Supporting Information

for

Cu-NHC Azide Complex: Synthesis and Reactivity

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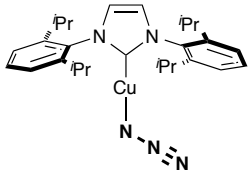
General considerations

All reactions were carried out under inert atmosphere (argon) using a glovebox. All reagents were purchased and used as received. All solvents were dried prior to use. ^{1}H and ^{13}C-{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded at 298K on a Brucker Advance 400 Ultrashield or on a Brucker Advance 500 Ultrashield spectrometer using the residual solvent peak (CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 53.84 ppm). Elemental analyses were performed by London Metropolitan University.

Synthesis and characterisation of complexes 1-8

Synthesis of [Cu(N_3)(IPr)], (**1**).



In a glovebox, a screw capped vial was charged with [Cu(OH)(IPr)] (300 mg, 0.64 mmol, 1.0 equiv.), $TMSN_3$ (126 µL, 0.96 mmol, 1.5 equiv.) and toluene (6 mL). The reaction mixture was stirred at room temperature for 16 h, after which pentane (10 mL) was added. The product was collected by filtration, washed with pentane (3 x 2 mL) and dried *in vacuo*. Complex **1** was obtained as a colourless solid (310 mg, 98 %).

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.55 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, $C_{Ar}H$), 7.35 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 4H, $C_{Ar}H$), 7.19 (s, 2H, H^4 and H^5 carbene), 2.54 (sept, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 4H, C*H*$(CH_3)_2$), 1.28 (d, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 12H, CH(C*H*$_3)_2$), 1.24 (d, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 12H, CH(C*H*$_3)_2$).

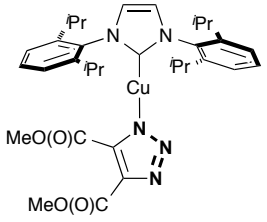
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K): δ (ppm) = 180.5 (s, C^2 carbene), 146.6 (s, C^{IV}), 135.2 (s, C^{IV}), 131.4 (s, $C_{Ar}H$), 125.1 (s, $C_{Ar}H$), 124.4 (s, C^4 and C^5 carbene), 29.6 (s, *C*H$(CH_3)_2$), 25.3 (s, CH(*C*H$_3)_2$), 24.4 (s, CH(*C*H$_3)_2$).

Anal. Calcd for $C_{27}H_{36}CuN_5$: C, 65.63; H, 7.34; N, 14.17. Found: C, 65.38, H, 7.59, N, 14.05

General procedure for reactions of [Cu(N_3)(IPr)] with organic substrates.

In a glovebox, a screw capped vial was charged with [Cu(N_3)(IPr)] (50 mg, 0.1 mmol, 1.0 equiv.), the organic substrate (0.12 mmol, 1.2 equiv.) and CH_2Cl_2 (1 mL). The reaction mixture was stirred at room temperature for the indicated time, after which pentane (3 mL) was added. The product was collected by filtration, washed with pentane (3 x 2 mL) and dried *in vacuo*.

Synthesis of [Cu(4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazol-1-yl)(IPr)], (**2**)



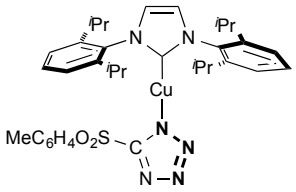
Reaction between **1** and dimethyl acetylenedicarboxylate (14.8 µL, 0.12 mmol) for 30 seconds lead to the isolation of **2** as a colourless solid (97%, 61.6 mg).

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.51 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, $C_{Ar}H$), 7.33 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 4H, $C_{Ar}H$), 7.24 (s, 2H, H^4 and H^5 carbene), 3.63 (s, 6H, OCH_3), 2.64 (sept, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 4H, C*H*$(CH_3)_2$), 1.28 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 12H, CH(C*H*$_3)_2$), 1.23 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 12H, CH(C*H*$_3)_2$).

^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K): δ (ppm) = 180.1 (s, C^2 carbene), 162.7 (s, C=O), 145.9 (s, C^{IV}), 137.3 (s, C^{IV}), 134.6 (s, C^{IV}), 130.5 (s, $C_{Ar}H$), 124.2 (s, $C_{Ar}H$), 123.8 (s, C^4 and C^5 carbene), 51.8 (s, OCH_3), 28.9 (s, *C*H$(CH_3)_2$), 24.4 (s, CH(*C*H$_3)_2$), 23.8 (s, CH(*C*H$_3)_2$).

Anal. Calcd for $C_{33}H_{42}CuN_5O_4$: C, 62.29; H, 6.65; N, 11.01. Found: C, 62.15; H, 6.74; N, 10.96

Synthesis of [Cu(5-tosyl-1*H*-tetrazol-1-yl)(IPr)], (**3**)



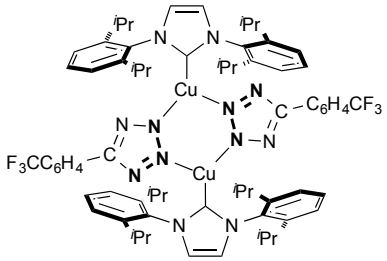
Reaction between **1** and sulfonylcyanide (21.8 mg, 0.12 mmol) for 30 seconds lead to the isolation of **3** as a colourless solid (98%, 66 mg).

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.54 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, $C_{Ar}H$), 7.50-7.41(bs, 2H, $C_{Ar}H$), 7.35 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, $C_{Ar}H$), 7.28 (s, 2H, H^4 and H^5 carbene), 7.19 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 4H, $C_{Ar}H$), 2.64 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 2.36 (s, 3H, CH_3), 1.28 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.24 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH(C*H*$_3)_2$).

^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K): δ (ppm) = 179.3 (s, C^2 carbene), 163.2 (s, C^{IV}), 145.9 (s, C^{IV}), 145.2 (s, C^{IV}), 136.8 (s, C^{IV}), 134.5 (s, C^{IV}), 130.6 (s, $C_{Ar}H$), 129.8 (s, $C_{Ar}H$), 128.0 (s, $C_{Ar}H$), 124.3 (s, $C_{Ar}H$), 124.0 (s, C^4 and C^5 carbene), 28.9 (s, *C*H$(CH_3)_2$), 24.4 (s, CH(*C*H$_3)_2$), 23.9 (s, CH(*C*H$_3)_2$), 21.4 (s, CH_3),.

Anal. Calcd for $C_{35}H_{43}CuN_6O_2S$: C, 62.24; H, 6.42; N, 12.44. Found: C, 62.15; H, 6.37; N, 12.49

Synthesis of [Cu(5-{4-(trifluoromethyl)phenyl}-2*H*-tetrazol-2-yl)(IPr)]$_2$, (**4**)



Reaction between **1** and 4-(trifluoromethyl)benzonitrile (20.5 mg, 0.12 mmol) at 50 °C for 16h lead to the isolation of **4** as a colourless solid (93%, 61.7 mg).

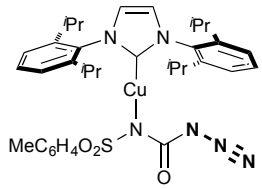
^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.78 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, $C_{Ar}H$), 7.57 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, $C_{Ar}H$), 7.42 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, $C_{Ar}H$), 7.36 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, $C_{Ar}H$), 7.28 (s, 2H, H^4 and H^5 carbene), 2.62 (sept, $^3J_{H\text{-}H}$ = 6.7 Hz, 4H, C*H*$(CH_3)_2$), 1.29-1.16 (m, 24H, CH(C*H*$_3)_2$).

^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K): δ (ppm) = 178.8 (s, C^2 carbene), 160.2 (s, C^{IV}), 142.7 (s, C^{IV}), 134.1 (s, C^{IV}), 133.0 (s, C^{IV}), 130.70 (s, $C_{Ar}H$), 129.7 (q, $^2J_{C\text{-}F}$= 32.5 Hz, C^{IV}), 126.8 (s, $C_{Ar}H$), 125.3 (q, $^4J_{C\text{-}F}$ = 3.6 Hz, $C_{Ar}H$), 124.2 (s, $C_{Ar}H$), 124.1 (q, $^1J_{C\text{-}F}$ = 272.0 Hz, C^{IV}), 123.9 (s, C^4 and C^5 carbene), 28.7 (s, *C*H$(CH_3)_2$), 24.4 (s, CH(*C*H$_3)_2$), 23.5 (s, CH(*C*H$_3)_2$),

^{19}F{^{1}H} NMR (376 MHz , CD_2Cl_2, 298K): δ (ppm) = - 63.0 (s).

Anal. Calcd for $C_{35}H_{40}CuF_3N_6$: C, 63.19; H, 6.06; N, 12.63. Found: C, 63.07; H, 6.18; N, 12.57

Synthesis of [Cu({*N*-(azidocarbonyl)-4-methylphenyl}sulfonamido)(IPr)], (**5**)

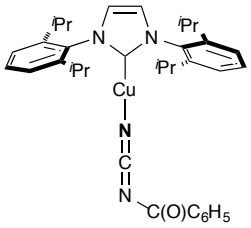


Reaction between **1** and *p*-toluenesulfonyl isocyanate (18.3 μL, 0.12 mmol) for 30 seconds lead to the isolation of **5** as a colourless solid (95%, 61.7 mg).

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.53 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, $C_{Ar}H$), 7.35 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 4H, $C_{Ar}H$), 7.29 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 4H, $C_{Ar}H$), 7.24 (s, 2H, H^4 and H^5 carbene), 7.09 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 4H, $C_{Ar}H$), 2.59 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.33 (s, 3H, CH_3), 1.28 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.22 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12H, CH(C*H*$_3)_2$).

^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K): δ (ppm) = 180.2 (s, C^2 carbene), 159.3 (s, C=O), 146.0 (s, C^{IV}), 142.5 (s, C^{IV}), 138.4 (s, C^{IV}), 134.7 (s, C^{IV}), 130.40 (s, $C_{Ar}H$), 128.6 (s, $C_{Ar}H$), 127.8 (s, $C_{Ar}H$), 124.1 (s, $C_{Ar}H$), 123.6 (s, C^4 and C^5 carbene), 28.9 (s, $CH(CH_3)_2$), 24.2 (s, $CH(CH_3)_2$), 24.0 (s, $CH(CH_3)_2$), 21.3 (s, CH_3).
Anal. Calcd for $C_{35}H_{43}CuN_6O_3S$: C, 60.80; H, 6.27; N, 12.16. Found: C, 60.66, H, 6.26; N, 12.09

Synthesis of [Cu((benzoylimino)methylene)amino)(IPr)], (**6**)

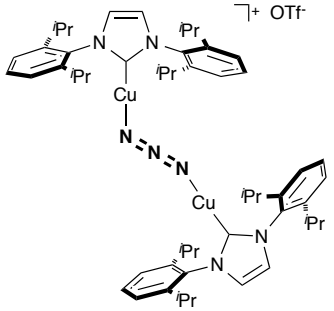


Reaction between **1** and benzoyl isothiocyanate (16.1 μL, 0.12 mmol) for 30 seconds lead to the isolation of **6** as a colourless solid (92%, 54.8 mg).
^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.91 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, $C_{Ar}H$), 7.55 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, $C_{Ar}H$), 7.40-7.32 (m, 5H, $C_{Ar}H$), 7.27 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, $C_{Ar}H$), 7.21 (s, 2H, H^4 and H^5 carbene), 2.53 (sept, $^3J_{H-H}$ = 6.9 Hz, 4H, $CH(CH_3)_2$), 1.28 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.23 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$).
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K): δ (ppm) = 178.6 (s, C^2 carbene), 175.8 (s, N=C=N), 145.5 (s, C^{IV}), 136.4 (s, C^{IV}), 134.0 (s, C^{IV}), 130.9 (s, $C_{Ar}H$), 130.6 (s, $C_{Ar}H$), 128.6 (s, $C_{Ar}H$), 127.5 (s, $C_{Ar}H$), 124.2 (s, $C_{Ar}H$), 123.6 (s, C^4 and C^5 carbene), 123.1 (s, C^{IV}), 28.6 (s, $CH(CH_3)_2$), 24.5 (s, $CH(CH_3)_2$), 23.5 (s, $CH(CH_3)_2$).
Anal. Calcd for $C_{35}H_{41}CuN_4O$: C, 70.38; H, 6.92; N, 9.38. Found: C, 70.28; H, 7.04; N, 9.28

General procedure for the synthesis of dinuclear copper azide complexes.

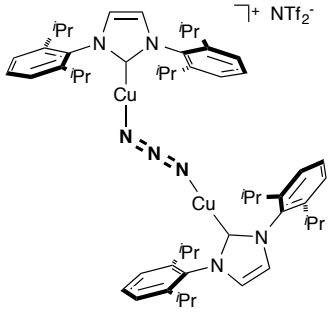
In a glovebox, a screw capped vial was charged with [Cu(N_3)(IPr)] (50 mg, 0.1 mmol, 1.0 equiv.), [Cu(X)(IPr)] (0.1 mmol, 1 equiv.), and CH_2Cl_2 (1 mL). The reaction mixture was stirred at room temperature for 5 min, after which the volatiles were removed *in vacuo* affording the correspondent complex.

Synthesis of [{Cu(IPr)}$_2$(μ-N_3)]OTf, (**7**).



Reaction between **1** and [Cu(OTf)(IPr)] (60.0 mg, 0.1 mmol) lead to the isolation of **7** as a colourless solid in quantitative yield (110 mg).
^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.50 (t, $^3J_{H-H}$ = 7.9 Hz, 4H, $C_{Ar}H$), 7.29 (d, $^3J_{H-H}$ = 7.9 Hz, 8H, $C_{Ar}H$), 7.21 (s, 4H, H^4 and H^5 carbene), 2.42 (sept, $^3J_{H-H}$ = 6.8 Hz, 8H, $CH(CH_3)_2$), 1.20 (d, $^3J_{H-H}$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.12 (d, $^3J_{H-H}$ = 6.8 Hz, 24H, $CH(CH_3)_2$).
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K): δ (ppm) = 177.1 (s, C^2 carbene), 145.4 (s, C^{IV}), 133.8 (s, C^{IV}), 130.6 (s, $C_{Ar}H$), 124.1 (s, $C_{Ar}H$), 124.0 (s, C^4 and C^5 carbene), 28.5 (s, $CH(CH_3)_2$), 24.4 (s, $CH(CH_3)_2$), 23.4 (s, $CH(CH_3)_2$).
^{19}F-{^{1}H} NMR (376 MHz , CD_2Cl_2, 298K): δ (ppm) = -78.9 (s).
Anal. Calcd for $C_{55}H_{72}Cu_2F_6N_8O_4S_2$: C, 60.31; H, 6.63; N, 8.95. Found: C, 60.39; H, 6.69; N, 8.85

Synthesis of $[\{Cu(IPr)\}_2(\mu\text{-}N_3)]NTf_2$, (**8**)



Reaction between **1** and $[Cu(NTf_2)(IPr)]$ (73.1 mg, 0.1 mmol) lead to the isolation of **8** as a colourless solid in quantitative yield (123 mg).

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.50 (t, $^3J_{H\text{-}H}$ = 7.9 Hz, 4H, $C_{Ar}H$), 7.29 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 8H, $C_{Ar}H$), 7.21 (s, 4H, H^4 and H^5 carbene), 2.42 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 8H, $CH(CH_3)_2$), 1.19 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.16 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 24H, $CH(CH_3)_2$).

^{13}C-{1H} NMR (100 MHz, CD_2Cl_2, 298K): δ (ppm) = 177.0 (s, C^2 carbene), 145.4 (s, C^{IV}), 133.8 (s, C^{IV}), 130.6 (s, $C_{Ar}H$), 124.1 (s, $C_{Ar}H$), 124.0 (s, C^4 and C^5 carbene), 28.5 (s, $CH(CH_3)_2$), 24.4 (s, $CH(CH_3)_2$), 23.4 (s, $CH(CH_3)_2$).

^{19}F-{1H} NMR (376 MHz , CD_2Cl_2, 298K): δ (ppm) = -79.3 (s).

Anal. Calcd for $C_{56}H_{72}Cu_2F_6N_8O_4S_2$: C, 54.84; H, 5.92; N, 9.14. Found:C, 55.02; H, 6.05, N, 8.93

Crystal data for complexes 1-8

[Cu(N$_3$)(IPr)], (1)

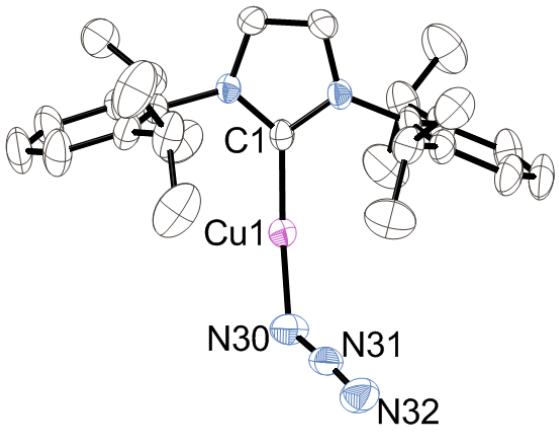


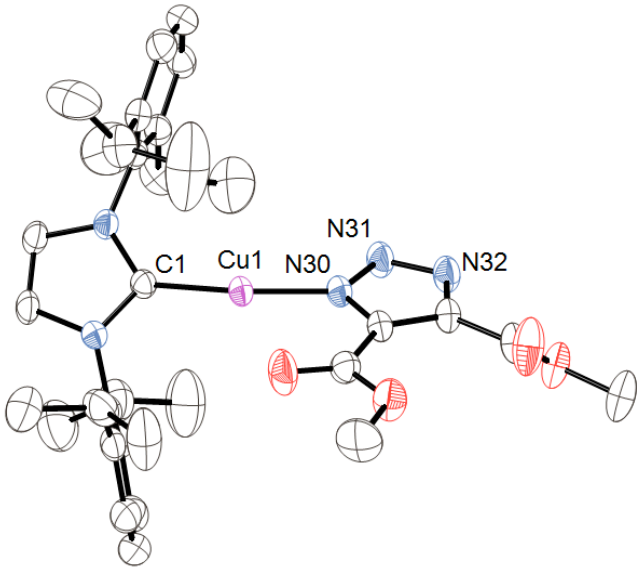
Figure S1. Molecular structure of **1**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Complex	**1**
CCDC number	**1541281**
Emperical formula	$C_{27}H_{36}CuN_5$
Formula Weight	494.16
Crystal color, Habit	colorless, prism
Temperature (K)	-100 °C
Crystal system	monoclinic
Space group	$P2_1/n$ (#14)
Unit cell dim.	0.210 X 0.140 X 0.040 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 10.7028(10) b = 19.841(2) c = 12.7079(16)
α,β,γ (°)	β = 94.549(3)
Volume (Å)^3	2690.1(5)
Z	4
Density calculated	1.220 g/cm^3
Absorption coefficient (cm^{-1})	8.344
F(000)	1048.00
Diffractometer	XtaLAB P200
Radiation	MoKα (γ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max} = 50.8^o$
Reflexions collected	Total: 32825

	Unique: 4929 (R_{int} = 0.0246)
Correction	Lorentz-polarization Absorption (trans. factors: 0.878 - 0.967)
Structure solution	Direct Methods (SIR2011)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	4929
No. variables	306
Reflection/parameter ratio	16.11
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	0.0255
R indices (all data)	0.0302
Maximum peak in Final Diff Map (e.$Å^{-3}$)	0.23 $e^-/Å^3$
Minimum peak in Final Diff Map (e.$Å^{-3}$)	-0.19 $e^-/Å^3$
Max shift/error in final cycle	0.000

[Cu(4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazol-1-yl)(IPr)], (2)

Figure S2. Molecular structure of **2**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.



Complex	**2**
CCDC number	**1541282**
Emperical formula	$C_{33}H_{42}CuN_5O_4$
Formula Weight	636.27
Crystal color, Habit	colorless, platelet
Temperature (K)	-100 °C
Crystal system	monoclinic
Space group	$P2_1/n$ (#14)
Unit cell dim.	0.180 X 0.070 X 0.020 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 15.7139(17) b = 21.668(2) c = 20.036(2)
α,β,γ (°)	β = 101.313(3)
Volume (Å)^3	6689.5(12)
Z	8
Density calculated	1.263 g/cm^3
Absorption coefficient (cm^{-1})	6.953
F(000)	2688.00
Diffractometer	XtaLAB P200
Radiation	MoKα (γ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max} = 50.8^o$
Reflexions collected	Total: 127565 Unique: 12225 (R_{int} = 0.0515)

Correction	Lorentz-polarization Absorption (trans. factors: 0.941 - 0.986)
Structure solution	Charge Flipping (Superflip)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	12225
No. variables	825
Reflection/parameter ratio	14.82
Goodness-of-fit on F^2	1.103
Final R indices [I>2sigma(I)]	0.0355
R indices (all data)	0.0562
Maximum peak in Final Diff Map ($e.Å^{-3}$)	0. 42 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0. 33 $e^-/Å^3$
Max shift/error in final cycle	0.000

[Cu(5-tosyl-1*H*-tetrazol-1-yl)(IPr)], (3)

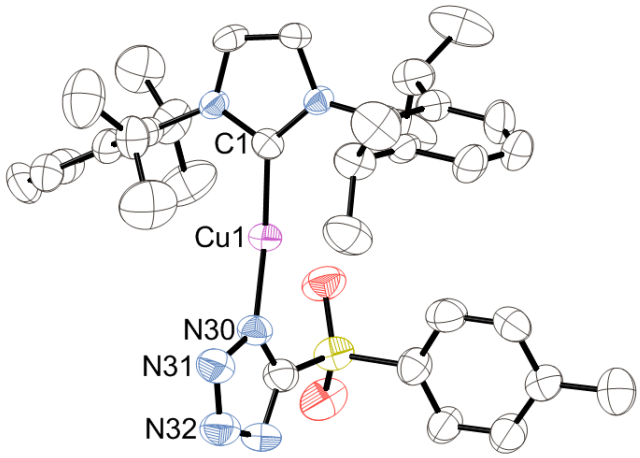


Figure S3. Molecular structure of **3**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Complex	**3**
CCDC number	**1541283**
Emperical formula	$C_{35.25}H_{43.5}Cl_{0.5}CuN_6O_2S$
Formula Weight	696.60
Crystal color, Habit	colorless, needle
Temperature (K)	-100 °C
Crystal system	orthorhombic
Space group	Pbca (#61)
Unit cell dim.	0.100 X 0.020 X 0.010 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 15.786(3) b = 22.886(4) c = 40.989(7)
Volume (Å)^3	14808(5)
Z	16
Density calculated	1.250 g/cm^3
Absorption coefficient (cm^{-1})	7.202
F(000)	5864.00
Diffractometer	XtaLAB P200
Radiation	MoKα (γ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max} = 50.8^o$
Reflexions collected	Total: 174222

	Unique: 13557 (R_{int} = 0.3537)
Correction	Lorentz-polarization Absorption (trans. factors: 0.751 - 0.993)
Structure solution	Charge Flipping (Superflip)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	13557
No. variables	851
Reflection/parameter ratio	15.93
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	0.0825
R indices (all data)	0.2380
Maximum peak in Final Diff Map ($e.Å^{-3}$)	1.29 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0. 37 $e^-/Å^3$
Max shift/error in final cycle	0.001

[Cu(5-(4-(trifluoromethyl)phenyl)-2*H*-tetrazol-2-yl)(IPr)]$_2$, (4)

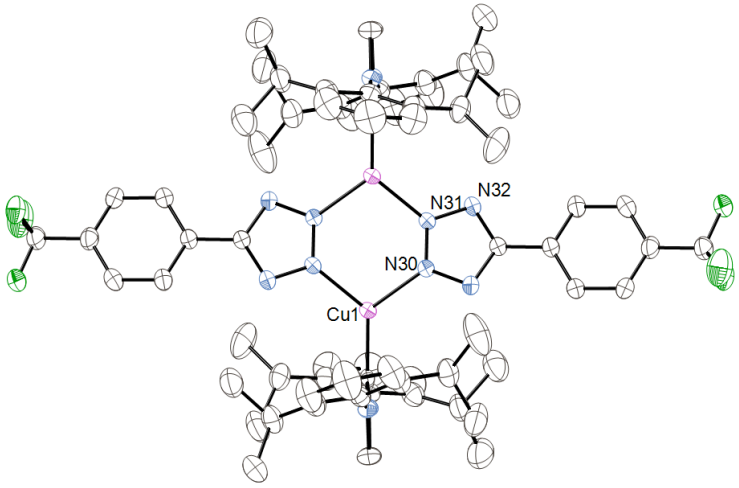


Figure S4. Molecular structure of **4**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Complex	**4**
CCDC number	**1541284**
Emperical formula	$C_{35}H_{44}CuF_3N_6O_2$
Formula Weight	701.31
Crystal color, Habit	colorless, prism
Temperature (K)	-100 °C
Crystal system	triclinic
Space group	P-1 (#2)
Unit cell dim.	0.180 X 0.140 X 0.040 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 12.2657(15) b = 12.5469(14) c = 14.0728(19)
α,β,γ (°)	α = 110.157(3) β = 107.483(2) γ = 91.4070(15)
Volume (Å)^3	1919.2(4)
Z	2
Density calculated	1.213 g/cm^3
Absorption coefficient (cm^{-1})	6.197
F(000)	736.00
Diffractometer	XtaLAB P200
Radiation	MoKα (γ = 0.71075 Å) multi-layer mirror monochromated

Voltage, Current	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max} = 50.7^{o}$
Reflexions collected	Total: 39708 Unique: 6979 ($R_{int} = 0.0261$)
Correction	Lorentz-polarization Absorption (trans. factors: 0.890 - 0.976)
Structure solution	Direct Methods (SIR2004)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	6979
No. variables	441
Reflection/parameter ratio	15.83
Goodness-of-fit on F^2	1.104
Final R indices [I>2sigma(I)]	0.0577
R indices (all data)	0.0624
Maximum peak in Final Diff Map ($e.Å^{-3}$)	1.76 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0. 45 $e^-/Å^3$
Max shift/error in final cycle	0.001

[Cu((N-(azidocarbonyl)-4-methylphenyl)sulfonamido)(IPr)], (5)

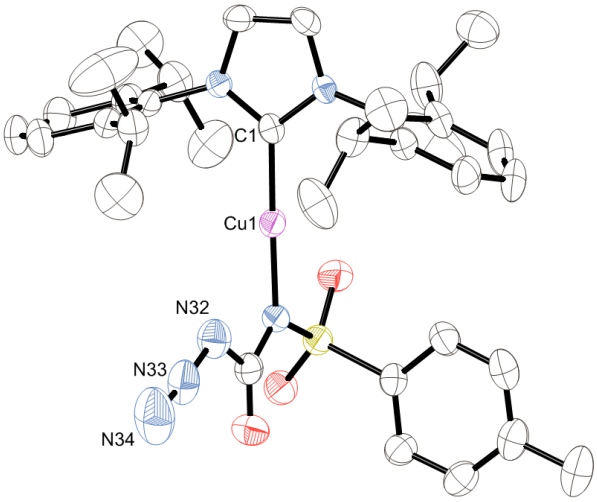


Figure S5. Molecular structure of **5**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Complex	**5**
CCDC number	**1541285**
Emperical formula	$C_{38}H_{46}CuN_6O_3S$
Formula Weight	730.43
Crystal color, Habit	colorless, prism
Temperature (K)	-100 °C
Crystal system	triclinic
Space group	P-1 (#2)
Unit cell dim.	0.230 X 0.060 X 0.040 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 10.2797(7) b = 12.4184(10) c = 16.0996(18)
α,β,γ (°)	α = 85.056(9) β = 75.371(7) γ = 71.777(7)
Volume (Å)^3	1888.8(3)
Z	2
Density calculated	1.284 g/cm^3
Absorption coefficient (cm^{-1})	6.769

F(000)	770.00
Diffractometer	XtaLAB P200
Radiation	MoKα (γ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max} = 50.8^{o}$
Reflexions collected	Total: 23049 Unique: 6857 (R_{int} = 0.0392)
Correction	Lorentz-polarization Absorption (trans. factors: 0.838 - 0.973)
Structure solution	Direct Methods (SIR2011)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	6857
No. variables	451
Reflection/parameter ratio	15.20
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	0.0481
R indices (all data)	0.0679
Maximum peak in Final Diff Map ($e.Å^{-3}$)	0.44 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0. 26 $e^-/Å^3$
Max shift/error in final cycle	0.000

Synthesis of [Cu((benzoylimino)methylene)amino)(IPr)], (6)

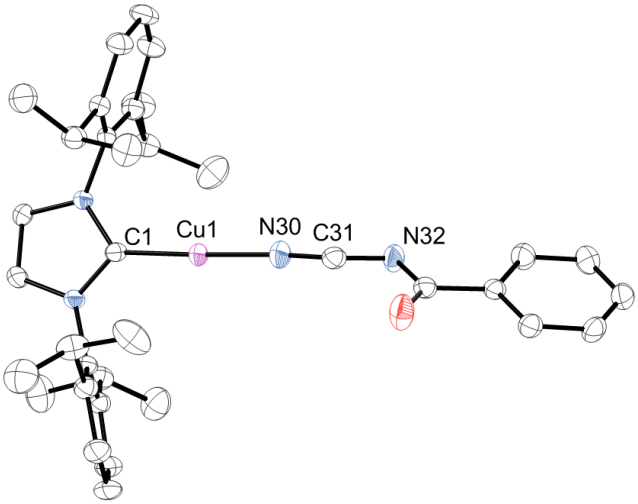


Figure S6. Molecular structure of **6**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Complex	**6**
CCDC number	**1541286**
Emperical formula	$C_{35}H_{41}CuN_4O$
Formula Weight	597.28
Crystal color, Habit	colorless, prism
Temperature (K)	-100 °C
Crystal system	triclinic
Space group	P-1 (#2)
Unit cell dim.	0.180 X 0.140 X 0.100 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 9.3577(9) b = 12.3850(13) c = 14.8513(15)
α,β,γ (°)	α = 109.819(3) β = 95.017(2) γ = 97.3442(16)
Volume (Å)^3	1590.1(3)
Z	2
Density calculated	1.247 g/cm^3
Absorption coefficient (cm^{-1})	7.194
F(000)	632.00
Diffractometer	XtaLAB P200
Radiation	MoKα (γ = 0.71075 Å) multi-layer mirror monochromated

Voltage, Current	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max} = 50.8^{o}$
Reflexions collected	Total: 19699 Unique: 5767 ($R_{int} = 0.0278$)
Correction	Lorentz-polarization Absorption (trans. factors: 0.776 - 0.931)
Structure solution	Charge Flipping (Superflip)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	5767
No. variables	378
Reflection/parameter ratio	15.26
Goodness-of-fit on F^2	1.172
Final R indices [I>2sigma(I)]	0.0290
R indices (all data)	0.0330
Maximum peak in Final Diff Map ($e.Å^{-3}$)	0.39 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0. 32 $e^-/Å^3$
Max shift/error in final cycle	0.001

{Cu(IPr)}$_2$(μ-N$_3$)]OTf, (7)

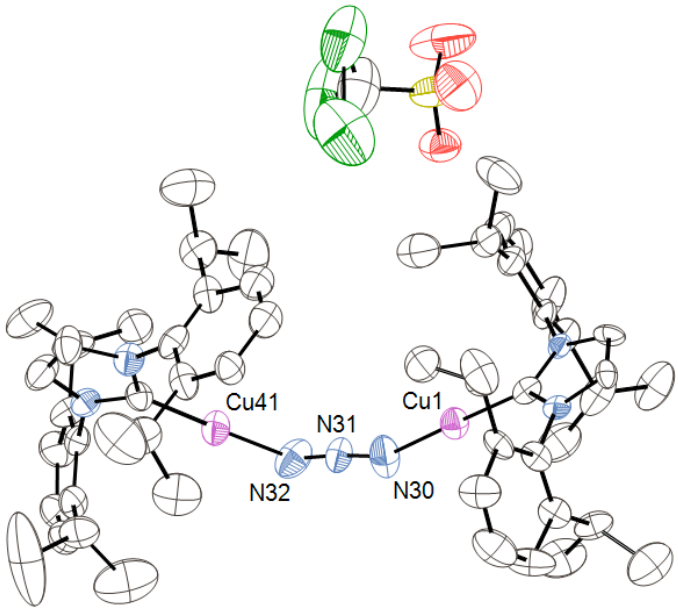


Figure S7. Molecular structure of **7**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Complex	**7**
CCDC number	**1541287**
Emperical formula	$C_{55}H_{72}Cu_2F_3N_7O_3S$
Formula Weight	1095.37
Crystal color, Habit	colorless, platelet
Temperature (K)	-100 °C
Crystal system	orthorhombic
Space group	$Pna2_1$ (#33)
Unit cell dim.	0.120 X 0.090 X 0.020 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 40.859(11) b = 10.950(3) c = 12.792(3)
Volume (Å)^3	5723(3)
Z	4
Density calculated	1.271g/cm^3
Absorption coefficient (cm^{-1})	8.358
F(000)	2304.00
Diffractometer	XtaLAB P200
Radiation	MoKα (γ = 0.71075 Å) multi-layer mirror monochromated

Voltage, Current	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max} = 50.7^{o}$
Reflexions collected	Total: 111777 Unique: 10471 ($R_{int} = 0.2086$) Parsons quotients (Flack x parameter): 1879
Correction	Lorentz-polarization Absorption (trans. factors: 0.860 - 0.983)
Structure solution	Charge Flipping (Superflip)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	10471
No. variables	656
Reflection/parameter ratio	15.96
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	0.0921
R indices (all data)	0.1705
Maximum peak in Final Diff Map ($e.Å^{-3}$)	0.89 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0.55 $e^-/Å^3$
Max shift/error in final cycle	0.000

[{Cu(IPr)}$_2$(μ-N$_3$)]NTf$_2$, (8)

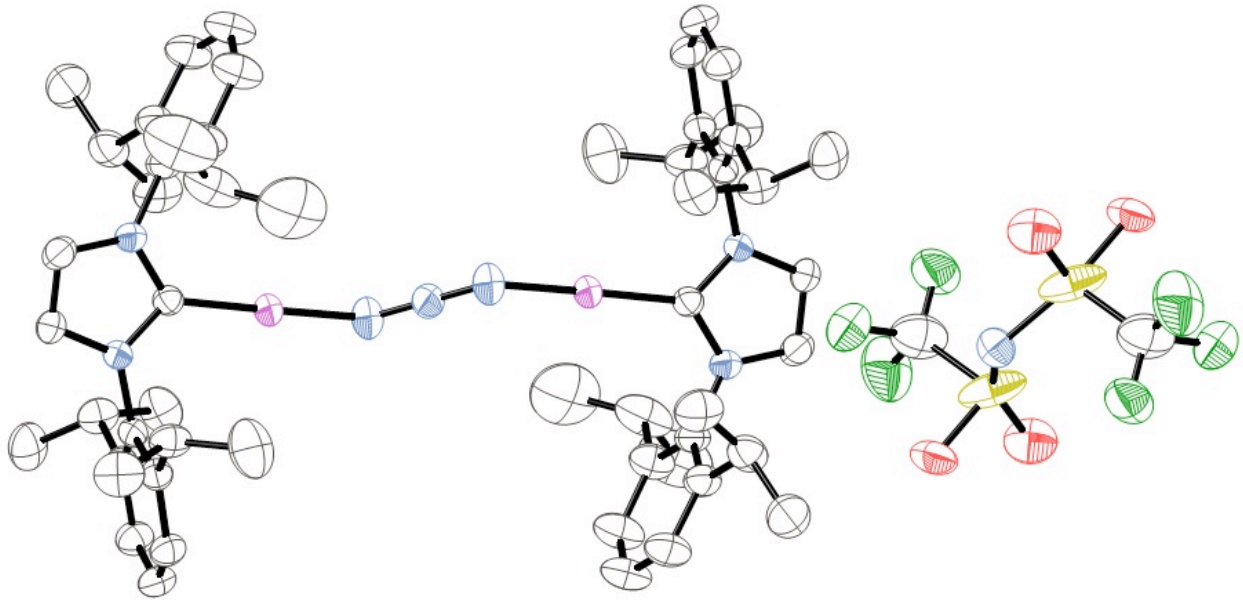


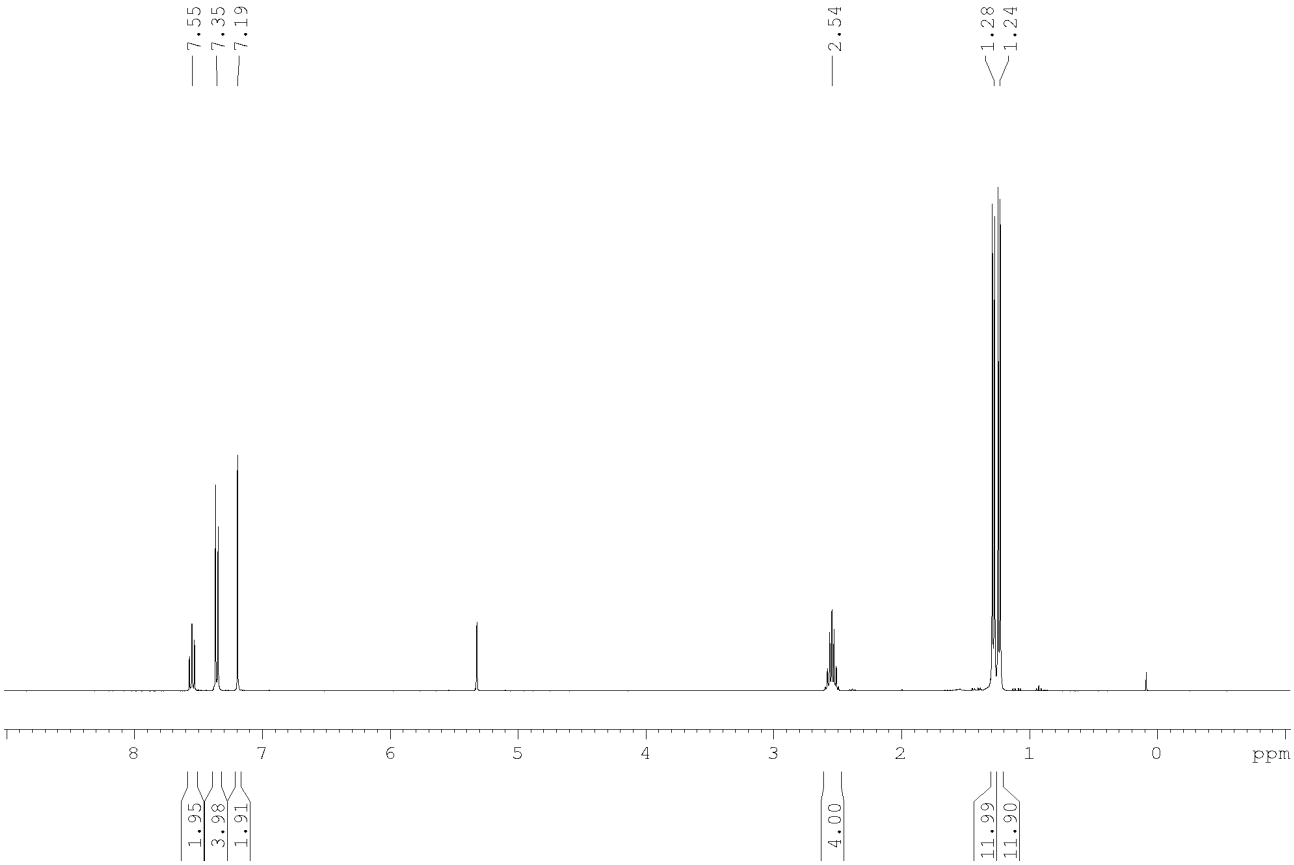
Figure S8. Molecular structure of **8**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Complex	**8**
CCDC number	**1541288**
Emperical formula	$C_{59}H_{78}Cu_2F_6N_8O_4S_2$
Formula Weight	1268.52
Crystal color, Habit	colorless, prism
Temperature (K)	-100 °C
Crystal system	triclinic
Space group	P-1 (#2)
Unit cell dim.	0.240 X 0.140 X 0.050 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 9.3135(7) b = 10.7161(8) c = 17.3225(10)
α,β,γ (°)	α = 80.201(5) β = 82.451(5) γ = 79.376(4)
Volume (Å)^3	1665.5(2)
Z	1
Density calculated	1.265g/cm^3
Absorption coefficient (cm^{-1})	7.653

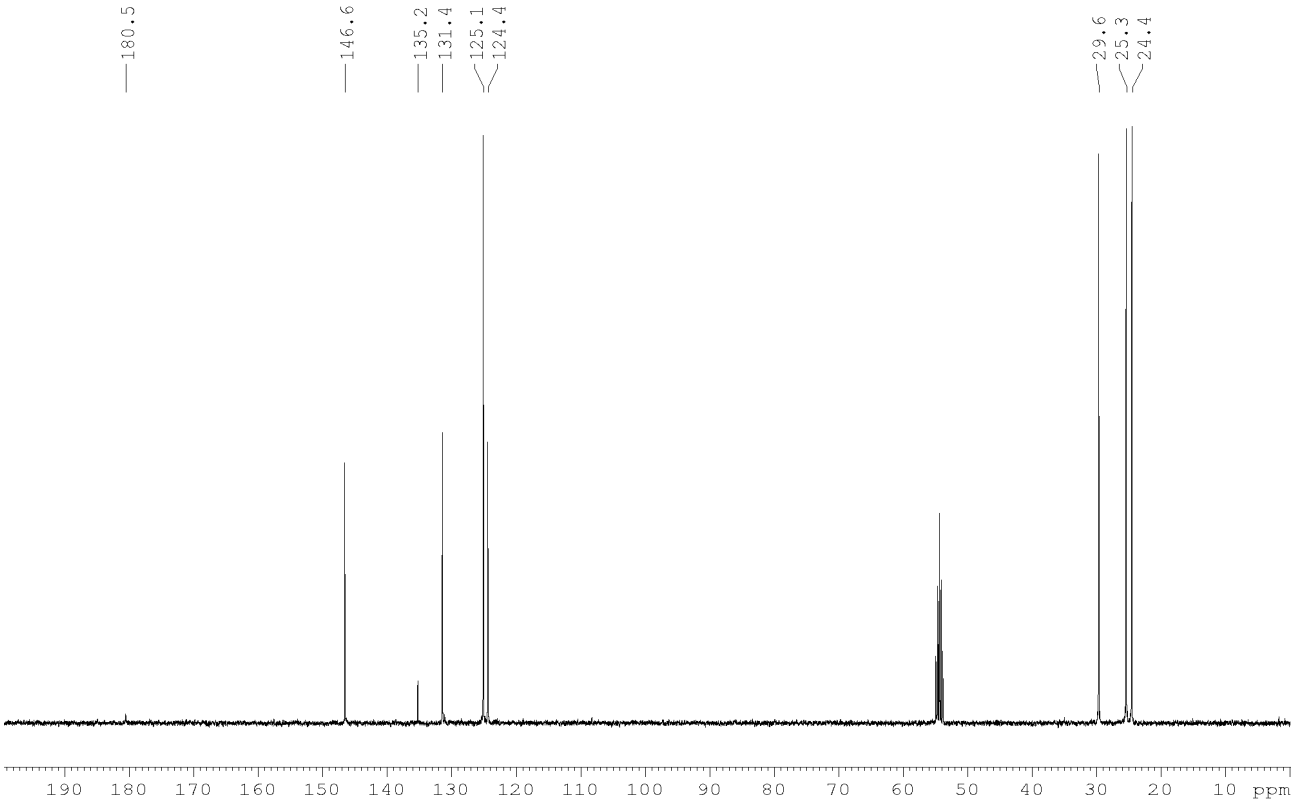
F(000)	664.00
Diffractometer	XtaLAB P200
Radiation	MoKα (γ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max} = 50.8^{o}$
Reflexions collected	Total: 34465 Unique: 6065 (R_{int} = 0.0330)
Correction	Lorentz-polarization Absorption (trans. factors: 0.805 - 0.962)
Structure solution	Direct Methods (SHELXT Version 2014/5)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	6065
No. variables	439
Reflection/parameter ratio	13.82
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	0.0498
R indices (all data)	0.0549
Maximum peak in Final Diff Map ($e.Å^{-3}$)	0.83 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0.85 $e^-/Å^3$
Max shift/error in final cycle	0.001

NMR spectra

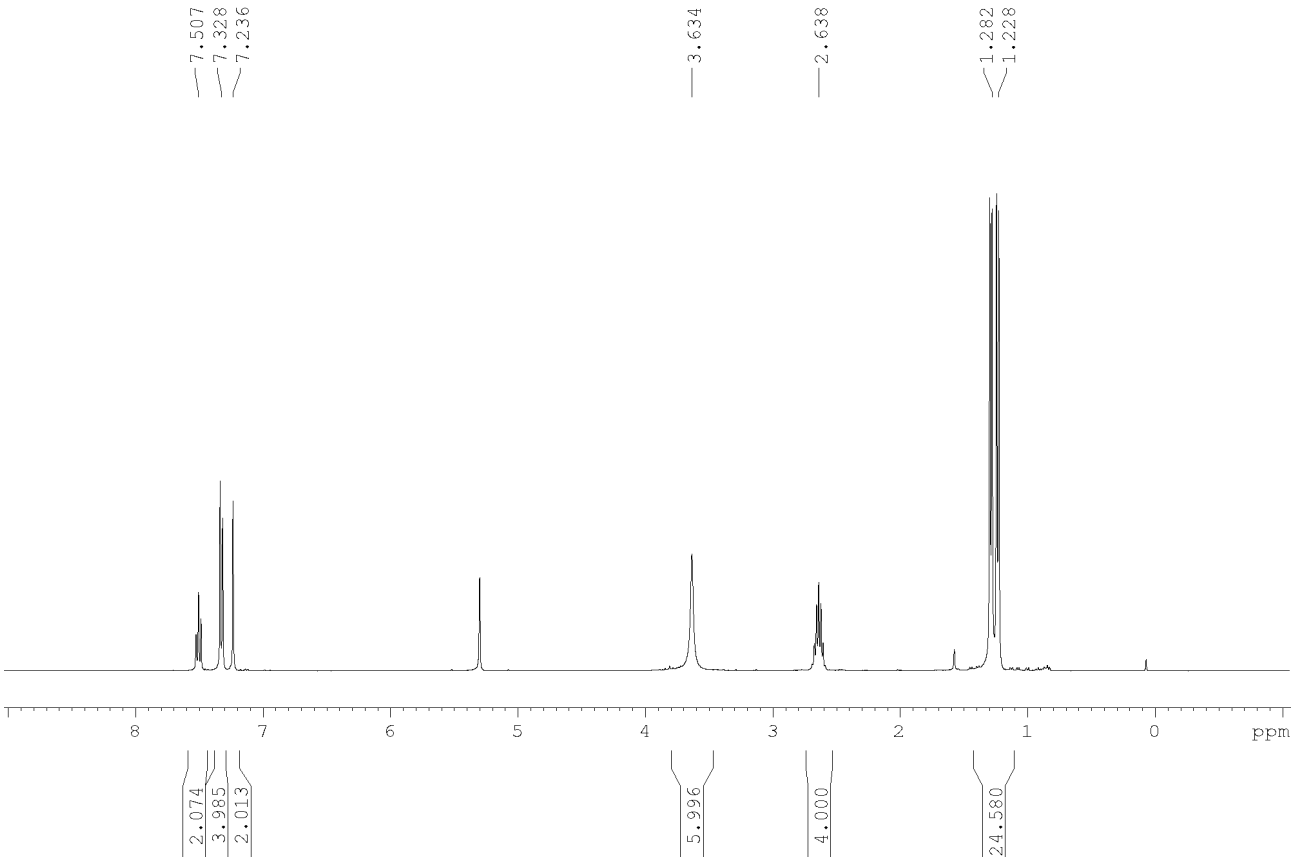
^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of [Cu(N_3)(IPr)], **1**



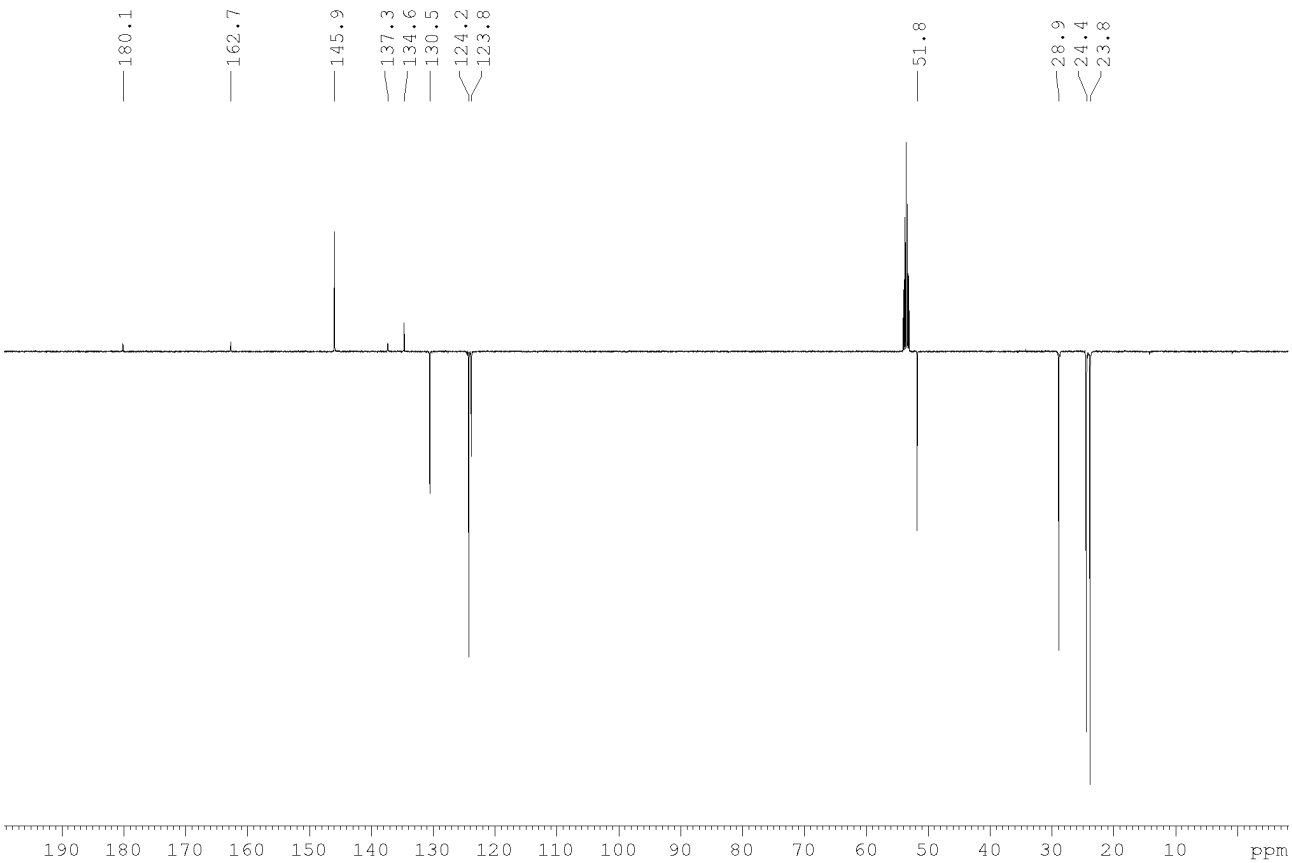
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K) of [Cu(N_3)(IPr)], **1**



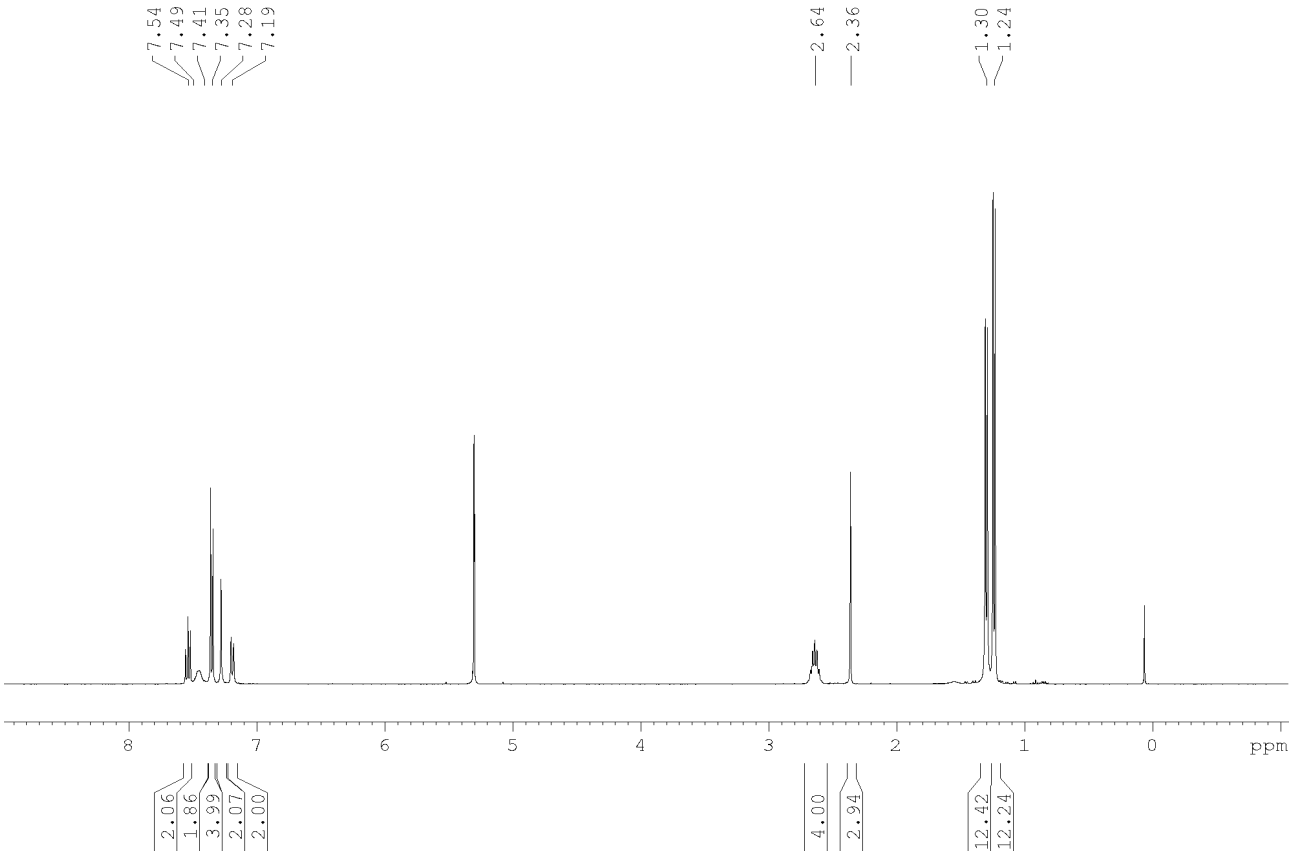
^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of [Cu(4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazol-1-yl)(IPr)], **2**



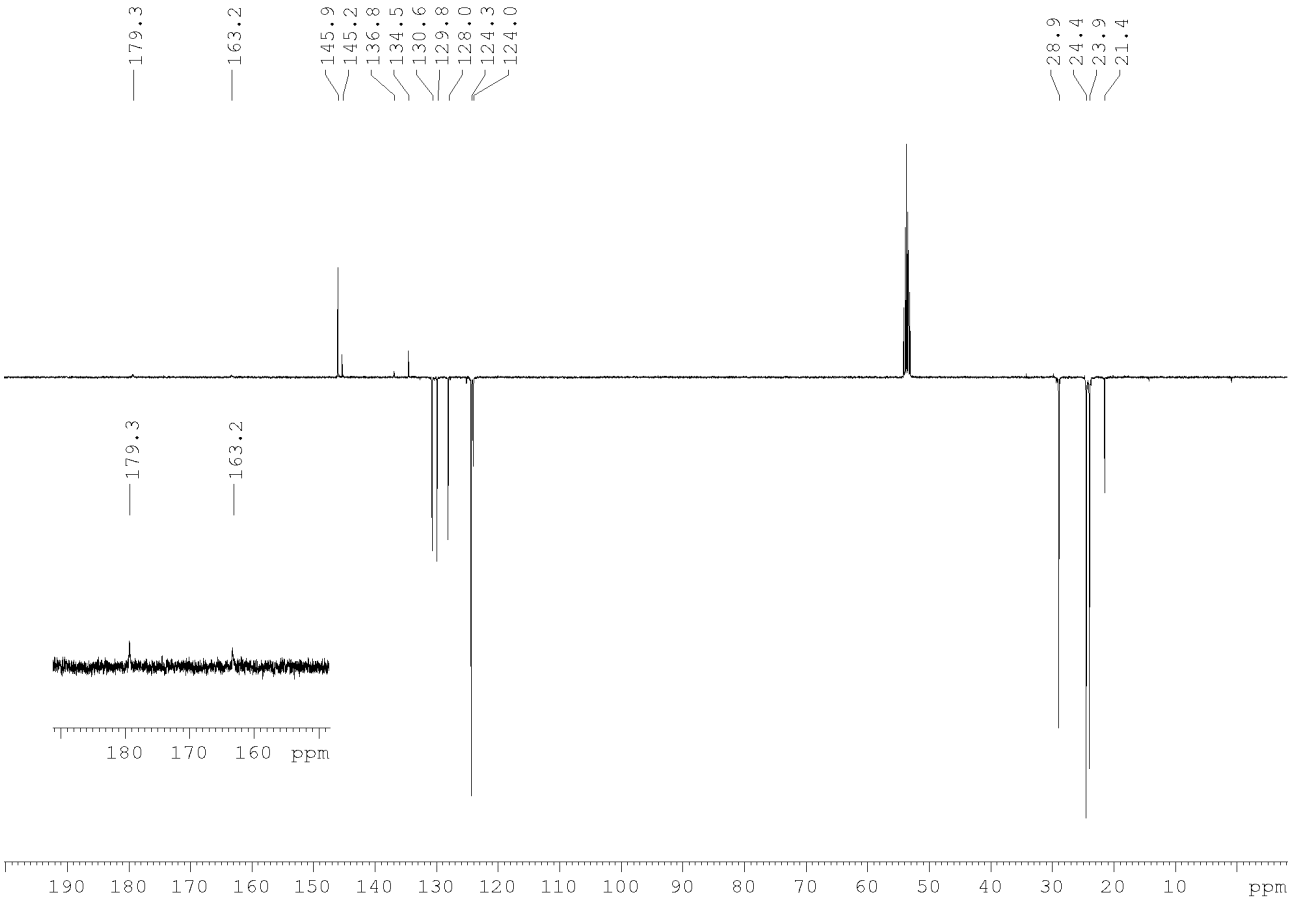
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K) of [Cu(4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazol-1-yl)(IPr)], **2**



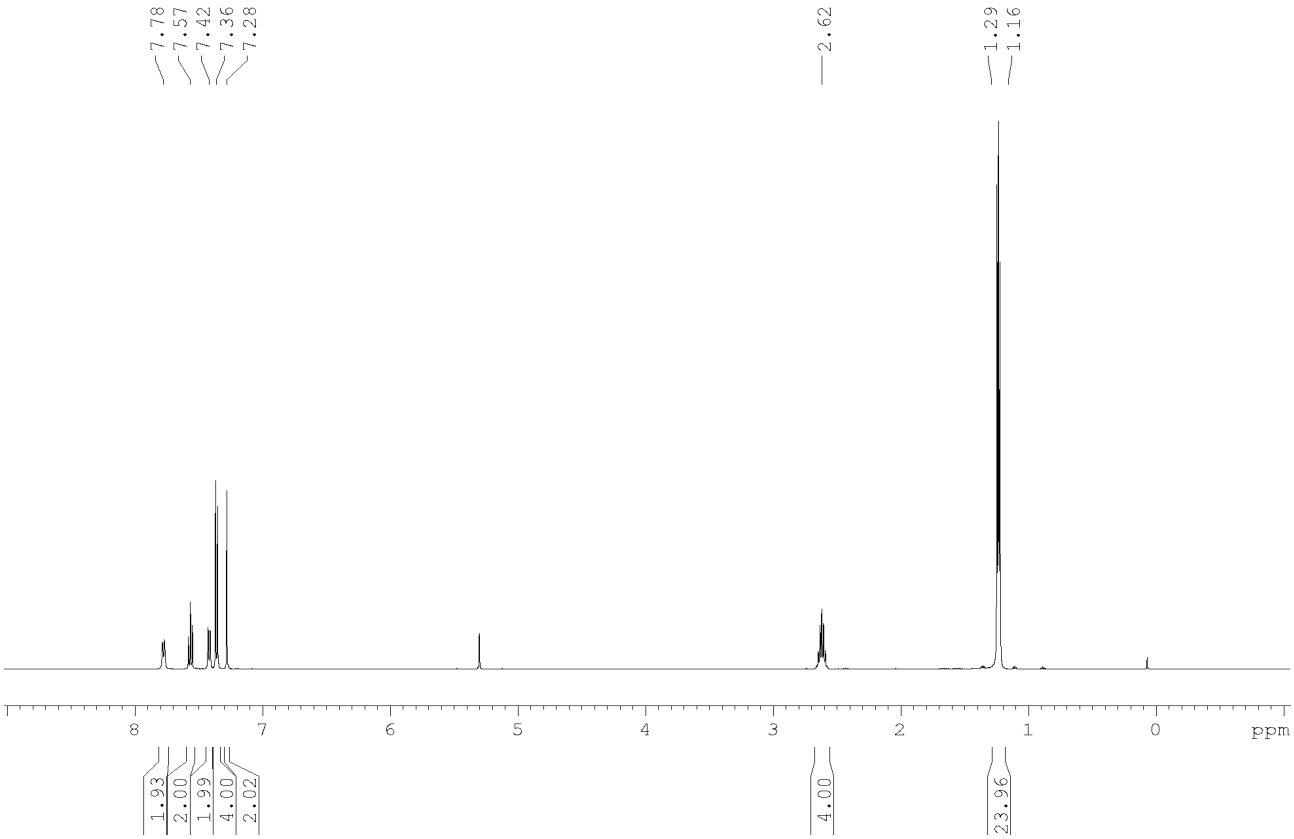
^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of [Cu(5-tosyl-1*H*-tetrazol-1-yl)(IPr)], **3**



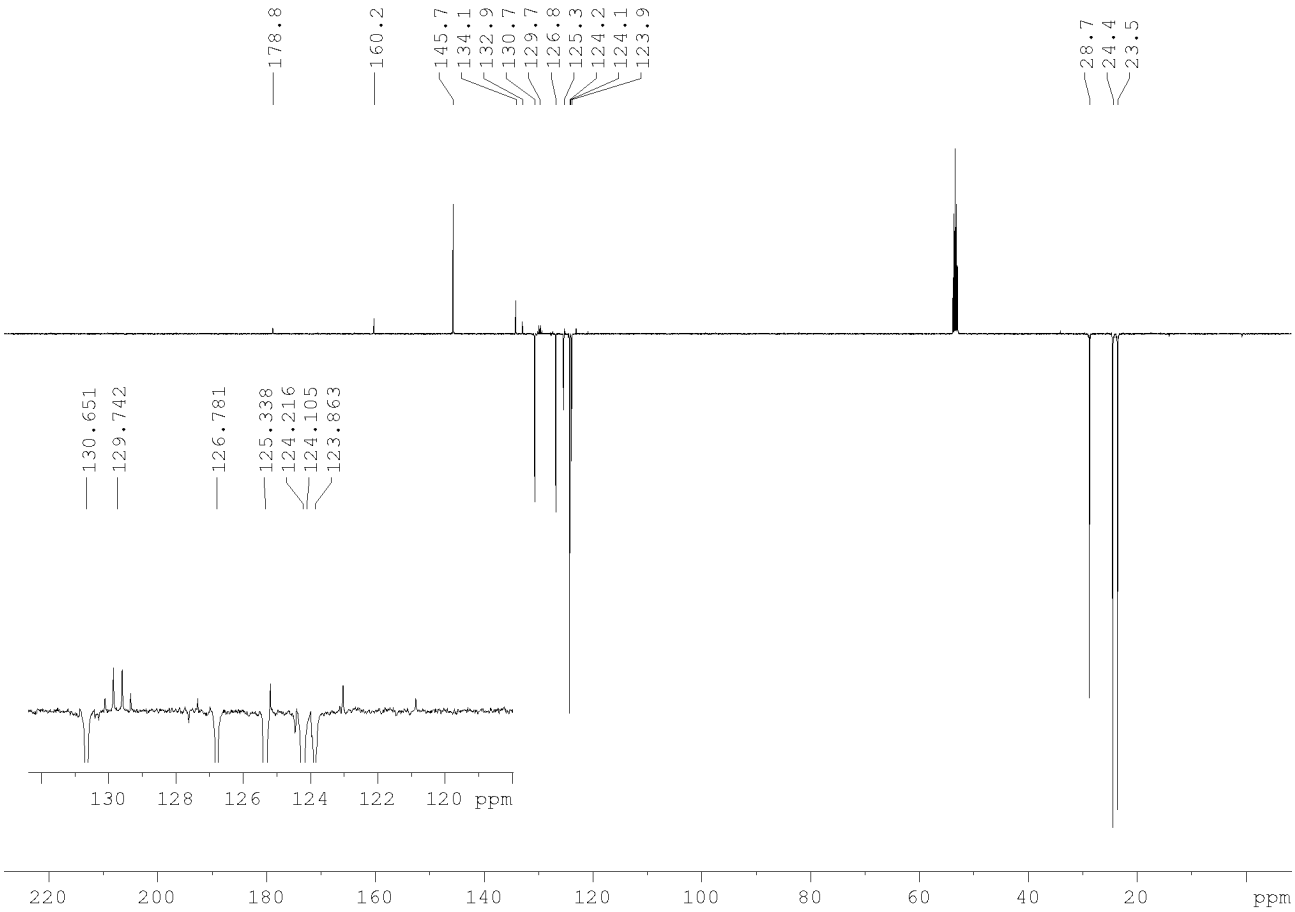
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K) of [Cu(5-tosyl-1*H*-tetrazol-1-yl)(IPr)], **3**



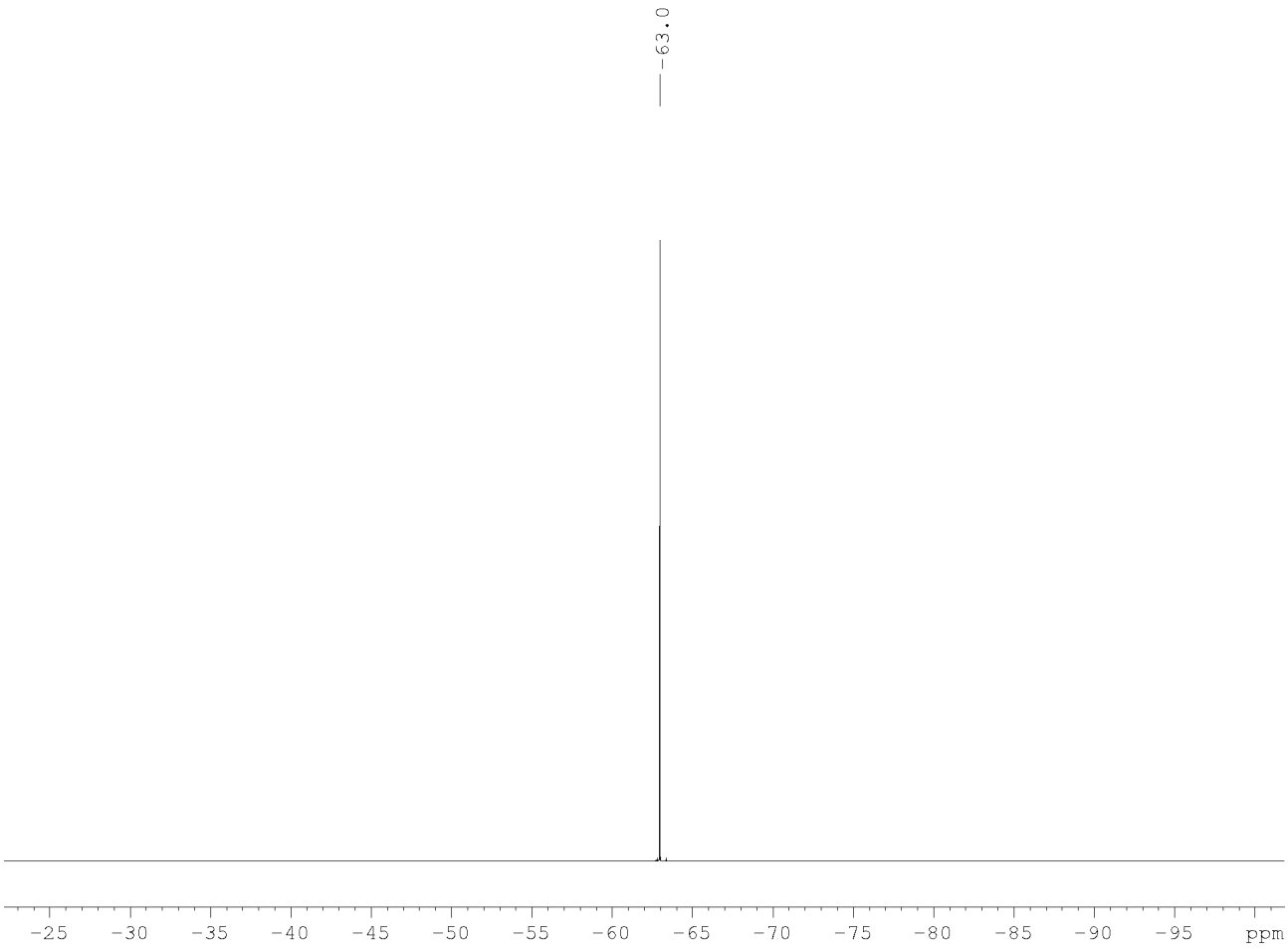
^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of [Cu(5-(4-(trifluoromethyl)phenyl)-2*H*-tetrazol-2-yl)(IPr)], **4**



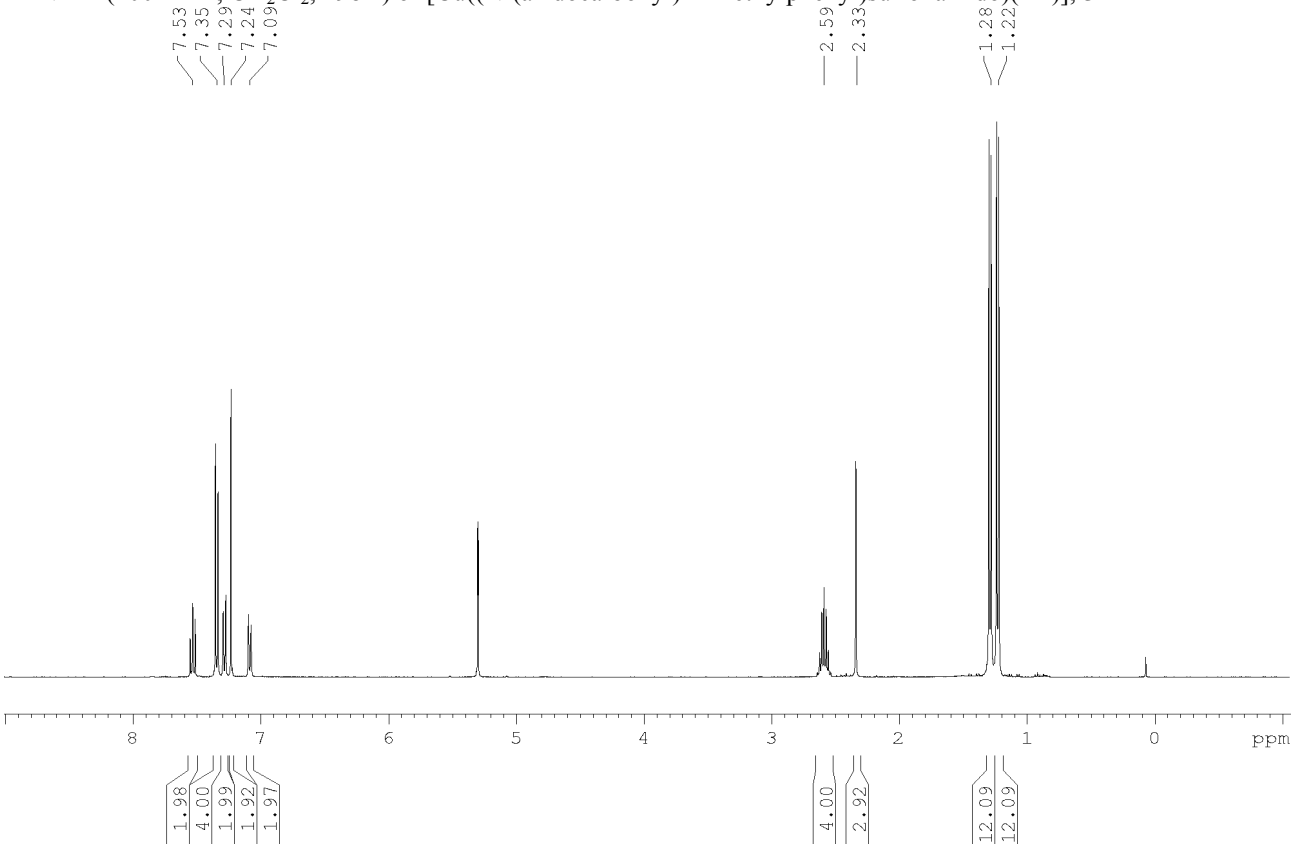
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K) of [Cu(5-(4-(trifluoromethyl)phenyl)-2*H*-tetrazol-2-yl)(IPr)], **4**



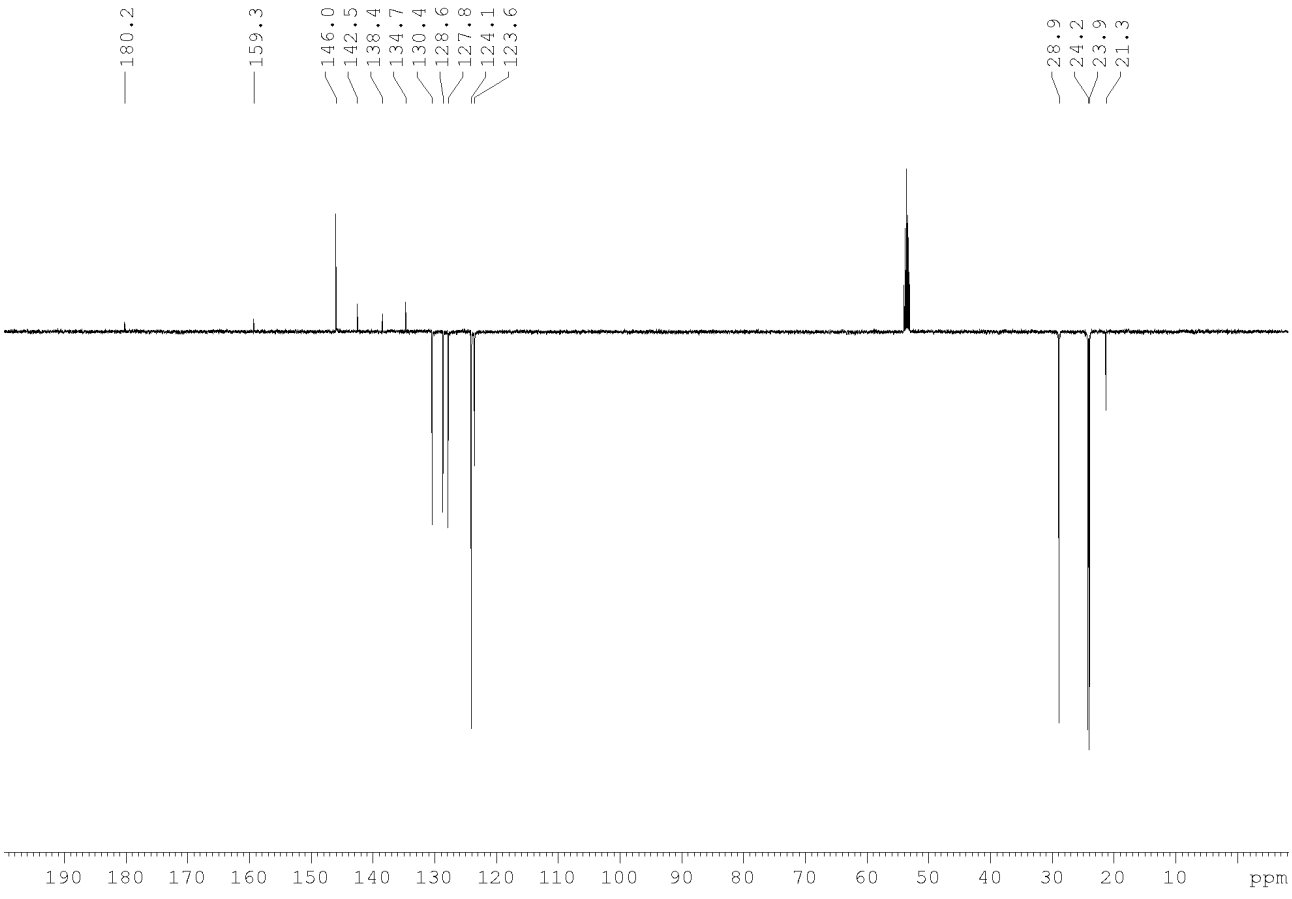
^{19}F-{^{1}H} NMR (376 MHz, CD_2Cl_2, 298K) of [Cu(5-(4-(trifluoromethyl)phenyl)-2*H*-tetrazol-2-yl)(IPr)], **4**



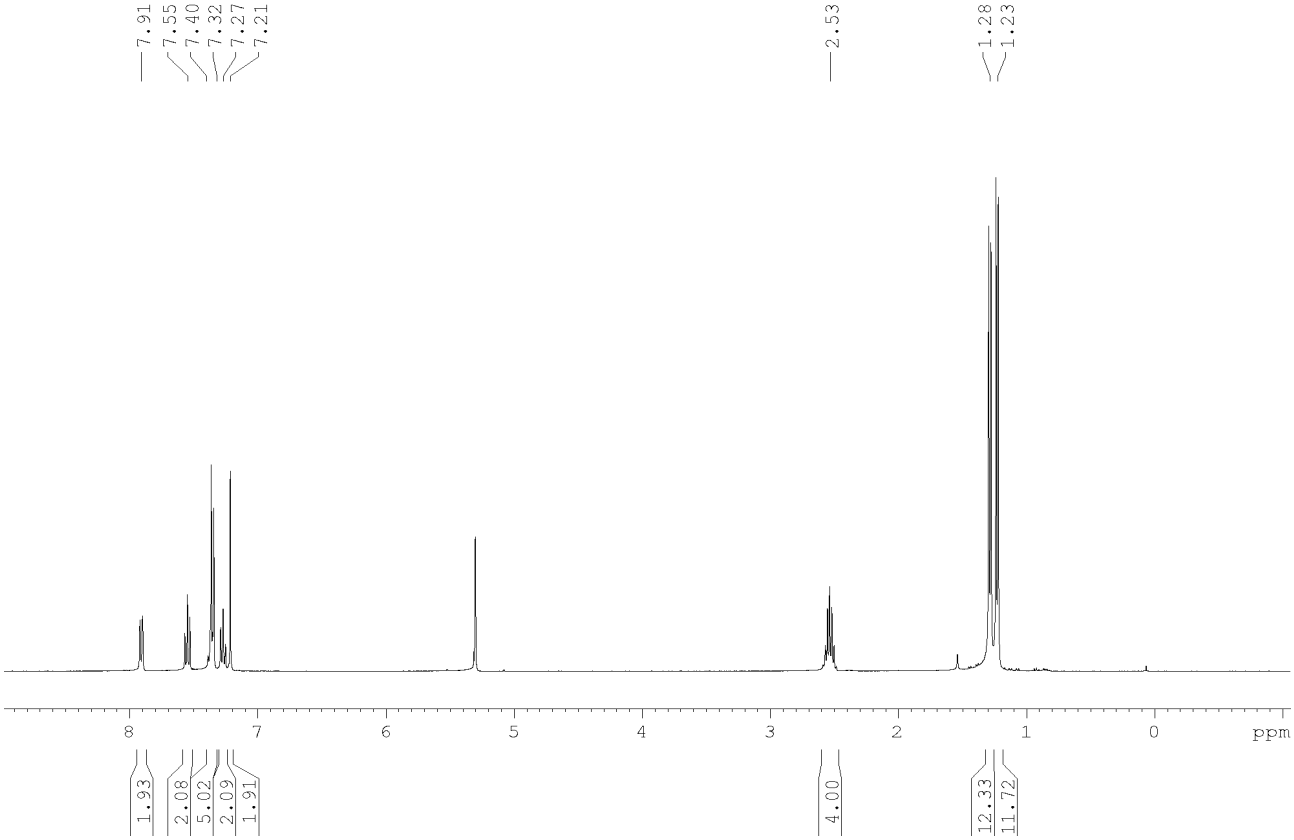
^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of [Cu((N-(azidocarbonyl)-4-methylphenyl)sulfonamido)(IPr)], **5**



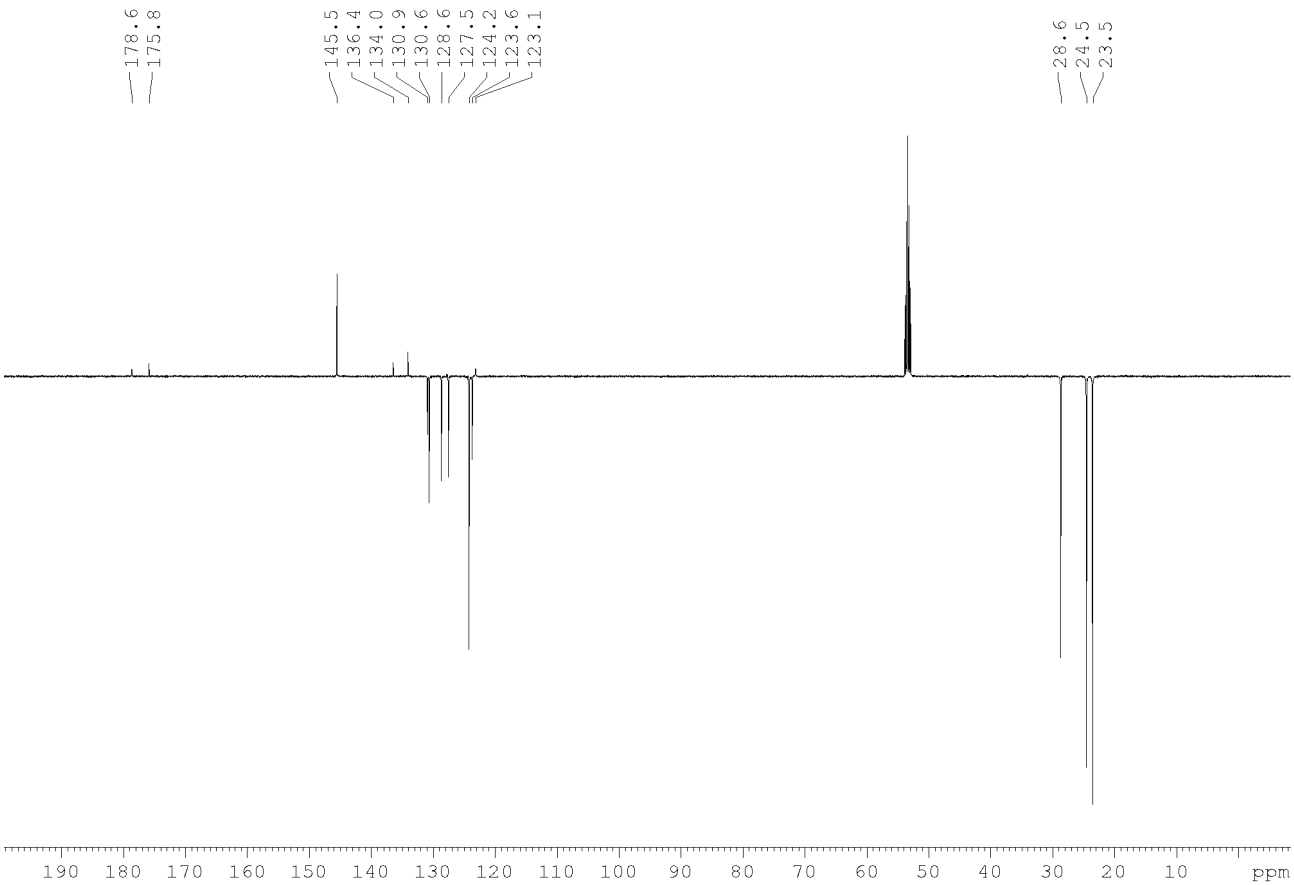
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K) of [Cu((N-(azidocarbonyl)-4-methylphenyl)sulfonamido)(IPr)], **5**



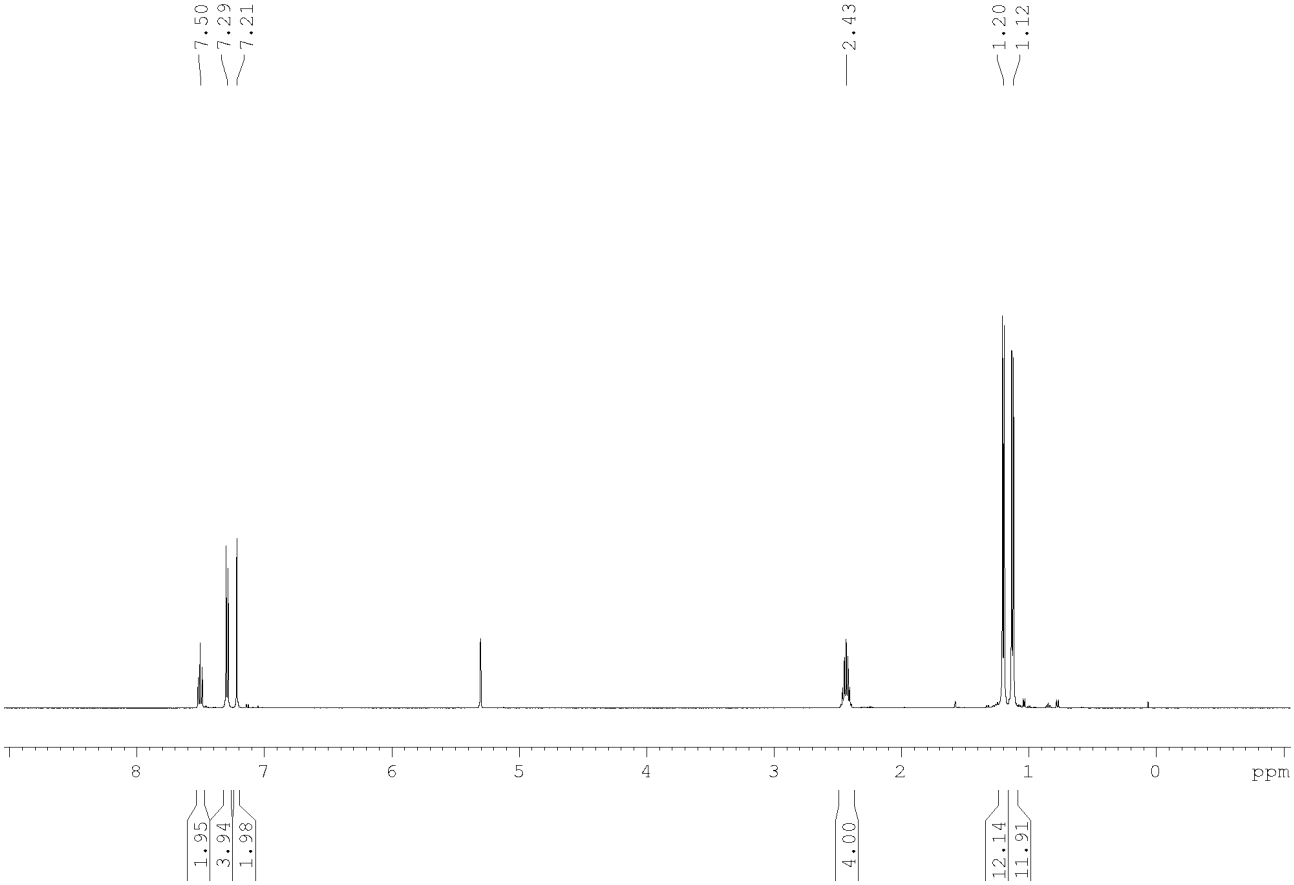
^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of [Cu((benzoylimino)methylene)amino)(IPr)], **6**



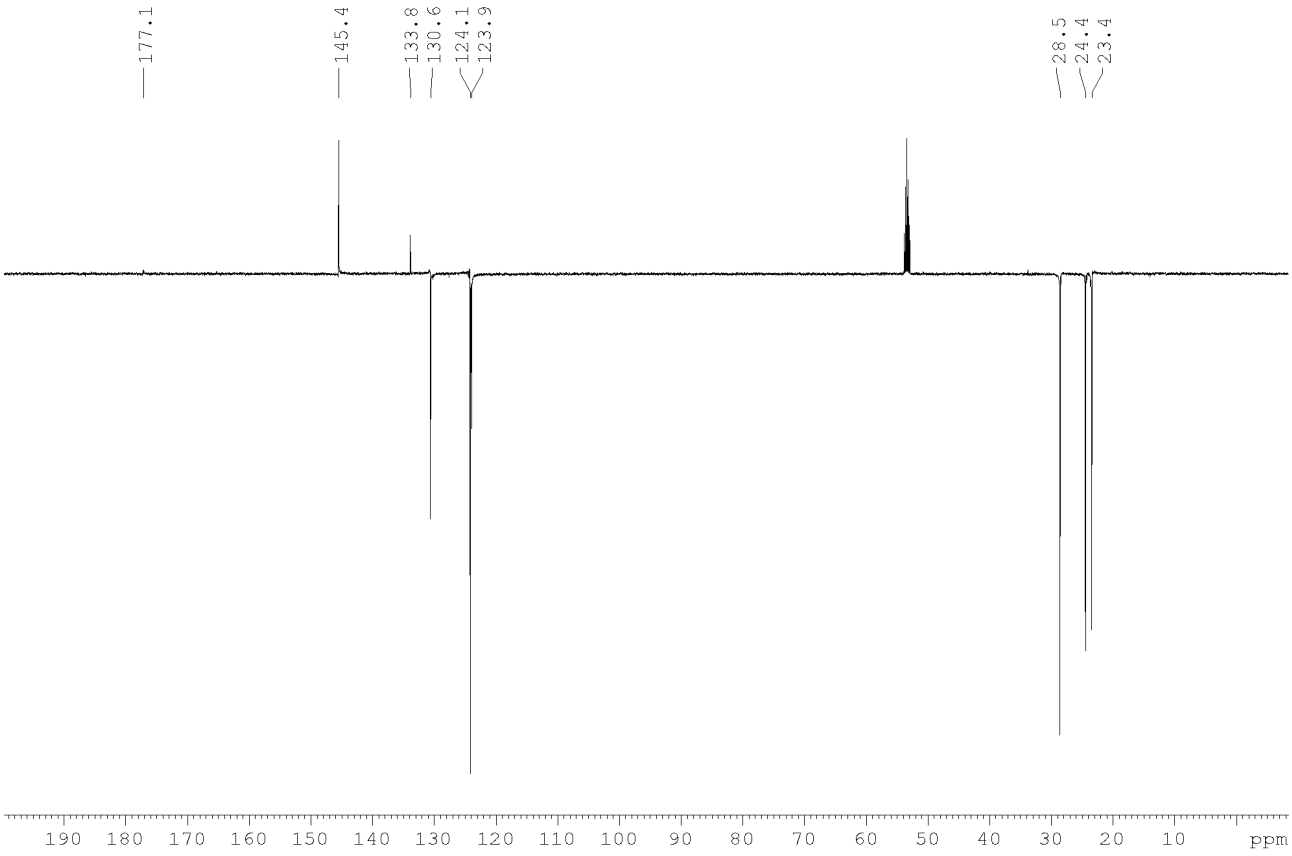
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K) of [Cu((benzoylimino)methylene)amino)(IPr)], **6**



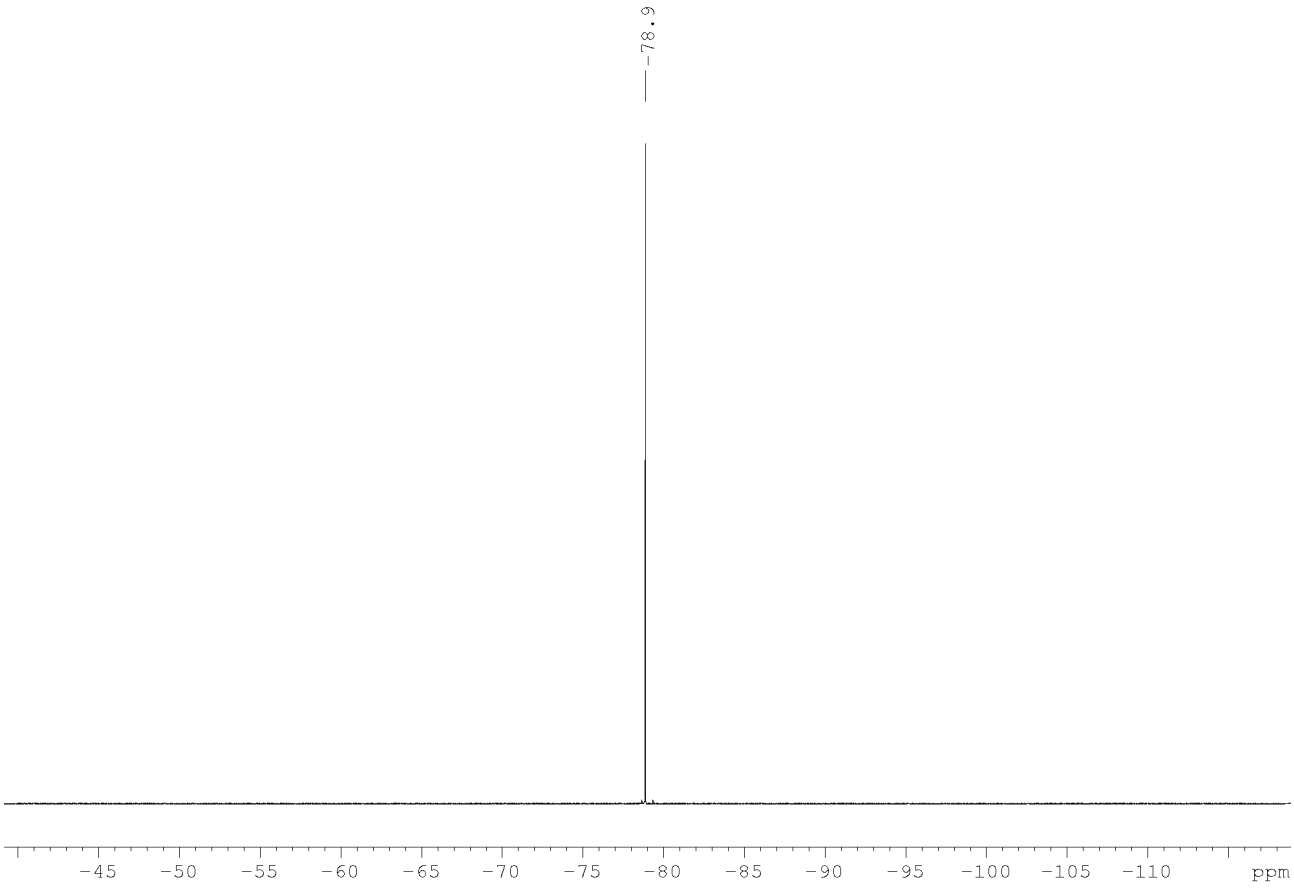
^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of [{Cu(IPr)}$_2$(μ-N_3)]OTf, **7**



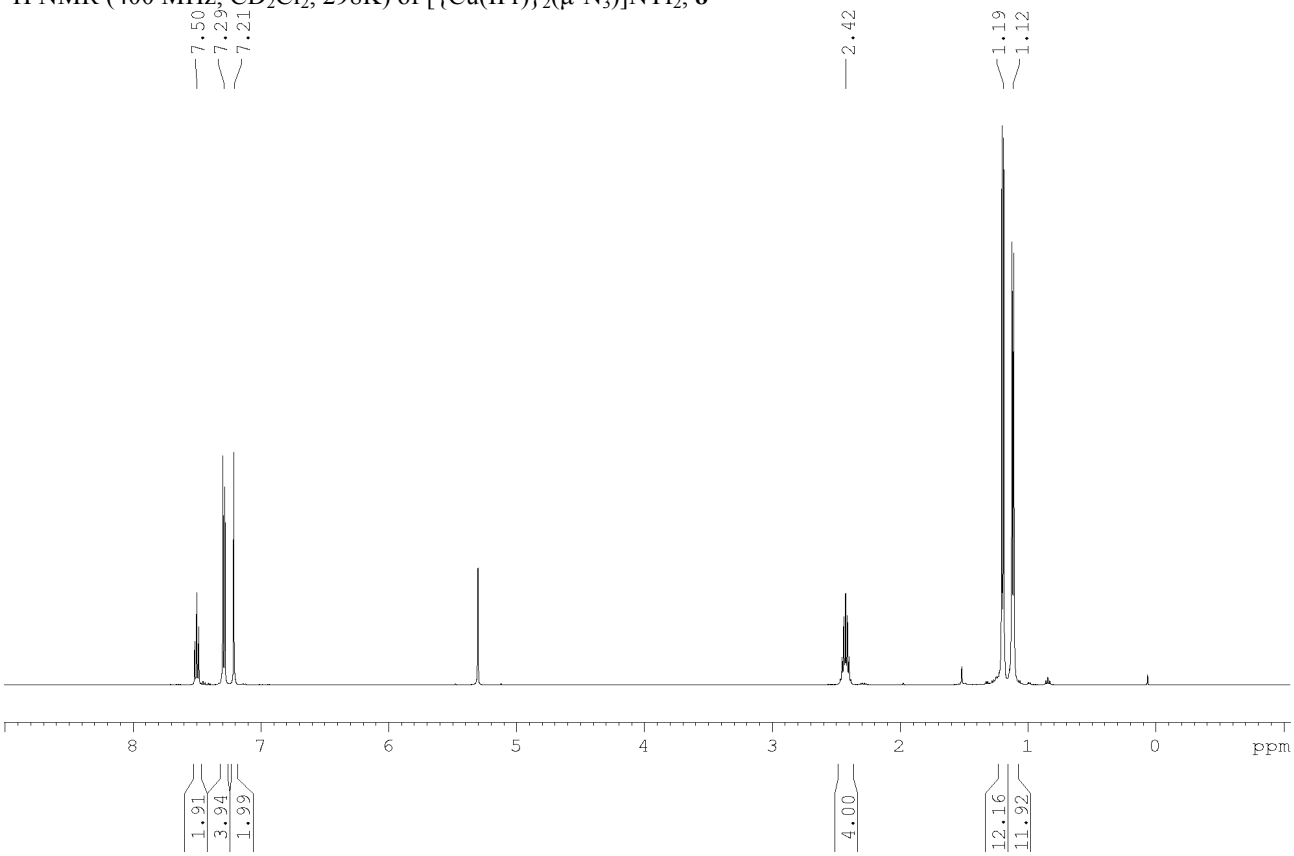
^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K) of [{Cu(IPr)}$_2$(μ-N_3)]OTf, **7**



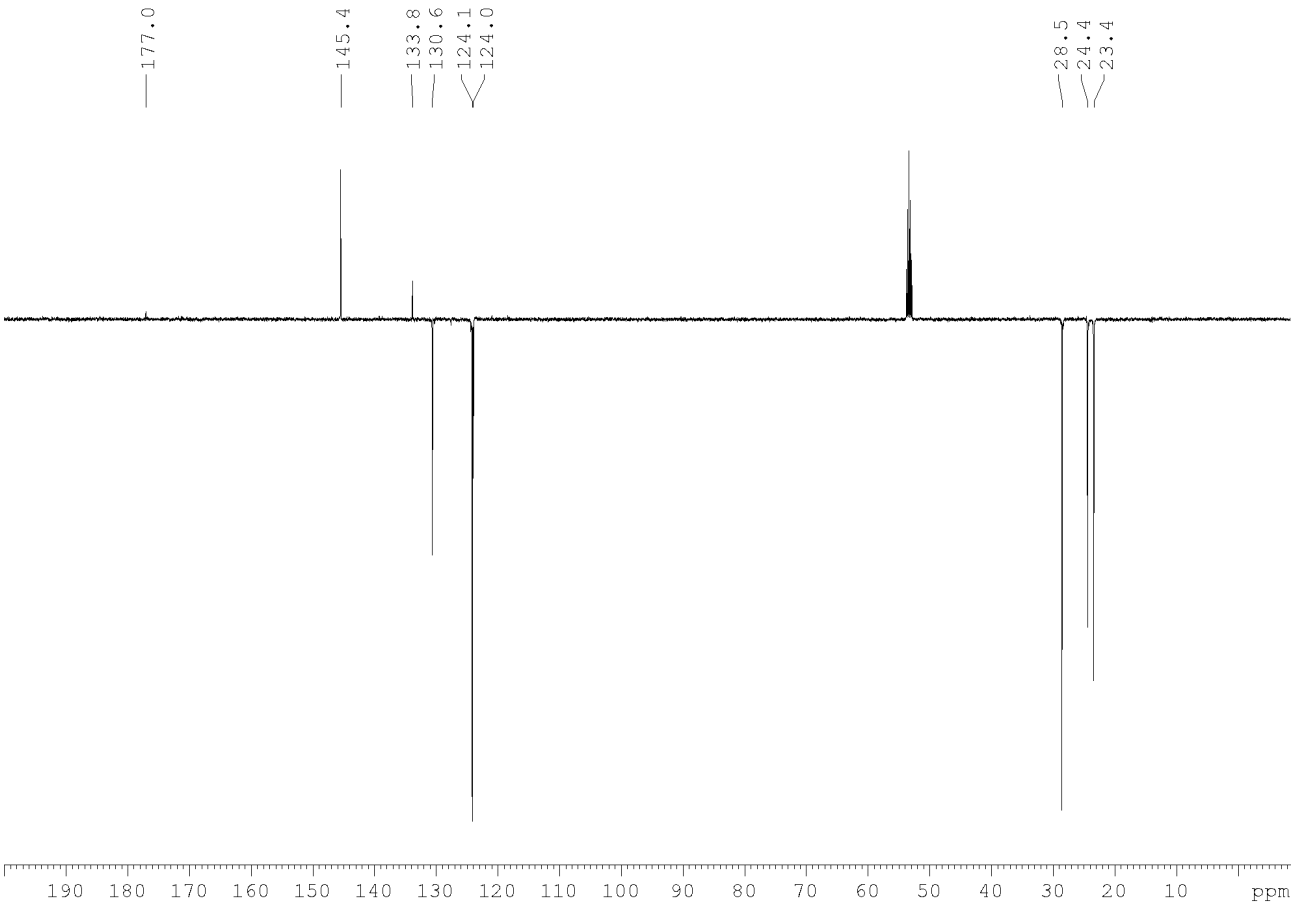
^{19}F-{^{1}H} NMR (376 MHz, CD_2Cl_2, 298K) of [{Cu(IPr)}$_2$(μ-N_3)]OTf, **7**



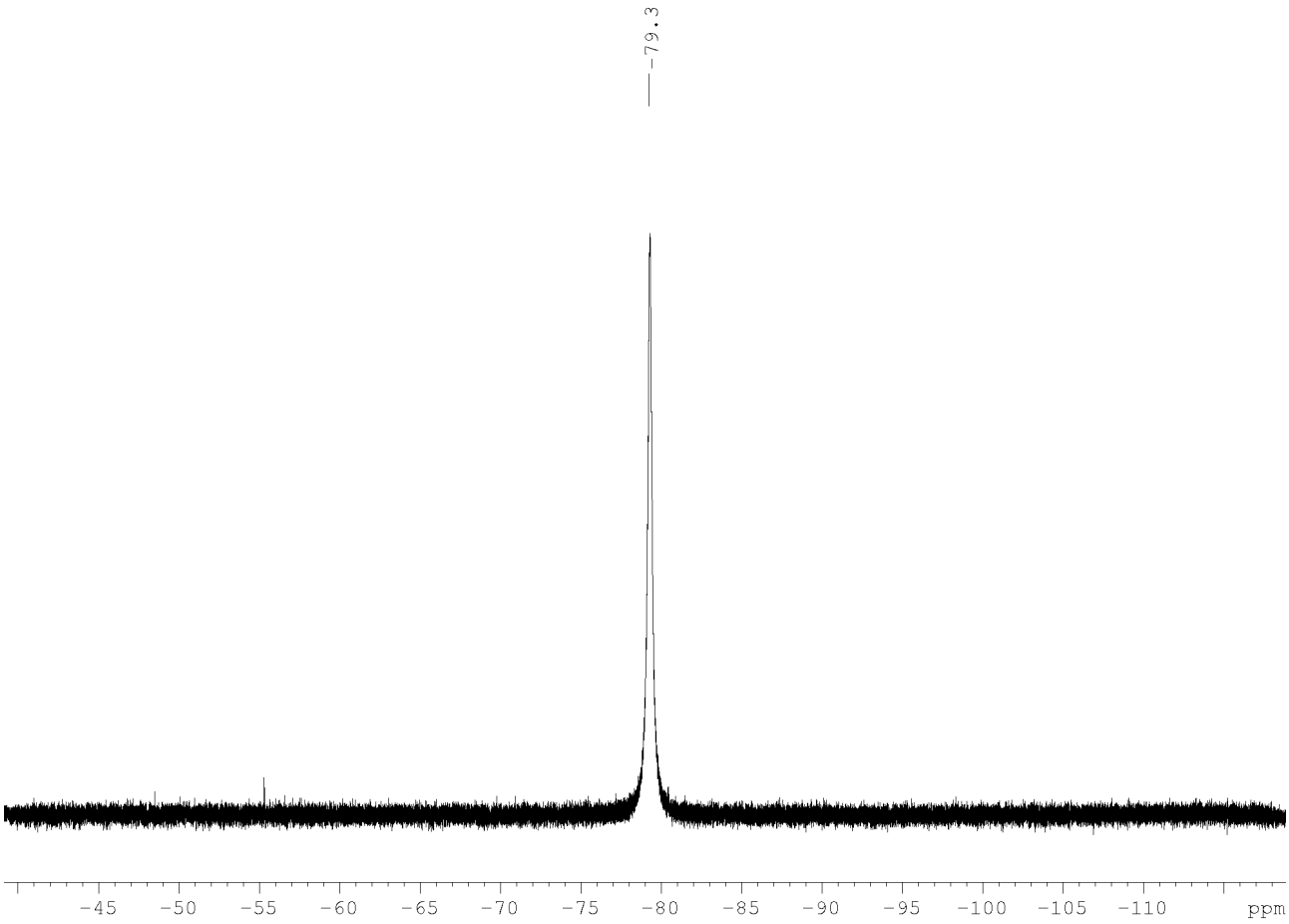
^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of [{Cu(IPr)}$_2$(μ-N_3)]NTf_2, **8**



^{13}C-{^{1}H} NMR (100 MHz, CD_2Cl_2, 298K) of [{Cu(IPr)}$_2$(μ-N_3)]NTf_2, **8**

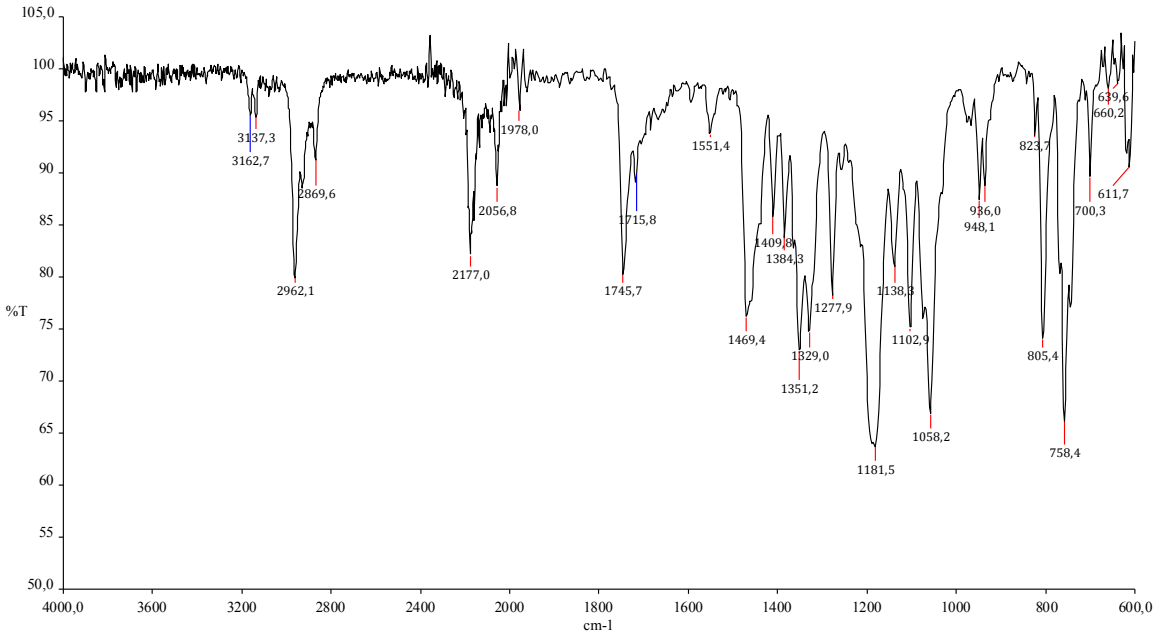


^{19}F-{^{1}H} NMR (376 MHz, CD_2Cl_2, 298K) of [{Cu(IPr)}$_2$(μ-N_3)]NTf_2, **8**

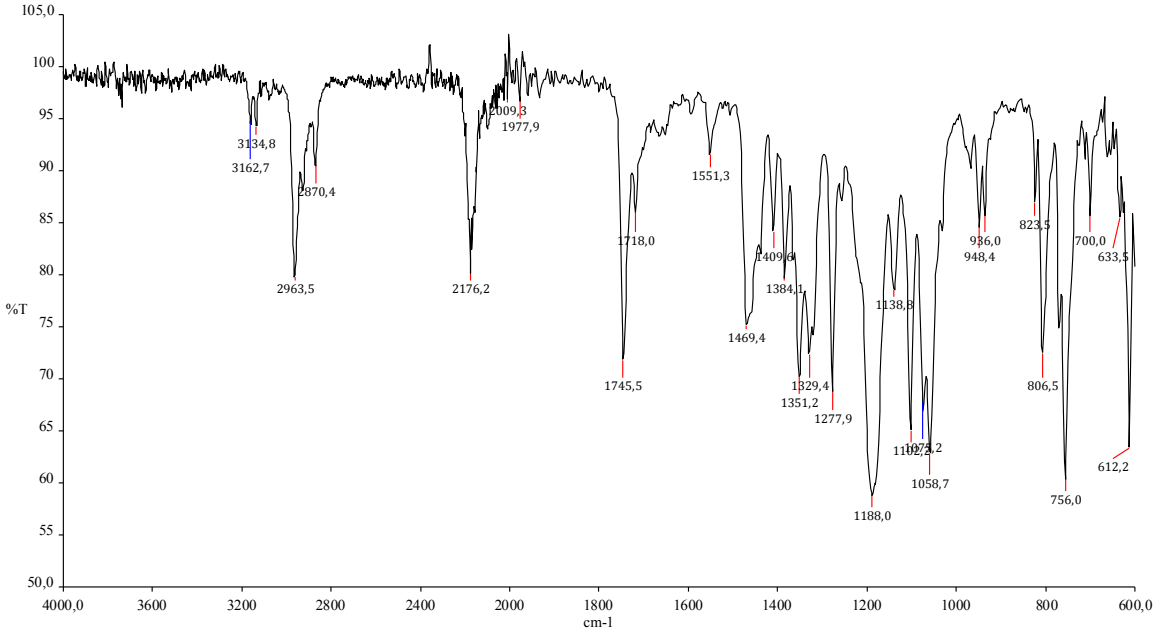


IR Spectra

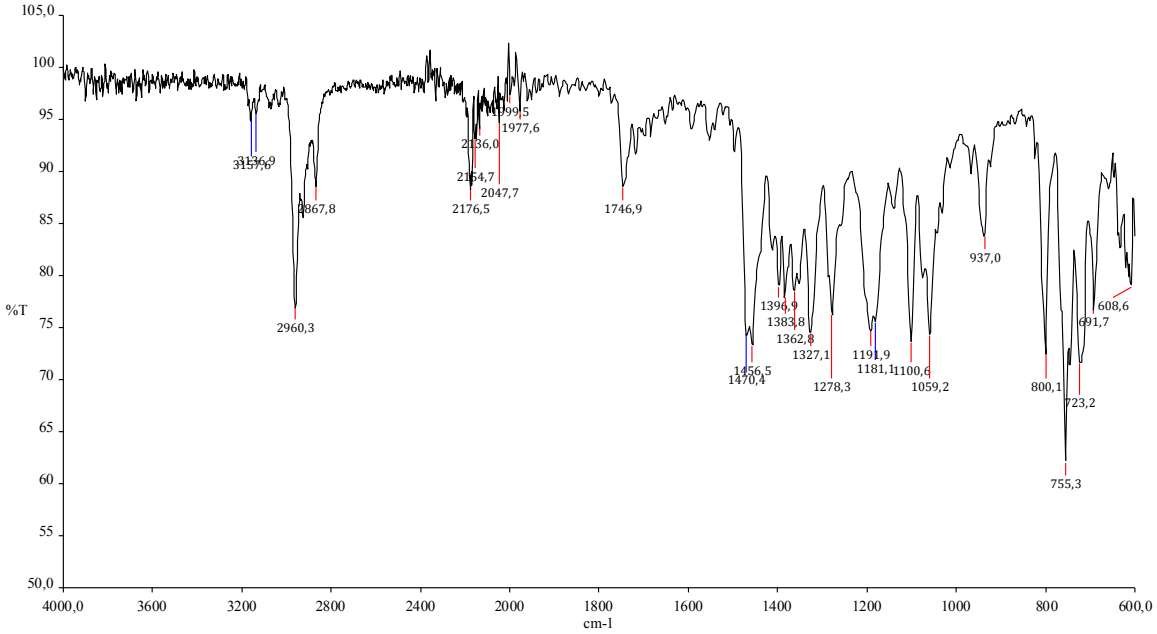
Complex 1



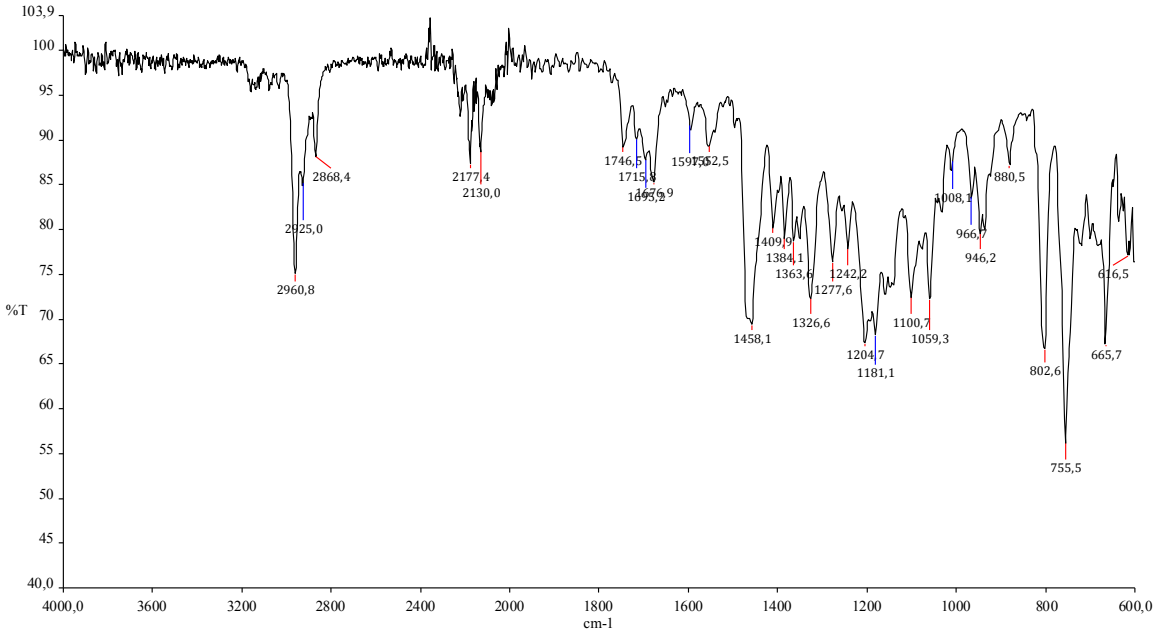
Complex 2



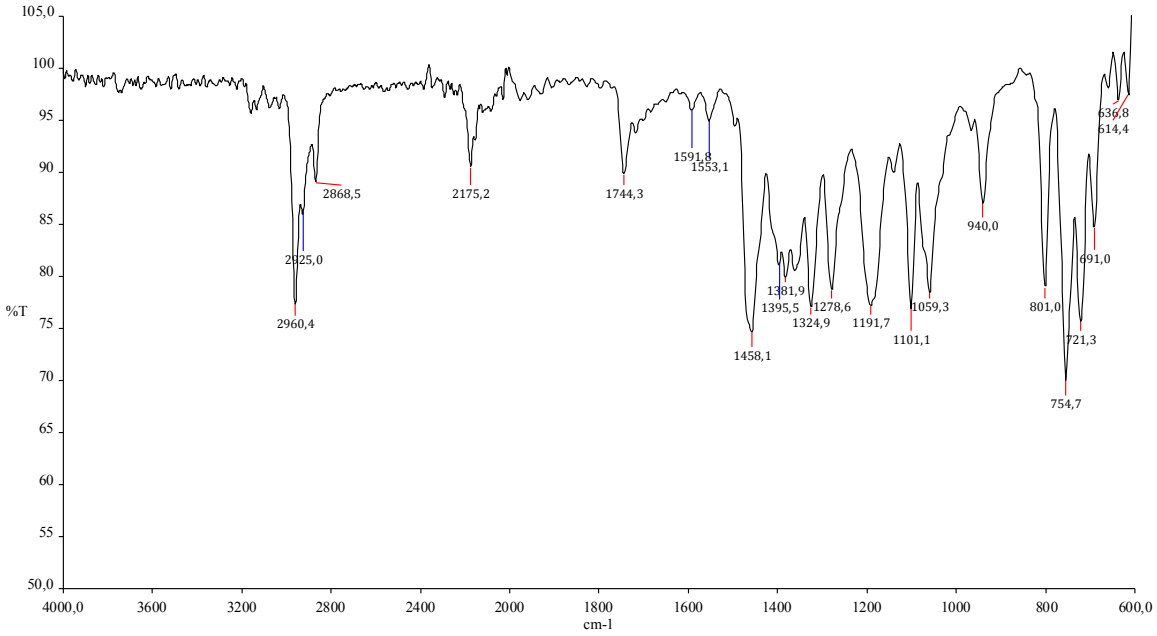
Complex 3



Complex 5



Complex 6



Complex 8