Supporting Information for

A Simply Accessible Organometallic System to Gauge Electronic Properties of N-Heterocyclic Carbenes

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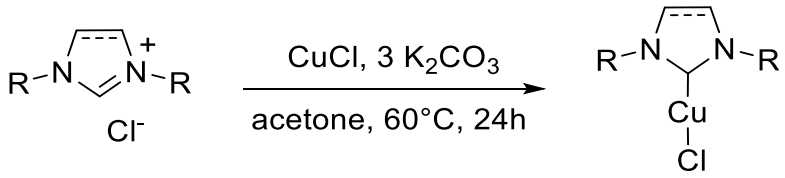
General Considerations

Dichloromethane and acetonitrile used were purified using a J.C. Meyer Phoenix Solvent Purification System in which solvents are dried over aluminium oxide using argon as carrier gas. Supporting electrolyte NBu_4PF_6 was purchased from TCI Chemicals and dried before use. [Cu(NHC)(Cl)] complexes were synthesized from their corresponding NHC·HCl salts using reported procedures and their formation was confirmed by comparing with literature reported ^{1}H-NMR data. ^{1}H-NMR spectra were recorded on a Bruker 300 or 400 MHz spectrometer using $CDCl_3$ as solvent. Spectra were referenced using the residual solvent peak ($CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.16) at 298 K. Electrochemical experiments were conducted inside a glovebox under Ar atmosphere using a three-electrode cell. The cyclic voltammograms (CV) were recorded at a Pt steady disk (ø = 3 mm). The counter-electrode is a Pt sheet electrode while the reference was a Ag/AgCl electrode separated from the solution by a bridge filled with a 0.1 M solution of $^nBu_4PF_6$ in the desired solvent. The potentiostat used is a Metrohm Autolab M204 using NOVA 2.1 as software.

Synthesis of [Cu(NHC)Cl] complexes

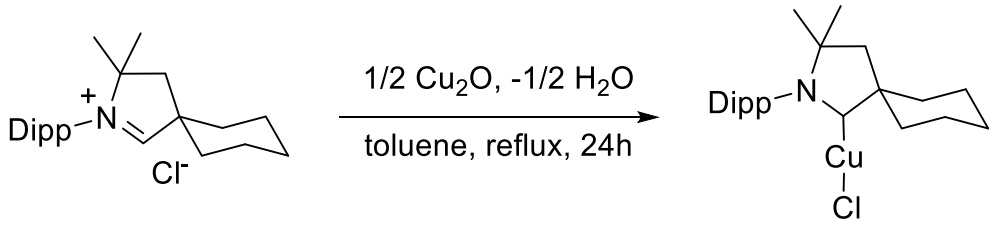
The general procedure is shown below.[1]



Scheme S1: General procedure for the synthesis of [Cu(NHC)Cl] complexes.

A vial was charged with CuCl (1.0 equiv.), NHC·HCl (1.0 equiv.) and K_2CO_3 (3.0 equiv.). The mixture was dissolved in acetone (2 mL) and stirred at 60°C for 24 hours. Conversion was checked with ^{1}H NMR until the H^2 peak of the imidazolium salt disappeared. The solution was then filtered through silica which was washed with acetone (2 mL). The solvent was evaporated *in vacuo* and CH_2Cl_2 (1 mL) and pentane (3 mL) were added to precipitate the desired compound. The compound was washed further with pentane and dried *in vacuo*.

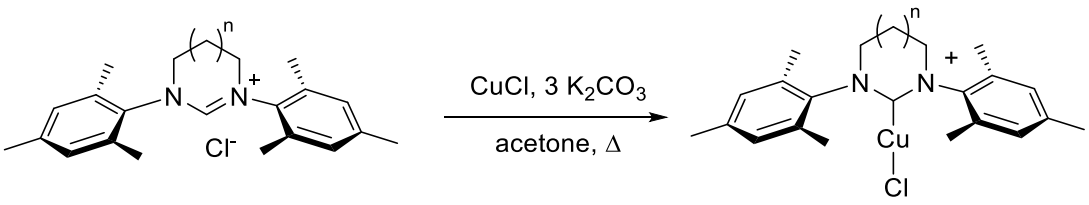
[Cu(CAAC^{Cy})Cl] was prepared using an adapted procedure:[2]



Scheme S2: Procedure for the synthesis of [Cu(CAAC^{Cy})Cl]

In a glovebox, a vial was charged with CAAC^{Cy}·HCl (1 equiv.), Cu_2O (0.5 equiv.), toluene (1 mL) and a magnetic stirring bar and removed from the glovebox. Then, under N_2-atmosphere, the reaction mixture was stirred at reflux for 24 hours. Then, the crude solid was dissolved in dichloromethane (2 mL) and filtered through celite and washed several times with pentane (3x 3 mL) to obtain the desired complex as a grey solid.

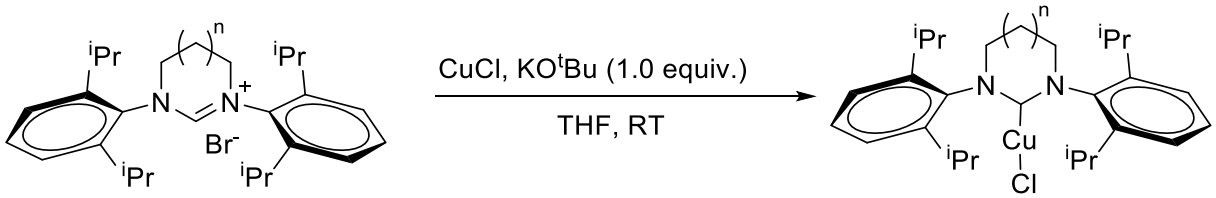
The synthesis of the ring-expanded NHC (RE-NHC) Mes-complexes followed a microwave procedure:[3]



Scheme S3:Procedure for the synthesis of [Cu(6Mes)Cl] and [Cu(7Mes)Cl] complexes.

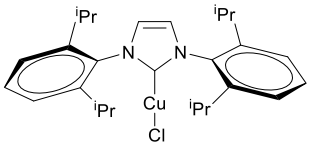
In a glovebox, a microwave vial was loaded with RE-NHC·HCl (1 equiv.), CuCl (1.2 equiv.) and K_2CO_3 (3 equiv.) and acetone (2mL). The mixture was heated in a microwave - 2 hours for [Cu(6Mes)Cl] and 10 hours for [Cu(7Mes)Cl)] - and reentered in a glovebox. The solution was filtered through silica and washed with dichloromethane (2 mL). The solvent was removed *in vacuo* to obtain the desired complex.

Lastly, the synthesis of the ring-expanded NHC (RE-NHC) Dipp-complexes followed a strong base route:[4]



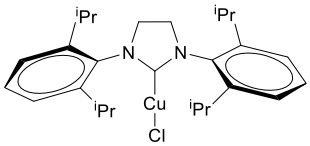
Scheme S4: Procedure for the synthesis of [Cu(6Dipp)Cl] and [Cu(7Dipp)Cl] complexes.

[Cu(IPr)(Cl)][1,5]



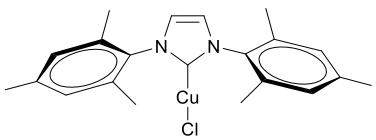
Was synthesized according to the general procedure from IPr·HCl (430 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 370 mg (75 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.49 (t, 2H), 7.29 (d, 4H), 7.13 (s, 2H), 2.57 (sept, 4H), 1.30 (d, 12H), 1.23 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(SIPr)(Cl)] [1,5]



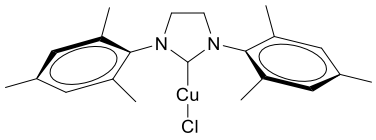
Was synthesized according to the general procedure from SIPr·HCl (431 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 390 mg (79 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.40 (t, 2H), 7.25 (d, 4H), 4.02 (s, 4H), 3.07 (sept, 4H), 1.41 (d, 12H), 1.30 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IMes)(Cl)] [1,5]



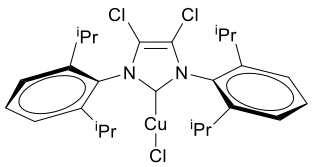
Was synthesized according to the general procedure from IMes·HCl (345 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 330 mg (81 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.08 (s, 2H), 7.00 (s, 4H), 2.34 (s, 6H), 2.10 (s, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(SIMes)(Cl)] [1,5]



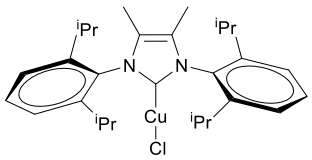
Was synthesized according to the general procedure from IMes·HCl (346 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 327 mg (80 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 6.95 (s, 4H), 3.92 (s, 2H), 2.18-2.42 (m, 18H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IPr^{Cl})(Cl)][6]



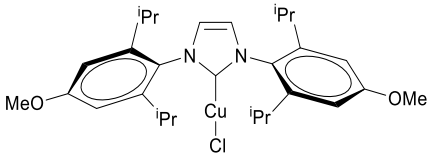
Was synthesized according to the general procedure from IMes·HCl (346 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 327 mg (80 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.55 (t, 2H), 7.33 (d, 4H), 2.47 (sept, 4H), 1.30 (d, 12H), 1.27 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IPr^{Me})(Cl)][6]



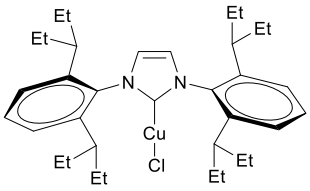
Was synthesized according to the general procedure from IPr^{Me}·HCl (458 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 412 mg (79 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.48 (t, 2H), 7.29 (d, 4H), 2.45 (sept, 4H), 1.92 (s, 6H), 1.28 (d, 12H), 1.23 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IPrOMe)(Cl)][7]



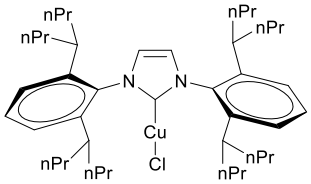
Was synthesized according to the general procedure from IPrOMe·HCl (492 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). Pale yellow solid; 422 mg (76 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.07 (d, 2H), 6.77 (s, 4H), 3.88 (s, 6H), 2.53 (sept, 4H), 1.92 (s, 6H), 1.29 (d, 12H), 1.21 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IPent)(Cl)][8]



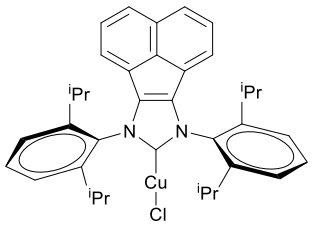
Was synthesized according to the general procedure from IPent·HCl (543 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). Off-white solid; 491 mg (81 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.48 (t, 2H), 7.21 (d, 4H), 7.00 (s, 2H), 2.15 (sept, 4H), 1.43-1.78 (m, 16H), 0.91 (d, 12H), 0.78 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IHept)(Cl)][8]



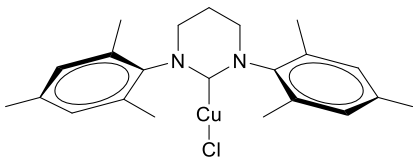
Was synthesized according to the general procedure from IHept·HCl (656 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). Off-white solid; 388 mg (54 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.27 (t, 2H), 7.54 (d, 4H), 7.23 (d, 2H), 1.99 (sept, 4H), 1.64-1.42 (m, 16H), 1.26-0.91 (m, 16H), 0.82 (d, 12H), 0.75 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(BIAN IPr)(Cl)][9]



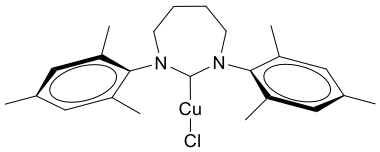
Was synthesized according to the general procedure from BIAN IPr·HCl (555 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). Yellow solid; 513 mg (83 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.65-7.54 (m, 2H), 7.50-7.33 (m, 6H), 7.00 (d, 2H), 2.84 (sept, 4H), 1.34 (d, 12H), 1.13 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(6Mes)(Cl)][3]



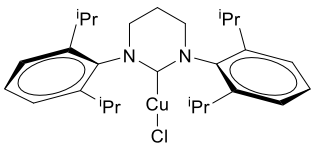
Was synthesized according to the microwave procedure from 6Mes·HCl (301 mg; 0.84 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 251 mg (71 % isolated yield).^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 6.93 (s, 4H), 3.35 (m, 4H), 2.20−2.36 (m, 20H) ppm. Spectroscopic data matched the literature reported information.

[Cu(7Mes)(Cl)][3]



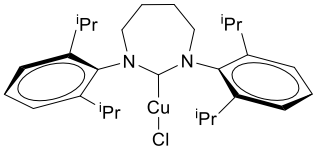
Was synthesized according to the microwave procedure from 7Mes·HCl (310 mg; 0.84 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 225 mg (63 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 6.92 (s, 4H), 3.87 (s, br, 4H), 2.35 (s, 12H), 2.14−2.32 (m, 10H) ppm. Spectroscopic data matched the literature reported information.

[Cu(6Dipp)(Cl)][3,4]



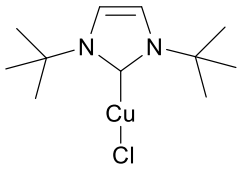
Was synthesized using the strong base procedure from 6Dipp·HBr (2.004 g; 4.27 mmol), CuCl (410 mg; 4.127 mmol) and KO^{t}Bu (0.463 mg; 4.127 mmol). White solid; 0568 mg (27 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.36 (t, 2H), 7.21 (d, 4H), 3.44 (t, 4H), 3.06 (sept, 4H), 2.37 (m, 2H), 1.35 (d, 12H), 1.31 (d, 12H). Spectroscopic data matched the literature reported information.

[Cu(7Dipp)(Cl)][3,4]



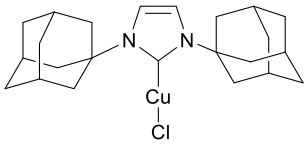
Was synthesized using the strong base procedure from 7Dipp·HBr (500 mg; 1 mmol), CuCl (0.099 mg; 1 mmol) and KO^{t}Bu (0.112 mg; 1 mmol). White solid; 0.202 mg (39 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.32 (t, 2H,), 7.19 (d, 4H), 3.98 (m, 4H), 3.25 (sept, 4H), 2.3 (q, 4H), 1.35 (d, 12H), 1.33 (d, 12H). Spectroscopic data matched the literature reported information.

[Cu(I^{t}Bu)(Cl)] [1,5]



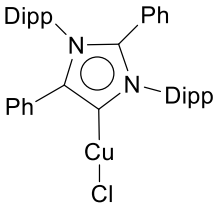
Was synthesized using the general procedure from I^{t}Bu·HCl (219 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 127 mg (45 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.04 (s, 2H), 1.79 (s, 18H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IAd)(Cl)][10]



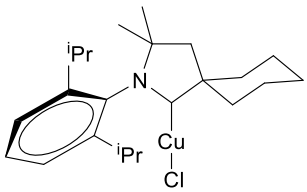
Was synthesized according to general procedure from IAd·HCl (377 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). White solid; 317 mg (72 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.03 (s, 2H), 2.35–2.45 (m, 12H), 2.21–2.26 (m, 6H), 1.68–1.84 (m, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(aNHC)(Cl)][11]



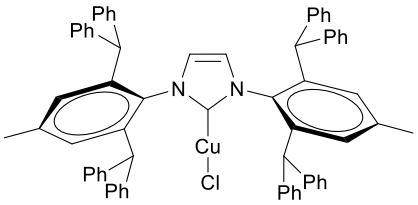
Was synthesized according to general procedure from aNHC·HCl (583 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). Pale yellow solid; 427 mg (66 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.41-7.51 (m, 4H), 7.16-7.25 (m, 8H), 7.05 (t, 2 H), 6.86 (d,2 H), 2.60-2.72 (m, 2H), 2.49-2.58 (m, 2H), 1.42 (d, 8H), 1.01 (d, 2H), 0.96 (d, 4H), 0.76-0.83 (m, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(CAAC^{Cy})(Cl)][12]



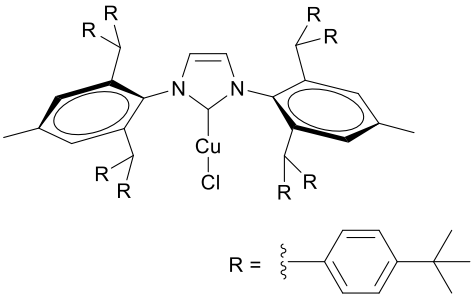
Was synthesized according to the adapted Cu_2O procedure from CAAC^{Cy}·HCl (362 mg; 1.0 mmol), Cu_2O (72 mg; 0.5 mmol). Off-white solid; 242 mg (61 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.39 (t, 1H), 7.27- 7.23 (m, 2H), 2.80 (sept, 2H), 2.39, (m, br, 2H), 2.07 (s, 2H), 1.86 (s, br, 3H), 1.72 (s, br, 2H), 1.50 (m, br, 3H), 1.34 (s, 6H), 1.27 (d, 12H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IPr*)(Cl)][1,5]



Was synthesized according to general procedure from IPr*·HCl (959 mg; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). Reaction time was 48 hours. White solid; 869 mg (85 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.09-7.23 (m, 24H), 7.05-7.09 (m, 8H), 6.92-6.96 (m, 8H), 6.84 (s, 4H), 5.80 (s, 2H), 5.19 (s, 4H), 2.22 (s, 6H) ppm. Spectroscopic data matched the literature reported information.

[Cu(IPr**)(Cl)][13]



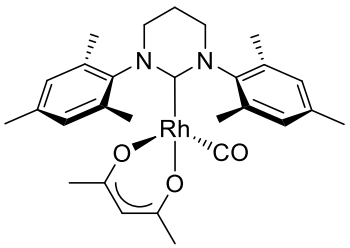
Was synthesized using the general procedure from IPr**·HCl (1.41 g; 1.01 mmol), CuCl (100 mg; 1.01 mmol) and K_2CO_3 (420 mg; 3.03 mmol). Reaction time was 48 hours. White solid; 1.16 g (79 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.17 (d, 8H), 7.16 (d, 8H), 7.02 (d, 8H), 6.80 (s, 4H), 6.72 (d, 8H), 5.70 (s, 2H), 5.21 (s, 4H), 2.17 (s, 6H), 1.18 (s, 72H) ppm. Spectroscopic data matched the literature reported information.

Synthesis of [Rh(NHC)(acac)(CO)] complexes

All [Rh(NHC)(acac)(CO)] complexes were synthesized by mixing [Rh(acac)$(CO)_2$], 1 equivalent of either the HCl or HBF_4 salt of the corresponding NHC, 5 equivalents of K_2CO_3, and 4mL of EtOAc. This reaction mixture was stirred overnight at 40°C until completion, which was confirmed by the disappearance of the imidazolium H^2 peak in ^{1}H-NMR. The solvent was then removed *in vacuo* and the remaining solids were dissolved in dichloromethane (2 mL). This mixture was filtered through silica to remove the base and the filtrate was concentrated *in vacuo*. Recrystallization using pentane resulted in the isolation of the desired compounds. For previously reported complexes the identity was confirmed by comparing the ^{1}H-NMR spectrum of the isolated compound to literature data.[14,15]

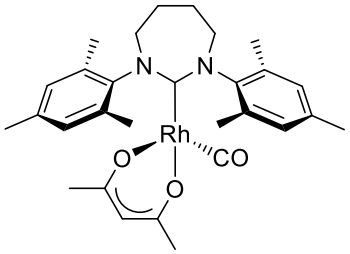
The only exception to this method is the synthesis of the [Rh(IAd)(acac)(CO)] complex. Both the HCl and the HBF_4 salt of *N,N'*-di-1-adamantyl-imidazol2-ylidene (IAd) proved to be unreactive using this "weak-base" approach. The complex was therefore synthesized by first isolating the free carbene of IAd using the method described by Arduengo and co-workers[16] and finally mixing this ligand with 1 equivalent of [Rh(acac)$(CO)_2$] in THF. The aforementioned work-up procedure was then followed to isolate the desired complex.

[Rh(6Mes)(acac)(CO)]



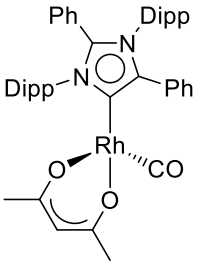
Was synthesized using the main procedure from [Rh(acac)$(CO)_2$] (25.8 mg; 0.1 mmol), 6MesHCl (35.7 mg; 0.1 mmol), and K_2CO_3 (69 mg; 0.5 mmol) in 1 mL of EtOAc. Yellow solid; 48.7 mg (88 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.93 (s, 2H, C*H* aryl); 6.83 (s, 2H, C*H* aryl); 5.12 (s, 1H, C*H* acac); 3.46 (m, 4H, N-CH_2); 2.45-2.17 (m, 20H, ortho-CH_3, para-CH_3, and (N-CH2)$_2$-CH_2); 1.81 (s, 3H, CH_3 acac); 1.74 (s, 3H, CH_3 acac) ppm. ^{13}C-{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 191.6 (N-*C*-N), 190.8 (Rh-*C*O), 186.9 (C^{acac}O), 183.4 ((C^{acac}O), 143.3 (C_{para}), 137.0 (C^{Ar}-N), 135.8 (C_{ortho}), 134.8 (C_{ortho}), 129.6 ($C_{meta}H$), 129.3 ($C_{meta}H$), 99.9 ($C^{acac}H$), 46.9 (*C*H_2-N), 27.8 ($C^{acac}H_3$), 26.7 ($C^{acac}H_3$),21.7 (CH_2-*C*H_2-CH_2), 21.2 ($C^{acac}H_3$), 18.6 (C_{para}-*C*H_3), 18.4 (C_{ortho}-*C*H_3). HRMS: m/s calculated for HRMS: m/z calculated for $C_{28}H_{36}N_2O_3Rh$, $[M+H]^+$: 552.1859, found 552.1860.

[Rh(7Mes)(acac)(CO)]



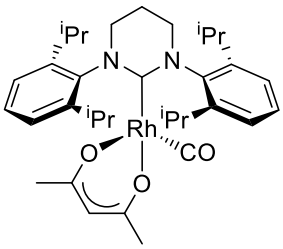
Was synthesized using the main procedure from [Rh(acac)$(CO)_2$] (25.8 mg; 0.1 mmol), 7MesHCl (37.1 mg; 0.1 mmol), and K_2CO_3 (69 mg; 0.5 mmol) in 1 mL of EtOAc. Yellow solid; 51.4 mg (90 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.92 (s, 2H, C*H* aryl); 6.82 (s, 2H, C*H* aryl); 5.10 (s, 1H, C*H* acac); 4.03-3.81 (m, 4H, N-CH_2); 2.37 (d, ortho-CH_3) 2.26-2.12 (overlapping s and m, 6H + 4H, para-CH_3 and (N-CH_2)-CH_2); 1.81 (s, 3H, CH_3 acac); 1.73 (s, 3H, CH_3 acac) ppm. ^{13}C-{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 145.0 (C_{para}), 136.7 (C^{Ar}-N), 135.7 (C_{ortho}), 134.6 (C_{ortho}), 129.8 (C_{meta}H), 129.4 (C_{meta}H), 99.8 (C^{acac}H), 54.2 (*C*H_2-N), 27.8 ($C^{acac}H_3$), 26.8 ($C^{acac}H_3$), 25.3 (CH_2-*C*H_2-CH_2), 22.3 ($C^{acac}H_3$), 21.2 (C_{para}-*C*H_3), 19.0 (C_{ortho}-*C*H_3).Elemental Analysis: calcd for C29H40N2O3Rh: C, 61.26; H, 7.27; N, 4.96. Found: C, 60.91; H, 7.28; N, 4.78.

[Rh(aNHC)(acac)(CO)]



Was synthesized using the main procedure from [Rh(acac)$(CO)_2$] (25.8 mg; 0.1 mmol), aNHCHBF_4 (62.8 mg; 0.1 mmol), and K_2CO_3 (69 mg; 0.5 mmol) in 1 mL of EtOAc. Yellow solid; 49.8 mg (64 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.78-7.67 (m, 2H, C*H* aryl); 7.37 (q, 2H, , $^3J_{H-H}$ = 7.69 Hz, C*H* aryl); 7.16 (d, 2H, , $^3J_{H-H}$ = 7.75 Hz, C*H* aryl); 7.12-6.99 (m, 6H, C*H* aryl); 6.93 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, C*H* aryl); 6.86-6.80 (m, 2H, C*H* aryl); 5.01 (s, 1H, C*H* acac); 2.90 (sept, 2H, $^3J_{H-H}$ = 6.7 Hz, $(CH_3)_2$-C*H*); 2.59 (sept, 2H, $^3J_{H-H}$ = 6.7 Hz, $(CH_3)_2$-C*H*); 1.82 (s, 3H, C*H*$_3$ acac); 1.37 (d, 6H, $^3J_{H-H}$ = 6.7 Hz, CH-(C*H*$_3$)); 1.23 (s, 3H, C*H*$_3$ acac); 0.84-0.69 (m, 18H, CH-(C*H*$_3$)) ppm. ^{13}C-{H}-NMR (400 MHz, CDCl3, 298 K) δ = 184.9 (*C*^{acac}O), 145.4 (*C*^{Ar}-N), 145.2 (*C*^{Ar}-N), 136.7 (C^{aryl}), 132.5 (C_{ortho}), 132.1 (C_{ortho}), 130.9 (C^{Aryl}H), 130.0 (C^{Aryl}H), 129.8(C^{Aryl}H), 128.1 (C^{Aryl}H), 127.0 (C^{Aryl}H), 126.8 (C^{Aryl}H), 125.2 (C^{Aryl}H), 125.0 (C^{Aryl}H), 124.6 (C^{Aryl}), 99.1 (*C*^{acac}*H*), 31.7 (N-C-N), 29.9 (C-N), 29.1 (*C*H-$(CH_3)_2$), 28.7 (*C*H-$(CH_3)_2$), 26.4 (CH-*C*H_3), 25.2 (*C*^{acac}*H*$_3$), 23.8 (*C*^{acac}*H*$_3$), 23.7 (*C*^{acac}*H*$_3$), 23.5 (CH-*C*H_3), 21.6 (CH-*C*H_3), 2.3 (CH-*C*H_3). Elemental Analysis: calcd for C45H52N2O3Rh: C, 70.03; H, 6.79; N, 3.63. Found: C, 69.99; H, 6.96; N, 3.59.

[Rh(6Dipp)(acac)(CO)]



Was synthesized using the main procedure from [Rh(acac)$(CO)_2$] (25.8 mg; 0.1 mmol), 6DippHCl (47.2 mg; 0.1 mmol), and K_2CO_3 (69 mg; 0.5 mmol) in 1 mL of EtOAc. Yellow solid; 51 mg (82 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.32 (t, 2H, para-C*H* aryl); 7.21 (t, 4H, meta-C*H* aryl); 5.20 (s, 1H, C*H* acac); 3.60 (m, 4H, N-C*H*$_2$); 3.55-3.23 (broad, 4H, C*H*-$(CH_3)_2$); 2.33 (m, 2, $(N\text{-}CH2)_2$-C*H*$_2$); 1.88 (s, 3H, C*H*$_3$ acac); 1.76 (s, 3H, C*H*$_3$ acac); 1.41-1.06 (broad, 24H, CH-C*H*$_3$) ppm.
^{13}C-{^{1}H}-NMR (400 MHz, CDCl3, 298 K) δ (ppm) = 191.7 (N-*C*-N), 190.9 (Rh-*C*O), 186.7 (*C*^{acac}O), 184.3 ((*C*^{acac}O), 145.9 (*C*^{Ar}-N), 143.9 (*C*$_{ortho}$), 136.0 (*C*$_{ortho}$), 131.4 (*C*$_{para}$*H*), 128.5 (*C*$_{meta}$*H*), 129.3 (*C*$_{meta}$*H*), 124.6 (*C*$_{para}$*H*), 99.8 (*C*^{acac}*H*), 50.4 (*C*H$_2$-N), 49.2 (*C*H$_2$-N), 29.0 (*C*H-$(CH_3)_2$), 28.6 (CH-*C*H_3), 27.8 (CH-*C*H_3), 25.0 (*C*^{acac}*H*$_3$), 24.9 (*C*^{acac}*H*$_3$), 21.7 (CH_2-*C*H_2-CH_2),. 19.5 (CH_2-*C*H_2-CH_2). Elemental Analysis: calcd for C45H52N2O3Rh: C, 70.03; H, 6.79; N, 3.63. Found: C, 69.99; H, 6.96; N, 3.59.

Electrochemical measurements

General procedure for cyclic voltammetry measurements of the complexes. All measurements were performed in the same manner. General procedure: all experiments were conducted inside a glovebox under an argon atmosphere. A stock solution of 0.1 M supporting electrolyte NBu_4PF_6 in dichloromethane or acetonitrile was made. Complexes were weighed inside the glovebox in 4mL vials. The vials were washed out thrice with the electrolyte solution to ensure all the complex is added to the electrochemical cell. 10 mL of the stock solution of electrolyte was added to result in a solution containing 1 mM (for the Cu-complexes) or 2 mM (for the Rh-complexes) of analyte. After addition of the solvent, the cell is stirred momentarily to assure proper mixing. The electrodes are then submersed in the solution and the voltammogram is recorded, started going to positive potentials first. For the assessment of the $E_{1/2}$, only the redox couple of interest is scanned.

CV of [Rh(IPr)(acac)(CO)]

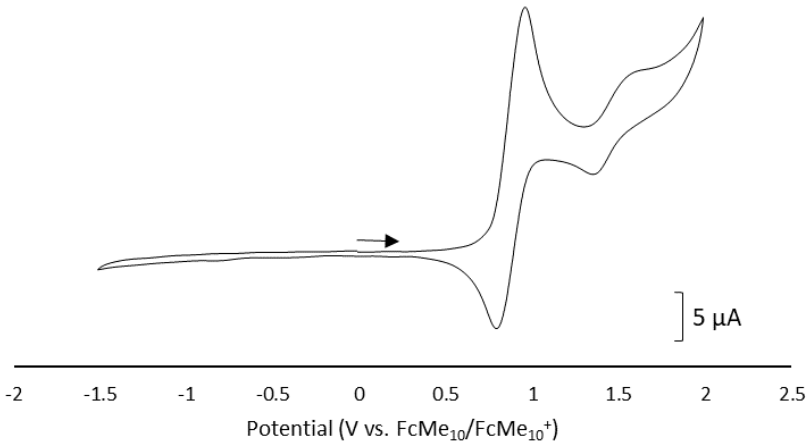


Figure S1: Full cyclic voltammogram of [Rh(IPr)(acac)(CO)].

Conditions: 25°C, 2 mM of analyte, 0.1 M NBu_4PF_6 in dichloromethane, Pt work and auxiliary electrode, scan rate 100 mVs^{-1}. Referenced to the decamethylferrocene couple determined at 0.15 V vs. Ag/Ag^+ under the same conditions.

CV of [Cu(IPr)Cl]

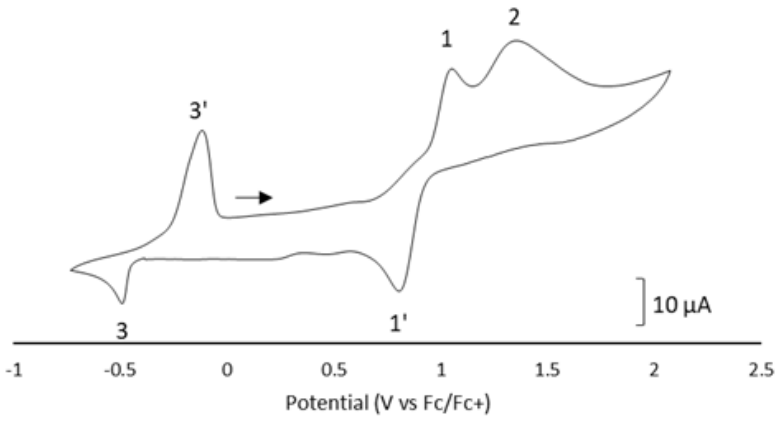
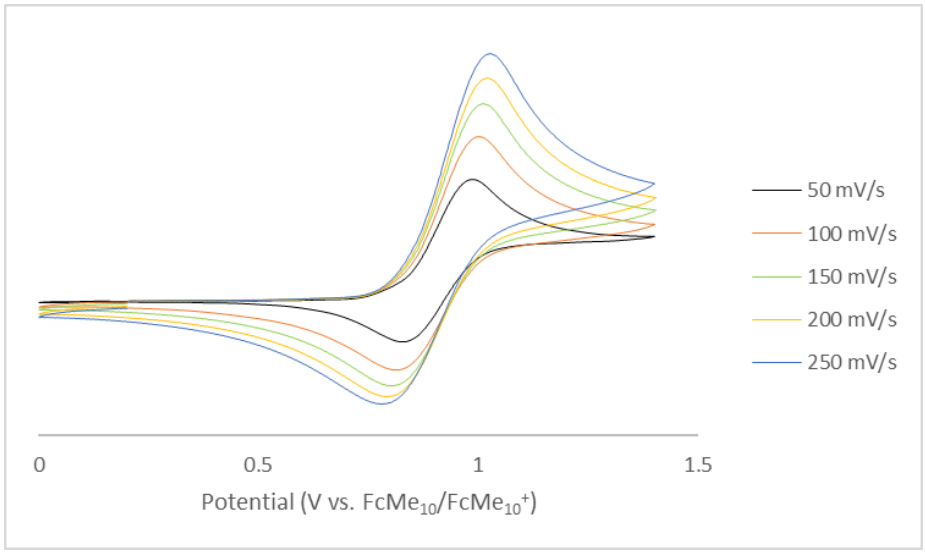


Figure S2: Full cyclic voltammogram of [Cu(IPr)Cl].

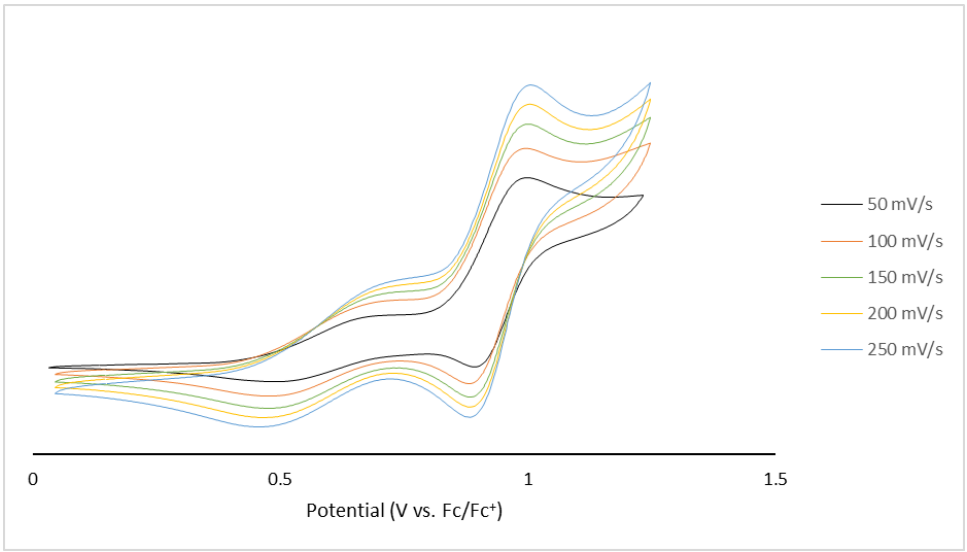
Conditions: 25°C, 1 mM of analyte, 0.1 M NBu_4PF_6 in acetonitrile, Pt work and auxiliary electrode, scan rate 100 mVs^{-1}. Referenced to the ferrocene couple determined at 0.13 V vs. Ag/Ag^+ under the same conditions.

Checking reversibility by varying the scan rate



v (mV/s)	ΔE_p (mV)
50	132
100	159
150	186
200	207
250	229

Figure S3: *Cyclic voltammograms of 2mM [Rh(IPr)(acac)(CO)] at varying scan rates in dichloromethane containing 0.1 M* NBu_4PF_6. .



v (mV/s)	ΔE_p (mV)
50	85
100	87
150	91
200	100
250	105

Figure S4: *(Top) Cyclic voltammograms of 2 mM [Cu(IPr)(Cl)] at varying scan rates in acetonitrile containing 0.1 M* NBu_4PF_6.

Additional data comparisons

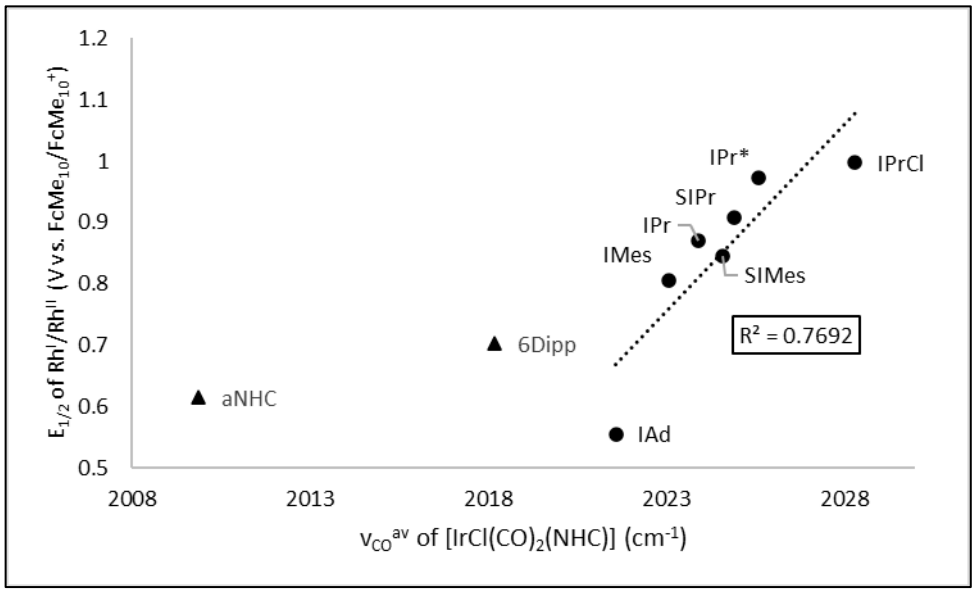


Figure S5: Comparison of the electrochemical data of [Rh(NHC)(acac)(CO)]] complexes to literature values of infrared measurements of $[IrCl(CO)_2(NHC)]$.

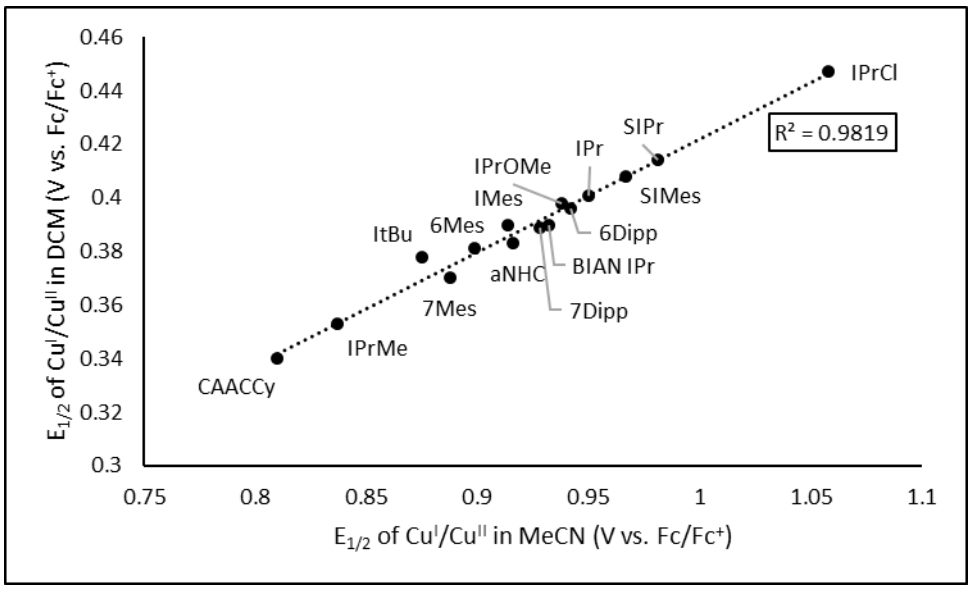


Figure S6: Comparison of electrochemical results of [Cu(NHC)(Cl)] in MeCN and results in DCM.

Cyclic voltammogram of [Cu(aNHC)Cl]

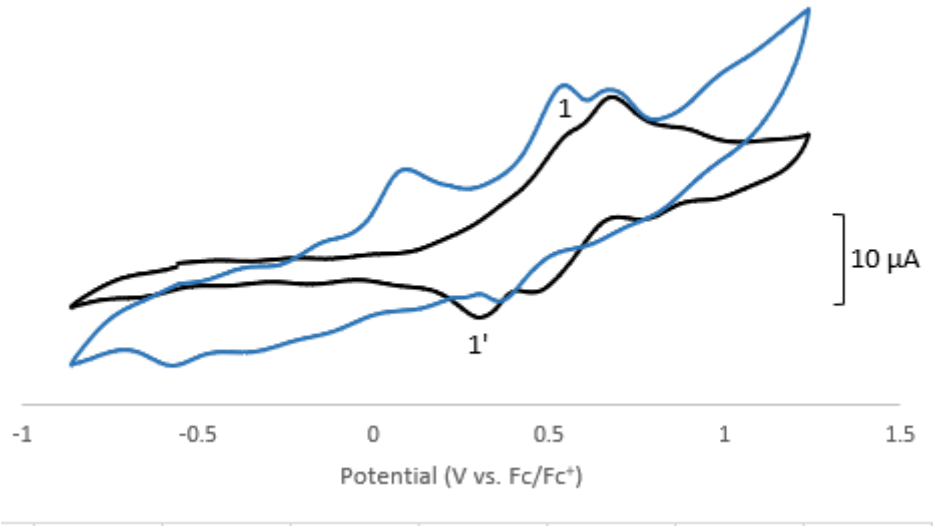


***Figure S7**: Cyclic voltammogram of [Cu(aNHC)Cl], black trace: first scan, blue trace: 3rd scan. Conditions: 25°C, 1 mM of analyte, 0.1 M NBu_4PF_6 in DCM, Pt work and auxiliary electrode, scan rate 100 mVs^{-1}. Referenced to the ferrocene couple determined at 0.46 V vs. Ag/Ag^+ under the same conditions*

Cyclic voltammogram of [Rh(BIAN IPr)(acac)(CO)]

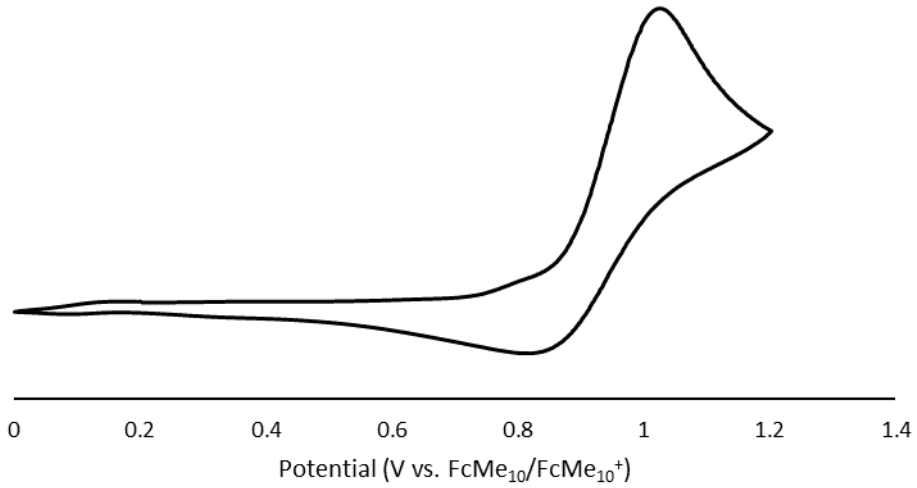


***Figure S8**: Cyclic voltammogram of [Rh (BIAN IPr)(acac)(CO)]. Conditions: 25°C, 2 mM of analyte, 0.1 M NBu_4PF_6 in DCM, Pt work and auxiliary electrode, scan rate 100 mVs^{-1}. Referenced to the decamethylferrocene couple determined at 0.15 V vs. Ag/Ag^+ under the same conditions*

Cyclic Voltammograms of Cu(IPent)Cl and Cu(IHept)Cl in dichloromethane

See remark c of Table 3

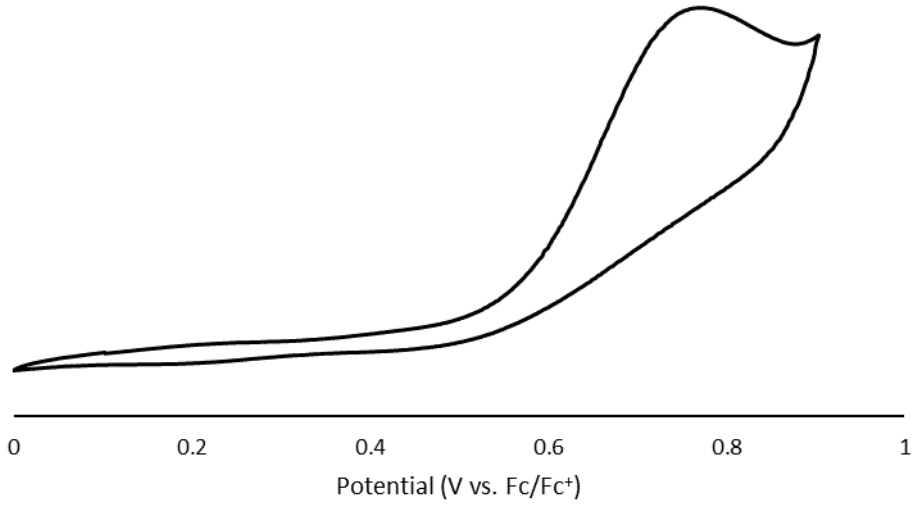


***Figure S9**: Cyclic voltammogram of [Cu(IPent)Cl]. Conditions: 25°C, 1 mM of analyte, 0.1 M NBu_4PF_6 in DCM, Pt work and auxiliary electrode, scan rate 100 mVs^{-1}. Referenced to the ferrocene couple determined at 0.46 V vs. Ag/Ag^+ under the same conditions*

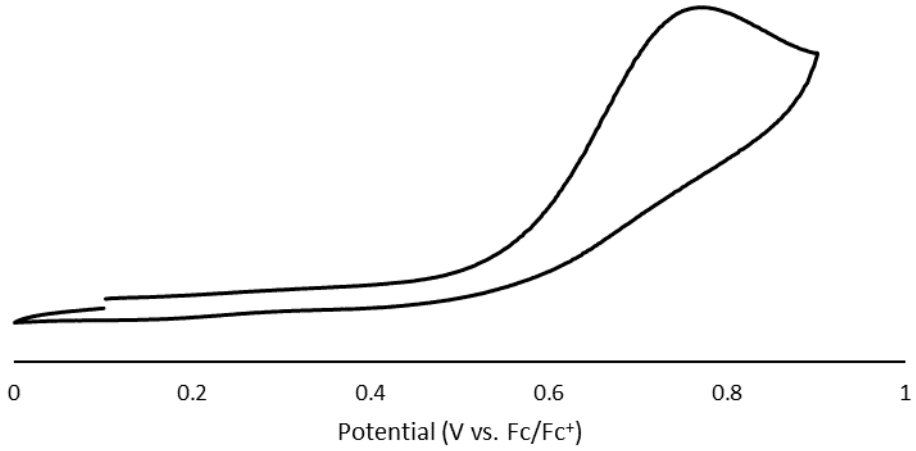


***Figure S10**: Cyclic voltammogram of [Cu(IHept)Cl]. Conditions: 25°C, 1 mM of analyte, 0.1 M NBu_4PF_6 in DCM, Pt work and auxiliary electrode, scan rate 100 mVs^{-1}. Referenced to the ferrocene couple determined at 0.46 V vs. Ag/Ag^+ under the same conditions*

VT-NMR investigation of [Rh(6Dipp)(acac)(CO)]

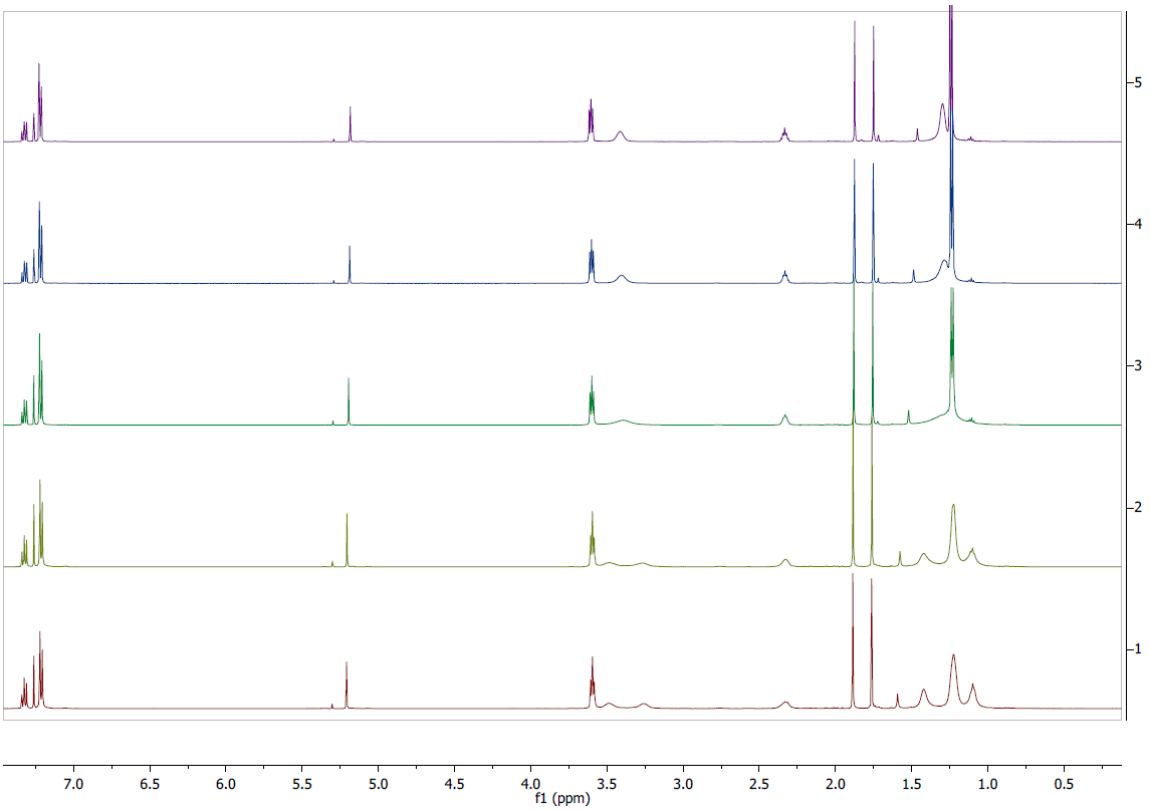


***Figure S11**: VT-^{1}H-NMR spectra of [Rh(6Dipp)(acac)(CO)] Solvent $CDCl_3$. Temperatures: Red - 283 K, Yellow - 288 K, Green - 308 K, Blue - 318 K, Purple - 328 K.*

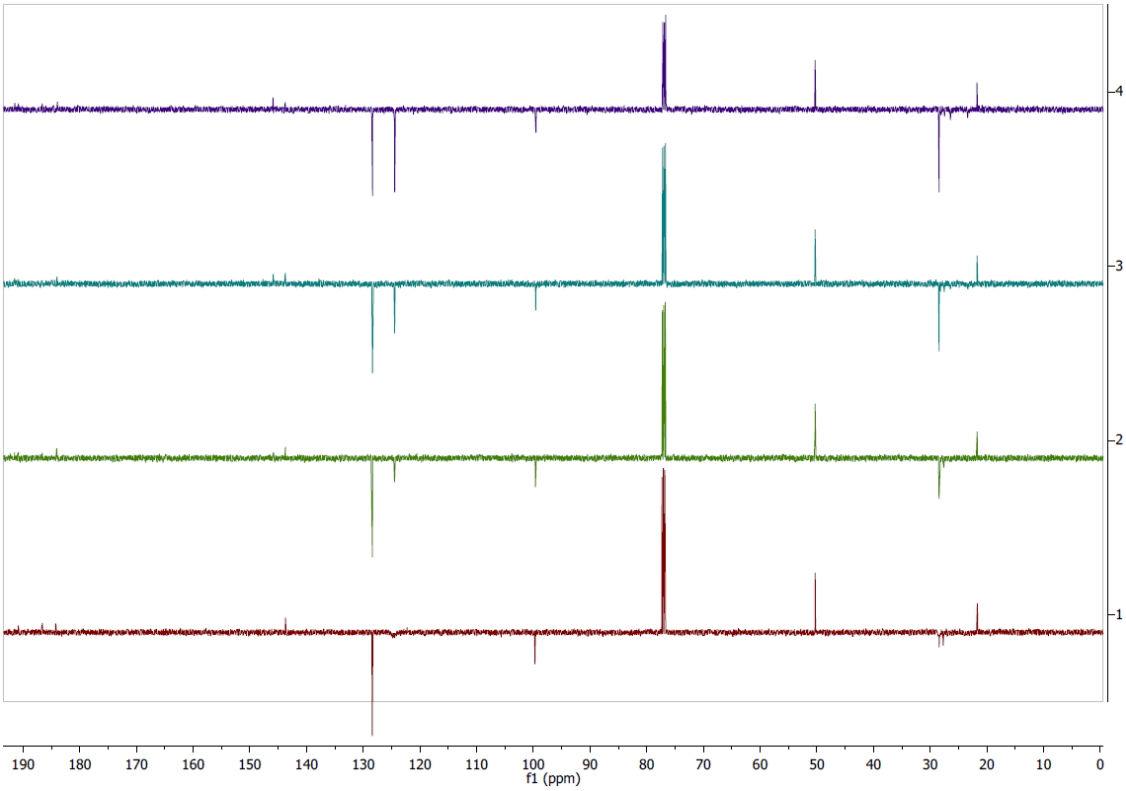


***Figure S12**: VT-^{13}C-{^{1}H}-NMR spectra of [Rh(6Dipp)(acac)(CO)] Solvent $CDCl_3$. Temperatures: Red - 288 K, Green - 308 K, Blue - 318 K, Purple - 328 K.*

Crystal data

Highlight of Crystal Structure of [Rh(6Dipp)(acac)(CO)]

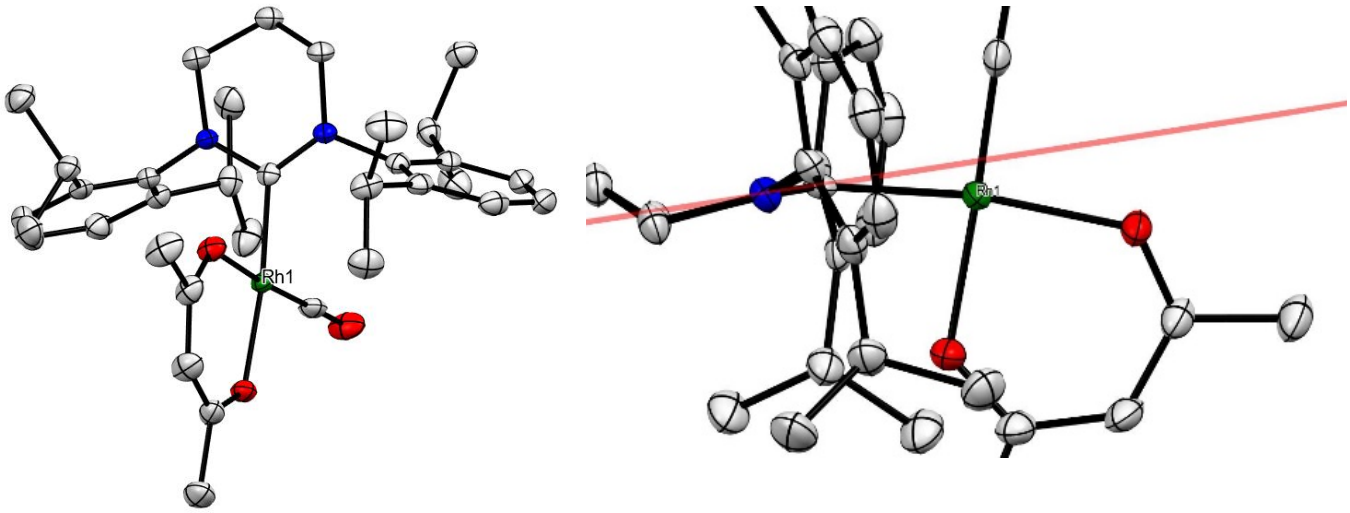


***Figure S13**: : (left) Crystal Structure of [Rh(6Dipp)(acac)(CO)]; (right) Highlight of the Rh atom being outside the N-C-N plane (plane indicated in red)*

Highlight of Crystal Structure of [Cu(7Dipp)Cl]

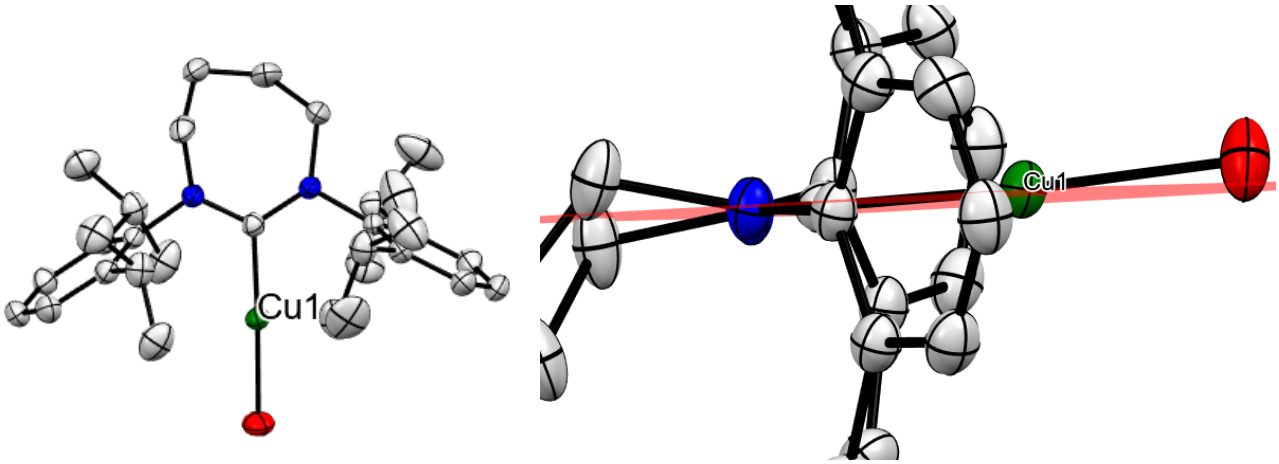
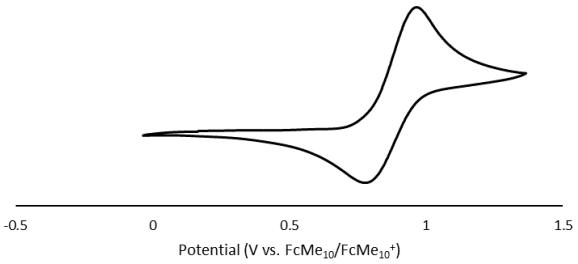


***Figure S14**: : (left) Crystal Structure of [Cu(7Dipp)Cl]; (right) Highlight of the Cu atom being inside the N-C-N plane (plane indicated in red)*

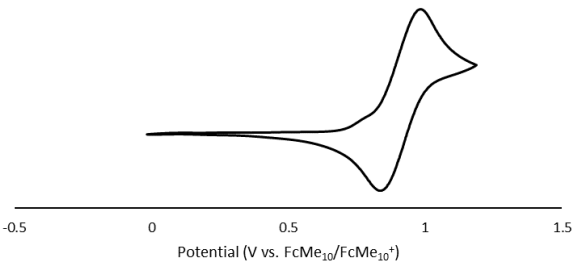
Representative cyclic voltammograms

Rh(NHC)(acac)(CO) complexes

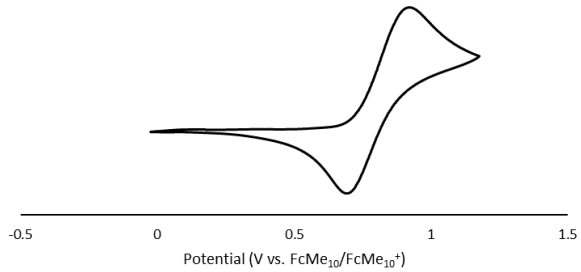
Rh(IPr)(acac)(CO)



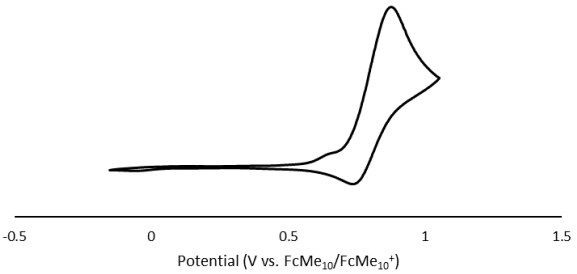
Rh(SIPr)(acac)(CO)



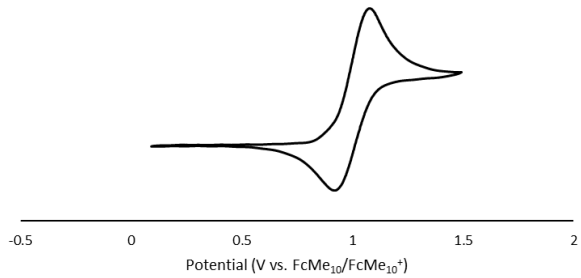
Rh(IMes)(acac)(CO)



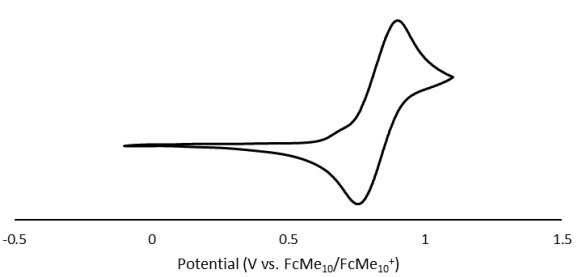
Rh(SIMes)(acac)(CO)



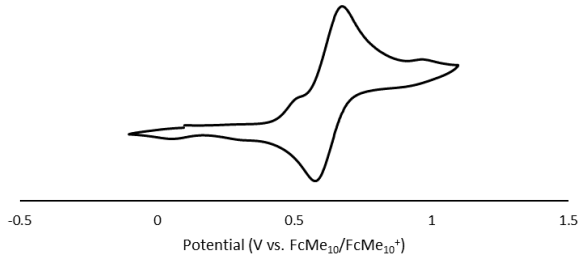
Rh(IPr^{Cl})(acac)(CO)



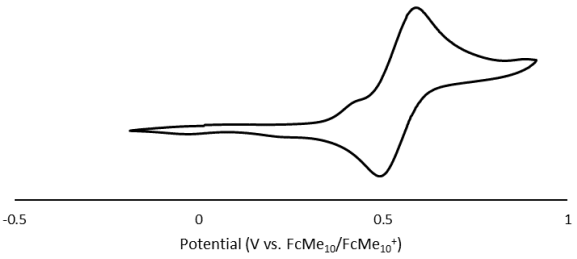
Rh(IPent)(acac)(CO)



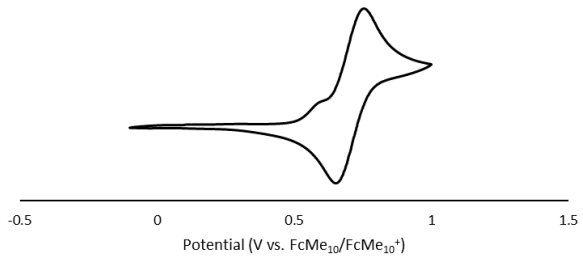
Rh(6Mes)(acac)(CO)



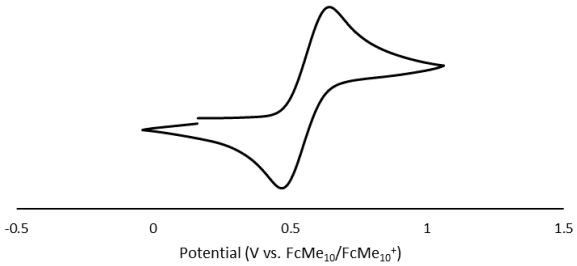
Rh(7Mes)(acac)(CO)



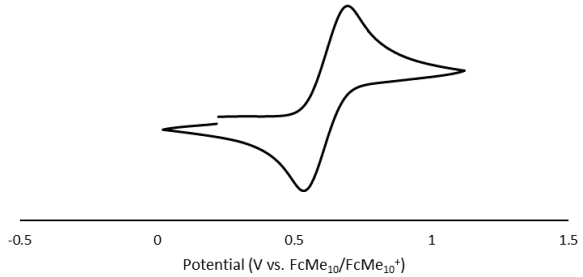
Rh(6Dipp)(acac)(CO)



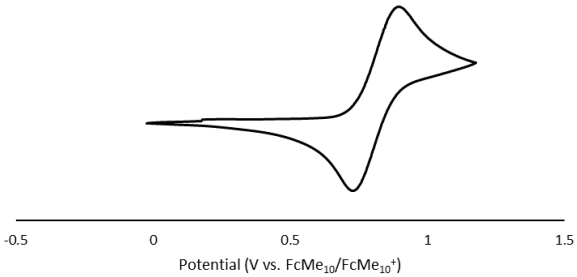
Rh(IAd)(acac)(CO)



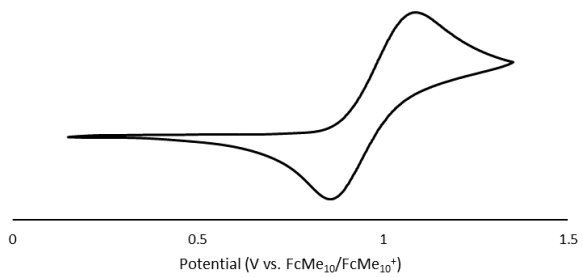
Rh(aNHC)(acac)(CO)



Rh(CAAC^{Cy})(acac)(CO)



Rh(IPr*)(acac)(CO)



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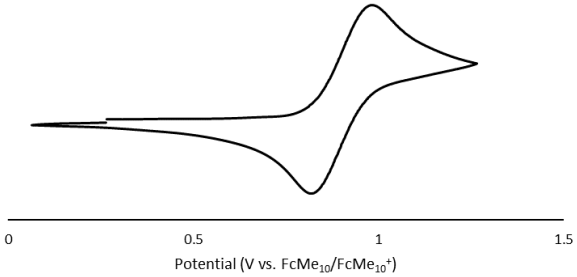
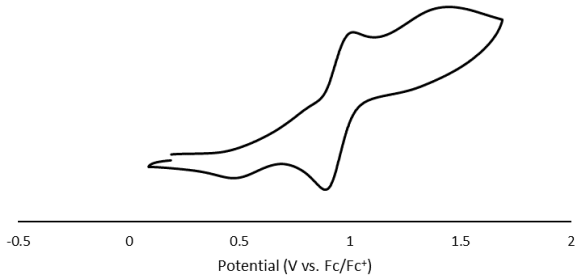


Cu(NHC)Cl complexes

Cu(IPr)Cl



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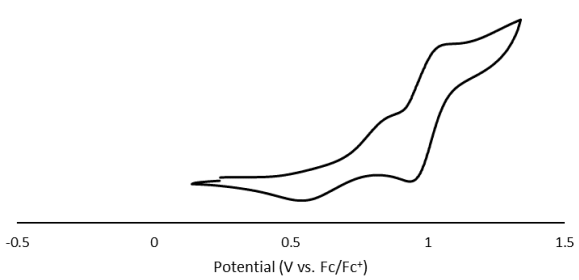
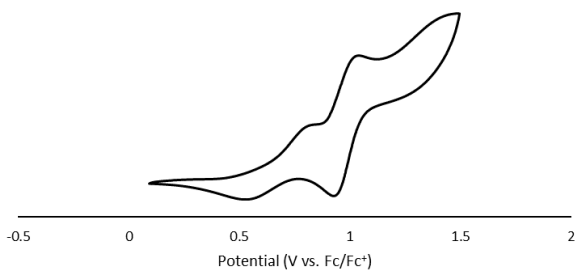


Cu(IMes)Cl



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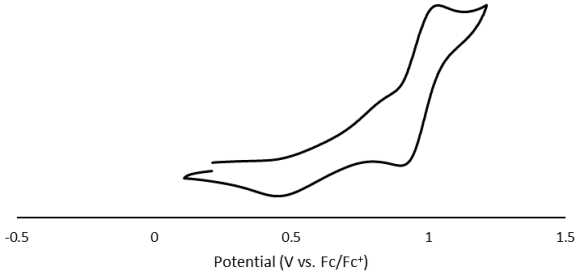
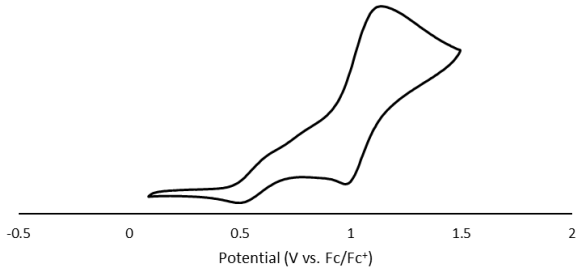
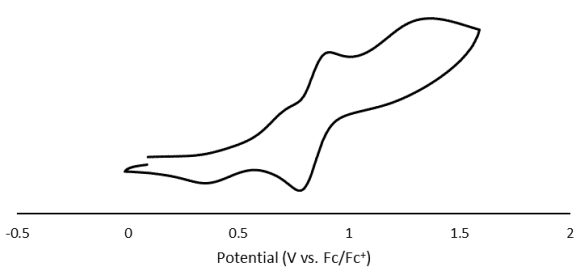


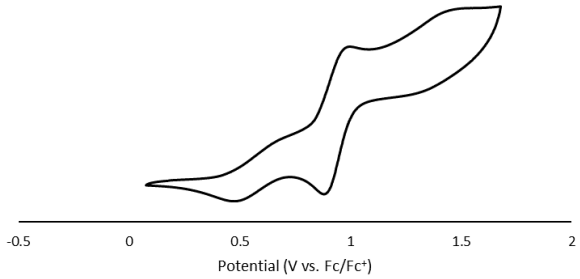
Cu(IPr^{Cl})Cl



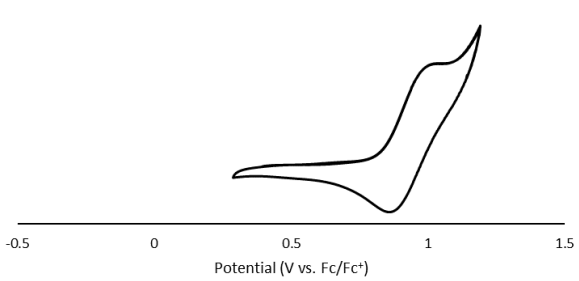
Cu(IPr^{Me})Cl



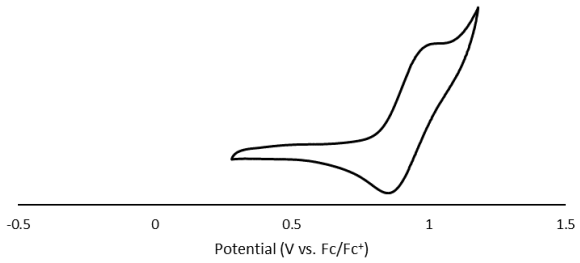
Cu(IPrOMe)Cl



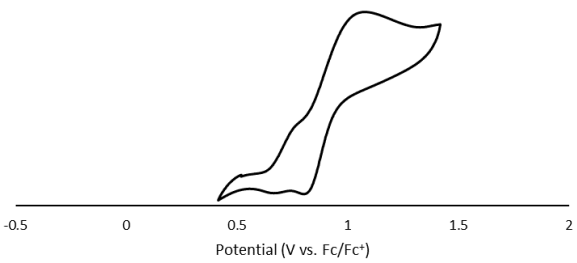
Cu(IPent)Cl



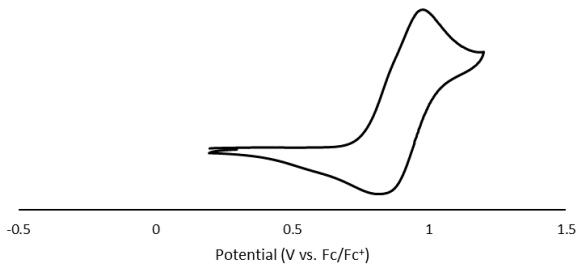
Cu(IHept)Cl



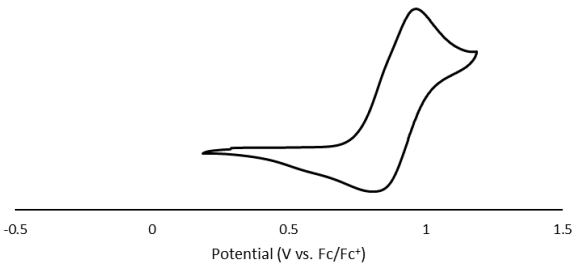
Cu(BIANIPr)Cl



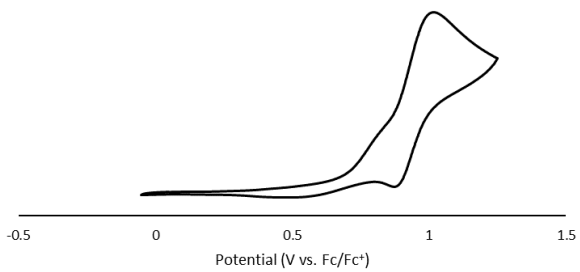
Cu(6Mes)Cl



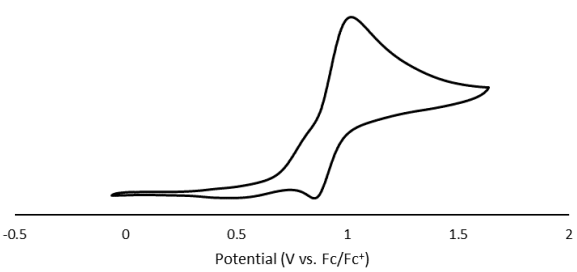
Cu(7Mes)Cl



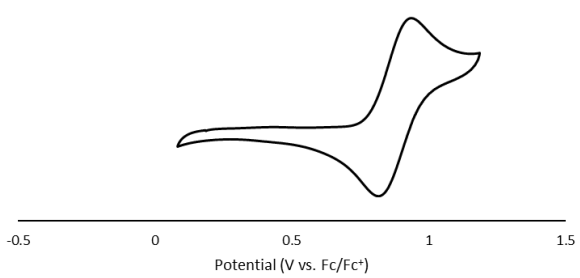
Cu(6Dipp)Cl



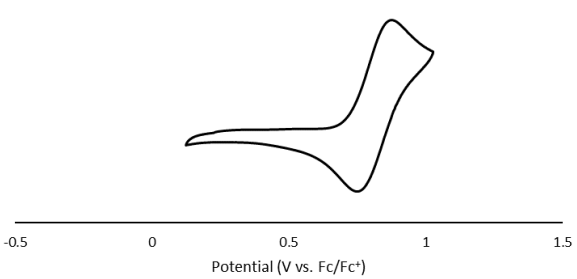
Cu(7Dipp)Cl



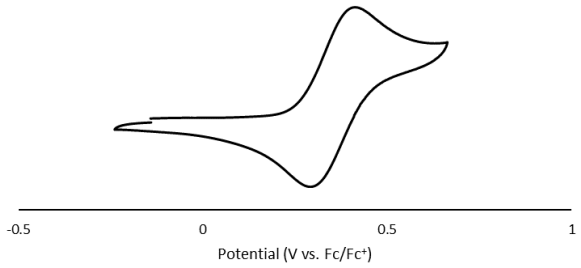
Cu(I^{t}Bu)Cl



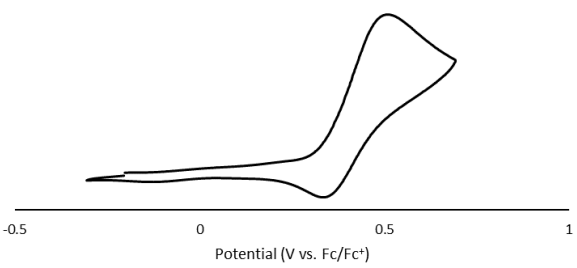
Cu(CAAC^{Cy})Cl



Cu(IAd)Cl



Cu(IPr*)Cl



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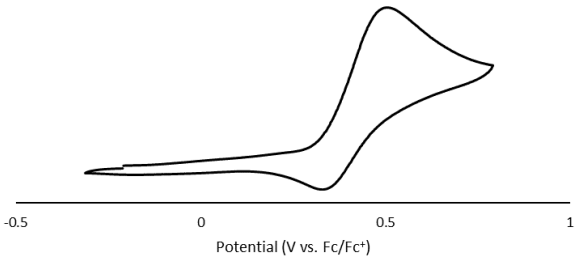
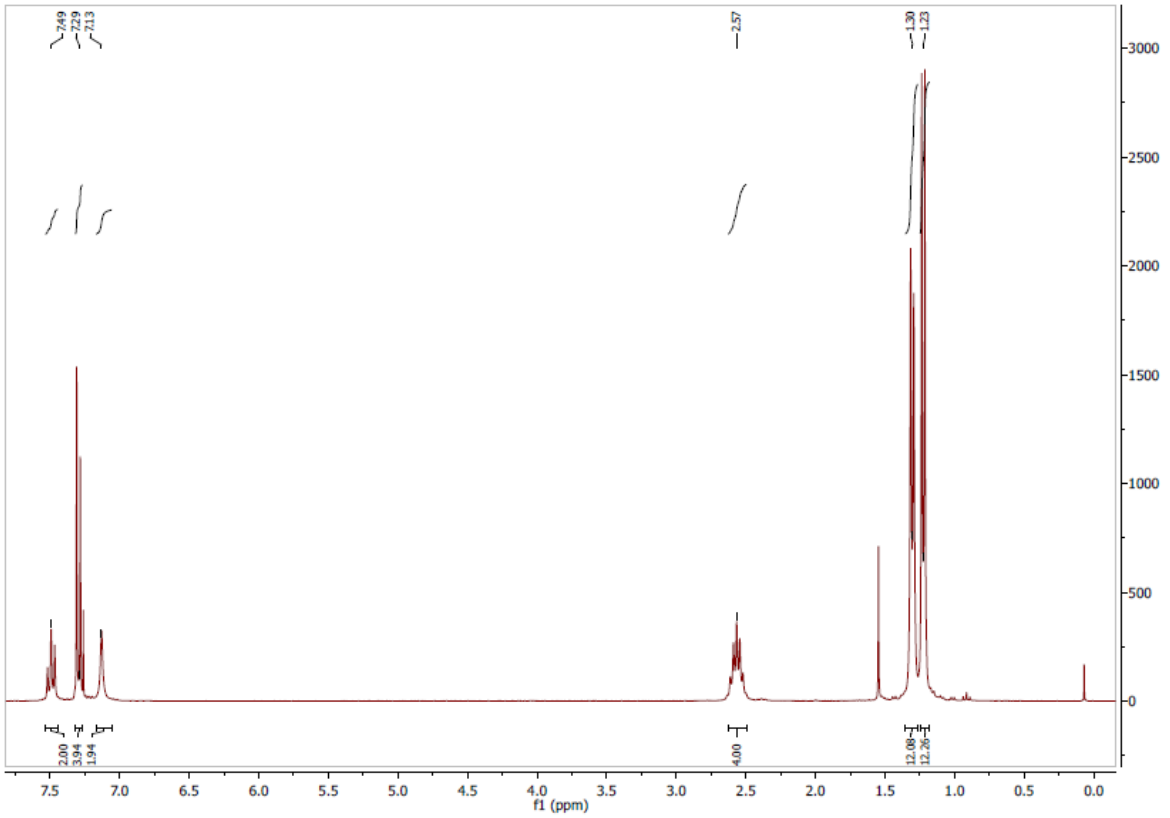
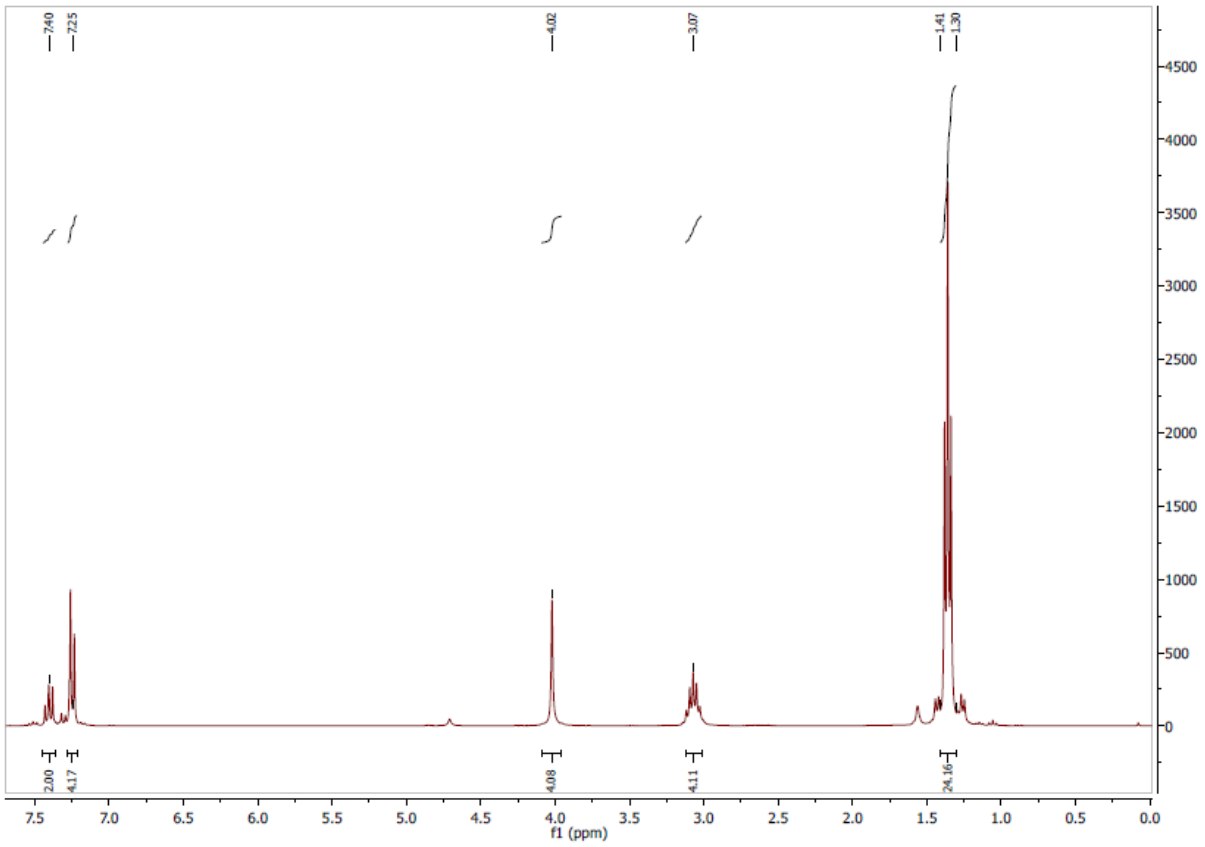


NMR spectra

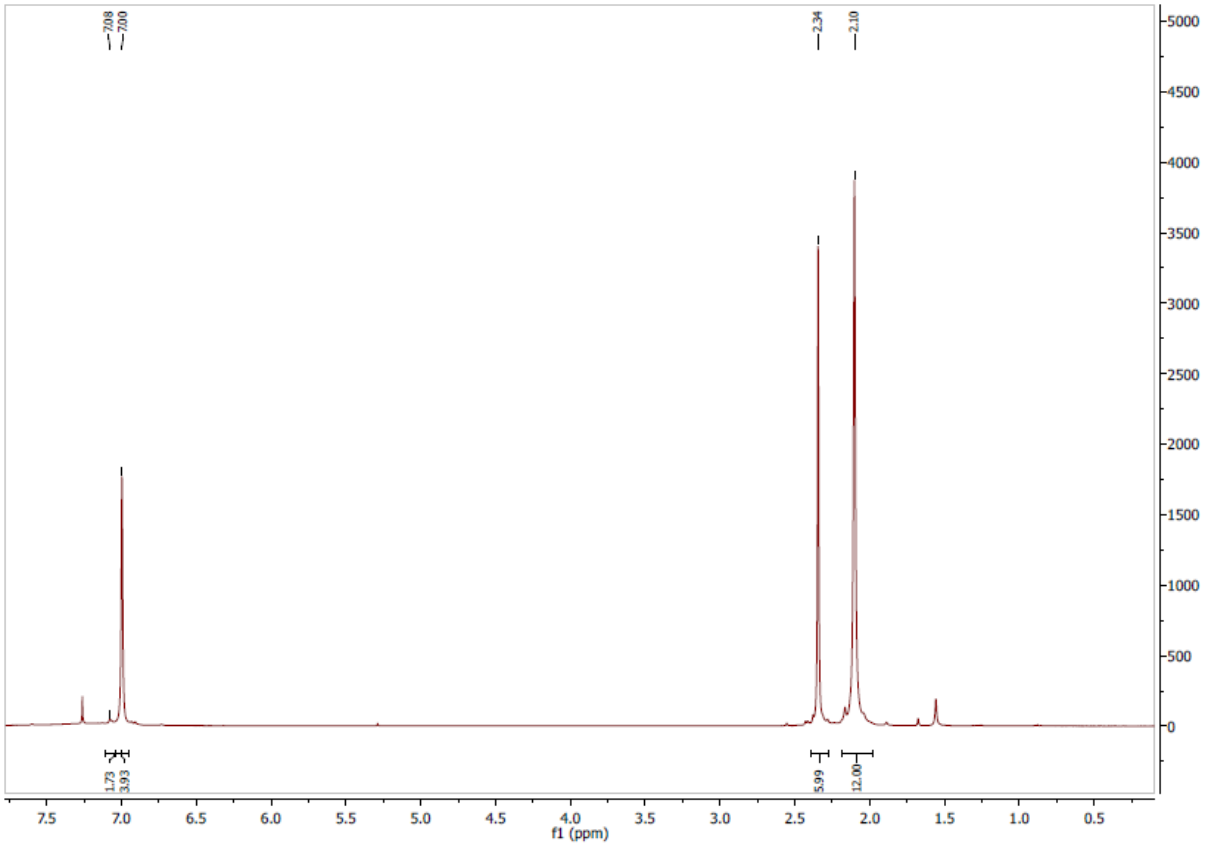
[Cu(Cl)(IPr)], ^{1}H NMR, $CDCl_3$, 298 K



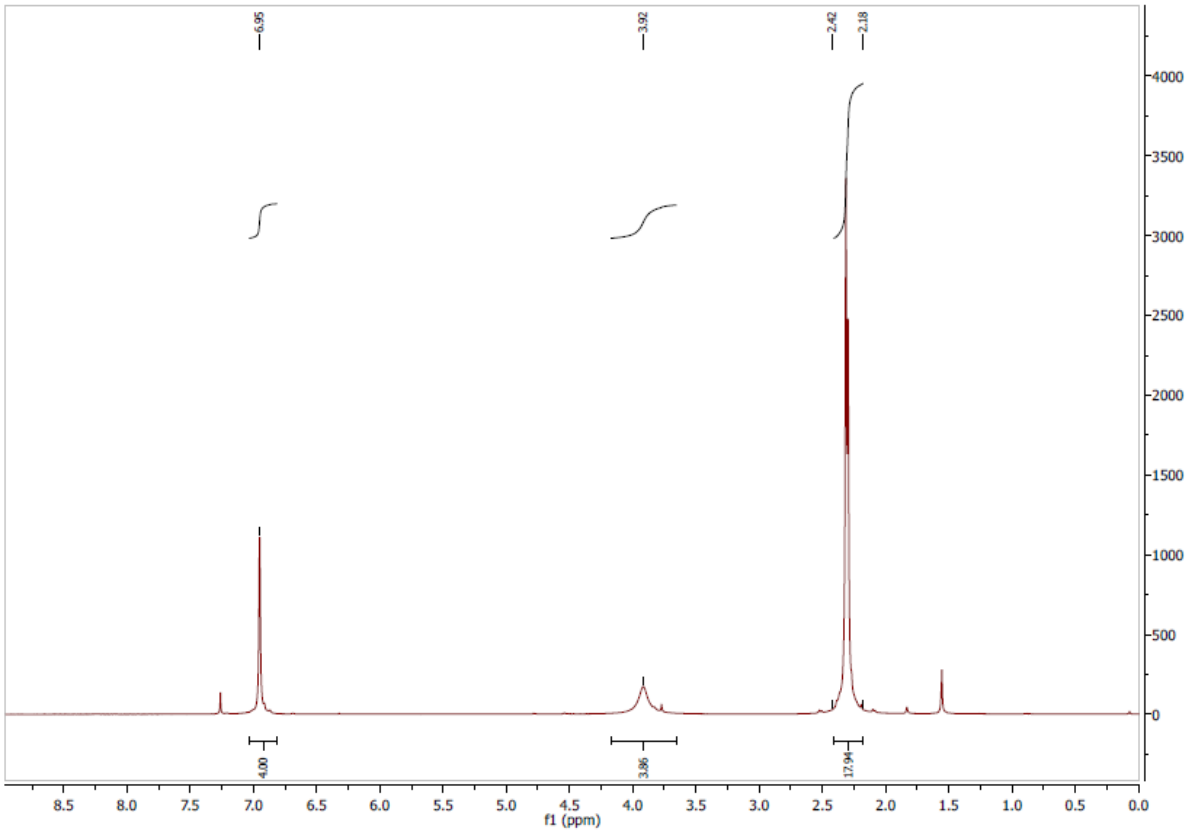
[Cu(Cl)(SIPr)], ^{1}H NMR, $CDCl_3$, 298 K



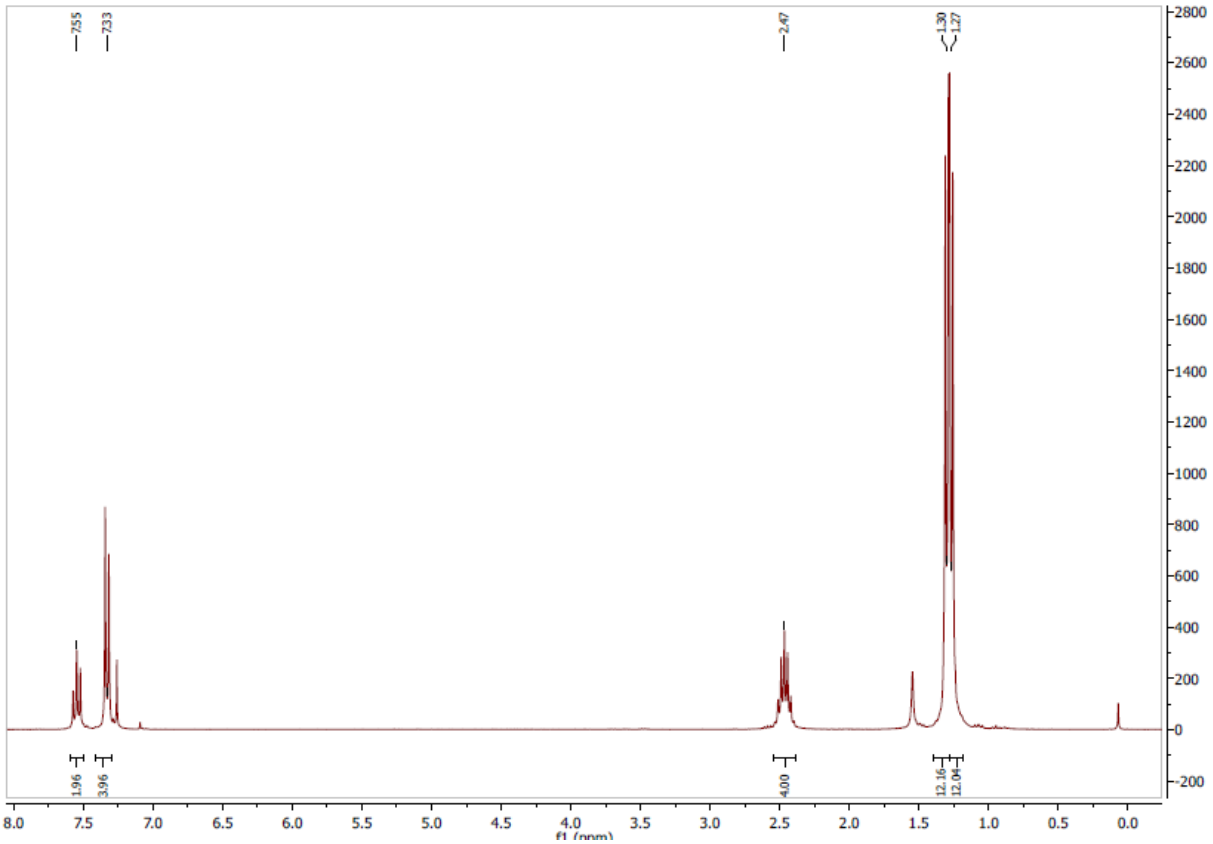
[Cu(Cl)(IMes)], ^{1}H NMR, $CDCl_3$, 298 K



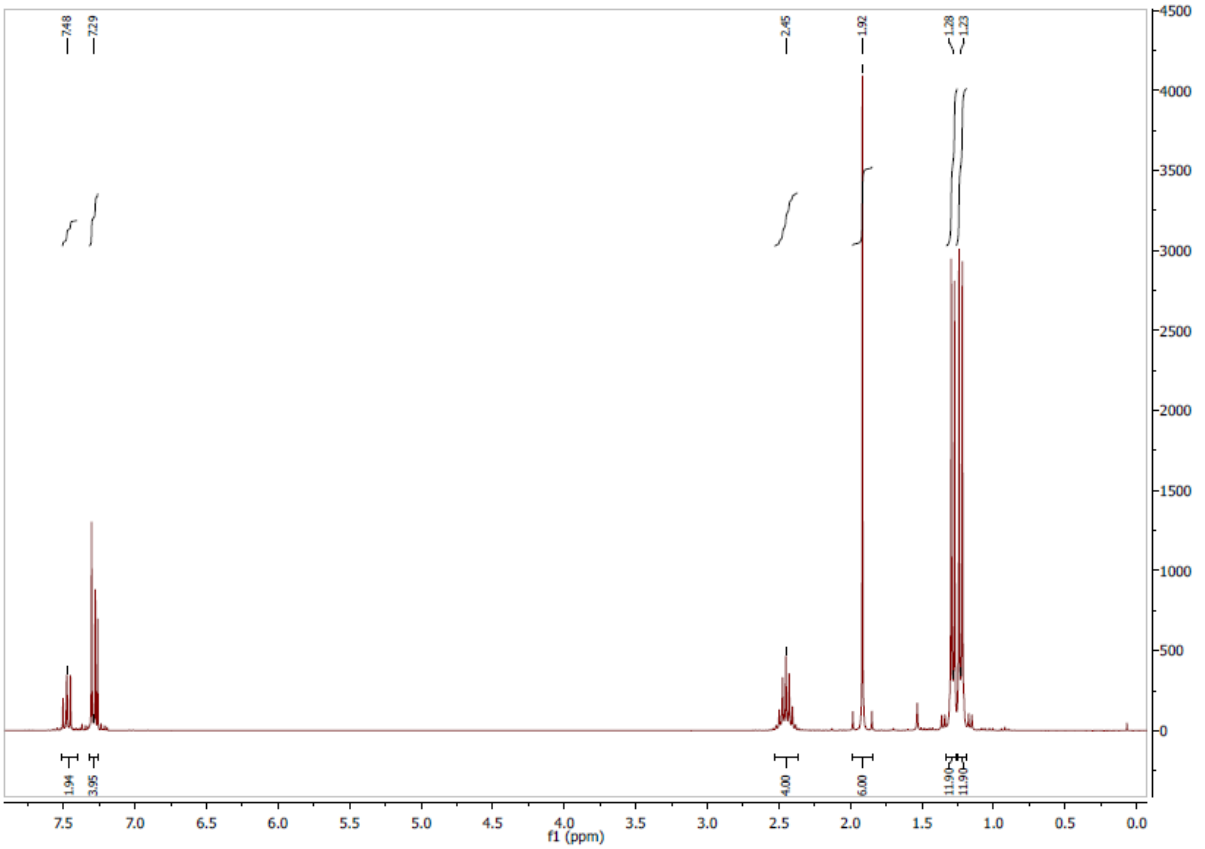
[Cu(Cl)(SIMes)], ^{1}H NMR, $CDCl_3$, 298 K



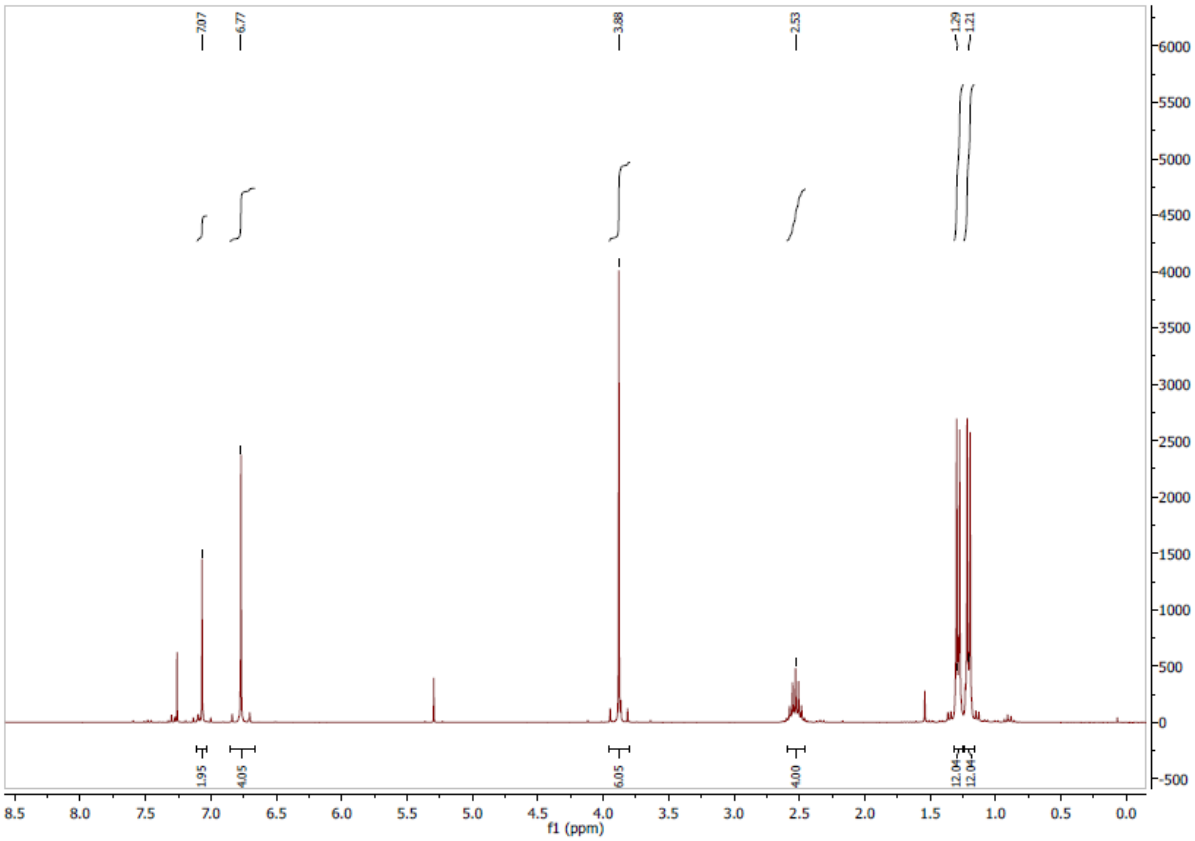
[Cu(Cl)(IPr^{Cl})], ^{1}H NMR, $CDCl_3$, 298 K



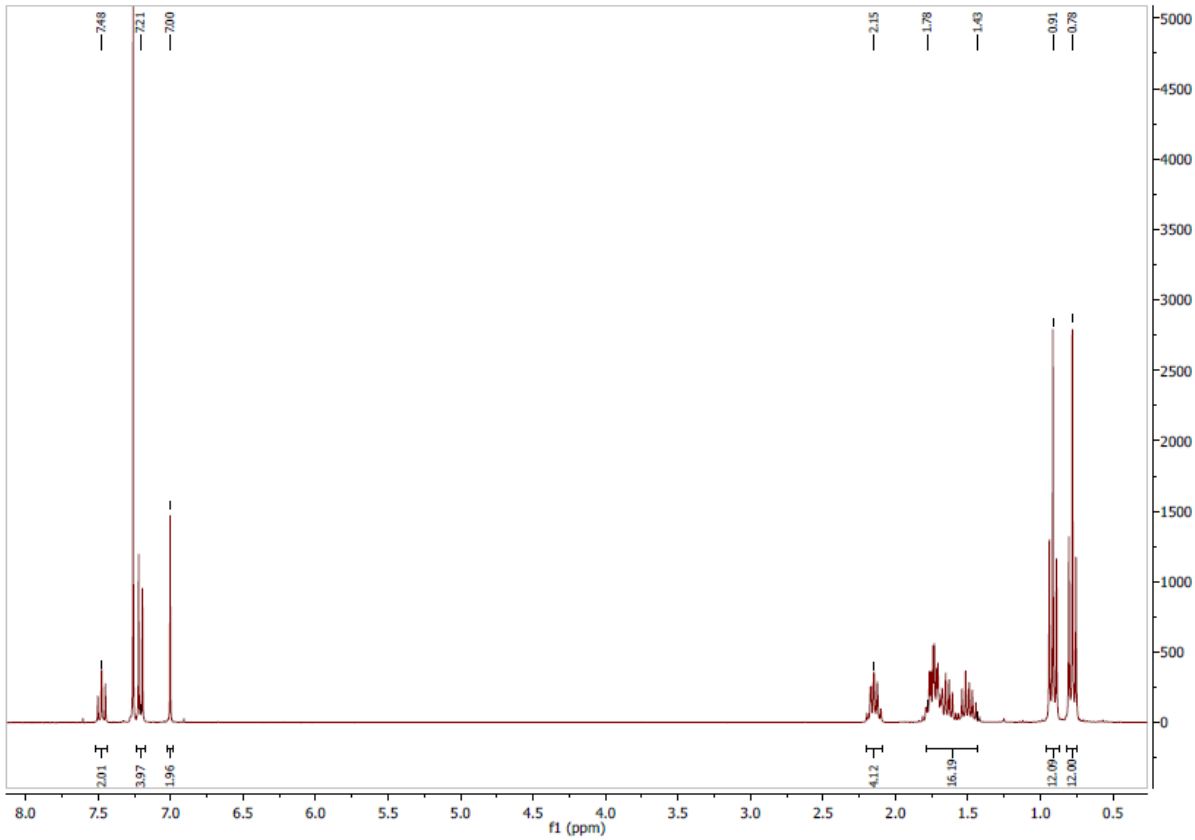
[Cu(Cl)(IPr^{Me})], ^{1}H NMR, $CDCl_3$, 298 K



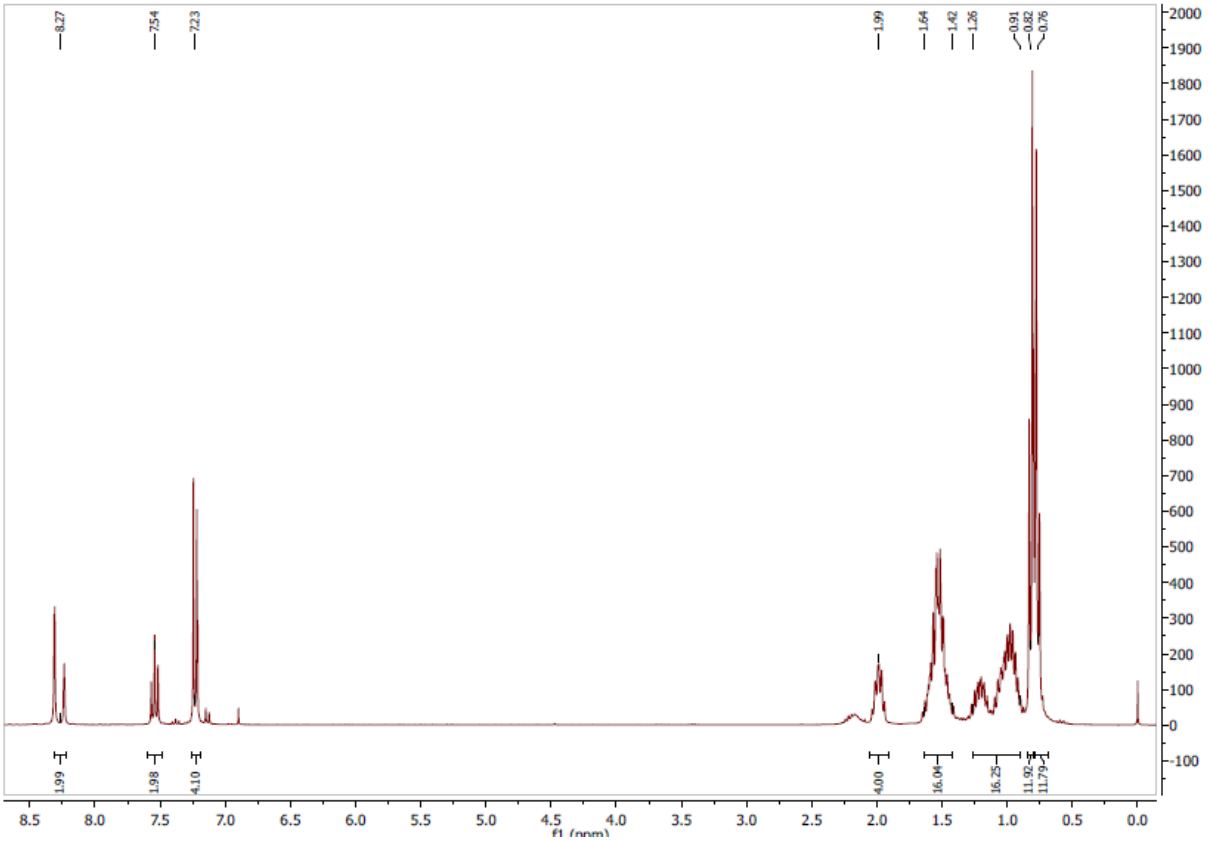
[Cu(Cl)(IPrOMe)], ^{1}H NMR, $CDCl_3$, 298 K



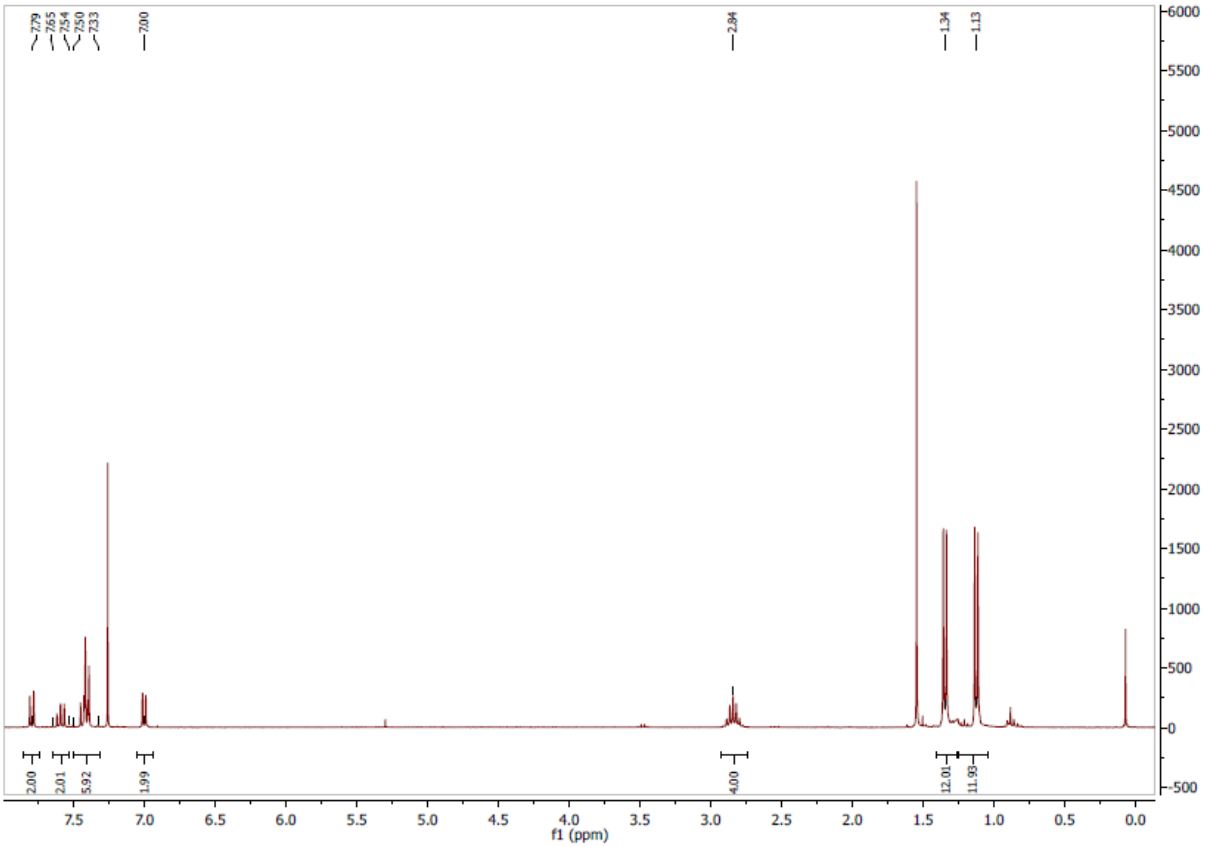
[Cu(Cl)(IPent)], ^{1}H NMR, $CDCl_3$, 298 K



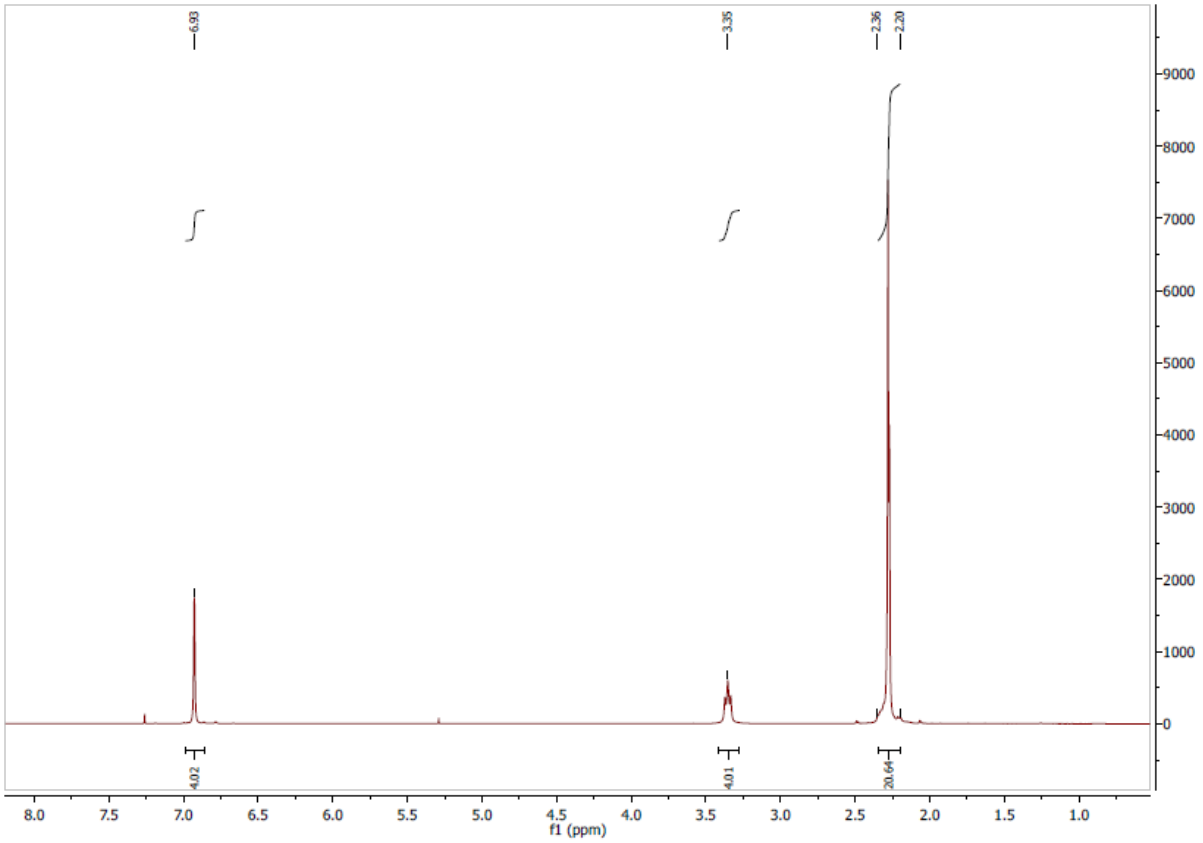
[Cu(Cl)(IHept)], ^{1}H NMR, $CDCl_3$, 298 K



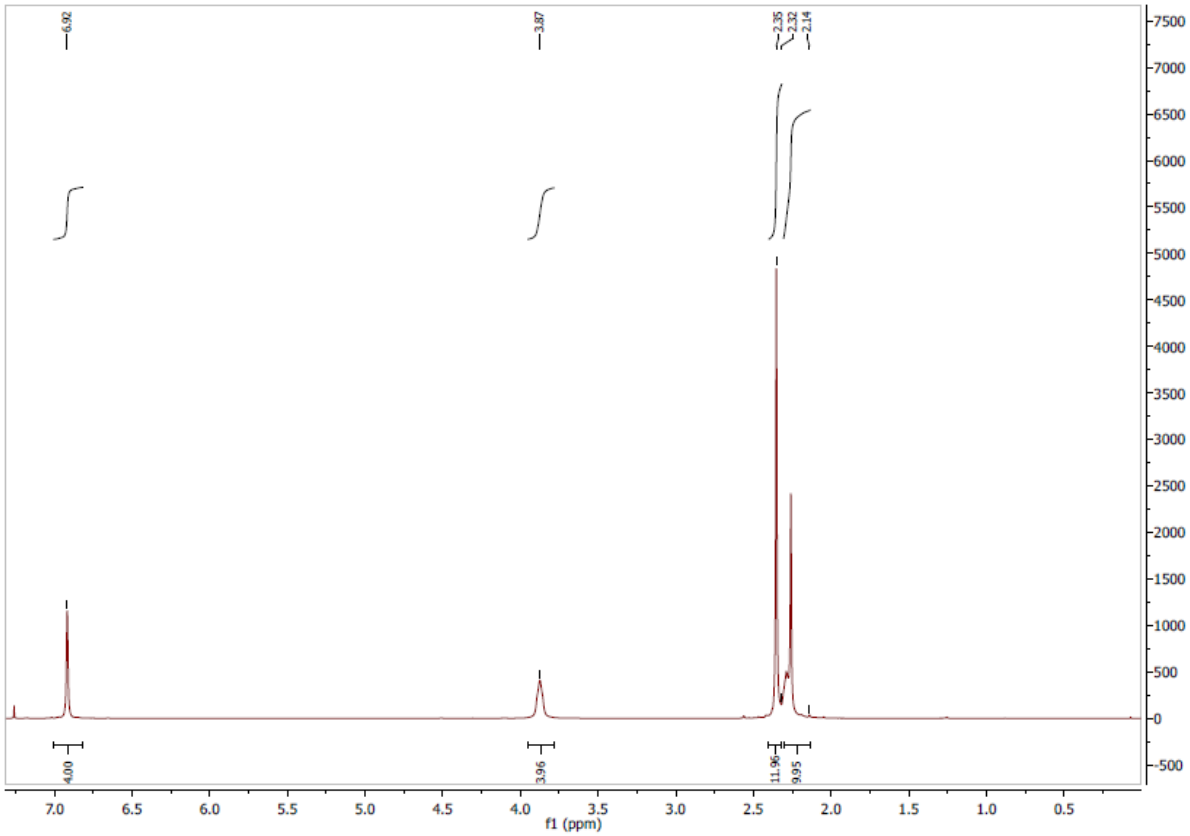
[Cu(Cl)(BIAN IPr)], ^{1}H NMR, $CDCl_3$, 298 K



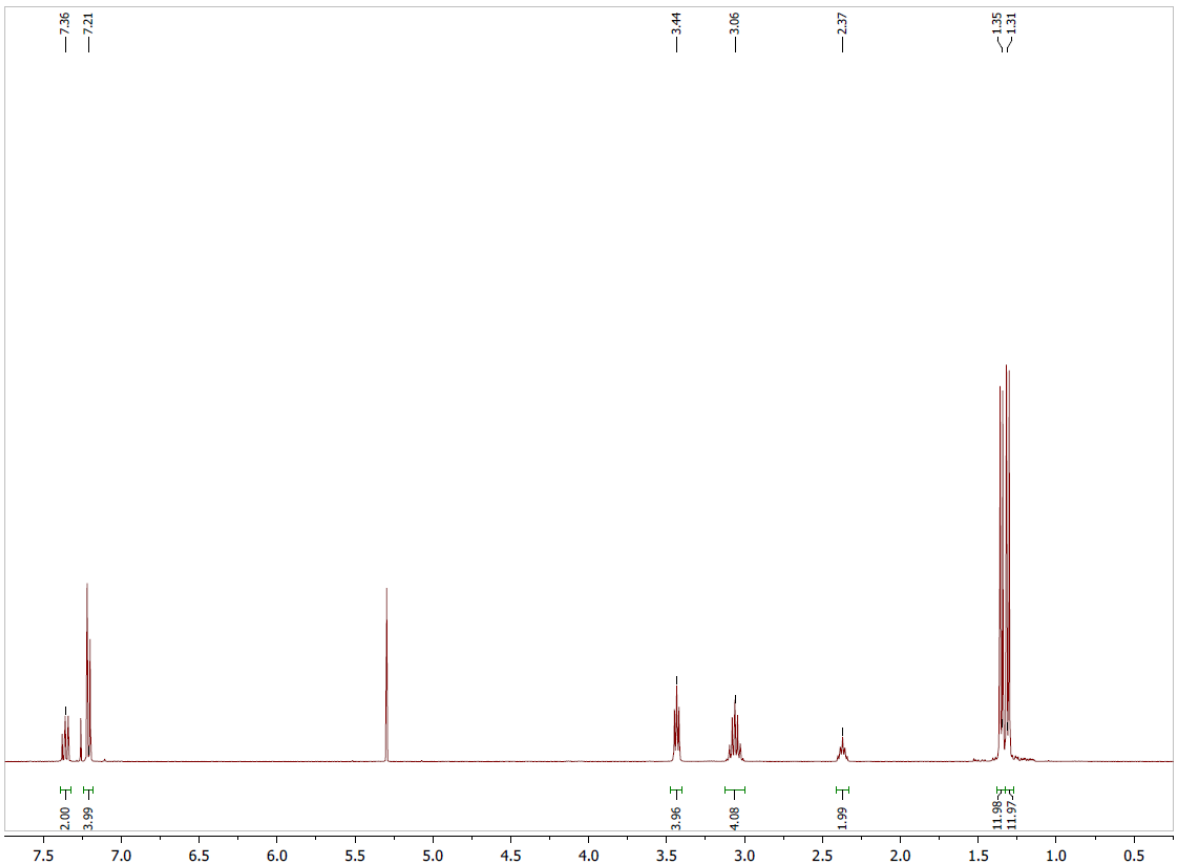
[Cu(Cl)(6Mes)], ^{1}H NMR, $CDCl_3$, 298 K



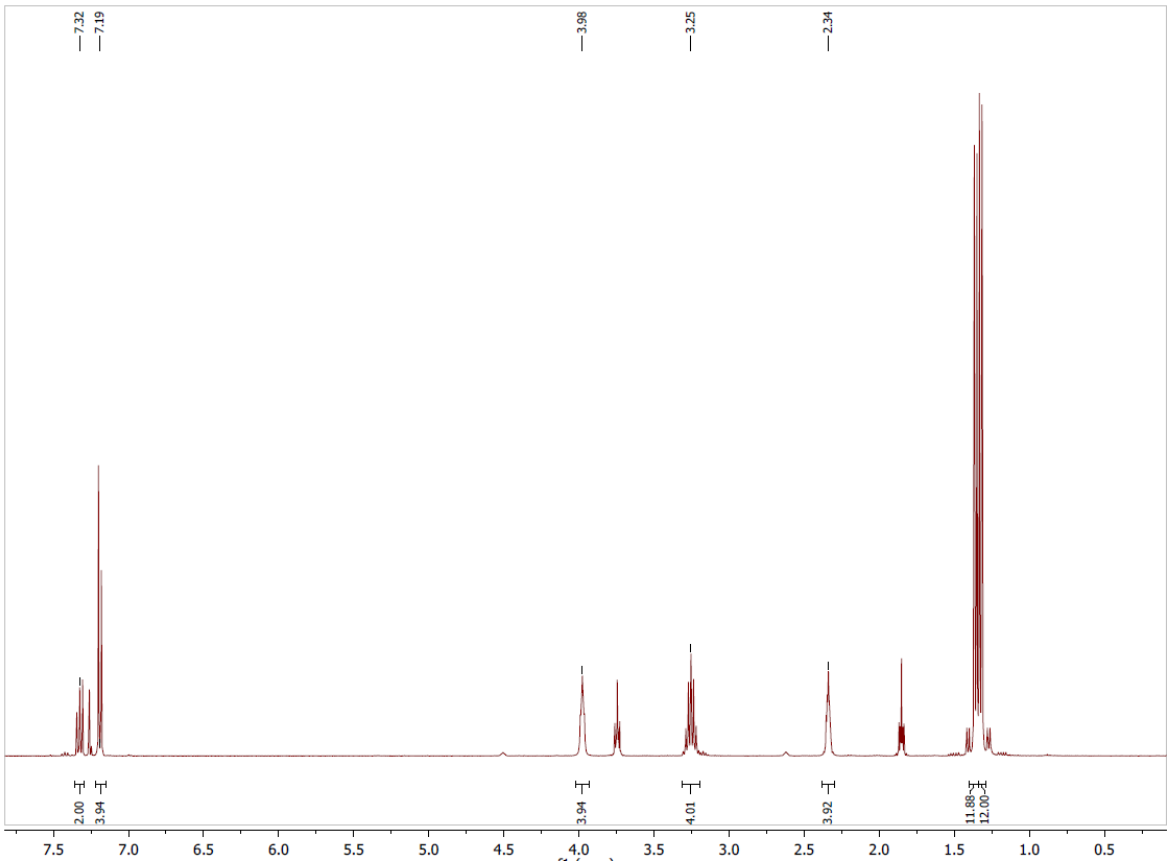
[Cu(Cl)(7Mes)], ^{1}H NMR, $CDCl_3$, 298 K



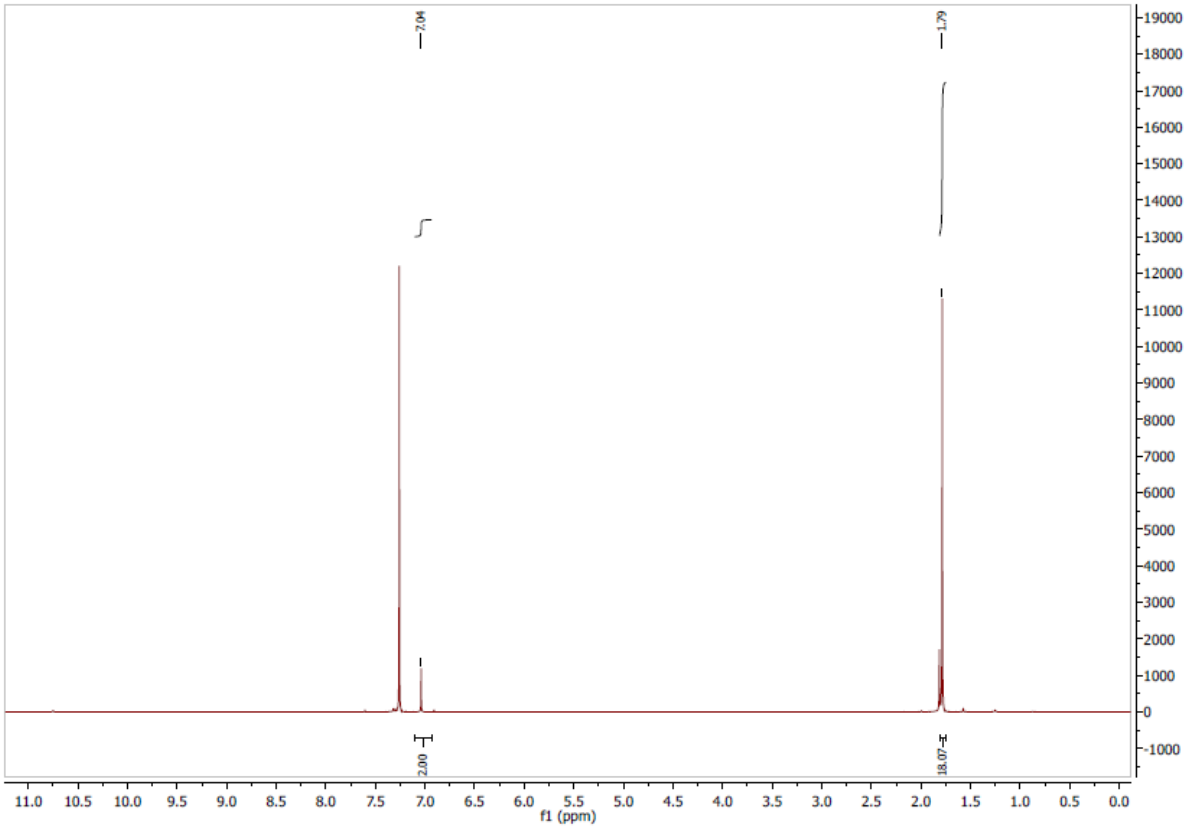
[Cu(Cl)(6Dipp)], ^{1}H NMR, $CDCl_3$, 298 K



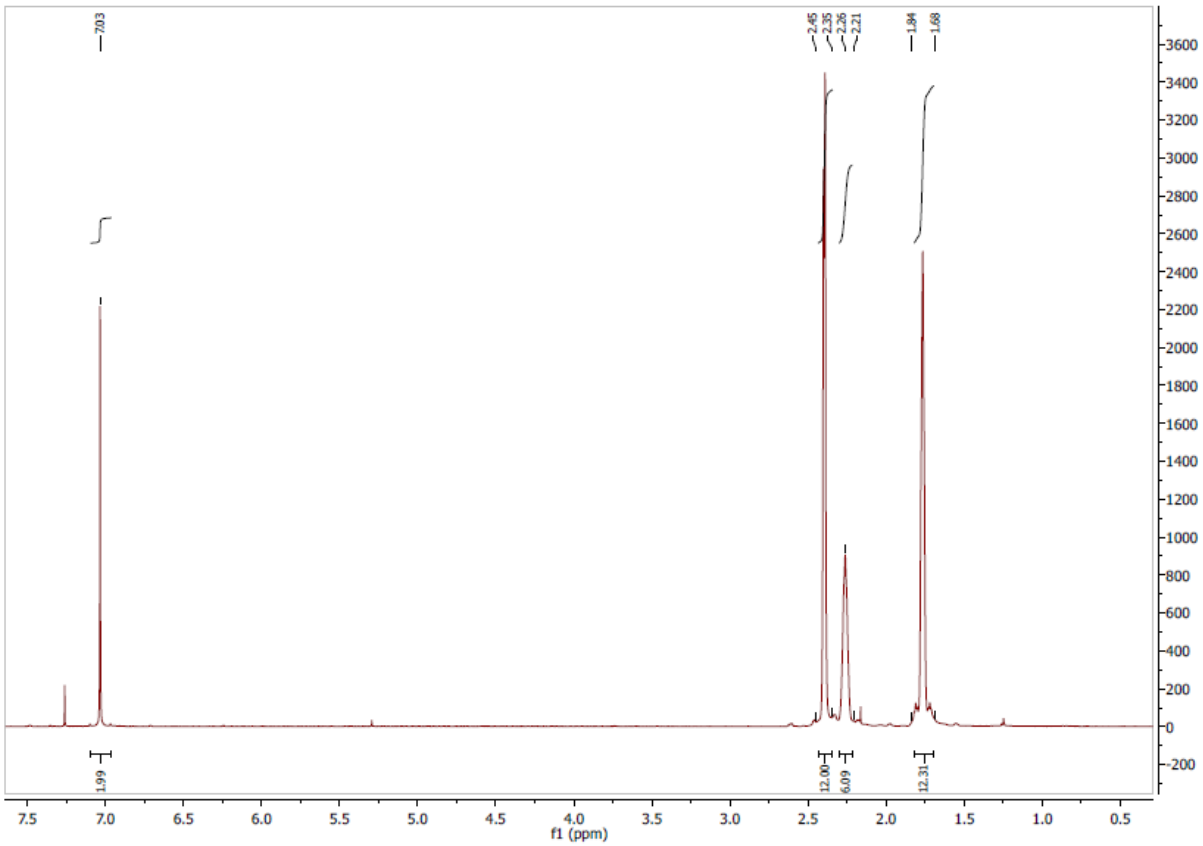
[Cu(Cl)(7Dipp)], ^{1}H NMR, $CDCl_3$, 298 K



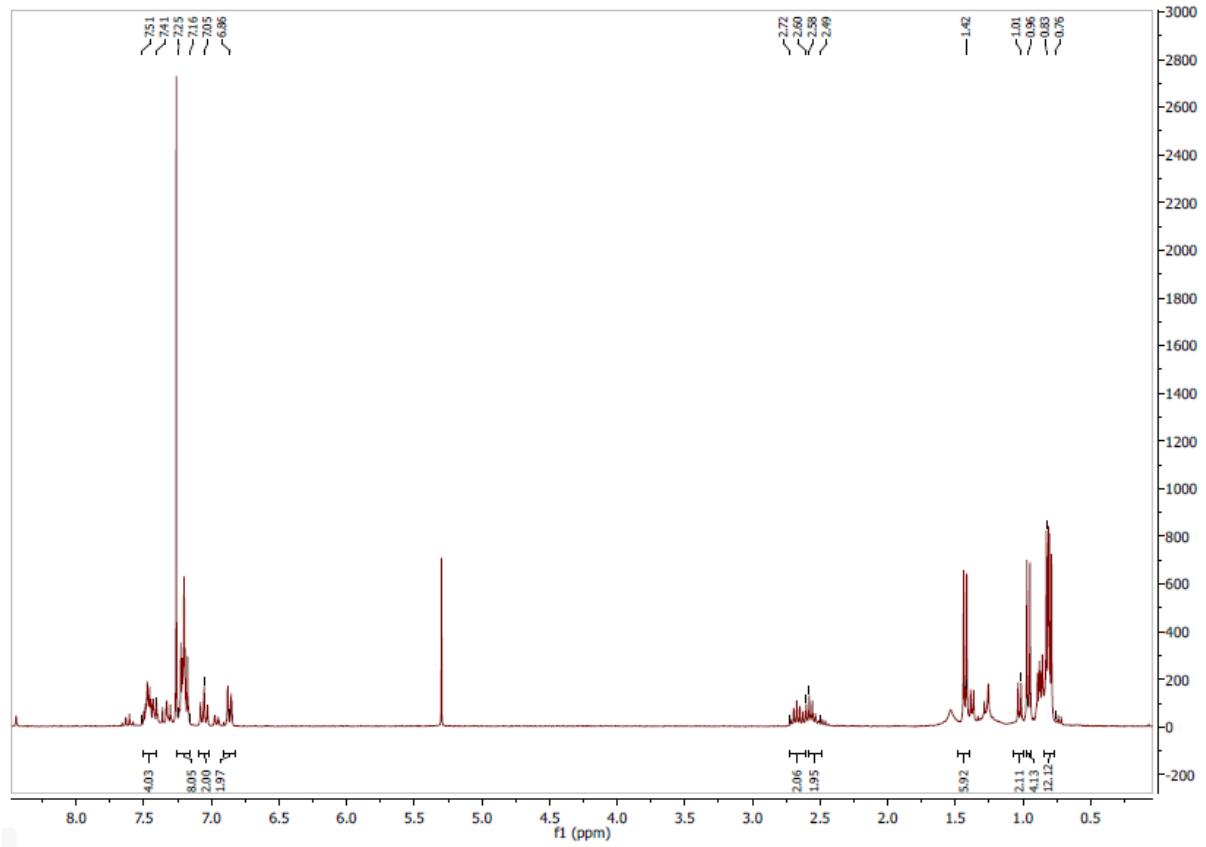
[Cu(Cl)(I^{t}Bu)], ^{1}H NMR, $CDCl_3$, 298 K



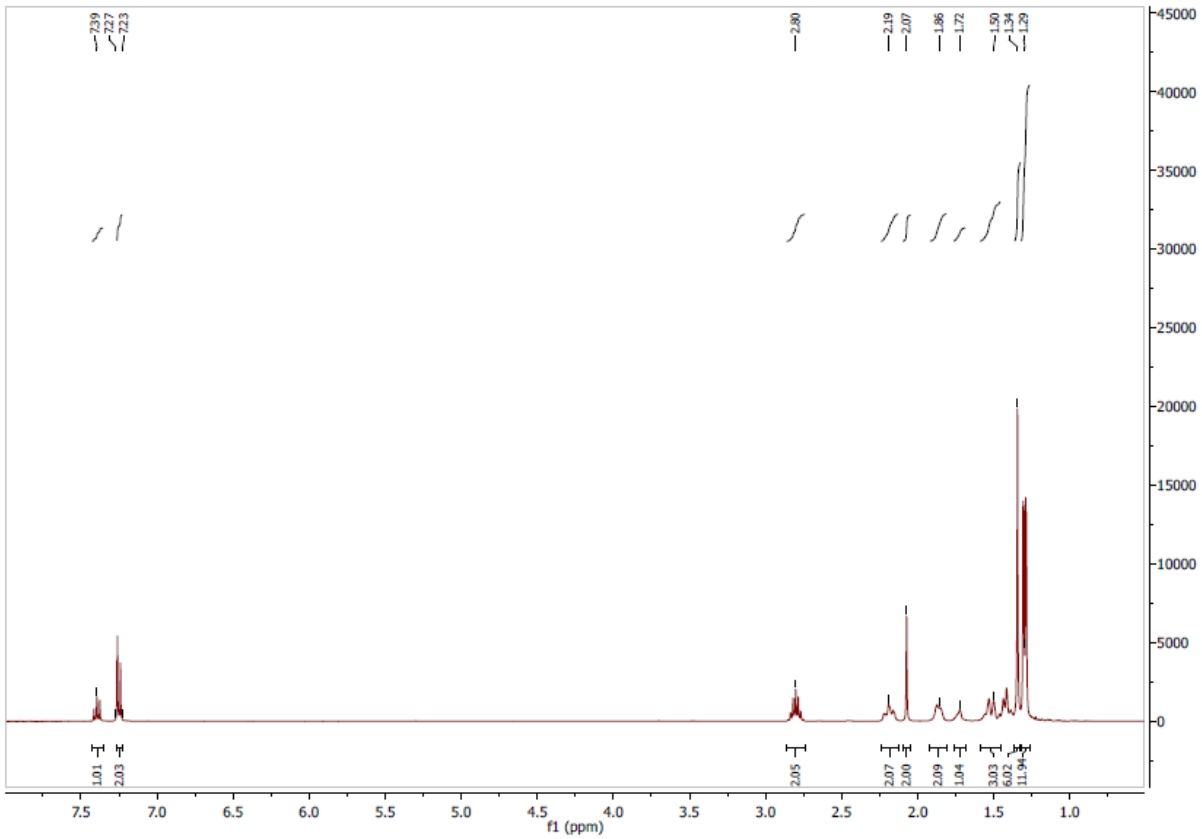
[Cu(Cl)(IAd)], ^{1}H NMR, $CDCl_3$, 298 K



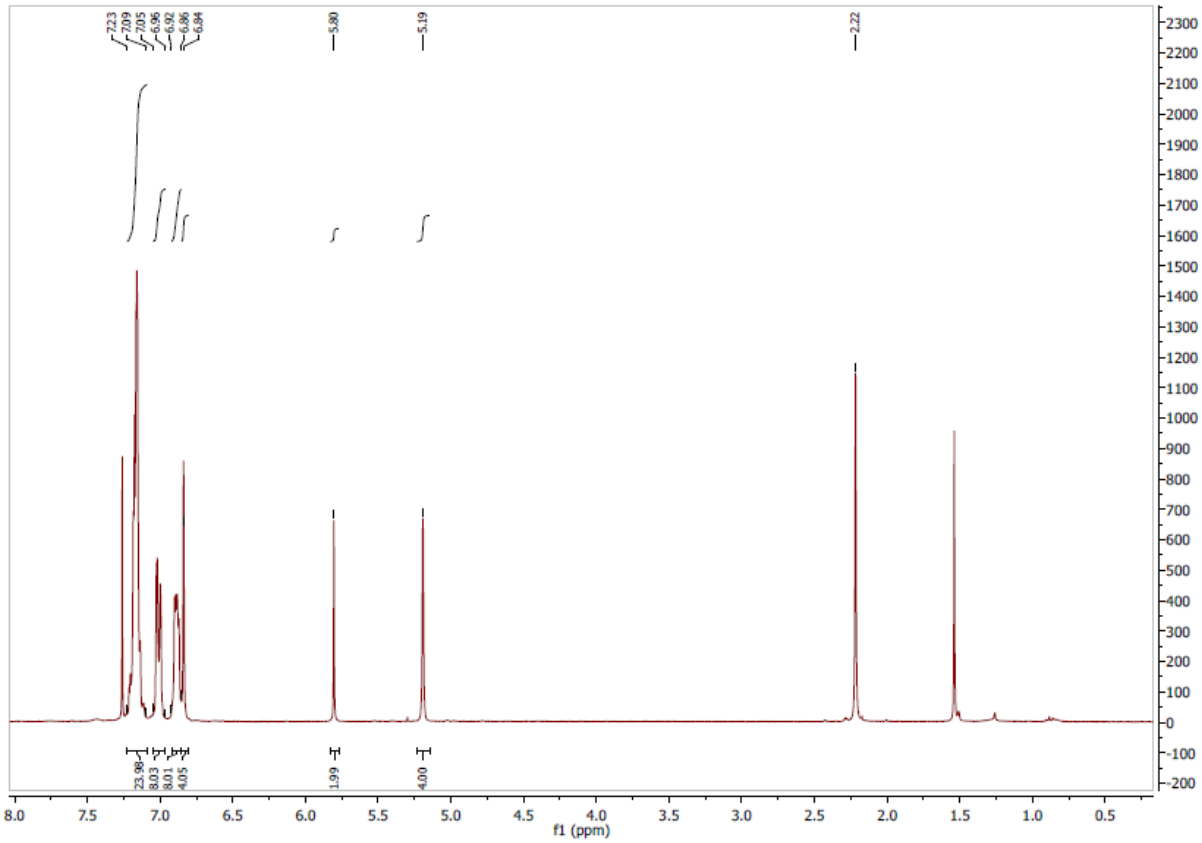
[Cu(Cl)(aNHC)], ^{1}H NMR, $CDCl_3$, 298 K



[Cu(Cl)(CAAC^{Cy})], ^{1}H NMR, $CDCl_3$, 298 K

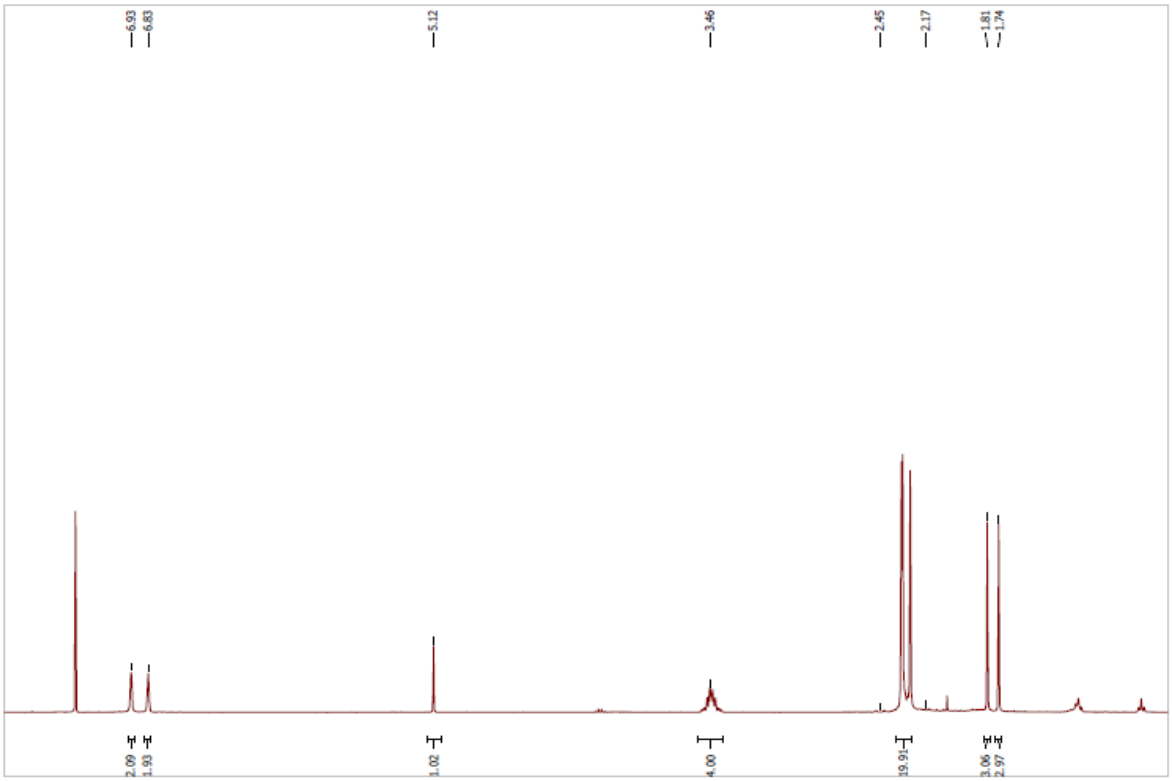


[Cu(Cl)(IPr*)], ^{1}H NMR, $CDCl_3$, 298 K

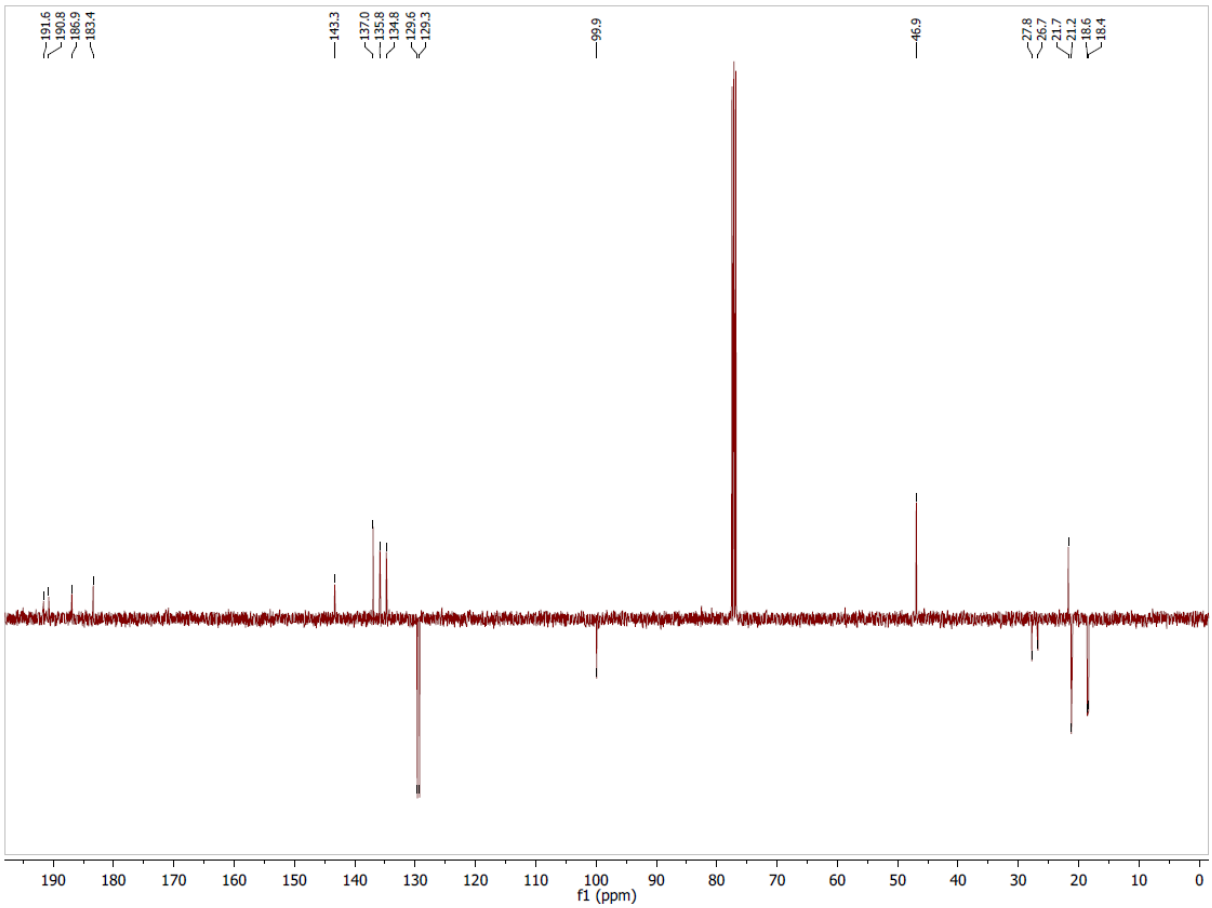


[Rh(6Mes)(acac)(CO)]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

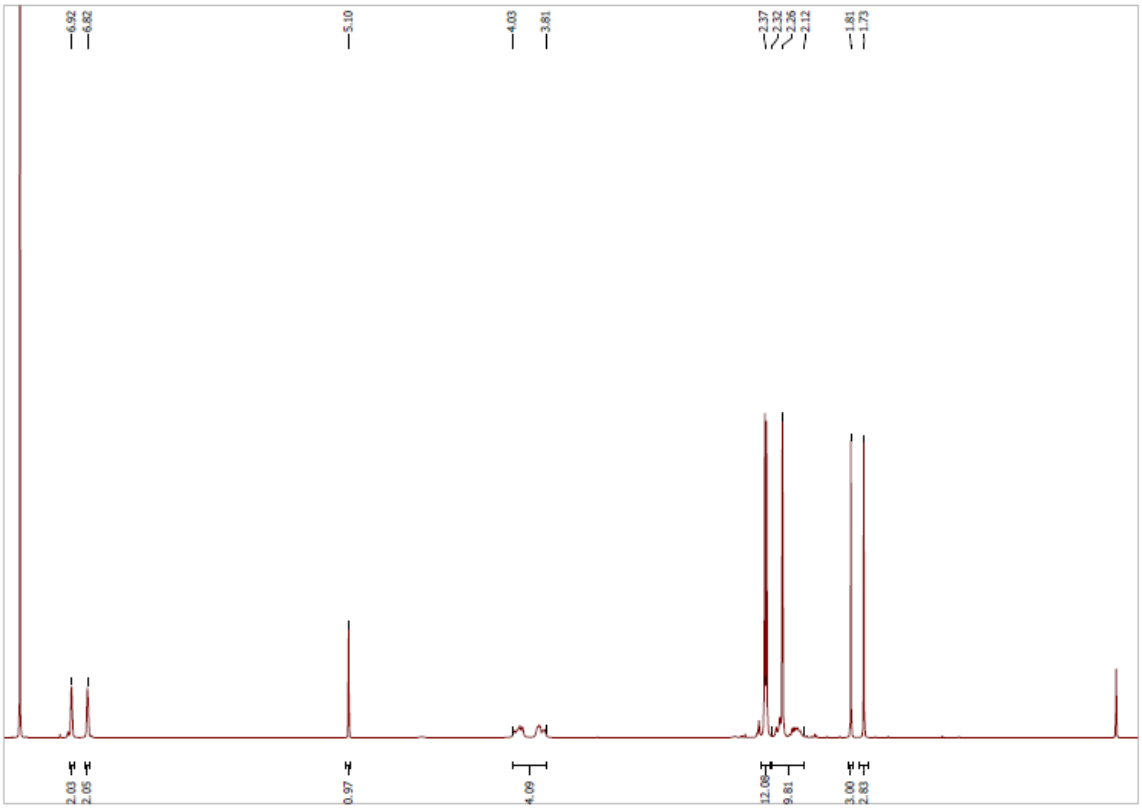


^{13}C-{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K)

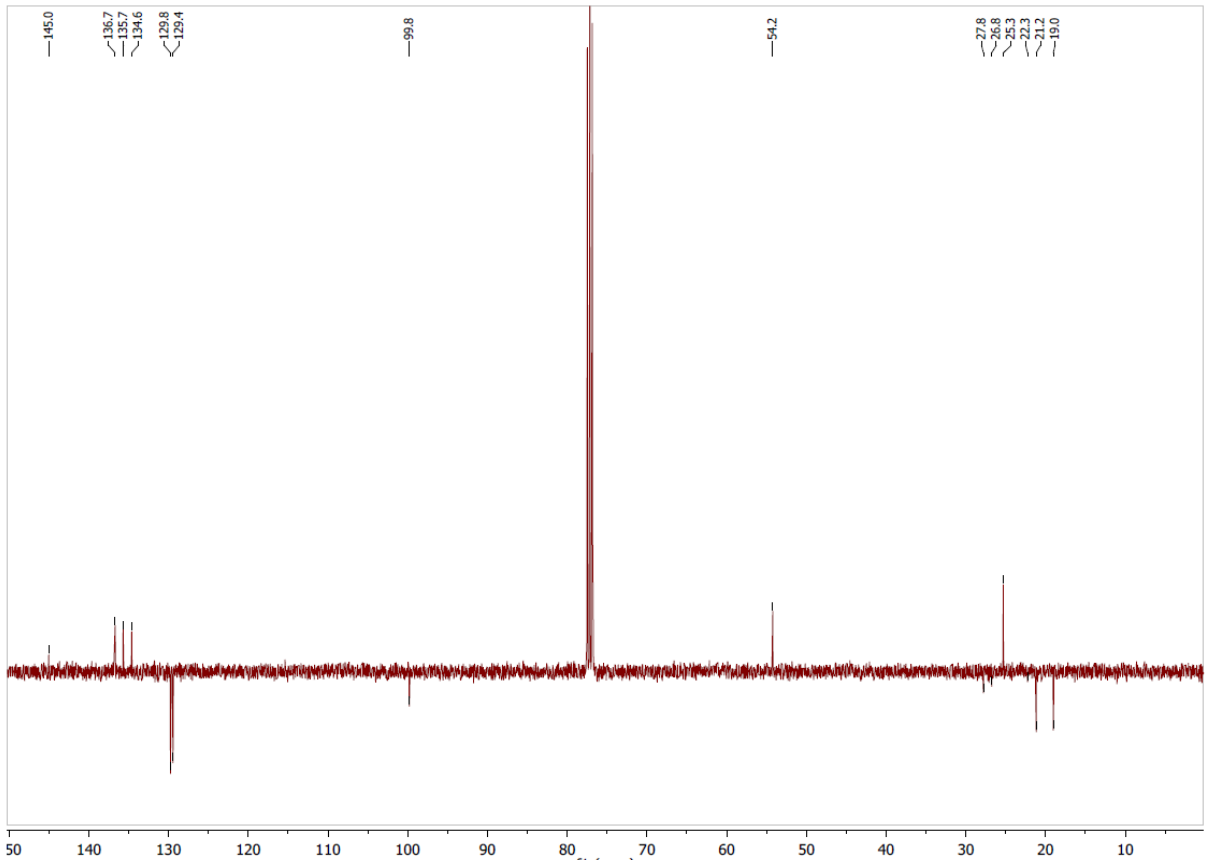


[Rh(7Mes)(acac)(CO)]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

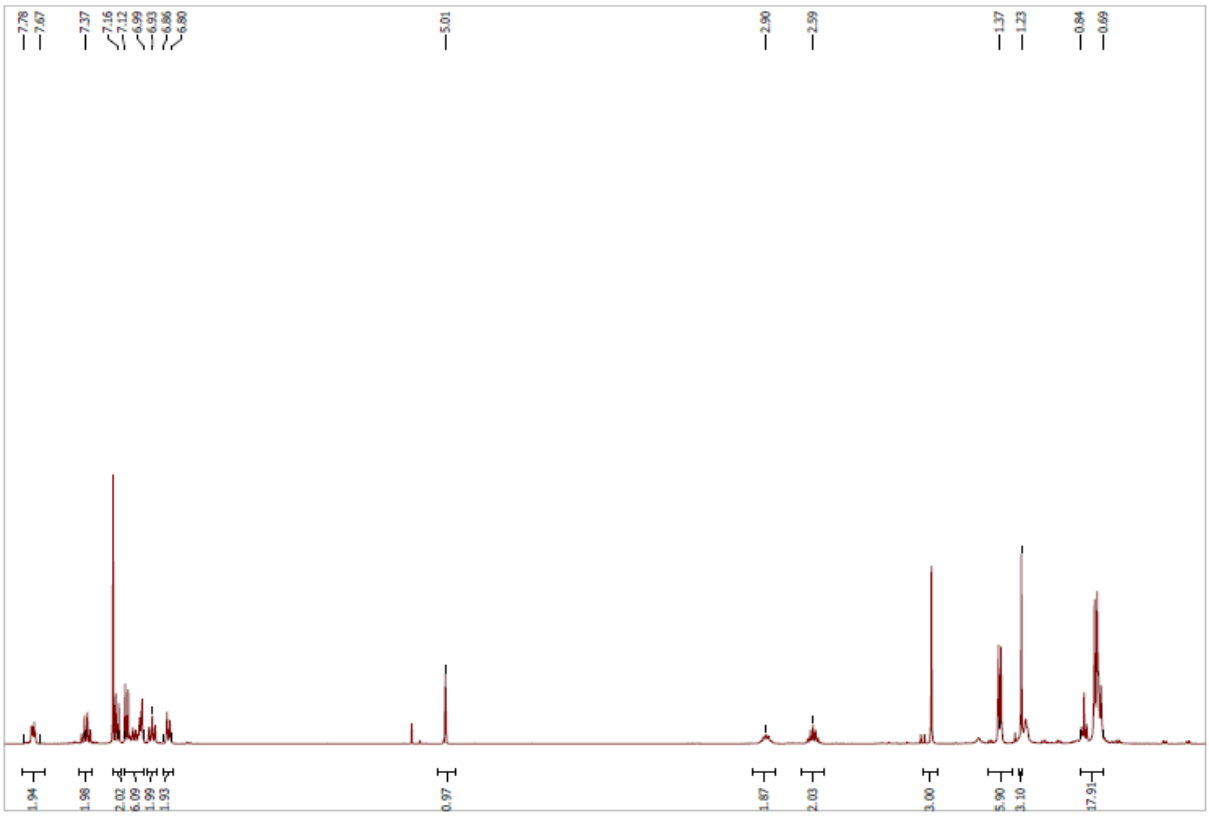


^{13}C-{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K)

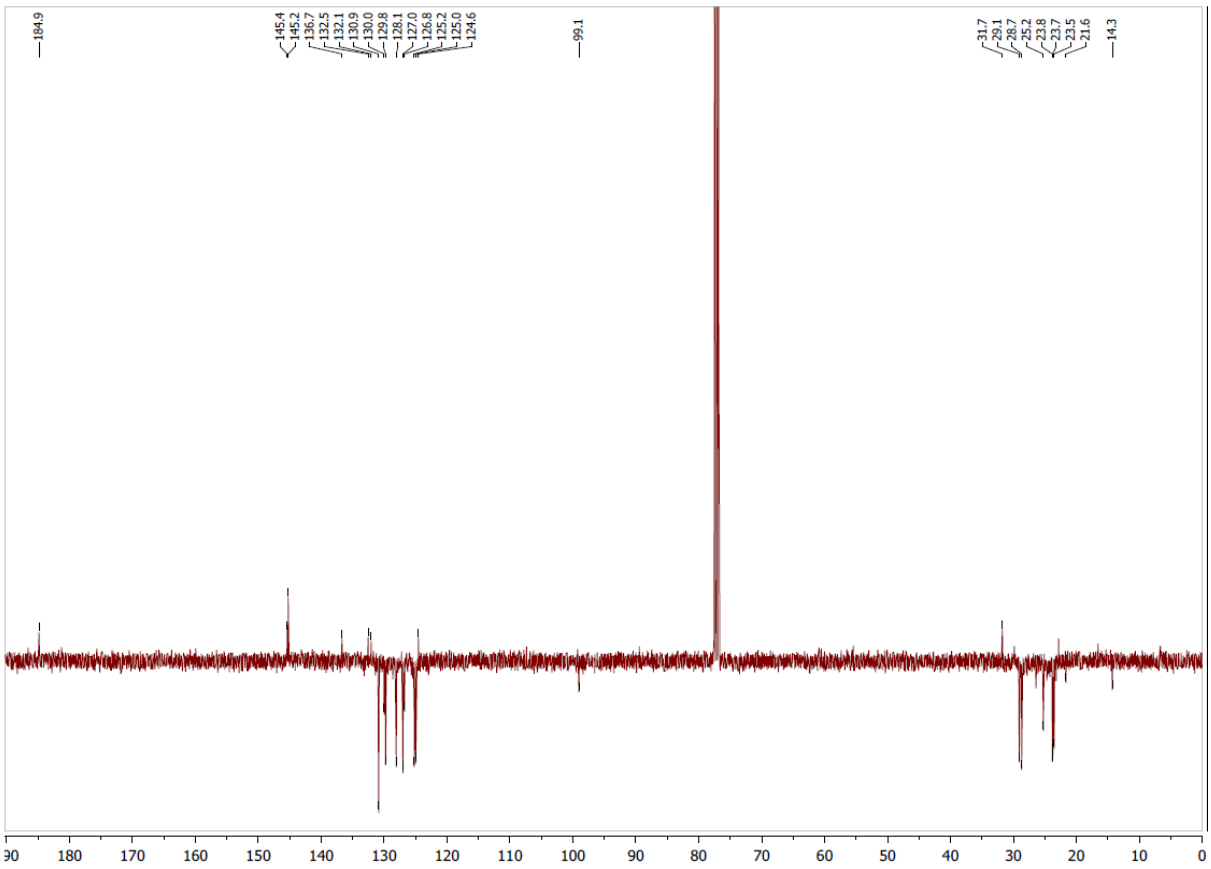


[Rh(aNHC)(acac)(CO)]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

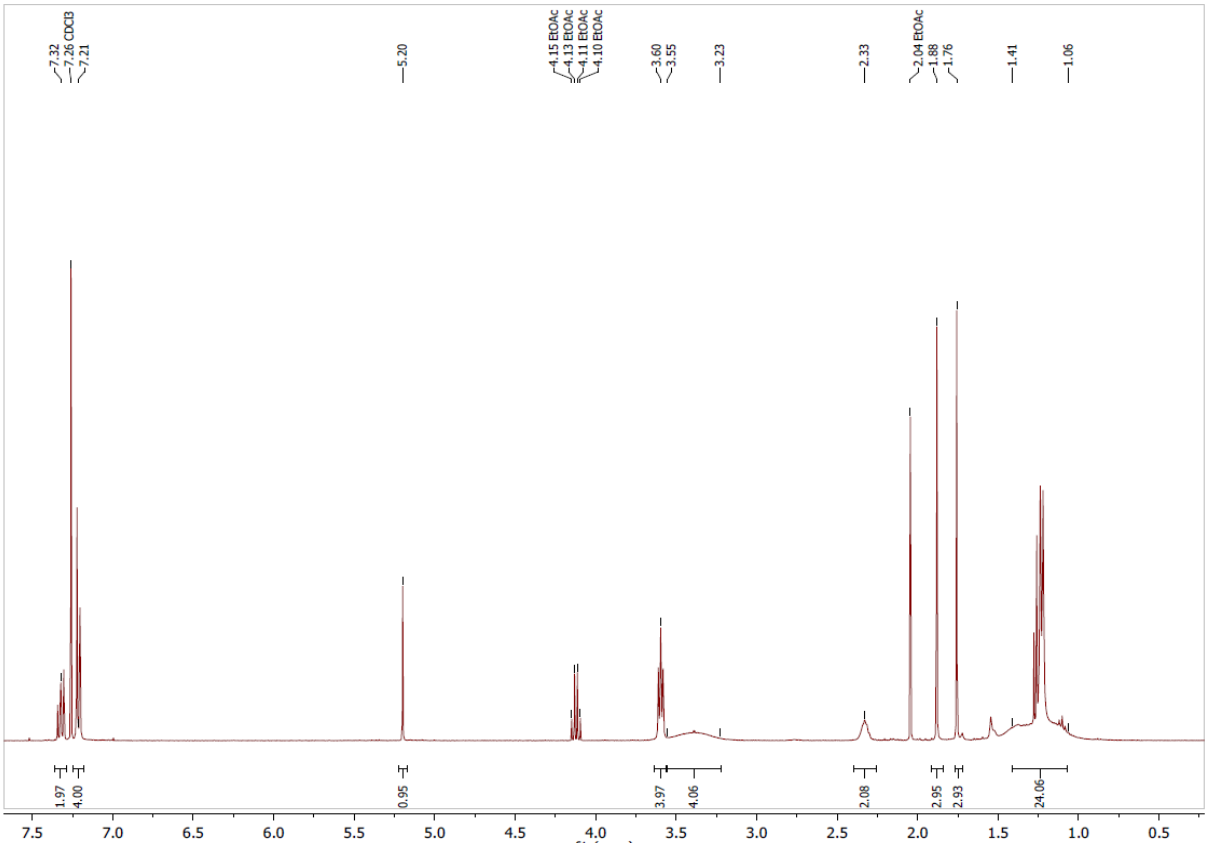


^{13}C-{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K)

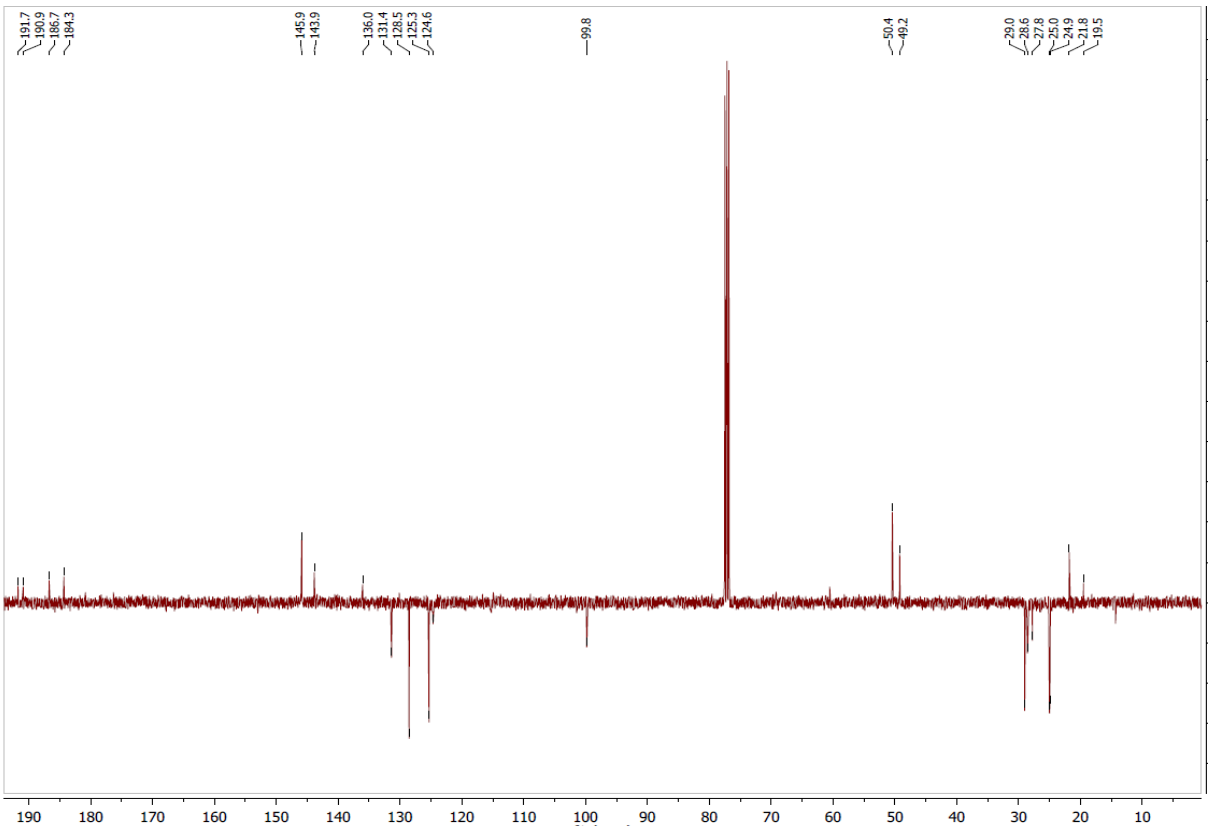


[Rh(6Dipp)(acac)(CO)]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



^{13}C-{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K)



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