Electronic Supplementary Materials

Sulfonimides versus Ketosulfonamides as Epoxidized Imidazolium Counterions: Towards a New Generation of Ionic Liquids Monomers

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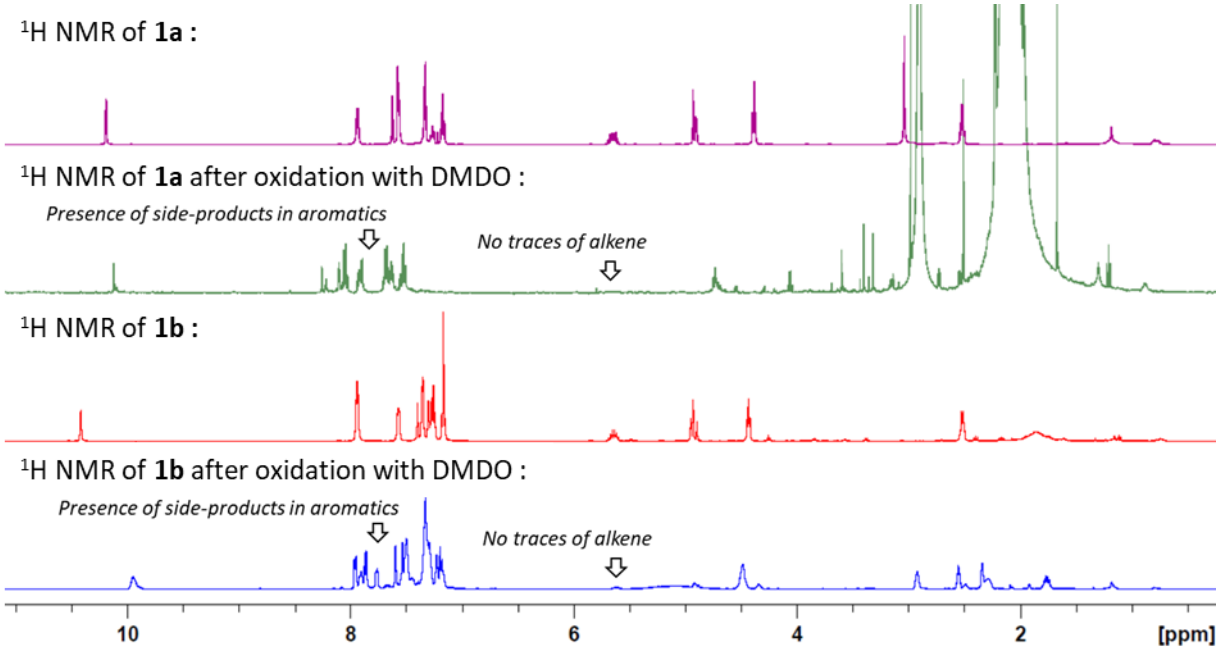
I. Epoxidation of imidazolium ketosulfonamides 1a-b or saccharinate 1c

UPLC : Acquity UPLC H-Class WATERS
Column: Waters Acquity UPLC CSH C18 1,7 µm
General procedure:

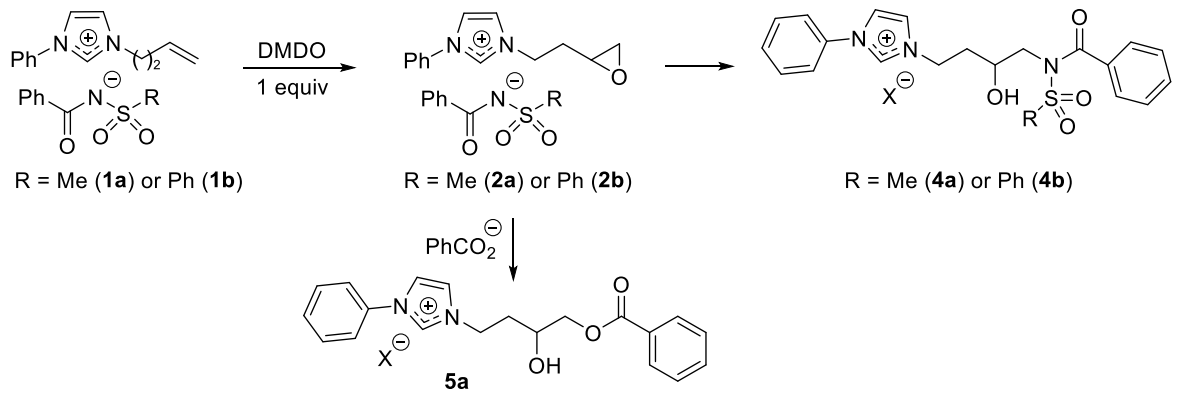
Gradient : H_2O/CH_3CN with 0.1% CH_3CO_2H or H_2O/CH_3CN (95/5 to 0/100).
Flow: 0,5 mL/min
Column température: 35 °C
Sample température: 20 °C

Mass spectrometry : Xevo G2-XS QTof WATERS
Positive ion mode (ES+) or negative ion mode (ES-)
Mass range : 50-1000 m/z
Source température: 120 °C
Desolvation température: 550 °C
Capillary tension: 0.3 kV
Cone tension: 50 V

I.1 Epoxidation results (NMR)

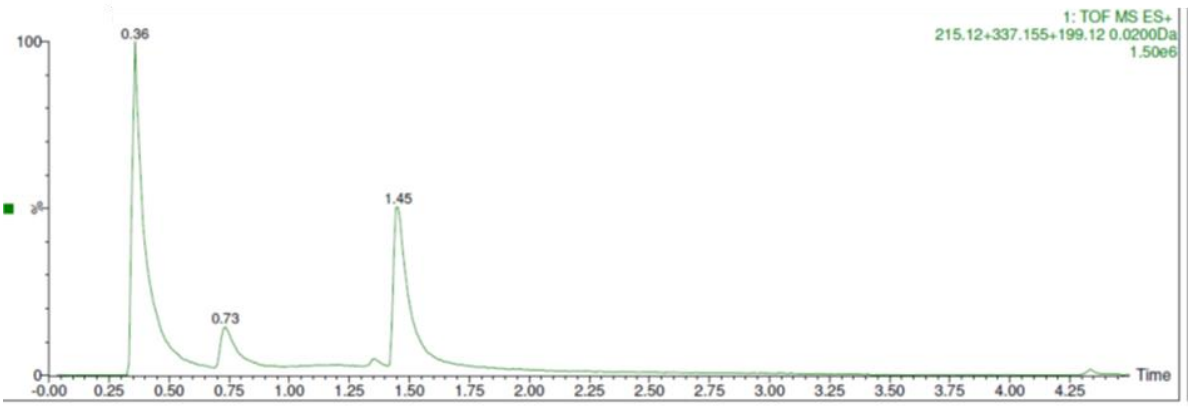


I.2 Suggested reactions after HRMS analyses

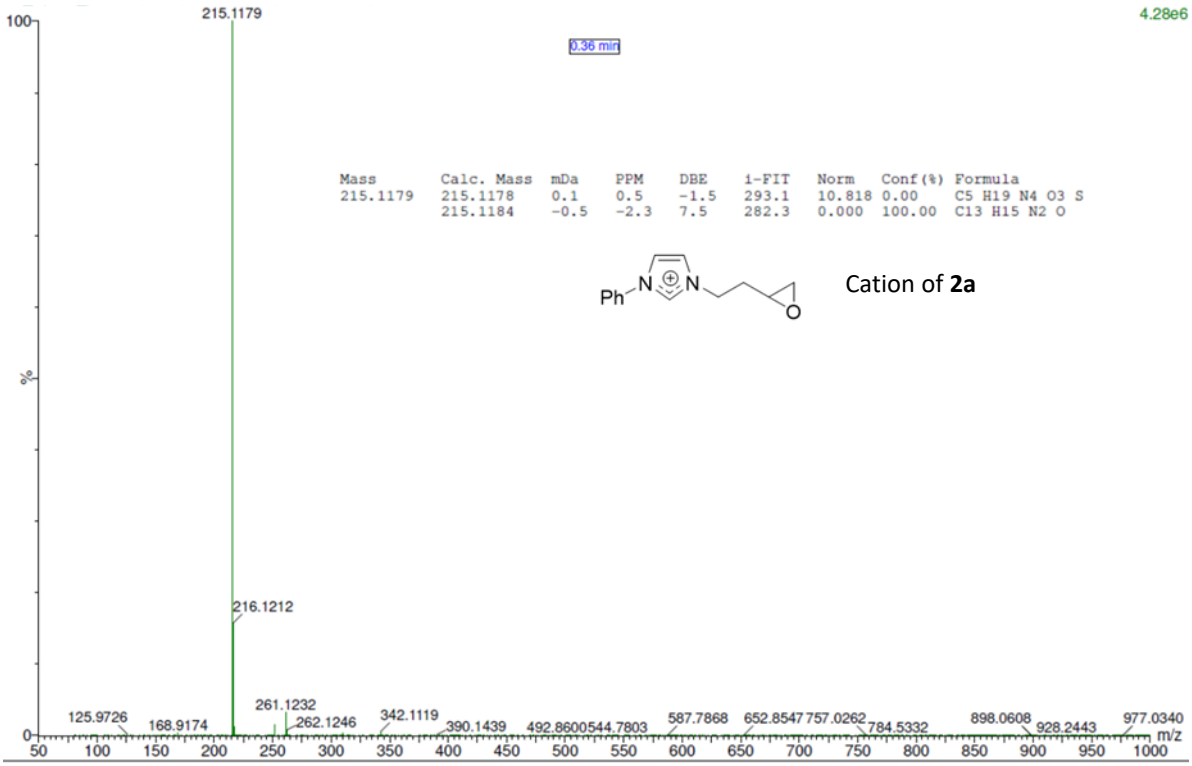


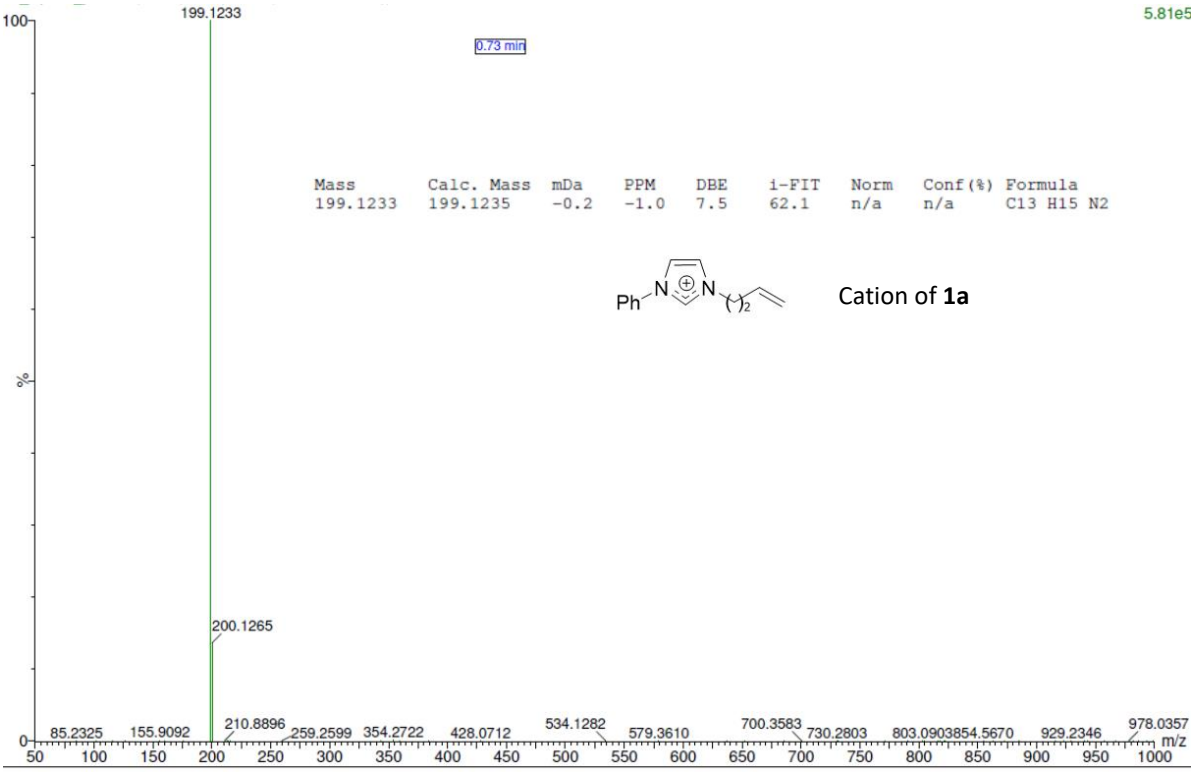
- UPLC-MS of compound <u>1a</u> after oxidation (TOF MS ES$^+$ then TOF MS ES$^-$)

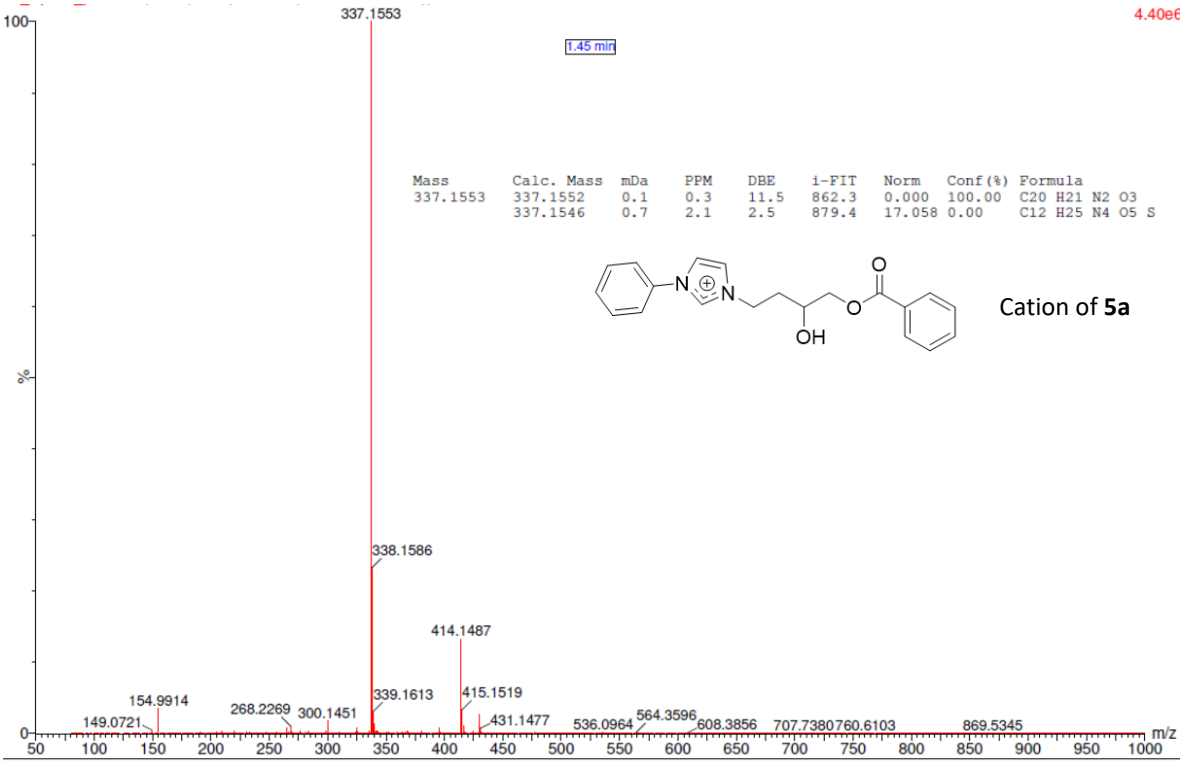
UPLC-MS (**ES$^+$**) :

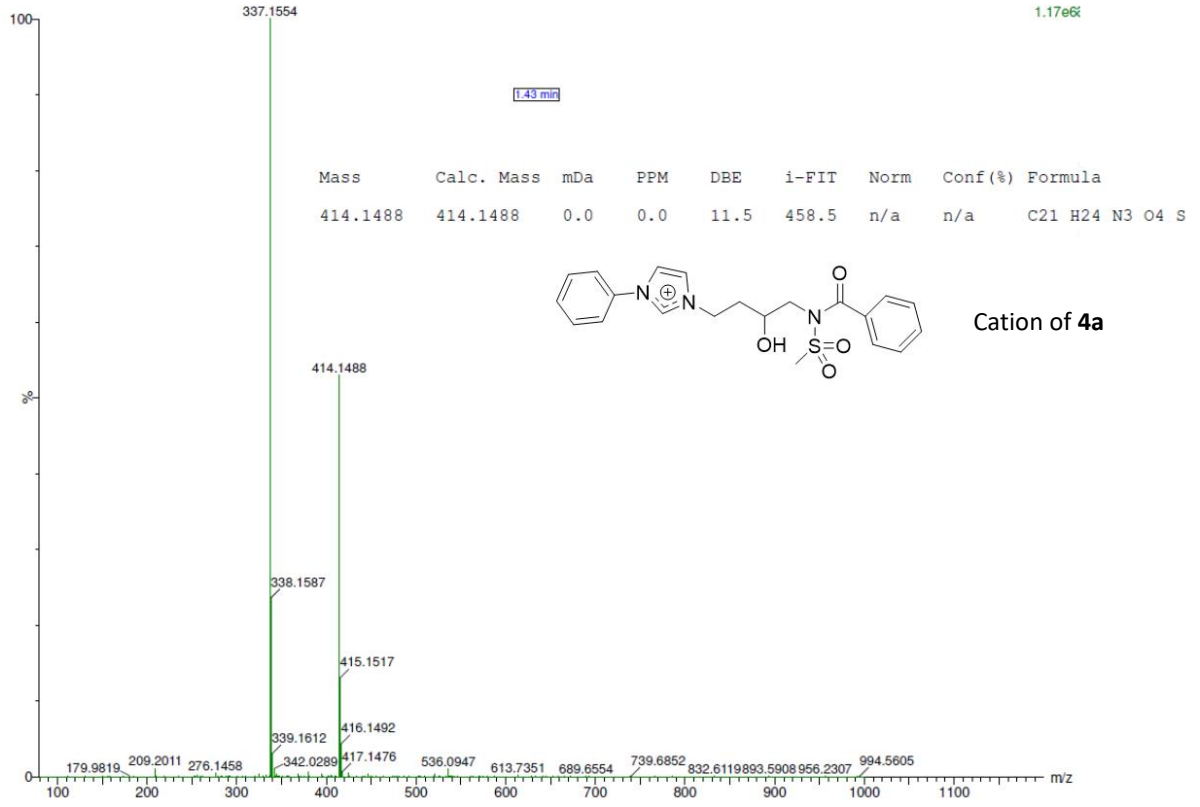


HRMS analyses :



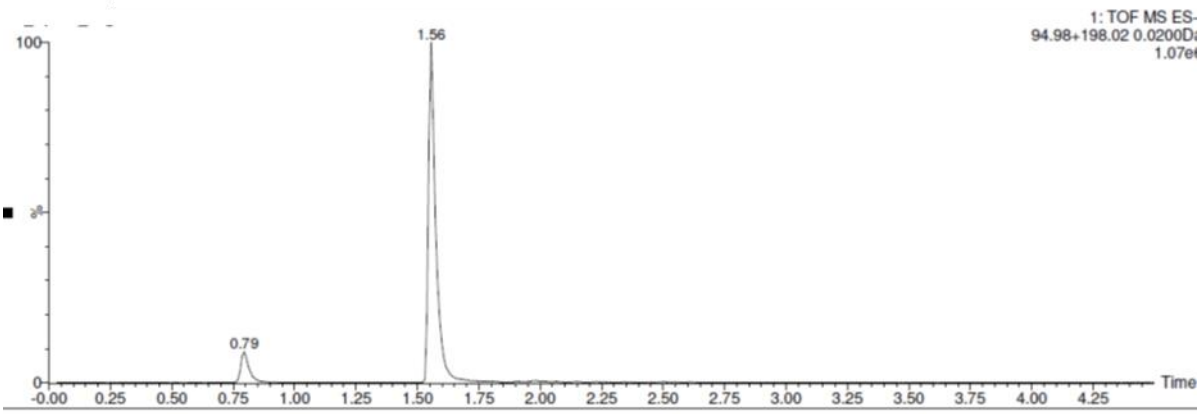

199.1233
5.81e5
0.73 min
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
199.1233 199.1235 -0.2 -1.0 7.5 62.1 n/a n/a C13 H15 N2
Ph
N
N
Cation of 1a
200.1265
85.2325 155.9092 210.8896 259.2599 354.2722 428.0712 534.1282 579.3610 700.3583 730.2803 803.0903854.5670 929.2346 978.0357
m/z


337.1553
4.40e6
1.45 min
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
337.1553 337.1552 0.1 0.3 11.5 862.3 0.000 100.00 C20 H21 N2 O3
337.1546 0.7 2.1 2.5 879.4 17.058 0.00 C12 H25 N4 O5 S
N
N
O
O
OH
Cation of 5a
338.1586
414.1487
154.9914
149.0721
268.2269
300.1451
339.1613
415.1519
431.1477
536.0964
564.3596
608.3856
707.7380760.6103
869.5345
m/z

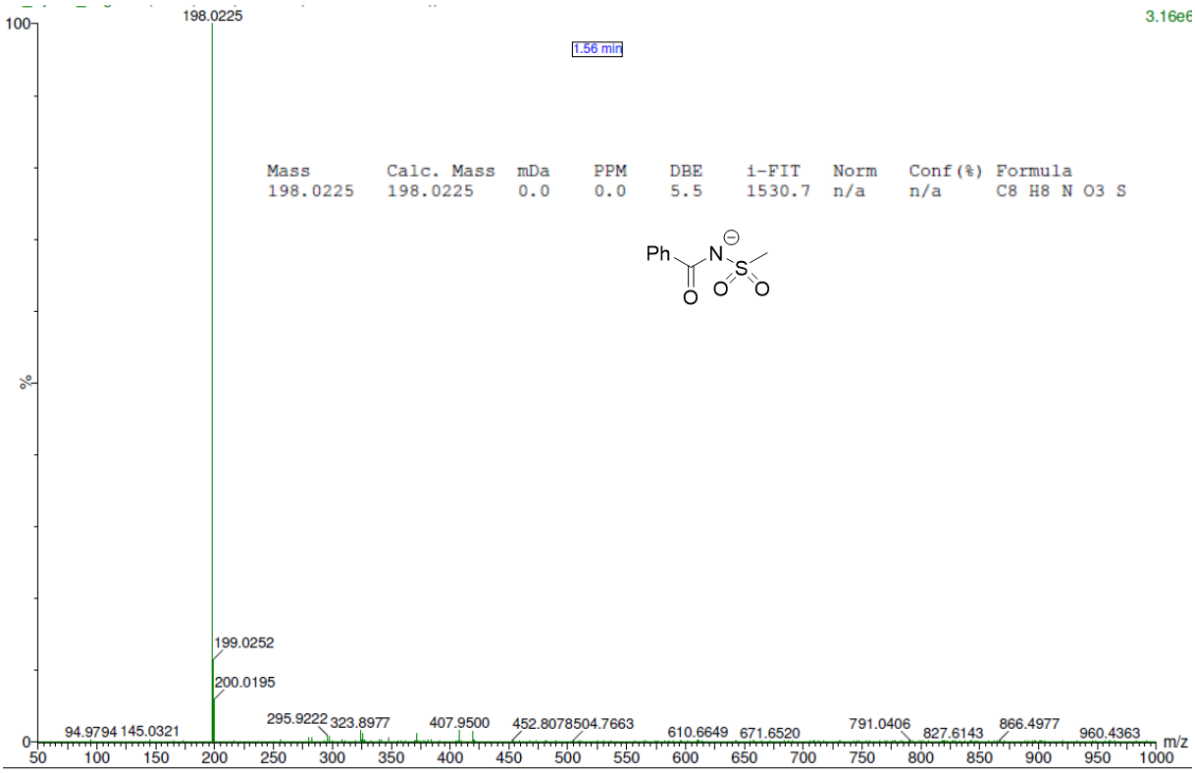


Cation of **4a**

UPLC-MS (**ES**$^-$) :

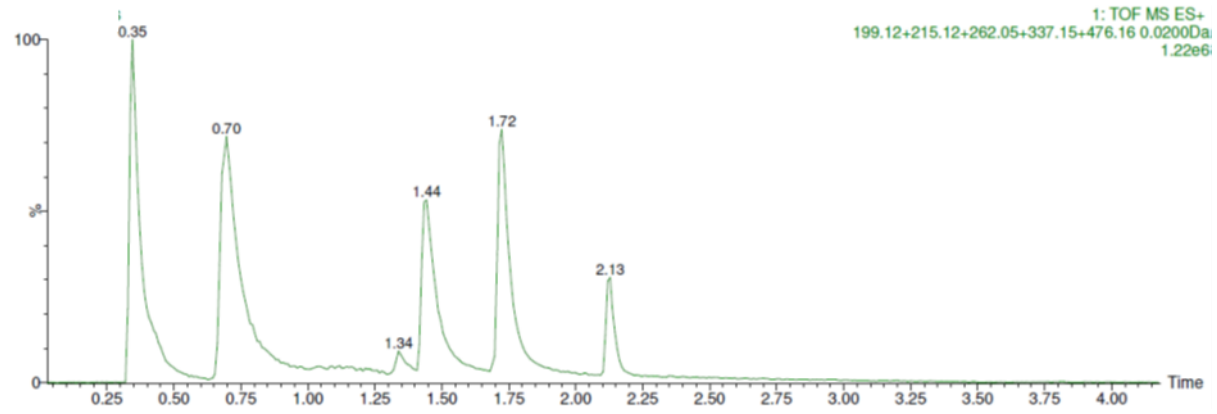


HRMS analyses :

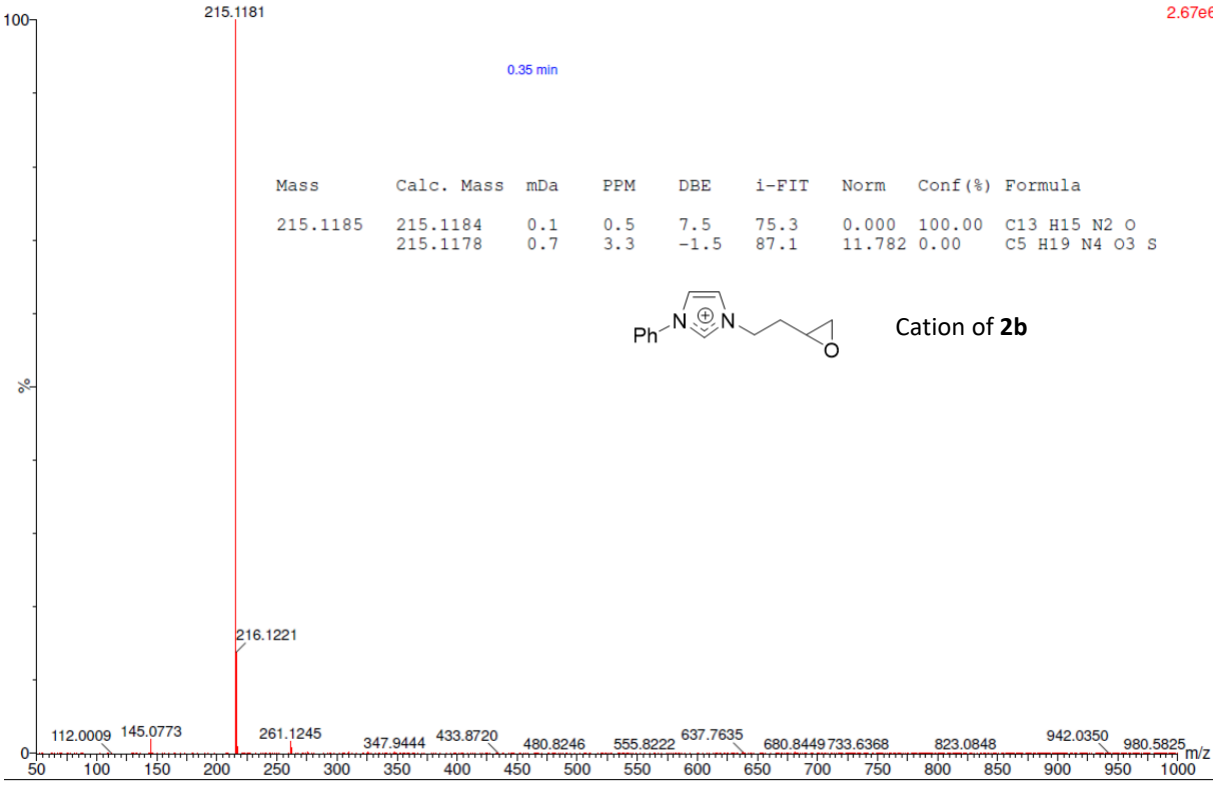


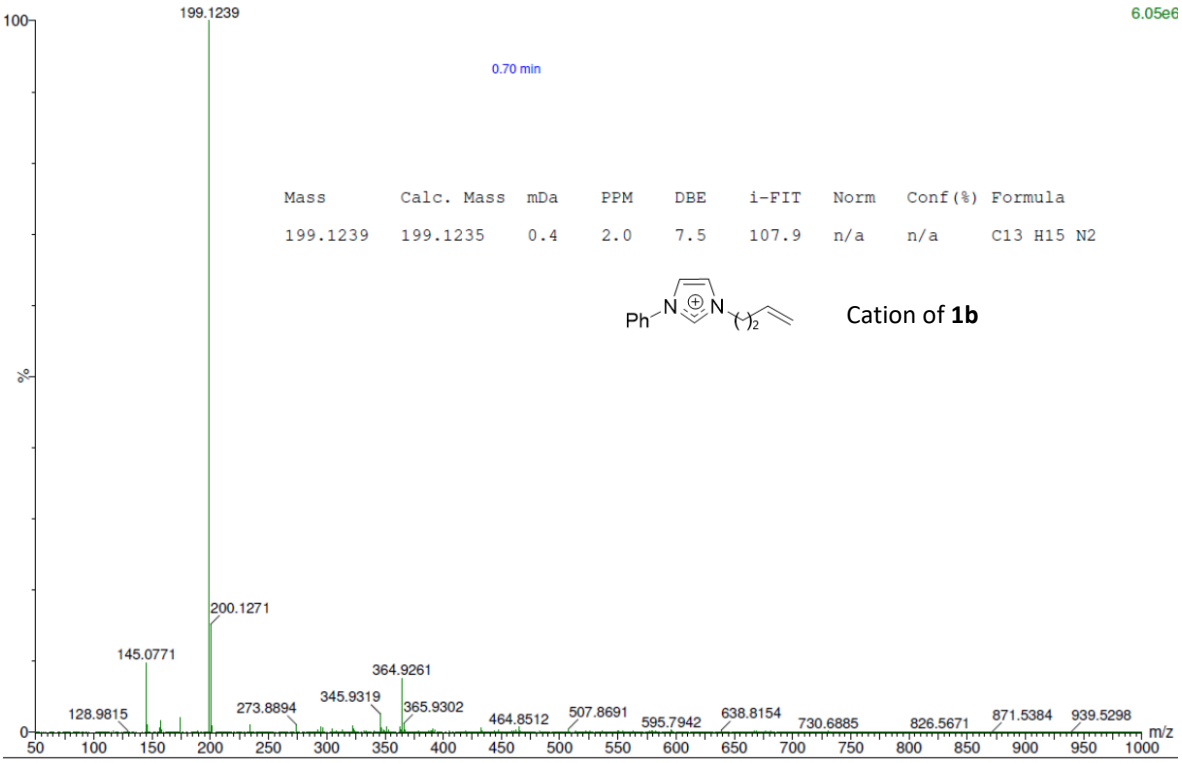
- UPLC-MS of compound <u>1b</u> after oxidation (TOF MS ES$^+$ then TOF MS ES$^-$) :

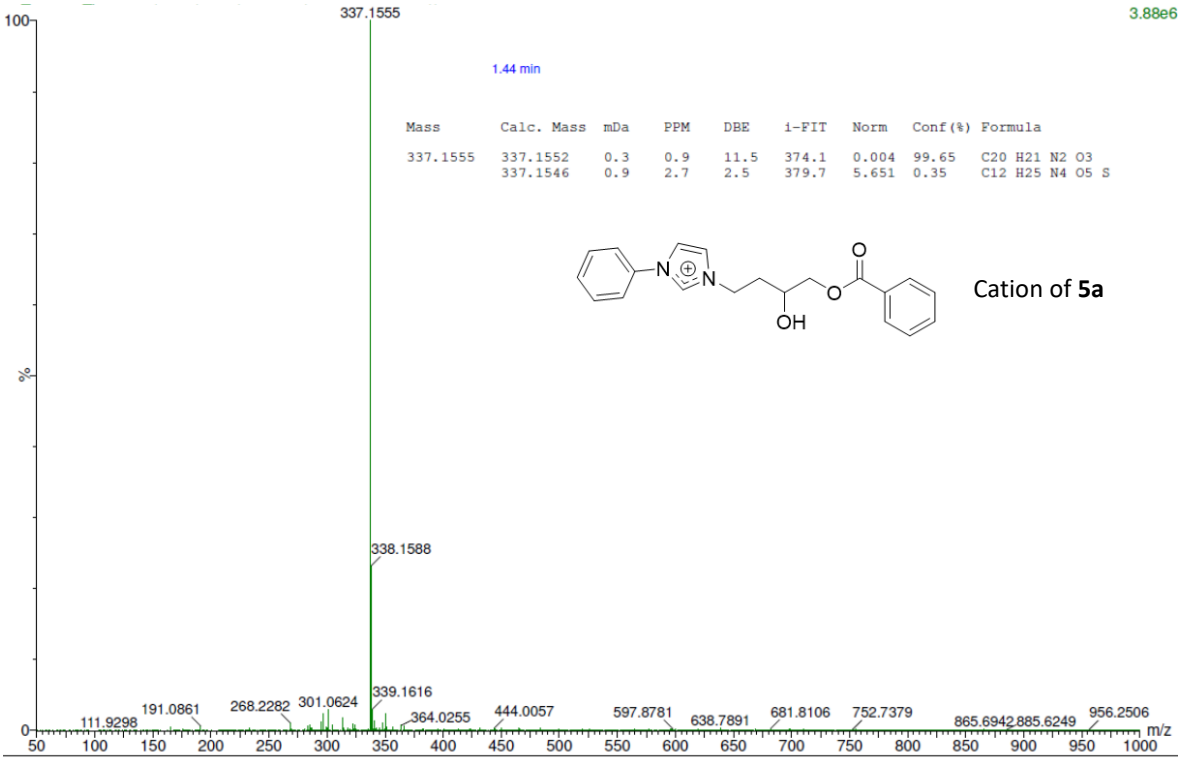
UPLC-MS (**ES$^+$**) :

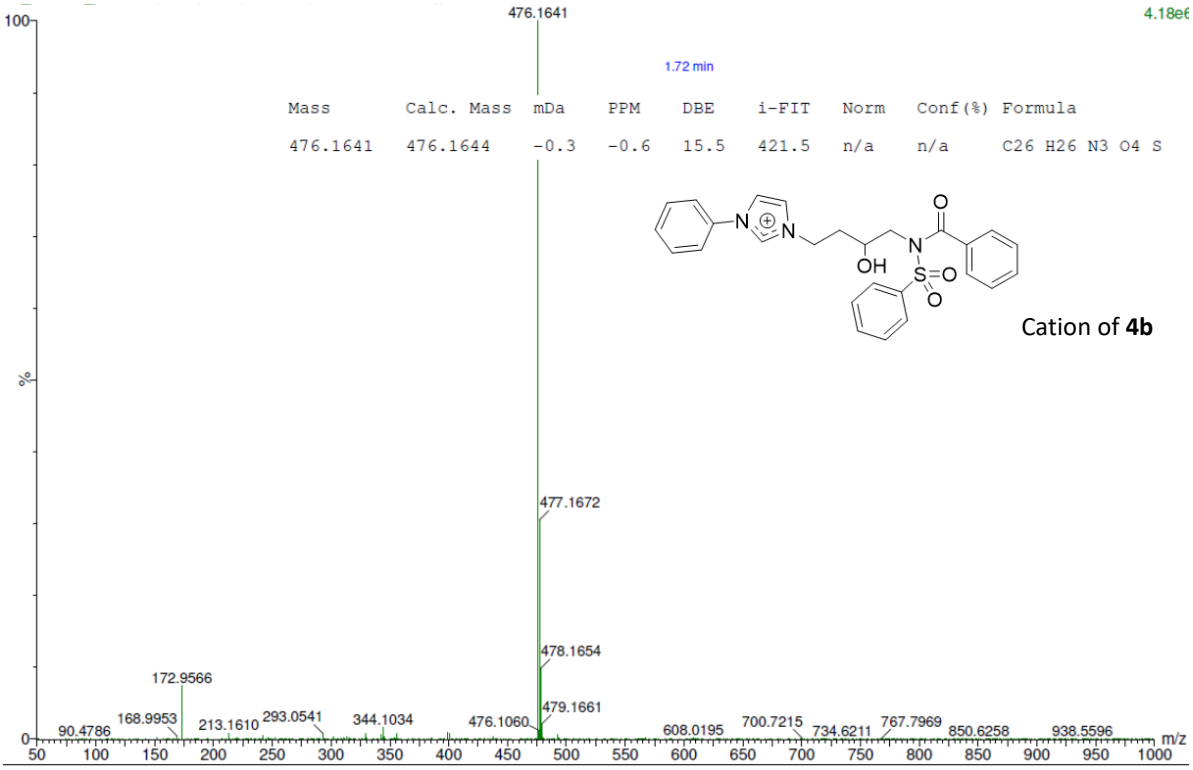


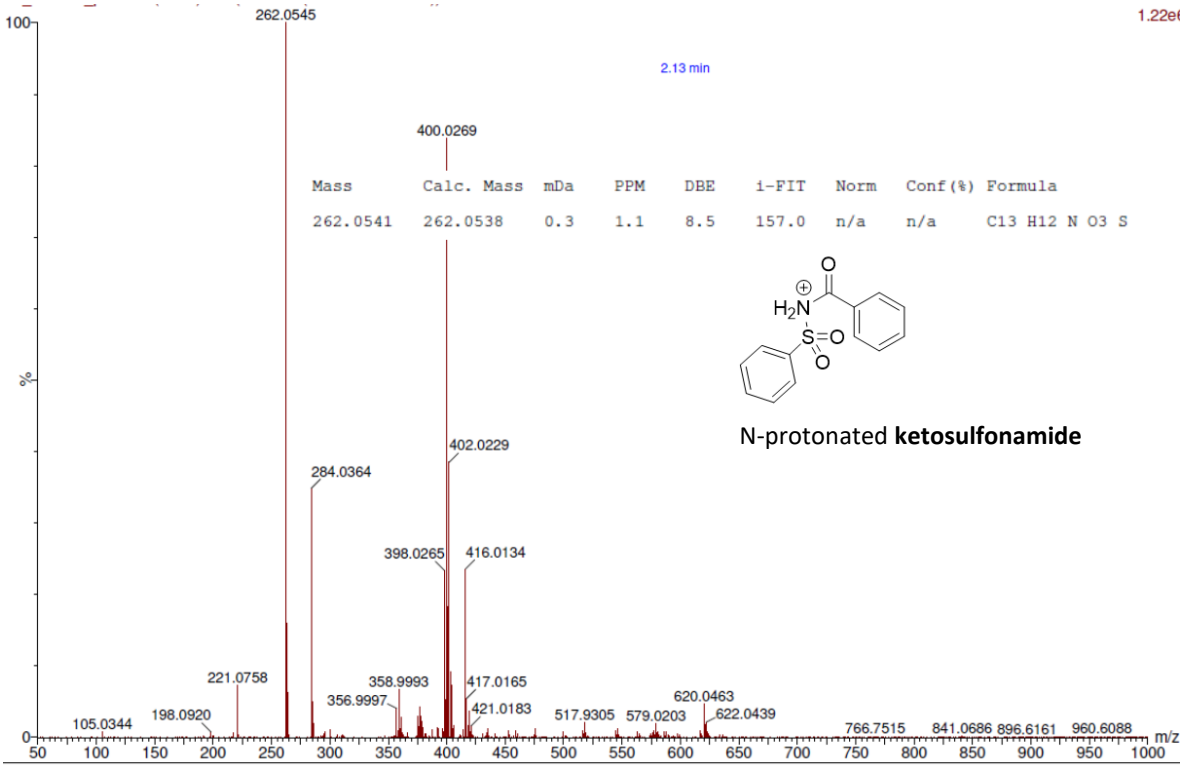
HRMS analyses :



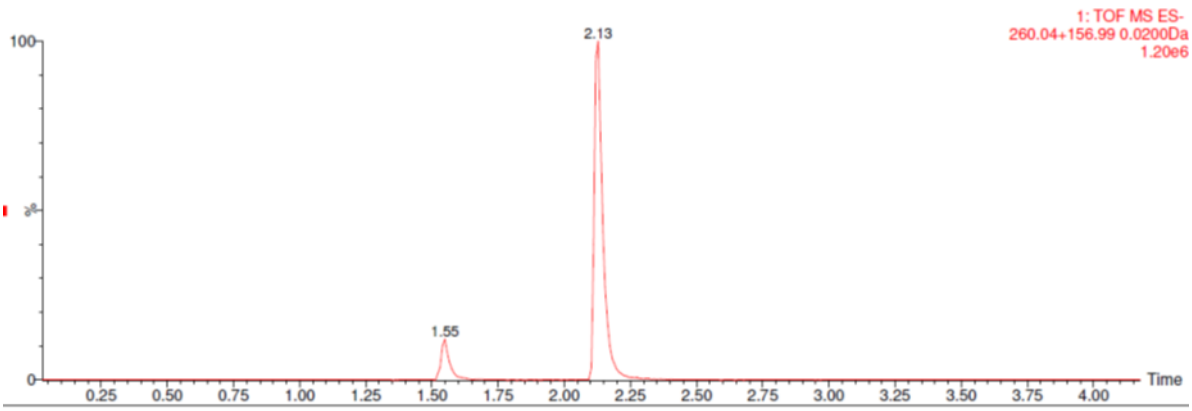

199.1239
6.05e6
0.70 min
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
199.1239 199.1235 0.4 2.0 7.5 107.9 n/a n/a C13 H15 N2
Ph
N
N
(-)2
Cation of 1b
%
200.1271
145.0771
364.9261
345.9319
365.9302
128.9815
273.8894
464.8512
507.8691
595.7942
638.8154
730.6885
826.5671
871.5384
939.5298
m/z


337.1555
3.88e6
1.44 min
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
337.1555 337.1552 0.3 0.9 11.5 374.1 0.004 99.65 C20 H21 N2 O3
337.1546 0.9 2.7 2.5 379.7 5.651 0.35 C12 H25 N4 O5 S
N
N
O
O
OH
Cation of 5a
%
338.1588
339.1616
191.0861
268.2282
301.0624
111.9298
364.0255
444.0057
597.8781
638.7891
681.8106
752.7379
865.6942
885.6249
956.2506
m/z

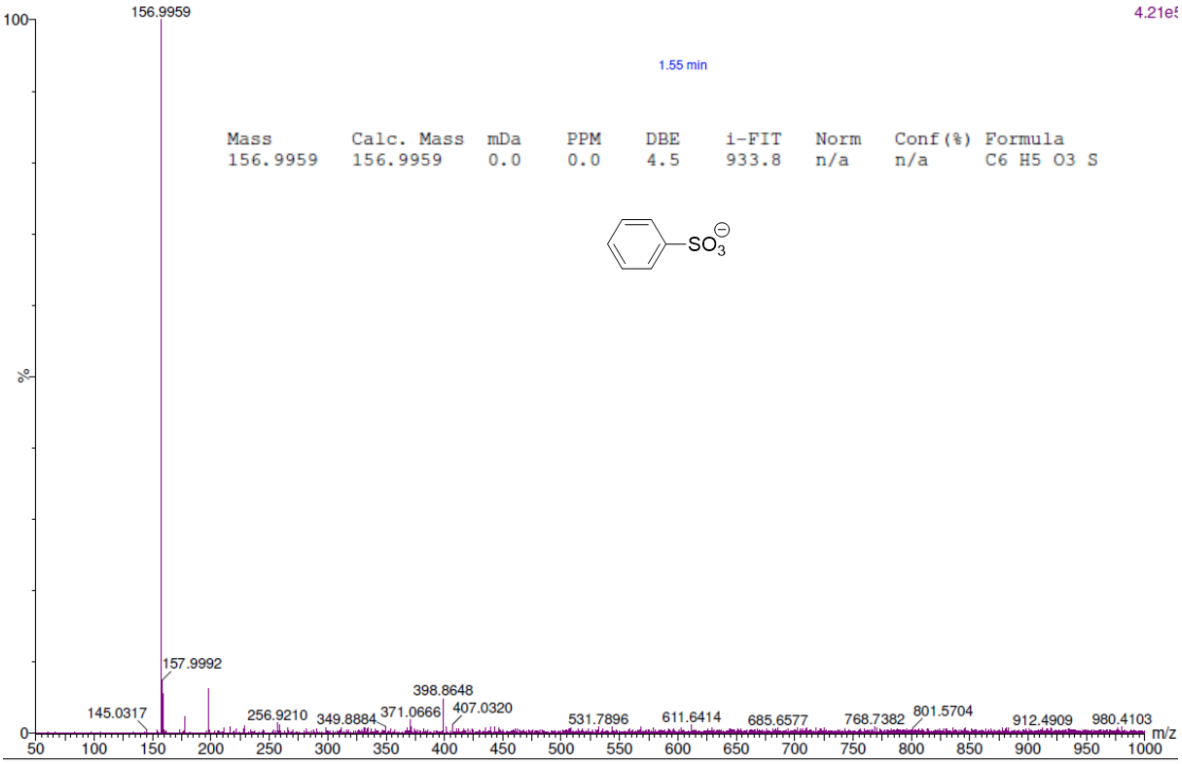

476.1641
4.18e6
1.72 min
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
476.1641 476.1644 -0.3 -0.6 15.5 421.5 n/a n/a C26 H26 N3 O4 S
Cation of 4b
477.1672
478.1654
479.1661
172.9566
168.9953
213.1610
293.0541
344.1034
476.1060
90.4786
608.0195
700.7215
734.6211
767.7969
850.6258
938.5596
%
m/z

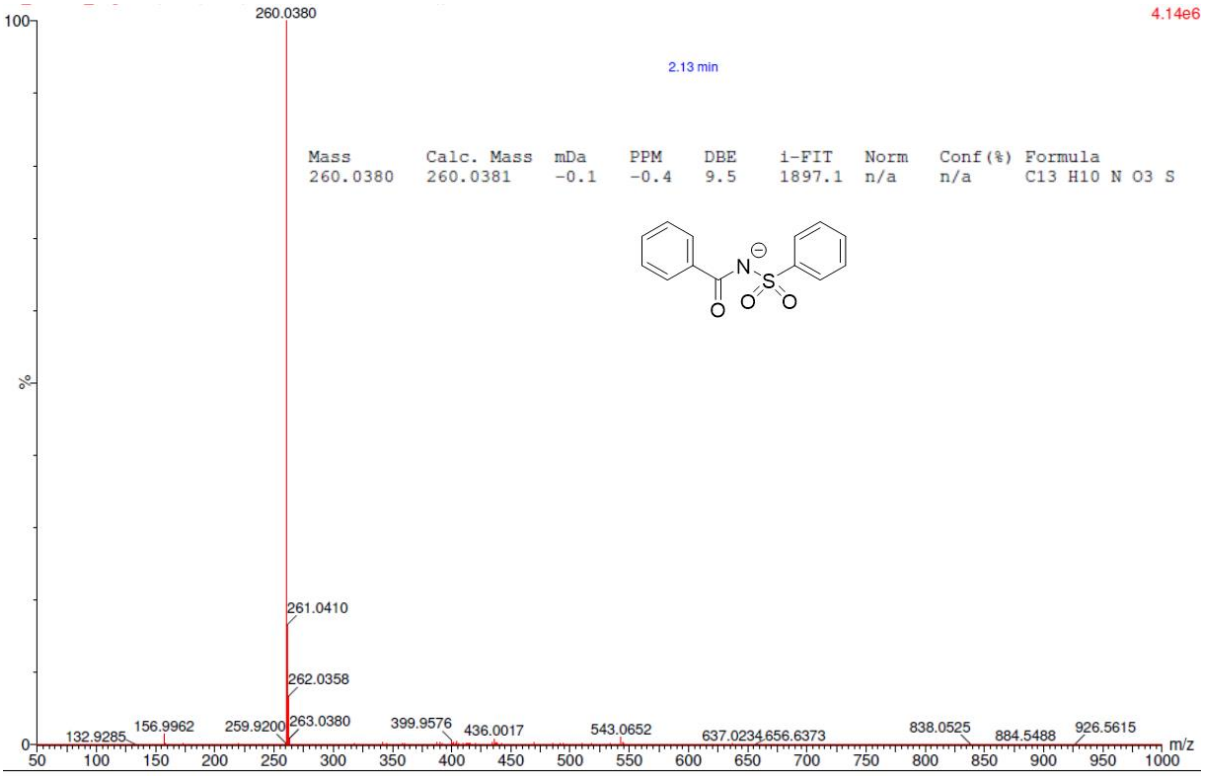

262.0545
1.22e6
2.13 min
400.0269
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
262.0541 262.0538 0.3 1.1 8.5 157.0 n/a n/a C13 H12 N O3 S
N-protonated ketosulfonamide
402.0229
284.0364
398.0265
416.0134
221.0758
358.9993
417.0165
356.9997
421.0183
620.0463
622.0439
105.0344
198.0920
517.9305
579.0203
766.7515
841.0686
896.6161
960.6088
%
m/z

UPLC-MS (**ES**$^-$) :



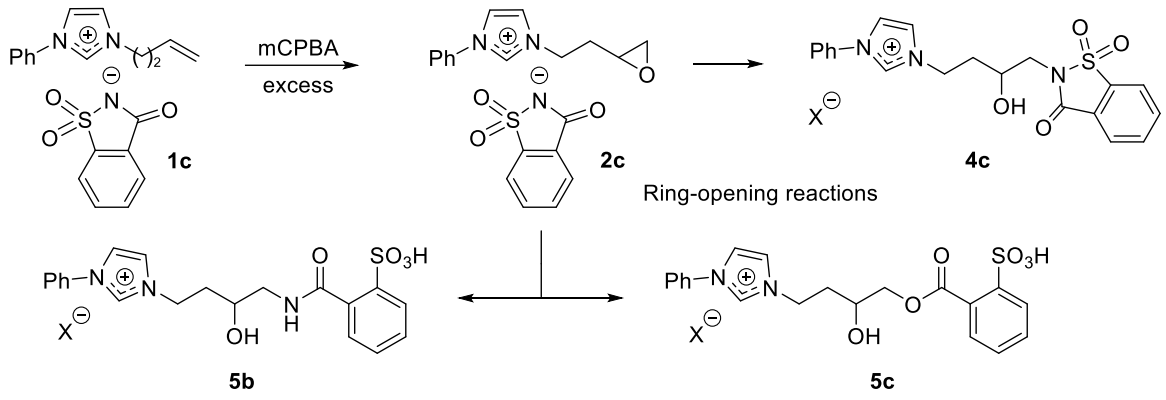
HRMS analyses :



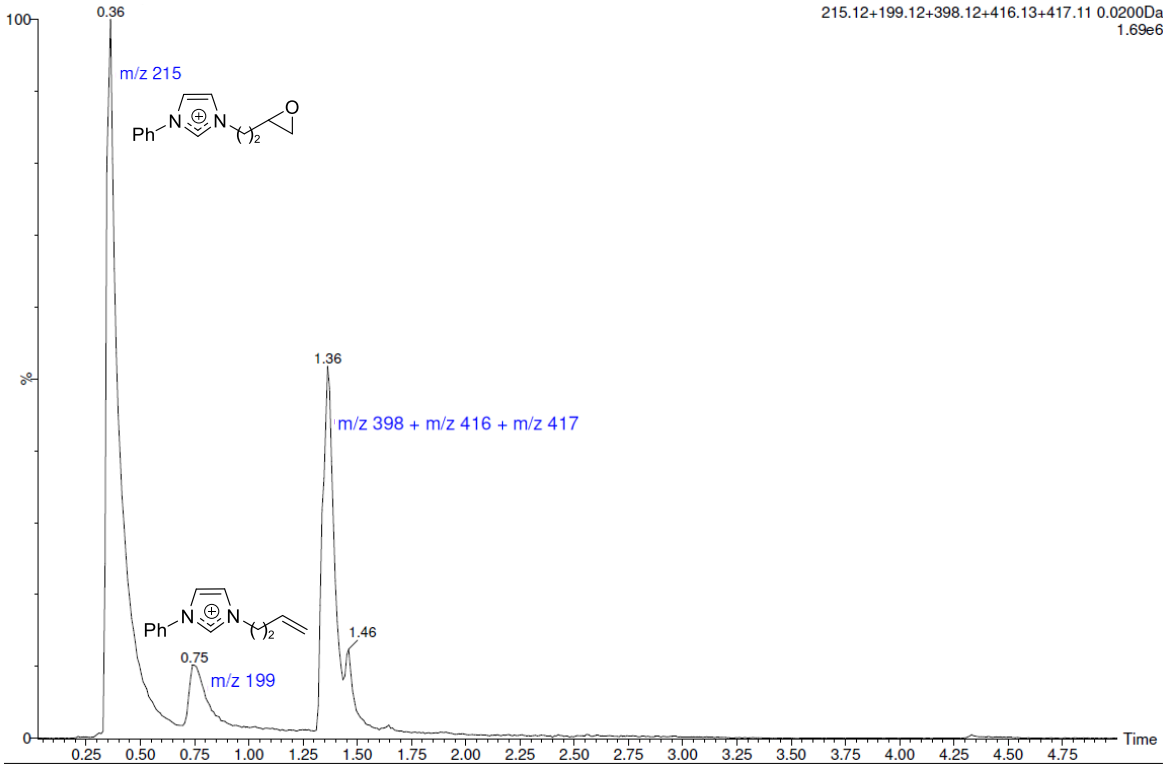


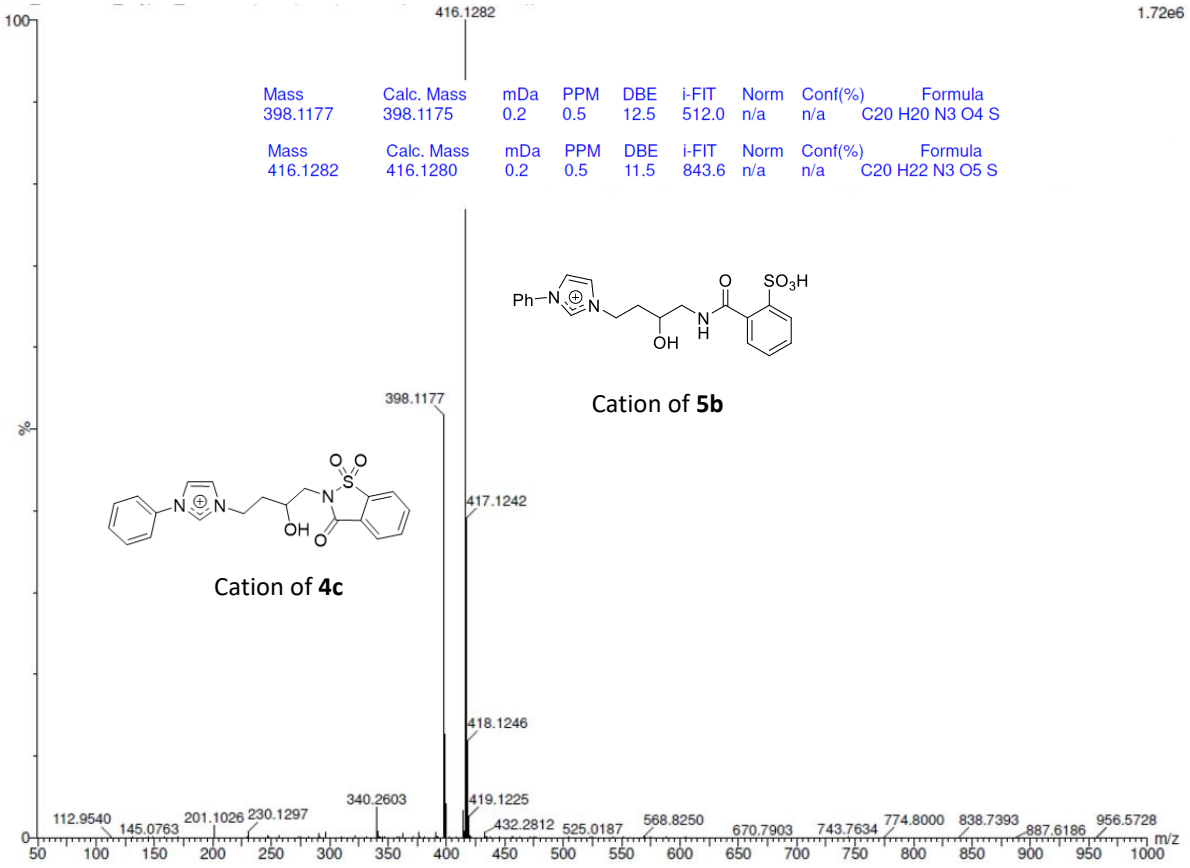
- UPLC-MS of imidazolium <u>saccharinate</u> 1c after oxidation (TOF MS ES$^+$ then TOF MS ES$^-$)

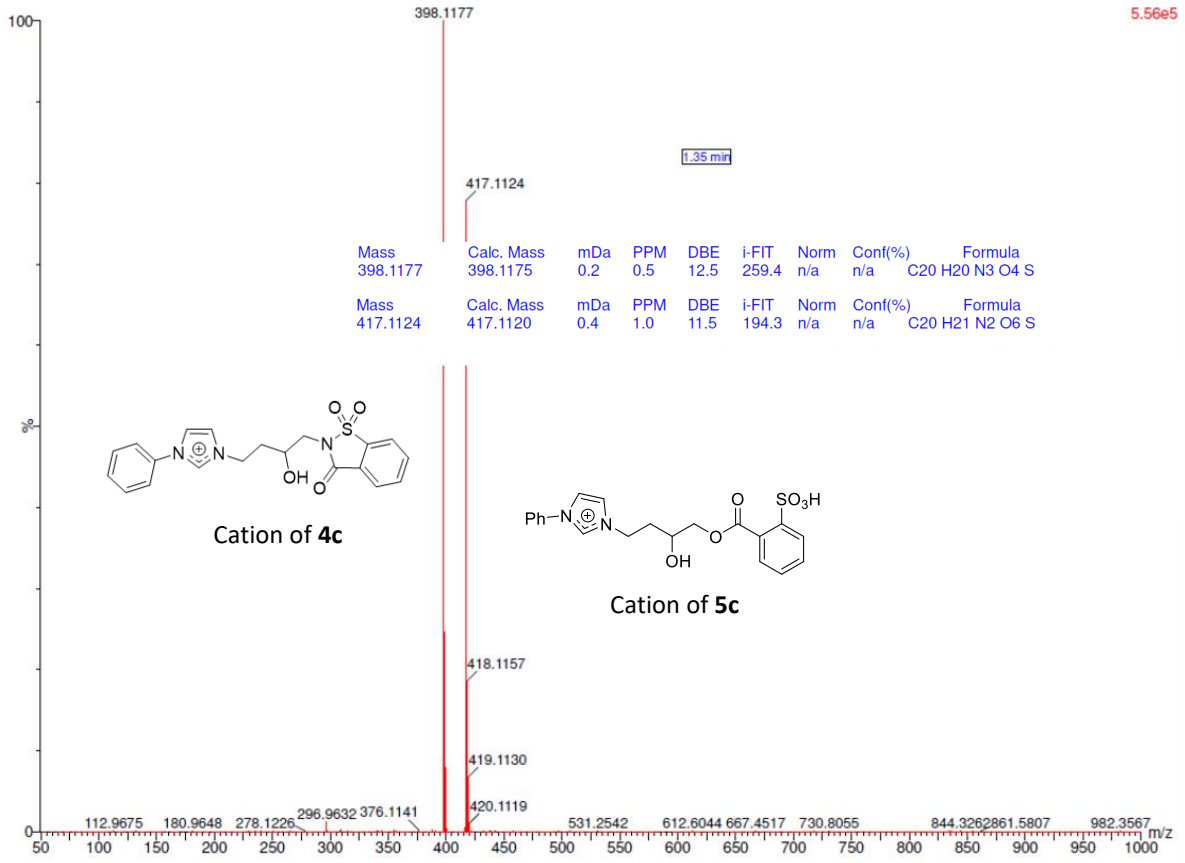
Suggested reactions in accordance with previous analyses:



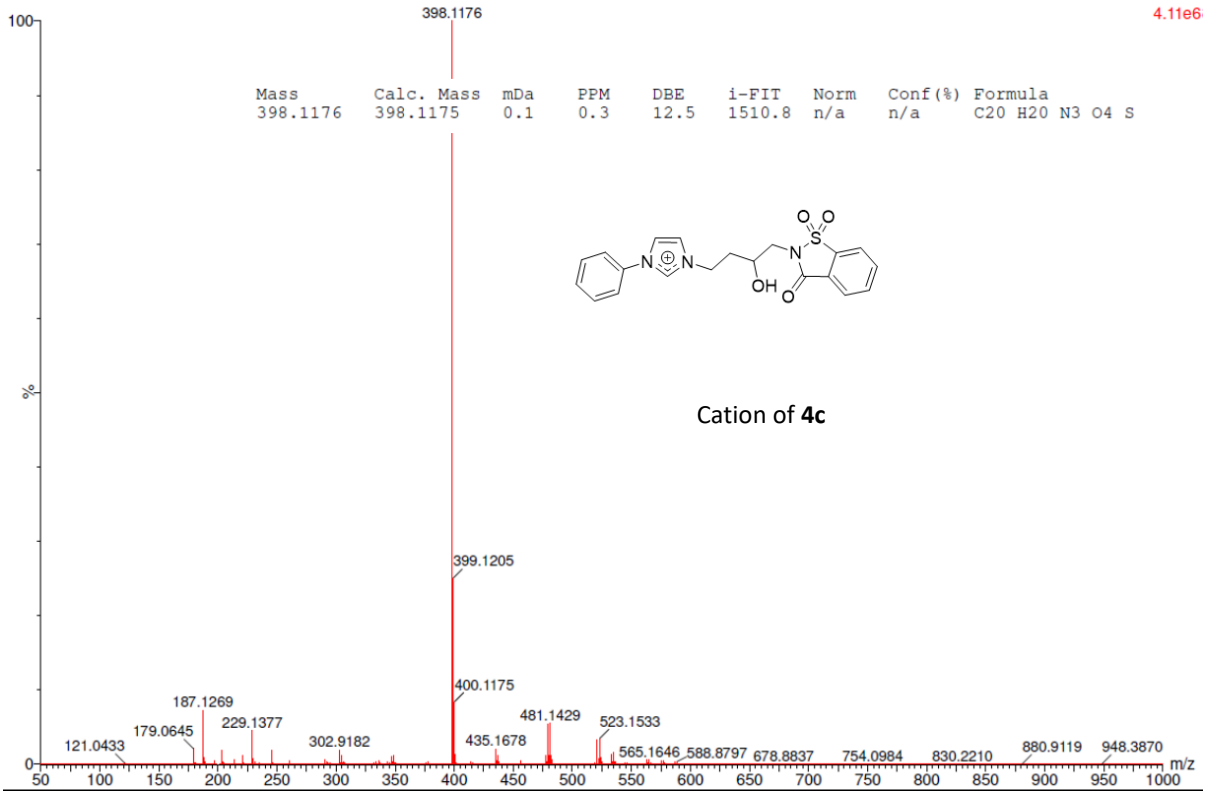
UPLC-MS (**ES$^+$**) :


215.12+199.12+398.12+416.13+417.11 0.0200Da
1.69e6
0.36
m/z 215
1.36
m/z 398 + m/z 416 + m/z 417
1.46
0.75
m/z 199
Time

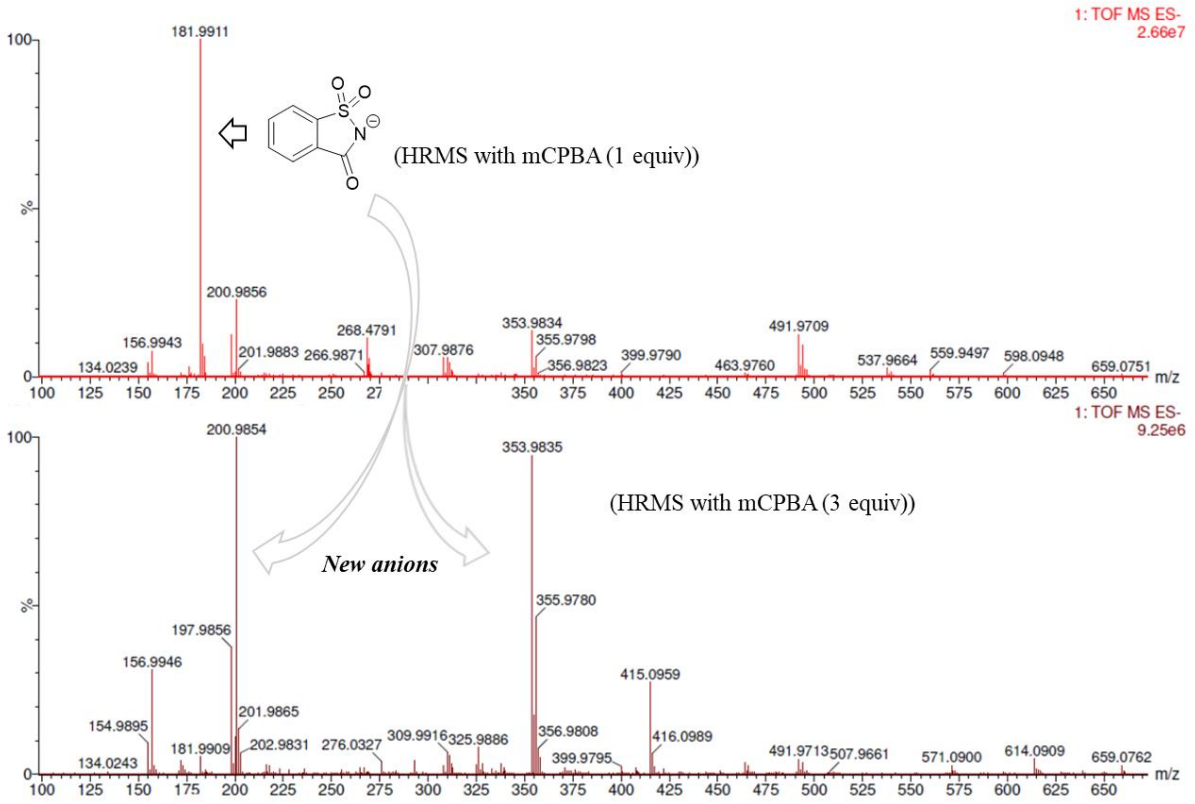

416.1282
1.72e6
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
398.1177 398.1175 0.2 0.5 12.5 512.0 n/a n/a C20 H20 N3 O4 S
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
416.1282 416.1280 0.2 0.5 11.5 843.6 n/a n/a C20 H22 N3 O5 S
Cation of 5b
398.1177
417.1242
Cation of 4c
418.1246
419.1225
340.2603
m/z



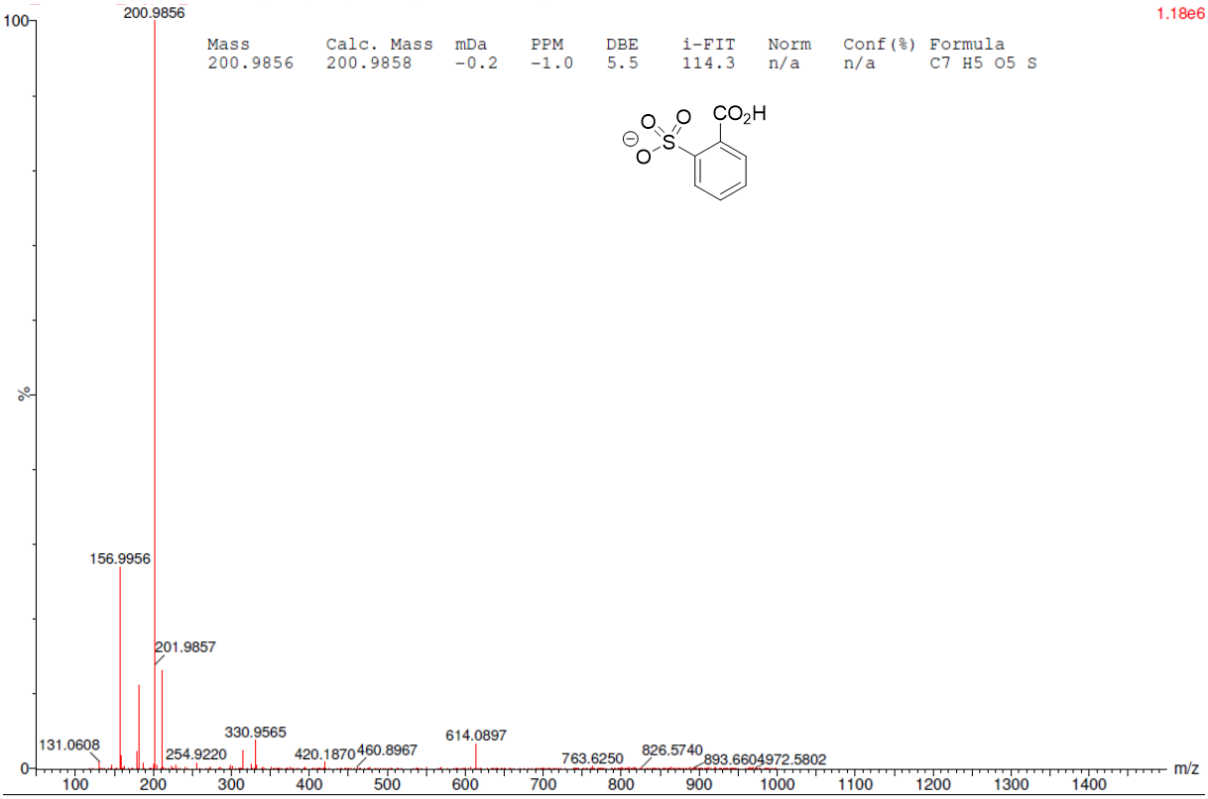
UPLC-MS analysis with a gradient 95% H_2O → 100% CH_3CN to separate **4c** (m/z = 398):

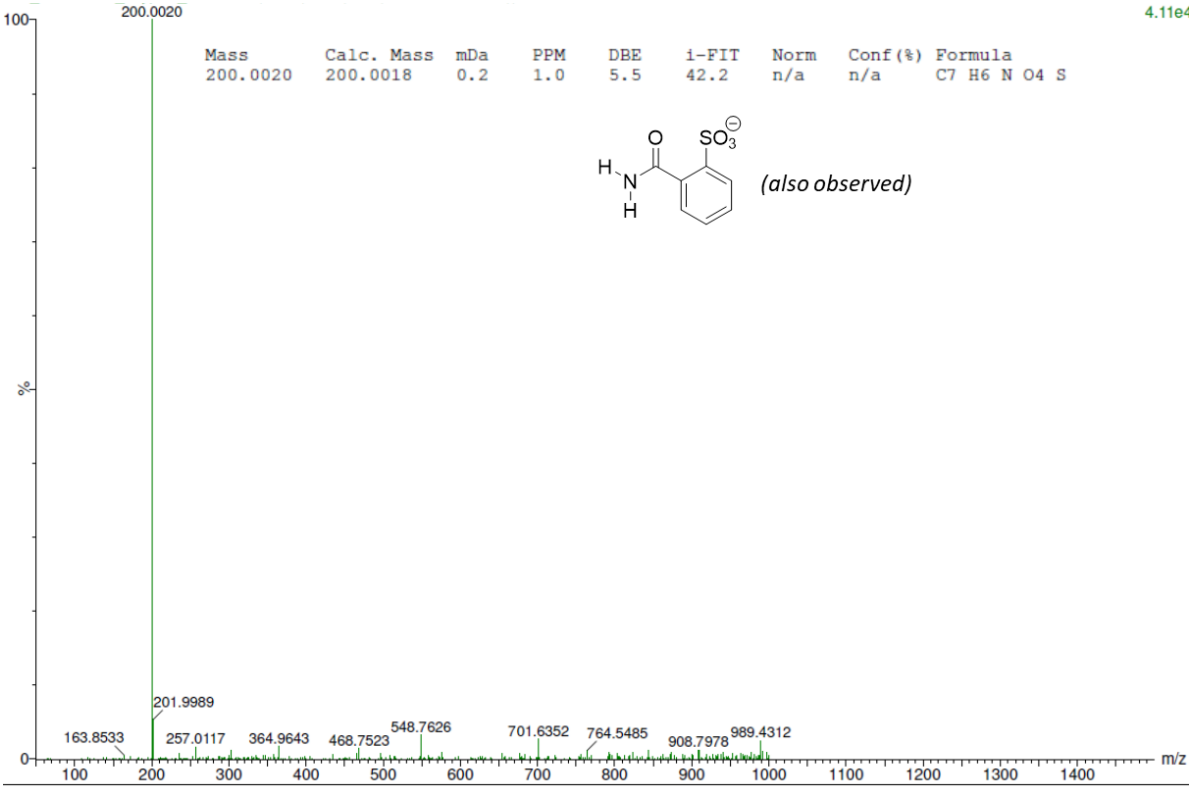


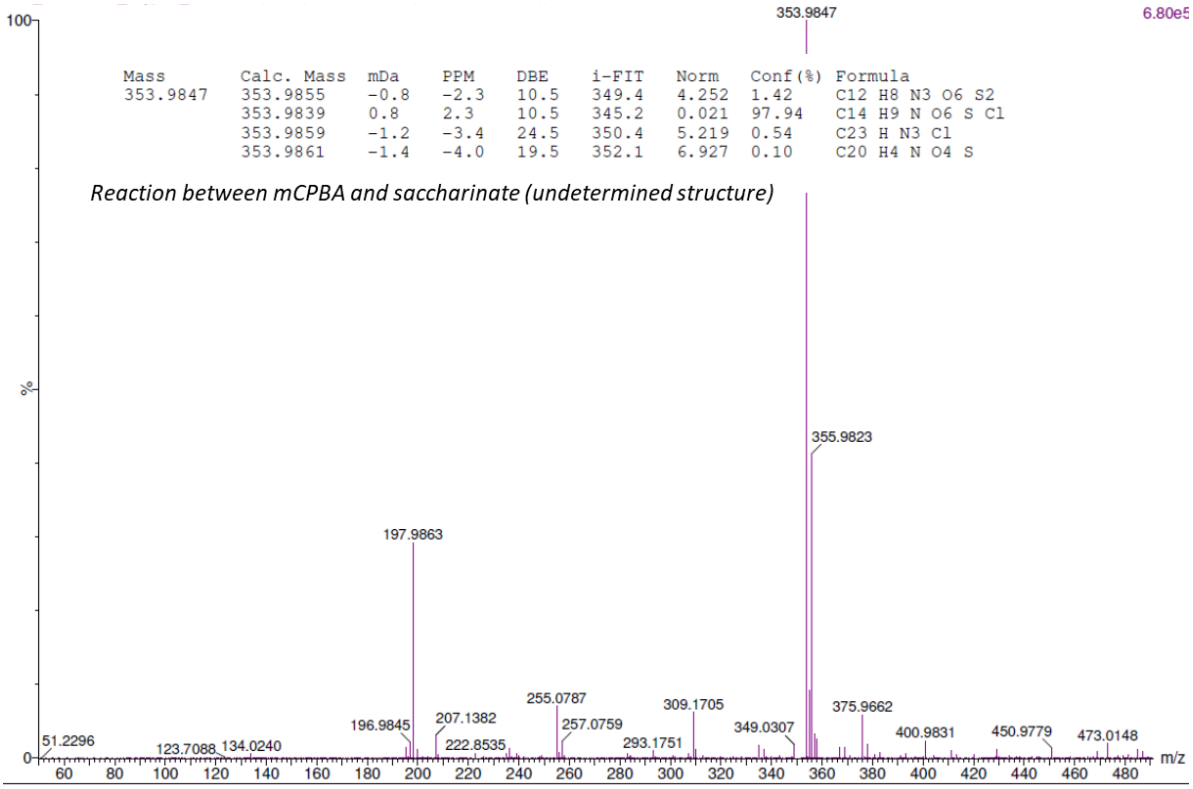
Study of the ring opening reaction (saccharinate) in the presence of one equivalent or an excess of mCPBA (direct infusion):



Analyses of these news anions by UPLC-MS :




200.0020
4.11e4
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
200.0020 200.0018 0.2 1.0 5.5 42.2 n/a n/a C7 H6 N O4 S
(also observed)
201.9989
163.8533
257.0117
364.9643
468.7523
548.7626
701.6352
764.5485
908.7978
989.4312
m/z


353.9847
6.80e5
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
353.9847 353.9855 -0.8 -2.3 10.5 349.4 4.252 1.42 C12 H8 N3 O6 S2
353.9839 0.8 2.3 10.5 345.2 0.021 97.94 C14 H9 N O6 S Cl
353.9859 -1.2 -3.4 24.5 350.4 5.219 0.54 C23 H N3 Cl
353.9861 -1.4 -4.0 19.5 352.1 6.927 0.10 C20 H4 N O4 S
Reaction between mCPBA and saccharinate (undetermined structure)
355.9823
197.9863
196.9845
207.1382
222.8535
255.0787
257.0759
293.1751
309.1705
349.0307
375.9662
400.9831
450.9779
473.0148
51.2296
123.7088
134.0240
m/z

II. General experimental and analytical data

All reagents were purchased from Sigma Aldrich, Alfa Aesar or TCI and were used without further purification and used as received : mCPBA (≤77% from Sigma Aldrich), 4-bromo-1-butene (97% from Alfa Aesar), Lithium bis(trifluoromethylsulfonyl)imide (>98% from Alfa Aesar), Anisole (>99% from Sigma Aldrich), chlorosulfonic acid (99% from Sigma Aldrich), ammonium hydroxide (28% from Sigma Aldrich), sodium hydride (60% from Sigma Aldrich), trifluoromethane sulfonamide (>98% from TCI), 4-fluorobenzenesulfonyl chloride (98% from Alfa Aesar), 4-methoxybenzenesulfonyl chloride (98% from Alfa Aesar), 4-(trifluoromethyl)benzenesulfonyl chloride (98% from Alfa Aesar). Solvents were used in RPE grade without further purification. Anhydrous solvents were obtained from a PURESOLV SPS400 apparatus developed by Innovative Technology Inc. All ionic liquids (**9**, **10**, **12a-c**, **13a-c**, **14a-b**, **15a-b**) were dried with a vane pump (3 mbar) at room temperature for 1-2 h. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker AvanceIII 400 MHz, 500 MHz or AvanceNEO 600 MHz spectrometer. Samples were dissolved in an appropriate deuterated solvent ($CDCl_3$, DMSO-d_6, acetone-d_6). The chemical shifts (δ) are expressed in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C nuclei, and coupling constants are indicated in Hz. Abbreviations for signal coupling are as follows: s=singlet; d=doublet; dd=doublet of doublets; t=triplet; q=quartet; quin=quintet; m=multiplet; br=broad signal. To assign the signals to the different proton and carbon atoms, as well as the relative stereochemistry of the cycloadducts, additional 2D NMR experiments (COSY, HSQC, HMBC) and NOESY experiments were performed. High-resolution mass spectra (HRMS) were performed on Acquity UPLC H-Class Xevo G2-XS QTof (WATERS) by electrospray ionization (ESI). Infrared (IR) spectra were recorded with a Perkin Elmer 16 PC FTIR ATR spectrometer, using the pure product (oil or solid). Thin Layer Chromatography (TLC) was run on pre-coated aluminum plates of silica gel 60 F-254 (Merck). Flash chromatography was performed on silica gel column (Merck silica gel, 40-63 mm) using air pressure.

Preparation of Dimethyldioxirane (DMDO). This reagent was prepared according to the procedure described by D. F. Taber.[1] Titration of different solutions prepared by this procedure afforded a DMDO concentration between 0.04 mol/L and 0.09 mol/L.[2]

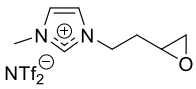
In a 1 mL volumetric test tube, a 0.7 M (C_{sol}) solution of thioanisole in acetone-d_6 is prepared, to a total volume of 1 mL (0.08 mL of thioanisole + 0.92 mL of acetone-d_6). A 0.6 mL portion of this solution is transferred to a tube and chilled to ca. 10 °C in a dry ice/water bath. Upon reaching 10 °C, 3.0 mL of the obtained DMDO solution is added to the thioanisole solution. The resulting solution is stirred for 10 min and then a portion of the solution is added directly to an NMR tube.

III. Preparation of the epoxidized salts

General procedure: To a solution of corresponding alkene in acetone (1 mL) was added freshly prepared DMDO. The reaction mixture was stirred at room temperature until the reaction is completed (^{1}H NMR monitoring). Two drops of dimethyl sulfide (DMS) was added to quench

the reaction mixture and neutralized the excess of DMDO. The crude was concentrated under reduced pressure.

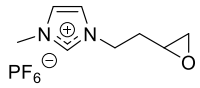
3-[2-(Oxiran-2-yl)ethyl]-1-methylimidazolium bis(trifluoromethanesulfonyl)imide (3a)



According to the general procedure, the title compound was prepared with 1-(3-Buten-1-yl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide[3] (100 mg, 0.240 mmol, 1.0 equiv) in acetone (1 mL) and freshly prepared DMDO (0.04 mol/L) (7.99 mL, 0.335 mmol, 1.4 equiv). The reaction mixture was stirred at room temperature for 6 h. The product **3a** was obtained as a yellow oil (103 mg, 99 %).

^{1}H NMR (400 MHz, acetone-d_6) δ 9.11 (s, 1H), 7.75-7.83 (m, 2H), 4.57 (t, J = 6.9 Hz, 2H), 4.10 (s, 3H), 3.01-3.04 (m, 1H), 2.70-2.72 (m, 1H), 2.47-2.49 (m, 1H), 2.35-2.40 (m, 1H), 1.97-2.05 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 137.7, 124.9, 123.7, 121.0 (q, J_{CF} = 322.4 Hz), 49.6, 48.0, 46.5, 36.7, 33.7. ^{19}F NMR (376 MHz, acetone-d_6) δ -80.0. IR (neat) cm^{-1} 3159, 3122, 1575, 1348, 1330, 1177, 1132, 1051, 789, 740. HRMS m/z (ESI): calcd. for $C_8H_{13}N_2O$ $[M]^+$: 153.1028, found: 153.1029.

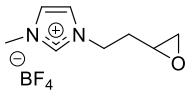
3-[2-(Oxiran-2-yl)ethyl]-1-methylimidazolium hexafluorophosphate (3b)



According to the general procedure, the title compound was prepared with 1-(3-Buten-1-yl)-3-methylimidazolium hexafluorophosphate[3] (100 mg, 0.354 mmol, 1.0 equiv) in acetone (1 mL) and freshly prepared DMDO (0.06 mol/L) (8.27 mL, 0.496 mmol, 1.4 equiv). The reaction mixture was stirred at room temperature for 6 h. The product **3b** was obtained as a yellow oil (85 mg, 80 %).

^{1}H NMR (400 MHz, acetone-d_6) δ 9.06 (s, 1H), 7.73-7.81 (m, 2H), 4.56 (t, J = 6.9 Hz, 2H), 4.08 (s, 3H), 3.00-3.05 (m, 1H), 2.70-2.72 (m, 1H), 2.47-2.49 (m, 1H), 2.31-2.39 (m, 1H), 1.96-2.10 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 137.7, 124.9, 123.7, 49.6, 47.9, 46.5, 36.7, 33.7. ^{19}F NMR (376 MHz, acetone-d_6) δ -71.6, -73.5. IR (neat) cm^{-1} 3171, 3125, 2971, 1576, 1464, 1429, 1168, 1024, 817, 749. HRMS m/z (ESI): calcd. for $C_8H_{13}N_2O$ $[M]^+$: 153.1028, found: 153.1029.

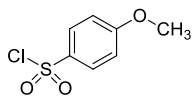
3-[2-(Oxiran-2-yl)ethyl]-1-methylimidazolium tetrafluoroborate (3c)



According to the general procedure, the tithe compound was prepared with 1-(3-Buten-1-yl)-3-methylimidazolium tetrafluoroborate[3] (100 mg, 0.4464 mmol, 1.0 equiv) in acetone (1 mL) and freshly prepared DMDO (0.07 mol/L) (8.93 mL, 0.625 mmol, 1.4 equiv). The reaction mixture was stirred at room temperature for 6 h. The product **3c** was obtained as a yellow oil (107 mg, 100 %).

^{1}H NMR (400 MHz, acetone-d_6) δ 9.06 (s, 1H), 7.72-7.80 (m, 2H), 4.55 (t, J = 6.9 Hz, 2H), 4.07 (s, 3H), 3.01-3.05 (m, 1H), 2.69-2.71 (m, 1H), 2.47-2.49 (m, 1H), 2.29-2.37 (m, 1H), 1.98-2.09 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 137.9, 124.8, 123.6, 49.6, 47.9, 46.5, 36.7, 33.7. ^{19}F NMR (376 MHz, acetone-d_6) δ -152.5, -152.6. IR (neat) cm^{-1} 3165, 2935, 1635, 1576, 1463, 1430, 1290, 1168, 1014, 952. HRMS m/z (ESI): calcd. for $C_8H_{13}N_2O$ $[M]^+$: 153.1028, found: 153.1025.

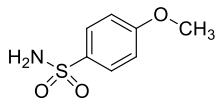
4-methoxybenzenesulfonyl chloride (6)



To a solution of anisole (1.84 g, 17.0 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) at -5 °C was added dropwise chlorosulfonic acid (4.95 g, 2.82 mL, 42.5 mmol, 2.5 equiv) in CH_2Cl_2 (10 mL) over 60 min. The reaction mixture was stirred for 1h then allowed to warm to room temperature. The reaction advancement was monitoring by NMR. After 1 h, the reaction mixture was concentrated under reduced pressure with membrane pump (10-15 mbar) at 40 °C. The product **6** was obtained as a colorless liquid and quickly used without any purification (3.19 g, 91 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.1 Hz, 2H), 7.05 (d, *J* = 9.1 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 136.2, 129.7, 114.8, 56.1. IR (neat) cm^{-1} 3102, 2947, 2845, 1591, 1495, 1369, 1264, 1160, 1083, 1020. HRMS m/z (ASAP): calcd. for $C_7H_7O_3SCl$ $[M]^+$: 205.9804, found: 205.9801.

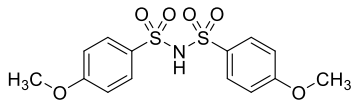
4-methoxybenzenesulfonamide (7)



A mixture of compound **6** (302 mg, 1.46 mmol, 1.0 equiv) and 28-30 % aqueous ammonium hydroxide (4 mL) with dichloromethane (3 mL) added to solubilize the mixture was prepared at 0 °C and stirred for 3-4 h. The reaction advancement was monitoring by TLC with cyclohexane/ethyl acetate (9/1). When the reaction was completed, the reaction mixture was warmed to room temperature and concentrated under reduced pressure with membrane pump (10-15 mbar). The product **7** was obtained as a white solid and was used without any purification (273 mg, 100 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 4.84 (bs, 2H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1, 133.7, 128.8, 114.4, 55.8. IR (neat) cm^{-1} 3343, 3266, 2983, 2923, 2850, 1596, 1499, 1300, 1255, 1102. Mp: 111.9 °C. HRMS m/z (ESI): calcd. for $C_7H_8NO_3S$ $[M-H]^-$: 186.0225, found: 186.0222.

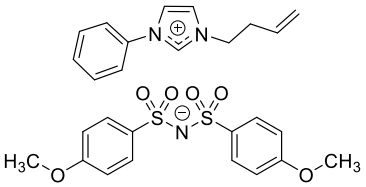
Bis(4-methoxybenzene)sulfonimide (8)



To a solution of compound **7** (374.44 mg, 2.00 mmol, 1.0 equiv) in anhydrous THF (10 mL) was added sodium hydride (168 mg, 4.2 mmol, 2.1 equiv) and the reaction mixture was stirred for 1 h at room temperature. 4-methoxybenzenesulfonyl chloride **6** (413.3 mg, 2.0 mmol, 1.0 equiv) in anhydrous THF (10 mL) was added dropwise to the reaction mixture followed by DMF (20 mL). The reaction advancement was monitored by TLC for 48 h with cyclohexane/ethyl acetate (4/6). The white precipitate formed was filtered and washed with diethyl ether. The filtrate was concentrated under reduced pressure with membrane pump (10-15 mbar). HCl 1M was added to the crude and the product was extracted with dichloromethane. The organic layer was concentrated under vacuum. The product **8** was obtained as a white solid (411 mg, 58 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 4H), 6.97 (d, *J* = 8.9 Hz, 4H), 3.89 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 131.1, 130.4, 114.4, 55.9. IR (neat) cm^{-1} 3100, 2976, 2923, 1593, 1497, 1365, 1261, 1150, 1086, 1020. Mp: 99.9 °C. HRMS m/z (ESI): calcd. for $C_{14}H_{14}NO_6S_2$ $[M-H]^-$: 356.0263, found: 356.0256.

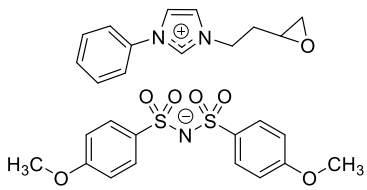
1-Phenyl-(3-buten-1-yl)imidazolium bis(4-methoxybenzene)sulfonimide (9)



To a solution of compound **8** (367 mg, 1.027 mmol, 1.0 equiv) in H_2O (100 mL) and CH_3CN (10 mL) was added NaOH (41.07 mg, 1.027 mmol, 1.0 equiv) and the reaction mixture was stirred for 1 h. Then, 3-(3-Buten-1-yl)-1-phenylimidazolium bromide[3] (287 mg, 1.027 mmol, 1.0 equiv) in H_2O (2 mL) was added and the solution was stirred at room temperature for 24 h. CH_3CN was removed under reduced pressure and the reaction mixture was extracted with dichloromethane. The organic layer was washed several times with water, dried with $MgSO_4$ and then concentrated under reduced pressure. The product **9** was obtained as a yellow oil (360 mg, 63 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.67-7.73 (m, 3H), 7.61-7.63 (m, 1H), 7.56 (d, *J* = 8.9 Hz, 4H), 7.42-7.53 (m, 3H), 6.65 (d, *J* = 8.9 Hz, 4H), 5.80 (ddt, *J* = 17.7, 10.8, 6.8 Hz, 1H), 5.00-5.07 (m, 2H), 4.56 (t, *J* = 6.8 Hz, 2H), 3.75 (s, 6H), 2.65 (q, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 136.3, 135.8, 134.7, 133.0, 130.6, 130.1, 128.8, 123.6, 122.0, 120.9, 119.5, 113.1, 55.5, 49.8, 34.5. IR (neat) cm^{-1} 3137, 3097, 2927, 2840, 1596, 1496, 1250, 1146, 1128, 1076. HRMS m/z (ESI): calcd. for $C_{14}H_{14}NO_6S_2$ $[M]^-$: 356.0263, found: 356.0264; calcd. for $C_{13}H_{15}N_2$ $[M]^+$: 199.1235, found: 199.1234.

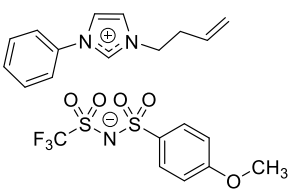
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium bis(4-methoxybenzene)sulfonimide (10)



To a solution of compound **9** (50 mg, 0.090 mmol, 1.0 equiv) in acetone (0.50 mL) was added freshly prepared DMDO (0.05 mol/L) (4.32 mL, 0.216 mmol, 2.4 equiv) also at -20 °C and the reaction mixture was stirred at room temperature for 7 h. Two drops of dimethyl sulfide (DMS) was added to quench the reaction mixture and neutralized the excess of DMDO. The reaction mixture was concentrated under reduced pressure and the product **10** was obtained as a yellow oil (51 mg, 100 %).

^{1}H NMR (500 MHz, acetone-d_6) δ 10.09 (s, 1H), 8.21-8.25 (m, 1H), 8.06-8.09 (m, 1H), 7.87-7.92 (m, 2H), 7.57-7.75 (m, 7H), 6.78-6.85 (m, 4H), 4.72 (t, *J* = 6.8 Hz, 2H), 3.81 (s, 6H), 3.10-3.16 (m, 1H), 2.67-2.71 (m, 1H), 2.50-2.54 (m, 1H), 2.37-2.45 (m, 1H), 2.09-2.15 (m, 1H). ^{13}C NMR (126 MHz, acetone-d_6) δ 161.0, 138.6, 136.2, 136.1, 130.3, 130.2, 129.8, 128.5, 123.8, 122.1, 121.2, 112.7, 55.4, 49.0, 47.5, 45.6, 32.8. IR (neat) cm^{-1} 3141, 3098, 3007, 2841, 1595, 1496, 1251, 1129, 1079, 1023. HRMS m/z (ESI): calcd. for $C_{14}H_{14}NO_6S_2$ $[M]^-$: 356.0263, found: 356.0272; calcd. for $C_{13}H_{15}N_2O$ $[M]^+$: 215.1184, found: 215.1189.

1-Phenyl-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-methoxybenzenesulfonyl)imide (12a)

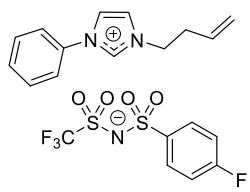


To a solution of trifluoromethanesulfonamide (721.5 mg, 4.84 mmol, 1.0 equiv) in anhydrous THF (20 mL) and DMF (2 mL) was added sodium hydride (406.5 mg, 10.16 mmol, 2.1 equiv) and the reaction mixture was stirred for 1 h and a solution of 4-methoxybenzenesulfonyl chloride **6** (1.0 g, 4.84 mmol, 1.0 equiv) in anhydrous THF (20 mL) was added dropwise. The reaction mixture was stirred for 48 h. The

white precipitate formed was filtered, washed with diethyl ether and the filtrate was concentrated under vacuum. The sulfonamide **11a** was obtained as a white solid (1.65 g, 100 %) and was used without any purification. To a solution of sulfonamide **11a** (1.65 g, 4.835 mmol, 1.0 equiv) in H_2O (100 mL) was added 3-(3-Buten-1-yl)-1-phenylimidazolium bromide[3] (1.35 g, 4.835 mmol, 1.0 equiv). The solution was stirred at room temperature for 24 h and then extracted with dichloromethane. The organic layer was washed several times with water, dried over $MgSO_4$, filtered and concentrated under vacuum. The product **12a** was obtained as a yellow oil (1.54 g, 62 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.56-7.65 (m, 4H), 7.47-7.55 (m, 3H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.78 (ddt, *J* = 17.1, 10.4, 6.8 Hz, 1H), 5.02-5.11 (m, 2H), 4.47 (t, *J* = 6.8 Hz, 2H), 3.79 (s, 3H), 2.65 (q, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 136.4, 135.1, 134.5, 132.6, 130.7, 130.5, 128.7, 123.5, 122.1, 121.2, 120.5 (q, J_{CF} = 322.4 Hz), 119.8, 113.6, 55.6, 49.8, 34.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.2. IR (neat) cm^{-1} 3140, 3102, 2922, 2846, 1597, 1497, 1318, 1172, 1132, 1045. HRMS m/z (ESI): calcd. for $C_8H_7NO_5F_3S_2$ $[M]^-$: 317.9718, found: 317.9720; calcd. for $C_{13}H_{15}N_2$ $[M]^+$: 199.1235, found: 199.1237.

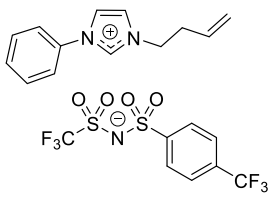
1-Phenyl-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide (12b)



To a solution of trifluoromethane sulfonamide (300 mg, 2.01 mmol, 1.0 equiv) in anhydrous THF (9 mL) and DMF (1 mL) was added NaH (169 mg, 4.22 mmol, 2.1 equiv) and the reaction mixture was stirred at room temperature for 1 h. Then, a solution of 4-fluorobenzenesulfonyl chloride (391 mg, 2.01 mmol, 1.0 equiv) in THF (9 mL) was added dropwise. The reaction was monitoring by CCM in cyclohexane/ethyl acetate (4/6). After the reaction was completed (12 h), the reaction mixture was concentrated under reduced pressure. The sulfonamide **11b** was obtained as a colorless liquid (662 mg, 100 %) and was used without any purification. To a solution of 3-(3-Buten-1-yl)-1-phenylimidazolium bromide[3] (560 mg, 2.01 mmol, 1.0 equiv) in distilled water (20 mL) was added sulfonamide **11b** (662 mg, 2.01 mmol, 1.0 equiv). The solution was stirred at room temperature for 24 h. The reaction mixture was extracted with dichloromethane and the organic layer was washed several times with water, dried with $MgSO_4$ and then concentrated under reduced pressure. The product **12b** was obtained as a yellow oil (709 mg, 72 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.87-7.93 (m, 2H), 7.49-7.66 (m, 7H), 7.01-7.08 (m, 2H), 5.80 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.04-5.14 (m, 2H), 4.50 (t, *J* = 7.0 Hz, 2H), 2.68 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4 (d, J_{CF} = 252.6 Hz), 140.2, 135.1, 134.4, 132.4, 130.7, 130.5, 129.3 (d, J_{CF} = 9.2 Hz), 123.4, 122.2, 121.2, 120.2 (CF_3, hidden peaks), 119.8, 115.3 (d, J_{CF} = 22.3 Hz), 49.8, 34.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.3, -107.9. IR (neat) cm^{-1} 2955, 2922, 2853, 1460, 1377, 1320, 1132, 1087, 1045, 819. HRMS m/z (ESI): calcd. for $C_7H_4NO_4S_2F_4$ $[M]^-$: 305.9518, found: 305.9528; calcd. for $C_{13}H_{15}N_2$ $[M]^+$: 199.1235, found: 199.1238.

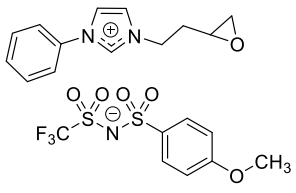
1-Phenyl-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide (12c)



To a solution of trifluoromethane sulfonamide (300 mg, 2.01 mmol, 1.0 equiv) in anhydrous THF (9 mL) and DMF (1 mL) was added NaH (169 mg, 4.22 mmol, 2.1 equiv) and the reaction mixture was stirred at room temperature for 1 h. Then, a solution of 4-(trifluoromethyl)benzenesulfonyl chloride (491 mg, 2.01 mmol, 1.0 equiv) in THF (9 mL) was added dropwise. The reaction was monitoring by CCM in cyclohexane/ethyl acetate (4/6). After the reaction was completed (12 h), the reaction mixture was concentrated under vacuum. The sulfonamide **11c** was obtained as a white solid (762 mg, 100 %) and was used without any purification. To a solution of 3-(3-Buten-1-yl)-1-phenylimidazolium bromide[3] (560 mg, 2.01 mmol, 1.0 equiv) in distilled water (20 mL) was added sulfonamide **11c** (762 mg, 2.01 mmol, 1.0 equiv). The solution was stirred at room temperature for 24 h. The reaction mixture was extracted with dichloromethane and the organic layer was washed several times with water, dried with $MgSO_4$ and then concentrated under reduced pressure. The product **12c** was obtained as a yellow oil (803 mg, 71 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.99-8.06 (m, 3H), 7.51-7.66 (m, 8H), 5.81 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.05-5.16 (m, 2H), 4.54 (t, *J* = 6.8 Hz, 2H), 2.70 (q, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 135.3, 133.0 (Cq, hidden peaks), 132.3, 130.7, 130.6, 127.2, 125.4 (q, J_{CF} = 3.7 Hz), 123.2, 122.2, 121.1, 120-125 (2*CF_3, hidden peaks) 119.8, 49.9, 34.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9, -78.3. IR (neat) cm^{-1} 3141, 3104, 2928, 1668, 1553, 1404, 1321, 1175, 1131, 1091. HRMS m/z (ESI): calcd. for $C_8H_4NO_4S_2F_6$ $[M]^-$: 355.9486, found: 355.9498; calcd. for $C_{13}H_{15}N_2$ $[M]^+$: 199.1235, found: 199.1237.

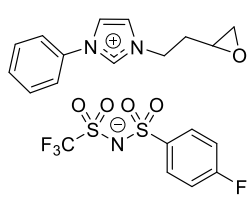
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-methoxybenzenesulfonyl)imide (13a)



To a solution of compound **12a** (50 mg, 0.0966 mmol, 1.0 equiv) in acetone (0.5 mL) was added freshly prepared DMDO (0.026 mol/L) (8.92 mL, 0.232 mmol, 2.4 equiv) also at -20 °C and the reaction mixture was stirred at room temperature for 2 h. Two drops of dimethyl sulfide (DMS) was added to quench the reaction mixture and neutralized the excess of DMDO. The reaction mixture was concentrated under reduced pressure and the product **13a** was obtained as a yellow oil (52 mg, 100 %).

^{1}H NMR (500 MHz, acetone-d_6) δ 9.70 (s, 1H), 8.21-8.24 (m, 1H), 8.06-8.09 (m, 1H), 7.78-7.86 (m, 4H), 7.61-7.71 (m, 3H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.70 (t, *J* = 6.8 Hz, 2H), 3.83 (s, 3H), 3.10-3.15 (m, 1H), 2.71-2.75 (m, 1H), 2.52-2.55 (m, 1H), 2.43-2.51 (m, 1H), 2.08-2.18 (m, 1H). ^{13}C NMR (126 MHz, acetone-d_6) δ 161.4, 138.7, 135.6, 135.2, 130.3, 130.2, 128.5, 123.9, 122.4, 121.8, 120.7 (q, J_{CF} = 324.0 Hz), 112.9, 54.9, 48.8, 47.7, 45.6, 32.6. ^{19}F NMR (471 MHz, acetone-d_6) δ -78.9. IR (neat) cm^{-1} 3142, 3104, 2931, 1597, 1497, 1319, 1173, 1133, 1089, 1045. HRMS m/z (ESI): calcd. for $C_8H_7NO_5S_2F_3$ $[M]^-$: 317.9718, found: 317.9728; calcd. for $C_{13}H_{15}N_2O$ $[M]^+$: 215.1184, found: 215.1186.

3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide (13b)

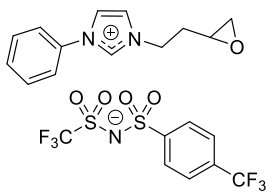


Procedure I. To a solution of compound **12b** (200 mg, 0.405 mmol, 1.0 equiv) in CH_3CN (20 mL), was added mCPBA (181 mg, 0.810 mmol, 2.0 equiv). The reaction mixture was stirred at 40 °C for 24 h. The crude was concentrated under reduced pressure and diethyl ether was added to extract the excess of mCPBA and 3-chlorobenzoic acid. The product **13b** was obtained as a colorless oil (187 mg, 89 %).

Procedure II. To a solution of compound **12b** (50 mg, 0.101 mmol, 1.0 equiv) in acetone (1 mL) was added freshly prepared DMDO (0.02 mol/L) (12 mL, 0.243 mmol, 2.4 equiv) also at -20 °C and the reaction mixture was stirred at room temperature for 2 h. Two drops of dimethyl sulfide (DMS) was added to quench the reaction mixture and neutralized the excess of DMDO. The reaction mixture was concentrated under reduced pressure and the product **13b** was obtained as a colorless oil (53 mg, 100 %).

^{1}H NMR (500 MHz, acetone-d_6) δ 9.69 (s, 1H), 8.23-8.26 (m, 1H), 8.07-8.10 (m, 1H), 7.89-7.95 (m, 2H), 7.81-7.87 (m, 2H), 7.66-7.72 (m, 3H), 7.14-7.21 (m, 2H), 4.68-4.74 (t, J = 7.0 Hz, 2H), 3.09-3.15 (m, 1H), 2.72-2.76 (m, 1H), 2.53-2.55 (m, 1H), 2.45-2.52 (m, 1H), 2.08-2.17 (m, 1H). ^{13}C NMR (126 MHz, acetone-d_6) δ 163.6 (d, J_{CF} = 247.9 Hz), 142.7, 135.5, 135.2, 130.4, 130.2, 129.3 (d, J_{CF} = 9.0 Hz), 123.8, 122.4, 121.8, 120.5 (CF_3, hidden peaks), 114.6 (d, J_{CF} = 22.5 Hz), 48.8, 47.7, 45.6, 32.6. ^{19}F NMR (471 MHz, acetone-d_6) δ -79.1, -111.7. IR (neat) cm^{-1} 3143, 3067, 2930, 1592, 1554, 1495, 1320, 1298, 1181, 1132. HRMS m/z (ESI): calcd. for $C_7H_4NO_4S_2F_4$ $[M]^-$: 305.9518, found: 305.9528; calcd. for $C_{13}H_{15}N_2O$ $[M]^+$: 215.1184, found: 215.1185.

3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide (13c)



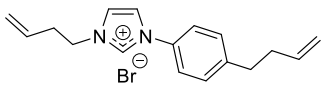
Procedure I. To a solution of compound **12c** (200 mg, 0.368 mmol, 1.0 equiv) in CH_3CN (20 mL), was added mCPBA (165 mg, 0.736 mmol, 2.0 equiv). The reaction mixture was stirred at 40 °C for 24 h. The crude was concentrated under reduced pressure and ether was added to extract the excess of mCPBA and 3-chlorobenzoic acid. The product **13c** was obtained as a white solid (143 mg, 68 %).

Procedure II. To a solution of compound **12c** (50 mg, 0.092 mmol, 1.0 equiv) in acetone (1 mL) was added freshly prepared DMDO (0.02 mol/L) (12 mL, 0.220 mmol, 2.4 equiv) also at -20 °C and the reaction mixture was stirred at room temperature for 2 h. Two drops of dimethyl sulfide (DMS) was added to quench the reaction mixture and neutralized the excess of DMDO. The reaction mixture was concentrated under reduced pressure and the product **13c** was obtained as a white solid (52 mg, 100 %).

^{1}H NMR (500 MHz, acetone-d_6) δ 9.72 (s, 1H), 8.22-8.26 (m, 1H), 8.04-8.10 (m, 3H), 7.76-7.86 (m, 4H), 7.61-7.72 (m, 3H), 4.71 (t, J = 6.8 Hz, 2H), 3.09-3.15 (m, 1H), 2.72-2.76 (m, 1H), 2.52-2.55 (m, 1H), 2.45-2.52 (m, 1H), 2.09-2.16 (m, 1H). ^{13}C NMR (126 MHz, acetone-d_6) δ 151.0, 136.5, 136.1, 132.5 (Cq, hidden peaks), 130.4, 130.2, 127.5, 125.1 (q, J_{CF} = 3.8 Hz), 123.8, 122.4, 121.8, 120-125 (2*CF_3, hidden peaks), 49.7, 48.6, 46.5, 33.5. ^{19}F NMR (471

MHz, acetone-d_6) δ -63.2, -79.1. IR (neat) cm^{-1} 3143, 3103, 3083, 1572, 1558, 1327, 1317, 1175, 1131, 1045. Mp: 79.8 °C. HRMS m/z (ESI): calcd. for $C_8H_4NO_4S_2F_6$ $[M]^-$: 355.9486, found: 355.9494; calcd. for $C_{13}H_{15}N_2O$ $[M]^+$: 215.1184, found: 215.1187.

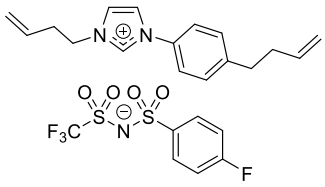
1-[4-(3-Buten-1-yl)phenyl]-3-(3-buten-1-yl)imidazolium bromide (diIm-Br)



To a solution of 1-[4-(3-Buten-1-yl)phenyl]-1*H*-Imidazole[3] (1.05 g, 5.27 mmol, 1.0 equiv) in CH_3CN (35 mL) was added 4-bromo-1-butene (1.06 mL, 10.54 mmol, 2.0 equiv). The mixture was refluxed at 80 °C for 48 h. After cooled to room temperature, the reaction mixture was concentrated under reduced pressure to obtain the product **diIm-Br** as a yellow oil (1.75 g, 100 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.63-7.72 (m, 4H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.72-5.94 (m, 2H), 4.95-5.12 (m, 4H), 4.71 (t, *J* = 6.7 Hz, 2H), 2.73-2.77 (m, 4H), 2.35 (q, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 137.1, 136.1, 132.7, 132.5, 130.7, 123.2, 121.8, 120.4, 119.7, 115.8, 49.6, 35.1, 34.9, 34.7. IR (neat) cm^{-1} 3049, 2855, 1640, 1566, 1550, 1515, 1438, 1198, 1071, 914. HRMS m/z (ESI): calcd. for $C_{17}H_{21}N_2$ $[M]^+$: 253.1705, found: 253.1704.

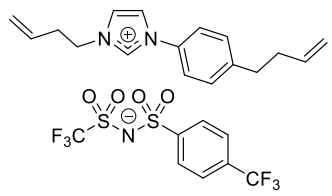
1-[4-(3-Buten-1-yl)phenyl]-3-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide (14a)



To a solution of trifluoromethane sulfonamide (300 mg, 2.01 mmol, 1.0 equiv) in anhydrous THF (9 mL) and DMF (1 mL) was added NaH (169 mg, 4.22 mmol, 2.1 equiv) and the reaction mixture was stirred at room temperature for 1 h. Then, a solution of 4-fluorobenzenesulfonyl chloride (391 mg, 2.01 mmol, 1.0 equiv) in THF (9 mL) was added dropwise. The reaction was monitoring by CCM in cyclohexane/ethyl acetate (4/6). After the reaction was completed (12 h), the reaction mixture was concentrated under reduced pressure. The sulfonamide **11b** was obtained as a colorless liquid (662 mg, 100 %) and was used without any purification. To a solution of **diIm-Br** (670 mg, 2.01 mmol, 1.0 equiv) in distilled water (20 mL) was added sulfonamide **11b** (662 mg, 2.01 mmol, 1.0 equiv). The solution was stirred at room temperature for 24 h. The reaction mixture was extracted with dichloromethane and the organic layer was washed several times with water, dried with $MgSO_4$ and then concentrated under reduced pressure. The product **14a** was obtained as a yellow oil (702 mg, 63 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.89-7.94 (m, 2H), 7.50-7.58 (m, 4H), 7.33-7.38 (m, 2H), 7.02-7.08 (m, 2H), 5.76-5.86 (m, 2H), 4.97-5.15 (m, 4H), 4.53 (t, *J* = 6.7 Hz, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.69 (q, *J* = 6.7 Hz, 2H), 2.38 (q, *J* = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5 (d, J_{CF} = 251.7 Hz), 145.0, 140.5, 137.2, 135.3, 132.5, 132.4, 130.7, 129.4 (d, J_{CF} = 8.7 Hz), 123.2, 122.1, 121.1, 120.3 (CF_3, hidden peaks), 119.9, 115.9, 115.4 (d, J_{CF} = 22.7 Hz), 49.2, 35.1, 34.9, 34.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.2, -108.0. IR (neat) cm^{-1} 2955, 2922, 2853, 1459, 1377, 1322, 1178, 1134, 1087, 1050. HRMS m/z (ESI): calcd. for $C_7H_4NO_4S_2F_4$ $[M]^-$: 305.9518, found: 305.9529; calcd. for $C_{17}H_{21}N_2$ $[M]^+$: 253.1705, found: 253.1706.

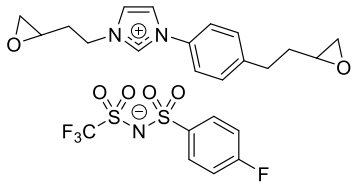
1-[4-(3-Buten-1-yl)phenyl]-3-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide (14b)



To a solution of trifluoromethane sulfonamide (300 mg, 2.01 mmol, 1.0 equiv) in anhydrous THF (9 mL) and DMF (1 mL) was added NaH (169 mg, 4.22 mmol, 2.1 equiv) and the reaction mixture was stirred at room temperature for 1 h. Then, a solution of 4-(trifluoromethyl)benzenesulfonyl chloride (491 mg, 2.01 mmol, 1.0 equiv) in THF (9 mL) was added dropwise. The reaction was monitoring by CCM in cyclohexane/ethyl acetate (4/6). After the reaction was completed (12 h), the reaction mixture was concentrated under vacuum and the sulfonamide **11c** was obtained as a white solid (762 mg, 100 %). To a solution of **diIm-Br** (670 mg, 2.01 mmol, 1.0 equiv) in distilled water (20 mL) was added sulfonamide **11c** (762 mg, 2.01 mmol, 1.0 equiv). The solution was stirred at room temperature for 24 h. The reaction mixture was extracted with dichloromethane and the organic layer was washed several times with water, dried with $MgSO_4$ and then concentrated under reduced pressure. The product **14b** was obtained as a yellow oil (594 mg, 48 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.49-7.56 (m, 4H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.75-5.88 (m, 2H), 4.96-5.18 (m, 4H), 4.53 (t, *J* = 6.7 Hz, 2H), 2.78 (t, *J* = 7.3 Hz, 2H), 2.70 (q, *J* = 6.7 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 145.2, 137.1, 135.2, 133.2 (Cq, J_{CF} = 32.8 Hz), 132.4, 132.4, 130.8, 127.4, 125.5 (q, J_{CF} = 3.7 Hz), 123.2, 122.2, 121.2, 120-125 (2*CF_3, hidden peaks), 120.0, 115.9, 50.0, 35.1, 34.9, 34.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9, -78.3. IR (neat) cm^{-1} 3140, 3112, 2924, 2855, 1553, 1515, 1316, 1189, 1131, 1043. HRMS m/z (ESI): calcd. for $C_8H_4NO_4S_2F_6$ $[M]^-$: 355.9486, found: 355.9492; calcd. for $C_{17}H_{21}N_2$ $[M]^+$: 253.1705, found: 253.1707.

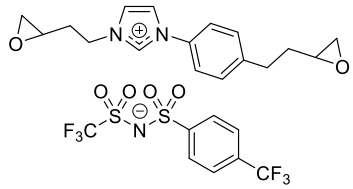
3-[2-(Oxiran-2-yl)ethyl]-1-{4-[2-(oxiran-2-yl)ethyl]phenyl}imidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide (15a)



To a solution of compound **14a** (200 mg, 0.357 mmol, 1.0 equiv) in acetone (1 mL) was added freshly prepared DMDO (0.05 mol/L) (23.6 mL, 1.179 mmol, 3.3 equiv) also at -20 °C and the reaction mixture was stirred at room temperature for 7 h. Two drops of dimethyl sulfide (DMS) was added to quench the reaction mixture and neutralized the excess of DMDO. The reaction mixture was concentrated under reduced pressure and the product **15a** was obtained as a yellow oil (211 mg, 100 %).

^{1}H NMR (500 MHz, acetone-d_6) δ 9.70 (s, 1H), 8.19-8.24 (m, 1H), 8.05-8.09 (m, 1H), 7.89-7.95 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.14-7.20 (m, 2H), 4.70 (t, *J* = 6.7 Hz, 2H), 3.09-3.15 (m, 1H), 2.85-2.95 (m, 3H), 2.71-2.76 (m, 1H), 2.65-2.69 (m, 1H), 2.52-2.55 (m, 1H), 2.42-2.52 (m, 2H), 2.07-2.17 (m, 1H), 1.86-1.96 (m, 1H), 1.77-1.86 (m, 1H). ^{13}C NMR (126 MHz, acetone-d_6) δ 164.6 (d, J_{CF} = 248.1 Hz), 145.3, 143.7, 136.4, 134.1, 131.1, 130.3 (d, J_{CF} = 9.1 Hz), 124.6, 123.2, 122.7, 121.5 (q, J_{CF} = 323.7 Hz), 115.6 (d, J_{CF} = 22.3 Hz), 51.7, 49.7, 48.5, 47.0, 46.5, 34.9, 33.5, 32.3. ^{19}F NMR (471 MHz, acetone-d_6) δ -79.1, -111.8. IR (neat) cm^{-1} 3140, 3071, 2999, 2930, 1591, 1494, 1321, 1180, 1138, 1048. HRMS m/z (ESI): calcd. for $C_7H_4NO_4S_2F_4$ $[M]^-$: 305.9518, found: 305.9522; calcd. for $C_{17}H_{21}N_2O_2$ $[M]^+$: 285.1603, found: 285.1602.

3-[2-(Oxiran-2-yl)ethyl]-1-{4-[2-(oxiran-2-yl)ethyl]phenyl}imidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide (15b)

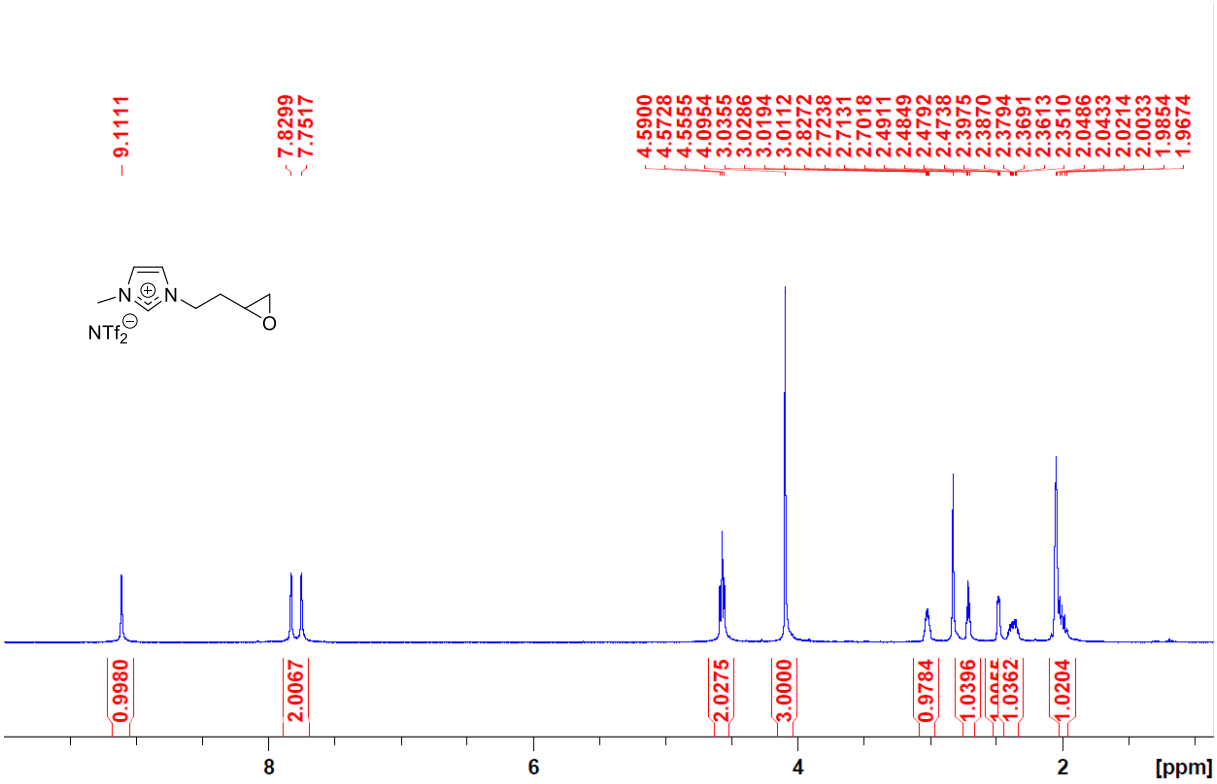


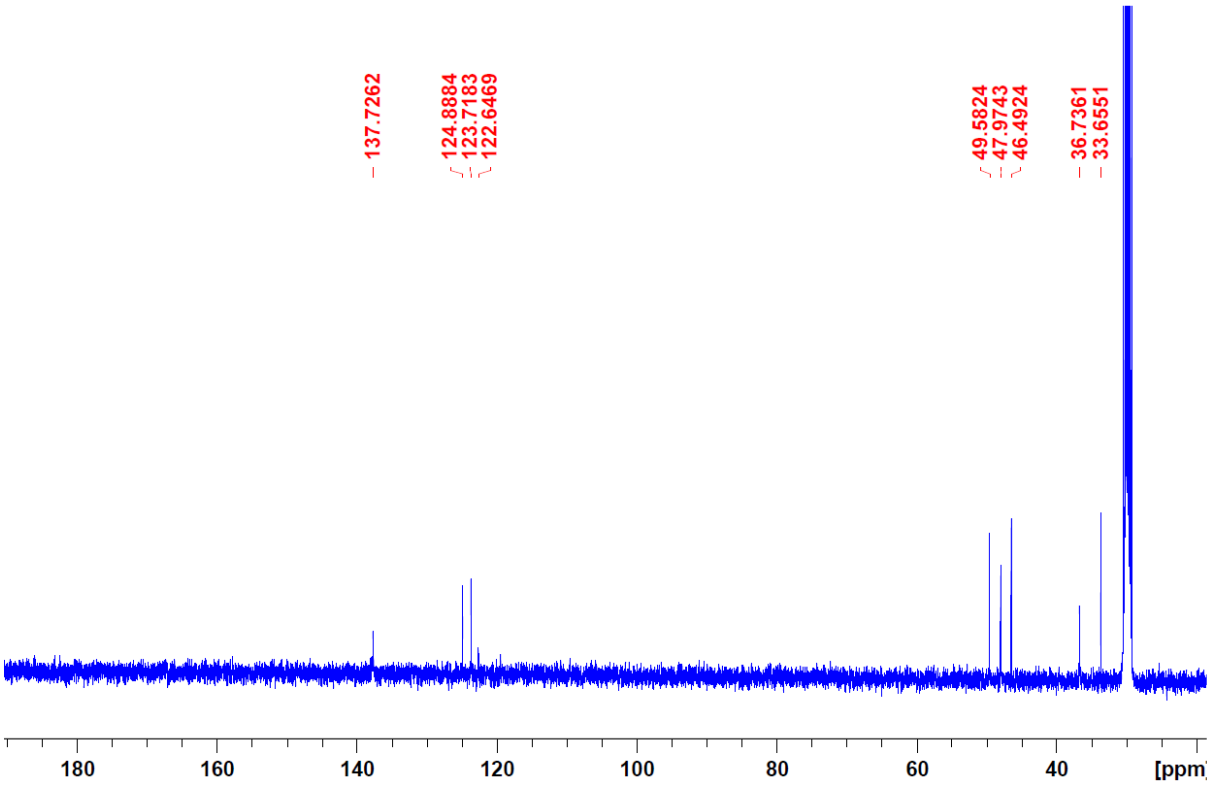
To a solution of compound **14b** (200 mg, 0.328 mmol, 1.0 equiv) in acetone (1 mL) was added freshly prepared DMDO (0.057 mol/L) (19 mL, 1.082 mmol, 3.3 equiv) also at -20 °C and the reaction mixture was stirred at room temperature for 7 h. Two drops of dimethyl sulfide (DMS) was added to quench the reaction mixture and neutralized the excess of DMDO. The reaction mixture was concentrated under reduced pressure and the product **15b** was obtained as a colorless oil (210 mg, 100 %).

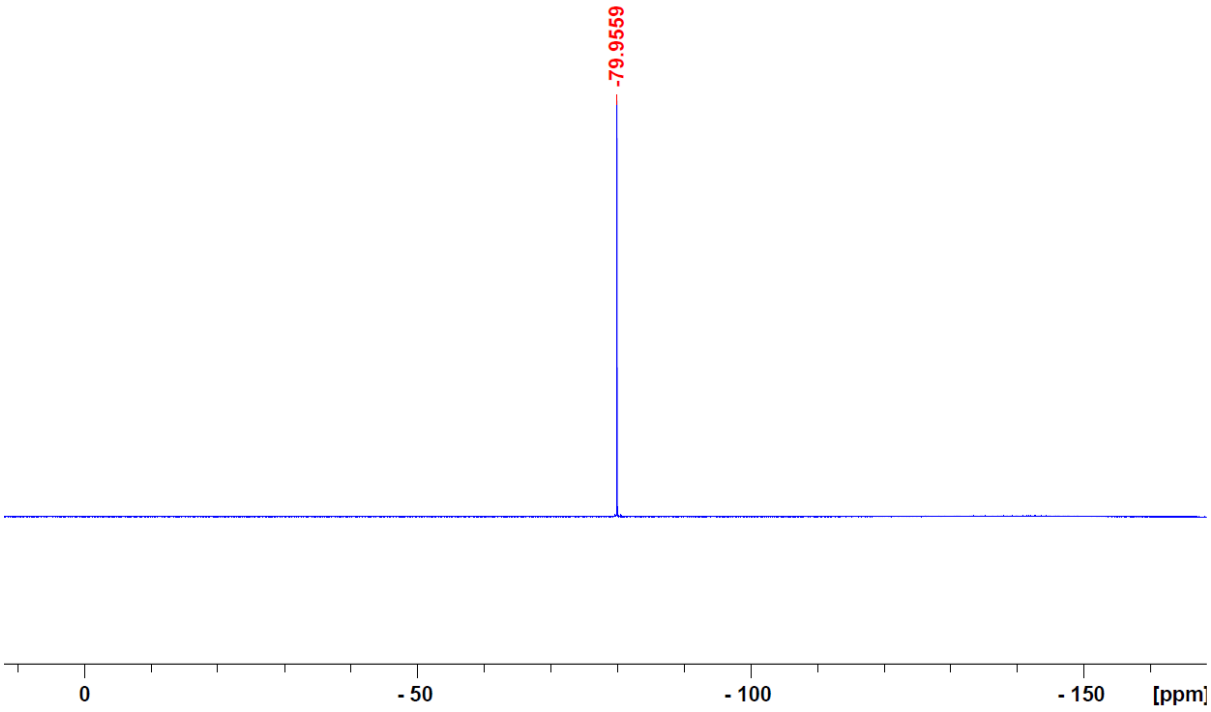
^{1}H NMR (500 MHz, acetone-d_6) δ 9.67 (s, 1H), 8.20-8.23 (m, 1H), 8.05-8.10 (m, 3H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 4.70 (m, 2H), 3.09-3.15 (m, 1H), 2.85-2.95 (m, 3H), 2.72-2.76 (m, 1H), 2.66-2.69 (m, 1H), 2.52-2.55 (m, 1H), 2.46-2.52 (m, 1H), 2.43-2.46 (m, 1H), 2.07-2.16 (m, 1H), 1.87-1.97 (m, 1H), 1.76-1.86 (m, 1H). ^{13}C NMR (126 MHz, acetone-d_6) δ 150.9, 145.3, 136.3, 134.1, 132.5 (q, J_{CF} = 31.8 Hz), 131.1, 128.4, 126.0 (q, J_{CF} = 3.8 Hz), 124.6, 123.2, 122.7, 120-125 (2*CF_3, hidden peaks), 51.7, 49.7, 48.6, 47.0, 46.5, 34.9, 33.5, 32.3. ^{19}F NMR (471 MHz, acetone-d_6) δ -63.2, -79.1. IR (neat) cm^{-1} 3141, 3104, 2999, 2929, 1554, 1404, 1321, 1178, 1131, 1053. HRMS m/z (ESI): calcd. for $C_8H_4NO_4S_2F_6$ $[M]^-$: 355.9486, found: 355.9494; calcd. for $C_{17}H_{21}N_2O_2$ $[M]^+$: 285.1603, found: 285.1601.

IV. NMR spectrum

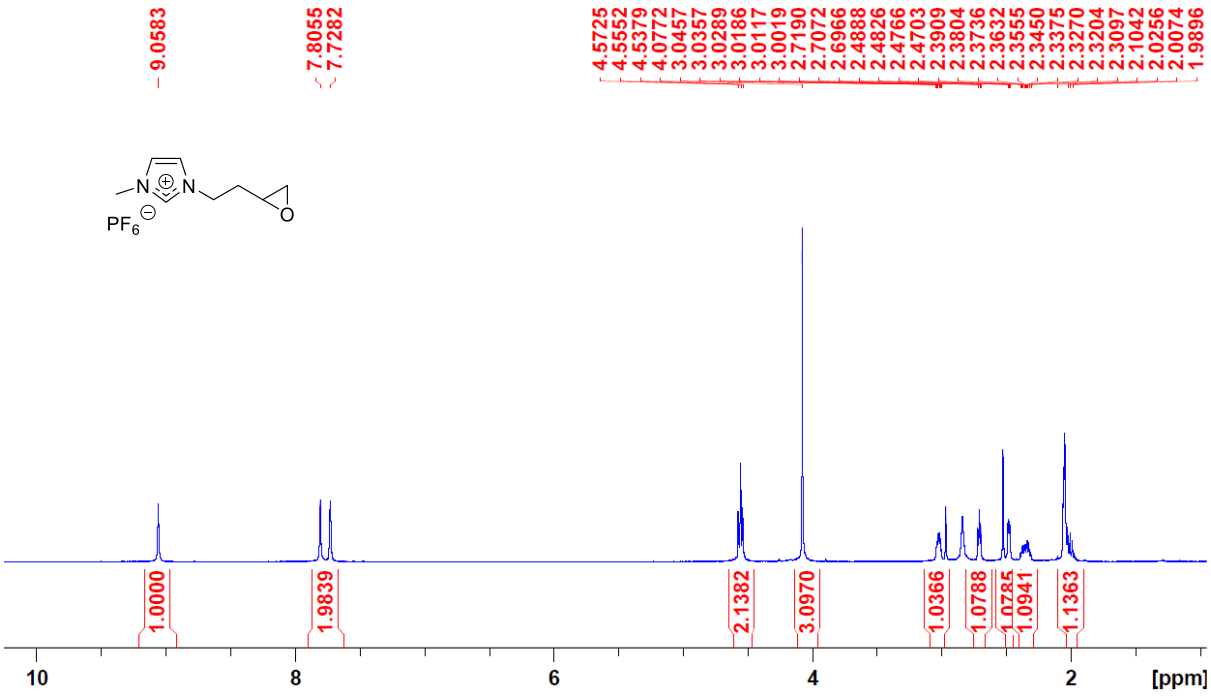
1-[2-(Oxiran-2-yl)ethyl]-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (3a)

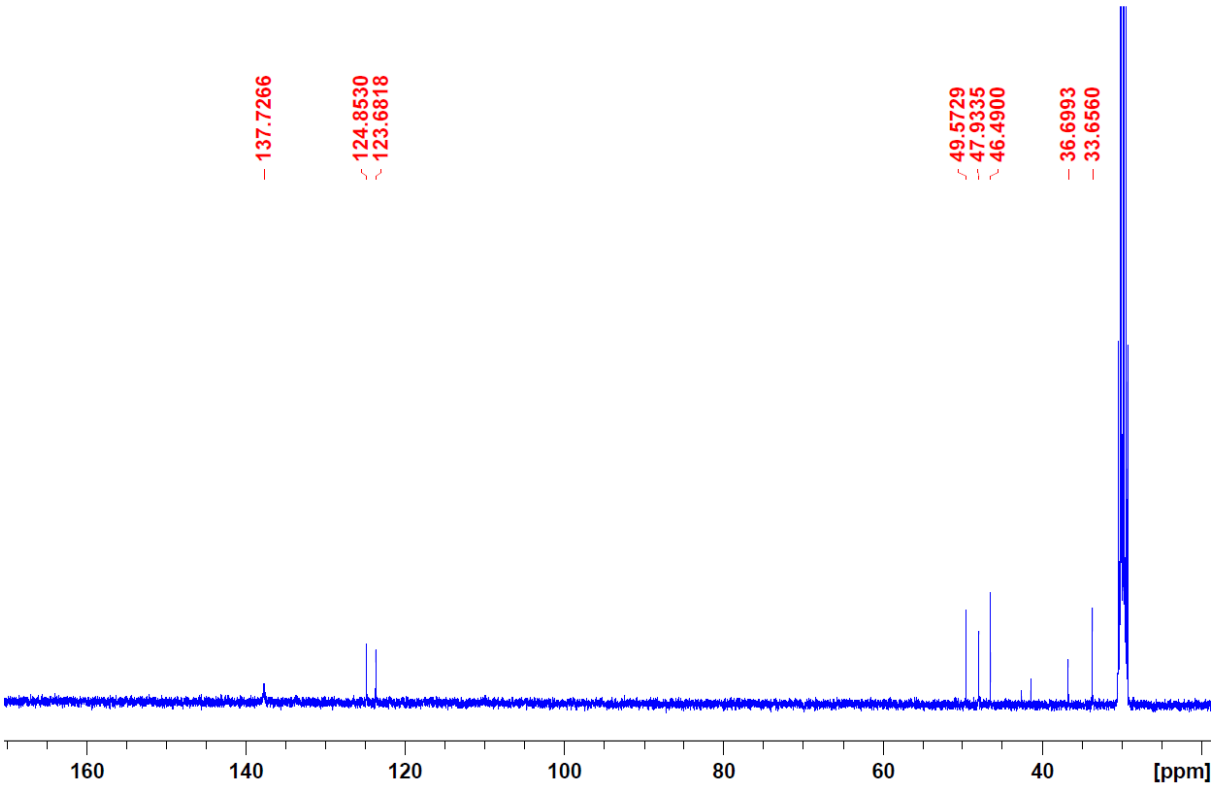






1-[2-(Oxiran-2-yl)ethyl]-3-methylimidazolium hexafluorophosphate (3b)




137.7266
124.8530
123.6818
49.5729
47.9335
46.4900
36.6993
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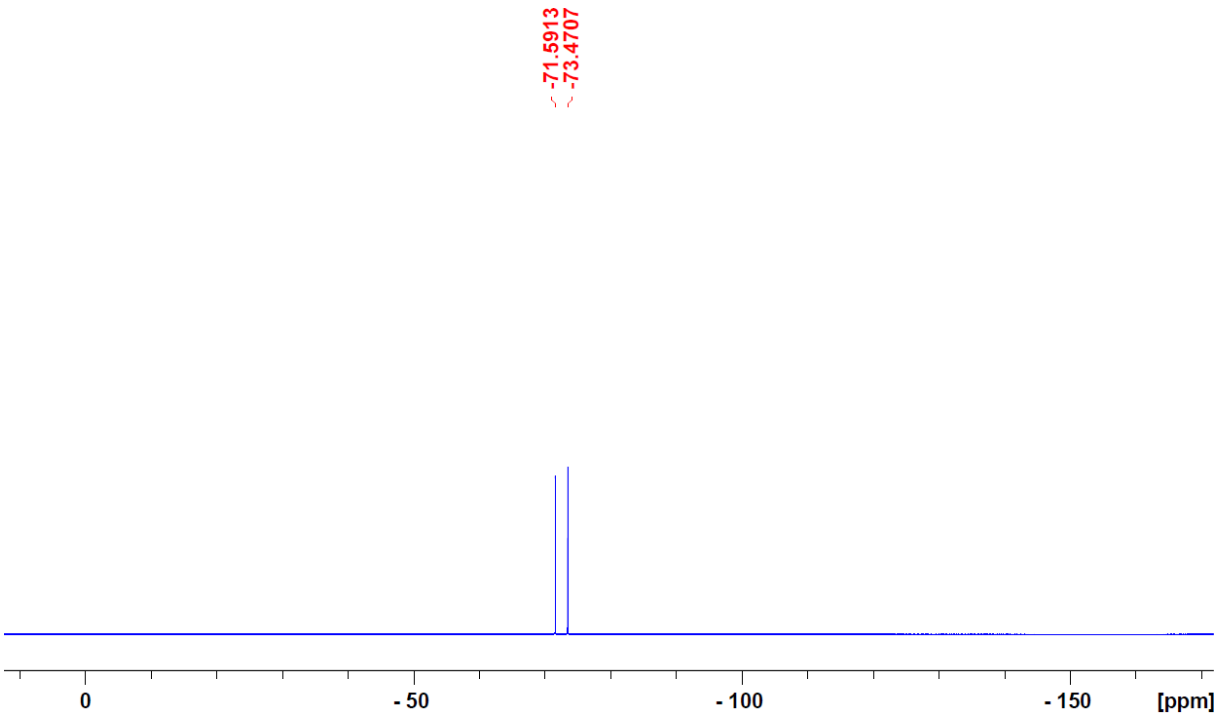
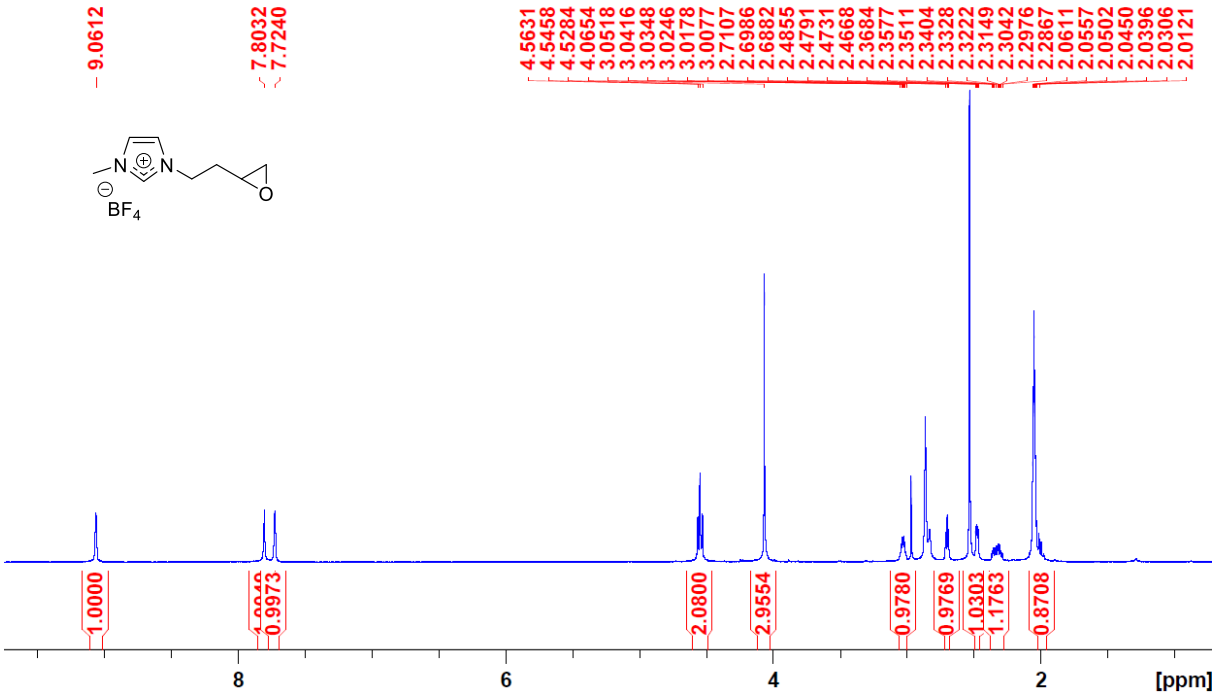
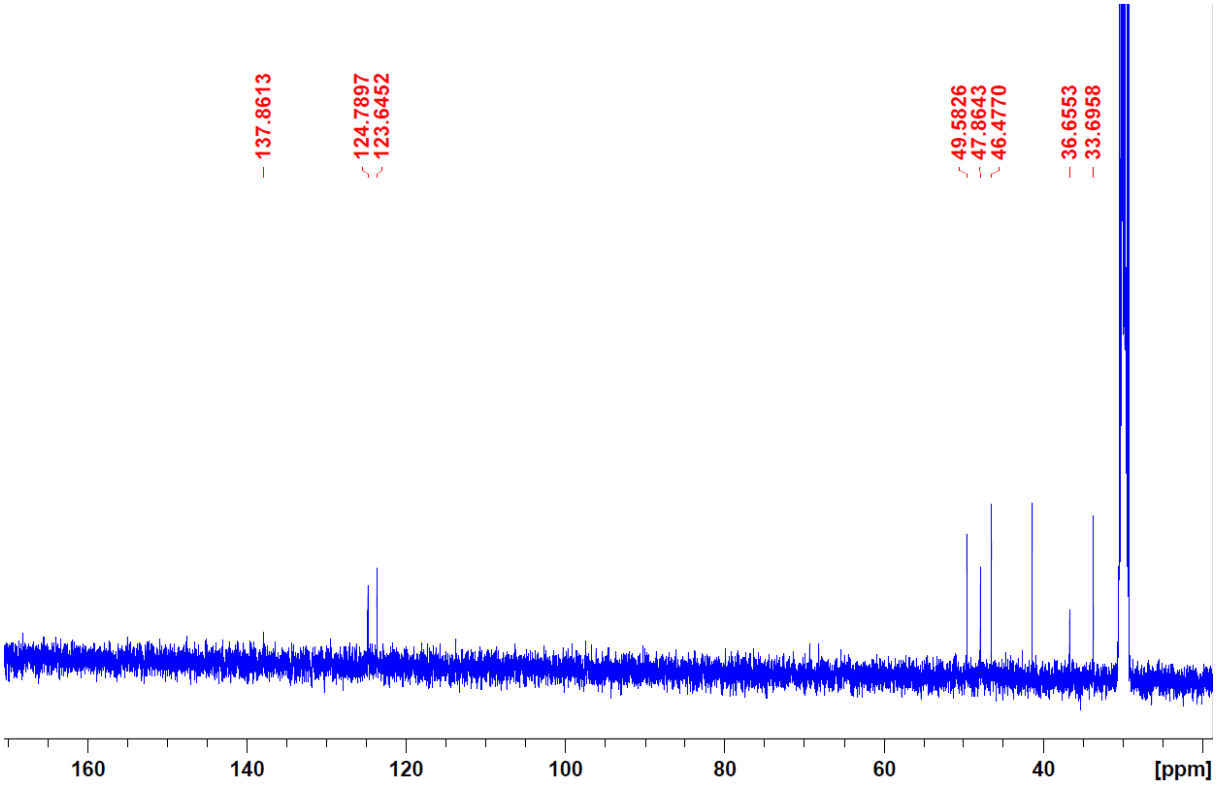
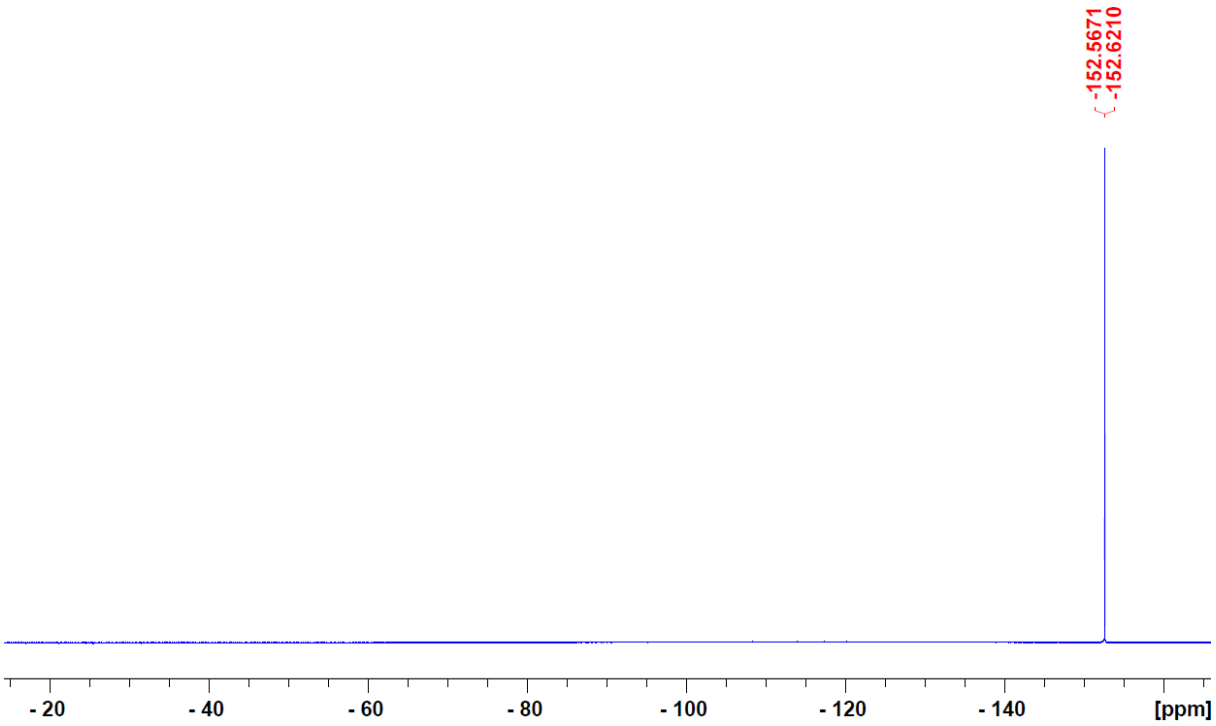
160
140
120
100
80
60
40
[ppm]


-71.5913
-73.4707
0
- 50
- 100
- 150
[ppm]

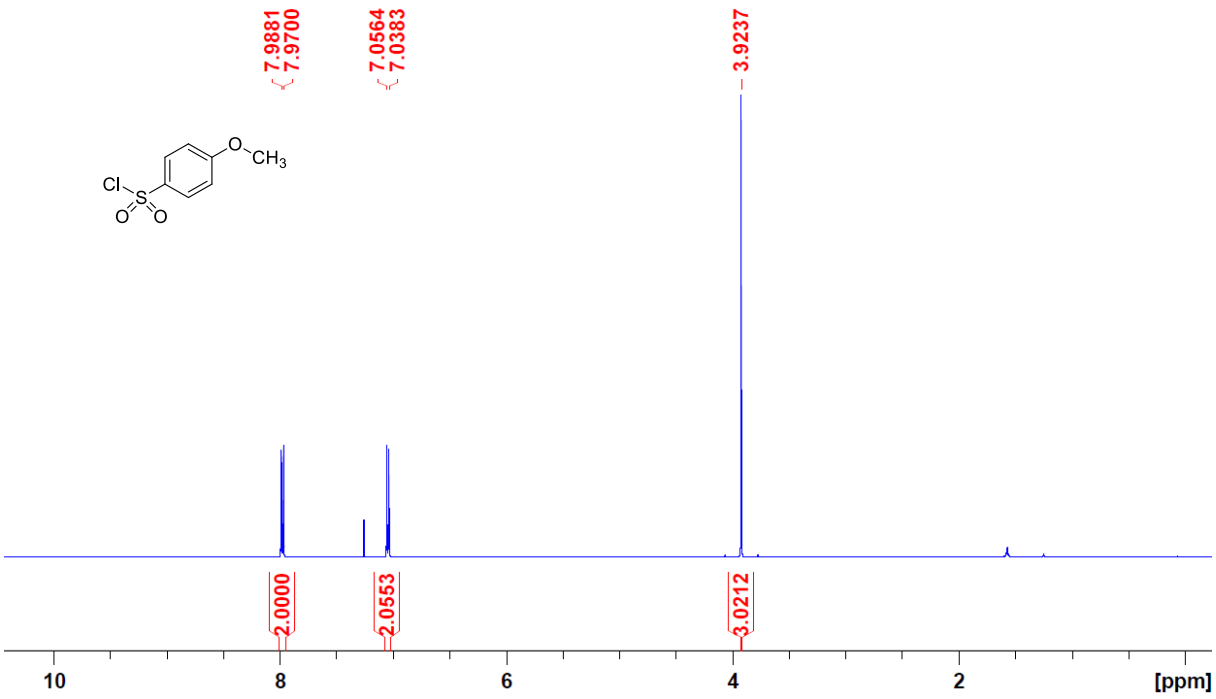
3-[2-(Oxiran-2-yl)ethyl]1-methylimidazolium tetrafluoroborate (3c)

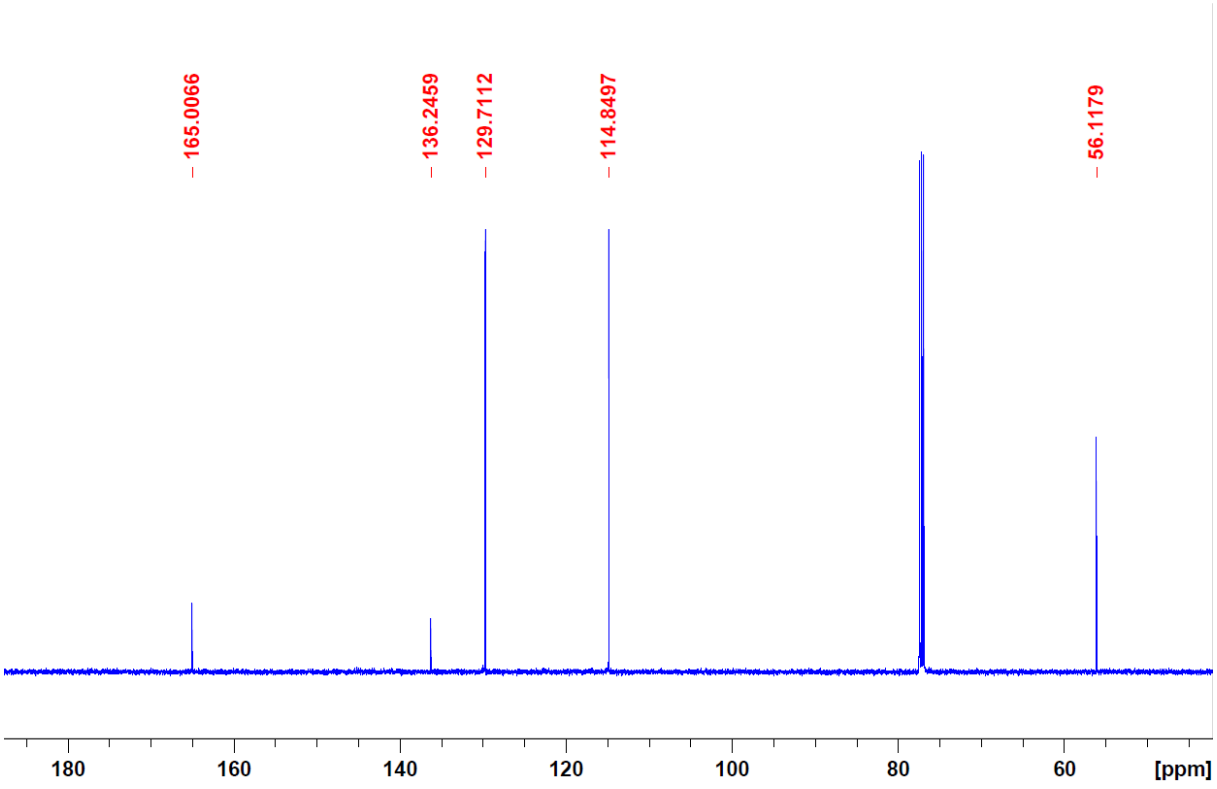




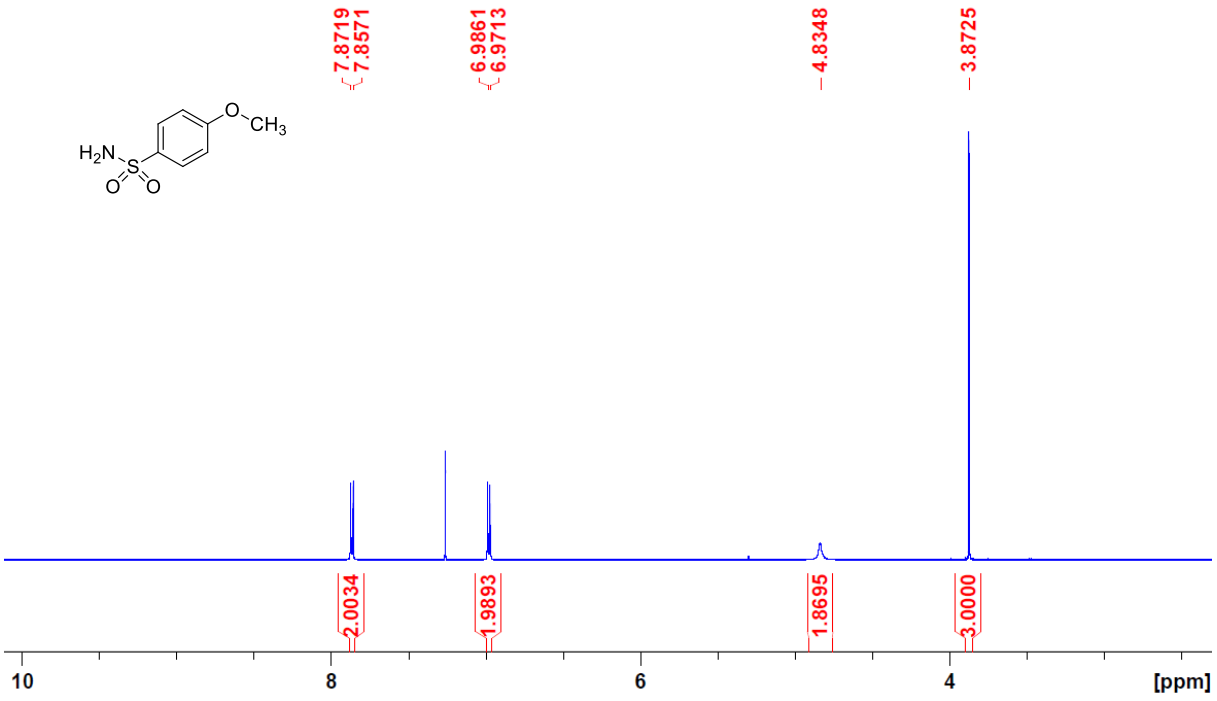


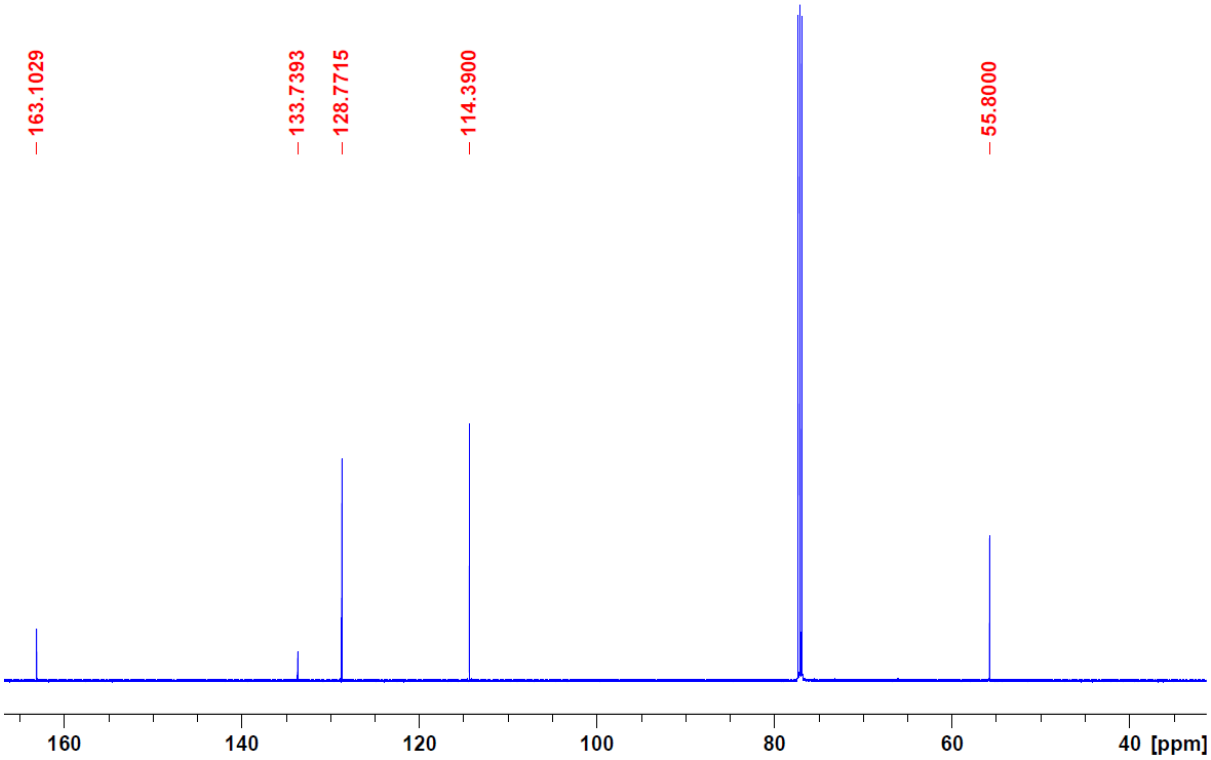
4-methoxybenzenesulfonyl chloride (6)



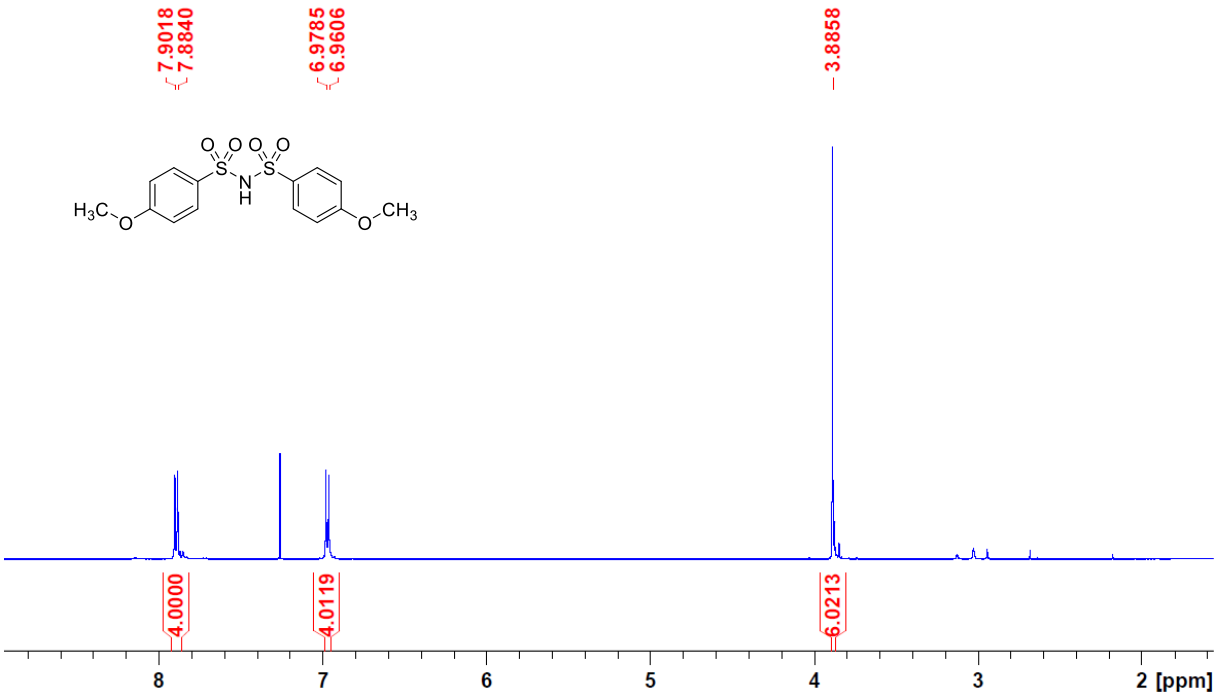


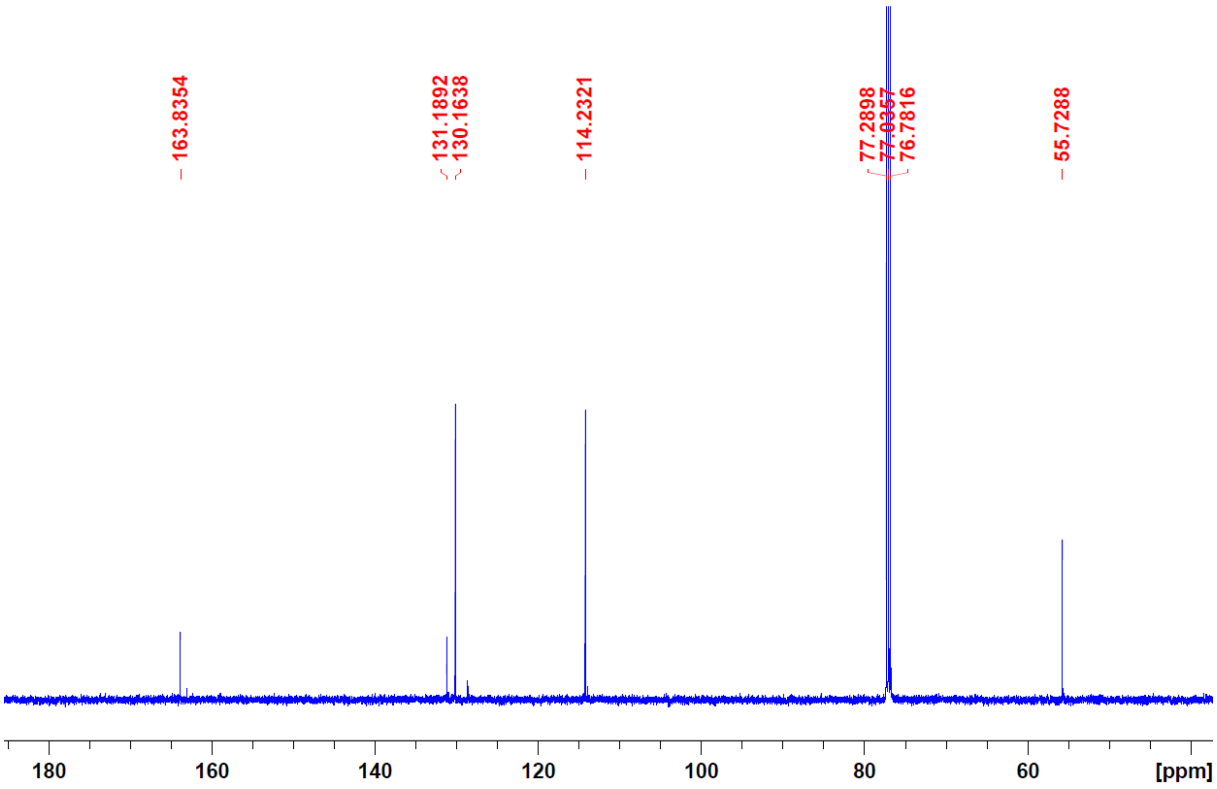
4-methoxybenzenesulfonamide (7)



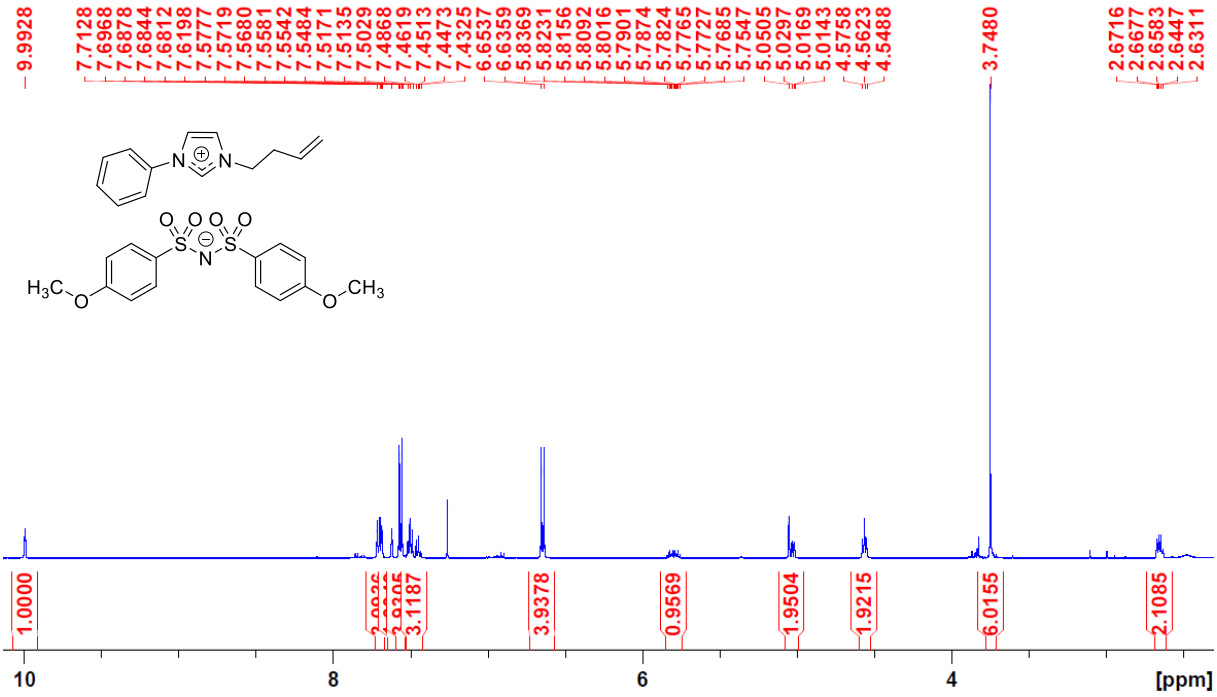


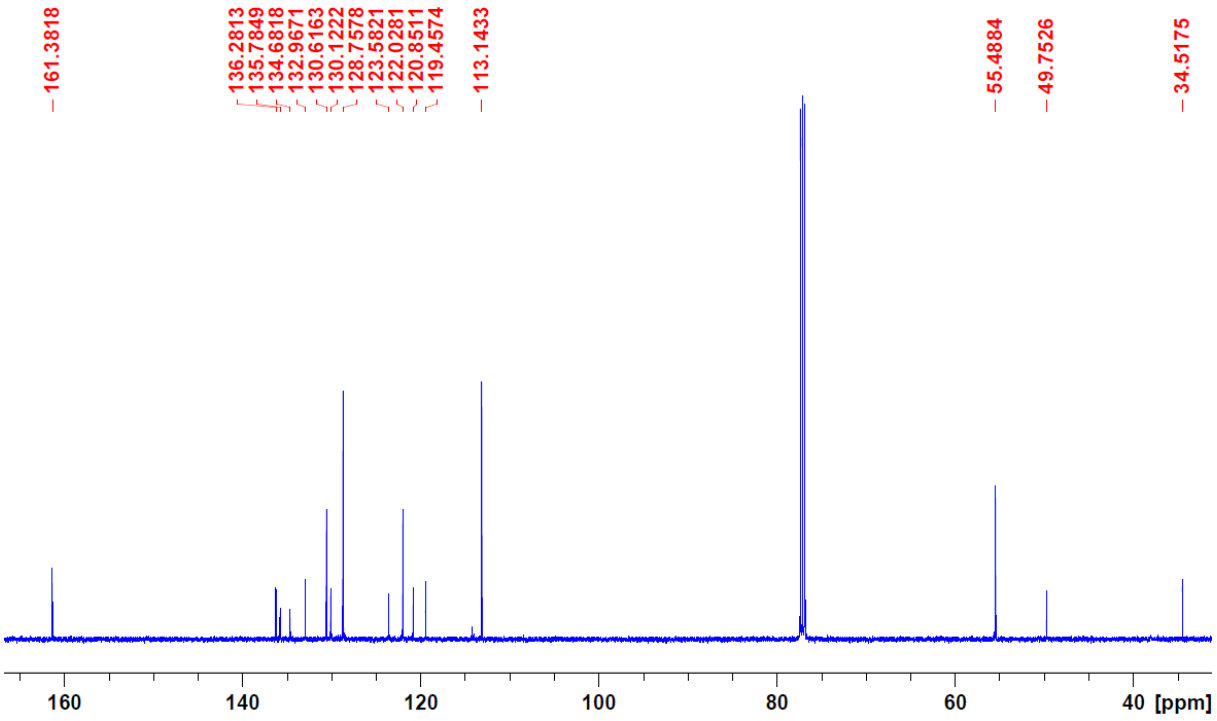
Bis(4-methoxybenzene)sulfonimide (8)



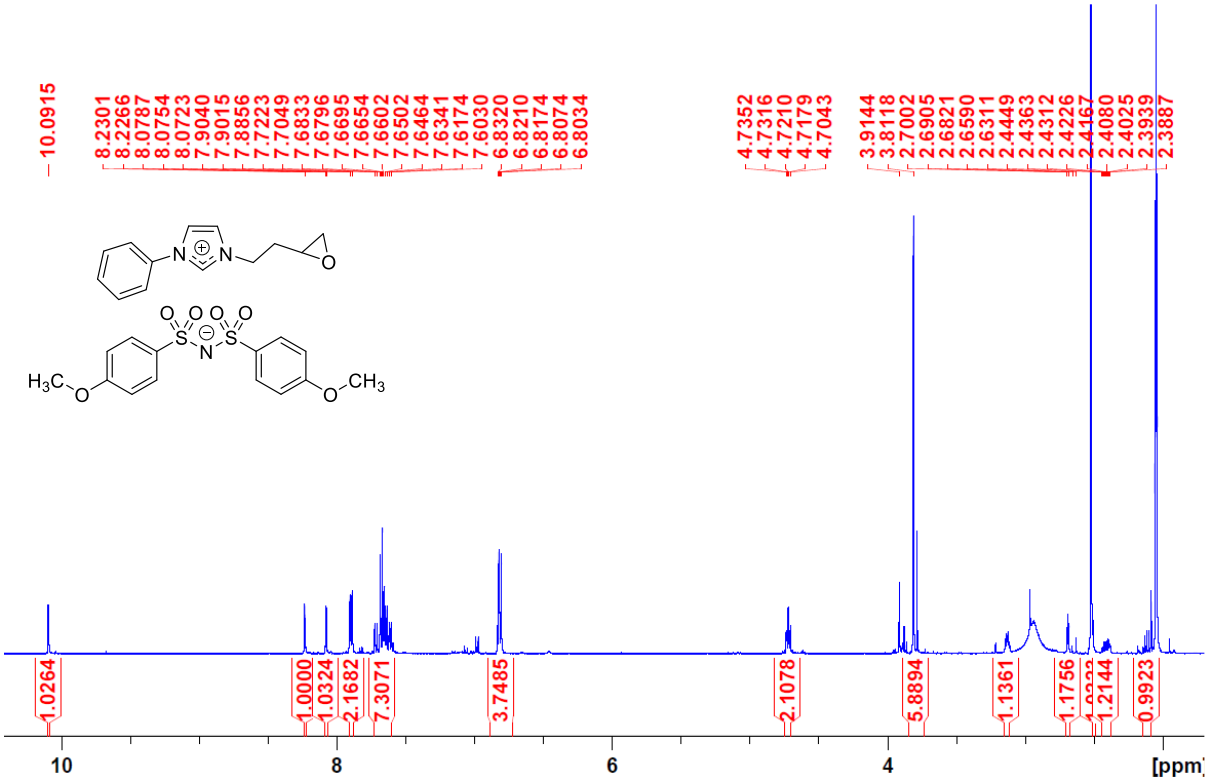


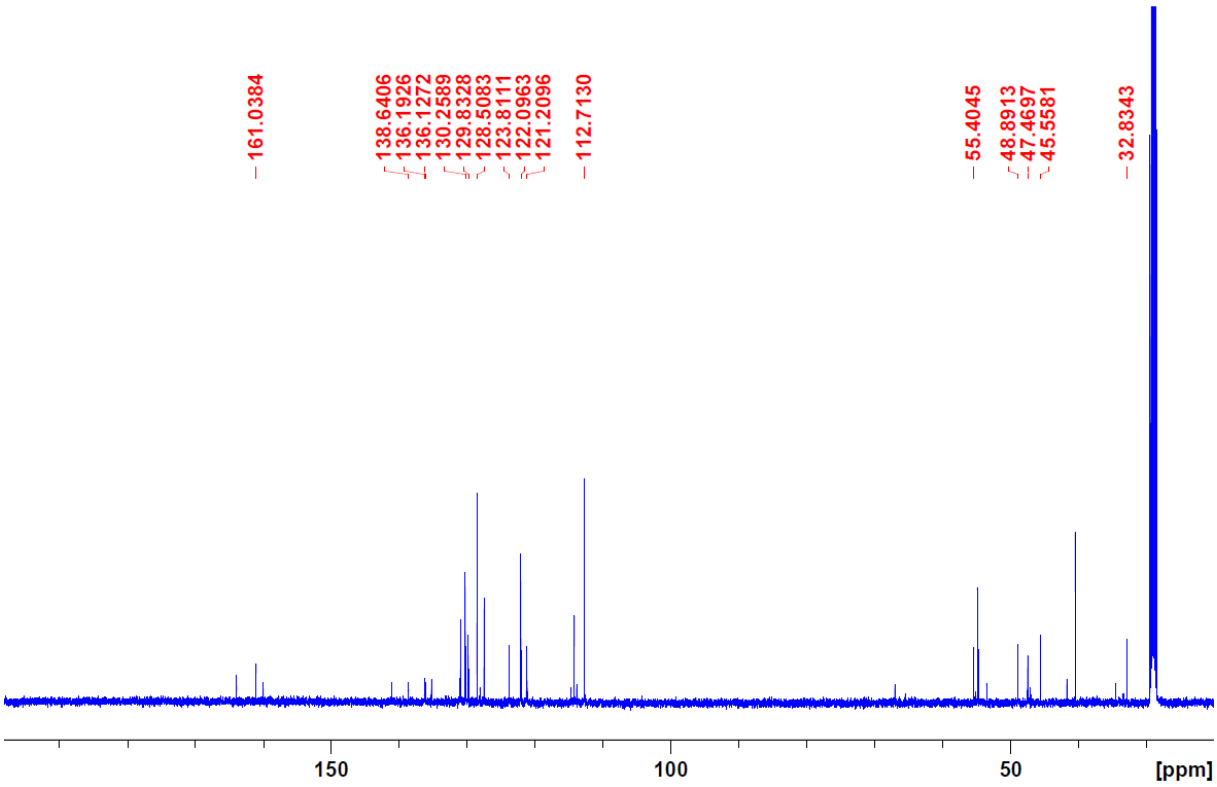
1-Phenyl-(3-buten-1-yl)imidazolium bis(4-methoxybenzene)sulfonimide (9)



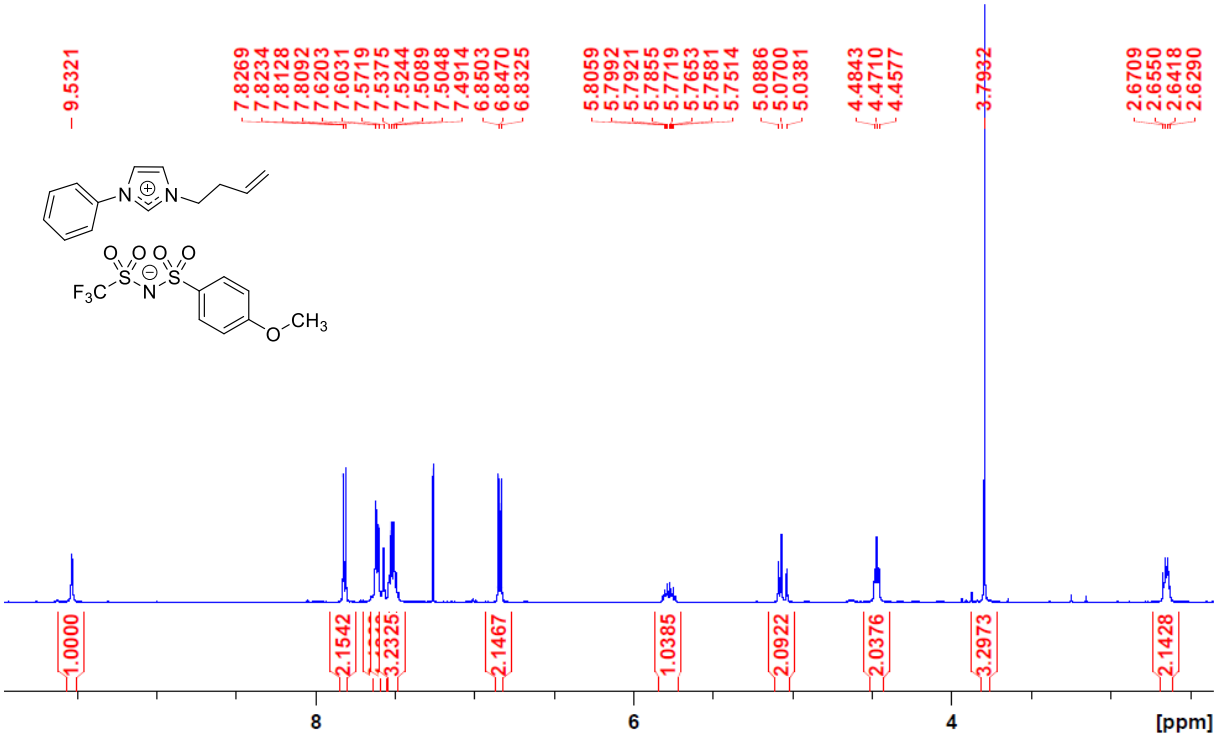


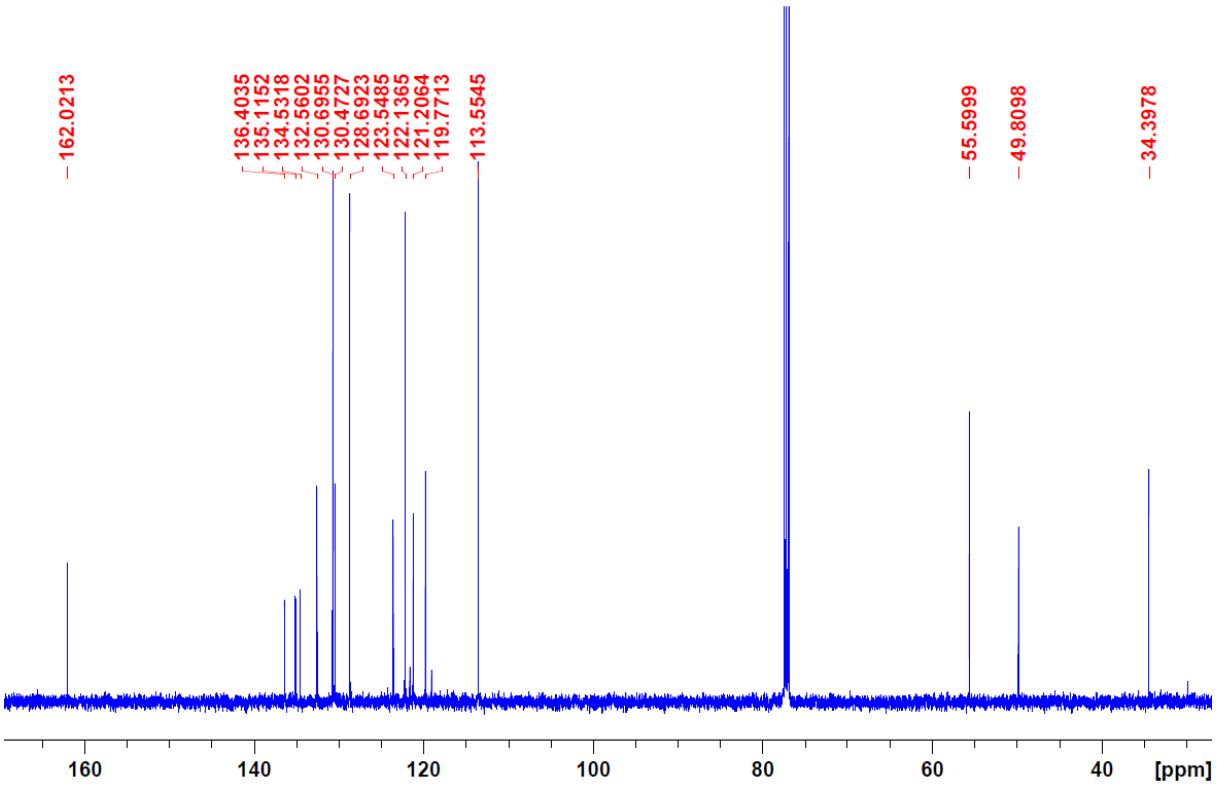
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium bis(4-methoxybenzene)sulfonimide (10)

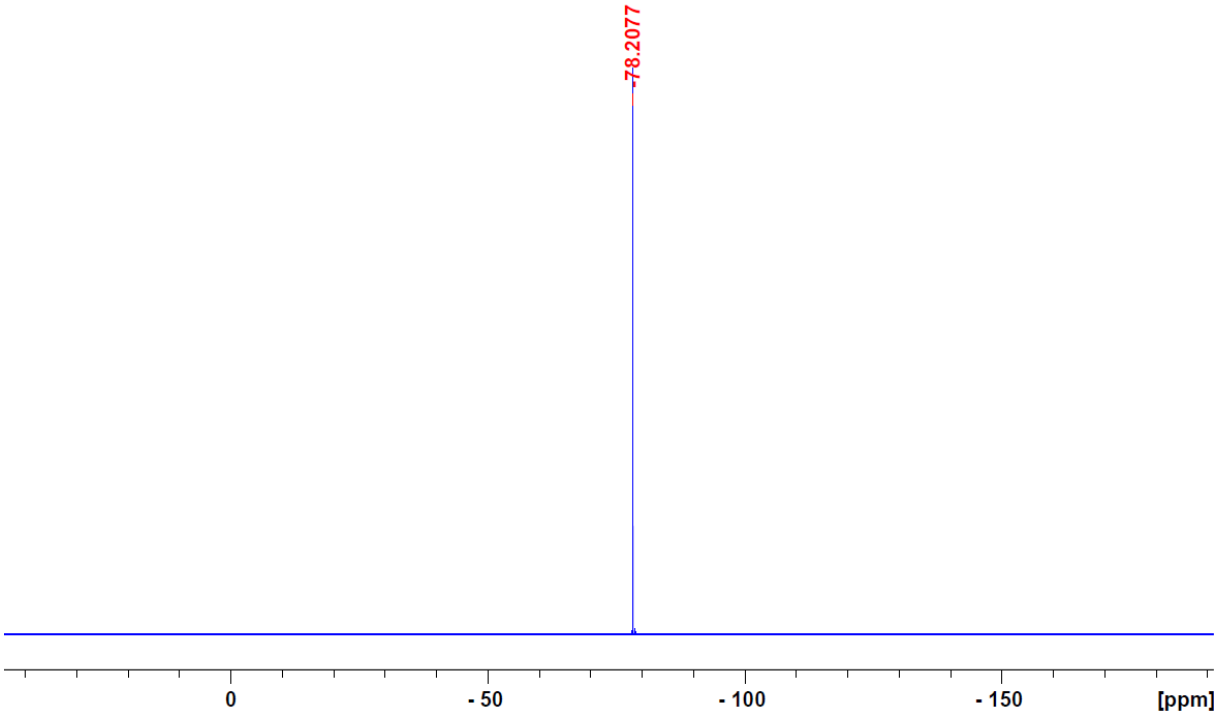




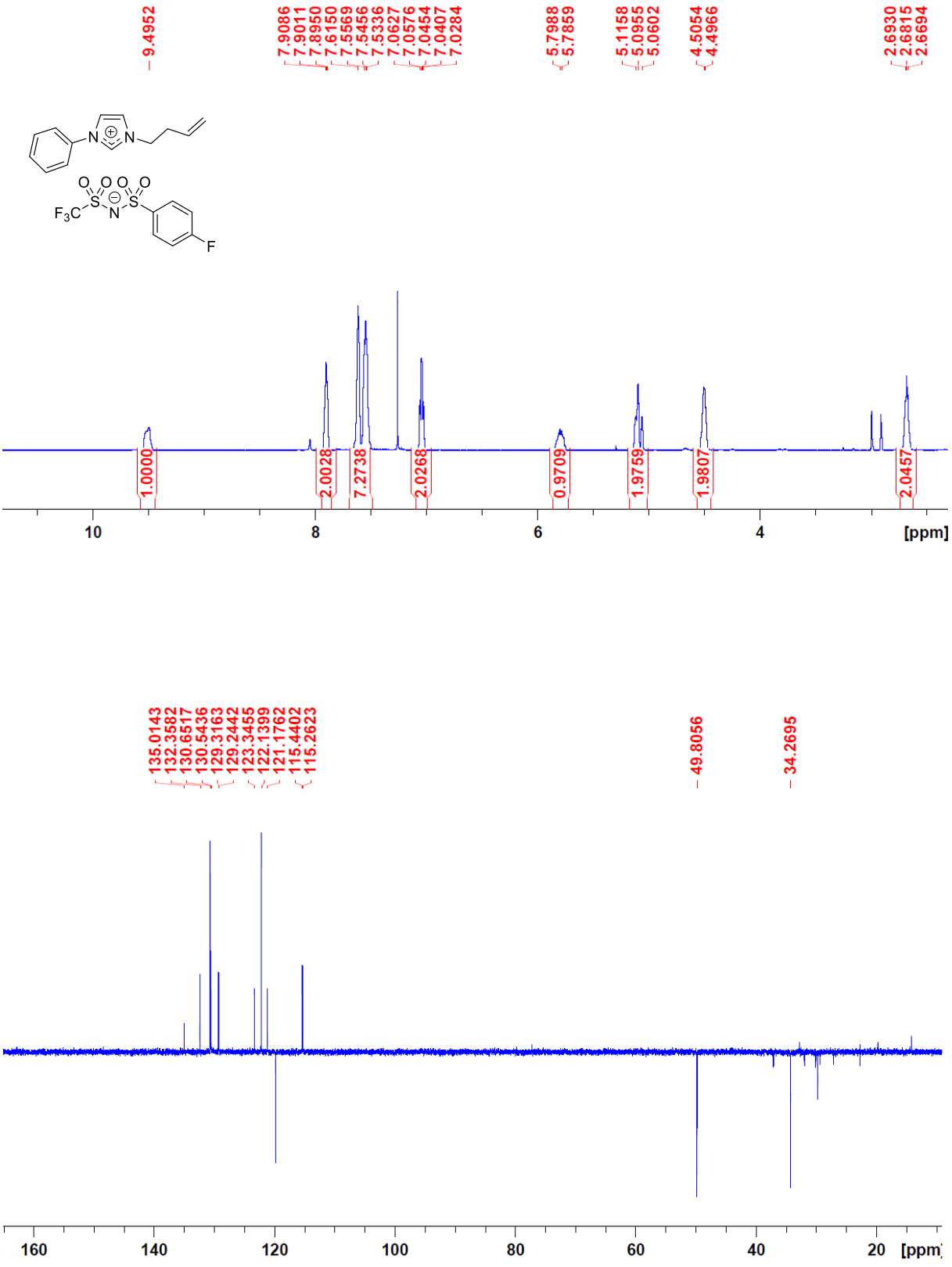
1-Phenyl-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-methoxybenzenesulfonyl)imide (12a)

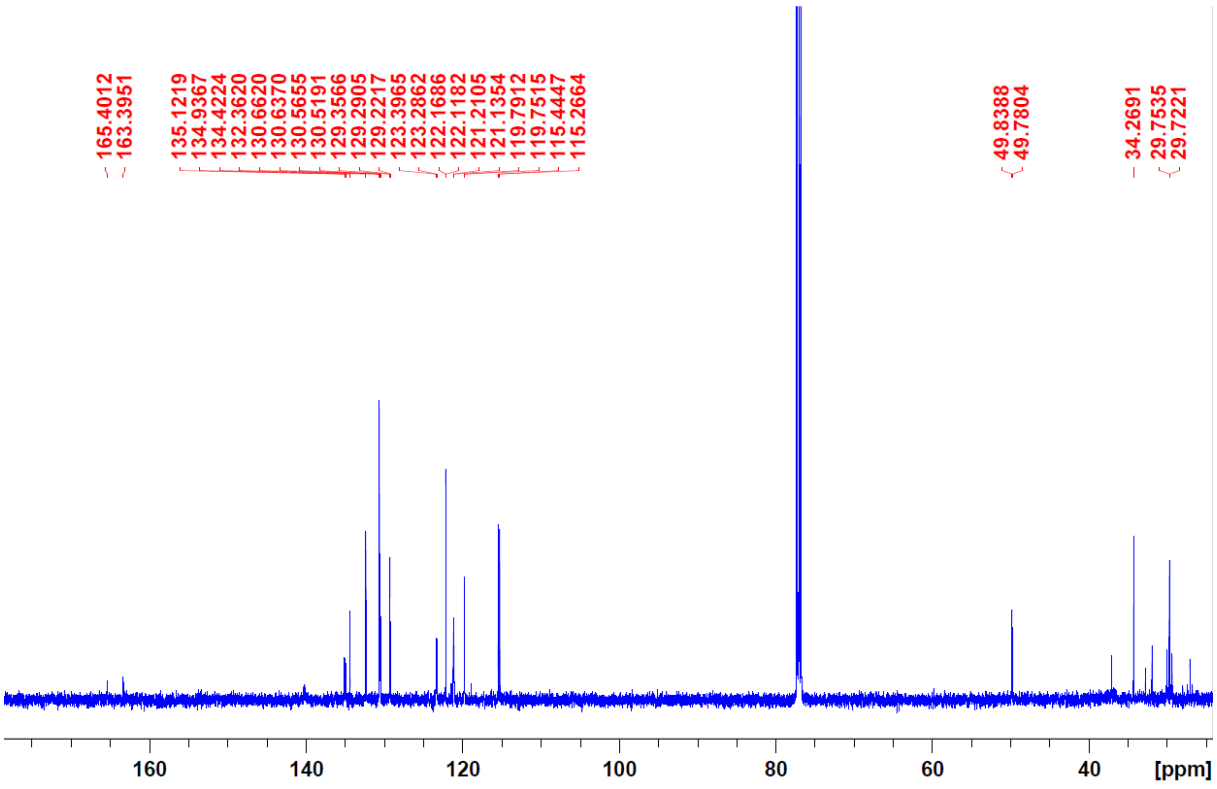


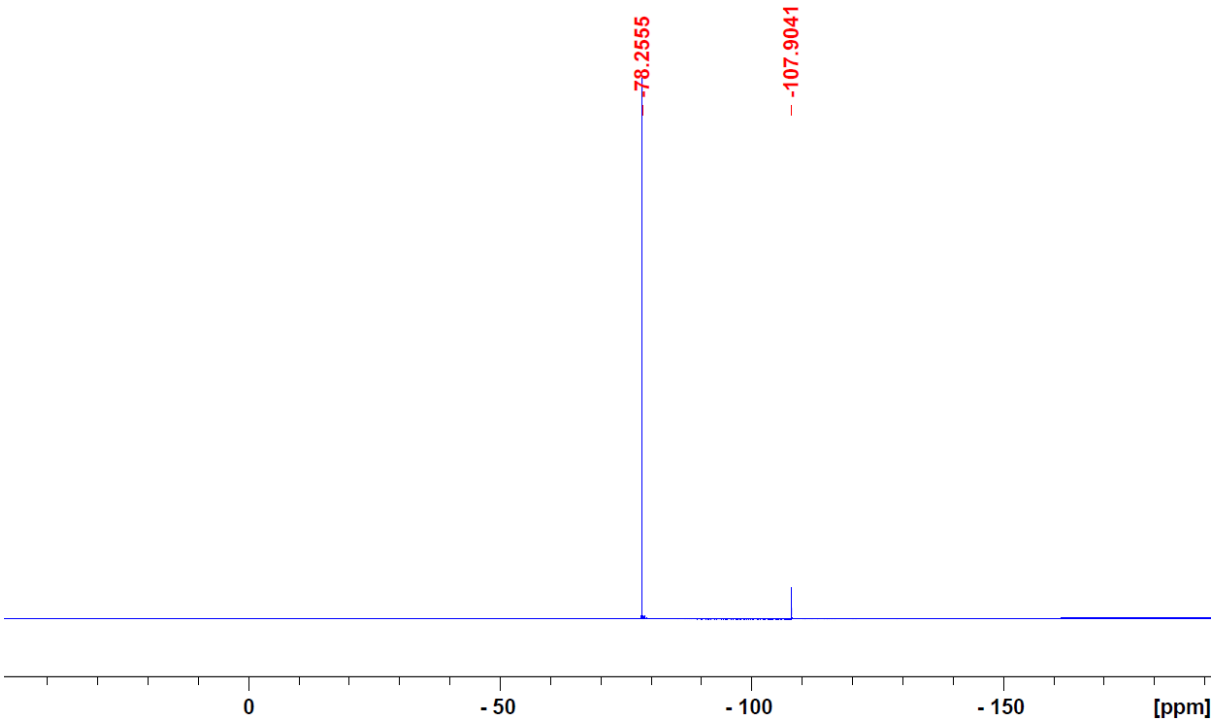

162.0213
136.4035
135.1152
134.5318
132.5602
130.6955
130.4727
128.6923
123.5485
122.1365
121.2064
119.7713
113.5545
55.5999
49.8098
34.3978
160
140
120
100
80
60
40
[ppm]


-78.2077
0
- 50
- 100
- 150
[ppm]

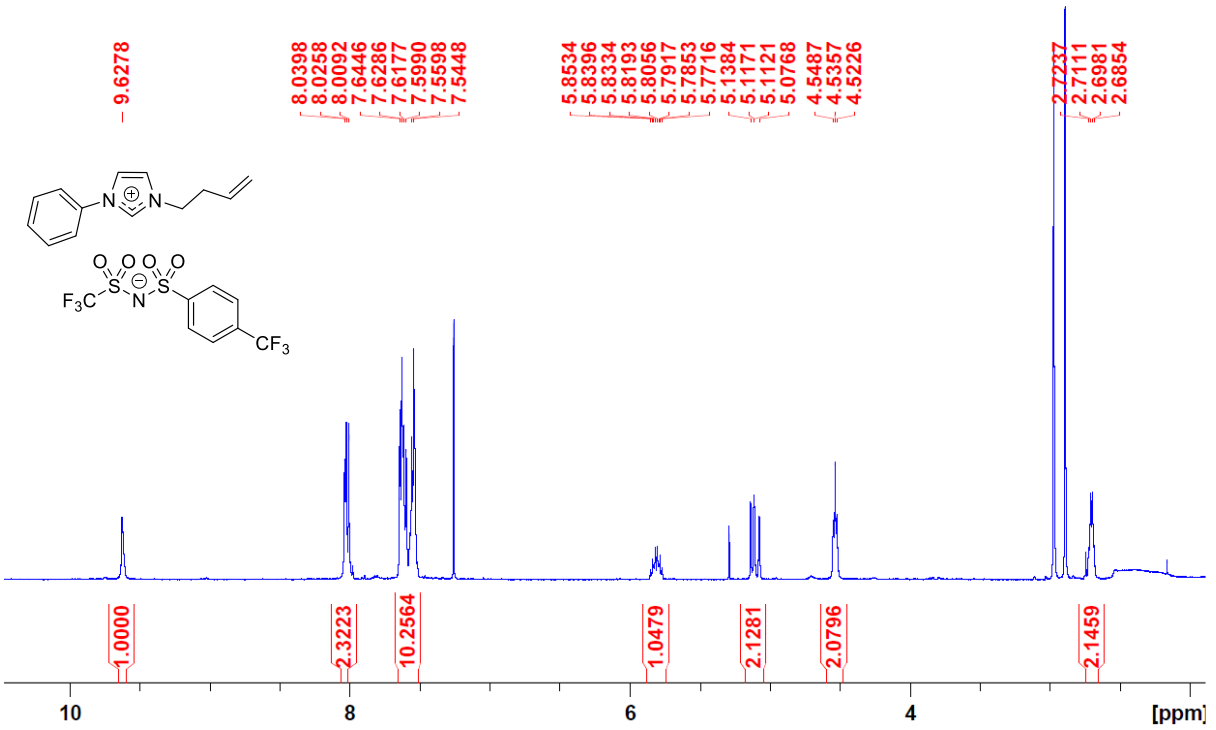
1-Phenyl-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide (12b)

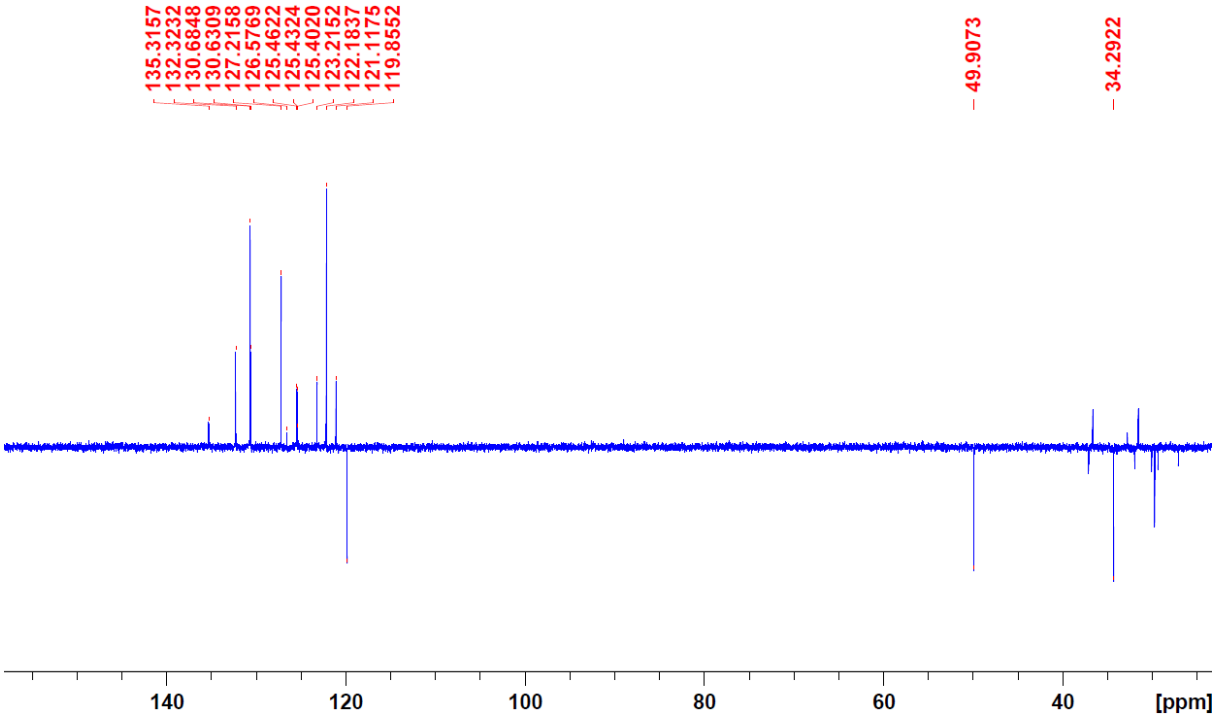


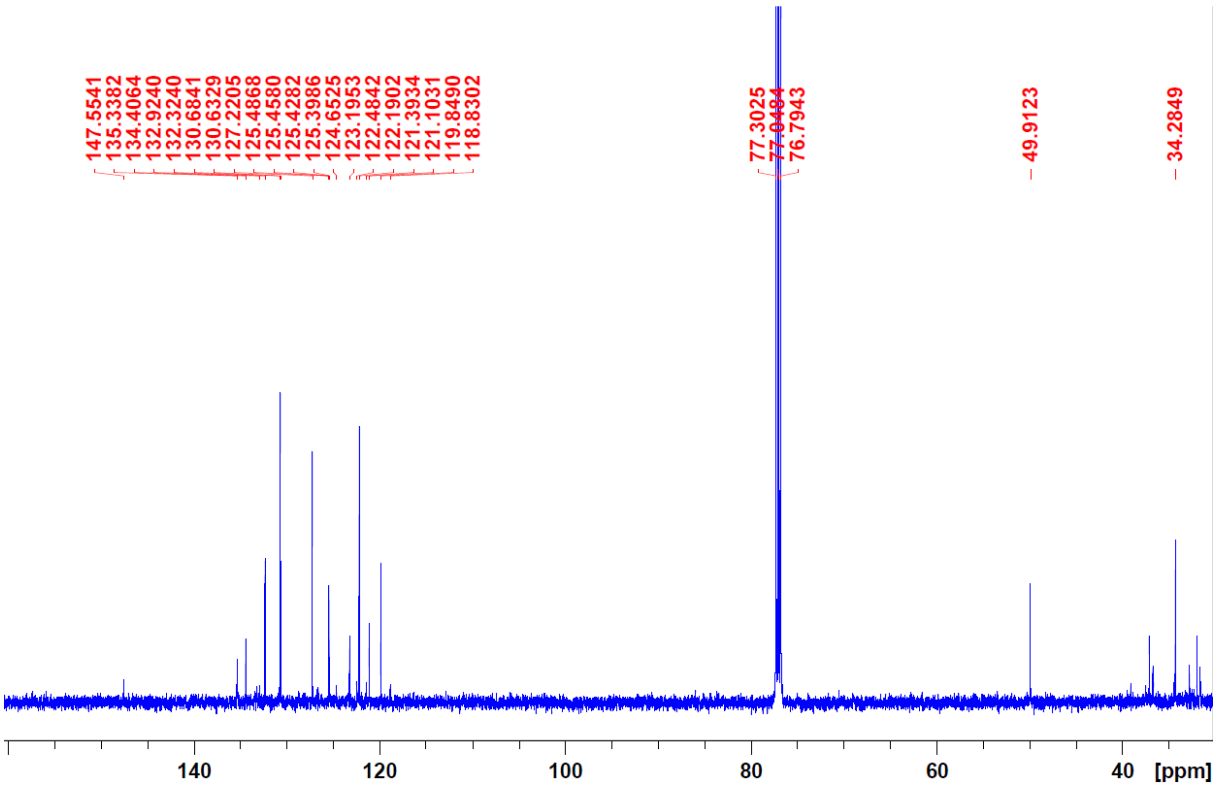

165.4012
163.3951
135.1219
134.9367
134.4224
132.3620
130.6620
130.6370
130.5655
130.5191
129.3566
129.2905
129.2217
123.3965
123.2862
122.1686
122.1182
121.2105
121.1354
119.7912
119.7515
115.4447
115.2664
49.8388
49.7804
34.2691
29.7535
29.7221
160
140
120
100
80
60
40
[ppm]

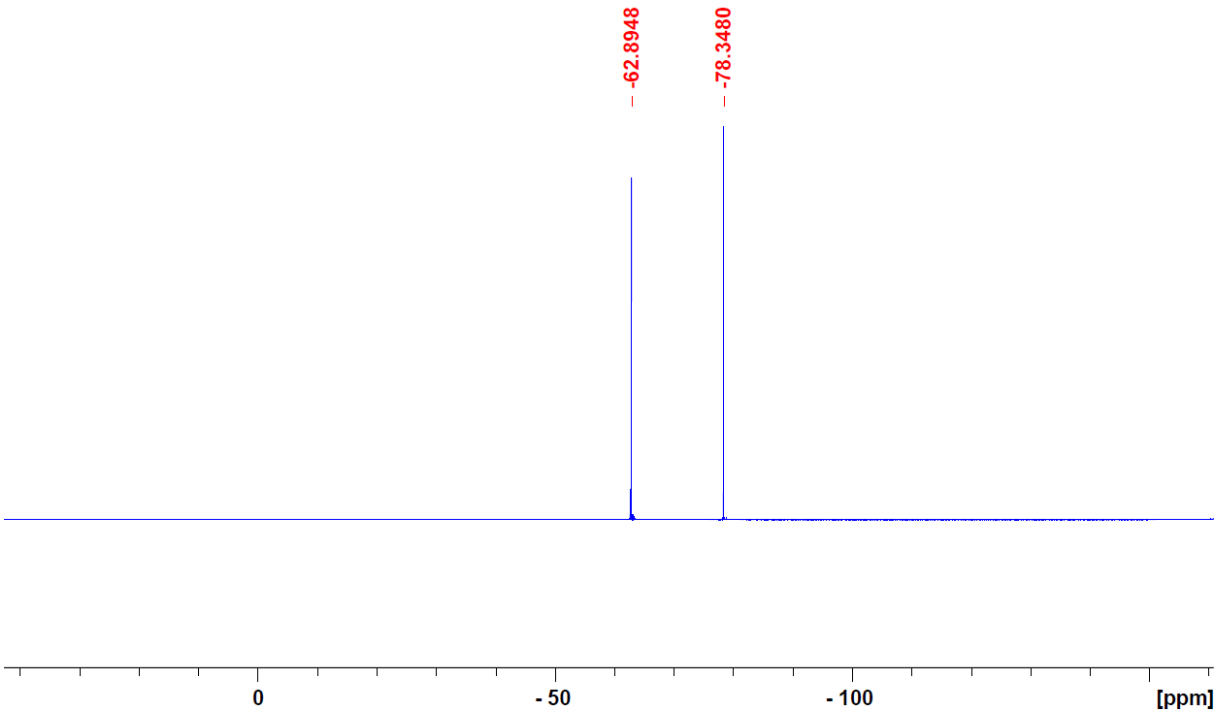

-78.2555
-107.9041
0
- 50
- 100
- 150
[ppm]

1-Phenyl-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide (12c)

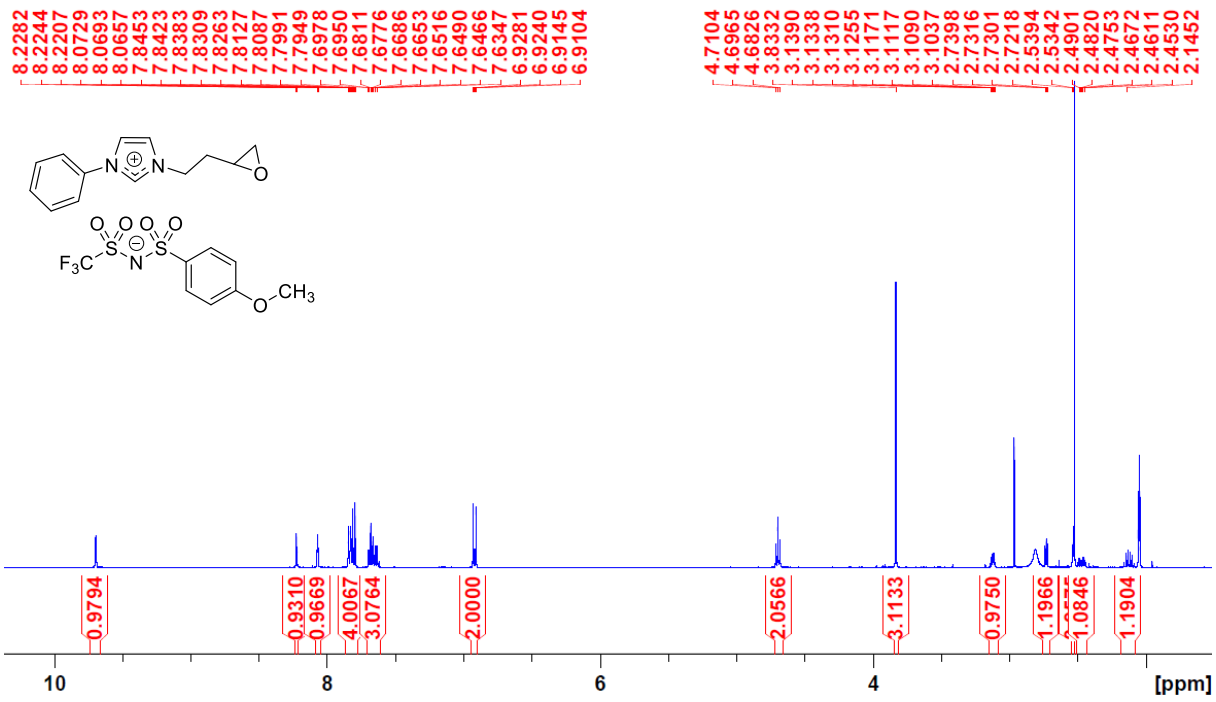


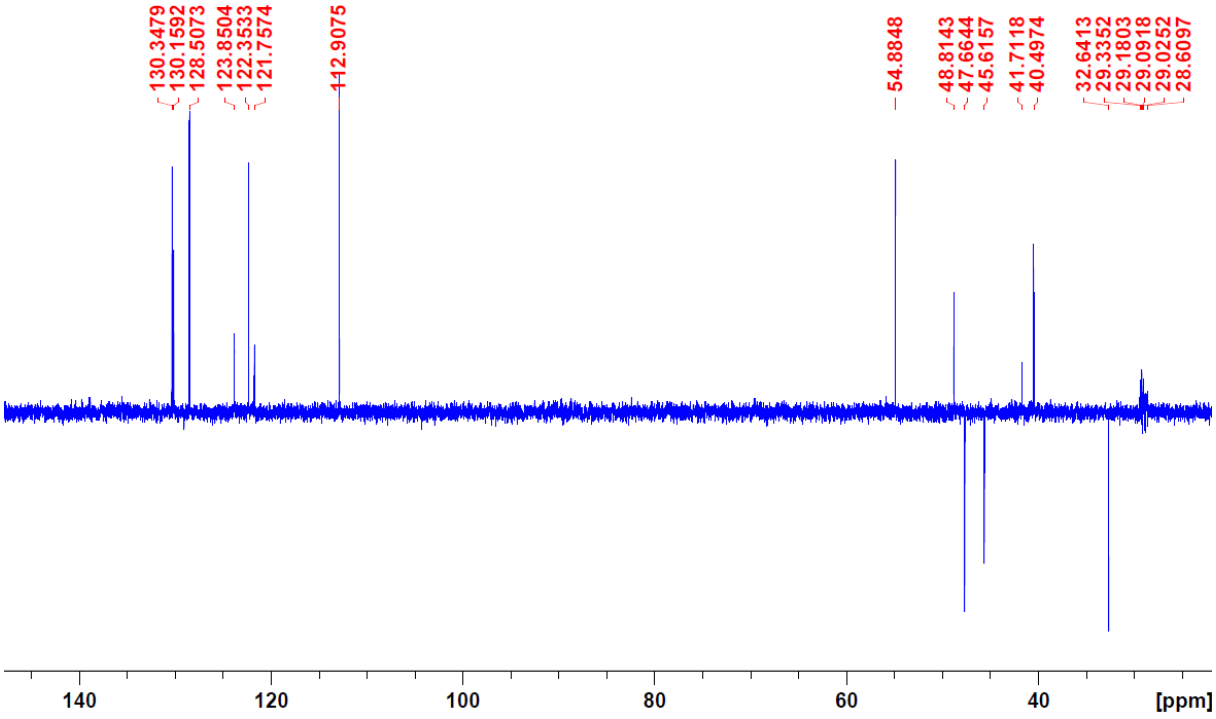


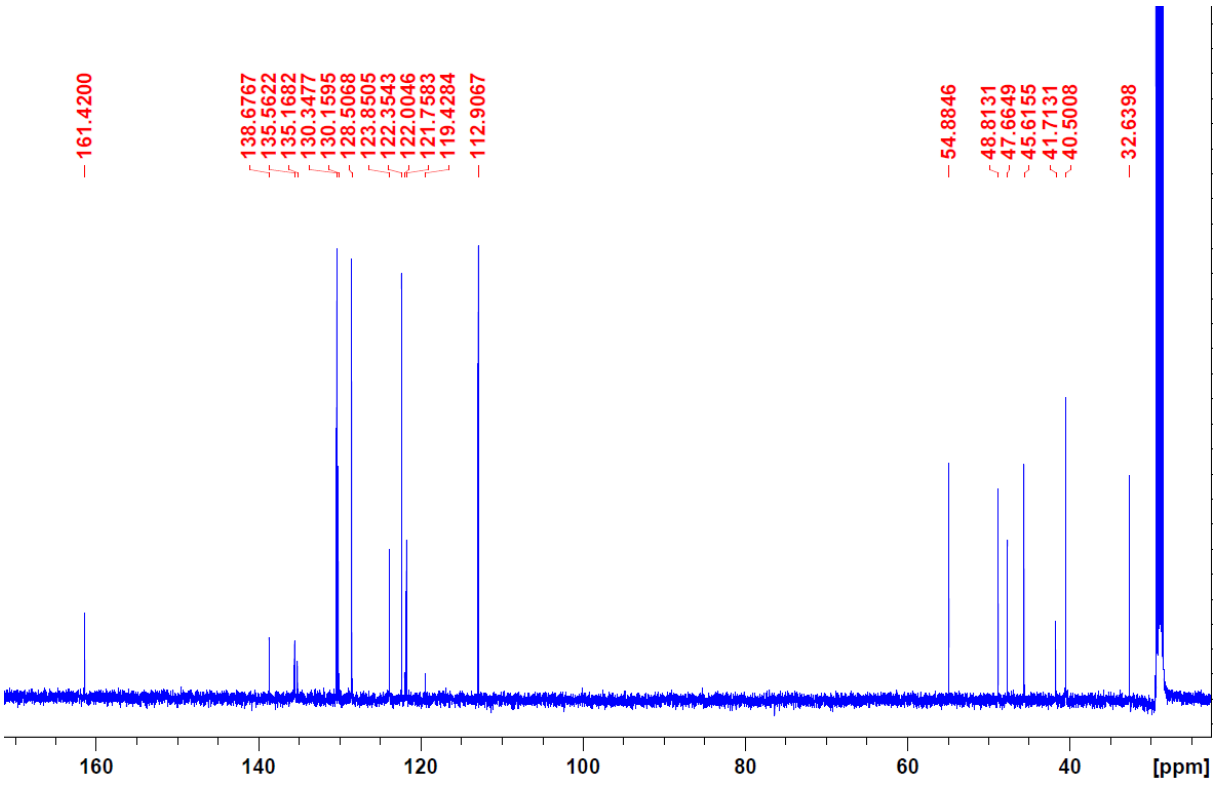

147.5541
135.3382
134.4064
132.9240
132.3240
130.6841
130.6329
127.2205
125.4868
125.4580
125.4282
125.3986
124.6525
123.1953
122.4842
122.1902
121.3934
121.1031
119.8490
118.8302
77.3025
77.0484
76.7943
49.9123
34.2849
140
120
100
80
60
40
[ppm]

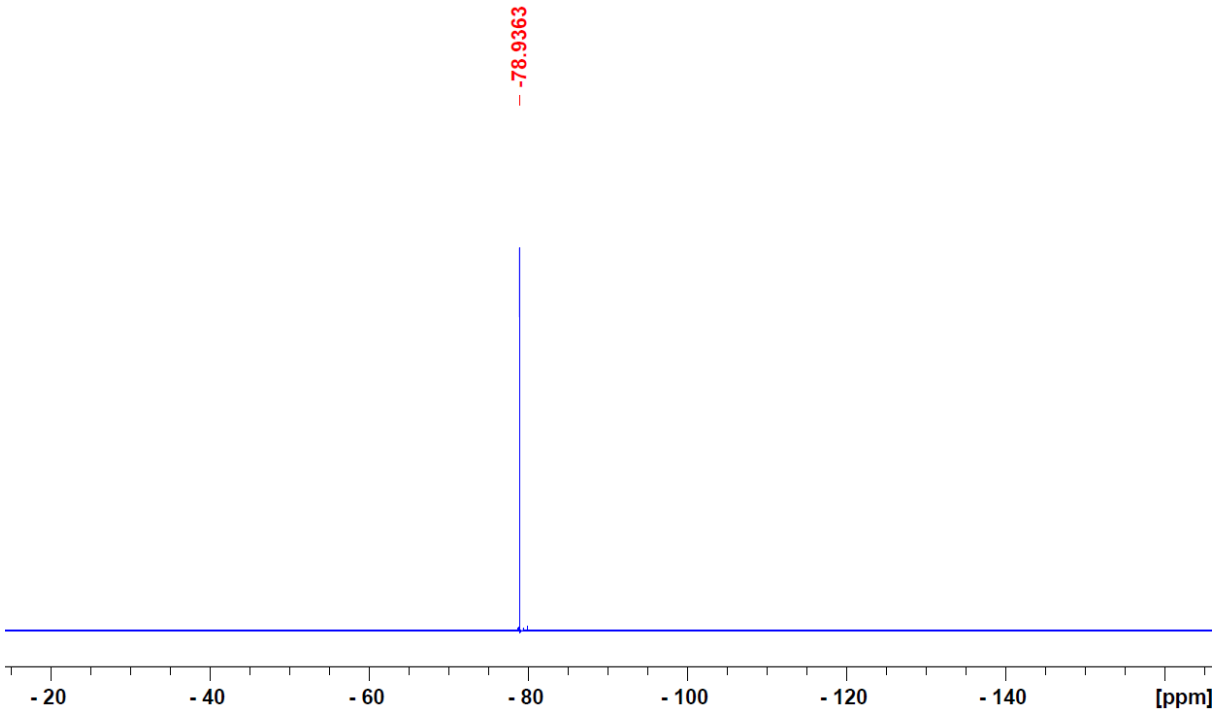

-62.8948
-78.3480
0
- 50
- 100
[ppm]

3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-methoxybenzenesulfonyl)imide (13a)

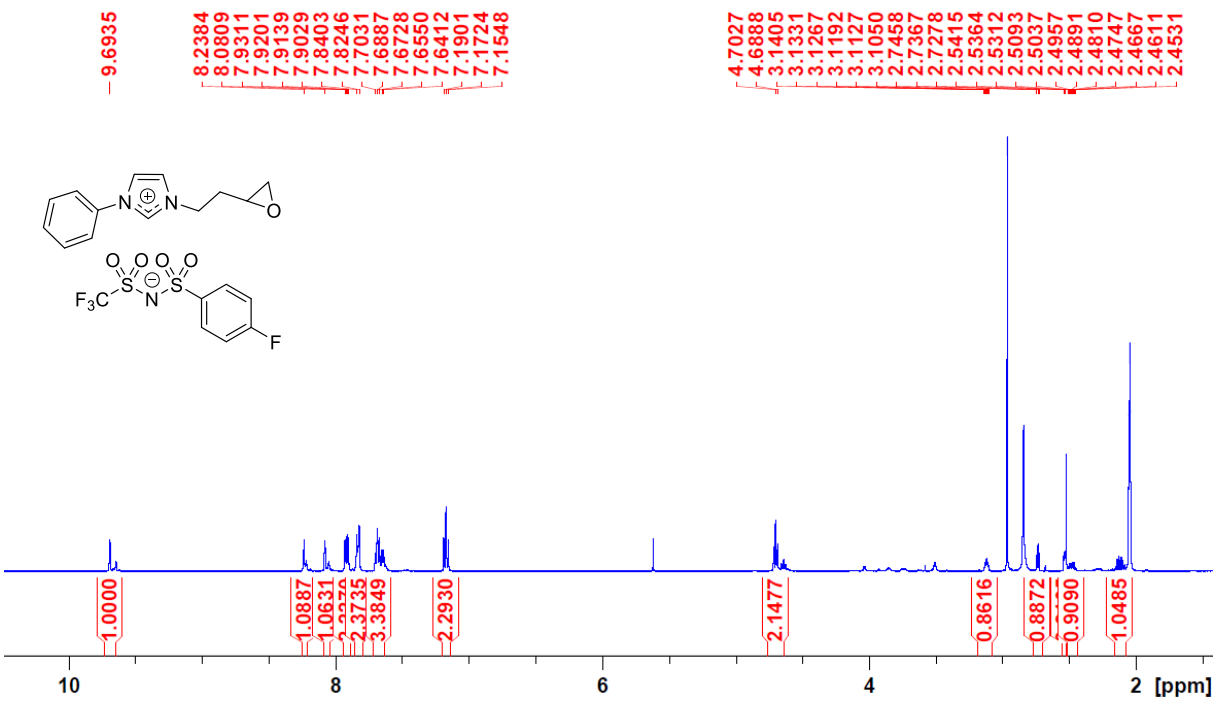


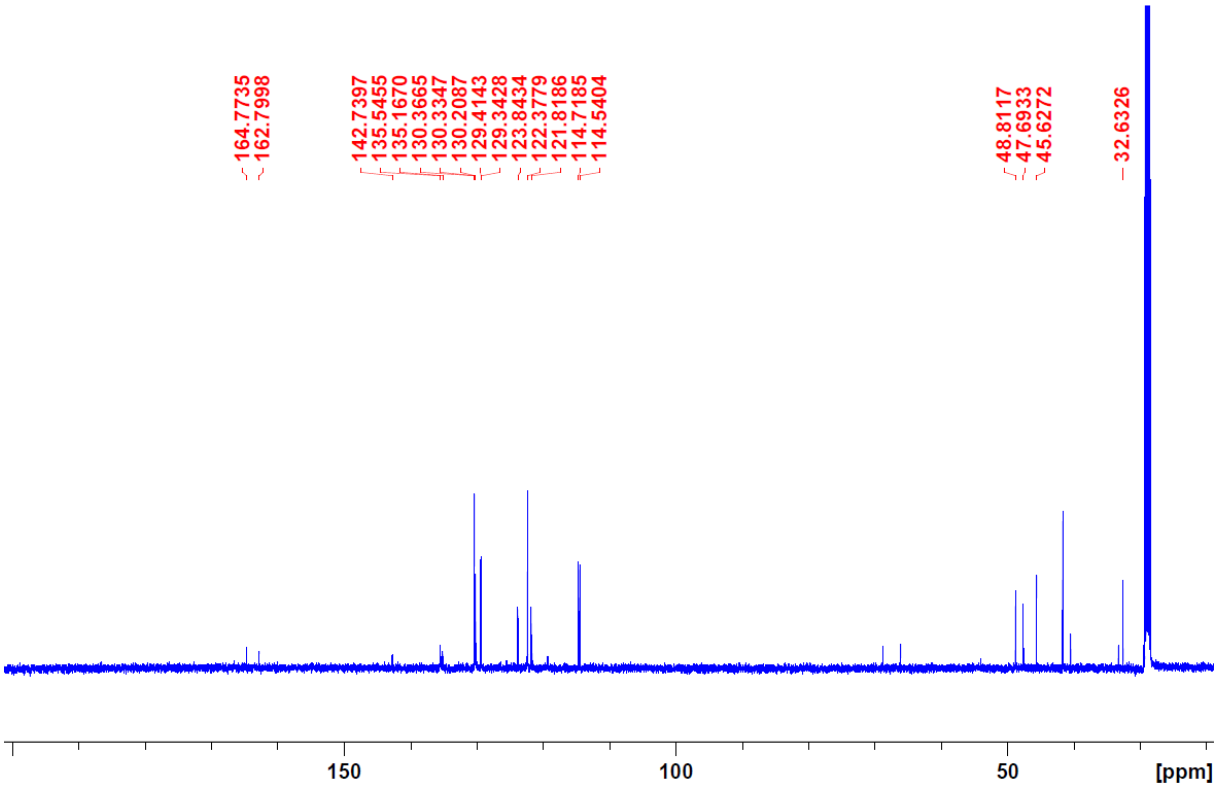


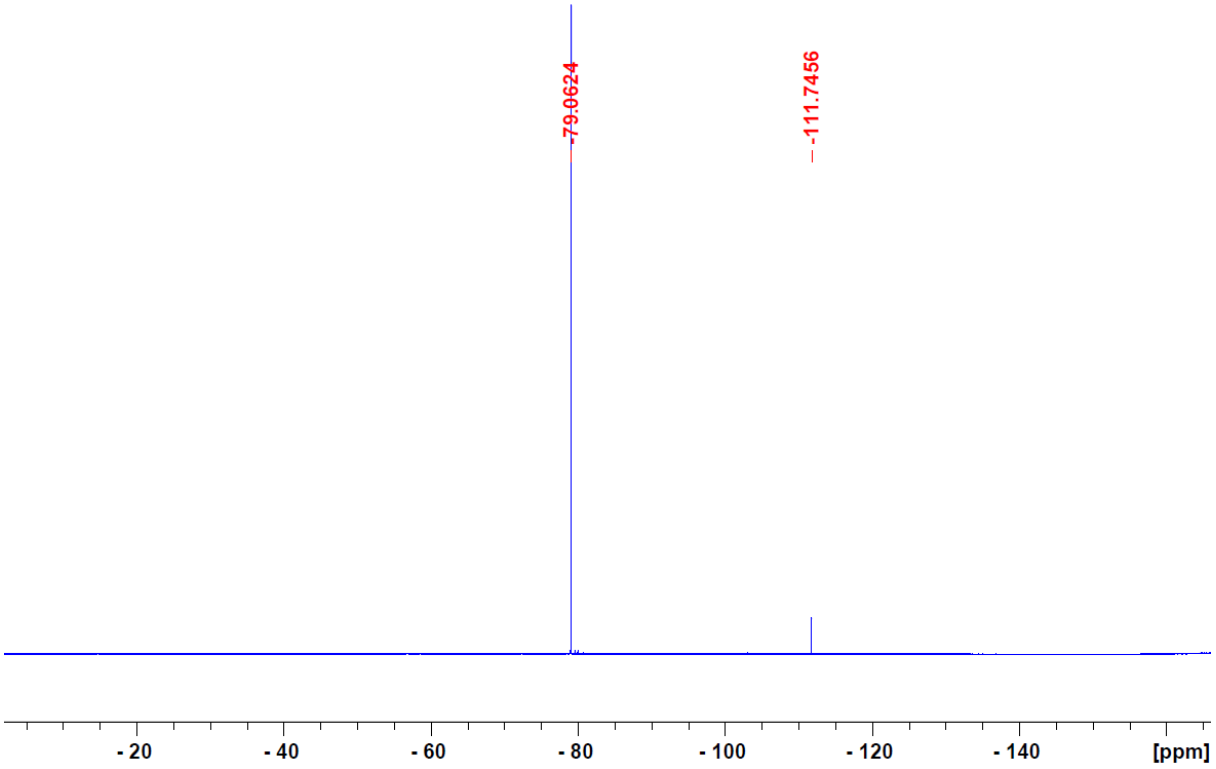

161.4200
138.6767
135.5622
135.1682
130.3477
130.1595
128.5068
123.8505
122.3543
122.0046
121.7583
119.4284
112.9067
54.8846
48.8131
47.6649
45.6155
41.7131
40.5008
32.6398
160
140
120
100
80
60
40
[ppm]


-78.9363
- 20
- 40
- 60
- 80
- 100
- 120
- 140
[ppm]

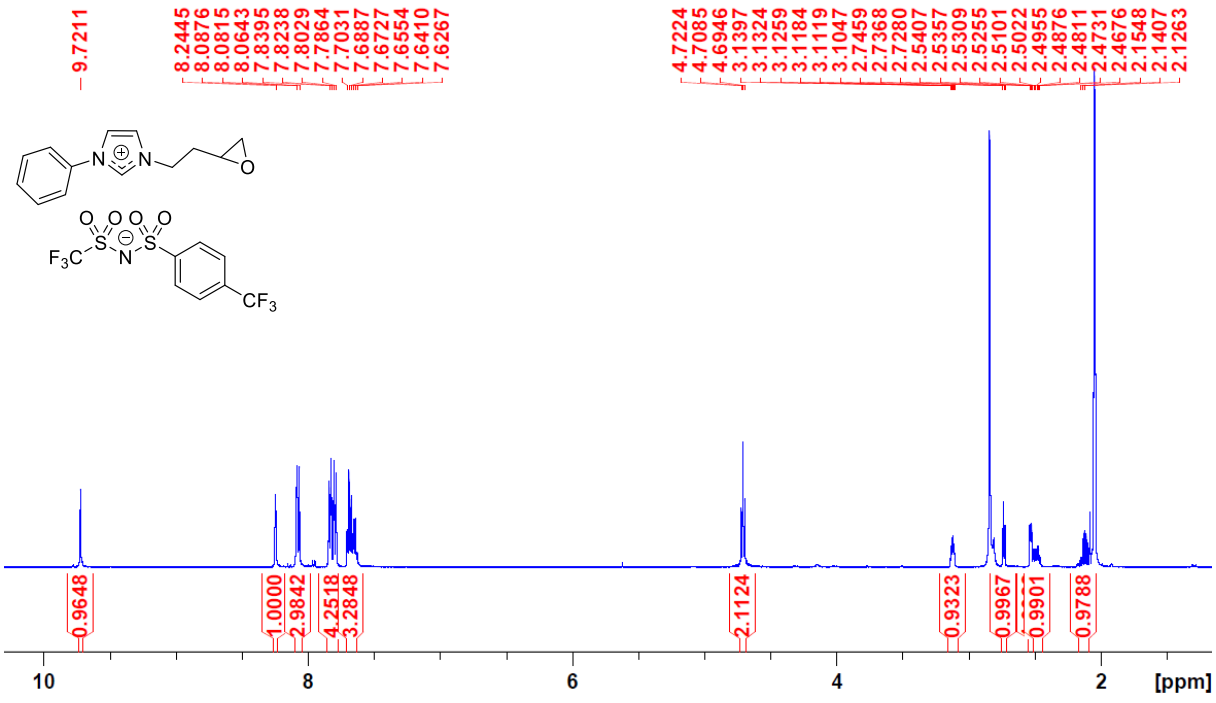
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide (13b)

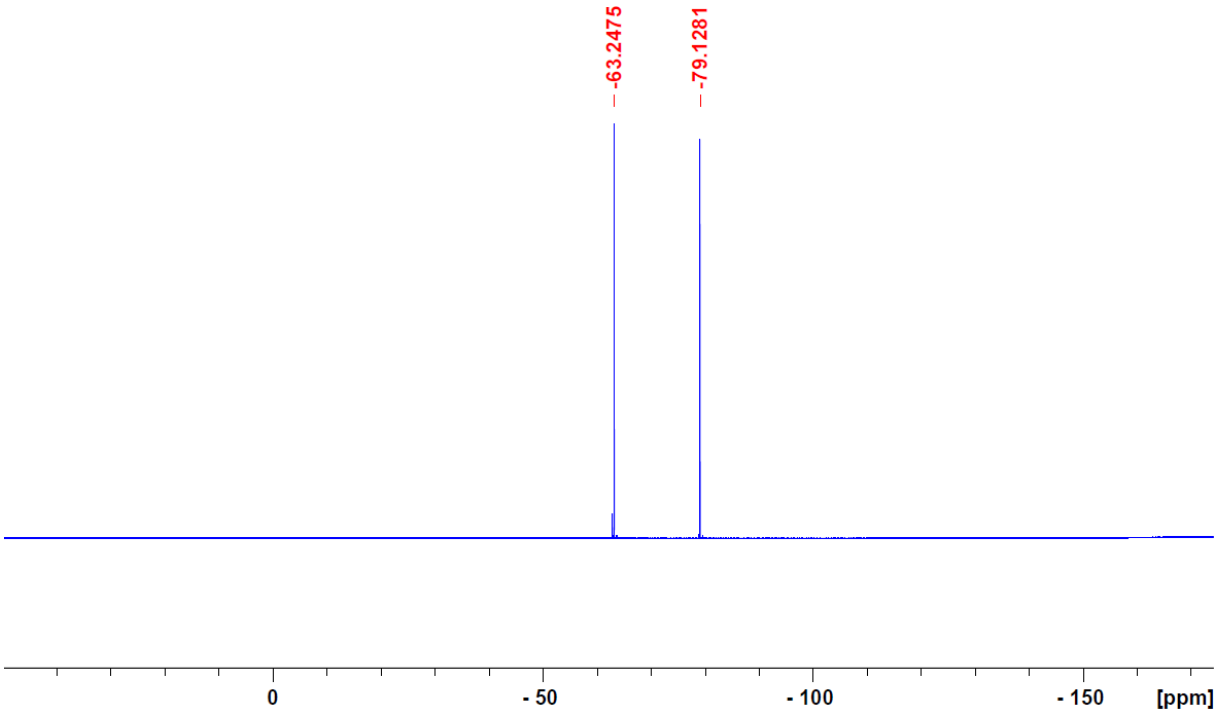




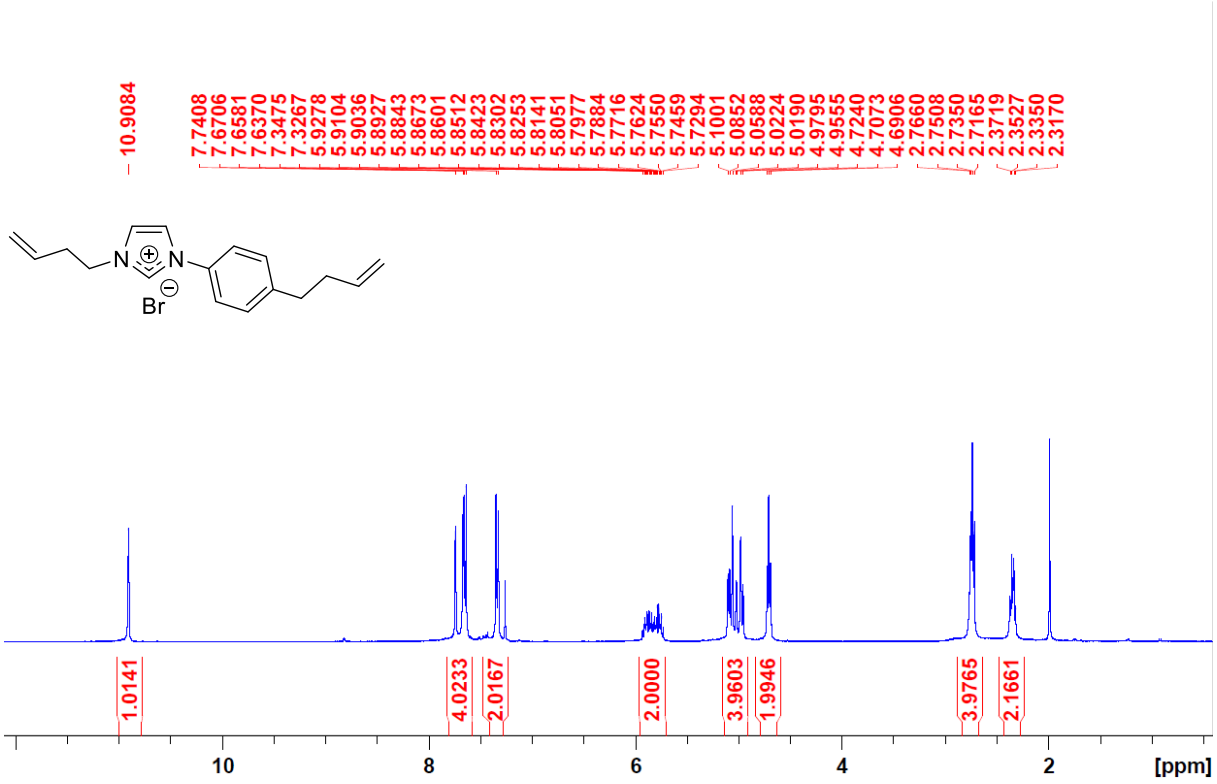


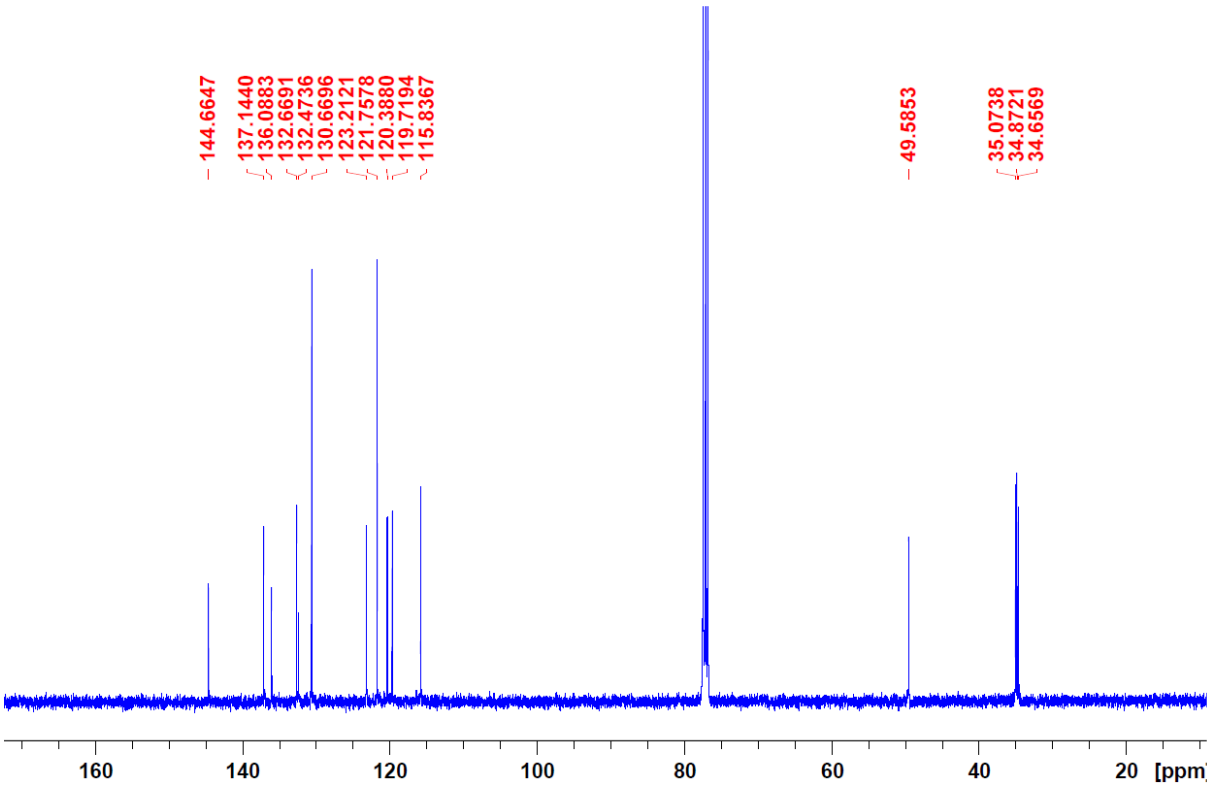
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide (13c)



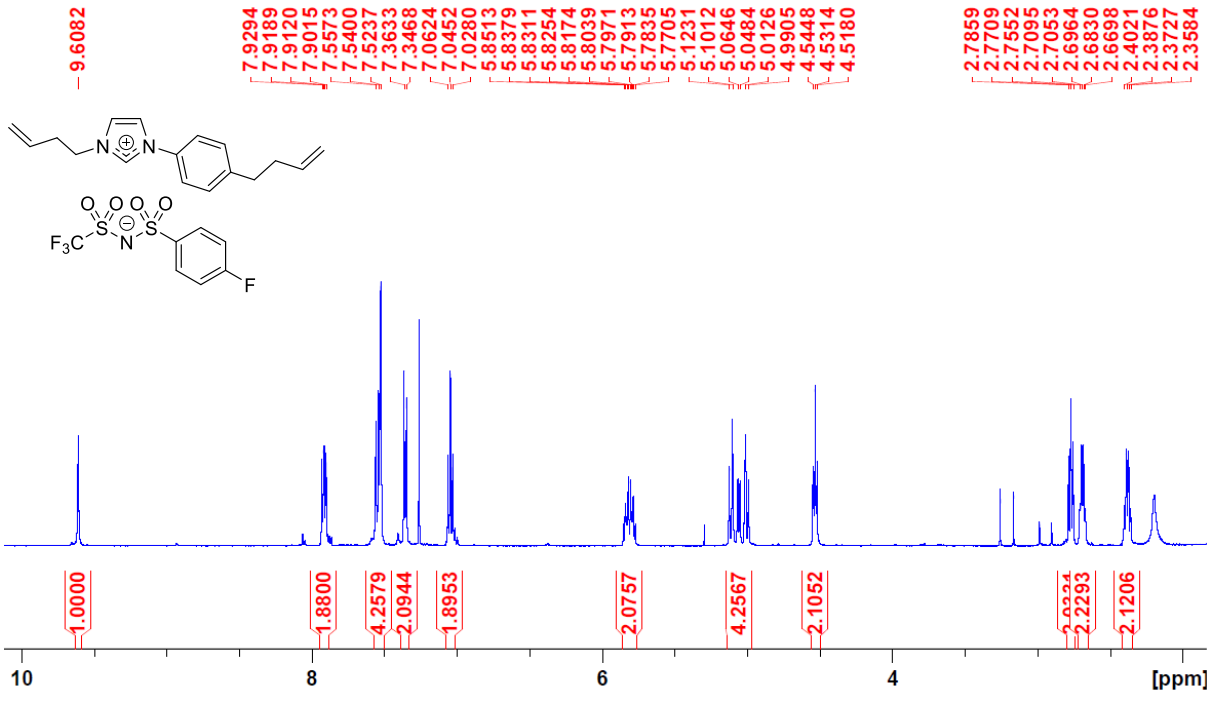


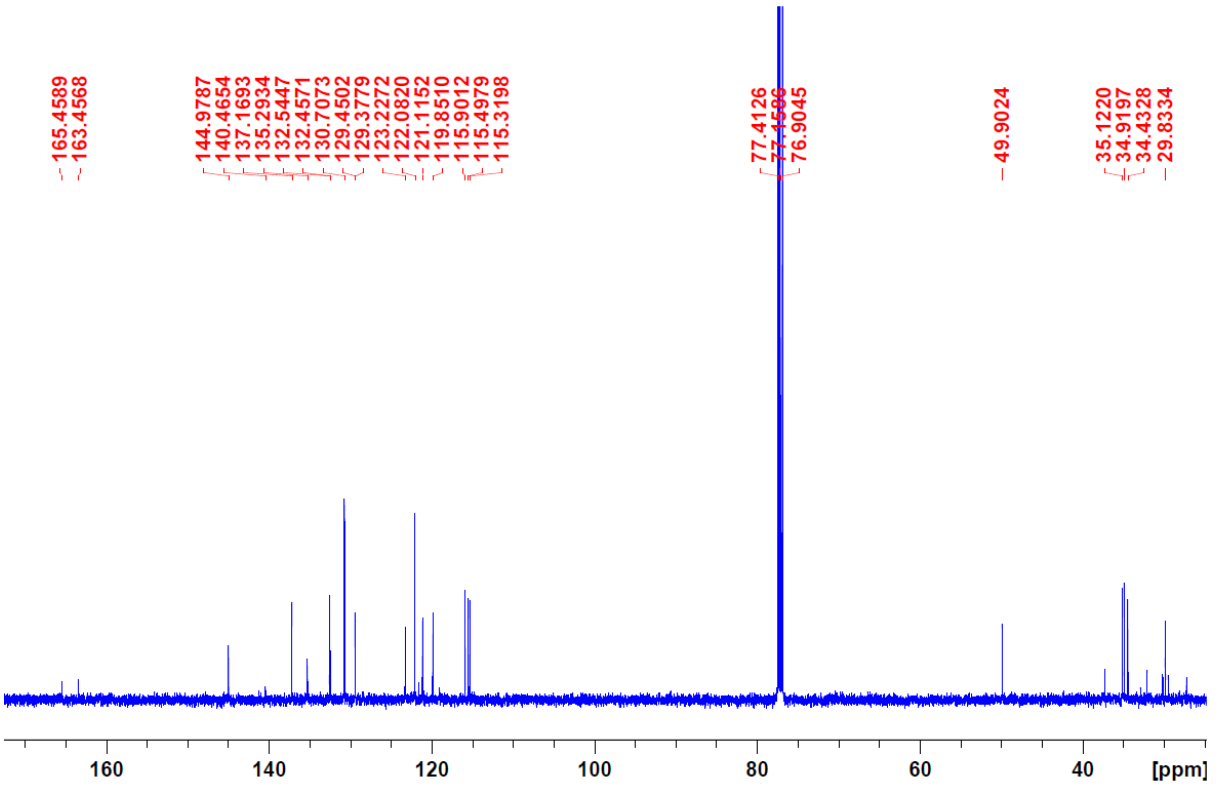
1-[4-(3-Buten-1-yl)phenyl]-3-(3-buten-1-yl)imidazolium bromide (diIm-Br)

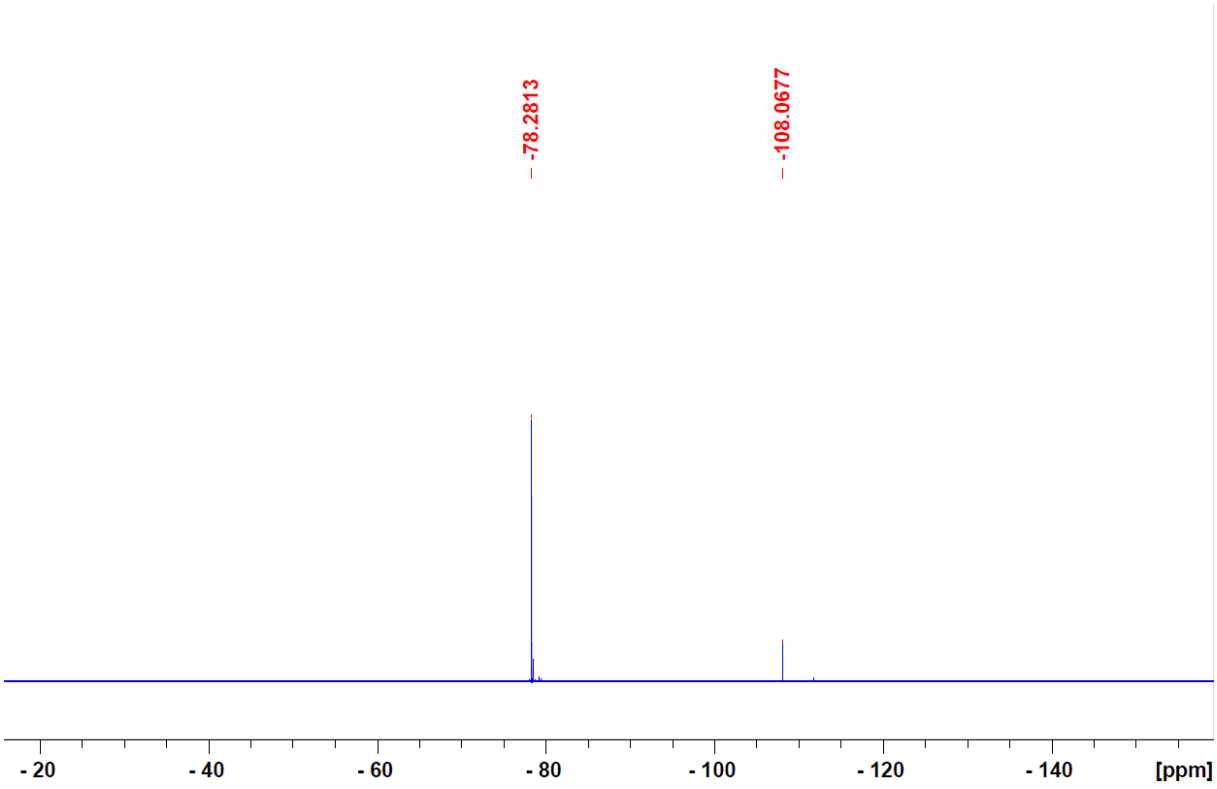




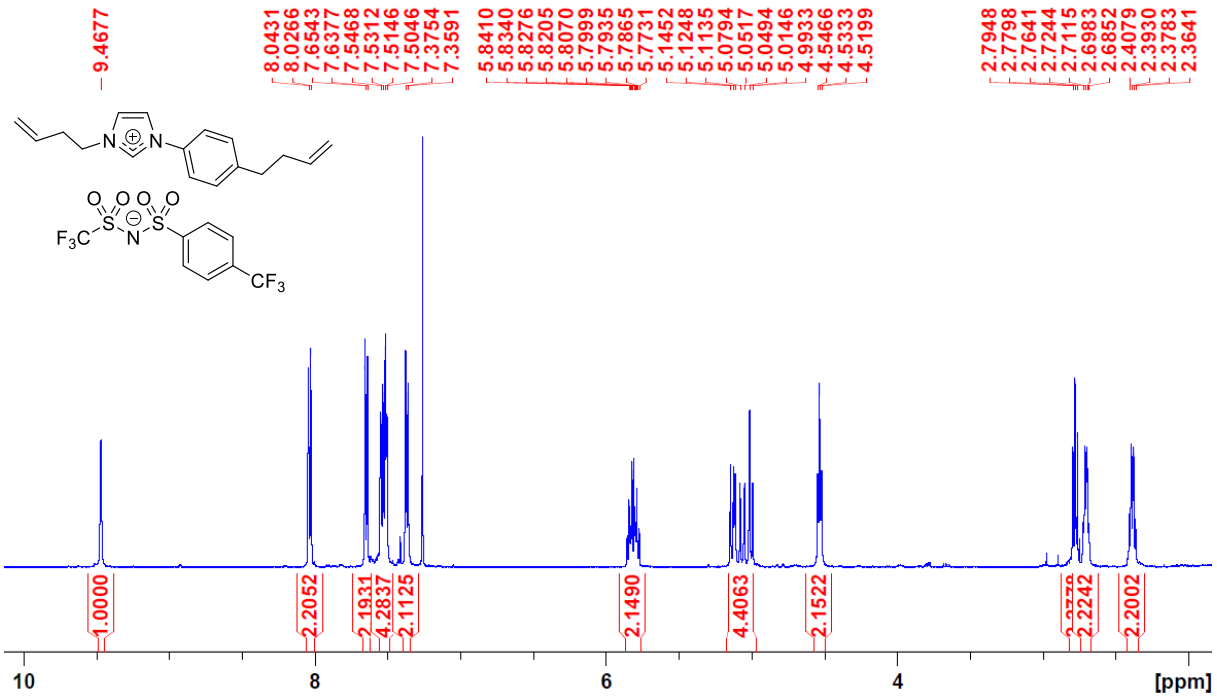
1-[4-(3-Buten-1-yl)phenyl]-3-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide (14a)

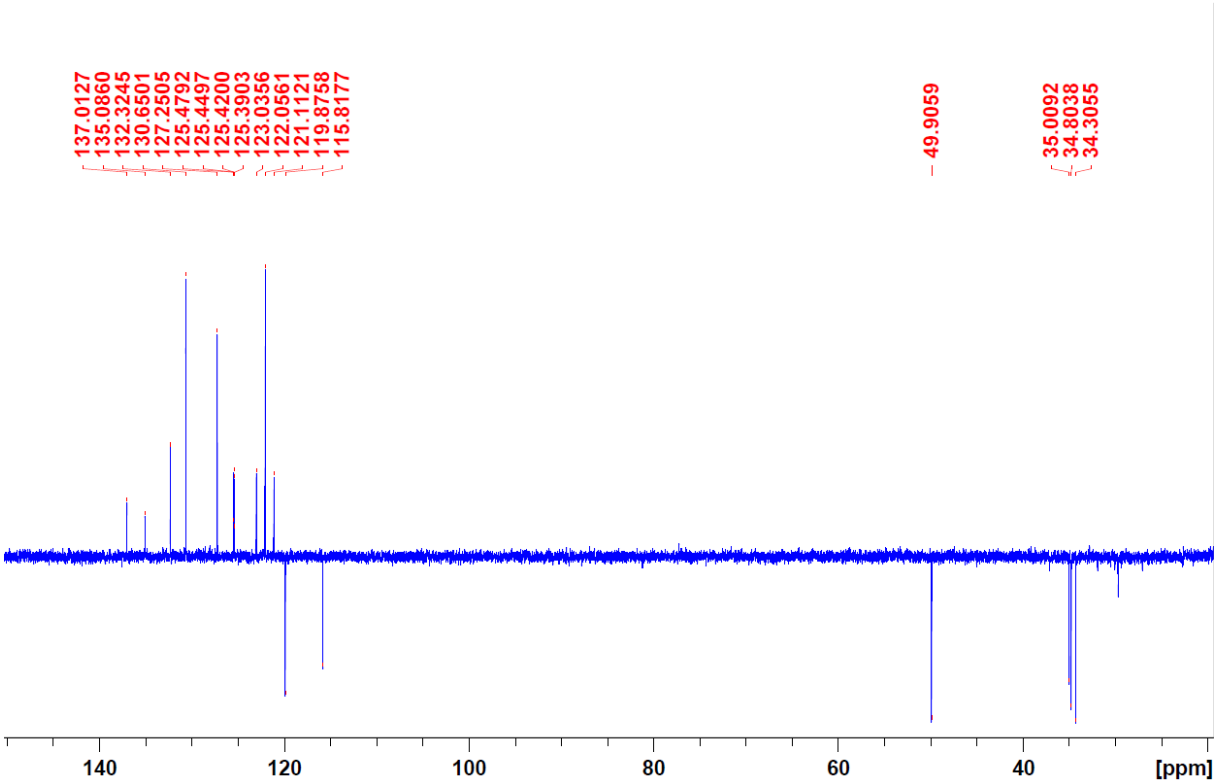


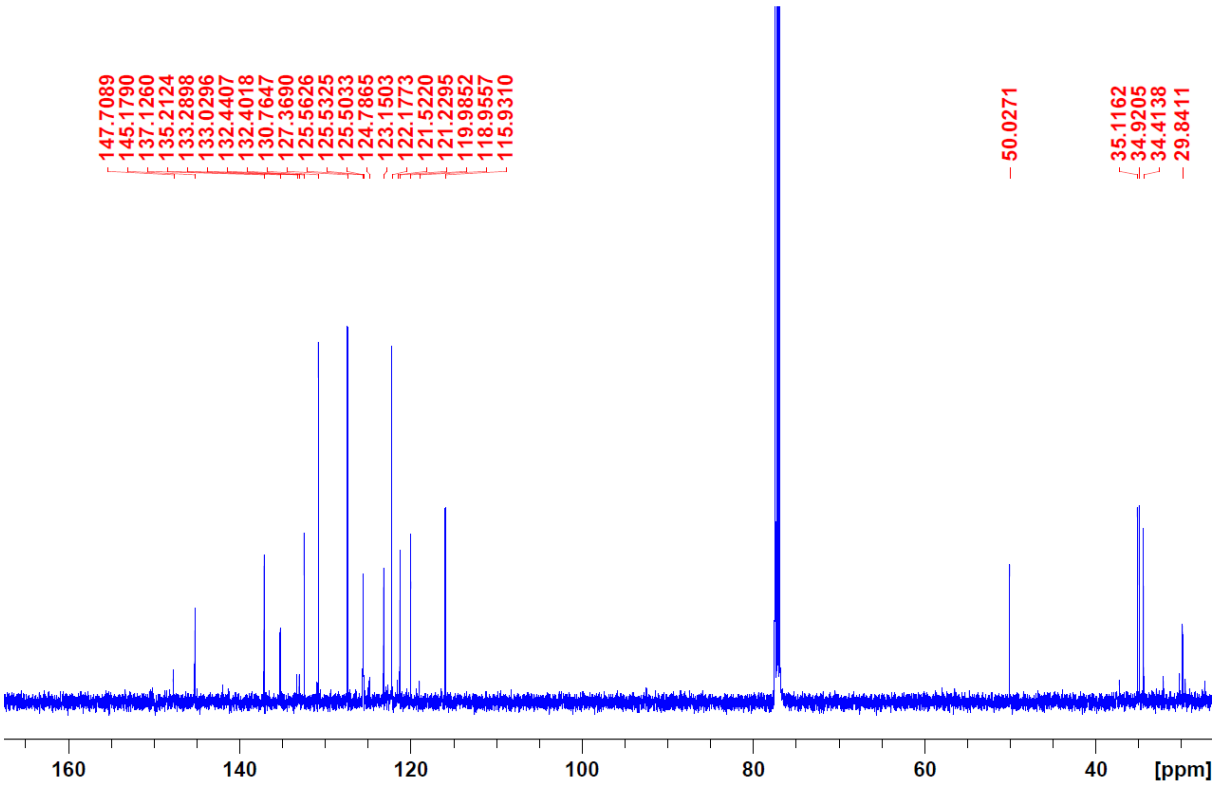

165.4589
163.4568
144.9787
140.4654
137.1693
135.2934
132.5447
132.4571
130.7073
129.4502
129.3779
123.2272
122.0820
121.1152
119.8510
115.9012
115.4979
115.3198
77.4126
76.9045
49.9024
35.1220
34.9197
34.4328
29.8334
160
140
120
100
80
60
40
[ppm]

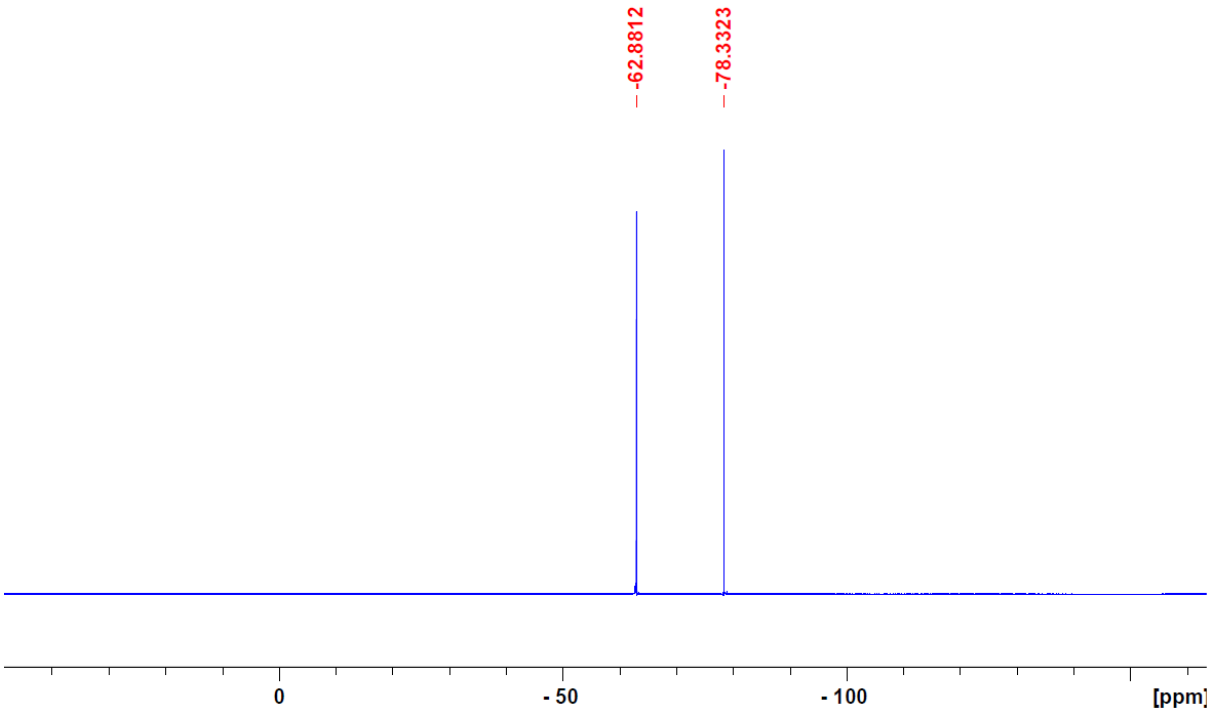

-78.2813
-108.0677
- 20
- 40
- 60
- 80
- 100
- 120
- 140
[ppm]

1-[4-(3-Buten-1-yl)phenyl]-3-(3-buten-1-yl)imidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide (14b)

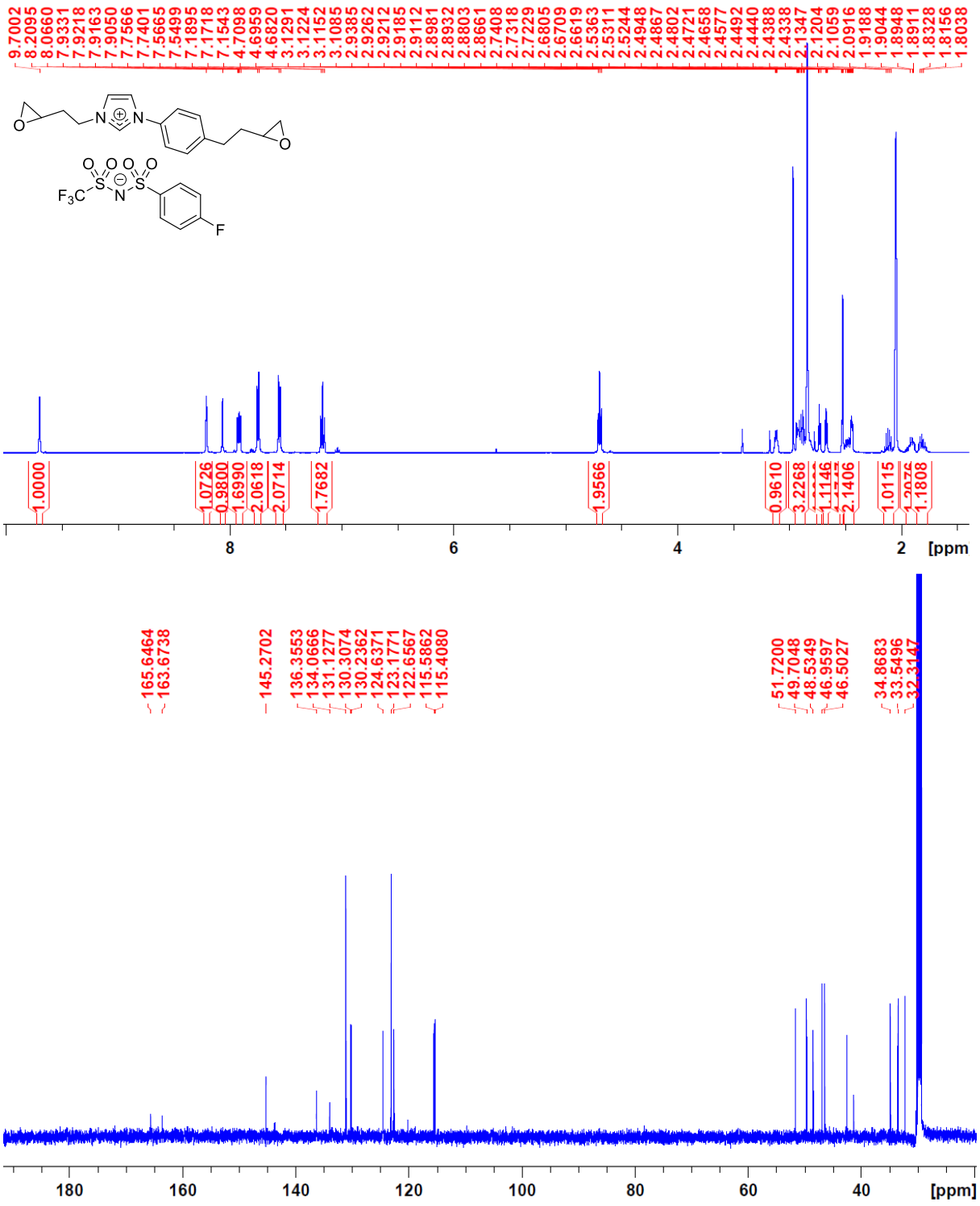


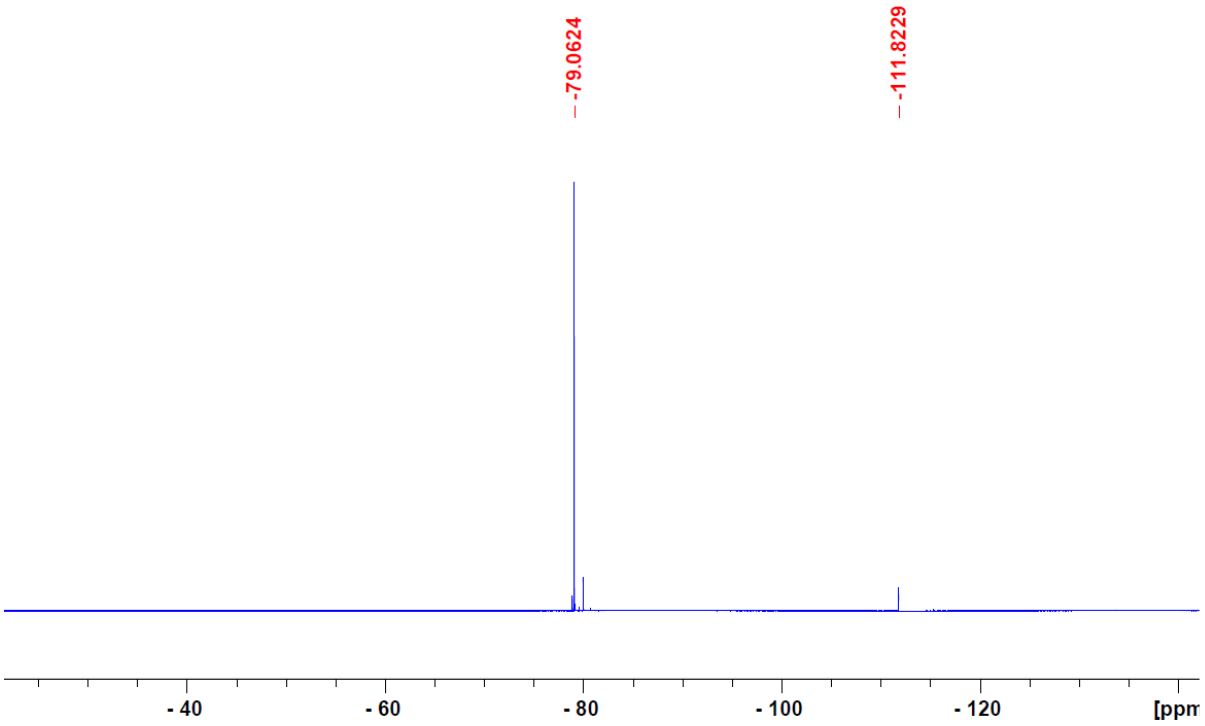



147.7089
145.1790
137.1260
135.2124
133.2898
133.0296
132.4407
132.4018
130.7647
127.3690
125.5626
125.5325
125.5033
124.7865
123.1503
122.1773
121.5220
121.2295
119.9852
118.9557
115.9310
50.0271
35.1162
34.9205
34.4138
29.8411
160
140
120
100
80
60
40
[ppm]

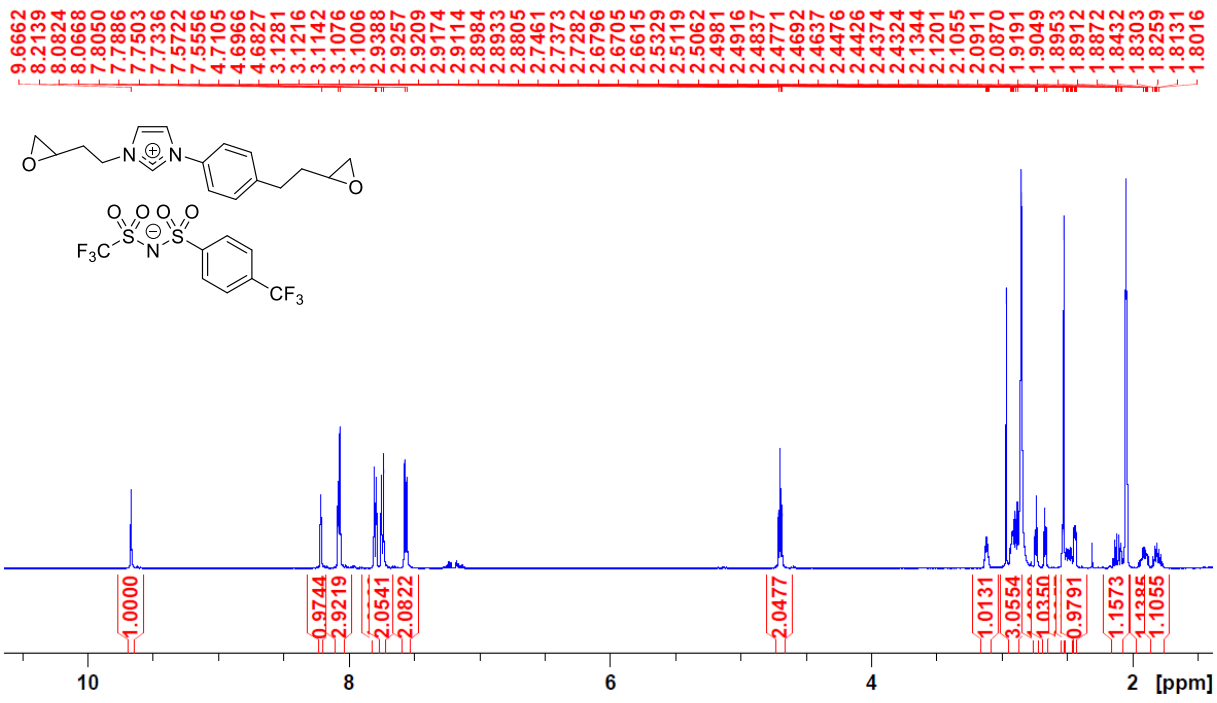

-62.8812
-78.3323
0
- 50
- 100
[ppm]

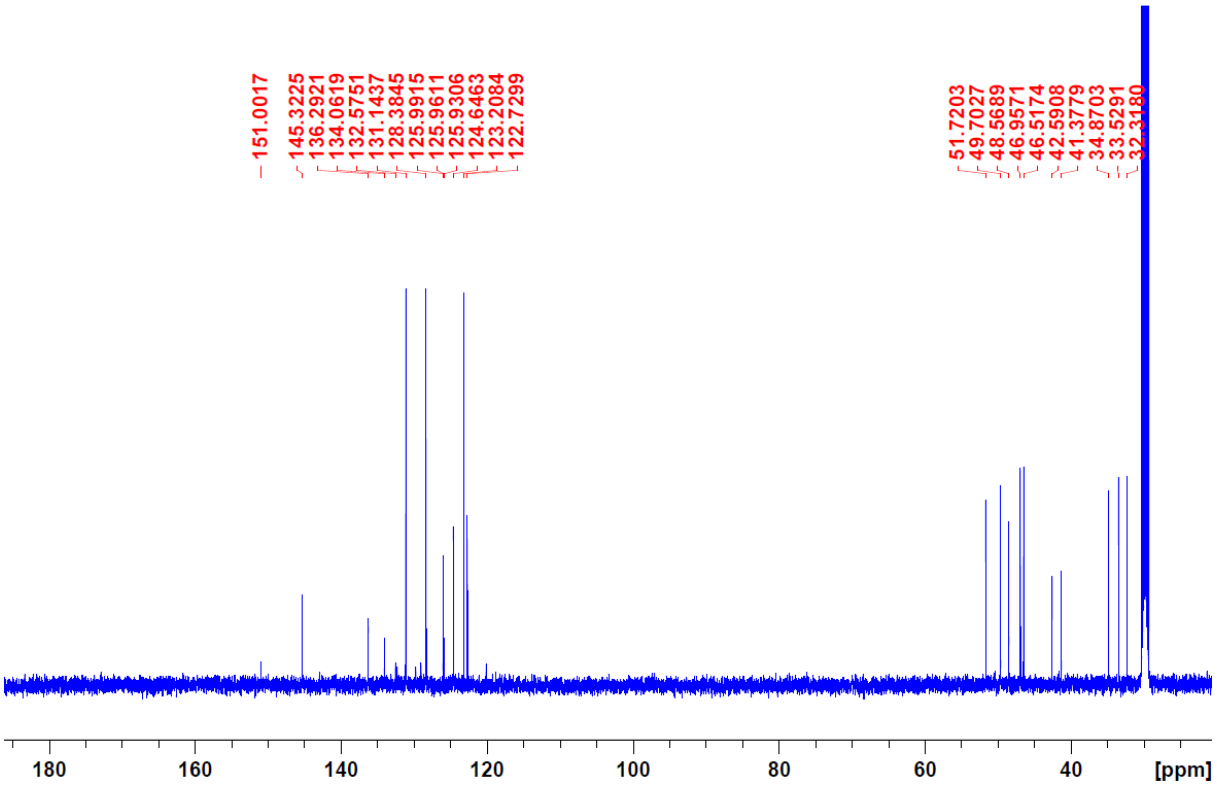
3-[2-(Oxiran-2-yl)ethyl]-1-{4-[2-(oxiran-2-yl)ethyl]phenyl}imidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide (15a)

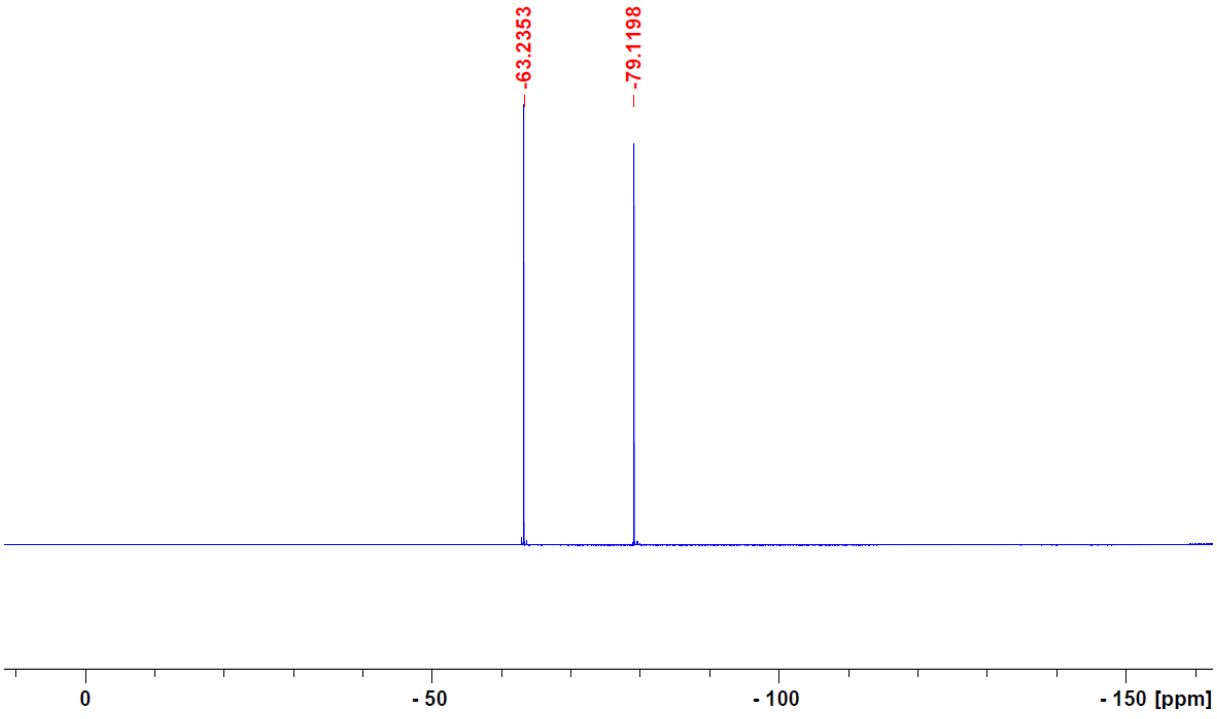




3-[2-(Oxiran-2-yl)ethyl]-1-{4-[2-(oxiran-2-yl)ethyl]phenyl}imidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide (15b)

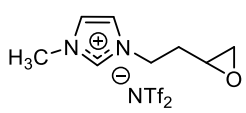



151.0017
145.3225
136.2921
134.0619
132.5751
131.1437
128.3845
125.9915
125.9611
125.9306
124.6463
123.2084
122.7299
51.7203
49.7027
48.5689
46.9571
46.5174
42.5908
41.3779
34.8703
33.5291
32.3180
180
160
140
120
100
80
60
40
[ppm]

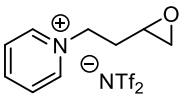

-63.2353
-79.1198
0
- 50
- 100
- 150 [ppm]

V. TGA and derivative curves of the epoxides

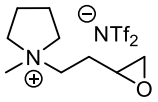
TGA of monoepoxide ionic liquids type "Cat-NTf_2" :



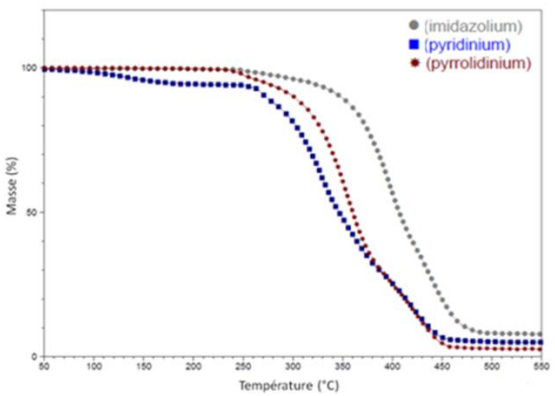
Imidazolium (1a)

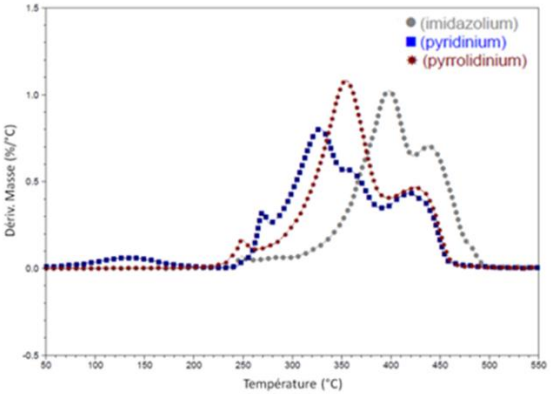


Pyridinium

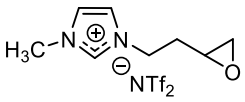


Pyrrolidinium

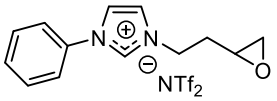




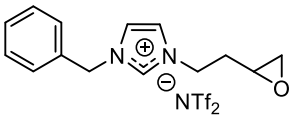
TGA of monoepoxide imidazolium type "Im-NTf_2" :



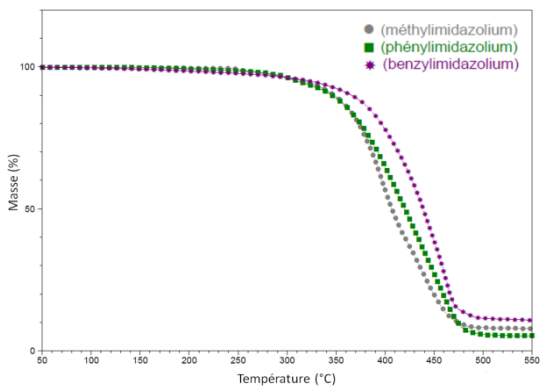
Methyl (1a)

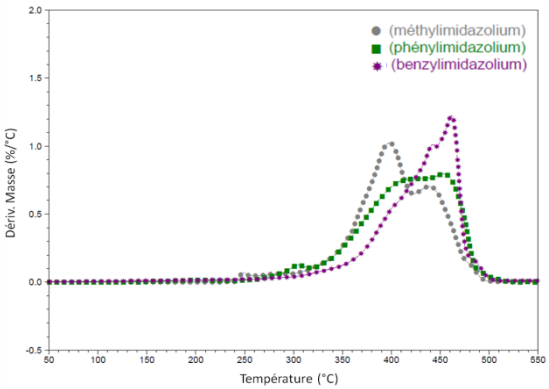


Phenyl

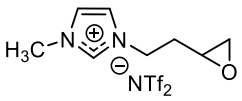


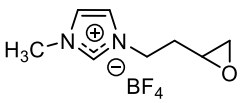
Benzyl

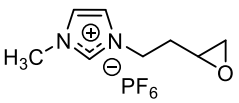


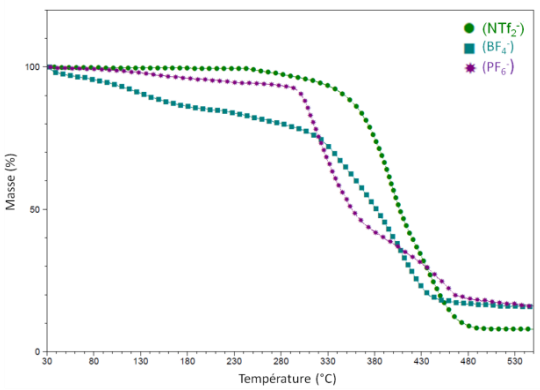


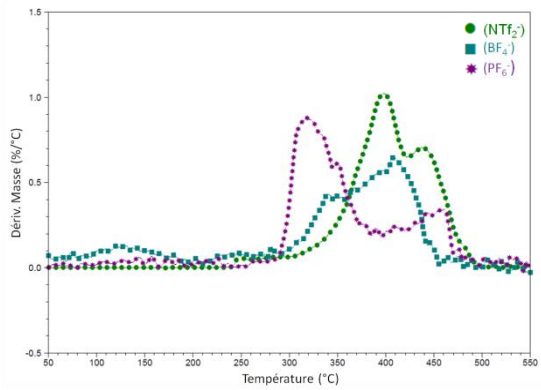
TGA of monoepoxide imidazolium type "Im-X" :



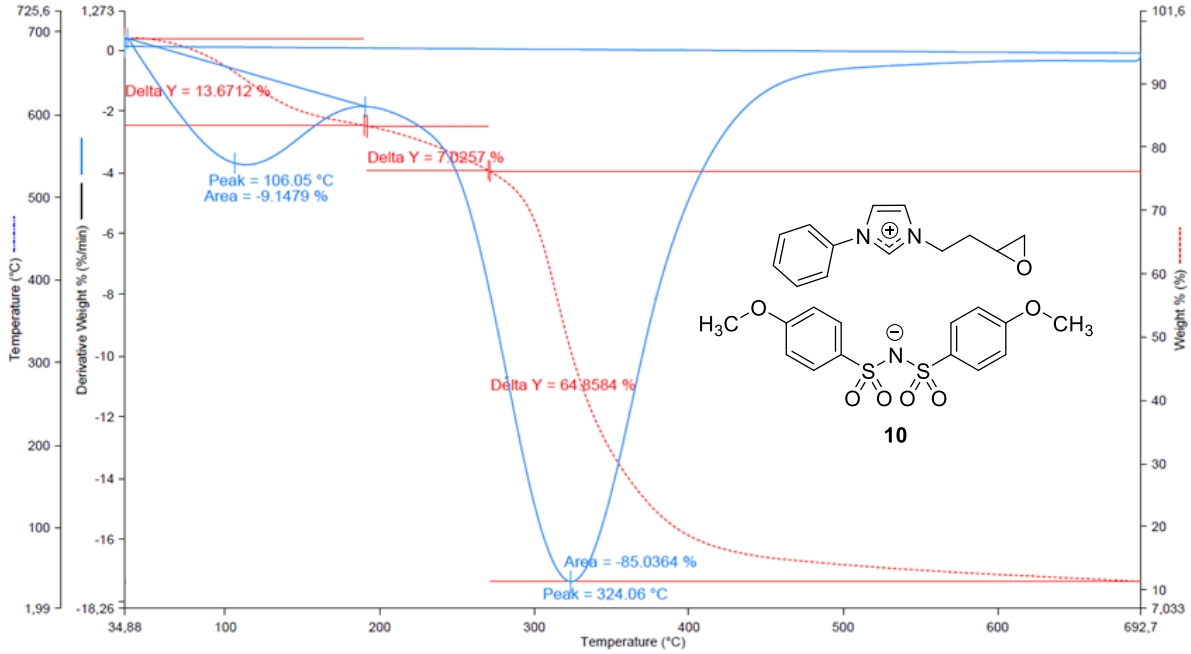




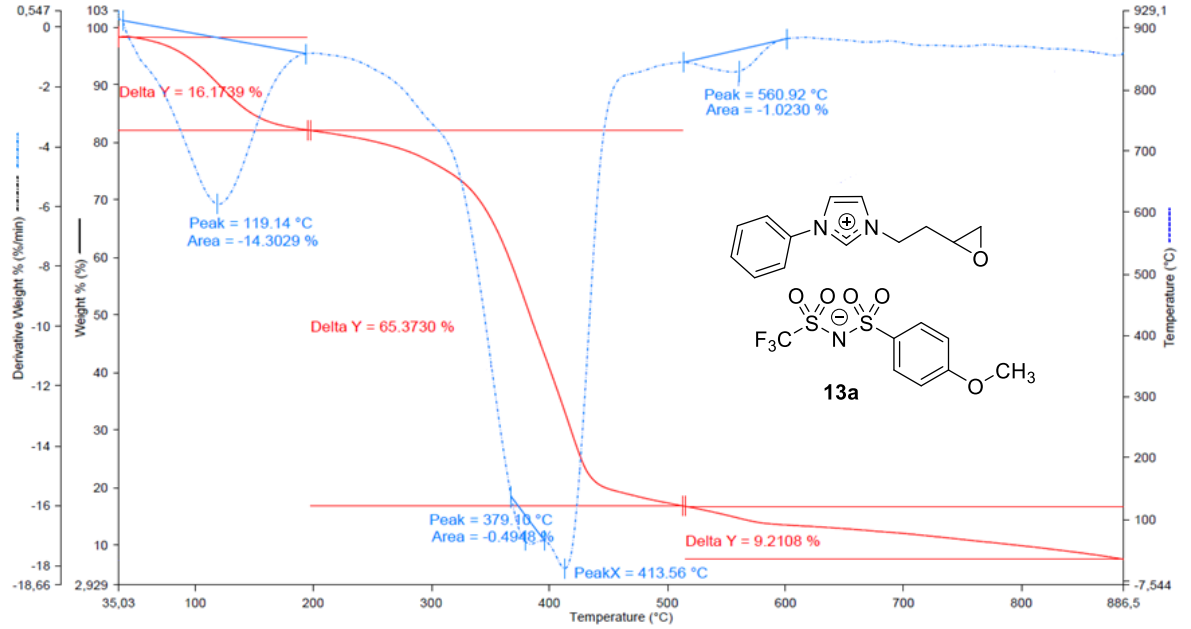




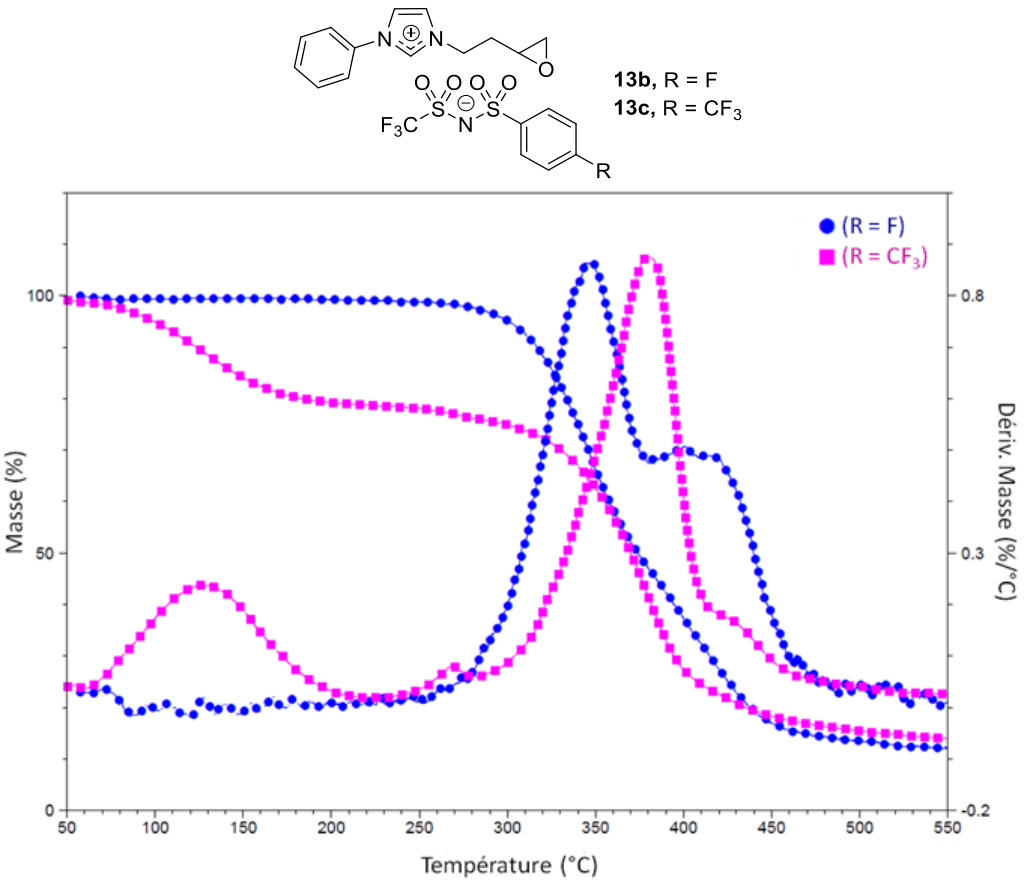
TGA of compound **10**



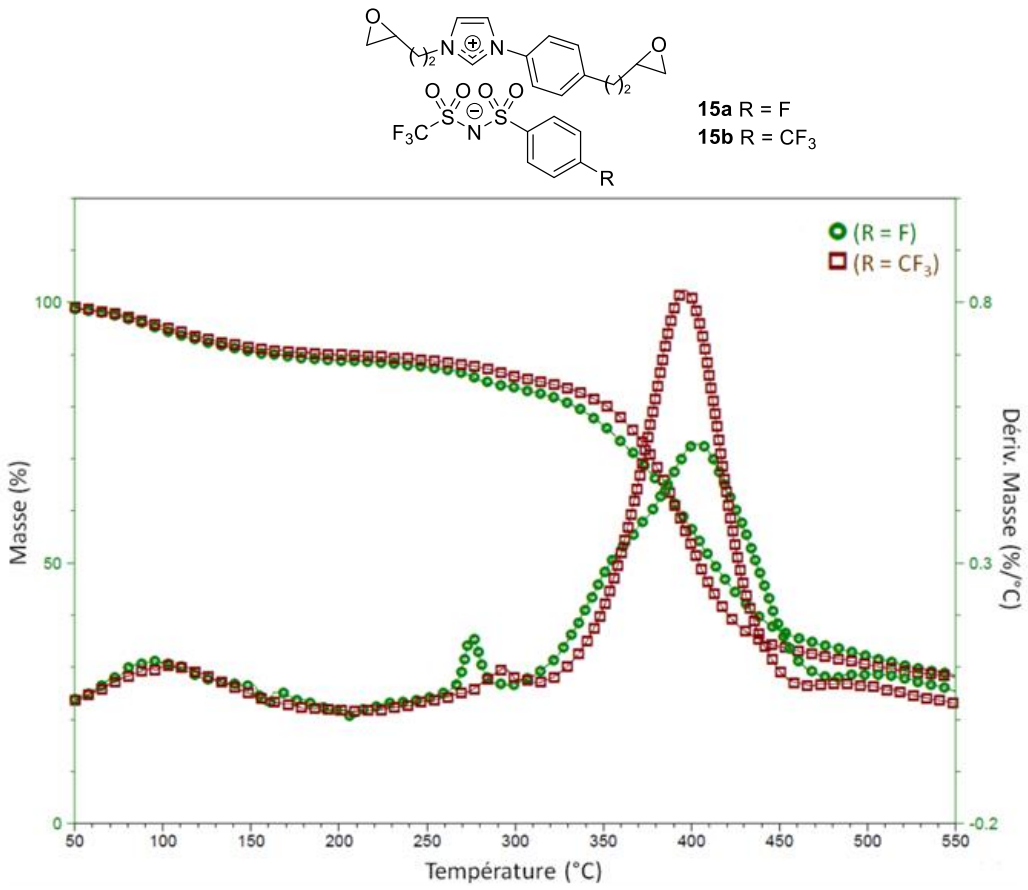
TGA of compound **13a**



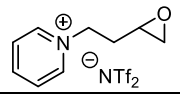
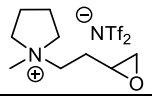
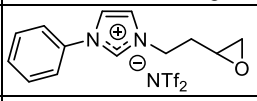
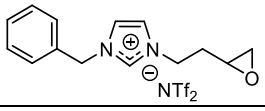
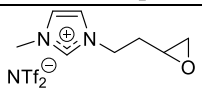
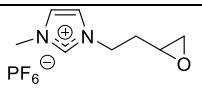
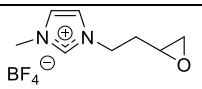
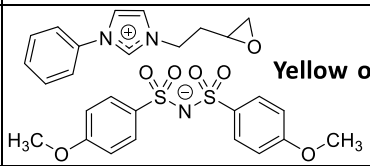
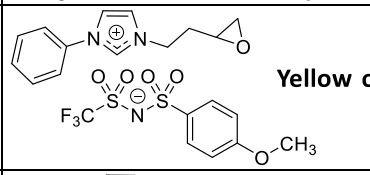
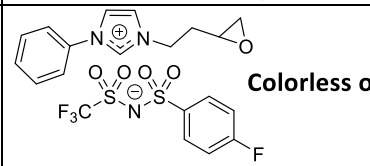
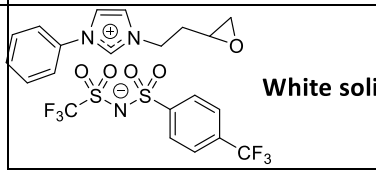
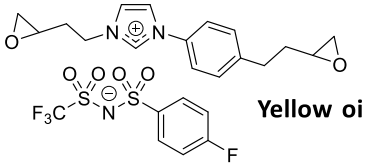
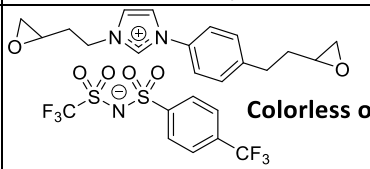
TGA of monoepoxide fluorinated salts **13b** and **13c**



TGA of diepoxide fluorinated salts **15a** and **15b**



Summary table :

Ionic liquid monomer	Structure / Appearance	Tonset weight loss (°C)	
		T5%	T10%
1-[2-(Oxiran-2-yl)ethyl]-pyridinium bis(trifluoromethanesulfonyl)imide	 Colorless oil	168	272
1-[2-(Oxiran-2-yl)ethyl]-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	 Brown oil	271	301
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium bis(trifluoromethanesulfonyl)imide	 Brown oil	310	346
3-[2-(Oxiran-2-yl)ethyl]-1-benzylimidazolium bis(trifluoromethanesulfonyl)imide	 Brown oil	322	365
3-[2-(Oxiran-2-yl)ethyl]-1-methylimidazolium bis(trifluoromethanesulfonyl)imide **(3a)**	 Yellow oil	316	348
3-[2-(Oxiran-2-yl)ethyl]-1-methylimidazolium hexafluorophosphate **(3b)**	 Yellow oil	219	302
3-[2-(Oxiran-2-yl)ethyl]-1-methylimidazolium tetrafluoroborate **(3c)**	 Yellow oil	89	136
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium bis(4-methoxybenzene)sulfonimide **(10)**	 Yellow oil	110	180
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-methoxybenzenesulfonyl)imide **(13a)**	 Yellow oil	115	135
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide **(13b)**	 Colorless oil	300	317
3-[2-(Oxiran-2-yl)ethyl]-1-phenylimidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide **(13c)**	 White solid	99	123
	Melting point/ Crystallization point (°C) **:** 79.8 °C		
3-[2-(Oxiran-2-yl)ethyl]-1-{4-[2-(oxiran-2-yl) ethyl]phenyl}imidazolium (trifluoromethylsulfonyl)(4-fluorobenzenesulfonyl)imide **(15a)**	 Yellow oil	97	165
3-[2-(Oxiran-2-yl)ethyl]-1-{4-[2-(oxiran-2-yl) ethyl]phenyl}imidazolium (trifluoromethylsulfonyl)(4-trifluoromethylbenzenesulfonyl)imide **(15b)**	 Colorless oil	104	199

VI. References

[1] D. F. Taber, P. W. DeMatteo and R. A. Hassan, *Org. Synth.*, 2013, **90**, 350.

[2] H. Mikula, D. Svatunek, D. Lumpi, F. Glöcklhofer, C. Hametner and J. Fröhlich, *Org. Process Res. Dev.*, 2013, **7**, 313.

[3] C. Chardin, J. Rouden, S. Livi and J. Baudoux, *Green Chem.***,** 2017, **19,** 5054.