Supporting information

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1. Synthetic procedures

1.1 General remarks

The milling treatments were carried out either in a planetary ball-mill Fritsch pulverisette 7 operated at 500 rpm. Milling load is defined as the sum of the mass of the reactants per free volume in the jar. All of the reactions using planetary ball-mill were made under air.

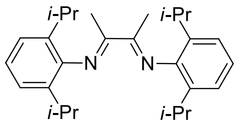
Analyses were performed at the 'Plateforme Technologique Laboratoire de Mesures Physiques' (IBMM, Université de Montpellier). ^{1}H NMR spectra were recorded on a Bruker Avance III HD 400 MHz or 500 MHz spectrometer and are reported in ppm using deuterated solvent for calibration ($CDCl_3$ at 7.26 ppm 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 a Bruker Avance III HD 101 MHz or 126 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). High resolution LC-UV-MS analyses were performed on UPLC Acquity H-Class from Waters with Kinetex C18 100 Å 2.1 x 2.6 mm column from Phenomenex hyphenated to a Synapt G2-S mass spectrometer with a dual ESI source from Waters.

1.2 Solution synthesis of the diimine precursors

General procedure A

Aniline (2.00 eq) was dissolved in methanol and a solution of 40% glyoxal in water (1.00 eq) or 2,3-butanedione (1.00 eq) and two or three drops of formic acid were added. The solution was stirred at room temperature for 24 h. The suspension was filtrated, washed with a minimum of methanol and dried under vacuum to afford the product.

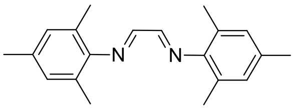
***N*,*N*'-Bis-(2,6-di*iso*propylphenyl)butane-2,3-diimine**



General procedure A was followed with 2,6-di*iso*propylaniline (15.0 g, 84.6 mmol, 2.00 eq), 2,3-butanedione (3.7 mL, 42.3 mmol, 1.00 eq) and methanol (42 mL) to afford *N*,*N*'-bis-(2,6-di*iso*propylphenyl)butane-2,3-diimine (11.2 g, 27.6 mmol, 65%) as a yellow powder.

^{1}H NMR (400 MHz, THF-d_8) δ 7.14 (d, *J* = 7.7 Hz, 4H), 7.03 (t, *J* = 7.7 Hz, 2H), 2.74 (sept, *J* = 6.9 Hz, 4H), 2.06 (s, 6H), 1.20 (d, *J* = 6.9 Hz, 12H), 1.15 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR (101 MHz, THF-d_8)** δ 168.8, 147.1, 135.4, 124.4, 123.5, 123.4, 29.2, 23.2, 22.7, 16.4. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[1]

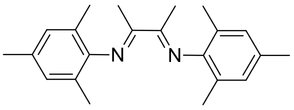
***N*,*N*'-Dimesitylethanediimine**



General procedure A was followed with 2,4,6-trimethylaniline (10.40 mL, 74.0 mmol, 2.00 eq), 40% glyoxal in water (4.23 mL, 37.0 mmol, 1.00 eq) and methanol (40 mL) to afford *N*,*N*'-dimesitylethanediimine (8.48 g, 29.0 mmol, 78%) as a yellow powder.

^{1}H NMR (400 MHz, THF-d_8) δ 8.07 (s, 2H), 6.87 (s, 4H), 2.24 (s, 6H), 2.11 (s, 12H); ^{13}C NMR (101 MHz, **THF-d_8**) δ 164.3, 148.6, 134.3, 129.4, 126.8, 20.7, 18.1. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[2]

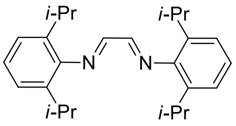
N,N'-Dimesityl-2,3-butanediimine



<u>General procedure A</u> was followed with 2,4,6-trimethylaniline (4.15 mL, 29.6 mmol, 2.00 eq), 2,3-butanedione (1.29 mL, 14.8 mmol, 1.00 eq) and methanol (29.6 mL) to afford *N,N'*-dimesityl-2,3-butanediimine (3.20 g, 10.0 mmol, 68%) as a yellow powder.

^{1}H NMR (400 MHz, THF-d_8) δ 6.85 (s, 4H), 2.24 (s, 6H), 1.99 (s, 6H), 1.96 (s, 12H); **^{13}C NMR (101 MHz, THF-d_8)** δ 168.7, 147.0, 132.6, 129.1, 124.8, 20.6, 17.7, 15.5. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[3]

N,N'-Bis(2,6-di*iso*propylphenyl)ethane-1,2-diimine



<u>General procedure A</u> was followed with 2,6-di*iso*propylaniline (3.00 g, 16.90 mmol, 2.00 eq), 40% glyoxal in water (975 µL, 8.45 mmol, 1.00 eq) and methanol (16.3 mL) to afford *N,N*'-bis(2,6-di*iso*propylphenyl)ethane-1,2-diimine (2.04 g, 5.42 mmol, 64%) as a yellow powder.

^{1}H NMR (400 MHz, THF-d_8) δ 8.11 (s, 2H), 7.16 (d, *J* = 7.2 Hz, 4H), 7.08 (t, *J* = 7.2 Hz, 2H), 2.96 (sept, *J* = 6.9 Hz, 4H), 1.19 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR (101 MHz, THF-d_8)** δ 164.2, 149.3, 137.0, 125.5, 123.6, 28.7, 23.4. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[2]

1.3 <u>Mechanosynthesis of the imidazolium salts</u>

General procedure B

Corresponding bisimine (1.00 eq) and a solution of paraformaldehyde (1.00 eq) in 4M hydrochloric acid in dioxane (1.00 eq) were introduced in a 20 mL zirconium oxide grinding bowl with eighty zirconium oxide balls (0.5 cm diameter). The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 3 hours at 500 rpm. Ethyl acetate was added and the resulting suspension was filtrated. The solid was washed two or three times with ethyl acetate and then dried under vacuum to afford the product.

General procedure C

Aniline (2.00 eq) and 2,3-butanedione (1.00 eq) were introduced in a 20 mL zirconium oxide grinding bowl with eighty zirconium oxide balls (0.5 cm diameter). The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 2 hours at 500 rpm. Then a solution of paraformaldehyde in 4M hydrochloric acid in dioxane (1.00 eq) was introduced. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 3 hours at 500 rpm. Ethyl acetate was added and the resulting suspension was filtrated. The solid was washed two or three times with ethyl acetate and then dried under vacuum to afford the product.

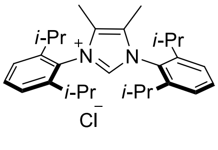
General procedure D

Aniline (2.00 eq), 40% glyoxal in water (1.00 eq) and few drops of formic acid were introduced in a 20 mL zirconium oxide grinding bowl with eighty zirconium oxide balls (0.5 cm diameter). The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 2 hours at 500 rpm. Then a solution of paraformaldehyde in 4M hydrochloric acid in dioxane (1.00 eq) was introduced. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 3 hours at 500 rpm. Products were recovered with two different procedures (see below).

Protocol 1: ethyl acetate was added and the resulting suspension was filtrated. The solid was washed two or three times with ethyl acetate and then dried under vacuum to afford the product.

Protocol 2: ethyl acetate and water were added. The aqueous layer was washed three times with ethyl acetate and concentrated under vacuum. The residue was dissolved in isopropanol, filtrated on celite and then concentrated under vacuum to afford the pure product.

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

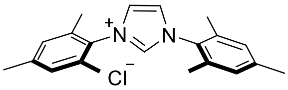


<u>Procedure in ball-mill starting from bisimine:</u>
<u>General procedure B</u> was followed with paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq), 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) and *N*,*N*'-bis-(2,6-di*iso*propylphenyl)butane-2,3-diimine (260.2 mg, 0.643 mmol, 1.00 eq) to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride **IPr^{Me}·HCl** (160.5 mg, 0.354 mmol, 55%) as a white powder.

<u>Procedure in ball-mill starting from aniline:</u>
<u>General procedure C</u> was followed with 2,6-di*iso*propylaniline (243 µL, 1.286 mmol, 2.00 eq), 2,3-butanedione (56 µL, 0.643 mmol, 1.00 eq), paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) and 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq). Protocol 1 was followed to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride **IPr^{Me}·HCl** (142.9 mg, 0.315 mmol, 49%) as a white powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) 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* = 6.7 Hz, 4H), 2.06 (s, 6H), 1.25 (d, *J* = 6.7 Hz, 12H), 1.11 (d, *J* = 6.7 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. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[4]

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



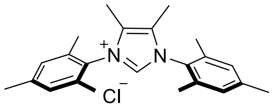
<u>Procedure in ball-mill starting from bisimine:</u>
<u>General procedure B</u> was followed with paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq), 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) and *N*,*N*'-dimesitylethanediimine (188 mg, 0.643 mmol, 1.00 eq) to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride **IMes·HCl** (184.1 mg, 0.540 mmol, 84%) as a white powder.

<u>Procedure in ball-mill starting from aniline:</u>
<u>General procedure D</u> was followed with 2,4,6-trimethylaniline (181 µL, 1.286 mmol, 2.00 eq), 40% glyoxal in water (73 µL, 0.643 mmol, 1.00 eq), paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) and

4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride **IMes·HCl** (190.0 mg, 0.558 mmol, 87%) as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.95 (s, 1H), 7.60 (s, 2H), 7.04 (s, 4H), 2.35 (s, 6H), 2.19 (s, 12H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.5, 140.1, 134.2, 130.8, 130.1, 124.4, 21.3, 17.8.

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



Procedure in ball-mill starting from bisimine:

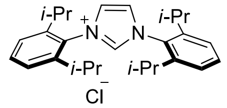
General procedure B was followed with paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq), 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) and *N,N'*-dimesityl-2,3-butanediimine (206.1 mg, 0.643 mmol, 1.00 eq) to afford [1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride **IMes^{Me}·HCl** (142.3 mg, 0.386 mmol, 60%) as a white powder.

Procedure in ball-mill starting from aniline:

General procedure C was followed with 2,4,6-trimethylaniline (181 µL, 1.286 mmol, 2.00 eq), 2,3-butanedione (56 µL, 0.643 mmol, 1.00 eq), paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) and 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) to afford [1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride **IMes^{Me}·HCl** (156.0 mg, 0.423 mmol, 66%) as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.56 (d, *J* = 0.7 Hz, 1H), 7.05 (s, 4H), 2.35 (s, 6H), 2.12 (s, 12H), 2.07 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.4, 137.8, 134.7, 130.1, 128.9, 127.5, 21.3, 17.7, 8.7.

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



Procedure in ball-mill starting from bisimine:

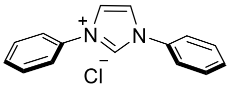
General procedure B was followed with paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq), 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) and *N*,*N*'-bis(2,6-di*iso*propylphenyl)ethane-1,2-diimine (242.1 mg, 0.643 mmol, 1.00 eq) to afford 1,3-bis-(2,6-di*iso*propylphenyl)imidazolium chloride **IPr·HCl** (268.0 mg, 0.630 mmol, 98%) as a white powder.

Procedure in ball-mill starting from aniline:

General procedure D was followed with 2,6-di*iso*propylaniline (243 µL, 1.286 mmol, 2.00 eq), 40% glyoxal in water (73 µL, 0.643 mmol, 1.00 eq), paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) and 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq). Protocol 1 was followed to afford 1,3-bis-(2,6-di*iso*propylphenyl)imidazolium chloride **IPr·HCl** (273.0 mg, 0.642 mmol, 100%) as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.14 (s, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 4H), 2.45 (sept, *J* = 6.8 Hz, 4H), 1.29 (d, *J* = 6.8 Hz, 12H), 1.24 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.2, 138.7, 132.3, 130.0, 126.9, 124.9, 29.3, 24.9, 23.9.

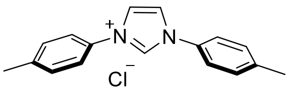
1,3-Bisphenylimidazolium chloride IPh·HCl



General procedure D was followed with aniline (117 µL, 1.286 mmol, 2.00 eq), 40% glyoxal in water (73 µL, 0.643 mmol, 1.00 eq), paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) and 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq). Protocol 1 was followed to afford 1,3-bisphenylimidazolium chloride **IPh·HCl** (148.2 mg, 0.578 mmol, 90%) as a brown powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 10.43 (s, 1H), 8.60 (d, *J* = 1.4 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 4H), 7.71 (t, *J* = 7.7 Hz, 4H), 7.66 – 7.60 (m, 2H); **^{13}C NMR (126 MHz, DMSO-*d$_6$*)** δ 134.7, 134.5, 130.1, 130.0, 129.6, 122.0, 121.9. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[5]

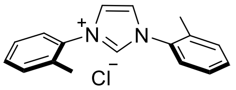
1,3-Bis(4-methylphenyl)imidazolium chloride I*p*-Tol·HCl



General procedure D was followed with *p*-toluidine (137.8 mg, 1.286 mmol, 2.00 eq), 40% glyoxal in water (73 µL, 0.643 mmol, 1.00 eq), paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) and 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) to afford 1,3-bis-(4-methylphenyl)imidazolium chloride **I*p*-Tol·HCl** (146.4 mg, 0.514, 80%) as a brown powder.

^{1}H NMR (500 MHz, CDCl$_3$) δ 11.71 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 4H), 7.74 (s, 2H), 7.40 (d, *J* = 8.0 Hz, 4H), 2.42 (s, 6H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.1, 135.5, 132.1, 131.2, 122.0, 121.0, 21.3.

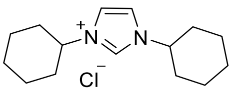
1,3-Bis-(2-methylphenyl)imidazolium chloride I*o*-Tol·HCl



General procedure D was followed with *o*-toluidine (137.8 µL, 1.286 mmol, 2.00 eq), 40% glyoxal in water (73 µL, 0.643 mmol, 1.00 eq), paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) and 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq). Protocol 1 was followed to afford 1,3-bis-(2-methylphenyl)imidazolium chloride **I*o*-Tol·HCl** (174.0 mg, 0.611 mmol, 95%) as a brown powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 9.87 (t, *J* = 1.5 Hz, 1H), 8.34 (d, *J* = 1.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.55 (m, 4H), 7.53 – 7.49 (m, 2H), 2.33 (s, 6H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 137.7, 134.1, 133.4, 131.6, 130.8, 127.3, 126.7, 124.1, 17.0.

1,3-Biscyclohexylimidazolium chloride ICy·HCl



General procedure D was followed with cyclohexylamine (148.1 µL, 1.286 mmol, 2.00 eq), 40% glyoxal in water (73 µL, 0.643 mmol, 1.00 eq), paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) and 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq). Protocol 2 was followed to afford 1,3-biscyclohexylimidazolium chloride **ICy·HCl** (138.5 mg, 0.515 mmol, 80%) as a brown powder.

^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 10.69 (s, 1H), 7.43 (d, *J* = 1.0 Hz, 2H), 4.48 (tt, *J* = 11.9, 3.8 Hz, 2H), 2.17 (d, *J* = 10.7 Hz, 4H), 1.88 (d, *J* = 13.7 Hz, 4H), 1.81 – 1.65 (m, 6H), 1.45 (qt, *J* = 13.0, 3.4 Hz, 4H), 1.25 (qt, *J* = 13.0, 3.4 Hz, 2H); **^{13}C NMR (101 MHz, DMSO-*d$_6$*)** δ 136.2, 120.0, 60.2, 33.8, 25.4, 25.1.

2. Calculation of green metrics

Different parameters can be used to evaluate the environmental impact of the different synthetic pathways. This part details the calculation of the E Factor (EF)[6] and Ecoscale score.[7]

2.1 Synthetic methods

Following methods were used for the calculation of the E Factor, and the Ecoscale score.

Synthesis of IMes·HCl

Procedure in the ball-mill
2,4,6-Trimethylaniline (181 µL, 1.286 mmol, 2.00 eq), 40% glyoxal in water (73 µL, 0.643 mmol, 1.00 eq) and few drops of formic acid were introduced in a 20 mL zirconium oxide grinding bowl with eighty zirconium oxide balls (0.5 cm diameter). Total mass of reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 2 hours at 500 rpm. Then a solution of paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) in 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) was introduced. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 3 hours at 500 rpm. Ethyl acetate was added and the resulting suspension was filtrated. The solid was washed two or three times with ethyl acetate and then dried under vacuum to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride **IMes·HCl** (190.0 mg, 0.558 mmol, 87%)as a white powder.

Procedure in solution
Literature procedure, described below,[2] was taken directly to calculate the mass of reagents:

2,4,6-Trimethylaniline (10.4 mL, 74.0 mmol, 2.00 eq) was dissolved in methanol (40 mL) and a solution of 40% glyoxal in water (4.23 mL, 37.0 mmol, 1.00 eq) and three drops of formic acid were added. The solution was warmed to room temperature and stirred during 3 hours. The suspension was filtrated, washed with a minimum of methanol and dried under vacuum to afford *N*,*N*'-dimesitylethanediimine (8.48 g, 29.0 mmol, 78%) as a yellow powder.

Paraformaldehyde (118.7 mg, 3.95 mmol, 1.40 eq) was suspended in a solution of 4M hydrochloric acid in dioxane (1.4 mL, 5.53 mmol, 1.40 eq) and stirred until complete dissolution of the white solid. This solution was added slowly into a solution of *N*,*N*'-dimesitylethanediimine (7.90 g, 27.0 mmol, 1.00 eq) in THF (8 mL). The resulting solution was stirred at room temperature for 2 days. Then the suspension was cooled to room temperature and the white precipitate was collected by filtration and washed with THF to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride **IMes·HCl** (1.01 g, 2.37 mmol, 75%) as a white powder.

Literature procedure
According to *Tetrahedron* **1999,** *55*, 14523: "*Preparation of Glyoxal-bis-(2,4,6-trimethylphenyl)imine 1a. To a solution of 67.61 g (0.5 mol) of 2,4,6-trimethylphenylamine in 300 ml of n-propanol were added at 23 °C a mixture of 36.3 g of a 40% aqueous solution of glyoxal (corresponding to 0.25 mol of glyoxal), 100 ml of n-propanol and 50 ml of water. The mixture was stirred for 16 h at 23 °C and then for 4 h at 60 °C. Upon addition of 200 ml of water, a yellow solid precipitated which was collected by filtration and dried in vacuo. Yield: 116.2 g (80%)*".[8]

According to *Org. Lett.* **2017,** *19*, 2750: "*1,3-dimesityl-1H-imidazol-3-ium chloride (IMesCl, 4): To a solution of (1E,2E)-N^1,N^2- dimesitylethane-1,2-diimine S2 (8.60 g, 29.4 mmol) in EtOAc (127 mL) was added paraformaldehyde (0.93 g, 30.9 mmol) at 70 °C, and a solution of TMSCl (4.30 mL, 33.89 mmol) in EtOAc (20.0 mL) was added dropwise. After being stirred at 70 °C for 2 h, the resulting suspension was cold -20 ºC, filtered and washed with cold EtOAc, Et_2O gave the title compound 4 (8.62 g, 86% yield) as a yellow powder*".[9]

Synthesis of IPr·HCl

Procedure in the ball-mill

2,6-Di*iso*propylaniline (243 µL, 1.286 mmol, 2.00 eq), 40% glyoxal in water (73 µL, 0.643 mmol, 1.00 eq) and few drops of formic acid were introduced in a 20 mL zirconium oxide grinding bowl with eighty zirconium oxide balls (0.5 cm diameter). Total mass of reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 2 hours at 500 rpm. Then a solution of paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) in 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) was introduced. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 3 hours at 500 rpm. Ethyl acetate was added and the resulting suspension was filtrated. The solid was washed two or three times with ethyl acetate and then dried under vacuum to afford 1,3-bis-(2,6-di*iso*propylphenyl)imidazolium chloride **IPr·HCl** (273.0 mg, 0.642 mmol, 100%) as a white powder.

Procedure in solution

Literature procedure, described below,[2] was taken directly to calculate the mass of reagents:

2,6-Di*iso*propylaniline (8.00 g, 45.1 mmol, 2.00 eq) was dissolved in methanol (23 mL) and a solution of 40% glyoxal in water (2.60 mL, 22.6 mmol, 1.00 eq) and two or three drops of formic acid were added. The solution was warmed to room temperature and stirred. The suspension was filtrated, washed with a minimum of methanol and dried under vacuum to afford *N*,*N*'-bis(2,6-di*iso*propylphenyl)ethane-1,2-diimine (5.90 g, 15.7 mmol, 69%) as a yellow powder.

Paraformaldehyde (119.5 mg, 3.98 mmol, 1.00 eq) was suspended in a 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 room temperature for two 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 **IPr·HCl** (988.1 mg, 2.32 mmol, 58%) as a white powder.

Literature procedure

According to *Nat. Protocols* **2011,** *6*, 69: "*Synthesis of diazabutadiene (3b)*
1| Weigh out 70.9 g (0.4 mol) of 2,6-diisopropylaniline in a 1 liter round-bottomed flask. 2| Add 200 ml of methanol (using a measuring cylinder) and stir the mixture for 5 min to dissolve aniline. 3| Transfer 58 ml (0.2 mol) of glyoxal (40% (wt/wt) aqueous solution) to the reaction mixture. 4| Add few drops of formic acid (with a Pasteur pipette). 5| Stir the reaction mixture at room temperature for 15 h. 6| Filter the yellow precipitate, wash it three times with methanol (i.e., 3 × 50 ml) and dry it under vacuum.

Synthesis of IMes-HCl (4ba). 7| In a three-necked flask, dissolve diazabutadiene (54 g, 0.184 mol) in 370 ml of ethyl acetate (0.5 M). 8| In a separate flask, weigh out 6.1 g (0.2 mol) of paraformaldehyde. Add a Teflon-coated stirring bar and transfer 69 ml (0.276 mol) of HCl (4 M in dioxane). 9| Stir the mixture until paraformaldehyde dissolves (~20 min) and gives a clear solution. 10| Transfer the solution of paraformadehyde to an addition funnel and connect the addition funnel to the three-necked flask. 11| Slowly add paraformaldehyde solution to the solution of diazabutadiene to maintain a gentle heating without reaching reflux of the solvent (1 h). 12| Stir the mixture overnight at room temperature. The reaction mixture turns from yellow to brown. A precipitate forms throughout the reaction. 13| Filter the precipitate and wash it three times with ethyl acetate (3 × 100 ml). Dry the product under vacuum (1.0×10^{-1} mbar for 16 h). 14| The product is an off-white solid".[2]

2.2 Calculation of E Factor

The E Factor is the ratio of the weight of generated waste to the total weight of the end product. It is a useful tool for rapid evaluation of processes based on generated waste.

$$\mathrm{EF} = \frac{\sum \mathrm{m(Raw\ materials)} + \sum \mathrm{m(solvent)} + \sum \mathrm{m(water)} - \mathrm{m(products)}}{\mathrm{m(products)}}$$

Due to the difficult measurement of solvent quantity in the work-up process and in particular in laboratory scale, their values will be omitted in the E Factor calculation.

Since both steps in solution are not on the same scale, the total mass of solvent and reagent of the second step was adjusted using the ratio of their scale.

E factor values are reported in the following table for the synthesis of **IMes·HCl** and **IPr·HCl** in the ball-mill and magnetic stirrer conditions.

Compounds	Stirring	Σm(Raw materials)	Σm(solvents)	Σm(water)	m(product)	EF
IMes·HCl	BM	0.254	0.166	0.056	0.19	**1.5**
	MS	15.151	110.14	3.23	7.38	**16.4**
	MS[a]	143.5	1871.3	54.5	117.3	**16.6**[8-9]
IPr·HCl	BM	0.308	0.166	0.056	0.273	**0.9**
	MS	11.142	177.372	1.965	3.845	**48.6**
	MS[a]	98.37	559.8	17.41	114.8	**4.9**[10]

BM = Ball-mill; MS = Magnetic stirring; [a] Conditions from lit.

2.3 Calculation of Ecoscale score

According to Van Aken *et al.*: "*The Ecoscale tool uses a scale from 0 to 100 with 0 representing a totally failed reaction (0% yield) and 100 representing the ideal reaction which is defined as follows: Compound **A** (substrate) undergoes a reaction with (or in the presence of) inexpensive compound(s) **B** to give the desired compound **C** in 100% yield at room temperature with a minimal risk for the operator and a minimal impact on the environment.*

Six general parameters which influence the quality of reaction conditions are analyzed. Within each of these parameters, individual penalty points of various relative weights are assigned that take into *account all possible situations when setting up an organic chemistry experiment. The penalty points are cumulative for all components of the preparation. In order to simplify the EcoScale design, the usual differentiation between solvents, reagents, auxiliary or co-reagents and catalysts is not made.*

Ecoscale can be summarizing by this simple equation: EcoScale = 100 - sum of individual penalties."[7]

Below, Ecoscale score tables for the synthesis of **IMes·HCl** and **IPr·HCl** using magnetic stirrer or ball-mill are displayed.

Ranking of reaction conditions is defined as follow: On a scale from 0 to 100 using the following scores: > 75 is excellent; > 50 is acceptable and < 50 is inadequate.

Parameters					**Penalty points**		
Homogenization technique					MS	Ball-mill	Lit.
Solvent					MeOH, THF	No solvent	Propanol, MeOH
1. Yield (%)					**59**	**87**	**69**
Penalty points					21	7	16
2. Reaction components	**Eq.**	**M**	**Price/g (Sigma-Aldrich)**	**Price to get 10mmol of product**			
2,4,6-Trimethylaniline	2,00	135,21	0,452	2,07	0		
2,4,6-Trimethylaniline	2,00	135,21	0,452	1,40		0	
2,4,6-Trimethylaniline	2,00	135,21	0,452	1,77			0
40% Glyoxal in water	1,00	86,09	0,05	0,07	0		
40% Glyoxal in water	1,00	86,09	0,05	0,05		0	
40% Glyoxal in water	1,00	86,09	0,05	0,06			0
Paraformaldehyde	1,00	30,03	0,02	0,01	0		
Paraformaldehyde	1,00	30,03	0,02	0,01		0	
Paraformaldehyde	1,05	30,03	0,02	0,01			0
HCl 4M dioxane	1,40	36,46	0,31	0,26	0		
HCl 4M dioxane	1,00	36,46	0,31	0,13		0	
Trimethylsilyl chloride	1,15	108,64	2,04	3,69			0
3. Safety							
2,4,6-Trimethylaniline (T)					5	5	5
THF (F)					5		
Paraformaldehyde (F, T+)					15	15	15
n-Propanol (F)							5
Diethyl ether (F+, T)							15
Ethyl acetate						0	
MeOH (F, T+)					15	-	15
HCl in dioxane (F, T+)					15	15	
Trimethylsilyl chloride (T, F)							10
4. Technical setup							
Magnetic stirrer					2		
Unconventional activation technique						2	
Dropwise addition							1
5. Temperature/ Time							
Room temperature < 24h					1	1	1
Heating > 1h							3
Cooling to -20°C							5
6. Workup and purification							
Filtration					0	0	0
Total					79	45	91
Ecoscale score					**22**	**56**	**10**
Ranking of reaction					Inadequate	Acceptable	Inadequate

Parameters					**Penalty points**		
Homogenization technique					MS	Ball-mill	Lit.
Solvent					MeOH, THF	No solvent	MeOH, THF
1. Yield (%)					**44**	**100**	**68**
Penalty points					28	0	16
2. Reaction components	**Eq.**	**M**	**Price/g (Sigma-Aldrich)**	**Price to get 10mmol of product**			
2,6-Diisopropylaniline	2,00	177,29	12,3	99,12	5		
2,6-Diisopropylaniline	2,00	177,29	12,3	43,61		5	
2,6-Diisopropylaniline	2,00	177,29	12,3	64,14			5
40% Glyoxal in water	1,00	86,09	0,05	0,10	0		
40% Glyoxal in water	1,00	86,09	0,05	0,04		0	
40% Glyoxal in water	1,00	86,09	0,05	0,06			0
Paraformaldehyde	1,00	30,03	0,02	0,0112	0		
Paraformaldehyde	1,00	30,03	0,02	0,0049		0	
Paraformaldehyde	1,00	30,03	0,02	0,0073			
HCl 4M dioxane	1,40	36,46	0,31	0,35	0		
HCl 4M dioxane	1,00	36,46	0,31	0,11		0	
HCl 4M dioxane	1,35	36,46	0,31	0,15			0
3. Safety							
THF (F, C)					5		5
Paraformaldehyde (F, T+)					15	15	15
Ethyl acetate					0	0	0
MeOH (F, T+)					15	-	15
HCl in dioxane (F, T+)					15	15	15
4. Technical setup							
Magnetic stirrer					0	-	0
Unconventional activation technique						2	
Dropwise addition							1
5. Temperature/ Time							
Room temperature < 24h					1	1	1
Cooling to 0°C					4		
6. Workup and purification							
Filtration					0	0	0
Total					88	38	73
Ecoscale score					**12**	**62**	**27**
Ranking of reaction					Inadequate	Acceptable	Inadequate

3. Calculation of the η ratio for the synthesis of IPr^{Me}·HCl

Reaction in ball-mill

2,6-Di*iso*propylaniline (243 µL, 1.286 mmol, 2.00 eq) and 2,3-butanedione (56 µL, 0.643 mmol, 1.00 eq) were introduced in a 20 mL zirconium oxide grinding bowl with eighty zirconium oxide balls (0.5 cm diameter). Total mass of reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 2 hours at 500 rpm. Then a solution of paraformaldehyde (19.3 mg, 0.643 mmol, 1.00 eq) in 4M hydrochloric acid in dioxane (161 µL, 0.643 mmol, 1.00 eq) was introduced. The bowl was closed, placed in the planetary ball-mill and subjected to grinding for 3 hours at 500 rpm. Ethyl acetate was added and the resulting suspension was filtrated. The solid was washed two or three times with ethyl acetate and then dried under vacuum to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dimethyl]imidazolium chloride **IPr^{Me}·HCl** (142.9 mg, 0.315 mmol, 49%) as a white powder.

Reaction in solution

2,6-Di*iso*propylaniline (10.0 g, 56.4 mmol, 2.00 eq) was dissolved in methanol (30 mL) and 2,3-butanedione (2.45 mL, 28.2 mmol, 1.00 eq) was added. The solution was warmed to room temperature and stirred during 3 hours. The suspension was filtrated, washed with a minimum of methanol and dried under vacuum to afford *N*,*N*'-bis-(2,6-di*iso*propylphenyl)butane-2,3-diimine (8.54 g, 21.1 mmol, 75%) as a yellow powder.

Paraformaldehyde (278.0 mg, 9.27 mmol, 1.25 eq) was suspended in a solution of 4M hydrochloric acid in dioxane (2.8 mL, 11.12 mmol, 1.50 eq) and stirred until complete dissolution of the white solid. THF (75 mL) followed by *N*,*N*'-bis-(2,6-diisopropylphenyl)butane-2,3-diimine (3.00 g, 7.41 mmol, 1.00 eq) were added slowly. The resulting solution was stirred at room temperature for two 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)-4,5-dimethyl]imidazolium chloride **IPr^{Me}·HCl** (471.2 mg, 1.04 mmol, 14%) as a white powder.

Literature conditions

According to *J. Org. Chem.* **2009,** *74*, 7935: "*General Synthesis A: 2,3-Substituted Imine-butane. A modification of a literature procedure was used to synthesize 3gMe and 3hMe. 2 To a round-bottom equipped with a stir-bar, EtOH, 2,3-butanedione (1 eq), substituted aniline (2 eq), and several drops of formic acid was added. This solution was allowed to stir for 15 hours. A yellow precipitate is formed after a few hours. The round-bottom was immersed in an ice bath and allowed to stir for 30 minutes prior to filtering the solution. 2,3-bis(2,6-diisopropylphenyl)imine-butane General procedure A was used with 2,6-diisopropyllphenylaniline (21.5 mL, 114 mmol), butanedione (4.5 mL, 51.3 mmol), and EtOH (250 mL) to afford 2,3- bis(2,6-diisopropylphenyl)imine-butane 3hMe as a yellow solid, (20.75 g, 91%)*".[11]

According to *ACS Appl. Mater. Inter.* **2016,** *8*, 14678: "*General Procedure A for the Synthesis of imidazolium salts. In a dry flamed Schlenk tube under argon atmosphere, the diimine (1 equiv.) was introduced in freshly distilled EtOAc (2.5 mL per mmol) and cooled down to 0 °C. In a test tube, paraformaldehyde (1.3 equiv.) was stirred in a 4 M dioxane solution of HCl (1.6 equiv.) for 10 minutes and added to the diimine solution at 0 °C. The reaction mixture was stirred at room temperature* *overnight. The precipitate was collected on a frit and washed with EtOAc. Then, the residue was dissolved in MeOH and anhydrous $NaHCO_3$ (2.5 equiv.) was added. The resulting mixture was stirred at room temperature for 1 hour. Diethyl ether was added affording a precipitate which was collected on a frit and dried under vacuum leading to the pure imidazolium salt.*" And "*Using diimine **S4** (3.15 g, 7.78 mmol) and following the general procedure **A**, pure product **S8** was obtained as a white powder (2.73 mg, 77% yield)*".[12]

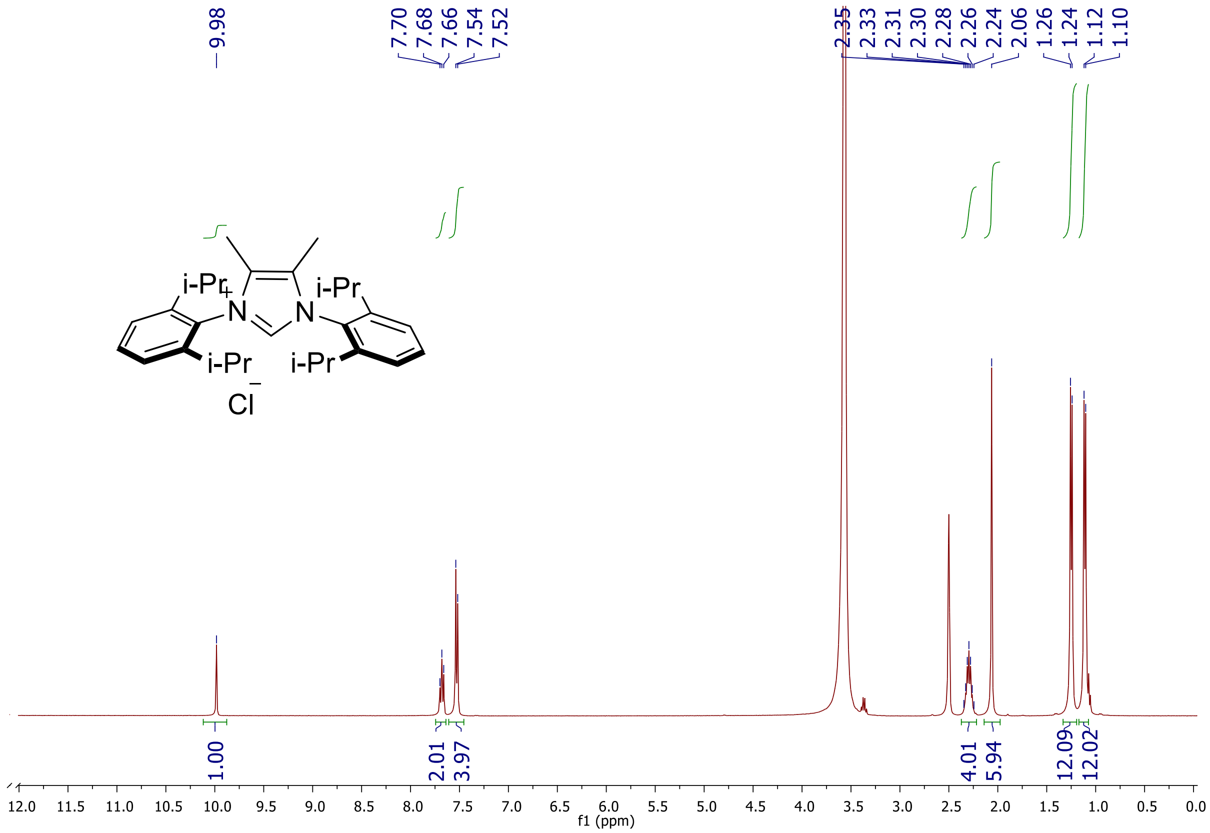
Since both steps in solution are not on the same scale, the total mass of solvent and reagent using during the second step was adjusted using the ratio of their scale.

Entry	**Conditions**	**Total masse of reagents (g)**	**Solvent quantity (mL)**	**η ratio**
1	BM	0.326	0.166	0.51
2	MS	27.22	326	12.0
3	Lit.	29.62	399	13.5

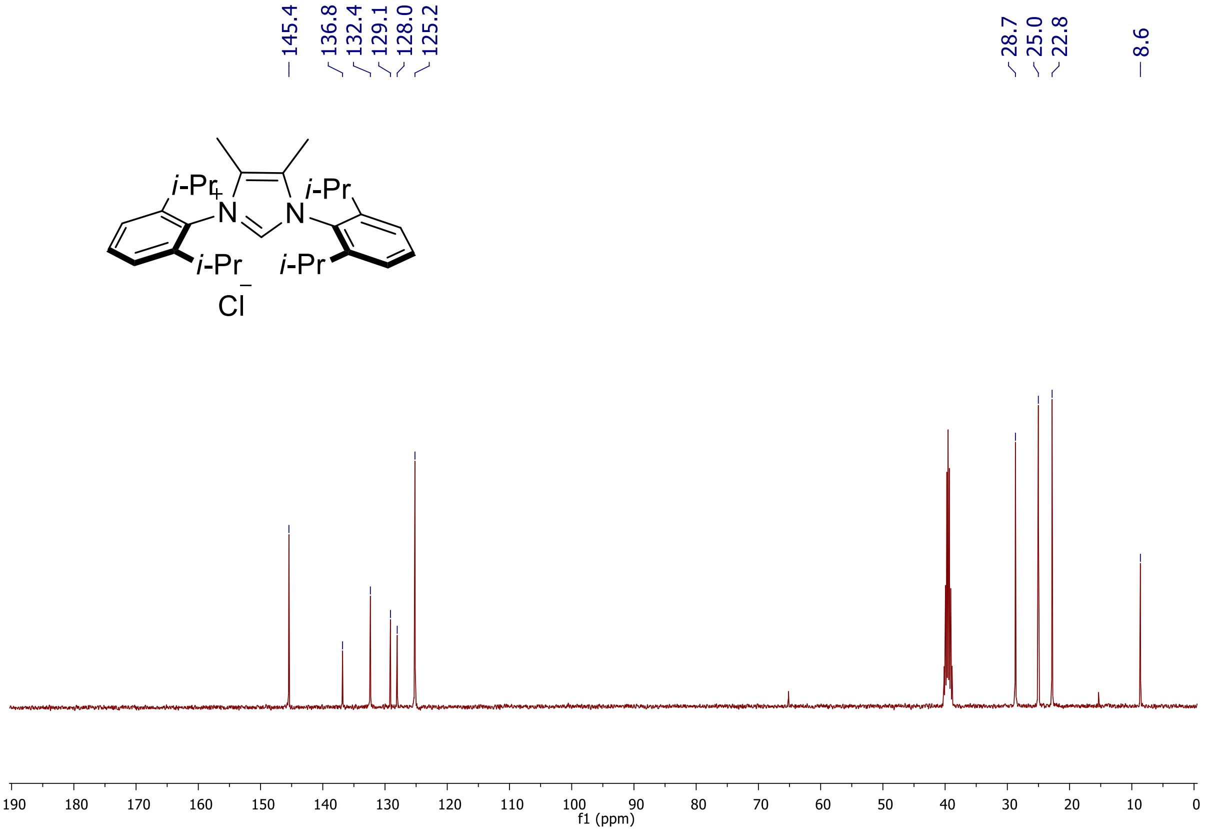
4. NMR

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

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

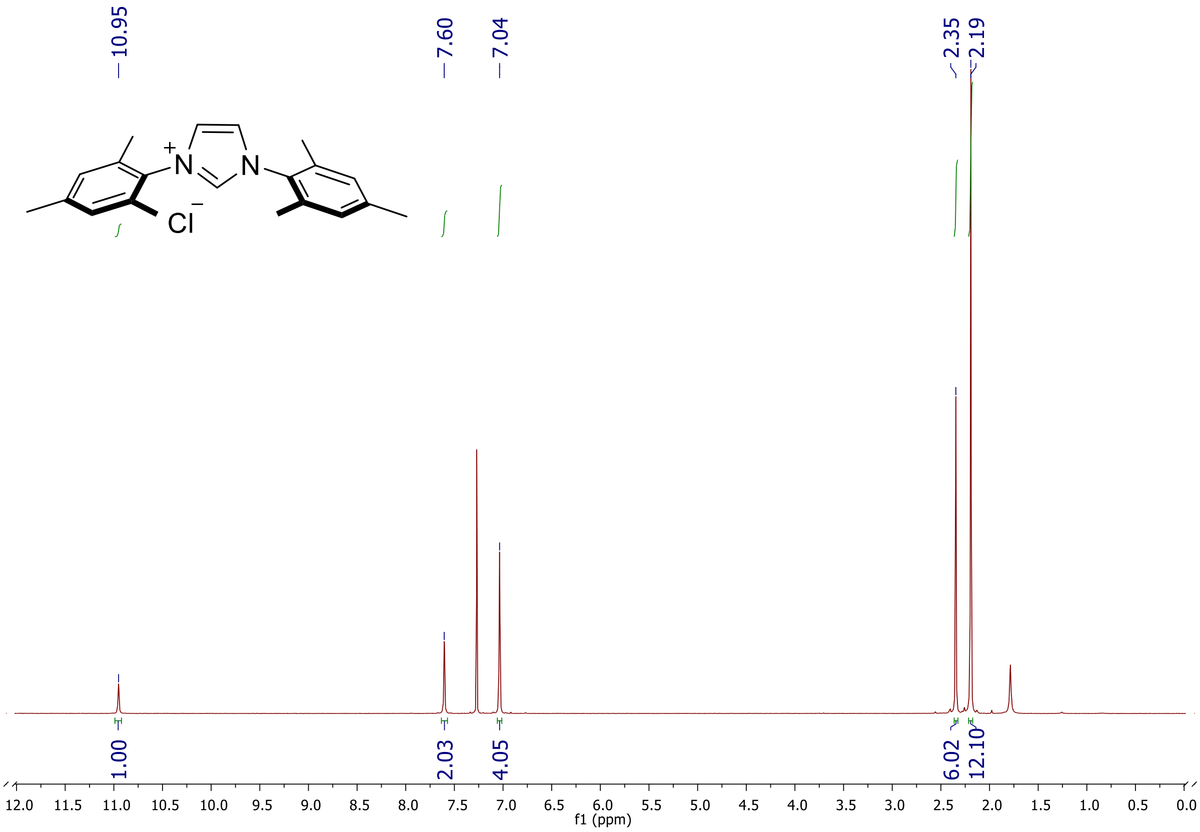


^{13}C NMR (101 MHz, DMSO-d_6)

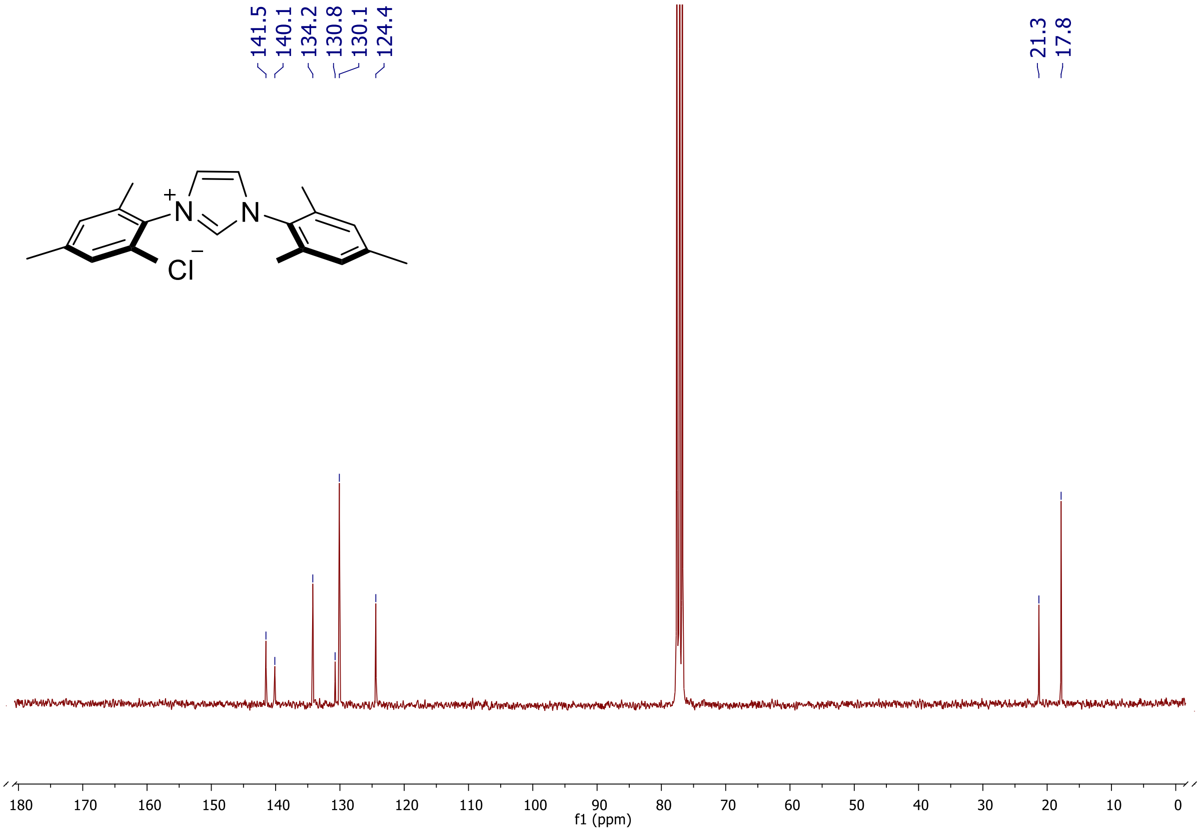


1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride IMes·HCl

^{1}H NMR (500 MHz, $CDCl_3$)

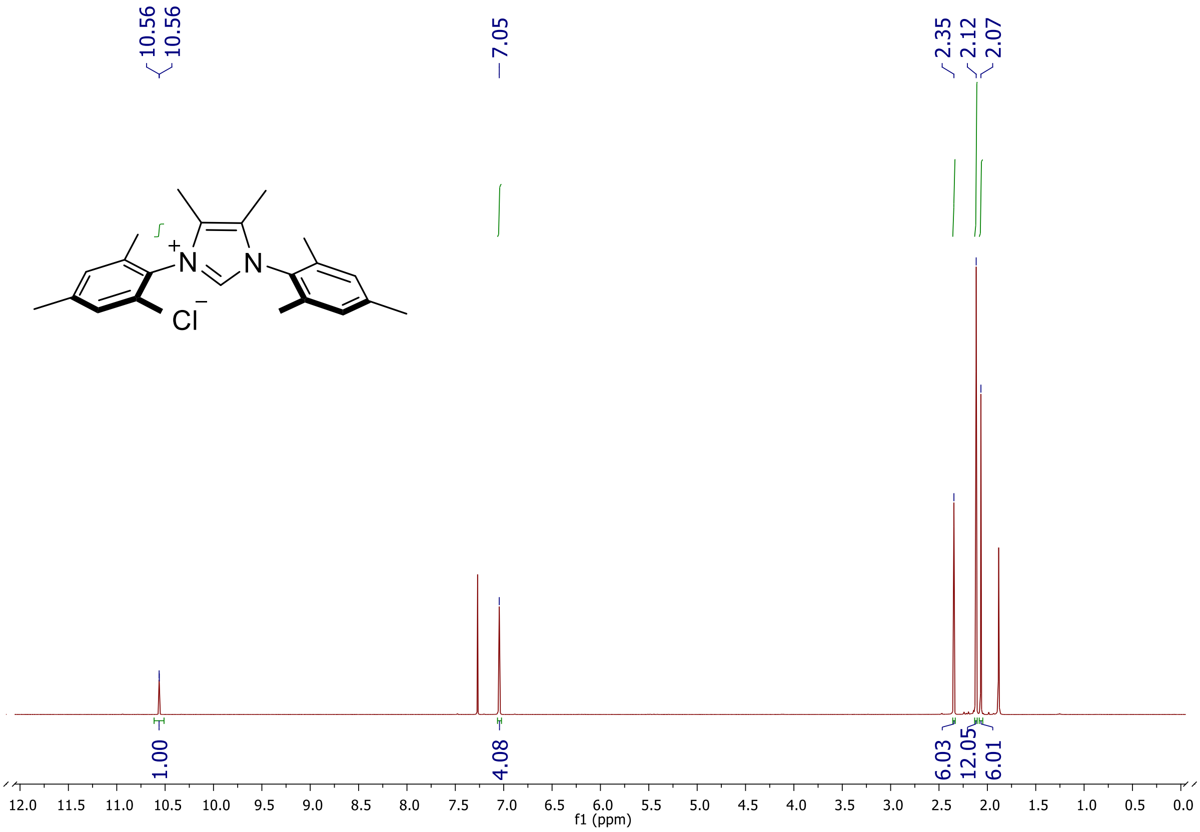


^{13}C NMR (126 MHz, $CDCl_3$)

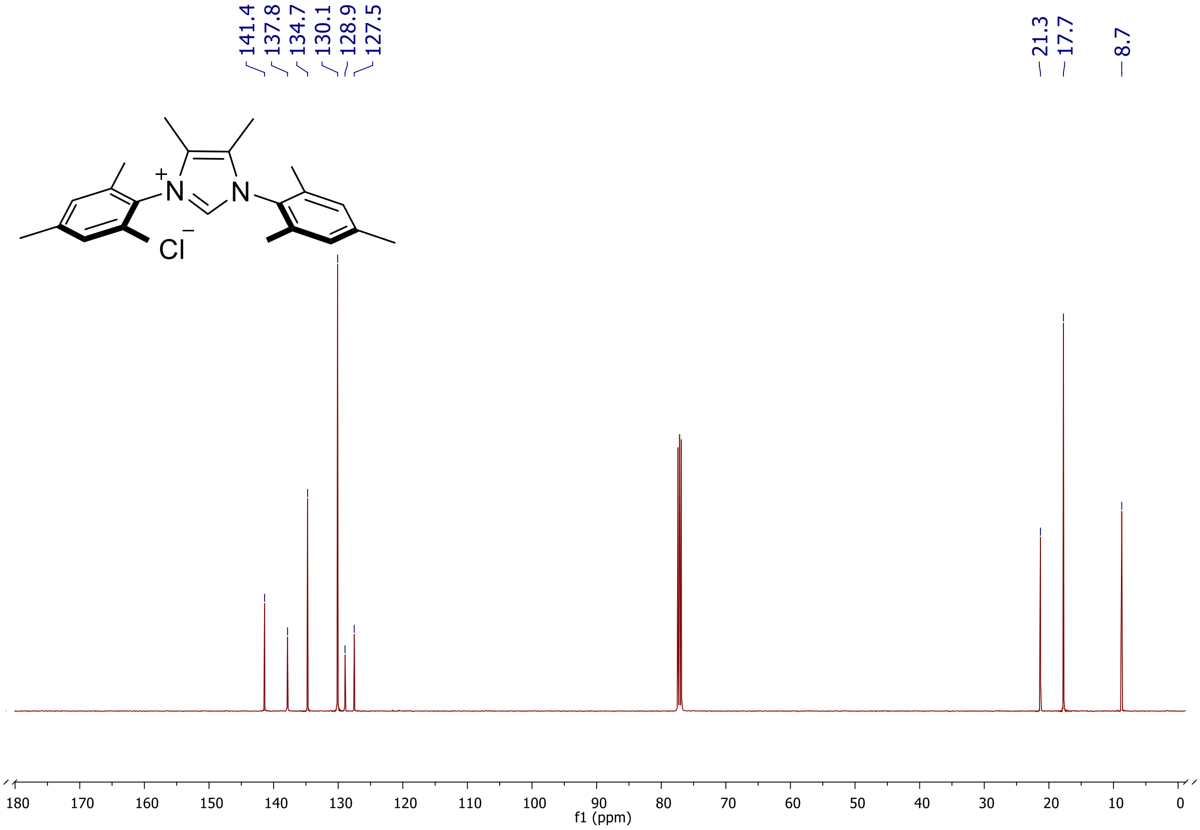


[1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethyl]imidazolium chloride IMes^{Me}·HCl

^{1}H NMR (500 MHz, CDCl$_3$)

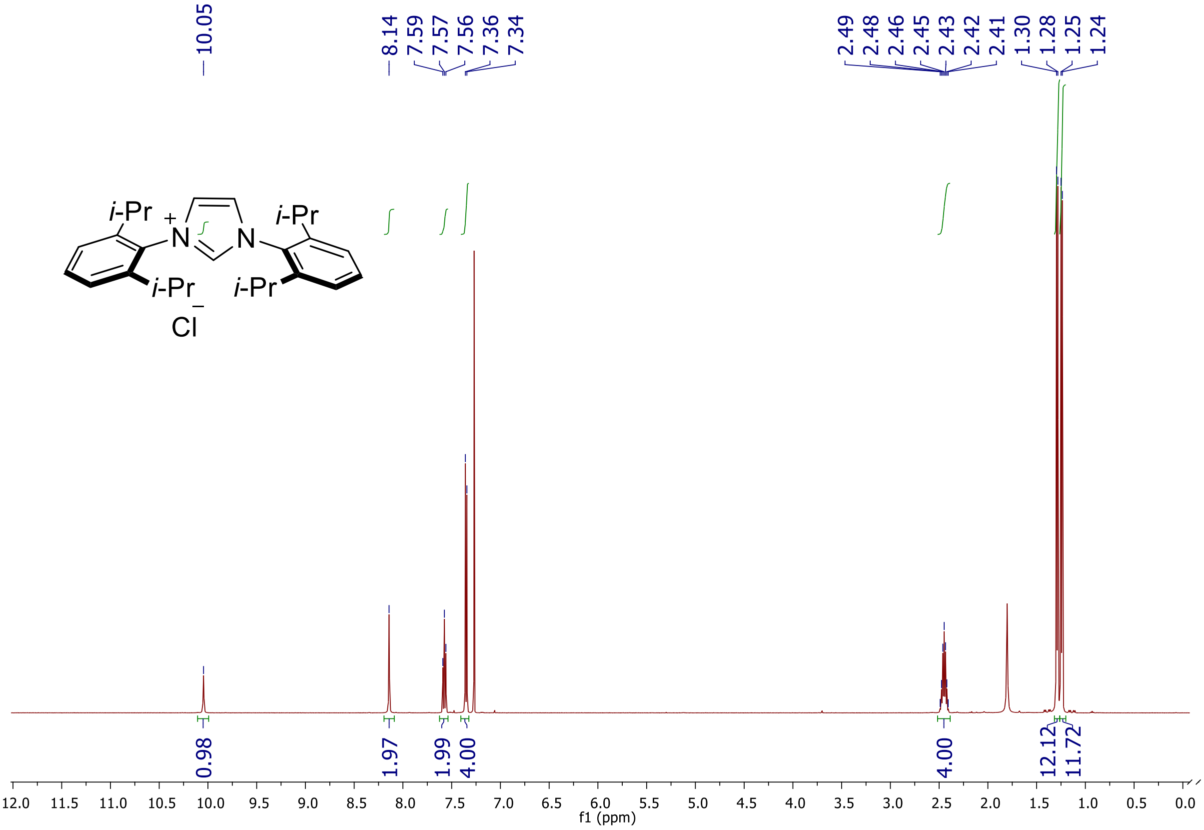


^{13}C NMR (126 MHz, CDCl$_3$)

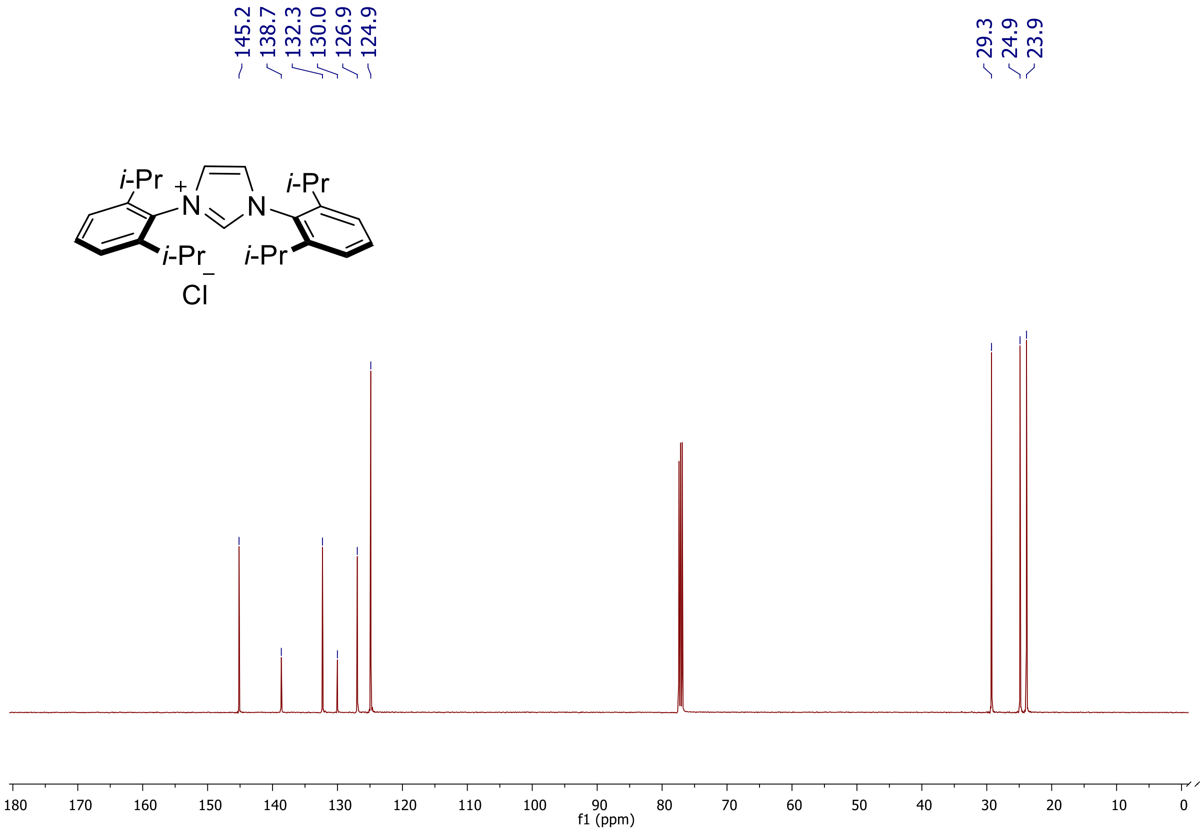


1,3-Bis-(2,6-di*iso*propylphenyl)imidazolium chloride IPr·HCl

^{1}H NMR (500 MHz, CDCl$_3$)

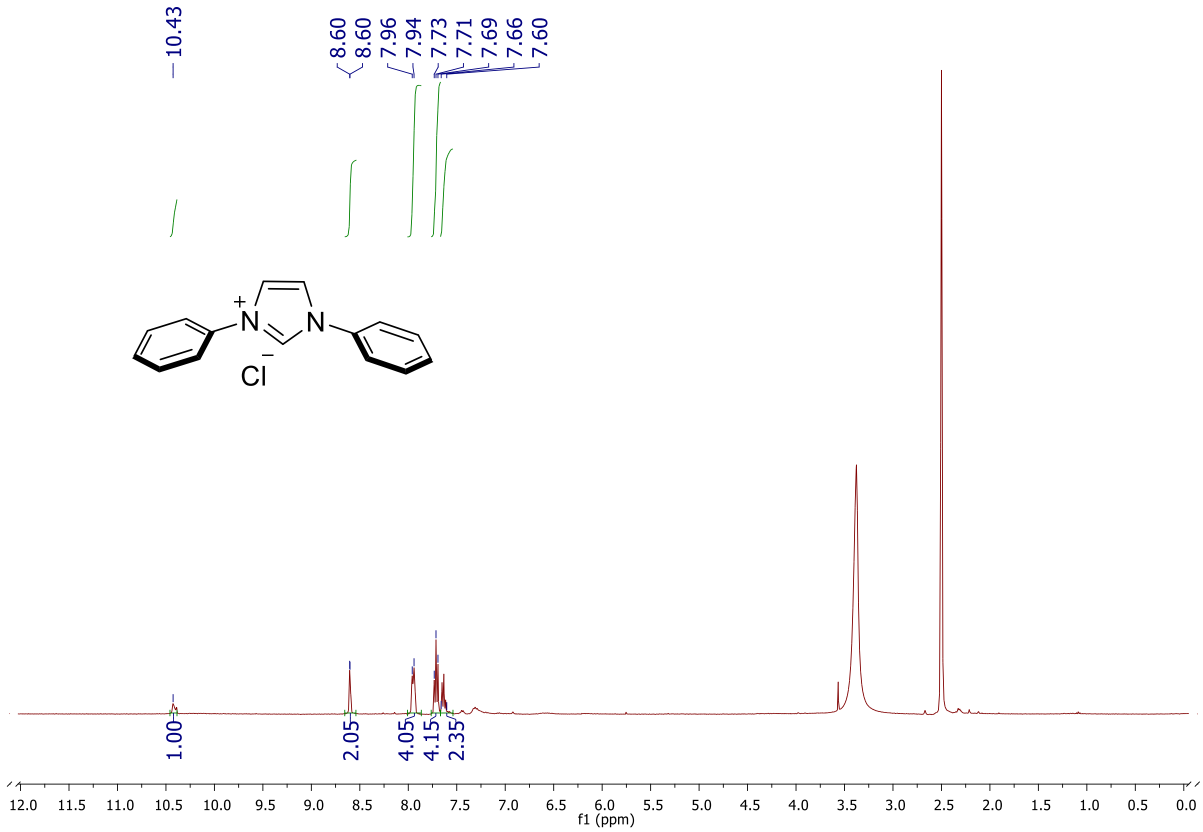


^{13}C NMR (126 MHz, CDCl$_3$)

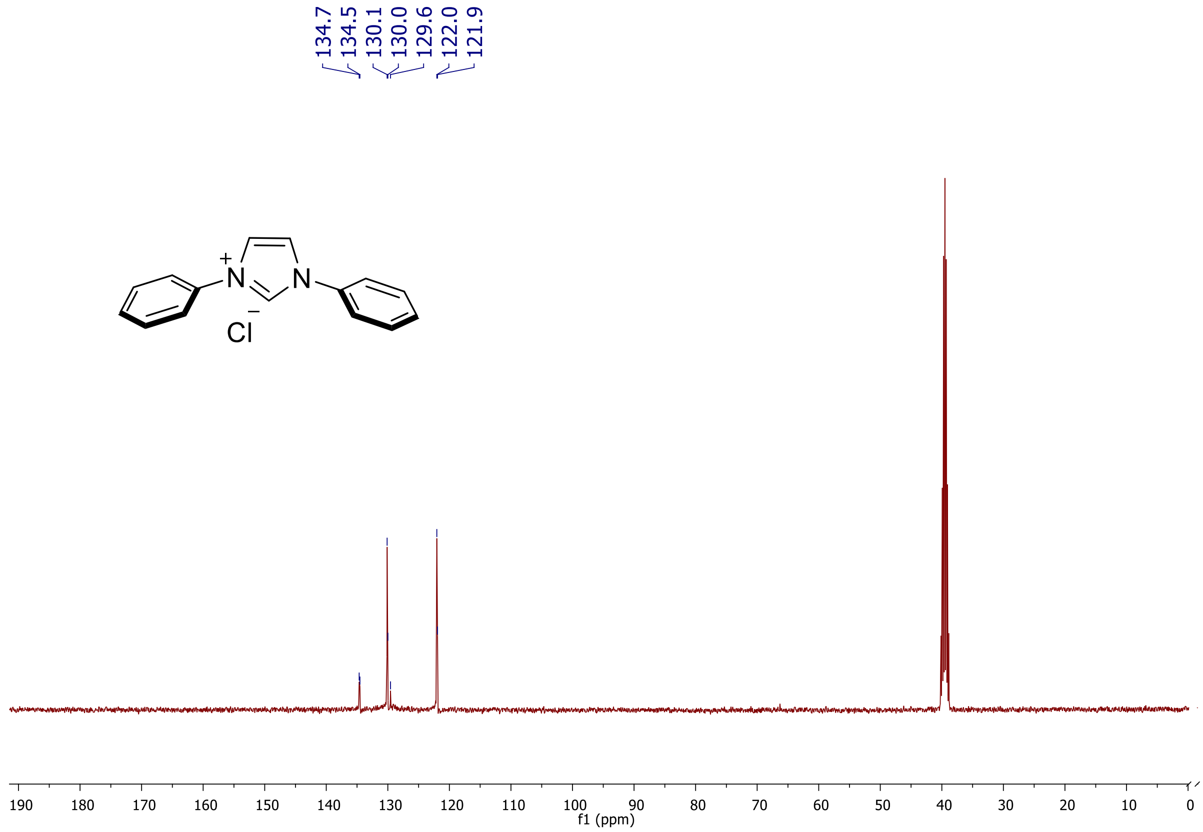


1,3-Bisphenylimidazolium chloride IPh·HCl

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

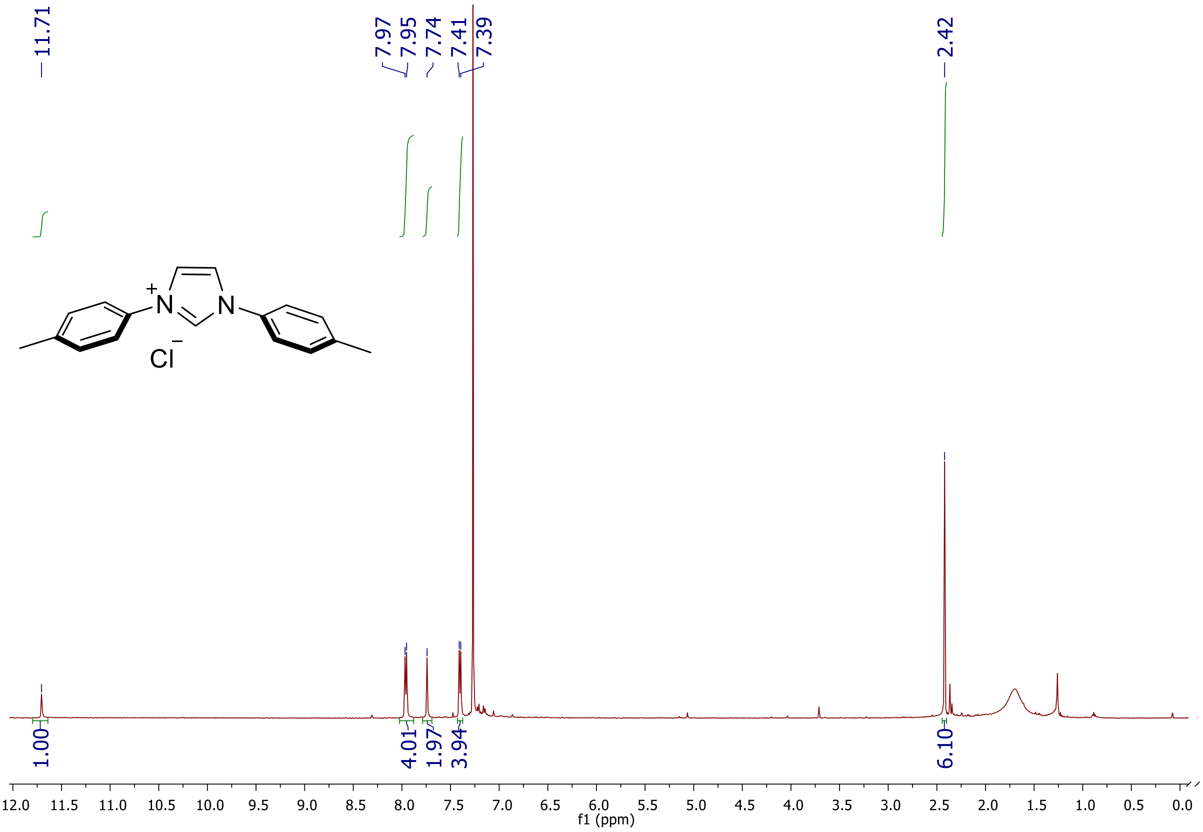


^{13}C NMR (126 MHz, DMSO-d_6)

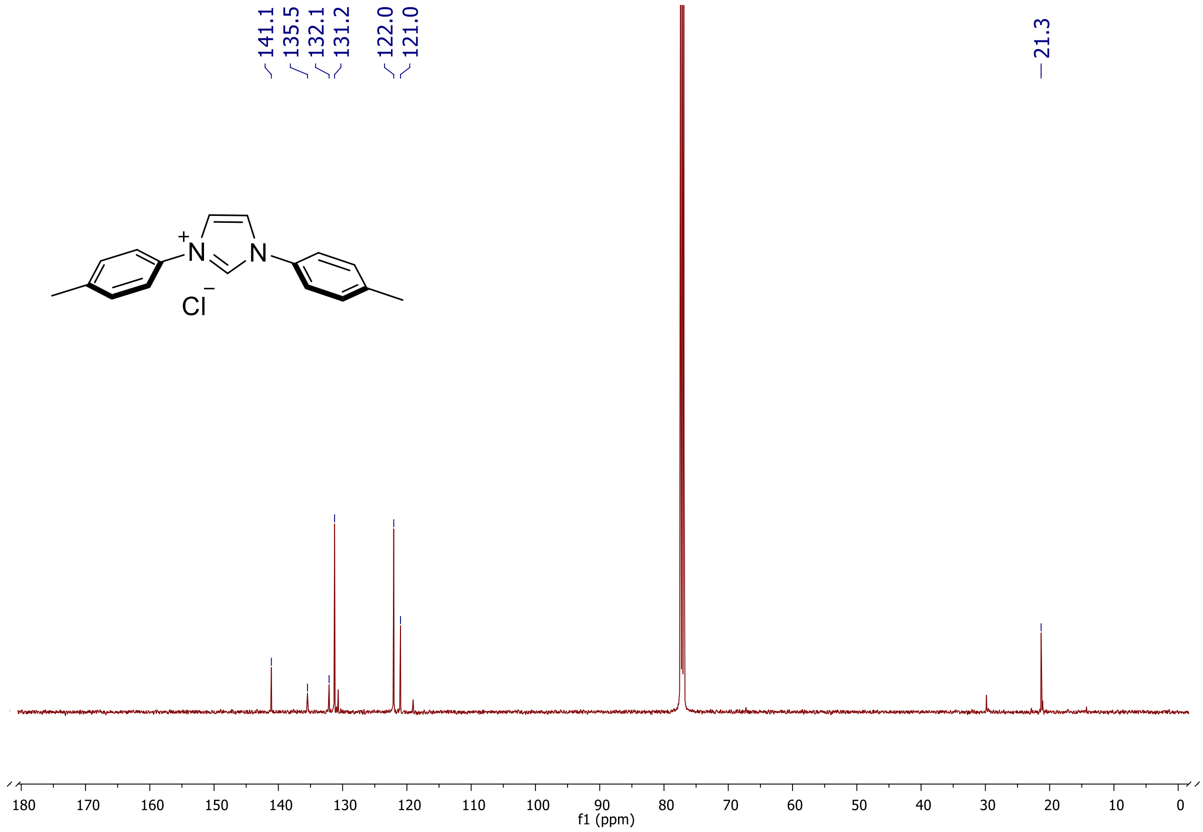


1,3-Bis(4-methylphenyl)imidazolium chloride I*p*-Tol·HCl

^{1}H NMR (500 MHz, CDCl$_3$)

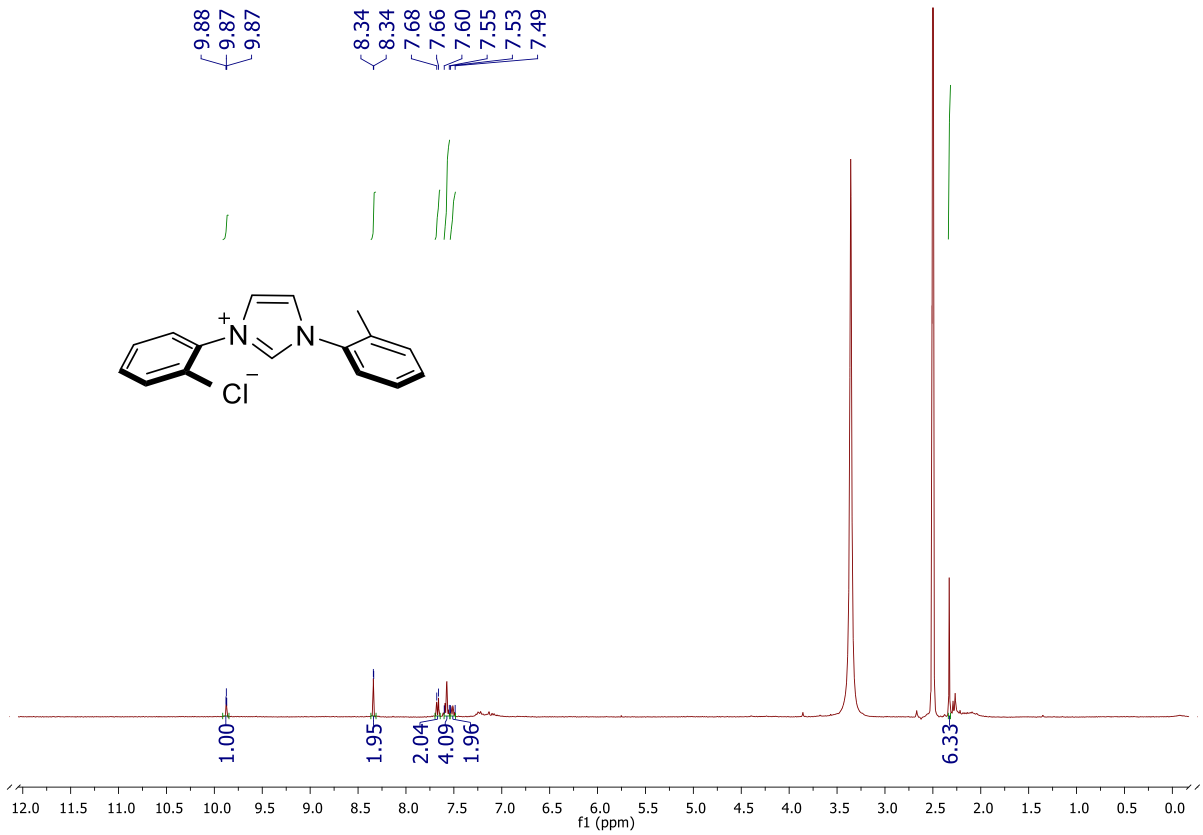


^{13}C NMR (126 MHz, CDCl$_3$)

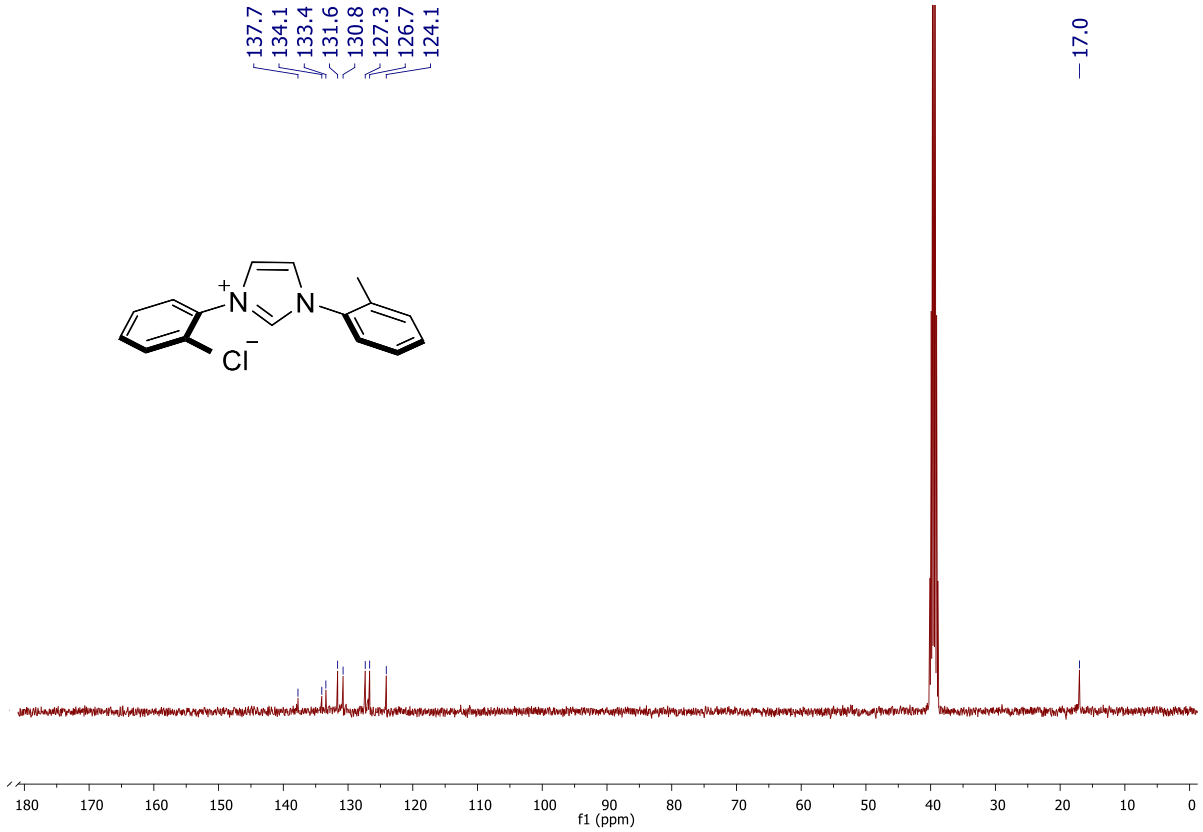


1,3-Bis-(2-methylphenyl)imidazolium chloride I*o*-Tol·HCl

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

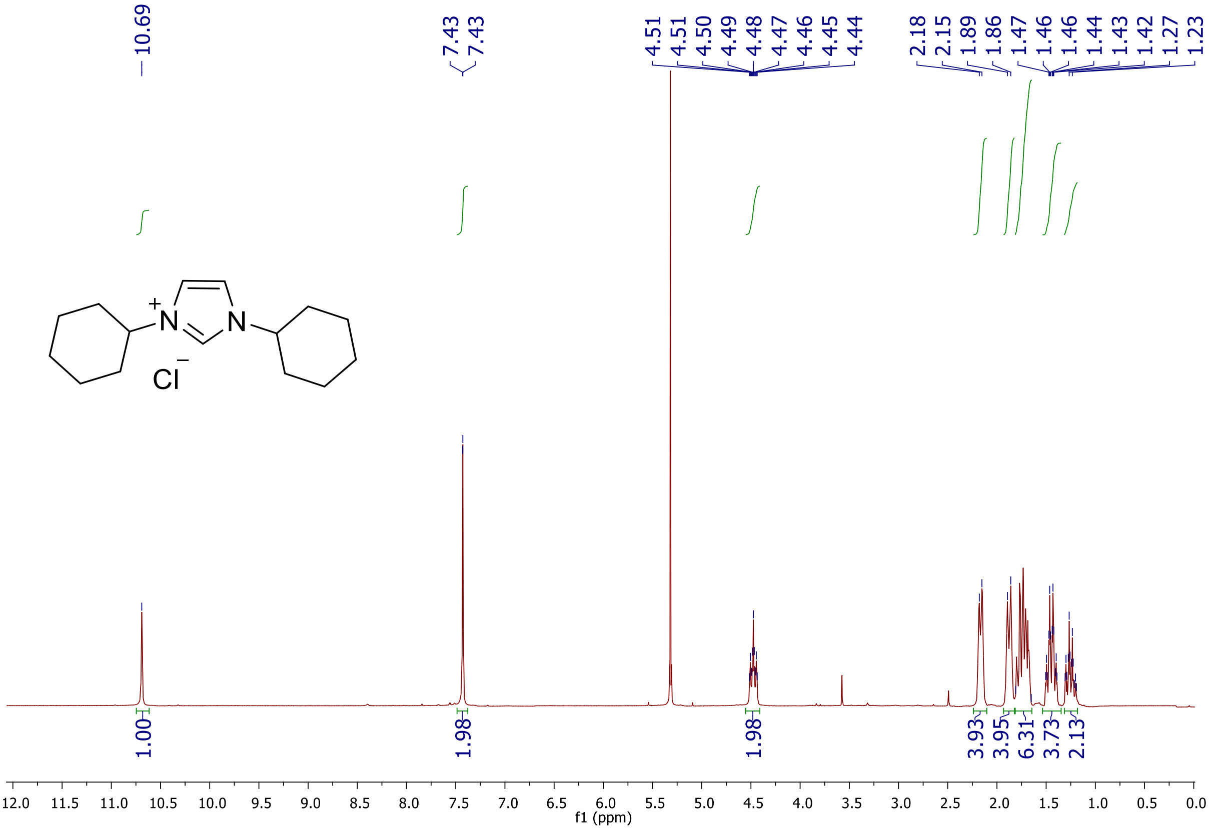


^{13}C NMR (101 MHz, DMSO-d_6)

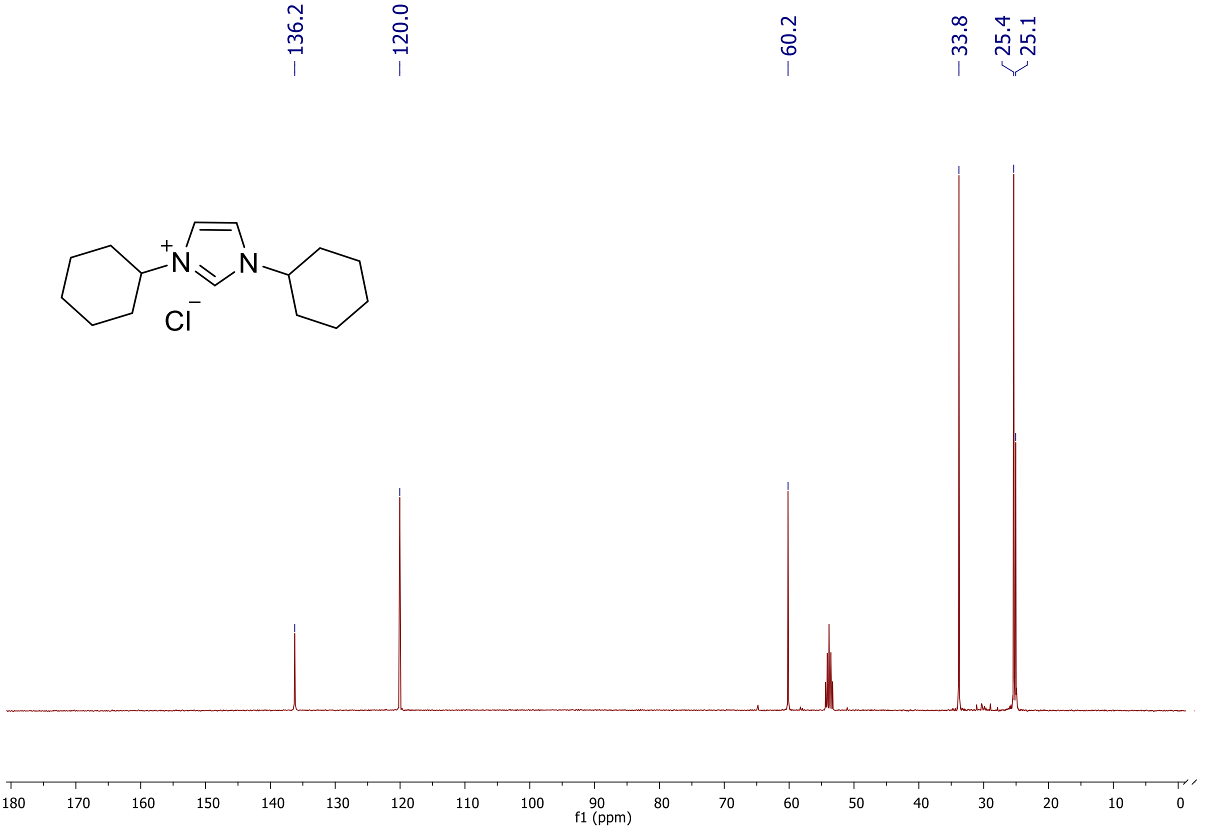


1,3-Biscyclohexylimidazolium chloride ICy·HCl

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



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



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