**Supporting Information**

**For**

# [Cu(NHC)(OR)] (R = $C(CF_3)_3$) complexes for N-H and S-H bond activation and as pre-catalysts in the Chan-Evans-Lam coupling

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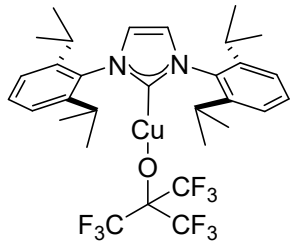
# General information

All reactions were performed in glass vials under air, unless otherwise mentioned. Solvents and all other reagents were purchased and used as received without any additional purification, except for $K_2CO_3$, which was finely grinded (using a mortar and pestle) and dried under high vacuum before use. $^1H$ and $^{13}C$-{1H} apt and $^{19}F$ NMR spectra were recorded in $C_6D_6$ or $CDCl_3$ using Bruker 300, 400 and 500 MHz spectrometers. Chemical shifts (ppm) in $^1H$ and $^{13}C$ NMR spectra are referenced to the residual solvent peak ($C_6D_6$: δH=7.16 ppm, δC=128.06 ppm); ($CDCl_3$: δH=7.26 ppm, δC=77.16 ppm); (DMSO-$d_6$: δH=2.50 ppm, δC=39.52 ppm) $^1H$ NMR splitting patterns are abbreviated as follows: broad signal (br), singlet (s), doublet (d), triplet (t), doublet of doublets (dd), doublet of triplets (dt), triplet of triplets (tt), quartet (q), quintet (quint), heptet (hept), multiplet (m). [(IPr)CuCl] [1], [(SIPr)CuCl] [1], [(IMes)CuCl] [1], [(SIMes)CuCl] [1], [(IPr*)CuCl] [1], [(IPr$^{Me}$)CuCl] [2] , [(IPr$^{OMe}$)CuCl] [2], [(BIAN-IPr)CuCl] [3], [(BIAN-IMes)CuCl] [4], [(IPr)CuOH] [5] were synthesized following the procedures described in the literature. All the HRMS analyses were conducted in MeCN as solvent and the measurement could only detect $[Cu(NHC)(MeCN)]^+$ and $[Cu(NHC)_2]^+$ as the main peaks unless otherwise stated.

## Synthesis of [Cu(IPr)(OC(CF$_3$)$_3$)] (1)




**Procedure A**

In a 4 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(IPr)(Cl)] (100 mg, 0.205 mmol), potassium carbonate (85 mg, 0.615 mmol), EtOH (1 mL) and nonafluoro-tert-butyl alcohol (31.3 µL, 0.225 mmol). The mixture was left to stir for 1 hour at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 95% yield (133 mg).

**Procedure B**

In a 20 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(IPr)(OH)] (500 mg, 1.066 mmol), EtOH (3 mL) and nonafluoro-tert-butyl alcohol (163 µL, 1.171 mmol). The mixture was left stirring for 1 hour at 25 °C. Then the solvent was evaporated under vacuum and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 98% yield (717 mg).

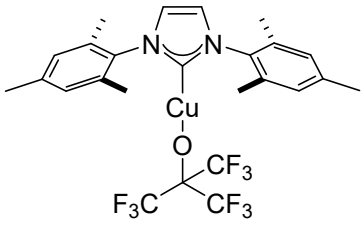
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.49 (t, J = 7.8 Hz, 2H, C$H_{Ar}$), 7.30 (d, J = 7.8 Hz, 4H, C$H_{Ar}$), 7.11 (s, 2H, C$H_{Imid}$), 2.58 (hept, J = 6.8 Hz, 4H, C*H*), 1.27 (d, J = 6.8 Hz, 12H, C$H_3$), 1.21 (d, J = 6.8 Hz, 12H, C$H_3$).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 180.48 (Cu-*C*), 145.55 ($C_{Ar}$), 134.77 ($C_{Ar}$), 130.53 ($CH_{Ar}$), 124.38 ($CH_{Ar}$), 123.43 ($CH_{Imid}$), 122,30 (d, $J_{CF}$= 295 Hz, $CF_3$), 28.84 (*C*H), 24.30 ($CH_3$), 24.06 ($CH_3$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -76.21.

**HRMS**: calculated *m/z* for $[Cu(IPr)(MeCN)]^+$ = 492.24400; found 492.24225.

# Synthesis of [Cu[(IMes)(OC(CF$_3$)$_3$)] (2)




In a 4 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(IMes)(Cl)] (100 mg, 0.247 mmol), potassium carbonate (102.4 mg, 0.741 mmol), EtOH (1 mL) and nonafluoro-tert-butyl alcohol (38 µL, 0.272 mmol). The mixture was left to stir for 1 hour at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 92% yield (138 mg).

**$^{1}$H NMR** (400 MHz, Chloroform-d) δ 6.98 (s, 2H, C$H_{Imid}$), 6.89 (s, 4H, C$H_{Ar}$), 2.41 (s, 6H, C$H_3$), 1.66 (s, 12H, C$H_3$).

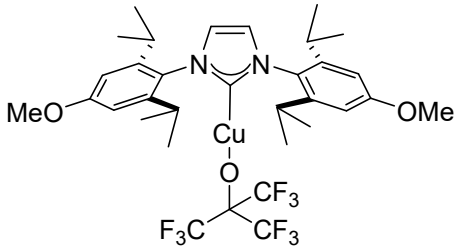
**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 177.65 (Cu-*C*), 139.66 ($C_{Ar}$), 134.53 ($2C_{Ar}$), 129.32 ($CH_{Ar}$), 123.98 (d, $J_{CF}$= 298 Hz, $CF_3$), 122.75 ($CH_{Imid}$), 21.22 ($CH_3$), 16.96 ($CH_3$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -76.70.

**HRMS**: calculated *m/z* for $[Cu(IMes)(MeCN)]^+$ = 408.15010; found 408.14911

calculated *m/z* for $[Cu(IMes)_2]^+$ = 671.31750; found 671.31585

## Synthesis of [Cu[(IPr$^{OMe}$)(OC(CF$_3$)$_3$)] (3)




In a 4 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(IPr$^{OMe}$)(Cl)] (100 mg, 0.182 mmol), potassium carbonate (75.6 mg, 0.547 mmol), EtOH (1 mL) and nonafluoro-tert-butyl alcohol (28 µL, 0.201 mmol). The mixture was left stirring for 1 hour at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated, and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 78% yield (107 mg).

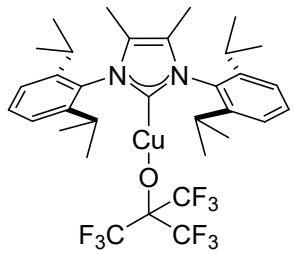
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.06 (s, 2H, C*H*$_{Imid}$), 6.78 (s, 4H, C*H*$_{Ar}$), 3.89 (s, 6H, OC*H*$_3$), 2.54 (hept, J = 6.8 Hz, 4H, C*H*), 1.25 (d, J = 6.8 Hz, 12H, C*H*$_3$), 1.19 (d, J = 6.8 Hz, 12H, C*H*$_3$).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 181.43 (Cu-*C*), 160.93 (*C*$_{Ar}$-OCH$_3$), 147.10 (*C*$_{Ar}$), 128.00 (*C*$_{Ar}$), 123.80 (*C*H$_{Imid}$), 123.18 (d, J$_{CF}$= 468 Hz, *C*F$_3$), 109.72 (*C*H$_{Ar}$), 55.64 (O*C*H$_3$), 29.01 (*C*H), 24.21 (*C*H$_3$), 23.98 (*C*H$_3$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -76.19.

**HRMS**: calculated *m/z* for [Cu(IPr$^{OMe}$)(MeCN)]$^+$ = 552.26513; found 552.26426

## Synthesis of [Cu[(IPr$^{Me}$)(OC(CF$_3$)$_3$)] (4)




In a 4 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(IPr$^{Me}$)(Cl)] (150 mg, 0.290 mmol), potassium carbonate (120.2 mg, 0.870 mmol), EtOH (1.5 mL) and nonafluoro-tert-butyl alcohol (44 µL, 0.319 mmol). The mixture was left stirring for 1 hour at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 72% yield (150 mg).

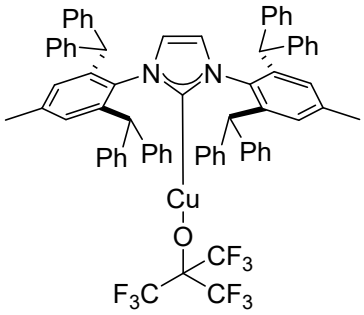
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.47 (t, J = 7.8 Hz, 2H, C*H*$_{Ar}$), 7.29 (d, J = 7.8 Hz, 4H, C*H*$_{Ar}$), 2.45 (hept, J = 6.9 Hz, 4H, C*H*), 1.91 (s, 6H, C*H*$_{3\ Imid}$), 1.23 (dd, J = 9.1, 6.9 Hz, 24H, C*H*$_3$).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 176.69 (Cu-*C*), 145.83 ($C_{Ar}$), 133.22 ($C_{Ar}$), 130.36 ($CH_{Ar}$), 126.23 ($CH_{Imid}$), 124.44 ($CH_{Ar}$), 122.33 (d, $J_{CF}$= 296 Hz, $CF_3$), 28.73 (*C*H), 24.79 (*C*H$_3$), 23.50 (*C*H$_3$), 9.69 *C*H$_{3\ Imid}$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -76.22.

**HRMS**: calculated *m/z* for $[Cu(IPr^{Me})(MeCN)]^+$ = 520.27530; found 520.27427

# Synthesis of [Cu[(IPr*)(OC(CF$_3$)$_3$)] (5)




In a 20 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(IPr*)(Cl)] (200 mg, 0.197 mmol), potassium carbonate (82 mg, 0.593 mmol), EtOH (3 mL) and nonafluoro-tert-butyl alcohol (30 µL, 0.217 mmol). The mixture was left to stir for 2 hours at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 95% yield (227 mg).

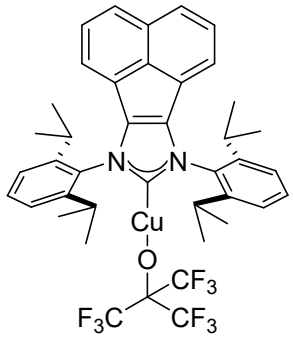
**$^{1}$H NMR** (400 MHz, Chloroform-d ) δ 7.24 – 7.16 (m, 12H, (Ph)C$H_{Ar}$), 7.16 – 7.09 (m, 12H, (Ph)C$H_{Ar}$), 7.09 – 7.01 (m, 8H, (Ph)C$H_{Ar}$), 6.91 – 6.78 (m, 12H, C$H_{Ar}$ + (Ph)C$H_{Ar}$), 5.58 (s, 2H, C$H_{Imid}$), 5.26 (s, 4H, C*H*), 2.24 (s, 6H, C$H_3$).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 180.21 (Cu-*C*), 143.36 ($C_{Ar}$), 142.60 ($C_{Ar}$), 140.88 ($C_{Ar}$), 140.09 ($C_{Ar}$), 134.25 ($C_{Ar}$), 130.14 ($CH_{Ar}$), 129.77 ($CH_{Ar}$), 129.42 ($CH_{Ar}$), 128.66 ($CH_{Ar}$), 128.42 ($CH_{Ar}$), 126.79 ($CH_{Ar}$), 126.73 ($CH_{Ar}$), 122.55 (d, $J_{CF}$= 295 Hz, $CF_3$), 123.39 ($CH_{Imid}$), 121.09, 51.54 (*C*H), 21.92 (*C*H$_3$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -75.97.

**HRMS**: calculated *m/z* for $[Cu(IPr^*)]^+$ = 975.37395; found 975.37146

## Synthesis of [Cu[(BIAN-IPr)(OC(CF$_3$)$_3$)] (6)



In a 4 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(BIAN-IPr)(Cl)] (100 mg, 0.163 mmol), potassium carbonate (68 mg, 0.490 mmol), EtOH (1mL) and nonafluoro-tert-butyl alcohol (25 µL, 0.179 mmol). The mixture was left to stir for 16 hours at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a pale orange solid in 85% yield (113 mg).

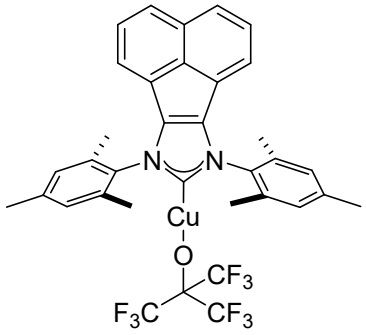
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.79 (d, J = 8.3 Hz, 2H, C*H*$_{\text{Naph top}}$), 7.59 (t, J = 7.8 Hz, 2H, C*H*$_{\text{Ar}}$), 7.46 – 7.38 (m(t+d), 6H, t=C*H*$_{\text{Naph}}$ + d=C*H*$_{\text{Ar}}$), 7.00 (d, J = 7.0 Hz, 2H, C*H*$_{\text{Naph down}}$), 2.85 (hept, J = 6.8 Hz, 4H, C*H*), 1.31 (d, J = 6.9 Hz, 12H, C*H*$_3$), 1.11 (d, J = 6.9 Hz, 12H, C*H*$_3$).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 185.75 (Cu-*C*), 145.56 (*C*$_{\text{Ar}}$), 138.94 (N-*C*=C), 133.52 (N-*C*$_{\text{Ar}}$), 130.92 (*C*$_{middle}$(C)$_3$), 130.78 (*C*H$_{\text{Ar}}$), 129.96 (*C*$_{down}$(C)$_3$), 128.44 (*C*H$_{\text{Naph top}}$), 127.93 (*C*H$_{\text{Naph middle}}$), 125.58 (*C*$_{top}$(C)$_3$), 124.68 (*C*H$_{\text{Ar}}$), 122.34 (d, J$_{\text{CF}}$= 296 Hz, *C*F$_3$), 121.16 (*C*H$_{\text{Naph down}}$), 29.02 (*C*H), 24.21 (*C*H$_3$), 24.01 (*C*H$_3$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -76.17.

**HRMS**: calculated *m/z* for [Cu(BIAN-IPr)(MeCN)]$^+$ = 617.281312; found 617.28284.

## Synthesis of [Cu[(BIAN-IMes)(OC(CF$_3$)$_3$)] (7)



In a 4 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(BIAN-IMes)(Cl)] (100 mg, 0.189 mmol), potassium carbonate (78.5 mg, 0.568 mmol), EtOH (1mL) and nonafluoro-tert-butyl alcohol (29 µL, 0.208 mmol). The mixture was left to stir for 16 hours at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by

filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a yellow solid in 81% yield (111 mg).

**$^{1}$H NMR** (400 MHz, Chloroform-d) δ 7.79 (d, J = 8.2 Hz, 2H, C$H_{\text{Naph top}}$), 7.41 (t, J = 7.7 Hz, 2H, C$H_{\text{Naph}}$), 7.05 – 6.99 (m=d+s, 6H, C$H_{\text{Ar}}$ +C$H_{\text{Naph down}}$), 2.50 (s, 6H, C$H_3$), 1.84 (s, 12H, C$H_3$).

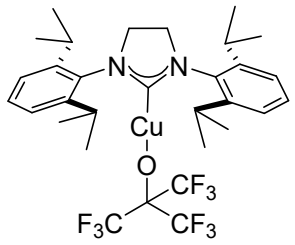
**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 182.63 (Cu-*C*), 140.03 ($C_{\text{Ar}}$), 138.24 (N-*C*=C), 134.44 ($C_{\text{Ar}}$), 133.33 (N-$C_{\text{Ar}}$), 130.81 ($C_{middle}(C)_3$) , 129.87 ($C_{down}(C)_3$), 129.75 (*C*H$_{\text{Ar}}$), 128.91 (*C*H$_{\text{Naph top}}$), 127.95 (*C*H$_{\text{Naph middle}}$), 124.61 ($C_{top}(C)_3$), 123.70 (d, $J_{CF}$= 298 Hz, *C*F$_3$), 121.38 (*C*H$_{\text{Naph down}}$), 21.38 (*C*H$_3$), 17.31 (*C*H$_3$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -76.37.

**HRMS**: calculated *m/z* for $[Cu(BIAN\text{-}IMes)(MeCN)]^+$ = 532.18140; found 532.18081.

calculated *m/z* for $[Cu(BIAN\text{-}IMes)_2]^+$ = 919.38010; found 919.37822.

# Synthesis of [Cu[(SIPr)(OC(CF$_3$)$_3$)] (8)




In a 20 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(SIPr)(Cl)] (200 mg, 0.408 mmol), potassium carbonate (169.5 mg, 1.225 mmol), EtOH (3mL) and nonafluoro-tert-butyl alcohol (63 µL, 0.449 mmol). The mixture was left to stir for 2 hours at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 88% yield (248 mg).

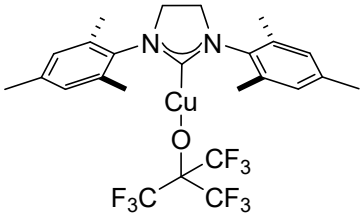
**$^{1}$H NMR** (400 MHz, Chloroform-d) δ 7.41 (t, J = 7.8 Hz, 2H, C$H_{\text{Ar}}$), 7.25 (d, J = 7.8 Hz, 2H, C$H_{\text{Ar}}$), 4.00 (s, 4H, C$H_2$), 3.05 (hept, J = 6.9 Hz, 4H, C*H*), 1.33 (d, J = 6.9 Hz, 24H, C$H_3$).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 203.63 (Cu-*C*), 146.60 ($C_{\text{Ar}}$), 134.74 ($C_{\text{Ar}}$), 129.83 (*C*H$_{\text{Ar}}$), 124.73 (*C*H$_{\text{Ar}}$), 122.24 (d, $J_{CF}$= 296 Hz, *C*F$_3$), 53.90 (*C*H$_2$), 29.01 (*C*H), 24.74 (*C*H$_3$), 24.34 (*C*H$_3$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -76.25.

**HRMS**: calculated *m/z* for $[Cu(SIPr)(MeCN)]^+$ = 494.25965; found= 494.25910.

## Synthesis of [Cu[(SIMes)(OC(CF$_3$)$_3$)] (9)



In a 20 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu(SIMes)(Cl)] (200 mg, 0.493 mmol), potassium carbonate (204.5 mg, 1.479 mmol), EtOH (3mL) and nonafluoro-tert-butyl alcohol (76 µL, 0.542 mmol). The mixture was left stirring for 1 hour at 25 °C. Then the solvent was evaporated under vacuum, and the residue was then microfiltered and filtered over a syringe microfilter using toluene (3 mL). The solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 90% yield (270 mg).

**$^1$H NMR** (400 MHz, Chloroform-d) δ 6.96 (s, 4H, C$H_{Ar}$), 3.93 (s, 4H, C$H_2$), 2.31 (s, 6H, C$H_3$), 2.28 (s, 12H, C$H_3$).

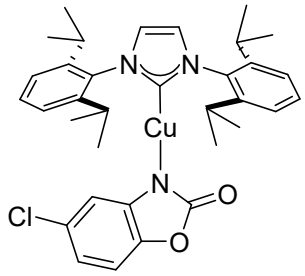
**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 202.88 (Cu-*C*), 138.80 (*C*$_{Ar}$), 135.67 (*C*$_{Ar}$), 135.13 (*C*$_{Ar}$), 129.76 (*C*H$_{Ar}$), 123.78, 120.86, 51.09 (*C*H$_2$), 21.11 (*C*H$_3$), 17.85 (*C*H$_3$).

**$^{19}$F NMR** (377 MHz, Chloroform-d) δ -76.34.

**HRMS**: calculated *m/z* for [Cu(SIMes)(MeCN)]$^+$ = 410.16575; found 410.16631.

calculated *m/z* for [Cu(SIMes)$_2$]$^+$ = 675.34880 ; found 675.34897.

## Synthesis of [Cu[(IPr)(chlorzoxazonyl)] (21)



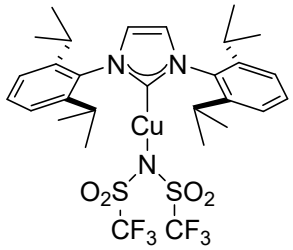
In a 20 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added Cu[(IPr)(OC(CF$_3$)$_3$)] (**1**) ( (100 mg, 0.145 mmol), toluene (3 mL) and chlorzoxazone (24.7 mg, 0.145 mmol). The mixture was left to stir for 24 hours at 110 °C. After the mixture was allowed to cool to room temperature, the solvent was evaporated under vacuum. Recrystallization in DCM/pentane and drying under vacuum afforded a white powder. The product was obtained in 99% yield (89.1 mg).

**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.57 (t, J = 7.8 Hz, 2H, C$H_{Ar}$), 7.37 (d, J = 7.8 Hz, 4H, C$H_{Ar}$), 7.23 (s, 2H, C$H_{Imid}$), 6.73 (d, J = 8.3 Hz, 1H, C$H_{Chlor}$), 6.63 (dd, J = 8.2, 2.2 Hz, 1H, C$H_{Chlor}$), 5.70 (d, J = 2.1 Hz, 1H, C$H_{Chlor}$), 2.62 (hept, J = 6.9 Hz, 4H, C*H*), 1.31 (d, J = 6.9 Hz, 12H, *C*H$_3$), 1.27 (d, J = 6.9 Hz, 12H, *C*H$_3$).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 180.63 (Cu-*C*), 163.51 (N-*C*$O_2$), 145.81 ($C_{Ar\ Chorz}$), 145.13 ($C_{Ar\ IPr}$), 142.77 ($C_{Ar\ Chorz}$), 134.35 ($C_{Ar\ IPr}$), 131.17 ($CH_{Ar\ IPr}$) , 126.84 ($C_{Ar\ Chorz}$), 124.51 ($CH_{Ar\ IPr}$), 123.52 ($CH_{Imid}$), 118.21 ($CH_{chorz}$), 110.68 ($CH_{chorz}$), 108.31 ($CH_{chorz}$), 28.98 (*C*H), 24.93 ($CH_3$), 24.04 ($CH_3$).

**HRMS**: calculated *m/z* for $[Cu(IPr)(MeCN)]^+$ = 492.24400; found 492.24340.

# Synthesis of [Cu(IPr)($NTf_2$)] (10)



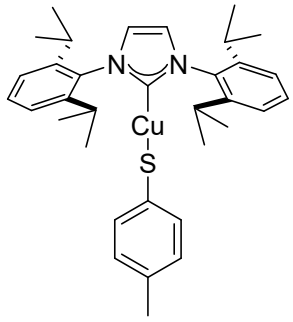

In a 4 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu[(IPr)($OC(CF_3)_3$)] (**1**) (30 mg, 0.044 mmol), EtOH (1 mL) and trifluoromethanesulfonimide (7.9 µL, 0.044 mmol). The mixture was left stirring for 1 hour at 25 °C. Then the solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 95% yield (31 mg). NMR spectra corresponded to the results reported in the literature.[5]

**$^{1}$H NMR** (300 MHz, Benzene-$d_6$) δ 7.22 (t, J = 7.8 Hz, 2H, C$H_{Ar}$), 7.05 (d, J = 7.8 Hz, 4H, C$H_{Ar}$), 6.30 (s, 2H, C$H_{Imid}$), 2.47 (hept, J = 6.7 Hz, 4H, C*H*), 1.33 (d, J = 6.8 Hz, 12H, C$H_3$), 1.03 (d, J = 6.9 Hz, 12H, C$H_3$).

**$^{13}$C NMR** (126 MHz, Benzene-$d_6$) δ 145.62 ($C_{Ar}$), 134.44 ($C_{Ar}$), 131.01 ($CH_{imid}$), 124.47 ($CH_{Ar}$), 123.41 ($CH_{Ar}$), 120 (d, J = 322 Hz, $CF_3$), 29.01 (*C*H), 24.28 (d, $CH_3$).

**$^{19}$F NMR** (471 MHz, Benzene-$d_6$) δ -76.65.

# Synthesis of [Cu(IPr)(SPhMe)] (11)



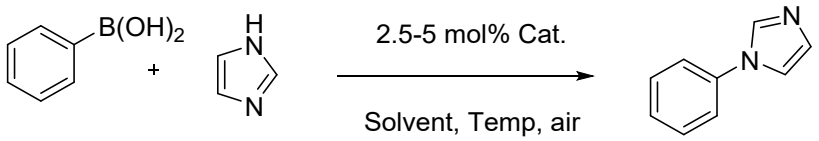

In a 4 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added [Cu[(IPr)($OC(CF_3)_3$)] (30 mg, 0.044 mmol), EtOH (1 mL) and p-thiocresol, (5.3 µL, 0.044 mmol). The mixture was left stirring for 1 hour at 25 °C. Then the solution was subsequently concentrated and pentane (10 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x5 mL) and dried under high vacuum. The final product was obtained as a white solid in 96% yield (24 mg). NMR spectra corresponded to the results reported in the literature. [5]

**$^1$H NMR** (300 MHz, Chloroform-d) δ 7.52 (t, J = 7.8 Hz, 2H, C$H_{Ar}$), 7.31 (d, J = 7.8 Hz, 4H, C$H_{Ar}$), 7.14 (s, 2H, C$H_{imid}$), 6.55 (dd, J = 28.8, 8.0 Hz, 4H, C$H_{cresol}$), 2.61 (hept, J = 6.9 Hz, 4H, C*H*), 2.14 (s, 3H, PhC$H_3$), 1.28 (d, J = 6.9 Hz, 12H, C$H_3$), 1.23 (d, J = 6.9 Hz, 12H, C$H_3$).

**$^{13}$C NMR** (75 MHz, Benzene-$d_6$) δ 182.37 (Cu-*C*), 145.82 ($C_{Ar}$), 142.69 (*C*-S), 133.60 ($C_{Ar}$), 132.48 ($CH_{cresol}$), 130.74 ($CH_{imid}$), 128.61 ($CH_{cresol}$), 125.06 ($CH_{cresol}$), 124.40 ($C_{Ar}$), 122.72 ($C_{Ar}$), 29.02 (*C*H), 25.02 ($CH_3$), 23.81 ($CH_3$), 21.07 ($CH_{3\ cresol}$).

# General procedure for Chan-Evans-Lam catalytic reactions

**Synthesis of N-Phenyl-imidazole (24)**

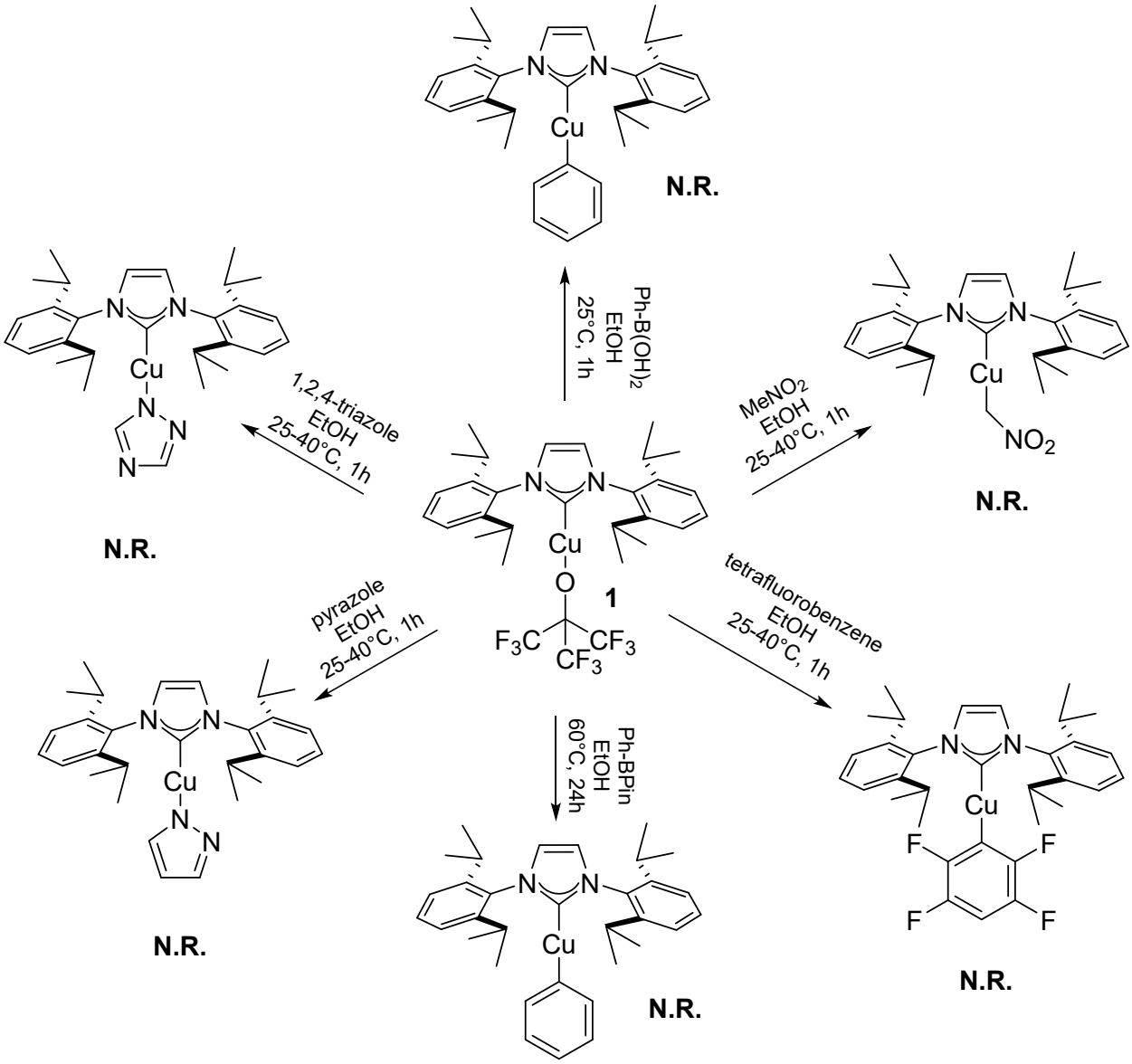



In a 20 mL vial equipped with a magnetic stirring bar and a septum-equipped cap were added phenylboronic acid (60.9 mg, 0.5 mmol, 2eq.), imidazole (17 mg, 0.25 mmol, 1 eq.), base (0.5 mmol, 2 eq.), the solvent (1-3 mL) and [Cu[(IPr)(OC($CF_3$)$_3$)] (**1**) or [Cu[(IPr)(Cl)] as catalyst (0.00625-0.01250 mmol, 2.5-5 mol%). The reaction mixture was allowed to stir at the indicated temperature for the indicated time. After the mixture was allowed to cool to room temperature, the solution was filtered with a syringe microfilter, and the solvent was evaporated under vacuum. The resulting residue was then purified by flash column chromatography on silica-gel using petroleum ether/ethyl acetate in a 1:1 ratio as the eluent to afford corresponding product N-phenyl-imidazole as a light-yellow oil ($R_f$= 0.22). NMR spectra corresponded to the results reported in the literature. [6]

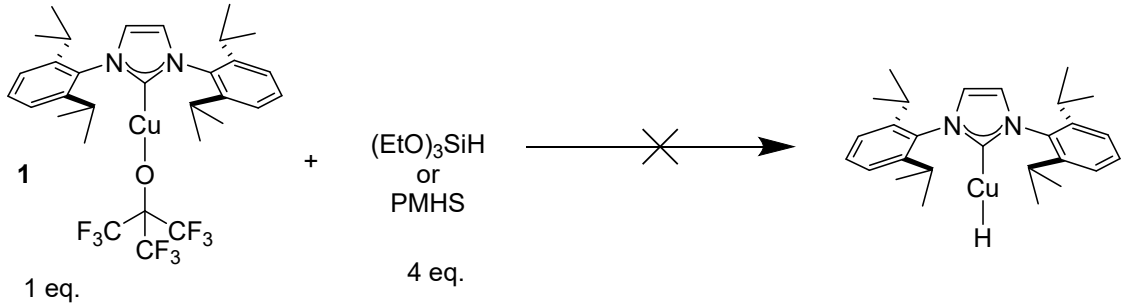
**$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 8.26 (s, 1H, N-CH-N), 7.74 (s, 1H, N-C*H*-CH), 7.65 (d, *J* = 7.4 Hz, 2H, C$H_{Ar}$), 7.51 (t, *J* = 7.4 Hz, 2H, C$H_{Ar}$), 7.35 (t, *J* = 7.4 Hz, 1H, C$H_{Ar}$), 7.12 (s, 1H, N-C*H*-CH).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 136.95 ($CH_{imid}$), 135.54 ($CH_{imid}$), 129.92 ($C_{Ar}$), 129.88 ($CH_{Ar}$), 126.89 ($CH_{Ar}$), 120.35 ($CH_{Ar}$), 118.02 ($CH_{Ar}$).

# Unsuccessful reactivity tests between [Cu(IPr)(OC($CF_3$)$_3$)] (1) and various substrates


Ph-B(OH)2
EtOH
25°C, 1h
N.R.
1,2,4-triazole
EtOH
25-40°C, 1h
N.R.
MeNO2
EtOH
25-40°C, 1h
N.R.
1
pyrazole
EtOH
25-40°C, 1h
N.R.
tetrafluorobenzene
EtOH
25-40°C, 1h
N.R.
Ph-BPin
EtOH
60°C, 24h
N.R.

## Unsuccessful reactions of [Cu(IPr)(OC(CF$_3$)$_3$)] (1) with silanes leading to Cu-H species. [a]




| Entry | Solvent | T (°C) | Time (h) |
|---|---|---|---|
| **1** | Toluene | 25 | 24 |
| **2** | Toluene | 80 | 2 |
| **3** | MeCN | 25 | 24 |
| **4** | MeCN | 70 | 2 |

[a] Reaction conditions: 1 (0.0145 mmol, 1 eq.) PMHS or $(EtO)_3SiH$ (0.0580 mmmol, 4 eq.), under air.

## Single-Crystal X-ray Diffraction Analysis

Complex **1** was crystallized by vapor diffusion of pentane into a solution of 3 mg of **1** in diethyl ether at 4-5 °C as colorless blocks. Complex **3** was crystallized by vapor diffusion of hexane into a solution of 3 mg of **3** in dichloromethane at 4-5 °C as yellowish blocks. Complex **5** was crystallized by vapor diffusion of pentane into a solution of 3 mg of **5** in tetrahydrofuran at 4-5 °C as colorless blocks. Compound **21** was crystallized by vapor diffusion of pentane into a solution of 6 mg of **21** in dichloromethane at 4-5 ° C as colorless plates. Crystals were covered in silicon oil and mounted on LithoLoops at ambient conditions. The diffraction data were collected at 100 K with a Rigaku Oxford Diffraction SuperNova diffractometer, using Cu Kα radiation ($\lambda = 1.54184$ Å). The intensity data were collected and processed using CrysAlis PRO software.[7] Data solution and model refinement were performed using Olex2-1.5 and all software packages within.[8] The structures were solved by direct methods with the program SHELXT 2018/2 [9] and refined by full-matrix least-squares method on $F^2$ with SHELXL 2018/3.[10] The carbon-bound hydrogen atoms were refined as riding on their carriers and their displacement parameters were set equal to 1.5 Ueq(C) for the methyl groups and 1.2 Ueq(C) for the remaining H atoms. CCDC 2392994-2392997 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

**[Cu(IPr)(OC(CF$_3$)$_3$)] (1)**

CCDC deposition number 2392994

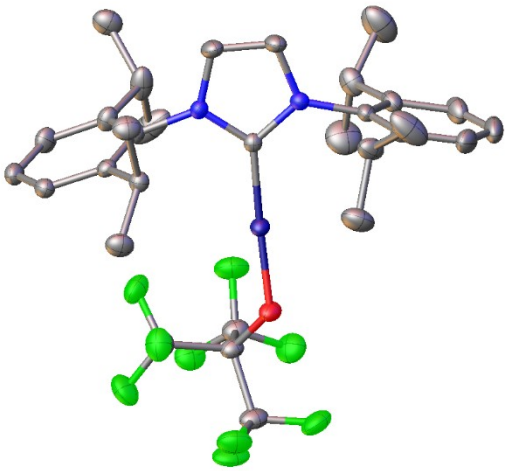


**Figure S1.** Molecular structure of (1). Thermal displacement ellipsoids shown at the 50% probability level. H-atoms are omitted for clarity. There are two molecules in the asymmetric unit. Selected bond distances (Å) and angles (°): Cu1-O1.8343(12); Cu1-C1 1.8532(16); Cu2-O2 1.8353(14); Cu2-C32 1.8618(17); N3-C32-N4 103.9(1); N1-C1-N2 103.8(1).

| **Table 1 Crystal data and structure refinement for 1.** | |
|---|---|
| Empirical formula | $C_{31}H_{36}CuF_9N_2O$ |
| Formula weight | 687.17 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 24.8398(6) |
| b/Å | 12.8584(2) |
| c/Å | 20.9327(4) |
| α/° | 90 |
| β/° | 106.149(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 6422.1(2) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.421 |
| μ/mm$^{-1}$ | 1.671 |
| F(000) | 2832.0 |
| Crystal size/mm$^3$ | 0.24 × 0.17 × 0.09 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 7.41 to 147.684 |
| Index ranges | $-29 \leq h \leq 30$, $-15 \leq k \leq 14$, $-25 \leq l \leq 25$ |
| Reflections collected | 61519 |

| | |
|---|---|
| Independent reflections | 12798 [$R_{int}$ = 0.0381, $R_{sigma}$ = 0.0254] |
| Data/restraints/parameters | 12798/20/823 |
| Goodness-of-fit on $F^2$ | 1.032 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0373, $wR_2$ = 0.0976 |
| Final R indexes [all data] | $R_1$ = 0.0459, $wR_2$ = 0.1034 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.74/-0.35 |

**[Cu[($IPr^{OMe}$)($OC(CF_3)_3$)] (3)**

CCDC deposition number 2392995

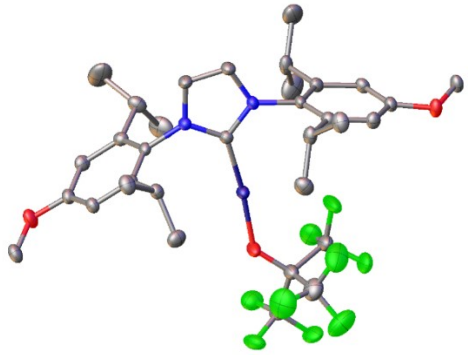


**Figure S2.** Molecular structure of (3). Thermal displacement ellipsoids shown at the 50% probability level. H-atoms are omitted for clarity. There are two molecules in the asymmetric unit. Selected bond distances (Å) and angles (°): Cu1-O1 1.8302(16); Cu1-C1 1.858(2); Cu2-O2 1.8403(18); Cu2-C2 1.861(2); N3-C2-N4 104.0(2); N1-C1-N2 103.8(2).

**Table 2 Crystal data and structure refinement for 3.**

| | |
|---|---|
| Empirical formula | $C_{36}H_{47}CuF_9N_2O_3$ |
| Formula weight | 790.29 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 20.4331(4) |
| b/Å | 19.1734(3) |
| c/Å | 21.8553(4) |
| α/° | 90 |
| β/° | 114.525(2) |
| γ/° | 90 |
| Volume/$Å^3$ | 7789.8(3) |
| Z | 8 |
| $\rho_{calc}g/cm^3$ | 1.348 |

| | |
|---|---|
| μ/mm$^{-1}$ | 1.487 |
| F(000) | 3288.0 |
| Crystal size/mm$^3$ | 0.28 × 0.16 × 0.08 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.404 to 147.644 |
| Index ranges | -19 ≤ h ≤ 25, -23 ≤ k ≤ 23, -26 ≤ l ≤ 26 |
| Reflections collected | 75383 |
| Independent reflections | 15547 [$R_{int}$ = 0.0450, $R_{sigma}$ = 0.0318] |
| Data/restraints/parameters | 15547/284/1001 |
| Goodness-of-fit on F$^2$ | 1.023 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0497, $wR_2$ = 0.1279 |
| Final R indexes [all data] | $R_1$ = 0.0646, $wR_2$ = 0.1388 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.00/-0.71 |

**[Cu[(IPr*)(OC(CF$_3$)$_3$)] (5)**

CCDC deposition number 2392996

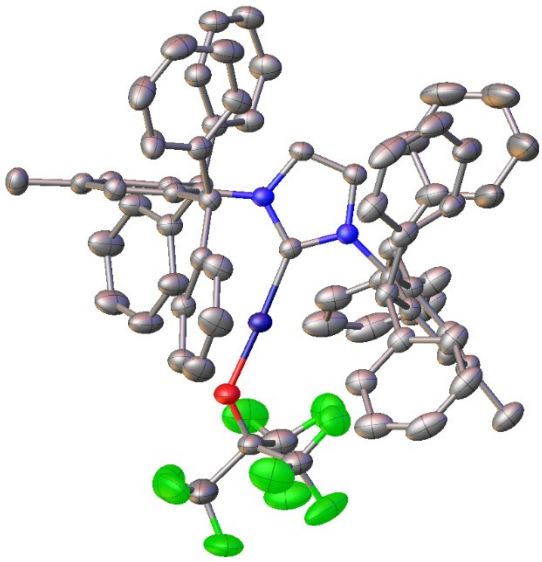


**Figure S3.** Molecular structure of (5). Thermal displacement ellipsoids shown at the 50% probability level. H-atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Cu1-O1 1.8369(18); Cu1-C1 1.861(2); N1-C1-N2 103.8(2).

| **Table 3 Crystal data and structure refinement for 5.** | |
|---|---|
| Empirical formula | $C_{73}H_{56}CuF_9N_2O$ |
| Formula weight | 1211.73 |
| Temperature/K | 293(2) |

| | |
|---|---|
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 13.5204(2) |
| b/Å | 20.7179(3) |
| c/Å | 21.7926(2) |
| α/° | 90 |
| β/° | 106.1960(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 5862.15(14) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.373 |
| μ/mm$^{-1}$ | 1.174 |
| F(000) | 2504.0 |
| Crystal size/mm$^3$ | 0.17 × 0.15 × 0.11 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.002 to 147.556 |
| Index ranges | -16 ≤ h ≤ 14, -25 ≤ k ≤ 25, -27 ≤ l ≤ 26 |
| Reflections collected | 56104 |
| Independent reflections | 11646 [$R_{int}$ = 0.0392, $R_{sigma}$ = 0.0293] |
| Data/restraints/parameters | 11646/0/777 |
| Goodness-of-fit on $F^2$ | 1.015 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0519, $wR_2$ = 0.1377 |
| Final R indexes [all data] | $R_1$ = 0.0690, $wR_2$ = 0.1513 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.88/-0.46 |

**[Cu[(IPr)(chlorzoxazonyl)] (21)**

CCDC deposition number 2392997

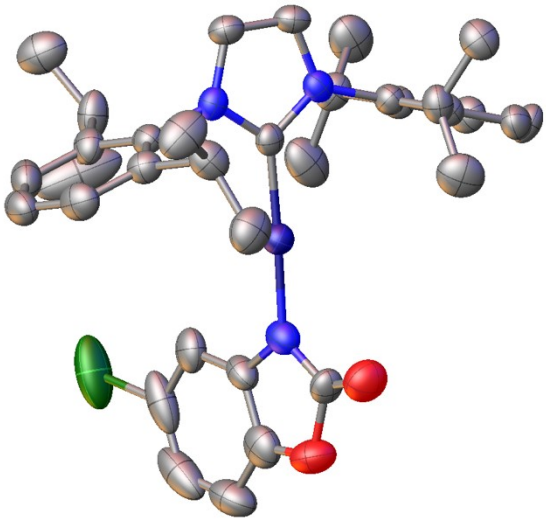


**Figure S4.** Molecular structure of (21). Therma displacement ellipsoids shown at the 50% probability level. H-atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Cu1-N3 1.888(6); Cu1-C1 1.875(6); N1-C1-N2 103.4(4).

| **Table 4 Crystal data and structure refinement for 21.** | |
|---|---|
| Empirical formula | $C_{136}H_{156}Cl_4Cu_4N_{12}O_8$ |
| Formula weight | 2482.68 |
| Temperature/K | 293(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 10.8667(5) |
| b/Å | 19.1255(7) |
| c/Å | 16.0322(7) |
| α/° | 90 |
| β/° | 107.662(5) |
| γ/° | 90 |
| Volume/Å$^3$ | 3174.9(2) |
| Z | 1 |
| $\rho_{calc}$g/cm$^3$ | 1.298 |
| μ/mm$^{-1}$ | 2.006 |
| F(000) | 1304.0 |
| Crystal size/mm$^3$ | 0.23 × 0.2 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 7.406 to 133.194 |
| Index ranges | $-12 \leq h \leq 12$, $-22 \leq k \leq 20$, $-19 \leq l \leq 19$ |
| Reflections collected | 28433 |
| Independent reflections | 5591 [$R_{int}$ = 0.0774, $R_{sigma}$ = 0.0527] |
| Data/restraints/parameters | 5591/0/378 |
| Goodness-of-fit on $F^2$ | 1.017 |

| | |
|---|---|
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0904, $wR_2$ = 0.1705 |
| Final R indexes [all data] | $R_1$ = 0.1130, $wR_2$ = 0.1808 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.23/-0.88 |

# List of metals bearing Nonafluoro-tert-butyl alkoxide as a ligand in complexes or salts

| | |
|---|---|
| **s-block** | **Li** [11], **Na** [12], **K** [13], **Mg** [14], **Ca** [15], **Sr** [15], **Ba** [15] |
| **p-block** | **Sn** [16], **Tl** [17] |
| **d-block** | **Sc** [18], **V** [19], **Fe** [20], **Co** [13], **Ni** [21], **Zn** [22], **Nb** [23] |
| **f-block** | **Ce** [24], **Nd** [24], **Eu** [12], **Dy** [25], **U** [26] |

Mo, W, Pd, Cu and Al has been already cited in the manuscript.

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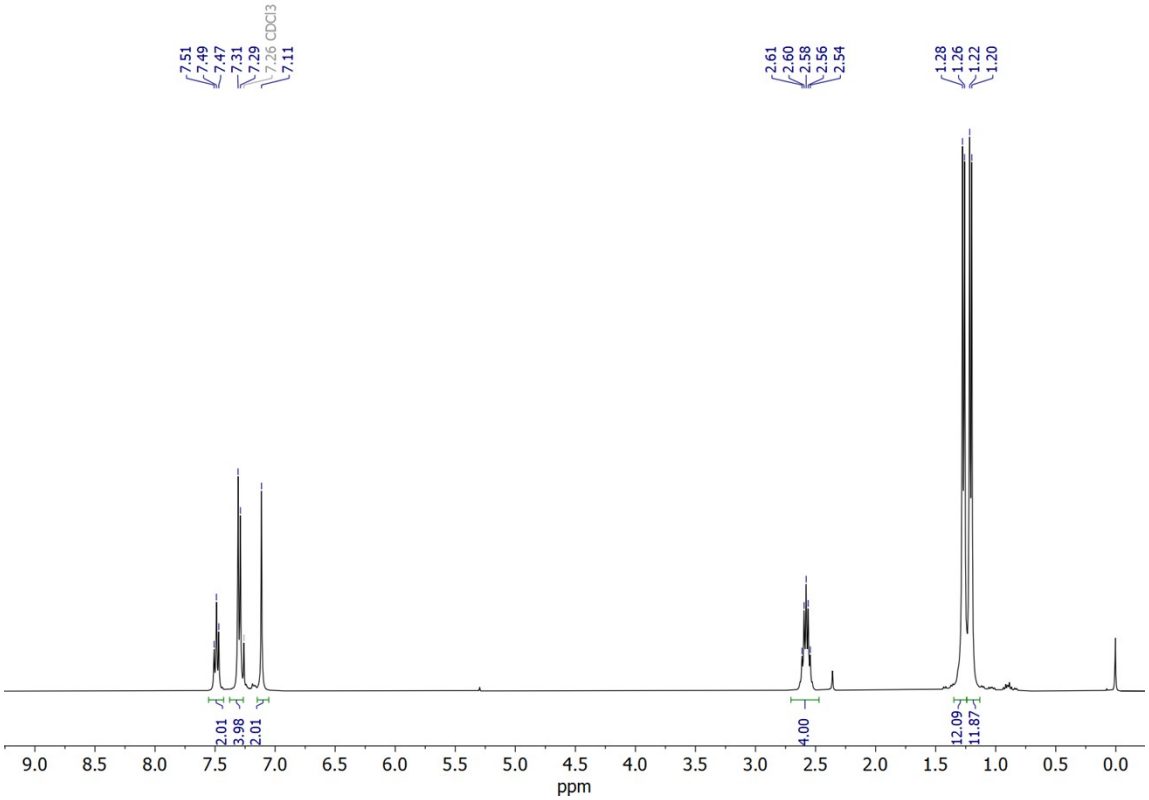
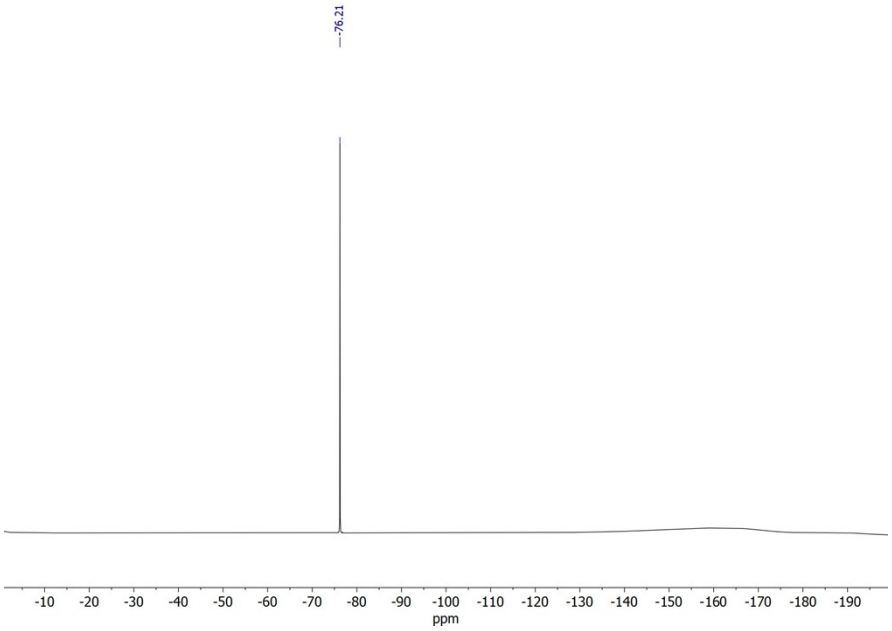
# NMR Spectra

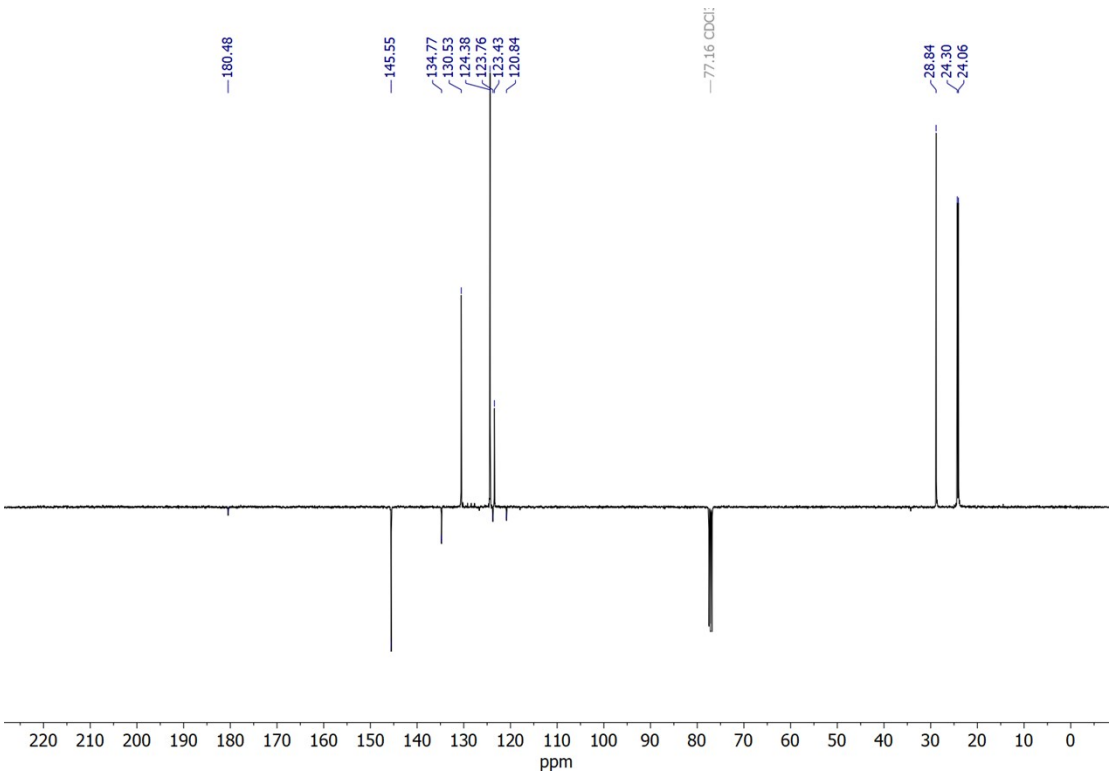
**[Cu(IPr)(OC(CF$_3$)$_3$)] (1) $^1$H NMR** (400 MHz, Chloroform-d)



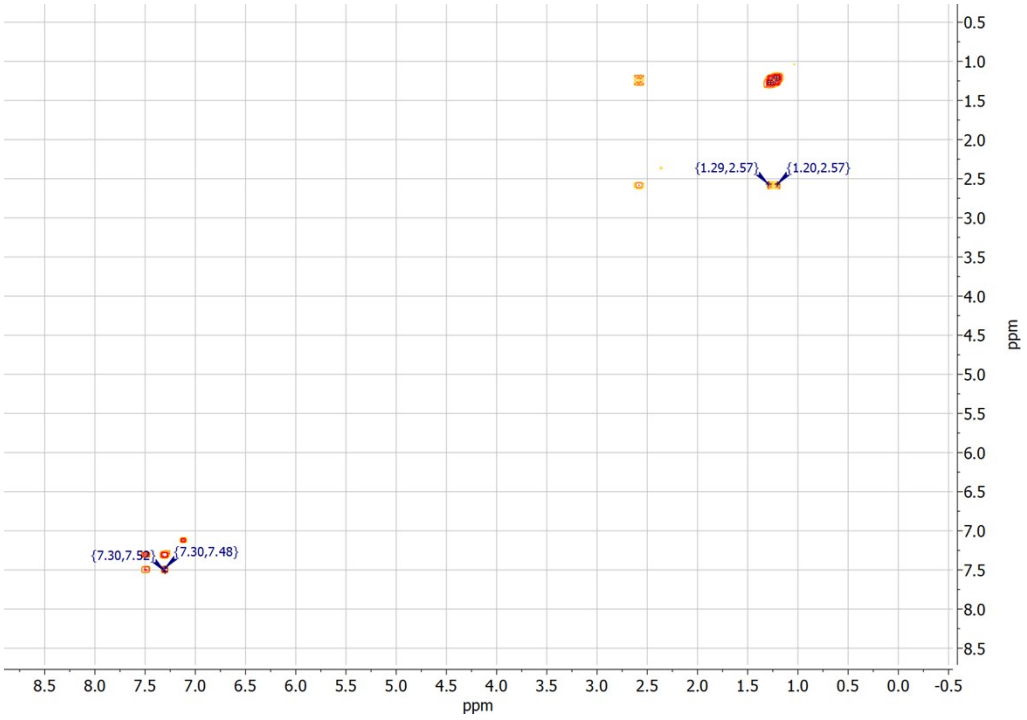

**[Cu(IPr)(OC(CF$_3$)$_3$)] (1) $^{19}$F NMR** (377 MHz, Chloroform-d)



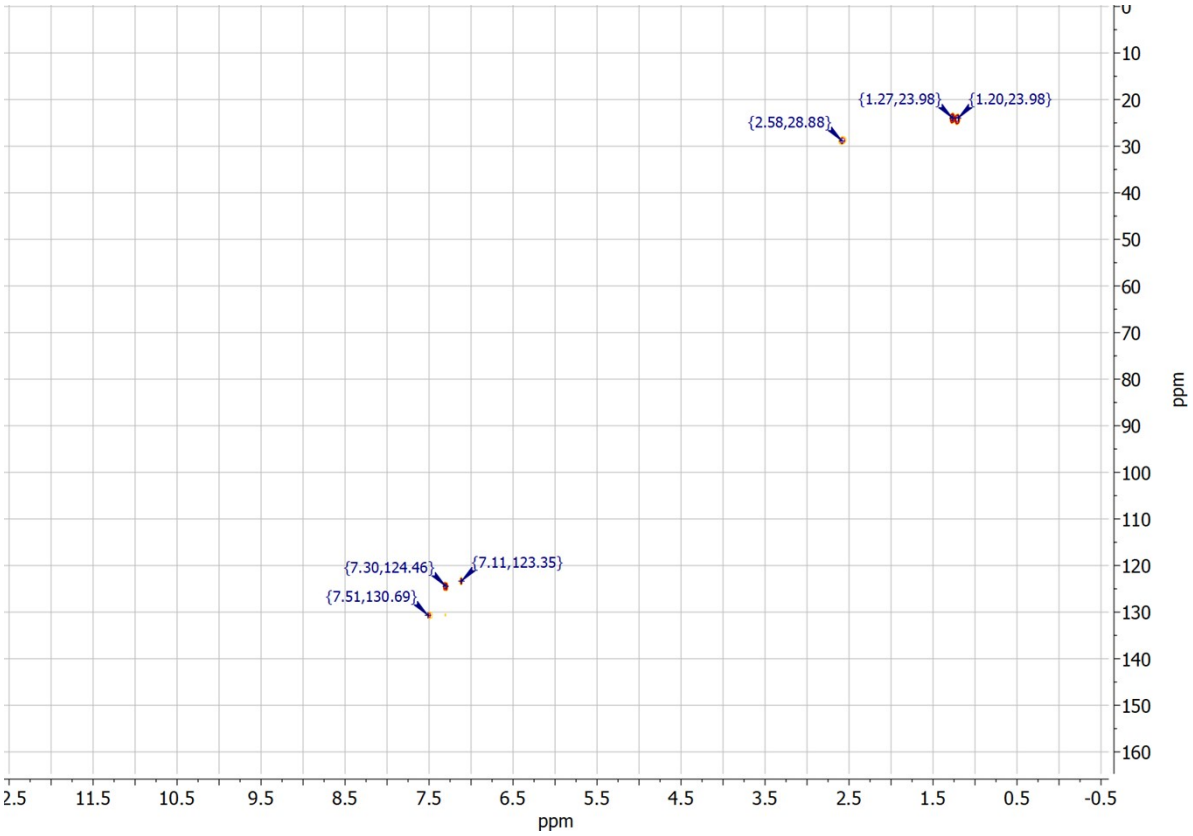

**[Cu(IPr)(OC(CF$_3$)$_3$)] (1) $^{13}$C NMR** (101 MHz, Chloroform-d)



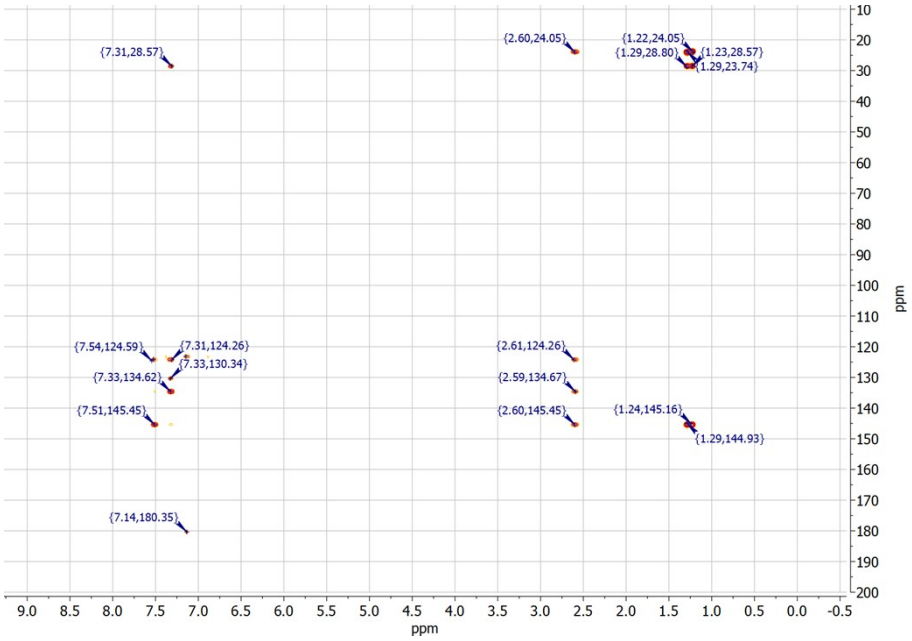

**[Cu(IPr)(OC(CF$_3$)$_3$)] (1) 2D COSY**



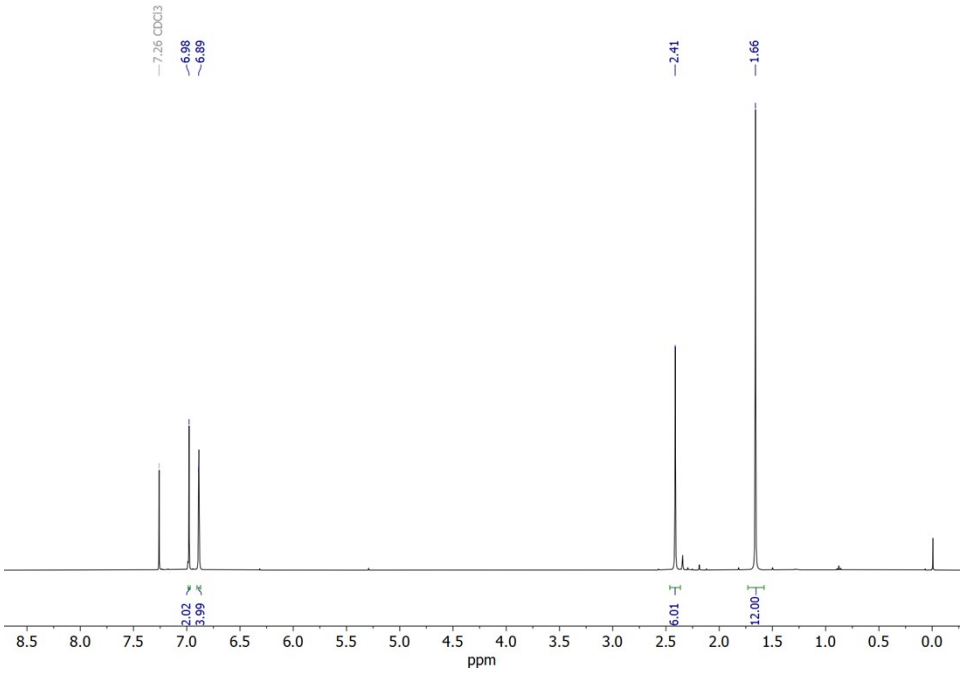

**[Cu(IPr)(OC(CF$_3$)$_3$)] (1) 2D HSQC**



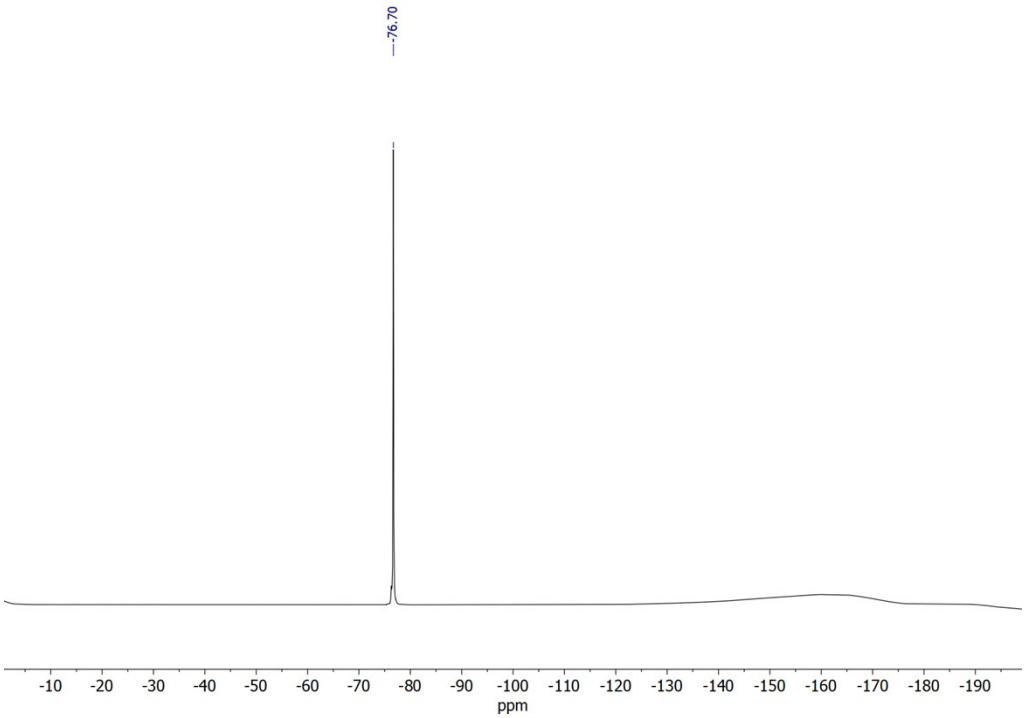

**[Cu(IPr)(OC(CF$_3$)$_3$)] (1) 2D HMBC**



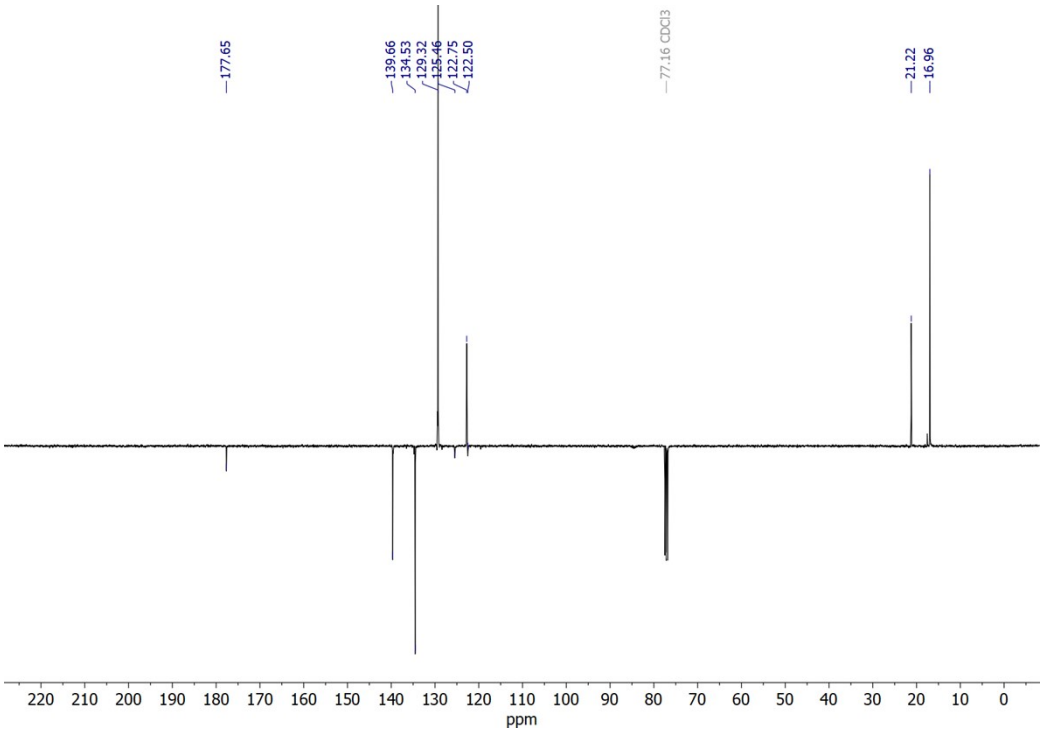

**[Cu[(IMes)(OC(CF$_3$)$_3$)] (2) $^1$H NMR** (400 MHz, Chloroform-d)



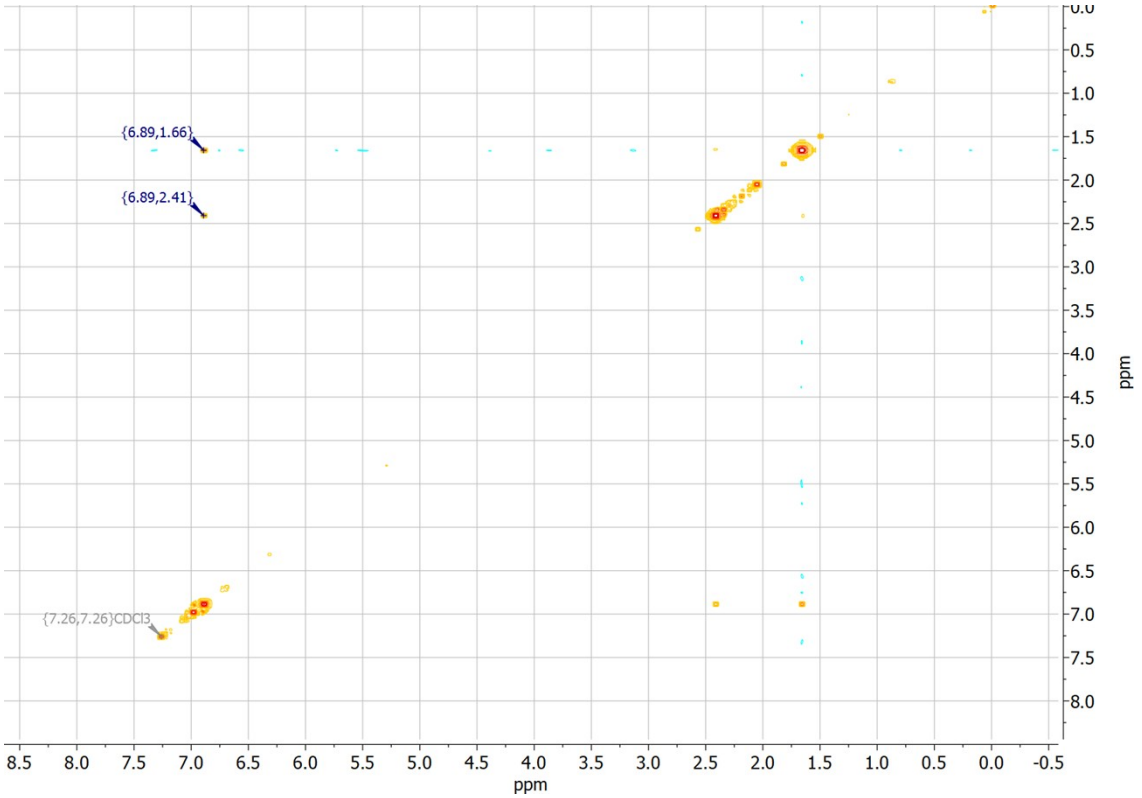

**[Cu[(IMes)(OC(CF$_3$)$_3$)] (2) $^{19}$F NMR** (377 MHz, Chloroform-d)



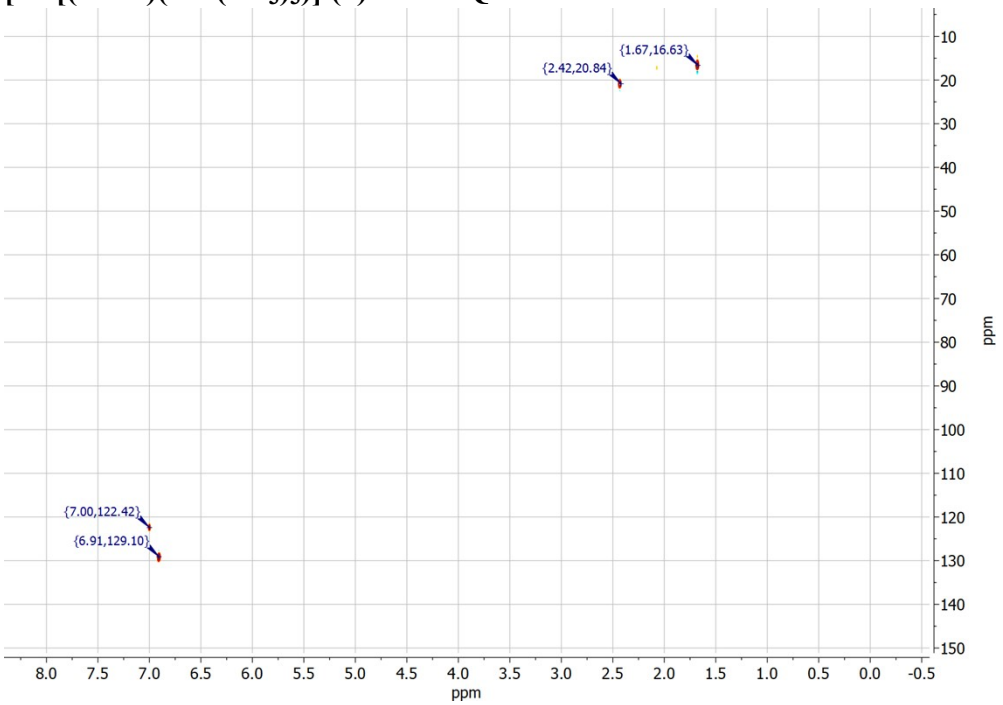

**[Cu[(IMes)(OC(CF$_3$)$_3$)] (2) $^{13}$C NMR** (101 MHz, Chloroform-d)



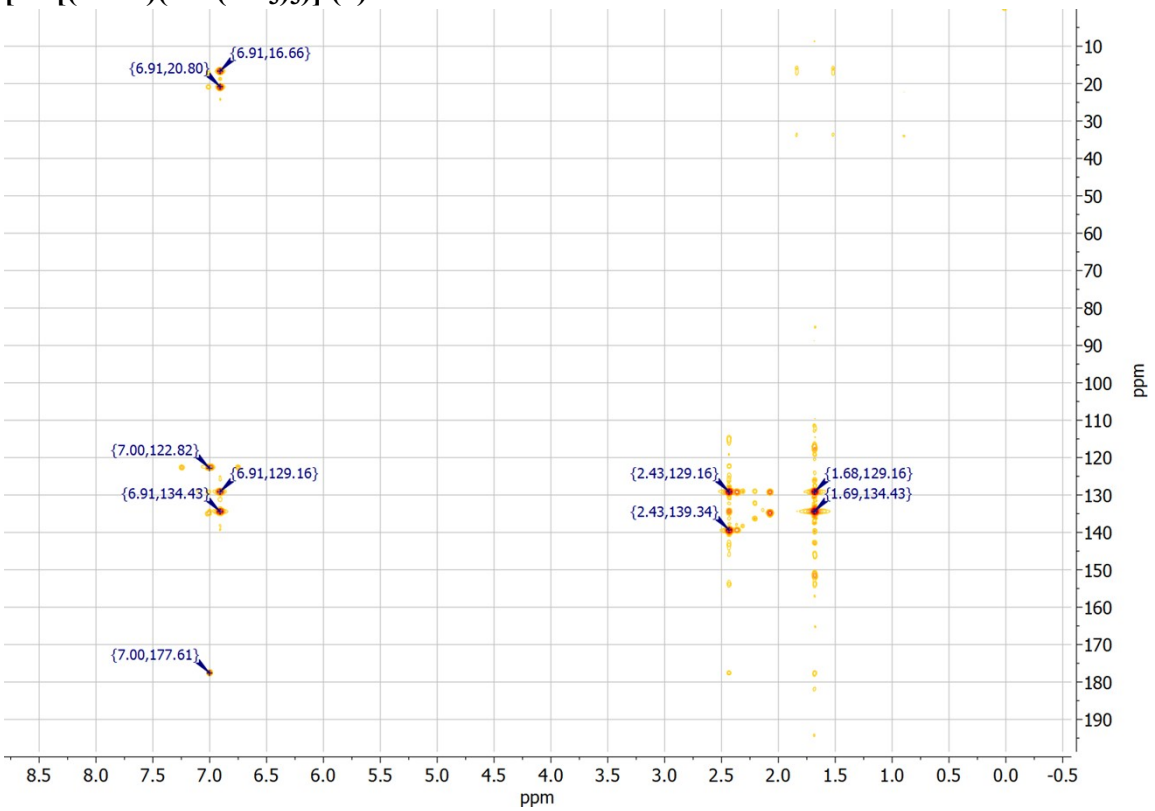

## [Cu[(IMes)(OC(CF$_3$)$_3$)] (2) 2D COSY



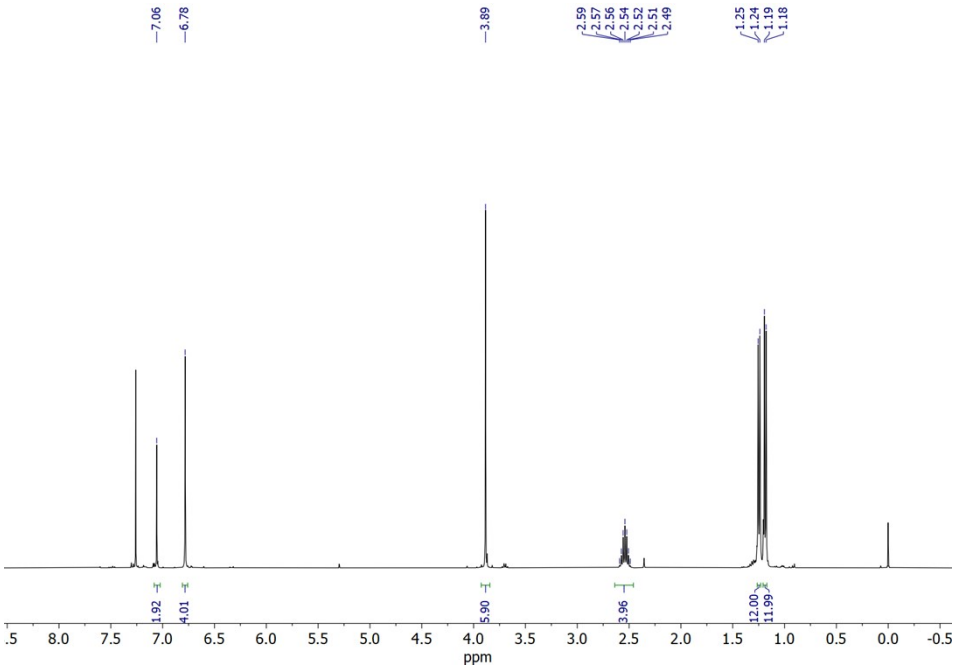
**[Cu[(IMes)(OC(CF$_3$)$_3$)] (2) 2D HSQC**



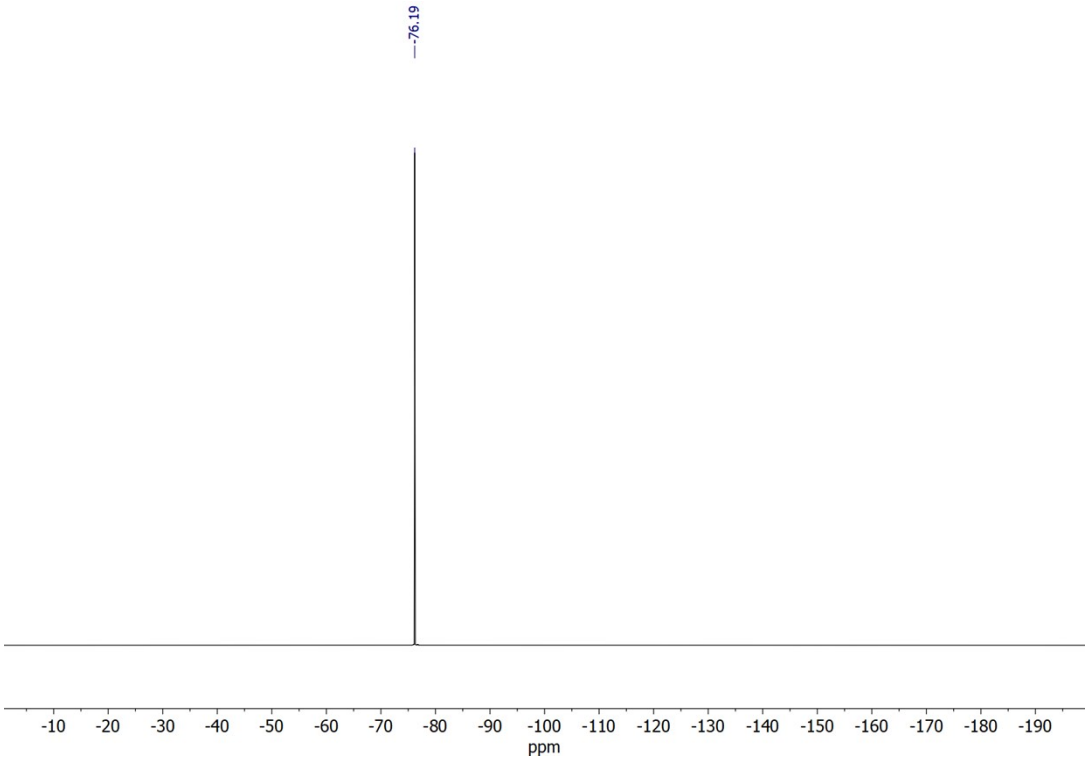

**[Cu[(IMes)(OC(CF$_3$)$_3$)] (2) 2D HMBC**



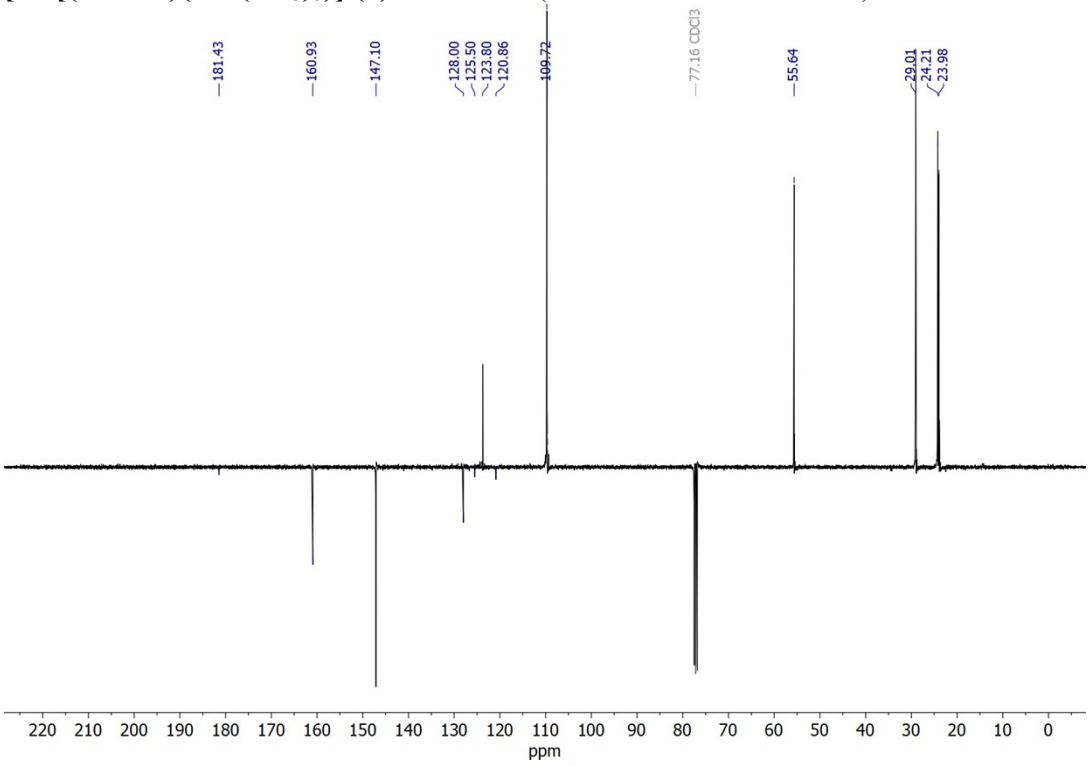
**[Cu[(IPr$^{OMe}$)(OC(CF$_3$)$_3$)] (3) $^1$H NMR** (400 MHz, Chloroform-d)



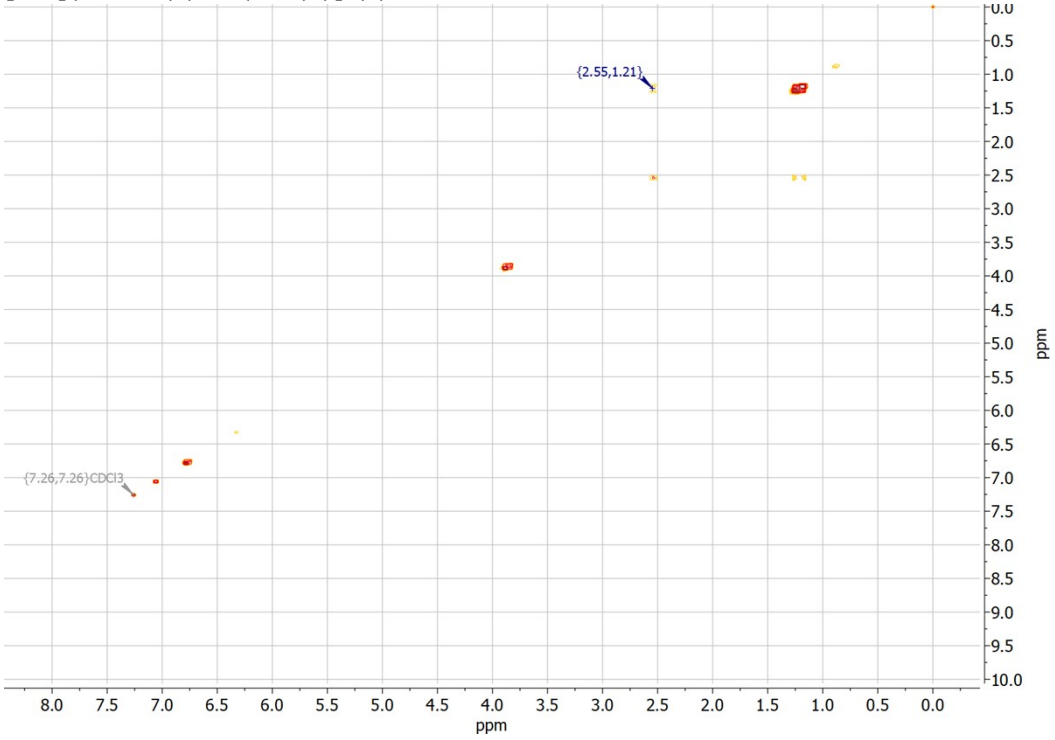

**[Cu[(IPr$^{OMe}$)(OC(CF$_3$)$_3$)] (3) $^{19}$F NMR** (377 MHz, Chloroform-d)



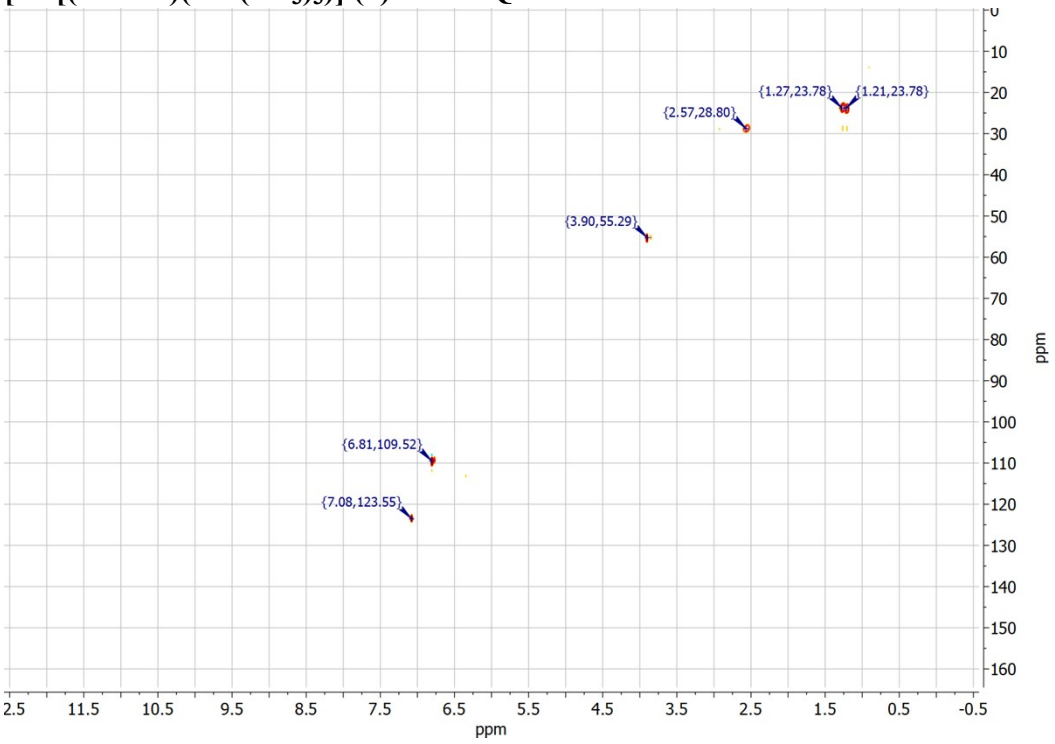
**[Cu[(IPr$^{OMe}$)(OC(CF$_3$)$_3$)] (3) $^{13}$C NMR** (101 MHz, Chloroform-d)



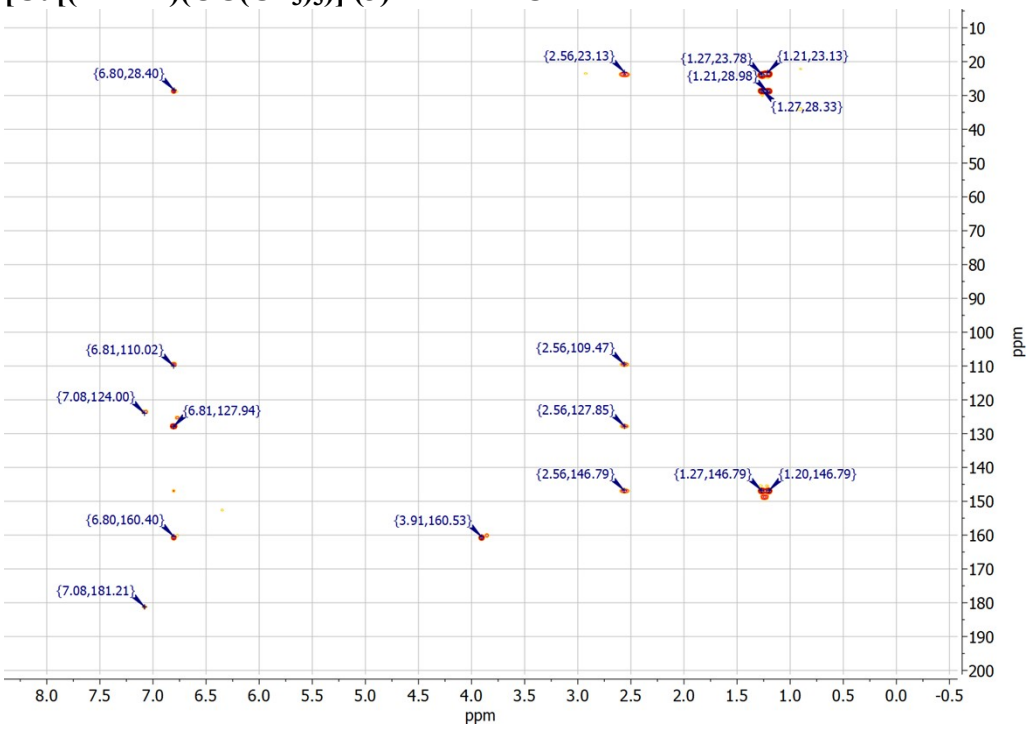

**[Cu[(IPr$^{OMe}$)(OC(CF$_3$)$_3$)] (3) 2D COSY**



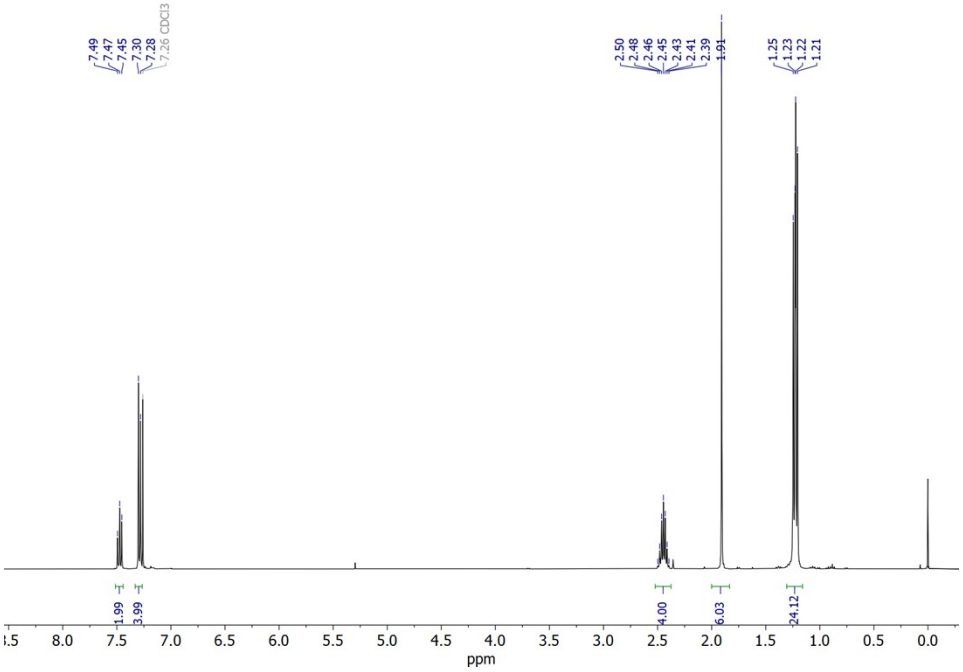
## [Cu[(IPr$^{OMe}$)(OC(CF$_3$)$_3$)] (3) 2D HSQC



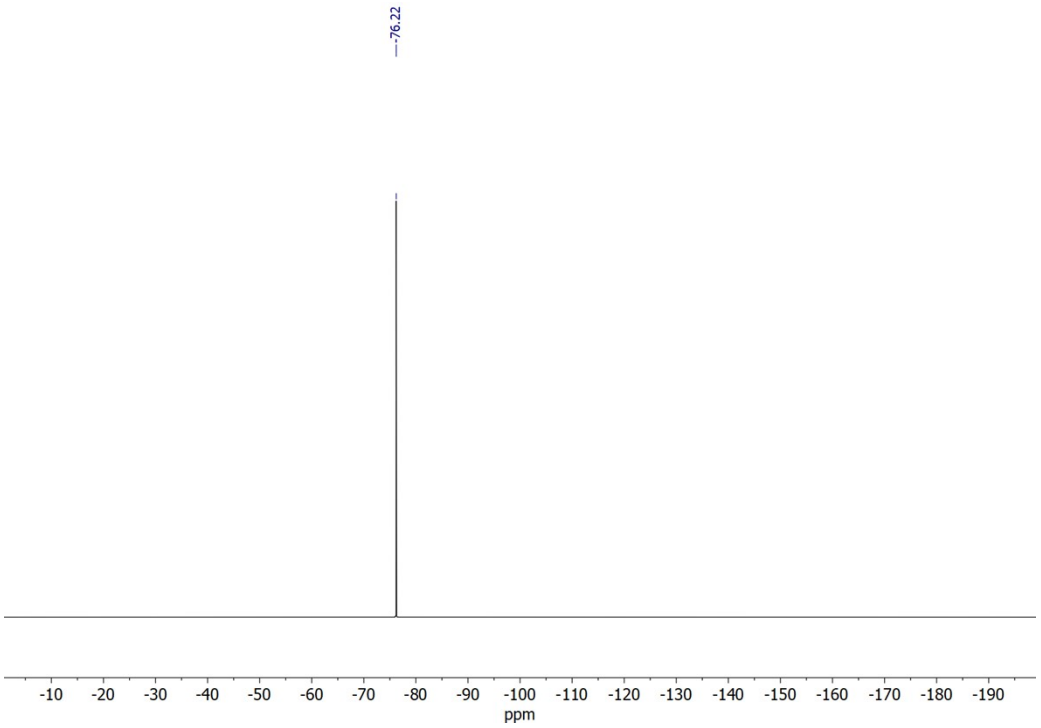

## [Cu[(IPr$^{OMe}$)(OC(CF$_3$)$_3$)] (3) 2D HMBC



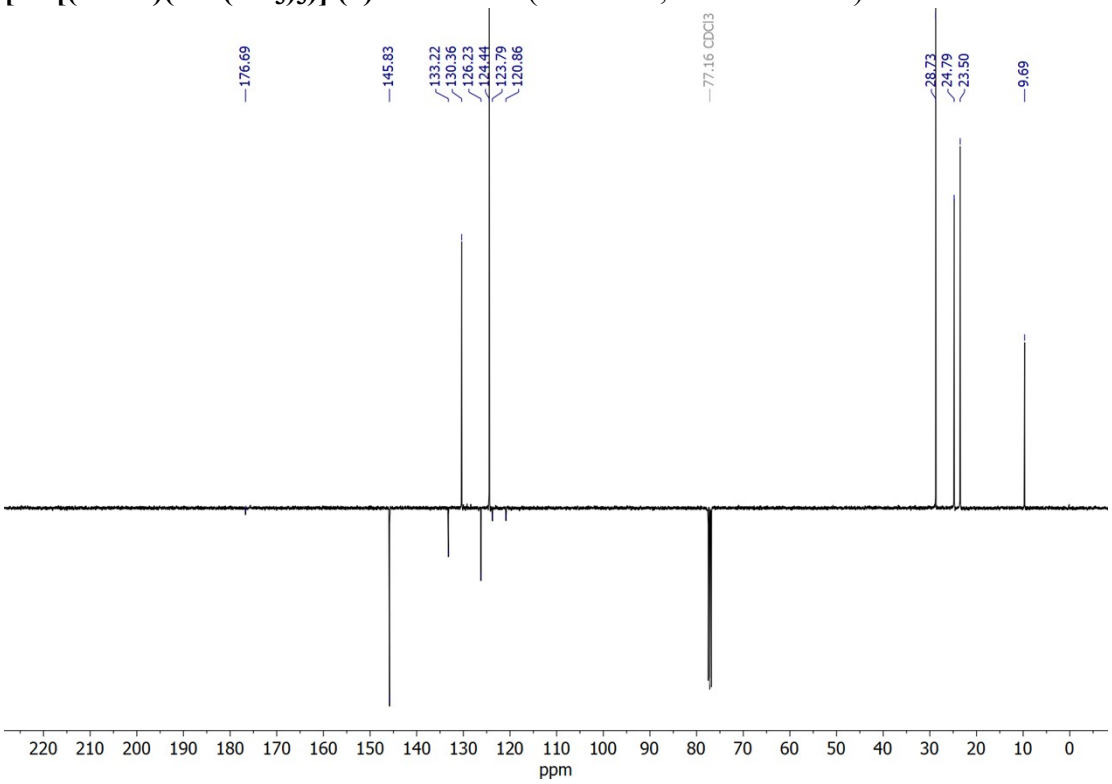
**[Cu[(IPr$^{Me}$)(OC(CF$_3$)$_3$)] (4) $^1$H NMR** (400 MHz, Chloroform-d)



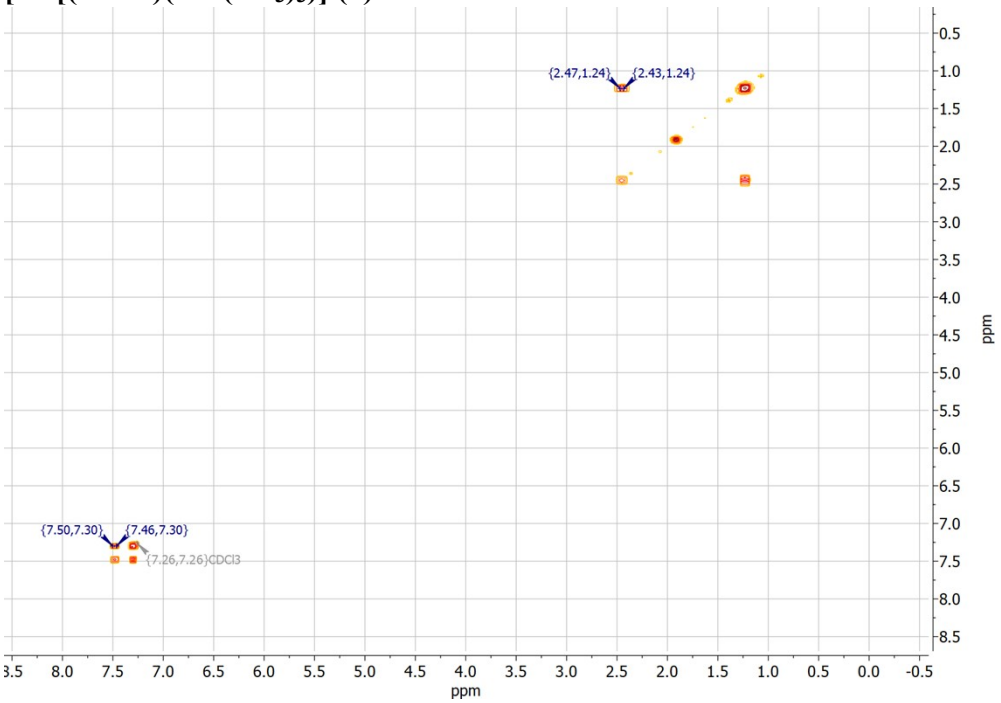

**[Cu[(IPr$^{Me}$)(OC(CF$_3$)$_3$)] (4) $^{19}$F NMR** (377 MHz, Chloroform-d)



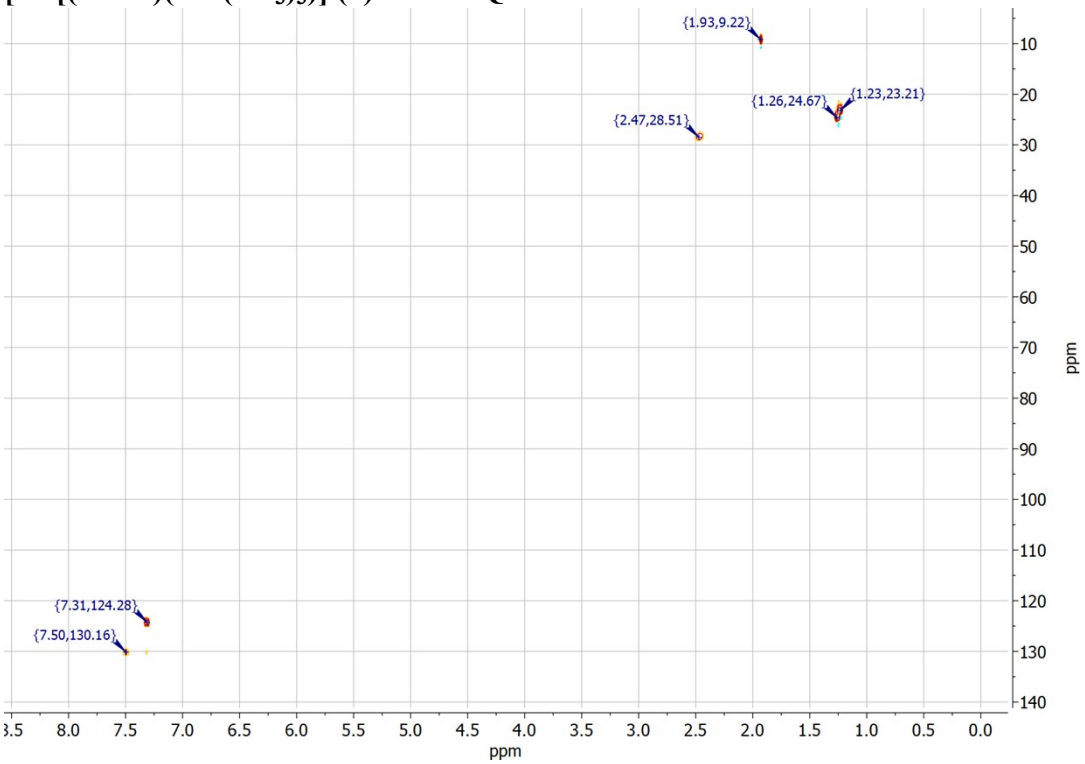
**[Cu[(IPr$^{Me}$)(OC(CF$_3$)$_3$)] (4) $^{13}$C NMR** (101 MHz, Chloroform-d)



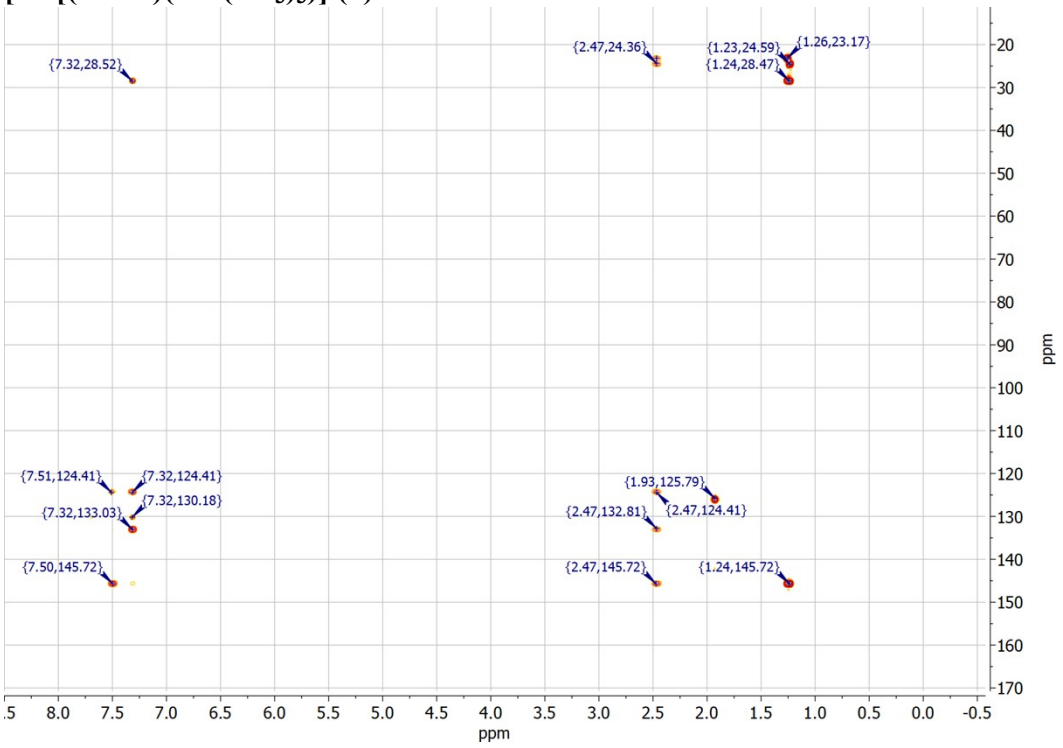

**[Cu[(IPr$^{Me}$)(OC(CF$_3$)$_3$)] (4) 2D COSY**



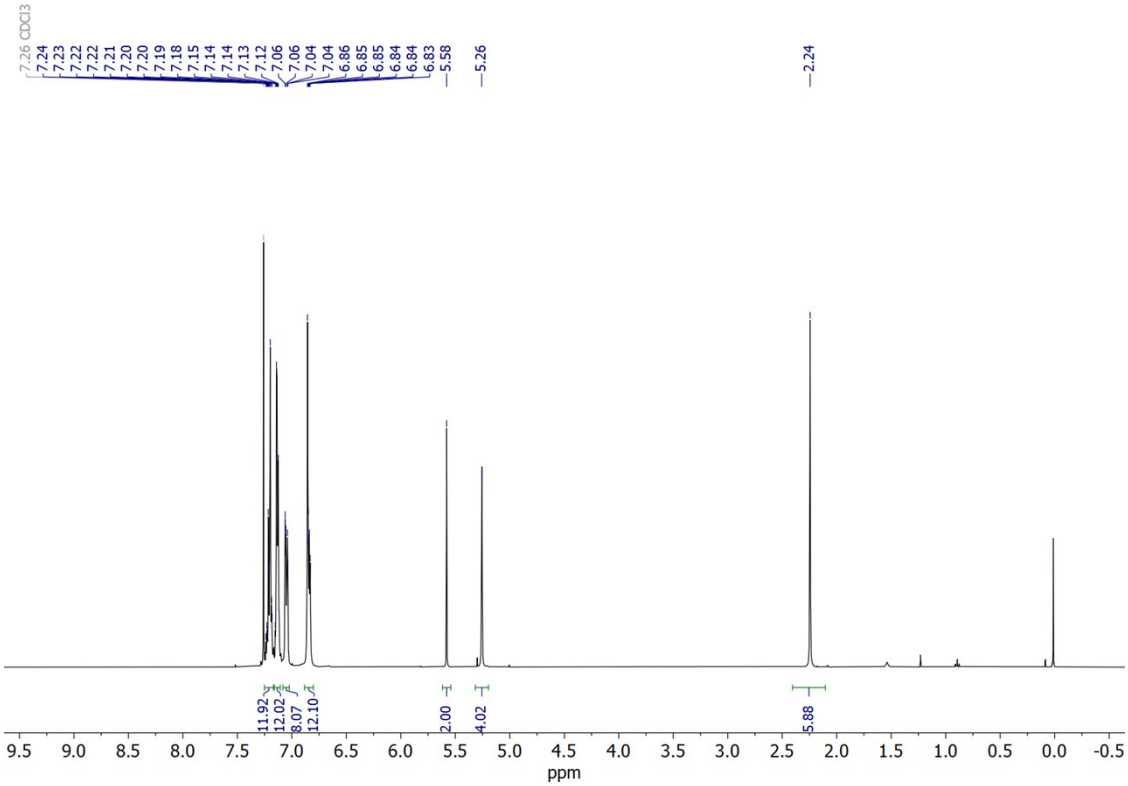
**[Cu[(IPr$^{Me}$)(OC(CF$_3$)$_3$)] (4) 2D HSQC**



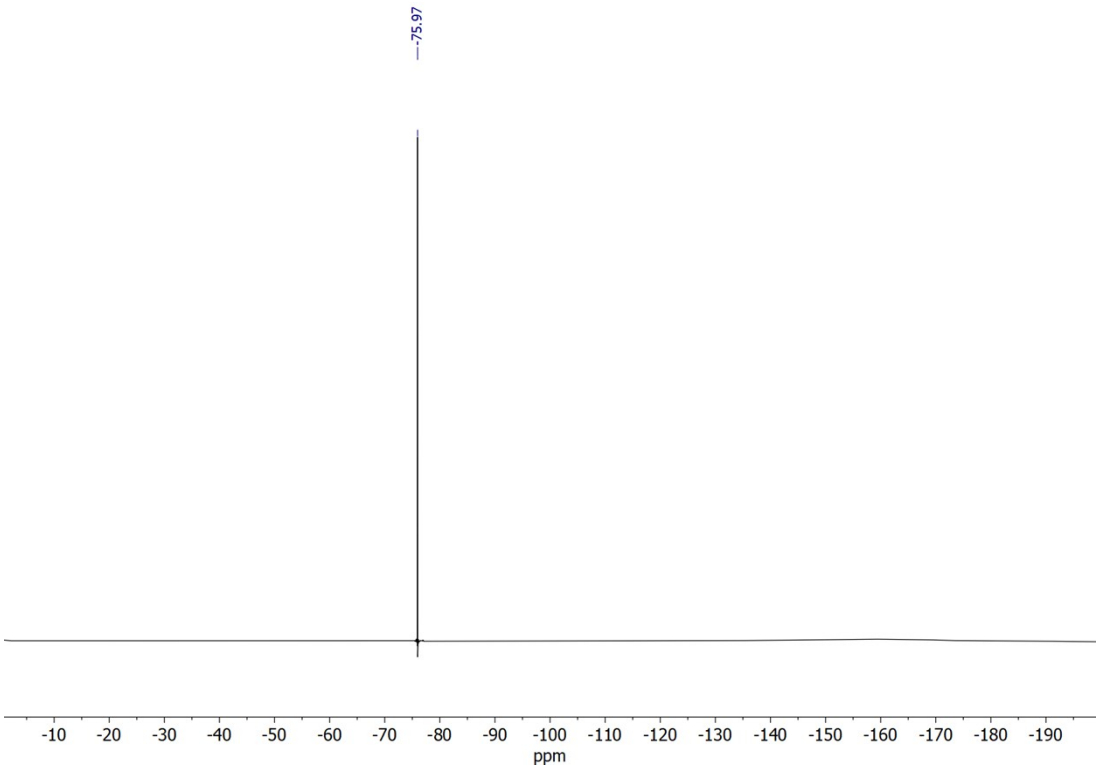

**[Cu[(IPr$^{Me}$)(OC(CF$_3$)$_3$)] (4) 2D HMBC**



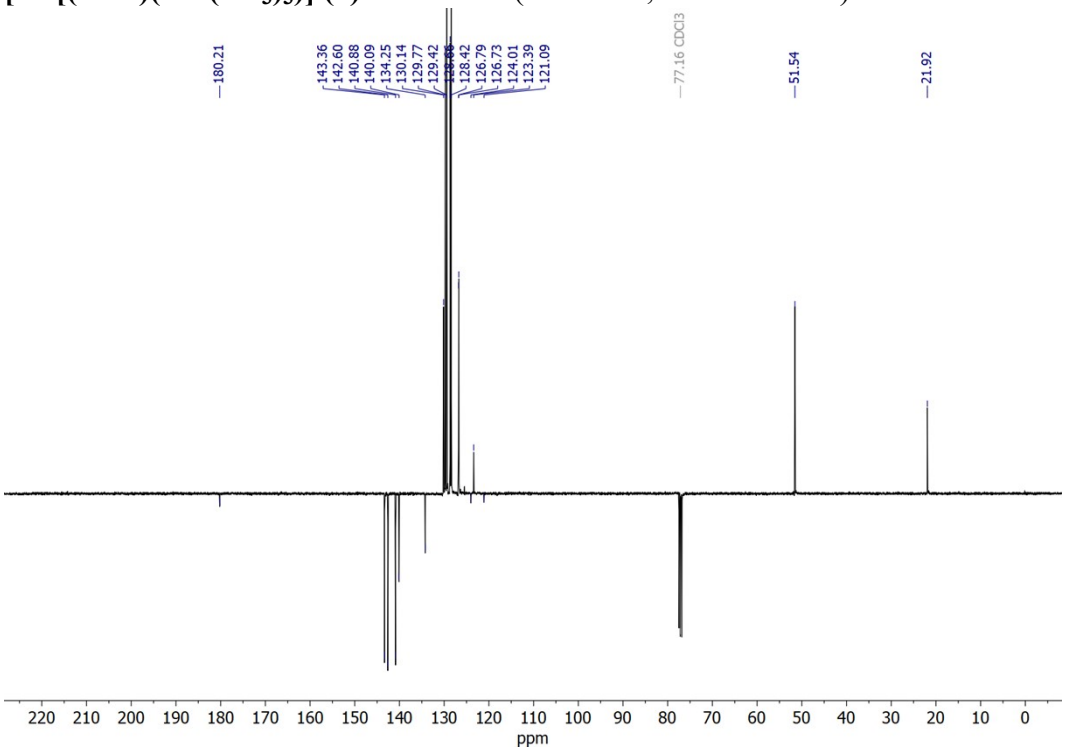
**[Cu[(IPr*)(OC(CF$_3$)$_3$)] (5) $^1$H NMR** (400 MHz, Chloroform-d )



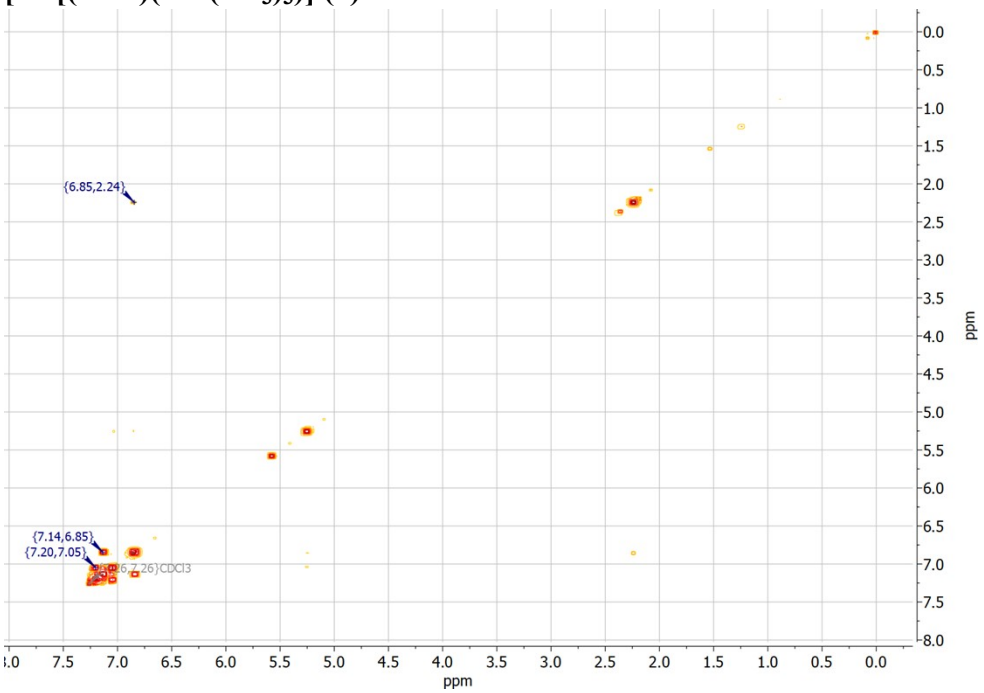

**[Cu[(IPr*)(OC(CF$_3$)$_3$)] (5) $^{19}$F NMR** (377 MHz, Chloroform-d)



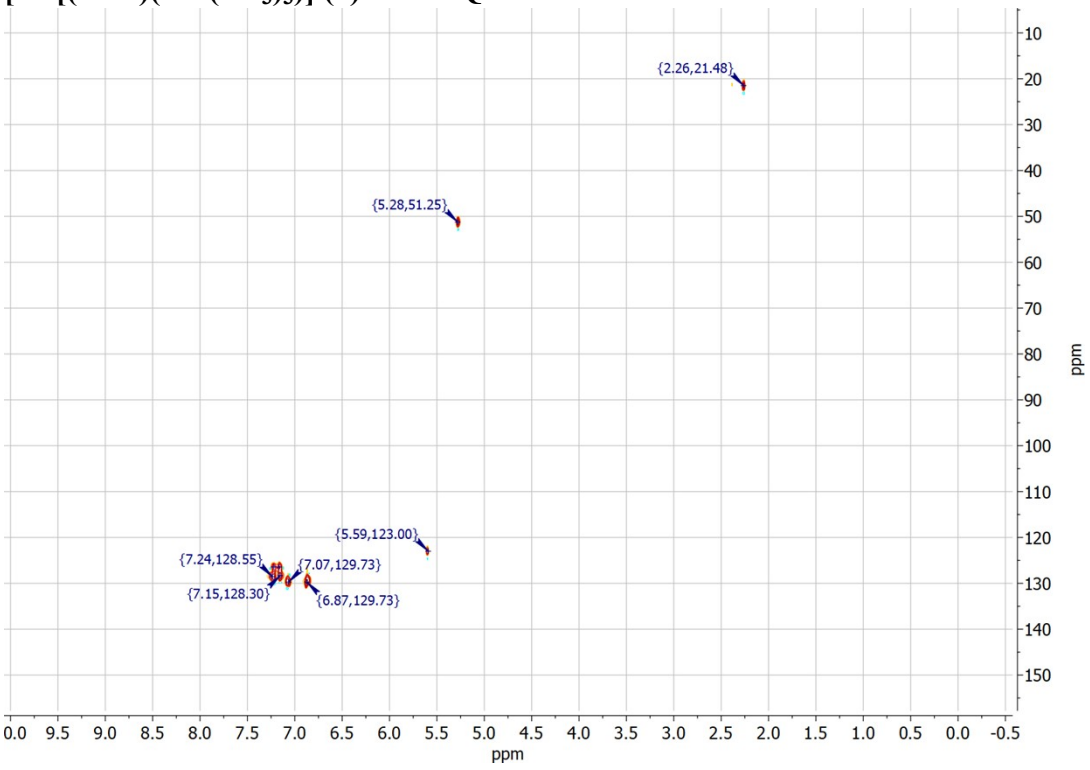
**[Cu[(IPr*)(OC(CF$_3$)$_3$)] (5) $^{13}$C NMR** (101 MHz, Chloroform-d)



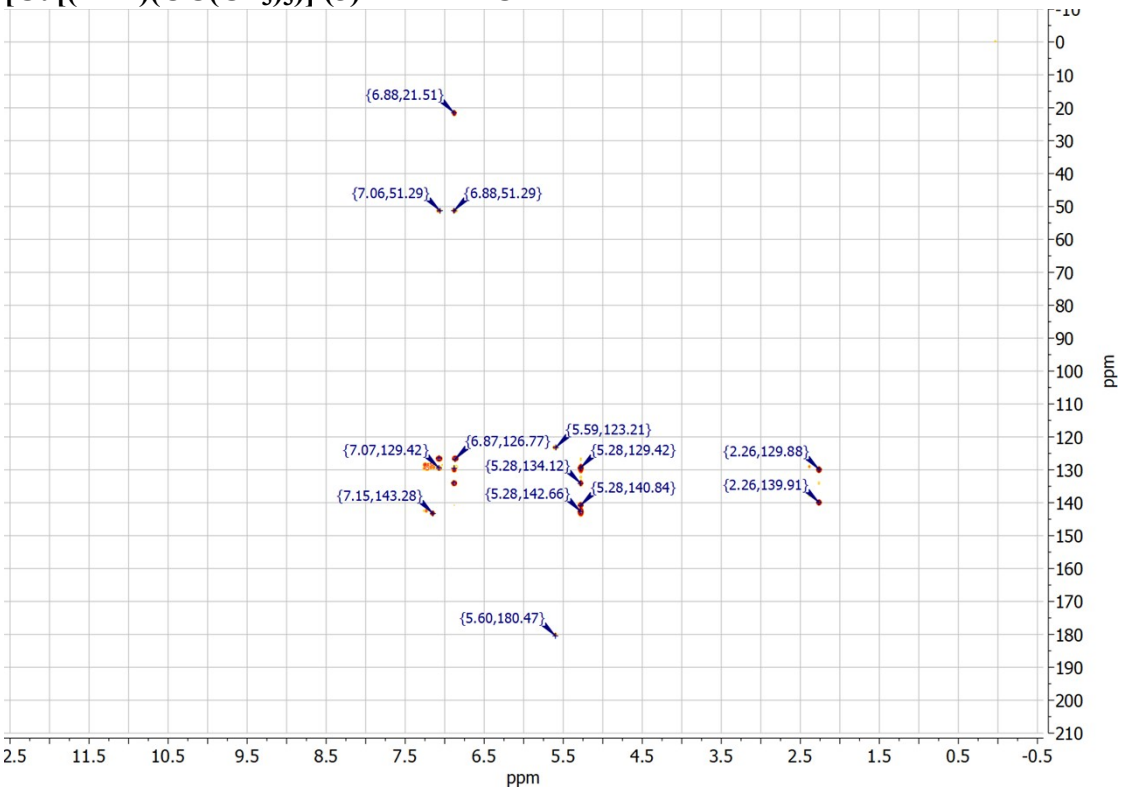

**[Cu[(IPr*)(OC(CF$_3$)$_3$)] (5) 2D COSY**



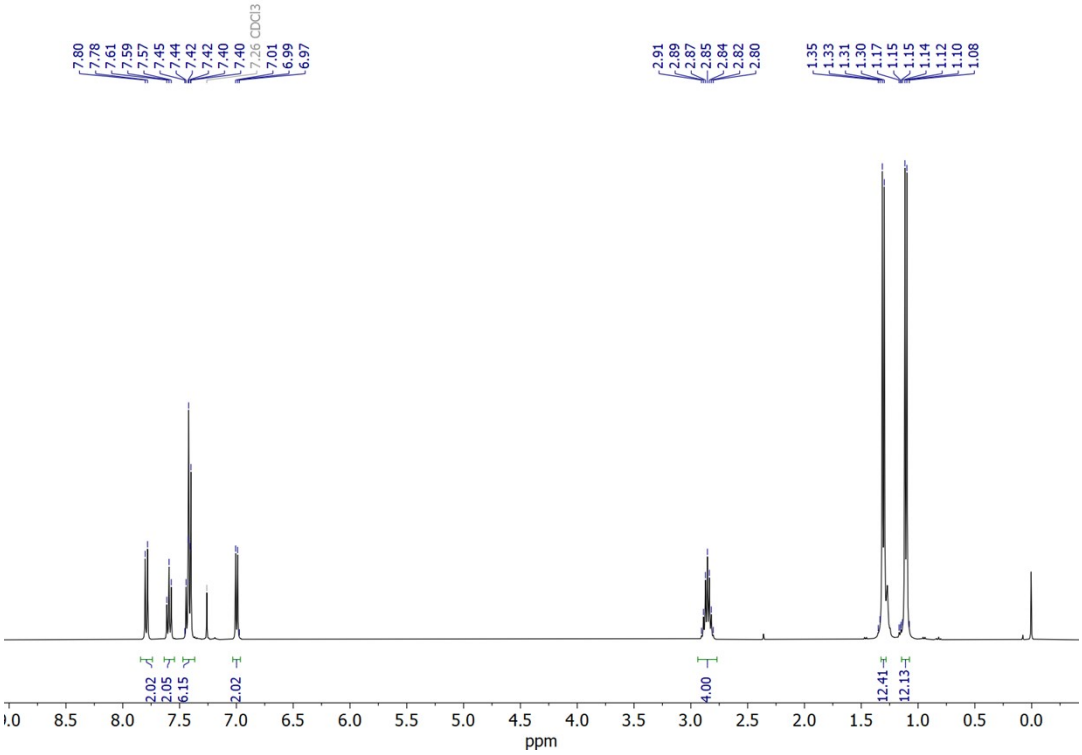
**[Cu[(IPr*)(OC(CF$_3$)$_3$)] (5) 2D HSQC**



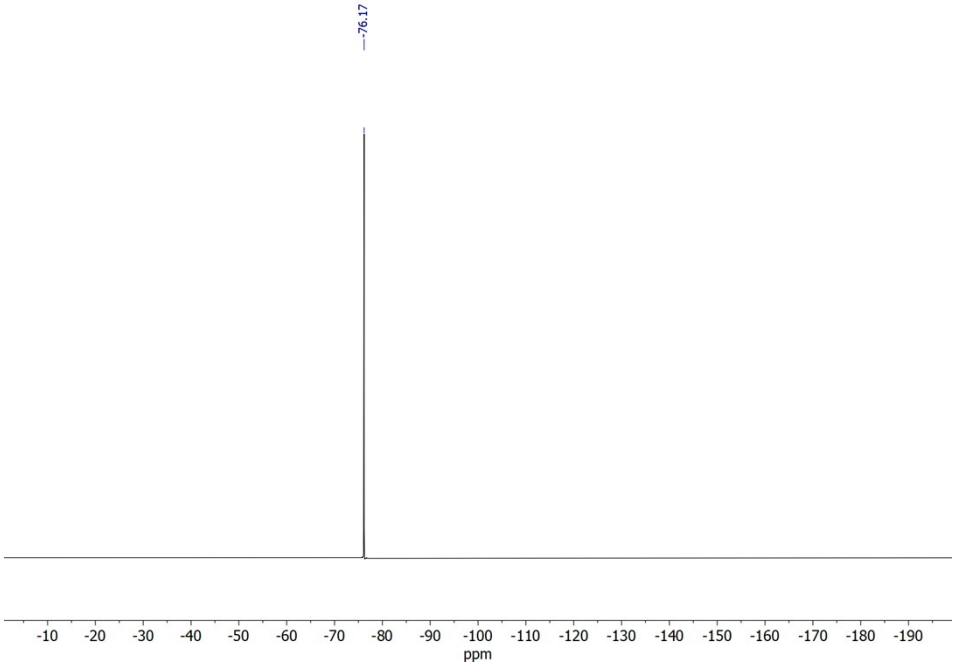

**[Cu[(IPr*)(OC(CF$_3$)$_3$)] (5) 2D HMBC**



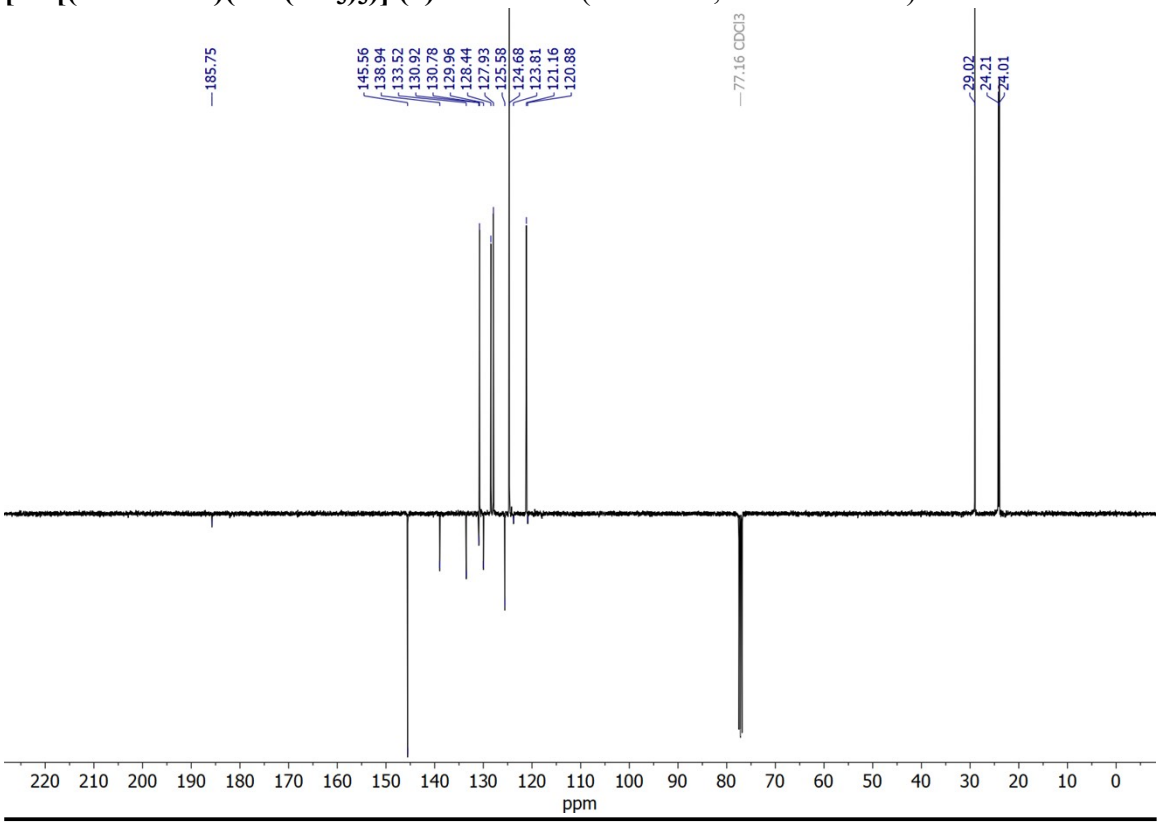
**[Cu[(BIAN-IPr)(OC($CF_3$)$_3$)] (6) $^1$H NMR** (400 MHz, Chloroform-d)



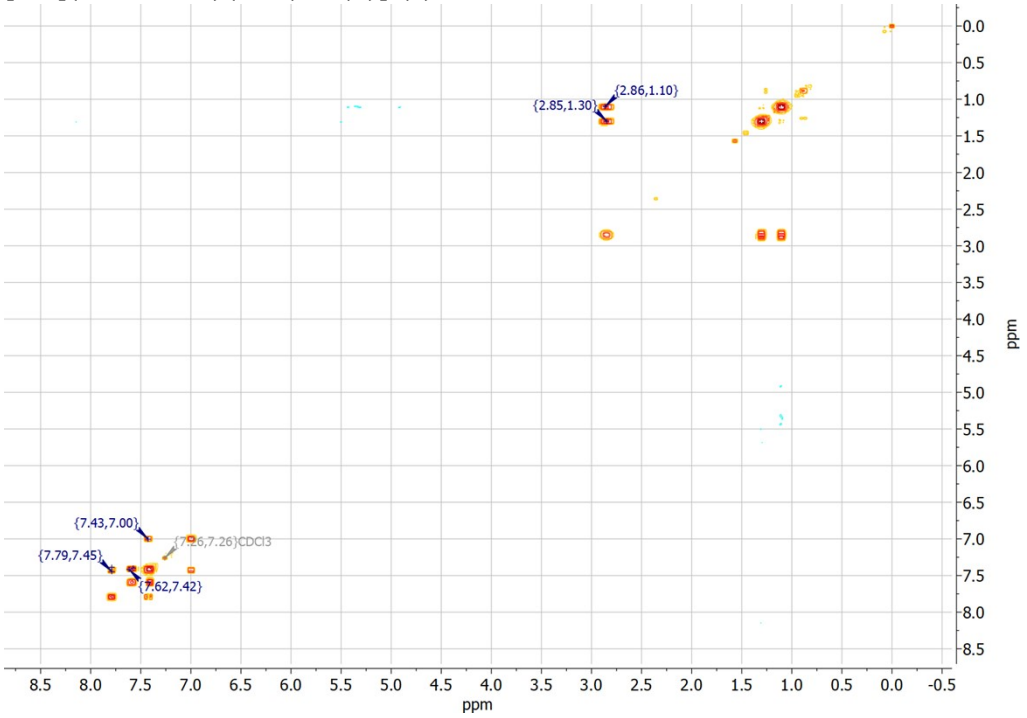

**[Cu[(BIAN-IPr)(OC($CF_3$)$_3$)] (6) $^{19}$F NMR** (377 MHz, Chloroform-d)



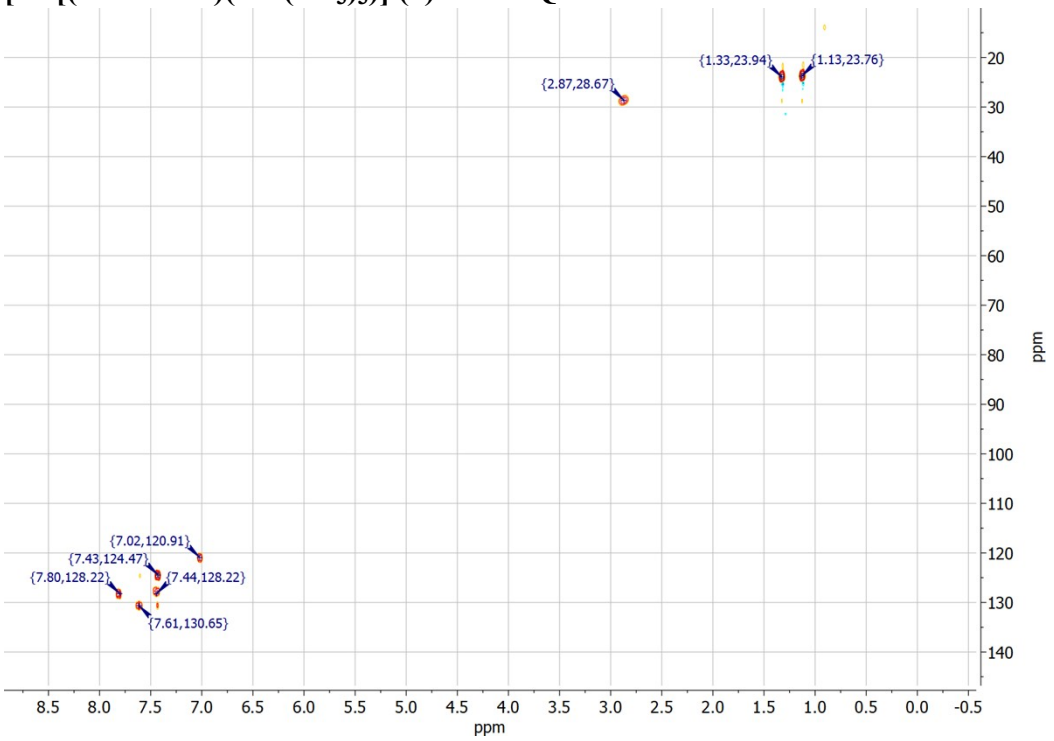
**[Cu[(BIAN-IPr)(OC(CF$_3$)$_3$)] (6) $^{13}$C NMR** (101 MHz, Chloroform-d)



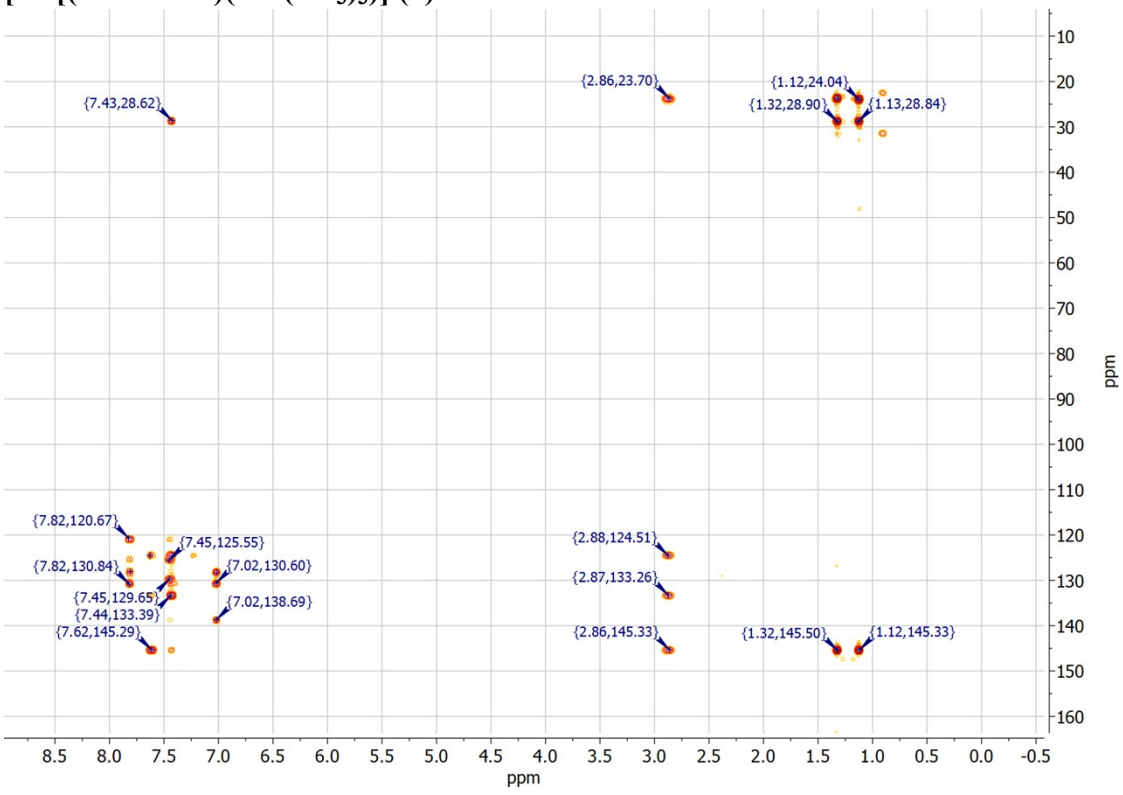

**[Cu[(BIAN-IPr)(OC(CF$_3$)$_3$)] (6) 2D COSY**



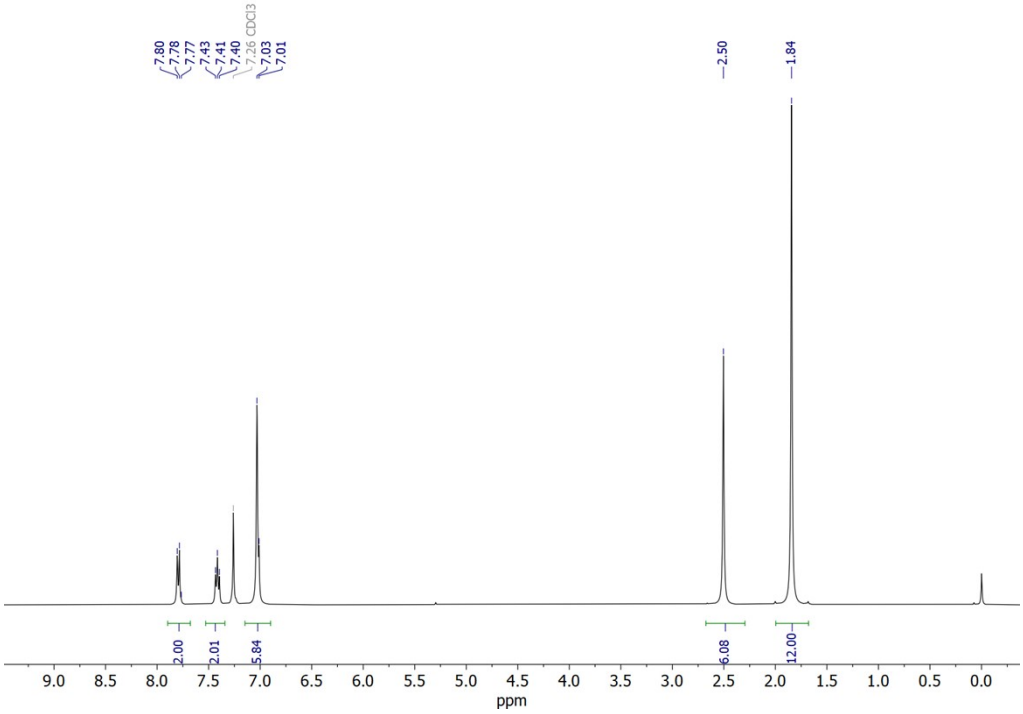
## [Cu[(BIAN-IPr)(OC(CF$_3$)$_3$)] (6) 2D HSQC



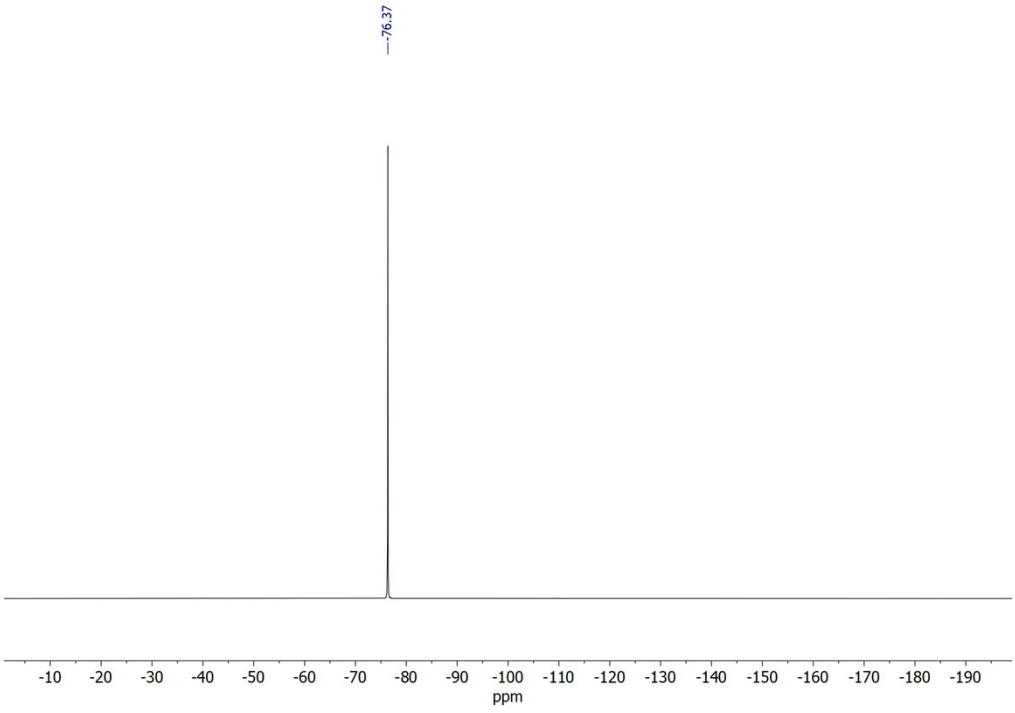

## [Cu[(BIAN-IPr)(OC(CF$_3$)$_3$)] (6) 2D HMBC



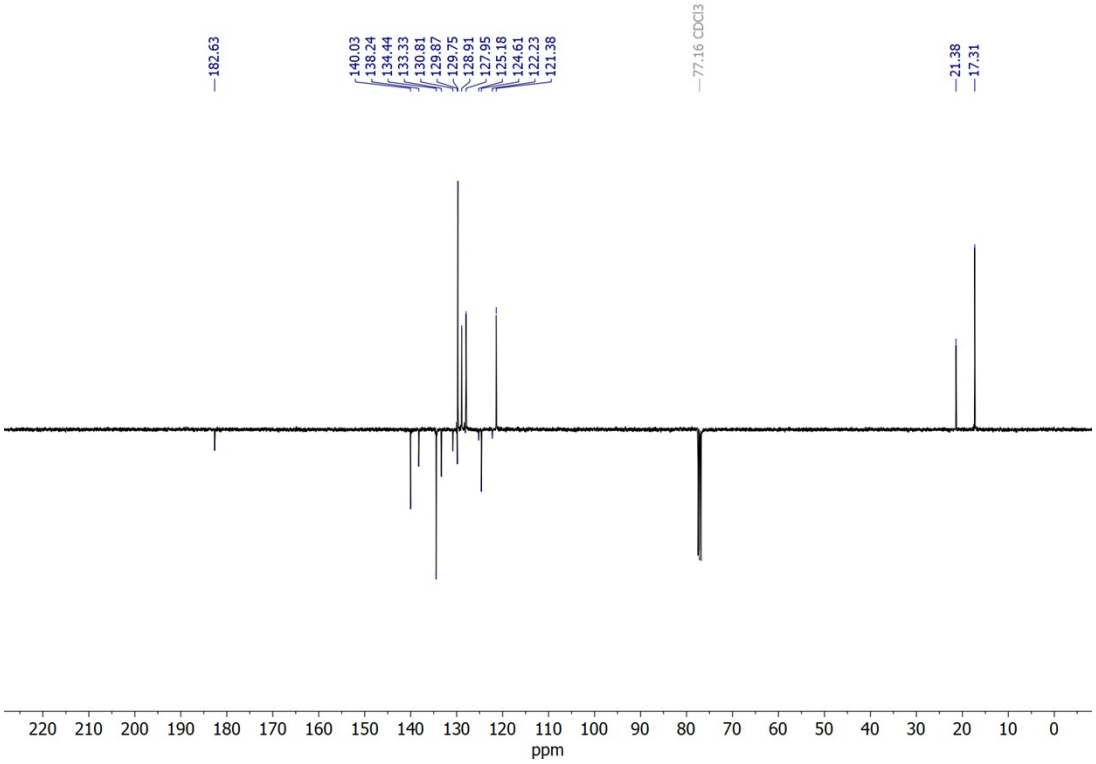
**[Cu[(BIAN-IMes)(OC($CF_3$)$_3$)] (7) $^1$H NMR** (400 MHz, Chloroform-d)



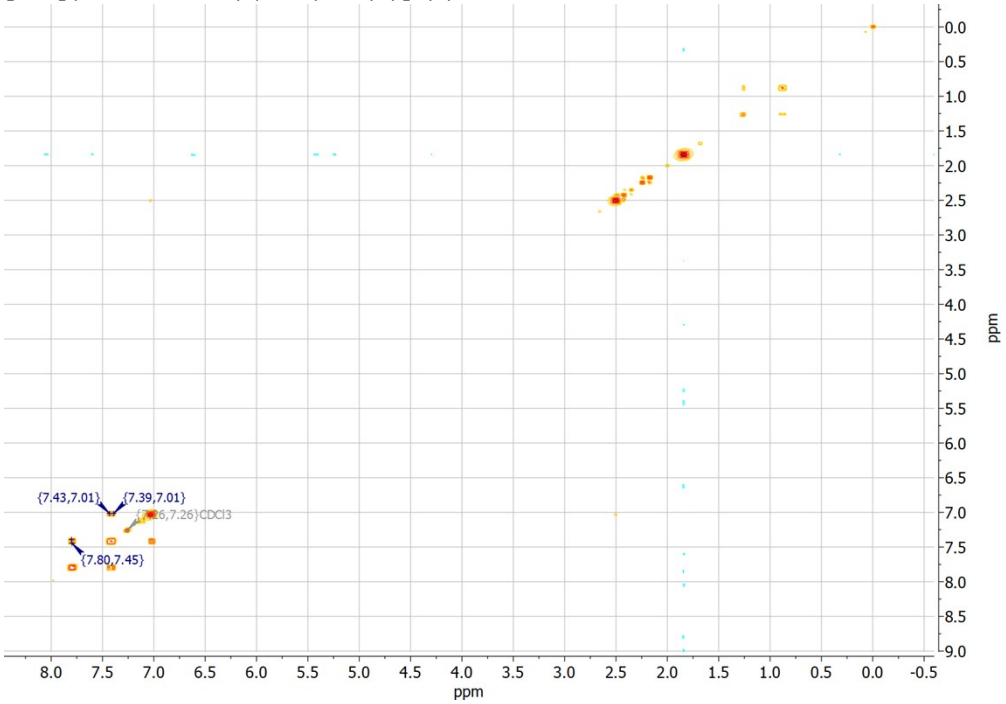

**[Cu[(BIAN-IMes)(OC($CF_3$)$_3$)] (7) $^{19}$F NMR** (377 MHz, Chloroform-d)



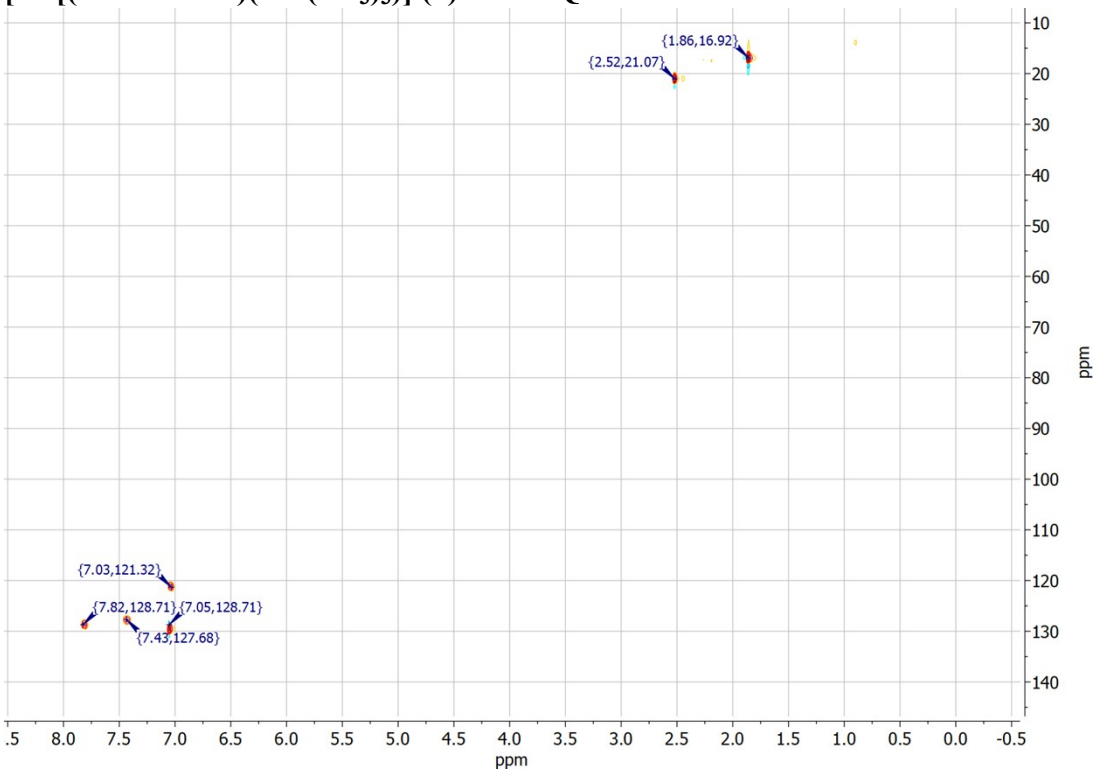
**[Cu[(BIAN-IMes)(OC(CF$_3$)$_3$)] (7) $^{13}$C NMR** (101 MHz, Chloroform-d)



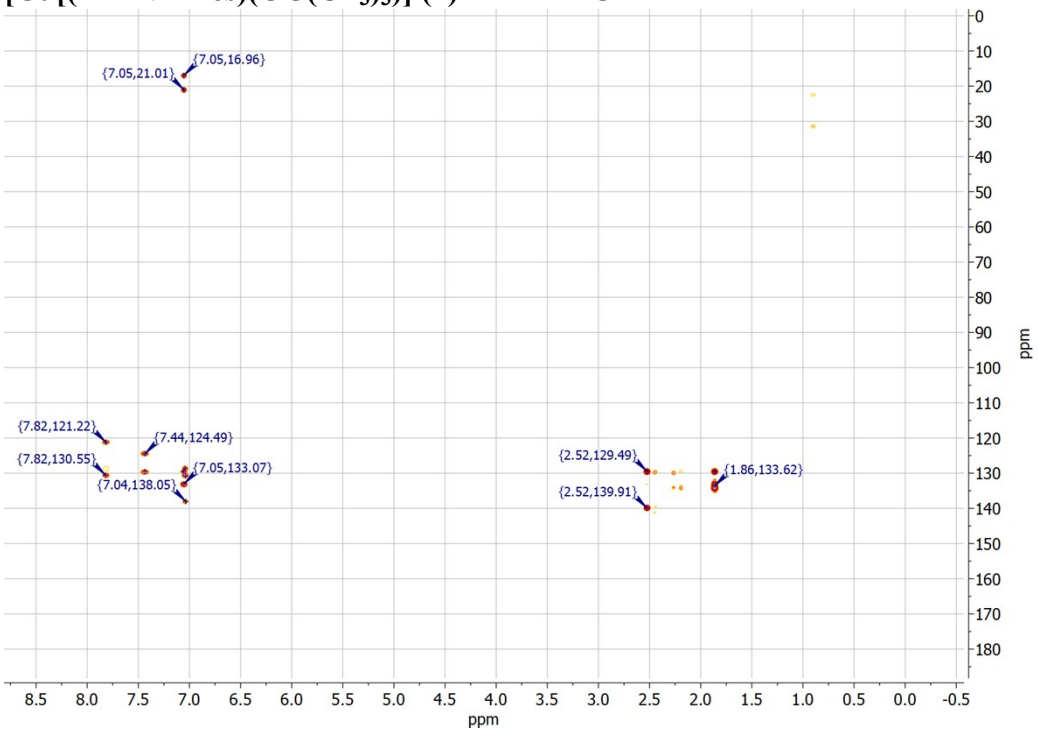

**[Cu[(BIAN-IMes)(OC(CF$_3$)$_3$)] (7) 2D COSY**



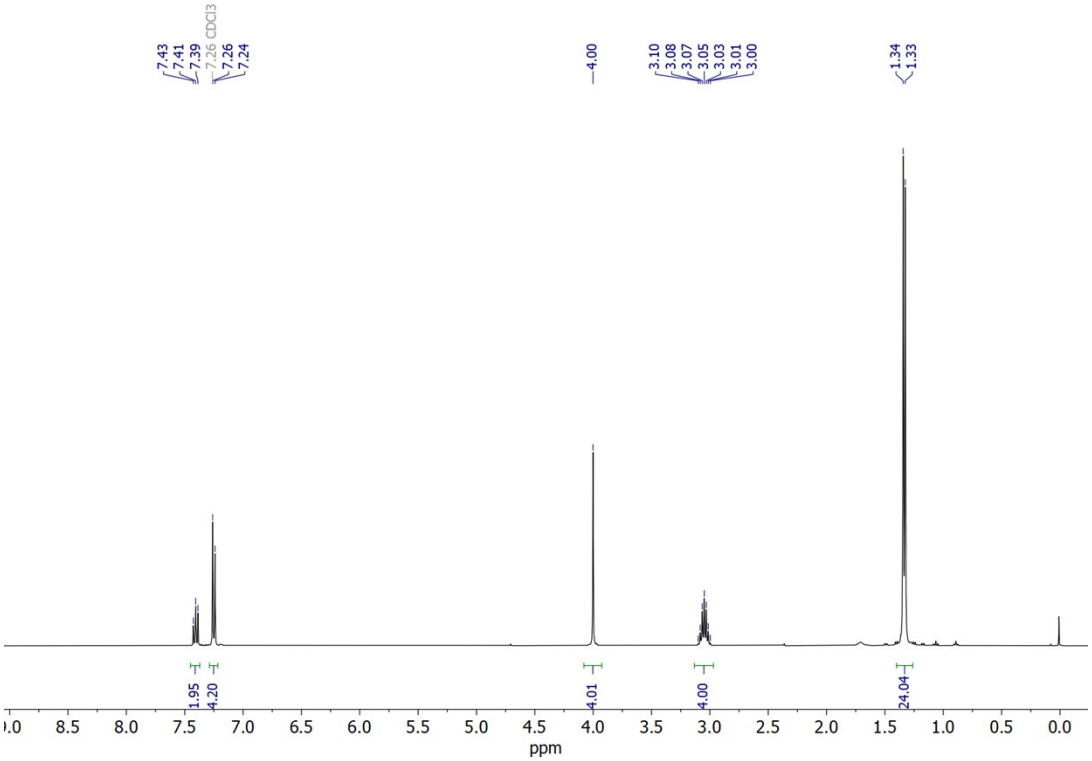
## [Cu[(BIAN-IMes)(OC($CF_3$)$_3$)] (7) 2D HSQC



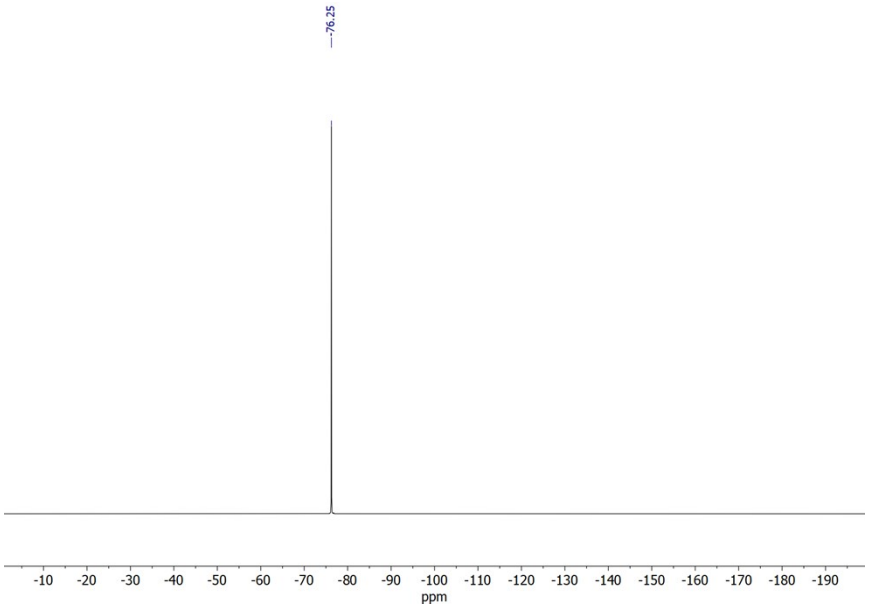

## [Cu[(BIAN-IMes)(OC($CF_3$)$_3$)] (7) 2D HMBC



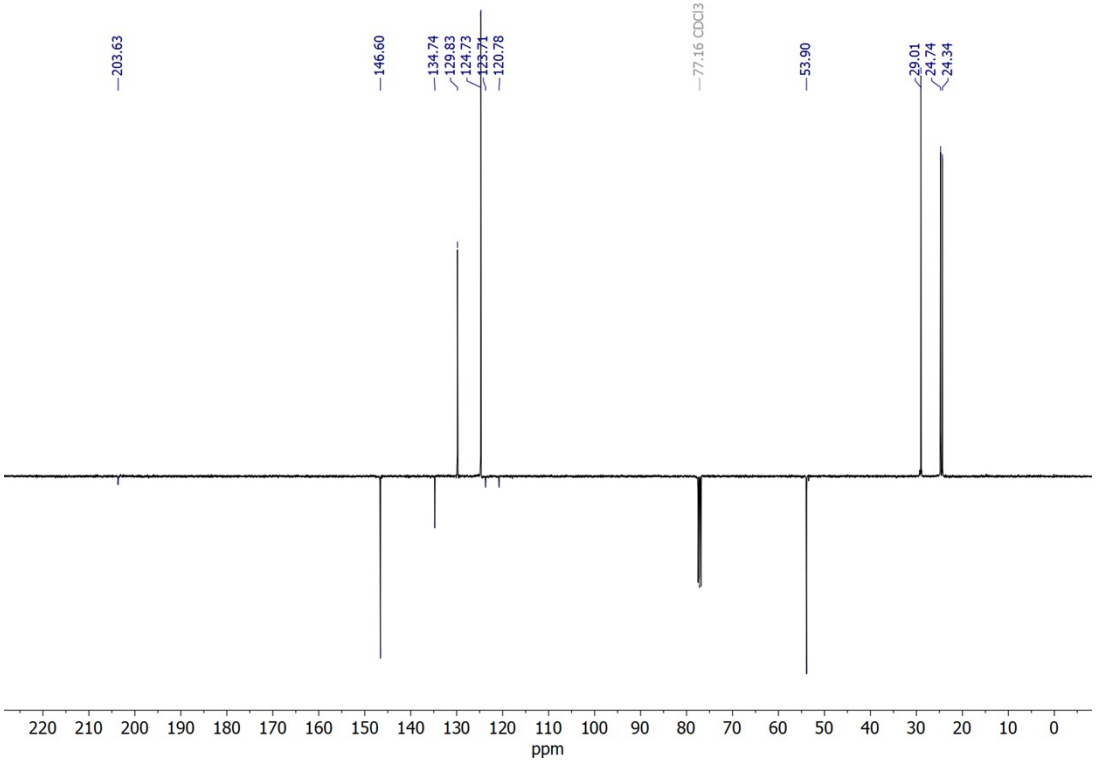
**[Cu[(SIPr)(OC(CF$_3$)$_3$)] (8) $^1$H NMR** (400 MHz, Chloroform-d)



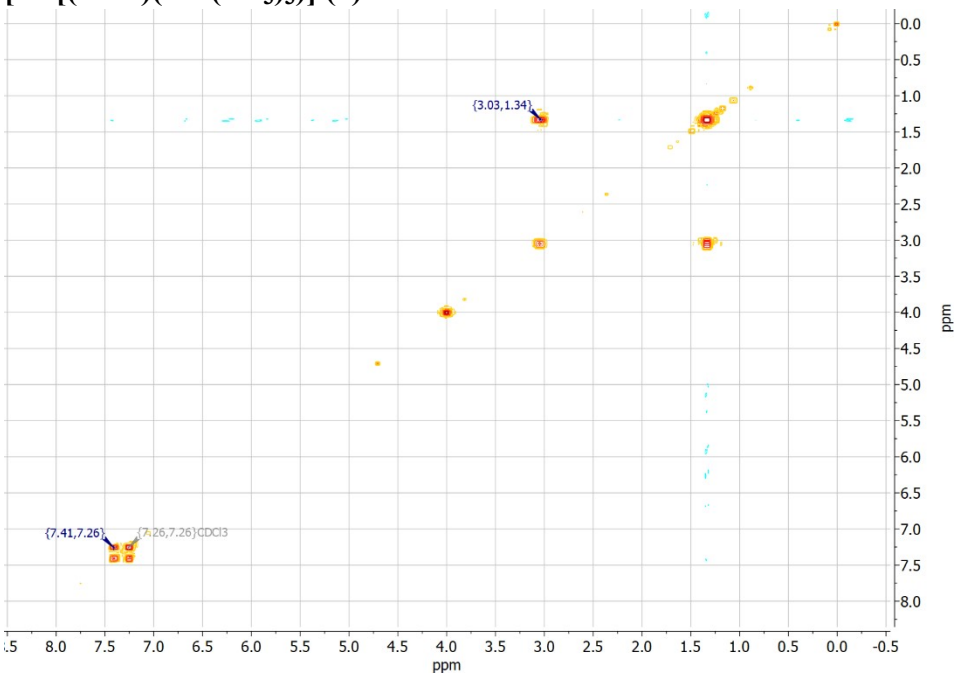

**[Cu[(SIPr)(OC(CF$_3$)$_3$)] (8) $^{19}$F NMR** (377 MHz, Chloroform-d)



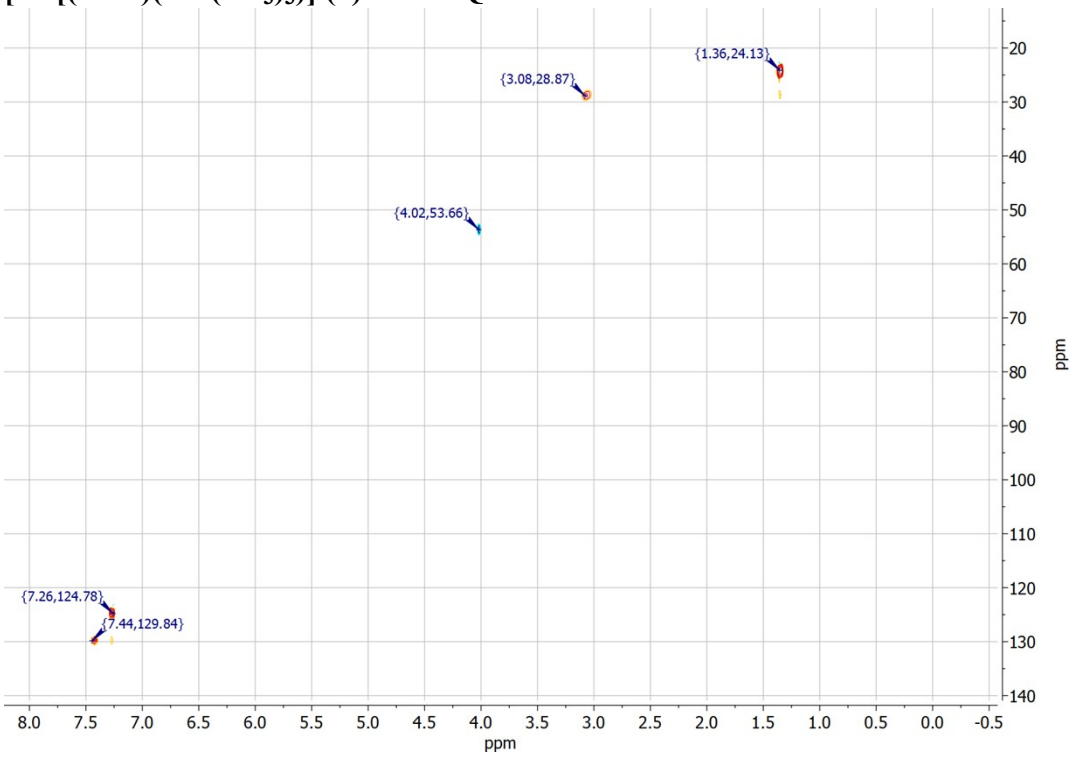
**[Cu[(SIPr)(OC(CF$_3$)$_3$)] (8) $^{13}$C NMR** (101 MHz, Chloroform-d)



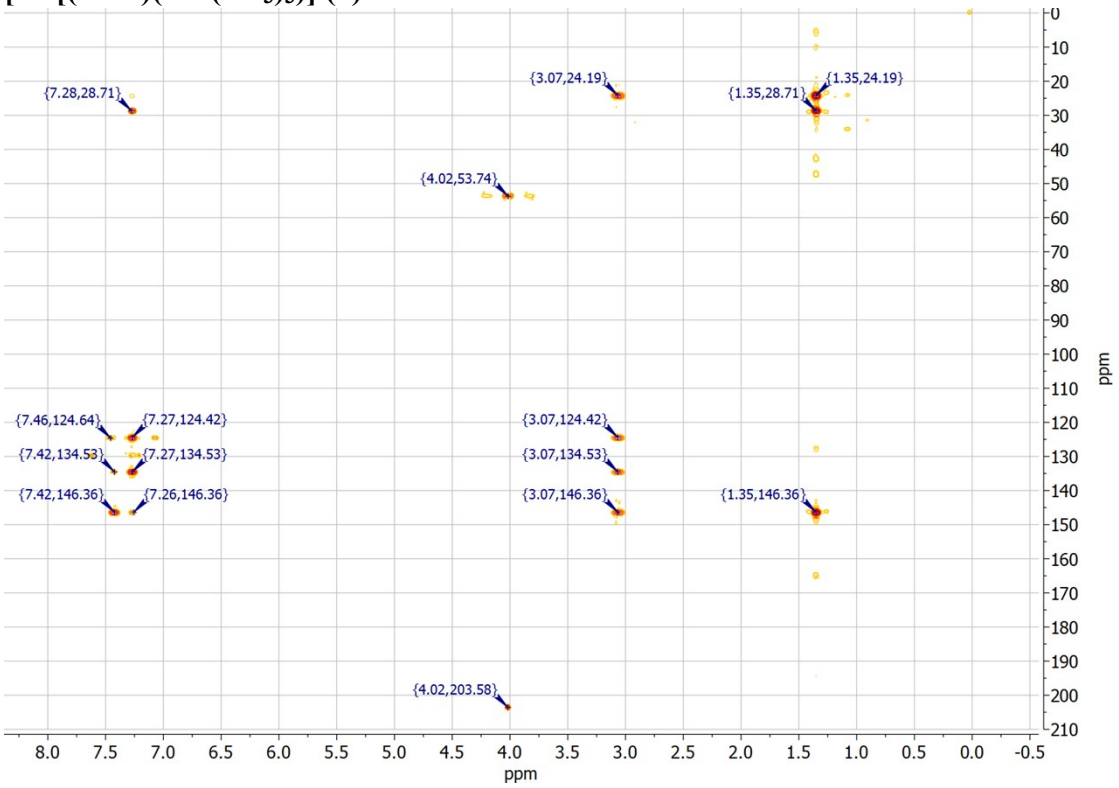

**[Cu[(SIPr)(OC(CF$_3$)$_3$)] (8) 2D COSY**



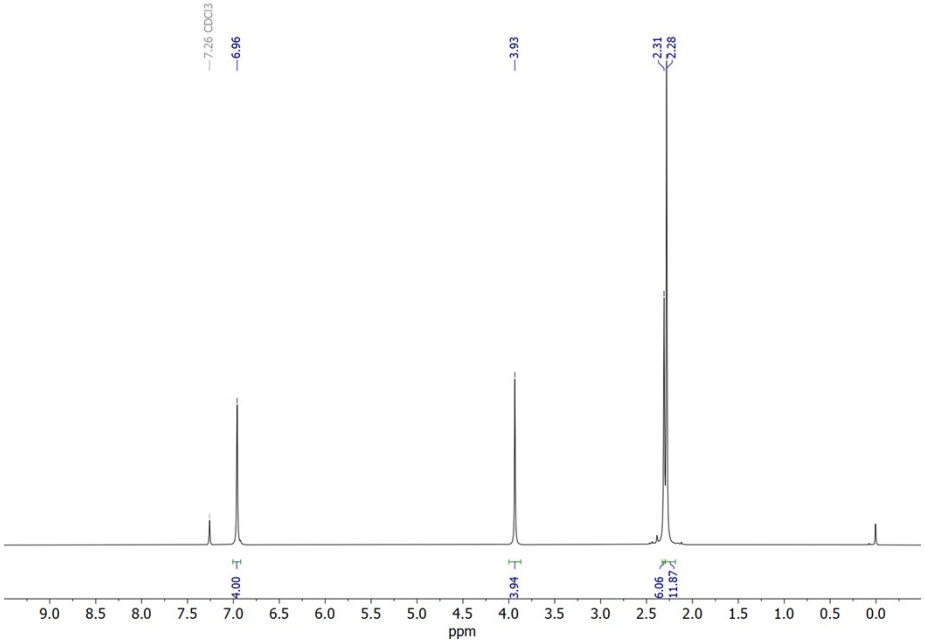
**[Cu[(SIPr)(OC(CF$_3$)$_3$)] (8) 2D HSQC**



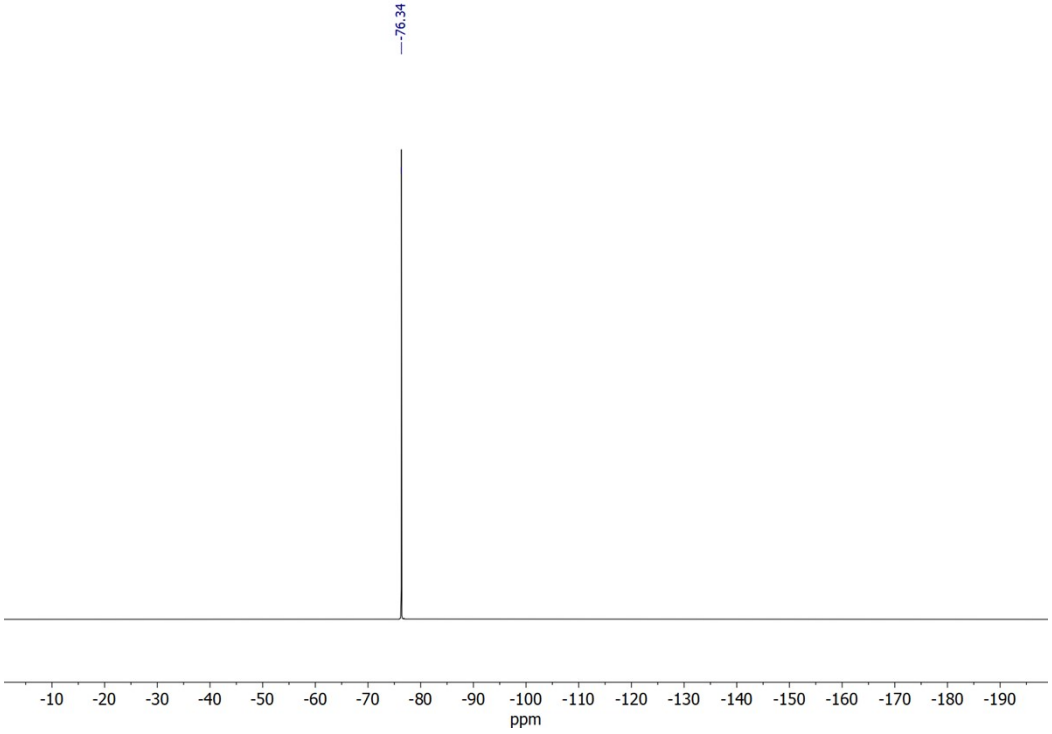

**[Cu[(SIPr)(OC(CF$_3$)$_3$)] (8) 2D HMBC**



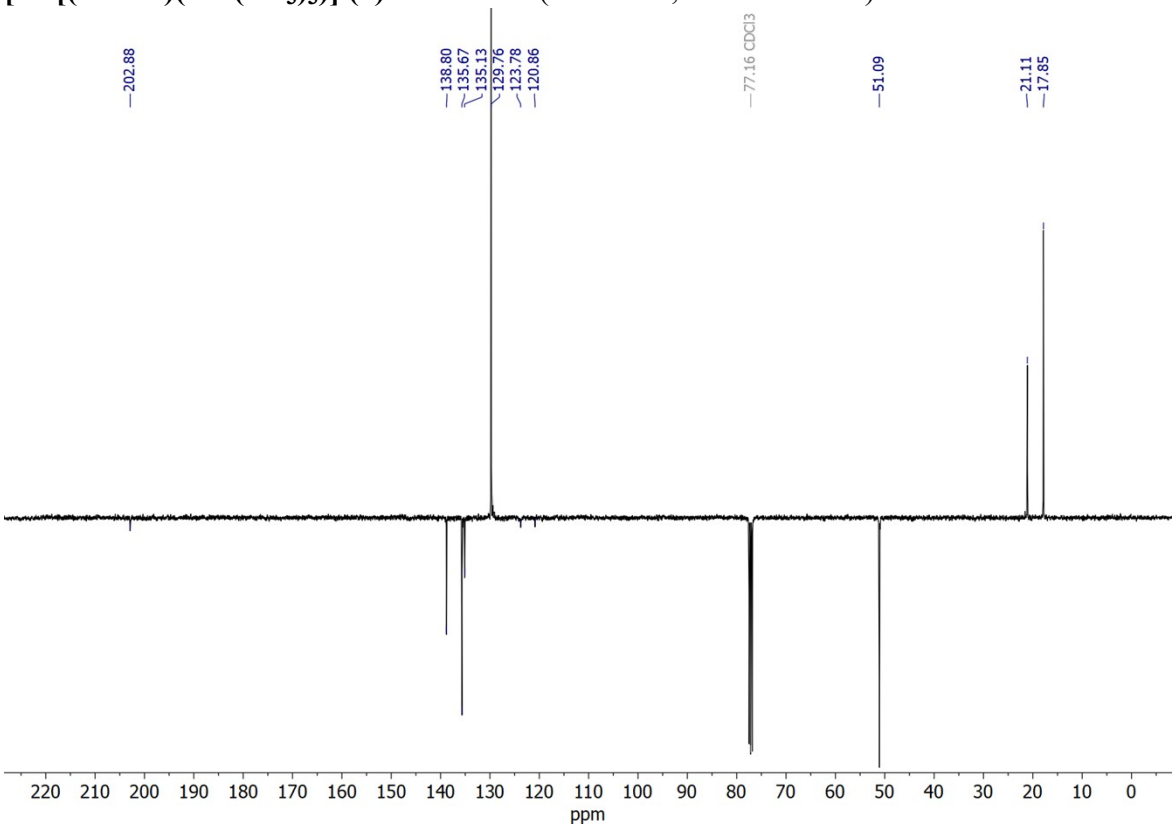
**[Cu[(SIMes)(OC($CF_3$)$_3$)] (9) $^1$H NMR** (400 MHz, Chloroform-d)



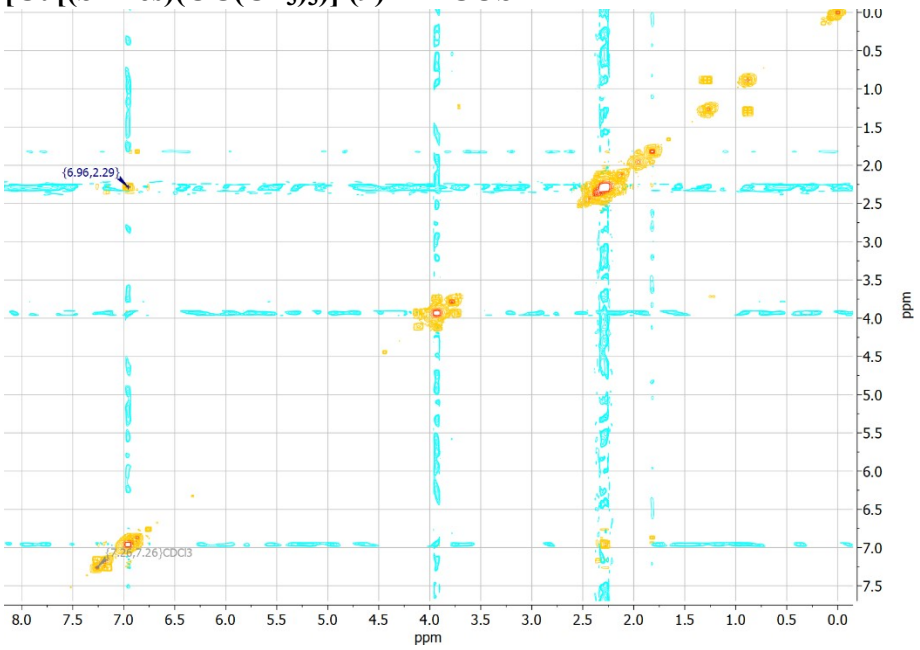

**[Cu[(SIMes)(OC($CF_3$)$_3$)] (9) $^{19}$F NMR** (377 MHz, Chloroform-d)



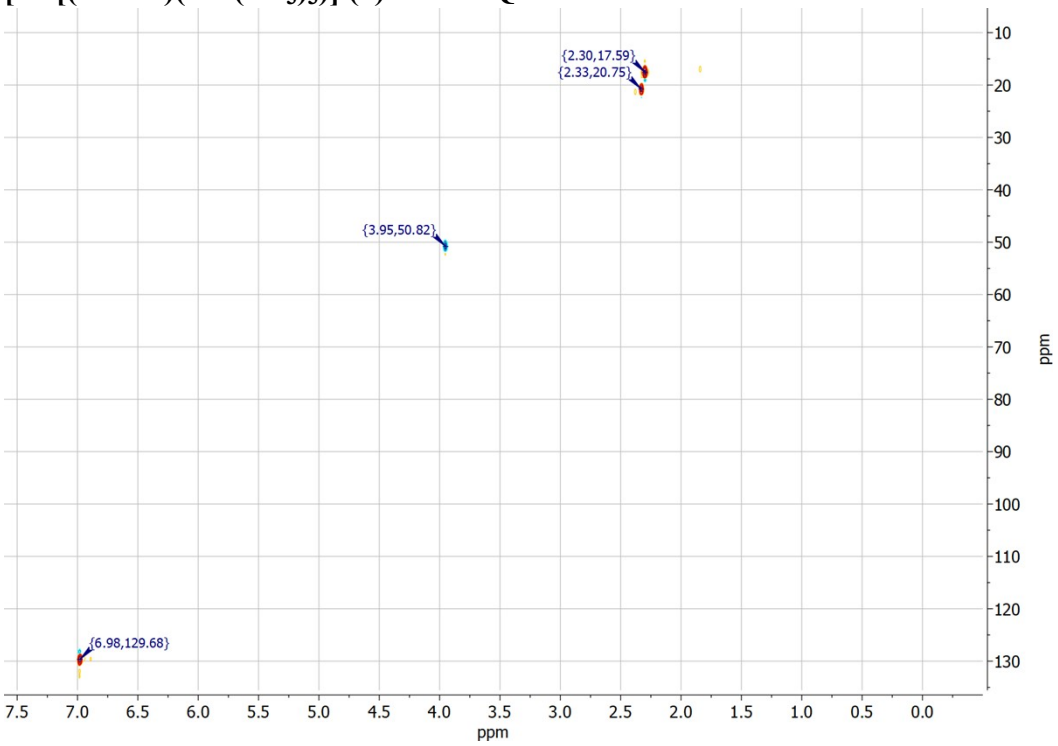
**[Cu[(SIMes)(OC(CF$_3$)$_3$)] (9) $^{13}$C NMR** (101 MHz, Chloroform-d)




**[Cu[(SIMes)(OC(CF$_3$)$_3$)] (9) 2D COSY**

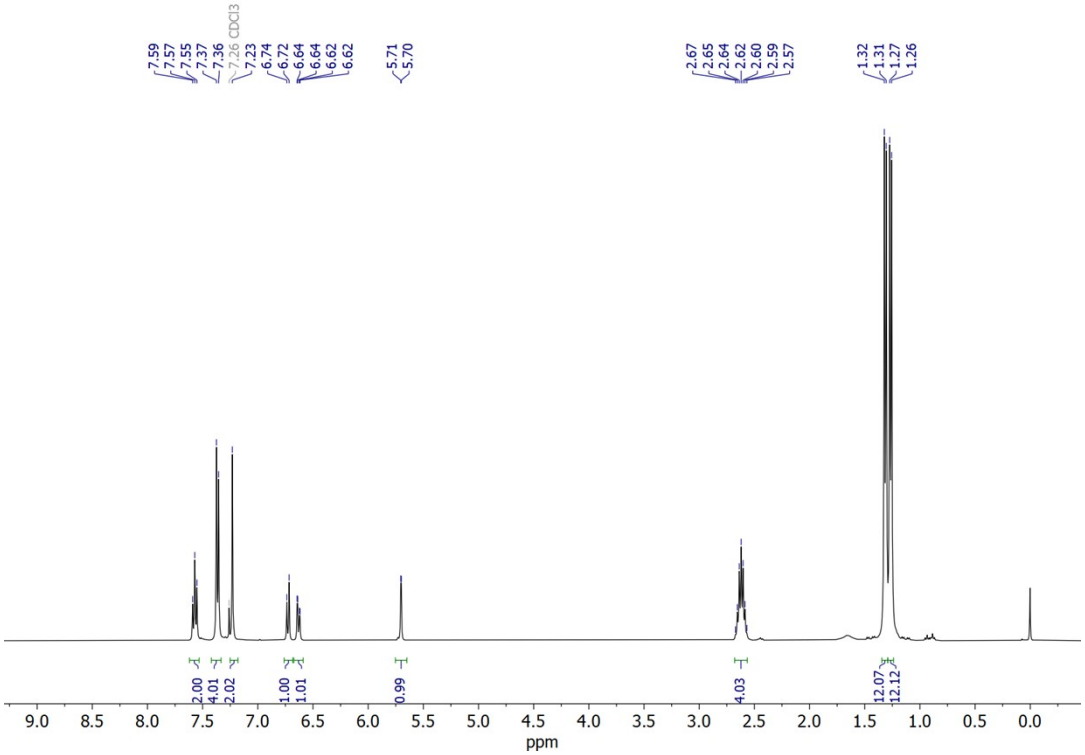


## [Cu[(SIMes)(OC($CF_3$)$_3$)] (9)  2D HSQC

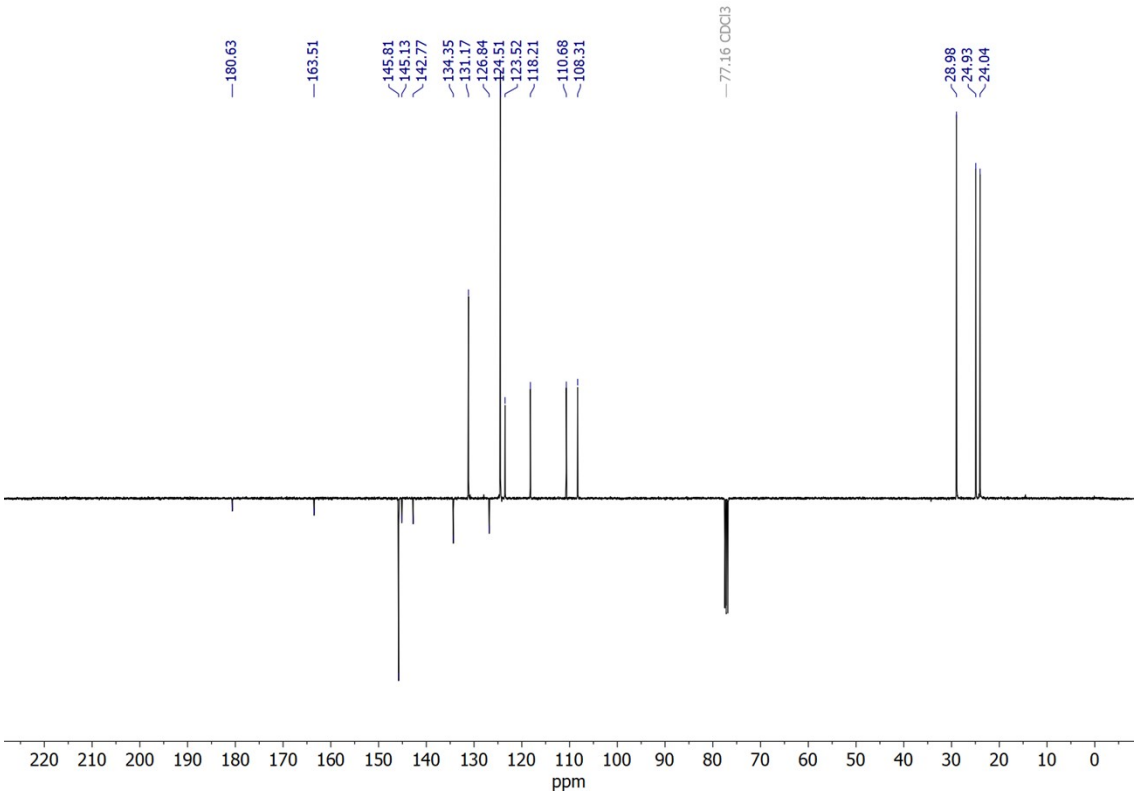



## [Cu[(SIMes)(OC($CF_3$)$_3$)] (9)  2D HMBC

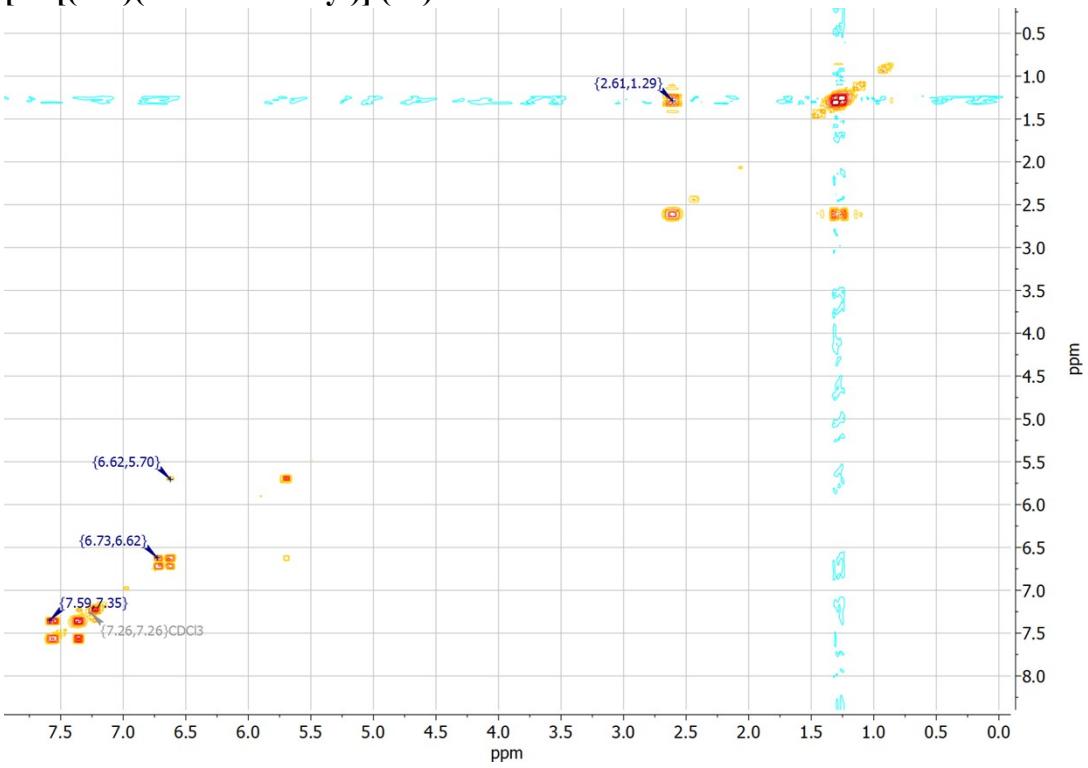
**[Cu[(IPr)(chlorzoxazonyl)] (21) $^{1}$H NMR** (400 MHz, Chloroform-d)



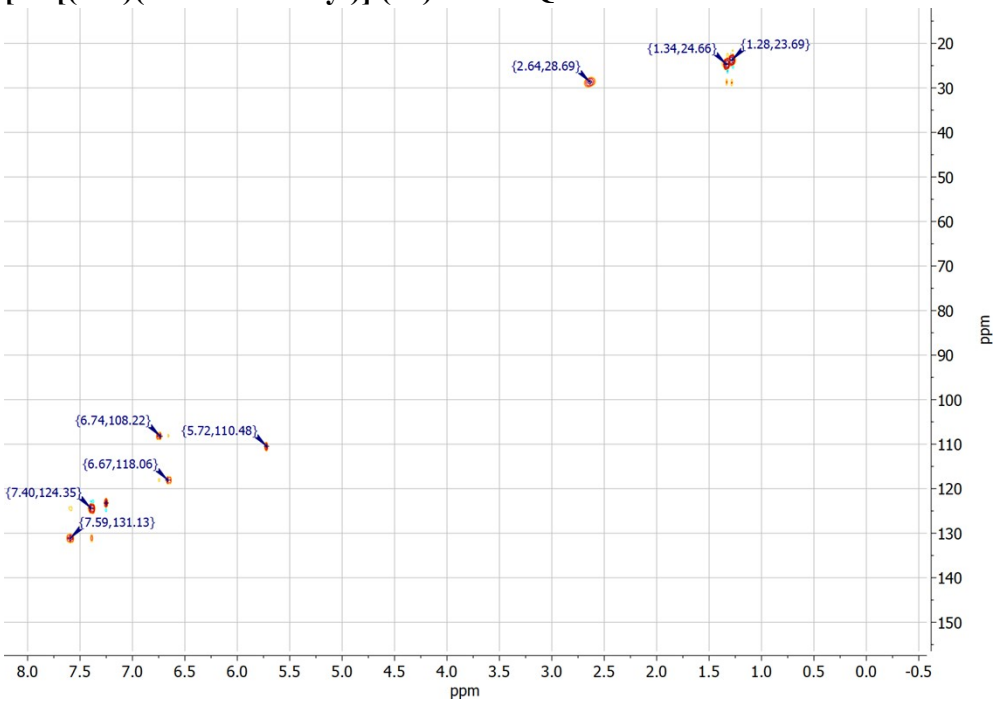

**[Cu[(IPr)(chlorzoxazonyl)] (21) $^{13}$C NMR** (101 MHz, Chloroform-d)



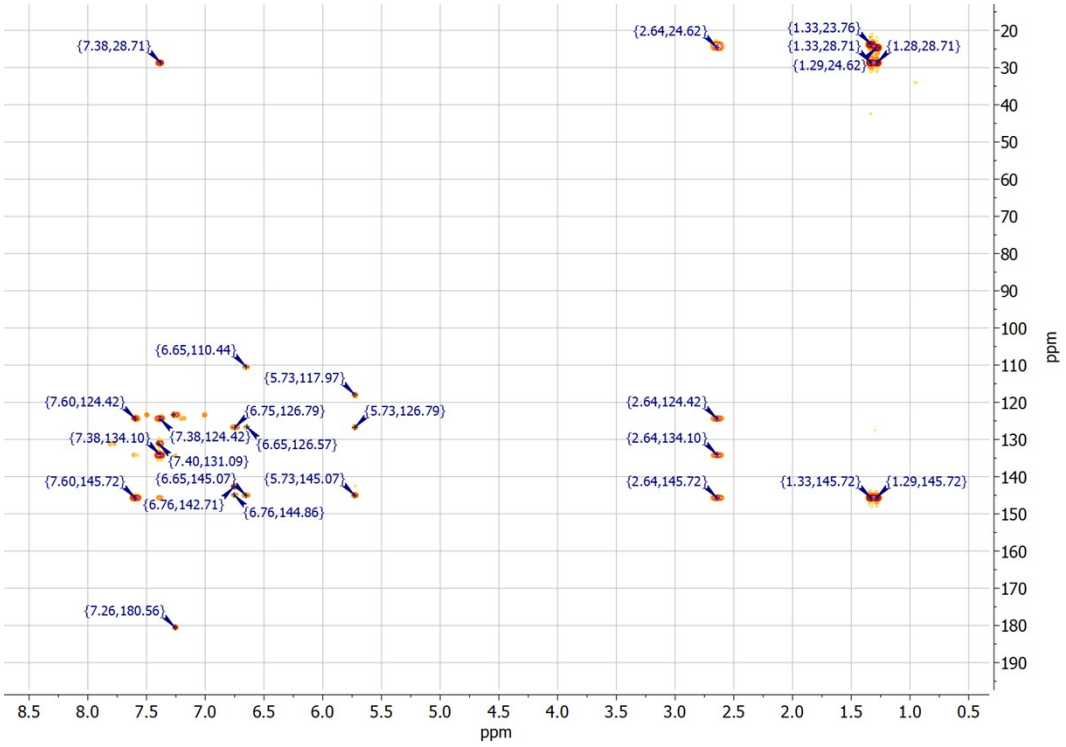
## [Cu[(IPr)(chlorzoxazonyl)] (21) 2D COSY



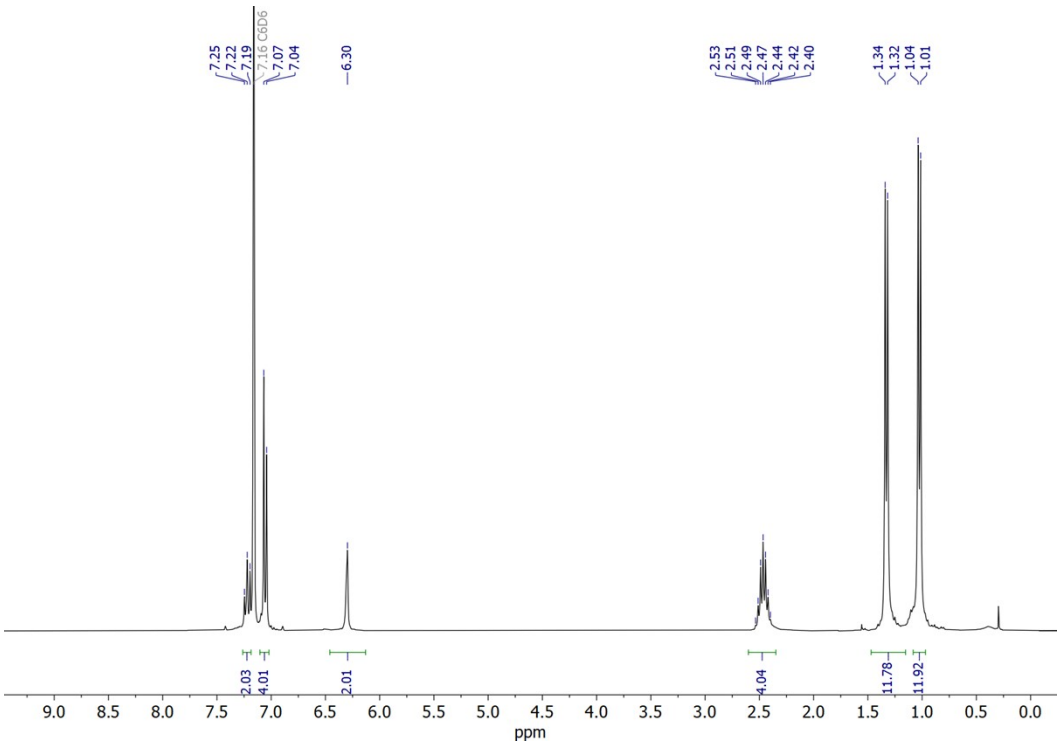

## [Cu[(IPr)(chlorzoxazonyl)] (21) 2D HSQC



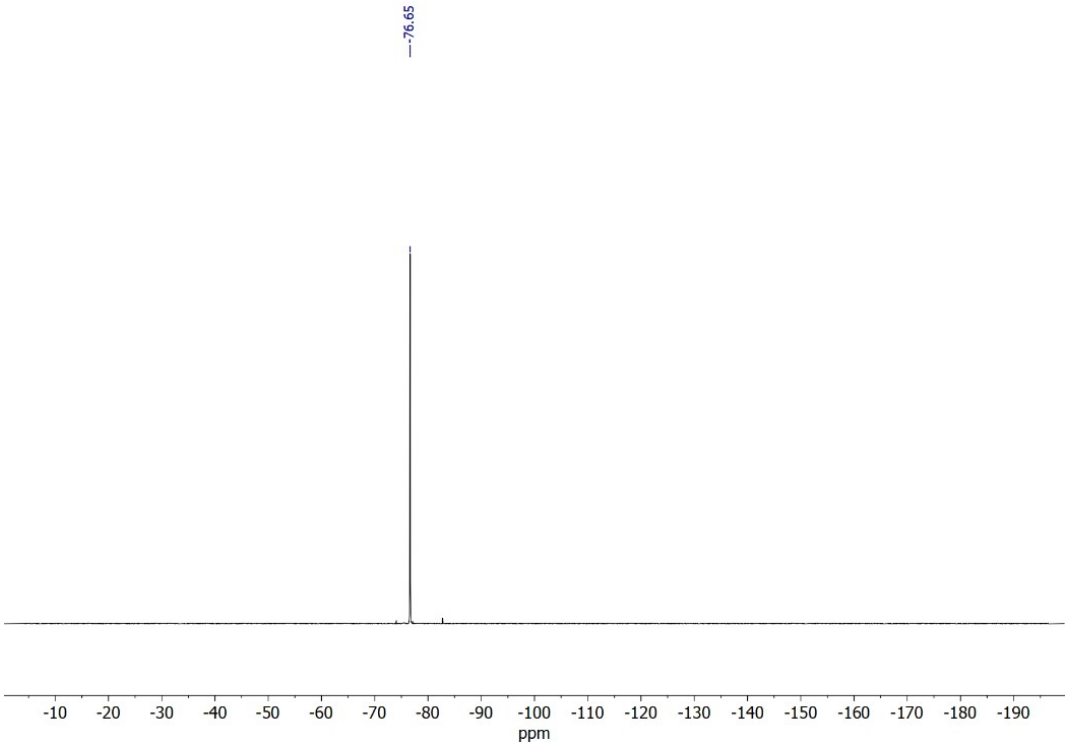
**[Cu[(IPr)(chlorzoxazonyl)] (21) 2D HMBC**



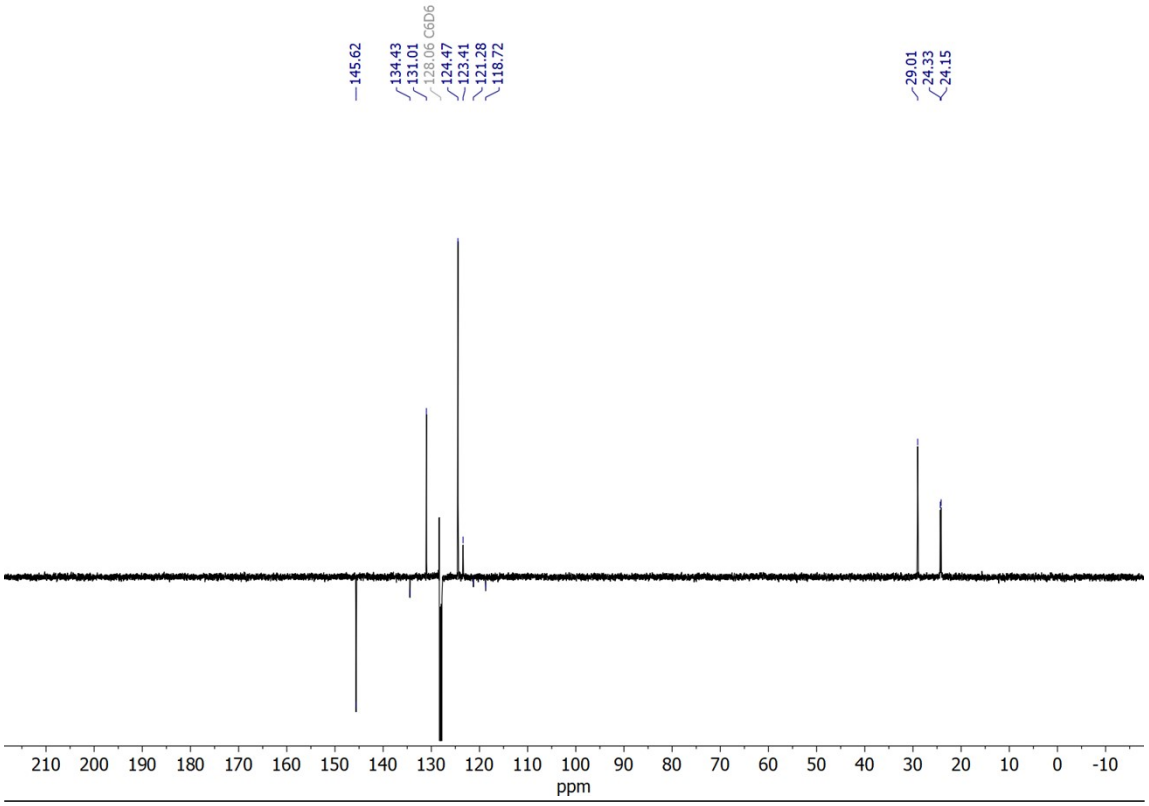

**[Cu(IPr)(NTf$_2$)] (10) $^1$H NMR** (300 MHz, Benzene-d$_6$)



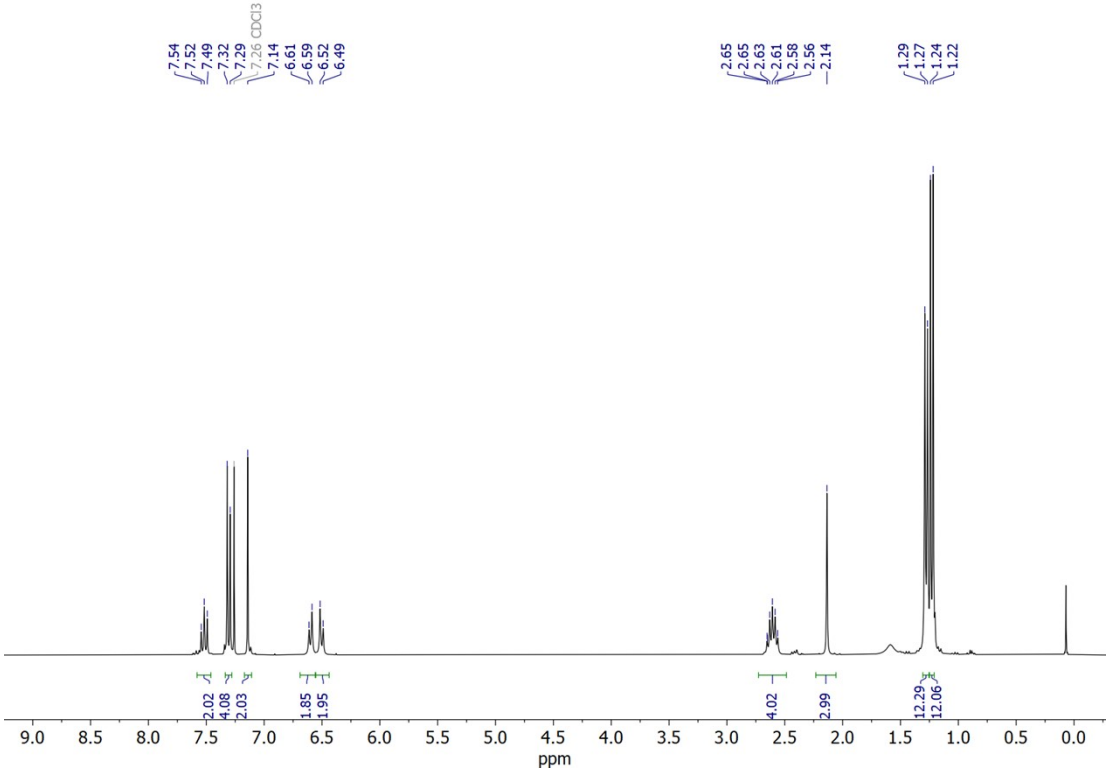
**[Cu(IPr)(NTf$_2$)] (10) $^{19}$F NMR** (471 MHz, Benzene-d$_6$)



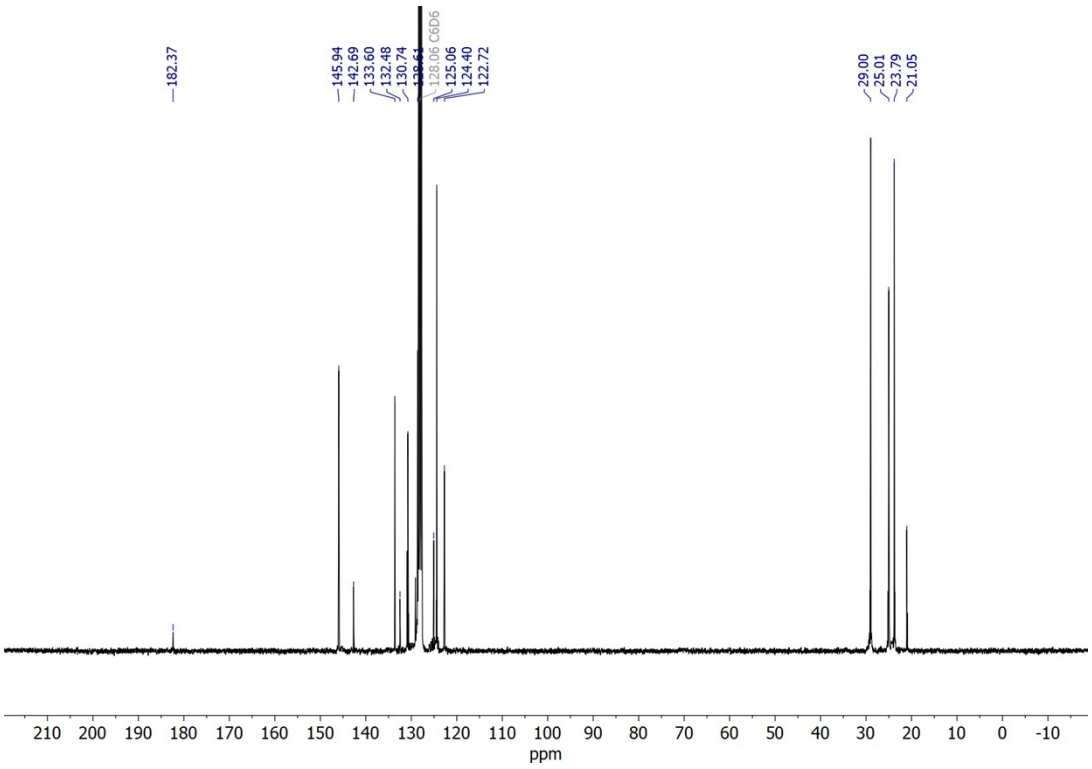

**[Cu(IPr)(NTf$_2$)] (10) $^{13}$C NMR** (126 MHz, Benzene-d$_6$)



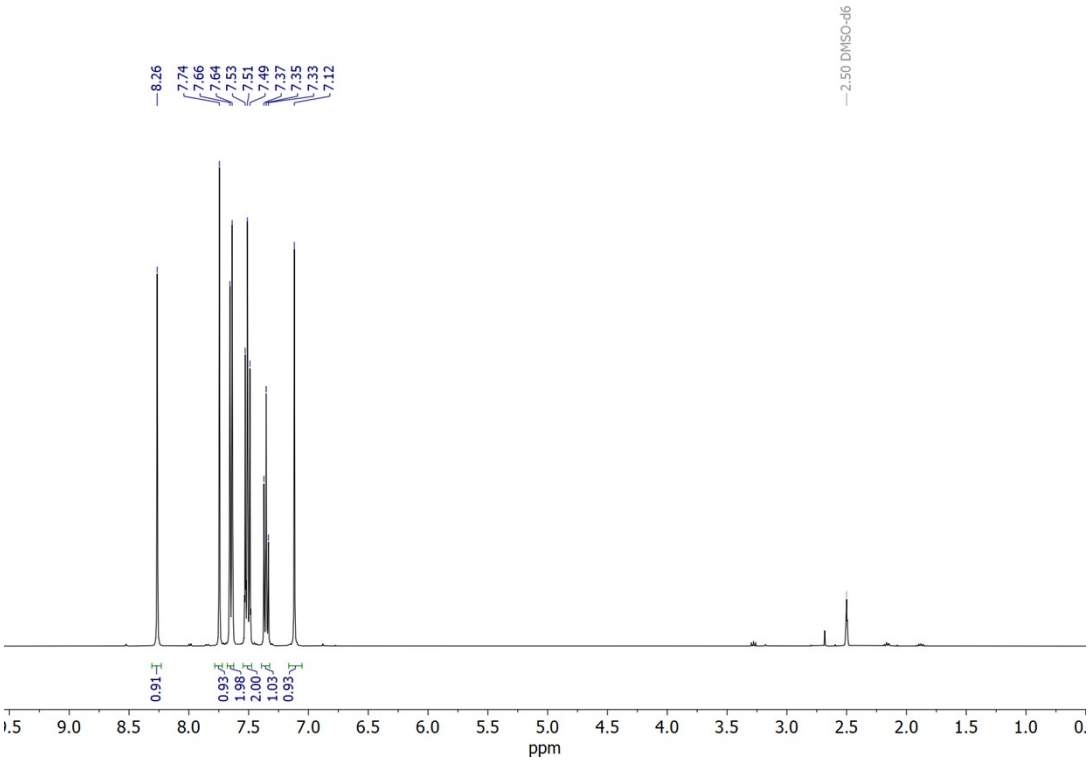
**[Cu(IPr)(SPhMe)] (11) $^{1}$H NMR** (300 MHz, Chloroform-d)




**[Cu(IPr)(SPhMe)] (11) $^{13}$C NMR** (75 MHz, Benzene-$d_6$)



**N-Phenyl-imidazole (24) $^{1}$H NMR** (400 MHz, Dimethylsulfoxide-$d_6$ )




**N-Phenyl-imidazole (24) $^{13}$C NMR** (101 MHz, Dimethylsulfoxide-$d_6$ )