Synthesis of a series of M(II) (M = Mn, Fe, Co) chloride complexes with both inter- and intra-ligand hydrogen bonding interactions

*Clare A. Leahy, Michael Drummond, Joshua Vura-Weis, and Alison R. Fout**

Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave. Urbana, IL 61801.

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General Considerations

All manipulations 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 except where specified otherwise. All glassware was oven- dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. Solvents were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves purchased from Strem following literature procedure prior to use.

2-bromo-6-acetylpyridine was synthesized using the same procedure as previously reported.[1] 2-phenol-6-acetylpyridine (**L1**) was synthesized according to a modified literature procedure.[2] NMR spectra were recorded at room temperature on a Varian spectrometer operating at 400 MHz or 500 MHz (^{1}H NMR) and 126 MHz (^{13}C NMR) and referenced to the residual solvent resonance (δ in parts per million and J in Hz). For paramagnetic molecules, the ^{1}H NMR data are reported with the chemical shift referenced to solvent peaks. Solid-state infrared spectra were recorded using a PerkinElmer Frontier FT-IR spectrophotometer equipped with a KRS5 thallium bromide/iodide universal attenuated total reflectance accessory. Elemental analyses were performed by the University of Illinois at Urbana−Champaign (UIUC) School of Chemical Sciences Microanalysis Laboratory in Urbana, IL. Samples submitted for elemental analyses were dried under vacuum for a minimum of 12 hours; solvates were confirmed by ^{1}H NMR. High-resolution mass spectra were recorded by the University of Illinois at Urbana-Champaign Mass Spectrometry Laboratory.

Synthesis of Ligands and Metal Complexes

2-phenol-6-acetyl-pyridine (L1). A modified literature procedure was used.[2] A 250 mL round-bottom flask was charged with 2-bromo-6-acetyl-pyridine (0.500 g, 2.50 mmol), 2-hydroxyphenylboronic acid (1.4 eq, 0.483 g, 3.50 mmol), $Pd(OAc)_2$ (0.010 g, 0.0445 mmol), triphenylphosphine (PPh_3, 0.027 g, 0.103 mmol), a solution of toluene:ethanol (2:1, total volume 15 mL) and 2 M K_2CO_3 (2.5 mL), and the reaction mixture was heated at 90 ^{o}C for 16 h. The resulting black reaction mixture was cooled to room temperature, H_2O_2 (0.25 mL, 30% in water) was added, and the mixture was stirred at room temperature in air for 30 minutes. The reaction mixture was then transferred to a separatory funnel and the organic portion collected. The aqueous portion was extracted with more toluene (4 x 10 mL) and the organic extractions combined and washed with brine (15 mL) and water (4 x 10 mL). The organic phase was finally dried with magnesium sulfate and filtered to removed solids. Volatiles were removed *in vacuo*, and the subsequent brown film was dissolved in a minimal amount of methanol. The resulting

mixture was stirred for 1 hour, and the desired product was collected as a powdery yellow precipitate via filtration. Yield, ^{1}H NMR, and IR data agreed with literature values.

^{Ph}OHPy(pi^{H})$_2$ (L2). A 20 mL scintillation vial was charged with 2-phenol-6-acetyl-pyridine (L1, 0.500 g, 2.34 mmol), pyrrole (0.5 mL, 7.21 mmol), and tetrahydrofuran (3 mL). While stirring, trifluoroacetic acid (20 drops) was added dropwise to the dark yellow-brown solution. The solution was stirred at room temperature for 24 h. Subsequently, the black solution was neutralized with saturated aqueous sodium bicarbonate solution and transferred to a separatory funnel. The aqueous portion was extracted with dichloromethane (3 x 10 mL), and the combined organic fractions were washed with brine (1 x 10 mL) and water (2 x 10 mL). Volatiles were removed *in vacuo*, resulting in a dark brown residue. The residue was dissolved in diethyl ether and filtered to produce a dark orange-brown filtrate that was discarded. Filtrate volatiles were removed *in vacuo*, giving the desired product as a light tan powder (0.588 g, 1.79 mmol, 76%). ^{1}H NMR ($CDCl_3$, 22 °C): δ = 13.41 (s, Ph-OH, 1H), 8.07 (bs, pyrr-NH, 2H), 7.77 (m, py & Ph, 3H), 7.28 (m, py, 1H), 7.11 (dd, J= 2.90 & 5.80 Hz, 1H), 6.97 (dd, J = 1.15 & 8.28 Hz, Ph, 1H), 6.90 (m, Ph, 1H), 6.73 (m, pyrr-H, 2H), 6.20 (m, pyrr-H, 2H), 5.99 (m, pyrr-H, 2H), 2.17 (s, -CH_3, 3H). ^{13}C NMR ($CDCl_3$, 22 °C): δ = 163.0, 159.5, 157.1, 138.5, 135.7, 131.6, 126.6, 119.7, 119.3, 119.0, 118.7, 117.7, 117.5, 108.6, 106.7, 46.7, 27.4. IR = 3288 cm^{-1} (N−H), 3412 cm^{-1} (O-H). ESI-MS: calculated $[C_{21}H_{20}N_3O]^+$: 330.1606, found: 330.1599.

^{Ph}OHPy(pi^{COH})$_2$ (L3). A 250 mL Schlenk flask was charged with **L2** (0.550 g, 1.67 mmol), dichloromethane (40 mL) and dimethylformamide (10 mL) and topped with an addition funnel. A solution of $POCl_3$ (2.5 eq, 0.640 g, 4.17 mmol) in dichloromethane (10 mL) was added to the addition funnel. The entire system was purged with nitrogen for 10 min. The $POCl_3$ solution was added dropwise over the course of 5 min while stirring vigorously, and the reaction solution was heated at reflux for 2 h. Sodium acetate (8 eq, 1.10 g, 13.4 mmol) in water was then added to the brown reaction solution, and the mixture was heated at 40^{o}C for 1 h. The dark brown reaction mixture was cooled to room temperature, neutralized with saturated sodium bicarbonate, and separated. The aqueous portion was extracted with dichloromethane (3 x 15 mL), and the combined organics were washed with brine (1 x 15 mL), and water (1 x 15 mL). The organic solution was subsequently dried with magnesium sulfate and filtered. Solvents were removed *in vacuo*, and the desired product was acquired as a yellow film (0.521 g, 1.35 mmol, 81%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 13.43 (s, OH, 1H), 10.91 (bs, pyrr-NH, 2H), 9.11 (s, COH, 2H), 7.80-7.75 (m, Ph, 3H), 7.28 (m, *p*-pyr-H, 1H), 7.15 (d(d), J= 7.3 Hz (0.8 Hz), *m*-pyr-H, 1H), 6.95 (d(d), J = 8.23 Hz (0.8 Hz), *m*-pyr-H, 1H), 6.91 (m, Ph, 1H), 6.88 (dd, J = 3.7 & 2.3 Hz, pyrr-H, 2H), 6.16 (dd, J = 3.5 & 2.6 Hz, pyrr-H, 2H), 2.23 (s, -CH_3, 3H). ^{13}C NMR ($CDCl_3$,25 °C): δ = 179.2, 160.4, 159.6, 157.2, 144.7, 138.8, 133.0, 131.8, 126.6, 122.1, 120.9, 119.1,

118.9, 118.7, 118.0, 111.0, 47.9, 27.4. IR = 1650 cm^{-1} (C=O), 3216, 3278 cm^{-1} (N-H). ESI-MS: calculated $[C_{23}H_{20}N_3O_3]^+$: 386.1505, found: 386.1502.

^{Ph}OHPy(pi^{Cy})$_2$. A 20 mL scintillation vial was charged with **L3** (0.520 g, 1.35 mmol), dichloromethane (5 mL), and cyclohexylamine (0.500 mL, 4.36 mmol). The dark red-brown solution was stirred overnight, and solvents were removed *in vacuo*. The resulting dark red film was dissolved in a small amount of diethyl either and left to sit for 20 min, precipitating out an off-white powder. This precipitate was collected by filtration and dried overnight under vacuum. The desired product was produced as a white-to-tan powder (0.599 g, 1.09 mmol, 81%). Prior to use in metal chemistry PhOHPy(pi^{Cy})$_2$ was brought into a glovebox, dissolved in dichloromethane and left to sit over 4Å molecular sieves for at least 18 h. Analysis for $C_{35}H_{41}N_5O$•0.6$C_6H_{13}N$•0.1CH_2Cl_2 (calc., found): C (75.49, 75.51), H (8.02, 8.00), N (12.74, 12.70). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.98 (bs, pyrr-NH, 2H), 7.76-7.73 (m, Ph, 3H), 7.25 (m, Ph 1H), 6.94 (dd, J= 8.3 & 1.0 Hz, Ph, 1H), 6.87 (m, Ph, 1H), 6.44 (d, J = 1.7 Hz, pyrr-H, 2H), 6.17 (dd, J = 3.6 Hz, pyrr-H, 2H), 3.06 (bm, Cy-CH, 2H), 2.16 (s, -CH_3, 3H), 1.82-0.99 (m, Cy, 20H). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 163, 159., 157, 150, 139, 139, 131, 127, 119.6, 119.6, 118.9, 117.7, 115, 109, 68.8, 47.3, 34.8, 27.0, 25.8, 25.0. IR = 1634 cm^{-1} (C=N), 3245 cm^{-1} (N−H), 3425 cm^{-1} (O-H).

General metalation procedure. A 20 mL scintillation vial was charged with ^{Ph}OHPy(pi^{Cy})$_2$ (27.0 mg, 0.049 mmol) and tetrahydrofuran (8 mL). While stirring, potassium hydride (2.0 mg, 0.050 mmol) was added. The reaction mixture was stirred for 10 min and filtered to remove excess potassium hydride, resulting in a light yellow solution. The metal dichloride salt (1 equiv, 0.049 mmol) was added, and the reaction was left to stir at room temperature for 18 h.

^{Ph}OPy(afa^{Cy})$_2$MnCl. After following the general procedure of complexation of MCl_2 salts (*vide supra*), the dark orange-yellow reaction solution had volatiles removed, and the remaining orange solids were dissolved in dichloromethane. This mixture was filtered through Celite™, and the filtrate collected. Solvents were removed *in vacuo*, and the desired product was collected as an orange film (28.4 mg, 0.0445 mmol, 91%). Dark orange crystals suitable for X-ray crystallography were grown from a vapour diffusion of diethyl ether into a concentrated solution of the product in dichloromethane. Analysis for $C_{35}H_{40}N_5OClMn$•0.1 CH_2Cl_2 (calc., found): C (65.30, 65.18), H (6.28, 6.22), N (10.85, 10.72). This complex presented as ^{1}H NMR silent. IR: 1640 cm^{-1} (C=N), 3161 (N-H). μ_{eff} = 6.10(22) μ_B.

^{Ph}OPy(afa^{Cy})$_2$FeCl. After following the general procedure of complexation of MCl_2 salts (*vide supra*), the dark red reaction solution was filtered through Celite™, with volatiles removed from the filtrate. The resulting dark red-brown solid was dissolved in

dichloromethane, filtered through Celite™, and solvents were removed in vacuo. The desired product was collected as a dark red solid (30.7 mg, 0.048 mmol, 98%). Red crystals suitable for X-ray crystallography were grown from a vapour diffusion of diethyl ether into a concentrated solution of the product in dichloromethane. Analysis for $C_{35}H_{40}N_5OClFe•0.75CH_2Cl_2$ (calc., found): C (61.19, 61.50), H (5.96, 6.35), N (9.98, 10.26). ^{1}H NMR (d_2-CD_2Cl_2, 500 MHz, 21^{o}C): 45, 43, 40, 39, 38, 35, 32, 29, 24, 8.8, 2.0, 1.5-0.9, 0.2, -1.2, -1.6, -3.5, -4.7, -6.3, -6.5, -8.6, -14, -15, -16, -18, -21, -22, -23, -25 ppm. IR: 1639 cm-1 (C=N), 3242 (broad, N-H). μ_{eff} = 5.26(12) μ_B.

^{Ph}OPy(afa^{Cy})$_2$CoCl. After following the general procedure of complexation of MCl_2 salts (*vide supra*), the dark green solution was filtered through Celite™, and the filtrate was had volatiles removed. The resulting dark green film was dissolved in a minimal amount of dichloromethane, filtered through Celite, and solvents removed *in vacuo*. The desired product was collected as a dark green solid (29.7 mg, 0.0434 mmol, 89%). Dark green-brown crystals suitable for X-ray crystallography were grown from a vapor diffusion of diethyl ether into a concentrated solution of the product in dichloromethane. Analysis for $C_{35}H_{40}N_5OClCo•0.25CH_2Cl_2$ (calc., found): C (63.92, 63.70), H (6.16, 6.12), N (10.57, 10.61). ^{1}H NMR (d_2-CD_2Cl_2, 500 MHz, 21^{o}C): 59.7, 53.5, 43.9, 43.4, 38.0, 29.5, 13.3, 10.8, 9.4, 6.3, 5.4, 4.3, 3.9, 3.8, 3.3, 2.1, 1.4, 1.2, 0.6, 0.4, -2.4, -14.8, -19.4 ppm IR: 1641 cm-^{1} (C=N), 3183 (N-H). μ_{eff} = 4.62(16) μ_B.

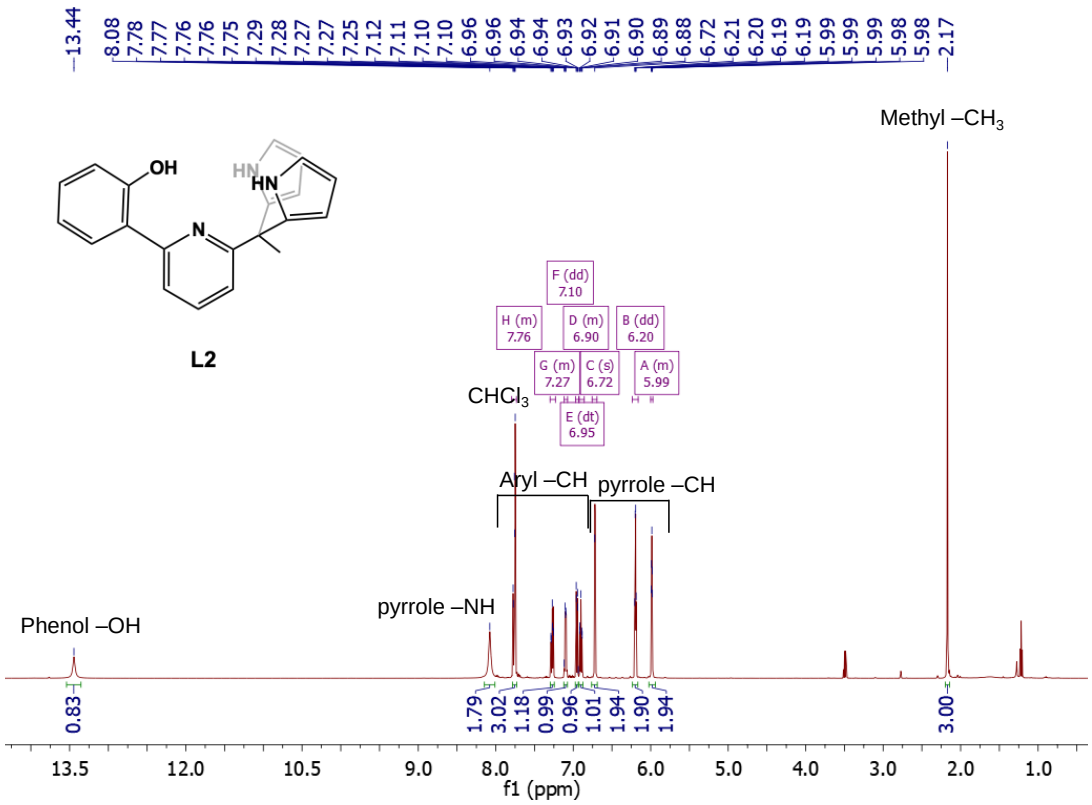

Figure S1 – ^{1}H NMR spectrum of **L2** in d_1-$CHCl_3$.

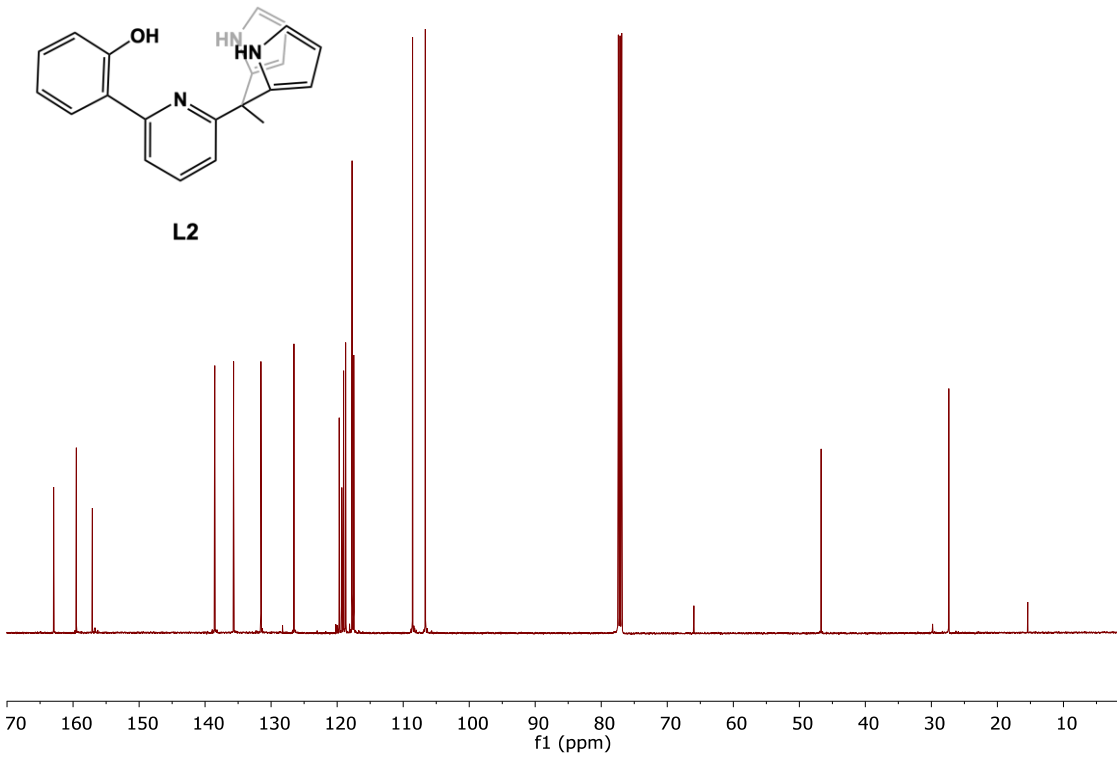

Figure S2 – ^{13}C NMR spectrum of **L2** in d_1-$CHCl_3$.

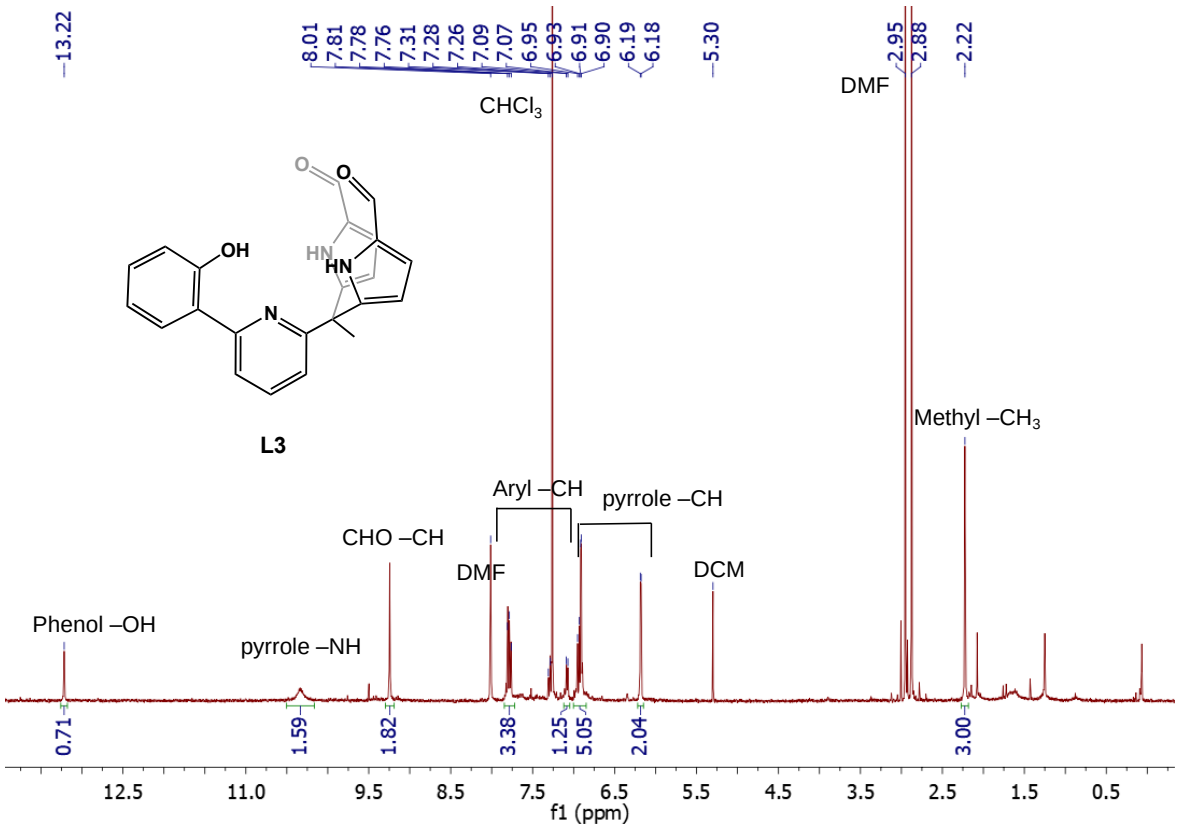

Figure S3 –^{1}H NMR spectrum of **L3** in d_1-$CHCl_3$.

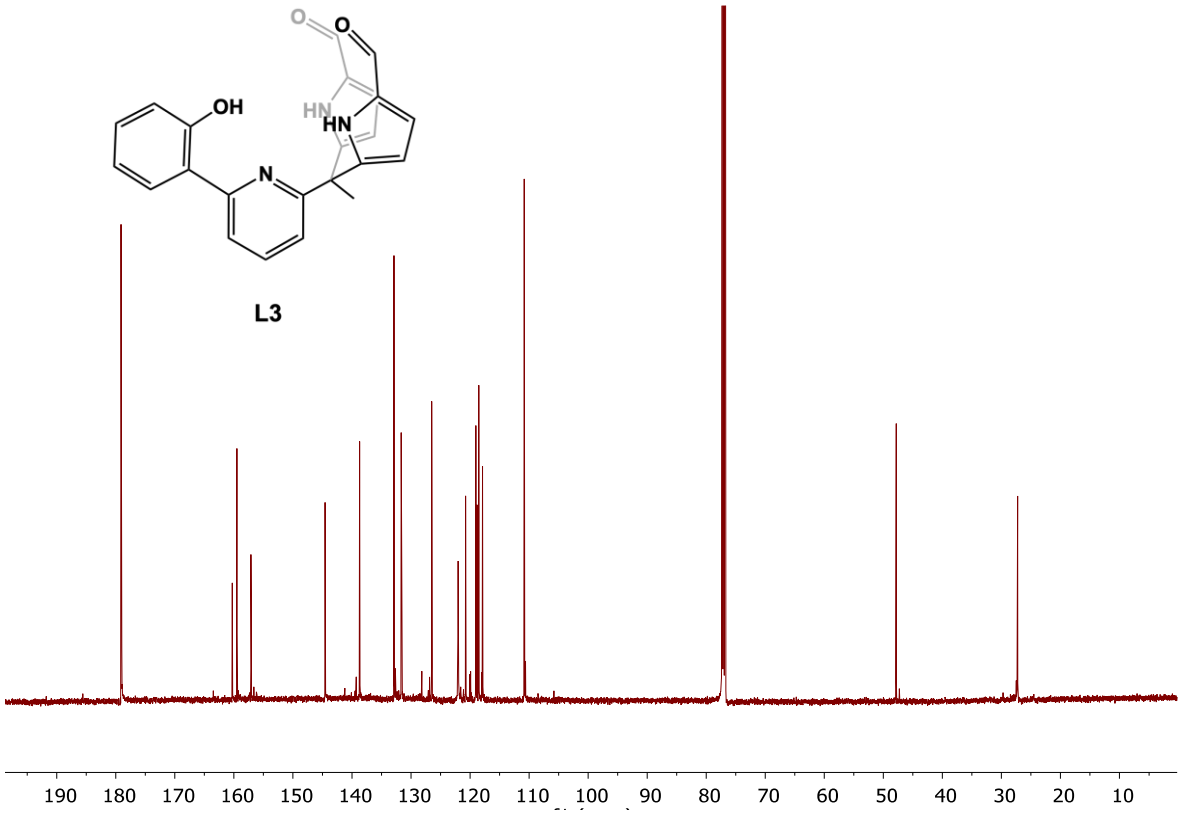

Figure S4 – ^{13}C NMR spectrum of **L3** in d_1-$CHCl_3$.

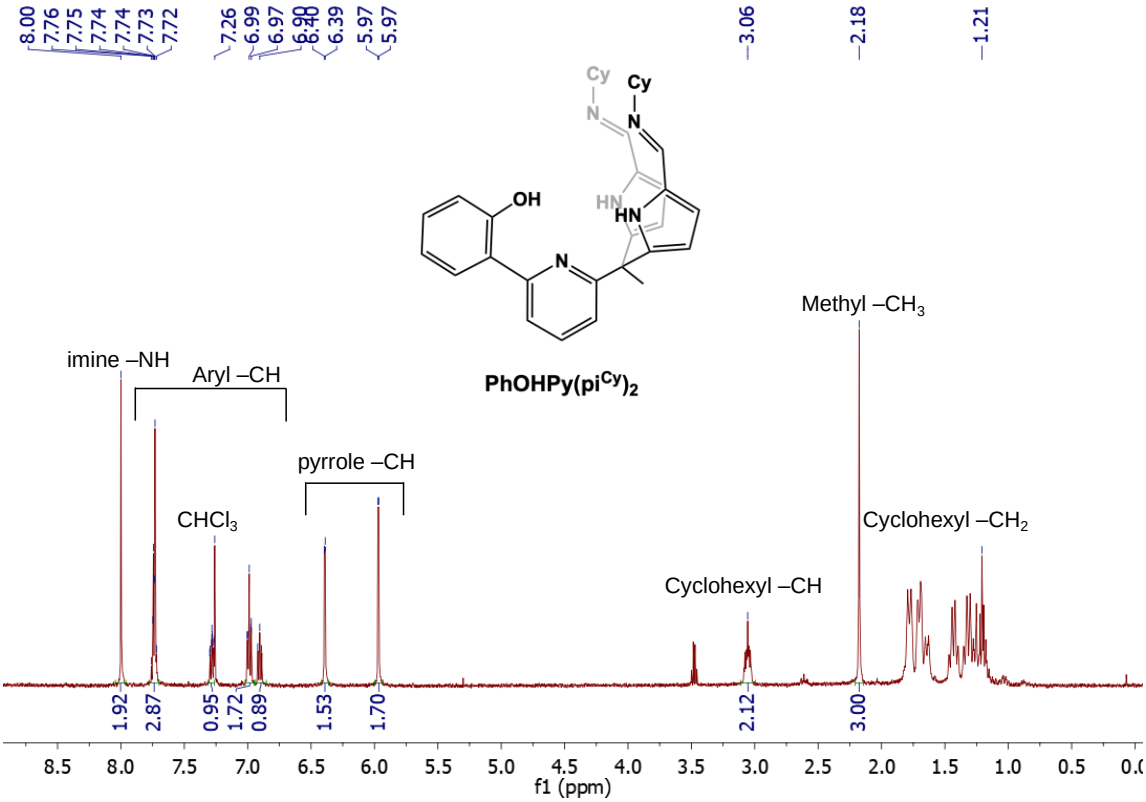

Figure S5 – ^{1}H NMR spectrum of ^{Ph}OHPy(pi^{Cy})$_2$ in d_1-$CHCl_3$

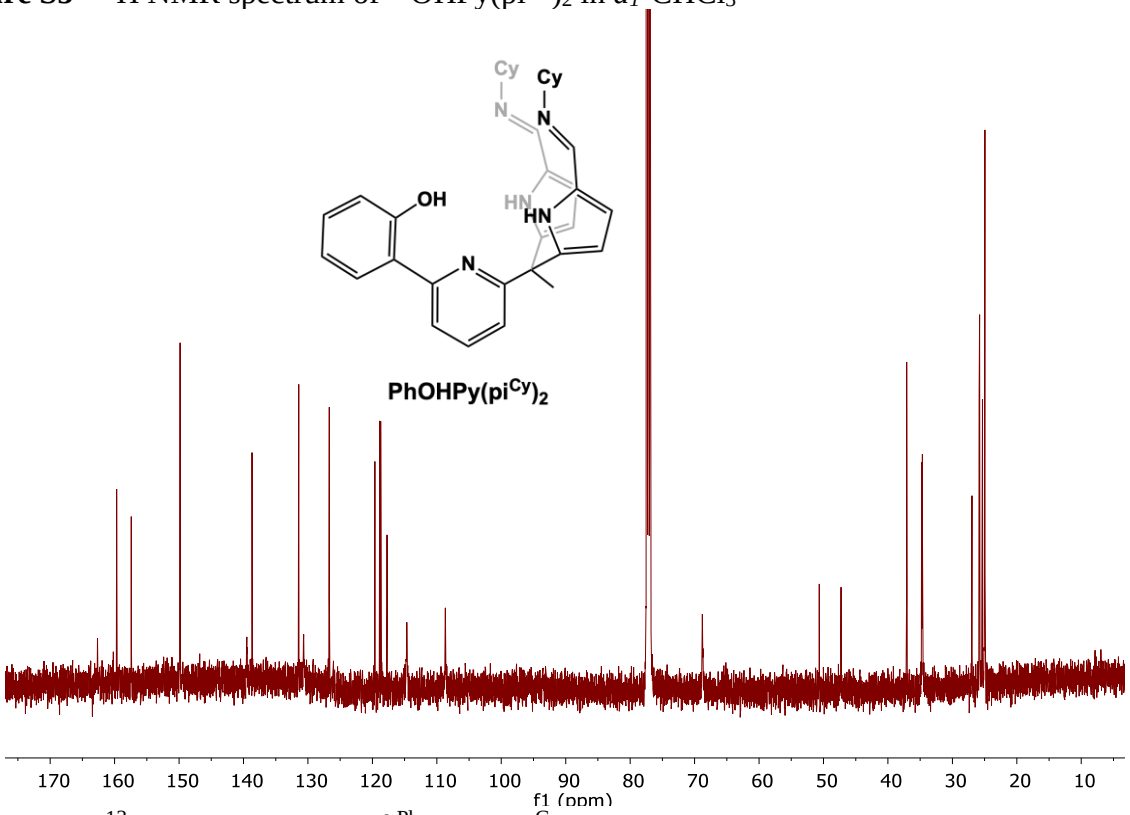

Figure S6 – ^{13}C NMR spectrum of ^{Ph}OHPy(pi^{Cy})$_2$ in d_1-$CHCl_3$

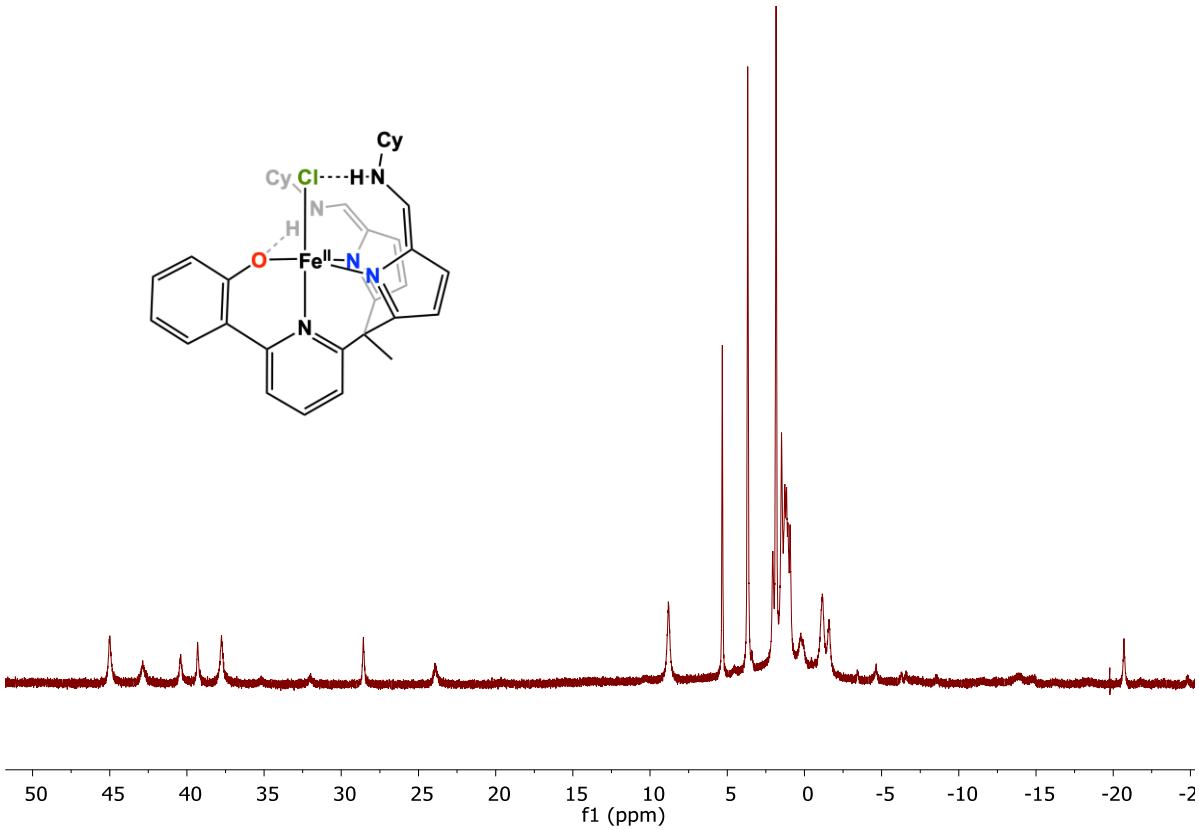

Figure S7 – ^{1}H NMR spectrum for **2** in d_2-CH_2Cl_2.

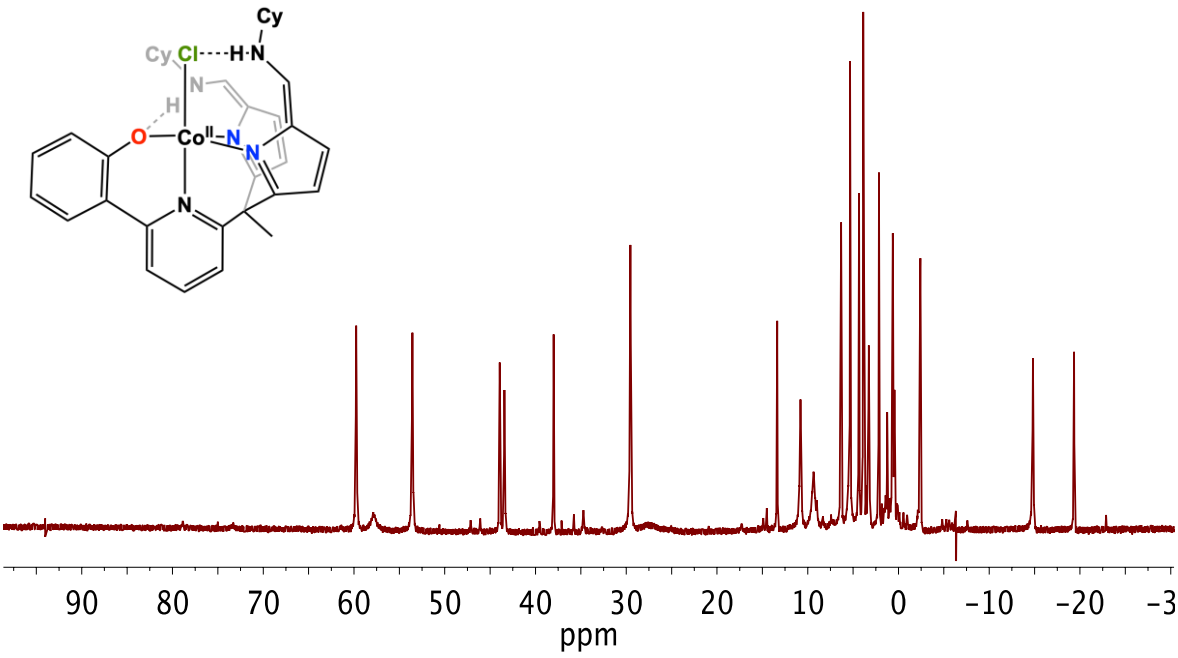

Figure S8 – ^{1}H NMR spectrum for **3** in d_2-CH_2Cl_2.

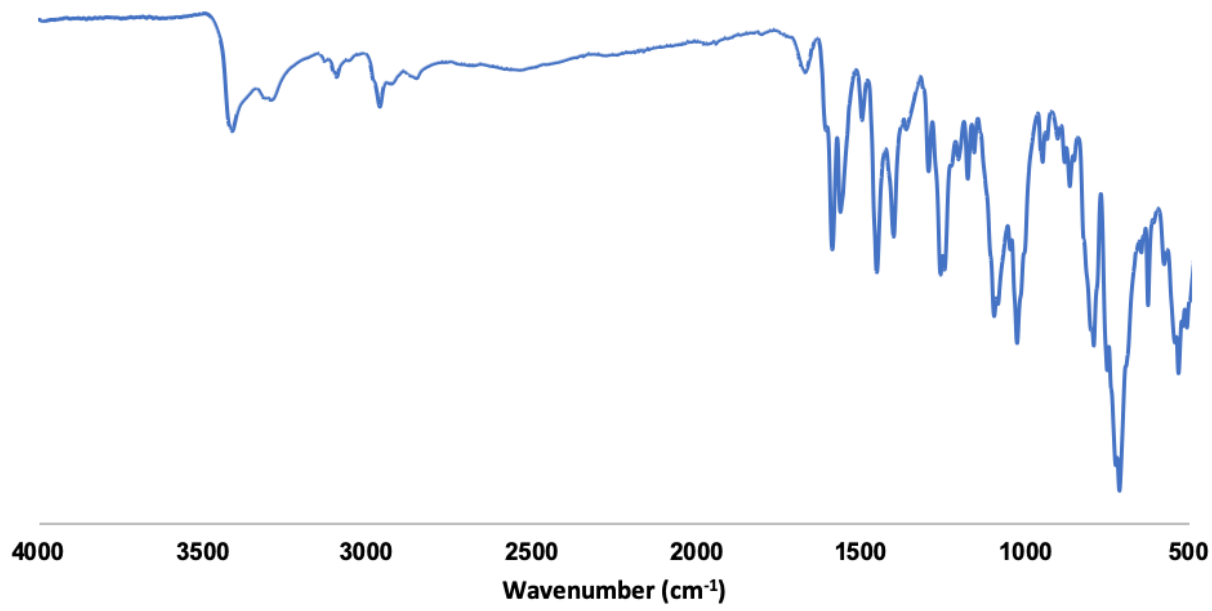

Figure S9 – IR spectrum for **L2**.

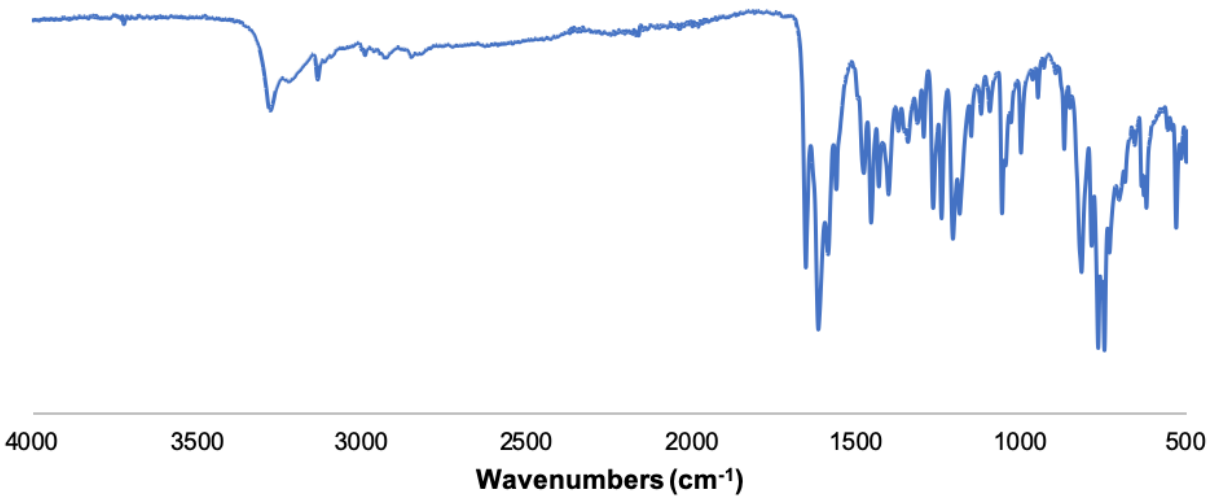

Figure S10 – IR spectrum for **L3**.

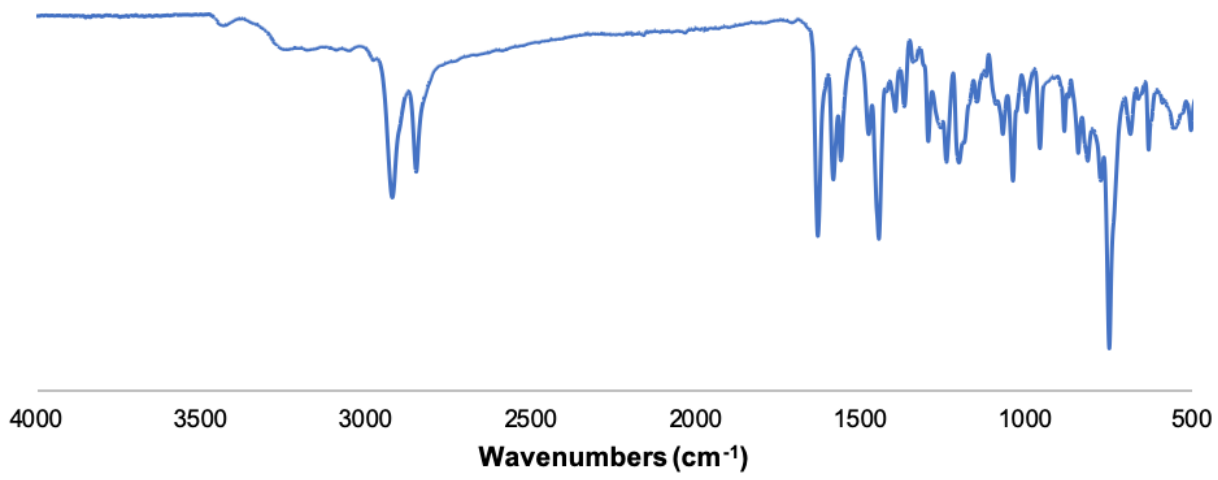

Figure S11 – IR spectrum for ^{Ph}OHPy(pi^{Cy})$_2$.

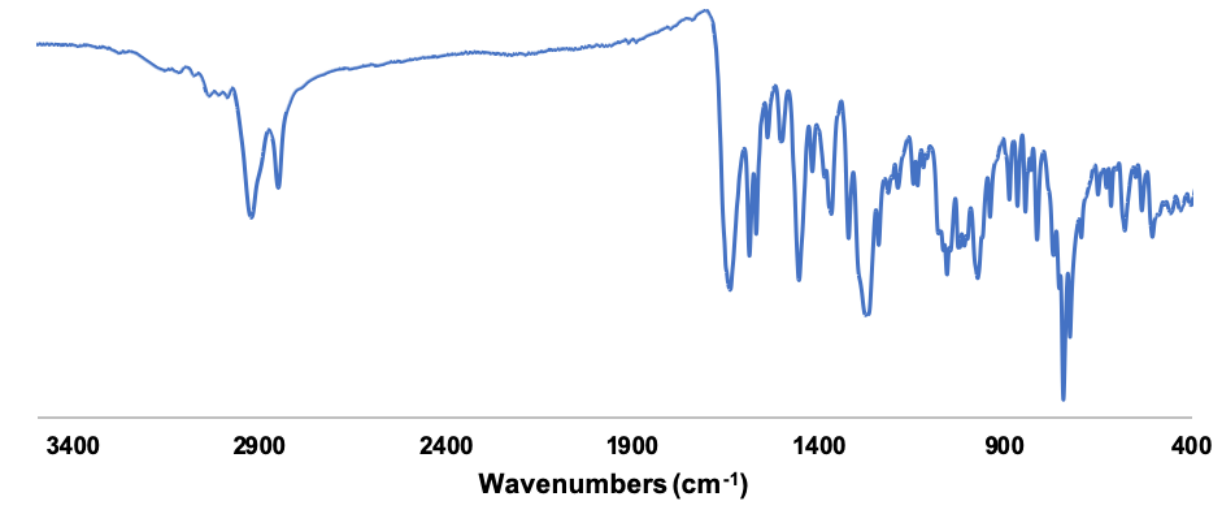

Figure S12 – IR spectrum for complex **1**.

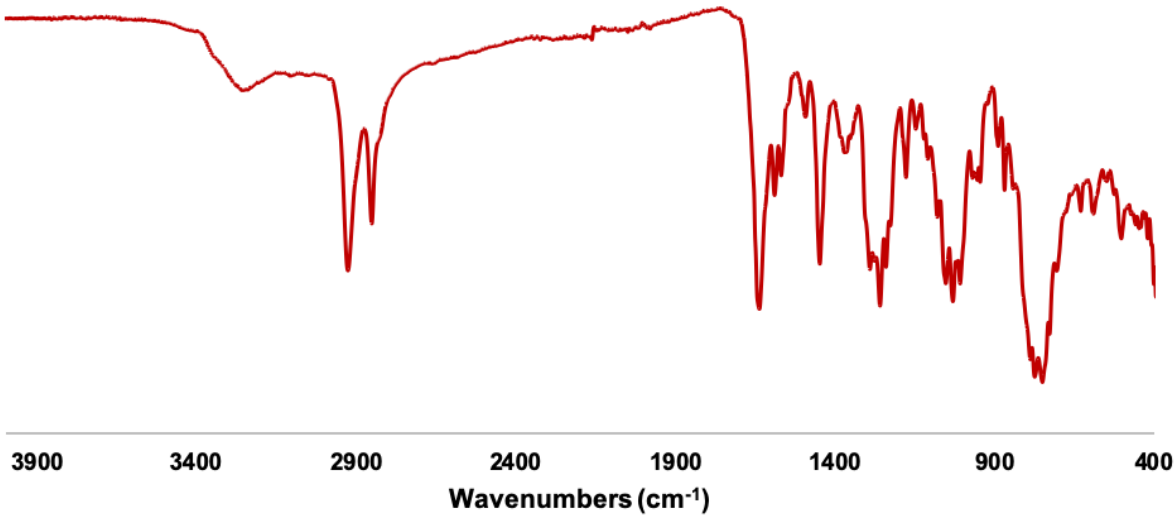

Figure S13 – IR spectrum for complex **2**.

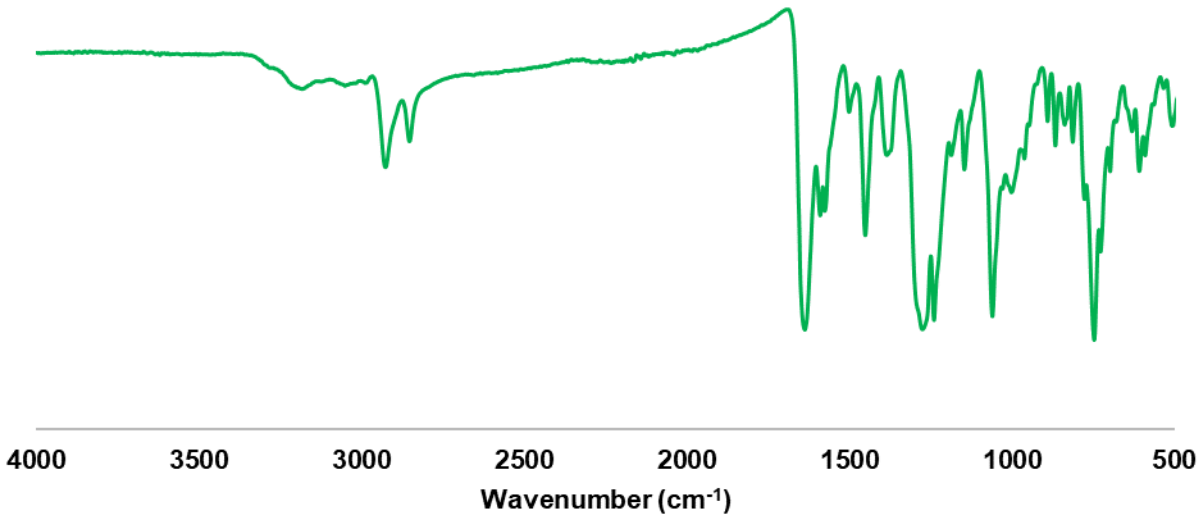

Figure S14 – IR spectrum for complex **3**.

$$\tau_5 = \frac{\beta - \alpha}{60°} = \frac{171.03° - 154.62°}{60°} = \frac{16.41°}{60°} = 0.27$$

Equation S1– Calculation of τ_5 for **1**

$$\tau_5 = \frac{\beta - \alpha}{60°} = \frac{178.32° - 154.10°}{60°} = \frac{24.22°}{60°} = 0.40$$

Equation S2– Calculation of τ_5 for **2**

$$\tau_5 = \frac{\beta - \alpha}{60°} = \frac{176.54° - 148.33°}{60°} = \frac{28.21°}{60°} = 0.47$$

Equation S3– Calculation of τ_5 for **3a**

$$\tau_5 = \frac{\beta - \alpha}{60°} = \frac{175.44° - 132.73°}{60°} = \frac{42.71°}{60°} = 0.71$$

Equation S4– Calculation of τ_5 for **3b**

Table S1 – Crystallographic parameters for complexes **1-3**

	^{Ph}OPy(afa^{Cy})$_2$MnCl **(1)** dd68n	^{Ph}OPy(afa^{Cy})$_2$FeCl (**2**) dm30h	^{Ph}OPy(afa^{Cy})$_2$CoCl (**3a,b**) dd29n
Empirical Formula	$C_{35}H_{40}ClMnN_5O$	C35H40ClFeN5O	$C_{71}H_{82}Cl_4Co_2N_{10}O_2$
Formula Weight	637.11 g/mol	638.02 g/mol	1367.12
Temperature	100.01 K	100.15 K	100.02
Wavelength	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	P-1	P-1	P-1
a (Å)	8.2117(2)	8.2743(3)	12.8543(4)
b (Å)	13.3475(4)	14.0697(5)	13.1875(4)
c (Å)	14.2019(4)	16.2126(6)	21.8904(7)
α (°)	98.8761(9)	107.625(2)	93.4590(10)
β (°)	95.6991(9)	99.068(2)	91.0240(10)
γ (°)	92.0161(9)	106.032(2)	106.6890(10)
Volume (Å^3)	1528.34(7)	1667.83(11)	3545.59(19)
Z	2	2	2
Reflections Collected	45633	24340	175399
Independent Reflections	5609	8309	13068
Goodness-of-fit on F2	1.098	1.053	1.064
Final R indices [I>2σ(I)]	R_1 = 0.0291, wR_2 = 0.0723	R_1 = 0.0417, wR_2 = 0.1140	R_1 = 0.0386, wR_2 = 0.0856
Final R indices [all data]	R_1 = 0.0337, wR_2 = 0.0751	R1 = 0.0532, wR2 = 0.1225	R_1 = 0.0450, wR_2 = 0.0892