Electronic Supporting Information

Straightforward synthesis of [Cu(NHC)alkynyl] and [Cu(NHC)thiolate] complexes (NHC = N-Heterocyclic Carbene)

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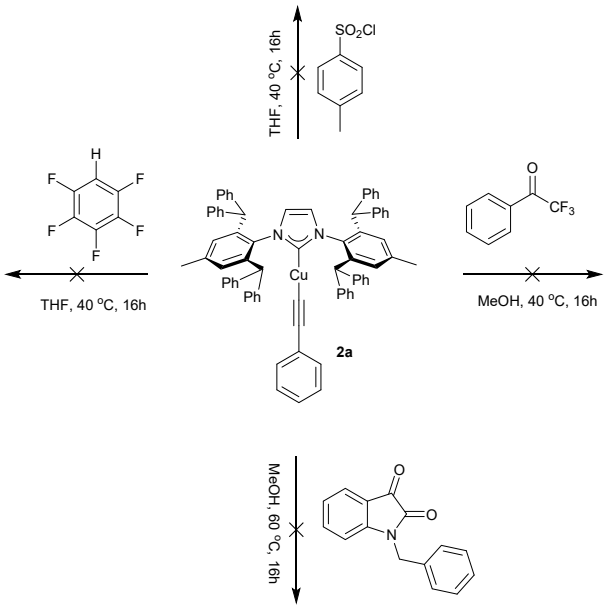
1. General Information

All reactions were carried out in air, unless otherwise noted. Solvents and all other reagents were purchased and used as received without further purification unless otherwise stated. Purification of compounds by filtration was performed using basic alumina or celite purchased from Sigma Aldrich, or syringe membrane filters purchased from Carl Roth. Unless otherwise noted, absolute ethanol, reagent grade acetone, deionized water and freshly crushed, anhydrous bases were used. ^{1}H, ^{13}C-{^{1}H, ^{19}F Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 Ultrashield, Bruker Avance 300 Ultrashield or a Bruker Avance 500 spectrometer at 298 K using the residual solvent peak as reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; C_6D_6: δ_H = 7.16 ppm, δ_C = 128.06 ppm). Peaks are assigned as: s (singlet), d (doublet), t (triplet), h (heptuplet) and m (multiplet). All chlorinated solvents (including the deuterated ones) were neutralized prior to use by filtration through dried basic alumina. Elemental analyses were performed at Université de Namur, rue de Bruxelles, 55 B-5000 Namur, Belgium.

2. Unsuccessful reactivity tests between **2a** and different substrates.



Scheme S1. The reactivity of complex **2a** with different substrates.

3. NMR study of spectra of IPr-Cu-alkynyl complexes

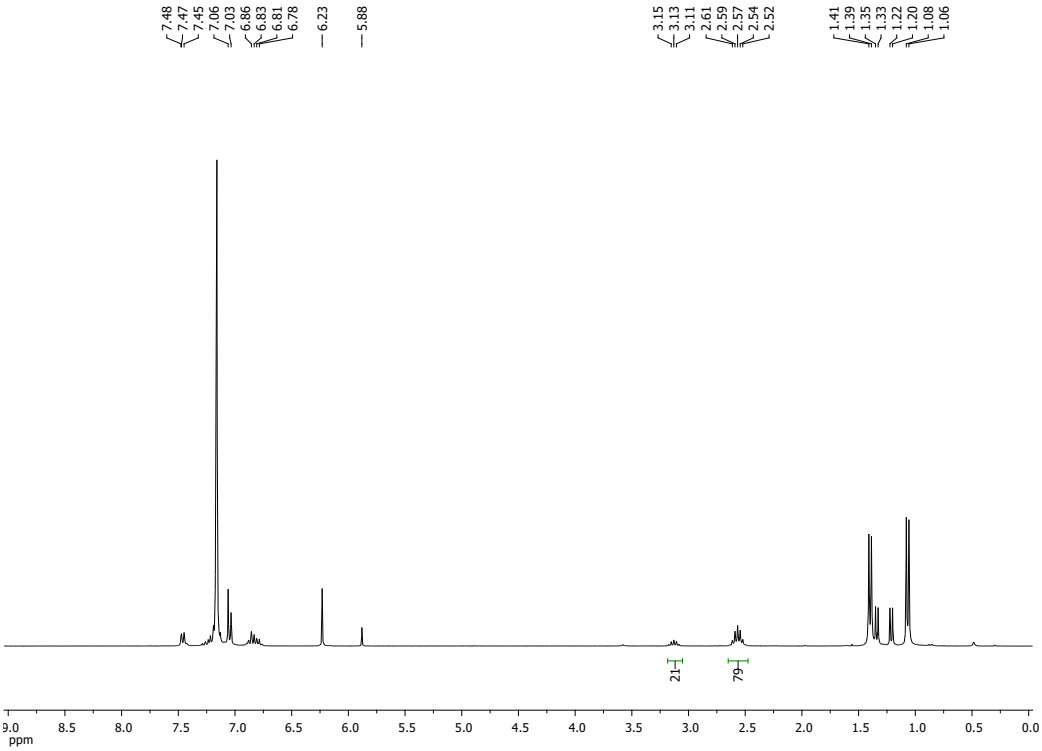


Figure S2. Disproportionation ratio of [Cu(IPr)(C≡CPh)] **1a** after 24h in benzene (79:21).

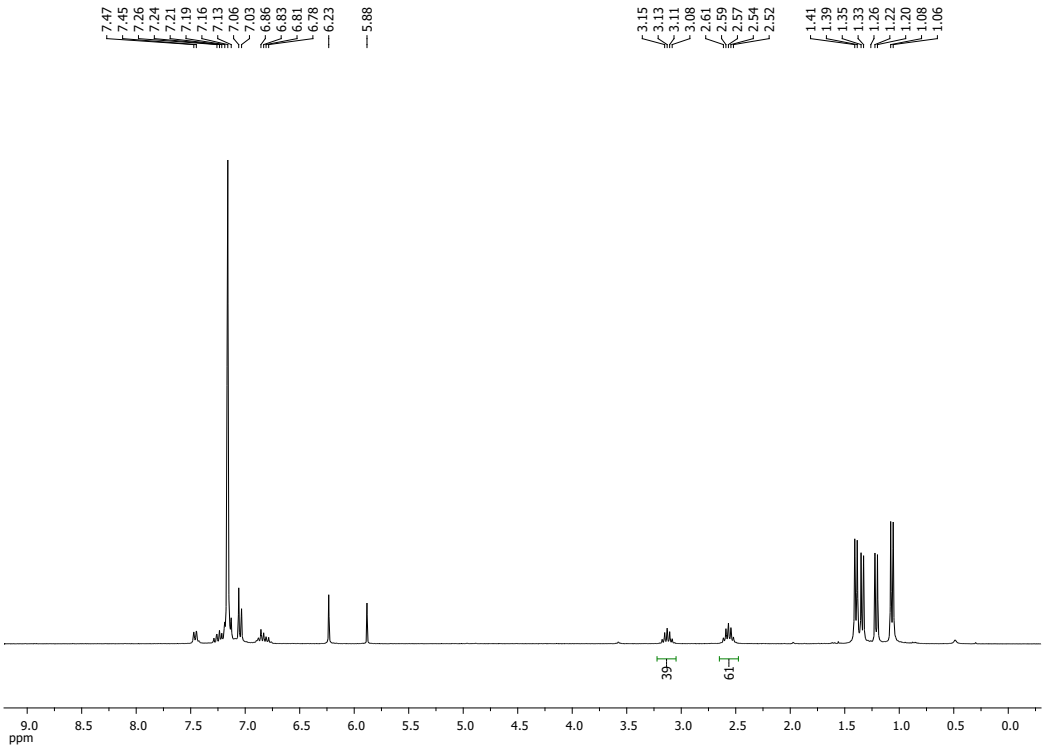


Figure S3. Disproportionation ratio of [Cu(IPr)(C≡CPh)] **1a** after 48h in benzene (61:39).

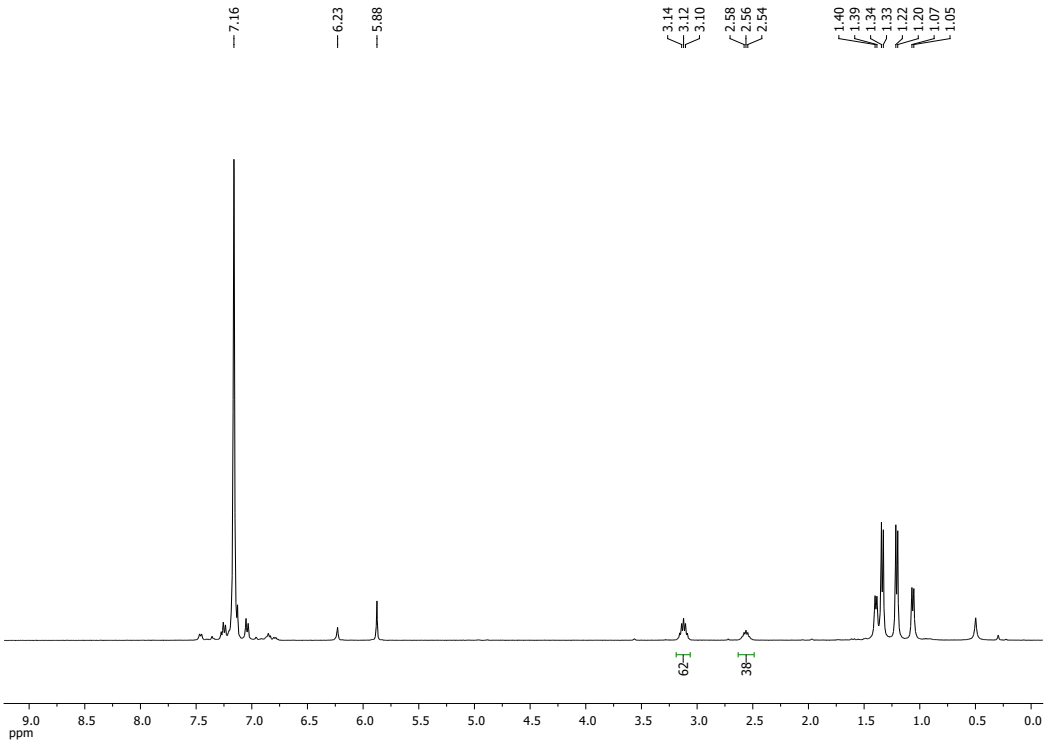


Figure S4. Disproportionation ratio of [Cu(IPr)(C≡CPh)] **1a** after 72h in benzene (68:62).

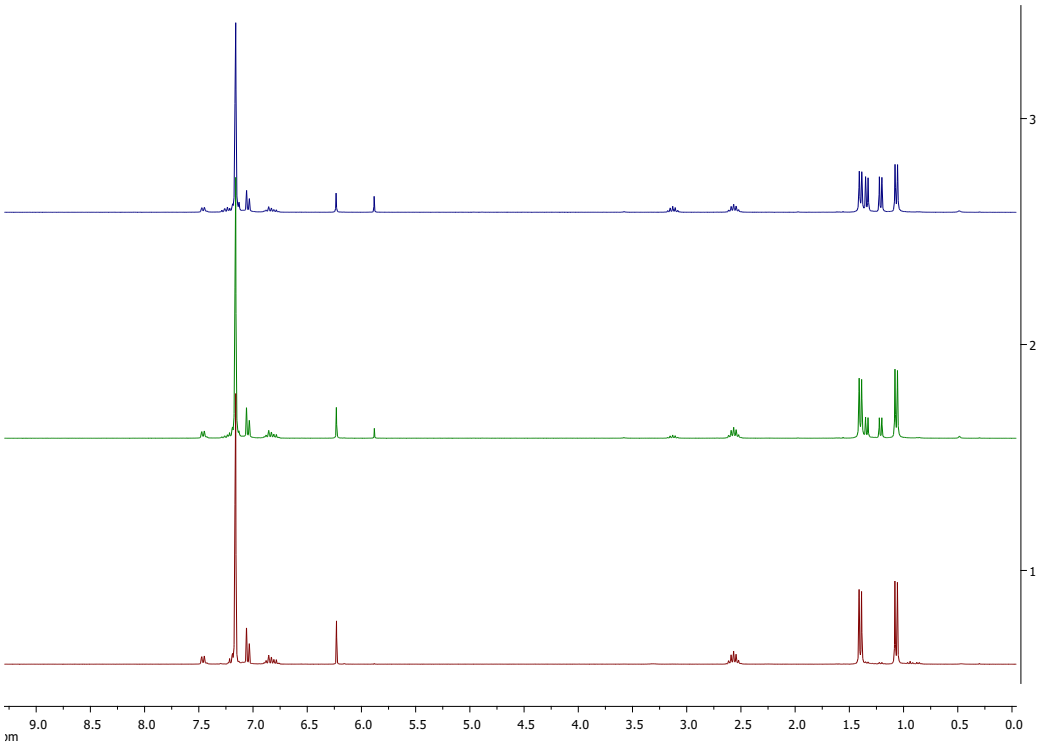
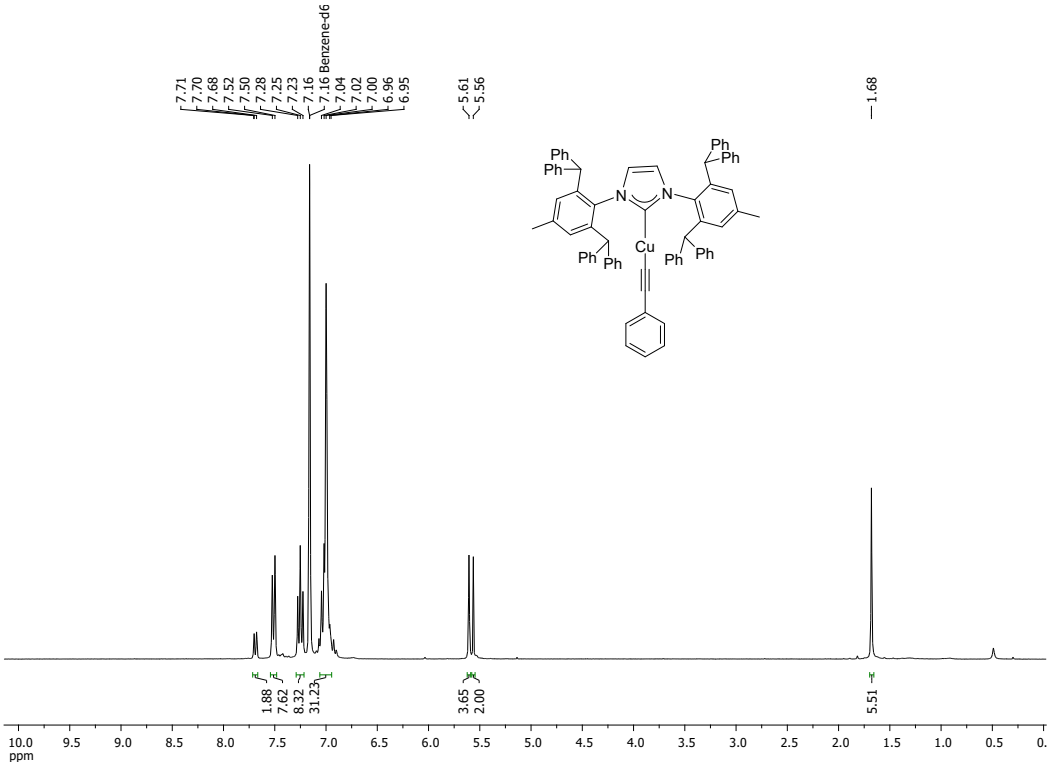
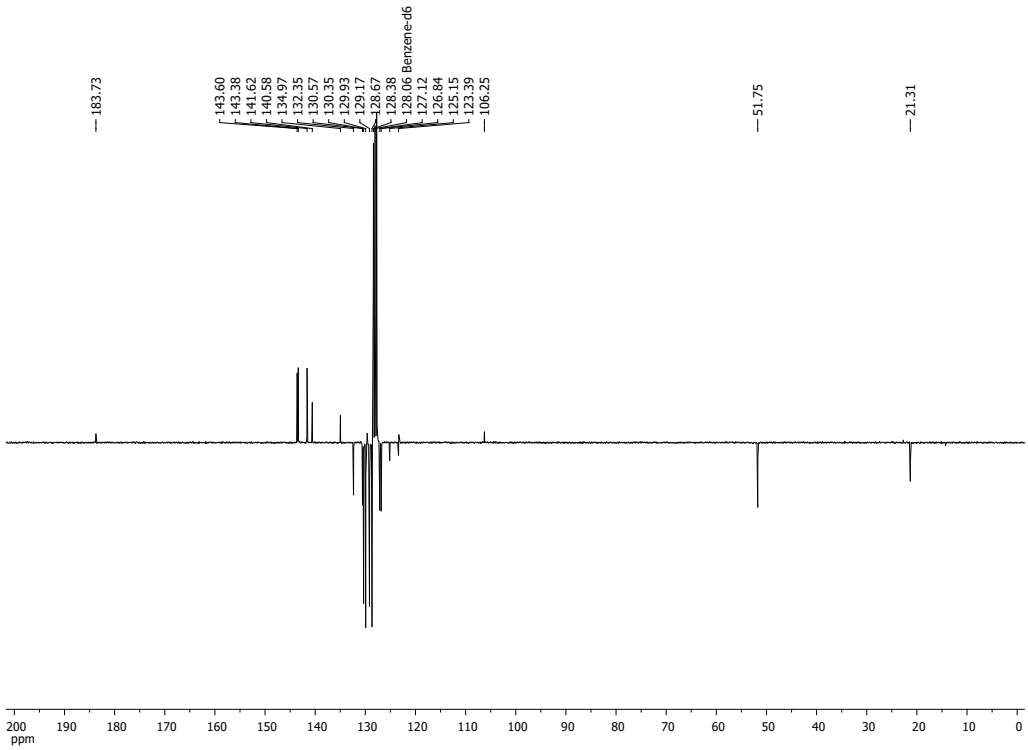


Figure S5. Disproportionation ratio of [Cu(IPr)(C≡CPh)] **1a** over 24h (1), 48h (2) and 72h (3) in benzene.

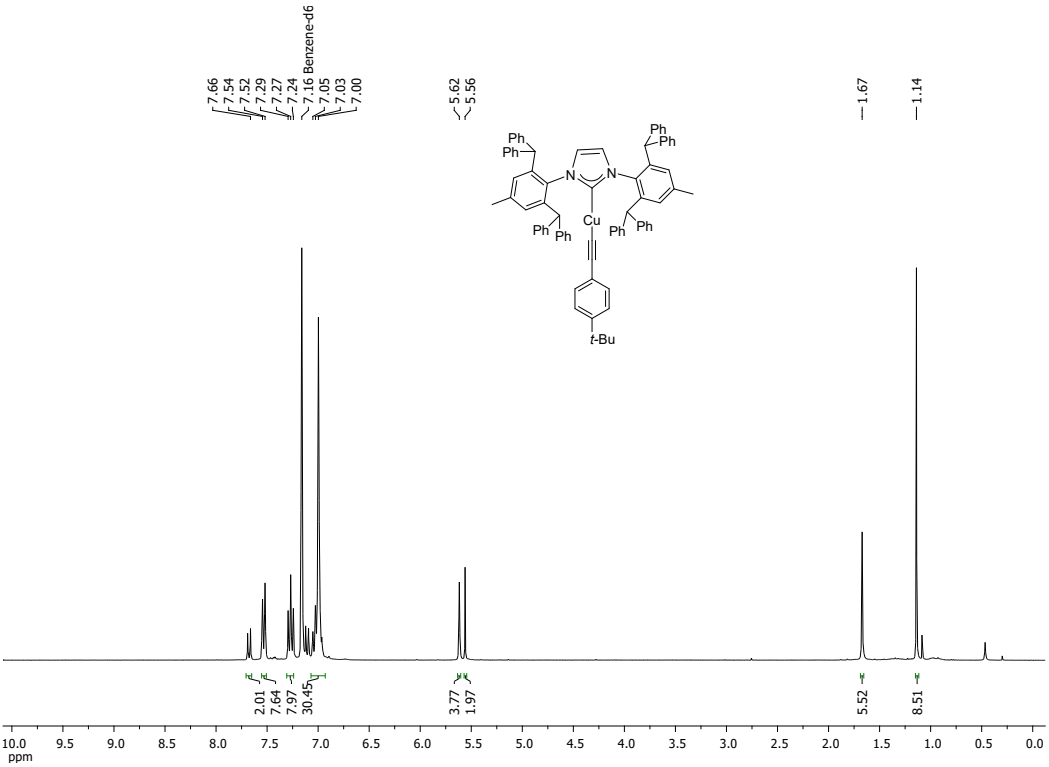
4. NMR spectra of IPr*-Cu-alkynyl complexes and their derivatives

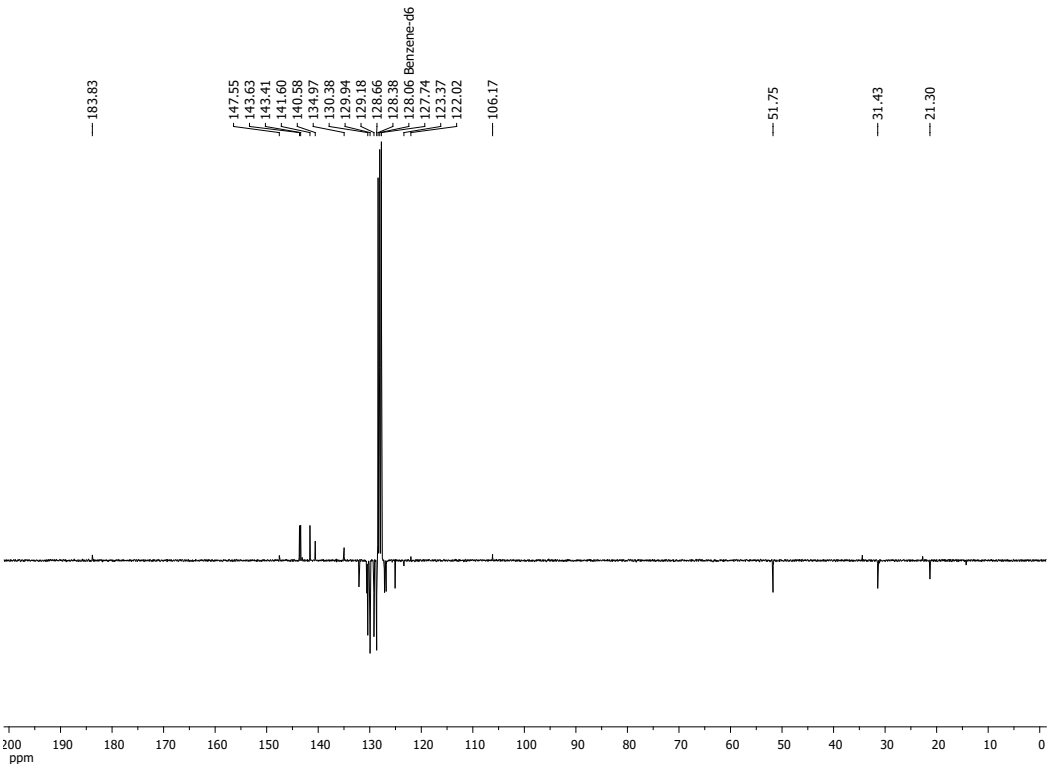
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of [Cu(IPr*)(phenylacetylide)] (2a)



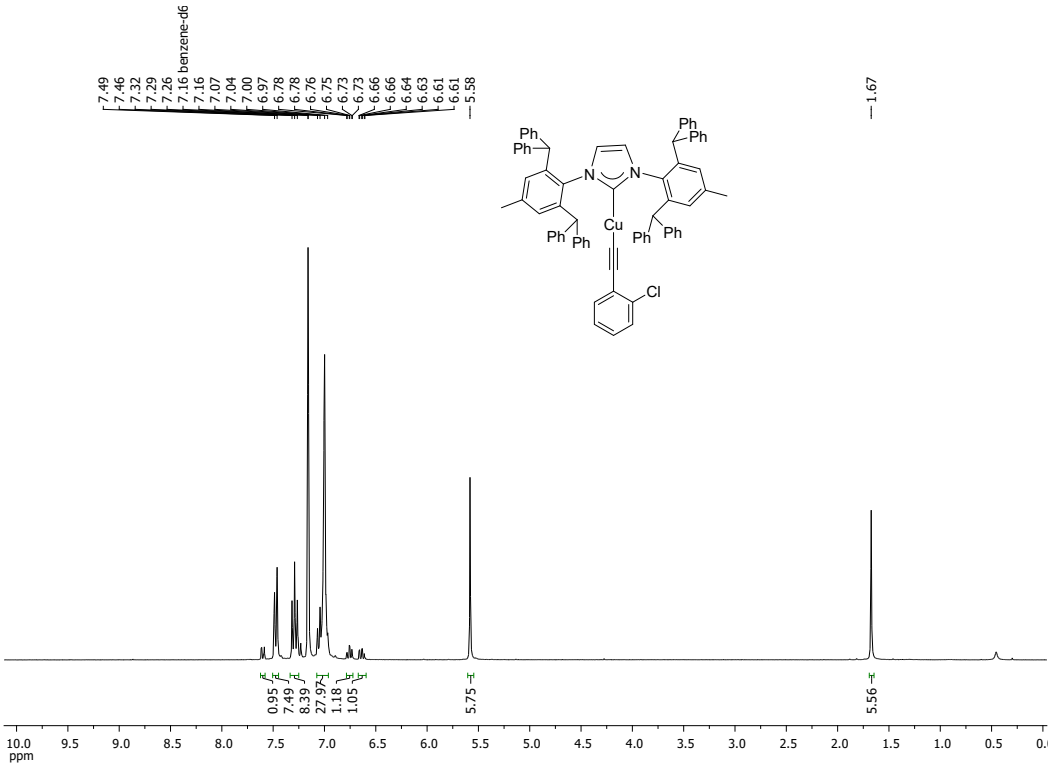


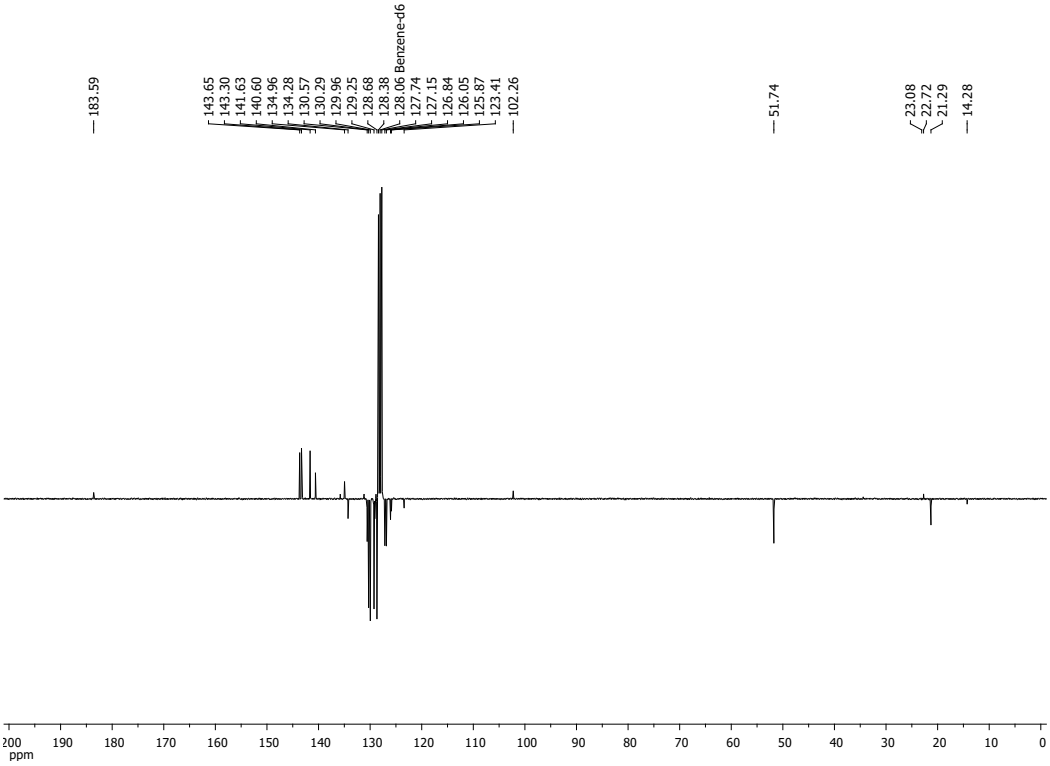
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of [Cu(IPr*)(4'-*t*-Bu-phenylacetylide)] (2b)



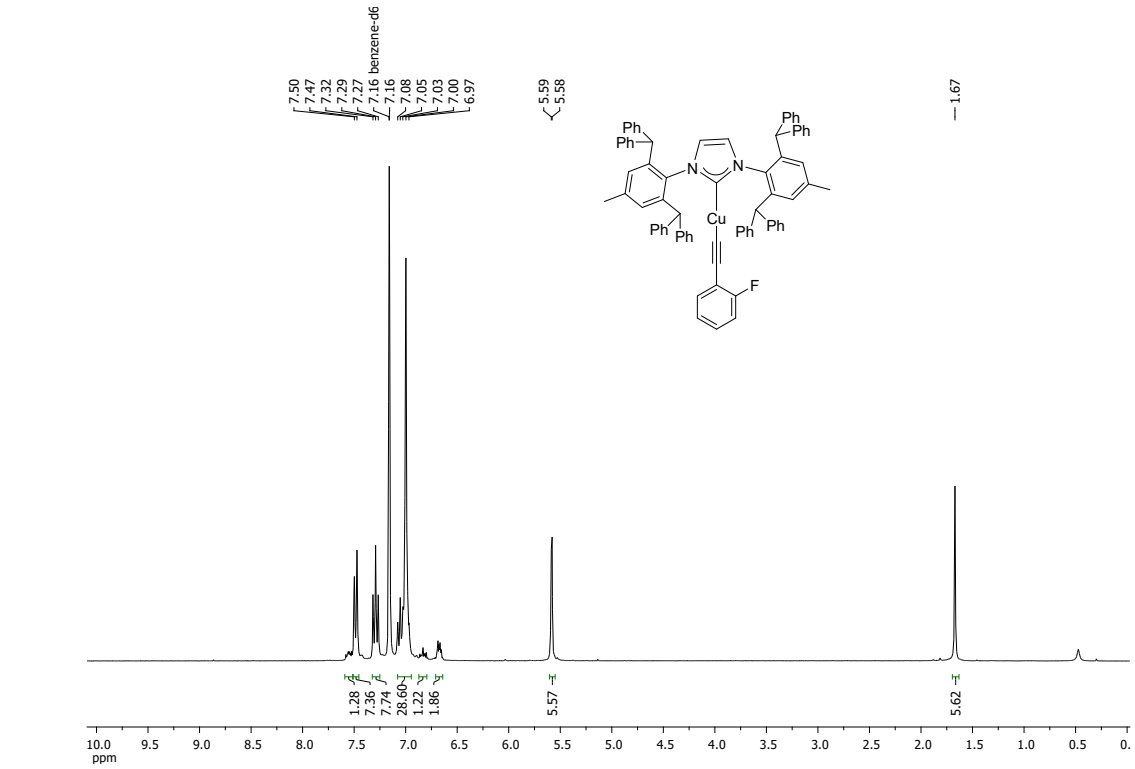


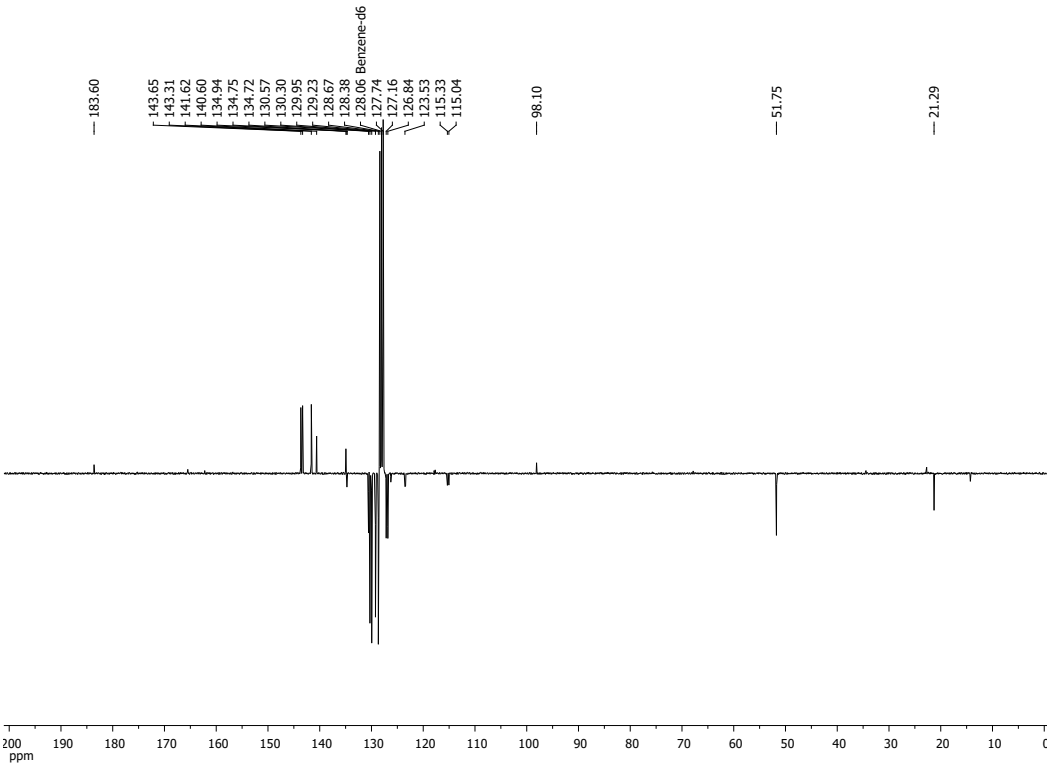
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of [Cu(IPr*)((2-Chlorophenyl)acetylene)] (2c)

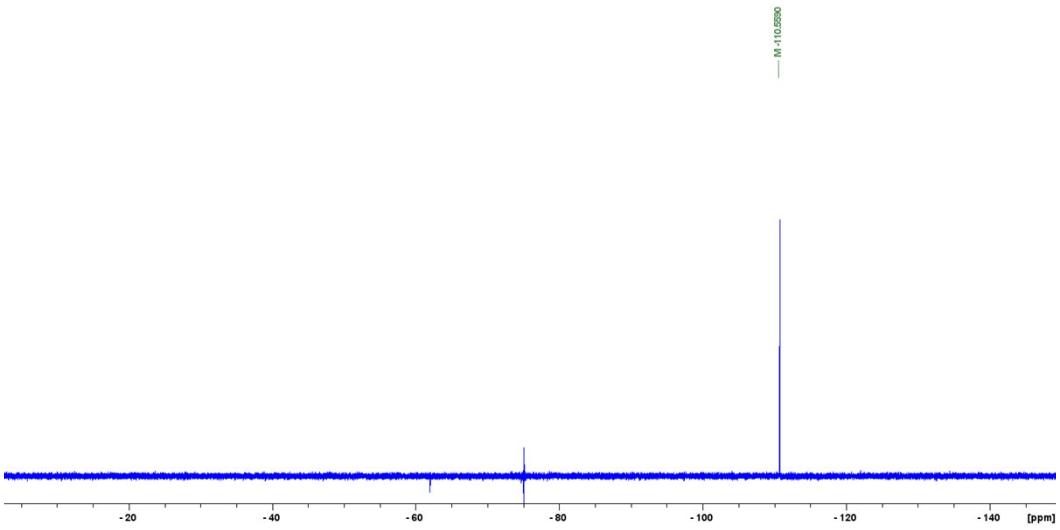




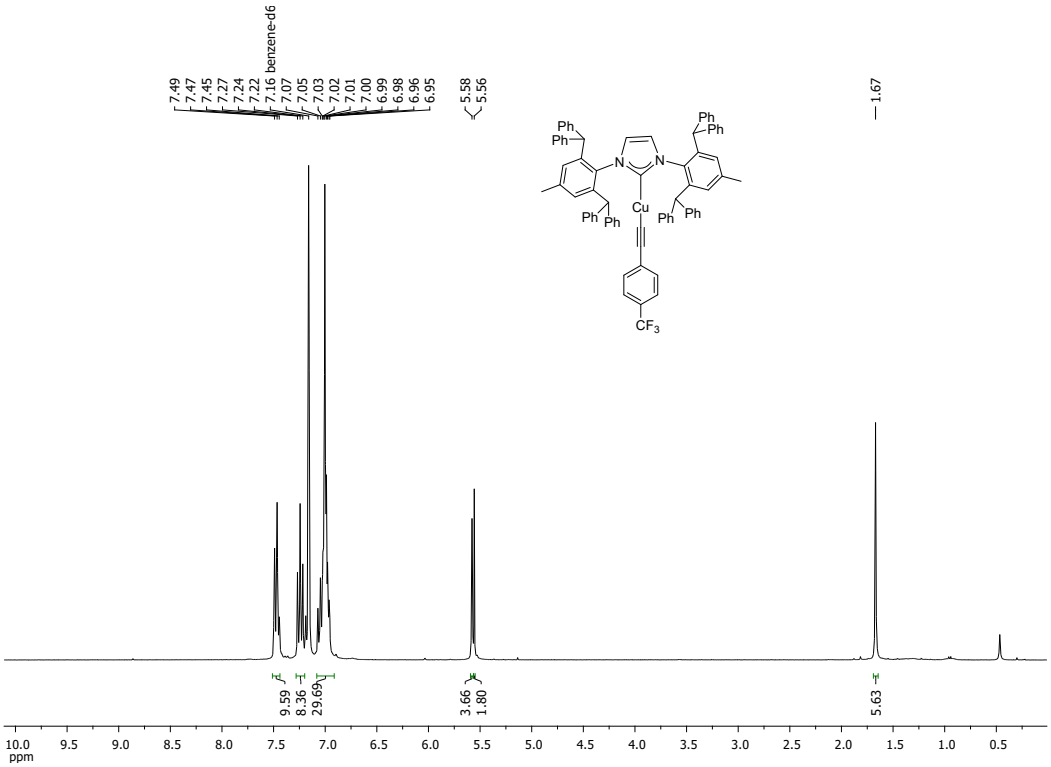
^{1}H NMR, ^{13}C{^{1}H} NMR and ^{19}F{^{1}H} NMR spectra of [Cu(IPr*)(2-fluorophenylacetylene)] (2d)

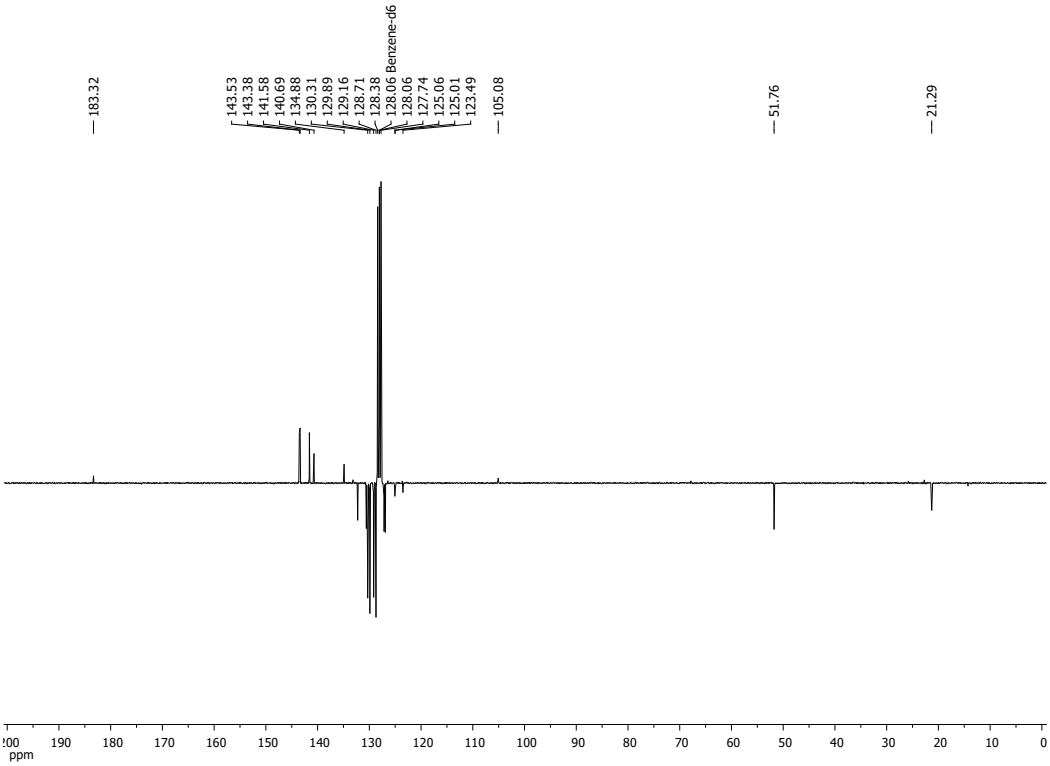






^{1}H NMR, ^{13}C{^{1}H} NMR and ^{19}F{^{1}H} NMR spectra of [Cu(IPr*)(4-(CF_3)phenylacetylene)] (2e)

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141.58
140.69
134.88
130.31
129.89
129.16
128.71
128.38
128.06 Benzene-d6
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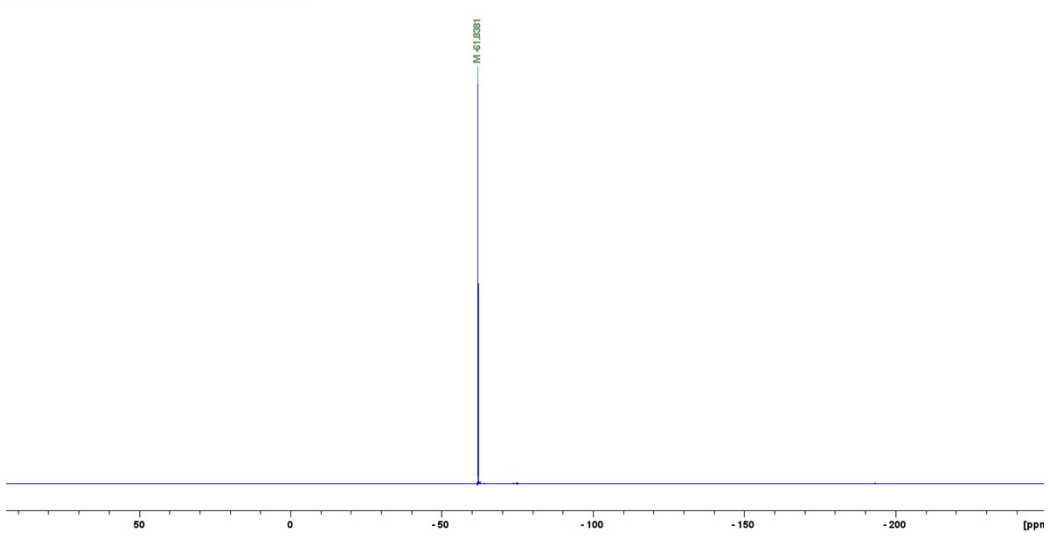
127.74
125.06
125.01
123.49
105.08
51.76
21.29
ppm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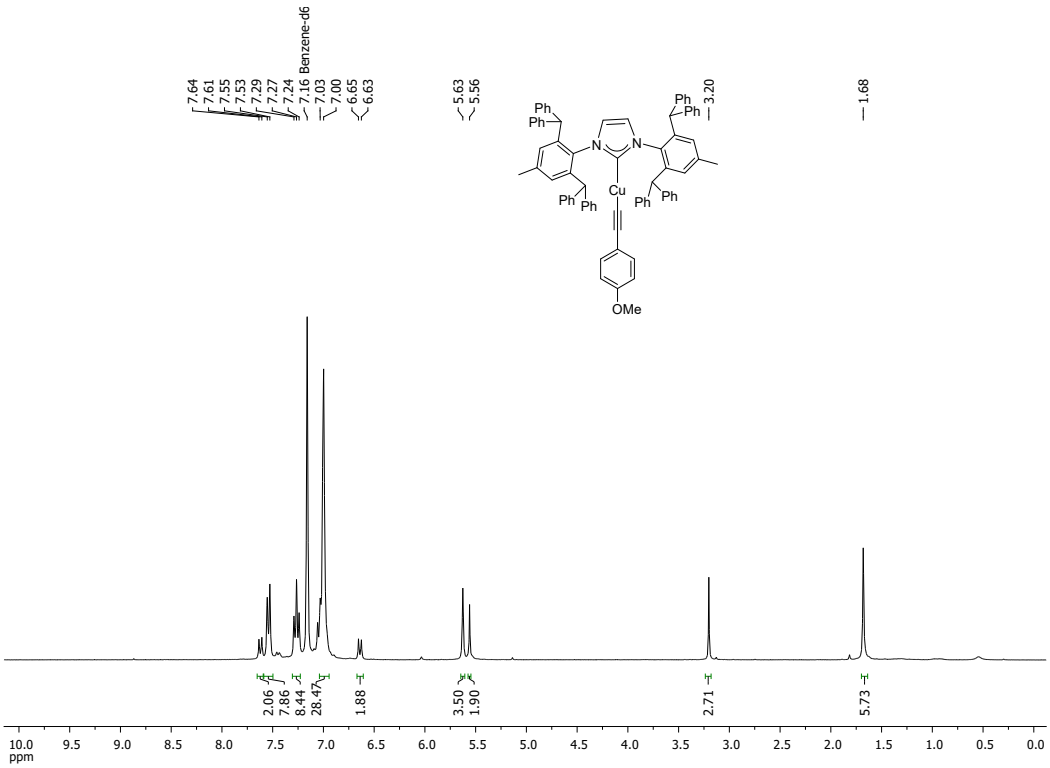
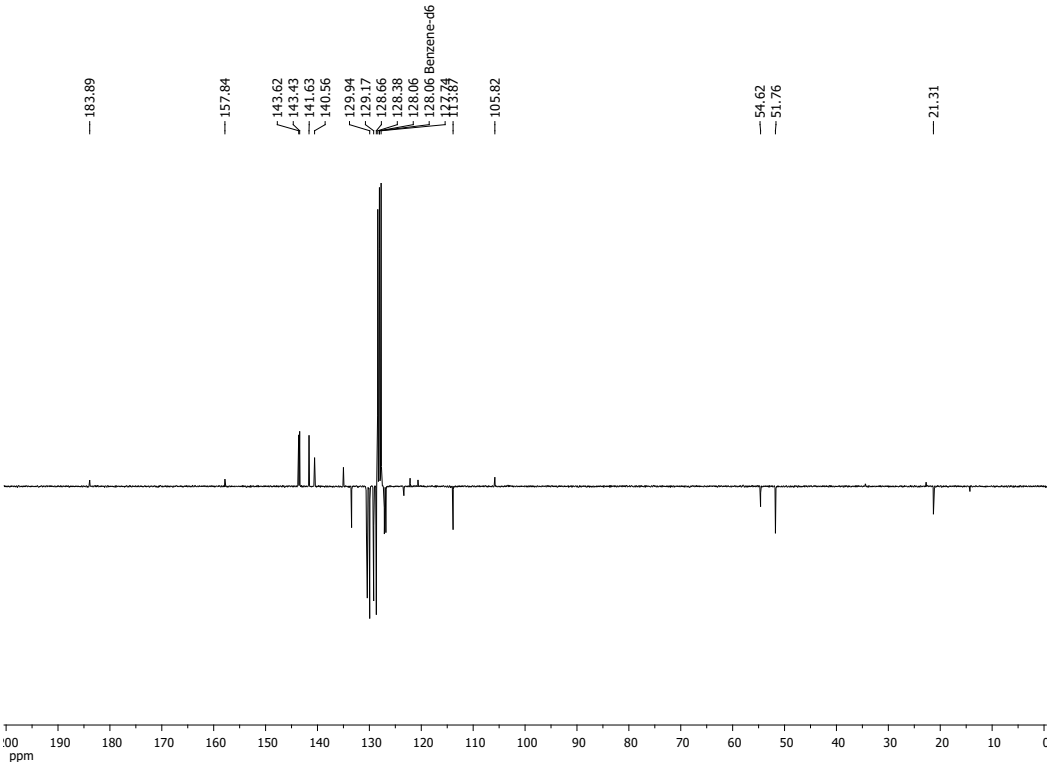
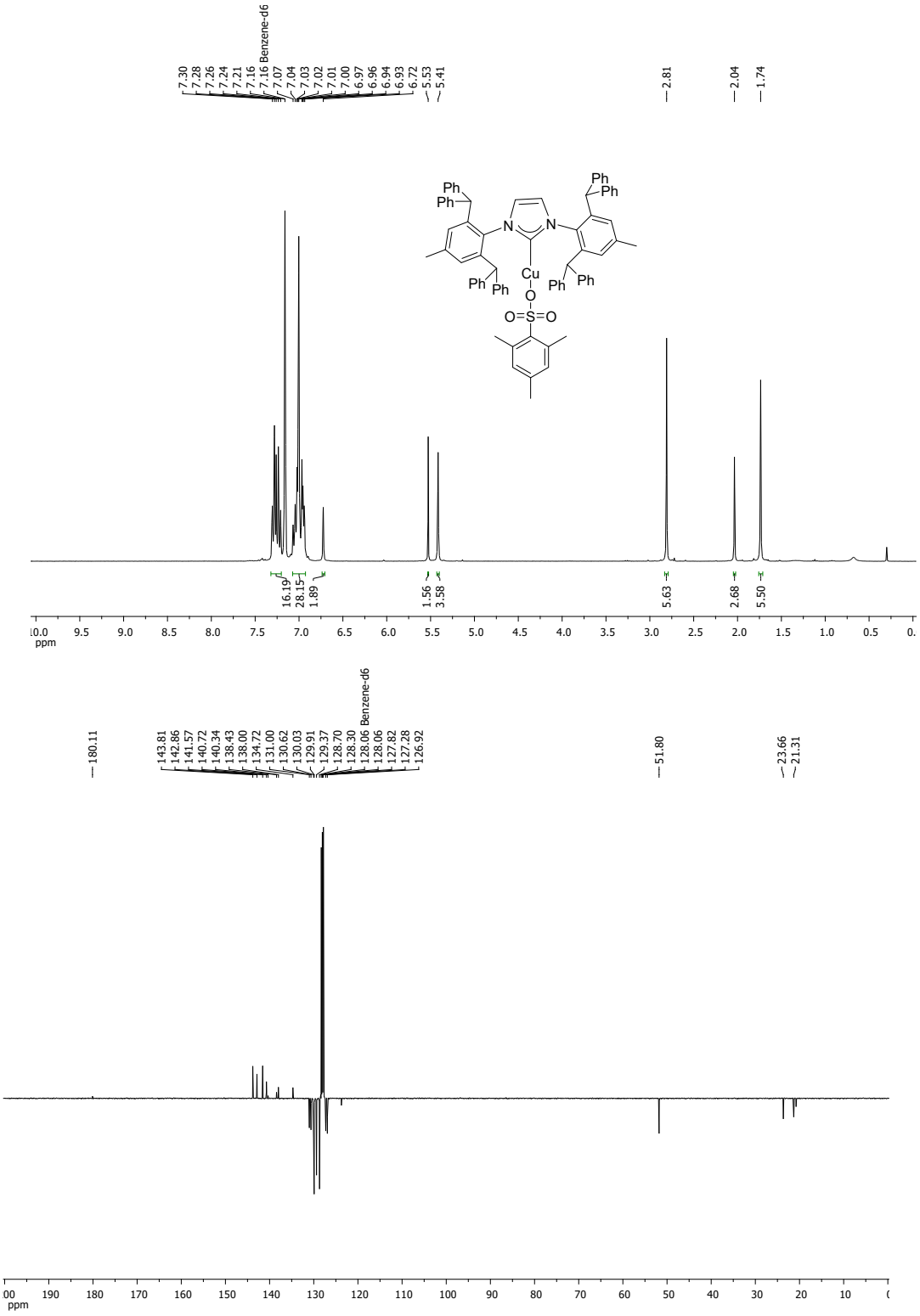
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of [Cu(IPr*)(4'-Methoxyphenylacetylene)] (2f)

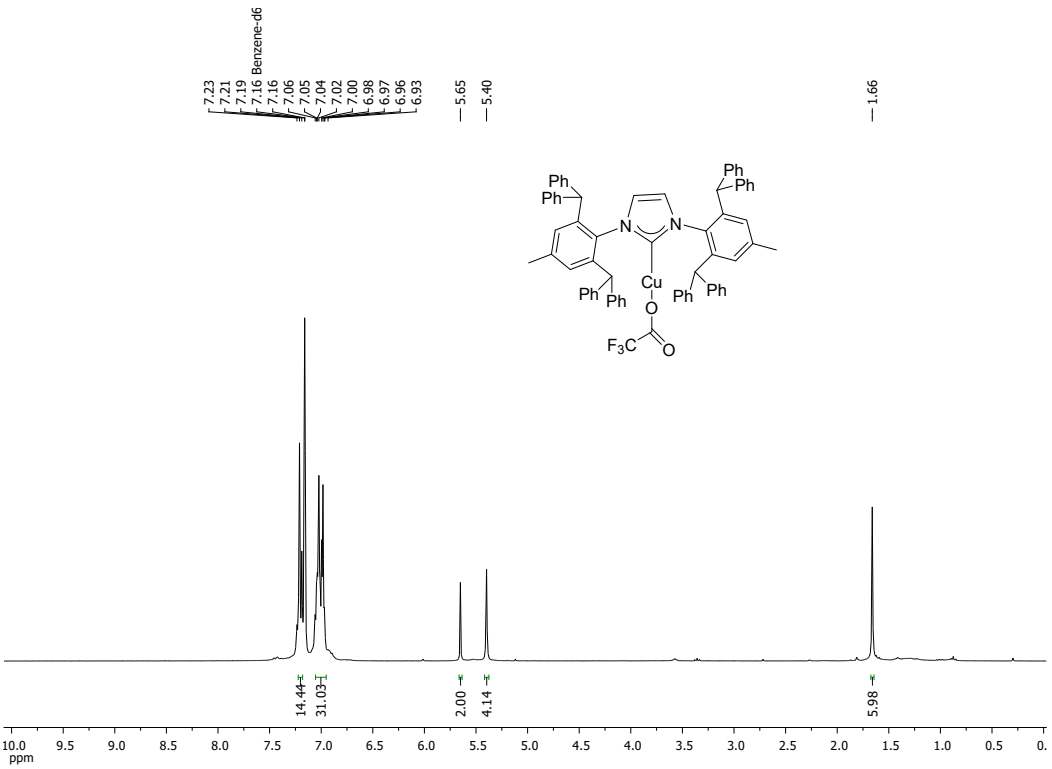




^{1}H NMR, $^{13}C\{^{1}H\}$ NMR and $^{19}F\{^{1}H\}$ NMR spectra of [Cu(IPr*)(OMess)] 2aa



^{1}H NMR, $^{13}C\{^{1}H\}$ NMR and $^{19}F\{^{1}H\}$ NMR spectra of [Cu(IPr*)(TFA)] 2ab


7.23
7.21
7.19
7.16 Benzene-d6
7.16
7.06
7.05
7.04
7.02
7.00
6.98
6.97
6.96
6.93
5.65
5.40
1.66
Ph
Ph
Ph
Ph
N
N
Cu
O
Ph
Ph
Ph
Ph
F3C
O
14.44
31.03
2.00
4.14
5.98
10.0
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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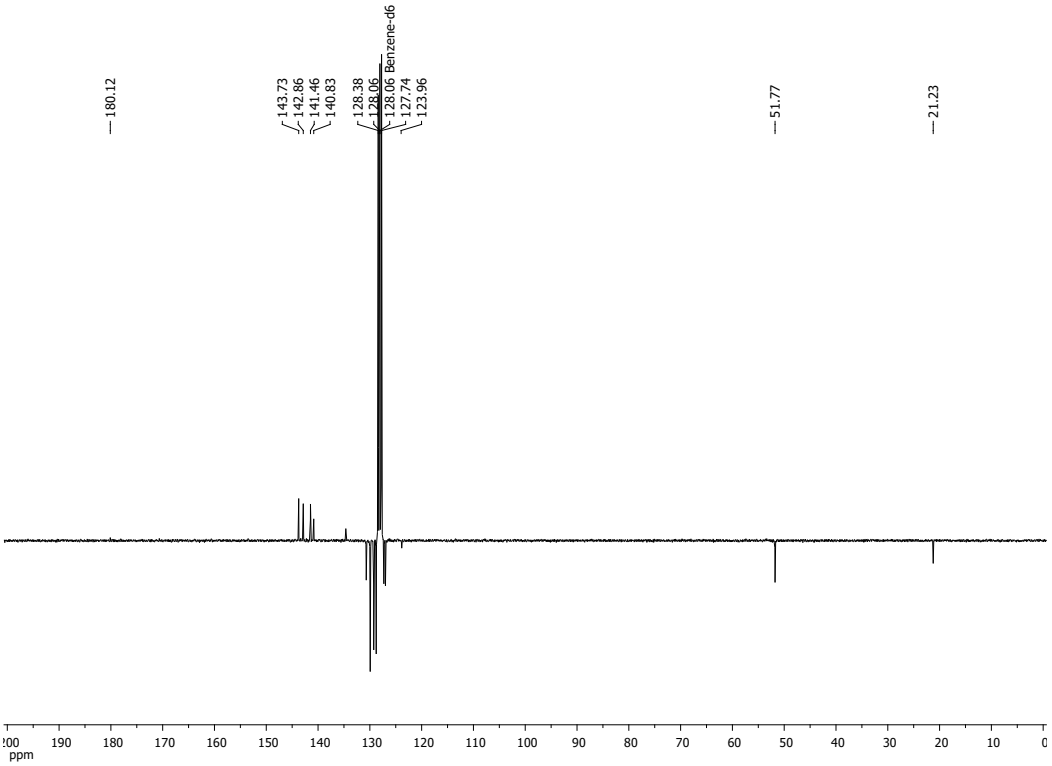
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127.74
123.96
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21.23
200
ppm
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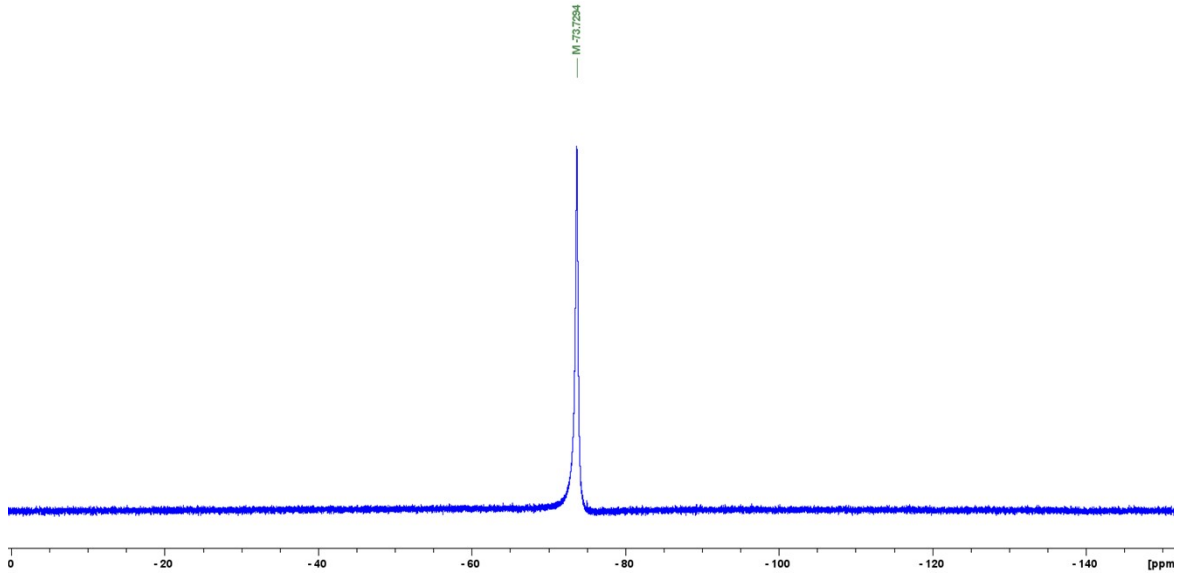
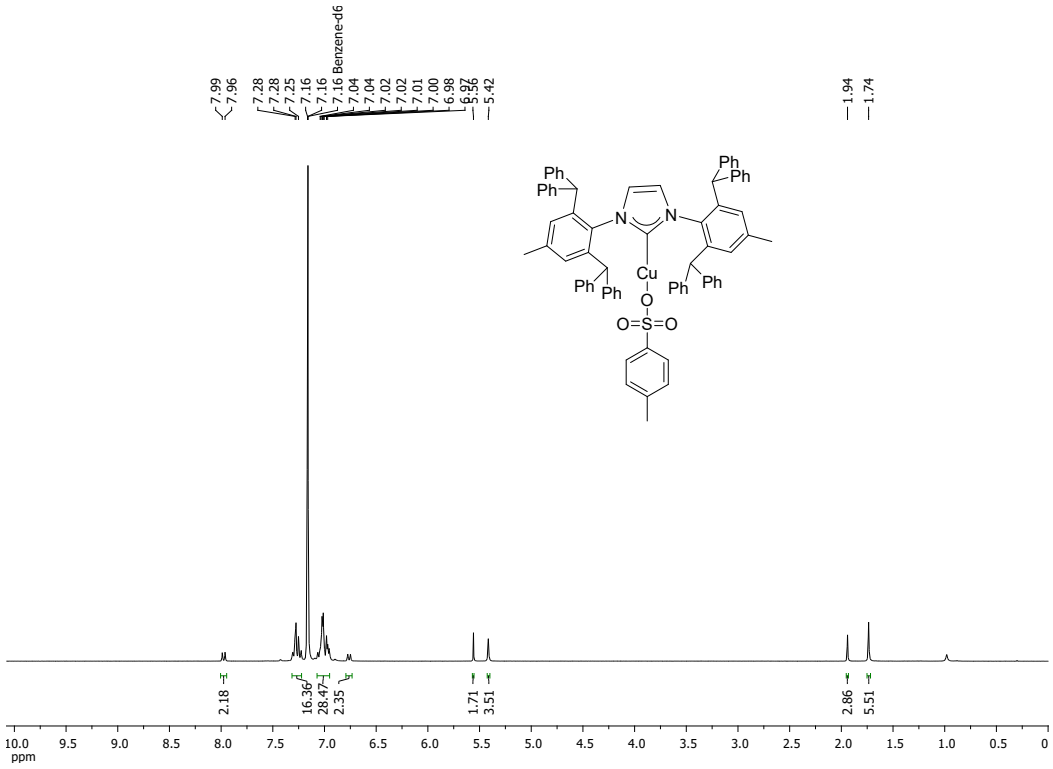
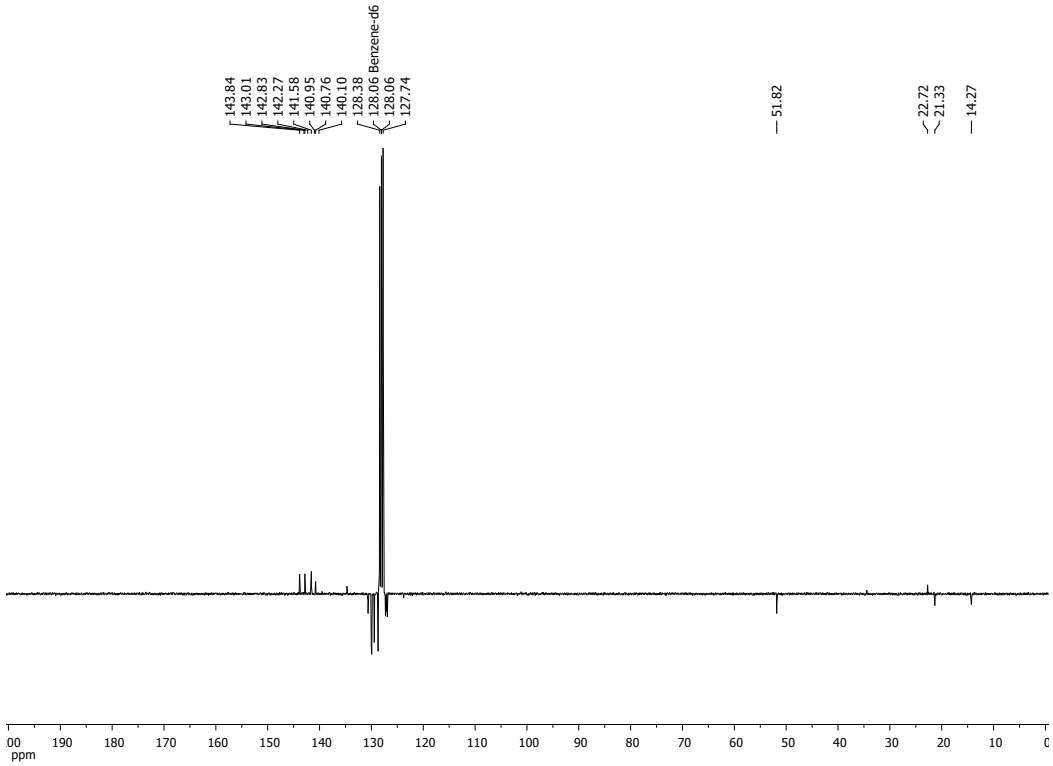
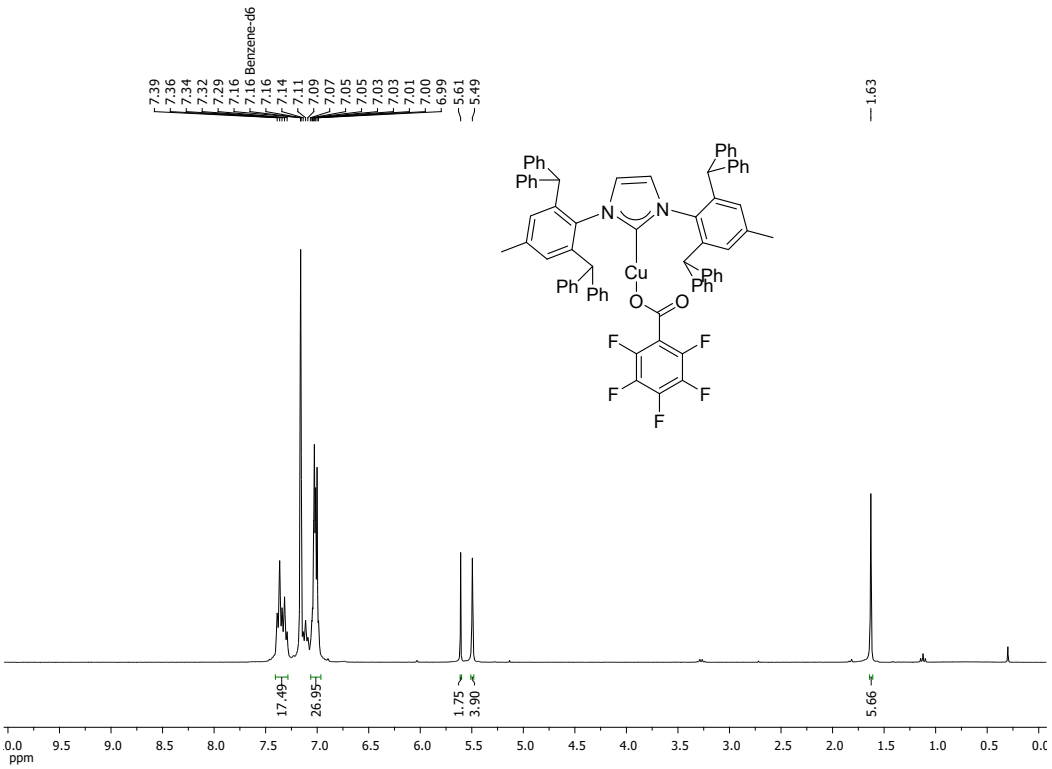


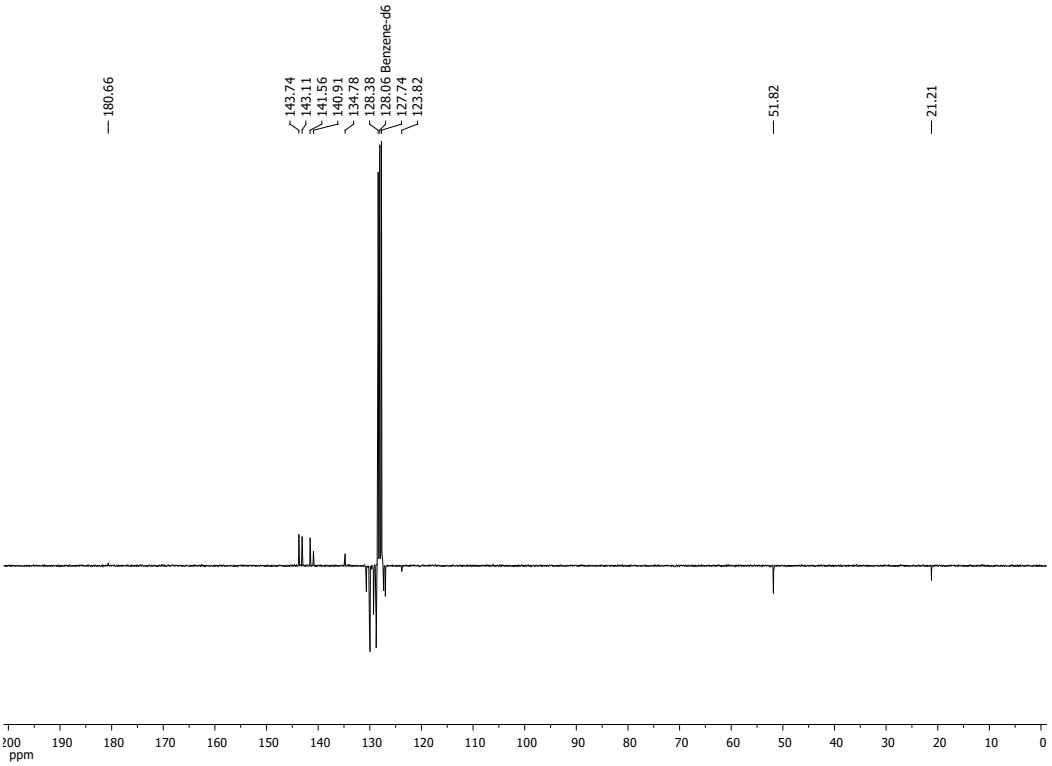
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of [Cu(IPr*)(OTs)] 2ac





^{1}H NMR, ^{13}C{^{1}H} NMR and ^{19}F{^{1}H} NMR spectra of [Cu(IPr*)((OCO)C$_6$F$_5$)] 2ad

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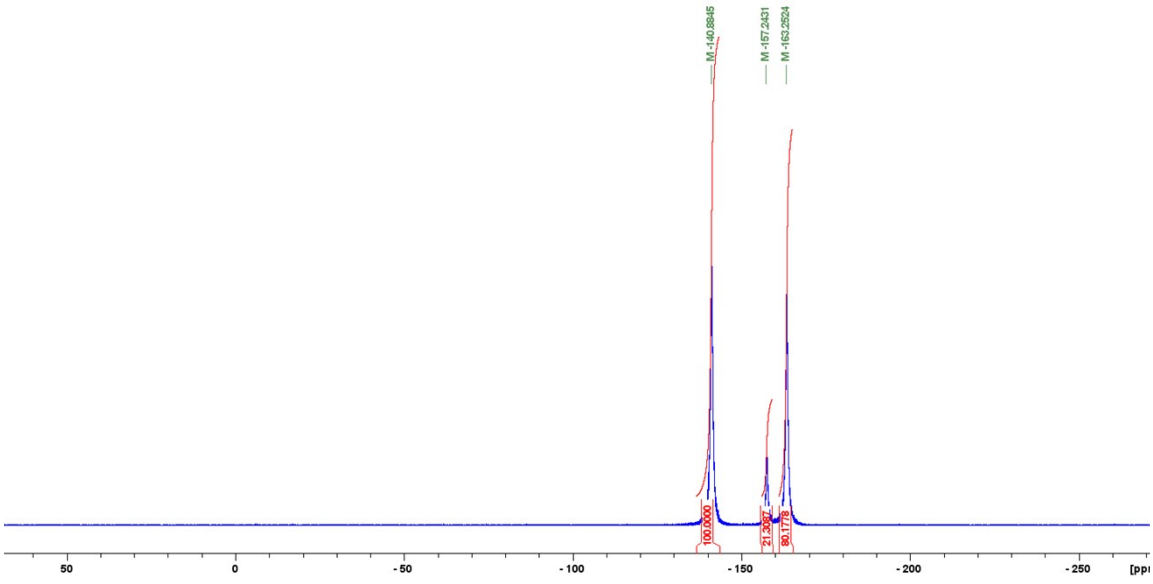
ppm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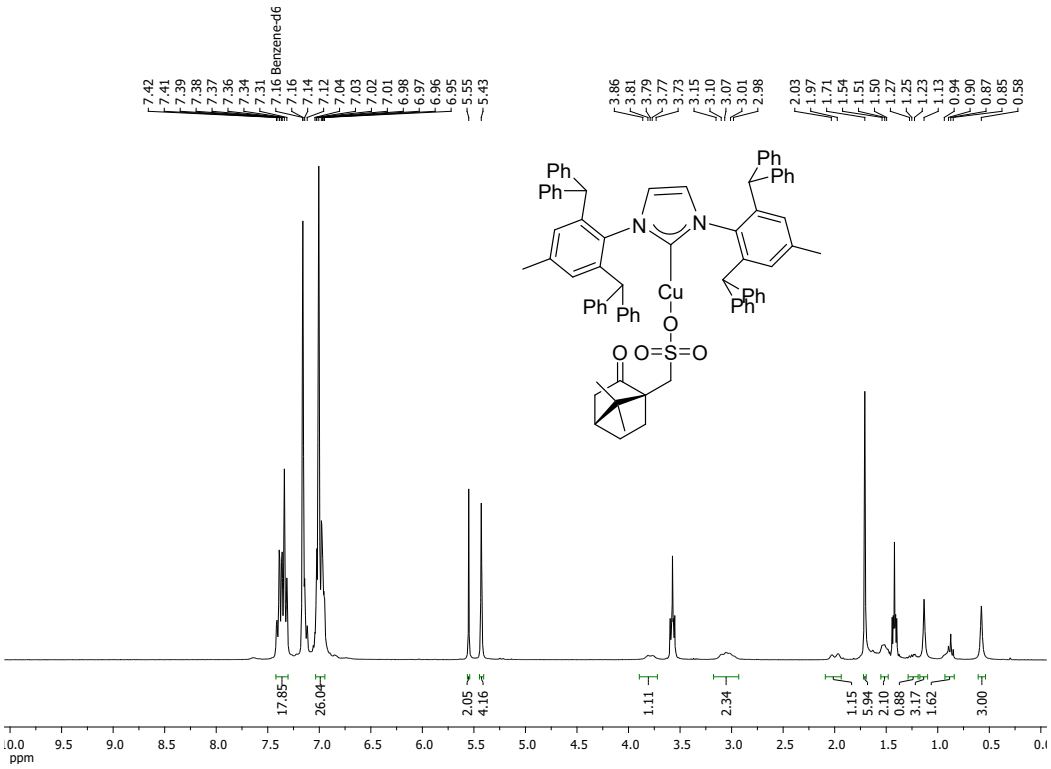
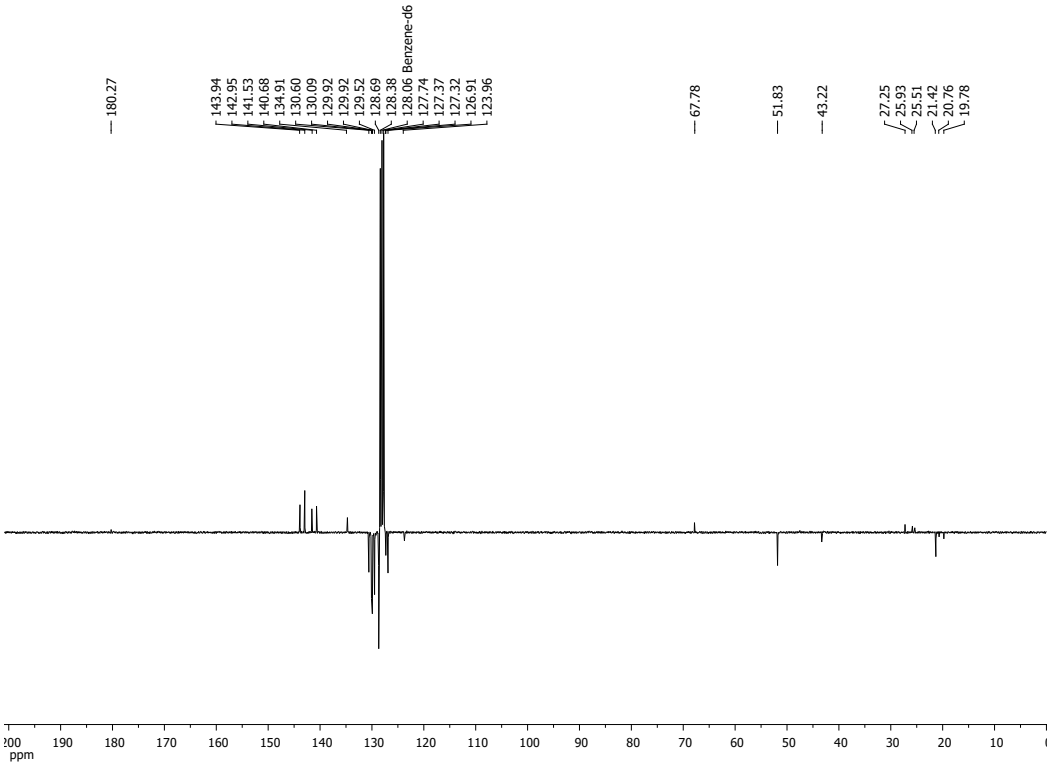
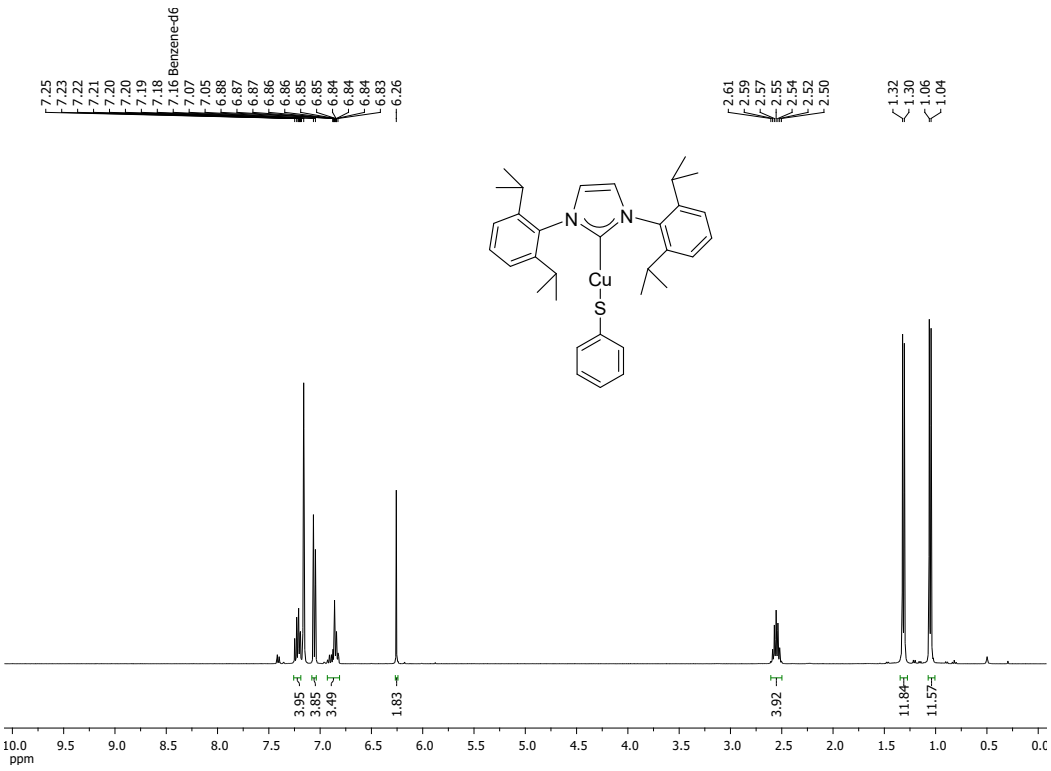
^{1}H NMR, $^{13}C\{^{1}H\}$ NMR and $^{19}F\{^{1}H\}$ NMR spectra of [Cu(IPr*)(OCs)] 2ae

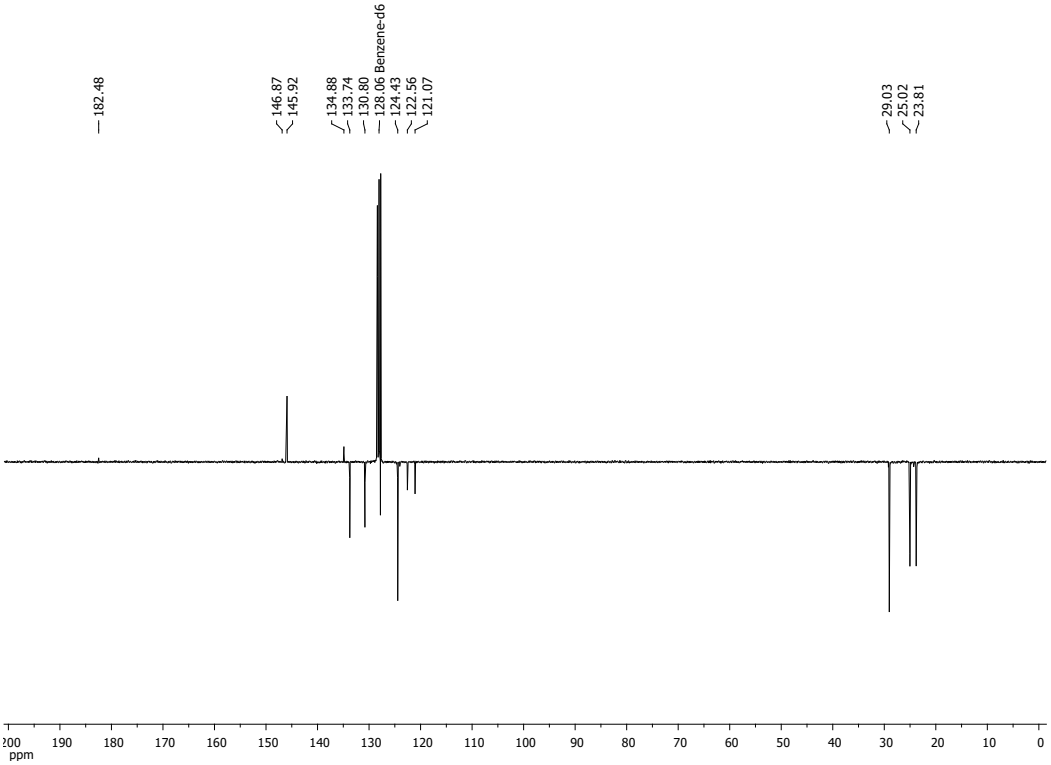




5. NMR spectra of NHC-Cu-thiolato complexes

^{1}H NMR and ^{13}C{^{1}H} NMR spectra of [Cu(IPr)(SPh)] (3a)





^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of [Cu(IPr*)(SPh)] (3b)