Borane-Substituted Imidazol-2-ylidenes: Syntheses in-vacuo

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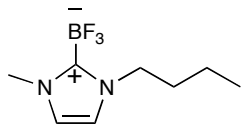
Supporting Information

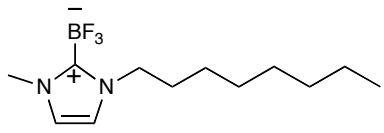
‡ *Analytical Data for Distillates of* $[C_nC_1Im][BF_4]$

*1-Butyl-3-methylimidazolium-2-trifluoroborate (**1**):* ^{1}H NMR, δ_H (300.1 MHz, DMSO-d_6), 7.51 (1H, d, J = 1.8 Hz), 7.45 (1H, d, J = 1.8 Hz), 4.17 (2H, t, J = 7.3 Hz), 3.80 (3H, s), 1.70 (2H, m), 1.24 (2H, m), 0.87 (3H, t, J = 7.2 Hz). ^{13}C NMR δ_c (125.8 MHz, DMSO-d_6), 157.01 (qq, $^{1}J_{CB}$ = 86 Hz, $^{2}J_{CF}$ = 62 Hz), 122.72, 121.16, 49.62, 36.74, 33.58, 20.09, 13.82. ^{19}F NMR δ_F (376.5 MHz, DMSO-d_6) -136.53 (q, J_{FB} = 37.7 Hz). ^{11}B NMR δ_B (128.4 MHz, DMSO-d_6) -0.25 (q, J_{BF} = 37.2 Hz). Anal. Found.: C, 46.0; H, 6.9; N, 13.6. Calc. for $C_8H_{14}N_2BF_3$: C, 46.6; H, 6.8; N, 13.6. ESI-MS m/z 187 $[C_8H_{14}N_2BF_2]^+$ (I = 100 %), 229 $[(C_8H_{14}N_2{}^{11}BF_3)Na]^+$ (I = 29.5. %). T_g = -65.3 °C.



(***1***)

*1-Octyl-3-methylimidazolium-2-trifluoroborate (**2**):* ^{1}H NMR, δ_H (300.1 MHz, DMSO-d_6), 7.52 (1H, d, J = 1.8 Hz), 7.46 (1H, d, J = 1.8 Hz), 4.14 (2H, t, J = 7.3 Hz), 3.78 (3H, s), 1.70 (2H, m), 1.22 (10H, m), 0.85 (3H, t, J = 6.8 Hz). ^{13}C NMR δ_c (125.8 MHz, DMSO-d_6), 157.12 (qq, $^{1}J_{CB}$ = 86 Hz, $^{2}J_{CF}$ = 62 Hz), 122.64, 121.13, 49.94, 36.81, 32.26, 31.16, 29.62, 29.56, 26.90, 23.14, 14.37. ^{19}F NMR δ_F (376.5 MHz, DMSO-d_6) -136.41 (q, J_{FB} = 37.5 Hz). ^{11}B NMR δ_B (128.4 MHz, DMSO-d_6) -0.29 (q, J_{BF} = 37.2 Hz). Anal. Found.: C, 54.8; H, 8.5; N, 10.6. Calc. for $C_{12}H_{22}N_2BF_3$: C, 55.0; H, 8.5; N, 10.7. ESI-MS m/z 243 $[C_{12}H_{22}N_2BF_2]^+$ (I = 100 %), 285 $[(C_{12}H_{22}N_2{}^{11}BF_3)Na]^+$ (I = 70.4 %). T_g = -62.5 °C; T_m = 41.8 °C.



(***2***)

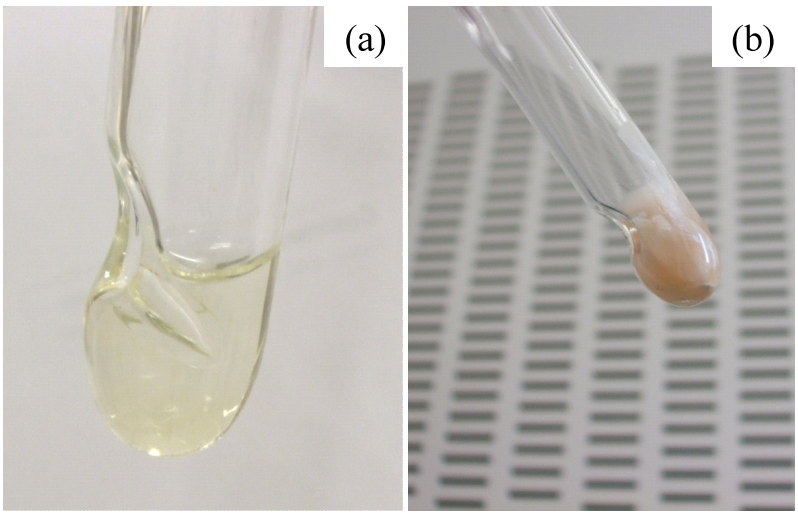


Fig. S1 Photographs of the distillates (a) *1-Butyl-3-methylimidazolium-2-trifluoroborate (**1**)* and (b) *1-Octyl-3-methylimidazolium-2-trifluoroborate (**2**)* in the receiving arm taken after removal from the distillation apparatus. *1-Octyl-3-methylimidazolium-2-trifluoroborate (2)* was initially a pink coloured liquid but crystallised 1 hour after removal from the distillation apparatus.

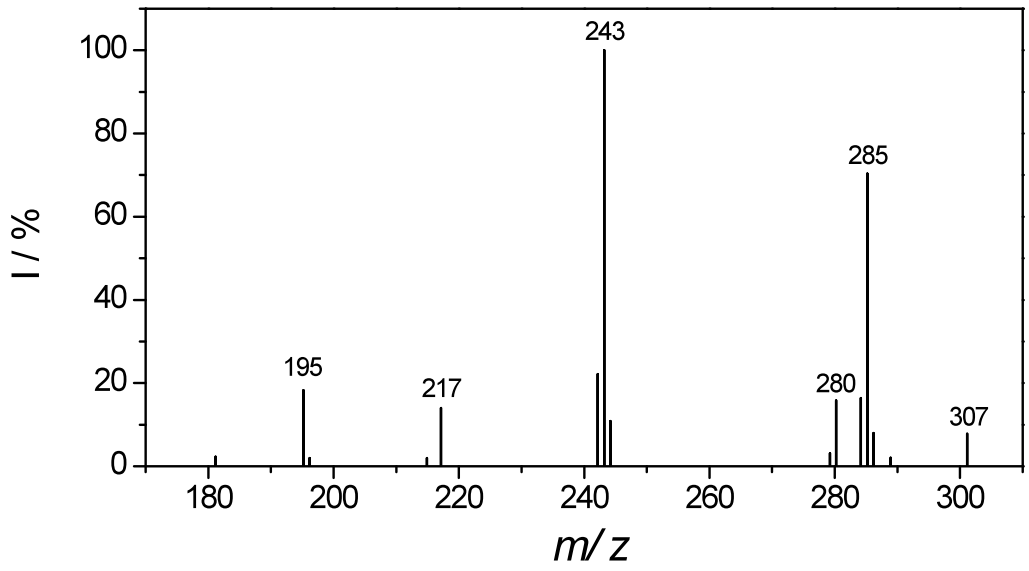
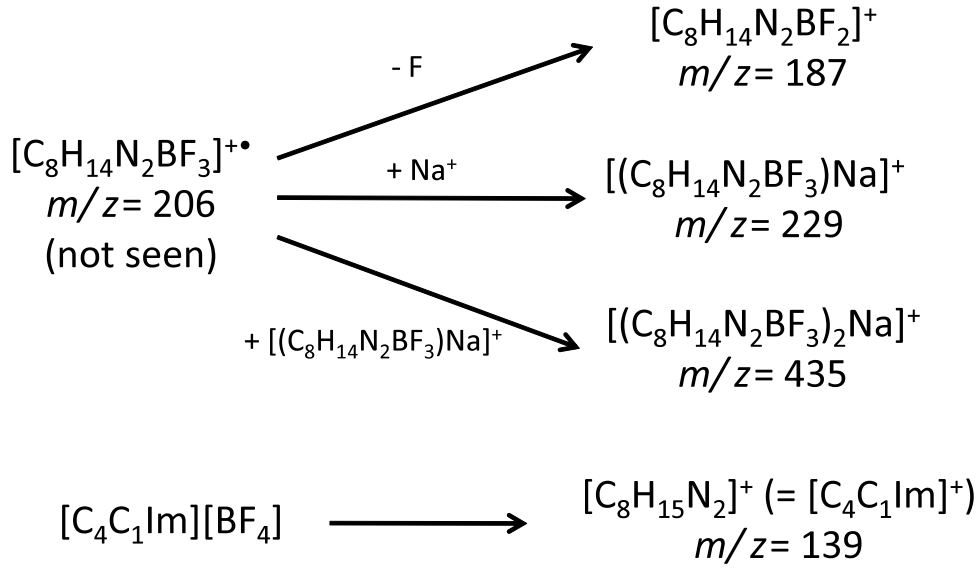


Fig. S2 ESI mass spectrum recorded of the distillate of $[C_8C_1Im][BF_4]$, *1-Octyl-3-methylimidazolium-2-trifluoroborate (**2**)*. The spectrum was recorded in low molecular weight positive mode. A list of peaks with their relative abundances is given in Table S1.

Table S1 Relative abundances and *m/z* values of the major peaks in the ESI mass spectrum recorded of the distillate of $[C_8C_1Im][BF_4]$, *1-Octyl-3-methylimidazolium-2-trifluoroborate (**2**)*.

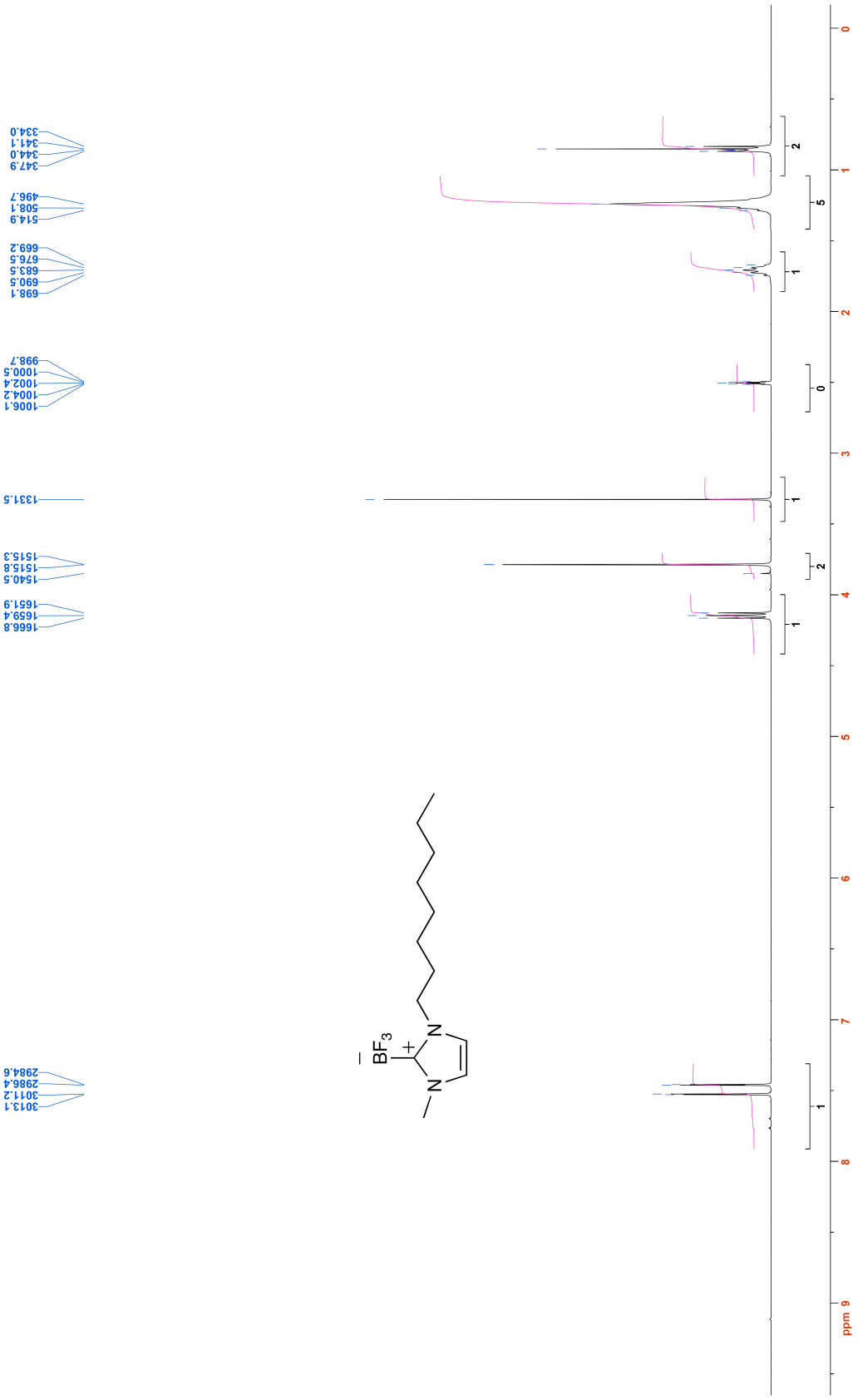
$[C_8C_1Im][BF_4]$		
m/z	*I* / %	Formula
195	18.3	$[C_{12}H_{23}N_2]^+$
217	14.0	unknown
242	22.2	$[C_{12}H_{22}N_2{}^{10}BF_2]^+$
243	100	$[C_{12}H_{22}N_2{}^{11}BF_2]^+$
244	10.9	$[{}^{13}C^{12}C_{11}H_{22}N_2{}^{11}BF_2]^+$
280	15.8	$[(C_{12}H_{14}N_2{}^{11}BF_3)NH_4]^+$
284	16.4	$[(C_{12}H_{14}N_2{}^{10}BF_3)Na]^+$
285	70.4	$[(C_{12}H_{14}N_2{}^{11}BF_3)Na]^+$
286	8.0	$[({}^{13}C^{12}C_{11}H_{14}N_2{}^{11}BF_3)Na]^+$



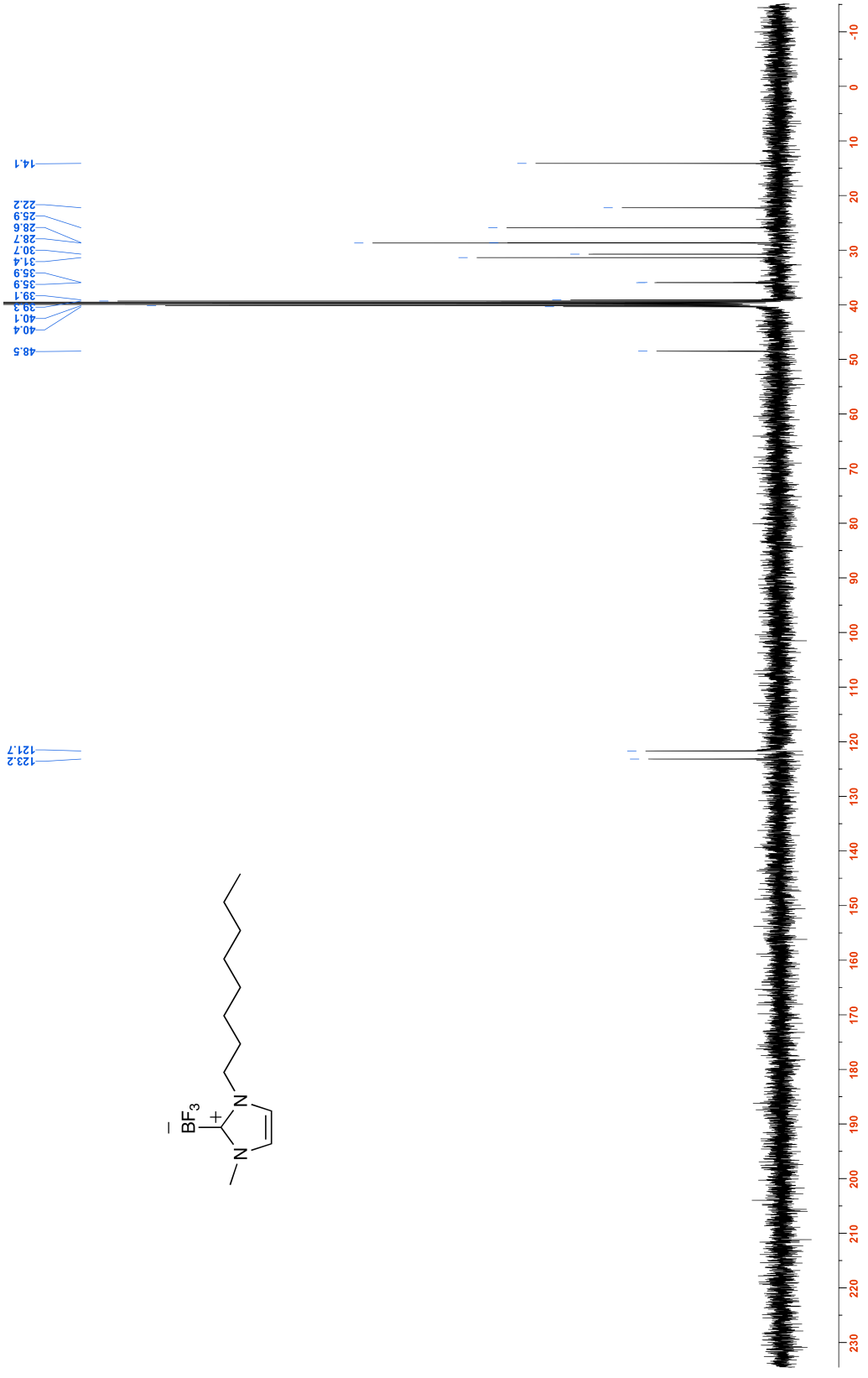
Scheme S1 Proposed fragmentation pattern giving rise to the fragments observed in the ESI-MS of the distillate of $[C_4C_1Im][BF_4]$, *1-butyl-3-methylimidazolium-2-trifluoroborate (**1**)*, as shown in Fig. 4 (main paper).

Figure S3 (a) ^{1}H (300.1 MHz), (b) ^{13}C (75.5 MHz), (c) ^{11}B (128.4 MHz) and (d) ^{19}F (376.5 MHz) NMR spectra in DMSO-d_6 of the distillate of $[C_8C_1Im][BF_4]$, *1-octyl-3-methylimidazolium-2-trifluoroborate*.

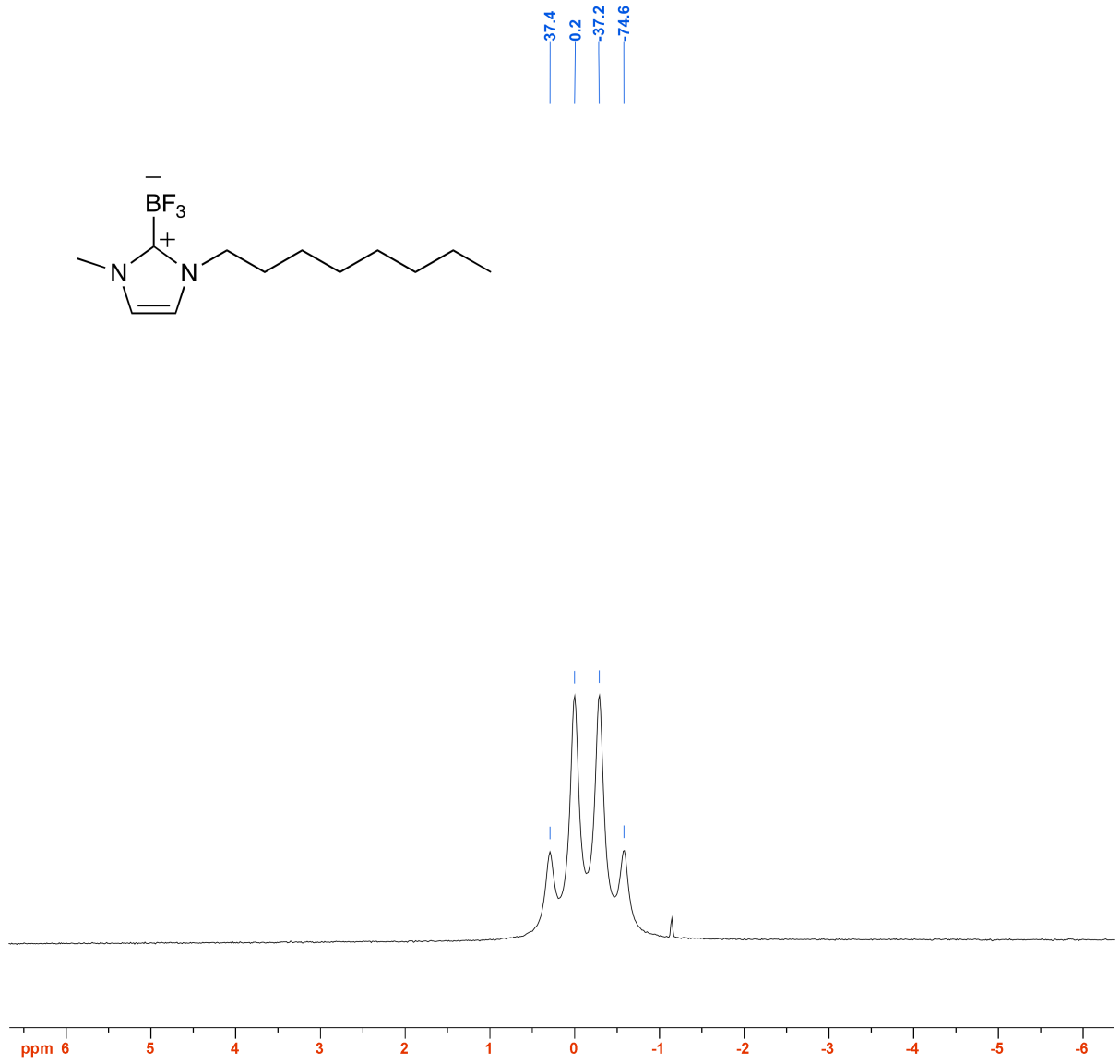
(a)



(b)


14.1
22.2
25.9
28.6
28.7
30.7
31.4
35.9
35.9
39.1
39.3
40.1
40.4
48.5
121.7
123.2
BF3
N
N

(c)



(d)

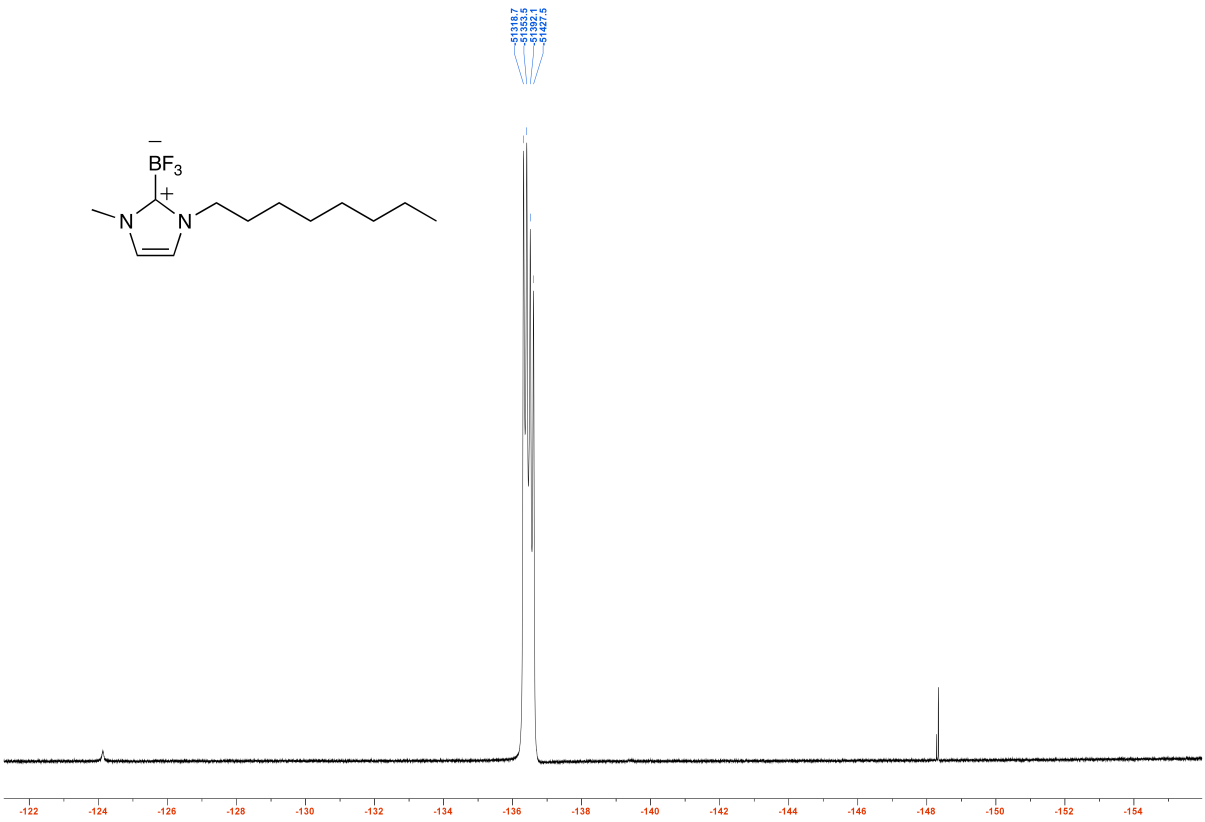
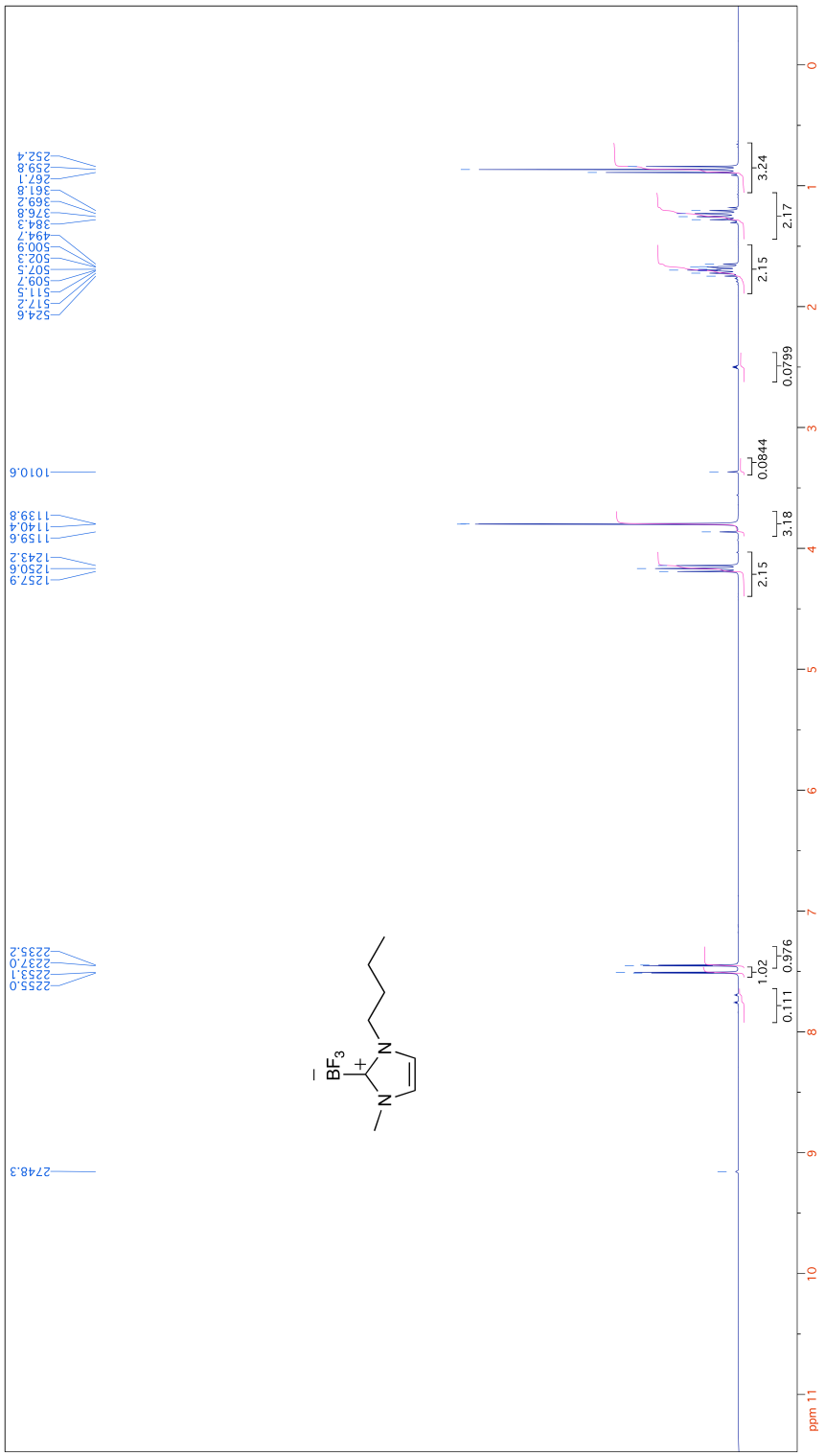
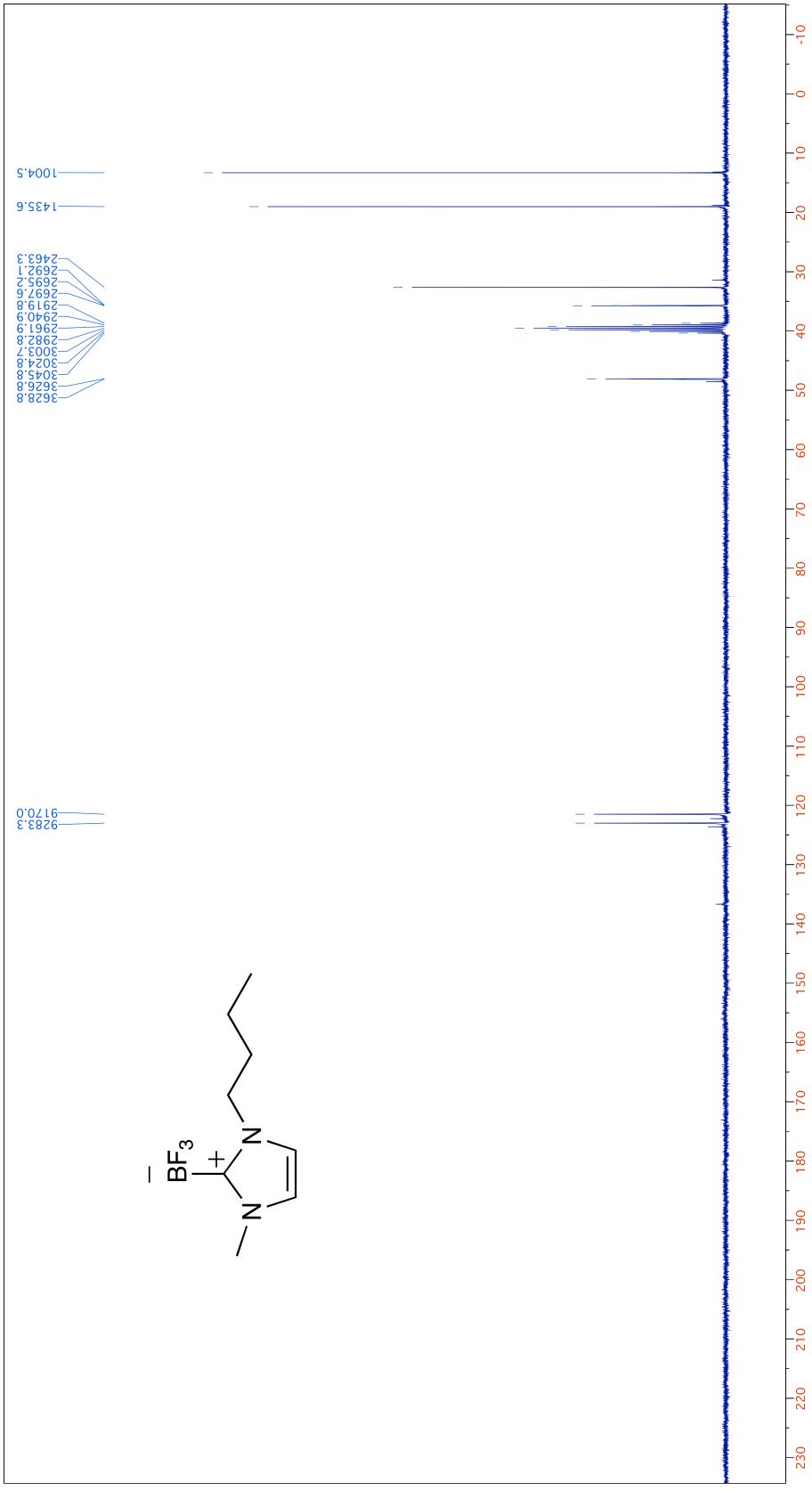

BF3
N
N
-131.8
-131.9
-132.0
-132.1
-132.2
-122
-124
-126
-128
-130
-132
-134
-136
-138
-140
-142
-144
-146
-148
-150
-152
-154

Figure S4 (a) ^{1}H (300.1 MHz), (b) ^{13}C (75.5 MHz), (c) ^{11}B (128.4 MHz) and (d) ^{19}F (376.5 MHz) NMR spectra in DMSO-d_6 of the distillate of $[C_4C_1Im][BF_4]$, *1-butyl-3-methylimidazolium-2-trifluoroborate.*

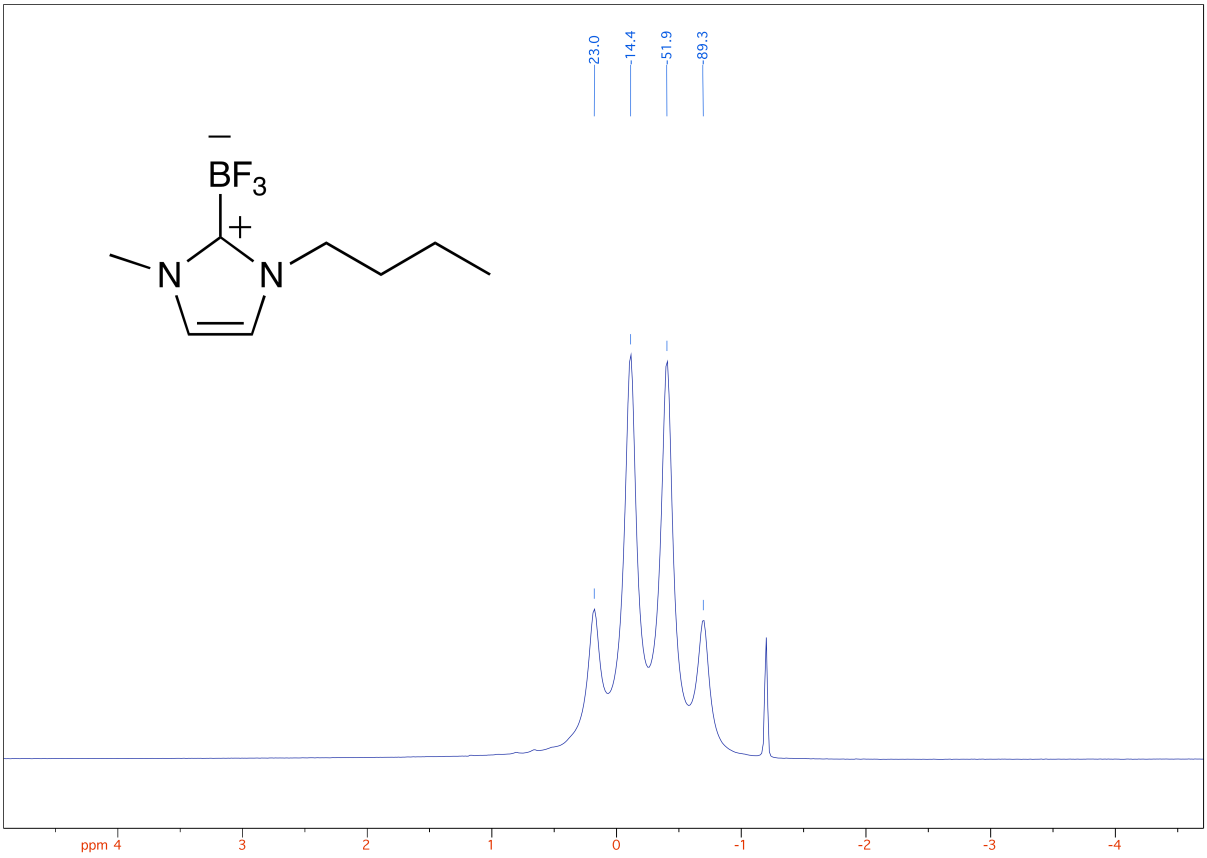
(a)



(b)


1004.5
1435.6
2463.3
2692.1
2695.2
2697.6
2919.8
2940.9
2961.9
2982.8
3003.7
3024.8
3045.8
3626.8
9283.3
9170.0
BF3
N
N

(c)



(d)

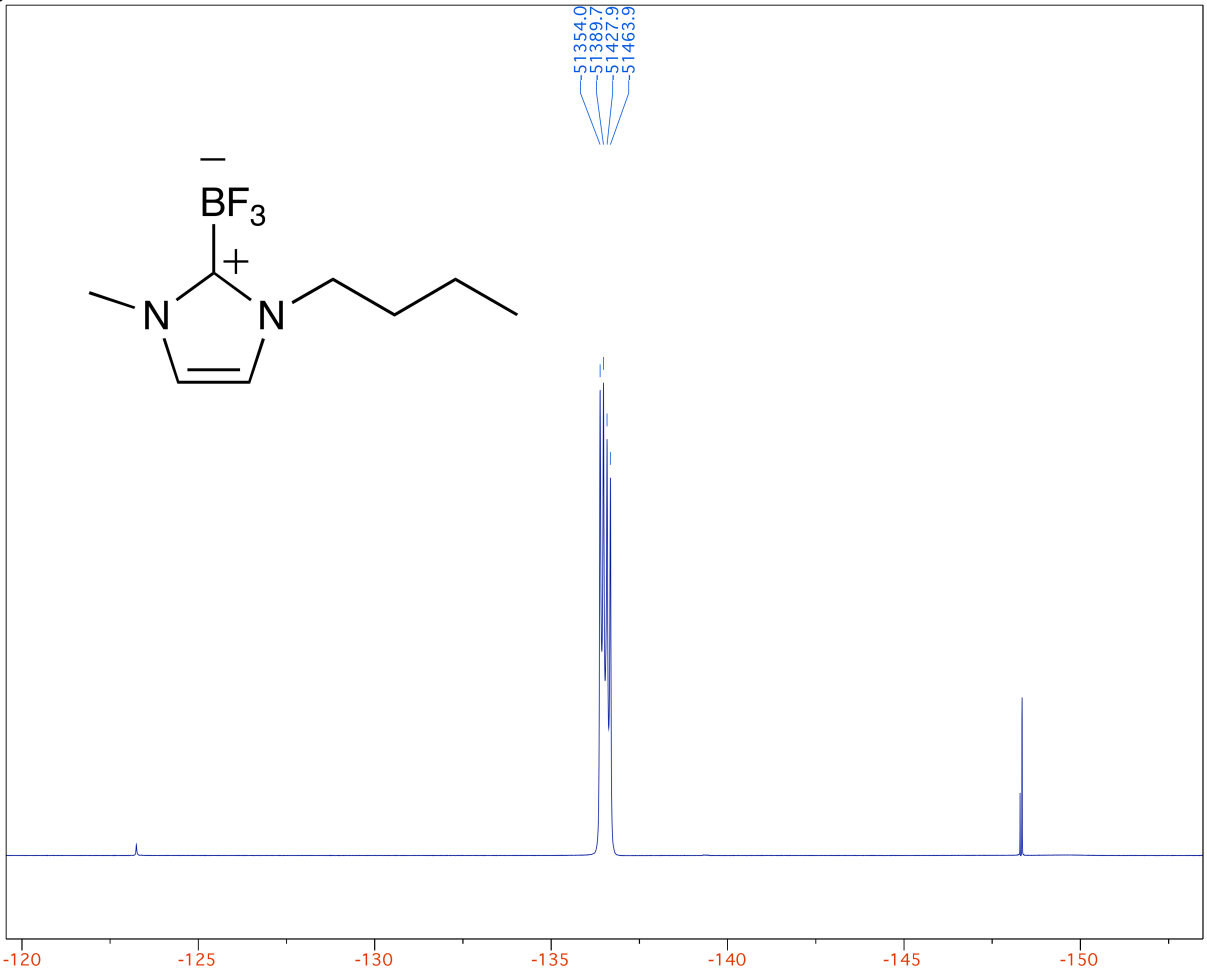
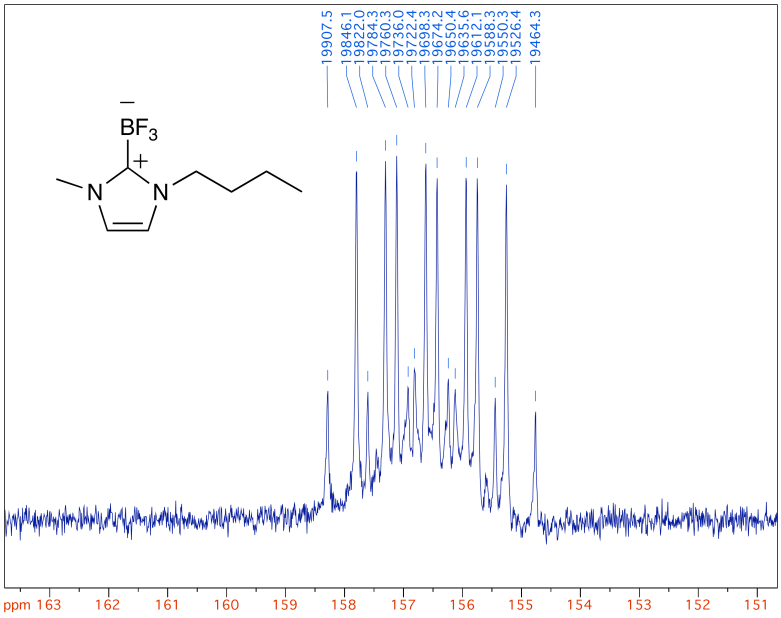
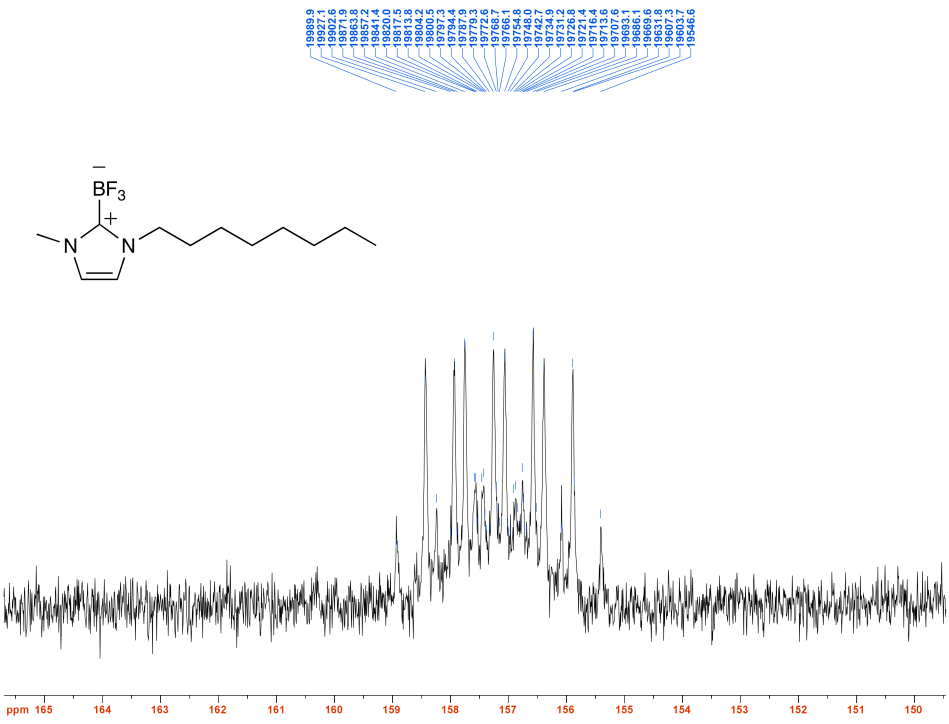

51354.0
51389.7
51427.9
51463.9
BF3
N
N
-120
-125
-130
-135
-140
-145
-150

Fig. S5, Expansion of ^{13}C NMR (Bruker DPX-500 MHz, CD_2Cl_2) for the distillate of (a) $[C_4C_1Im][BF_4]$ and (b) $[C_8C_1Im][BF_4]$. The NMR spectra were recorded with an extended d1 relaxation time of 10 secs in order to observe the C^2 signal of the imidazolium group. This signal is commonly unobserved in carbon-borane NMR spectra, due to coupling to the rapid relaxing quadropolar B nucleus. The coupling constants, $J_{C\text{-}B}$ (86 Hz) and $^2J_{C\text{-}F}$ (62 Hz), furthered confirmed the attachment of the BF_3 group to the C^2 carbon of the imidazolium ring. The signals are interpreted with the generic splitting diagram (c).

(a)



(b)



(c)

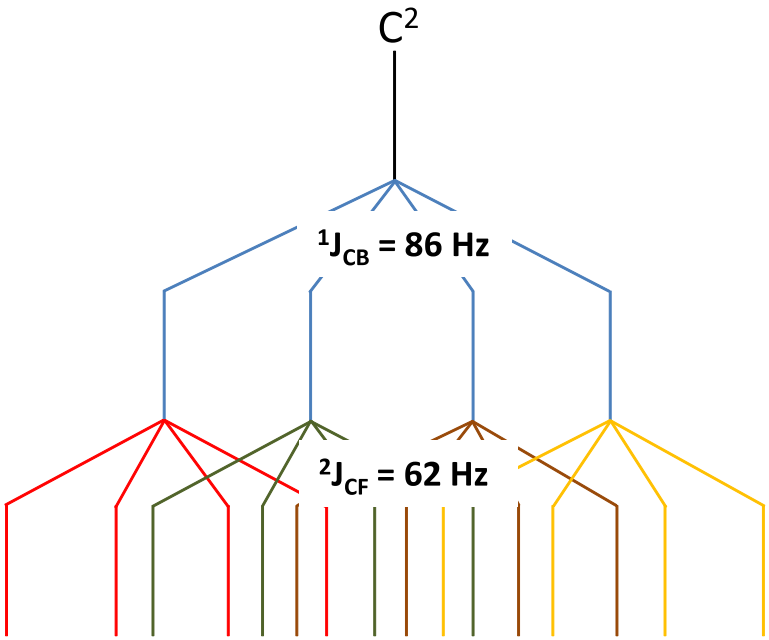
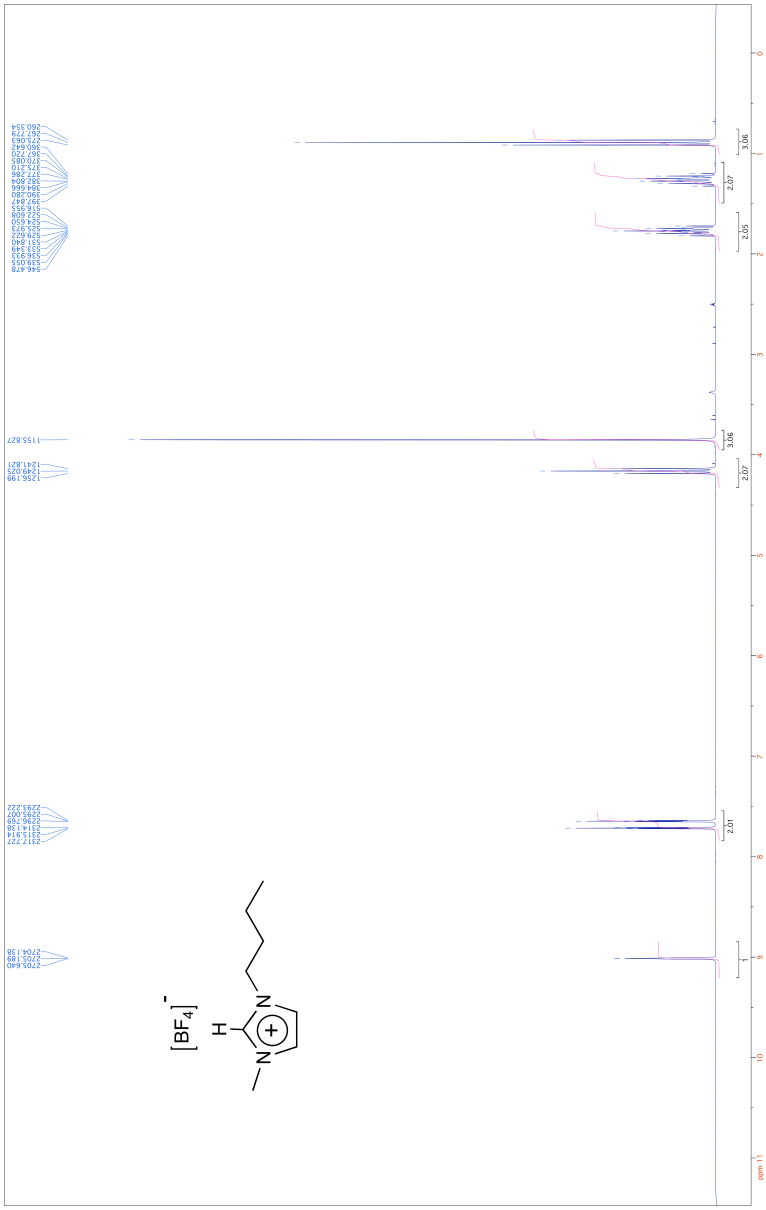


Figure S6 (a) ^{1}H (300.1 MHz) and (b) ^{13}C (75.5 MHz), NMR reference spectra of $[C_4C_1Im][BF_4]$ in DMSO-d_6

(a)



(b)

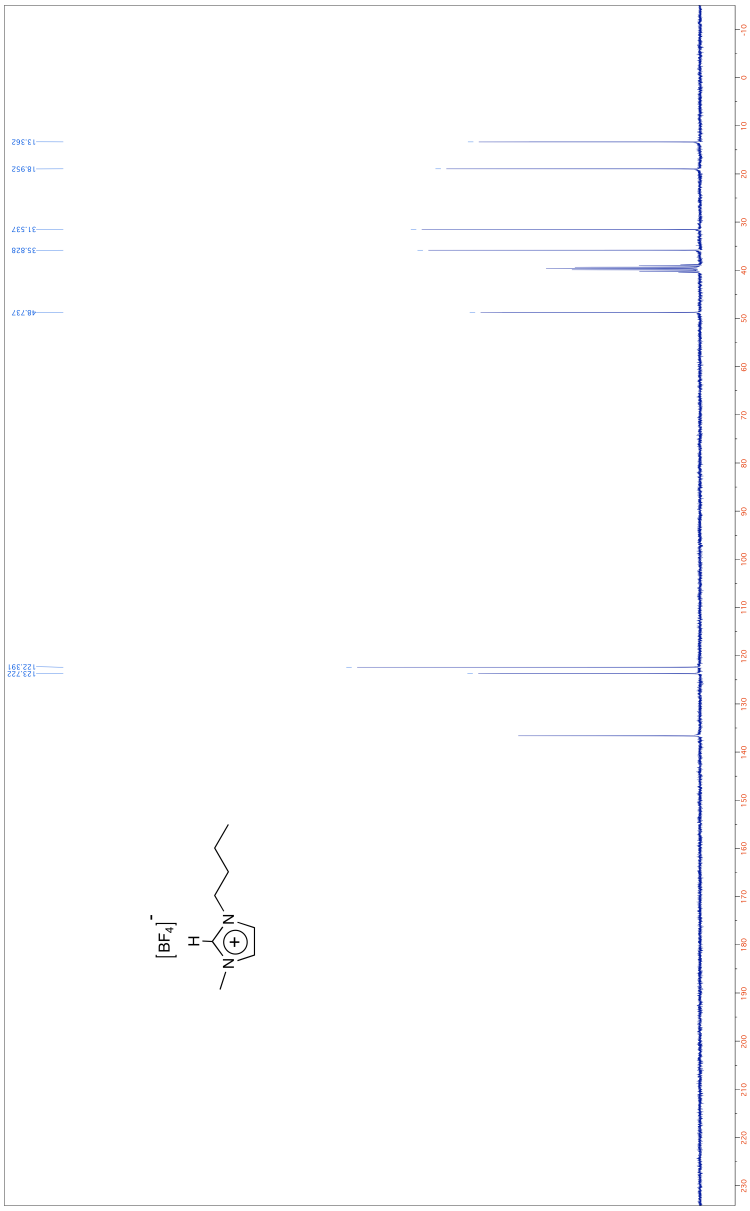
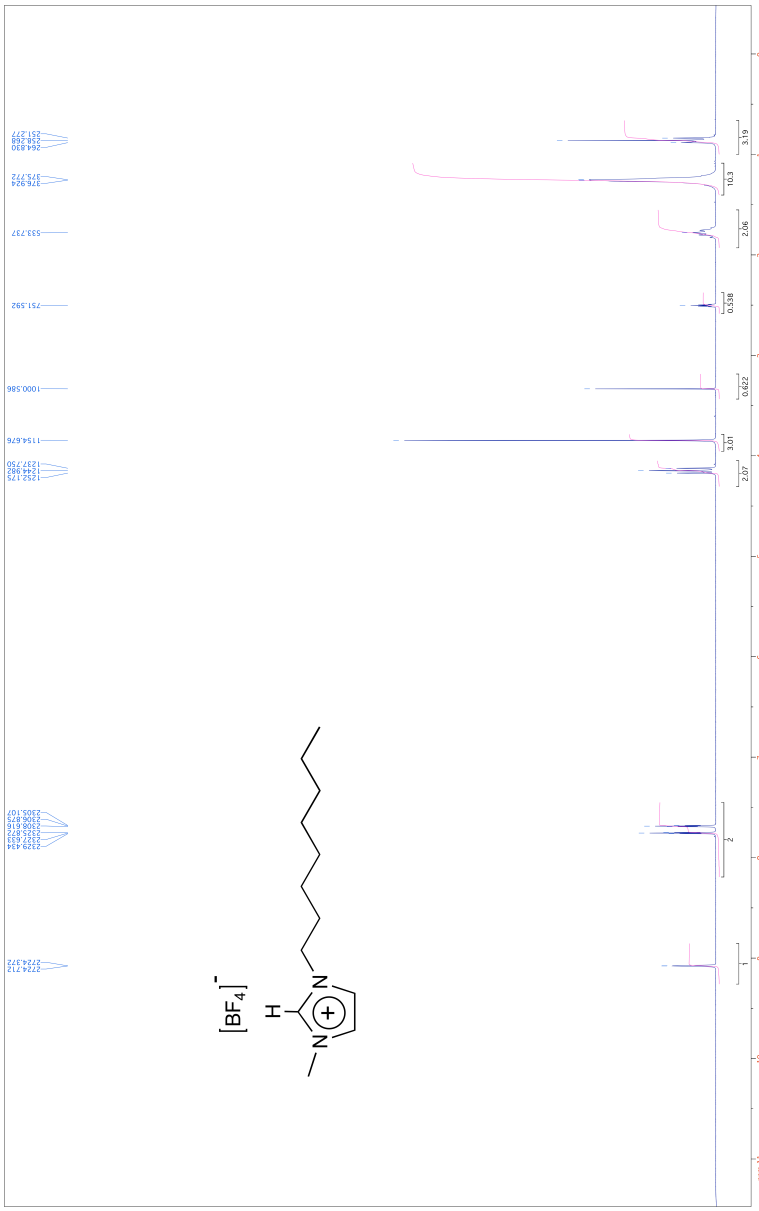
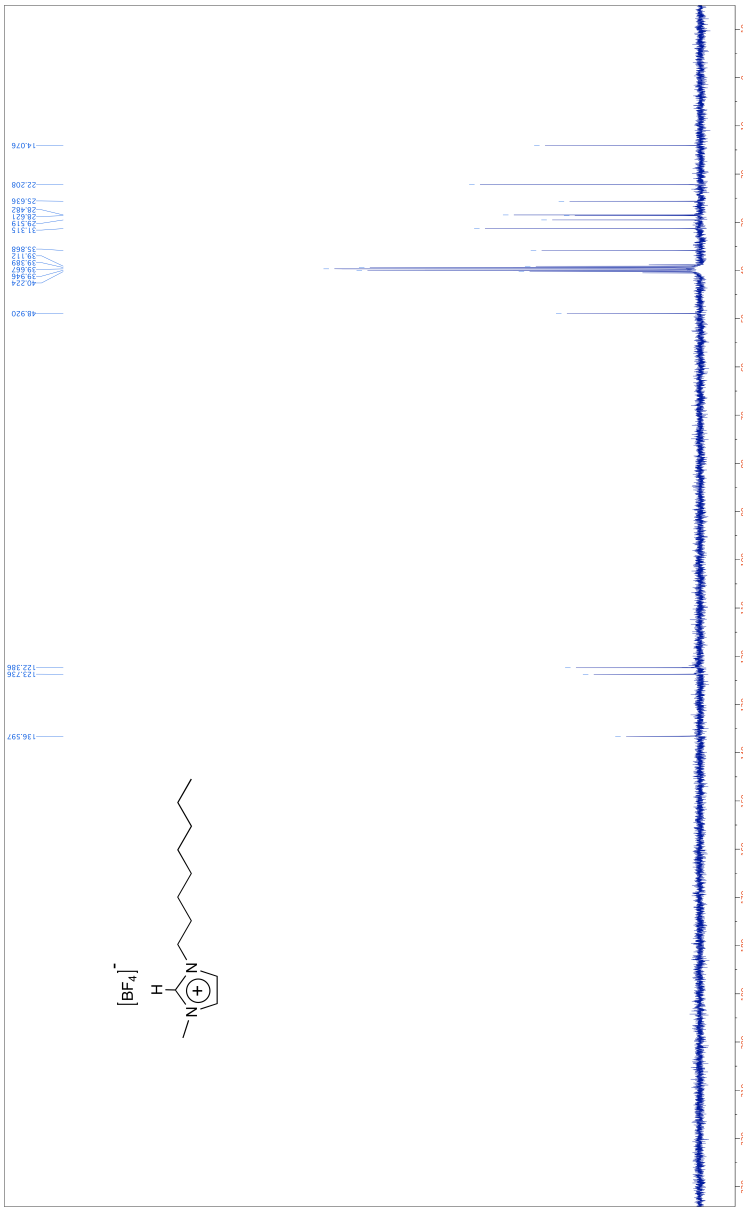


Figure S7 (a) ^{1}H (300.1 MHz) and (b) ^{13}C (75.5 MHz), NMR reference spectra of $[C_8C_1Im][BF_4]$ in DMSO-d_6

(a)



(b)


14.076
22.208
25.636
26.462
28.621
29.519
31.315
33.068
39.109
39.112
39.546
40.224
44.920
122.386
123.736
136.597
[BF4]-
H
N
N