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Supporting Information

Mechanochemistry for a facilitated access to *N*,*N*-diaryl NHC metal 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, CNRS, Université Montpellier, ENSCM, Université de Montpellier Campus Triolet, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

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

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1. Synthetic procedures

1.1 General remarks

All reagents were purchased from Aldrich Chemical Co., Fluka and Alfa Aesar and used without further purification. The milling treatments were carried out either in a vibrating Retsch Mixer Mill 200 (vbm) or in a Retsch PM100 Planetary Mill (pbm). Milling load is defined as the sum of the mass of the reactants per free volume in the jar. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 300 MHz, 400 MHz or Bruker Avance III 600 MHz spectrometer and are reported in ppm using deuterated solvent used 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, m = multiplet, sept = septuplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on Bruker Avance AM 75 MHz or 101 MHz spectrometers and are reported in ppm using deuterated solvent used for calibration ($CDCl_3$ at 77.2 ppm or DMSO-d6 at 39.5 ppm). HRMS analysis was performed on a Q-Tof (Waters, ESI, 2001) spectrometer.

All of reactions mixture were recovered with a solvent and filtrated over celite to remove metallic particles lost by the reactor during ball milling.

All of the reactions using vibratory ball mill were made at 25 Hz or 30 Hz under air with no interruption of the milling.

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 dichloromethane and filtrated over celite. The filtrate was concentrated under vacuum to afford product.

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

Method C: 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 to afford product.

Method D: 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 to afford product.

Method E: The solid was recovered with dichloromethane and filtrated over a short pad of silica. The filtrate was concentrated under vacuum and the product was recrystallized by slow diffusion of hexane into a dichloromethane solution of the crude product. The precipitate was filtered, washed three times with hexane and dried under vacuum to afford product.

Method F: The solid was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum and the resulting solid was put on silica, filtrated with cyclohexane to remove excesses of allylpalladium chloride dimer and ethyl acetate to collect the desired product. Ethyl acetate was evaporated under vacuum to afford the pure product.

1.2.1 General table for the mechanosynthesis of silver-NHC complexes

Entry	Product	Reagent	Aspect bp or mp °C	Eq.	Quantity (mmol)	Ball mill (frequency)	Time (h)	Aspect of reaction mixture	Treatment	Yields (%)	Product aspect
1a	[AgCl(IMes)]	IMesHCl	White powder	1.00	0.389	vbm (25Hz)	1h40	Grey powder	Method A	82	White powder
		Silver oxide	Black powder mp : 280	0.55	0.214						
1b	[AgCl(IMes)]	IMesHCl	White powder	1.00	0.358	pbm (450 rpm)	2	Grey powder	Method A	88	White powder
		Silver oxide	Black powder mp : 280	0.55	0.197						
2	[AgCl(SIMes)]	SIMesHCl	White powder	1.00	0.387	vbm (30Hz)	1.5	Grey powder	Method A	89	White powder
		Silver oxide	Black powder mp : 280	0.55	0.213						
3	[AgCl(IPr)]	IPrHCl	White powder	1.00	0.329	vbm (30Hz)	3	Grey powder	Method B	89	White powder
		Silver oxide	Black powder mp : 280	0.55	0.181						
4	[AgCl(SIPr)]	SIPrHCl	White powder	1.00	0.328	vbm (30Hz)	3	Grey powder	Method C	73	White powder
		Silver oxide	Black powder mp : 280	0.55	0.180						
5	[AgCl(IMes^{Me})]	IMes^{Me}HCl	White powder	1.00	0.367	vbm (30Hz)	3	Grey powder	Method A	81	White powder
		Silver oxide	Black powder mp : 280	0.55	0.202						
6	[AgCl(SIMes$^{Me\text{-}cis}$)]	SIMes$^{Me\text{-}cis}$HCl dia 1	White powder	1.00	0.365	vbm (30Hz)	3	Grey powder	Method A	86	White powder
		Silver oxide	Black powder mp : 280	0.55	0.201						
7	[AgCl(SIMes$^{Me\text{-}trans}$)]	SIMes$^{Me\text{-}trans}$HCl dia 2	White powder	1.00	0.365	vbm (30Hz)	3	Grey powder	Method A	86	White powder
		Silver oxide	Black powder mp : 280	0.55	0.201						
8	[AgCl(IPr^{Me})]	IPr^{Me}HCl	White powder	1.00	0.320	vbm (30Hz)	4	Grey powder	Method A	82	White powder
		Silver oxide	Black powder mp : 280	0.55	0.176						

9	[AgCl(SIPr^{Me})]	SIPr^{Me}AgCl Silver oxide	White powder Black powder mp : 280	1.00 0.55	0.312 0.172	vbm (30Hz)	3	Grey powder	Method D	77	White powder
10	[AgCl(TPT)]	TPTHCl Silver oxide	White powder Black powder mp : 280	1.00 0.55	0.394 0.217	vbm (30Hz)	3	Grey powder	Method A	89	Brown powder

Reactions were carry out with a milling load of 19.2 mg/mL

1.2.2 General table for the transmetalation of silver-NHC complexes

Entry	Product	Reagent	Aspect bp or mp °C	Eq.	Quantity (mmol)	Ball mill (frequency)	Time (h)	Aspect of reaction mixture	Treatment	Yields (%)	Product aspect
1a	[CuCl(IMes)]	[AgCl(IMes)] Copper (I) chloride	White powder Green powder mp : 426	1.00 1.50	0.305 0.458	vbm (25Hz)	1	White powder	Method A	100	White powder
2	[AuCl(IMes)]	[AgCl(IMes)] AuCl(DMS)	White powder White powder decomp. 110-160	1.00 1.20	0.227 0.273	vbm (25Hz)	1	Yellow powder	Method E	96	Pale yellow powder
3	[PdCl(η^3-allyl)(IMes)]	[AgCl(IMes)] [Pd(η^3-allyl)Cl]$_2$	White powder Brown powder	1.00 0.65	0.265 0.173	vbm (25Hz)	1h30	Black powder	Method F	94	Pale yellow powder

Reactions were carry out with a milling load of 19.2 mg/mL

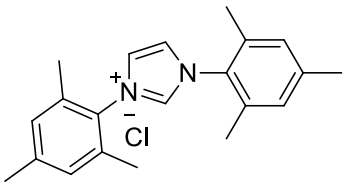
1.2.3 General table of one-pot two-step generation of metal-NHC complexes

Entry	Product	1st step						2nd step						Yields (%)	Product aspect
		Reagent	Aspect	Eq.	Quantity (mmol)	Aspect of reaction mixture	Time	Reagent	Aspect	Eq.	Quantity (mmol)	Aspect of reaction mixture	Time		
1	[CuCl(IMes)]	IMesHCl Silver oxide	White powder Black powder mp : 280	1.00 0.55	0.295 0.162	Grey powder	1h40	Copper chloride	Green powder mp : 426	1.50	0.442	Grey powder	1h	90	White powder
2	[AuCl(IMes)]	IMesHCl Silver oxide	White powder Black powder mp : 280	1.00 0.55	0.221 0.122	Grey powder	1h40	AuCl(DMS)	White powder	1.20	0.266	Grey powder	1h30	76	Pale yellow powder
3	[PdCl(η^3-allyl)(IMes)]	IMesHCl Silver oxide	White powder Black powder mp : 280	1.00 0.55	0.258 0.142	Grey powder	1h40	Pd(allyl)Cl dimer	Yellow powder	0.65	0.167	Black powder	1h30	88	Pale yellow powder

Reactions were carry out with a milling load of 19.2 mg/mL

1.3 Synthesis of imidazolium salts

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

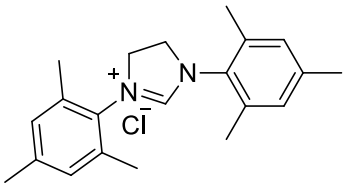


2,4,6-Trimethylaniline (10.4 mL, 74.0 mmol, 2.00 eq) was dissolved in methanol (40 mL). The resulting solution was cooled to 0 °C, and glyoxal 40% in water (4.23 mL, 37.0 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred during two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

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

^{1}H NMR (300 MHz, $CDCl_3$)[2] δ 10.95 (s, 1H), 7.60 (s, 2H), 7.04 (s, 4H), 2.35 (s, 6H), 2.19 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 141.4, 140.0, 134.1, 130.6, 129.9, 124.3, 21.1, 17.7

1,3-Dimesitylimidazolinium chloride SIMes•HCl

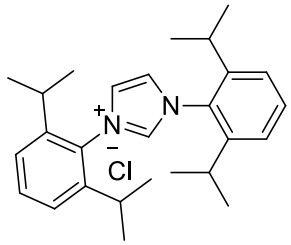


As reported in the littérature[3] : *N*,*N*'-dimesitylethanediimine (4.02 g, 13.7 mmol, 1.00 eq) was dissolved in a mixture of methanol (55 mL) and THF (82 mL). The reaction was agitated at room temperature and sodium borohydride (5.20 g, 137.4 mmol, 10.00 eq) was added. After 2 h at room temperature, a saturated solution of ammonium chloride was added. The resulting solution was extracted three times with diethyl ether. The combined organic layer was washed with water, dried with $MgSO_4$, filtrated and concentrated under vaccum to furnish 1,2-bis(mesitylamino)ethane (3.78 g, 12.8 mmol, 93 %). ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[4]

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

^{1}H NMR (400 MHz, $CDCl_3$)[5] δ 9.34 (s, 1H), 6.94 (s, 4H), 4.54 (s, 4H), 2.36 (s, 12H), 2.27 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.9, 140.5, 134.9, 130.2, 130.0, 51.9, 21.0, 18.0

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

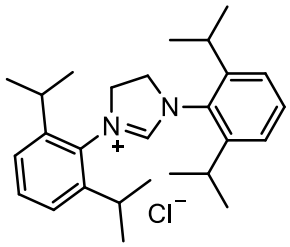


2,6-Diisopropylaniline (3.00 g, 16.9 mmol, 2.00 eq) was dissolved in methanol (16.3 mL). The resulting solution was cooled to 0 °C, and glyoxal 40% in water (975 µL, 8.45 mmol, 1.00 eq) and two or three drops of formic acid were added. The solution was warmed to room temperature and stirred during three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

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

^{1}H NMR (400 MHz, DMSO-d_6)[2] δ 10.41 (s, 1H), 8.74 (s, 2H), 7.83 (t, *J* = 6.8 Hz, 2H), 7.67 (d, *J* = 6.8 Hz, 4H), 2.64 (s, 4H), 1.41 (d, *J* = 5.6 Hz, 12H), 1.31 (d, *J* = 5.6 Hz, 12H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 145.3, 139.8, 132.3, 130.5, 126.7, 125.1, 29.1, 24.6, 23.6.

1,3-Bis(2,6-diisopropylphenyl)imidazolidinium chloride SIPr•HCl

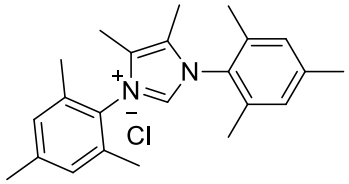


N,*N*'-Bis(2,6-diisopropylphenyl)ethane-1,2-diimine (500 mg, 1.33 mmol, 1.00 eq) was disolved in a mixture of THF (6 mL) and MeOH (5.3 mL). Sodium borohydride (503.2 mg, 13.3 mmol, 10.00 eq) was added and the mixture was stirred at 80°C for three hours under Argon. The reaction mixture was cooled to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

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

^{1}H NMR (400 MHz, $CDCl_3$)[5] δ 8.69 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.22 (m, 4H), 4.76 (s, 4H), 2.99 (sept, *J* = 6.6 Hz, 4H), 1.37 (d, *J* = 6.6 Hz, 12H), 1.24 (d, *J* = 6.6 Hz, 12H) ; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 146.1, 131.6, 129.4, 125.0, 55.3, 29.3, 25.5, 23.8 ; **HRMS** calcd for C27H39N2 [M – Cl^-]$^+$: 391.3113; found: 391.3115;

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

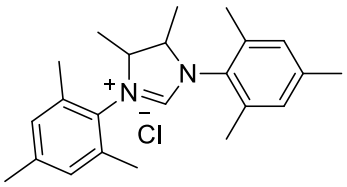


2,4,6-Trimethylaniline (4.15 mL, 29.6 mmol, 2.00 eq) was dissolved in methanol (29.6 mL). The resulting solution was cooled to 0 °C, and 2,3-butanedione (1.29 mL, 14.8 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred two days. The yellow suspension was filtrated, washed with a minimum of methanol and diethyl ether to afford *N,N*'-dimesityl-2,3-butanediimine (3.20 g, 10.0 mmol, 68%) as a yellow powder. ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[7]

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

^{1}H NMR (400 MHz, $CDCl_3$)[8] δ 10.59 (s, 1H), 7.01 (s, 4H), 2.31 (s, 6H), 2.08 (s, 12H), 2.04 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.2, 137.7, 134.7, 130.0, 128.9, 127.5, 21.2, 17.7, 8.7

[1,3-Bis(2,4,6-trimethylphenyl)-4,5-bis(methyl)]imidazolinium chloride SIMes^{Me}•HCl



N,N'-Dimesityl-2,3-butanediimine (6.00 g, 18.7 mmol, 1.00 eq) was dissolved in methanol (75 mL). Cyanoborohydride (5.90 g, 93.6 mmol, 5.00 eq) was added slowly to the resulting solution. Bromo cresol green and 0.1M HCl was added until the solution change from blue to yellow. The resulting solution was stirred at reflux for three days. Two diasteroisomeres were obtained in 25:75 (dia1:dia2). Then, cooling down to room temperature, 0.1N KOH (15 mL) and water (150 mL) were added. The aqueous layer was extracted three times with dichloromethane (3*100 mL). The combined organic layer was washed two times with water, dried with $MgSO_4$ and concentrated under vacuum. The crude mixture was purified and both diastereoisomeres were separated by column chromatography with a gradient from cyclohexane to cyclohexane/ethyl acetate 2% to afford both 2,3-*cis*-bis(mesitylamino)butane (581,4 mg, 1.79 mmol, 10%) and 2,3-*trans*-bis(mesitylamino)butane (3.26 g, 10.04 mmol, 54%) as white powders.

Cis diastereoisomer:

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

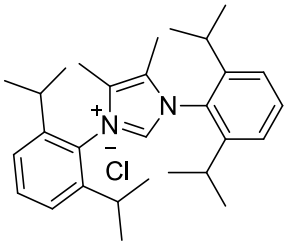
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 6.94 (s, 2H), 6.92 (s, 2H), 5.10 (s, 2H), 2.40 (s, 6H), 2.35 (s, 6H), 2.26 (s, 6H), 1.30 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.0, 140.2, 135.7, 135.3, 130.4, 130.3, 128.9, 62.3, 21.1, 19.0, 18.6, 12.3; **HRMS** calcd for $C_{23}H_{31}N_2$ [M –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

Trans diastereoisomer:

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 6.93 (s, 2H), 6.90 (s, 2H), 4.41 – 4.30 (m, 2H), 2.36 (s, 6H), 2.32 (s, 6H), 2.25 (s, 6H), 1.43 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.5, 140.2, 136.2, 134.6, 130.34, 130.31, 128.8, 66.8, 21.0, 19.0, 18.4, 17.8; **HRMS** calcd for $C_{23}H_{31}N_2$ [M – Cl^-]+: 335.2488; found : 335.2489; **HRMS** calcd for $C_{29}H_{43}N_2$ [M – Cl^-]$_+$: 419.3430; found: 419.3426;

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

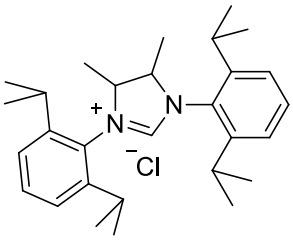


2,6-Di*iso*propylaniline (15.0 g, 84,6 mmol, 2.00 eq) was dissolved in methanol (42,3 mL). The resulting solution was cooled to 0 °C, and 2,3-butanedione (3.7 mL, 42,3 mmol, 1.00 eq) and one or two drops of formic acid were added. The solution was warmed to room temperature and stirred overnight. The yellow suspension was filtrated, washed with a minimum of methanol and diethyl ether to afford *N*,*N*'-bis-(2,6-diisopropylphenyl)butane-2,3-diimine (11.15 g, 27.6 mmol, 65%) as a yellow powder. ^{1}H and ^{13}C NMR spectrum of the product was found to be identical to literature data.[9]

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

^{1}H NMR (400 MHz, DMSO-d_6)[10] δ 9.98 (s, 1H), 7.68 (t, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 4H), 2.29 (sept, *J* = 6.8 HZ, 4H), 2.06 (s, 6H), 1.25 (d, *J* = 6.8 Hz, 12H), 1.11 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 145.4, 136.8, 132.4, 129.1, 128.0, 125.2, 28.7, 25.0, 22.8, 8.6

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

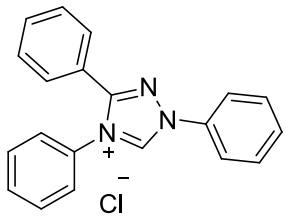


N,*N*'-bis-(2,6-di*iso*propylphenyl)butane-2,3-diimine (6.00 g, 14.8 mmol, 1.00 eq) was dissolved in methanol (60 mL). Sodium cyanoborohydride (4.70 g, 74.1 mmol, 5.00 eq) was added to resulting solution slowly. Bromo cresole green and HCl 0.1M was added until the solution change from blue to yellow. The resulting solution was stirred at reflux for three days. Two diasteroisomeres were obtained in 6:4. Then, cooling down to room temperature, KOH 0.1N (15 mL) and water (150 mL) were added. The aqueous layer was extracted three times with dichloromethane (3*100 mL). The combined organic layer was washed two times with water, dried with $MgSO_4$ and concentrated under vacuum to afford 2,3-bis(2,6-di*iso*propylphenylamino)butane (5.27 g, 12.9 mmol, 87%).

2,3-Bis(2,6-di*iso*propylphenylamino)butane (5.20 g, 17.53 mmol, 1.00 eq), ammonium chloride (1.03 g, 19.28 mmol, 1.10 eq) and triethyl orthoformate (17.5 mL, 15.59 mmol, 6.00 eq) were stirred at 110°C overnight. Diethyl ether was added, the resulting suspension was filtrated and washed with diethyl ether and acetone to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolinium chloride (1.70 g, 4.97 mmol, 28%) as a white solid.

^{1}H RMN (400 MHz, DMSO-d_6) δ 9.55 (s, 1H, 57%), 9.44 (s, 1H, 43%), 7.57 (t, *J* = 7.8 Hz, 2H, 57%), 7.56 (t, *J* = 7.8 Hz, 2H, 43%), 7.47 – 7.41 (m, 4H), 5.10 – 5.01 (m, 2H, 43%), 4.60 – 4.51 (m, 2H, 57%), 3.14 – 2.89 (m, 4H), 1.42 (d, *J* = 5.4 Hz, 6H), 1.38 – 1.32 (m, 12H), 1.28 (d, *J* = 5.5 Hz, 6H), 1.23 – 1.13 (m, 12H) ; Major diastereoisomer: **^{13}C NMR (101 MHz, DMSO-d_6)** 158.9, 147.2, 146.3, 131.2, 127.8, 125.0, 124.9, 68.2, 28.63, 28.57, 28.5, 25.2, 24.8, 23.34, 22.7, 16.1 ; Minor diastereoisomer : **^{13}C NMR (101 MHz, DMSO-d_6)** 159.9, 146.8, 146.4, 131.1, 127.9, 125.0, 124.9, 63.2, 28.63, 28.57, 28.5, 25.3, 24.9, 23.27, 22.8, 11.9 ; **HRMS** calcd for $C_{29}H_{43}N_2$ $[M - Cl^-]_+$: 419.3430; found: 419.3426;

1,3,4-Triphenyl-1,2,4-triazolium chloride TPT•HCl

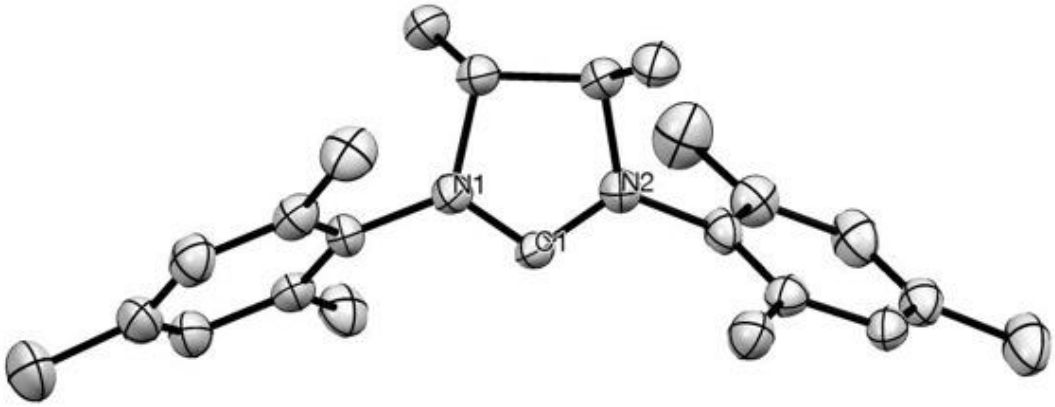


Benzoyl chloride (1.16 mL, 10.0 mmol, 1.00 eq) and aniline (913 µL, 10.0 mmol, 1.00 eq) were stirred together in toluene (10 mL) for 90 min at room temperature under Argon. A white precipitate appears quickly. After this time, the reaction mixture was heated to 130 °C for 2 h until the precipitate disappear. 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.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.68 (s, 1H), 8.17 (d, *J* = 7.7 Hz, 2H), 7.82 – 7.61 (m, 9H), 7.54 (d, *J* = 3.9 Hz, 4H) ; **^{13}C NMR (101 MHz, DMSO-d_6)** δ 153.1, 143.3, 134.9, 132.2, 132.1, 131.4, 130.7, 130.3, 130.1, 129.3, 129.2, 126.6, 122.4, 120.6; **HRMS** calcd for $C_{20}H_{16}N_3$ $[M - Cl^-]_+$: 298.1344; found: 298.1347;

1.4 X-Ray diffraction of SIMes$^{Me\text{-}trans}$•HCl

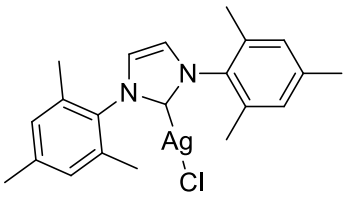


X-Ray diffraction of SIMes$^{Me\text{-}trans}$•HCl (CCDC 1487556) indicating the *trans* configuration.

	SIMes$^{Me\text{-}trans}$•HCl
Formula	$C_{23}H_{31}ClN_2$
M / g.mol^{-1}	370.95
Crystal system	Monoclinic
Space group	P 21/n
a / Å	8.9790 (3)
b / Å	15.1223 (5)
c / Å	15.7117 (8)
α / Å	90
β / Å	100.137 (4)
γ / Å	90
V (Å^3)	2100.08 (11)
Z	4
ρ_{calcd} / g.cm^{-3}	1.173
μ (Mo Kα) / mm^{-1}	1.652
T / K	175
Number of reflections	4293
Number of unique reflections	1954
R_{int}	0.104
R1, wR2 ($I > 2\sigma(I)$)	0.0678, 0.0709
R1, wR2 (all data)	0.0751, 0.0720
GOF	1.0291

1.5 Synthesis of NHC-Silver complexes

[1,3-Bismesitylimidazol-2-ylidene]silver chloride [AgCl(IMes)]

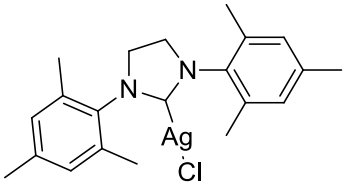


Method A: 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (132.4 mg, 0.389 mmol, 1.00 eq) and silver oxide (49.5 mg, 0.214 mmol, 0.55 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 1 hour and 40 minutes in the vibratory ball mill operated at 25 Hz. The grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]silver chloride (142.3 mg, 0.318 mmol, 82%) as a pale brown solid.

Method B: 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (122.0 mg, 0.358 mmol, 1.00 eq) and silver oxide (45.6 mg, 0.197 mmol, 0.55 eq) were introduced in a 12 mL stainless steel grinding bowl with fifty stainless steel balls (5 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 planetory ball mill operated at 450 rpm. The grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]silver chloride (140.3 mg, 0.313 mmol, 88%) as a pale brown solid.

^{1}H NMR (300 MHz, $CDCl_3$)[11] δ 7.14 (d, *J* = 1.5 Hz, 2H), 7.00 (s, 4H), 2.36 (s, 6H), 2.08 (s, 12H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.1 (dd, *J* = 256.0, 18.3 Hz), 139.9, 135.3, 134.7, 129.7, 122.9, 122.8, 21.2, 17.8.

[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]silver chloride [AgCl(SIMes)]

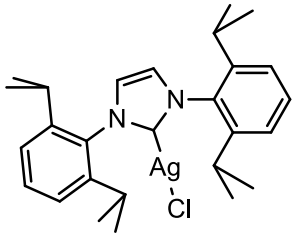


1,3-Dimesitylimidazolinium chloride (132.7 mg, 0.387 mmol, 1.00 eq), and silver oxide (49.3 mg, 0.213 mmol, 0.55 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 3*1 hour in the vibratory ball mill operated at 30 Hz. The grey 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 two times with water, once with diethyl ether and dry under vacuum to afford [1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]silver chloride (116.1 mg, 0.258 mmol, 69%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$)[11] δ 6.96 (s, 4H), 4.01 (s, 4H), 2.31 (s, 6H), 2.30 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 138.9, 135.4, 135.1, 129.9, 51.2, 51.1, 21.0, 17.9.

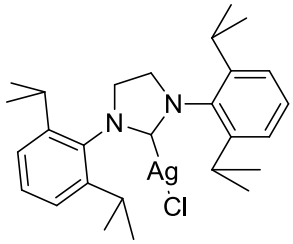
[1,3-Bis[2,6-di*iso*propylphenyl)]imidazol-2-ylidene]silver chloride [AgCl(IPr)]



1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium chloride (140.0 mg, 0.329 mmol, 1.00 eq) and silver oxide (42.0 mg, 0.181 mmol, 0.55 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 grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum. The solid was washed with water and dried under vacuum to [1,3-bis[2,6-di*iso*propylphenyl)]imidazol-2-ylidene]silver chloride (155 mg, 0.440 mmol, 89%) as a white powder.

After purification, a mixture of [AgCl(IPr)] and [$AgCl(IPr)_2$] were obtained in 95:5 ratio. Peaks for [AgCl(IPr)] (major product) are reported: **^{1}H NMR (400 MHz, $CDCl_3$)**[11] δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 4H), 7.22 (d, *J* = 1.8 Hz, 2H), 2.62 – 2.47 (m, 4H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.22 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 184.6 (dd, *J* = 258.5, 21.4 Hz), 145.7, 134.6, 130.9, 124.5, 123.8, 123.7, 28.8, 24.8, 24.1.

[1,3-Bis[2,6-(di*iso*propylphenyl)]imidazolidin-2-ylidene]silver chloride [AgCl(SIPr)]

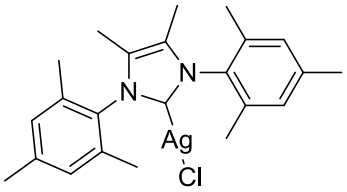


1,3-Bis(2,6-di*iso*propylphenyl)imidazolidinium chloride (140.1 mg, 0.328 mmol, 1.00 eq) and silver oxide (41.8 mg, 0.180 mmol, 0.55 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling

load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 3*1 hour in the vibratory ball mill operated at 30 Hz. The grey 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, dried with $MgSO_4$ and concentrated 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)]imidazolidin-2-ylidene]silver chloride (127.8, 0.239 mmol, 73%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$)[11] δ 7.42 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 4H), 4.06 (s, 4H), 3.05 (hept, *J* = 6.9 Hz, 4H), 1.342 (d, *J* = 6.9 Hz, 12H), 1.337 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ ^{13}C of carbene was not observed, 146.7, 134.6, 130.2, 124.9, 54.1, 54.0, 29.0, 25.6, 24.2.

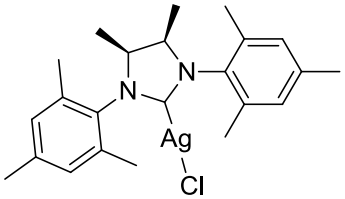
[(1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver chloride [AgCl(IMes^{Me})]



[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride (135.2 mg, 0.367 mmol, 1.00 eq) and silver oxide (46.7 mg, 0.202 mmol, 0.55 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 grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]silver chloride (142.3 mg, 0.299 mmol, 81%) as a pale brown solid.

A mixture of [AgCl(IMes^{Me})] and [AgCl(IMes^{Me})$_2$] were obtained in 90:10 ratio. Peaks for [AgCl(IMes^{Me})] (major product) are reported: **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.99 (s, 4H), 2.35 (s, 6H), 2.01 (s, 12H), 1.91 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.8 (dd, *J* = 258.4, 18.4 Hz), 139.5, 135.0, 134.0, 129.7, 126.13, 126.07, 21.2, 17.8, 9.3; **HRMS** calcd for $C_{23}H_{28}N_2Ag$ [M – Cl^-]$^+$: 439.1303; found: 439.1308.

[(1,3-Bis-(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazolidin-2-ylidene]silver chloride [AgCl(SIMes$^{Me\text{-}cis}$)]

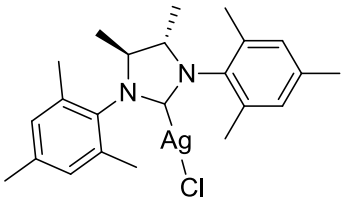


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-*cis*-dimethyl]imidazolinium chloride (135.4 mg, 0.365 mmol, 1.00 eq), and silver oxide (46.5 mg, 0.201 mmol, 0.55 eq) were introduced in a 10 mL stainless steel

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 grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [(1,3-bis-(2,4,6-trimethylphenyl)-4,5-*cis*-dimethyl)imidazolidin-2-ylidene]silver chloride (149.4 mg, 0.313 mmol, 86%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.94 (s, 2H), 4.47 (s, 2H), 2.36 (s, 6H), 2.30 (s, 6H), 2.27 (s, 6H), 1.19 (d, *J* = 5.5 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 206.1 (dd, *J* = 242.4, 17.4 Hz), 138.5, 136.3, 135.5, 134.1, 130.1, 130.0, 61.4, 61.3, 21.0, 19.1, 18.1, 13.0; **HRMS** calcd for $C_{46}H_{60}N_4Ag$ [M – Cl^-]$^+$: 775.3869; found: 775.3879.

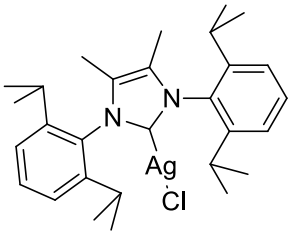
[(1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl)imidazolidin-2-ylidene]silver chloride [AgCl(SIMes$^{Me\text{-}trans}$)]



[1,3-Bis(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl]imidazolinium chloride (135.4 mg, 0.365 mmol, 1.00 eq), and silver oxide (46.5 mg, 0.201 mmol, 0.55 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 grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [(1,3-bis(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl)imidazolidin-2-ylidene]silver chloride (150.1 mg, 0.314 mmol, 86%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.91 (s, 34H), 4.07 – 3.91 (m, 2H), 2.32 (s, 6H), 2.28 (s, 6H), 2.26 (s, 6H), 1.28 (d, *J* = 5.8 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 207.64 (dd, *J* = 242.0, 17.4 Hz), 138.6, 136.6, 135.3, 134.0, 130.1, 130.0, 66.64, 66.54, 21.0, 19.1, 18.4, 18.0; **HRMS** calcd for $C_{46}H_{60}N_4Ag$ [M – Cl^-]+: 775.3869; found: 775.3870.

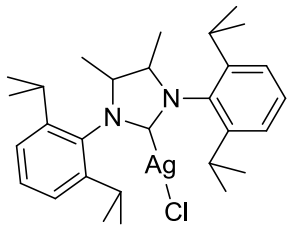
[(1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver chloride [AgCl(IPr^{Me})]



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride (144.9 mg, 0.320 mmol, 1.00 eq), and silver oxide (40.8 mg, 0.176 mmol, 0.55 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 grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver chloride (146.2 mg, 0.261 mmol, 82%) as a white solid.

After purification, a mixture of [AgCl(IPr^{Me})] and [AgCl(IPr^{Me})$_2$] were obtained in 97:3 ratio. Peaks for [AgCl(IPr^{Me})] (major product) are reported: **^{1}H NMR (400 MHz, DMSO-*d*$_6$)**[10] δ 7.60 – 7.53 (m, 2H), 7.44 (d, *J* = 7.7 Hz, 4H), 2.39 (sept, *J* = 6.8 Hz, 4H), 1.95 (s, 6H), 1.22 (d, *J* = 6.8 Hz, 12H), 1.18 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 178.9 (dd, *J* = 253.1, 18.1 Hz), 146.0, 133.2, 131.1, 127.3, 127.2, 124.9, 28.6, 25.5, 23.4, 9.6.

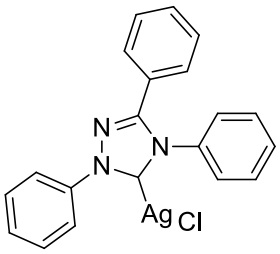
[(1,3-Bis[2,6-di*iso*propylphenyl]-4,5-dimethyl)imidazolidin-2-ylidene]silver chloride [AgCl($SIPr^{Me}$)] racemic



[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolinium chloride (139.5 mg, 0.333 mmol, 1.00 eq), and silver oxide (39.8 mg, 0.172 mmol, 0.55 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 grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum. The solid was washed with diethyl ether and dried to afford [(1,3-bis[2,6-di*iso*propylphenyl]-4,5-dimethyl) imidazolidin-2-ylidene]silver chloride (135.0 mg, 0.240 mmol, 77%) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.46 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 6.7 Hz, 4H), 4.57 (s, 2H, 43%), 4.01 (s, 2H, 57%), 3.26 (sept, *J* = 6.8 Hz, 2H, 57%), 3.15 (sept, *J* = 6.9 Hz, 2H, 43%), 3.06 (sept, *J* = 6.9 Hz, 2H, 43%), 2.95 (sept, *J* = 6.8 Hz, 2H, 57%), 1.35 – 1.26 (m, 18H), 1.23 (d, *J* = 6.7 Hz, 12H, 57%), 1.19 (d, *J* = 6.7 Hz, 6H, 43%), 1.14 (d, *J* = 4.8 Hz, 6H, 43%); Major diastereoisomer: **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 206.3 (dd, *J* = 201.0, 17.2 Hz), 147.5, 146.8, 132.9, 129.8, 124.7, 124.4, 68.3, 68.2, 28.2, 28.1, 25.9, 25.1, 23.6, 22.8, 17.4; Minor diastereoisomer: **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 203.9 (dd, *J* = 201.2, 17.8 Hz), 147.4, 146.8, 133.2, 129.6, 124.5, 63.0, 62.9, 28.3, 28.0, 25.9, 25.2, 23.4, 23.1, 12.8; **HRMS** calcd for $C_{29}H_{42}N_2Ag$ [M – Cl^-]$^+$: 525.2399; found: 525.2404.

[1,3,4-Triphenyl-1,2,4-triazol-2-ylidene]silver chloride [AgCl(TPT)]

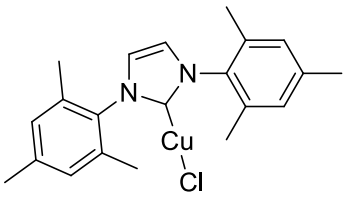


1,3,4-Triphenyl-1,2,4-triazolium chloride (131.4 mg, 0.394 mmol, 1.00 eq) and silver oxide (50.3 mg, 0.217 mmol, 0.55 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding for 3*1 hours in the vibratory ball mill operated at 30 Hz. The brown powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3,4-triphenyl-1,2,4-triazol-2-ylidene]silver chloride (152.7 mg, 0.349, 89%) as a brown crystallized powder.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.08 – 8.00 (m, 2H), 7.64 – 7.48 (m, 9H), 7.46 – 7.41 (m, 4H); **^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 183.5, 154.1, 139.5, 137.0, 131.6, 130.6, 130.3, 130.0, 129.6, 129.2, 127.5, 124.7, 123.3; **HRMS** calcd for $C_{20}H_{15}N_3Ag$ $[M - Cl^-]^+$: 404.0317; found: 404.0317.

1.6 Synthesis of NHC-Copper complex

[1,3-Bismesitylimidazol-2-ylidene]copper chloride [CuCl(IMes)]



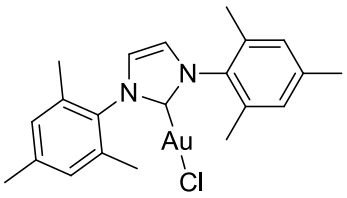
Method A: [1,3-Bismesitylimidazol-2-ylidene]silver chloride (136.6 mg, 0.305 mmol, 1.00 eq) and copper(I) chloride (45.3 mg, 0.458 mmol, 1.50 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that 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 25 Hz. The white powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]copper chloride (122.7 mg, 0.304 mmol, 100%) as a white powder.

Method B: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (100.6 mg, 0.295 mmol, 1.00 eq) and silver oxide (37.6 mg, 0.162 mmol, 0.55 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 1 hour and 40 minutes in the vibratory ball mill operated at 25 Hz. The bowls was open and copper(I) chloride (43.8 mg, 0.442 mmol, 1.50 eq) was 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 1 hour in the vibratory ball mill operated at 25 Hz. The grey powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]copper chloride (107.2 mg, 0.266 mmol, 90%) as a white powder.

^{1}H NMR (300 MHz, $CDCl_3$)[12] δ 7.07 (s, 2H), 7.01 (s, 4H), 2.36 (s, 6H), 2.11 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 179.9, 139.6, 135.5, 134.5, 129.6, 129.2, 122.6, 121.9, 21.2, 17.8

1.7 Synthesis of NHC-Gold complex

[1,3-Bismesitylimidazol-2-ylidene]gold chloride [AuCl(IMes)]



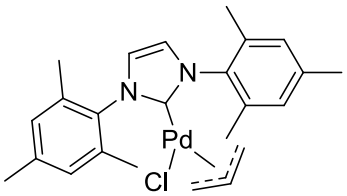
Method A: [1,3-Bismesitylimidazol-2-ylidene]silver chloride (101.7 mg, 0.227 mmol, 1.00 eq) and chloro(dimethylsulfide)gold (80.3 mg, 0.273 mmol, 1.20 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated 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 25 Hz. The yellow powder was recovered with dichloromethane and the suspension was filtrated over silica. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]gold chloride (117.5 mg, 0.219 mmol, 96%) as pale yellow powder.

Method B: 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (75.5 mg, 0.221 mmol, 1.00) and silver oxide (28.2 mg, 0.122 mmol, 0.55 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 1 hour and 40 minutes in the vibratory ball mill operated at 25 Hz. Afterwards, chloro(dimethylsulfide)gold (78.3 mg, 0.266 mmol, 1.20 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 1 hour and 30 minutes in the vibratory ball mill operated at 25 Hz. The grey powder was recovered with dichloromethane and the suspension was filtrated over silica. The filtrate was concentrated under vacuum to afford [1,3-bismesitylimidazol-2-ylidene]gold chloride (90.2 mg, 0.168 mmol, 76%) as a pale yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$)[13] δ 7.10 (s, 1H), 6.99 (s, 2H), 2.35 (s, 3H), 2.11 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.5, 139.8, 134.71, 134.68, 129.5, 122.4, 21.2, 17.8

1.8 Synthesis of NHC-Palladium complex

[1,3-Bismesitylimidazol-2-ylidene](η^3-2-propen-1-yl)palladium chloride [PdCl(η^3-allyl)(IMes)]



Method A: [1,3-Bismesitylimidazol-2-ylidene]silver chloride (118.8 mg, 0.265 mmol, 1.00 eq) and allylpalladium chloride dimer (63.1 mg, 0.173 mmol, 0.65 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 and 30 minutes 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 and the resulting solid was put on silica, filtrated with cyclohexane to remove excesses of allylpalladium chloride dimer and ethyl acetate to collect the desired product. Ethyl acetate was evaporated to afford [1,3-bismesitylimidazol-2-ylidene](η^3-2-propen-1-yl)palladium chloride (122.0 mg, 0.250 mmol, 94%) as pale yellow powder.

Method B: 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (87.8 mg, 0.258 mmol, 1.00) and silver oxide (32.8 mg, 0.142 mmol, 0.55 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 1 hour and 40 minutes in the vibratory ball mill operated at 25 Hz. Afterwards, allylpalladium chloride dimer (61.3 mg, 0.167 mmol, 0.65 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 1 hour and 30 minutes 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 and the resulting solid was put on silica, filtrated with cyclohexane to remove excesses of allylpalladium chloride dimer and ethyl acetate to collect the desired product. Ethyl acetate was evaporated to afford [1,3-bismesitylimidazol-2-ylidene](η^3-2-propen-1-yl)palladium chloride (110.8 mg, 0.227 mmol, 88%) as a pale yellow solid.

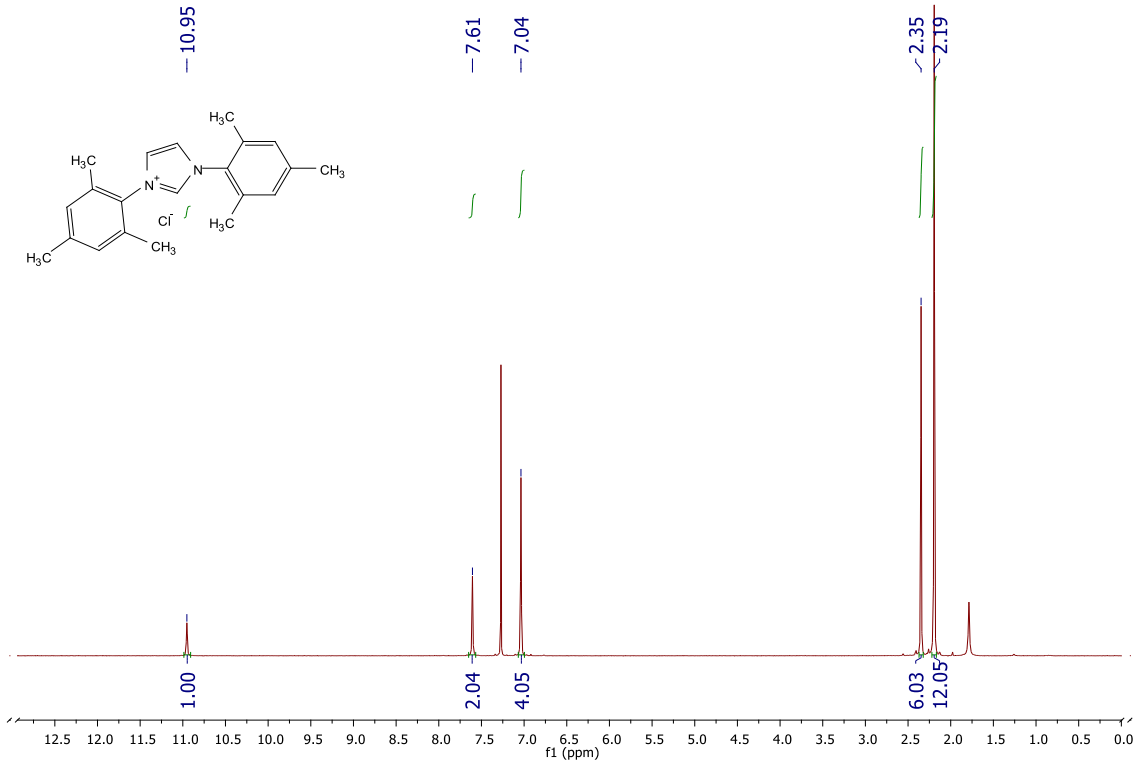
^{1}H NMR (400 MHz, $CDCl_3$)[14] δ 7.09 (s, 2H), 6.97 (s, 4H), 4.93 – 4.77 (m, 1H), 3.94 – 3.83 (m, 1H), 3.39 (d, *J* = 6.1 Hz, 1H, 25%), 3.20 (d, *J* = 6.1 Hz, 1H, 75%), 2.81 (d, *J* = 13.5 Hz, 1H, 75%), 2.76 (d, *J* = 13.4 Hz, 1H, 25%), 2.33 (s, 6H), 2.23 (s, 6H), 2.20 (s, 6H), 1.87 (d, *J* = 12.1 Hz, 1H, 25%), 1.80 (d, *J* = 11.8 Hz, 1H, 75%); Major diastereoisomer: **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.8, 139.0, 136.0, 135.6, 129.2, 129.1, 123.1, 114.4, 72.5, 49.3, 21.3, 18.43, 18.37 ; Minor diastereoisomer: **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.3, 139.0, 136.0, 135.5, 129.3, 129.2, 123.2, 113.9, 71.7, 52.5, 21.3, 18.71, 18.66

2. NMR spectra

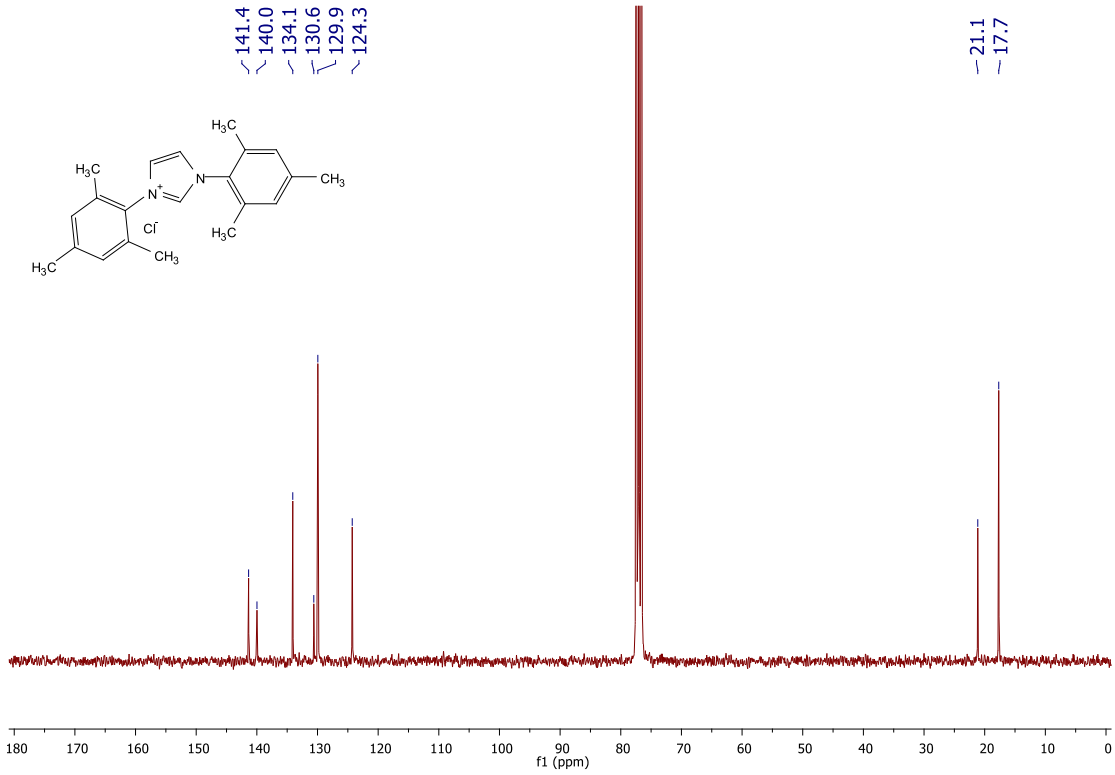
2.1 Imidazolium salts

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

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

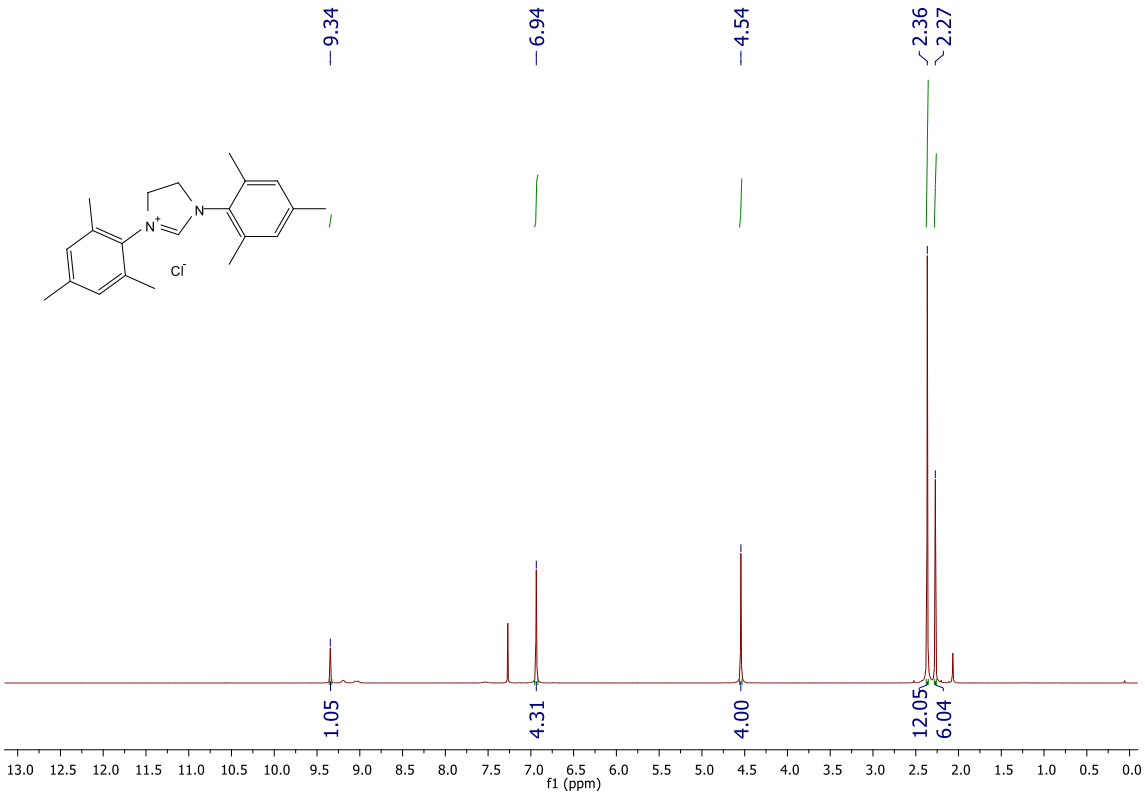


^{13}C NMR (75 MHz, $CDCl_3$)

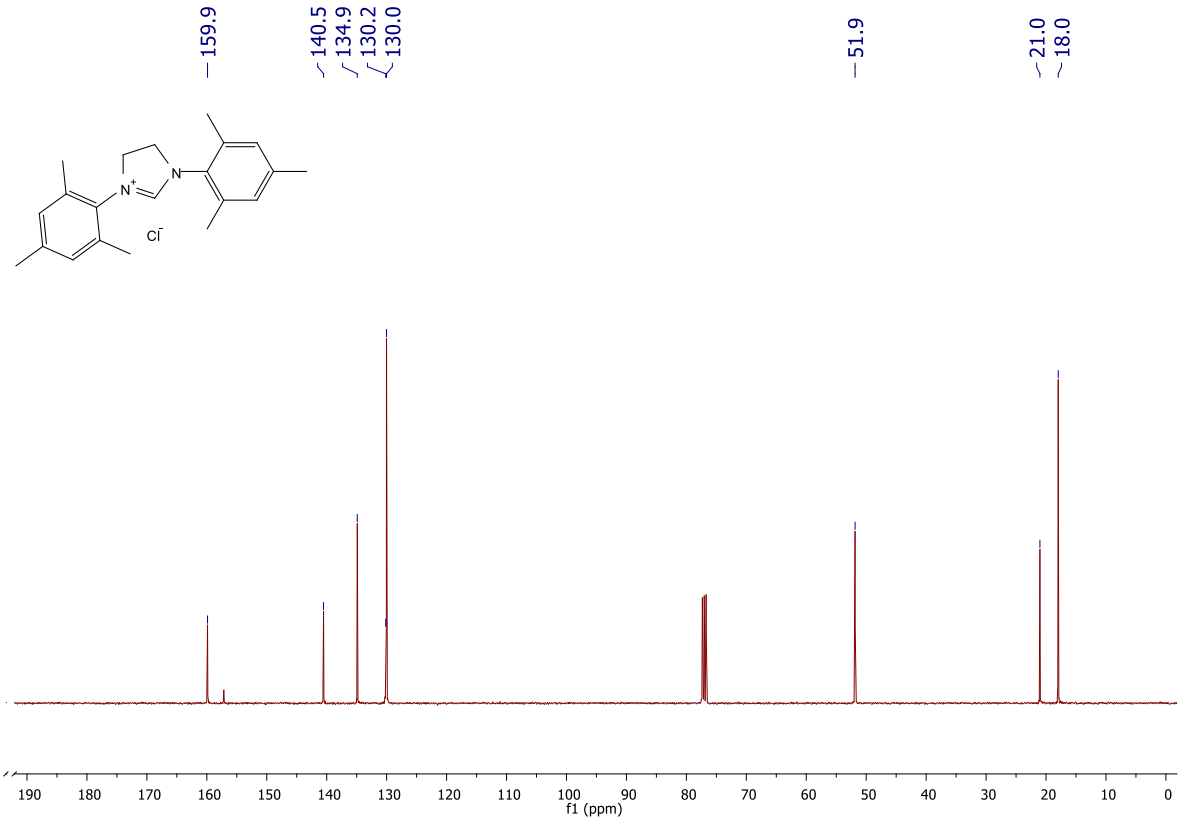


1,3-Dimesitylimidazolinium chloride SIMes•HCl

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

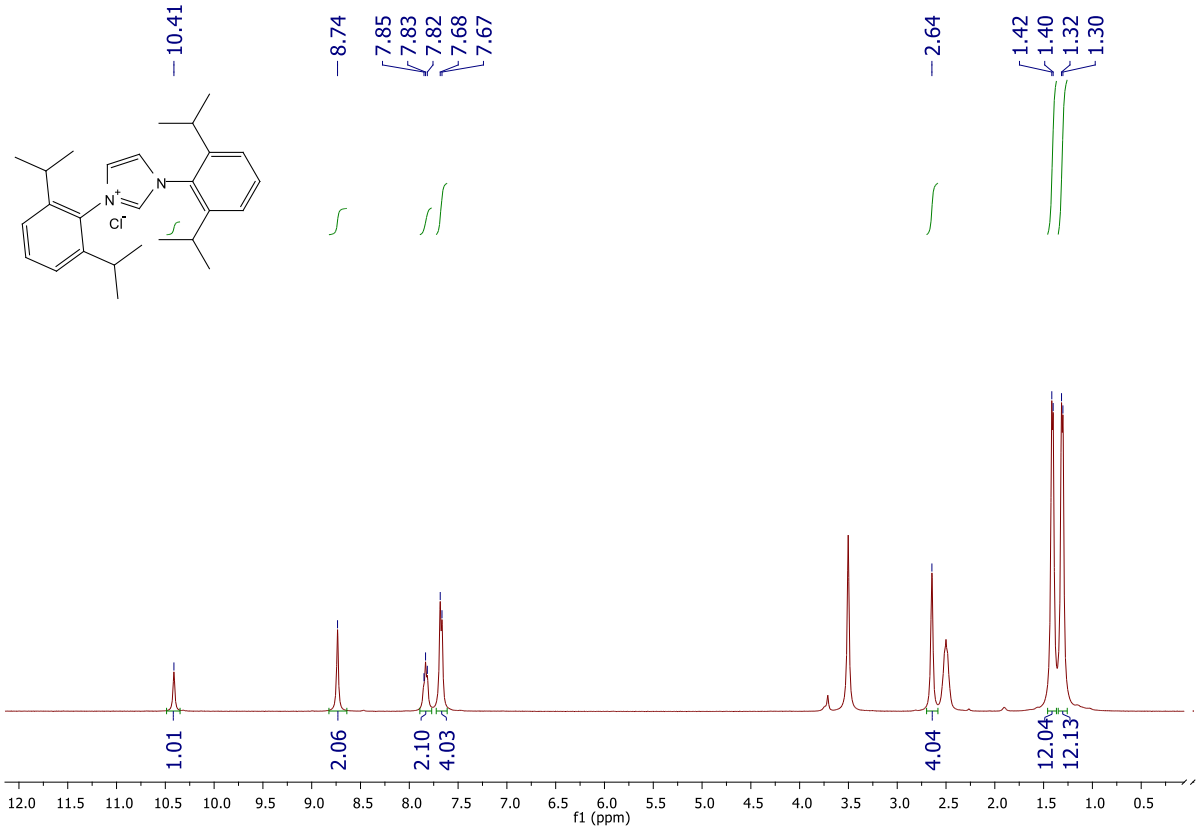


^{13}C NMR (101 MHz, $CDCl_3$)

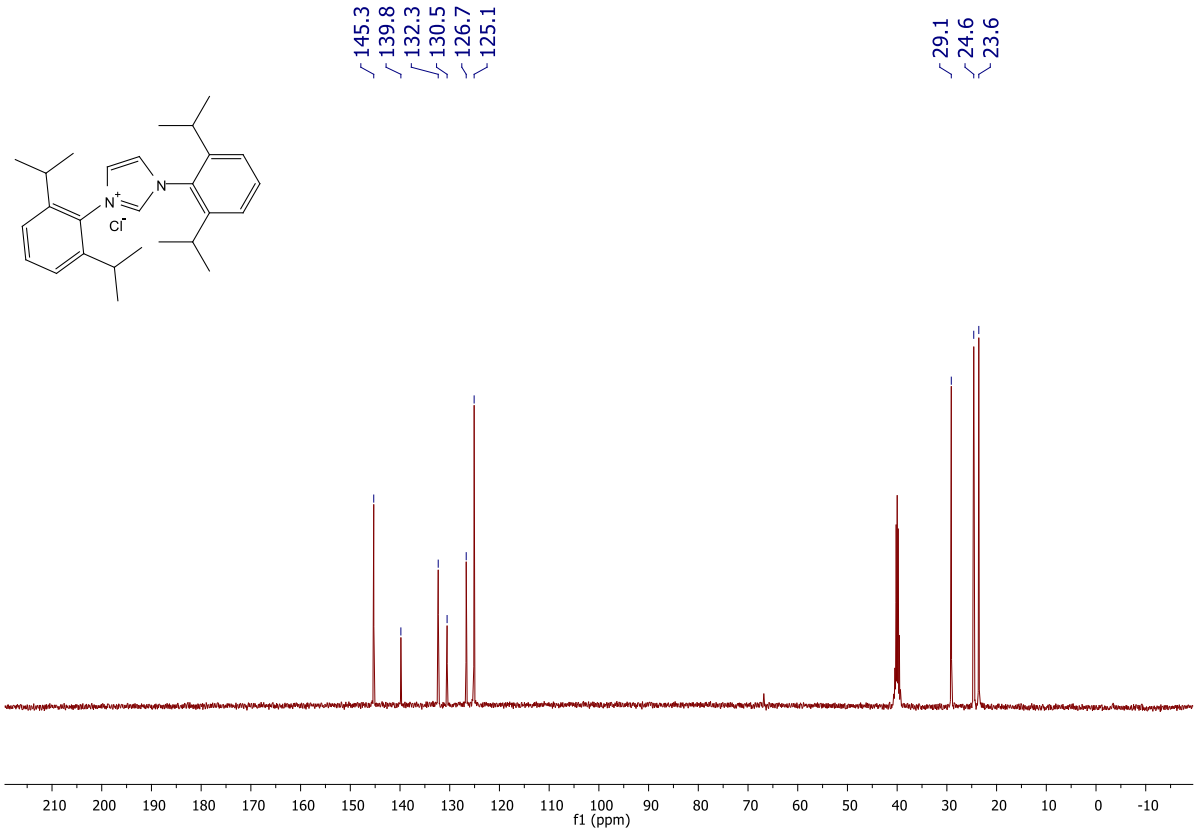


1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium chloride IPr•HCl

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

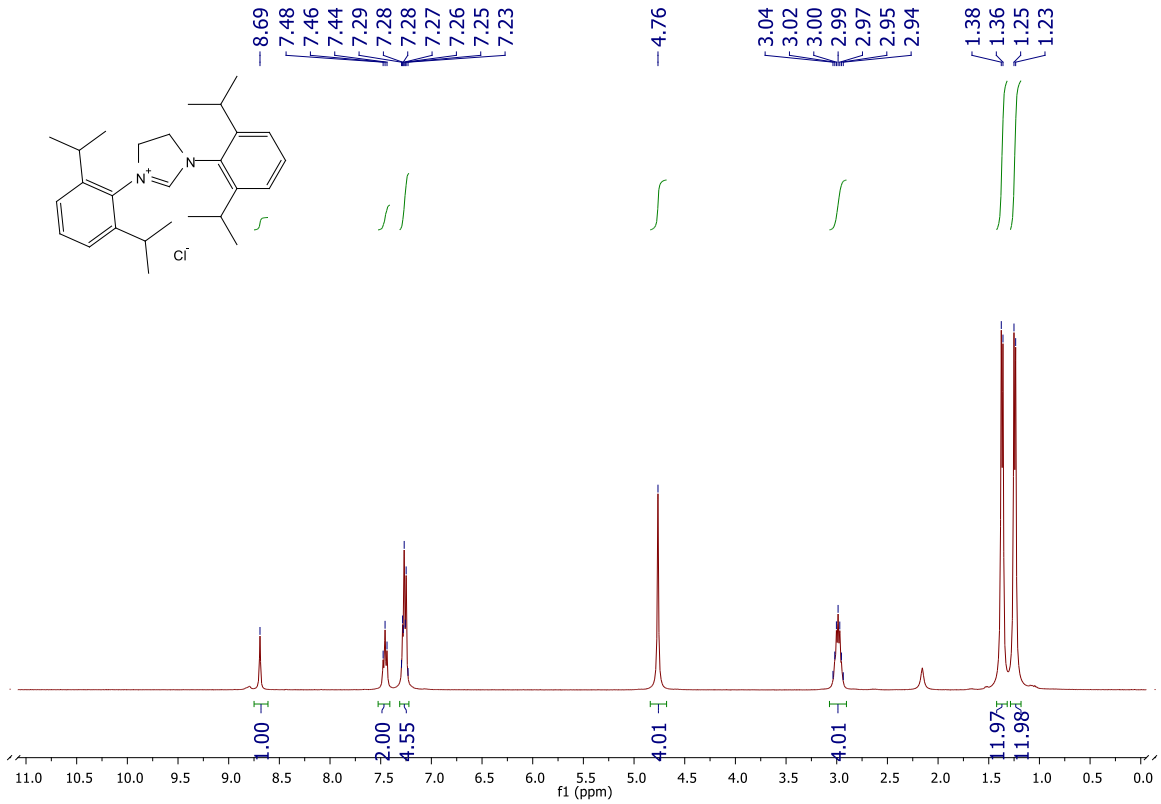


^{13}C NMR (75 MHz, $CDCl_3$)

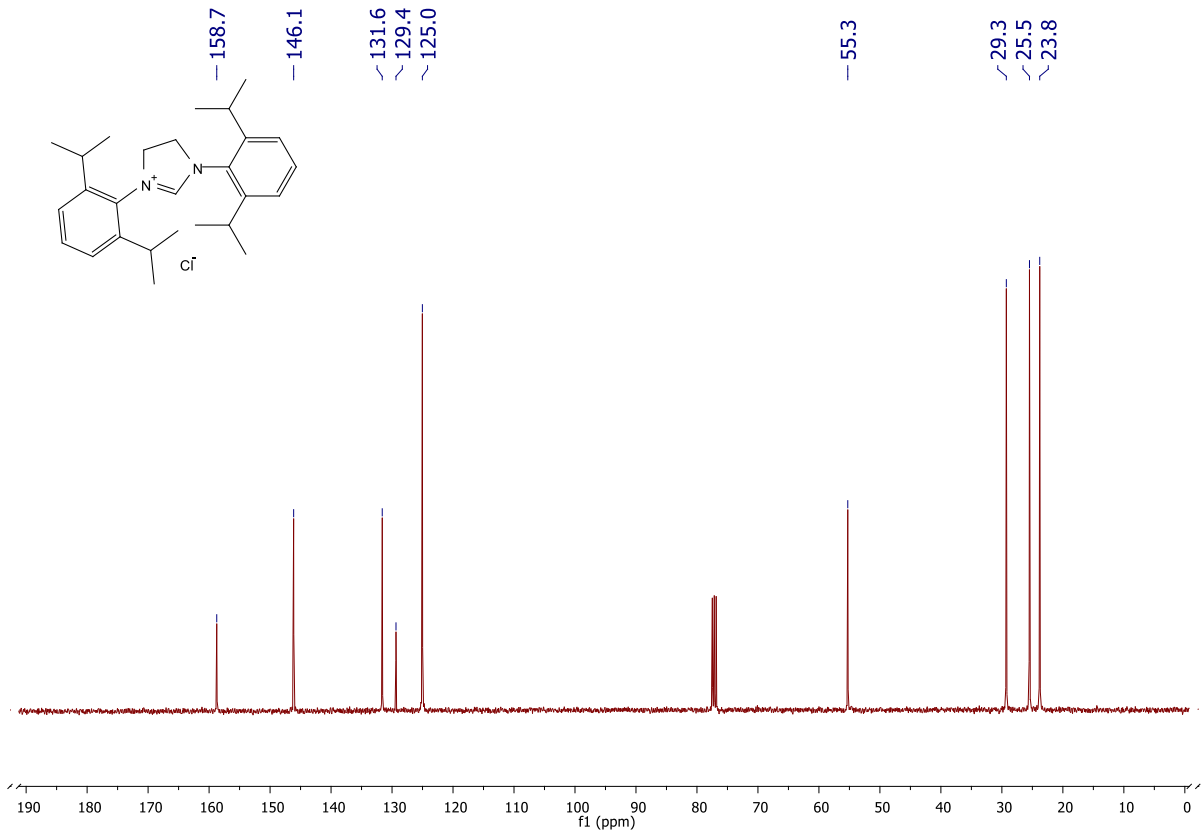


1,3-Bis(2,6-diisopropylphenyl)imidazolidinium chloride SIPr•HCl

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

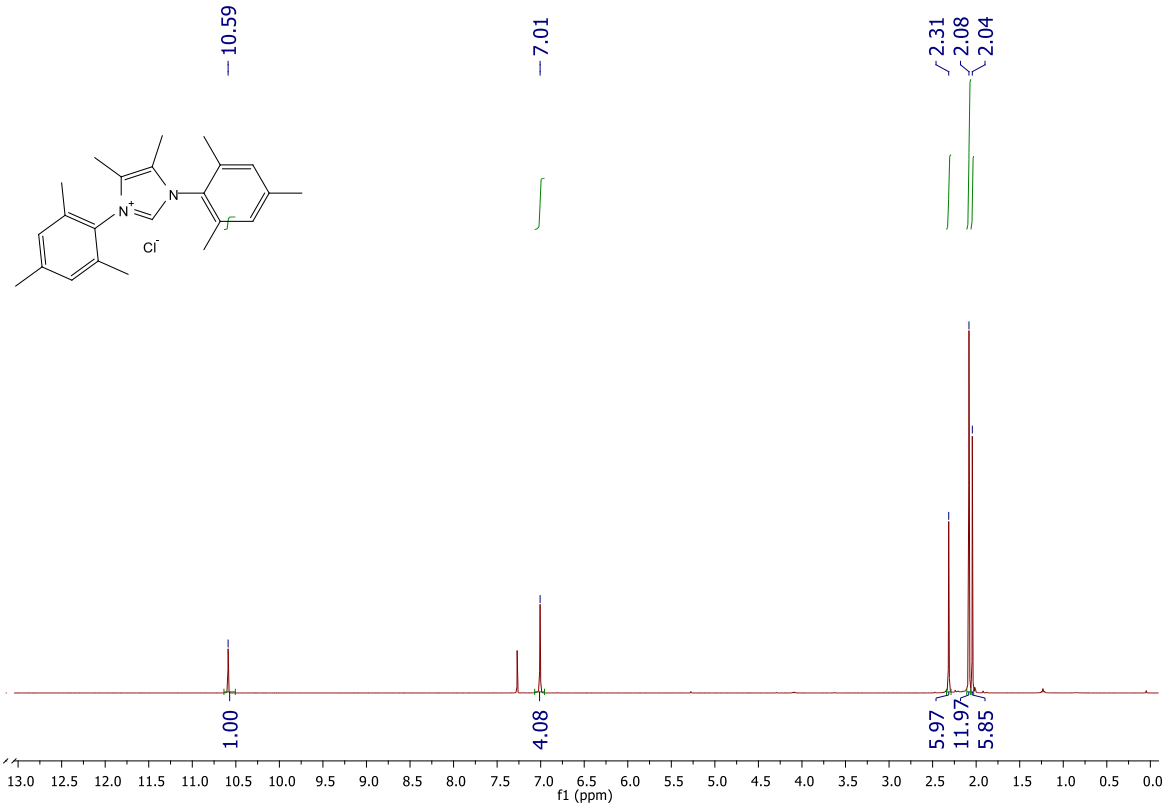


^{13}C NMR (101 MHz, $CDCl_3$)

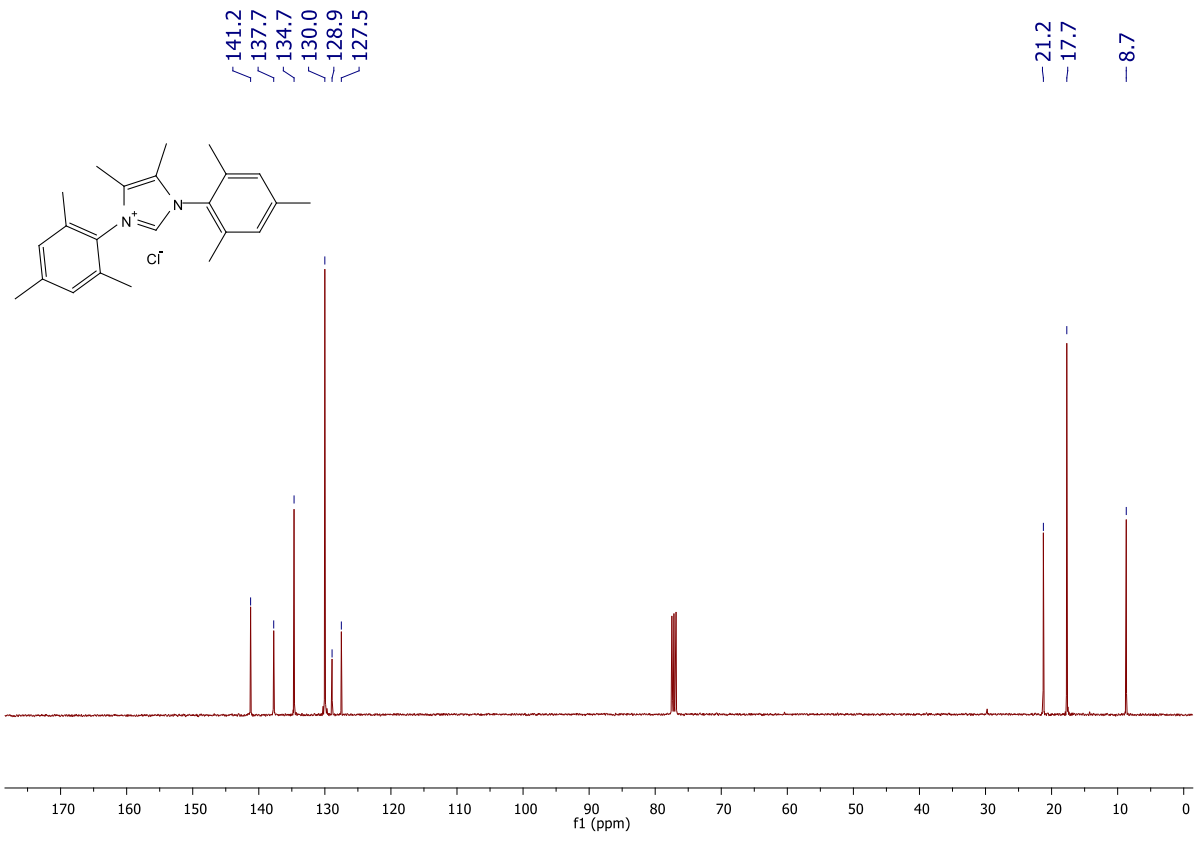


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride IMes^{Me}•HCl

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

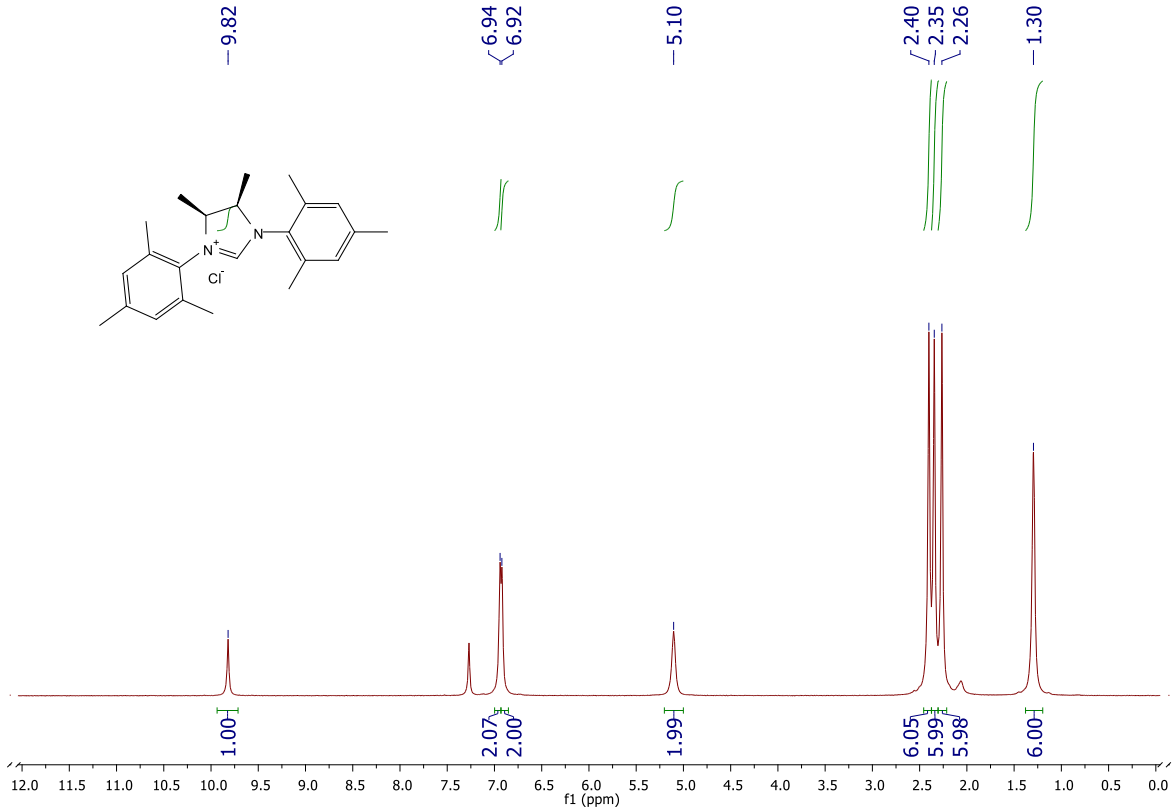


^{13}C NMR (101 MHz, $CDCl_3$)

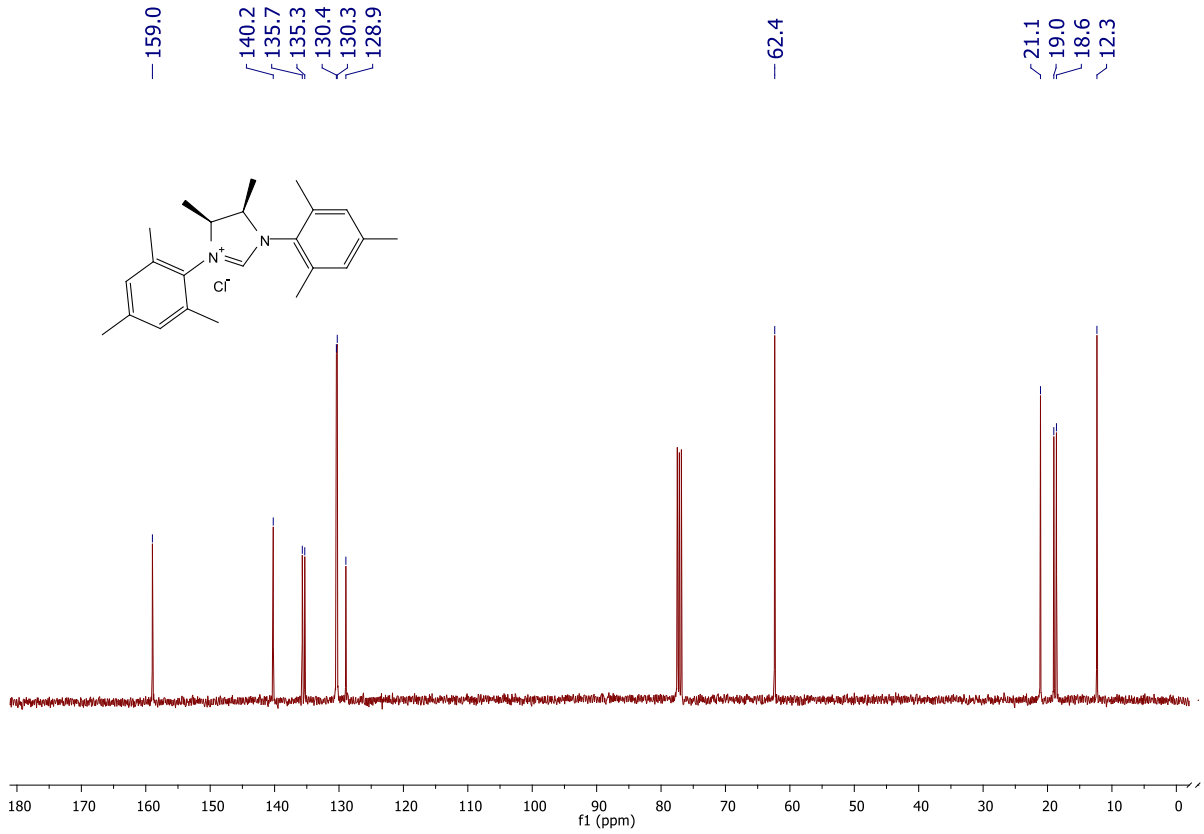


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-*cis*-dimethyl]imidazolinium chloride SIMes$^{Me\text{-}cis}$•HCl

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

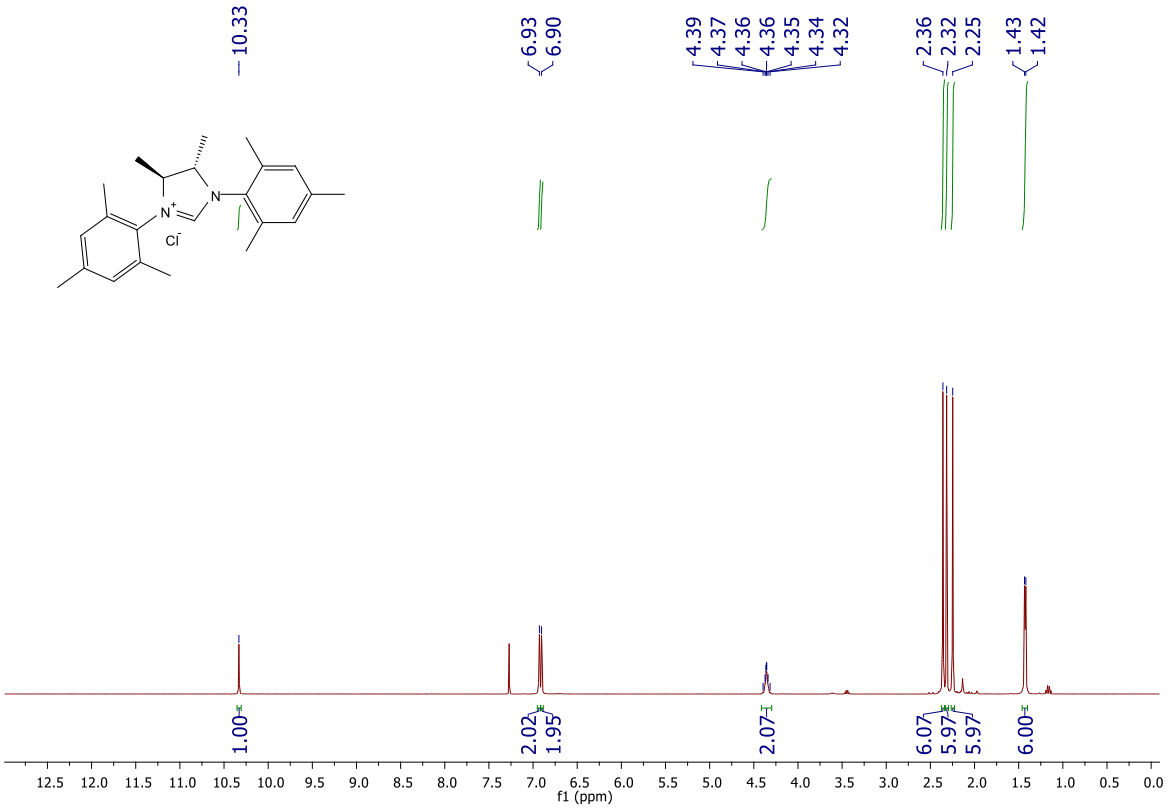


^{13}C NMR (101 MHz, $CDCl_3$)

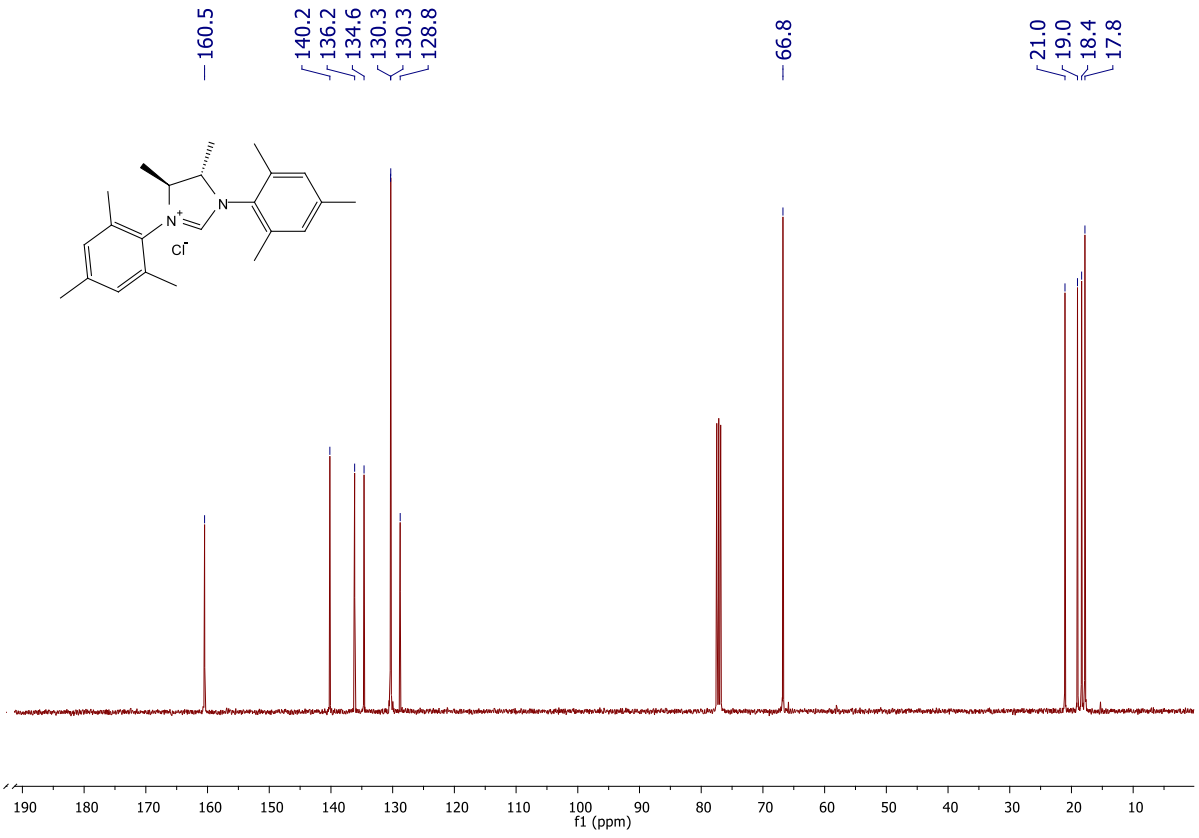


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl]imidazolinium chloride SIMes$^{Me\text{-}trans}$•HCl

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

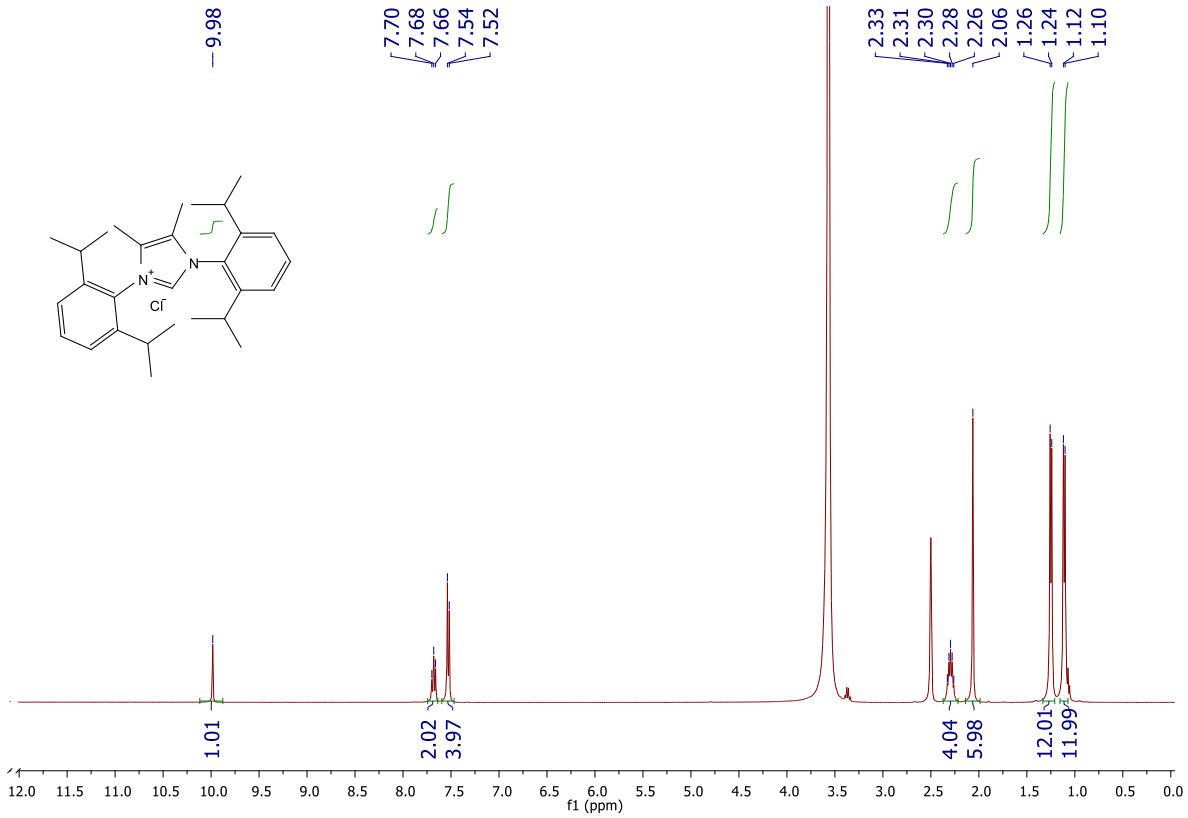


^{13}C NMR (101 MHz, $CDCl_3$)

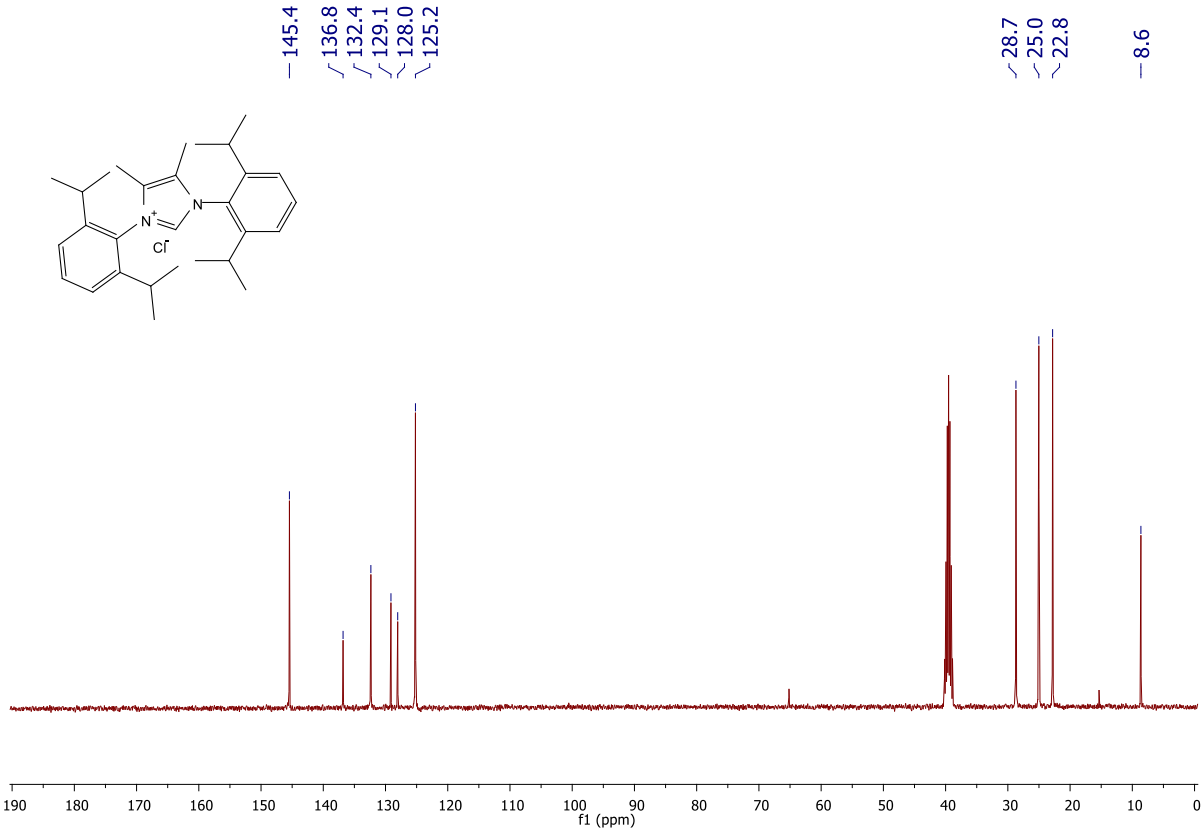


[4,5-Dimethyl-1,3-bis(2,6-di*iso*propylphenyl)]imidazolium chloride IPr^{Me}•HCl

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

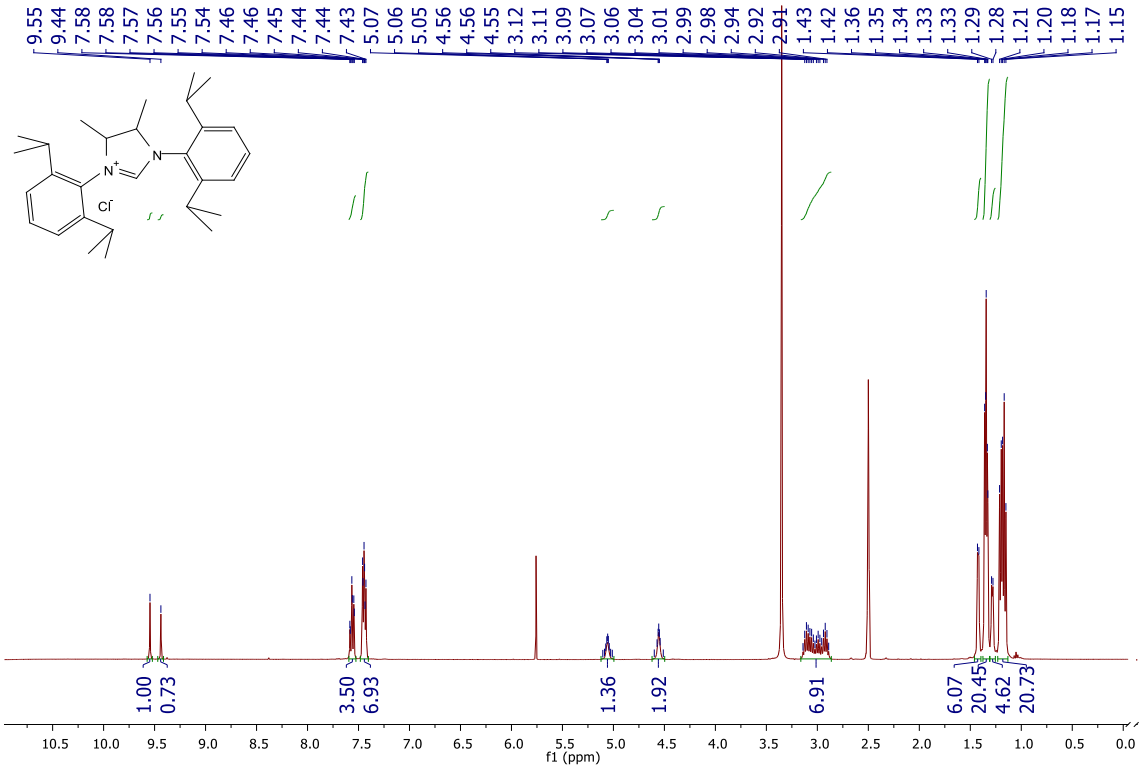


^{13}C NMR (101 MHz, DMSO-d_6)

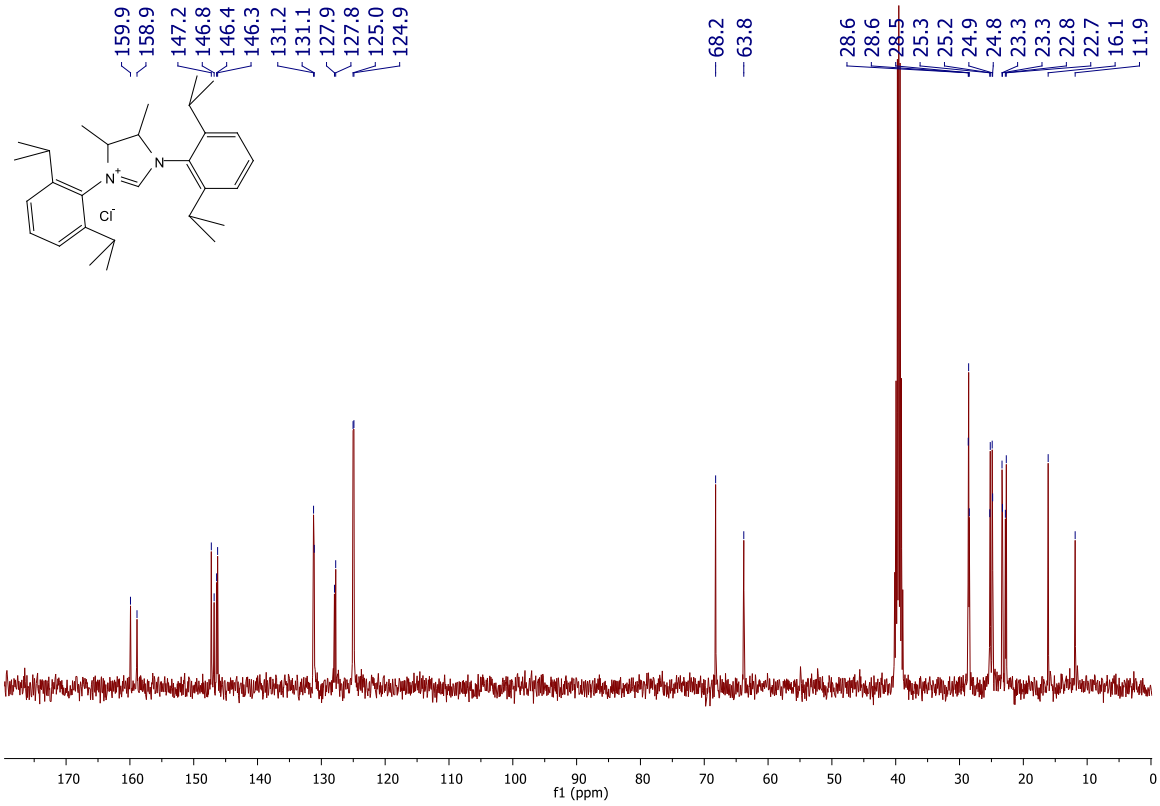


[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolinium chloride SIPr^{Me}•HCl

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

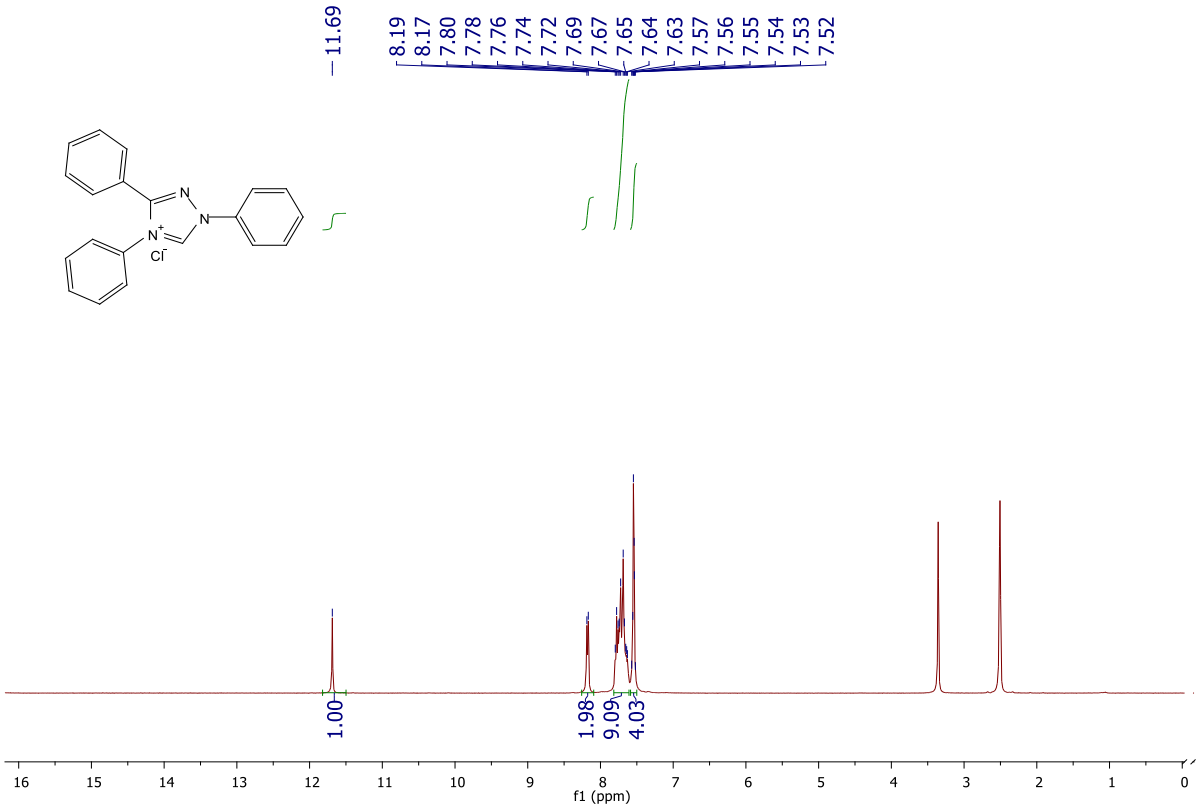


^{13}C NMR (101 MHz, DMSO-d_6)

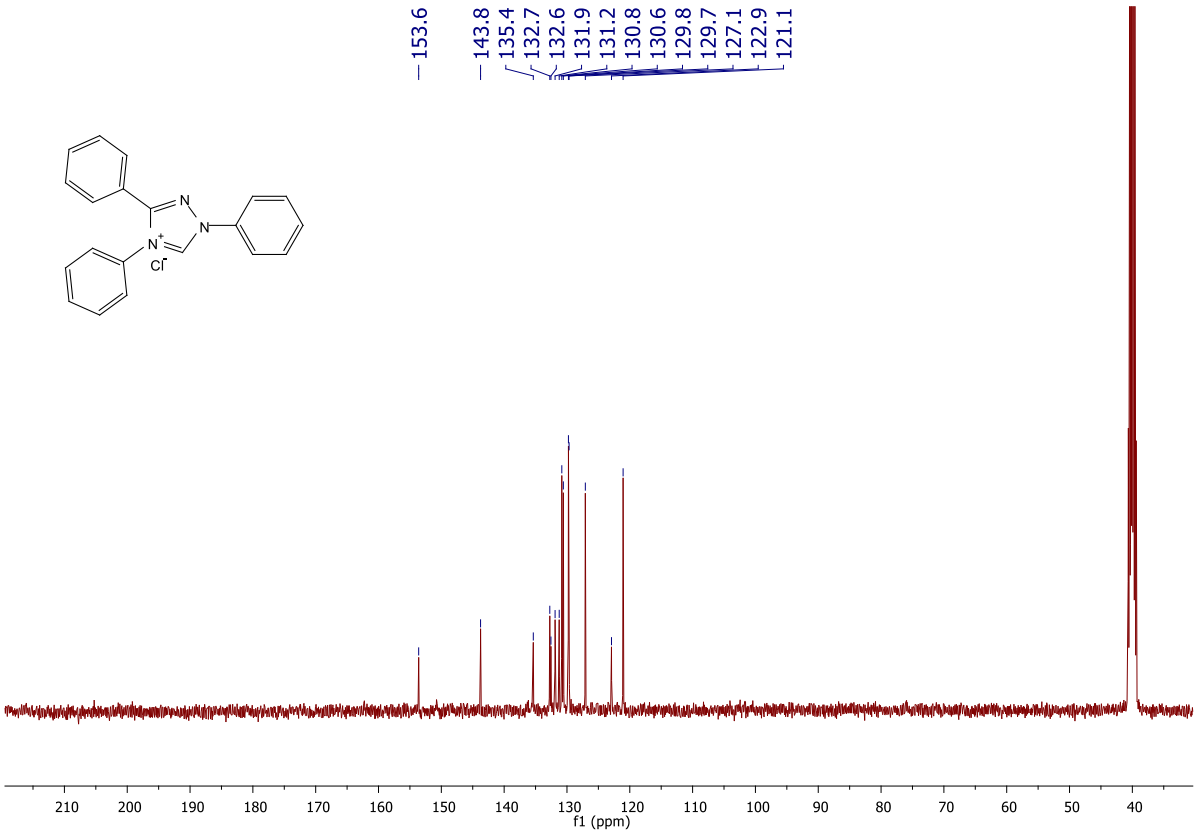


1,3,4-Triphenyl-1,2,4-triazolium chloride TPT•HCl

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



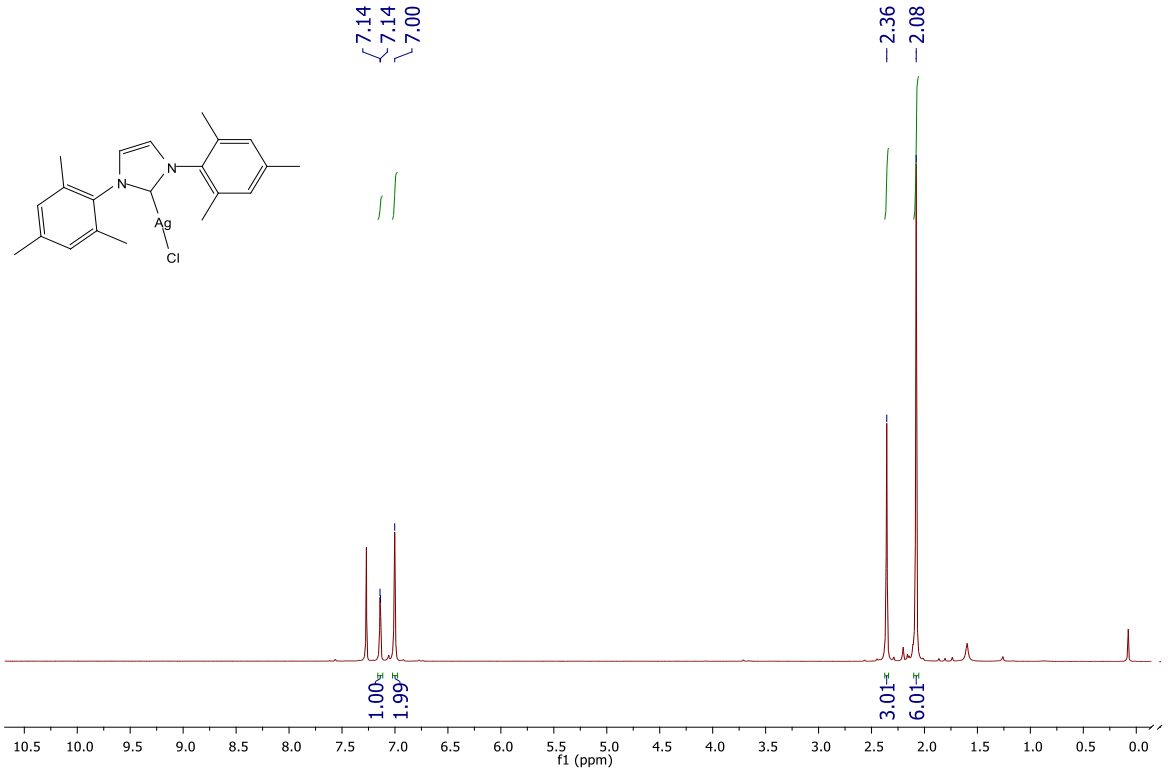
^{13}C NMR (101 MHz, DMSO-d_6)



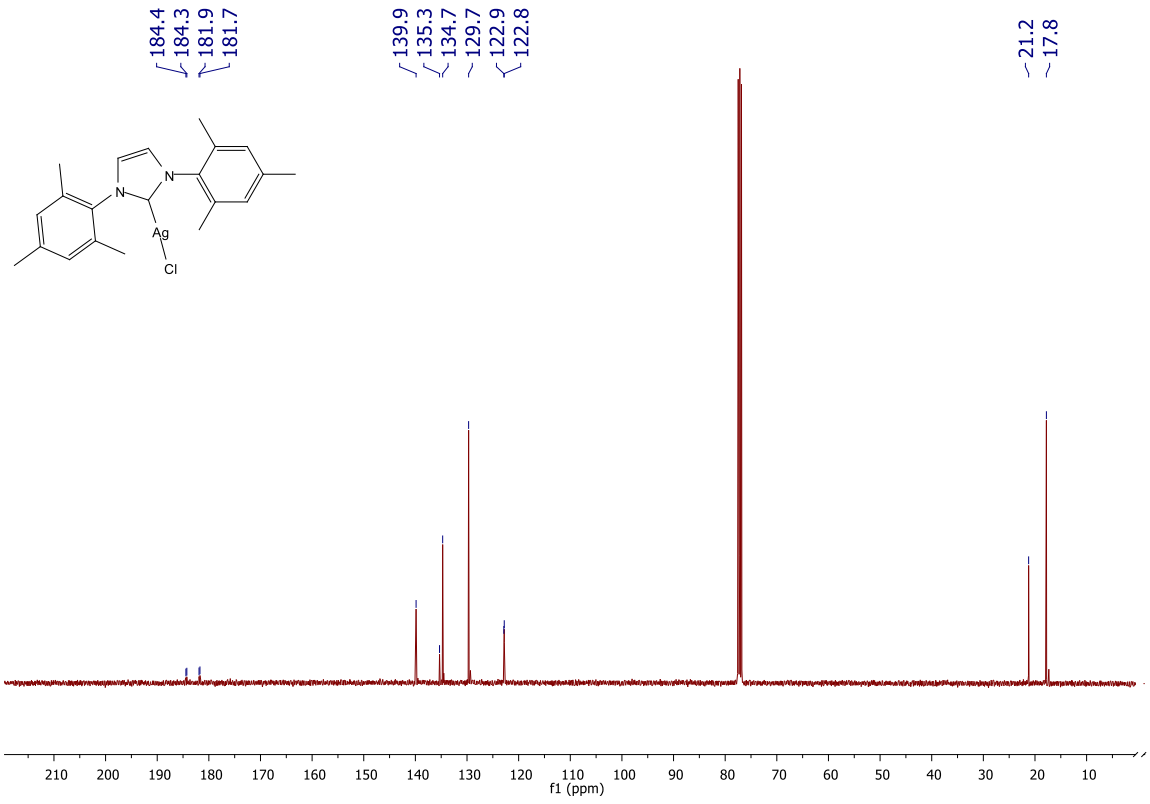
2.2 NHC-Silver complexes

[1,3-Bismesitylimidazol-2-ylidene]silver chloride [AgCl(IMes)]

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

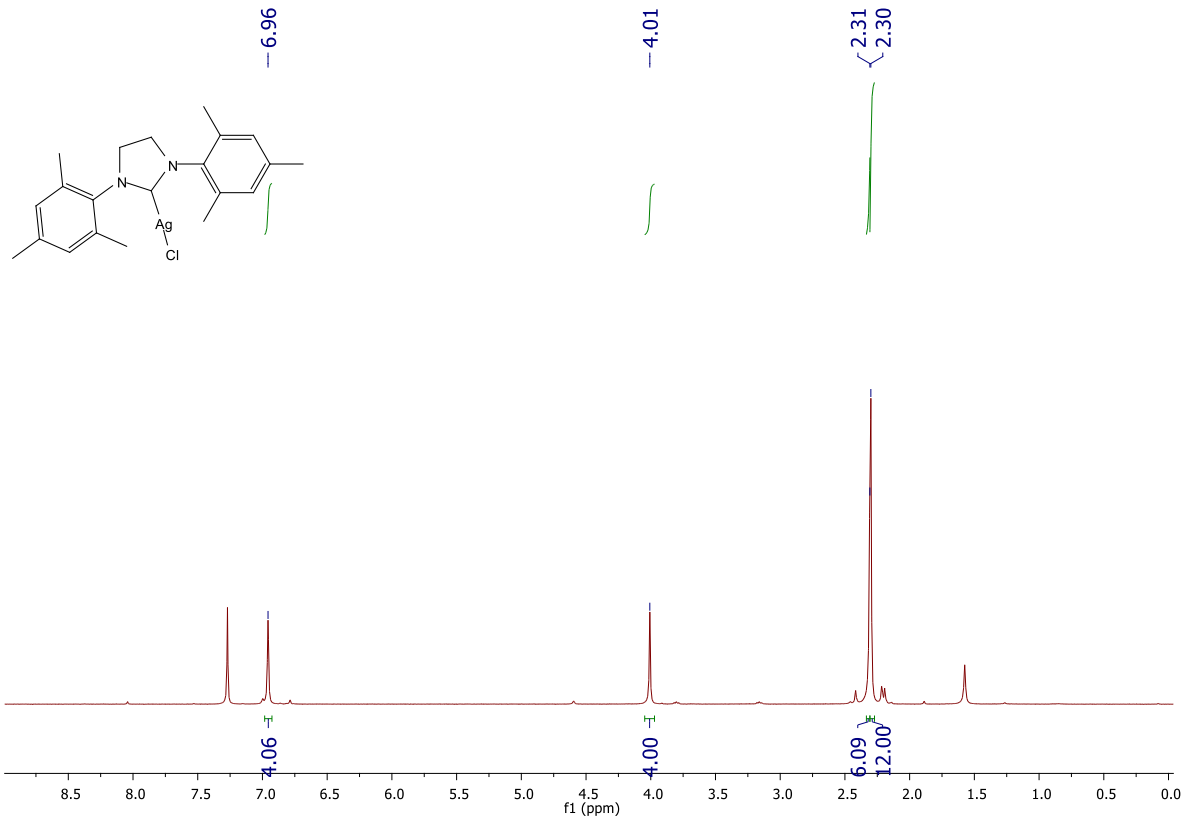


^{13}C NMR (101 MHz, $CDCl_3$)

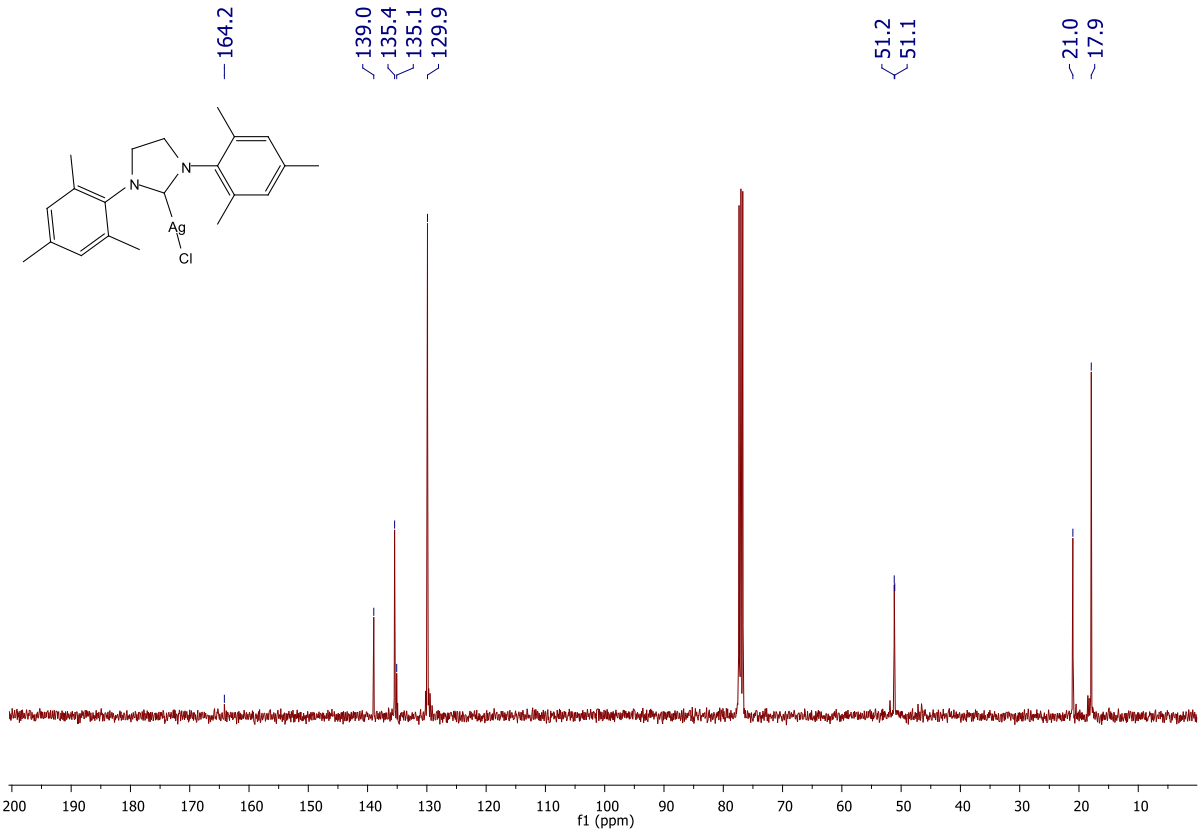


[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]silver chloride [AgCl(SIMes)]

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

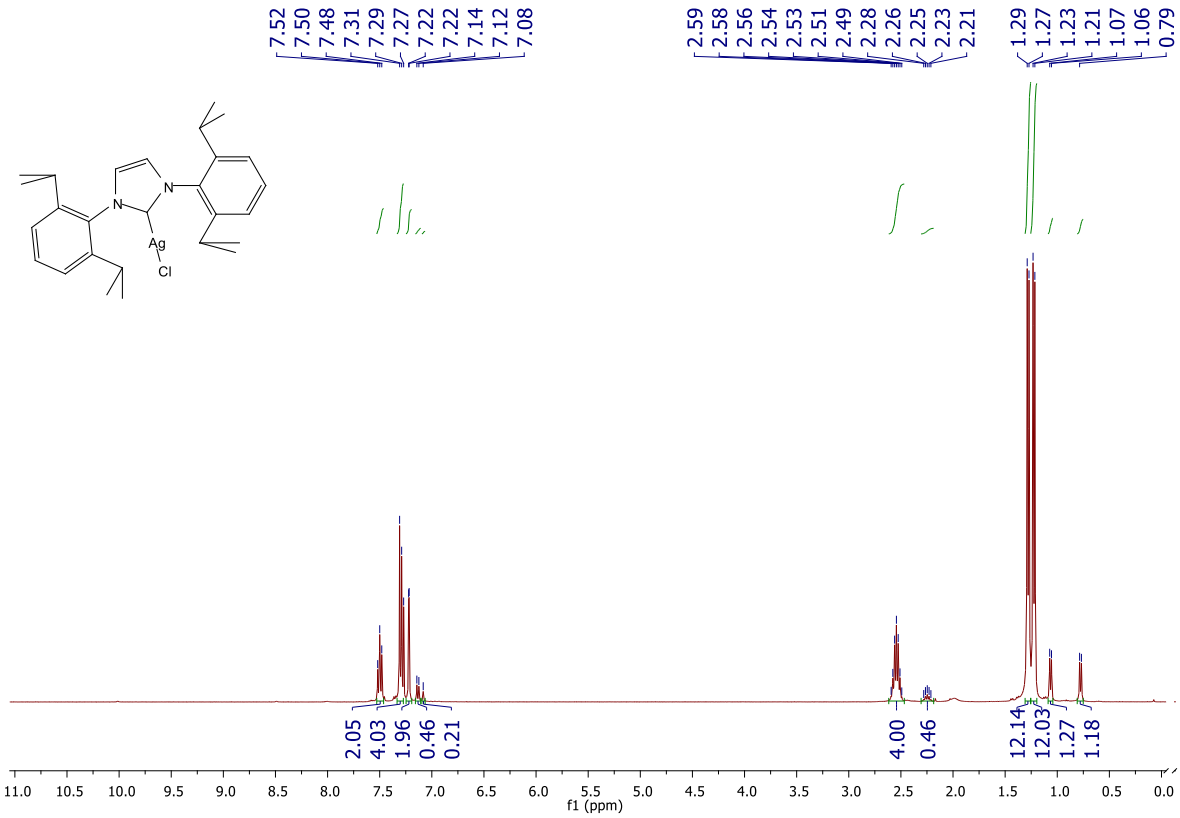


^{13}C NMR (101 MHz, DMSO-d_6)

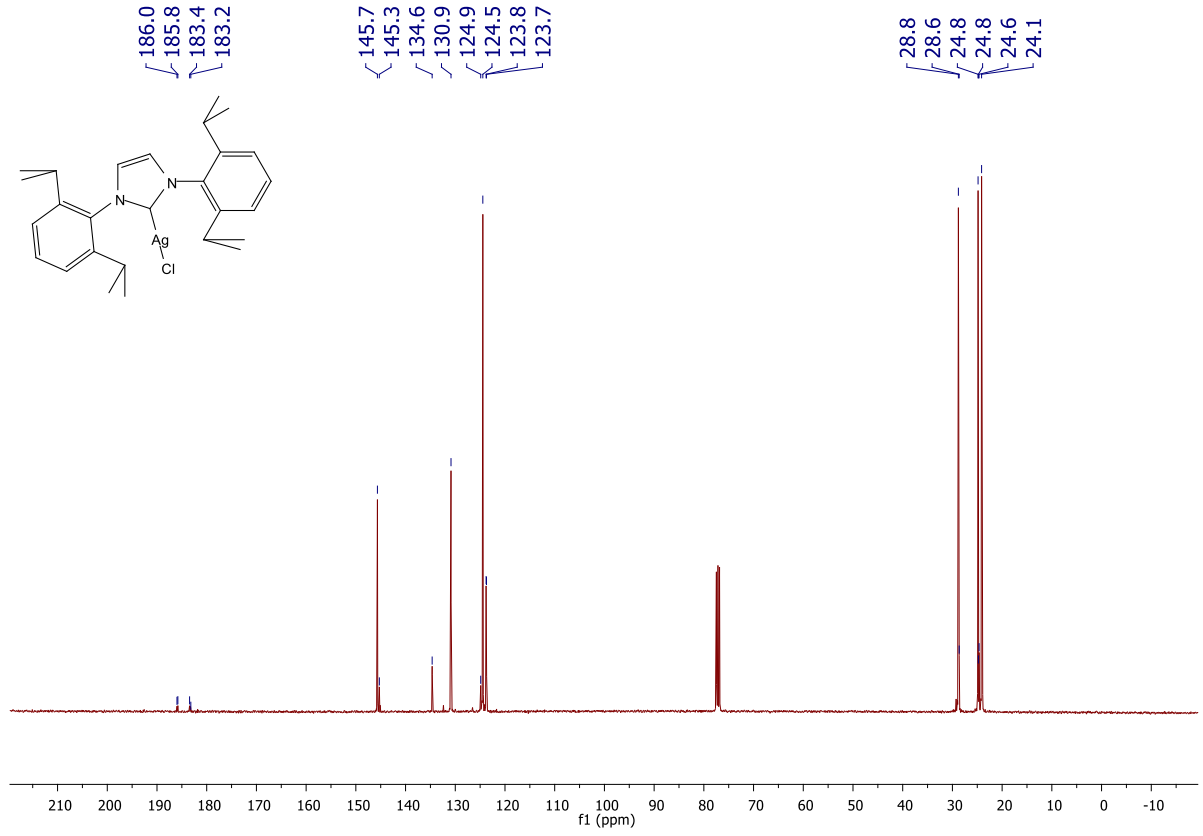


[1,3-Bis[2,6-di*iso*propylphenyl)]imidazol-2-ylidene]silver chloride [AgCl(IPr)]

^{1}H NMR (400MHz, $CDCl_3$): 5% of dimer

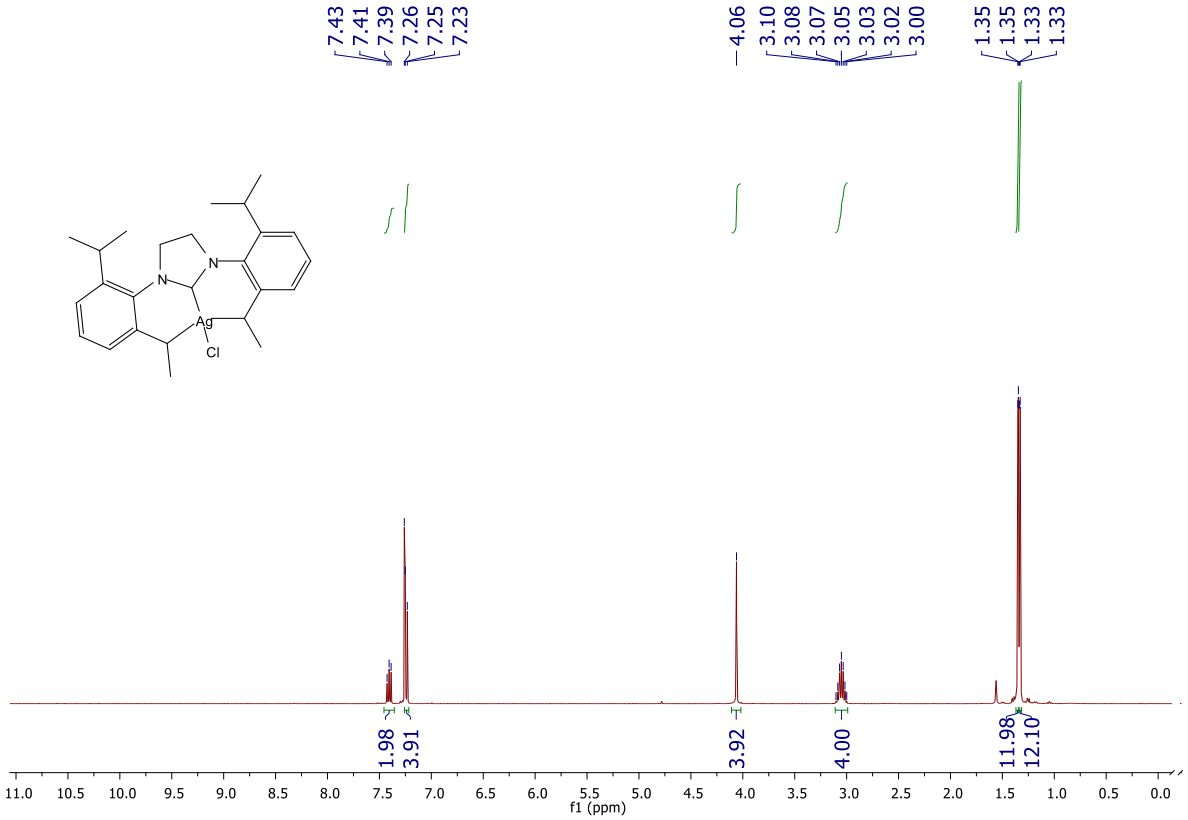


^{13}C NMR (101 MHz, $CDCl_3$

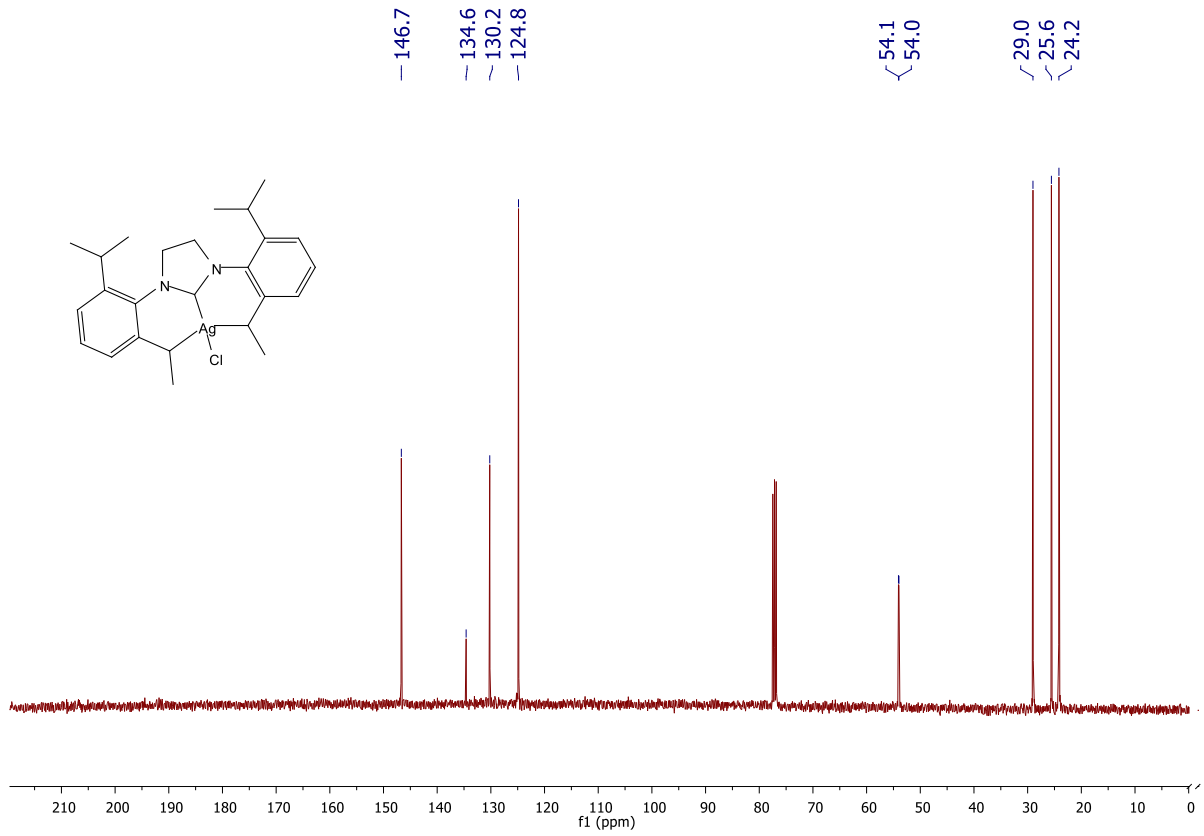


[1,3-Bis[2,6-(di*iso*propylphenyl)]imidazolidin-2-ylidene]silver chloride [AgCl(SIPr)]

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

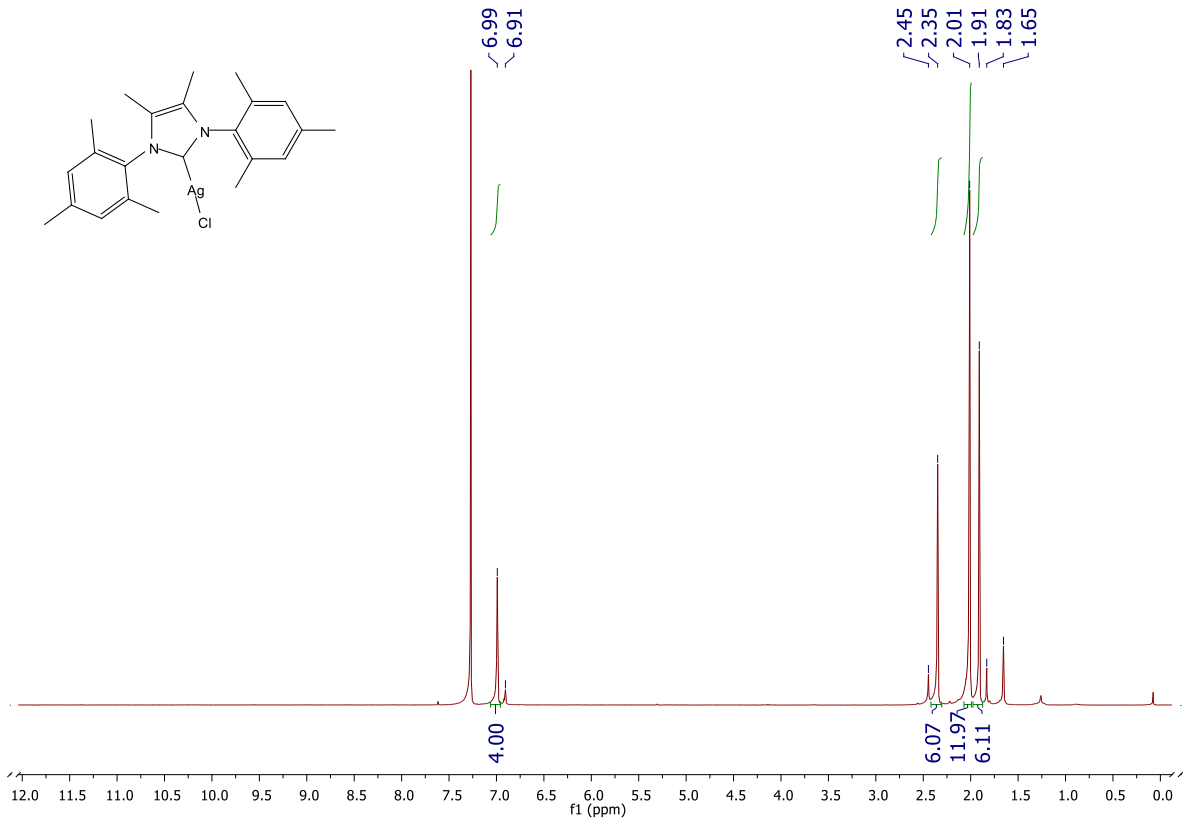


^{13}C NMR (101 MHz, $CDCl_3$)

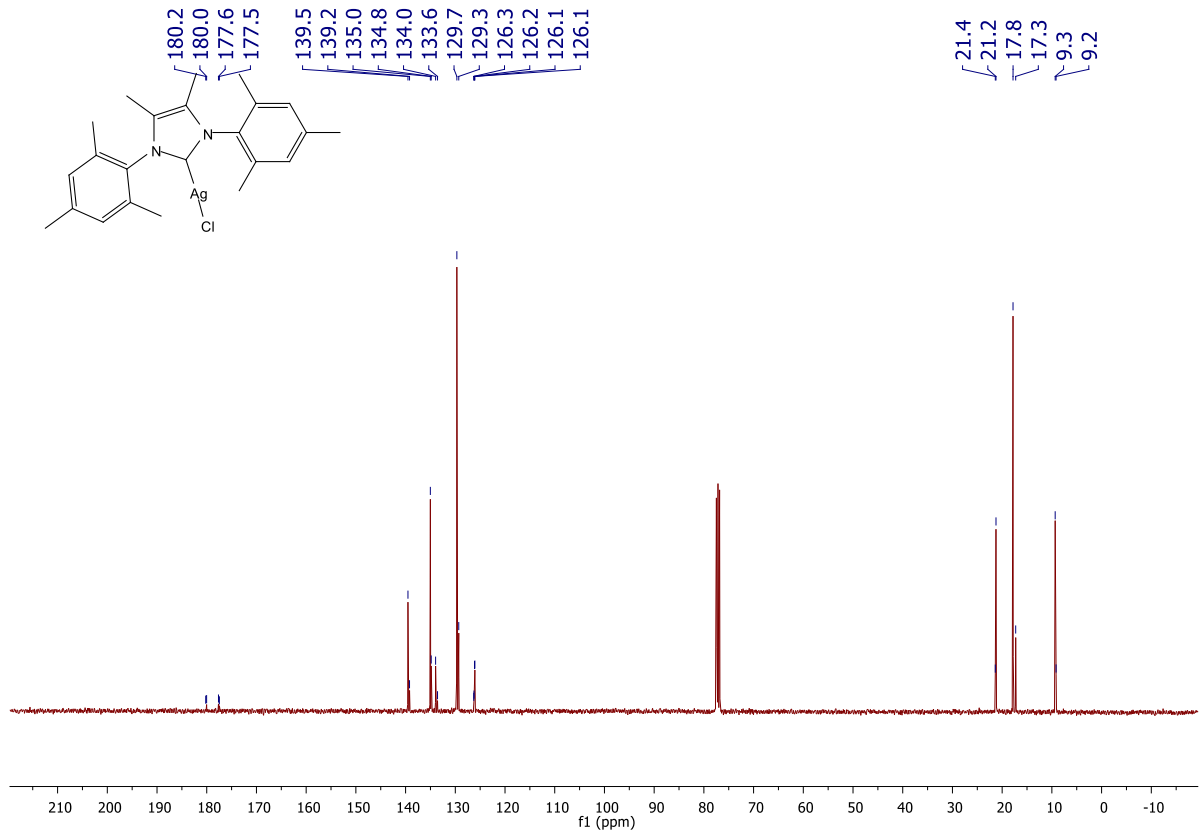


[(1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl)imidazol-2-ylidene]silver chloride [AgCl(IMes^{Me})]

^{1}H NMR (300MHz, $CDCl_3$): 10% of dimer

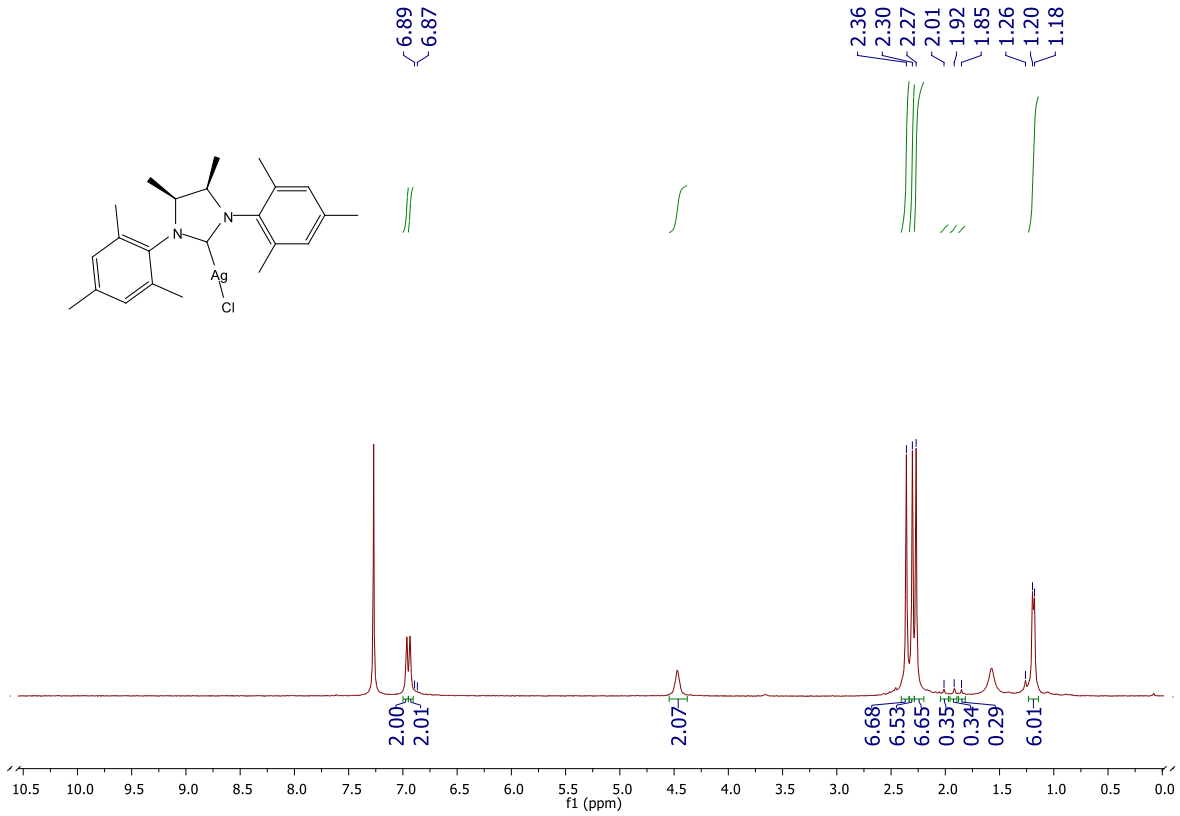


^{13}C NMR (101 MHz, DMSO-d_6)

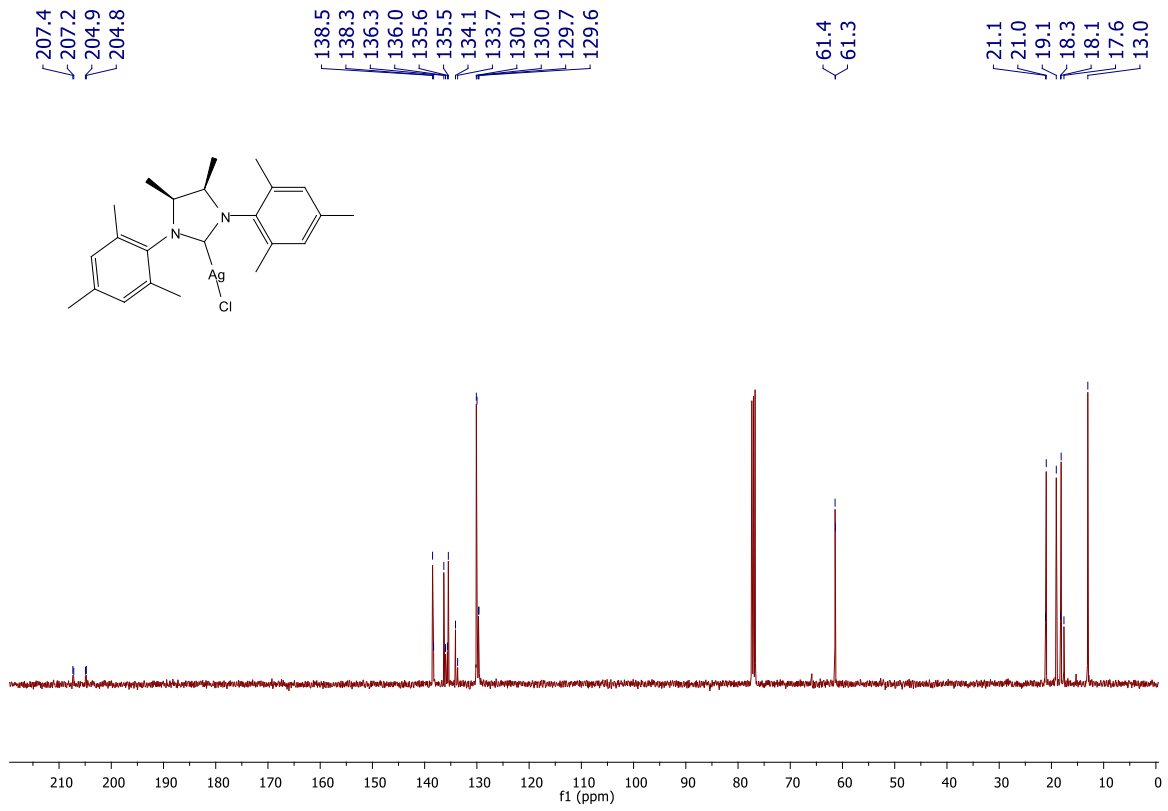


[(1,3-Bis-(2,4,6-trimethylphenyl)-4,5-*cis*-dimethyl)imidazolidin-2-ylidene]silver chloride [AgCl(SIMes$^{Me\text{-}cis}$)]

^{1}H NMR (400MHz, $CDCl_3$): 2% of dimer

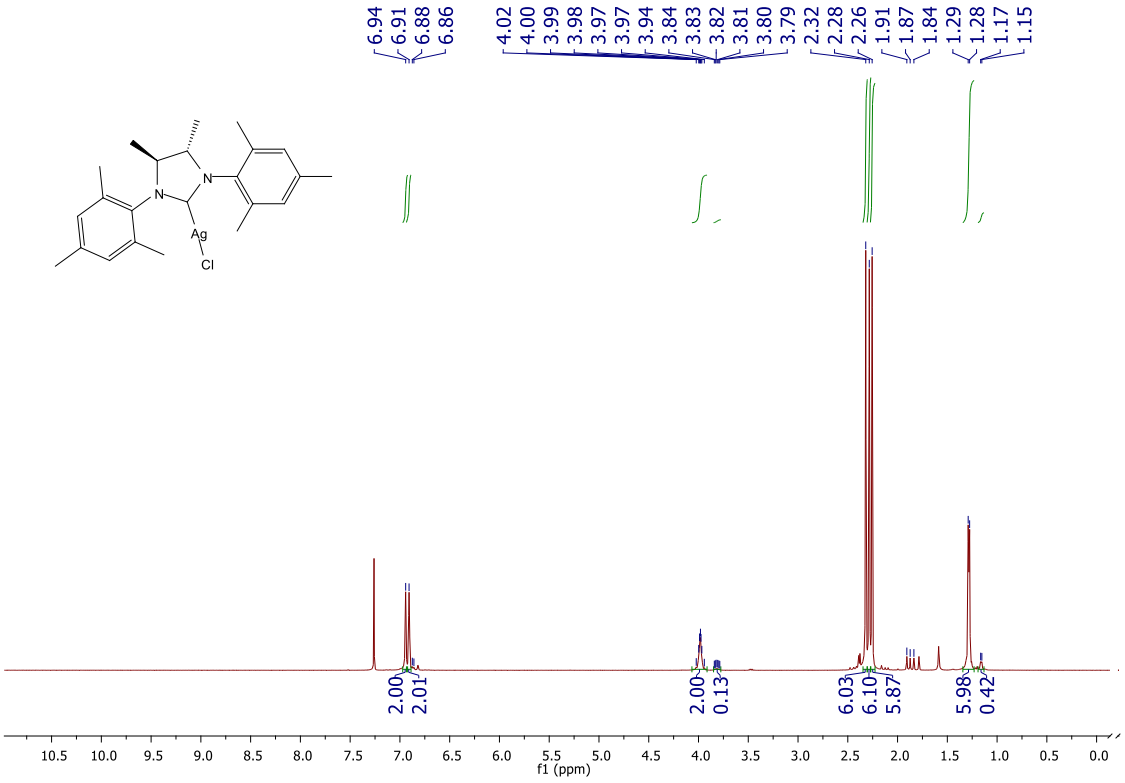


^{13}C NMR (101 MHz, $CDCl_3$)

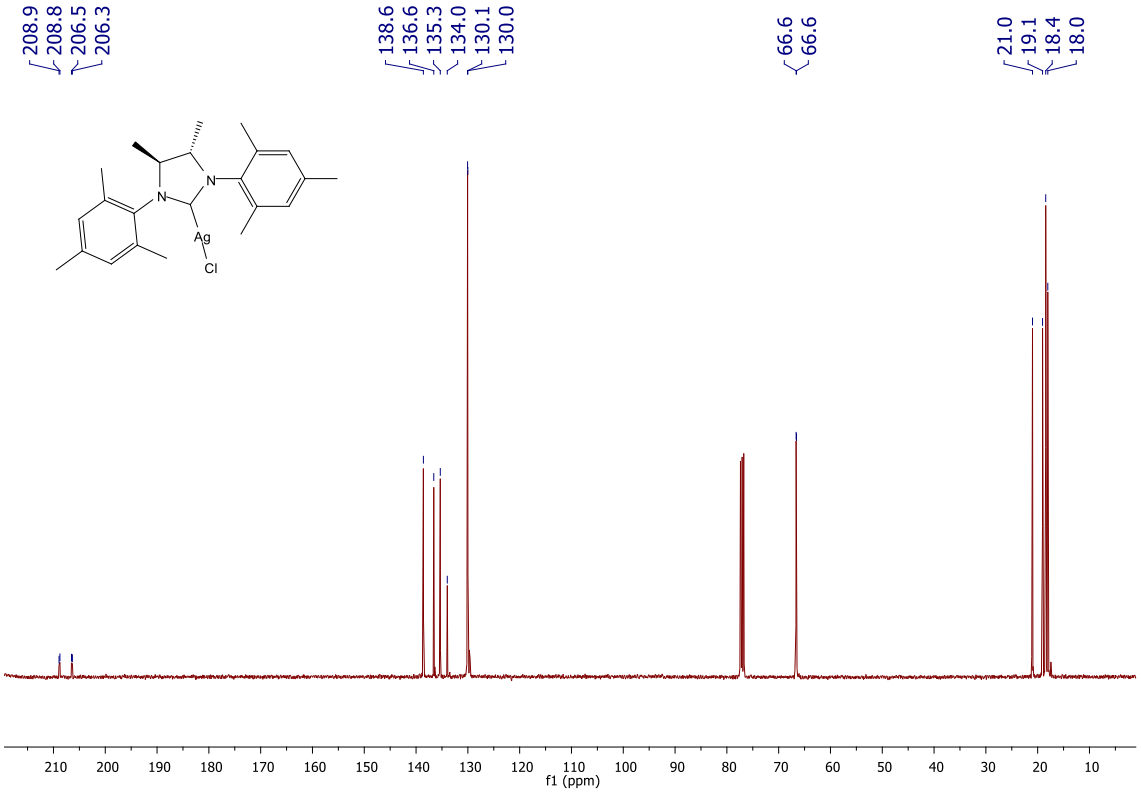


[(1,3-Bis-(2,4,6-trimethylphenyl)-4,5-*trans*-dimethyl)imidazolidin-2-ylidene]silver chloride [AgCl(SIMes$^{Me\text{-}trans}$)]

^{1}H NMR (400MHz, $CDCl_3$): 3% of dimer

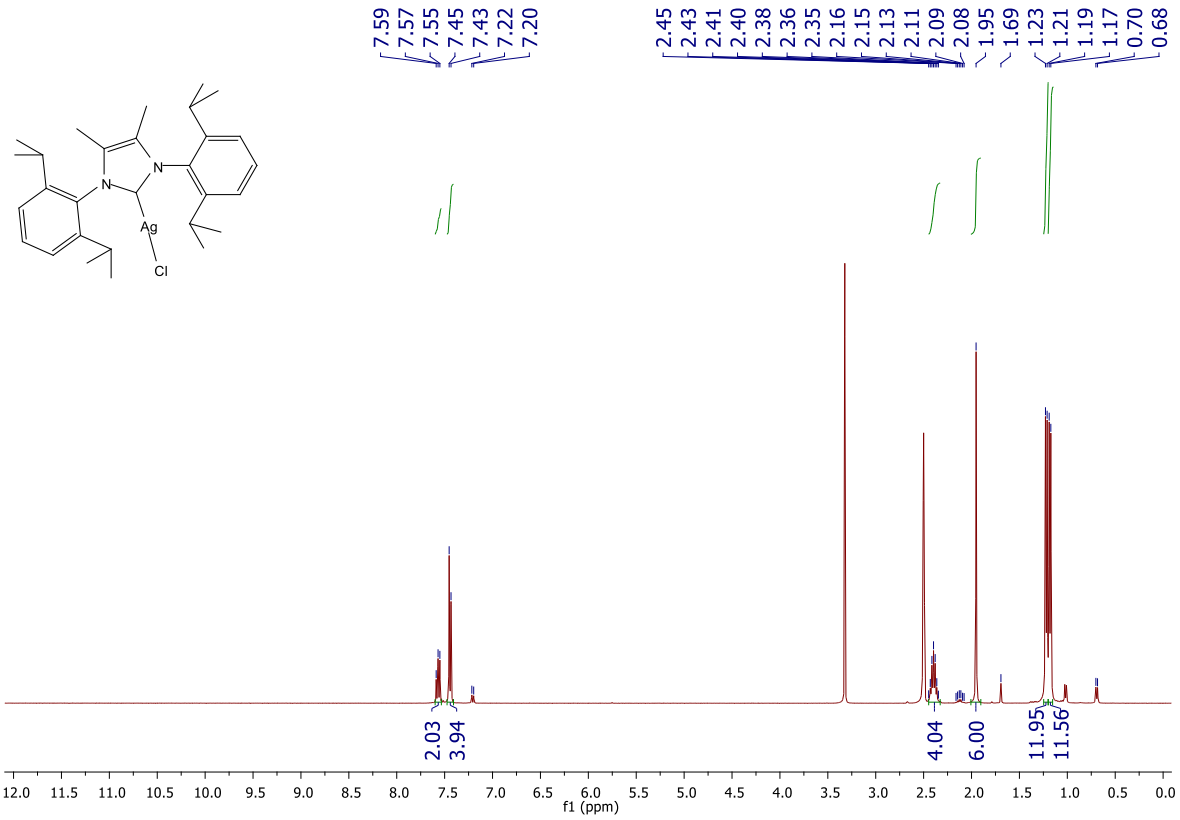


^{13}C NMR (101 MHz, $CDCl_3$)

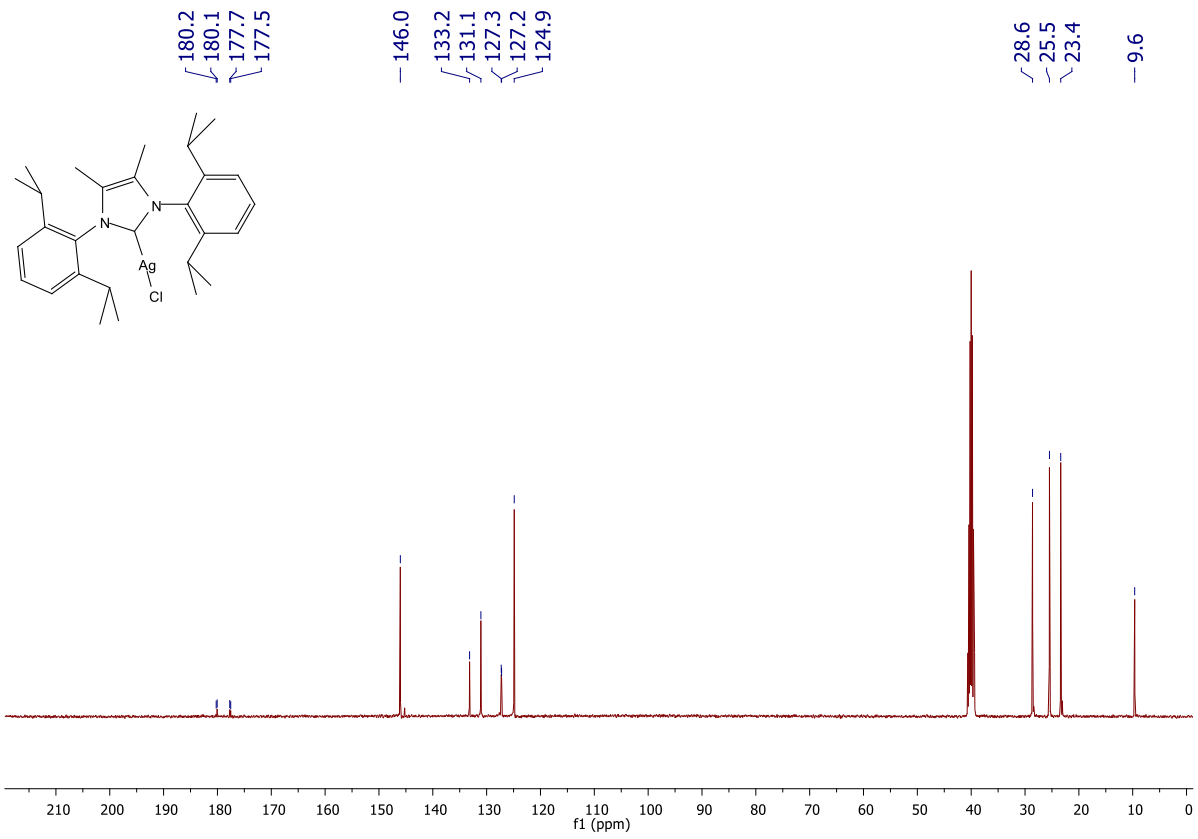


[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]silver chloride [AgCl(IPr^{Me})]

^{1}H NMR (400MHz, DMSO-d_6): 3% of dimer

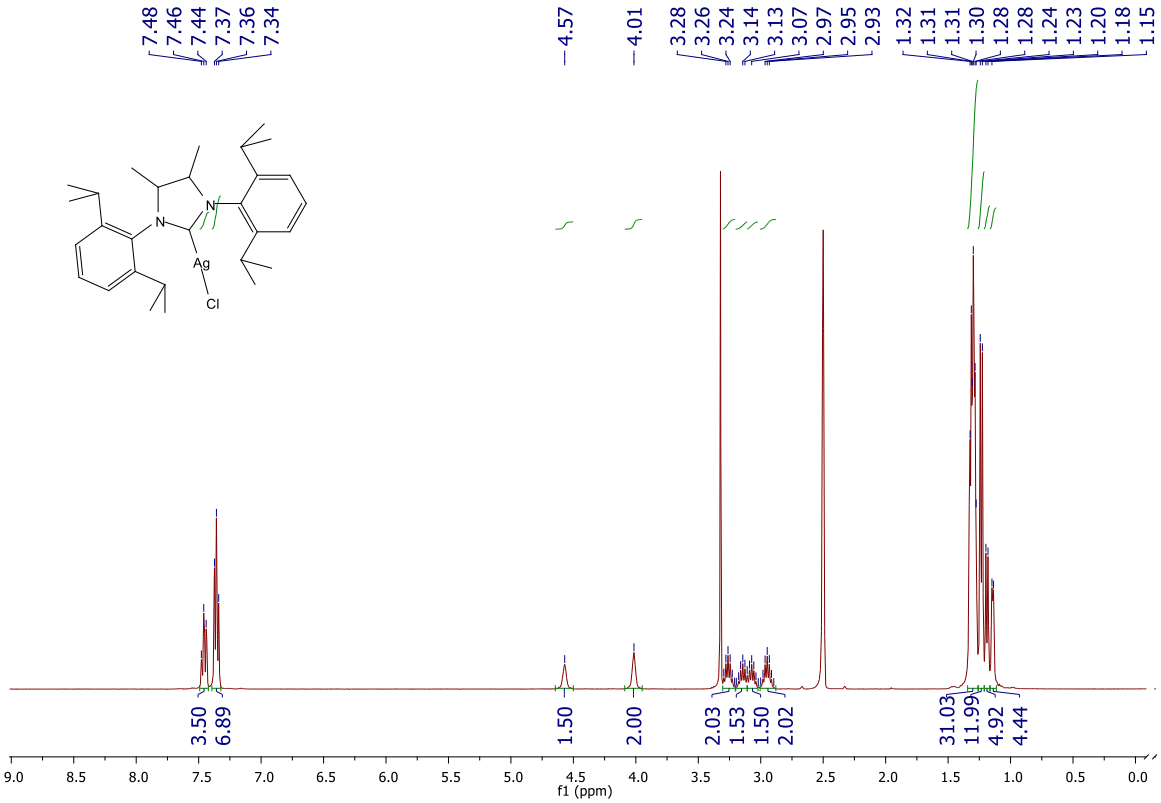


^{13}C NMR (101 MHz, DMSO-d_6)

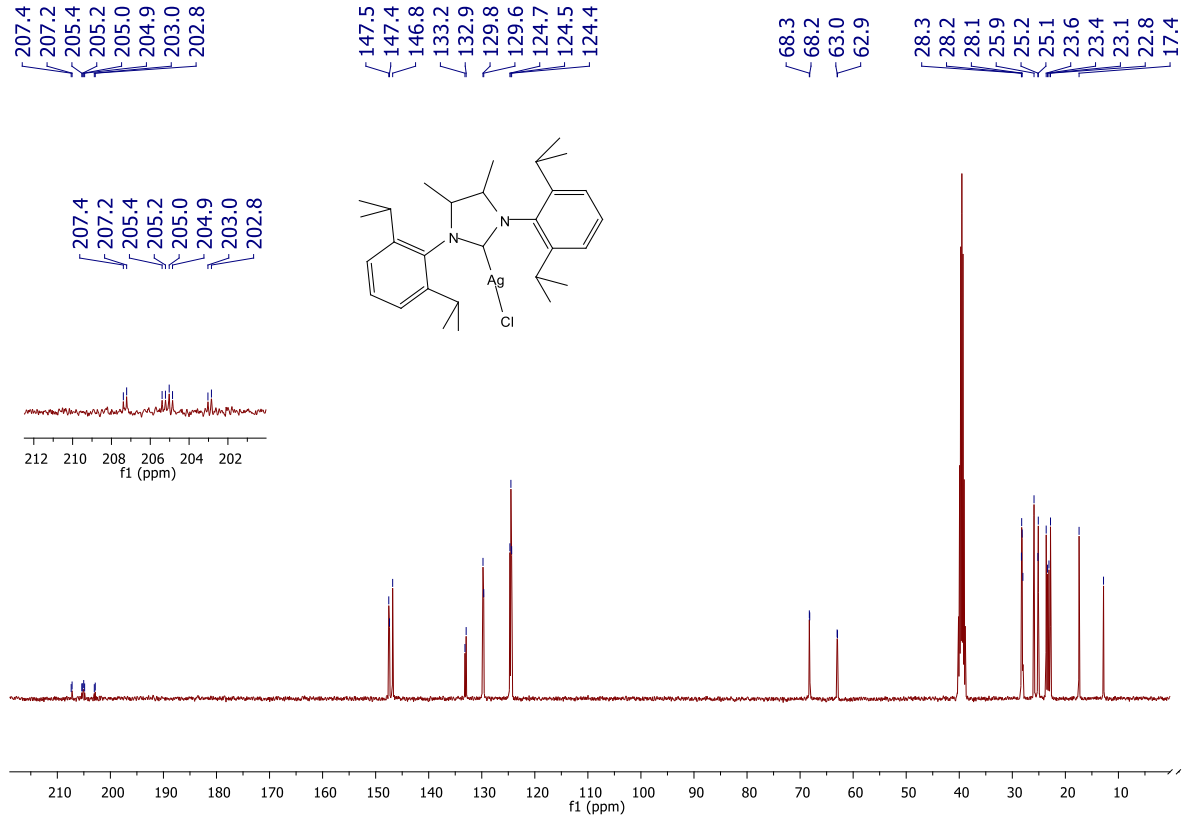


[(1,3-Bis[2,6-di*iso*propylphenyl]-4,5-dimethyl)imidazolidin-2-ylidene]silver chloride [AgCl(SIPr^{Me})] racemic

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

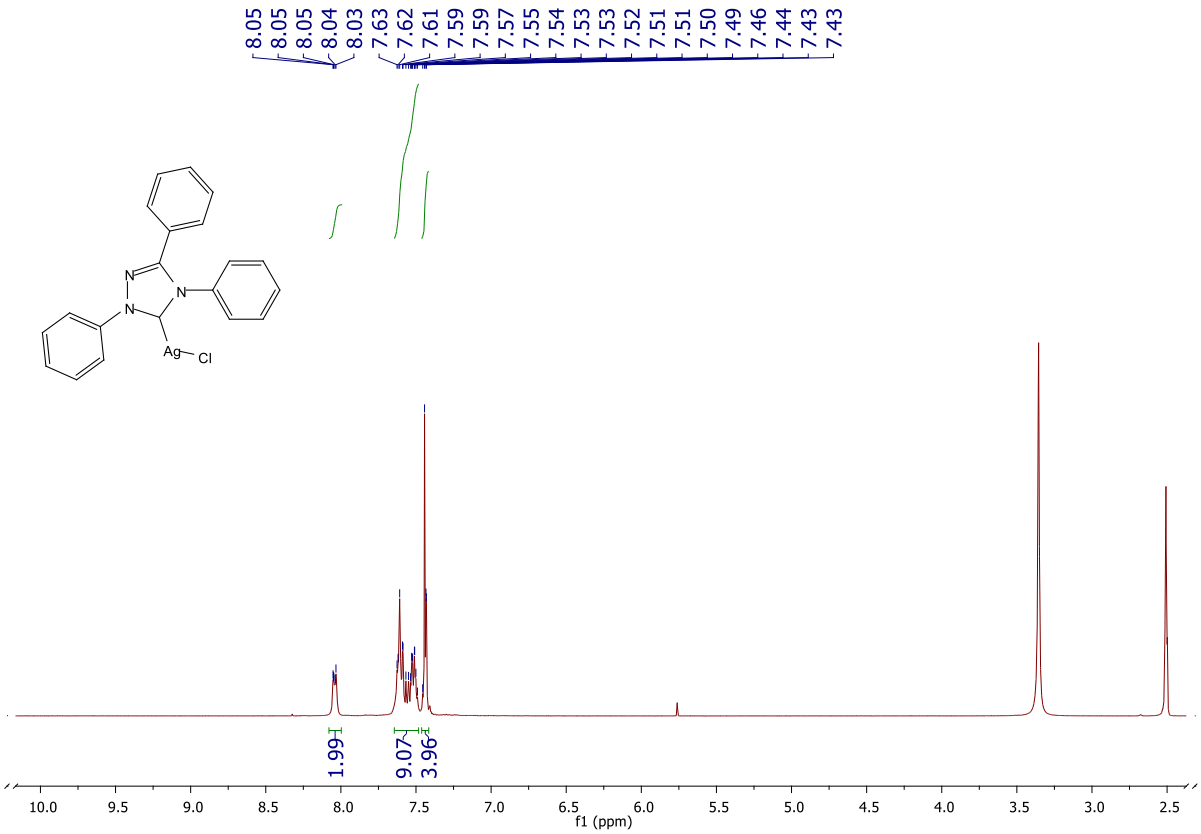


^{13}C NMR (101 MHz, DMSO-d_6)

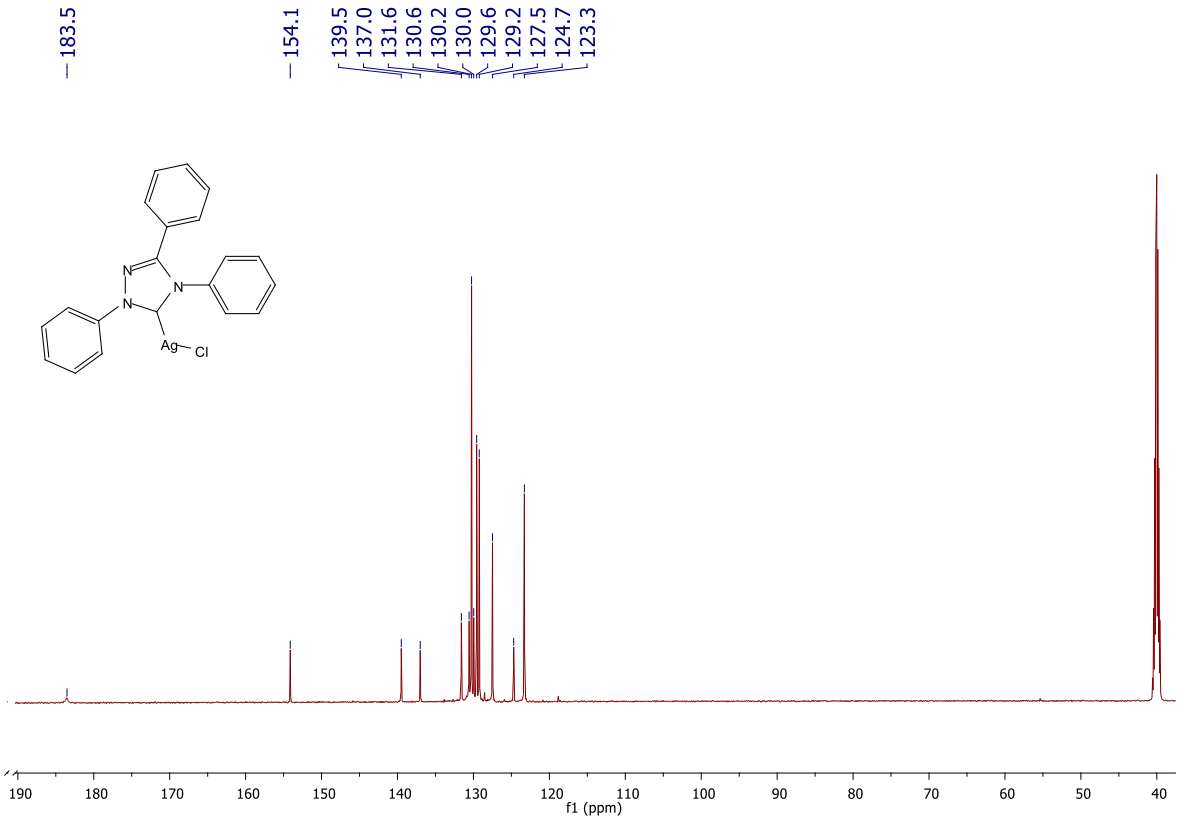


[1,3,4-Triphenyl-1,2,4-triazol-2-ylidene]silver chloride [AgCl(TPT)]

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



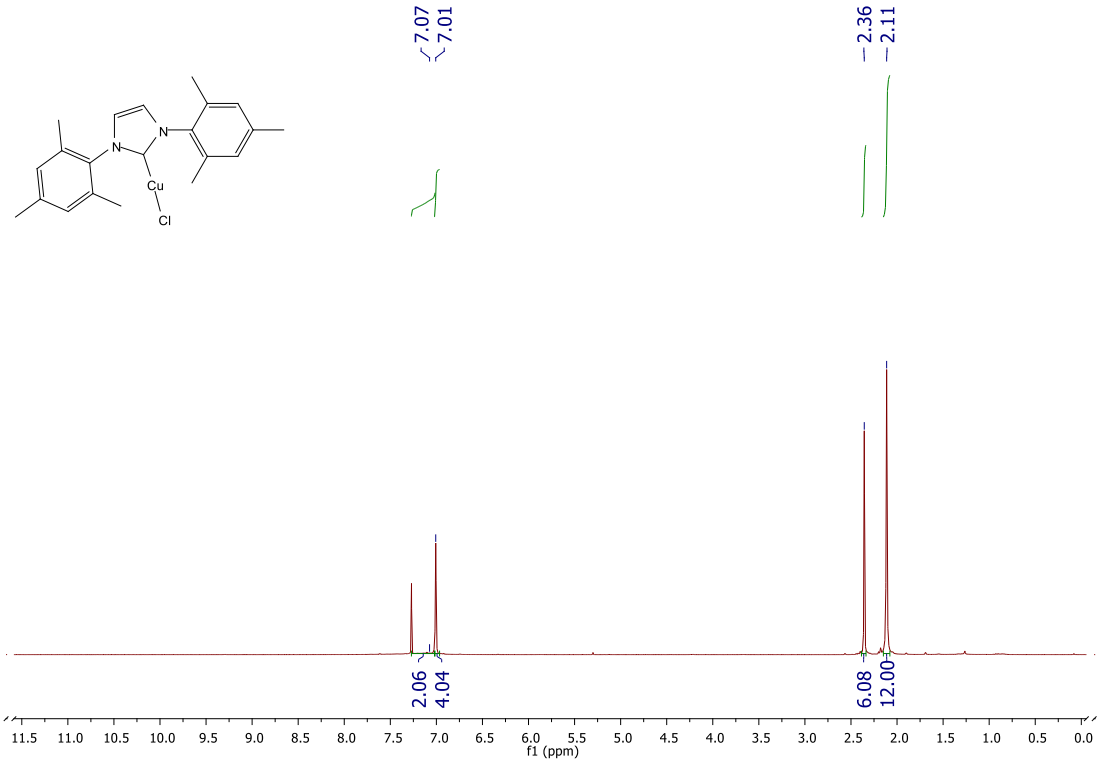
^{13}C NMR (101 MHz, $CDCl_3$)



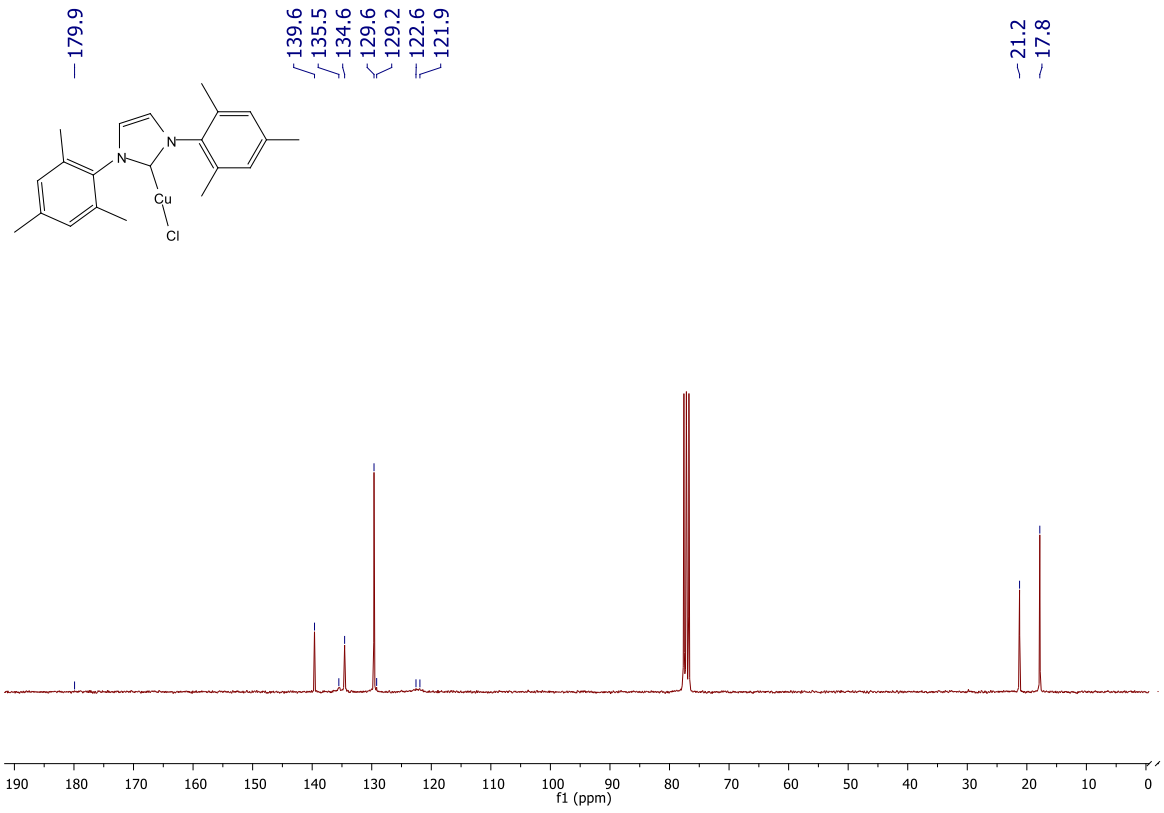
2.3 NHC-Copper complex

[1,3-Bismesitylimidazol-2-ylidene]copper chloride[CuCl(IMes)]

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



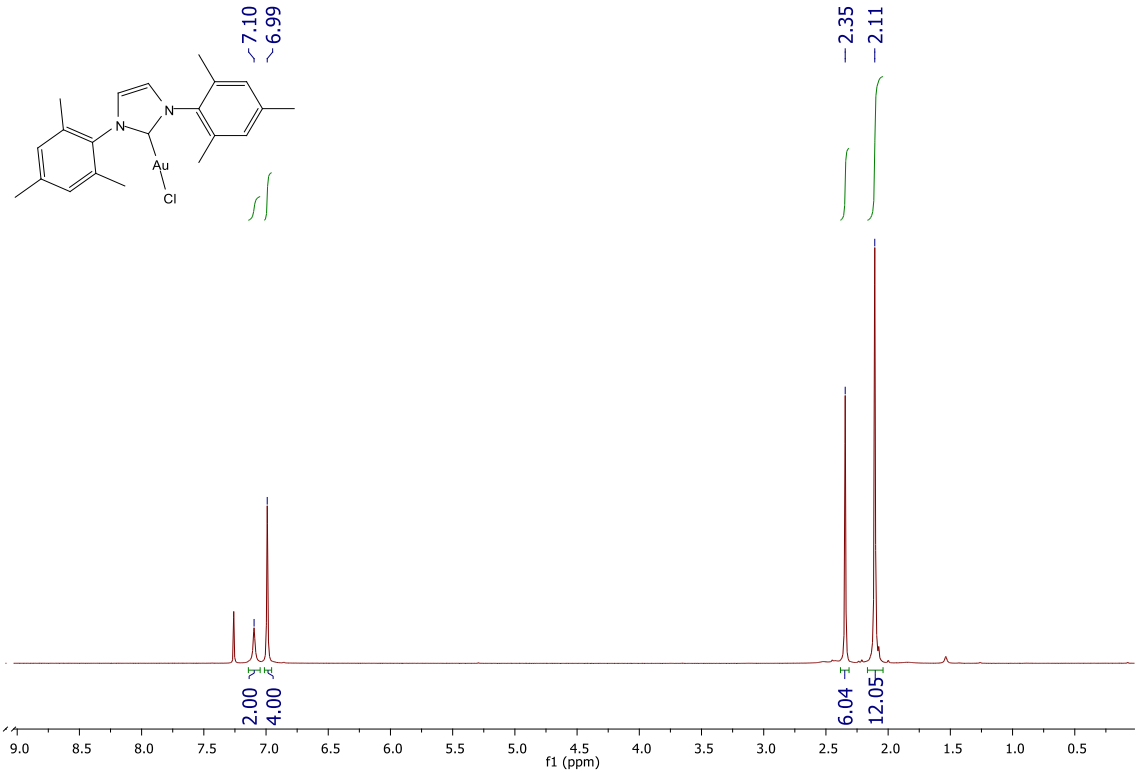
^{13}C NMR (75 MHz, $CDCl_3$)



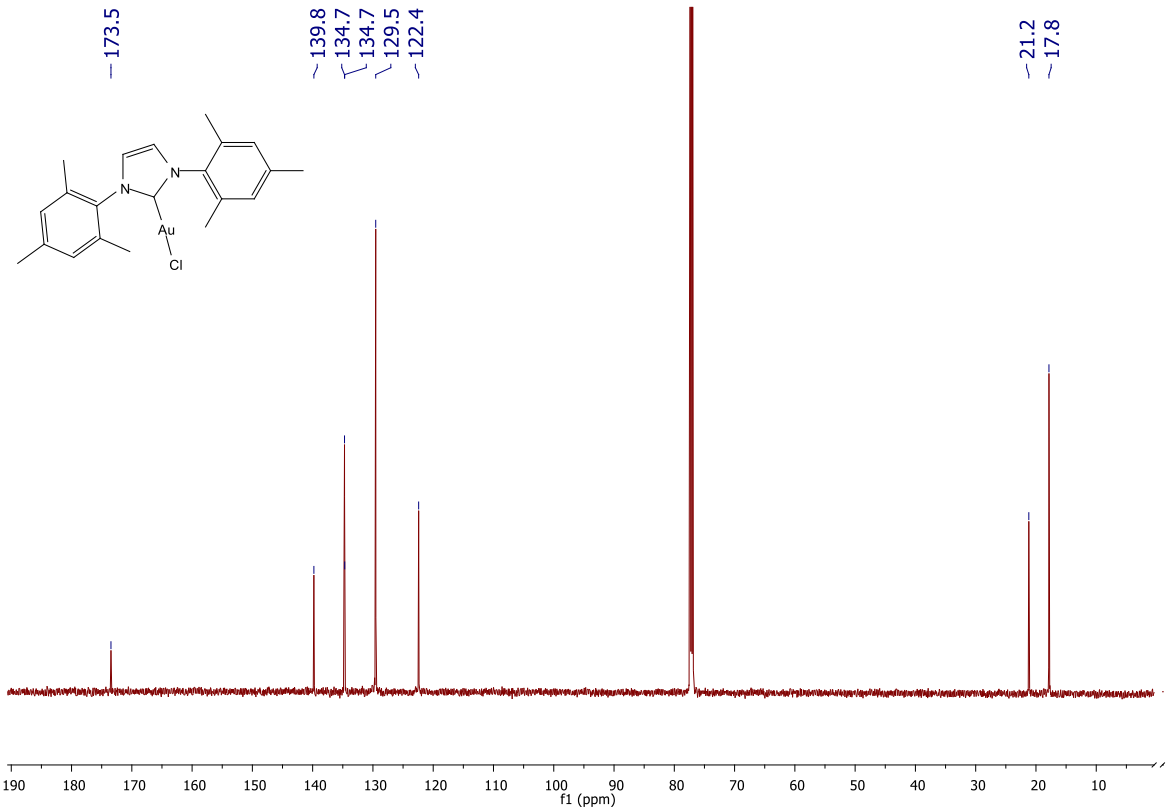
2.4 NHC-Gold complex

[1,3-Bismesitylimidazol-2-ylidene]gold chloride [AuCl(IMes)]

^{1}H NMR (600MHz, $CDCl_3$)



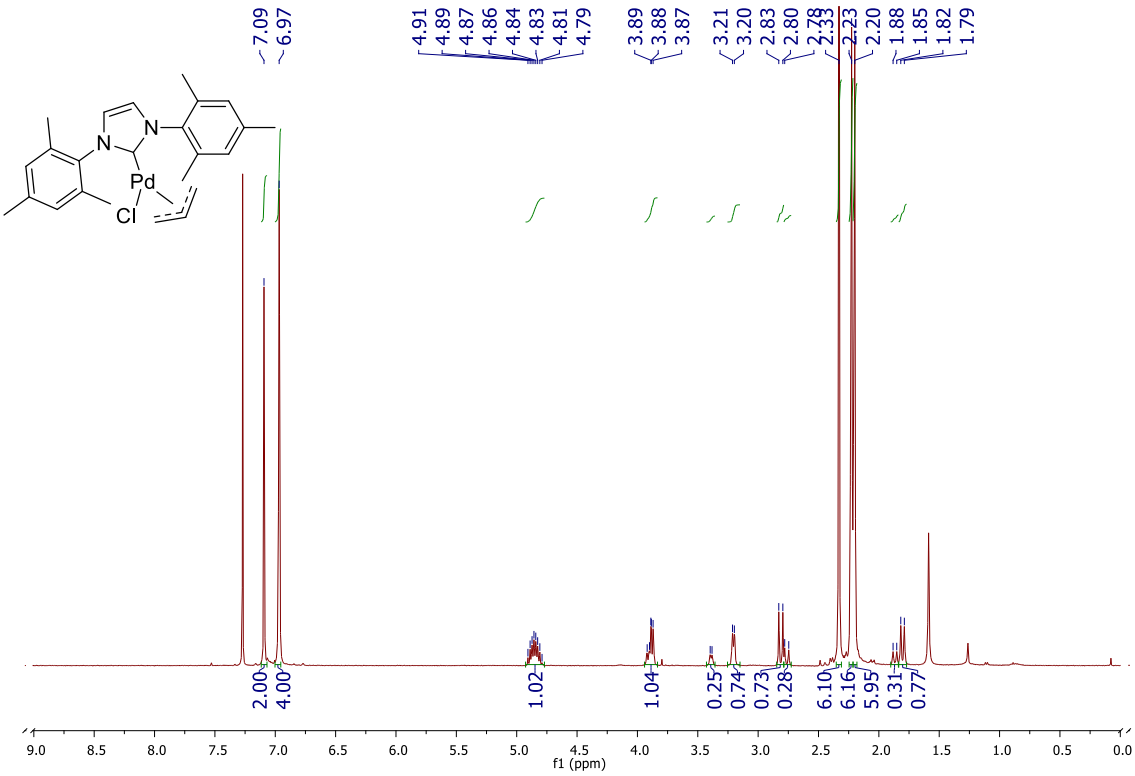
^{13}C NMR (151 MHz, $CDCl_3$)



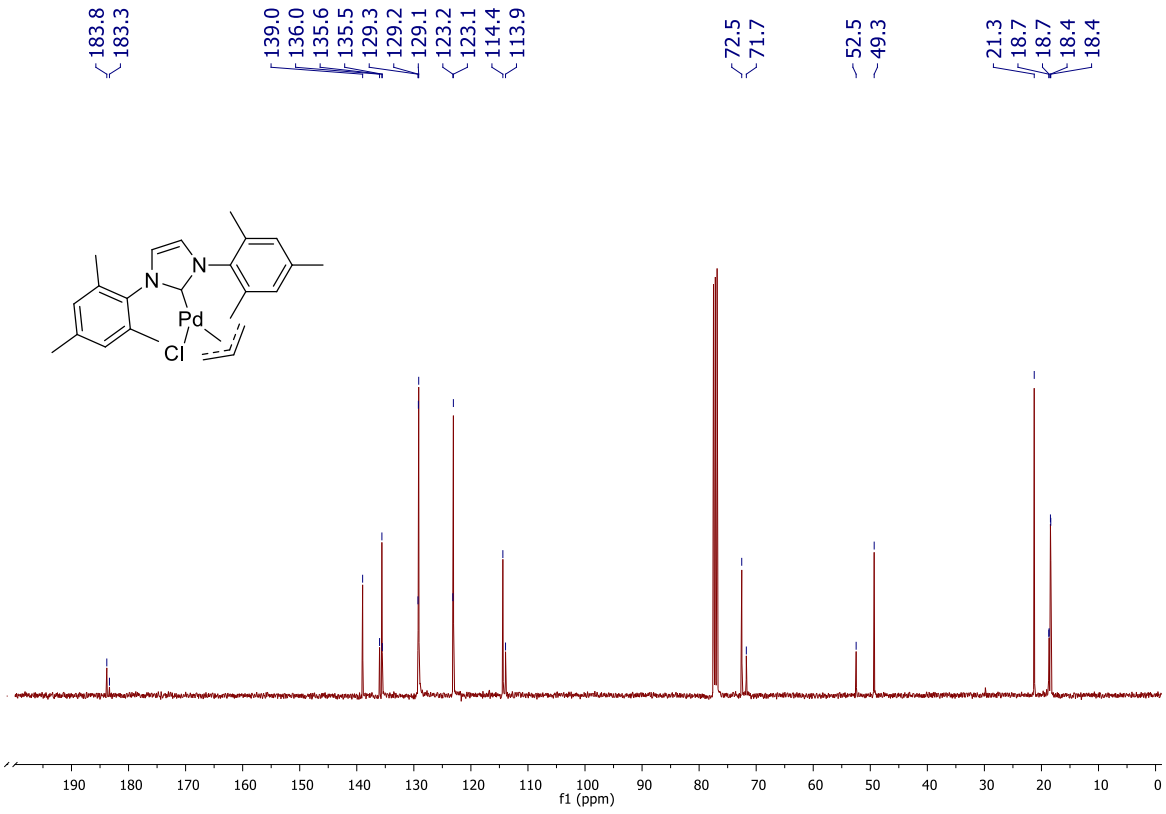
2.5 NHC-Palladium complex

[1,3-Bismesitylimidazol-2-ylidene](η³-2-propen-1-yl)palladium chloride [PdCl(η³-allyl)(IMes)]

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



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



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