Electronic Supplementary Information

Chiral protic imidazolium salts with (–)-menthol fragment in the cation – synthesis, properties and use in the Diels-Alder reaction

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ESI Contents

S1. Experimental. Materials. Analytical methods. Synthesis methods of substrates and chiral aprotic salts

Experimental

Materials

(1*R*,2*S*,5*R*)-(–)-Menthol (Aldrich, ≥99%), (1*S*,2*R*,5*S*)-(+)-Menthol (Aldrich, ≥99%), (±)-Menthol (Aldrich, ≥98%), paraformaldehyde (Sigma-Aldrich, 95%), imidazole (Sigma-Aldrich, ≥99,5%), lithium bis(trifluoromethanesulfonyl)imide, $LiNTf_2$ (IoLiTec, 99%), potassium hexafluorophosphate, KPF_6 (Sigma, ≥99%), sodium trifluoromethanesulfonate, NaOTf (Sigma-Aldrich, 98%), triethylamine anhydrous (Avantor Performance Materials Poland, min. 99.5%), hydrochloric acid (37%) were used to the synthesis of protic salts. 1-Methylimidazole (99%), 1-butylimidazole (98%), 1-bromodecane (98%), 1-hexanol (≥99%), sodium (cubes, contains mineral oil, 99.9% trace metals basis), sulfuric acid (≥96%) were used for the preparation of quaternary agents and aprotic ionic liquids and were purchased from Sigma-Aldrich. [Tetrabutylammonium][Δ-tris(tetrachloro-1,2-benzenediolato)phosphate(V)], in brief Δ-TRISPHAT tetrabutylammonium salt was supplied by Sigma-Aldrich.

Solvents such as hexane, toluene, acetone, methanol, ethanol, 1-propanol, DMSO, DMF, dichloromethane, chloroform, diethyl ether, ethyl acetate, 1,2-dichloroethane and acetonitrile were generally available products with high purity. Some of them before use were dried with commonly known methods. The drying agents, such as sodium sulphate (anhydrous, pure) and phosphorus pentoxide (powder, anhydrous, ≥98%) were provided by P.O.Ch (Gliwice, Poland).

Analytical methods

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ as the solvent on a Bruker DPX spectrometer (400.13 MHz for ^{1}H NMR and 100.62 MHz for ^{13}C NMR) or Bruker DRX spectrometer (600 MHz for ^{1}H and 75 MHz for ^{13}C) or Varian VNMRS spectrometer (600 MHz for ^{1}H and 150 MHz for ^{13}C). The chemical shifts were referred to TMS as the internal standard.

Elemental analyses were carried out for all synthesized salts and ionic liquids using VARIO EL-III. High-resolution mass spectra (HRMS) were recorded on a LCT Premier XE Waters spectrometer in positive ESI+ and negative ESI– ionization mode (TOF MS ES+/ TOF MS ES–). Sample was introduced through a standard electrospray ion source into the instrument.

The water content in the chiral ionic liquids was determined by Karl-Fischer titration using 831 KF Coulometer (Metrohm). The concentration of water in the chiral ionic liquids was below 150 ppm. The concentration of the proper metal (Na, K, Li) in the prepared salts was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) with Perkin-Elmer Optima 5300 DV instrument. Solutions were prepared by microwave-oven digestion of samples (125 mg) with Suprapur® nitric acid (3 ml) for 24 h. These were then diluted with deionized water to 25 ml. Standard solutions of Na, K or Li (0.5, 0.75 and 1.0 mg/L) were used for calibration. The metal concentrations in the synthesized salts were below 50 ppm based on the weight of the sample and the volume of the reconstituted solution.

The refractive index at 1000 mbar, n_D, for the studied new protic ionic liquid with bis(trifluoromethylsulfonyl)imide anion was measured on an Automatic Digital Refractometer RX-5000α (Atago

company) with an uncertainty of ± 0.00004 n_D units and a temperature probe measurement accuracy ± 0.1 °C. The testes were performed over a wide temperature range, from 20 °C till 60 °C. Before each measurement, the refractive index of pure distilled water was measured and compared with known literature values. The specific rotation $[\alpha]^{20}_D$ was measured on a AUTOPOL IV (Rudolph Research Analytical) polarimeter for solutions in ethanol.

Thermogravimetric analyses used a thermobalance TG 209 F1 Libra (Netzsch). The sample was loaded in an Al_2O_3 crucible and heated from 25 °C to 1000 °C at 5 °C/min in air (25 ml/min) with nitrogen (10 ml/min) as the purge gas. The TGA temperature calibration used five calibration standards (indium, bismuth, zinc, aluminium and silver; each was over > 99.999% pure) in nitrogen atmosphere.

Modulated differential scanning calorimetry (MDSC) was performed using a TA Instruments model Q100 DSC. The sample was loaded on an aluminium pan sealed with pinhole cap. The liquid salt data was collected at a constant cooling/heating rate of 5 °C·min^{-1} in nitrogen atmosphere. This was first cooled from 20 °C to -90 °C and then heated from -90 °C to 150 °C. The second cooling mode was from 150 °C to -90 °C. The modulation period was 60 s, and the modulation amplitude was ±0.8 °C. Phase transition temperatures were determined according to ISO 11357-1:2009(E) using the midpoint temperature. Indium and mercury were used as standards to calibrate the temperature. Heat calibration used indium.

Synthesis of substrates

Chloromethyl (1*R*,2*S*,5*R*)-(−)-menthyl ether was obtained by passing HCl through a mixture of paraformaldehyde and (1*R*,2*S*,5*R*)-(−)-menthol similar to Pernak et al.[1] In the same way chloromethyl (1*S*,2*R*,5*S*)-(+)-menthyl ether and chloromethyl (±)-menthyl ether were prepared from (+)-menthol and (±)-menthol as starting material respectively. Imidazole was freshly recrystallized from benzene (mp 90-91 °C). The 1-methylimidazole and 1-butylimidazole were purchased, and 1-decylimidazole was obtained following published method[2]. Triethylamine was distilled twice - the first from phthalic anhydride to remove lower amines resulting from autoxidation during storage. Chloromethyl hexyl ether was prepared by passing HCl through a mixture of formaldehyde and decanol as described previously[3] and then with 1-hexyloxymethylimidazole. The 1-pyridine was dried by azeotropic distillation with chloroform. Those substrates were freshly distilled each time before using them.

The **1-(1*R*,2*S*,5*R*)-(−)-menthoxymethylimidazole (–)[Ment-Im]** and **(±)-menthoxymethylimidazole (±)[Ment-Im]** were synthesized through a two-step reaction using trimethylamine, chloromethyl (1*R*,2*S*,5*R*)-(−)-menthyl ether or chloromethyl (±)-menthyl ether and imidazole following the method of Feder-Kubis et al.[4] The crude product was crystallized from hexane-acetone to form long needles with the same melting point (48-50 °C) as reported previously.

Synthesis of aprotic imidazolium salts

Synthesis of aprotic ionic liquids with (1*R*,2*S*,5*R*)-(−)-menthol moiety having 1-alkylimidazoles, or 1-alkoxymethylimidazole or pyridinium part in the cation were obtained according the procedures described previously: 1-[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]pyridinium bis(trifluoromethanesulfonyl)imide (–)[Ment-Py][NTf_2],[5]

3-alkyl-1-[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium bis(trifluoromethanesulfonyl)imides (with alkyl chain: methyl, butyl and decyl) (–)[C_1-Ment-Im][NTf_2], (–)[C_4-Ment-Im][NTf_2], (–)[C_{10}-Ment-Im][NTf_2],[2] 3-hexyloxymethyl-1-(1*R*,2*S*,5*R*)-(−)-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)imide (–)[C_6O-Ment-Im][NTf_2].[3]

3-butyl-1-[(1*S*,2*R*,5*S*)-(+)-menthoxymethyl]imidazolium bis(trifluoromethanesulfonyl)imide, (+)[C_4-Ment-Im][NTf_2], as representative of aprotic chiral ionic liquid with (+)-menthol moiety in the cation, was prepared in analogous way to other aprotic salts.

Solubility

The solubility of the salts was determined according to Vogel's Textbook of Practical Organic Chemistry.[6] The analyses were performed for all of the new protic salts ((–)[H-Ment-Im][Cl], (–)[H-Ment-Im][NTf_2], (–)[H-Ment-Im][OTf], (–)[H-Ment-Im][PF_6]) at 25 ºC and at 50 ºC under ambient pressure using commonly used solvents. The phrase *complete solubility* describes salts that are soluble (0.1 g in 1 mL of solvent); *limited solubility* describes salts in which 0.1 g of salt is soluble in 3 mL of a solvent. The phrase *insoluble* describes insolubility (less than 0.1 g of the salt in 3 mL of a solvent).

S2. Reaction yield, HRMS analyses and elemental analyses of 1-(1*R*,2*S*,5*R*)-(–)-menthoxymethylimidazole, (±)-menthoxymethylimidazole and chiral aprotic salts

1-(1*R*,2*S*,5*R*)-(–)-Menthoxymethylimidazole (–)[Ment-Im].

Yield: 97.5%.

Elemental analysis calc. (%) for $[C_{14}H_{24}N_2O+H]^+$ (236.35): C 71.14, H 10.23, N 11.85, found: C 71.22, H 10.34, N 11.73.

(±)-Menthoxymethylimidazole (±)[Ment-Im].

Yield: 87%.

Spectroscopic data were the same as for (–)**[Ment-Im][4].**

1-[(1*R*,2*S*,5*R*)-(–)-Menthoxymethyl]pyridinium bis(trifluoromethanesulfonyl)imide (–)[Ment-Py][NTf_2].

Yield: 93.5%.

Elemental analysis calc. (%) for $C_{18}H_{26}F_6N_2O_5S_2$ (528.53): C 40.90, H 4.96, N 5.30, found: C 40.82, H 5.09, N 5.33.

HRMS (ESI+): m/z (%) calcd for $[C_{16}H_{26}NO]^+$: 248.2014, found: 248.2014.

1-[(1*R*,2*S*,5*R*)-(–)-Menthoxymethyl]-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (–)[C_1-Ment-Im][NTf_2]

Yield: 99.0%.

Elemental analysis calc. (%) for $C_{17}H_{27}F_6N_3O_5S_2$ (531.53): C 38.41, H 5.12, N 7.905, found: C 38.50, H 5.23, N 7.82.

HRMS (ESI+): m/z (%) calcd for $[C_{15}H_{27}N_2O]^+$: 251.2123, found: 251.2118.

HRMS (ESI–): m/z (%) calcd for $[C_2F_6NO_4S_2]^-$: 279.9173, found: 279.9178.

3-Butyl-1-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethanesulfonyl)imide (–)[C_4-Ment-Im][NTf_2]

Yield: 99.0%.

Elemental analysis calc. (%) for $C_{20}H_{33}F_6N_3O_5S_2$ (573.61): C 41.88, H 5.80, N 7.325, found: C 41.95, H 5.91, N 7.20.

HRMS (ESI+): m/z (%) calcd for $[C_{18}H_{33}N_2O]^+$: 293.2593, found: 293.2608.

HRMS (ESI–): m/z (%) calcd for $[C_2F_6NO_4S_2]^-$: 279.9173, found: 279.9177.

3-Butyl-1-[(1*S*,2*R*,5*S*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethanesulfonyl)imide (+)[C_4-Ment-Im][NTf_2]

Yield: 97.0; $[\alpha]^{20}_D = +53.07$

Elemental analysis calc. (%) for $C_{20}H_{33}F_6N_3O_5S_2$ (573.61): C 41.88, H 5.80, N 7.325, found: C 41.99, H 5.93, N 7.17

3-decyl-1-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethanesulfonyl)imide (–)[C_{10}-Ment-

Im][NTf_2]

Yield: 98.0%.

Elemental analysis calc. (%) for $C_{26}H_{45}F_6N_3O_5S_2$ (657.27): C 47.47, H 6.90, N 6.39, found: C 47.35, H 7.03, N 6.49.

HRMS (ESI+): m/z (%) calcd for $[C_{24}H_{45}N_2O]^+$: 377.3532, found: 377.3531.

HRMS (ESI–): m/z (%) calcd for $[C_2F_6NO_4S_2]^-$: 279.9173, found: 279.9179.

3-Hexyloxymethyl-1-(1*R*,2*S*,5*R*)-(–)-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)imide (–)[C_6O-Ment-Im][NTf_2]

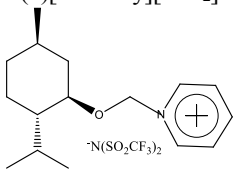
Yield: 94.5%.

Elemental analysis calc. (%) for $C_{23}H_{39}F_6N_3O_6S_2$ (631.69): C 43.73, H 6.22, N 6.65, found: C 43.81, H 6.35, N 6.49.

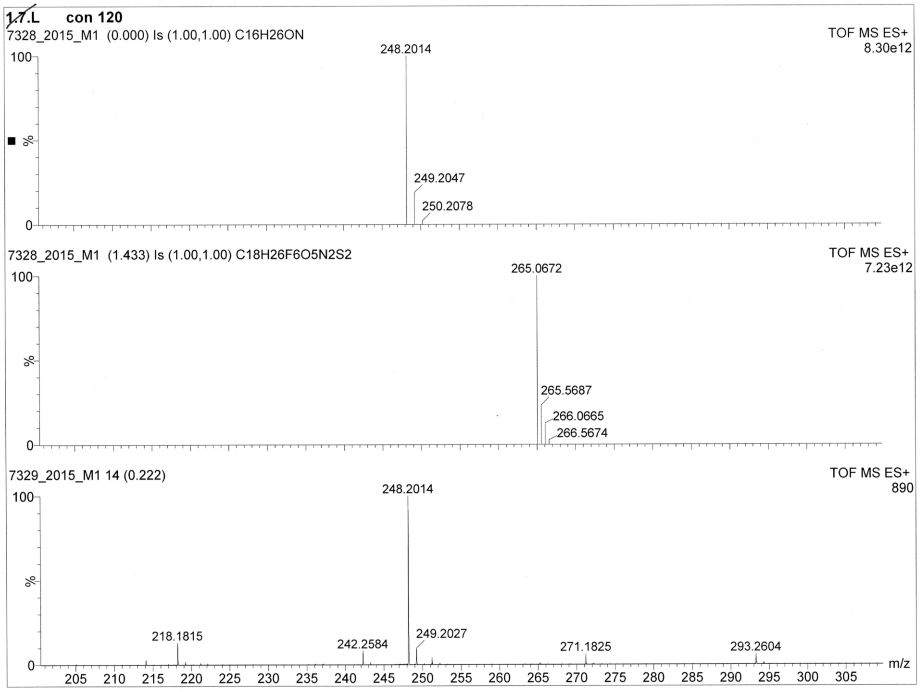
HRMS (ESI+): m/z (%) calcd for $[C_{21}H_{39}N_2O_2]^+$: 351.3011, found: 351.3001.

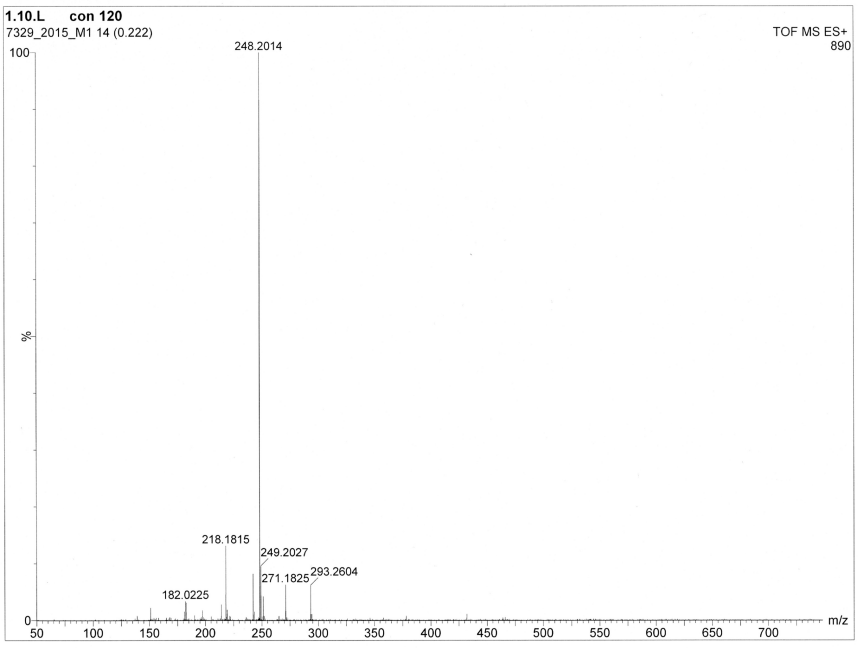
S3. Copies of HRMS spectra of aprotic salts

HRMS spectrum of 1-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]pyridinium bis(trifluoromethanesulfonyl)imide, (–)[Ment-Py][NTf_2]

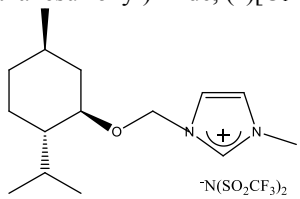


HRMS (ESI +) of (–)[Ment-Py][NTf_2]

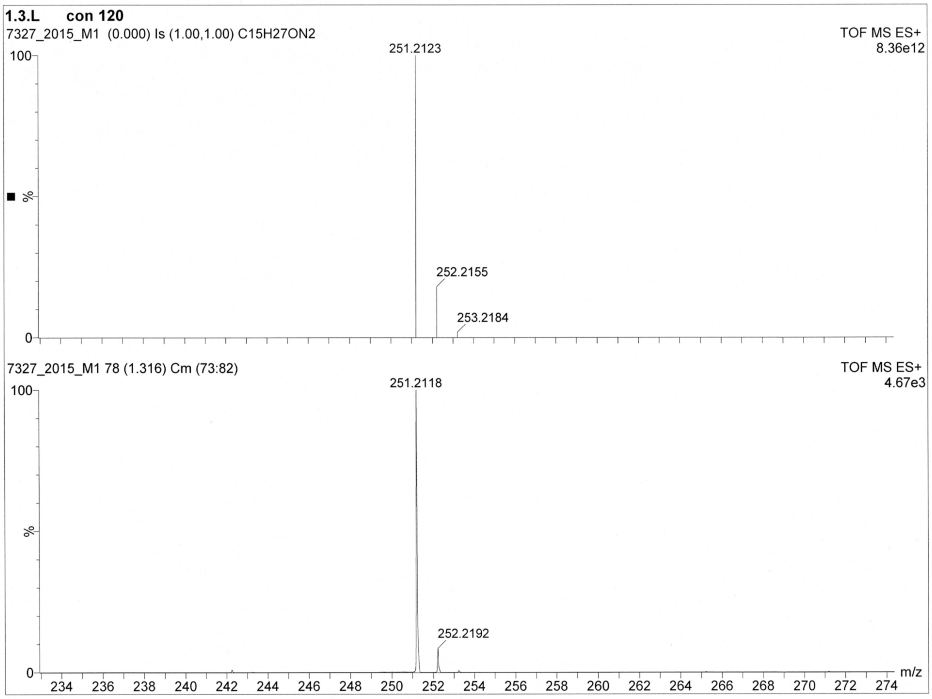


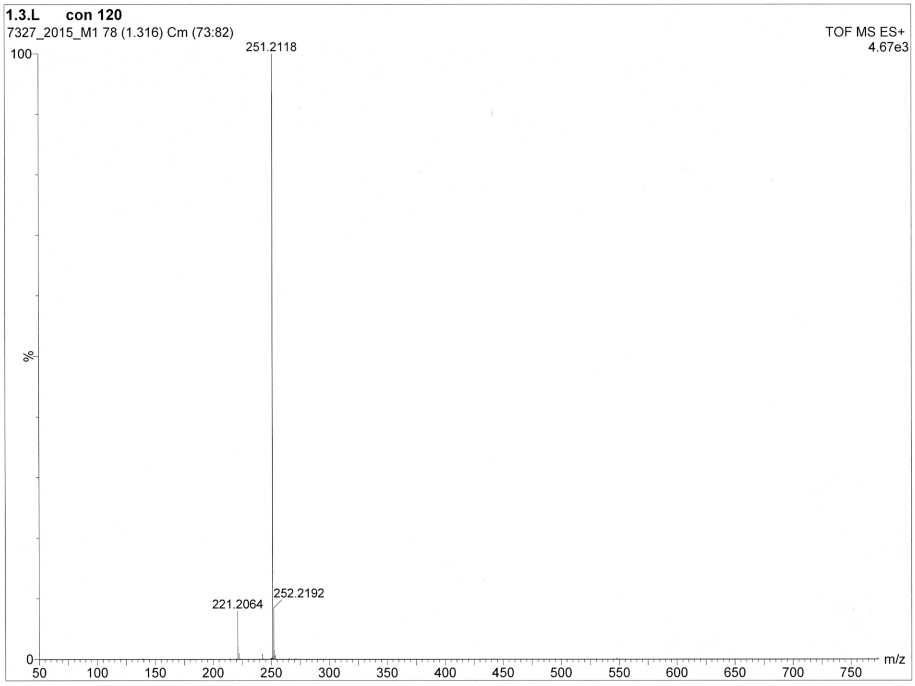


HRMS spectrum of 1-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, (–)[C_1-Ment-Im][NTf_2]

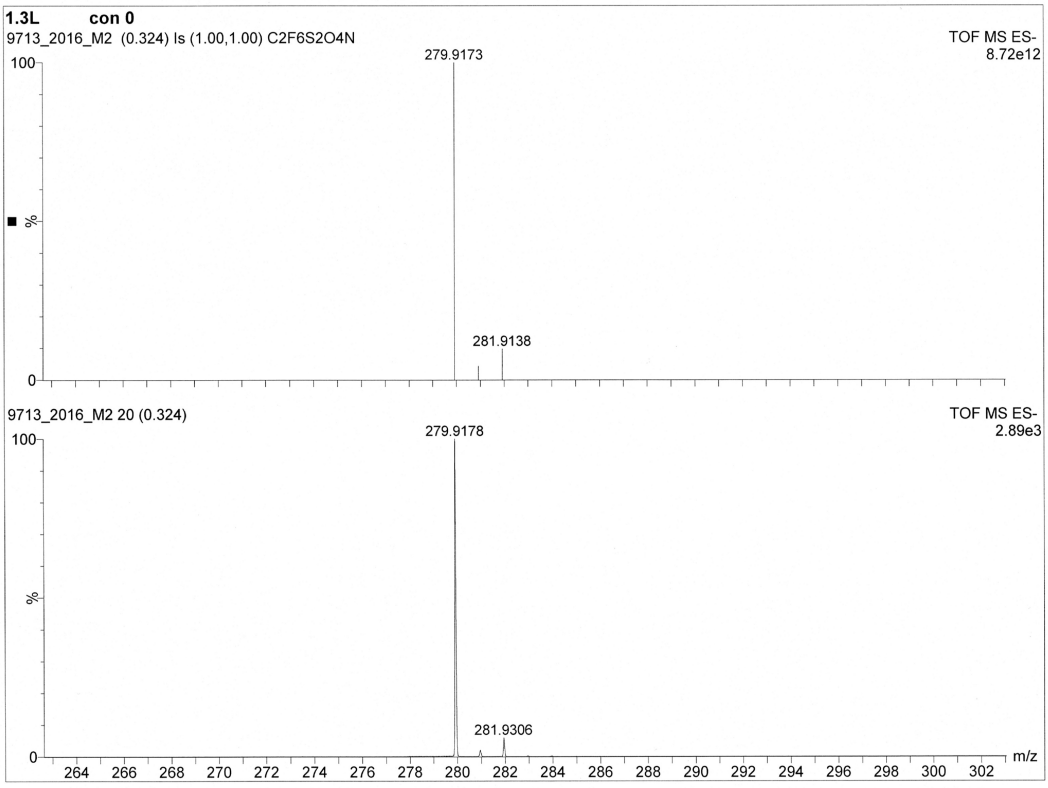


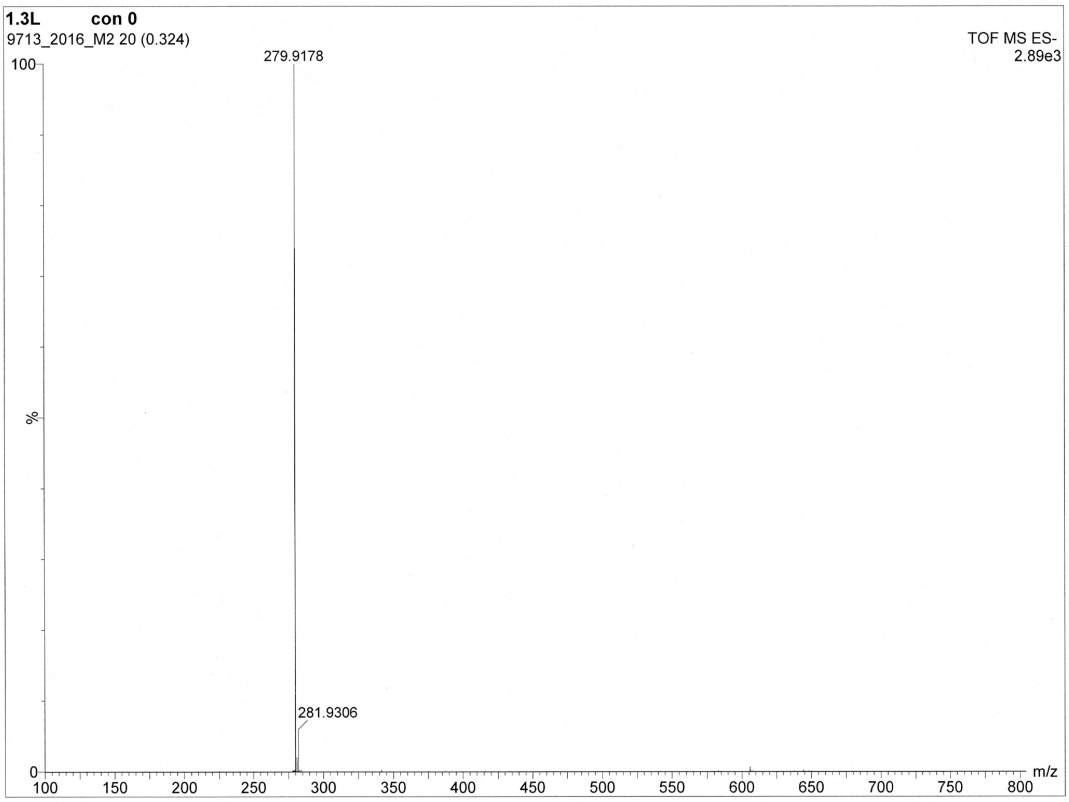
HRMS (ESI +) of (–)[C_1-Ment-Im][NTf_2]



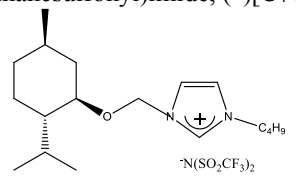


HRMS (ESI –) of (–)[C_1-Ment-Im][NTf_2]

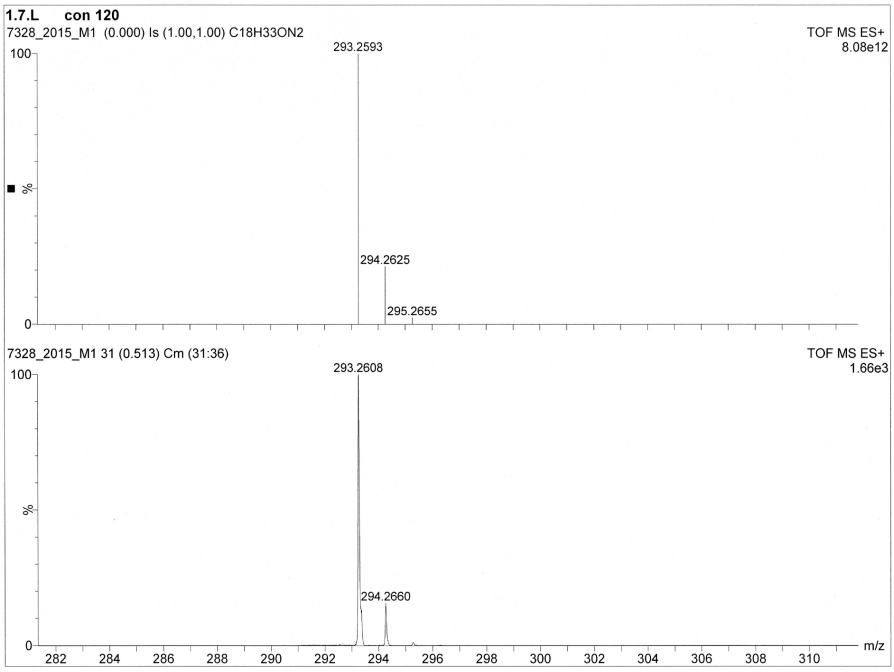


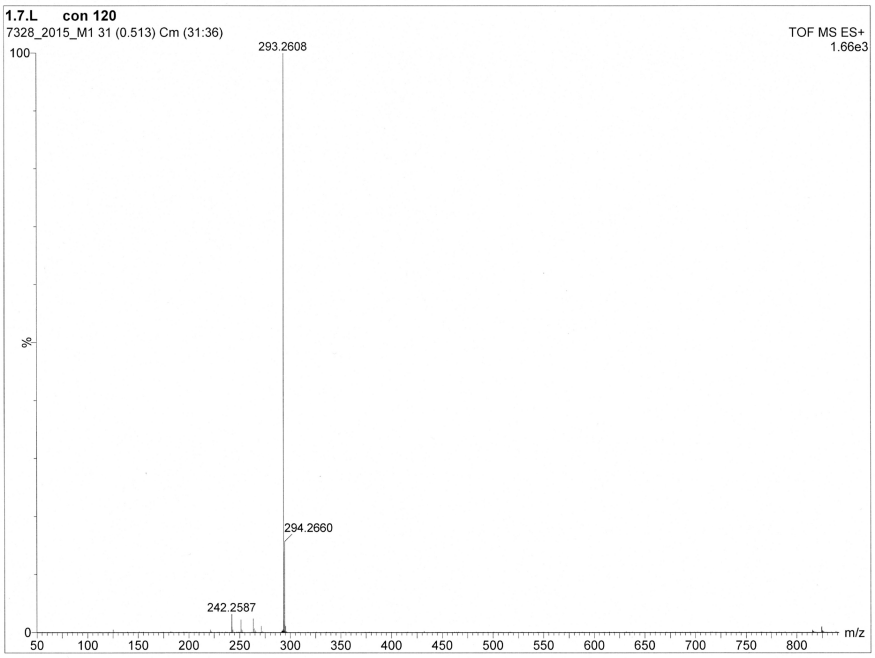


HRMS spectrum of 3-butyl-1-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethanesulfonyl)imide, (–)[C_4-Ment-Im][NTf_2]

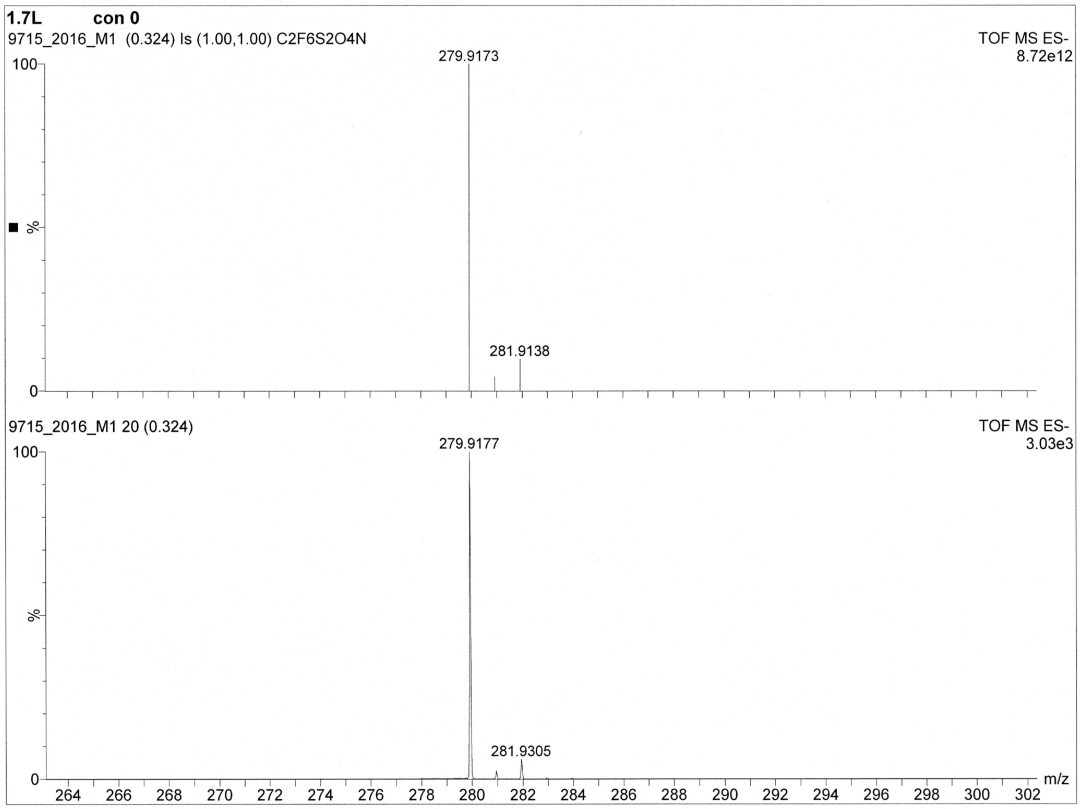


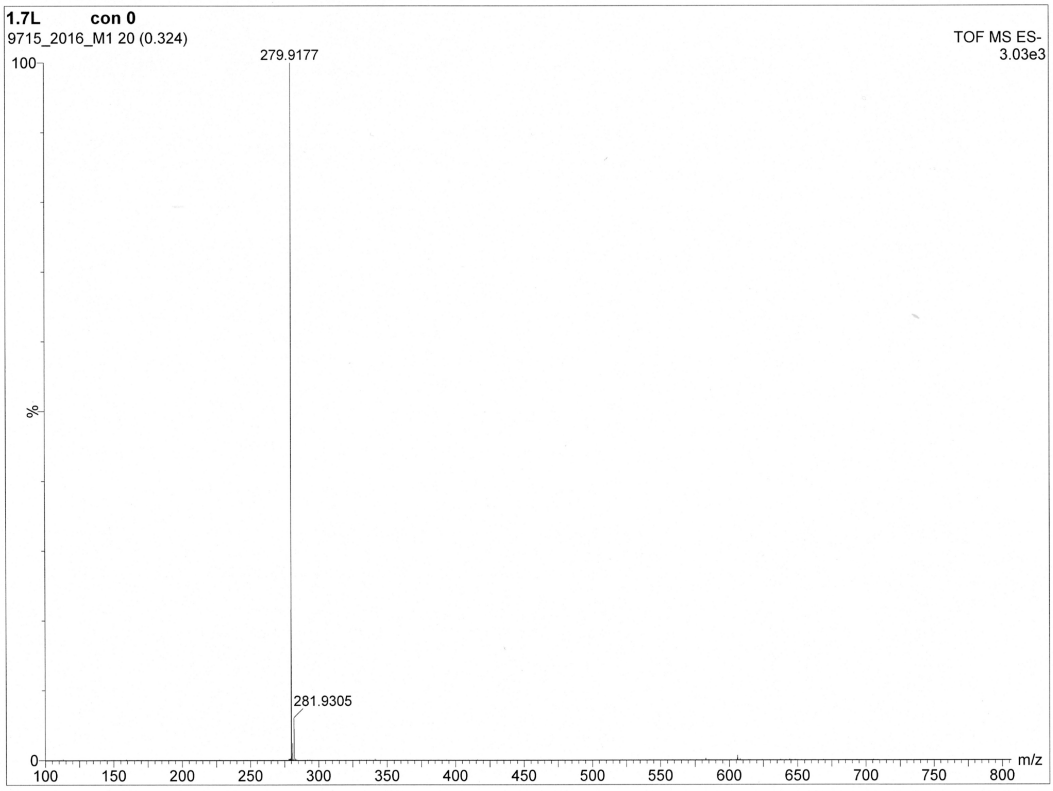
HRMS (ESI +) of (–)[C_4-Ment-Im][NTf_2]



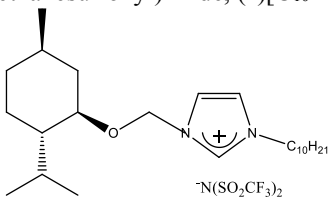


HRMS (ESI –) of (–)[C_4-Ment-Im][NTf_2]

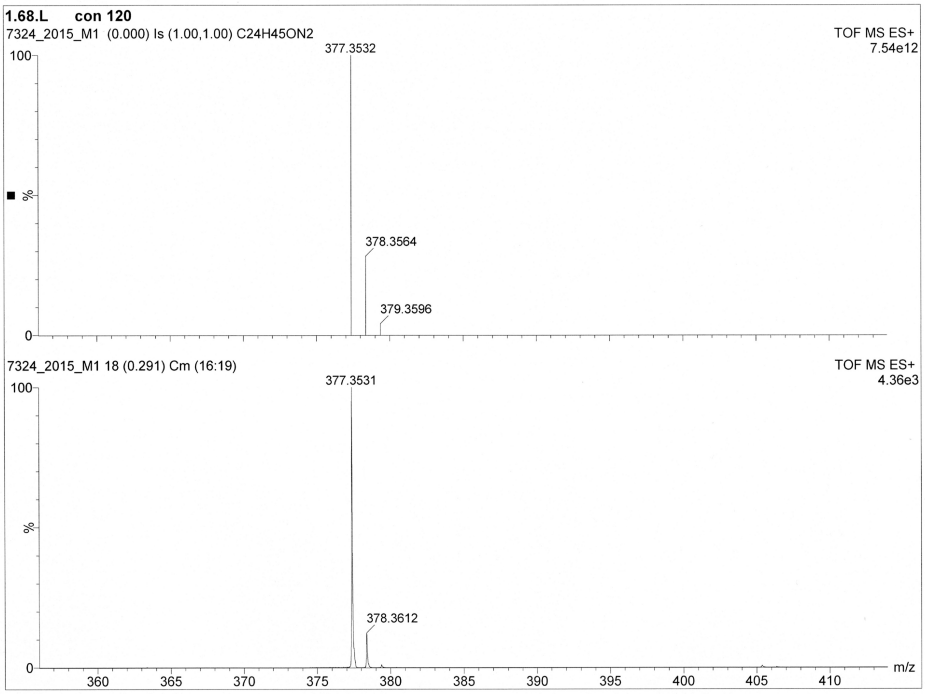


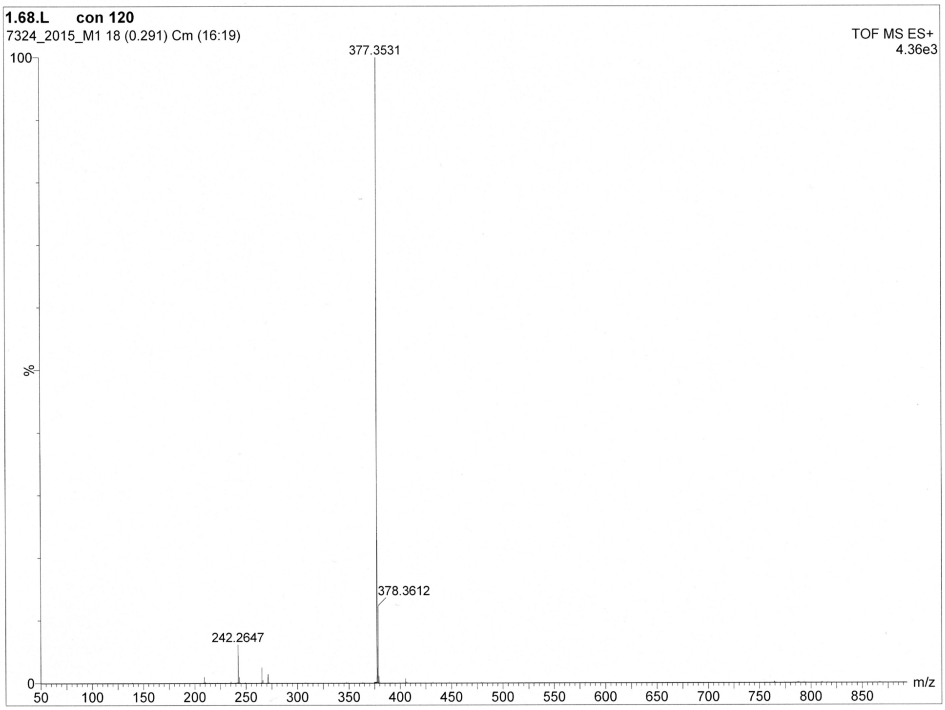


HRMS spectrum of 3-decyl-1-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethanesulfonyl)imide, (–)[C_{10}-Ment-Im][NTf_2]

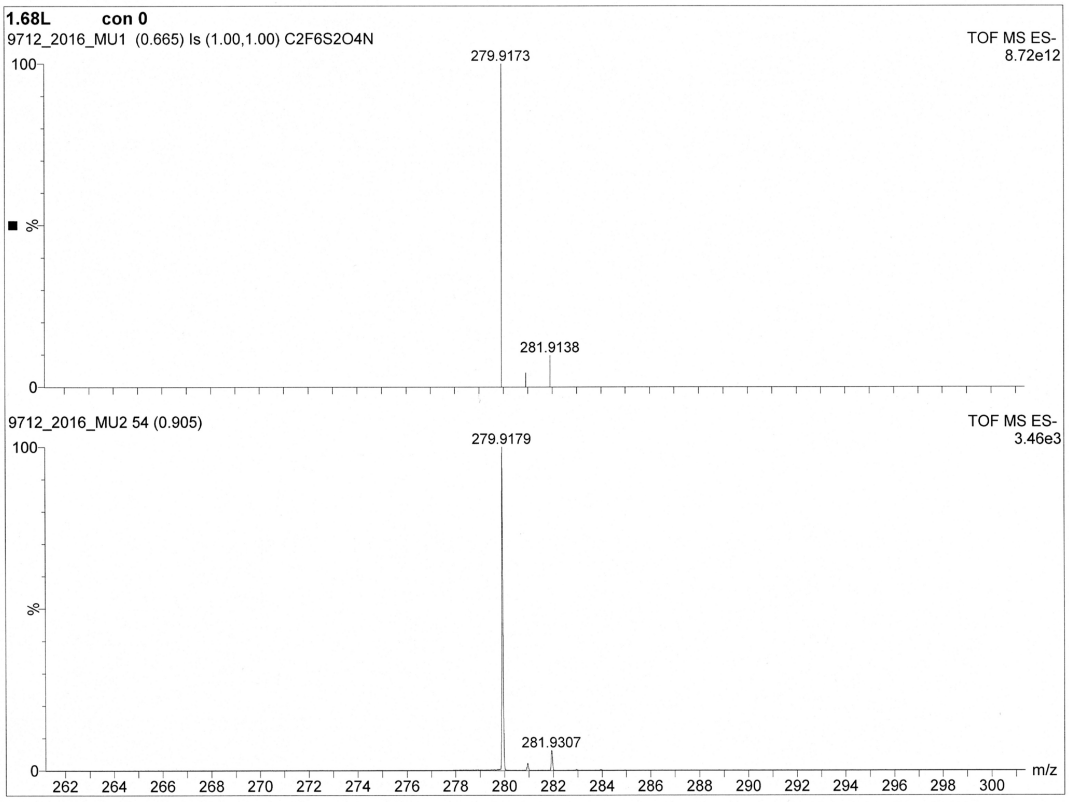


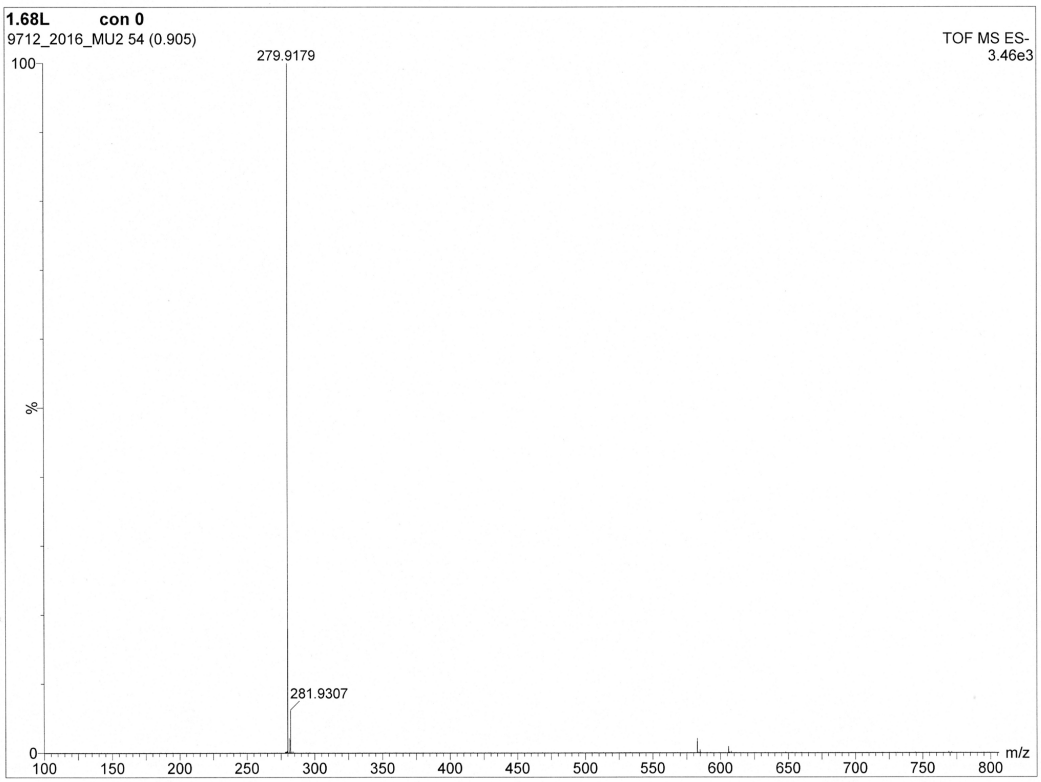
HRMS (ESI +) of (–)[C_{10}-Ment-Im][NTf_2]



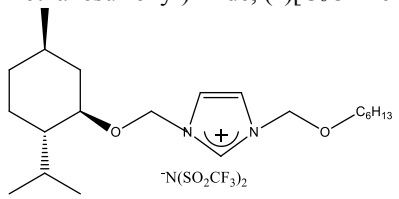


HRMS (ESI –) of (–)[C_{10}-Ment-Im][NTf_2]

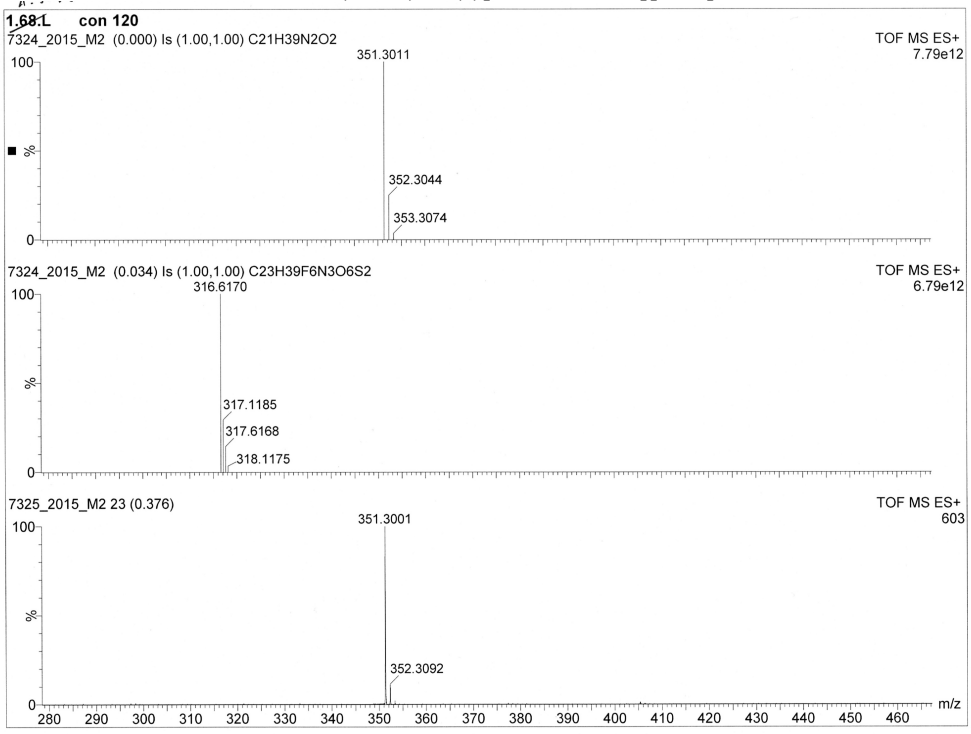


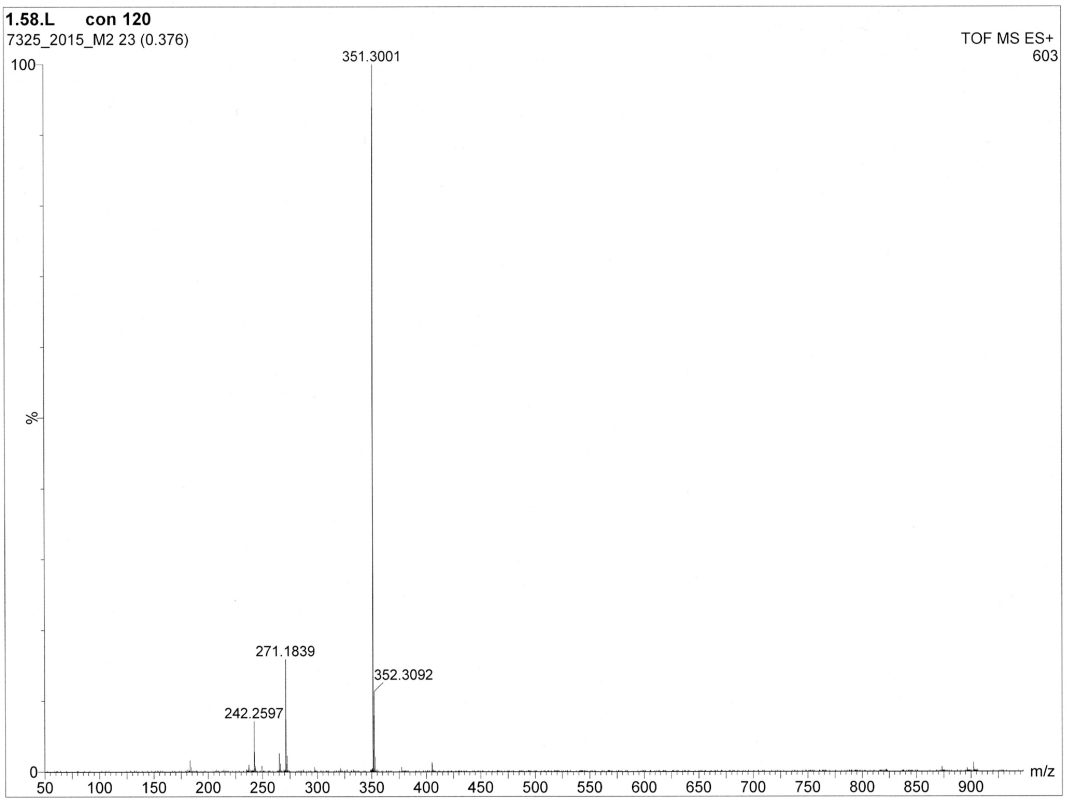


HRMS spectrum of 3-hexyloxymethyl-1-(1*R*,2*S*,5*R*)-(–)-menthoxymethylimidazolium bis(trifluoromethanesulfonyl)imide, (–)[C_6O-Ment-Im][NTf_2]



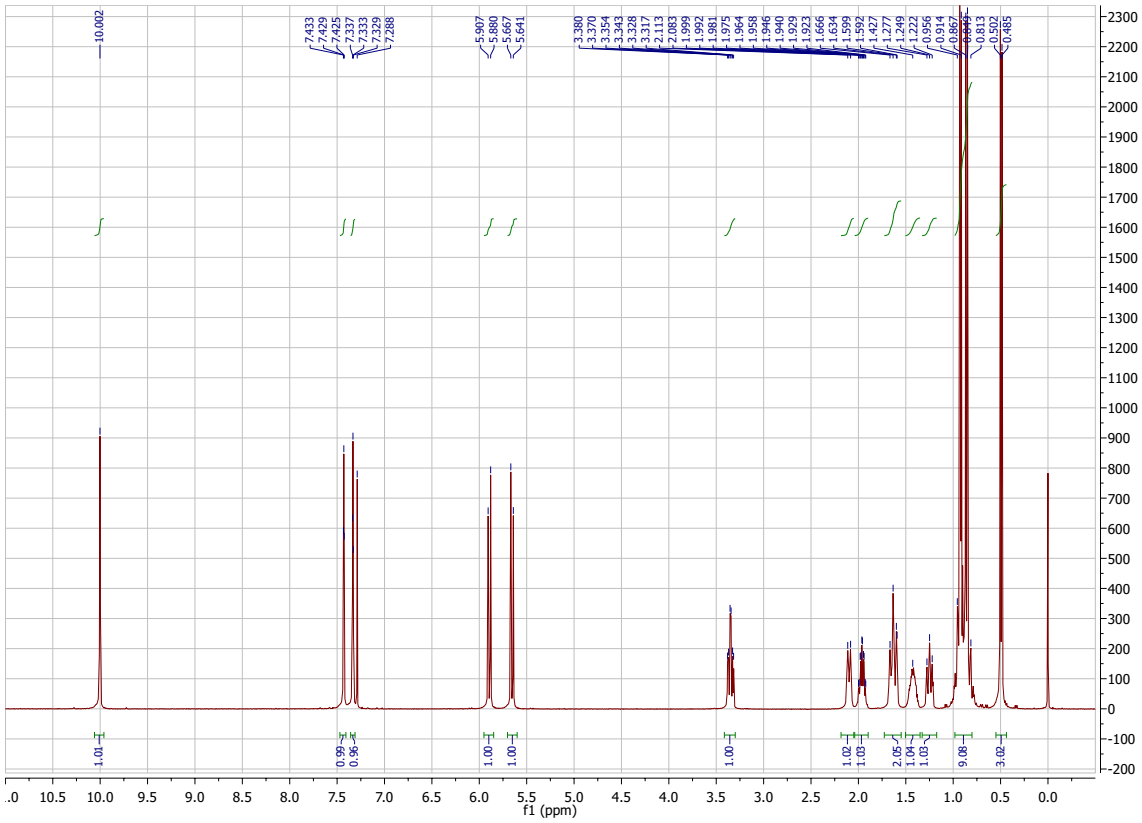
HRMS (ESI +) of (–)[C_6O-Ment-Im][NTf_2]



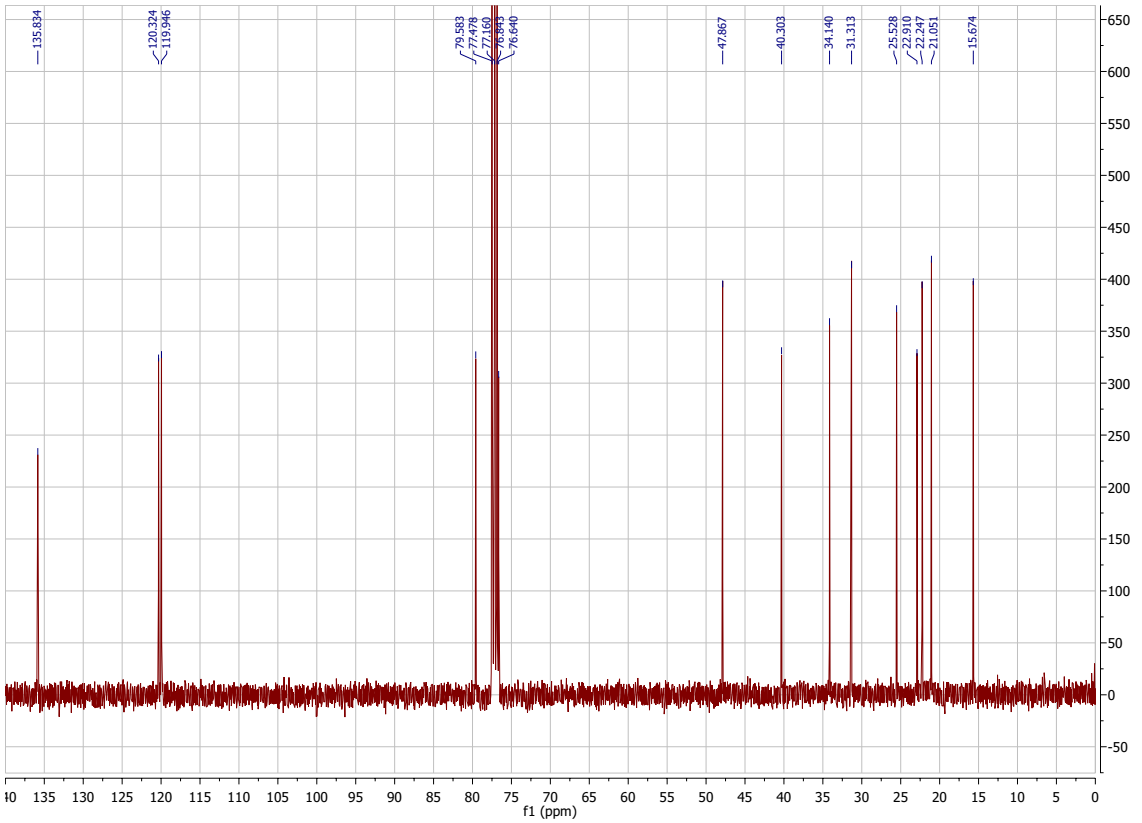


S4. Copies of ^{1}H NMR, ^{13}C NMR and HRMS spectra of 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium chloride, (–)[H-Ment-Im][Cl]

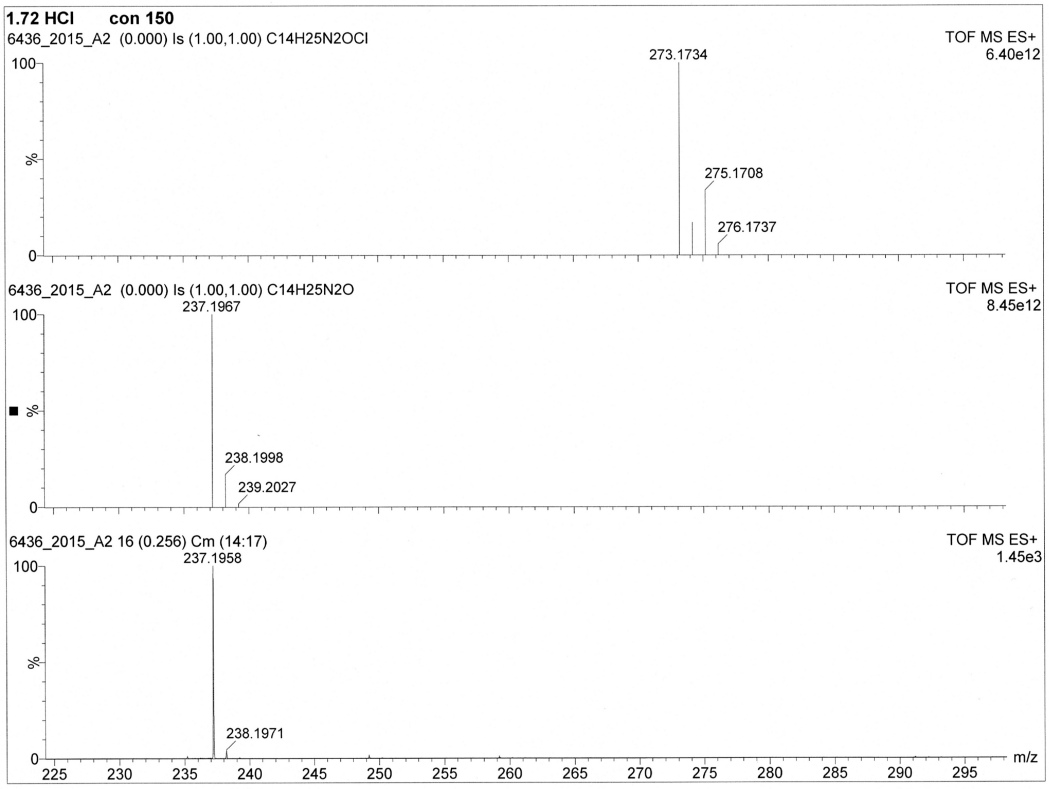
^{1}H NMR spectrum of (–)[H-Ment-Im][Cl] (400 MHz,$CDCl_3$)

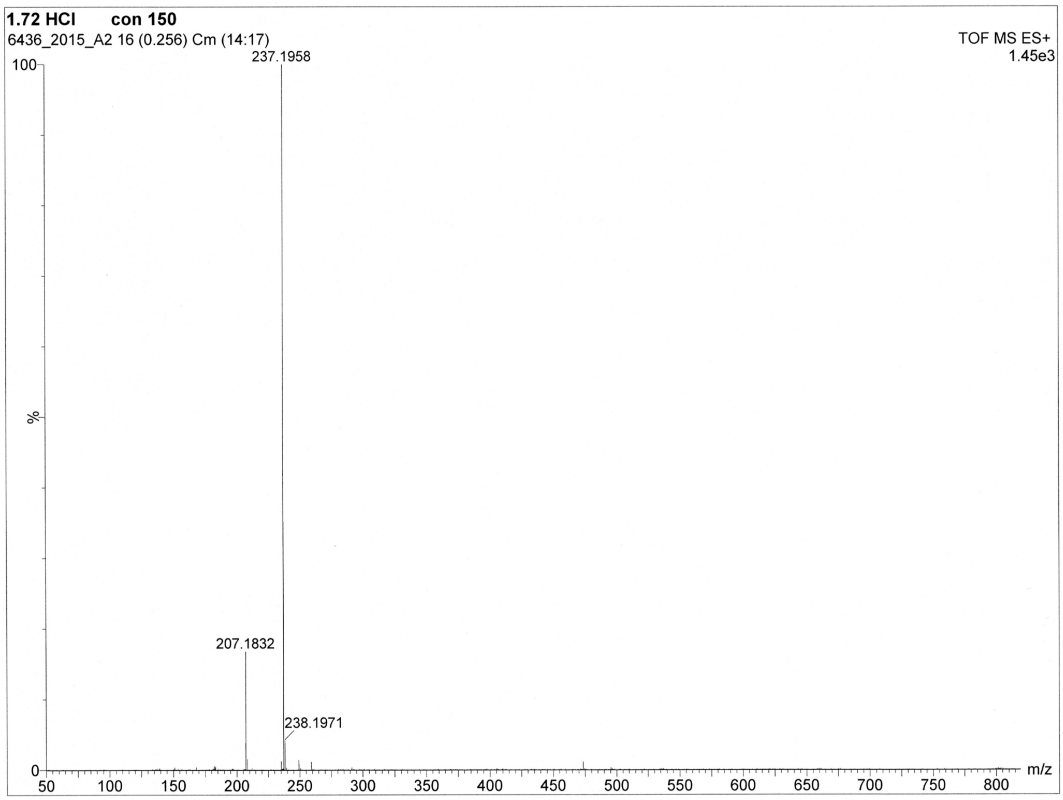


^{13}C NMR spectrum of (–)[H-Ment-Im][Cl] (100 MHz,$CDCl_3$)



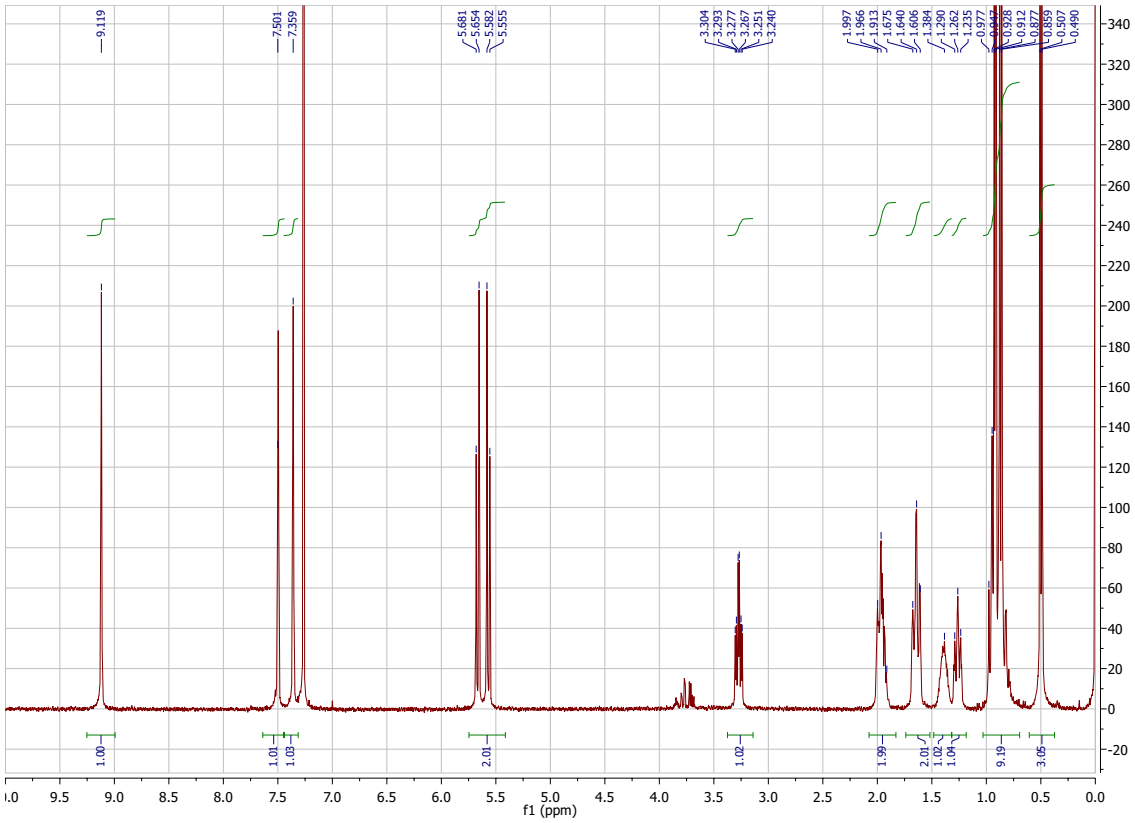
HRMS (ESI +) of (–)[H-Ment-Im][Cl]



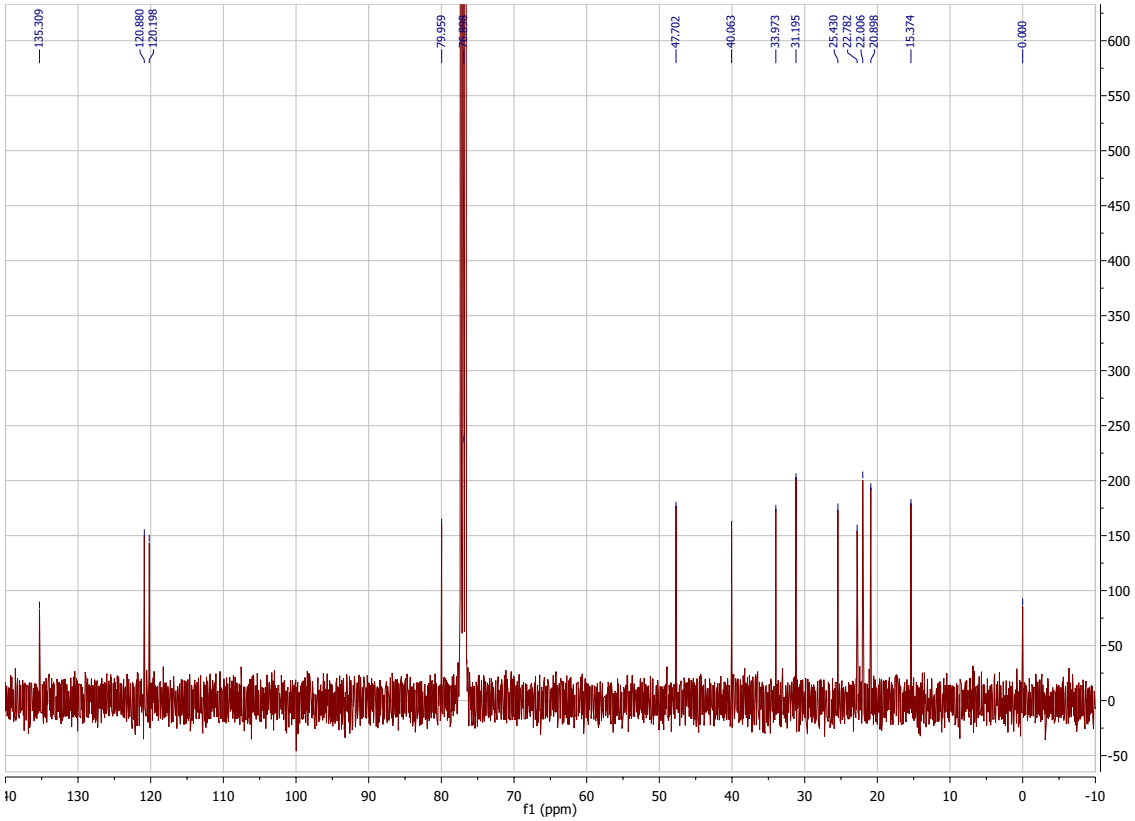


S5. Copies of ^{1}H and ^{13}C NMR spectra of chiral protic imidazolium salts

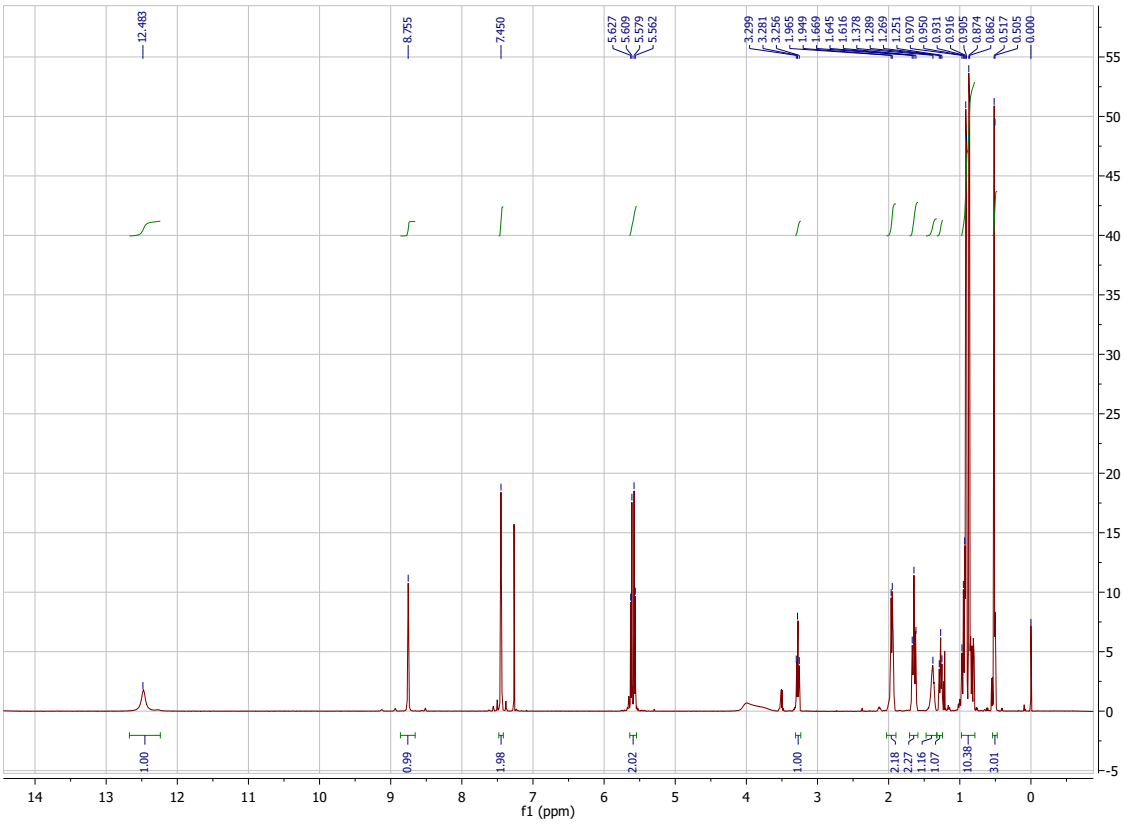
^{1}H NMR spectrum of 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium trifluoromethanesulfonate, (–)[H-Ment-Im][OTf] (400 MHz,$CDCl_3$)



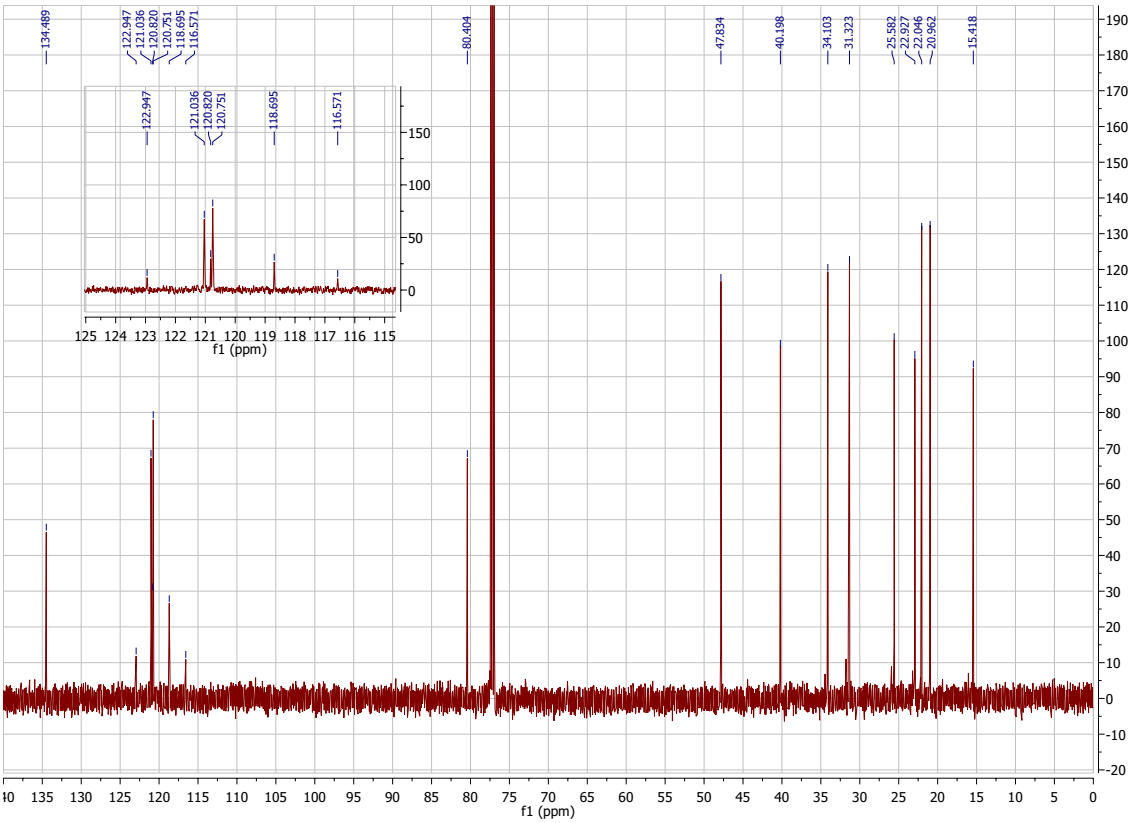
^{13}C NMR spectrum of 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium trifluoromethanesulfonate, (–)[H-Ment-Im][OTf] (100 MHz, $CDCl_3$)



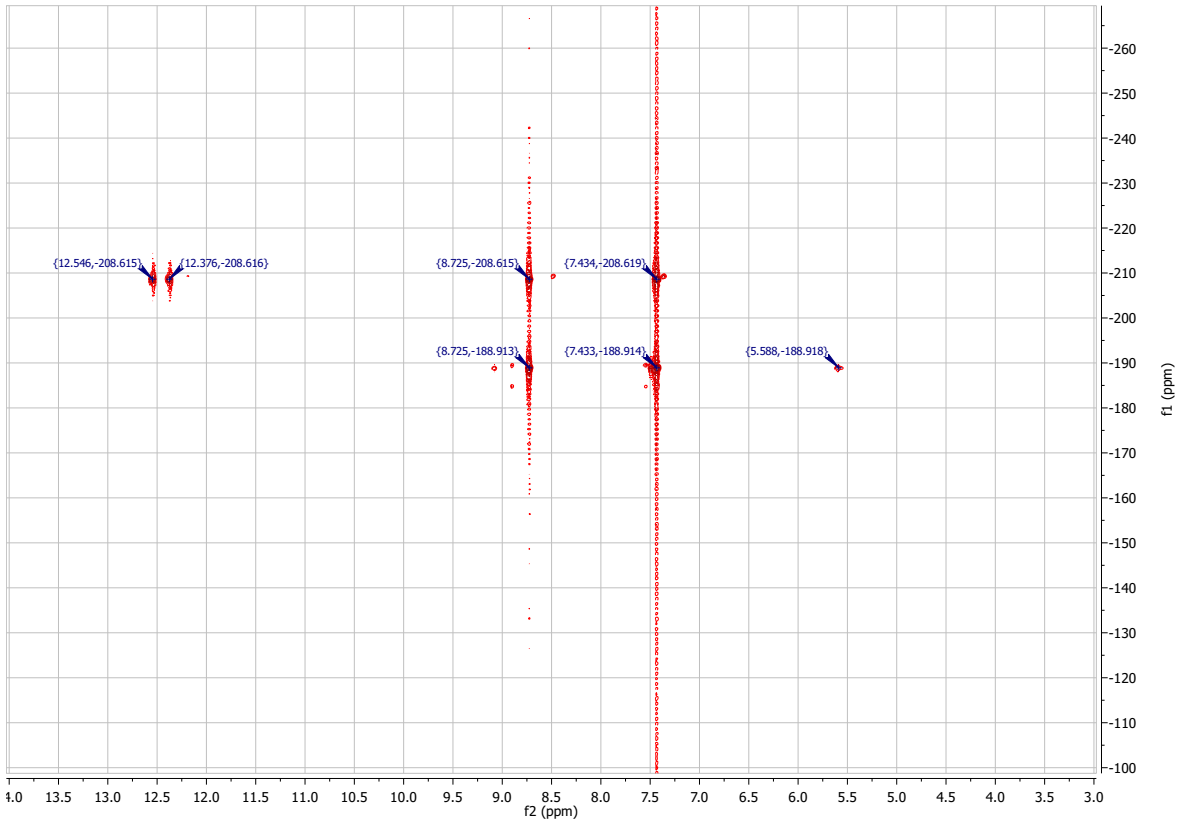
^{1}H NMR spectrum of 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethylsulfonyl)imide, (–)[H-Ment-Im][NTf_2] (600 MHz,$CDCl_3$)



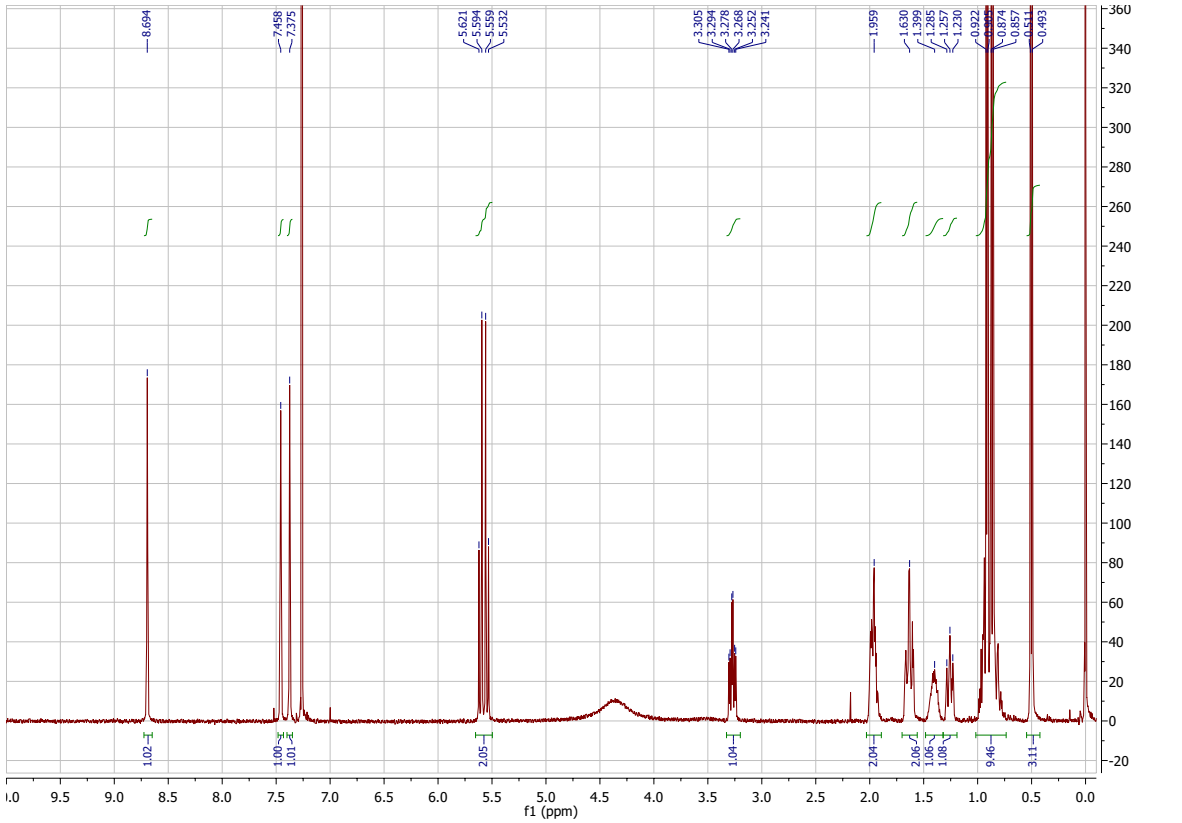
^{13}C NMR spectrum of 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethylsulfonyl)imide, (–)[H-Ment-Im][NTf_2] (150 MHz,$CDCl_3$)



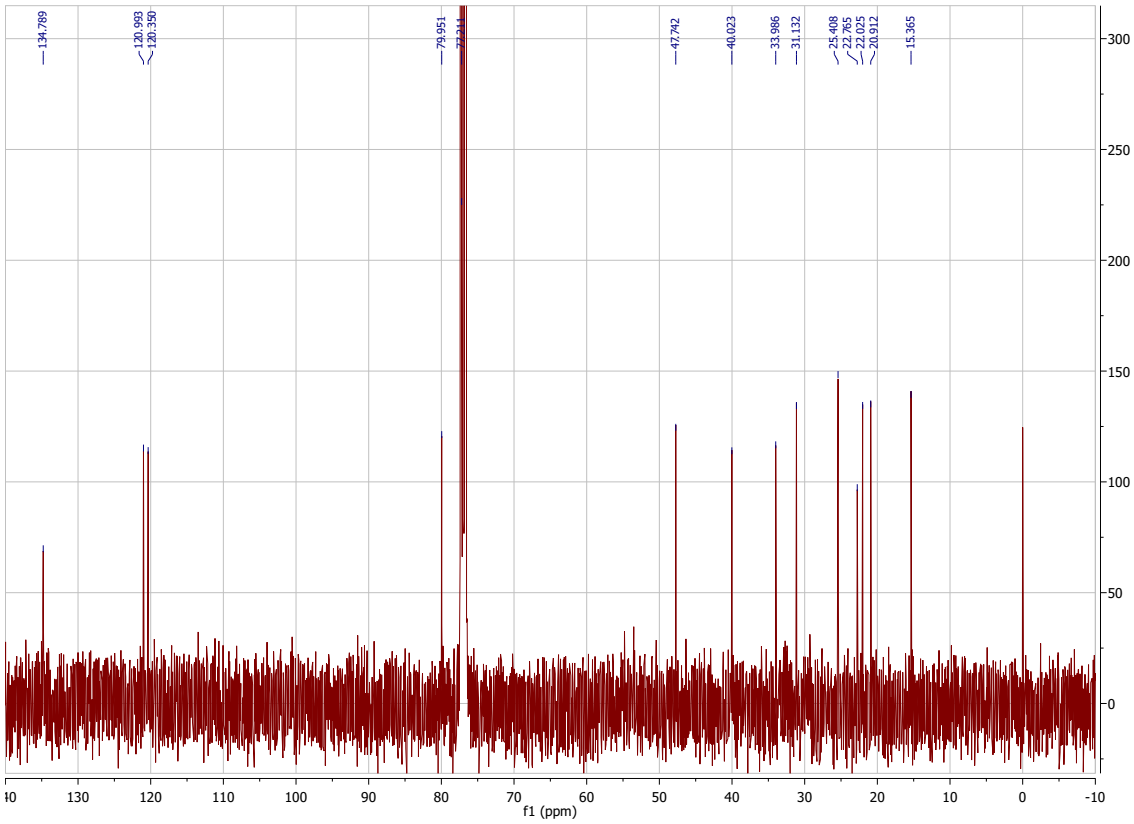
$^{1}H(^{15}N)$ HMBCAD spectrum of 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethylsulfonyl)imide, (–)[H-Ment-Im][NTf_2]



^{1}H NMR spectrum of 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium hexafluorophosphate, (–)[H-Ment-Im][PF_6] (400 MHz,$CDCl_3$)

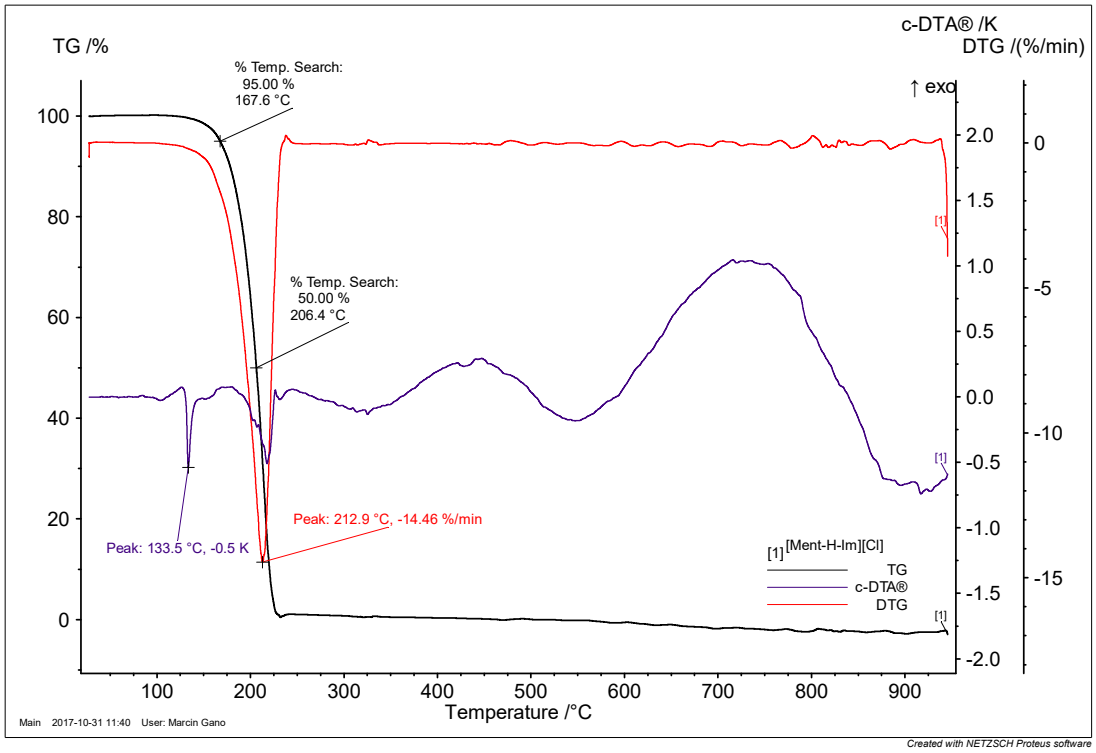


^{13}C NMR spectrum of 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium hexafluorophosphate, (–)[H-Ment-Im][PF_6] (100 MHz,$CDCl_3$)

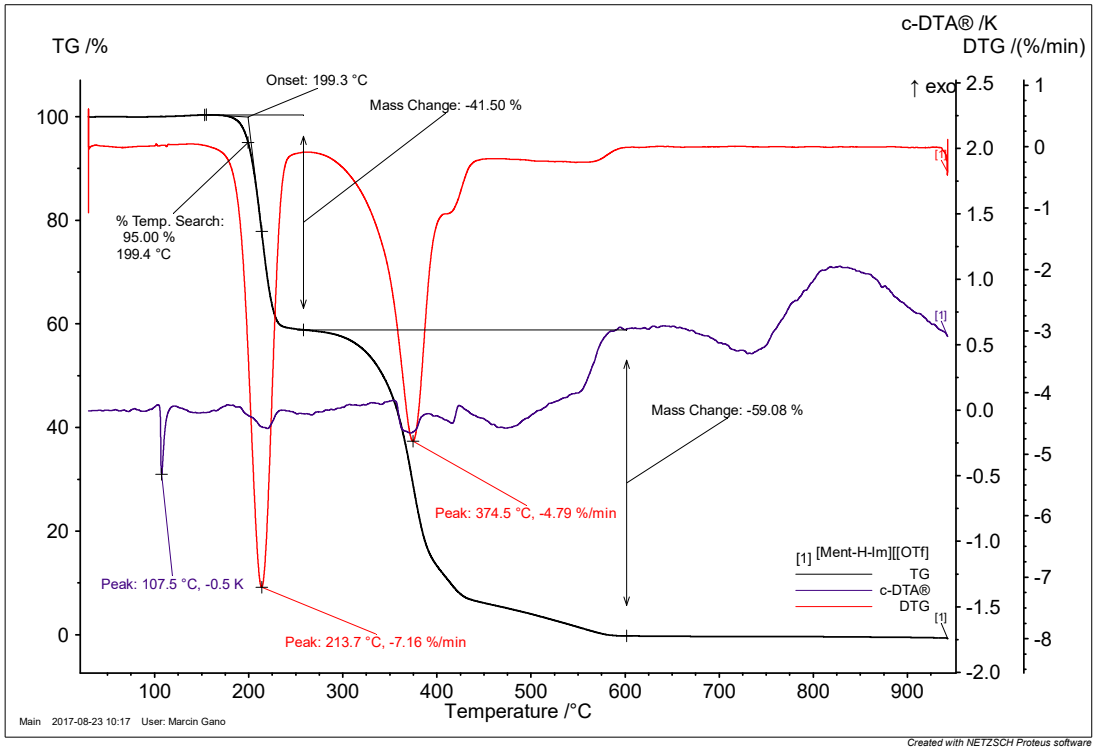


S6. Curves from thermogravimetric analysis of chiral protic imidazolium salts

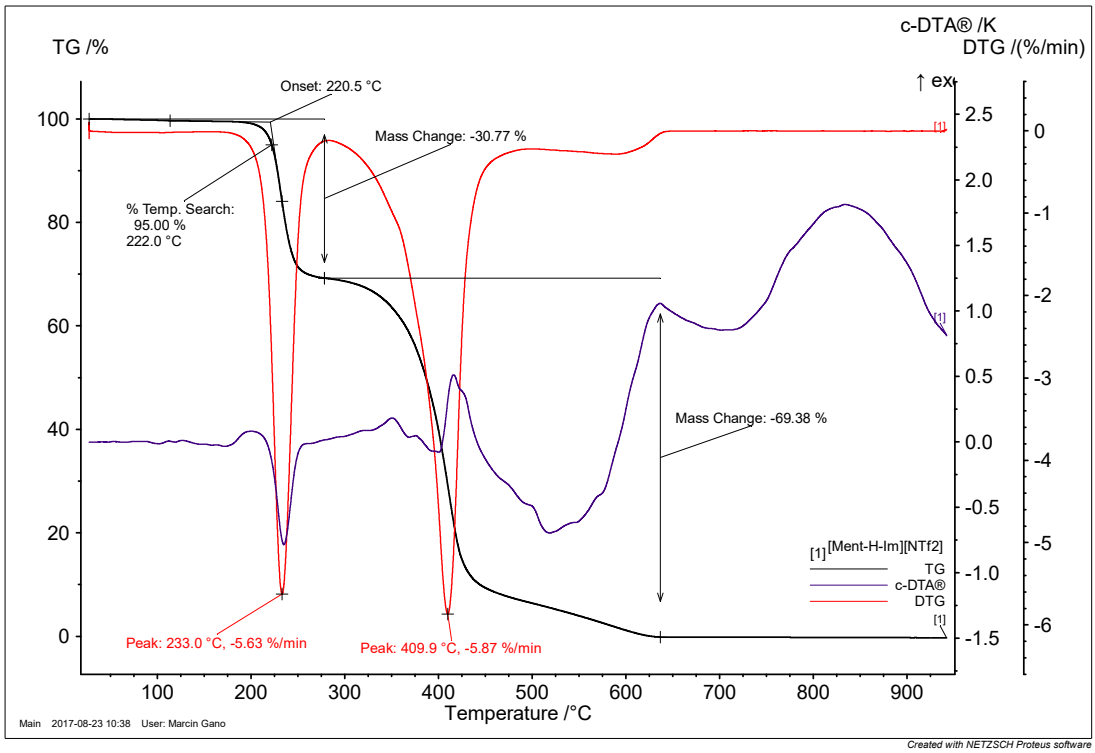
TG, DTG and c-DTA curves for 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium chloride, (–)[H-Ment-Im][Cl]



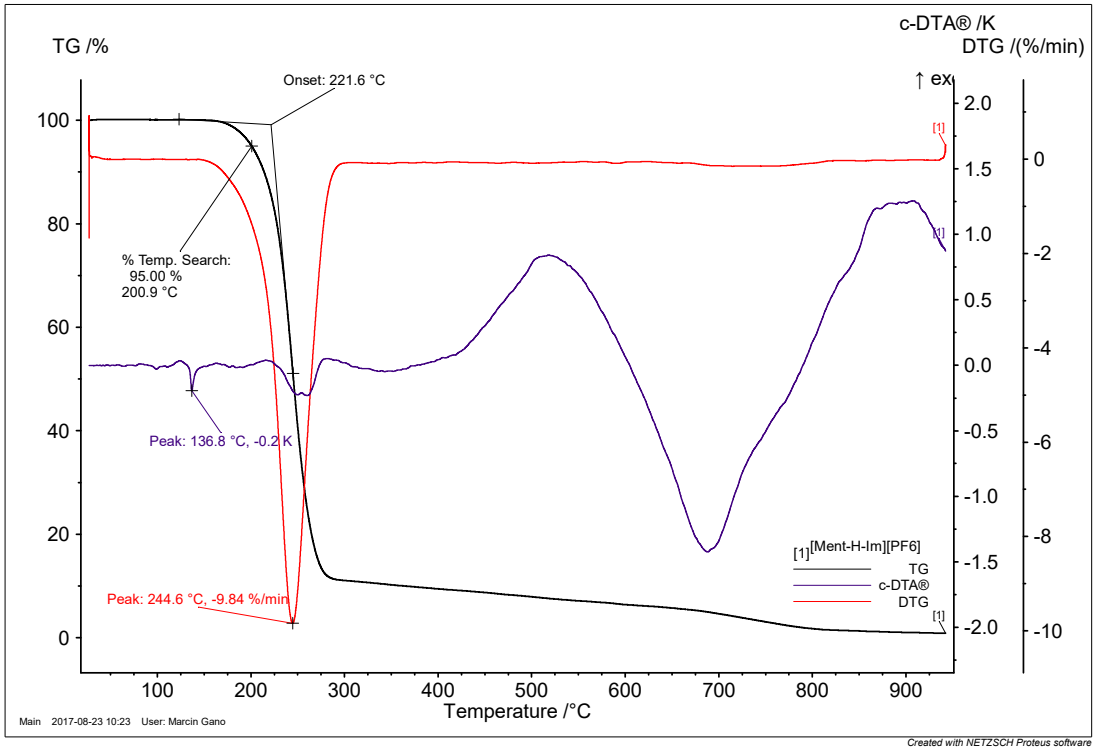
TG, DTG and c-DTA curves for 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium trifluoromethanesulfonate, (–)[H-Ment-Im][OTf]



TG, DTG and c-DTA curves for 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethanylsulfonyl)imide, (–)[H-Ment-Im][NTf_2]

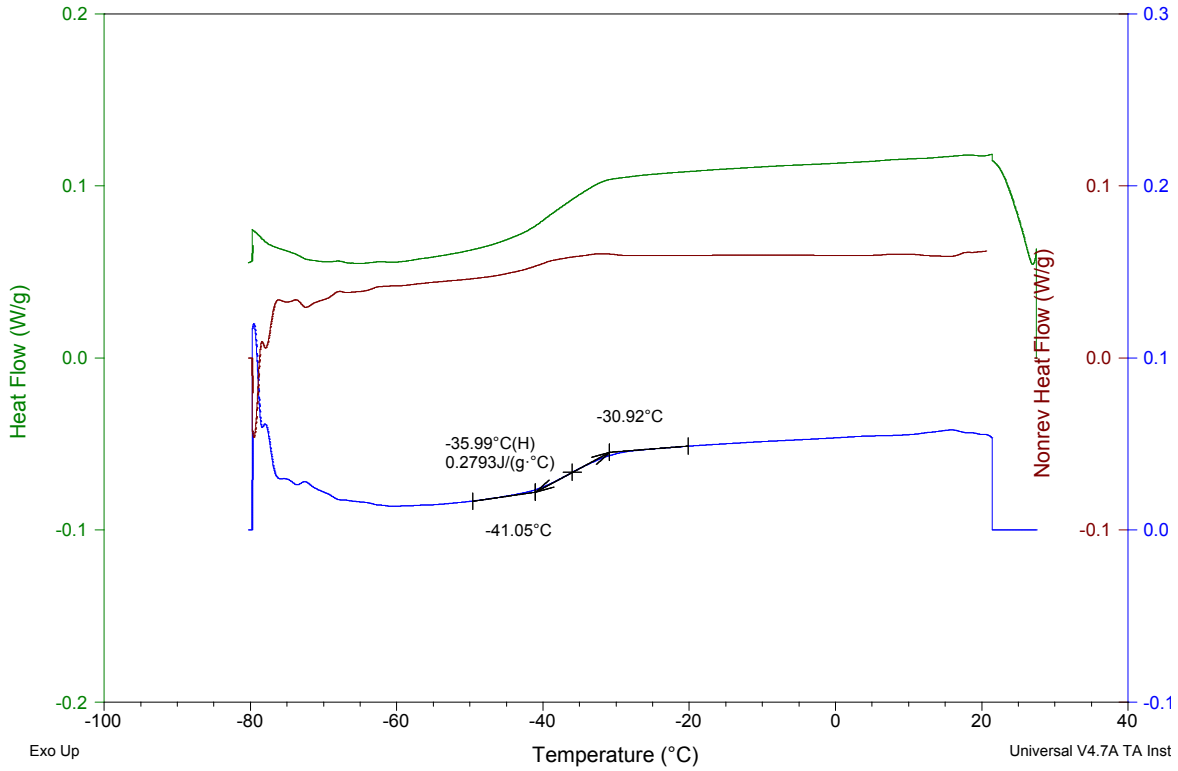


TG, DTG and c-DTA curves for 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium hexafluorophosphate, (–)[H-Ment-Im][PF_6]

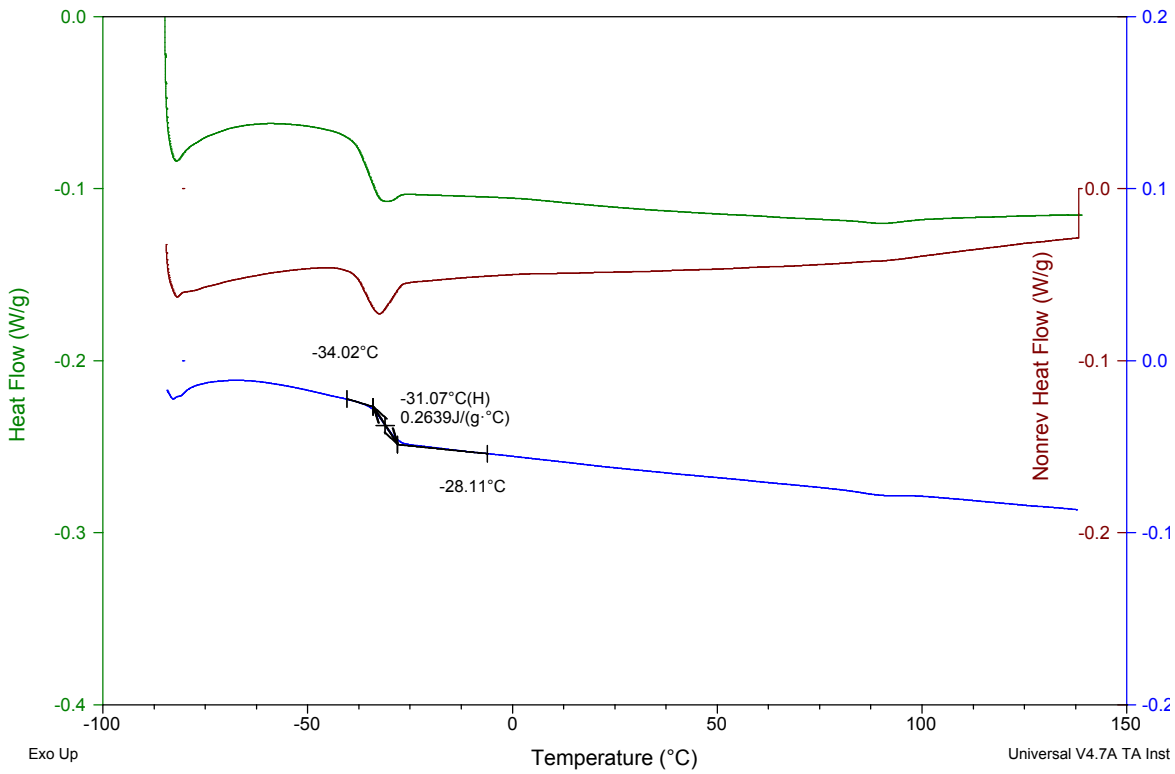


S7. MDSC measurements for 1-*H*-3-[(1*R*,2*S*,5*R*)-(–)-menthoxymethyl]imidazolium bis(trifluoromethanylsulfonyl)imide, (–)[H-Ment-Im][NTf_2]

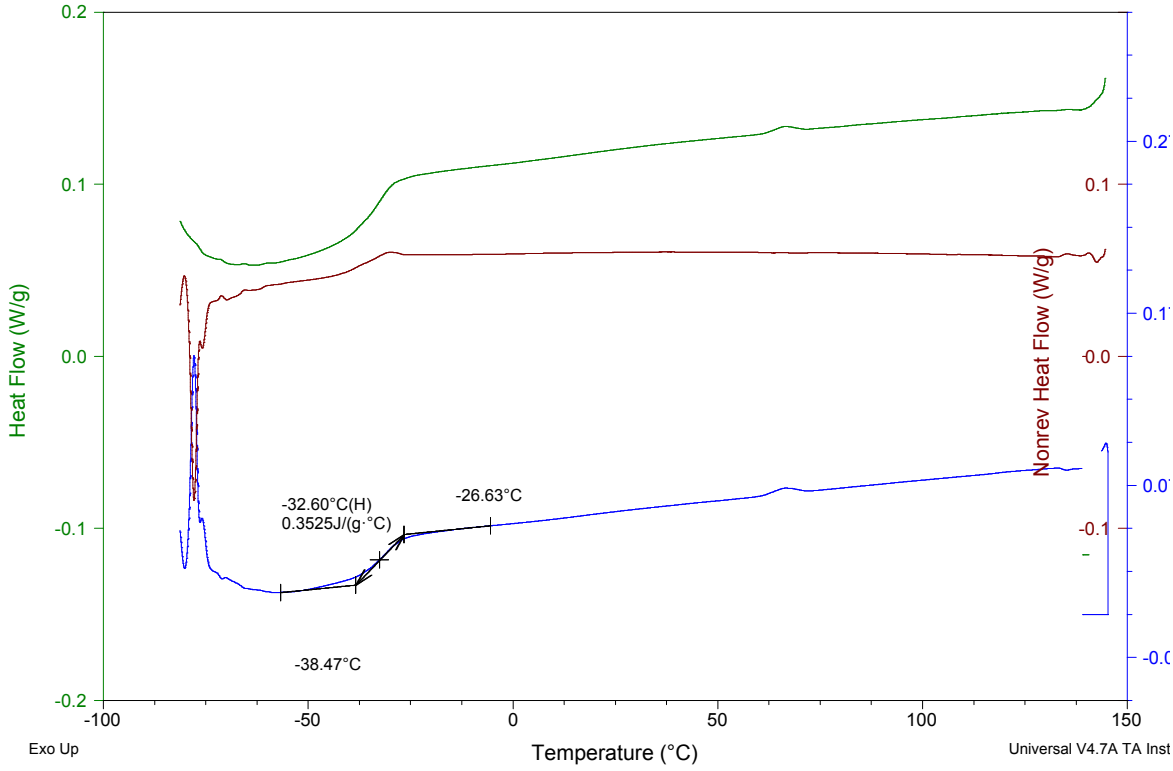
MDSC in 1st cooling mode from 20 ºC to -90 ºC



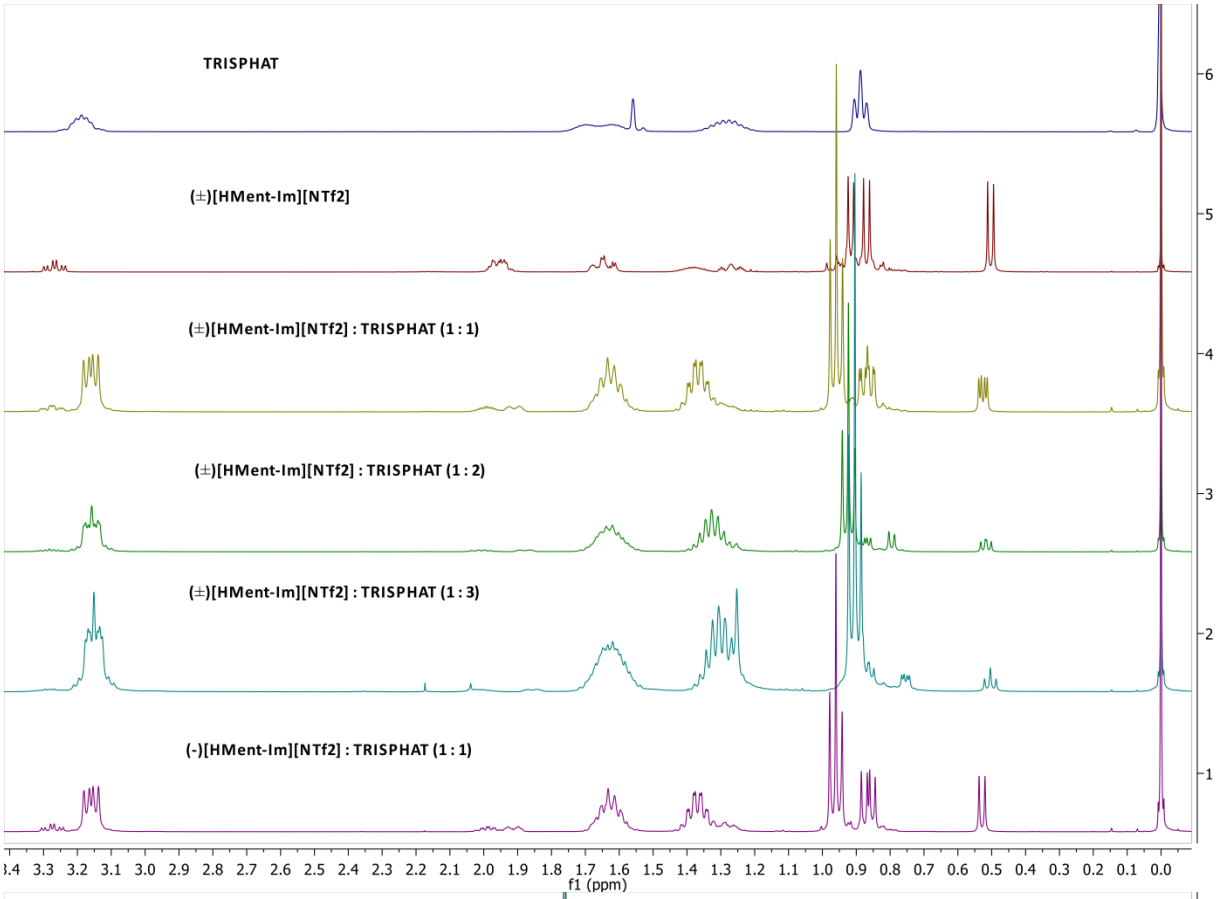
MDSC in heating mode from -90 ºC to 150 ºC

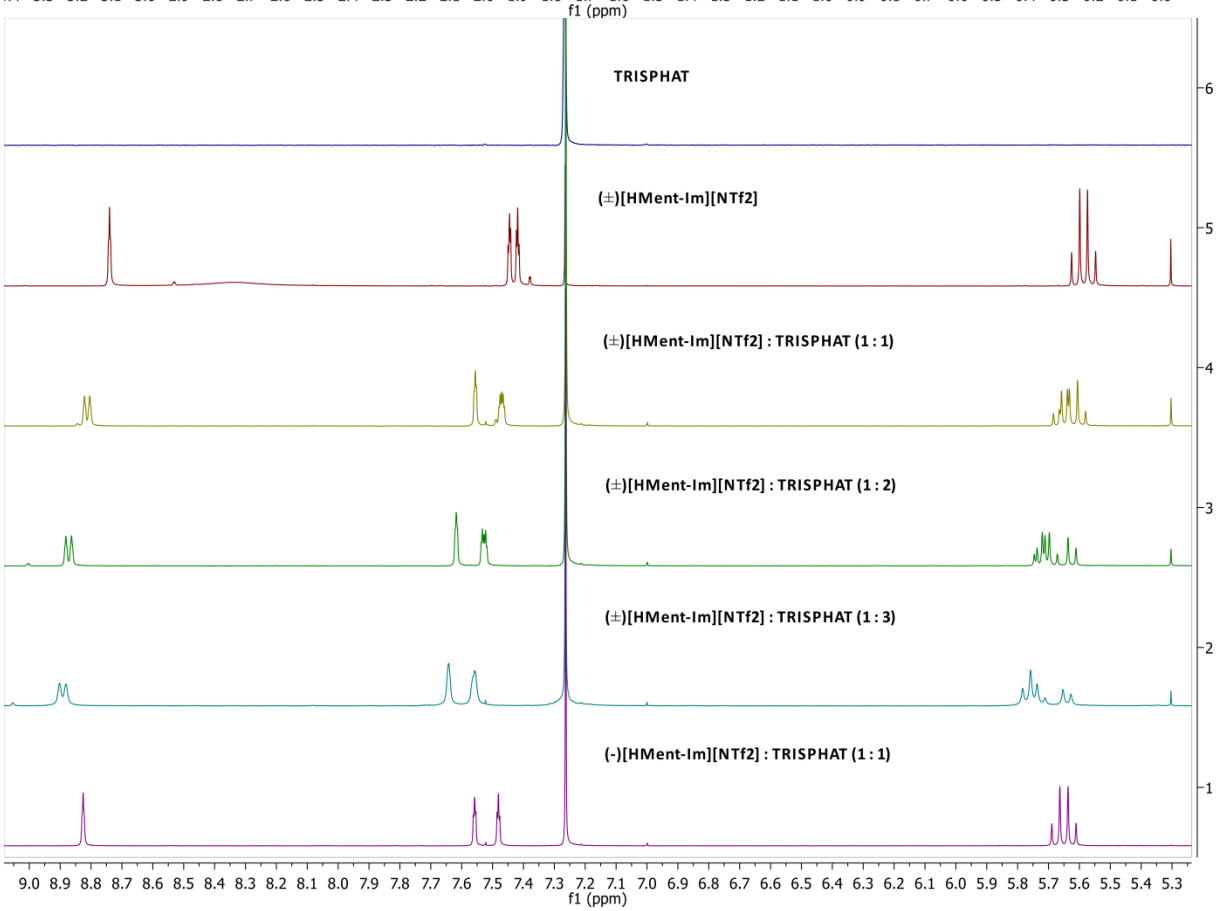


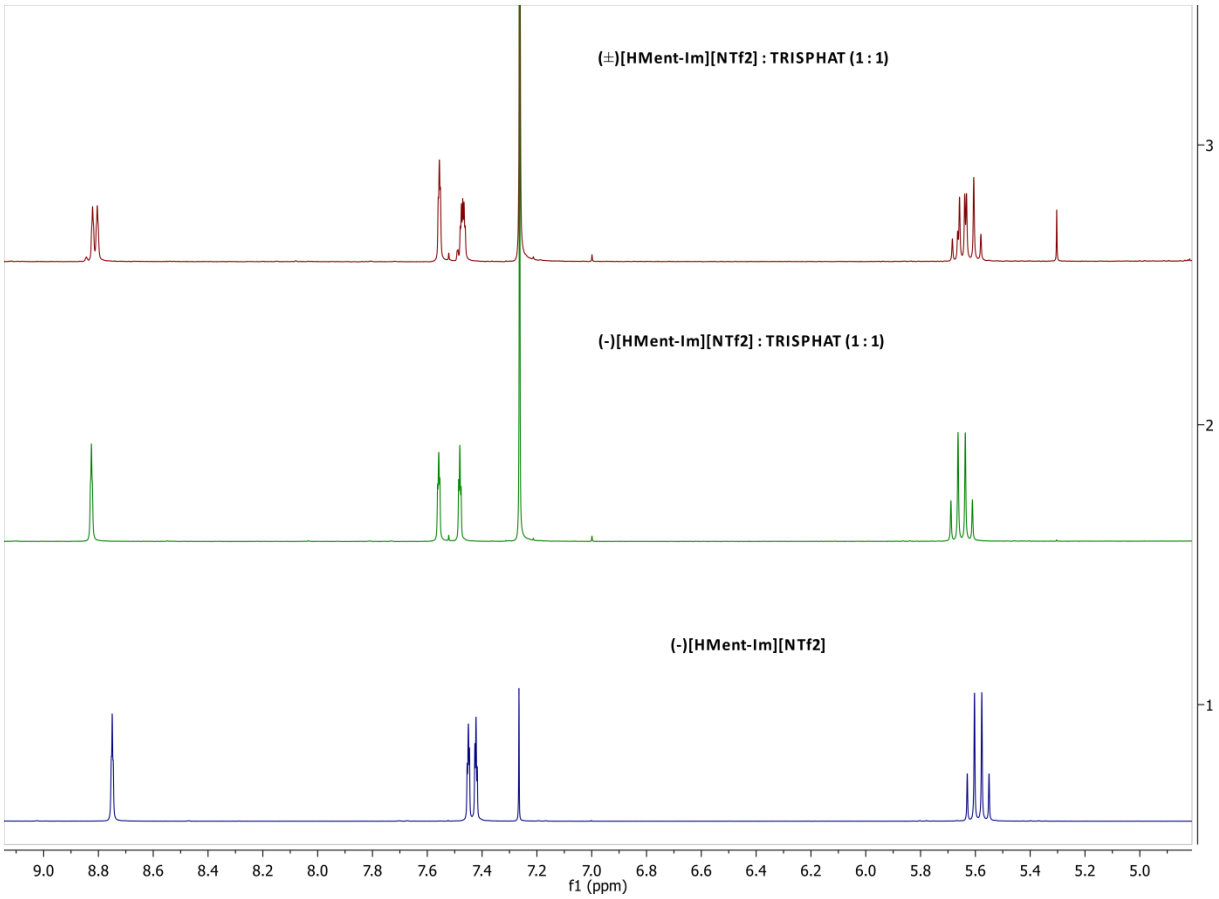
MDSC in 2nd cooling mode from 150 ºC to -90 ºC

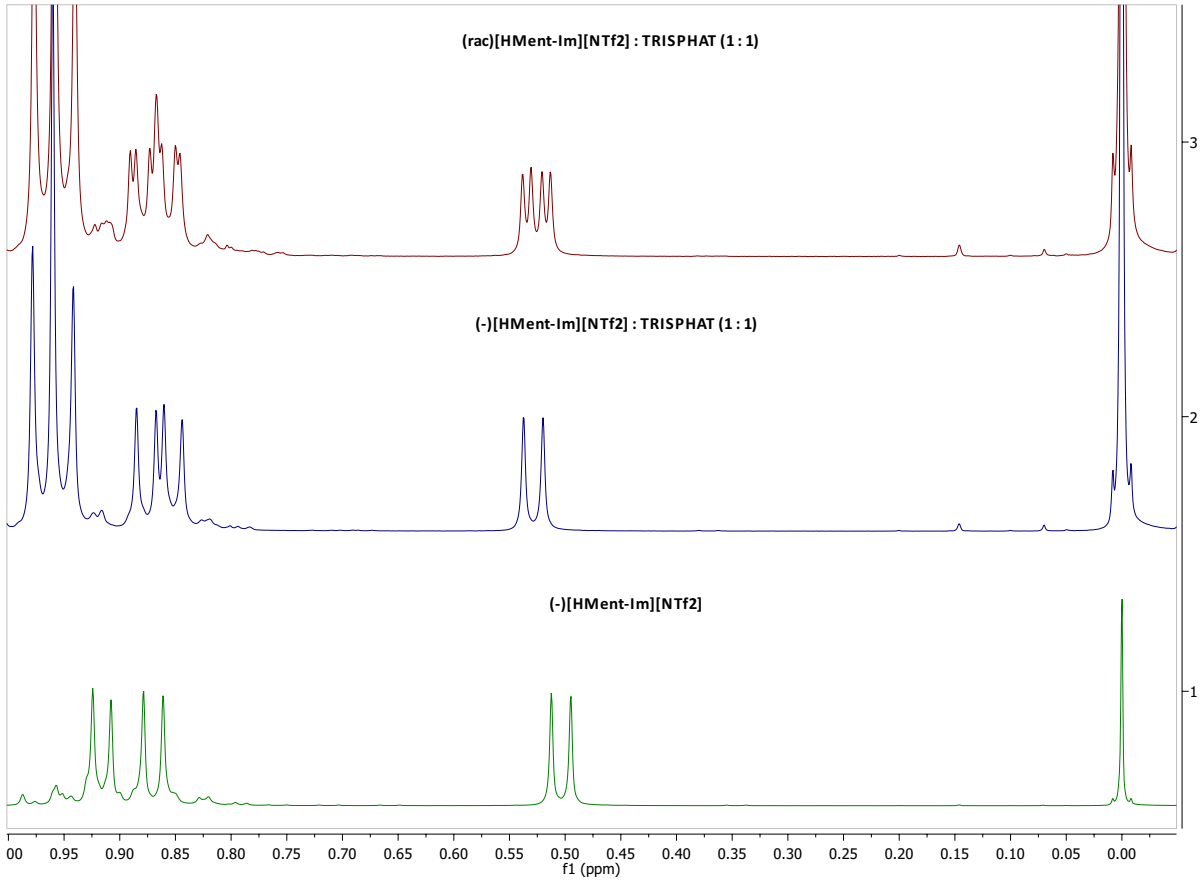


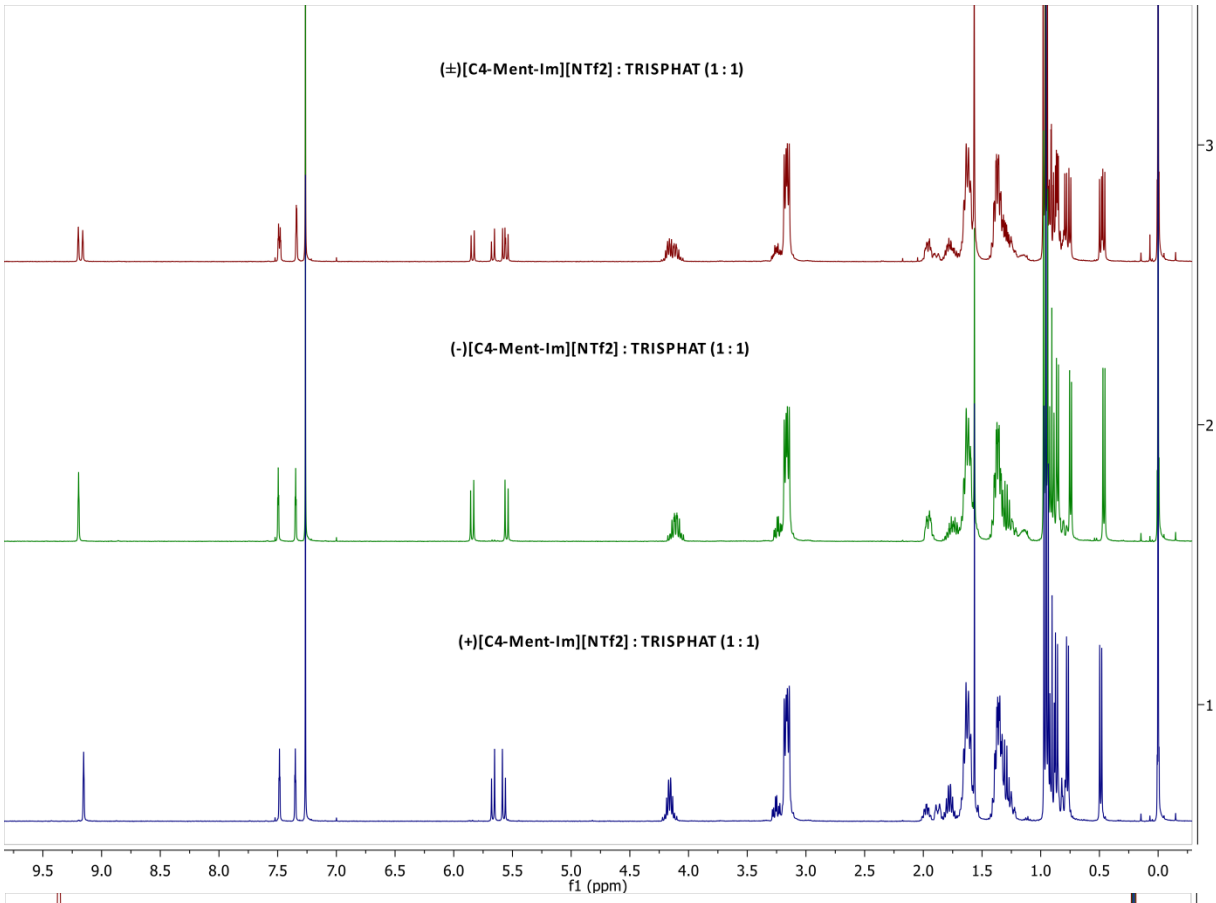
S8. ^{1}H NMR spectra of chiral protic and aprotic salts with chiral shift reagent Δ-TRISPHAT tetrabutylammonium salt

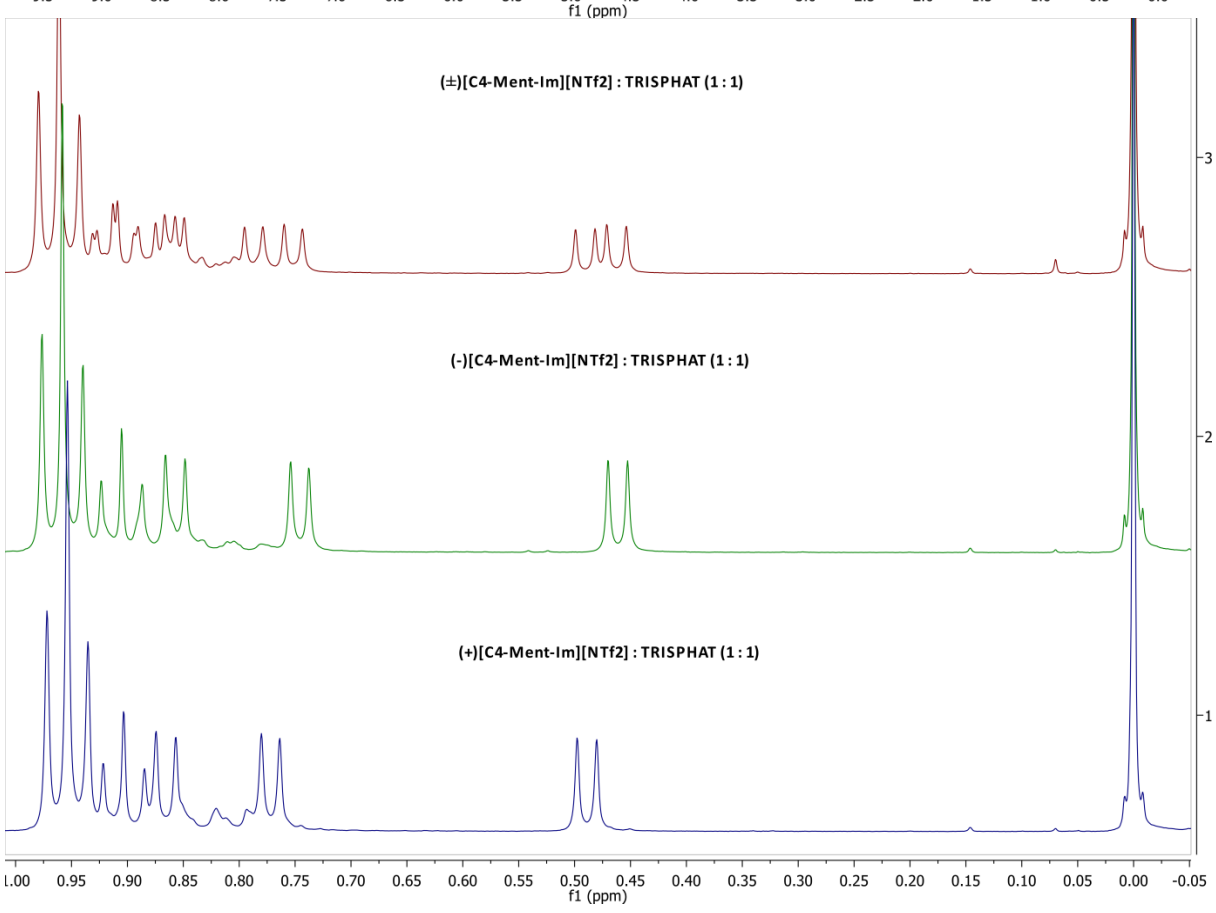


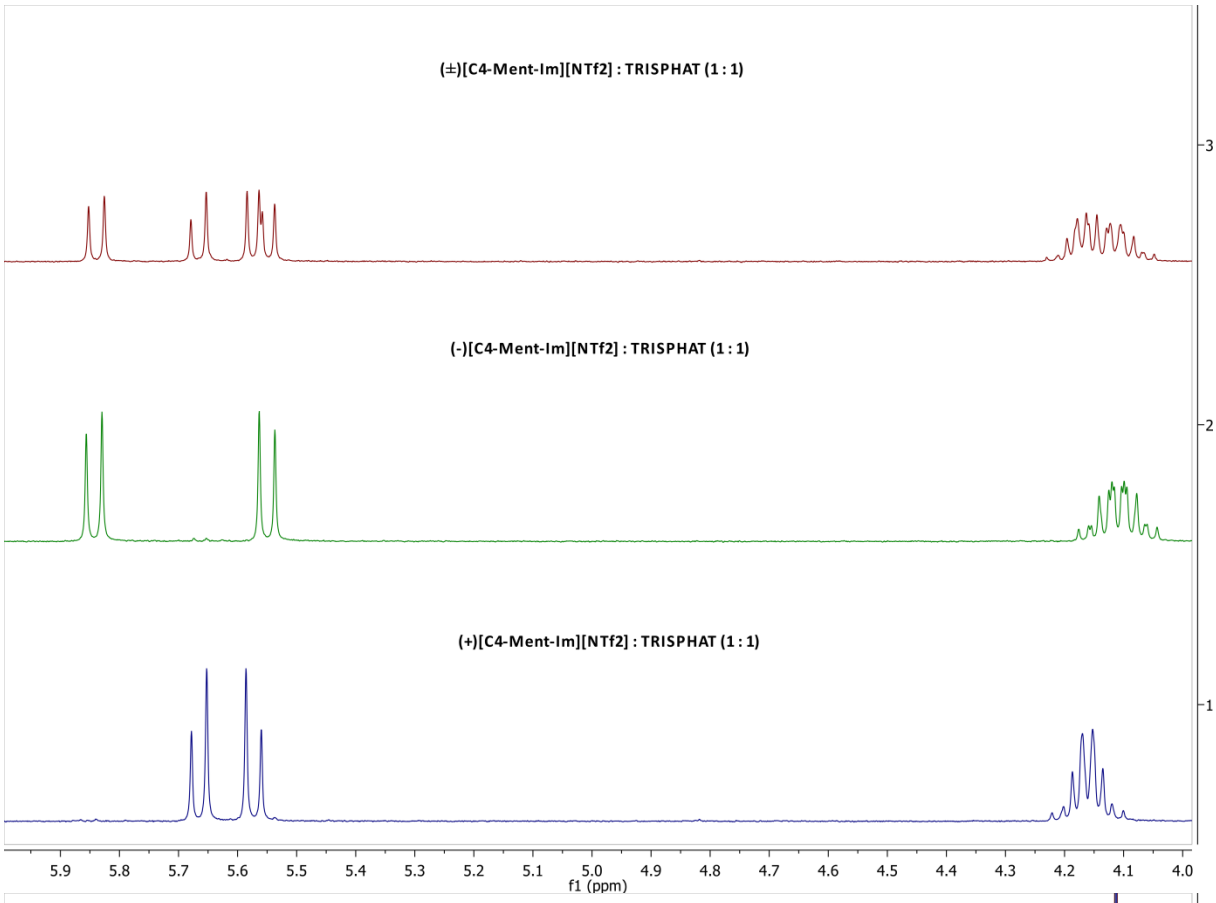


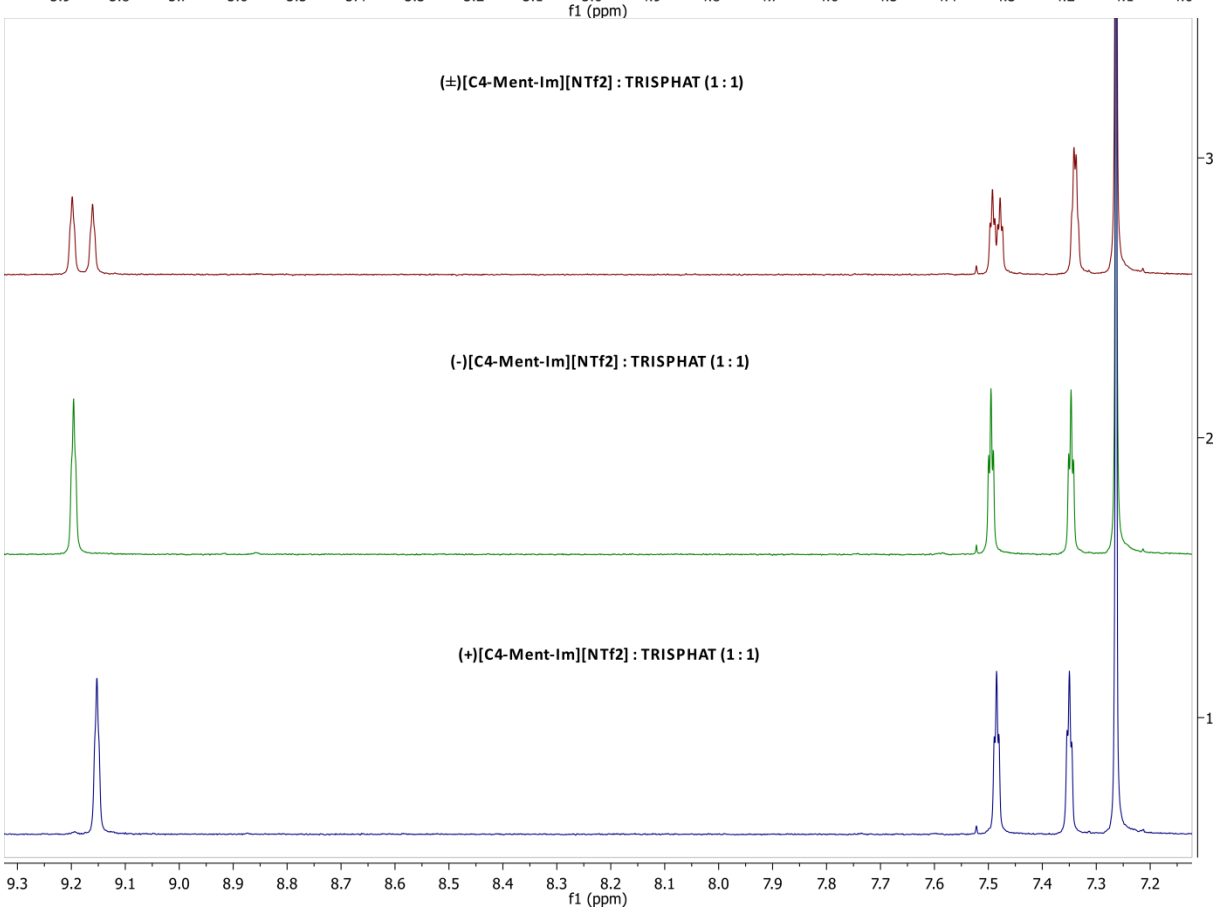

(±)[HMent-Im][NTf2] : TRISPHAT (1 : 1)
(-)[HMent-Im][NTf2] : TRISPHAT (1 : 1)
(-)[HMent-Im][NTf2]
3
2
1
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0
f1 (ppm)

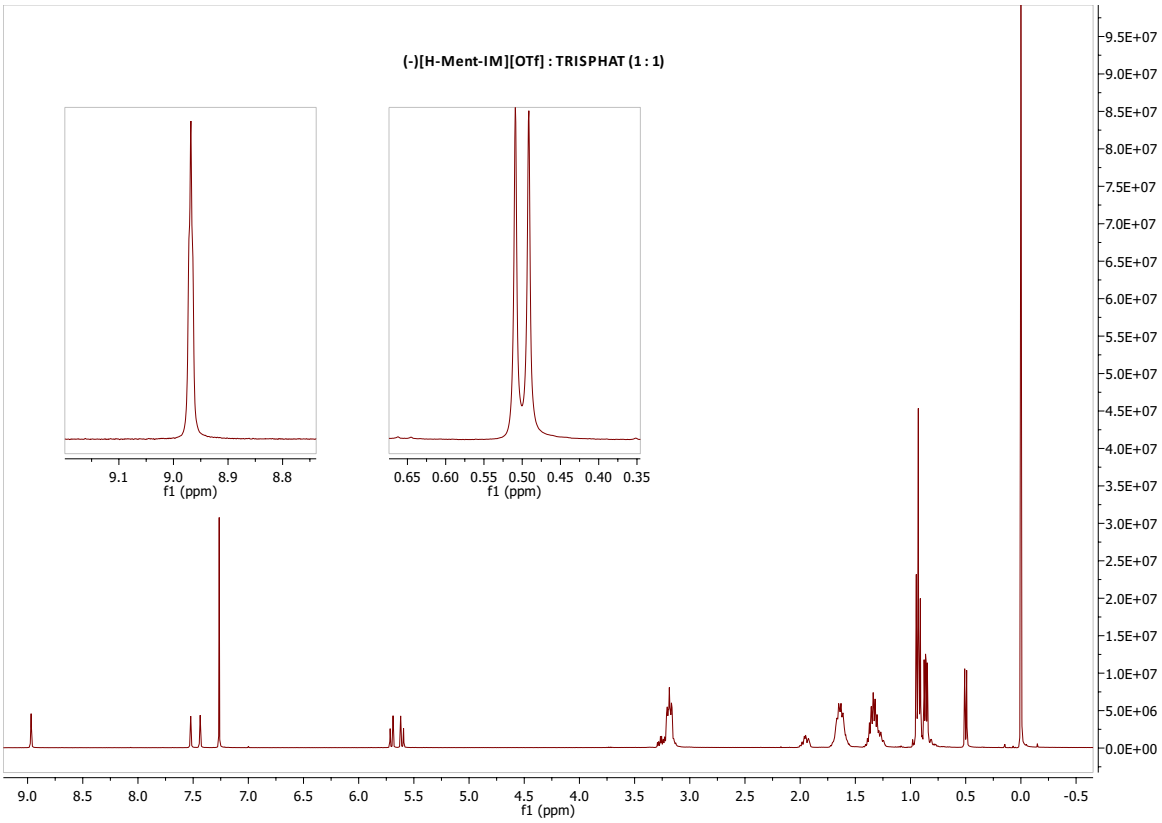

(rac)[HMent-Im][NTf2] : TRISPHAT (1 : 1)
(-)[HMent-Im][NTf2] : TRISPHAT (1 : 1)
(-)[HMent-Im][NTf2]
3
2
1
00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.60 0.55 0.50 0.45 0.40 0.35 0.30 0.25 0.20 0.15 0.10 0.05 0.00
f1 (ppm)

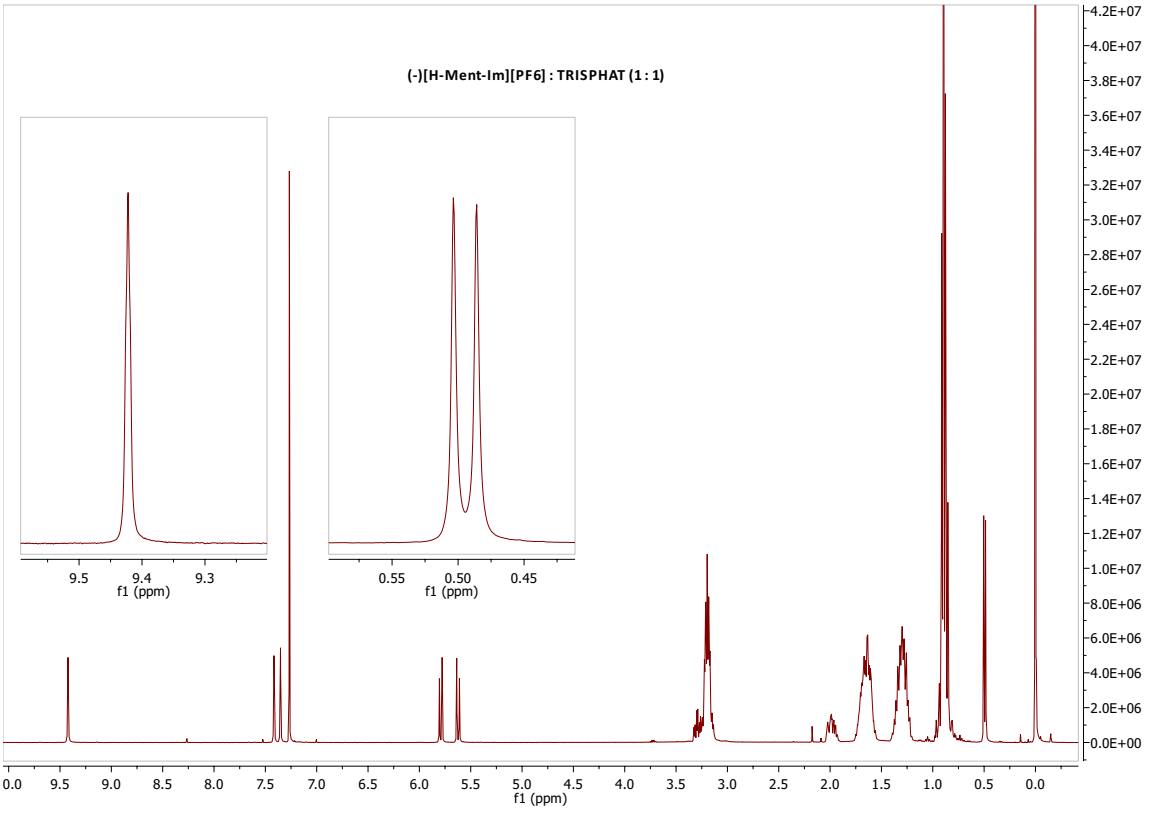

(±)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
(-)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
(+)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
3
2
1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

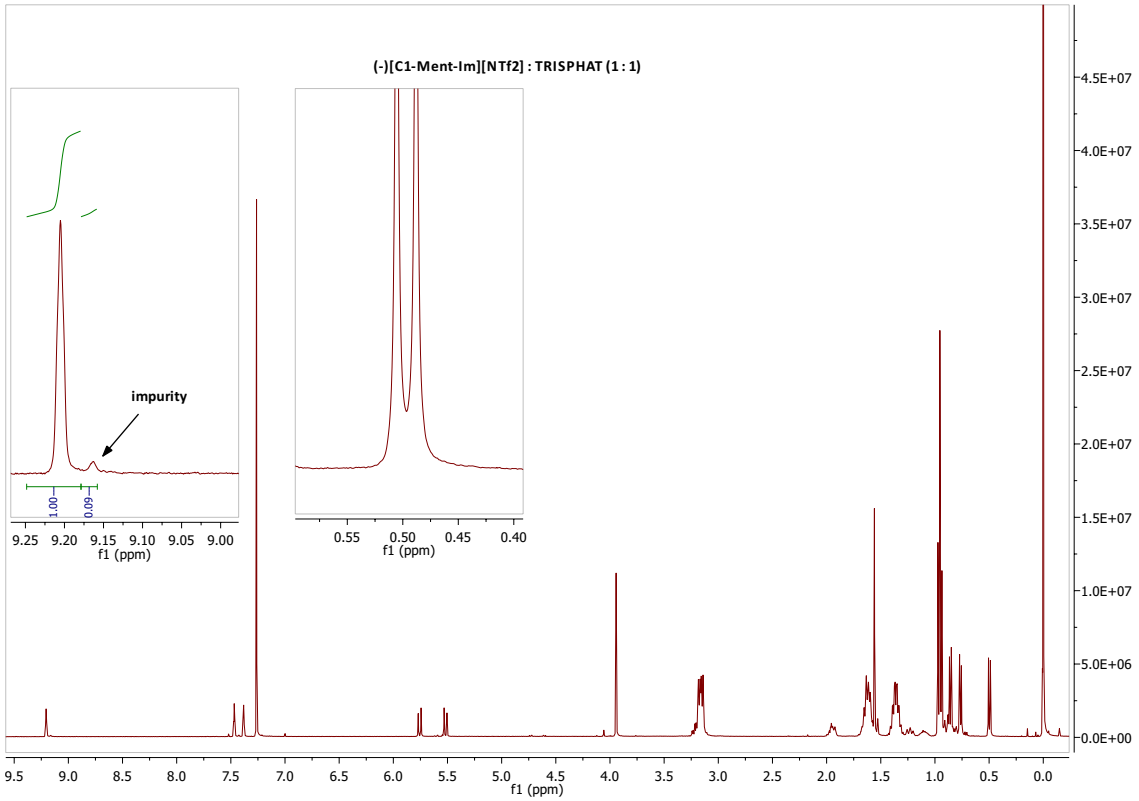

(±)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
(-)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
(+)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
3
2
1
1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.60 0.55 0.50 0.45 0.40 0.35 0.30 0.25 0.20 0.15 0.10 0.05 0.00 -0.05
f1 (ppm)

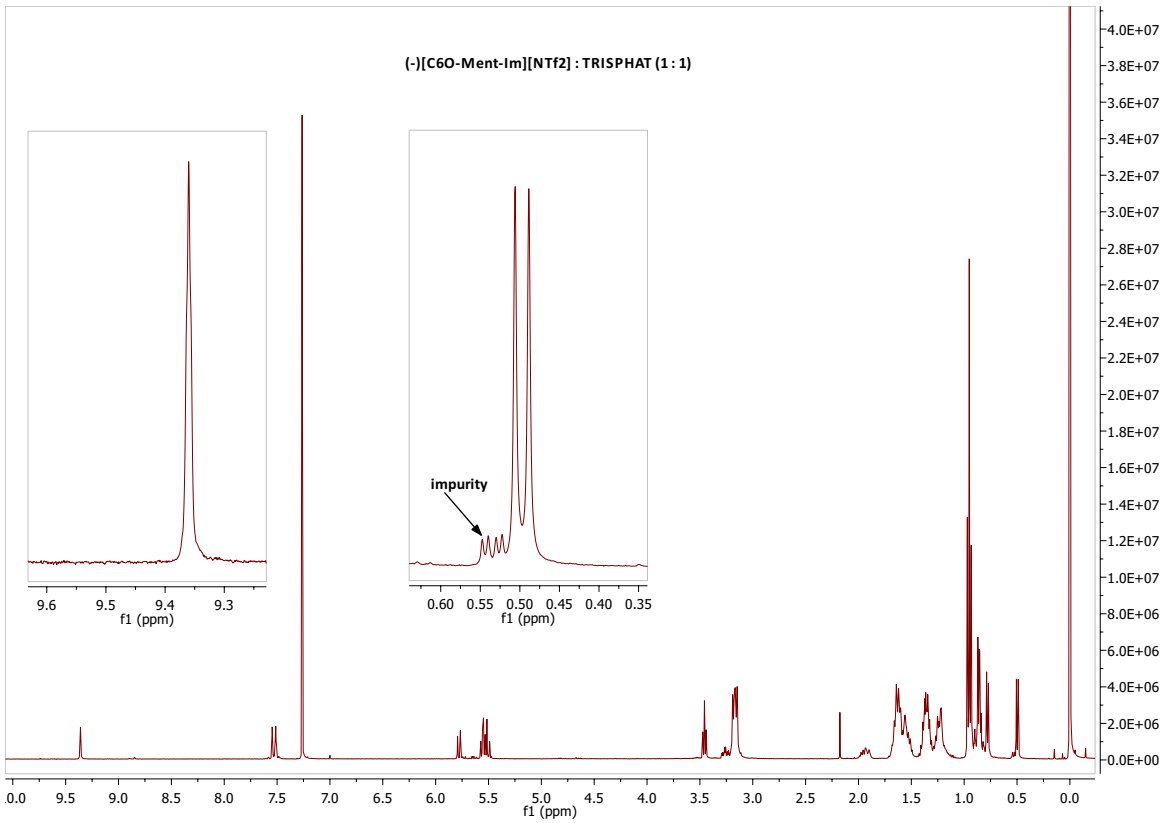

(±)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
(-)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
(+)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
3
2
1
5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0
f1 (ppm)

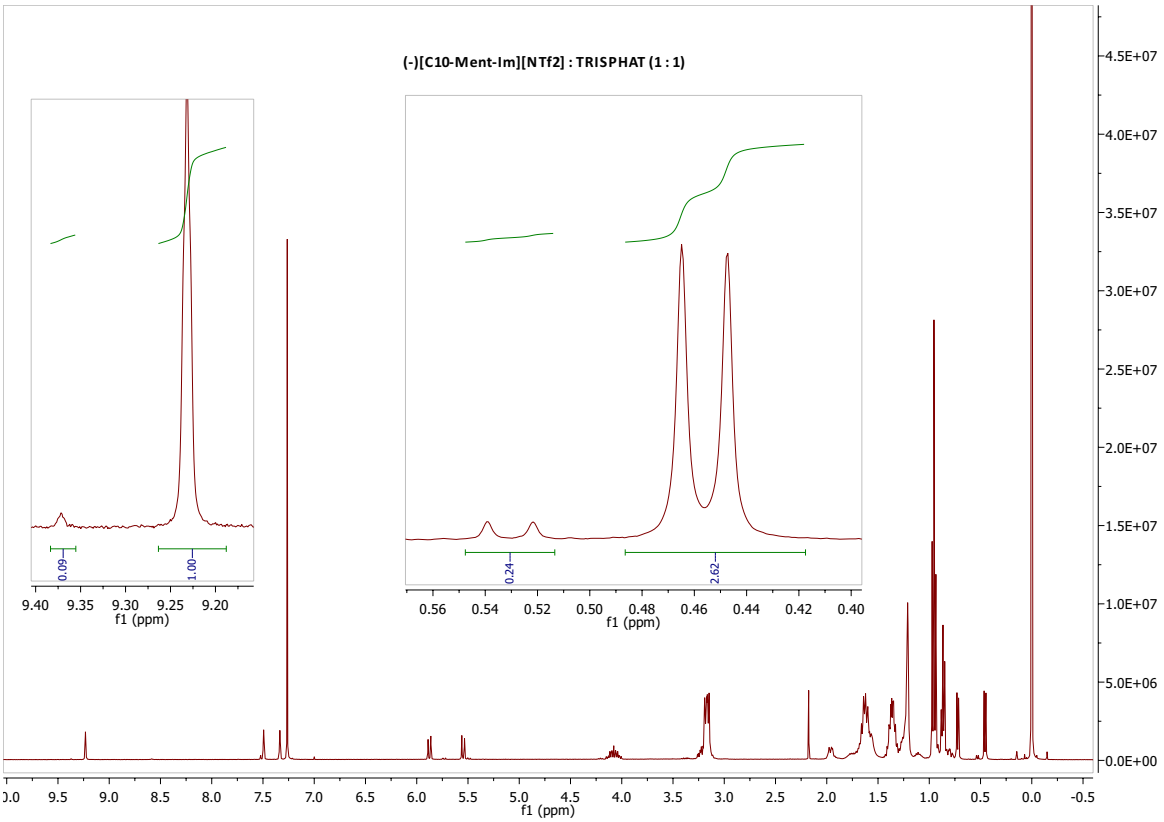

(±)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
(-)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
(+)[C4-Ment-Im][NTf2] : TRISPHAT (1 : 1)
3
2
1
9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)

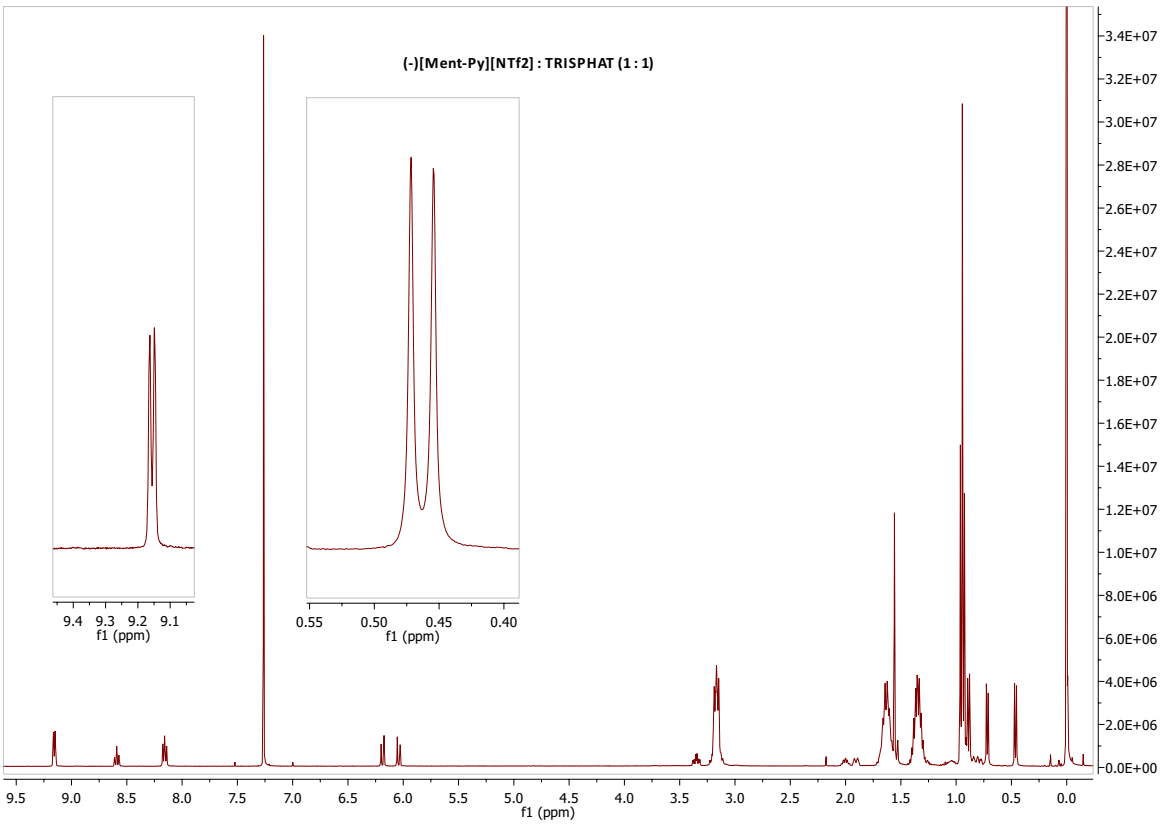

(-)[H-Ment-IM][OTf] : TRISPHAT (1 : 1)
f1 (ppm)
f1 (ppm)
f1 (ppm)


(-)[H-Ment-Im][PF6] : TRISPHAT (1 : 1)
f1 (ppm)
f1 (ppm)
f1 (ppm)

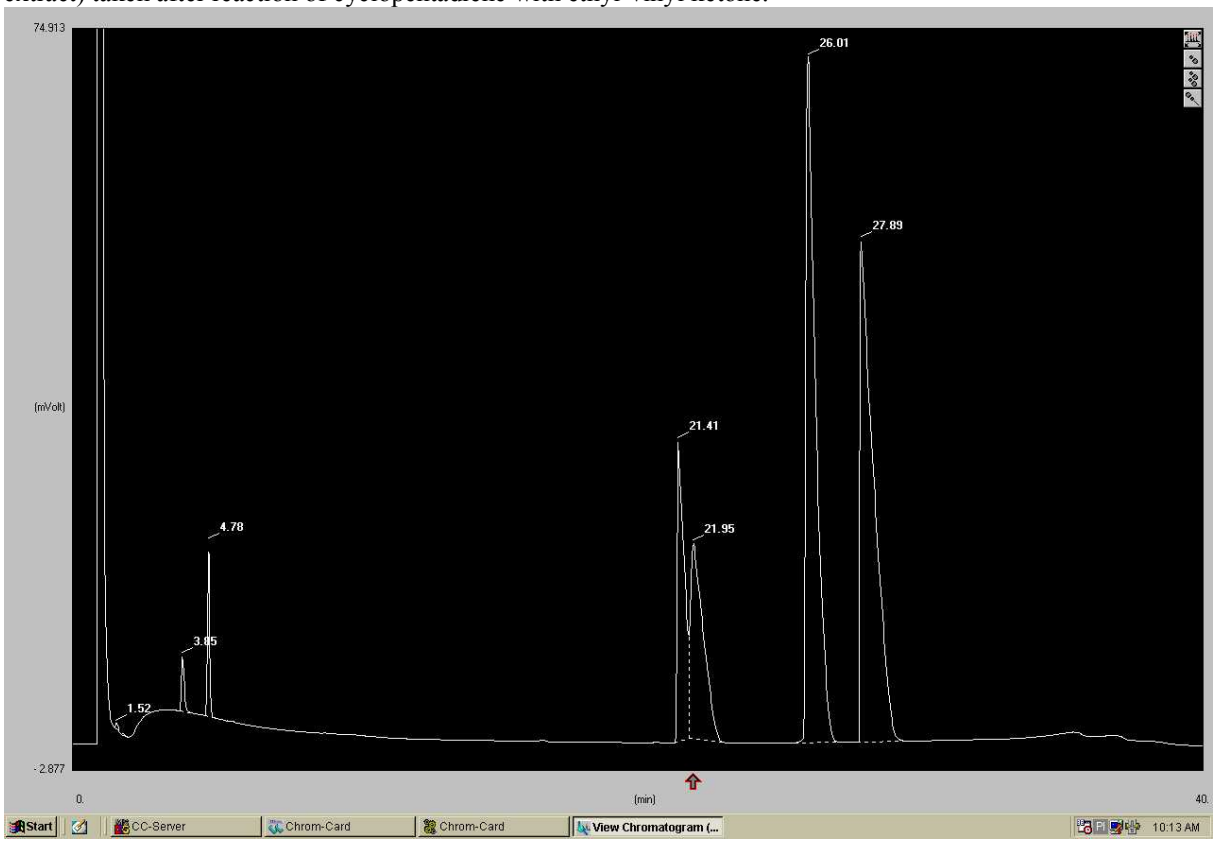

(-)[C1-Ment-Im][NTf2] : TRISPHAT (1 : 1)
impurity
1.00
0.09
f1 (ppm)


(-)[C6O-Ment-Im][NTf2] : TRISPHAT (1 : 1)
impurity
f1 (ppm)


(-)[C10-Ment-Im][NTf2] : TRISPHAT (1 : 1)
0.09
1.00
0.24
2.62
f1 (ppm)

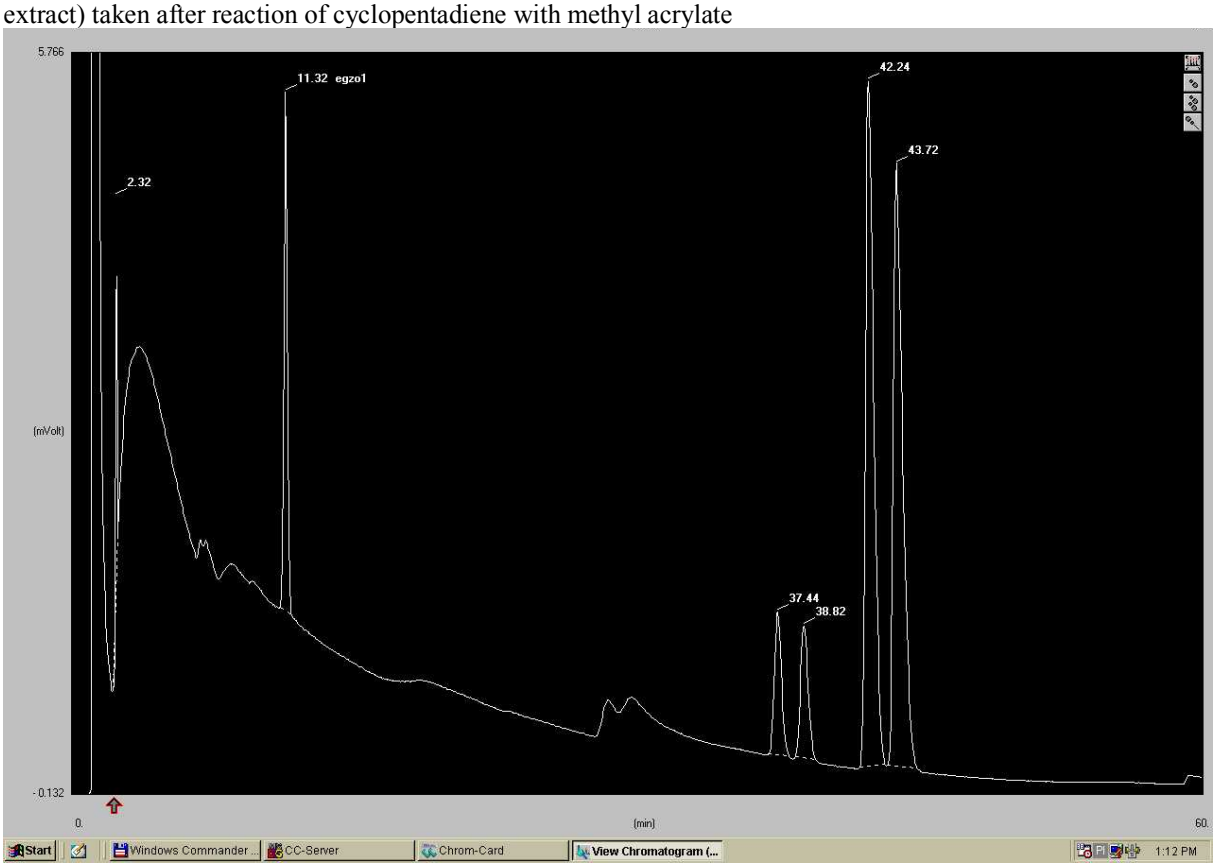

(-)[Ment-Py][NTf2] : TRISPHAT (1 : 1)
f1 (ppm)

S9. The representative chromatogram registered on chiral RT-BetaDEXsa GC column for the sample (hexane extract) taken after reaction of cyclopentadiene with ethyl-vinyl ketone.



Peaks with retention time 21.41 min and 21.95 min, correspond to two enantiomers of 2-*egzo*-ethylcarbonyl-5-norbornene; peaks with retention time 26.01 min and 27.09 min correspond to two enantiomers of 2-*endo*-ethylcarbonyl-5-norbornene;

S10. The representative chromatogram registered on chiral RT-BetaDEXsa GC column for the sample (hexane extract) taken after reaction of cyclopentadiene with methyl acrylate



Peaks with retention time 37.44 min and 38.02 min, correspond to two enantiomers of 2-*egzo*-methoxycarbonyl-5-norbornene; peaks with retention time 42.24 min and 43.72 min correspond to two enantiomers of 2-*endo*-methoxycarbonyl-5-norbornene;

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