Synthesis of the Chiral Tripyridyldiamine Ligand Bn-CDPy3 and Characterization of its Co(III) Complex [Co(Bn-CDPy3)Cl]Cl$_2$

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Supporting Information

(24 Pages)

Part A. General Considerations

All reagents were purchased from commercial suppliers and used as received. Dipyridyldiamine (*rac*-**4**) was prepared using a known procedure.[1,2] NMR spectra were recorded on a Varian FT-NMR Mercury-300 or 400 MHz Spectrometer. Mass spectra were recorded on a Waters ZQ2000 single quadrupole mass spectrometer using an electrospray ionization source. IR spectra were recorded on a Nicolet FT-IR spectrophotometer. UV-vis spectra were recorded on a Varian Cary 50 spectrophotometer. All reactions were performed under ambient atmosphere unless otherwise noted. Conductivity measurements were performed with an Omega portable conductivity meter (Model CDH-280). X-ray crystallographic data were collected on a Bruker *P4/CCD* diffractometer. Molecular modeling studies were performed with the program Spartan 04.

Part B. Experimental procedures and tabulated characterization data for new compounds

Chemical Formula: $C_{24}H_{27}N_5$
Molecular Weight: 385.50
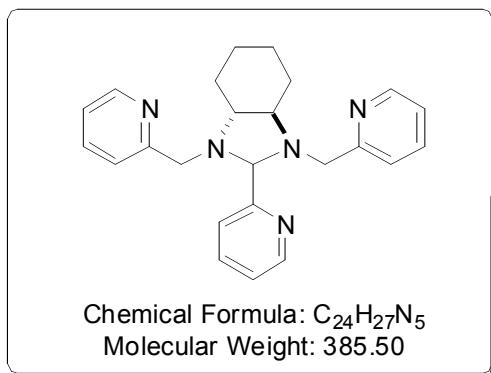
Trans-2-(pyridin-2-yl)-1,3-bis(pyridin-2-ylmethyl)octahydro-1H-benzo[d]imidazole (*rac*-5)

Dipyridyldiamine (*rac*-4) (3.18 g, 10.7 mmol) was dissolved in dry ether (65 mL). 4 Å molecular sieves and picolinaldehyde (1.02 mL, 10.7 mmol) were added to the mixture. The resultant mixture was maintained overnight at rt resulting in the formation of a small amount of gray precipitate. The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to give the resultant aminal as a yellow oil (4.14 g, 100%). The crude product was purified by alumina chromatography (CH_2Cl_2 to 1% MeOH: CH_2Cl_2) to obtain a pure light yellow oil (3.62 g, 88%). ^{1}H NMR ($CDCl_3$) δ 8.28 (m, 3H), 7.45 (m, 2H), 7.31 (m, 3H), 7.13 (d, J = 7.94 Hz, 1H), 6.93 (m, 3H), 4.84 (s, 1H), 3.96 (d, J = 14.3 Hz, 1H), 3.86 (d, J = 14.3 Hz, 1H), 3.61 (d, J = 15.6 Hz, 1H), 3.54 (d, J = 15.6 Hz, 1H), 2.90 (m, 1H), 2.56 (m, 1H), 1.62 (m, 4H), 1.16 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 161.1, 160.9, 159.7, 148.4, 148.3, 148.2, 135.8, 135.5, 135.5, 123.7, 123.4, 122.5, 122.2, 121.4, 121.3, 87.7, 77.2, 69.1, 67.4, 58.6, 54.7, 29.9, 29.7, 24.3 ppm; IR (thin film) 3395, 3053, 3009, 2933, 2859, 1590, 1570, 1474, 1434, 1352, 1338, 1310, 1219, 1185, 1147, 1120, 1080, 1046, 994, 976, 913, 837, 662, 621 cm^{-1}; LRMS (ESMS) calc'd for $C_{24}H_{27}N_5$ (M+H)[+]: 386, found: 386.

Chemical Formula: $C_{24}H_{29}N_5$
Molecular Weight: 387.52
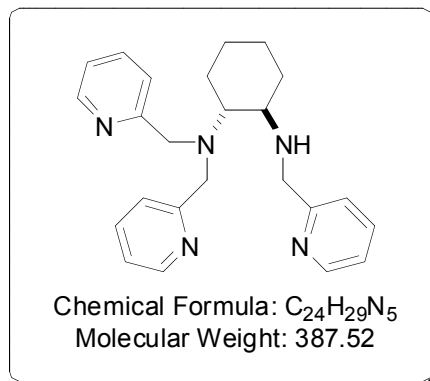
***Trans*-N^1,N^1,N^2-tris(pyridine-2-ylmethyl)cyclohexane-1,2-diamine (*rac*-6)**

The aminal intermediate *rac*-**5** (1.92 g, 4.99 mmol) was dissolved in dry MeOH (80 mL, dried over 4 Å molecular sieves) and placed under N_2 atmosphere. To this solution, a suspension of $NaCNBH_3$ (0.382 g, 5.99 mmol) in dry MeOH (10 mL) was added, followed by trifluoroacetic acid (0.75 mL, 9.98 mmol) dropwise.[3] The reaction mixture was maintained overnight at rt and progress was monitored by TLC. When the reaction was complete, as judged by TLC analysis, 80 mL of sodium hydroxide was added and the mixture was stirred for 6 hours at rt. The solution was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated to give *rac*-**6** (1.84 g, 96%) as light yellow oil. The product, shown to be pure by ^{1}H NMR analysis, was taken to the next step without purification; ^{1}H NMR ($CDCl_3$) δ 8.41 (bm, *J* = 4.9 Hz, 3H), 7.59 (m, 3H), 7.54 (m, 3H), 7.27 (s, 1H), 7.06 (m, 3H), 3.85 (m, 6H), 2.49 (bm, 2H), 2.09 (bm, 2H), 1.72 (bm, 3H), 1.21 (bm, 3H); ^{13}C NMR ($CDCl_3$) δ 160.3, 149.0, 148.7, 136.3, 136.1, 123.0, 122.2, 121.7, 121.6, 63.9, 57.8, 56.6, 56.2, 52.5, 31.8, 25.6, 24.6, 22.9 ppm; IR (thin film) 3310, 3049, 3007, 2928, 2855, 1590, 1569, 1473, 1450, 1433, 1355, 1308, 1243, 1148, 1120, 1087, 1048, 994, 879, 841, 759, 621 cm^{-1}; LRMS (ESMS) calc'd for $C_{24}H_{29}N_5$ (M+H)[+]: 388, found: 388.

Chemical Formula: $C_{31}H_{35}N_5$
Molecular Weight: 477.64
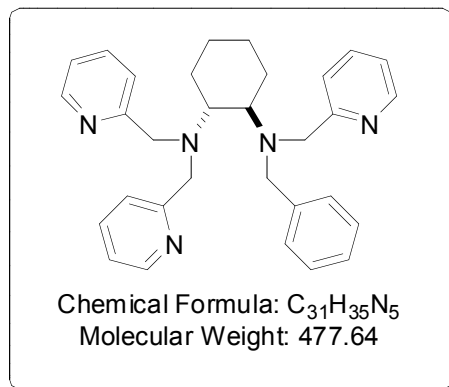
Trans-N^1-benzyl-N^1,N^2,N^2-tris(pyridin-2-ylmethyl)cyclohexane-1,2-diamine (_rac_-2)

Tripyridyldiamine (_rac_-6) (1.84 g, 4.75 mmol) was suspended in acetonitrile (50 mL). Benzyl bromide (0.57 mL, 4.75 mmol) and iPr$_2$EtN (1.65 mL, 9.50 mmol) were added to this solution. The reaction mixture was maintained overnight at rt under nitrogen atmosphere. Volatiles were removed _in vacuo_ to furnish a red-brown residue. To this residue were added CH$_2$Cl$_2$ (50 mL), water (30 mL) and 1 N sodium hydroxide to achieve a pH of 10. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The organic layers were combined and dried over Na$_2$SO$_4$, filtered and concentrated to give _rac_-2 as a light brown residue, (2.23 g, 99%); ^{1}H NMR (CDCl$_3$) δ 8.45 (d, _J_ = 4.9 Hz, 3H), 7.67 (d, _J_ = 7.3 Hz, 1H), 7.61 (d, _J_ = 8.1 Hz, 2H), 7.40 (m, 3H), 7.29 (d, _J_ = 8.1 Hz, 2H), 7.11 (m, 6H), 3.60 (m, 8H), 2.67 (m, 2H), 2.15 (m, 2H), 1.70 (m, 2H), 1.09 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 161.1, 160.6, 148.7, 148.6, 139.9, 135.8, 128.9, 127.9, 126.6, 123.3, 123.2, 121.6, 121.5, 59.9, 58.8, 55.6, 55.2, 53.7, 25.8, 25.7, 24.4, 24.2 ppm; IR (thin film) 3060, 3008, 2932, 2855, 1664, 1591, 1569, 1494, 1473, 1434, 1368, 1216, 1148, 1113, 1047, 996, 979, 757, 700, 663, 622 cm^{-1}; LRMS (ESMS) calc'd for C$_{31}$H$_{35}$N$_5$ (M+H)$^+$: 478, found: 478.

[Co^{III}(Bn-CDPy3)Cl]Cl$_2$ (_rac_-3)

The compound _trans_-[Co(py)$_4$Cl$_2$]Cl•6H$_2$O [4,5] (587 mg, 0.995 mmol) was added to a solution of _rac_-2 (477 mg, 0.995 mmol) in CH$_2$Cl$_2$ (7 mL). The mixture was stirred for 24 hours in the dark. A dark purple solid was formed. The resultant solid was isolated by filtration (501 mg, 79%). ^{1}H NMR analysis of the purple solid in CD$_3$OD (after filtration) indicated the presence of two isomers, one major and one minor, in a ratio of

approximately 1:5, as judged by integration of resonances at 9.84 and 9.69 ppm, respectively, along with trace amounts of other isomers. This purple precipitate was recrystallized from EtOH with Et_2O vapor diffusion resulting in large purple blocks of *rac*-**3** that were subjected to X-ray analysis. Crystallization was performed in the dark to avoid formation of an unidentified blue microcrystalline solid. ^{1}H NMR analysis indicated that ratio of isomers after recrystallization was >10:1. ^{1}H NMR (CD_3OD) δ 9.70 (d, J = 6.1 Hz, 1H), 9.04 (d, J = 5.5 Hz, 1H), 8.2 (dt, J = 7.9, 1.2 Hz, 2H), 8.1 (dt, J = 7.9, 1.2 Hz, 1H), 7.9 (t, J = 8.6 Hz, 2H), 7.67 (m, 6H), 7.46 (m, 3H), 7.34 (d, J = 6.1 Hz, 1H), 6.13 (d, J = 18.9 Hz, 1H), 5.32 (d, J = 16.5 Hz, 1H), 4.94 (d, J = 18.3 Hz, 2H), 4.62 (d, J = 12.8 Hz, 1H), 4.31 (d, J = 12.8 Hz, 1H), 4.19 (m, 1H), 3.24 (d, J = 13.4 Hz, 1H), 2.79 (m, 1H), 2.28 (m, 1H), 2.05 (m, 1H), 1.71 (m, 1H), 1.35 (m, 4H), 1.08 (m, 2H); ^{13}C NMR (CD_3OD) δ 166.1, 164.6, 164.2, 154.8, 152.2, 151.4, 143.4, 143.2, 142.4, 133.7, 132.8, 132.5, 131.1, 130.2, 129.8, 128.9, 128.5, 128.0, 127.3, 124.9, 124.3, 77.0, 76.4, 69.6, 68.0, 65.1, 62.4, 32.8, 28.1, 24.7, 24.5 ppm; IR (KBr) 3385, 3111, 3033, 2930, 2865, 1609, 1571, 1483, 1448, 1382, 1293, 1266, 1222, 1163, 1061, 1035, 972, 933, 893, 855, 765, 708, 677, 617, 589, 573, 544, 528, 489 cm^{-1}; LRMS (ESMS) calc'd for $C_{31}H_{34}N_5CoCl$ (M^{+2}): 286, found: 286. *Anal. Calc*. for $C_{31}H_{45}Cl_3CoN_5O_5$ (*rac*-**3**·$5H_2O$): C, 50.79; H, 6.19; N, 9.55. Found: C, 50.45; H, 6.02; N, 9.33.

Part C. X-ray Crystallographic Data

Diffraction data were collected on a Bruker *P4/CCD* diffractometer equipped with Mo radiation and a graphite monochromator at 100 K. Data were measured at 10 s/frames and 0.3 degree between frames. Frame data were indexed and integrated with the manufacturer's *SMART*, *SAINT* and *SADABS* software.[6] Parameters were refined using Sheldrick's *SHELX-97* software.[7] The complex crystallized as violet plates. 92682 reflections were measured, of which 17503 were independent. The solvent region indicated some ethanol and water disordered about the center of symmetry. Spek's PLATON/SQUEEZE[8] software was used to account for the disordered solvent. The asymmetric unit contains 2 cations, 4 Cl anions, 6 waters (1 SQUEEZED), and 1 ethanol (SQUEEZED).

Figure S1. Molecular structure of the two dications [Co(Bn-CDPy3)Cl]$^{2+}$ present in the asymmetric unit showing 50% probability thermal ellipsoids for all non-hydrogen atoms. Hydrogen atoms, lattice solvent molecules and chloride anions are omitted for clarity.
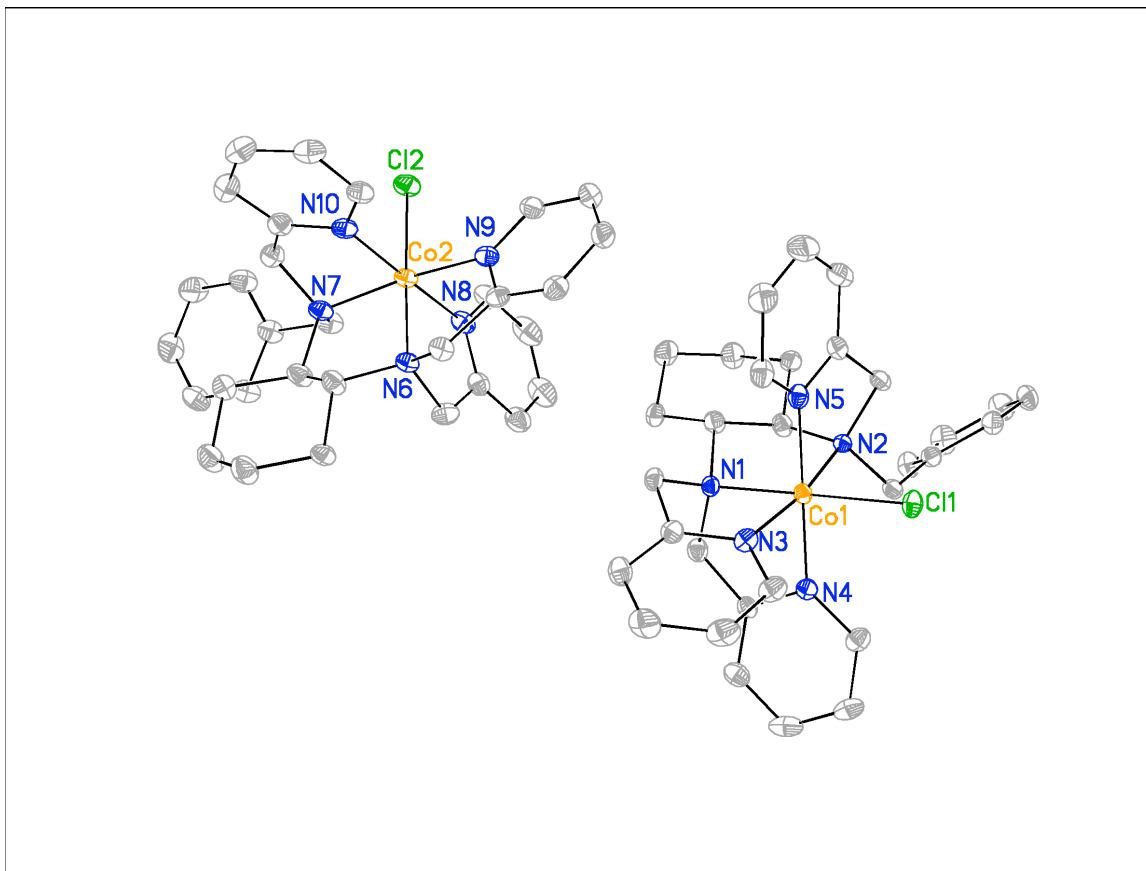
Table S1. Crystal data and structure refinement for *rac*-**3**.

	[Co^{III}(Bn-CDPy3)Cl]Cl$_2$·½EtOH·3H$_2$O
Formula	C32 H44 Cl3 Co1 N5 O3.5
Formula Weight	720.00
Space Group	Triclinic, P-1
a (Å)	14.5658(3)
b (Å)	14.8438(3)
c (Å)	18.4793(4)
α (º)	107.3480(10)
β (º)	105.8420(10)
γ (º)	96.4300(10)
V (Å^3)	3586.56(13)
Z	4
ρ$_{calc}$, (mg/m^3)	1.333
T (K)	100(2)
μ(Mo Kα) (mm^{-1})	0.742
θ limits (º)	1.86 to 28.35
Total number of data	92682
Number of unique data	17502
Number of parameters	775
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1222
R indices (all data)	R1 = 0.0642, wR2 = 0.1296
Maximum, minimum peaks (e/Å^3)	2.179, -0.518

Table S2. Selected bond lengths (Å) and angles (deg) for *rac*-**3**.[a]

bond length		bond angle	
Co(1)-N(3)	1.942 (2)	N(3)-Co(1)-N(5)	94.16(8)
Co(1)-N(5)	1.946(2)	N(3)-Co(1)-N(4)	84.63(8)
Co(1)-N(4)	1.952(2)	N(5)-Co(1)-N(4)	178.68(8)
Co(1)-N(1)	1.962(2)	N(3)-Co(1)-N(1)	84.11(8)
Co(1)-N(2)	2.015(2)	N(5)-Co(1)-N(1)	94.50(8)
Co(1)-Cl(1)	2.241(1)	N(4)-Co(1)-N(1)	85.90(8)
		N(3)-Co(1)-N(2)	170.58(8)
		N(5)-Co(1)-N(2)	84.09(8)
		N(4)-Co(1)-N(2)	97.19(7)
		N(1)-Co(1)-N(2)	86.80(7)
		N(3)-Co(1)-Cl(1)	94.74(6)
		N(5)-Co(1)-Cl(1)	85.39(6)
		N(4)-Co(1)-Cl(1)	94.18(6)
		N(1)-Co(1)-Cl(1)	178.83(6)
		N(2)-Co(1)-Cl(1)	94.34(5)

bond length		bond angle	
Co(2)-N(9)	1.946(2)	N(9)-Co(2)-N(8)	87.25(8)
Co(2)-N(10)	1.951(2)	N(9)-Co(2)-N(10)	93.58(8)
Co(2)-N(8)	1.949(2)	N(8)-Co(2)-N(10)	177.93(8)
Co(2)-N(6)	1.957(2)	N(9)-Co(2)-N(6)	84.23(8)
Co(2)-N(7)	2.026(2)	N(8)-Co(2)-N(6)	86.24(8)
Co(2)-Cl(2)	2.238(1)	N(10)-Co(2)-N(6)	95.73(8)
		N(9)-Co(2)-N(7)	169.89(8)
		N(8)-Co(2)-N(7)	96.14(8)
		N(10)-Co(2)-N(7)	83.36(8)
		N(6)-Co(2)-N(7)	86.49(8)
		N(9)-Co(2)-Cl(2)	94.74(6)
		N(8)-Co(2)-Cl(2)	92.87(6)
		N(10)-Co(2)-Cl(2)	85.17(6)
		N(6)-Co(2)-Cl(2)	178.67(6)
		N(7)-Co(2)-Cl(2)	94.60(6)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure S1.

Figure S2. Molecular structures of the possible isomers of *rac*-**3**.
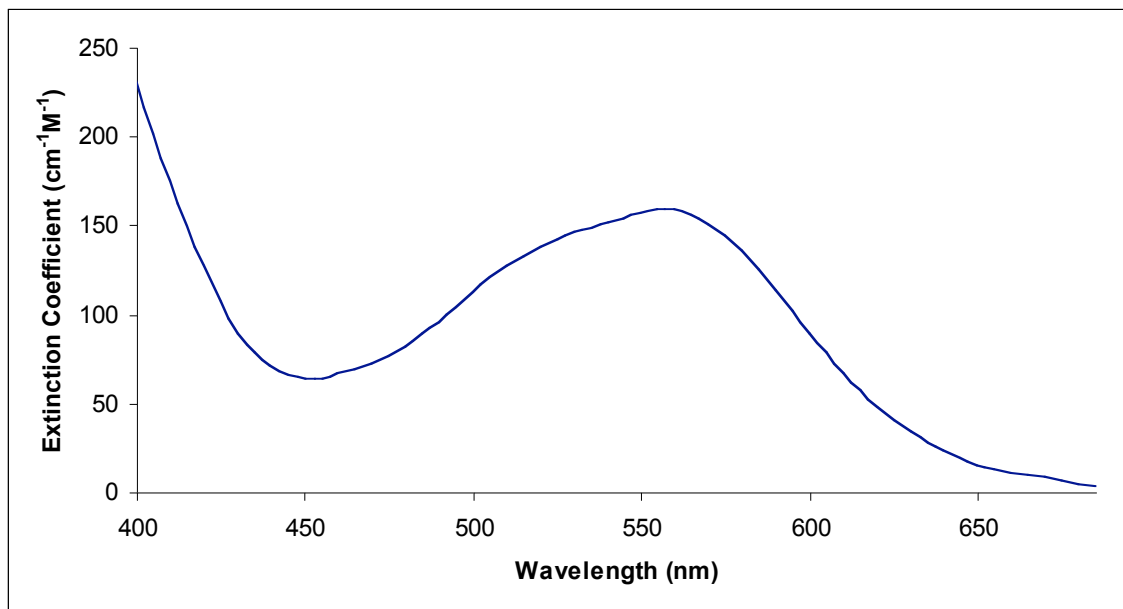
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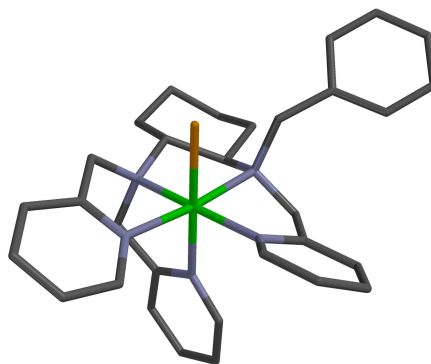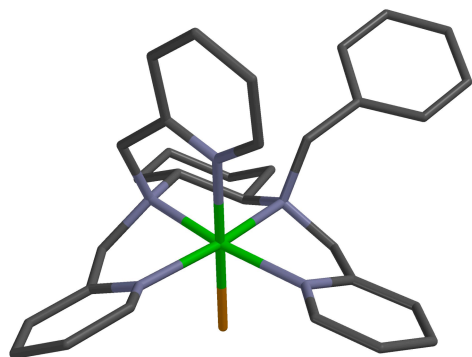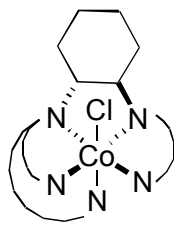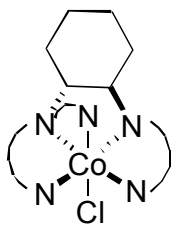
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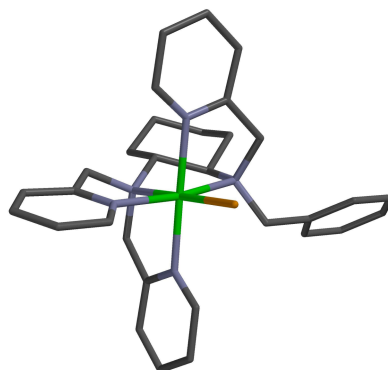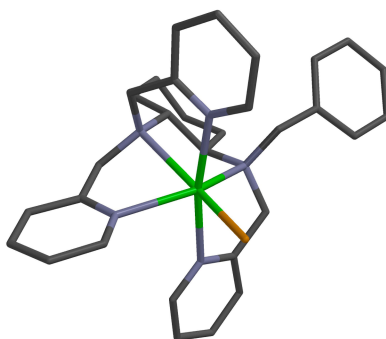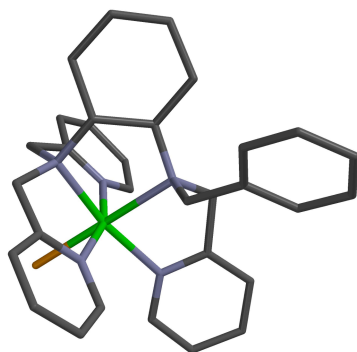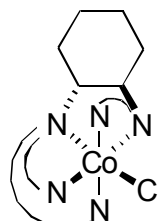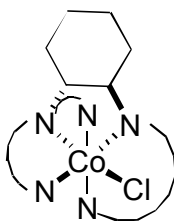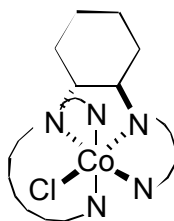
Part D. UV-vis Data.

Figure S3. The UV-vis spectrum of *rac*-**3**, 1 mM in MeOH.

Part E. Molar Conductivity Data.

The conductivity meter was calibrated with a 0.01 M KCl solution which has a known conductivity of 1.413 mS/cm at 25 °C. The specific conductivities of 0.25 − 2.0 mM MeOH solutions of *rac*-**3** were measured at ambient temperature in MeOH (~25°C).[9] Molar conductivities (Λ_M) were calculated from these values.

Table S3. Conductivities for *rac*-**3** in MeOH at 25 °C.

[*rac*-3] in MeOH (mM)	Λ_M (S•cm^2•mol^{-1})
2.0	143.0
1.5	143.3
1.0	148.8
0.5	176.8
0.25	207.2

Part F. References

1) S. Schoumacker, O. Hamelin, J. Pecaut and M. Fontecave, *Inorg. Chem*., 2003, **42**, 8110-8116.

2) W. Park, M. H. Shin, J. H. Chung, J. Park, M. S. Lah and D. Lim, *Tetrahedron Lett*., 2006, **47**, 8841-8845.

3) P. Mialane, A. Nivorojkine, G. Pratviel, L. Azema, M. Slany, F. Godde, A. Simaan, F. Banse, T. Kargar-Grisel, G. Bouchoux, J. Sainton, O. Horner, J. Guilhem, L. Tchertanova, B. Meunier and J.-J. Girerd, *Inorg. Chem*., 1999, **38**, 1085-1092.

4) J. Springborg and C. E. Schaeffer, *Acta Chem. Scand*., 1973, 27, 3312-3322.

5) C. N. Elgy and C. F. Wells, *J. Chem. Soc., Dalton Trans*., 1980, 2405-2409.

6) *APEX II, SMART, SAINT and SADABS* collection and processing programs are distributed by the manufacturer. Bruker AXS Inc., Madison WI, USA.

7) G. Sheldrick, *SHELX-97*, University of Gottingen, Germany, 1997.

8) A. L. Speck, "PLATON, a multipurpose crystallographic tool." Utrecht University, Utrecht, The Netherlands, 2001.

9) W. J. Geary, *Coord. Chem. Rev*., 1971, 7, 81-122.

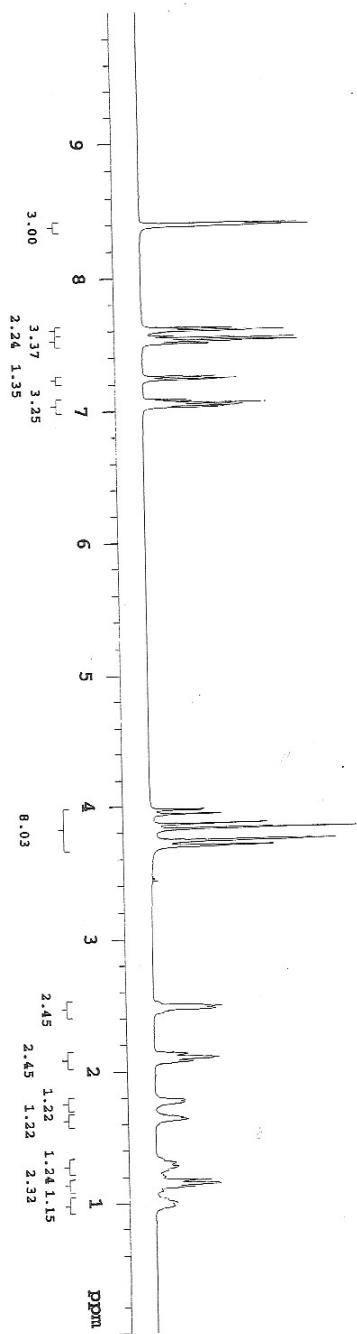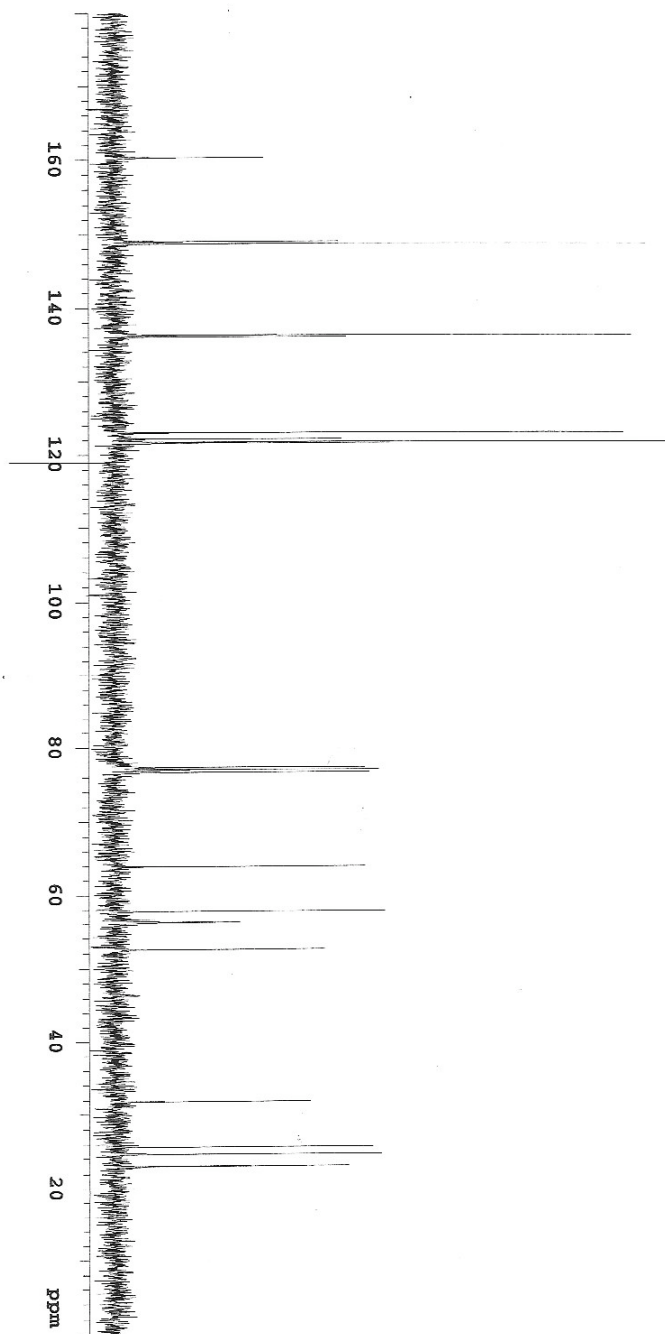**Part G.** ^{1}H and ^{13}C NMR spectra for all new compounds

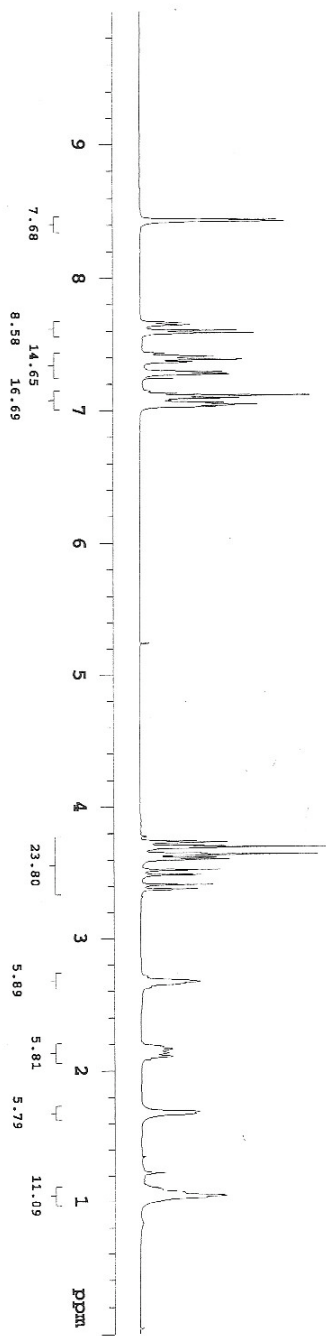^{1}H NMR for *rac*-**5**
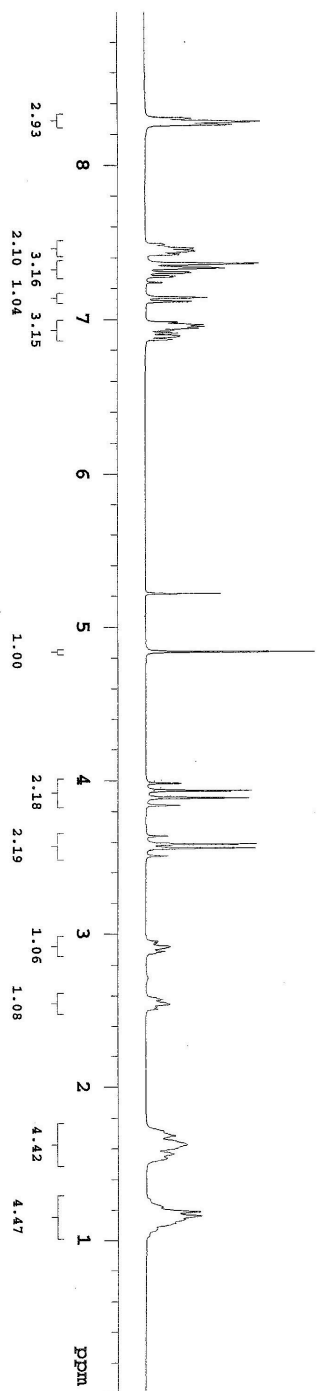
^{13}C NMR for *rac*-**5**
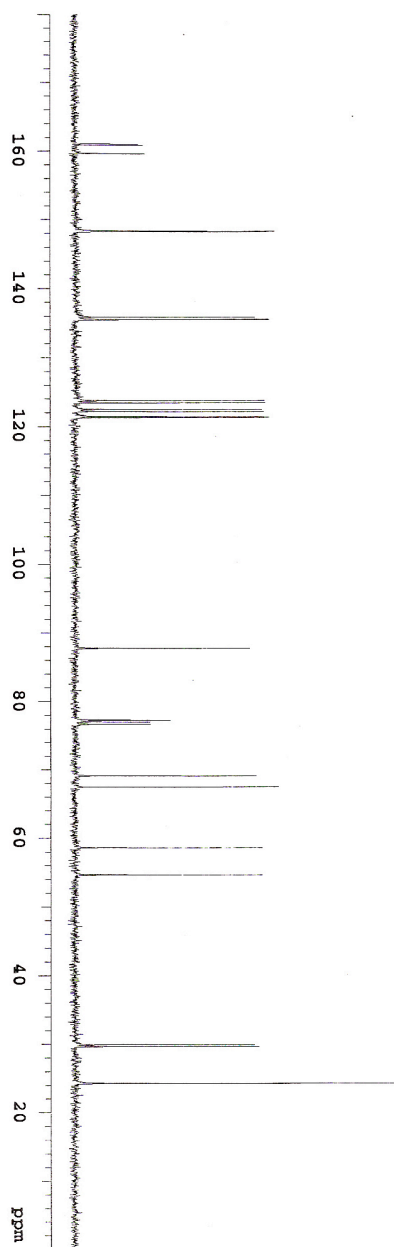
^{1}H NMR for *rac*-**6**

^{13}C NMR for *rac*-**6**

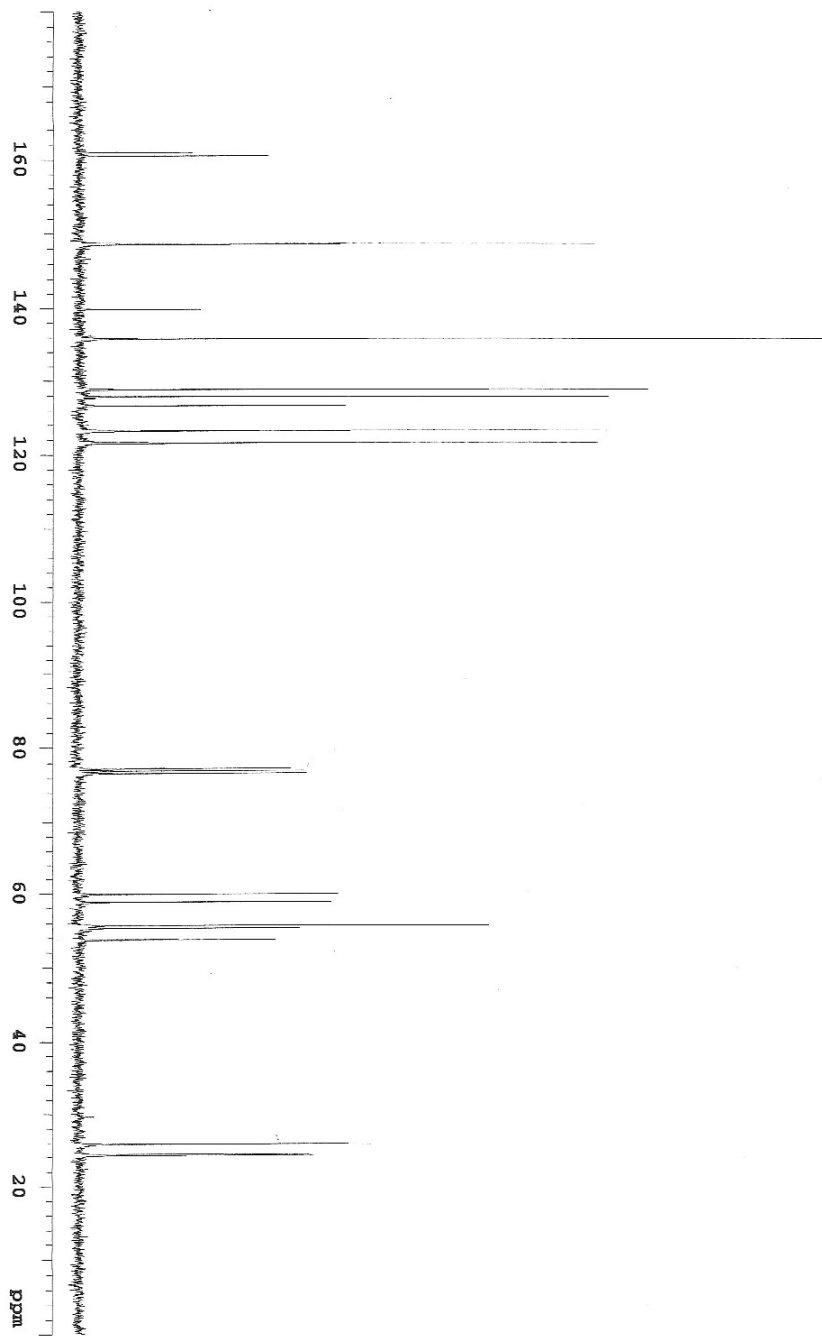¹H NMR for *rac*-**2**

¹³C NMR for *rac*-**2**
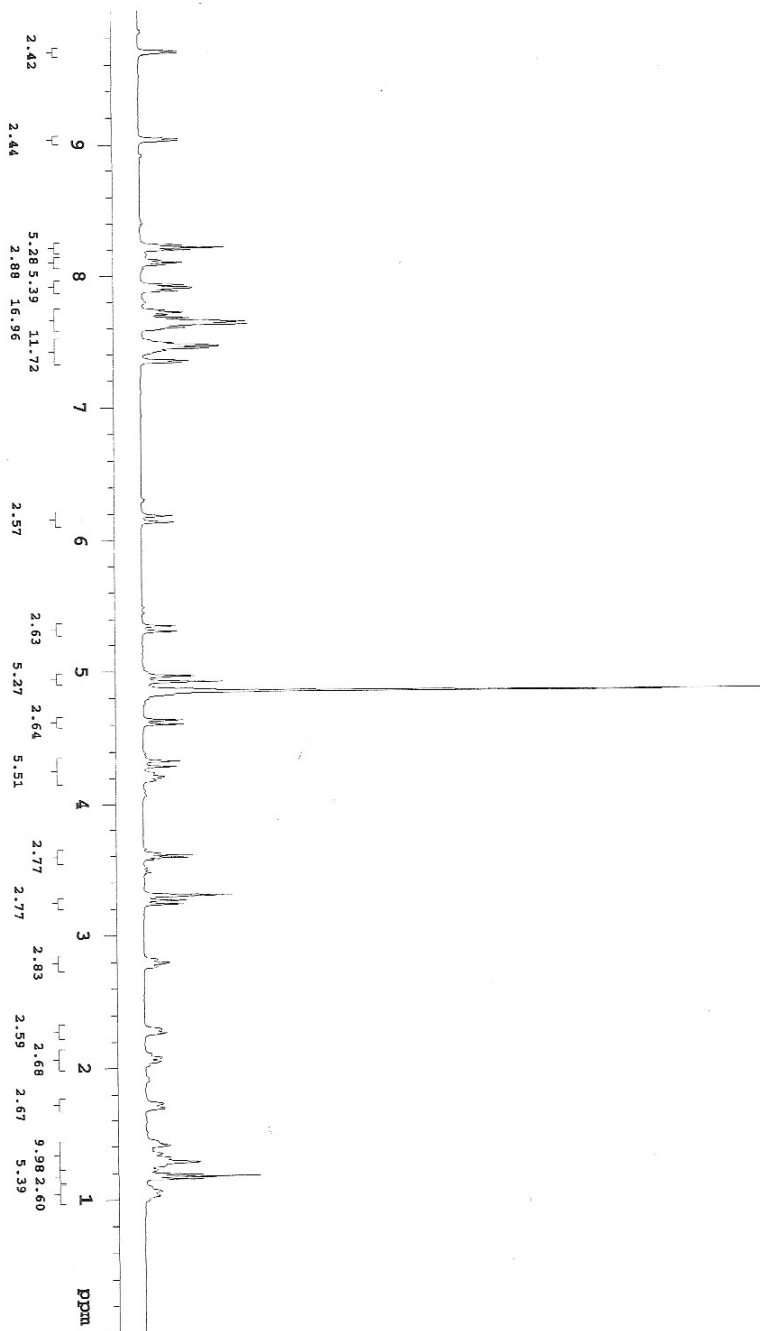
¹H NMR for *rac*-**3**

^{13}C NMR for *rac*-**3**

IR for *rac*-**3**