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**SUPPORTING INFORMATION**

# 1-Alkyl-3-methylimidazolium 4-organyloxy-2,3,5,6-tetrafluorophenyltrifluoroborates as a new platform for ionic liquids with specific properties

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**The viscosity measurements of ionic liquids**

The viscosity of prepared ionic liquids was measured by capillary viscosimeter (capillary tube diameter 0.49 mm, the constant of viscosimeter $K$ = 0.03321 $mm^2/sec^2$) at 60°C.

The kinematic viscosity were calculated by formulas (**1**) and (**2**), respectively

$$\nu = \frac{g}{9.807} \cdot K \cdot t \qquad (\mathbf{1})$$

$$\eta = \nu \cdot d \qquad (\mathbf{2})$$

Whereas

$\nu$ – kinematic viscosity, $mm^2/sec$

$g$ – the acceleration of gravity at the point of measurement, 9.815 $m/sec^2$

$K$ – the constant of viscosimeter, 0.03321 $mm^2/sec^2$

$t$ – time of flowing liquid, sec

$\eta$ – dynamic viscosity, MPa·sec

$d$ – density of liquid, $kg/m^3$

The results are presented in Table:

| **Ionic liquid** | **t, sec** | **v, $mm^2/sec$** | **d, $kg/m^3$** | **n, MPa·sec** |
|---|---|---|---|---|
| $BMIM[BF_4]$ | 547 | 18,18 | 1177 | 21398,67 |
| $EMIM[C_6F_5BF_3]$ (**3b**) | 683 | 22,70 | 1486 | 33733,59 |
| $BMIM[C_6F_5BF_3]$ (**3c**) | 962 | 31,97 | 1331 | 42557,50 |
| $OMIM[C_6F_5BF_3]$ (**3d**) | 1244 | 41,35 | 1265 | 52303,88 |
| $BMMIM[C_6F_5BF_3]$ (**3e**) | 1593 | 52,95 | 1357 | 71848,65 |

**The spectral data of prepared ionic liquids**

The NMR spectra were recorded on a Bruker AVANCE III 500 ($^{1}$H at 500.13 MHz, $^{11}$B at 160.46 MHz, $^{13}$C at 125.76 MHz, and $^{19}$F at 470.59 MHz) spectrometer. The chemical shifts were referenced to TMS ($^{1}$H, $^{13}$C), $BF_3O(C_2H_5)_2$ in $CDCl_3$ (15% v/v) ($^{11}$B), and $CCl_3F$ ($^{19}$F, with $C_6F_6$ as secondary reference (−162.9 ppm)).

As a convention for the presentation of the NMR spectral data, the labeling of the carbon atoms in imidazolium alkyl groups is presented by Greek symbols, e.g., $CH_3^{\beta}–CH_2^{\alpha}–N$.

Elemental analysis was performed in the Collective Service Center of SB RAS (Novosibirsk).

**1-Butyl-3-methylimidazolium tetrafluoroborate**

**$^{1}$H NMR** ($CDCl_3$): δ 8.83 (s, 1H, *H*-2); 7.31 (s, 1H, *H*-4); 7.26 (s, 1H, *H*-5); 4.16 (t, 2H, $^{3}J_{HH}$ 7.4 Hz, α-C*H*$_2$); 3.94 (s, 3H, NC*H*$_3$); 1.84 (tt, 2H, $^{3}J_{HH}$ 7.4 Hz, $^{3}J_{HH}$ 7.4 Hz, β-C*H*$_2$); 1.35 (qt, 2H, $^{3}J_{HH}$ 7.4 Hz, $^{3}J_{HH}$ 7.5 Hz, γ-C*H*$_2$); 0.84 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, δ-C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ -0.99 (q, $^{1}J_{BF}$ 1.2 Hz, *B*F$_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 136.91 (s, *C*H-2); 123.78 (s, *C*H-4); 122.19 (s, *C*H-5); 50.13 (s, α-*C*H$_2$) 36.58 (s, N*C*H$_3$) 32.11 (s, β-*C*H$_2$); 19.61 (s, γ-*C*H$_2$); 13.51 (s, δ-*C*H$_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -152.67 (s, 4F, B*F*$_4$).

**1-Butyl-2,3-dimethylimidazolium tetrafluoroborate**

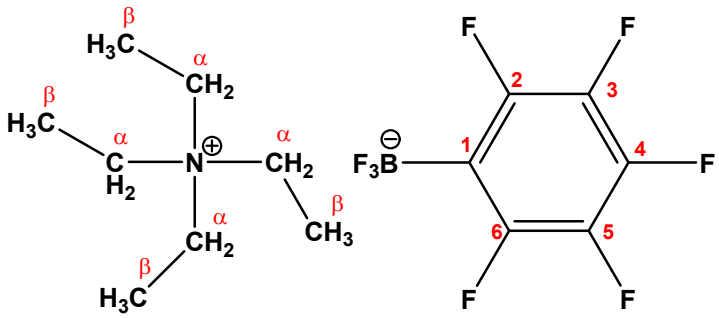
**$^{1}$H NMR** ($CDCl_3$): δ 7.28 (d, 1H, $^{3}J_{HH}$ 2.1 Hz, *H*-4); 7.20 (d, 1H, $^{3}J_{HH}$ 2.1 Hz, *H*-5); 4.04 (t, 2H, $^{3}J_{HH}$ 7.5 Hz, α-C*H*$_2$); 3.78 (s, 3H, NC*H*$_3$); 2.58 (s, 3H, C2-C*H*$_3$); 1.75 (tt, 2H, $^{3}J_{HH}$ 7.6 Hz, $^{3}J_{HH}$ 7.6 Hz, β-C*H*$_2$); 1.35 (qt, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.5 Hz, γ-C*H*$_2$); 0.92 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, δ-C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ -1.24 (s, *B*F$_4$).

**$^{13}$C NMR** ($CDCl_3$): δ 143.95 (s, *C*-2); 122.62 (s, *C*H-4); 120.80 (s, *C*H-5); 48.42 (s, α-*C*H$_2$) 35.15 (s, N*C*H$_3$) 31.55 (s, β-*C*H$_2$); 19.51 (s, γ-*C*H$_2$); 13.41 (s, δ-*C*H$_3$); 9.41 (s, C2-*C*H$_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -153.84 (s, B*F*$_4$).

**Tetraethylammonium pentafluorophenyltrifluoroborate (3a)**



**$^{1}$H NMR** ($CDCl_3$): δ 3.26 (q, 2H, $^{3}J_{HH}$ 7.3 Hz, C*H*$_2$); 1.28 (tt, 3H, $^{3}J_{HH}$ 7.3 Hz, $^{3}J_{HN}$ 1.8 Hz, C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 1.86 (q, $^{1}J_{BF}$ 44.8 Hz, *B*$F_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.34 (dm, $^{1}J_{CF}$ 239.8 Hz, *C*-2,6); 139.37 (dm, $^{1}J_{CF}$ 247.5 Hz, *C*-4); 136.91 (dm, $^{1}J_{CF}$ 248.0 Hz, *C*-3,5); 117.90 (bm, *C*-1); 52.68 (s, *C*$H_2$); 7.35 (s, *C*$H_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -135.93 (q, 3F, $^{2}J_{BF}$ 43.9 Hz, B*F*$_3$); -136.69 (ddq, 2F, $^{3}J_{FF}$ 23.3 Hz; $^{5}J_{FF}$ 11.5 Hz; $^{4}J_{FF(BF3)}$ 11.6 Hz, *F*-2,6); -161.22 (t, 1F, $^{3}J_{FF}$ 19.7 Hz, *F*-4); -166.30 (ddd, 2F, $^{3}J_{FF}$ 23.1 Hz, $^{3}J_{FF}$ 21.3 Hz, $^{5}J_{FF}$ 9.1 Hz, *F*-3,5).

Anal. calcd for $C_{14}H_{20}BF_8N$ (365.11): C, 46.05; H, 5.52; F, 41.63; N, 3.84; found: C, 46.11; H, 5.42; F, 41.60; N, 3.81.

The NMR spectra are presented in Fig. S1-S4.

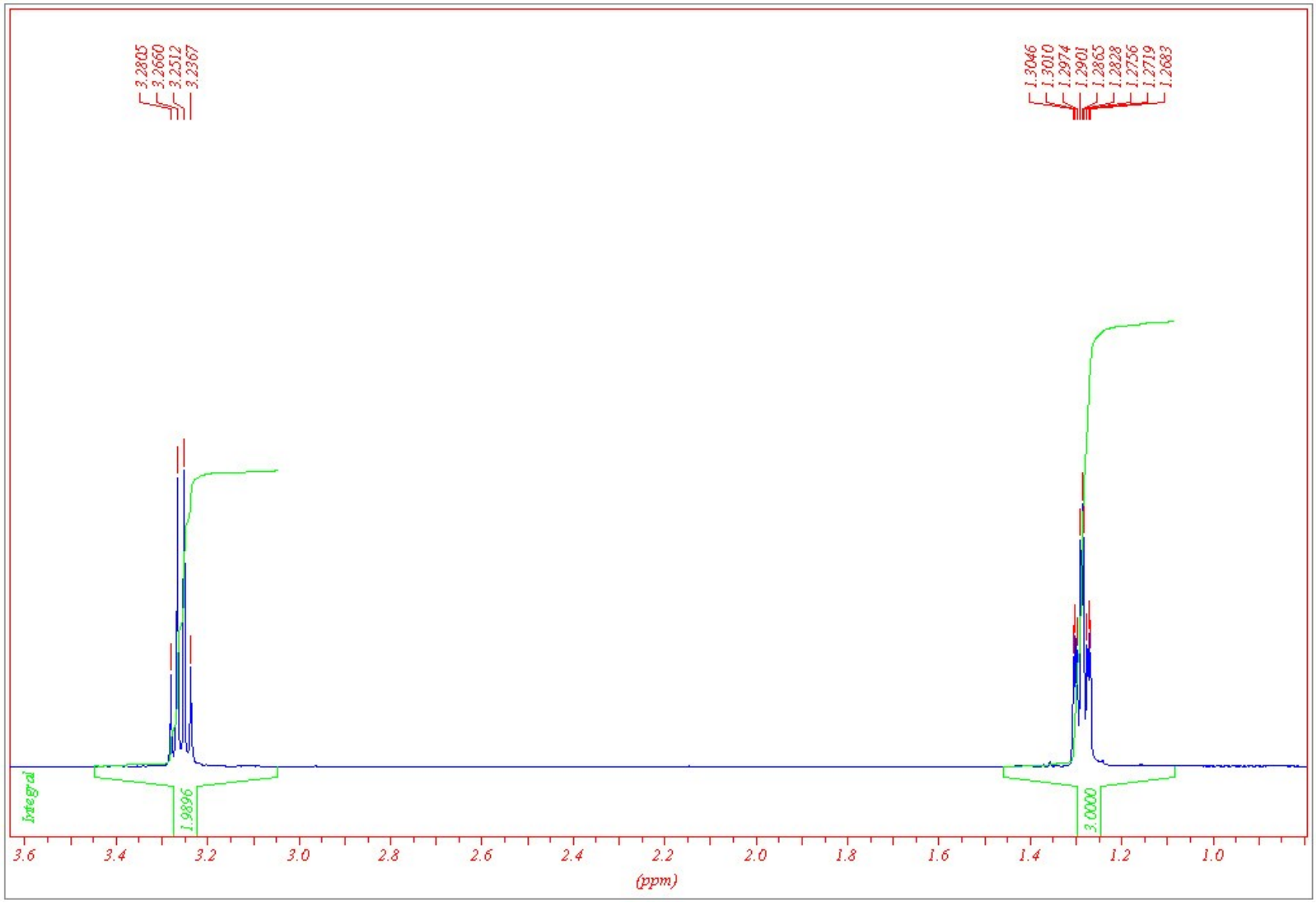



Figure S1. $^{1}H$ NMR spectra of tetraethylammonium pentafluorophenyltrifluoroborate (**3a**)

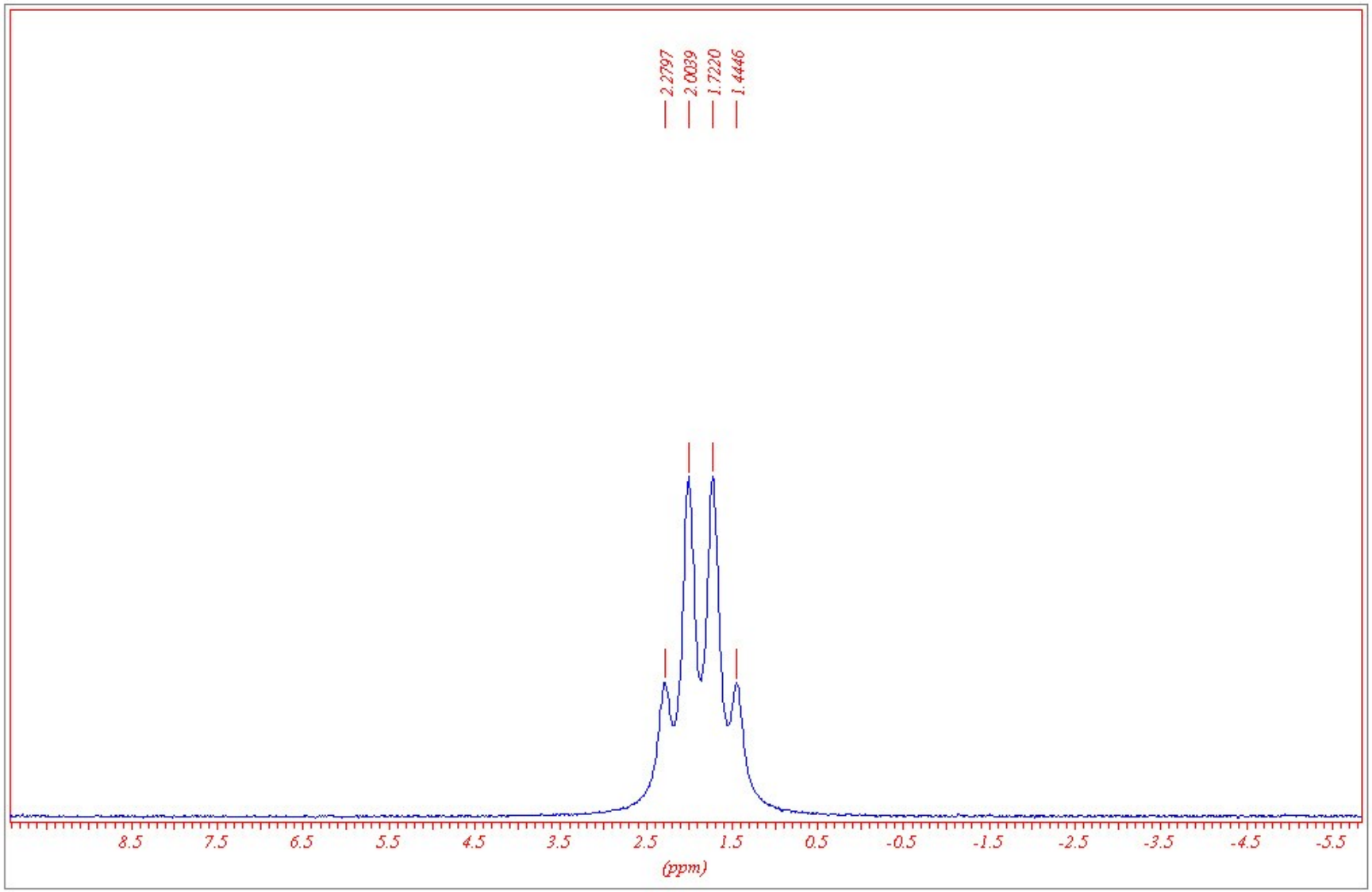



Figure S2. $^{11}B$ NMR spectra of tetraethylammonium pentafluorophenyltrifluoroborate (**3a**)

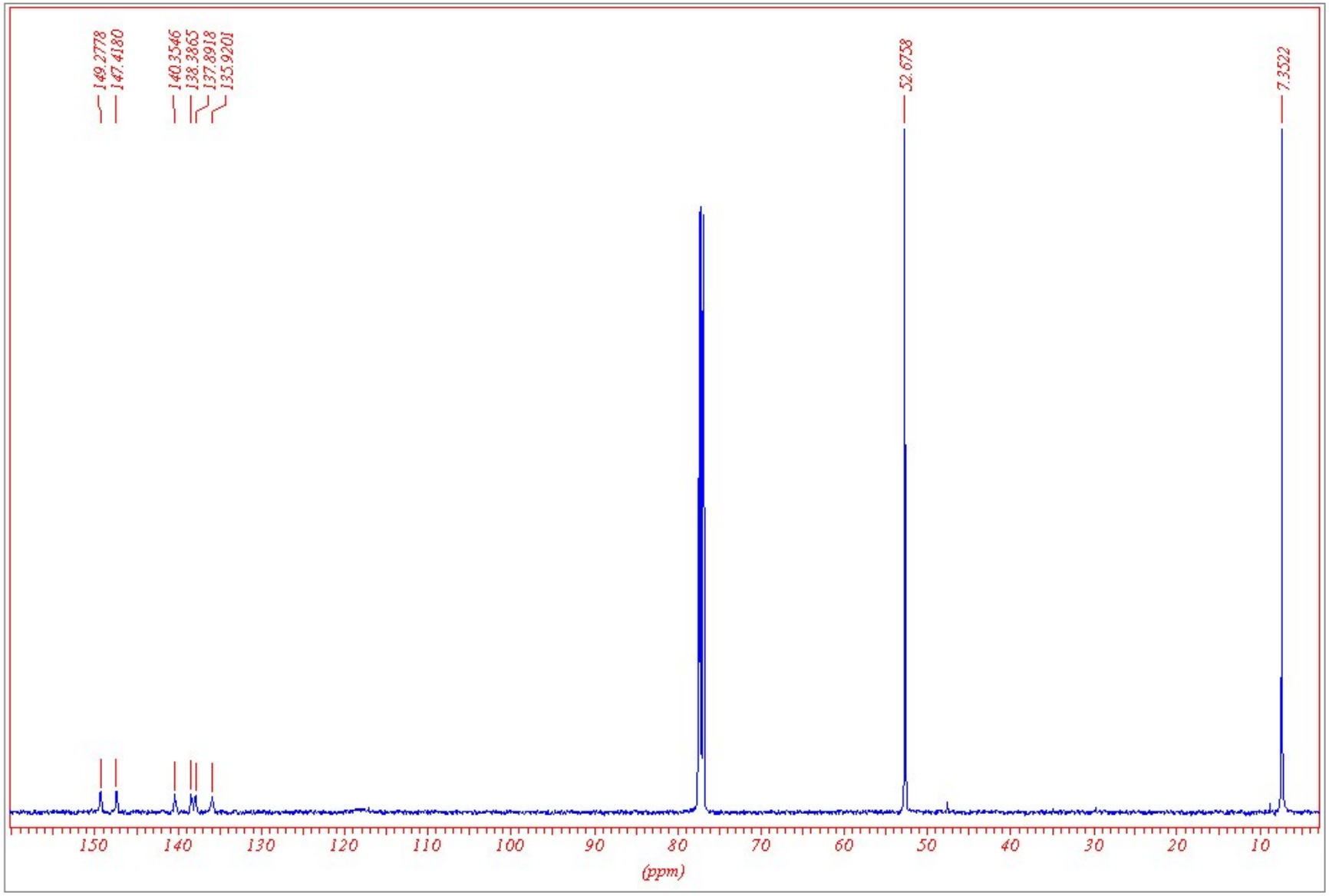



Figure S3. $^{13}C$ NMR spectra of tetraethylammonium pentafluorophenyltrifluoroborate (**3a**)

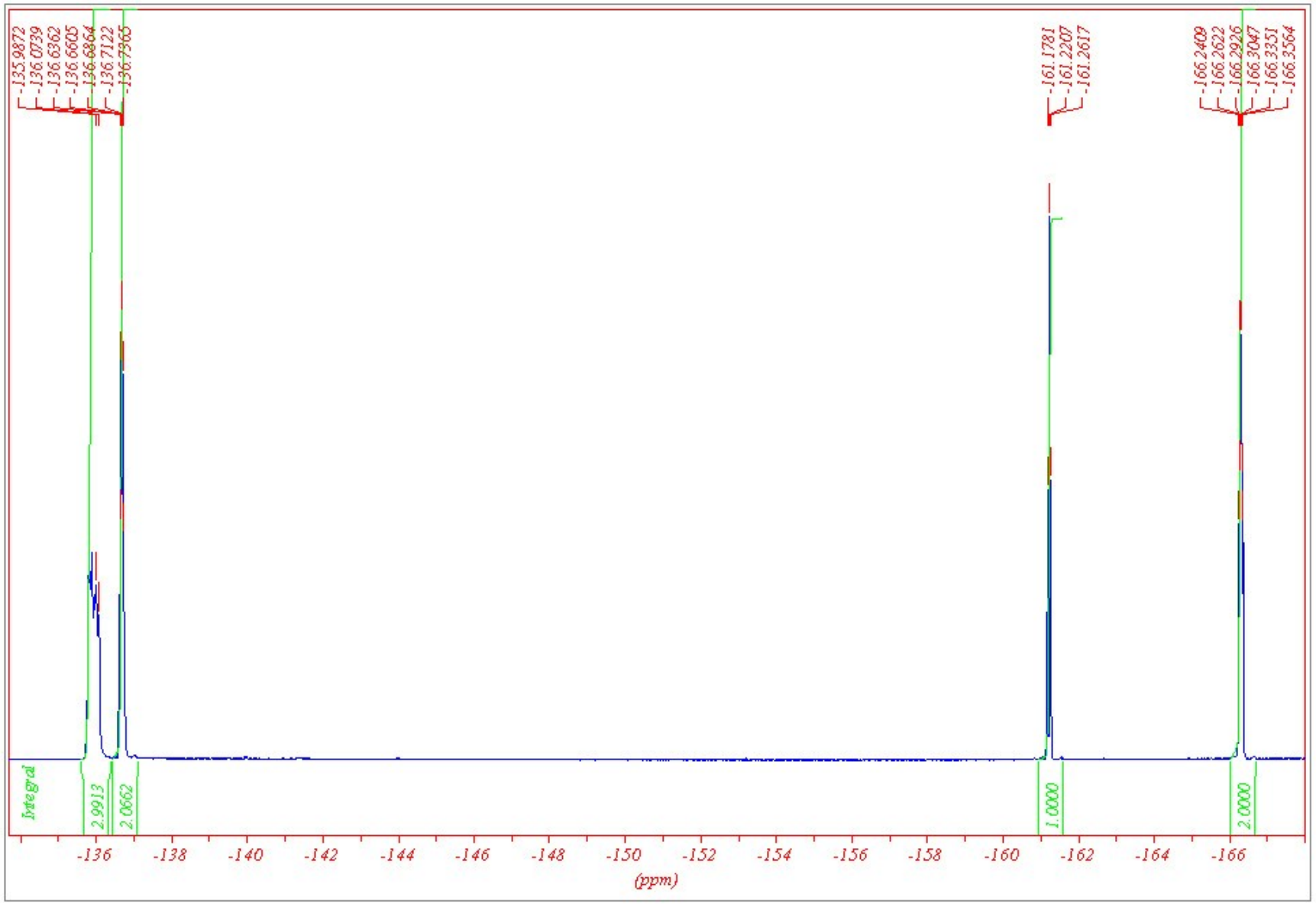
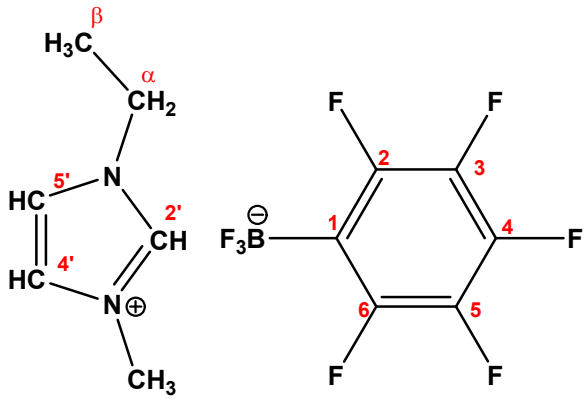



Figure S4. $^{19}F$ NMR spectra of tetraethylammonium pentafluorophenyltrifluoroborate (**3a**)

**1-Ethyl-3-methylimidazolium pentafluorophenyltrifluoroborate (3b)**




**$^{1}$H NMR** ($CDCl_3$): δ 9.00 (s, 1H, *H*-2'); 7.31 (s, 2H, *H*-4',5'); 4.25 (q, 2H, $^{3}J_{HH}$ 7.4 Hz, α-C*H*$_2$); 3.96 (s, 3H, NC*H*$_3$); 1.53 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, β-C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.05 (q, $^{1}J_{BF}$ 45.0 Hz, *B*$F_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.29 (ddddd, $^{1}J_{CF}$ 239.5 Hz, $^{2}J_{CF}$ 17.5 Hz, $^{3}J_{CF}$ 8.3 Hz, 4.1 Hz, $^{4}J_{CF}$ 4.1 Hz, *C*-2,6); 139.54 (dtt, $^{1}J_{CF}$ 248.3 Hz, $^{2}J_{CF}$ 13.3 Hz, $^{3}J_{CF}$ 6.6 Hz, *C*-4); 136.97 (dm, $^{1}J_{CF}$ 247.1 Hz, *C*-3,5); 136.64 (s, *C*H-2'); 123.65 (s, *C*H-4'); 121.78 (s, *C*H-5'); 117.06 (bm, *C*-1); 45.41 (s, α-*C*$H_2$) 36.39 (s, N*C*$H_3$) 15.11 (s, β-*C*$H_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -135.00 (q, 3F $^{2}J_{BF}$ 41.5 Hz, B*F*$_3$); -137.23 (ddq, 2F, $^{3}J_{FF}$ 23.5 Hz; $^{5}J_{FF}$ 11.8 Hz; $^{4}J_{FF(BF3)}$ 11.7 Hz, *F*-2,6); -160.66 (t, 1F, $^{3}J_{FF}$ 20.0 Hz, *F*-4); -166.00 (ddd, 2F, $^{3}J_{FF}$ 23.3 Hz, $^{3}J_{FF}$ 21.1 Hz, $^{5}J_{FF}$ 9.3 Hz, *F*-3,5).

Anal. calcd for $C_{12}H_{11}BF_8N_2$ (346.03): C, 41.65; H, 3.20; F, 43.92; N, 8.10; found: C, 41.58; H, 3.38; F, 43.84; N, 8.13.

The NMR spectra are presented in Fig. S5-S8.

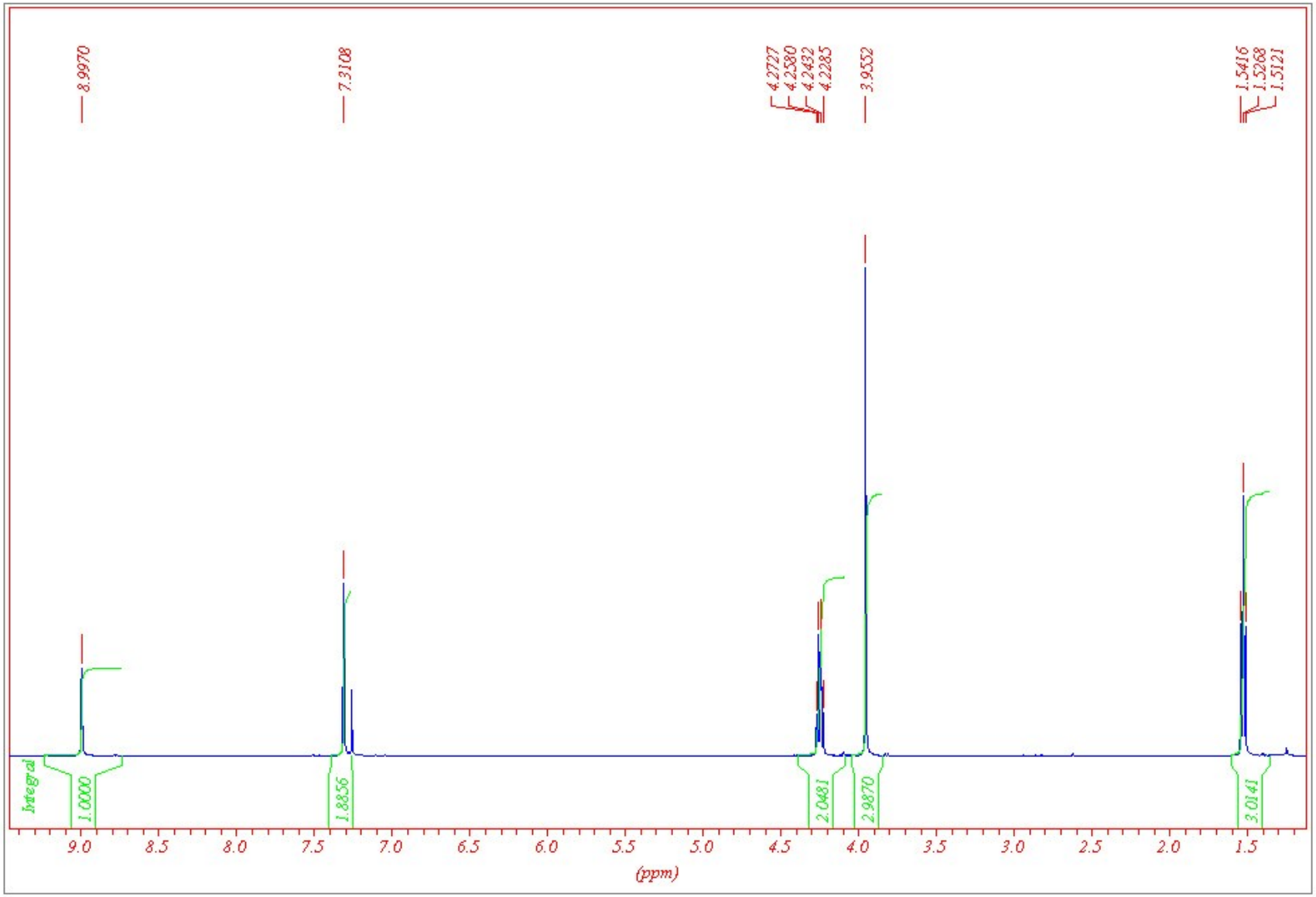



Figure S5. $^{1}H$ NMR spectra of 1-Ethyl-3-methylimidazolium pentafluorophenyltrifluoroborate (**3b**)

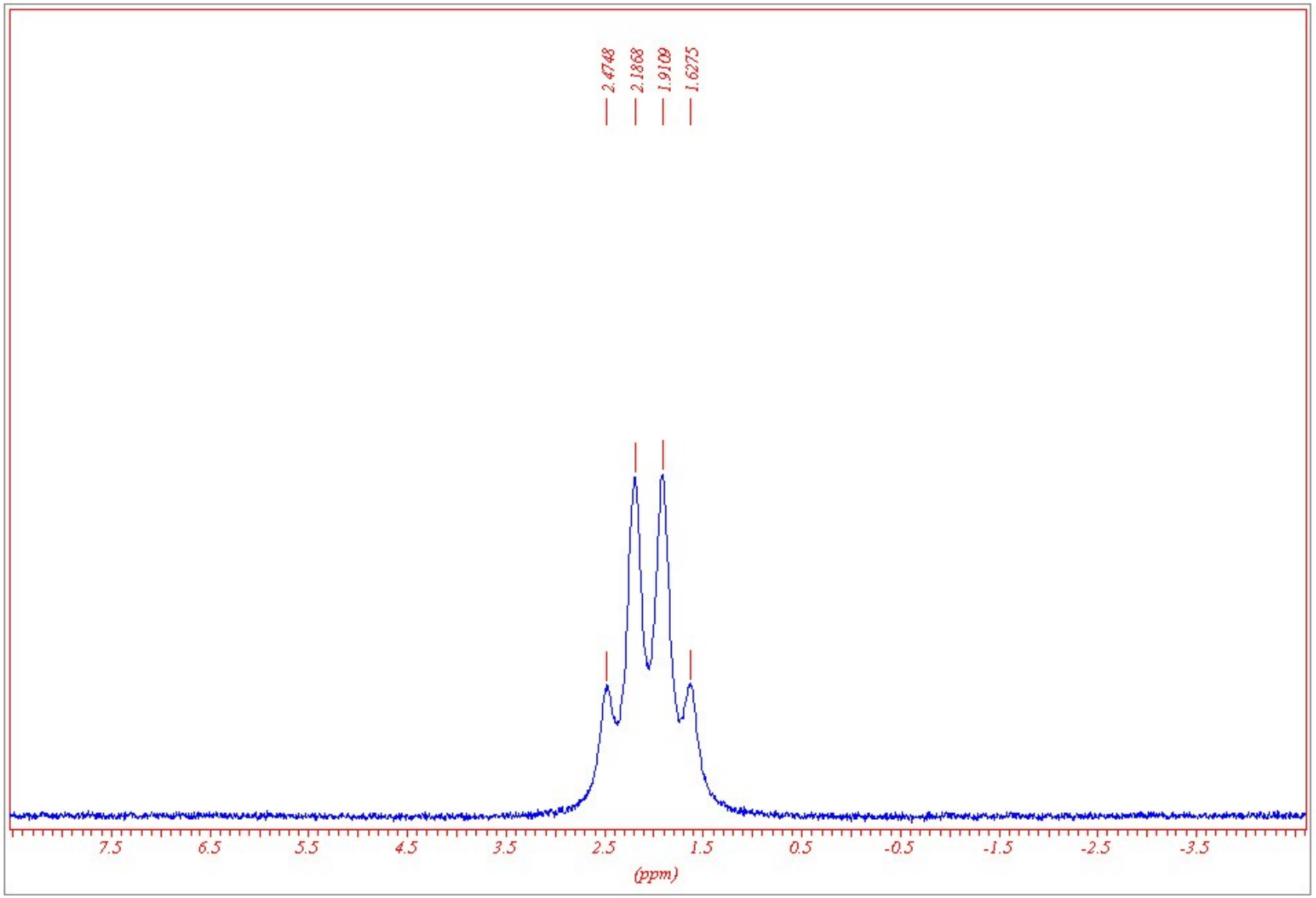



Figure S6. $^{11}B$ NMR spectra of 1-Ethyl-3-methylimidazolium pentafluorophenyltrifluoroborate (**3b**)

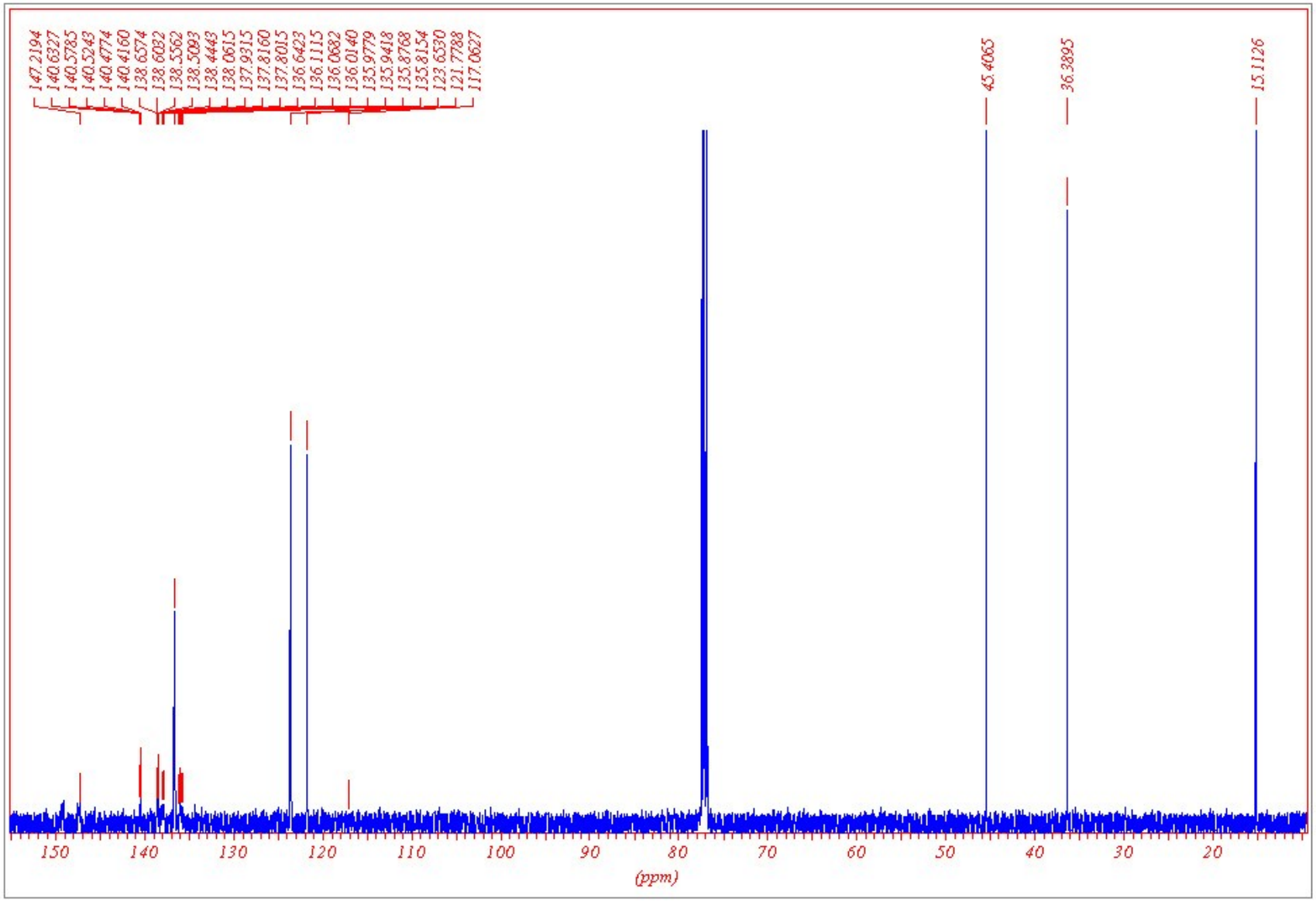



Figure S7. $^{13}C$ NMR spectra of 1-Ethyl-3-methylimidazolium pentafluorophenyltrifluoroborate (**3b**)

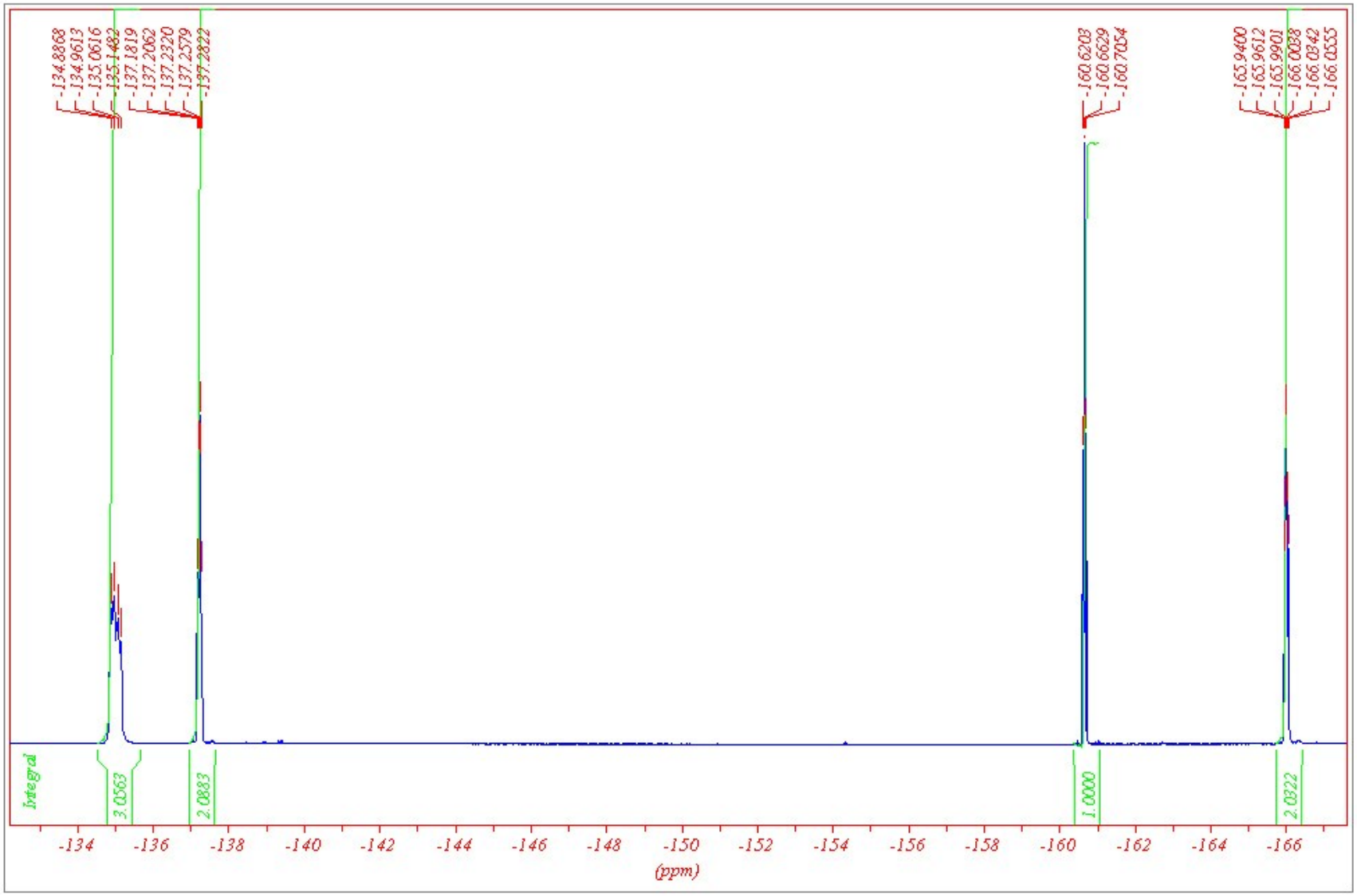
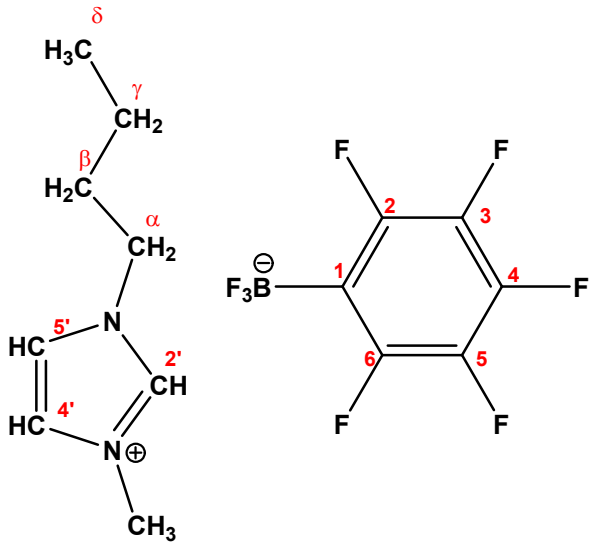



Figure S8. $^{19}F$ NMR spectra of 1-Ethyl-3-methylimidazolium pentafluorophenyltrifluoroborate (**3b**)

**1-Butyl-3-methylimidazolium pentafluorophenyltrifluoroborate (3c)**




**$^{1}$H NMR** ($CDCl_3$): δ 8.89 (s, 1H, *H*-2'); 7.34 (s, 1H, *H*-4'); 7.31 (s, 1H, *H*-5'); 4.15 (t, 2H, $^{3}J_{HH}$ 7.4 Hz, α-C*H*$_2$); 3.93 (s, 3H, NC*H*$_3$); 1.80 (tt, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.5 Hz, β-C*H*$_2$); 1.30 (qt, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.5 Hz, γ-C*H*$_2$); 0.88 (t, 3H, $^{3}J_{HH}$ 7.3 Hz, δ-C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.03 (q, $^{1}J_{BF}$ 45.3 Hz, *B*F$_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.30 (ddddd, $^{1}J_{CF}$ 239.3 Hz, $^{2}J_{CF}$ 17.7 Hz, $^{3}J_{CF}$ 8.5 Hz, 4.3 Hz, $^{4}J_{CF}$ 4.3 Hz, *C*-2,6); 139.50 (dtt, $^{1}J_{CF}$ 247.8 Hz, $^{2}J_{CF}$ 13.3 Hz, $^{3}J_{CF}$ 6.5 Hz, *C*-4); 136.94 (dm, $^{1}J_{CF}$ 248.8 Hz, *C*-3,5); 136.60 (s, *C*H-2'); 123.78 (s, *C*H-4'); 122.27 (s, *C*H-5'); 117.48 (bm, *C*-1); 49.98 (s, α-*C*H$_2$) 36.28 (s, NCH$_3$) 31.96 (s, β-*C*H$_2$); 19.40 (s, γ-*C*H$_2$); 13.15 (s, δ-*C*H$_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.83 (q, 3F $^{2}J_{BF}$ 41.0 Hz, B*F*$_3$); -137.13 (ddq, 2F, $^{3}J_{FF}$ 22.6 Hz; $^{5}J_{FF}$ 11.4 Hz; $^{4}J_{FF(BF3)}$ 11.2 Hz, *F*-2,6); -160.81 (t, 1F, $^{3}J_{FF}$ 20.0 Hz, *F*-4); -166.06 (ddd, 2F, $^{3}J_{FF}$ 23.2 Hz, $^{3}J_{FF}$ 20.7 Hz, $^{5}J_{FF}$ 9.3 Hz, *F*-3,5).

Anal. calcd for $C_{14}H_{15}BF_8N_2$ (374.08): C, 44.95; H, 4.04; F, 40.63; N, 7.49; found: C, 44.84; H, 4.17; F, 40.58; N, 7.52.

The NMR spectra are presented in Fig. S9-S12.

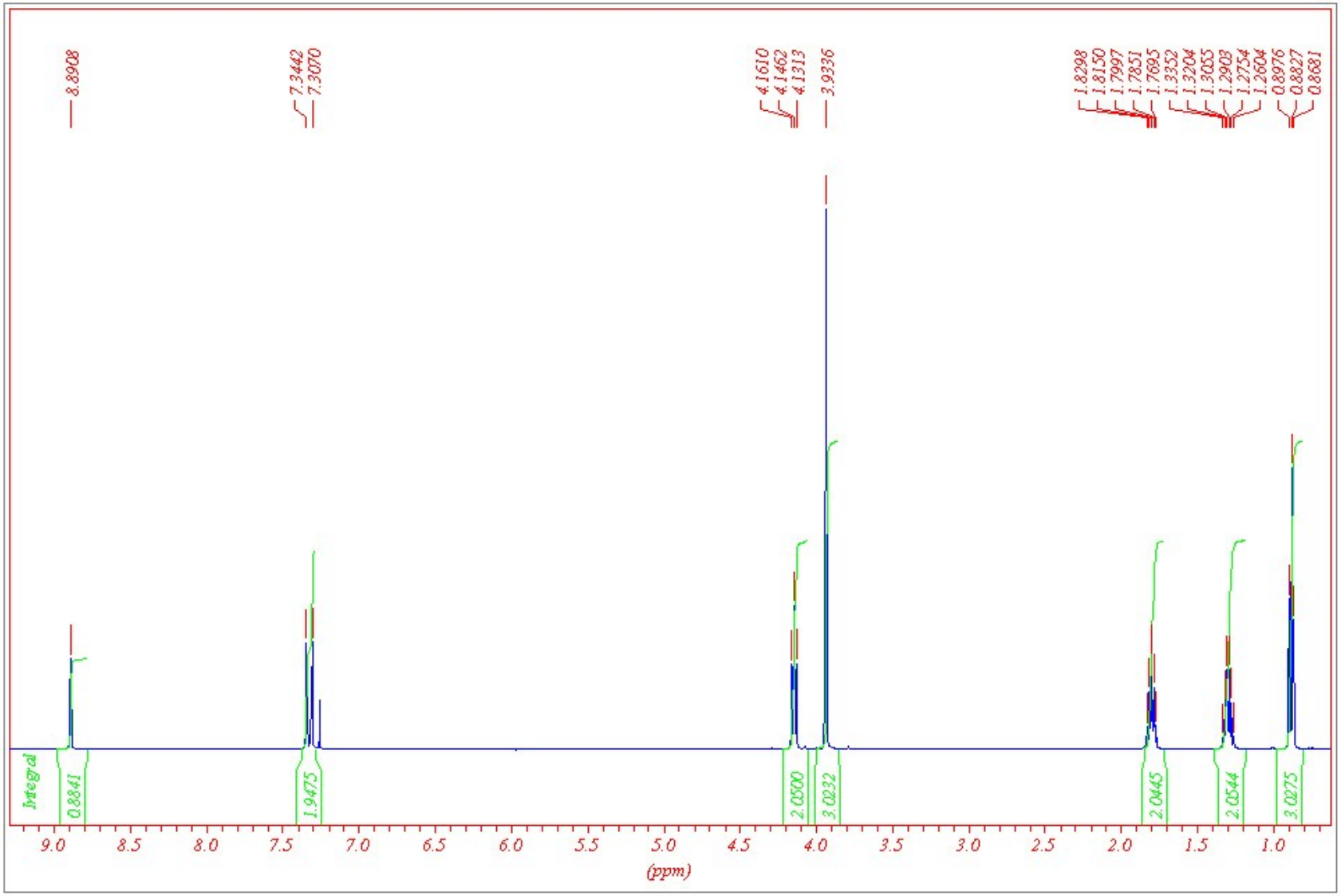



Figure S9. $^{1}H$ NMR spectra of 1-Butyl-3-methylimidazolium pentafluorophenyltrifluoroborate (**3c**)

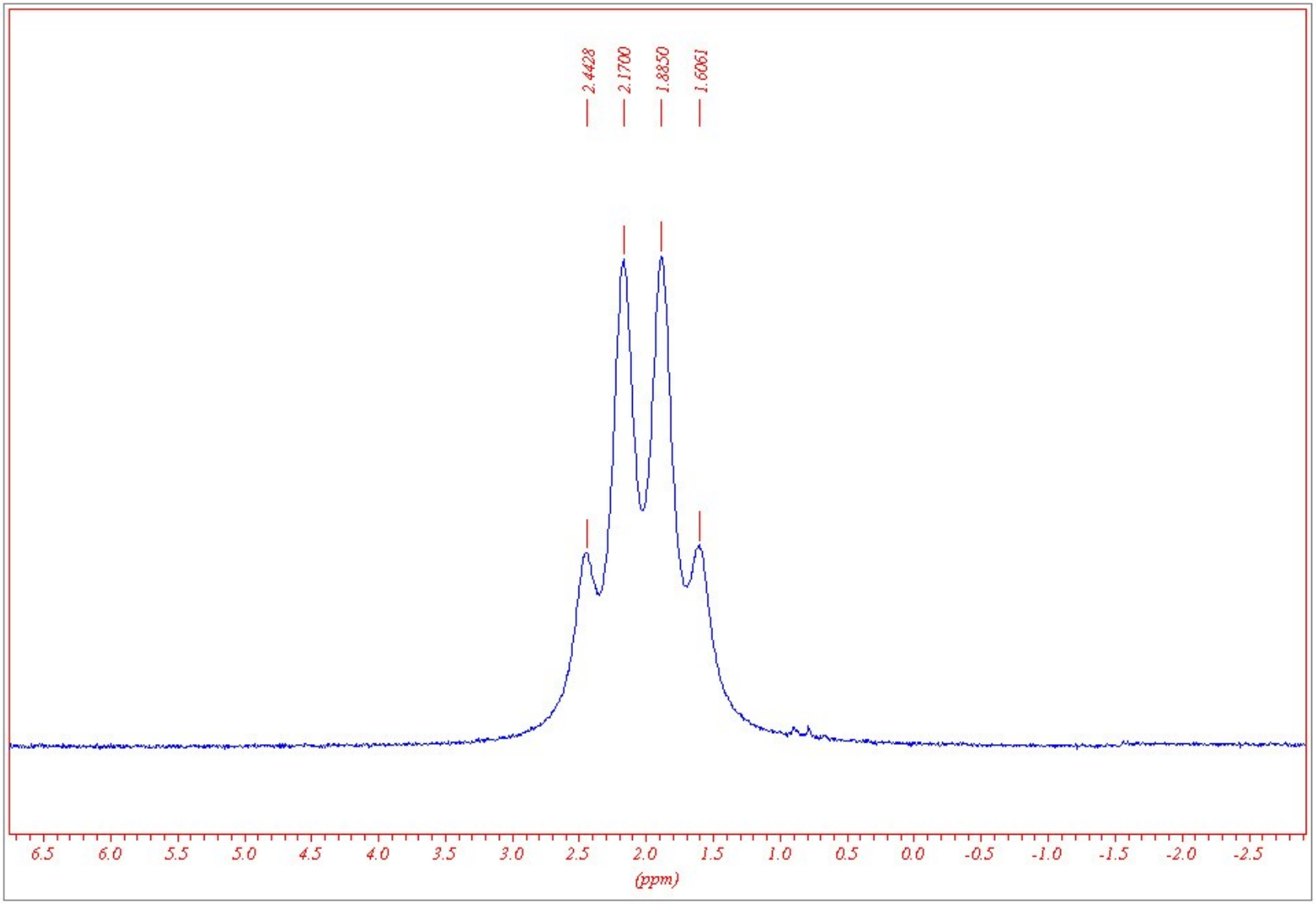



Figure S10. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium pentafluorophenyltrifluoroborate (**3c**)

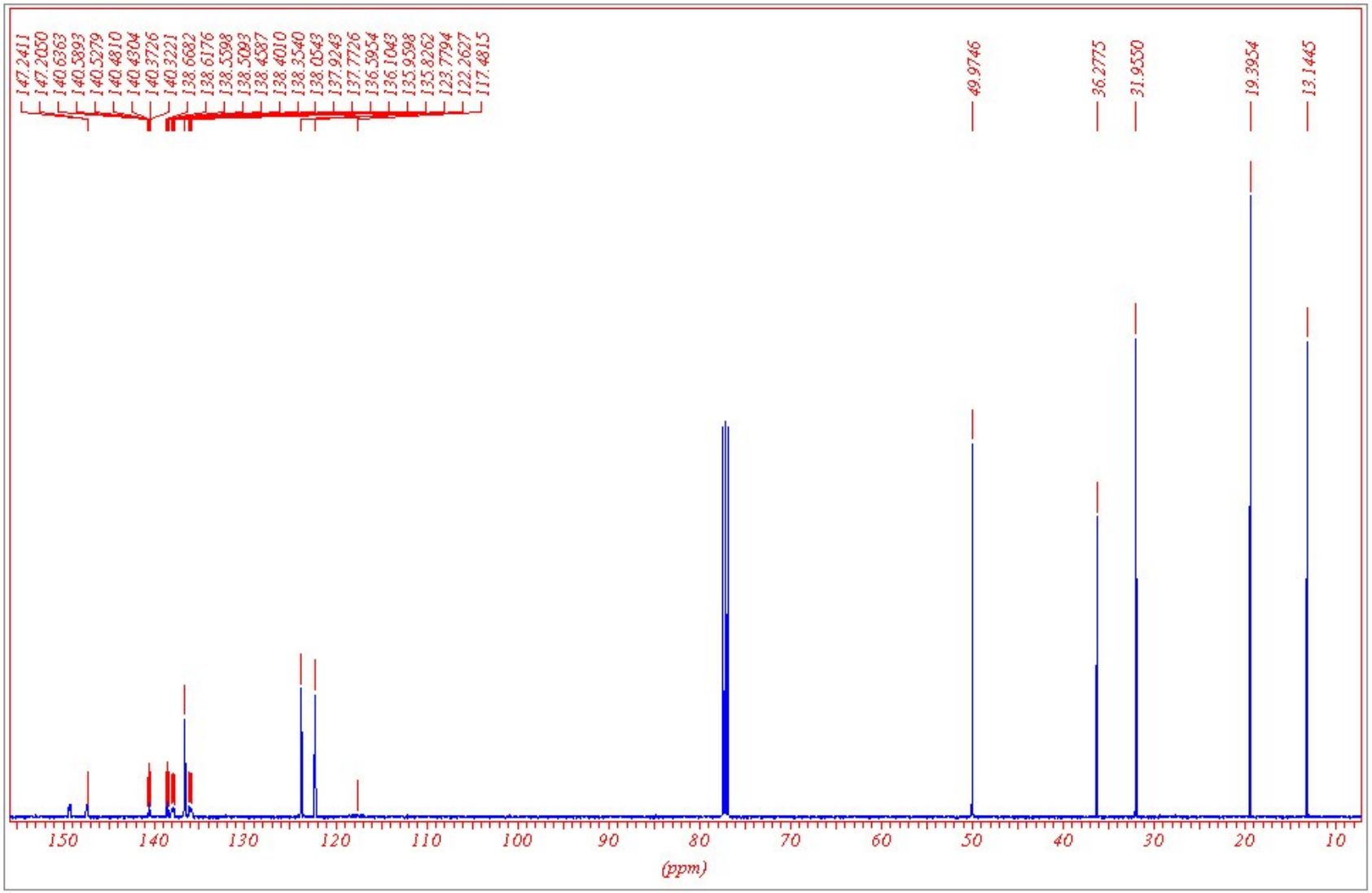



Figure S11. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium pentafluorophenyltrifluoroborate (**3c**)

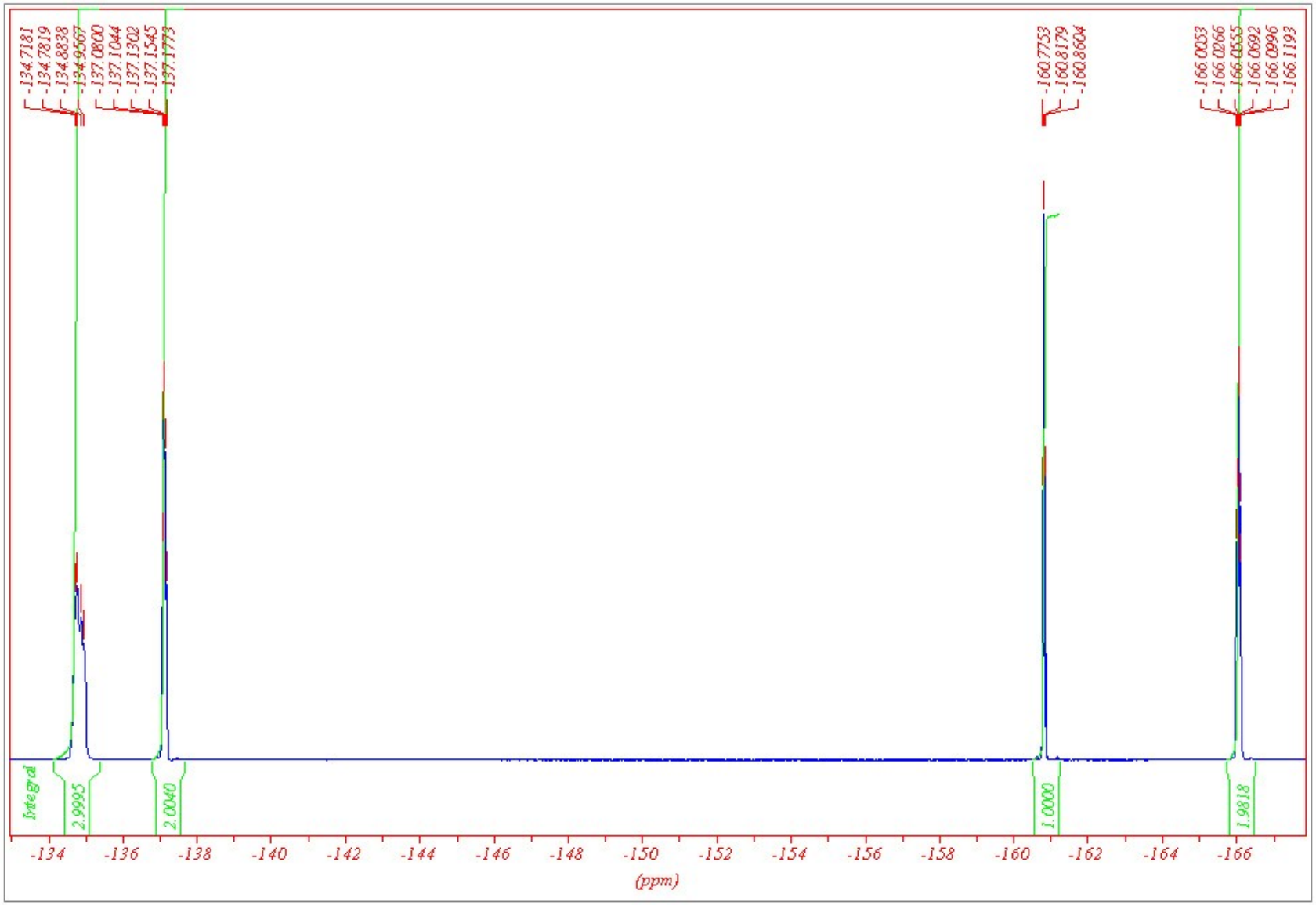
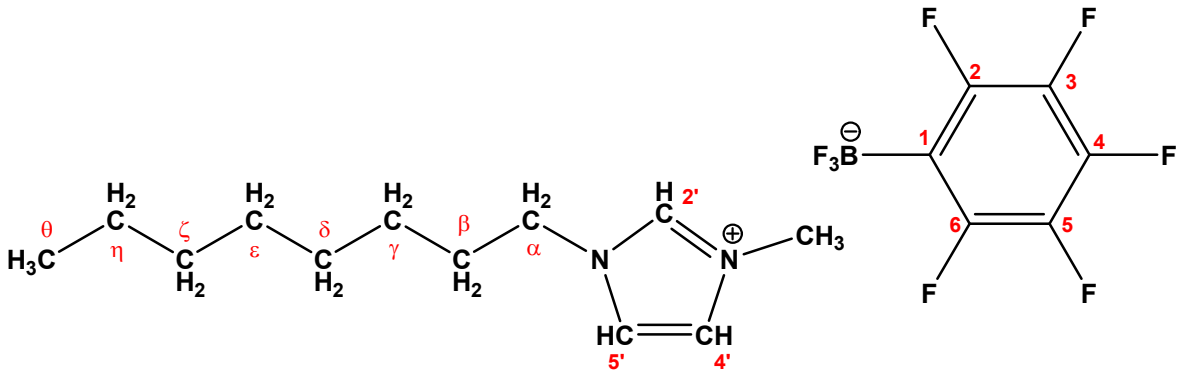



Figure S12. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium pentafluorophenyltrifluoroborate (**3c**)

**1-Methyl-3-octylimidazolium pentafluorophenyltrifluoroborate (3d)**



**$^{1}$H NMR** ($CDCl_3$): δ 8.90 (s, 1H, *H*-2'); 7.35 (s, 1H, *H*-5'); 7.30 (s, 1H, *H*-4'); 4.13 (t, 2H, $^{3}J_{HH}$ 7.5 Hz, *α*-C*H*$_2$); 3.94 (s, 3H, NC*H*$_3$); 1.81 (tt, 2H, $^{3}J_{HH}$ 7.3 Hz, $^{3}J_{HH}$ 7.3 Hz, *β*-C*H*$_2$); 1.11-1.30 (m, 10H, *γ*-*CH*$_2$ – *η*-C*H*$_2$); 0.82 (t, 3H, $^{3}J_{HH}$ 7.1 Hz, *θ*-C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.03 (q, $^{1}J_{BF}$ 45.3 Hz, *B*F$_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.30 (ddddd, $^{1}J_{CF}$ 239.3 Hz, $^{2}J_{CF}$ 17.7 Hz, $^{3}J_{CF}$ 8.6 Hz, 4.3 Hz, $^{4}J_{CF}$ 4.3 Hz, *C*-2,6); 139.50 (dtt, $^{1}J_{CF}$ 247.8 Hz, $^{2}J_{CF}$ 13.3 Hz, $^{3}J_{CF}$ 6.6 Hz, *C*-4); 136.94 (dm, $^{1}J_{CF}$ 248.4 Hz, *C*-3,5); 136.57 (s, *C*H-2'); 123.80 (s, *C*H-5'); 122.22 (s, *C*H-4'); 117.55 (bm, *C*-1); 50.26 (s, α-*C*H$_2$) 36.29 (s, N*C*H$_3$) 31.67 (s, β-*C*H$_2$); 30.10 (s, γ-*C*H$_2$); 28.98 (s, δ-*C*H$_2$); 28.89 (s, ε-*C*H$_2$); 26.22 (s, *ζ*-*C*H$_2$); 22.55 (s, η-*C*H$_2$); 13.93 (s, θ-*C*H$_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.79 (q, 3F $^{2}J_{BF}$ 42.4 Hz, *BF*$_3$); -137.09 (ddq, 2F, $^{3}J_{FF}$ 23.8 Hz; $^{5}J_{FF}$ 11.8 Hz; $^{4}J_{FF(BF3)}$ 11.7 Hz, *F*-2,6); -160.76 (t, 1F, $^{3}J_{FF}$ 20.0 Hz, *F*-4); -165.98 (ddd, 2F, $^{3}J_{FF}$ 23.4 Hz, $^{3}J_{FF}$ 21.3 Hz, $^{5}J_{FF}$ 9.5 Hz, *F*-3,5).

Anal. calcd for $C_{18}H_{23}BF_8N_2$ (430.19): C, 50.26; H, 5.39; F, 35.33; N, 6.51; found: C, 50.38; H, 5.62; F, 35.21; N, 6.54.

The NMR spectra are presented in Fig. S13-S16.

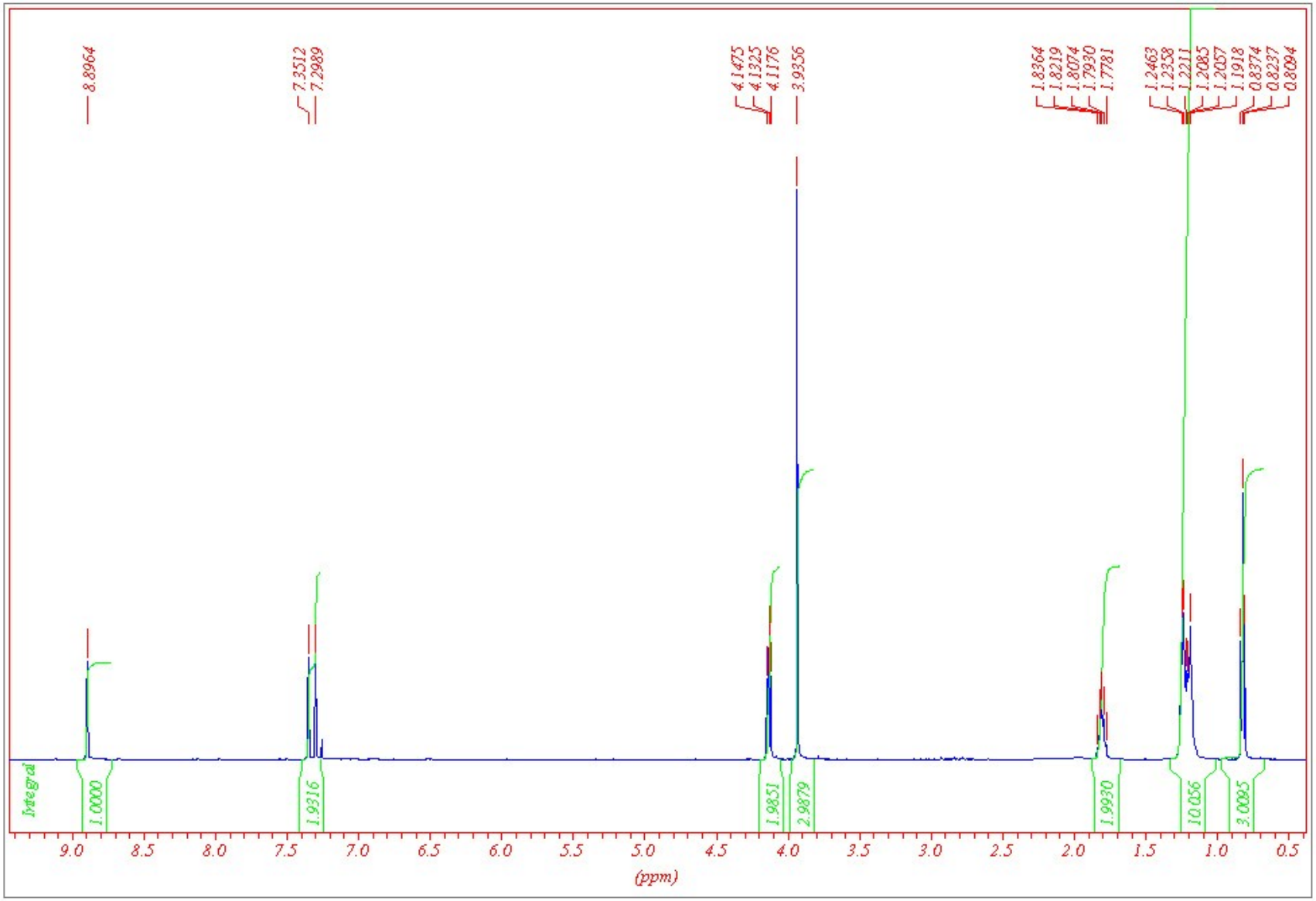



Figure S13. $^{1}H$ NMR spectra of 1-Methyl-3-octylimidazolium pentafluorophenyltrifluoroborate (**3d**)

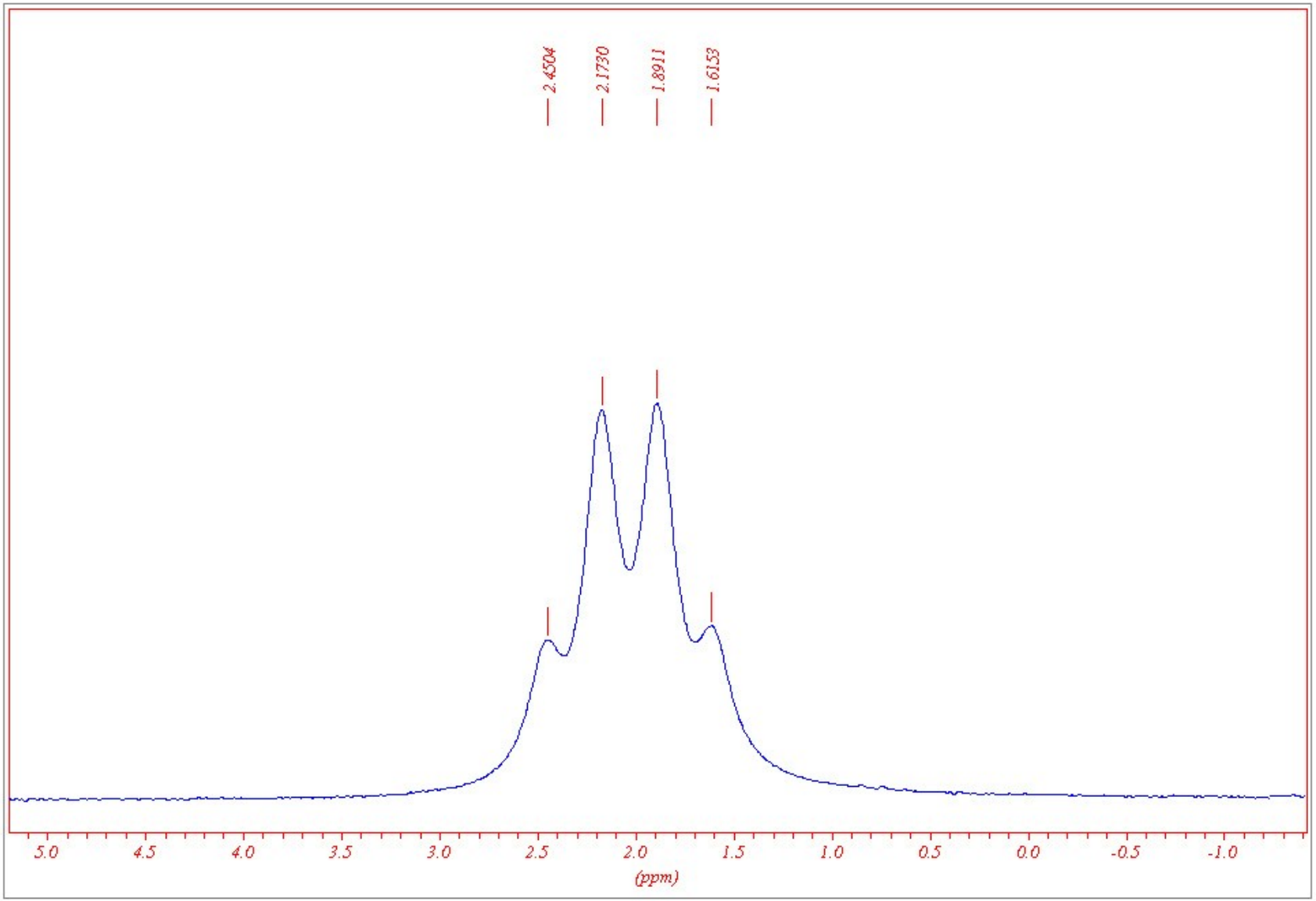



Figure S14. $^{11}B$ NMR spectra of 1-Methyl-3-octylimidazolium pentafluorophenyltrifluoroborate (**3d**)

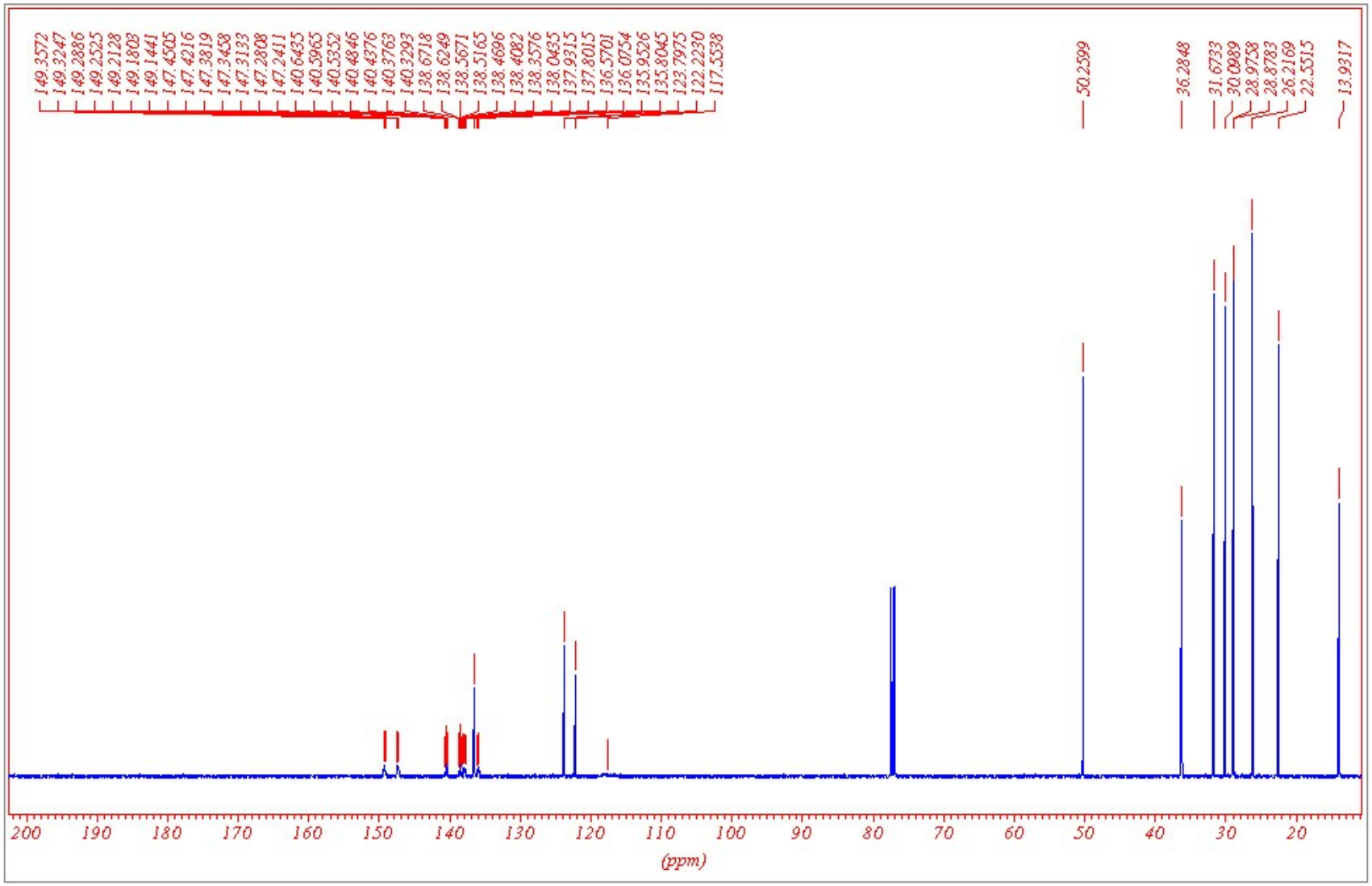



Figure S15. $^{13}C$ NMR spectra of 1-Methyl-3-octylimidazolium pentafluorophenyltrifluoroborate (**3d**)

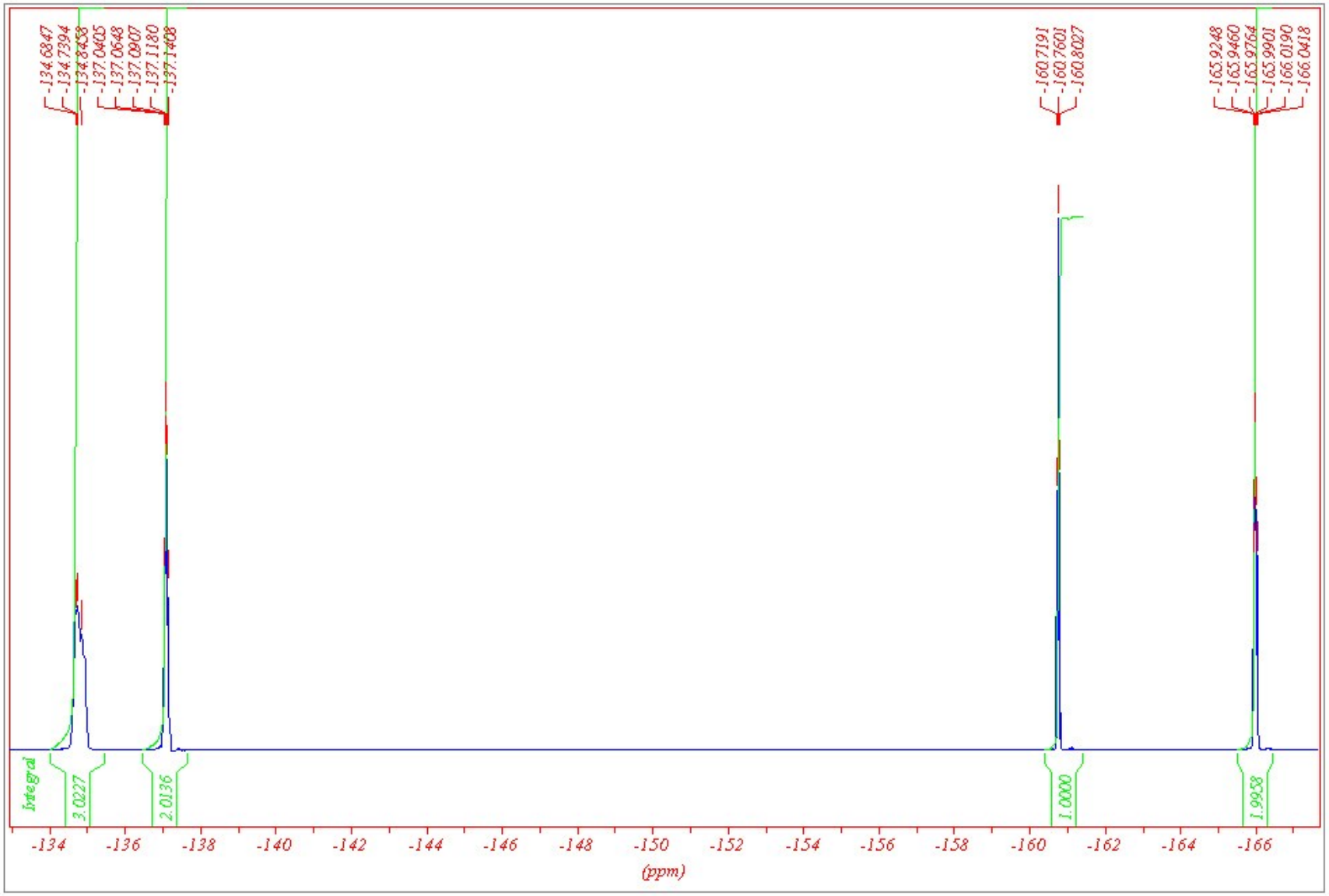
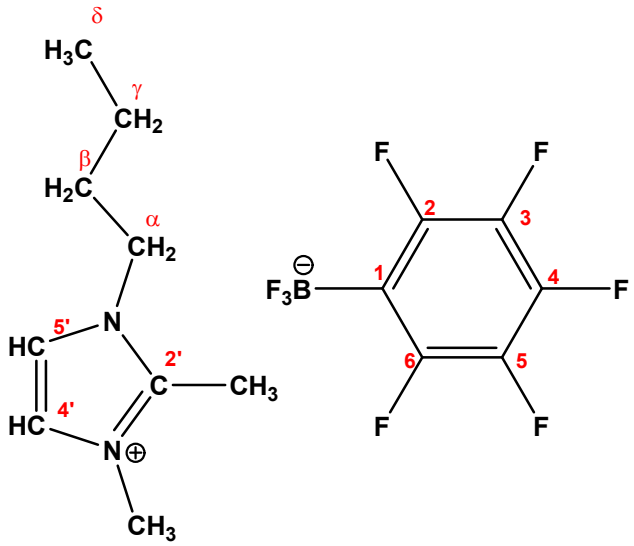



Figure S16. $^{19}F$ NMR spectra of 1-Methyl-3-octylimidazolium pentafluorophenyltrifluoroborate (**3d**)

**1-Butyl-2,3-dimethylimidazolium pentafluorophenyltrifluoroborate (3e)**




**$^{1}$H NMR** ($CDCl_3$): δ 7.27 (s, 1H, *H*-4'); 7.20 (s, 1H, *H*-5'); 4.02 (t, 2H, $^{3}J_{HH}$ 7.5 Hz, α-C$H_2$); 3.79 (s, 3H, NC$H_3$); 2.58 (s, 3H, C2'-C$H_3$); 1.71 (tt, 2H, $^{3}J_{HH}$ 7.6 Hz, $^{3}J_{HH}$ 7.4 Hz, β-C$H_2$); 1.31 (qt, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.5 Hz, γ-C$H_2$); 0.88 (t, 3H, $^{3}J_{HH}$ 7.3 Hz, δ-C$H_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 1.76 (q, $^{1}J_{BF}$ 44.7 Hz, *B*$F_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.25 (ddddd, $^{1}J_{CF}$ 239.3 Hz, $^{2}J_{CF}$ 17.7 Hz, $^{3}J_{CF}$ 8.5 Hz, 4.3 Hz, $^{4}J_{CF}$ 4.3 Hz, *C*-2,6); 144.02 (s, *C*-2'); 139.30 (dtt, $^{1}J_{CF}$ 247.6 Hz, $^{2}J_{CF}$ 13.3 Hz, $^{3}J_{CF}$ 6.5 Hz, *C*-4); 136.83 (dm, $^{1}J_{CF}$ 248.8 Hz, *C*-3,5); 122.74 (s, *C*H-4'); 120.93 (s, *C*H-5'); 118.27 (bm, *C*-1); 48.57 (s, α-*C*$H_2$) 35.24 (s, NCH$_3$) 31.59 (s, β-CH$_2$); 19.53 (s, γ-CH$_2$); 13.29 (s, δ-CH$_3$); 9.40 (s, C2'-*C*$H_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -136.14 (q, 3F $^{2}J_{BF}$ 40.8 Hz, B*F*$_3$); -136.77 (ddq, 2F, $^{3}J_{FF}$ 21.6 Hz; $^{5}J_{FF}$ 11.0 Hz; $^{4}J_{FF(BF3)}$ 10.7 Hz, *F*-2,6); -161.35 (t, 1F, $^{3}J_{FF}$ 19.7 Hz, *F*-4); -166.38 (ddd, 2F, $^{3}J_{FF}$ 22.9 Hz, $^{3}J_{FF}$ 20.7 Hz, $^{5}J_{FF}$ 8.9 Hz, *F*-3,5).

Anal. calcd for $C_{15}H_{17}BF_8N_2$ (388.11): C, 46.42; H, 4.42; F, 39.16; N, 7.22; found: C, 46.38; H, 4.40; F, 39.22; N, 7.18.

The NMR spectra are presented in Fig. S17-S20.

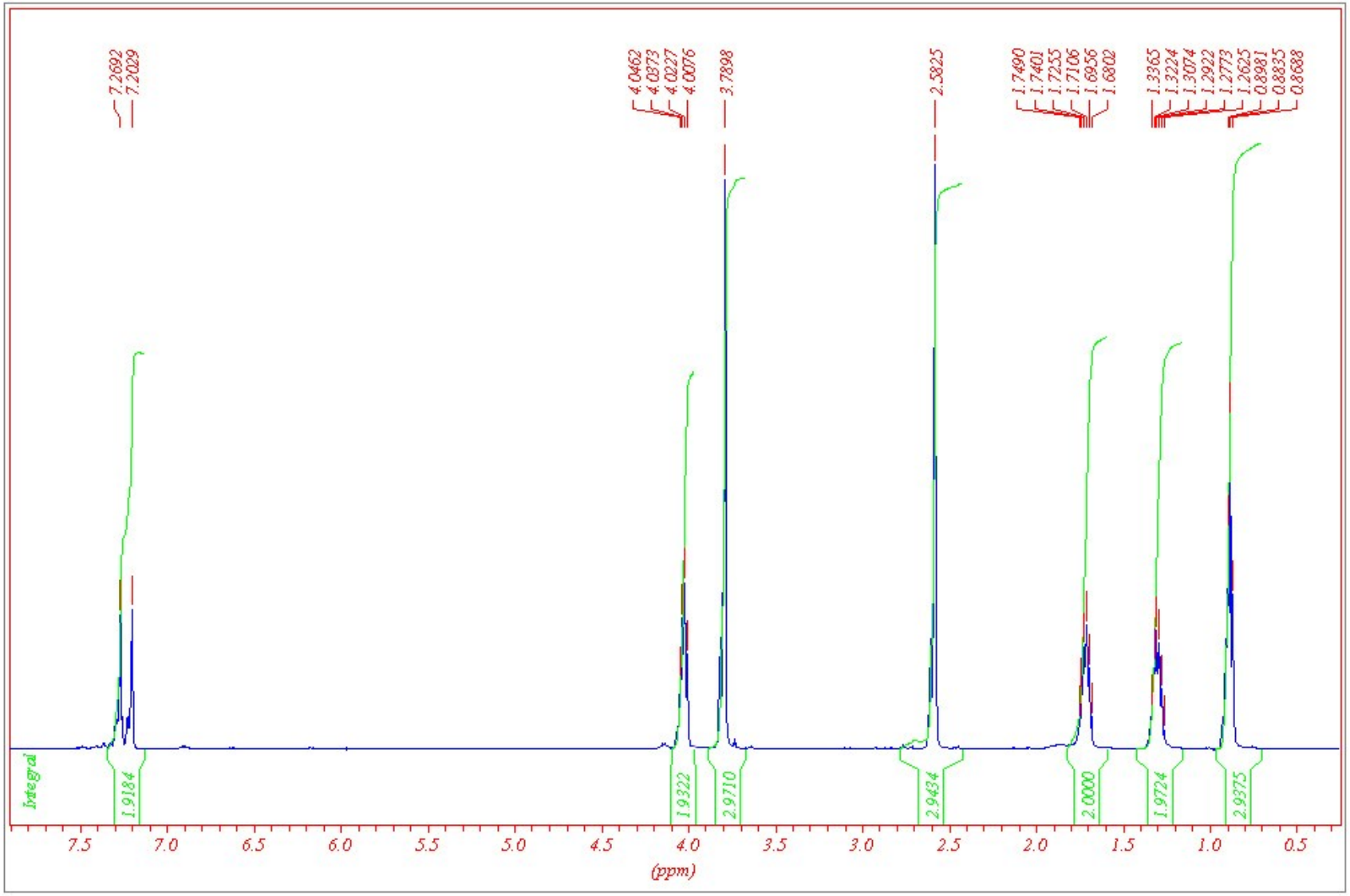



Figure S17. $^{1}H$ NMR spectra of 1-Butyl-2,3-dimethylimidazolium pentafluorophenyltrifluoroborate (**3e**)

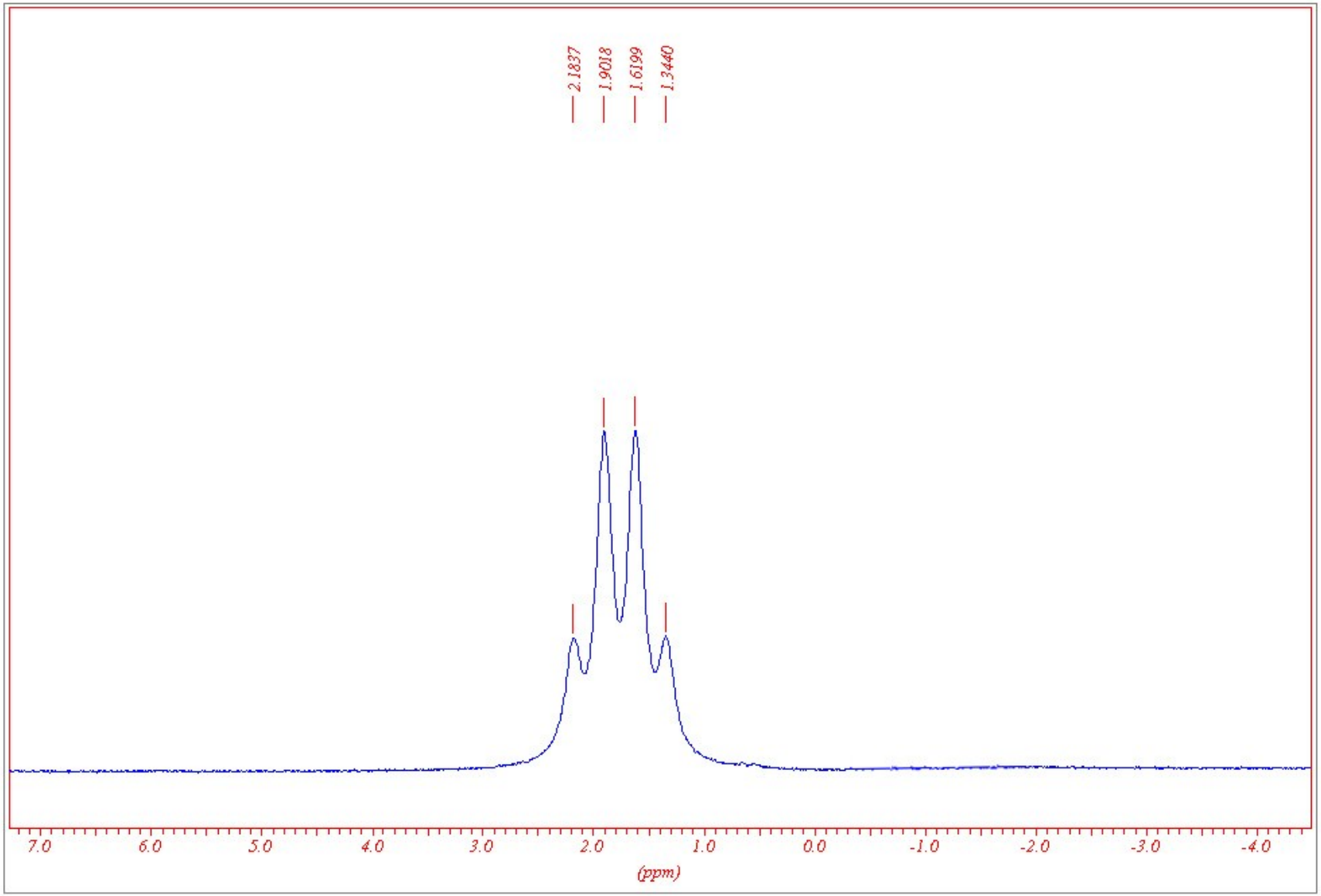



Figure S18. $^{11}B$ NMR spectra of 1-Butyl-2,3-dimethylimidazolium pentafluorophenyltrifluoroborate (**3e**)

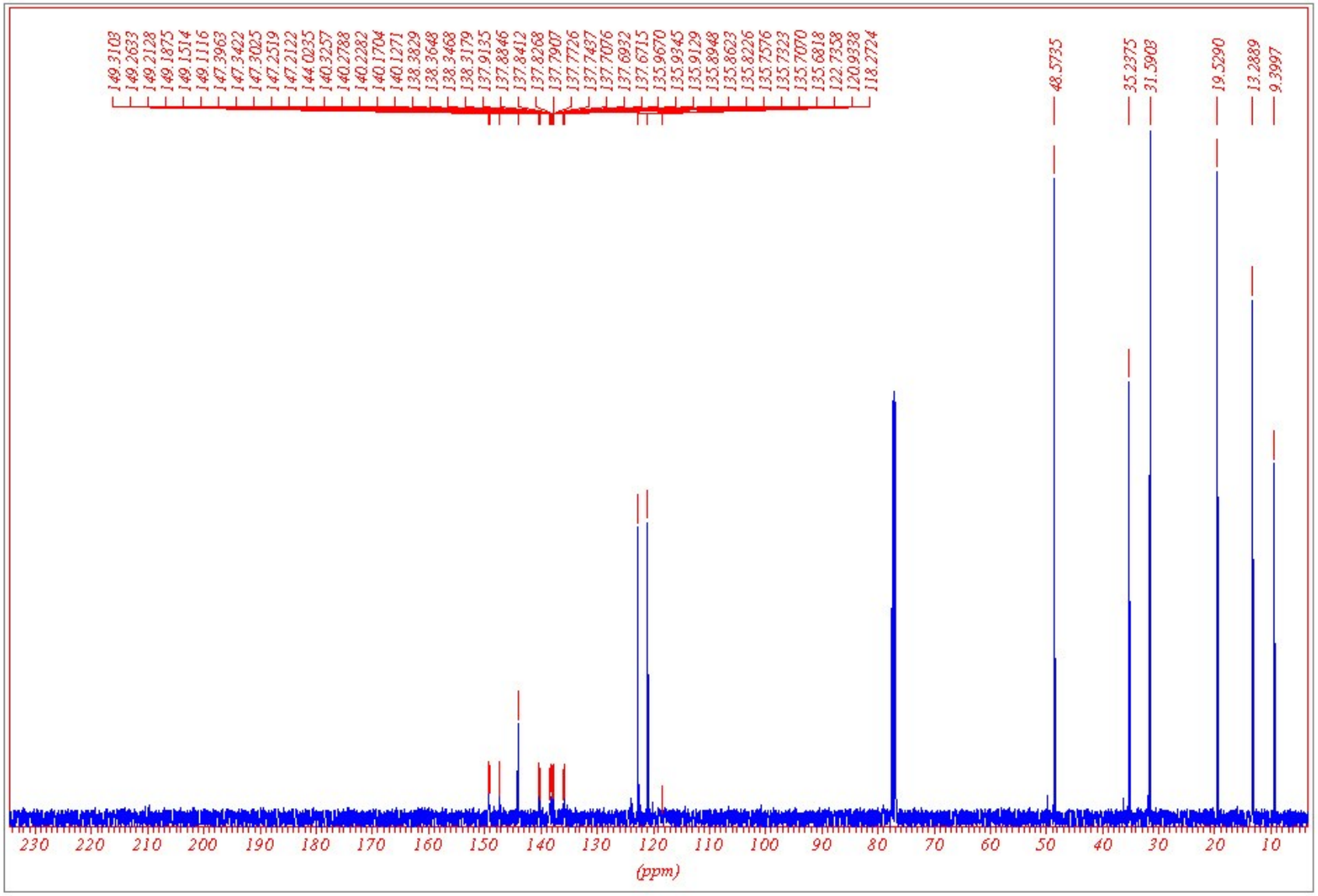



Figure S19. $^{13}C$ NMR spectra of 1-Butyl-2,3-dimethylimidazolium pentafluorophenyltrifluoroborate (**3e**)

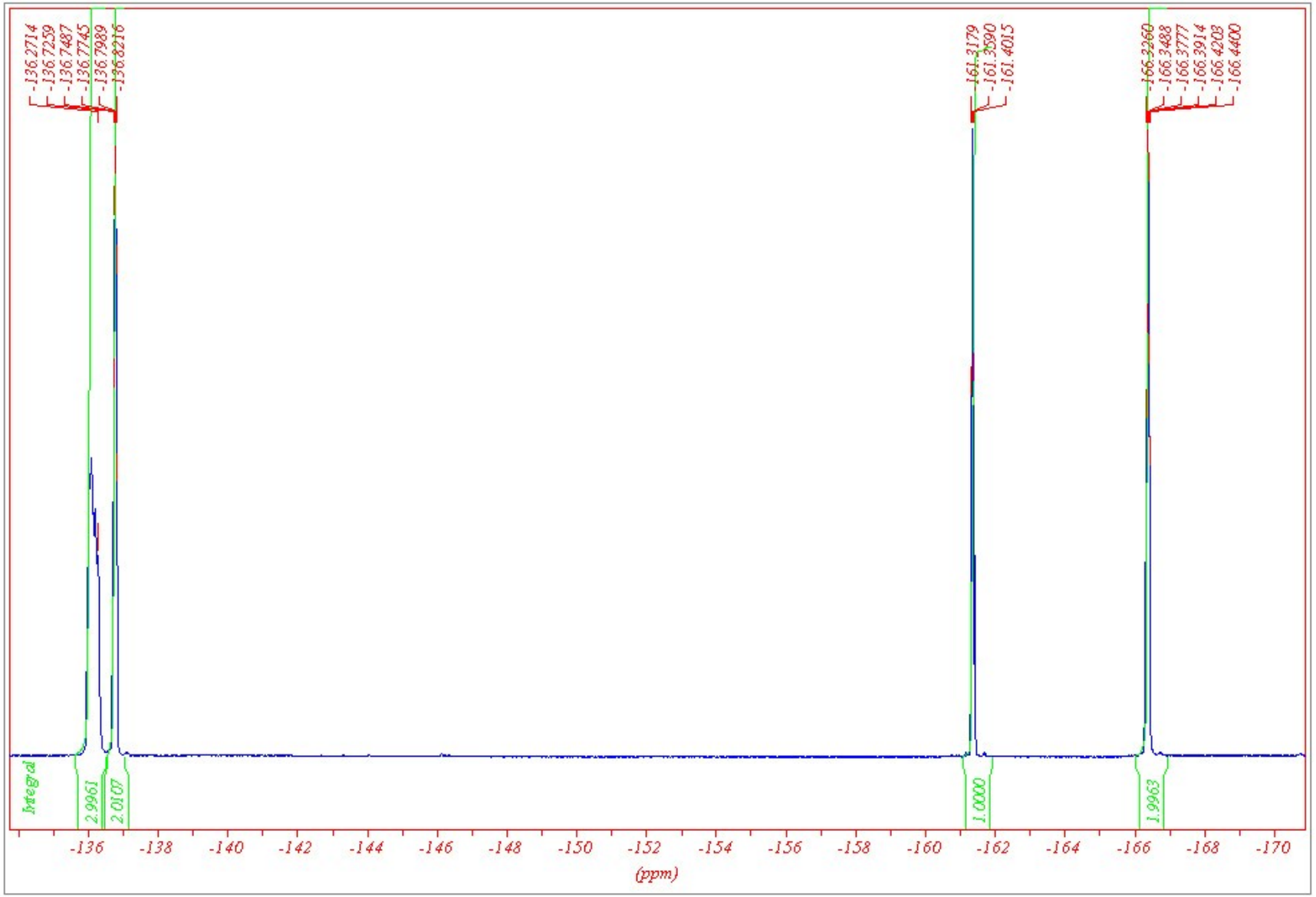
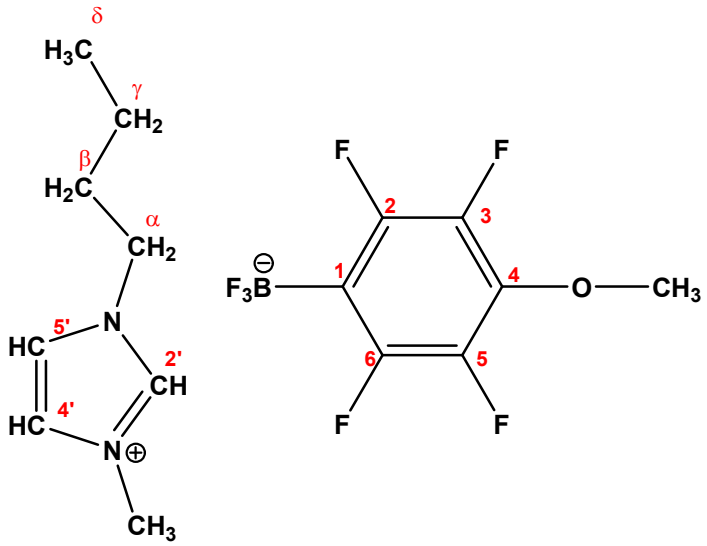



Figure S20. $^{19}F$ NMR spectra of 1-Butyl-2,3-dimethylimidazolium pentafluorophenyltrifluoroborate (**3e**)

**1-Butyl-3-methylimidazolium 4-methoxytetrafluorophenyltrifluoroborate (5a)**




**$^{1}$H NMR** ($CDCl_3$): δ 8.99 (s, 1H, *H*-2'); 7.36 (s, 1H, *H*-4'); 7.32 (s, 1H, *H*-5'); 4.13 (t, 2H, $^{3}J_{HH}$ 7.4 Hz, α-C*H*$_2$); 3.95 (s, 3H, OC*H*$_3$); 3.92 (s, 3H, NC*H*$_3$); 1.79 (tt, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.5 Hz, β-C*H*$_2$); 1.28 (qt, 2H, $^{3}J_{HH}$ 7.6 Hz, $^{3}J_{HH}$ 7.6 Hz, γ-C*H*$_2$); 0.87 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, δ-C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.14 (q, $^{1}J_{BF}$ 45.5 Hz, *B*F$_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.55 (dddd, $^{1}J_{CF}$ 237.6 Hz, $^{2}J_{CF}$ 18.5 Hz, $^{3}J_{CF}$ 10.3 Hz, $^{4}J_{CF}$ 3.5 Hz, *C*-2,6); 140.80 (dd, $^{1}J_{CF}$ 244.7 Hz, $^{2}J_{CF}$ 19.1 Hz, *C*-3,5); 136.71 (s, *C*H-2'); 136.28 (tt, $^{2}J_{CF}$ 12.7 Hz, $^{3}J_{CF}$ 4.3 Hz, *C*-4); 123.79 (s, *C*H-4'); 122.26 (s, *C*H-5'); 116.50 (bm, *C*-1); 62.00 (s, O*C*H$_3$); 49.87 (s, α-*C*H$_2$) 36.25 (s, N*C*H$_3$) 31.98 (s, β-*C*H$_2$); 19.40 (s, γ-*C*H$_2$); 13.22 (s, δ-*C*H$_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.6 (bs, 3F, B*F*$_3$); -138.40 (ddq, 2F, $^{3}J_{FF}$ 23.2 Hz; $^{5}J_{FF}$ 11.5 Hz; $^{4}J_{FF(BF3)}$ 11.6 Hz, *F*-2,6); -161.25 (dd, 2F, $^{3}J_{FF}$ 24.0 Hz, $^{5}J_{FF}$ 11.1 Hz, *F*-3,5).

Anal. calcd for $C_{15}H_{18}BF_7N_2O$ (386.12): C, 46.66; H, 4.70; F, 34.44; N, 7.26; found: C, 46.51; H, 4.82; F, 34.41; N, 7.21.

The NMR spectra are presented in Fig. S21-S24.

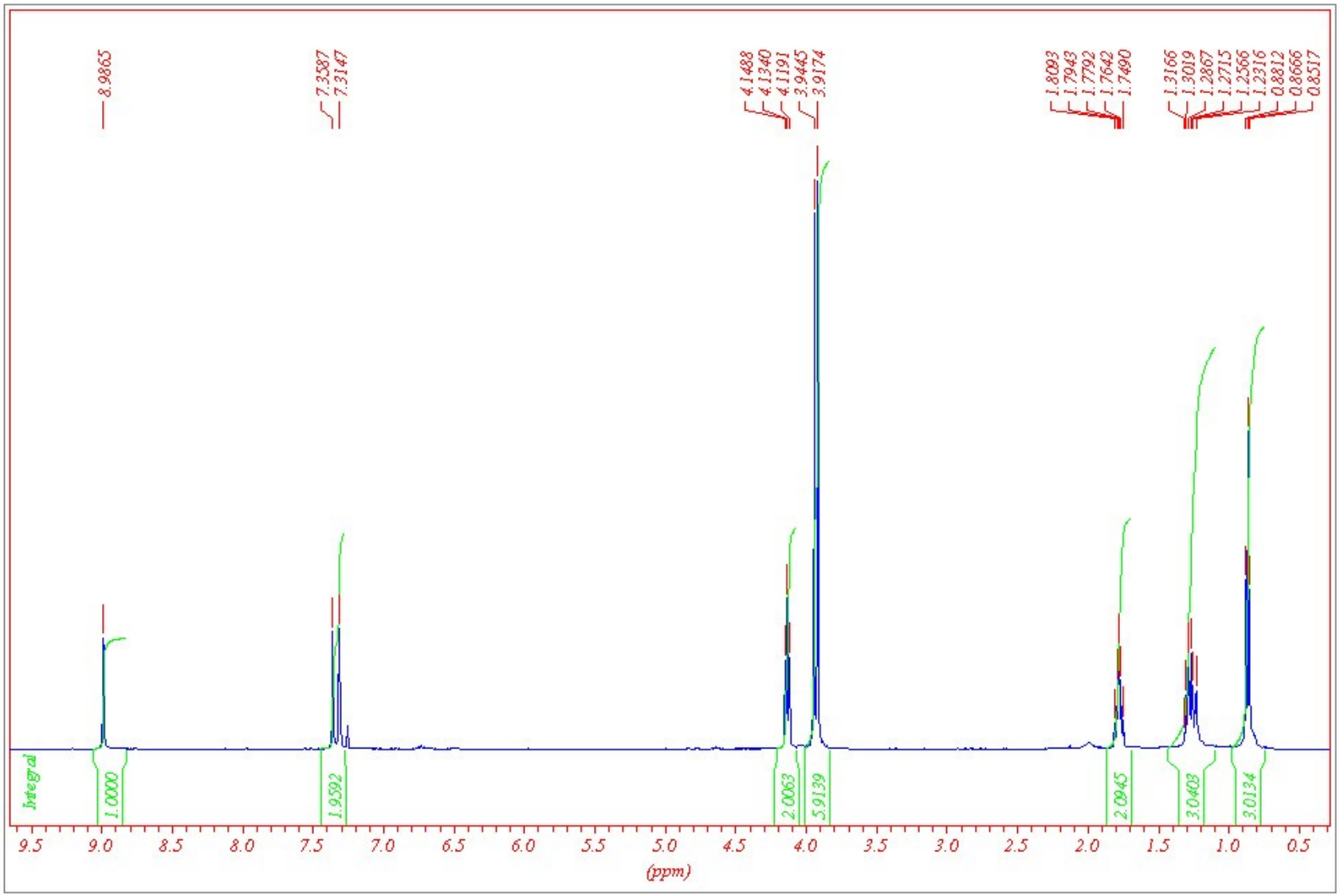



Figure S21. $^{1}H$ NMR spectra of 1-Butyl-3-methylimidazolium 4- methoxytetrafluorophenyltrifluoroborate (**5a**)

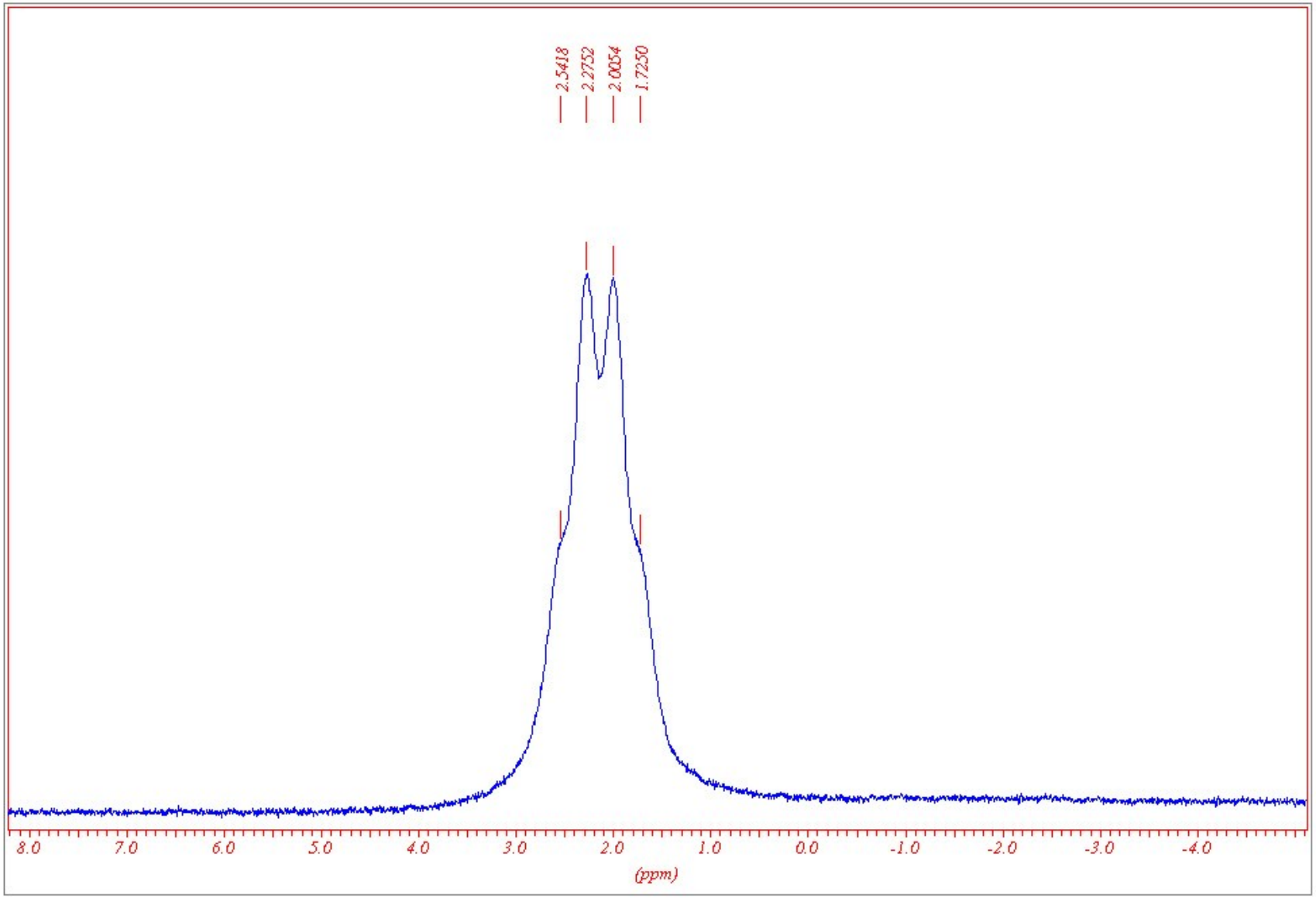



Figure S22. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium 4- methoxytetrafluorophenyltrifluoroborate (**5a**)

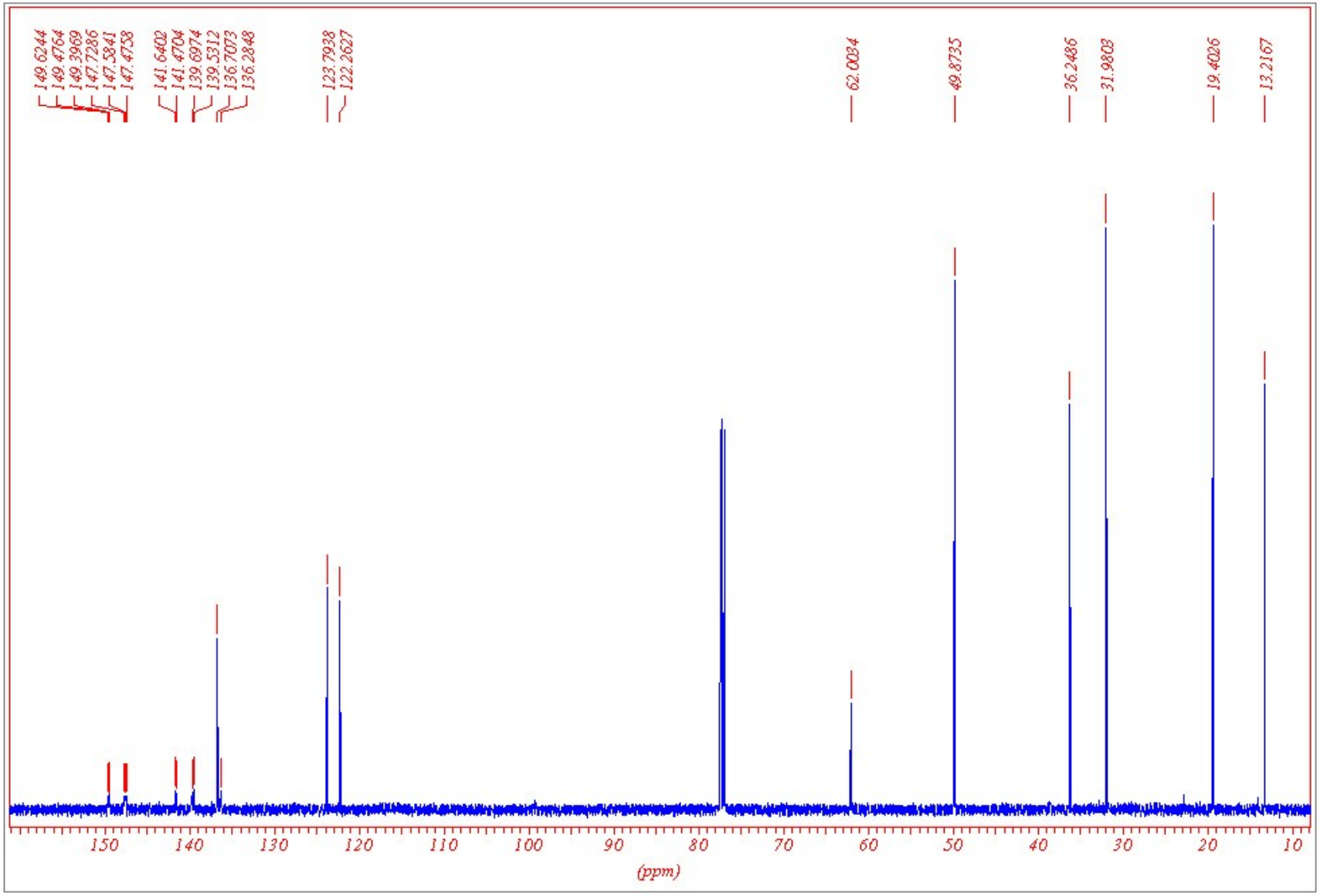



Figure S23. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium 4- methoxytetrafluorophenyltrifluoroborate (**5a**)

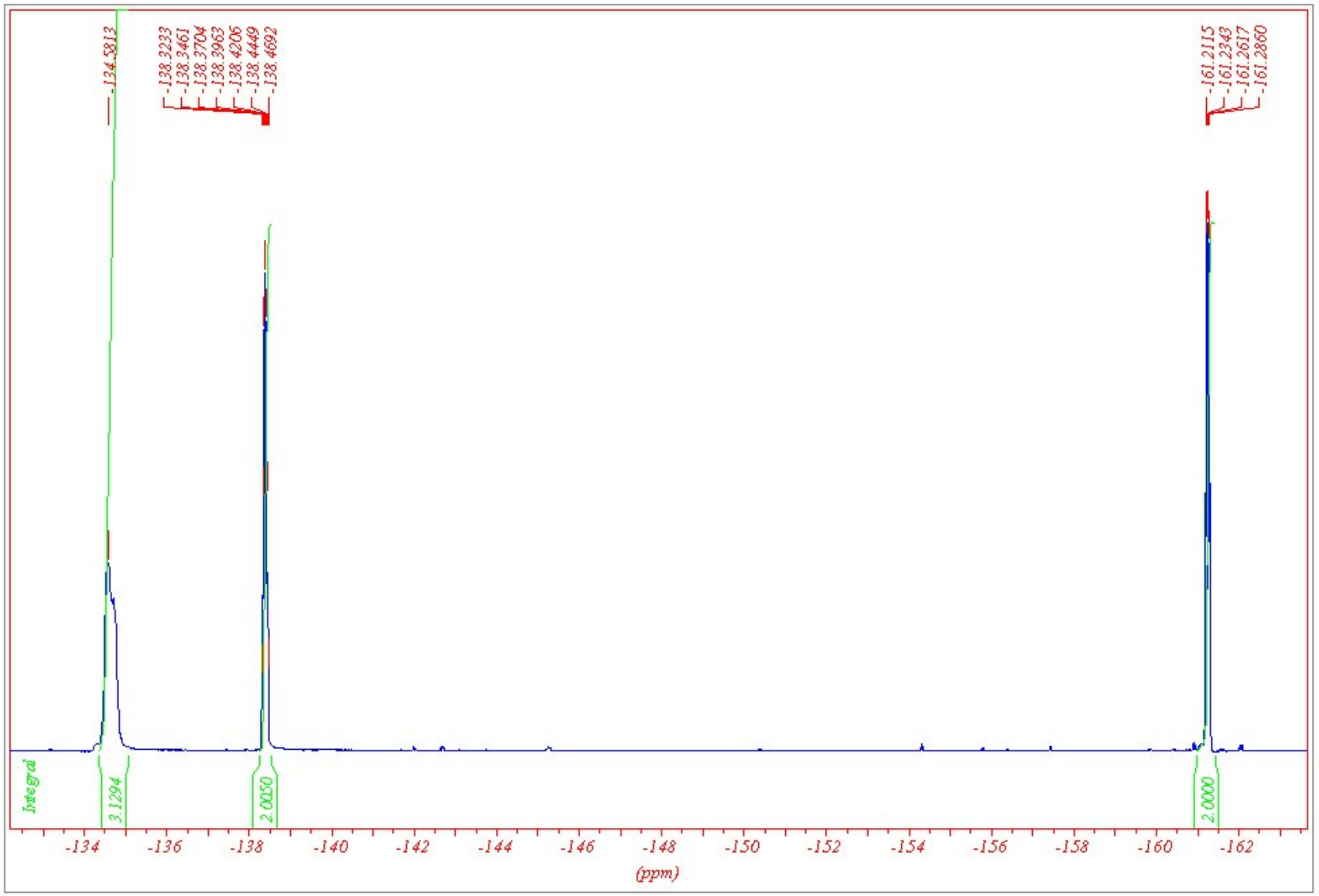
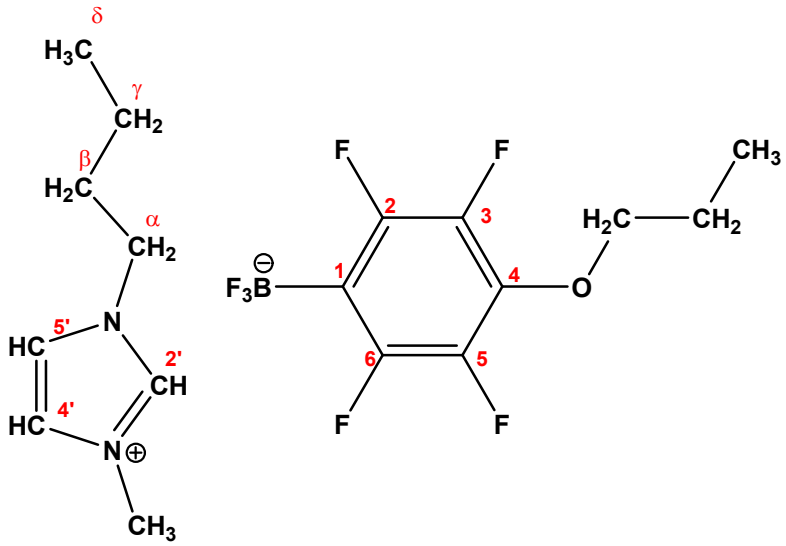



Figure S24. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium 4- methoxytetrafluorophenyltrifluoroborate (**5a**)

**1-Butyl-3-methylimidazolium 4-propoxytetrafluorophenyltrifluoroborate (5b)**




**$^{1}$H NMR** ($CDCl_3$): δ 8.79 (s, 1H, *H*-2'); 7.39 (s, 1H, *H*-5'); 7.30 (s, 1H, *H*-4'); 4.03 (t, 2H, $^{3}J_{HH}$ 7.3 Hz, α-C*H*$_2$); 3.96 (t, 2H, $^{3}J_{HH}$ 6.6 Hz, OC*H*$_2$CH$_2$CH$_3$); 3.82 (s, 3H, NC*H*$_3$); 1.56-1.73 (m, 4H, OCH$_2$*CH*$_2$CH$_3$ and *β*-*CH*$_2$); 1.17 (qt, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.5 Hz, γ-C*H*$_2$); 0.88 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, δ-C*H*$_3$), 0.75 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, OCH$_2$CH$_2$C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.08 (bs, *B*F$_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.43 (dddd, $^{1}J_{CF}$ 237.8 Hz, $^{2}J_{CF}$ 18.3 Hz, $^{3}J_{CF}$ 10.2 Hz, $^{4}J_{CF}$ 3.2 Hz, *C*-2,6); 140.80 (ddd, $^{1}J_{CF}$ 244.7 Hz, $^{2}J_{CF}$ 19.1 Hz, $^{3}J_{CF}$ 2.0 Hz, *C*-3,5); 136.37 (s, *C*H-2'); 135.41 (tt, $^{2}J_{CF}$ 12.7 Hz, $^{3}J_{CF}$ 4.3 Hz, *C*-4); 123.75 (s, *C*H-4'); 122.34 (s, *C*H-5'); 116.39 (bm, *C*-1); 76.53 (s, OC*H*$_2$CH$_2$CH$_3$); 49.70 (s, α-*C*H$_2$) 36.04 (s, NCH$_3$) 31.87 (s, β-*C*H$_2$); 23.16 (s, OCH$_2$*CH*$_2$CH$_3$); 19.27 (s, γ-*C*H$_2$); 13.07 (s, δ-*C*H$_3$); 9.98 (s, OCH$_2$CH$_2$*CH*$_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.4 (bs, 3F, B*F*$_3$); -138.60 (ddq, 2F, $^{3}J_{FF}$ 23.2 Hz; $^{5}J_{FF}$ 11.5 Hz; $^{4}J_{FF(BF3)}$ 11.6 Hz, *F*-2,6); -160.66 (dd, 2F, $^{3}J_{FF}$ 24.0 Hz, $^{5}J_{FF}$ 11.1 Hz, *F*-3,5).

Anal. calcd for $C_{17}H_{22}BF_7N_2O$ (414.17): C, 49.30; H, 5.35; F, 32.11; N, 6.76; found: C, 49.34; H, 5.42; F, 32.08; N, 6.64.

The NMR spectra are presented in Fig. S25-S28.

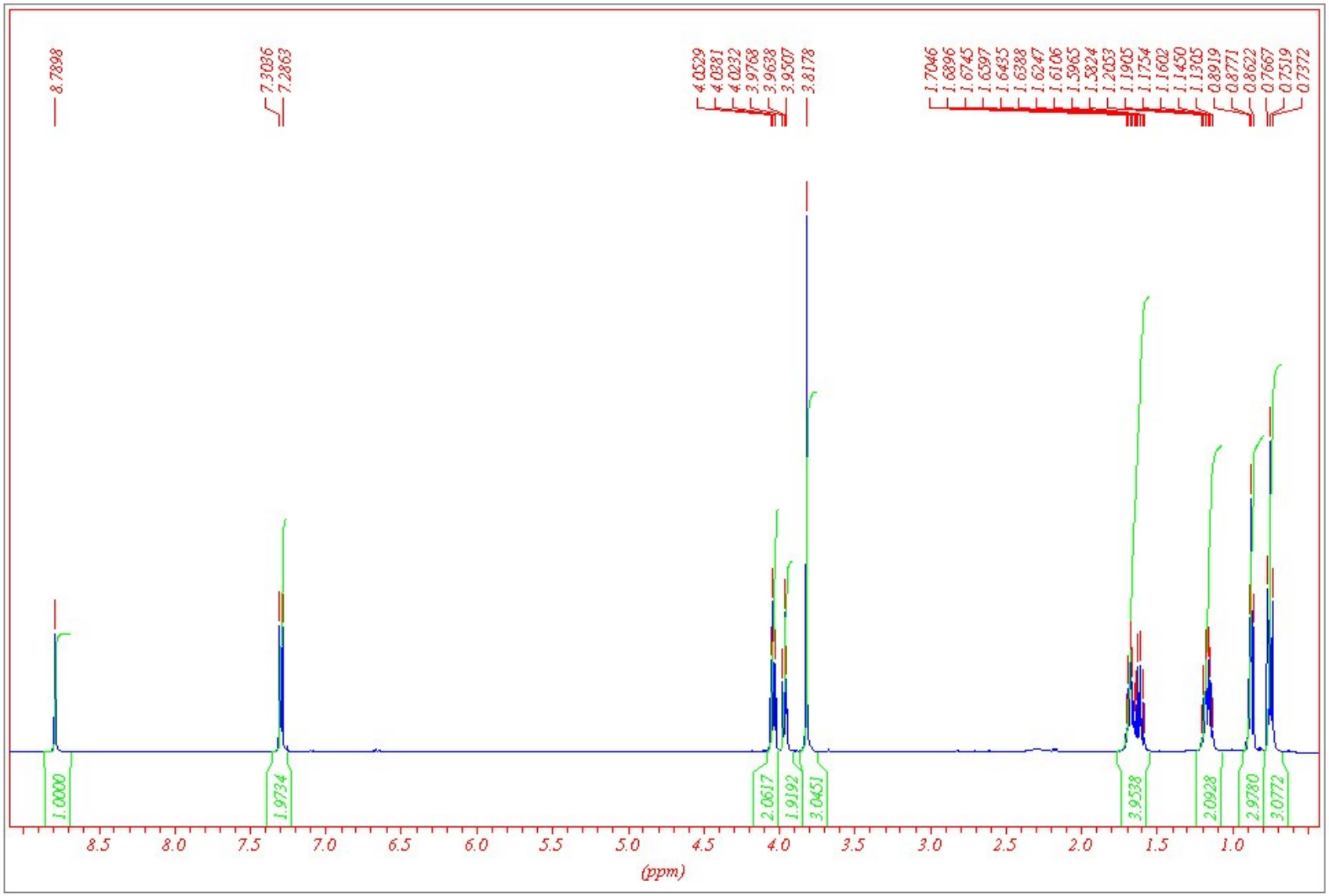



Figure S25. $^{1}H$ NMR spectra of 1-Butyl-3-methylimidazolium 4- propoxytetrafluorophenyltrifluoroborate (**5b**)

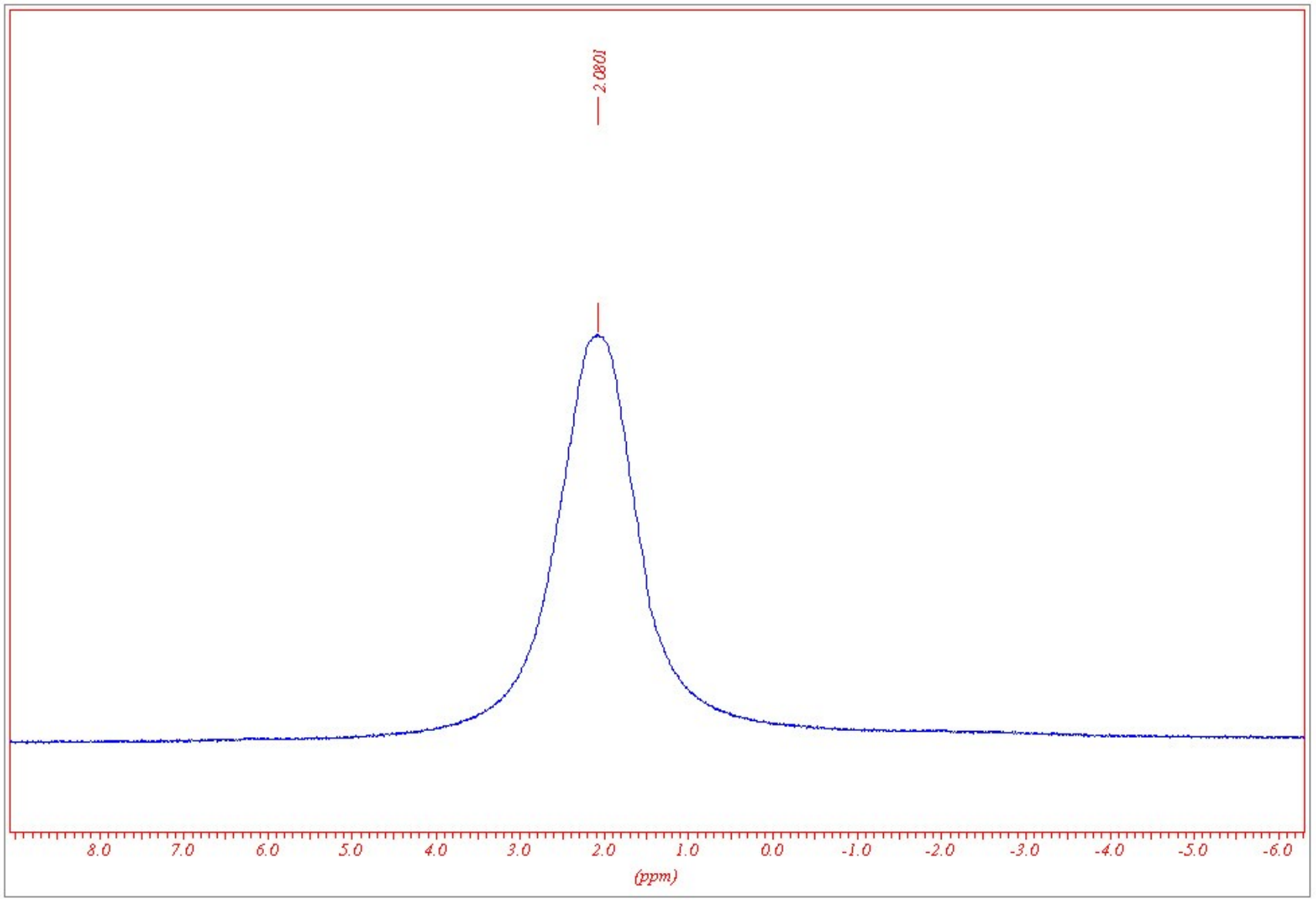



Figure S26. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium 4- propoxytetrafluorophenyltrifluoroborate (**5b**)

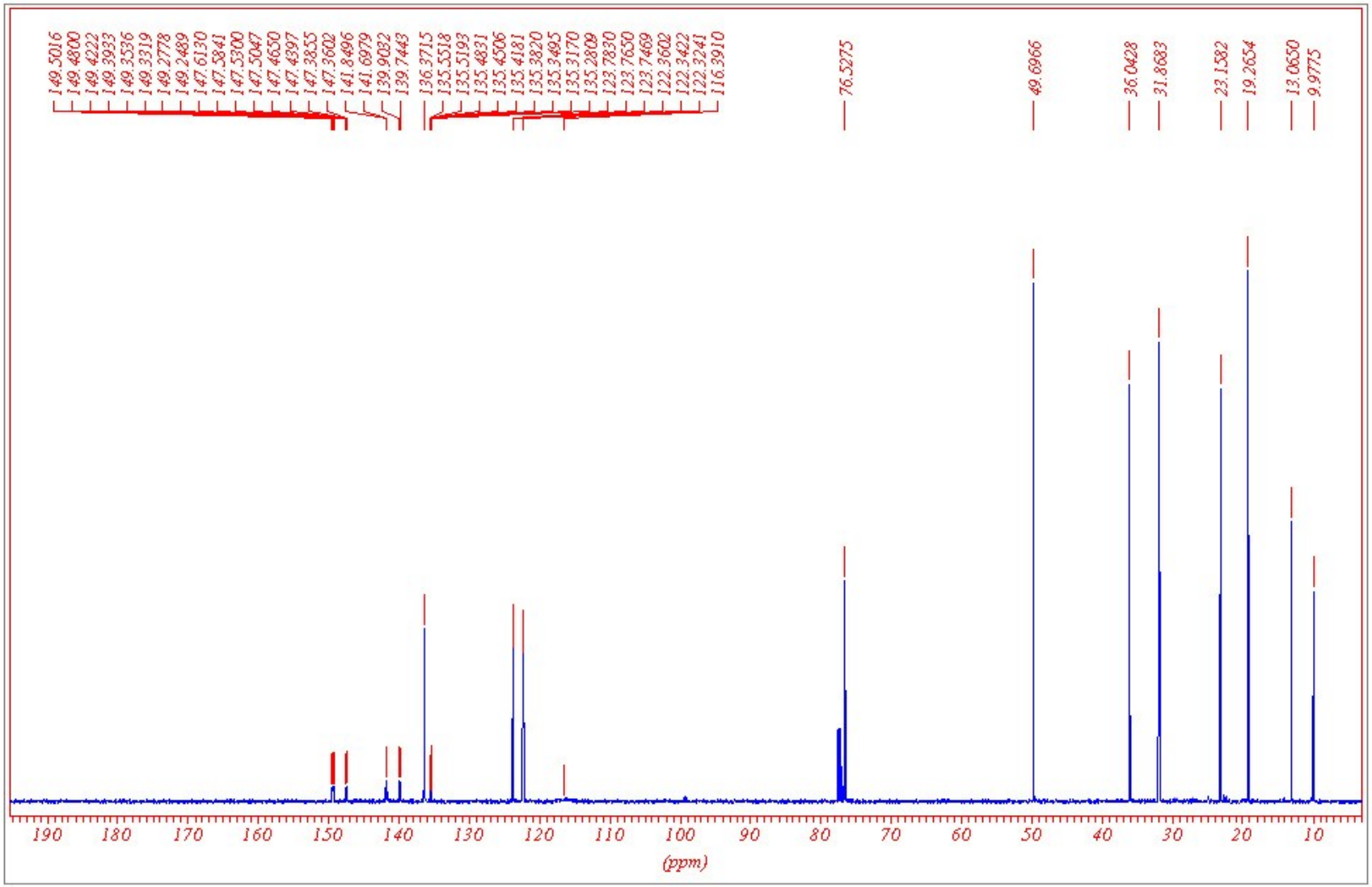



Figure S27. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium 4- propoxytetrafluorophenyltrifluoroborate (**5b**)

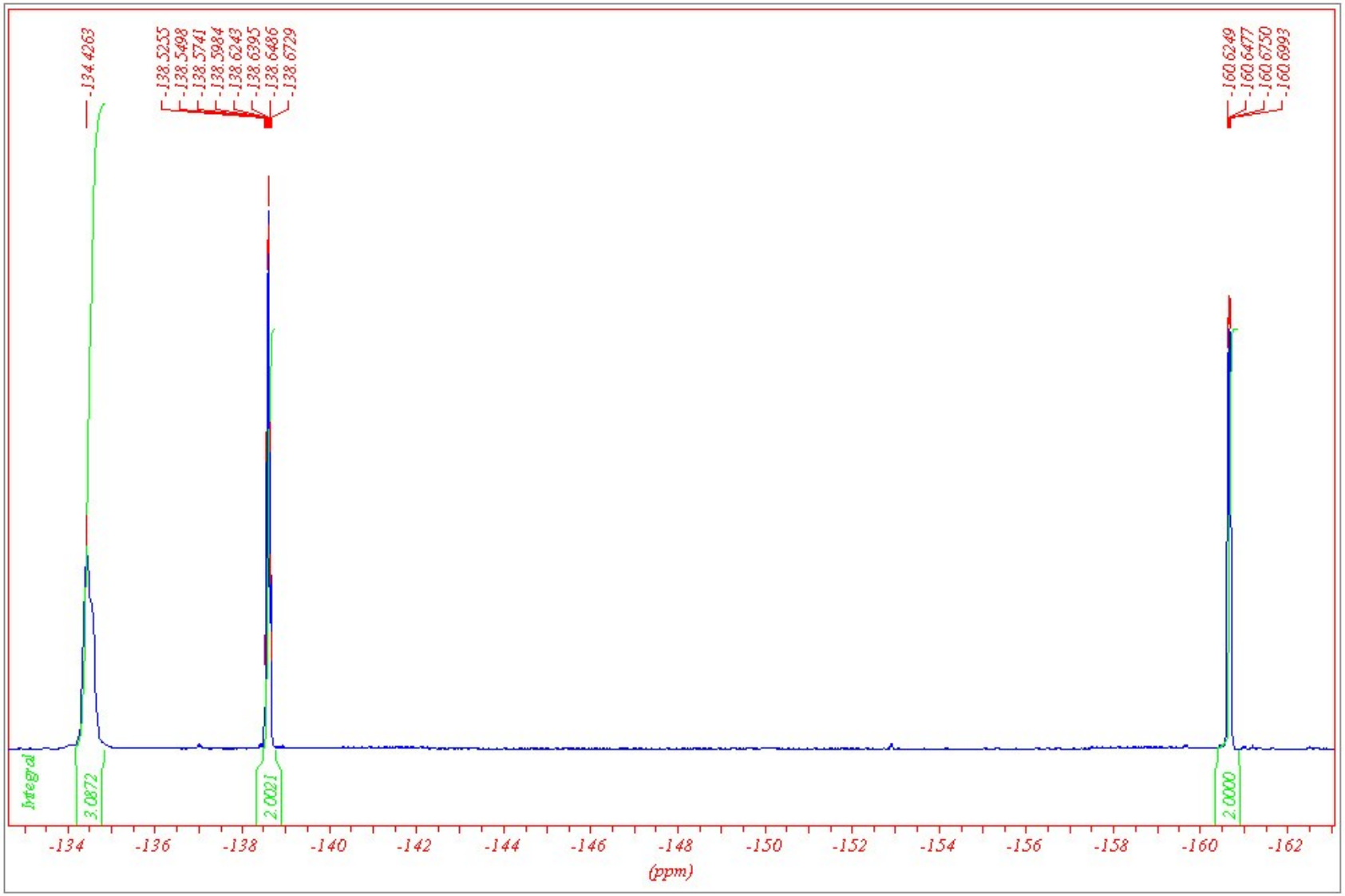
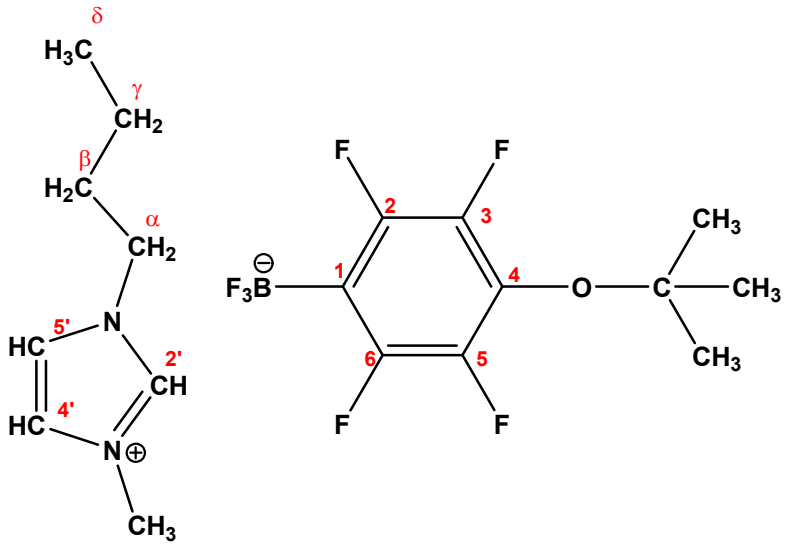



Figure S28. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium 4- propoxytetrafluorophenyltrifluoroborate (**5b**)

**1-Butyl-3-methylimidazolium 4-*tert*-butoxytetrafluorophenyltrifluoroborate (5c)**




**$^{1}$H NMR** ($CDCl_3$): δ 8.68 (s, 1H, *H*-2'); 7.24 (s, 2H, *H*-4', 5'); 3.97 (t, 2H, $^{3}J_{HH}$ 7.2 Hz, α-C*H*$_2$); 3.75 (s, 3H, NC*H*$_3$); 1.60 (tt, 2H, $^{3}J_{HH}$ 7.0 Hz, $^{3}J_{HH}$ 6.9 Hz, β-C*H*$_2$); 1.15 (s, 9H, (C*H*$_3$)$_3$C); 1.08 (qt, 2H, $^{3}J_{HH}$ 7.4 Hz, $^{3}J_{HH}$ 7.5 Hz, γ-C*H*$_2$); 0.66 (t, 3H, $^{3}J_{HH}$ 7.2 Hz, δ-C*H*$_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.12 (bs, *B*F$_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.34 (dddd, $^{1}J_{CF}$ 238.0 Hz, $^{2}J_{CF}$ 18.1 Hz, $^{3}J_{CF}$ 11.0 Hz, $^{4}J_{CF}$ 3.0 Hz, *C*-2,6); 142.61 (dd, $^{1}J_{CF}$ 245.7 Hz, $^{2}J_{CF}$ 17.3 Hz, *C*-3,5); 136.19 (s, *C*H-2'); 131.60 (t, $^{2}J_{CF}$ 13.6 Hz, *C*-4); 123.66 (s, *C*H-4'); 122.34 (s, *C*H-5'); 118.02 (bm, *C*-1); 83.65 (s, *C*(CH$_3$)$_3$); 49.60 (s, α-CH$_2$) 35.92 (s, NCH$_3$) 31.76 (s, β-*C*H$_2$); 28.16 (s, C(*C*H$_3$)$_3$); 19.16 (s, γ-*C*H$_2$); 12.96 (s, δ-*C*H$_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.40 (bs, 3F, B*F*$_3$); -138.74 (ddq, 2F, $^{3}J_{FF}$ 23.1 Hz; $^{5}J_{FF}$ 11.5 Hz; $^{4}J_{FF(BF3)}$ 11.4 Hz, *F*-2,6); -155.35 (dd, 2F, $^{3}J_{FF}$ 24.3 Hz, $^{5}J_{FF}$ 10.7 Hz, *F*-3,5).

Anal. calcd for $C_{18}H_{24}BF_7N_2O$ (428.20): C, 50.49; H, 5.65; F, 31.06; N, 6.54; found: C, 50.61; H, 5.79; F, 31.01; N, 6.51.

The NMR spectra are presented in Fig. S29-S32.

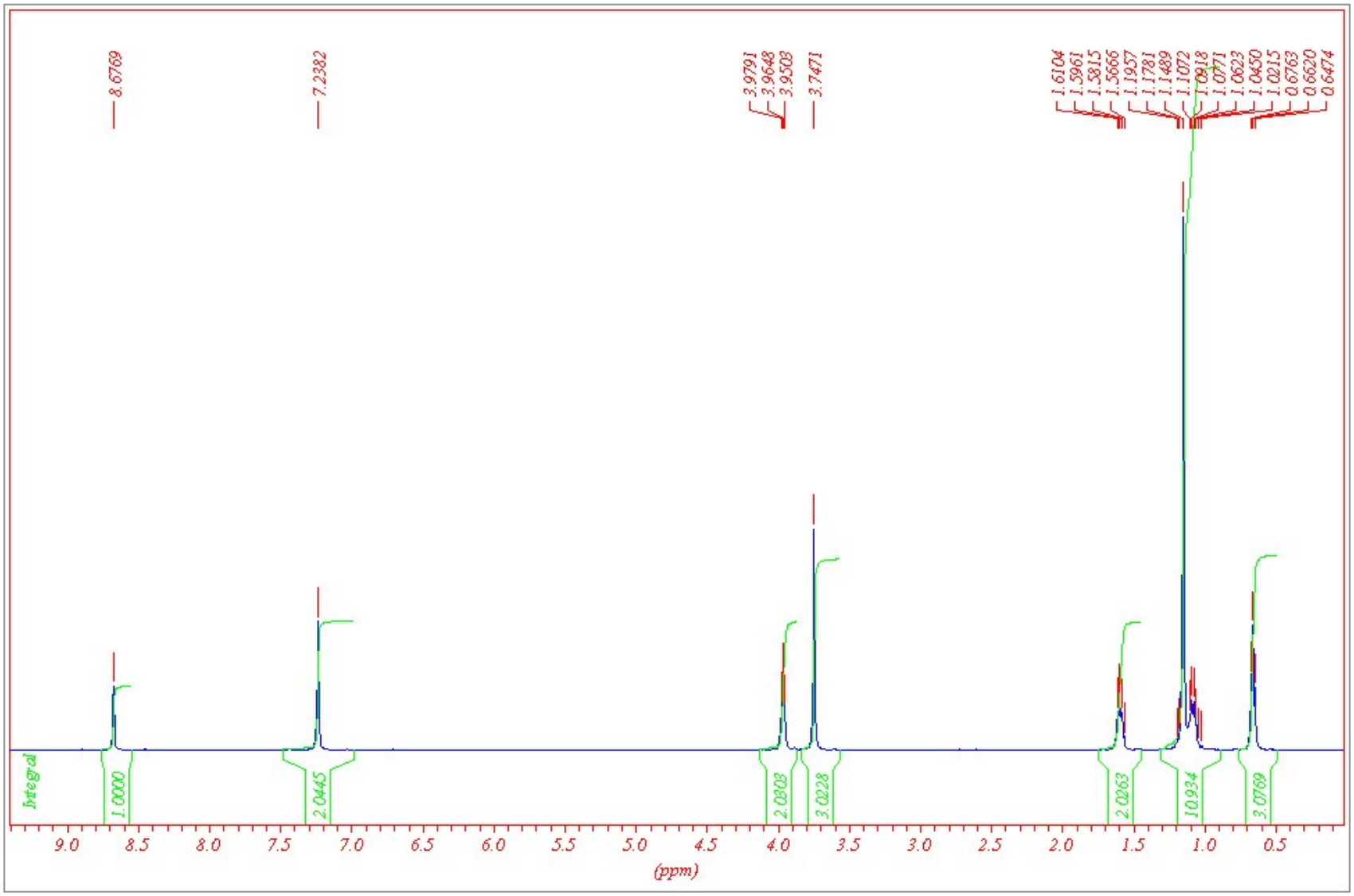



Figure S29. $^{1}$H NMR spectra of 1-Butyl-3-methylimidazolium 4-*tert*- butoxytetrafluorophenyltrifluoroborate (**5c**)

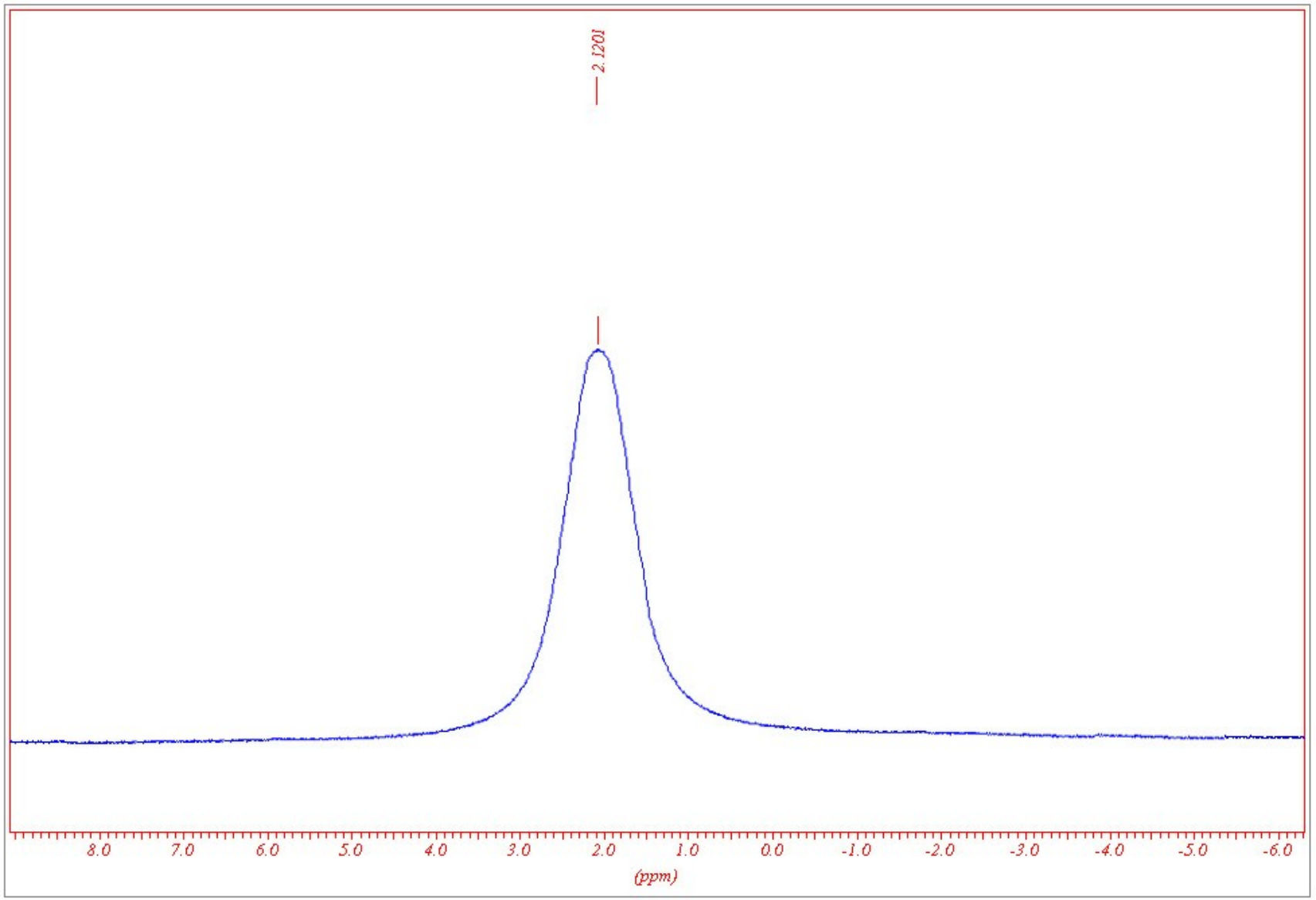



Figure S30. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium 4-*tert*- butoxytetrafluorophenyltrifluoroborate (**5c**)

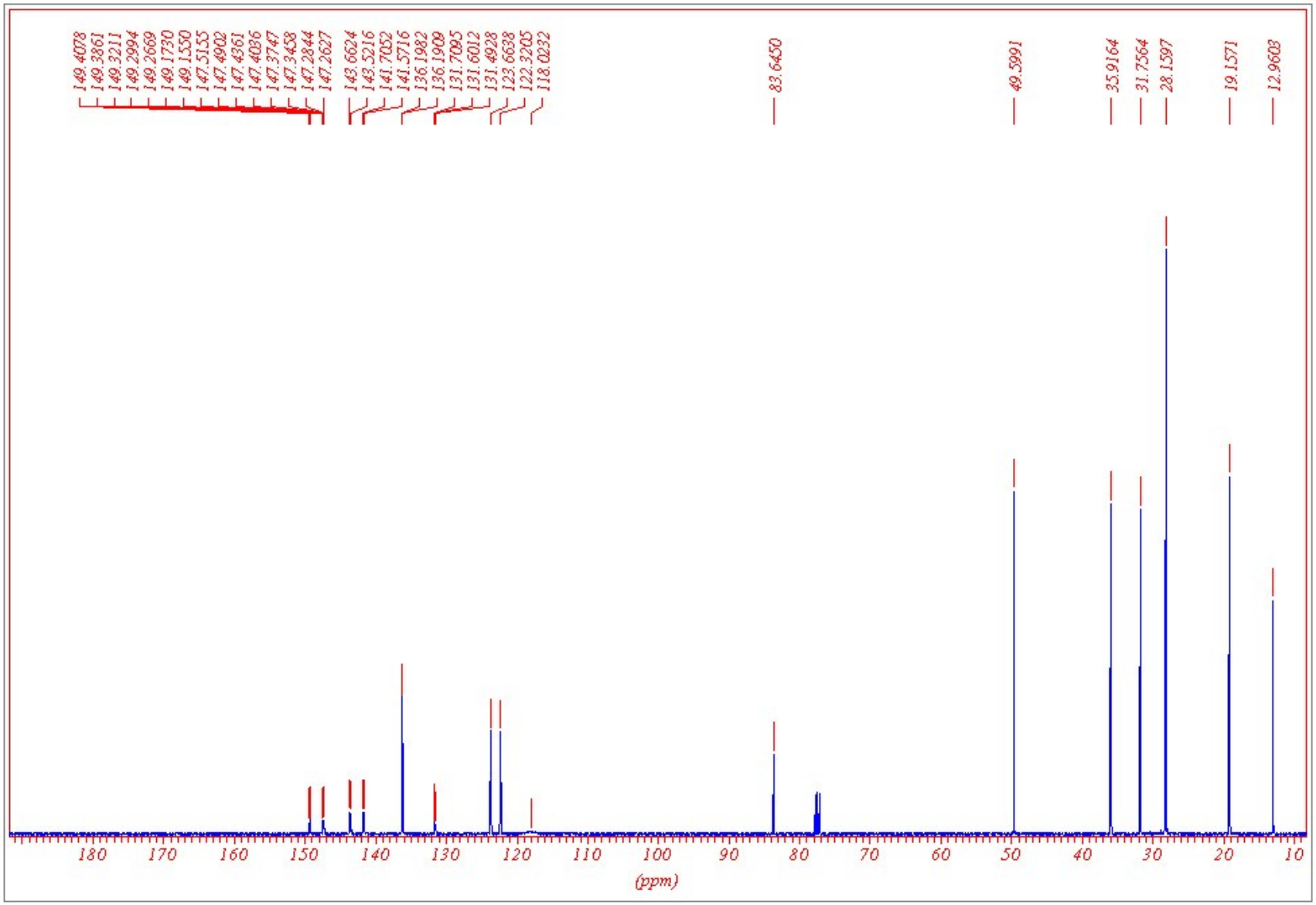



Figure S31. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium 4-*tert*- butoxytetrafluorophenyltrifluoroborate (**5c**)

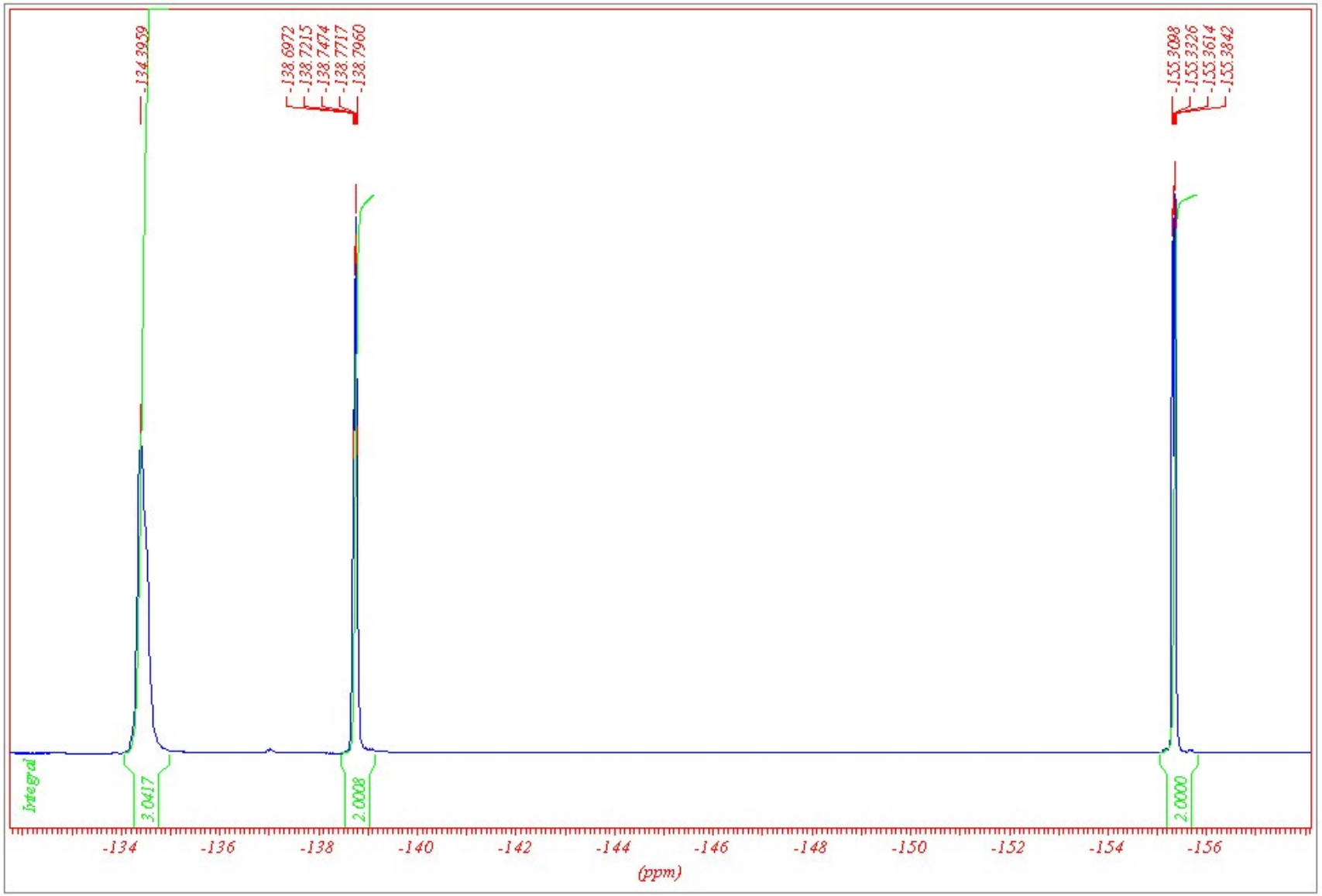
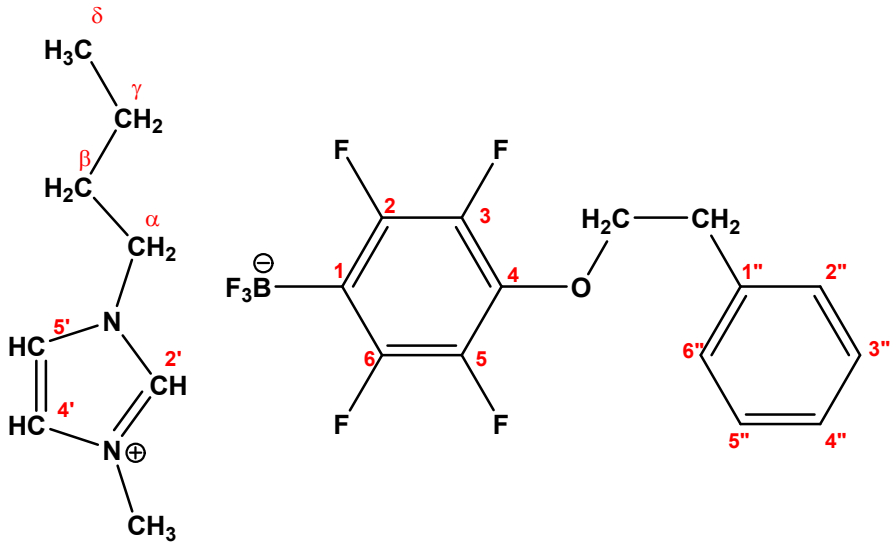



Figure S32. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium 4-*tert*- butoxytetrafluorophenyltrifluoroborate (**5c**)

**1-Butyl-3-methylimidazolium 4-(2-phenylethoxy)tetrafluorophenyltrifluoroborate (5d)**



**$^{1}$H NMR** ($CDCl_3$): δ 8.90 (s, 1H, *H*-2'); 7.23-7.31 (m, 4H, *H*-2",3",5",6"); 7.26 (s, 2H, *H*-4',5'); 7.20 (tt, 1H, $^{3}J_{HH}$ 7.0 Hz, $^{4}J_{HH}$ 1.6 Hz, *H*-4"); 4.33 (t, 2H, $^{3}J_{HH}$ 7.2 Hz, $PhCH_2CH_2O$); 4.12 (t, 2H, $^{3}J_{HH}$ 7.5 Hz, α-$CH_2$); 3.91 (s, 3H, $NCH_3$); 3.05 (t, 2H, $^{3}J_{HH}$ 7.2 Hz, $PhCH_2CH_2O$); 1.78 (tt, 2H, $^{3}J_{HH}$ 7.6 Hz, $^{3}J_{HH}$ 7.6 Hz, β-$CH_2$); 1.29 (qt, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.5 Hz, γ-$CH_2$); 0.88 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, δ-$CH_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.20 (bs, $BF_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.60 (dddd, $^{1}J_{CF}$ 238.2 Hz, $^{2}J_{CF}$ 18.4 Hz, $^{3}J_{CF}$ 10.3 Hz, $^{4}J_{CF}$ 3.5 Hz, *C*-2,6); 140.80 (dd, $^{1}J_{CF}$ 245.2 Hz, $^{2}J_{CF}$ 20.5 Hz, *C*-3,5); 137.74 (s, *C-1"*); 136.69 (s, *C*H-2'); 135.27 (tt, $^{2}J_{CF}$ 12.7 Hz, $^{3}J_{CF}$ 4.3 Hz, *C*-4); 129.06 (s, *C*-2",6"); 128.58 (s, *C*-3",5"); 126.64 (s, *C*-4"); 123.73 (s, *C*H-4'); 122.17 (s, *C*H-5'); 116.55 (bm, *C*-1); 75.25 (s, $PhCH_2CH_2O$); 49.93 (s, α-$CH_2$); 36.48 (s, $PhCH_2CH_2O$); 36.29 (s, $NCH_3$) 31.96 (s, β-$CH_2$); 19.43 (s, γ-$CH_2$); 13.25 (s, δ-$CH_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.63 (bs, 3F, $BF_3$); -138.34 (dddq, 2F, $^{3}J_{FF}$ 23.2 Hz, $^{5}J_{FF}$ 11.7 Hz; $^{4}J_{FF(BF3)}$ 11.6 Hz, $^{4}J_{FF}$ 3.6 Hz; *F*-2,6); -160.23 (dd, 2F, $^{3}J_{FF}$ 24.0 Hz, $^{5}J_{FF}$ 11.1 Hz, *F*-3,5).

Anal. calcd for $C_{22}H_{24}BF_7N_2O$ (476.24): C, 55.48; H, 5.08; F, 27.92; N, 5.88; found: C, 55.41; H, 5.19; F, 27.88; N, 5.92.

The NMR spectra are presented in Fig. S33-S36.

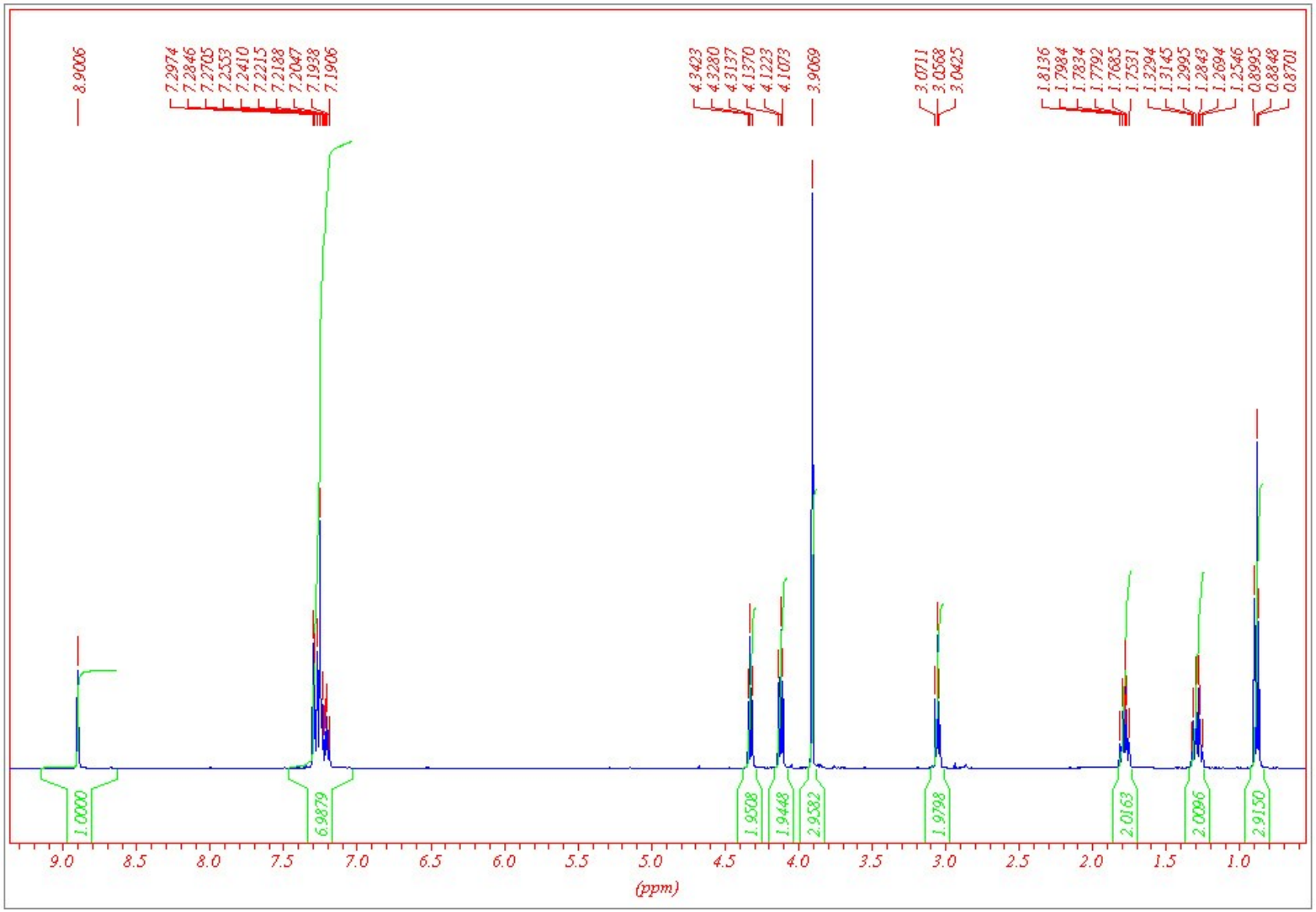



Figure S33. $^{1}H$ NMR spectra of 1-Butyl-3-methylimidazolium 4-(2- phenylethoxy)tetrafluorophenyltrifluoroborate (**5d**)

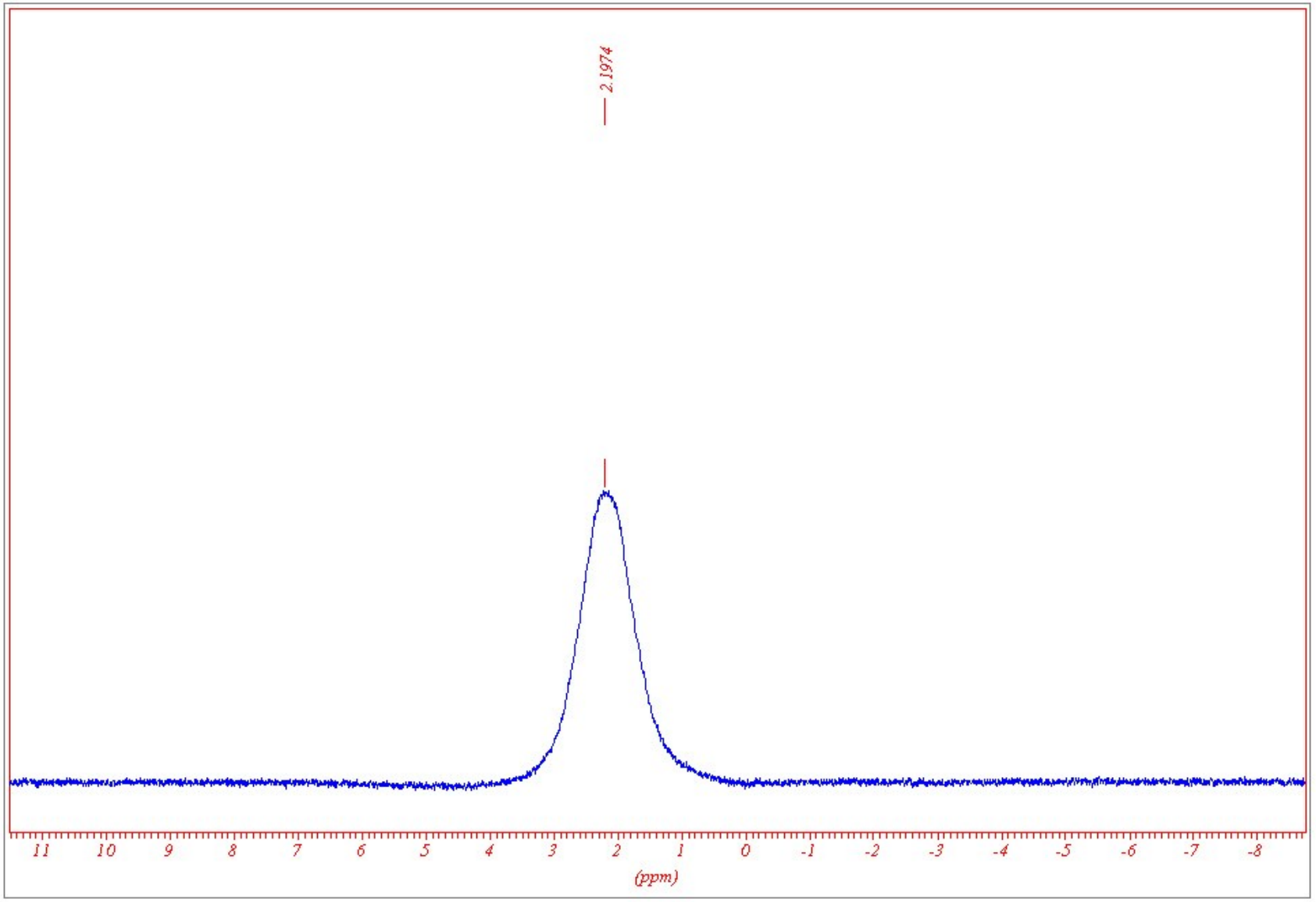



Figure S34. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium 4-(2- phenylethoxy)tetrafluorophenyltrifluoroborate (**5d**)

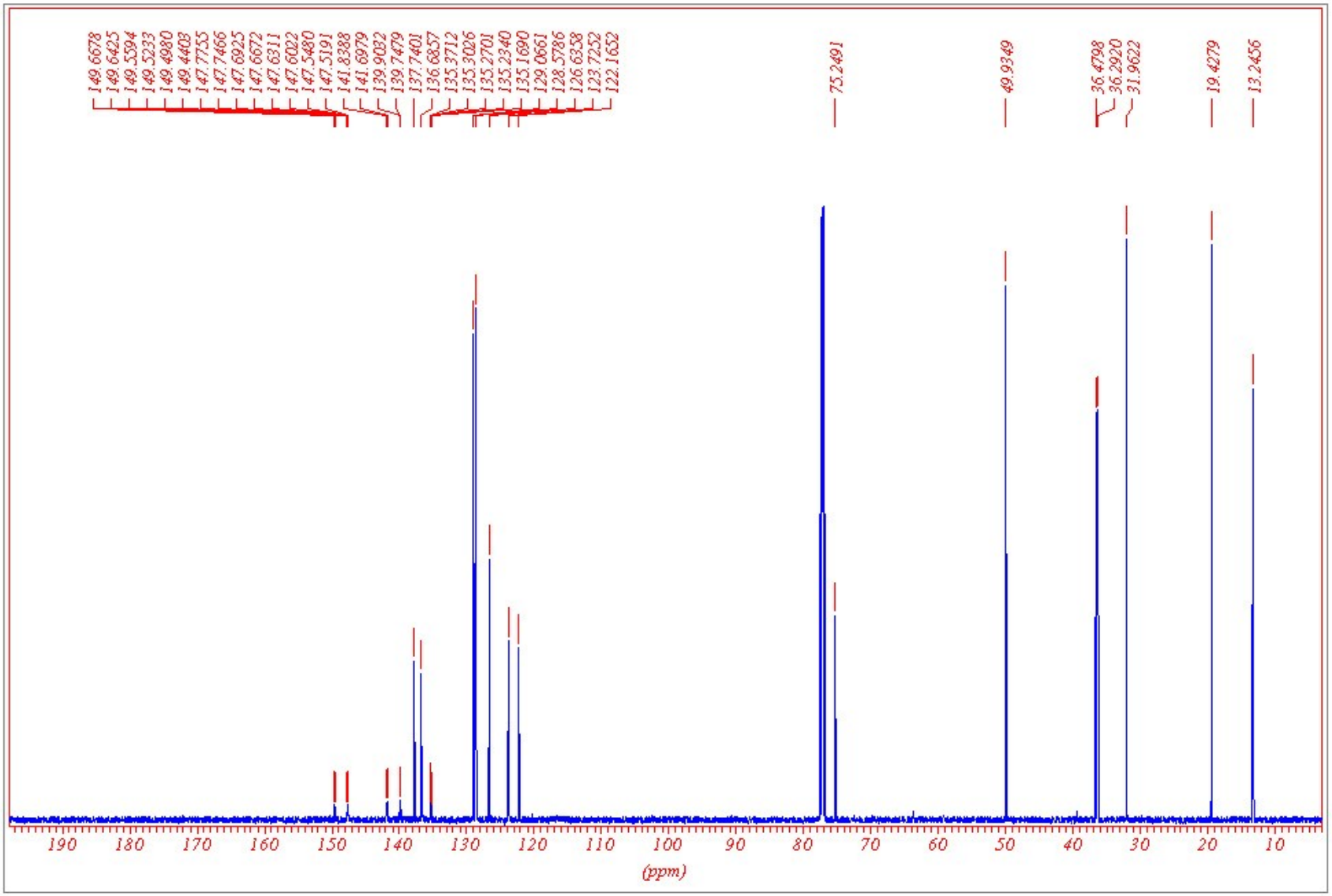



Figure S35. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium 4-(2- phenylethoxy)tetrafluorophenyltrifluoroborate (**5d**)

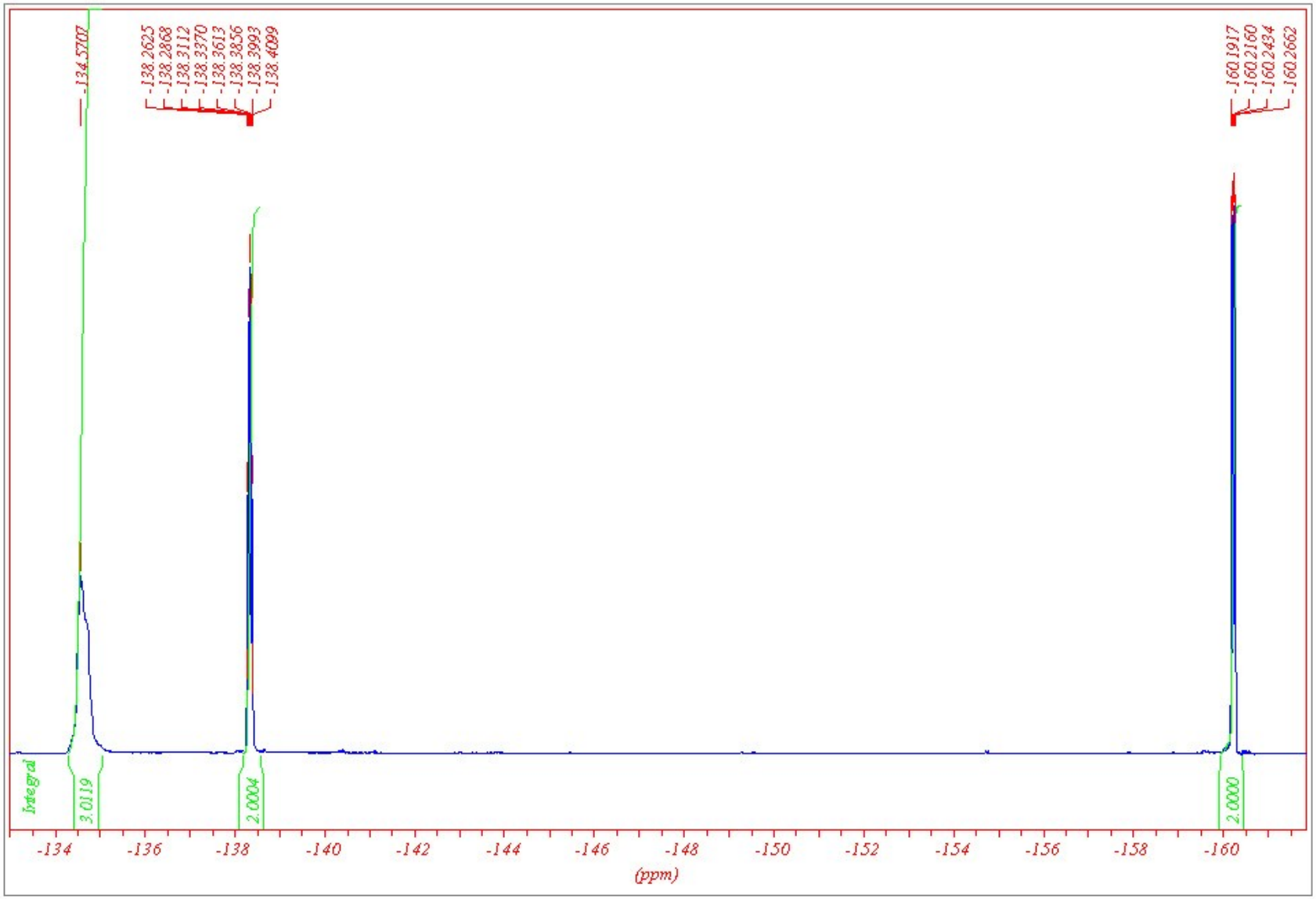
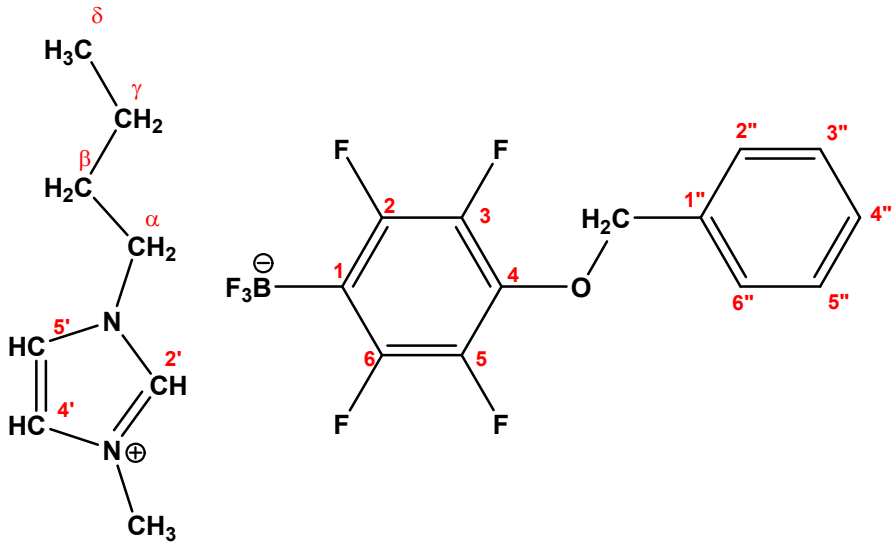



Figure S36. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium 4-(2- phenylethoxy)tetrafluorophenyltrifluoroborate (**5d**)

**1-Butyl-3-methylimidazolium 4-benzoxytetrafluorophenyltrifluoroborate (5e)**




**$^{1}$H NMR** ($CDCl_3$): δ 9.00 (s, 1H, *H*-2'); 7.22-7.44 (m, 7H, *H2"-H6",* C*H*-4', C*H*-5'); 5.15 (s, 2H, PhC$H_2$O); 4.12 (t, 2H, $^{3}J_{HH}$ 7.4 Hz, α-C$H_2$); 3.89 (s, 3H, NC$H_3$); 1.78 (tt, 2H, $^{3}J_{HH}$ 7.6 Hz, $^{3}J_{HH}$ 7.6 Hz, β-C$H_2$); 1.29 (qt, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.5 Hz, γ-C$H_2$); 0.89 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, δ-C$H_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.20 (bs, $BF_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.36 (dddd, $^{1}J_{CF}$ 237.2 Hz, $^{2}J_{CF}$ 18.1 Hz, $^{3}J_{CF}$ 10.1 Hz, $^{4}J_{CF}$ 3.4 Hz, *C*-2,6); 140.84 (dd, $^{1}J_{CF}$ 246.1 Hz, $^{2}J_{CF}$ 20.1 Hz, *C*-3,5); 136.63 (s, *C*-1"); 136.24 (s, *C*H-2'); 134.67 (tt, $^{2}J_{CF}$ 12.1 Hz, $^{3}J_{CF}$ 4.0 Hz, *C*-4); 128.57 (s, *C*-3",5"); 128.53 (s, *C*-4"); 128.33 (s, *C*-2",6"); 123.55 (s, *C*H-4'); 121.98 (s, *C*H-5'); 115.50 (bm, *C*-1); 76.15 (s, Ph*C*$H_2$O); 49.77 (s, α-*C*$H_2$); 36.19 (s, N*C*$H_3$) 31.89 (s, β-*C*$H_2$); 19.33 (s, γ-*C*$H_2$); 13.24 (s, δ-*C*$H_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.67 (bs, 3F, B$F_3$); -138.31 (dddq, 2F, $^{3}J_{FF}$ 23.4 Hz, $^{5}J_{FF}$ 11.6 Hz; $^{4}J_{FF(BF3)}$ 11.7 Hz, $^{4}J_{FF}$ 3.7 Hz; *F*-2,6); -159.65 (dd, 2F, $^{3}J_{FF}$ 24.0 Hz, $^{5}J_{FF}$ 11.1 Hz, *F*-3,5).

Anal. calcd for $C_{21}H_{22}BF_7N_2O$ (462.21): C, 54.57; H, 4.80; F, 28.77; N, 6.06; found: C, 54.49; H, 4.88; F, 28.64; N, 6.01.

The NMR spectra are presented in Fig. S37-S40.

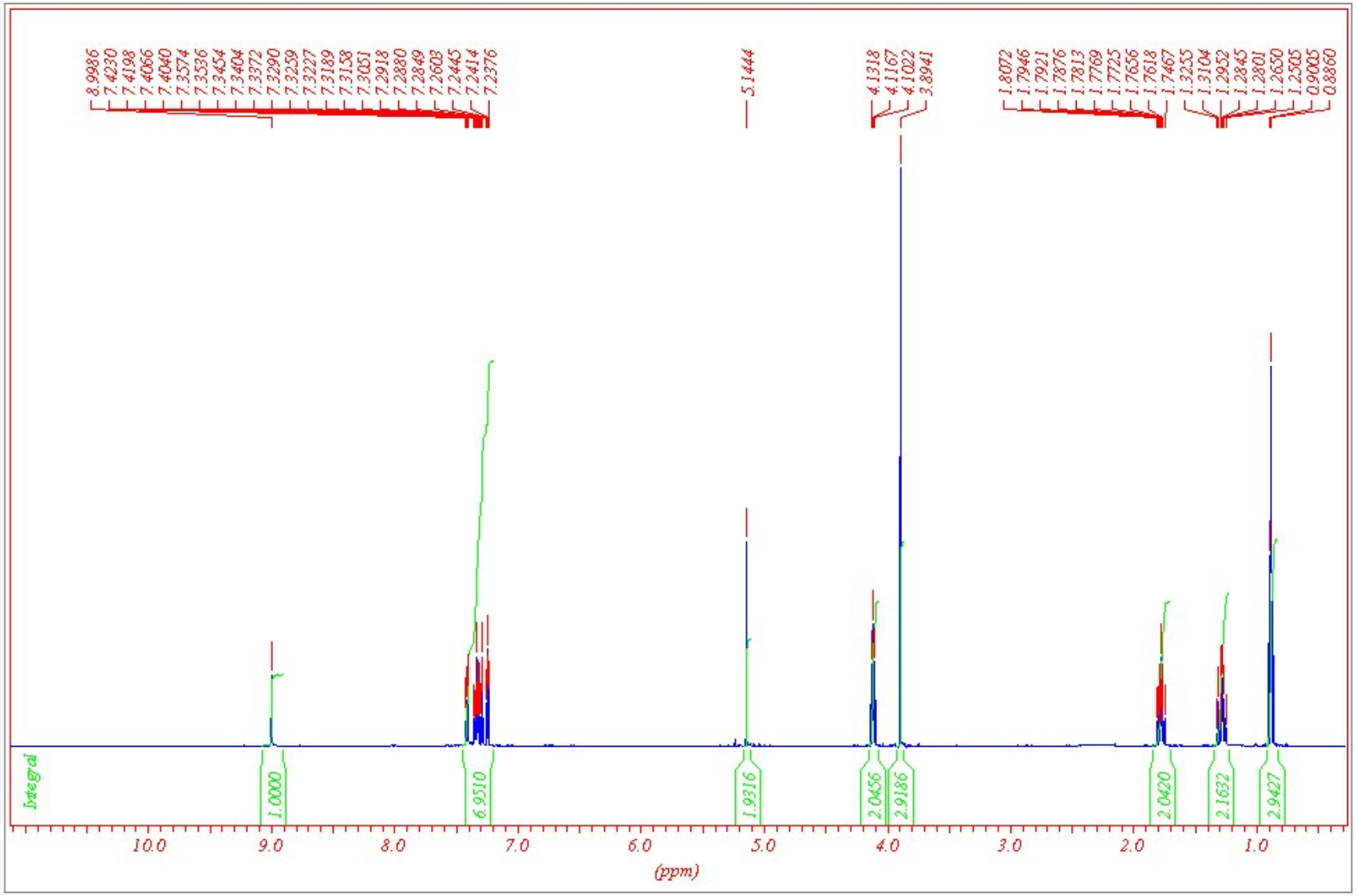



Figure S37. $^{1}H$ NMR spectra of 1-Butyl-3-methylimidazolium 4- benzoxytetrafluorophenyltrifluoroborate **(5e)**

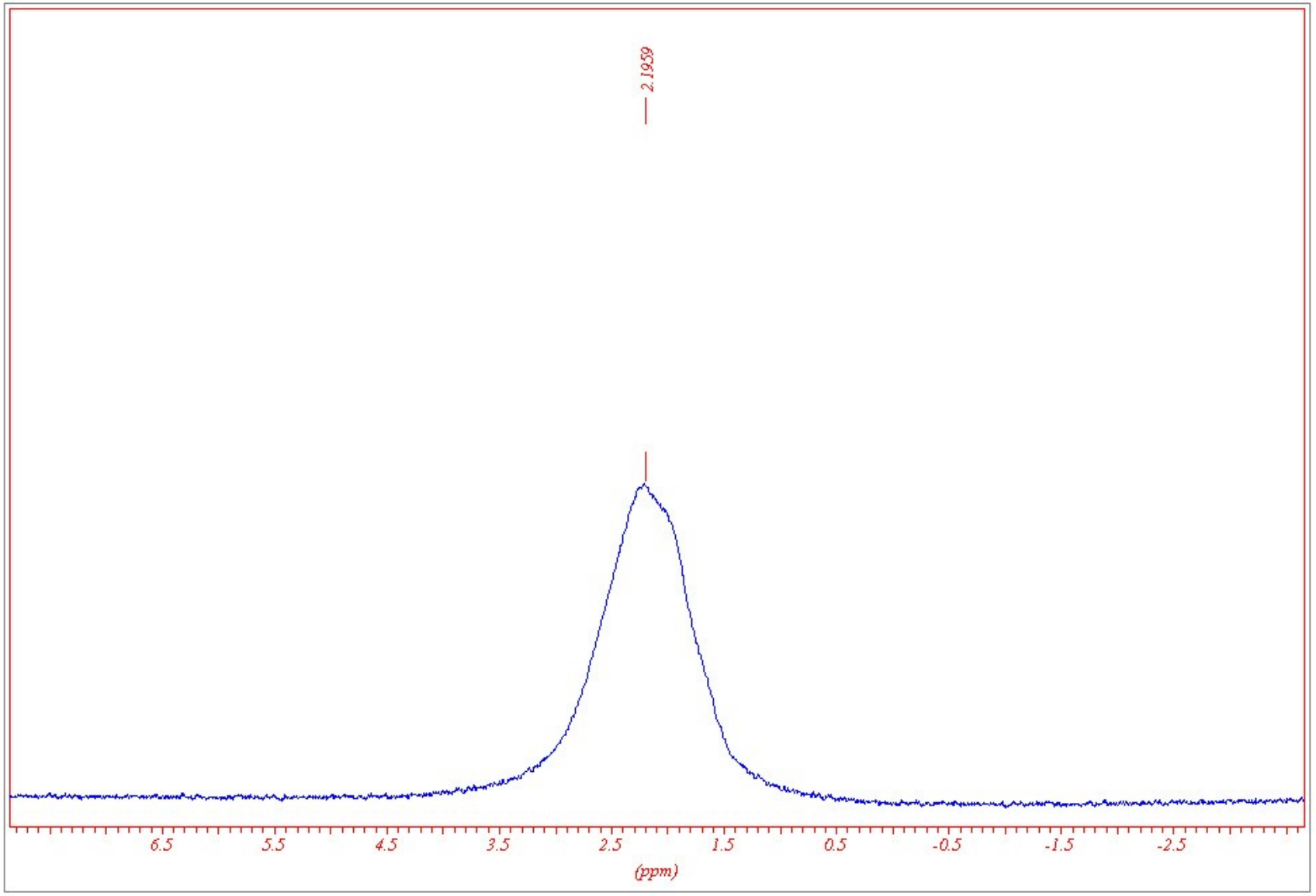



Figure S38. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium 4- benzoxytetrafluorophenyltrifluoroborate **(5e)**

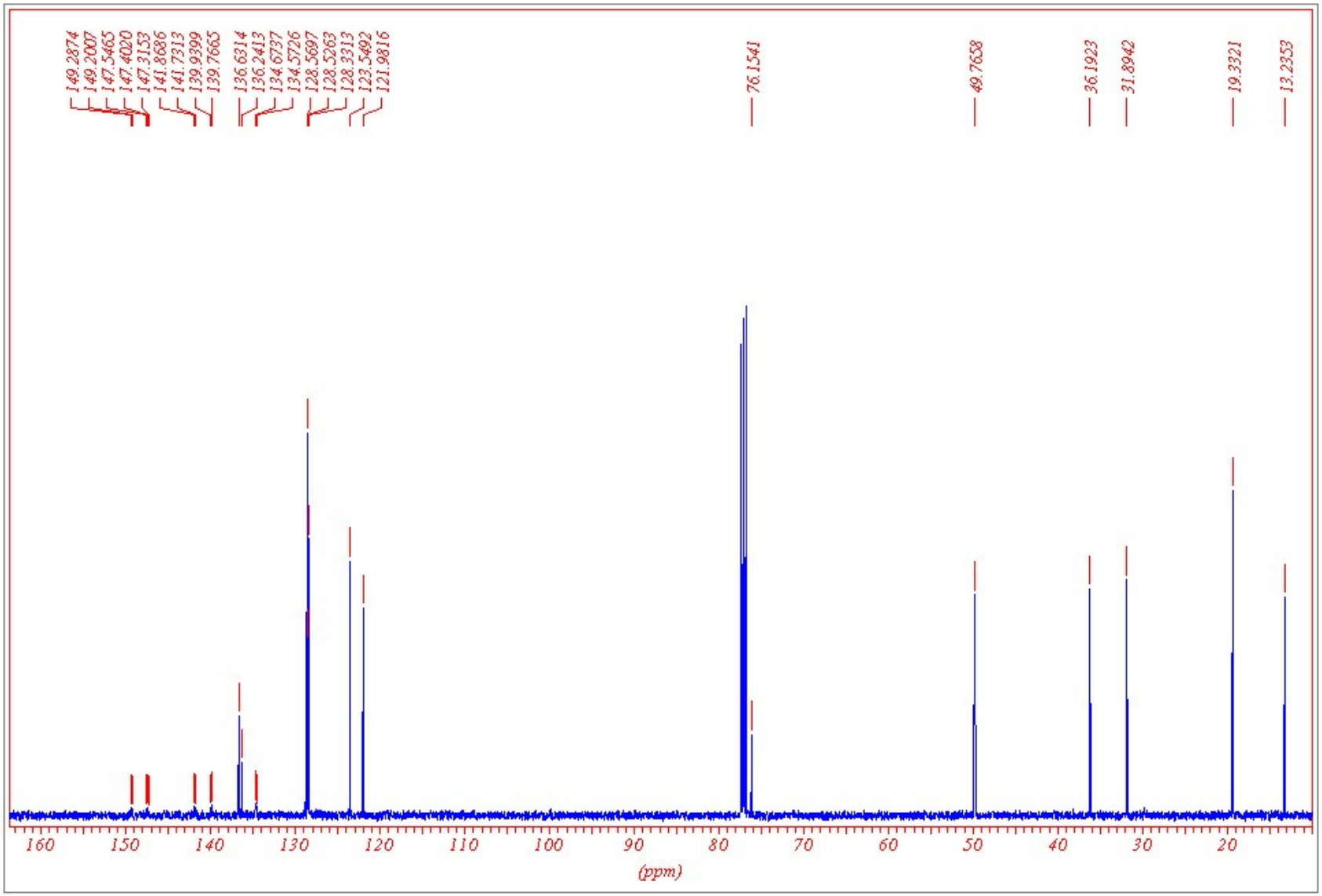



Figure S39. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium 4- benzoxytetrafluorophenyltrifluoroborate **(5e)**

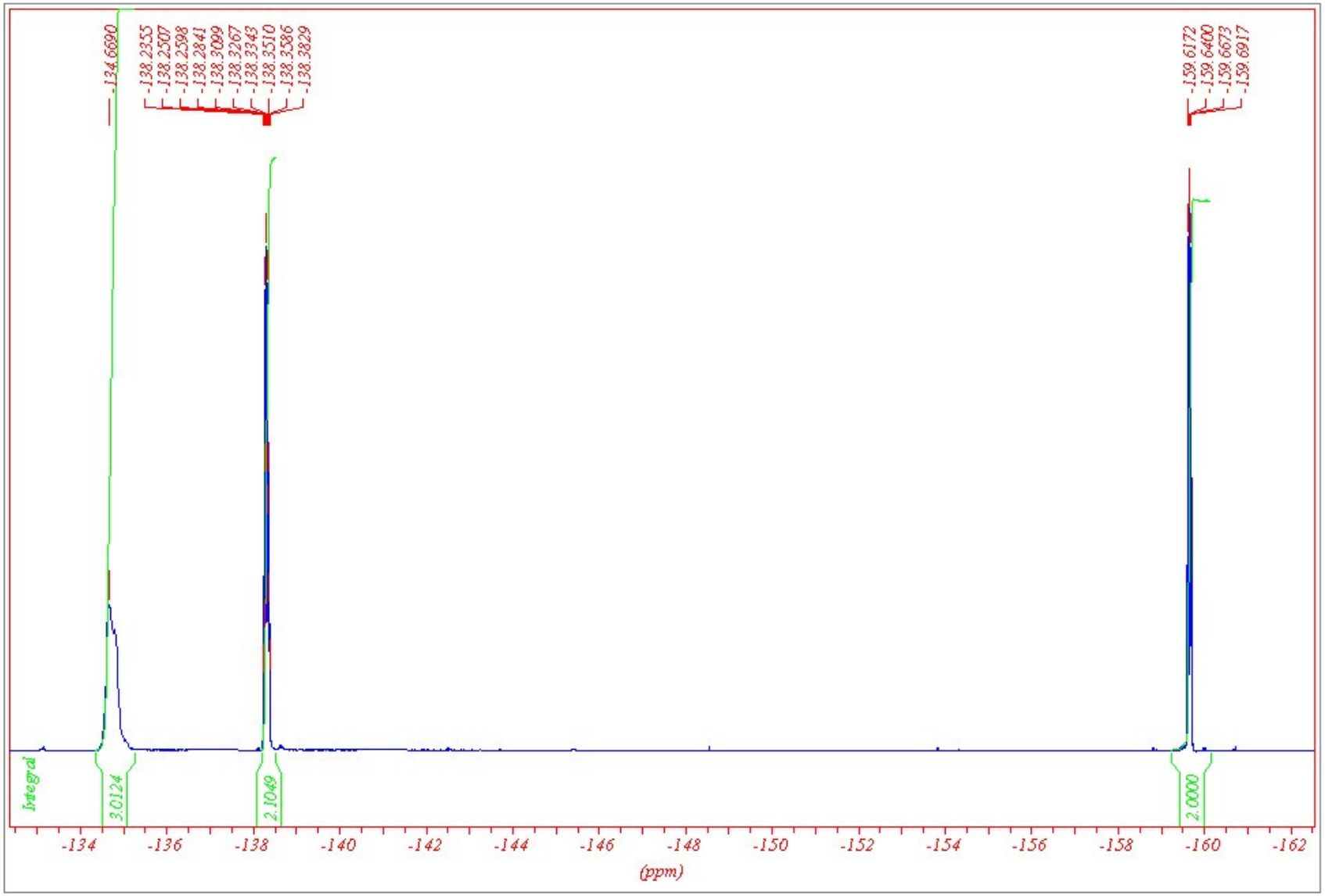
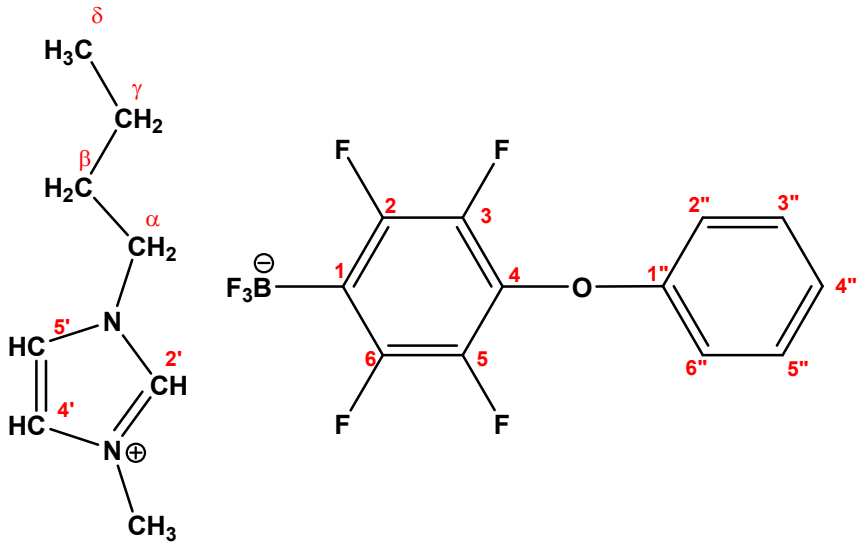



Figure S40. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium 4- benzoxytetrafluorophenyltrifluoroborate **(5e)**

**1-Butyl-3-methylimidazolium 4-phenoxytetrafluorophenyltrifluoroborate (5f)**




**$^{1}$H NMR** ($CDCl_3$): δ 8.77 (s, 1H, *H-2'*); 7.26 (s, 2H, *H-4',5'*); 7.22 (dd, 2H, $^{3}J_{HH}$ 7.0 Hz, $^{3}J_{HH}$ 7.0 Hz, *H*-3",5"); 6.98 (t, 1H, $^{3}J_{HH}$ 6.9 Hz, *H*-4"); 6.86 (d, 2H, $^{3}J_{HH}$ 7.4 Hz, *H*-2",6"); 4.06 (t, 2H, $^{3}J_{HH}$ 6.5 Hz, α-C$H_2$); 3.80 (s, 3H, NC$H_3$); 1.71 (tt, 2H, $^{3}J_{HH}$ 7.2 Hz, $^{3}J_{HH}$ 7.2 Hz, β-C$H_2$); 1.21 (qt, 2H, $^{3}J_{HH}$ 7.0 Hz, $^{3}J_{HH}$ 6.9 Hz, γ-C$H_2$); 0.79 (t, 3H, $^{3}J_{HH}$ 6.6 Hz, δ-C$H_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.19 (bs, *B*$F_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 157.68 (s, *C*-1"); 148.71 (dddd, $^{1}J_{CF}$ 239.3 Hz, $^{2}J_{CF}$ 17.9 Hz, $^{3}J_{CF}$ 9.4 Hz, $^{4}J_{CF}$ 2.2 Hz, *C*-2,6); 140.98 (dd, $^{1}J_{CF}$ 248.6 Hz, $^{2}J_{CF}$ 20.2 Hz, *C*-3,5); 136.24 (s, *C*H-2'); 131.14 (t, $^{2}J_{CF}$ 13.6 Hz, *C*-4); 129.88 (s, *C*-3",5"); 123.78 (s, *C*H-4'); 123.42 (s, *C*-4"); 122.39 (s, *C*H-5'); 119.67 (bm, *C*-1); 115.43 (s, *C*-2",6"); 49.81 (s, α-*C*$H_2$) 36.10 (s, N-*C*$H_3$) 31.87 (s, β-*C*$H_2$); 19.32 (s, γ-*C*$H_2$); 13.12 (s, δ-*C*$H_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.49 (bs, 3F, B*F*$_3$); -137.01 (ddq, 2F, $^{3}J_{FF}$ 22.9 Hz; $^{5}J_{FF}$ 11.3 Hz; $^{4}J_{FF(BF3)}$ 11.4 Hz, *F*-2,6); -158.39 (dd, 2F, $^{3}J_{FF}$ 23.6 Hz, $^{5}J_{FF}$ 10.7 Hz, *F*-3,5).

Anal. calcd for $C_{20}H_{20}BF_7N_2O$ (448.19): C, 53.60; H, 4.50; F, 29.67; N, 6.25; found: C, 53.69; H, 4.68; F, 29.59; N, 6.33.

The NMR spectra are presented in Fig. S41-S44.

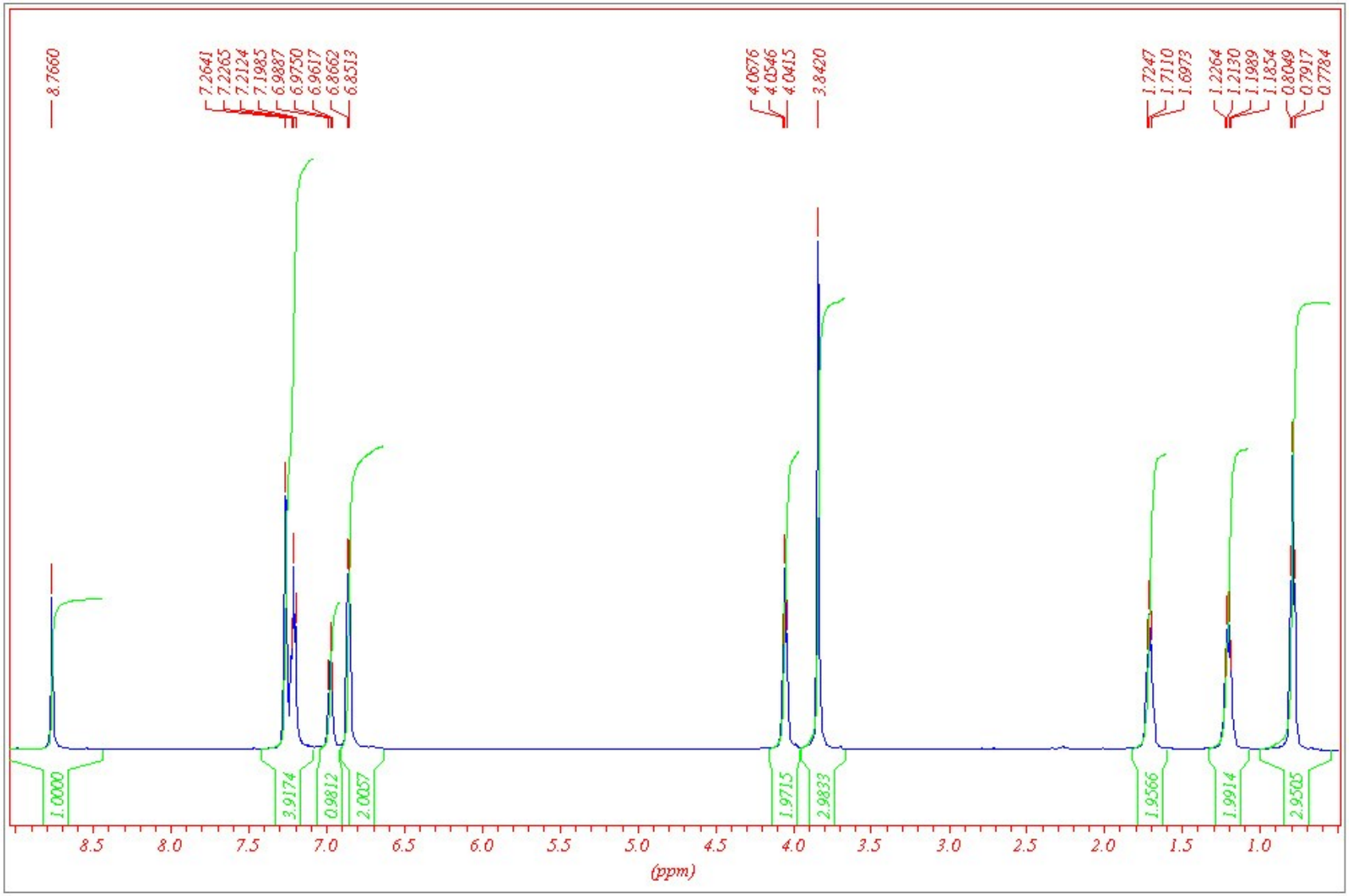



Figure S41. $^{1}H$ NMR spectra of 1-Butyl-3-methylimidazolium 4- phenoxytetrafluorophenyltrifluoroborate (**5f**)

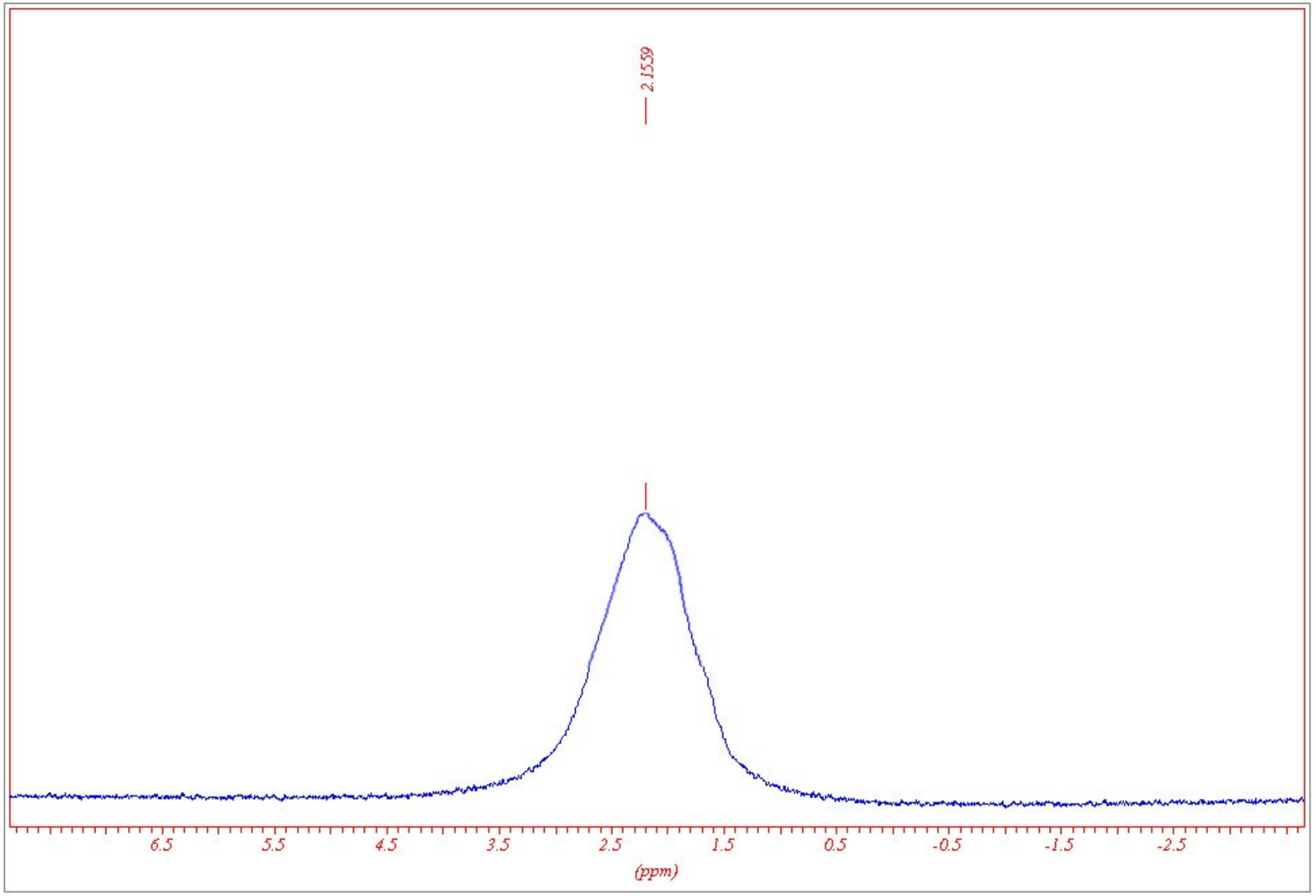



Figure S42. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium 4- phenoxytetrafluorophenyltrifluoroborate (**5f**)

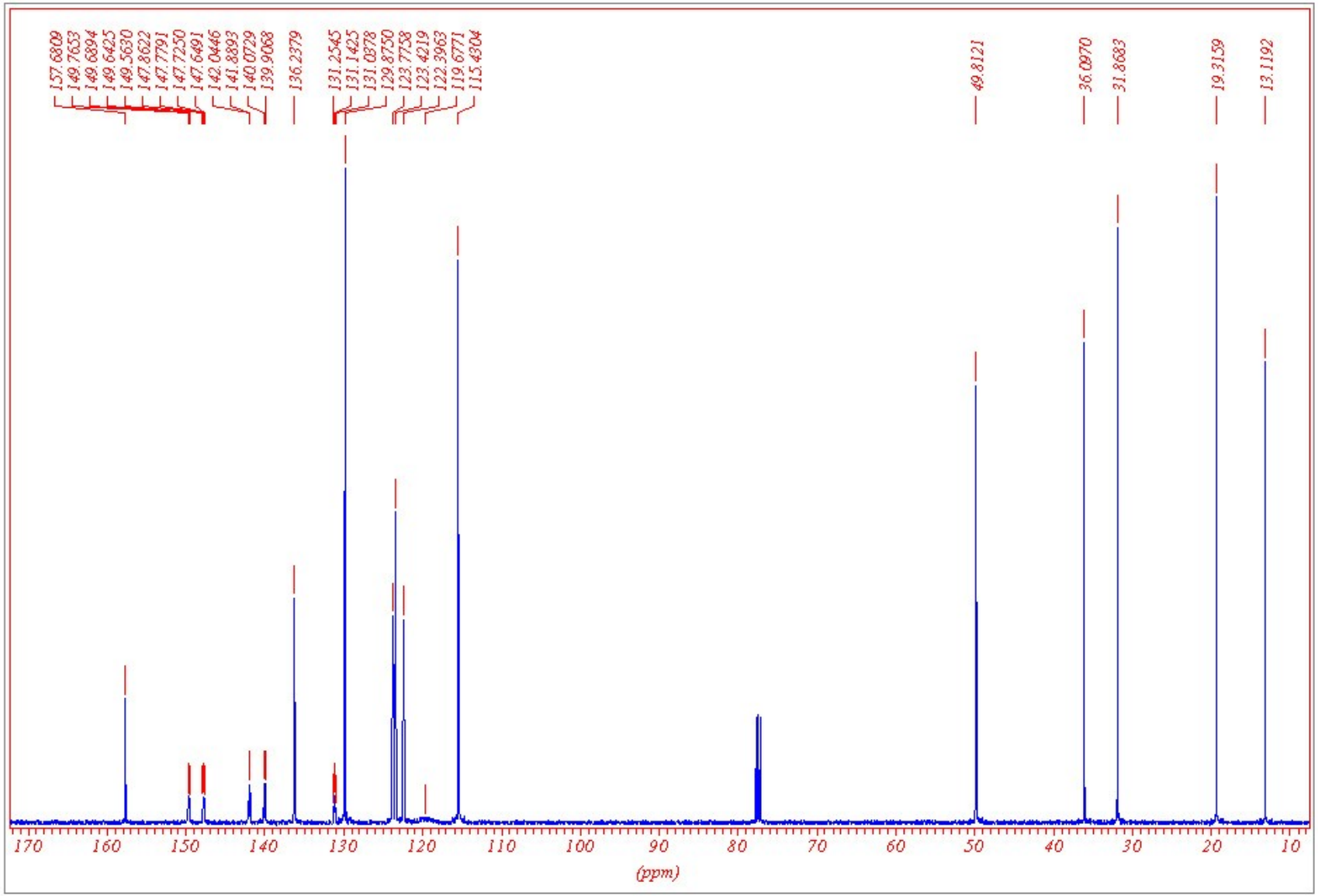



Figure S43. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium 4- phenoxytetrafluorophenyltrifluoroborate (**5f**)

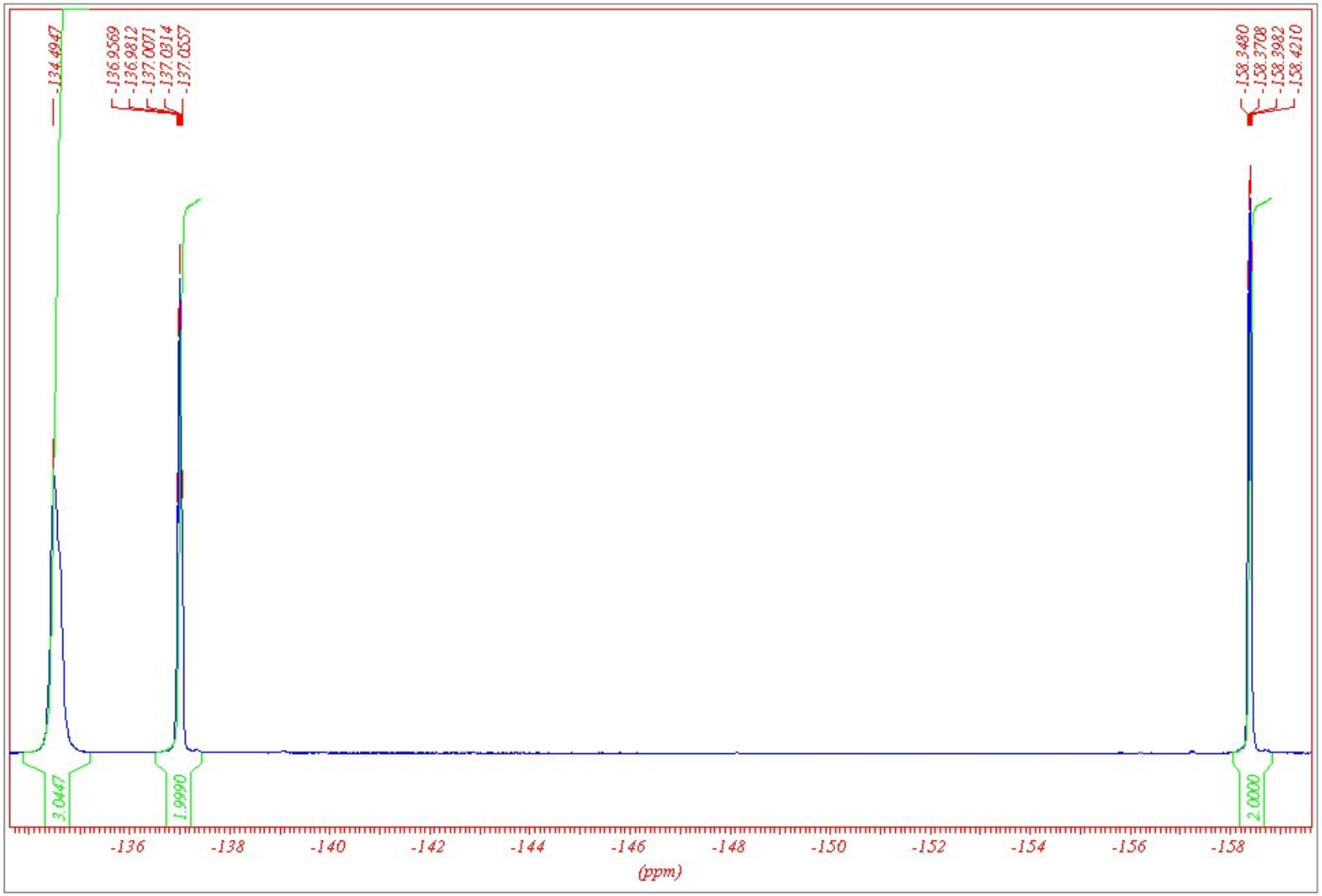
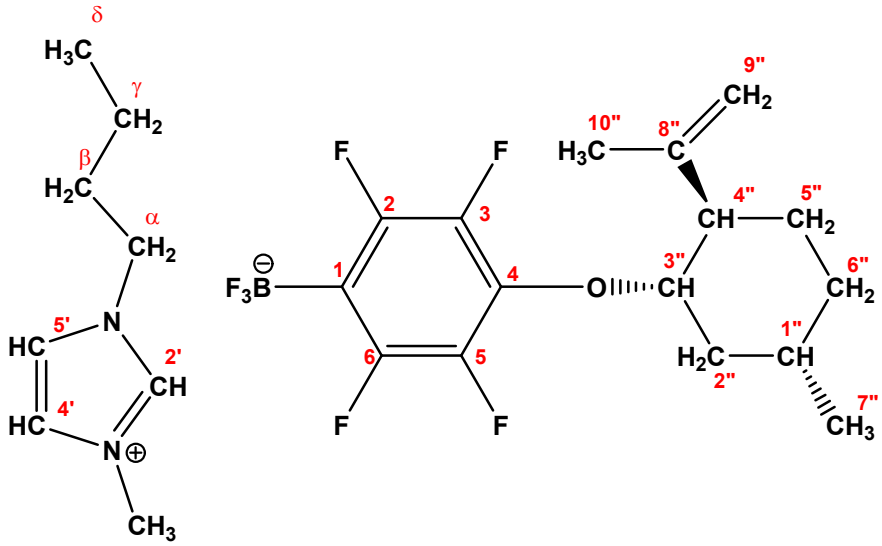



Figure S44. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium 4- phenoxytetrafluorophenyltrifluoroborate (**5f**)

**1-Butyl-3-methylimidazolium 4-[(1R,2S,5R)-5-methyl-2-(prop-1-en-2-yl)cyclohexyloxy] tetrafluorophenyltrifluoroborate (5g)**



**$^{1}$H NMR** ($CDCl_3$): δ 8.93 (s, 1H, *H*-2'); 7.33 (s, 1H, *H*-4'); 7.28 (s, 1H, *H-5'*); 4.87 (s, 1H, C*H*-9"); 4.80 (s, 1H, C*H*-9"*)*); 4.19 (d, 1H, $^{3}J_{HH}$ 3.8 Hz, C*H*-3"); 4.15 (t, 2H, $^{3}J_{HH}$ 7.4 Hz, α-C$H_2$); 3.94 (s, 3H, N-C$H_3$); 2.28 (ddd, 1H, $^{3}J_{HH}$ 11.3 Hz, $^{3}J_{HH}$ 11.3 Hz, $^{3}J_{HH}$ 2.3 Hz, C*H*-4"); 1.82 (t, 2H, $^{3}J_{HH}$ 7.4 Hz, β-C$H_2$); 1.78 (s, *3H, C$H_3$-10")*; 1.68 (m, 2H, C*H*-5", C*H*-6"); 1.40 (m, 2H, C*H*-1", C*H*-5"); 1.31 (tq, 2H, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HH}$ 7.6 Hz, γ-C$H_2$); 1.08 (m, 2H, C$H_2$-2"); 0.99 (dddd, 1H, $^{3}J_{HH}$ 12.8 Hz, $^{3}J_{HH}$ 12.7 Hz, $^{3}J_{HH}$ 12.7 Hz, $^{3}J_{HH}$ 2.8 Hz, C*H*-6"); 0.91 (d, 3H, $^{3}J_{HH}$ 7.5 Hz, C$H_3$-7"); 0.90 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, δ-C$H_3$).

**$^{11}$B NMR** ($CDCl_3$): δ 2.31 (bs, *B*$F_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.51 (dddd, $^{1}J_{CF}$ 238.0 Hz, $^{2}J_{CF}$ 18.5 Hz, $^{3}J_{CF}$ 10.3 Hz, $^{4}J_{CF}$ 3.5 Hz, *C*-2,6); 146.84 (s, *C*-8"); 141.41 (dd, $^{1}J_{CF}$ 244.6 Hz, $^{2}J_{CF}$ 18.9 Hz, *C*-3,5); 136.61 (s, *C*H-2'); 133.83 (tt, $^{2}J_{CF}$ 12.8 Hz, $^{3}J_{CF}$ 4.2 Hz, *C*-4); 123.59 (s, *C*H-4'); 122.02 (s, *C*H-5'); 116.09 (bm, *C*-1); 111.64 (s, *C*-9"); 82.78 (s, *C*-3"); 51.90 (s, *C*-4"); 49.82 (s, α-$CH_2$); 39.95 (s, *C*-2"); 36.23 (s, N-$CH_3$); 34.16 (s, *C*-6"); 31.88 (s, β-$CH_2$); 31.39 (s, *C*-1"); 31.03 (s, *C*-5"); 22.01 (s, *C*-7"); 19.32 (s, *C*-10"); 19.29 (s, γ-$CH_2$); 13.19 (s, δ-$CH_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.61 (bs, 3F, B$F_3$); -138.76 (ddq, 2F, $^{3}J_{FF}$ 23.2 Hz; $^{5}J_{FF}$ 11.6 Hz; $^{4}J_{FF(BF3)}$ 11.6 Hz, *F-2,6*); -158.63 (dd, 2F, $^{3}J_{FF}$ 24.0 Hz, $^{5}J_{FF}$ 11.1 Hz, *F-3,5*).

Anal. calcd for $C_{24}H_{32}BF_7N_2O$ (508.32): C, 56.71; H, 6.35; F, 26.16; N, 5.51; found: C, 56.68; H, 6.39; F, 26.01; N, 5.53.

The NMR spectra are presented in Fig. S45- S48.

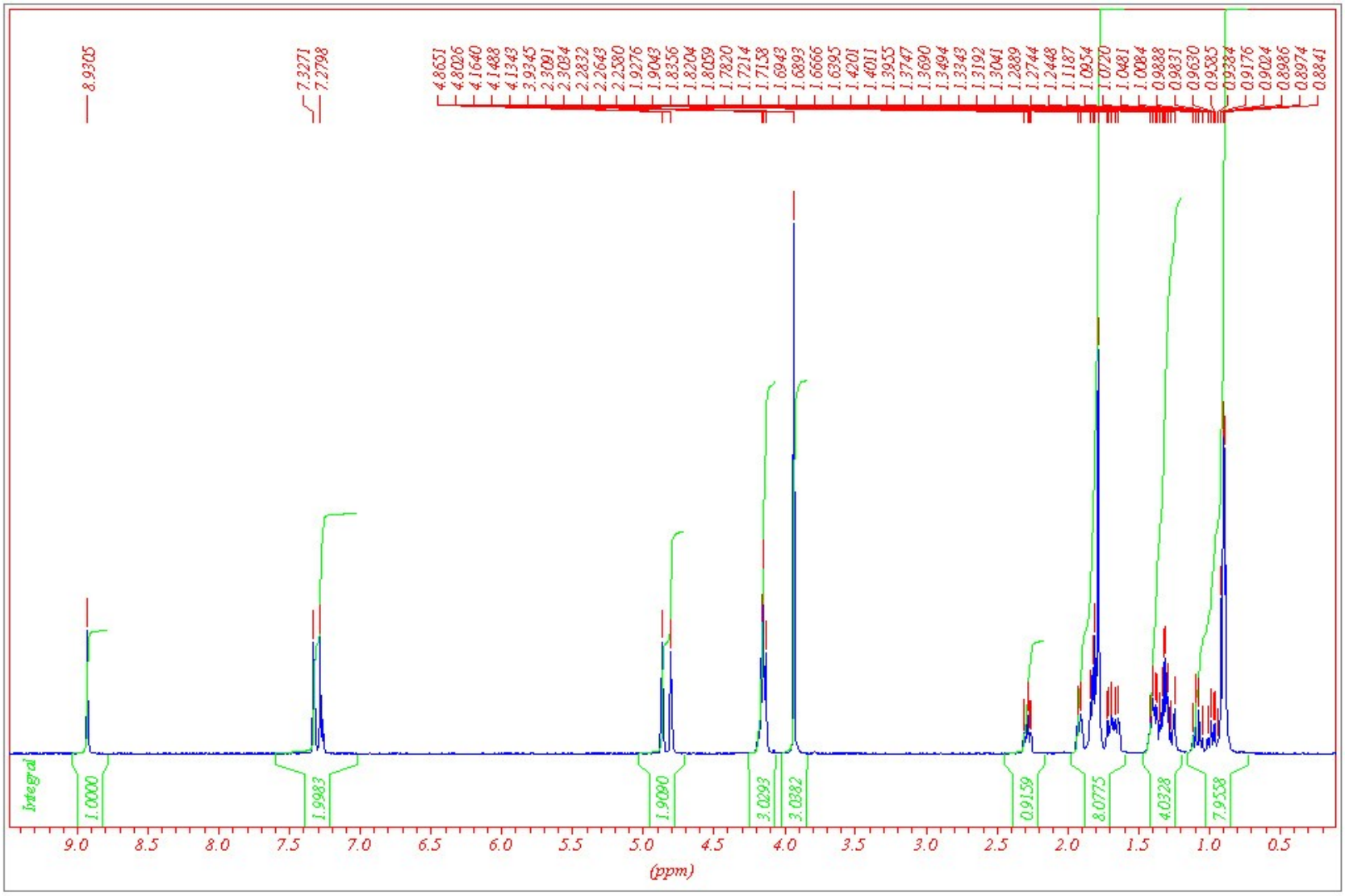



Figure S45. $^{1}H$ NMR spectra of 1-Butyl-3-methylimidazolium 4-[(1R,2S,5R)-5-methyl-2-(prop-1-en-2-yl)cyclohexyloxy] tetrafluorophenyltrifluoroborate (**5g**)

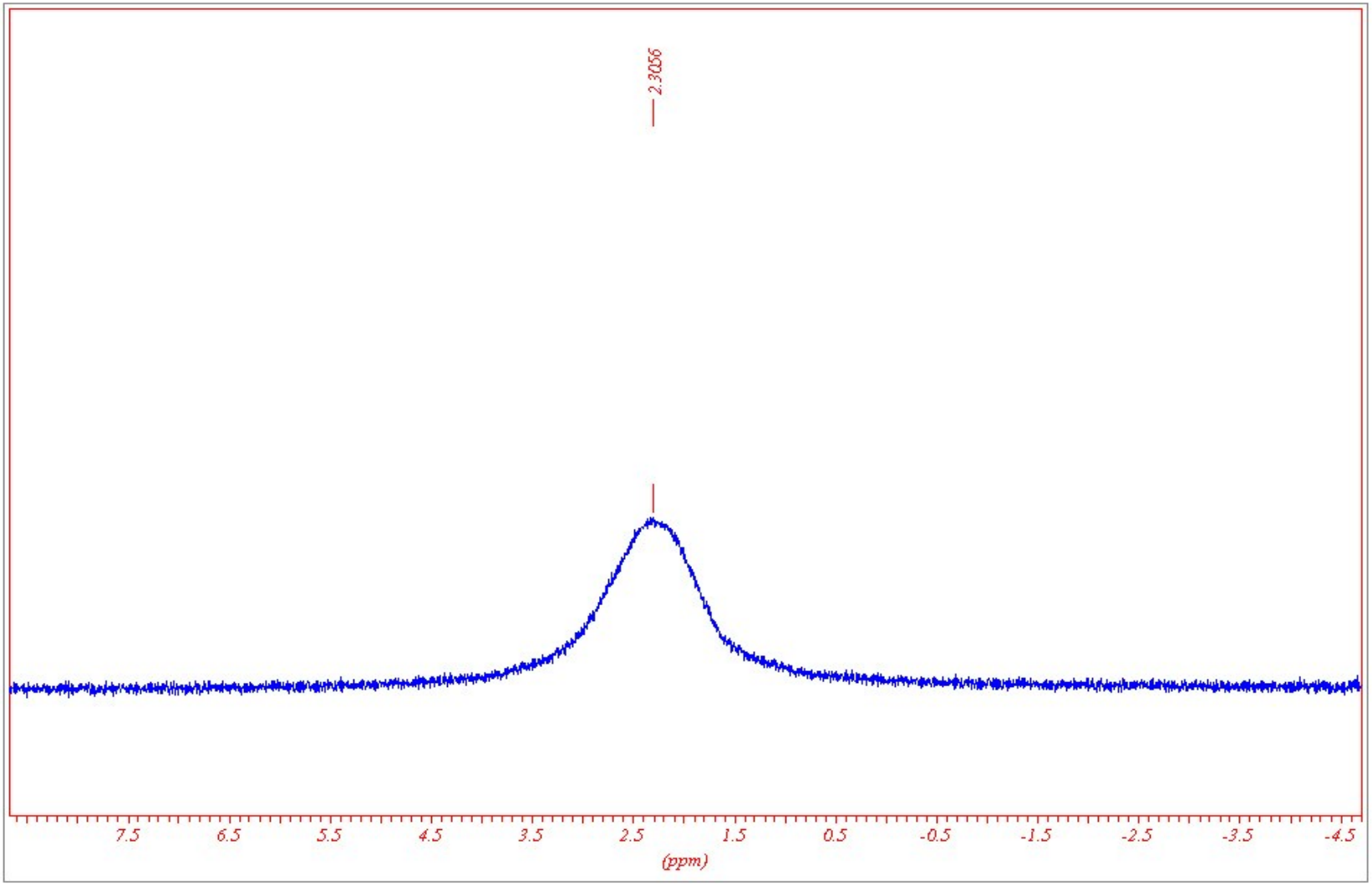



Figure S46. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium 4-[(1R,2S,5R)-5-methyl-2-(prop-1-en-2-yl)cyclohexyloxy] tetrafluorophenyltrifluoroborate (**5g**)

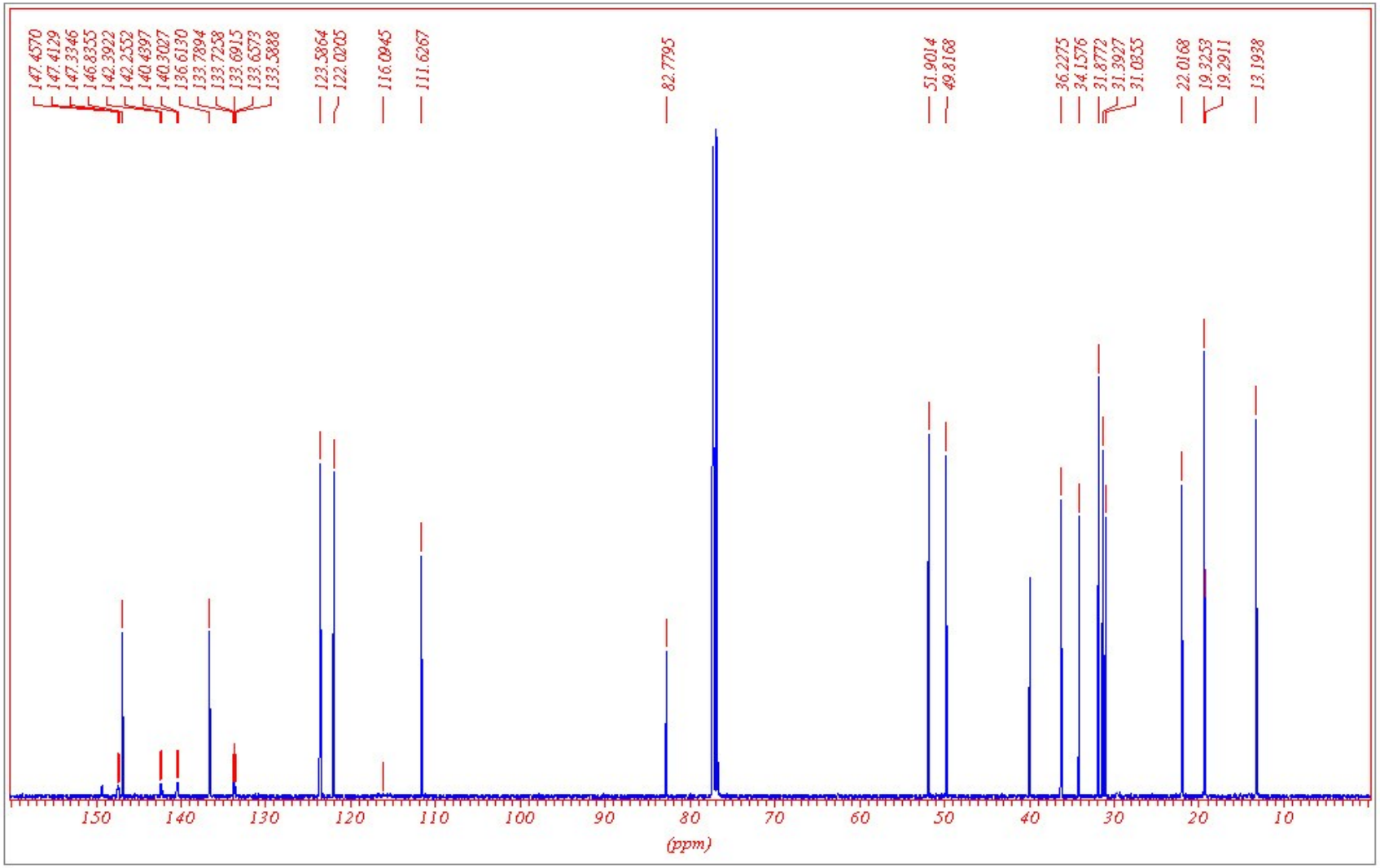



Figure S47. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium 4-[(1R,2S,5R)-5-methyl-2-(prop-1-en-2-yl)cyclohexyloxy] tetrafluorophenyltrifluoroborate (**5g**)

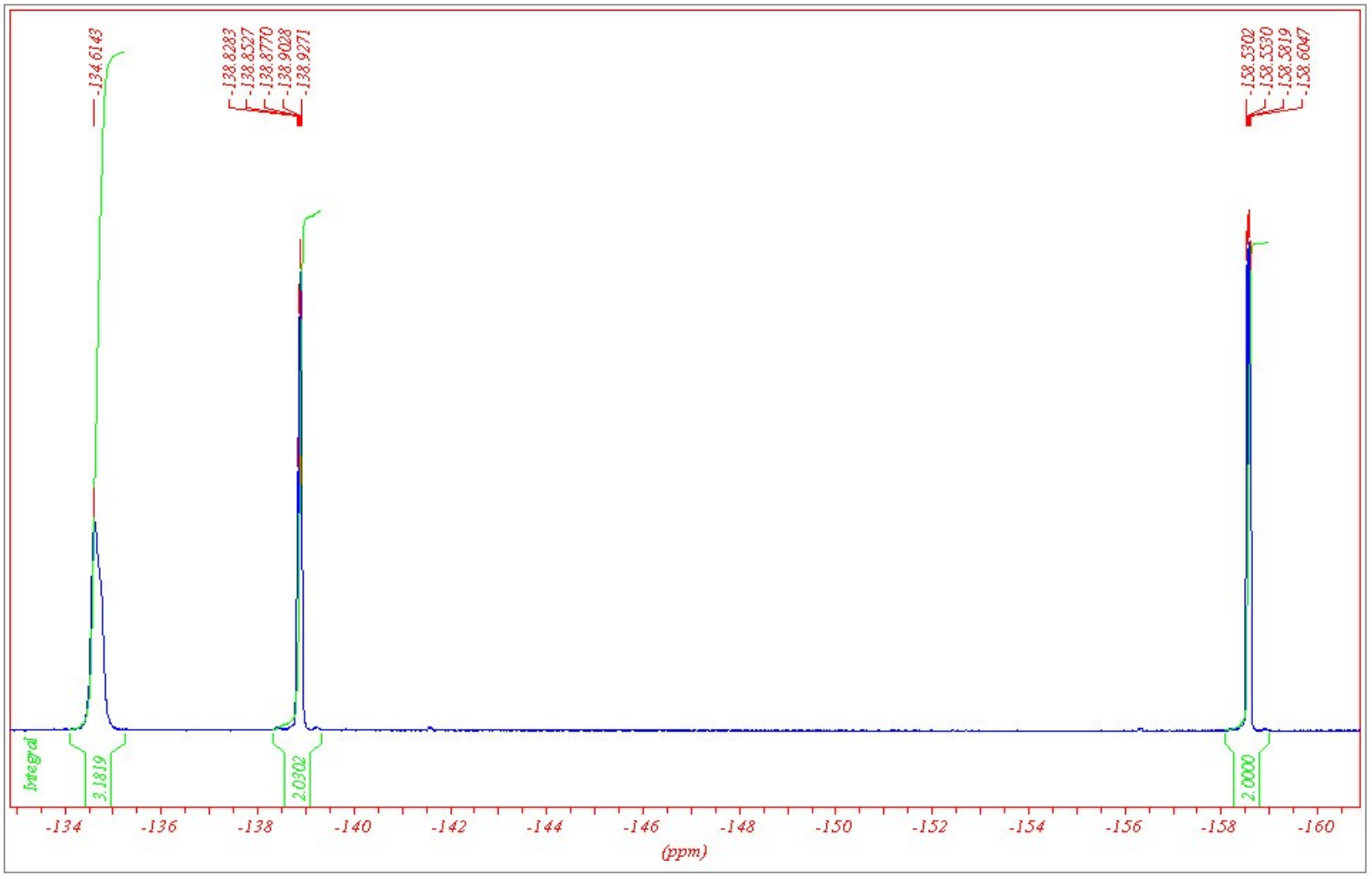
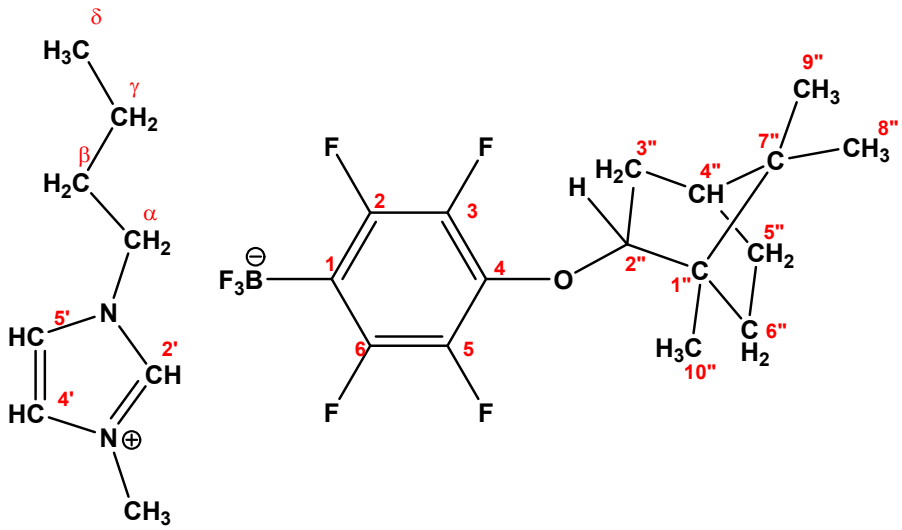



Figure S48. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium 4-[(1R,2S,5R)-5-methyl-2-(prop-1-en-2-yl)cyclohexyloxy] tetrafluorophenyltrifluoroborate (**5g**)

**1-Butyl-3-methylimidazolium 4-bornyloxytetrafluorophenyltrifluoroborate (5h)**



**$^{1}$H NMR** ($CDCl_3$): δ 8.93 (s, 1H, *H*-2'); 7.33 (s, 1H, *H*-4'); 7.29 (s, 1H, *H*-5'); 4.40 (d, 1H; $^{3}J_{HH}$ 8.7 Hz, *H*-2); 4.14 (t, 2H, $^{3}J_{HH}$ 7.5 Hz, α-C*H*$_2$); 3.94 (s, 3H, NC*H*$_3$); 2.25 (ddd, 1H, $^{3}J_{HH}$ 12.6 Hz, $^{3}J_{HH}$ 10.2 Hz, $^{2}J_{HH}$ 5.4 Hz, *H*-3"); 2.18 (dddd, 1H, $^{3}J_{HH}$ 13.7 Hz, $^{3}J_{HH}$ 9.3 Hz, $^{2}J_{HH}$ 4.5 Hz, $^{4}J_{HH}$ 3.6 Hz, *H*-3"); 1.70-1.85 (m, 3H, *H*-5" *and* β-C*H*$_2$); 1.67 (dd, 1H, $^{3}J_{HH}$ 4.5 Hz; $^{3}J_{HH}$ 4.5 Hz, *H*-4"); 1.22-1.39 (m, 5H, *H*-3", 5", 6" and γ-C*H*$_2$); 0.92 (s, 3H, *H*-8"); 0.89 (t, 3H, $^{3}J_{HH}$ 7.4 Hz, δ-C*H*$_3$); 0.87 (s, 3H, *H*-9"); 0.83 (s, 3H, *H*-10").

**$^{11}$B NMR** ($CDCl_3$): δ 2.24 (bs, *B*F$_3$).

**$^{13}$C NMR** ($CDCl_3$): δ 148.61 (dddd, $^{1}J_{CF}$ 237.9 Hz, $^{2}J_{CF}$ 18.5 Hz, $^{3}J_{CF}$ 10.3 Hz, $^{4}J_{CF}$ 3.9 Hz, *C*-2,6); 141.00 (ddd, $^{1}J_{CF}$ 244.7 Hz, $^{2}J_{CF}$ 20.0 Hz, $^{4}J_{CF}$ 2.0 Hz, *C*-3,5); 136.79 (s, *C*H-2'); 136.05 (tt, $^{2}J_{CF}$ 12.4 Hz, $^{3}J_{CF}$ 4.1 Hz, *C*-4); 123.74 (s, *C*H-4'); 122.16 (s, *C*H-5'); 115.78 (bm, *C*-1); 90.78 (s, *C*-2"*);* 50.20 (s, *C*-1"*);* 49.96 (s, α-*C*H$_2$); 48.17 (s, *C*-7"*);* 45.11 (s, *C*-4"*);* 36.61 (s, N-*C*H$_3$); 36.59 (s, *C*-3"*);* 31.98 (s, β-*C*H$_2$); 28.20 (s, *C*-5"*);* 26.38 (s, *C*-6"*);* 19.88 (s, *C*-8"*);* 19.45 (s, γ-*C*H$_2$); 18.89 (s, *C*-9"*);* 13.49 (s, *C*-10"); 13.25 (s, δ-*C*H$_3$).

**$^{19}$F NMR** ($CDCl_3$): δ -134.54 (bs, 3F, B*F*$_3$); -138.75 (ddq, 2F, $^{3}J_{FF}$ 23.3 Hz; $^{5}J_{FF}$ 11.6 Hz; $^{4}J_{FF(BF3)}$ 11.6 Hz, *F*-2,6); -159.67 (dd, 2F, $^{3}J_{FF}$ 24.3 Hz, $^{5}J_{FF}$ 10.7 Hz, *F*-3,5).

Anal. calcd for $C_{24}H_{32}BF_7N_2O$ (508.32): C, 56.71; H, 6.35; F, 26.16; N, 5.51; found: C, 56.78; H, 6.41; F, 26.08; N, 5.45.

The NMR spectra are presented in Fig. S49-S52.

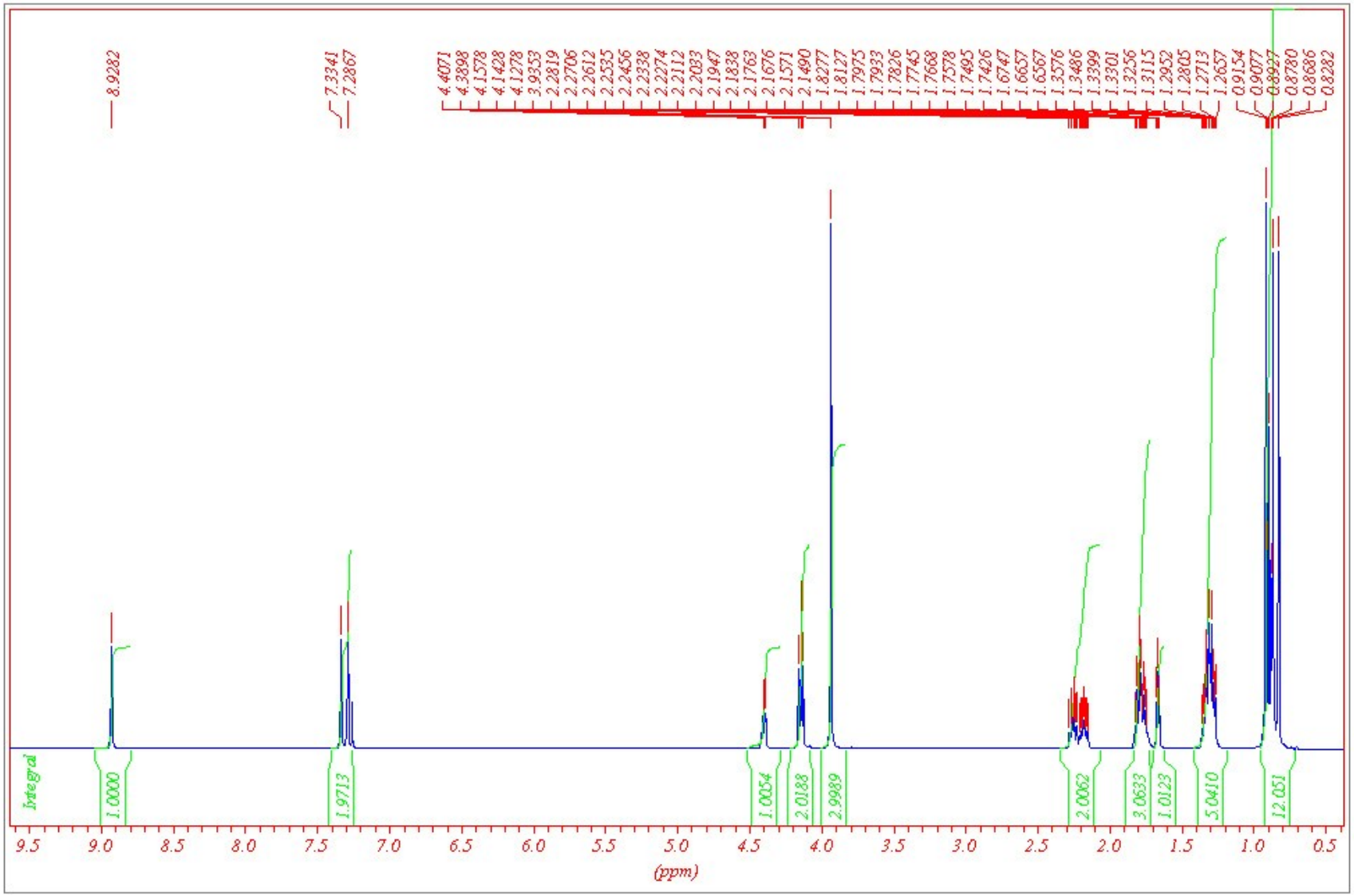



Figure S49. $^{1}H$ NMR spectra of 1-Butyl-3-methylimidazolium 4- bornyloxytetrafluorophenyltrifluoroborate (**5h**)

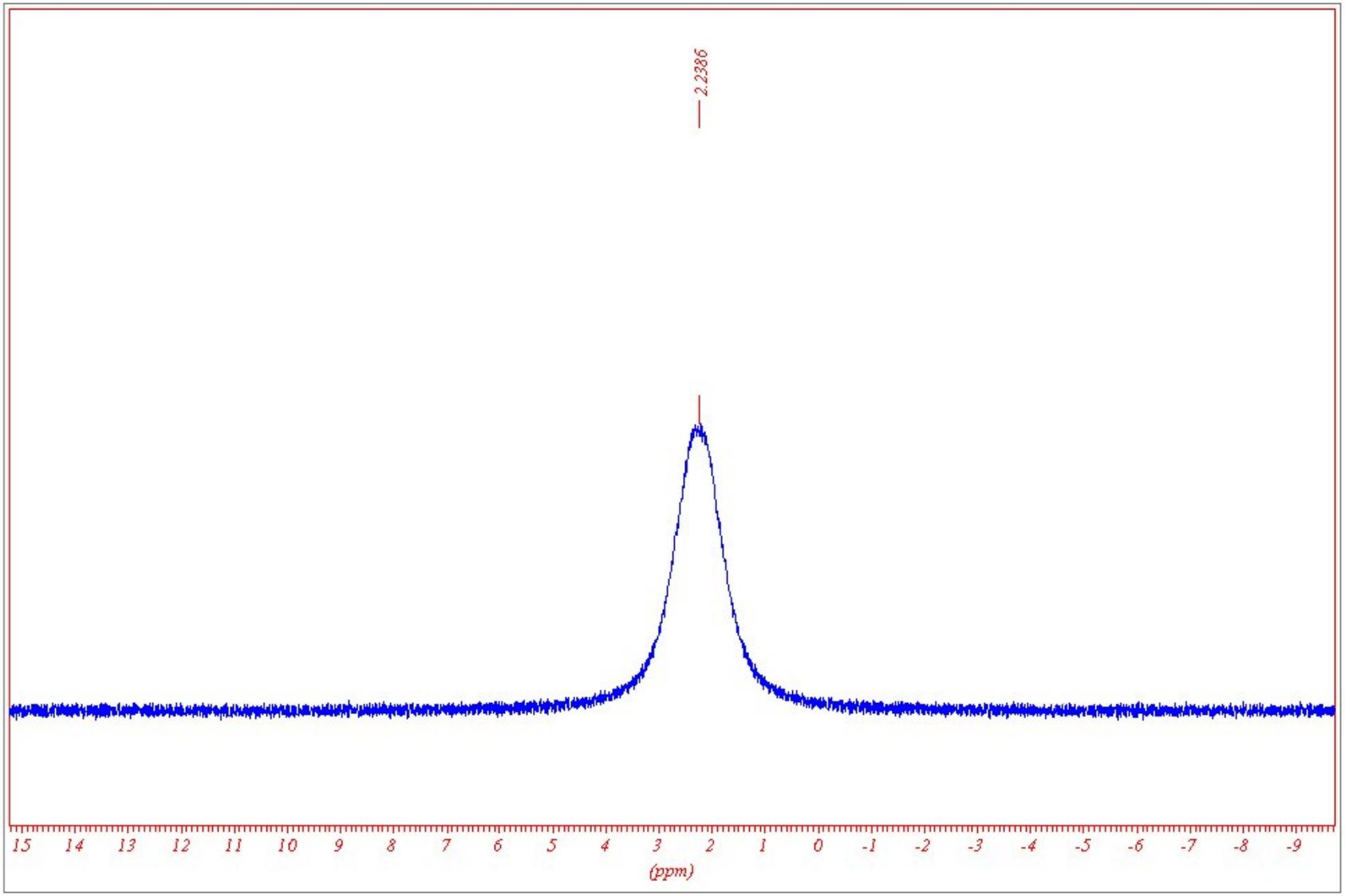



Figure S50. $^{11}B$ NMR spectra of 1-Butyl-3-methylimidazolium 4- bornyloxytetrafluorophenyltrifluoroborate (**5h**)

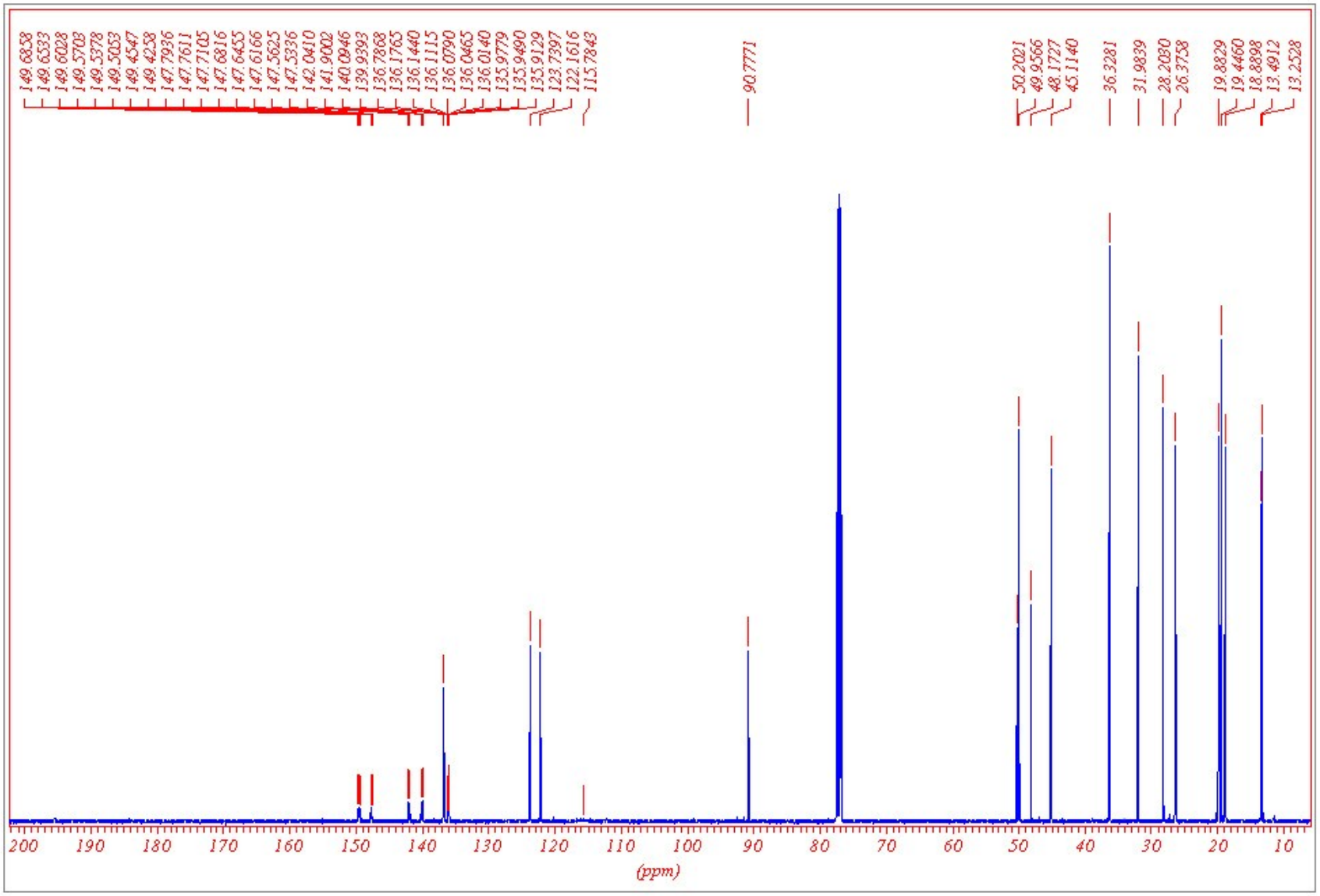



Figure S51. $^{13}C$ NMR spectra of 1-Butyl-3-methylimidazolium 4- bornyloxytetrafluorophenyltrifluoroborate (**5h**)

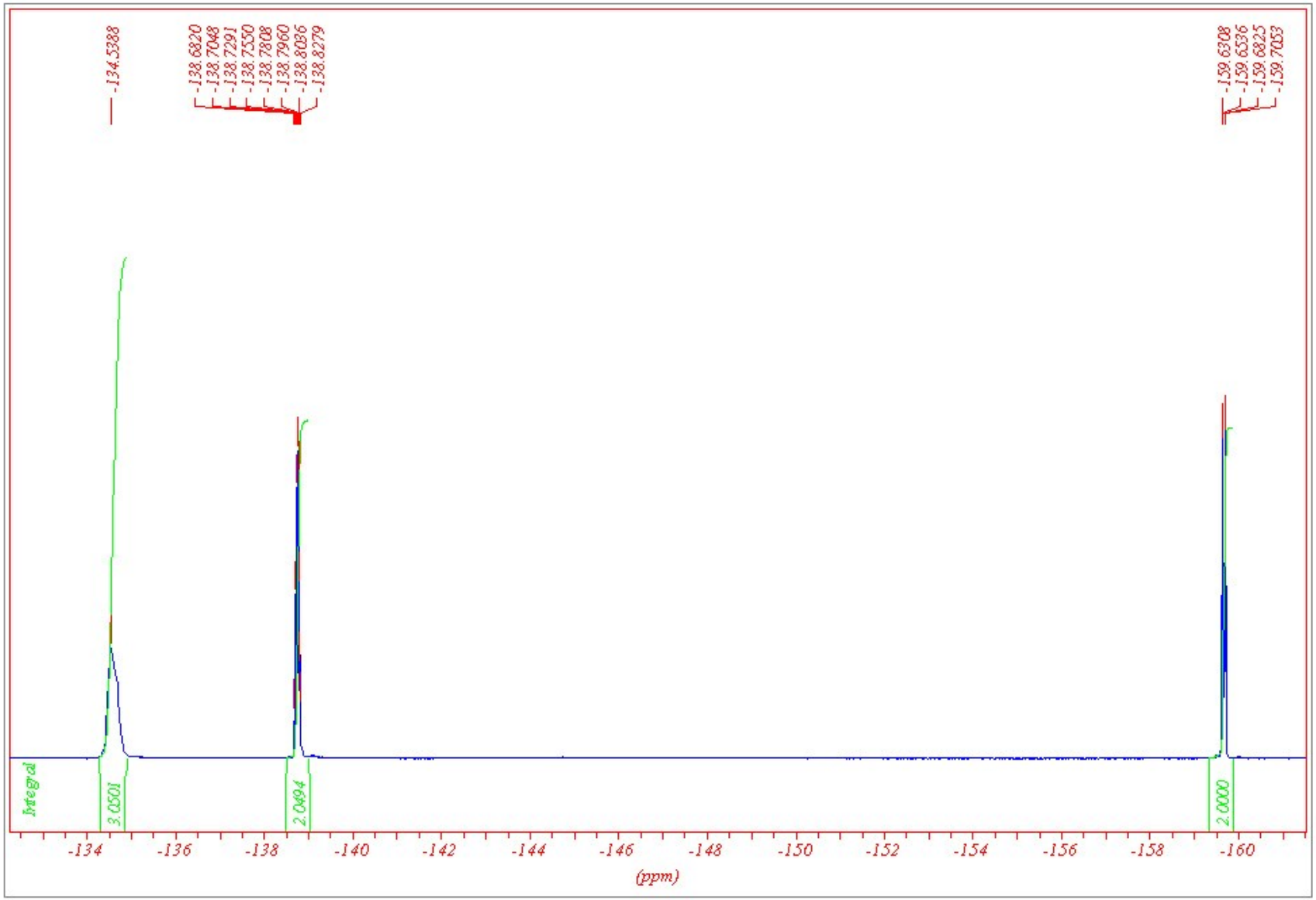



Figure S52. $^{19}F$ NMR spectra of 1-Butyl-3-methylimidazolium 4- bornyloxytetrafluorophenyltrifluoroborate (**5h**)