



Supporting Information

for

Selectfluor and alcohol-mediated synthesis of bicyclic oxyfluorination compounds by Wagner–Meerwein rearrangement

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Experimental procedures, copies of ^1H NMR, ^{13}C NMR, and HRMS(Q-TOF) spectra

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Experimental

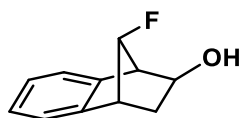
General

All chemicals and solvents, purchased from Sigma-Aldrich, were used without further purification. Reactions that require heating were carried out under oil bath conditions. Reactions were monitored by thin-layer chromatography using Merck TLC Silica gel 60 F254 and the plates were inspected by 254 nm or 365 nm UV-light and/or by acquiring ^1H -NMR spectra. Column chromatography was performed over Merck Silica gel 60F (70–230 mesh ASTM). The ^1H and ^{13}C NMR spectra were recorded on a Varian-400 or a Bruker-400 spectrometer in CDCl_3 using tetramethylsilane as the internal reference. All spectra were recorded at 25 °C and coupling constants (J values) are given in Hz. Chemical shifts are given in parts per million (ppm). Abbreviations used to define the multiplicities are as follows: s = singlet; d = doublet; dd = doublet of doublets; m = multiplet. Optical rotations were determined with a 589 nm spectropolarimeter at 25 °C. IR Spectra spectra were recorded with VERTEX 70v FT-IR spectrometer. Mass spectra of unknown compounds were recorded on an AB-Sciex 4600 QTOF-MS.

General procedure

Benzonorbornadiene (**1a**) or (+)-camphene (**1b**) (0.5 mmol), selectfluor (215 mg, 0.61 mmol) and alcohol derivatives (2.4 mmol) were dissolved in 2 mL CH_3CN in an ACE pressure tube. The reaction mixture was stirred at 90 °C for 2 hours. The mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography on silica gel (*n*-hexane/EtOAc (9:1)).

(1*R*(S),4*R*(S),9*R*(S))-9-Fluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-ol (3a):



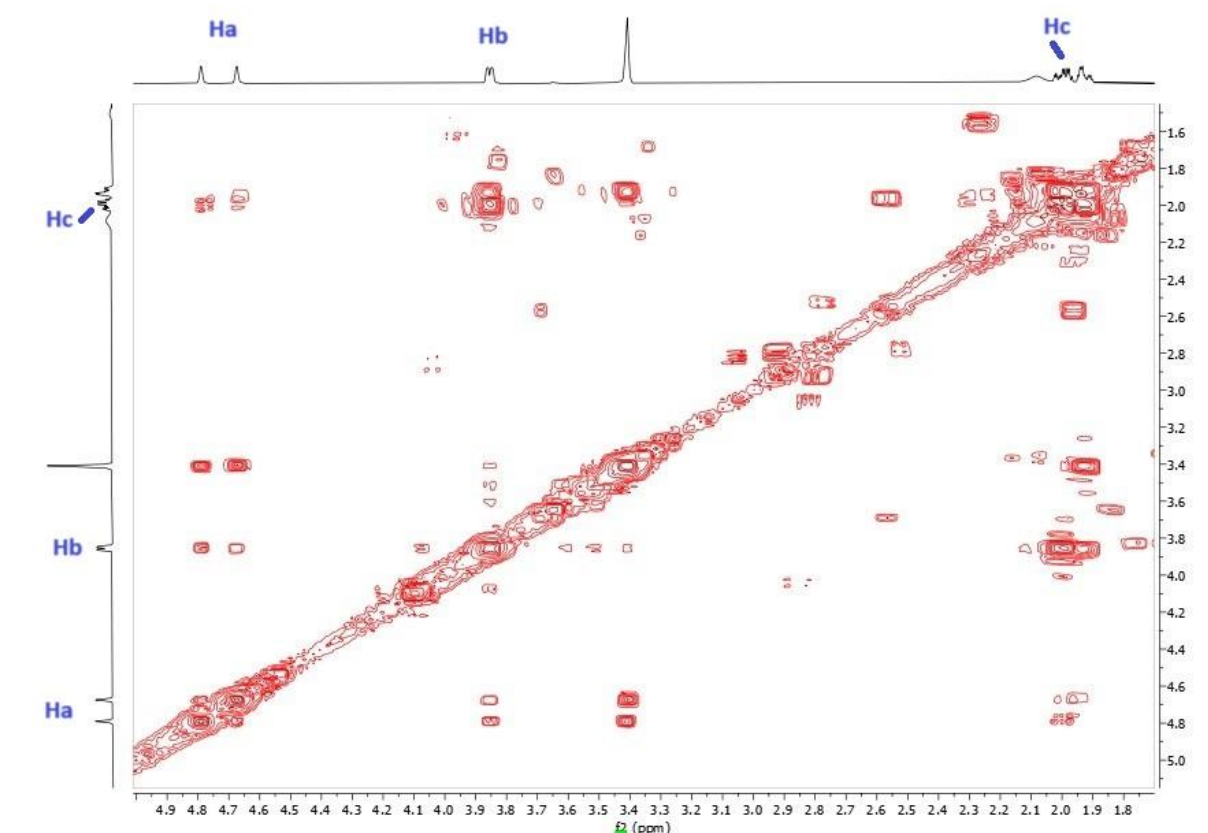
Colorless oil (97 mg, 94%). ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.19 (m, 1H), 7.18 – 7.14 (m, 3H), 4.81 (d, J = 57.2 Hz, 1H), 4.00–3.88 (m, 1H), 3.54–3.47 (m, 2H), 2.18 (s, 1H), 2.10 – 2.01 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.8 (d, J = 8.1 Hz), 138.8 (d, J = 10.6 Hz), 127.7, 127.2, 123.1, 122.2, 100.6 (d, J = 206.4 Hz), 74.1, 54.0 (d, J = 14.9 Hz), 46.4 (d, J = 18.4 Hz), 36.7. ^{19}F NMR (376 MHz, CDCl_3) δ -177.17 (d, J = 58.3 Hz). IR (KBr cm^{-1}): 2932, 2887, 2857, 1732, 1452, 1391, 1184, 1082, 991, 980. (TOF MS) m/z (%): $[(\text{M}-\text{H}_2\text{O})+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_9\text{F}$ 161.0761; found: 161,0773.

Structure:

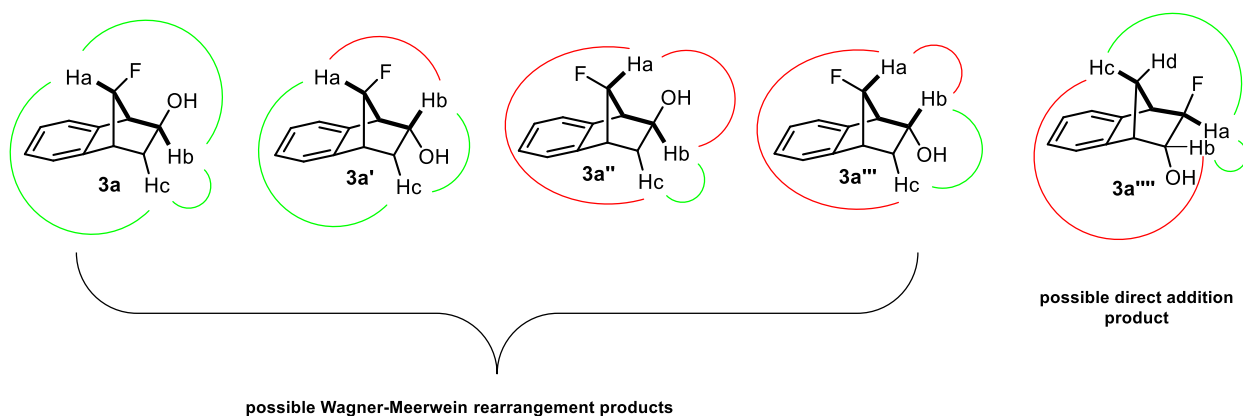
The rearrangement mechanisms of addition reactions in norbornene-derived bicyclic systems and the products formed as a result of this mechanism are well known. In these systems, *syn-anti* and *endo-exo* configurations can be easily determined using

^1H NMR and 2D NMR (NEO, NEOSY, COSY, etc.) techniques (Daştan et al., 1996; Gültekin et al., 2023; Wakchaure et al., 2024; Zky et al. 1998; Moreno-Dorado et al., 2003).

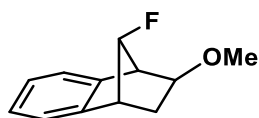
Although the structures of the products formed as a result of alkene additions in norbornene-derived systems are well known, COSY 2D-NMR experiments of compound **3a** were performed to confirm the configurations of the products. When the COSY spectrum is examined, it is seen that Ha interacts with Hb and Hc, Hb interacts with Ha and Hc, and Hc interacts with Ha and Hc.



In norbornene-derived bicyclic systems, long-distance interactions of protons through four bonds are observed when they are zigzag (M or W) oriented. Otherwise, no interaction is observed (Balci, 2005). In the light of this information, when the possible structures for **3a** are evaluated together with the COSY spectrum; the only structure in which all Ha, Hb and Hc protons can interact with each other is the **3a** structure. This proves the correctness of the configuration given for structure **3** in the manuscript, with fluorine as anti and OH as exo.

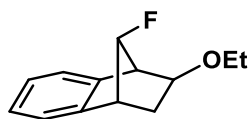


(1*R*(S),4*R*(S),9*R*(S))-9-Fluoro-2-methoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3b):



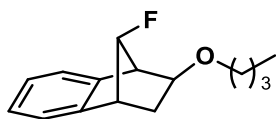
Colorless oil (101 mg, 98%). ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.20 (m, 1H), 7.19-7.11 (m, 3H), 4.68 (d, $J = 57.3$ Hz, 1H), 3.62-3.55 (m, 1H), 3.53-3.47 (m, 1H), 3.47-3.43 (m, 1H), 3.41 (s, 3H), 2.15-2.06 (m, 1H), 1.98-1.89 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.3 (d, $J = 7.6$ Hz), 139.4 (d, $J = 10.4$ Hz), 127.5, 127.1, 122.9, 122.3, 98.7 (d, $J = 213.4$ Hz), 83.0 (d, $J = 2.3$ Hz), 57.7, 50.6 (d, $J = 16.3$ Hz), 46.3 (d, $J = 18.6$ Hz), 32.9. ^{19}F NMR (376 MHz, CDCl_3) δ -178.50 (d, $J = 57.9$ Hz). IR (KBr cm^{-1}): 2980, 2943, 2886, 2820, 1734, 1464, 1350, 1242, 1209, 1099, 1047, 1003, 937, 750, 635, 505, 422. (TOF MS) m/z (%): $(\text{M}+\text{H})^+$ calcd for $\text{C}_{12}\text{H}_{13}\text{FO}$ 193.1023; found: 193.1022

(1*R*(S),4*R*(S),9*R*(S))-2-Ethoxy-9-fluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3c):



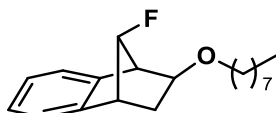
Colorless oil (101 mg, 98%). ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.19 (m, 1H), 7.19 – 7.14 (m, 3H), 4.67 (d, $J = 57.1$ Hz, 1H), 3.63 – 3.51 (m, 4H), 3.47 – 3.40 (m, 1H), 2.19-2.10 (m, 1H), 1.96-1.86 (m, 1H), 1.26 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2 (d, $J = 7.6$ Hz), 139.6 (d, $J = 10.4$ Hz), 127.4, 127.0, 122.7, 122.2, 98.6 (d, $J = 213.3$ Hz), 81.0, 65.3, 51.0 (d, $J = 16.0$ Hz), 46.3 (d, $J = 18.4$ Hz), 33.1, 15.5. ^{19}F NMR (376 MHz, CDCl_3) δ -178.31 (d, $J = 57.7$ Hz). IR (KBr cm^{-1}): 2974, 2945, 1734, 1466, 1348, 1240, 1194, 1103, 1051, 1011, 750, 634. (TOF MS) m/z (%): $(\text{M}+\text{H})^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{FO}$ 207.1180; found: 207.1180.

(1*R*(*S*),4*R*(*S*),9*R*(*S*))-2-Butoxy-9-fluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3d):



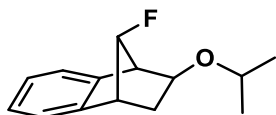
Colorless oil (98 mg, 95%). ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.21 (m, 1H), 7.20 – 7.14 (m, 3H), 4.68 (d, J = 57.1 Hz, 1H), 3.65 – 3.42 (m, 5H), 2.21 – 2.09 (m, 1H), 2.00–1.86 (m, 1H), 1.68 – 1.56 (m, 2H), 1.50–1.36 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2 (d, J = 7.7 Hz), 139.6 (d, J = 10.3 Hz), 127.3, 127.0, 122.7, 122.1, 98.6 (d, J = 213.9 Hz), 81.0, 69.8, 50.9 (d, J = 19.2 Hz), 46.2 (d, J = 18.3 Hz), 33.0, 32.0, 19.5, 14.0. ^{19}F NMR (376 MHz, CDCl_3) δ -178.34 (d, J = 57.6 Hz). IR (KBr cm^{-1}): 2955, 2926, 2866, 1724, 1464, 1348, 1194, 1092, 1051, 939, 748, 634, 494, 422. (TOF MS) m/z (%): ($\text{M}+\text{H}$) $^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{FO}$ 235,1493; found: 235,1495.

(1*R*(*S*),4*R*(*S*),9*R*(*S*))-9-Fluoro-2-(octyloxy)-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3e):



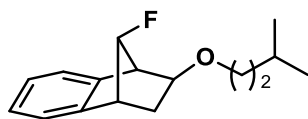
Colorless oil (133 mg, 92%). ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.20 (m, 1H), 7.20 – 7.12 (m, 3H), 4.68 (d, J = 57.1 Hz, 1H), 3.61 – 3.43 (m, 5H), 2.18–2.08 (m, 1H), 1.96–1.86 (m, 1H), 1.65 – 1.59 (m, 2H), 1.36 – 1.27 (m, 10H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.3 (d, J = 7.7 Hz), 139.6 (d, J = 10.5 Hz), 127.4, 127.0, 122.8, 122.2, 98.6 (d, J = 214.2 Hz), 81.1, 70.2, 50.9 (d, J = 17.2 Hz), 46.3 (d, J = 18.1 Hz), 33.0, 31.9, 30.0, 29.6, 29.4, 26.3, 22.8, 14.2. ^{19}F NMR (376 MHz, CDCl_3) δ -178.26 (d, J = 57.3 Hz). IR (KBr cm^{-1}): 2926, 2855, 1464, 1348, 1105, 1053, 1009, 748, 494, 422. (TOF MS) m/z (%): ($\text{M}+\text{H}$) $^+$ calcd for $\text{C}_{19}\text{H}_{27}\text{FO}$ 291.2119; found: 291.2116.

(1*R*(*S*),4*R*(*S*),9*R*(*S*))-9-Fluoro-2-isopropoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3f):



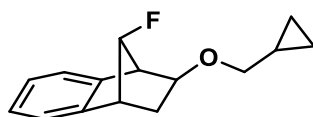
Colorless oil (105 mg, 96%). ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.21 (m, 1H), 7.20 – 7.15 (m, 3H), 4.68 (d, J = 57.2 Hz, 1H), 3.77 – 3.66 (m, 2H), 3.54–3.48 (m, 1H), 3.47–3.40 (m, 1H), 2.19–2.08 (m, 1H), 1.97–1.87 (m, 1H), 1.24 (d, J = 6.1 Hz, 3H), 1.20 (d, J = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2 (d, J = 7.6 Hz), 139.8 (d, J = 10.4 Hz), 127.3, 126.9, 122.7, 122.2, 98.6 (d, J = 213.6 Hz), 78.5, 70.7 (d, J = 2.0 Hz), 51.8 (d, J = 16.5 Hz), 46.4 (d, J = 18.4 Hz), 33.6, 22.6, 22.5. ^{19}F NMR (376 MHz, CDCl_3) δ -178.04 (d, J = 57.6 Hz). IR (KBr cm^{-1}): 2973, 2947, 2879, 1468, 1370, 1330, 1241, 1151, 1134, 1085, 1053, 1013, 986, 749, 638, 499. (TOF MS) m/z (%): ($\text{M}+\text{H}$) $^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{FO}$ 221,1336; found: 221,1338.

(1*R*(*S*),4*R*(*S*),9*R*(*S*))-9-Fluoro-2-(isopentyloxy)-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3g):



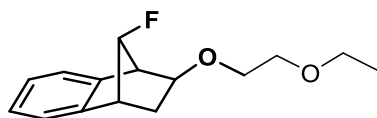
Colorless oil (116 mg, 94%). ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.20 (m, 1H), 7.19 – 7.14 (m, 3H), 4.68 (d, J = 57.1 Hz, 1H), 3.64 – 3.40 (m, 5H), 2.20–2.05 (m, 1H), 2.00–1.83 (m, 1H), 1.77 – 1.68 (m, 1H), 1.57 – 1.47 (m, 2H), 0.94 (d, J = 2.5 Hz, 3H), 0.92 (d, J = 2.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.3 (d, J = 7.7 Hz), 139.6 (d, J = 10.0 Hz), 127.4, 127.0, 122.8, 122.2, 98.6 (d, J = 213.7 Hz), 81.1 (d, J = 2.1 Hz), 68.5, 50.9 (d, J = 16.2 Hz), 46.3 (d, J = 18.7 Hz), 38.8, 33.1, 25.2, 22.8. ^{19}F NMR (376 MHz, CDCl_3) δ -178.30 (d, J = 57.1 Hz). IR (KBr cm^{-1}): 2961, 2933, 2866, 1473, 1354, 1197, 1102, 1055, 1022, 936, 751, 641, 494. (TOF MS) m/z (%): ($\text{M}+\text{H}$) $^+$ calcd for $\text{C}_{16}\text{H}_{21}\text{FO}$ 249.1649; found: 249.1647.

(1*R*(*S*),4*R*(*S*),9*R*(*S*))-2-(Cyclopropylmethoxy)-9-fluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3h):



Colorless oil (106 mg, 92%). ^1H NMR (400 MHz, CDCl_3) δ 7.22–7.19 (m, 1H), 7.18–7.14 (m, 3H), 4.67 (d, J = 57.2 Hz, 1H), 3.66–3.60 (m, 1H), 3.60–3.56 (m, 1H), 3.46–3.42 (m, 1H), 3.35 (d, J = 6.8 Hz, 2H), 2.18 – 2.11 (m, 1H), 1.95–1.86 (m, 1H), 1.14–1.06 (m, 1H), 0.58–0.54 (m, 2H), 0.25 – 0.21 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.3 (d, J = 7.7 Hz), 139.6 (d, J = 10.0 Hz), 127.4, 127.0, 122.8, 122.2, 98.6 (d, J = 213.3 Hz), 80.8 (d, J = 2.2 Hz), 74.8, 51.0 (d, J = 16.3 Hz), 46.3 (d, J = 18.6 Hz), 33.1, 10.9, 3.4. ^{19}F NMR (376 MHz, CDCl_3) δ -178.24 (d, J = 57.7 Hz). IR (KBr cm^{-1}): 3071, 2984, 2948, 2870, 1726, 1471, 1352, 1193, 1084, 1052, 1016, 943, 751, 642, 500. (TOF MS) m/z (%): ($\text{M}+\text{H}$) $^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{FO}$ 233.1336; found: 233.1337.

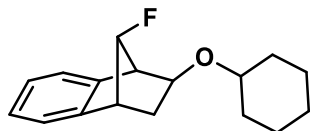
(1*R*(*S*),4*R*(*S*),9*R*(*S*))-2-(2-Ethoxyethoxy)-9-fluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3i):



Colorless oil (117 mg, 94%). ^1H NMR (400 MHz, CDCl_3) δ 7.21 – 7.18 (m, 1H), 7.17 – 7.13 (m, 3H), 4.66 (dd, J = 57.0, 1.9 Hz, 1H), 3.69 – 3.59 (m, 6H), 3.55 (q, J = 6.8 Hz, 2H), 3.46–3.41 (m, 1H), 2.18–2.11 (m, 1H), 1.95–1.88 (m, 1H), 1.21 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2 (d, J = 7.7 Hz), 139.5 (d, J = 10.7 Hz), 127.4, 127.1, 122.9, 122.2, 98.6 (d, J = 213.4 Hz), 81.7 (d, J = 2.2 Hz), 70.0, 69.4, 66.8, 50.9 (d, J = 16.6 Hz), 46.3 (d, J = 18.4 Hz), 33.1, 15.3. ^{19}F NMR (376 MHz, CDCl_3) δ -178.23 (d, J = 57.1 Hz). IR (KBr cm^{-1}): 2986, 2944, 2868, 1734, 1469, 1357, 1239, 1173, 1102,

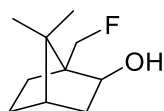
1050, 755, 643, 495. (TOF MS) m/z (%): $[(M-C_4H_9O_2)+H]^+$ calcd for $C_{11}H_{10}F$ 161.0767; found: 161.0761

(1*R*(*S*),4*R*(*S*),9*R*(*S*))-2-(Cyclohexyloxy)-9-fluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3j):



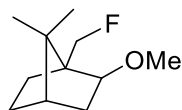
Colorless oil (118 mg, 91%). 1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.18 (m, 1H), 7.18 – 7.09 (m, 3H), 4.65 (d, J = 57.2 Hz, 1H), 3.78-3.66 (m, 1H), 3.52 – 3.39 (m, 2H), 3.37-3.24 (m, 1H), 2.18-2.06 (m, 1H), 2.02 – 1.83 (m, 3H), 1.81 – 1.71 (m, 2H), 1.58 – 1.51 (m, 1H), 1.39 – 1.16 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 (d, J = 7.6 Hz), 139.7 (d, J = 10.6 Hz), 127.2, 126.8, 122.6, 122.1, 98.6 (d, J = 213.8 Hz), 78.3, 77.2, 51.8 (d, J = 16.8 Hz), 46.3 (d, J = 18.3 Hz), 33.6, 32.9, 32.8, 25.7, 24.5, 24.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.00 (d, J = 57.2 Hz). IR (KBr cm^{-1}): 2983, 2935, 2858, 1470, 1358, 1198, 1087, 1059, 903, 729, 652, 522. (TOF MS) m/z (%): $(M+H)^+$ calcd for $C_{17}H_{21}FO$ 261.1649; found: 261.1648.

(1*R*,4*S*)-1-(Fluoromethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol (4a):



Colorless oil (79 mg, 92%). $[\alpha]_D = -5.0$ (c = 1.0, EtOH). 1H NMR (400 MHz, $CDCl_3$) δ 4.79 (dd, J = 47.7, 9.3 Hz, 1H), 4.48 (dd, J = 47.7, 9.3 Hz, 1H), 3.95 (dd, J = 7.9, 3.9 Hz, 1H), 1.80 – 1.70 (m, 4H), 1.27 – 1.20 (m, 2H), 1.12 (s, 3H), 1.08 – 1.04 (m, 1H), 0.97-0.93 (m, 1H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.8 (d, J = 161.9 Hz), 52.9 (d, J = 15.9 Hz), 46.9 (d, J = 7.0 Hz), 46.2, 40.3, 29.4 (d, J = 2.5 Hz), 27.1, 21.1, 20.6 (2C signal overlaps). ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.6 (ddd, J = 293.1, J_{H-F} = 57.3, 55.5 Hz). IR (KBr cm^{-1}): 2966, 2890, 1729, 1453, 1376, 1259, 1083, 1061, 1010, 916, 807, 753, 631, 518. (TOF MS) m/z (%): $(M+Na)^+$ calcd for $C_{10}H_{17}FO$ 195.1156; found: 195.1154.

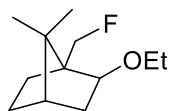
(1*R*,4*S*)-1-(Fluoromethyl)-2-methoxy-7,7-dimethylbicyclo[2.2.1]heptane (4b):



Colorless oil (91mg, 98%). $[\alpha]_D = -4.92$ (c = 1.42, EtOH). 1H NMR (400 MHz, $CDCl_3$) δ 4.71 (dd, J = 47.3, 9.3 Hz, 1H), 4.42 (dd, J = 48.1, 9.3 Hz, 1H), 3.36 (dd, J = 7.6, 3.5 Hz, 1H), 3.24 (s, 3H), 1.82 – 1.62 (m, 5H), 1.26 – 1.15 (m, 2H), 1.04 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.2, 83.9 (d, J = 163.0 Hz), 56.9, 53.0 (d, J = 16.6 Hz), 46.9 (d, J = 6.3 Hz), 46.1, 38.0, 29.4 (d, J = 2.8 Hz), 27.1, 21.2, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.34 (dd, J = 292.6, J_{H-F} = 55.6 Hz). IR (KBr cm^{-1}): 3312, 2961,

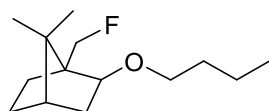
2886, 1653, 1539, 1459, 1369, 1298, 1203, 1099, 981, 914, 729, 649, 592. (TOF MS) m/z (%): [(M-MeOH)+H]⁺ calcd for C₁₀H₁₅F 155.1231; found: 155.1230.

(1*R*,4*S*)-2-Ethoxy-1-(fluoromethyl)-7,7-dimethylbicyclo[2.2.1]heptane (4c):



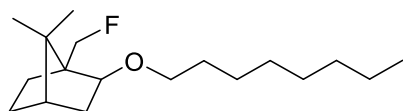
Colorless oil (98 mg, 98%). $[\alpha]_D = -10.34$ ($c = 1.45$, EtOH). ¹H NMR (400 MHz, CDCl₃) δ 4.73 (dd, $J = 47.3, 9.2$ Hz, 1H), 4.42 (dd, $J = 48.2, 9.2$ Hz, 1H), 3.52 – 3.42 (m, 2H), 3.39 – 3.29 (m, 1H), 1.83 – 1.62 (m, 6H), 1.27 – 1.25 (m, 1H), 1.13 (s, 3H), 1.07 (s, 3H), 0.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 84.1 (d, $J = 2.6$ Hz), 84.1 (d, $J = 162.7$ Hz), 64.8, 52.9 (d, $J = 16.4$ Hz), 46.9 (d, $J = 6.2$ Hz), 46.2, 38.9, 29.3 (d, $J = 2.8$ Hz), 27.1, 21.3, 20.6, 15.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -126.99 (ddd, $J = 290.8, J_{H-F} = 57.8, 54.5$ Hz). IR (KBr cm⁻¹): 2962, 2885, 1724, 1684, 1643, 1463, 1377, 1268, 1178, 1110, 1092, 1007, 989, 803. (TOF MS) m/z (%): [(M-EtOH)+H]⁺ calcd for C₁₀H₁₅F 155.1231; found: 155.1229.

(1*R*,4*S*)-2-Butoxy-1-(fluoromethyl)-7,7-dimethylbicyclo[2.2.1]heptane (4d):



Colorless oil (109 mg, 96%). $[\alpha]_D = -7.07$ ($c = 0.99$, EtOH). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.73 (dd, $J = 47.3, 9.2$ Hz, 1H), 4.42 (dd, $J = 48.2, 9.2$ Hz, 1H), 3.44 – 3.37 (m, 2H), 3.28-3.23(m, 1H), 1.82 – 1.68 (m, 5H), 1.64 – 1.58 (m, 2H), 1.51 – 1.43 (m, 2H), 1.37 – 1.33 (m, 2H), 1.06 (s, 3H), 0.92 – 0.87 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 84.2, 84.1 (d, $J = 162.3$ Hz), 69.0, 52.9 (d, $J = 16.4$ Hz), 46.9 (d, $J = 6.1$ Hz), 46.1, 38.7, 32.3, 29.2 (d, $J = 2.8$ Hz), 27.1, 21.3, 20.6, 19.7, 14.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -123.43 (dd, $J = 290.3, 55.0$ Hz), -127.01 (ddd, $J = 289.8, J_{H-F} = 60.3, 55.0$ Hz), -130.59 (dd, $J = 289.9, 60.3$ Hz). IR (KBr cm⁻¹): 2958, 2939, 2874, 1728, 1464, 1377, 1187, 1099, 984, 804. (TOF MS) m/z (%): (M+Na)⁺ calcd for C₁₄H₂₅FO 251.1782; found: 251.1832.

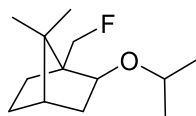
(1*R*,4*S*)-1-(Fluoromethyl)-7,7-dimethyl-2-(octyloxy)bicyclo[2.2.1]heptane (4e):



Colorless oil (134 mg, 95%). $[\alpha]_D = -6.97$ ($c = 1.29$, EtOH). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.73 (dd, $J = 47.3, 9.2$ Hz, 1H), 4.43 (dd, $J = 48.2, 9.2$ Hz, 1H), 3.48 – 3.35 (m, 2H), 3.32 – 3.18 (m, 1H), 1.84 – 1.46 (m, 9H), 1.31 – 1.25 (m, 10H), 1.06 (s, 3H), 0.92 – 0.84 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 84.3 (d, $J = 2.9$ Hz), 84.0, (d, $J = 163.0$ Hz), 69.4, 52.9 (d, $J = 16.5$ Hz), 46.9 (d, $J = 5.9$ Hz), 46.2, 38.8, 32.0, 30.2, 29.6, 29.5, 29.3 (d, $J = 2.9$ Hz), 27.1, 26.5, 22.8, 21.3, 20.6, 14.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -127.00 (ddd, $J = 291.2, J_{H-F} = 57.6, 54.7$ Hz). IR (KBr cm⁻¹): 2925, 2846,

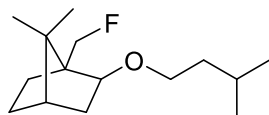
1455, 1371, 1185, 1096, 988. (TOF MS) m/z (%): $(M+Na)^+$ calcd for $C_{18}H_{35}FO$ 309.2564; found: 309.2573.

(1*R*,4*S*)-1-(Fluoromethyl)-2-isopropoxy-7,7-dimethylbicyclo[2.2.1]heptane (4f):



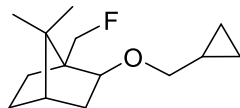
Colorless oil (103 mg, 97%). $[\alpha]_D = -10.32$ ($c = 1.55$, EtOH). 1H NMR (101 MHz, $CDCl_3$) δ 4.72 (dd, $J = 47.3, 9.1$ Hz, 1H), 4.40 (dd, $J = 48.2, 9.1$ Hz, 1H), 3.55 – 3.47 (m, 2H), 1.87 – 1.60 (m, 6H), 1.10 – 1.05 (m, 9H), 0.89 (s, 3H), 0.88 – 0.86 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.3 (d, $J = 162.4$ Hz), 81.9 (d, $J = 2.5$ Hz), 70.9, 52.7 (d, $J = 16.3$ Hz), 47.0 (d, $J = 6.8$ Hz), 46.2, 40.2, 29.3 (d, $J = 2.7$ Hz), 27.1, 23.4, 22.3, 21.3, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.31 (ddd, $J = 288.7, J_{H-F} = 58.1, 53.7$ Hz). IR (KBr cm^{-1}): 3418, 2958, 2932, 2871, 1721, 1454, 1381, 1122, 1075, 978. (TOF MS) m/z (%): $[(M-C_3H_7OH)+H]^+$ calcd for $C_{10}H_{15}F$ 155.1231; found: 155.1229.

(1*R*,4*S*)-1-(Fluoromethyl)-2-(isopentyloxy)-7,7-dimethylbicyclo[2.2.1]heptane (4g):



Colorless oil (110 mg, 91%). $[\alpha]_D = -7.25$ ($c = 1.24$, EtOH). 1H NMR (101 MHz, $CDCl_3$) δ 4.72 (dd, $J = 47.3, 9.1$ Hz, 1H), 4.42 (dd, $J = 48.2, 9.2$ Hz, 1H), 3.45 – 3.40 (m, 2H), 3.31 – 3.23 (m, 1H), 1.81 – 1.63 (m, 7H), 1.43 – 1.35 (m, 3H), 1.06 (s, 3H), 0.90 – 0.87 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.3 (d, $J = 3.0$ Hz), 84.1 (d, $J = 162.6$ Hz), 67.6, 52.9 (d, $J = 16.7$ Hz), 46.2, 39.1, 38.7, 29.3, 29.2, 27.1, 25.2, 22.8, 22.7, 21.3, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.01 (ddd, $J = 291.5, J_{H-F} = 60.7, 57.6$ Hz). IR (KBr cm^{-1}): 2960, 2937, 2872, 1731, 1462, 1365, 1259, 1189, 1088, 977, 805. (TOF MS) m/z (%): $[(M-C_5H_{10}OH)+H]^+$ calcd for $C_{10}H_{15}F$ 155.1231; found: 155.1230.

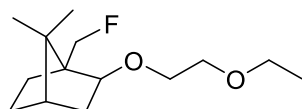
(1*R*,4*S*)-2-(Cyclopropylmethoxy)-1-(fluoromethyl)-7,7-dimethylbicyclo[2.2.1]heptane (4h):



Colorless oil (100 mg, 90%). $[\alpha]_D = -5.71$ ($c = 0.7$, EtOH). 1H NMR (101 MHz, $CDCl_3$) δ 4.73 (dd, $J = 47.3, 9.2$ Hz, 1H), 4.42 (dd, $J = 48.2, 9.2$ Hz, 1H), 3.45 (dd, $J = 7.7, 3.5$ Hz, 1H), 3.21 (dd, $J = 6.4, 1.5$ Hz, 2H), 1.81 – 1.67 (m, 4H), 1.63 – 1.58 (m, 1H), 1.27 – 1.22 (m, 1H), 1.07 (s, 3H), 1.04 (s, 1H), 0.93 (s, 1H), 0.89 (s, 3H), 0.46 – 0.42 (m, 2H), 0.19 – 0.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.0 (d, $J = 162.9$ Hz), 83.9 (d, $J = 2.8$ Hz), 73.6, 52.9 (d, $J = 16.4$ Hz), 46.9 (d, $J = 5.7$ Hz), 46.1, 38.8, 29.3 (d, $J = 2.9$ Hz), 27.1, 23.9, 23.1, 21.2, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.98 (ddd, $J = 292.1, J_{H-F} = 58.9, 53.5$ Hz). IR (KBr cm^{-1}): 3081, 2957, 2884, 1463, 1391, 1189, 1089, 1022, 974,

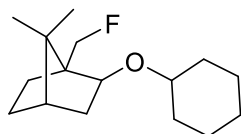
820. (TOF MS) m/z (%): $[(M-C_4H_7OH)+H]^+$ calcd for $C_{10}H_{15}F$ 155.1231; found: 155.1230.

(1*R*,4*S*)-2-(2-Ethoxyethoxy)-1-(fluoromethyl)-7,7-dimethylbicyclo[2.2.1]heptane (4i):



Colorless oil (112 mg, 94%). $[\alpha]_D = -2.42$ ($c = 1.24$, EtOH). 1H NMR (101 MHz, $CDCl_3$) δ 4.73 (dd, $J = 47.2, 9.2$ Hz, 1H), 4.41 (dd, $J = 48.2, 9.2$ Hz, 1H), 3.62 – 3.40 (m, 7H), 1.88– 1.56 (m, 6H), 1.17 (t, $J = 7.0$ Hz, 4H), 1.05 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.7 (d, $J = 2.5$ Hz), 83.9 (d, $J = 162.9$ Hz), 70.1, 69.0, 66.7, 52.9 (d, $J = 16.8$ Hz), 46.1, 38.6, 29.20, 29.17, 27.0, 21.2, 20.6, 15.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.86 (ddd, $J = 353.6, 292.7, J_{H-F} = 60.3, 57.4$ Hz). IR (KBr cm^{-1}): 2950, 2882, 1463, 1404, 1188, 1105, 977, 843. (TOF MS) m/z (%): $[(M-C_4H_{10}O_2)+H]^+$ calcd for $C_{10}H_{15}F$ 155.1231; found: 155.1231.

(1*R*,4*S*)-2-(Cyclohexyloxy)-1-(fluoromethyl)-7,7-dimethylbicyclo[2.2.1]heptane (4j):

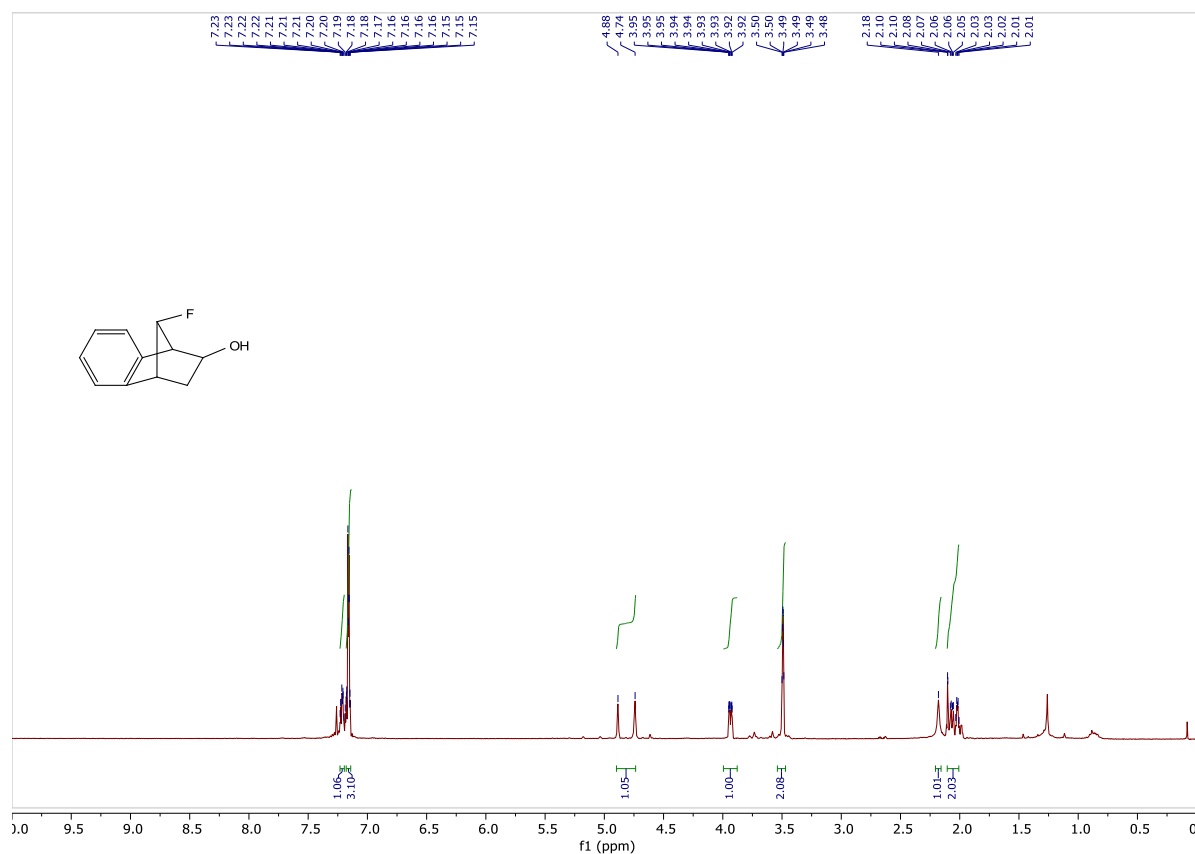


Colorless oil (76 mg, 60%). $[\alpha]_D = -3.42$ ($c = 1.49$, EtOH). 1H NMR (101 MHz, $CDCl_3$) δ 4.74 (dd, $J = 47.3, 9.1$ Hz, 1H), 4.41 (dd, $J = 48.2, 9.1$ Hz, 1H), 3.54 (dd, $J = 7.7, 3.5$ Hz, 1H), 3.29-3.20 (m, 1H), 1.83 – 1.65 (m, 10H), 1.31 – 1.21 (m, 7H), 1.09 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.3 (d, $J = 162.5$ Hz), 81.9 (d, $J = 2.9$ Hz), 76.6, 52.8 (d, $J = 16.5$ Hz), 47.0 (d, $J = 6.3$ Hz), 46.4, 40.2, 33.6, 32.1, 29.3 (d, $J = 2.8$ Hz), 27.2, 26.1, 24.00, 23.98, 21.3, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.26 (ddd, $J = 290.5, 60.0, 54.7$ Hz). IR (KBr cm^{-1}): 2933, 2891, 2864, 1733, 1457, 1393, 1374, 1186, 1080, 979. (TOF MS) m/z (%): $(M+Na)^+$ calcd for $C_{16}H_{27}FO$ 277.1938; found: 277.1936.

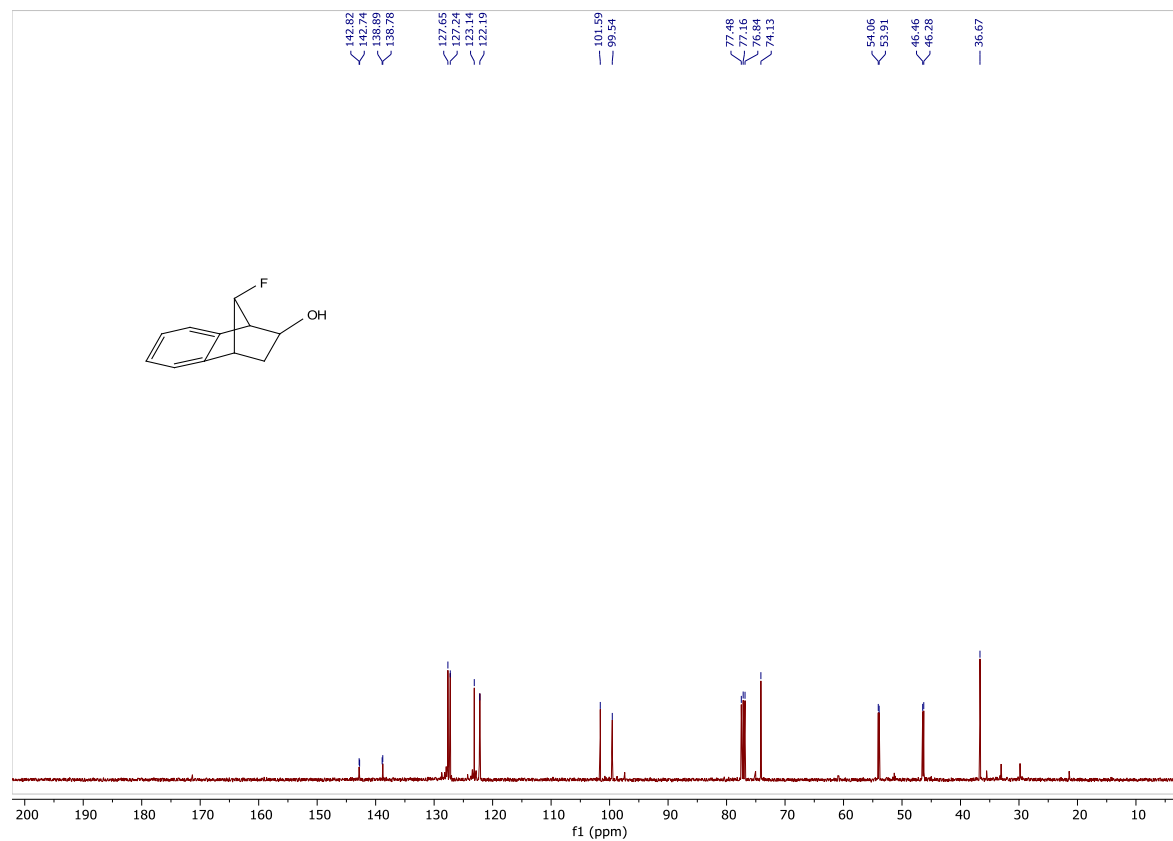
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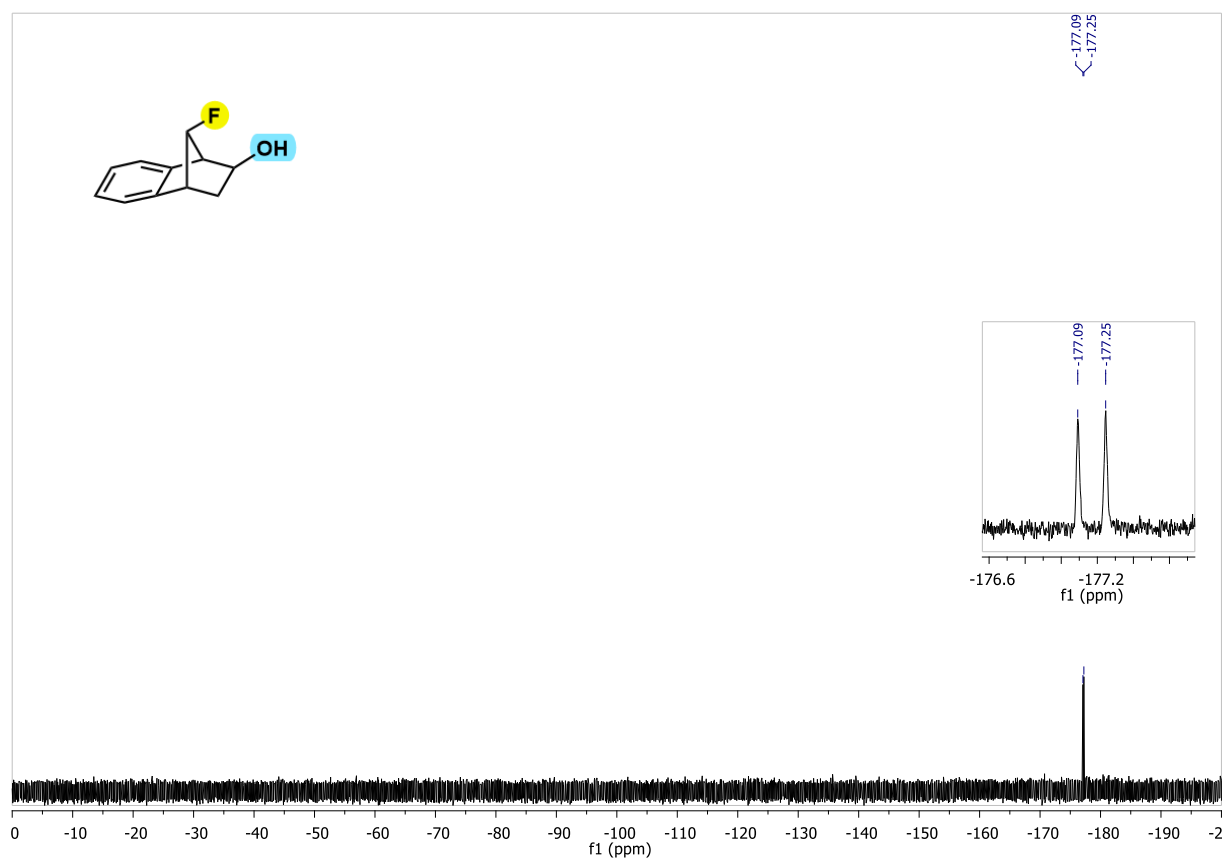
¹H NMR, ¹³C NMR, ¹⁹F NMR, and HRMS Spectra



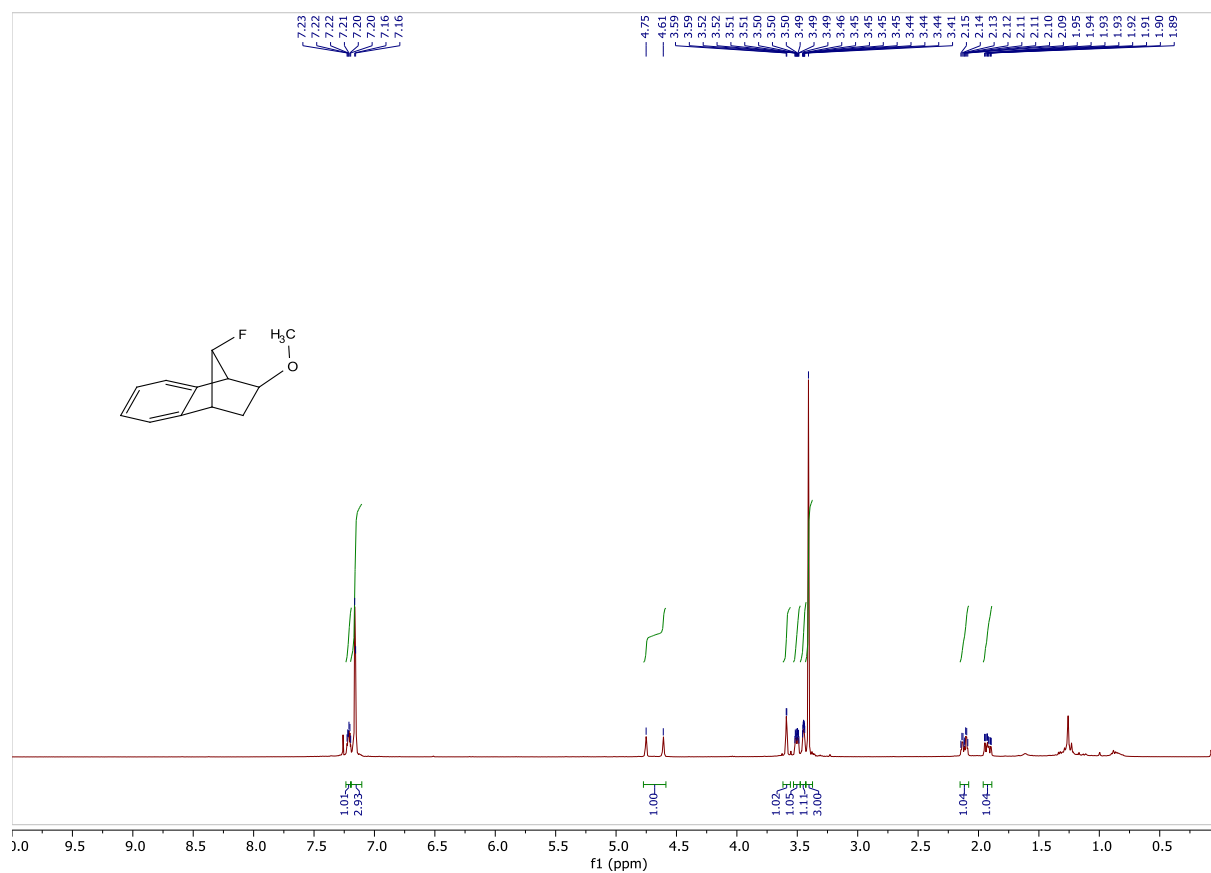
400 MHz ¹H-NMR spectrum of **3a** (CDCl₃)



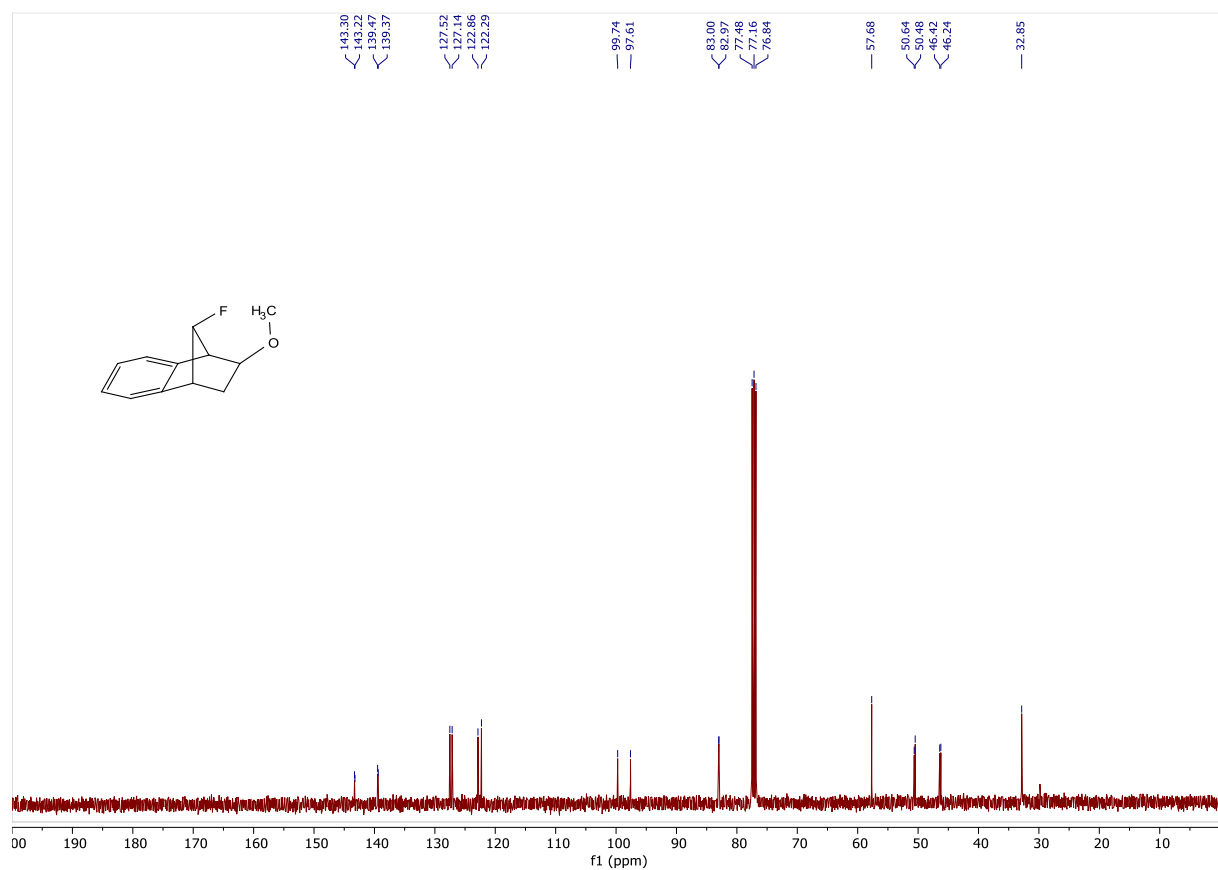
101 MHz ¹³C-NMR spectrum of **3a** (CDCl₃)



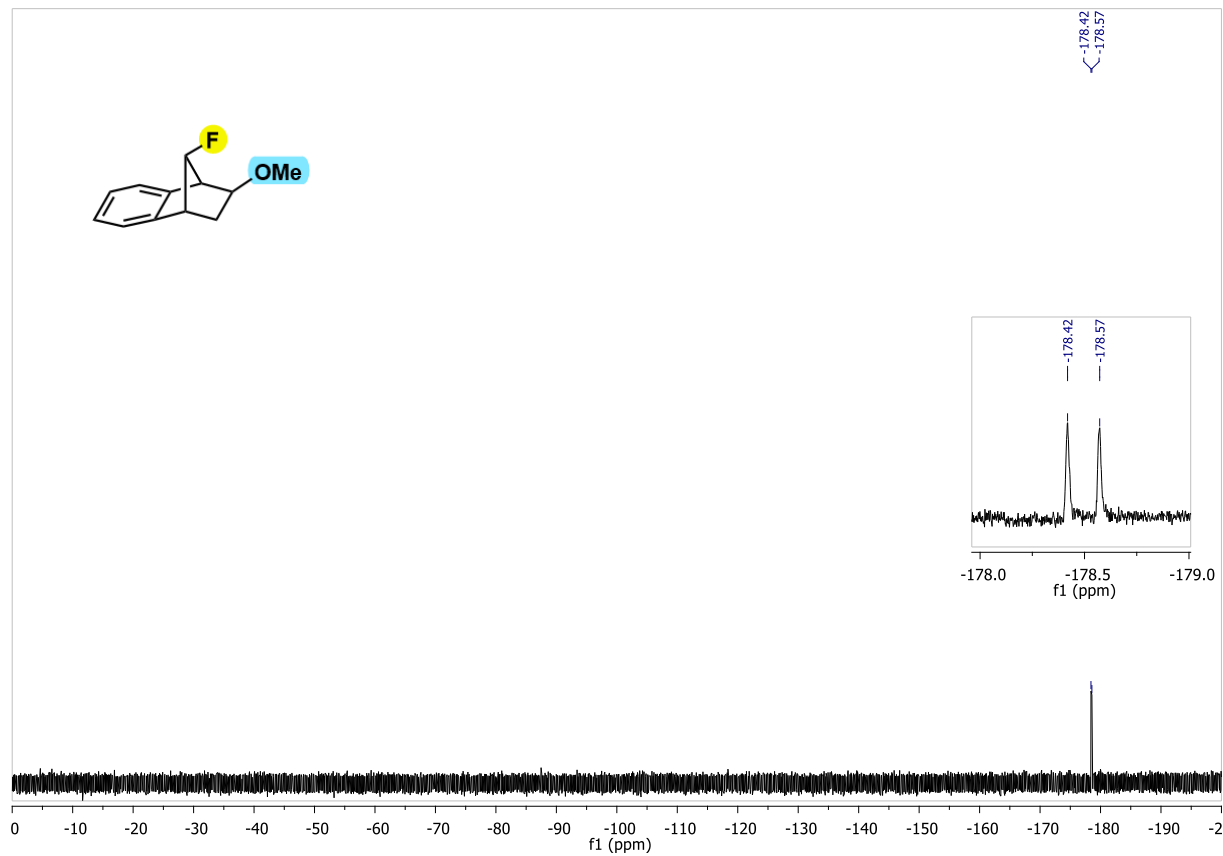
376 MHz ^{19}F -NMR spectrum of **3a** (CDCl_3)



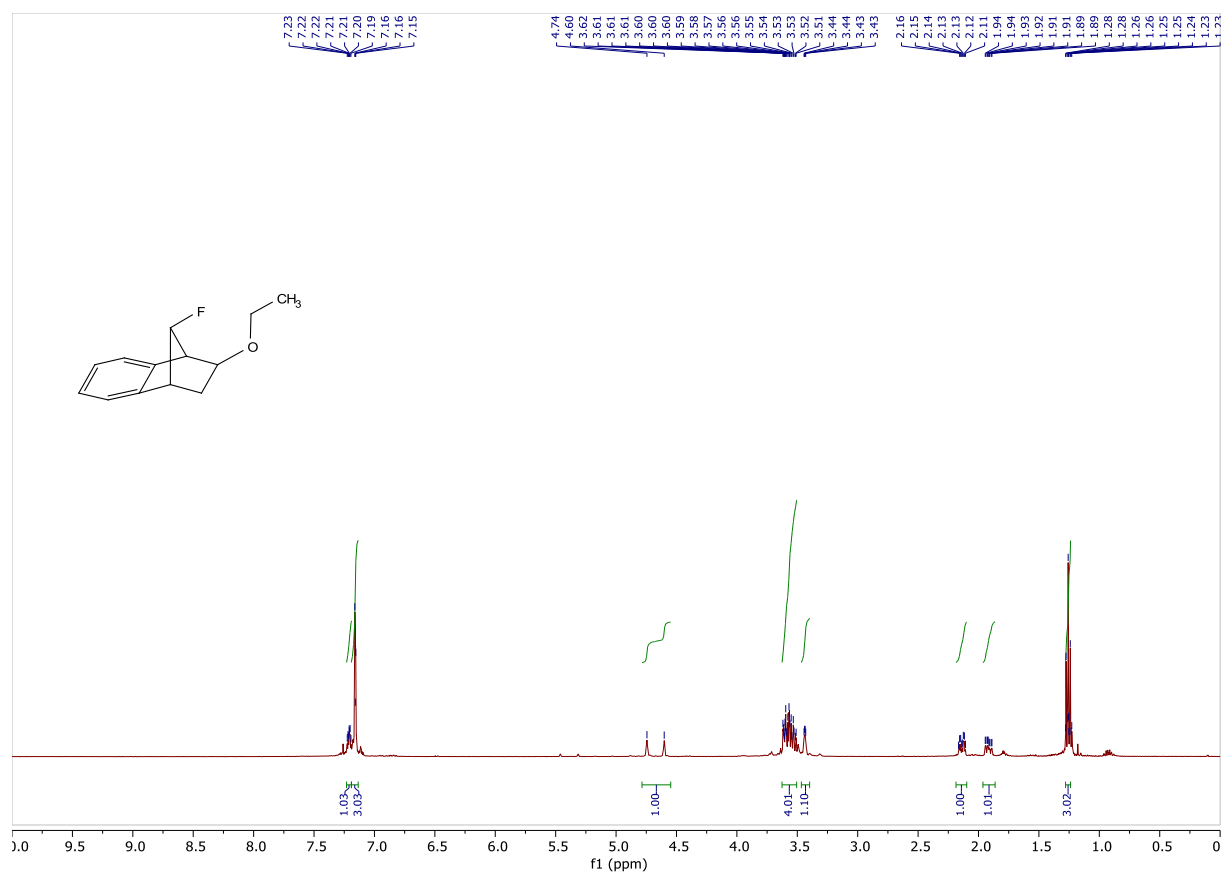
400 MHz ^1H -NMR spectrum of **3b** (CDCl_3)



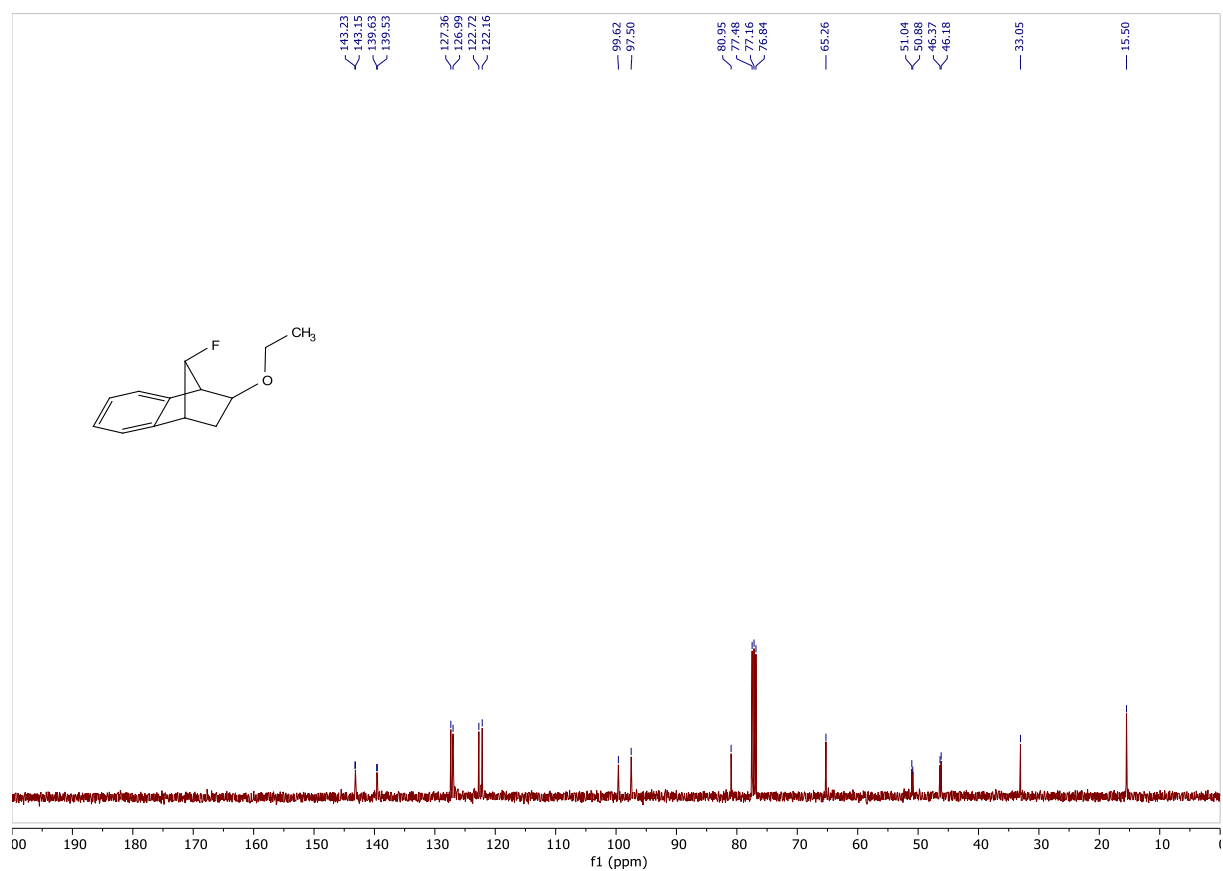
101 MHz ^{13}C -NMR spectrum of **3b** (CDCl_3)



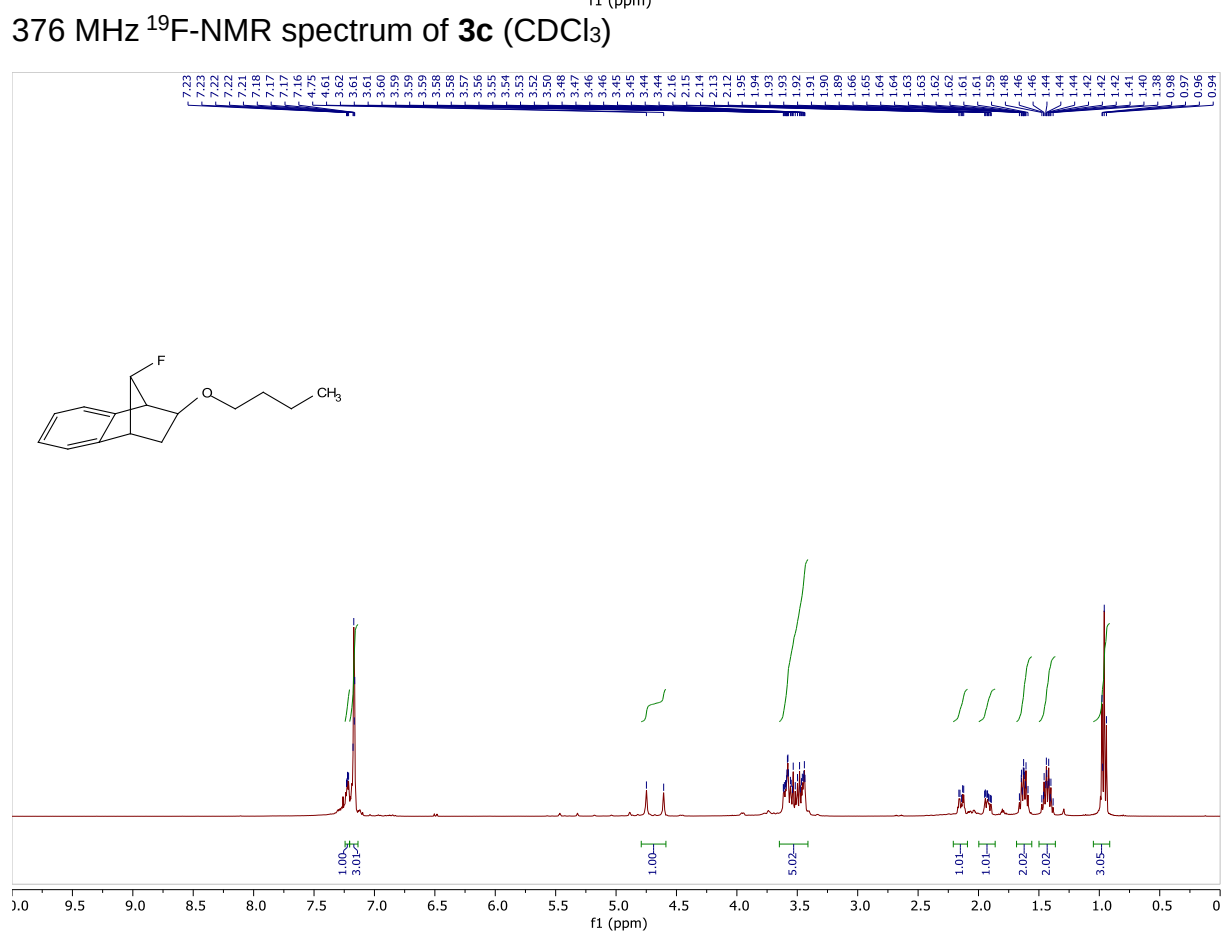
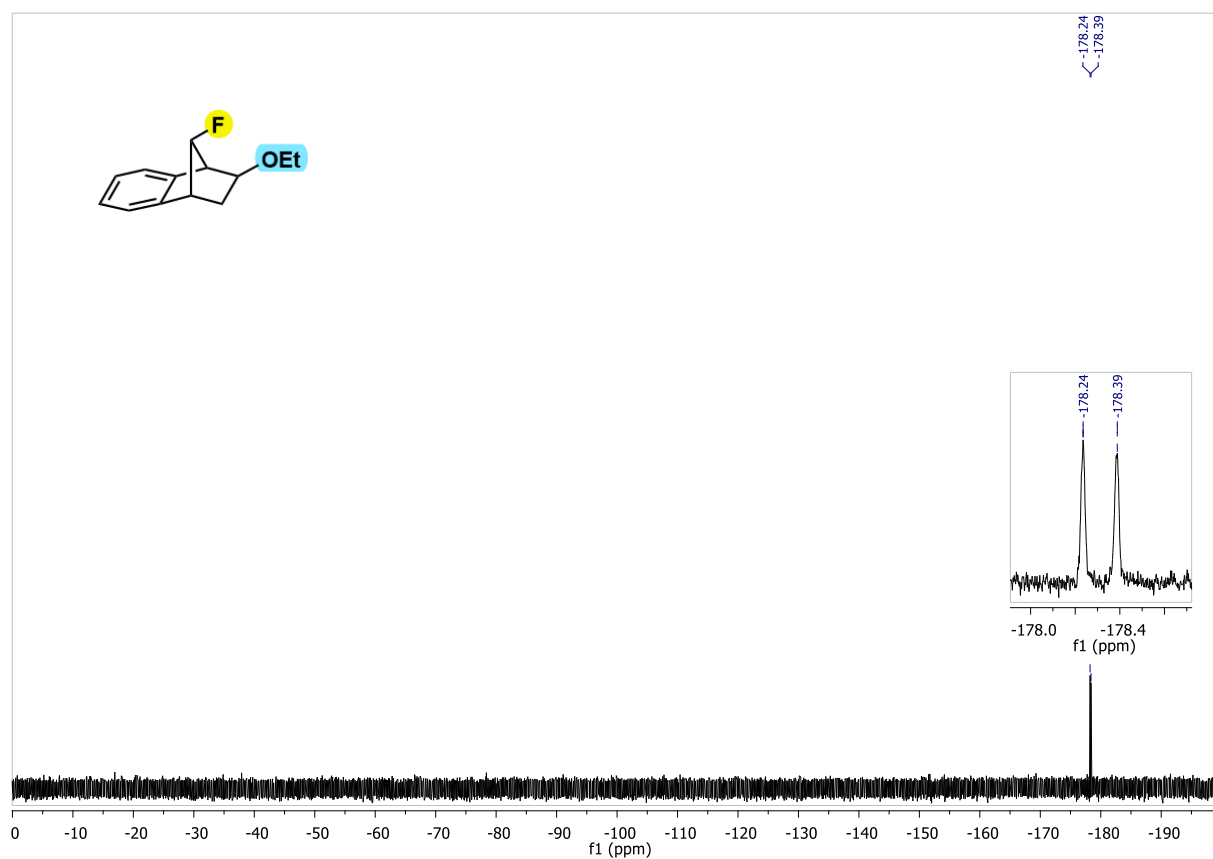
376 MHz ^{19}F -NMR spectrum of **3b** (CDCl_3)



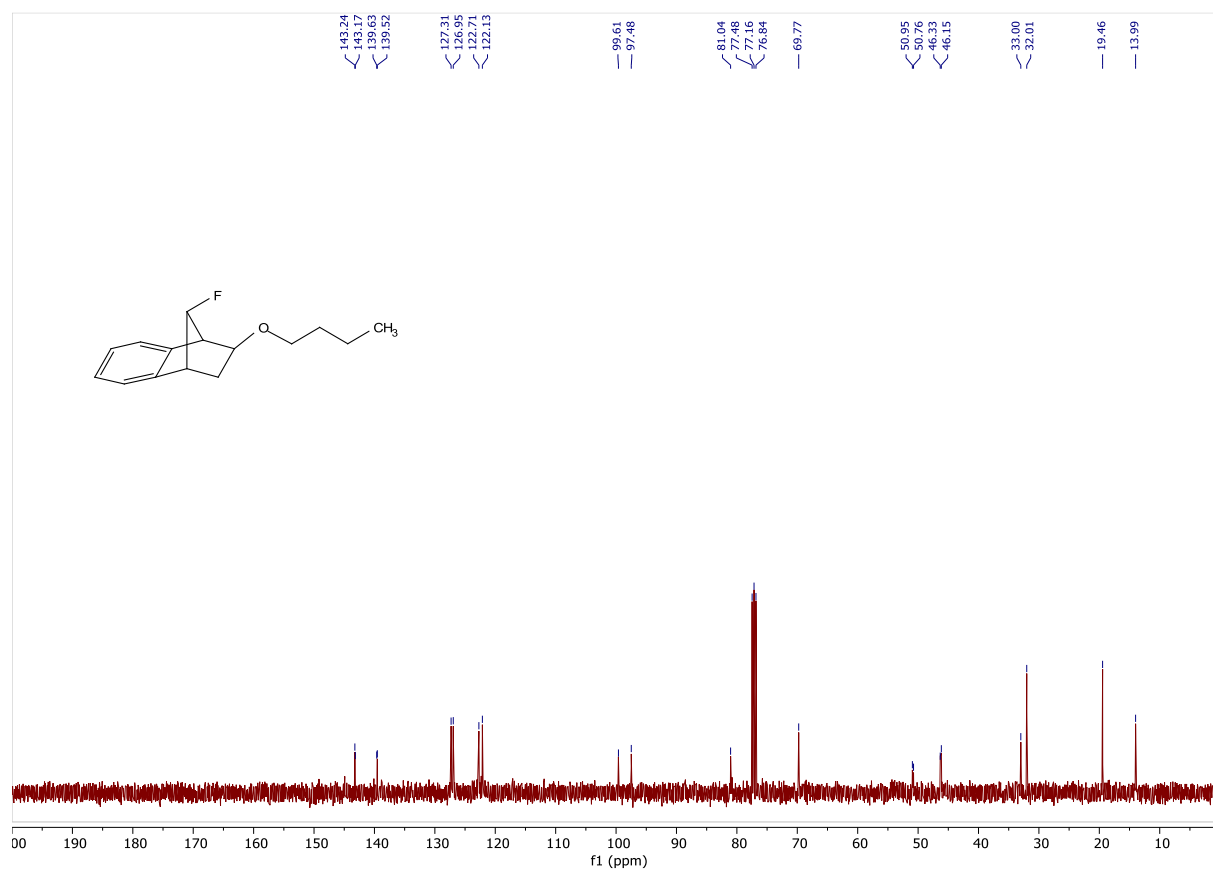
400 MHz ^1H -NMR spectrum of **3c** (CDCl_3)



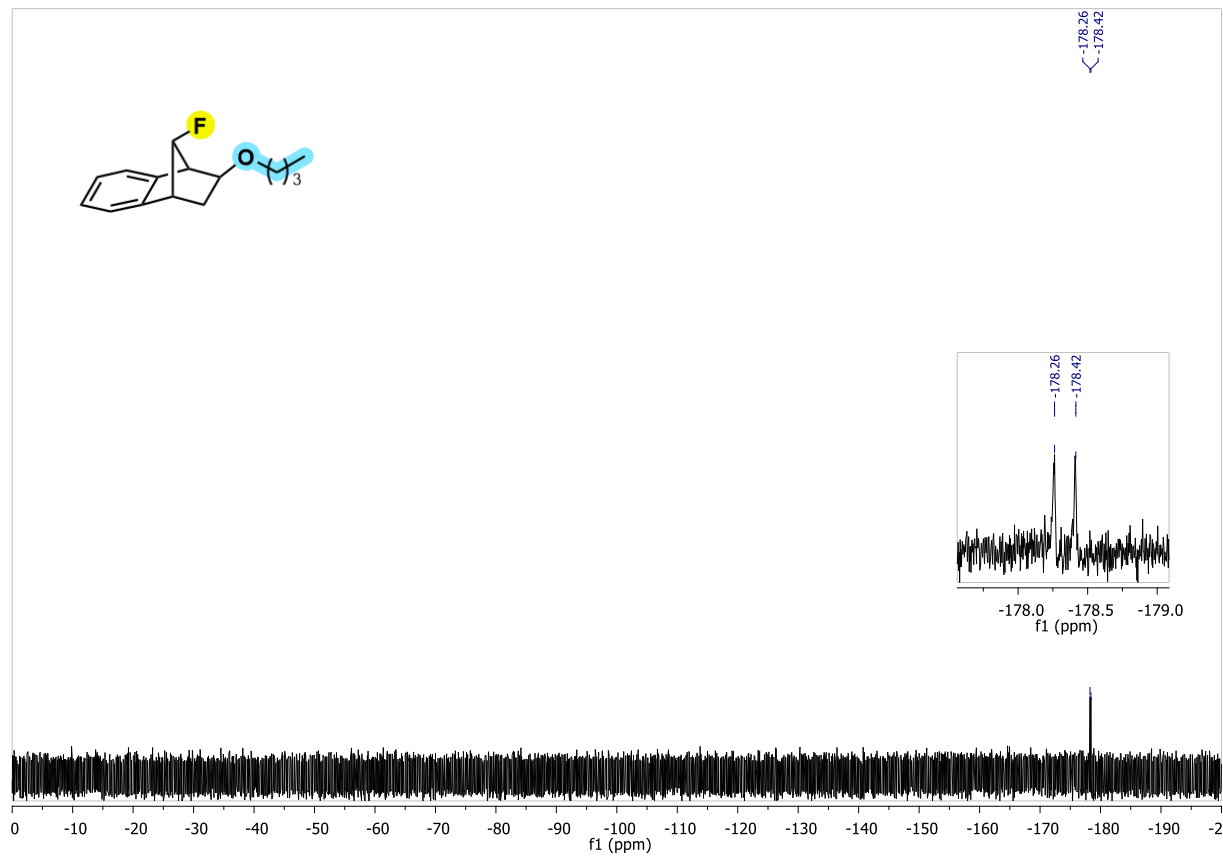
101 MHz ^{13}C -NMR spectrum of **3c** (CDCl_3)



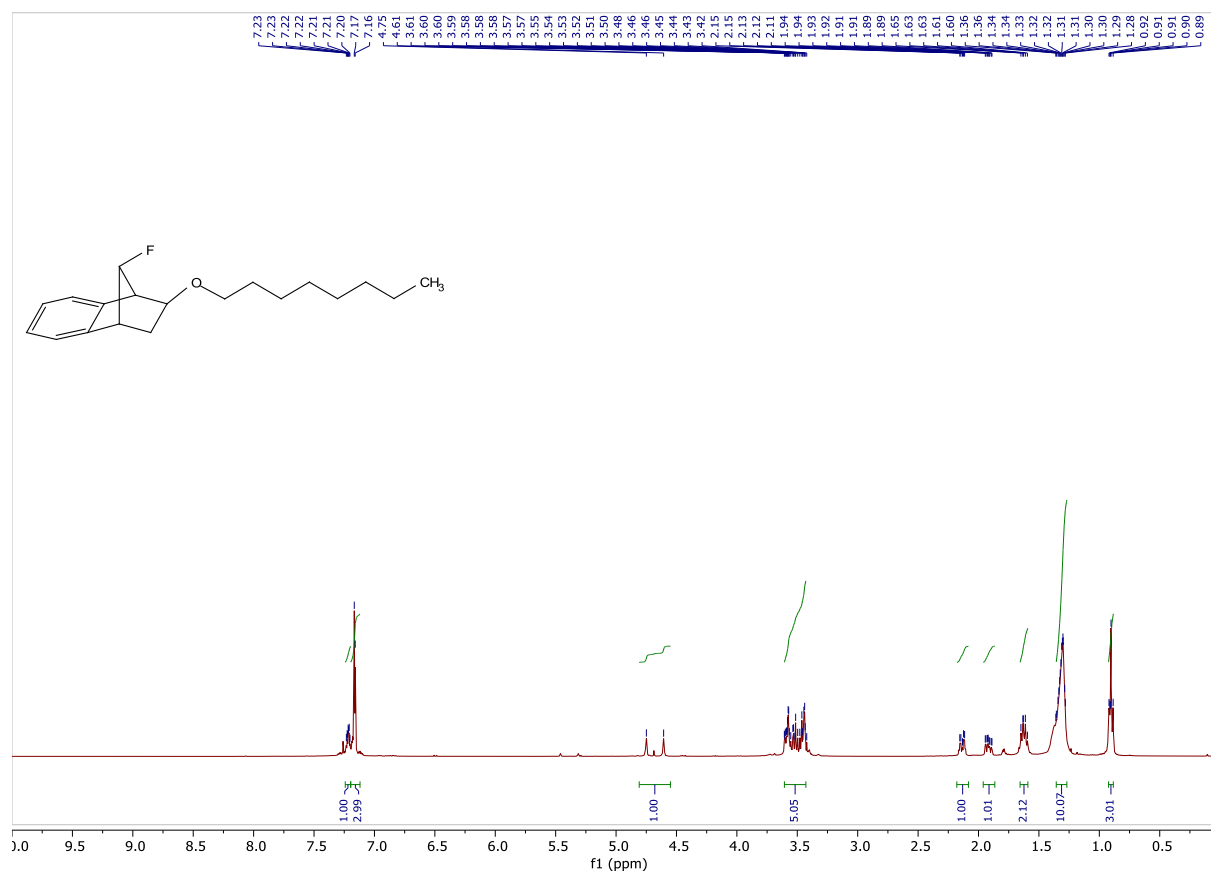
400 MHz ^1H -NMR spectrum of **3d** (CDCl_3)



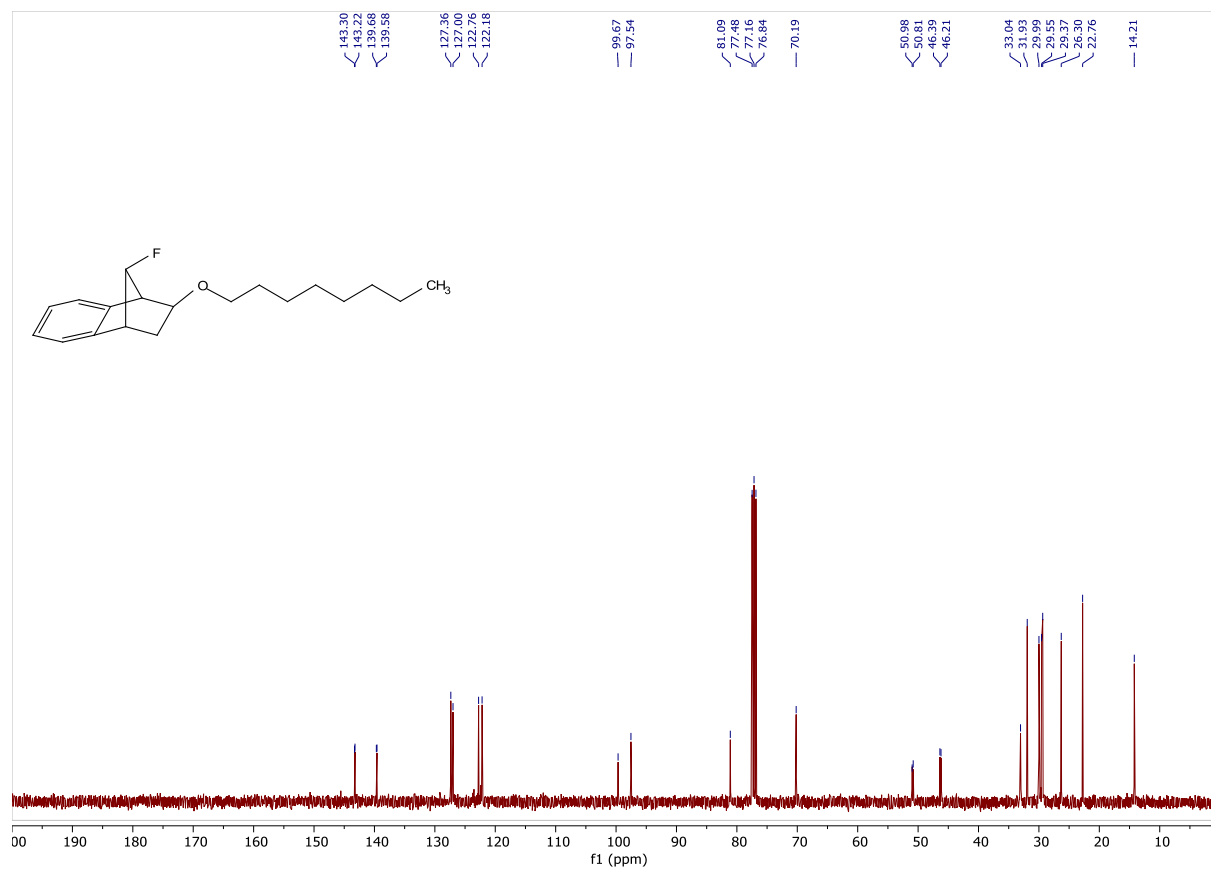
101 MHz ¹³C-NMR spectrum of **3d** (CDCl₃)



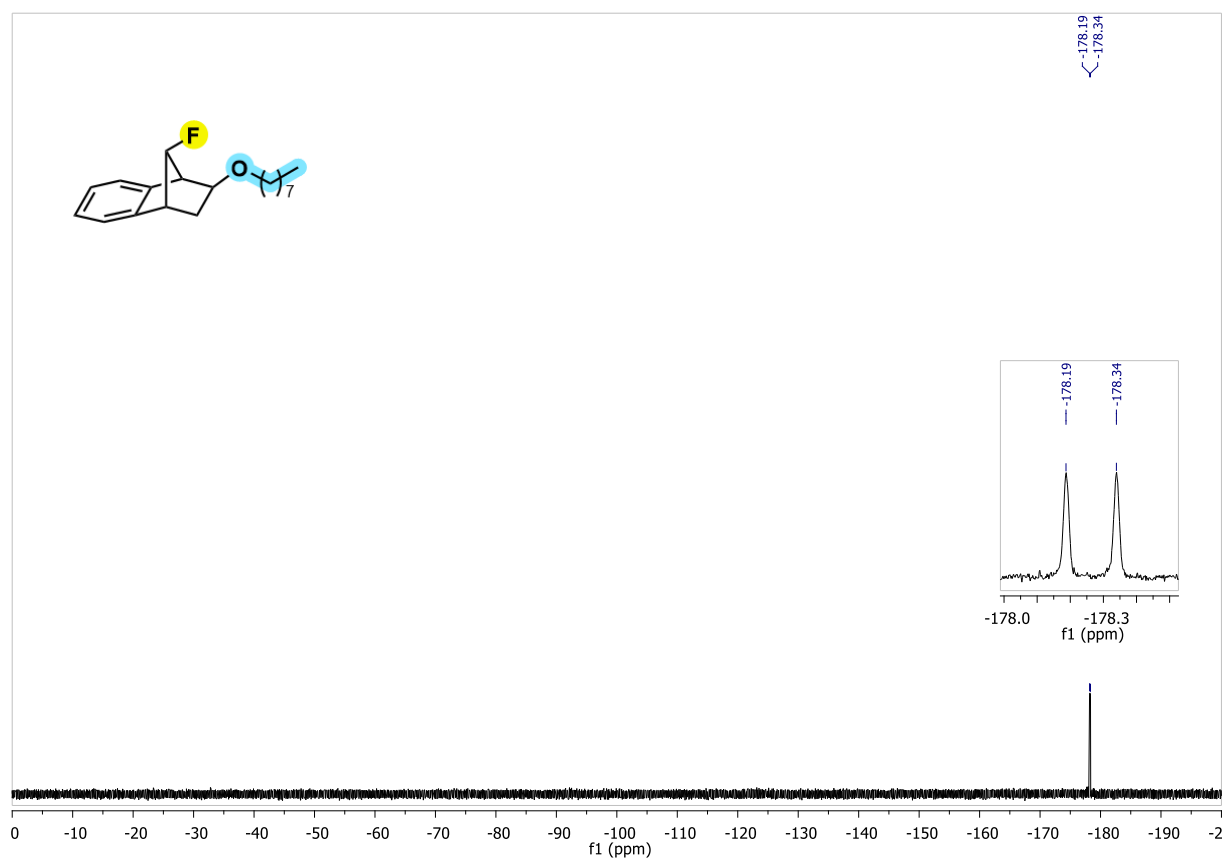
376 MHz ¹⁹F-NMR spectrum of **3d** (CDCl₃)



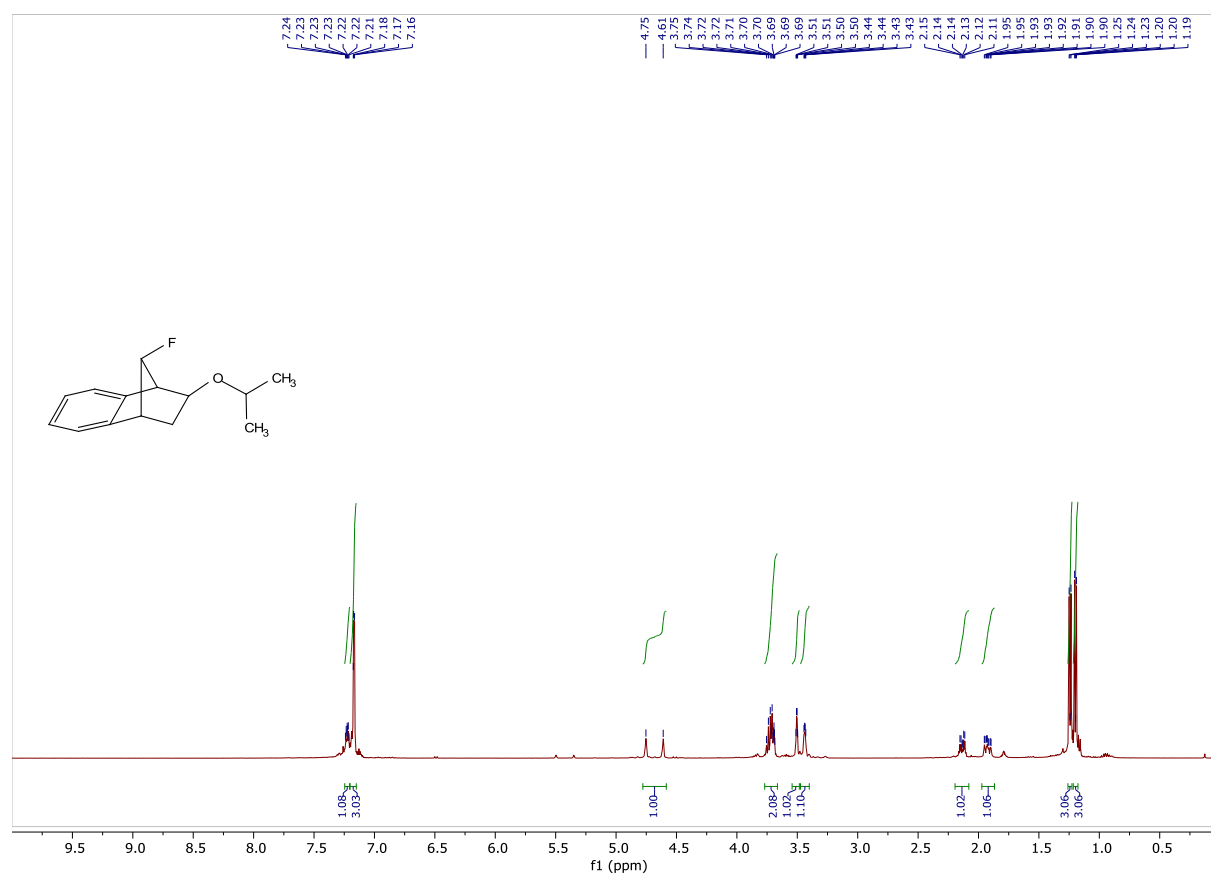
400 MHz ¹H-NMR spectrum of **3e** (CDCl₃)



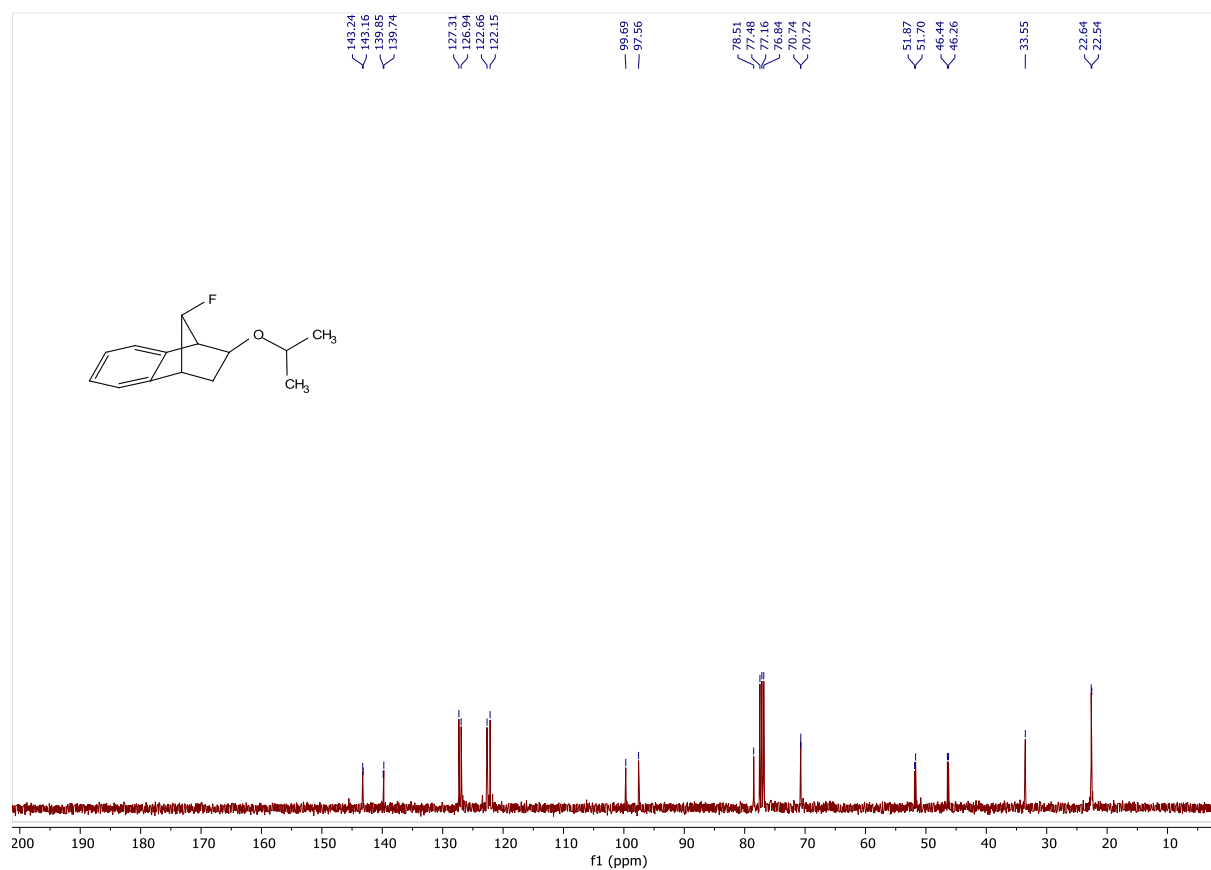
101 MHz ¹³C-NMR spectrum of **3e** (CDCl₃)



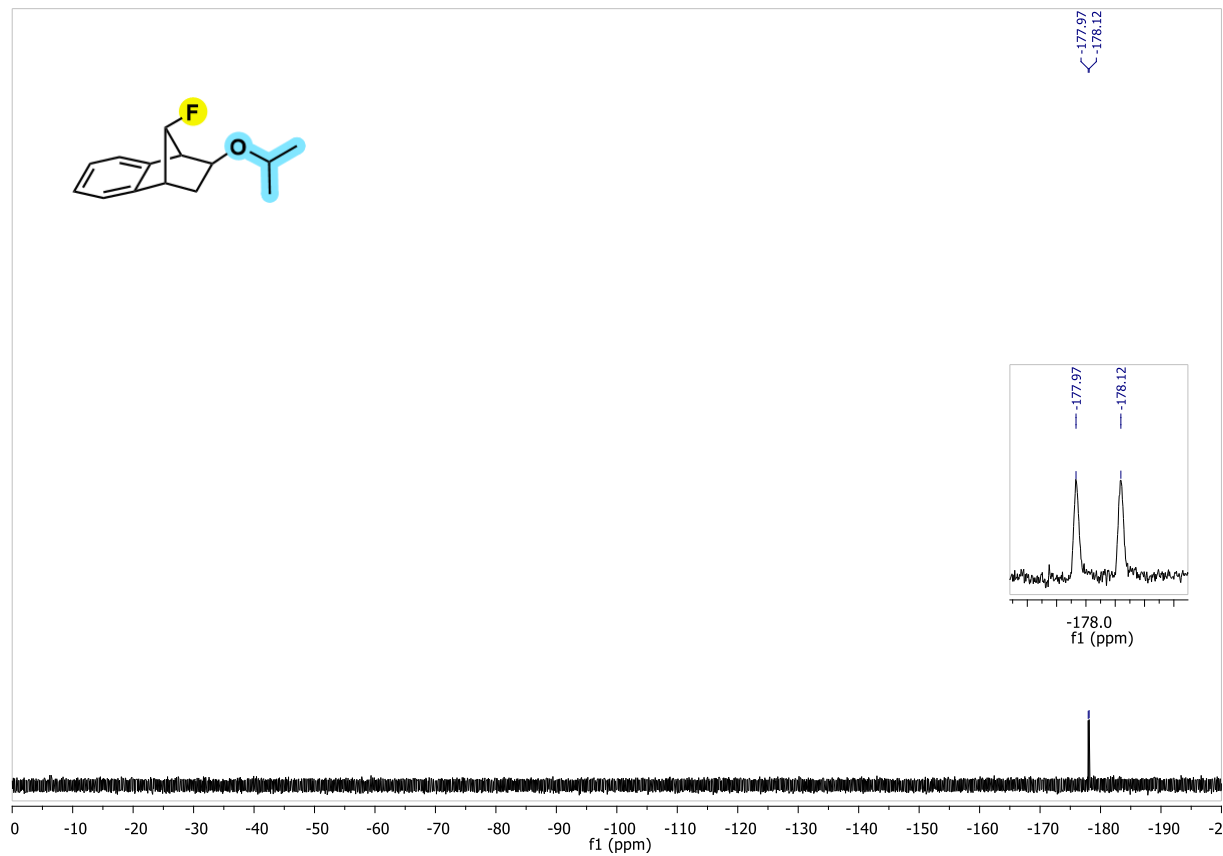
376 MHz ^{19}F -NMR spectrum of **3e** (CDCl_3)



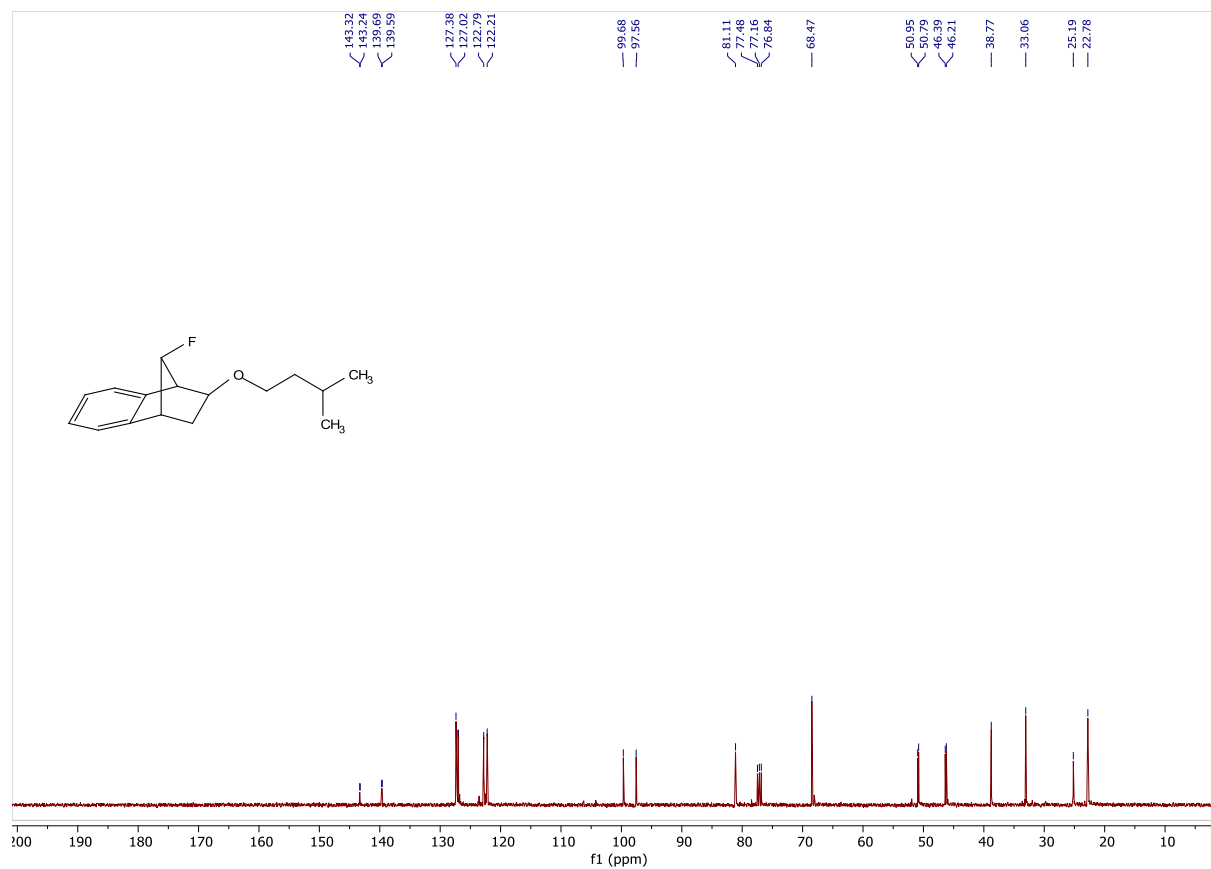
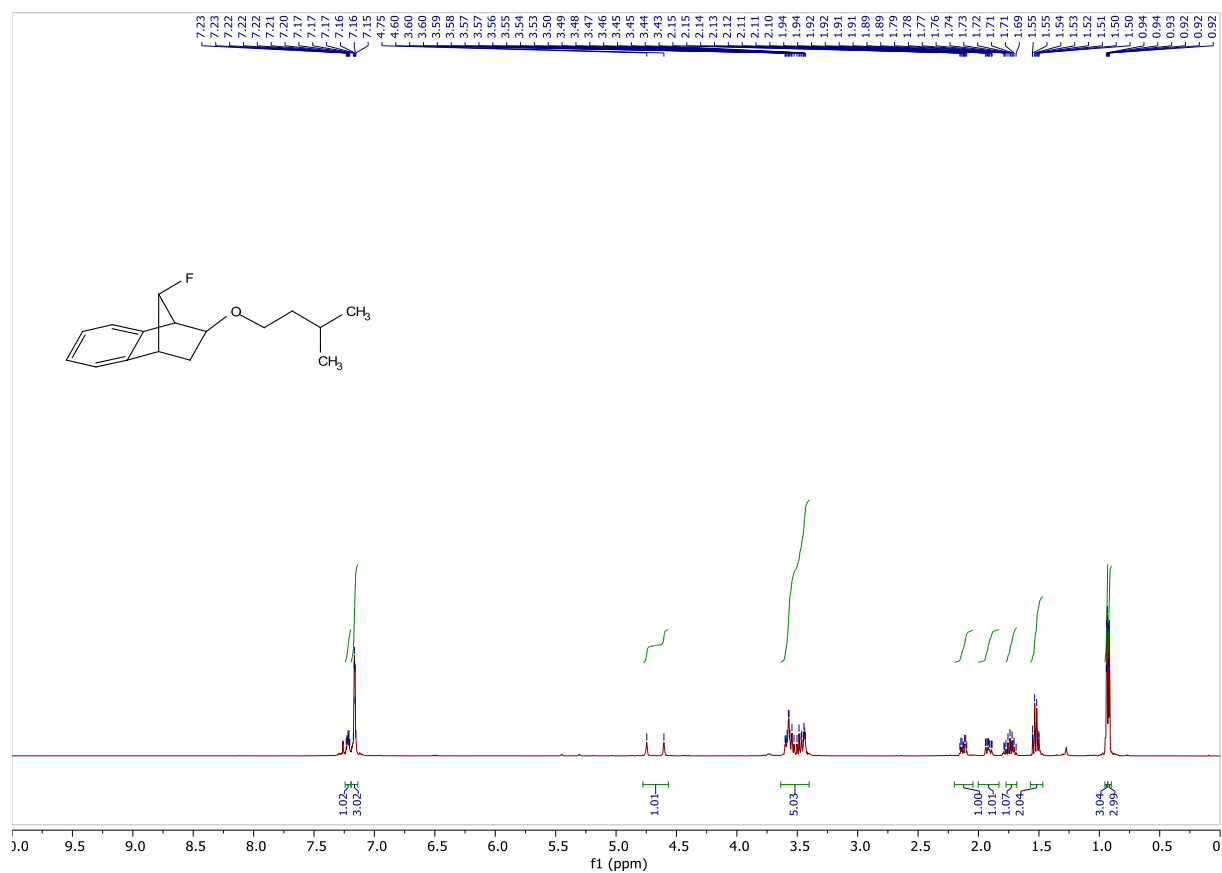
400 MHz ^1H -NMR spectrum of **3f** (CDCl_3)

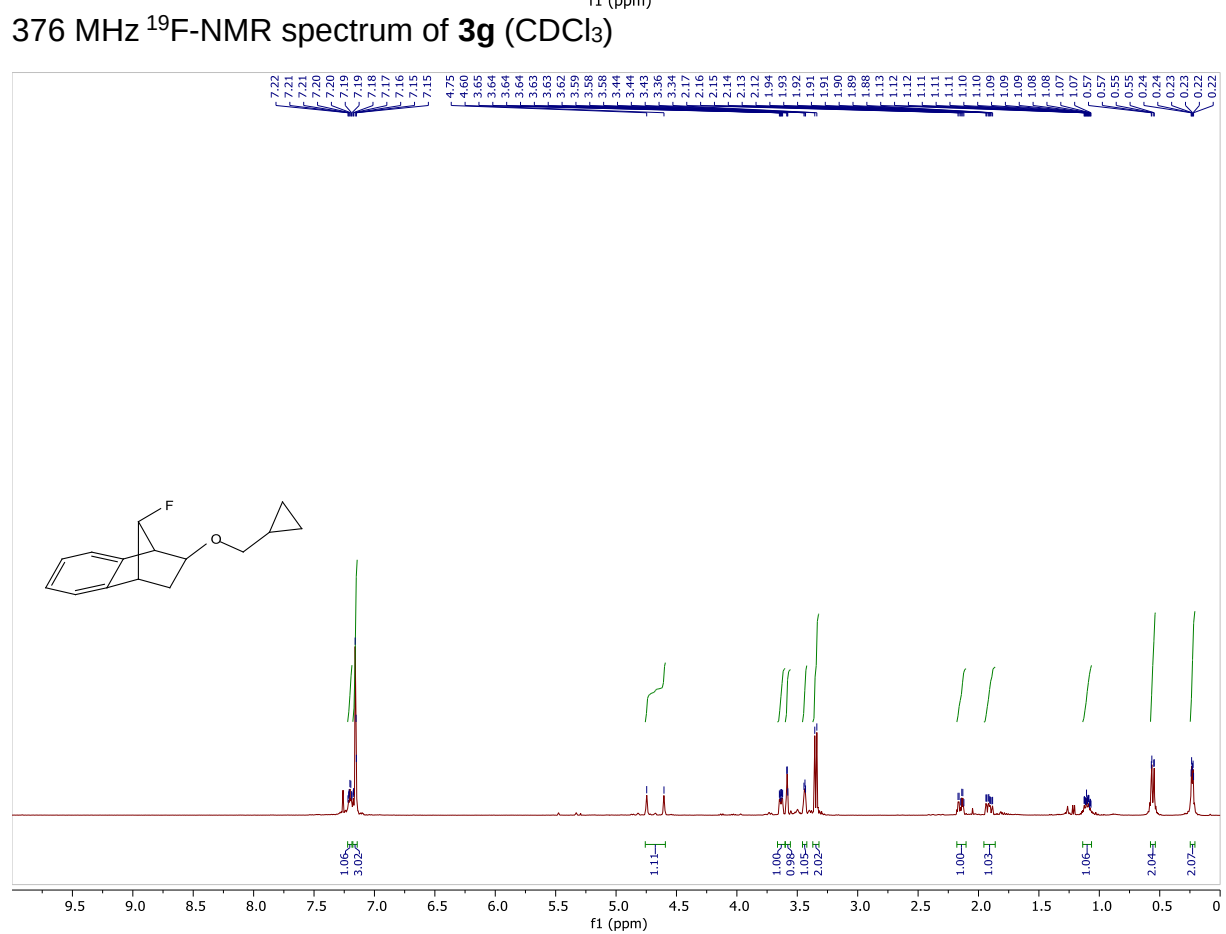
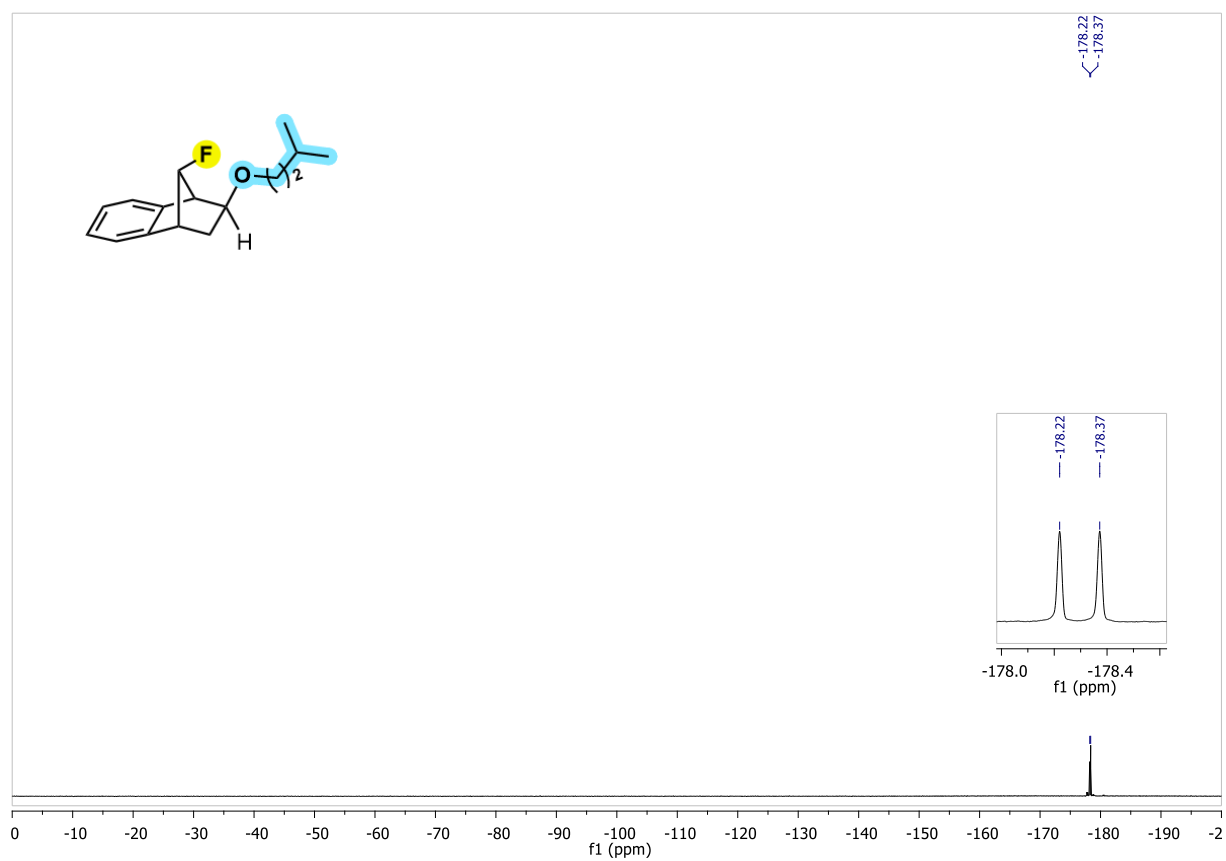


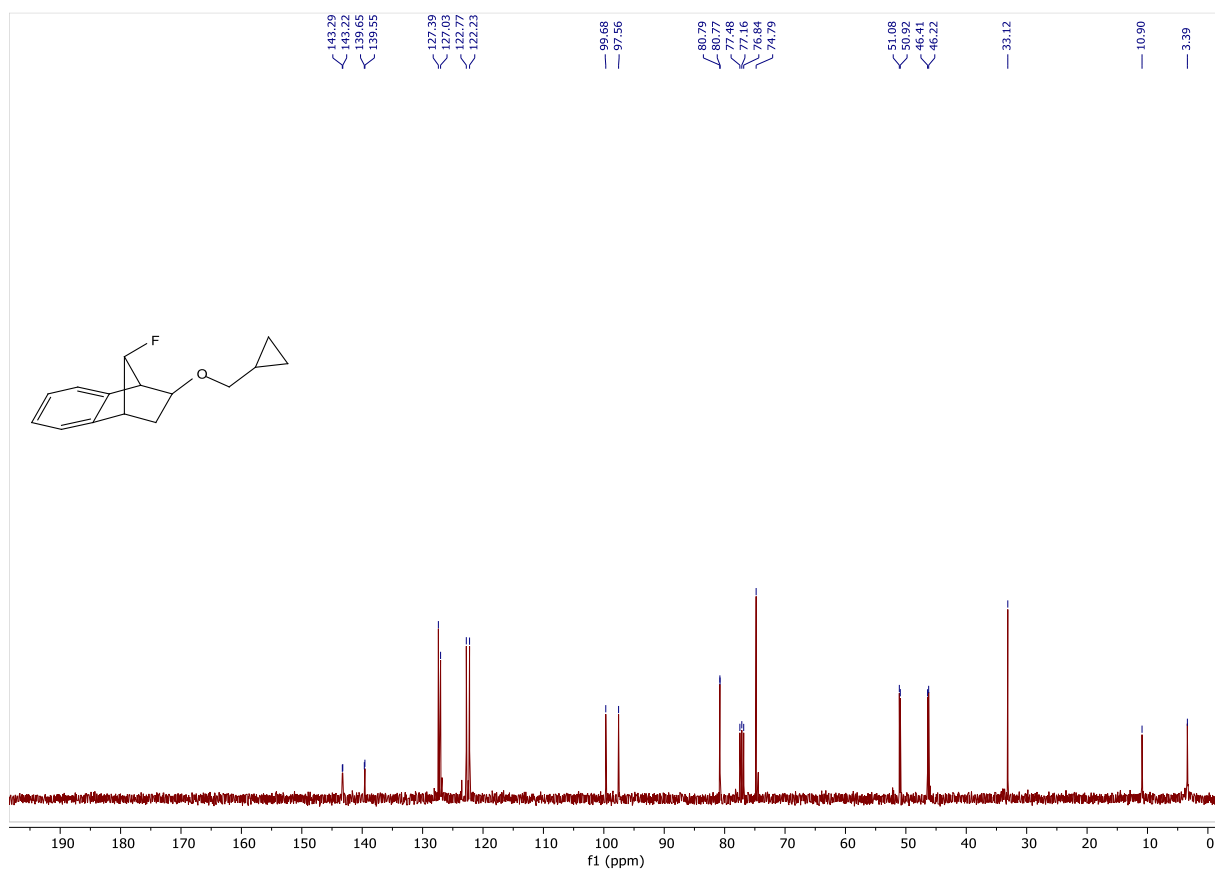
101 MHz ¹³C-NMR spectrum of **3f** (CDCl₃)



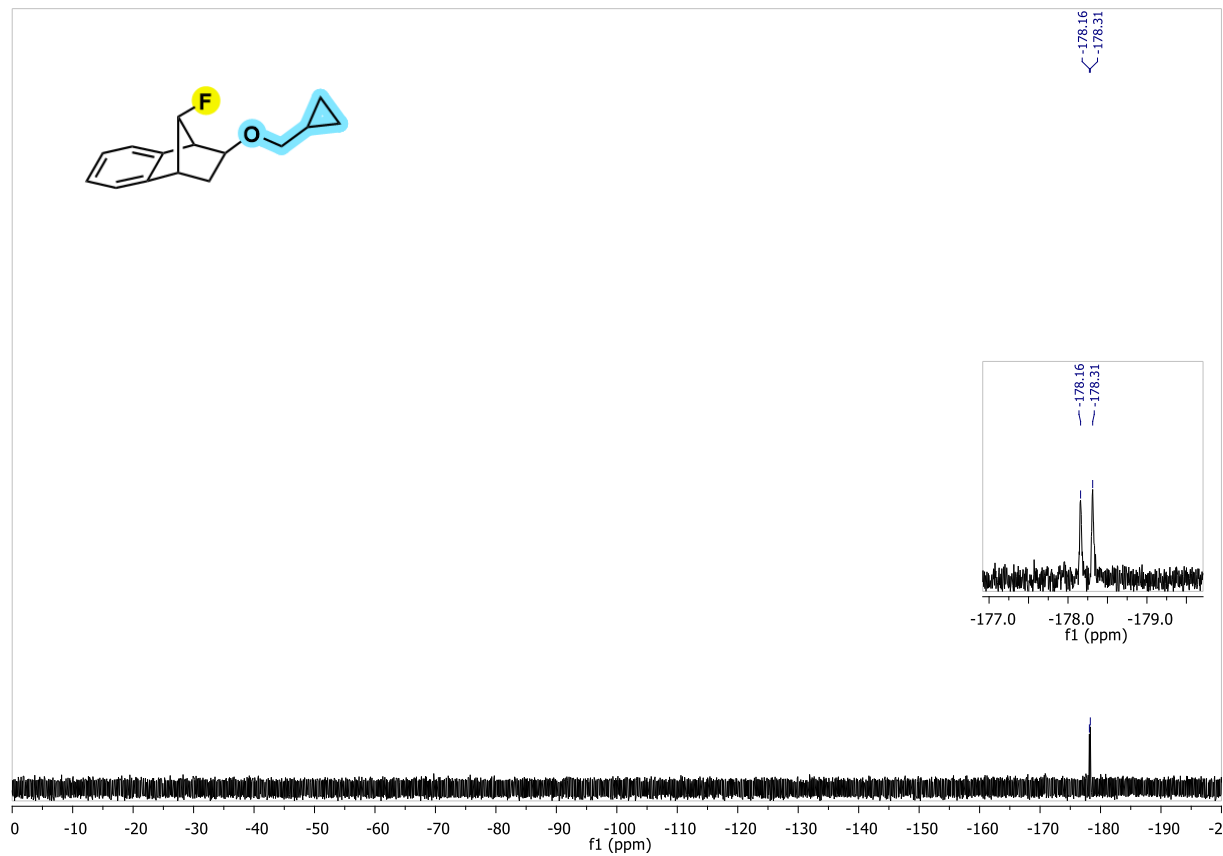
376 MHz ¹⁹F-NMR spectrum of **3f** (CDCl₃)



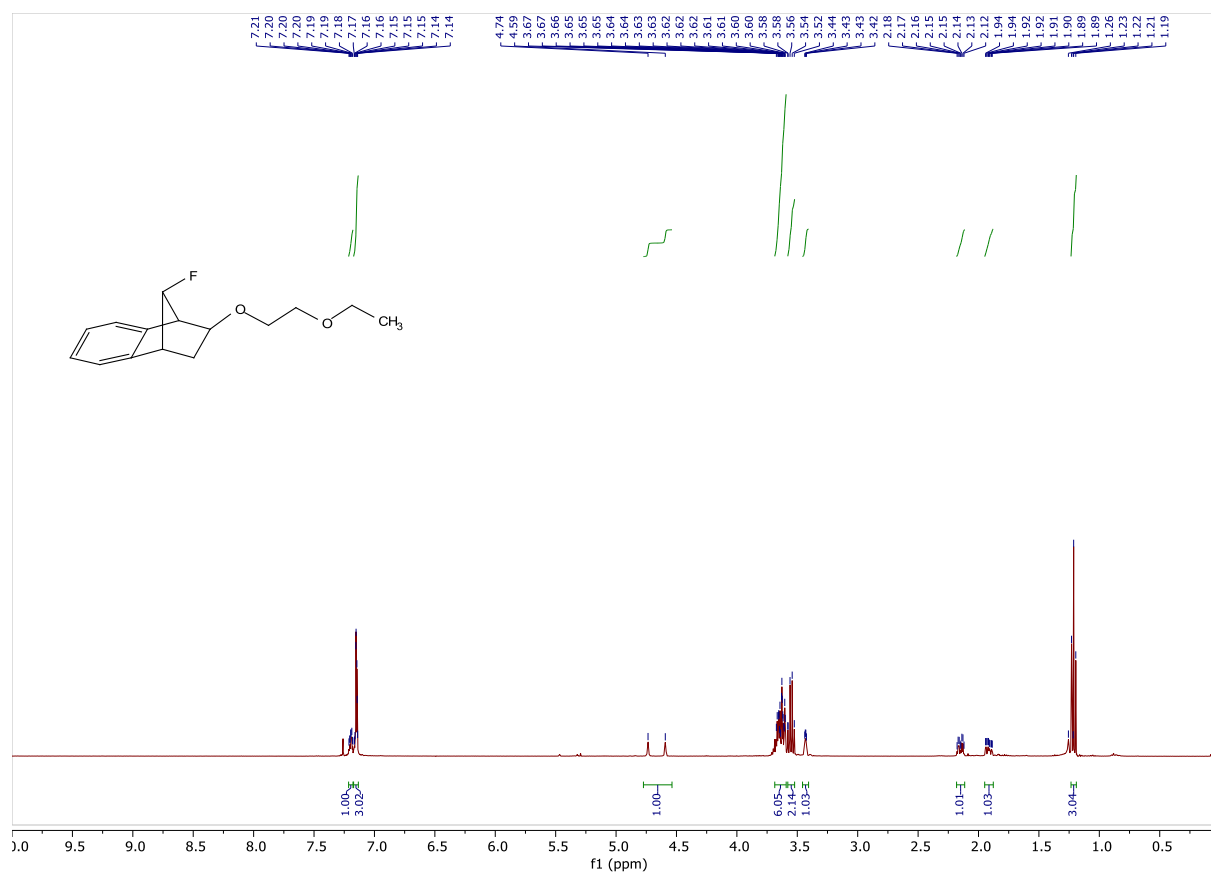




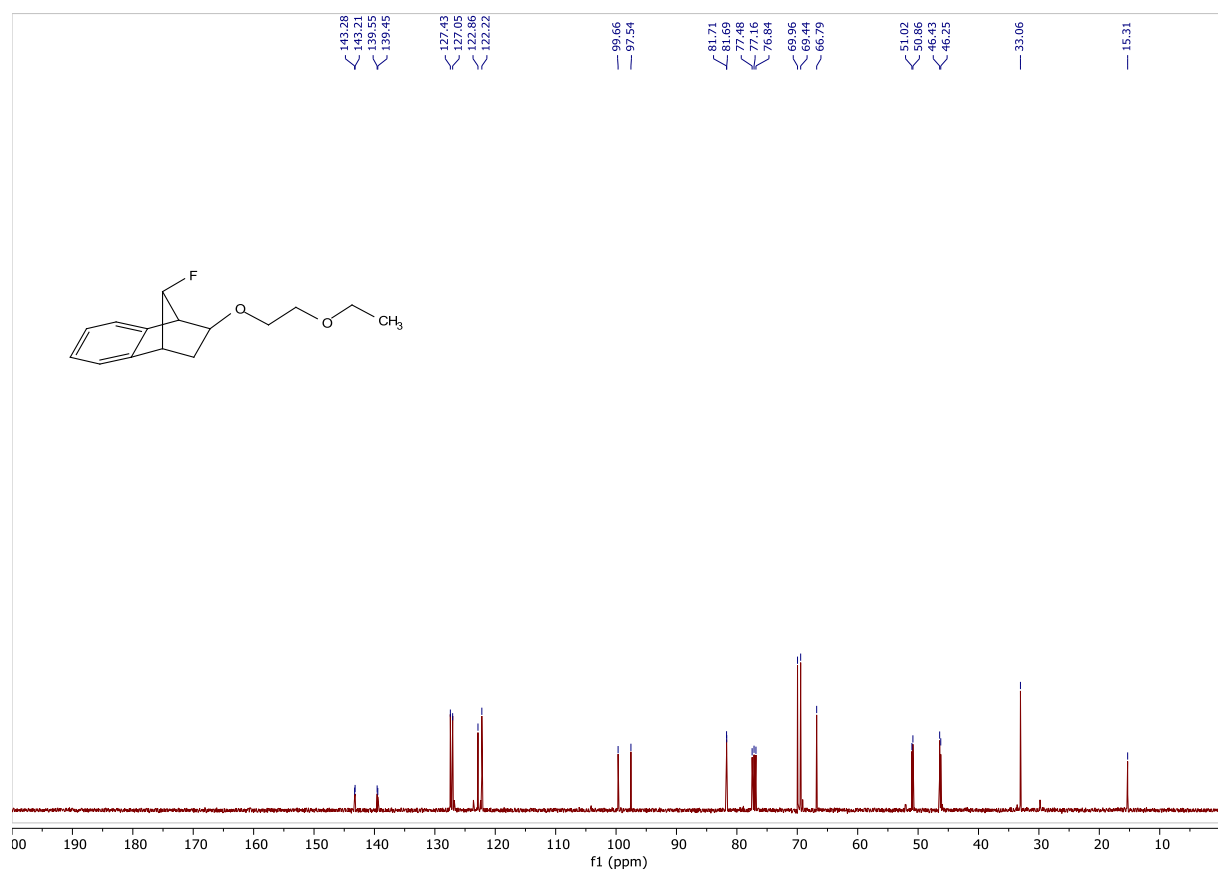
101 MHz ^{13}C -NMR spectrum of **3h** (CDCl_3)



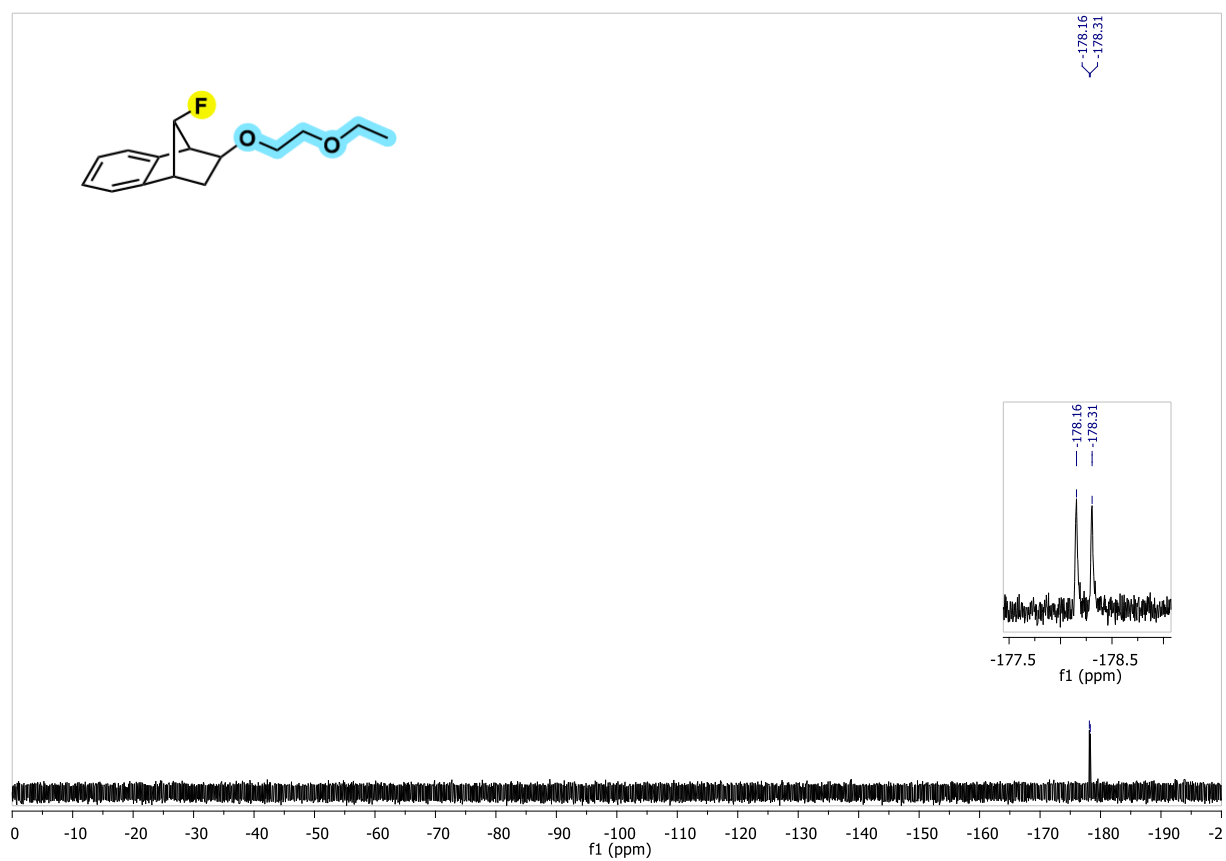
376 MHz ^{19}F -NMR spectrum of **3h** (CDCl_3)



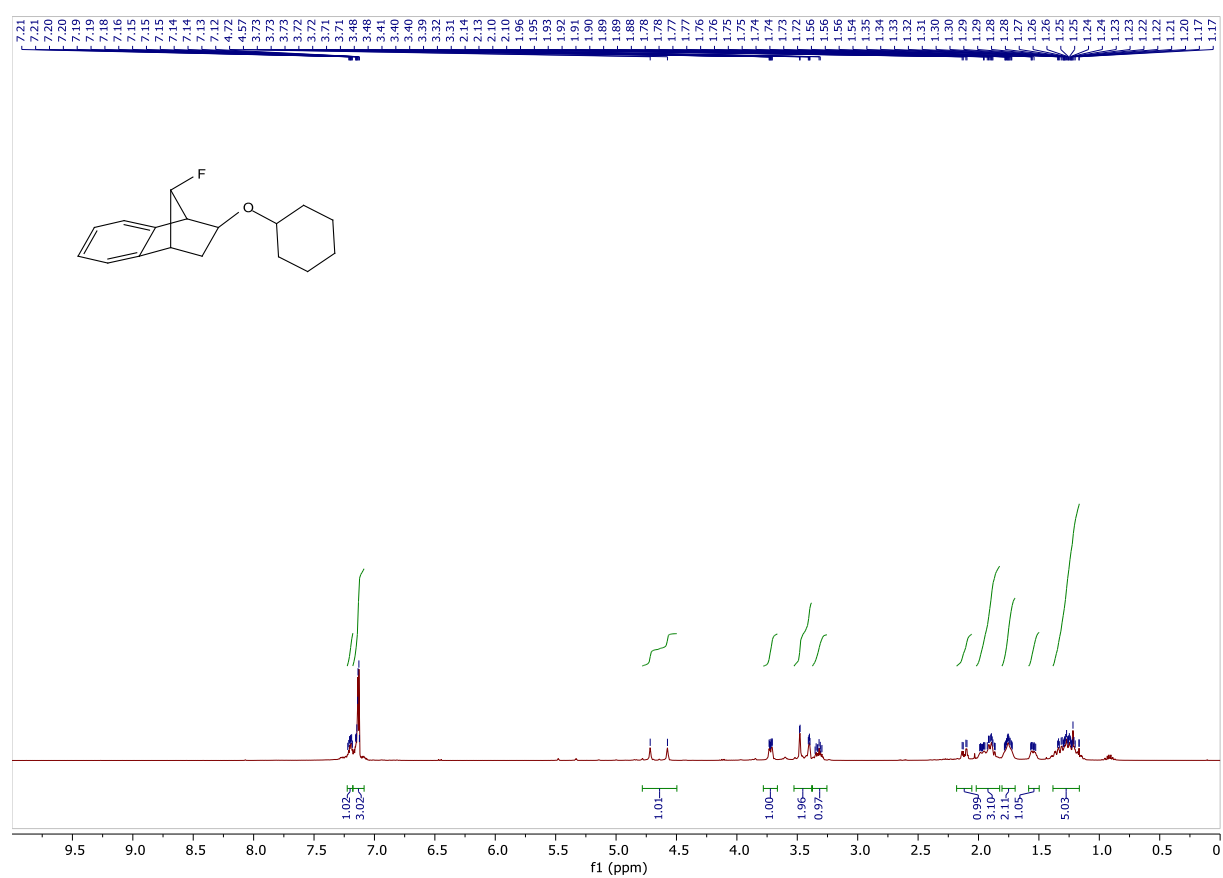
400 MHz ^1H -NMR spectrum of **3i** (CDCl_3)



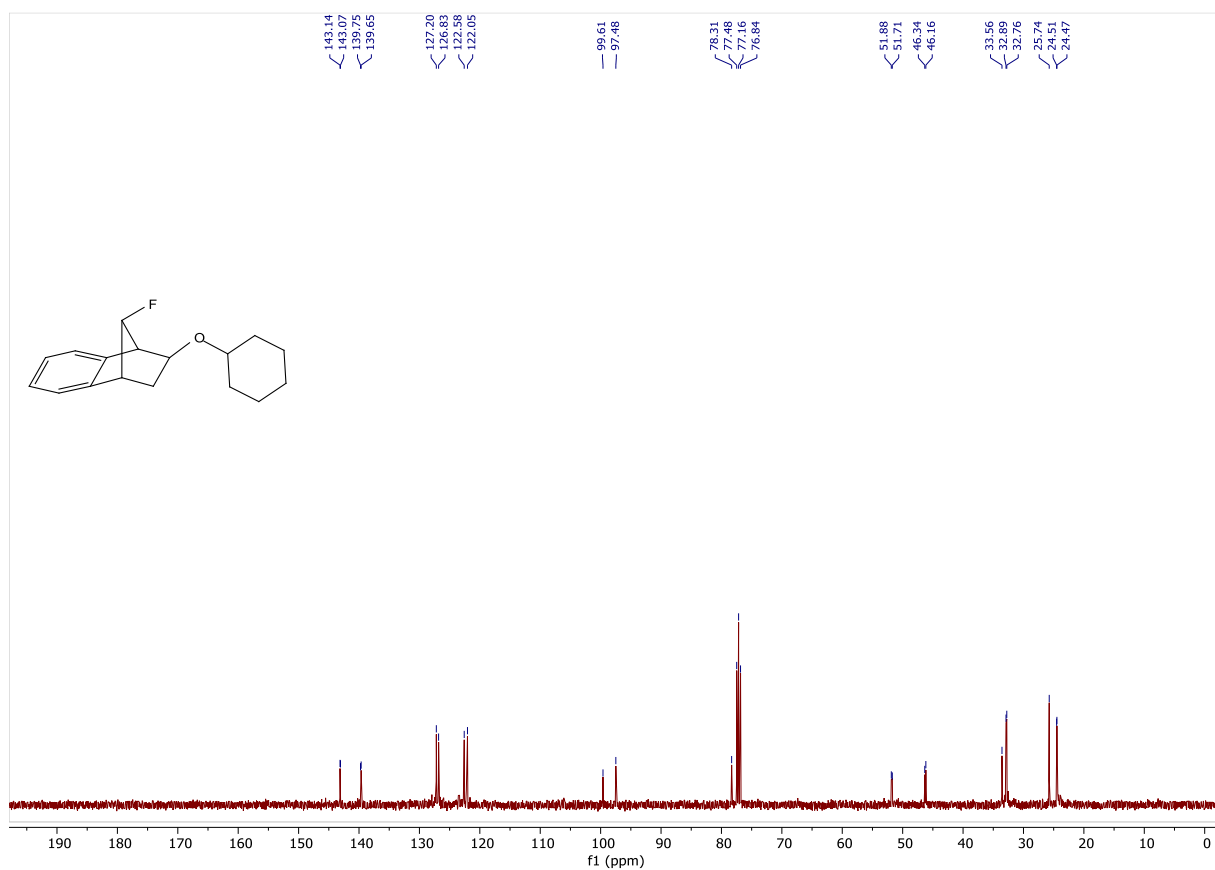
101 MHz ^{13}C -NMR spectrum of **3i** (CDCl_3)



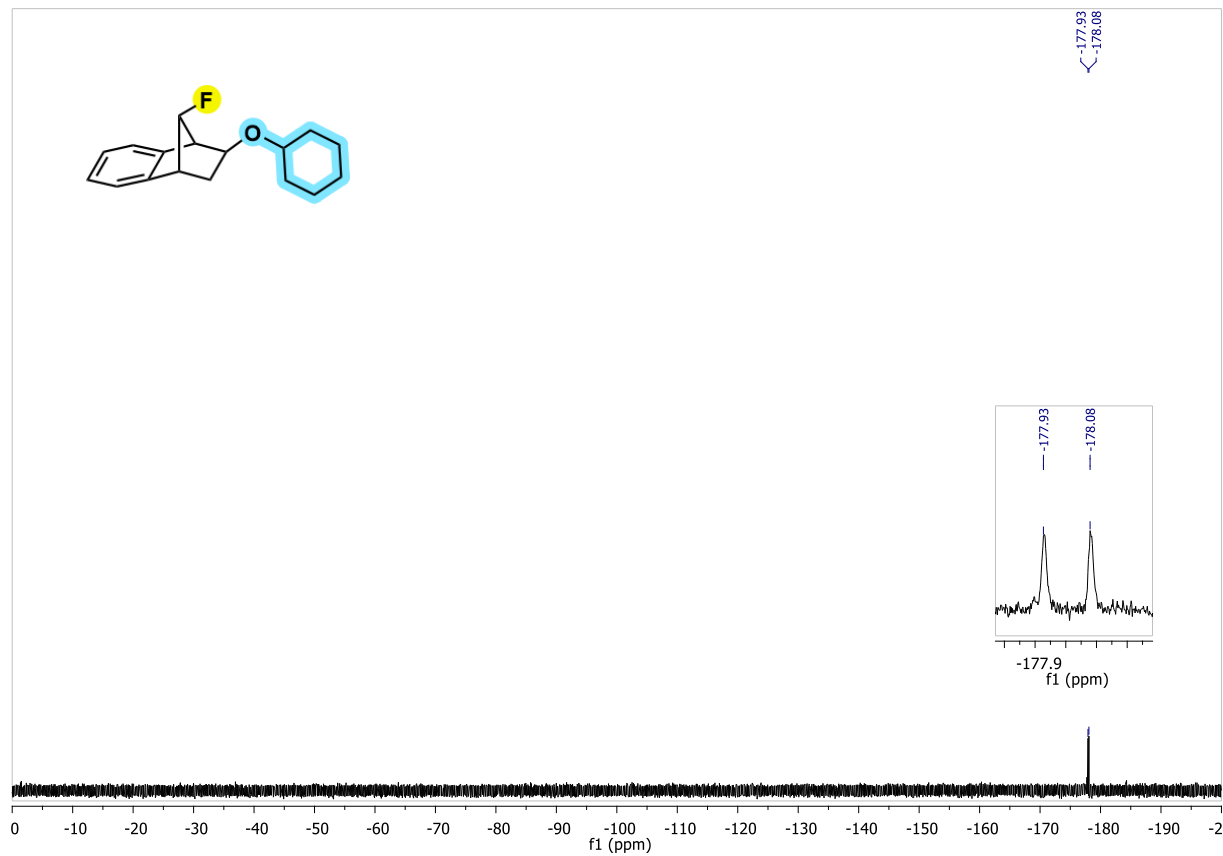
376 MHz ^{19}F -NMR spectrum of **3i** (CDCl_3)



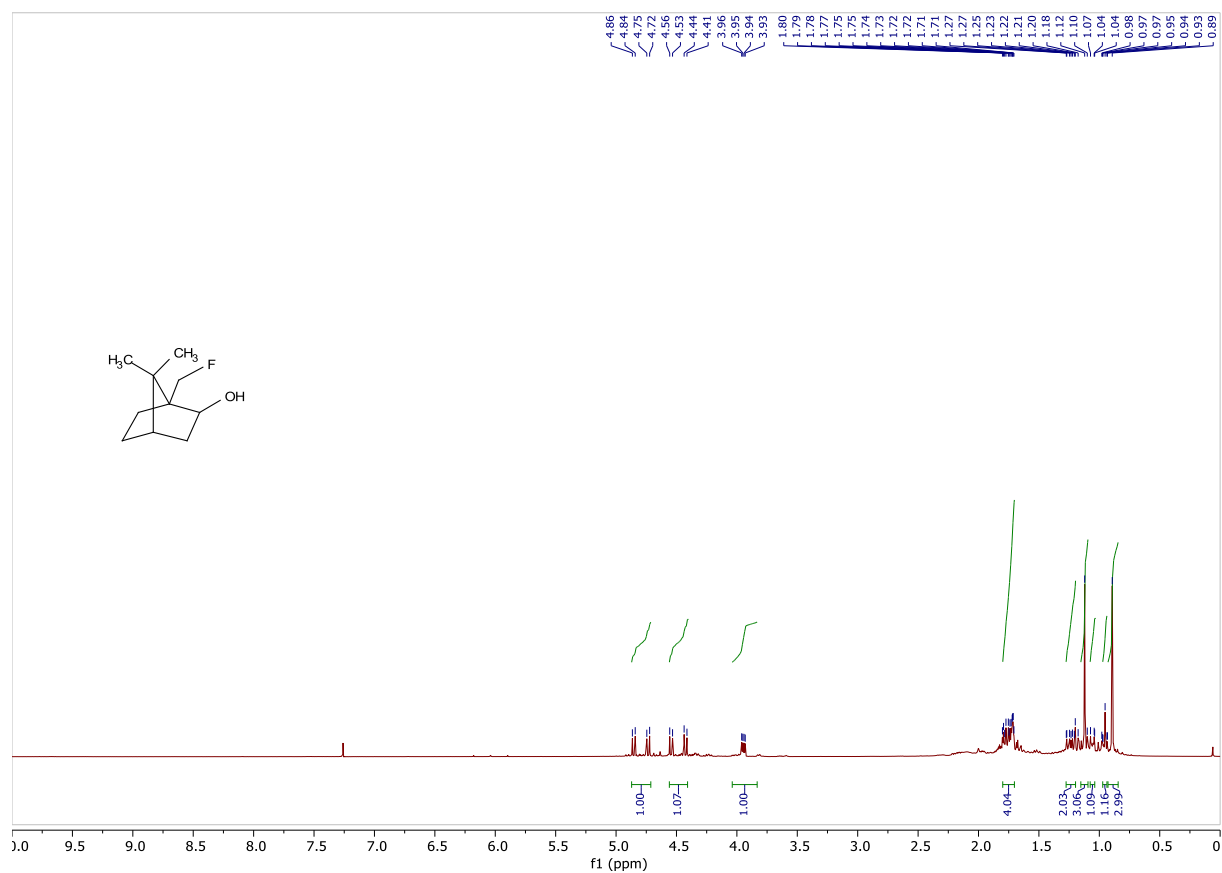
400 MHz ^1H -NMR spectrum of **3j** (CDCl_3)



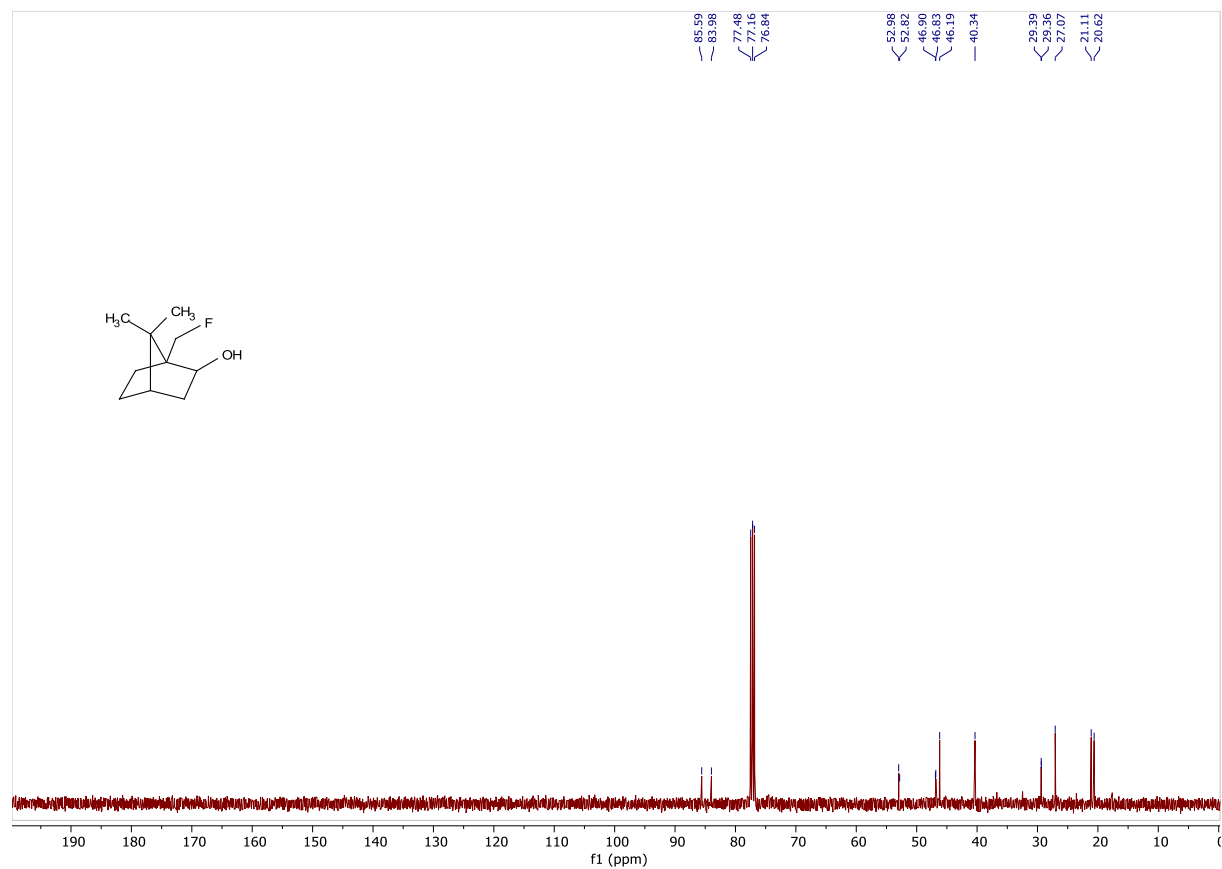
101 MHz ¹³C-NMR spectrum of **3j** (CDCl₃)



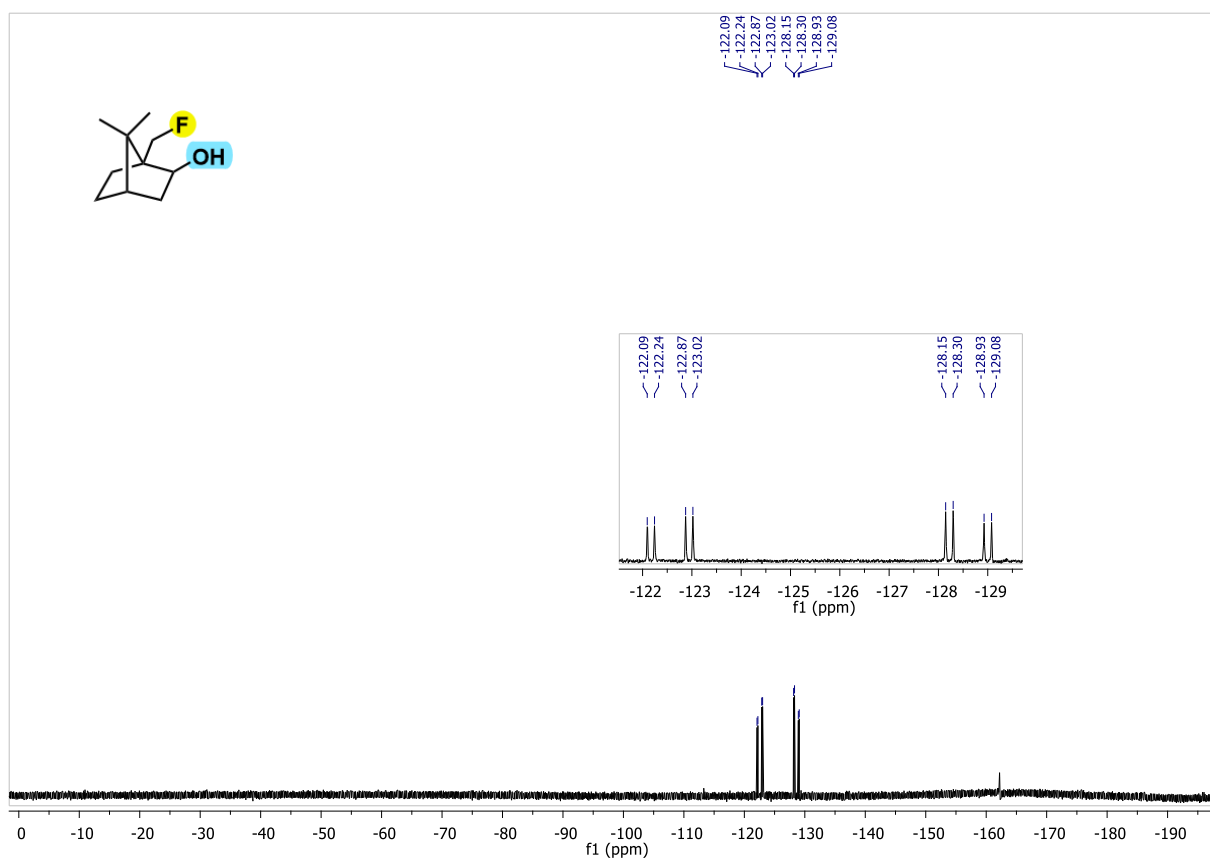
376 MHz ¹⁹F-NMR spectrum of **3j** (CDCl₃)



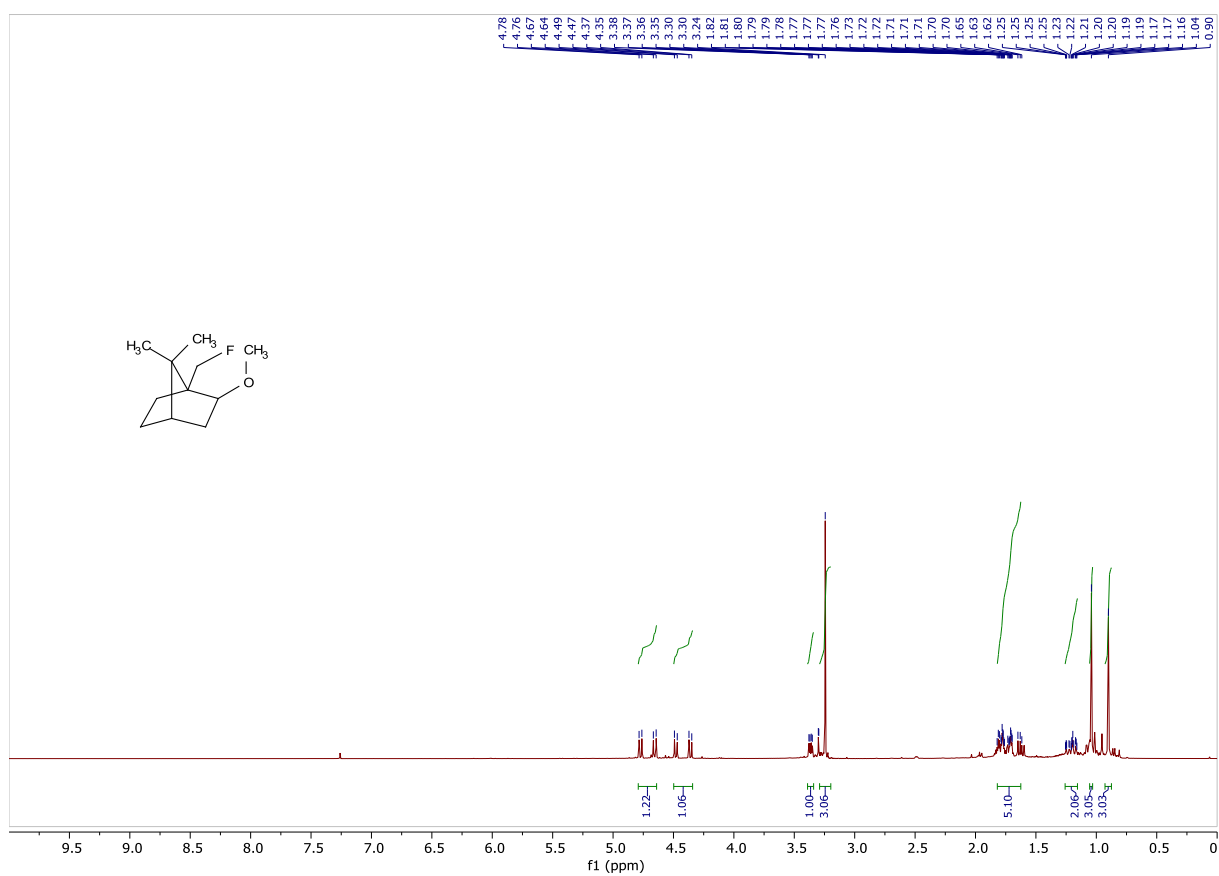
400 MHz ¹H-NMR spectrum of **4a** (CDCl₃)



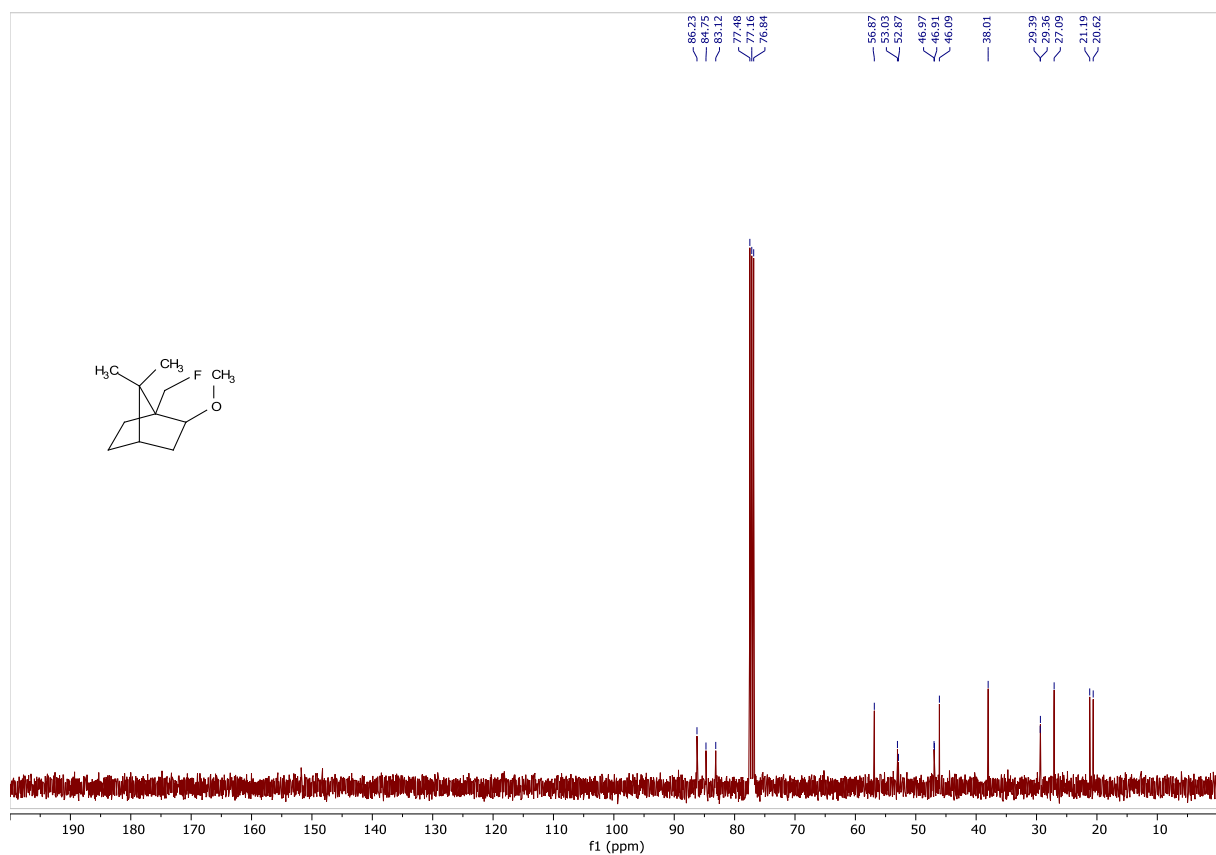
101 MHz ¹³C-NMR spectrum of **4a** (CDCl₃)



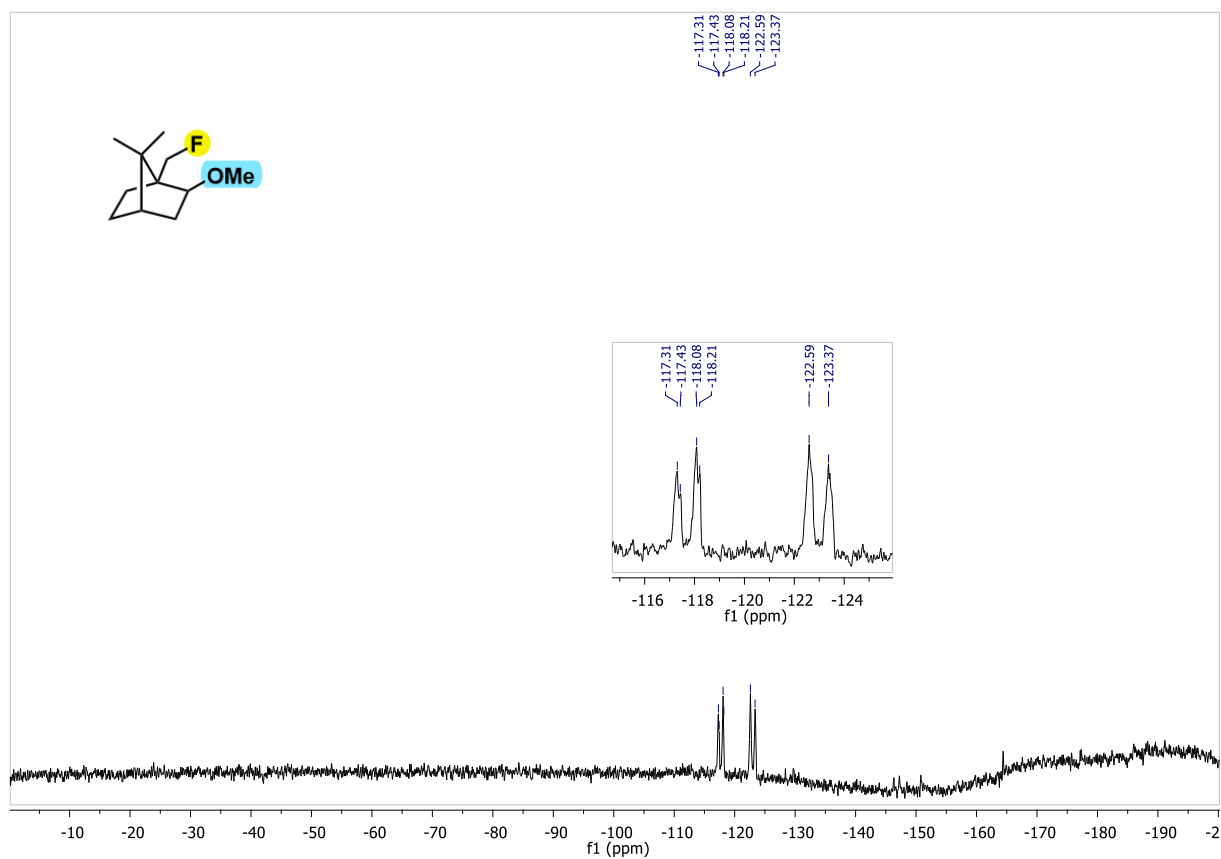
376 MHz ^{19}F -NMR spectrum of **4a** (CDCl_3)



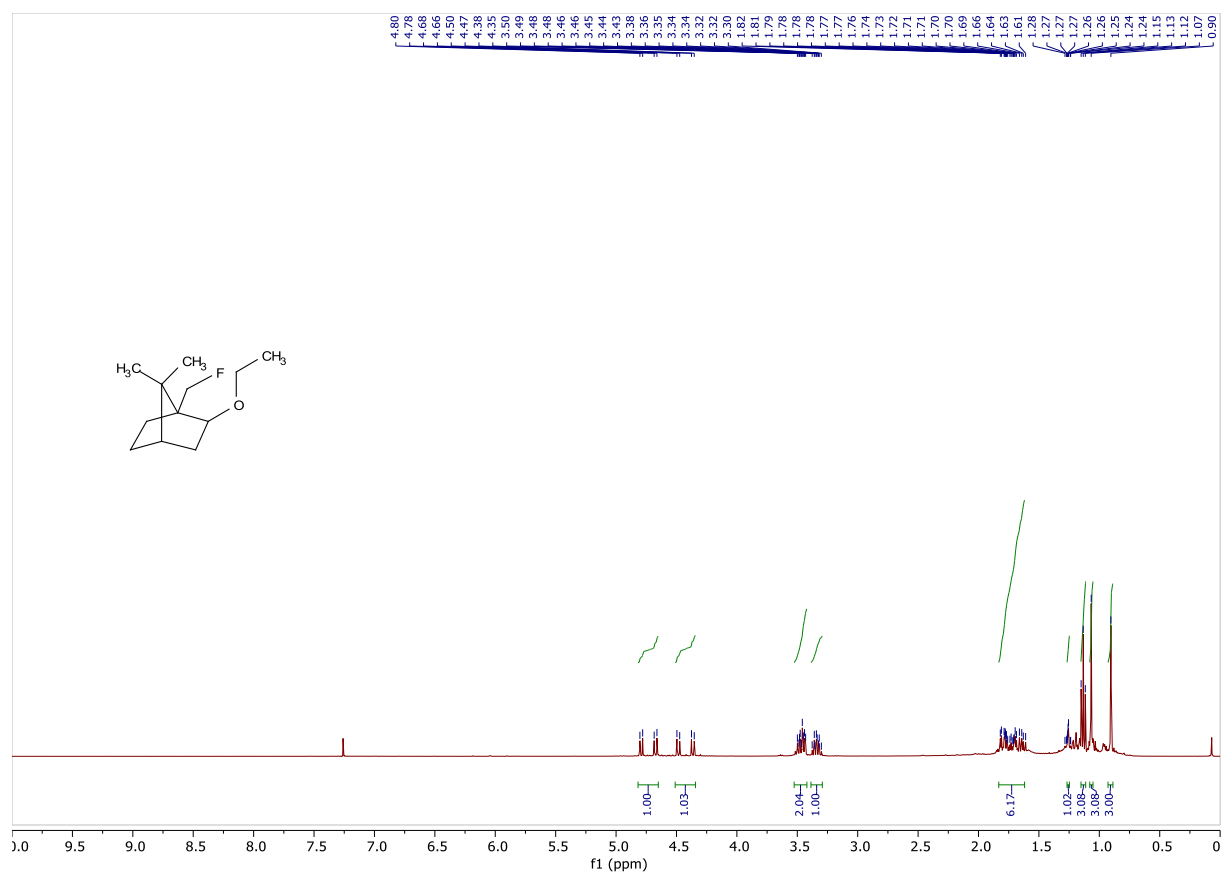
400 MHz ^1H -NMR spectrum of **4b** (CDCl_3)



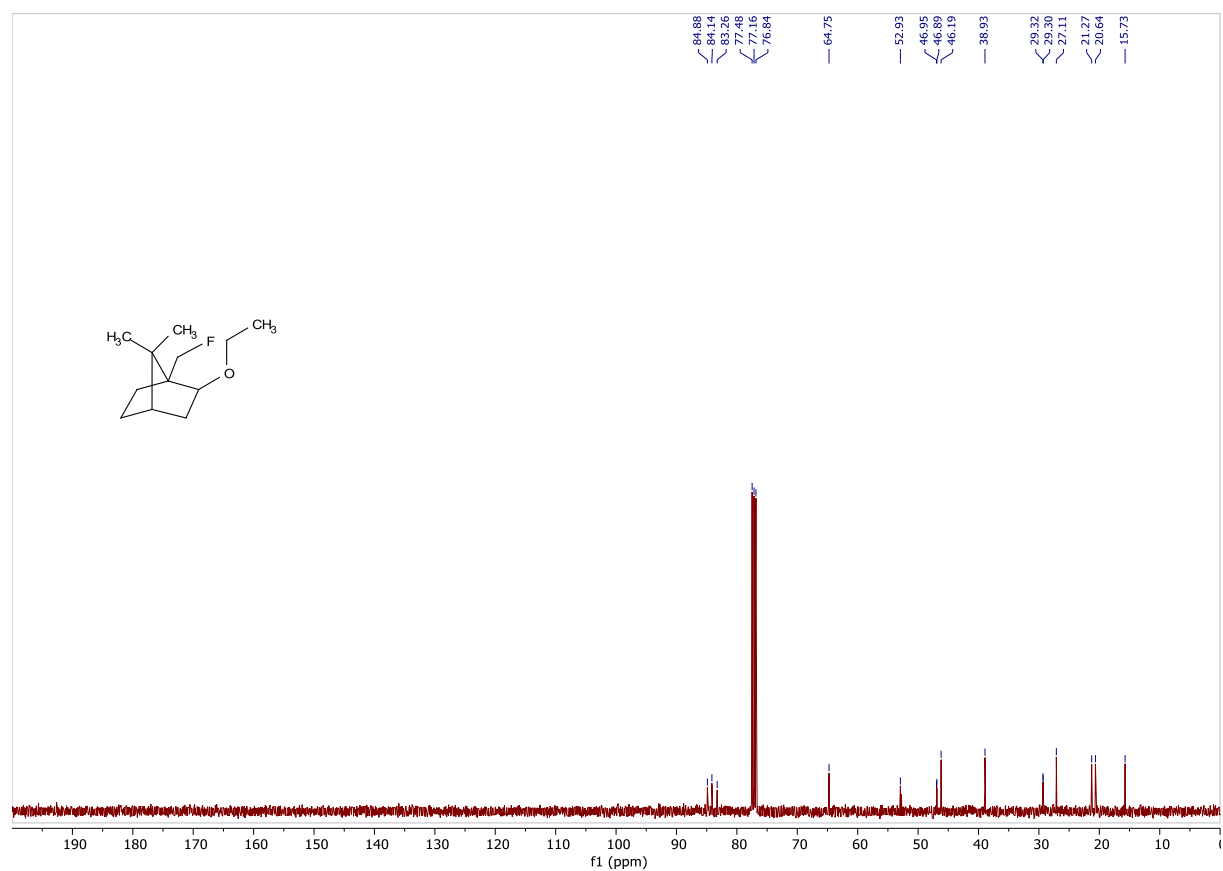
101 MHz ^{13}C -NMR spectrum of **4b** (CDCl_3)



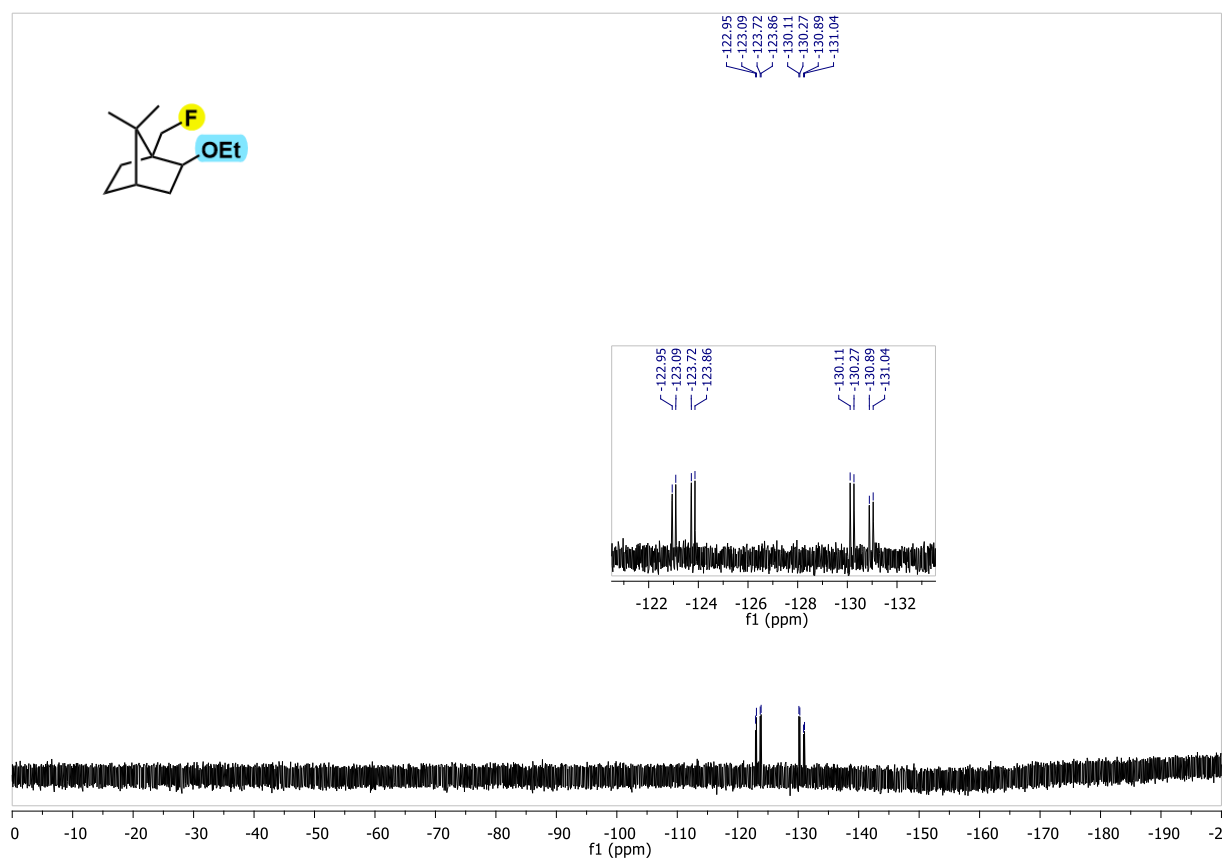
376 MHz ^{19}F -NMR spectrum of **4b** (CDCl_3)



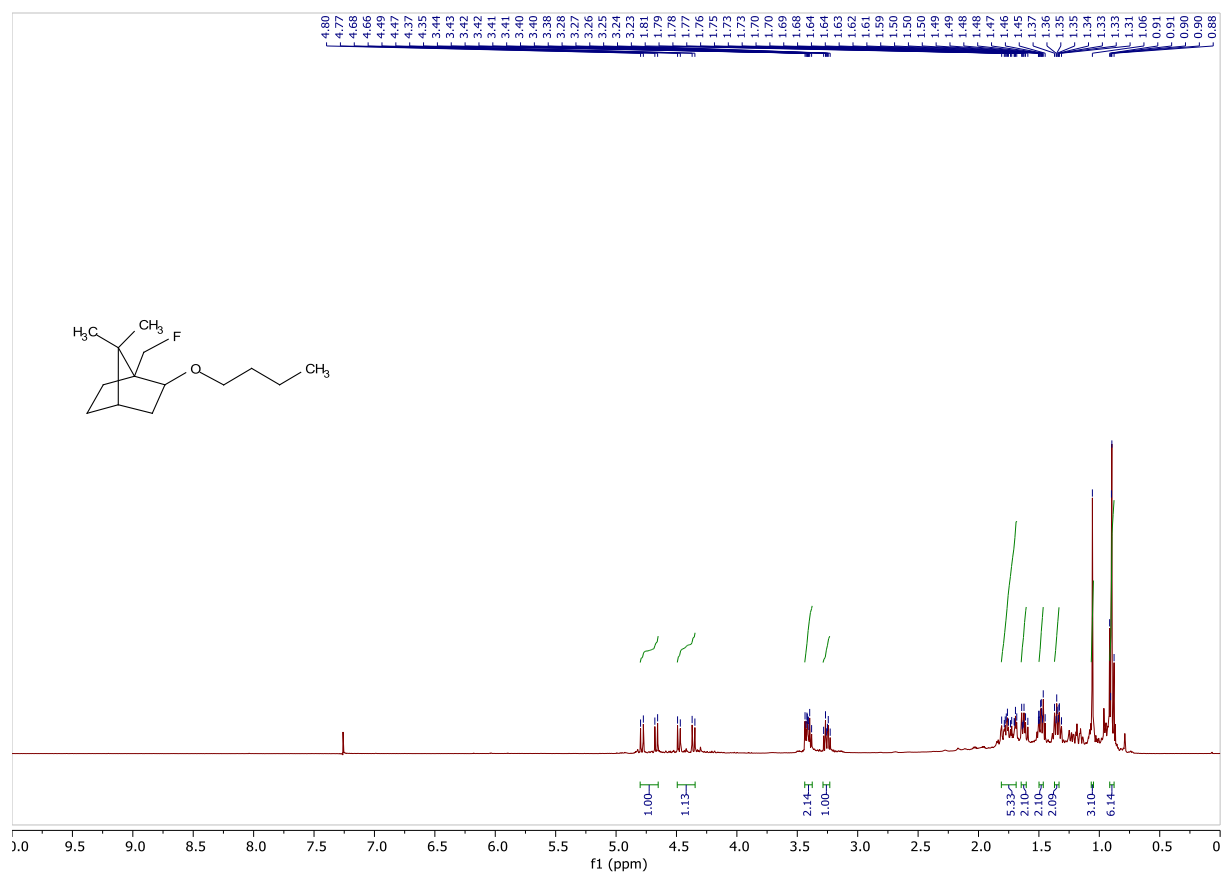
400 MHz ^1H -NMR spectrum of **4c** (CDCl_3)



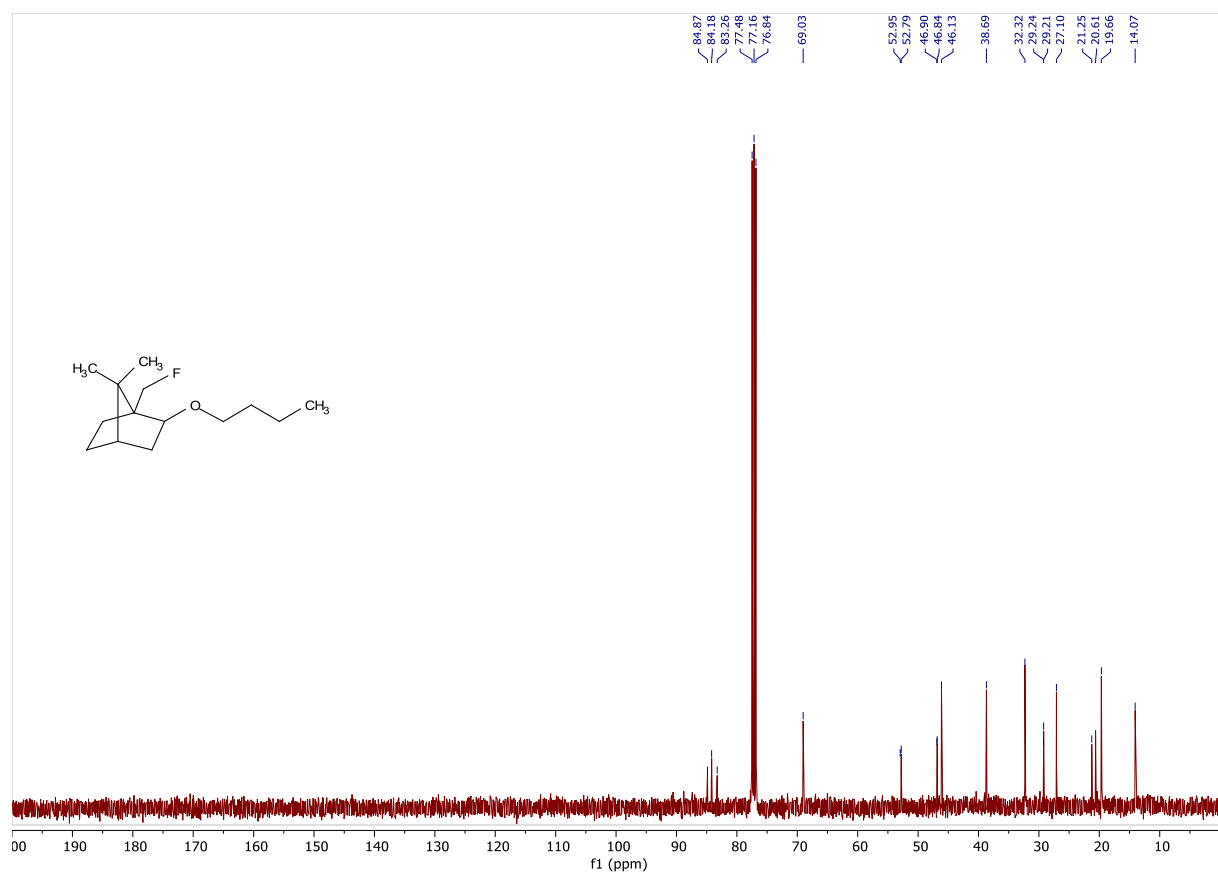
101 MHz ^{13}C -NMR spectrum of **4c** (CDCl_3)



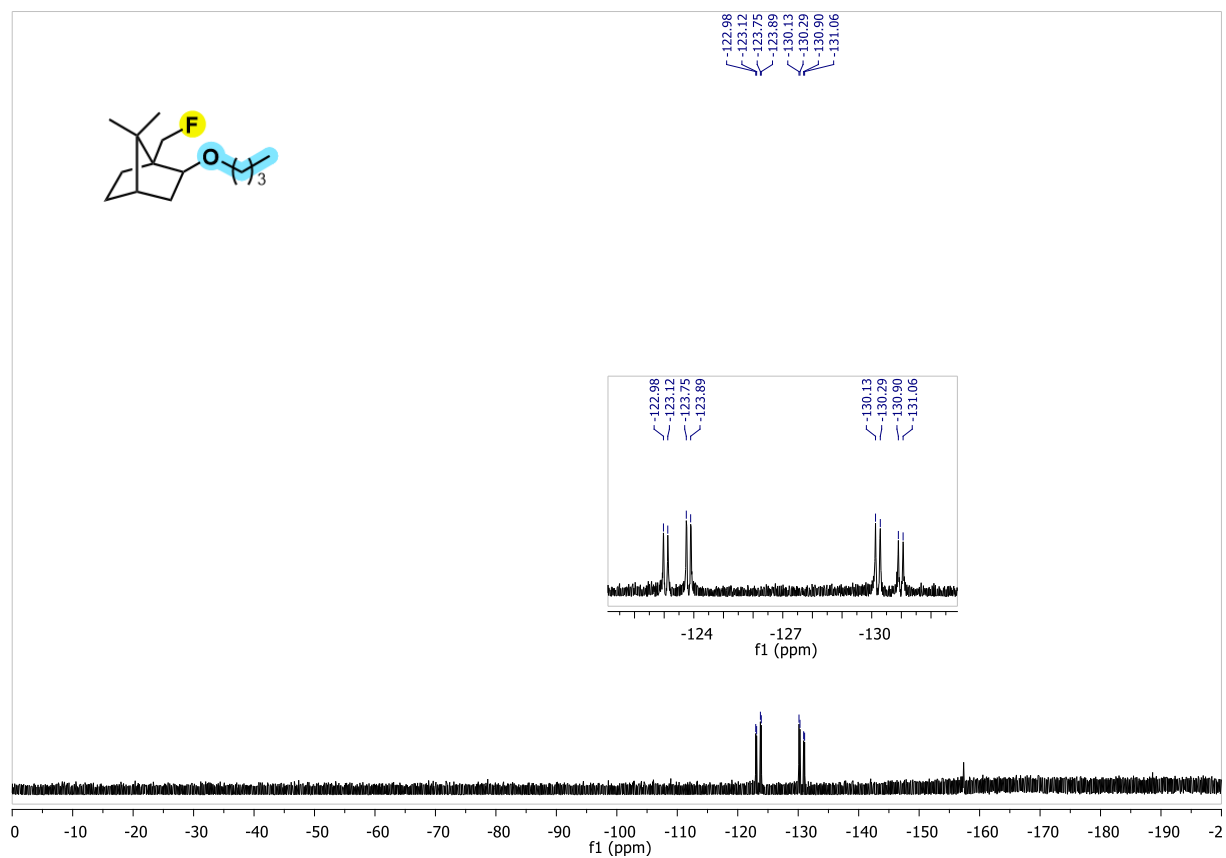
376 MHz ^{19}F -NMR spectrum of **4c** (CDCl_3)



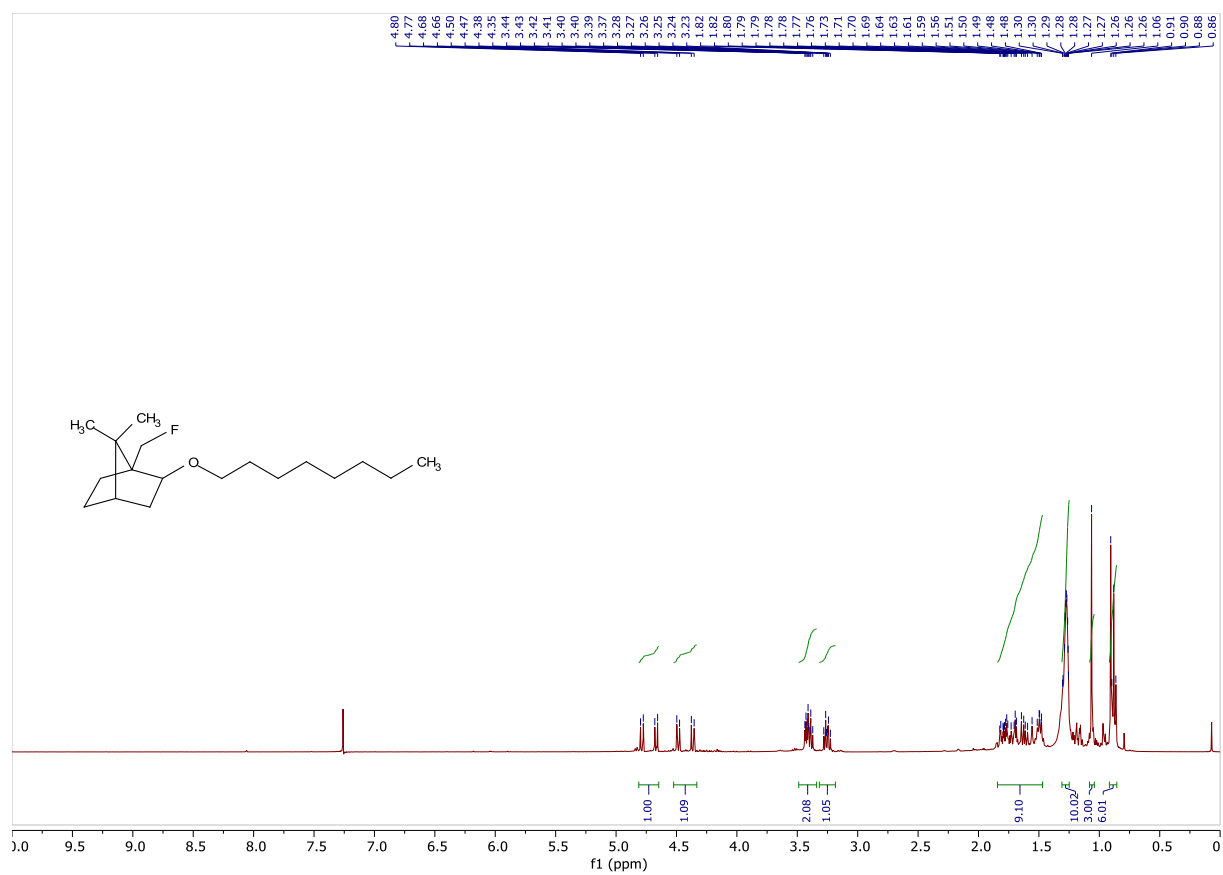
400 MHz ^1H -NMR spectrum of **4d** (CDCl_3)



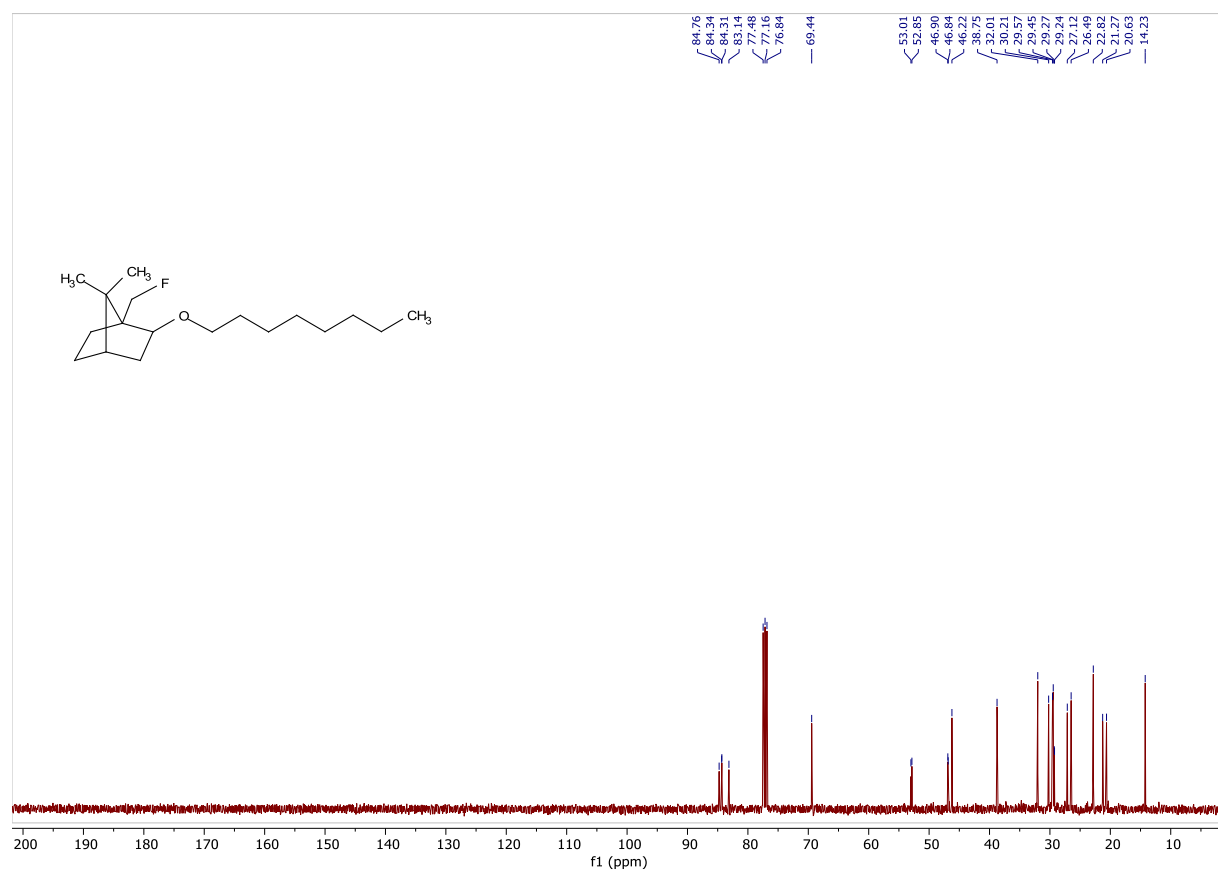
101 MHz ^{13}C -NMR spectrum of **4d** (CDCl_3)



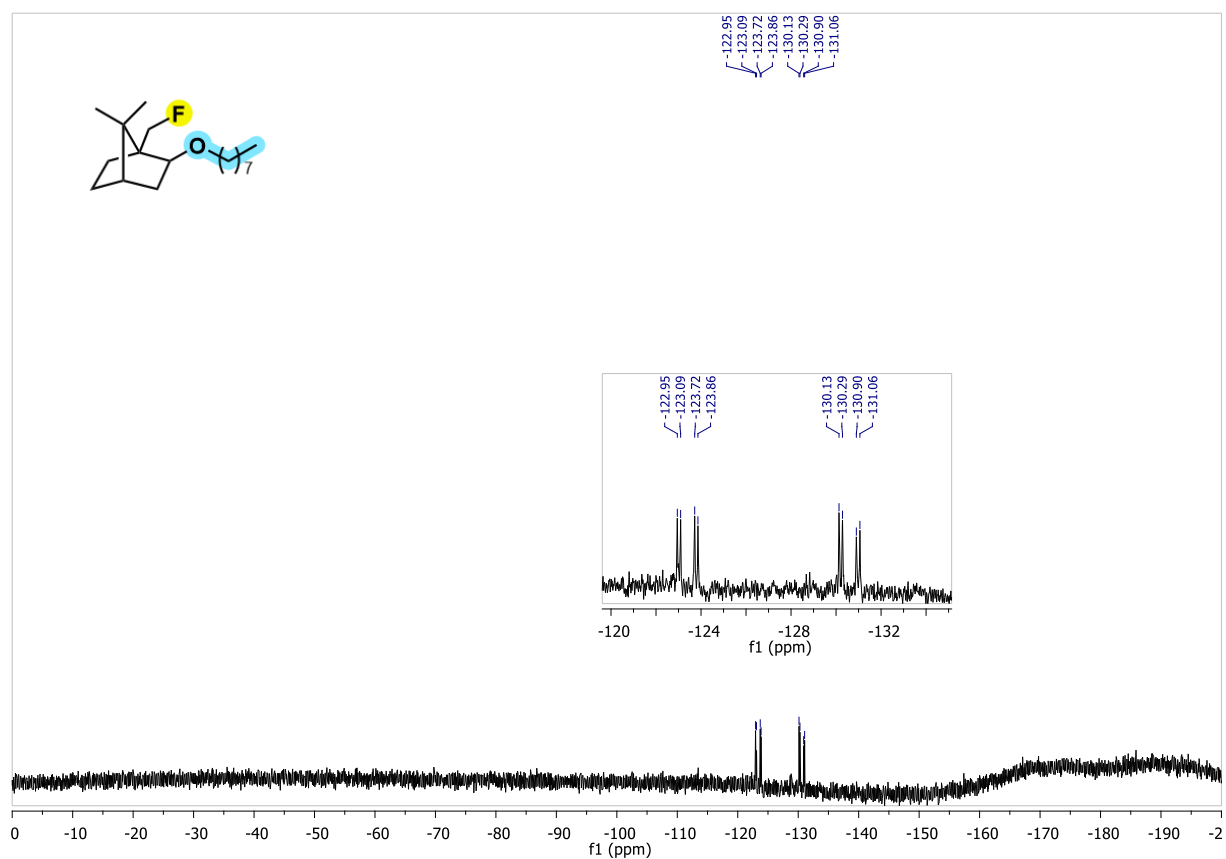
376 MHz ^{19}F -NMR spectrum of **4d** (CDCl_3)



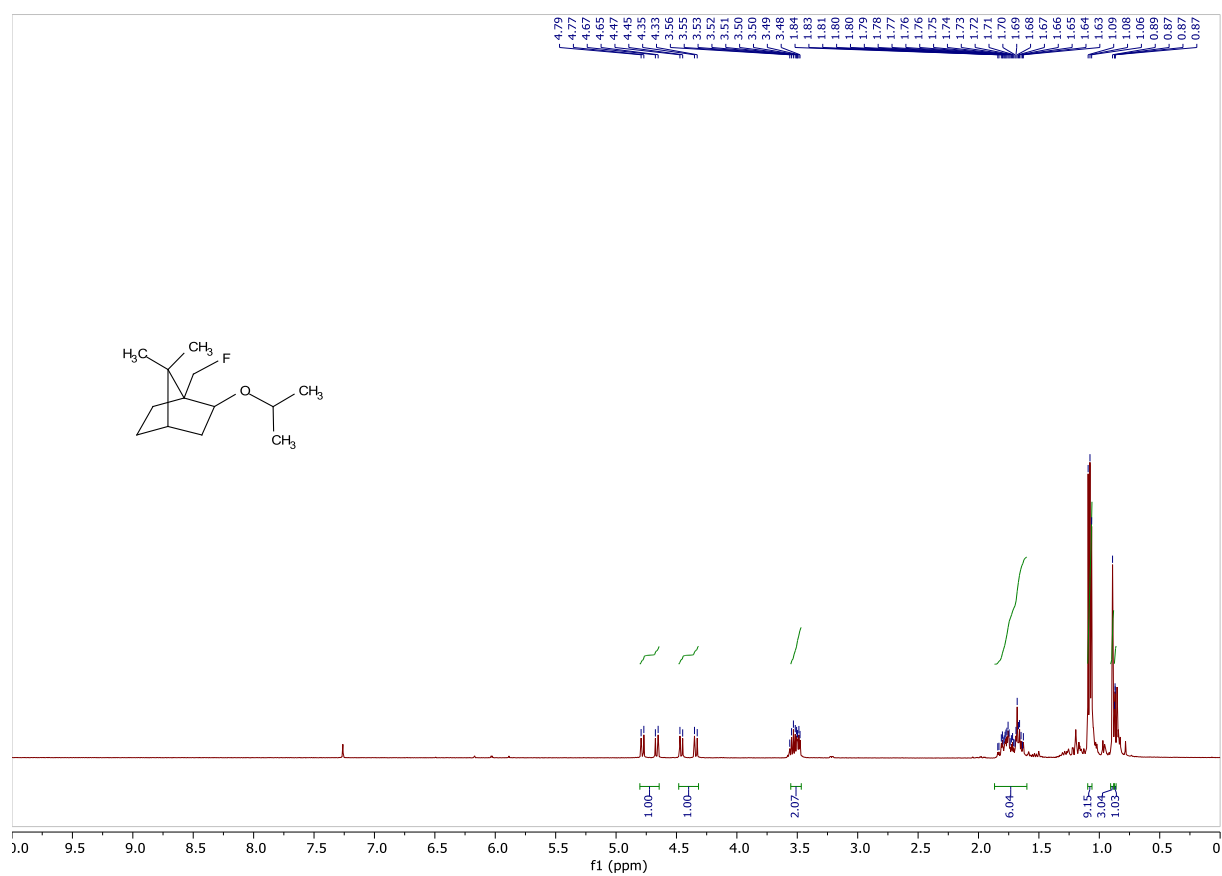
400 MHz ^1H -NMR spectrum of **4e** (CDCl_3)



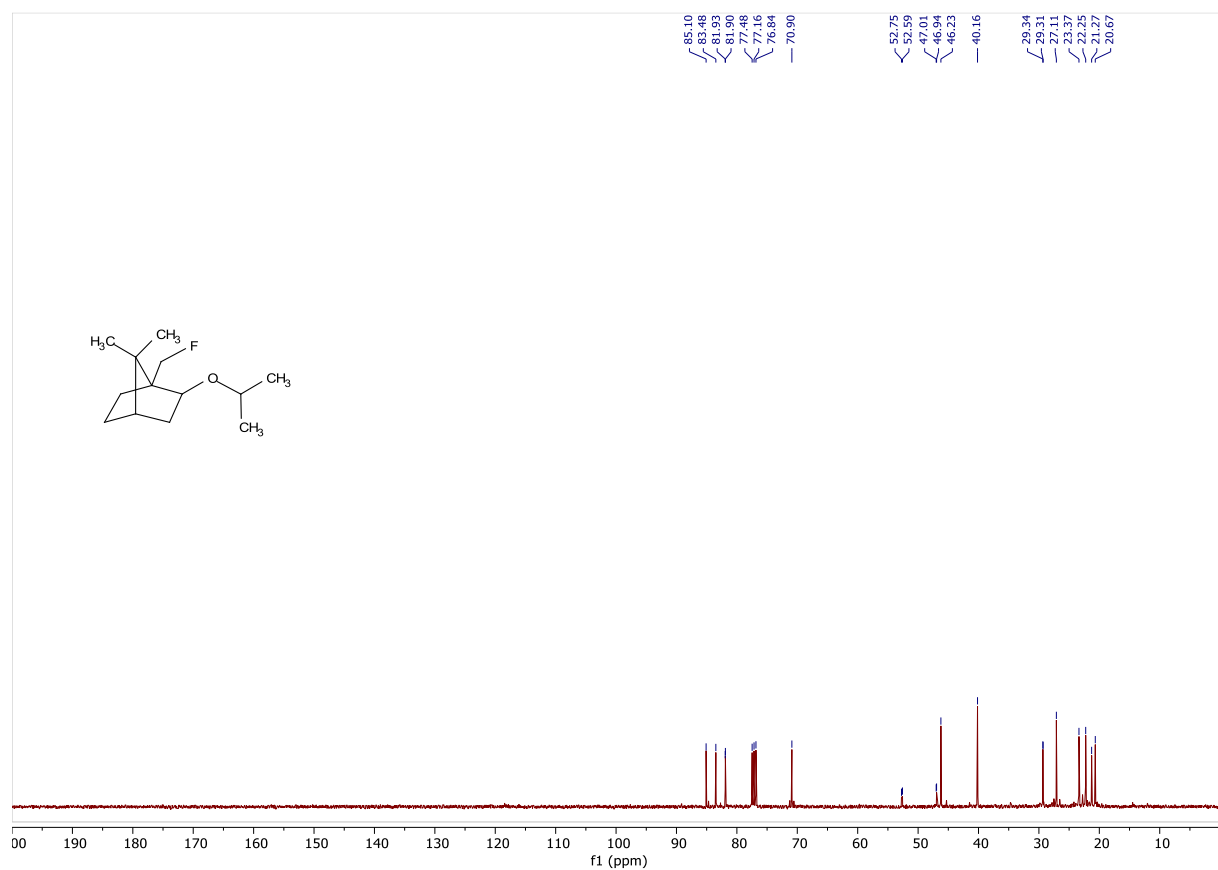
101 MHz ^{13}C -NMR spectrum of **4e** (CDCl_3)



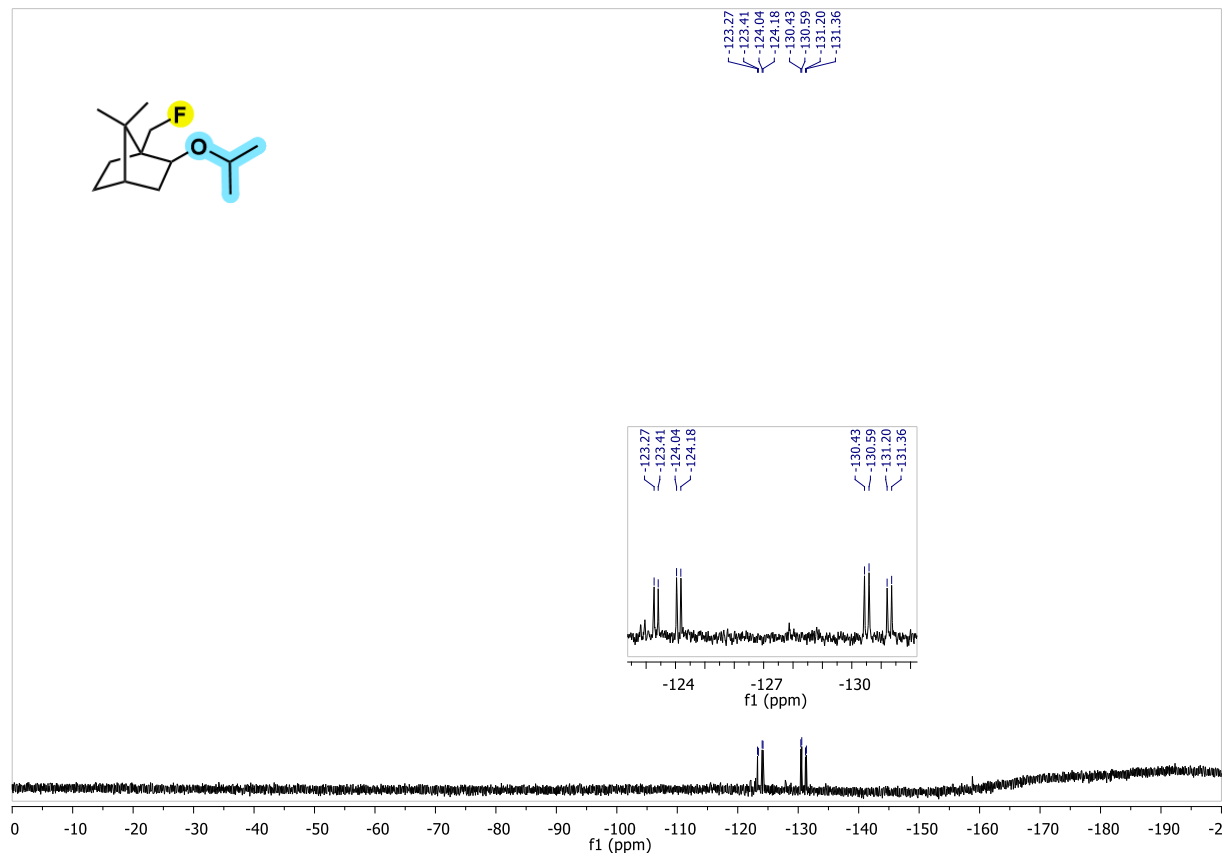
376 MHz ^{19}F -NMR spectrum of **4e** (CDCl_3)



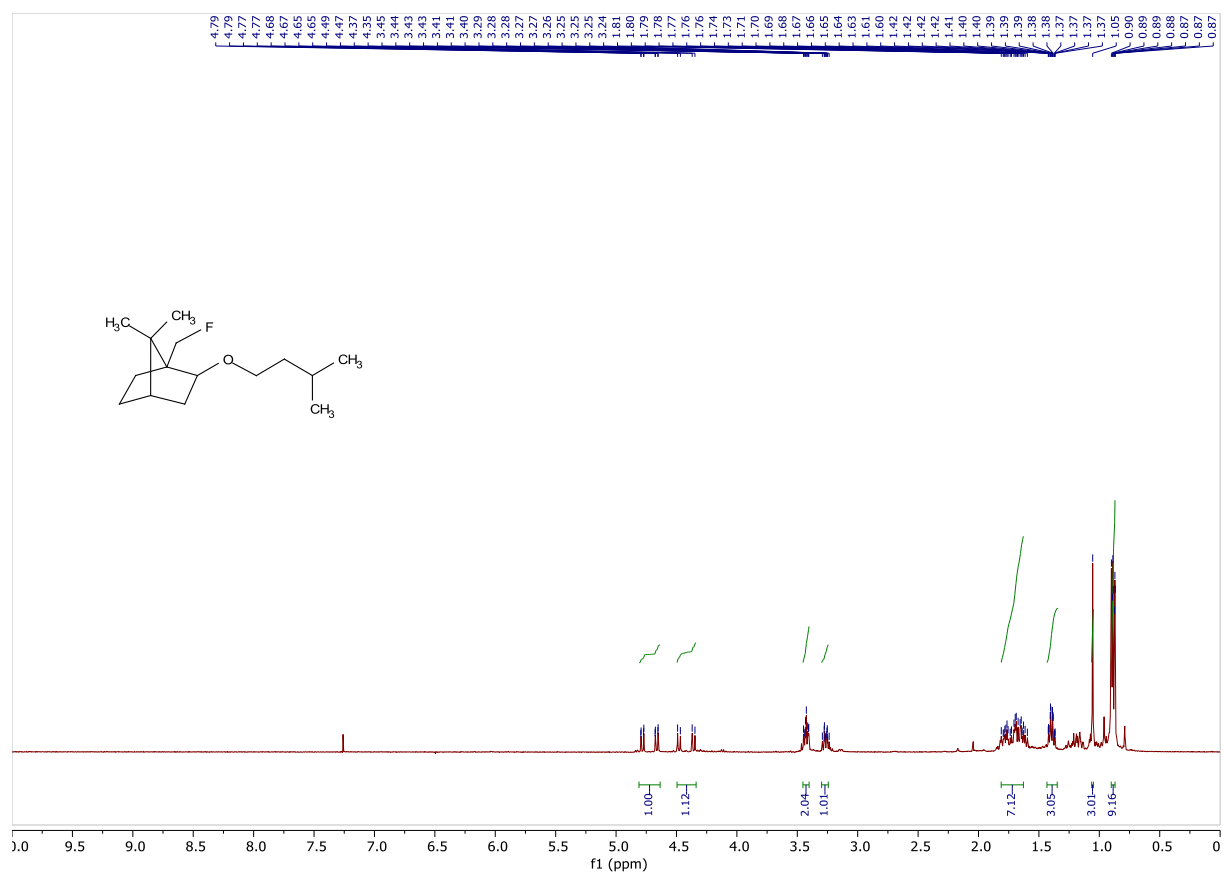
400 MHz ^1H -NMR spectrum of **4f** (CDCl_3)



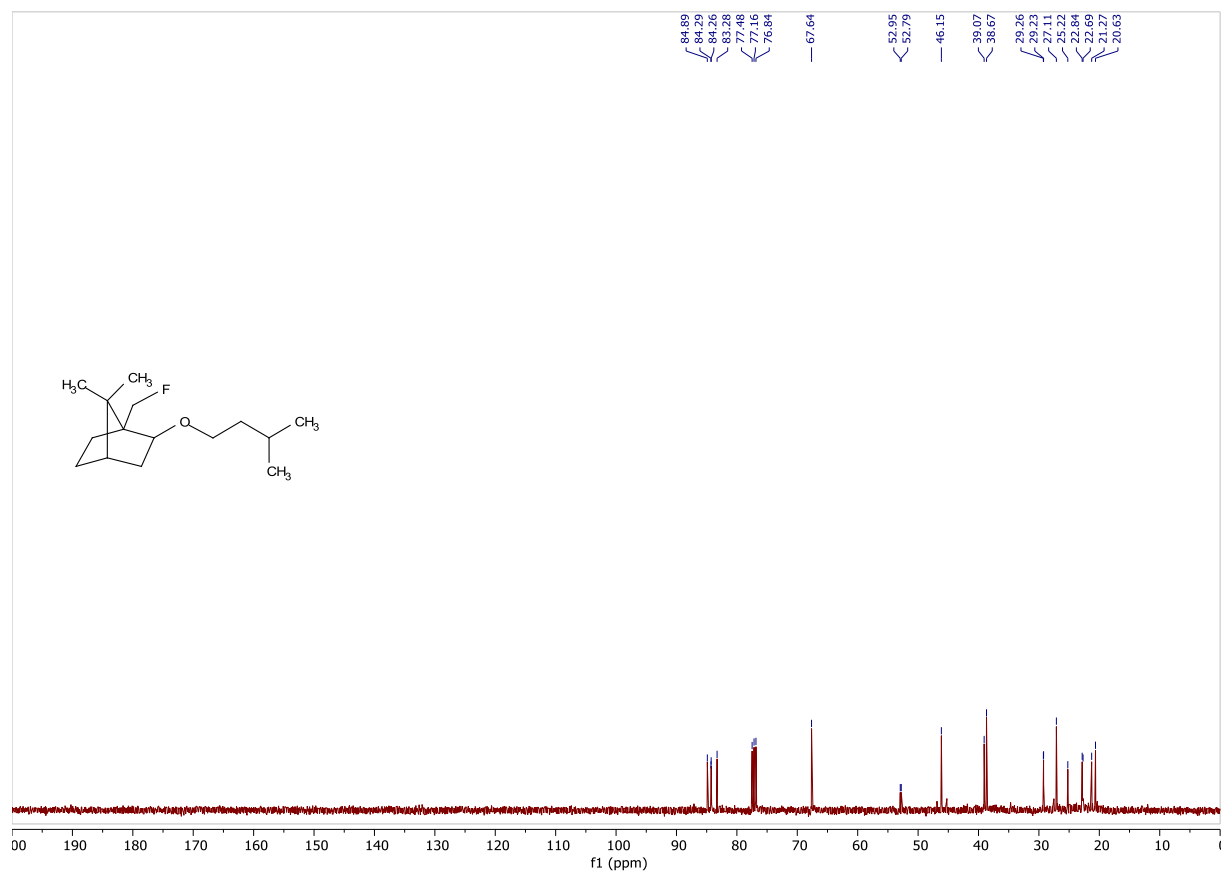
101 MHz ^{13}C -NMR spectrum of **4f** (CDCl_3)



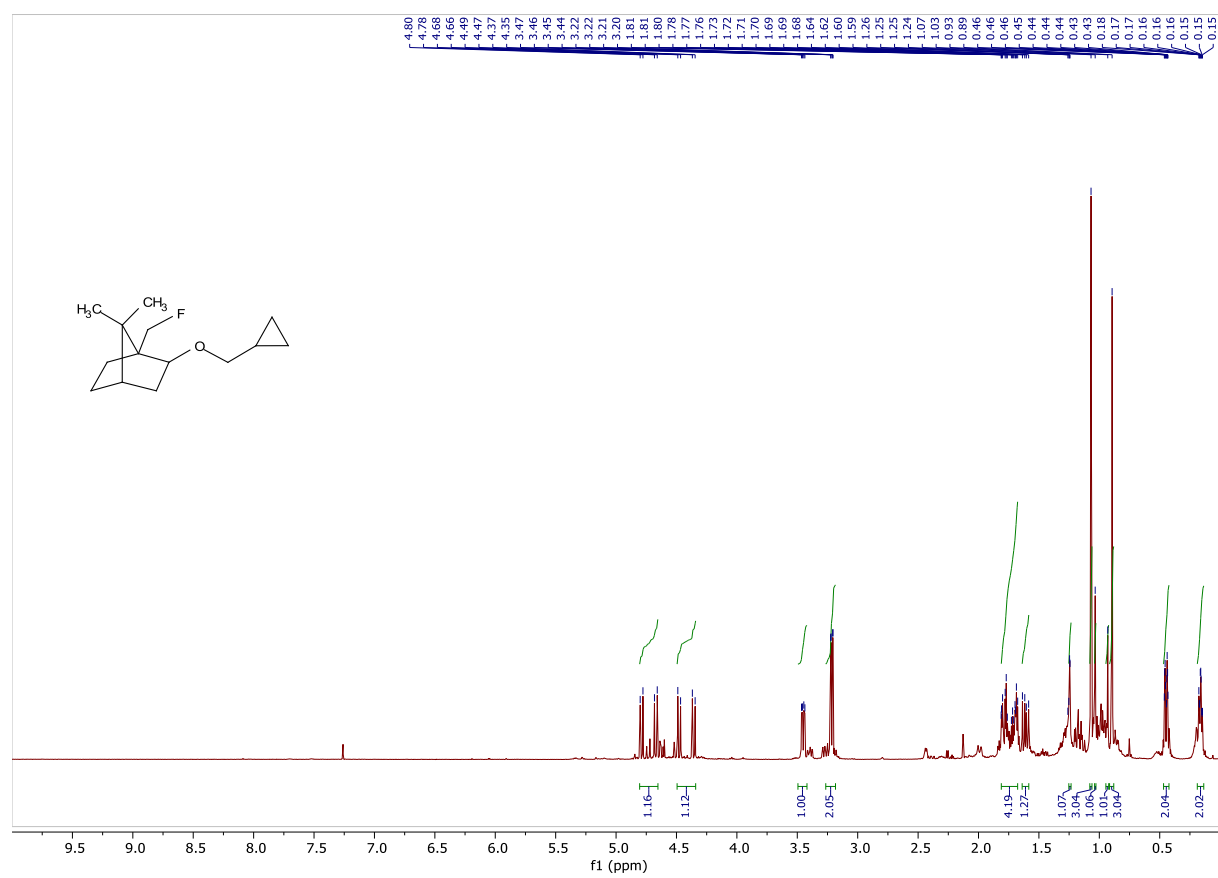
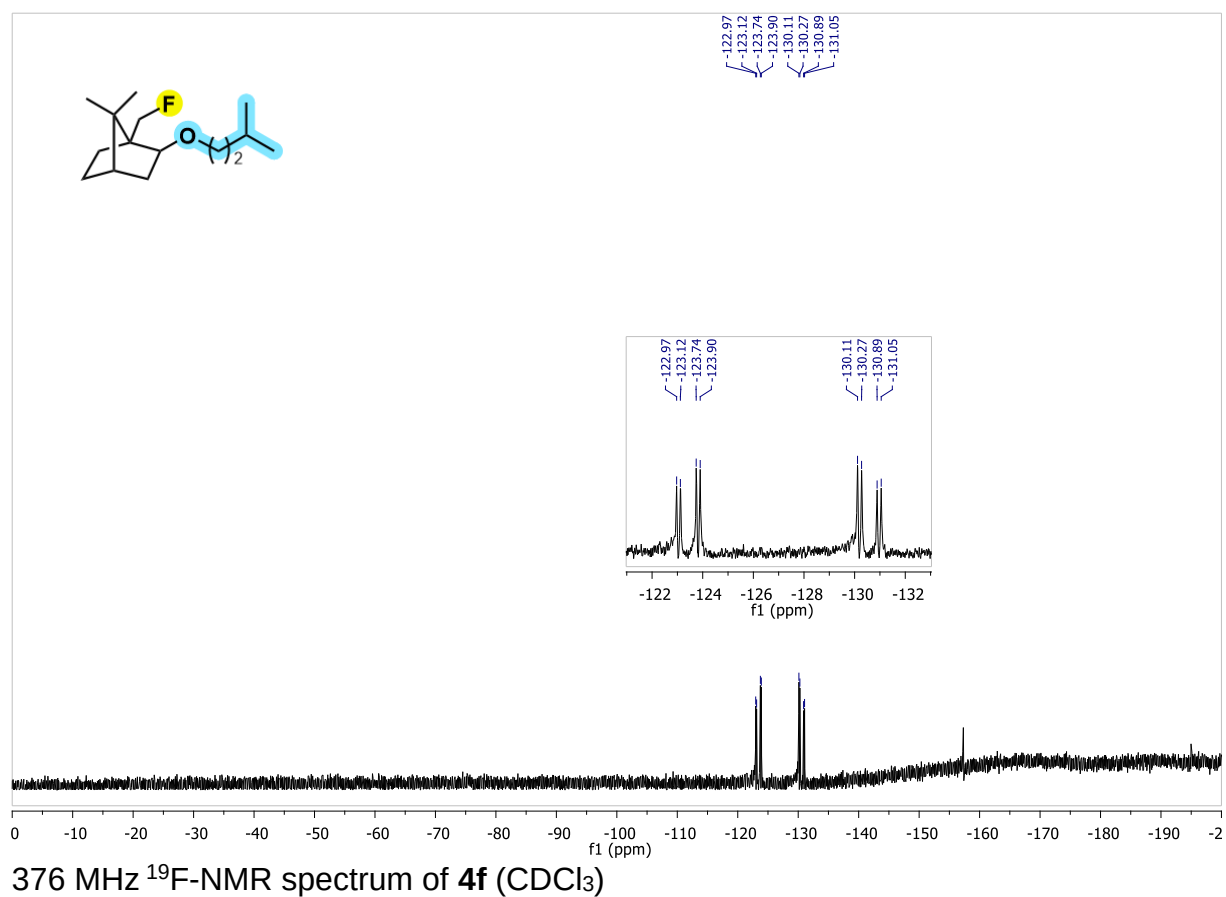
376 MHz ^{19}F -NMR spectrum of **4f** (CDCl_3)

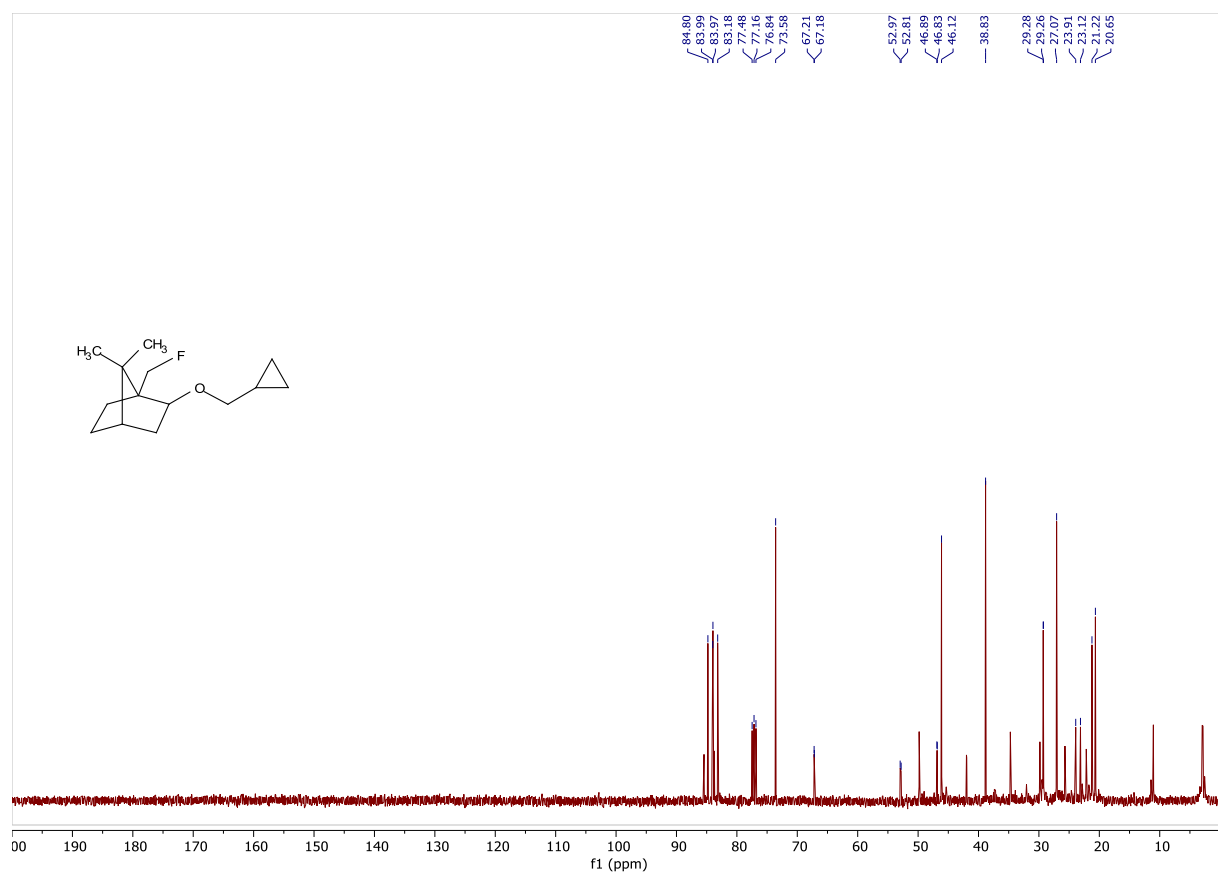


400 MHz ¹H-NMR spectrum of **4g** (CDCl₃)

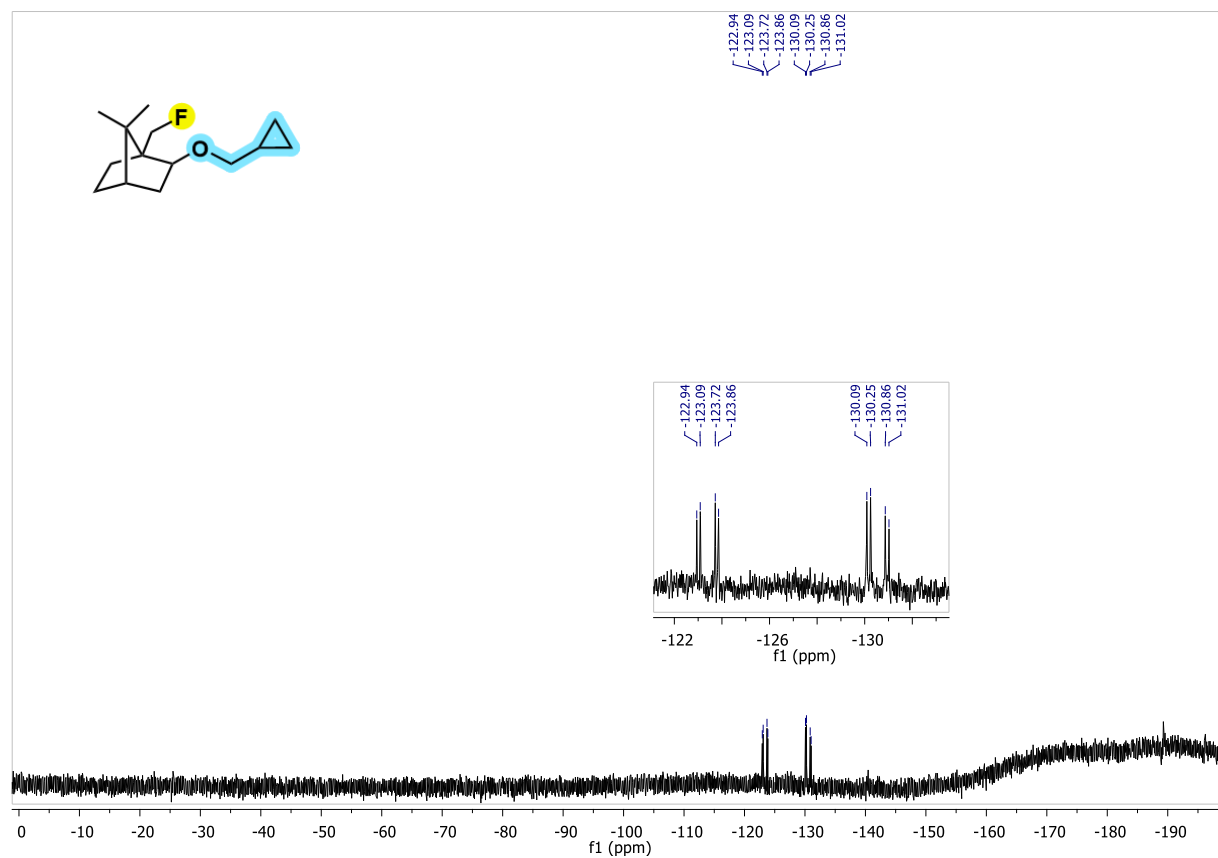


101 MHz ¹³C-NMR spectrum of **4g** (CDCl₃)

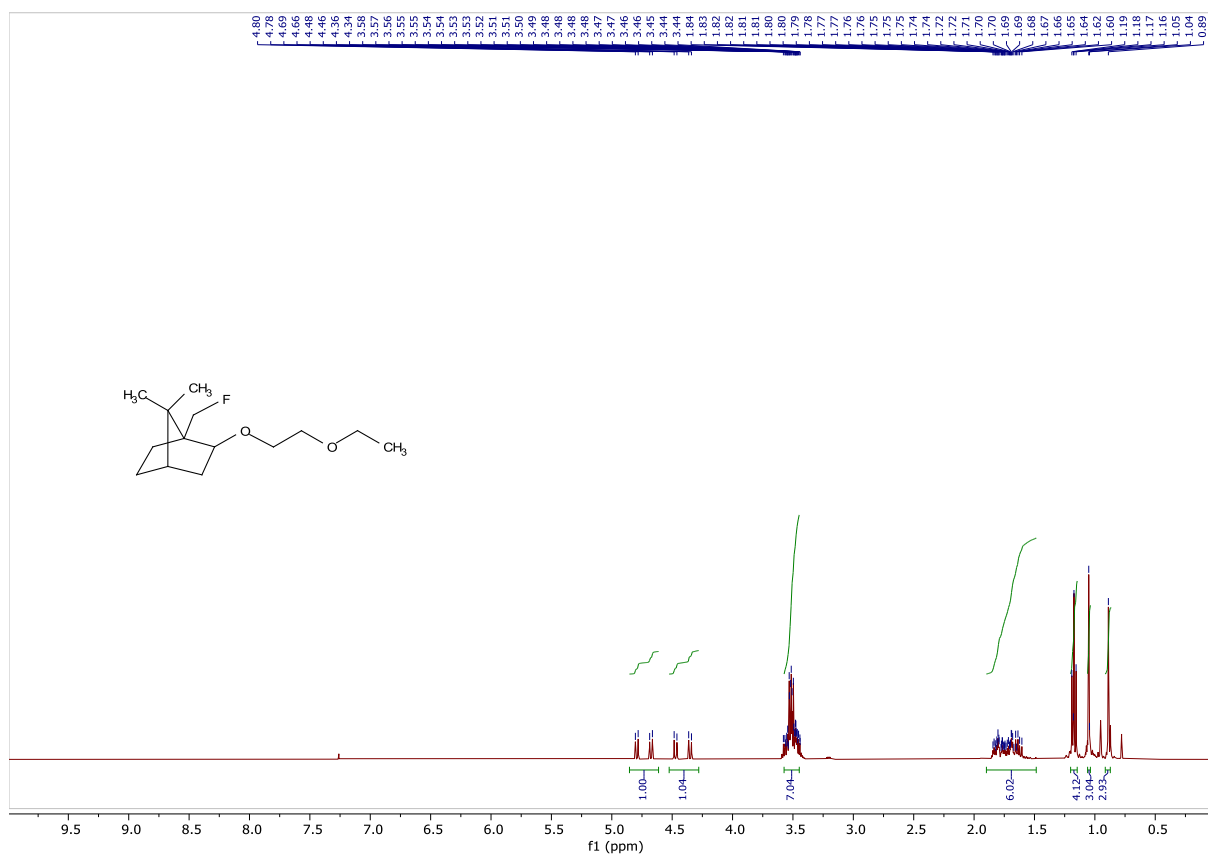




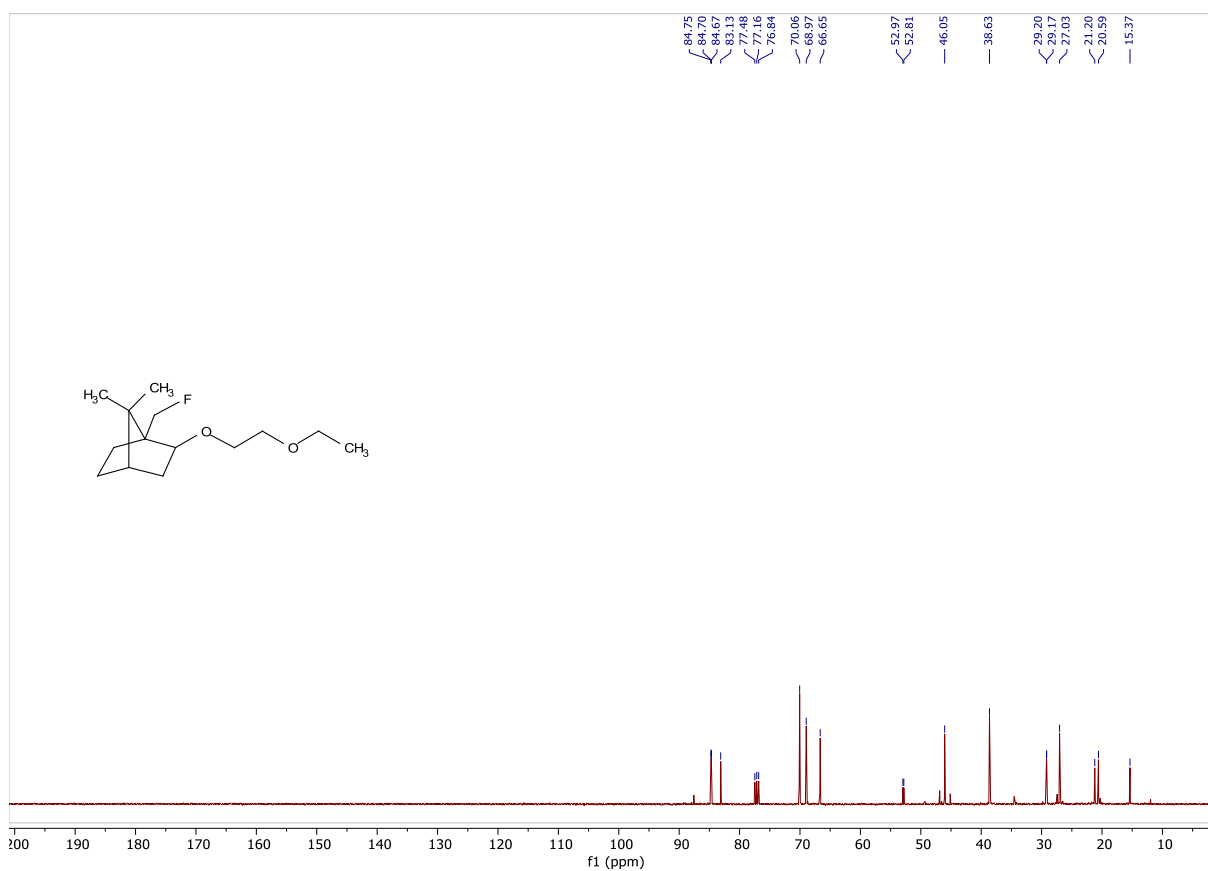
101 MHz ^{13}C -NMR spectrum of **4h** (CDCl_3)



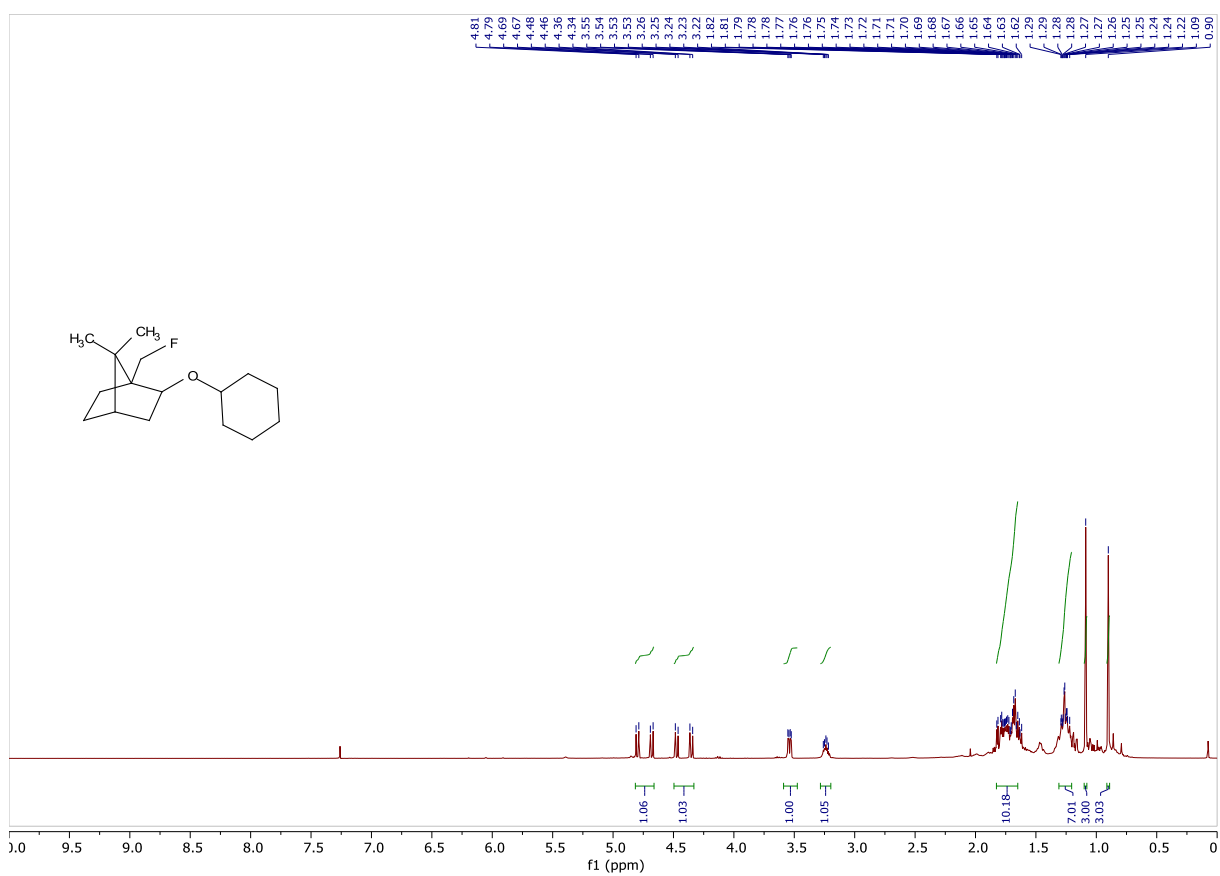
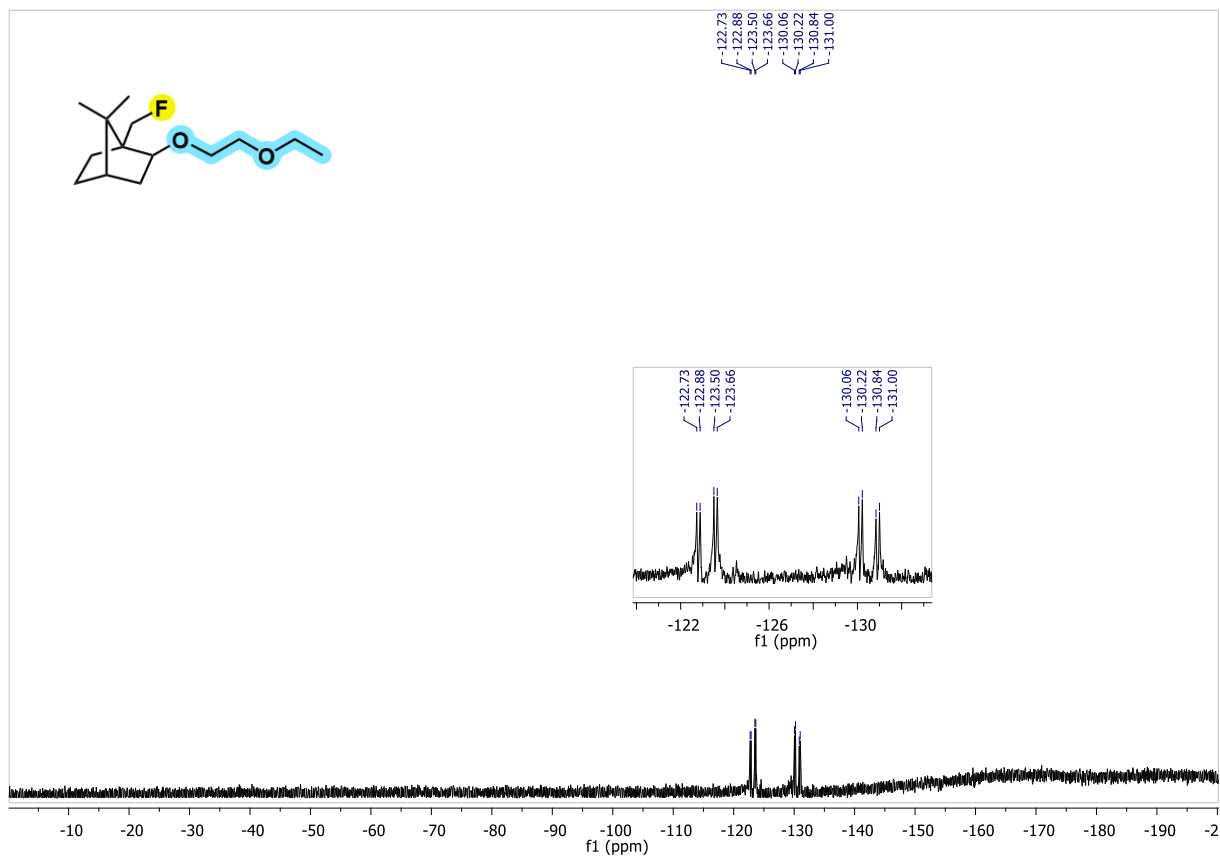
376 MHz ^{19}F -NMR spectrum of **4h** (CDCl_3)



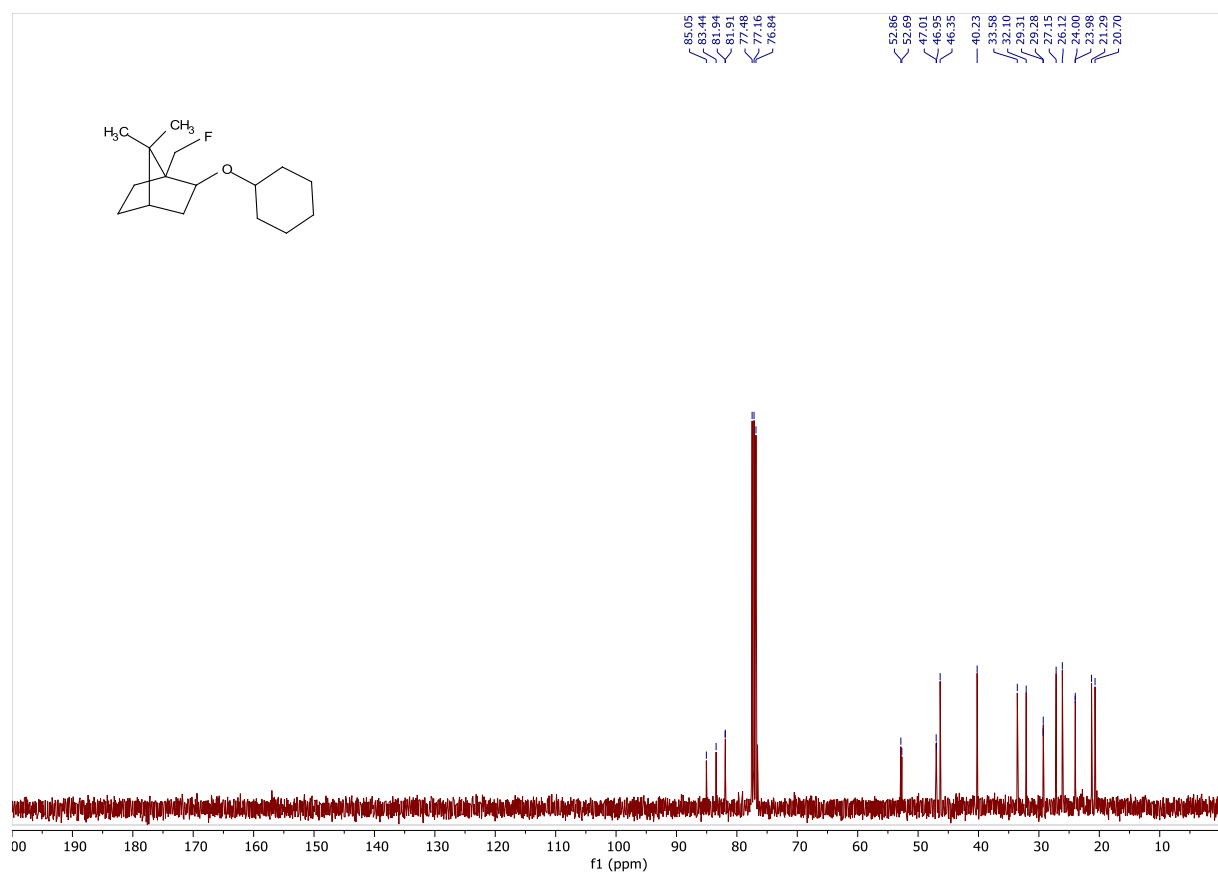
400 MHz ^1H -NMR spectrum of **4i** (CDCl_3)



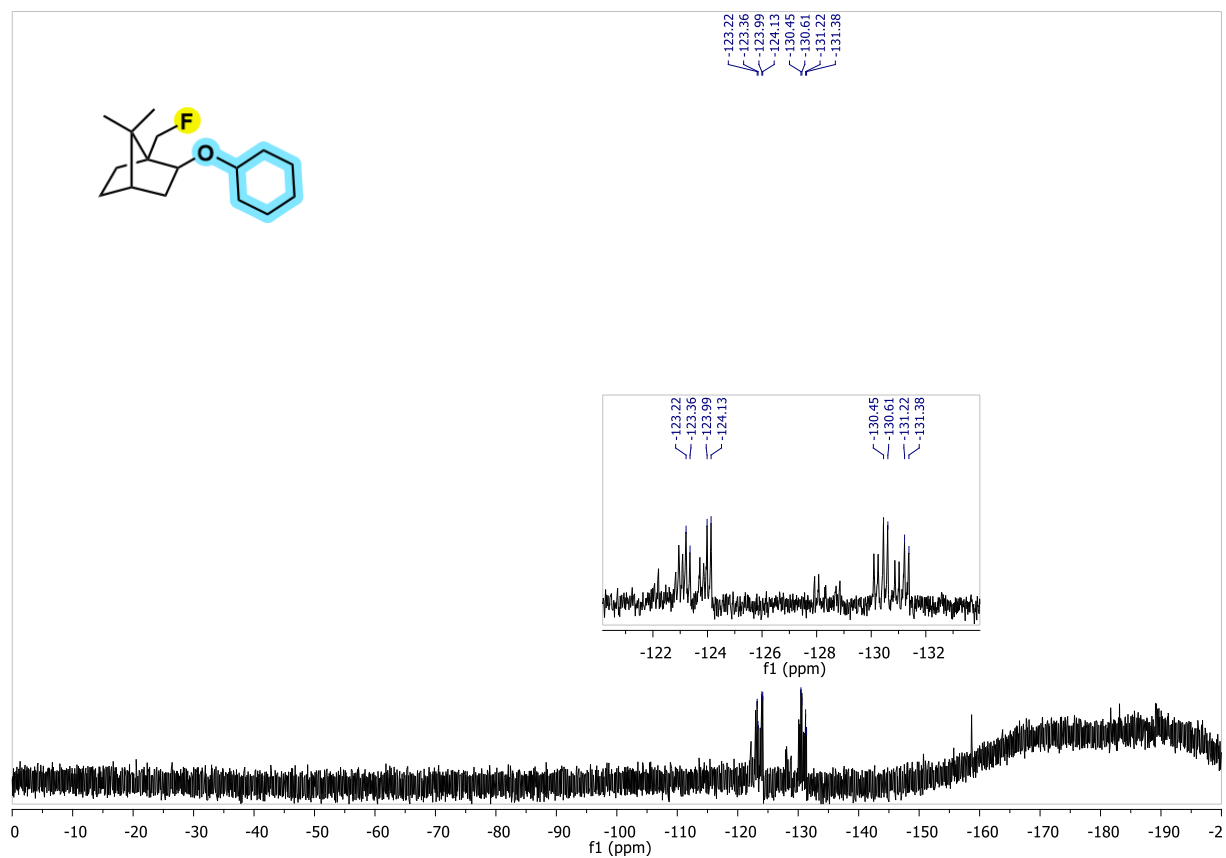
101 MHz ^{13}C -NMR spectrum of **4i** (CDCl_3)



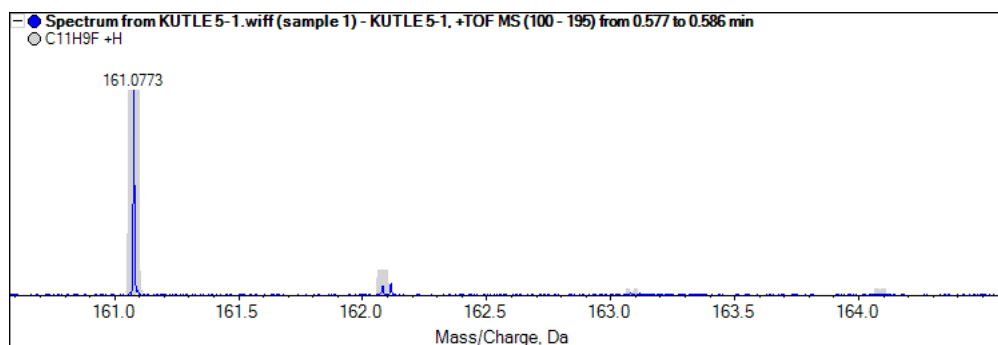
400 MHz ^1H -NMR spectrum of **4j** (CDCl_3)



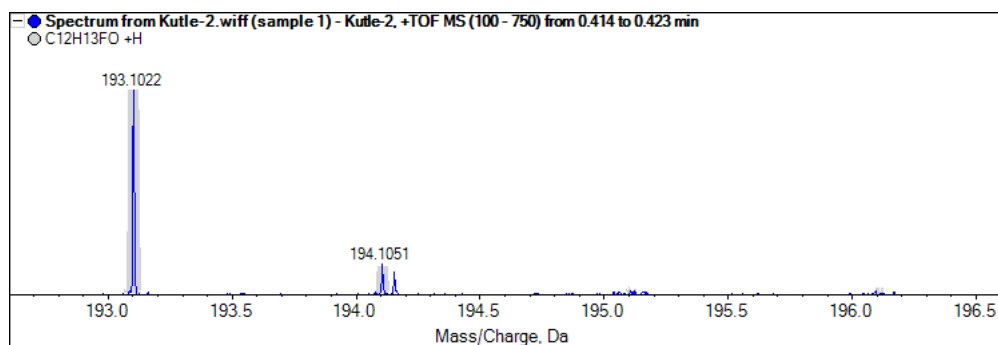
101 MHz ^{13}C -NMR spectrum of **4j** (CDCl_3)



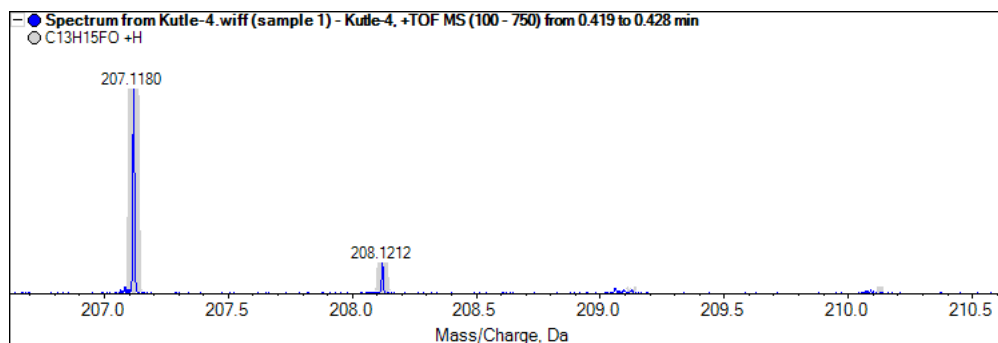
376 MHz ^{19}F -NMR spectrum of **4j** (CDCl_3)



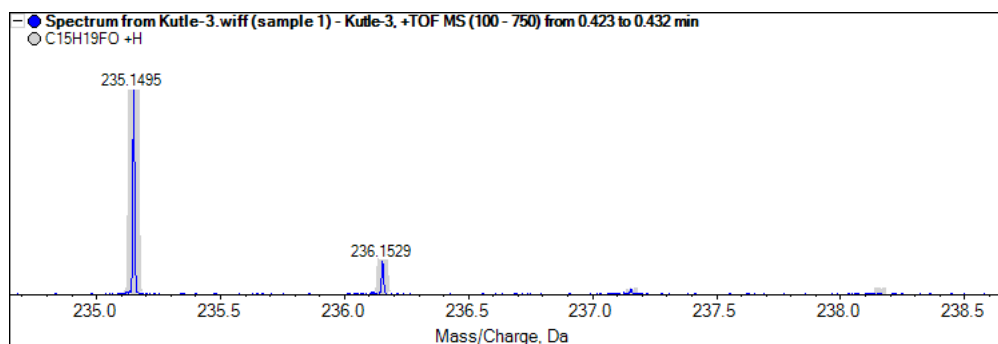
(TOF MS) spectrum of **3a**.



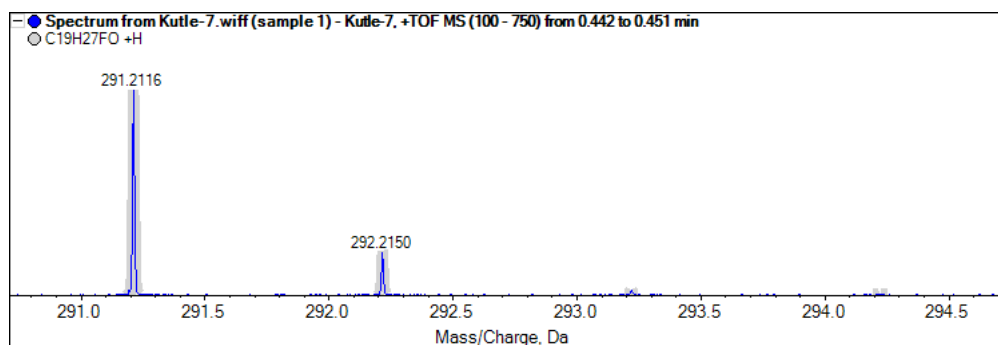
(TOF MS) spectrum of **3b**.



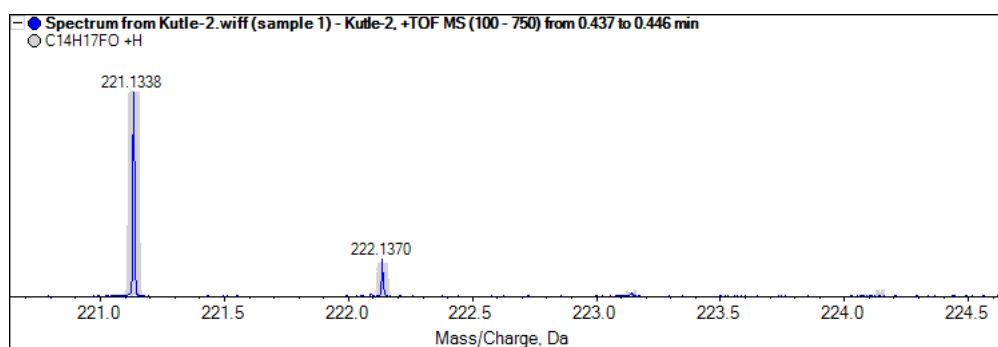
(TOF MS) spectrum of **3c**.



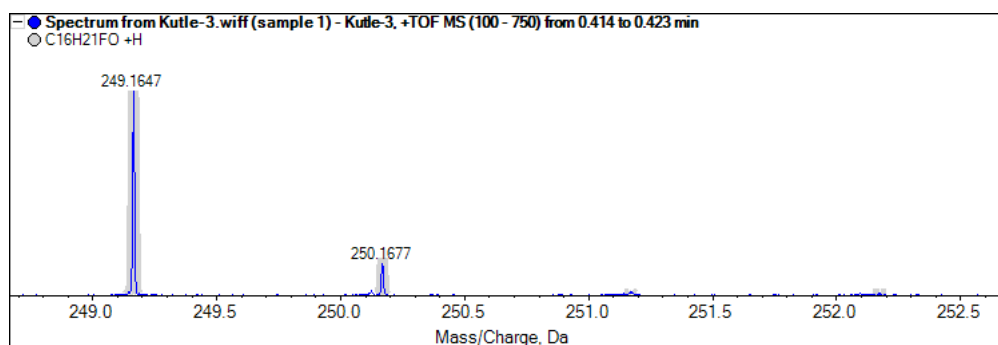
(TOF MS) spectrum of **3d**.



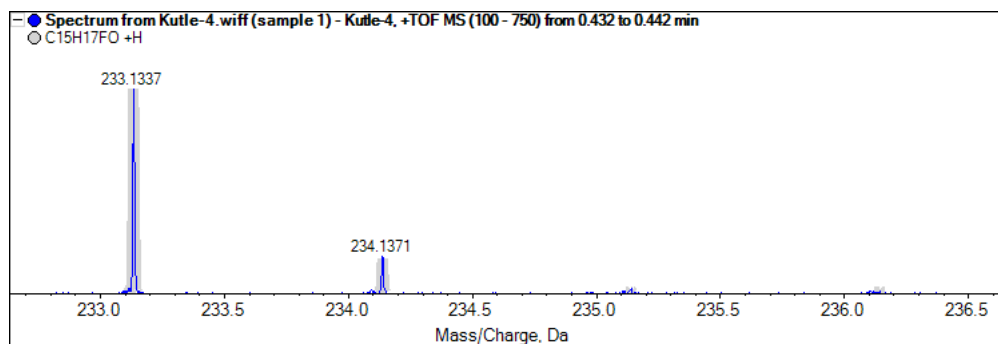
(TOF MS) spectrum of **3e**.



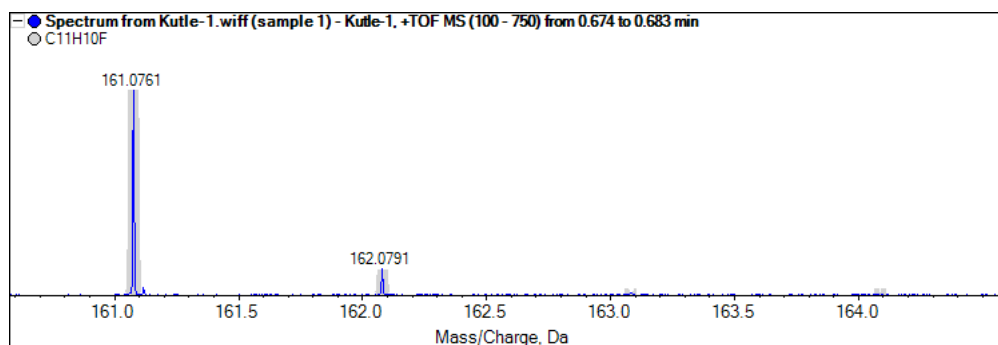
(TOF MS) spectrum of **3f**.



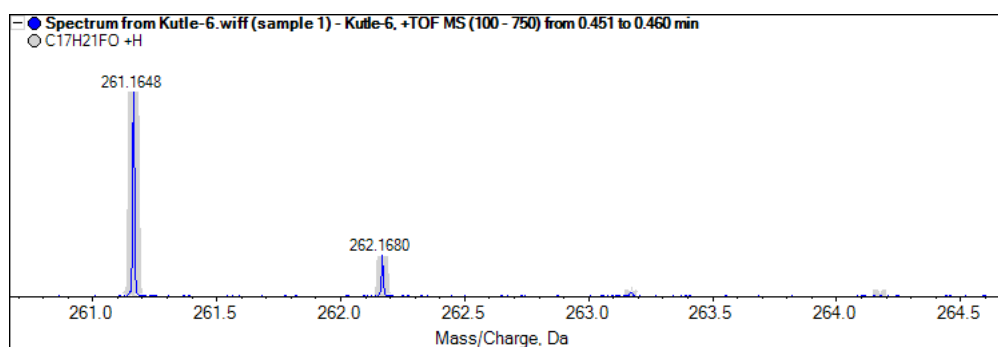
(TOF MS) spectrum of **3g**.



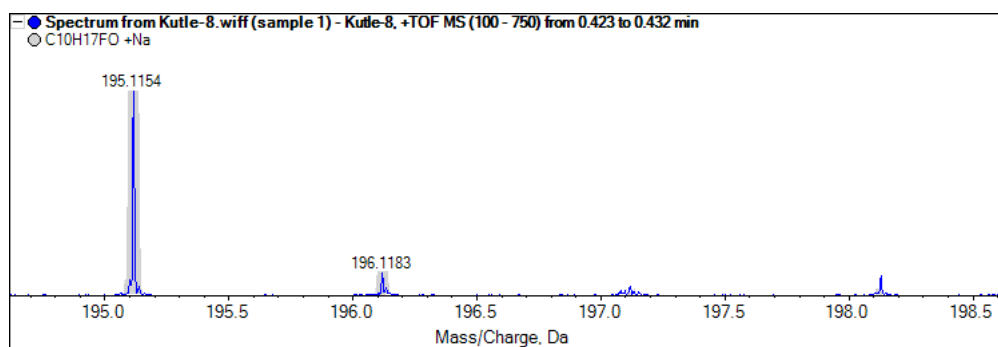
(TOF MS) spectrum of **3h**.



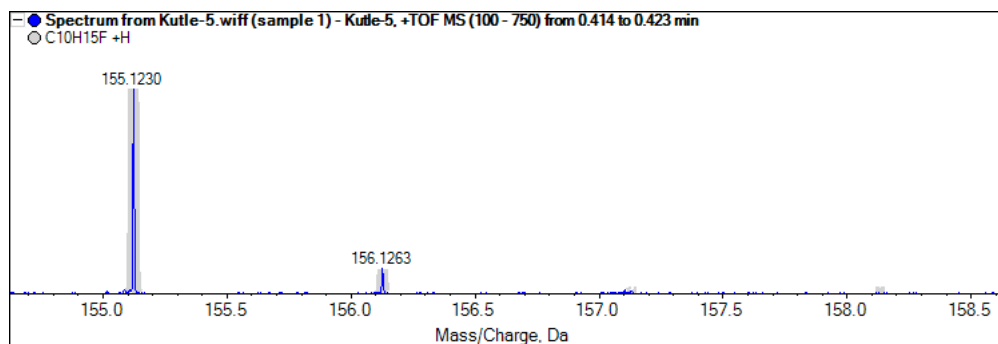
(TOF MS) spectrum of **3i**.



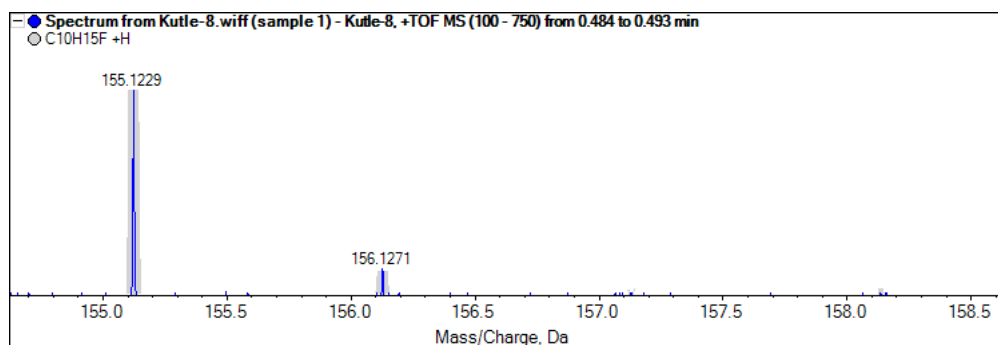
(TOF MS) spectrum of **3j**.



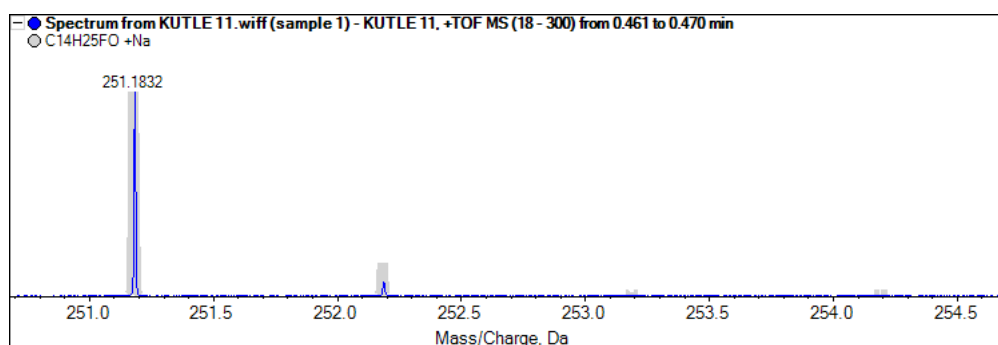
(TOF MS) spectrum of **4a**.



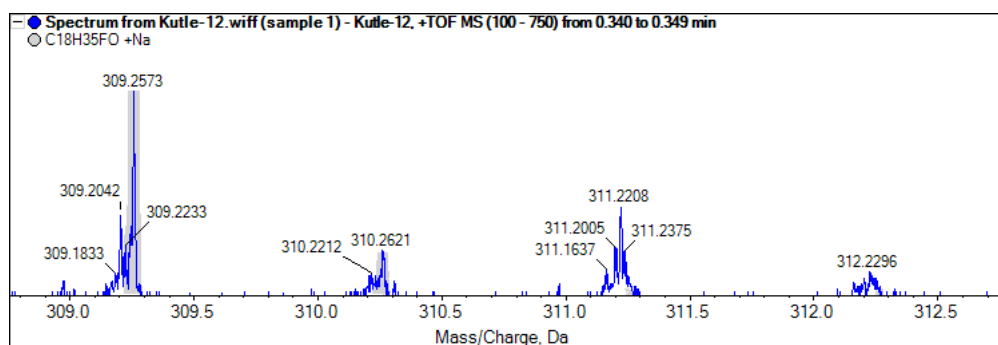
(TOF MS) spectrum of **4b**.



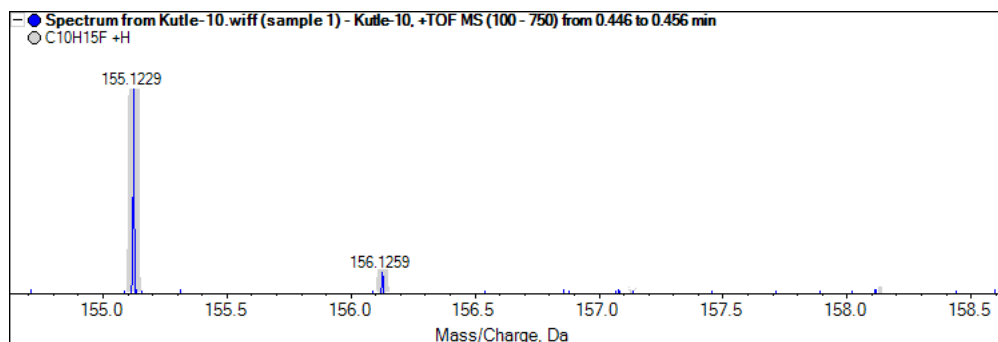
(TOF MS) spectrum of **4c**.



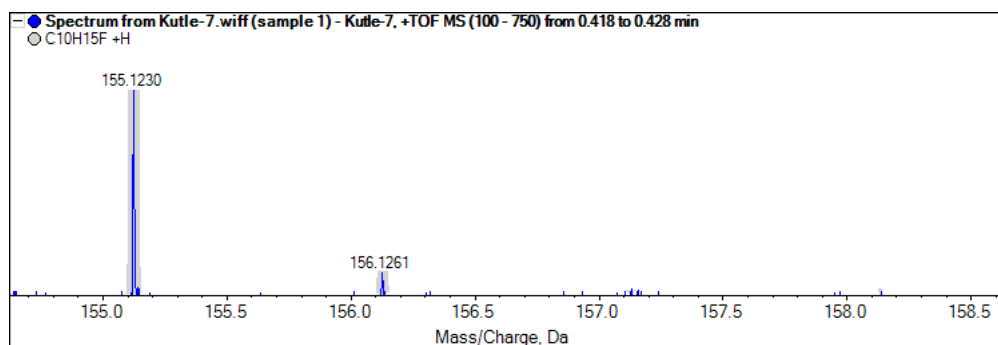
(TOF MS) spectrum of **4d**.



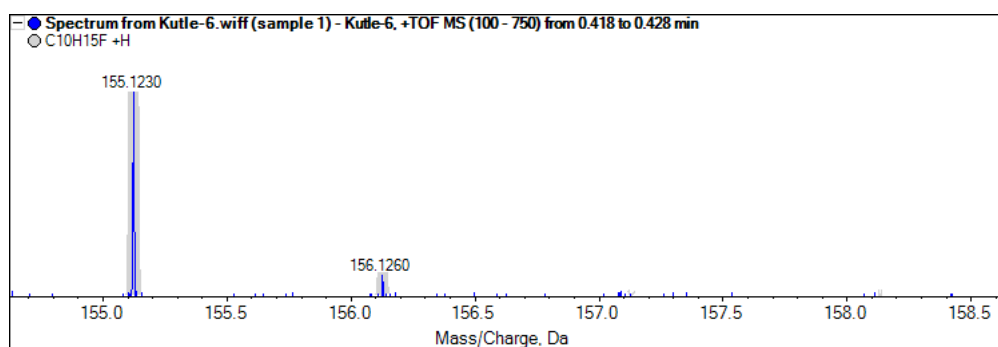
(TOF MS) spectrum of **4e**.



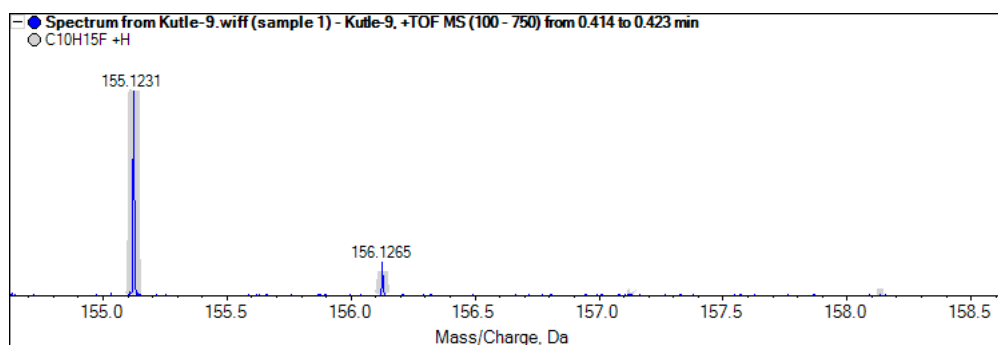
(TOF MS) spectrum of **4f**.



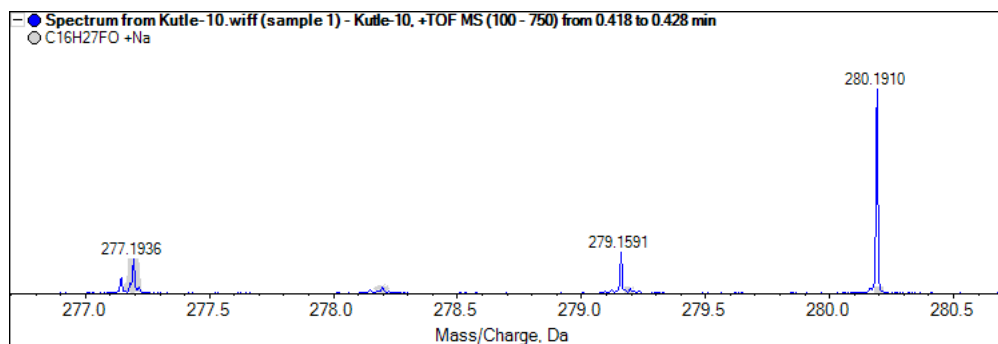
(TOF MS) spectrum of **4g**.



(TOF MS) spectrum of **4h**.



(TOF MS) spectrum of **4i**.



(TOF MS) spectrum of **4i**.