Supporting Information

Table of contents

1. Synthetic procedures

1.1 General remarks

All reagents were purchased from Aldrich Chemical Co., Fluka and Alfa Aesar and used without further purification. The milling treatments were carried out either in a Retsch MM200 or MM400 vibrating ball-mill operated at 25 Hz or in a Retsch PM100 Planetary Mill (pbm) operated at 450 rpm. Milling load is defined as the sum of the mass of the reactants per free volume in the bowl. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 200 MHZ, 300 MHz or 400 MHz spectrometer and are reported in ppm using deuterated solvent for calibration ($CDCl_3$ at 7.26 ppm or DMSO-d_6 at 2.50 ppm). Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on Bruker Avance AM 50 MHz, 75 MHz or 101 MHz spectrometers and are reported in ppm using deuterated solvent for calibration ($CDCl_3$ at 77.2 ppm or DMSO-d_6 at 39.5 ppm). HRMS analysis was performed on a Q-Tof (Waters, ESI, 2001) spectrometer.

1.2 General table

Methods utilized for the treatment of reaction mixtures are described hereunder.

Method A: Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum to afford the desired product.

Method B: Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum and the resulting powder was washed three times with water. The resulting powder was dried under vacuum to afford the product.

Method C: Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum and washed with water and diethyl ether and dried under vacuum to afford the product.

Method D: Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The solid was washed with diethyl ether, filtrated and dried under vacuum to afford the product.

Method E: Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum and dissolved in a minimum of dichloromethane. Diethyl ether was added to precipitate the product. After filtration, the solid was washed three times with diethyl ether and dried under vacuum to afford the product.

Method F: Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum and washed three times with diethyl ether and dried under vacuum to afford the product.

1.2.1 General table for the synthesis of [CuCl(NHC)]

Entry	Product	Reagent	Aspect bp or mp (°C)	Eq.	Quantity (mmol)	Ball-mill (frequency)	Time	Aspect of reaction mixture	Treatment	Yield[a] (%)	Product aspect
1	[CuCl(IMes)]	IMes·HCl	White powder mp: 351 – 352[1]	1.00	0.389	pbm (450 rpm)	5 h	Brown and compact solid	Method A	85	White powder
		Copper powder	Red powder <45µm mp: 1083.4	2.00	0.778						
		Water	Transparent liquid	7.14	2.778						
2	[CuCl(SIMes)]	SIMes·HCl	White powder mp: 252 – 254[2]	1.00	0.357	pbm (450 rpm)	5 h	Brown and compact solid	Method A	76	White powder
		Copper powder	Red powder <45µm mp: 1083.4	2.00	0.713						
		Water	Transparent liquid	7.78	2.778						
3	[CuCl(IPr)]	IPr·HCl	White powder 260 – 262[2]	1.00	0.226	pbm (450 rpm)	6 h	Brown solid	Method B	82	White powder
		Copper powder	Red powder <45µm mp: 1083.4	5.00	1.128						
		Water	Transparent liquid	12.30	2.778						
4	[CuCl(SIPr)]	SIPr·HCl	White solid mp: 220 – 222[2]	1.00	0.225	pbm (450 rpm)	9 h	Brown solid	Method C	65	White powder
		Copper powder	Red powder <45µm mp: 1083.4	5.00	1.125						
		Water	Transparent liquid	12.35	2.778						

5	[CuCl(IMes^{Me})]	IMes^{Me}·HCl	White solid	1.00	0.338	pbm (450 rpm)	6 h	Grey solid	Method D	82	White powder
		Copper powder	Red powder <45µm mp: 1083.4	2.00	0.676						
		Benzonitrile	Transparent liquid	0.69	0.485						
6	[CuCl(SIMes^{Me})] trans	SIMes^{Me}·HCl trans	White solid	1.00	0.336	pbm (450 rpm)	6 h	Brown and compact solid	Method A	90	White powder
		Copper powder	Red powder <45µm mp: 1083.4	2.00	0.673						
		Water	Transparent liquid	8.27	2.778						
7	[CuCl(IPr^{Me})]	IPr^{Me}·HCl	White solid	1.00	0.217	pbm (450 rpm)	12 h	Brown-red and compact solid	Method D	89	White powder
		Copper powder	Red powder <45µm mp: 1083.4	5.00	1.087						
		Benzonitrile	Transparent liquid	2.24	0.485						

[a] Yield of isolated product; [b] Few milligram of reaction mixture were dissolved in deuterated solvent, filtrated and analyzed by ^{1}H NMR.

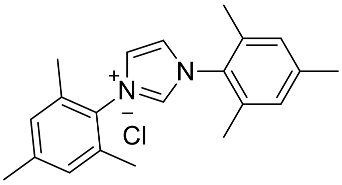
1.2.2 General table for the synthesis of $[Cu(NHC)_2]Y$ (Y = BF_4 or PF_6)

Entry	Product	Reagent	Aspect bp or mp °C	Eq.	Quantity (mmol)	Ball-Mill (frequency)	Time	Aspect of reaction mixture	Treatment	Yield (%)	Product aspect
1	$[Cu(IMes)_2]BF_4$	IMes·HBF_4	White solid 240 – 243[2]	1.00	0.267	pbm (450 rpm)	3 h	Red-Brown powder	Method A	79	White powder
		Copper powder	Red powder <45µm mp: 1083.4	3.00	0.802						
		NaOH	Sticky white powder	1.10	0.294						
2	$[Cu(IMes)_2]PF_6$	IMes·HPF_6	White solid > 300[3]	1.00	0.245	pbm (450 rpm)	6 h	Brown powder	Method A	87	White powder
		Copper powder	Red powder <45µm mp: 1083.4	3.00	0.734						
		NaOH	Sticky white powder	1.10	0.269						
3	$[Cu(IPr)_2]BF_4$	IPr·HBF_4	White solid	1.00	0.200	pbm (450 rpm)	6 h	Brown powder	Method F	85	White powder
		Copper powder	Red powder <45µm mp: 1083.4	5.00	1.000						
		NaOH	Sticky white powder	1.10	0.220						
4	$[Cu(IPr)_2]PF_6$	IPr·HPF_6	White solid	1.00	0.156	pbm (450 rpm)	6 h	Brown powder	Method F	89	White powder
		Copper powder	Red powder <45µm mp: 1083.4	5.00	0.782						
		KHMDS	White solid	1.10	0.172						
5	$[Cu(IMes^{Me})_2]BF_4$	$IMes^{Me}$·HBF_4	White solid	1.00	0.256	pbm (450 rpm)	6 h	Brown powder	Method A	91	Brown solid
		Copper powder	Red powder <45µm mp: 1083.4	3.00	0.768						
		NaOH	Sticky white powder	1.10	0.281						
6	$[Cu(IMes^{Me})_2]PF_6$	$IMes^{Me}$·HPF_6	White solid	1.00	0.235	pbm (450 rpm)	6 h	Brown powder	Method A	97	Brown solid
		Copper powder	Red powder <45µm mp: 1083.4	3.00	0.705						
		NaOH	Sticky white powder	1.10	0.258						

7	$[Cu(IPr^{Me})_2]BF_4$	$IPr^{Me}\cdot HBF_4$	White solid	1.00	0.161	pbm (450 rpm)	6 h	Brown powder	Method F	72	White powder
		Copper powder	Red powder <45µm mp: 1083.4	5.00	0.804						
		KHMDS	White solid	1.10	0.177						
8	$[Cu(IPr^{Me})_2]PF_6$	$IPr^{Me}\cdot HPF_6$	White solid	1.00	0.089	pbm (450 rpm)	6h	Brown powder	Method F	78	White powder
		Copper powder	Red powder <45µm mp: 1083.4	5.00	0.446						
		KHMDS	White solid	5.00	0.446						

1.3 Imidazolium salts synthesis

1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride IMes·HCl

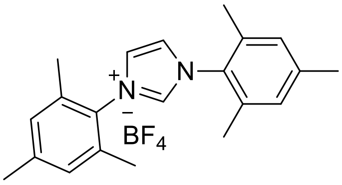


2,4,6-Trimethylaniline (10.4 mL, 74.0 mmol, 2.00 eq) was dissolved in methanol (40 mL). The resulting solution was cooled to 0 °C, and a solution of 40% glyoxal in water (4.23 mL, 37.0 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred during two days. The yellow suspension was filtrated, washed with a minimum of methanol and diethyl ether to afford *N*,*N*'-dimesitylethanediimine (8.48 g, 29.0 mmol, 78%) as a yellow powder. ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[1]

Paraformaldehyde (811 mg, 27.0 mmol, 1.00 eq) was suspended in a solution of 4M Hydrochloric acid in dioxane (9.45 mL, 37.8 mmol, 1.40 eq) and stirred until complete dissolution of the white solid. THF (54 mL) followed by *N*,*N*'-dimesitylethanediimine (7.90 g, 27.0 mmol, 1.00 eq) were added slowly. The resulting solution was stirred at 40°C for 2 days. Then the suspension was cooled to room temperature and the white precipitate was collected by filtration, washed with THF and diethyl ether to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (7.14 g, 20.9 mmol, 78%) as a white powder.

^{1}H NMR (300 MHz, CDCl$_3$)[4] δ 10.95 (s, 1H), 7.60 (s, 2H), 7.04 (s, 4H), 2.35 (s, 6H), 2.19 (s, 12H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 141.4, 140.0, 134.1, 130.6, 129.9, 124.3, 21.1, 17.7

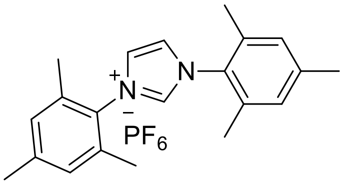
1,3-Bis-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate IMes·HBF$_4$



1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (306.8 mg, 0.900 mmol, 1.00 eq) and sodium tetrafluoroborate (163.2 mg, 0.954 mmol, 1.06 eq) were introduced in a 25 mL Teflon grinding bowl with one Teflon ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 30 minutes in the vibrating ball-mill operated at 25 Hz. The white powder was recovered with water and the suspension was filtrated. The white solid was washed three times with water and dried under vacuum to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate (334.9 mg, 0.854 mmol, 95%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[2] δ 9.65 (s, 1H), 8.27 (s, 2H), 7.22 (s, 4H), 2.37 (s, 6H), 2.13 (s, 12H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 140.7, 138.5, 134.3, 131.0, 129.4, 124.8, 20.6, 16.9; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.2

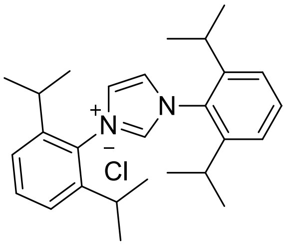
1,3-Bis-(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate IMes·HPF$_6$



1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (285.2 mg, 0.837 mmol, 1.00 eq) and potassium hexafluorophosphate (184.8 mg, 1.004 mmol, 1.20 eq) were introduced in a 25 mL Teflon grinding bowl with one Teflon ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 30 minutes in the vibrating ball-mill operated at 25 Hz. The white powder was recovered with water and the suspension was filtrated. The white solid was washed three times with water and dried under vacuum to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate (353.3 mg, 0.784 mmol, 94%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[3] δ 9.65 (s, 1H), 8.28 (s, 2H), 7.21 (s, 4H), 2.36 (s, 6H), 2.13 (s, 12H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 140.6, 138.5, 134.3, 131.0, 129.4, 124.8, 20.6, 16.8; **^{31}P NMR (162 MHz, DMSO-*d$_6$*)** δ -144.2 (sept, *J* = 711.2 Hz) ; **^{19}F NMR (282 MHz, DMSO-*d$_6$*)** δ -70.2 (d, *J* = 711.2 Hz).

1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium chloride IPr·HCl

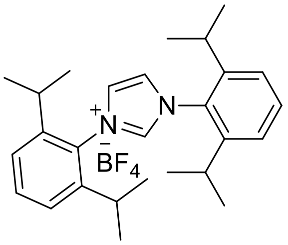


2,6-Di*iso*propylaniline (3.00 g, 16.9 mmol, 2.00 eq) was dissolved in methanol (16.3 mL). The resulting solution was cooled to 0 °C, and 40% glyoxal in water (975 µL, 8.45 mmol, 1.00 eq) and two or three drops of formic acid were added. The solution was warmed to room temperature and stirred during three days. The yellow suspension was filtrated, washed with a minimum of methanol and diethyl ether to afford *N*,*N*'-bis(2,6-diisopropylphenyl)ethane-1,2-diimine (2.04 g, 5.42 mmol, 64%) as a yellow powder. ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[1]

Paraformaldehyde (119.5 mg, 3.98 mmol, 1.00 eq) was suspended in as solution of 4M Hydrochloric acid in dioxane (1.40 mL, 5.57 mmol, 1.40 eq) and stirred until complete dissolution of the white solid. THF (30 mL) followed by *N*,*N*'-bis(2,6-di*iso*propylphenyl)ethane-1,2-diimine (1.50 g, 3.98 mmol, 1.00 eq) were added slowly. The resulting solution was stirred at 40°C for three days. Then the suspension was cooled to room temperature and the white precipitate was collected by filtration, washed with THF and diethyl ether to afford 1,3-bis-(2,6-di*iso*propylphenyl)imidazolium chloride (988.1 mg, 2.32 mmol, 58%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d₆*)[4] δ 10.27 (s, 1H), 8.59 (s, 2H), 7.69 (t, *J* = 6.8 Hz, 2H), 7.53 (d, *J* = 6.8 Hz, 4H), 2.41 – 2.29 (m, 4H), 1.26 (d, *J* = 5.6 Hz, 12H), 1.16 (d, *J* = 5.6 Hz, 12H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 145.3, 139.8, 132.3, 130.5, 126.7, 125.1, 29.1, 24.6, 23.6.

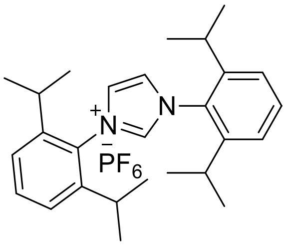
1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium tetrafluoroborate IPr·HBF$_4$



1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium chloride (368.9 mg, 0.868 mmol, 1.00 eq) and sodium tetrafluoroborate (101.0 mg, 0.920 mmol, 1.06 eq) were introduced in a 25 mL Teflon grinding bowl with one Teflon ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 30 minutes in the vibrating ball-mill operated at 25 Hz. The white powder was recovered with water and the suspension was filtrated. The white solid was washed three times with water and dried under vacuum to afford 1,3-bis-(2,6-di*iso*propylphenyl)imidazolium tetrafluoroborate (398.0 mg, 0.835 mmol, 96%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6)[5] δ 10.17 (s, 1H), 8.56 (d, *J* = 1.1 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 4H), 2.36 (sept, *J* = 6.7 Hz, 4H), 1.27 (d, *J* = 6.8 Hz, 12H), 1.17 (d, *J* = 6.8 Hz, 12H) ; **^{13}C NMR (101 MHz, DMSO-d_6)** δ 144.8, 139.3, 131.8, 130.0, 126.2, 124.6, 28.6, 24.1, 23.1; **^{19}F NMR (376 MHz, DMSO-d_6)** δ -148.3

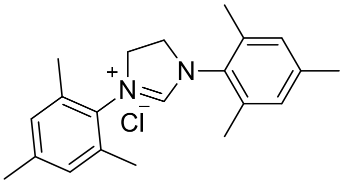
1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium hexafluorophosphate IPr·HPF$_6$



1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium chloride (308.3 mg, 0.728 mmol, 1.00 eq) and potassium hexafluorophosphate (160.7 mg, 0.873 mmol, 1.20 eq) were introduced in a 25 mL Teflon grinding bowl with one Teflon ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 30 minutes in the vibrating ball-mill operated at 25 Hz. The white powder was recovered with water and the suspension was filtrated. The white solid was washed three times with water and dried under vacuum to afford 1,3-bis-(2,6-di*iso*propylphenyl)imidazolium hexafluorophosphate (350.3 mg, 0.655 mmol, 90%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$)[5] δ 10.16 (s, 1H), 8.56 (s, 2H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 4H), 2.36 (sept, *J* = 6.8 Hz, 4H), 1.27 (d, *J* = 6.8 Hz, 12H), 1.17 (d, *J* = 6.8 Hz, 12H) ; **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 145.3, 139.7, 132.3, 130.5, 126.7, 125.1, 29.1, 24.6, 23.6; **^{31}P NMR (162 MHz, DMSO-*d*$_6$)** δ -144.2 (sept, *J* = 711.2 Hz) ; **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -70.1 (d, *J* = 711.2 Hz) ;

1,3-Dimesitylimidazolidinium chloride SIMes·HCl

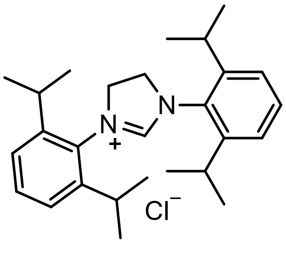


N,*N*'-Dimesitylethanediimine (4.02 g, 13.7 mmol, 1.00 eq) was dissolved in a mixture of methanol (55 mL) and THF (82 mL). The resulting solution was agitated at room temperature and sodium borohydride (5.20 g, 137.4 mmol, 10.00 eq) was added slowly. After 2 h at room temperature, a saturated solution of ammonium chloride was added. The resulting solution was extracted three times with diethyl ether. The combined organic layer was washed with water, dried with $MgSO_4$, filtrated and concentrated under vaccum to furnish 1,2-bis(mesitylamino)ethane (3.78 g, 12.8 mmol, 93%). ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[6]

1,2-Bis(mesitylamino)ethane (3.66 g, 12.40 mmol, 1.00 eq), ammonium chloride (729.6 mg, 13.64 mmol, 1.10 eq) and triethyl orthoformate (5.20 mL, 31.00 mmol, 2.50 eq) were agitated at 110°C for 2 h. The reaction mixture was cooled to room temperature and diethyl ether was added. The resulting suspension was filtrated and the white solid washed with acetone to afford 1,3-dimesitylimidazolidinium chloride (2.81 g, 8.19 mmol, 66%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$)[7] δ 9.34 (s, 1H), 6.94 (s, 4H), 4.54 (s, 4H), 2.36 (s, 12H), 2.27 (s, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.9, 140.5, 134.9, 130.2, 130.0, 51.9, 21.0, 18.0

1,3-Bis(2,6-di*iso*propylphenyl)imidazolidinium chloride SIPr·HCl

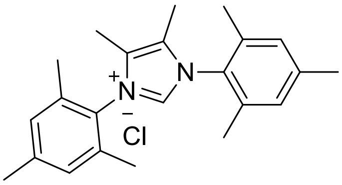


N,*N*'-Bis(2,6-di*iso*propylphenyl)ethane-1,2-diimine (500 mg, 1.33 mmol, 1.00 eq) was disolved in a mixture of THF (6 mL) and MeOH (5.3 mL). Sodium borohydride (503.2 mg, 13.3 mmol, 10.00 eq) was added and the mixture was stirred at 80°C for three hours under Argon. The reaction mixture was cooled to room temperature and a saturated aqueous solution of NH_4Cl was added. Diethyl ether was added and the aqueous phase was extracted three times with diethyl ether. The combined organic layer was washed with water, dried with $MgSO_4$, and concentrated under vacuum to afford *N*,*N*'-bis(2,6-di*iso*propylphenyl)ethylenediamine (455 mg, 1.20 mmol, 90%). ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[2]

N,*N*'-Bis(2,6-di*iso*propylphenyl)ethylenediamine (455 mg, 1.20 mmol, 1.00 eq), ammonium chloride (70.6 mg, 1.32 mmol, 1.10 eq) and triethyl orthoformate (795 µL, 4.78 mmol, 4.00 eq) were agitated at 110°C for 4 h. The reaction mixture was cooled to room temperature and diethyl ether was added. The resulting suspension was filtrated and dried under vacuum to afford 1,3-bis(2,6-di*iso*propylphenyl)imidazolidinium chloride (262.8 mg, 0.615 mmol, 51%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$)[7] δ 8.69 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.22 (m, 4H), 4.76 (s, 4H), 2.99 (sept, *J* = 6.6 Hz, 4H), 1.37 (d, *J* = 6.6 Hz, 12H), 1.24 (d, *J* = 6.6 Hz, 12H) ; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 146.1, 131.6, 129.4, 125.0, 55.3, 29.3, 25.5, 23.8 ; **HRMS** calcd for $C_{27}H_{39}N_2$ $[M - Cl^-]^+$: 391.3113; found: 391.3115

[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride IMes^{Me}·HCl

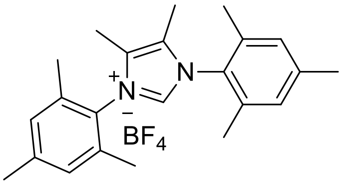


2,4,6-Trimethylaniline (4.15 mL, 29.6 mmol, 2.00 eq) was dissolved in methanol (29.6 mL). The resulting solution was cooled to 0 °C, and 2,3-butanedione (1.29 mL, 14.8 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred two days. The yellow suspension was filtrated, washed with a minimum of methanol and diethyl ether to afford *N,N'*-dimesityl-2,3-butanediimine (3.20 g, 10.0 mmol, 68%) as a yellow powder. ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[8]

Paraformaldehyde (973 mg, 32.4 mmol, 1.20 eq) was suspended in as solution of 4M Hydrochloric acid in dioxane (9.45 mL, 37.8 mmol, 1.40 eq) and stirred until complete dissolution of the white solid. *N,N'*-dimesityl-2,3-butanediimine (8.646 g, 27.0 mmol, 1.00 eq) dissolved in THF (270 mL) was added slowly. The resulting solution was stirred at room temperature for 3 days. Then the suspension was filtrated, washed with THF and diethyl ether and dried under vaccum. The brown solid was dissolved in a saturated aqueous solution of $NaHCO_3$, the aqueous layer was washed four times with ethyl acetate and extracted three times with dichloromethane. The combined organic layer resulting from dichloromethane extraction was dried with $MgSO_4$ and concentrated under vacuum to afford [1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride (751.3 mg, 2.04 mmol, 8%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$)[9] δ 10.59 (s, 1H), 7.01 (s, 4H), 2.31 (s, 6H), 2.08 (s, 12H), 2.04 (s, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 141.2, 137.7, 134.7, 130.0, 128.9, 127.5, 21.2, 17.7, 8.7

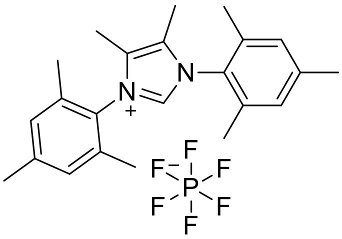
[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium tetrafluoborate IMes^{Me}·HBF$_4$



Paraformaldehyde (117.0 mg, 3.90 mmol, 1.25 eq) was suspended in a solution of 4M hydrochloric acid in dioxane (1.21 mL, 4.84 mmol, 1.55 eq) and stirred until complete dissolution of the white solid. This solution was added to a suspension of *N,N'*-dimesityl-2,3-butanediimine (1.00 g, 3.12 mmol, 1.00 eq) in ethyl acetate (12.5 mL). The resulting suspension was stirred 8 h at room temperature. The white solid was recovered by filtration and was dissolved in water (20 mL). Sodium tetrafluoroborate (410.6 mg, 3.74 mmol, 1.2 eq) was added to the solution. After 30 minutes the solid was filtrated and washed three times with water to afford [1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium tetrafluoborate (434.9 mg, 1.03 mmol, 33%) as a brown solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[10] δ 9.35 (s, 1H), 7.19 (s, 4H), 2.33 (s, 6H), 2.03 (s, 12H), 2.01 (s, 6H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 141.4, 135.9, 135.2, 130.0, 129.4, 128.5, 21.1, 17.1, 8.4 ; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.2; **HRMS** calcd for $C_{23}H_{29}N_2$ $[M – BF_4^-]^+$: 333.2330; found: 333.2331

[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate IMes^{Me}·HPF$_6$

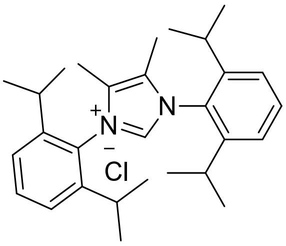


Paraformaldehyde (117.0 mg, 3.90 mmol, 1.25 eq) was suspended in a solution of 4M hydrochloric acid in dioxane (1.21 mL, 4.84 mmol, 1.55 eq) and stirred until complete dissolution of the white solid. This solution was added to a suspension of *N,N'*-dimesityl-2,3-butanediimine (1.00 g, 3.12 mmol, 1.00 eq) in ethyl acetate (12.5 mL). The resulting suspension was stirred during 8 h at room temperature. The white solid was recovered by filtration and dissolved in water (20 mL). Potassium hexafluorophosphate (688.4 mg, 3.74 mmol, 1.2 eq) was added to the solution. After 30 minutes the solid was filtrated and washed three times with water to afford [1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate (429.2 mg, 0.897 mmol, 29%) as a beige solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 9.35 (s, 1H), 7.19 (s, 4H), 2.33 (s, 6H), 2.09 – 1.95 (m, 18H) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 141.3, 135.8, 135.2, 129.9, 129.3, 128.4, 21.0, 17.1, 8.4 ; **^{31}P NMR (162 MHz,**

DMSO-d_6) δ -144.26 (sept, *J* = 711.3 Hz) ; **^{19}F NMR (376 MHz, DMSO-d_6)** δ -70.1 (d, *J* = 711.5 Hz) ; **HRMS** calcd for $C_{23}H_{29}N_2$ [M – PF_6^-]$^+$: 333.2331; found: 333.2333

[1,3-Bis(2,6-diisopropylphenyl)-4,5-dimethyl]imidazolium chloride IPr^{Me}·HCl

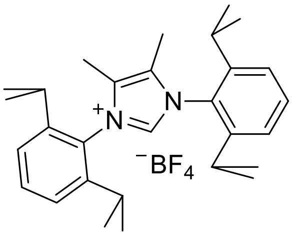


2,6-Di*iso*propylaniline (15.0 g, 84,6 mmol, 2.00 eq) was dissolved in methanol (42,3 mL). The resulting solution was cooled to 0 °C, and 2,3-butanedione (3.7 mL, 42,3 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred overnight. The yellow suspension was filtrated, washed with a minimum of methanol and diethyl ether to afford *N*,*N*'-bis-(2,6-di*iso*propylphenyl)butane-2,3-diimine (11.15 g, 27.6 mmol, 65%) as a yellow powder. ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[10]

Paraformaldehyde (288.0 mg, 9.59 mmol, 1.25 eq) was suspended in a solution of 4M hydrochloric acid in dioxane (2.89 mL, 11.6 mmol, 1.50) and stirred until complete dissolution of the white solid. The resulting solution was added dropwise to a solution of *N*,*N*'-bis-(2,6-diisopropylphenyl)butane-2,3-diimine (3.11 g, 7.67 mmol, 1.00 eq) in THF (76.7 mL) at 0°C. The resulting solution was stirred at room temperature overnight. Then the white precipitate was collected by filtration, washed with THF and diethyl ether to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride (806.6 mg, 1.78 mmol, 23%) as a white powder.

^{1}H NMR (400 MHz, DMSO-d_6)[11] δ 9.98 (s, 1H), 7.68 (t, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 4H), 2.29 (sept, *J* = 6.8 HZ, 4H), 2.06 (s, 6H), 1.25 (d, *J* = 6.8 Hz, 12H), 1.11 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 145.4, 136.8, 132.4, 129.1, 128.0, 125.2, 28.7, 25.0, 22.8, 8.6

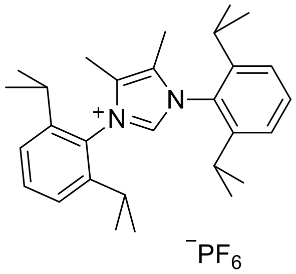
[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium tetrafluoroborate IPr^{Me}·HBF$_4$



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride (250 mg, 0.552 mmol, 1.00 eq) was dissolved in water (20 mL) and sodium tetrafluroroborate (72.7 mg, 0.662 mmol, 1.20 eq) was added. The resulting suspension was stirred for 30 minutes and filtrated under vacuum. The solid was washed with water and diethyl ether and dried under vacuum to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium tetrafluoroborate (221.7 mg, 0.439 mmol, 80%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d_6*) δ 9.98 (s, 1H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 4H), 2.32 (sept, *J* = 6.7 Hz, 4H), 2.09 (s, 6H), 1.27 (d, *J* = 6.7 Hz, 12H), 1.13 (d, *J* = 6.7 Hz, 12H) ; **^{13}C NMR (101 MHz, DMSO-*d_6*)** δ 145.2, 136.6, 132.1, 128.9, 127.8, 125.0, 28.4, 24.8, 22.6, 8.4 ; **^{19}F NMR (376 MHz, DMSO-*d_6*)** δ -148.3; **HRMS** calcd for $C_{29}H_{41}N_2$ $[M – BF_4^-]^+$: 417.3270; found: 417.3269

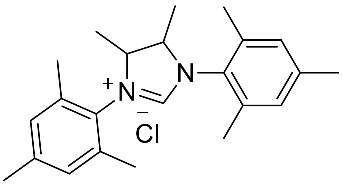
[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate IPr^{Me}·HPF$_6$



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride (350 mg, 0.772 mmol, 1.00 eq) was dissolved in water (40 mL) and potassium hexafluorophosphate (170.6 mg, 0.927 mmol, 1.20 eq) was added. The resulting suspension was stirred for 30 minutes and filtrated under vacuum. The solid was washed with water and diethyl ether and dried under vacuum to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate (341 mg, 0.606 mmol, 78%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d_6*) δ 9.97 (s, 1H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 4H), 2.38 – 2.25 (m, 4H), 2.08 (s, 6H), 1.26 (d, *J* = 6.7 Hz, 12H), 1.12 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (101 MHz, DMSO-*d_6*)** δ 145.3, 136.6, 132.1, 129.0, 127.9, 125.0, 28.5, 24.9, 22.6, 8.5; **^{31}P NMR (162 MHz, DMSO-*d_6*)** δ -144.2 (sept, *J* = 711.2 Hz) ; **^{19}F NMR (376 MHz, DMSO-*d_6*)** δ -70.2 (d, *J* = 711.2 Hz); **HRMS** calcd for $C_{29}H_{41}N_2$ $[M – PF_6^-]^+$: 417.3270; found: 417.3272

[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolidinium chloride SIMes^{Me}·HCl



N,N'-Dimesityl-2,3-butanediimine (6.00 g, 18.7 mmol, 1.00 eq) was dissolved in methanol (75 mL). Cyanoborohydride (5.90 g, 93.6 mmol, 5.00 eq) was added slowly to the resulting solution. Bromo cresol green and 0.1M HCl aqueous solution was added until the solution changed from blue to yellow. The resulting solution was stirred at reflux for three days. Then, reaction mixture was cooled down to room temperature, 0.1N KOH aqueous solution (15 mL) and water (150 mL) were added.

The aqueous layer was extracted three times with dichloromethane (3*100 mL). The combined organic layer was washed two times with water, dried with $MgSO_4$ and concentrated under vacuum. The crude mixture was purified by column chromatography with a gradient ranging from cyclohexane to cyclohexane/ethyl acetate 2% to afford both *cis*-2,3-bis(mesitylamino)butane (581,4 mg, 1.79 mmol, 10%) and *trans*-2,3-bis(mesitylamino)butane (3.26 g, 10.04 mmol, 54%) as white powders.

Cis diastereoisomer:

Cis-2,3-bis(mesitylamino)butane (347.0 mg, 1.07 mmol, 1.00 eq), ammonium chloride (57.2 mg, 1.07 mmol, 1.00 eq) and triethyl orthoformate (1.07 mL, 6.41 mmol, 6.00 eq) were stirred at 110°C overnight. Then, reaction mixture was cooled down to room temperature, diethyl ether was added, the white solid was filtrated and washed with diethyl ether and acetone to afford [1,3-bis(2,4,6-trimethylphenyl)-4,5-*cis*-dimethyl]imidazolidinium chloride (202.9 mg, 0.547 mmol, 51%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 6.94 (s, 2H), 6.92 (s, 2H), 5.10 (s, 2H), 2.40 (s, 6H), 2.35 (s, 6H), 2.26 (s, 6H), 1.30 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.0, 140.2, 135.7, 135.3, 130.4, 130.3, 128.9, 62.3, 21.1, 19.0, 18.6, 12.3; **HRMS** calcd for $C_{23}H_{31}N_2$ $[M - Cl^-]^+$: 335.2487; found : 335.2489

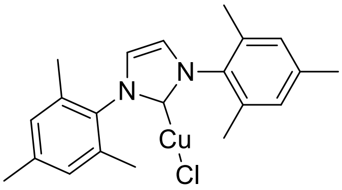
Trans diastereoisomer:

Trans-2,3-bis(mesitylamino)butane (2.68 g, 8.25 mmol, 1.00 eq), ammonium chloride (441 mg, 8.25 mmol, 1.00 eq) and triethyl orthoformate (8.25 mL, 49.5 mmol, 6.00 eq) were stirred at 110°C overnight. Then, reaction mixture was cooled down to room temperature, diethyl ether was added, the white solid was filtrated and washed with diethyl ether and acetone to afford [1,3-bis(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl]imidazolidinium chloride (1.19 g, 3.20 mmol, 39%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 6.93 (s, 2H), 6.90 (s, 2H), 4.41 – 4.30 (m, 2H), 2.36 (s, 6H), 2.32 (s, 6H), 2.25 (s, 6H), 1.43 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.5, 140.2, 136.2, 134.6, 130.34, 130.31, 128.8, 66.8, 21.0, 19.0, 18.4, 17.8; **HRMS** calcd for $C_{23}H_{31}N_2$ $[M - Cl^-]^+$: 335.2488; found : 335.2489

1.4 [CuCl(NHC)] synthesis

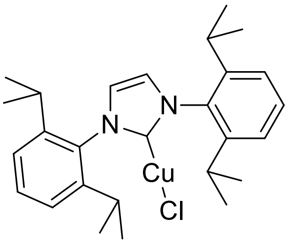
[1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper(I) chloride [CuCl(IMes)]



1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (122.1 mg, 0.358 mmol, 1.00 eq), copper powder (45.5 mg, 0.716 mmol, 2.00 eq) and water (50 µL) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 5 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper(I) chloride (123.3 mg, 0.306 mmol, 85%) as a white solid.

^{1}H NMR (300 MHz, CDCl$_3$)[12] δ 7.06 (s, 2H), 7.01 (s, 4H), 2.35 (s, 6H), 2.11 (s, 12H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 179.5, 139.9, 135.4, 134.9, 129.8, 122.6, 21.4, 18.1

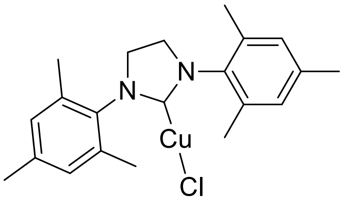
[1,3-Bis-(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper(I) chloride [CuCl(IPr)]



1,3-bis-(2,6-di*iso*propylphenyl)imidazolium chloride (95.9 mg, 0.226 mmol, 1.00 eq), copper powder (71.7 mg, 1.128 mmol, 5.00 eq) and water (50 µL) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting white powder was washed three times with water and dried under vacuum to afford [1,3-bis-(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper(I) chloride (90.3 mg, 0.185 mmol, 82%) as a white powder.

^{1}H NMR (400 MHz, CDCl$_3$)[12] δ 7.50 (s, 2H), 7.31 (s, 4H), 7.14 (s, 2H), 2.59 (s, 4H), 1.31 (s, 12H), 1.25 (s, 12H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 180.7, 145.7, 134.5, 130.7, 124.3, 123.3, 28.9, 24.9, 24.0

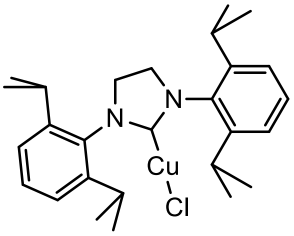
[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]copper(I) chloride [CuCl(SIMes)]



1,3-Dimesitylimidazolidinium chloride (122.3 mg, 0.357 mmol, 1.00 eq), copper powder (45.3 mg, 0.713 mmol, 2.00 eq) and water (50 µL) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting white powder was washed with diethyl ether to afford [1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]copper(I) chloride (107 mg, 0.264 mmol, 76%) as a white powder.

^{1}H NMR (300 MHz, CDCl$_3$)[12] δ 6.96 (s, 4H), 3.96 (s, 4H), 2.32 (s, 12H), 2.31 (s, 6H) ; **^{13}C NMR (101 MHz, CDCl$_3$)** δ 138.7, 135.2, 134.9, 129.7, 50.94, 50.85, 20.8, 17.7.

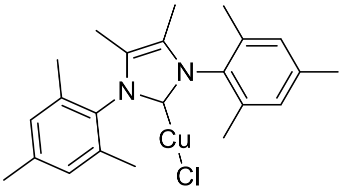
[1,3-Bis(2,6-di*iso*propylphenyl)imidazolidin-2-ylidene]copper(I) chloride [CuCl(SIPr)]



1,3-Bis(2,6-di*iso*propylphenyl)imidazolidinium chloride (96.1 mg, 0.225 mmol, 1.00 eq), copper powder (71.5 mg, 1.125 mmol, 5.00 eq) and water (50 µL) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting white powder was washed with water and diethyl ether to afford [1,3-bis(2,6-di*iso*propylphenyl)imidazolidin-2-ylidene]copper(I) chloride (71.9 mg, 0.147 mmol, 65%) as a white powder.

^{1}H NMR (400 MHz, DMSO-d_6)[13] δ 7.46 – 7.39 (m, 2H), 7.33 (d, J = 7.6 Hz, 4H), 4.07 (s, 4H), 3.10 (sept, J = 6.8 Hz, 4H), 1.31 (d, J = 6.8 Hz, 12H), 1.26 (d, J = 6.8 Hz, 12H) ; **^{13}C NMR (101 MHz, DMSO-d_6)** δ 200.9, 146.5, 134.6, 129.5, 124.3, 53.6, 28.1, 25.2, 23.4.

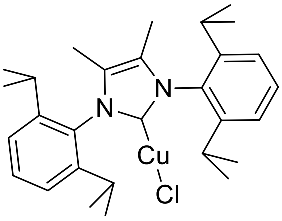
[(1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper(I) chloride [CuCl(IMes^{Me})]



[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride (124.6 mg, 0.338 mmol, 1.00 eq), copper powder (42.9 mg, 0.676 mmol, 2.00 eq) and benzonitrile (50 µL) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum to afford [(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper(I) chloride (118.9 mg, 0.276 mmol, 82%) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 4H), 2.34 (s, 6H), 2.03 (s, 12H), 1.88 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.4, 139.3, 135.0, 133.8, 129.6, 125.5, 21.2, 17.9, 9.2;

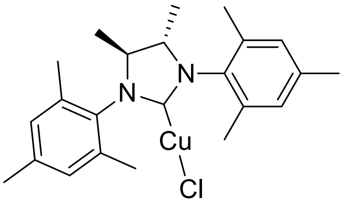
[(1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper(I) chloride [CuCl(IPr^{Me})]



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride (98.5 mg, 0.217 mmol, 1.00 eq), copper powder (69.1 mg, 1.087 mmol, 5.00) and benzonitrile (50 µL) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vaccum. The resulting white solid was washed with diethyl ether and dried under vacuum to afford [(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper(I) chloride (99.4 mg, 0.193 mmol, 89%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d_6*)[14] δ 7.56 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 4H), 2.46 – 2.35 (m, 4H), 1.91 (s, 6H), 1.21 (d, *J* = 7.6 Hz, 12H), 1.19 (d, 7.6 Hz, 12H) ; **^{13}C NMR (101 MHz, DMSO-*d_6*)** δ 175.3, 145.6, 132.5, 130.5, 126.2, 124.3, 28.2, 25.1, 22.8, 9.0

[(1,3-Bis-(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl)imidazolidin-2-ylidene]copper(I) chloride [CuCl(SIMes^{Me})]

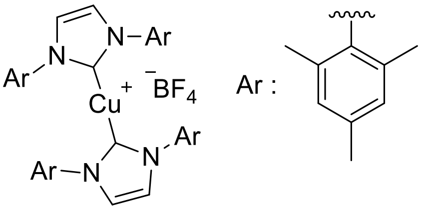


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl]imidazolidinium chloride (124.8 mg, 0.336 mmol, 1.00 eq), copper powder (42.8 mg, 0.673 mmol, 2.00 eq) and water (50 µL) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting white powder was washed with diethyl ether to afford [(1,3-bis-(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl)imidazolidin-2-ylidene]copper(I) chloride (130.7 mg, 0.302 mmol, 90%) as a white powder.

^{1}H NMR (300 MHz, CDCl$_3$) δ 6.96 (s, 2H), 6.92 (s, 2H), 4.05 – 3.88 (m, 2H), 2.37 (s, 6H), 2.30 (s, 6H), 2.28 (s, 6H), 1.28 (d, *J* = 5.6 Hz, 6H) ; The product was not stable in solution but peaks were identified as followed: **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.8, 138.5, 136.70, 135.4, 133.9, 130.1, 66.4, 21.1, 19.3, 18.5, 18.2 ; **HRMS** calcd for $C_{46}H_{60}N_4Cu$ [M – Cl$^-$]$^+$: 731.4114; found: 731.4105

1.5 [Cu(NHC)$_2$]Y (Y = BF_4 or PF_6) synthesis

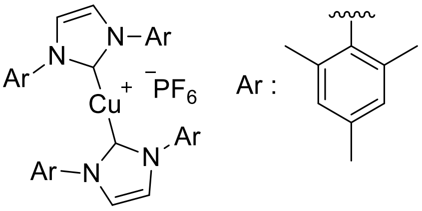
Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper tetrafluoroborate [Cu(IMes)$_2$]BF_4



1,3-Bis-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate (104.9 mg, 0.267 mmol, 1.00 eq), copper powder (51.0 mg, 0.802 mmol, 3.00 eq) and sodium hydroxide (11.8 mg, 0.294 mmol, 1.10 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 3 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper tetrafluoroborate (79.7 mg, 0.105 mmol, 79%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[13] δ 7.51 (s, 4H), 6.98 (s, 8H), 2.38 (s, 12H), 1.61 (s, 24H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 176.9, 139.3, 134.9, 134.5, 129.2, 123.6, 21.1, 16.9; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.2

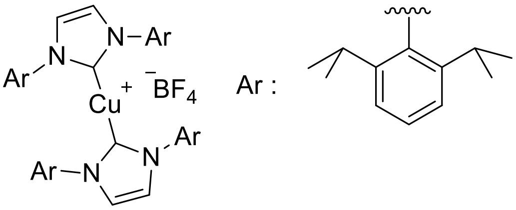
Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper hexafluorophosphate [Cu(IMes)$_2$]PF_6



1,3-Bis-(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate (110.2 mg, 0.245 mmol, 1.00 eq), copper powder (46.6 mg, 0.734 mmol, 3.00 eq) and sodium hydroxide (10.8 mg, 0.269 mmol, 1.10 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hour at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper hexafluorophosphate (87.0 mg, 0.106 mmol, 87%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[12] δ 7.51 (s, 4H), 6.98 (s, 8H), 2.38 (s, 12H), 1.61 (s, 24H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 176.9, 139.3, 134.9, 134.5, 129.2, 123.6, 21.1, 16.8**; ^{31}P NMR (162 MHz, DMSO-*d$_6$*)** δ -144.2 (sept, *J* = 711.2 Hz) ; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -70.1 (d, *J* = 711.3 Hz)

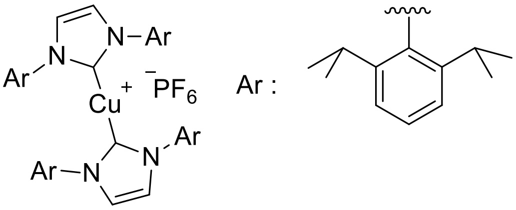
Bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper tetrafluoroborate [Cu(IPr)$_2$]BF$_4$



1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium tetrafluoroborate (95.3 mg, 0.200 mmol, 1.00 eq), copper powder (63.5 mg, 1.00 mmol, 5.00 eq) and sodium hydroxide (8.8 mg, 0.220 mmol, 1.10 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 5 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting white powder was washed three times with diethyl ether and dried under vacuum to afford bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper tetrafluoroborate (78.9 mg, 0.0851 mmol, 85%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[15] δ 7.66 (s, 4H), 7.49 (t, *J* = 7.8 Hz, 4H), 7.18 (d, *J* = 7.8 Hz, 8H), 2.24 (sept, *J* = 6.9 Hz, 8H), 0.97 (d, *J* = 6.9 Hz, 24H), 0.80 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 176.5, 144.6, 134.7, 130.3, 126.0, 124.2, 28.3, 23.9, 23.8; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.3

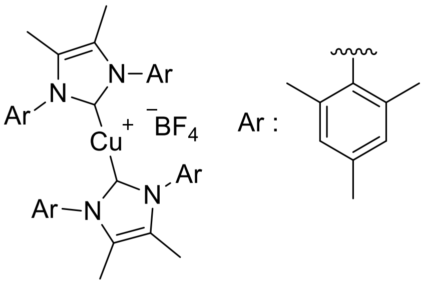
Bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper hexafluorophosphate [Cu(IPr)$_2$]PF$_6$



1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium hexafluorophosphate (83.6 mg, 0.156 mmol, 1.00 eq), copper powder (49.7 mg, 0.782 mmol, 5.00 eq) and potassium bis(trimethylsilyl)amide (34.3 mg, 0.172 mmol, 1.10 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting white powder was washed three times with diethyl ether and dried under vacuum to afford bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper hexafluorophosphate (68.8 mg, 0.0698 mmol, 89%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[15] δ 7.68 (s, 4H), 7.49 (t, *J* = 7.8 Hz, 4H), 7.18 (d, *J* = 7.8 Hz, 8H), 2.24 (hept, *J* = 6.7 Hz, 8H), 0.97 (d, *J* = 6.8 Hz, 24H), 0.81 (d, *J* = 6.9 Hz, 24H) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 176.4, 144.5, 134.6, 130.2, 126.0, 124.2, 28.2, 23.9, 23.8 ; **^{31}P NMR (162 MHz, DMSO-*d$_6$*)** δ -144.2 (hept, *J* = 711.2 Hz) ; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -70.2 (d, *J* = 711.2 Hz)

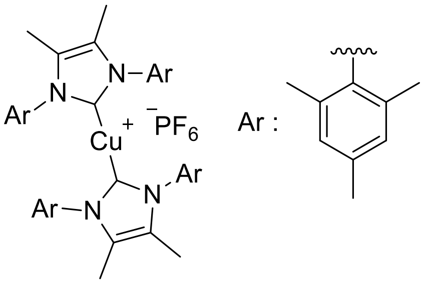
Bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper tetrafluoroborate [Cu(IMes^{Me})$_2$]BF$_4$



[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium tetrafluoborate (107.5 mg, 0.256 mmol, 1.00 eq), copper powder (48.8 mg, 0.768 mmol, 3.00 eq) and sodium hydroxide (11.3 mg, 0.768 mmol, 1.10 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting powder was washed with diethyl ether and dried under vacuum to afford bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper tetrafluoroborate (95.0 mg, 0.117 mmol, 91%) as a brown powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 7.01 (s, 8H), 2.41 (s, 12H), 1.76 (s, 12H), 1.56 (s, 24H) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 173.4, 138.7, 134.4, 132.9, 128.9, 125.5, 20.7, 16.5, 8.3 ; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.3 ; **HRMS** calcd for $C_{46}H_{56}N_4Cu$ $[M – BF_4^-]^+$: 727.3801; found: 727.3802

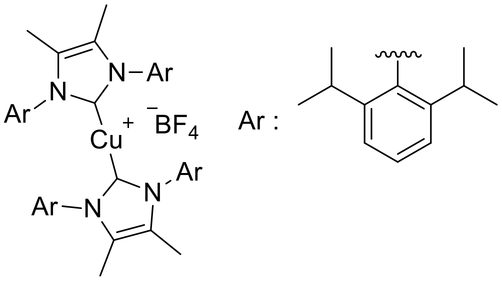
Bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper hexafluorophosphate [Cu(IMes^{Me})$_2$]PF$_6$



[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate (112.4 mg, 0.235 mmol, 1.00 eq), copper powder (44.8 mg, 0.705 mmol, 3.00 eq) and sodium hydroxide (10.3 mg, 0.258 mmol, 1.10 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrated was concentrated under vacuum. The resulting powder was washed with diethyl ether and dried under vacuum to afford bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper hexafluorophosphate (100.0 mg, 0.114 mg, 97%) as a brown powder.

^{1}H NMR (400 MHz, DMSO-*d₆*) δ 7.01 (s, 8H), 2.41 (s, 12H), 1.76 (s, 12H), 1.56 (s, 24H) ; **^{13}C NMR (101 MHz, DMSO-*d₆*)** δ 173.6, 138.7, 134.4, 132.9, 128.9, 125.6, 20.7, 16.5, 8.3 ; **^{31}P NMR (162 MHz, DMSO-*d₆*)** δ -144.2 (sept, *J* = 711.3 Hz) ; **^{19}F NMR (376 MHz, DMSO-*d₆*)** δ -70.1 (d, *J* = 711.3 Hz) ; **HRMS** calcd for $C_{46}H_{56}N_4Cu$ $[M - PF_6^-]^+$: 727.3801; found: 727.3800

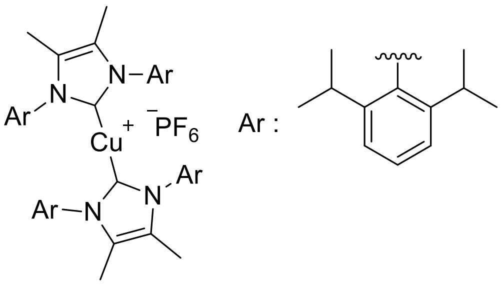
Bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper tetrafluoroborate [Cu(IPr^{Me})$_2$]BF$_4$



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium tetrafluoroborate (81.2 mg, 0.161 mmol, 1.00 eq), copper powder (51.1 mg, 0.804 mmol, 5.00 eq) and potassium bis(trimethylsilyl)amide (35.3 mg, 0.177 mmol, 1.10 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting solid was washed with diethyl ether and dried under vacuum to afford bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper tetrafluoroborate (57.2 mg, 0.0582 mmol, 72%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d₆*) δ 7.53 (t, *J* = 7.5 Hz, 4H), 7.40 (d, *J* = 7.5 Hz, 8H), 2.45 – 2.34 (m, 8H), 1.89 (s, 12H), 1.20 (d, *J* = 6.0 Hz, 48H); **^{13}C NMR (101 MHz, DMSO-*d₆*)** δ 145.5, 133.0, 130.2, 125.8, 124.1, 28.2, 25.0, 22.9, 9.0 ; **^{19}F NMR (376 MHz, DMSO-*d₆*)** δ -148.3 ; **HRMS** calcd for $C_{58}H_{80}N_4Cu$ $[M - BF_4^-]^+$: 895.5679; found: 895.5664

Bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper hexafluorophosphate [Cu(IPr^{Me})$_2$]PF$_6$



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate (50.2 mg, 0.0892 mmol, 1.00 eq), copper powder (51.1 mg, 0.446 mmol, 5.00 eq) and potassium bis(trimethylsilyl)amide (28.4 mg, 0.446 mmol, 5.00 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball mill and subjected to grinding for 6 hours at 450 rpm. Reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The resulting solid was washed with diethyl ether and dried under vacuum to afford a mixture of bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper hexafluorophosphate and a second copper complex of unidentified structure (36.1 mg, 0.0347 mmol, 78%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 7.55 – 7.50 (4H, $[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$ and second complex), 7.40 (d, *J* = 7.6 Hz, 8H, $[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 7.21 (d, *J* = 7.8 Hz, second complex), 2.39 (m, 8H, $[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 2.18 (sept, *J* = 6.7 Hz, second complex), 1.89 (s, 12H, $[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 1.60 (s, second complex), 1.20 (d, *J* = 6.5 Hz, 48H, $[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 0.97 (d, *J* = 6.8 Hz, second complex), 0.73 (d, *J* = 6.9 Hz, second complex) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** 145.5 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 144.7, 133.0 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 130.5, 130.2 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 127.5, 125.7 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 124.5, 124.1 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 28.2 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 28.1, 25.0 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 24.8, 22.9 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$), 22.5, 9.3, 9.0 ($[(\mathrm{IPr}^{\mathrm{Me}})_2\mathrm{Cu}]\mathrm{PF}_6$); **^{31}P NMR (162 MHz, DMSO-*d$_6$*)** δ -144.2 (sept, *J* = 711.3 Hz) ; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -70.2 (d, *J* = 711.5 Hz); **HRMS** calcd for $C_{58}H_{80}N_4Cu$ $[M - PF_6^-]^+$: 895.5679; found: 895.5662

2. Influence of reagent stoichiometry for the production of [CuCl(IMes)]

2.1 Influence of copper stoichiometry

General procedure with water in a ball-mill: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride IMes·HCl (1.00 eq), copper powder (1.00 – 5.00 eq) and water (50 µL, 0.3µL/mg) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding at 450 rpm during a given amount of time. Reaction mixture samples were regularly withdrawn from the bowl. In each cases, grinding was stopped less than five minutes to prepare each samples.

General procedure without water in a ball-mill: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride IMes·HCl (1.00 eq) and copper powder (1.00 – 5.00 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding at 450 rpm during a given amount of time. Reaction mixture samples were regularly withdrawn from the bowl. In each cases, grinding was stopped less than five minutes to prepare each samples.

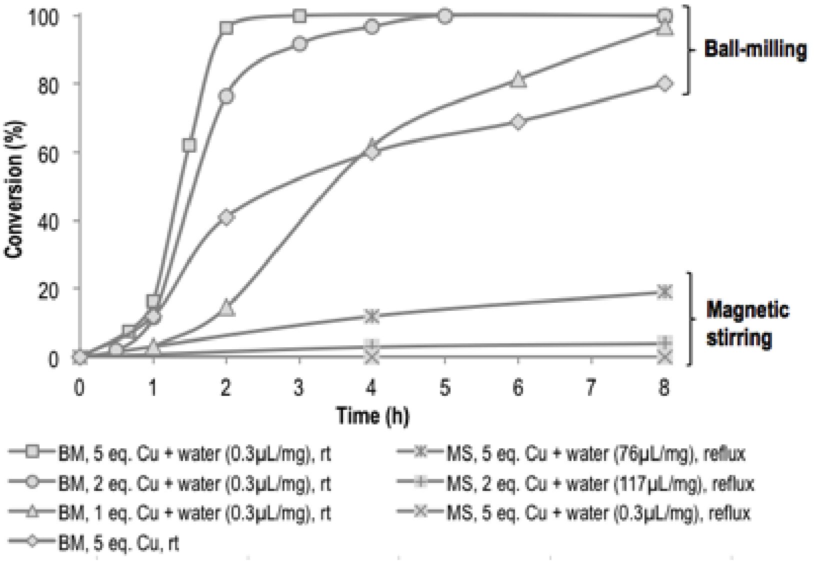
To prepare NMR samples, 1 or 2 mg of the reaction mixture were dissolved in 0.6 mL of deuterated chloroform, filtrated over celite and analyzed by ^{1}H NMR to determine conversion.

Entry	IMes·HCl		Copper powder		Water (µL;eq.)	NMR conv. (%)										**Yield (%)**
	Eq.	Quantity (mmol)	Eq.	Quantity (mmol)		30 min	40 min	1h	1.5h	2h	3h	4h	5h	6h	8h	
1	1.00	0.414	1.00	0.414	50;6.7			3		15		62		81	**97**	**79**
2	1.00	0.358	2.00	0.716	50;7.8	2		12		76	92	97	**100**			**85**
3					0;0			0		0		8		13	34	**-**
4	1.00	0.254	5.00	1.272	50;10.9	8	8	16	62	96	**100**					**85**
5					0;0			12		41		60		69	80	**-**

General procedure in diluted aqueous conditions under magnetic stirring: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride IMes·HCl (1.00 eq) was introduced in a round-bottom flask equipped with a condenser and dissolved in water (0.02M; 117µL/mg for 2 eq. of copper, 76µL/mg for 5 eq. of copper). Copper powder (2.00 – 5.00 eq) was added and the resulting reaction mixture was heated at reflux under air. After four hours, 1 mL of the hot reaction mixture was withdrawn from the reaction mixture, filtrated over celite and concentrated under vacuum. The resulting white solid was dissolved in deuterium chloroform and analyzed by ^{1}H NMR to determine conversion. After eight hours, another sample was prepared as described above.

General procedure in concentrated aqueous conditions under magnetic stirring: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride IMes·HCl (1.00 eq) and copper powder (2.00 – 5.00 eq) were introduced in a round-bottom flask equipped with a condenser. Water (50 µL, 0.3µL/mg) was added and the resulting reaction mixture was stirred and heated at 100°C under air. After four hours, the reaction mixture was cooled down to room temperature and few milligrams of the reaction mixture were withdrawn from the flask, dissolved in deuterated chloroform, filtrated over celite and analyzed by ^{1}H NMR to determine conversion. After eight hours, another sample was prepared as described above.

Entry	IMes·HCl		Copper powder		Water (mL;eq.)	NMR conv. (%)	
	Eq.	Quantity (mmol)	Eq.	Quantity (mmol)		4h	8h
1	1.00	0.358	2.00	0.716	17.9;2778	3	4
2					0.050;7.7	0	0
3	1.00	0.254	5.00	1.272	12.7;2778	12	19
4					0.050;10.9	0	0



MS = Magnetic stirring; BM = Ball-milling.

2.2 Influence of dioxygen stoichiometry

General procedure: Two bowls were prepared as follows: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride **IMes·HCl** (1.00 eq) and **copper powder** (5.00 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). The bowls were closed hermetically with parafilm, placed together in the planetary ball-mill and subjected to grinding at 450 rpm during **T_1**. Then, one bowl was removed and the second bowl (without opening) was subjected to grinding during **T_2**. For the first bowl after **T_1** and the second bowl after **T_1+T_2**, reaction mixture was recovered with dichloromethane and filtrated over celite. The filtrates were concentrated under vacuum and analyzed by ^{1}H NMR to determine conversion. This reaction was repeated with changing the total amount of material (IMes·HCl + copper powder) introduced in the bowl to vary the amount of O_2 present inside the hermetically closed bowl. To confirm the good homogenization of the reaction mixture inside the bowl, three samples of the reaction mixture with the highest milling load (entries 10 and 11) were withdrawn at three different spots inside the bowl. ^{1}H NMR analysis of these samples indicated identical conversion for the three different spots, confirming perfect homogeneization of the reaction mixture. All data are reported in the following table.

Entry	IMes·HCl (mmol)	Cu powder (mmol)	Milling Load (mg/mL)	O_2 (µmol)	O_2 (eq)	Vf (mL)	Time (h)		NMR conv. (%)	Yield[a] (%)
							T_1	T_2		
1	0.254	1.270	19.4	80.8	1.27	8.64	-	6	100	83
2	0.317	1.586	24.2	80.6	1.02	8.62	7	-	70	55
3	0.317	1.586	24.2	80.6	1.02		7	6	67	60
4	0.419	2.095	32.2	80.3	0.77	8.58	12	-	47	40
5	0.419	2.095	32.2	80.3	0.77		12	5	43	40
6	0.617	3.084	47.7	79.6	0.52	8.52	15	-	29	27
7	0.617	3.084	47.7	79.6	0.52		15	5	28	27
8	1.169	5.846	92.5	77.8	0.27	8.32	18	-	5	5
9	1.169	5.846	92.5	77.8	0.27		18	6	5	5
10	1.560	7.801	125.6	76.5	0.20	8.18	21	-	0	0
11	1.560	7.801	125.6	76.5	0.20		21	9	0	0

[a] Yields were calculated by using the isolated yield of the crude product and the NMR conversion.

The equivalents of O_2, corresponding to the O_2/IMes·HCl ratio, was determined based on the following oxido-reduction reaction leading to the formation of Cu(I) from Cu(0) and O_2:

$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O$$

$$Cu \longrightarrow Cu^+ + e^-$$

$$\Longrightarrow O_2 + 4Cu + 4H^+ \longrightarrow 4Cu^+ + 2H_2O$$

One molecule of dioxygen oxidize four copper atoms and one IMes·HCl molecule reacts with one copper atom. Then, only 0.25 eq of dioxygen should be necessary to obtain complete conversion of IMes·HCl. In other words, $n_{dioxygen} = 0.25\ n_{IMes\cdot HCl}$

The moles of dioxygen present in the bowl was calculated as follows:
$n_{dioxygen} = V_{dioxygen} / 22.414$
and $V_{dioxygen} = 0.2095\ V_f$
where V_f: free volume

V_f was calculated using the following equation:

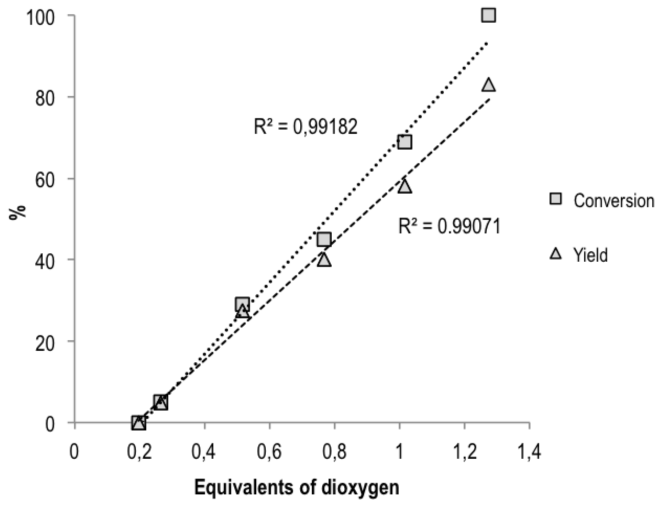
$$V_f = V_t - n_b * V_b - \sum V_{reagent}$$

where
V_t: total volume of the bowl
n_b: number of balls
V_b: volume of one ball
$V_{reagent}$: reagent volume

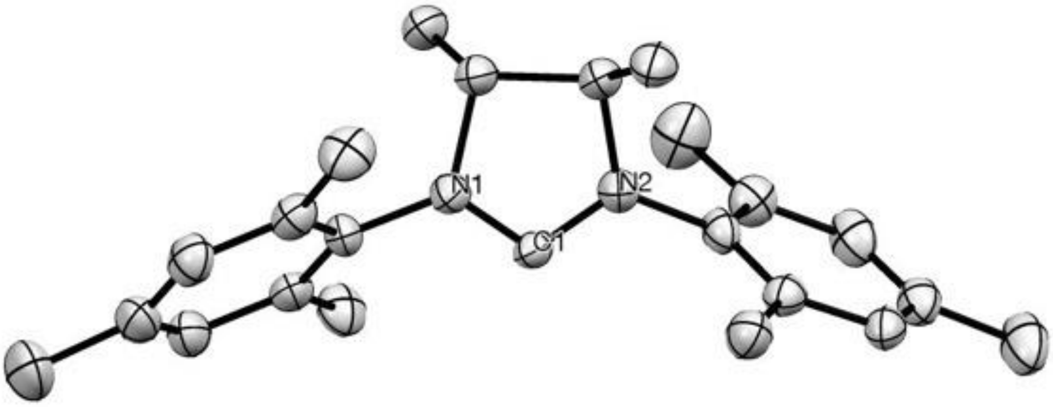
$V_{reagent}$ was calculated based on the mass of the reactants introduced in the bowl and on their density. Density of IMes·HCl was calculated as being 1.09 g.mL^{-1}, SIMes·HCl as being 1.07 g.mL^{-1}, IPr·HCl as being 0.954 g.mL^{-1} and SIPr·HCl as being 0.997 g.mL^{-1}. Density of copper powder is 8.94 g.mL^{-1}. M (IMes·HCl) = 340.89 g.moL^{-1}. M (Cu) = 63.55 g.moL^{-1}.

As an example, for the first entry: $V_f = 12 - 50 * 0.0654 - (\frac{0.0807}{8.94} + \frac{0.0866}{1.09})$ = 8.64 mL
and $n_{dioxygen}$ = 0.2095 x 0.00864 / 22.414 = 80.9 µmol

$$4\ \text{IMes}\cdot\text{HCl} + 4\ \text{Cu(0)} + \text{O}_2 \xrightarrow[\text{pbm, 450 rpm}]{} 4\ [\text{CuCl(IMes)}] + 2\ \text{H}_2\text{O}$$



3. X-Ray data



X-Ray diffraction of SIMes^{Me}·HCl (CCDC 1487556) indicating the trans configuration.

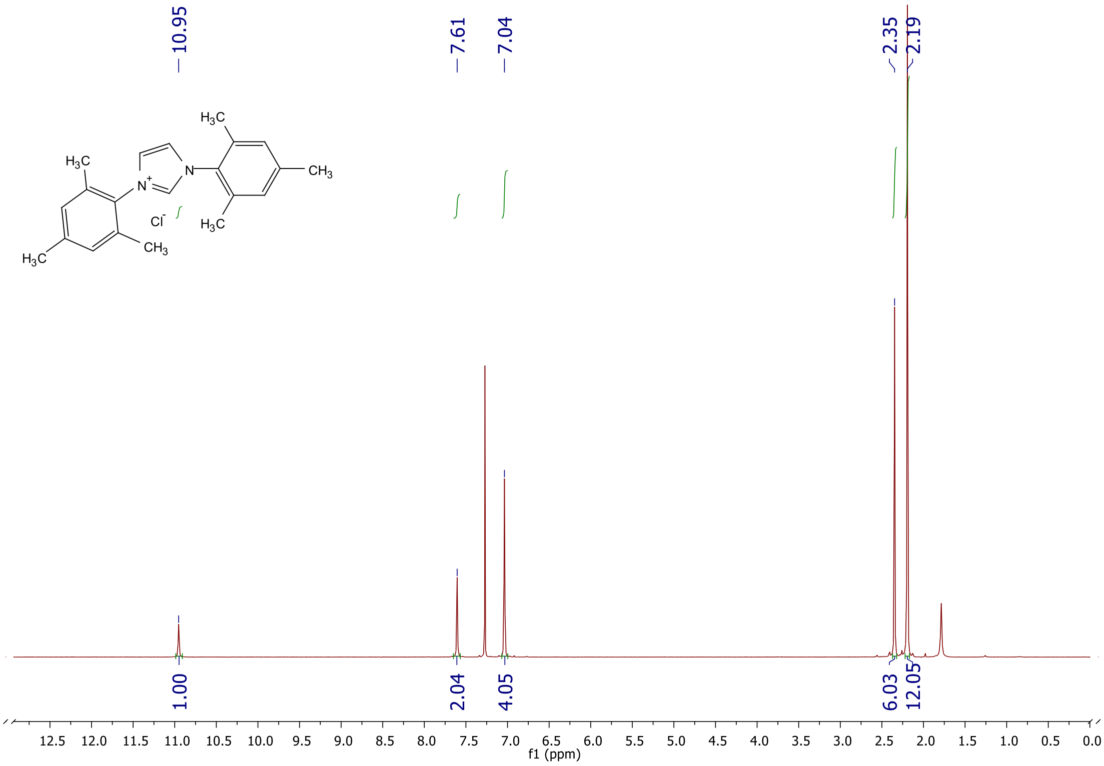
	SIMes^{Me}·HCl
Formula	$C_{23}H_{31}ClN_2$
M / g.mol^{-1}	370.95
Crystal system	Monoclinic
Space group	P 21/n
a / Å	8.9790 (3)
b / Å	15.1223 (5)
c / Å	15.7117 (8)
α / Å	90
β / Å	100.137 (4)
γ / Å	90
V (Å^3)	2100.08 (11)
Z	4
ρ_{calcd} / g.cm^{-3}	1.173
μ (Mo Kα) / mm^{-1}	1.652
T / K	175
Number of reflections	4293
Number of unique reflections	1954
R_{int}	0.104
*R*1, w*R*2 (I > 2σ(I))	0.0678, 0.0709
*R*1, w*R*2 (all data)	0.0751, 0.0720
GOF	1.0291

4. NMR Spectra

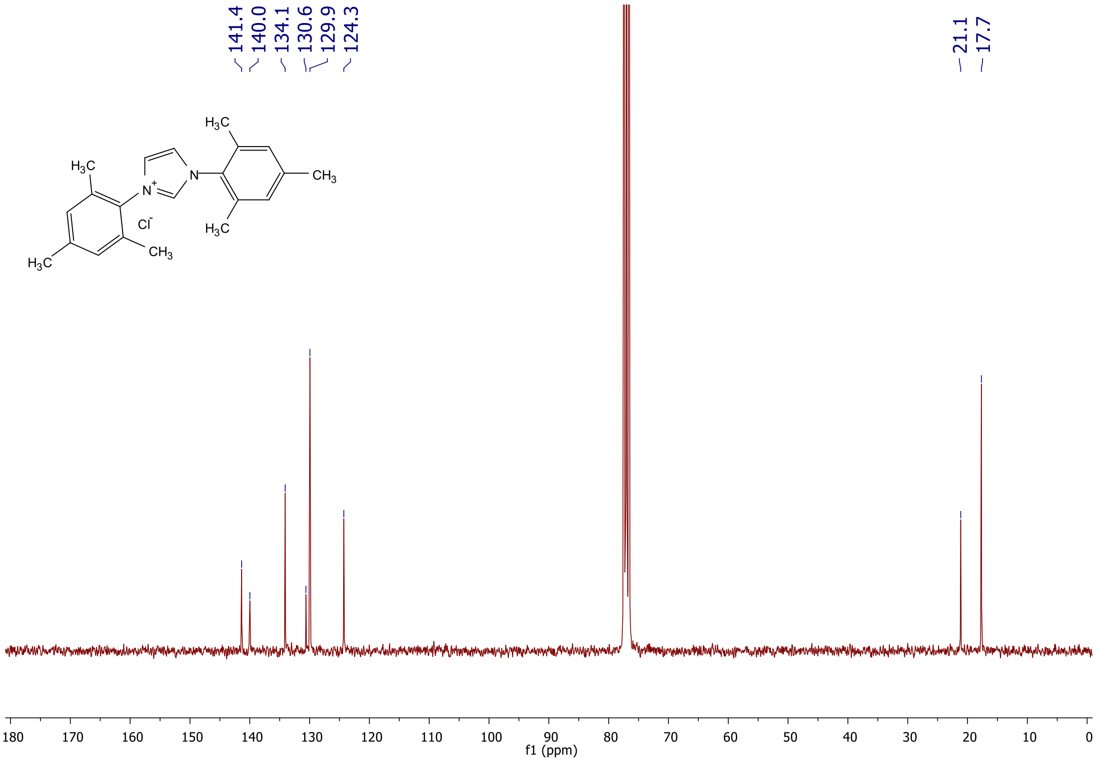
4.1 Imidazolium salts

1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride IMes·HCl

^{1}H NMR (300MHz, $CDCl_3$)

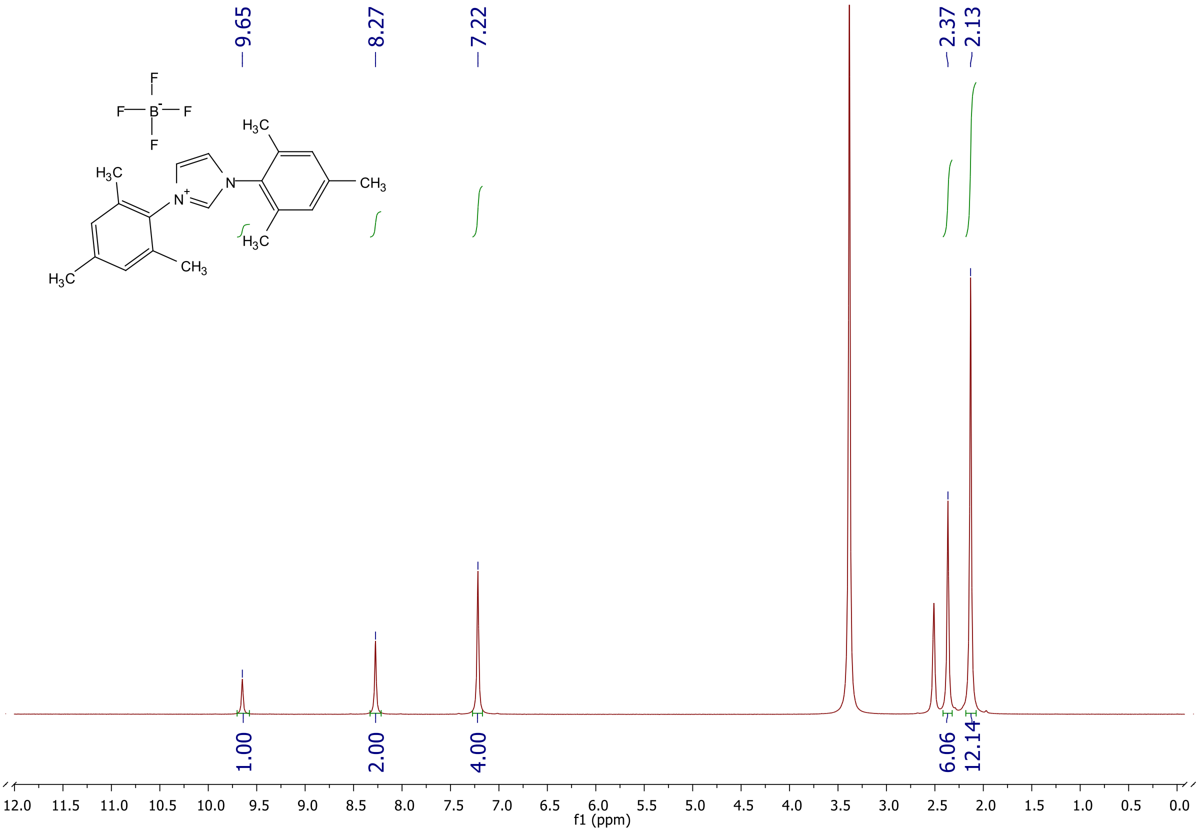


^{13}C NMR (75 MHz, $CDCl_3$)

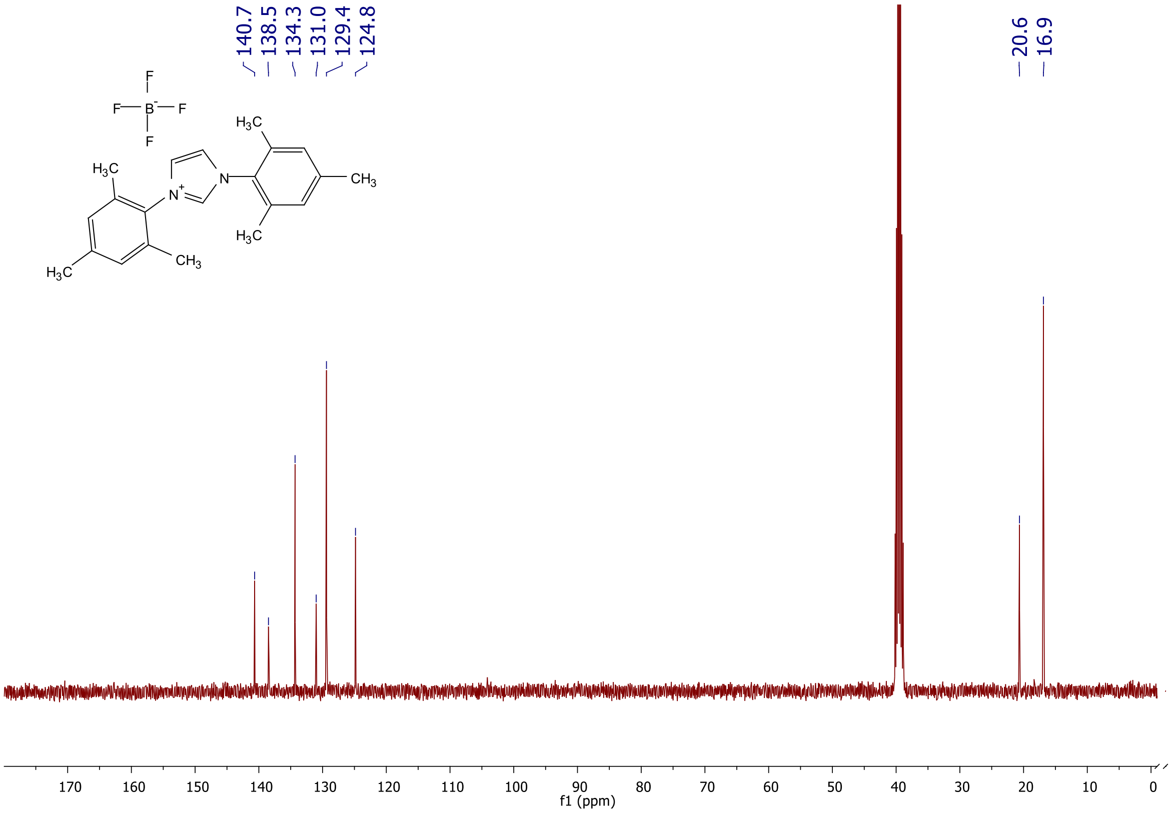


1,3-Bis-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate IMes·HBF_4

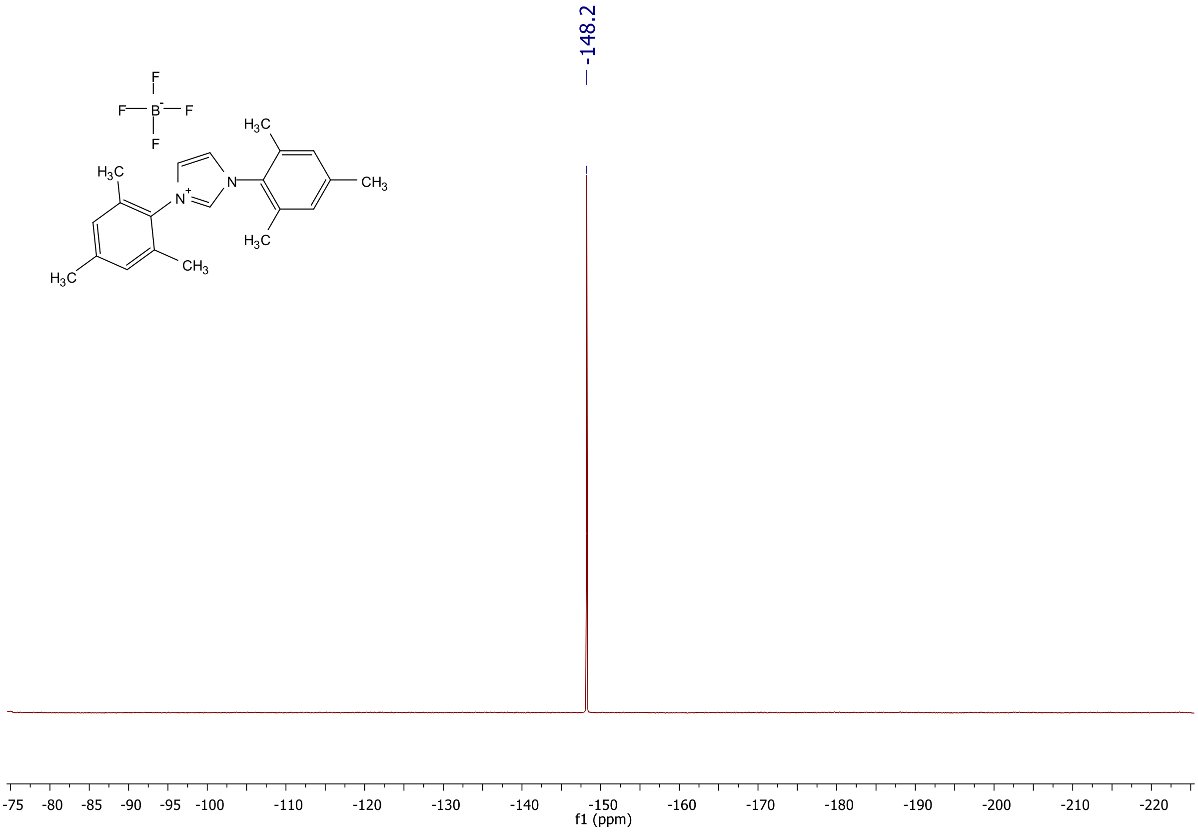
^1H NMR (400MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

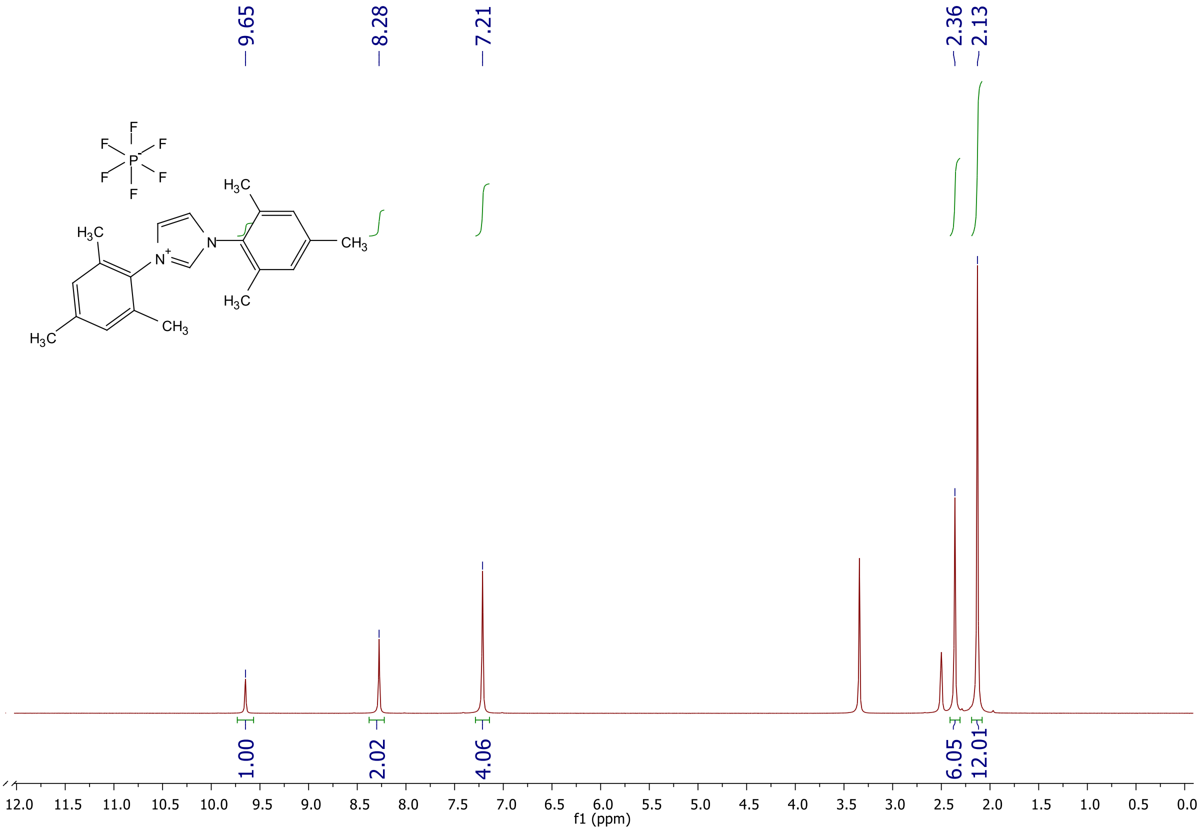


^{19}F NMR (376 MHz, DMSO-d_6)

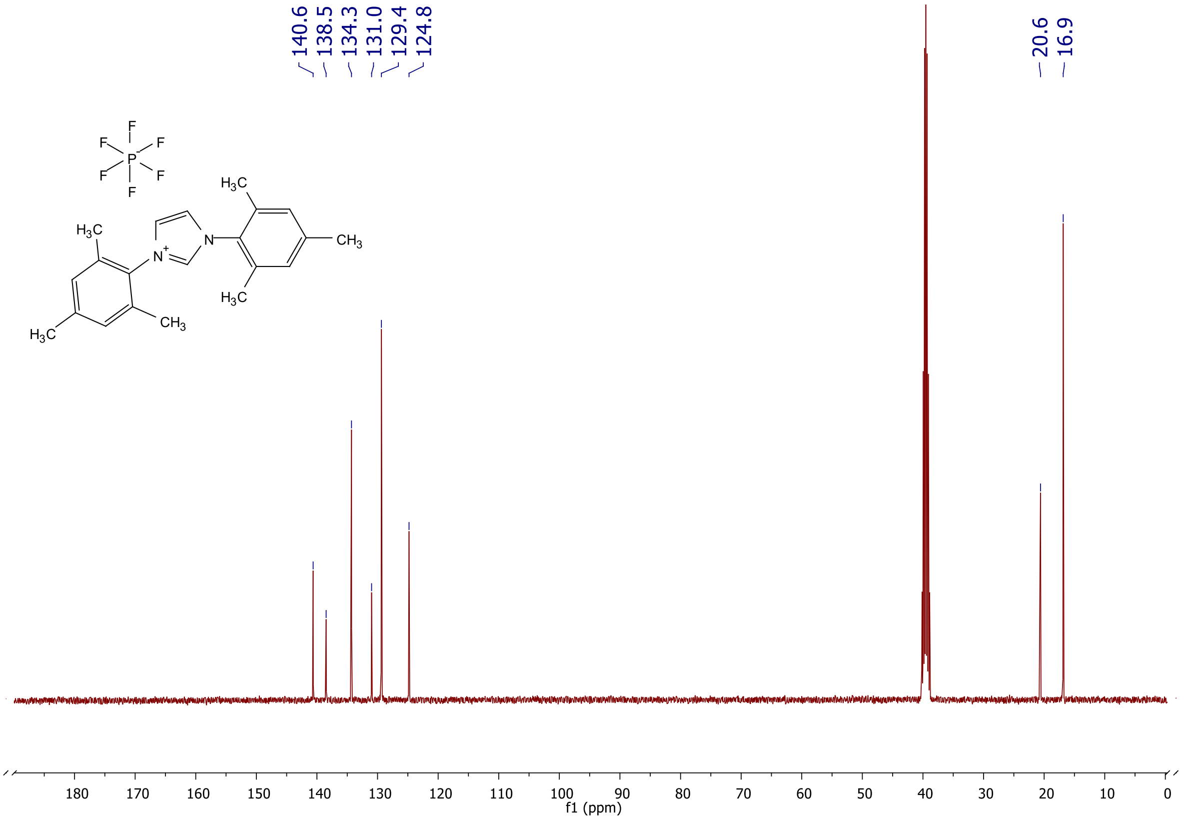


1,3-Bis-(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate IMes·HPF_6

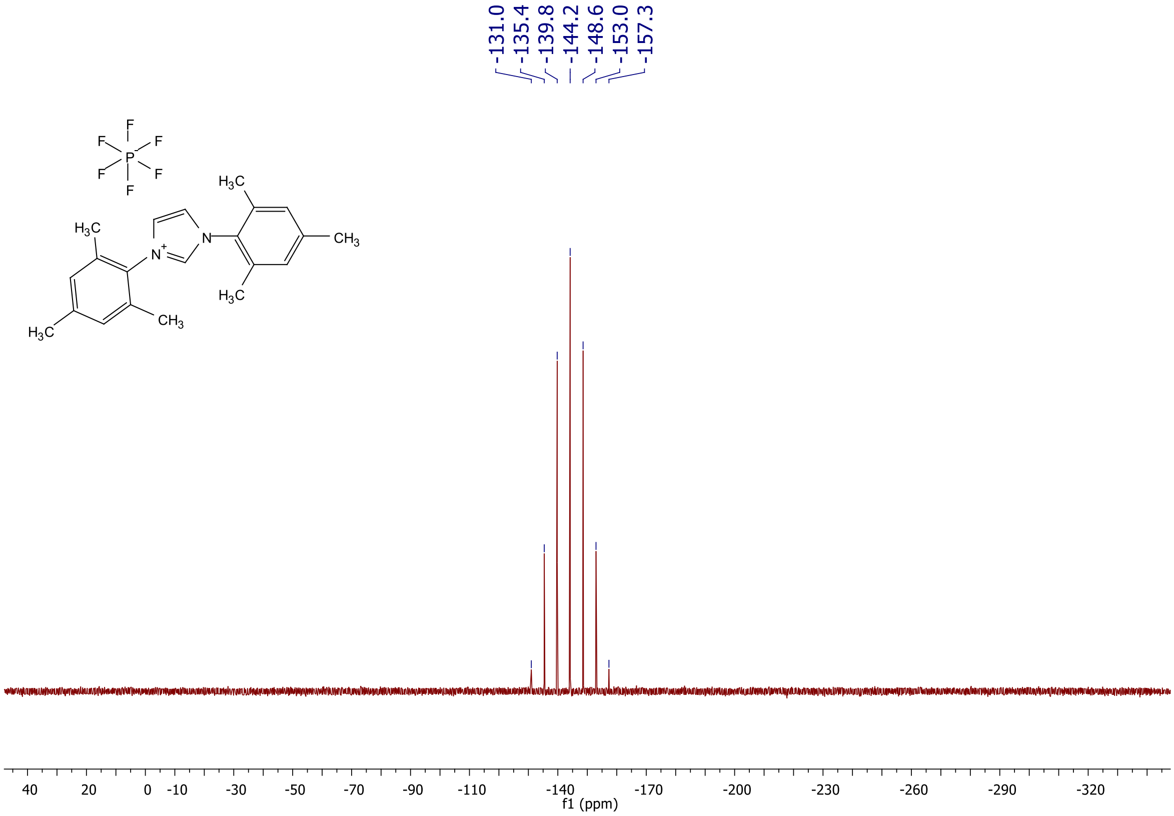
^1H NMR (400MHz, DMSO-d_6)



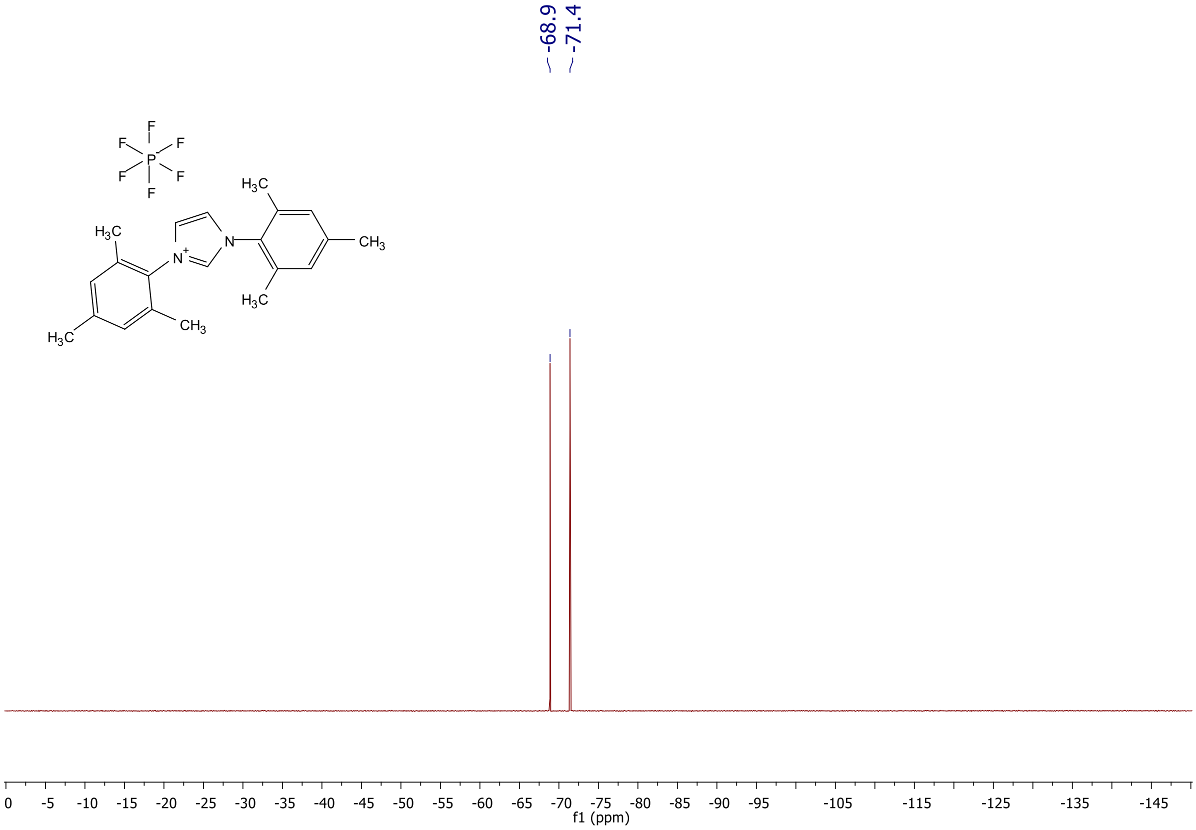
^{13}C NMR (101 MHz, DMSO-d_6)



^{31}P NMR (162 MHz, DMSO-d_6)

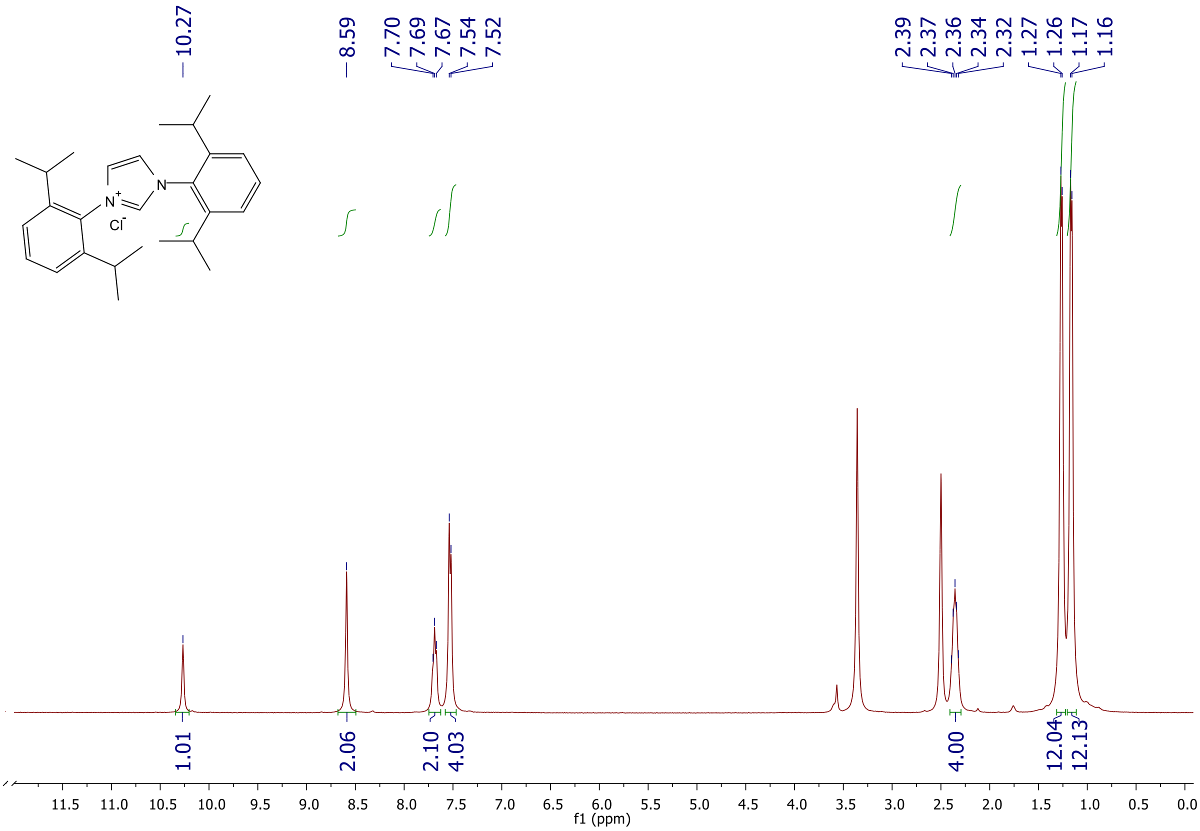


^{19}F NMR (376 MHz, DMSO-d_6)

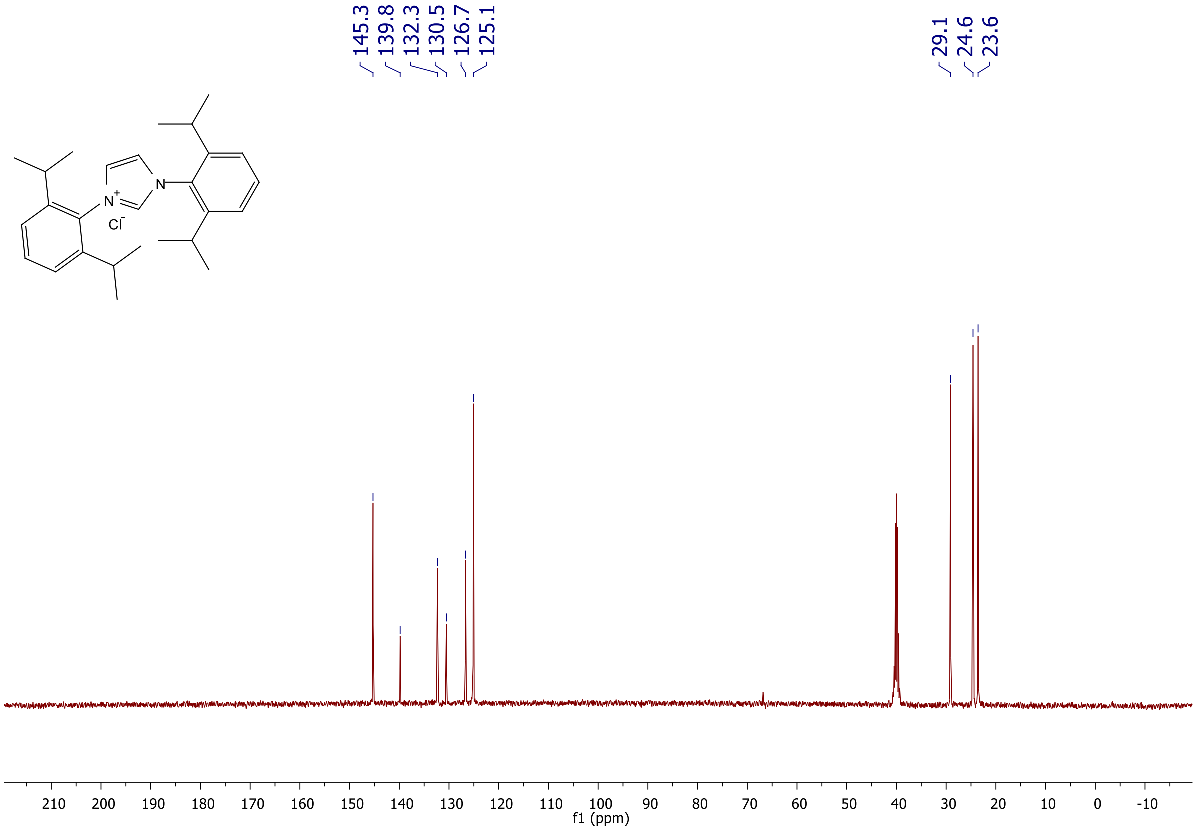


1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium chloride IPr·HCl

^{1}H NMR (400MHz, $CDCl_3$)

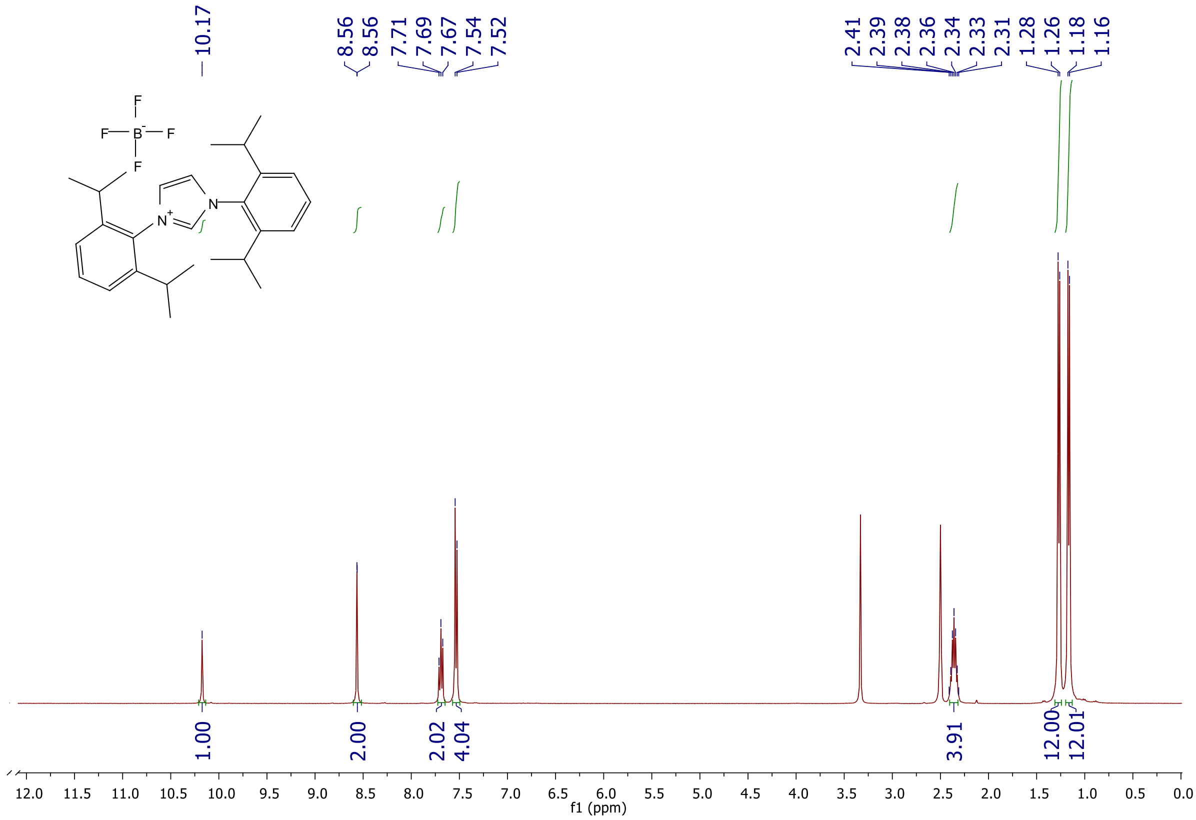


^{13}C NMR (75 MHz, $CDCl_3$)

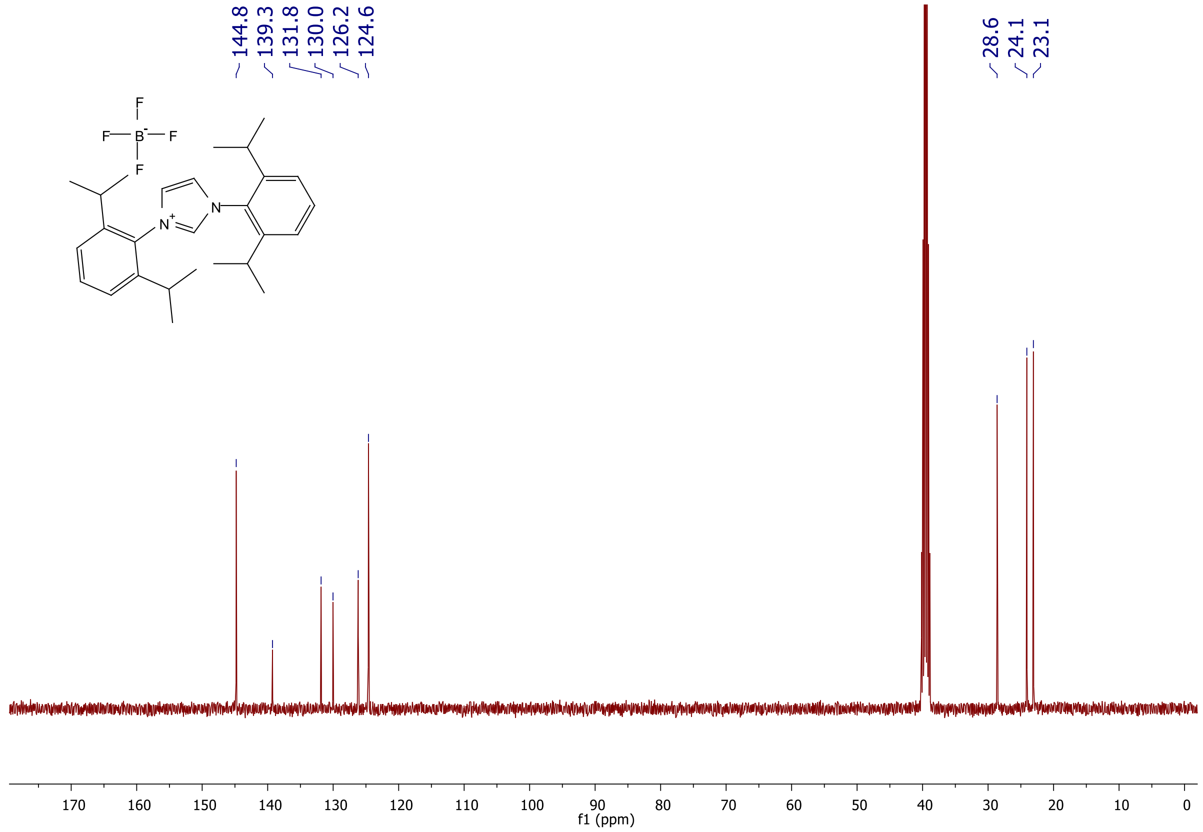


1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium tetrafluoroborate IPr·HBF$_4$

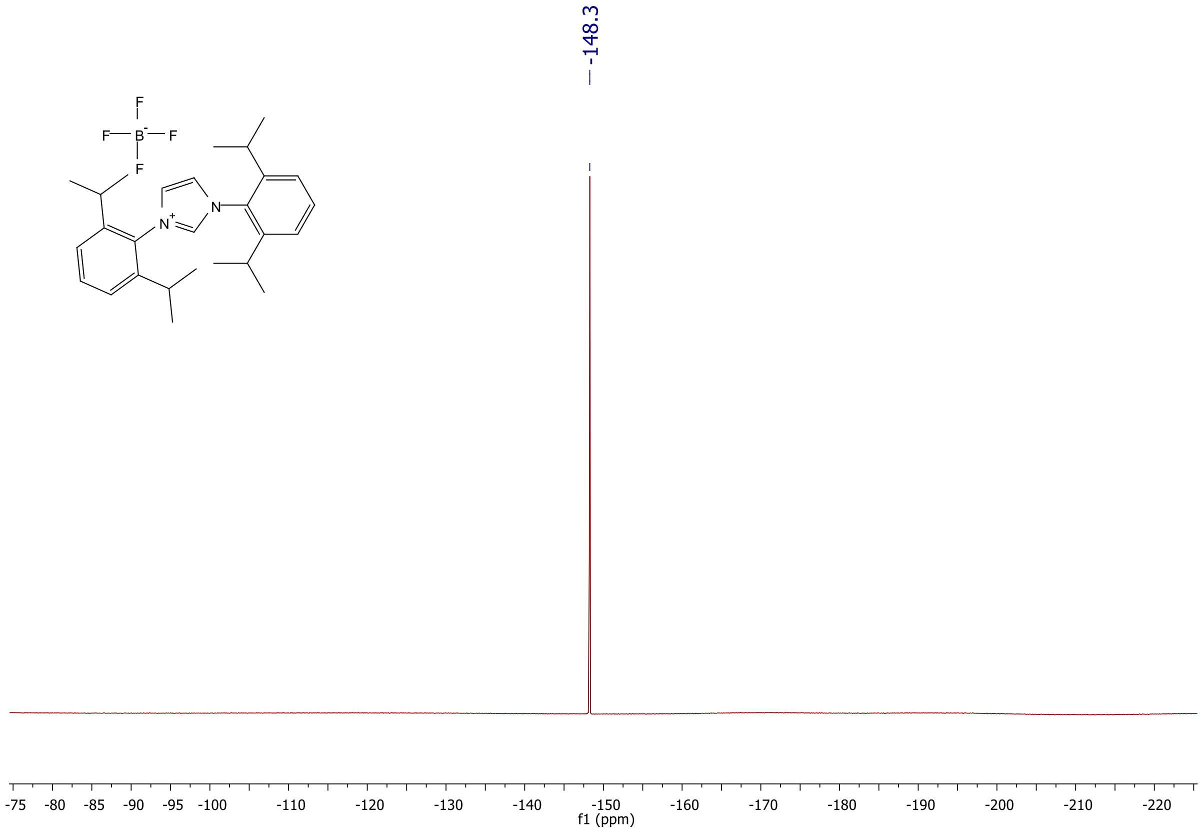
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

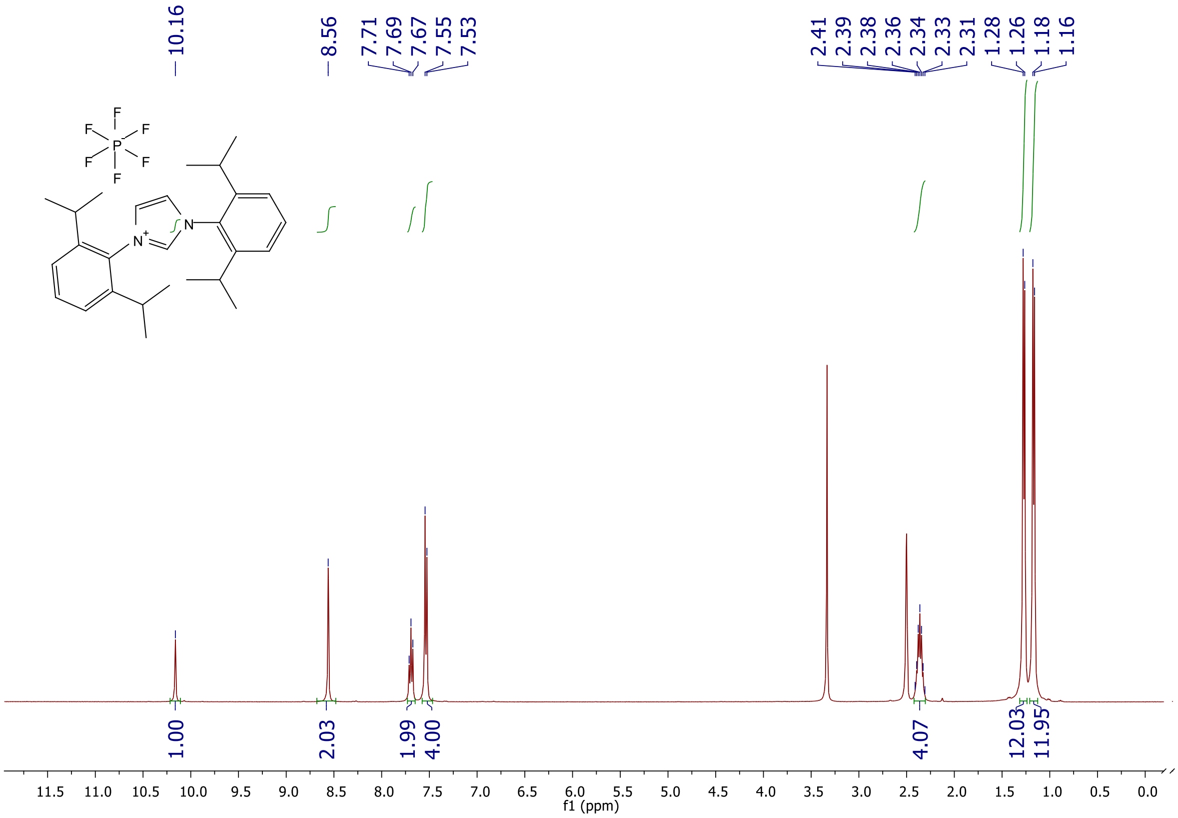


^{19}F NMR (376 MHz, DMSO-d_6)

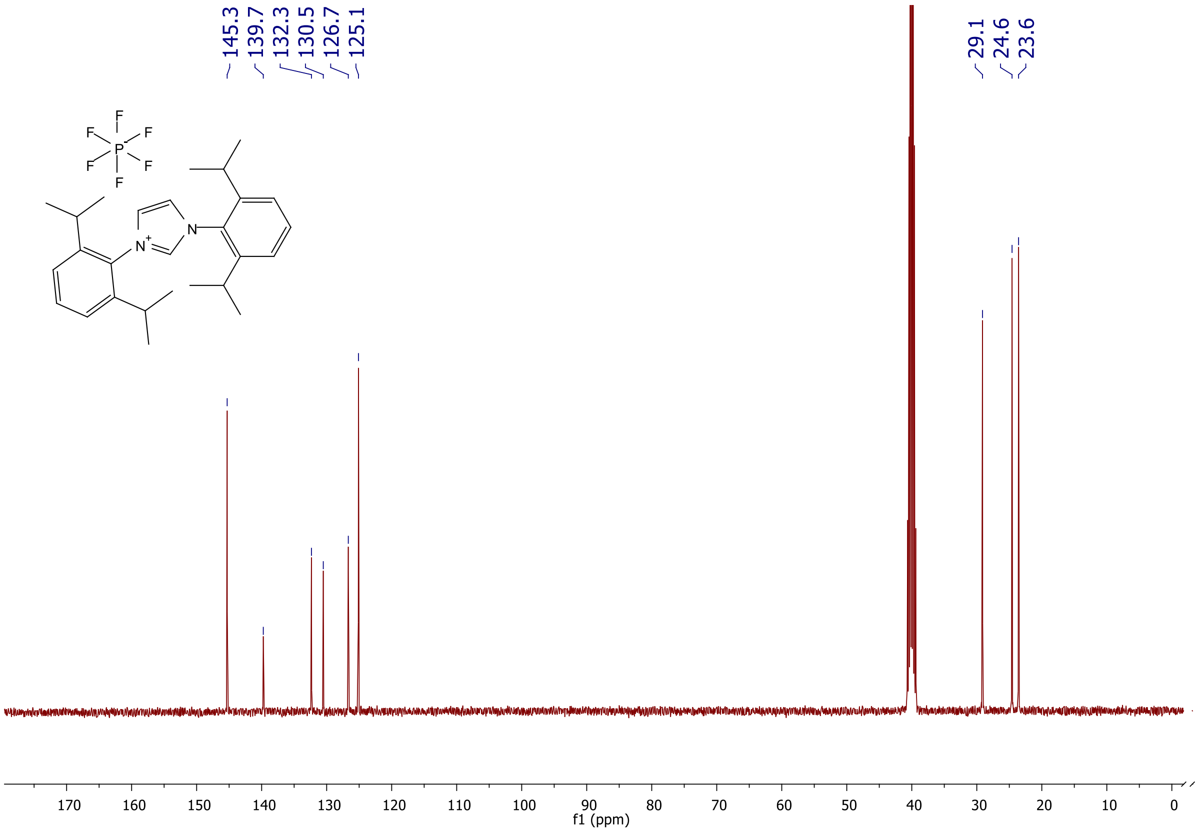


1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium hexafluorophosphate IPr·HPF_6

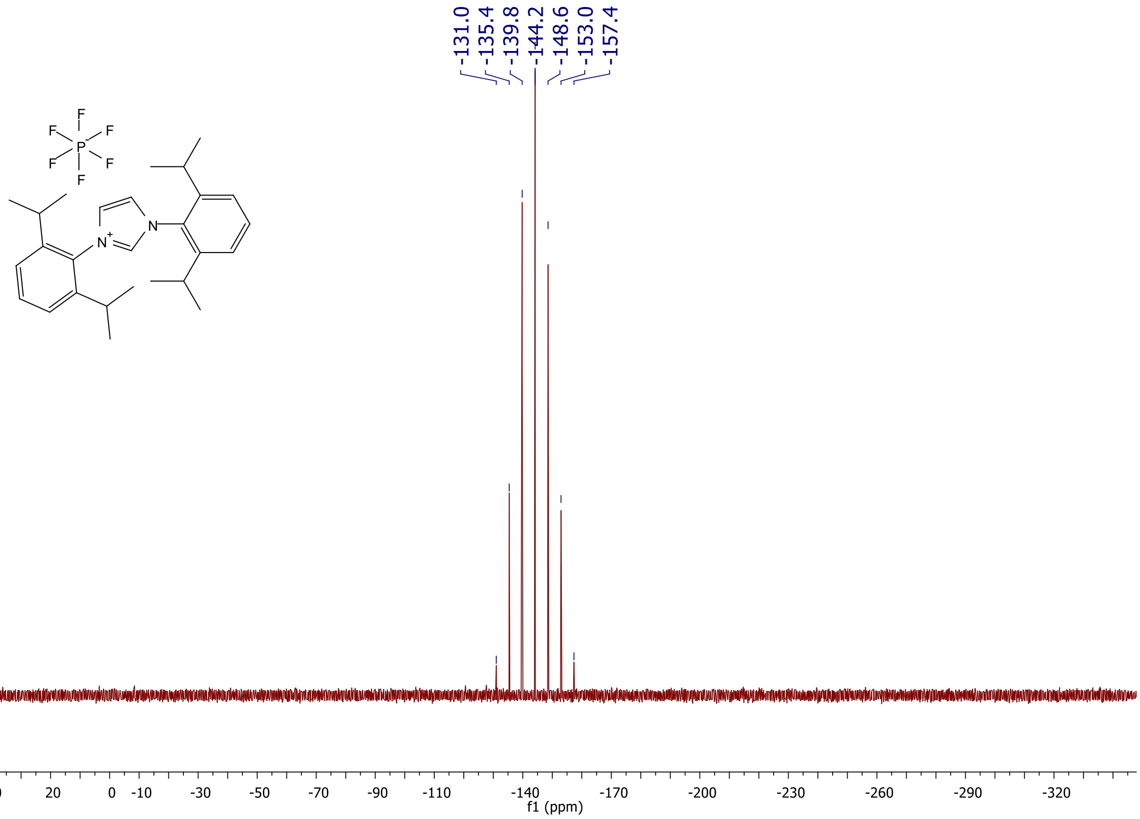
^{1}H NMR (400MHz, DMSO-d_6)



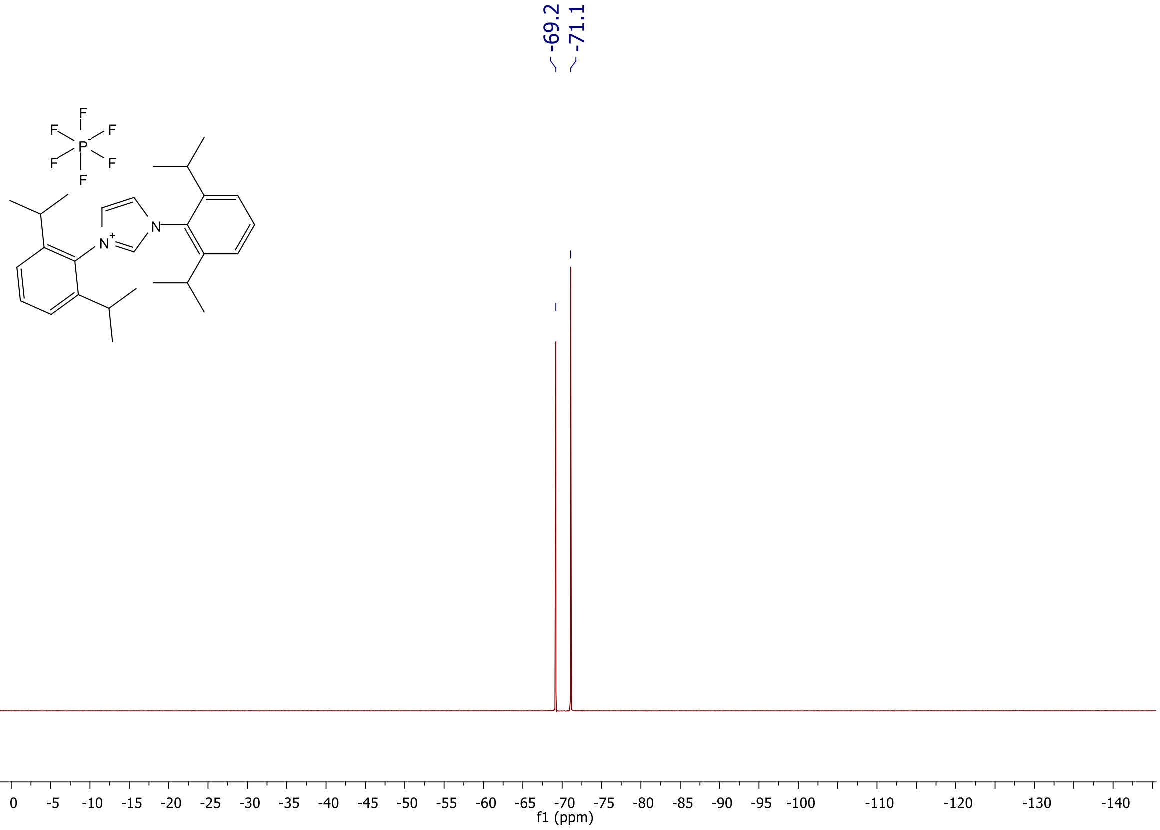
^{13}C NMR (101 MHz, DMSO-d_6)



^{31}P NMR (162 MHz, DMSO-d_6)

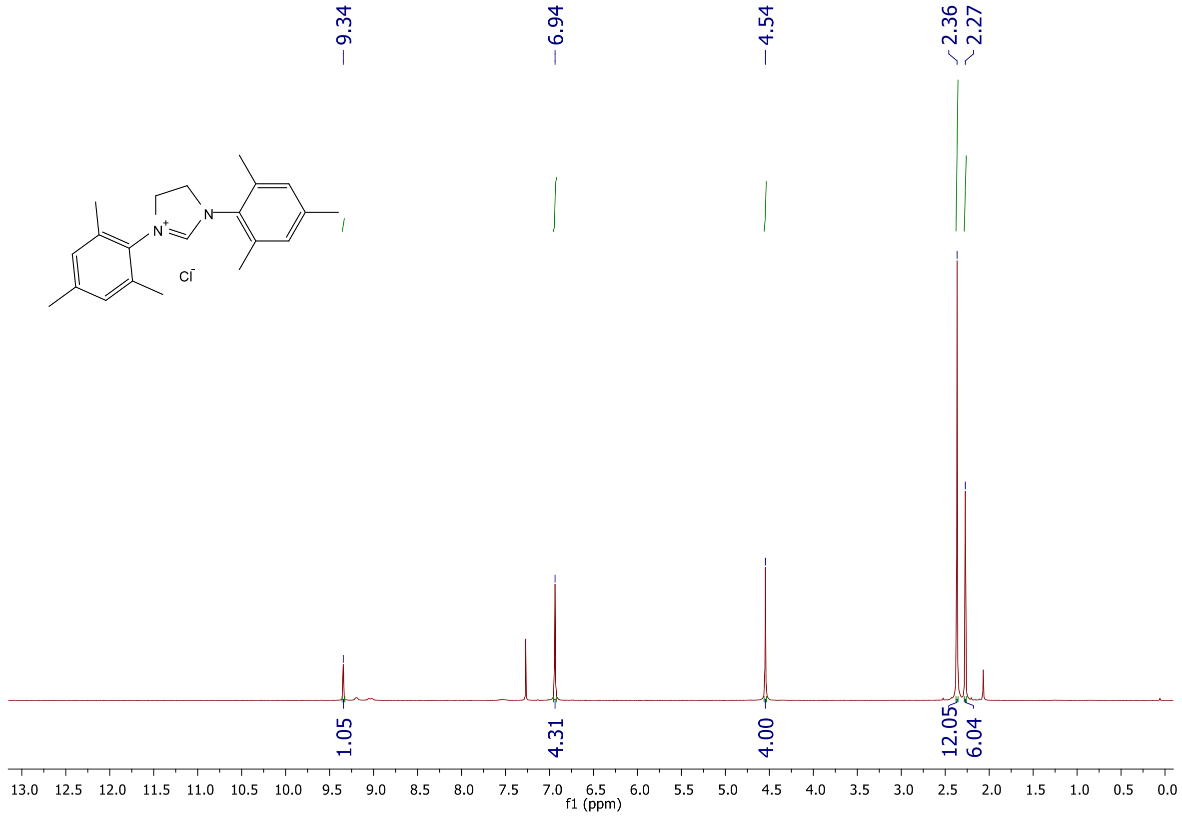


^{19}F NMR (376 MHz, DMSO-d_6)

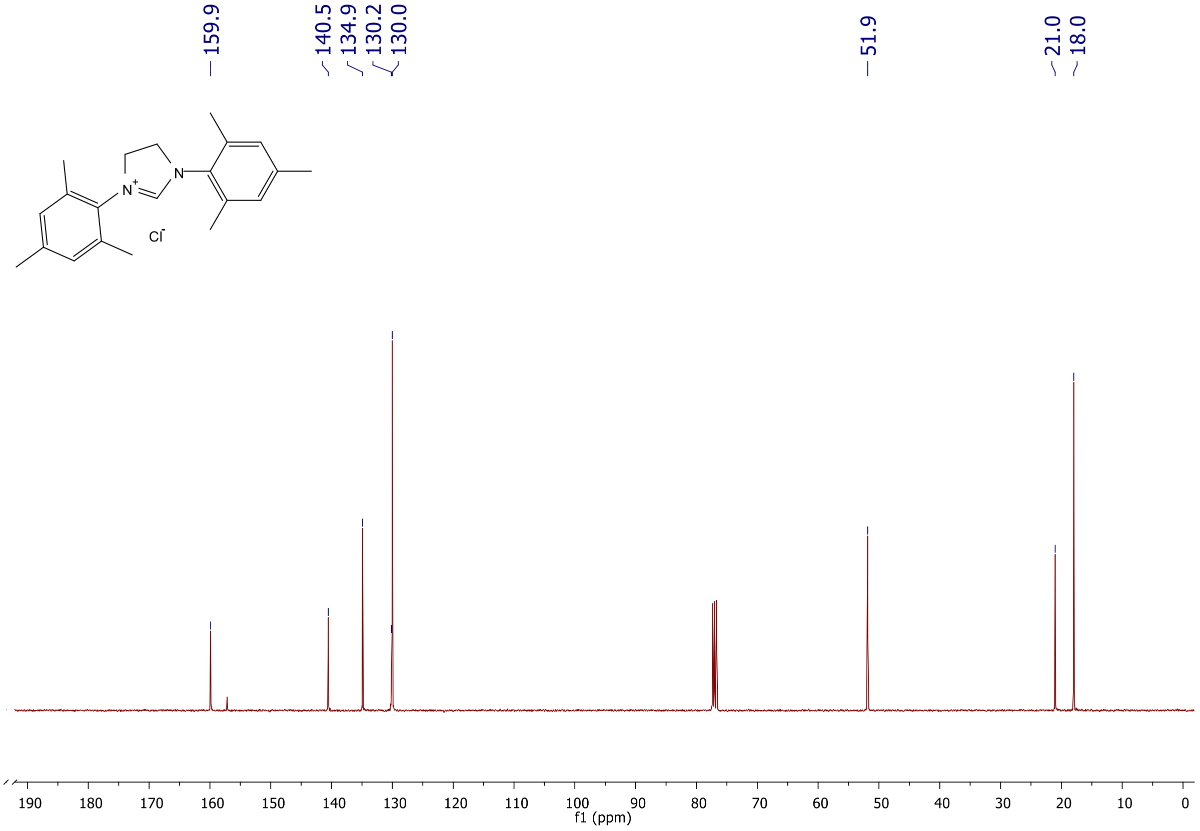


1,3-Dimesitylimidazolidinium chloride SIMes·HCl

^{1}H NMR (400MHz, $CDCl_3$)

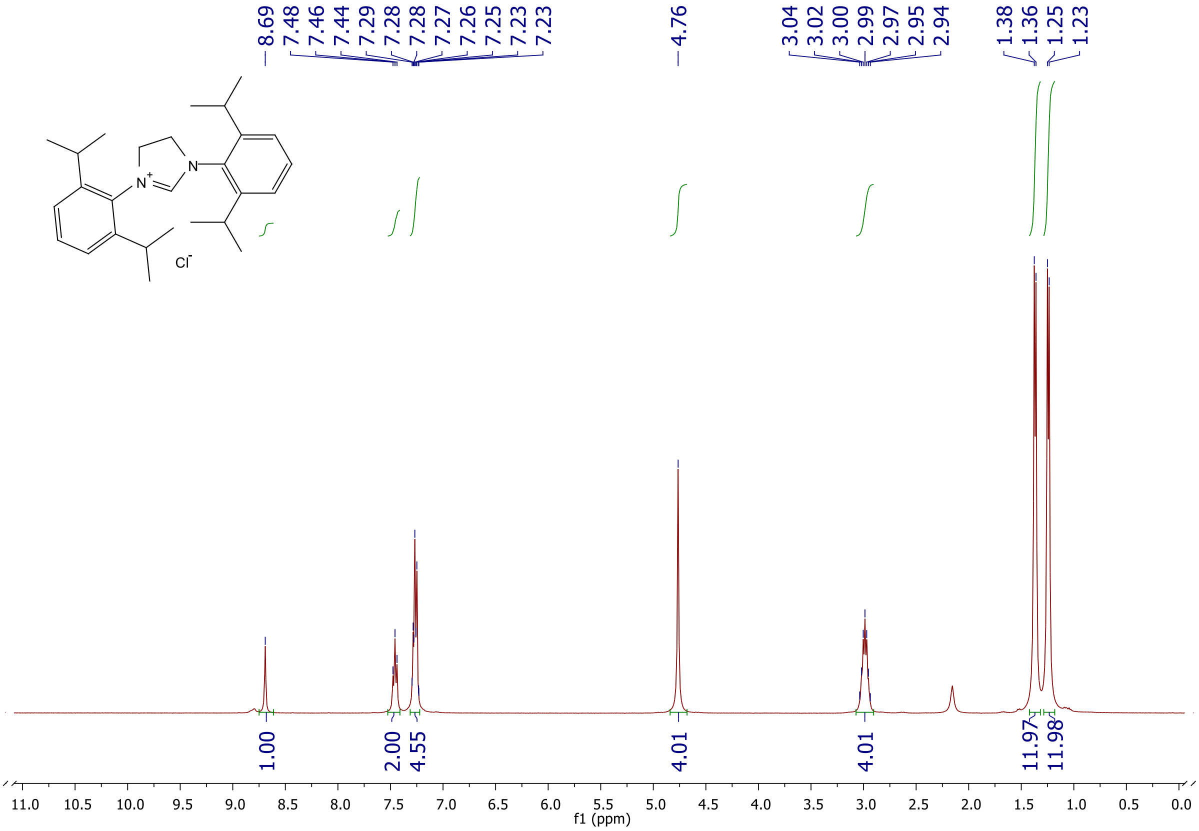


^{13}C NMR (101 MHz, $CDCl_3$)

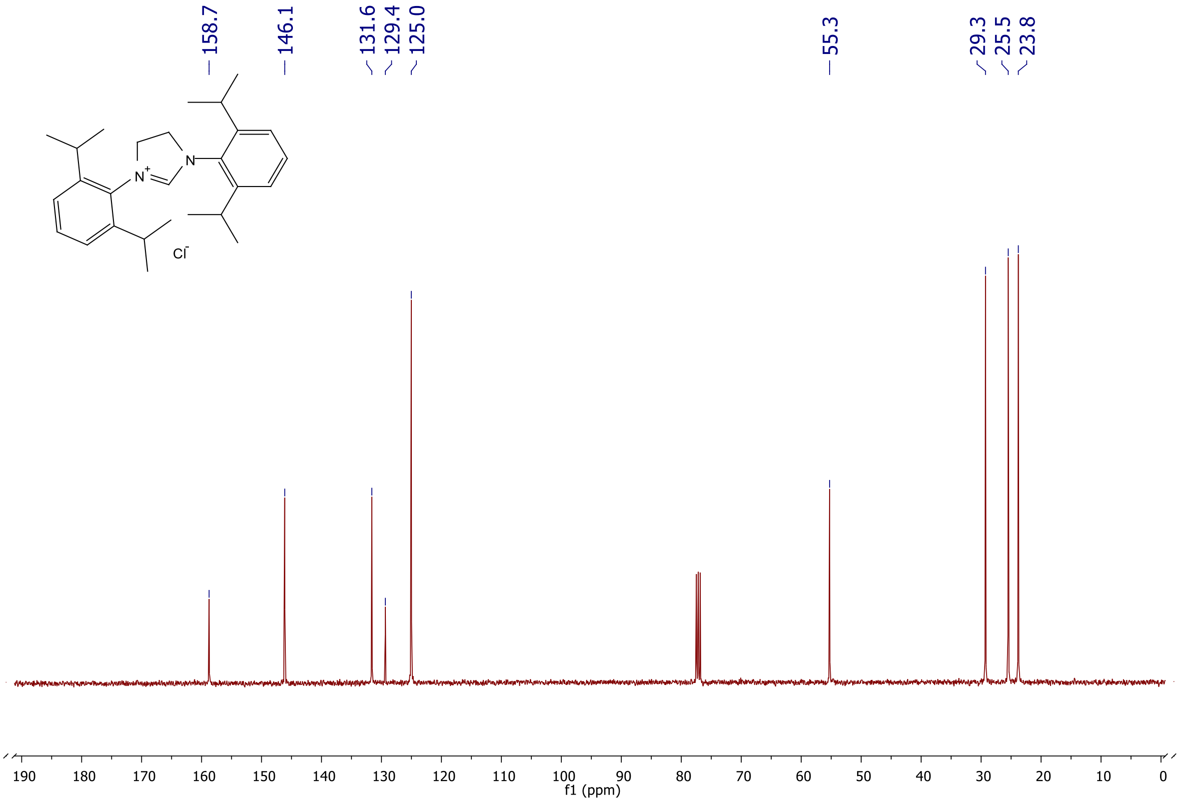


1,3-Bis(2,6-di*iso*propylphenyl)imidazolidinium chloride SIPr·HCl

^{1}H NMR (400MHz, $CDCl_3$)

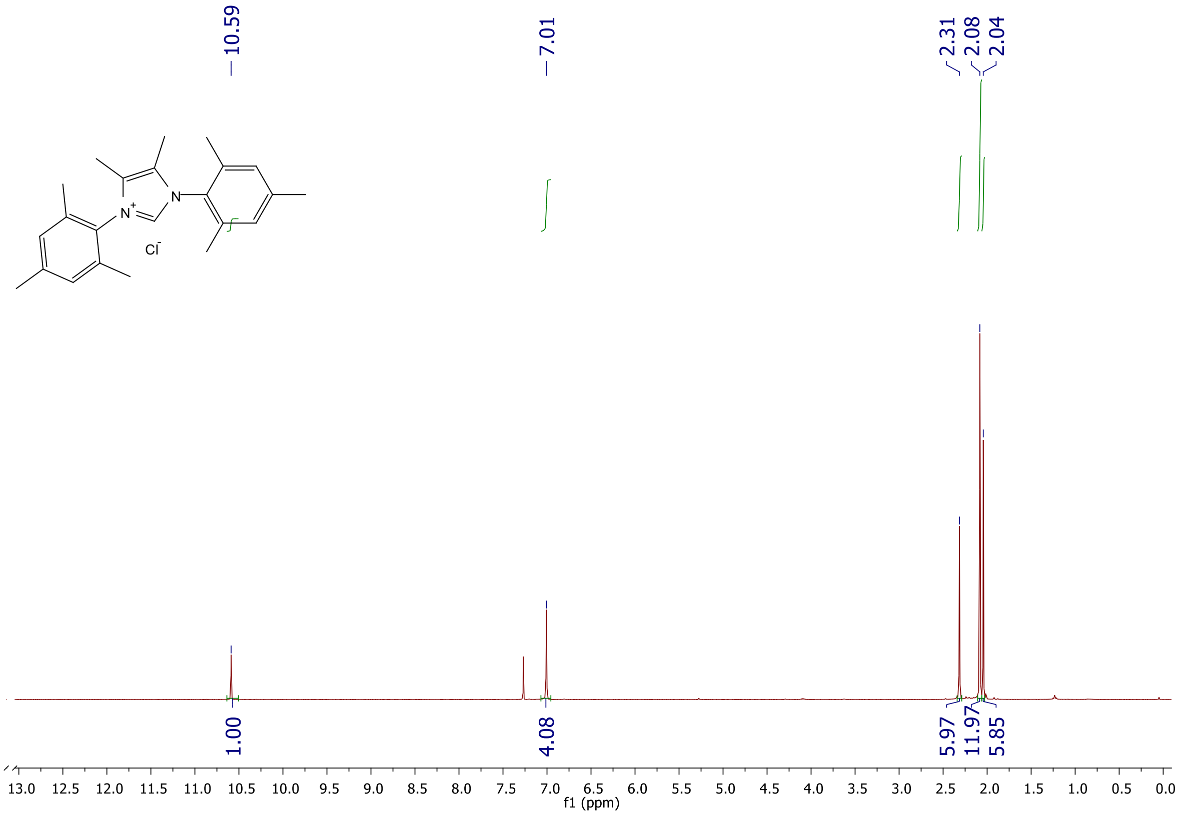


^{13}C NMR (101 MHz, $CDCl_3$)

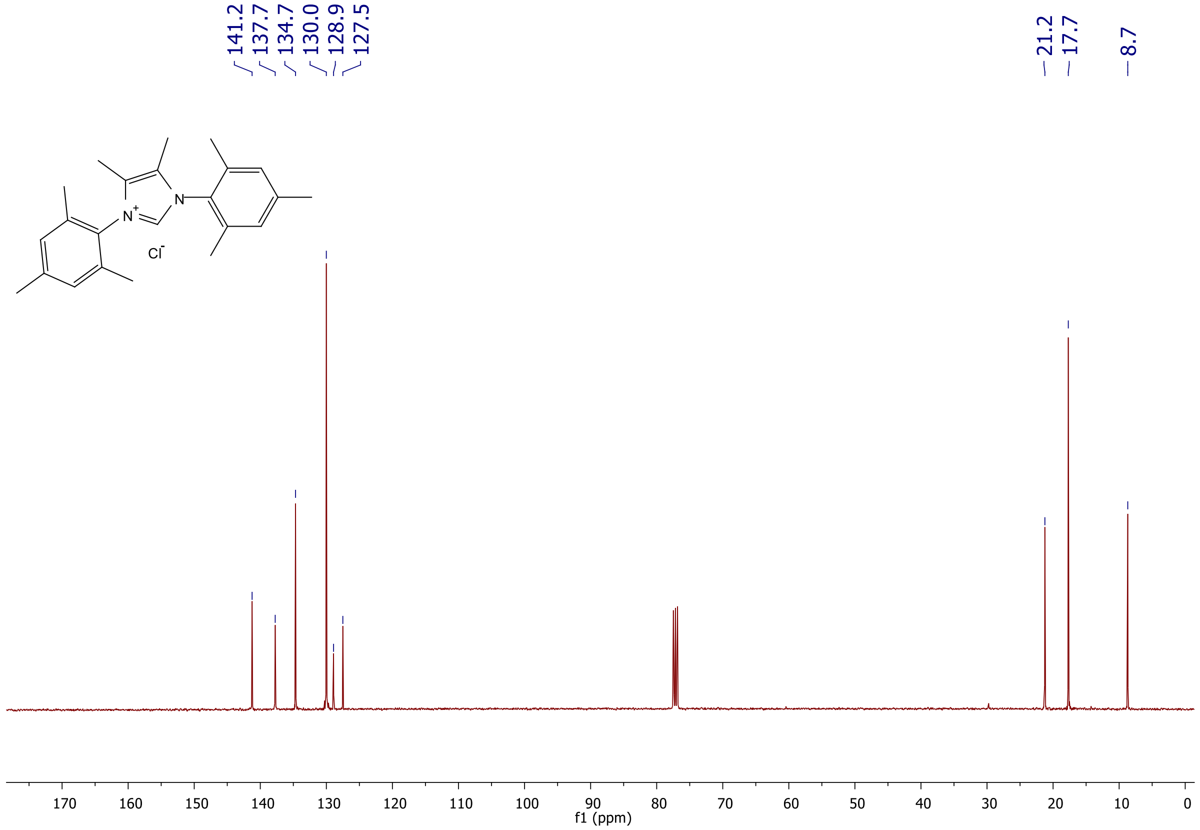


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride IMes^{Me}·HCl

^{1}H NMR (400MHz, CDCl$_3$)

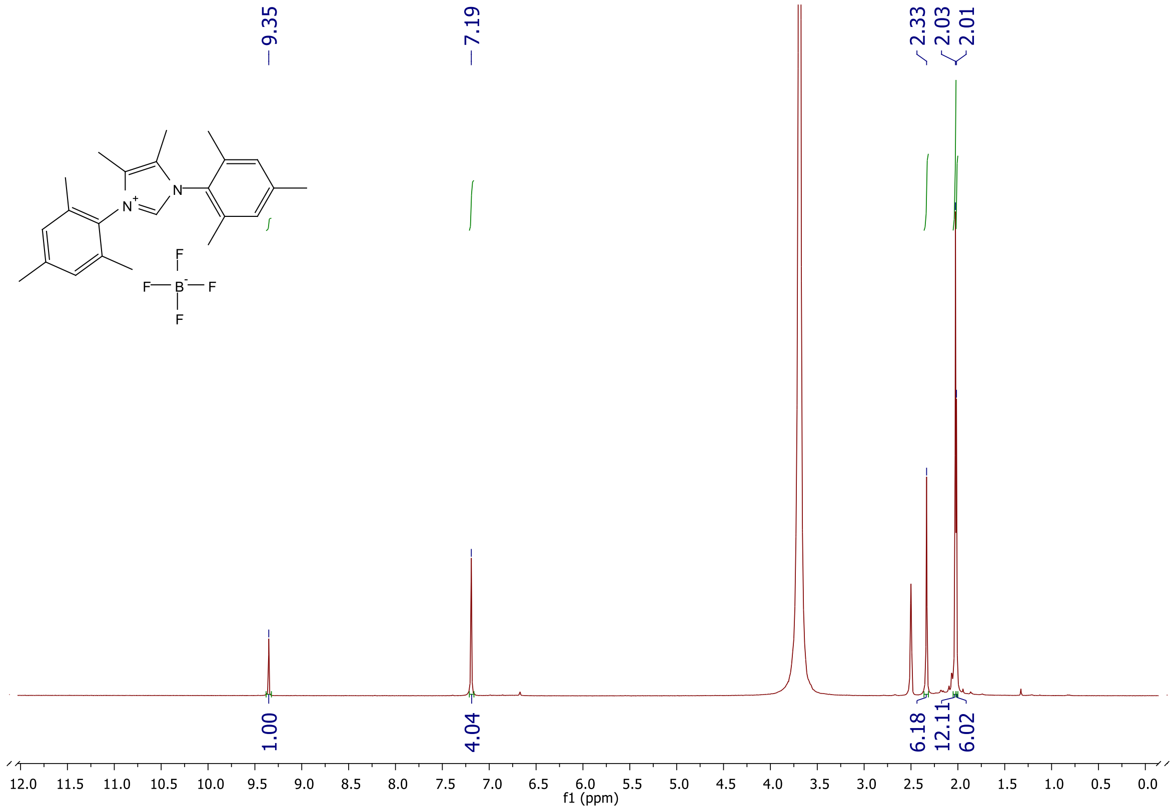


^{13}C NMR (101 MHz, CDCl$_3$)

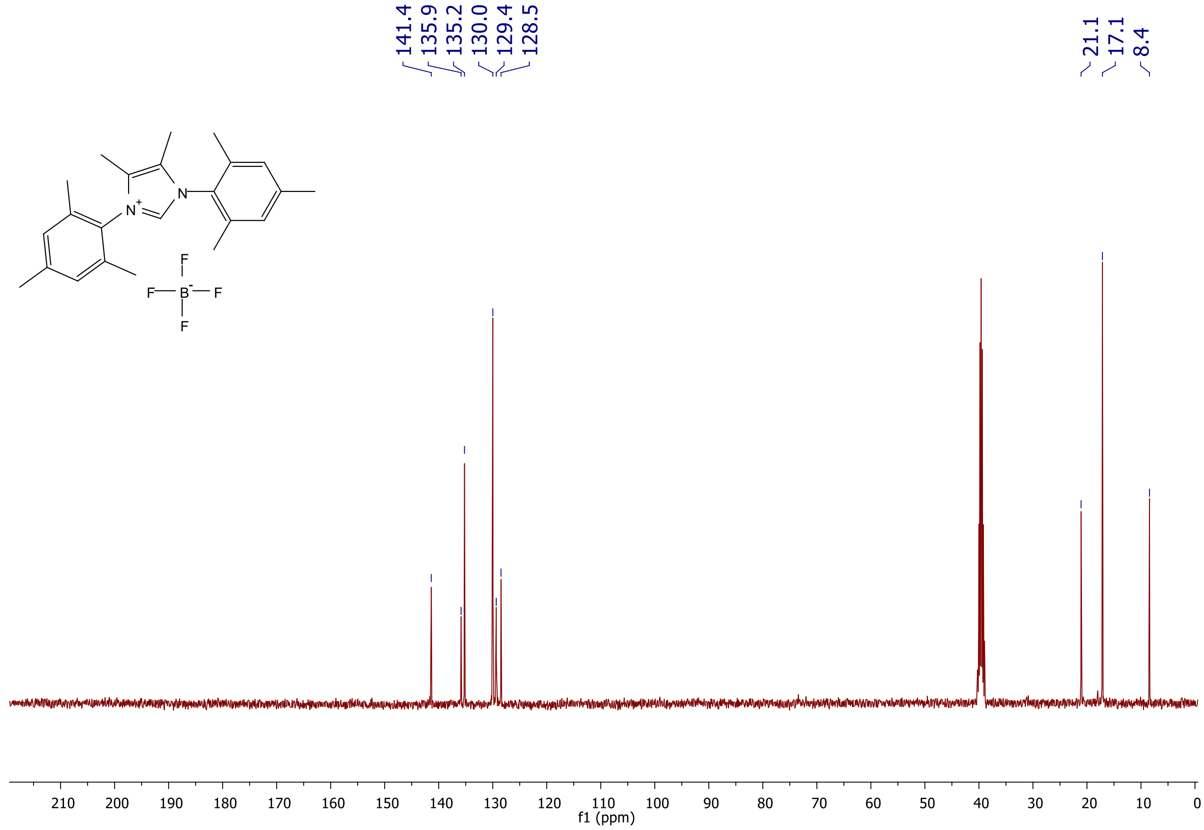


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium tetrafluoborate IMes^{Me}·HBF$_4$

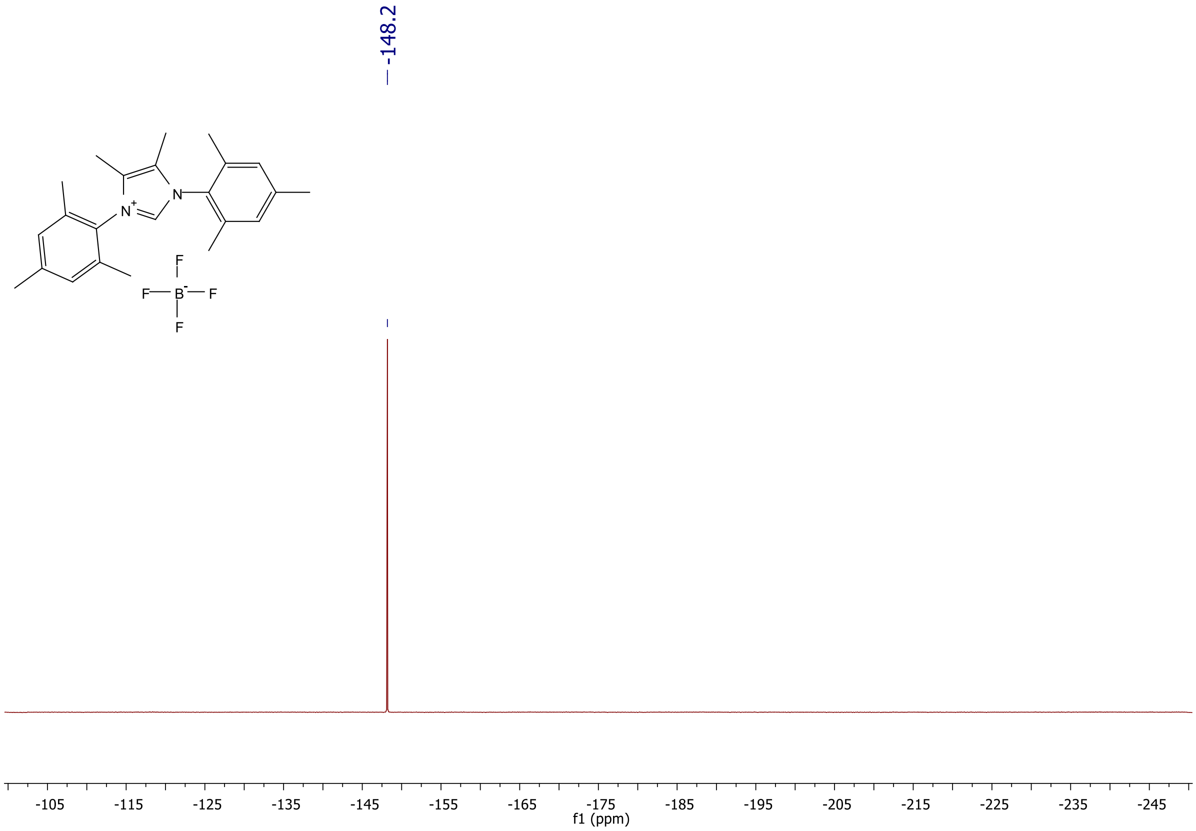
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

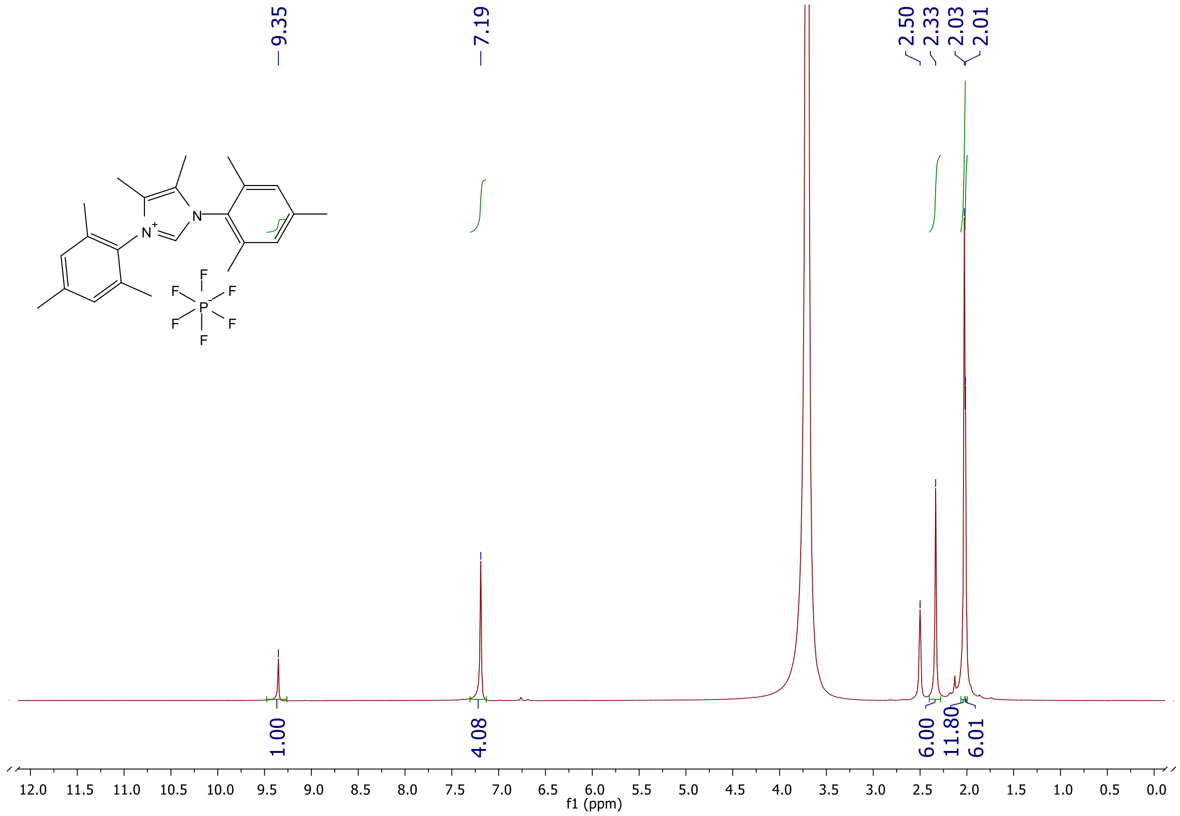


^{19}F NMR (376 MHz, DMSO-d_6)

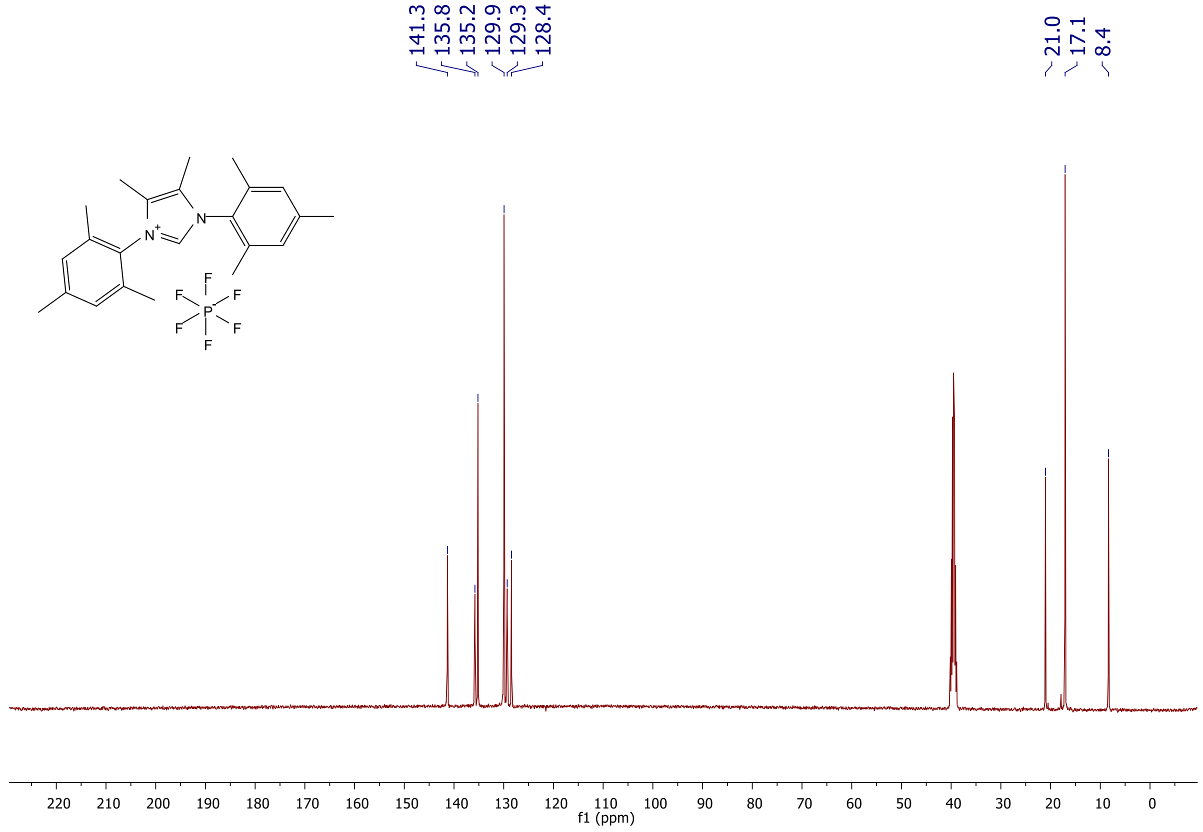


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate IMes^{Me}·HPF$_6$

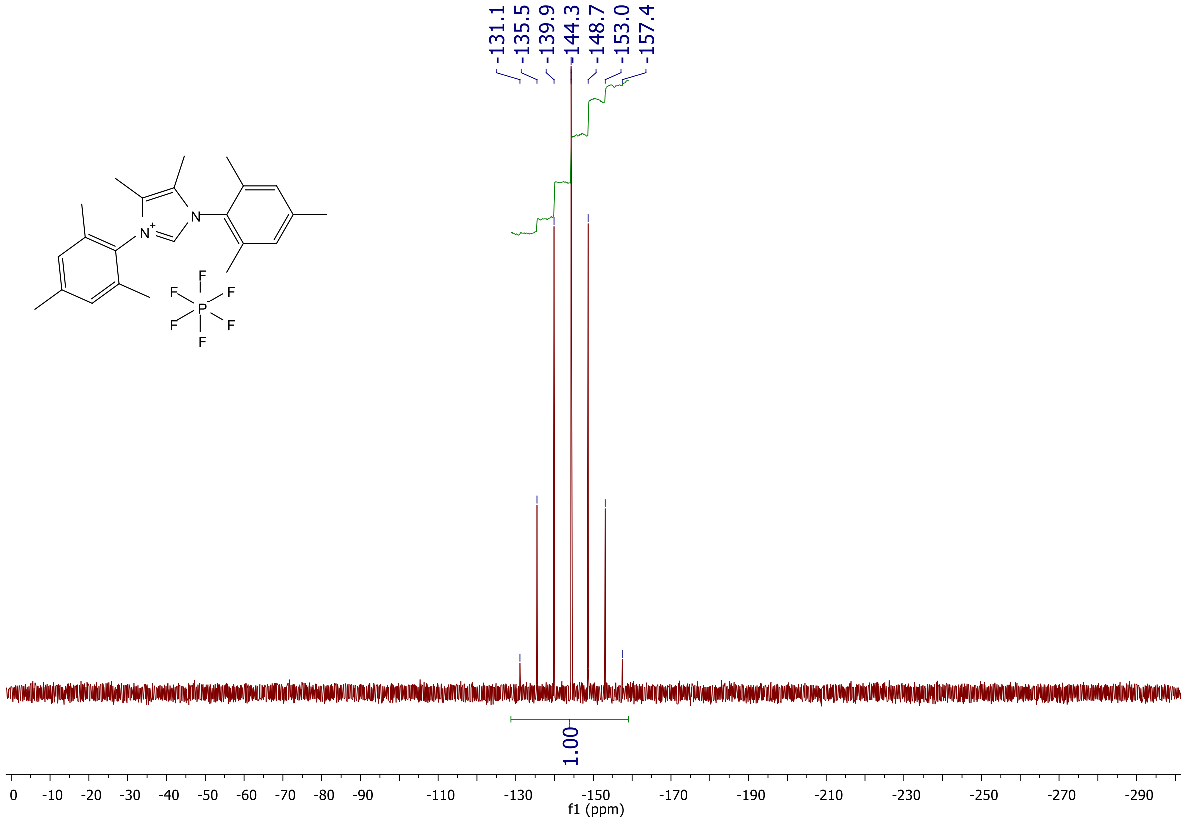
^{1}H NMR (400MHz, DMSO-*d$_6$*)



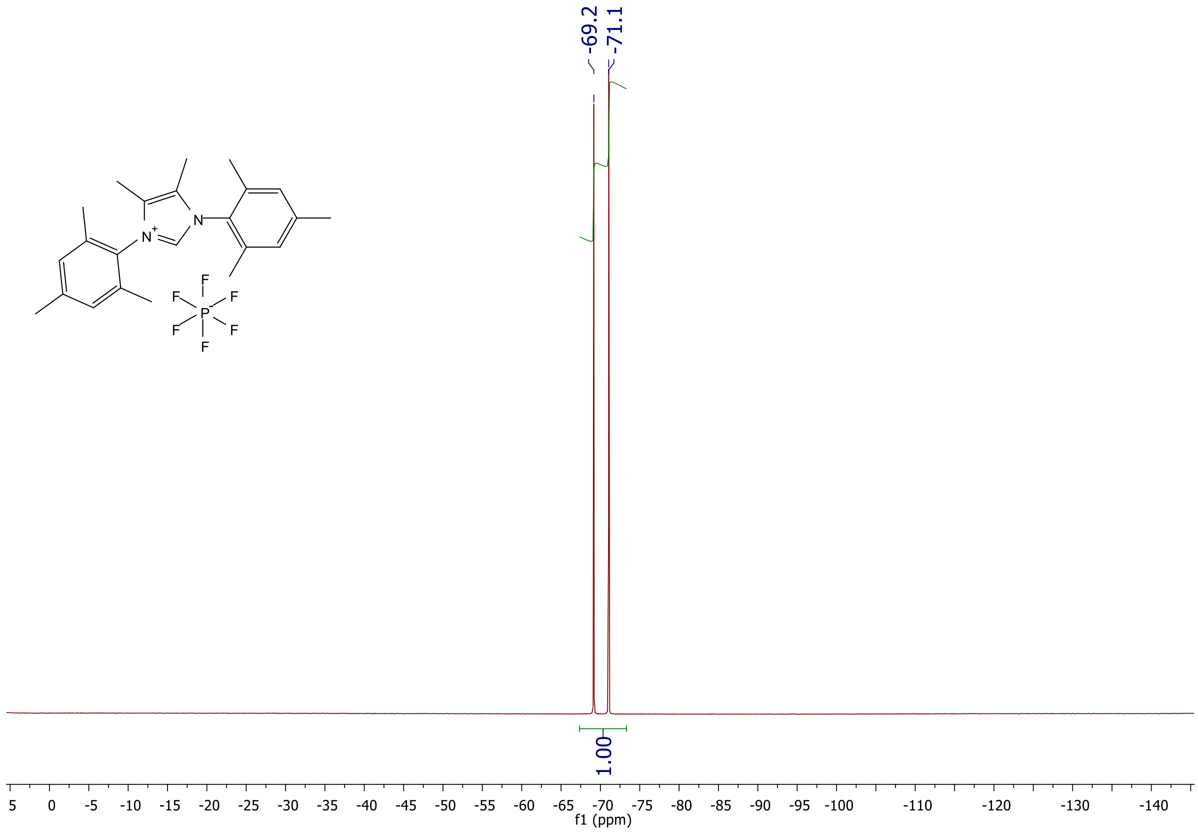
^{13}C NMR (101 MHz, DMSO-*d$_6$*)



^{31}P NMR (162 MHz, DMSO-d_6)

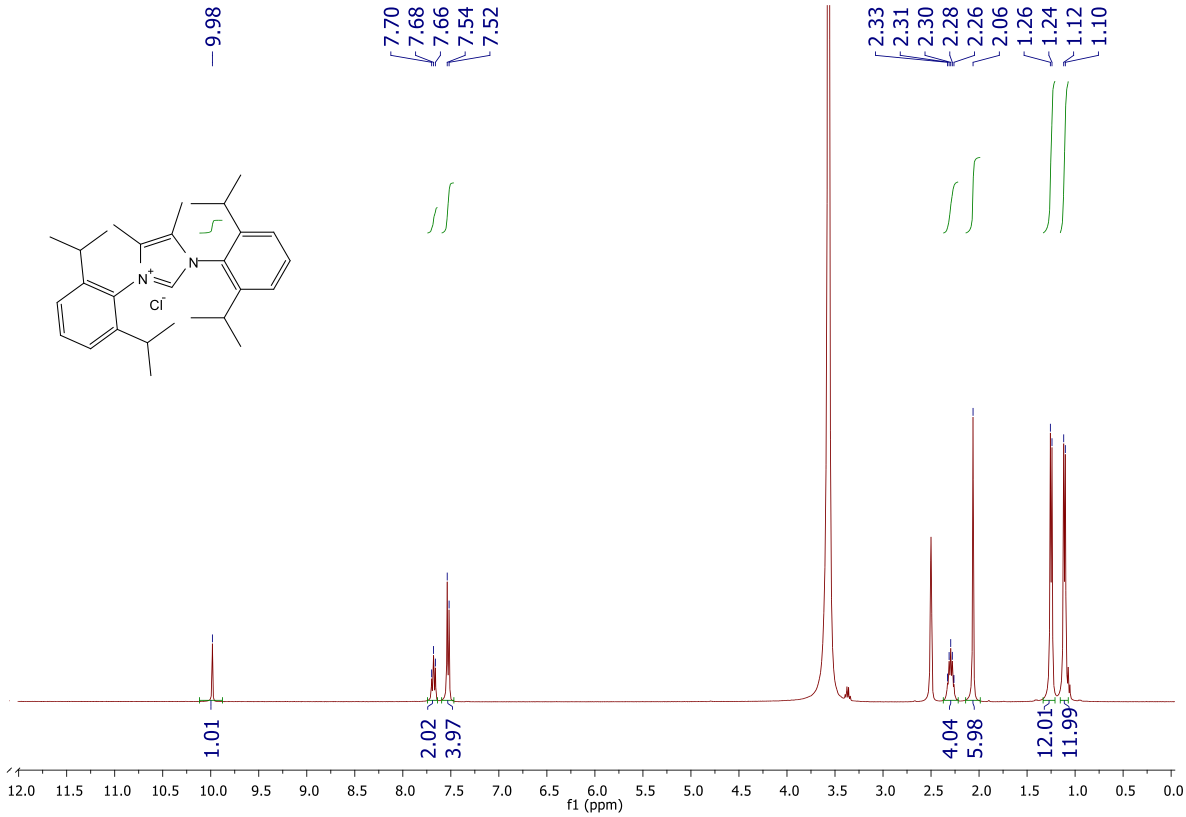


^{19}F NMR (376 MHz, DMSO-d_6)

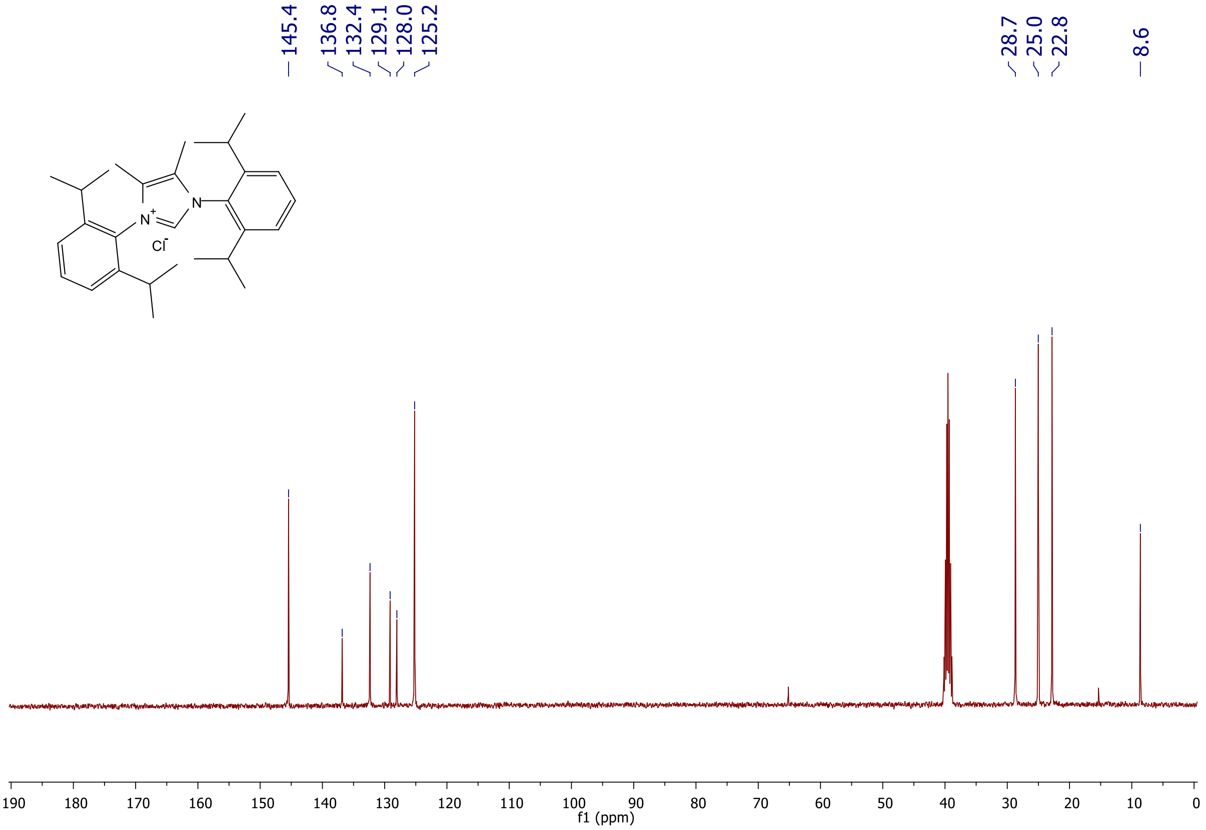


[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride IPr^{Me}·HCl

^{1}H NMR (400MHz, DMSO-d_6)

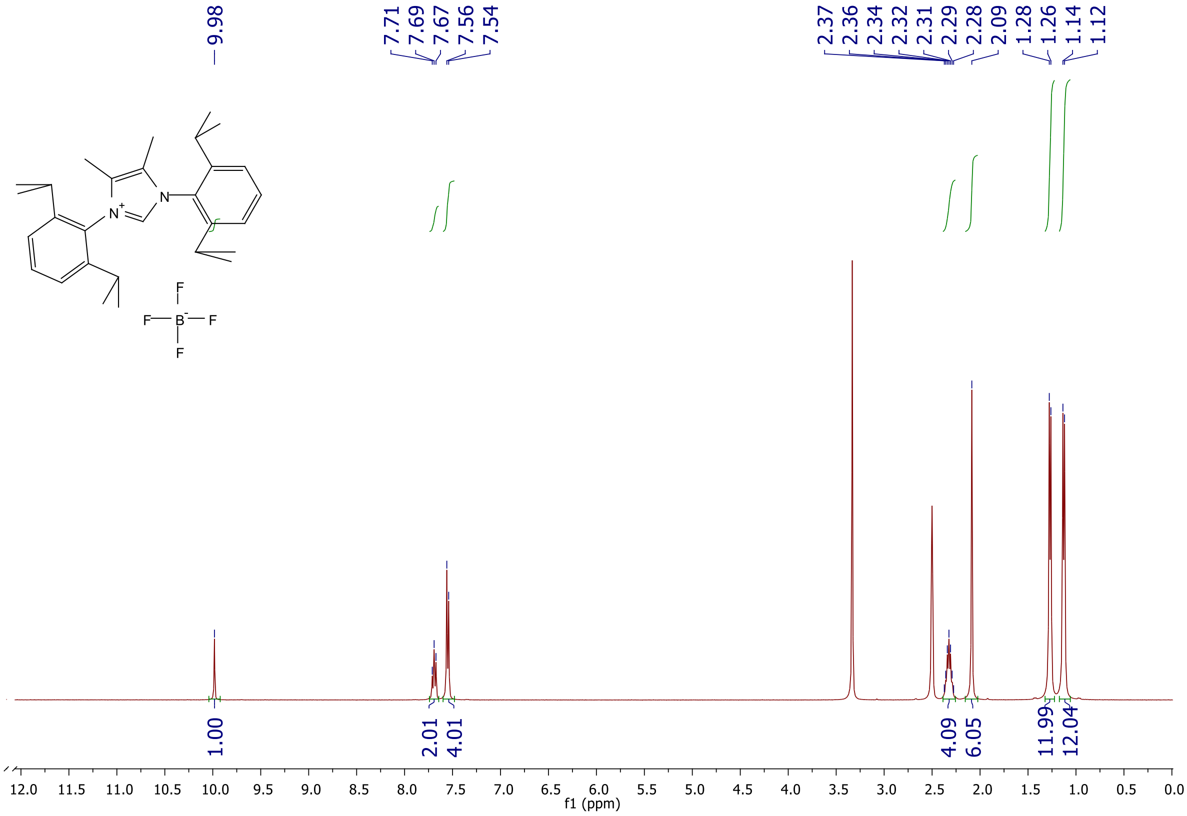


^{13}C NMR (101 MHz, DMSO-d_6)

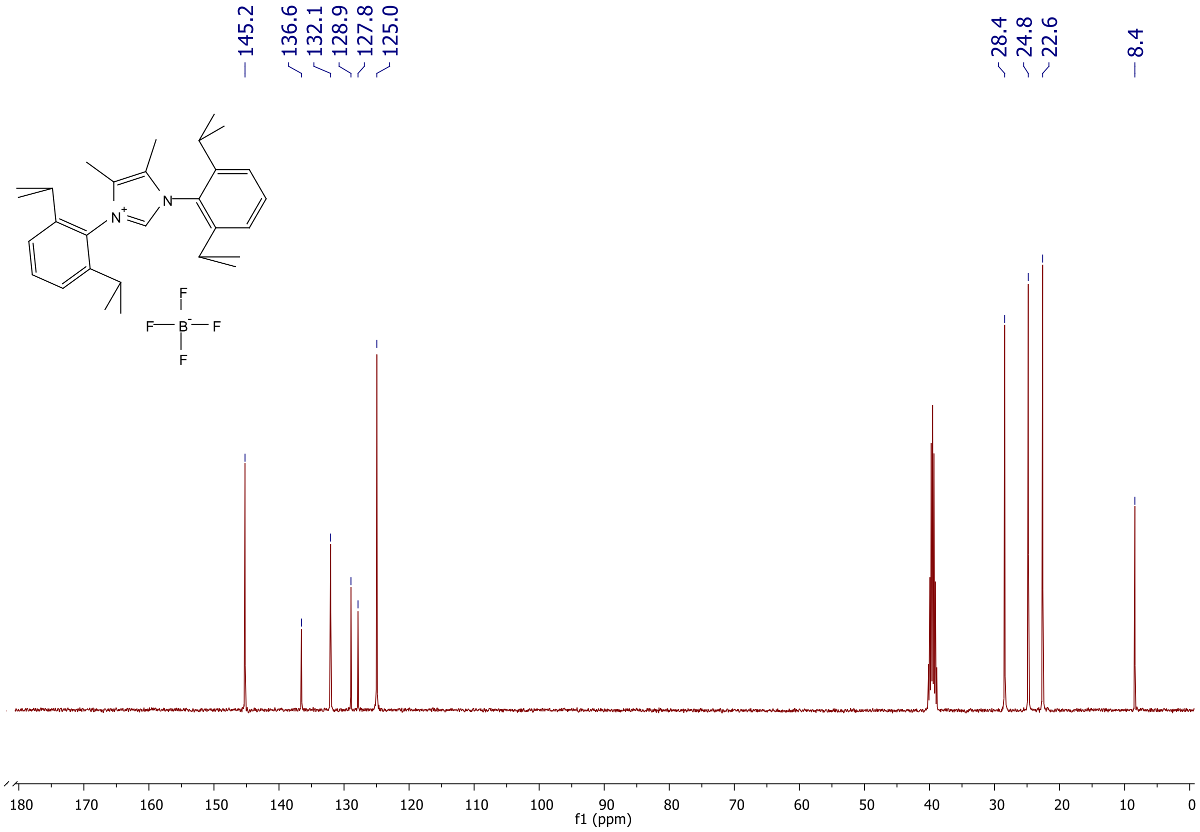


[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium tetrafluoroborate $\mathrm{IPr^{Me}\cdot HBF_4}$

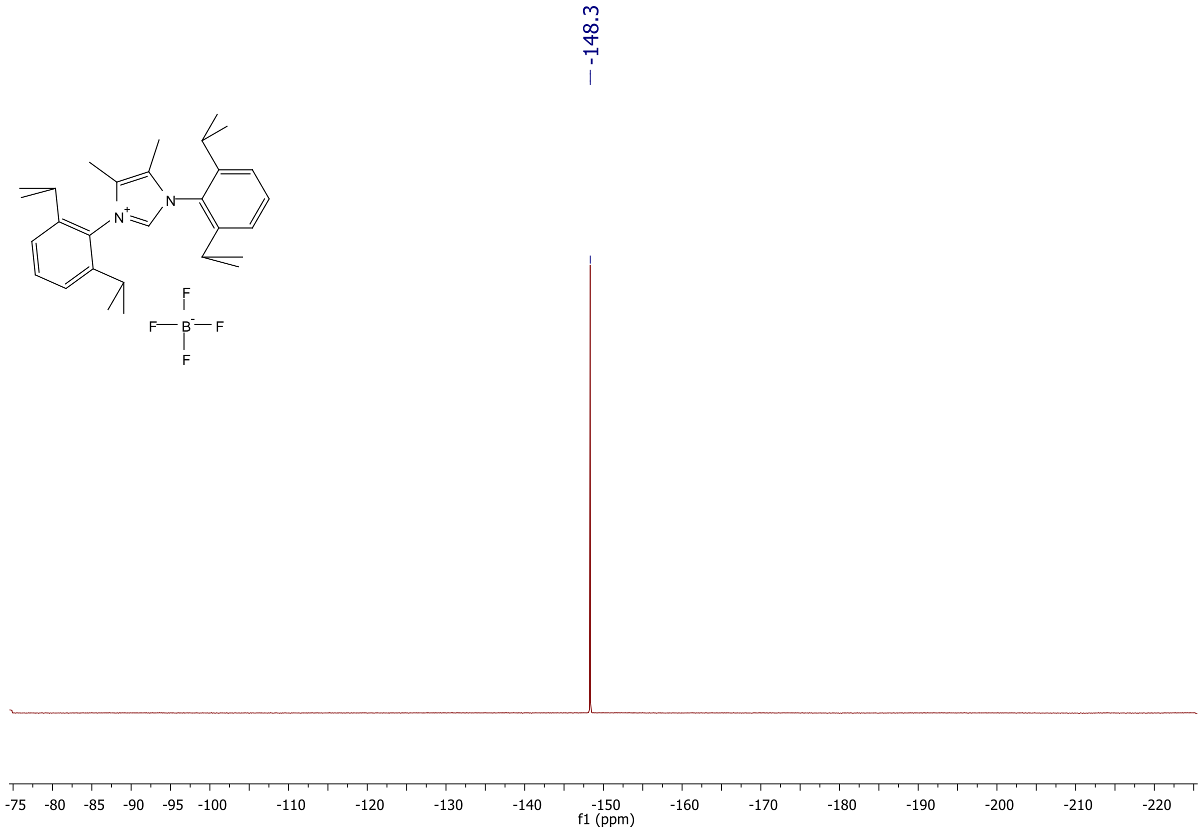
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

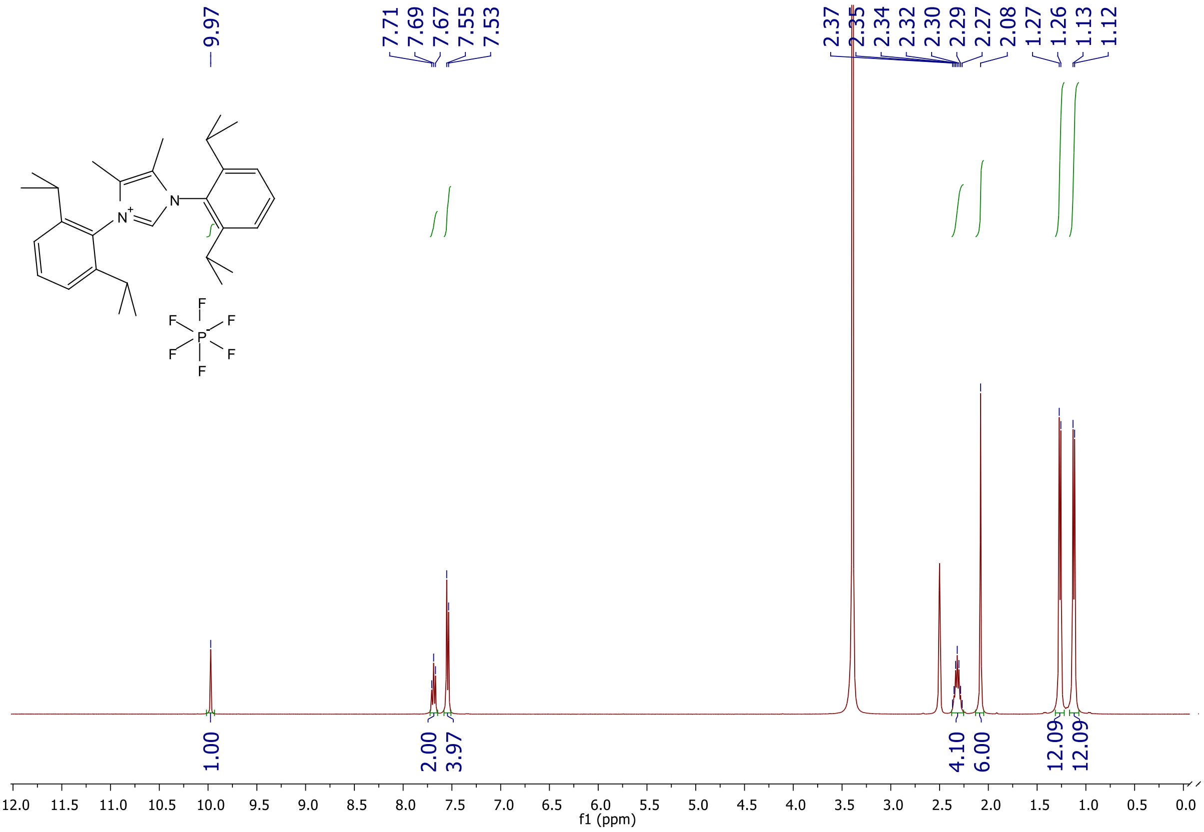


^{19}F NMR (376 MHz, DMSO-d_6)

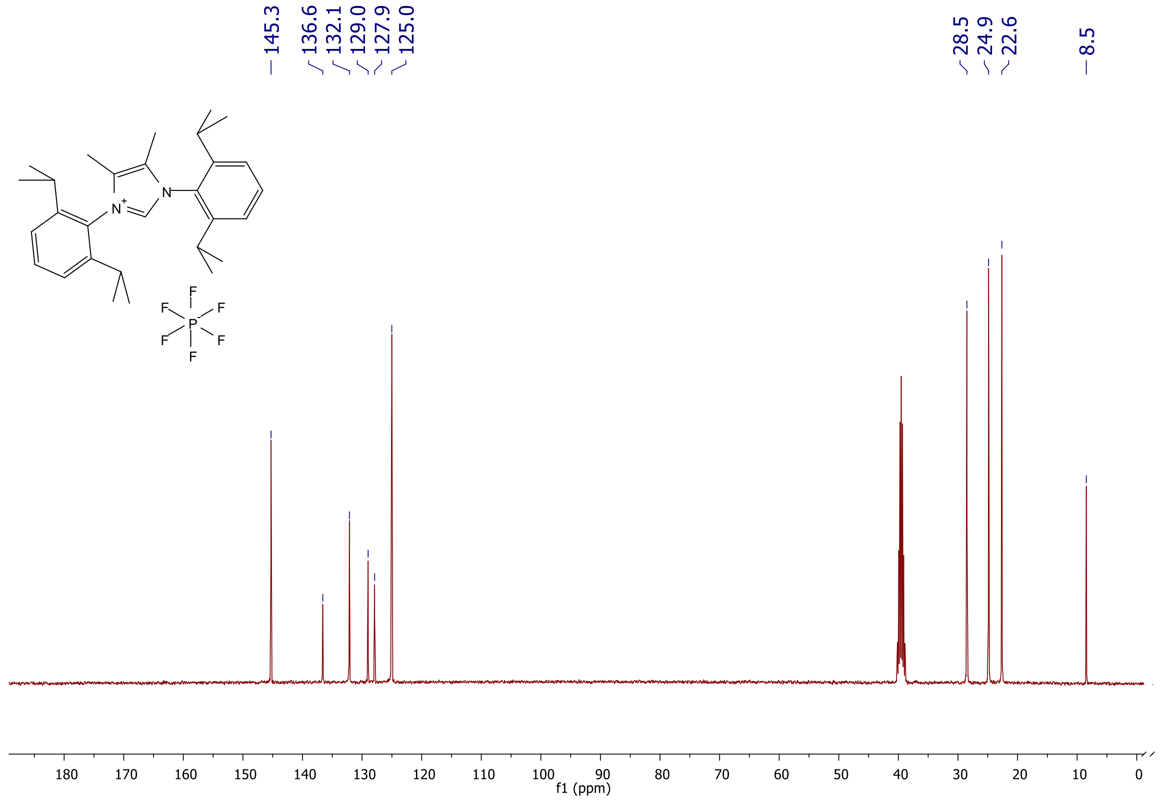


[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate IPr^{Me}·HPF$_6$

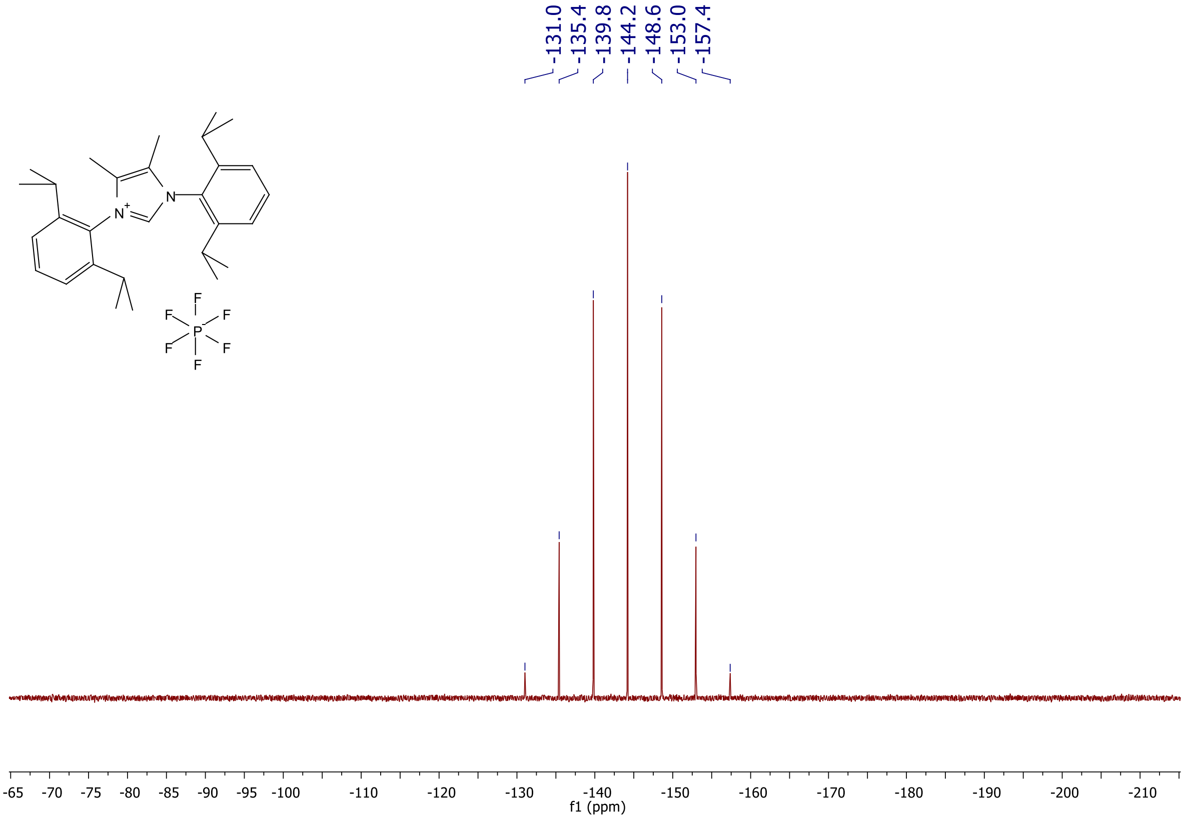
^{1}H NMR (400MHz, DMSO-d_6)



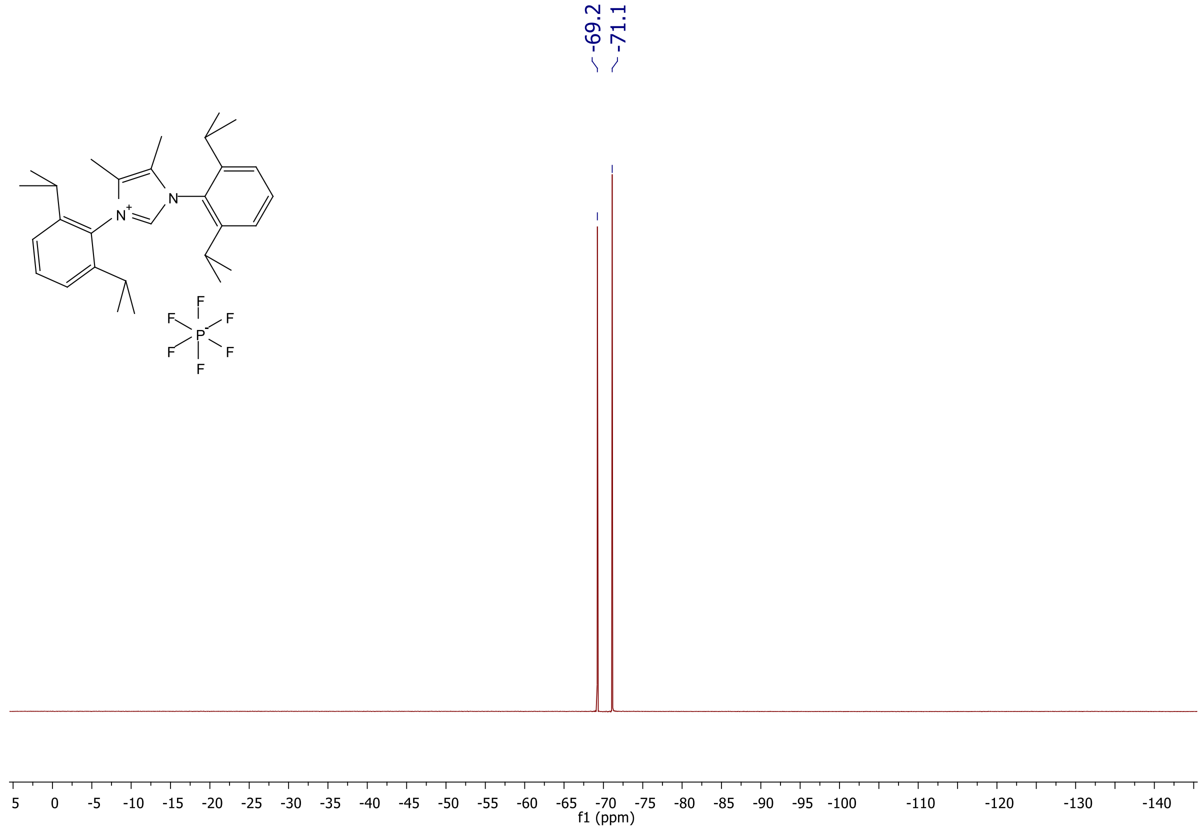
^{13}C NMR (101 MHz, DMSO-d_6)



^{31}P NMR (162 MHz, DMSO-d_6)

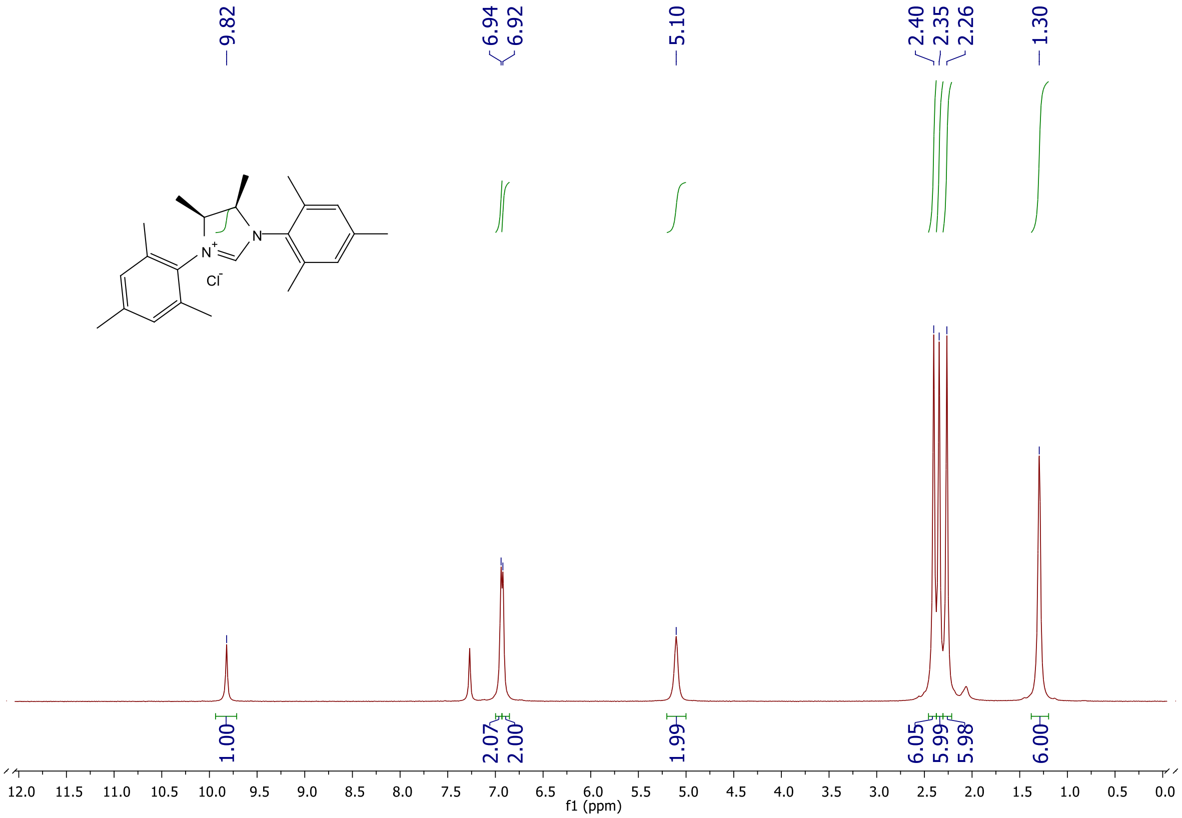


^{19}F NMR (376 MHz, DMSO-d_6)

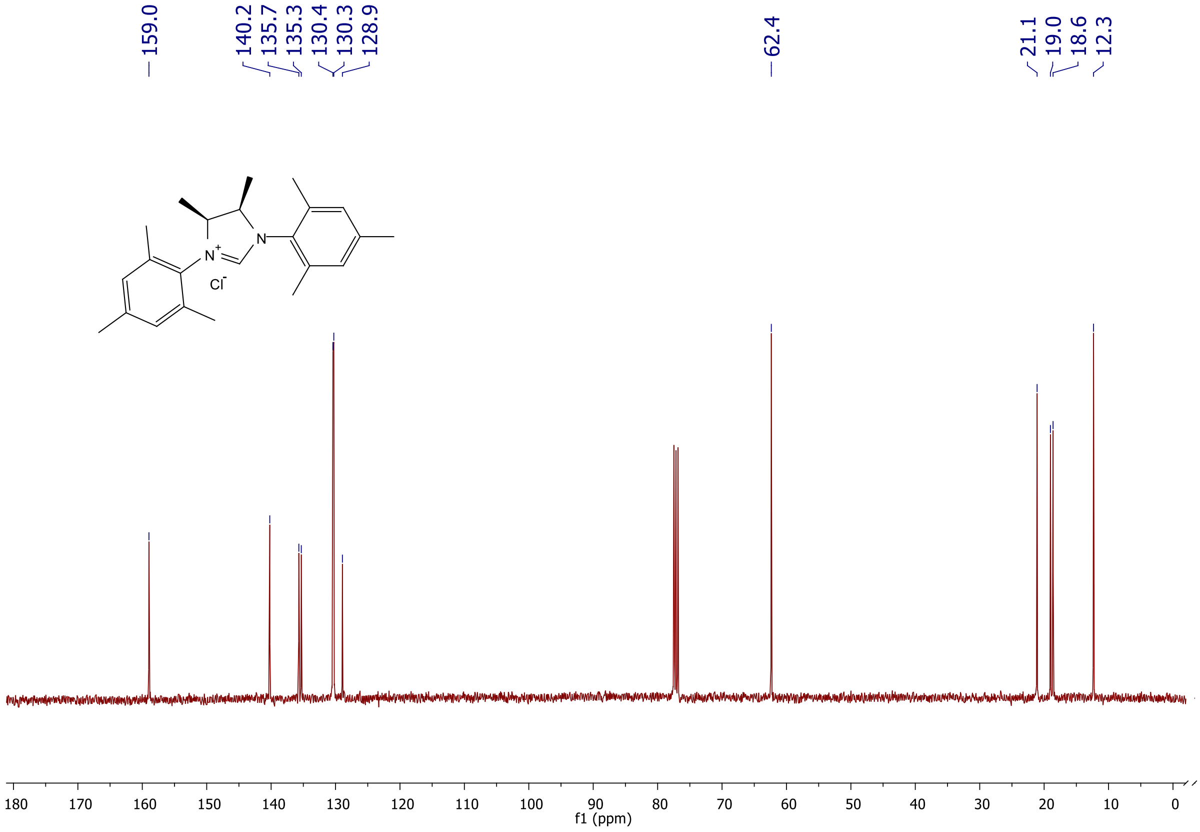


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-cis-dimethyl]imidazolidinium chloride SIMes^{Me}·HCl

^{1}H NMR (400MHz, $CDCl_3$)

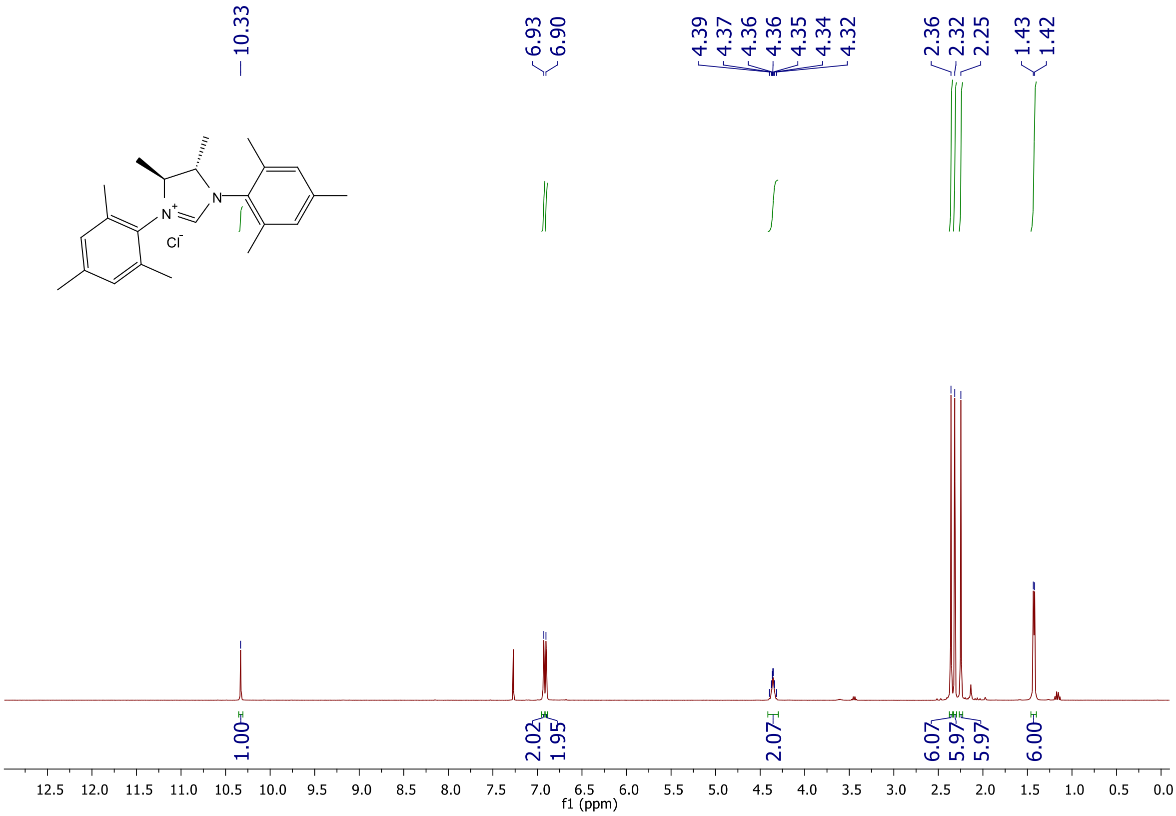


^{13}C NMR (101 MHz, $CDCl_3$)

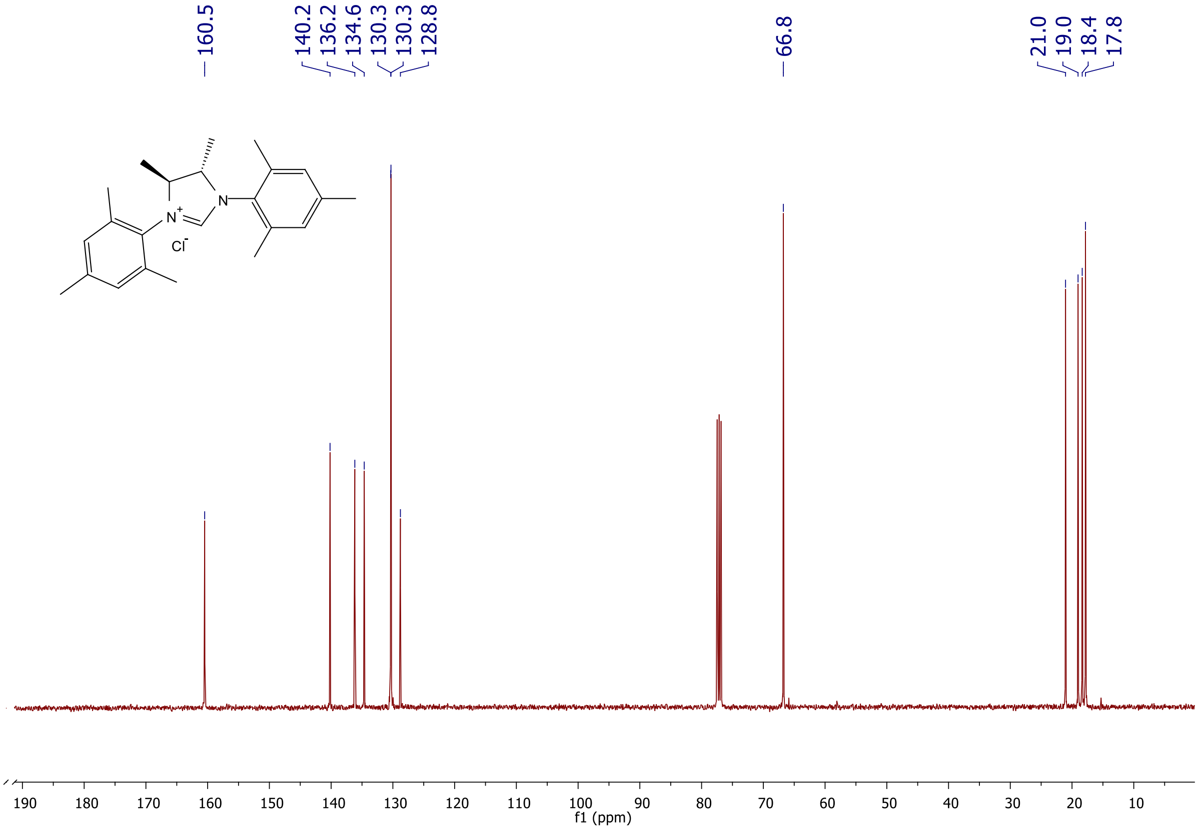


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-trans-dimethyl]imidazolidinium chloride SIMes^{Me}·HCl

^{1}H NMR (400MHz, $CDCl_3$)



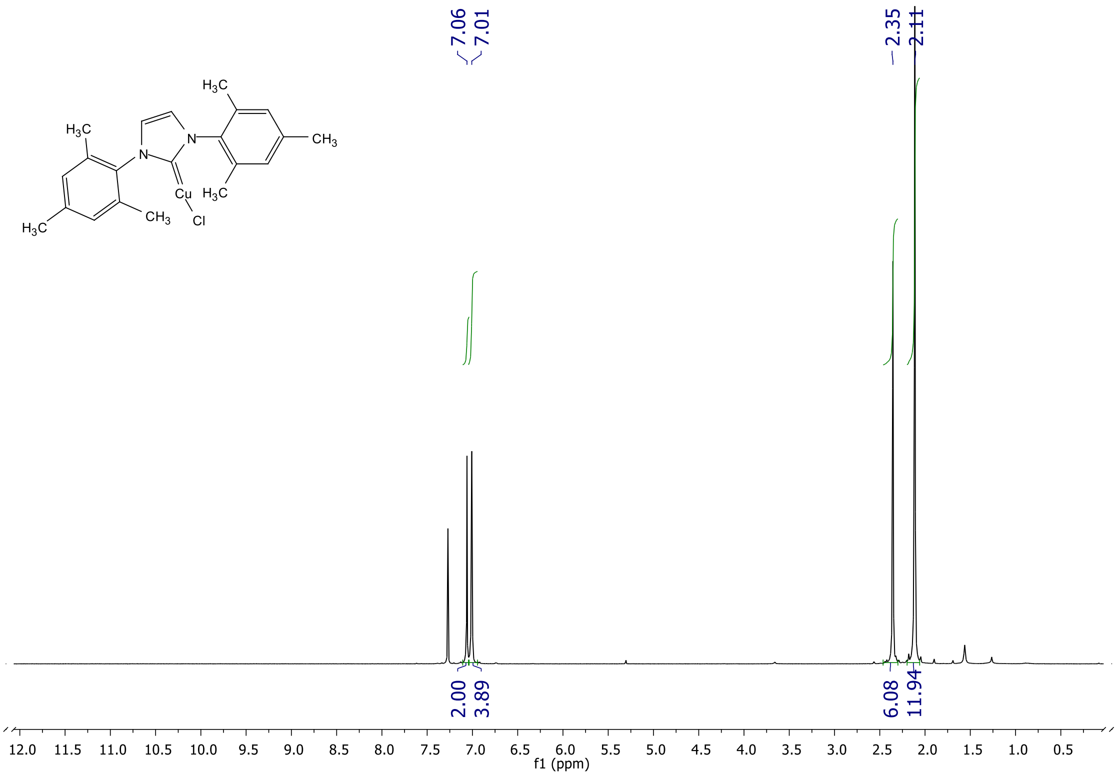
^{13}C NMR (101 MHz, $CDCl_3$)



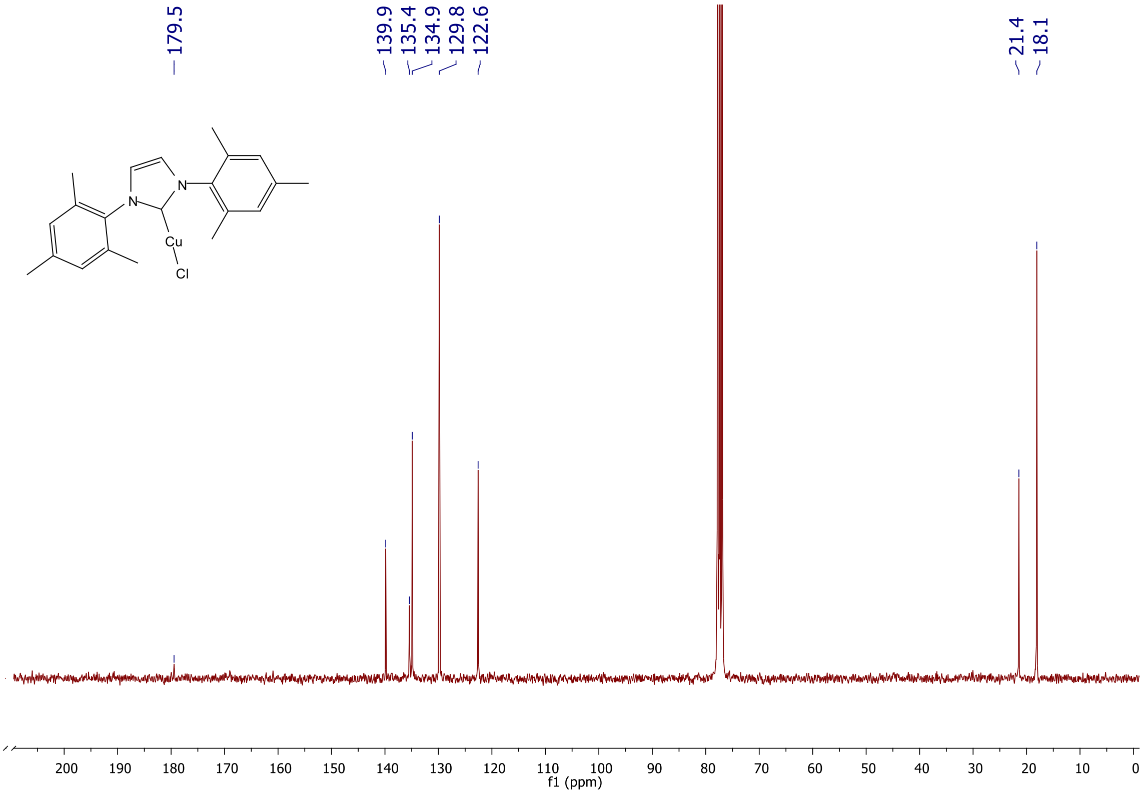
4.2 [CuCl(NHC)]

[1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper(I) chloride [CuCl(IMes)]

^{1}H NMR (300MHz, $CDCl_3$)

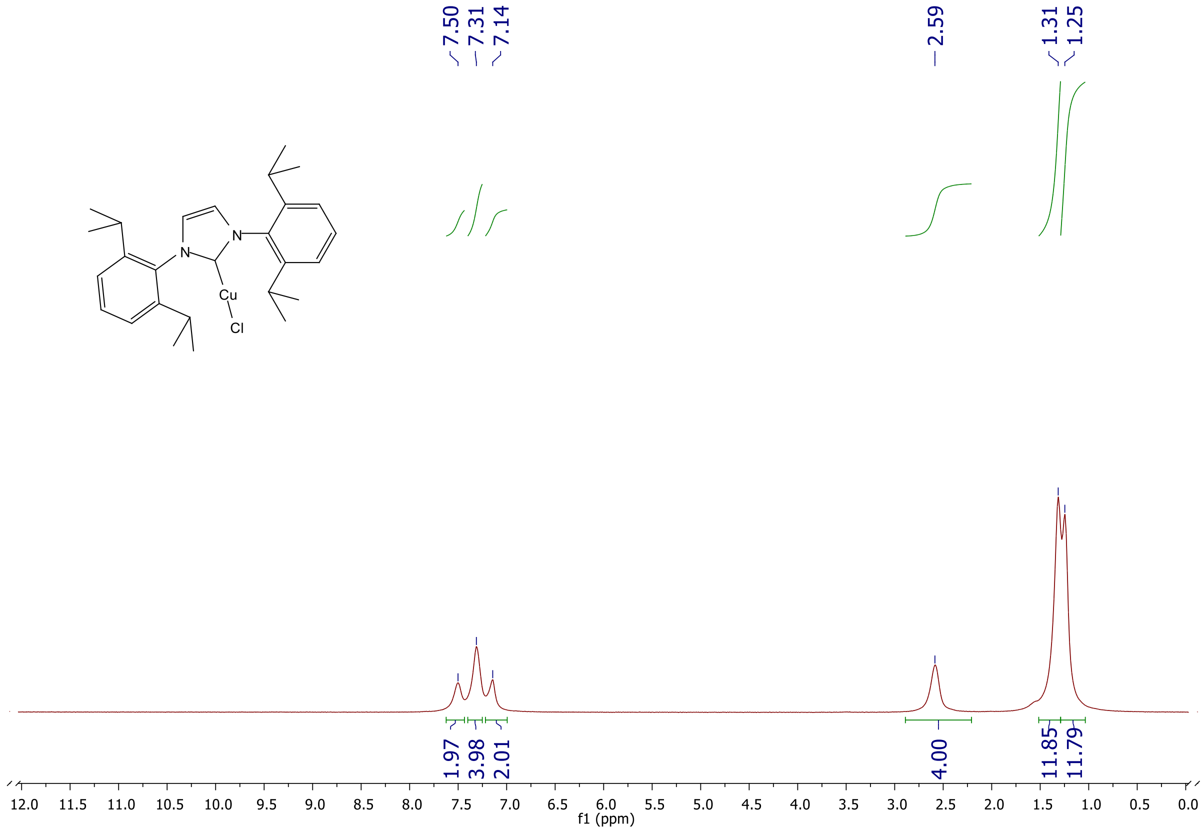


^{13}C NMR (75 MHz, $CDCl_3$)

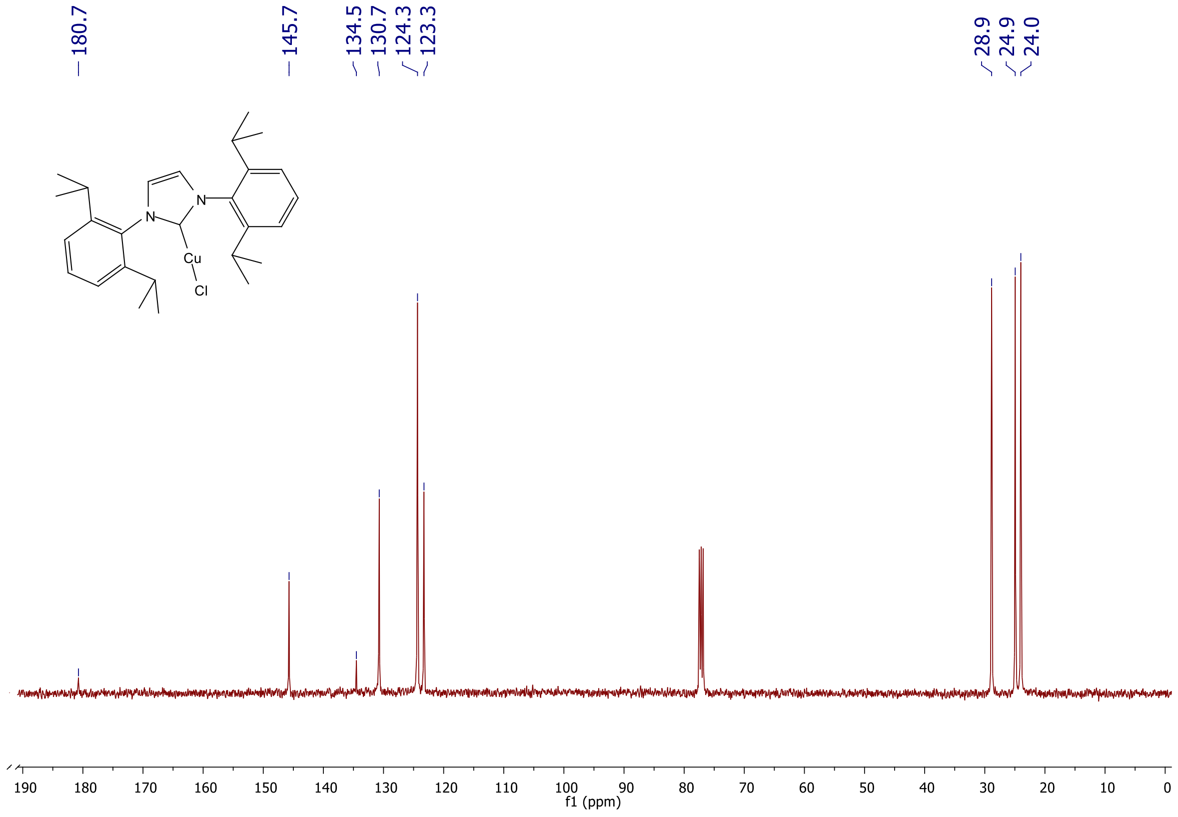


[1,3-Bis-(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper(I) chloride [CuCl(IPr)]

^{1}H NMR (400MHz, $CDCl_3$)

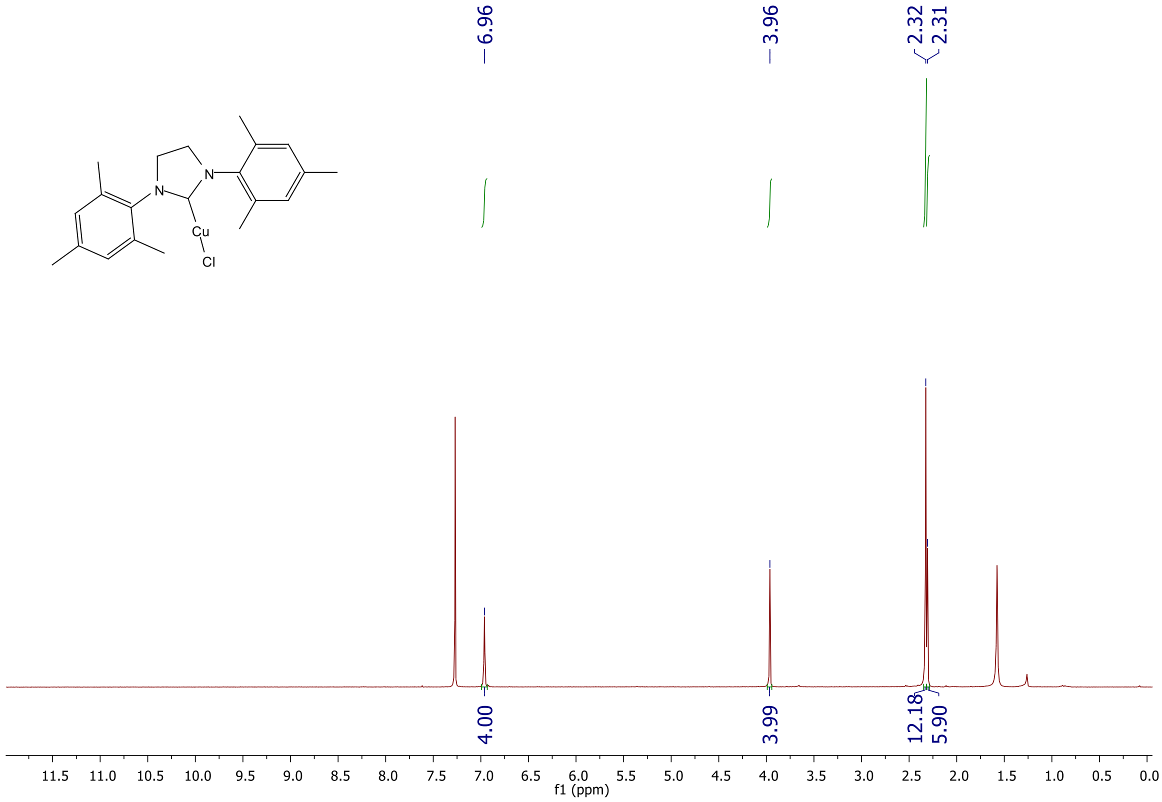


^{13}C NMR (101 MHz, $CDCl_3$)

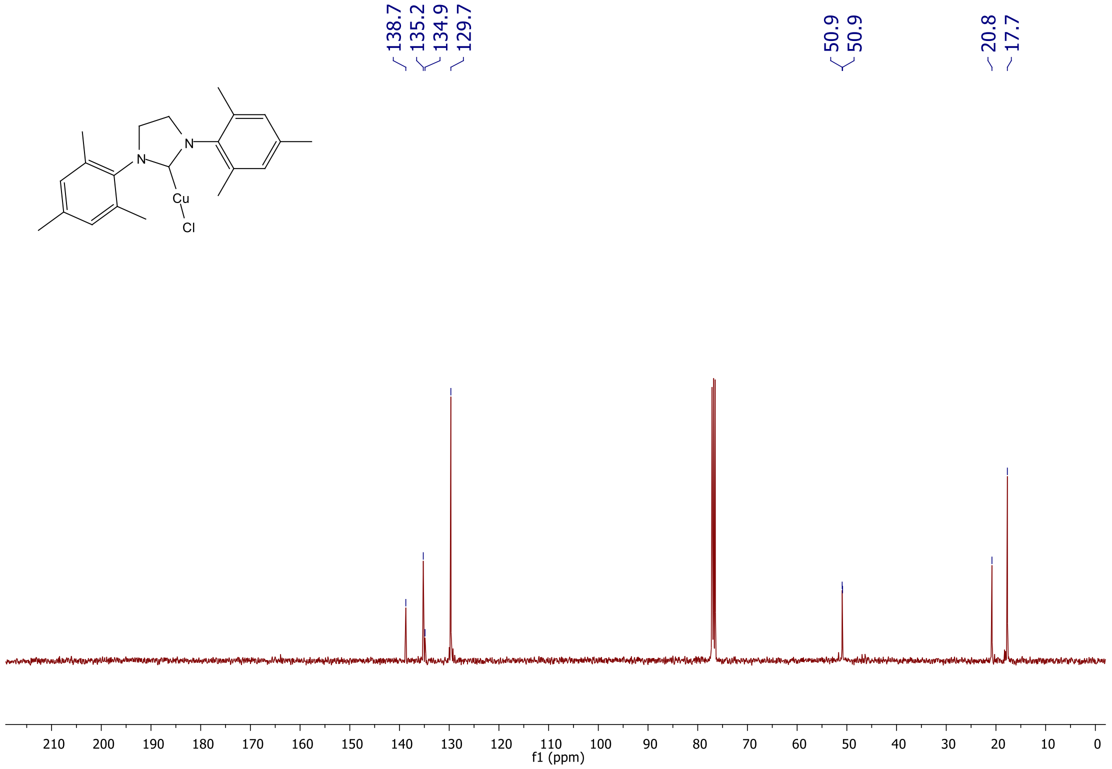


[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]copper(I) chloride [CuCl(SIMes)]

^{1}H NMR (300MHz, $CDCl_3$)

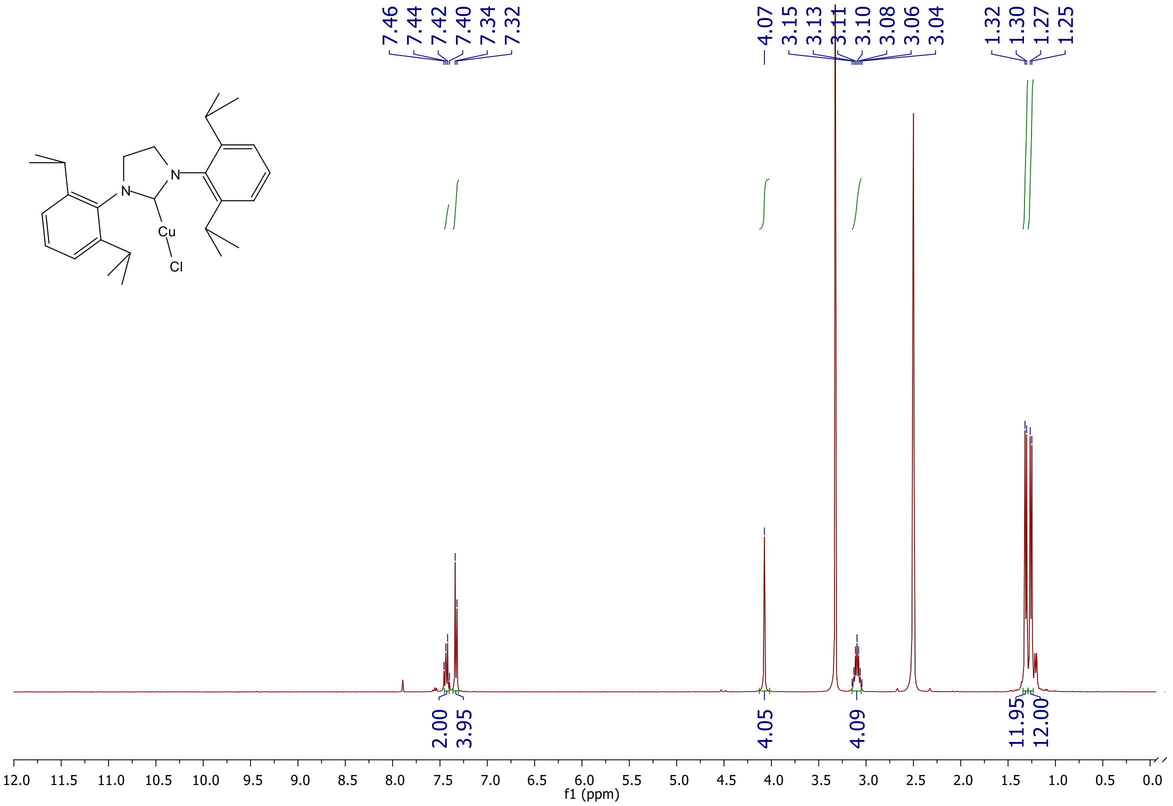


^{13}C NMR (101 MHz, $CDCl_3$)

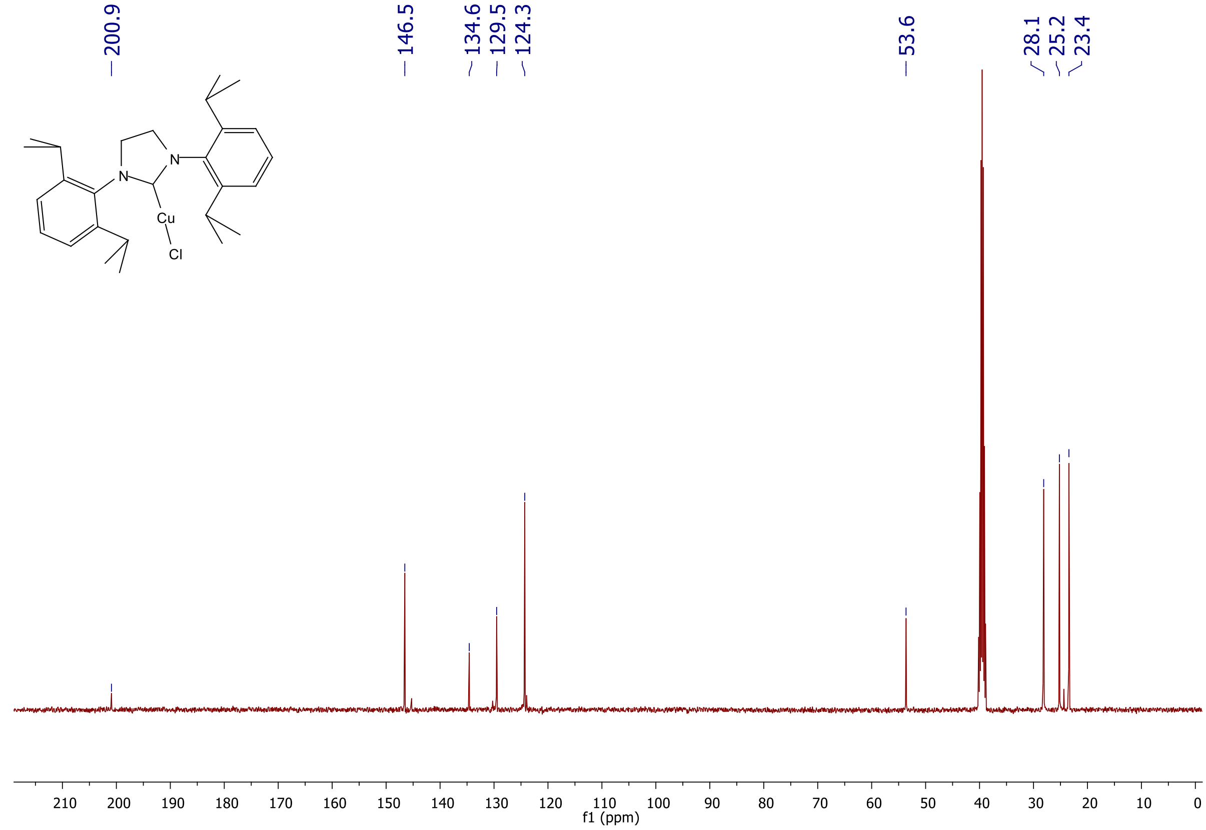


[1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene]copper(I) chloride [CuCl(SIPr)]

^{1}H NMR (400MHz, DMSO-d_6)

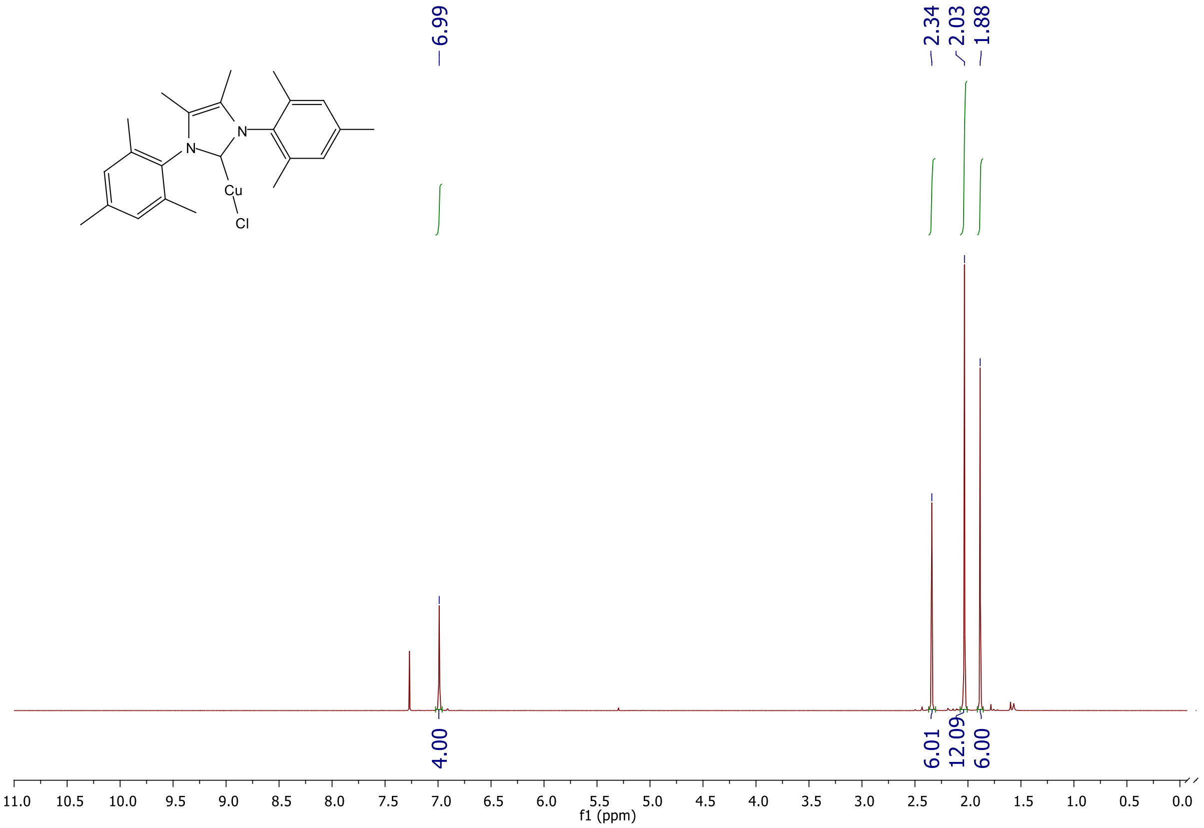


^{13}C NMR (101 MHz, DMSO-d_6)

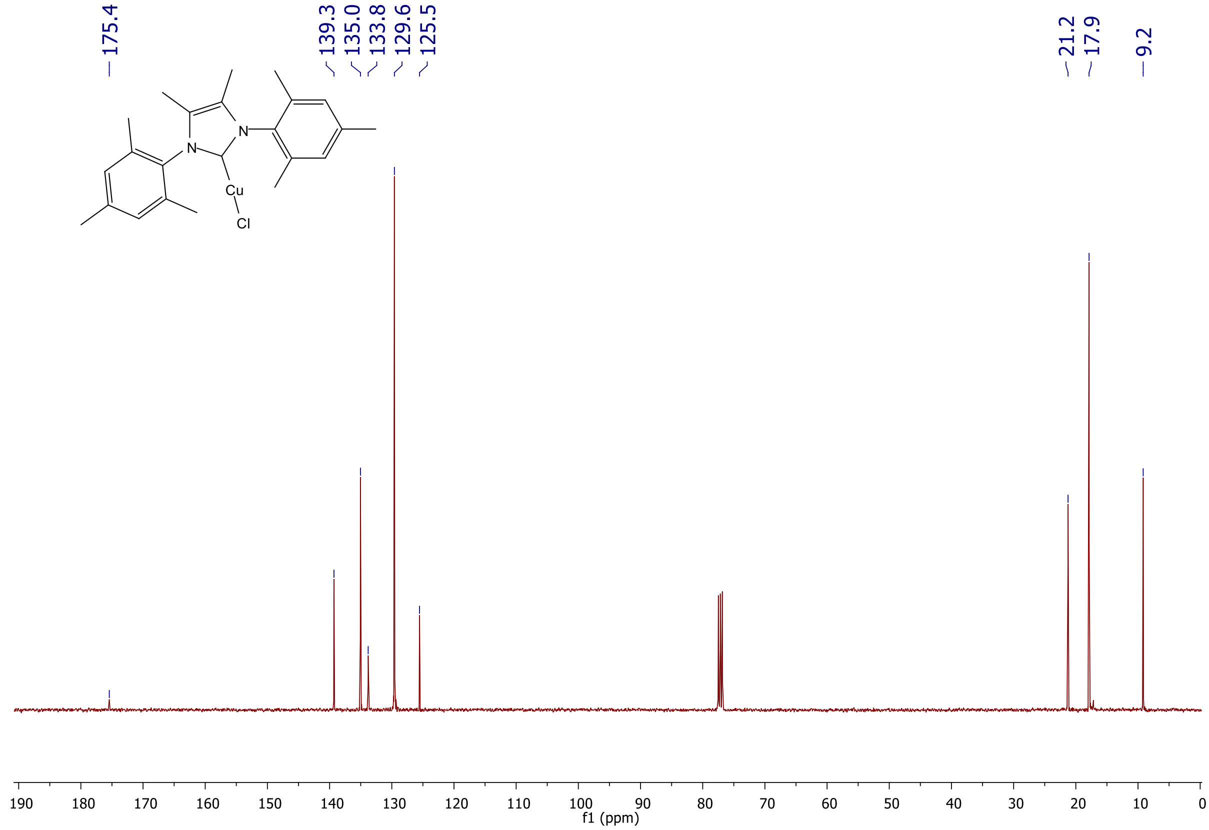


[(1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper(I) chloride [CuCl(IMes^{Me})]

^{1}H NMR (400MHz, CDCl$_3$)

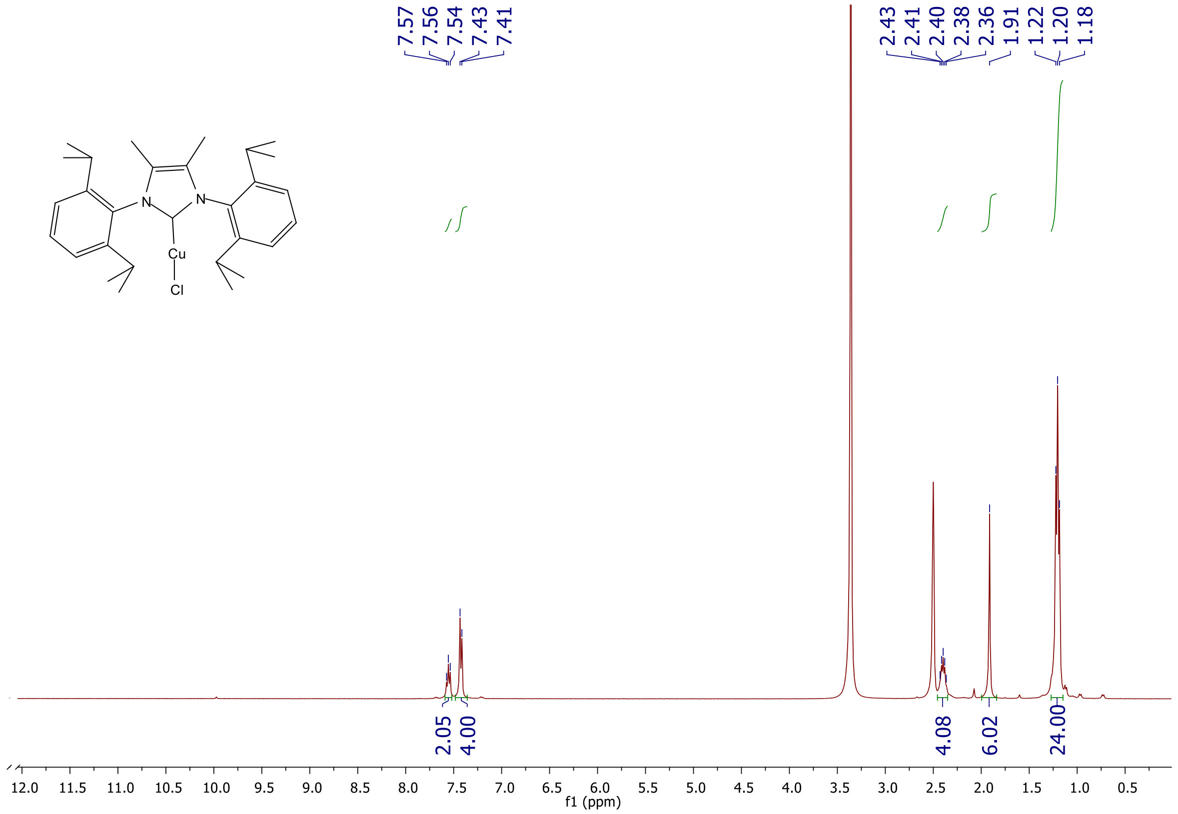


^{13}C NMR (101 MHz, CDCl$_3$)

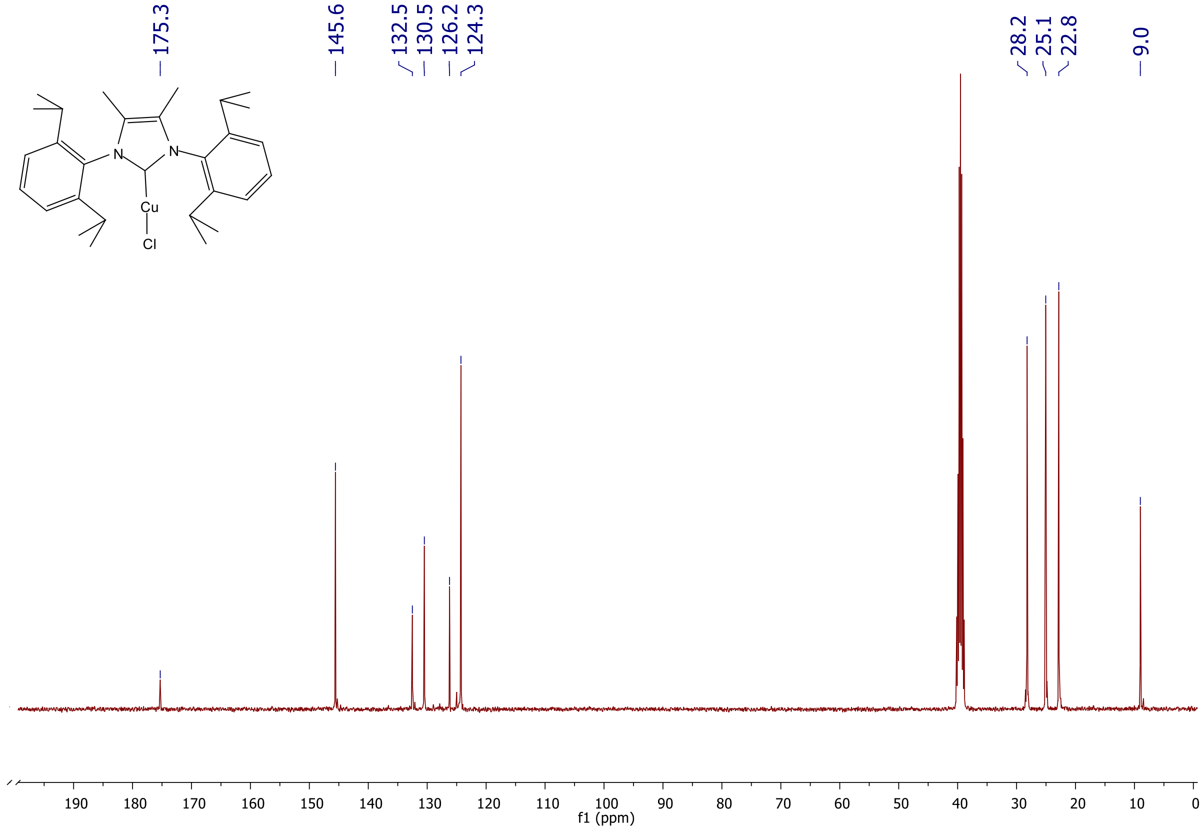


[(1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazole-2-ylidene]copper(I) chloride [CuCl(IPr^{Me})]

^{1}H NMR (400MHz, DMSO-d_6)

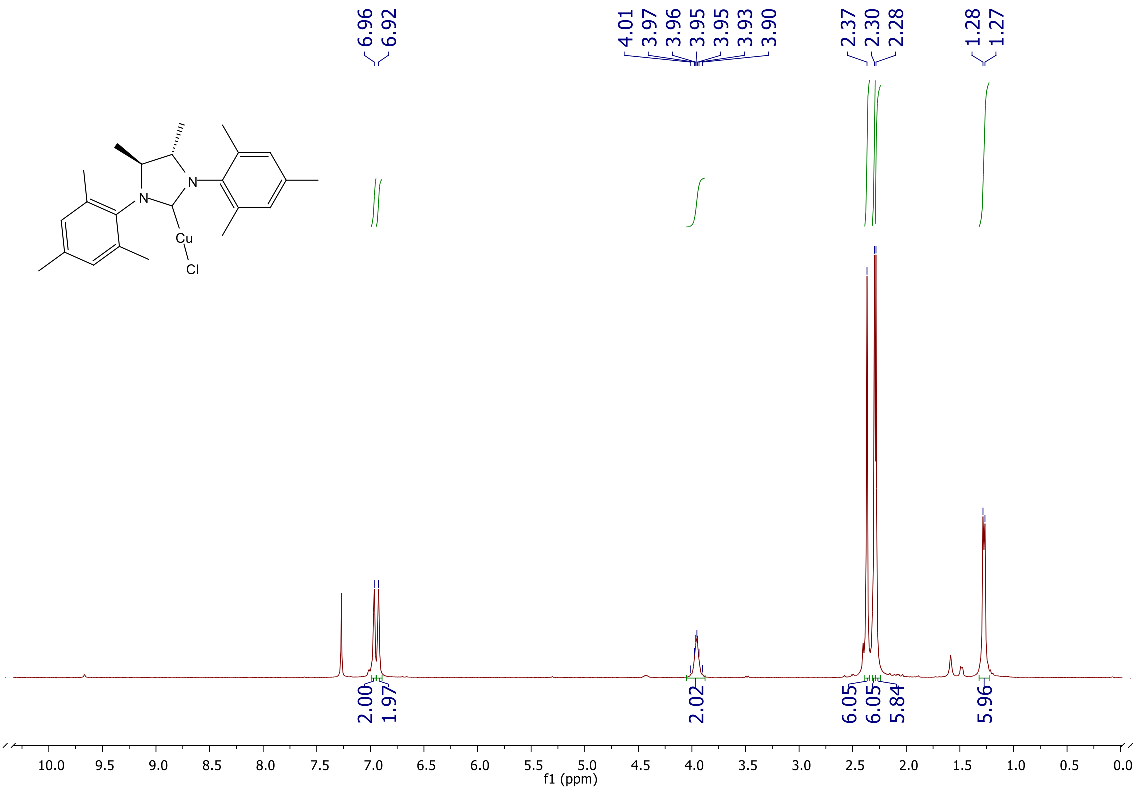


^{13}C NMR (101 MHz, DMSO-d_6)

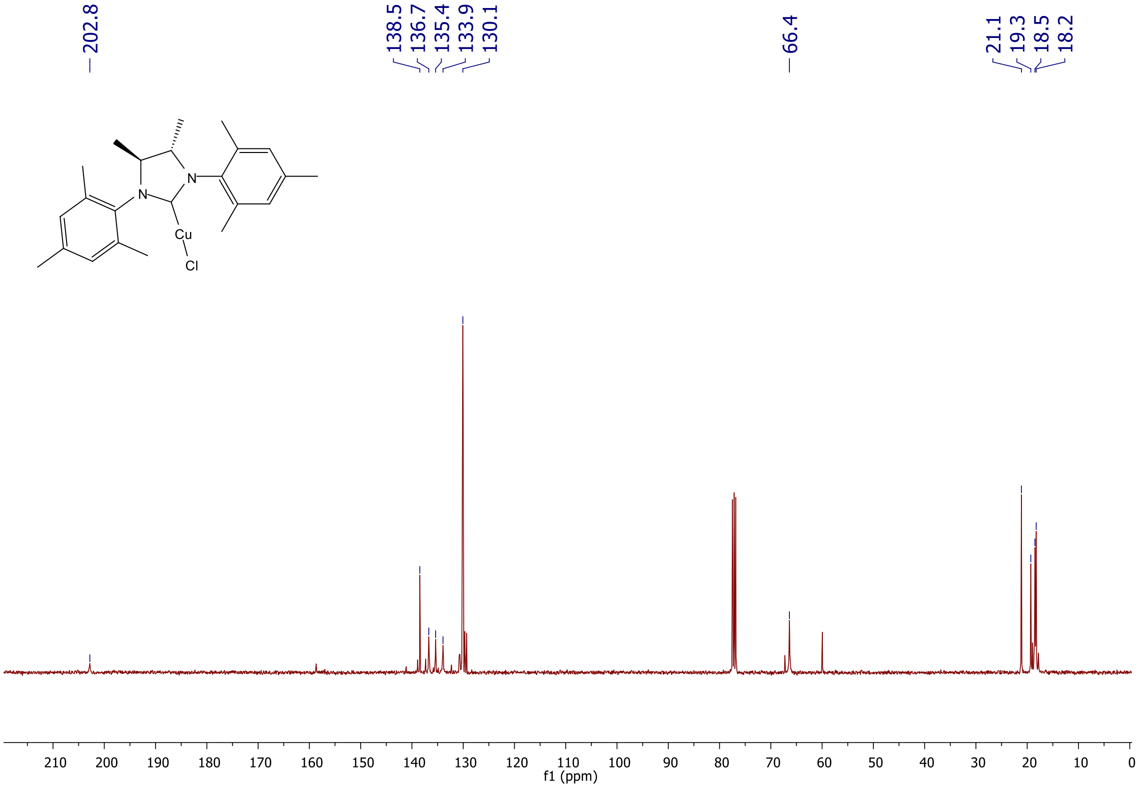


[(1,3-Bis-(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl)imidazolidin-2-ylidene]copper(I) chloride $SIMes^{Me}CuCl$

^1H NMR (300MHz, $CDCl_3$)



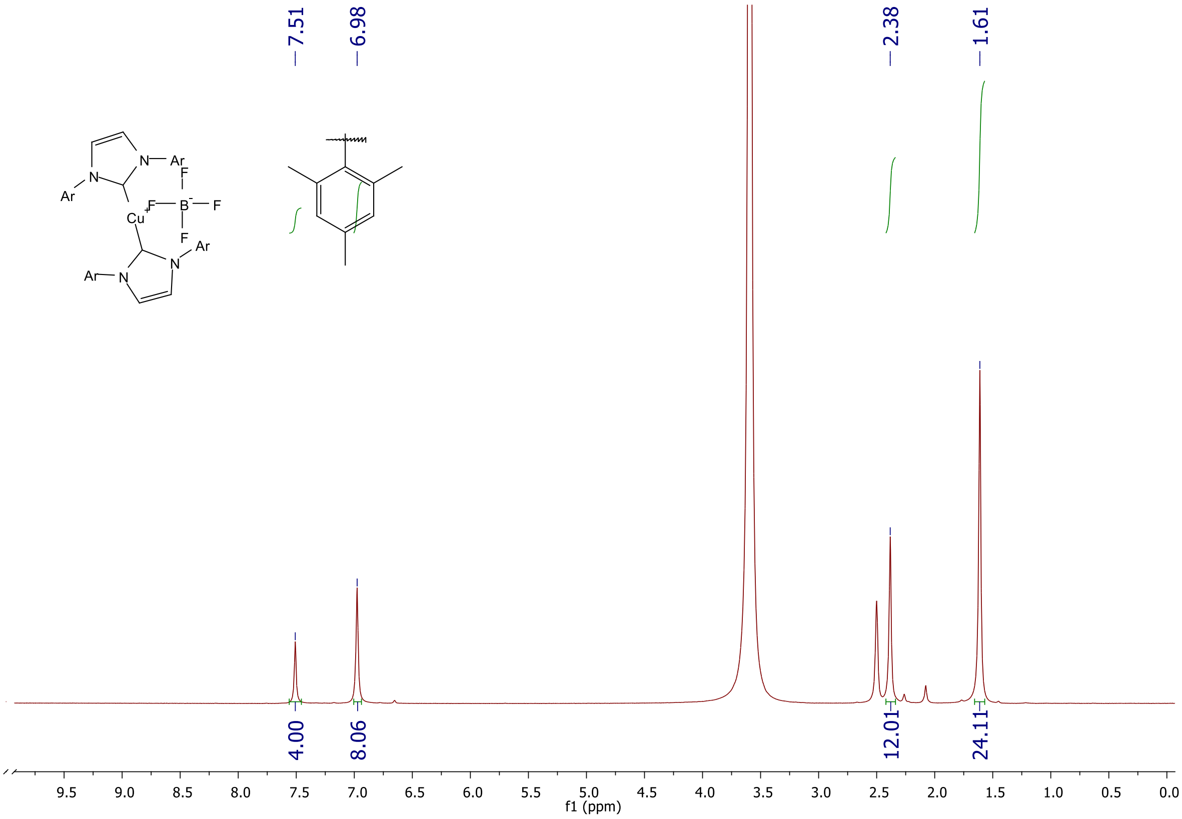
^{13}C NMR (101 MHz, $CDCl_3$)



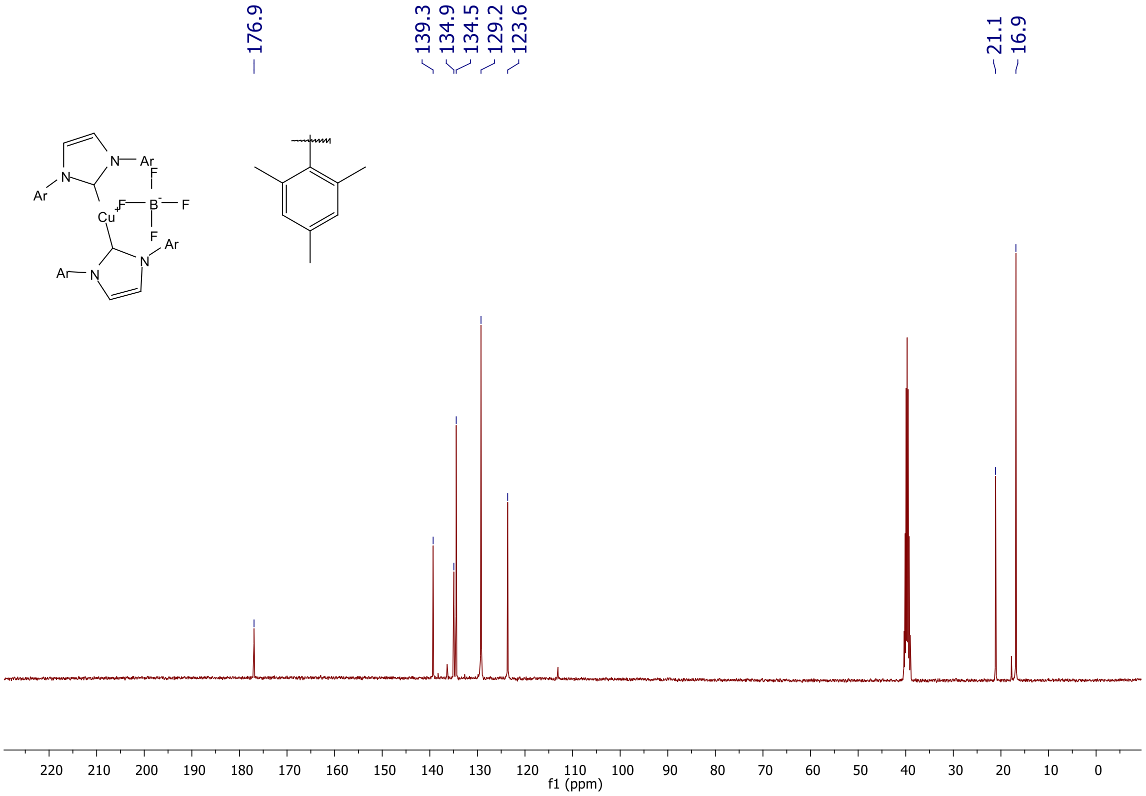
4.3 [Cu(NHC)$_2$]Y (Y = BF_4 or PF_6)

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper tetrafluoroborate [Cu(IMes)$_2$]BF_4

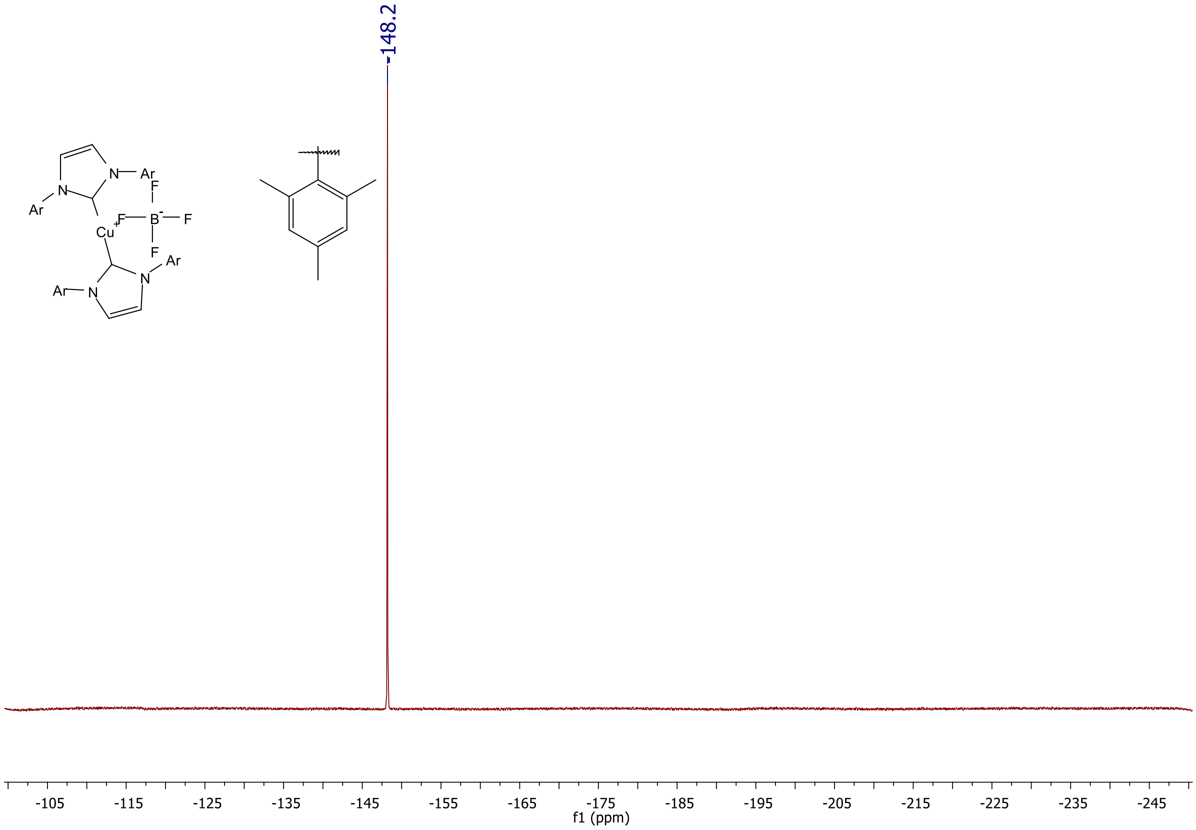
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

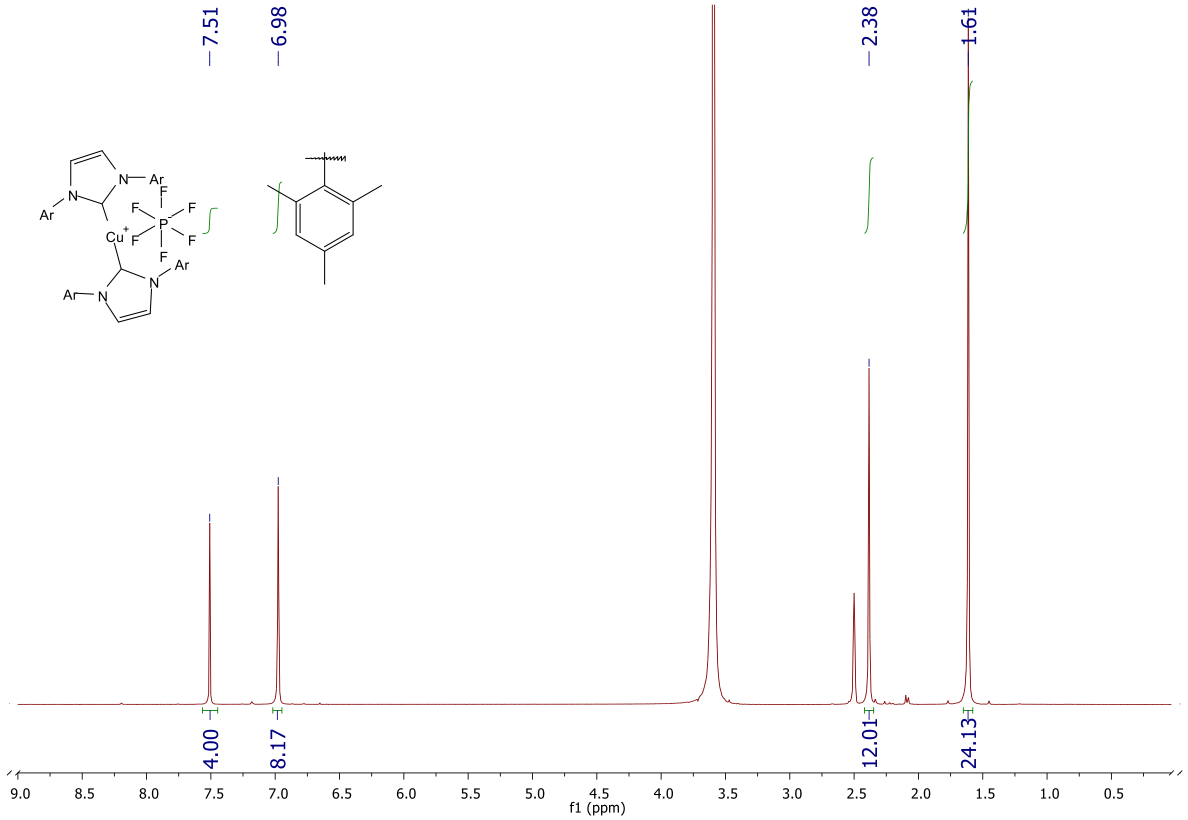


^{19}F NMR (376 MHz, DMSO-d_6)

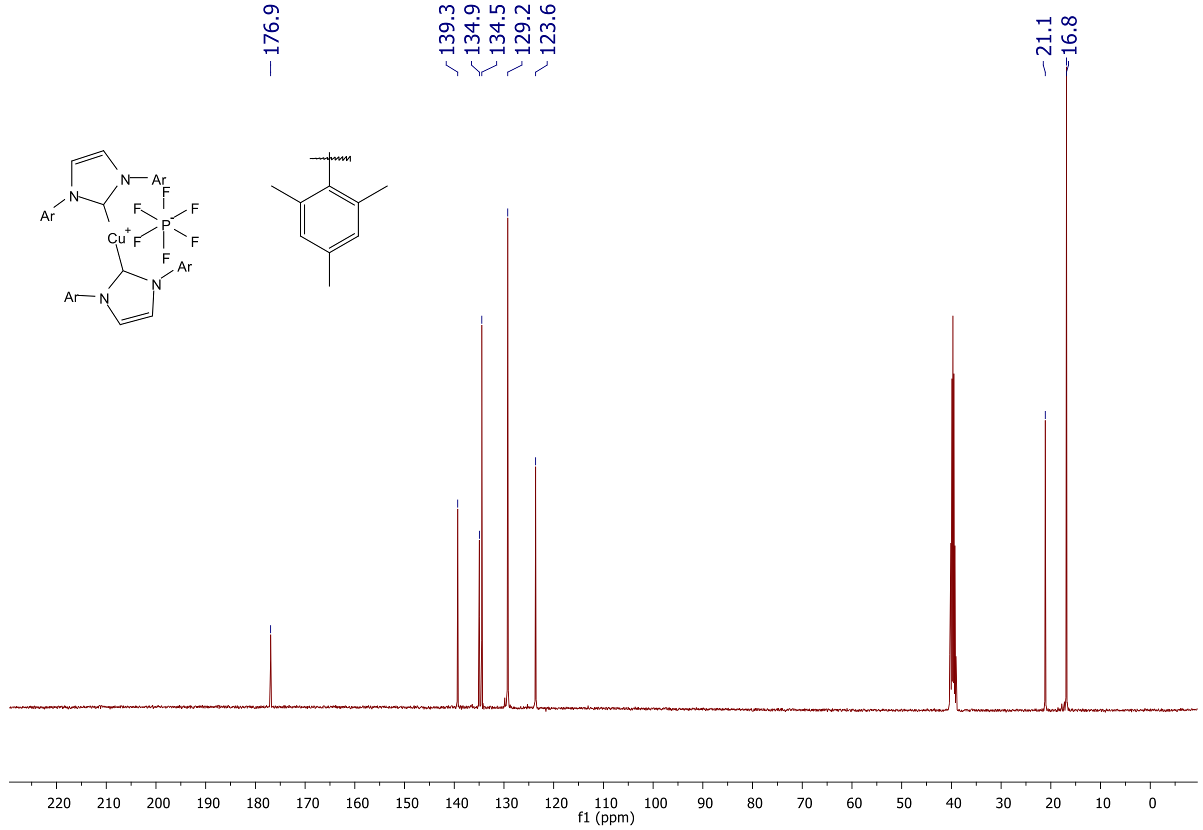


Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper hexafluorophosphate [Cu(IMes)$_2$]PF$_6$

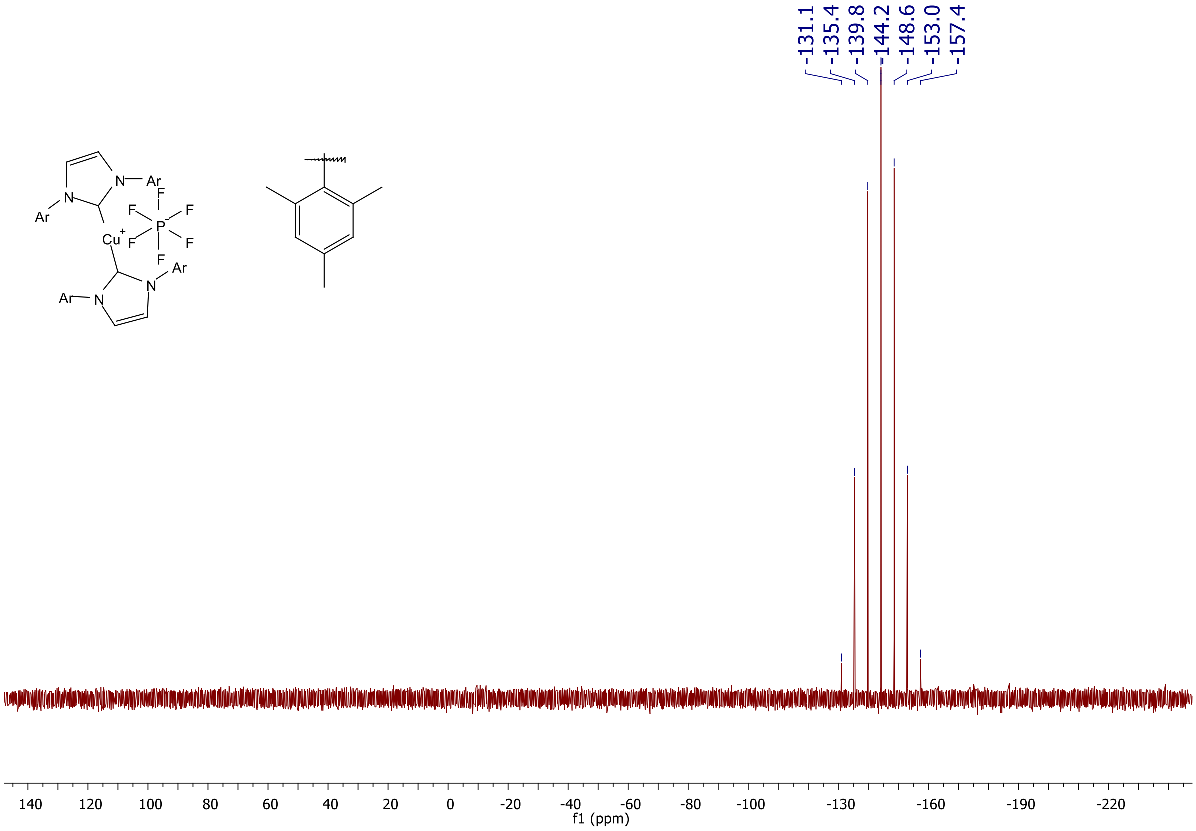
^{1}H NMR (400MHz, DMSO-d_6)



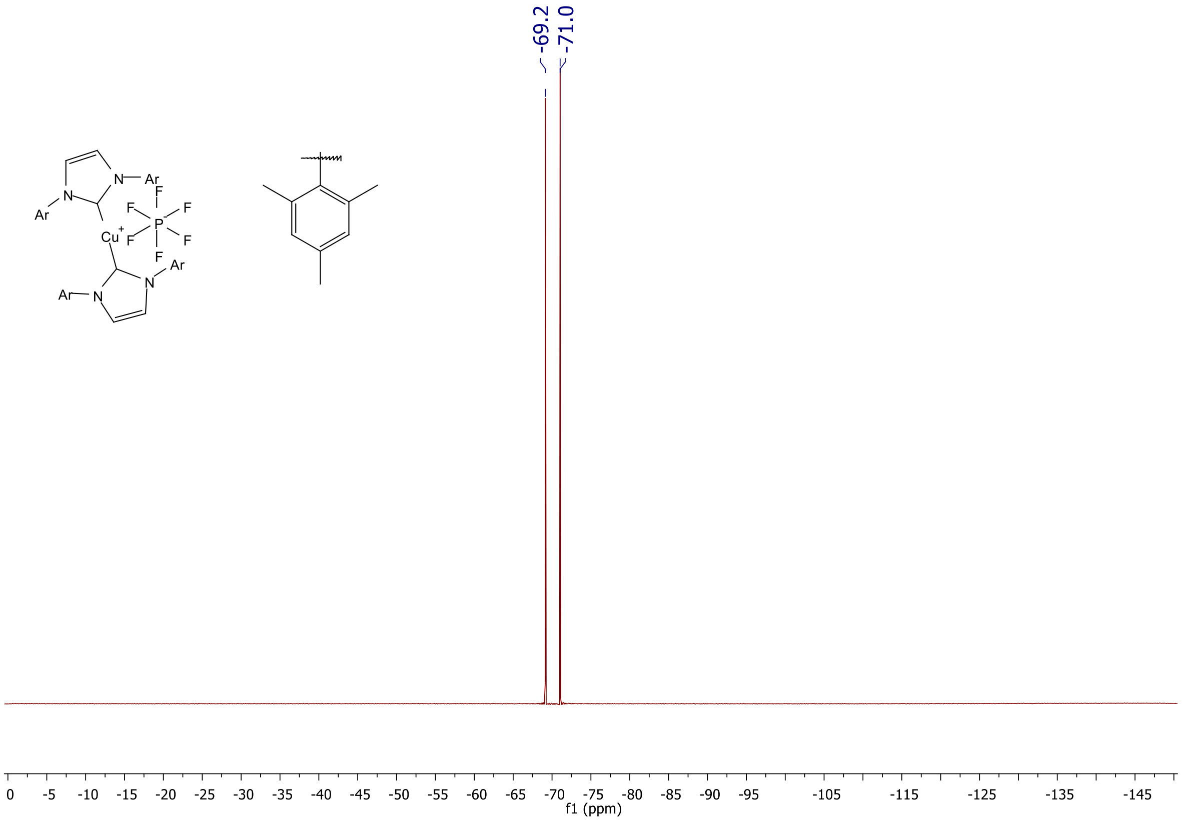
^{13}C NMR (101 MHz, DMSO-d_6)



^{31}P NMR (162 MHz, DMSO-d_6)

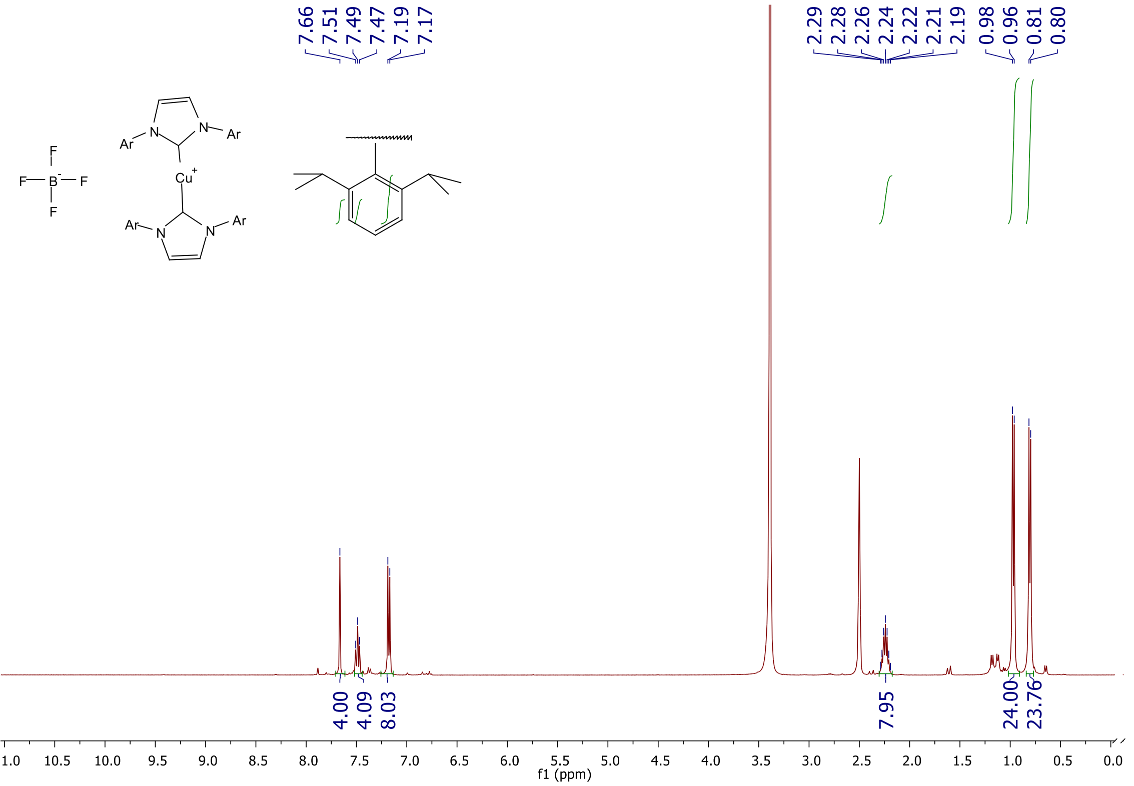


^{19}F NMR (376 MHz, DMSO-d_6)

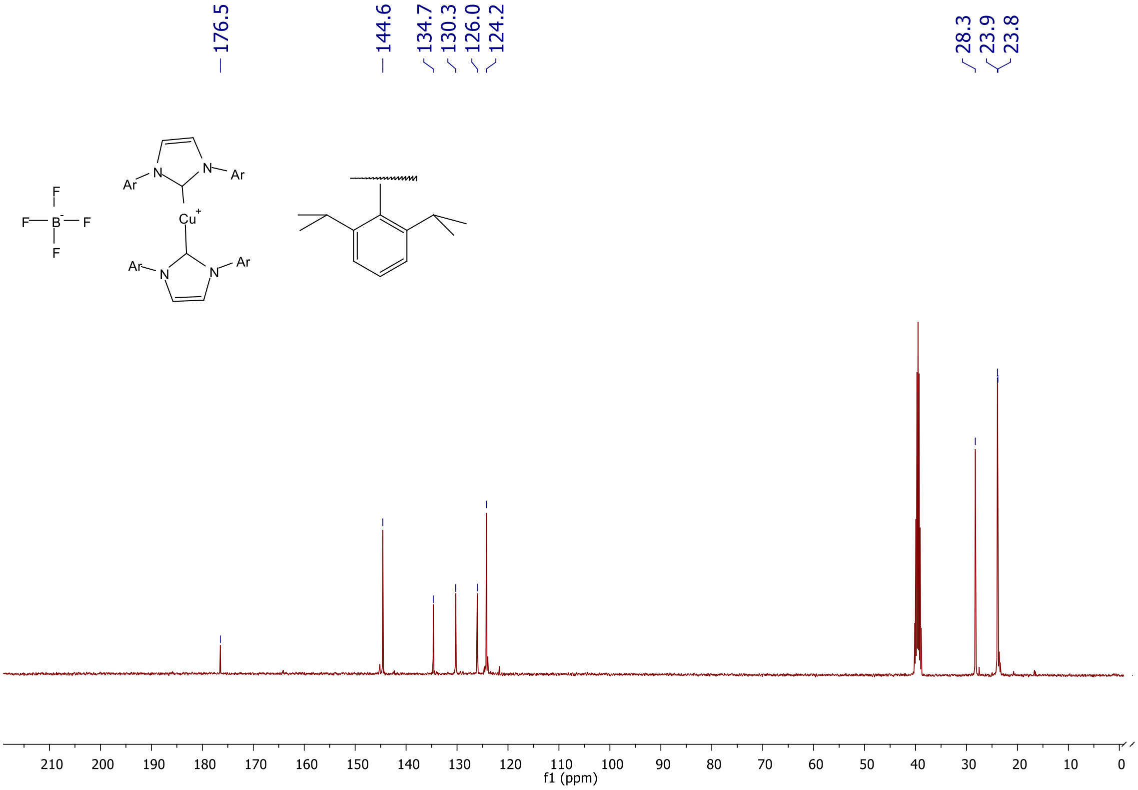


Bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper tetrafluoroborate [Cu(IPr)$_2$]BF$_4$

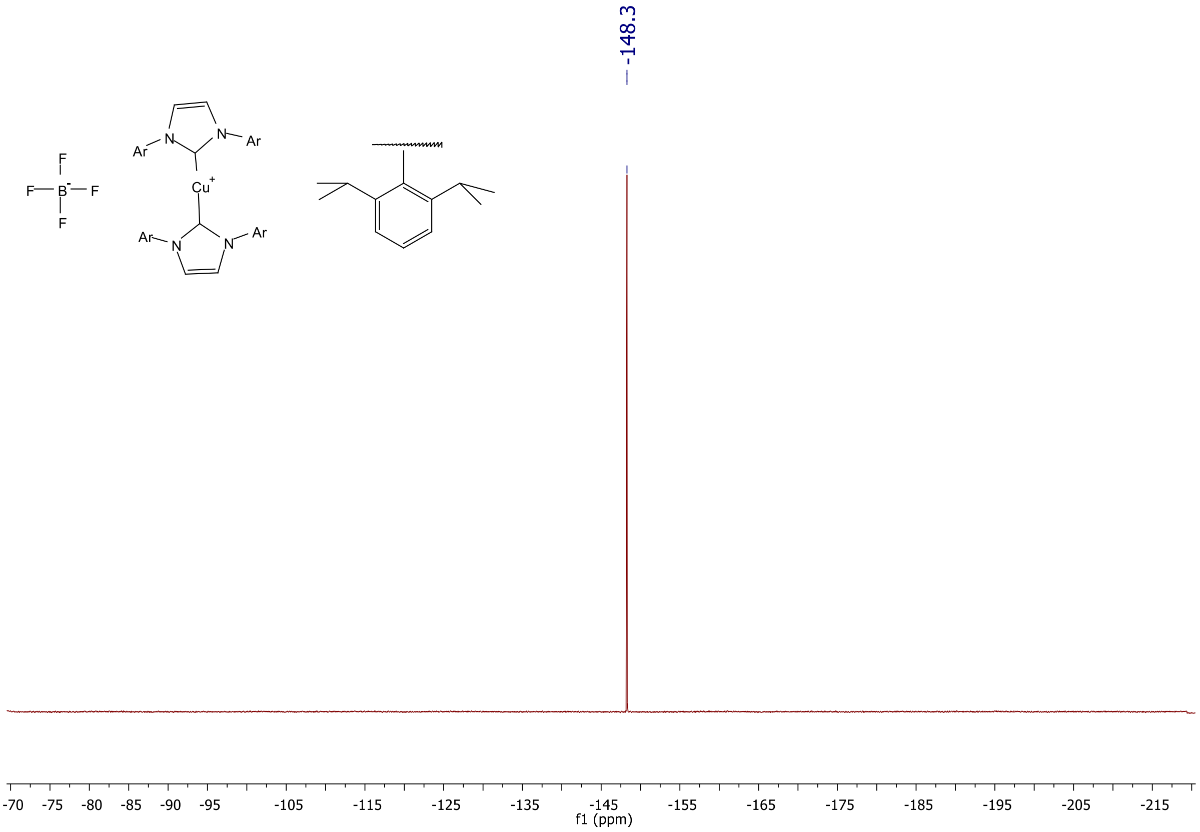
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (101MHz, DMSO-d_6)

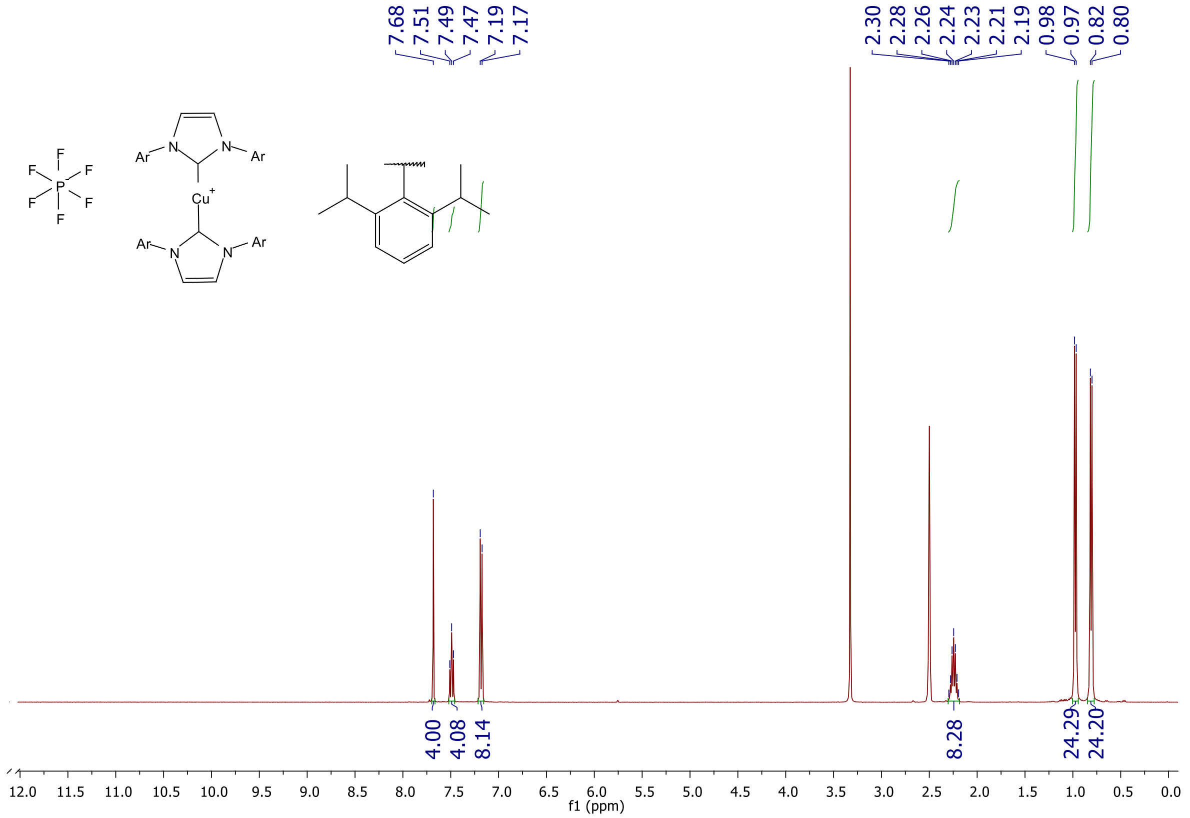


^{19}F NMR (376 MHz, DMSO-d_6)

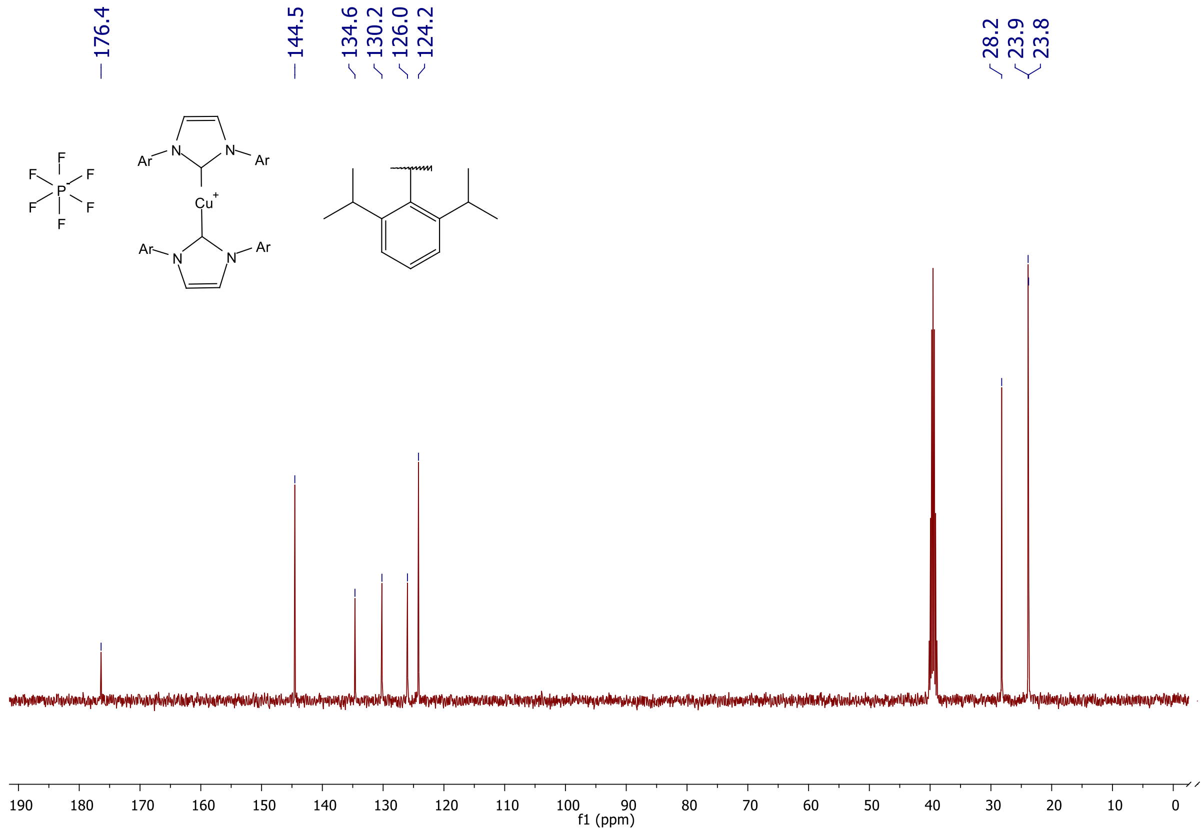


Bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]copper hexafluorophosphate [Cu(IPr)$_2$]PF$_6$

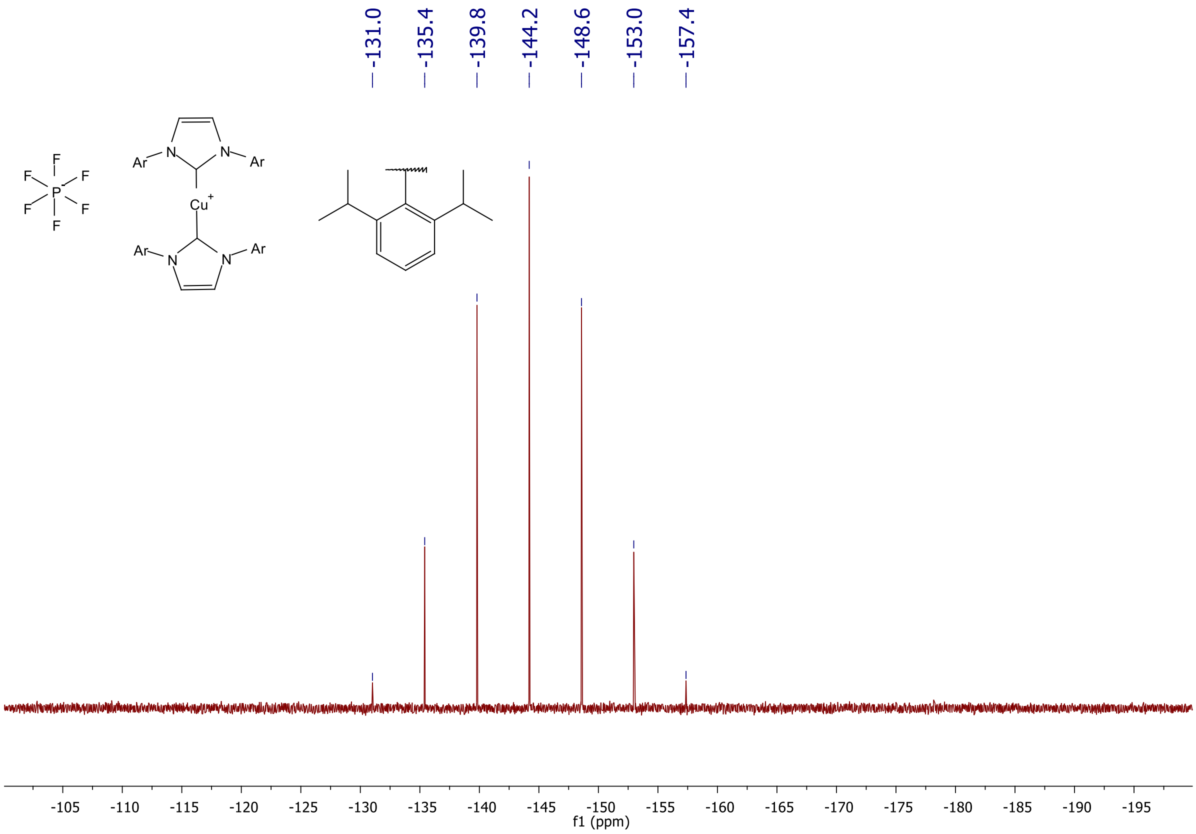
^{1}H NMR (400MHz, DMSO-d_6)



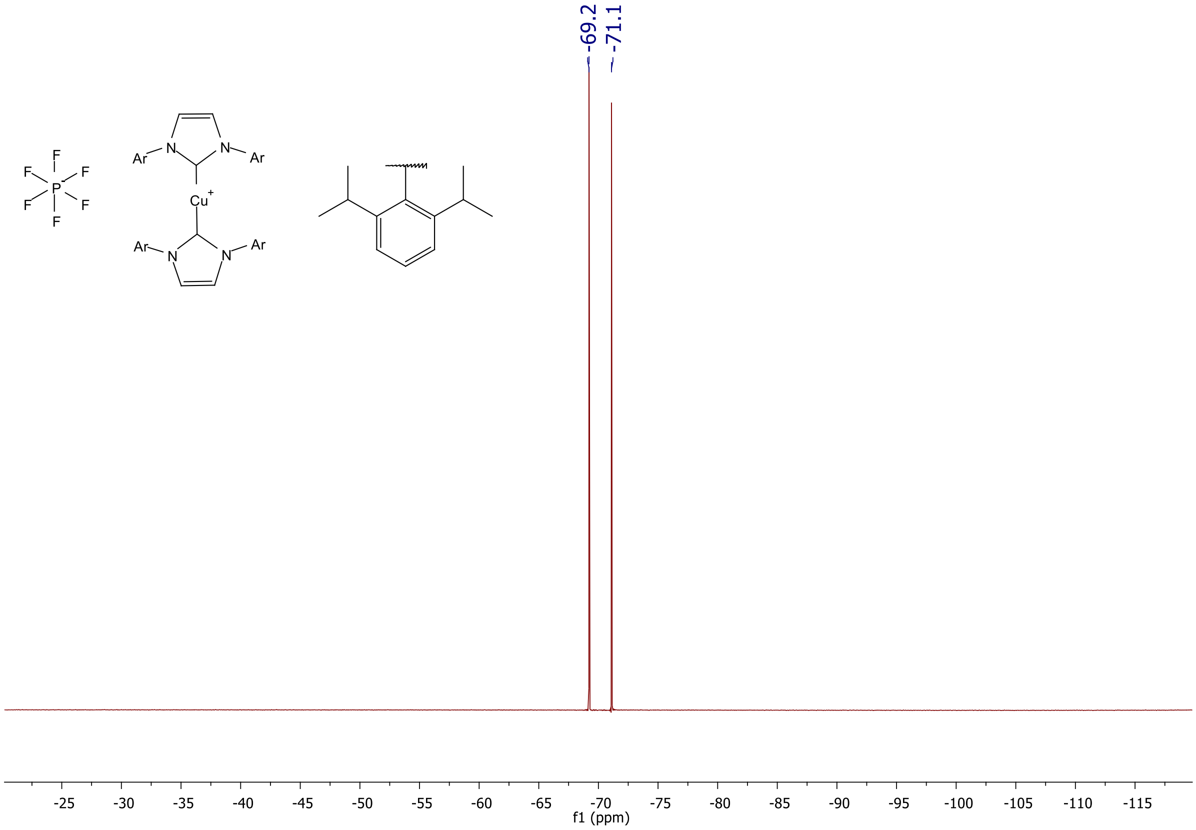
^{13}C NMR (101MHz, DMSO-d_6)



^{31}P NMR (162 MHz, DMSO-d_6)

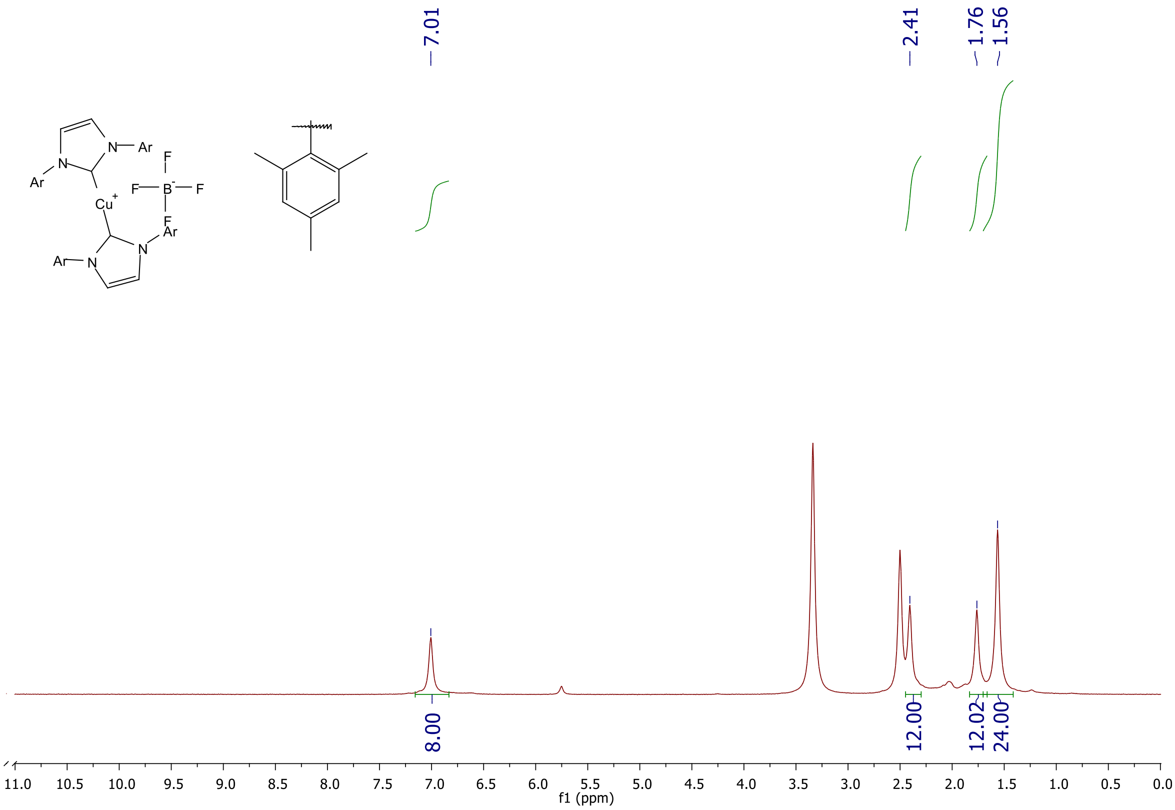


^{19}F NMR (376 MHz, DMSO-d_6)

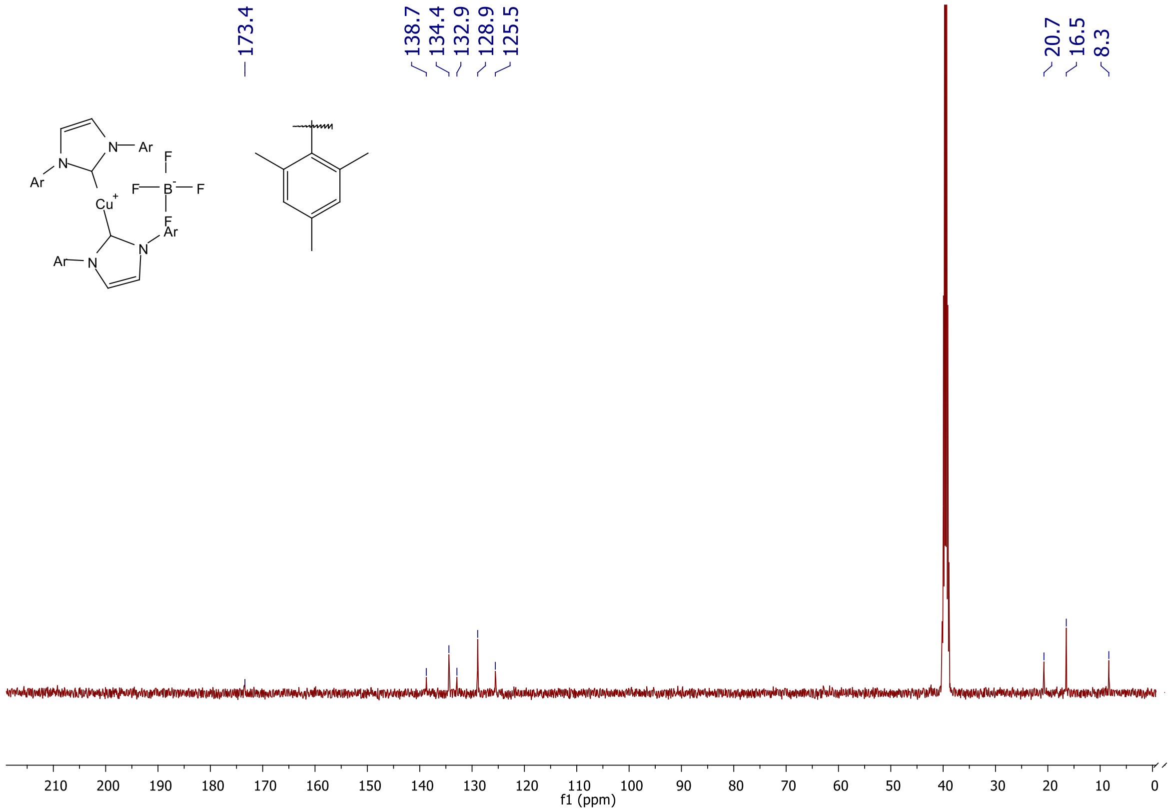


Bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper tetrafluoroborate [Cu(IMes^{Me})$_2$]BF$_4$

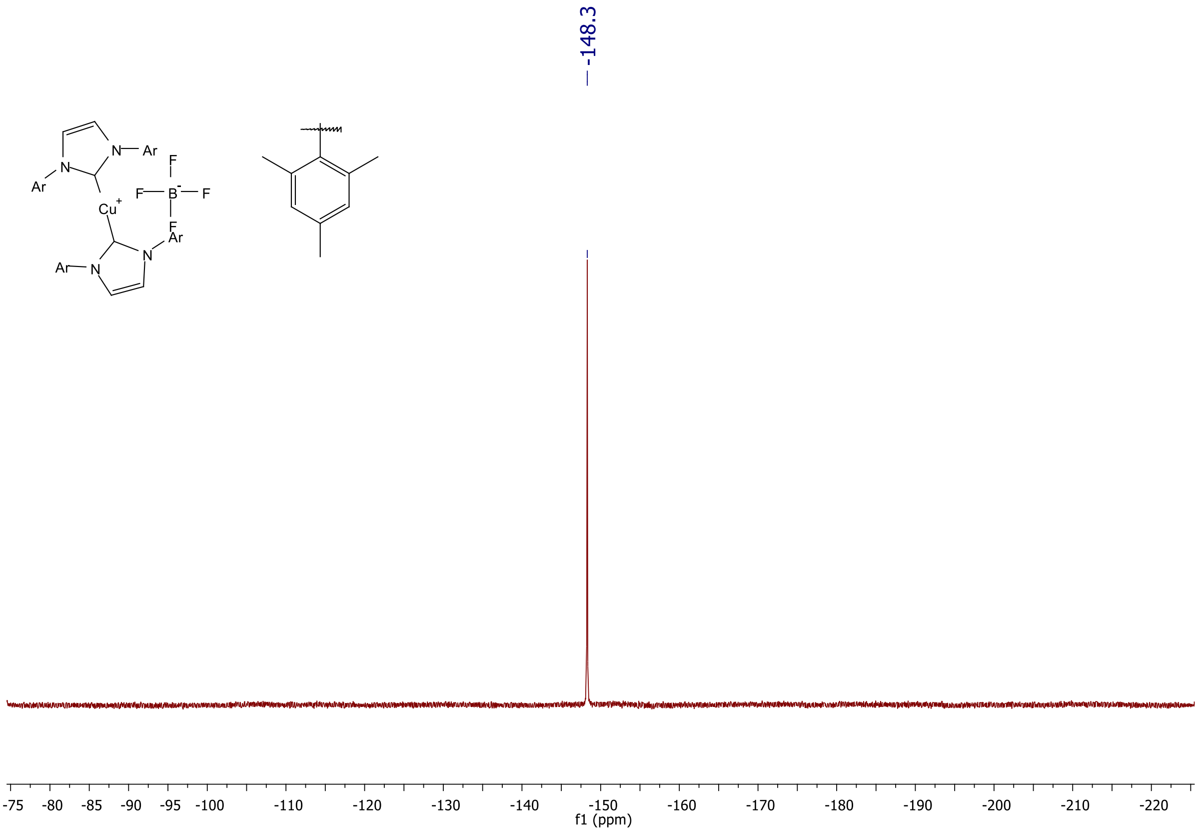
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

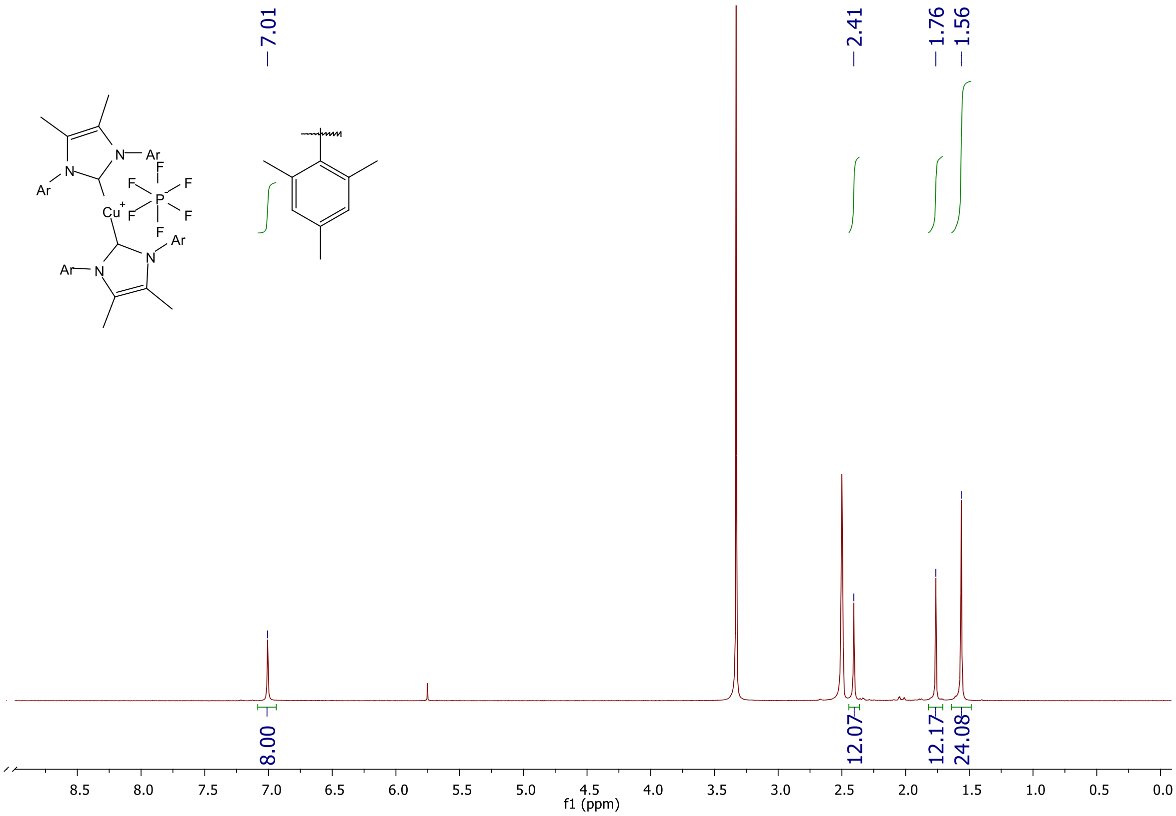


^{19}F NMR (376 MHz, DMSO-d_6)

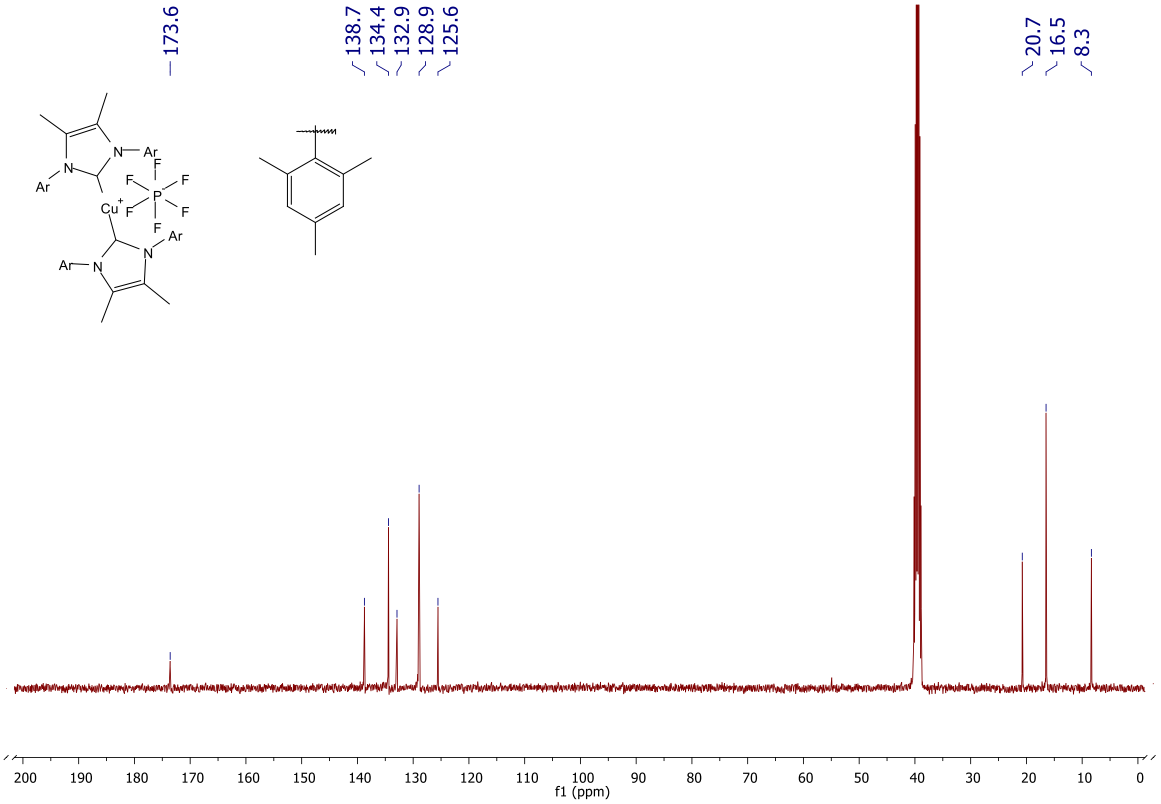


Bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper hexafluorophosphate [Cu(IMes^{Me})$_2$]PF$_6$

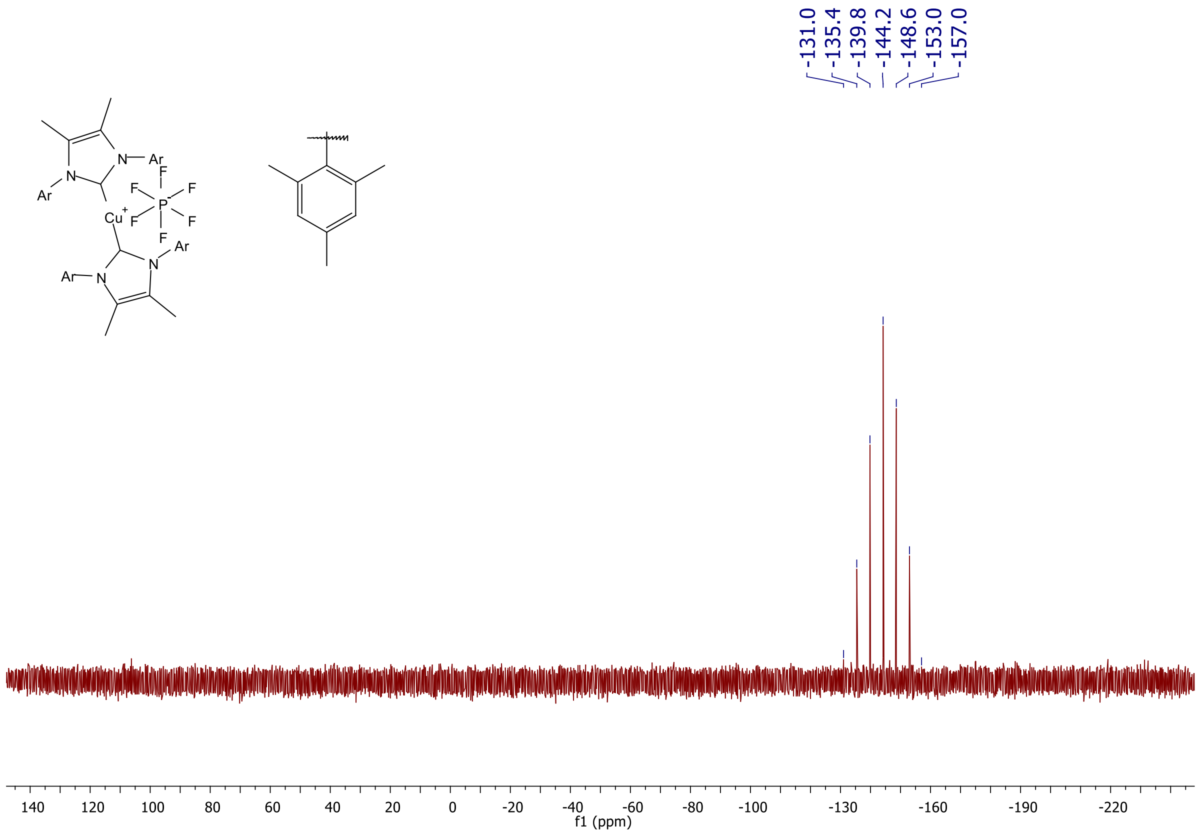
^{1}H NMR (400MHz, DMSO-d_6)



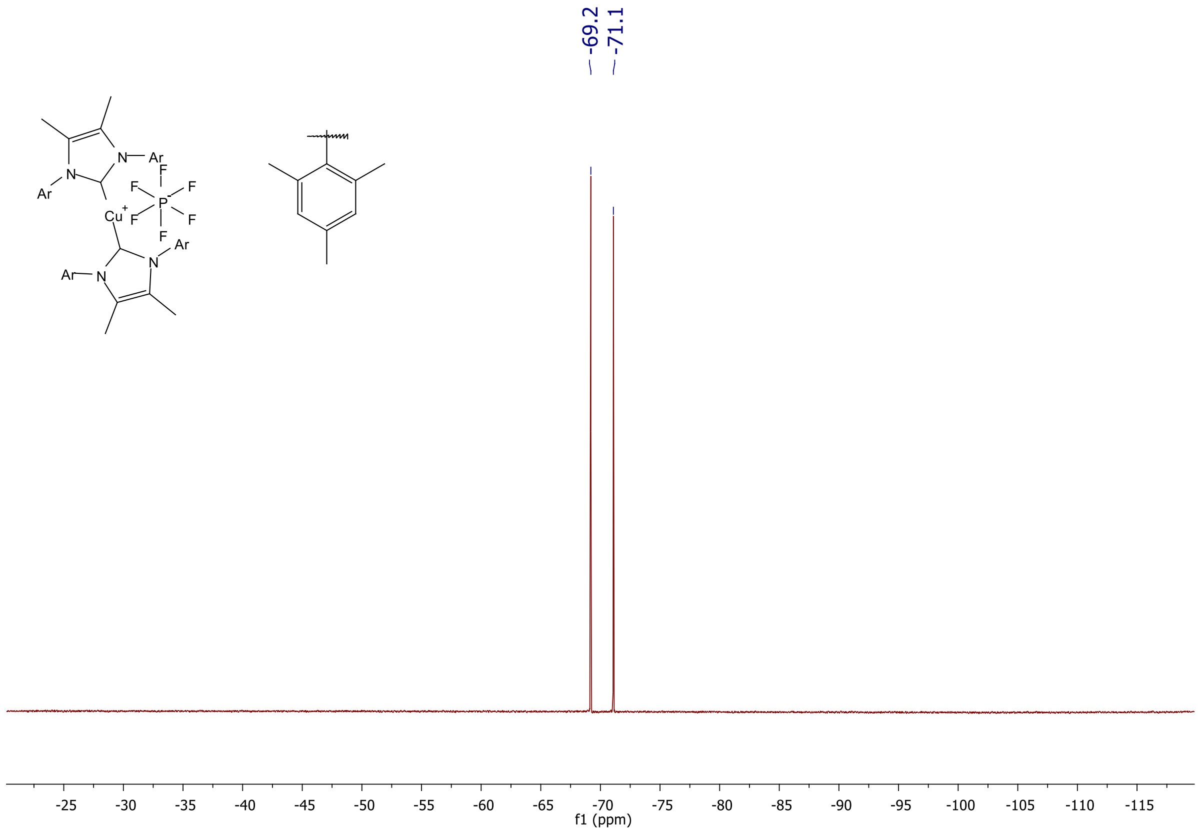
^{13}C NMR (101 MHz, DMSO-d_6)



^{31}P NMR (162 MHz, DMSO-d_6)

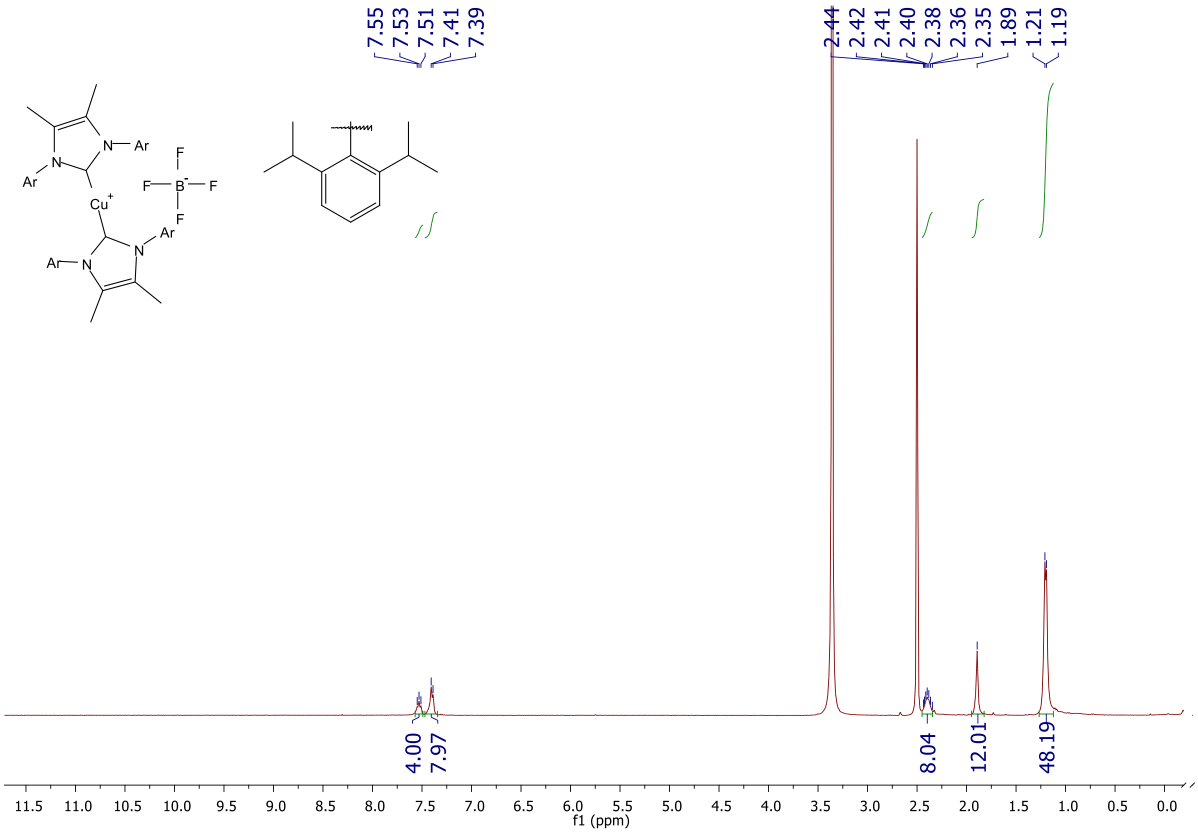


^{19}F NMR (376 MHz, DMSO-d_6)

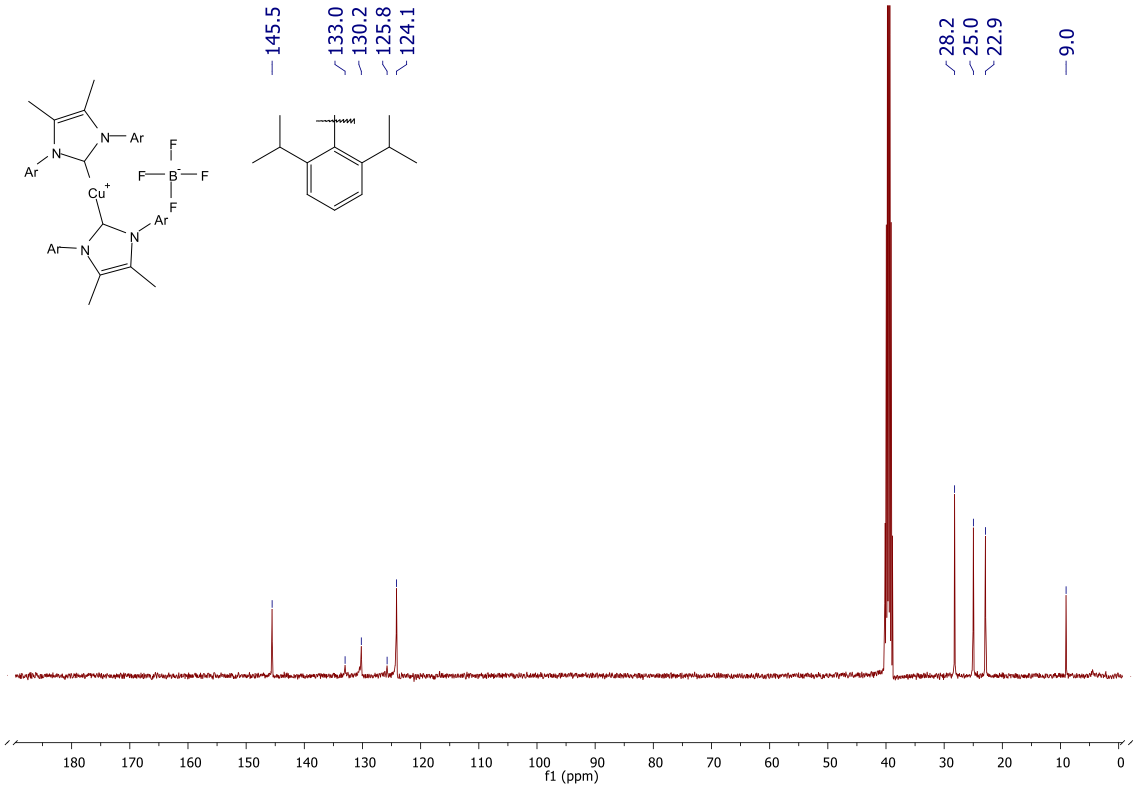


Bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper tetrafluoroborate [Cu(IPr^{Me})$_2$]BF$_4$

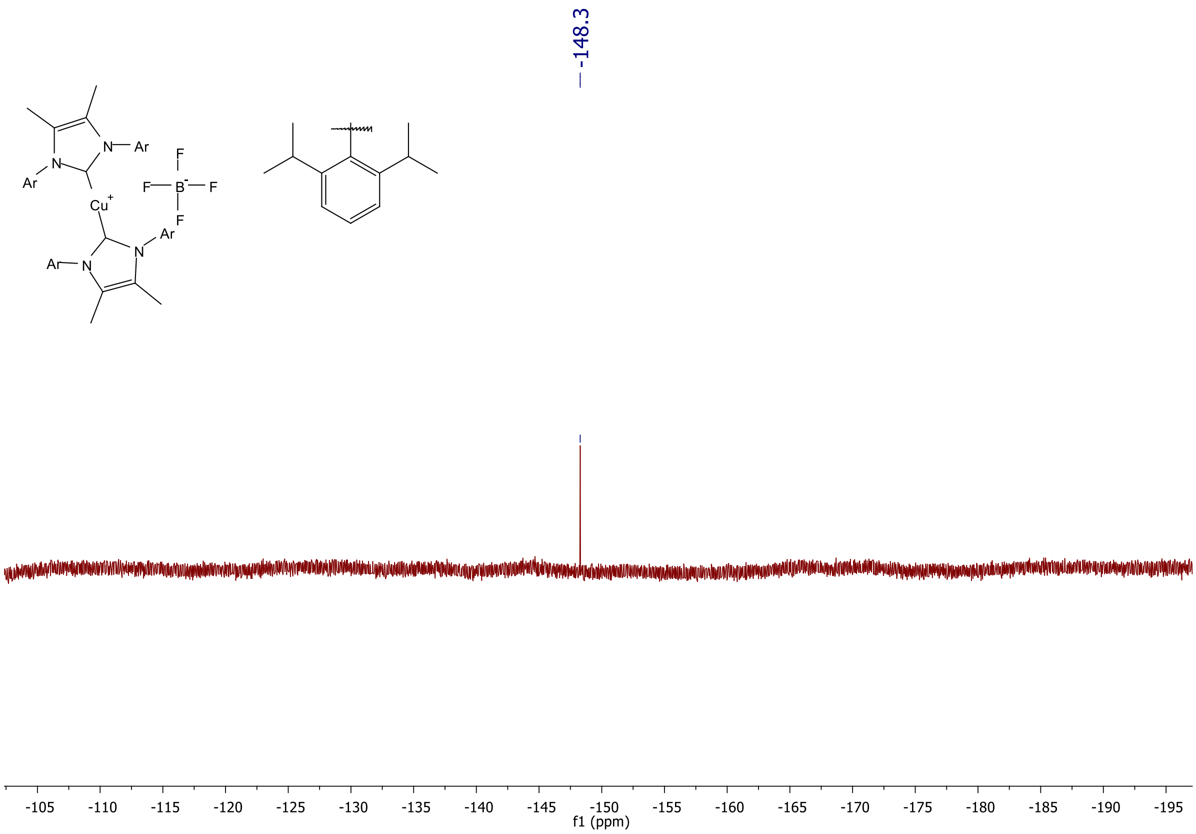
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

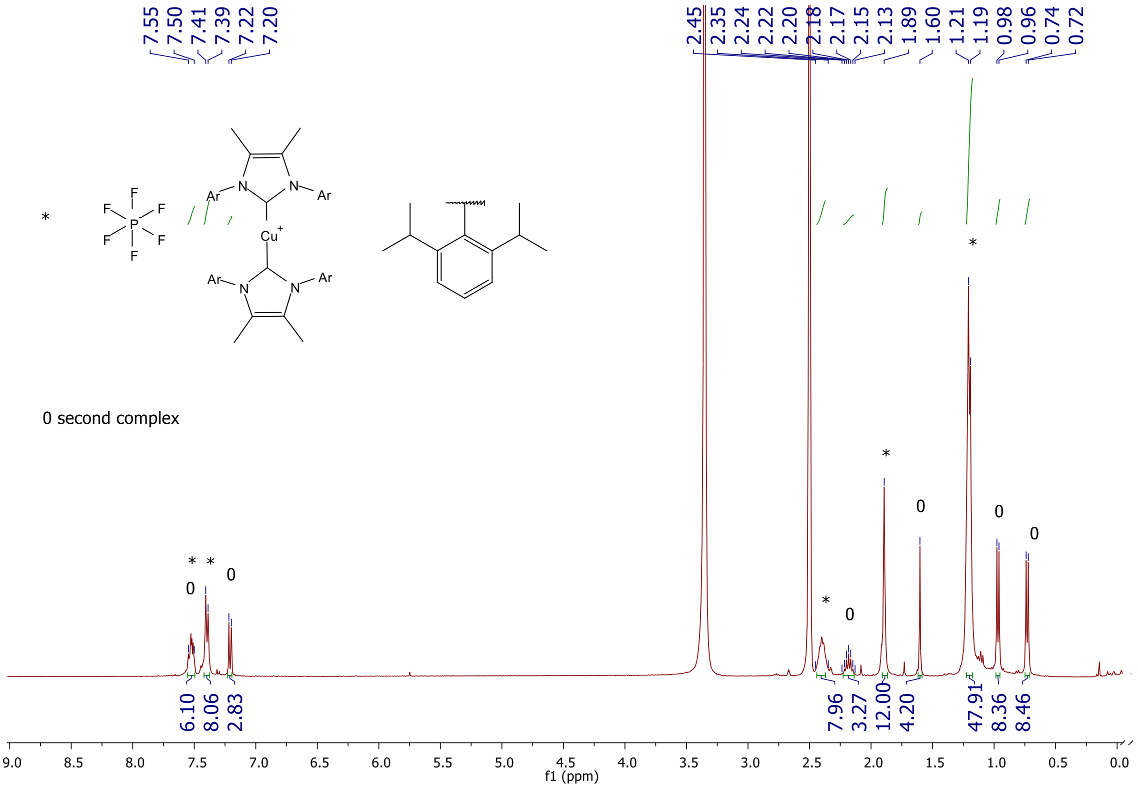


^{19}F NMR (376 MHz, DMSO-d_6)

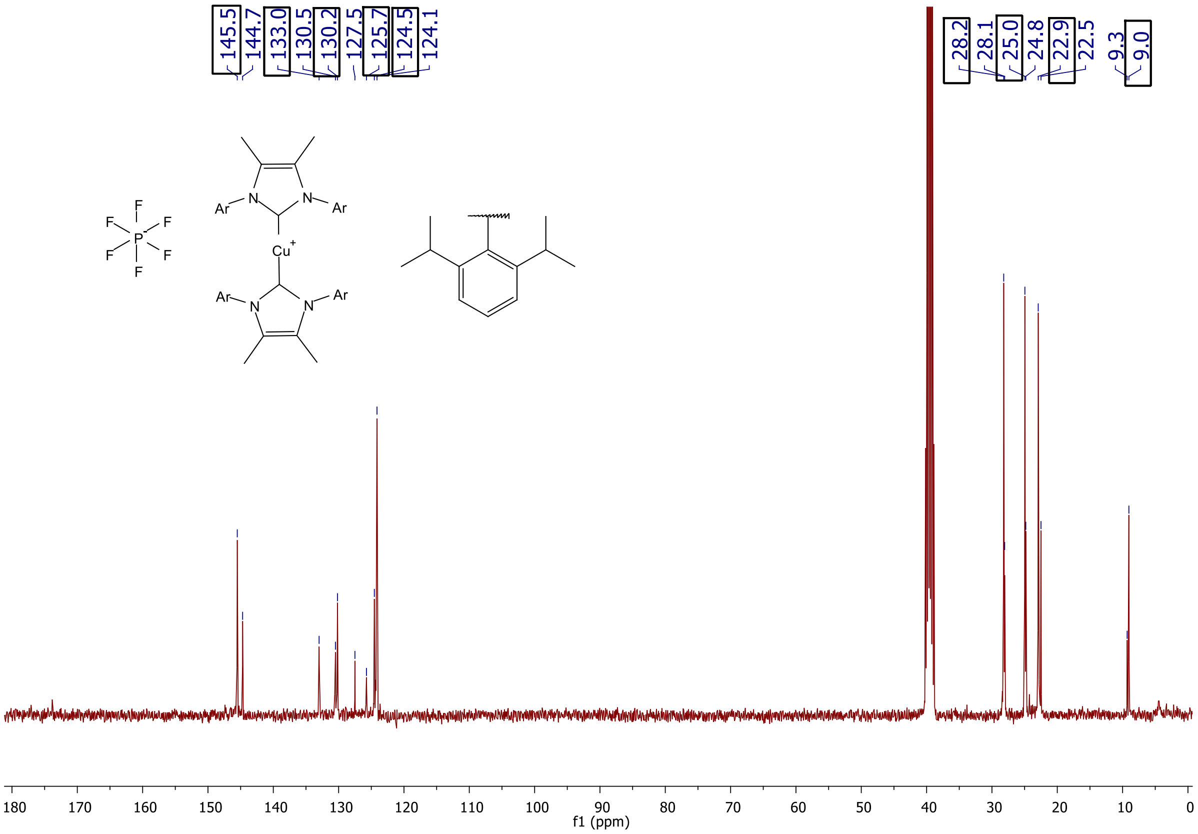


Bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]copper hexafluorophosphate [Cu(IPr^{Me})$_2$]PF$_6$

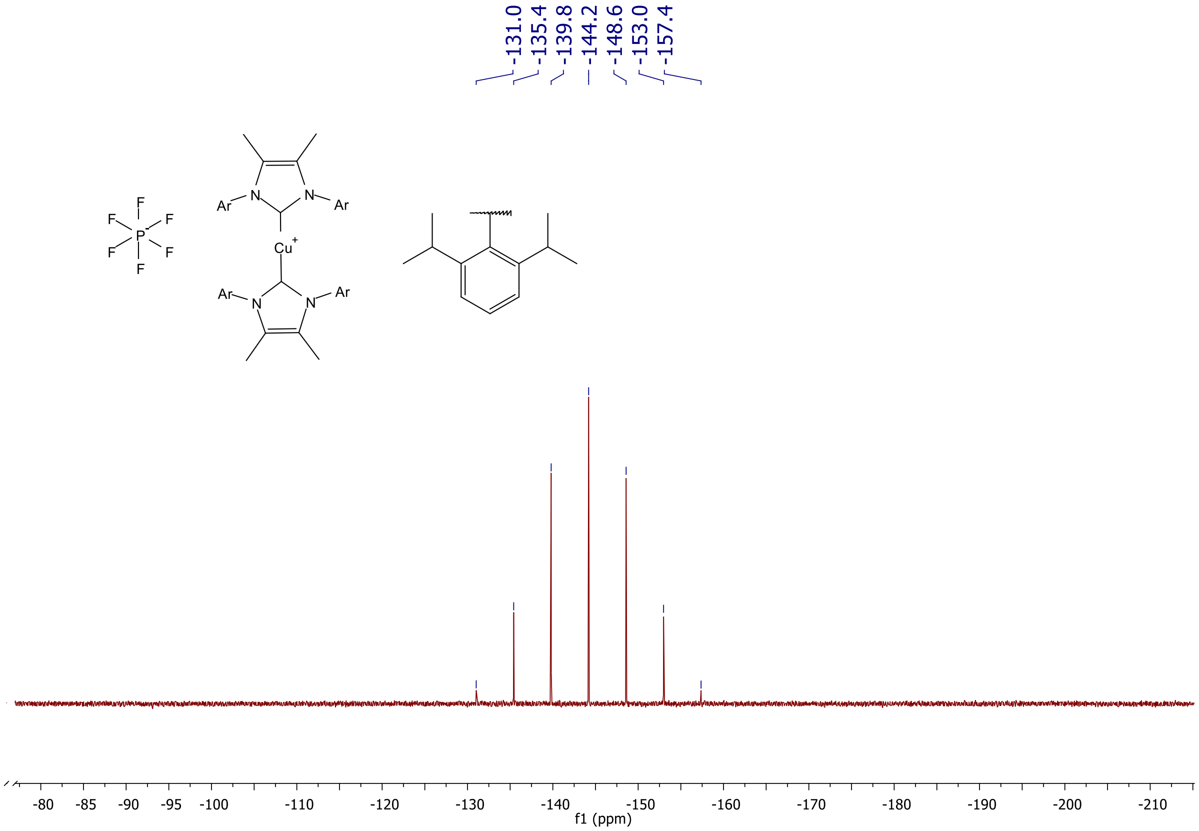
^{1}H NMR (400MHz, DMSO-d_6)



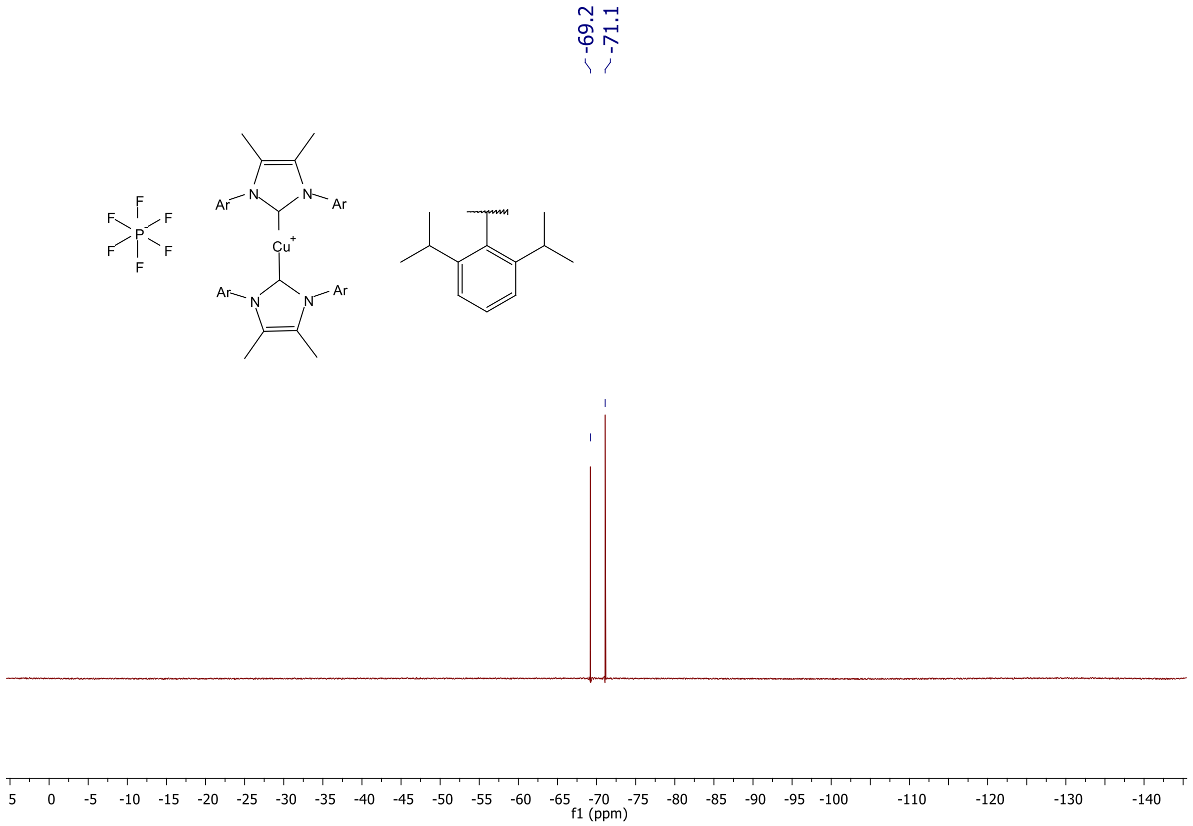
^{13}C NMR (101 MHz, DMSO-d_6)



^{31}P NMR (162 MHz, DMSO-d_6)



^{19}F NMR (376 MHz, DMSO-d_6)



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