Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The Enthalpies of Vaporisation of Ionic Liquids: New measurements and Predictions

Supporting Information

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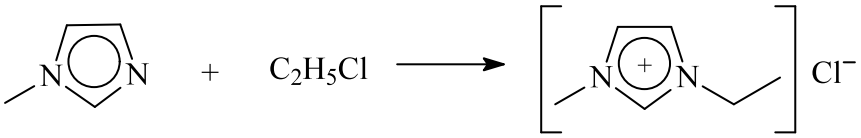
The IL syntheses are arranged in order of compound number (**1** to **7**) as listed in the paper, table 1. The syntheses of any precursors are described immediately before the synthesis of the IL.

Experimental

Materials: All reagents and solvents were analytical grade materials purchased from commercial sources (Aldrich, Acros Organics) and were used without further purification, unless stated otherwise. 1-Methylimidazole, 1-chlorobutane, 1-chlorohexane, toluene and dichloromethane were dried and distilled from CaH_2 prior to use. Acetonitrile and acetone were purified by distillation after standing 24 hr over molecular sieves (3Å). Lithum tris(pentafluoroethyl)trifluorophosphate was prepared according to a literature method.[1] Lithium bis(pentafluoroethyl)phosphinate was prepared by neutralization of bis(pentafluoroethyl)phosphinic acid.[2]

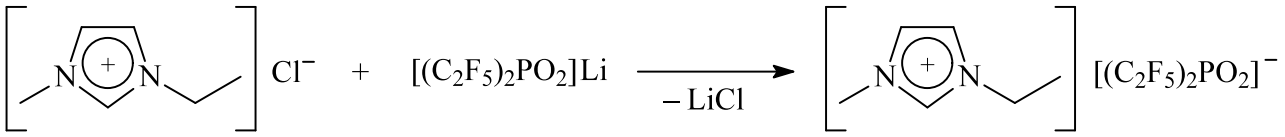
Methods: FT-IR spectra were recorded with a Nicolet Protégé 460 spectrometer in the region 4000-400 cm^{-1} as liquid films. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker AM300 instrument at 300 and 75 MHz, respectively, as solutions in DMSO-d_6, chemical shifts (δ) are reported as ppm with respect to trace resonances of protonated solvents or TMS as an internal standard.

1-Ethyl-3-methylimidazolium chloride, $[C_2C_1Im][Cl]$.[3].



An 250-mL autoclave was charged with 103 g of 1-methylimidazole (1.26 mol, freshly distilled from KOH) and cooled to 0°C under an argon atmosphere. 1-Chloroethane (100 g, 1.55 mol) was condensed into a partially evacuated 200-mL Schlenk tube and transferred to the autoclave, which was then sealed and pressurised to 5 bar with argon. The autoclave was heated at 75°C for 48 hr. The reactor contents were transferred to a round-bottomed flask under argon and the excess of 1-chloroethane was removed with heating at 70°C under reduced pressure. The resulting colourless viscous liquid was dried *in vacuo* at 50°C for 12 hr and cooled to give a white solid. Yield 181.5 g (99%). All spectroscopy was consistent with that in the literature.

1-Ethyl-3-methylimidazolium bis(pentafluoroethyl)phosphinate, $[C_2C_1Im][PO_2(C_2F_5)_2]$. Compound 1



A 500-mL, one-necked, round-bottomed flask was equipped with a magnetic stirrer and charged with 154 g (0.5 mol, 1 equiv) of lithim bis(pentafluoroethyl)phosphinate, and 73.3 g (0.5 mol, 1 equiv) of 1-ethyl-3-methylimidazolium chloride dissolved in 100 mL of distilled water. The reaction mixture was stirred at room temperature for 1 hr affording a two-phase system. Then 100 mL of dichloromethane was added. The lower organic layer was separated and washed with water (5 × 10 mL) until the aqueous fraction was observed to be free of chloride ($AgNO_3$). The dichloromethane solution was mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr, the suspension was filtered and the volatile material was removed by rotary evaporation. The resulting colourless viscous liquid was dried under reduced pressure (0.5 mmHg) at 70°C for 12 hr. Yield 189.6 g (92 %)

^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 1.41 (3H, t, $NCH_2C\underline{H_3}$), 3.85 (3H, s, $NC\underline{H_3}$), 4.19 (2H, quart., $NC\underline{H_2}CH_3$), 7.70 (1H, m, $C_{im}(5)\underline{H}$), 77.9 (1H, m, $C_{im}(4)\underline{H}$), 9.14 (1H, s, $C_{im}(2)\underline{H}$).

^{13}C NMR (75 MHz, DMSO-d_6, δ/ppm): 14.79 ($\underline{C}H_3$), 35.48 ($\underline{C}H_3N$), 44.19 ($\underline{C}H_2N$), 122.03 ($\underline{C}_{im}HNCH_2$), 123.60($\underline{C}_{im}HNCH_3$), 136.47 ($N\underline{C}_{im}HN$), 107-125 (m, $\underline{C}F_2\underline{C}F_3$).

FT-IRS (neat, KRS-5, ν): 3154, 3104, 2995, 1574, 1464, 1433, 1392, 1309, 1212, 1159, 1146, 1107, 1089, 977, 874, 805, 751, 703, 651, 625, 597, 564, 505, 463, 431 cm^{-1}.

Analysis, found: C 29.08%, H 2.77%, F 45.93%, N 6.89, P 7.66%, calculated for $C_{10}H_{11}F_{10}N_2O_2P$: C 29.14%, H 2.69%, F 46.09%, N 6.80, O 7.76%, P 7.52%.

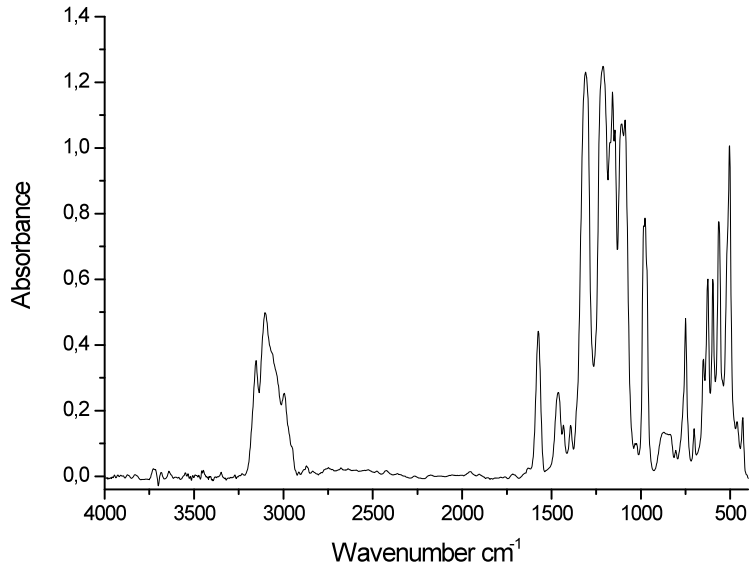


Fig. 1. FT-IR-spectra of 1-ethyl-3-methylimidazolium bis(pentafluoroethyl)phosphinate.

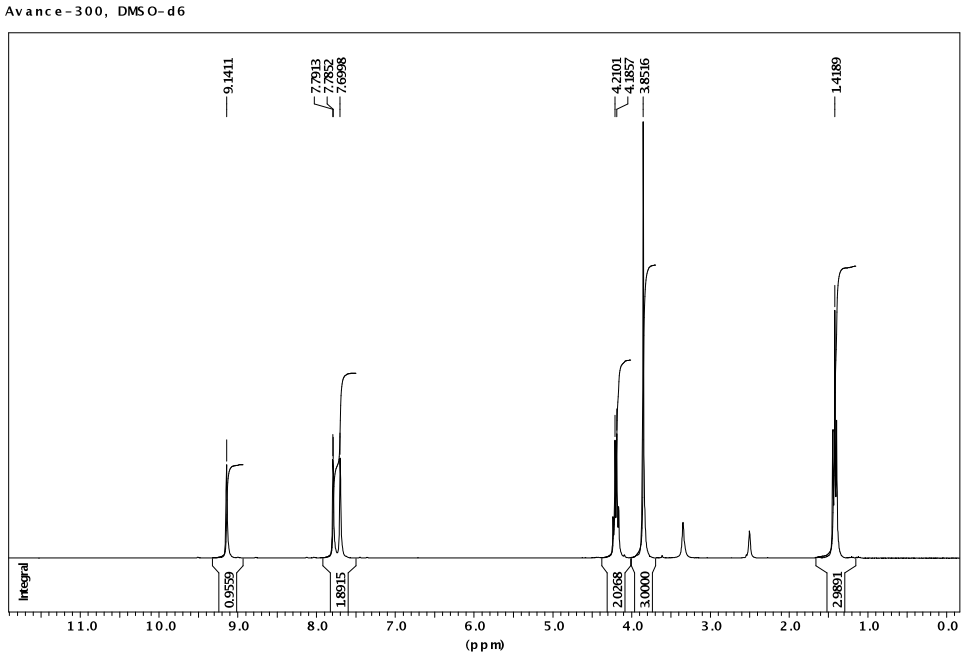


Fig. 2. ^{1}H NMR spectra of 1-ethyl-3-methylimidazolium bis(pentafluoroethyl)phosphinate.

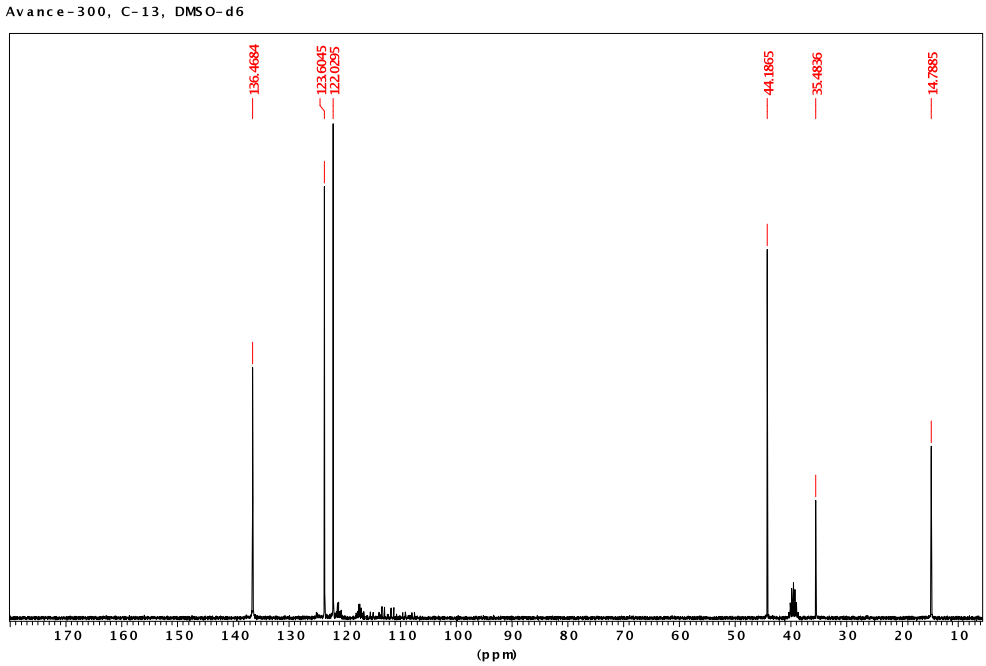
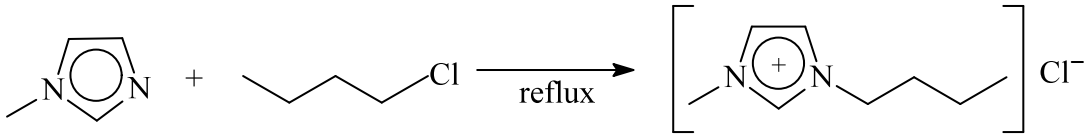


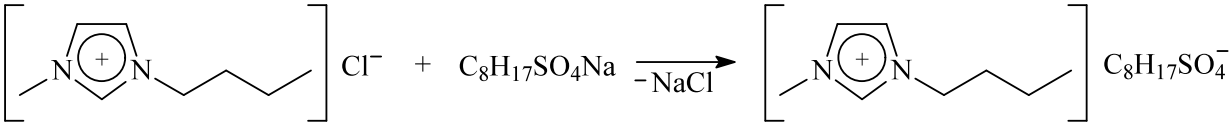
Fig. 3. ^{13}C NMR spectra of 1-ethyl-3-methylimidazolium bis(pentafluoroethyl)phosphinate.

1-Butyl-3-methylimidazolium chloride, $[C_4C_1Im][Cl]$[4].



A 2-L, three-necked, round-bottomed flask was equipped with a heating bath, an argon inlet adapter, an internal thermometer adapter, an overhead mechanical stirrer and a reflux condenser. The flask was flushed with argon and charged with 328.8 g (4.01 mol, 1 equiv) of freshly distilled 1-methylimidazole, 556.6 g (6.01 mol, 1.5 equiv) of 1-chlorobutane and 300 mL of dry toluene and brought to a gentle reflux (75-80°C internal temperature). The solution was heated under reflux for 48 hr and then cooled to room temperature. The remaining light-yellow oil was washed with dry toluene and the volatile material was removed under reduced pressure. The resulting light-yellow ionic liquid was dissolved in 500 mL dry dichloromethane, stirred with activated charcoal for 12 hr and filtered. The dichloromethane was removed from solution under reduced pressure (0.5 mmHg) at 70°C for 3 hr. After cooling to room temperature the imidazolium salt began to crystallize forming a white solid. Yield 645 g (92%). Spectroscopy was consistent with that published in the literature.[4]

1-Butyl-3-methylimidazolium octylsulfate, $[C_4C_1Im][C_8OSO_3]$. Compound 2[5]



A 250-mL, one-necked, round-bottomed flask was equipped with a magnetic stirrer and charged with 33.4 g (0.144 mol, 1 equiv) of sodium octylsulfate and 27.62 g (0.158 mol, 1.1 equiv) of 1-butyl-3-methylimidazolium chloride in 50 mL of distilled water. The reaction mixture was stirred at room temperature for 2 hr and water was removed *in vacuo*. Then, 250 mL of dichloromethane was added. The resulting precipitate of sodium chloride was removed by filtration and washed with dry dichloromethane. The dichloromethane solution was washed with water (4 × 30 mL) until the aqueous fraction was observed to be free of chloride ($AgNO_3$), mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr, the suspension was filtered and the volatile material was removed by rotary evaporation. The resulting colourless viscous liquid was dried under reduced pressure (0.5 mmHg) at 50°C for 12 hr. Yield 37.8 g (75.4 %)

^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 0.90 (6H, m, oct-C$\underline{H}_3$, but-C$\underline{H}_3$), 1.25 (12H, m, NCH$_2$CH$_2$C$\underline{H}_2$CH$_3$, OCH$_2$CH$_2$(C$\underline{H}_2$)$_5$CH$_3$), 1.47 (2H, p, OCH$_2$C$\underline{H}_2$(CH$_2$)$_4$CH$_2$CH$_3$), 1.76 (2H, p, NCH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 3.67 (2H, t, OC$\underline{H}_2$CH$_2$(CH$_2$)$_4$CH$_2$CH$_3$), 3.85 (3H, s, NC$\underline{H}_3$), 4.16 (2H, t, NC$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 7.70 (1H, m, C$_{im}$(5)$\underline{H}$), 7.77 (1H, m, C$_{im}$(4)$\underline{H}$), 9.11 (1H, s, C$_{im}$(2)$\underline{H}$).

^{13}C NMR (75 MHz, DMSO-d_6, δ/ppm): 13.10 (oct-$\underline{C}$H$_3$), 13.69 (but-$\underline{C}$H$_3$), 18.80 ($\underline{C}$H$_2$CH$_3$-oct), 22.14 ($\underline{C}$H$_2$CH$_3$-but), 25.58 ($\underline{C}$H$_2$CH$_2$CH$_2$OS) 28.78 ($\underline{C}$H$_2$CH$_2$CH$_2$CH$_2$OS) 28.84 ($\underline{C}$H$_2$CH$_2$OS) 29.16 (CH$_3$CH$_2$$\underline{C}H_2CH_2$-oct), 31.34 (CH$_3CH_2CH_2$$\underline{C}H_2$-oct), 31.60 (CH$_2$$\underline{C}H_2CH_2$-but), 35.54 (CH$_3$N), 48.47 ($\underline{C}H_2$N), 65.79 ($\underline{C}H_2$OS), 122.31 ($\underline{C}_{im}$HNCH$_2$), 123.53 ($\underline{C}_{im}$HNCH$_3$), 136.79 (N$\underline{C}_{im}$HN).

FT-IRS (neat, KRS-5, ν): 3149, 3106, 2957, 2926, 2871, 2858, 1573, 1465, 1430, 1379, 1341, 1248, 1223, 1172, 1118, 1057, 1044, 1006, 985, 958, 907, 836, 788, 754, 655, 624, 578 cm^{-1}.

Analysis, found: C 54.91%, H 9.25%, N 7.91, S 8.98%; calculated for $C_{16}H_{32}N_2O_4S$: C 55.14%, H 9.26%, N 8.04, S 9.20%.

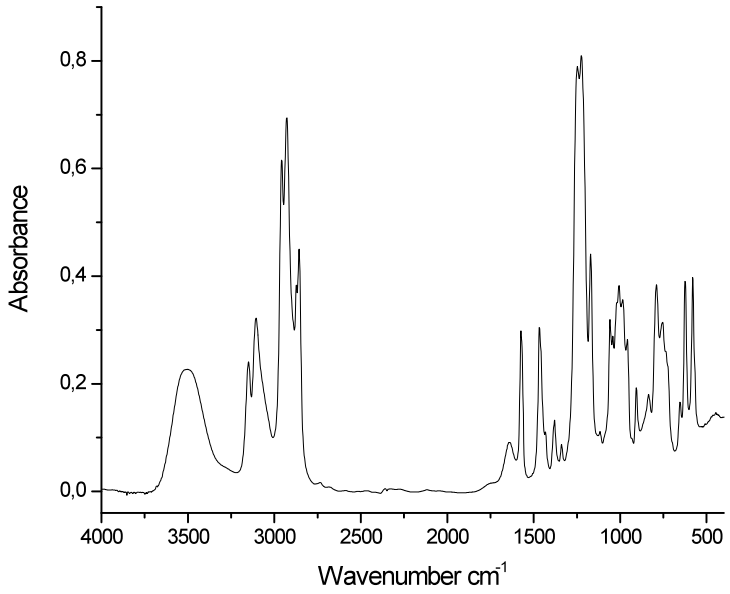


Fig. 4. FT-IR-spectra of 1-butyl-3-methylimidazolium octylsulfate.

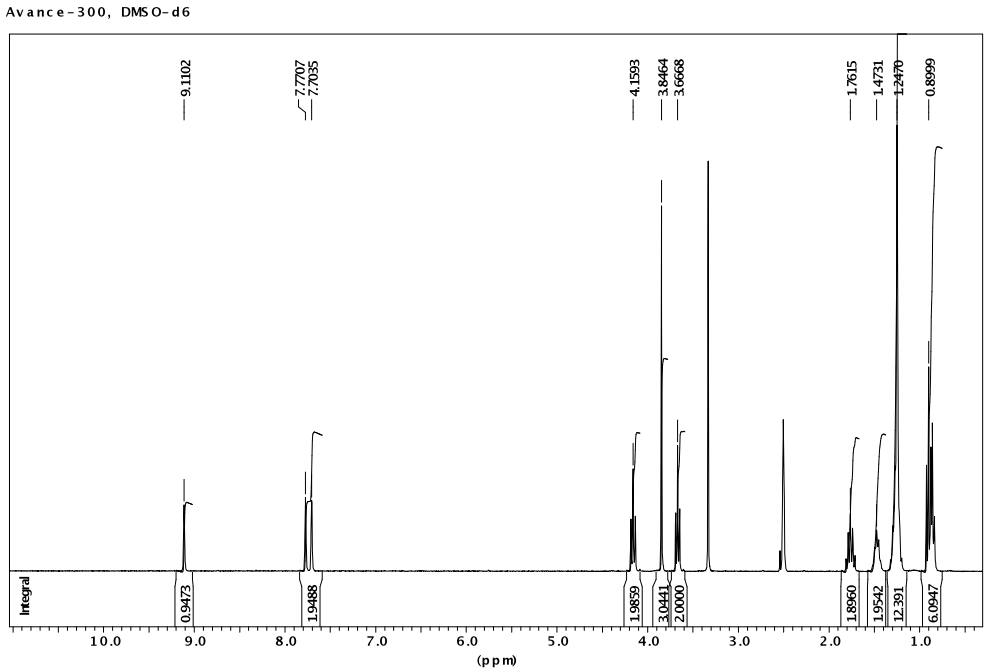


Fig. 5. ^{1}H NMR spectra of 1-butyl-3-methylimidazolium octylsulfate.

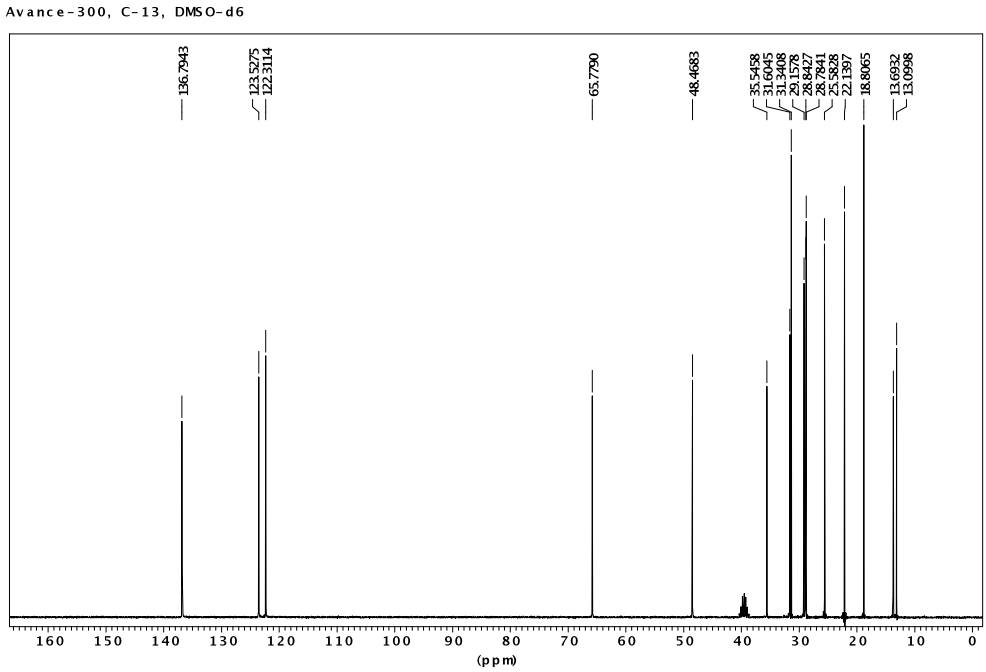
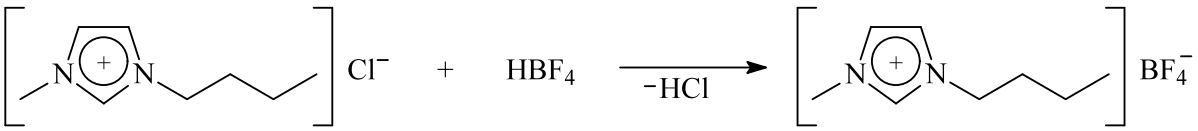


Fig. 6. ^{13}C NMR spectra of 1-butyl-3-methylimidazolium octylsulfate.

1-Butyl-3-methylimidazolium tetrafluoroborate, $[C_4C_1Im][BF_4]$. Compound 3[6]



A 1-L, one-necked, round-bottomed flask was equipped with a magnetic stirrer and charged with 380 g (2.18 mol, 1 equiv) of 1-butyl-3-methylimidazolium chloride in 400 mL of distilled water. Tetrafluoroboric acid (382.44 g, 2.18 mol, 1 equiv, 50 wt.% solution in water) was added slowly to a rapidly stirred solution of 1-butyl-3-methylimidazolium chloride in water. The reaction mixture was stirred at room temperature for 2 hr and extracted with dichloromethane (3 × 200 mL). The organic layer was collected and washed with water (7 × 10 mL) until the aqueous fraction was observed to be free of chloride ($AgNO_3$). The dichloromethane solution was mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr of standing the suspension was filtered and dichloromethane was removed by rotary evaporation. The resulting colourless or light-yellow viscous liquid was dried under reduced pressure (0.5 mm Hg) at 70°C for 24 hr. Yield 327.5 g (66.5 %).

^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 0.89 (3H, t, $NCH_2CH_2CH_2C\underline{H_3}$), 1.26 (2H, m, $NCH_2CH_2C\underline{H_2}CH_3$), 1.76 (2H, p, $NCH_2C\underline{H_2}CH_2CH_3$), 3.84 (3H, s, $NC\underline{H_3}$), 4.15 (2H, t, $NC\underline{H_2}CH_2CH_2CH_3$), 7.72 (2H, m, C(5)<u>H</u>, C(4)<u>H</u>), 9.08 (1H, s, C(2)<u>H</u>).

^{13}C NMR (75 MHz, DMSO-d_6, δ/ppm): 13.24 ($\underline{C}H_3$), 19.00 ($\underline{C}H_2CH_3$), 31.62 ($CH_2\underline{C}H_2CH_2$), 35.75 ($\underline{C}H_3N$), 48.90 ($\underline{C}H_2N$), 122.37 ($\underline{C}_{im}HNCH_2$), 123.68 ($\underline{C}_{im}HNCH_3$), 136.67 ($N\underline{C}_{im}HN$).

FT-IRS (neat, KRS-5, ν): 3160, 3120, 2964, 2937, 2877, 1576, 1466, 1432, 1385, 1342, 1284, 1173, 1064, 848, 753, 652, 628, 518 cm^{-1}.

Analysis, found: C 42.62%, H 6.79%, B 4.75%, F 33.56%, N 12.40; calculated for $C_8H_{15}BF_4N_2$: C 42.51%, H 6.69%, B 4.78%, F 33.62%, N 12.39%.

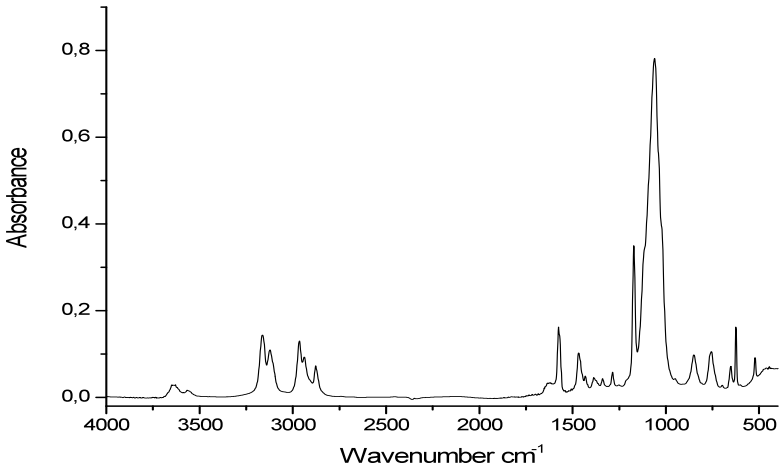


Fig. 7. FT-IR-spectra of 1-butyl-3-methylimidazolium tetrafluorborate.

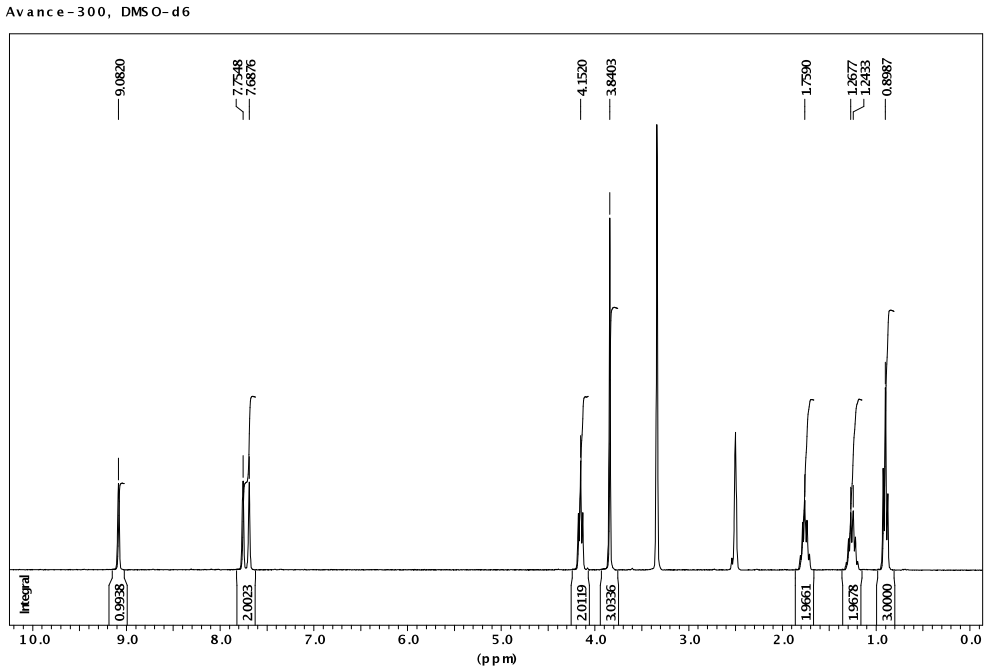


Fig. 8. ^{1}H NMR spectra of 1-butyl-3-methylimidazolium tetrafluorborate.

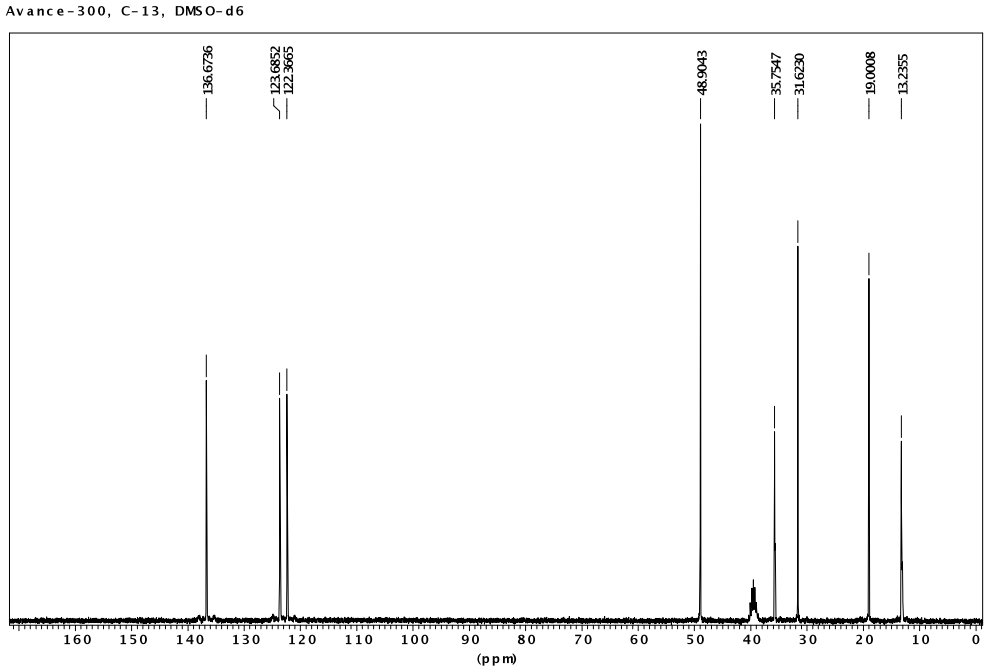
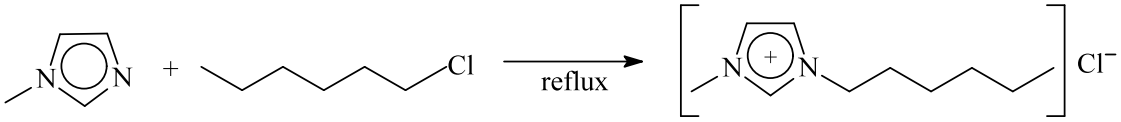


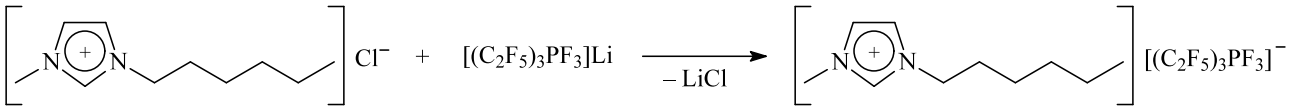
Fig. 9. ^{13}C NMR spectra of 1-butyl-3-methylimidazolium tetrafluorborate.

1-Hexyl-3-methylimidazolium chloride, [C_6C_1Im][Cl].



The same procedure was used as for [C_4C_1Im][Cl]. From 41.5 g (0.5 mol) of 1-methylimidazole and 90.47 g (0.75 mol, 1.5 equiv) of 1-chlorohexane, there was obtained 97.30 g of [C_6C_1Im][Cl] (96%), as a white solid.

1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [C_6C_1Im][FAP]. Compound 4



A 500-mL, one-necked, round-bottomed flask was equipped with a magnetic stirrer and charged with 126.5 g (0.28 mol, 1 equiv) of lithim tris(pentafluoroethyl)trifluorophosphate, and 56.8 g (0.28 mol, 1 equiv) of 1-hexyl-3-methylimidazolium chloride dissolved in 100 mL of distilled water. The reaction mixture was stirred at room temperature for 1 hr affording a two-phase system. Then 100 mL of dichloromethane was added. The lower organic layer was separated and washed with water (5 × 10 mL) until the aqueous fraction was observed to be free of chloride ($AgNO_3$). The dichloromethane solution was mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr, the suspension was filtered and the volatile material was removed by rotary evaporation. The resulting colourless viscous liquid was dried under reduced pressure (0.5 mmHg) at 70°C for 12 hr. Yield 157.7 g (92 %)

^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 0.86 (3H, t, $NCH_2CH_2(CH_2)_3C\underline{H_3}$), 1.27 (6H, m, $NCH_2CH_2(C\underline{H_2})_3CH_3$), 1.77 (2H, p, $NCH_2C\underline{H_2}(CH_2)_3CH_3$), 3.84 (3H, s, $NC\underline{H_3}$), 4.15 (2H, t, $NC\underline{H_2}CH_2(CH_2)_3CH_3$), 7.68 (1H, m, C(5)H), 7.75 (H, m, C(4)H), 9.11 (1H, s, C(2)H).

^{13}C NMR (75 MHz, DMSO-d_6, δ/ppm): 13.44 ($NCH_2CH_2CH_2CH_2C\underline{H_3}$), 21.92 ($NCH_2CH_2CH_2C\underline{H_2}CH_2CH_3$), 25.31 ($NCH_2CH_2\underline{C}H_2CH_2CH_2CH_3$), 29.53 ($NCH_2\underline{C}H_2CH_2CH_2CH_2CH_3$), 30.66 ($NCH_2CH_2CH_2\underline{C}H_2CH_2CH_3$), 35.54 ($\underline{C}H_3N$), 49.09 ($N\underline{C}H_2CH_2CH_2CH_2CH_2CH_3$), 122.31 ($\underline{C}_{im}HNCH_2$), 123.65 ($\underline{C}_{im}HNCH_3$), 136.76 ($N\underline{C}_{im}HN$), 107-126 (m, $\underline{C}F_2\underline{C}F_3$).

FT-IRS (neat, KRS-5, ν): 3178, 3125, 2965, 2937, 2866, 1600, 1571, 1469, 1433, 1383, 1314, 1301, 1218, 1189, 1137, 1100, 1071, 814, 761, 744, 722, 620, 583, 534, 497, 431 cm^{-1}.

Analysis, found: C 31.01%, H 3.71.00%, F 56.82%, N 4.50, P 4.66%; calculated for $C_{16}H_{19}F_{18}N_2P$: C 31.39%, H 3.13%, F 55.85%, N 4.57, P 5.06%,.

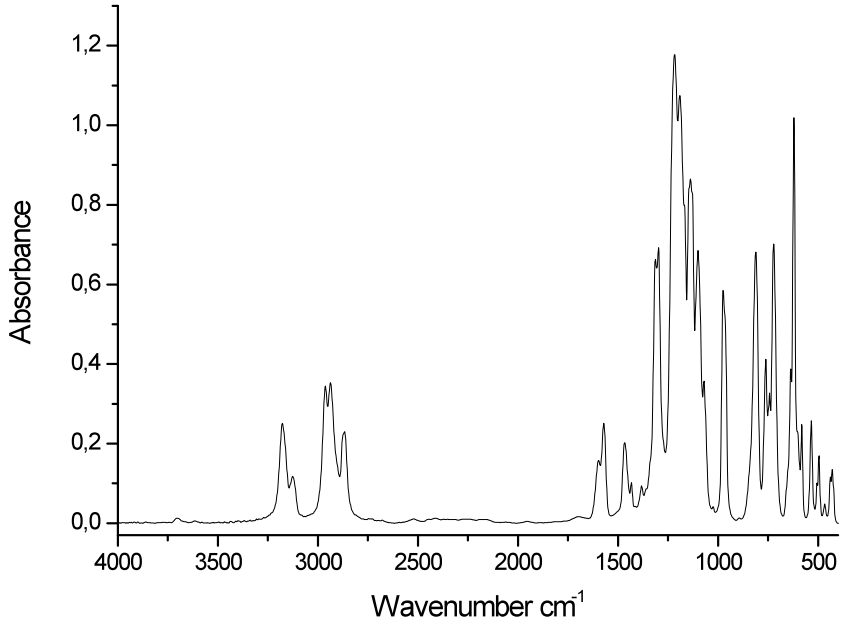


Fig. 10. FT-IR-spectra of 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate.

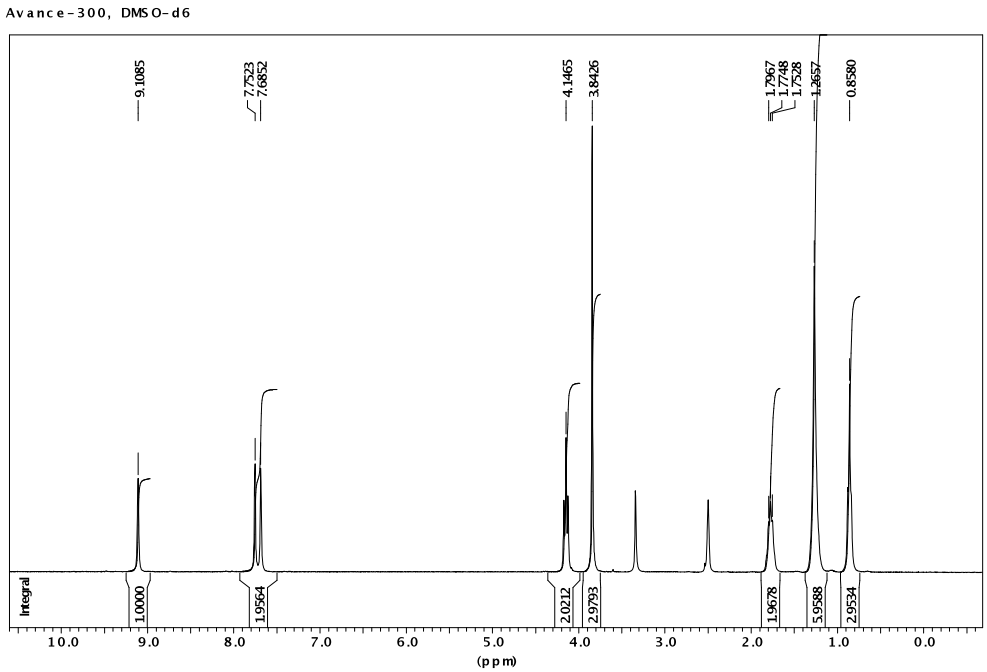


Fig. 11. ^{1}H NMR spectra of 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate.

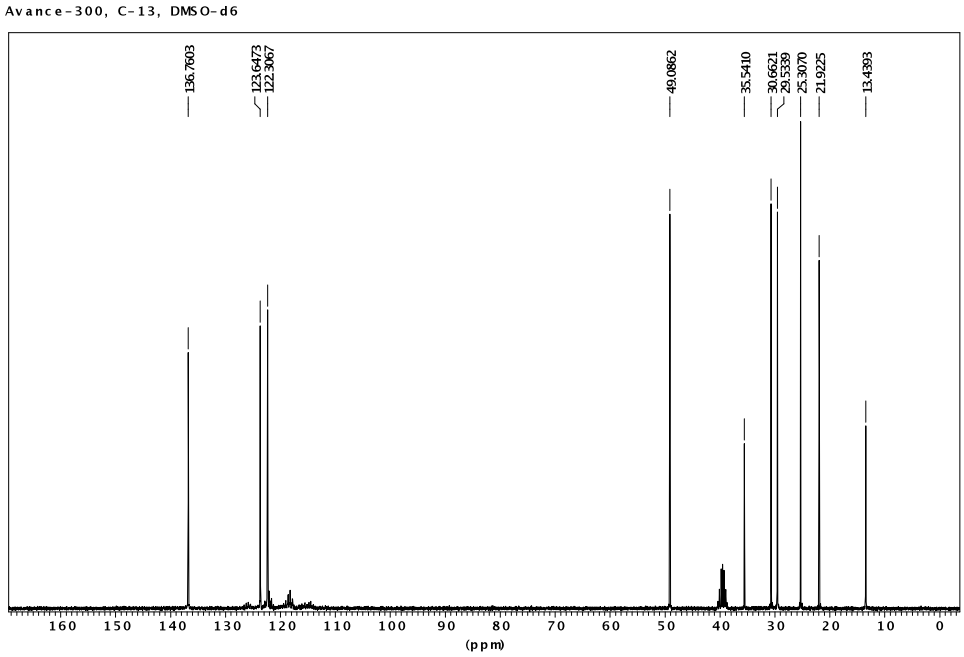
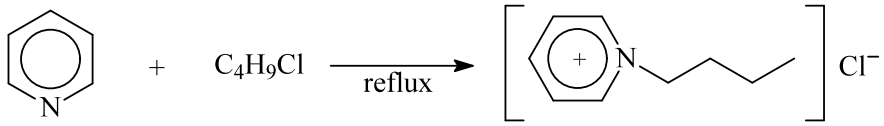


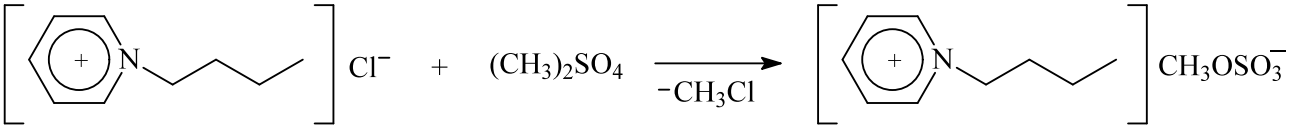
Fig. 12. ^{13}C NMR spectra of 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate.

N-Butylpyridinium chloride, [C_4Py][Cl].[7]



A 500-mL, three-necked, round-bottomed flask was equipped with a heating bath, an argon inlet adapter, an internal thermometer adapter, a magnetic stirrer and a reflux condenser. The flask was flushed with argon and charged with 98.9 g (1.25 mol) of freshly distilled pyridine, 138.9 g (1.50 mol, 1.2 equiv) of 1-chlorobutane and, 100 mL of dry acetonitrile. The mixture was heated under reflux for 72 hr and then cooled to room temperature. The product was recrystallized from acetonitrile/ethyl acetate (9:1, v/v) twice, filtered and dried under reduced pressure at 70-80°C for 12 hr. Yield 137 g (80 %). All spectroscopy was consistent with that in the literature.[7]

N-Butylpyridinium methylsulfate, [C_4Py][$MeSO_4$]. Compound 5[8]



A 100-mL, three-necked, round-bottomed flask was equipped with a magnetic stirrer, an argon inlet adapter and an internal thermometer adapter. The flask was flushed with argon and charged with 15 g (0.087 mol) of N-butylpyridinium chloride. Then, 11 g (0.087 mol) of dimethylsulphate was added by a syringe through a rubber septa during intensive stirring. The reaction mixture stirred for 5 minutes and the volatile material was removed under reduced pressure at 40-50°C for 12 hr. The Yield 21.3 g (99 %).

^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 0.91 (3H, t, $NCH_2CH_2CH_2C\underline{H_3}$), 1.27 (2H, sext, $NCH_2CH_2C\underline{H_2}CH_3$), 1.90 (2H, quin, $NCH_2C\underline{H_2}CH_2CH_3$), 3.38(3H, s, $SOC\underline{H_3}$), 4.60 (2H, t, $NC\underline{H_2}CH_2CH_2CH_3$), 8.16 (2H, m, C_{py}(3,5)$\underline{H}$), 8.61 (1H, m, C_{py}(4)$\underline{H}$), 9.08 (2H, m, C_{py}(2,6)$\underline{H}$)

^{13}C NMR (75 MHz, DMSO-d_6, δ/ppm): 13.26 ($\underline{C}H_3$), 18.75 ($\underline{C}H_2CH_3$), 32.71 ($CH_2\underline{C}H_2CH_2$), 53.13 ($\underline{C}H_3OS$), 60.62 ($\underline{C}H_2N$), 128.17 ($\underline{C_{py}}$(3,5)H), 144.85($\underline{C_{py}}$(2,6)H), 145.60 ($\underline{C_{py}}$(4)H).

FT-IRS (neat, KRS-5, ν): 3136, 3066, 2963, 2873, 1633, 1490, 1465, 1385, 1322, 1251, 1228, 1174, 1060, 1009, 747, 687, 610, 579, 553, 499, 430 cm^{-1}.

Analysis, found: C 48.40%, H 7.01%, N 5.63, S 12.92%; calculated for $C_{10}H_{17}NO_4S$: C 48.57%, H 6.93%, N 5.66%, O 25.88%, S 12.96%.

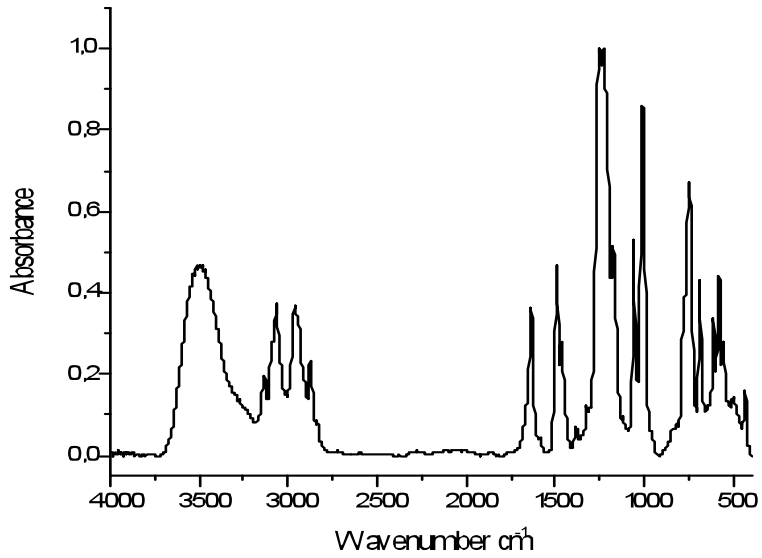


Fig. 13. FT-IR-spectra of N-butylpyridinium methylsulfate.

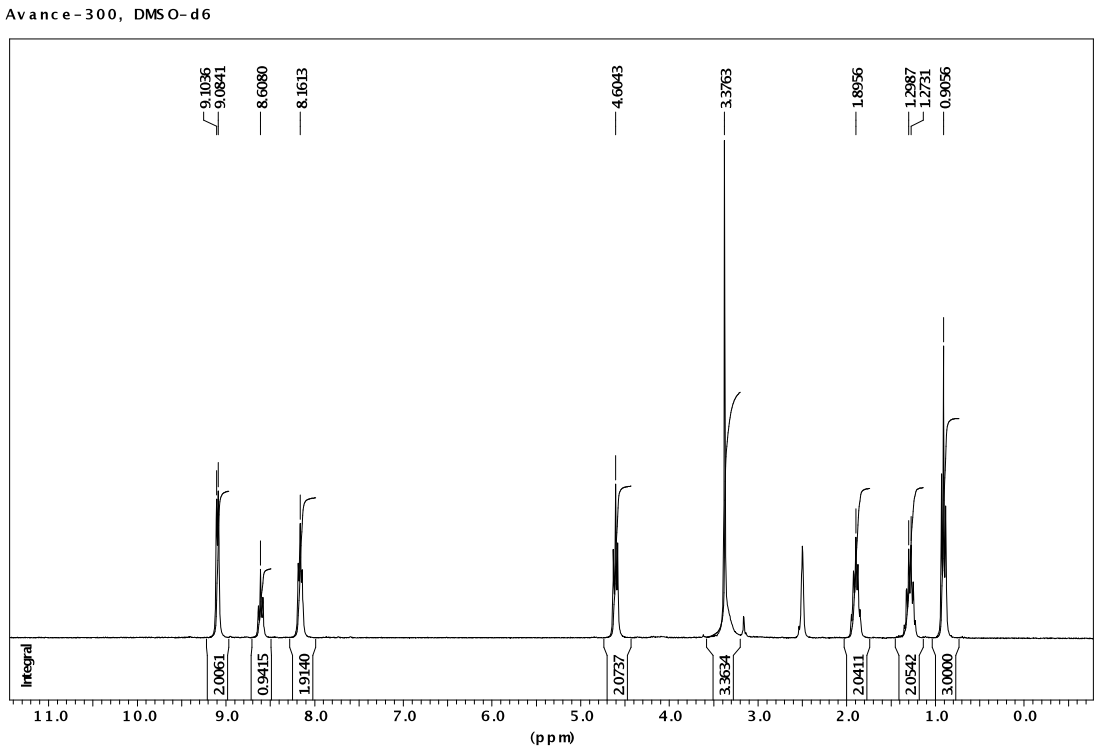


Fig. 14. ^{1}H NMR spectra of N-butylpyridinium methylsulfate.

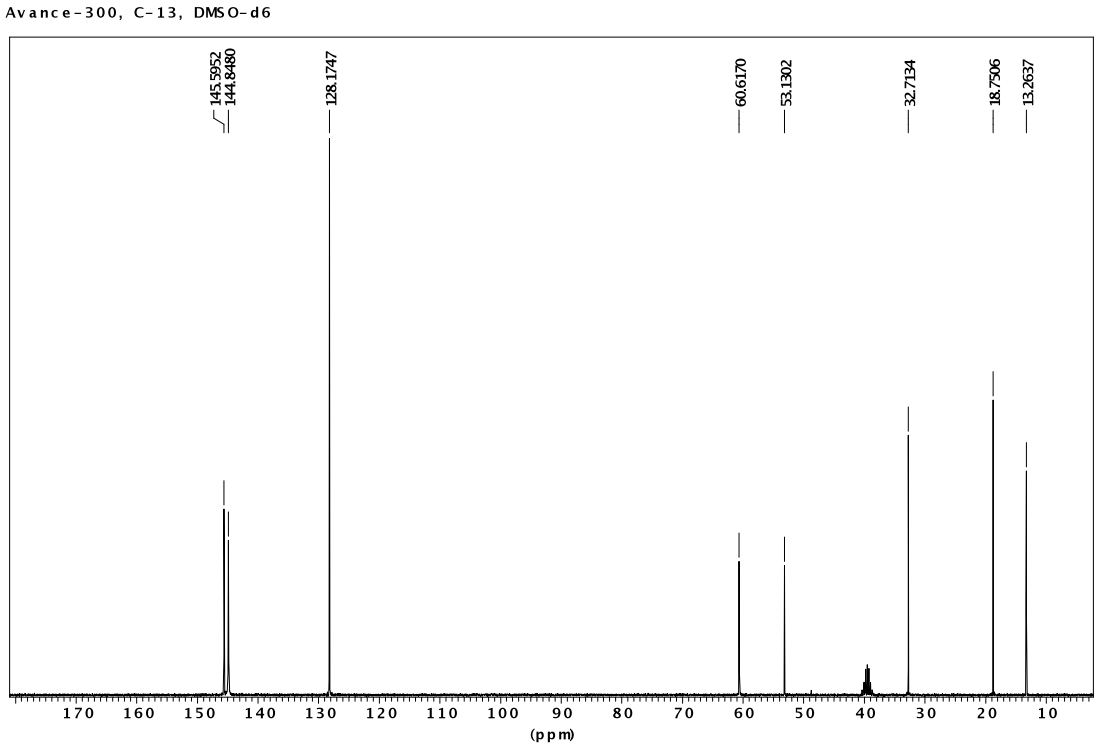
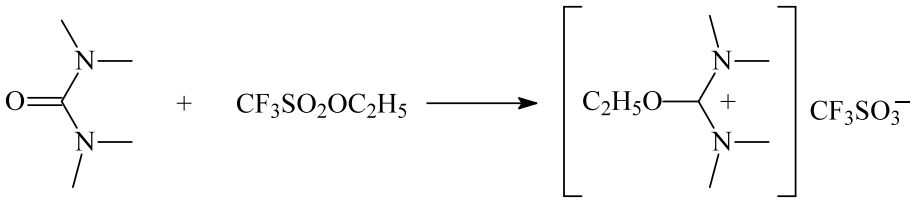


Fig. 15. ^{13}C NMR spectra of N-butylpyridinium methylsulfate.

O-Ethyl-N,N,N',N'-tetramethylisouronium trifluoromethanesulfonate, $[C_2(C_1)_4iU][TFO]$. Compound 6[9]



A 250 mL round-bottomed flask was equipped with a magnetic stirrer and charged with 20.0 g (0.17 mol) N,N,N',N'-tetramethylurea in 100 mL of anhydrous pentane. The stirred solution was cooled to 0°C under an argon atmosphere and 32.0 g (0.18 mol, 1.05 equiv) of ethyl triflate was added dropwise over 30 minutes. The reaction mixture was allowed to warm to room temperature and stirred for a further 10 min. The lower liquid phase was separated and washed with pentane (3 × 30 mL). The resulting viscous liquid was dried under reduced pressure (0.5 mmHg) at 50°C for 24 hr. Yield 49.7 g (99.5 %).

^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 1.35 (3H, t, $OCH_2C\underline{H_3}$), 3.02 (12H, s, $NC\underline{H_3}$), 4.36 (2H, quart., $OC\underline{H_2}CH_3$).

^{13}C NMR (75 MHz, DMSO-d_6, δ/ppm): 14.59 ($OCH_2\underline{C}H_3$), 39.40 ($\underline{C}H_3$), 71.41 ($O\underline{C}H_2CH_3$), 118-127 (t., $\underline{C}F_2\underline{C}F_3$), 163.21 (-N-$\underline{C}$-N-).

FT-IRS (neat, KRS-5, ν): 2990, 2953, 2819, 1656, 1544, 1470, 1413, 1390, 1268, 1225, 1156, 1058, 1031, 995, 909, 867, 755, 637, 574, 518 cm^{-1}.

Analysis, found: C 32.11%, H 6.09%, F 19.89%, N 9.33, S 10.35%, calculated for $C_8H_{17}F_3N_2O_4S$: C 32.65%, H 5.82%, F 19.37%, N 9.52, O 21.75, S 10.89%.

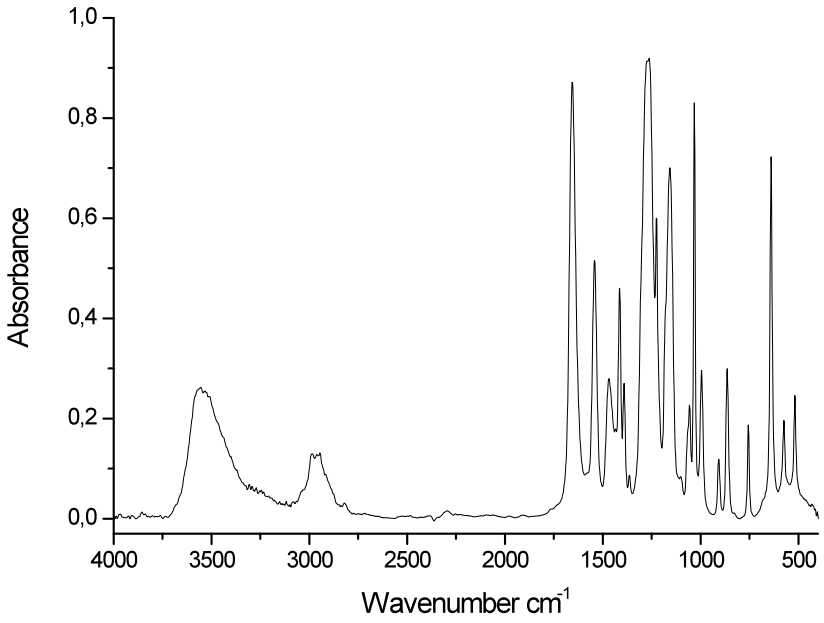


Fig. 16. FT-IR-spectra of O-ethyl-N,N,N',N'-tetramethylisouronium trifluoromethanesulfonate.

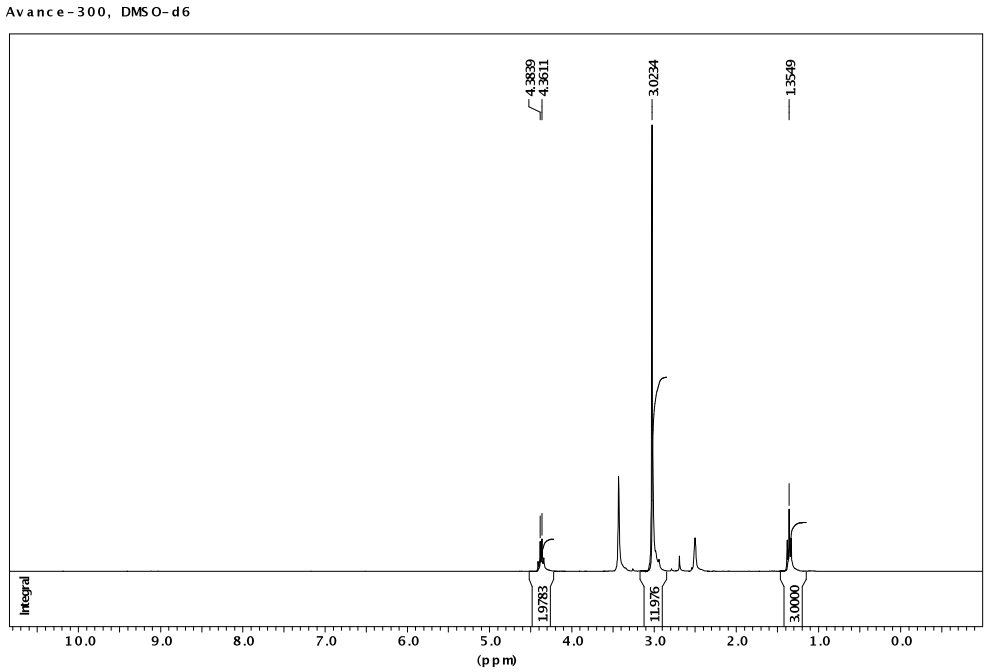


Fig. 17. ^{1}H NMR spectra of O-ethyl-N,N,N',N'-tetramethylisouronium trifluoromethanesulfonate.

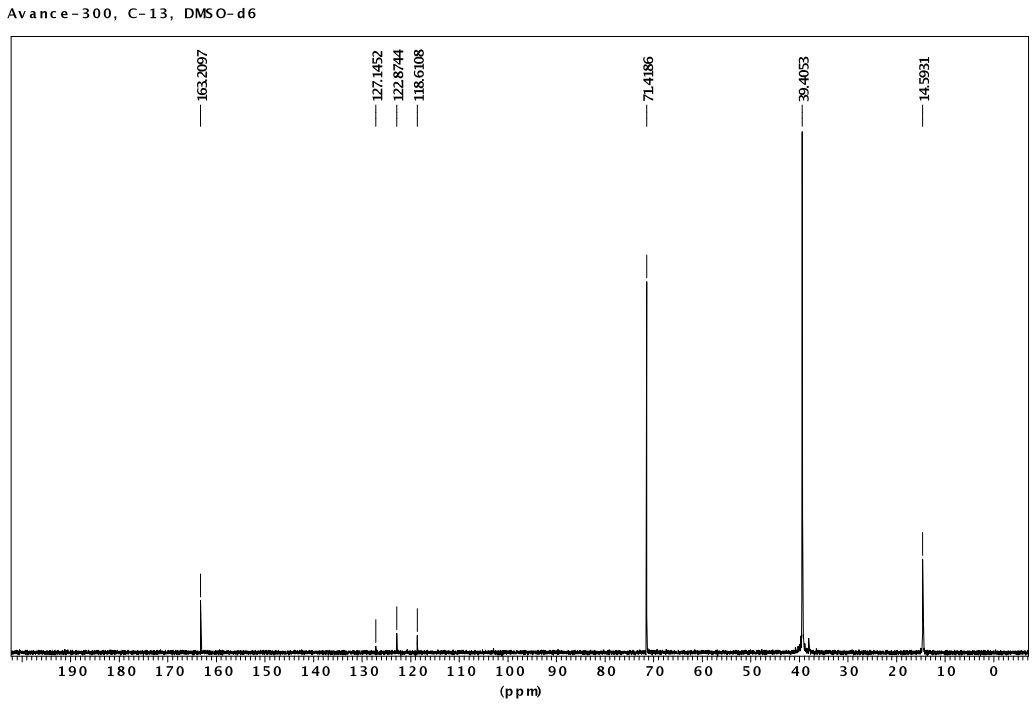
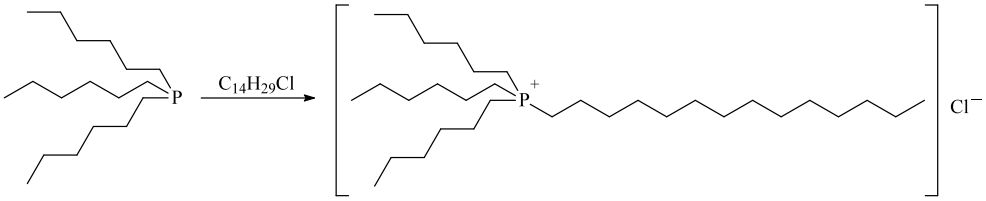


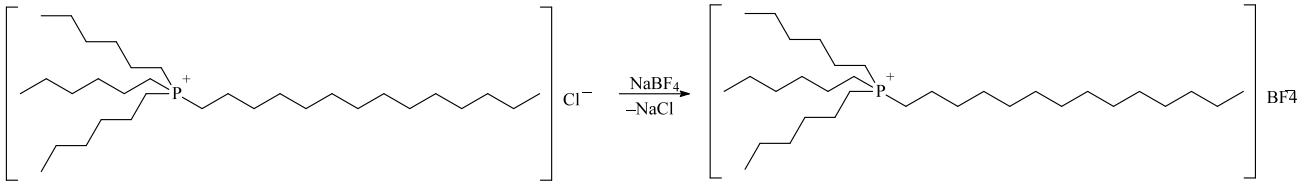
Fig. 18. ^{13}C NMR spectra of O-ethyl-N,N,N',N'-tetramethylisouronium trifluoromethanesulfonate.

Trihexyl(tetradecyl)phosphonium chloride, $[P_{6,6,6,14}][Cl]$.[10]



A 2L round-bottomed flask fitted with a condenser was charged with trihexylphosphine 286.0 g (1.0 mol) and was heated to 145 C. Then, 1-chlorotetradecane 261.0 g (1.20 mol) was added over 2.75 hr. The temperature was maintained at 140 C overnight (approximately 16 hr of postaddition reaction). The progress of the reaction was monitored by ^{31}P NMR spectroscopy. The mixture was then vacuum stripped at 100 C (0.5 mm Hg) to remove the excess of 1-chlorotetradecane and volatile by-product impurities. The product was obtained as a colourless oil (495.0 g, 97.2%). All spectroscopy was consistent with that in the literature.[10]

Trihexyl(tetradecyl)phosphonium tetrafluoroborate, $[P_{6,6,6,14}]$ $[BF_4]$. Compound 7



A 1L round-bottomed flask was equipped with a magnetic stirrer and charged with 250 mL of acetone and 100 g (0.20 mol) of trihexyl(tetradecyl)phosphonium chloride. To this solution was added 33 g (0.30 mol, 1.5 equiv.) of sodium tetrafluoroborate. The mixture was stirred vigorously for 1 hr at room temperature. Afterwards, the suspension was filtered to remove the excess sodium tetrafluoroborate and precipitated sodium chloride. The clear acetone solution containing trihexyl(tetradecyl)phosphonium tetrafluoroborate then was heated under reduced pressure to remove the solvent. Then, 250 mL of dichloromethane was added. The resulting precipitate of sodium chloride was removed by filtration and washed with dry dichloromethane. The dichloromethane solution was washed with water (4 × 30 mL) until the aqueous fraction was observed to be free of chloride ($AgNO_3$), mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr, the suspension was filtered and the volatile material removed by rotary evaporation. The resulting colourless oil was dried under reduced pressure (0.5 mm Hg) at 100°C for 12 hr. Yield 103.0 g (94 %)

^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 0.87 (12H, m, $CH_2C\underline{H}_3$), 1.28 (48H, m, $(C\underline{H}_2)_{24}$), 2.17 (8H, m, $PC\underline{H}_2$).

^{13}C NMR (75 MHz, DMSO-d_6, δ/ppm): 13.58 ($\underline{C}H_3$, hex.), 13.63 ($\underline{C}H_3$, tetradec), 17.26 ($P\underline{C}H_2$, hex., tetradec.), 17.88 ($P\underline{C}H_2$, hex., tetradec.), 20.49 ($PCH_2\underline{C}H_2$, hex., tetradec.), 20.55 ($PCH_2\underline{C}H_2$, hex., tetradec.), 21.68 ($CH_3\underline{C}H_2$, hex.), 21.95 ($CH_3\underline{C}H_2$, tetradec.), 28.05 ($\underline{C}H_2$, tetradec.), 28.60 ($\underline{C}H_2$, tetradec.), 28.90 ($\underline{C}H_2$, tetradec.), 29.56 ($PCH_2CH_2\underline{C}H_2$, hex.), 29.77 ($PCH_2CH_2\underline{C}H_2$, hex.), 29.82 ($PCH_2CH_2\underline{C}H_2$, tetradec.), 30.02 ($PCH_2CH_2\underline{C}H_2$, tetradec.), 30.30 ($CH_3CH_2\underline{C}H_2$, hex.), 31.19 ($CH_3CH_2\underline{C}H_2$, tetradec.).

FT-IRS (neat, KRS-5, ν): 2968, 2939, 2865, 1471, 1419, 1382, 1307, 1263, 1220, 1062, 872, 817, 725, 521 cm^{-1}.

Analysis, found: C 67.29%, H 12.10%, B 2.02, F 13.21, P 5.48%; calculated for $C_{32}H_{68}PBF_4$: C 67.35%, H 12.01%, B 1.89, F 13.32, P 5.43%.

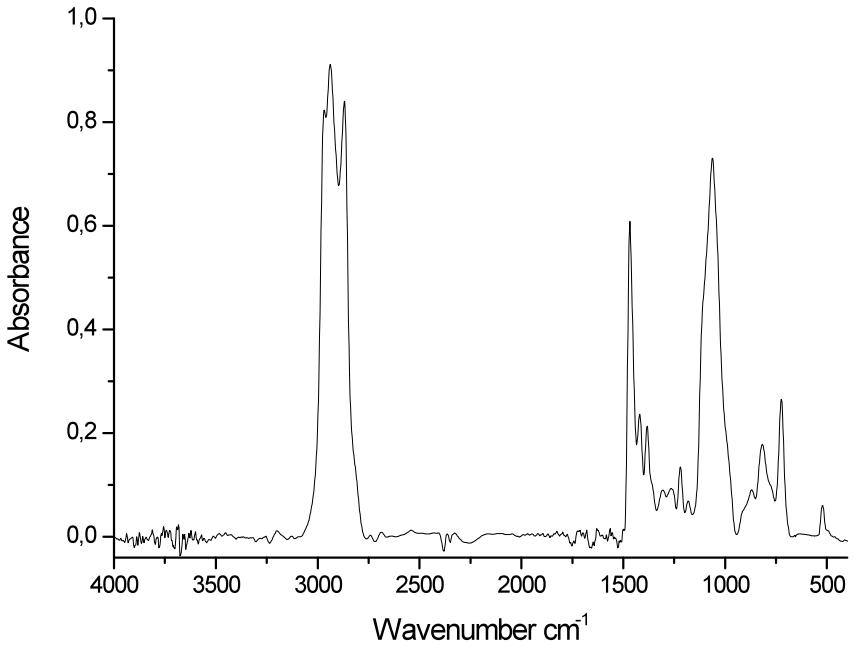


Fig. 19. FT-IR-spectra of trihexyl(tetradecyl)phosphonium tetrafluoroborate.

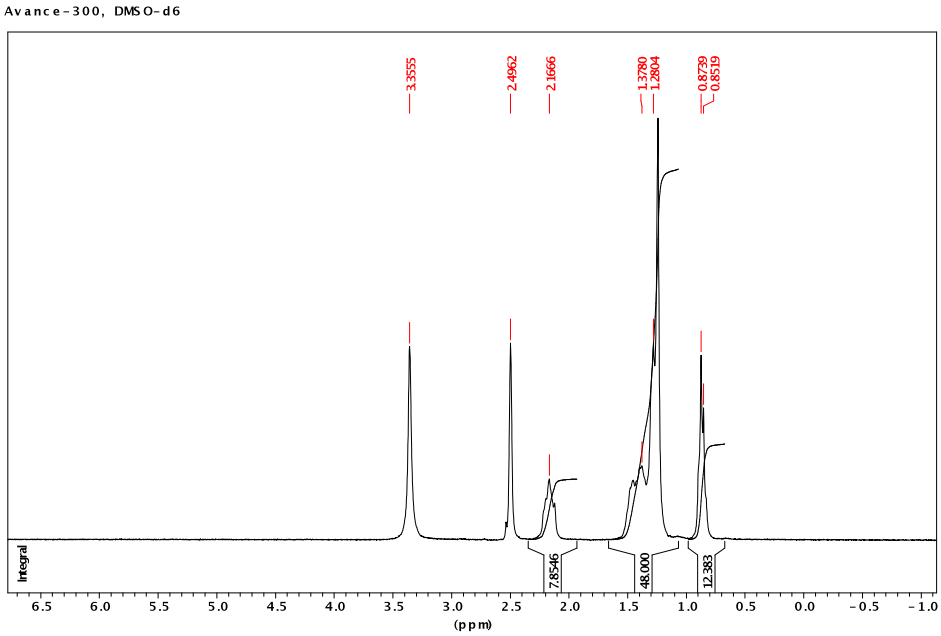


Fig. 20. ^{1}H NMR spectra of trihexyl(tetradecyl)phosphonium tetrafluoroborate.

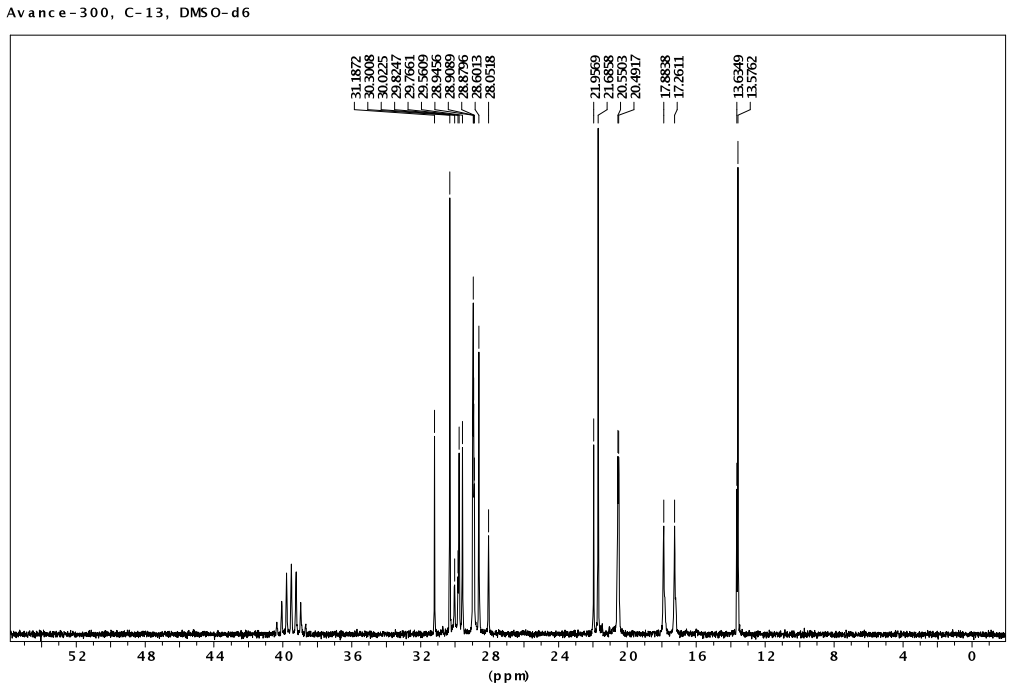


Fig. 21. ^{13}C NMR spectra of trihexyl(tetradecyl)phosphonium tetrafluoroborate.

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