ELECTRONIC SUPPLEMENTARY INFORMATION

Supramolecular Interaction of Non-Racemic Benzimidazolium Based Ion Pairs with Chiral Substrates†

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1. General procedures

All oxygen and moisture sensitive operations were carried out under argon atmosphere using standard vacuum-line and Schlenk techniques. Solvents were purchased from Sigma-Aldrich as HPLC grade and dried by means of an Inert Puresolv MD purification system. All reagents were purchased from Sigma Aldrich and purified when required by literature procedures.[1] Chemical shifts of ^{1}H and ^{13}C NMR are reported in ppm, the solvent was used as internal standard. Signals are quoted as s (singlet), d (doublet), dd (doublet of doublets), m (multiplet), q (quartet) dt (doublet of triplets), td (triplet of doublets), ddd (doublet of doublet of doublets), dddd (doublet of doublet of doublet of doublets), dtd (doublet of triplet of doublets), qdt (quartet of doublet of triplets), pd (pentet of doublets), ddt (doublet of doublet of triplets), tt (triplet of triplets), ttt (triplet of triplet of triplets), dq (doublet of quartets) and hept (heptet) in ^{1}H NMR.

Nuclear Magnetic Resonance (NMR)

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX400 400 MHz nuclear magnetic resonance spectrometer.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on a TA instruments Discovery from -90 to 150 °C at a rate of 10°C/min under nitrogen atmosphere.

Electrospray Ionization Mass spectrometry (ESI-MS)

ESI-MS analyses were carried out on a Bruker ESI-TOF MicroTOF II.

Fourier Transform Infrared Spectroscopy (ATR FT-IR)

ATR FT-IR measurements were performed on a Bruker Alpha Series FT-IR spectrometer equipped with an attenuated total reflectance (ATR) module. The ATR FT-IR spectra were recorded by collecting 16 scans of a compound in the ATR module.

Polarimetry

Polarimetry measurements were carried out on an Anton Parr MCP 100 at 20°C and with methanol as solvent.

2. Synthetic procedures

2a. Synthesis of chiral Acetals 2a–c

All acetals were synthesized by the previously reported method.[2] 5 g of chiral alcohol and 6.67 g of paraformaldehyde were dissolved in dry distilled toluene (150 mL). Next, a few crystals of *p*-toluene sulfonic acid were added as a catalyst to the reaction mixture. The apparatus was set with a dean stark distillation head and azeotropic distillation was carried out. The reaction was monitored by TLC. After

completion, the reaction mixture was cooled to room temperature (R.T.) and excess toluene was removed under reduced pressure. The crude product was extracted with 3 x 20 mL ethyl acetate. The combined organic layer was washed with brine and a saturated solution of $NaHCO_3$. The collected organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using 2% ethyl acetate/ hexane as eluent.

bis(((1*S*, 2*S*)-2-Isopropyl-5-methylcyclohexyl)oxy)methane (2a). White crystals, mp 58°C, $[\alpha]_D^{25}$ = 8.40 (c = 5 mg / 20 mL $CHCl_3$). Yield = 80%, IR: υ (cm^{-1}) 2927, 2869, 1454, 1385, 1104. ^{1}H NMR (300 MHz, Chloroform-d): δ 4.84 (2H, s), 3.30 (2H, dt, *J* = 4.5, 10.8 Hz), 2.24 – 2.12 (4H, m), 1.70 – 1.60 (4H, m), 1.41 – 1.40 (2H, m), 1.34 – 1.30 (2H, m), 1.20 –1.20 (2H, m) , 1.01 – 0.99 (4H, m), 0.93 (6H, d, *J* = 3.0 Hz), 0.91 (6H, d, *J* = 3.6 Hz), 0.80 (6H, d, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 95.3, 88.9, 48.6, 42.4, 34.4, 31.6, 29.7, 23.1, 22.3, 21.2, 16.1. GCMS: 324 (M+) 185, 169, 156, 139, 125. IR signals, and ^{1}H and ^{13}C{^{1}H} NMR data were consistent with those previously reported.[2]

bis(((1R,2R,4S)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methane (2b). Yellow thick liquid, $[\alpha]_D^{25}$ = 1.73 (c = 5 mg / 20 mL $CHCl_3$). Yield = 85%, IR: υ (cm^{-1}) 2847, 1366, 1115. ^{1}H NMR (300 MHz, Chloroform-d): δ 4.62 (2H, s), 3.16 (2H, d, *J* = 1.5 Hz), 1.78 – 1.72 (4H, m), 1.69 – 1.68 (2H, m), 1.63 – 1.62 (4H, m), 1.47 – 1.38 (4H, m), 1.06 (6H, s), 0.95 (6H, s), 0.87 (6H, s). ^{13}C NMR: (75 MHz, $CDCl_3$): δ 91.0, 85.1, 52.0, 47.9, 41.4, 40.1, 36.4, 30.7, 20.2, 19.8, 19.7. GCMS: 320 (M^+), 183, 168, 153, 137, 95. IR signals, and ^{1}H and ^{13}C{^{1}H} NMR data were consistent with those previously reported.[3]

bis(((1S,2S,3S,5R)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methane (2c). Yellow thick liquid, $[\alpha]_D^{25}$ = 6.3 (c = 5 mg/ 20 mL $CHCl_3$). Yield = 83%, IR: υ (cm^{-1}) 2904, 1367, 1258, 1024. ^{1}H NMR (400 MHz, Chloroform-d): δ 4.79 (2H, s), 4.04 (2H, ddd, *J* = 9.5, 5.3, 4.5 Hz), 2.50 – 2.40 (2H, m), 2.33 (2H, dtd, *J* = 9.7, 6.2, 2.3 Hz), 2.11 – 2.01 (2H, m), 1.94 (2H, tt, *J* = 6.0, 3.1 Hz), 1.79 (4H, dtd, *J* = 8.7, 4.5, 2.7 Hz), 1.21 (6H, s), 1.14 (6H, d, *J* = 7.4 Hz), 1.04 (2H, d, *J* = 9.7 Hz), 0.92 (6H, s). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 90.9, 75.0, 47.8, 44.7, 41.6, 38.4, 35.6, 33.7, 27.6, 23.8, 21.3. GCMS: 236 (M^+), 193, 167, 137, 95, 81.

2b. Synthesis of alkoxymethyl chlorides 3a–c

All alkoxymethyl chlorides were synthesized by the previously reported method.[2] Over 5 g acetal of chiral alcohol, few drops of dry, distilled methanol was added under inert conditions and 1.5 mL of freshly distilled acetyl chloride was added dropwise with a syringe. The mixture was stirred for 36 hours at R.T. After the completion of time the corresponding alkoxymethyl chloride was ready to use without any workup.

2c. Synthesis of ionic liquids 4a-c

1.1 equiv. of chloromethyl alkyl ether were placed in a round bottom flask under inert atmosphere and 1.0 equiv. of 1-methylbenzimidazole was added dropwise. Immediately, a solid starts to appear upon addition. The reaction mixture was further stirred for 30 minutes to ensure complete reaction. Afterwards, the mixture was diluted with dry diethyl ether, stirred for 5 minutes and filtered under vacuum. The final product was washed three times with diethyl ether and dried under vacuum, obtaining a white powder which was purified by column chromatography using 5% methanol/ chloroform as an eluent.

1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-3-methylbenzimidazolium chloride (4a). White solid, $[\alpha]_D^{20}$ = +136.50 (c = 20 mg/ 5 mL MeOH). Yield = 97%. IR: υ (cm^{-1}) 3389, 2917, 1563, 1452, 1073. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 12.12 (1H, s), 7.92 – 7.86 (1H, m), 7.71 – 7.65 (3H, m), 6.23 (1H, d, *J* = 12.0 Hz, N–C*H*$_2$–O), 5.95 (1H, d, *J* = 12.0 Hz, N–C*H*$_2$–O), 4.28 (3H, s), 3.41 (1H, td, *J* = 10.6, 4.3 Hz), 2.29 – 2.22 (1H, m), 1.81 – 1.71 (1H, m), 1.67 – 1.58 (1H, m), 1.59 – 1.43 (2H, m), 1.26 – 1.17 (1H, m), 0.96 – 0.77 (3H, m), 0.92 (3H, d, *J* = 6.6 Hz), 0.73 (3H, d, *J* = 8.0 Hz), 0.14 (3H, d, *J* = 8.0 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.38, 132.35, 131.05, 127.62, 127.56, 114.54, 112.57, 79.37, 75.43, 47.95, 40.19, 34.25, 33.81, 31.26, 25.43, 22.84, 22.29, 20.98, 15.25. ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{29}N_2O$ 301.2274; found 301.2283.

3-methyl-1-(((1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-benzimidazolium chloride (4b). White solid, $[\alpha]_D^{20}$ = +39.8 (c = 20 mg/ 5 mL MeOH). Yield = 95%. IR: υ (cm^{-1}) 2951, 1567, 1464, 1095, 1013. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 12.03 (1H, s), 7.91 – 7.86 (1H, m), 7.71 – 7.65 (3H, m), 6.05 (1H, d, *J* = 10.7 Hz, N–C*H*$_2$–O), 6.00 (1H, d, *J* = 10.8 Hz, N–C*H*$_2$–O), 4.29 (3H, s), 3.32 (1H, d, *J* = 1.9 Hz), 1.69 – 1.60 (3H, m), 1.51 – 1.45 (1H, m), 1.42 – 1.34 (1H, m), 1.09 – 1.00 (4H, m), 0.99 – 0.92 (1H, m), 0.81 (3H, s), 0.74 (3H, s). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.39, 132.35, 130.98, 127.59, 127.56, 114.63, 112.72, 93.87, 78.32, 49.09, 48.55, 41.23, 39.67, 33.81, 31.42, 26.01, 25.93, 21.11, 19.44. ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{27}N_2O$ 299.2118; found 299.2125.

3-methyl-1-((((1S,2S,3S,5R)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methyl)-benzimidazolium chloride (4c). White solid, $[\alpha]_D^{20}$ = +37.8 (c = 20 mg/ 5 mL MeOH). Yield = 93%. IR: υ (cm^{-1}) 3371, 2921, 1565, 1436, 1098. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.00 (1H, s), 7.96 – 7.90 (1H, m), 7.74 – 7.61 (3H, m), 6.18 (1H, d, *J* = 10.7 Hz, N–C*H*$_2$–O), 6.01 (1H, d, *J* = 10.7 Hz, , N–C*H*$_2$–O), 4.29 (3H, s), 3.92 (1H, dt, *J* = 9.2, 4.6 Hz), 2.60 (1H, ddt, *J* = 14.4, 9.1, 2.9 Hz), 2.33 (1H, dtd, *J* = 9.8, 6.1, 2.2 Hz), 2.06 – 1.98 1H, m), 1.92 (1H, dt, *J* = 5.9, 3.5 Hz), 1.77 – 1.67 (2H, m), 1.17 (3H, s), 0.97 (1H, d, *J* = 9.8 Hz), 0.87 – 0.80 (6H, m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.33, 132.40, 131.04, 127.61, 127.58,

114.73, 112.73, 79.56, 76.66, 47.45, 44.47, 41.39, 38.44, 35.47, 33.87, 33.77, 27.50, 24.10, 20.95. ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{27}N_2O$ 299.2118; found 299.2119.

3. Anion exchange experiments

A solution of 1 equiv. of chloride salt **4a**–**c** in distilled water (5 mL) was treated with 1.1 equiv. of chosen salt ($NaBF_4$, KPF_6 or $LiNTf_2$). The reaction mixture was stirred at R.T. for 2 h. Then, water was completely removed under vacuum to give a solid. Dichloromethane was added and the residual solid was filtered and the filtrate was evaporated under reduced pressure to yield the desired products **5**–**7.**

1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-3-methylbenzimidazolium tetrafluroborate (5a). White solid, $[\alpha]_D^{20}$ = +147.50 (c = 20 mg/ 5 mL MeOH). Yield = 99%. IR: υ (cm^{-1}) 2928, 1567, 1454, 1008. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.65 (1H, s), 7.92 – 7.86 (1H, m), 7.76 – 7.62 (3H, m), 5.95 (1H, d, *J* = 11.1 Hz, N–C*H*$_2$–O), 5.87 (1H, d, *J* = 11.1 Hz, N–C*H*$_2$–O), 4.20 (3H, s), 3.37 (1H, td, *J* = 10.6, 4.3 Hz), 2.15 – 2.06 (1H, m), 1.81 (1H, pd, *J* = 7.0, 2.6 Hz), 1.65 – 1.59 (1H, m), 1.58 – 1.43 (2H, m), 1.26 – 1.18 (1H, m), 0.96 – 0.77 (3H, m), 0.90 (3H, d, *J* = 6.5 Hz), 0.75 (3H, d, *J* = 7.0 Hz), 0.17 (3H, d, *J* = 7.0 Hz).^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.43, 132.17, 130.74, 127.30, 127.20, 114.09, 112.52, 78.95, 75.35, 47.71, 39.70, 33.95, 33.42, 30.77, 25.07, 22.47, 21.95, 20.70, 14.84. ^{11}B NMR (128 MHz, Chloroform-*d*) δ: -0.92 (s). ^{19}F NMR (376 MHz, Chloroform-*d*): δ -150.95 – (-150.97) (m, $[^{10}BF_4]^-$), -151.01 (q, *J* = 1.5 Hz, $[^{11}BF_4]^-$). ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{29}N_2O$ 301.2274; found 301.2282.

1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-3-methylbenzimidazolium hexaflurophosphate (6a). White solid, $[\alpha]_D^{20}$ = +94.50 (c = 20 mg/ 5 mL MeOH). Yield = 99%. IR: υ (cm^{-1}) 2927, 1571, 1330, 1099, 1008. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.40 (1H, s), 7.94 – 7.89 (1H, m), 7.74 – 7.67 (3H, m), 5.90 (1H, d, *J* = 11.1 Hz, N–C*H*$_2$–O), 5.85 (1H, d, *J* = 11.1 Hz, N–C*H*$_2$–O), 4.18 (3H, s), 3.35 (1H, td, *J* = 10.6, 4.3 Hz), 2.12 – 2.04 (1H, m), 1.81 (1H, pd, *J* = 7.0, 2.5 Hz), 1.67 – 1.45 (3H, m), 1.28 – 1.21 (1H, m), 0.97 – 0.88 (3H, m), 0.91 (3H, d, *J* = 6.6 Hz), 0.76 (3H, d, *J* = 8.0 Hz), 0.17 (3H, d, *J* = 8.0 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.09, 132.43, 131.03, 127.86, 127.77, 114.52, 112.77, 79.46, 75.72, 48.02, 39.99, 34.24, 33.74, 31.03, 25.41, 22.77, 22.22, 21.00, 15.12. ^{31}P NMR (162 MHz, Chloroform-*d*): δ -144.17 (hept, *J* = 712.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*): δ -71.92 (d, *J* = 713.0 Hz). ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{29}N_2O$ 301.2274; found 301.2284. $[M]^-$ calcd for PF_6 144.9647; found 144.9645.

1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-3-methylbenzimidazolium bis(trifluoromethylsulfonyl)amine (7a). Clear oil, $[\alpha]_D^{20}$ = +96.50 (c = 20 mg/ 5 mL MeOH). Yield = 99%. IR: υ (cm^{-1}) 2927, 1571, 1347, 1185. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.64 (1H, s), 7.94 – 7.88 (1H, m), 7.78 – 7.69 (3H, m), 5.93

(1H, d, *J* = 11.0 Hz, N–C*H*$_2$–O), 5.86 (1H, d, *J* = 11.0 Hz, N–C*H*$_2$–O), 4.19 (3H, s), 3.31 (1H, td, *J* = 10.6, 4.3 Hz), 2.12 – 2.04 (1H, m), 1.78 (1H, pd, *J* = 7.0, 2.6 Hz), 1.67– 1.54 (2H, m), 1.48 – 1.36 (1H, m), 1.27 – 1.19 (1H, m), 0.97 – 0.78 (3H, m), 0.91 (3H, d, *J* = 6.6 Hz), 0.75 (3H, d, *J* = 7.1 Hz), 0.17 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.83, 132.41, 131.05, 128.02, 127.94, 119.90 (q, *J* = 321.1 Hz, *C*F$_3$), 114.46, 112.87, 79.70, 75.62, 47.89, 40.03, 34.20, 33.75, 31.22, 25.41, 22.80, 22.10, 20.93, 15.08. ^{19}F NMR (376 MHz, Chloroform-*d*): δ -78.91 (s). ESI-HRMS *m*/*z*: [M]$^+$ calcd for $C_{19}H_{29}N_2O$ 301.2274; found 301.2281. [M]$^-$ calcd for $C_2F_6NO_4S_2$ 279.9178; found 279.9188.

3-methyl-1-(((1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-benzimidazolium tetrafluroborate (5b). White solid, $[\alpha]_D^{20}$ = +38.20 (c = 20 mg/ 5 mL MeOH). Yield = 98%. IR: υ (cm^{-1}) 2951, 1567, 1463, 1150, 1006. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.68 (1H, s), 7.92 – 7.85 (1H, m), 7.76 – 7.64 (3H, m), 5.89 (1H, d, *J* = 11.0 Hz, N–C*H*$_2$–O), 5.80 (1H, d, *J* = 11.0 Hz, N–C*H*$_2$–O), 4.20 (3H, s), 3.26 (1H, d, J = 1.8 Hz), 1.69 – 1.62 (3H, m), 1.53 – 1.45 (1H, m), 1.43 – 1.33 (1H, m), 1.05 (1H, d, *J* = 10.3 Hz), 1.00 – 0.90 (1H, m), 0.98 (3H, s), 0.81 (3H, s), 0.74 (3H, s). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.65, 132.44, 130.97, 127.65, 127.60, 114.49, 112.94, 93.74, 78.43, 49.07, 48.53, 41.18, 39.57, 33.75, 31.22, 25.96, 21.07, 19.26. ^{11}B NMR (128 MHz, Chloroform-*d*): δ -0.93 (s). ^{19}F NMR (376 MHz, Chloroform-*d*): δ -150.67 – (-150.72) (m, [^{10}BF$_4$]$^-$), -150.72 – (-150.79) (m, [^{11}BF$_4$]$^-$). ESI-HRMS *m*/*z*: [M]$^+$ calcd for $C_{19}H_{27}N_2O$ 299.2118; found 299.2121.

3-methyl-1-(((1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-benzimidazolium hexaflurophosphate (6b). White solid, $[\alpha]_D^{20}$ = +45 (c = 20 mg / 5 mL MeOH). Yield = 99%, IR: υ (cm^{-1}) 2960, 1573, 1347, 1098. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 10.06 (1H, s), 7.93 – 7.86 (1H, m), 7.76 – 7.65 (3H, m), 5.92 (1H, d, *J* = 10.9 Hz, N–C*H*$_2$–O), 5.85 (1H, d, *J* = 10.9 Hz, N–C*H*$_2$–O), 4.22 (3H, s), 3.27 (1H, d, *J* = 1.6 Hz), 1.67 – 1.61 (3H, m), 1.51 – 1.46 (1H, m), 1.42 – 1.34 (1H, m), 1.05 (1H, dd, *J* = 10.4, 1.6 Hz), 1.00 – 0.91 (1H, m), 0.99 (3H, s), 0.81 (3H, s), 0.74 (3H, s). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.88, 132.30, 130.81, 127.62, 127.56, 114.38, 112.82, 93.66, 78.39, 48.96, 48.38, 41.01, 39.45, 33.57, 31.07, 25.88, 25.84, 21.01, 19.02. ^{31}P NMR (162 MHz, Chloroform-*d*): δ -142.22 (hept, *J* = 712.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*): δ -71.79 (d, *J* = 712.9 Hz). ESI-HRMS *m*/*z*: [M]$^+$ calcd for $C_{19}H_{27}N_2O$ 299.2118; found 299.2122. [M]$^-$ calcd for PF_6 144.9647; found 144.9648.

3-methyl-1-(((1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-benzimidazolium bis(trifluoromethylsulfonyl)amine (7b). Clear oil, $[\alpha]_D^{20}$ = +22.50 (c = 20 mg / 5 mL MeOH). Yield = 99%. IR: υ (cm^{-1}) 2958, 1569, 1333, 1188, 1128. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.65 (1H, s), 7.94 – 7.88 (1H, m), 7.76 – 7.68 (3H, m), 5.89 (1H, d, *J* = 10.8 Hz, N–C*H*$_2$–O), 5.81 (1H, d, *J* = 10.8 Hz, N–

C*H*$_2$–O), 4.20 (3H, s), 3.21 (1H, d, *J* = 1.8 Hz), 1.68 – 1.63 (3H, m), 1.50 – 1.45 (1H, m), 1.44 – 1.37 (1H, m), 1.08 (1H, dd, J = 10.4, 1.5 Hz), 1.02 – 0.94 (1H, m), 0.97 (3H, s), 0.80 (3H, s), 0.77 (3H, s). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.90, 132.38, 130.99, 128.03, 128.01, 119.89 (q, *J* = 321.2 Hz, *C*F$_3$), 114.61, 112.92, 94.53, 78.48, 49.14, 48.50, 41.20, 39.62, 33.79, 31.19, 25.95, 21.05, 19.30. ^{19}F NMR (376 MHz, Chloroform-*d*): δ -78.87 (s). ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{27}N_2O$ 299.2118; found 299.2122. $[M]^-$ calcd for $C_2F_6NO_4S_2$ 279.9178; found 279.9191.

3-methyl-1-((((1S,2S,3S,5R)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methyl)-benzimidazolium tetrafluroborate (5c). White solid, $[\alpha]_D^{20}$ = +41.00 (c = 20 mg/ 5 mL MeOH). Yield = 98 %. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.87 (1H, s), 7.99 – 7.91 (1H, m), 7.76 – 7.64 (3H, m), 5.96 (1H, d, *J* = 10.8 Hz, N–C*H*$_2$–O), 5.90 (1H, d, *J* = 10.8 Hz, N–C*H*$_2$–O), 4.22 (3H, s), 3.91 – 3.84 (1H, m), 2.58 – 2.47 (1H, m), 2.34 (1H, dtd, *J* = 9.8, 6.1, 2.3 Hz), 2.09 – 2.00 (1H, m), 1.93 (1H, tt, *J* = 5.9, 3.1 Hz), 1.77 – 1.68 (2H, m), 1.18 (3H, s), 0.99 (1H, d, *J* = 9.8 Hz), 0.88 – 0.76 (6H, m). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.84, 132.51, 131.08, 127.73, 114.72, 112.85, 79.62, 76.90, 47.46, 44.48, 41.39, 38.45, 35.17, 33.82, 33.75, 27.51, 23.89, 20.92. ^{11}B NMR (128 MHz, Chloroform-*d*): δ -0.87 (s). ^{19}F NMR (376 MHz, Chloroform-*d*): δ -150.99 – (-151.02) (m, $[^{10}BF_4]^-$), -151.03 – (-151.08) (m, $[^{11}BF_4]^-$). ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{27}N_2O$ 299.2118; found 299.2122.

3-methyl-1-((((1S,2S,3S,5R)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methyl)-benzimidazolium hexaflurophosphate (6c). White solid, $[\alpha]_D^{20}$ = +55.00 (c = 20 mg/ 5 mL MeOH). Yield = 99%. IR: υ (cm^{-1}) 2926, 1578, 1348, 1099. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.35 (1H, s), 7.97 – 7.90 (1H, m), 7.75 – 7.64 (3H, m), 5.90 – 5.83 (2H, m, N–C*H*$_2$–O), 4.18 (3H, s), 3.88 – 3.82 (1H, m), 2.56 – 2.44 (1H, m), 2.34 (1H, dtd, *J* = 9.9, 6.1, 2.3 Hz), 2.06 (1H, tt, *J* = 7.4, 5.1 Hz), 1.93 (1H tt, *J* = 5.9, 3.1 Hz), 1.76 (1H, td, *J* = 5.8, 2.1 Hz), 1.70 (1H, ddd, *J* = 13.8, 4.1, 2.8 Hz), 1.18 (3H, s), 1.00 (1H, d, *J* = 9.8 Hz), 0.85 (6H, t, *J* = 3.7 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.03, 132.51, 131.04, 127.80, 127.77, 114.72, 112.94, 79.62, 76.97, 47.44, 44.50, 41.37, 38.43, 35.03, 33.86, 33.76, 27.49, 23.80, 20.89. ^{31}P NMR (162 MHz, Chloroform-*d*): δ -144.22 (hept, *J* = 712.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.00 (d, *J* = 712.9 Hz). ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{27}N_2O$ 299.2118; found 299.2125. $[M]^-$ calcd for PF_6 144.9647; found 144.9649.

3-methyl-1-((((1S,2S,3S,5R)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methyl)-benzimidazolium bis(trifluoromethylsulfonyl)amine (7c). Light brown oil, $[\alpha]_D^{20}$ = +30.00 (c = 20 mg/ 5 mL MeOH). Yield = 98%. IR: υ (cm^{-1}) 2927, 1572, 1347, 1187, 1100. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.67 (1H, s), 7.98 – 7.92 (1H, m), 7.78 – 7.68 (3H, m), 5.93 (1H, d, *J* = 10.8 Hz, N–C*H*$_2$–O), 5.88 (1H, d, *J* = 12.0 Hz, N–C*H*$_2$–O), 4.21 (3H, s), 3.87 – 3.81 (1H, m), 2.50 – 2.41 (1H, m), 2.35 (1H, dtd, *J* = 9.9, 6.1,

2.3 Hz), 2.09 – 2.01 (1H, m), 1.93 (1H tt, *J* = 5.9, 3.1 Hz), 1.77 (1H, td, *J* = 5.8, 2.1 Hz), 1.70 (1H, ddd, *J* = 13.8, 4.1, 2.7 Hz), 1.19 (3H, s), 0.99 (1H, d, *J* = 9.9 Hz), 0.91 – 0.76 (6H, m). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.90, 132.46, 131.07, 128.04, 128.02, 119.89 (q, *J* = 321.2 Hz, *C*F_3), 114.72, 112.93, 80.03, 76.90, 47.42, 44.45, 41.33, 38.41, 35.21, 33.81, 33.73, 27.46, 23.81, 20.88. ^{19}F NMR (376 MHz, Chloroform-*d*): δ -78.89 (s). ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{19}H_{27}N_2O$ 299.2118; found 299.2123. $[M]^-$ calcd for $C_2F_6NO_4S_2$ 279.9178; found 279.9187.

4. Synthesis of ILs 8 and 9

1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-3-methylimidazolium chloride (8)

Procedure adapted from reference 4. (1*S*,2*R*,4*S*)-(+)-Chloromethyl menthyl ether (0.582 g, 7.09 mmol) and 1-methylimidazole (1.596 g, 7.80 mmol) were dissolved in acetonitrile (20 mL) in a round bottom flask. The reaction mixture was heated for 24 h at 90 °C under reflux. Afterwards, the solution was cooled to R.T. and the solvent was evaporated under vacuum. The final product was washed three times with diethyl ether and dried under vacuum, obtaining a white powder.[4]

^{1}H NMR (400 MHz, Chloroform-*d*): δ 11.19 (1H, s), 7.42 (1H, t, *J* = 1.7 Hz), 7.41 (1H, t, *J* = 1.7 Hz), 5.90 (1H, d, *J* = 10.4 Hz, N-C*H*$_2$-O), 5.65 (1H, d, *J* = 10.4 Hz, N-C*H*$_2$-O), 4.12 (3H, s), 3.37 (1H, td, *J* = 10.6, 4.3 Hz), 2.15 – 2.06 (1H, m), 1.93 (1H, pd, *J* = 7.0, 2.6 Hz), 1.67 – 1.56 (2H, m), 1.49 – 1.36 (1H, m), 1.27 – 1.19 (1H, m), 0.98 – 0.74 (3H, m), 0.90 (3H, d, *J* = 6.6 Hz), 0.84 (3H, d, *J* = 7.1 Hz), 0.50 (3H, d, *J* = 7.0 Hz).

^{1}H NMR data were consistent with those previously reported.[5]

1-((1*S*,2*R*,4*S*)-(+)-menthoxymethyl)-2,3-dimethylimidazolium chloride (9)

Procedure adapted from reference 4. (1*S*,2*R*,4*S*)-(+)-Chloromethyl menthyl ether (4.85 g, 23.7 mmol) and 1,2-dimethyl-1*H*-imidazole (0.981 g, 22.6 mmol) were dissolved in acetonitrile (75 mL) in a round bottom flask. The reaction mixture was heated for 24 h at 90 °C under reflux. Afterwards, the solution was cooled to R.T. and the solvent was evaporated under vacuum. The final product was washed three times with diethyl ether and dried under vacuum, obtaining a white powder.[4]

White powder, $[\alpha]_D^{20}$ = +68.2 (c = 20 mg/ 5 mL CH_2Cl_2). Yield = 94%. IR: υ (cm^{-1}) 3080, 2956, 2918, 2851, 1453, 1401, 1237, 1080, 1052. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.88 (1H, d, *J* = 2.1 Hz), 7.77 (1H, d, *J* = 2.1 Hz), 5.71 (1H, d, *J* = 10.9 Hz, N-C*H*$_2$-O), 5.65 (1H, d, *J* = 10.9 Hz, N-C*H*$_2$-O), 4.02 (3H, s), 3.30 (1H, td, *J* = 10.6, 4.3 Hz), 2.83 (3H, s), 2.09 – 2.02 (1H, m), 1.97 – 1.86 (2H, m), 1.68 - 1.56 (2H, m), 1.46 – 1.31 (1H, m), 1.27 – 1.17 (1H, m), 0.94 – 0.78 (2H, m), 0.91 (3H, d, *J* = 6.5 Hz), 0.85 (3H, d, *J* = 7.0 Hz), 0.51 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 145.11, 123.02,

121.83, 79.60, 76.45, 47.94, 40.38, 35.87, 34.17, 31.43, 25.65, 22.95, 22.27, 21.02, 15.70, 10.81. ESI-HRMS *m*/*z*: $[M]^+$ calcd for $C_{16}H_{29}N_2O$ 265.2274; found 265.2276.

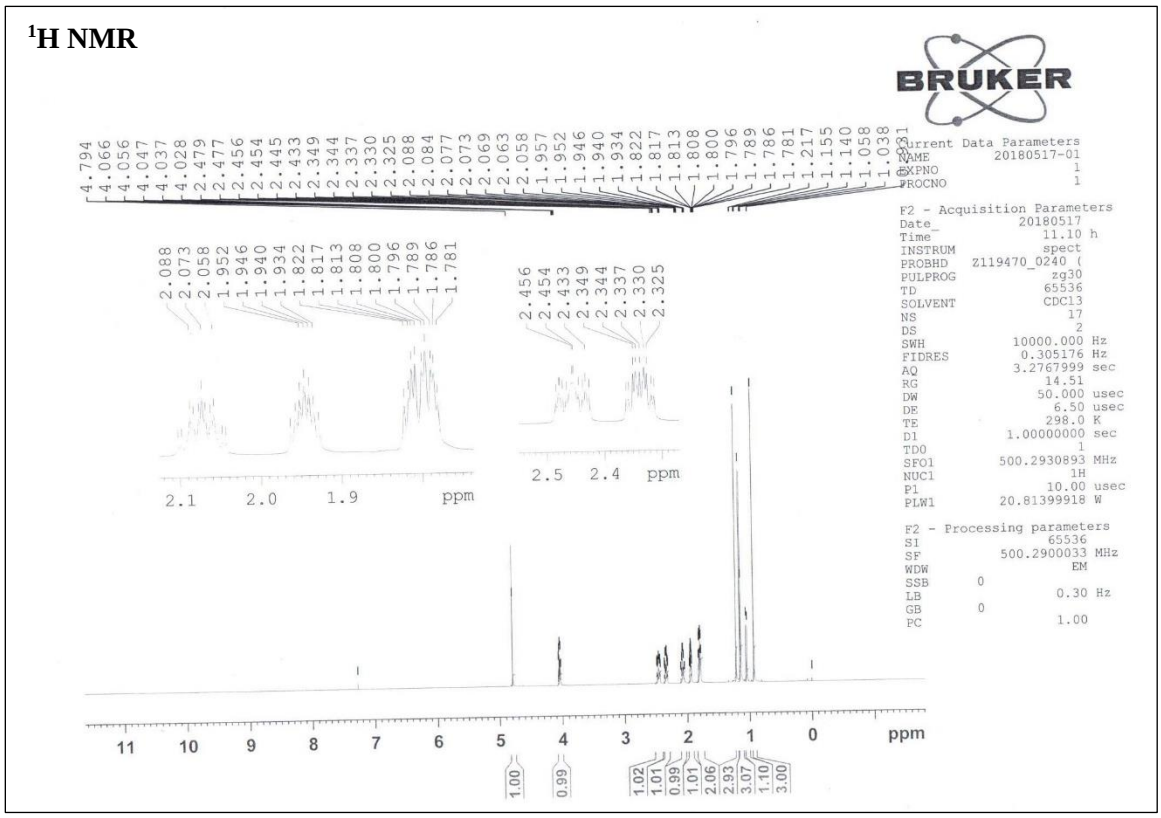
5. Chiral recognition experiments

0.05 mmol of racemic Mosher acid's potassium salt was mixed with the chosen amount of chiral ionic liquid (1 mmol for general experiments) in 0.6 mL of a specific deuterated solvent at R.T., sonicated for 3-5 seconds if required and analyzed by ^{19}F NMR spectroscopy

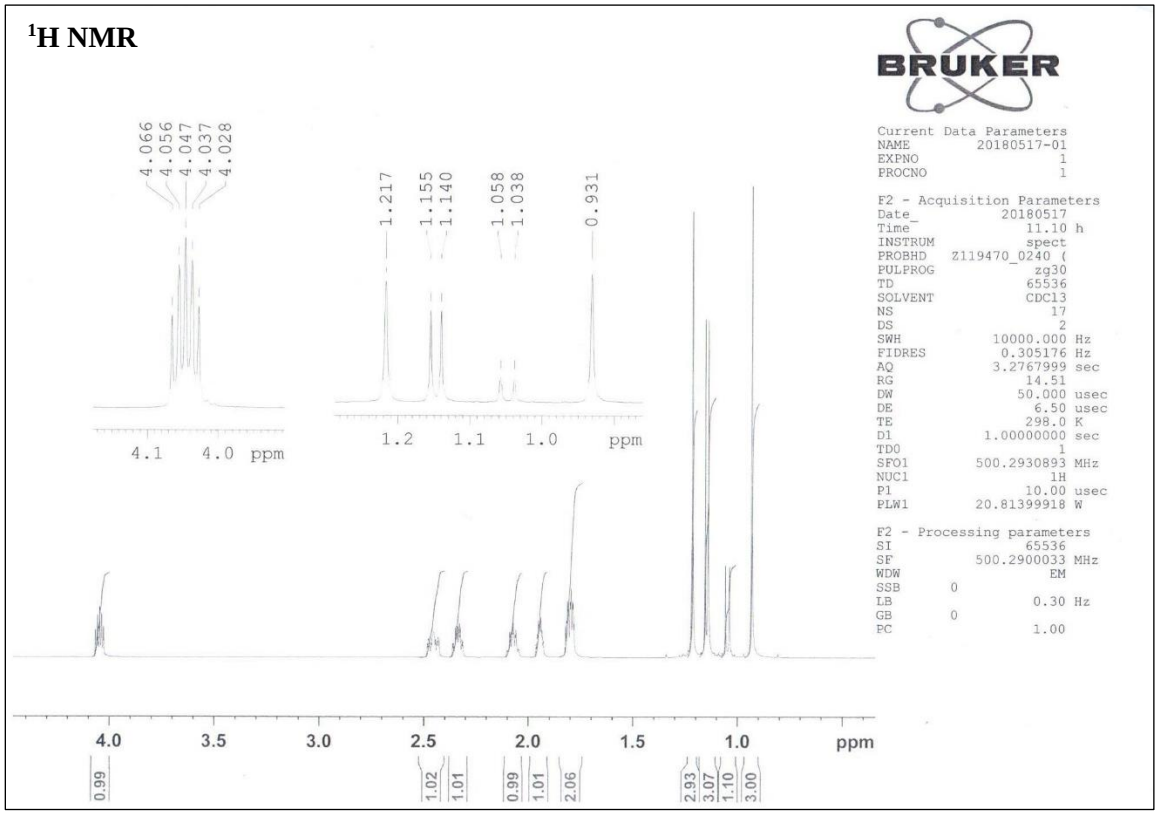
6. NMR spectra

bis(((1S,2S,3S,5R)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methane (2c).

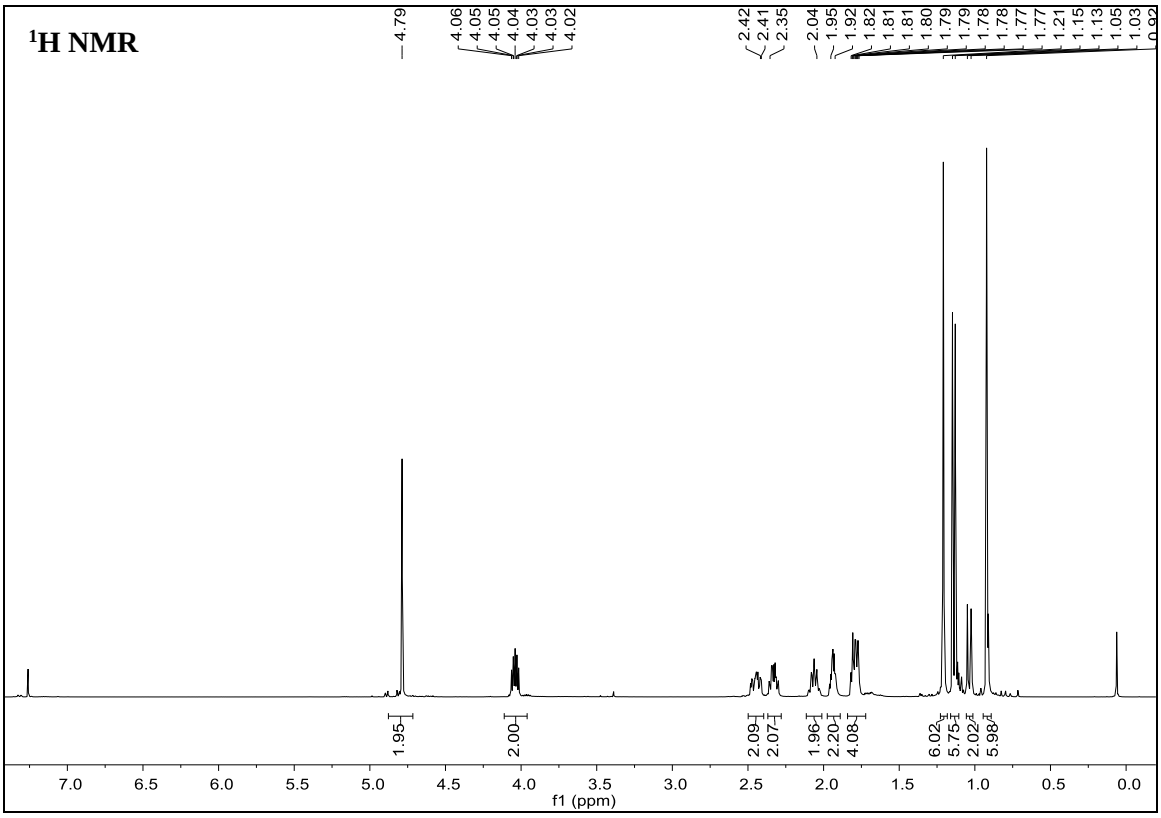
^{1}H NMR



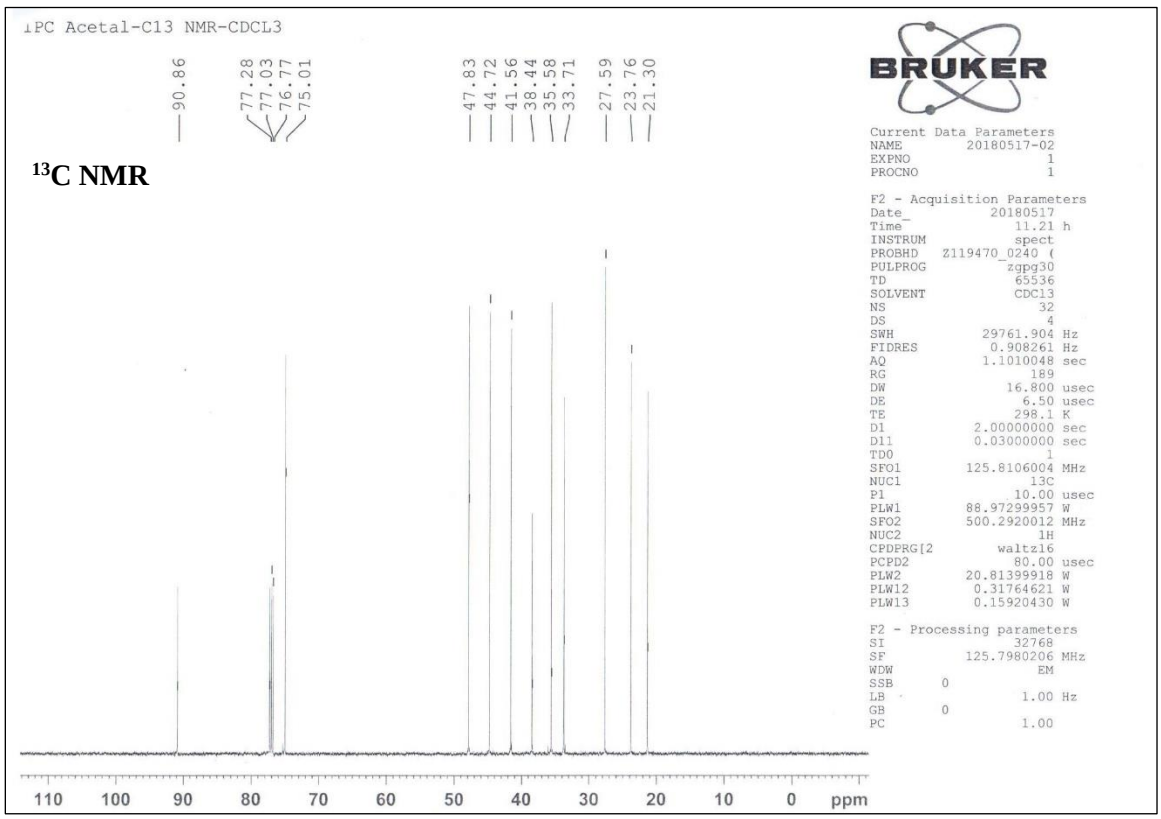
^{1}H NMR



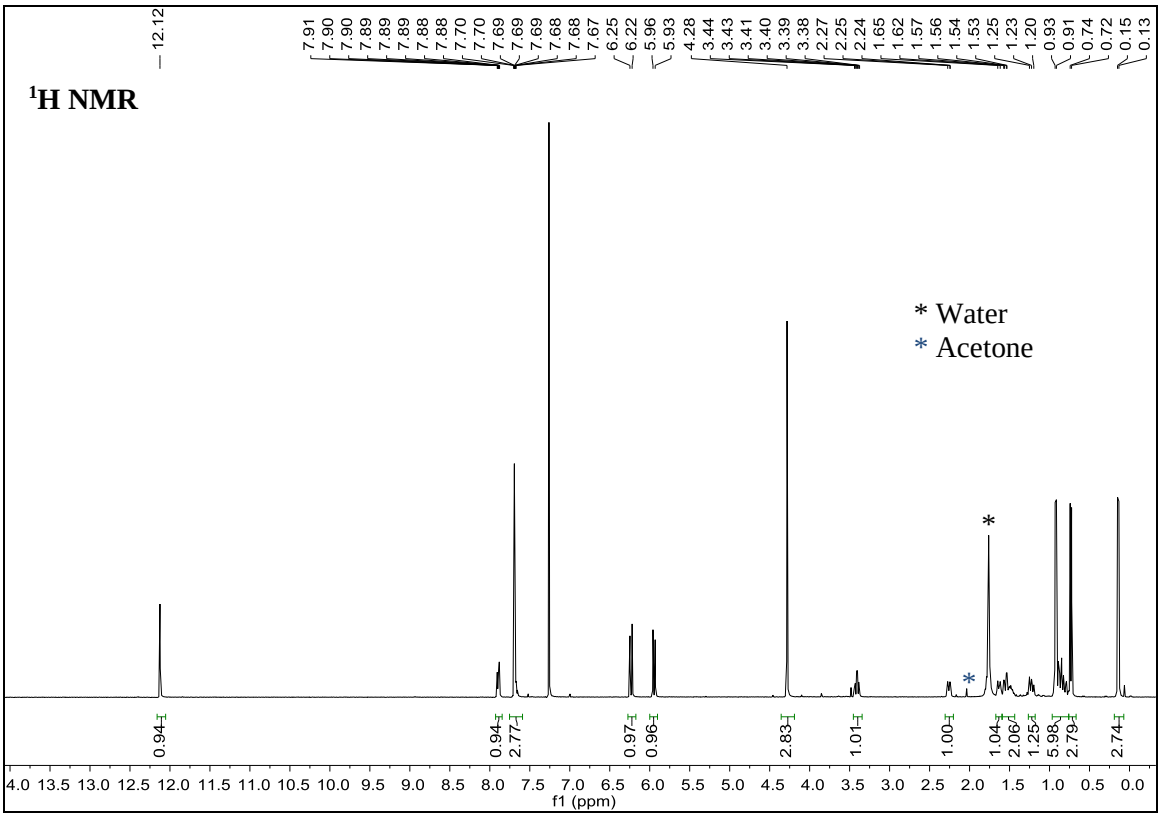
^{1}H NMR

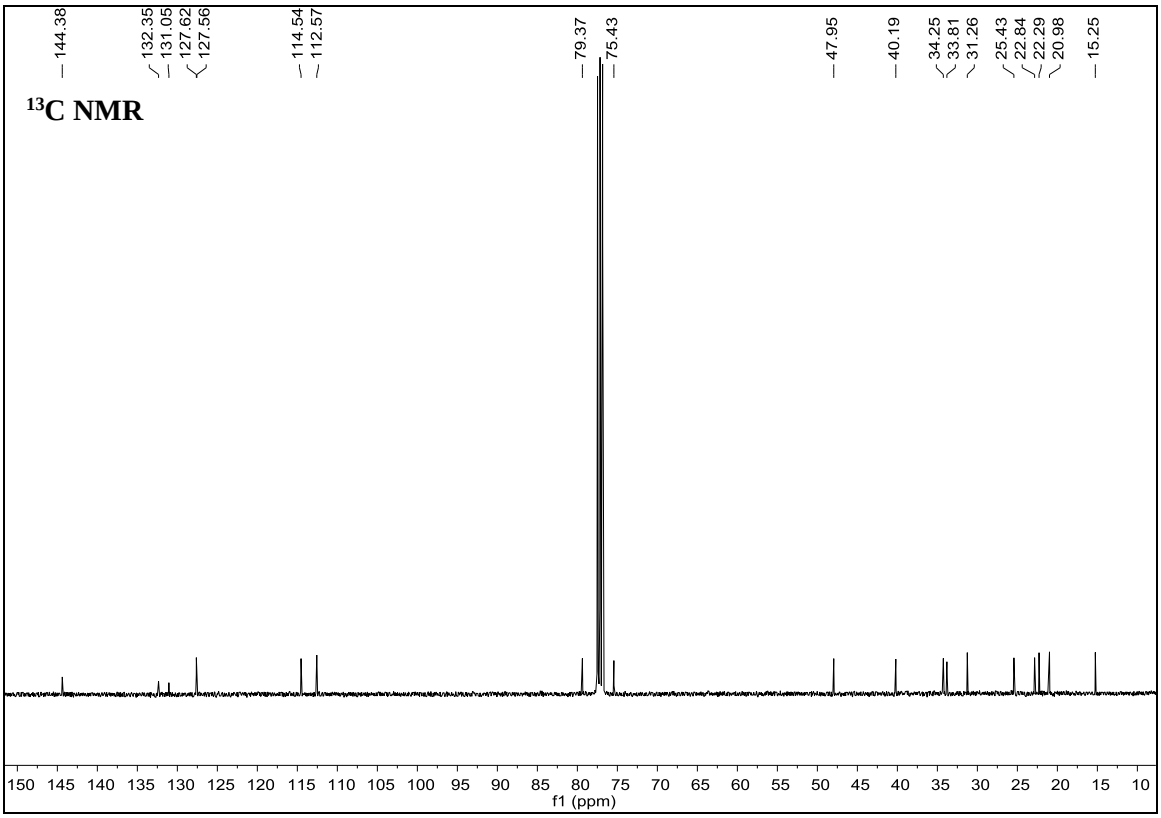


^{13}C NMR

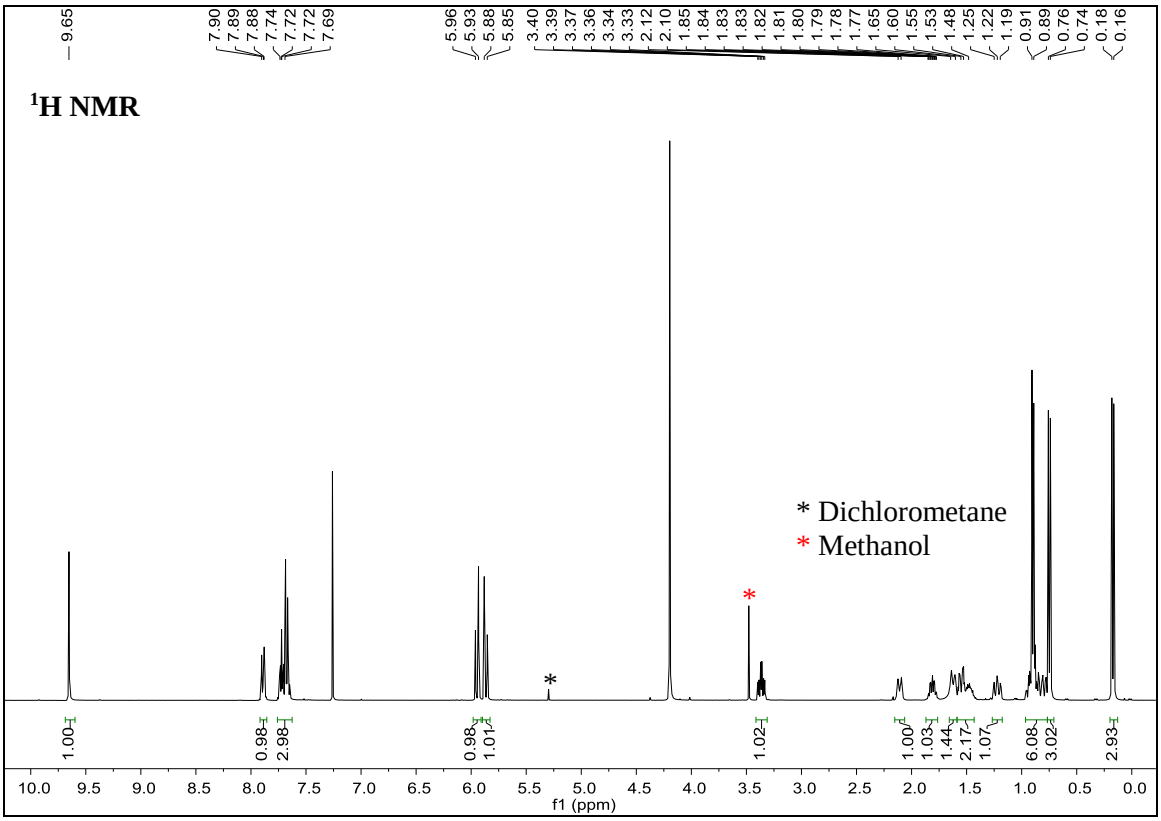


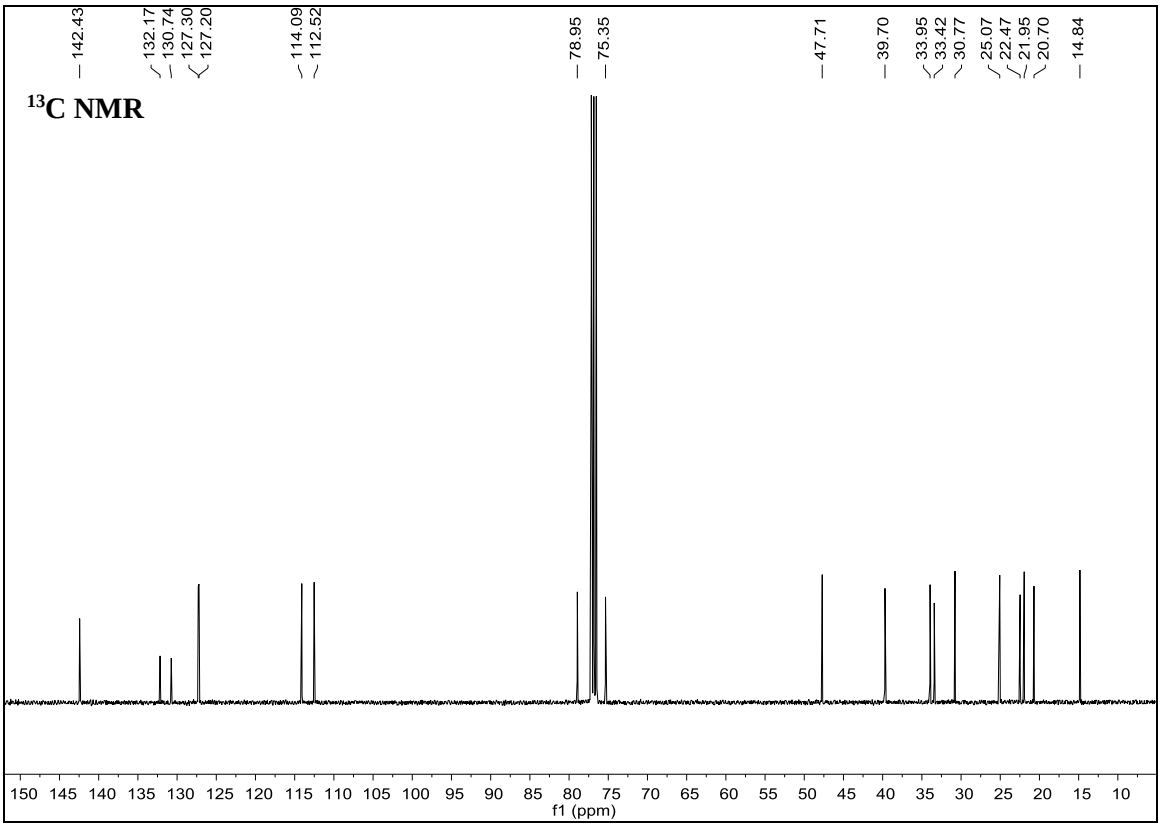
1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-benzimidazolium chloride (4a).



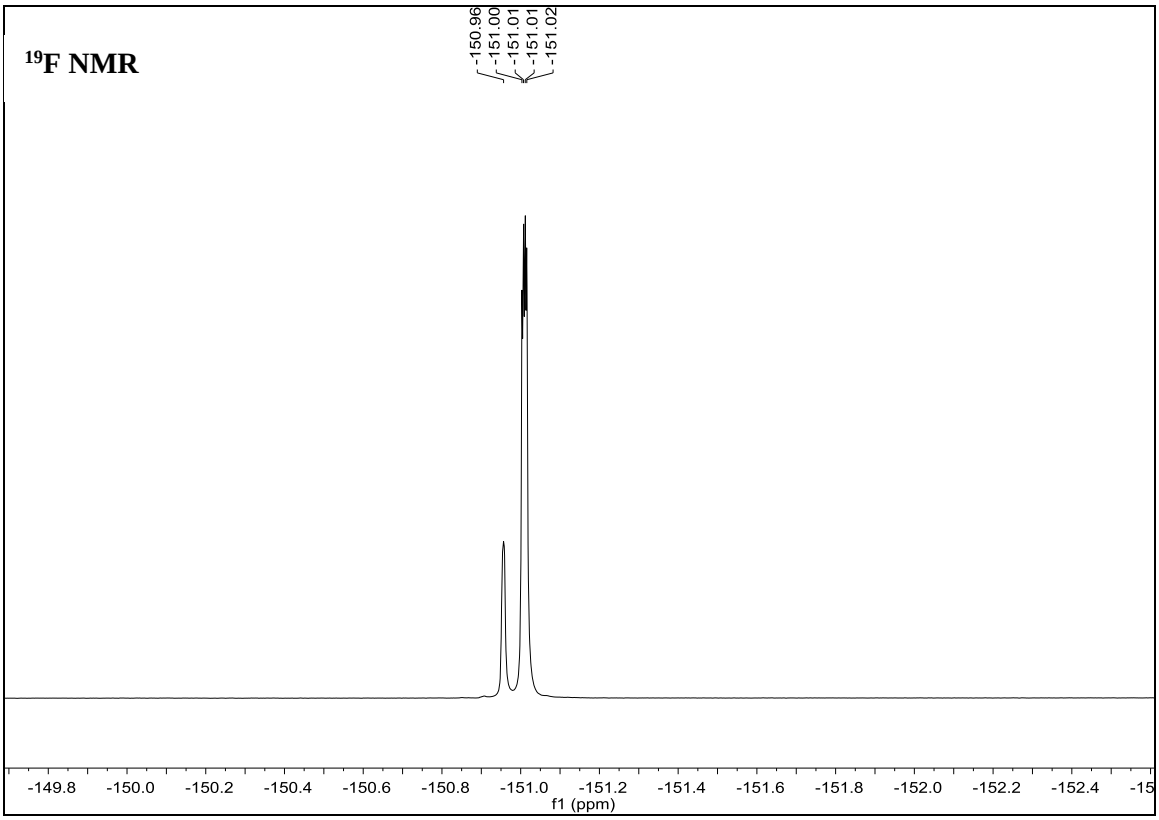


1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-benzimidazolium tetrafluroborate (5a).

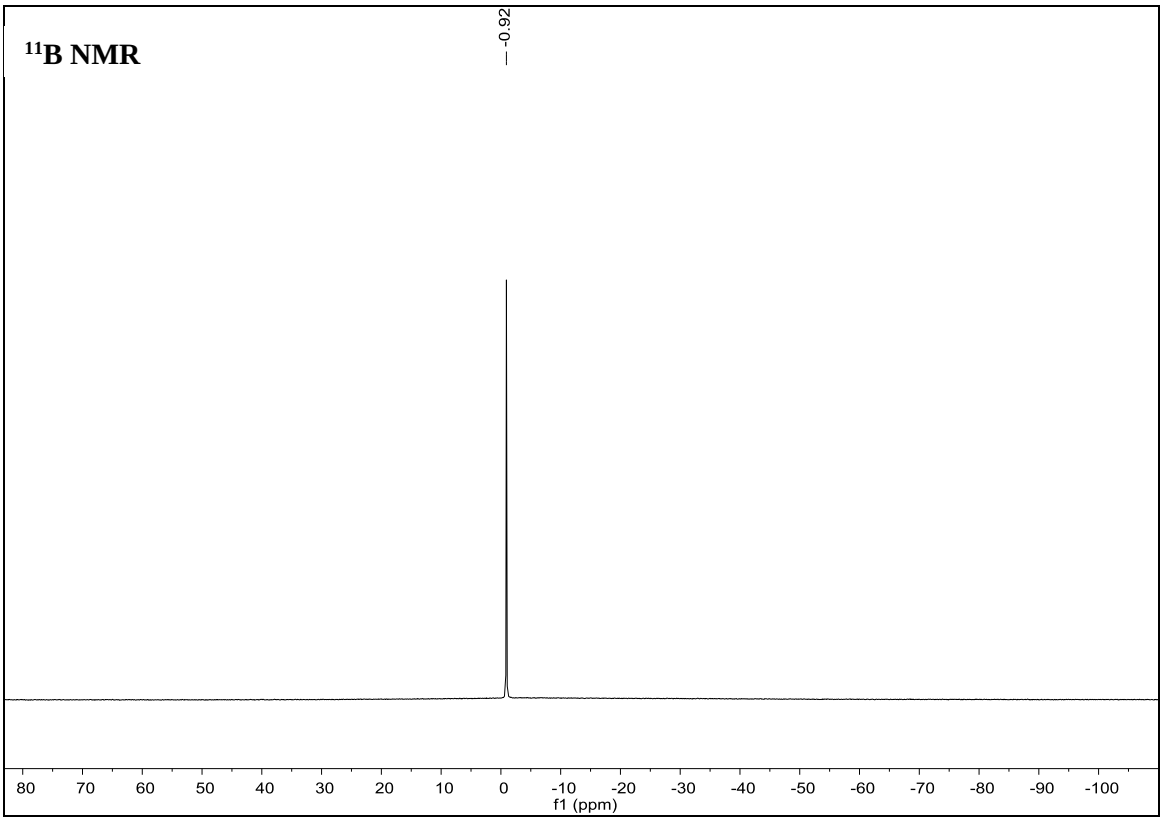




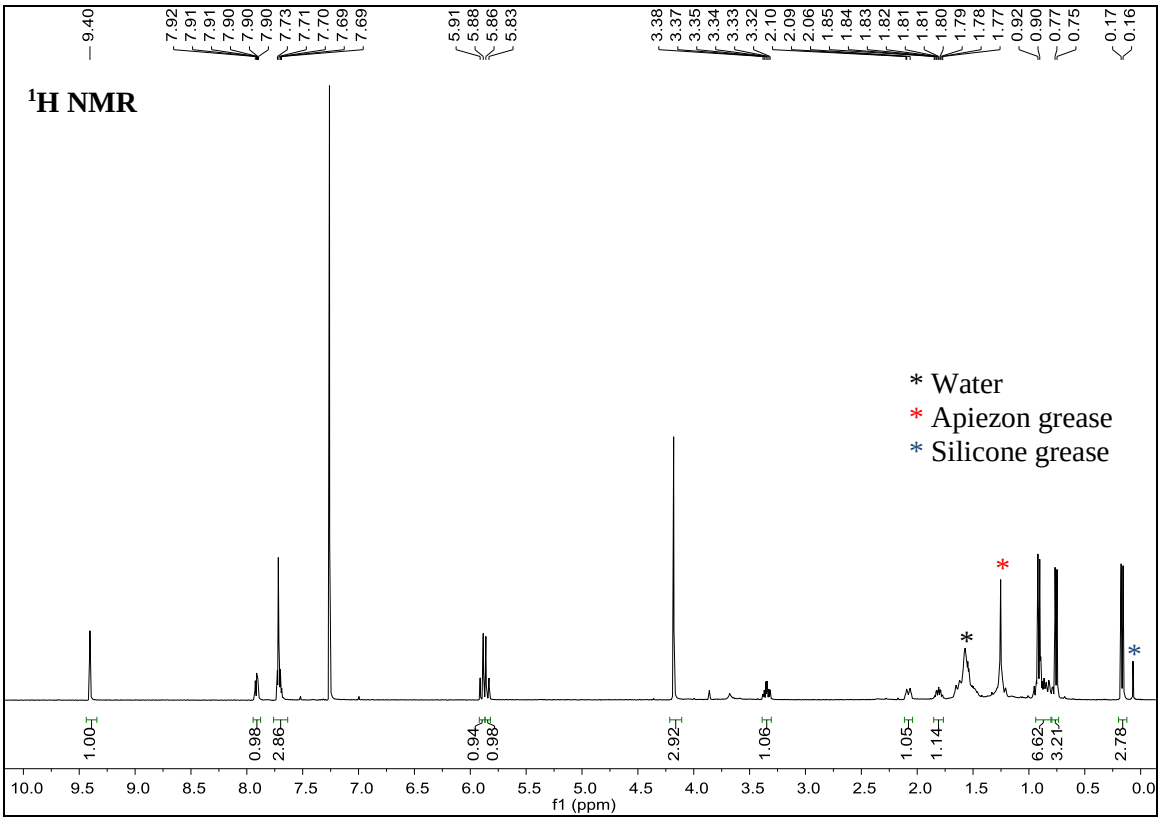
^{19}F NMR

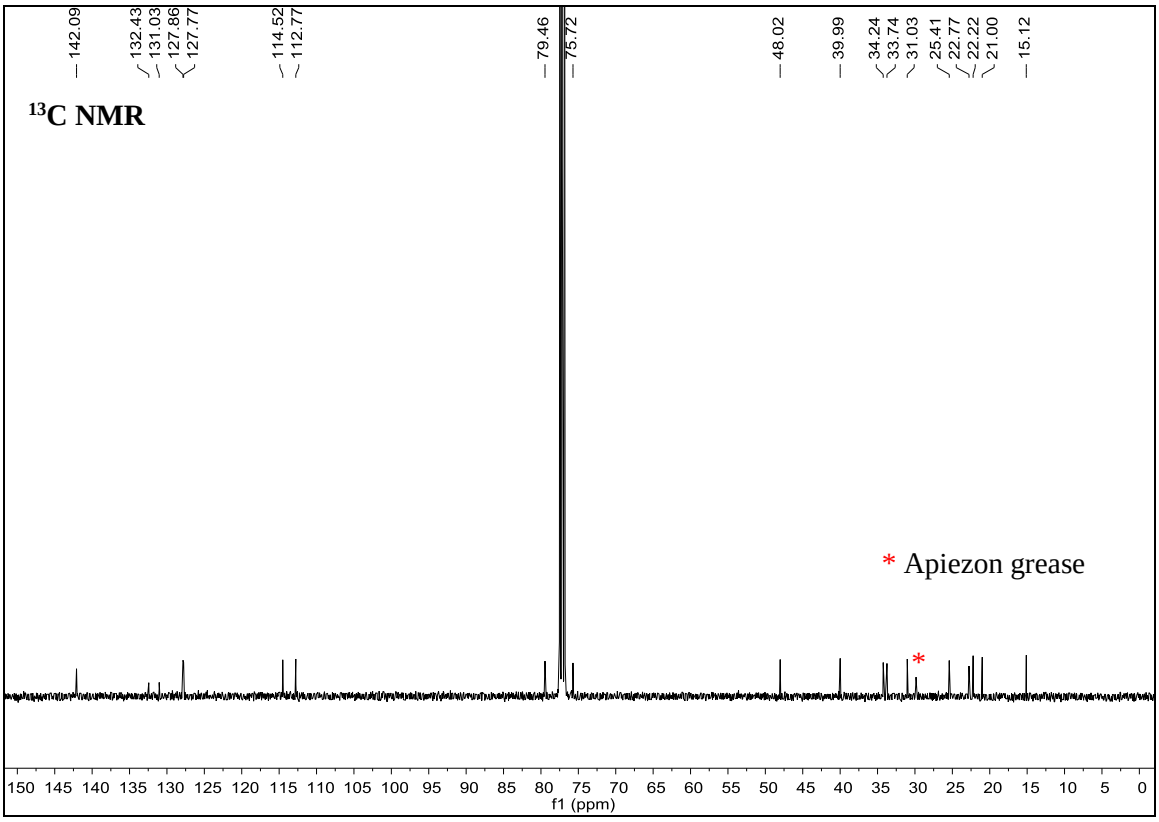


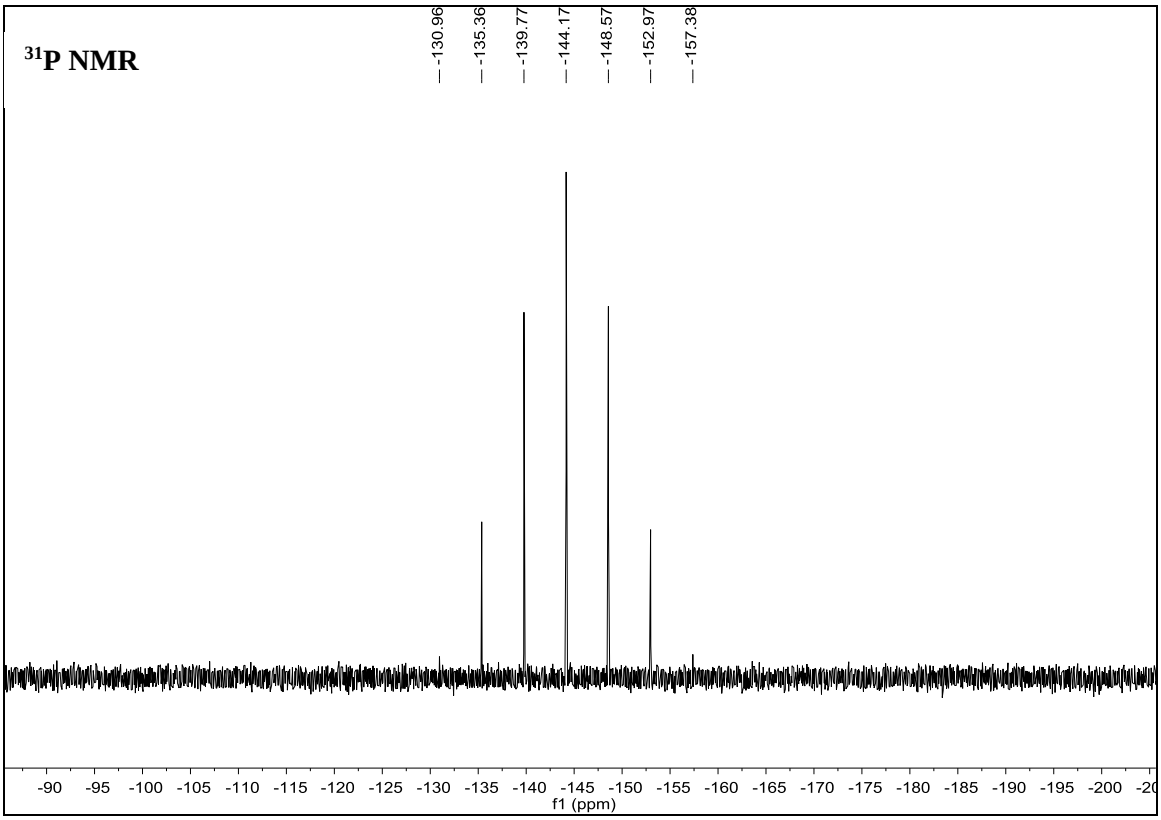
^{11}B NMR

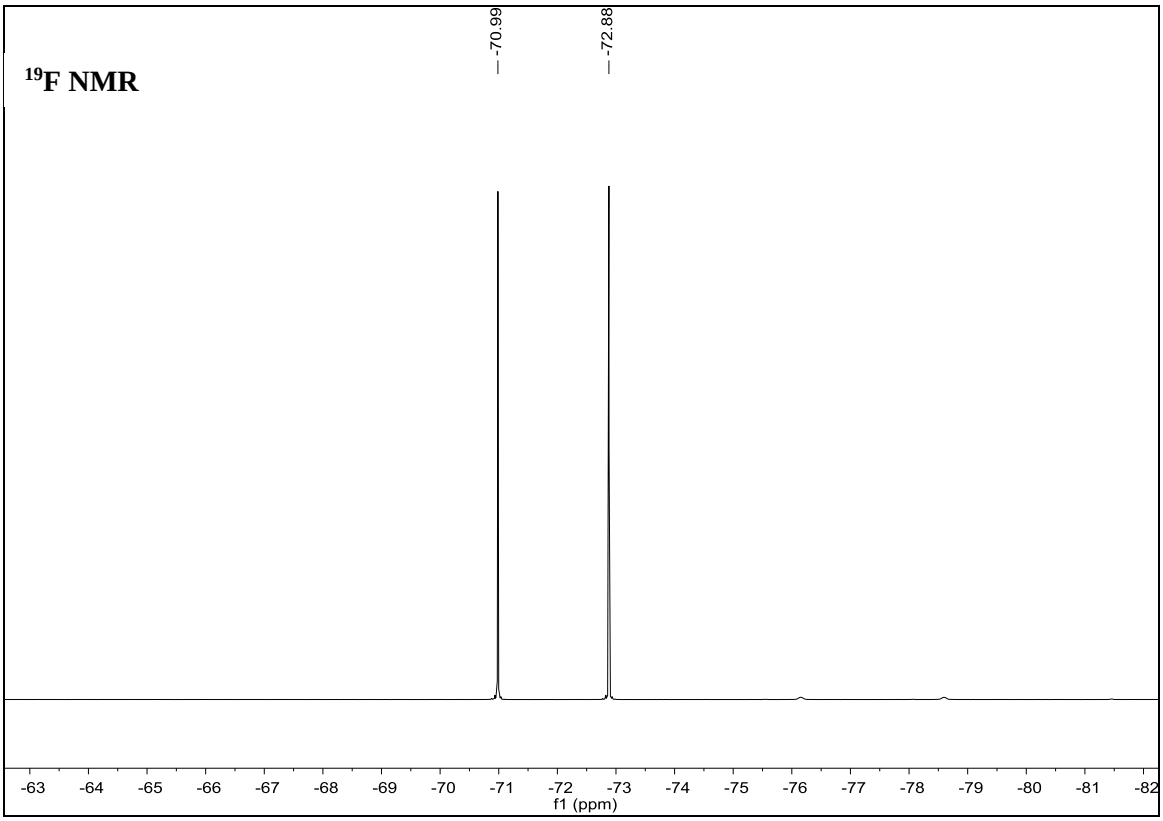


1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-benzimidazolium hexaflurophosphate (6a).

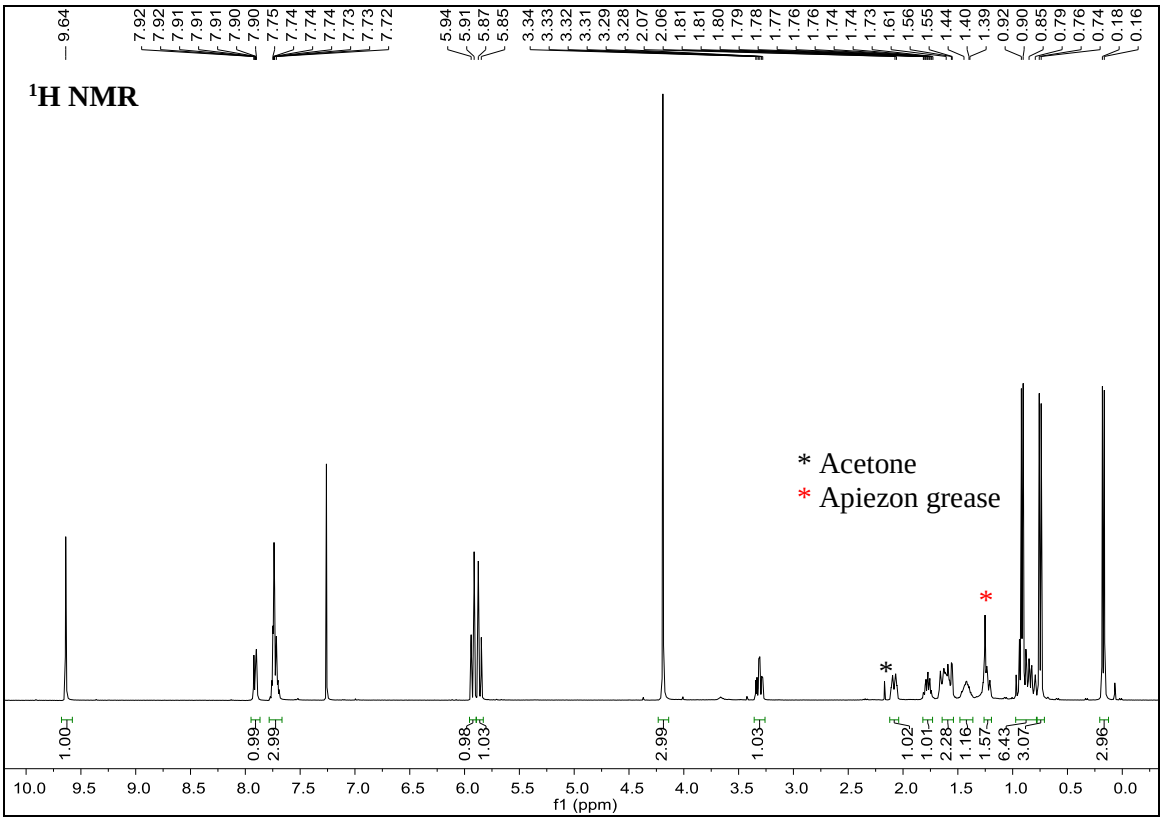


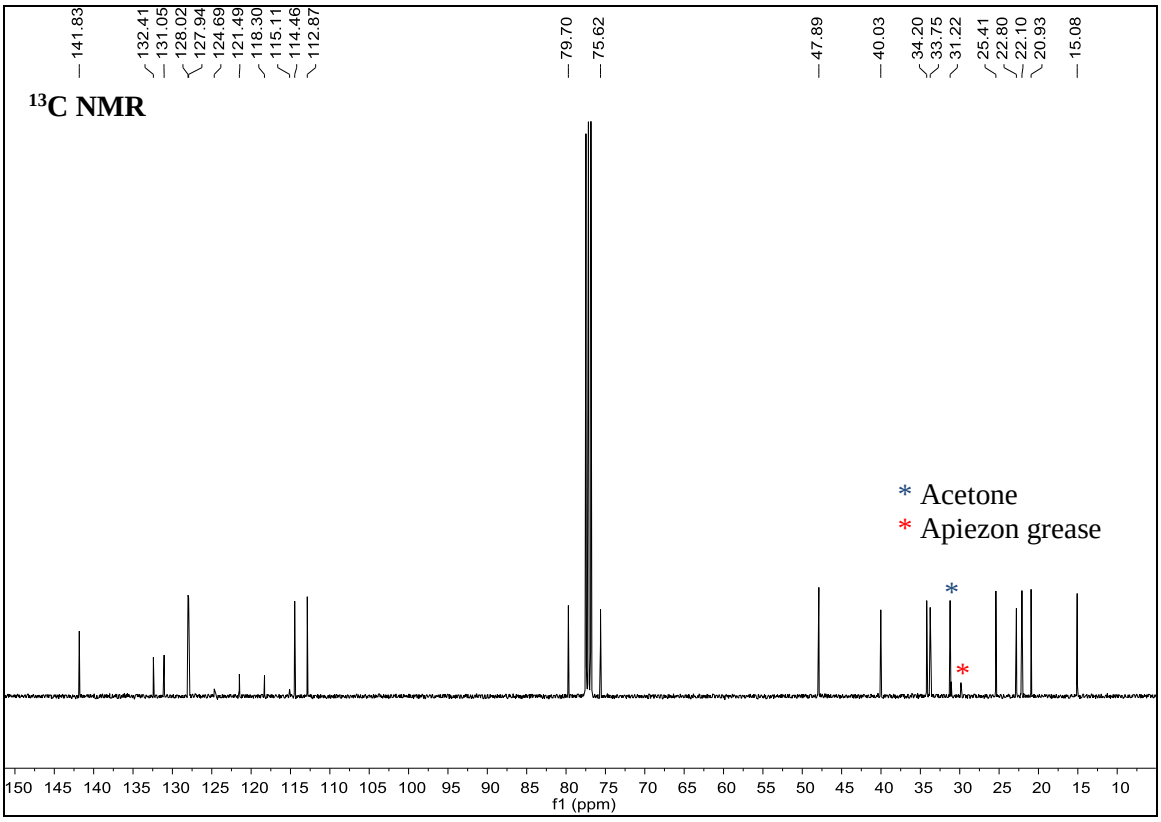



31P NMR
-130.96
-135.36
-139.77
-144.17
-148.57
-152.97
-157.38
-90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200
f1 (ppm)

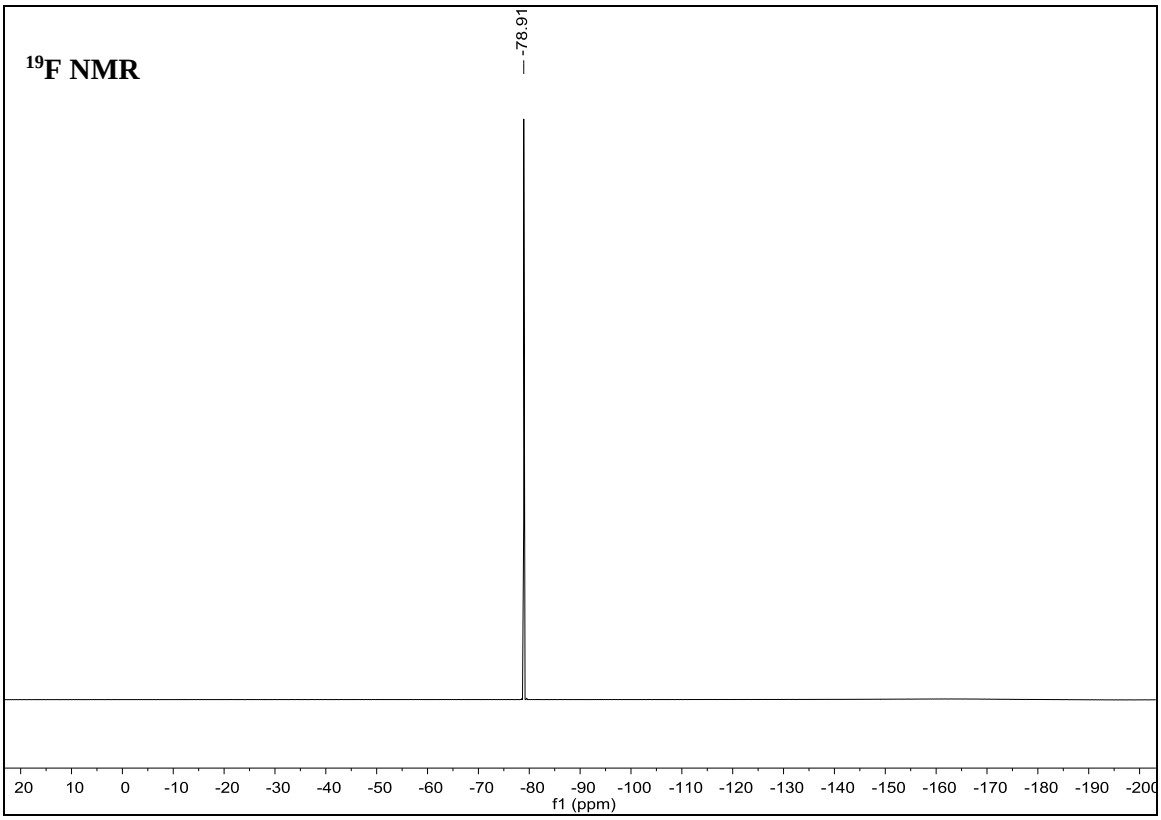

19F NMR
-70.99
-72.88
-63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82
f1 (ppm)

1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-benzimidazolium bis(trifluoromethylsulfonyl)amine (7a).

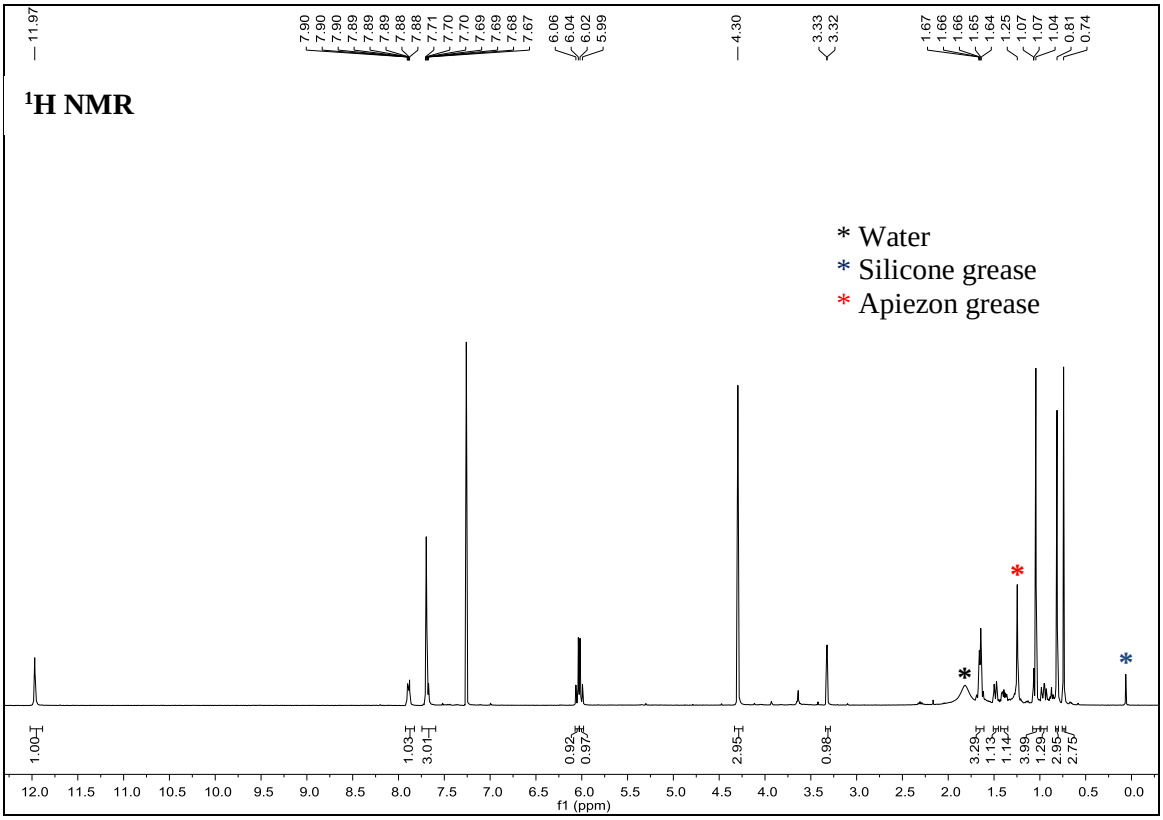


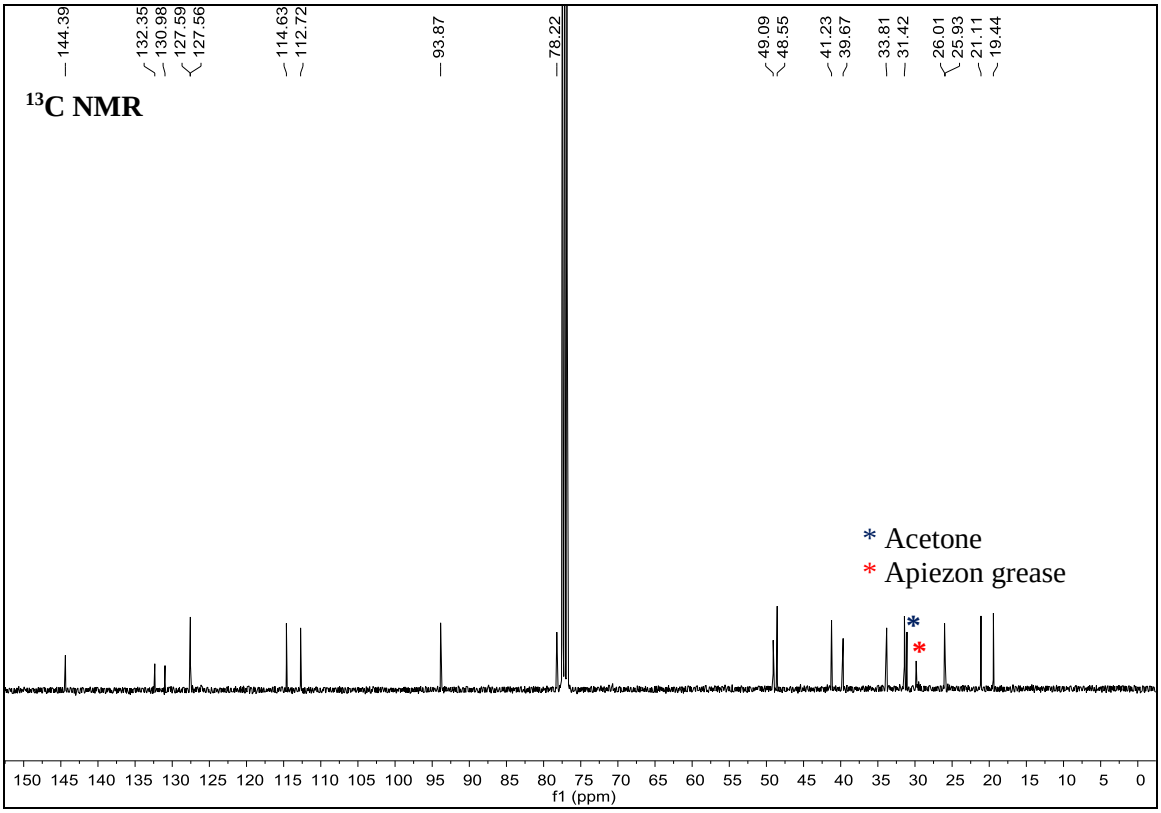


^{19}F NMR

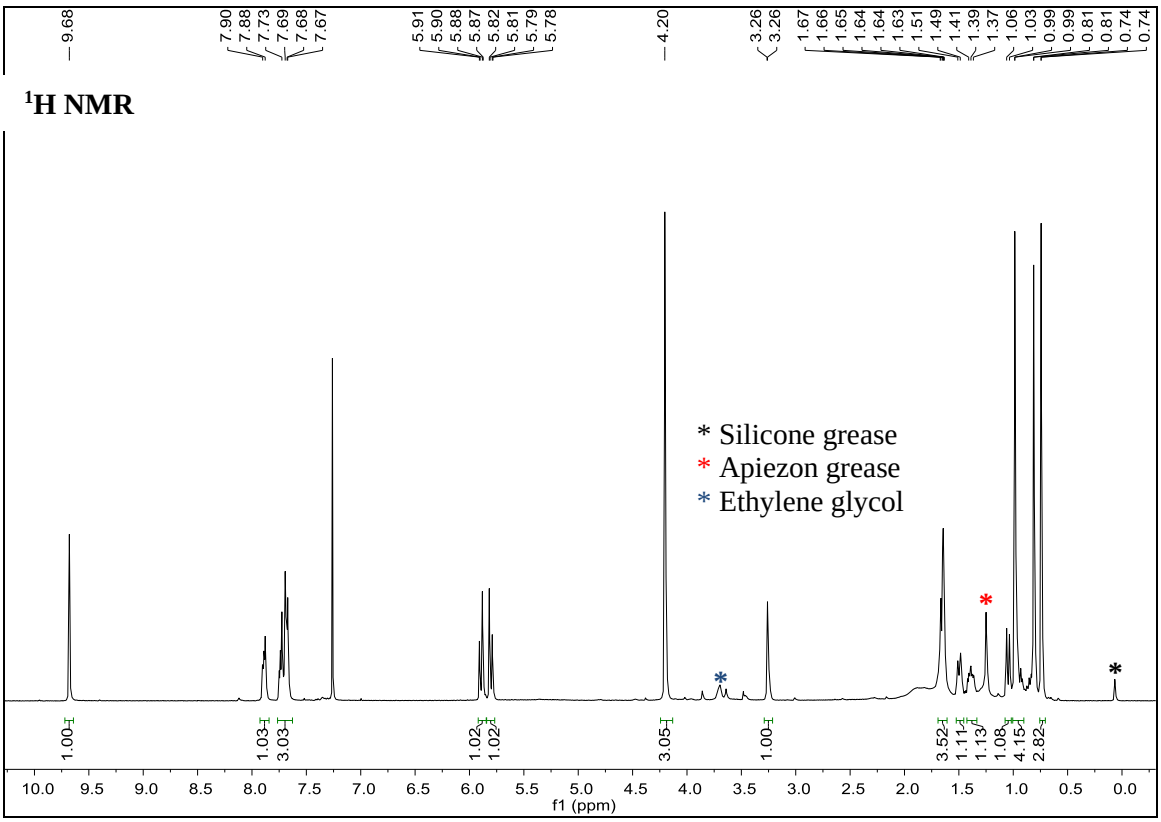

-78.91
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

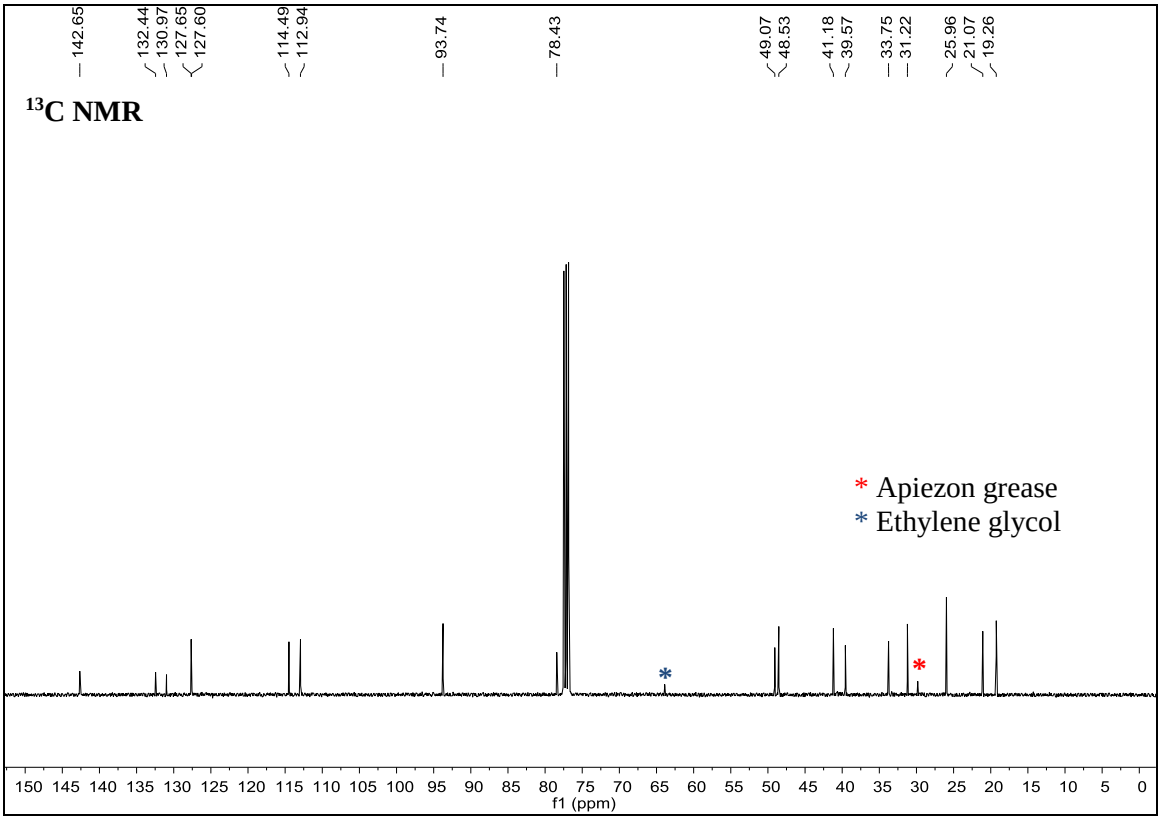
1-(((1R,2R,4S)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-benzimidazolium chloride (4b).



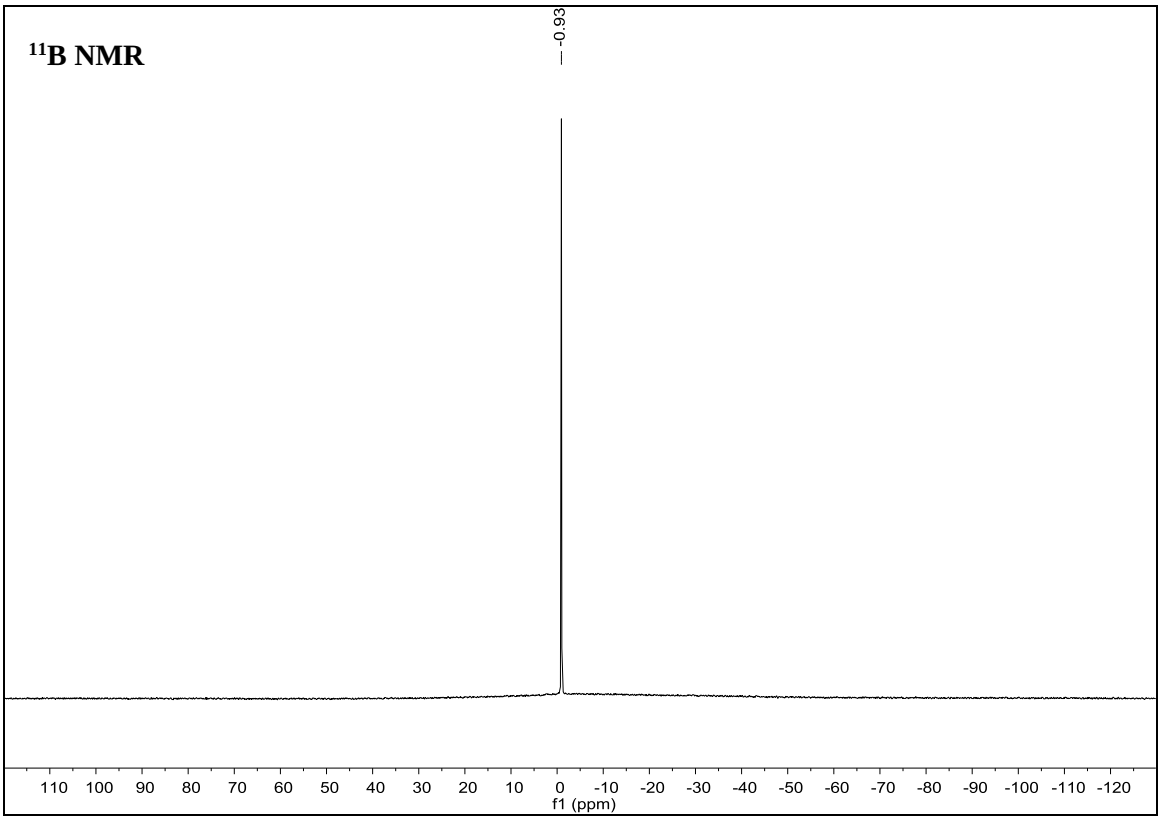


1-(((1R,2R,4S)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-benzimidazolium tetrafluroborate (5b).

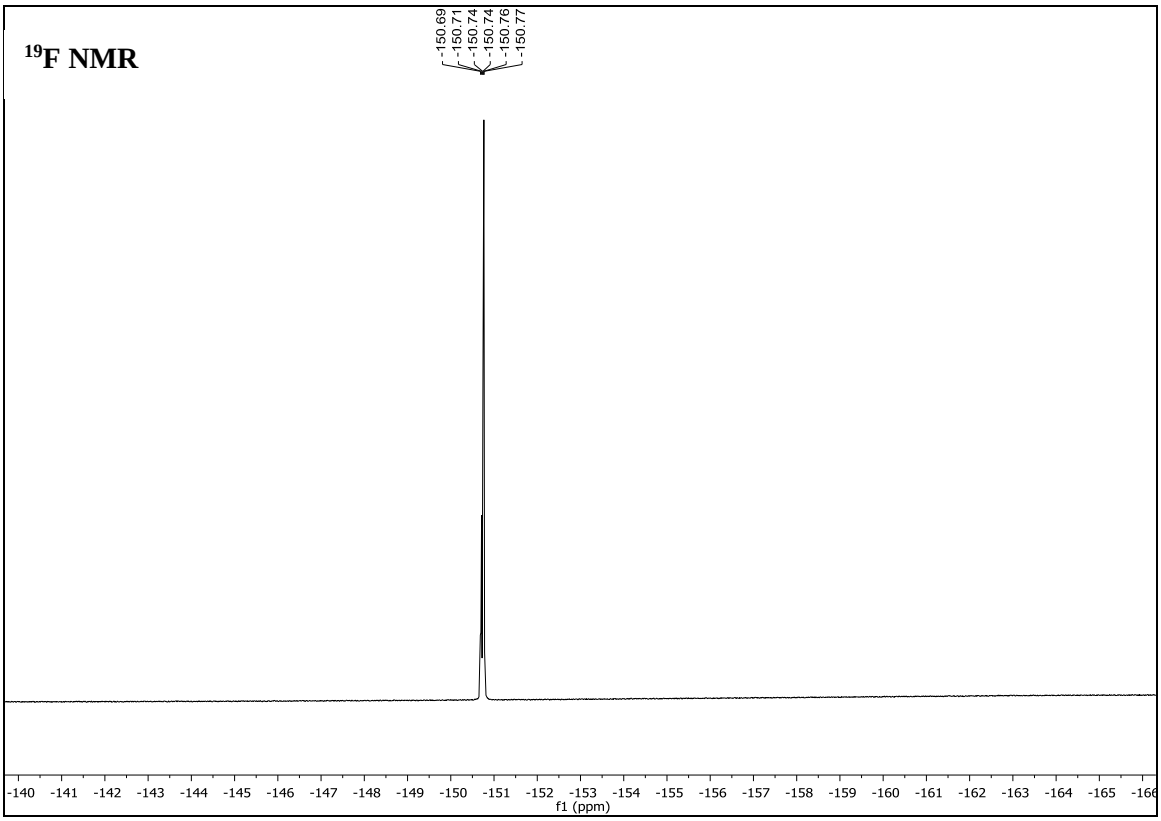




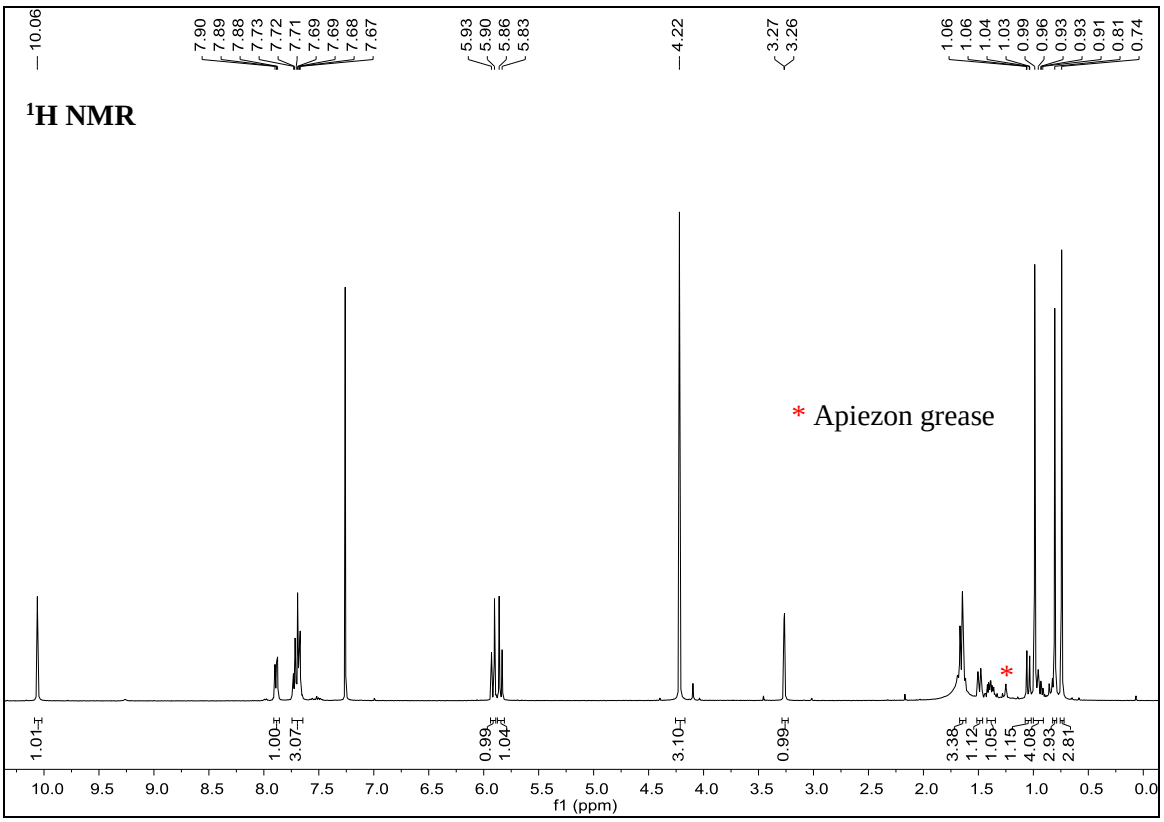
^{11}B NMR

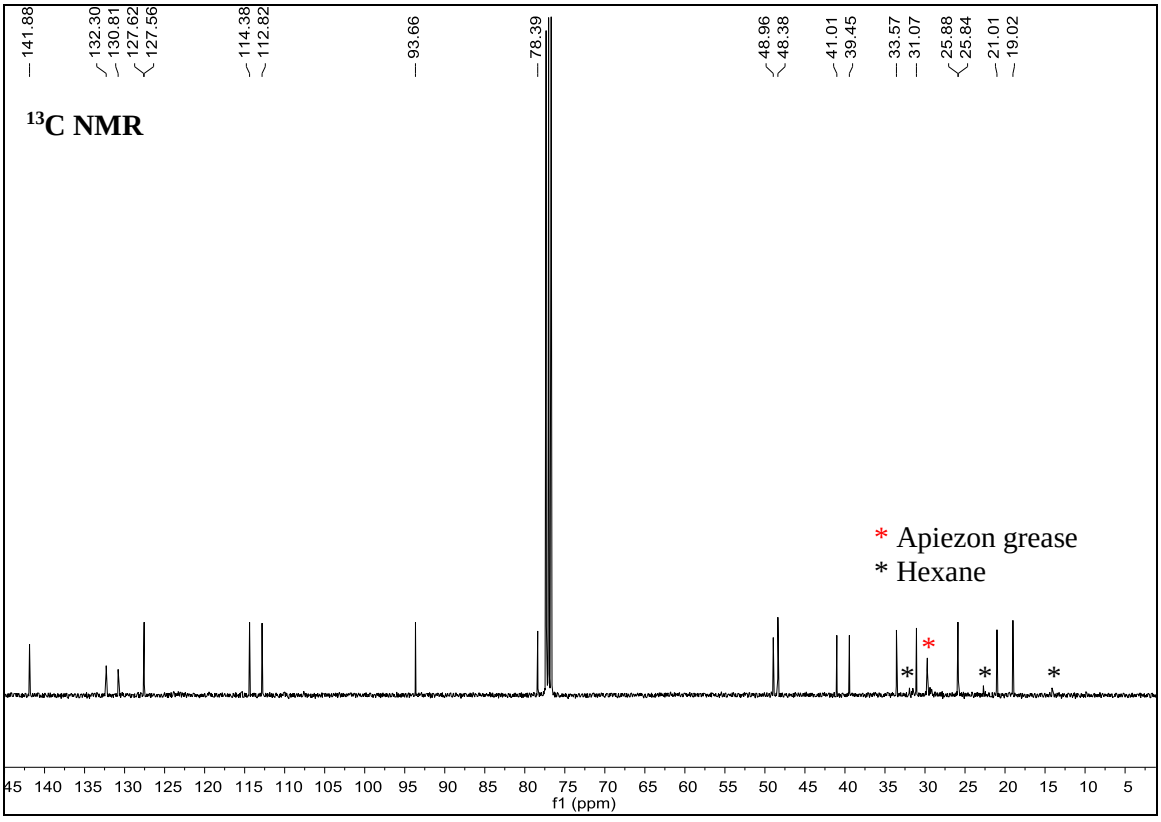


^{19}F NMR

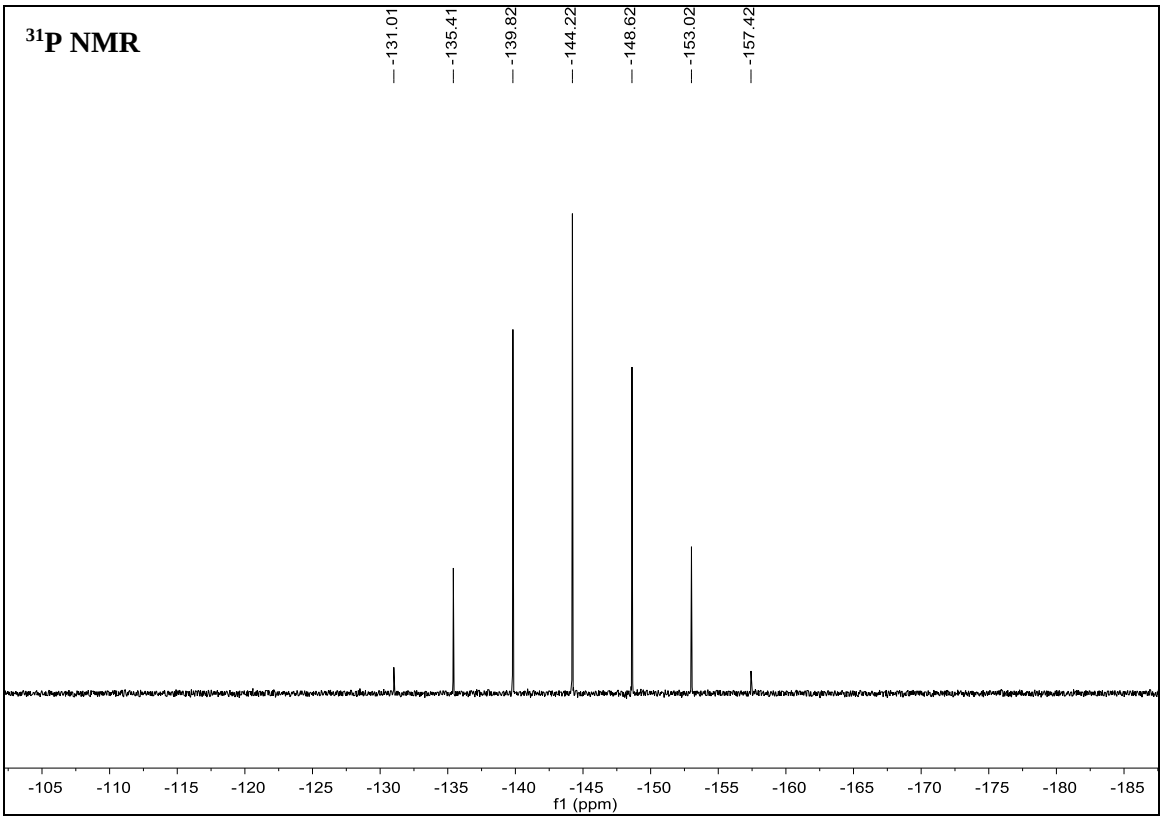


1-(((1R,2R,4S)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-benzimidazolium hexaflurophosphate (6b).

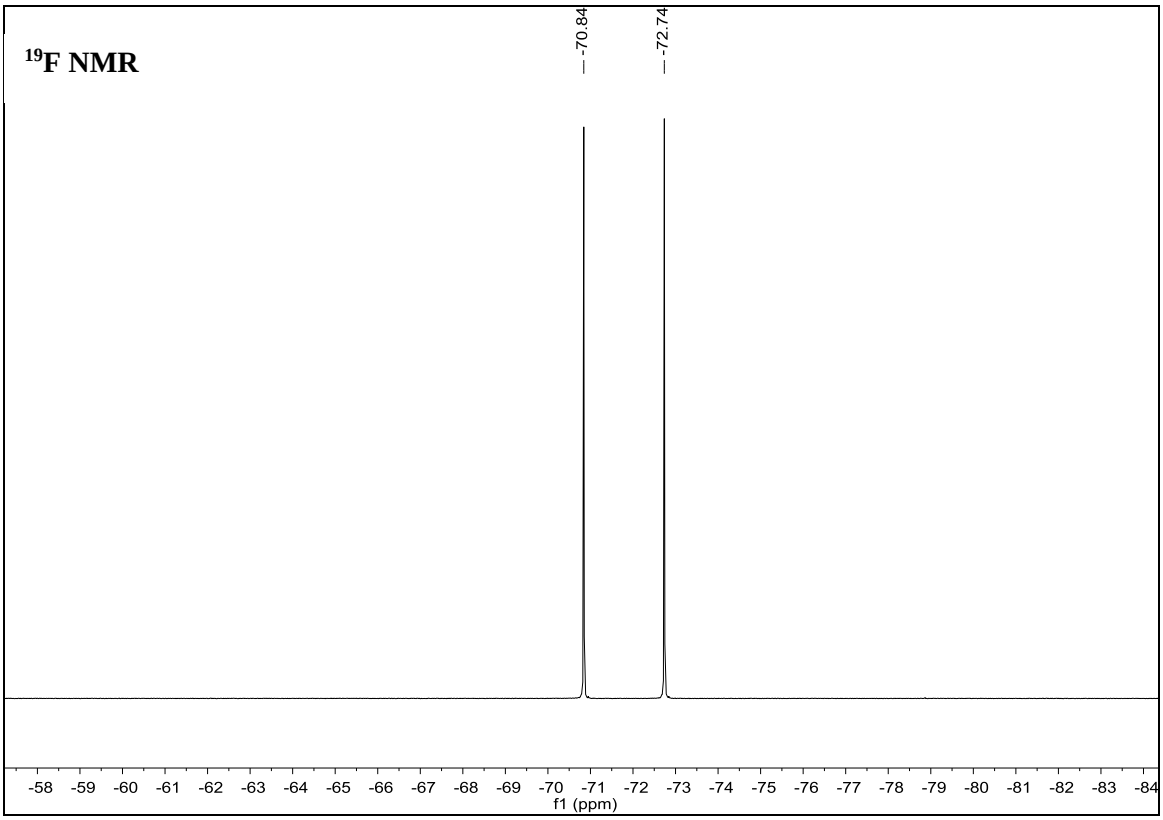




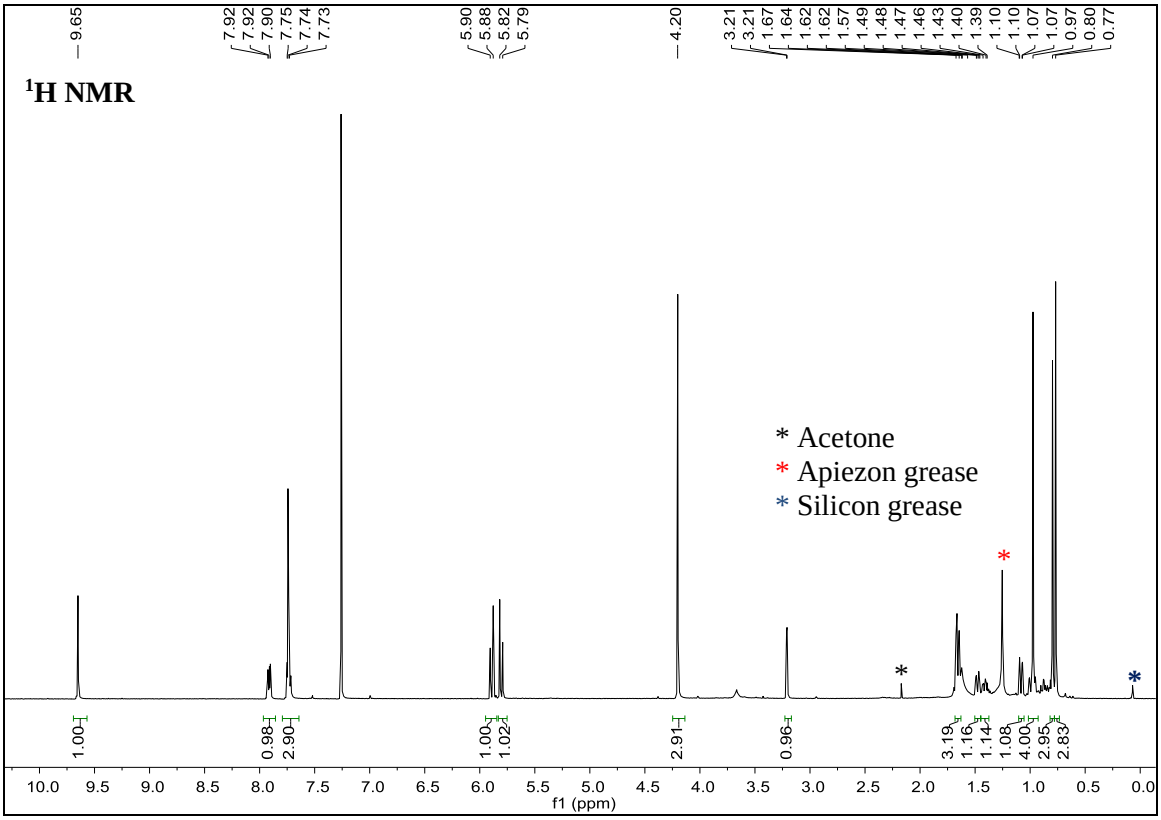
^{31}P NMR

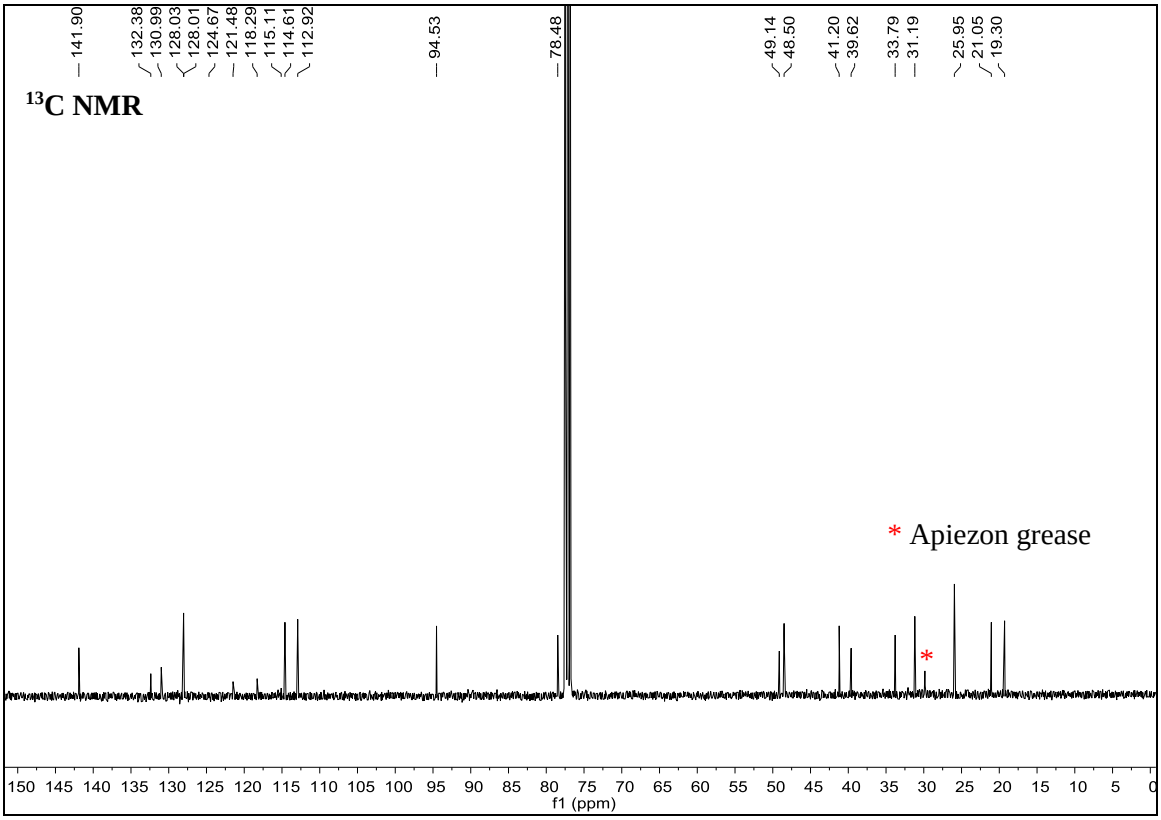


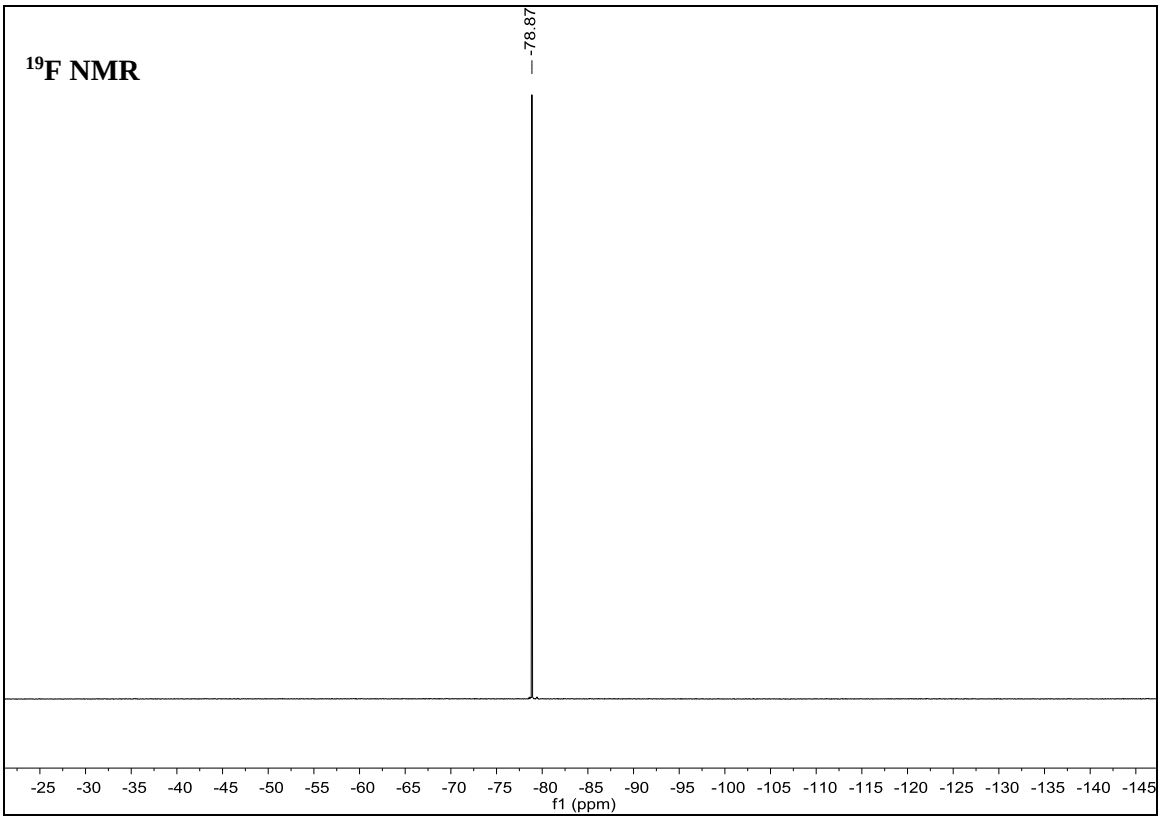
^{19}F NMR



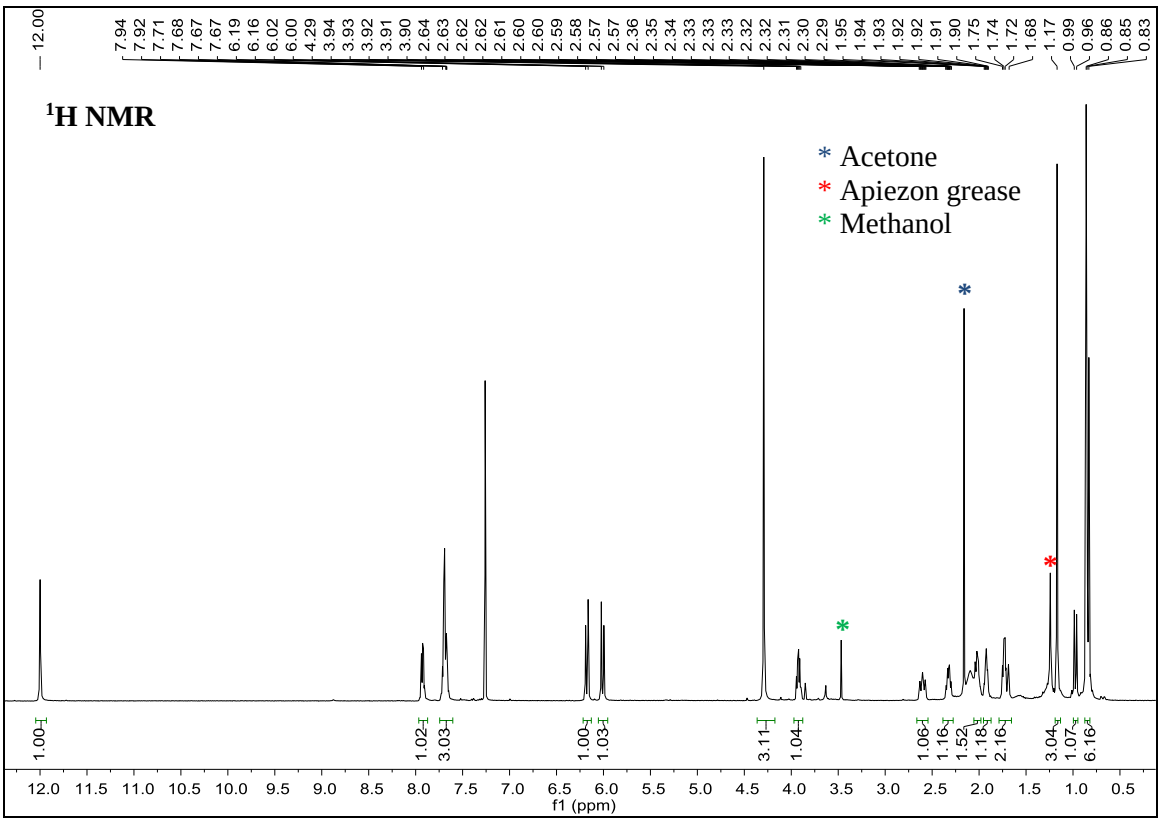
1-(((1R,2R,4S)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-benzimidazolium bis(trifluoromethylsulfonyl)amine (7b).

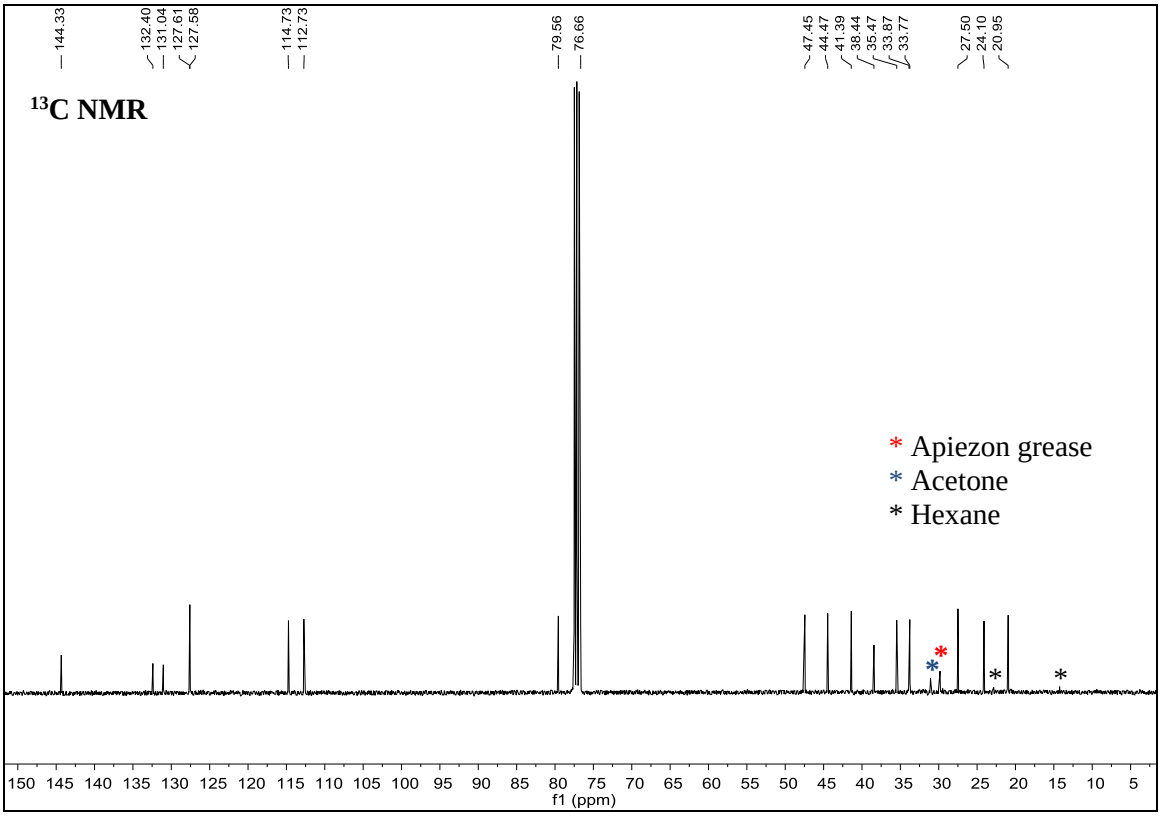




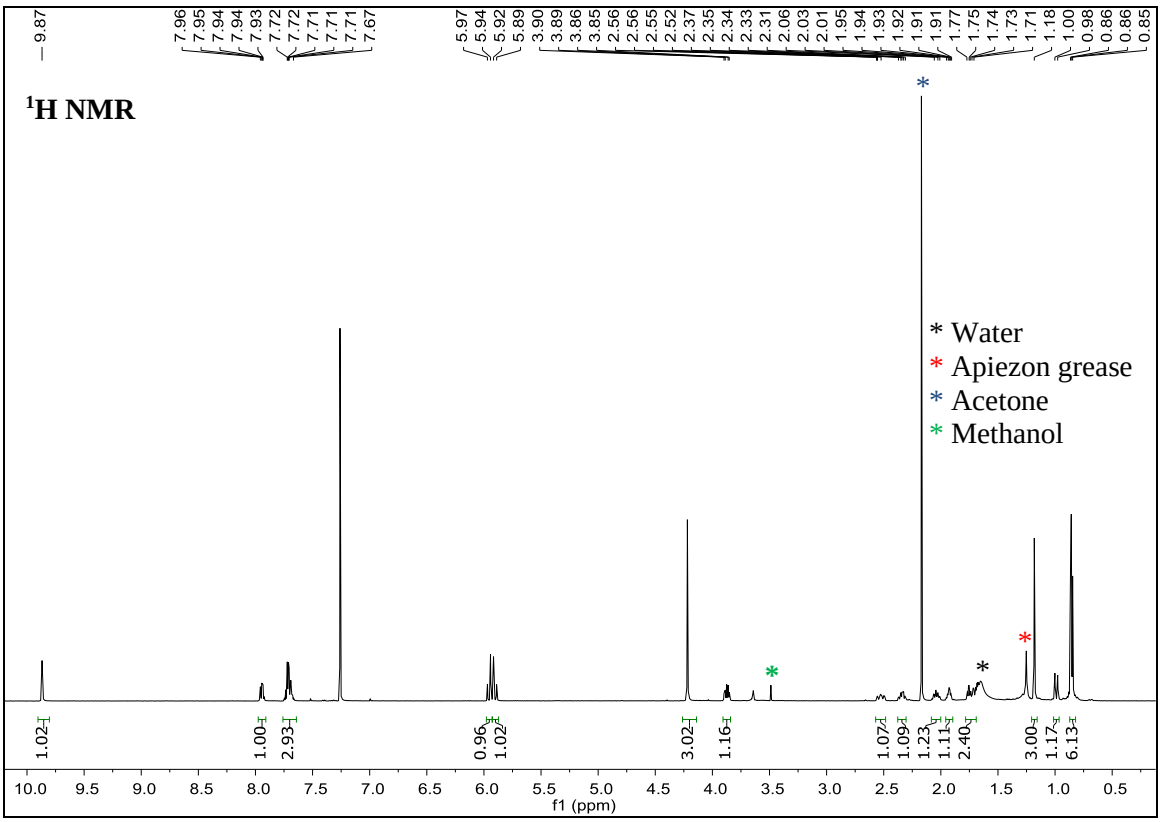

19F NMR
-78.87
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

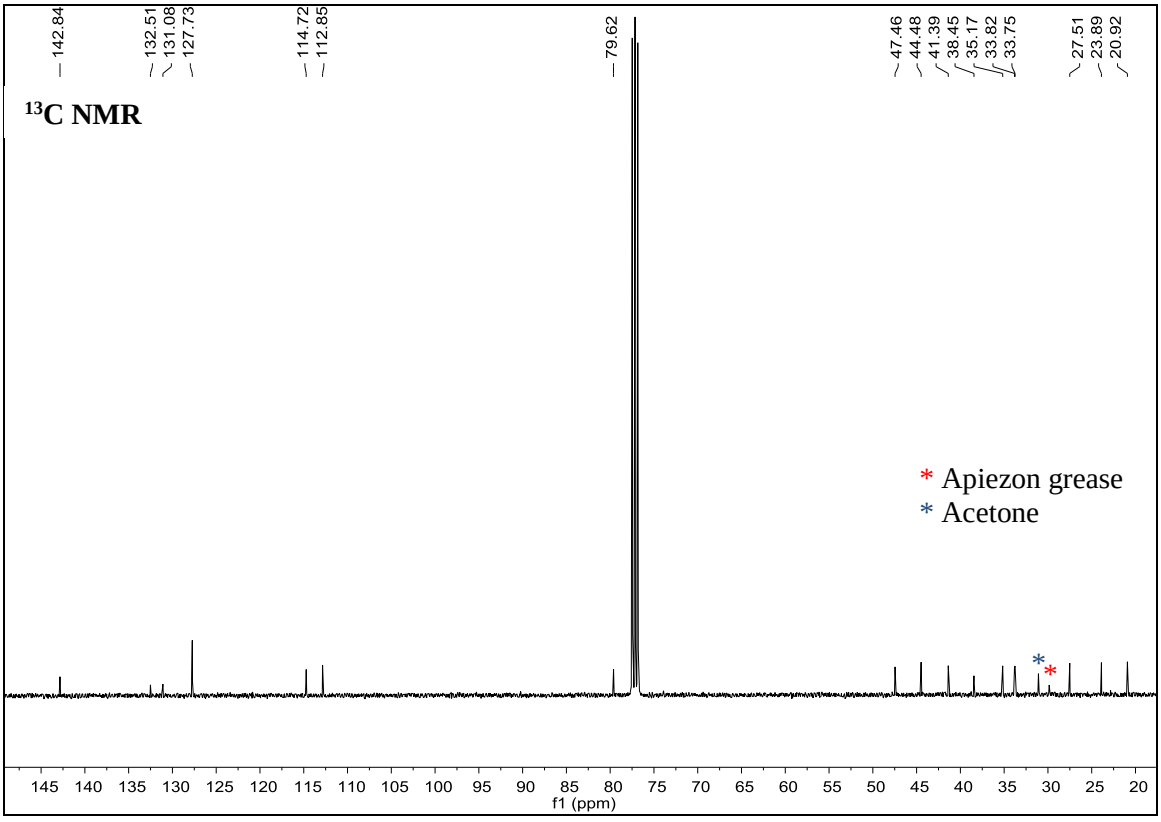
1-((((1S,2S,3S,5R)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methyl)-benzimidazolium chloride (4c).



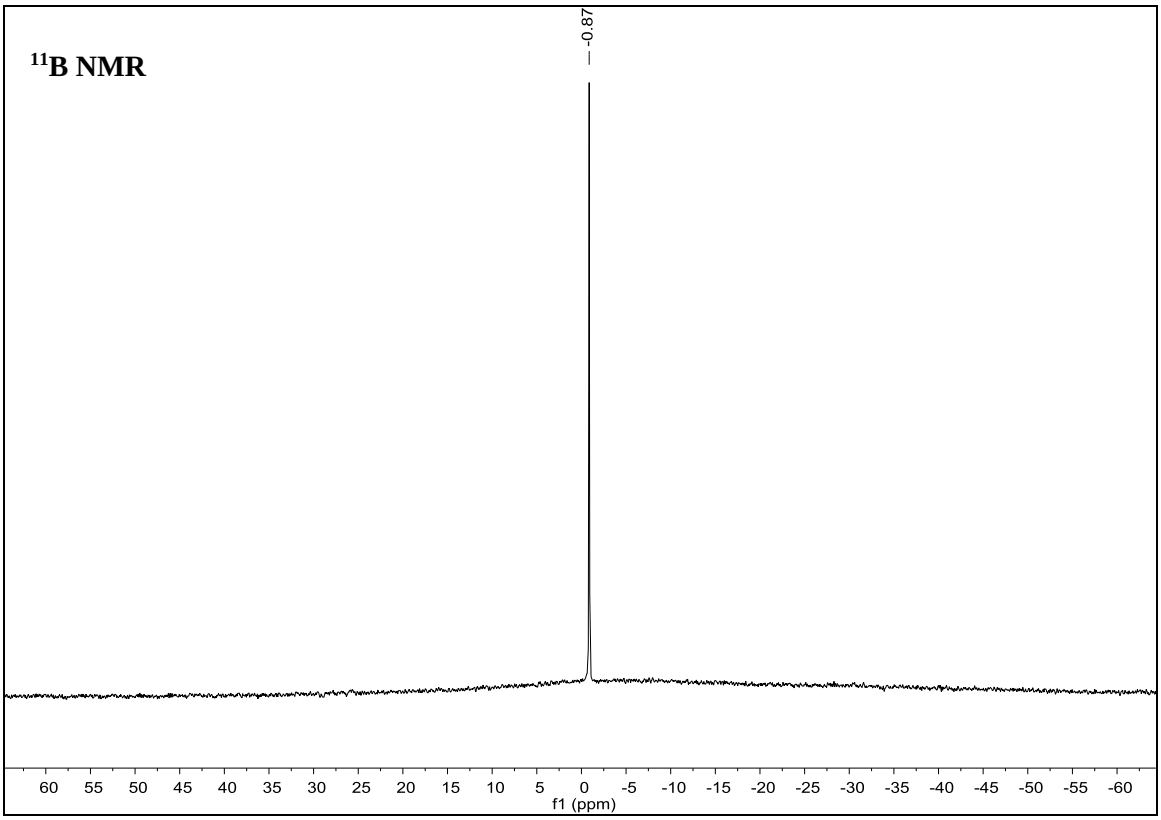


1-((((1S,2S,3S,5R)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methyl)-benzimidazolium tetrafluroborate (5c).

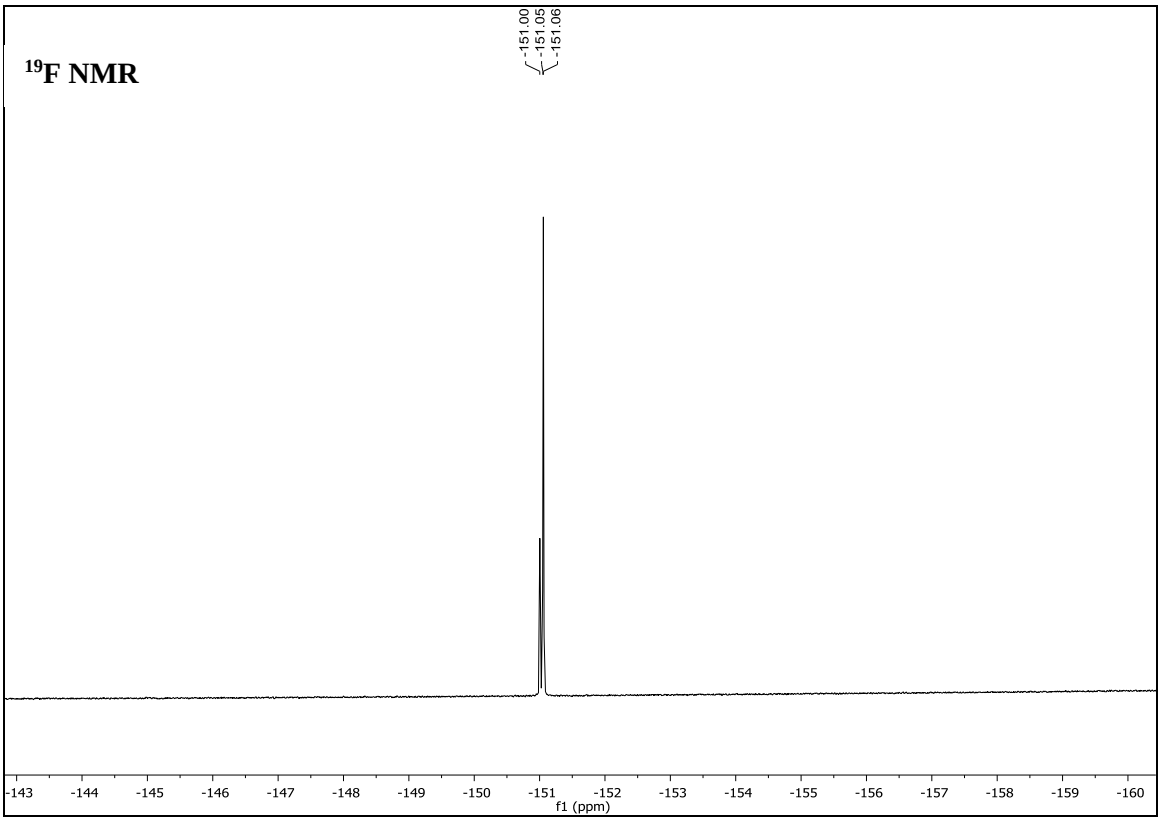




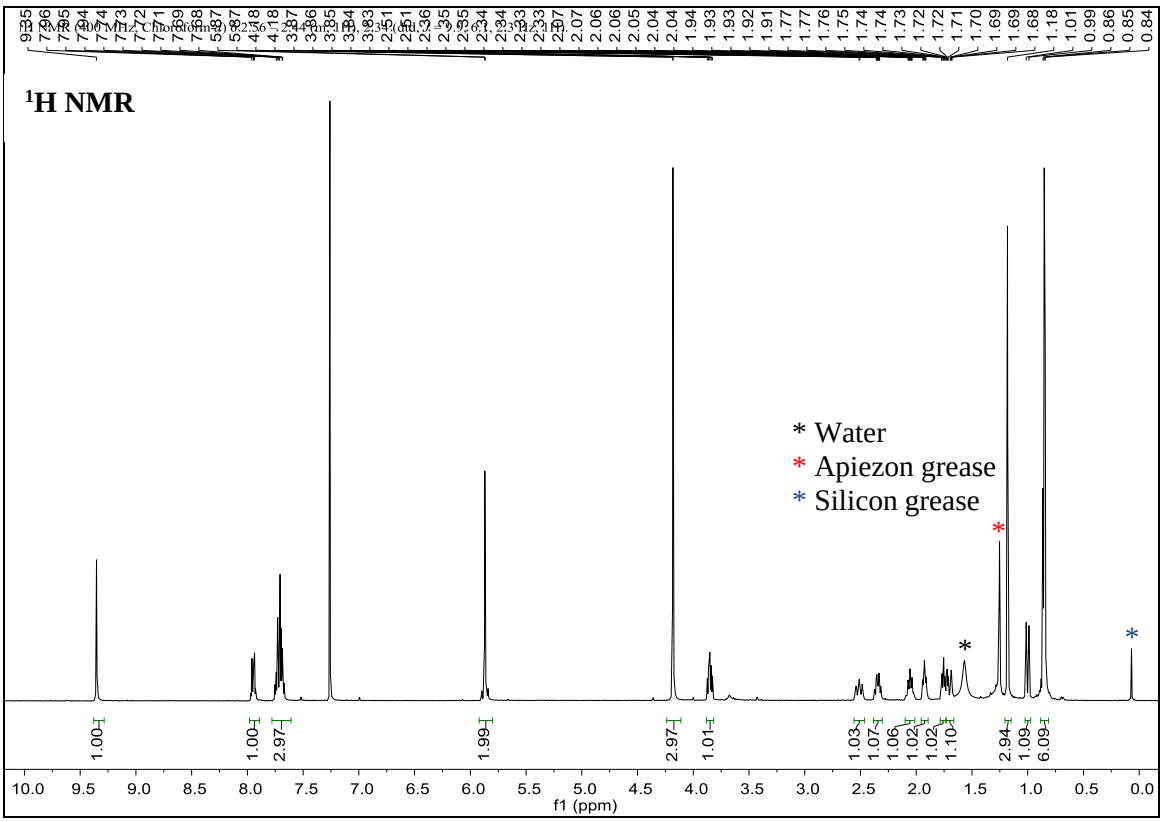
^{11}B NMR

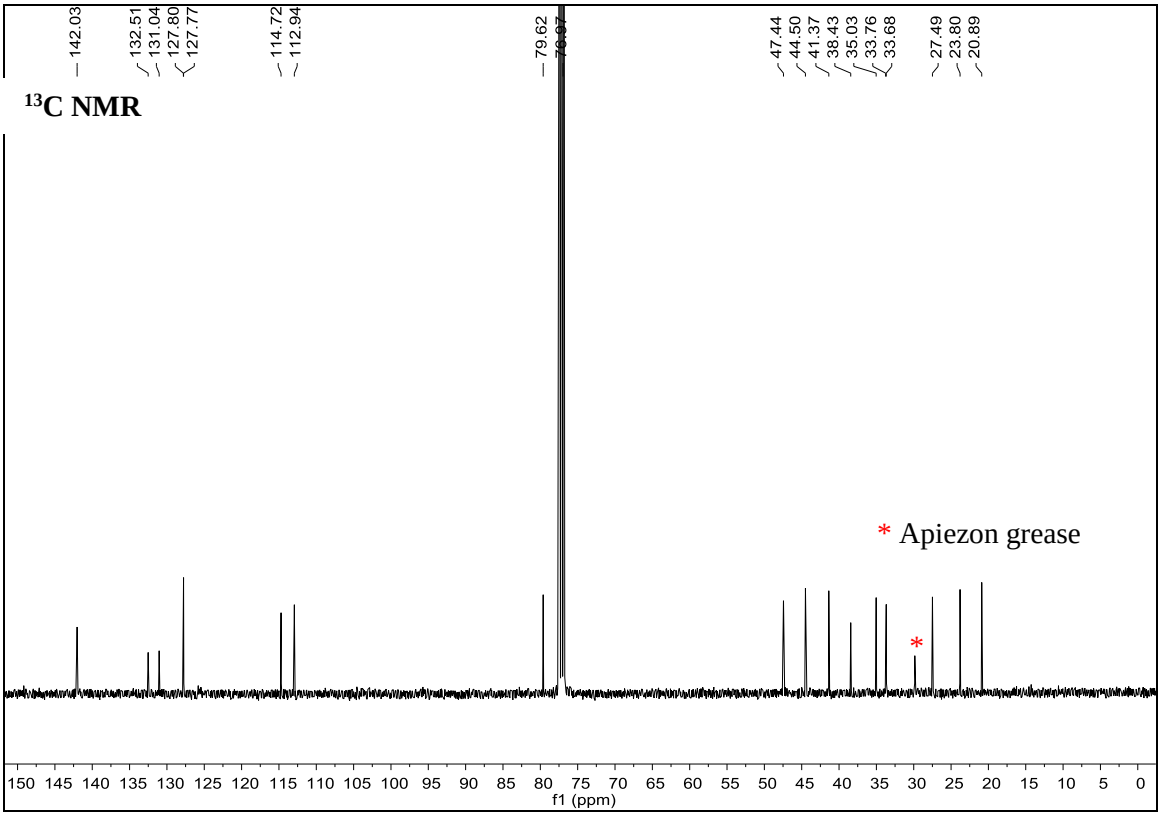


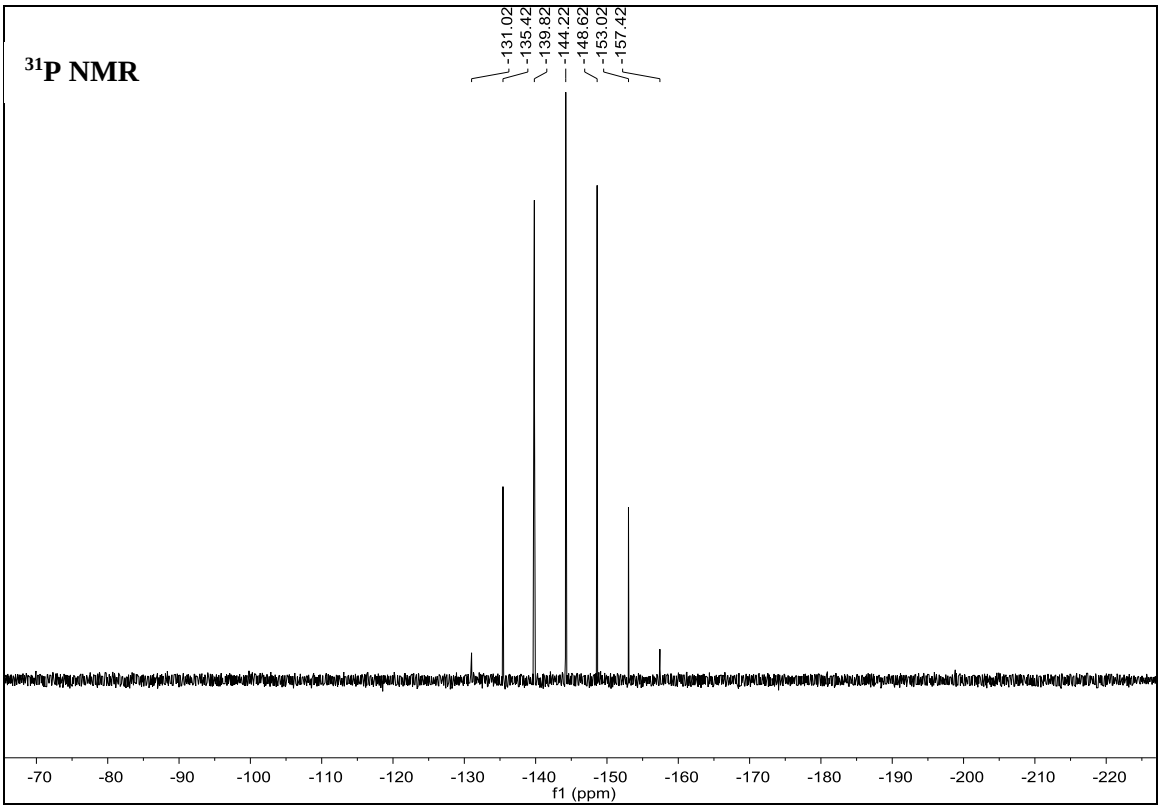
^{19}F NMR

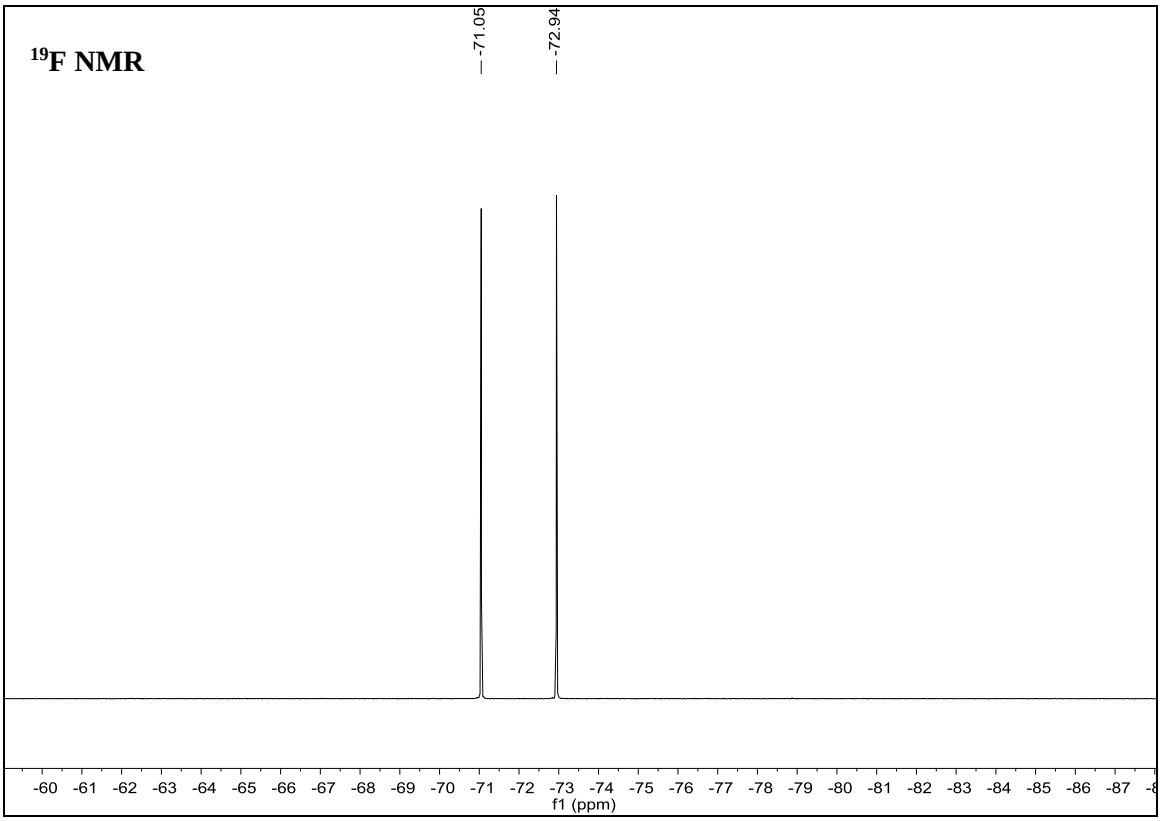


1-((((1S,2S,3S,5R)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methyl)-benzimidazolium hexaflurophosphate (6c).

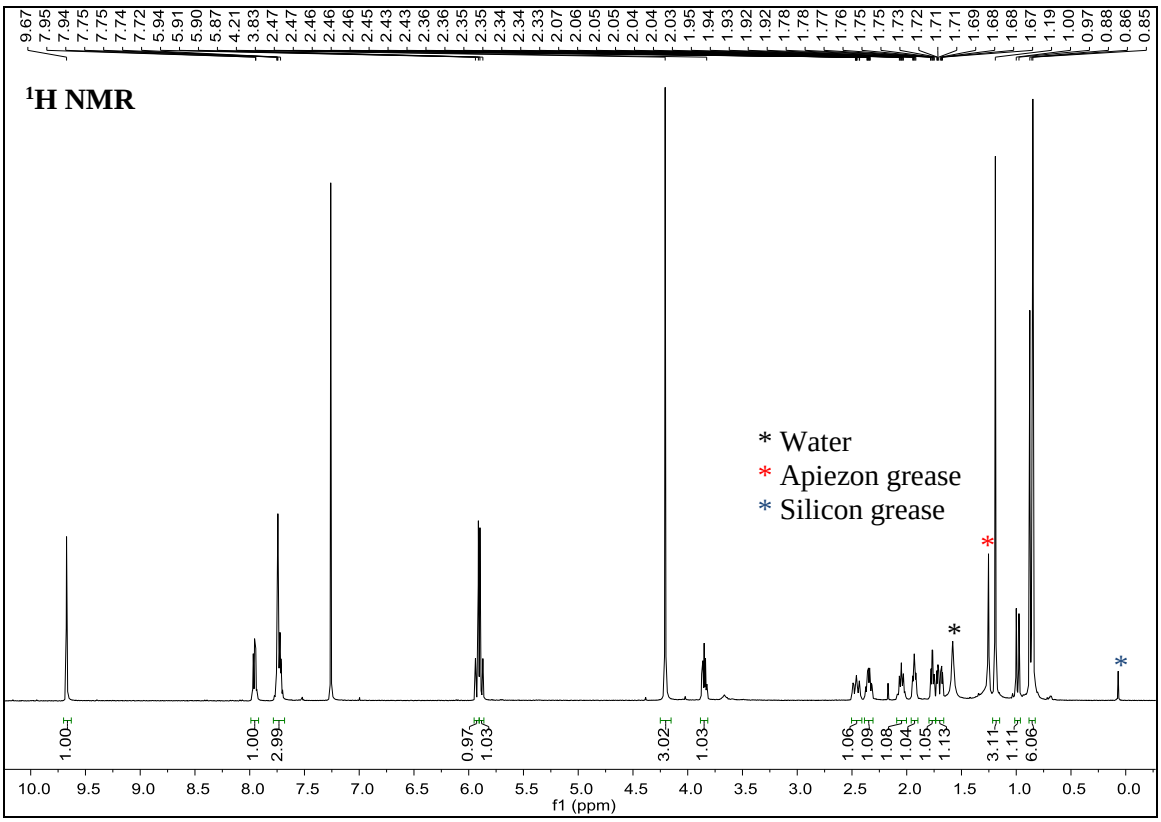


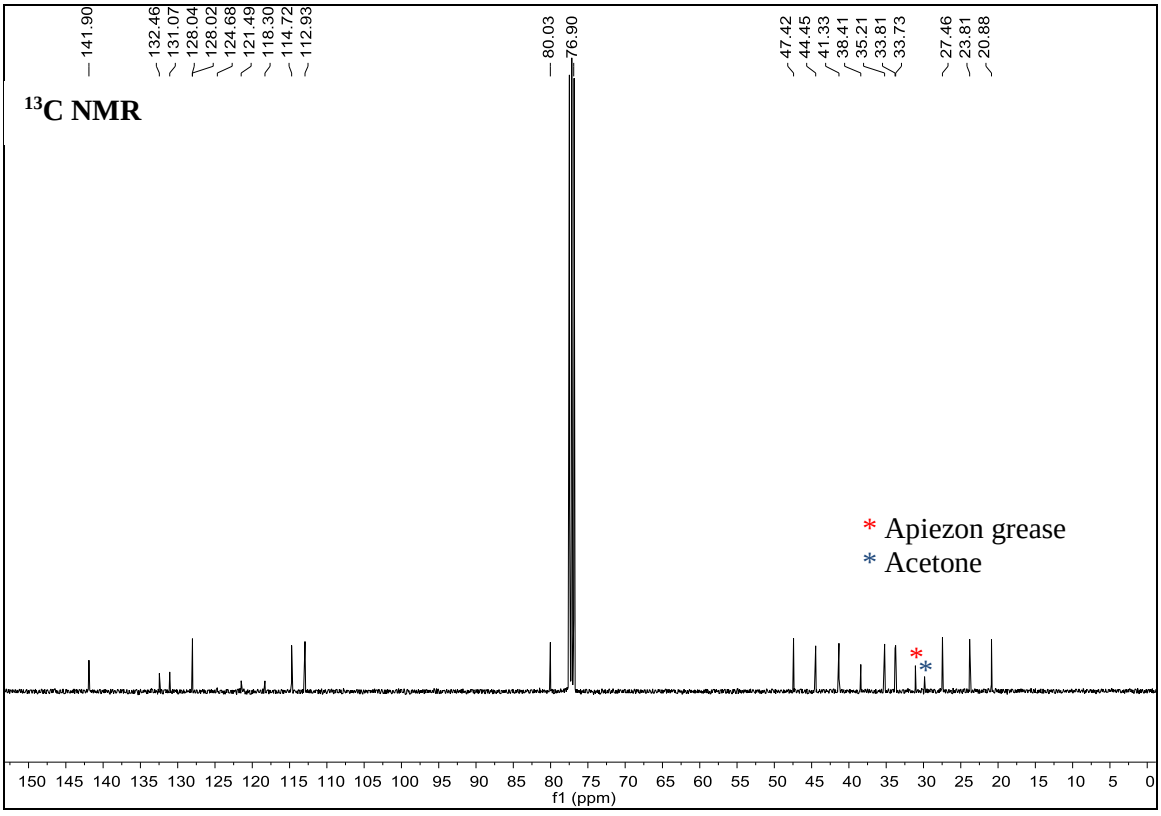


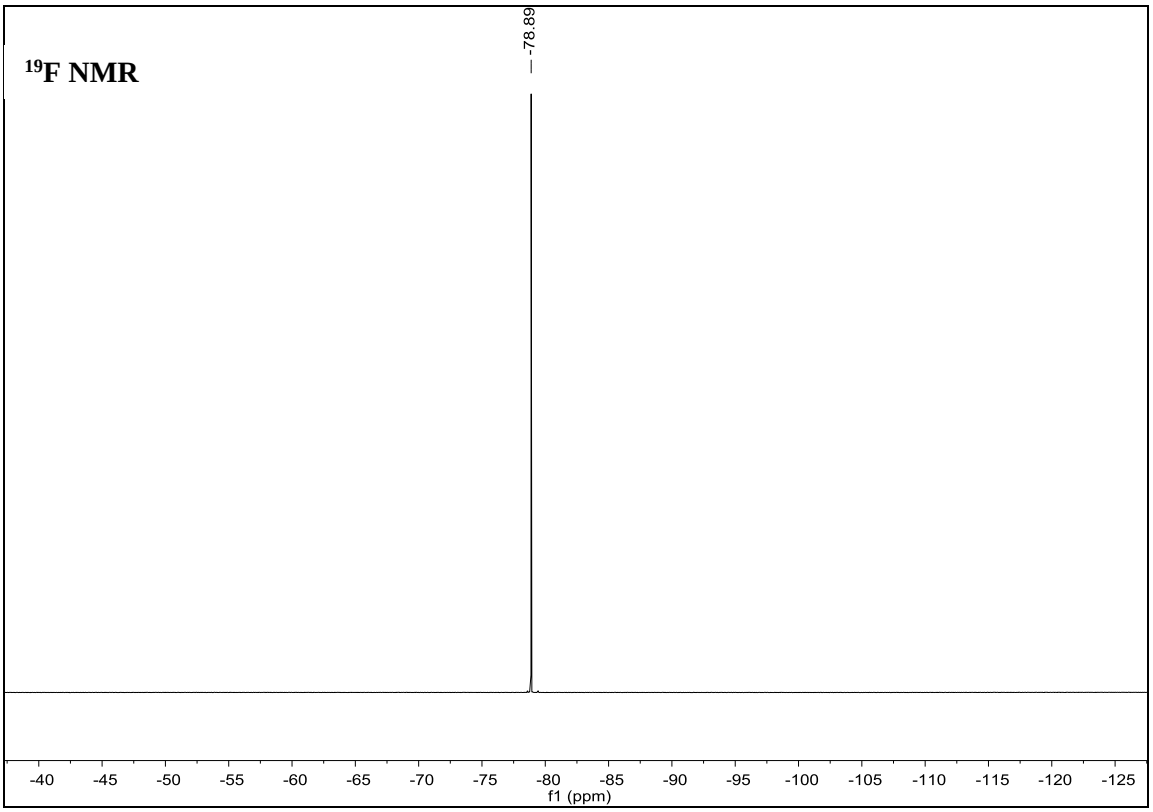

31P NMR
-131.02
-135.42
-139.82
-144.22
-148.62
-153.02
-157.42
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


19F NMR
-71.05
-72.94
-60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86 -87
f1 (ppm)

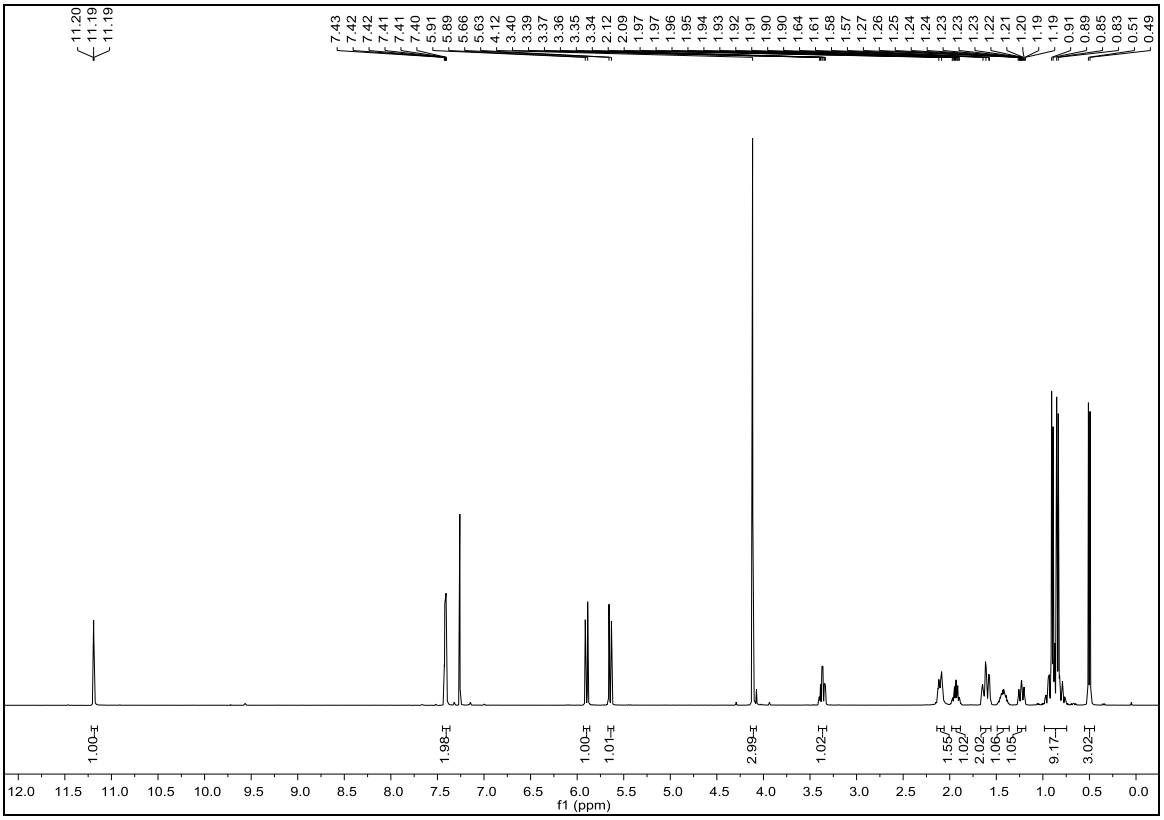
1-((((1S,2S,3S,5R)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl)oxy)methyl)-benzimidazolium bis(trifluoromethylsulfonyl)amine (7c).



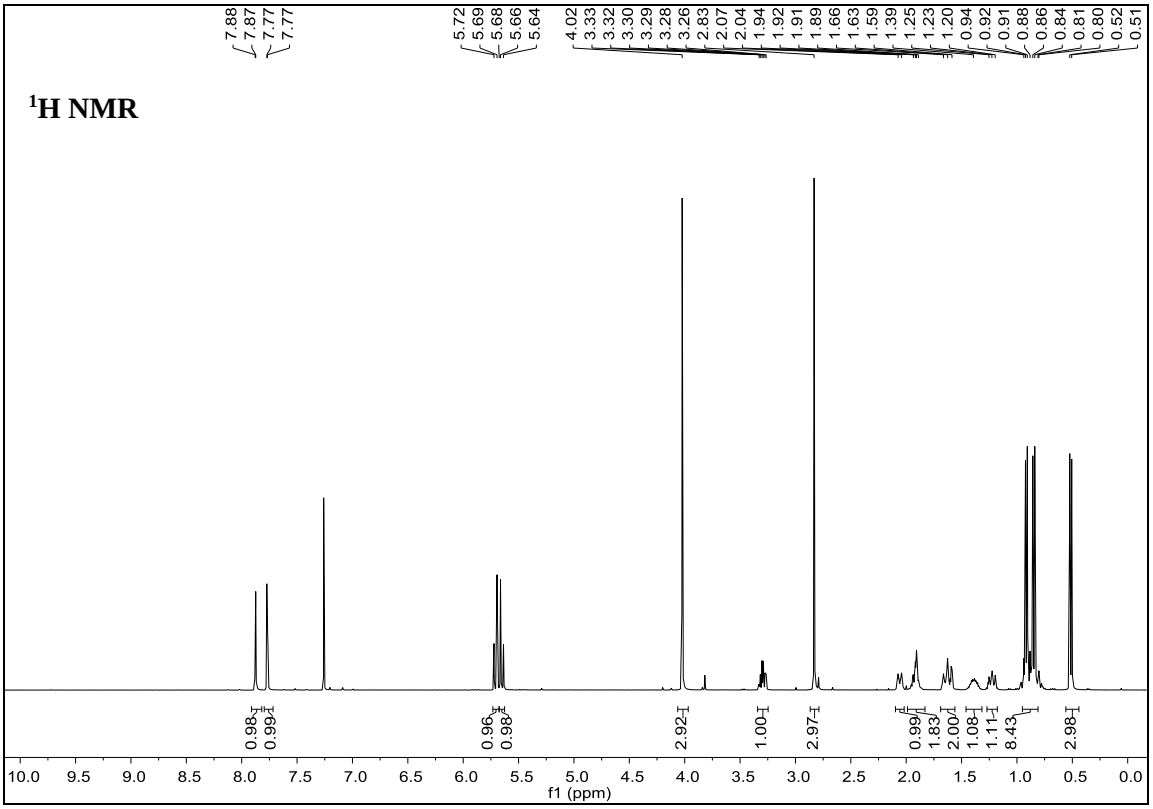


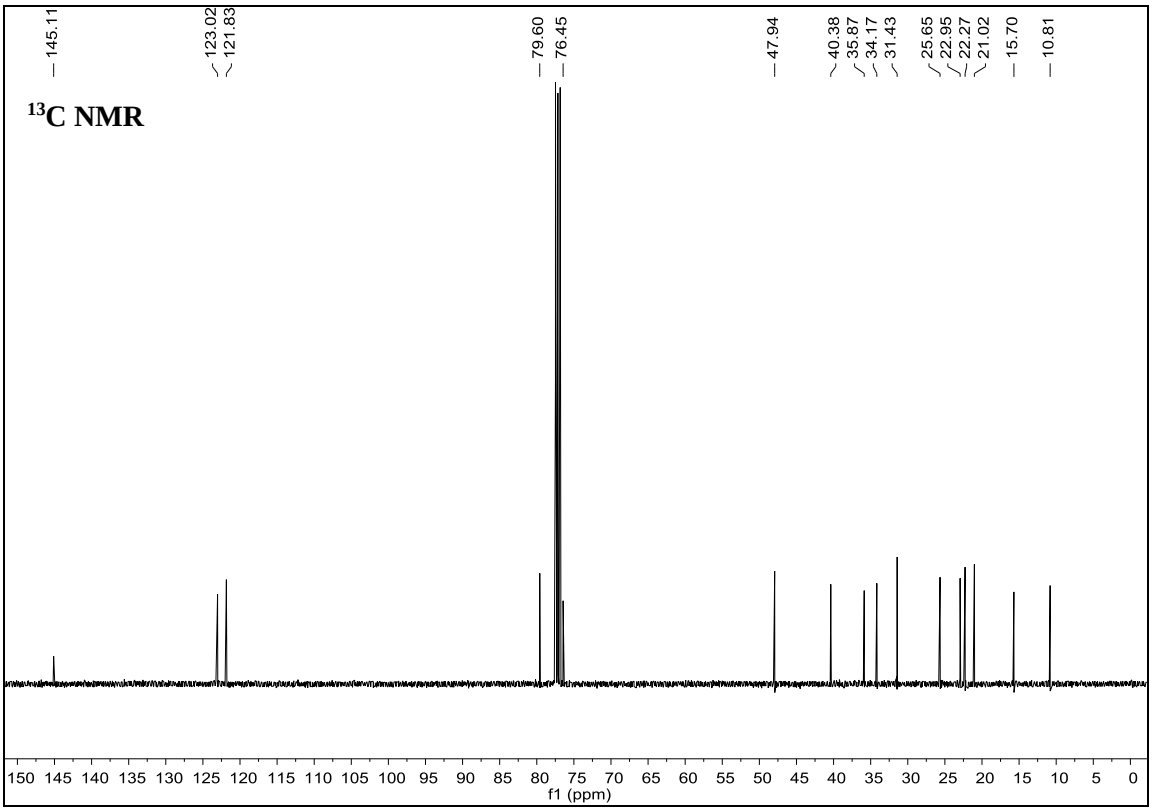

19F NMR
-78.89
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
f1 (ppm)

1-((1*S*,2*R*,4*S*)-(+)-Menthoxymethyl)-3-methylimidazolium chloride (8)



1-((1*S*,2*R*,4*S*)-(+)-menthoxymethyl)-2,3-dimethylimidazolium chloride (9)





7. References

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