Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

For

An Air-stable [Cu(NHC)(OR)] (R = $C(H)(CF_3)_2$) Complex for C–H, N–H and S–H Bond Activation

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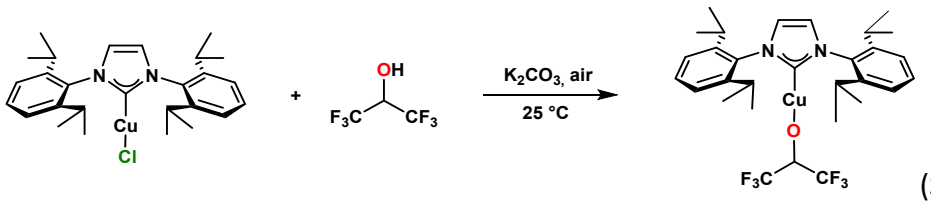
General information

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. Elemental analyses were performed at Université de Namur, Rue de Bruxelles 55, B-5000 Namur, Belgium. ^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). ^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). [Cu(IPr)Cl][1] and [Cu(IPr)(OH)][2] were synthesized following the procedures described in the literature.

Optimisation of [Cu(IPr)(OC(H)(CF_3)$_2$]synthesis with [Cu(IPr)Cl]



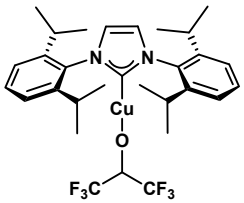
(S1)

Table S1. Optimization of [Cu(IPr)OCH(CF_3)$_2$] synthesis

Entry	Solvent	Base	Time [h]	Yield [%][a]
1	EtOH	K_2CO_3	2	99
2	EtOH	K_2CO_3	0.25	99
3	EtOH	NEt_3	16	NR
4	EtOH	NaOAc	16	NR
5	benzene	K_2CO_3	2	97
6	DCM	K_2CO_3	16	91
7	H_2O	K_2CO_3	0.25	99

Reaction conditions: [Cu(IPr)Cl] (200 mg, 1 eq); HFIP (1.1 eq); solvent (1 mL); 25 °C; [a]insulation yield; [b]<25 °C

Procedure for the synthesis of Cu[(IPr)(OC(H)(CF_3)$_2$)] (4)



Procedure A: A 4 mL scintillation vial equipped with a magnetic stirring bar and a septum-equipped cap was charged with [Cu(IPr)(OH)] (100 mg, 0.213 mmol) which was suspended in EtOH (1 mL) and HFIP (1.1 equiv., 0.028 mL, 0.234 mmol) was added via a micropipette. The mixture became a clear solution at once, and was left to stir for 1 hour at 25 °C. The solution was subsequently concentrated on the rotary evaporator until a viscous oil remained and pentane (5 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x3 mL) and dried under high vacuum. The final product was obtained as a white solid in 95% yield (133 mg).

Procedure B:

Small scale:

A 4 mL scintillation vial equipped with a magnetic stirring bar and a septum-equipped cap was charged with [Cu(IPr)Cl] (200 mg, 0.409 mmol) and K_2CO_3 (3 equiv., 170 mg, 1227 mmol) which were suspended in ethanol or water (1 mL). HFIP (1.1 equiv., 0.047 mL, 0.450 mmol) was added and the reaction was left to stir at room temperature 25 °C for 0.25 hour. The solvent was evaporated, and the residue was then microfiltered and filtered over basic alumina using toluene (8 mL). The solution was subsequently concentrated on the rotary evaporator until a viscous oil remained and pentane (5 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x3 mL) and dried under high vacuum. The final product was obtained as a white solid in 99% yield (251 mg).

Large scale:

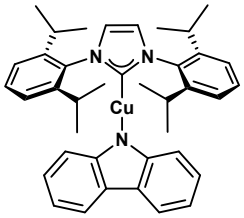
A 15 mL scintillation vial equipped with a magnetic stirring bar and a septum-equipped cap was charged with [Cu(IPr)Cl] (1000 mg, 2045 mmol) and K_2CO_3 (3 equiv., 850 mg, 6135 mmol) which were suspended in ethanol (3 mL). HFIP (1.1 equiv., 0.235 mL, 2.250 mmol) was added and the reaction was left to stir at 25 °C for 2 hours. The solvent was evaporated, and the residue was then microfiltered and filtered over basic alumina using toluene (8 mL). The solution was subsequently concentrated on the rotary evaporator until a viscous oil remained

and pentane (5 mL) was added to precipitate the product, which was collected by filtration, washed with pentane (2x3 mL) and dried under high vacuum. The final product was obtained as a white solid in 98% yield (1.255 g).

^{1}H NMR (300 MHz, C_6D_6) δ 7.26 – 7.17 (t, *J* = 7.7 Hz, 2H, CH_{Ar}), 7.05 (d, *J* = 7.7 Hz, 4H, CH_{Ar}), 6.27 (s, 2H, NCH_{Imid}), 4.53 (hept, *J* = 6.4 Hz, 1H, $CH(CF_3)$), 2.51 (hept, *J* = 6.9 Hz, 4H, $CH(CH_3)_2$), 1.33 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.05 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$). **^{13}C-{^{1}H} NMR** (75 MHz, C_6D_6) δ 181.91 (Cu-C), 145.65 (C_{Ar}), 134.91 (C_{Ar}), 130.77 (CH_{Ar}), 125.31 – 125.18 (m, CF_3), 124.35 (CH_{Ar}), 123.06 – 122.22 (m, CF_3), 122.81 (NCH_{Imid}), 74.84 (p, *J* = 30.0 Hz, (CH-CF_3)), 28.95 ($CH(CH_3)_2$), 24.54 ($CH(CH_3)_2$), 23.87 ($CH(CH_3)_2$). **^{19}F-{^{1}H} NMR** (376 MHz, C_6D_6) δ -77.15 (s, CF_3).

Anal. Calcd: $C_{30}H_{37}CuF_6N_2O$: C, 58.20; H, 6.02; N, 4.52. **Found**: C, 58.14; H, 6.08; N, 4.55.

Synthesis of [Cu(IPr)(Cbz)] (5)

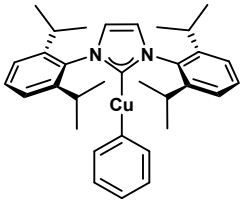


A 4 mL scintillation vial equipped with a magnetic stirring bar and a septum-equipped cap was charged with [Cu(IPr)(OC(H)(CF_3)$_2$] (100 mg, 0.161 mmol) and ethanol (1 mL). Carbazole, (1 equiv., 27 mg, 0.161 mmol) was added and the reaction was left to stir at 25 °C for 1 hour. The solvent was subsequently stripped in vacuo to approximately 0.25 mL, at which point the product was precipitated from solution with the addition of pentane. The products were filtered from the solution, washed with pentane (3x3 mL), and dried under reduced pressure The final product was obtained as a white solid in 98% yield (98 mg). NMR spectra corresponded to the results reported in the literature.[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.76 – 7.64 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 4H), 7.30 (s, 2H), 6.96 (dt, *J* = 15.6, 8.0 Hz, 4H), 6.36 (d, *J* = 8.0 Hz, 2H), 2.85 – 2.62 (m, 4H), 1.32 (overlapping d, J = 7.0 Hz, 24H, $CH(C\mathit{H}_3)_2$).

^{13}C NMR (75 MHz, C_6D_6) δ 182.45 (Cu-C), 150.22 (C_{Ar}), 146.19 (C_{Ar}), 134.78 (C_{Ar}), 130.70 (C_{Ar}), 124.44 (C_{Ar}), 124.30 (C_{Ar}), 123.32 (C_{Ar}), 119.42 (C_{imid}), 115.26 (C_{Ar}), 114.32 (C_{Ar}), 28.99 ($CH(CH_3)_2$), 24.89 ($CH(\mathit{C}H_3)_2$), 23.93 ($CH(\mathit{C}H_3)_2$).

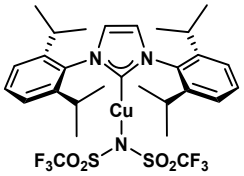
Synthesis of [Cu(IPr)(Ph)] (6)



A 4 mL scintillation vial equipped with a magnetic stirring bar and a septum-equipped cap was charged with [Cu(IPr)(OC(H)(CF_3)$_2$] (100 mg, 0.161 mmol) and ethanol (1 mL). Phenylboronic acid pinacol ester, (1 equiv., 33 mg, 0.161 mmol) was added and the reaction was left to stir at 25 °C for 1 hour. The solvent was subsequently stripped in vacuo to approximately 0.25 mL, at which point the product was precipitated from solution with the addition of pentane. The products were filtered from the solution, washed with pentane (3x3 mL), and dried under reduced pressure The final product was obtained as a white solid in 95% yield (81 mg). NMR spectra corresponded to the results reported in the literature.[7]

^{1}H NMR (C_6D_6): δ 7.65 (d, *J* = 6 Hz, 2H, Ph), 7.18 (br t, *J* = 7 Hz, 3H, overlap of *p*-aryl of IPr and Ph), 7.03 (br d, *J* = 7 Hz, 3H, overlap of *m*-aryl of IPr and Ph), 6.30 (s, 2H, C*H*$_{imid}$), 2.61 (sept, *J* = 6 Hz, 4H, C*H*(CH_3)$_2$), 1.28 (d, *J* = 6.1 Hz, 12H, CH(C*H*$_3$)$_2$), 1.23 (d, *J* = 6.1 Hz, 12H, CH(C*H*$_3$)$_2$). **^{13}C-{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 180.57 (Cu-C), 145.63 (C_{Ar}), 134.81 (C_{Ar}), 130.59 (C_{Ar}), 124.75 (C_{Ar}), 124.54 (C_{Ar}), 123.47 (C_{Ar}), 120.64 (*C*H(CH_3)$_2$), 28.86 (CH(*C*H$_3$)$_2$), 24.28 (CH(*C*H$_3$)$_2$), 24.20 (CH(*C*H$_3$)$_2$).

Synthesis of [Cu(IPr)(N(SO_2CF_3)$_2$)] (7)

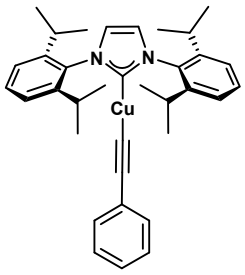


A 4 mL scintillation vial equipped with a magnetic stirring bar and a septum-equipped cap was charged with [Cu(IPr)(OC(H)(CF_3)$_2$] (100 mg, 0.161 mmol) and ethanol (1 mL). Trifluoromethanesulfonimide, (1 equiv., 45 mg, 0.161 mmol) was added and the reaction was left to stir at 25 °C for 1 hour. The solvent was subsequently stripped in vacuo to approximately 0.25 mL, at which point the product was precipitated from solution with the addition of pentane. The products were filtered from the solution, washed with pentane (3x3 mL), and

dried under reduced pressure The final product was obtained as a white solid in 96% yield (107 mg). NMR spectra corresponded to the results reported in the literature.[5]

^{1}H NMR (300 MHz, C_6D_6) δ 7.22 (t, *J* = 7.8 Hz, 2H, (C*H*$_{Ar}$)), 7.06 (d, *J* = 7.8 Hz, 4H, (C*H*$_{Ar}$)), 6.30 (s, 2H, (C*H*$_{imid}$)), 2.54 – 2.38 (m, 4H, C*H*$(CH_3)_2$)), 1.33 (d, *J* = 6.8 Hz, 12H, CH$(CH_3)_2$)), 1.03 (d, *J* = 6.9 Hz, 12H, CH(*CH*$_3)_2$)). **^{13}C NMR-{^{1}H}** (126 MHz, C_6D_6) δ 145.62 (C*H*$_{Ar}$), 134.44 (C*H*$_{Ar}$), 131.01 (*C*H$_{imid}$), 124.47 (C_{Ar}), 123.41 (C_{Ar}), 119.72 (q, 1 *J*F = 322 Hz, CF_3), 29.01 (*C*H$(CH_3)_2$), 24.28 (d, CH(*C*H$_3)_2$). **^{19}F-{^{1}H} NMR** (300 MHz, C_6D_6) δ -76.65 (s, CF_3).

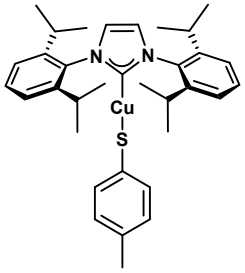
Synthesis of [Cu(IPr)(CCPh)] (8)



A 4 mL scintillation vial equipped with a magnetic stirring bar and a septum-equipped cap was charged with [Cu(IPr)(OC(H)$(CF_3)_2$] (100 mg, 0.161 mmol) and ethanol (1 mL). Phenylacetylene, (1 equiv., 18 µL, 0.161 mmol) was added and the reaction was left to stir at 25 °C for 1 hour. The solvent was subsequently stripped in vacuo to approximately 0.25 mL, at which point the product was precipitated from solution with the addition of pentane. The products were filtered from the solution, washed with pentane (3x3 mL), and dried under reduced pressure The final product was obtained as a white solid in 98% yield (87 mg). NMR spectra corresponded to the results reported in the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.7 Hz, 2H, (C_{Ar})), 7.27 – 7.15 (m, 6H, (C_{Ar})), 7.13 – 6.91 (m, 5H, (C_{Ar} and C_{imid})), 2.67 – 2.42 (m, 4H, (*C*H$(CH_3)_2$), 1.28 (d, *J* = 6.9 Hz, 12H, (CH(*C*H$_3)_2$), 1.15 (d, *J* = 6.9 Hz, 12H, (CH(*C*H$_3)_2$). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 184.31 (Cu-C), 145.73 (C_{Ar}), 134.53 (C_{Ar}), 132.28 (C_{Ar}), 130.73 (C_{Ar}), 129.56 (C_{Ar}), 128.45(C_{Ar}), 124.37 (C_{Ar}), 123.96 (C_{Ar}), 123.27 (C_{Ar} and C_{imid}), 106.34 (Cu-C≡*C*), 102.48 (Cu-*C*≡C), 28.89 (*C*H$(CH_3)_2$), 24.95 (CH(*C*H$_3)_2$), 24.03 (CH(*C*H$_3)_2$).

Synthesis of [Cu(IPr)(SPh-*p*Me)] (9)

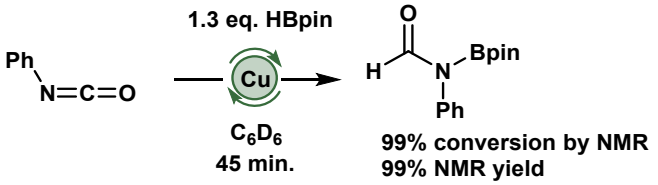


A 4 mL scintillation vial equipped with a magnetic stirring bar and a septum-equipped cap was charged with [Cu(IPr)(OC(H)(CF_3)$_2$] (100 mg, 0.161 mmol) and ethanol (1 mL). *p*-Thiocresol, (1 equiv., 20 mg, 0.161 mmol) was added and the reaction was left to stir at 25 °C for 1 hour. The solvent was subsequently stripped in vacuo to approximately 0.25 mL, at which point the product was precipitated from solution with the addition of pentane. The products were filtered from the solution, washed with pentane (3x3 mL), and dried under reduced pressure The final product was obtained as a pink-white solid in 98% yield (91 mg). NMR spectra corresponded to the results reported in the literature.[2]

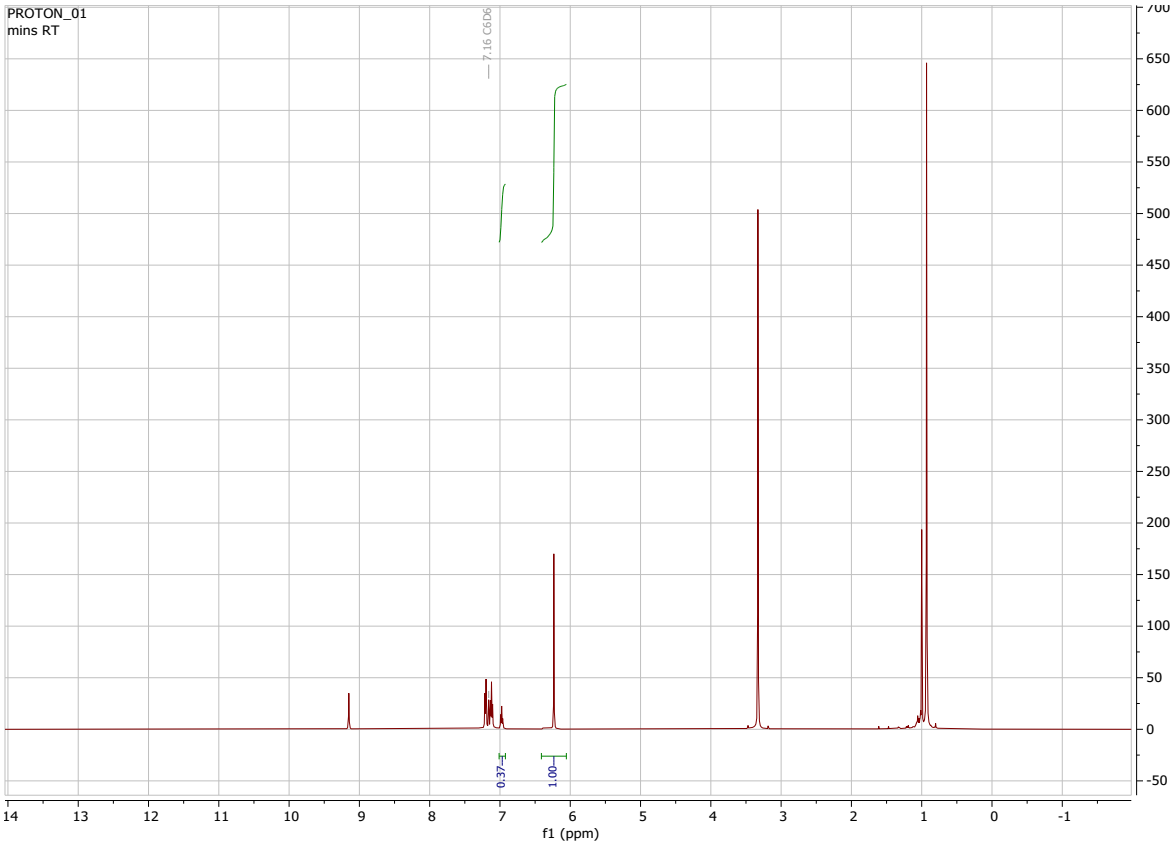
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.8 Hz, 2H, (CH_{Ar})), 7.31 (d, *J* = 7.8 Hz, 4H, (CH_{Ar})), 7.14 (s, 2H, (CH_{imid})), 6.55 (dd, *J* = 28.8, 8.0 Hz, 4H, (CH_{cresol})), 2.61 (hept, *J* = 6.9 Hz, 4H, ($CH(CH_3)_2$)), 2.14 (s, 3H, ($PhCH_3$)), 1.28 (d, *J* = 6.9 Hz, 12H, ($CH(CH_3)_2$)), 1.23 (d, *J* = 6.9 Hz, 12H, ($CH(CH_3)_2$)).

^{13}C NMR (75 MHz, C_6D_6) δ 182.37 (Cu-C), 145.82 (C_{Ar}), 142.69 (C-S), 133.60 (C_{Ar}), 132.48 (CH_{cresol}), 130.74 (C_{imid}), 128.61 (CH_{cresol}), 125.06 (CH_{cresol}), 124.40 (C_{Ar}), 122.72 (C_{Ar}), 29.02 (C-CH_3), 25.02 (C-CH_3), 23.81 (C-CH_3), 21.07 ($CH_{3cresol}$).

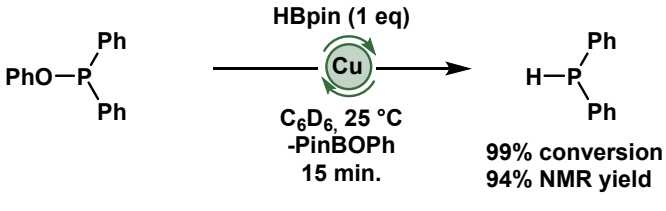
Catalytic activity of [Cu(IPr)(OC(H)(CF$_3$)$_2$)] (4) in insertion and cross-metathesis reactions



(S3)



1,3,5-trimethoxybenzene (89 µmol, 14.9 mg) and [Cu(IPr)(OC(H)(CF$_3$)$_2$)] (0.02 eq., 1.5 mg) was dissolved was dissolved in 500 µL C_6D_6 and the solution was transferred to a J. Young's NMR tube. Phenyl isocyanate (0.1 mmol, 10.9 µL) was added, followed by PinBH (1.3 eq., 18.8 µL) Reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy.



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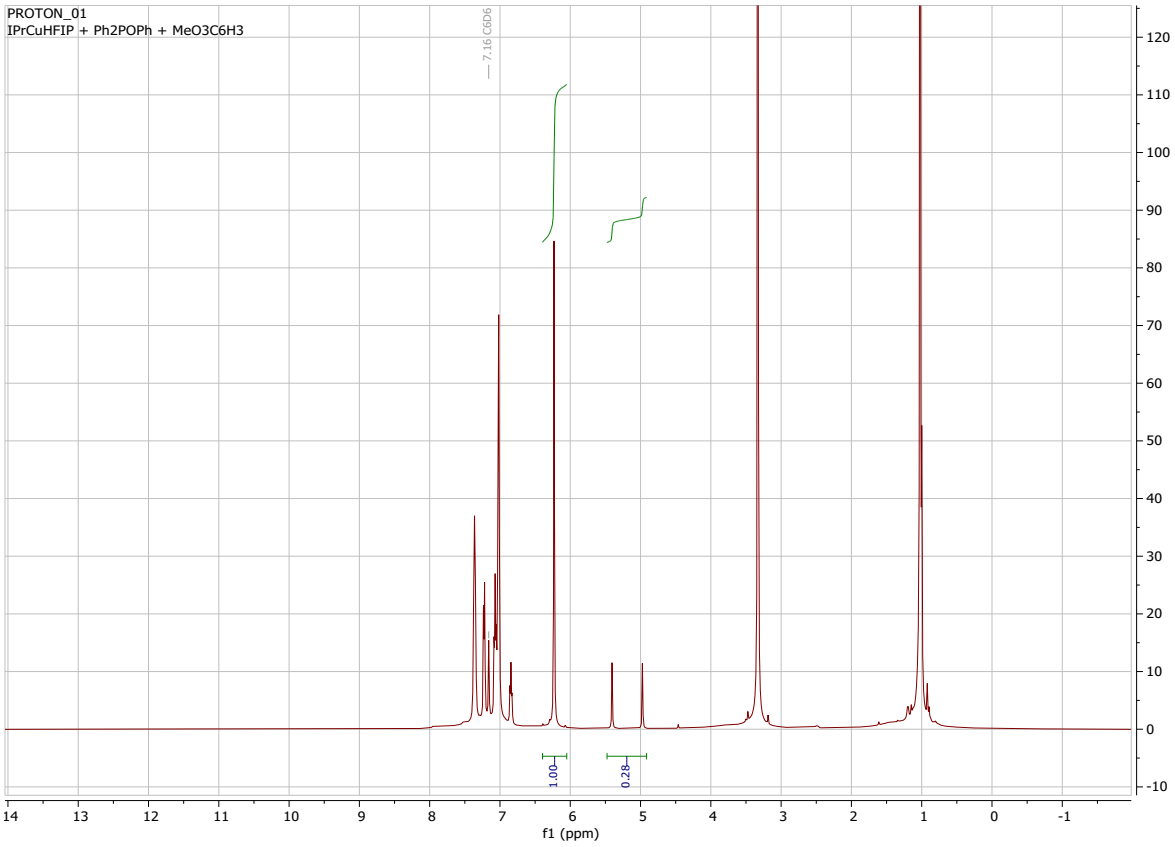
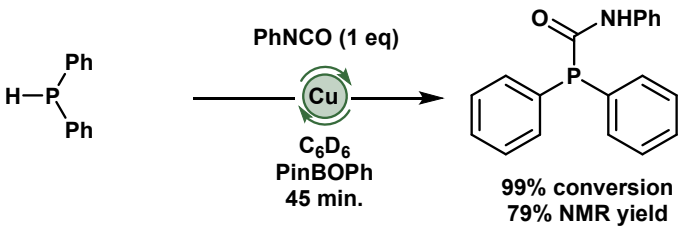
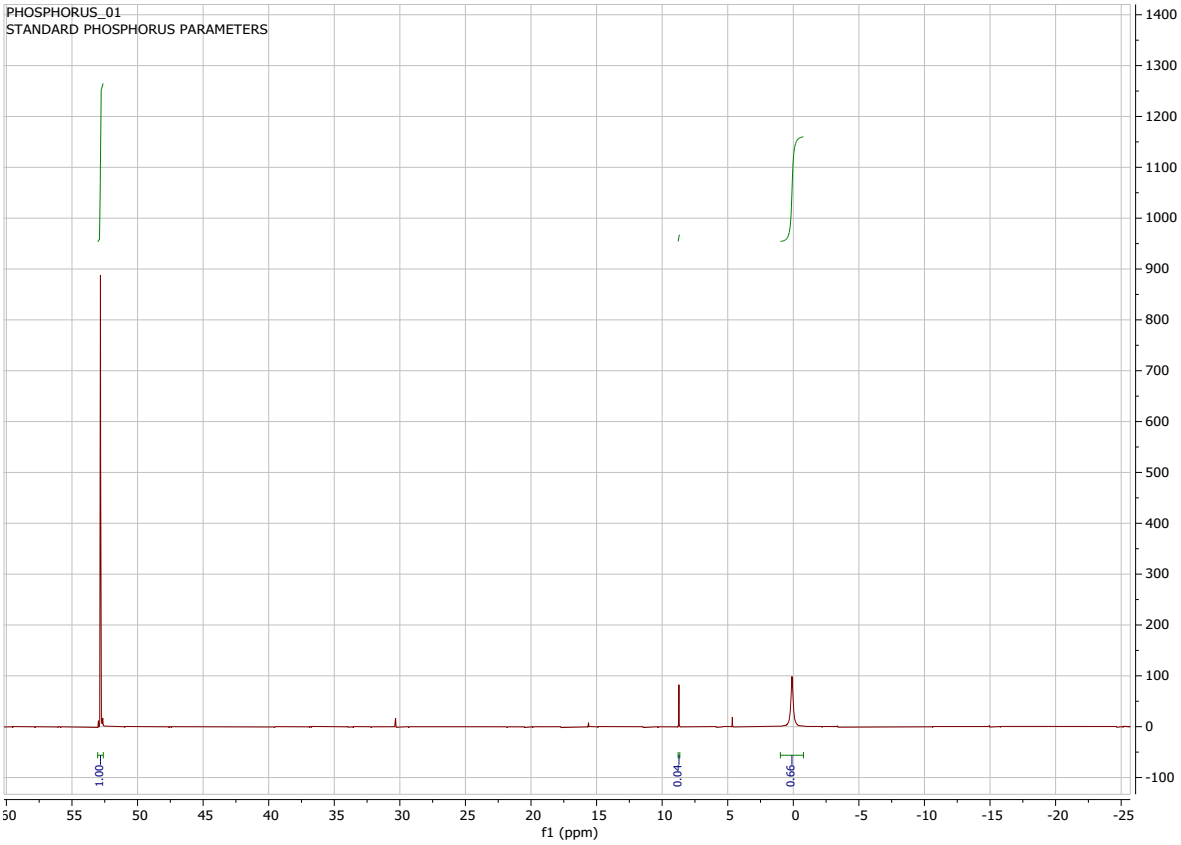


In a vial in a glovebox, to a C_6D_6 solution (0.5 mL) of 1,3,5-trimethoxybenzene (17.8 mg, 106 µmol), [Cu(IPr)(OC(H)(CF_3)$_2$] (0.02 eq., 1.5 mg), and diphenyl phosphinite (27.8 mg, 0.1 mmol) The reaction mixture was transferred to an NMR tube and was added PinBH (1 eq, 14.5 µL). The tube was sealed with a J. Young's valve then removed from the glovebox and the reaction monitored by NMR spectroscopy.



(S5)



In the glovebox, to the resultant solution of the previous reaction was added phenyl isocyanate (0.1 mmol, 10.9 µL) was then added. The tube was sealed with a J. Young's valve then removed from the glovebox and the reaction monitored by NMR spectroscopy. Yield was calculated relative to NMR yield of Ph_2PH (*vide supra*) by adding triethylphosphine oxide (0.111 mmol 14.9 mg) and exchanging the solvent for $CDCl_3$. A 94:6 ratio of single and double insertion (to give $HN(Ph)C(O)N(Ph)C(O)PPh_2$) was observed.

References

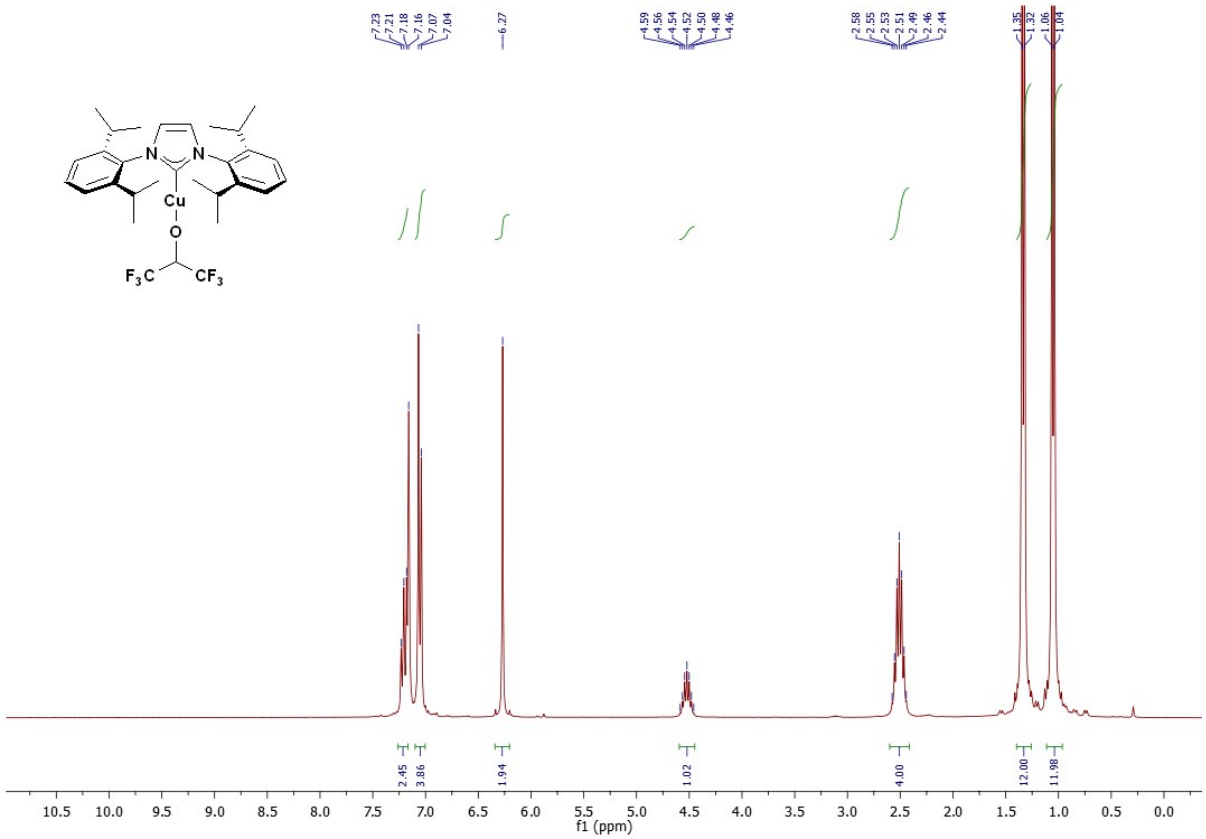
1 O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan and C. S. J. Cazin, *Chem. Commun.*, 2013, **49**, 10483–10485.

2 G. C. Fortman, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2010, **29**, 3966–3972.

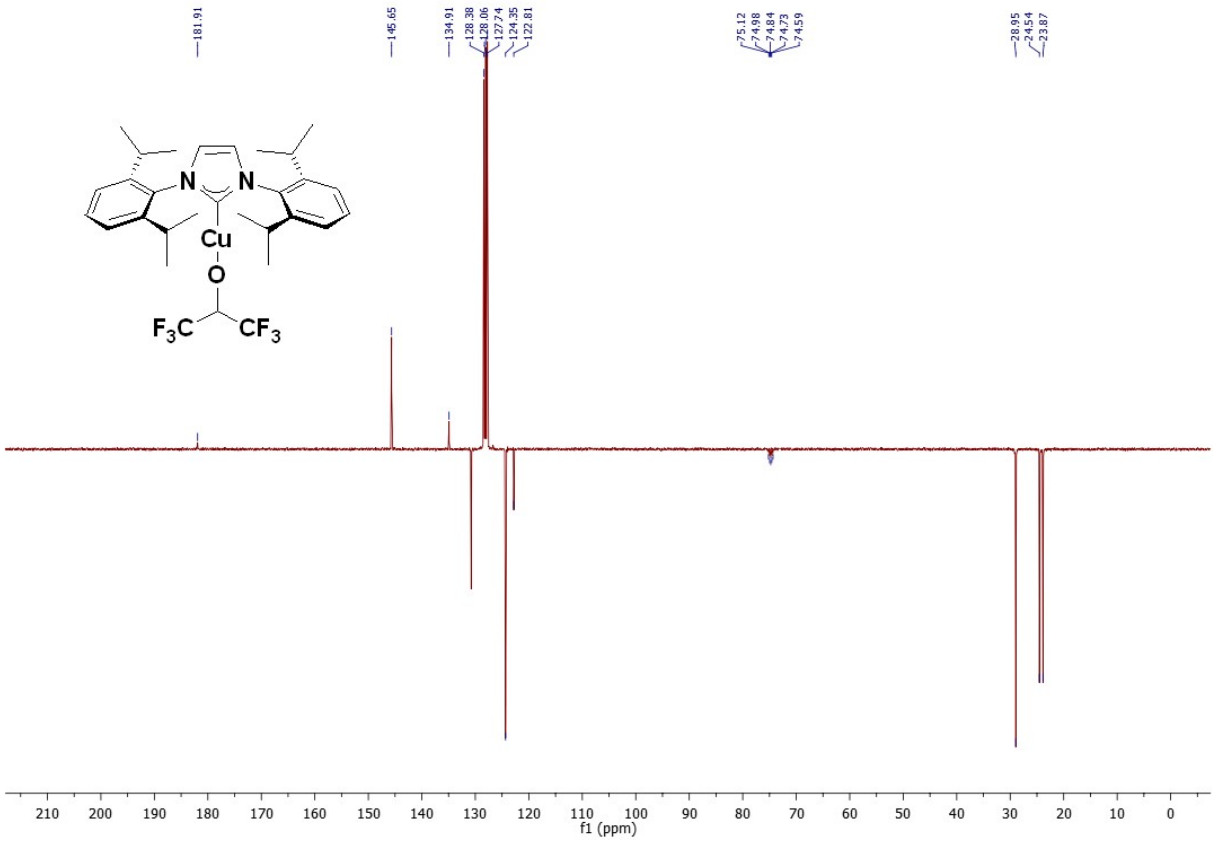
3 N. V. Tzouras, E. A. Martynova, X. Ma, T. Scattolin, B. Hupp, H. Busen, M. Saab, Z. Zhang, L. Falivene, G. Pisanò, K. Van Hecke, L. Cavallo, C. S. J. Cazin, A. Steffen and S. P. Nolan, *Chem. - A Eur. J.*, 2021, **27**, 11904–11911.

4 J. Plotzitzka and C. Kleeberg, *Inorg. Chem.* 2017, **56**, 11, 6671–6680**.**

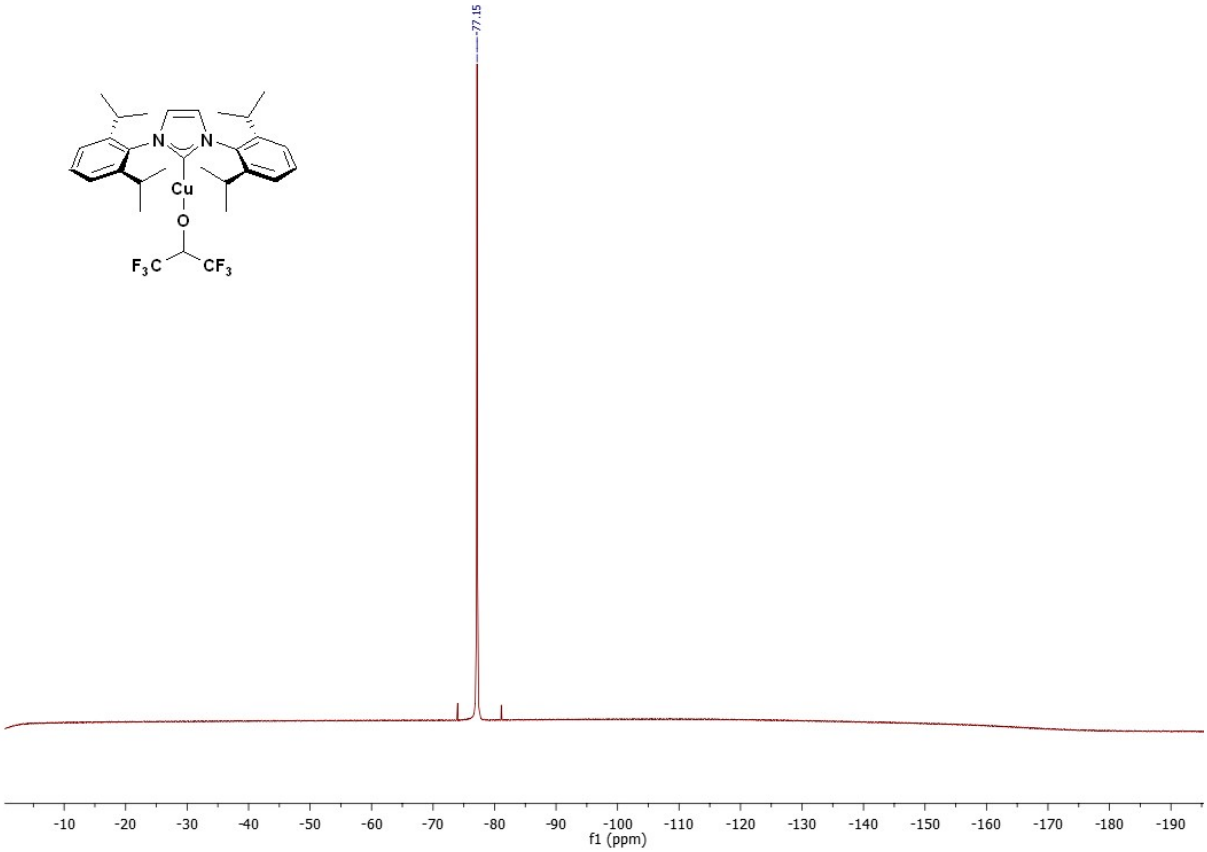
NMR spectrum: [Cu(IPr)(OC(H)(CF_3)$_2$] (**4**) ^{1}H NMR (C_6D_6)



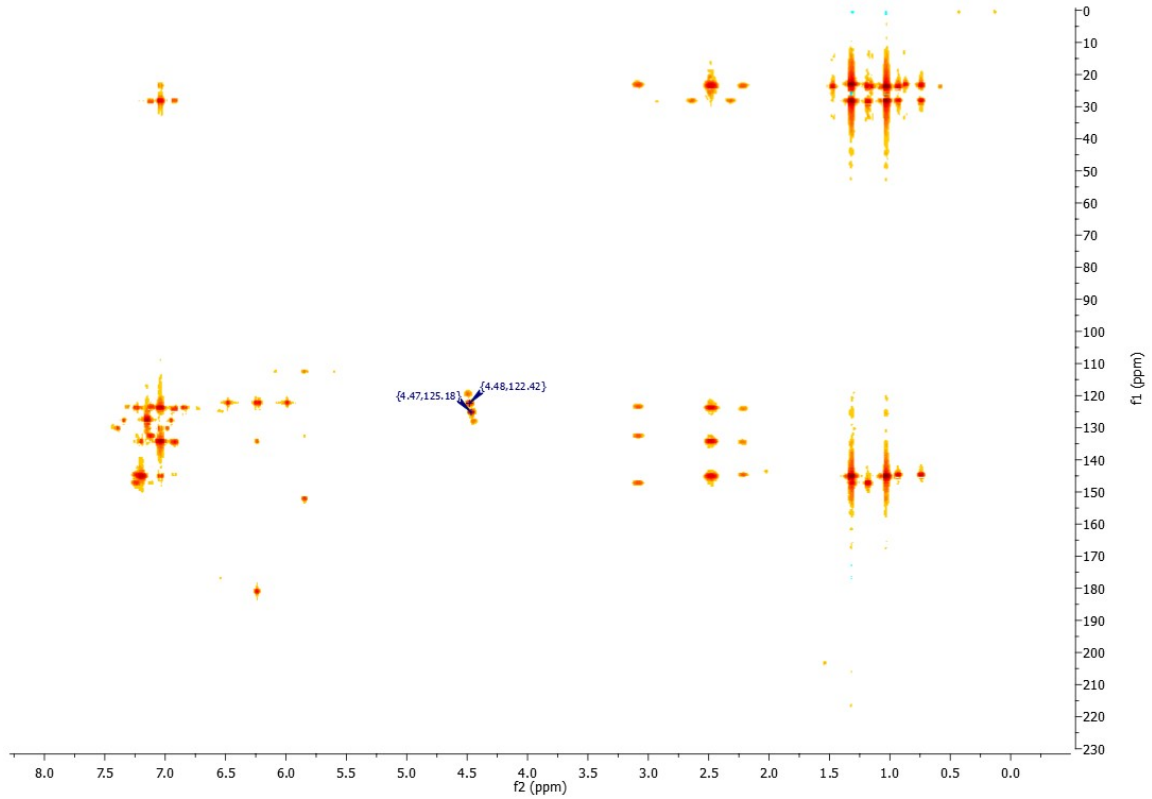
[Cu(IPr)(OC(H)(CF_3)$_2$] (**4**) ^{13}C NMR (C_6D_6)



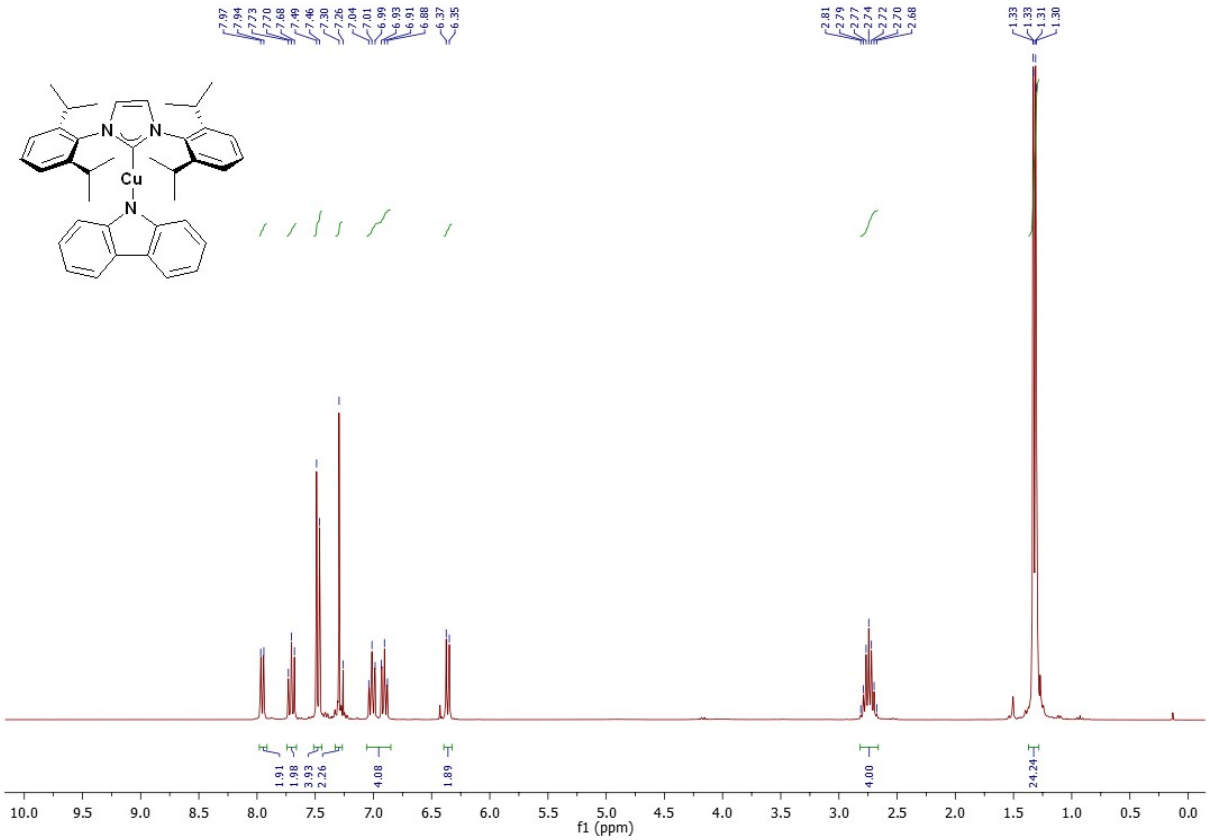
[Cu(IPr)(OC(H)(CF_3)$_2$] (**4**) ^{19}F NMR (C_6D_6)



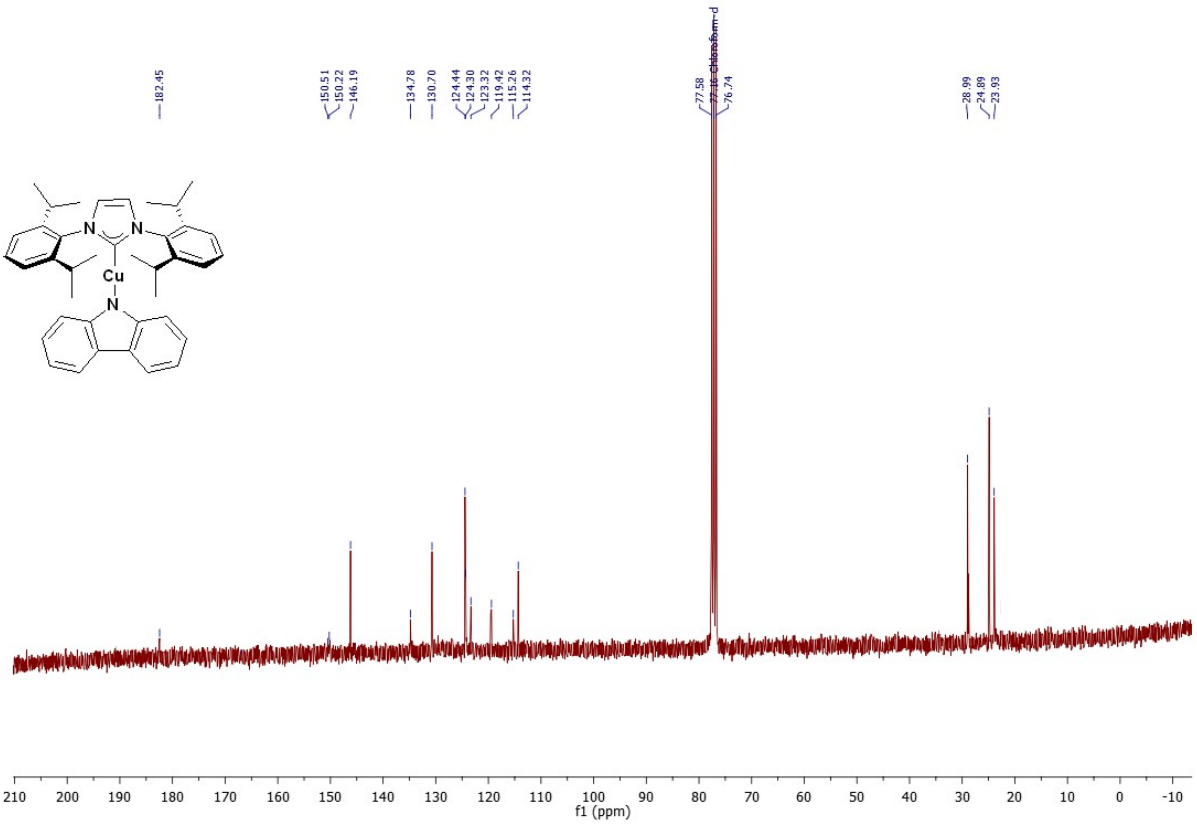
2D HMBC of [Cu(IPr)(OC(H)(CF_3)$_2$] (**4**) showing the chemical shift of the CF_3 groups by correlation to the O-CH signa



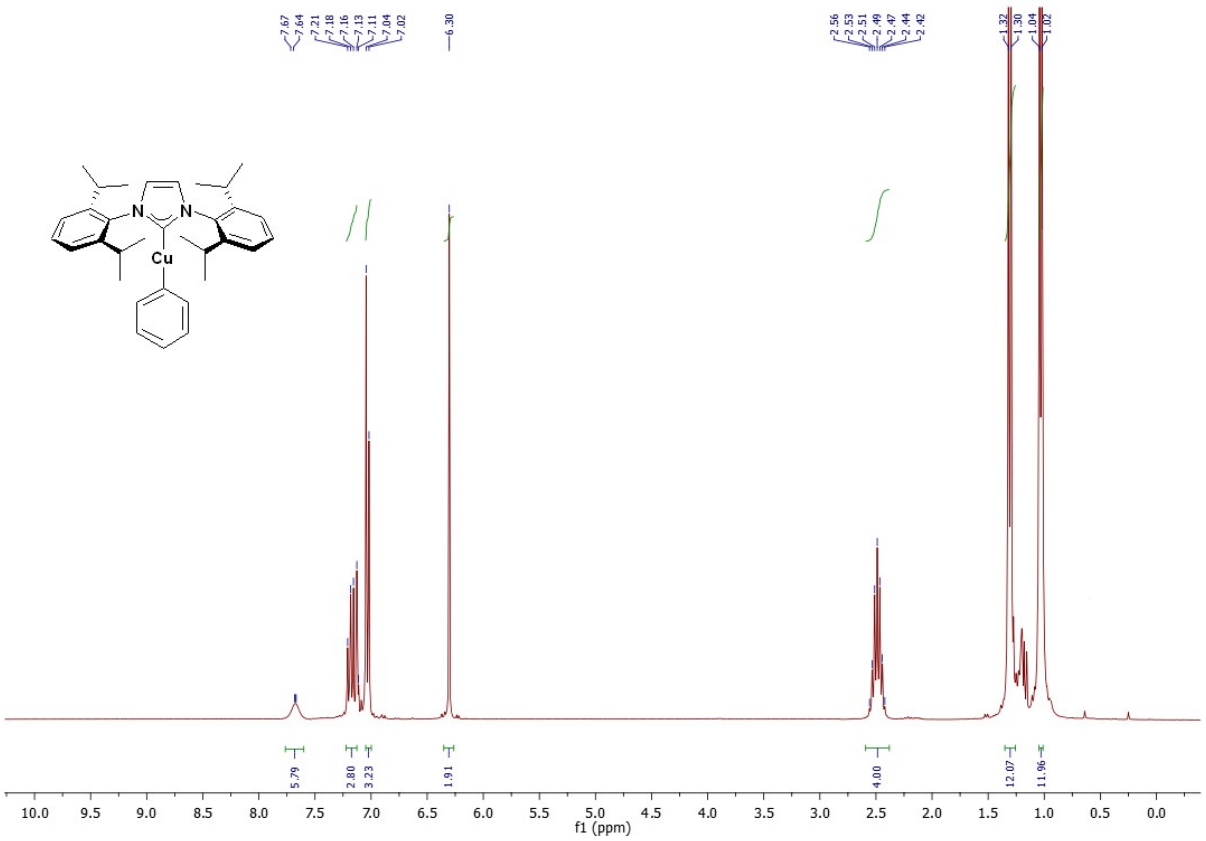
[Cu(IPr)(Cbz)] (**5**) ^{1}H NMR (C_6D_6)



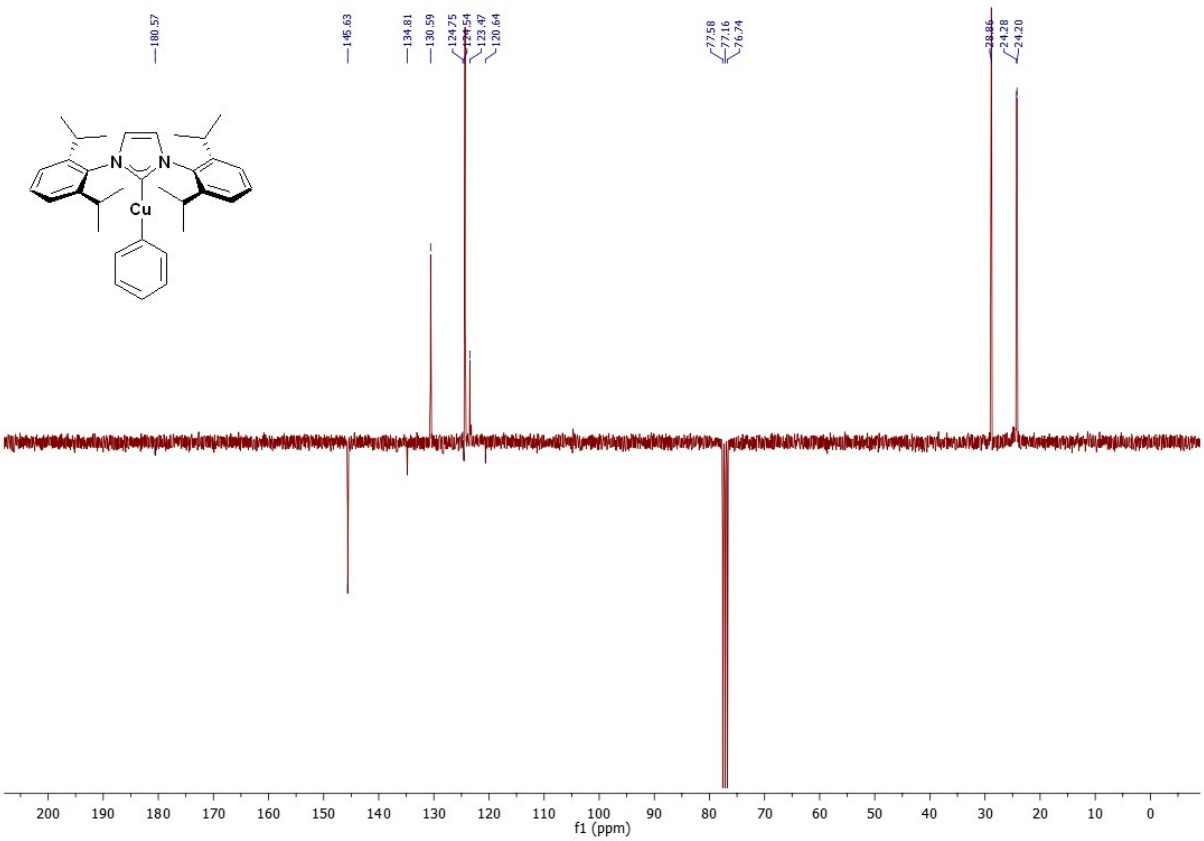
[Cu(IPr)(Cbz)] (**5**) ^{13}C NMR ($CDCl_3$)



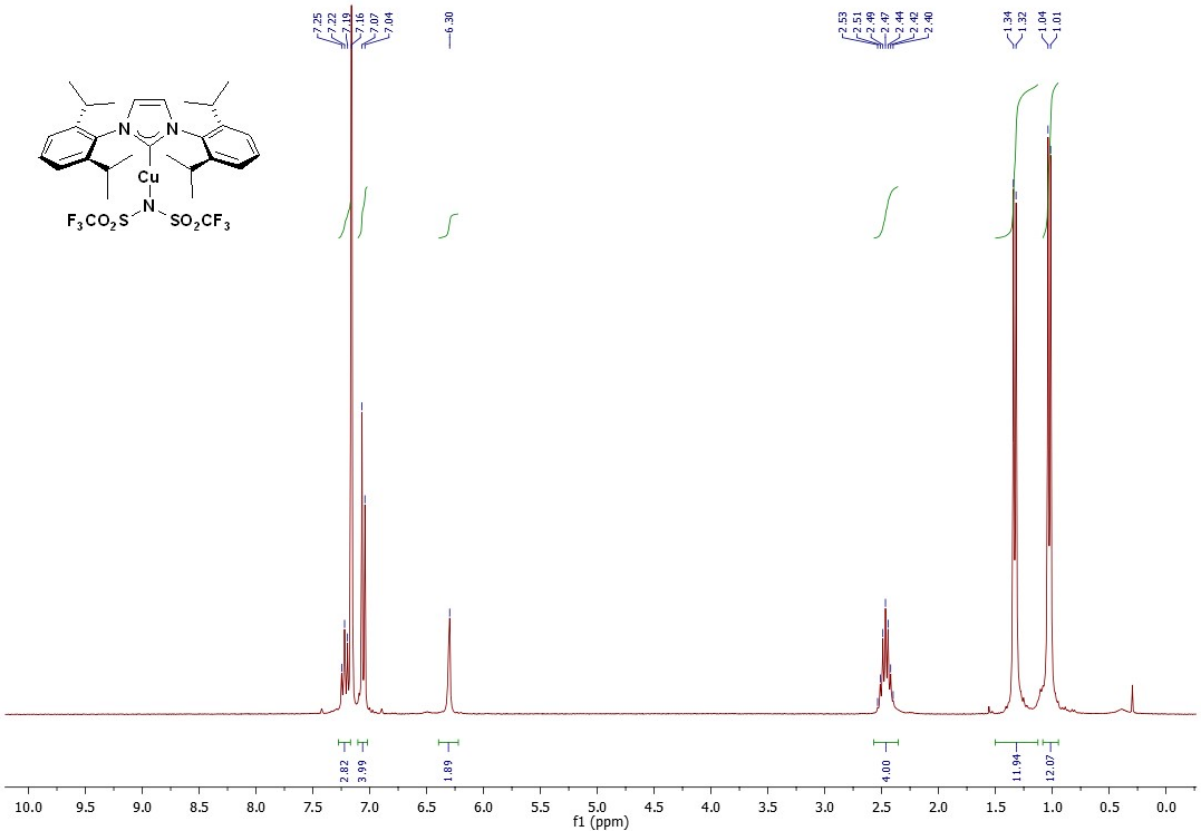
[Cu(IPr)(Ph)] (**6**) ^{1}H NMR (C_6D_6)



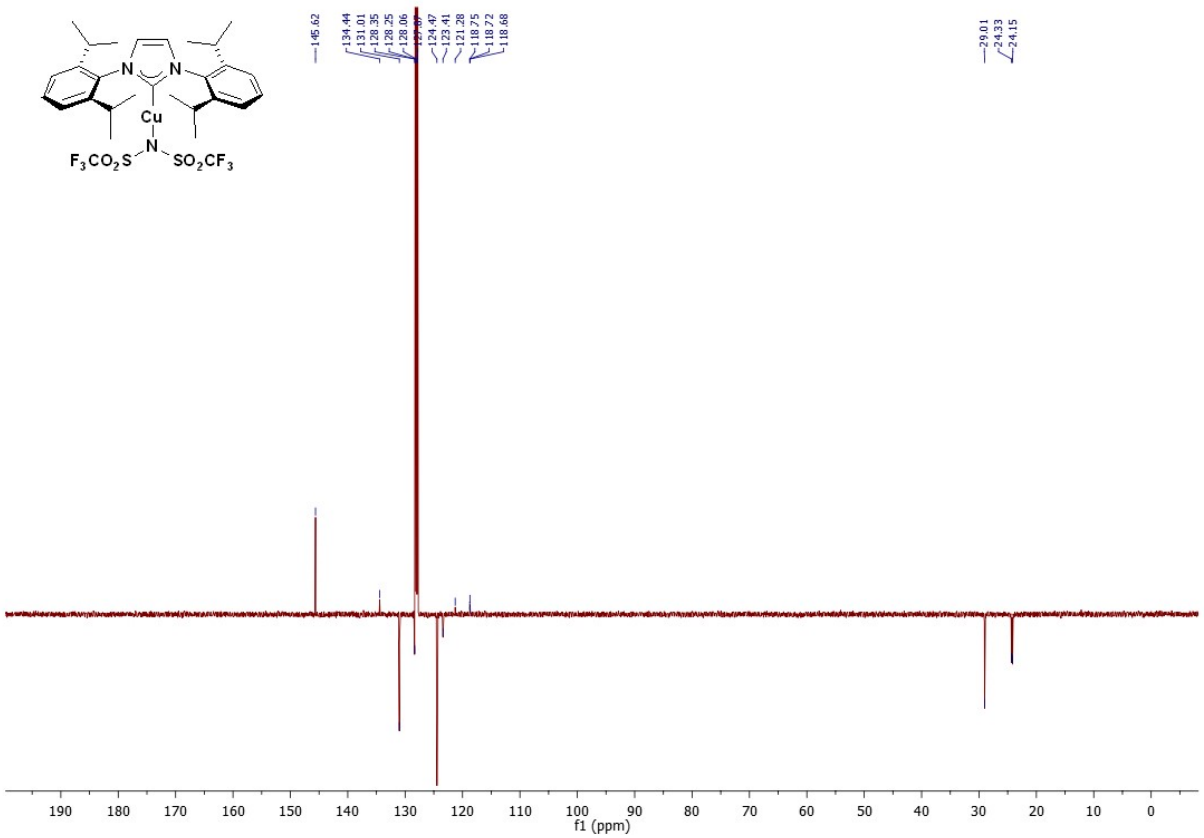
[Cu(IPr)(Ph)] (**6**) ^{1}H NMR ($CDCl_3$)



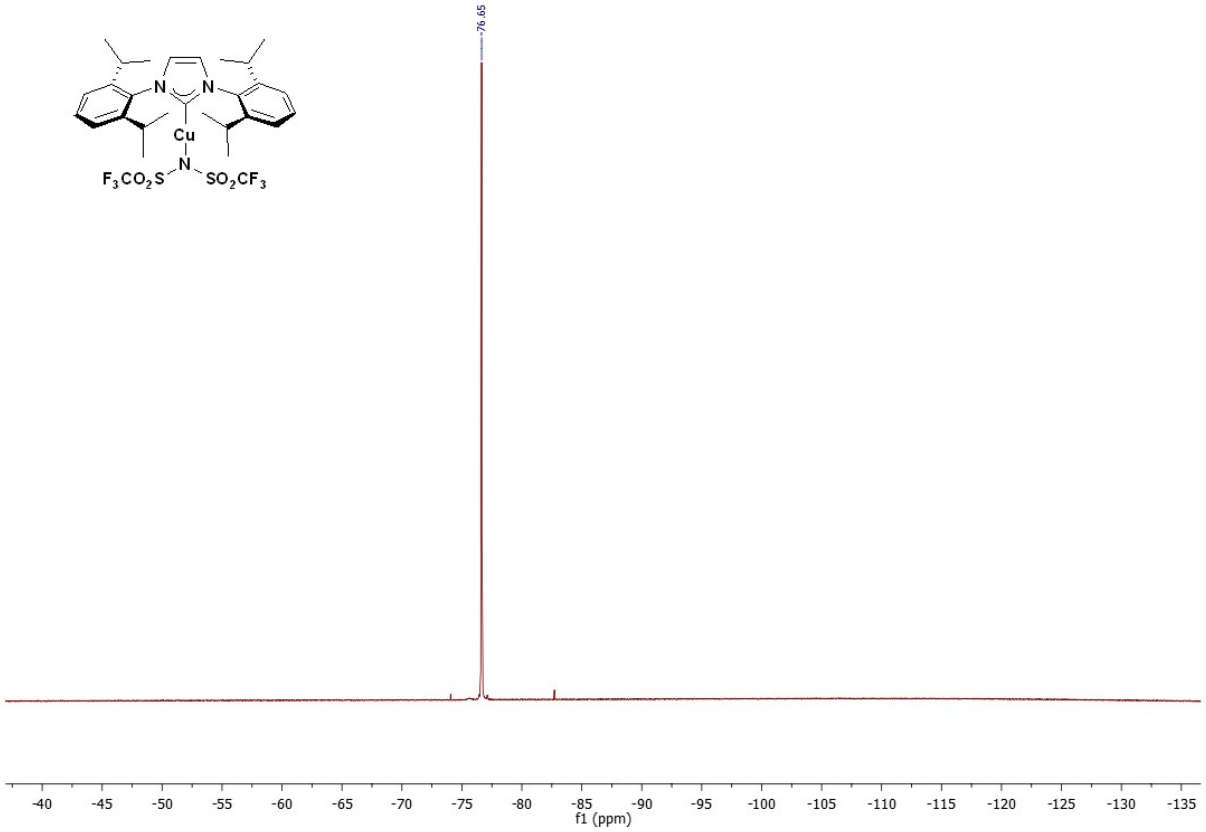
[Cu(IPr)(NTf$_2$)] (**7**) ^{1}H NMR (C_6D_6)



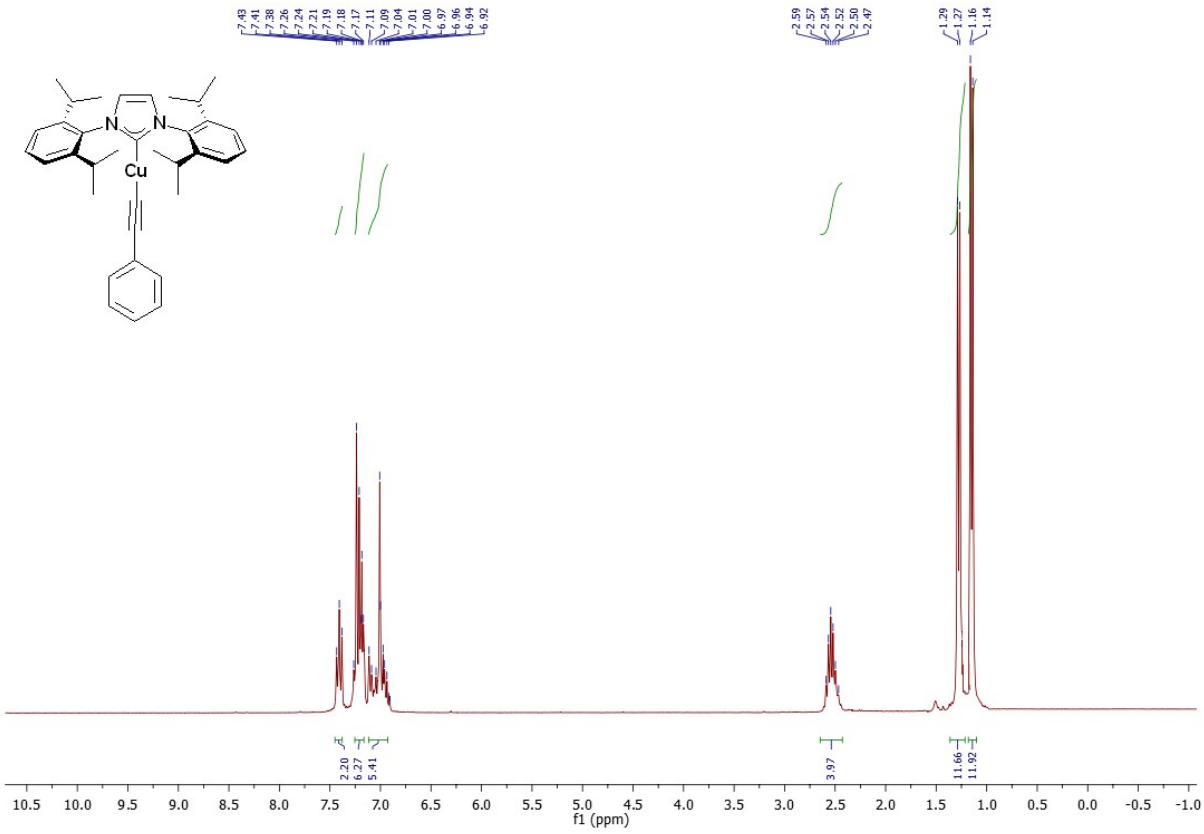
[Cu(IPr)(NTf$_2$)] (**7**) ^{13}C NMR (C_6D_6)



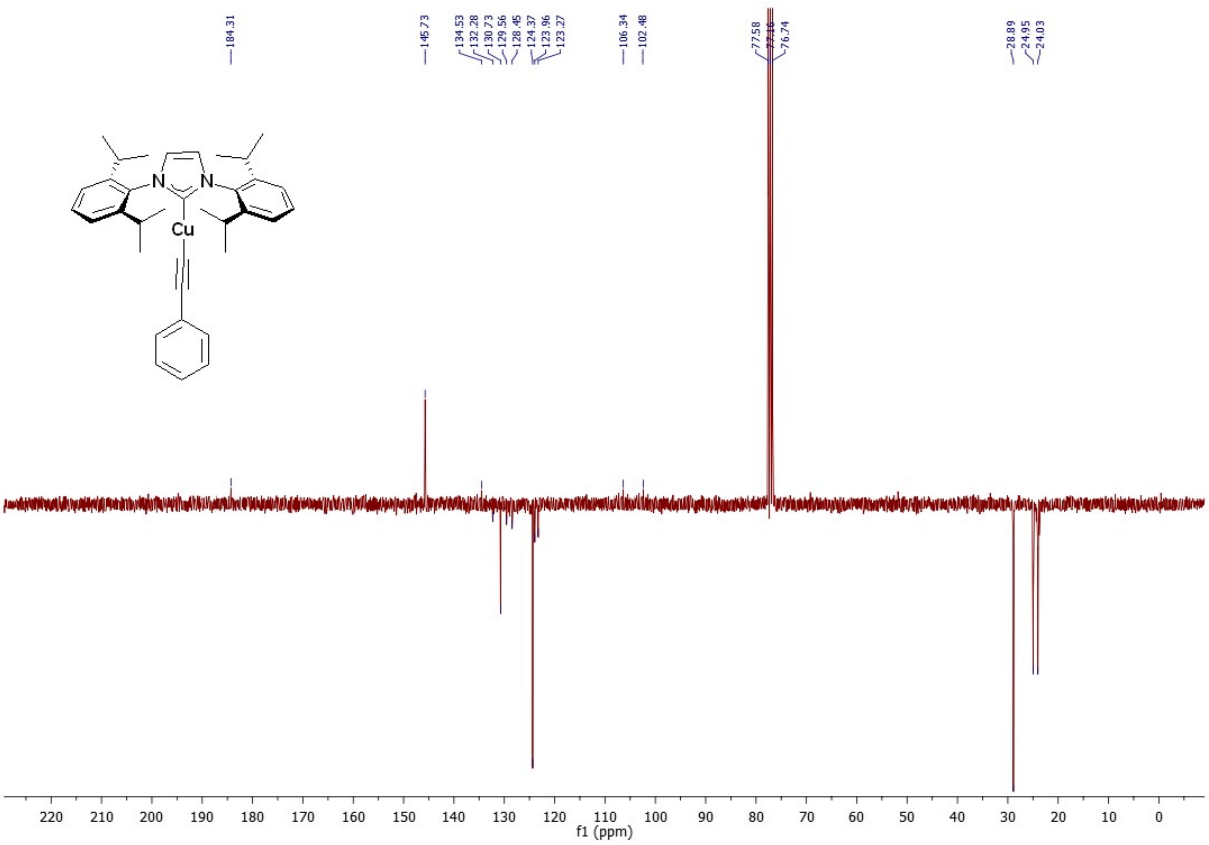
[Cu(IPr)(NTf_2)] (**7**) $^{19}F\{H\}$ NMR (C_6D_6)



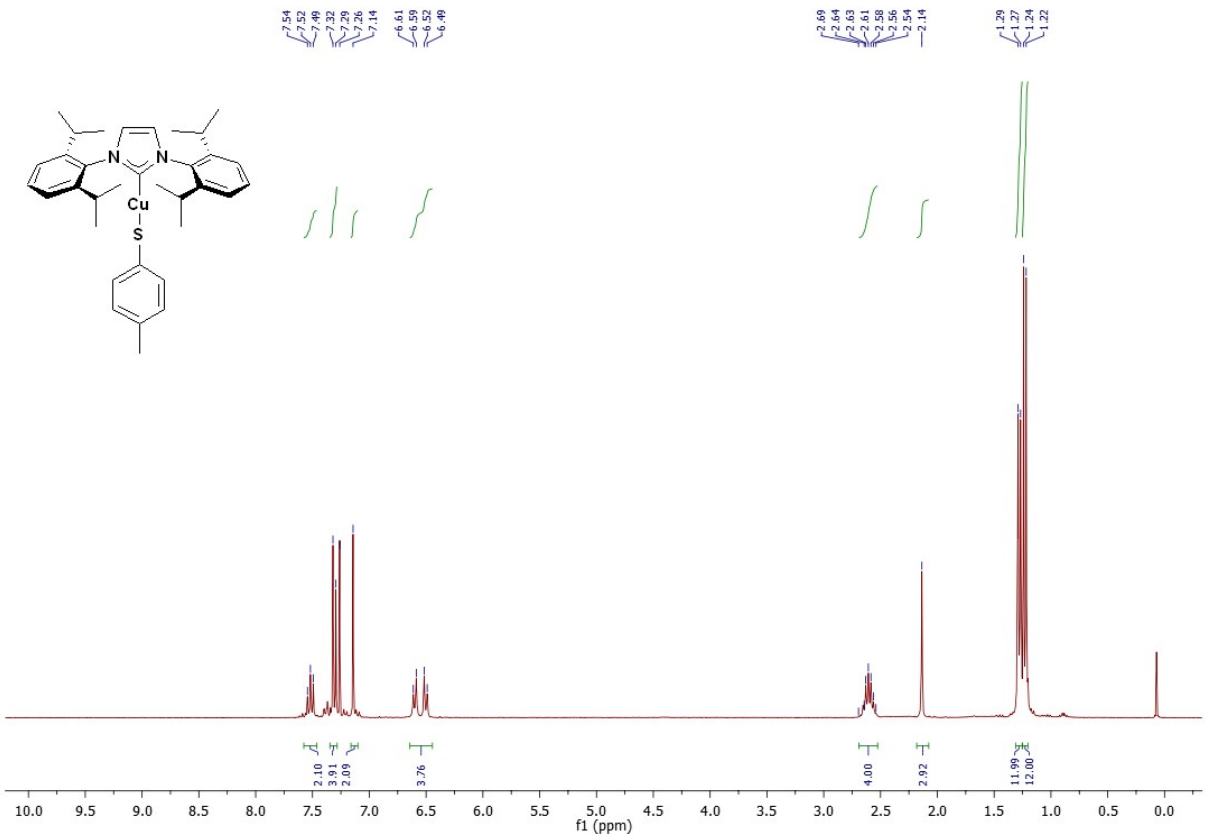
[Cu(IPr)(CCPh)] (**8**) ^{1}H NMR ($CDCl_3$)



[Cu(IPr)(CCPh)] (**8**) ^{13}C NMR ($CDCl_3$)



[Cu(IPr)(SPhMe)] (**9**) ^{1}H NMR (C_6D_6)



[Cu(IPr)(SPhMe)] (**9**) ^{13}C NMR (C_6D_6)