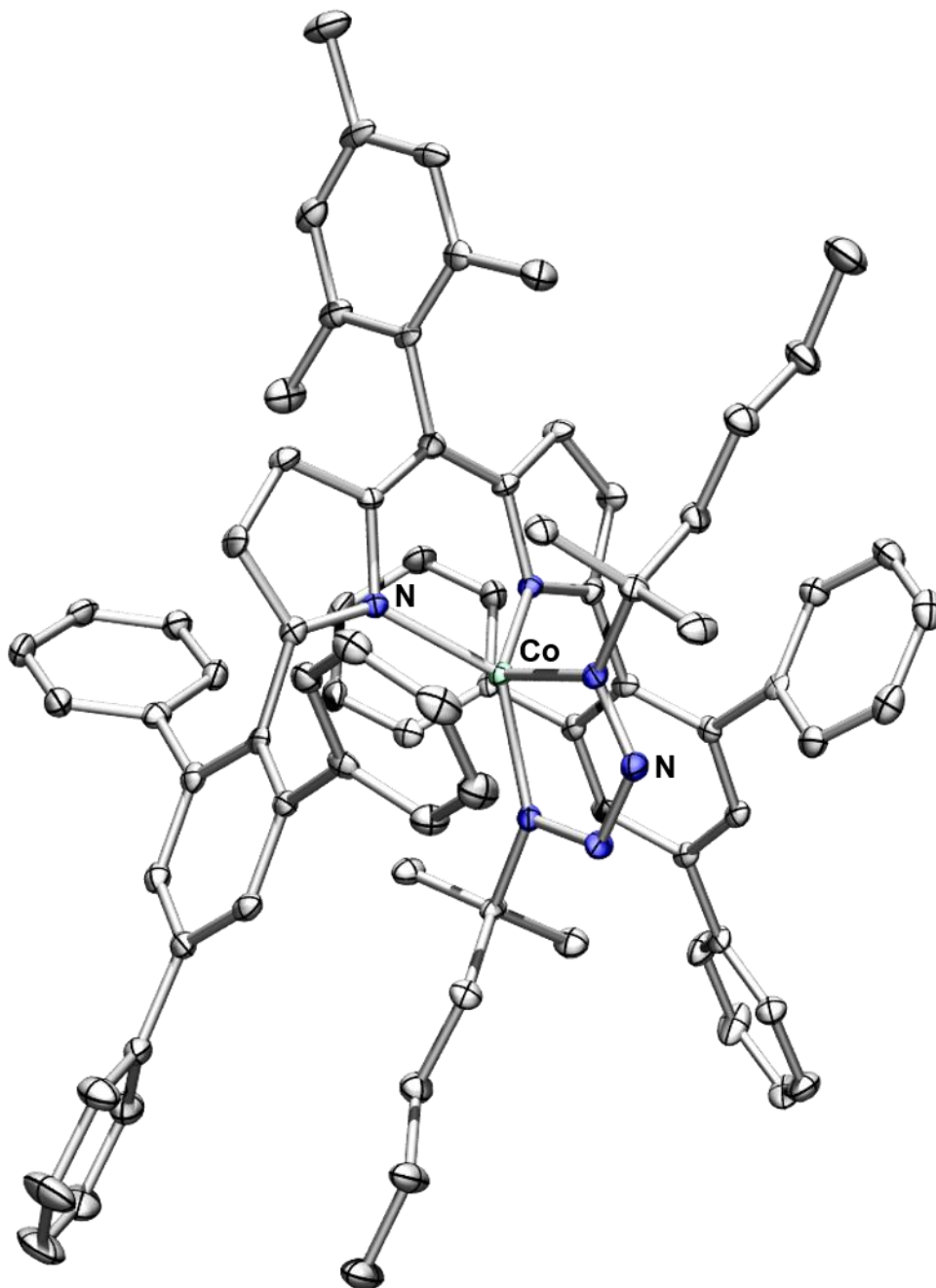
**Figure S-46.** Solid-state molecular structure for ( $A^L$ )Co(NR'),  $R' = C(CH_3)_2(CH_2)_3CH_3$  (**3**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.



**Figure S-47.** Solid-state molecular structure for ( $^{\text{Ar}}\text{L}$ )Co(NR'), R' = C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> (**4**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

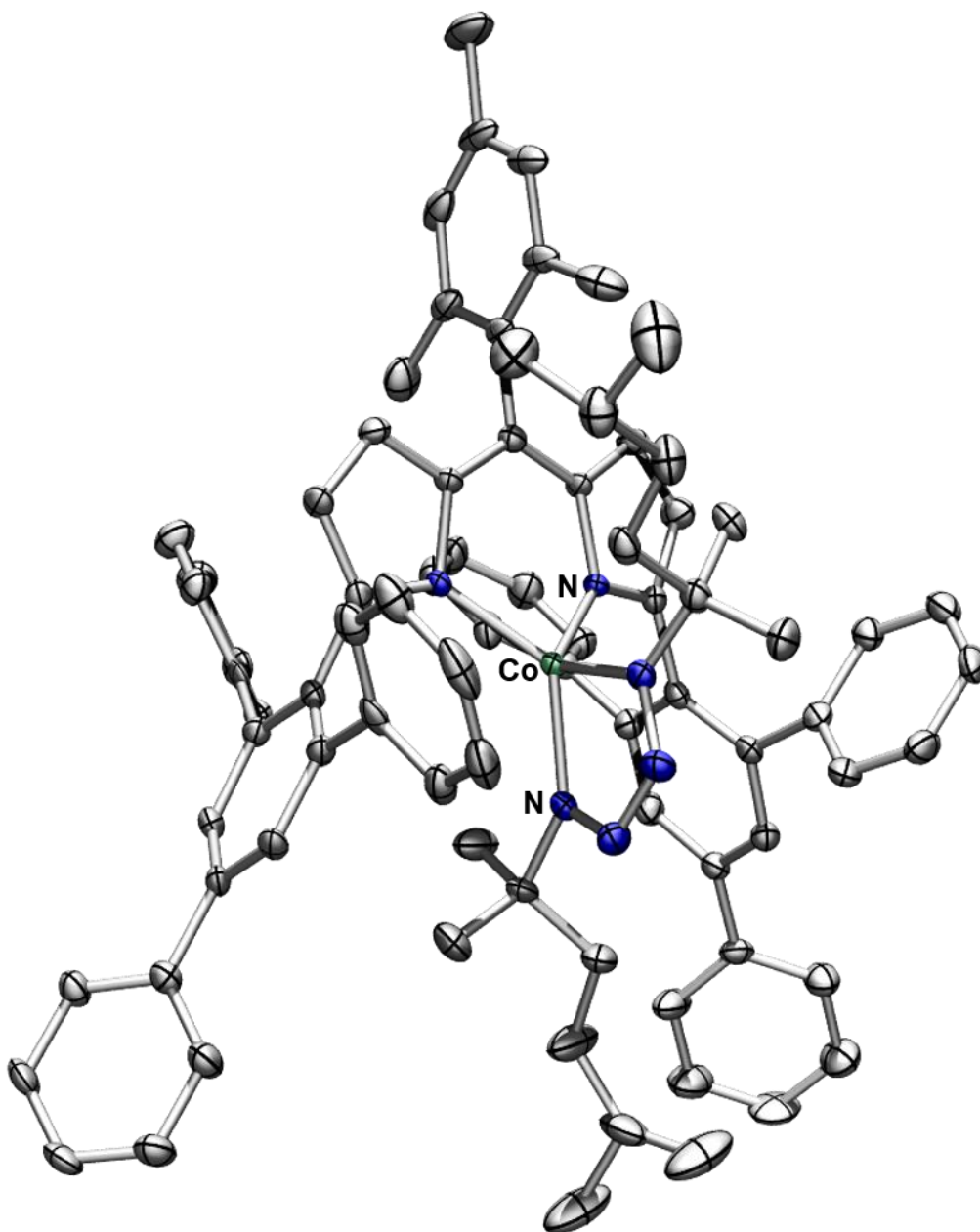


**Figure S-48.** Solid-state molecular structure for (<sup>Ar</sup>L)Co(NAd) (**10**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

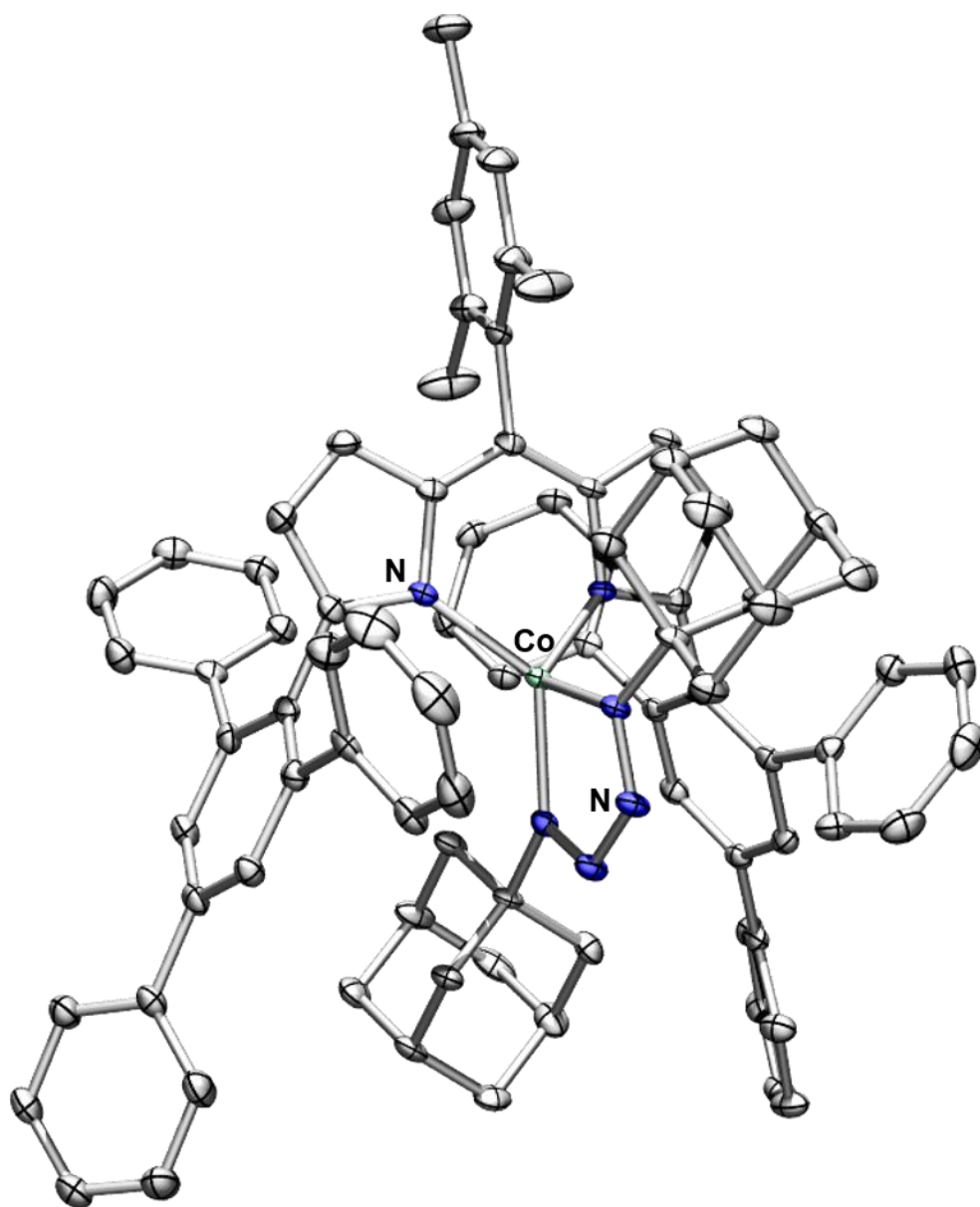


**Figure S-49** Solid-state molecular structure for  $(^{\text{Ar}}\text{L})\text{Co}(\kappa^2\text{-N}_4\text{R}'_2)$ ,  $\text{R}' = \text{C}(\text{CH}_3)_2(\text{CH}_2)_3\text{CH}_3$  (**5**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.





**Figure S-50.** Solid-state molecular structure for ( $^{\text{Ar}}\text{L}$ )Co( $\kappa^2\text{-N}_4\text{R}'_2$ ),  $\text{R}' = \text{C}(\text{CH}_3)_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$  (**6**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.



**Figure S-51.** Solid-state molecular structure for  $(^{\text{Ar}}\text{L})\text{Co}(\kappa^2\text{-N}_4\text{Ad}_2)$  (**11**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

### Computational Methods.

Computations were carried out utilizing the ORCA 4.0.1.2 program package.<sup>23</sup> All calculations employed the def2-TZVP<sup>24</sup> (Co, N) and def2-SV(P)<sup>25</sup> (C, H) basis sets. Further, the def2-TSVP/J (Co, N) and def2-SV(P)/J (C, H) auxiliary basis sets were employed to utilize the RIJCOSX<sup>26</sup> approximation for accelerating the calculation. The B3LYP<sup>27</sup> functional was chosen based on good agreement of the optimized structure of **10** with its crystallographic data.

**Table S-10.** Summary of the geometry optimized results of **10-py**.

	<i>S</i> = <b>0</b> model	<i>S</i> = <b>1</b> model	<i>S</i> = <b>2</b> model
Co–N <sub>imido</sub> (Å)	1.70	1.82	1.79
Co–N <sub>dipyrin</sub> (Å)	2.04/2.05	2.07/2.07	2.07/2.11
Co–N <sub>pyridine</sub> (Å)	2.07	2.15	2.18
Co–N <sub>imido</sub> –C (°)	176.4	143.7	152.5
$\tau_4$ <sup>28</sup>	0.77	0.75	0.76
Relative energy (kcal/mol)	+7.7	+1.6	0

<sup>23</sup> Neese, F. *The ORCA program system*, Wiley Interdiscip. Rev.: Comput. Mol. Sci., **2012**, 2, 73.

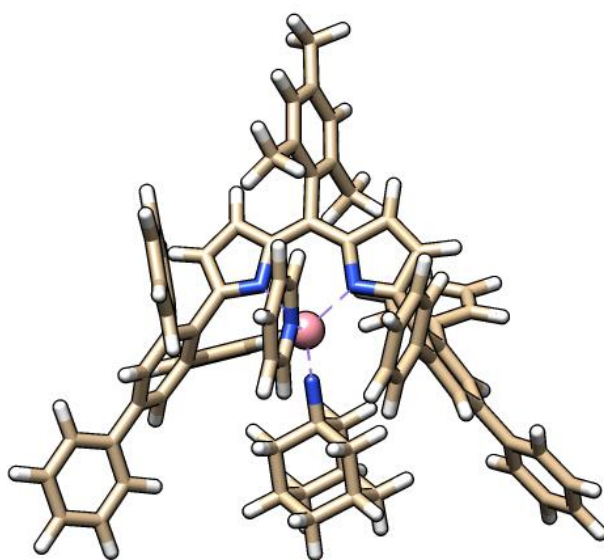
<sup>24</sup> Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, 7, 3297

<sup>25</sup> Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, 8, 1057

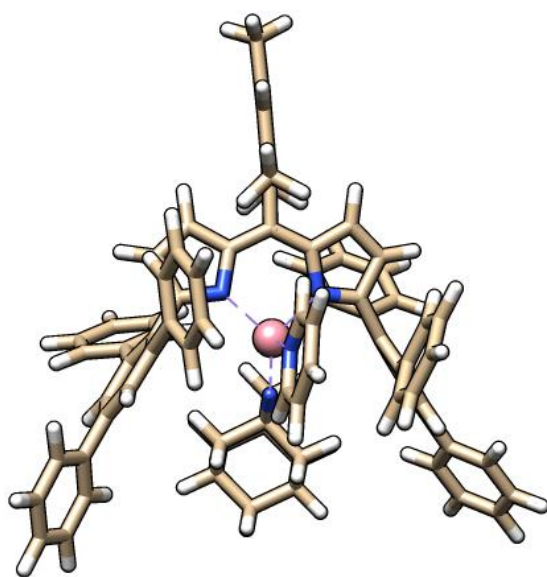
<sup>26</sup> Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. *Chem. Phys.* **2009**, 356, 98

<sup>27</sup> (a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648 (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys Rev. B*, **1988**, 33, 785

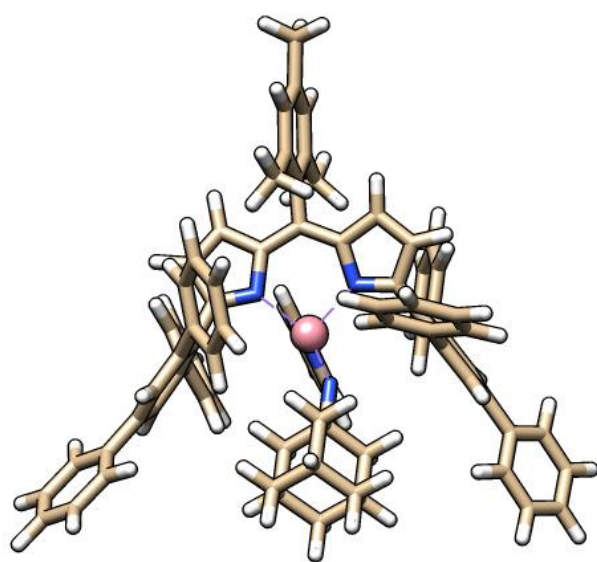
<sup>28</sup> Yang L.; Powell D. R.; Houser R. P. *Dalton Trans.* **2007**, 955



**Figure S-52.** Geometry optimized molecular structure of (<sup>Ar</sup>L)Co(py)(NAd) (**10-py**) with an  $S = 0$  spin state. Hydrogens omitted for clarity.



**Figure S-53.** Geometry optimized molecular structure of (<sup>Ar</sup>L)Co(py)(NAd) (**10-py**) with an  $S = 1$  spin state. Hydrogens omitted for clarity.



**Figure S-54.** Geometry optimized molecular structure of (<sup>Ar</sup>L)Co(py)(NAd) (**10-py**) with an  $S = 2$  spin state. Hydrogens omitted for clarity.



**Table S-11.** Coordinates of optimized molecular structure for (<sup>Ar</sup>L)Co(NAd) (**10**).Singlet ( $S = 0$ )

Co	11.689614	18.334845	6.020368
N	9.752576	18.348816	5.628457
N	11.929432	16.596658	5.110569
C	9.011786	17.274051	5.123749
C	9.706394	23.306561	7.438708
C	9.212363	20.668615	6.456763
C	10.077599	22.928650	6.139521
C	8.867713	19.316525	5.941881
N	12.593448	19.301748	7.079479
C	9.853091	21.636077	5.636599
C	13.108125	16.013733	4.814433
C	16.873584	17.279613	6.531486
C	15.946965	16.528232	7.271879
C	9.435783	20.835263	3.256174
C	14.408228	16.453682	5.386631
C	13.791263	15.308643	7.577601
C	7.534616	18.890377	5.673169
C	10.292661	21.379799	4.230244
C	9.062475	22.342656	8.226054
C	9.560029	16.091596	4.591861
C	14.727424	16.108168	6.724706
C	8.607018	15.047041	4.068161
C	7.624693	17.611025	5.157307
C	8.114579	20.114877	8.712449
C	8.798131	21.044137	7.761415
C	10.935657	15.817929	4.515684
C	8.019114	18.048486	10.003435
C	11.583751	21.775542	3.829544
C	13.188053	20.088282	8.104215
C	9.850707	20.709871	1.926837
C	13.363264	14.025223	7.193496
C	20.471315	18.808642	8.369140
C	12.916032	14.874706	3.984086
C	15.355670	17.156815	4.602671
C	15.124696	17.458593	3.156868
C	18.124109	17.790844	7.155818
C	18.648360	19.045886	6.787842
C	11.526125	26.577587	8.133806
C	8.623967	18.839906	9.022395
C	11.549412	14.732155	3.820704
C	19.807745	19.548185	7.384075
C	18.809047	17.055892	8.143102
C	6.964861	20.554255	9.396078
C	13.322386	15.824654	8.798465
C	11.131963	21.120972	1.542142
C	16.565381	17.558369	5.191188
C	10.028412	24.650914	7.989339



C	12.472645	13.296755	7.986925
C	11.184478	25.342646	7.576880
C	8.130022	14.041605	4.941183
C	7.219818	13.091166	4.451982
C	14.726600	17.976752	0.405992
C	9.560855	26.486146	9.534548
C	9.217672	25.254311	8.971364
C	15.898253	17.348444	0.842251
C	16.095088	17.094847	2.203174
C	12.444464	19.853940	9.453569
C	13.761975	18.359062	1.343691
C	7.274450	14.096127	2.276419
C	19.964773	17.560210	8.745968
C	12.002204	21.646568	2.502191
C	14.691435	19.750786	8.307470
C	6.779328	13.097081	3.123696
C	11.992496	13.835809	9.185564
C	15.295750	20.626390	9.426538
C	6.884729	18.504754	10.684018
C	10.720471	27.151951	9.122640
C	13.960435	18.105528	2.703431
C	14.545047	20.374099	10.749106
C	13.074838	21.595266	7.737048
C	6.353104	19.759500	10.369851
C	8.179192	15.070105	2.720310
C	12.428948	15.100063	9.593731
C	13.056111	20.728766	10.567097
C	13.679565	22.466684	8.856024
C	8.575380	13.972361	6.385333
C	12.927531	22.214756	10.178816
C	15.168651	22.114141	9.038512
C	5.820088	12.050953	2.604983
C	8.676189	16.120737	1.755054
H	6.356211	11.259070	2.045903
H	5.269966	11.557693	3.425334
H	5.078887	12.491832	1.913434
H	6.841944	12.323161	5.136622
H	6.939625	14.126161	1.233216
H	9.668805	13.833432	6.469952
H	8.332480	14.901225	6.931954
H	8.082774	13.135533	6.908371
H	9.775353	16.080348	1.646388
H	8.227633	15.980778	0.757072
H	8.426545	17.139718	2.102635
H	11.017111	13.960965	3.265026
H	13.710294	14.240732	3.591958
H	6.814456	16.969518	4.812771
H	6.638458	19.487776	5.838366
H	6.539246	21.531398	9.147205
H	5.459577	20.125163	10.886352
H	6.414795	17.882351	11.452521
H	8.447869	17.070643	10.246039

H	9.514244	18.472053	8.506170
H	8.797726	22.582902	9.257346
H	10.535809	23.666368	5.476086
H	11.846221	24.892824	6.831780
H	8.297932	24.758535	9.294502
H	8.913230	26.931017	10.297338
H	10.996700	28.111685	9.570511
H	12.434806	27.088048	7.798957
H	12.273859	22.178646	4.576131
H	13.011489	21.958392	2.216245
H	11.454654	21.032562	0.499254
H	9.160709	20.297058	1.184153
H	8.426377	20.524430	3.535809
H	13.207330	18.428051	3.424936
H	12.846574	18.863385	1.020394
H	14.565023	18.173853	-0.659383
H	16.660762	17.041400	0.119213
H	17.003548	16.581235	2.533492
H	18.441101	16.068147	8.434429
H	20.480145	16.966412	9.508081
H	21.375242	19.204738	8.842395
H	20.192647	20.526107	7.077403
H	18.122456	19.651267	6.043871
H	12.147761	12.303632	7.659670
H	11.287826	13.268937	9.802951
H	12.061670	15.535087	10.529126
H	13.733692	13.589662	6.263685
H	13.645231	16.817464	9.119567
H	16.163863	16.273392	8.312377
H	17.282574	18.109522	4.577320
H	15.231470	19.910522	7.358132
H	14.799625	18.682025	8.554791
H	13.601733	21.773717	6.781794
H	12.015810	21.848687	7.579776
H	12.516804	18.784770	9.722927
H	11.374165	20.087475	9.323676
H	12.507319	20.538090	11.507803
H	13.345567	22.855030	10.978021
H	11.863335	22.494534	10.069083
H	13.571958	23.529243	8.569471
H	15.727803	22.312083	8.104085
H	15.619305	22.753386	9.820956
H	16.361124	20.360133	9.550589
H	14.985189	20.986540	11.558425
H	14.652374	19.316045	11.054584

**Table S-12.** Coordinates of optimized molecular structure for (<sup>Ar</sup>L)Co(py)(NAd) (**10-py**).

Singlet ( $S = 0$ )

Co	5.466741	8.573359	21.396388
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N	4.151207	7.186641	22.094531
N	4.769510	10.026735	22.666154
N	4.287682	9.174799	19.809787
N	7.078004	8.205058	21.000749
C	3.090792	7.478910	22.961028
C	4.051597	5.881292	21.793569
C	3.831072	9.774700	23.672356
C	5.015305	4.793923	19.680006
C	6.804003	3.331840	21.253507
H	7.465322	2.742060	21.891915
C	6.775696	3.083072	19.874437
C	5.304147	11.231671	22.939069
C	7.632408	12.074660	22.415502
C	5.777551	12.757036	20.967742
C	8.203650	11.454454	23.652689
C	6.064672	4.383045	23.356346
C	4.335200	12.959312	20.605374
C	3.841754	10.855523	24.610300
H	3.223351	10.929154	25.503724
C	5.986958	3.207740	24.130112
H	5.781442	2.253676	23.635420
C	4.023294	5.410101	18.745381
C	6.697319	13.478059	20.187227
H	6.321165	14.051128	19.337203
C	6.153774	3.241748	25.516913
H	6.087221	2.313997	26.094703
C	1.909382	8.691801	24.785273
C	5.971712	4.281658	21.865347
C	5.056306	5.034325	21.077377
C	6.254292	11.989740	22.069479
C	2.111507	8.043678	26.027840
C	5.887942	3.849969	19.108542
H	5.833215	3.687161	18.029223
C	2.987461	8.649195	23.734977
C	7.925974	10.131321	24.042947
H	7.275117	9.512639	23.423151
C	8.507967	12.820324	21.605401
H	9.564716	12.869636	21.880662
C	7.598702	1.997082	19.273656
C	8.068112	13.508177	20.468292
C	2.279817	6.311101	23.122150
H	1.382266	6.240166	23.734668
C	4.783750	11.757341	24.160466
H	5.079801	12.703187	24.614008
C	9.000174	14.257689	19.583248
C	7.114885	1.247304	18.183551
H	6.128700	1.474104	17.769549
C	3.946575	12.996303	19.251122
H	4.676203	12.743816	18.477576
C	4.454571	5.996163	17.539699
H	5.527775	6.103780	17.351064
C	6.309482	5.599290	24.020045

H	6.387368	6.521575	23.440917
C	2.893827	5.305604	22.406678
H	2.593749	4.260322	22.329976
C	2.965311	9.356965	19.923769
H	2.534078	9.147504	20.903486
C	8.499002	9.586137	25.195989
H	8.263822	8.553347	25.473808
C	4.862096	9.409678	18.619842
H	5.939555	9.240298	18.572883
C	3.372599	7.256205	26.302992
H	3.483427	6.404288	25.611648
H	3.377869	6.858426	27.332602
H	4.271800	7.883509	26.171694
C	2.647606	13.346493	18.872243
H	2.380618	13.373526	17.810171
C	9.653019	11.662547	25.614622
H	10.321454	12.275584	26.228466
C	1.690995	13.662416	19.840573
H	0.676169	13.947948	19.544839
C	10.263494	13.734913	19.246846
H	10.573329	12.770226	19.659780
C	0.721809	9.418430	24.549022
C	9.077356	12.208303	24.463488
H	9.299470	13.245635	24.195863
C	2.638689	5.293411	18.965580
H	2.276067	4.826780	19.882723
C	2.169283	9.780827	18.861377
H	1.096457	9.921289	19.016772
C	1.128054	8.158040	27.017775
H	1.293332	7.664340	27.982203
C	8.857263	1.649696	19.803200
H	9.272040	2.227436	20.634607
C	6.478380	5.632733	25.407980
H	6.677207	6.588485	25.903881
C	-0.234963	9.504250	25.572554
H	-1.152844	10.073932	25.389263
C	7.852830	0.188929	17.647683
H	7.445183	-0.384514	16.808652
C	11.107384	14.410968	18.360914
H	12.076119	13.975138	18.095445
C	8.623004	15.492324	19.020627
H	7.662433	15.936271	19.298396
C	3.358426	13.286395	21.566151
H	3.625060	13.303113	22.622988
C	4.144766	9.837459	17.504219
H	4.667741	10.014978	16.560228
C	2.055509	13.626174	21.190092
H	1.325124	13.885897	21.962794
C	-0.048462	8.892903	26.817339
C	1.719307	5.735114	18.010644
H	0.647746	5.613152	18.203232
C	9.365054	10.346285	25.988616

H	9.812909	9.915408	26.889833
C	6.402760	4.457200	26.162125
H	6.542944	4.487876	27.247773
C	9.594230	0.587233	19.272429
H	10.566533	0.332522	19.706518
C	9.464985	16.168979	18.134671
H	9.146054	17.125655	17.708456
C	3.536250	6.444696	16.586053
H	3.899536	6.902345	15.659742
C	9.095818	-0.149559	18.192550
H	9.672931	-0.982307	17.778097
C	0.458899	10.086663	23.215066
H	1.268415	10.783048	22.935934
H	-0.488307	10.653322	23.235708
H	0.384172	9.339027	22.403050
C	2.766595	10.024628	17.623953
H	2.169327	10.359594	16.770645
C	10.709256	15.626961	17.794892
H	11.368702	16.152404	17.096484
C	2.162993	6.312383	16.815785
H	1.442912	6.657227	16.067035
C	-1.069634	9.022578	27.923451
H	-1.454817	8.035860	28.242712
H	-1.932167	9.635058	27.609854
H	-0.627066	9.496995	28.819472
H	9.794732	5.966591	18.000471
H	10.116991	8.444870	17.751895
C	9.824622	6.608414	18.899983
H	7.865360	7.501458	18.503408
H	11.629597	7.653331	18.251683
C	10.603365	7.900934	18.584727
C	8.381982	6.964055	19.320751
H	7.798600	6.050553	19.527074
H	11.540844	5.552986	19.746120
C	10.518737	5.849494	20.050610
H	9.966082	4.916599	20.274808
C	10.645227	8.793397	19.841331
H	8.689113	9.706403	19.456394
C	8.397630	7.864431	20.591590
H	11.199514	9.724457	19.616011
C	9.205568	9.154512	20.263809
C	10.566512	6.743553	21.305893
H	12.385797	7.796934	20.711987
C	11.342570	8.038449	20.992387
C	9.128966	7.099082	21.736074
H	8.560317	6.185354	21.984016
H	11.066949	6.202673	22.130341
H	9.212780	9.812294	21.149097
H	11.387836	8.680275	21.892571
H	9.143820	7.731781	22.641100

**Table S-13.** Coordinates of optimized molecular structure for (<sup>Ar</sup>L)Co(py)(NAd) (**10-py**).Triplet ( $S = 1$ )

Co	5.413860	8.621601	21.238753
N	4.260671	7.129519	22.096473
N	4.871360	10.092717	22.590838
N	4.247491	9.190359	19.529372
N	7.004013	8.323347	20.404876
C	3.252093	7.464712	23.013827
C	4.125175	5.813514	21.848662
C	3.979262	9.813416	23.632939
C	4.977232	4.832884	19.647847
C	6.801559	3.243863	21.043001
H	7.475510	2.596081	21.607253
C	6.760723	3.138156	19.645919
C	5.366443	11.323039	22.834869
C	7.637744	12.267277	22.252845
C	5.722757	12.821941	20.820978
C	8.261432	11.720640	23.501012
C	6.050164	4.036831	23.254616
C	4.265643	12.940813	20.478125
C	3.978375	10.906581	24.555311
H	3.386243	10.969445	25.466761
C	6.007332	2.766527	23.864703
H	5.853947	1.879056	23.243642
C	3.910000	5.466372	18.814367
C	6.592017	13.575019	20.013310
H	6.174515	14.118580	19.163705
C	6.135687	2.619380	25.247960
H	6.092511	1.620644	25.695429
C	2.122984	8.728360	24.829547
C	5.972716	4.120718	21.761121
C	5.061637	4.958383	21.057970
C	6.259772	12.106274	21.930533
C	2.378840	8.154215	26.097427
C	5.844269	3.955745	18.972172
H	5.760258	3.884770	17.885093
C	3.169382	8.663745	23.747401
C	8.010879	10.422839	23.985307
H	7.330248	9.768236	23.441192
C	8.461590	13.027741	21.402762
H	9.521457	13.130195	21.648118
C	7.594718	2.132245	18.930263
C	7.964548	13.673594	20.265022
C	2.444065	6.310330	23.263536
H	1.578972	6.271924	23.923717
C	4.869772	11.839792	24.066313
H	5.140306	12.802296	24.499691
C	8.840728	14.457236	19.352764
C	7.100611	1.465361	17.791834

H	6.099487	1.701118	17.420957
C	3.862516	12.982838	19.127517
H	4.596439	12.786886	18.342022
C	4.229518	6.118239	17.608648
H	5.280235	6.286238	17.351844
C	6.218800	5.159024	24.085949
H	6.258419	6.156184	23.644709
C	3.008154	5.271705	22.554649
H	2.694710	4.227898	22.535310
C	2.918630	9.344489	19.583944
H	2.442466	9.113066	20.540763
C	8.637308	9.946337	25.140249
H	8.420025	8.931451	25.488724
C	4.881553	9.443635	18.376151
H	5.962324	9.273672	18.403591
C	3.662991	7.401165	26.366283
H	3.766031	6.523728	25.706104
H	3.705496	7.043766	27.409763
H	4.546949	8.039632	26.184928
C	2.542691	13.264464	18.765446
H	2.267503	13.300174	17.705825
C	9.791072	12.049315	25.385969
H	10.480150	12.701633	25.932607
C	1.576228	13.499743	19.746576
H	0.544024	13.731741	19.464195
C	10.113162	13.983281	18.981802
H	10.470699	13.030734	19.384297
C	0.913379	9.416679	24.591342
C	9.161663	12.524276	24.231919
H	9.362915	13.547019	23.900452
C	2.550557	5.276333	19.124704
H	2.275496	4.754579	20.042645
C	2.167190	9.769772	18.489716
H	1.085048	9.887638	18.588757
C	1.427354	8.309466	27.113446
H	1.633721	7.874307	28.097920
C	8.875197	1.775619	19.396945
H	9.298346	2.292936	20.262480
C	6.356965	5.012085	25.469567
H	6.505499	5.900187	26.091941
C	-0.010637	9.543362	25.639699
H	-0.945002	10.084949	25.455258
C	7.850488	0.476419	17.149901
H	7.434841	-0.035318	16.275812
C	10.906666	14.693995	18.076388
H	11.883791	14.296365	17.783655
C	8.398857	15.675819	18.802593
H	7.429093	16.081049	19.106570
C	3.276496	13.180797	21.451744
H	3.547270	13.187503	22.507545
C	4.209784	9.876250	17.232554
H	4.771607	10.074848	16.315253

C	1.952470	13.449771	21.092059
H	1.213369	13.643574	21.876007
C	0.230540	9.011545	26.911655
C	1.545639	5.707073	18.254921
H	0.497166	5.523789	18.514530
C	9.532686	10.754829	25.847394
H	10.023803	10.379212	26.750766
C	6.314487	3.744141	26.058341
H	6.423421	3.631174	27.142255
C	9.625016	0.783957	18.758421
H	10.614328	0.520104	19.146096
C	9.191216	16.387277	17.898135
H	8.824598	17.331399	17.482417
C	3.225232	6.556947	16.741080
H	3.500520	7.068533	15.813113
C	9.115409	0.126656	17.633499
H	9.701814	-0.652508	17.136062
C	0.598202	10.004890	23.231749
H	1.380155	10.708988	22.898117
H	-0.364871	10.544103	23.246532
H	0.529943	9.214692	22.460916
C	2.824473	10.042482	17.288662
H	2.264027	10.381133	16.411391
C	10.446225	15.894537	17.524799
H	11.066234	16.447651	16.811734
C	1.878673	6.347664	17.056826
H	1.093811	6.684488	16.372353
C	-0.759926	9.187269	28.039509
H	-1.166563	8.216933	28.382646
H	-1.612232	9.818234	27.734802
H	-0.284284	9.662609	28.917586
H	10.381554	5.683827	18.700833
H	11.013819	8.110316	18.573739
C	10.146215	6.356857	19.545940
H	8.577552	7.429256	18.459246
H	12.155260	7.211834	19.603384
C	11.107396	7.561370	19.530675
C	8.696791	6.866426	19.403620
H	7.990828	6.017224	19.368108
H	11.338576	5.199622	20.968665
C	10.306226	5.589316	20.875819
H	9.627825	4.715131	20.891107
C	10.771165	8.498927	20.707951
H	9.189611	9.563420	19.624710
C	8.316751	7.806312	20.590642
H	11.451097	9.370726	20.694333
C	9.318548	9.006752	20.570201
C	9.980297	6.526356	22.056758
H	11.982818	7.393311	22.156960
C	10.936078	7.735242	22.039568
C	8.528066	7.025623	21.919206
H	7.832655	6.170192	21.941606



H	10.092050	5.975965	23.009829
H	9.073507	9.697048	21.394439
H	10.715741	8.407097	22.890150
H	8.269311	7.684305	22.767336

**Table S-14.** Coordinates of optimized molecular structure for (<sup>Ar</sup>L)Co(py)(NAd) (**10-py**).

Quintet ( $S = 2$ )

Co	5.398841	8.538821	21.394908
N	4.181064	7.059414	22.163331
N	4.785675	10.017850	22.766139
N	4.326023	9.005770	19.556079
N	7.075023	8.853056	20.848621
C	3.109222	7.395663	22.999605
C	4.007079	5.770468	21.806664
C	3.816243	9.721902	23.733278
C	4.840921	4.586869	19.705337
C	6.827148	3.289653	21.176224
H	7.552667	2.747960	21.786776
C	6.660472	2.934441	19.830854
C	5.303230	11.207715	23.099240
C	7.636934	12.089295	22.712201
C	5.853607	12.722400	21.154393
C	8.146278	11.463575	23.972909
C	6.341197	4.497282	23.258503
C	4.426577	12.855154	20.716355
C	3.780472	10.783914	24.700371
H	3.126235	10.832095	25.569391
C	5.390324	4.360037	24.285482
H	4.353684	4.129105	24.035793
C	3.801322	5.164053	18.793226
C	6.797496	13.452243	20.414789
H	6.457950	14.000718	19.533136
C	5.760327	4.488345	25.628155
H	5.003152	4.360533	26.408260
C	1.882068	8.630459	24.777391
C	6.029148	4.256373	21.811693
C	4.990149	4.903823	21.081716
C	6.284377	11.983894	22.289323
C	2.099925	8.124917	26.080643
C	5.686160	3.635381	19.109138
H	5.540864	3.415145	18.049132
C	2.994123	8.584226	23.761461
C	7.846970	10.137912	24.341868
H	7.230852	9.521108	23.686126
C	8.540146	12.843860	21.942971
H	9.581015	12.912039	22.269798
C	7.425731	1.811439	19.221228
C	8.150138	13.508318	20.773300
C	2.232443	6.275782	23.104190

H	1.315093	6.239104	23.689495
C	4.734222	11.698684	24.317336
H	5.009505	12.631991	24.808131
C	9.122394	14.243127	19.921117
C	6.846903	1.011378	18.215686
H	5.828973	1.222561	17.877068
C	4.093673	12.779483	19.349830
H	4.867972	12.518060	18.624249
C	4.201315	5.781803	17.591327
H	5.267506	5.946337	17.403702
C	7.674378	4.762898	23.629504
H	8.434145	4.868762	22.850259
C	2.797222	5.257102	22.356533
H	2.430276	4.237151	22.239583
C	3.001530	8.837365	19.446223
H	2.495625	8.413127	20.317423
C	8.356884	9.584162	25.520260
H	8.105220	8.550704	25.780013
C	4.995277	9.509613	18.510288
H	6.069386	9.637318	18.664999
C	3.414456	7.477573	26.458890
H	3.738363	6.737889	25.708122
H	3.339697	6.968513	27.435639
H	4.224391	8.226742	26.530797
C	2.793627	13.032496	18.901262
H	2.566972	12.972010	17.831474
C	9.495488	11.655544	26.005975
H	10.134674	12.262160	26.656364
C	1.786421	13.365658	19.811021
H	0.770460	13.573929	19.459606
C	10.398421	13.711078	19.653521
H	10.683940	12.752175	20.096480
C	0.652193	9.239041	24.445504
C	8.981157	12.209670	24.830272
H	9.220758	13.247106	24.579089
C	2.425762	4.967484	19.008878
H	2.087971	4.470136	19.918779
C	2.293276	9.174189	18.292256
H	1.213321	9.012753	18.250820
C	1.085645	8.264956	27.036519
H	1.258288	7.877976	28.047387
C	8.724056	1.480067	19.656145
H	9.213413	2.093236	20.418441
C	8.044933	4.897989	24.970771
H	9.087833	5.111513	25.227178
C	-0.335453	9.351919	25.436109
H	-1.285579	9.833612	25.179569
C	7.534131	-0.073891	17.666210
H	7.054206	-0.683124	16.893102
C	11.283143	14.367044	18.793029
H	12.261309	13.923084	18.580385
C	8.773700	15.465699	19.316368

H	7.801249	15.915154	19.539297
C	3.401334	13.201796	21.616792
H	3.628512	13.306943	22.678452
C	4.372252	9.863562	17.312996
H	4.966361	10.271129	16.490109
C	2.098628	13.446857	21.171816
H	1.326215	13.723195	21.896393
C	-0.135060	8.887954	26.741457
C	1.484187	5.360848	18.052574
H	0.421097	5.172649	18.238589
C	9.183488	10.338614	26.358550
H	9.583812	9.902373	27.279569
C	7.086569	4.760300	25.978929
H	7.373985	4.856903	27.031359
C	9.409085	0.388639	19.114896
H	10.412925	0.146390	19.478587
C	9.656852	16.122520	18.455919
H	9.360331	17.071153	17.996677
C	3.261876	6.179413	16.636238
H	3.601778	6.659128	15.712495
C	8.818792	-0.394283	18.116696
H	9.356348	-1.248520	17.693126
C	0.386991	9.763185	23.049750
H	1.179421	10.455186	22.715448
H	-0.577217	10.298809	23.003431
H	0.350103	8.939694	22.312151
C	2.989863	9.699686	17.202900
H	2.462947	9.972938	16.282809
C	10.914663	15.572343	18.185492
H	11.606747	16.081638	17.507111
C	1.897854	5.964194	16.860296
H	1.161653	6.265109	16.107941
C	-1.186025	9.070167	27.812077
H	-1.439314	8.113310	28.305932
H	-2.116225	9.494576	27.396763
H	-0.831063	9.755172	28.605305
H	9.565486	5.943452	18.267549
H	9.860319	8.292216	17.422381
C	9.665800	6.777919	18.985813
H	7.683189	7.587170	18.543760
H	11.409735	7.609254	17.965130
C	10.415902	7.948138	18.316284
C	8.263489	7.250741	19.423912
H	7.696986	6.421756	19.886163
H	11.446296	5.918705	19.914678
C	10.451367	6.295557	20.221654
H	9.920082	5.449485	20.699357
C	10.561802	9.109940	19.319806
H	8.588373	9.960182	18.892259
C	8.368202	8.429330	20.441300
H	11.102709	9.947680	18.840630
C	9.162174	9.587047	19.761979

C	10.597125	7.458222	21.223693
H	12.365221	8.300592	20.253467
C	11.350784	8.625528	20.554251
C	9.198953	7.936515	21.664104
H	8.644403	7.124009	22.165683
H	11.159735	7.114772	22.111994
H	9.243757	10.428153	20.473845
H	11.477357	9.455179	21.275720
H	9.288988	8.760778	22.392674