Supplementary Information for

A remarkable chiral recognition of racemic mosher's acid salt by naturally derived chiral ionic liquids using ^{19}F NMR

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Contents

1. Supplementary Methods

1.1 General Information

Solvents and Reagents

All the solvents were concentrated under reduced pressure was performed by rotary evaporation at the appropriate pressure and temperature. All the air and moisture sensitive reactions were performed using dry solvents, which were dried according to the procedures prior to use. Deuterated solvents were purchased from Sigma-Aldrich chemical Co. (USA) and used as supplied. Reagents used were obtained from commercial suppliers or purified according to standard procedures.

Chromatography

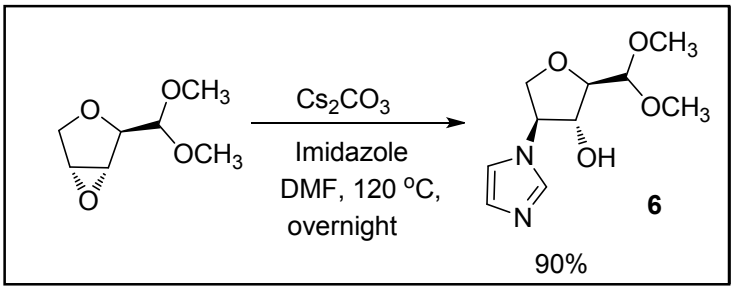
Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 plates and TLC plates were stained with Phosphomolybdic acid solution. Column chromatography was performed on silica gel (100 -200 µm) and Aluminum Oxide (neutral) using technical grade solvents that were used as supplied.

Instrumentation

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Bruker 400, 100, 376.5 MHz and 160 Hz respectively. Chemical shifts are quoted in parts per million (δ) relative to tetramethyl silane or $CHCl_3$ (residual chloroform in $CDCl_3$). For ^{19}F NMR, trifluorotoluene in $CDCl_3$ were used as internal standards. Optical rotations were measured using Rudolph Digi Pol 781 M6U NOVA automatic polarimeter. Mass spectra were recorded on a High Resolution Q-TOF Mass Spectrometer (Model: QSTAR XL, Applied Bio systems, USA).

1.2 Synthesis and characterization of compound 6

(2R, 3R, 4S)-2-(dimethoxymethyl)-4-(1H-imidazol-1-yl) tetrahydrofuran-3-ol (6)

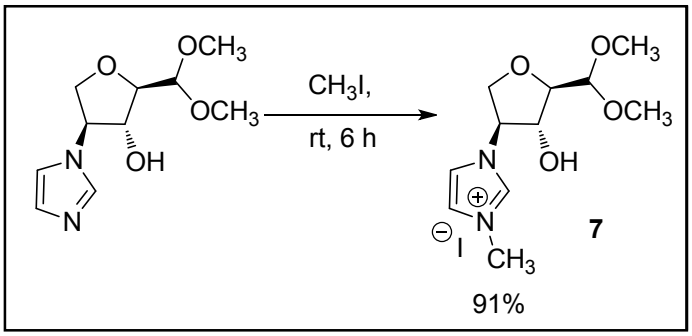


To a stirred solution of $CsCO_3$ (203 mg, 0.624 mmol) in dry DMF 3 mL, charged compound **5** (500 mg, 3.121 mmol) and imidazole 212 mg, 3.121 mmol) under nitrogen atmosphere. Heated the reaction mass at 120 ˚C overnight. After completion, removed the solvent by rotary evaporation under vacuum and the crude compound was purified using column chromatography (silica gel-100-200 mesh) eluted with 10% methanol/chloroform.

Yield: 90%, brown color liquid; **$[\alpha]_D^{25}$** = 47.2 (*c* 1, MeOH); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 24.4 Hz, 1H), 7.05 (s, 1H), 6.98 (d, *J* = 17.6 Hz, 1H), 4.66 (dq, *J* = 5.1, 2.6 Hz, 1H), 4.51 – 4.44 (m, 1H), 4.37 (ddd, *J* = 25.7, 5.2, 2.6 Hz, 1H), 4.25 – 4.07 (m, 2H), 4.03 – 3.86 (m, 1H), 3.55 – 3.44 (m, 7H);
HRMS (ESI) exact calculated mass for [M+1] ($C_{10}H_{17}O_4N_2$) requires *m/z* 229.1183, found *m/z* 229.1179

1.3 Synthesis and Characterization of CCIL 7

1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium iodide (7)



To a stirred solution of compound **6** (641 mg, 2.808 mmol) in dry acetonitrile (2 mL), charged methyl iodide (598 mg/ 0.26 mL, 4.212 mmol). Stirred the reaction mass at room temperature for 6 h. Upon completion of the reaction, removed the solvent by vacuum distillation. The crude compound was dissolved in 50% methanol/chloroform and passed through neutral alumina, afforded colorless liquid compound **7** in 91% yield.

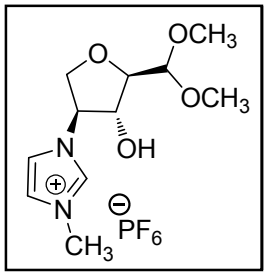
Yield: 90%, Light brown color liquid; **$[\alpha]_D^{25}$** = +88.8 (*c* 1, MeOH); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 7.72 (t, *J* = 2.0 Hz, 1H), 7.17 (t, *J* = 2.0 Hz, 1H), 5.41 (d, *J* = 4.8 Hz, 1H), 4.61 (d, *J* = 4.8 Hz, 1H), 4.51 (d, *J* = 3.6 Hz, 1H), 4.30 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.20 (d, *J* = 11.2 Hz, 1H), 4.00 (s, 3H), 3.98 (dd, *J* = 4.8, 3.2 Hz, 1H), 3.46 (s, 3H), 3.44 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.50, 122.69, 121.37, 103.66, 85.67, 78.69, 70.92, 68.34, 55.99, 55.55, 36.91; **HRMS** (ESI) exact calculated mass for [M+] ($C_{11}H_{19}O_4N_2$)requires *m/z* 243.1339, found *m/z* 243.1336; LR-MS (ESI) ES^+: 243.2, ES^-: 126.9.

1.4 General procedure for the synthesis and Characterization of CCILs 8 to 11

To a stirred solution of CCIL **7** (0.270 mmol) in water (2 mL), charged LiX (0.324 mmol) and continued the reaction for 24 h at room temperature. Reaction mixture was cconcentrated under reduced pressure by rotary evaporation and the crude compounds were dissolved in

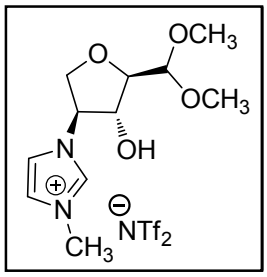
$CHCl_3$washed with cold water (for CCILs**8** and **11**). For CCILs **9** and **10** the crude compounds were rinsed with $CHCL_3$ (3 x 5 mL)[CCILs **9** and **10** were in soluble in $CHCl_3$].

1.4.1 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium hexafluorophosphate (V) (8).



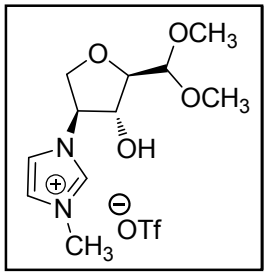
Yield: 72%, Light brown color liquid; $[\alpha]_D^{25}$ = +20.6 (*c* 1, MeOH);**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.56 (s, 1H), 7.72 (t, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 2.0 Hz, 1H), 5.31 (d, *J* = 5.2 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 4.52 (d, *J* = 3.6 Hz, 1H), 4.29 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.22 (dd, *J* = 10.8, 1.6 Hz, 1H), 4.01 (s, 3H), 3.95 (t, *J* = 4.0 Hz, 1H), 3.46 (s, 3H), 3.44 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.85, 123.04, 121.59, 103.64, 85.53, 78.12, 71.04, 68.11, 56.24, 55.71, 37.10; **^{19}F NMR** (376.5 MHz, Chloroform-*d*) δ -66.71, -68.59; **HRMS** (ESI) exact calculated mass for [M+] ($C_{11}H_{19}O_4N_2$)requires *m/z* 243.13393, found *m/z* 243.13390

1.4.2 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium bis ((trifluoromethyl) sulfonyl) amide (9).



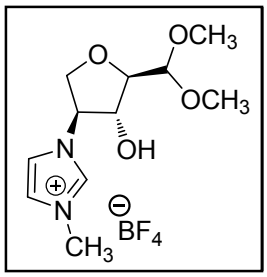
Yield: 82%, Light brown color liquid; $[\alpha]_D^{25}$ = +56.8 (*c*0.9, MeOH);**^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.68 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 4.78 (s, 1H), 4.52 (d, *J* = 3.6 Hz, 1H), 4.43 – 4.38 (m, 1H), 4.32 – 4.22 (m, 2H), 3.95 (s, 3H), 3.87 (t, *J* = 4.0 Hz, 1H), 3.46 (s, 3H), 3.45 (s, 3H); **^{13}C NMR** (100 MHz, Methanol-d_4) δ 125.02, 123.34, 122.60, 120.18, 105.29, 87.34, 78.86, 71.42, 69.26, 56.65, 55.84, 36.60; **^{19}F NMR** (376.5 MHz, Methanol-*d4*) δ -80.73; **HRMS** (ESI) exact calculated mass for [M+] ($C_{11}H_{19}O_4N_2$)requires *m/z* 243.1339, found *m/z* 243.1335; LR-MS (ESI) ES^+: 243.2, ES^-: 279.9.

1.4.3 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium trifluoromethanesulfonate (10).



Yield: 76%, Light brown color liquid; $[\alpha]_D^{25}$ = +33.0 (*c*1, MeOH);**^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.99 (s, 1H), 7.69 (t, *J* = 1.6 Hz, 1H), 7.62 (t, *J* = 1.6 Hz, 1H), 4.79 (s, 1H), 4.53 (d, *J* = 3.6 Hz, 1H), 4.44 – 4.40 (m, 1H), 4.28 (t, *J* = 4.5 Hz, 2H), 3.96 (s, 3H), 3.88 (t, *J* = 4.0 Hz, 1H), 3.47 (d, *J* = 1.6 Hz, 3H), 3.45 (d, *J* = 1.6 Hz, 3H); **^{13}C NMR** (100 MHz, Methanol-d_4) δ 125.04, 122.79, 122.61, 119.61, 105.31, 87.37, 78.86, 71.42, 69.27, 56.66, 55.86, 36.64; **^{19}F NMR** (376.5 MHz, Methanol-d_4) δ -80.14; **HRMS** (ESI) exact calculated mass for [M+] ($C_{11}H_{19}O_4N_2$)requires *m/z* 243.1339, found *m/z* 243.1340.

1.4.4 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium tetrafluoroborate (11).



Yield: 62%, Light brown color liquid; $[\alpha]_D^{25}$ = +18.2 (*c*1, MeOH);**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.71 (s, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.18 (t, *J* = 1.6 Hz, 1H), 5.36 (d, *J* = 5.2 Hz, 1H), 4.61 (d, *J* = 4.8 Hz, 1H), 4.52 (d, *J* = 3.2 Hz, 1H), 4.30 (dd, *J* = 10.8, 4.8 Hz, 1H), 4.20 (d, *J* = 11.2 Hz, 1H), 4.00 (s, 3H), 3.97 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.46 (s, 3H), 3.44 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.99, 122.90, 121.63, 103.63, 85.55, 78.18, 71.03, 68.17, 56.18, 55.69, 37.05; **^{19}F NMR** (376.5 MHz, Chloroform-*d*) δ -151.06 (d, *J* = 19.2 Hz); **HRMS** (ESI) exact calculated mass for [M+] ($C_{11}H_{19}O_4N_2$)requires *m/z* 243.1339, found *m/z* 243.1340; LR-MS (ESI) ES^+: 243.2, ES^-: 87.1.

1.5 Procedure for ^{19}F NMR Experiment for Chiral Recognition studies of CCILs

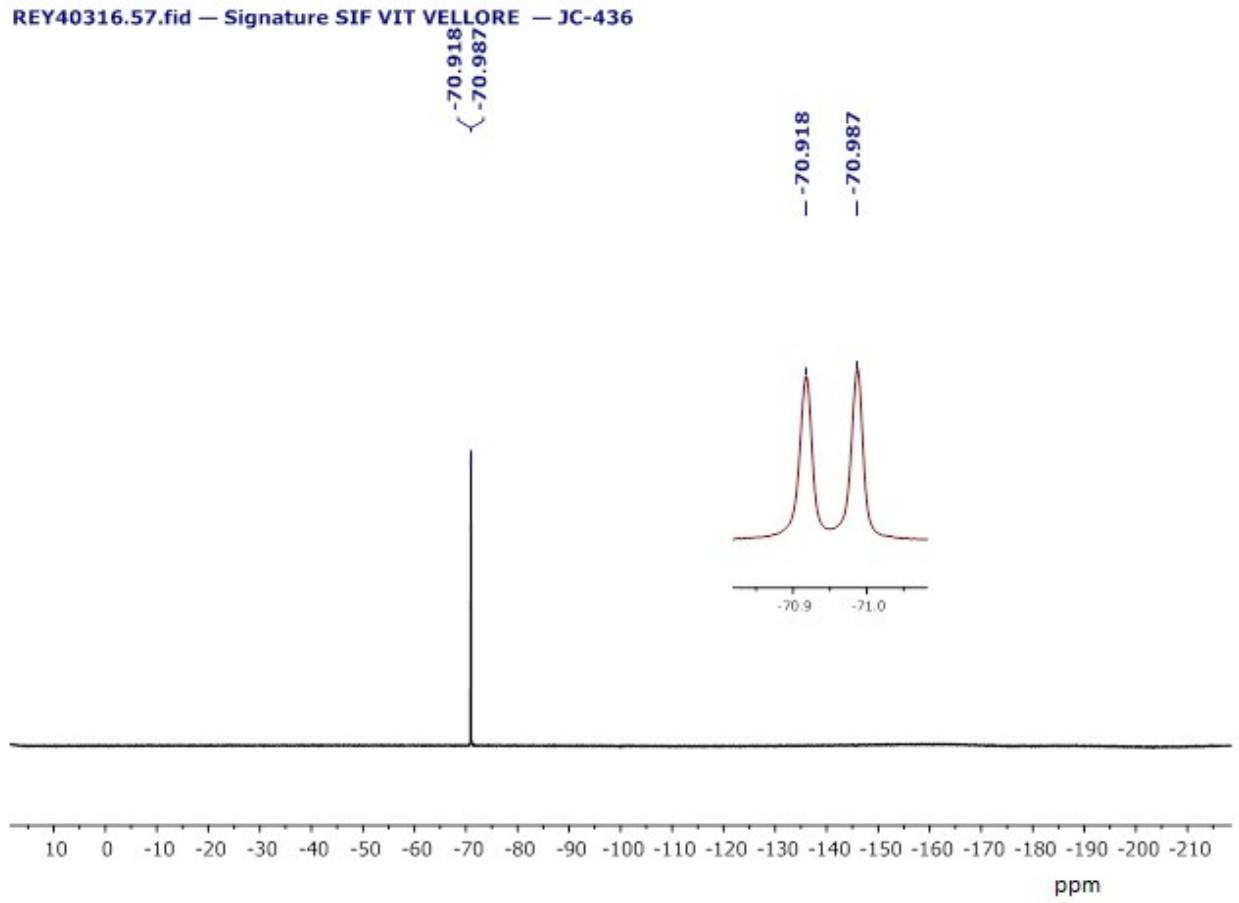
The racemic Mosher's acid silver salt (4.6 mg, 0.013 mmol) was mixed with CCIL **7** (10 mg, 0.027 mmol) in 0.6 mL of CD_3CN and stirred for 10 min at room temperature to exchange anions. The AgI precipitate thus formed was filtered and filtrate was analyzed by ^{19}F NMR (376.5 MHz). For CCILs **8**-**11,** the racemic salt (1 equiv.) was mixed with each CIL (10 mg, 2equiv.) separately in dry ACN and stirred for 10 min. Filtered the formed salts and concentrated the filtrate under

reduced pressure using rotary evaporator. The residual compound was dissolved in $CDCl_3$, analyzed by ^{19}F NMR.

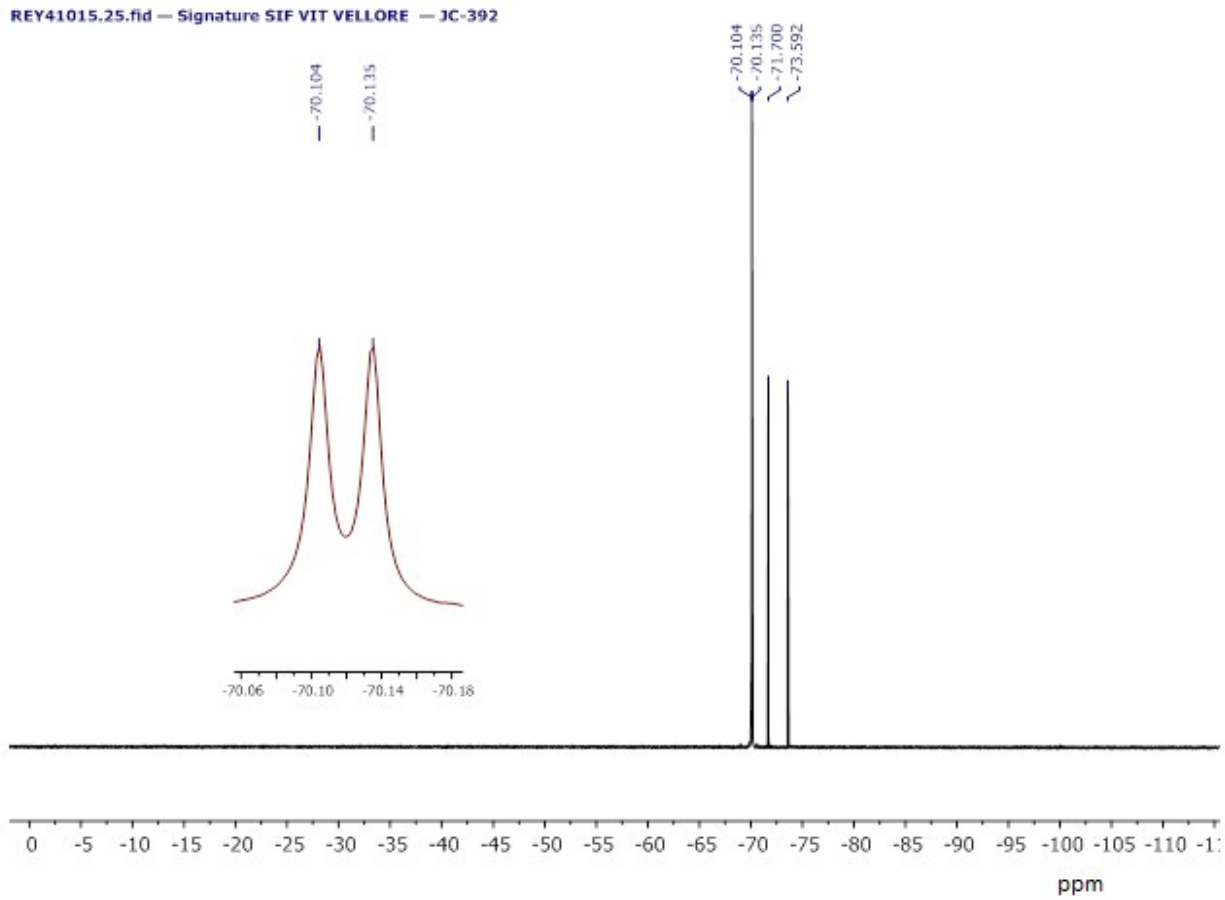
Effect of CCIL 7 concentration: In another set of experiment, each time different concentrations of CCIL **7** (1 eq, 4 eq, and 6 eq) was mixed with racemic salt and studied the effect of concentration of CCIL **7** for chiral discrimination by ^{19}F NMR.

2. Supplementary Data

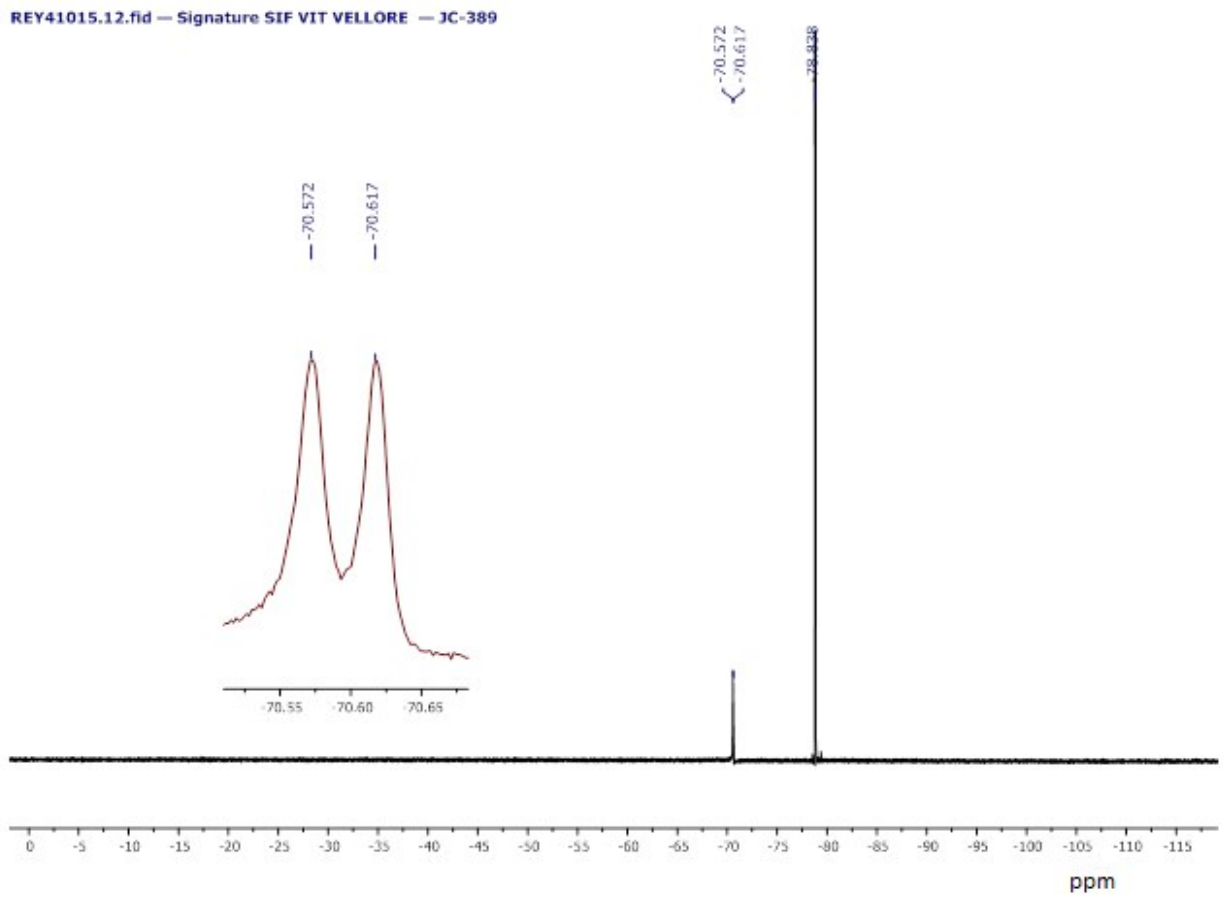
2.1 Copies of ^{19}F NMR Spectra for Chiral Recognition Experiments.



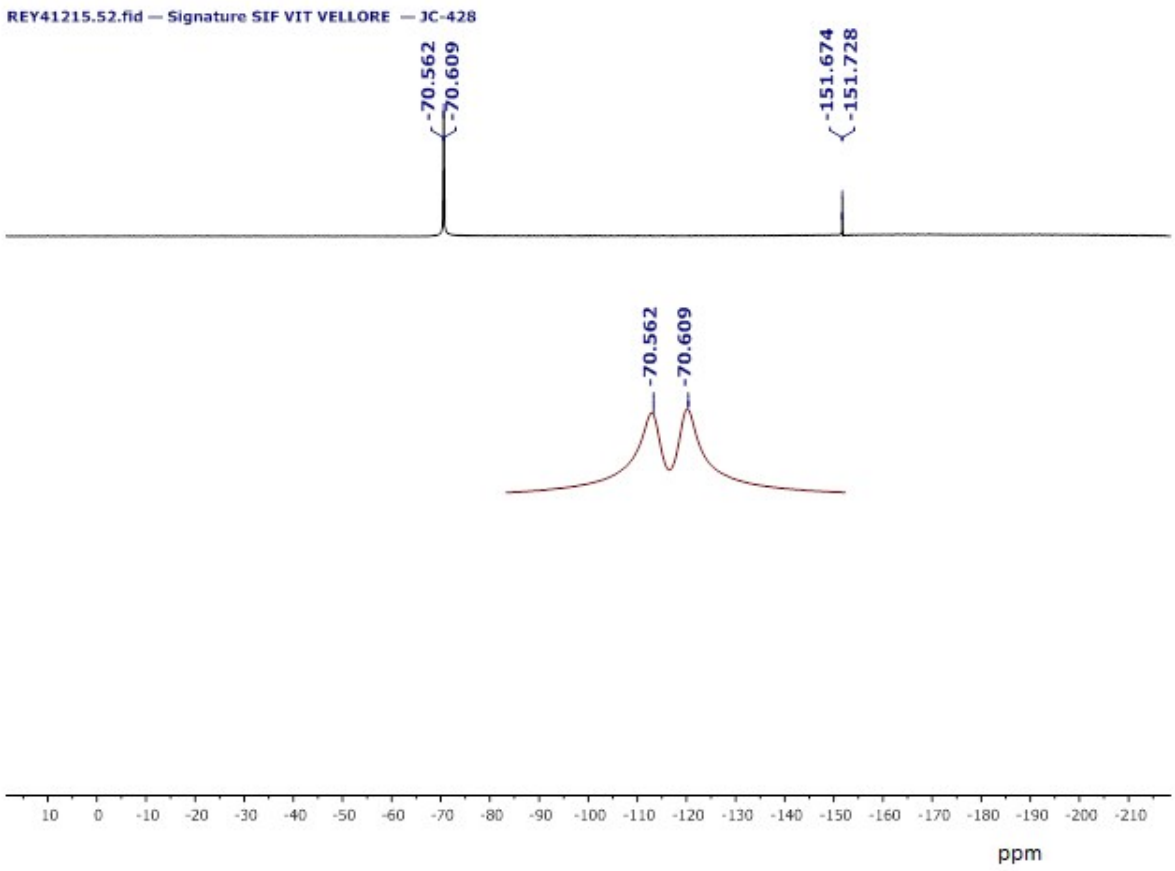
^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 7 (2 equiv.) and Mosher's acid salt.



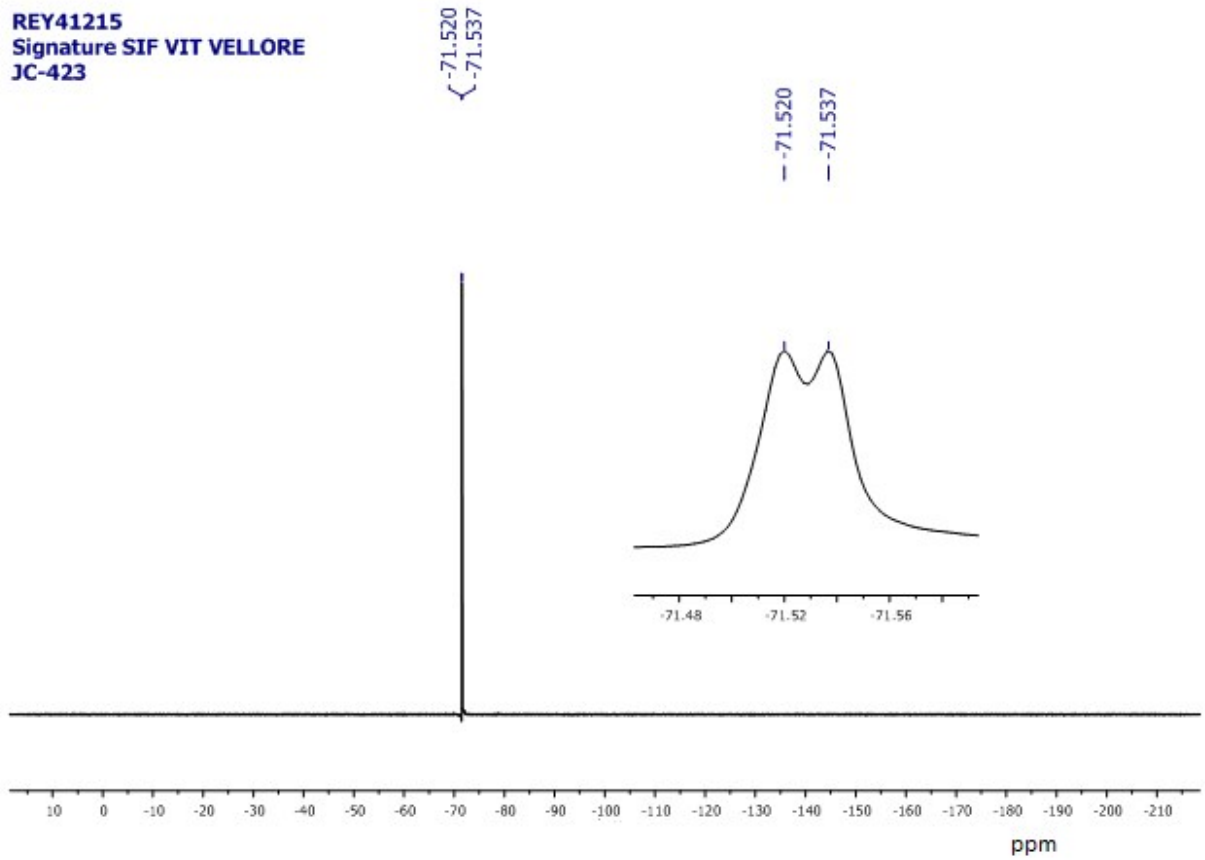
^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 8 (2 equiv.) and Mosher's acid salt.



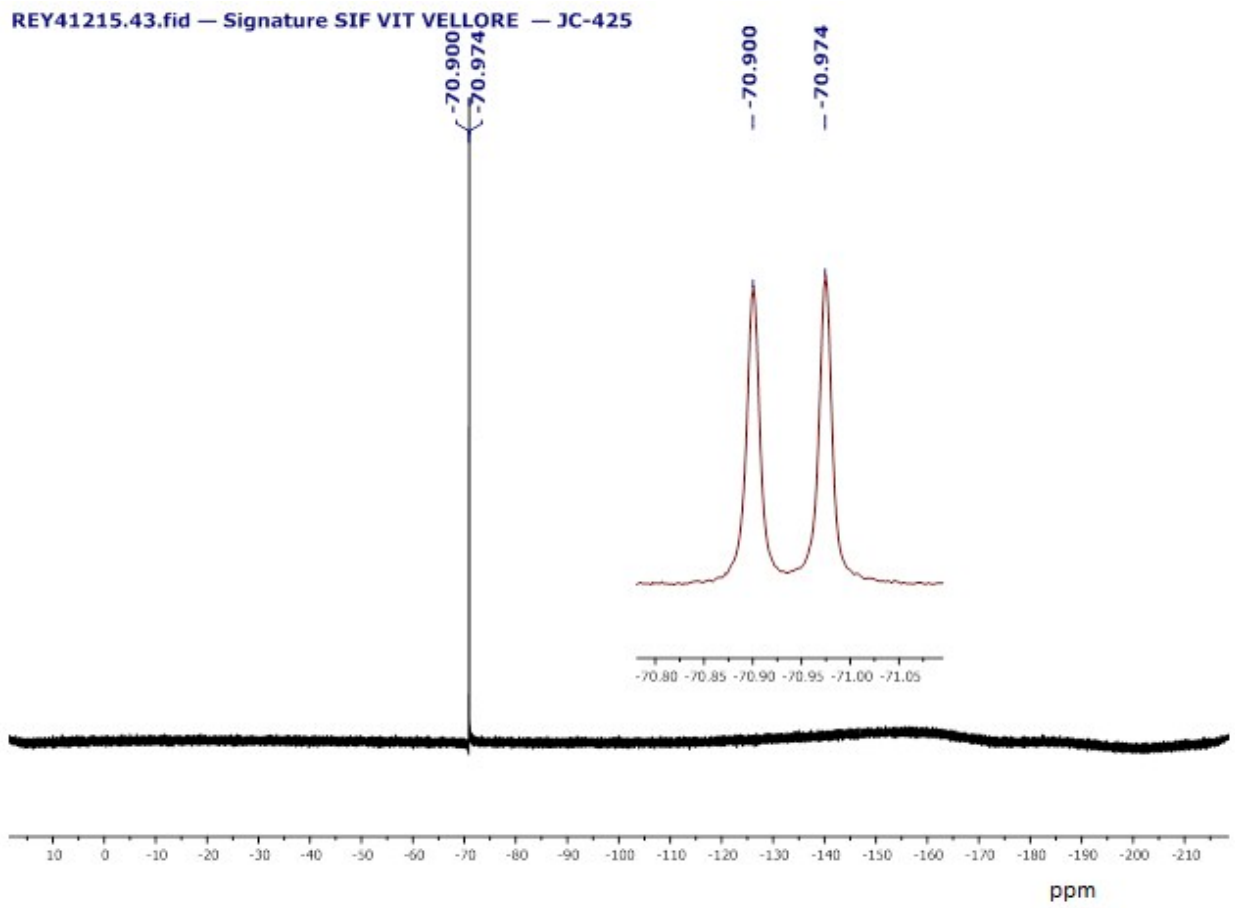
^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 9 (2 equiv.) and Mosher's acid salt.



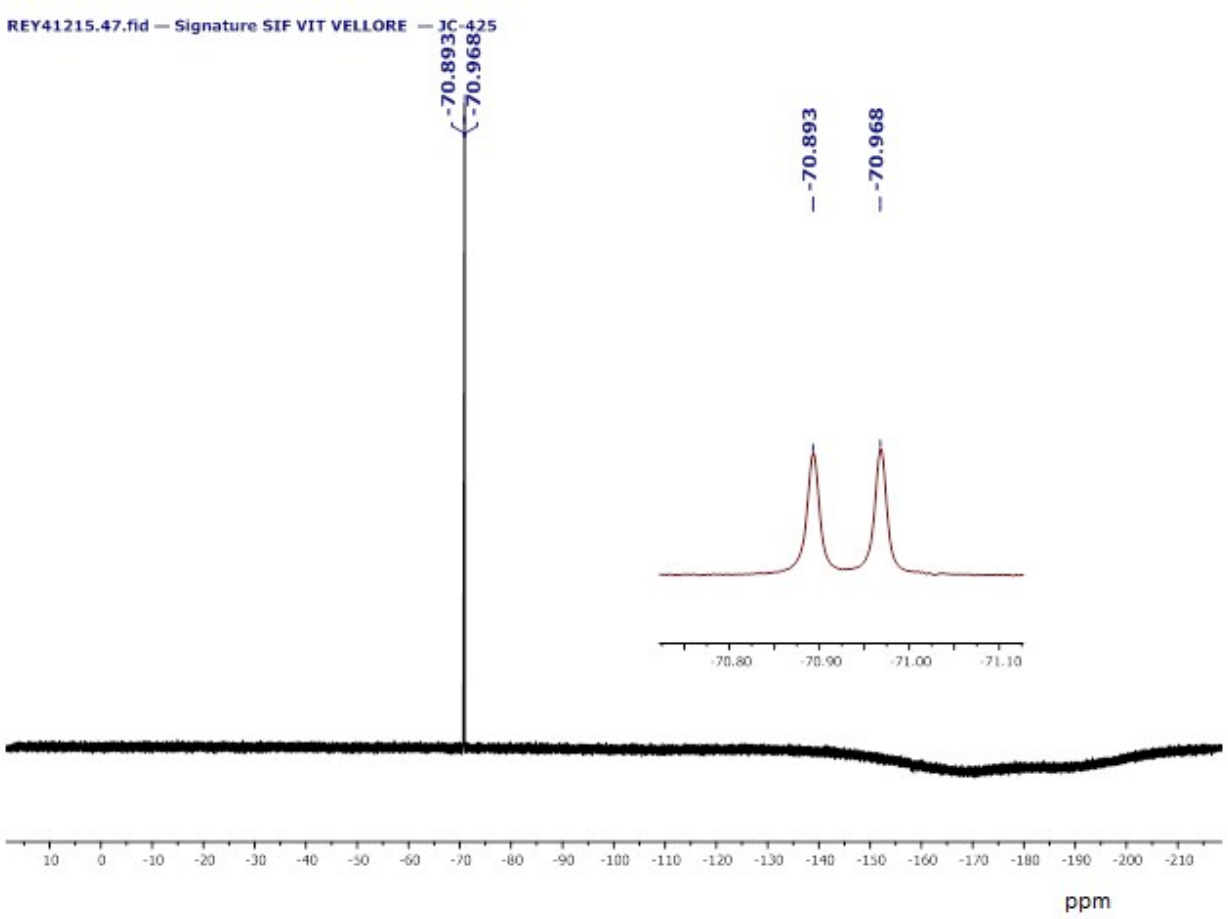
^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 11 (2 equiv.) and Mosher's acid salt.



^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 7 (1 equiv.) and Mosher's acid salt.

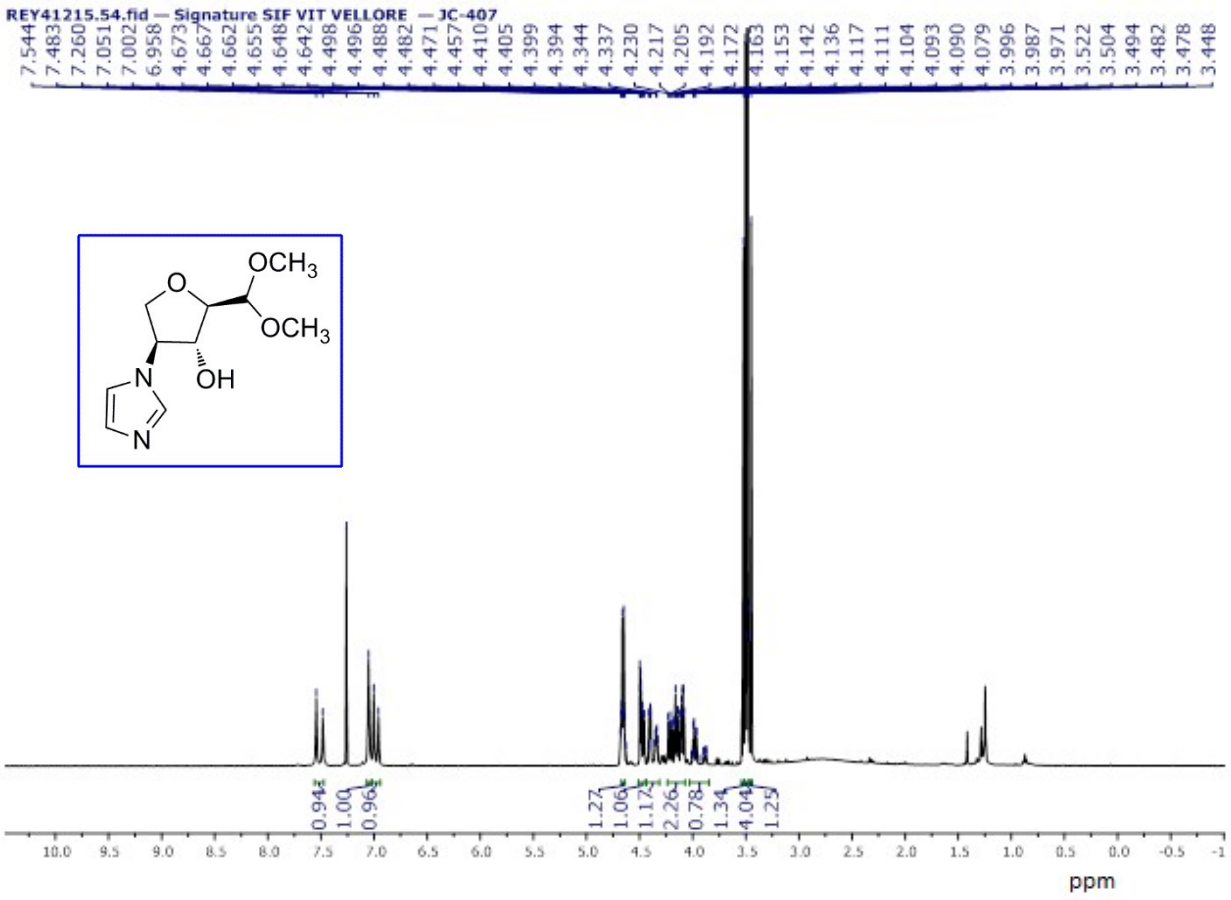


^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 7 (4 equiv.) and Mosher's acid salt.

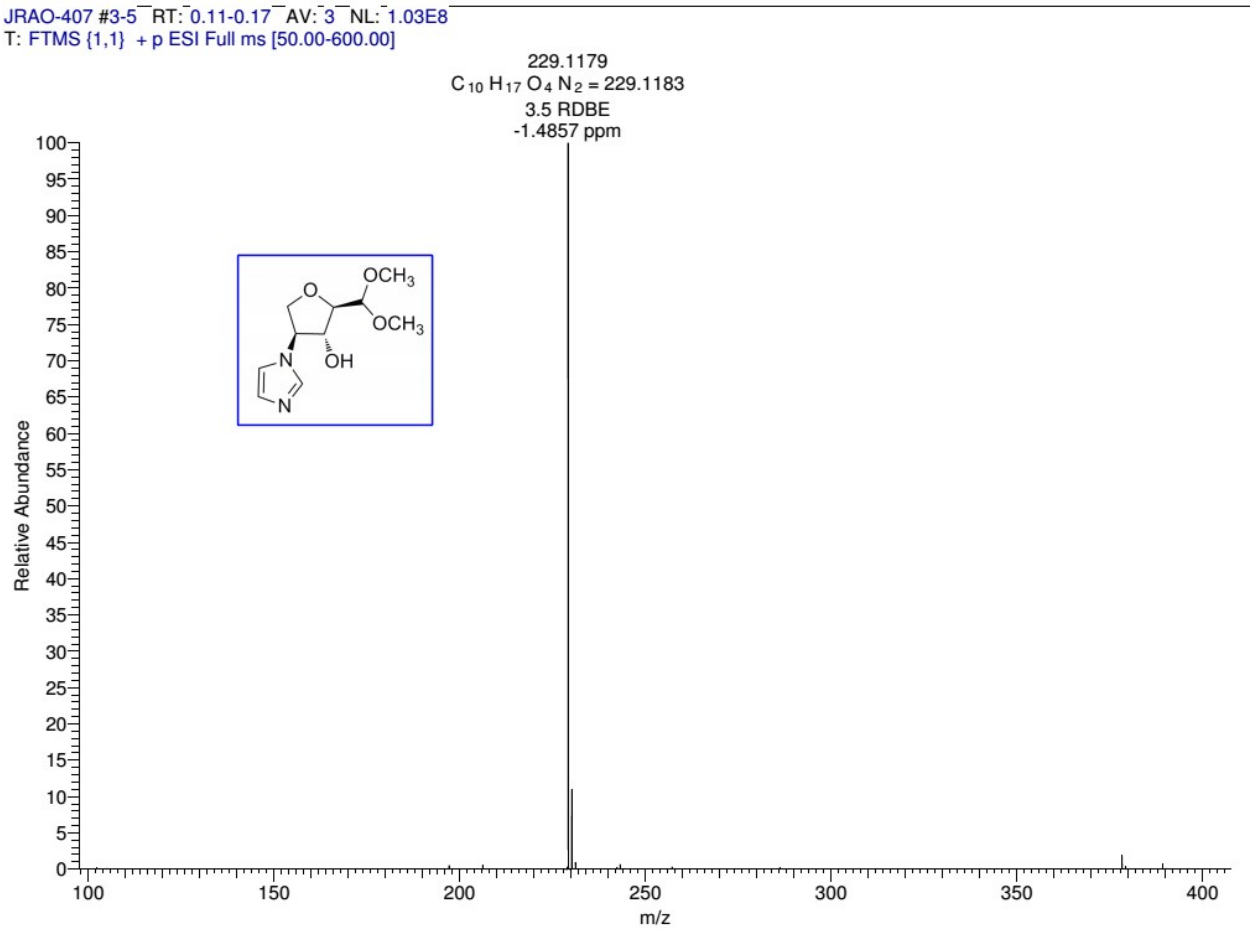


^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 7 (6 equiv.) and Mosher's acid salt.

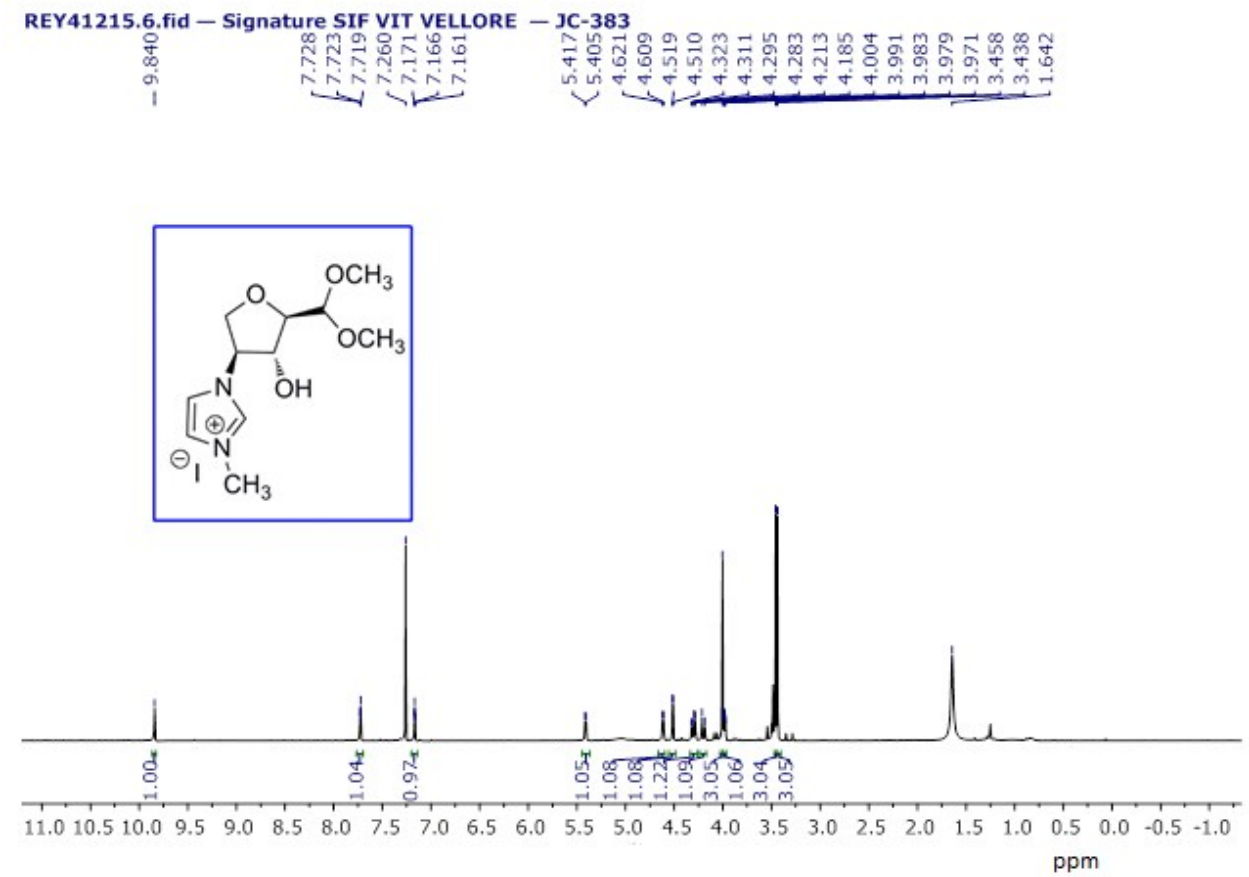
2.2 Copies of NMR, ESI and HR-MS Spectra



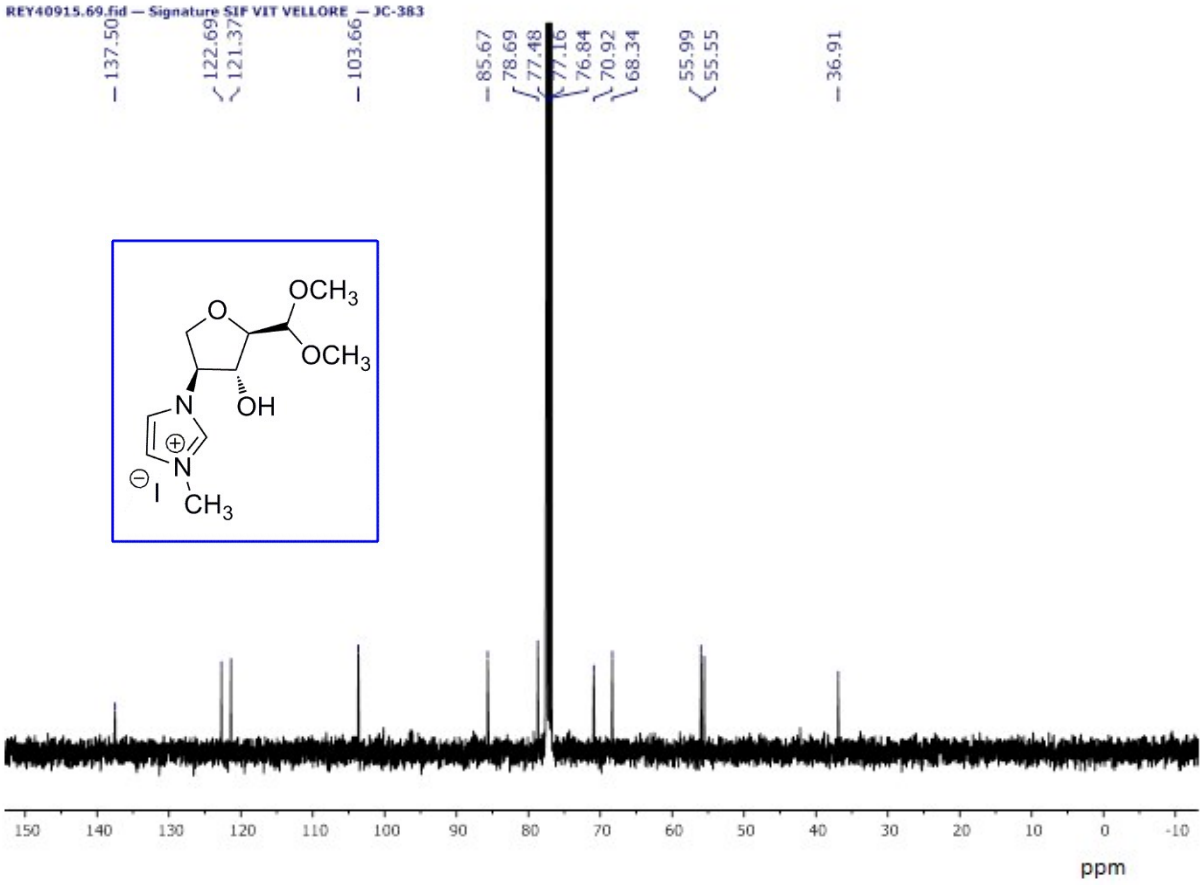
^{1}H NMR Spectrum of (2R, 3R, 4S)-2-(dimethoxymethyl)-4-(1H-imidazol-1-yl) tetrahydrofuran-3-ol (6).



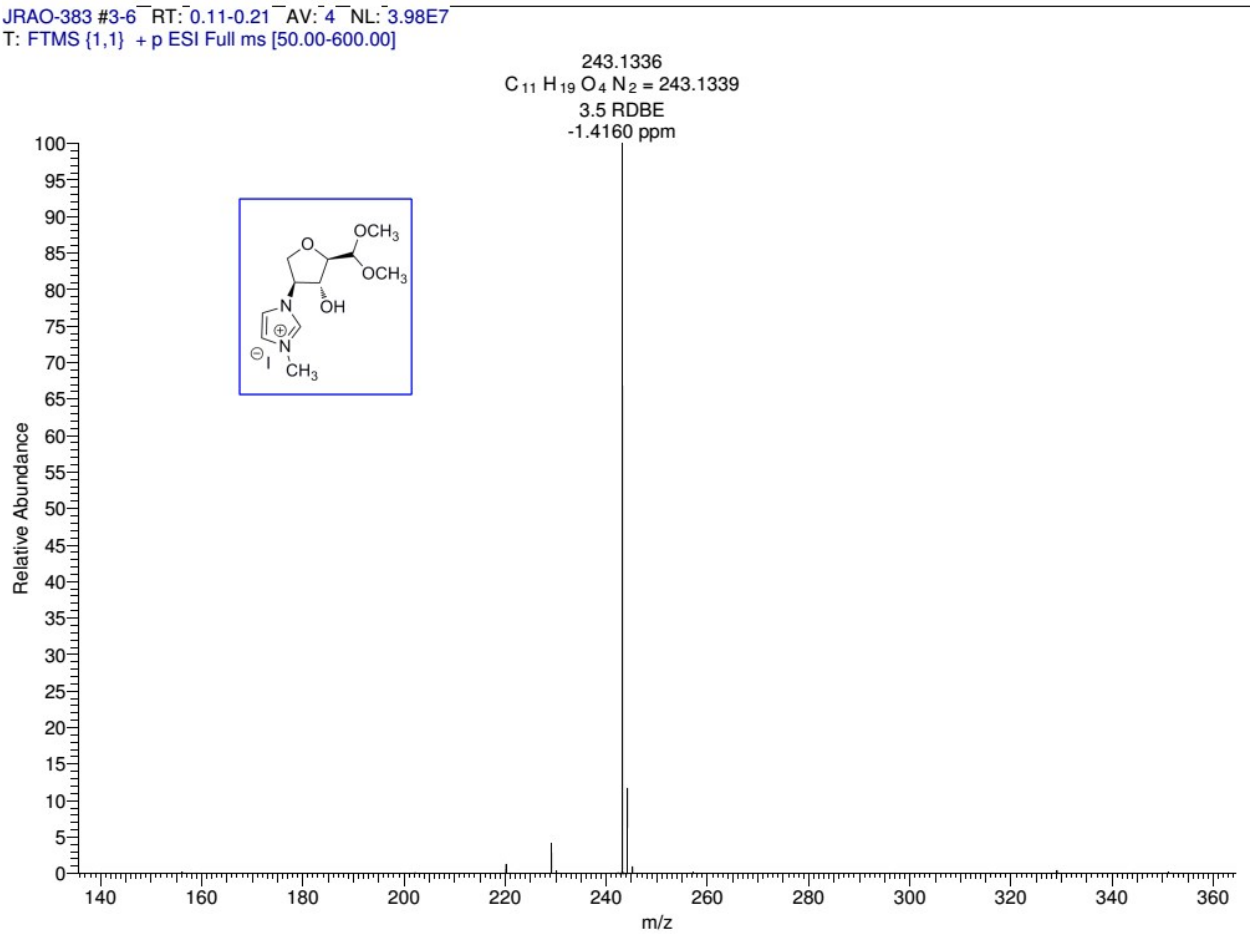
HR-MS Spectrum of (2R, 3R, 4S)-2-(dimethoxymethyl)-4-(1H-imidazol-1-yl) tetrahydrofuran-3-ol (6).



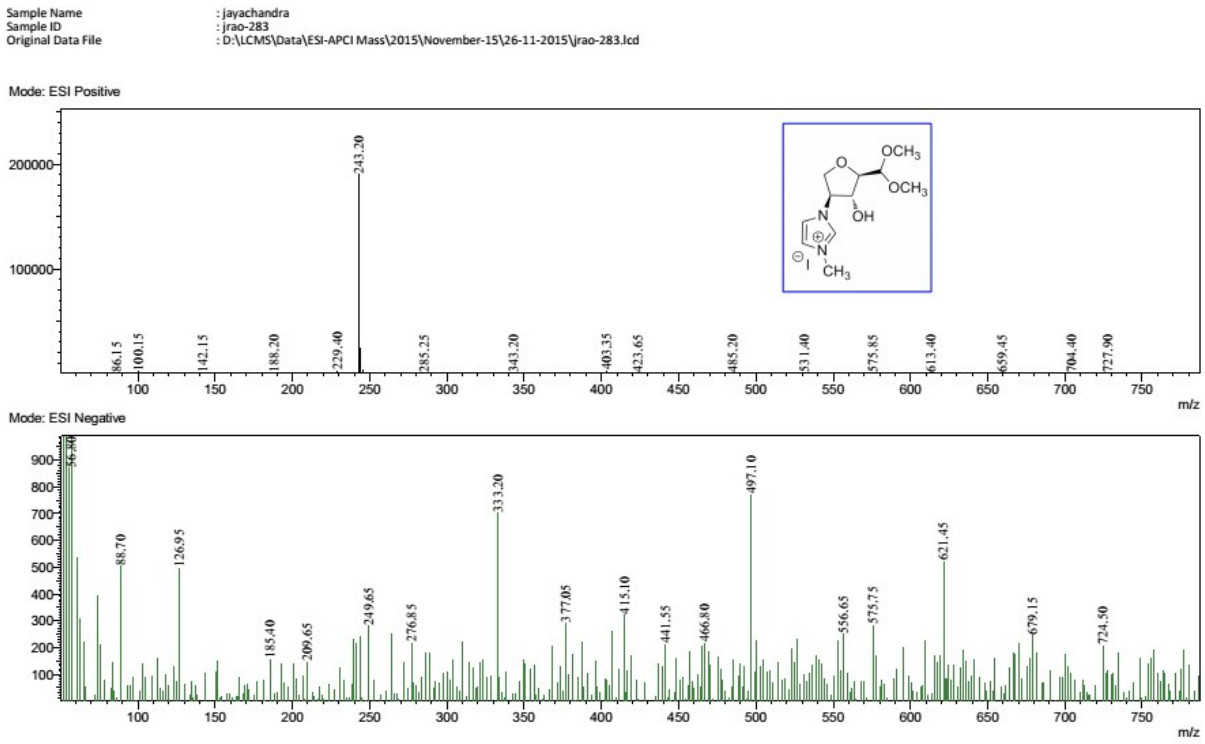
^{1}H NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium iodide (7).



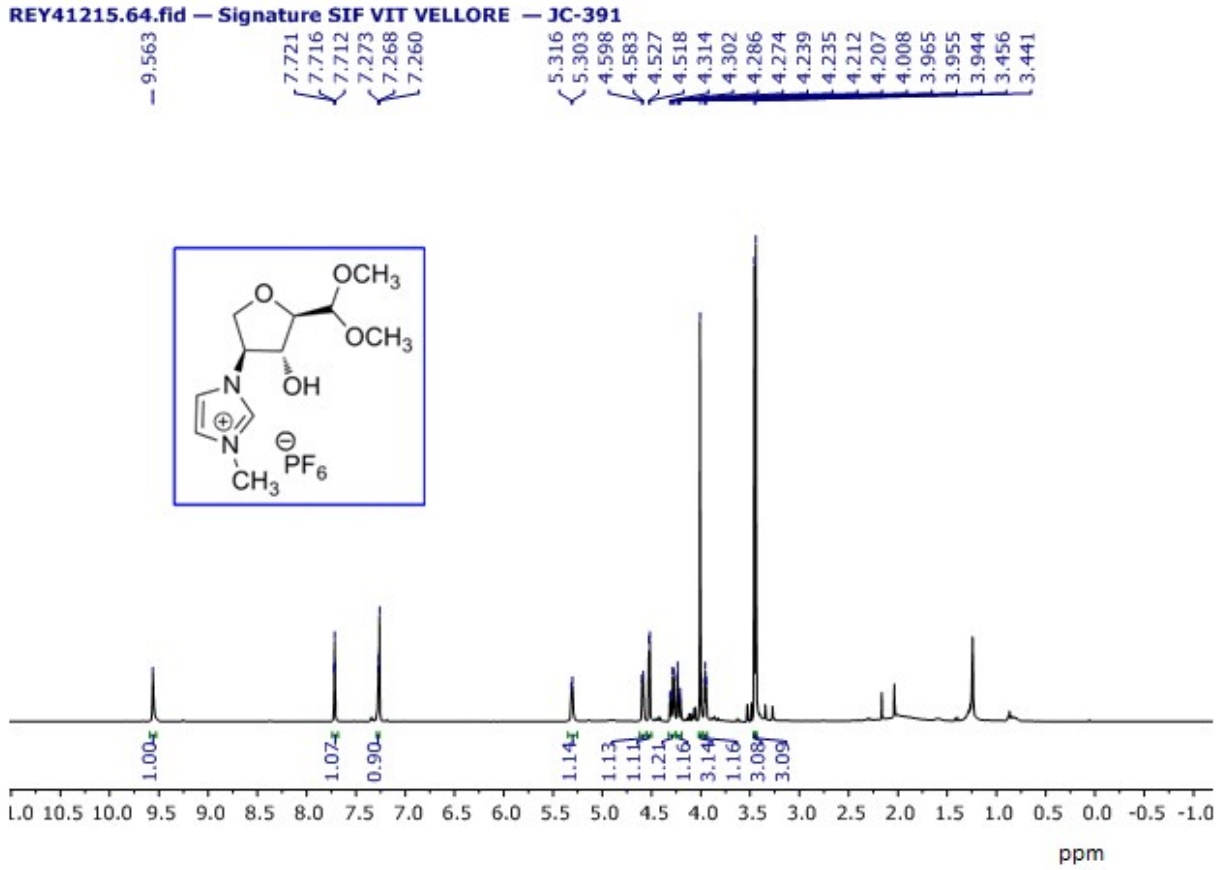
^{13}C NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium iodide (7).



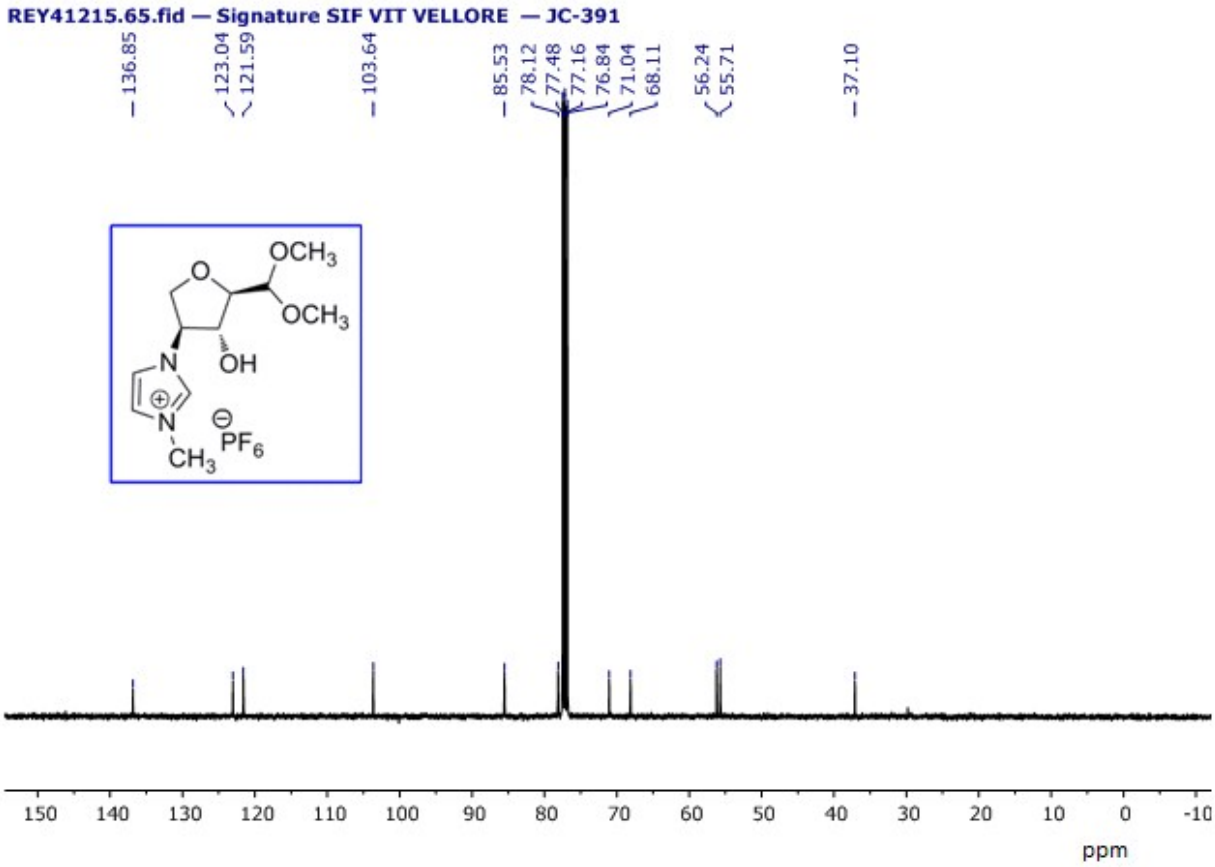
HR-MS Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium iodide (7)



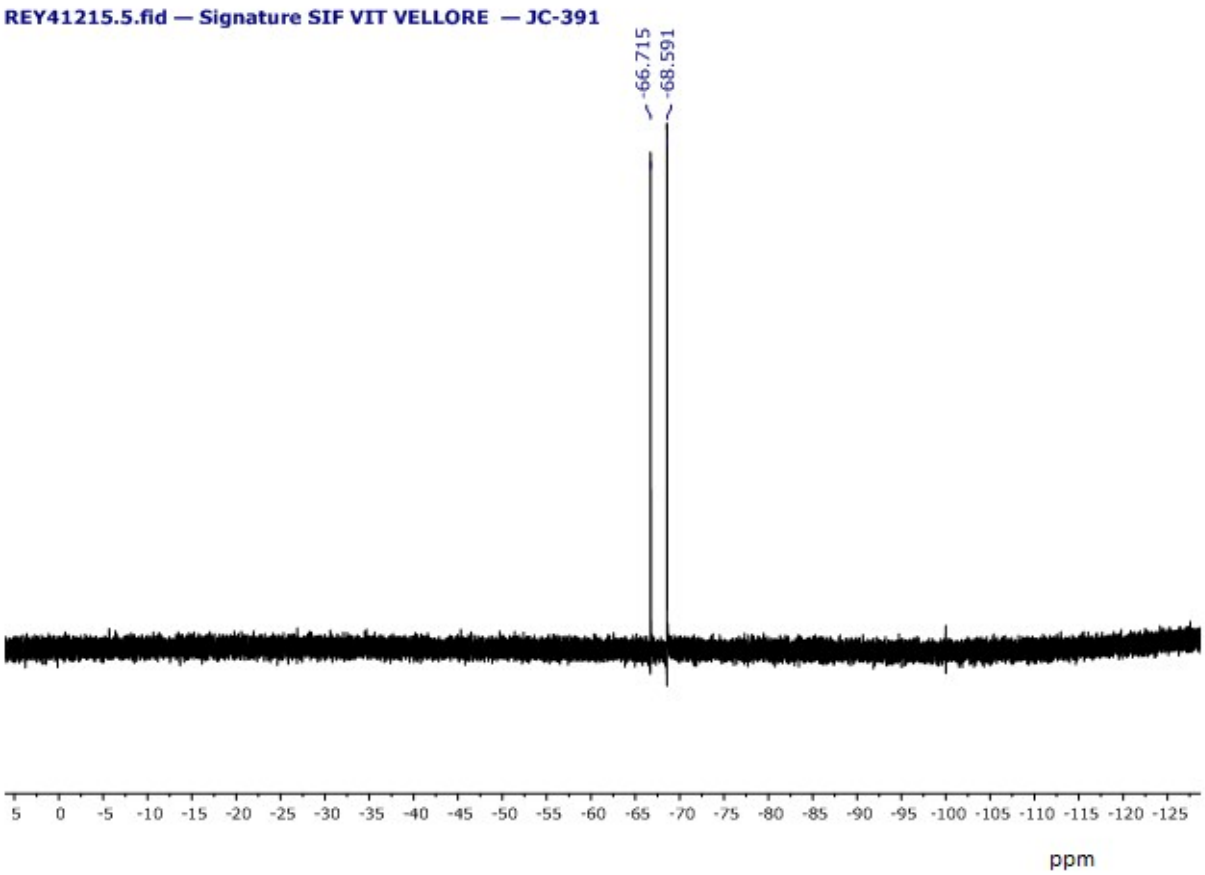
LR-MS (ESI) Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium iodide (7) (Positive and negative modes).



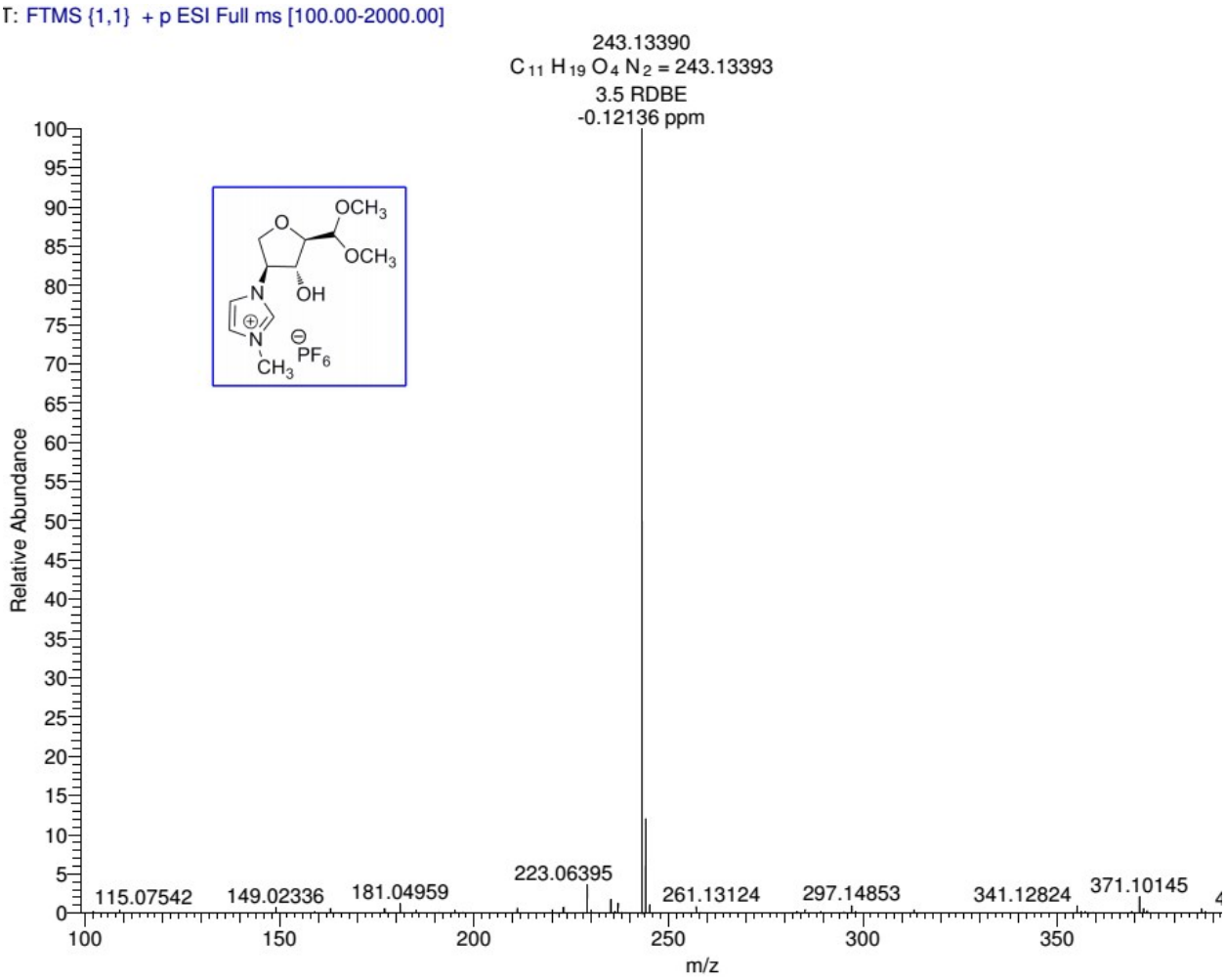
^{1}H NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium hexafluorophosphate (V) (8).



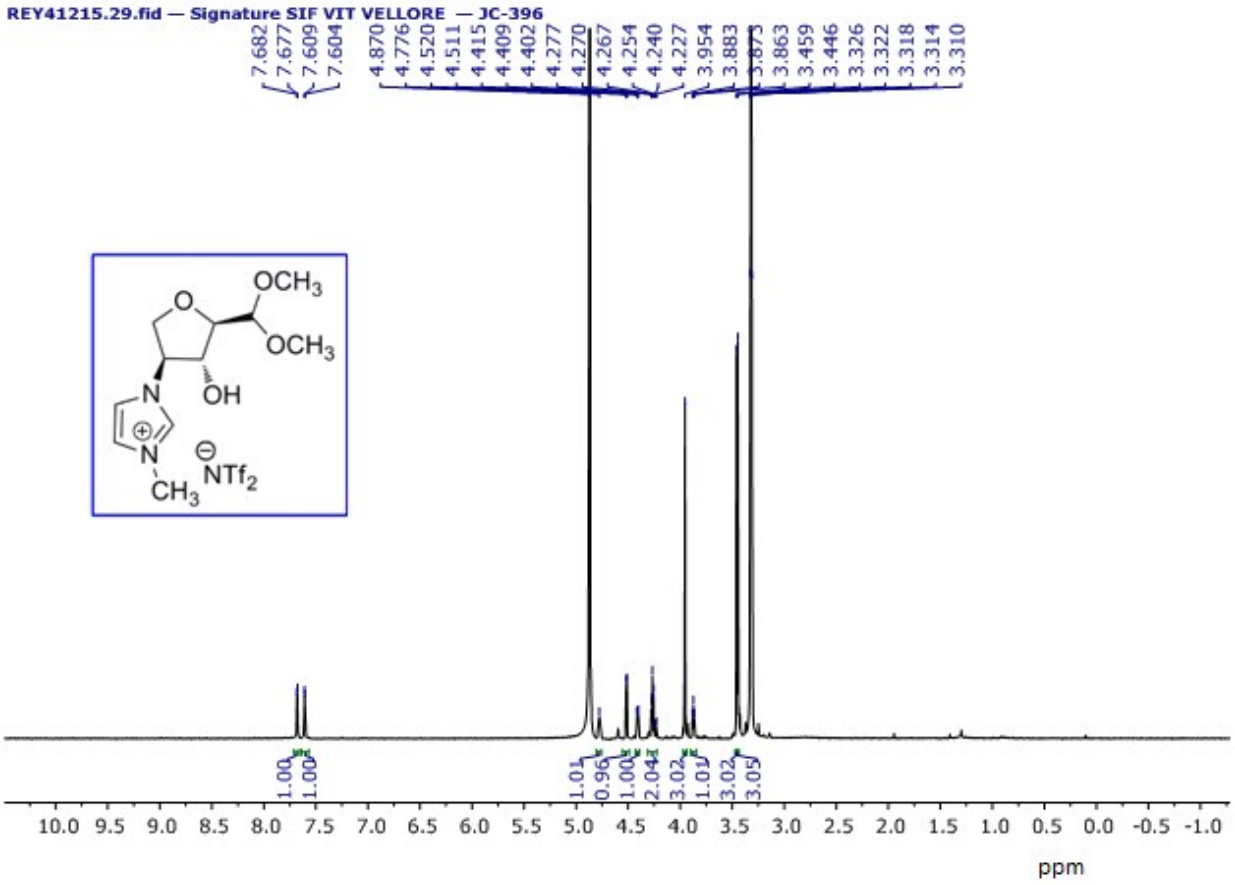
^{13}C NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium hexafluorophosphate (V) (8).



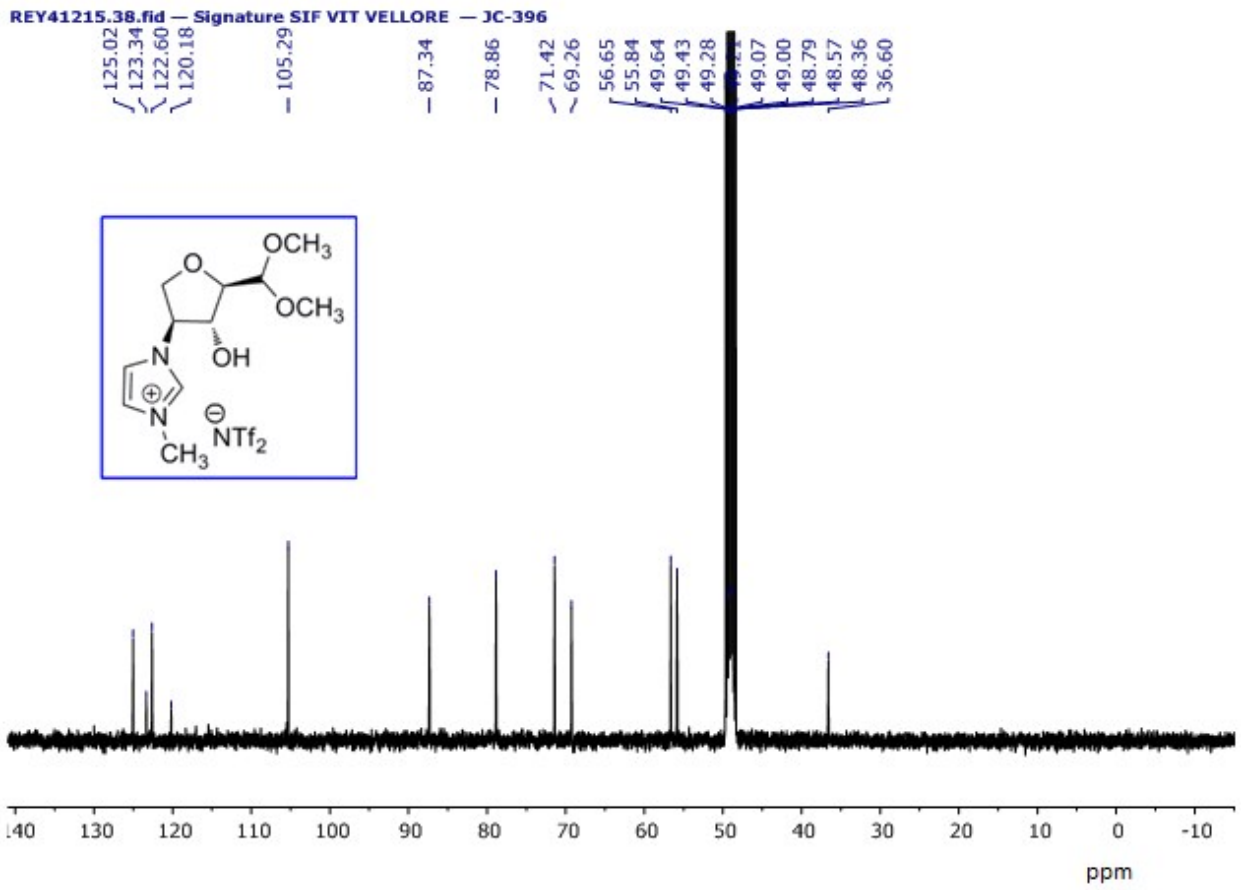
^{19}F NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium hexafluorophosphate (V) (8).



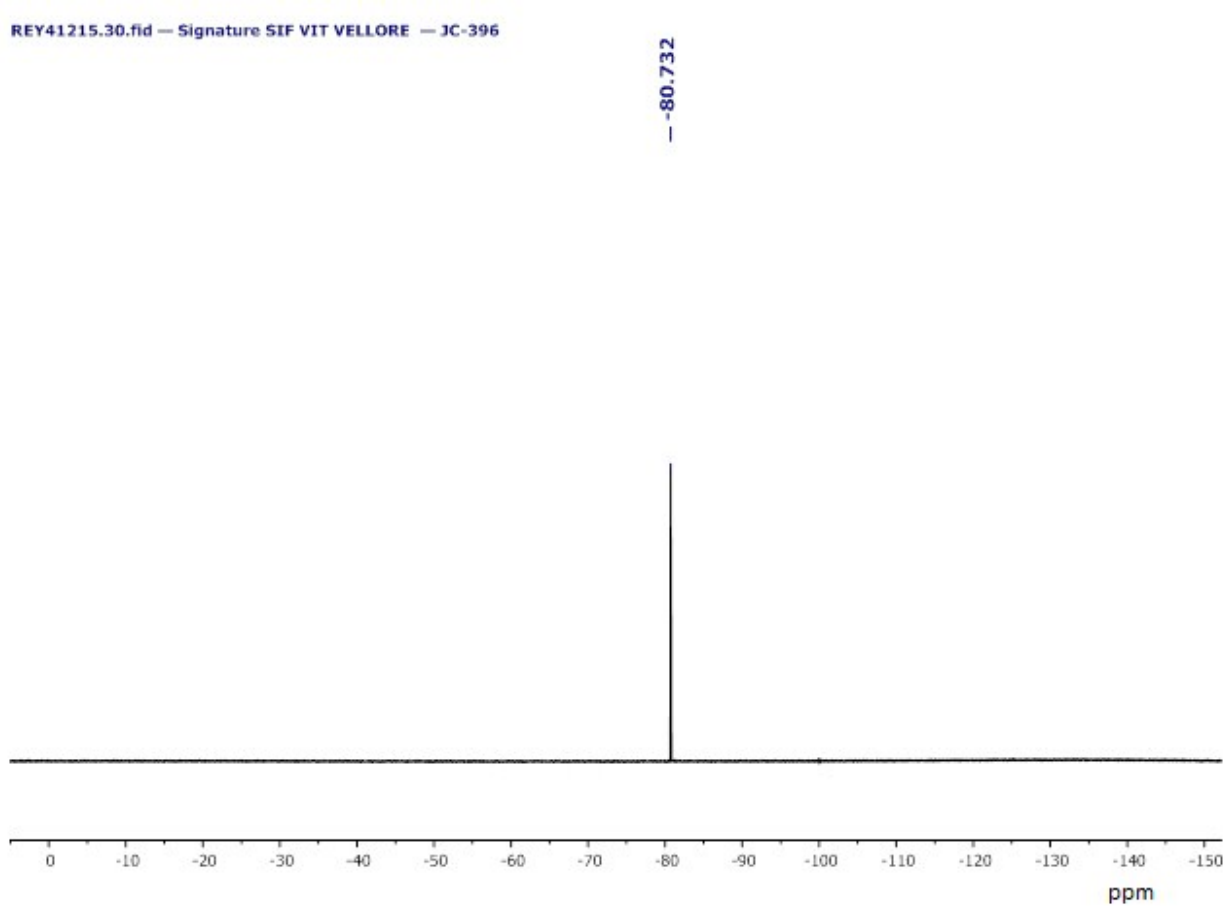
HR-MS Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium hexafluorophosphate (V) (8).



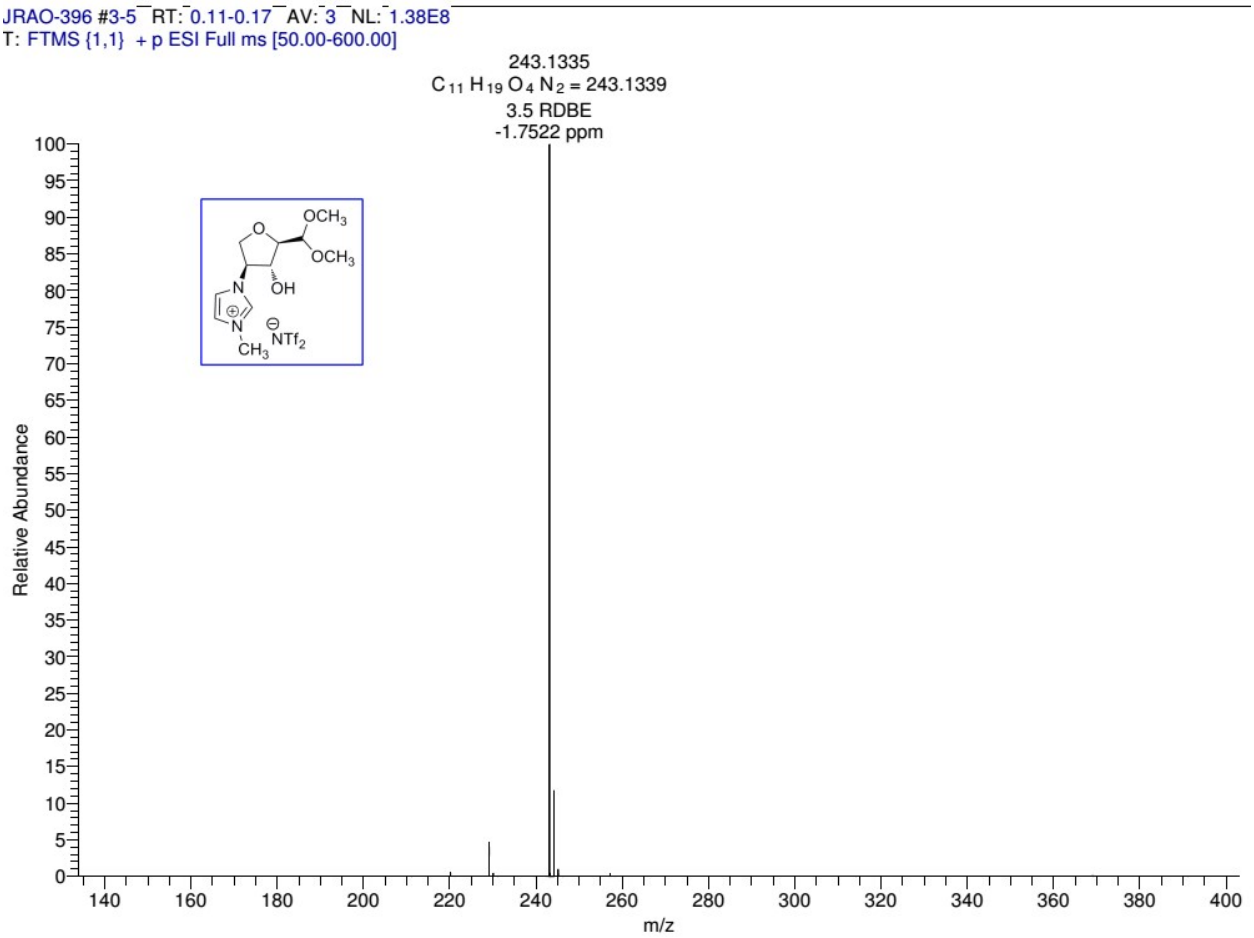
^{1}H NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium bis ((trifluoromethyl) sulfonyl) amide (9).



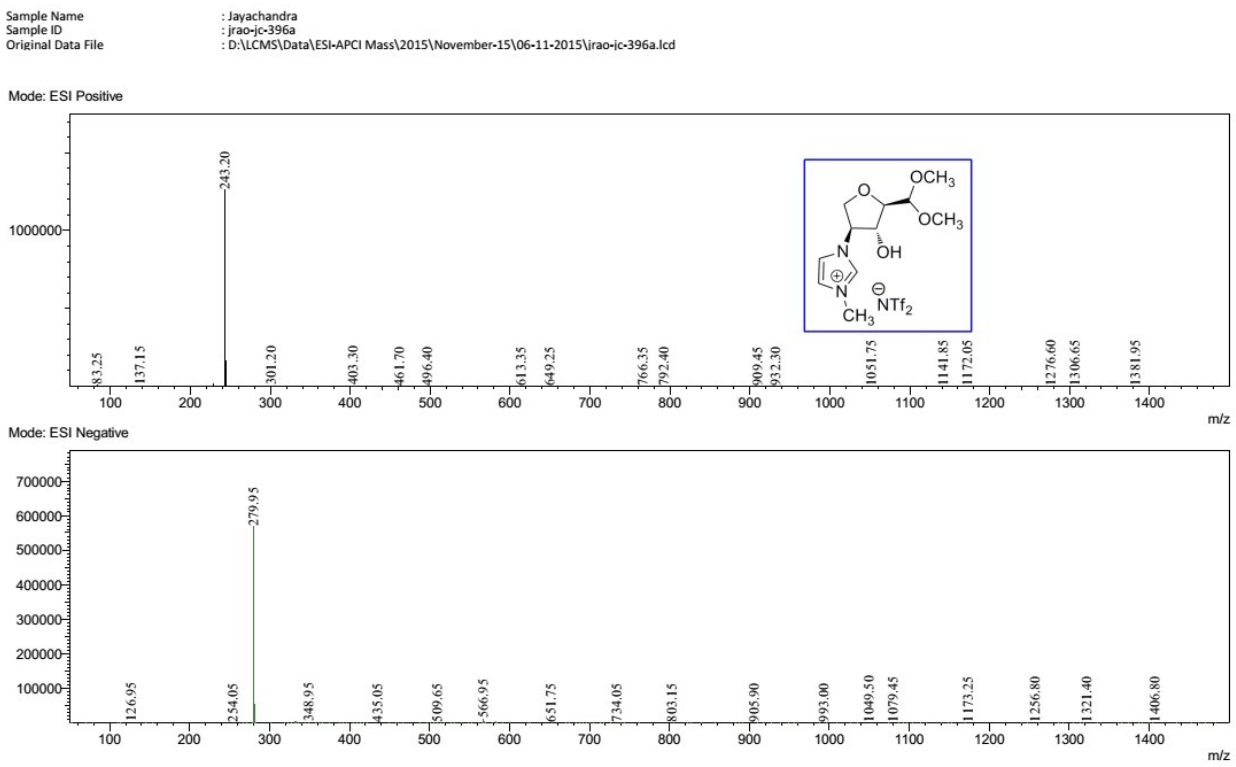
^{13}C NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium bis ((trifluoromethyl) sulfonyl) amide (9).



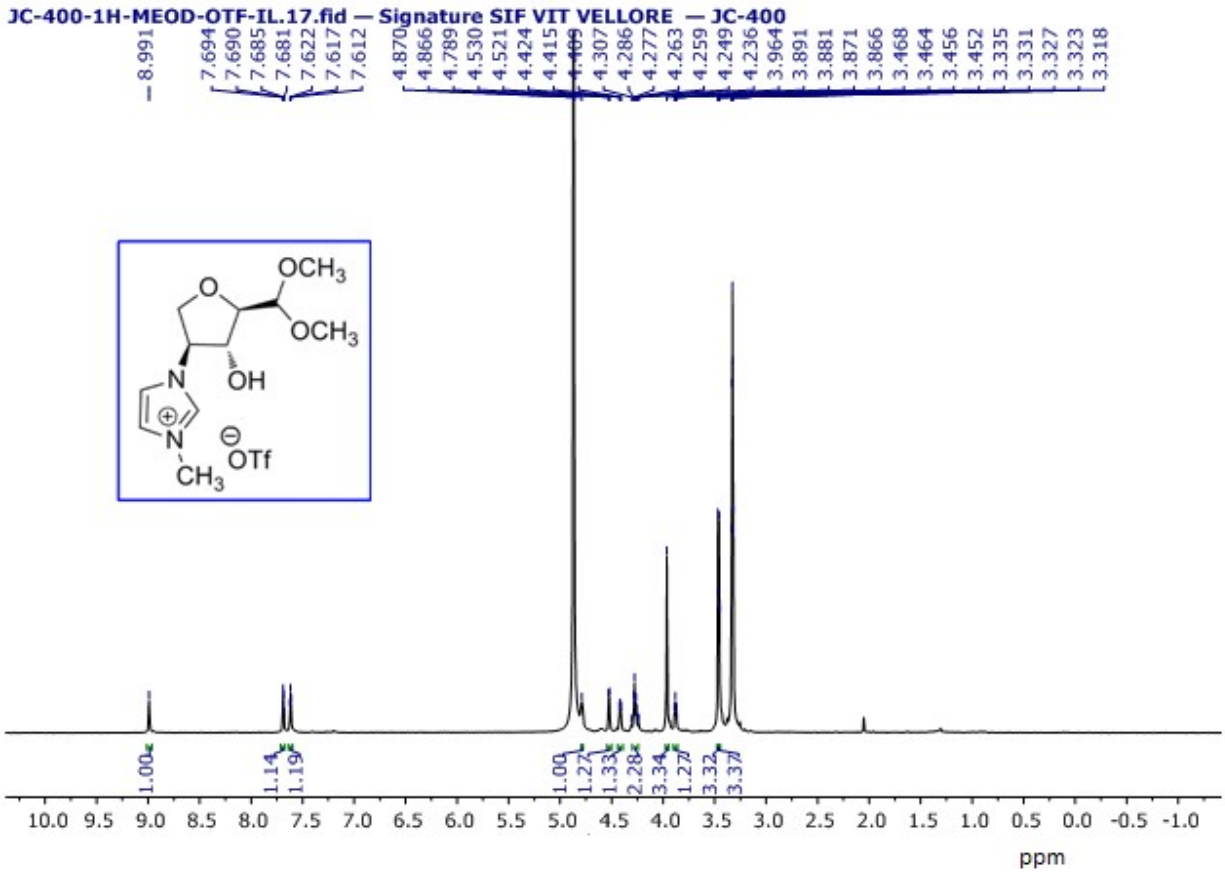
^{19}F NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium bis ((trifluoromethyl) sulfonyl) amide (9).



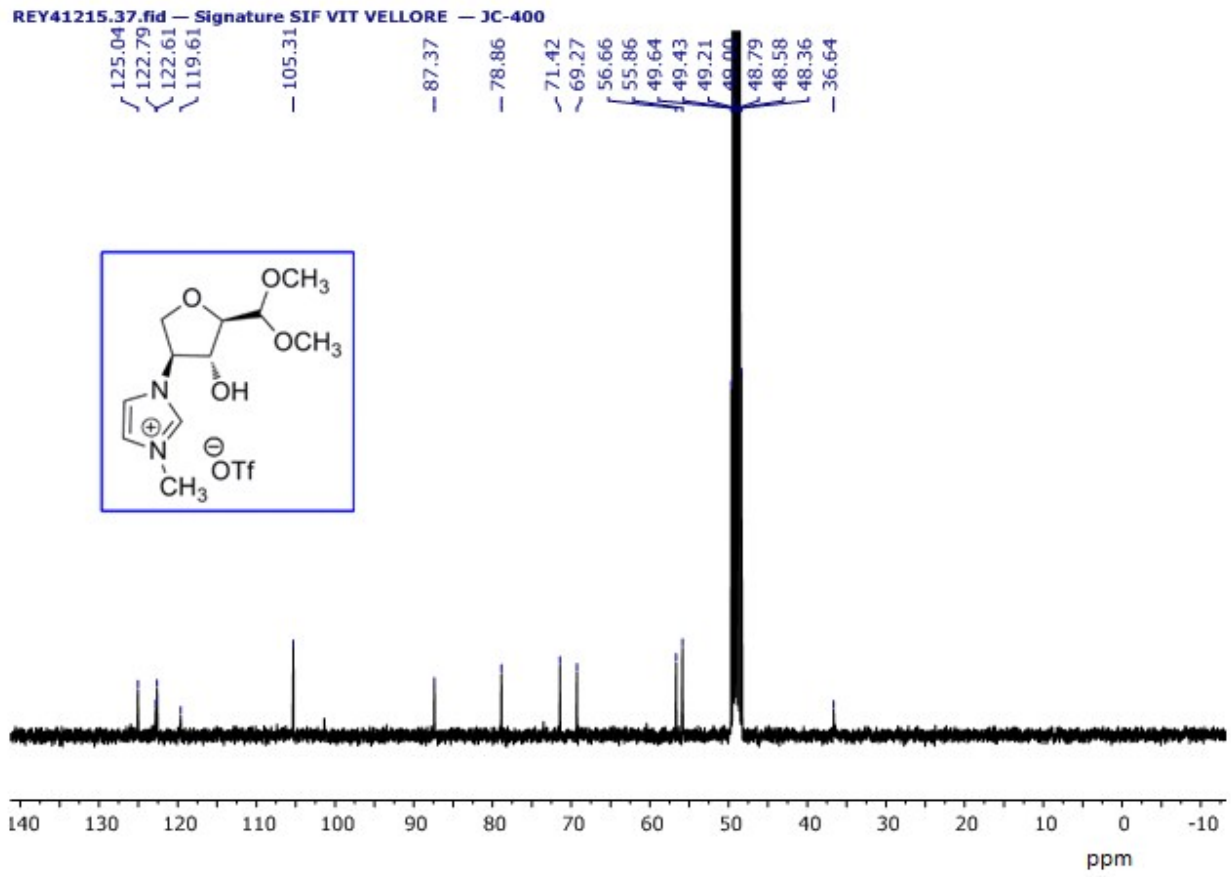
HR-MS (ESI) Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium bis ((trifluoromethyl) sulfonyl) amide (9).



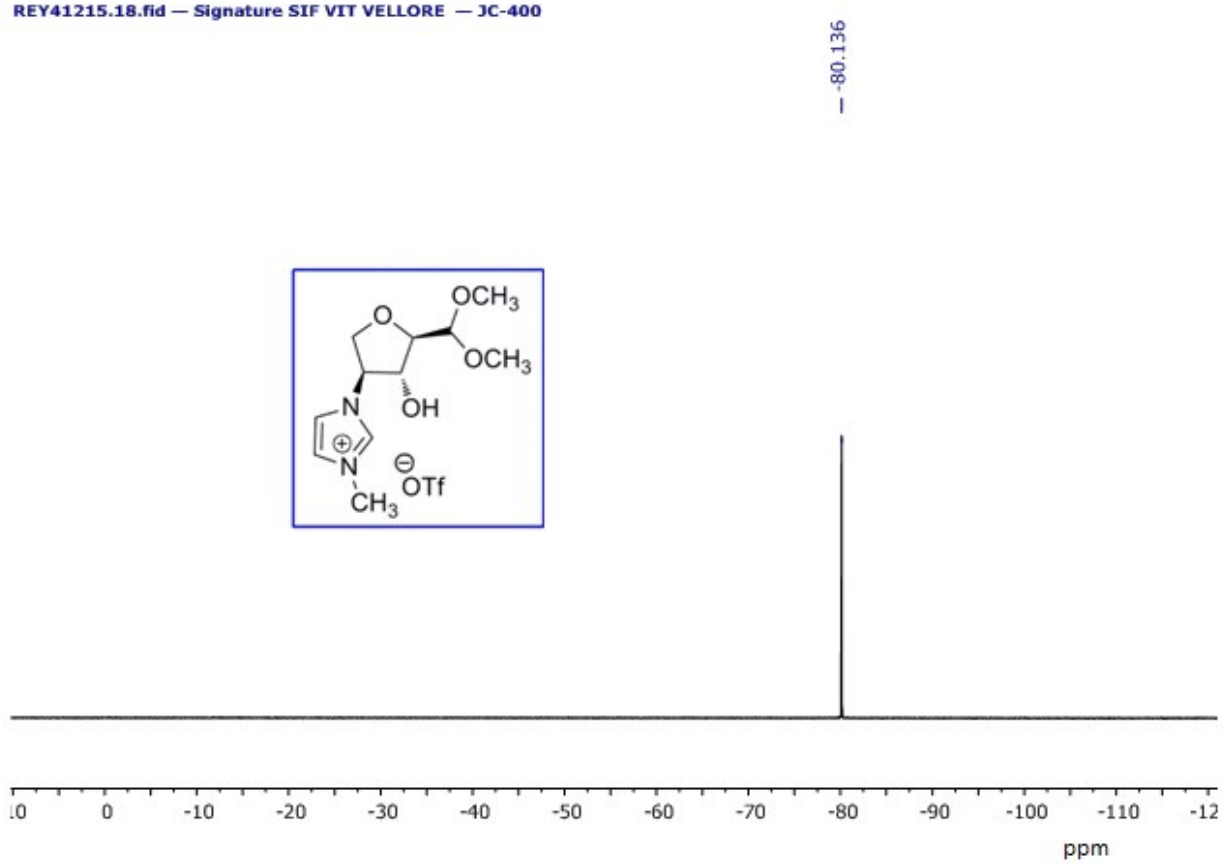
LR-MS (ESI) Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium bis ((trifluoromethyl) sulfonyl) amide (9) (Positive and negative modes).



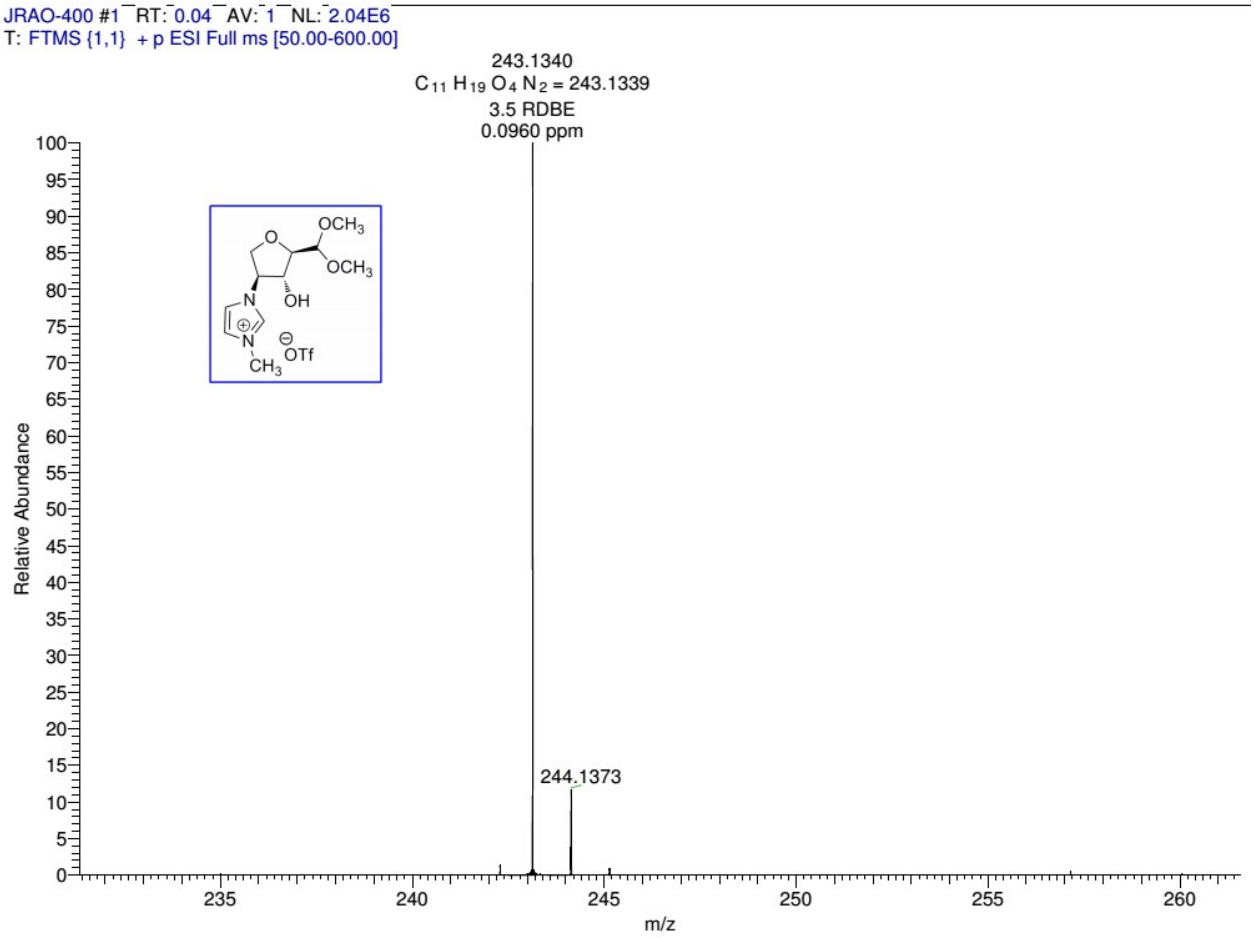
^{1}H NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium trifluoromethanesulfonate (10).



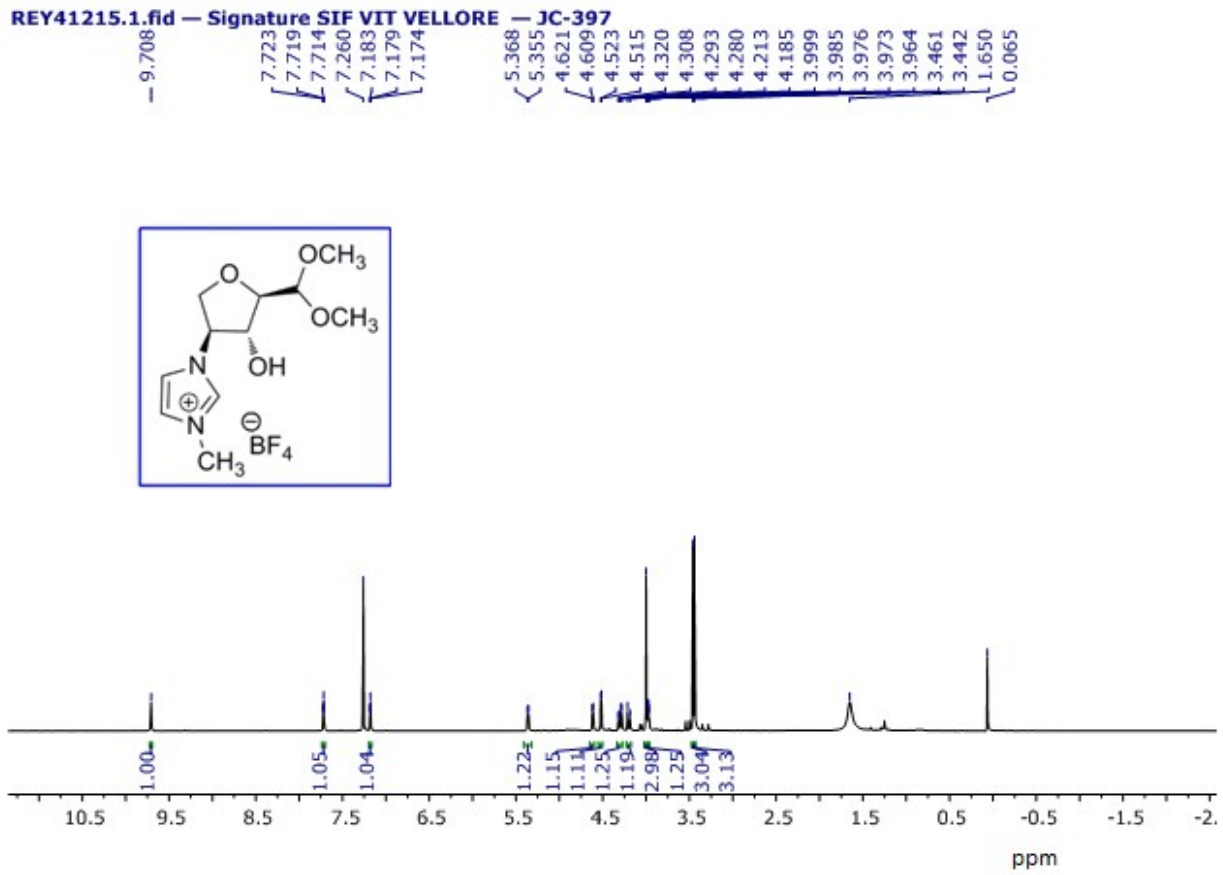
^{13}C NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium trifluoromethanesulfonate (10).



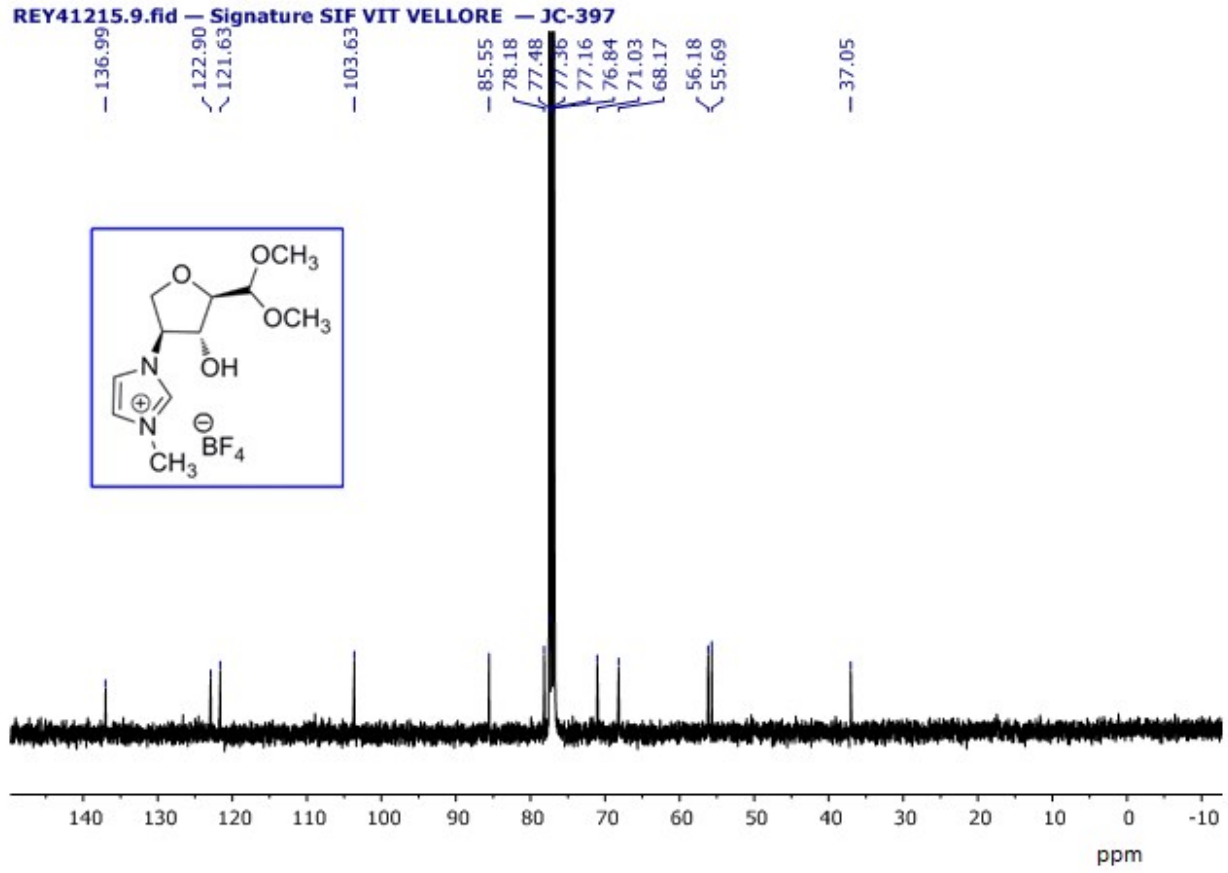
^{19}F NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium trifluoromethanesulfonate (10).



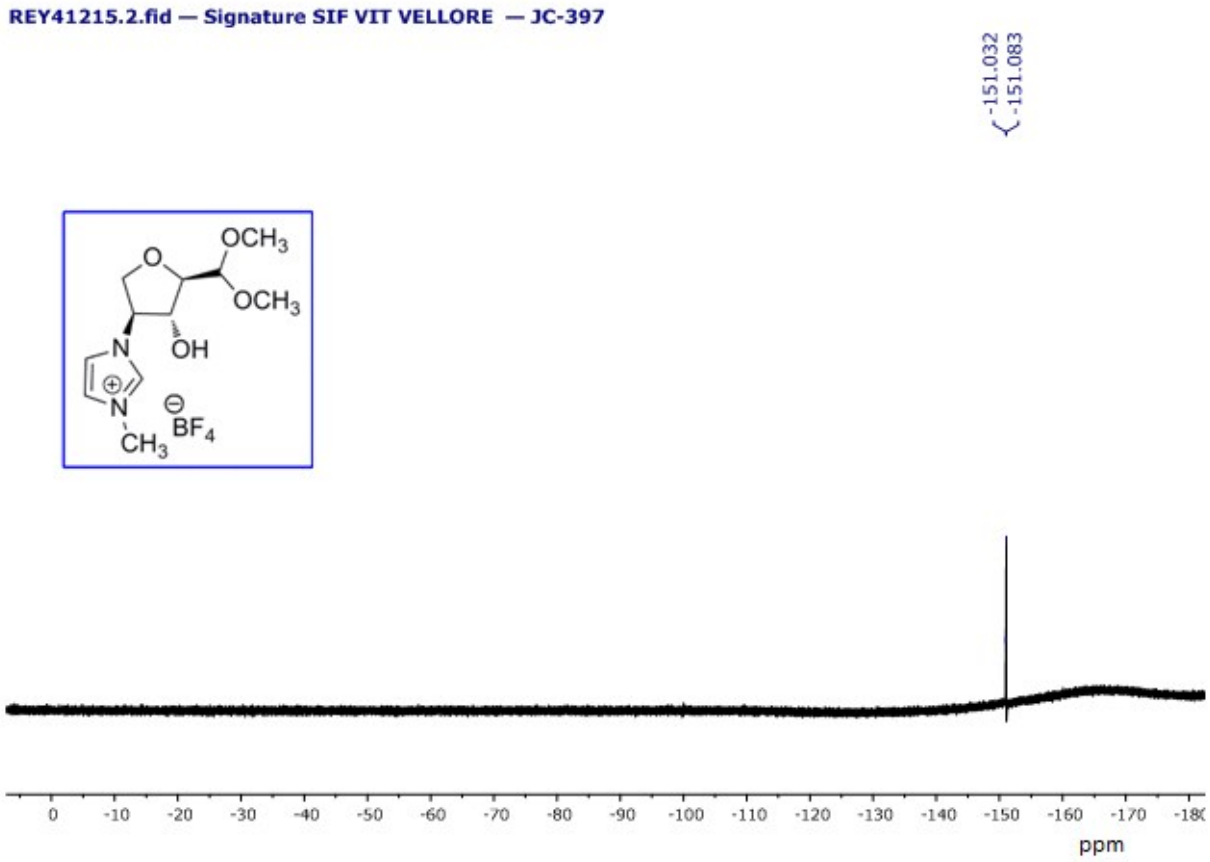
HR-MS Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium trifluoromethanesulfonate (10).



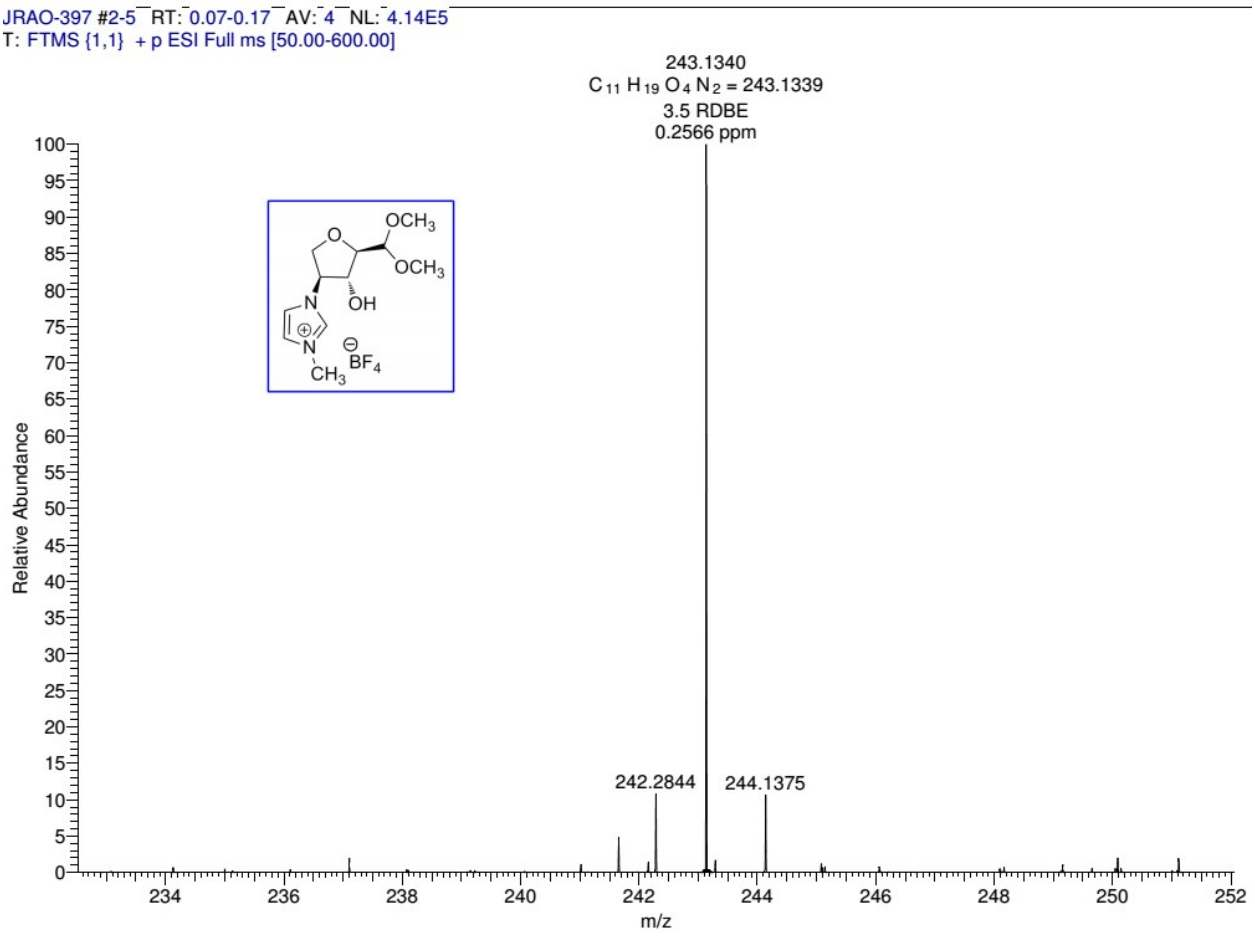
^{1}H NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium tetrafluoroborate (11).



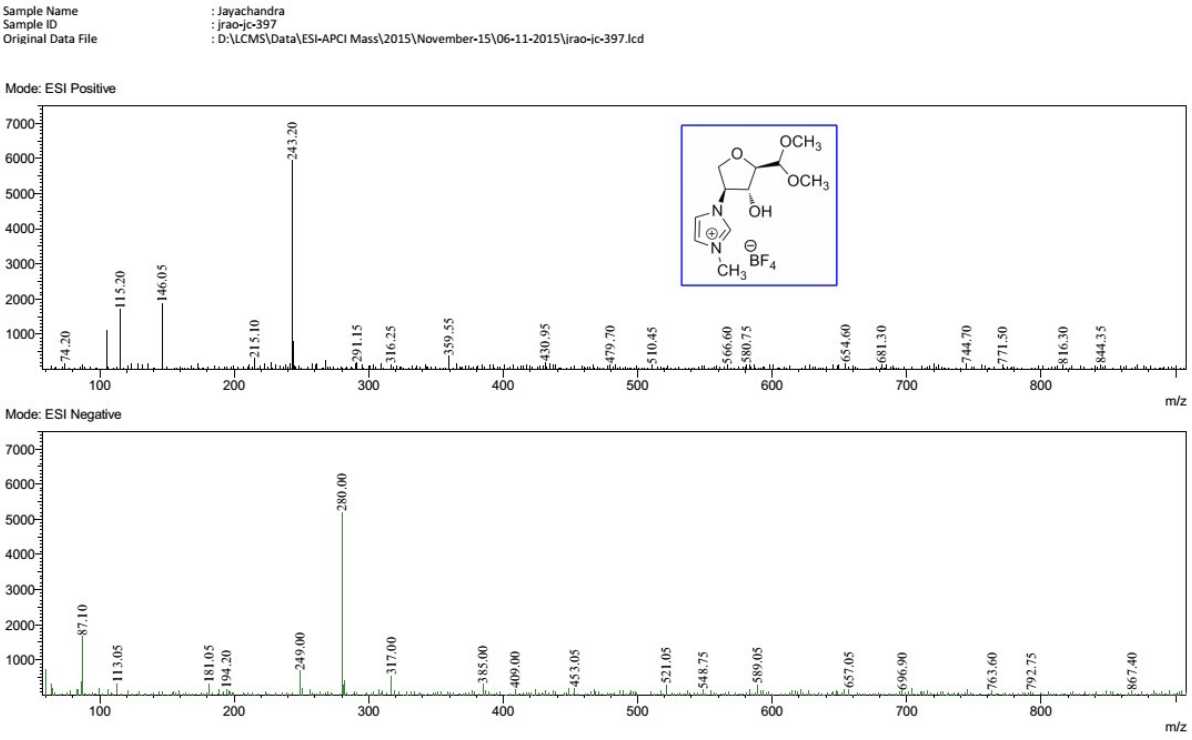
^{13}C NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium tetrafluoroborate (11).



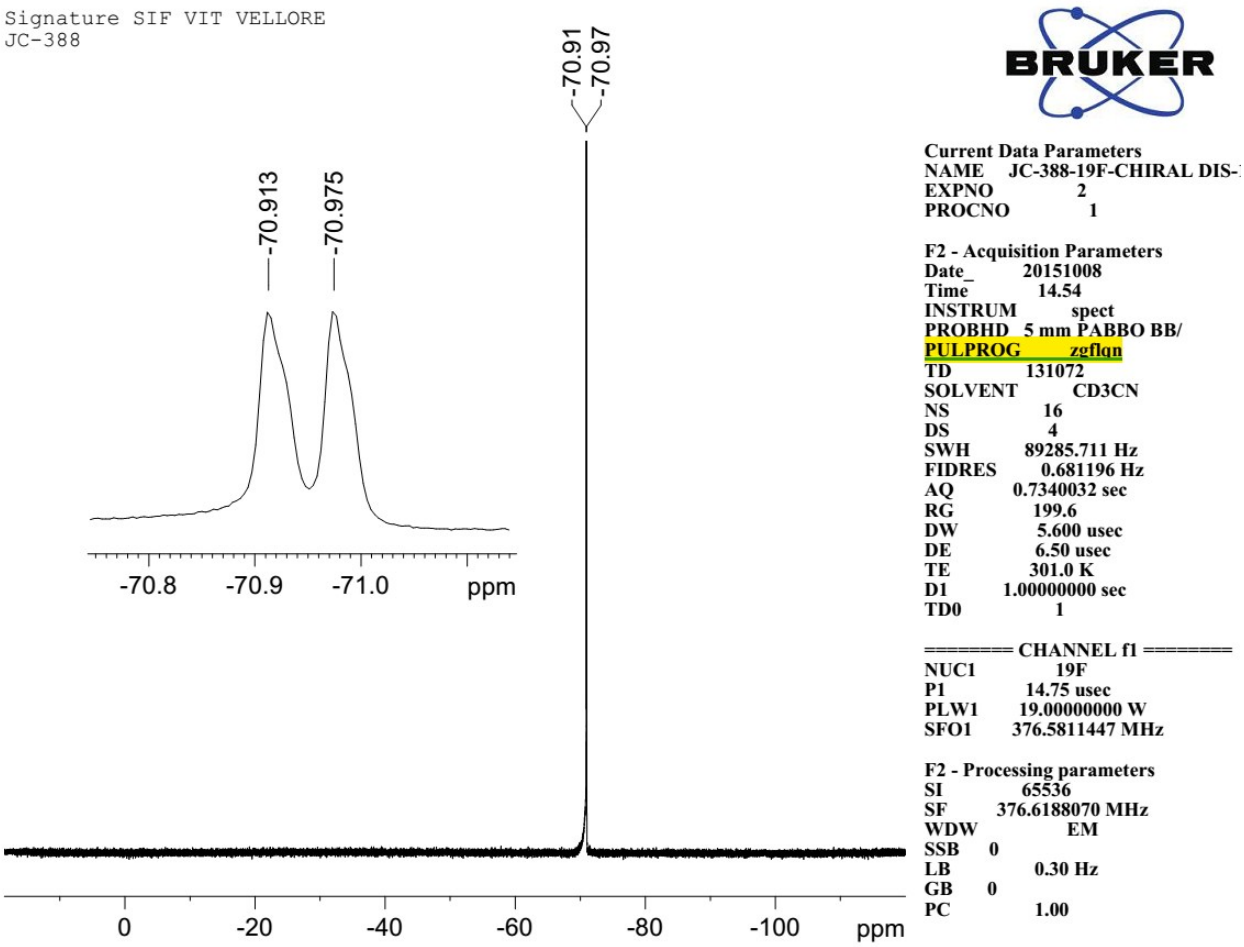
^{19}F NMR Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium tetrafluoroborate (11).



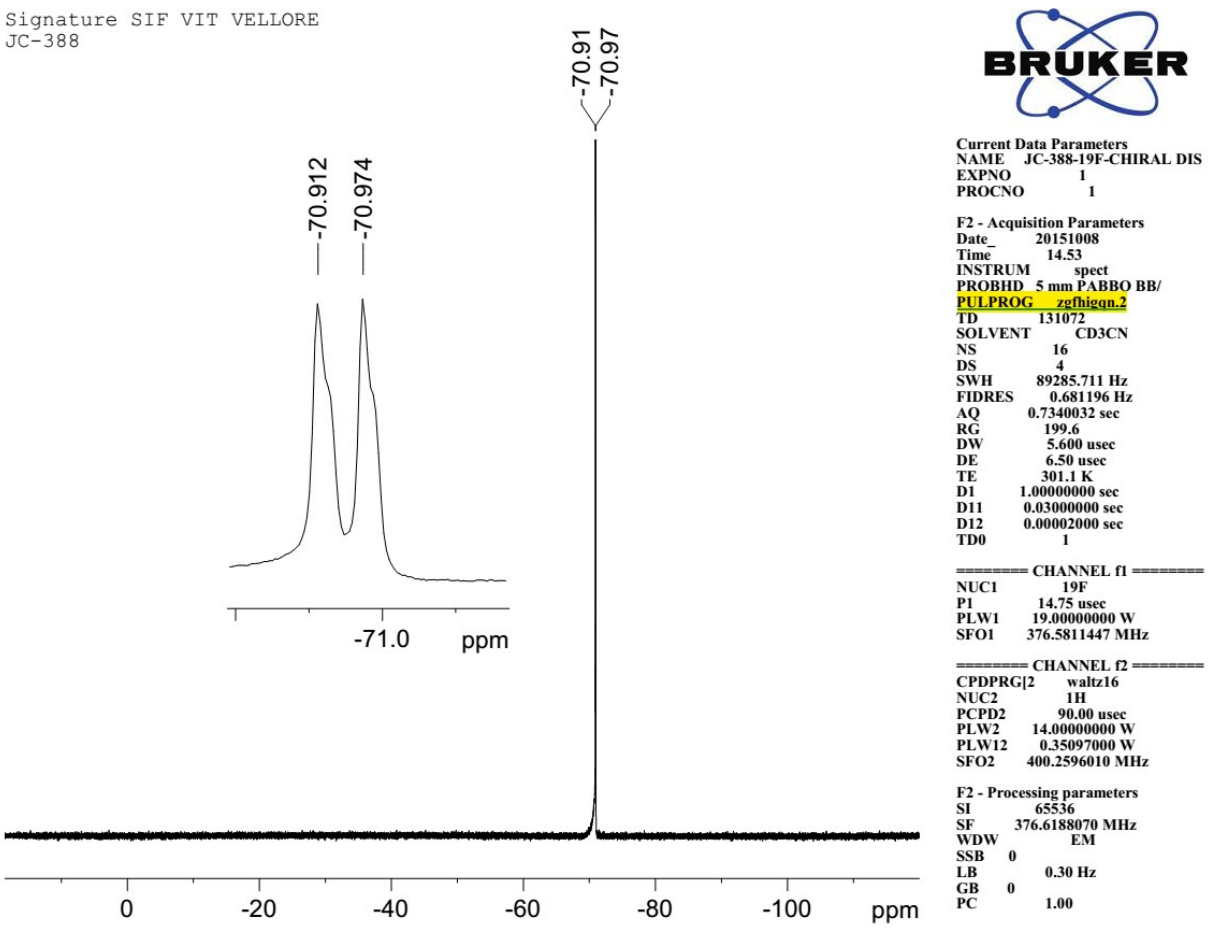
HR-MS (ESI) Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium tetrafluoroborate (11).



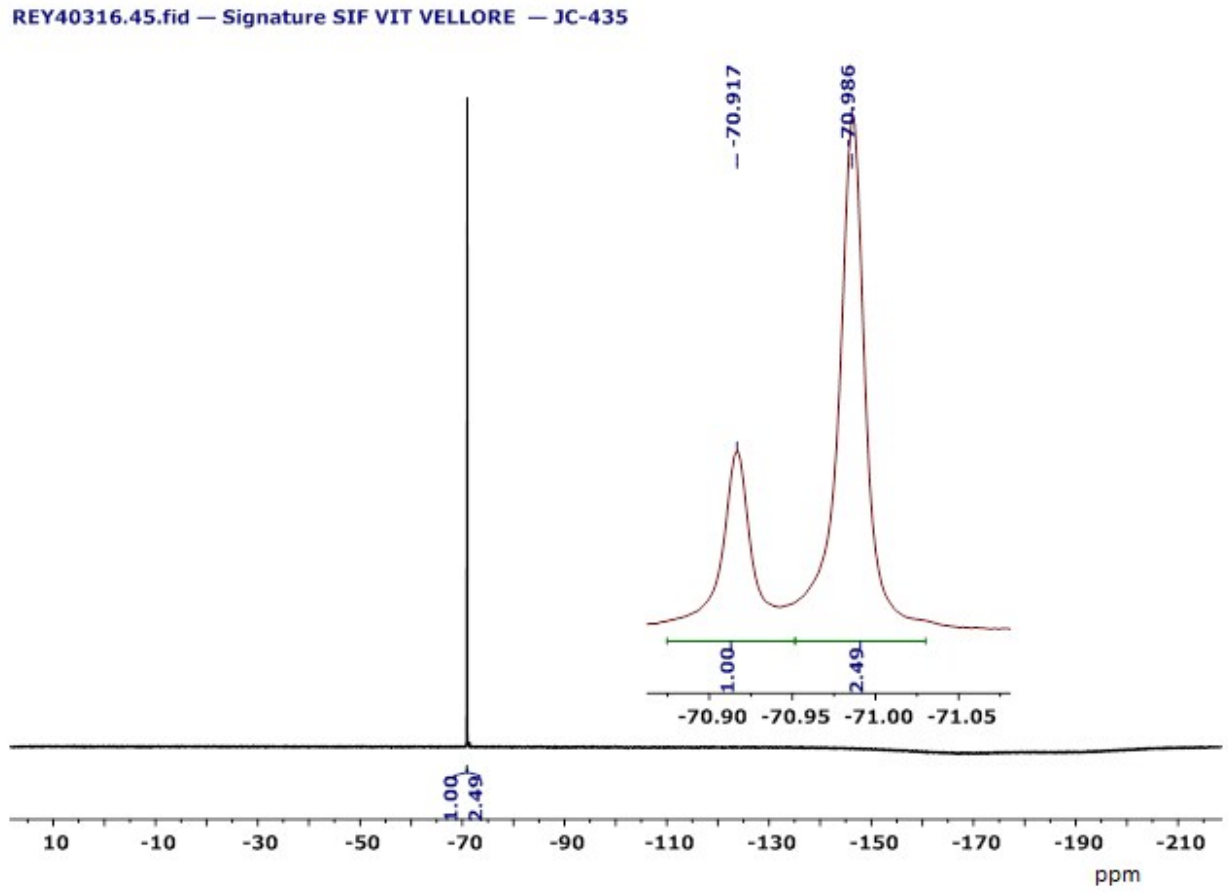
LR-MS (ESI) Spectrum of 1-((3S, 4R, 5R)-5-(dimethoxymethyl)-4-hydroxytetrahydrofuran-3-yl)-3-methyl-1H-imidazol-3-ium tetrafluoroborate (11) (Positive and negative modes).



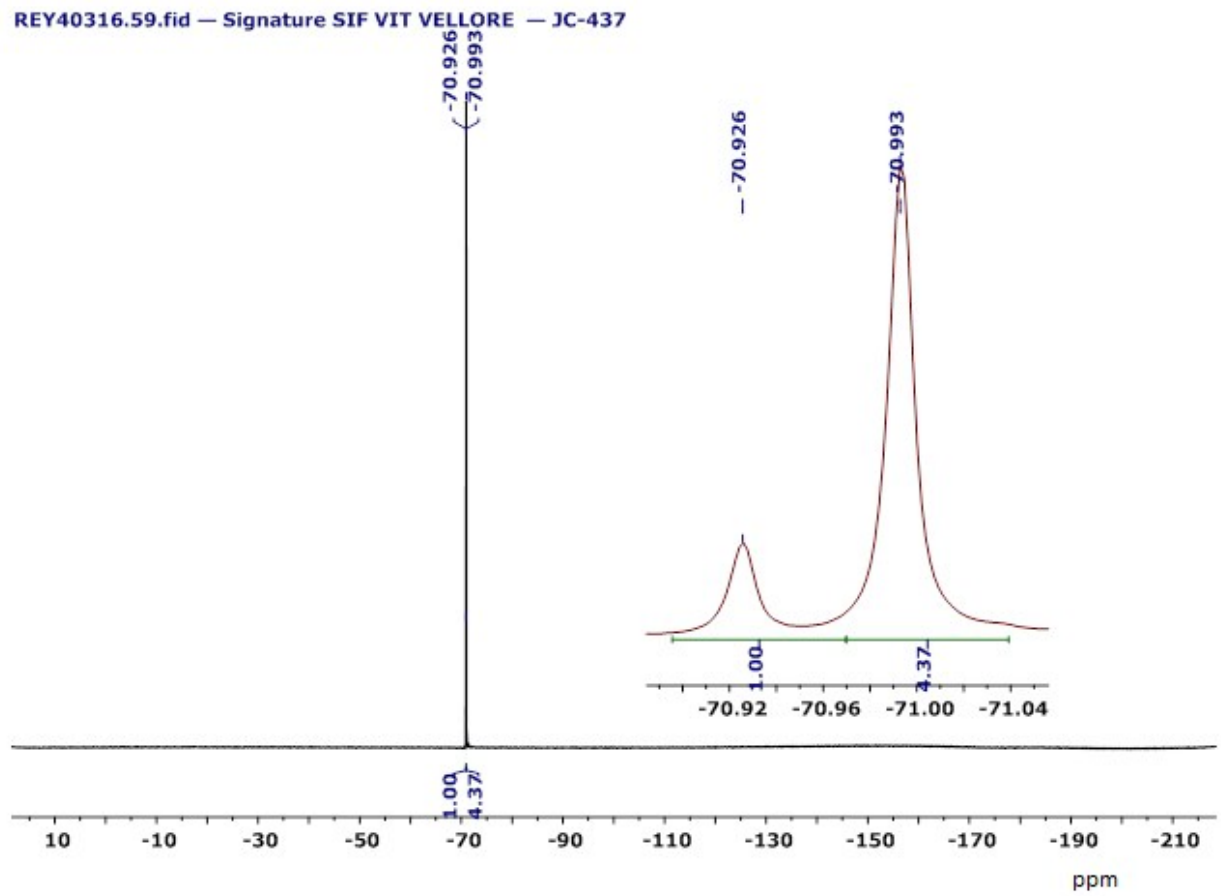
^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 7 (2 equiv.) and Mosher's acid salt (Proton Half decoupled spectrum).



^{19}F NMR Spectrum for the Chiral Recognition Experiment between CCIL 7 (2 equiv.) and Mosher's acid salt (Completely Proton decoupled spectrum).



^{19}F NMR spectrum for non-racemic Mosher's acid salt for the calculation of ee.



^{19}F NMR spectrum for non-racemic Mosher's acid salt for the calculation of ee.

LIST OF ABBREVATIONS

CCIL	**CARBOHYDRATE BASED CHIRAL IONIC LIQUID**
CIL	**CHIRAL IONIC LIQUID**
IL	**IONIC LIQUID**
$CuSO_4$	**COPPER SULPHATE**
H_2SO_4	**SULPHURIC ACID**
Me_2CO	**ACETONE**
DCM	**DICHLOROMETHANE**
HCl	**HYDROCHLORIC ACID**
TsCl	***p*-TOLUENE SULPHONYL CHLORIDE**
TEA	**TRIETHYLAMINE**
TFA	**TRIFLUOROACETIC ACID**
MeOH	**METHANOL**
K_2CO_3	**POTASSIUM CARBONATE**
Cs_2CO_3	**CESIUM CARBONATE**
DMF	**DIMETHYLFORMAMIDE**
CH_3I	**METHYL IODIDE**
Li	**LITHIUM**