An Acidity Scale of 1,3-Dialkylimidazolium Salts in Dimethylsulfoxide Solution

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Supporting Information

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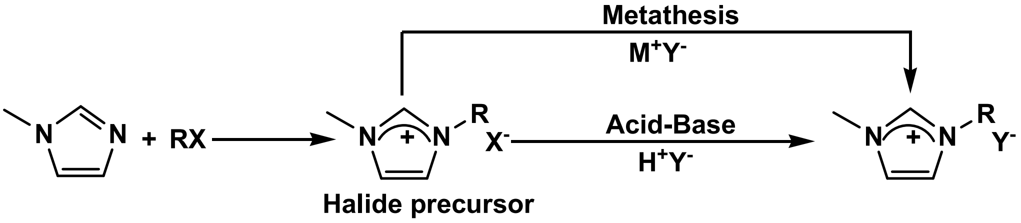
Preparative Procedures and Characterization Data of Ionic Liquids

Ionic liquids used in this work were synthesized following the published procedure. All the syntheses were carried out under dry argon using standard schlenk techniques. Solvents (acetone, dichloromethane and toluene) were used after handling over 3Å molecular sieves. In all the syntheses, we used distilled and deionized water. *N*-methylimidazole and halohydrocarbon were used after distillation under reduced pressure and storage over 3Å molecular sieves. All other reagents were obtained from commercial sources and used as received.

Scheme S1.



1-*n*-butyl-3-methylimidazolium bromide (IL **14**).[1] Under vigorous stirring, freshly distilled 1-bromobutane (10.0 mmol) was added dropwise to a solution of 1-methylimidazole (6.0 mmol) in toluene (30 mL). The mixture, already turbid, was heated at 90°C for 2h. The resulted imidazolium salt was decanted from the hot solution in a separatory funnel, washed three times with toluene and dried at 70°C for 3h under reduced pressure. The product was obtained as a white solid with 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.22 (s, 1H), 7.79 (s, 1H), 7.71 (s, 1H), 4.15 (t, 2H), 3.83 (s, 3H), 1.75 (quintet, 2H), 1.21 (sextet, 2H), 0.85 (t, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.2, 124.2, 122.9, 49.1, 36.4, 32.0, 19.4, 14.0 ppm.

1-*n*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **3**).[2] A solution of IL **14** (5.0 mmol) in 10 mL H_2O was added dropwise to a solution of lithium bis(trifluoromethanesulfonyl)imide (5.0 mmol) in 10 mL H_2O. The solution was stirred at 70°C for 2h and then cooled to room temperature. The lower phase was then collected and washed several times with fresh water until the "*$AgNO_3$ test*" was negative (as described below). The product was then dried at 70°C for 3h under reduced pressure to afford a colorless liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.07 (s, 1H), 7.72 (s, 1H), 7.66 (s, 1H), 4.13 (t, 2H), 3.82 (s, 3H), 1.74 (quintet, 2H), 1.25 (sextet, 2H), 0.88 (t, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.1, 124.2, 122.9, 121.7, 118.5, 49.2, 36.4, 32.0, 19.4, 13.8 ppm.

1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (IL **1**). The halide precursor, 1,3-dimethylimidazolium iodide was synthesized as the same procedure used for IL **14**. From methyl iodide (10.0 mmol) and 1-methylimidazole (6.0 mmol), there was obtained 1,3-dimethylimidazolium iodide as a pale yellow solid. IL **1** was then synthesized as the same procedure used for IL **3** and obtained as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.99 (s, 1H), 7.64 (s, 2H), 3.81 (s, 6H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.7, 124.1, 121.8, 118.6, 36.3 ppm.

1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **2**). The halide precursor, 1-ethyl-3-methylimidazolium bromide was synthesized as the same procedure used for IL **14**. From bromoethane (10.0 mmol) and 1-methylimidazole (6.0 mmol), there was obtained 1-ethyl-3-methylimidazolium bromide as a white solid. IL **2** was then synthesized as the same procedure used for IL **3** and obtained as a colorless liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.08 (s, 1H), 7.75 (s, 1H), 7.66 (s, 1H), 4.16 (quartet, 2H), 3.81 (s, 3H), 1.38 (t, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 136.9, 124.2, 122.6, 121.8, 118.6, 44.8, 36.3, 15.7 ppm.

1-*n*-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **4**). The halide precursor, 1-*n*-octyl-3-methylimidazolium bromide was synthesized as the same procedure used for IL **14**. From 1-bromooctane (10.0 mmol) and 1-methylimidazole (6.0 mmol), there was obtained 1-*n*-octyl-3-methylimidazolium bromide as a white solid. IL **4** was then synthesized as the same procedure used for IL **3** and obtained as a pale yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.06 (s, 1H), 7.73 (s, 1H), 7.66 (s, 1H), 4.11 (t, 2H), 3.81 (s, 3H), 1.76-1.73 (m, 2H), 1.22 (br. s, 10H), 0.83 (t, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.1, 124.2, 122.9, 121.7, 118.5, 49.5, 36.3, 31.8, 30.0, 29.1, 29.0, 26.1, 22.7, 14.4 ppm.

1-benzyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **7**). The halide precursor, 1-benzyl-3-methylimidazolium bromide was synthesized as the same procedure used for IL **14**. From benzyl bromide (10.0 mmol) and 1-methylimidazole (6.0 mmol), there was obtained 1-benzyl-3-methylimidazolium bromide as a yellow liquid. IL **7** was then synthesized as the same procedure used for IL **3** and obtained as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.17 (s, 1H), 7.75 (s, 1H), 7.68 (s, 1H), 7.43-7.36 (m, 5H), 5.39 (s, 2H), 3.83 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.3, 135.5, 129.6, 129.4, 128.9, 124.6, 123.0, 121.8, 118.6, 52.6, 36.5 ppm.

1-(*p*-methylbenzyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **8**). The halide precursor, 1-(*p*-methylbenzyl)-3-methylimidazolium bromide was synthesized as the same procedure used for IL **14**. From 4-methylbenzyl bromide (10.0 mmol) and 1-methylimidazole (6.0 mmol), there was obtained 1-(*p*-methylbenzyl)-3-methylimidazolium bromide as a yellow liquid. IL **8** was then synthesized as the same procedure used for IL **3** and obtained as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.14 (s, 1H), 7.73 (d, 1H), 7.66 (d, 1H), 7.30 (d, 2H), 7.22 (d, 2H), 5.33 (s, 2H), 3.82 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C

NMR (100.6 MHz, DMSO-d_6): δ 138.9, 137.2, 132.4, 130.2, 129.0, 124.6, 122.9, 121.8, 118.6, 52.4, 36.5, 21.3 ppm.

1-(*p*-bromobenzyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **9**). The halide precursor, 1-(*p*-bromobenzyl)-3-methylimidazolium bromide was synthesized as the same procedure used for IL **14**. From 4-bromobenzyl bromide (10.0 mmol) and 1-methylimidazole (6.0 mmol), there was obtained 1-(*p*-bromobenzyl)-3-methylimidazolium bromide as a yellow liquid. IL **9** was then synthesized as the same procedure used for IL **3** and obtained as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.15 (s, 1H), 7.74 (d, 1H), 7.68 (d, 1H), 7.62 (d, 2H), 7.37 (d, 2H), 5.37 (s, 2H), 3.83 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.4, 134.8, 132.6, 131.2, 124.7, 123.0, 122.8, 121.8, 118.6, 51.8, 36.5 ppm.

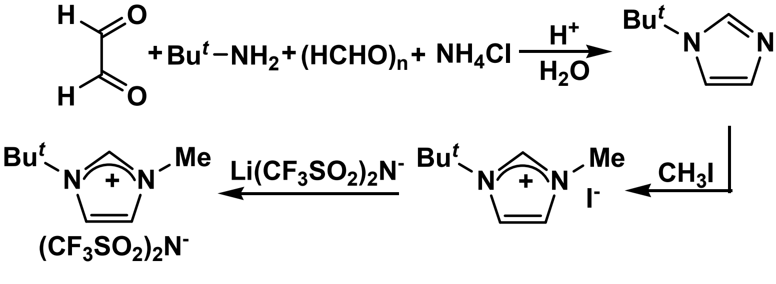
1-methoxylmethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **10**). The halide precursor, 1-methoxylmethyl-3-methylimidazolium chloride was synthesized as the same procedure used for IL **14**. From chloromethyl methyl ether (10.0 mmol) and 1-methylimidazole (6.0 mmol), there was obtained 1-methoxylmethyl-3-methylimidazolium chloride as a pale yellow liquid. IL **10** was then synthesized as the same procedure used for IL **3** and obtained as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.28 (s, 1H), 7.85 (s, 1H), 7.76 (s, 1H), 5.51 (s, 2H), 3.89 (s, 3H), 3.32 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.2, 124.0, 121.9, 121.6, 117.3, 79.4, 56.7, 35.9 ppm.

1-*n*-butyl-3-methylimidazolium chloride (IL **13**). IL **13** was synthesized as the same procedure used for IL **14**. From 1-chlorobutane (10.0 mmol) and 1-methylimidazole (6.0 mmol), there was obtained IL **13** as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.70 (s, 1H), 7.95 (s, 1H), 7.86 (s, 1H), 4.18 (t, 2H), 3.86 (s, 3H), 1.71 (quintet, 2H), 1.18 (sextet, 2H), 0.81 (t, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.5, 124.2, 122.9, 49.0, 36.3, 32.1, 19.4, 13.9 ppm.

1-*n*-butyl-3-methylimidazolium tetrafluoroborate (IL **15**).[2] Under vigorous stirring, a solution of $NaBF_4$ (15.0 mmol) in acetone (20 mL) was added to IL **14** (10.0 mmol) in acetone (20 mL). The mixture was then stirred at room temperature until the IL **14** reacted completely. The reaction mixture was filtered through celite and concentrated under reduced pressure. The obtained viscous liquids was dissolved in water and extracted by dichloromethane. Then the solution was evaporated and the resulted product was dried at 70°C for 3h under vacuum as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.05 (s, 1H), 7.72 (s, 1H), 7.66 (s, 1H), 4.12 (t, 2H), 3.81 (s, 3H), 1.73 (quintet, 2H), 1.24 (sextet, 2H), 0.87 (t, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.1, 124.2, 122.9, 49.2, 36.3, 32.0, 19.4, 13.9 ppm.

1-*n*-butyl-3-methylimidazolium hexafluorophosphate (IL **16**). IL **16** was synthesized as the same procedure used for IL **3**. A solution of HPF_6 (15.0 mmol) in water (20 mL) was added to IL **14** (10.0 mmol) in water (20 mL) and IL **16** was obtained as a colorless liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.06 (s, 1H), 7.72 (s, 1H), 7.65 (s, 1H), 4.13 (t, 2H), 3.81 (s, 3H), 1.74 (quintet, 2H), 1.24 (sextet, 2H), 0.87 (t, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 137.0, 124.0, 122.6, 49.2, 36.1, 31.9, 19.3, 13.5 ppm.

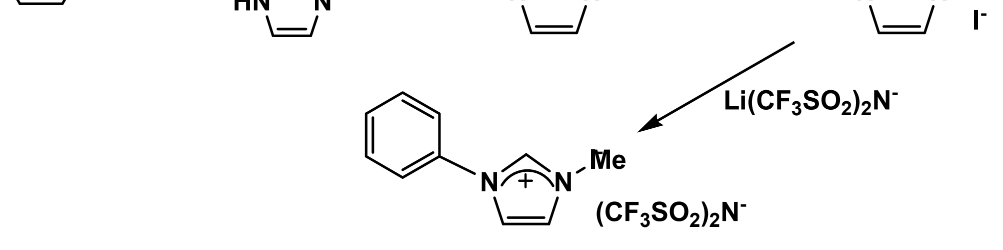
Scheme S2.



1-*t*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **5**).[3] 250 mL flask equipped with mechanical stirrer, dropping funnel and reflux condenser was loaded with glyoxal (0.1 mol), formaldehyde (0.1 mol) and *t*-butylammonium salt (0.1 mol) which had been obtained by acidification of the *t*-butylamine solution in 15 mL of water with phosphoric acid until the pH = 2. The reaction mixture was warmed to 90-95°C and a saturated aqueous solution of 0.1 mol ammonium chloride was added to the stirred reaction mixture over a period of 1h. After an additional 2h of stirring at 95°C, the solution was chilled, solid KOH was added and the mixture was extracted with ethyl acetate three times. The combined extract was evaporated and distilled in vacuum (105°C/12mmHg), 1-*t*-butylimidazole then could be obtained as a colorless liquid with 20% yield.

The halide precursor, 1-*t*-butyl-3-methylimidazolium iodide was synthesized as the same procedure used for IL **14**. From methyl iodide (10.0 mmol) and 1-*t*-butylimidazole (6.0 mmol), there was obtained 1-*t*-butyl-3-methylimidazolium iodide as a white solid. IL **5** was then synthesized as the same procedure used for IL **3** and obtained as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.17 (s, 1H), 7.95 (s, 1H), 7.71 (s, 1H), 3.81 (s, 3H), 1.55 (s, 9H) ppm; ^{13}C NMR (100.6 MHz, DMSO-*d*$_6$): δ 135.6, 124.4, 121.8, 120.7, 118.6, 60.0, 36.3, 29.6 ppm.

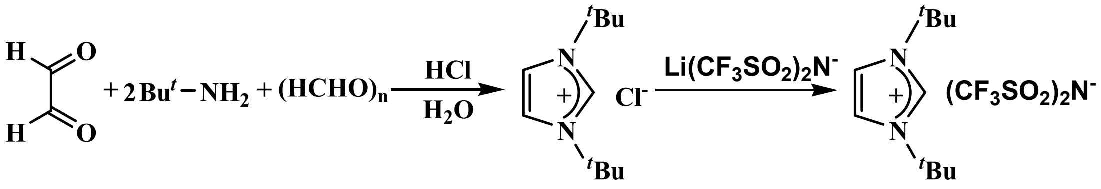
Scheme S3.



1-phenyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL **6**).[4] Phenylboronic acid (16.0 mmol), imidazole (13.0 mmol) and copper(□) iodide (0.6 mmol) were mixed in methanol (100 mL). The mixture solution was refluxing 5h with pumping air continuously. Then the solvent was evaporated under reduced pressure and extracted by ether. The extract phase was concentrated under reduced pressure. The residue was filtered through celite, the corresponding *N*-phenylimidazole was gotten in almost quantitative yields.

The halide precursor, 1-phenyl-3-methylimidazolium iodide was synthesized as the same procedure used for IL **14**. From methyl iodide (10.0 mmol) and *N*-phenylimidazole (6.0 mmol), there was obtained 1-phenyl-3-methylimidazolium iodide as a white solid. IL **6** was then synthesized as the same procedure used for IL **3** and obtained as a colorless liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.71 (s, 1H), 8.26 (s, 1H), 7.91 (s, 1H), 7.74-7.54 (m, 5H), 3.92 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 136.7, 135.4, 130.8, 130.4, 125.1, 122.5, 121.8, 121.7, 118.6, 36.8 ppm.

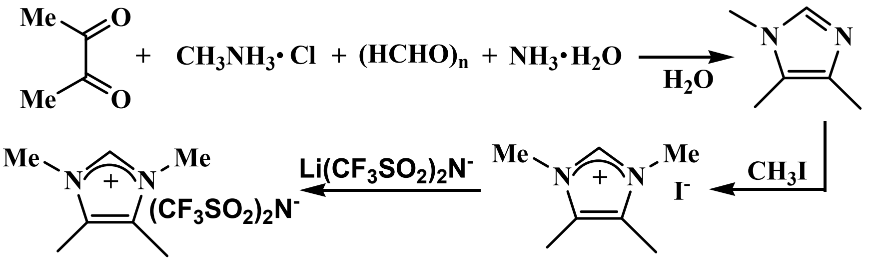
Scheme S4.



1,3-di-*t*-butylimidazolium bis(trifluoromethanesulfonyl)imide (IL **11**).[5] A total of 10 mmol formaldehyde was dissolved in 10 mL of toluene and *tert*-butyl amine (10 mmol) were added dropwise. The mixture was stirred and heated until a clear solution formed. After cooling to 0°C another 10 mmol of *tert*-butyl amine was added. A total of 10 mmol of a 3 M aqueous HCl was added dropwise. Then the glyoxal (10 mmol) were added dropwise. The reaction mixture was stirred at 40°C for 15 h. After dilution with a saturated $NaHCO_3$(aq.) solution, the water of the aqueous phase was then removed by evaporation and the crude product obtained was extracted three times with 5 ml of CH_2Cl_2. After evaporation of the organic solvent under reduced pressure, 1,3-di-*t*-butylimidazolium chloride was obtained as a viscous liquid.

IL **11** was then synthesized as the same procedure used for IL **3** and obtained as a colorless needle crystals. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.98 (s, 1H), 8.03 (s, 2H), 1.57 (s, 18H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 132.2, 121.6, 120.4, 117.3, 59.6, 29.1 ppm.

Scheme S5.



1,3,4,5-tetramethylimidazolium bis(trifluoromethanesulfonyl)imide (IL **12**).[6] 250 mL flask was loaded with formaldehyde (0.1 mol), methylamine hydrochloride (0.18 mol) and ammonium hydroxide (50.0 mL). After stirring uniformly, butandione (60.0 mmol) was added and the mixture was maintained in an oil bath at 100°C for 15 min. The cold reaction mixture was extracted with dichloromethane. The organic phase was dried with Na_2SO_4 and the solvent was removed. The 1,4,5-trimethylimidazole could be obtained after the vacuum distillation (100°C/1mmHg).

The halide precursor, 1,3,4,5-tetramethylimidazolium iodide was synthesized as the same procedure used for IL **14**. From methyl iodide (10.0 mmol) and 1,4,5-trimethylimidazole (6.0 mmol), there was obtained 1,3,4,5-tetramethylimidazolium iodide as a white solid. IL **12** was then synthesized as the same procedure used for IL **3** and obtained as a yellow liquid. ^{1}H

NMR (400 MHz, DMSO-d_6): δ 8.87 (s, 1H), 3.69 (s, 6H), 2.19 (s, 6H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 135.5, 127.5, 121.8, 118.6, 33.6, 8.1 ppm.

References

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The “$AgNO_3$ test”

The “$AgNO_3$ test” is a qualitative test which is based on the formation of halogenated silver precipitate when an $AgNO_3$ acid aqueous solution is contacted with a halide ion source.

In the case of hydrophobic ionic liquids, the test is operated during aqueous washing of the ionic liquid on a sample of the aqueous layer. For hydrophilic ionic liquids, the test was realized directly on a sample of the neat ionic liquid. This simple visual method permits the determination of halide ion amount as low as 3×10^{-3} mol/L.

Copies of ^{1}H NMR and ^{13}C NMR spectra for Ionic Liquids

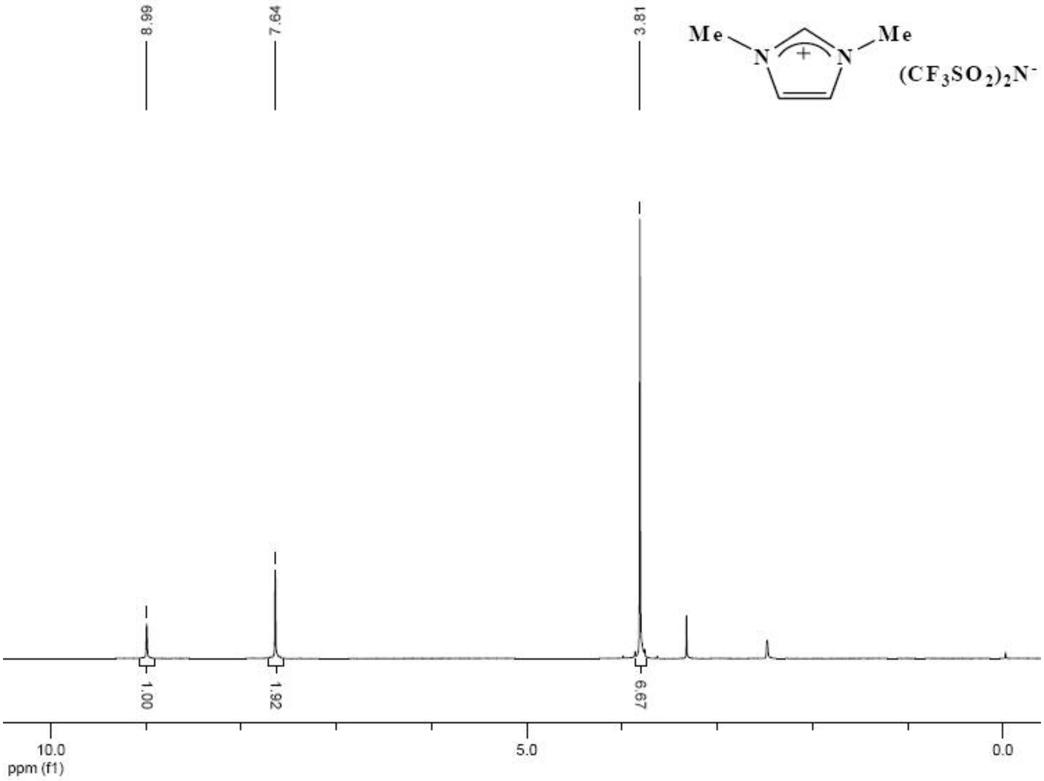

Figure 1 ^{1}H NMR spectrum of 1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

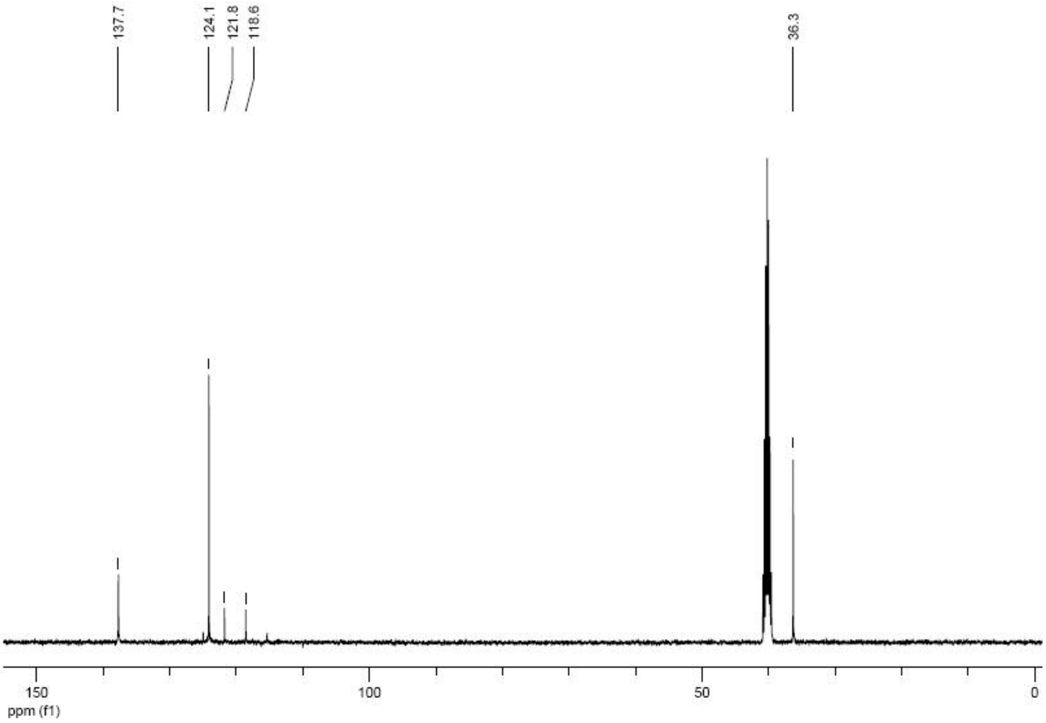

Figure 2 ^{13}C NMR spectrum of 1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

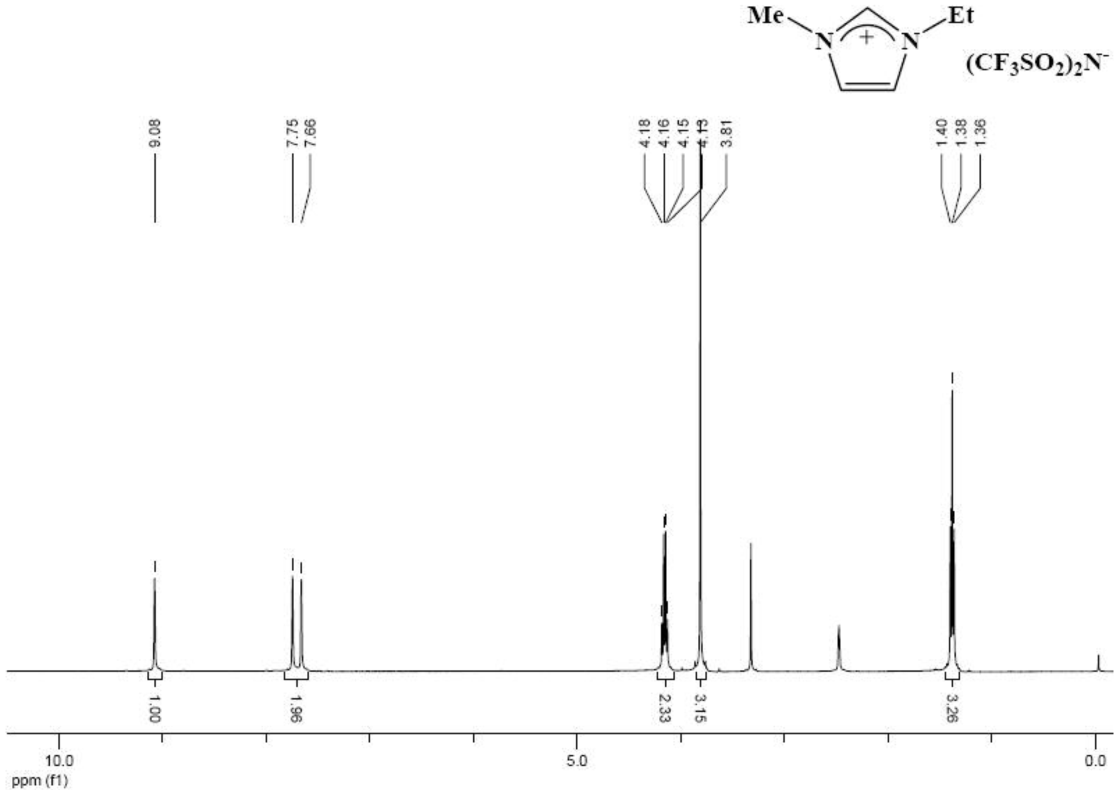

Figure 3 ^{1}H NMR spectrum of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

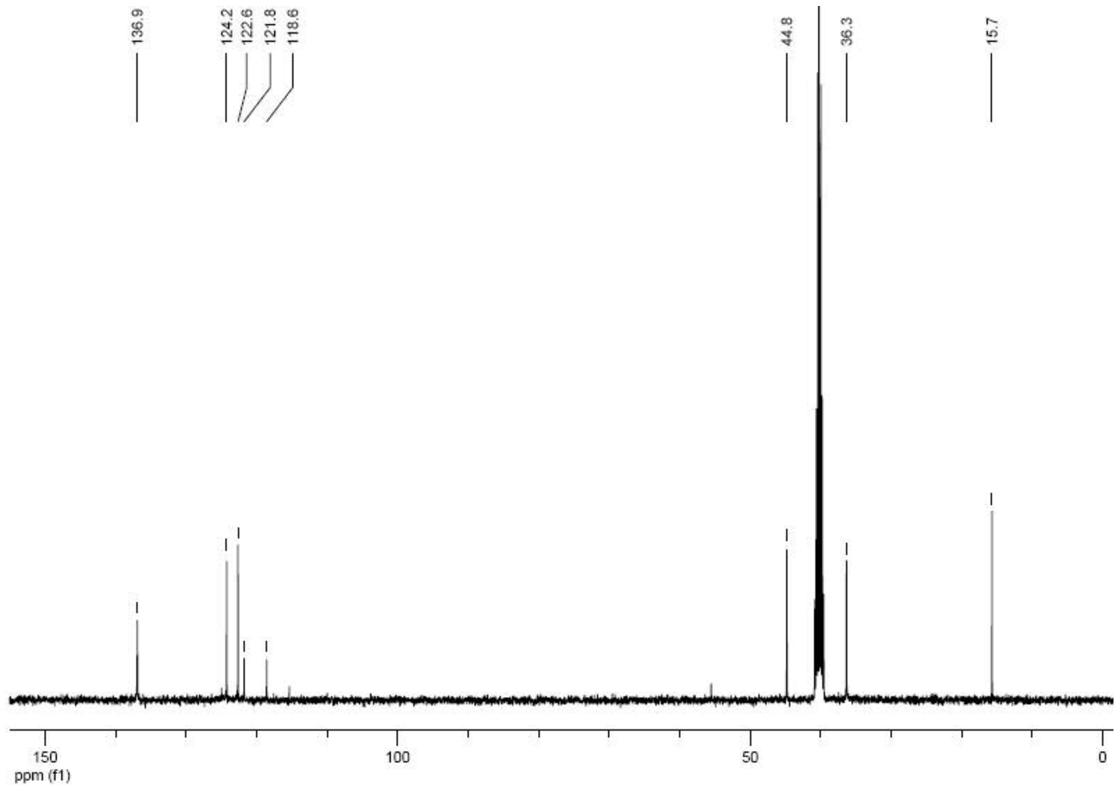

Figure 4 ^{13}C NMR spectrum of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

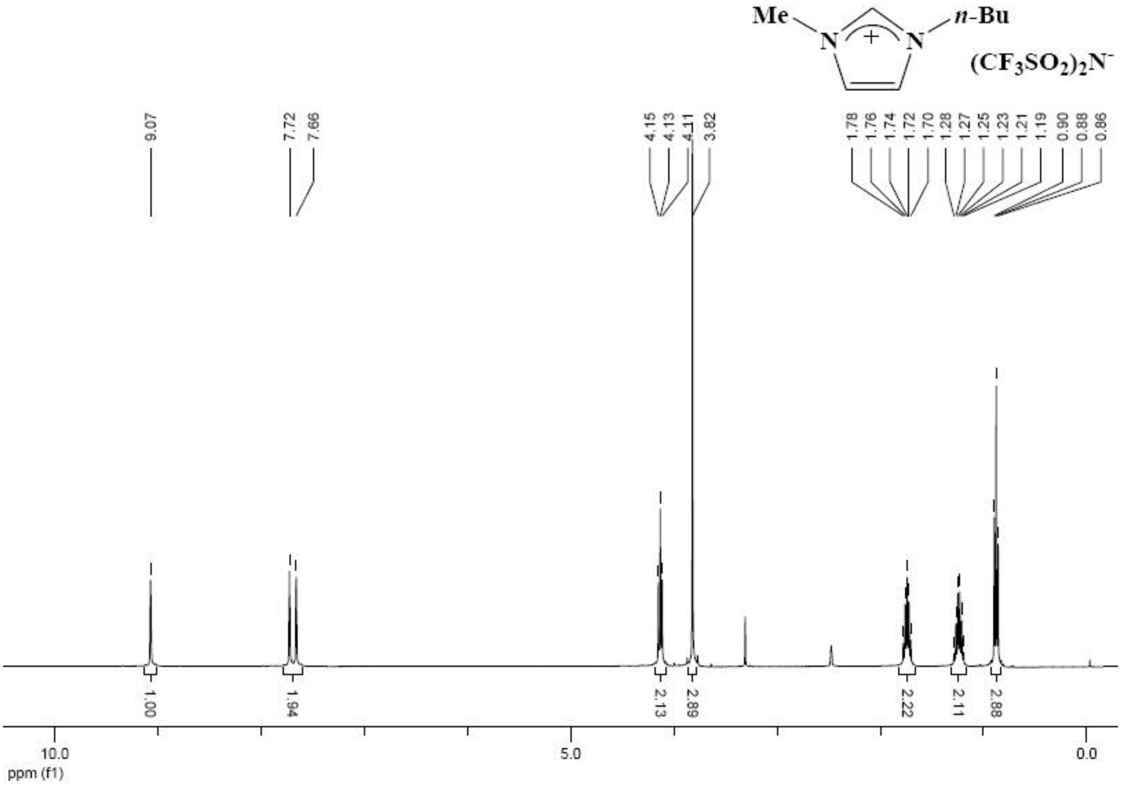

Figure 5 ^{1}H NMR spectrum of 1-*n*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

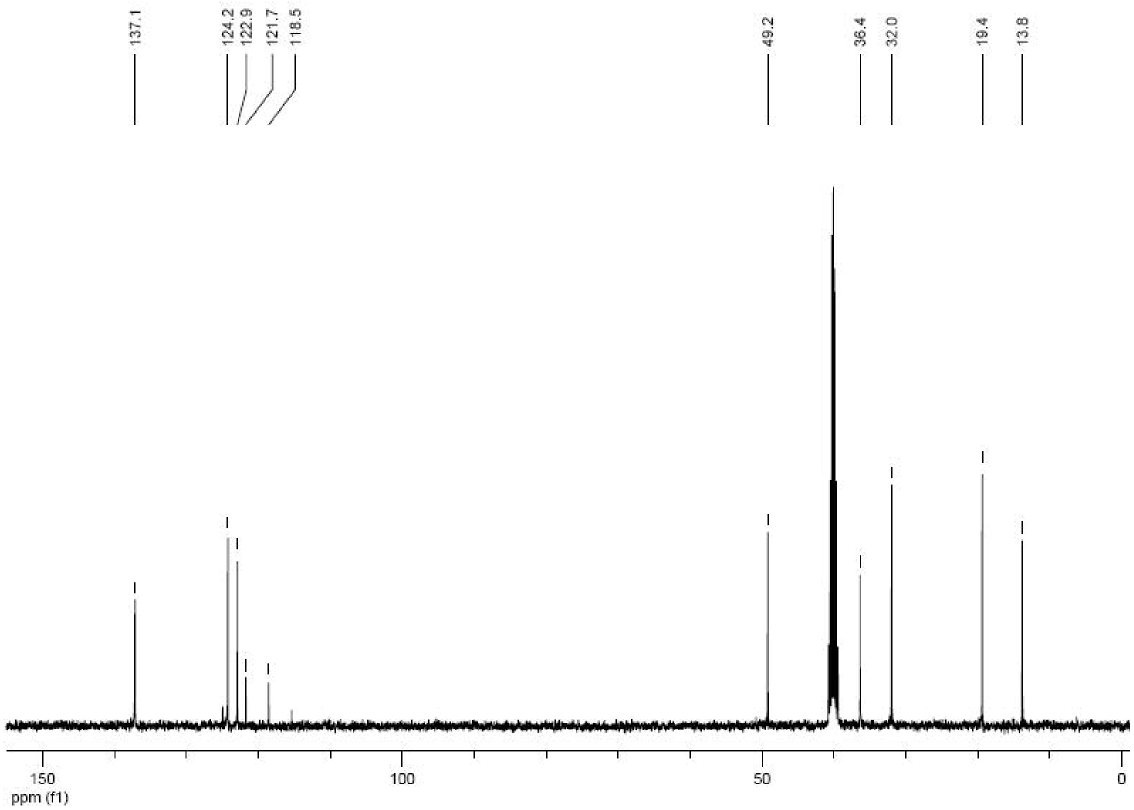

Figure 6 ^{13}C NMR spectrum of 1-*n*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

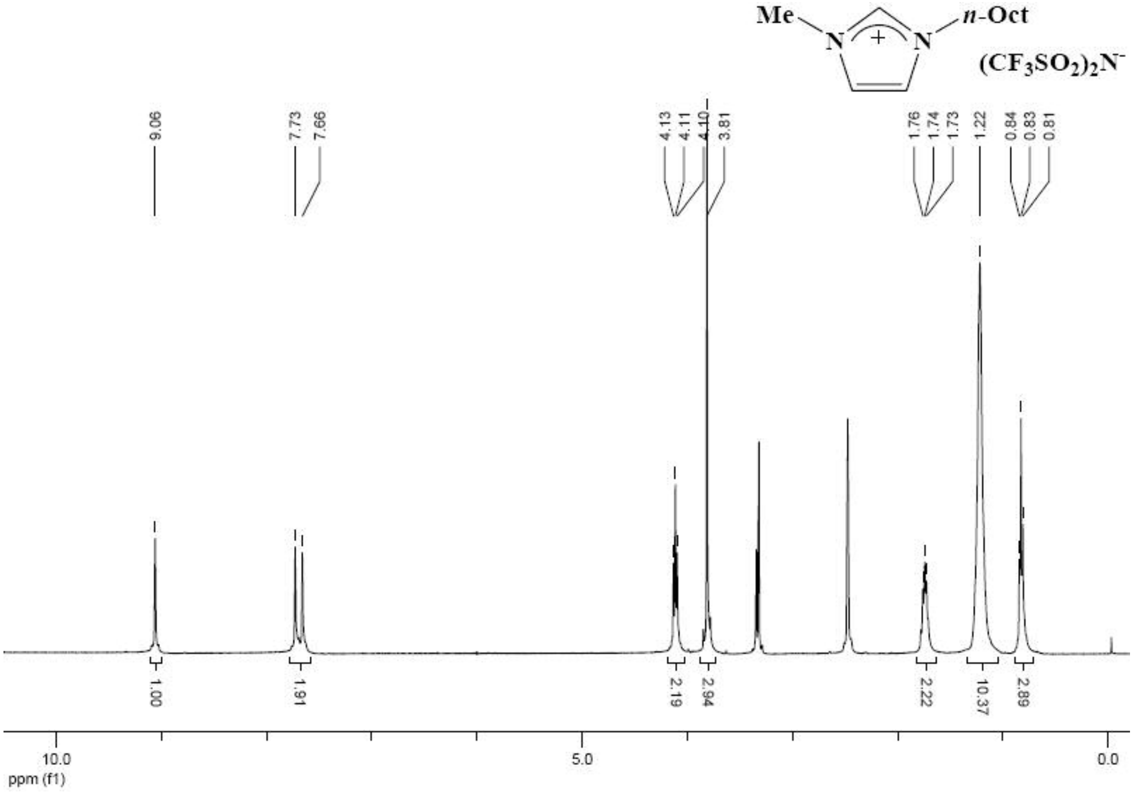

Figure 7 ^{1}H NMR spectrum of 1-*n*-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

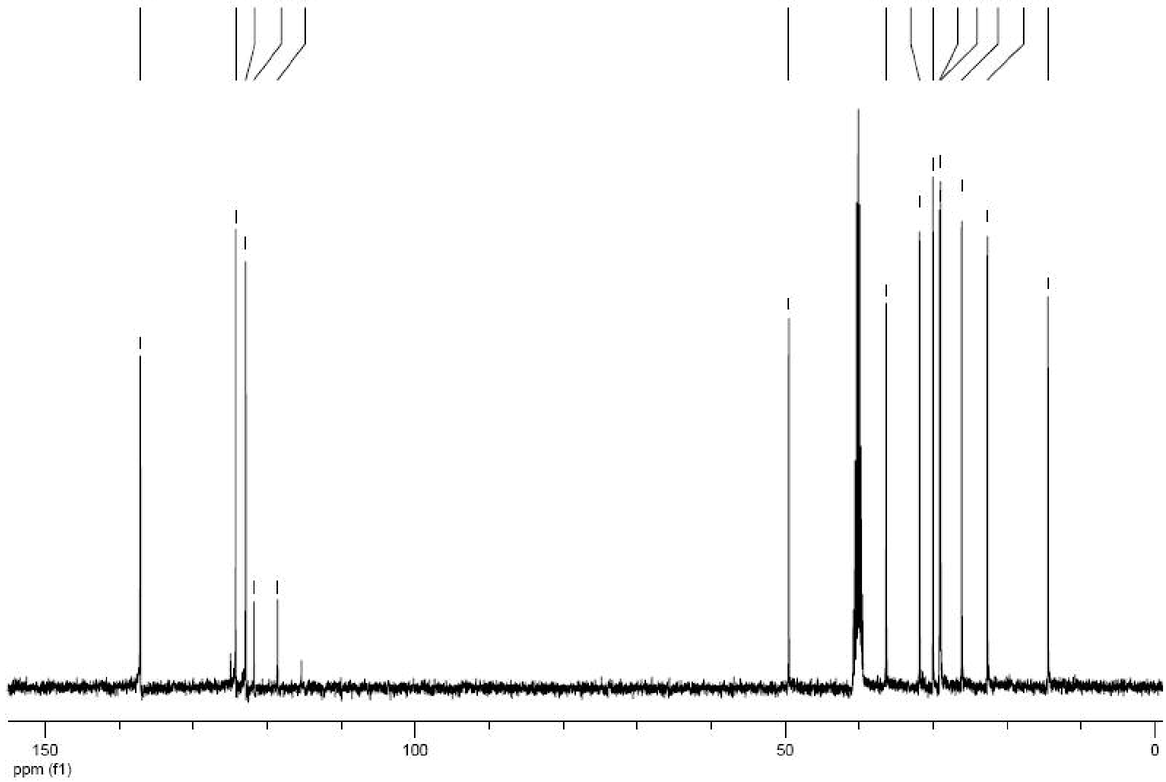

Figure 8 ^{13}C NMR spectrum of 1-*n*-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

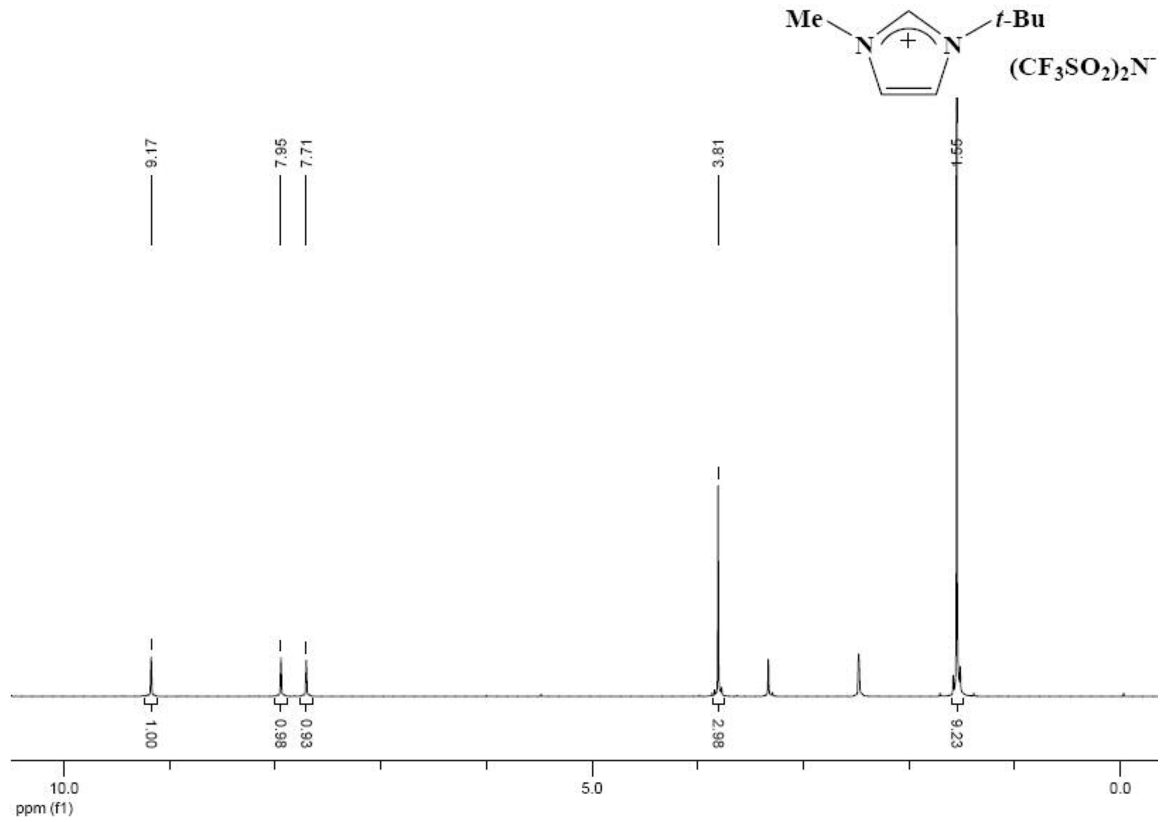

Figure 9 ^{1}H NMR spectrum of 1-*t*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

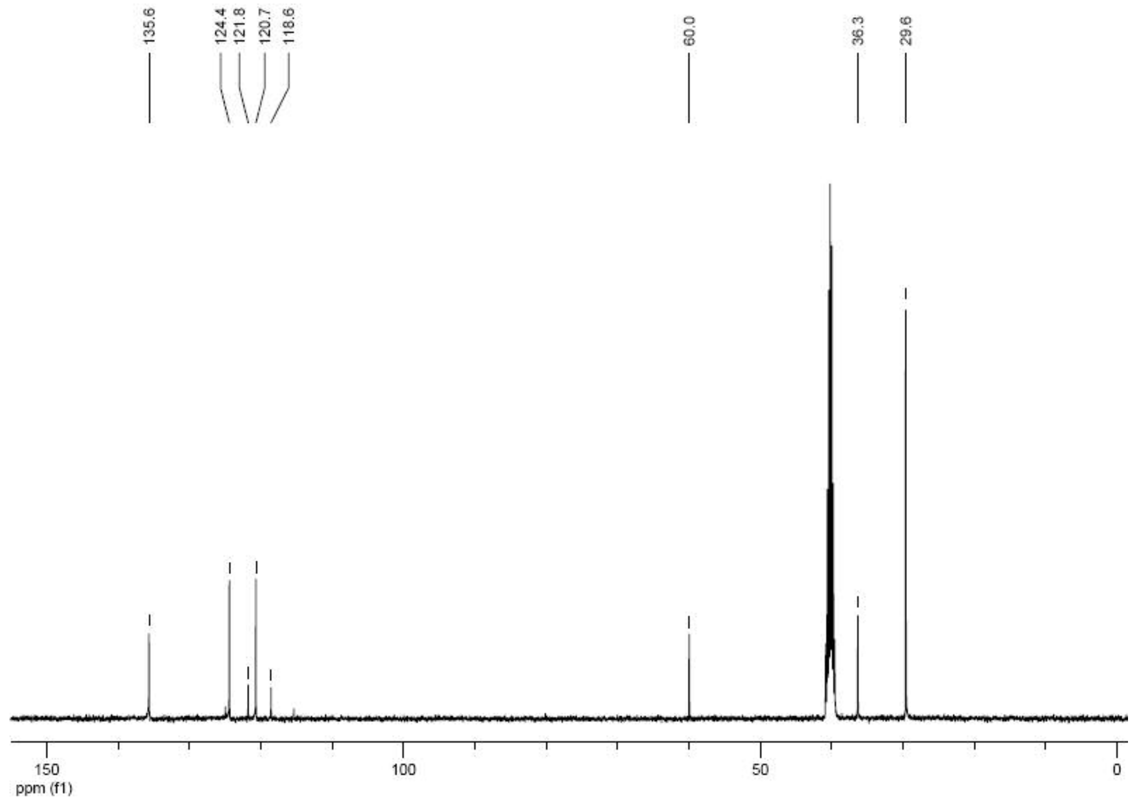

Figure 10 ^{13}C NMR spectrum of 1-*t*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

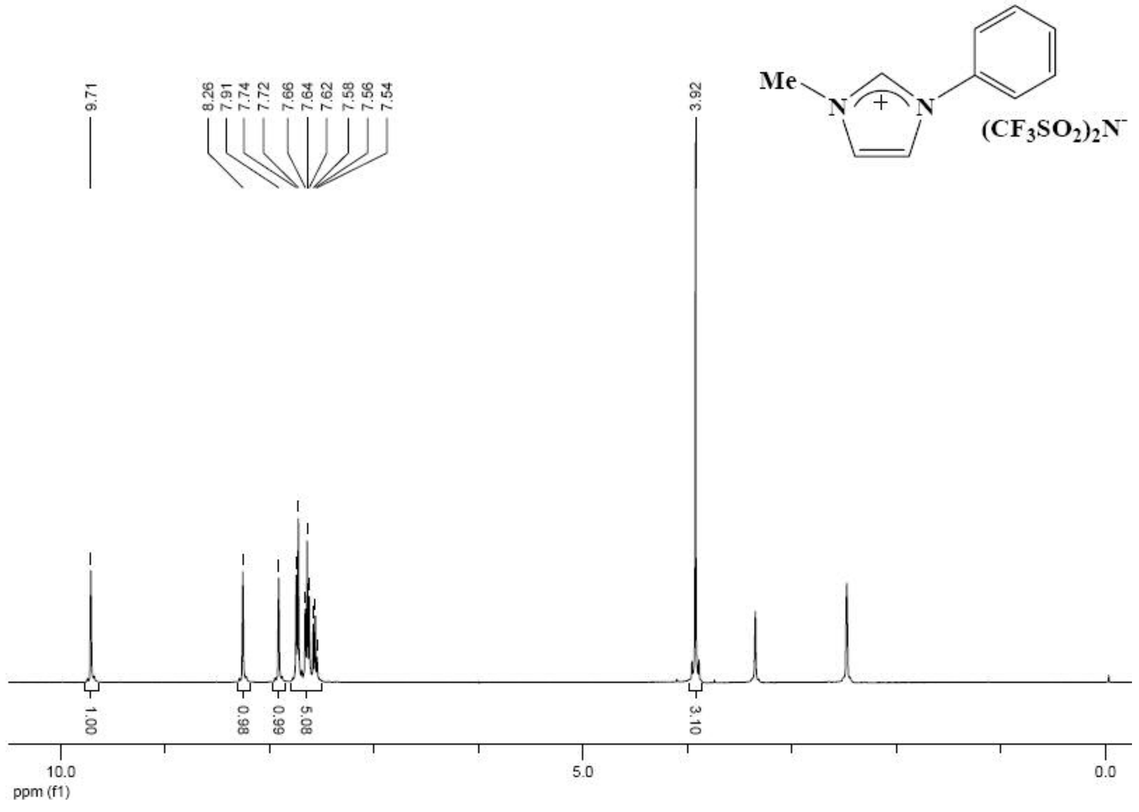

Figure 11 ^{1}H NMR spectrum of 1-phenyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

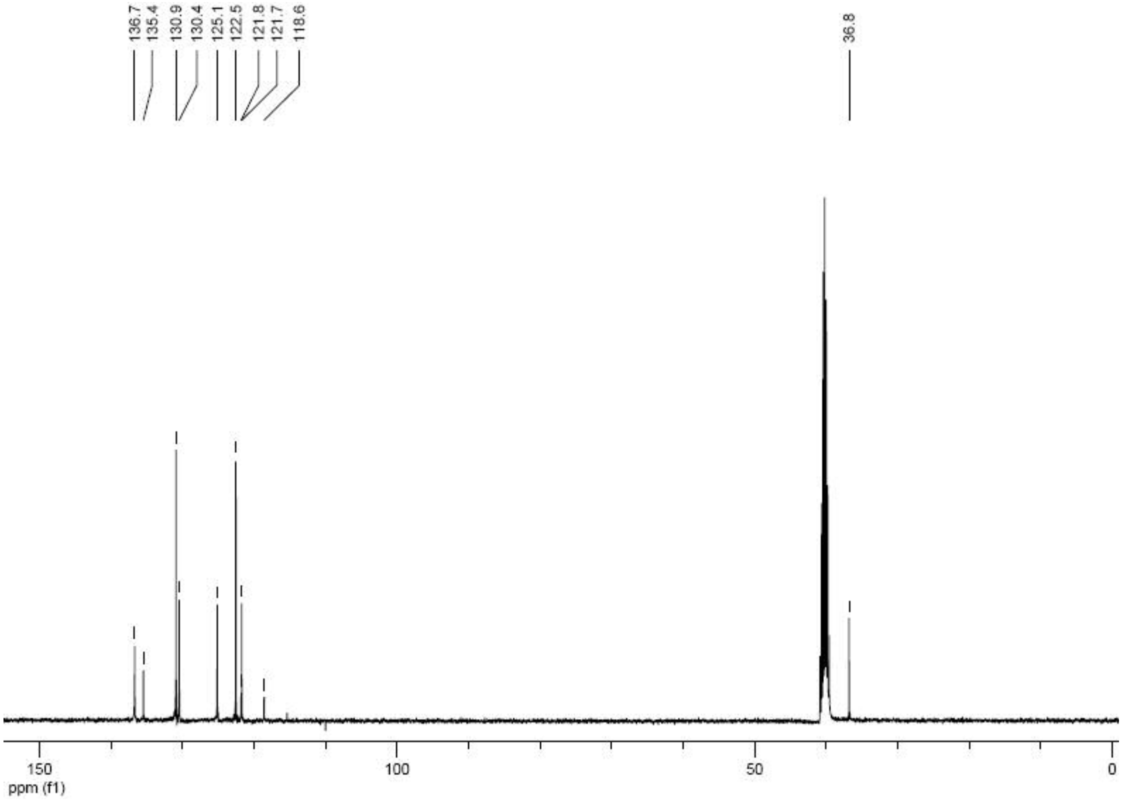

Figure 12 ^{13}C NMR spectrum of 1-phenyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

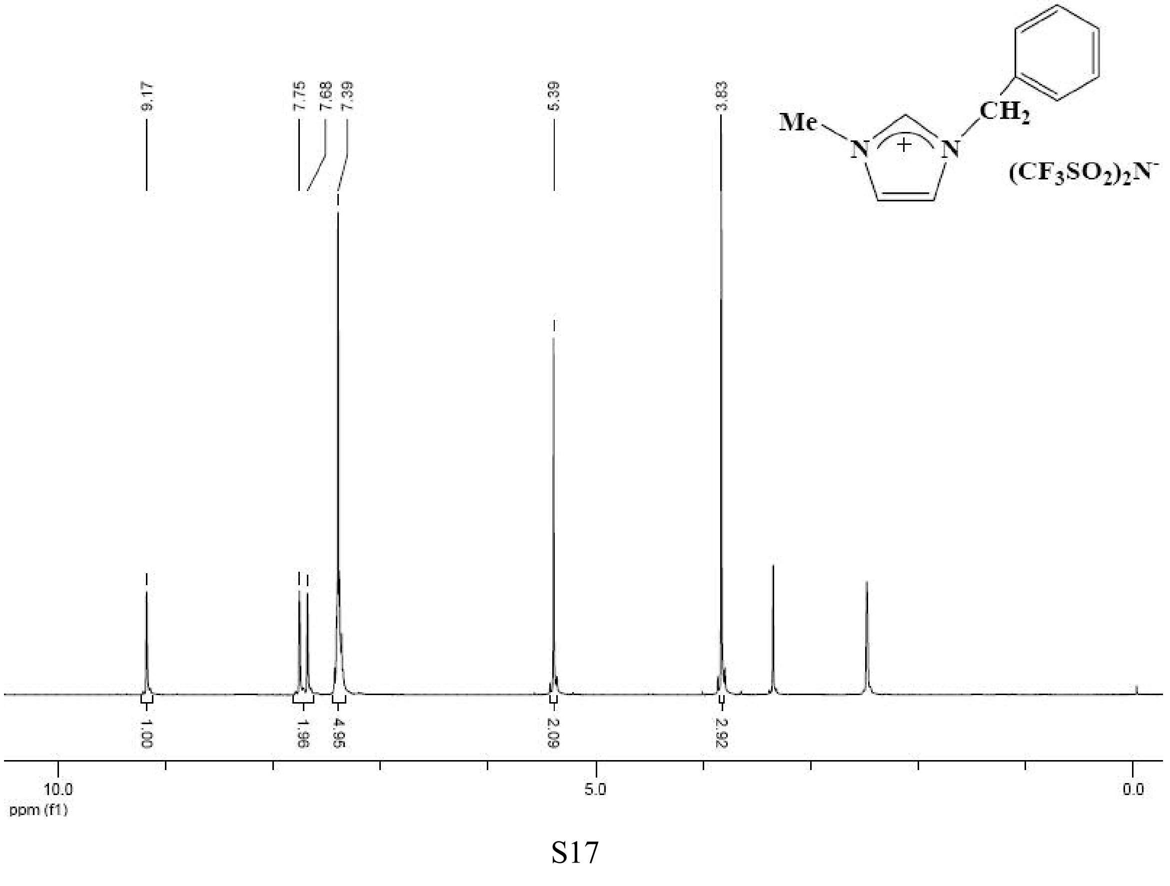

Figure 13 ^{1}H NMR spectrum of 1-benzyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

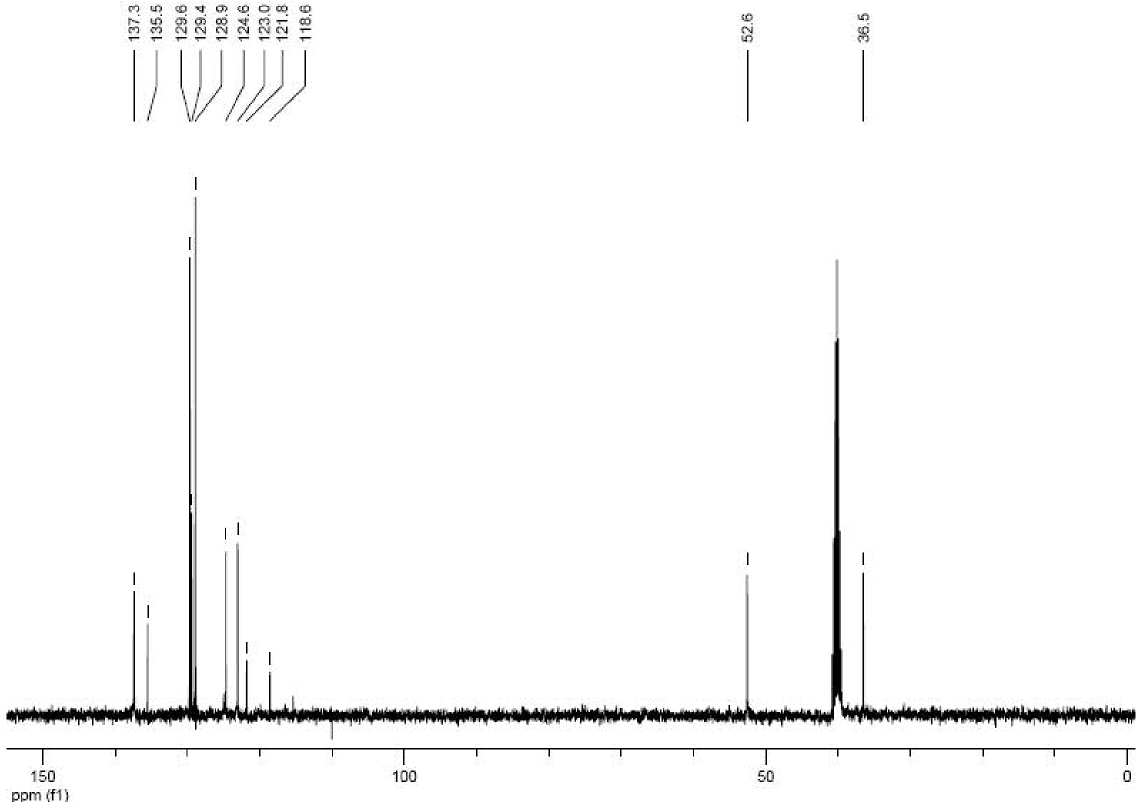

Figure 14 ^{13}C NMR spectrum of 1-benzyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

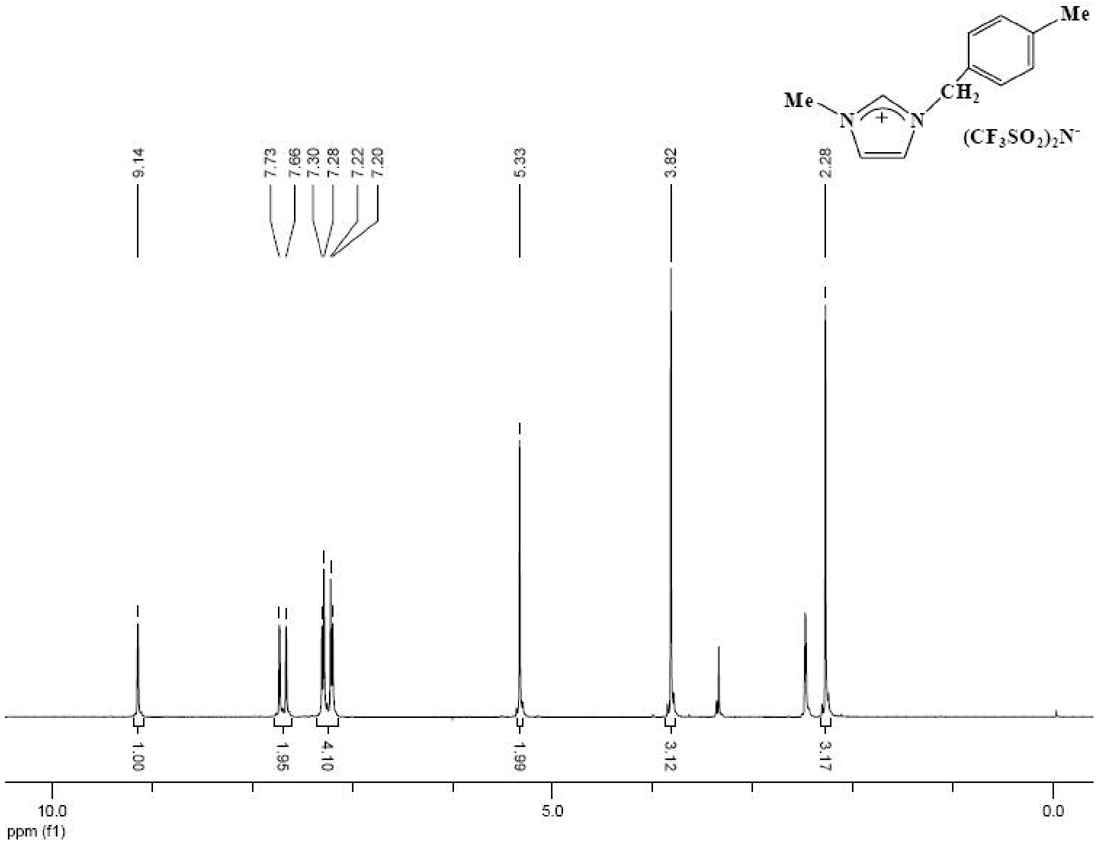

Figure 15 ^{1}H NMR spectrum of 1-(*p*-methylbenzyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

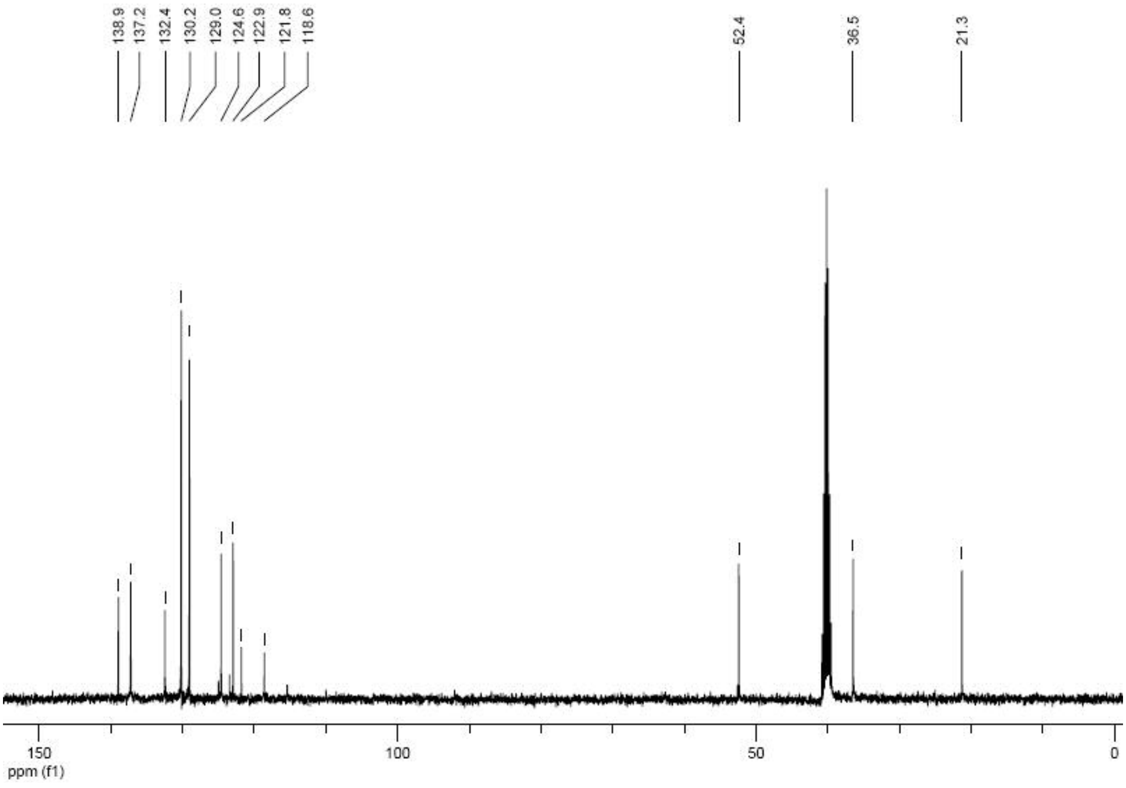

Figure 16 ^{13}C NMR spectrum of 1-(*p*-methylbenzyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

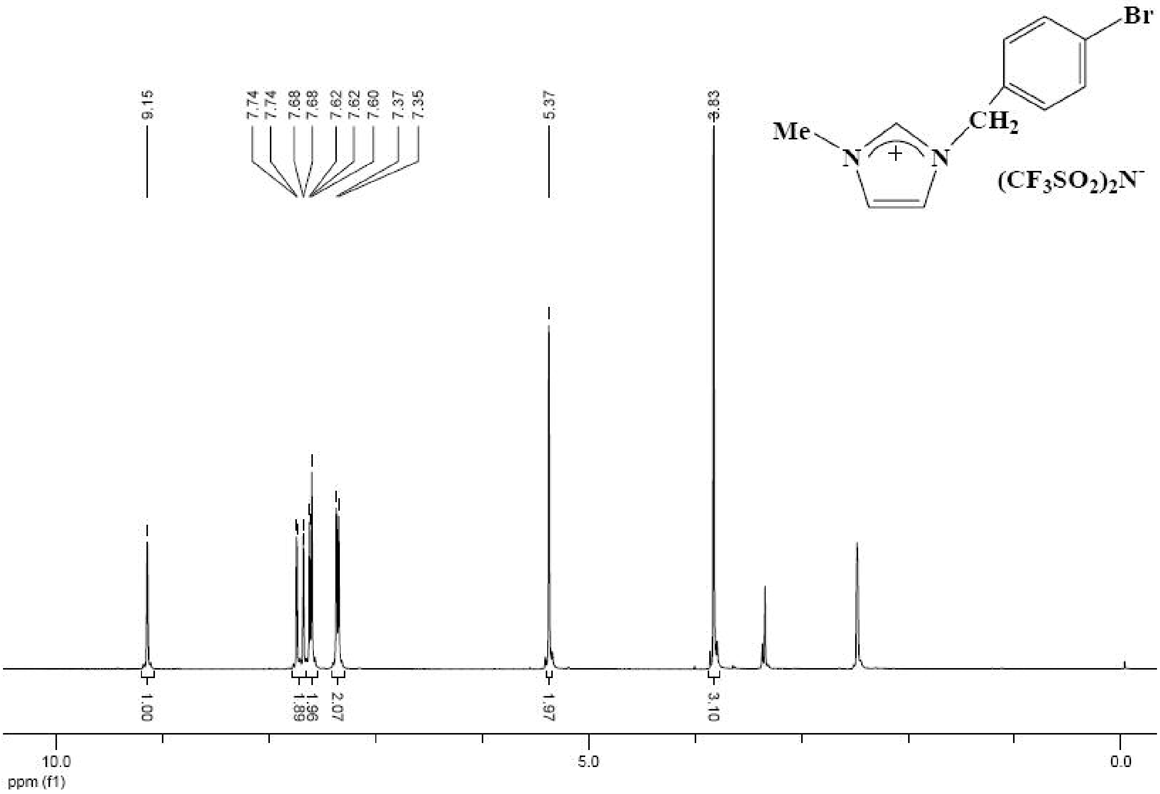

Figure 17 ^{1}H NMR spectrum of 1-(*p*-bromobenzyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

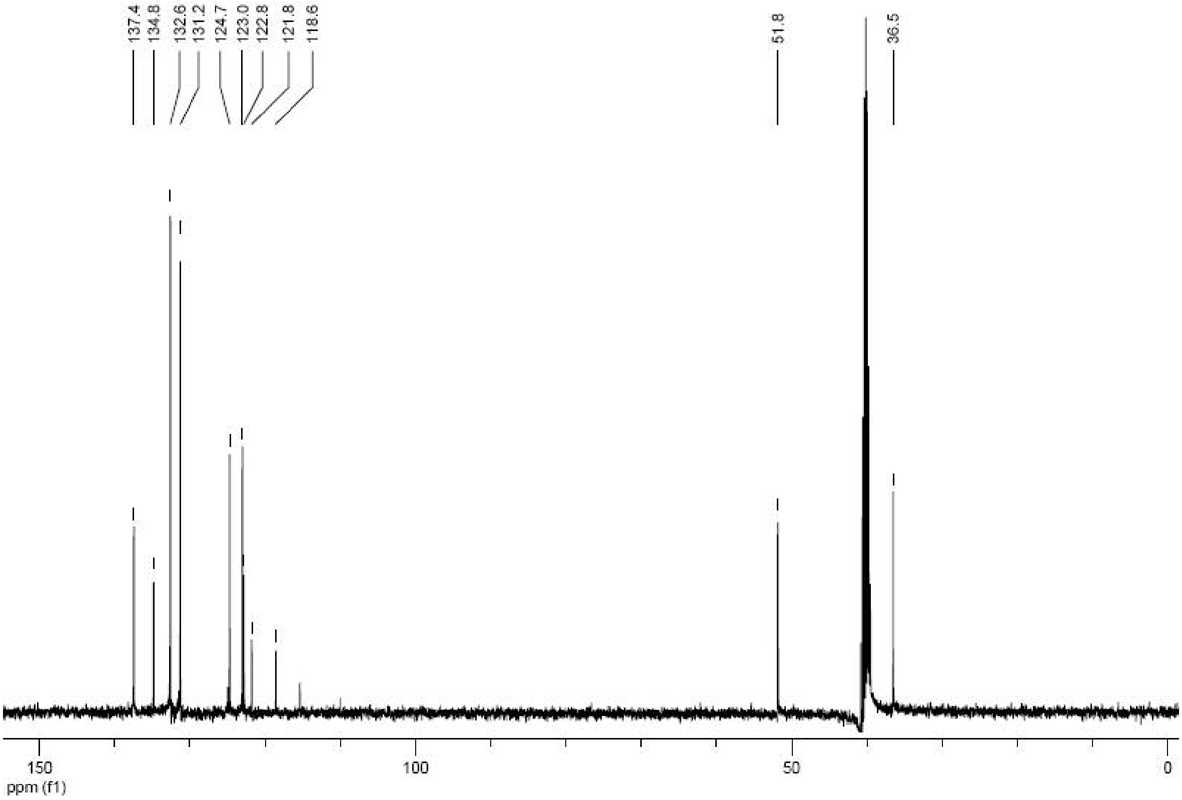

Figure 18 ^{13}C NMR spectrum of 1-(*p*-bromobenzyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

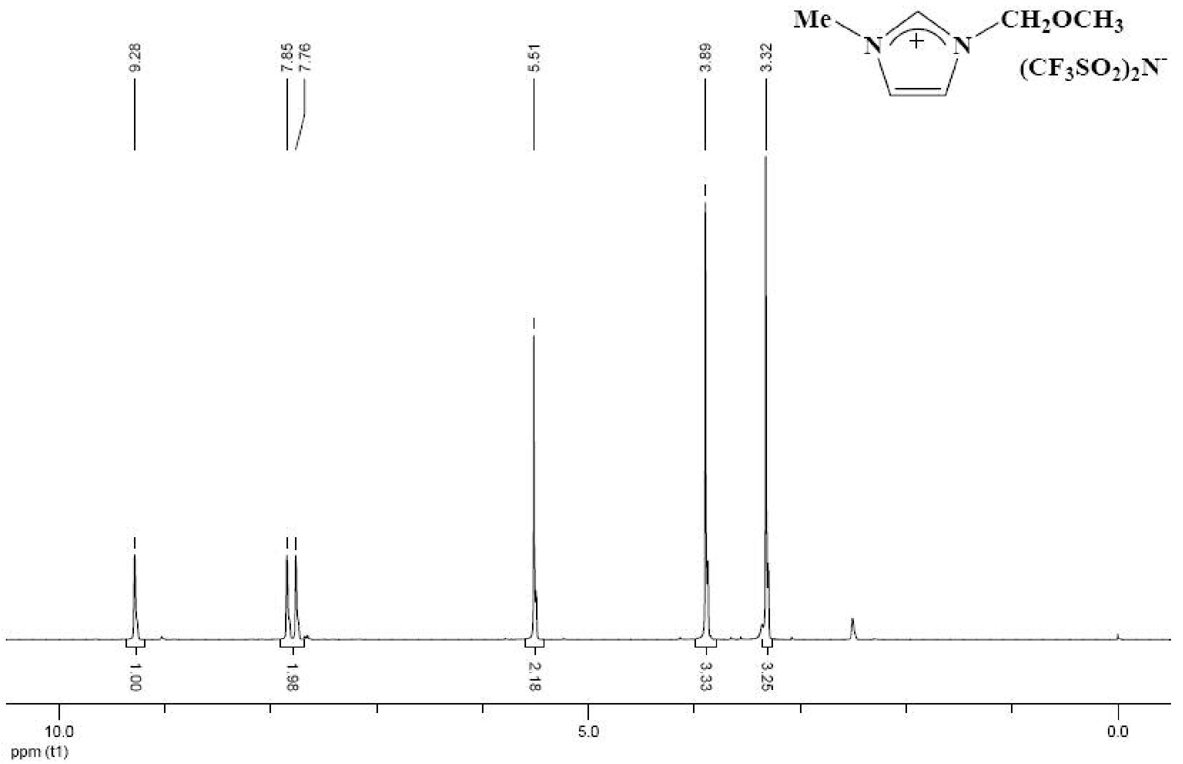

Figure 19 ^{1}H NMR spectrum of 1-methoxylmethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

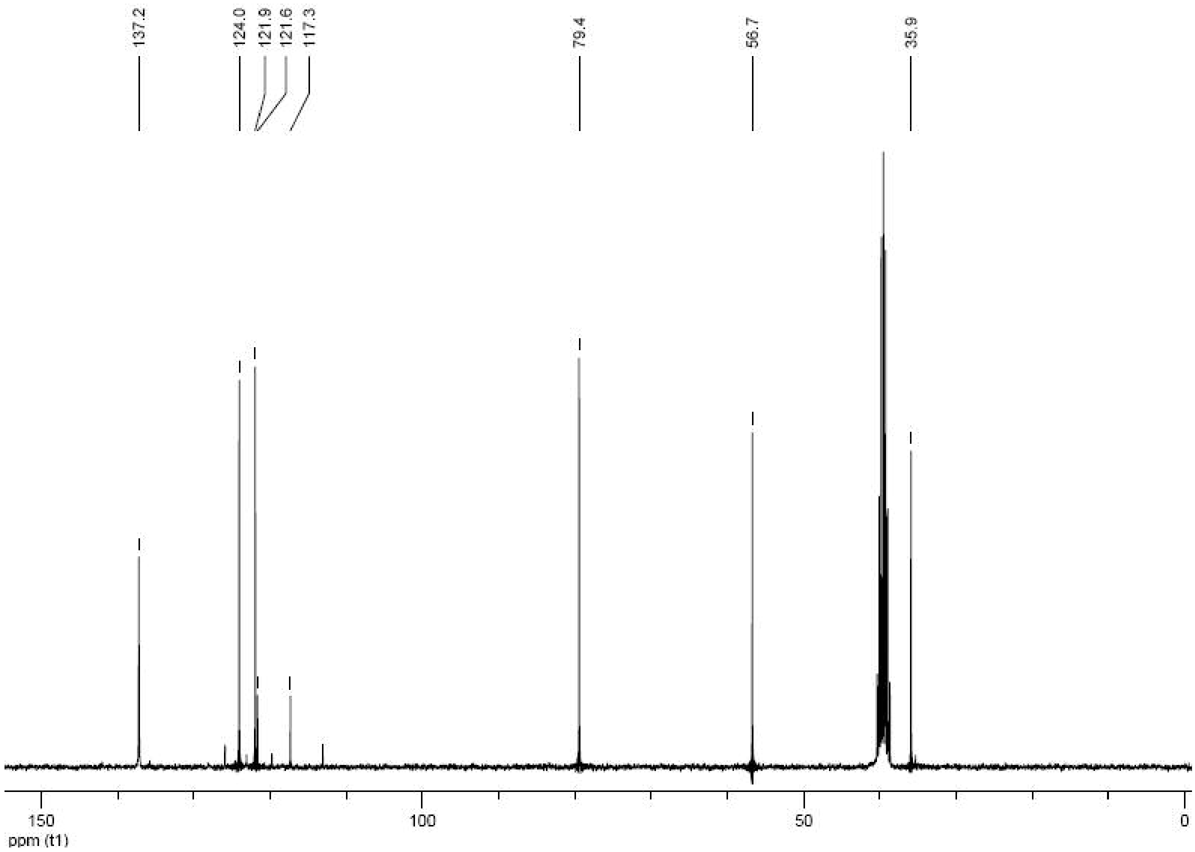

Figure 20 ^{13}C NMR spectrum of 1-methoxylmethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

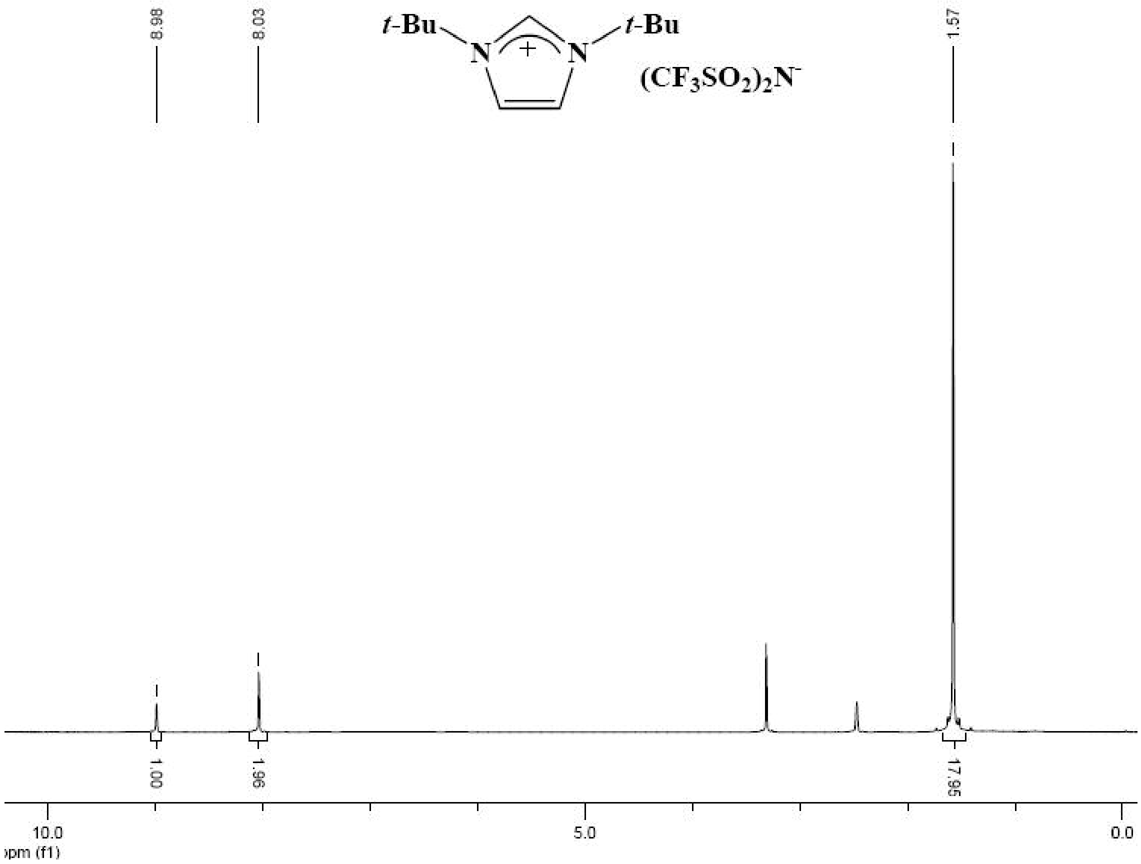

Figure 21 ^{1}H NMR spectrum of 1,3-Di-*t*-butylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

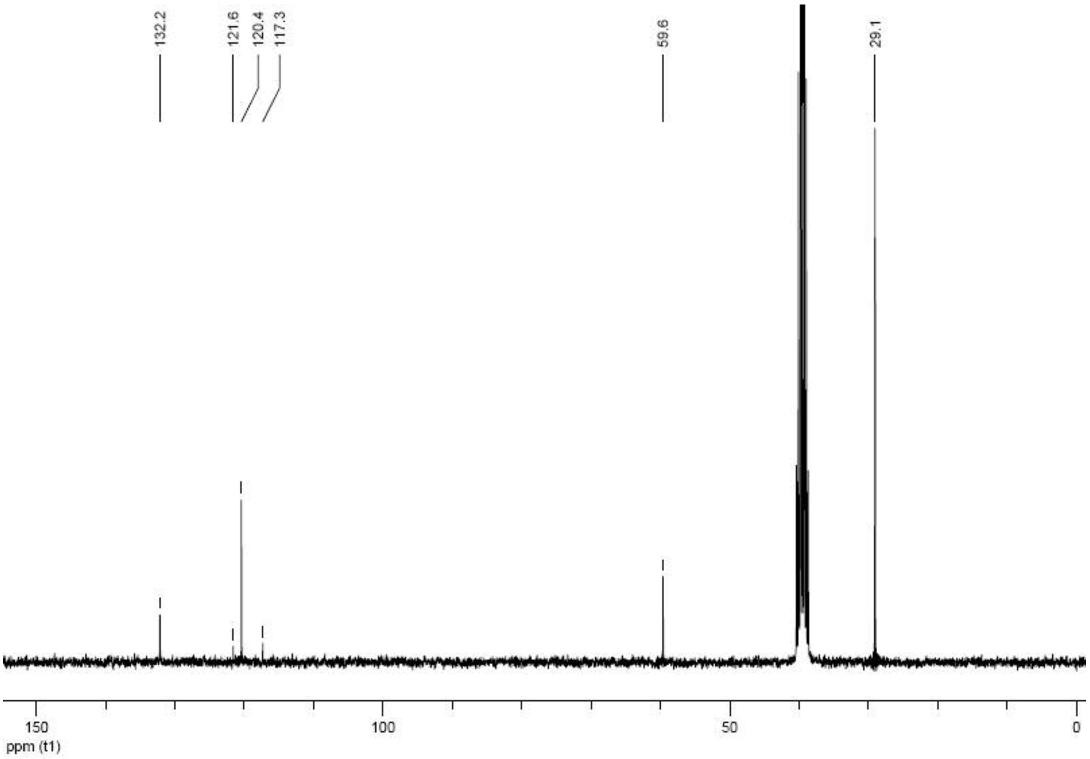

Figure 22 ^{13}C NMR spectrum of 1,3-Di-*t*-butylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

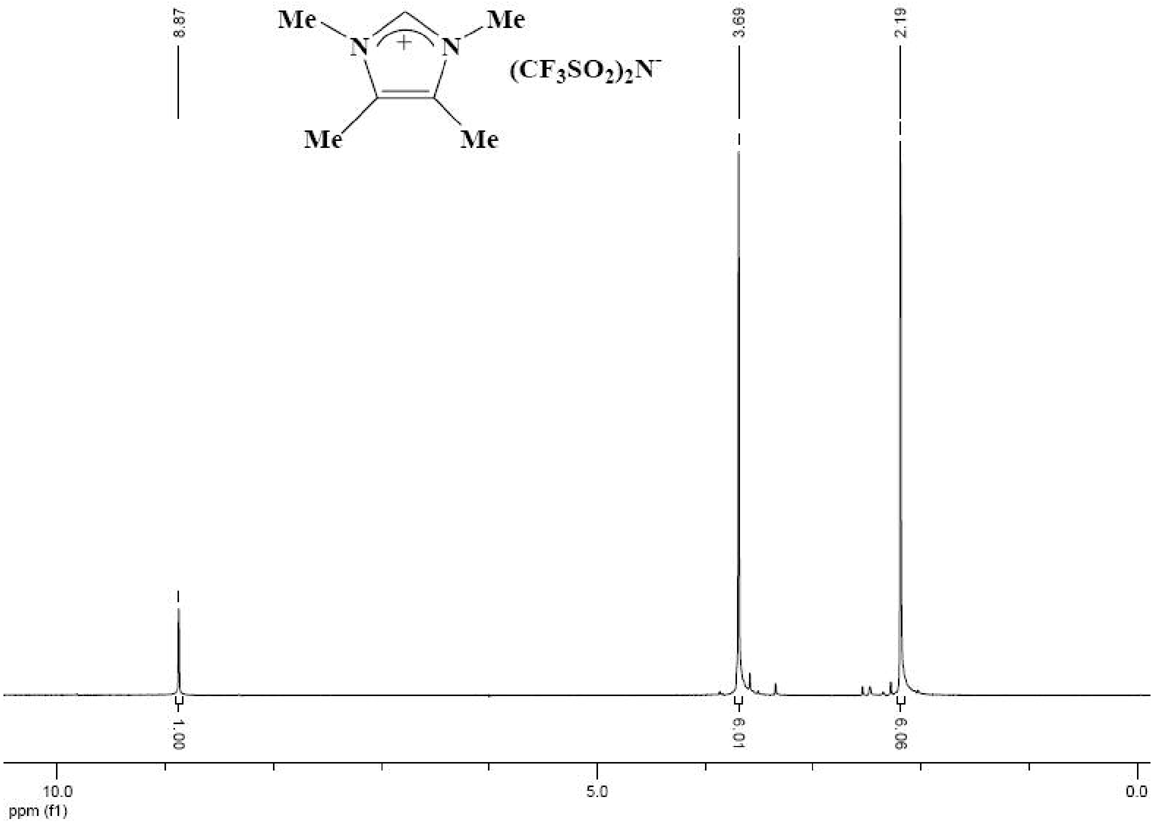

Figure 23 ^{1}H NMR spectrum of 1,3,4,5-tetramethylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

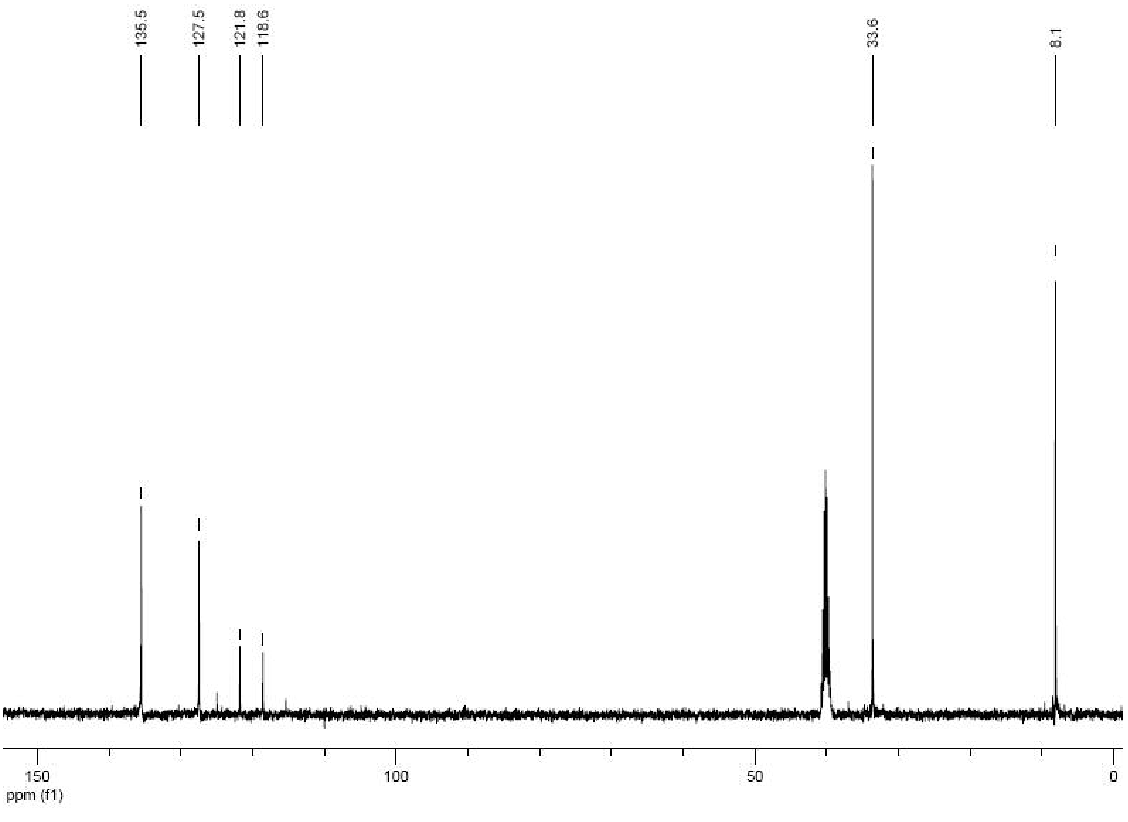

Figure 24 ^{13}C NMR spectrum of 1,3,4,5-tetramethylimidazolium bis(trifluoromethanesulfonyl)imide in DMSO-d_6.

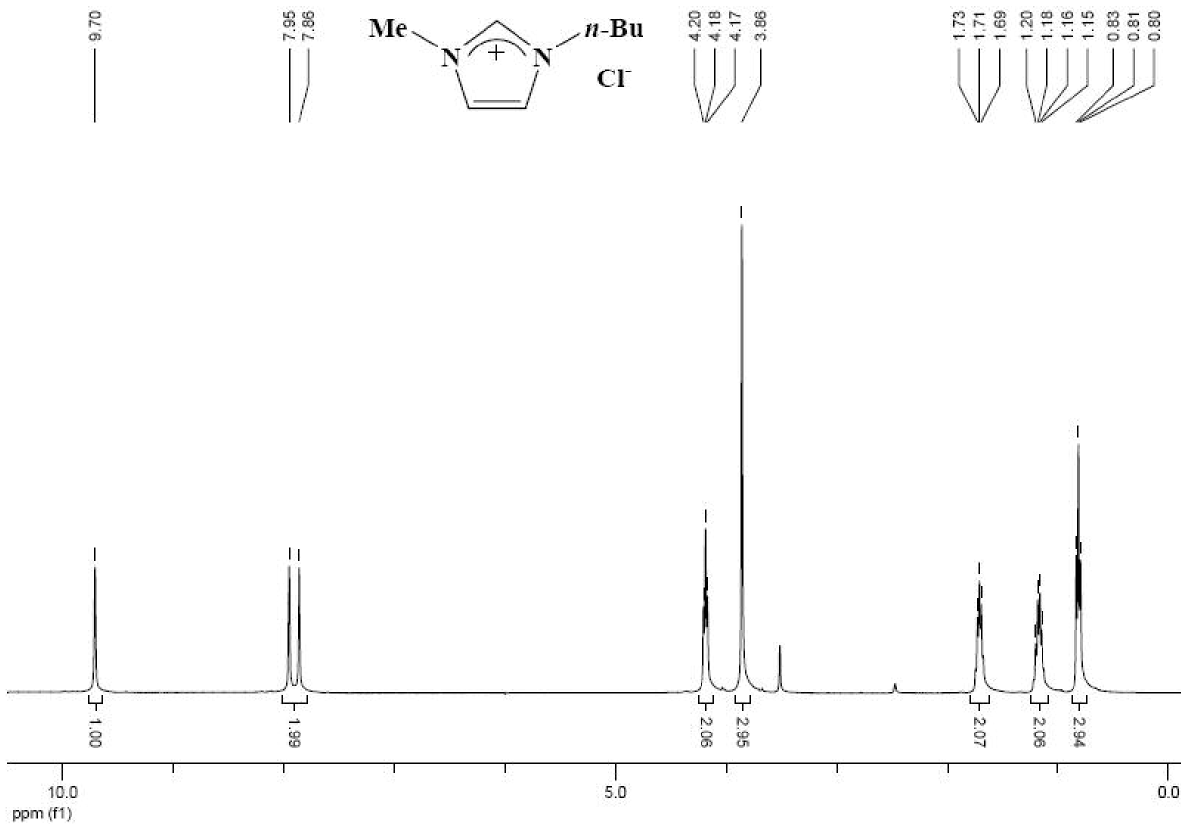

Figure 25 ^{1}H NMR spectrum of 1-*n*-butyl-3-methylimidazolium chloride in DMSO-d_6.

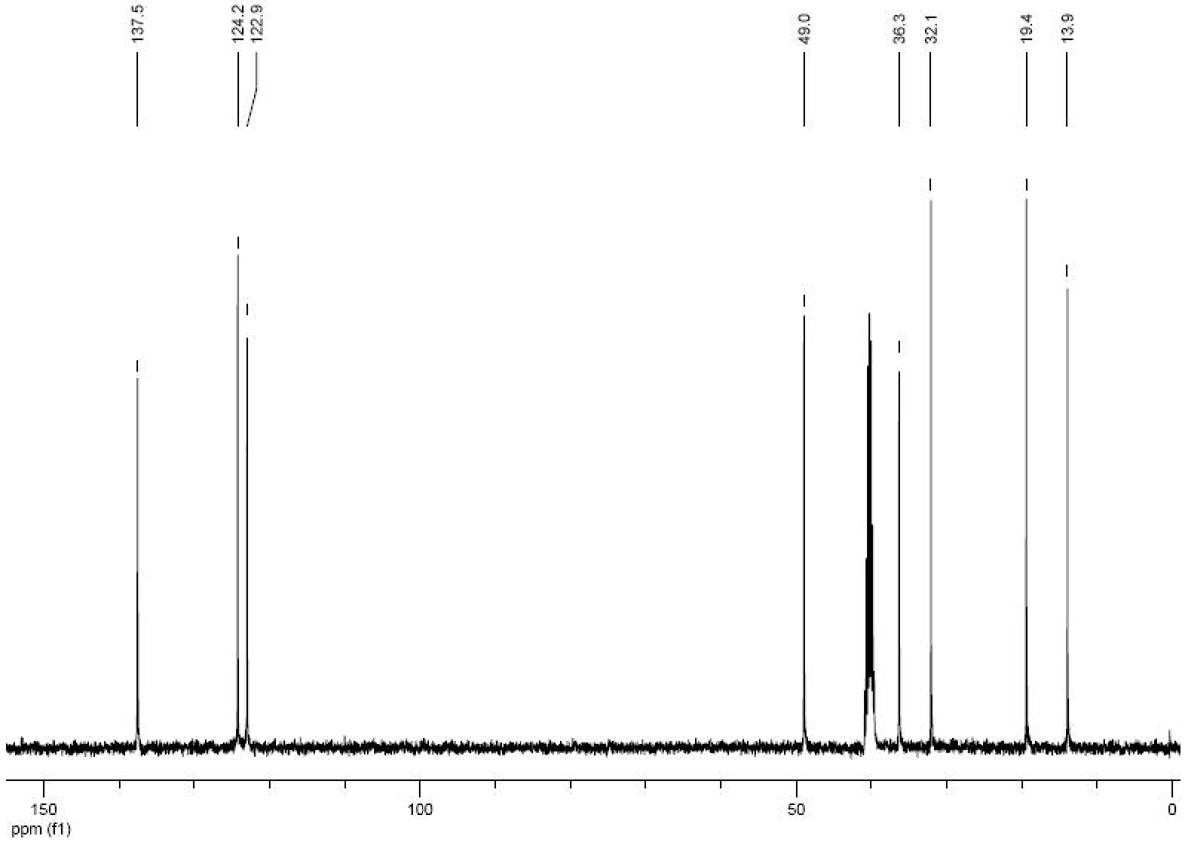

Figure 26 ^{13}C NMR spectrum of 1-*n*-butyl-3-methylimidazolium chloride in DMSO-d_6.

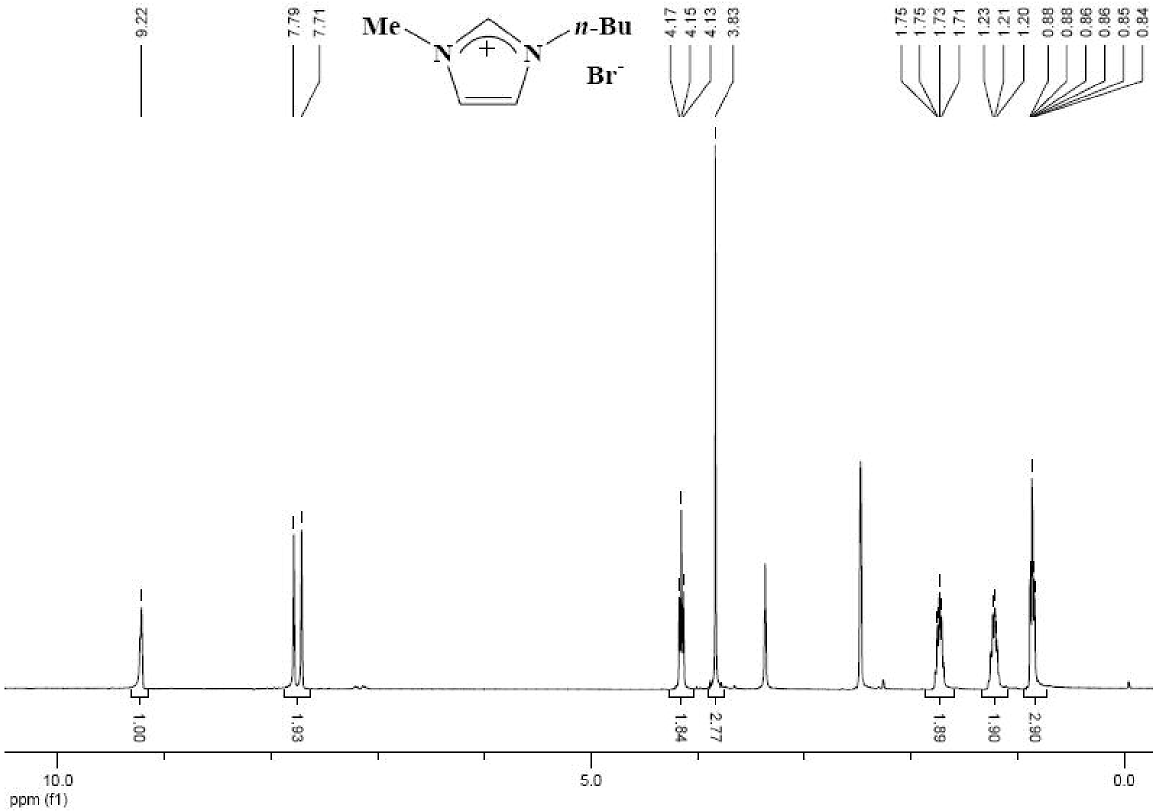

Figure 27 ^{1}H NMR spectrum of 1-*n*-butyl-3-methylimidazolium bromide in DMSO-d_6.

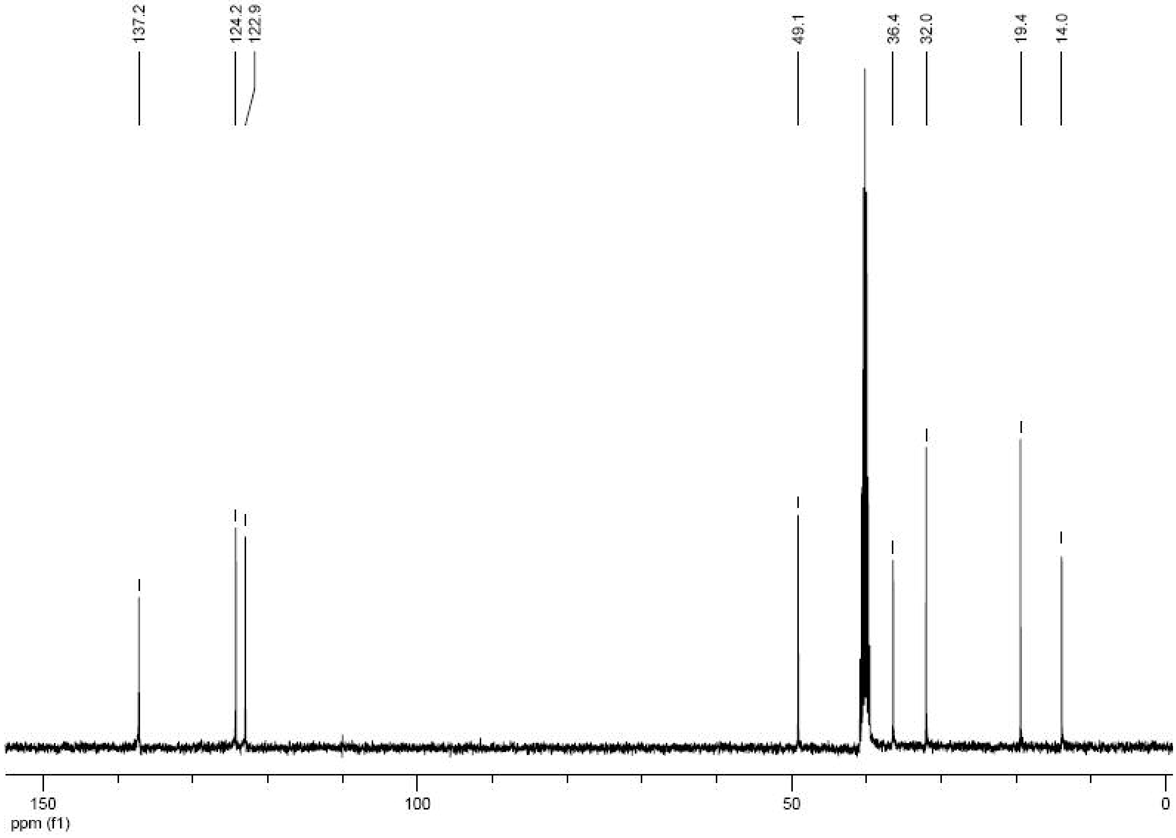

Figure 28 ^{13}C NMR spectrum of 1-*n*-butyl-3-methylimidazolium bromide in DMSO-d_6.

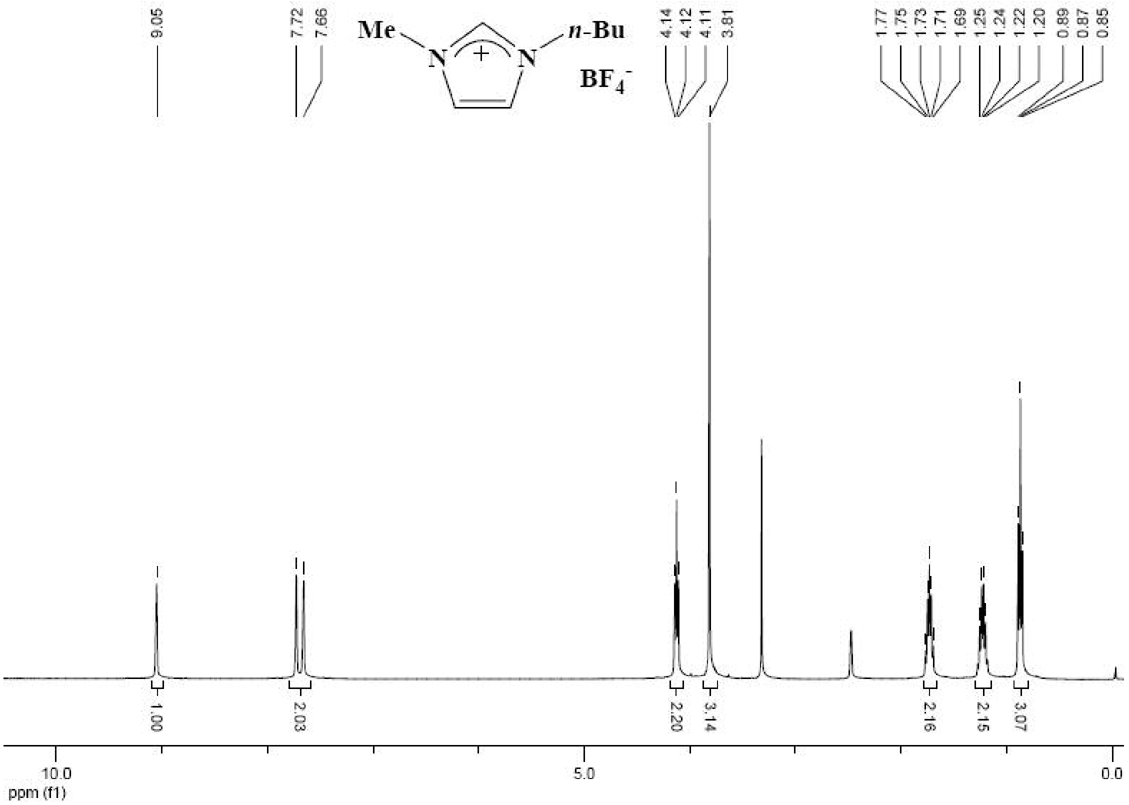

Figure 29 ^{1}H NMR spectrum of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate in DMSO-d_6.

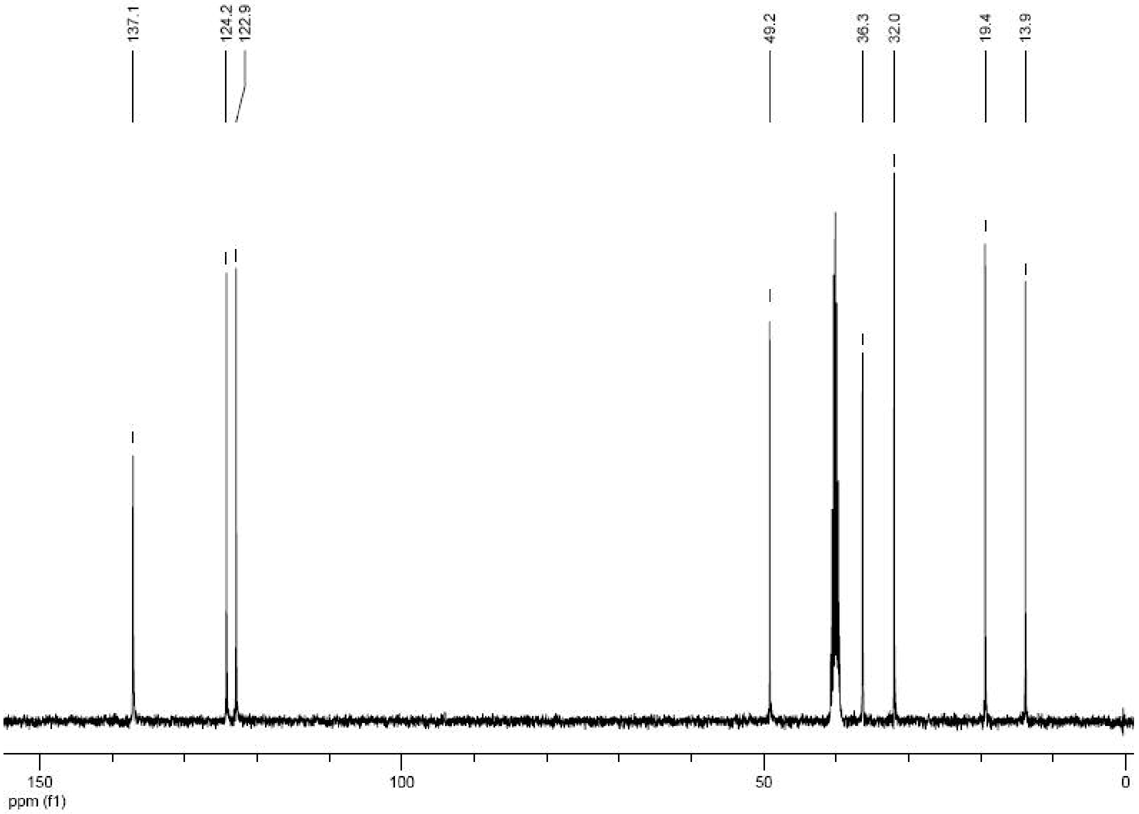

Figure 30 ^{13}C NMR spectrum of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate in DMSO-d_6.

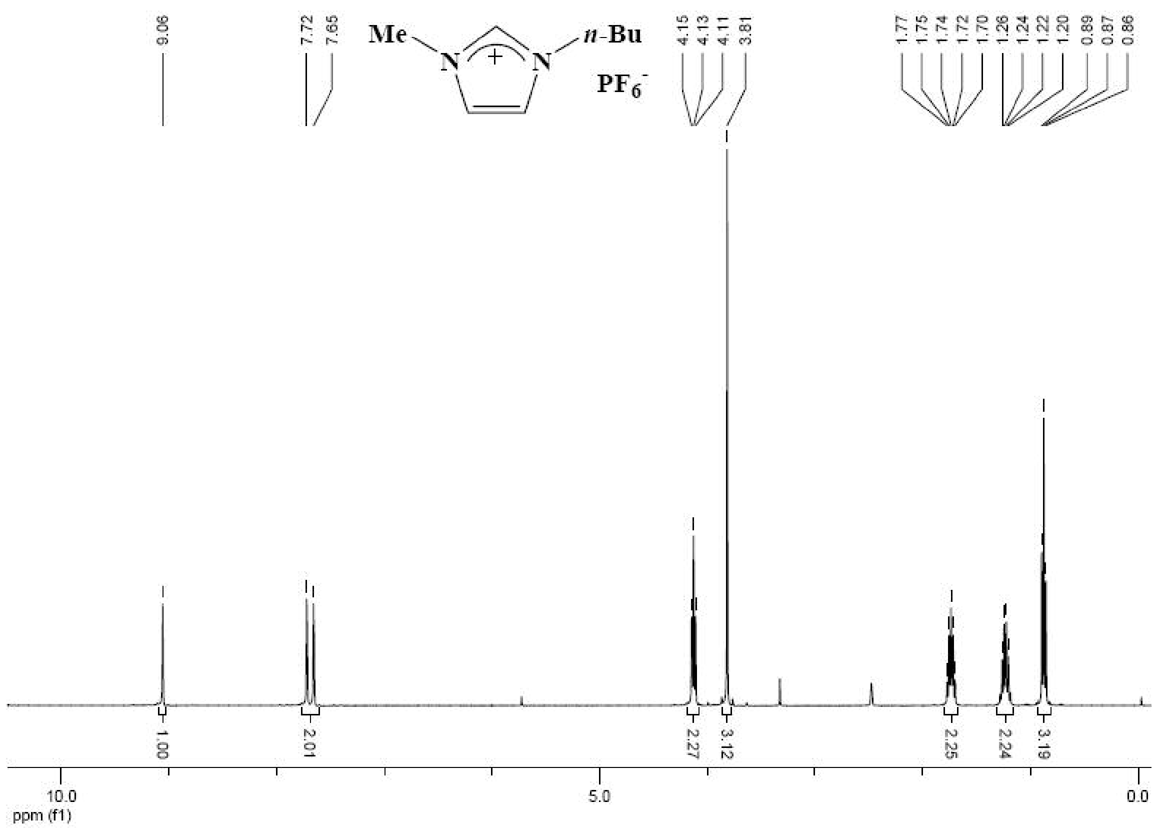

Figure 31 ^{1}H NMR spectrum of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate in DMSO-d_6.

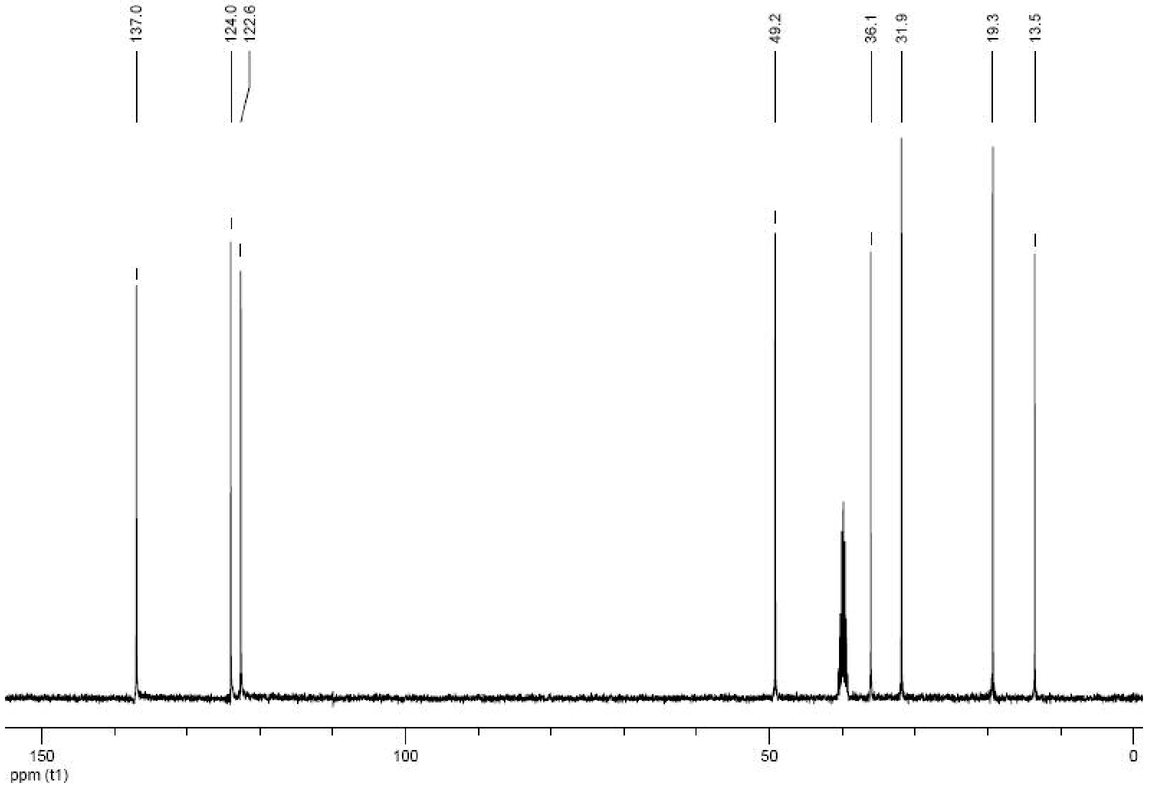

Figure 32 ^{13}C NMR spectrum of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate in DMSO-d_6.

Details of model experimental operation

The UV spectrum measurements were performed on a Hitachi U-3000 UV/vis spectrometer. The exact amount of DMSO (usually 10-25 mL) and indicator (usually 100 mg) were determined gravimetrically to prepare the solution of indicator whose concentration was about 50 mmol/L. The pK_a's determined with a given set of solutions are usually reproducible to within ±0.05 pK unit. Measurements for the same IL with freshly prepared solutions are generally within ±0.1 pK unit.

Scheme 6.

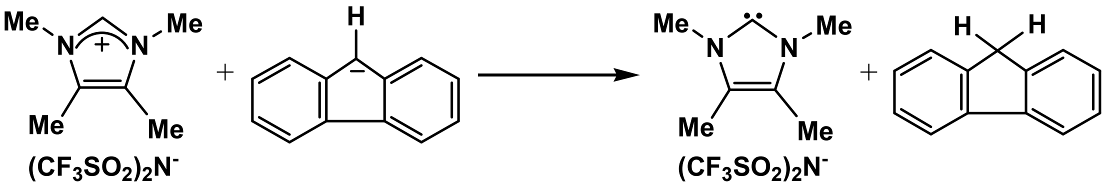

Figure S33: Absorption spectra of fluorenide ion for various added amount of fluorene during the internal dimsyl titration in DMSO at 25°C. The inlet is the correlation between absorption of fluorenide ion and added amount of fluorene.

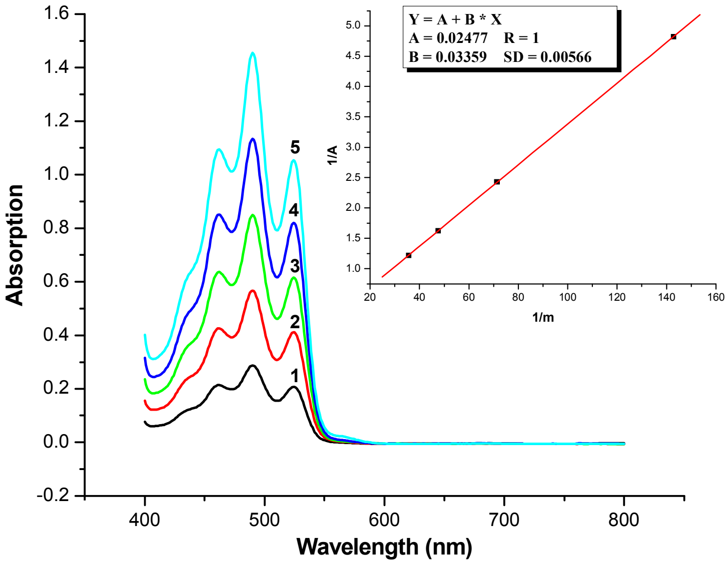

Figure S34: Absorption spectra of fluorenide ion for various added amount of IL **12** in DMSO at 25°C presented in Scheme S6.