Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Expedient mechanosynthesis of homoleptic [Ag(NHC)$_2$]Y (Y=BF$_4$, PF$_6$) complexes

Audrey Beillard,[a] Xavier Bantreil,*[a] Thomas-Xavier Métro,*[a] Jean Martinez,[a] and Frédéric Lamaty*[a]

[a] Institut des Biomolécules Max Mousseron (IBMM), UMR 5247, Université de Montpellier, CNRS, ENSCM, Université de Montpellier, Campus Triolet, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

E-mail: xavier.bantreil@umontpellier.fr; thomas-xavier.metro@umontpellier.fr; frederic.lamaty@umontpellier.fr

Table of content

1. Synthetic procedure

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 30 Hz. 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). ^{19}F NMR spectra were recorded on Bruker Avance AM 282 MHz or 376 MHz spectrometers and are reported in ppm. ^{31}P NMR spectra were recorded on Bruker Avance AM 162 MHz spectrometer and are reported in ppm. HRMS analysis were performed on a Q-Tof (Waters, ESI, 2001) spectrometer.

1.2. General table

Used methods for the treatment of reactions are described in the following tables. Those tables include important parameters for ball-mill syntheses.

Method A: The solid was recovered with water and the suspension was filtrated. The white solid was washed three times with water and dried under vacuum to afford product

Method B: The solid was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum to afford product.

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

Method D: The solid was recovered with dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum. The solid was dissolved in a minimum of dichloromethane, washed three times with water, dried with $MgSO_4$ and concentrated under vacuum. The solid was washed with water and diethyl ether and dried under vacuum to afford product.

1.2.1 General table for the mechanosynthesis of imidazolium tetrafluoroborate and hexaflurorophosphate

Entry	Product	Reagent	Aspect bp or mp °C	Eq.	Quantity (mmol)	Ball Mill	Time	Aspect of reaction mixture	Treatment	Yield (%)	Product Aspect
1	$1a\cdot HBF_4$	$1a\cdot HCl$	White powder	1.00	0.900	vbm (25 Hz)	30 min	White powder	Method A	95	White powder
		$NaBF_4$	White powder mp: 384	1.06	0.954						
2	$1b\cdot HBF_4$	$1a\cdot HCl$	White powder	1.00	0.868	vbm (25 Hz)	30 min	White powder	Method A	96	White powder
		$NaBF_4$	White powder mp: 384	1.06	0.920						
3	$1a\cdot HPF_6$	$1a\cdot HCl$	White powder	1.00	0.837	vbm (25 Hz)	30 min	White powder	Method A	94	White powder
		KPF_6	White powder mp: 575	1.20	1.004						
4	$1b\cdot HPF_6$	$1a\cdot HCl$	White powder	1.00	0.728	vbm (25 Hz)	30 min	White powder	Method A	90	White powder
		KPF_6	White powder mp: 575	1.20	0.973						

1.2.2 General table for the mechanosynthesis of silver-NHC complexes

Entry	Product	Reagent	Aspect bp or mp °C	Eq.	Quantity (mmol)	Ball Mill (Frequency)	Time	Aspect of reaction mixture	Treatment	Yield (%)	Product Aspect
1	$[Ag(1a)_2]BF_4$	$1a\cdot HBF_4$	White powder	1.00	0.323	vbm (25Hz)	2h	Black powder	Method B	91	White powder
		Silver oxide	Black powder mp: 280	0.55	0.178						
		NaOH	White solid mp: 318	1.10	0.355						
2	$[Ag(1b)_2]BF_4$	$1b\cdot HBF_4$	White powder	1.00	0.314	vbm (30Hz)	3h	Black powder	Method B	86	White powder
		Silver oxide	Black powder mp: 280	0.50	0.157						
		NaOH	White solid mp: 318	1.10	0.345						

3	[Ag(1c)$_2$]BF$_4$	IPr·HBF$_4$	White powder	1.00	0.286	vbm (30Hz)	3h	Black powder	Method C	91	White powder
		Silver oxide	Black powder mp: 280	0.50	0.143						
		NaOH	White solid mp: 318	1.10	0.315						
4	[Ag(1d)$_2$]BF$_4$	1d·HBF$_4$	White powder	1.00	0.274	vbm (30Hz)	3h	Black powder	Method B	86	White powder
		Silver oxide	Black powder mp: 280	0.50	0.137						
		NaOH	White solid mp: 318	1.10	0.301						
5	[Ag(1e)$_2$]BF$_4$	1e·HBF$_4$	White solid	1.00	0.422	vbm (30Hz)	1h	Black powder	Method B	92	White powder
		Silver oxide	Black powder mp: 280	0.55	0.232						
		NaOH	White solid mp: 318	1.10	0.464						
6	[Ag(1f)$_2$]BF$_4$	Bn$_2$Im·HBF$_4$	White powder	1.00	0.367	vbm (30Hz)	2h	Black sticky powder	Method B	85	White powder
		Silver oxide	Black powder mp: 280	0.50	0.183						
		NaOH	White solid mp: 318	1.10	0.404						
7	[Ag(1g)$_2$]BF$_4$	1g·HBF$_4$	White powder	1.00	0.334	vbm (30Hz)	3h	Black powder	Method B	74	White powder
		Silver oxide	Black powder mp: 280	0.50	0.167						
		NaOH	White solid mp: 318	1.10	0.387						
8	[Ag(1a)$_2$]PF$_6$	1a·HPF$_6$	White powder	1.00	0.293	vbm (25Hz)	2h	Black powder	Method B	91	White solid
		Silver oxide	Black powder mp: 280	0.55	0.161						
		NaOH	White solid mp: 318	1.10	0.322						

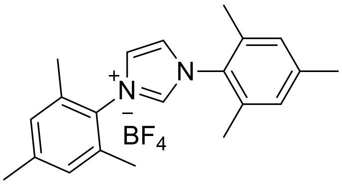
9	$[Ag(1b)_2]PF_6$	1b·HPF_6	White powder	1.00	0.285	vbm (30Hz)	3h	Black powder	Method B	91	White solid
		Silver oxide	Black powder mp: 280	0.50	0.143						
		NaOH	White solid mp: 318	1.10	0.314						
10	$[Ag(1c)_2]PF_6$	1c·HPF_6	White powder	1.00	0.262	vbm (30Hz)	3h	Black powder	Method D	72	White powder
		Silver oxide	Black powder mp: 280	0.50	0.131						
		NaOH	White solid mp: 318	1.10	0.288						
11	$[Ag(1d)_2]PF_6$	1d·HPF_6	White powder	1.00	0.252	vbm (30Hz)	3h	Black powder	Method B	91	White powder
		Silver oxide	Black powder mp: 280	0.50	0.126						
		NaOH	White solid mp: 318	1.10	0.277						
12	$[Ag(1e)_2]PF_6$	BnMeIm·HPF_6	White powder	1.00	0.321	vbm (30Hz)	1h	Black powder	Method B	94	White powder
		Silver oxide	Black powder mp: 280	0.55	0.177						
		NaOH	White solid mp: 318	1.10	0.353						
13	$[Ag(1f)_2]PF_6$	1f·HPF_6	White powder	1.00	0.328	vbm (30Hz)	2h	Black powder	Method B	85	White powder
		Silver oxide	Black powder mp: 280	0.50	0.164						
		NaOH	White solid mp: 318	1.10	0.361						
14	$[Ag(1g)_2]PF_6$	TPT·HPF_6	White powder	1.00	0.302	vbm (30Hz)	3h	Black powder	Method B	73	White powder
		Silver oxide	Black powder mp : 280	0.50	0.151						
		NaOH	White solid mp: 318	1.10	0.332						

1.2.3 General table for the one-pot two-step mechanosynthesis of silver-NHC complexes

Entry	Product	1st step						2nd step						Treatment	Yield (%)
		Reagent	Aspect mp or bp °C	Eq.	Quantity (mmol)	Time	Aspect of reaction mixture	Reagent	Aspect mp or bp °C	Eq.	Quantity (mmol)	Time	Aspect of reaction mixture		
1	[Ag(1a)$_2$]BF$_4$	1a·HCl	White powder	1.00	0.295	20 min	White powder	Silver oxide	Black powder mp: 280	0.50	0.148	2h30	Grey powder	Method B	84
		NaBF$_4$	White solid mp: 384	1.05	0.310			NaOH	White solid mp: 318	1.10	0.325				
2	[Ag(1a)$_2$]PF$_6$	1a·HCl	White powder	1.00	0.262	20 min	White powder	Silver oxide	Black powder mp: 280	0.50	0.131	2h30	Grey powder	Method B	78
		KPF$_6$	White solid mp: 575	1.05	0.275			NaOH	White solid mp: 318	1.10	0.288				

1.3. Imidazolium tetrafluoroborate synthesis

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



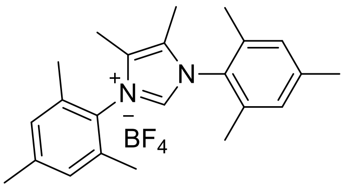
2,4,6-Trimethylaniline (10.4 mL, 74.0 mmol, 2.00 eq) was dissolved in methanol (40 mL). The resulting solution was cooled to 0 °C, and glyoxal 40% in water (4.23 mL, 37.0 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred two days. The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

Hydrochloric acid 4M in dioxane (9.45 mL, 37.8 mmol, 1.40 eq) and paraformaldehyde (811 mg, 27.0 mmol, 1.00 eq) were 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 ether to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (7.14 g, 20.9 mmol, 78%) as white powder. Product was found to be identical by NMR to literature data.[2]

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 vibratory 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$_6$*)[3] 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)-4,5-dimethyl]imidazolium tetrafluoborate 1b·HBF_4

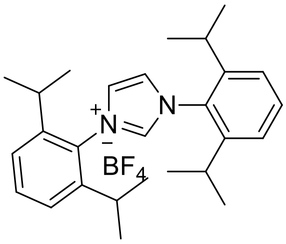


2,4,6-Trimethylaniline (4.15 mL, 29.6 mmol, 2.00 eq) was dissolved in methanol (29.6 mL). The resulting solution was cooled to 0 °C, and 2,3-butanedione (1.29 mL, 14.8 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred two days. The yellow suspension was filtrated, washed with a minimum of methanol and ether to afford *N,N'*-dimesityl-2,3-butanediimine (3.20 g, 10.0 mmol, 68%) as a yellow powder. Product was found to be identical by NMR to literature data.[5]

Paraformaldehyde (117.0 mg, 3.90 mmol, 1.25 eq) and hydrochloric acid 4M in dioxane (1.21 mL, 4.84 mmol, 1.55 eq) were 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 for 8 h at room temperature. The white solid was recovered by filtration and 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*$_6$)[6] 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-(2,6-di*iso*propylphenyl)imidazolium tetrafluoroborate 1c·HBF_4



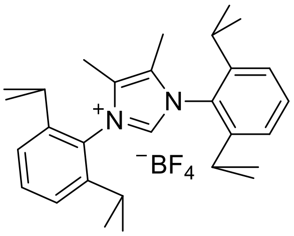
2,6-Diisopropylaniline (3.00 g, 16.9 mmol, 2.00 eq) was dissolved in methanol (16.3 mL). The resulting solution was cooled to 0 °C, and glyoxal 40% in water (975 µL, 8.45 mmol, 1.00 eq) and two or three drops of formic acid were added. The solution was warmed to room temperature and stirred three days.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

Hydrochloric acid 4M in dioxane (1.40 mL, 5.57 mmol, 1.40 eq) and paraformaldehyde (119.5 mg, 3.98 mmol, 1.00 eq) were stirred until complete dissolution of the white solid. THF (30 mL) followed by *N*,*N*'-bis(2,6-diisopropylphenyl)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 ether to afford 1,3-bis-(2,6-di*iso*propylphenyl)imidazolium chloride (988.1 mg, 2.32 mmol, 58%) as white powder. Product was found to be identical by NMR to literature data.[2]

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 vibratory 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$_6$*)[4] 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)-4,5-dimethyl]imidazolium tetrafluroborate 1d·HBF$_4$



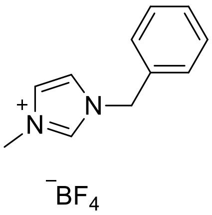
2,6-Diisopropylaniline (15.0 g, 84,6 mmol, 2.00 eq) was dissolved in methanol (42,3 mL). The resulting solution was cooled to 0 °C, and 2,3-butanedione (3.7 mL, 42,3 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred overnight. The yellow suspension was filtrated, washed with a minimum of methanol and ether to afford *N*,*N*'-bis-(2,6-diisopropylphenyl)butane-2,3-diimine (11.15 g, 27.6 mmol, 65%%) as a yellow powder. Product was found to be identical by NMR to literature data.[6]

Hydrochloric acid 4M in dioxane (2.89 mL, 11.6 mmol, 1.50) and paraformaldehyde (288.0 mg, 9.59 mmol, 1.25 eq) were stirred until complete dissolution of the white solid. The resulting solution was added dropwise at 0°C to a solution of *N*,*N*'-bis-(2,6-di*iso*propylphenyl)butane-2,3-diimine (3.11 g, 7.67 mmol, 1.00 eq) in THF (76.7 mL). The resulting solution was stirred at room temperature overnight. Then the white precipitate was collected by filtration, washed with THF and ether to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride (806.6 mg, 1.78 mmol, 23%) as white powder. Product was found to be indentical by NMR to literature data.[7]

[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 tetraflurorоborate (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 tetrafluroborate (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-Benzyl-3-methylimidazolium tetrafluoroborate 1e·HBF$_4$

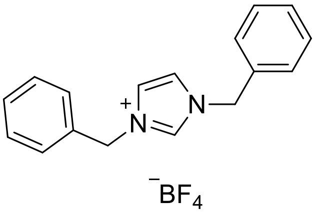


Method A: benzyl bromide (153 µL, 1.28 mmol, 1.00 eq) and *N*-methylimidazole (137 µL, 1.34 mmol, 1.05 eq) were introduced in a 25 mL teflon grinding bowl with one teflon balls (1 cm diameter). The bowl was closed, placed in the vibratory ball mill, subjected to grinding for 1 hour at 25 Hz and sodium tetrafluoroborate (148 mg, 1.35 mmol, 1.06 eq) was added. Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the vibratory ball mill and subjected to grinding for 30 minutes. The product was recovered with a mixture of dichloromethane and a saturated solution of sodium tetrafluoroborate. The organic layer was washed three times with a saturated solution of sodium tetrafluoroborate, dry with $MgSO_4$, filtrated and concentrated under vacuum to afford 1-benzyl-3-methylimidazolium tetrafluoroborate (261 mg, 1.00 mmol, 79%) as a white solid.

Method B: benzyl bromide (890 µL, 11.17 mmol, 1.00 eq) and *N*-methylimidazole (1.27 mL , 10.64 mmol, 1.05 eq) were introduced in a 250 mL stainless steel grinding bowl with eighty two stainless steel balls (1 cm diameter). The bowl was closed, placed in the planetary ball mill, subjected to grinding for 1 hour at 300 rpm and sodium tetrafluoroborate (1.24 g, 11.28 mmol, 1.20 eq) was added. Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the vibratory ball mill and subjected to grinding for 30 minutes. The product was precipitated with water, filtrated and dry under vacuum to afford 1-benzyl-3-methylimidazolium tetrafluoroborate (2.258 g, 8.68 mmol, 82%) as a white solid.

^{1}H NMR (300 MHz, DMSO-*d$_6$*)[9] δ 9.22 (s, 1H), 7.81 (s, 1H), 7.74 (s, 1H), 7.53 – 7.40 (m, 5H), 5.45 (s, 2H), 3.89 (s, 3H) ; **^{13}C NMR (75 MHz, DMSO-*d$_6$*)** δ 136.7, 134.9, 129.0, 128.8, 128.3, 124.0, 122.4, 51.9, 35.9 ; **^{19}F NMR (282 MHz, DMSO-*d$_6$*)** δ -148.2.

1,3-Dibenzylimidazolium tetrafluoroborate 1f·HBF$_4$

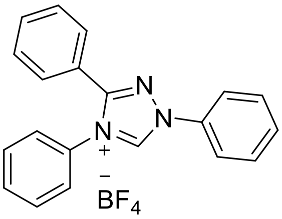


Benzyl bromide (1.91 mL, 16.00 mmol, 2.50 eq), sodium hydrogencarbonate (806 mg, 9.59 mmol, 1.50 eq) and imidazole (435 mg, 6.40 mmol, 1.00 eq) were introduced in a 250 mL stainless steel grinding bowl with eighty two stainless steel balls (1 cm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 2 hours in the planetary ball mill operated at 400 rpm. The white sticky oil was recovered with a mixture of water and ethyl acetate and the organic layer was extracted three times with water. The combined aqueous layer was concentrated under vacuum. The residue was dissolved in isopropanol, dried with $MgSO_4$ and filtrated over celite. The filtrate was concentrated under vacuum to afford 1,3-dibenzylimidazolium bromide (2.08 g, 6.32 mmol, 99%) as a white solid. Product was found to be identical to literature data.[10]

1,3-Dibenzylimidazolium bromide (700 mg, 2.13 mmol, 1.00 eq) was dissolved in water (10 ml). Sodium tetrafluoroborate (245.1 mg, 2.23 mmol, 1.05 eq) was added. The reaction mixture was stirred for 30 minutes. Then the precipitate was filtrated, washed with water and diethyl ether and dried under vaccum to afford 1,3-dibenzylimidazolium tetrafluoroborate (420.6 mg, 1.25 mmol, 59%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[11] δ 9.35 (s, 1H), 7.78 (d, *J* = 1.5 Hz, 2H), 7.52 – 7.30 (m, 10H), 5.41 (s, 4H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 136.4, 134.8, 129.3, 129.1, 128.5, 123.1, 52.4; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.2.

1,3,4-Triphenyl-1,2,4-triazolium tetrafluoroborate 1g·HBF$_4$



Benzoyl chloride (1.16 mL, 10.0 mmol, 1.00 eq) and aniline (913 µL, 10.0 mmol, 1.00 eq) were stirred together in toluene (10 mL) for 90 min at room temperature under Argon. A white precipitate appears quickly. After this time, the reaction mixture was heated to 130 °C for 2 h until the precipitate disappear. Then the reaction mixture was cooled to 50°C, a white precipitate appear and $SOCl_2$ (2.18 mL, 30.0 mmol, 3.00 eq) was added slowly. The reaction mixture was heated to 80 °C for 2 days with vigorous stirring until the precipitate disappear. The mixture was cooled to room temperature and the volatiles (residual $SOCl_2$ and toluene) were removed in vacuum. The residue was dissolved in THF (10 mL) and Et_3N (2.09 mL, 15.0 mmol, 1.50 eq) was added followed by the addition of phenylhydrazine (983 µL, 10.0 mmol, 1.00 eq) dropwise. The reaction mixture was stirred overnight at room temperature. After the solvent was removed in vacuum, the viscous residue was treated with aq 2% HOAc (16 mL) and warmed to 70 °C and stirred until the viscous oil solidified. The solid was collected on a Buchner funnel, washed with H_2O and MeOH and dried in air. N-phenylbenzamide phenylhydrazone was obtained (1.2485 g, 4.34 mmol, 43%) as a white solid. This product was sufficiently pure to be used in the next step without further purification.

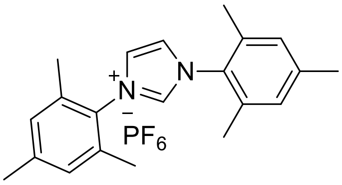
N-phenylbenzamide phenylhydrazone (1.00 g, 3.48 mmol, 1.00 eq), ammonium chloride (186 mg, 3.48 mmol, 1.00 eq) and triethyl orthoformiate (3.2 mL, 19.49 mmol, 5.60 eq) were agitated at 110°C for 24 hours. After cooling to room temperature, n-hexane was added to precipitate the product. The black solid was filtrated under vacuum and the solid was washed with acetone to obtain 1,3,4-triphenyl-1,2,4-triazolium chloride (460.5 mg, 1.38 mmol, 40%) as a beige solid. Product was found to be identical to literature data.

1,3,4-Triphenyl-1,2,4-triazolium chloride (1.00 g, 3.00 mmol, 1.00 eq) was dissolved in water (15 mL) and sodium tetrafluoroborate (394 mg, 3.59 mmol, 1.20 eq) was added. The resulting suspension was stirred for 15 minutes and filtrated under vacuum. The solid was washed with water, diethyl ether and dried under vacuum to afford 1,3,4-triphenyl-1,2,4-triazolium tetrafluoroborate (996 mg, 2.59 mmol, 93%) as a beige powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*)[8] δ 11.35 (s, 1H), 8.10 (d, *J* = 7.5 Hz, 2H), 7.78 (t, *J* = 7.5 Hz 2H), 7.72 – 7.63 (m, 7H), 7.58 – 7.50 (m, 4H) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 153.7, 143.6, 135.3, 132.8, 132.5, 132.0, 131.3, 130.9, 130.7, 129.7, 127.0, 122.8, 121.0; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.3.

1.4. Imidazolium hexafluorophosphate synthesis

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



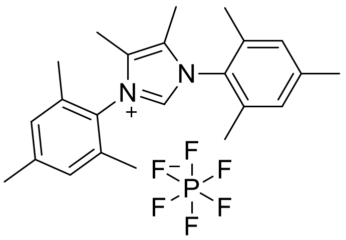
2,4,6-Trimethylaniline (10.4 mL, 74.0 mmol, 2.00 eq) was dissolved in methanol (40 mL). The resulting solution was cooled to 0 °C, and glyoxal 40% in water (4.23 mL, 37.0 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred two days. The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

Hydrochloric acid 4M in dioxane (9.45 mL, 37.8 mmol, 1.40 eq) and paraformaldehyde (811 mg, 27.0 mmol, 1.00 eq) were 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 ether to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (7.14 g, 20.9 mmol, 78%) as white powder. Product was found to be identical by NMR to literature data.[2]

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 vibratory 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$_6$*)[12] 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(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate 1b·HPF_6

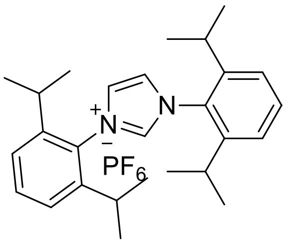


2,4,6-Trimethylaniline (4.15 mL, 29.6 mmol, 2.00 eq) was dissolved in methanol (29.6 mL). The resulting solution was cooled to 0 °C, and 2,3-butanedione (1.29 mL, 14.8 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred two days. The yellow suspension was filtrated, washed with a minimum of methanol and ether to afford *N,N'*-dimesityl-2,3-butanediimine (3.20 g, 10.0 mmol, 68%) as a yellow powder. Product was found to be identical by NMR to literature data.[5]

Paraformaldehyde (117.0 mg, 3.90 mmol, 1.25 eq) and hydrochloric acid 4M in dioxane (1.21 mL, 4.84 mmol, 1.55 eq) were 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 for 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 -144.3 (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-di*iso*propylphenyl)imidazolium hexafluorophosphate 1c·HPF_6



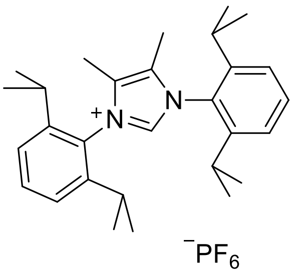
2,6-Diisopropylaniline (3.00 g, 16.9 mmol, 2.00 eq) was dissolved in methanol (16.3 mL). The resulting solution was cooled to 0 °C, and glyoxal 40% in water (975 µL, 8.45 mmol, 1.00 eq) and two or three drops of formic acid were added. The solution was warmed to room temperature and stirred three days.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

Hydrochloric acid 4M in dioxane (1.40 mL, 5.57 mmol, 1.40 eq) and paraformaldehyde (119.5 mg, 3.98 mmol, 1.00 eq) were stirred until complete dissolution of the white solid. THF (30 mL) followed by *N*,*N*'-bis(2,6-diisopropylphenyl)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 ether to afford 1,3-bis-(2,6-di*iso*propylphenyl)imidazolium chloride (988.1 mg, 2.32 mmol, 58%) as white powder. Product was found to be identical by NMR to literature data.[2]

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 vibratory 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*$_6$)[4] 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-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate 1d·HPF$_6$



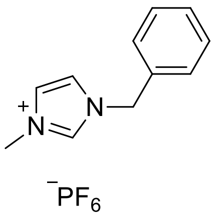
2,6-Diisopropylaniline (15.0 g, 84,6 mmol, 2.00 eq) was dissolved in methanol (42,3 mL). The resulting solution was cooled to 0 °C, and 2,3-butanedione (3.7 mL, 42,3 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred overnight. The yellow suspension was filtrated, washed with a minimum of methanol and ether to afford *N*,*N*'-bis-(2,6-diisopropylphenyl)butane-2,3-diimine (11.15 g, 27.6 mmol, 65%%) as a yellow powder. Product was found to be identical by NMR to literature data.[6]

Hydrochloric acid 4M in dioxane (2.89 mL, 11.6 mmol, 1.50) and paraformaldehyde (288.0 mg, 9.59 mmol, 1.25 eq) were stirred until complete dissolution of the white solid. The resulting solution was added dropwise at 0°C to a solution of *N*,*N*'-bis-(2,6-di*iso*propylphenyl)butane-2,3-diimine (3.11 g, 7.67 mmol, 1.00 eq) in THF (76.7 mL). The resulting solution was stirred at room temperature overnight. Then the white precipitate was collected by filtration, washed with THF and ether to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride (806.6 mg, 1.78 mmol, 23%) as white powder. Product was found to be indentical by NMR to literature data. [7]

[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-Benzyl-3-methylimidazolium hexafluorophosphate 1e·HPF$_6$

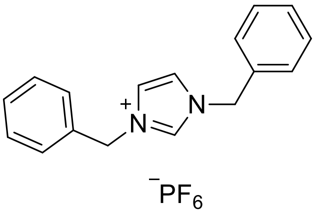


Method A: benzyl bromide (120 µL, 0.997 mmol, 1.00 eq) and *N*-methylimidazole (86 mg, 1.047 mmol, 1.05 eq) were introduced in a 25 mL teflon grinding bowl with one teflon balls (1 cm diameter). The bowl was closed, placed in the vibratory ball mill, subjected to grinding for 1 hour at 25 Hz and KPF_6 (220 mg, 1.196 mmol, 1.2 eq) was added. Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the vibratory ball mill and subjected to grinding for 30 minutes. The product was precipitated with water, filtrated and dry under vacuum to afford 1-benzyl-3-methylimidazolium hexafluoridophosphate (224 mg, 0.704 mmol, 71%) as a white powder.

Method B: benzyl bromide (995 µL, 8.32 mmol, 1.00 eq) and *N*-methylimidazole (696 µL, 8.731 mmol, 1.05 eq) were introduced in a 250 mL stainless steel grinding bowl with eighty two stainless steel balls (1 cm diameter). The bowl was closed, placed in the planetary ball mill, subjected to grinding for 1 hour at 300 rpm and KPF_6 (1.84 g, 9.978 mmol, 1.2 eq) was added. Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the vibratory ball mill and subjected to grinding for 30 minutes. The product was precipitated with water, filtrated and dry under vacuum to afford 1-benzyl-3-methylimidazolium hexafluorophosphate (2.41 g, 6.11 mmol, 74%) as a white powder.

^{1}H NMR (300 MHz, DMSO-*d$_6$*)[13] δ 9.20 (s, 1H), 7.78 (s, 1H), 7.70 (s, 1H), 7.48 - 7.32 (m, 5H), 5.41 (s, 2H), 3.85 (s, 3H); **^{13}C NMR (75 MHz, DMSO-*d$_6$*)** δ 136.7, 134.9, 129.0, 128.8, 128.3, 124.0, 122.4, 51.9, 35.9 ; **^{31}P NMR (162 MHz, DMSO-*d$_6$*)** δ -144.2 (sept, *J* = 711 Hz) ;**^{19}F NMR (282 MHz, DMSO-*d$_6$*)** δ -70.1 (d, *J* = 711 Hz).

1,3-Dibenzylimidazolium hexafluorophosphate 1f·HPF$_6$

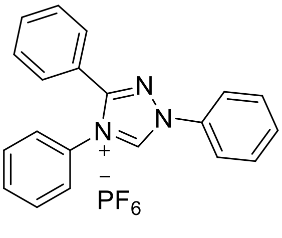


Method A: benzyl bromide (159 µL, 1.33 mmol, 2.00 eq), *N*-methylimidazole (45 mg, 0.667 mmol, 1.00 eq) and hydrogencarbonate (56 mg, 0.667 mmol, 1 eq) were introduced in a 25 mL teflon grinding bowl with one teflon balls (1 cm diameter). The bowl was closed, placed in the vibratory ball mill, subjected to grinding for 1 hour and 20 minutes at 25 Hz and potassium hexafluorophosphate (147 mg, 0.800 mmol, 1.20 eq) was added. Total mass of the reagents was calculated so that miling load equals 19.2 mg/mL. The bowl was closed, placed in the vibratory ball mill and subjected to grinding for 30 minutes. The product was precipitated with water, filtrated and dry under vacuum to afford 1,3-dibenzylimidazolium hexafluorophosphate (191 mg, 0.484 mmol, 73%) as a white powder.

Method B: benzyl bromide (352 µL, 2.95 mmol, 2.00 eq), *N*-methylimidazole (100.3 mg, 1.47 mmol, 1.00 eq) and hydrogencarbonate (123.7 mg, 1.47 mmol, 1.00 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel balls (1 cm diameter). Total mass of the reagents was calculated so that miling load equals 76.8 mg/mL. The bowl was closed, placed in the vibratory ball mill, subjected to grinding for 2 hours at 25 Hz. Reaction mixture was recovered with water washed one time with ethyl acetate. Potassium hexafluorophosphate (325.4 mg, 1.77 mmol, 1.20 eq) was added in the aqueous layer. The precipitate was filtrated, washed with water and dry under vacuum to afford 1,3-dibenzylimidazolium hexafluorophosphate (500.4 mg, 1.27 mmol, 86%) as a white powder.

^{1}H NMR (300 MHz, DMSO-*d$_6$*)[14] δ 9.38 (s, 1H), 7.82 (s, 2H), 7.48 – 7.36 (m, 10H), 5.43 (s, 4H); **^{13}C NMR (75 MHz, DMSO-*d$_6$*)** δ 136.3, 134.7, 129.1, 128.8, 128.3, 122.9, 52.1; **^{19}F NMR (282 MHz, DMSO-*d$_6$*)** δ -70.1 (d, *J* = 711 Hz).

1,3,4-Triphenyl-1,2,4-triazolium hexafluorophosphate 1g·HPF$_6$



Benzoyl chloride (1.16 mL, 10.0 mmol, 1.00 eq) and aniline (913 µL, 10.0 mmol, 1.00 eq) were stirred together in toluene (10 mL) for 90 min at room temperature under Argon. A white precipitate appears quickly. After this time, the reaction mixture was heated to 130 °C for 2 h until the precipitate disappear. Then the reaction mixture was cooled to 50°C, a white precipitate appear and $SOCl_2$ (2.18 mL, 30.0 mmol, 3.00 eq) was added slowly. The reaction mixture was heated to 80 °C for 2 days with vigorous stirring until the precipitate disappear. The mixture was cooled to room temperature and the volatiles (residual $SOCl_2$ and toluene) were removed in vacuum. The residue was dissolved in THF (10 mL) and Et_3N (2.09 mL, 15.0 mmol, 1.50 eq) was added followed by the addition of phenylhydrazine (983 µL, 10.0 mmol, 1.00 eq) dropwise. The reaction mixture was stirred overnight at room temperature. After the solvent was removed in vacuum, the viscous residue was treated with aq 2% HOAc (16 mL) and warmed to 70 °C and stirred until the viscous oil solidified. The solid was collected on a Buchner funnel, washed with H_2O and MeOH and dried in air. N-phenylbenzamide phenylhydrazone was obtained (1.2485 g, 4.34 mmol, 43%) as a white solid. This product was sufficiently pure to be used in the next step without further purification.

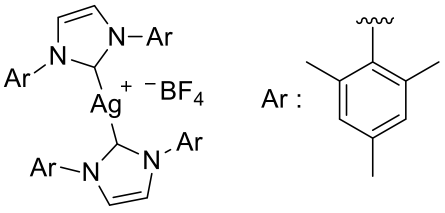
N-phenylbenzamide phenylhydrazone (1.00 g, 3.48 mmol, 1.00 eq), ammonium chloride (186 mg, 3.48 mmol, 1.00 eq) and triethyl orthoformiate (3.2 mL, 19.49 mmol, 5.60 eq) were agitated at 110°C for 24 hours. After cooling to room temperature, n-hexane was added to precipitate the product. The black solid was filtrated under vacuum and the solid was washed with acetone to obtain 1,3,4-triphenyl-1,2,4-triazolium chloride (460.5 mg, 1.38 mmol, 40%) as a beige solid. Product was found to be identical to literature data.

1,3,4-triphenyl-1,2,4-triazolium chloride (1.00 g, 3.00 mmol, 1.00 eq) was dissolved in water (15 mL) and potassium hexafluorophosphate (661 mg, 3.59 mmol, 1.20 eq) was added. The resulting suspension was stirred for 15 minutes and filtrated under vacuum. The solid was washed with water and dried under vacuum to afford 1,3,4-triphenyl-1,2,4-triazolium hexafluorophosphate (1.214 g, 2.74 mmol, 91%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.35 (s, 1H), 8.10 (d, *J* = 7.1 Hz, 2H), 7.79 (t, *J* = 7.8 Hz, 2H), 7.73 – 7.61 (m, 7H), 7.58 – 7.50 (m, 4H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 153.7, 143.6, 135.3, 132.8, 132.5, 132.0, 131.3, 130.9, 130.7, 129.7, 127.0, 122.8, 121.0; **^{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* = 711.3 Hz).

1.4. Synthesis of [Ag(NHC)$_2$]BF$_4$

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1a)$_2$]BF$_4$

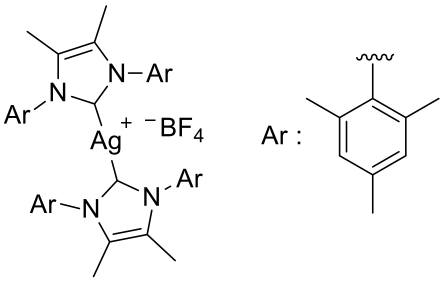


Method A: 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate (126.6 mg, 0.323 mmol, 1.00 eq), silver oxide (41.1 mg, 0.178 mmol, 0.55 eq) and sodium hydroxide (14.2 mg, 0.355 mmol, 1.1 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). 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 2 hours in the vibratory ball mill operated at 25 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene]silver tetrafluoroborate (117.6 mg, 0.146 mmol, 91%) as a white solid.

Method B: 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (100.7 mg, 0.295 mmol, 1.00 eq) and sodium tetrafluoroborate (34.1 mg, 0.310 mmol, 1.05 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). The bowl was closed and subjected to grinding for 20 minutes in the vibratory ball mill operated at 25 Hz. Afterwards, silver oxide (39.2 mg, 0.148 mmol, 0.50 eq) and sodium hydroxide (13.0 mg, 0.325 mmol, 1.10 eq) were added. 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 2 hours and 30 minutes. The black powder 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]silver tetrafluoroborate (100.0 mg, 0.124 mmol, 84%) as a white solid.

^{1}H NMR (300 MHz, DMSO-*d$_6$*) δ 7.67 (d, *J* = 1.4 Hz, 4H), 6.99 (s, 8H), 2.41 (s, 12H), 1.67 (s, 24H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 181.4 (dd, *J* = 192.4, 13.8 Hz), 138.8, 134.9, 134.0, 128.8, 123.63, 123.58, 20.7, 16.7; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.3 ; **HRMS** calcd for $C_{42}H_{48}N_4Ag$ [M – BF_4^-]$^+$: 715.2930 ; found : 715.2932.

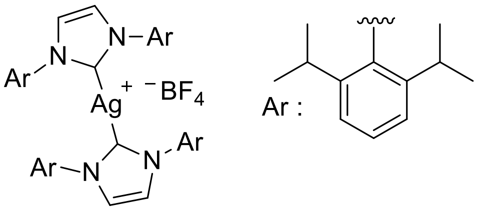
Bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1b)$_2$]BF$_4$ (unprecedented)



[1,3-Bis(2,4,6-trimethylphenyl-4,5-dimethyl)]imidazolium tetrafluoborate (131.8 mg, 0.314 mmol, 1.00 eq), silver oxide (36.3 mg, 0.157 mmol, 0.50 eq) and sodium hydroxide (13.8 mg, 0.345 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 3 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver tetrafluoroborate (117.8 mg, 0.137 mmol, 86%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.00 (s, 8H), 2.42 (s, 12H), 1.81 (s, 12H), 1.61 (s, 24H) ; **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.3 (dd, *J* = 190.6, 13.7 Hz), 138.7, 134.4, 133.2, 128.9, 125.94, 125.89, 20.7, 16.6, 8.5; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -143.6 ; **HRMS** calcd for $C_{46}H_{56}N_4Ag$ $[M - BF_4^-]^+$: 771.3536 ; found : 771.3565.

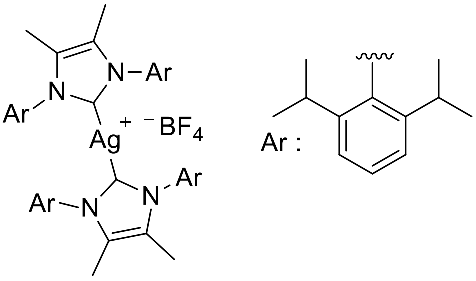
Bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1c)$_2$]BF$_4$ (unprecedented)



1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium tetrafluoroborate (136.2 mg, 0.286 mmol, 1.00 eq), silver oxide (33.1 mg, 0.143 mmol, 0.50 eq) and sodium hydroxide (12.6 mg, 0.315 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 3 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum. The yellow solid was washed with diethyl ether and dried under vacuum to afford bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]silver tetrafluoroborate (126.5 mg, 0.130 mmol, 91%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d_6*) δ 7.76 (s, 4H), 7.50 (t, *J* = 7.8 Hz, 4H), 7.18 (d, *J* = 7.8 Hz, 8H), 2.27 – 2.13 (m, 8H), 1.01 (d, *J* = 6.8 Hz, 24H), 0.75 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR (101 MHz, DMSO-*d_6*)** δ 181.4 (dd, *J* = 201.9, 14.4 Hz), 144.7, 134.5, 130.3, 125.71, 125.65, 124.1, 28.1, 24.0, 23.7 ; **^{19}F NMR (376 MHz, DMSO-*d_6*)** δ -148.3 ; **HRMS** calcd for $C_{54}H_{72}N_4Ag$ $[M - BF_4^-]^+$: 883.4808 ; found : 883.4803.

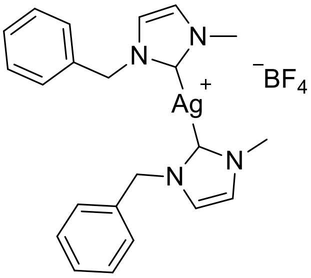
Bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1d)$_2$]BF$_4$ (unprecedented)



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium tetrafluoroborate (138.2 mg, 0.274 mmol, 1.00 eq), silver oxide (31.7 mg, 0.137 mmol, 0.50 eq) and sodium hydroxide (12.1 mg, 0.301 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 3 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver tetrafluoroborate (120.5 mg, 0.117 mmol, 86%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d_6*) δ 7.53 (t, *J* = 7.8 Hz, 4H), 7.21 (d, *J* = 7.8 Hz, 8H), 2.13 (sept, *J* = 6.9 Hz, 8H), 1.69 (s, 12H), 1.02 (d, *J* = 6.9 Hz, 24H), 0.69 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR (101 MHz, DMSO-*d_6*)** δ 178.4 (dd, *J* = 204.3, 14.7 Hz), 144.7, 132.7, 130.5, 127.2, 127.1, 124.4, 27.9, 25.0, 22.6, 9.2 ; **^{19}F NMR (376 MHz, DMSO-*d_6*)** δ -148.3 ; **HRMS** calcd for $C_{58}H_{80}N_4Ag$ $[M - BF_4^-]^+$: 939.5434; found : 939.5429.

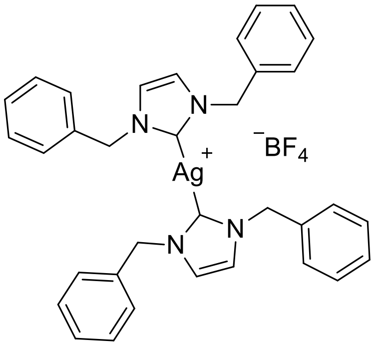
Bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1e)$_2$]BF$_4$ (unprecedented)



1-Benzyl-3-methylimidazolium tetrafluoroborate (109.7 mg, 0.422 mmol, 1.00 eq), silver oxide (53.7 mg, 0.232 mmol, 0.55 eq) and sodium hydroxide (18.6 mg, 0.464 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 1 hour in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate (104.3 mg, 0.193 mmol, 92%) as a white powder.

^{1}H NMR (300 MHz, DMSO-*d$_6$*) δ 7.56 (s, 2H), 7.47 (s, 2H), 7.41 – 7.15 (m, 10H), 5.32 (s, 4H), 3.77 (s, 6H) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 137.5, 128.9, 128.1, 127.6, 123.4, 122.5, 54.1, 38.3 (The ^{13}C of carbene was not observed due to the low concentration of the sample) ; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.3; **HRMS** calcd for $C_{22}H_{24}N_4Ag$ [M – BF_4^-]$^+$: 451.1052; found: 451.1050.

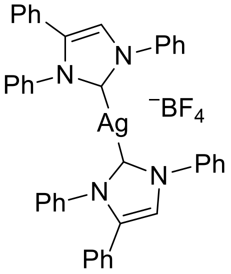
Bis[1,3-dibenzylimidazol-2-ylidene]silver tetrafluoroborate [Ag(1f)$_2$]BF$_4$ (unprecedented)



1,3-Dibenzylimidazolium tetrafluoroborate (123.3 mg, 0.367 mmol, 1.00 eq), silver oxide (42.5 mg, 0.183 mmol, 0.50 eq) and sodium hydroxide (16.1 mg, 0.404 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 2 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-dibenzylimidazol-2-ylidene]silver tetrafluoroborate (107.7 mg, 0.156 mmol, 85%) as a white powder.

^{1}H NMR (300 MHz, DMSO-*d$_6$*) δ 7.57 (s, 4H), 7.31 – 7.22 (m, 12H), 7.21 – 7.15 (m, 8H), 5.27 (s, 8H)**;** **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 137.3, 128.8, 128.1, 127.5, 122.9, 54.3 (The ^{13}C of carbene was not observed due to the low concentration of the sample) ; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.3 ; **HRMS** calcd for $C_{34}H_{32}N_4Ag$ [M – BF_4^-]$^+$: 603.1678; found: 603.1681.

Bis[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver tetrafluoroborate [Ag(1g)$_2$]BF$_4$ (unprecedented)

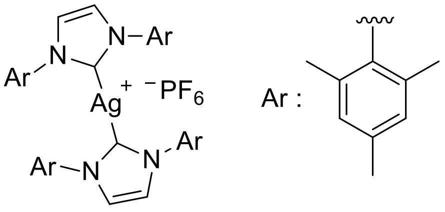


1,3,4-Triphenyl-1,2,4-triazolium tetrafluoroborate (128.6 mg, 0.334 mmol, 1.00 eq), silver oxide (38.7 mg, 0.167 mmol, 0.50 eq) and sodium hydroxide (14.7 mg, 0.367 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 3 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver tetrafluoroborate (97.7 mg, 0.124 mmol, 74%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 7.90 (d, *J* = 7.4 Hz, 4H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.55 – 7.48 (m, 12H), 7.46 – 7.37 (m, 12H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 183.0 (d, *J* = 194.2 Hz), 153.8, 138.8, 136.3, 131.2, 130.1, 129.8, 129.6, 129.1, 128.8, 126.8, 124.1, 122.6; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -148.3; **HRMS** calcd for $C_{40}H_{30}N_6Ag$ [M – BF$_4^-$]$^+$: 701.1578; found: 701.1584.

1.5. Synthesis of $[Ag(NHC)_2]PF_6$

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol -2-ylidene]silver hexafluorophosphate $[Ag(1a)_2]PF_6$

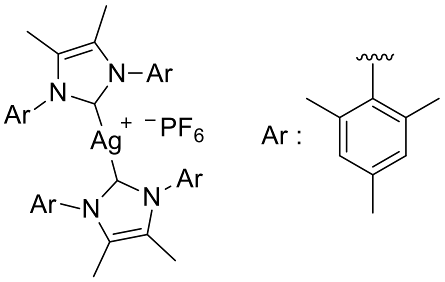


Method A: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate (131.8 mg, 0.293 mmol, 1.00 eq), silver oxide (37.3 mg, 0.761 mmol, 0.55 eq) and sodium hydroxide (12.9 mg, 0.322 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). 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 2 hours in the vibratory ball mill operated at 25 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]silver hexafluorophosphate (115.3 mg, 0.144 mmol, 91%) as a white solid.

Method B: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (89.3 mg, 0.262 mmol, 1.00 eq) and potassium hexafluorophosphate (50.8 mg, 0.275 mmol, 1.05 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). The bowl was closed and subjected to grinding for 20 minutes in the vibratory ball mill operated at 25 Hz. Afterwards, silver oxide (30.3 mg, 0.131 mmol, 0.50 eq) and sodium hydroxide (11.5 mg, 0.288 mmol, 1.10 eq) were added. 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 2 hours and 30 minutes. The black powder 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]silver hexafluorophosphate (83 mg, 0.0963 mmol, 78%).

^{1}H NMR (300 MHz, DMSO-*d$_6$*)[15] δ 7.67 (d, *J* = 1.2 Hz, 1H), 7.00 (s, 2H), 2.41 (s, 3H), 1.68 (s, 6H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 181.4 (dd, *J* = 192.4, 13.8 Hz), 138.7, 134.9, 134.0, 128.8, 123.62, 123.55, 20.7, 16.6; **^{31}P NMR (162 MHz, DMSO-*d$_6$*)** δ -144.2 (sept, *J* = 711.4 Hz); **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -70.1 (d, *J* = 711.4 Hz).

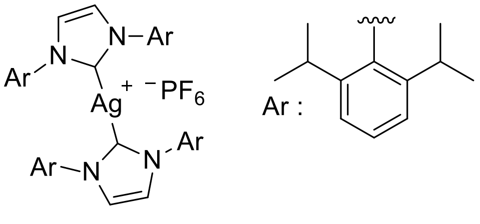
Bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver hexafluorophosphate [Ag(1b)$_2$]PF$_6$ (unprecedented)



[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate (136.4 mg, 0.285 mmol, 1.00 eq), silver oxide (33.0 mg, 0.143 mmol, 0.50 eq) and sodium hydroxide (12.5 mg, 0.314 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 3 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver hexafluorophosphate (119.0 mg, 0.130 mmol, 91%) as a beige solid.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 6.99 (s, 8H), 2.41 (s, 12H), 1.80 (s, 12H), 1.61 (s, 24H) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 178.3 (dd, *J* = 190.6, 14.1 Hz), 138.7, 134.4, 133.2, 128.9, 126.0, 20.8, 16.6, 8.6 ; **^{31}P NMR (162 MHz, DMSO-*d$_6$*)** δ -144.2 (hept, *J* = 711.4 Hz) ; **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -70.2 (d, *J* = 711.4 Hz) **HRMS** calcd for $C_{46}H_{56}N_4Ag$ [M – PF_6^-]$^+$: 771.3536 ; found : 771.3545.

Bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]silver hexafluorophosphate [Ag(1c)$_2$]PF$_6$

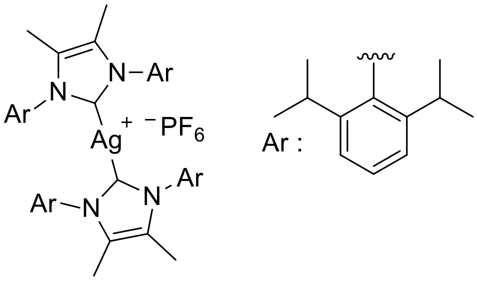


1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium hexafluorophosphate (140.1 mg, 0.262 mmol, 1.00 eq), silver oxide (30.3 mg, 0.131 mmol, 0.50 eq) and sodium hydroxide (11.5 mg, 0.288 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 3 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum. The white solid was dissolved in a minimum of dichloromethane, washed three times with water and concentrated under vacuum. The solid was washed with water and diethyl ether and dry under vacuum to afford bis[1,3-bis(2,6-

di*iso*propylphenyl)imidazol-2-ylidene]silver hexafluorophosphate (96.9 mg, 94.1 µmol, 72%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6)[15] δ 7.77 (d, *J* = 0.9 Hz, 4H), 7.51 (t, *J* = 7.8 Hz, 4H), 7.18 (d, *J* = 7.8 Hz, 8H), 2.20 (sept, *J* = 6.9 Hz, 8H), 1.01 (d, *J* = 6.9 Hz, 24H), 0.75 (d, *J* = 6.9 Hz, 24H) ; **^{13}C NMR (101 MHz, DMSO-d_6)** δ 181.4 (dd, *J* = 201.6, 14.5 Hz), 144.6, 134.5, 130.3, 125.7, 125.6, 124.0, 28.1, 24.0, 23.7 ; **^{31}P NMR (162 MHz, DMSO-d_6)** δ -144.2 (hept, *J* = 711.3 Hz); **^{19}F NMR (376 MHz, DMSO-d_6)** δ -70.2 (d, *J* = 711.3 Hz).

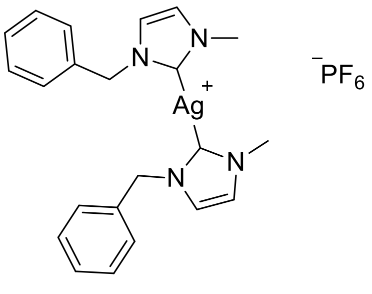
Bis[1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]silver hexafluorophosphate [Ag(1d)$_2$]PF$_6$ (unprecedented)



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate (141.7 mg, 0.252 mmol, 1.00 eq), silver oxide (29.2 mg, 0.126 mmol, 0.50 eq) and sodium hydroxide (11.1 mg, 0.277 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 3 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]silver hexafluorophosphate (124.1 mg, 0.114 mmol, 91%) as a white powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (t, *J* = 7.8 Hz, 4H), 7.20 (d, *J* = 7.8 Hz, 8H), 2.18 – 2.05 (m, 8H), 1.69 (s, 12H), 1.01 (d, *J* = 6.9 Hz, 24H), 0.69 (d, *J* = 6.9 Hz, 24H) ; **^{13}C NMR (101 MHz, DMSO-d_6)** δ 145.2, 133.1, 130.9, 127.6, 124.8, 28.4, 25.4, 23.1, 9.7; **^{31}P NMR (162 MHz, DMSO-d_6)** δ -133.2 – -157.4 (m). **^{19}F NMR (376 MHz, DMSO-d_6)** δ -70.1 (d, *J* = 711.2 Hz); **HRMS** calcd for $C_{58}H_{80}N_4Ag$ [M – PF_6^-]$^+$: 939.5434; found : 939.5433.

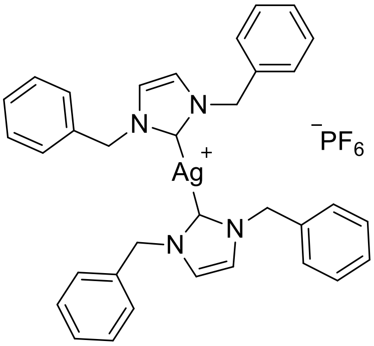
Bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver hexafluorophosphate [Ag(1e)$_2$]PF$_6$



1-Benzyl-3-methylimidazolium hexafluorophosphate (126.9 mg, 0.321 mmol, 1.00 eq), silver oxide (40.9 mg, 0.177 mmol, 0.55 eq) and sodium hydroxide (14.1 mg, 0.353 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 1 hour in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver hexafluorophosphate (90 mg, 0.151 mmol, 94%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 7.55 (d, *J* = 1.7 Hz, 2H), 7.46 (d, *J* = 1.7 Hz, 2H), 7.34 – 7.24 (m, 10H), 5.32 (s, 4H), 3.77 (s, **6H**) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 137.4, 128.8, 128.0, 127.5, 123.3, 122.4, 54.0, 38.2 (The ^{13}C of carbene was not observed due to the low concentration of the sample) ; **^{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* = 711.4 Hz) ; **HRMS** calcd for $C_{22}H_{24}N_4Ag$ [M – PF_6^-]$^+$: 451.1052; found: 451.1052.

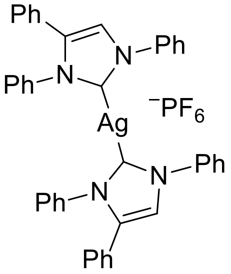
Bis[1,3-dibenzylimidazol-2-ylidene]silver hexafluorophosphate [Ag(1f)$_2$]PF$_6$ (unprecedented)



1,3-Dibenzylimidazolium hexafluorophosphate (129.5 mg, 0.328 mmol, 1.00 eq), silver oxide (38.0 mg, 0.164 mmol, 0.50 eq) and sodium hydroxide (14.4 mg, 0.361 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 2 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3-dibenzylimidazol-2-ylidene]silver hexafluorophosphate (104.7 mg, 0.140 mmol, 85%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 7.56 (s, 4H), 7.31 – 7.23 (m, 12H), 7.21 – 7.15 (m, 8H), 5.27 (s, 8H) ; **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 137.2, 128.7, 128.0, 127.4, 122.8, 54.2 (The ^{13}C of carbene was not observed due to the low concentration of the sample) ;**^{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); **HRMS** calcd for $C_{34}H_{32}N_4Ag$ [M – PF_6^-]$^+$: 603.1678; found: 603.1680.

Bis[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver hexafluorophosphate [Ag(1g)$_2$]PF$_6$ (unprecedented)



1,3,4-Triphenyl-1,2,4-triazolium hexafluorophosphate (133.7 mg, 0.302 mmol, 1.00 eq), silver oxide (35.0 mg, 0.151 mmol, 0.50 eq) and sodium hydroxide (13.3 mg, 0.332 mmol, 1.10 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel 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 3 hours in the vibratory ball mill operated at 30 Hz. The black powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford bis[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver hexafluorophosphate (93.8 mg, 0.111 mmol, 73%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.55 – 7.47 (m, 6H), 7.45 – 7.37 (m, 6H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 183.1 (d, *J* = 200.0 Hz), 153.8, 138.8, 136.3, 131.2, 130.1, 129.8, 129.5, 129.1, 128.8, 126.8, 124.1, 122.6; **^{31}P NMR (162 MHz, DMSO-*d$_6$*)** δ -144.2 (sept, *J* = 711.4 Hz); **^{19}F NMR (376 MHz, DMSO-*d$_6$*)** δ -70.2 (d, *J* = 711.4 Hz); **HRMS** calcd for $C_{40}H_{30}N_6Ag$ [M – PF$_6^-$]$^+$: 701.1583; found: 701.1584.

2. Synthesis of silver complexes in solution

General procedure for the synthesis of silver complexes in solution:

Method A[16]: imidazolium tetrafluoroborate or hexafluorophosphate (1.00 eq) was dissolved in acetonitrile (0.04 M). Silver oxide (0.50 – 0.55 eq) was added and the resulting suspension was stirred at 70°C in the dark.

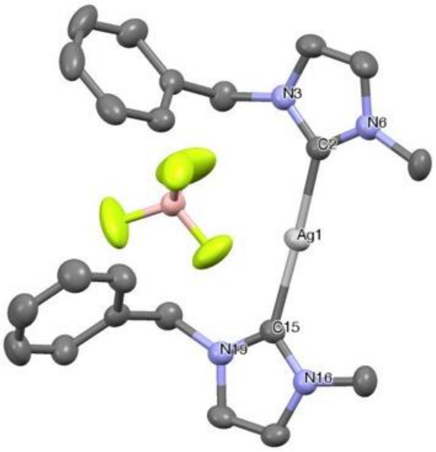
Method B: imidazolium tetrafluoroborate or hexafluorophosphate (1.00 eq) was dissolved in acetonitrile (0.04 M). Silver oxide (0.50 – 0.55 eq) and sodium hydroxide were added and the resulting suspension was stirred at room temperature in the dark.

NMR samples were prepared as followed: 300 µL of reaction mixture was withdrawn and filtrated. The filtrate was concentrated under vacuum. The white solid was dissolved in DMSO-*d*$_6$ and analyzed in ^{1}H NMR.

Entry	**[Ag(NHC)$_2$]Y**	**NHC·HY**			**Silver oxide**			**Sodium hydroxide**			**Acetonitrile (mL)**	**Method**	**Time (h)**	**NMR conv. (%)**
		m (mg)	**n (mmol)**	**Eq.**	**m (mg)**	**n (mmol)**	**Eq.**	**m (mg)**	**n (mmol)**	**Eq.**				
1	[Ag(1e)$_2$]BF$_4$	109.7	0.422	1.00	97.8	0.422	1.00	-	-	-	10.6	Method A	17	75
2		109.7	0.422	1.00	53.7	0.232	0.55	18.6	0.464	1.10	10.6	Method B	17	67
3		**109.7**	**0.422**	**1.00**	**53.5**	**0.232**	**0.55**	**18.6**	**0.464**	**1.10**	**-**	**vbm (30Hz)**	**1**	**100**
3	[Ag(1d)$_2$]BF$_4$	138.2	0.274	1.00	63.5	0.274	1.00	-	-	-	6.9	Method A	17	32
4		138.2	0.274	1.00	31.7	0.137	0.50	12.1	0.301	1.10	6.9	Method B	17	86
5		**138.2**	**0.274**	**1.00**	**31.7**	**0.137**	**0.50**	**12.1**	**0.301**	**1.10**	**-**	**vbm (30 Hz)**	**3**	**100**
6	[Ag(1d)$_2$]PF$_6$	141.7	0.252	1.00	58.4	0.252	1.00	-	-	-	6.3	Method A	17	7
7		141.7	0.252	1.00	29.2	0.126	0.50	11.1	0.277	1.10	6.3	Method B	17	Traces
8		**141.7**	**0.252**	**1.00**	**29.2**	**0.126**	**0.50**	**11.1**	**0.277**	**1.10**	**-**	**vbm (30 Hz)**	**3**	**100**

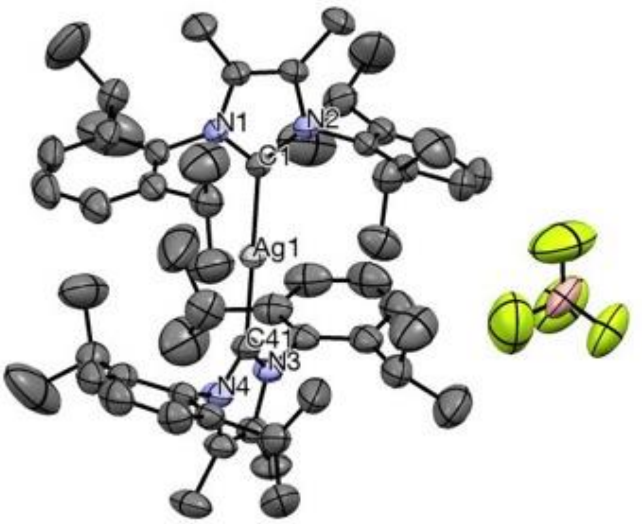
3. X-Ray Data

3.1. X-Ray Data of bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1e)$_2$]BF$_4$



CCDC 1495358	**[Ag(1e)$_2$]BF$_4$**
Formula	$C_{22}H_{24}AgBF_4N_4$
M / g.mol^{-1}	539.13
Crystal system	Triclinic
Space group	P -1
a / Å	10.3636 (8)
b / Å	11.3101 (6)
c / Å	11.3849 (7)
α / Å	106.948 (5)
β / Å	90.923 (6)
γ / Å	114.698 (6)
V (Å^3)	1145.04 (7)
Z	2
ρ_{calcd} / g.cm^{-3}	1.564
μ (Mo Kα) / mm^{-1}	0.929
T / K	175
Number of reflections	9665
Number of unique reflections	5224
R_{int}	0.031
*R*1, w*R*2 (I > 2σ(I))	0.0412, 0.0394
*R*1, w*R*2 (all data)	0.0501, 0.0425
GOF	1.1045

3.2. X-Ray data of bis-[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1d)$_2$]BF$_4$



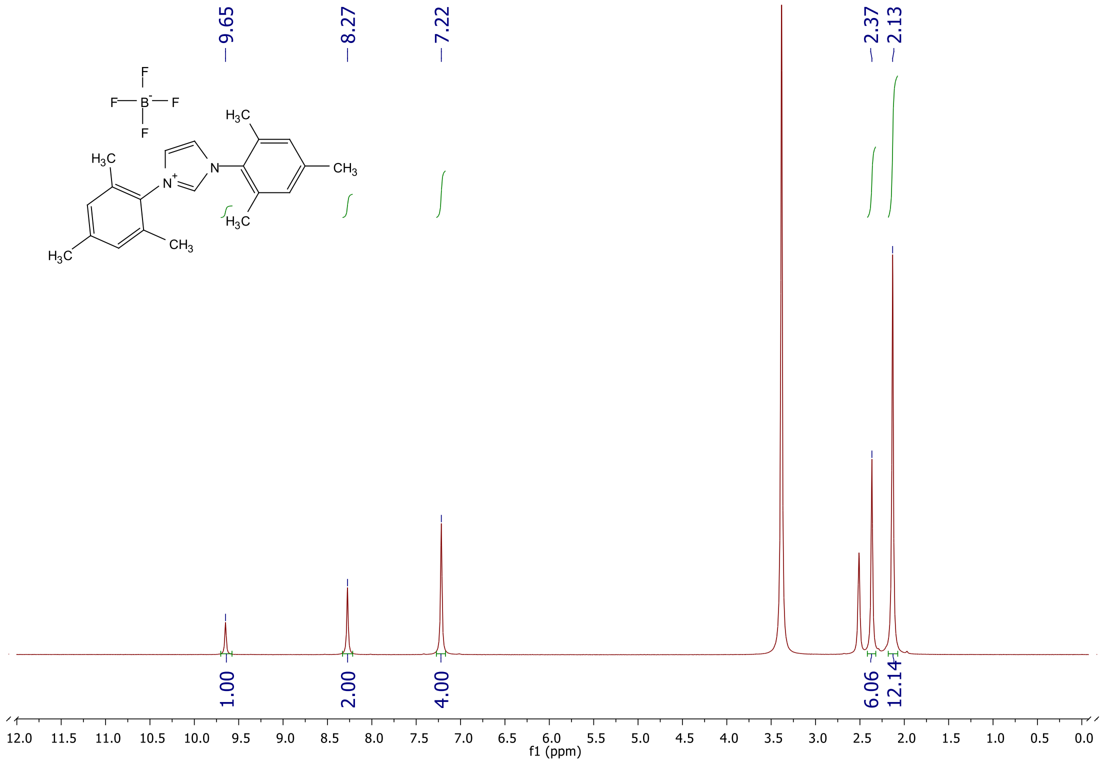
CCDC 1495341	**[Ag(1d)$_2$]BF$_4$**
Formula	$C_{58}H_{80}AgN_4$, BF_4, $C_4H_{10}O$
M / g.mol^{-1}	1102,05
Crystal system	Monoclinic
Space group	P 21/c
a / Å	13.5877 (4)
b / Å	19.4556 (6)
c / Å	23.8843 (9)
α / Å	90
β / Å	101.506 (3)
γ / Å	90
V (Å^3)	6187.1 (4)
Z	4
ρ_{calcd} / g.cm^{-3}	1.183
μ (Mo Kα) / mm^{-1}	0.378
T / K	293
Number of reflections	16008
Number of unique reflections	10183
R_{int}	0.0714
R1, wR2 ($I > 2\sigma(I)$)	0.0492, 0.1181
R1, wR2 (all data)	0.0940, 0.1315
GOF	0.991

4. NMR spectra

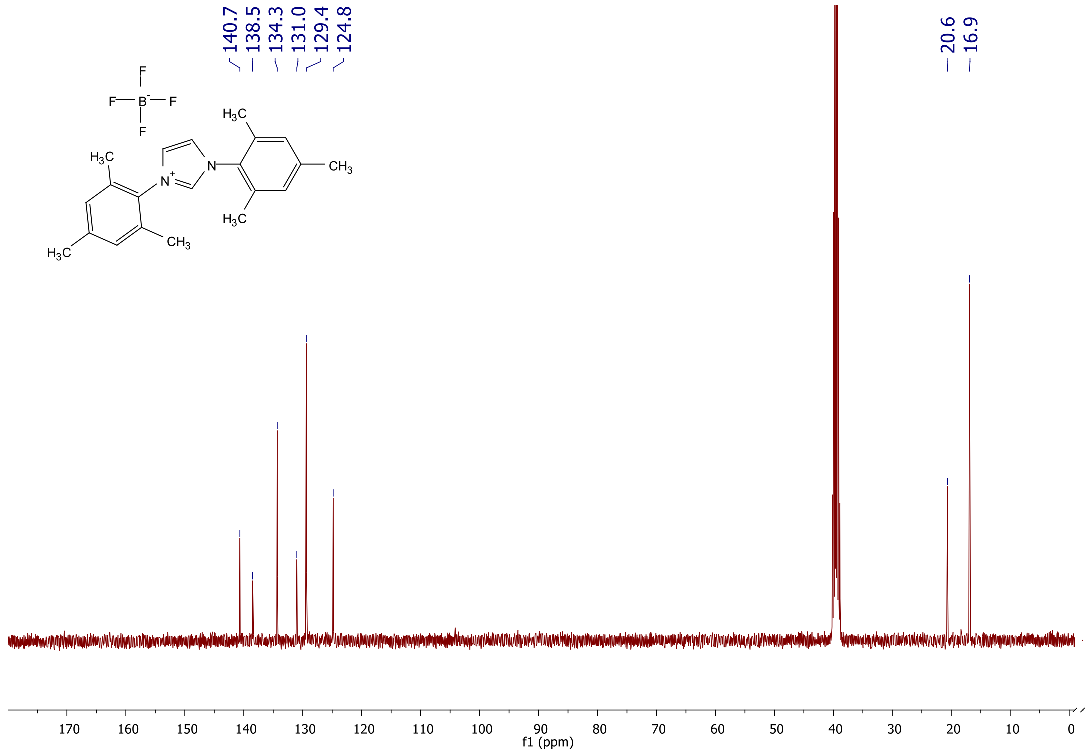
4.1. Imidazolium tetrafluoroborate

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

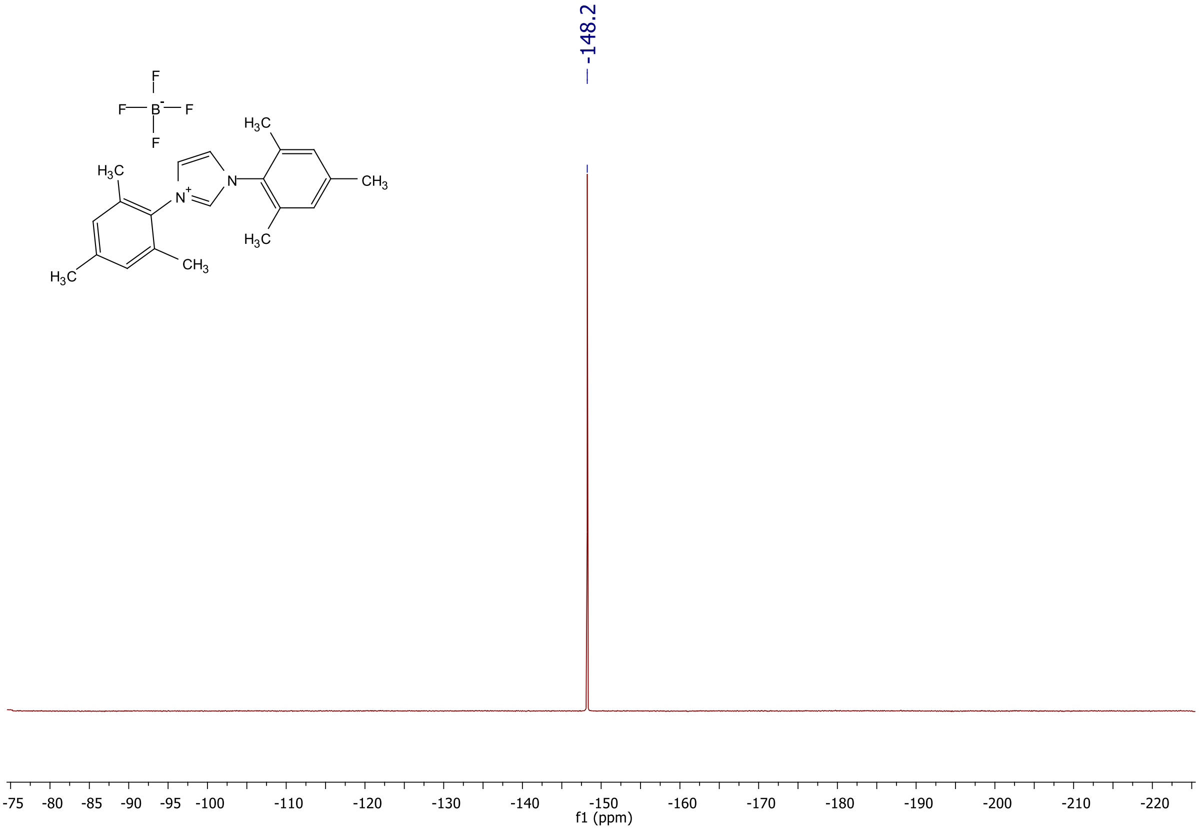
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)

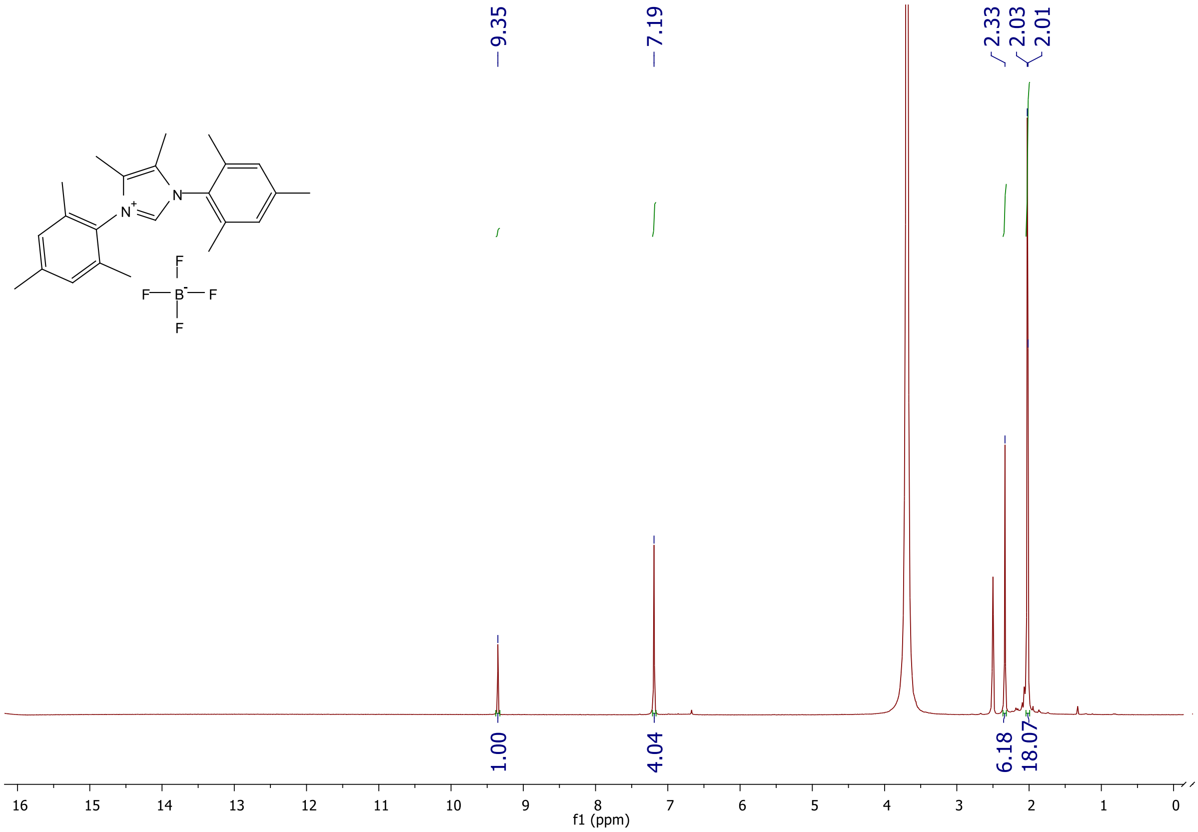


^{19}F NMR (376 MHz, DMSO-d_6)

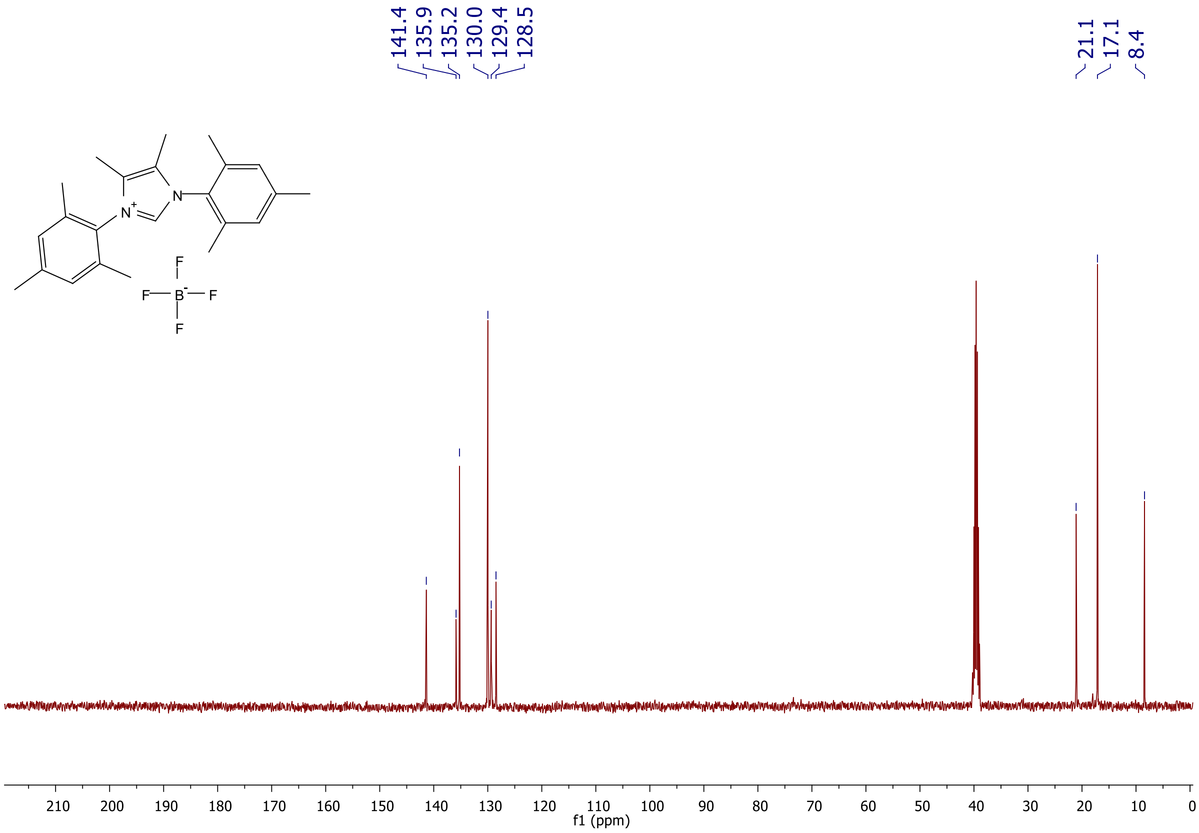


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium tetrafluoroborate 1b·HBF_4

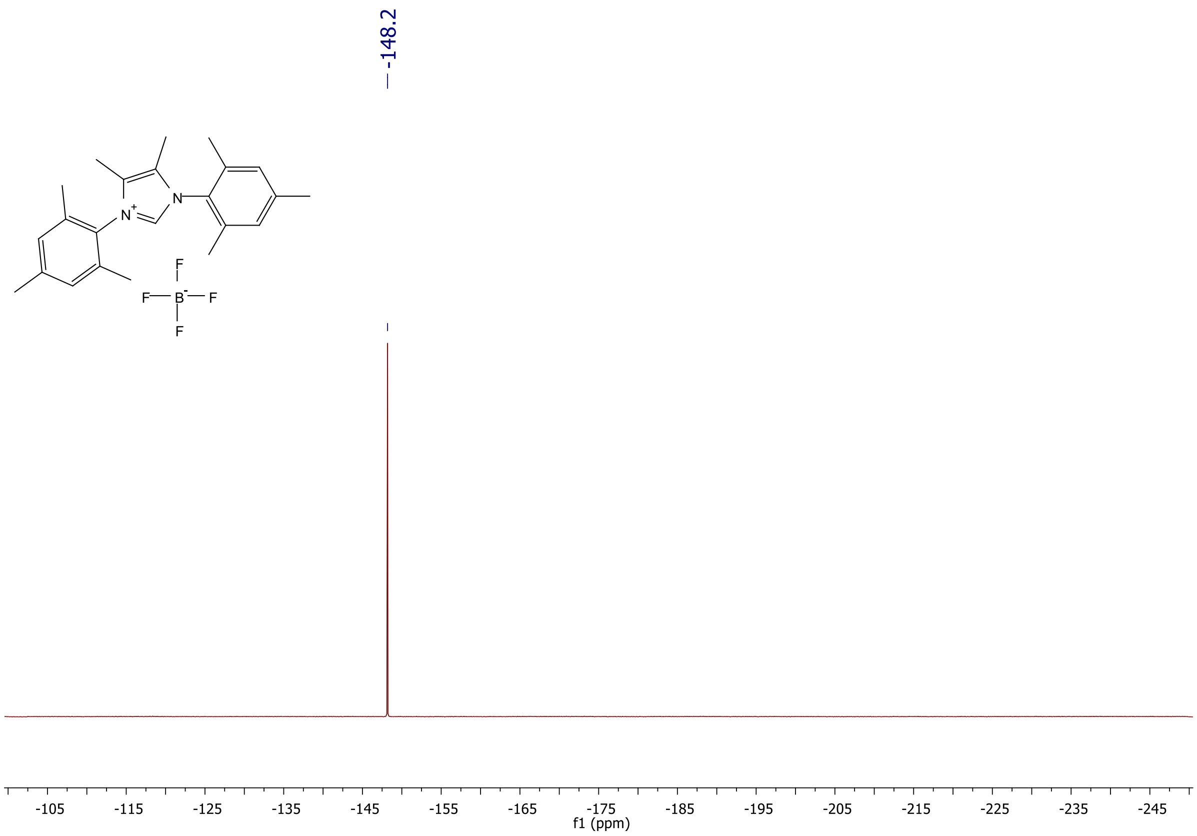
^1H NMR (400MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)

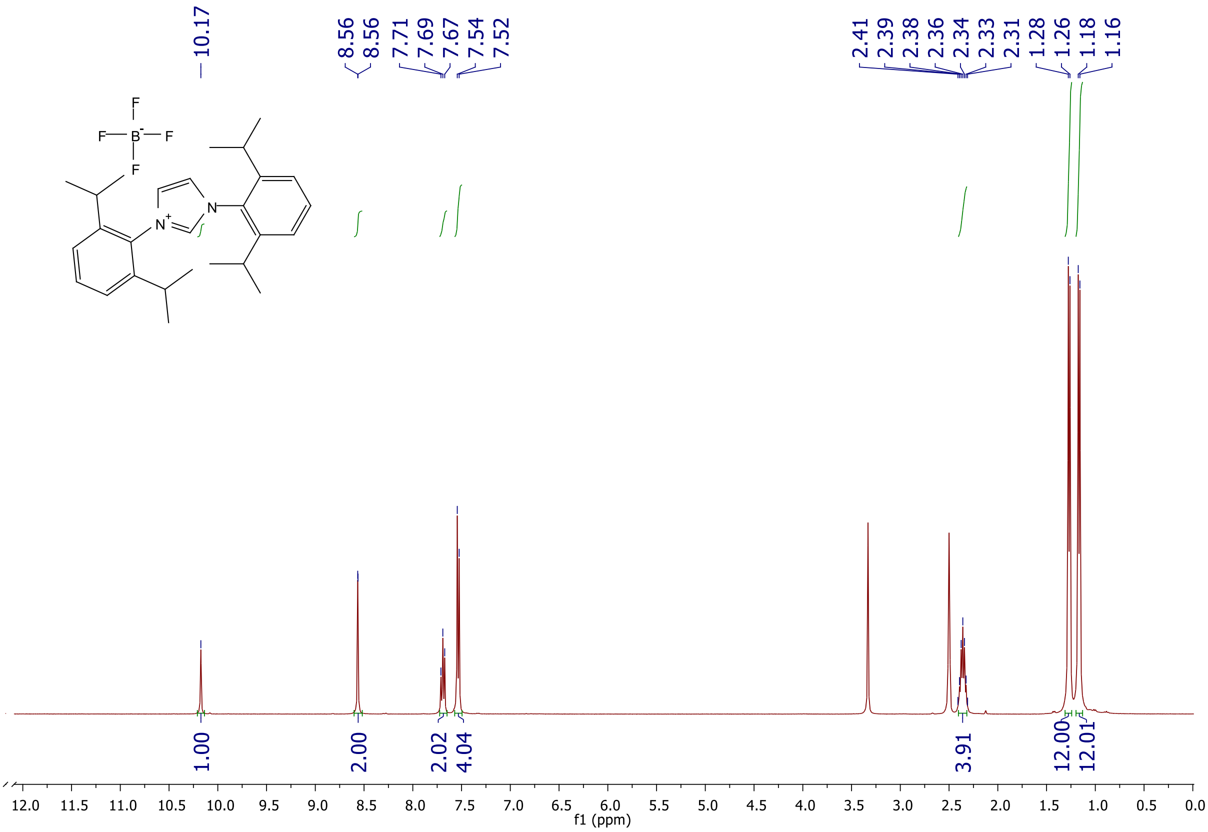


^{19}F NMR (376 MHz, DMSO-d_6)

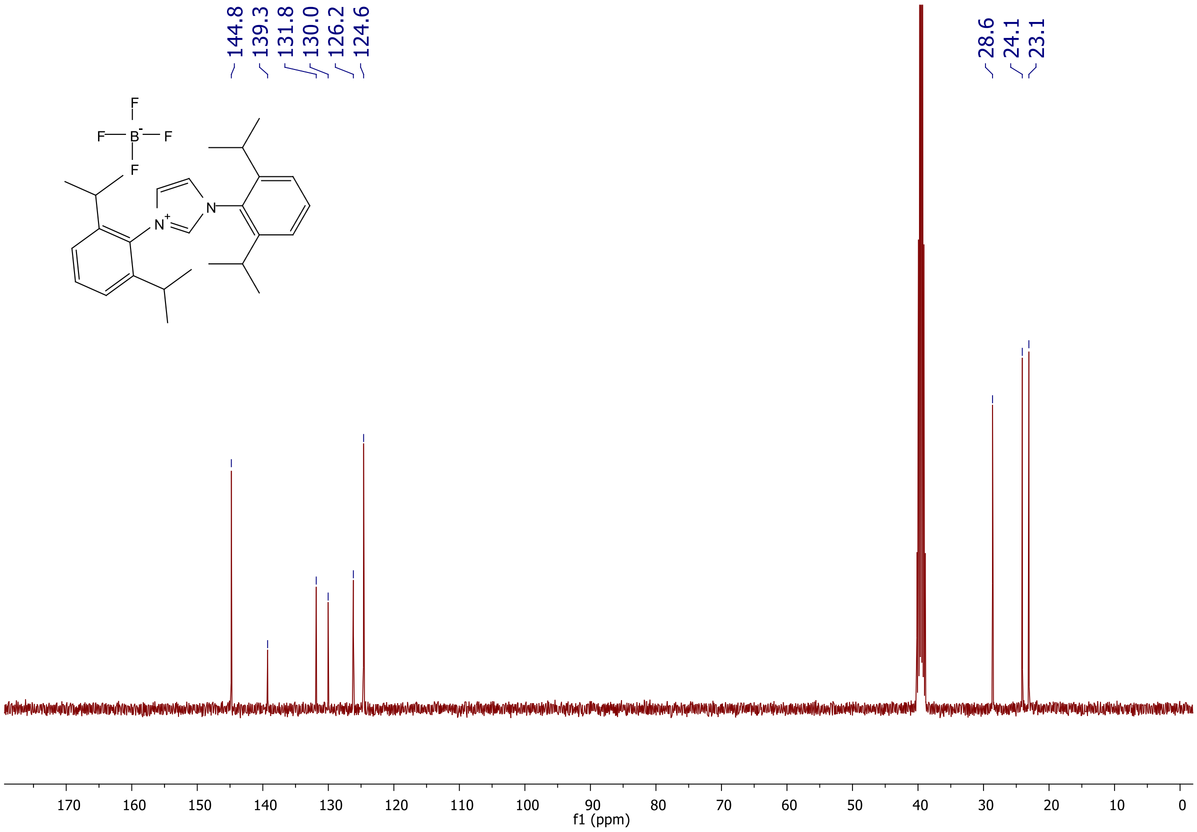


1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium tetrafluoroborate 1c·HBF$_4$

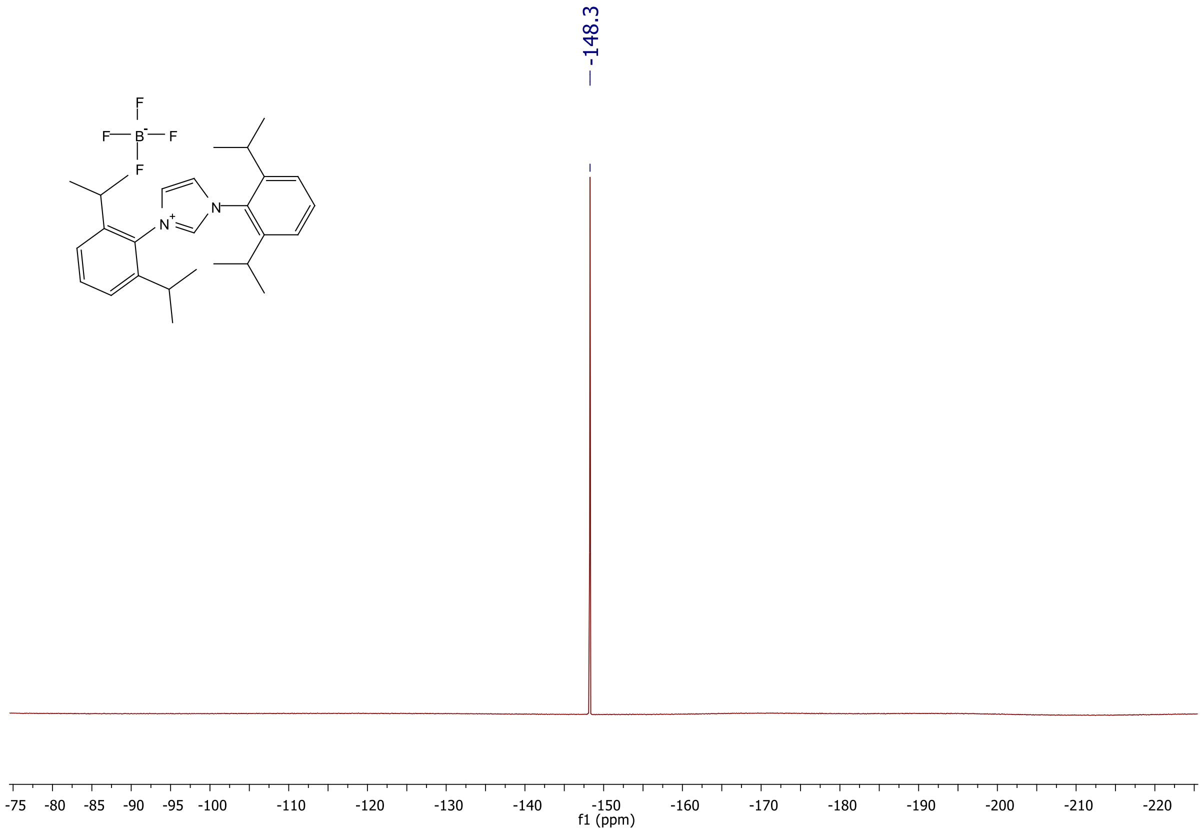
^{1}H NMR (400MHz, DMSO-*d*$_6$)



^{13}C NMR (110 MHz, DMSO-*d*$_6$)

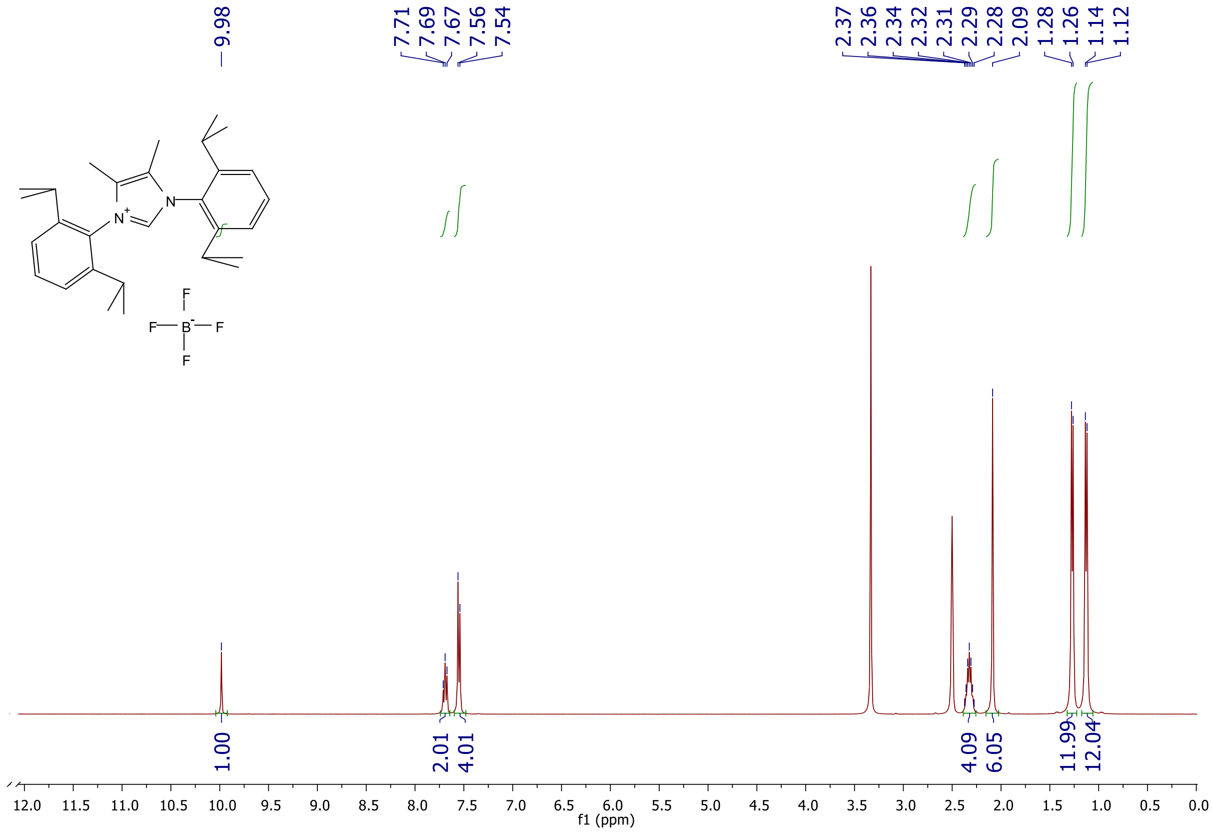


^{19}F NMR (376 MHz, DMSO-d_6)

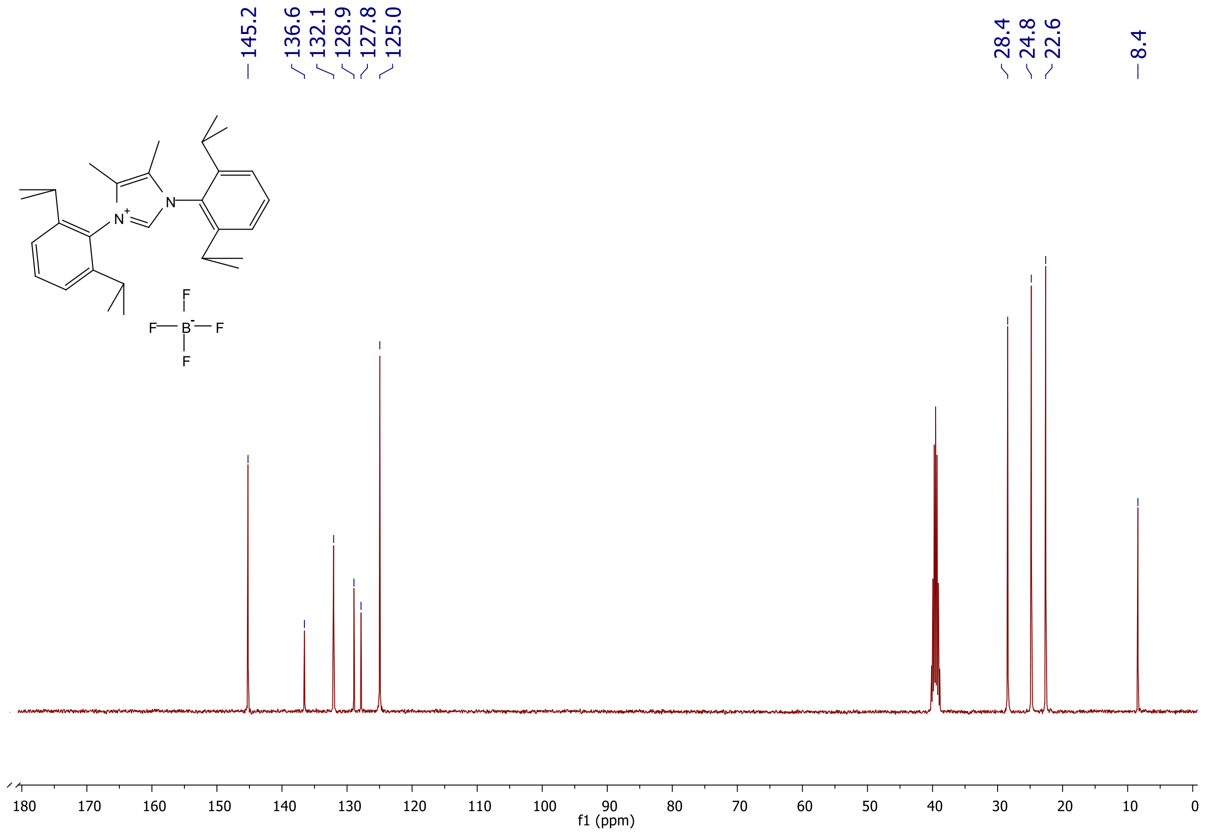


[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium tetrafluroborate 1d·HBF$_4$

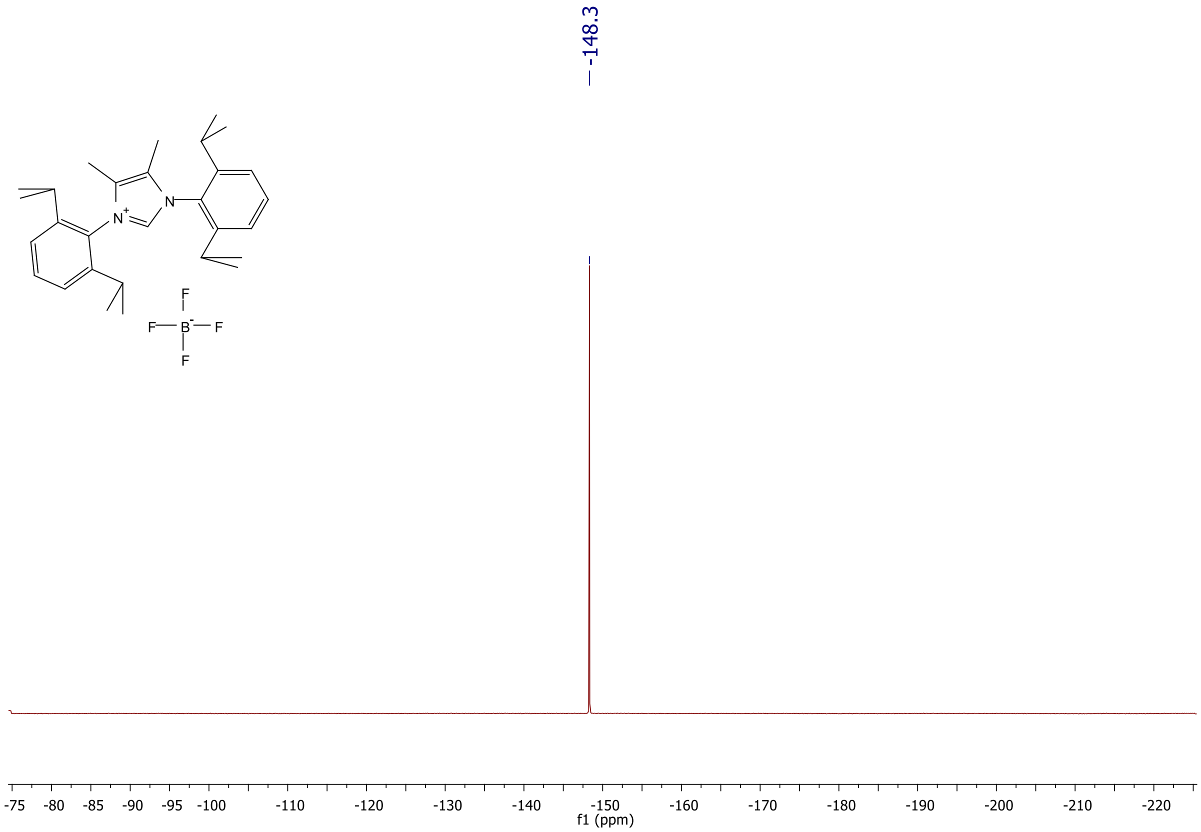
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)

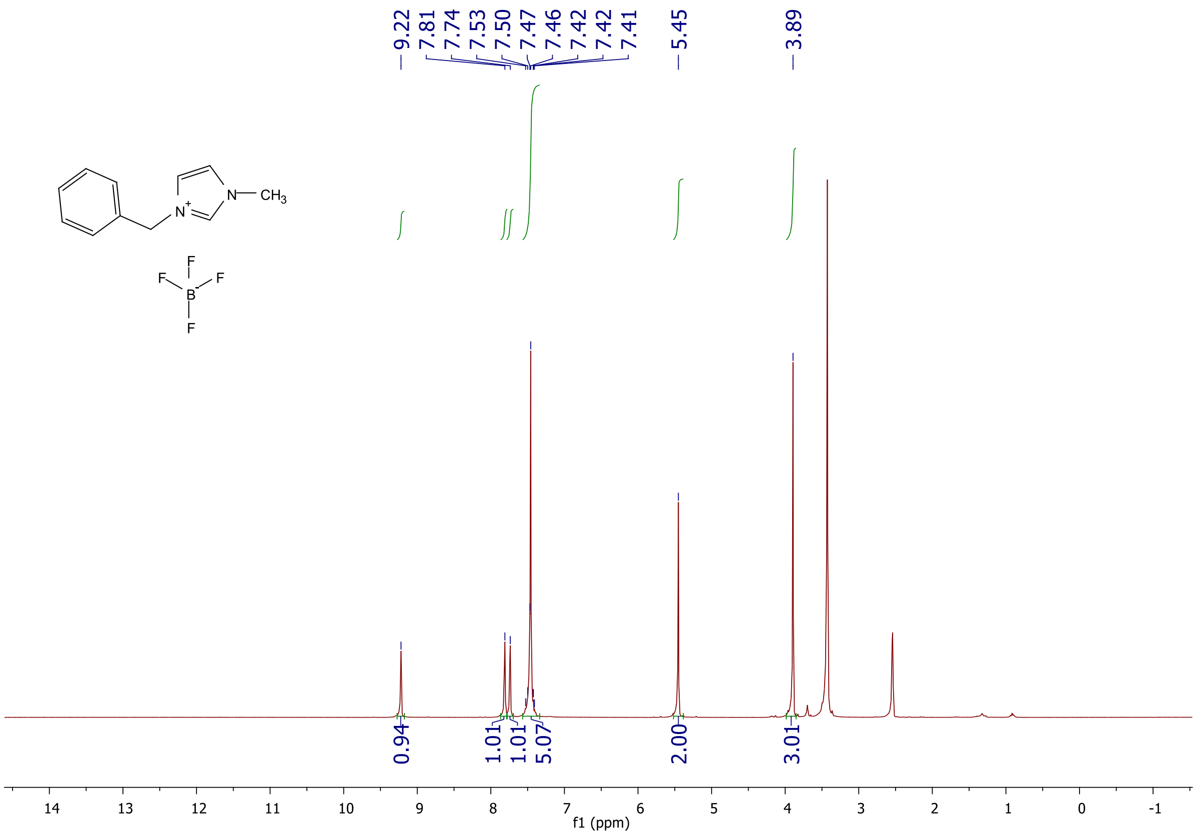


^{19}F NMR (376 MHz, DMSO-d_6)

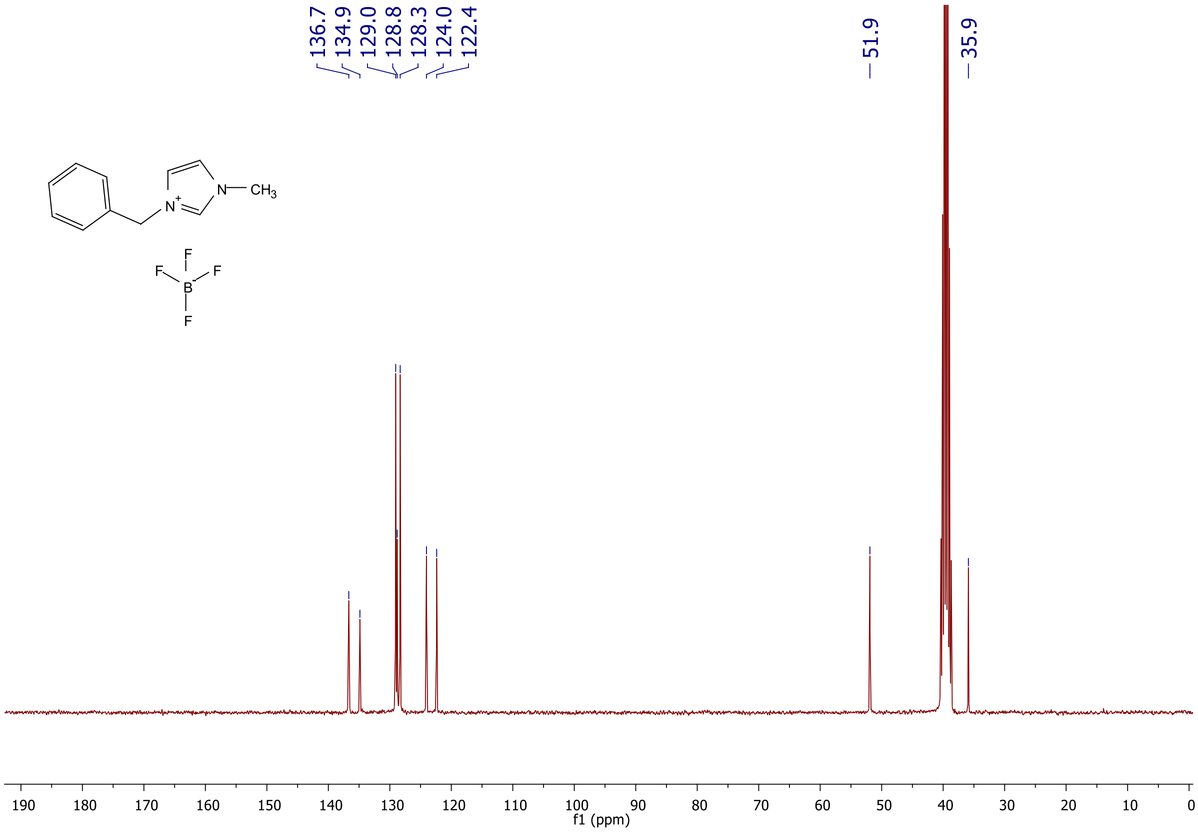


1-Benzyl-3-methylimidazolium tetrafluoroborate 1e·HBF$_4$

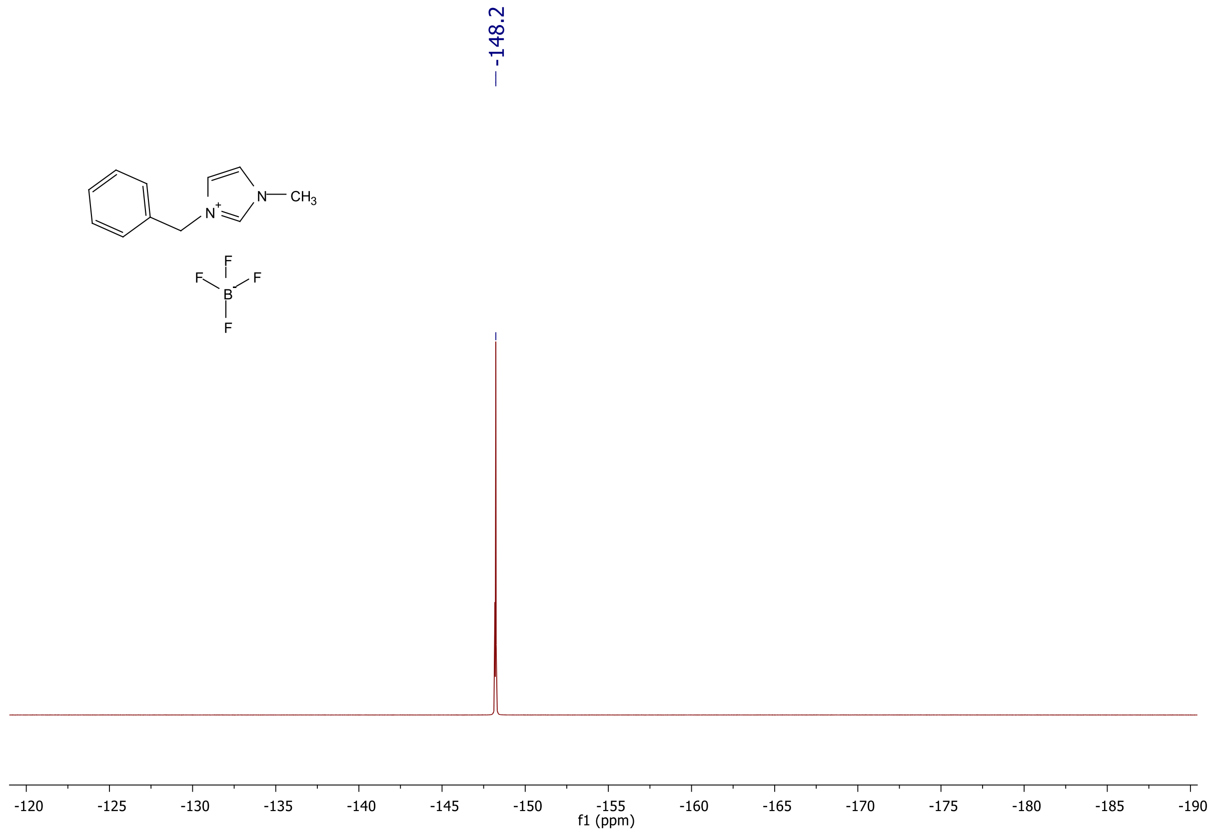
^{1}H NMR (300MHz, DMSO-*d$_6$*)



^{13}C NMR (75 MHz, DMSO-*d$_6$*)

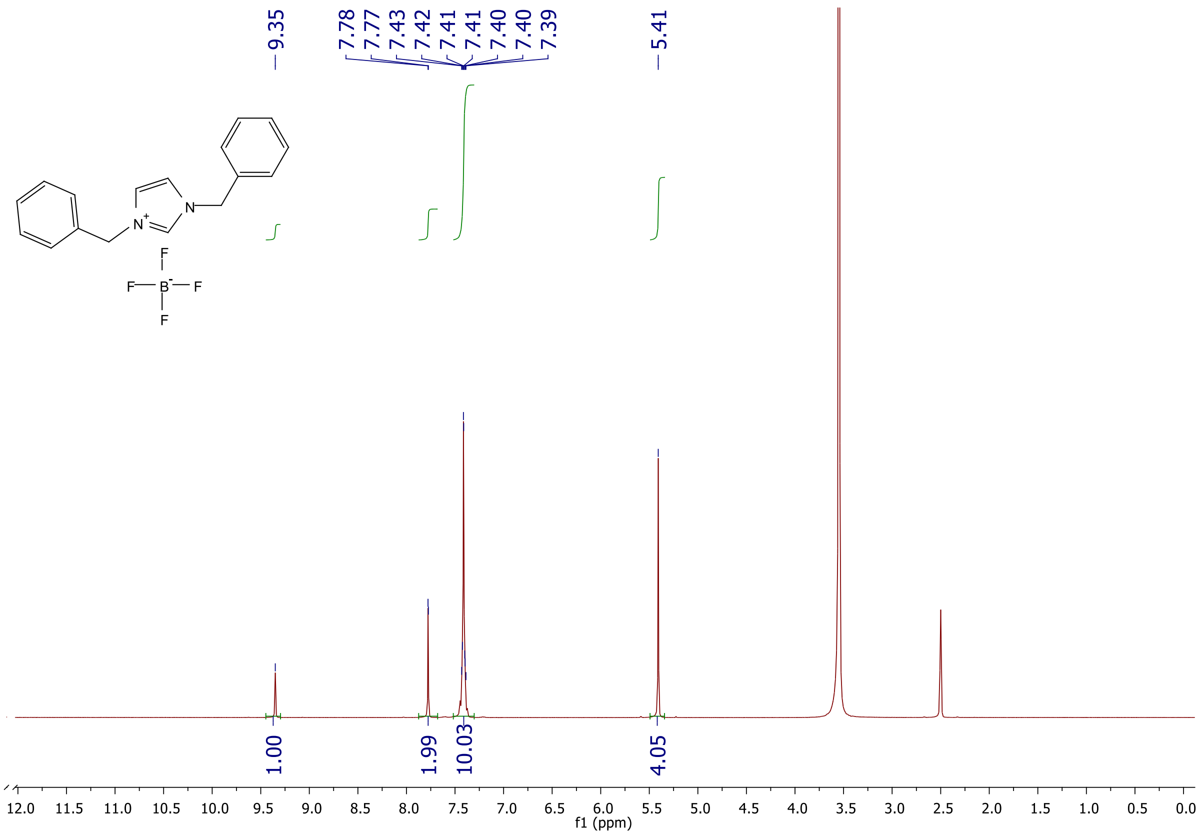


^{19}F NMR (282 MHz, DMSO-d_6)

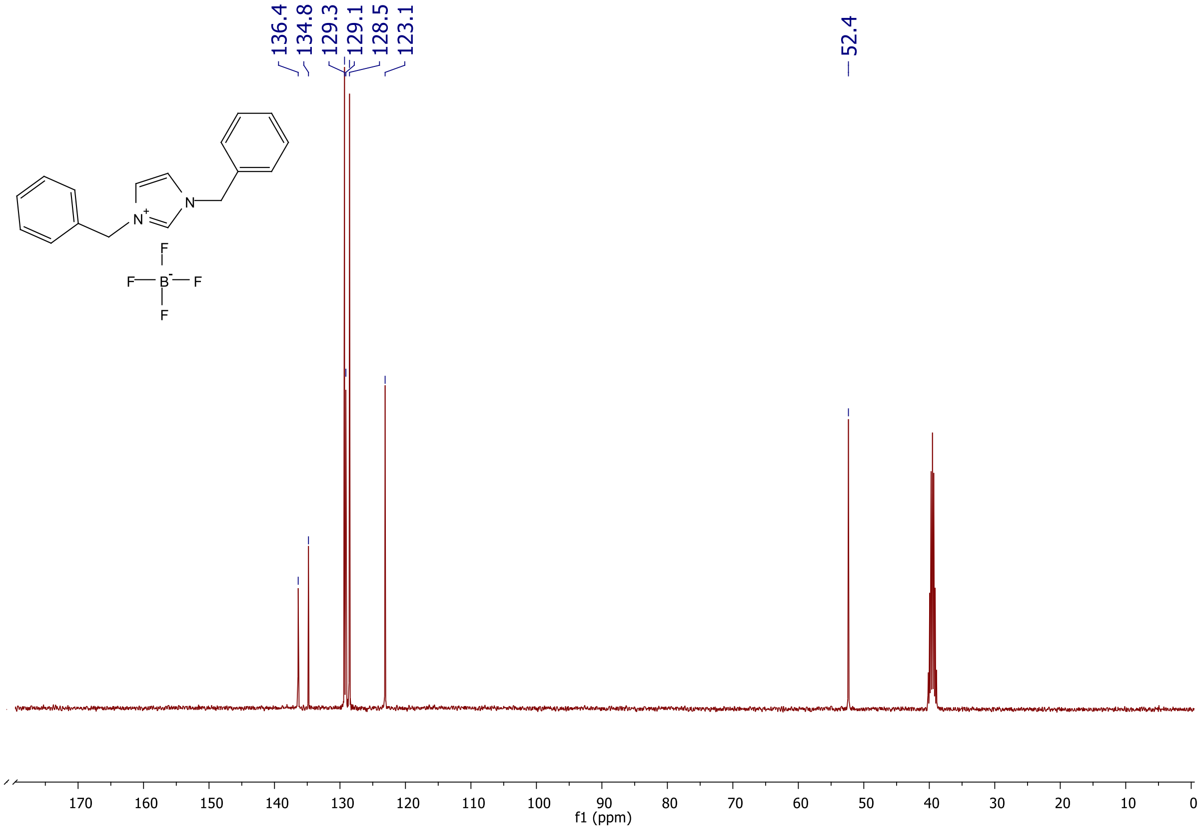


1,3-Dibenzylimidazolium tetrafluoroborate 1f·HBF_4

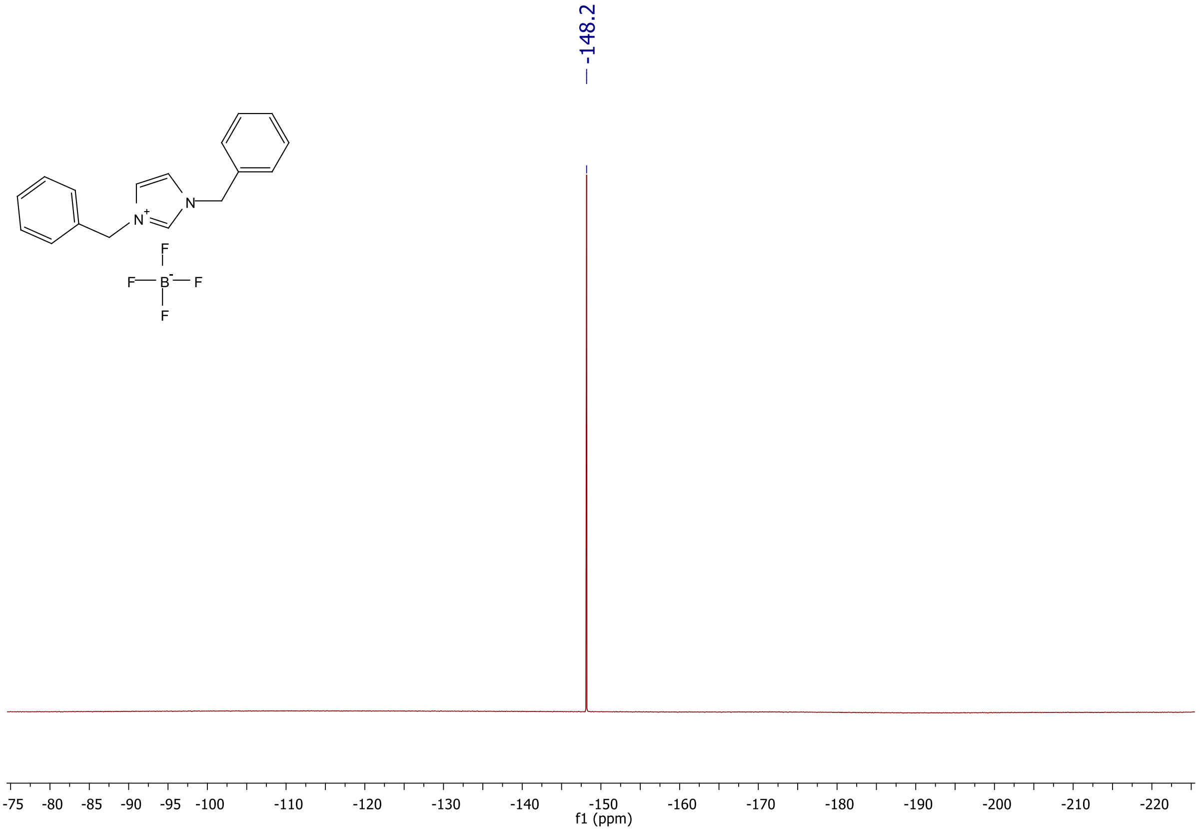
^{1}H NMR (300MHz, DMSO-d_6)



^{13}C NMR (75 MHz, DMSO-d_6)

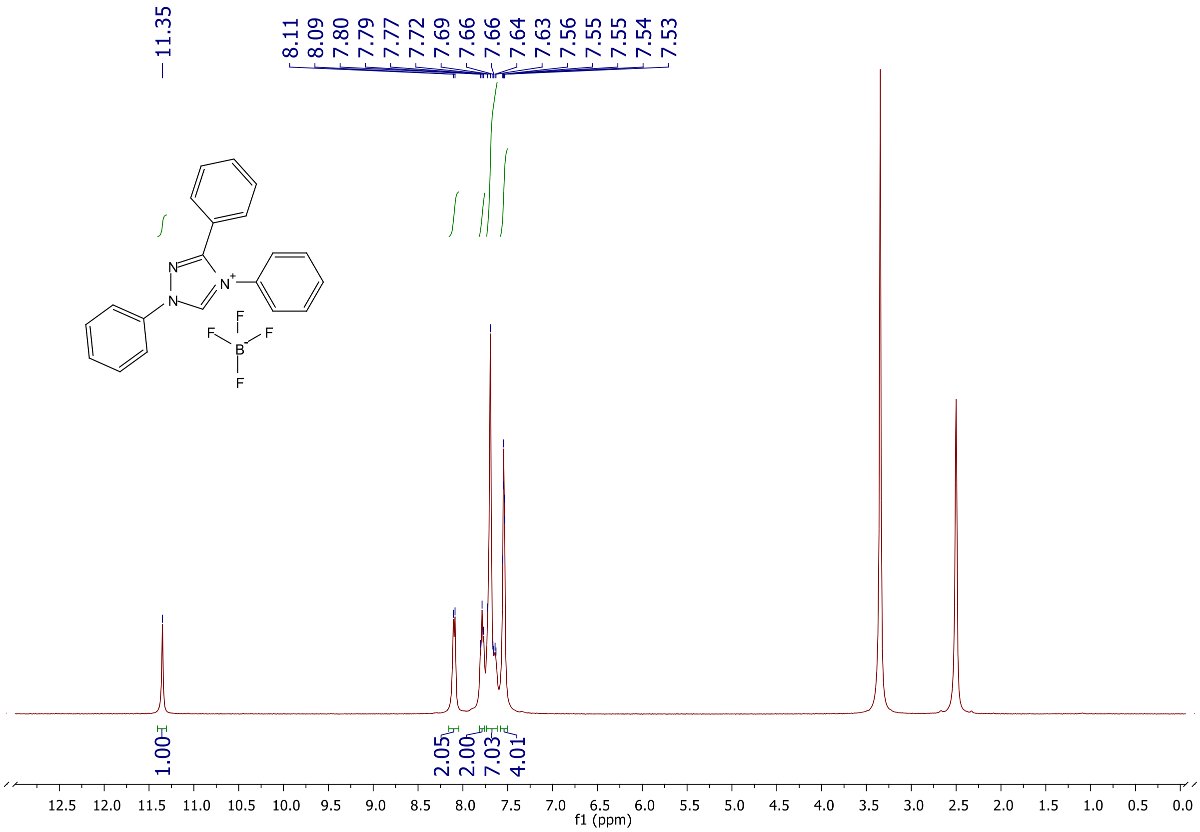


^{19}F NMR (282 MHz, DMSO-d_6)

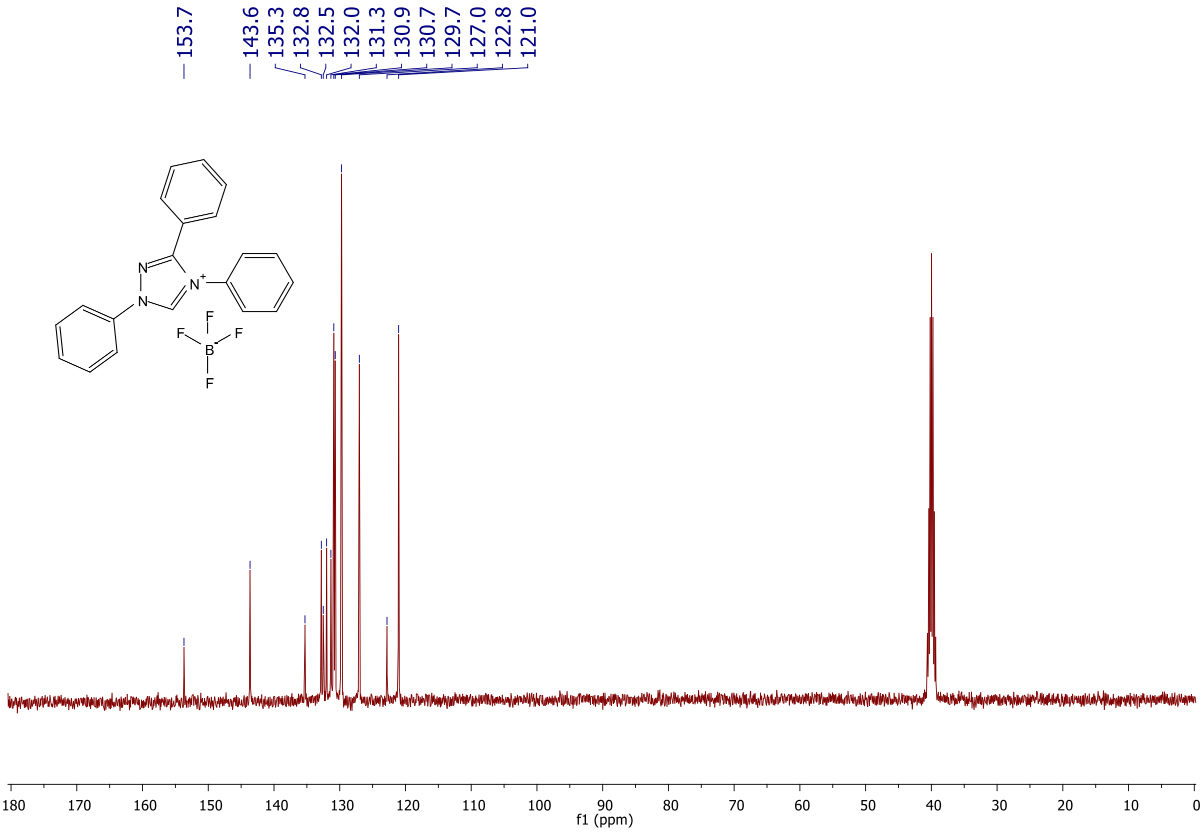


1,3,4-Triphenyl-1,2,4-triazolium tetrafluoroborate 1g·HBF_4

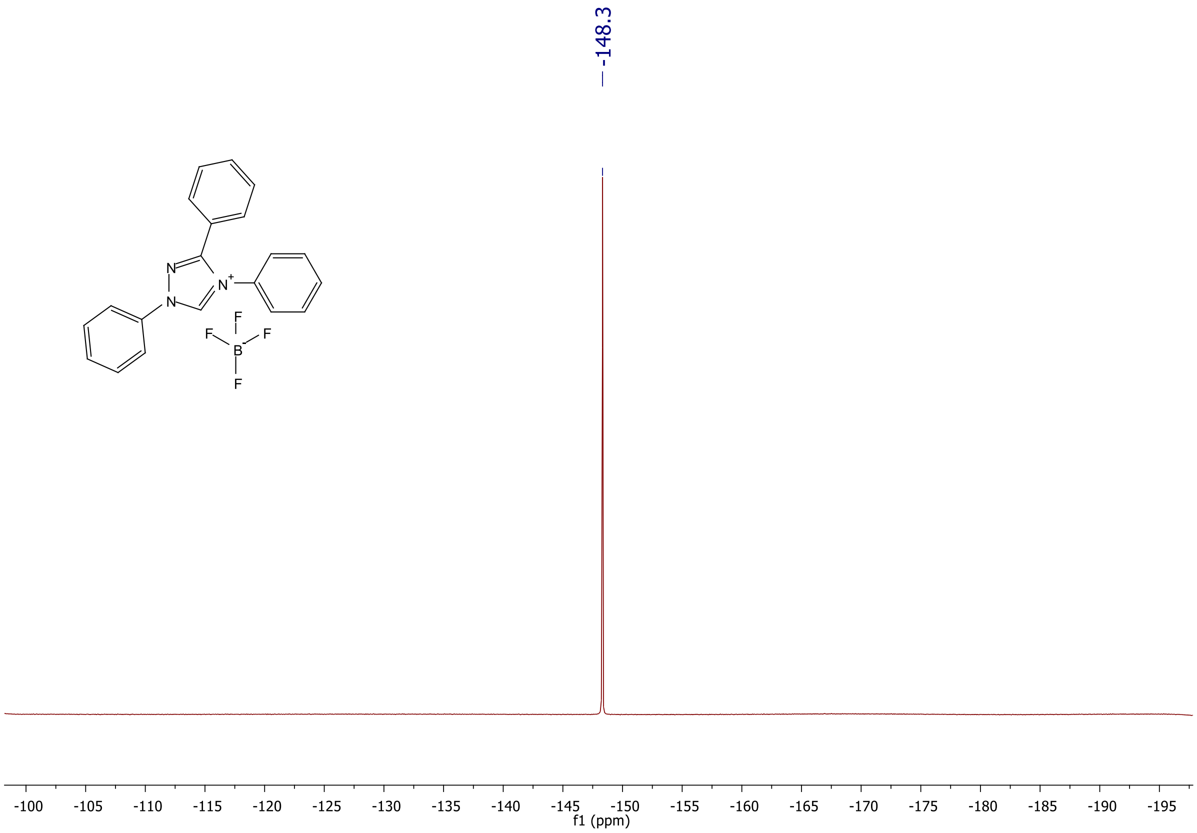
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)



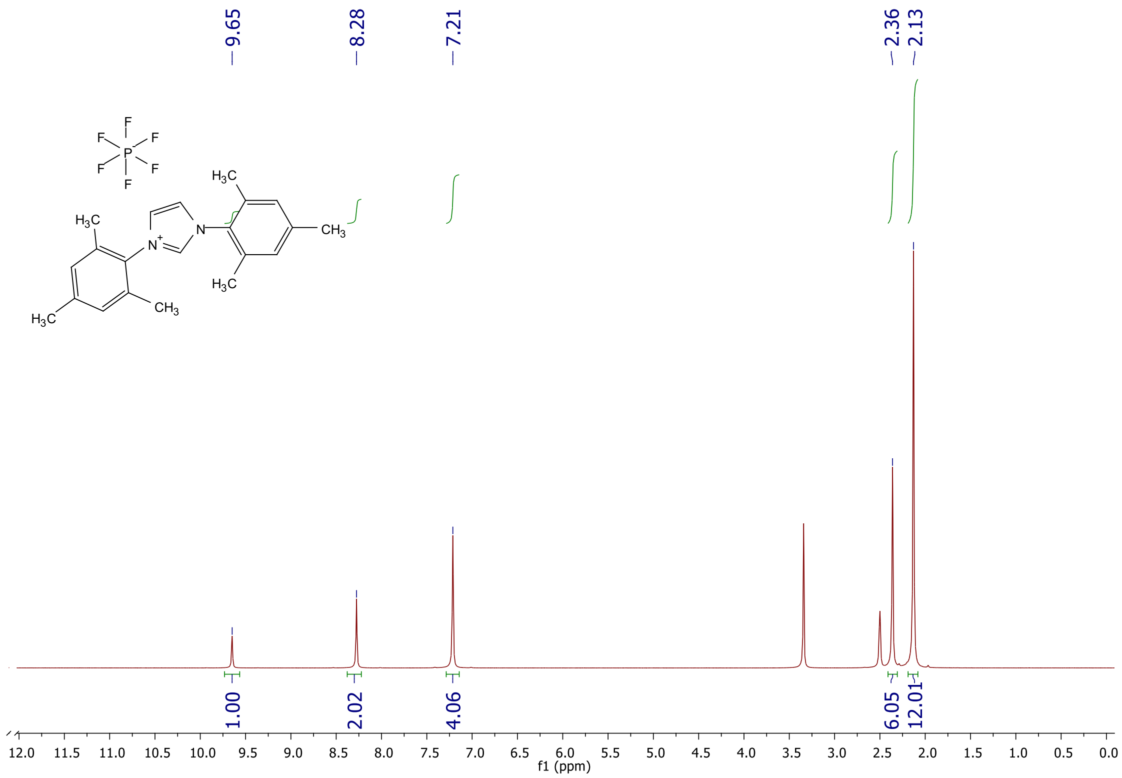
^{19}F NMR (376 MHz, DMSO-d_6)



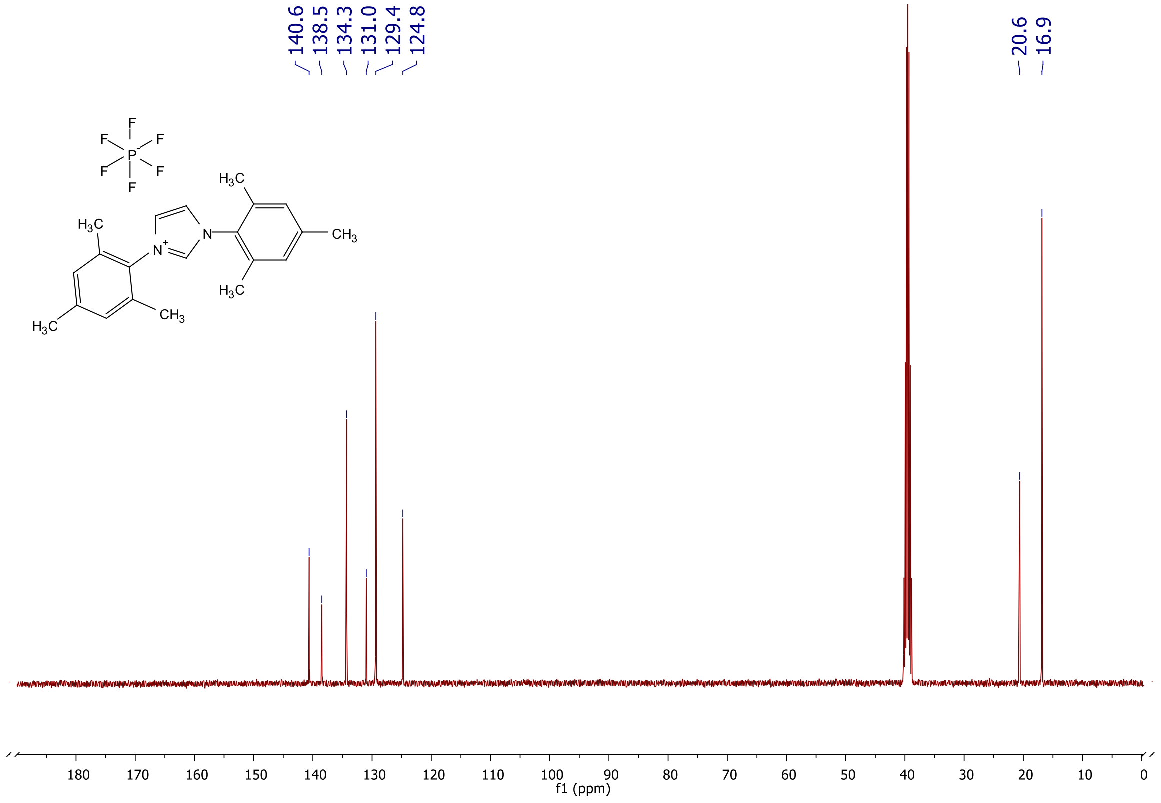
4.2. Imidazolium hexafluorophosphate

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

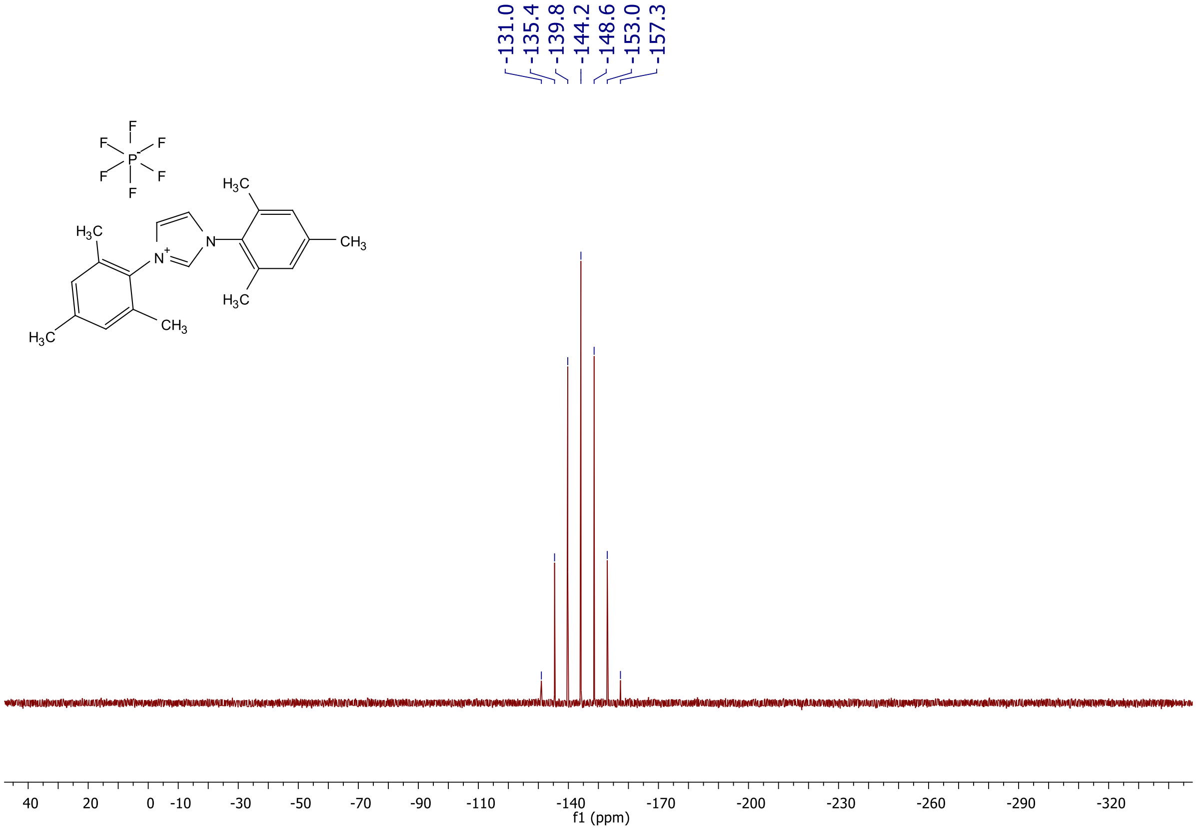
^{1}H NMR (400MHz, DMSO-d_6)



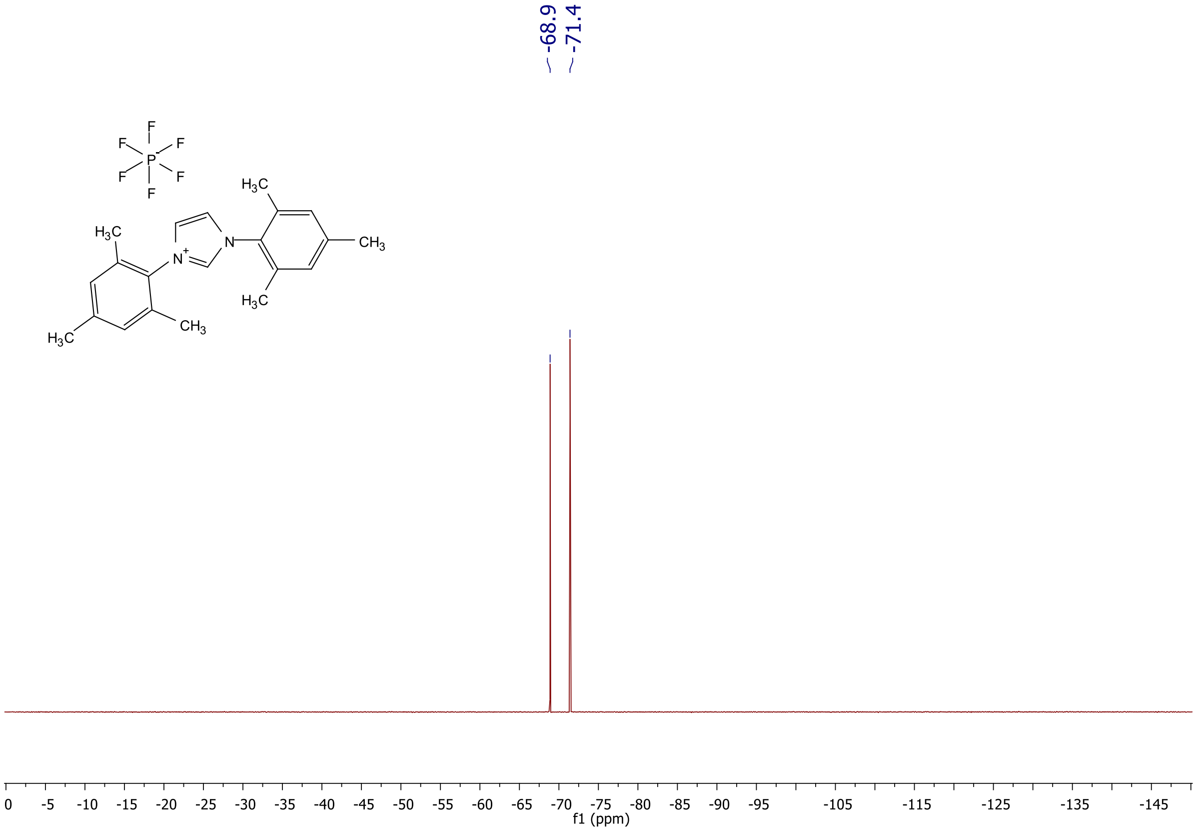
^{13}C NMR (110 MHz, DMSO-d_6)



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

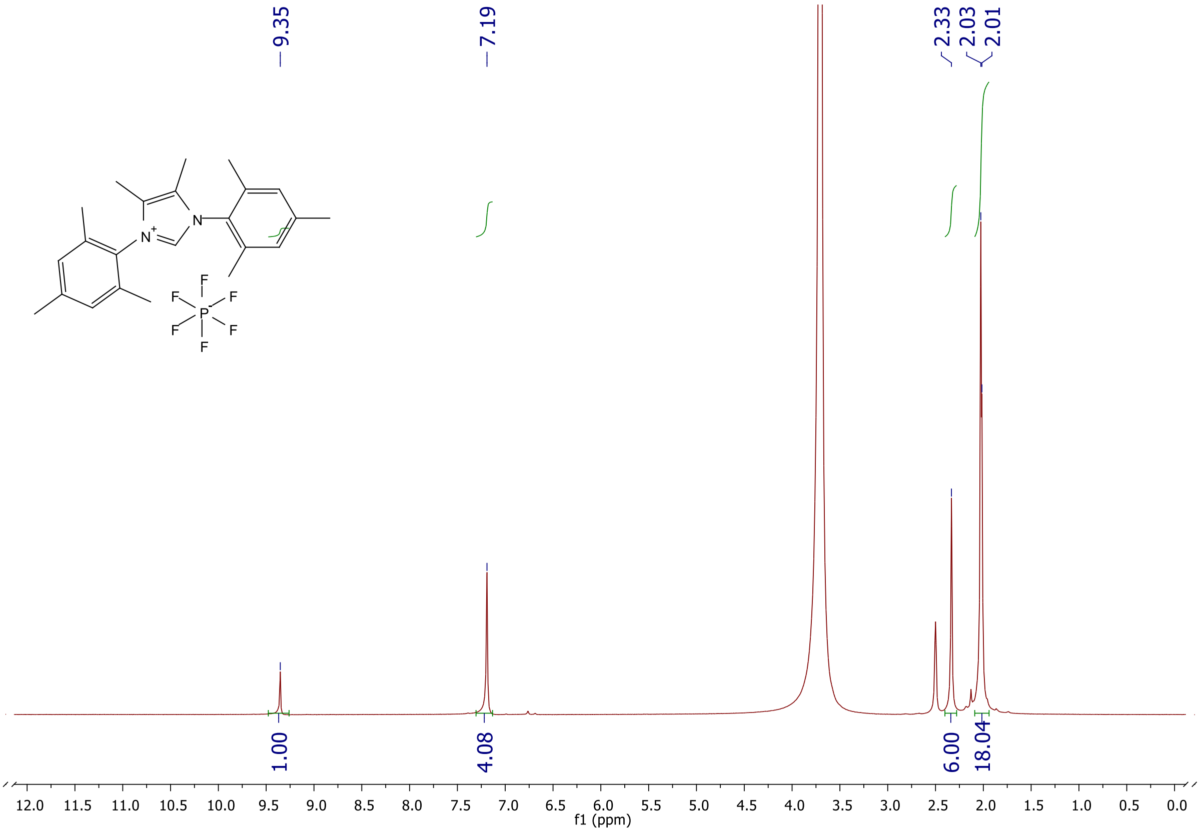


^{19}F NMR (376 MHz, DMSO-d_6)

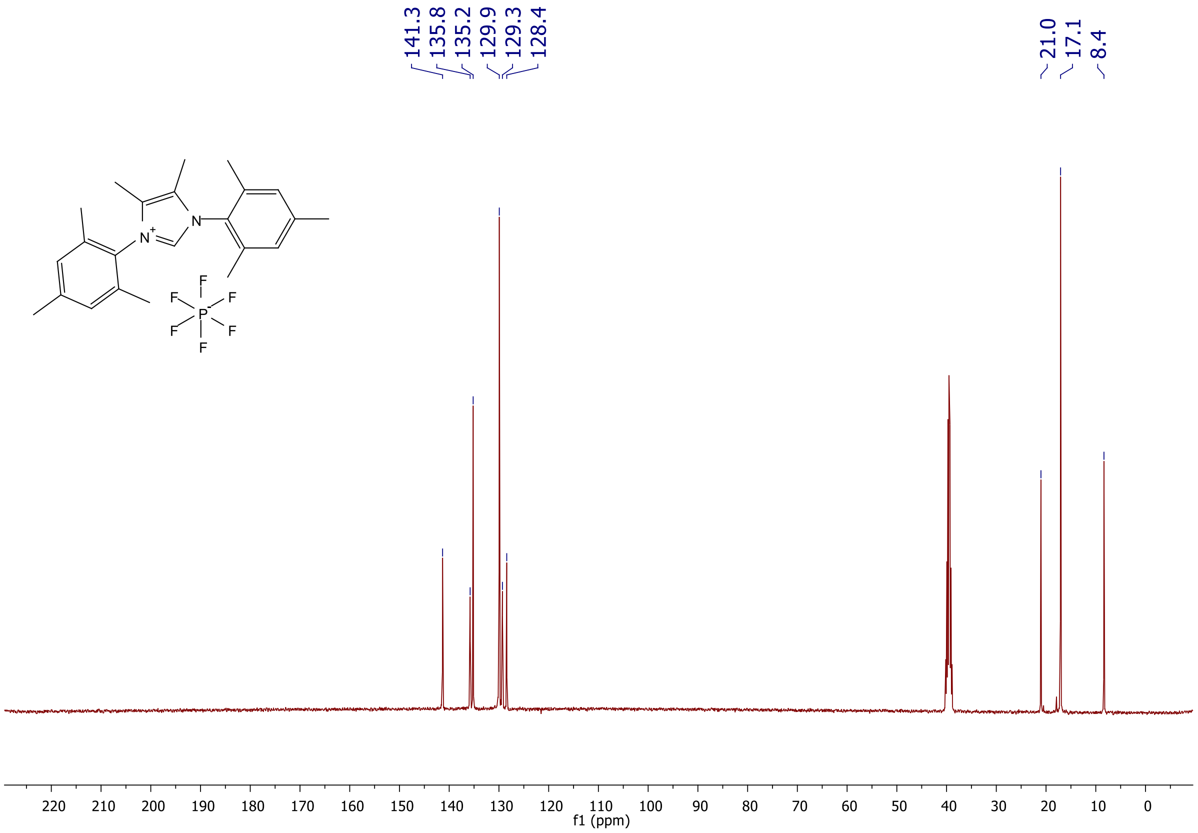


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate 1b·HPF$_6$

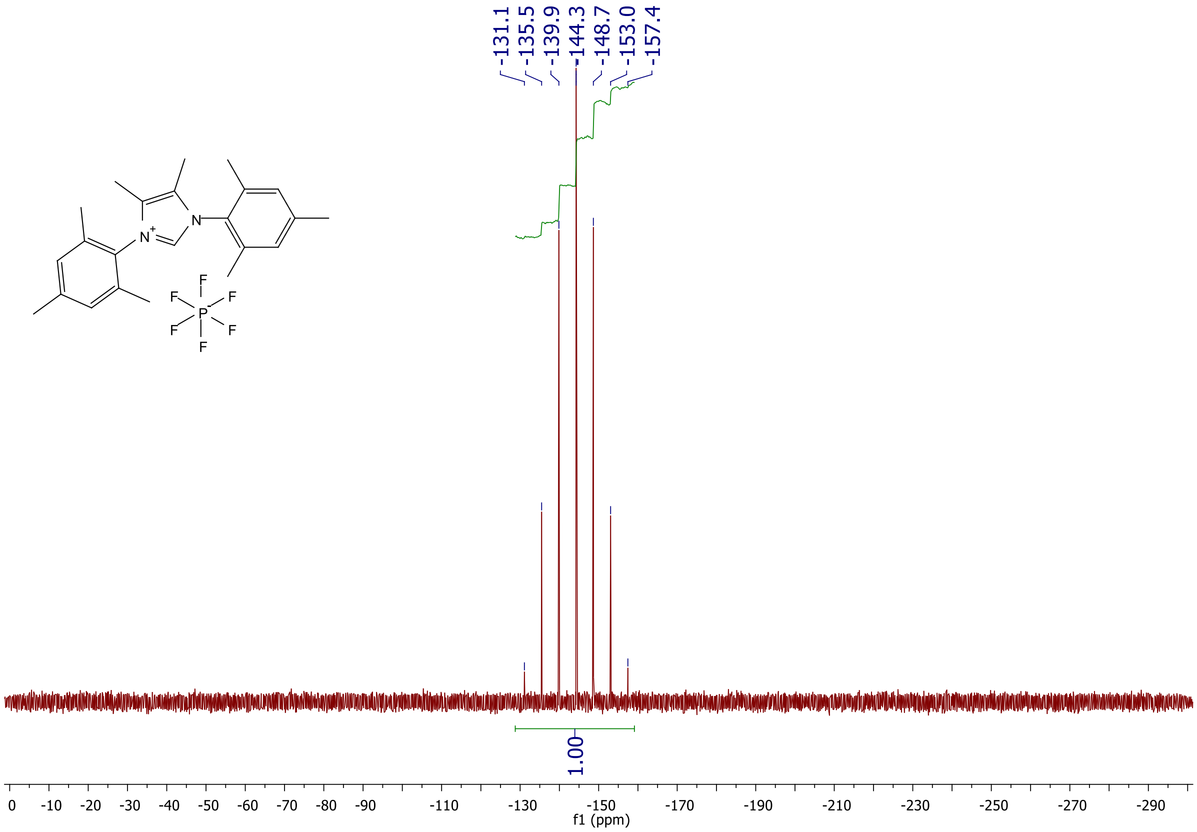
^{1}H NMR (400MHz, DMSO-d_6)



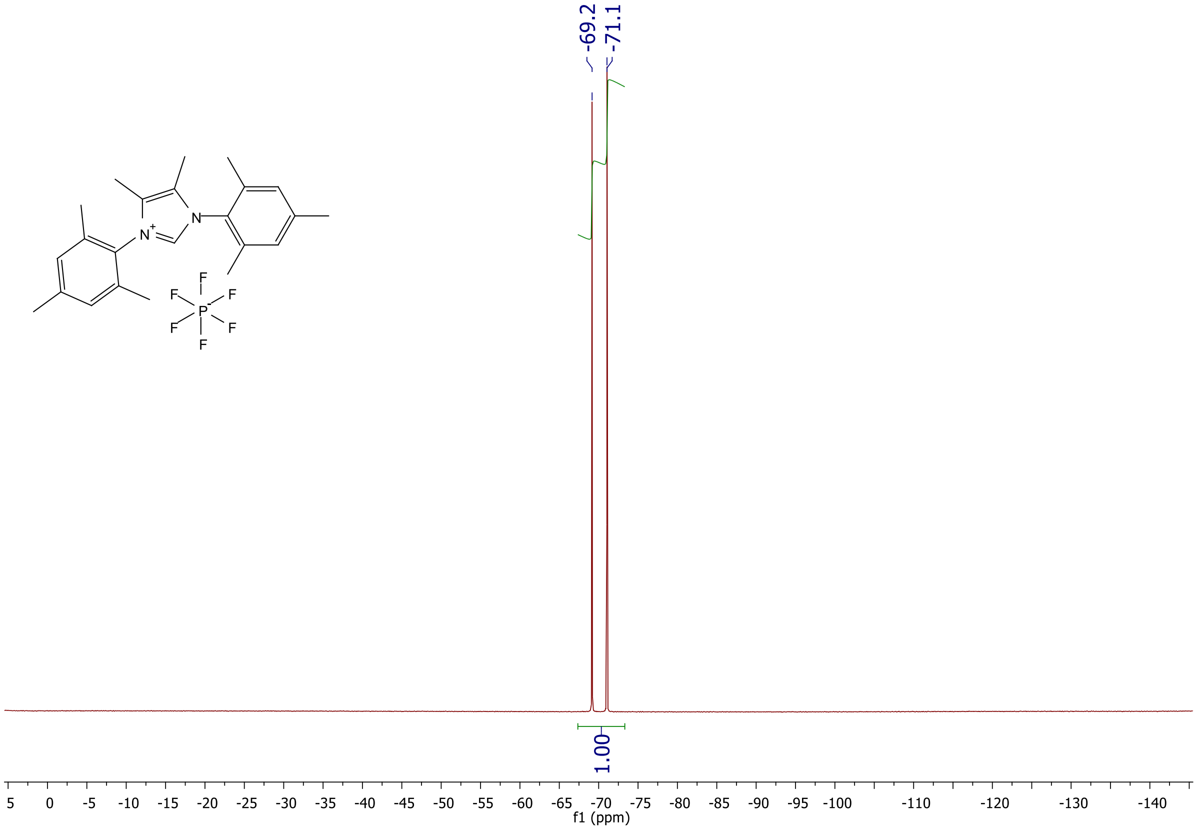
^{13}C NMR (110 MHz, DMSO-d_6)



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

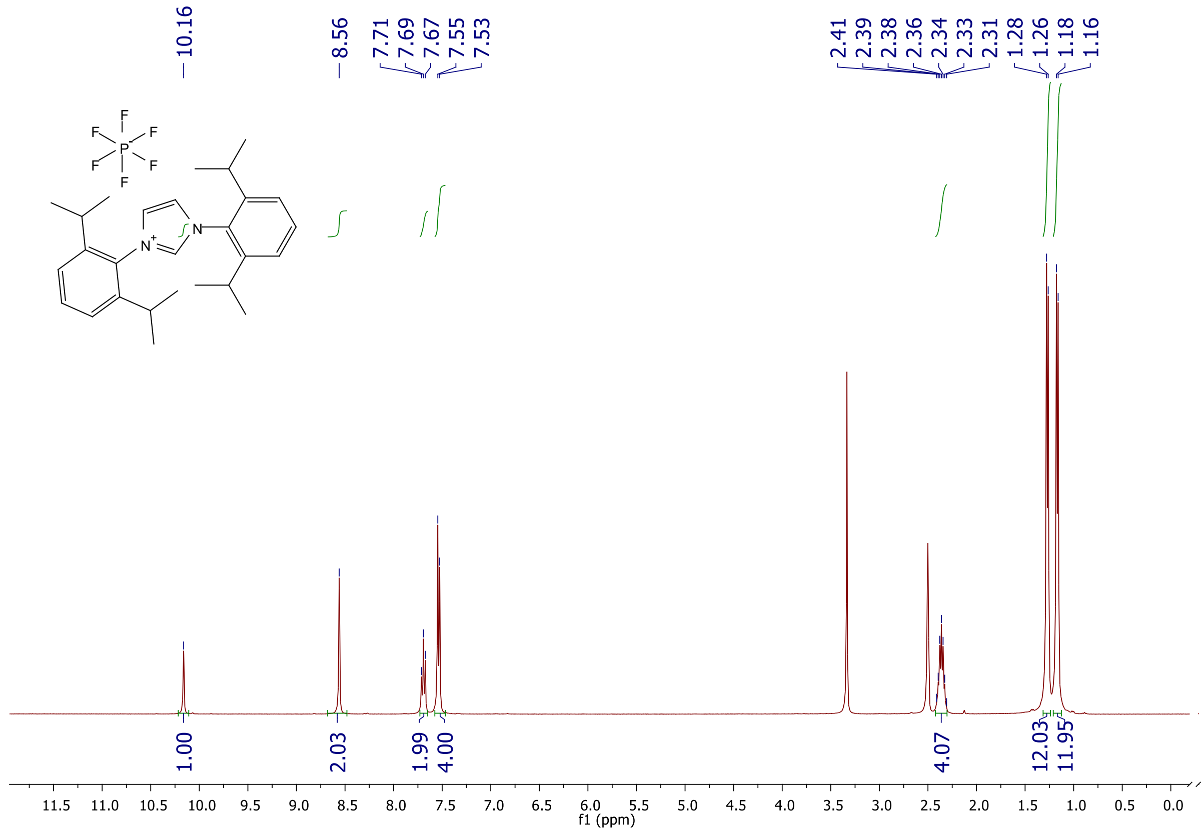


^{19}F NMR (376 MHz, DMSO-d_6)

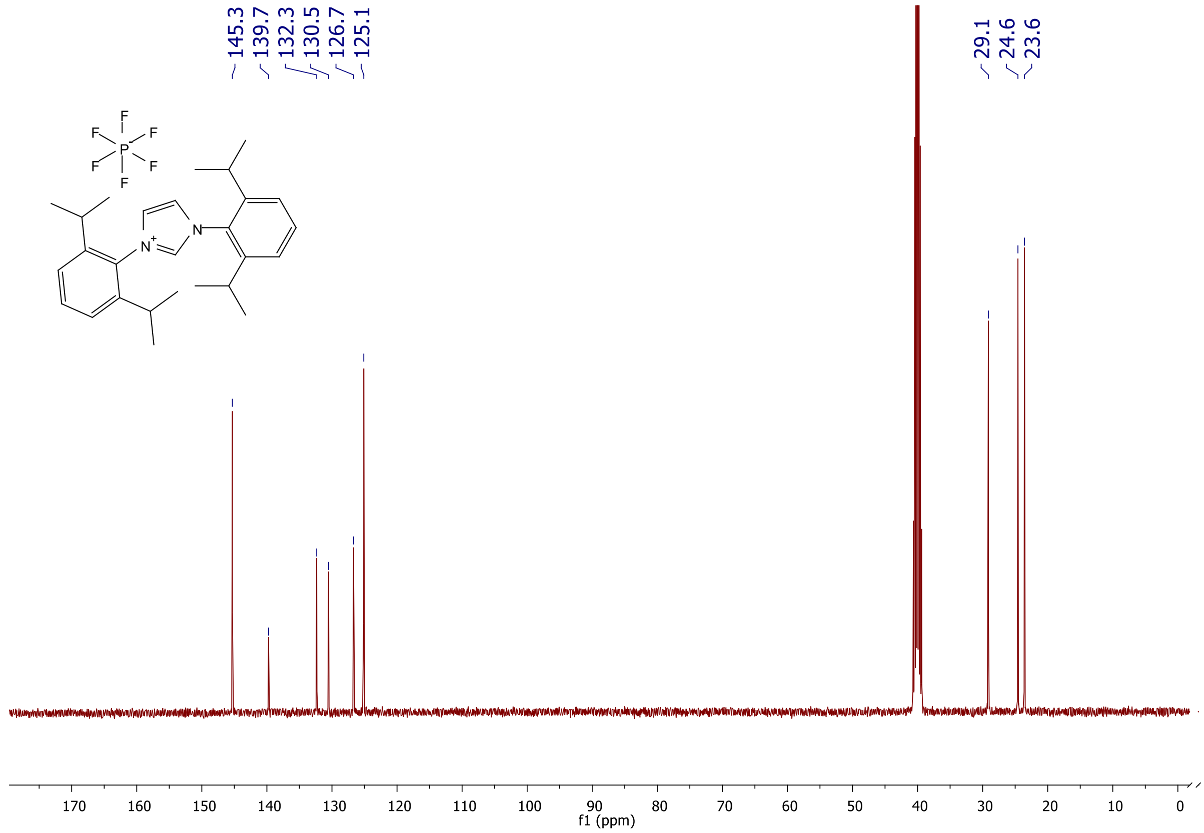


1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium hexafluorophosphate 1c·HPF$_6$

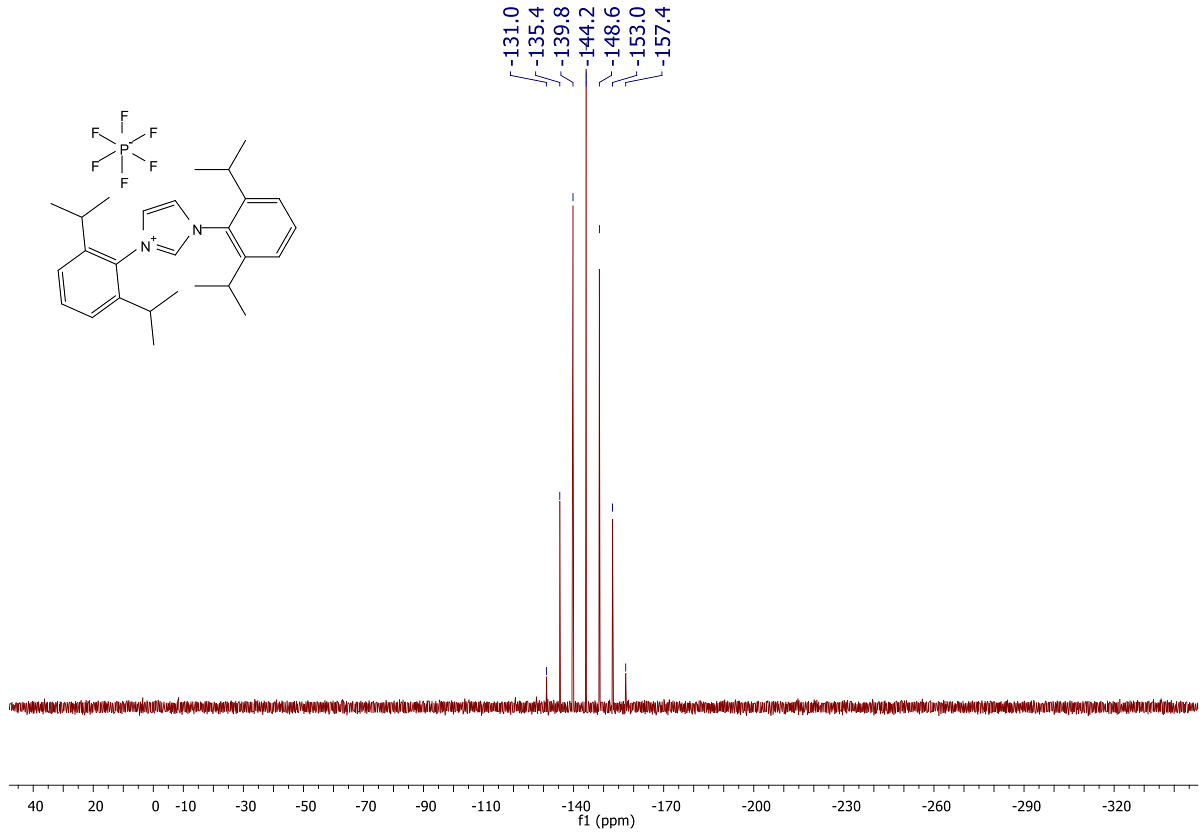
^{1}H NMR (400MHz, DMSO-d_6)



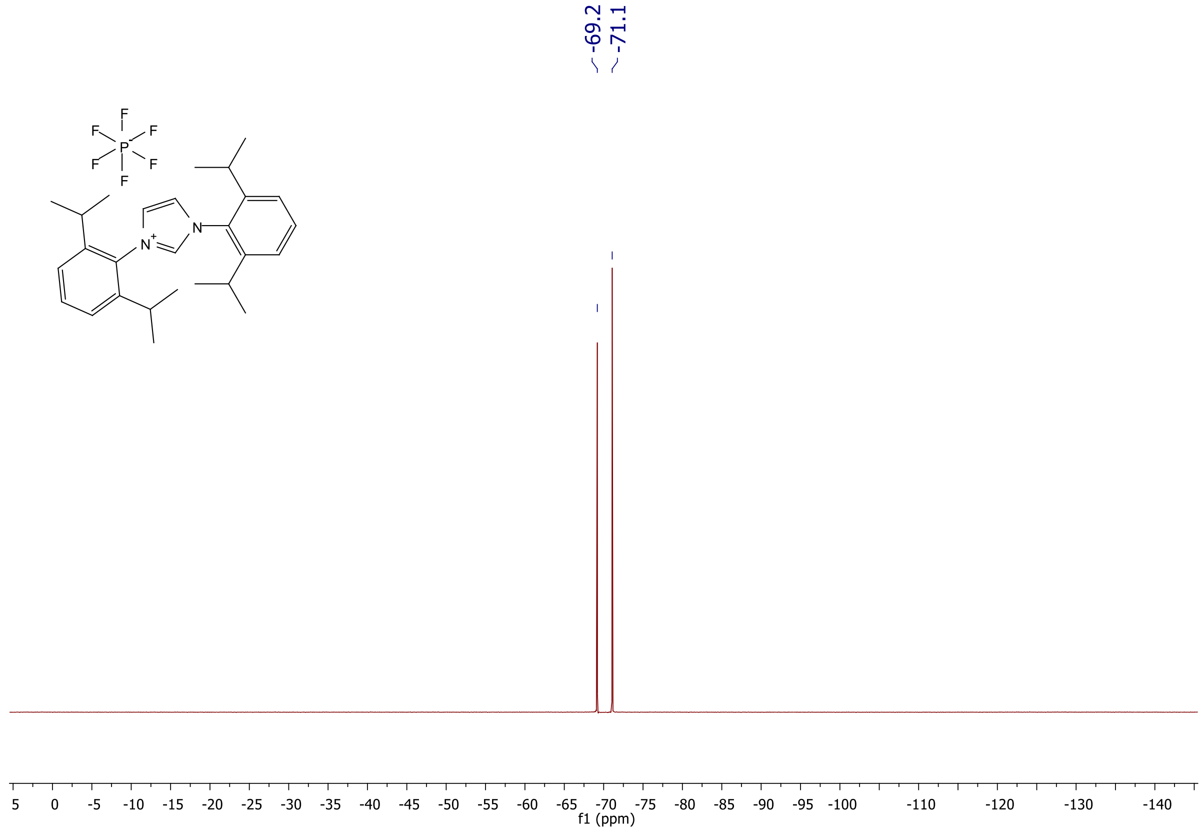
^{13}C NMR (110 MHz, DMSO-d_6)



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

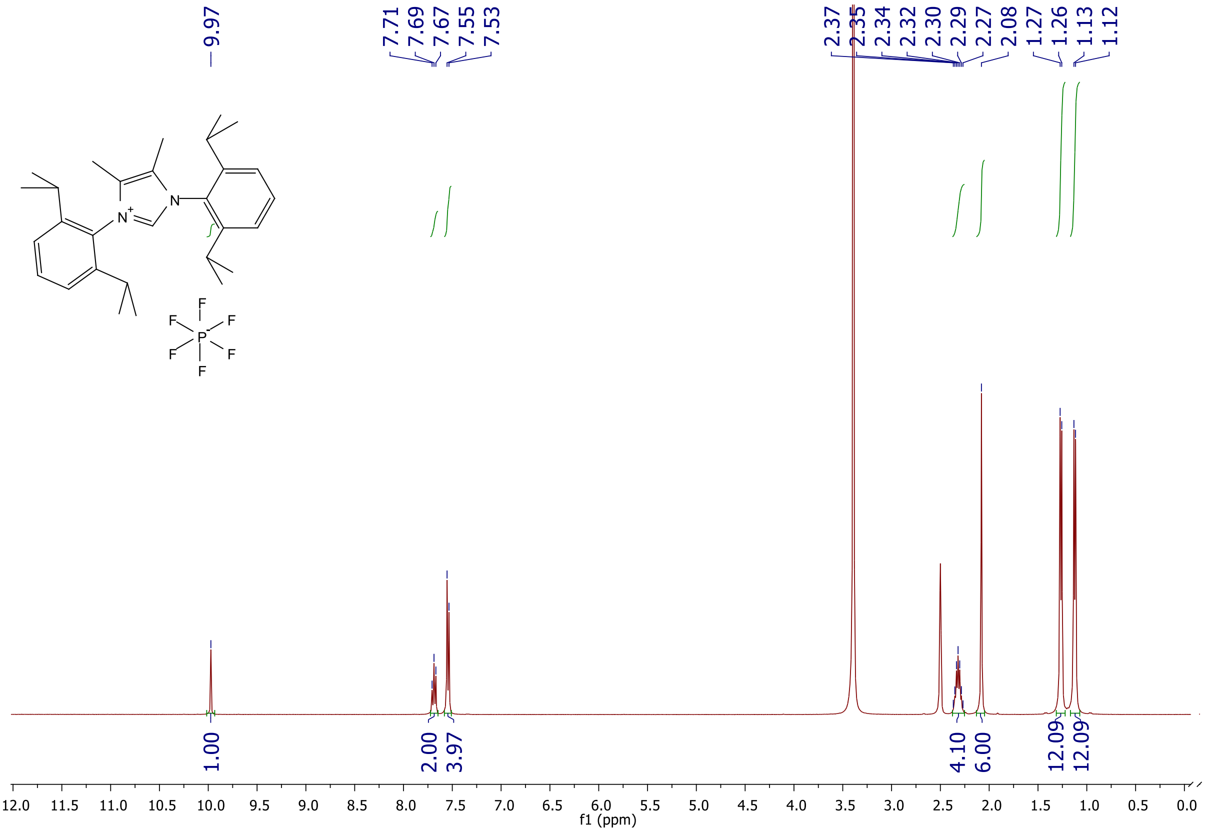


^{19}F NMR (376 MHz, DMSO-d_6)

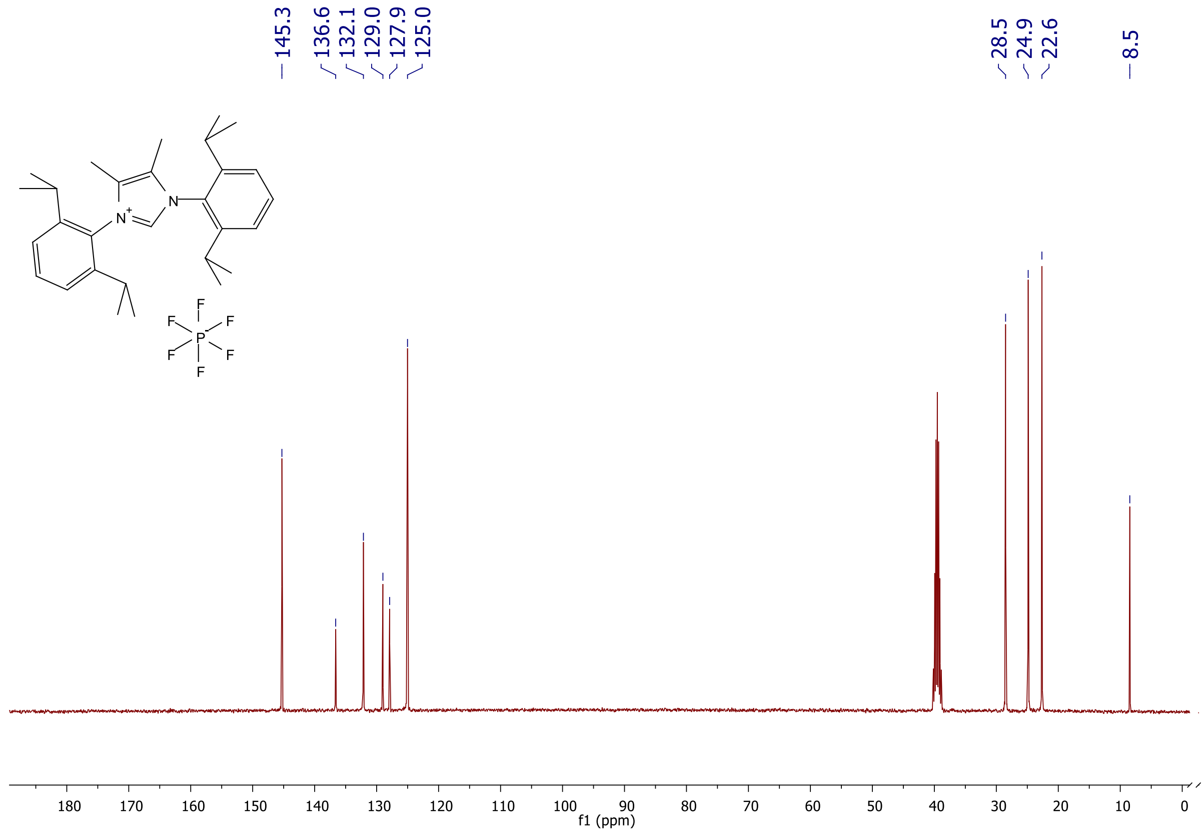


[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium hexafluorophosphate 1d·HPF$_6$

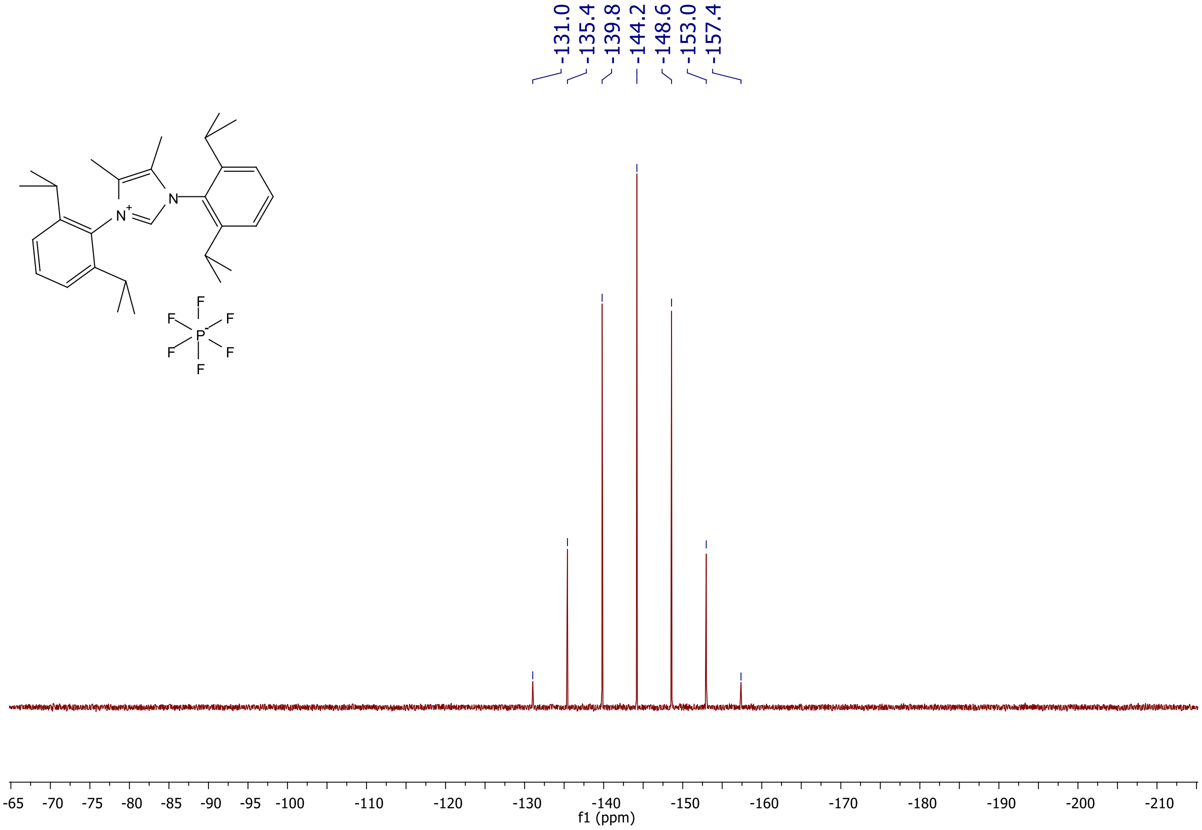
^{1}H NMR (400MHz, DMSO-d_6)



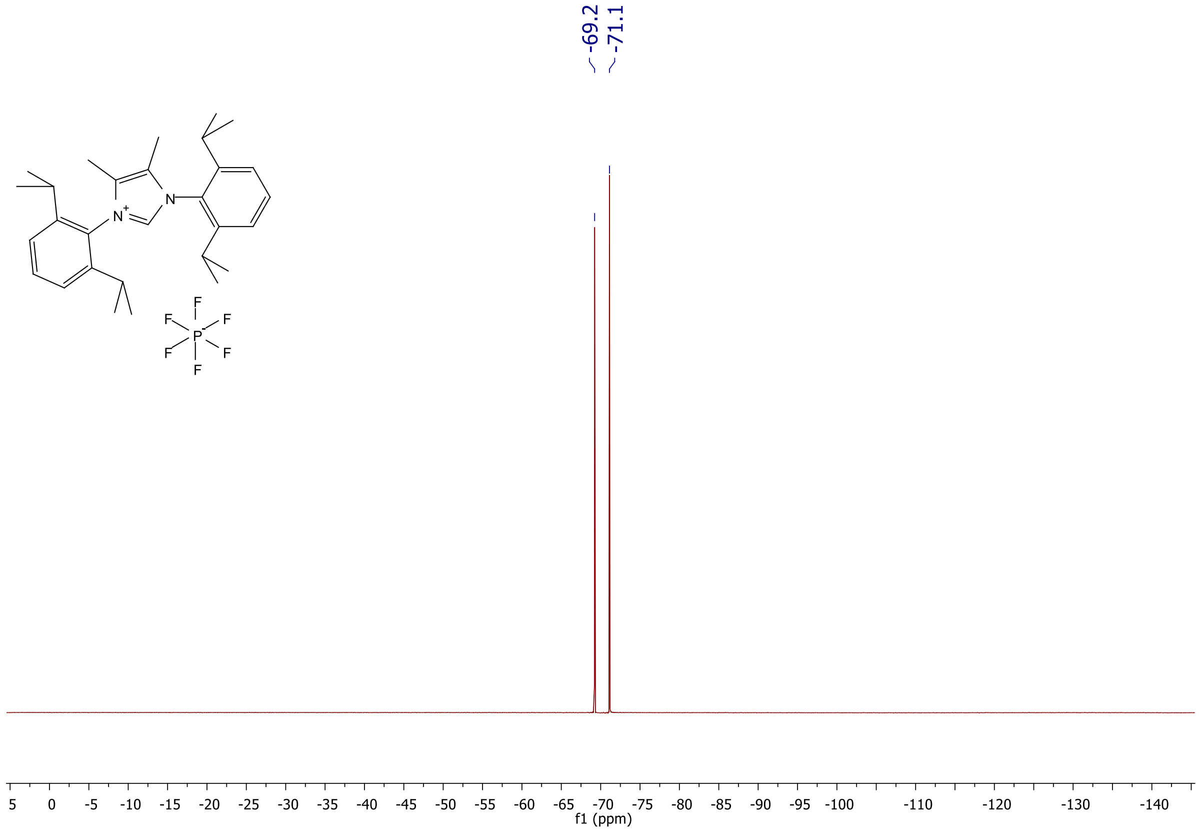
^{13}C NMR (110 MHz, DMSO-d_6)



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

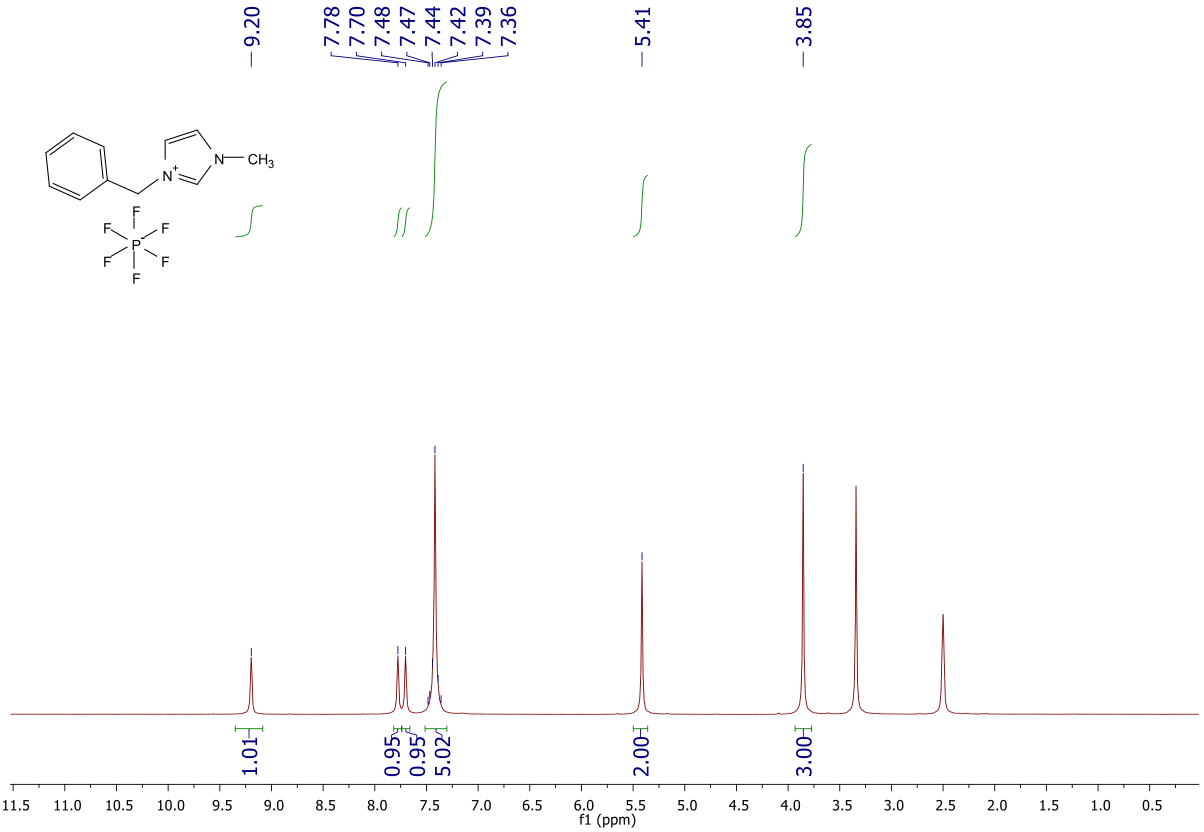


^{19}F NMR (376 MHz, DMSO-d_6)

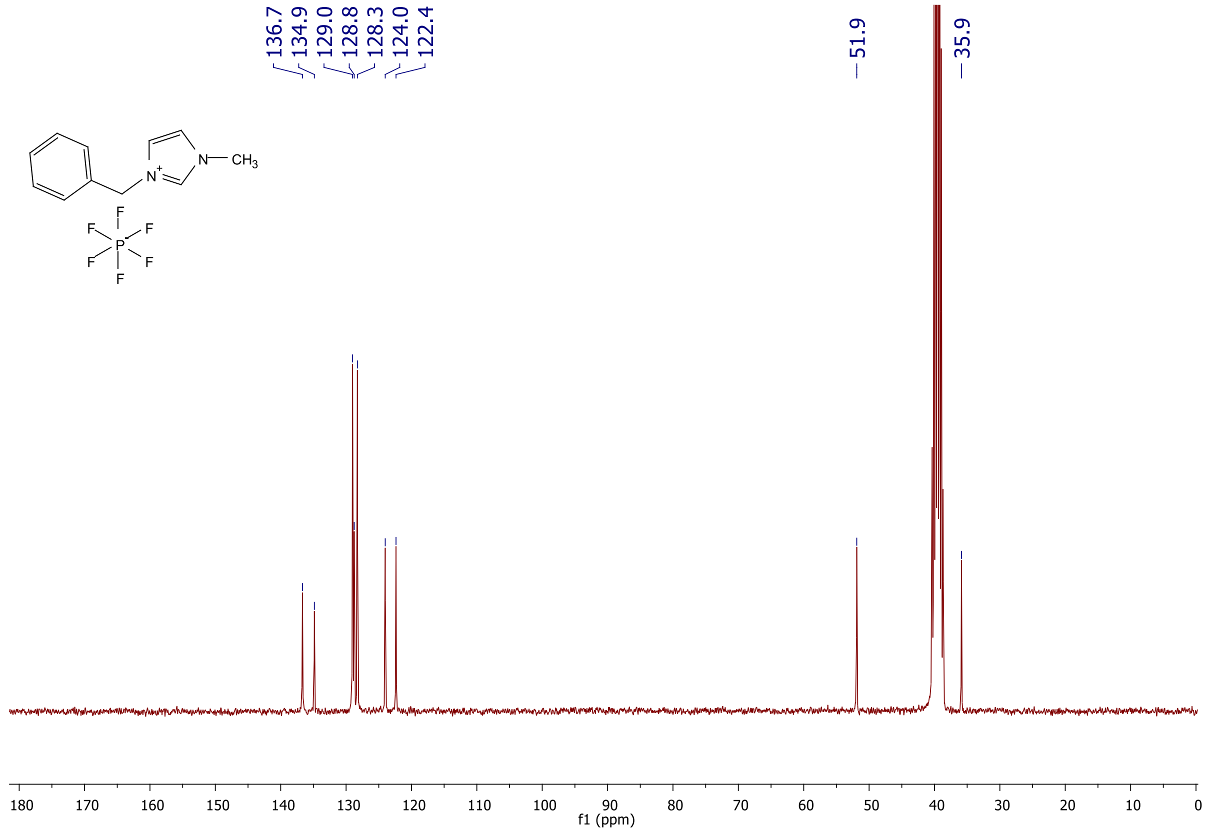


1-Benzyl-3-methylimidazolium hexafluorophosphate 1e·HPF_6

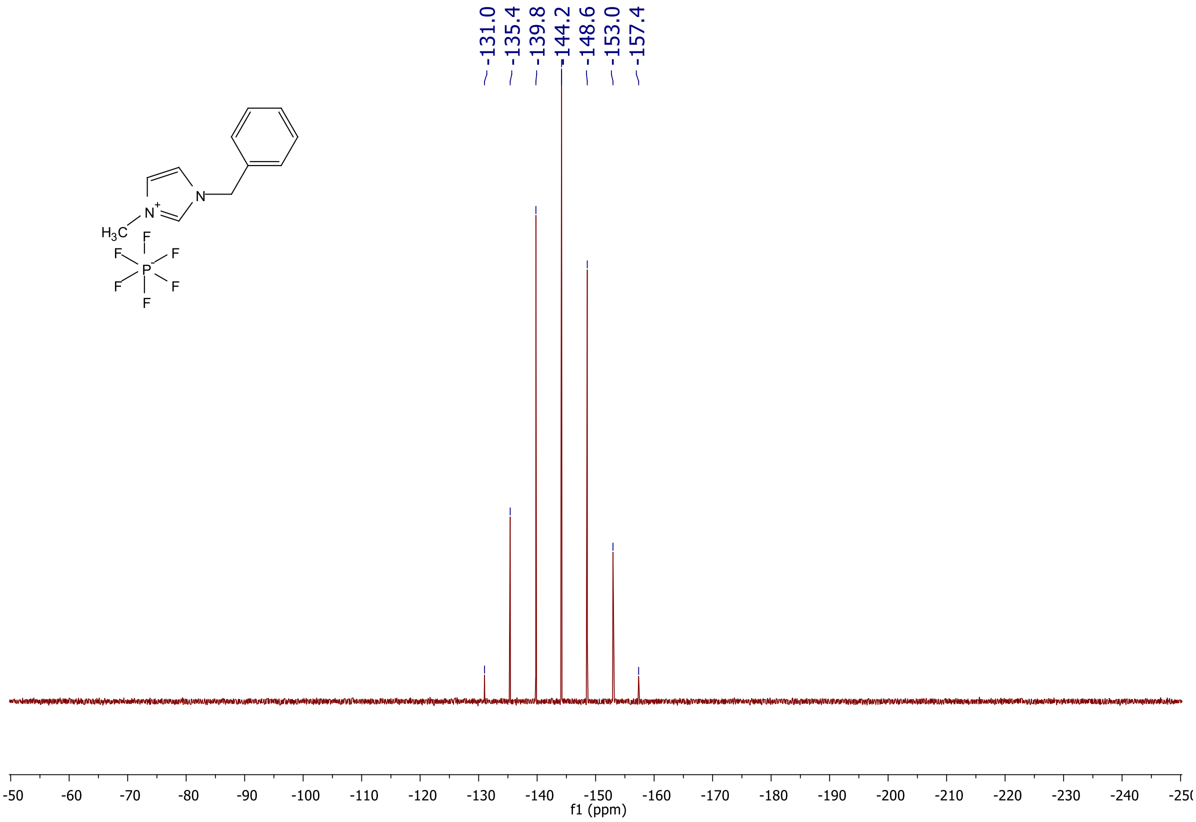
^{1}H NMR (300MHz, DMSO-d_6)



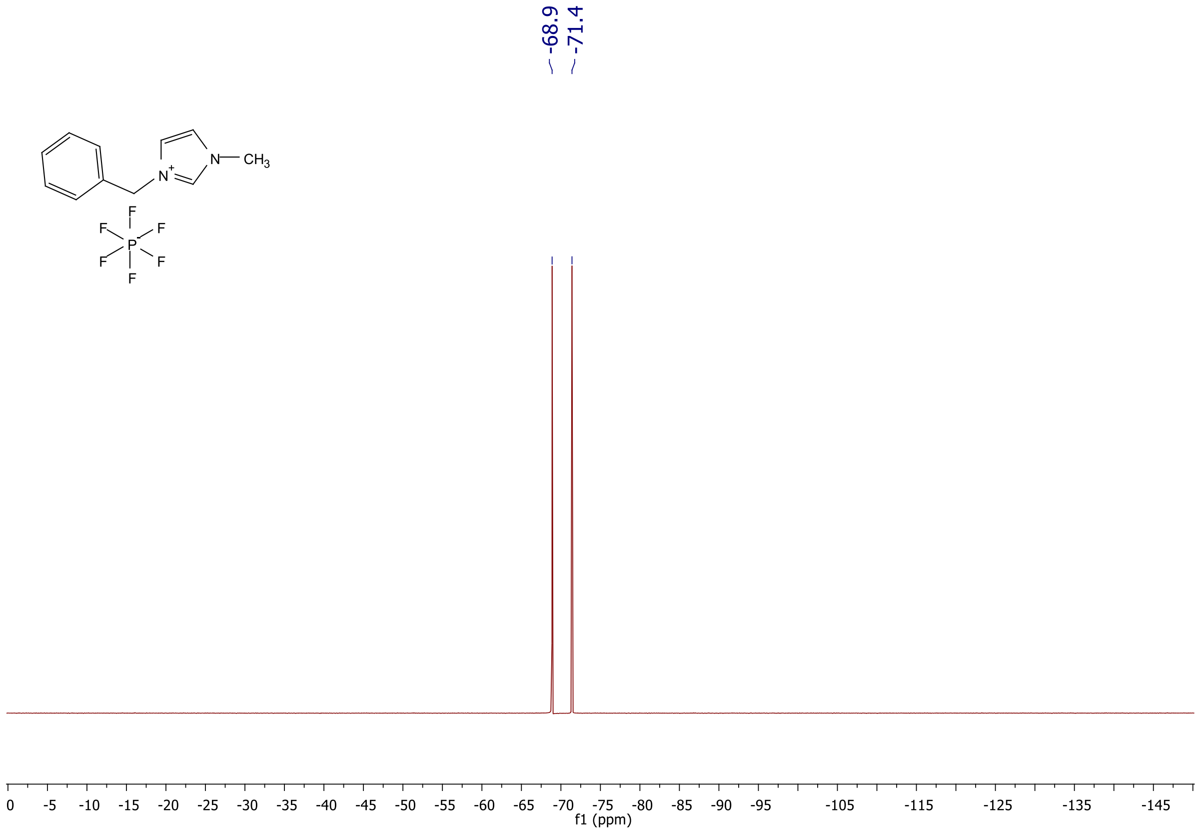
^{13}C NMR (75 MHz, DMSO-d_6)



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

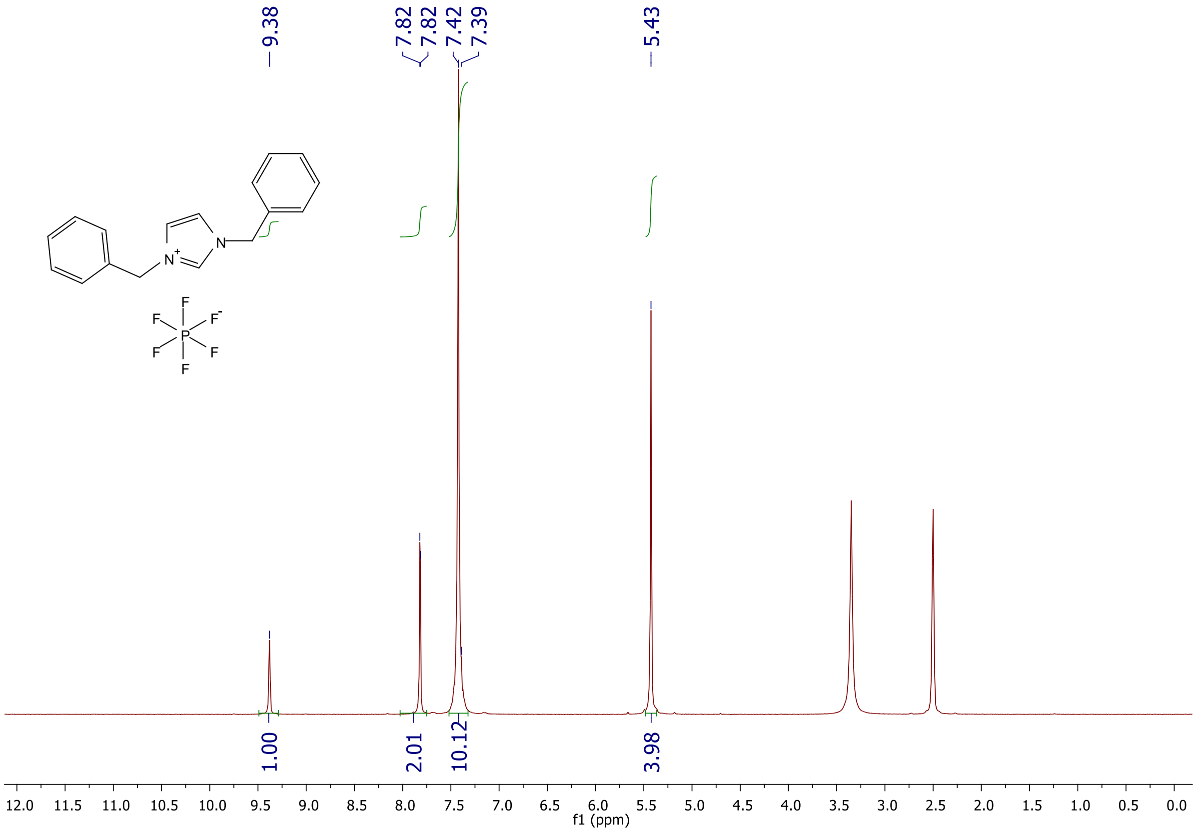


^{19}F NMR (282 MHz, DMSO-d_6)

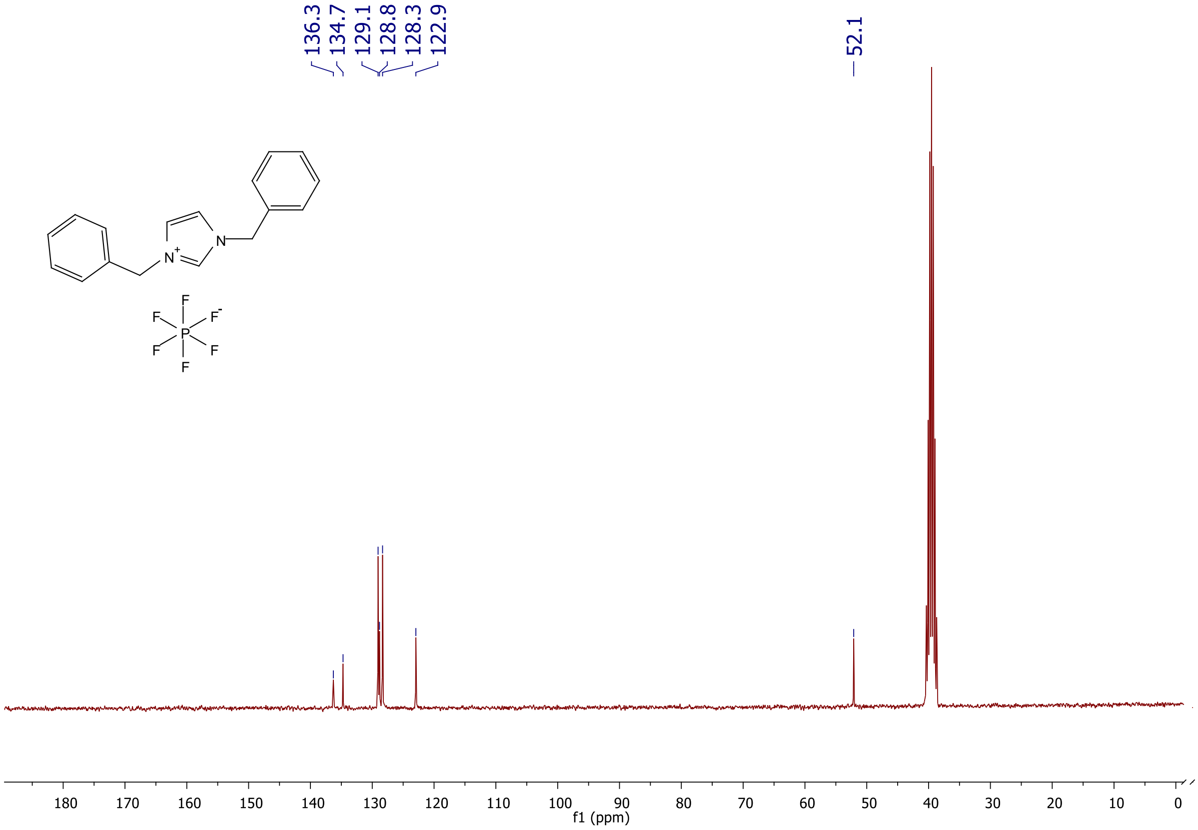


1,3-Dibenzylimidazolium hexafluorophosphate 1f·HPF_6

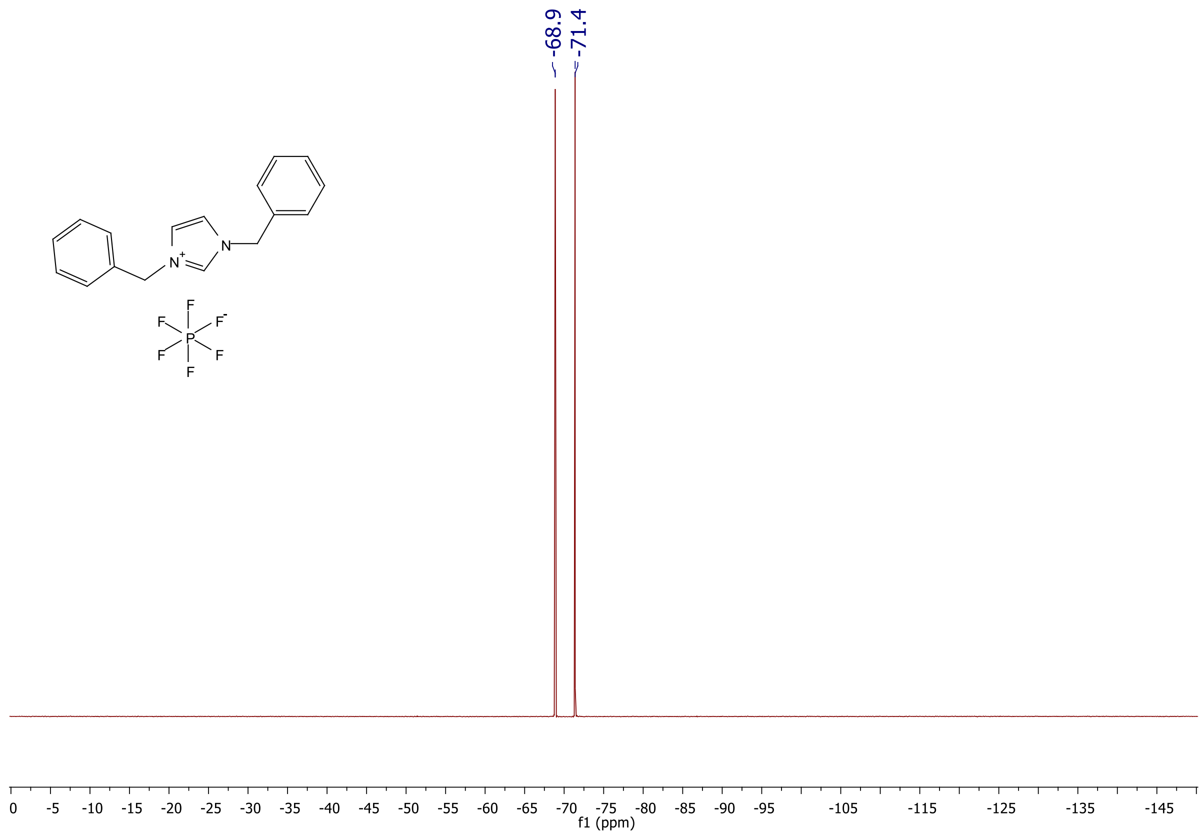
^{1}H NMR (300MHz, DMSO-d_6)



^{13}C NMR (75 MHz, DMSO-d_6)

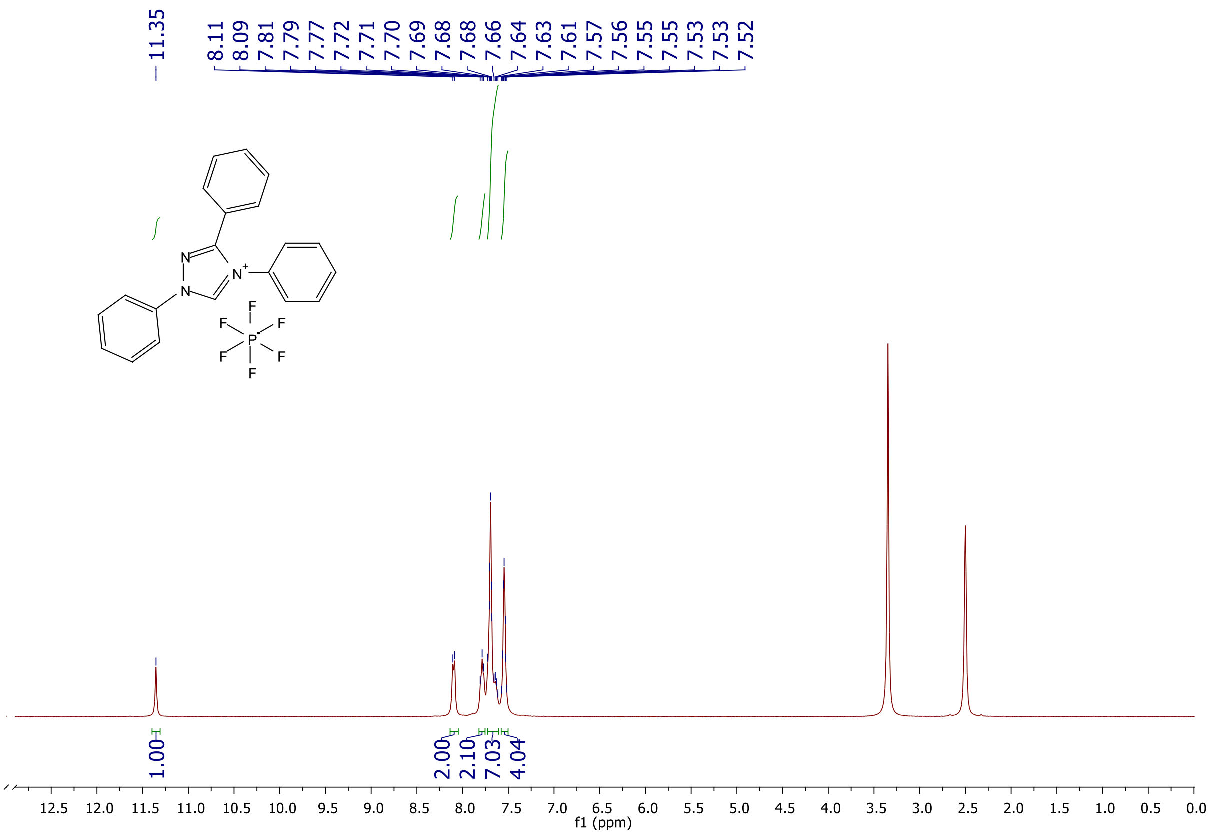


^{19}F NMR (282 MHz, DMSO-d_6)

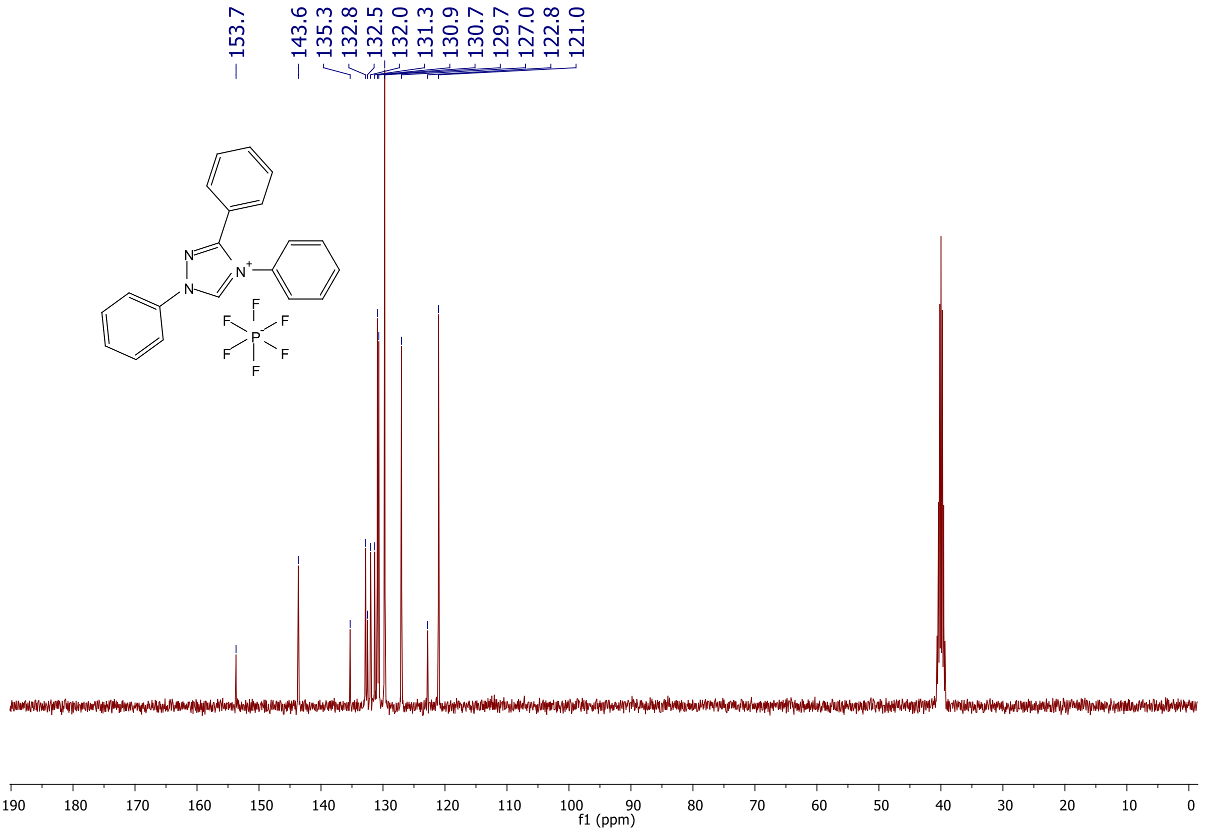


1,3,4-Triphenyl-1,2,4-triazolium hexafluorophosphate 1g·HPF_6

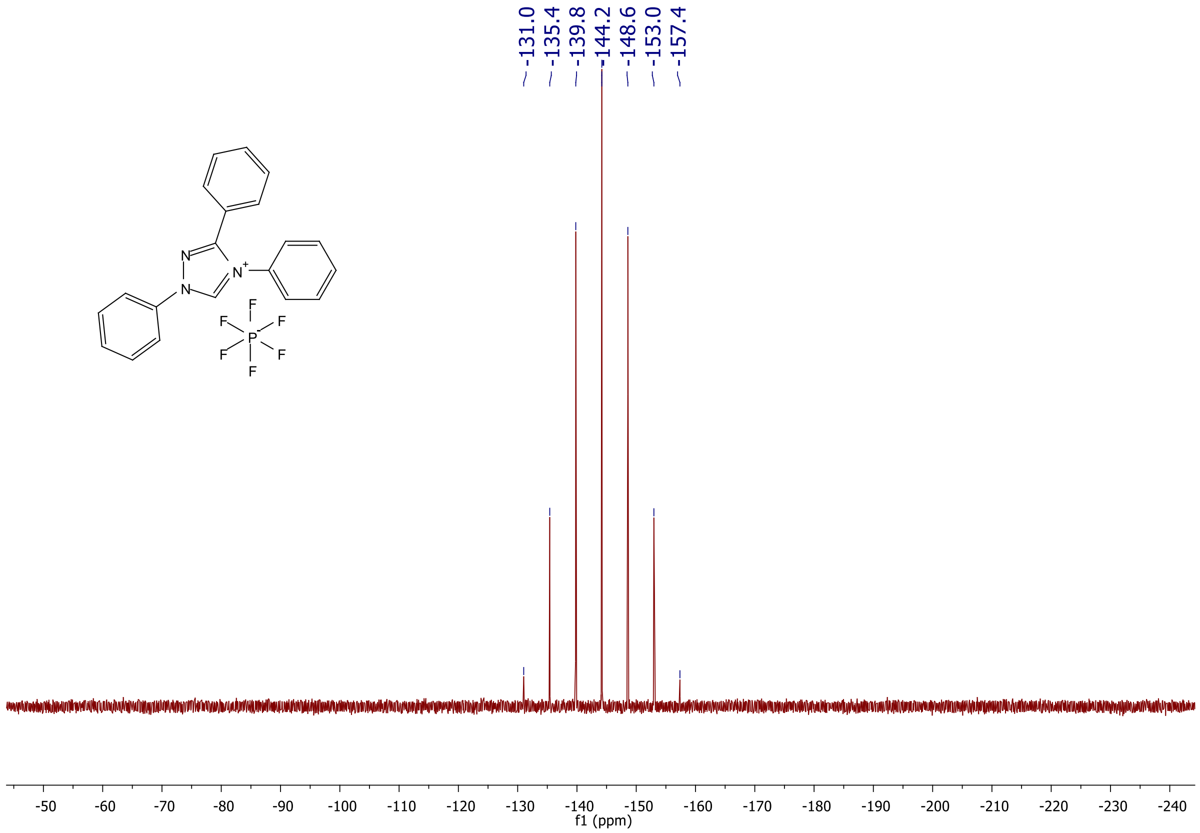
^1H NMR (400MHz, DMSO-d_6)



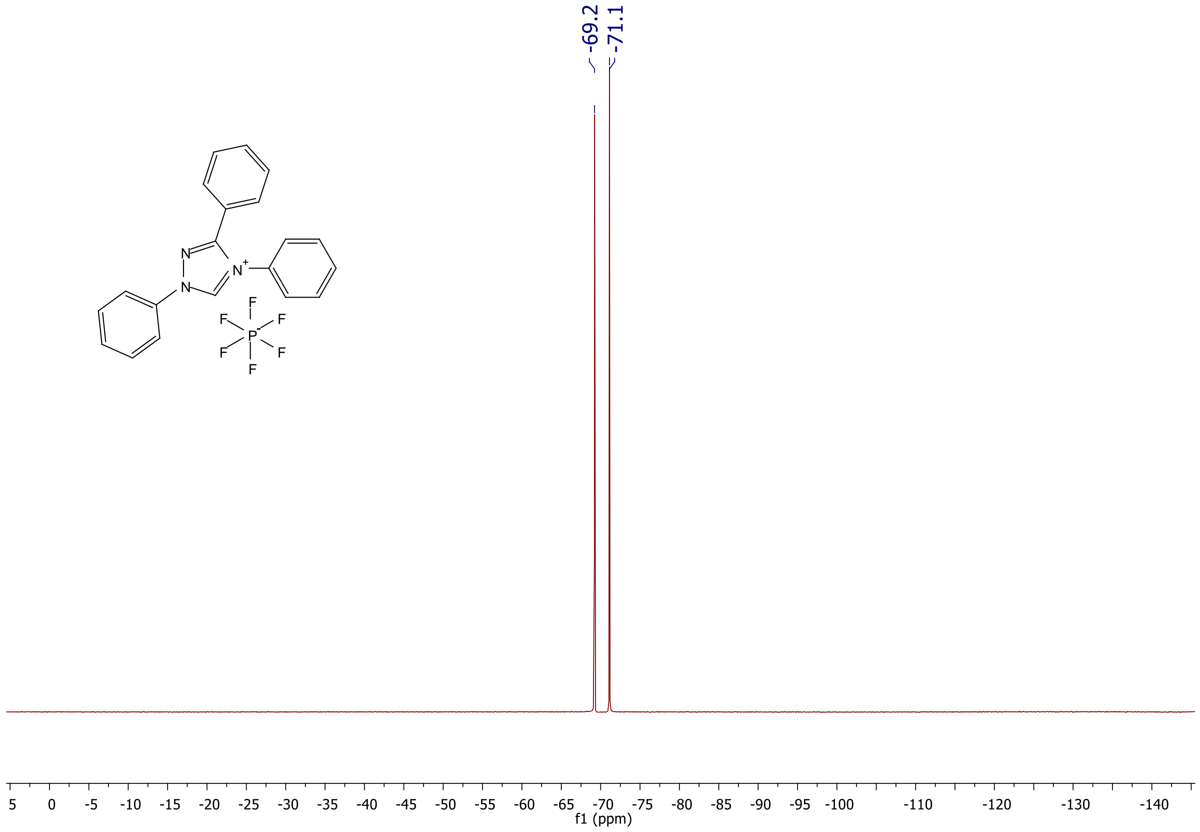
^{13}C NMR (110 MHz, DMSO-d_6)



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



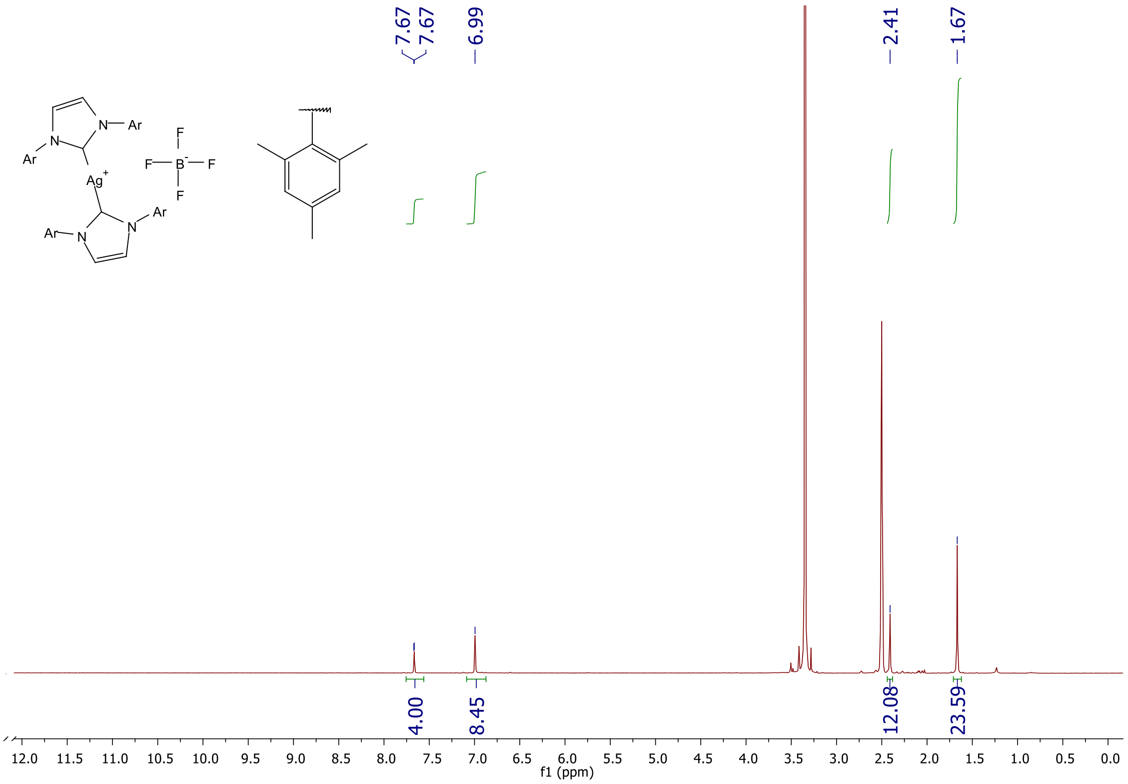
^{19}F NMR (376 MHz, DMSO-d_6)



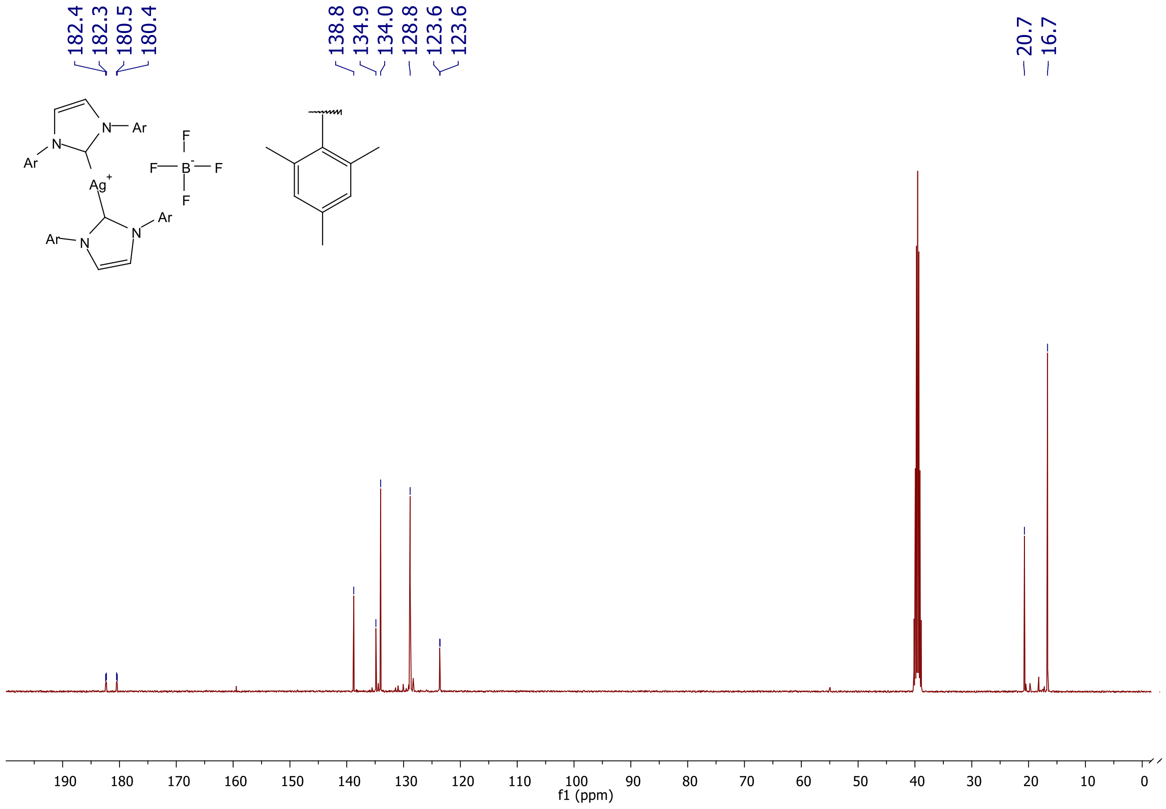
4.3. [Ag(NHC)$_2$]BF$_4$

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1a)$_2$]BF$_4$

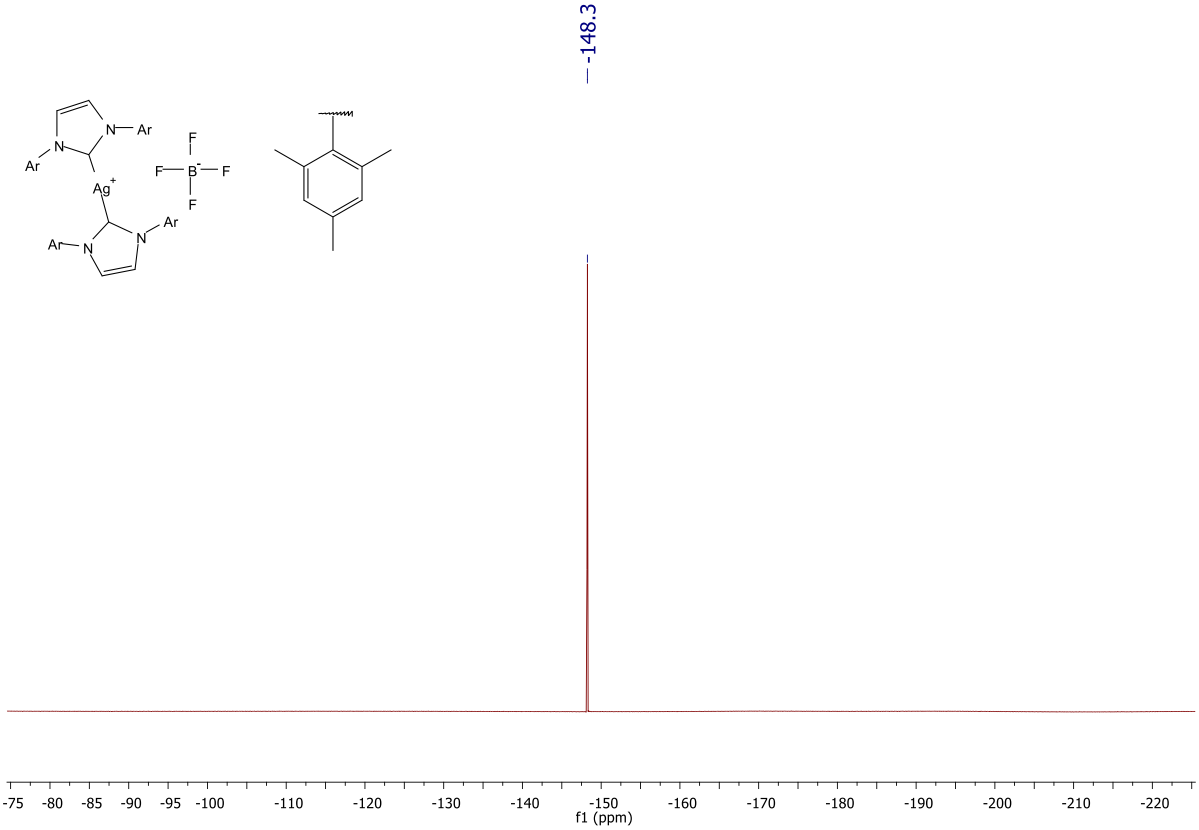
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)

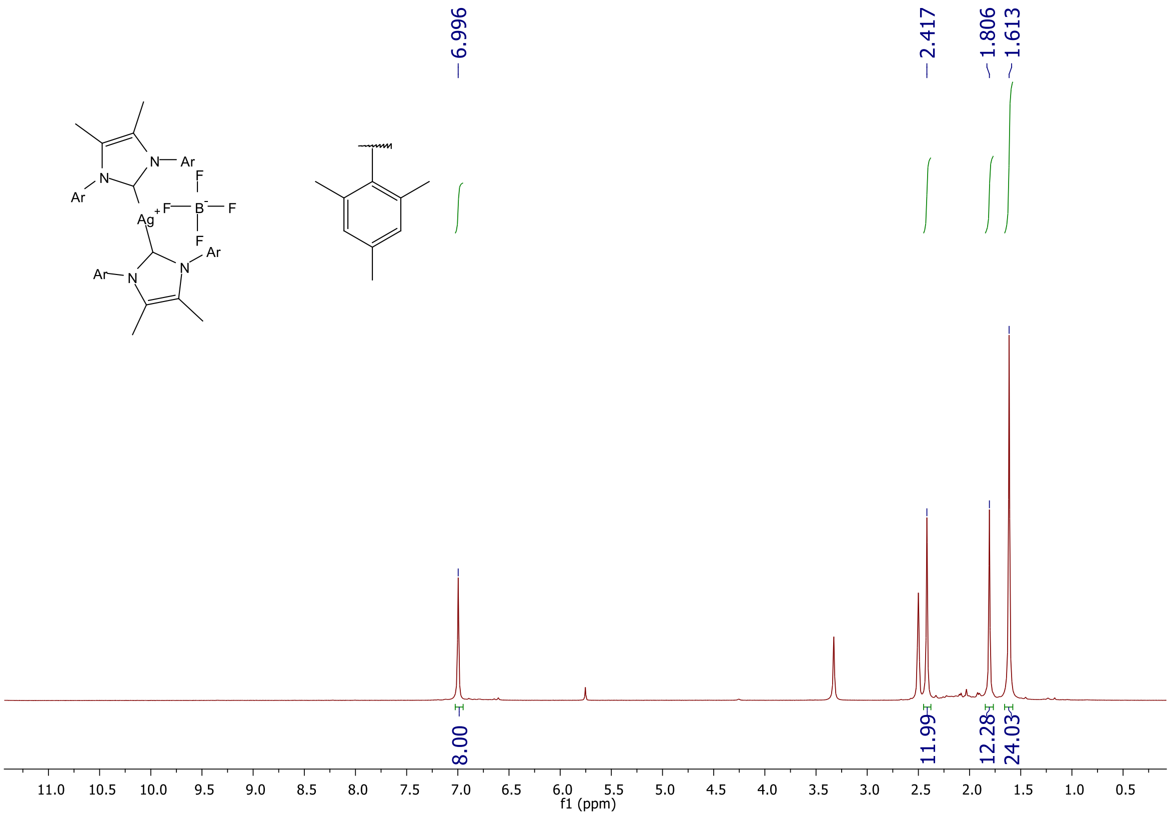


^{19}F NMR (376 MHz, DMSO-d_6)

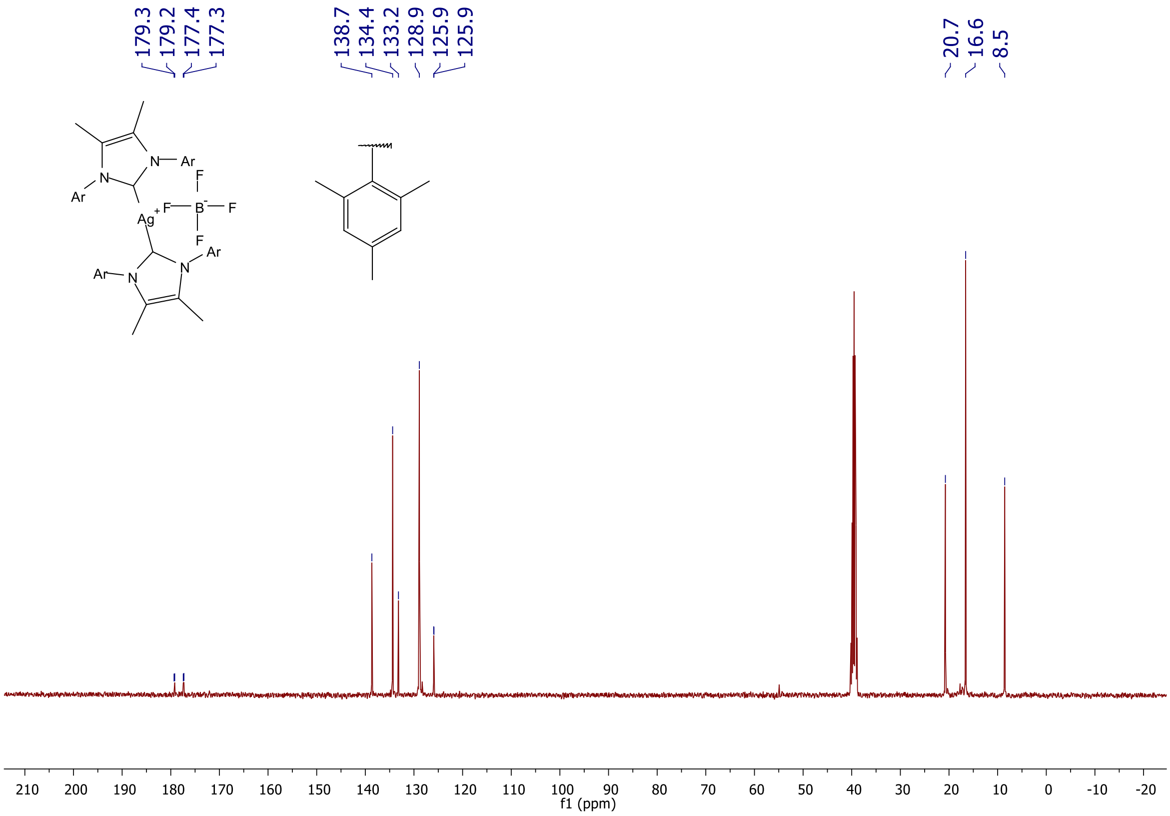


Bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1b)$_2$]BF$_4$

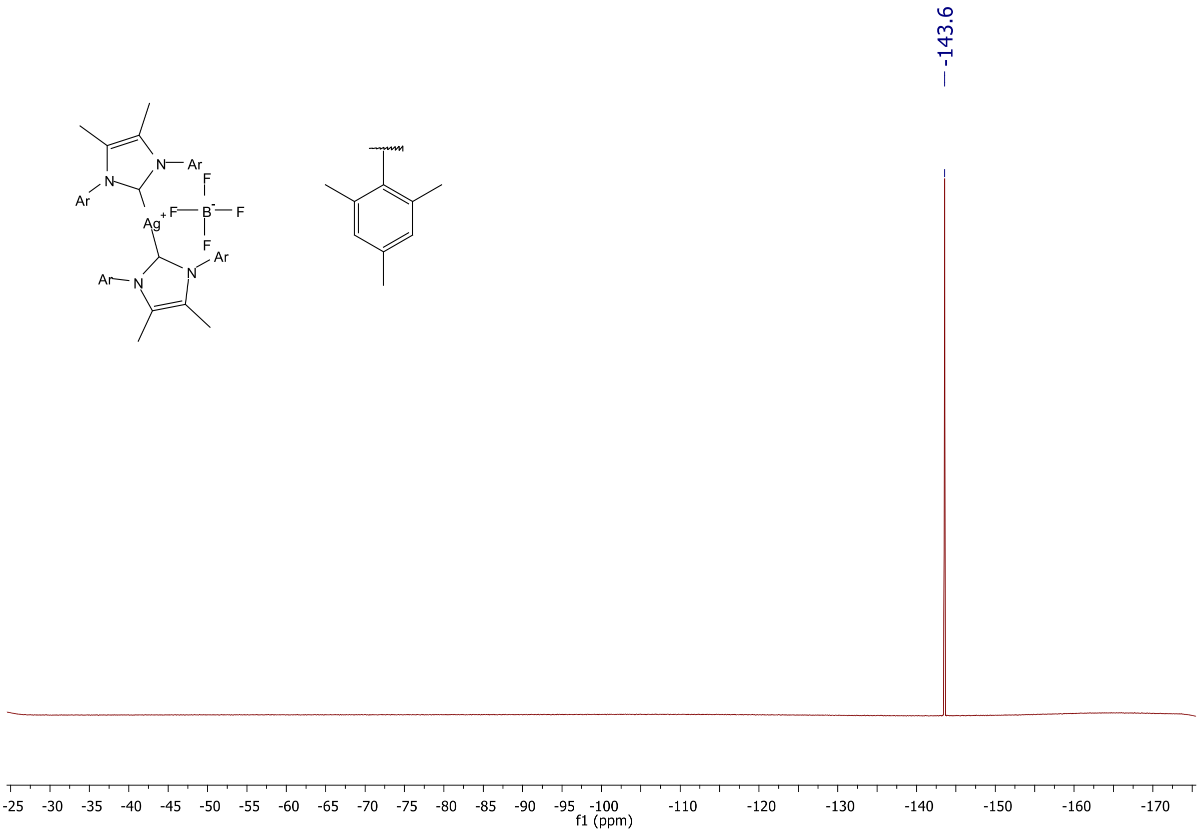
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)

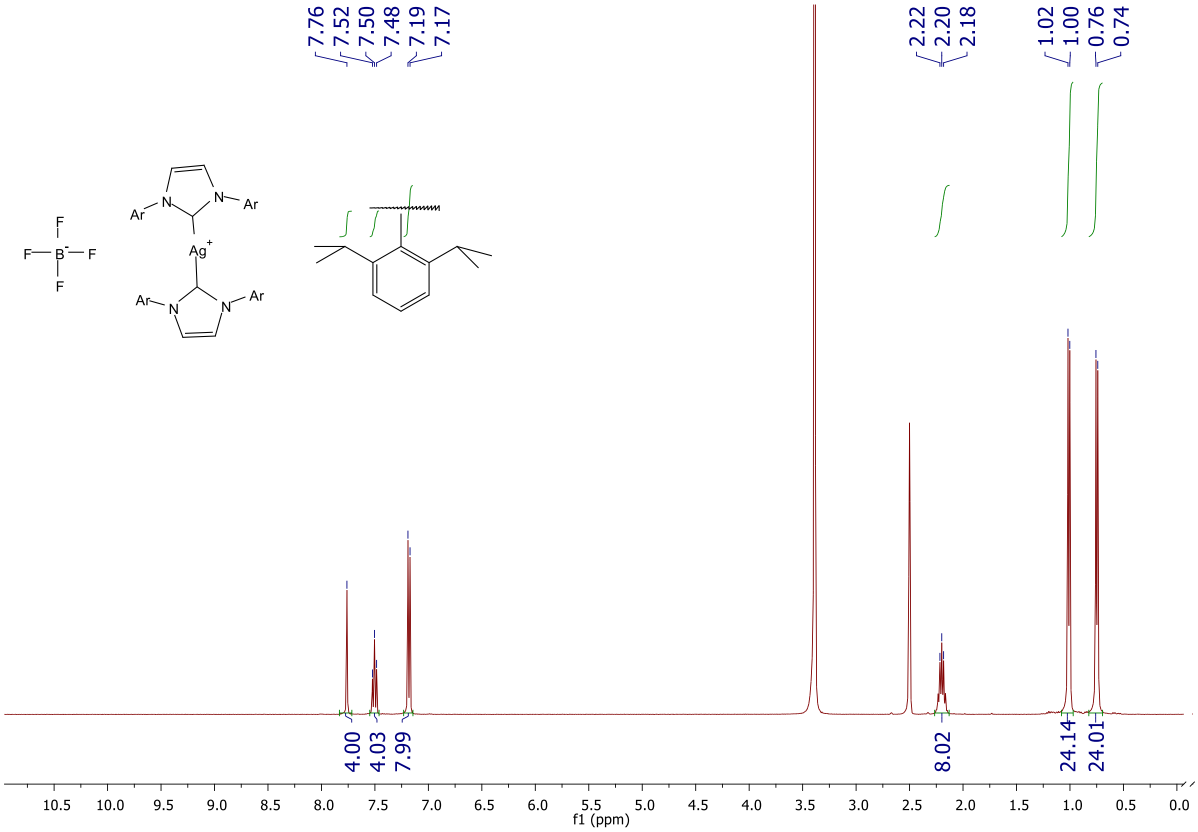


^{19}F NMR (376 MHz, DMSO-d_6)

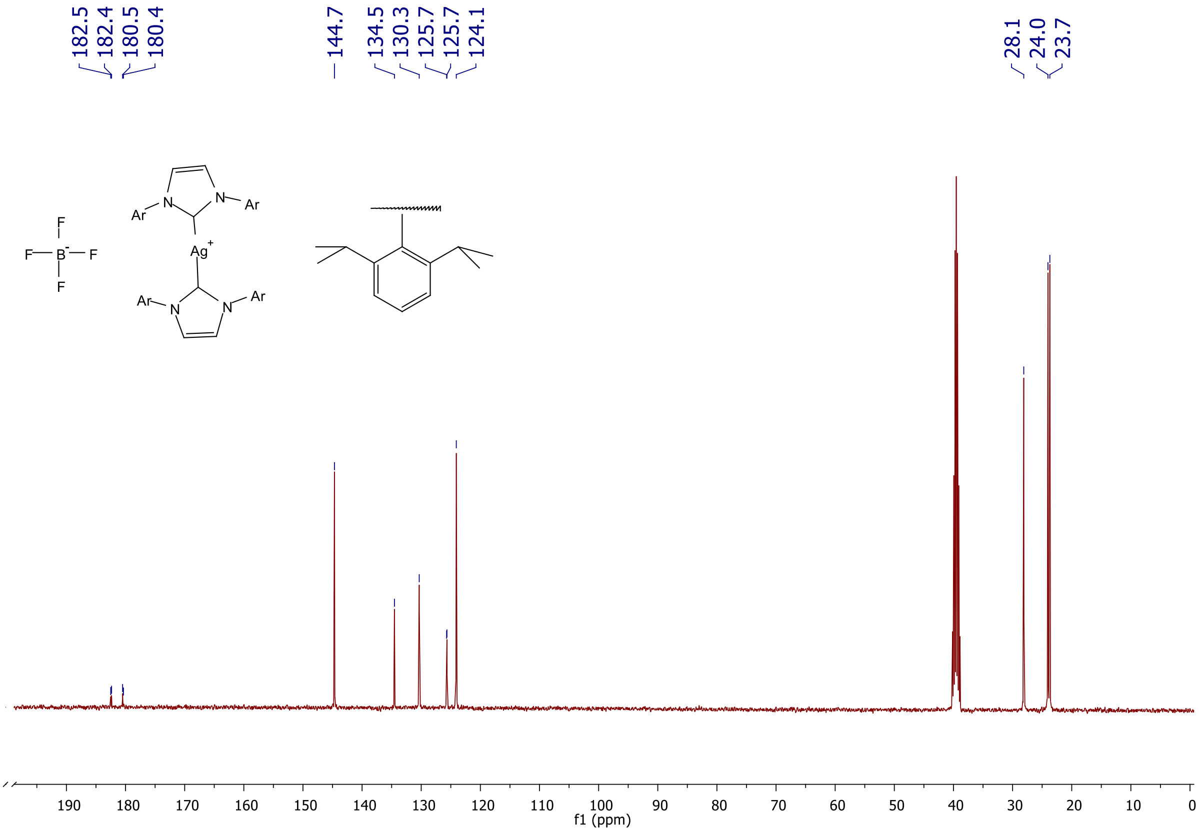


Bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1c)$_2$]BF$_4$

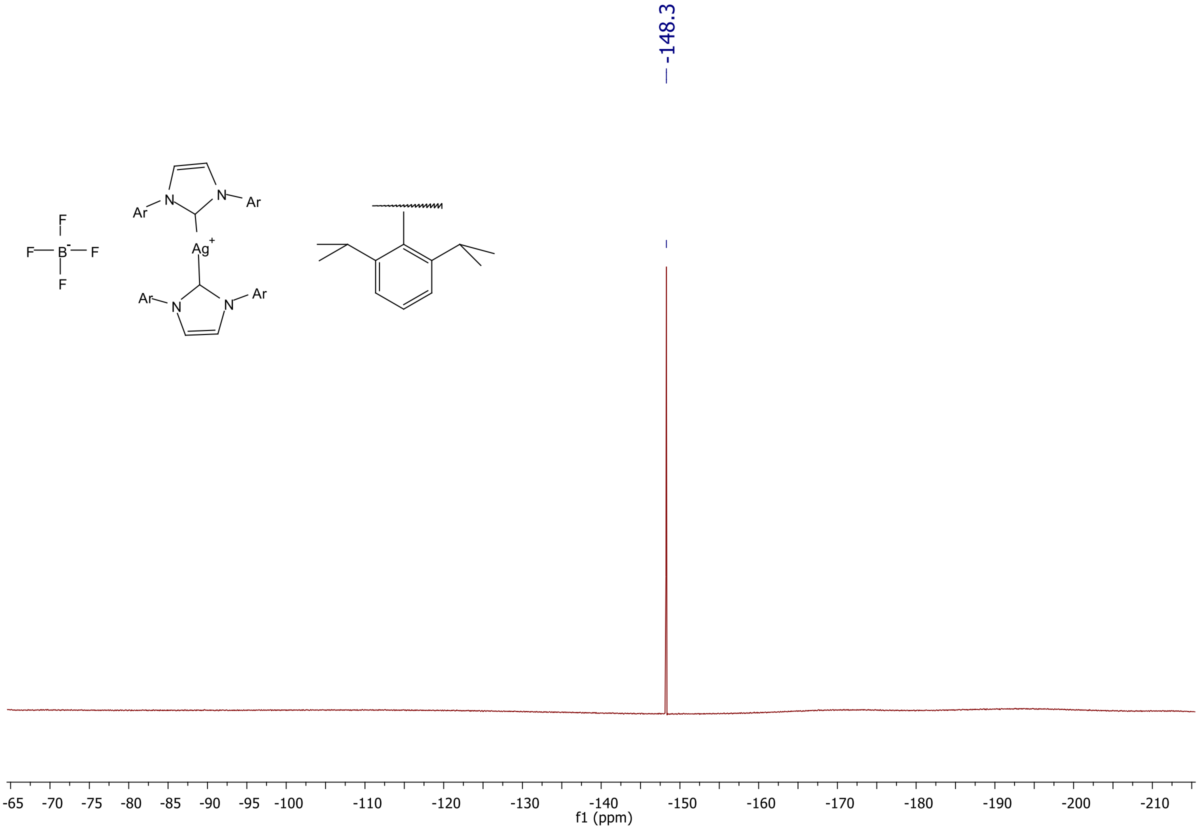
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)

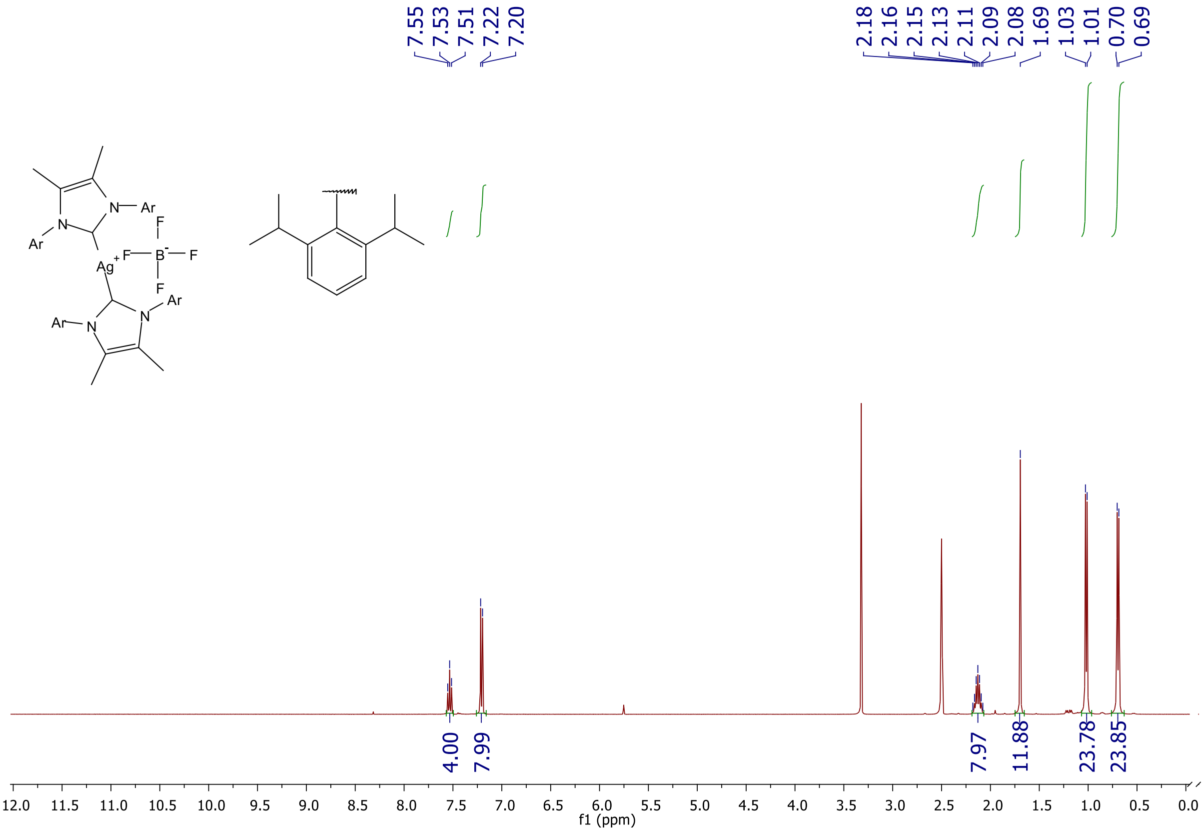


^{19}F NMR (376 MHz, DMSO-d_6)

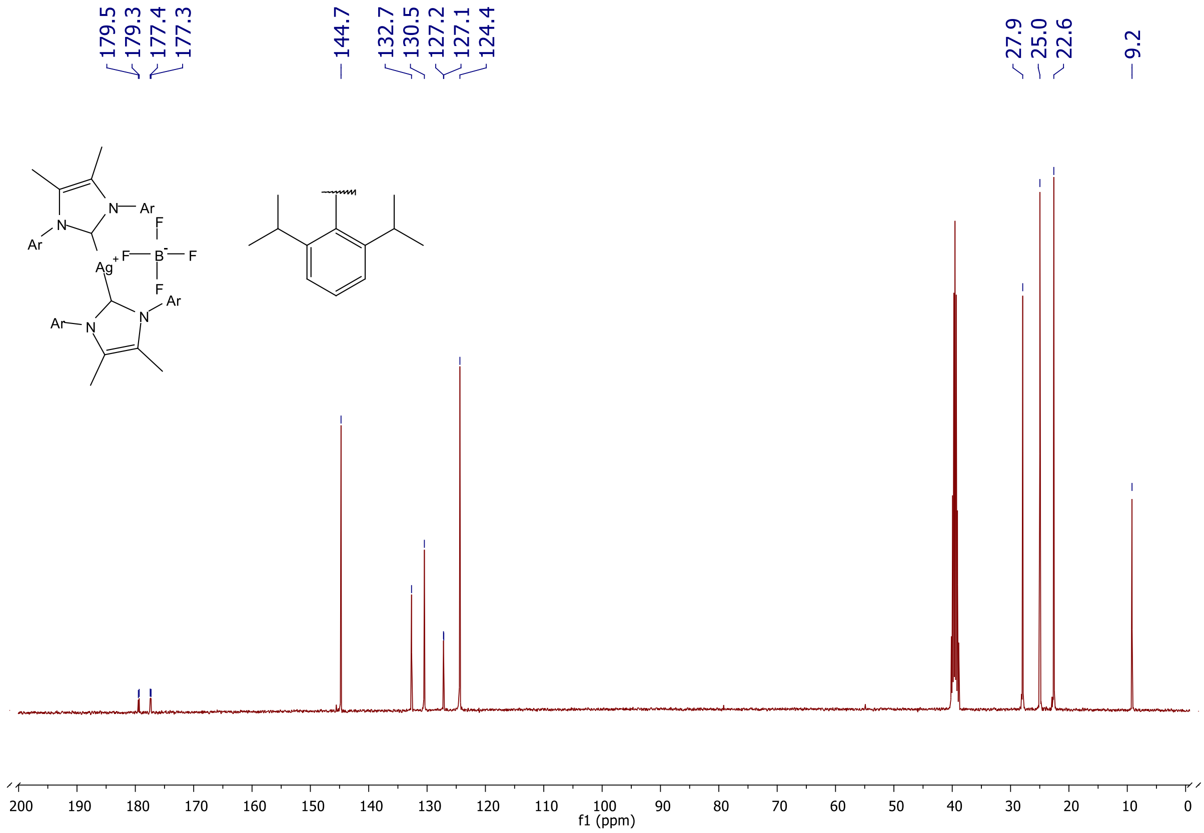


Bis-[1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]silver tetrafluoroborate [Ag(1d)$_2$]BF$_4$

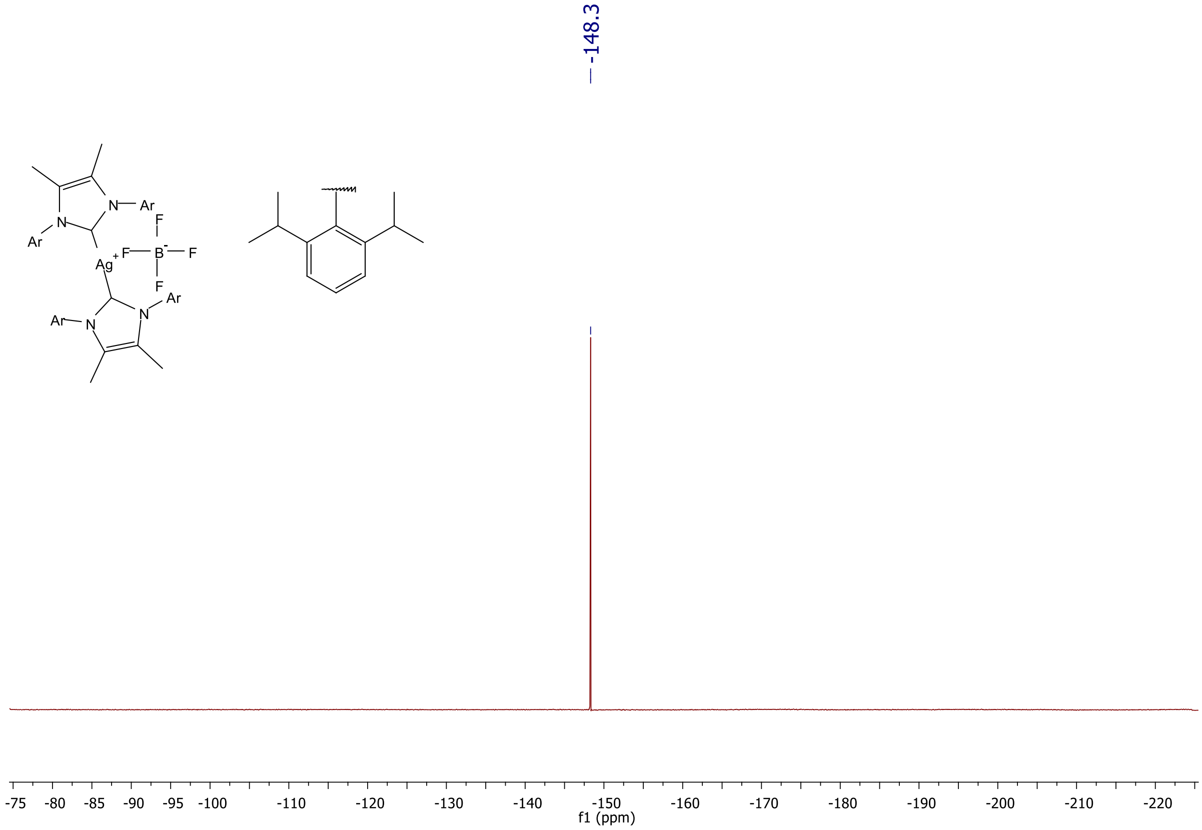
^{1}H NMR (400MHz, DMSO-*d*$_6$)



^{13}C NMR (110 MHz, DMSO-*d*$_6$)

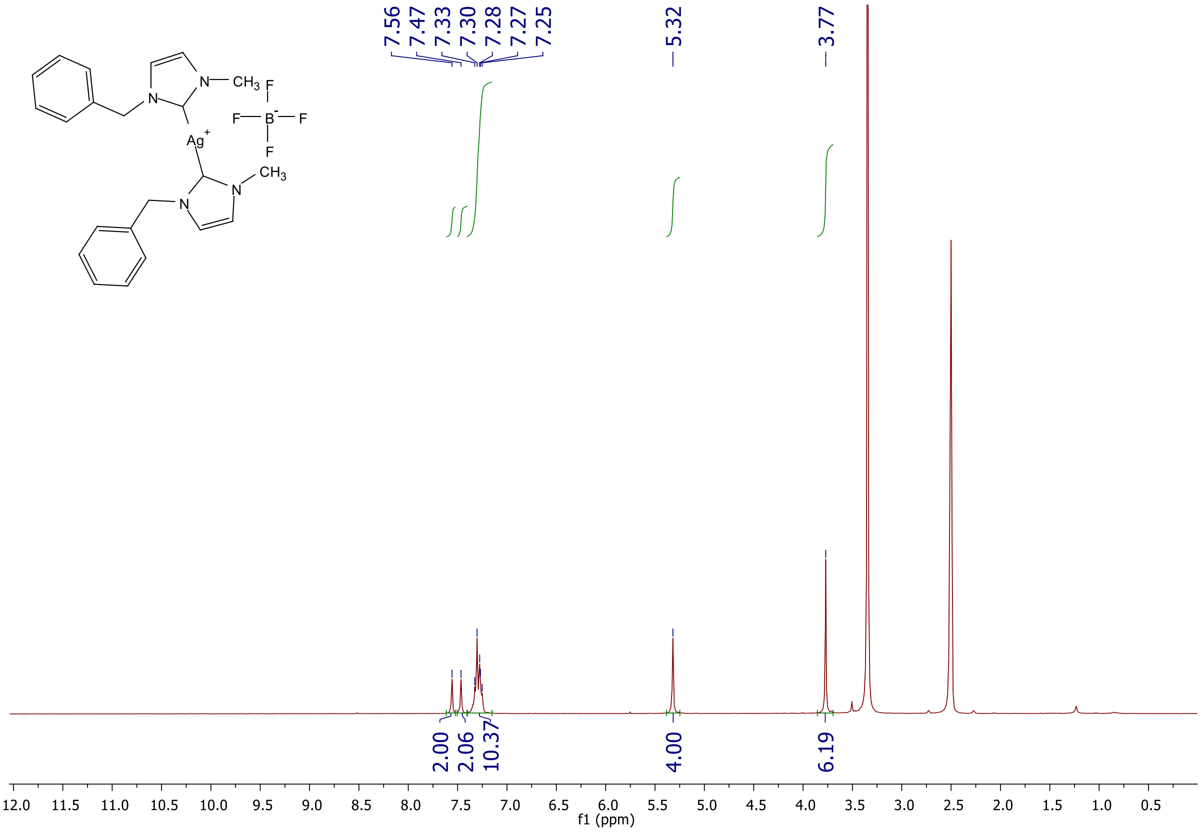


^{19}F NMR (376 MHz, DMSO-d_6)

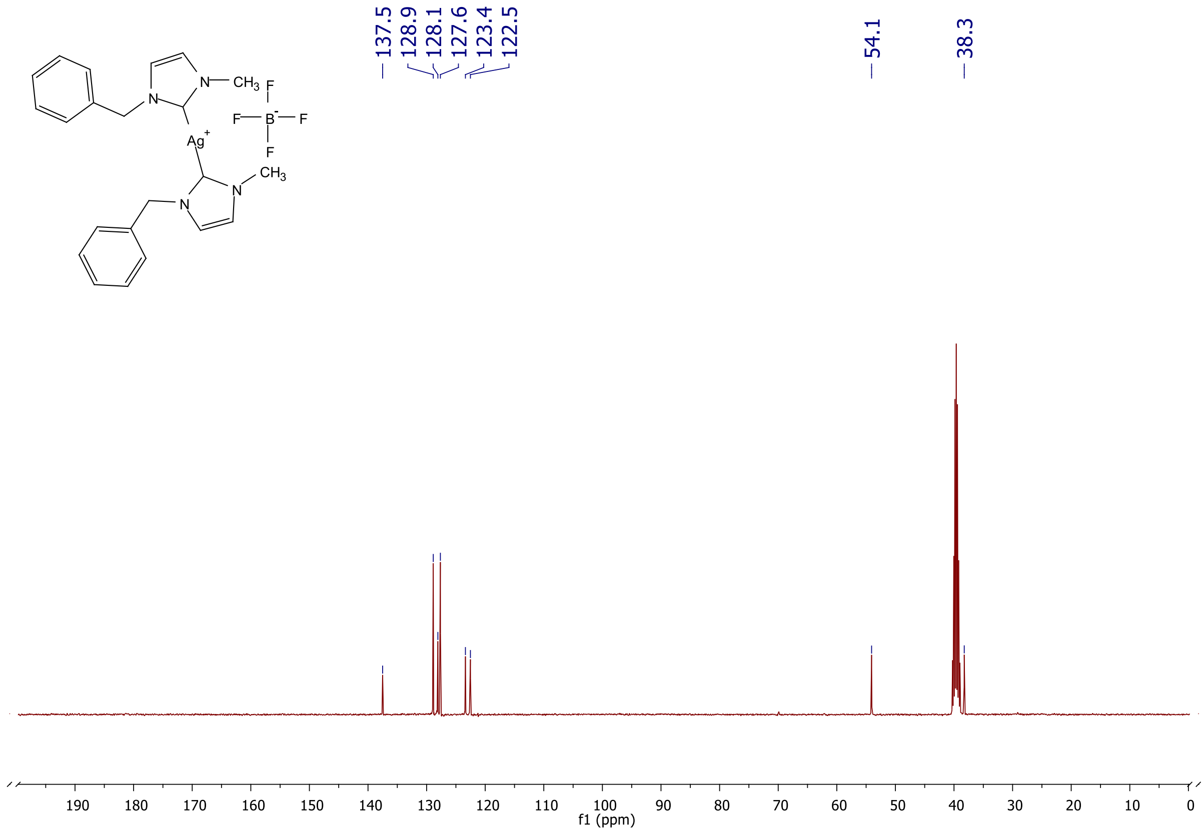


Bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver tetrafluoroborate [Ag(1e)$_2$]BF$_4$

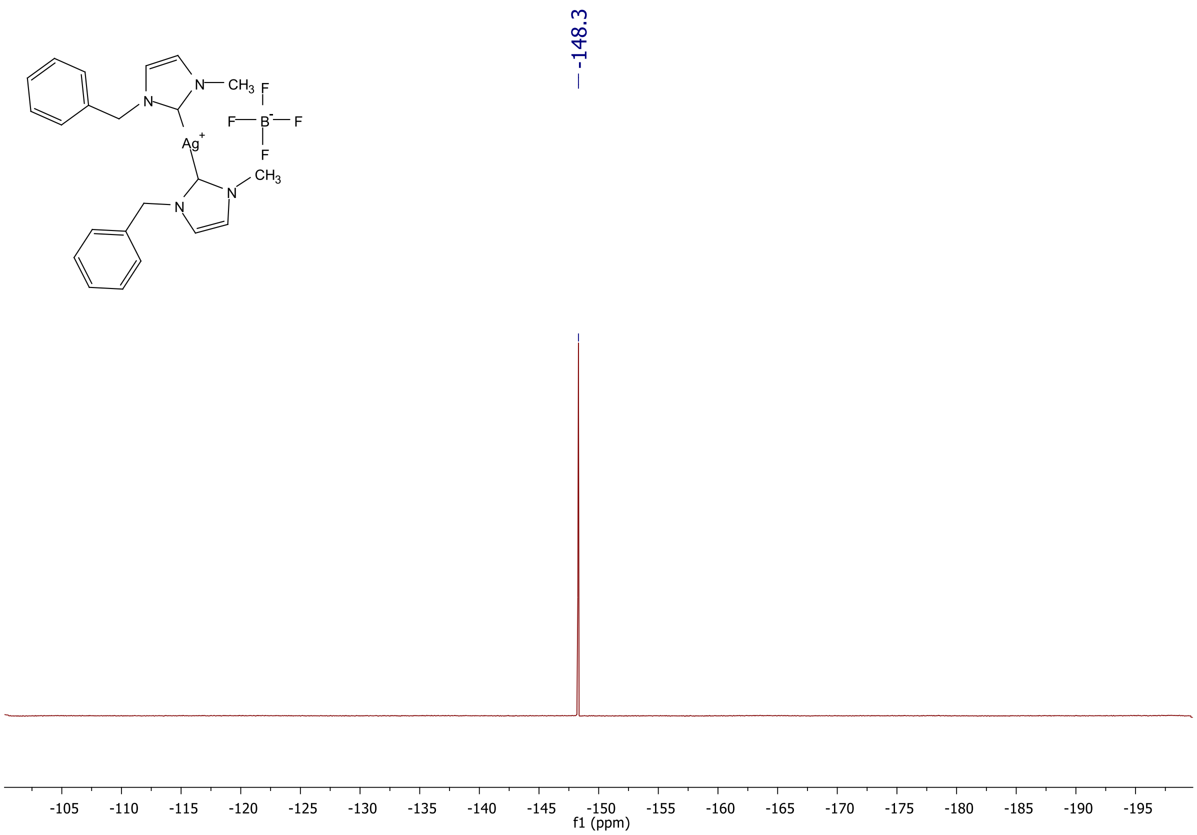
^{1}H NMR (300MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)

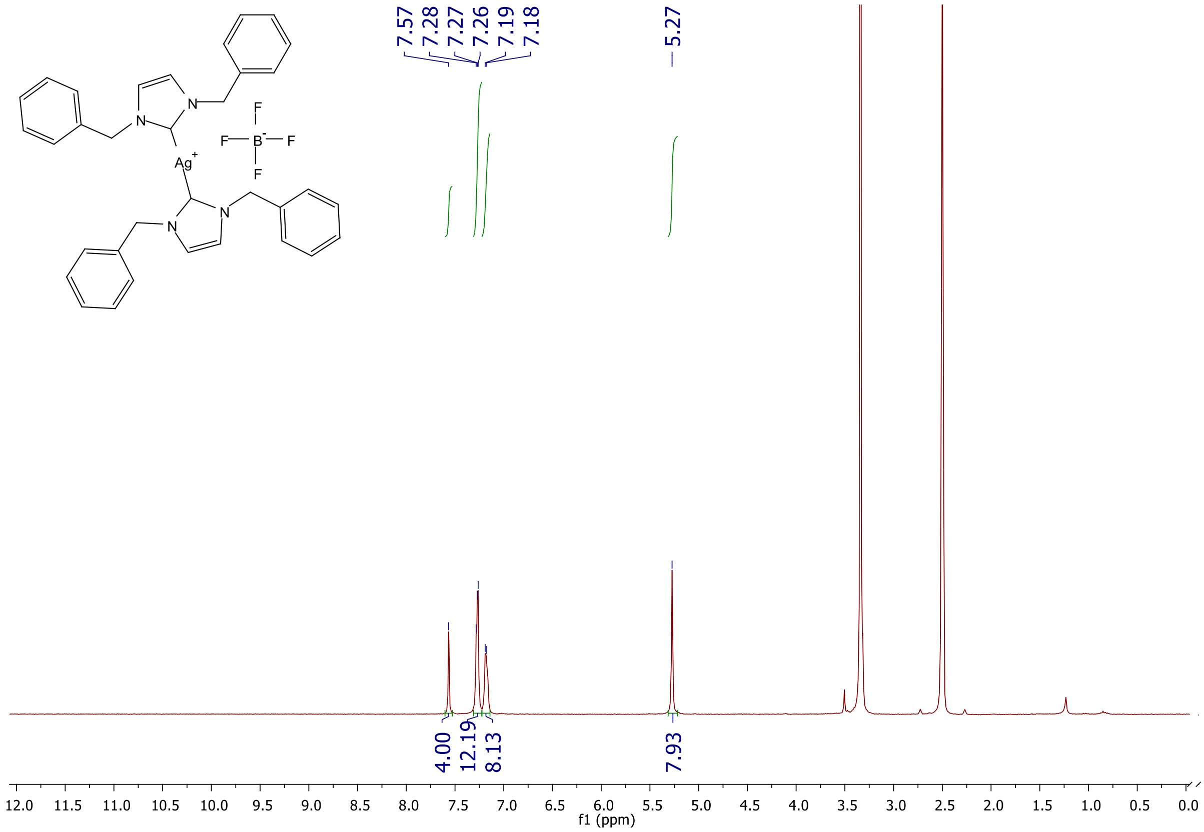


^{19}F NMR (376 MHz, DMSO-d_6)

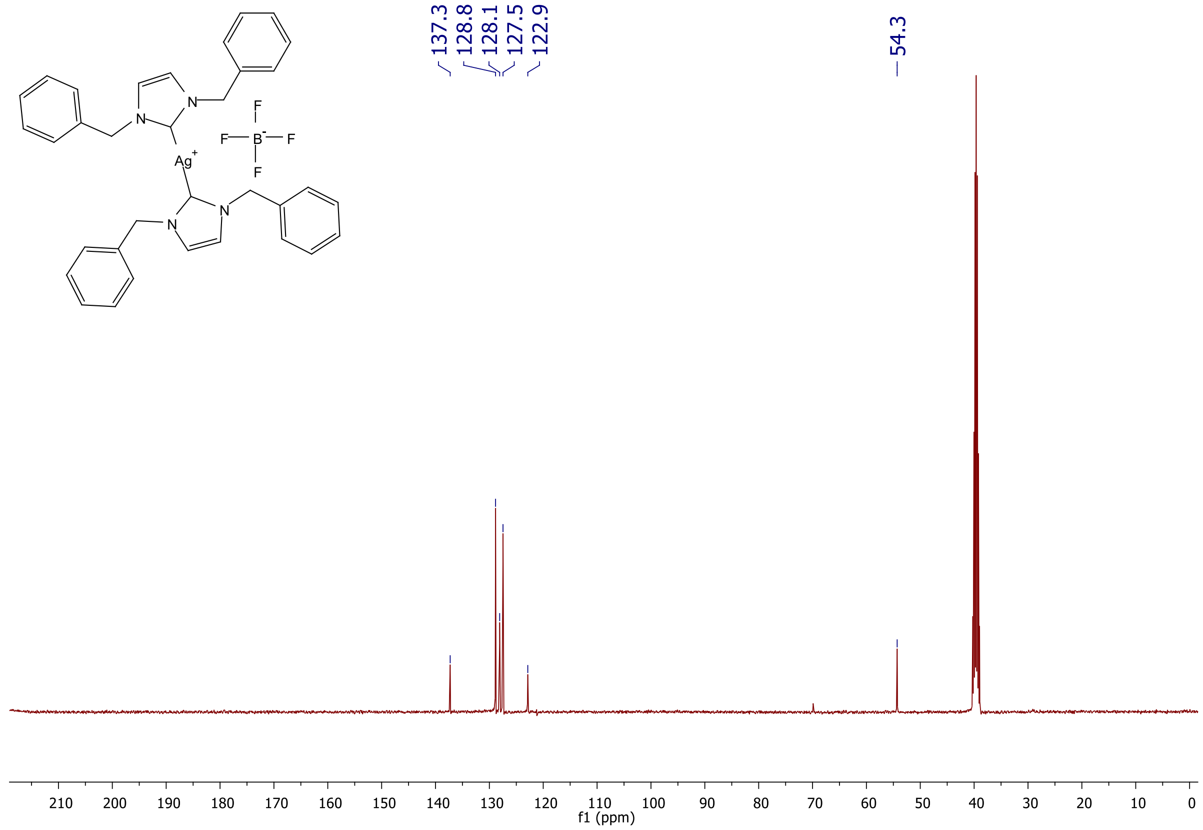


Bis[1,3-dibenzylimidazol-2-ylidene]silver tetrafluoroborate [Ag(1f)$_2$]BF$_4$

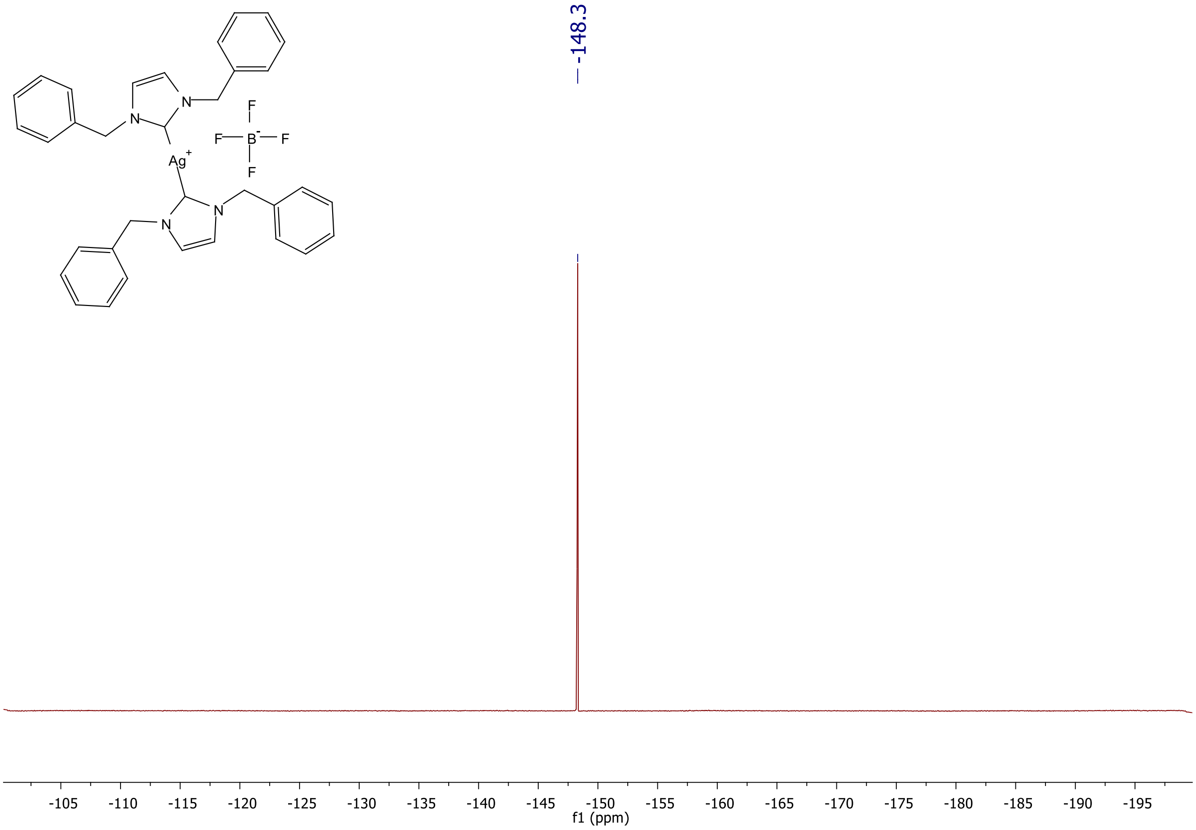
^{1}H NMR (300MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)

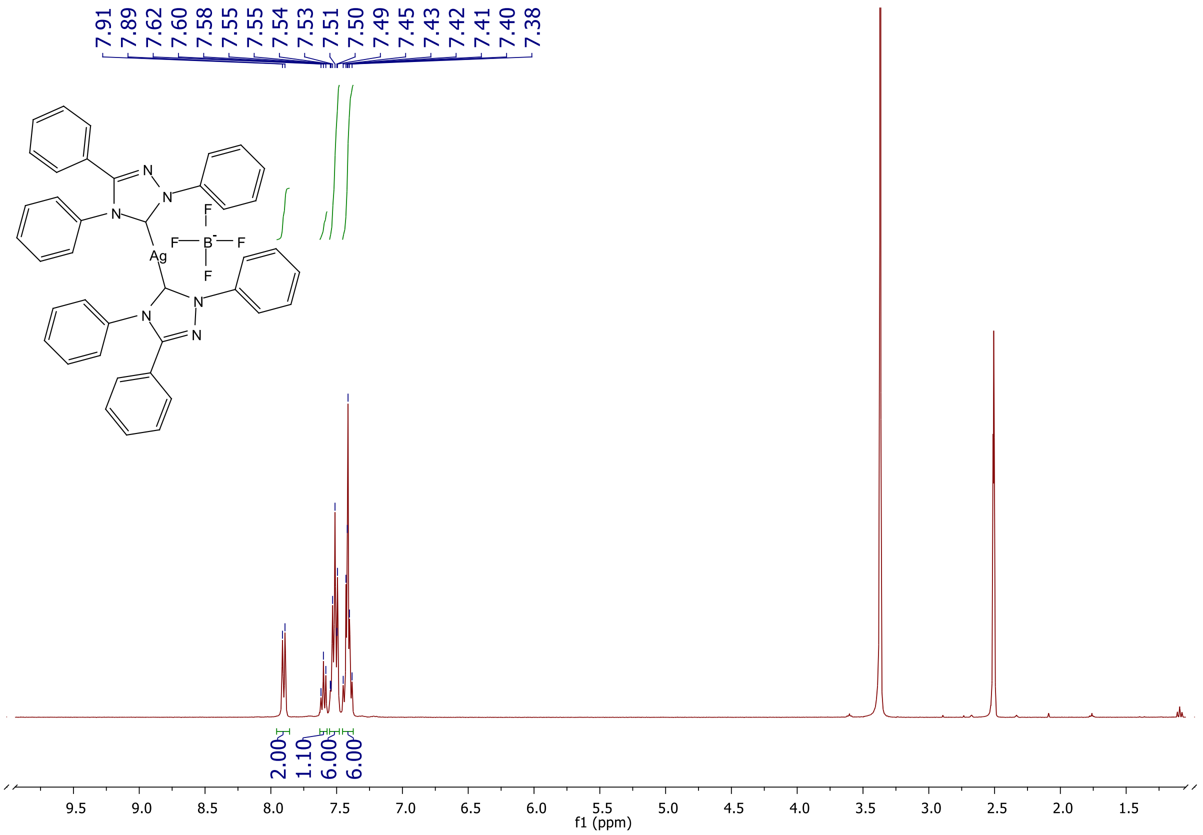


^{19}F NMR (376 MHz, DMSO-d_6)

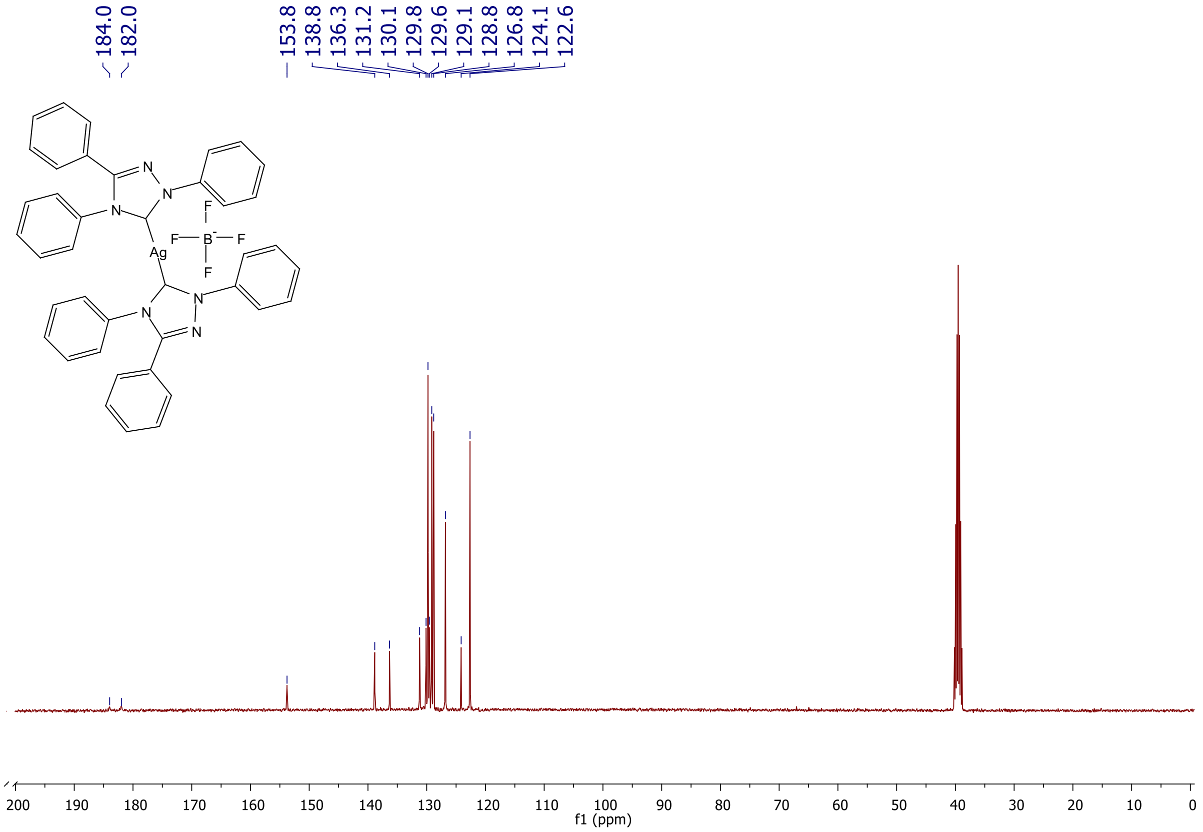


Bis[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver tetrafluoroborate [Ag(1g)$_2$]BF$_4$

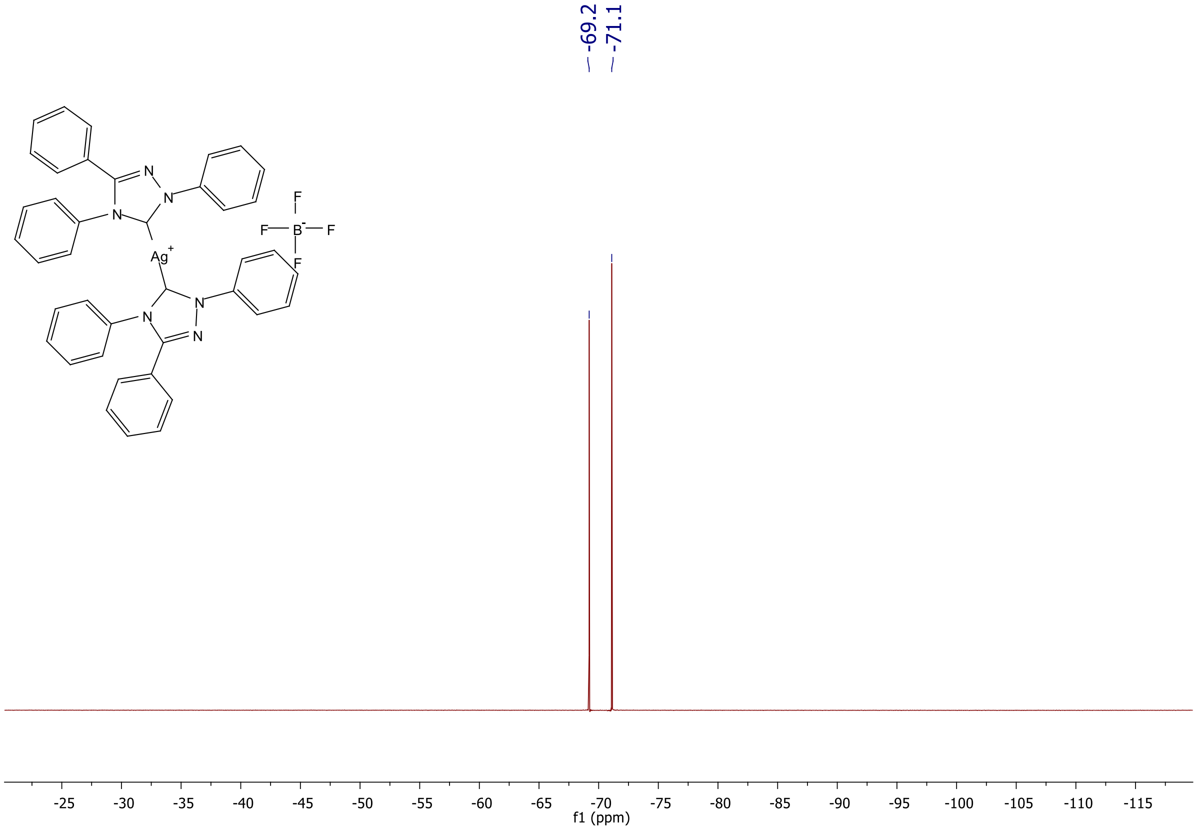
^{1}H NMR (400MHz, DMSO-*d$_6$*)



^{13}C NMR (110 MHz, DMSO-*d$_6$*)



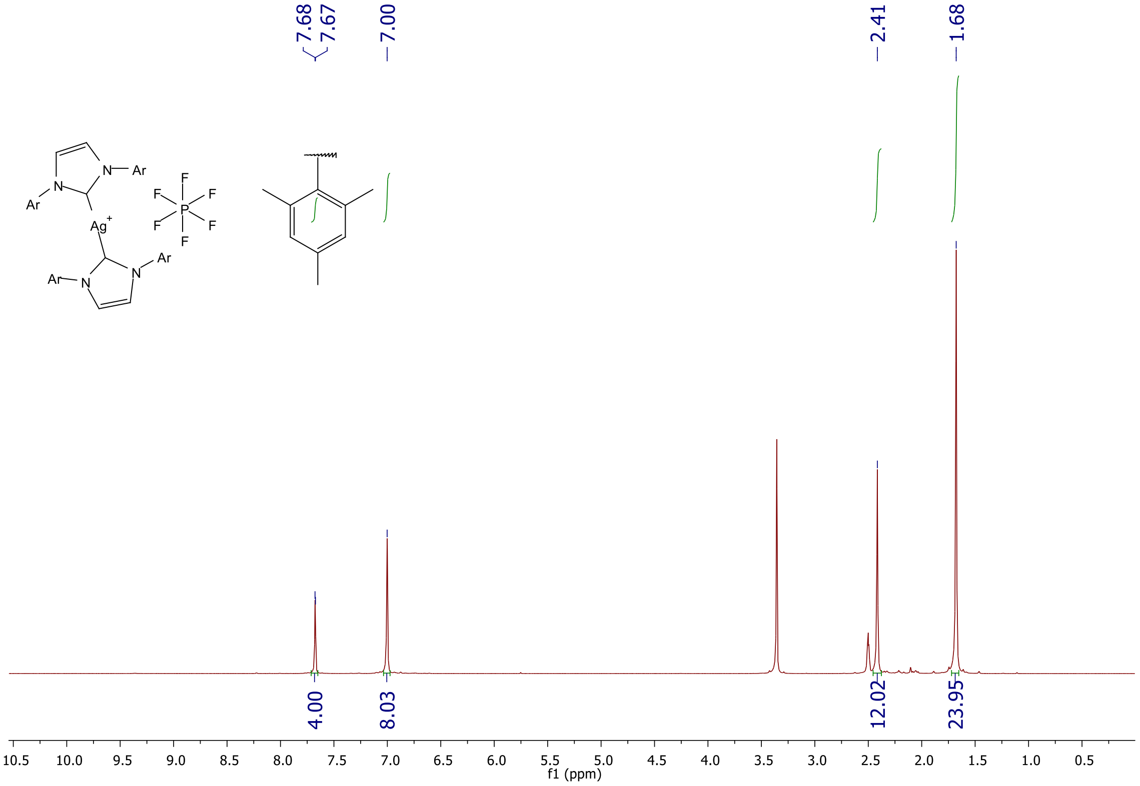
^{19}F NMR (376 MHz, DMSO-d_6)



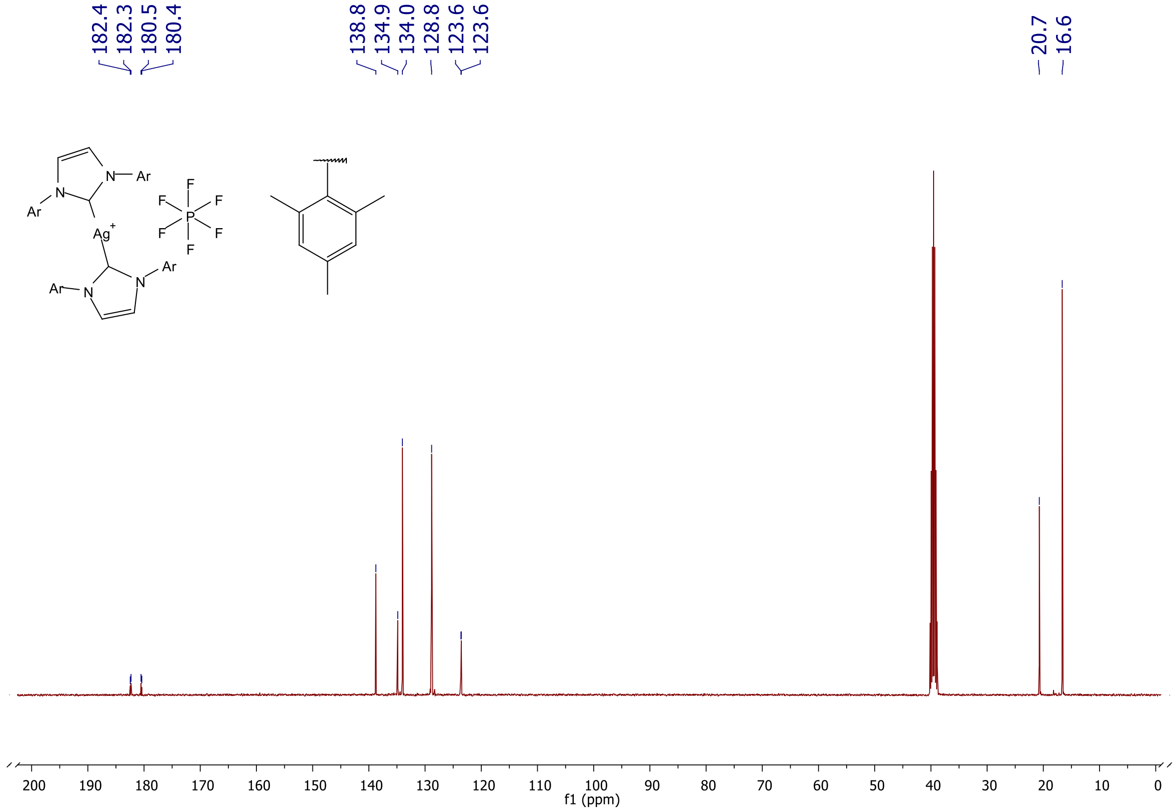
4.4. [Ag(NHC)$_2$]PF$_6$

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazol -2-ylidene]silver hexafluorophosphate [Ag(1a)$_2$]PF$_6$

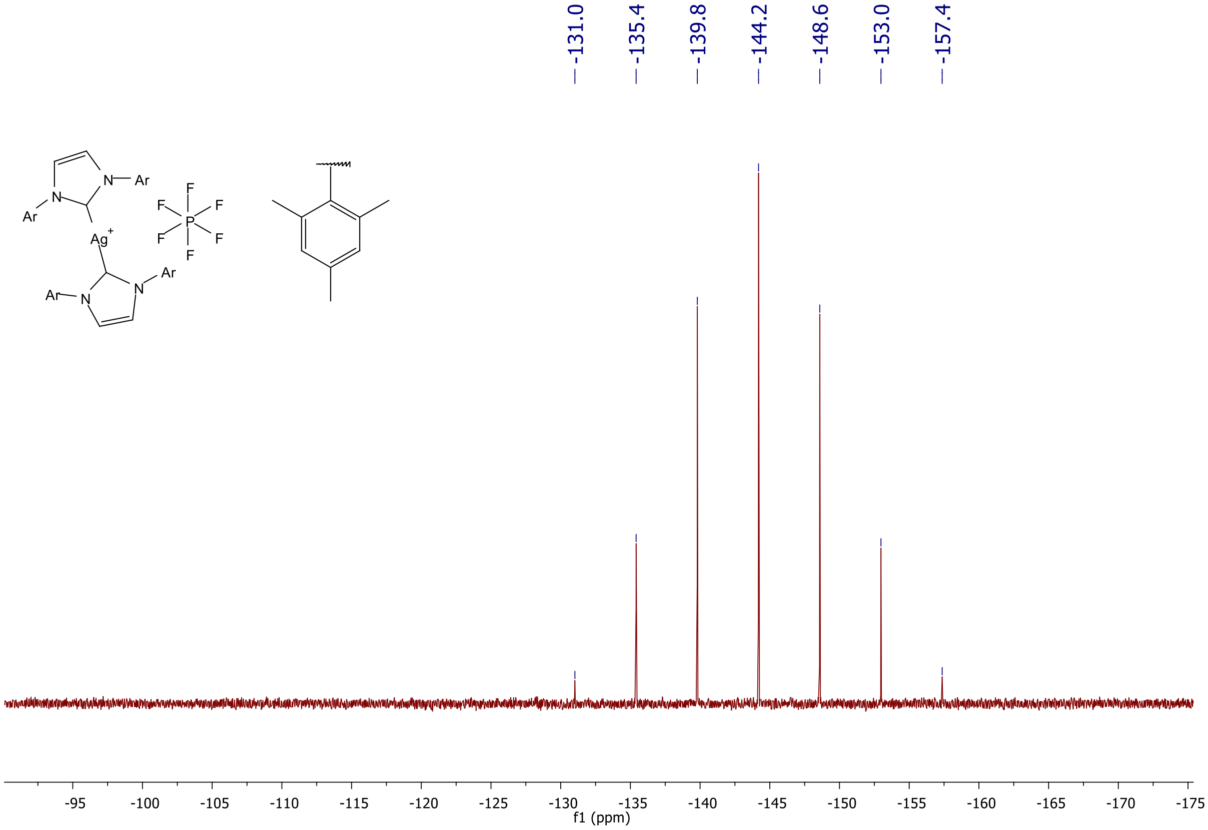
^{1}H NMR (300MHz, DMSO-d_6)



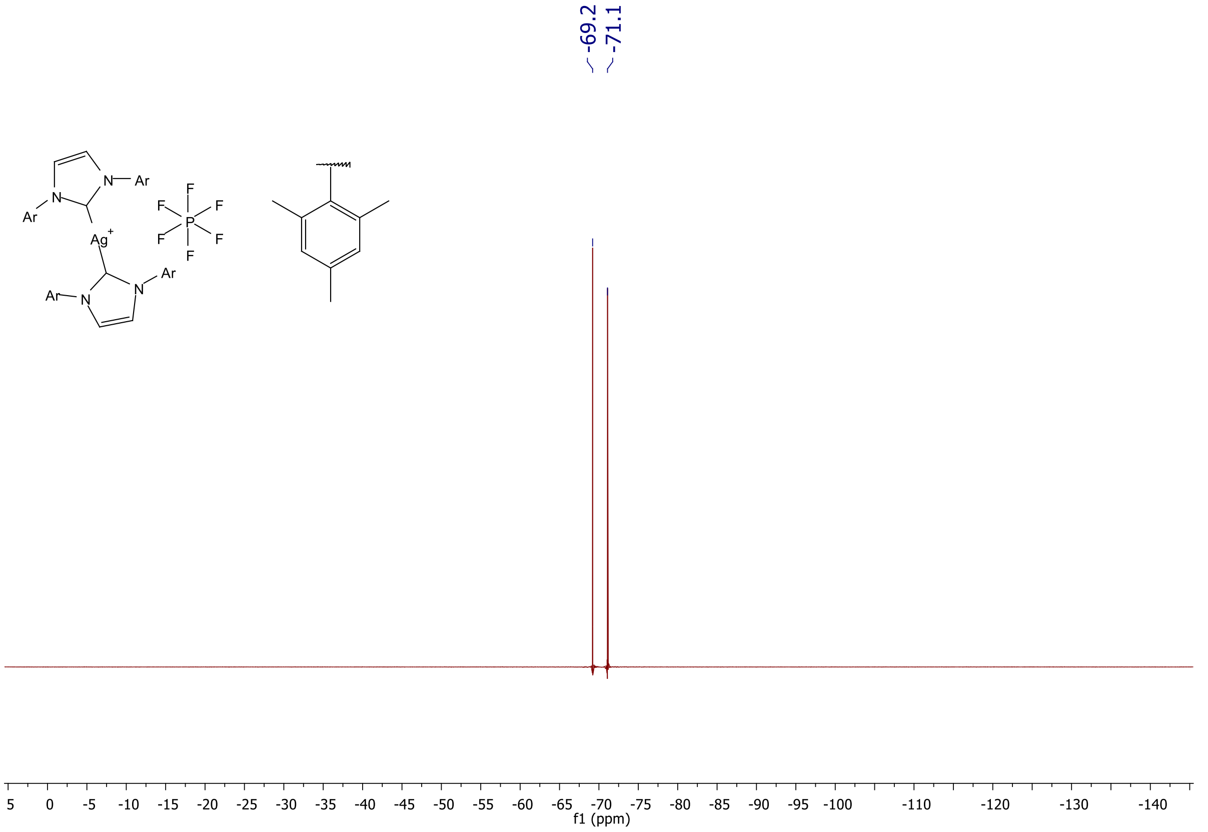
^{13}C NMR (110 MHz, DMSO-d_6)



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

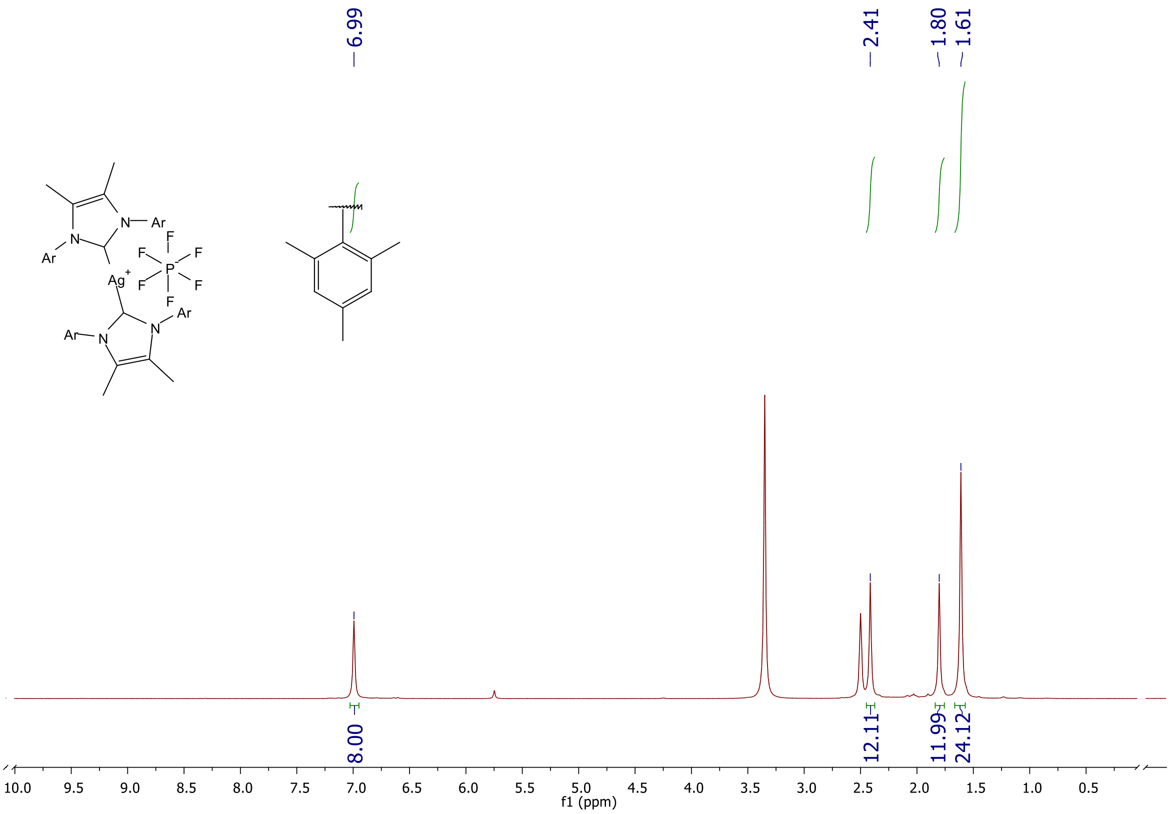


^{19}F NMR (376 MHz, DMSO-d_6)

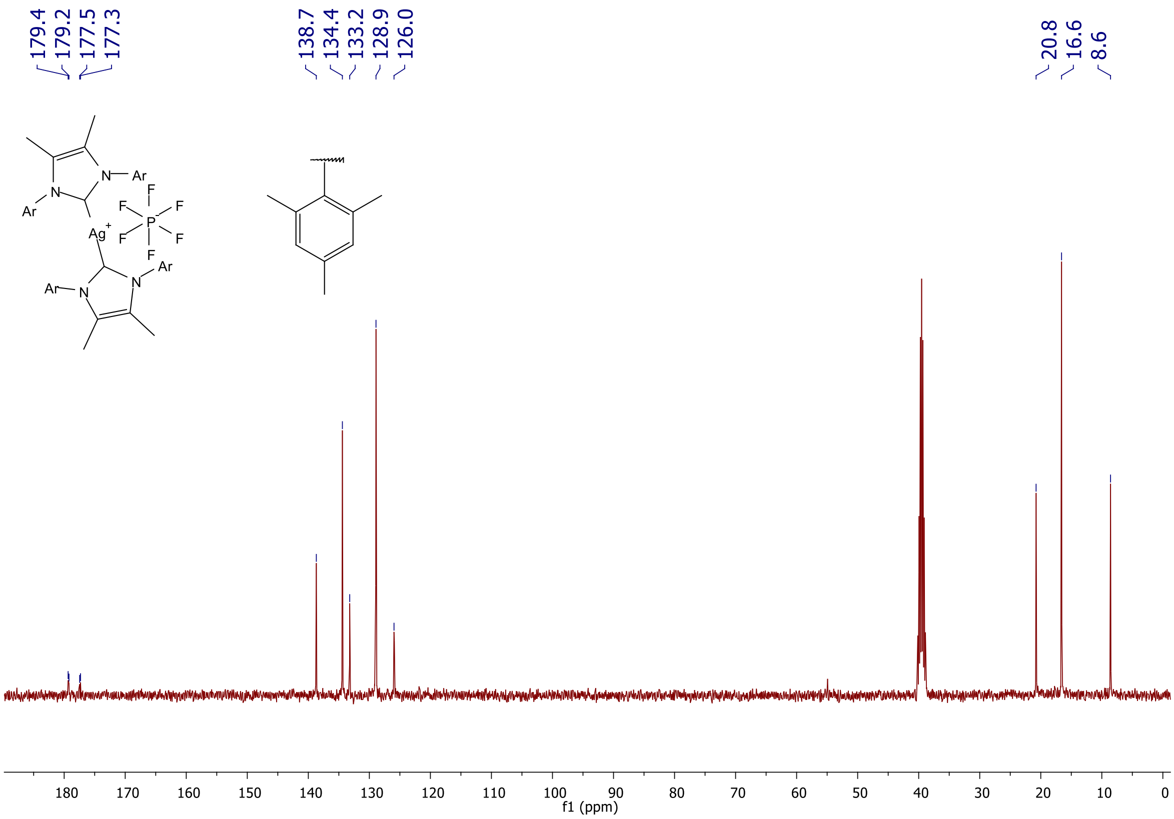


Bis[(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver hexaflurophosphate [Ag(1b)$_2$]PF$_6$

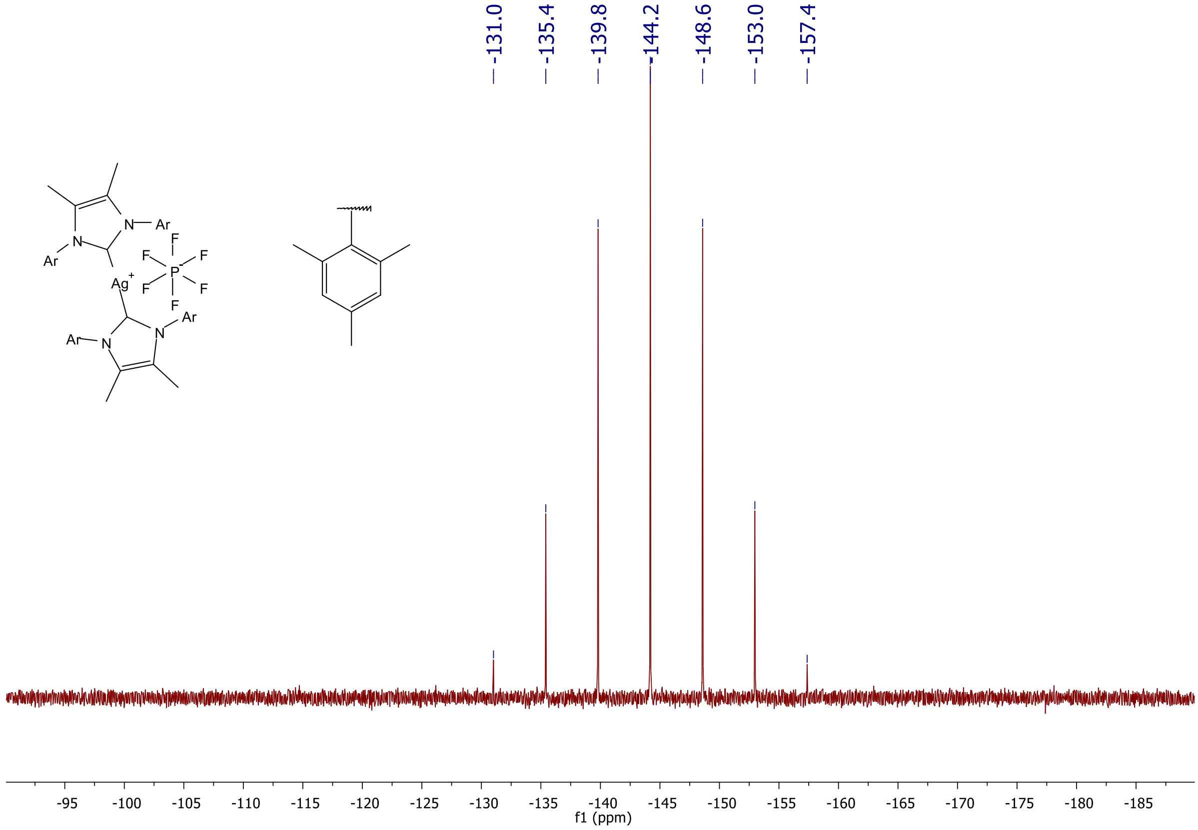
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (110 MHz, DMSO-d_6)



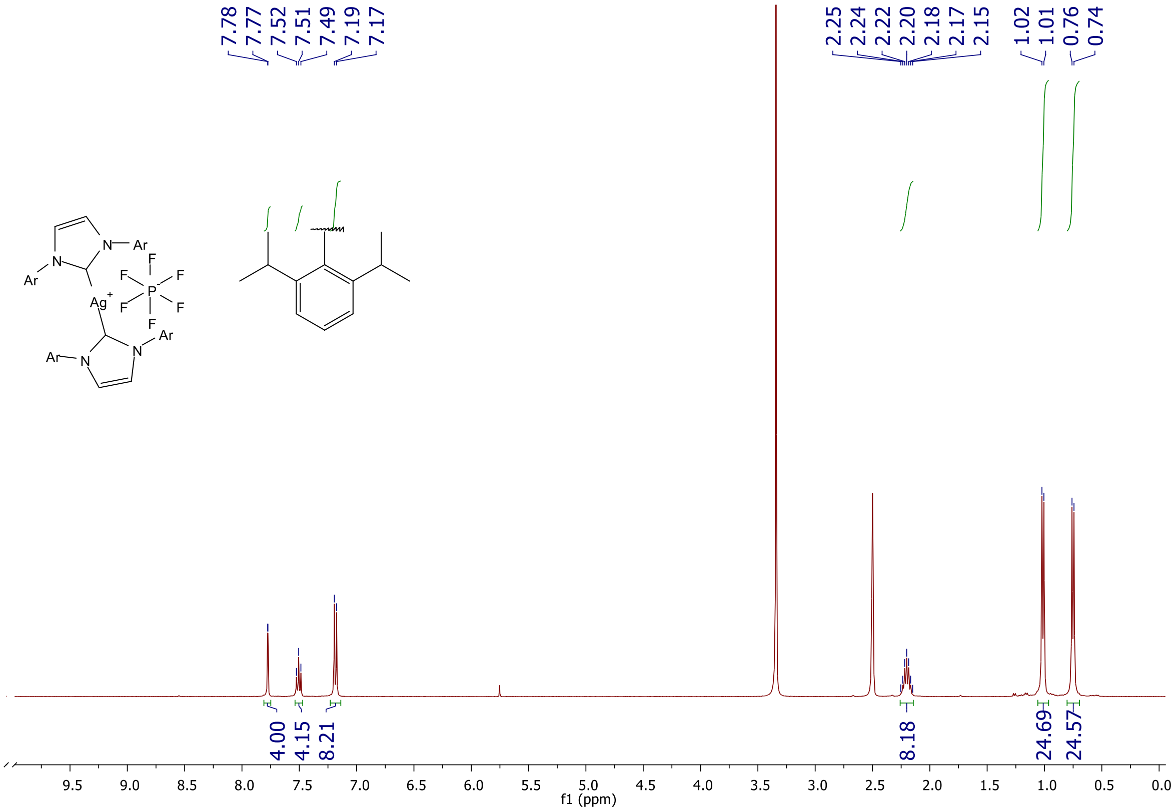
^{31}P NMR (162 MHz, DMSO-d_6)



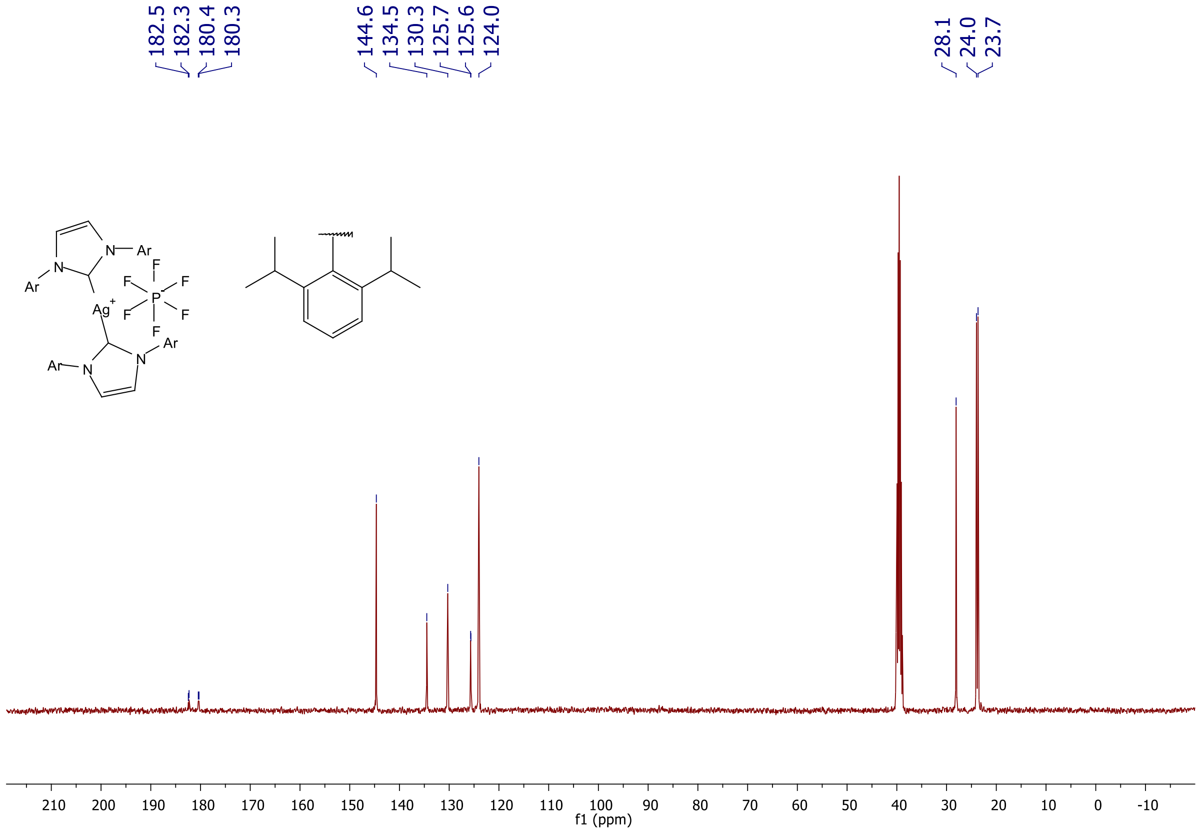
^{19}F NMR (376 MHz, DMSO-d_6)

Bis[1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene]silver hexafluorophosphate [Ag(1c)$_2$]PF$_6$

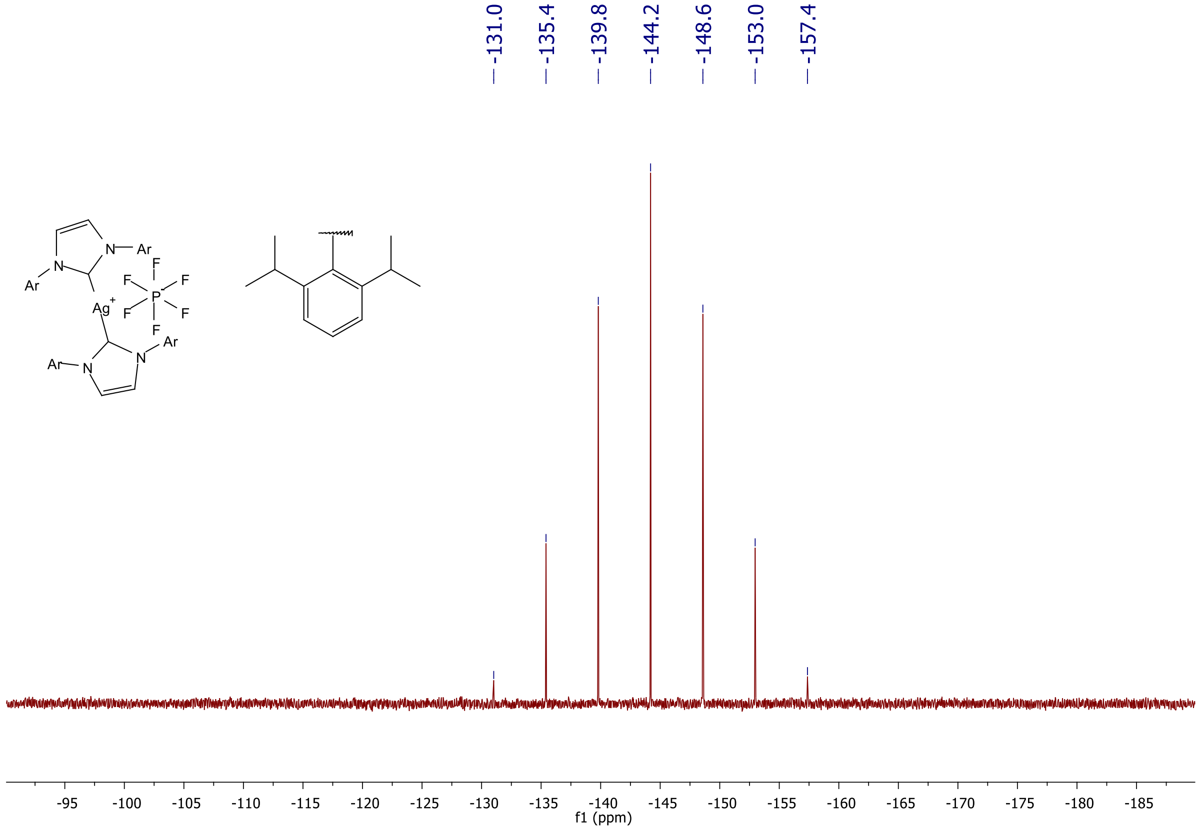
^{1}H NMR (400MHz, DMSO-d_6)



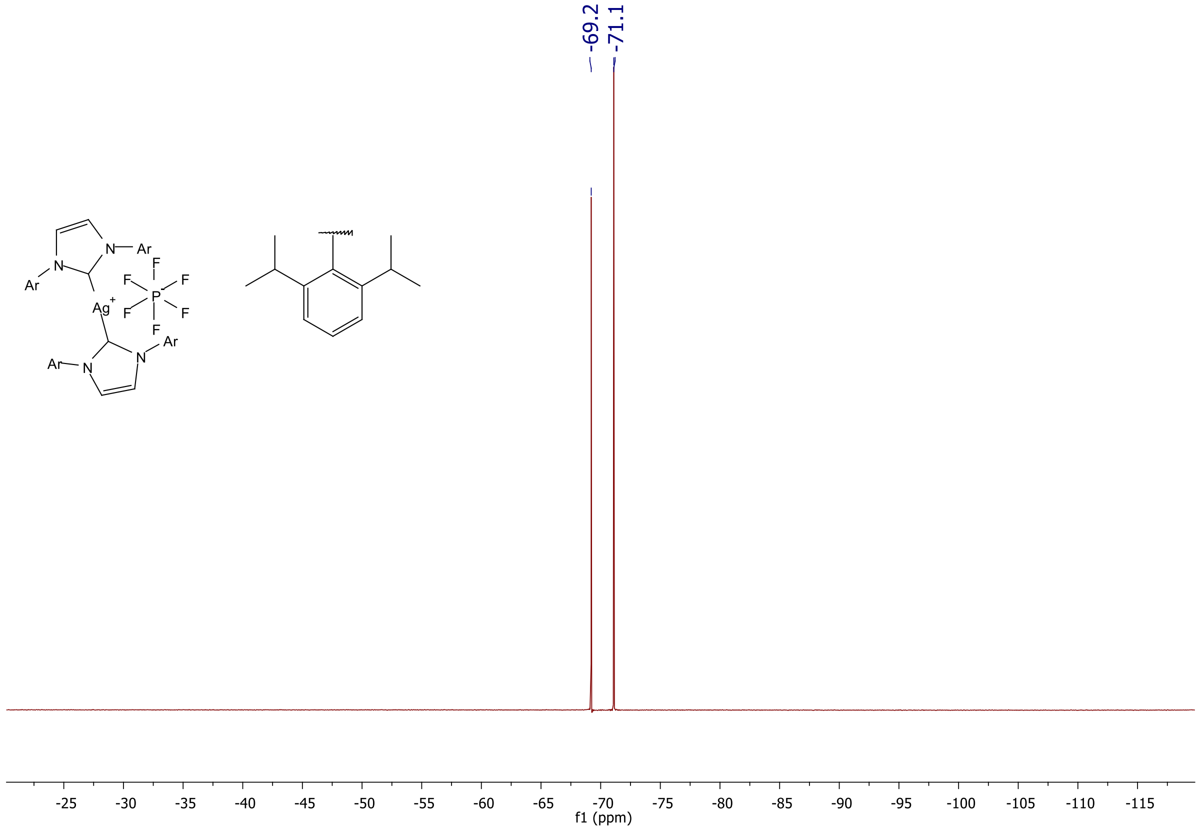
^{13}C NMR (110 MHz, DMSO-d_6)



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

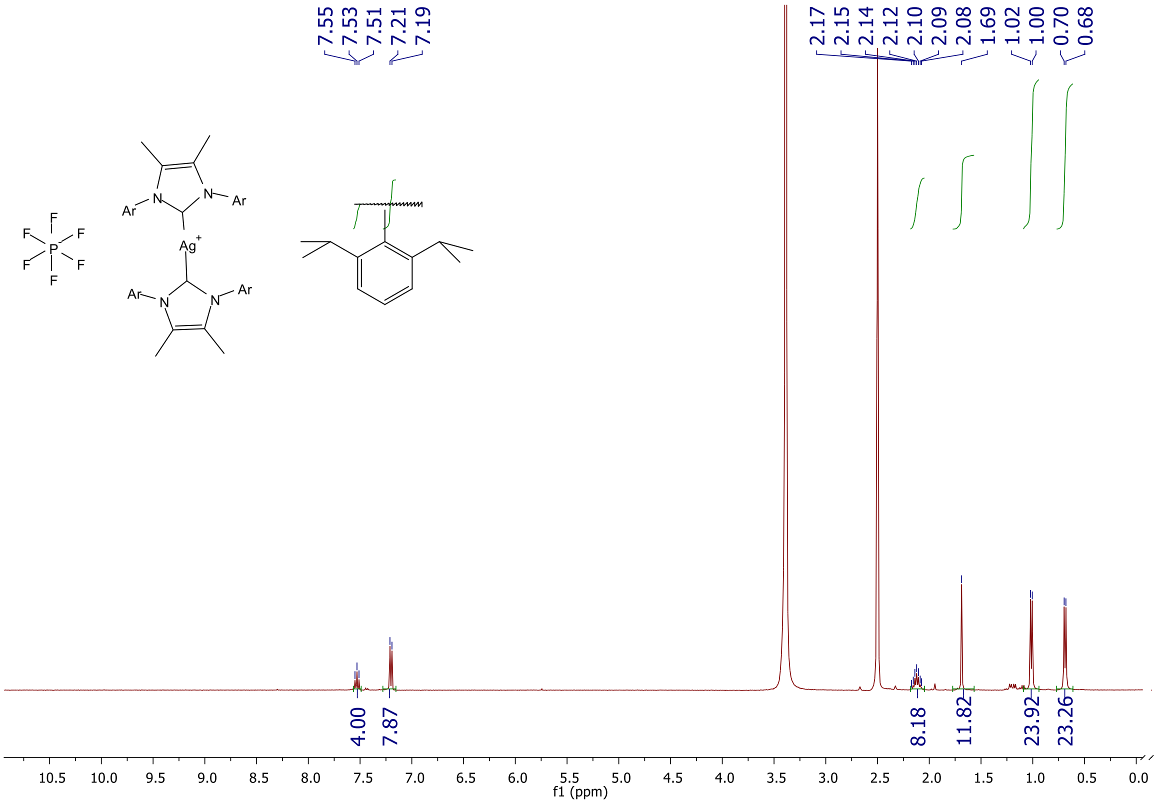


^{19}F NMR (376 MHz, DMSO-d_6)

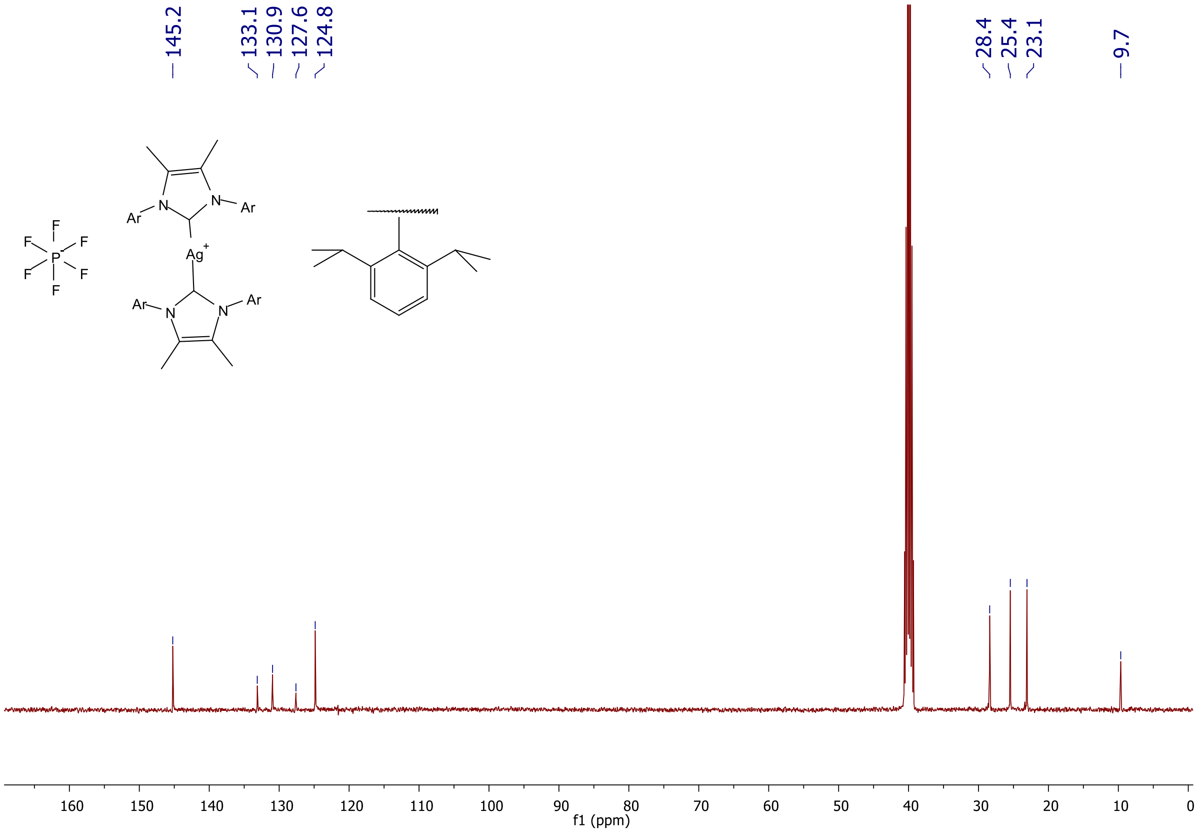


Bis-[1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]silver hexafluorophosphate [Ag(1d)$_2$]PF$_6$

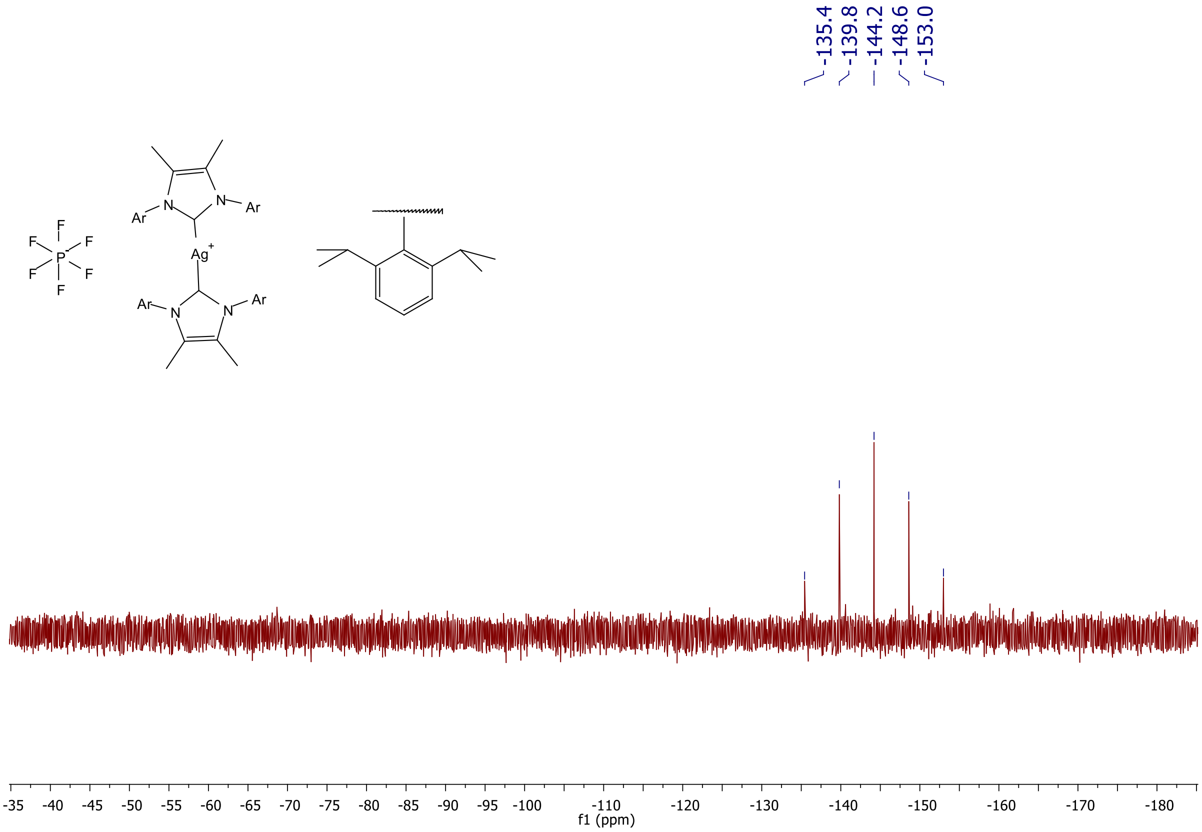
^{1}H NMR (400MHz, DMSO-*d$_6$*)



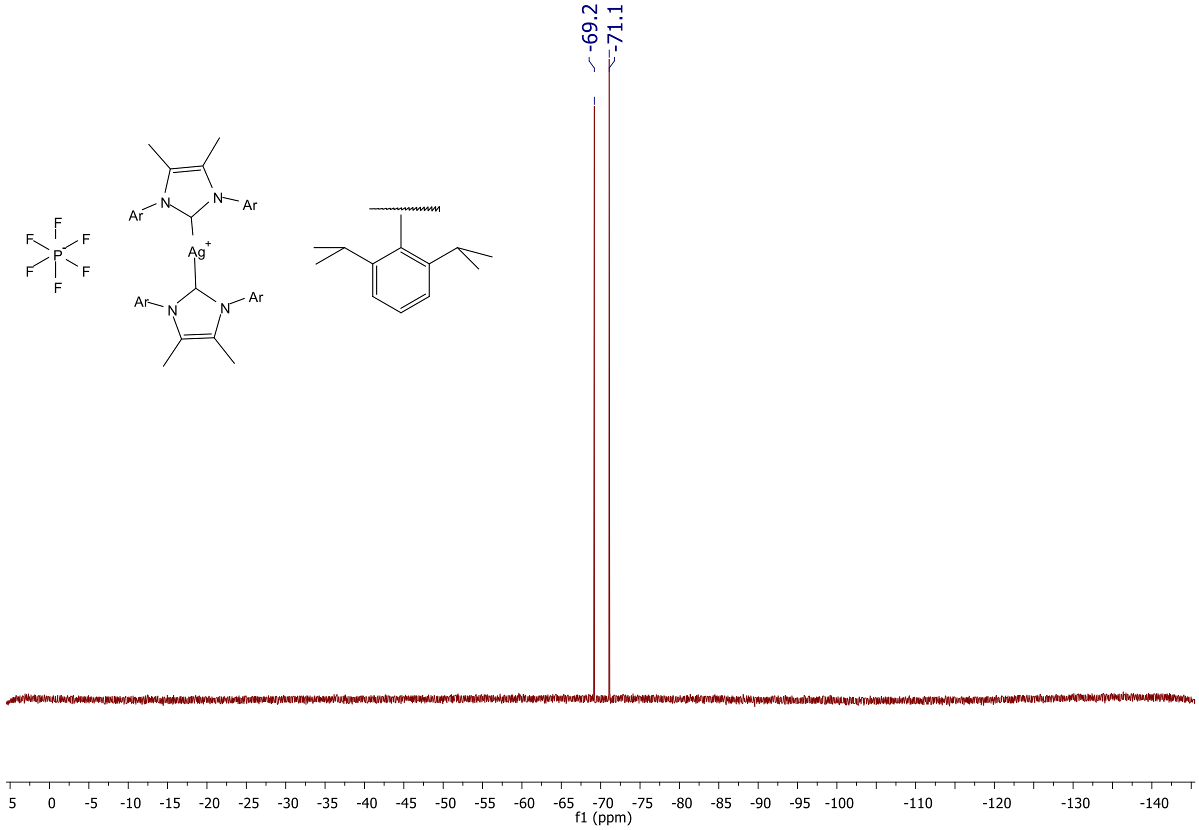
^{13}C NMR (110 MHz, DMSO-*d$_6$*)



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

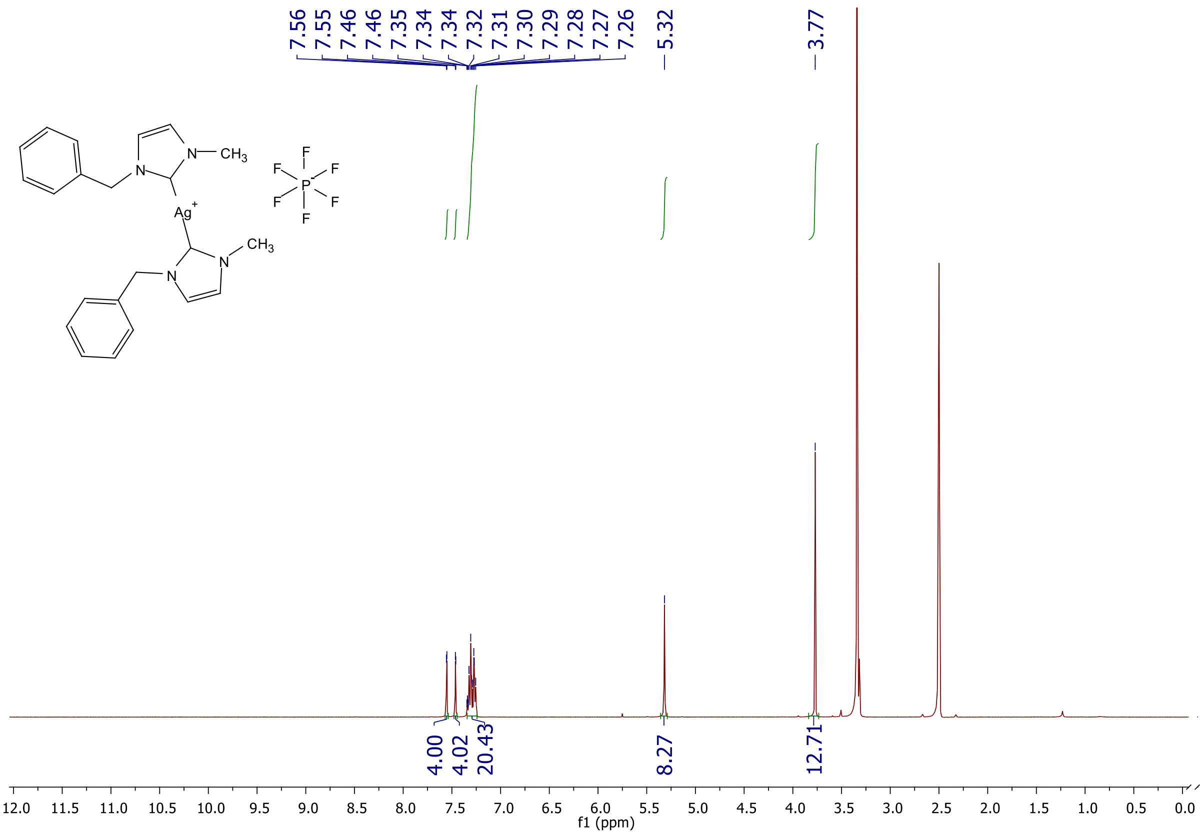


^{19}F NMR (376 MHz, DMSO-d_6)

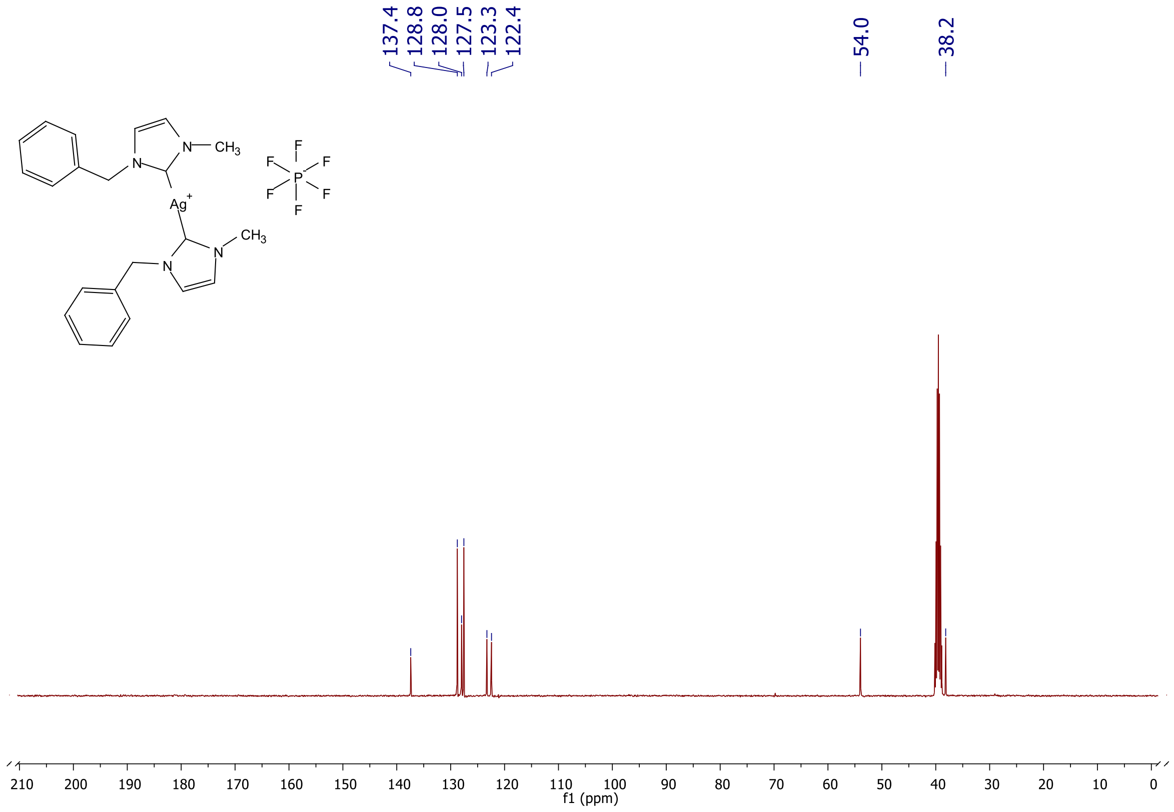


Bis[(1-benzyl-3-methyl)imidazol-2-ylidene]silver hexafluorophosphate [Ag(1e)$_2$]PF$_6$

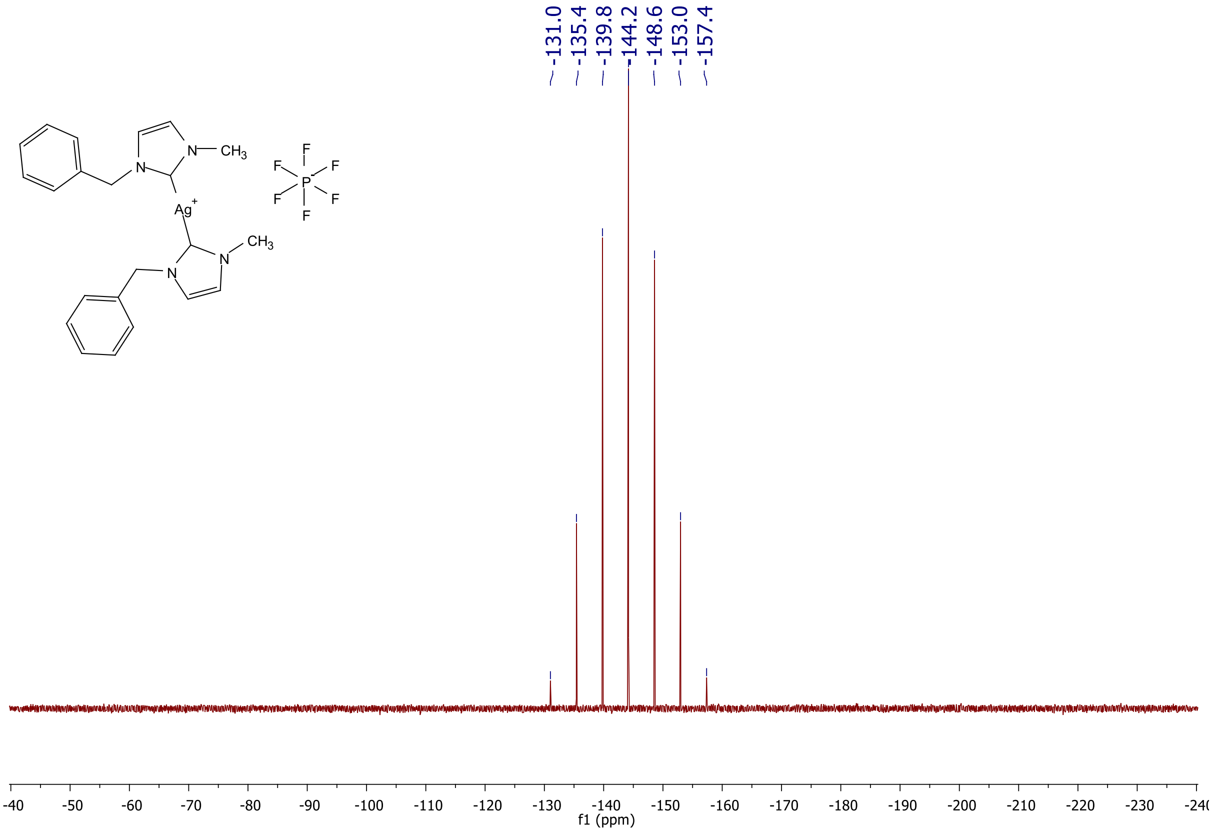
^{1}H NMR (400MHz, DMSO-d_6)



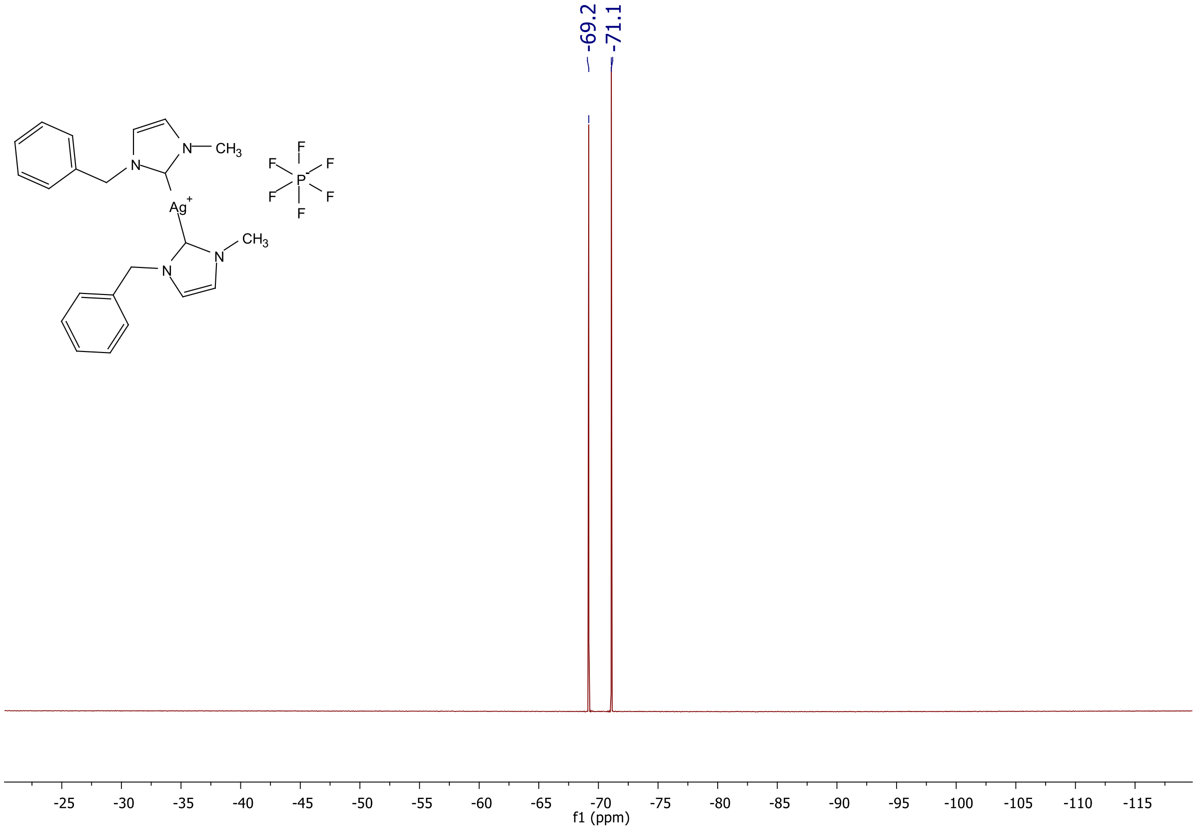
^{13}C NMR (110 MHz, DMSO-d_6)



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

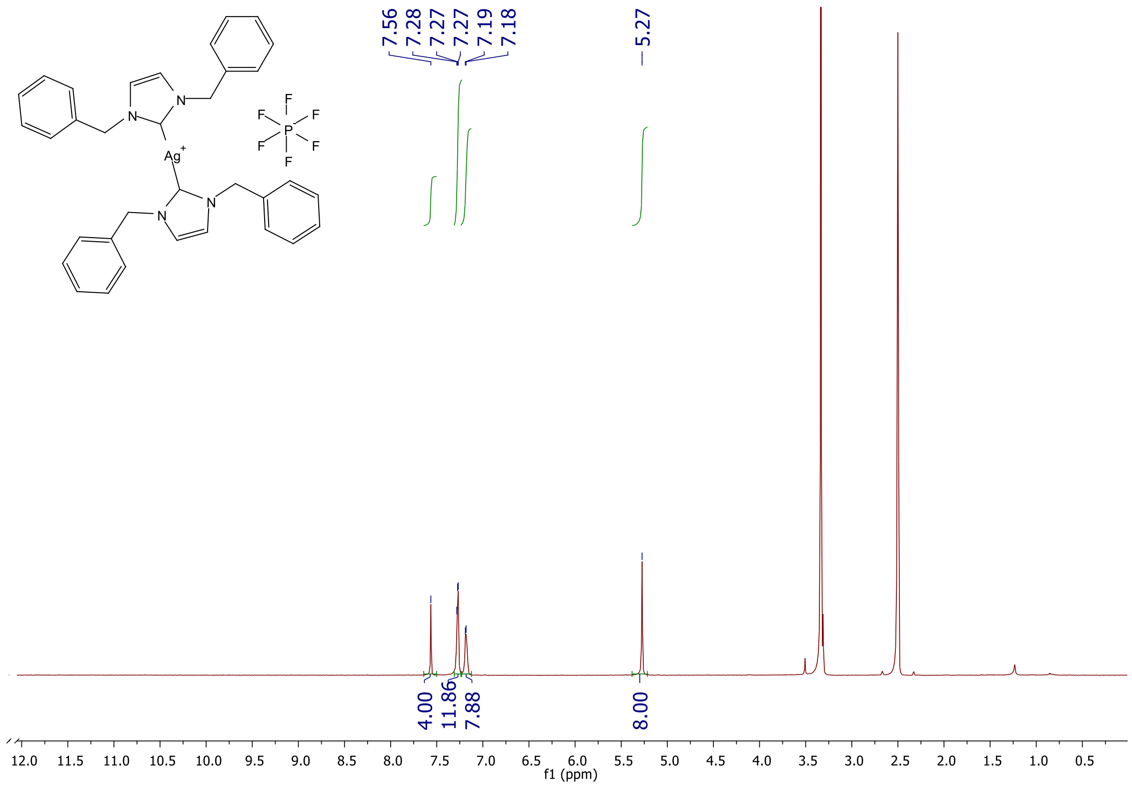


^{19}F NMR (376 MHz, DMSO-d_6)

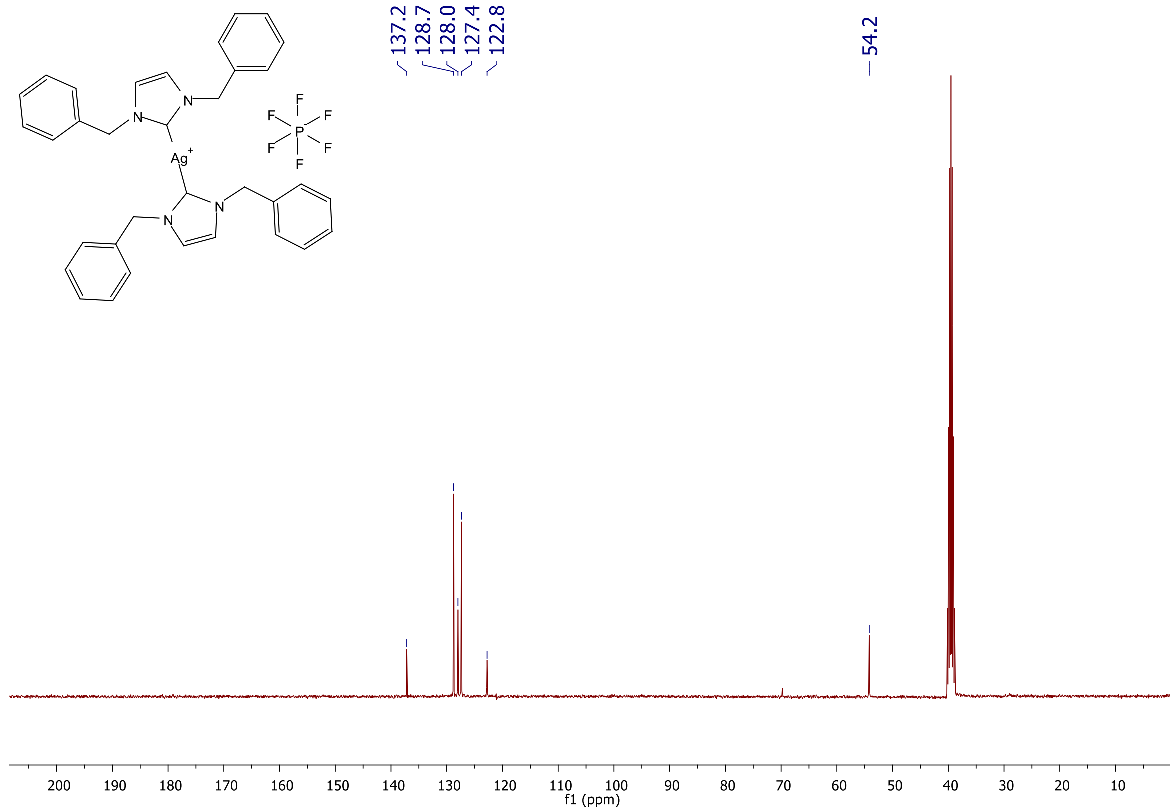


Bis[1,3-dibenzylimidazol-2-ylidene]silver hexafluorophosphate [Ag(1f)$_2$]PF$_6$

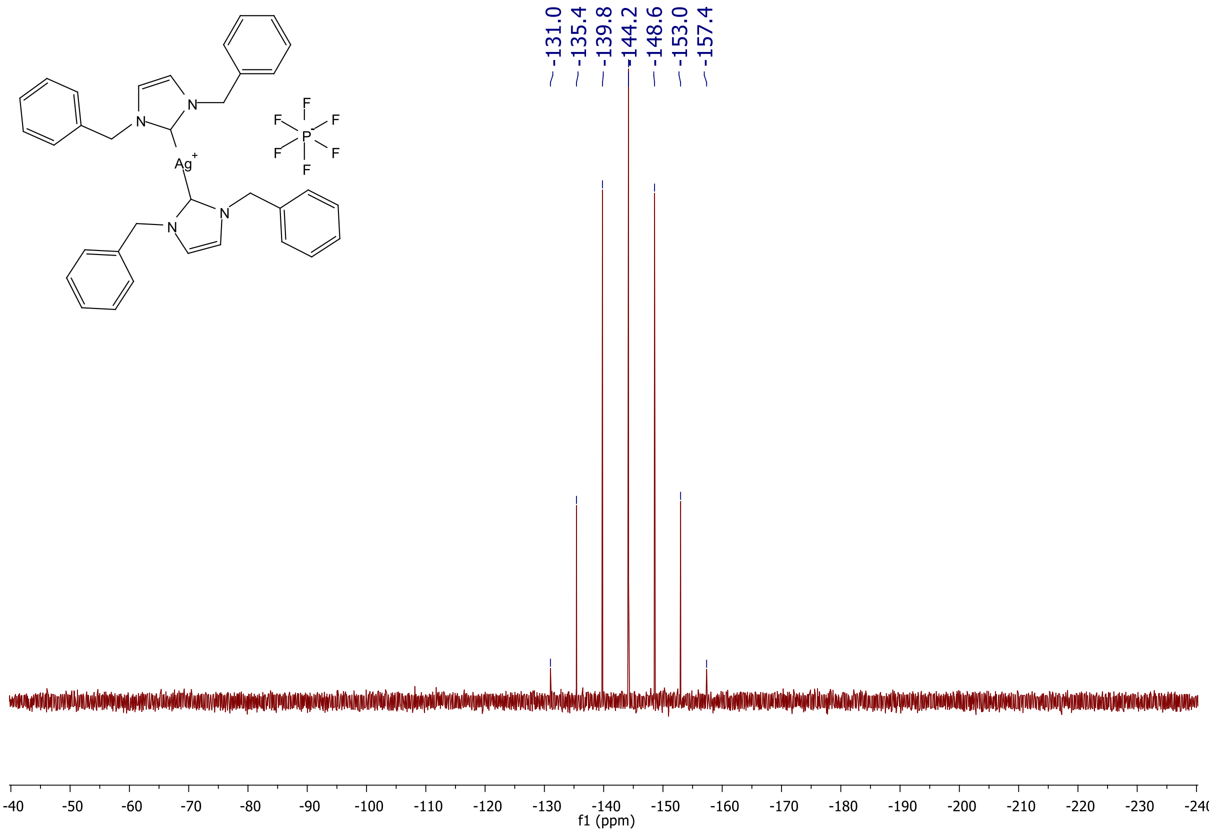
^{1}H NMR (400MHz, DMSO-d_6)



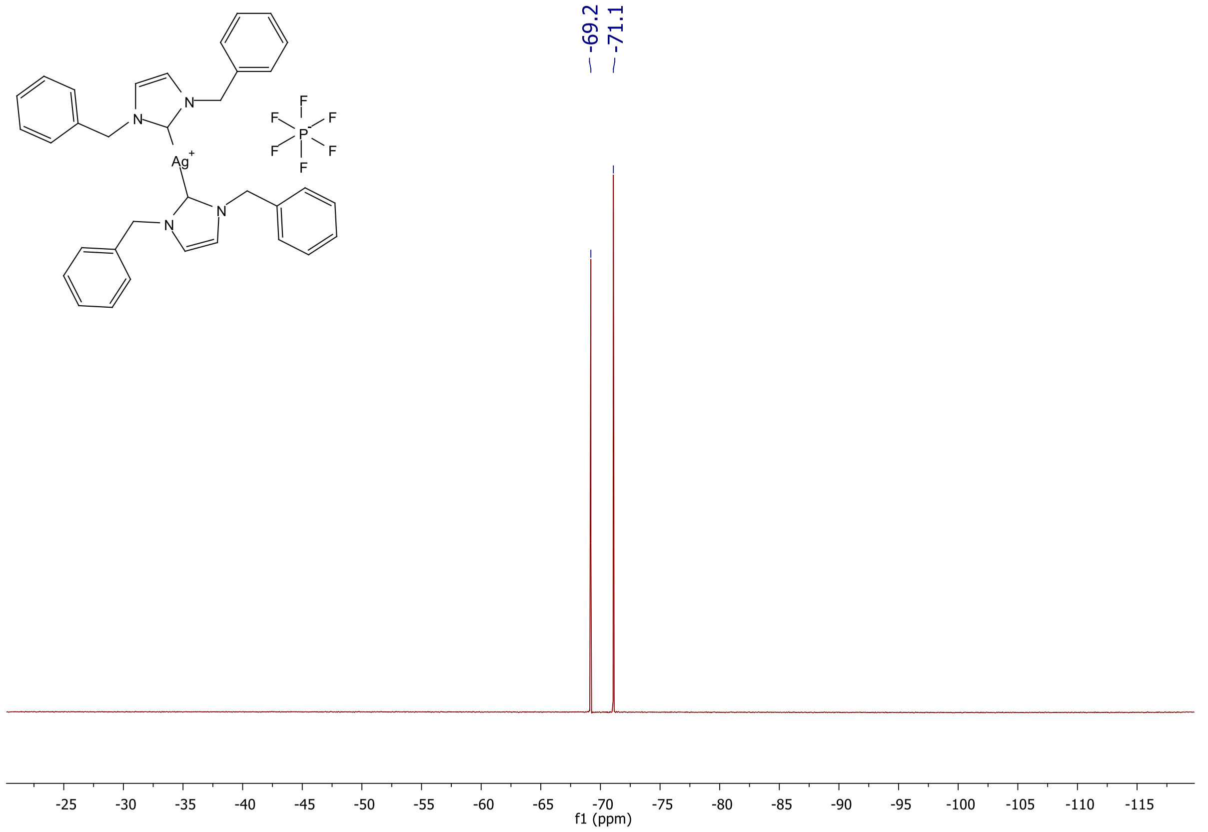
^{13}C NMR (110 MHz, DMSO-d_6)



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

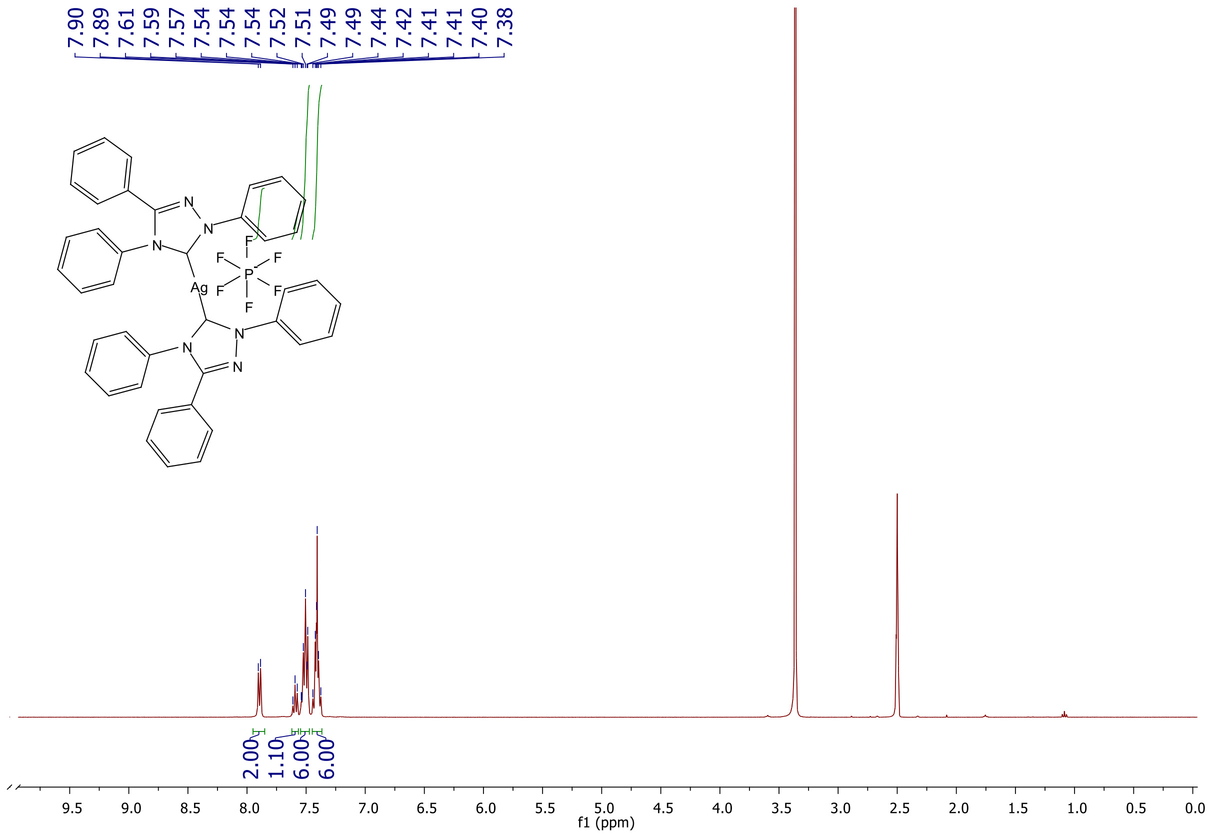


^{19}F NMR (376 MHz, DMSO-d_6)

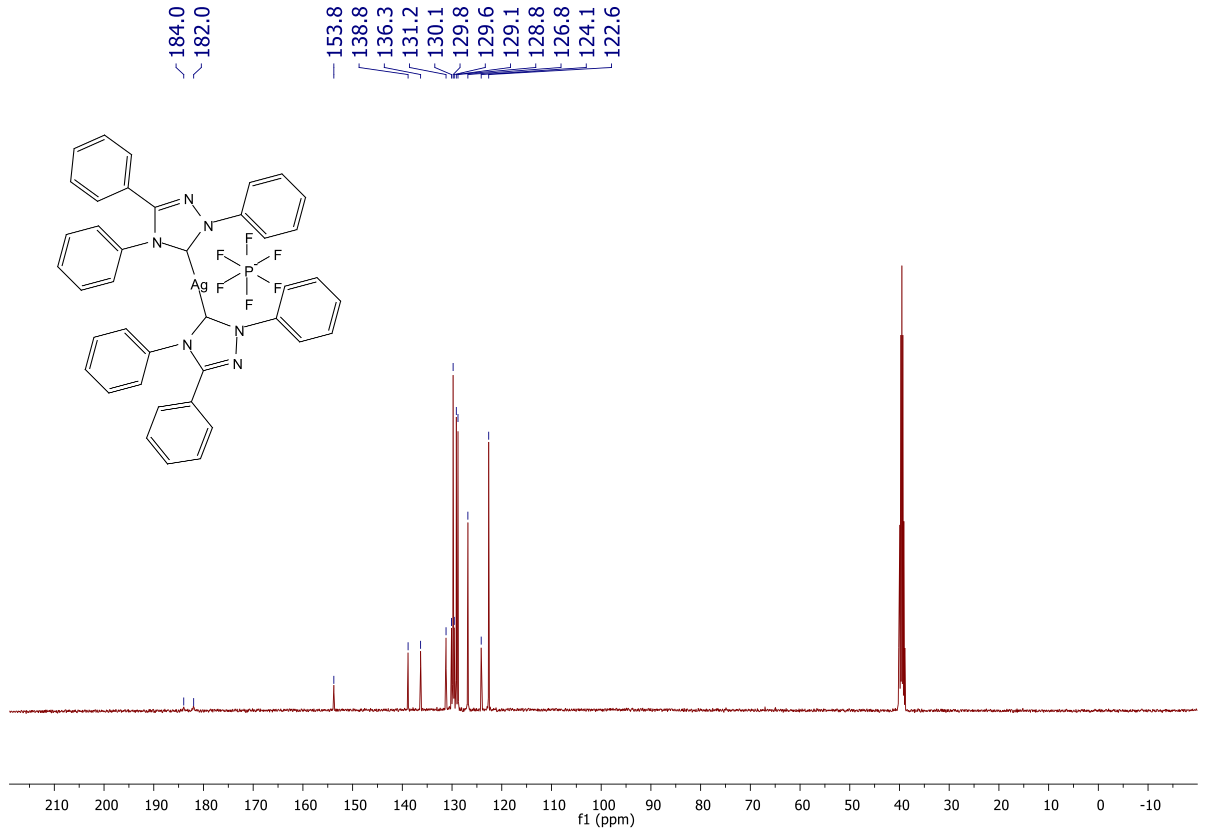


Bis[1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver hexafluorophosphate [Ag(1g)$_2$]PF$_6$

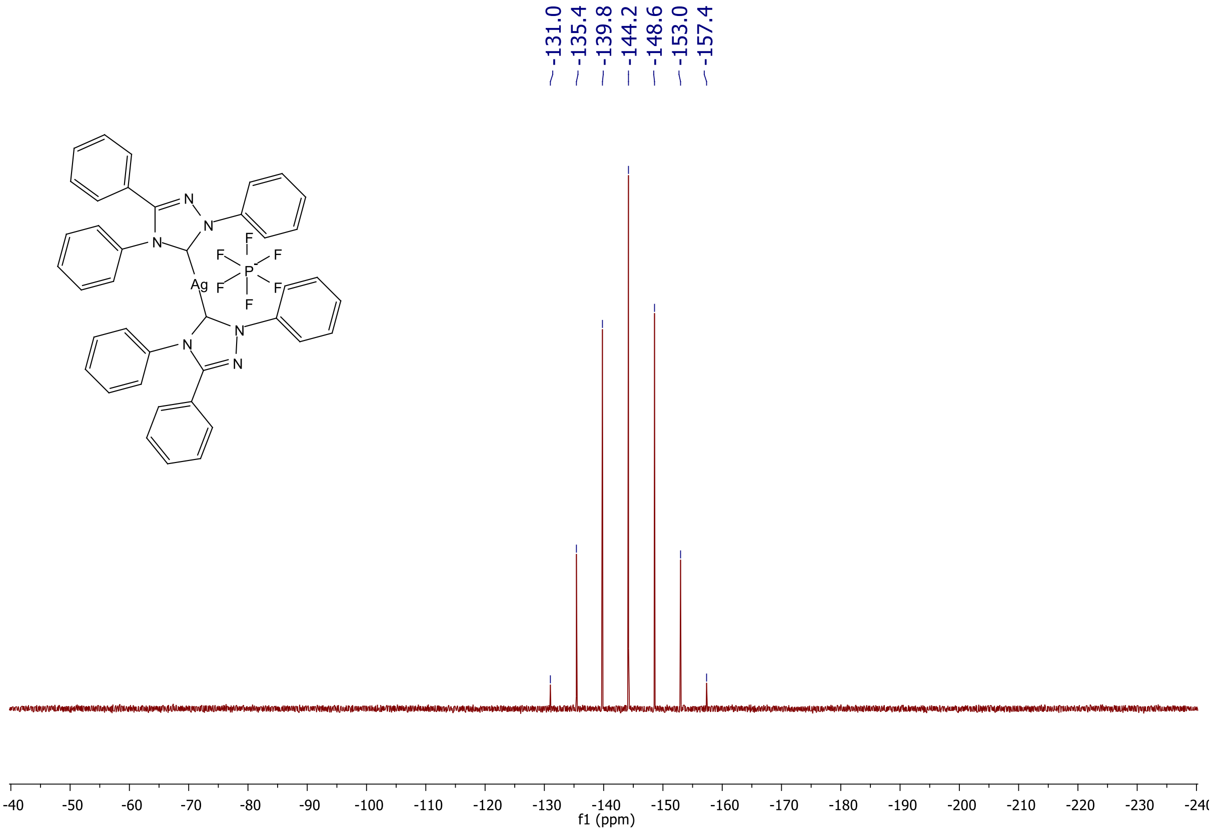
^{1}H NMR (400MHz, DMSO-d_6)



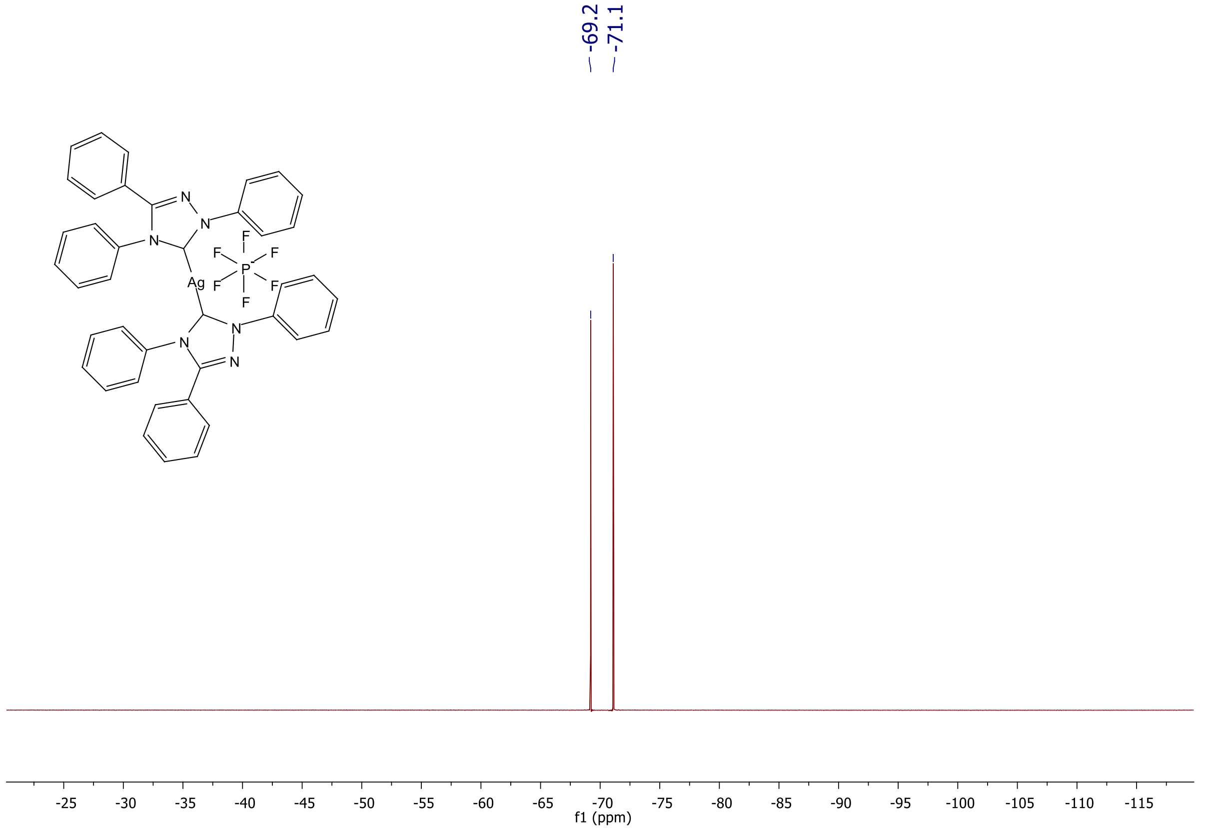
^{13}C NMR (110 MHz, DMSO-d_6)



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



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



5. References

[1] X. Bantreil, S. P. Nolan, *Nat. Protocols* **2011**, *6*, 69-77.

[2] C. Huerta-Aguilar, J. M. Talamantes Gómez, P. Thangarasu, I. Camacho-Arroyo, A. González-Arenas, J. Narayanan, R. Srivastava, *Appl. Organomet. Chem.* **2013**, *27*, 578-587.

[3] J. E. Thomson, C. D. Campbell, C. Concellón, N. Duguet, K. Rix, A. M. Z. Slawin, A. D. Smith, *J. Org. Chem.* **2008**, *73*, 2784-2791.

[4] S. Wei, X.-G. Wei, X. Su, J. You, Y. Ren, *Chem. Eur. J.* **2011**, *17*, 5965-5971.

[5] H. A. Zhong, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2002**, *124*, 1378-1399.

[6] H. Clavier, A. Correa, L. Cavallo, E. C. Escudero-Adán, J. Benet-Buchholz, A. M. Z. Slawin, S. P. Nolan, *Eur. J. Inorg. Chem.* **2009**, *2009*, 1767-1773.

[7] S. Gaillard, X. Bantreil, A. M. Z. Slawin, S. P. Nolan, *Dalton Trans.* **2009**, 6967-6971.

[8] B. Bostai, Z. Novák, A. C. Bényei, A. Kotschy, *Org Lett* **2007**, *9*, 3437-3439.

[9] S. Petit, R. Azzouz, C. Fruit, L. Bischoff, F. Marsais, *Tetrahedron Lett.* **2008**, *49*, 3663-3665.

[10] A. Beillard, E. Golliard, V. Gillet, X. Bantreil, T.-X. Métro, J. Martinez, F. Lamaty, *Chem. Eur. J.* **2015**, *21*, 17614-17617.

[11] K.-T. Chan, Y.-H. Tsai, W.-S. Lin, J.-R. Wu, S.-J. Chen, F.-X. Liao, C.-H. Hu, H. M. Lee, *Organometallics* **2010**, *29*, 463-472.

[12] D. M. Lindsay, D. McArthur, *Chem. Commun.* **2010**, *46*, 2474-2476.

[13] J. J. Peng, J. Y. Li, Y. Bai, W. H. Gao, H. Y. Qiu, H. Wu, Y. Deng, G. Q. Lai, *J. Mol. Catal. A: Chem.* **2007**, *278*, 97-101.

[14] L. Leclercq, M. Simard, A. R. Schmitzer, *J. Mol. Struct.* **2009**, *918*, 101-107.

[15] X.-Y. Yu, B. O. Patrick, B. R. James, *Organometallics* **2006**, *25*, 2359-2363.

[16] R. A. Haque, A. W. Salman, C. K. Whai, C. K. Quah, H. K. Fun, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2011**, *67*, m97-m98.