Supporting Information

for

Simple Synthesis of Neutral and Cationic Cu-NHC Complexes

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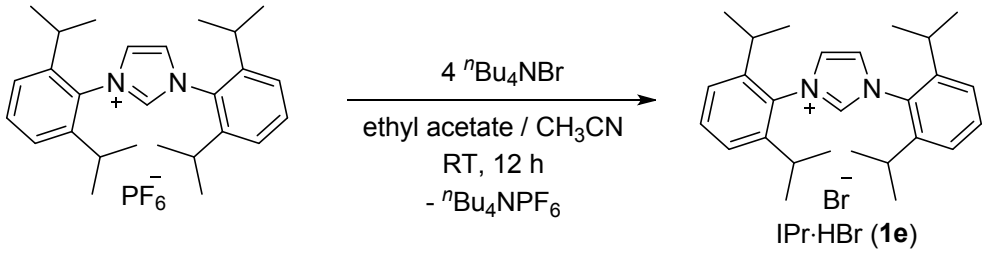
I General Information

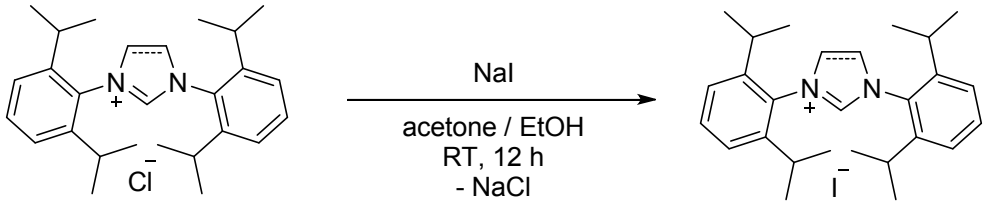
All chemicals were obtained from commercial suppliers and used as received without further purification. ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded at 400 and 100 MHz respectively on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm and coupling constants (J) are expressed in Hz. All NMR spectra were recorded at 298 K in deuterated solvent using the residual solvent peak as reference ($CHCl_3$ δ_H = 7.26 ppm, δ_C = 77.16 ppm; acetone δ_H = 2.05 ppm, δ_C = 29.84, 206.26 ppm; DMSO δ_H = 2.50 ppm, δ_C = 39.52 ppm; CH_3CN δ_H = 1.94 ppm, δ_C = 1.32, 118.26 ppm). Single-crystal X-ray diffraction data were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with a Mo Kα radiation (λ = 0.71073 Å).

II Preparation of N-Heterocyclic Carbene Precursors



IPr·HBr, 1e. IPr·HPF_6[1] (1.0 mmol, 535 mg) was dissolved in 21 mL of ethyl acetate/CH_3CN (v/v = 6/1), and tetrabutylammonium bromide (4.0 mmol, 1288 mg) was dissolved in 4 mL of ethyl acetate/ CH_3CN (v/v = 1/1). Then the imidazolium salt solution was added into the $^{n}Bu_4NBr$ solution, and the mixture was stirred at room temperature overnight. The resulting off-white precipitate was filtered, washed with ethyl acetate/CH_3CN (v/v = 6/1) (3 mL × 3) and diethyl ether (5 mL × 3). The desired product was obtained after dried in vacuo. Yield: 318 mg (68%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6 (v/v=2/1)): δ 10.18 (s, 1H, NC*H*N), 8.09 (d, J = 1.2 Hz, 2H, NC*H*C*H*N), 7.64 (t, J = 7.6, 8.0 Hz, 2H, Ar-*H*), 7.41 (d, J = 7.6 Hz, 4H, Ar-*H*), 2.35-2.46 (m, 4H, C*H*$(CH_3)_2$), 1.31, 1.22 (both d, J = 6.8 Hz, each 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6 (v/v=2/1)):

δ 144.4, 139.1, 131.5, 129.5, 125.5, 124.1, 28.5, 24.0, 23.0.

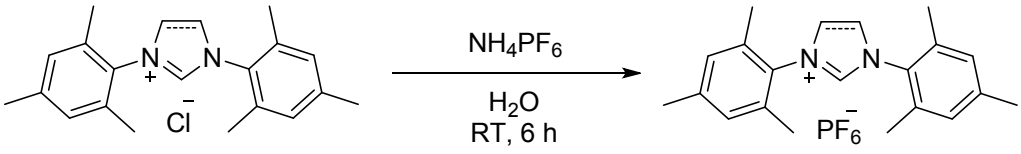


IPr·HI (**1f**)
SIPr·HI (**1g**)

IPr·HCl[2] or SIPr·HCl[2] (3.0 mmol) was dissolved in the mixture solvent of acetone/EtOH (15 mL/2 mL). NaI (3.0 mmol, 450 mg) was added into the solution, and the mixture was stirred at room temperature for 12 h. The resulting precipitate NaCl was removed via filtration, and the filtrate was concentrated. Addition of diethyl ether into the filtrate gave the desired product.

IPr·HI, 1i.[3] Yield: 923 mg (60%), off-white powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.16 (br. s, 1H, NC*H*N), 8.56, 8.55 (both s, each 1H, NC*H*CHN), 7.69 (t, J = 7.6, 8.0 Hz, 2H, Ar-*H*), 7.53 (d, J = 7.6 Hz, 4H, Ar-*H*), 2.31-2.37 (m, 4H, C*H*$(CH_3)_2$), 1.26, 1.16 (both d, J = 6.8 Hz, each 12 H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.8, 139.2, 131.9, 130.0, 126.2, 124.6, 28.6, 24.1, 23.1.

SIPr·HI, 1j.[3a] Yield: 1232 mg (79%), pale yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.44 (s, 1H, NC*H*N), 7.55 (t, J = 8.0, 7.6 Hz, 2H, Ar-*H*), 7.42 (d, J = 7.6 Hz, 4H, Ar-*H*), 4.54 (s, 4H, NCH_2CH_2N), 3.00-3.13 (m, 4H, C*H*$(CH_3)_2$), 1.35 (d, J = 6.4 Hz, 12H, CH_3), 1.19 (d, J = 6.8 Hz, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.1, 146.1, 131.1, 129.8, 124.8, 53.7, 28.3, 25.0, 23.3.



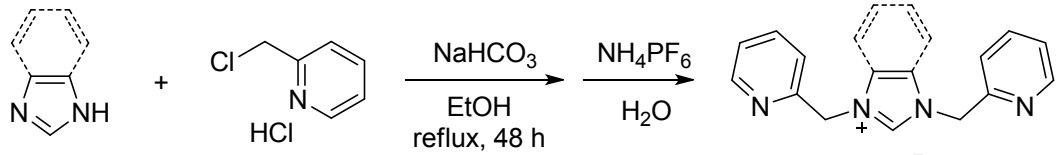
IMes·HPF$_6$ (**1h**)
SIMes·HPF$_6$ (**1i**)

IMes·HCl[2] or SIMes·HCl[2] (3.0 mmol) was dissolved in 25 mL of water. NH_4PF_6 (10.0 mmol, 1630 mg) was added into the solution, and the mixture was allowed to be stirred at room temperature

for 6 h. The resulting white precipitate was isolated via filtration, washed with water, and dried in vacuo.

IMes·HPF$_6$, 1h. Yield: 1242 mg (92%), white powder. ^{1}H NMR(400 MHz, DMSO-d_6): δ 9.68 (s, 1H, NC*H*N), 8.29 (s, 2H, NC*H*C*H*N), 7.23 (s, 4H, Ar-*H*), 2.38 (s, 6H, CH_3), 2.16 (s, 12H, CH_3). ^{13}C NMR(100 MHz, DMSO-d_6): δ 140.7, 138.5, 134.3, 131.0, 129.4, 124.9, 20.6, 16.9.

SIMes·HPF$_6$, 1i. Yield: 1288 mg (95%), white powder. ^{1}H NMR(400 MHz, DMSO-d_6): δ 9.04 (s, 1H, NC*H*N), 7.12 (s, 4H, Ar-*H*), 4.48 (s, 4H, NCH_2CH_2N), 2.39 (s, 12H, CH_3), 2.32 (s, 6H, CH_3). ^{13}C NMR(100 MHz, DMSO-d_6): δ 160.4, 139.7, 135.4, 130.9, 129.5, 50.9, 20.5, 17.2.



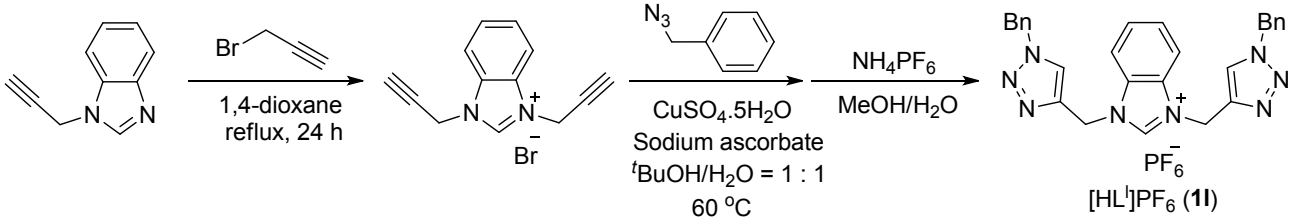
[HL^j]PF$_6$ (**1j**)
[HL^k]PF$_6$ (**1k**)
(benzimidazolium)

The mixture of imidazole or benzimidazole (20.0 mmol), 2-(chloromethyl)pyridine hydrochloride (45.0 mmol, 7380 mg), and $NaHCO_3$ (80.0 mmol, 6720 mg) suspended in 50 mL of EtOH was refluxed for 48 h. The mixture was filtered, and the filtrate was dried under reduced pressure. The residue was washed with CH_3CN, and dissolved in water. The aqueous solution was filtered and added into the aqueous solution of an excess of NH_4PF_6. The resulting precipitate was isolated by filtration, and washed with EtOH and diethyl ether. The desired product was obtained after dried in vacuo.

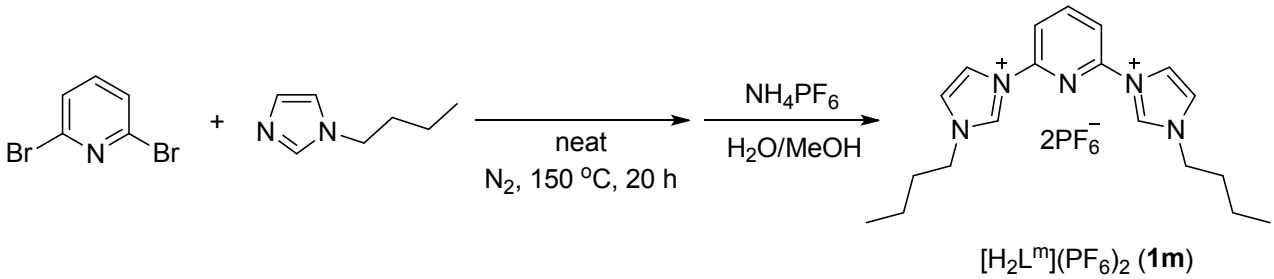
[HL^j]PF$_6$, 1j.[4] Yield: 3960 mg (50%), off-white solid. ^{1}H NMR(400 MHz, DMSO-d_6): δ 9.44 (s, 1H, NC*H*N), 8.56 (d, J = 4.4 Hz, 2H, 6-Py), 7.90 (t, J = 7.8 Hz, 2H, 4-Py), 7.82 (s, 2H, NC*H*C*H*N), 7.49 (d, J = 8.0 Hz, 2H, 3-Py), 7.41 (t, J = 5.2, 5.6 Hz, 2H, 5-Py), 5.63 (s, 4H, NCH_2). ^{13}C NMR(100

MHz, DMSO-d_6): δ 153.5, 149.6, 137.7, 137.6, 123.7, 123.3, 122.5, 53.2.

[HL^k]PF$_6$, 1k.[4] Yield: 4816 mg (54%), off-white solid. ^{1}H NMR(400 MHz, DMSO-d_6): δ 10.15 (s, 1H, NC*H*N), 8.52 (br. s, 2H), 7.95-8.03 (m, 2H), 7.92 (t, J = 7.6 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.57-7.66 (m, 2H), 7.38 (br. s, 2H), 6.02 (s, 4H, NCH_2). ^{13}C NMR(100 MHz, DMSO-d_6): δ 153.0, 149.7, 144.0, 137.6, 131.3, 126.8, 123.8, 122.7, 113.9, 51.0.

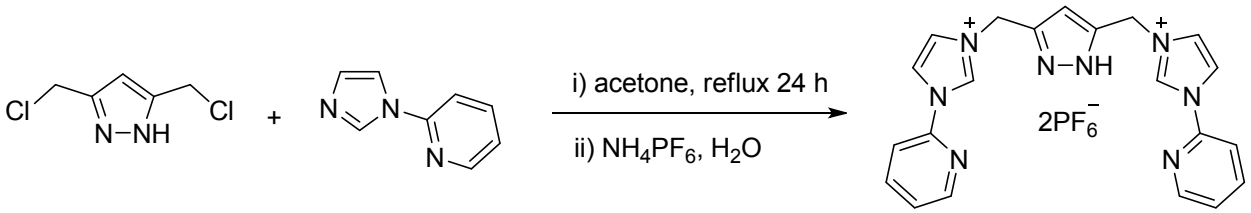


[HL^l]PF$_6$, 1l.[5] A solution of 1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazole[6] (4680 mg, 30 mmol) and 3-bromoprop-1-yne (3570 g, 30 mmol) in 30 mL of 1,4-dioxane was refluxed for 24 h. The resulting pale yellow solid was filtered, washed with 1,4-dioxane (10 mL × 3), diethyl ether (10 mL × 3) and dried in vacuo. The formed bromide salt (2750 mg, 10 mmol), (azidomethyl)benzene (3990 mg, 30 mmol), copper sulfate pentahydrate (250 mg, 1 mmol), and sodium ascorbate (400 mg, 2 mmol) were added into water/^{t}BuOH (20 mL/20 mL). The mixture was stirred at 60 ºC for 24 h. The reaction mixture was diluted with methanol (60 mL), and the yellow solution was added into an aqueous solution of an excess of NH_4PF_6. The resulting precipitate was collected by filtration and dried in vacuo. Yield: 4300 mg (71%), white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.96 (s, 1H, NC*H*N), 8.37 (s, 2H, 5-triazole *H*), 8.06 (m, 2H, benzimidazole *H*), 7.67 (m, 2H, benzimidazole *H*), 7.35-7.27 (m, 10H, Ph-*H*), 5.87 (s, 4H, CH_2), 5.62 (s, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.6, 140.3, 135.7, 131.0, 128.9, 128.3, 128.1, 126.9, 125.0, 114.1, 53.1, 41.9.



$[H_2L^m](PF_6)_2$ (**1m**)

[H₂L^m](PF₆)₂, 1m.[7] A mixture of 2,6-dibromopyridine (13.5 mmol, 3200 mg) and 1-butyl-1*H*-imidazole (40 mmol, 4960 mg) was heated at 150 ºC under nitrogen for 20 h. After the mixture was cooled to room temperature, 50 mL of chloroform and 250 mL of diethyl ether were added into the mixture. The precipitate was collected, and purified via recrystallization from Et_2O/MeOH solution. The white solid was dissolved in MeOH, filtered and added into the aqueous solution of an excess of NH_4PF_6. The resulting precipitate was isolated by filtration, and washed with EtOH and diethyl ether. The desired product was obtained after dried in vacuo. Yield: 3489 mg (42%), white solid. ^{1}H NMR(400 MHz, DMSO-d_6): δ 10.26 (s, 2H, NC*H*N), 8.79, 8.14 (both br. s, each 2H, NC*H*C*H*N), 8.60 (t, J = 8.0 Hz, 1H, 4-Py), 8.21 (d, J = 8.0 Hz, 2H, 3,5-Py), 4.32 (t, J = 6.8, 7.2 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 1.87-1.96 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.32-1.43 (m, 4H, $NCH_2CH_2CH_2CH_3$), 0.96 (t, J = 7.2 Hz, 6H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.3, 144.7, 135.6, 123.7, 119.4, 114.3, 49.7, 31.1, 18.9, 13.3.



$[H_2L^n](PF_6)_2$ (**1n**)

[H₂L^n](PF₆)₂, 1n.[8] A solution of 3,5-bis(chloromethyl)pyrazole[9] (6.0 mmol, 990 mg) and 2-(1*H*-imidazol-1-yl)pyridine (24.0 mmol, 3480 mg) in acetone was refluxed for 24 h. The resulting precipitate was filtered and dissolved in 50 mL of water. The aqueous solution was filtered and

added into the solution of an excess of NH_4PF_6 in water. The generating solid was collected by filtration, washed with water, and dried in vacuo. Yield: 1618 mg (40%), white solid. ^{1}H NMR(400 MHz, DMSO-d_6): δ 13.33 (s, 1H, N*H*), 10.17 (s, 2H, NC*H*N), 8.68 (d, J = 4.8 Hz, 2H), 8.54 (s, 2H), 8.22 (t, J = 7.2 Hz, 2H), 8.07 (d, J = 8.0 Hz, 2H), 8.00 (s, 2H), 7.69 (dd, J = 4.8, 7.2 Hz, 2H), 6.62 (s, 1H, pyrazole-*H*), 5.60 (s, 4H, NCH_2).

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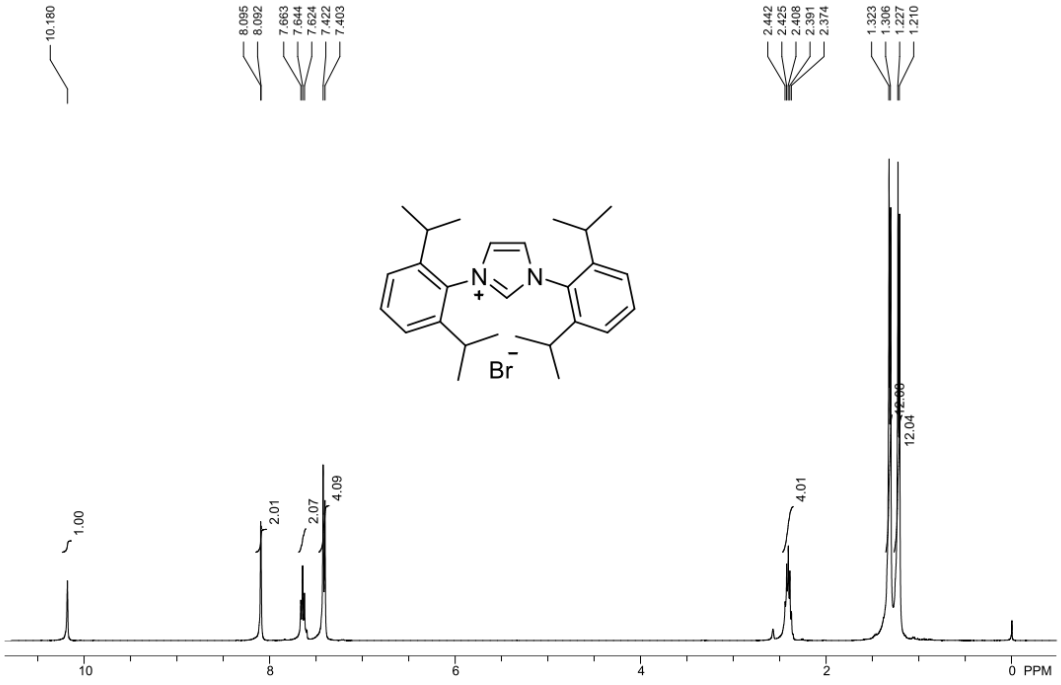
III Crystallographic Data of Cu(I)-NHC Complexes 2l and 2m

Table S1. Summary of the Crystallographic Data for 2l and 2m.

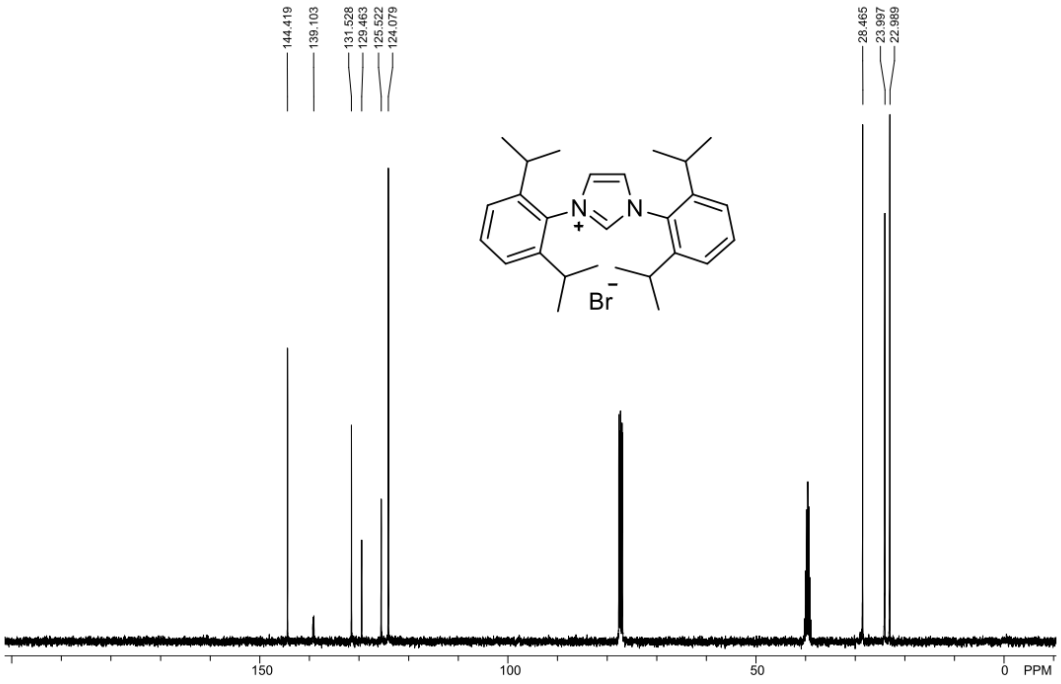
	2l	**2m**
Formula	$C_{81}H_{72}Cu_3F_{18}N_{24}P_3$	$C_{38}H_{50}Cu_2F_{12}N_{10}P_2$
Fw	2007.16	1063.90
Temperature	293(2) K	293(2) K
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
a, Å	19.3418(6)	23.3578(14)
b, Å	20.3706(5)	12.8016(6)
c, Å	25.5215(7)	17.0511(9)
α, deg.	90	90
β, deg.	97.939(2)	116.390(7)
γ, deg.	90	90
V, Å^3	9959.2(5)	4567.3(4)
Z	4	4
D_{calcd}, Mg/m^3	1.339	1.547
Reflections collected	19305	9824
Reflections independent, R_{int}	8750, 0.0334	4020, 0.0299
Goodness-of-fit on F^2	1.029	0.994
$R1$, $wR2$ ($I>2\sigma(I)$)	0.0703, 0.1771	0.0566, 0.1425
$R1$, $wR2$ (all data)	0.0945, 0.1884	0.0752, 0.1579

IV ^{1}H and ^{13}C-{^{1}H} NMR Spectra of Carbene Precursors

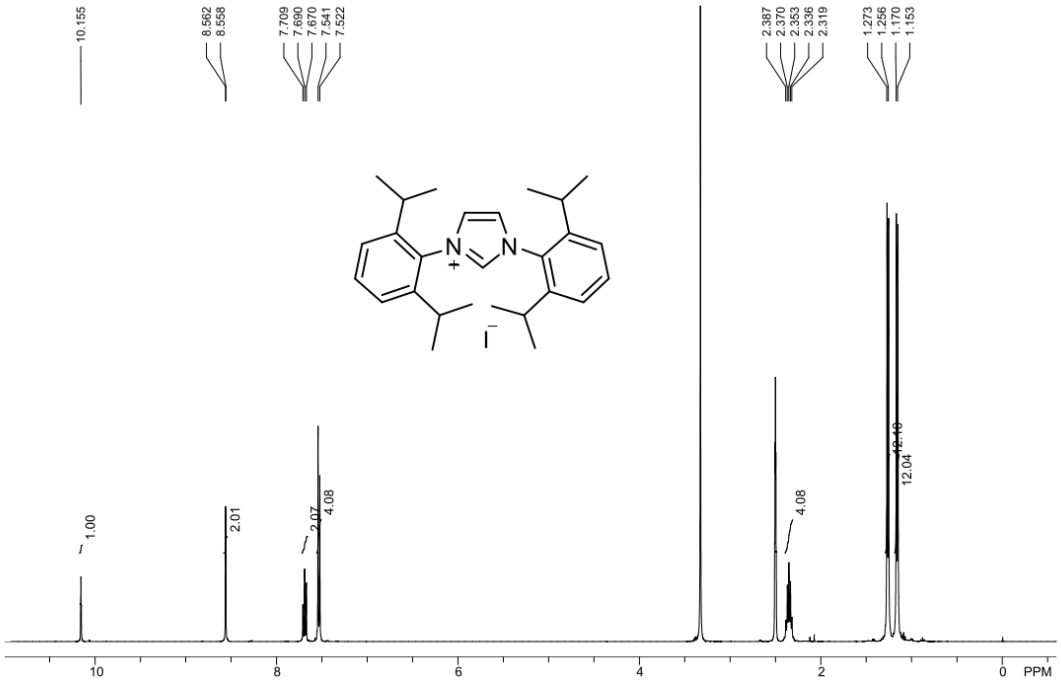
^{1}H NMR spectrum of IPr·HBr (**1e**) at 298 K ($CDCl_3$+DMSO-d_6 (v/v=2/1), 400 MHz)



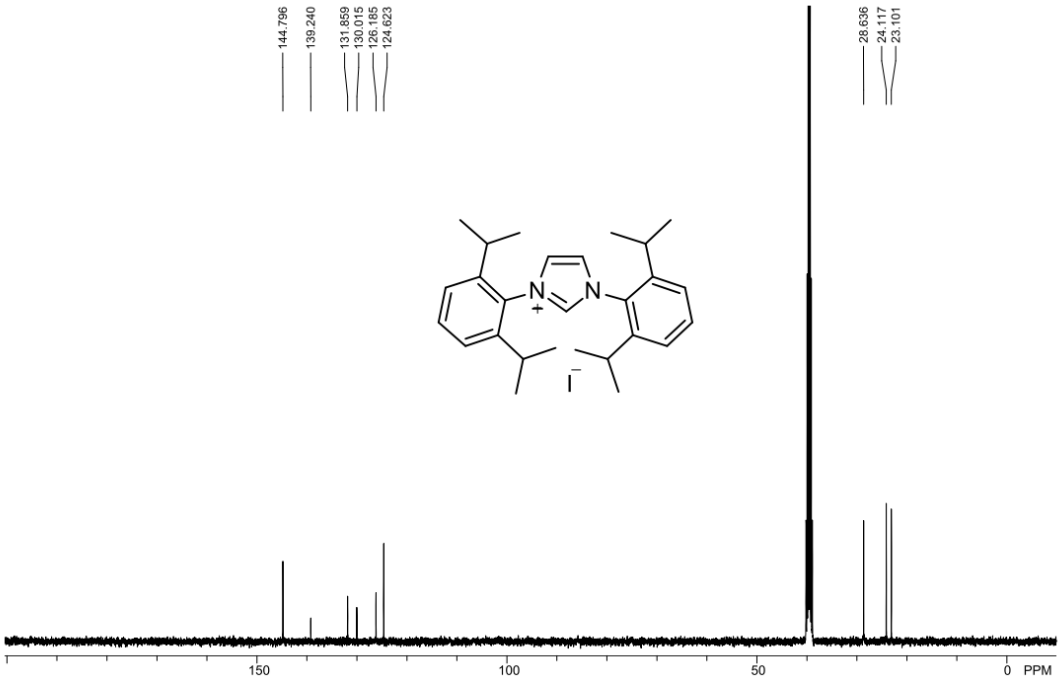
^{13}C NMR spectrum of IPr·HBr (**1e**) at 298 K ($CDCl_3$+DMSO-d_6 (v/v=2/1), 100 MHz)



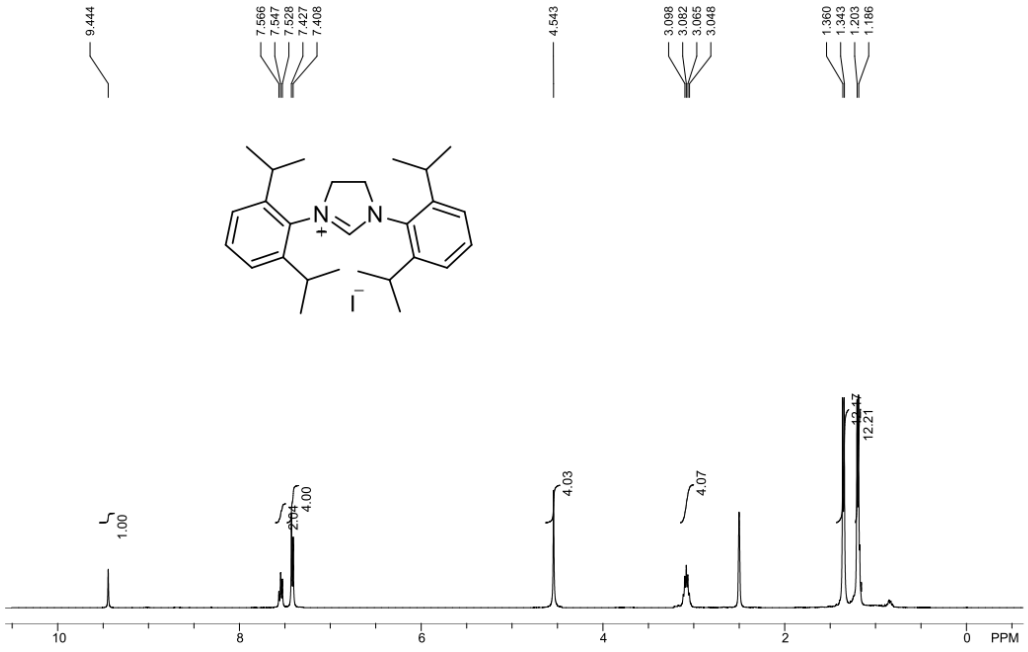
^{1}H NMR spectrum of IPr·HI (**1f**) at 298 K (DMSO-d_6, 400 MHz)



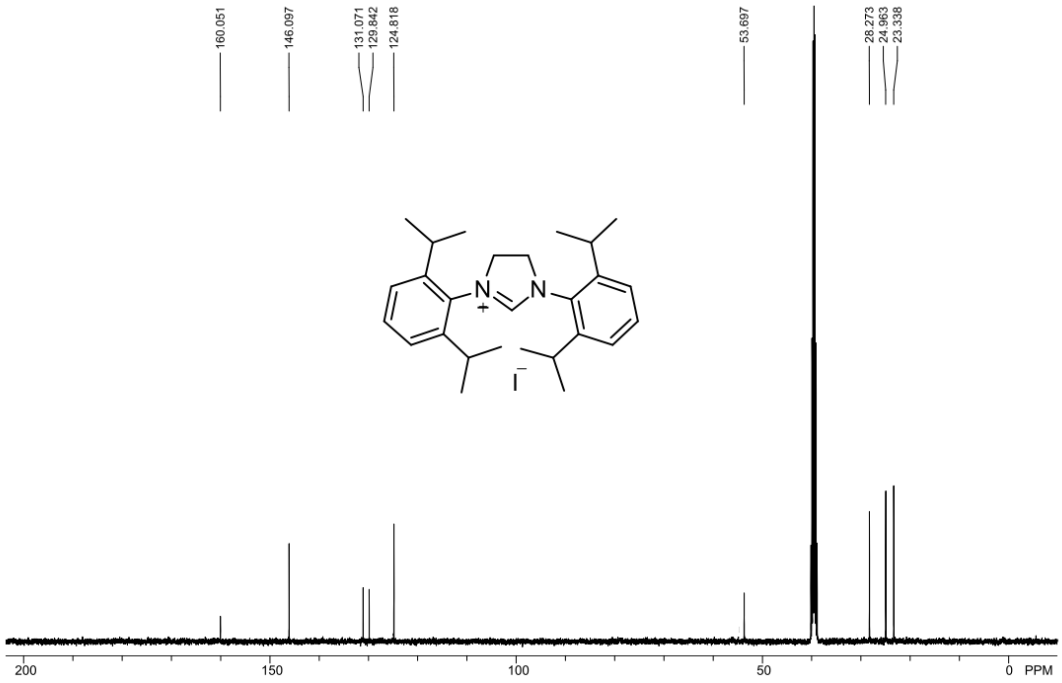
^{13}C NMR spectrum of IPr·HI (**1f**) at 298 K (DMSO-d_6, 100 MHz)



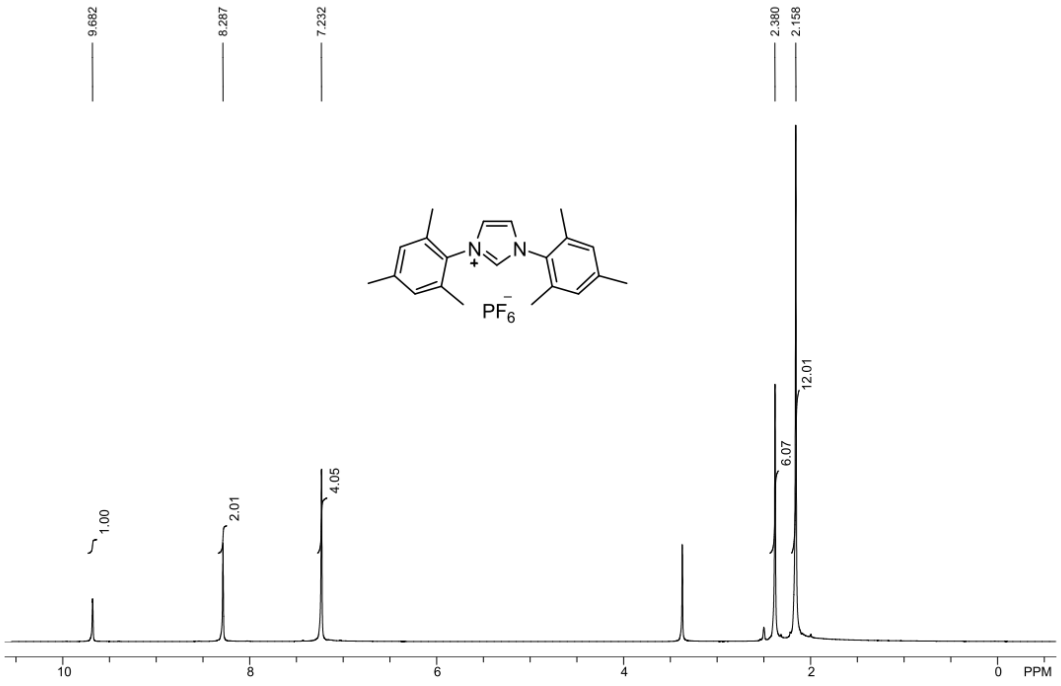
^{1}H NMR spectrum of SIPr·HI (**1g**) at 298 K (DMSO-d_6, 400 MHz)



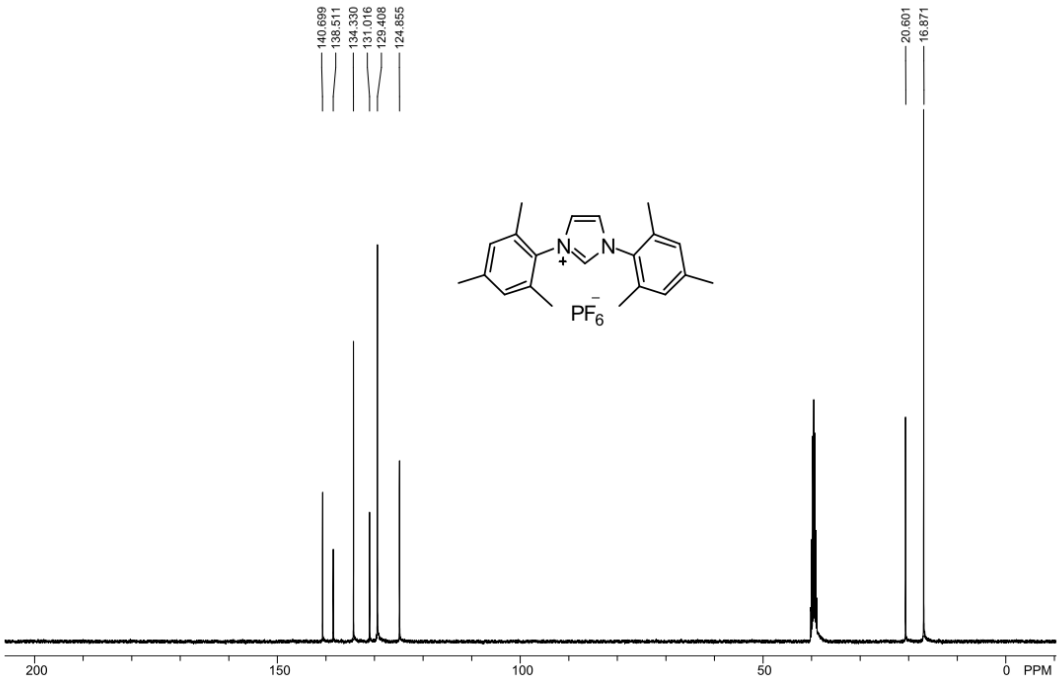
^{13}C NMR spectrum of SIPr·HI (**1g**) at 298 K (DMSO-d_6, 100 MHz)



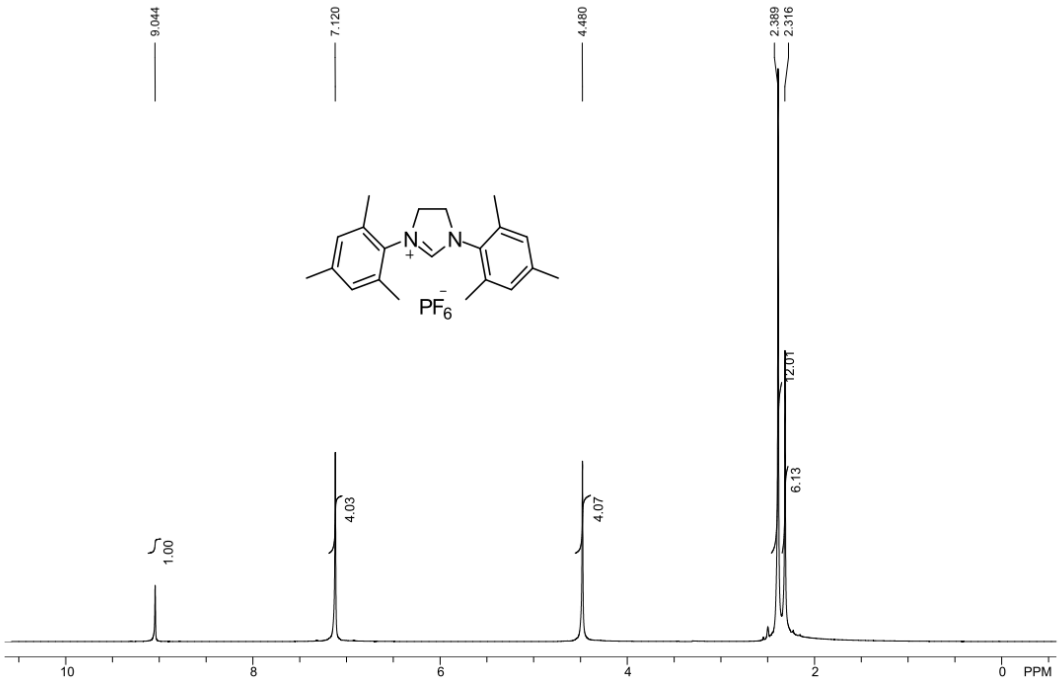
^{1}H NMR spectrum of IMes·HPF$_6$ (**1h**) at 298 K (DMSO-d_6, 400 MHz)



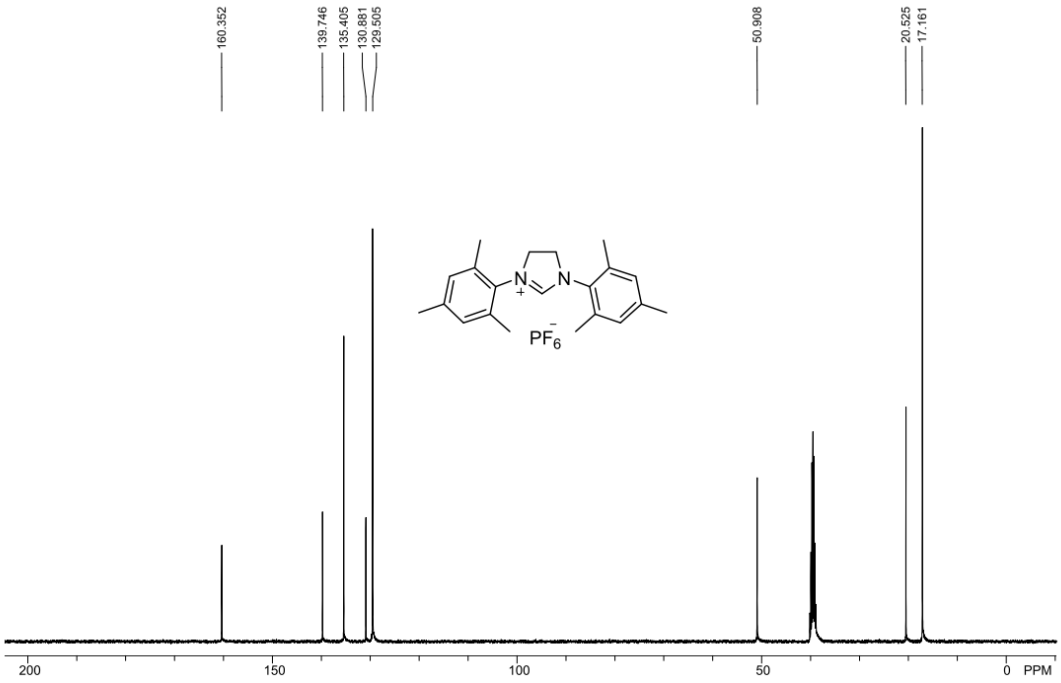
^{13}C NMR spectrum of IMes·HPF$_6$ (**1h**) at 298 K (DMSO-d_6, 100 MHz)



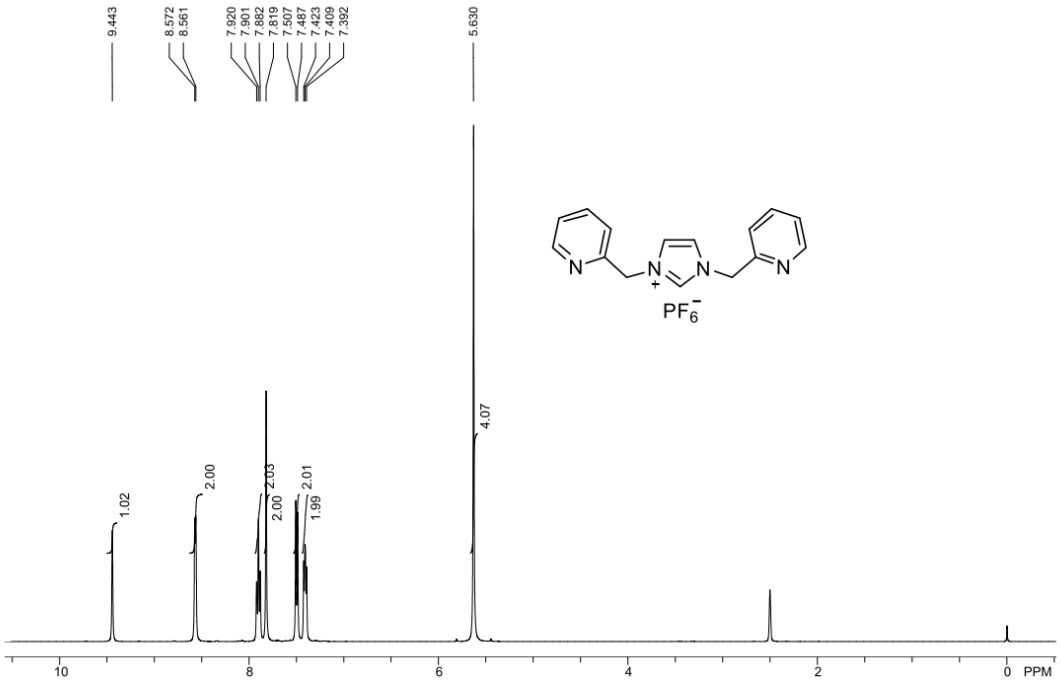
^{1}H NMR spectrum of SIMes·HPF$_6$ (**1i**) at 298 K (DMSO-d_6, 400 MHz)



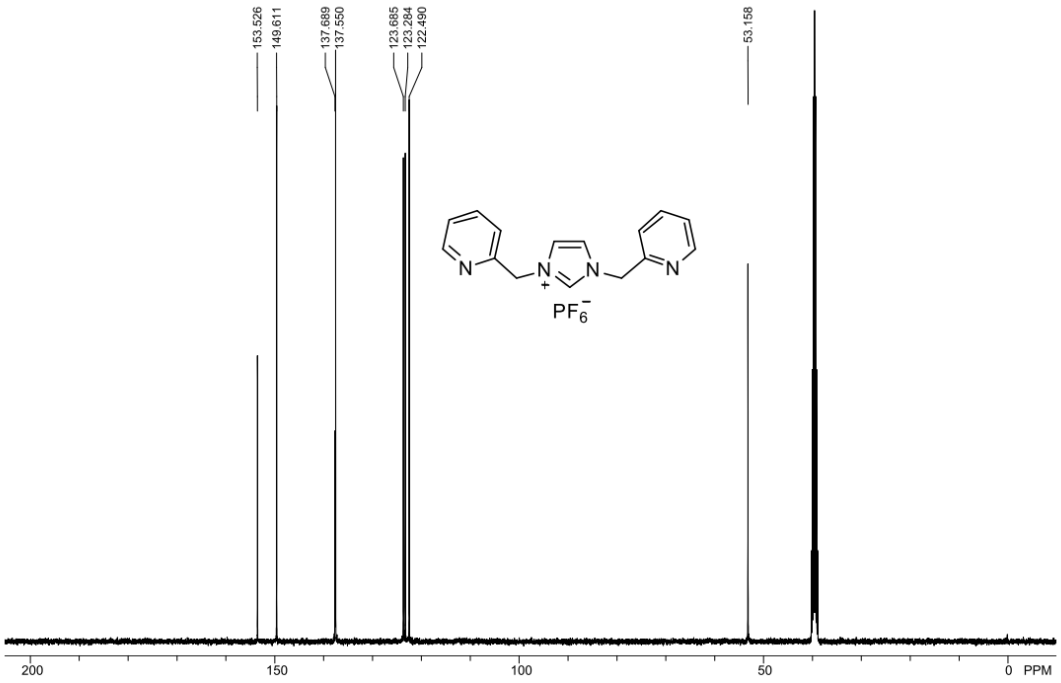
^{13}C NMR spectrum of SIMes·HPF$_6$ (**1i**) at 298 K (DMSO-d_6, 100 MHz)



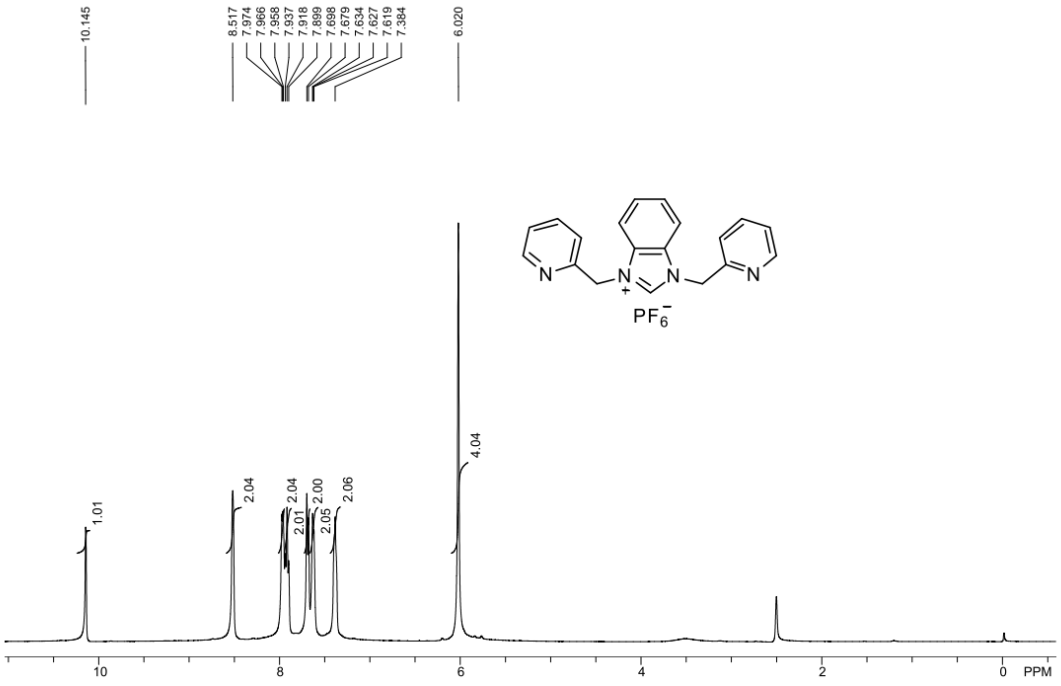
^{1}H NMR spectrum of [HL^{j}](PF$_6$) (**1j**) at 298 K (DMSO-d_6, 400 MHz)



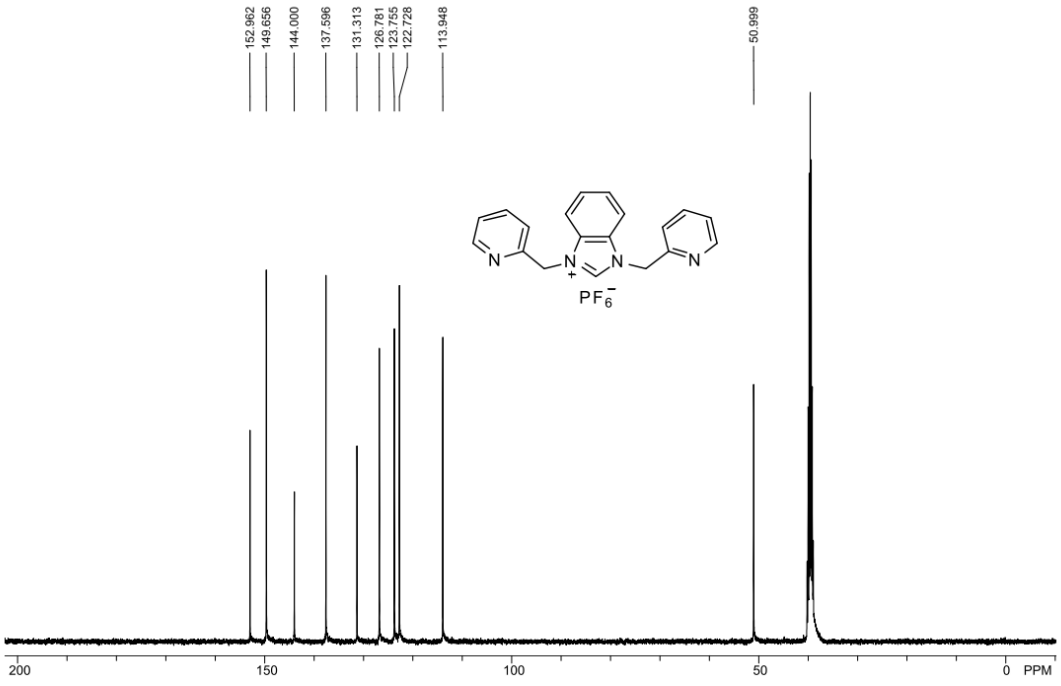
^{13}C NMR spectrum of [HL^{j}](PF$_6$) (**1j**) at 298 K (DMSO-d_6, 100 MHz)



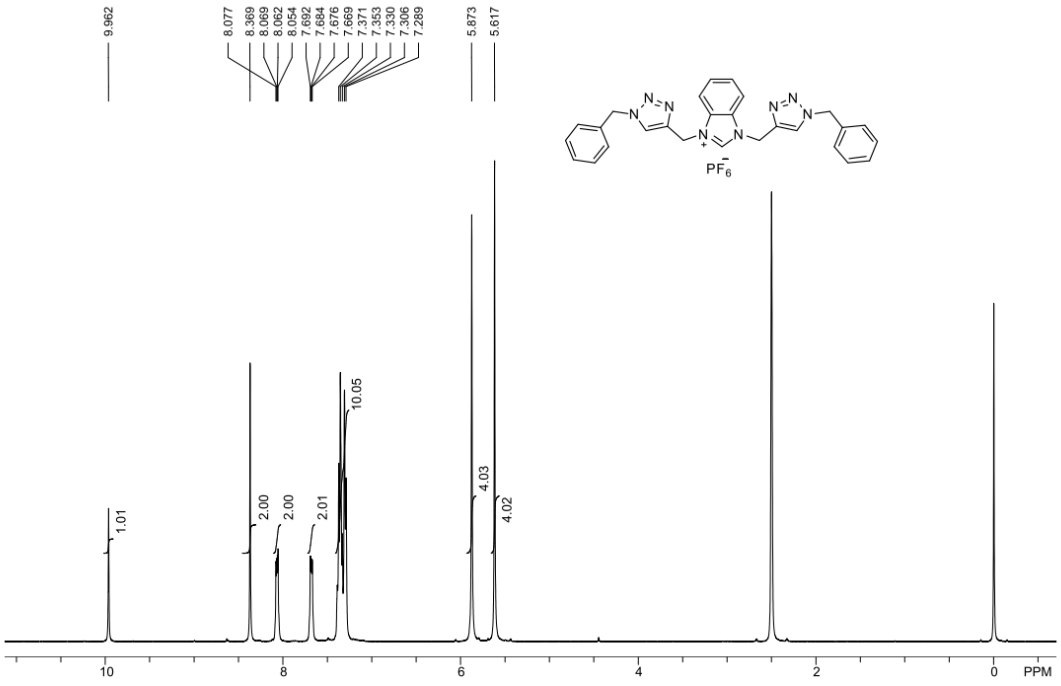
^{1}H NMR spectrum of [HL^{k}](PF$_6$) (**1k**) at 298 K (DMSO-d_6, 400 MHz)



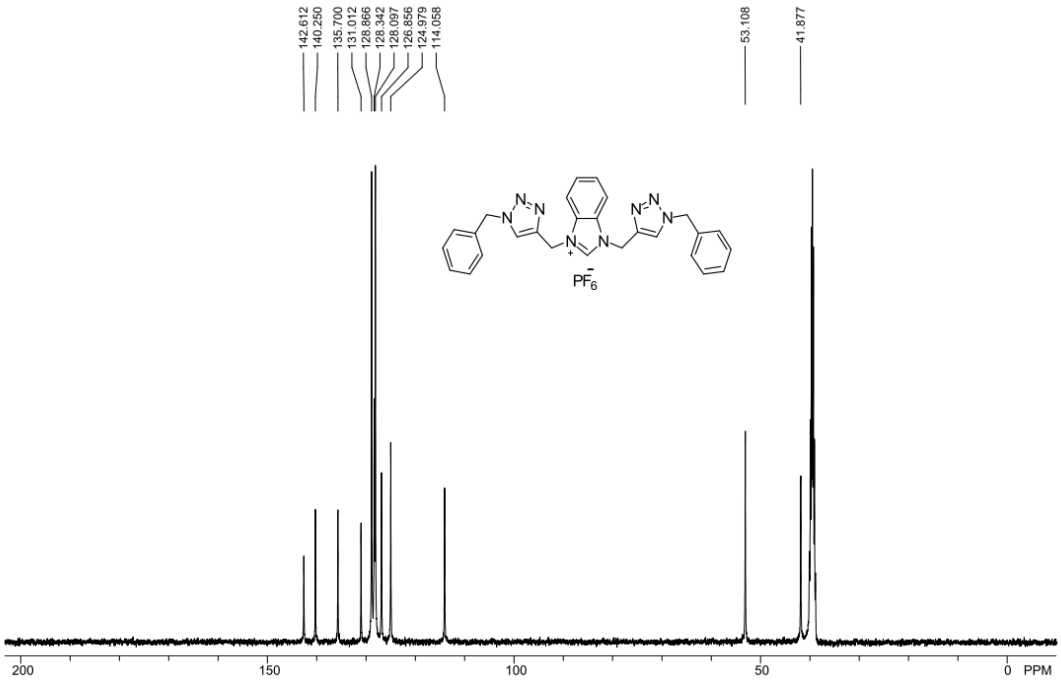
^{13}C NMR spectrum of [HL^{k}](PF$_6$) (**1k**) at 298 K (DMSO-d_6, 100 MHz)



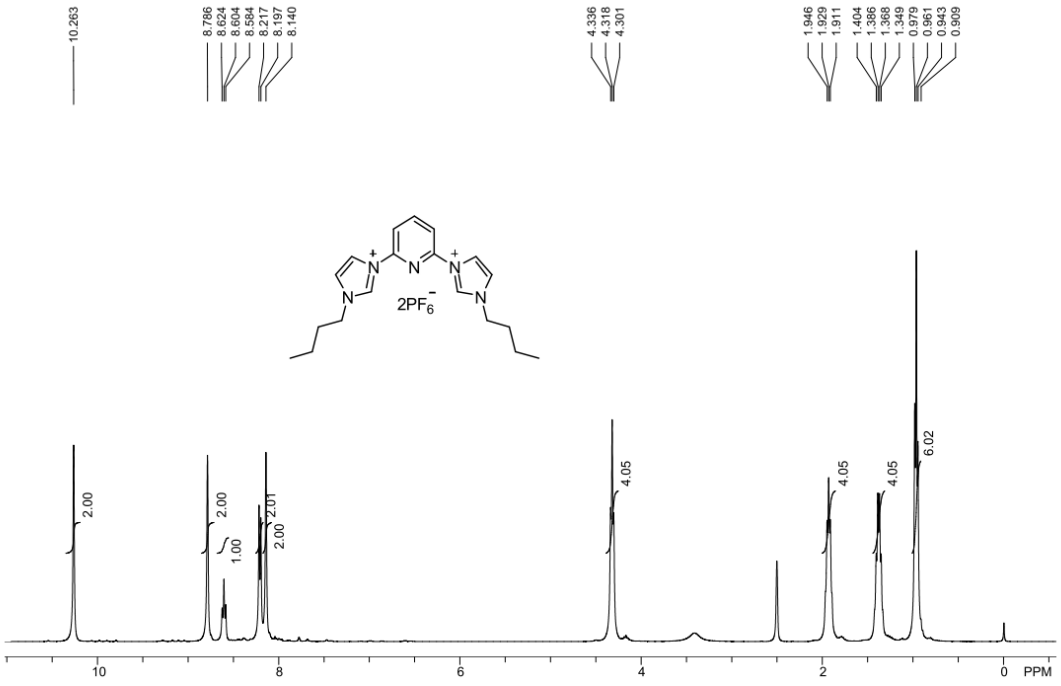
^{1}H NMR spectrum of [HL^{l}](PF$_6$) (**1l**) at 298 K (DMSO-d_6, 400 MHz)



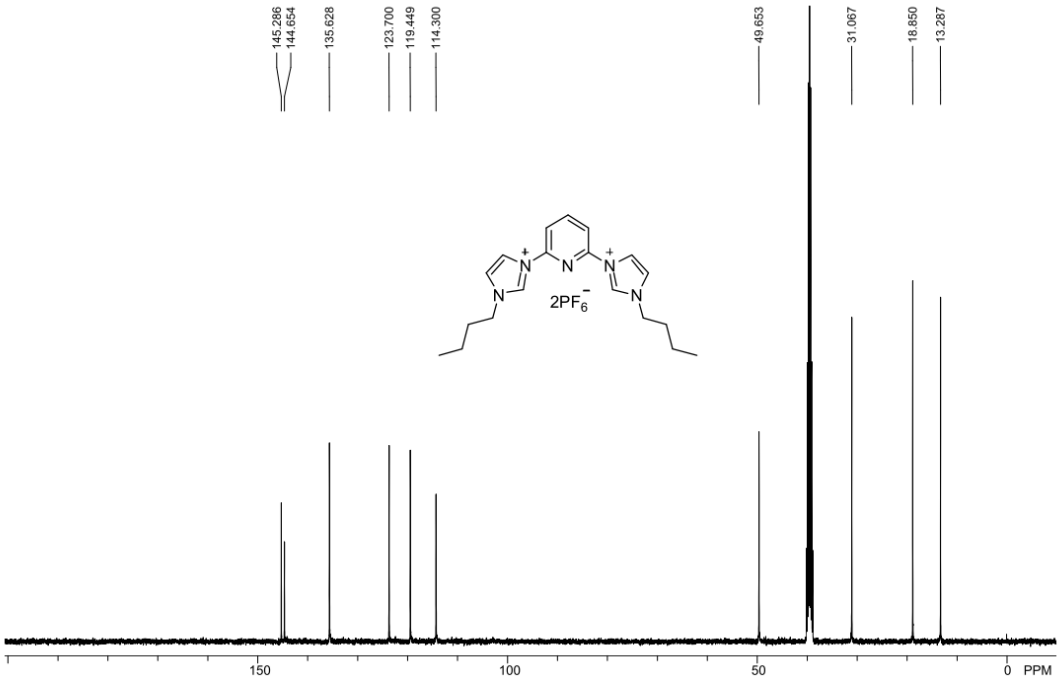
^{13}C NMR spectrum of [HL^{l}](PF$_6$) (**1l**) at 298 K (DMSO-d_6, 100 MHz)



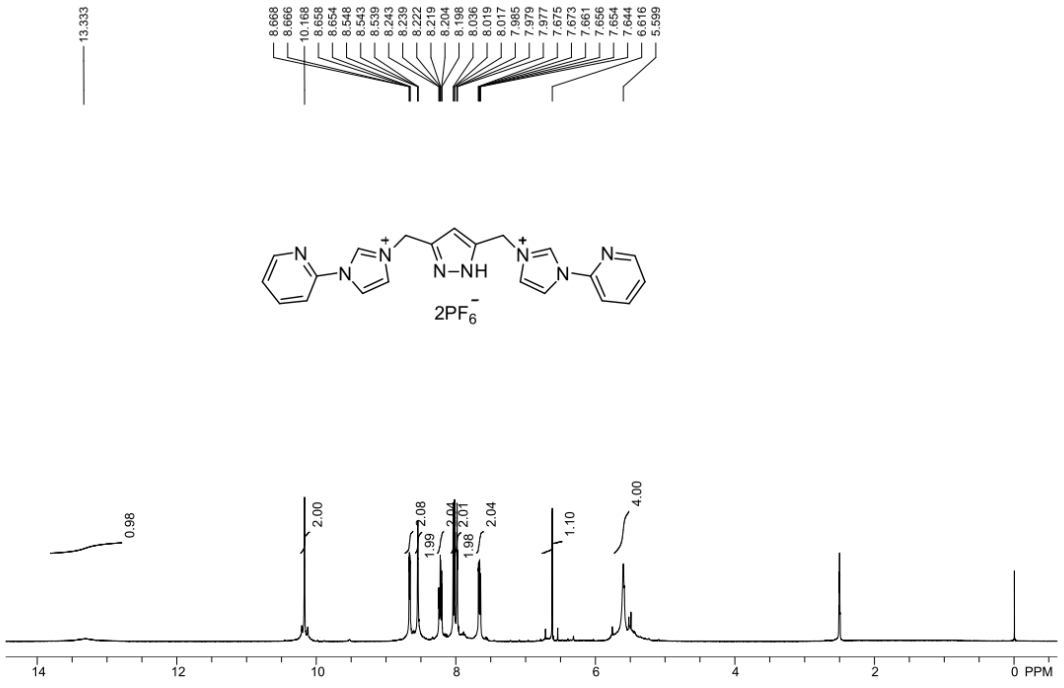
^{1}H NMR spectrum of $[H_2L^m](PF_6)_2$ (**1m**) at 298 K (DMSO-d_6, 400 MHz)



^{13}C NMR spectrum of $[H_2L^m](PF_6)_2$ (**1m**) at 298 K (DMSO-d_6, 100 MHz)

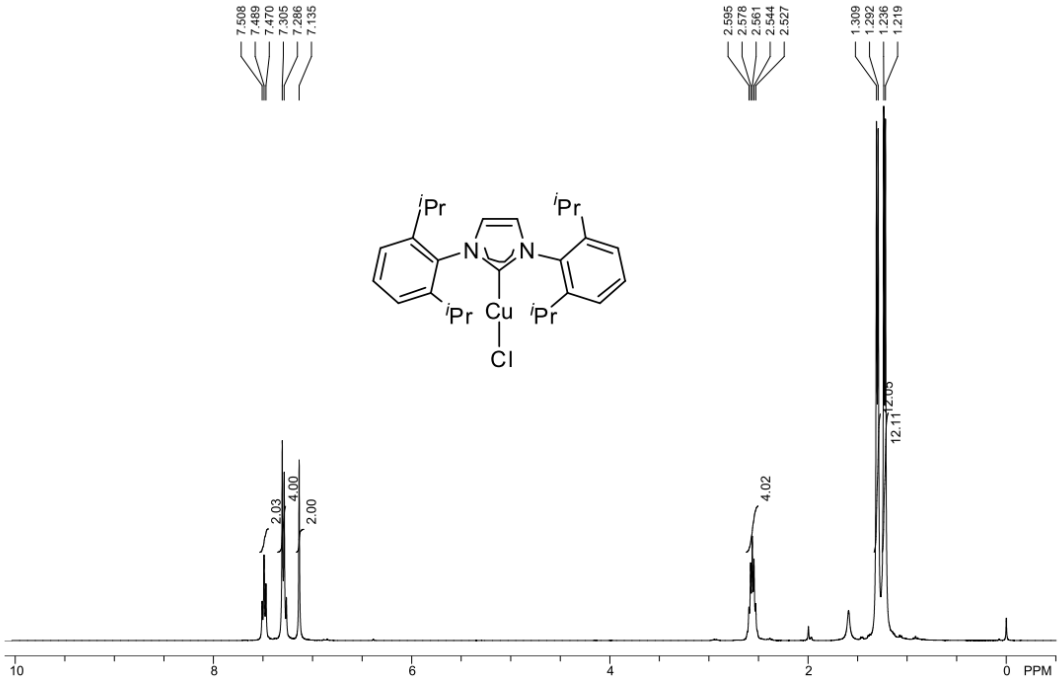


^{1}H NMR spectrum of $[H_2L^n](PF_6)_2$ (**1n**) at 298 K (DMSO-d_6, 400 MHz)

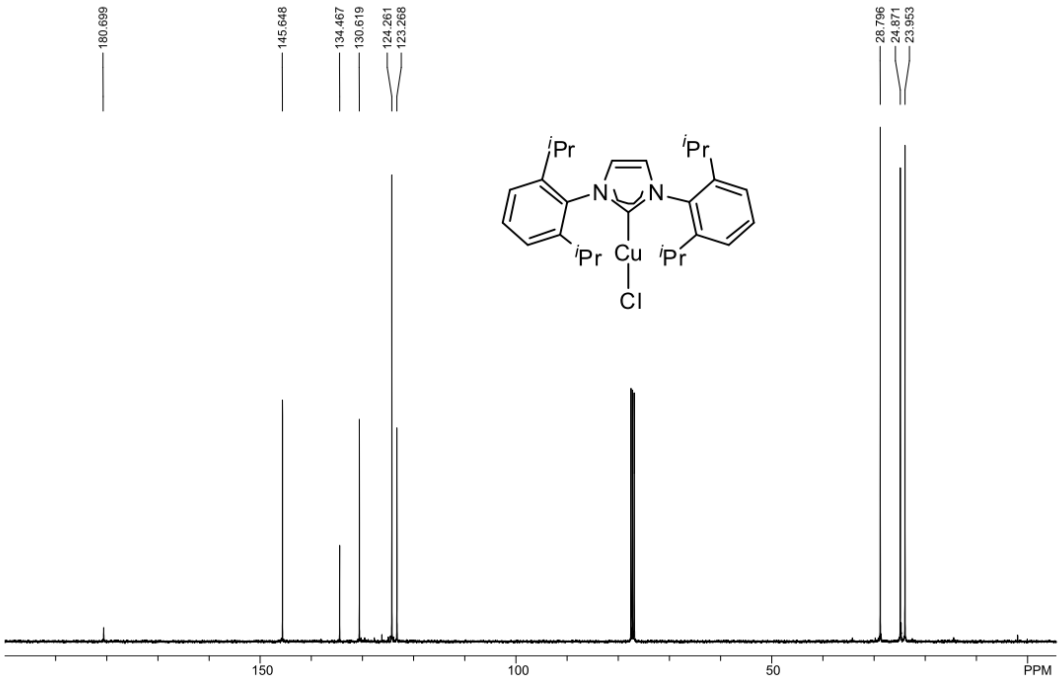


V ^{1}H and ^{13}C-{^{1}H} NMR spectra of Cu(I)-NHC Products

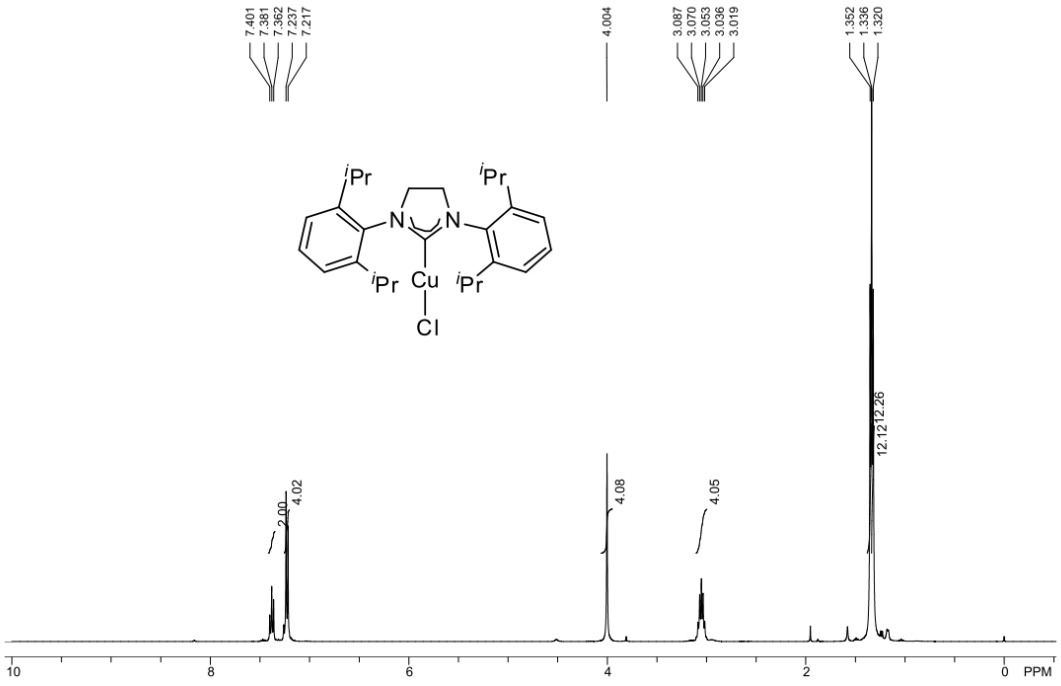
^{1}H NMR spectrum of [(IPr)CuCl] (**2a**) at 298 K ($CDCl_3$, 400 MHz)



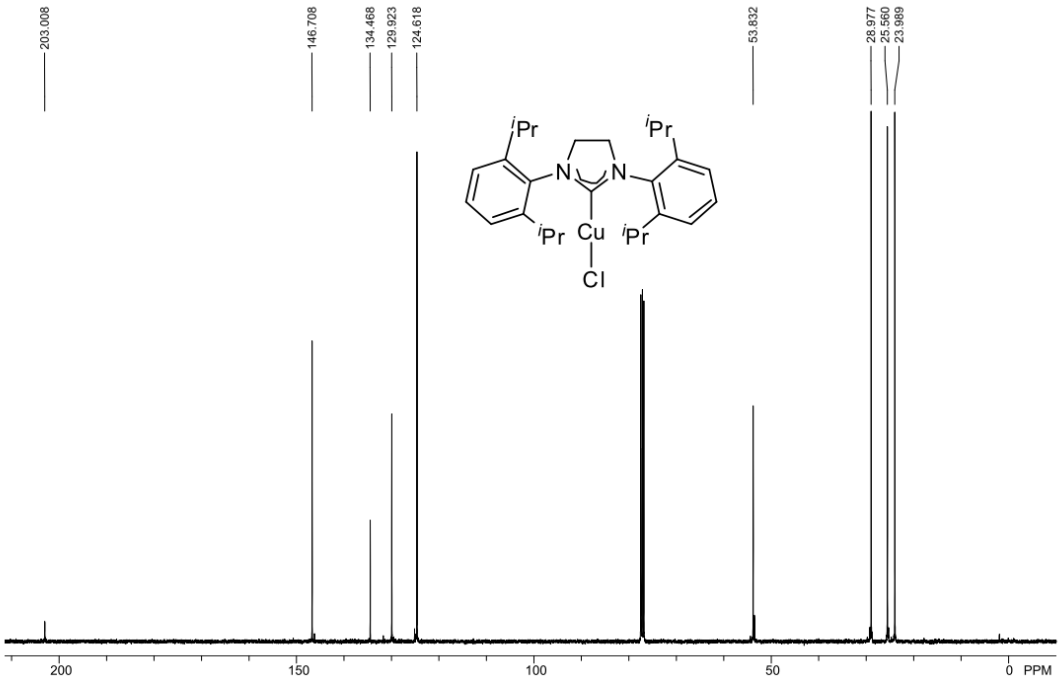
^{13}C NMR spectrum of [(IPr)CuCl] (**2a**) at 298 K ($CDCl_3$, 100 MHz)



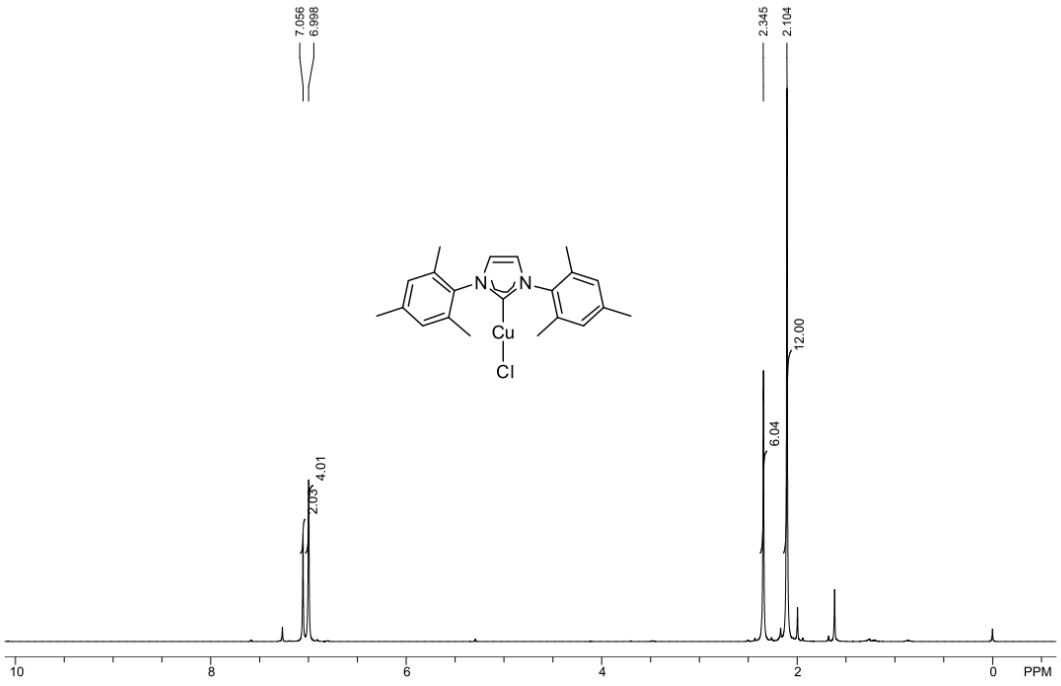
^{1}H NMR spectrum of [(SIPr)CuCl] (**2b**) at 298 K ($CDCl_3$, 400 MHz)



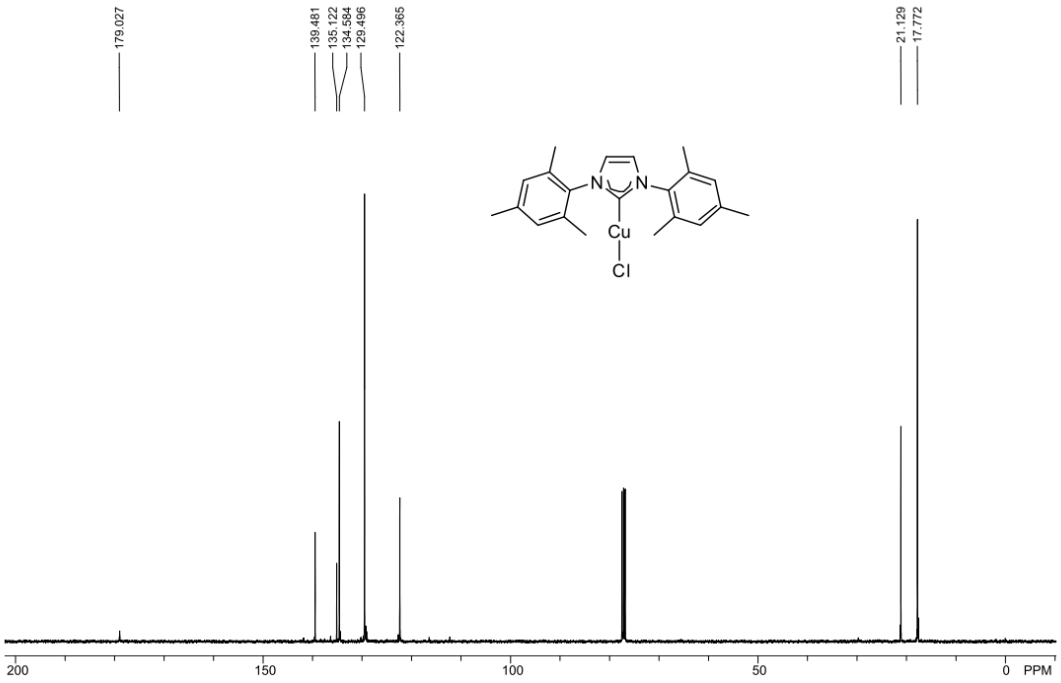
^{13}C NMR spectrum of [(SIPr)CuCl] (**2b**) at 298 K ($CDCl_3$, 100 MHz)



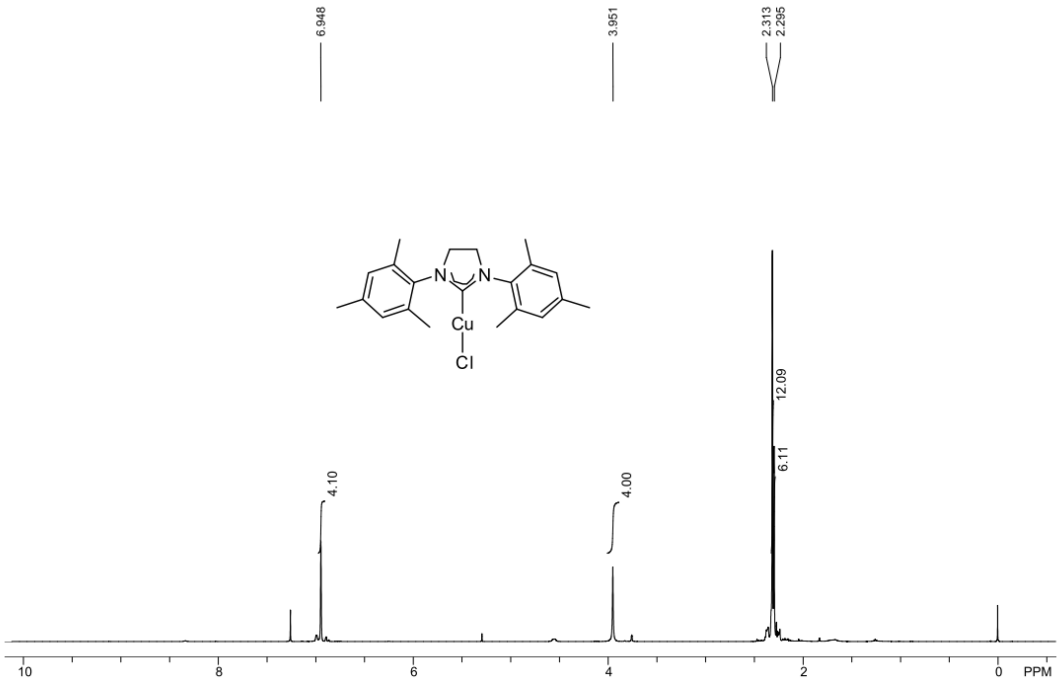
^{1}H NMR spectrum of [(IMes)CuCl] (**2c**) at 298 K ($CDCl_3$, 400 MHz)



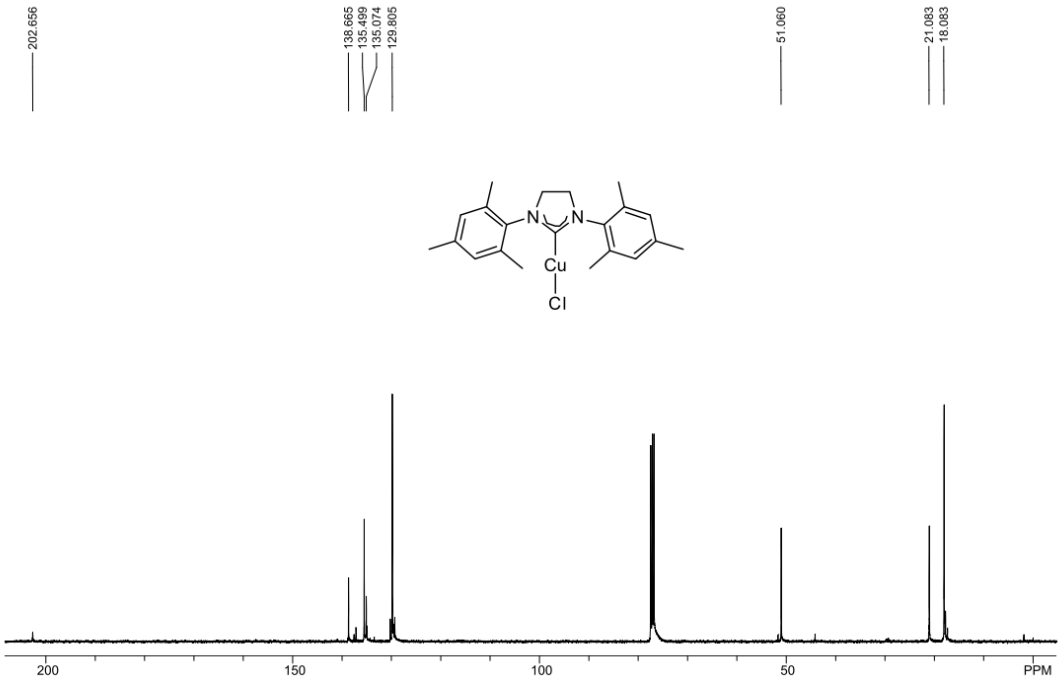
^{13}C NMR spectrum of [(IMes)CuCl] (**2c**) at 298 K ($CDCl_3$, 100 MHz)



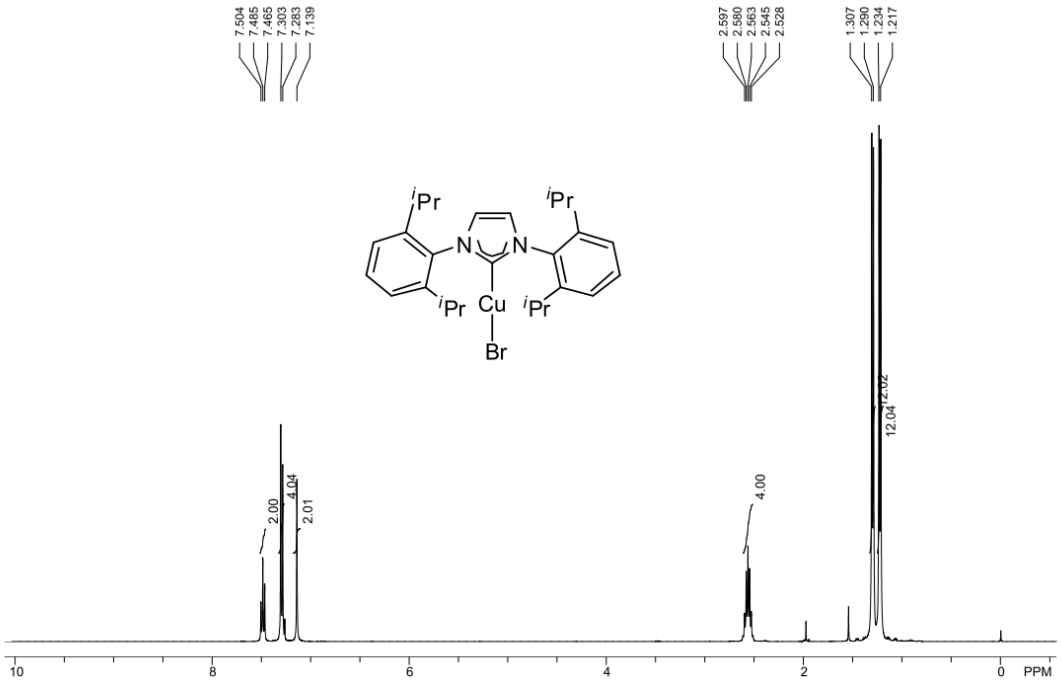
^{1}H NMR spectrum of [(SIMes)CuCl] (**2d**) at 298 K ($CDCl_3$, 400 MHz)



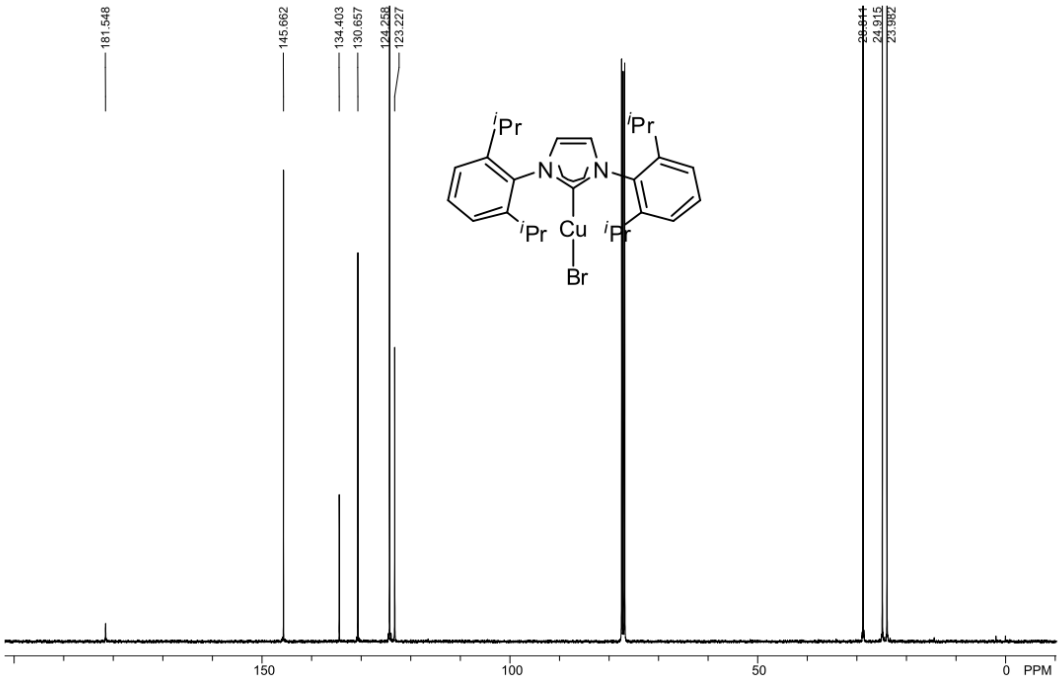
^{13}C NMR spectrum of [(SIMes)CuCl] (**2d**) at 298 K ($CDCl_3$, 100 MHz)



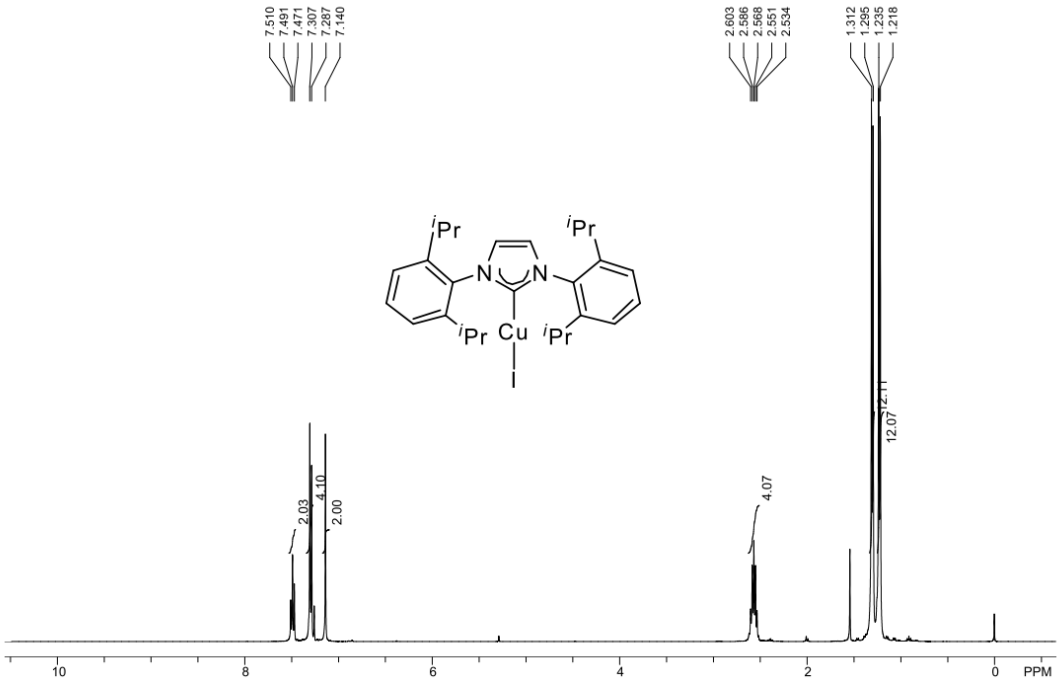
^{1}H NMR spectrum of [(IPr)CuBr] (**2e**) at 298 K ($CDCl_3$, 400 MHz)



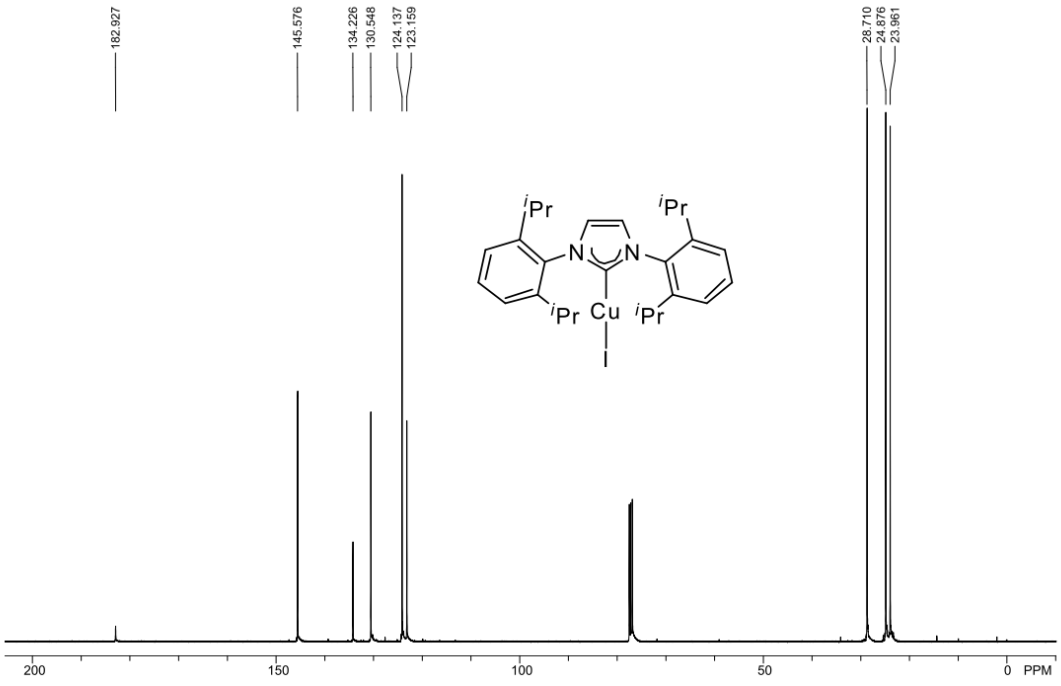
^{13}C NMR spectrum of [(IPr)CuBr] (**2e**) at 298 K ($CDCl_3$, 100 MHz)



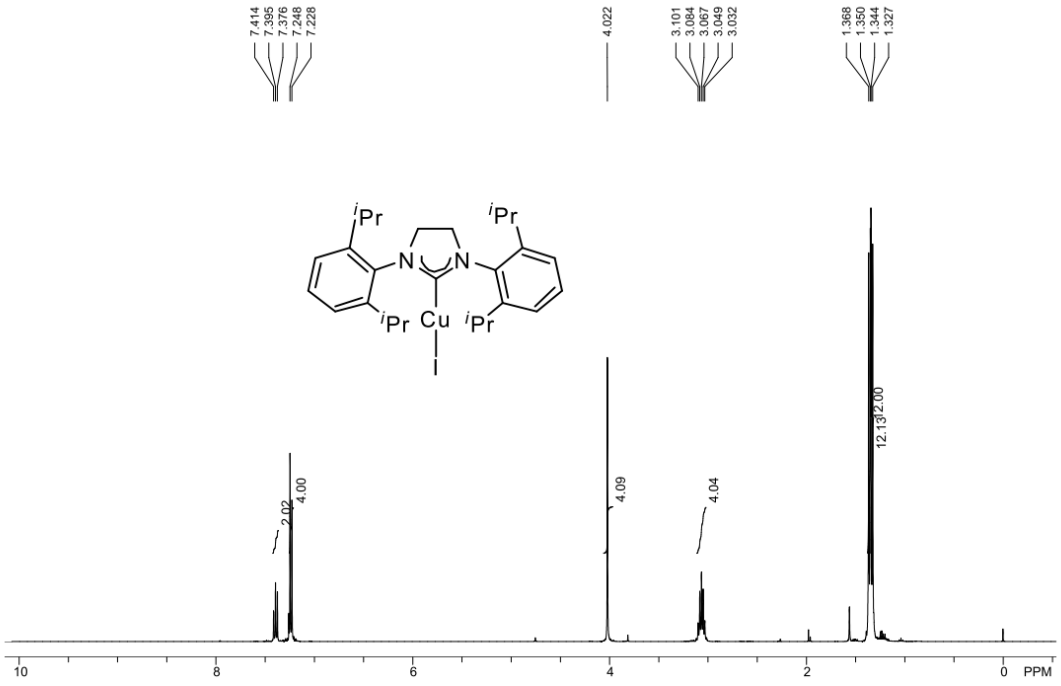
^{1}H NMR spectrum of [(IPr)CuI] (**2f**) at 298 K ($CDCl_3$, 400 MHz)



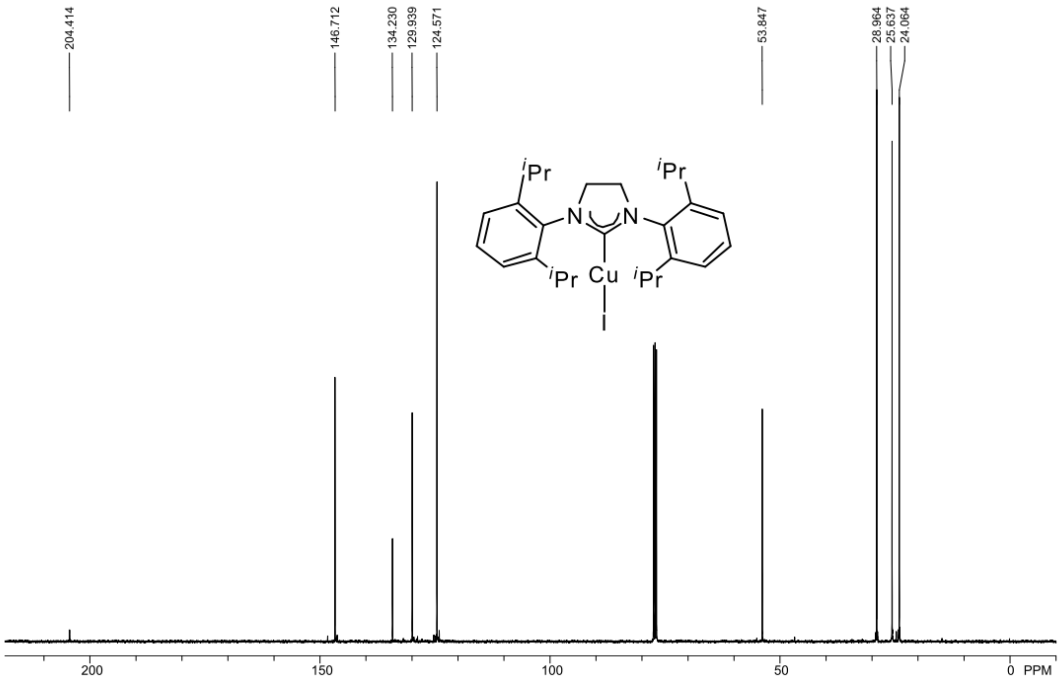
^{13}C NMR spectrum of [(IPr)CuI] (**2f**) at 298 K ($CDCl_3$, 100 MHz)



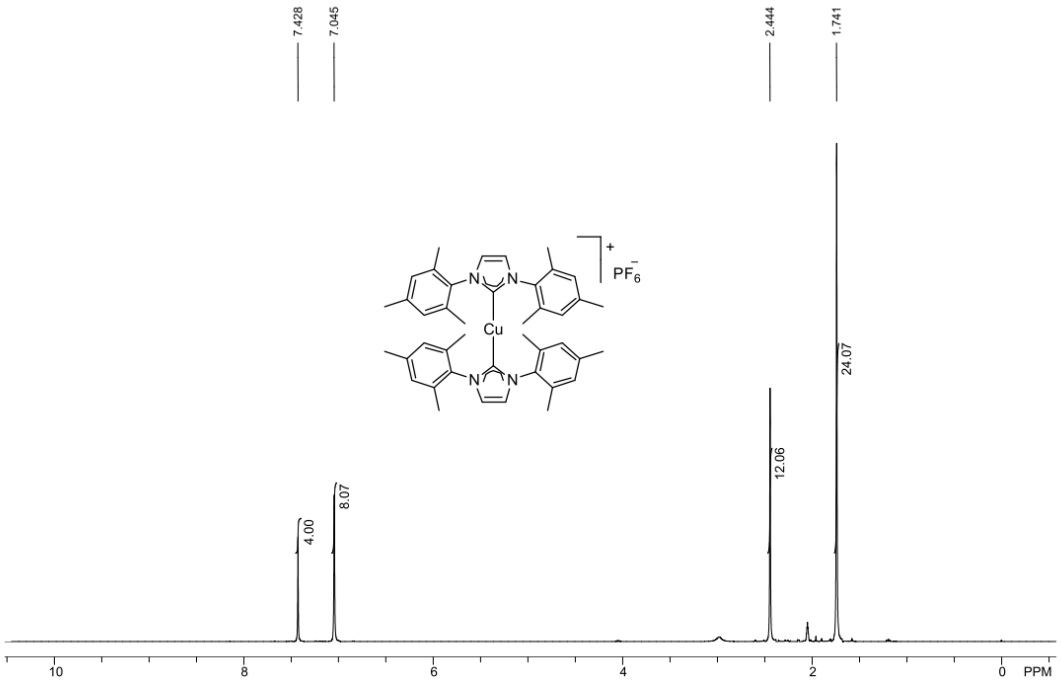
^{1}H NMR spectrum of [(SIPr)CuI] (**2g**) at 298 K ($CDCl_3$, 400 MHz)



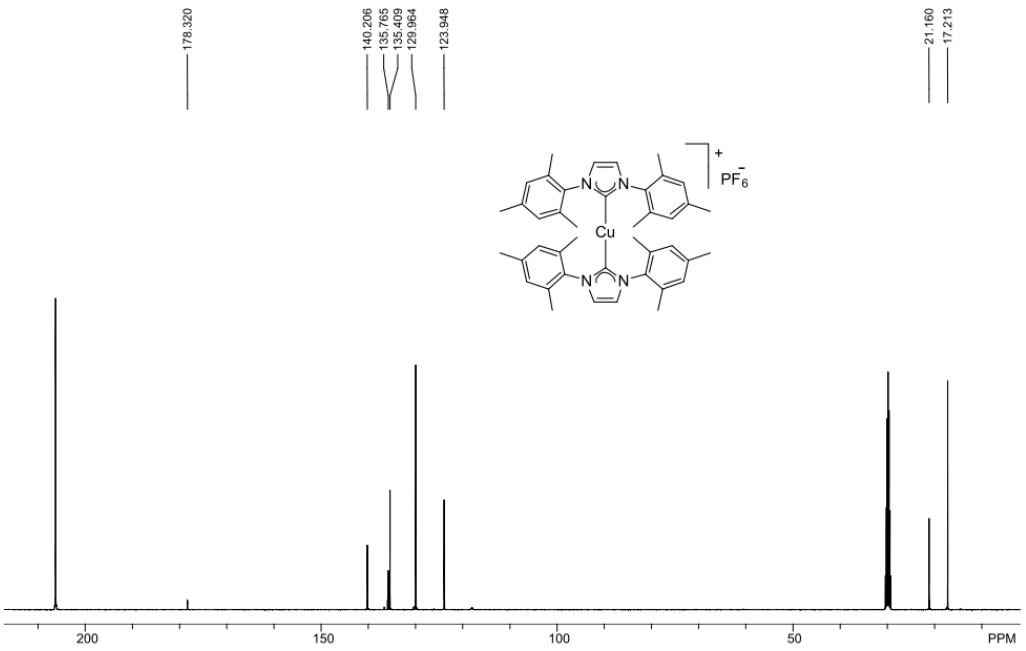
^{13}C NMR spectrum of [(SIPr)CuI] (**2g**) at 298 K ($CDCl_3$, 100 MHz)



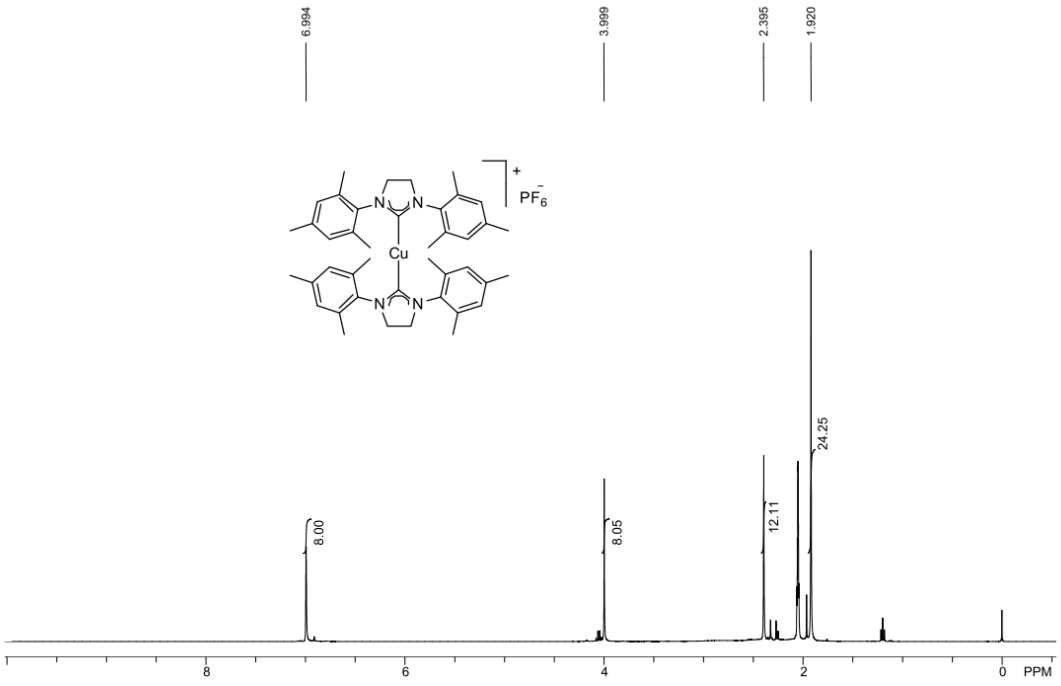
^{1}H NMR spectrum of $[(IMes)_2Cu]PF_6$ (**2h**) at 298 K (acetone-d_6, 400 MHz)



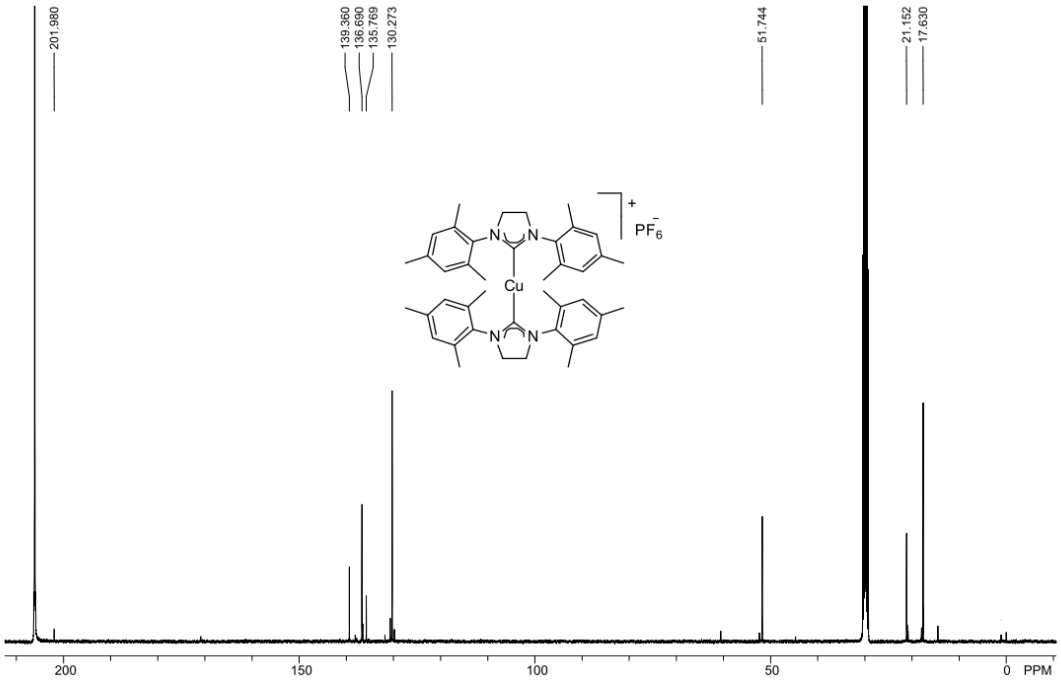
^{13}C NMR spectrum of $[(IMes)_2Cu]PF_6$ (**2h**) at 298 K (acetone-d_6, 100 MHz)



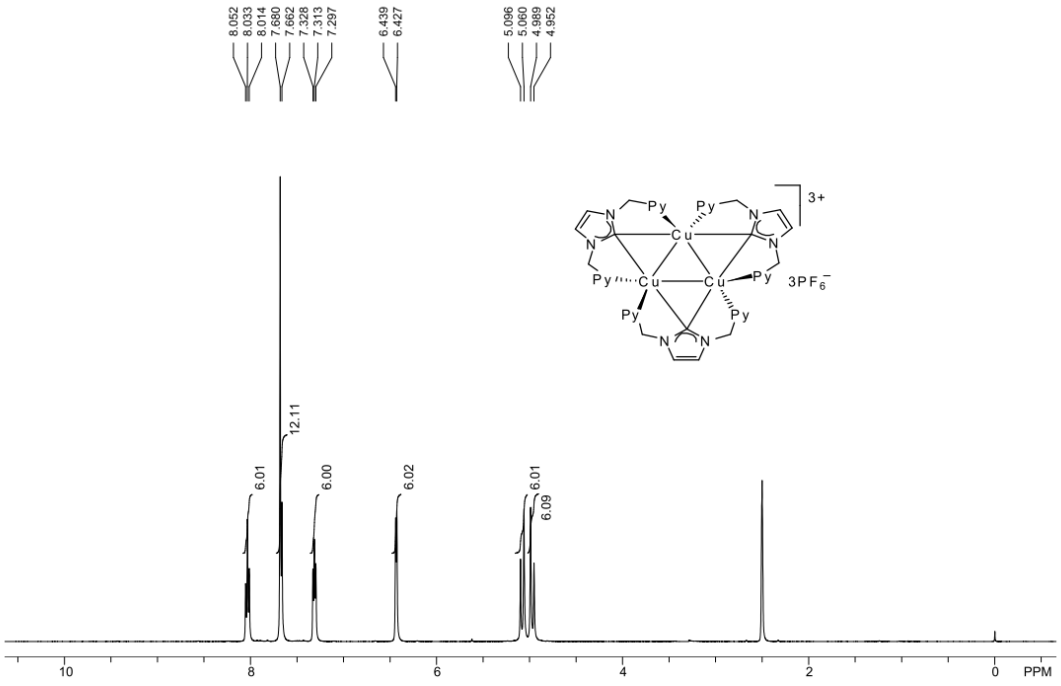
^{1}H NMR spectrum of [(SIMes)$_2$Cu]PF$_6$ (**2i**) at 298 K (acetone-d_6, 400 MHz)



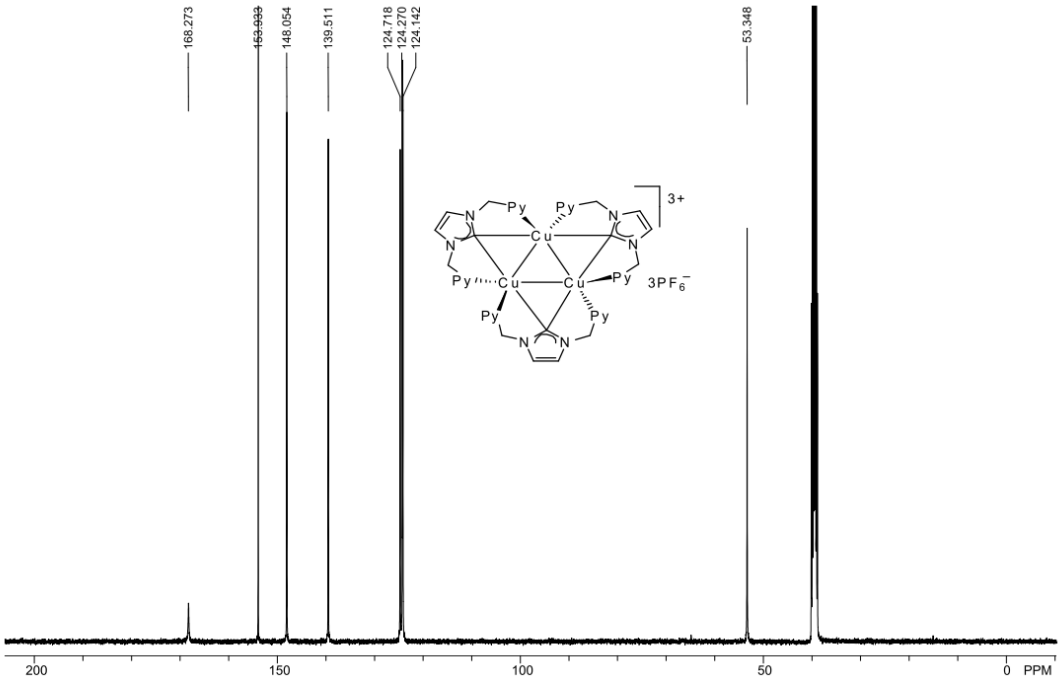
^{13}C NMR spectrum of [(SIMes)$_2$Cu]PF$_6$ (**2i**) at 298 K (acetone-d_6, 100 MHz)



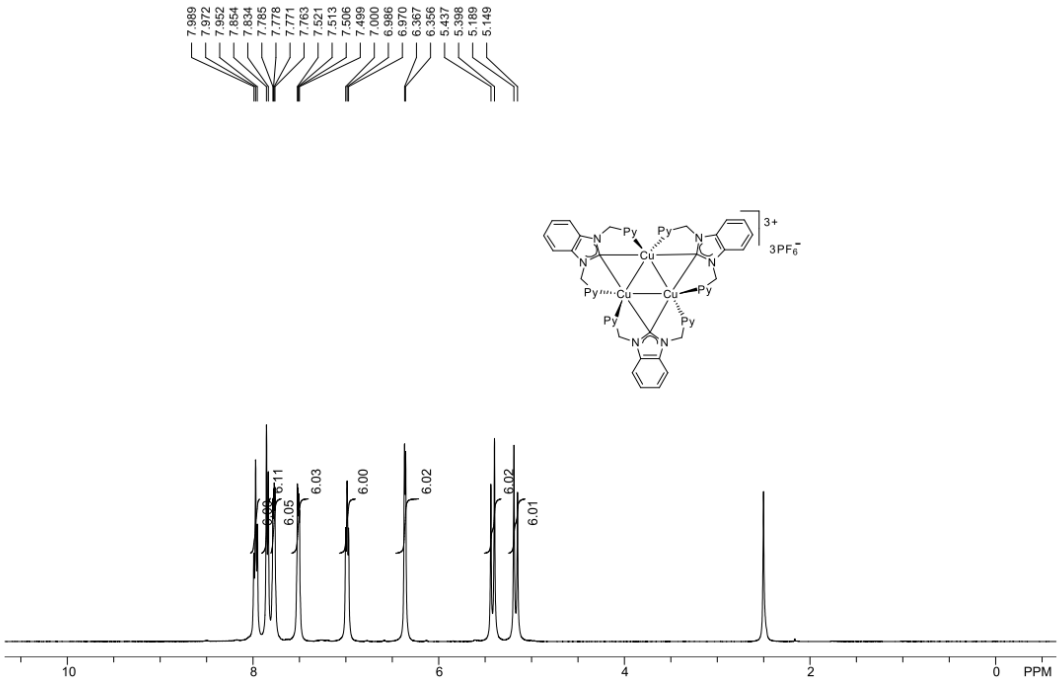
^{1}H NMR spectrum of $[Cu_3L^{j}_3](PF_6)_3$ (**2j**) at 298 K (DMSO-d_6, 400 MHz)



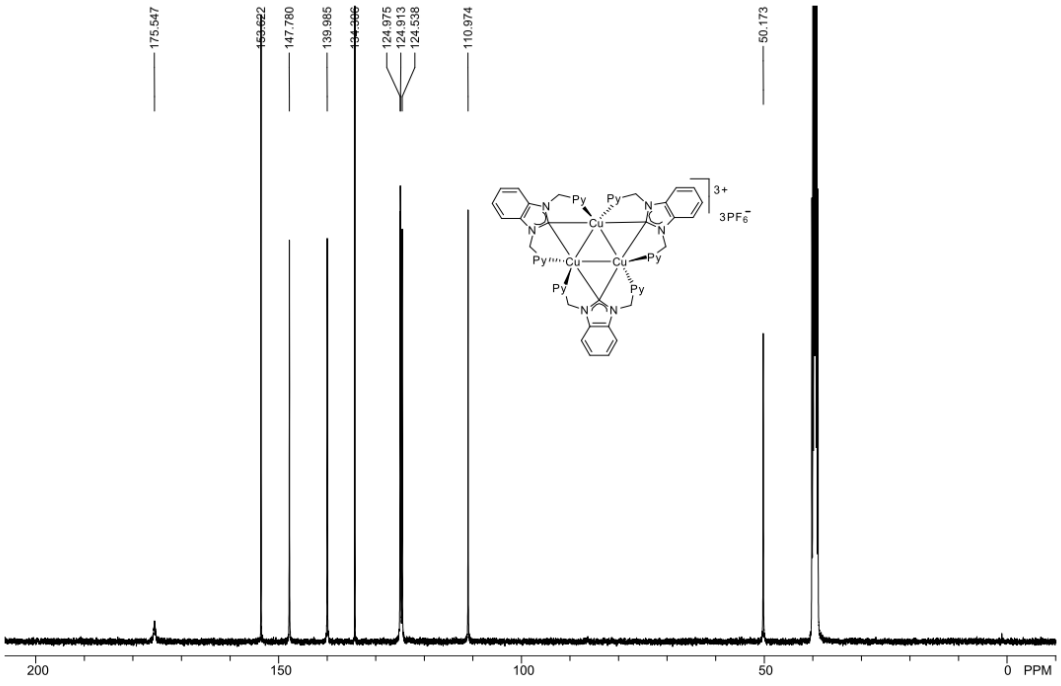
^{13}C NMR spectrum of $[Cu_3L^{j}_3](PF_6)_3$ (**2j**) at 298 K (DMSO-d_6, 100 MHz)



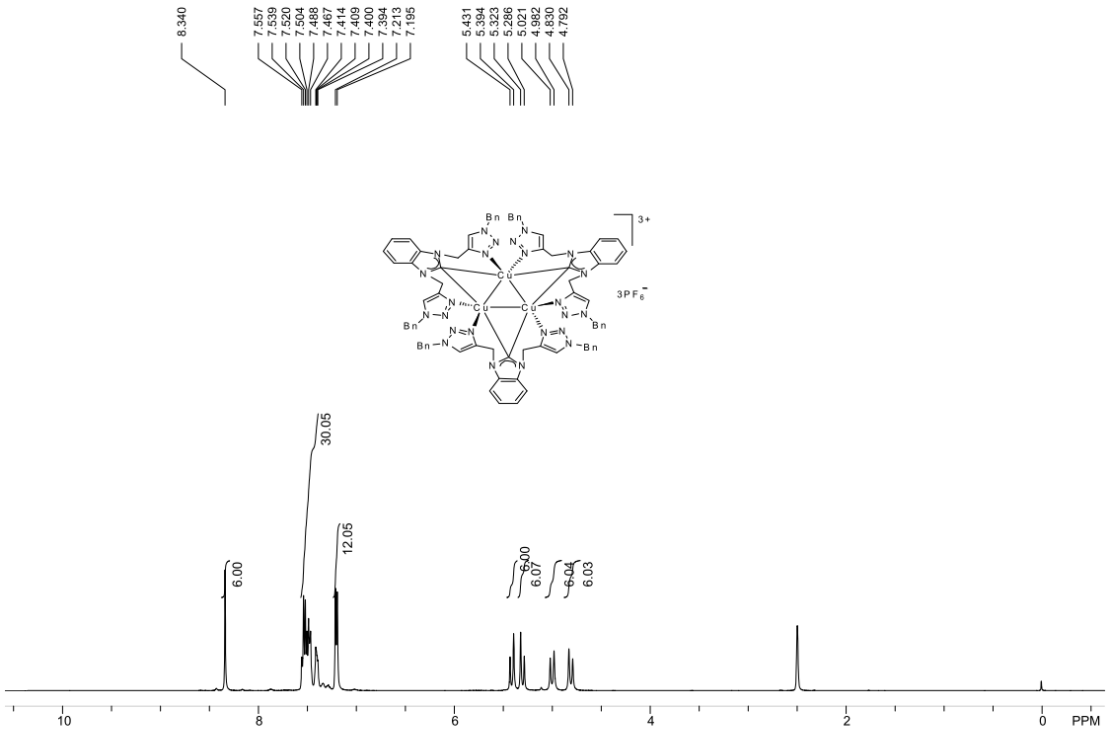
^{1}H NMR spectrum of $[Cu_3L^k_3](PF_6)_3$ (**2k**) at 298 K (DMSO-d_6, 400 MHz)



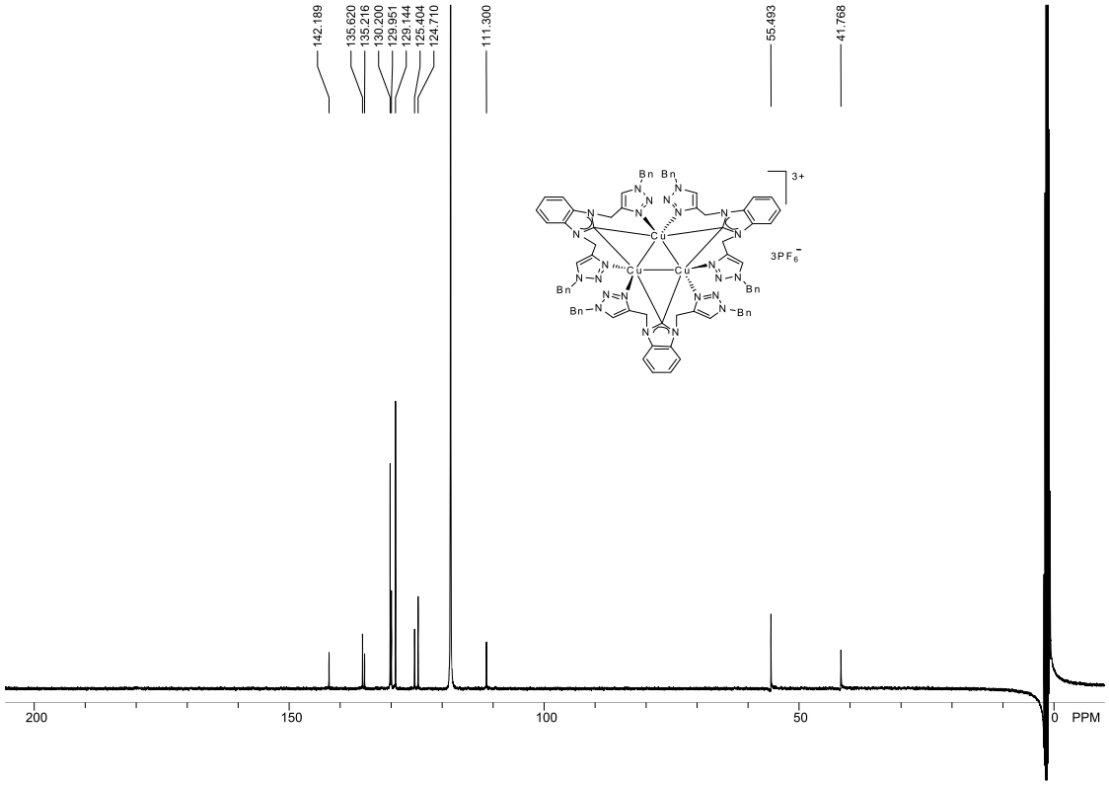
^{13}C NMR spectrum of $[Cu_3L^k_3](PF_6)_3$ (**2k**) at 298 K (DMSO-d_6, 100 MHz)



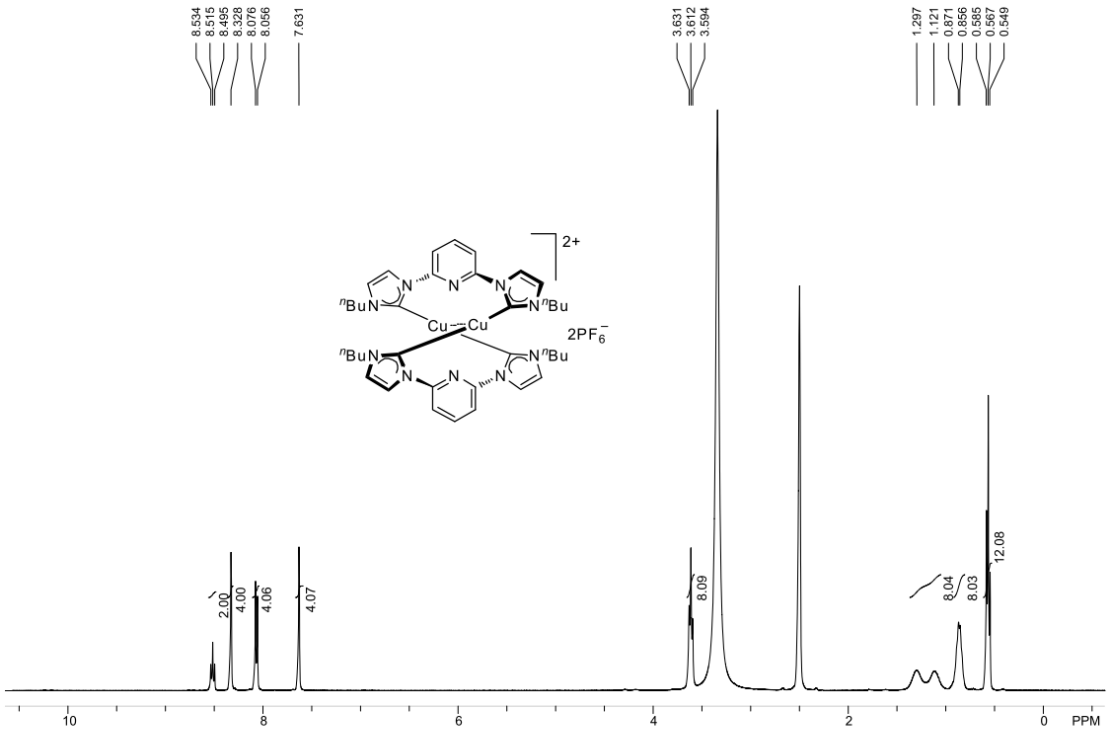
^{1}H NMR spectrum of $[Cu_3L^1_3](PF_6)_3$ (**2l**) at 298 K (DMSO-d_6, 400 MHz)



^{13}C NMR spectrum of $[Cu_3L^1_3](PF_6)_3$ (**2l**) at 298 K (CD_3CN, 100 MHz)



^{1}H NMR spectrum of $[Cu_2L^m{}_2](PF_6)_2$ (**2m**) at 298 K (DMSO-d_6, 400 MHz)



^{13}C NMR spectrum of $[Cu_2L^m{}_2](PF_6)_2$ (**2m**) at 298 K (DMSO-d_6, 100 MHz)