Supporting Information

I_2-mediated convenient ring-opening of simple gem-difluorocyclopropanes

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Preparation of gem-difluorocyclopropanes

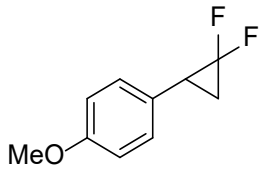
Method A

To a mixture of KI (2.0 or 4.0 equiv) and an alkene (1.0 equiv) in EtCN (1.0 M to alkene) was added methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (MDFA, 2.0 or 4.0 equiv) at room temperature, and the resultant solution was stirred at 50 °C (oil bath temperature) for 24 h. After cooling to room temperature, the reaction mixture was quenched by water and extracted by hexane three times. The combined hexane layer was successively washed with water, saturated aqueous $NaHCO_3$, and brine. After drying over anhydrous Na_2SO_4, followed by concentration under reduced pressure, the crude product was purified by silica gel column chromatography.

Method B

To a mixture of NaI (0.2 equiv) and an alkene (1.0 equiv) in anhydrous THF (3.4 M to alkene) under argon atmosphere was added $TMSCF_3$ (2.5 equiv), and the resultant solution was stirred at 65 °C (oil bath temperature) until the starting material was disappeared (judged by TLC). After cooling to room temperature and evaporation to dryness under reduced pressure, water (20 mL) was added to the residue, which was extracted by Et_2O three times. The combined extract was washed with water, saturated aqueous $Na_2S_2O_3$, and brine. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography.

1-(2,2-Difluorocyclopropyl)-4-methoxybenzene (**1a**) [52178-85-5][1]



Method B, 3.66 g (19.84 mmol, 95%).

Colorless oil.

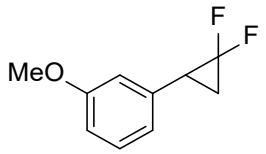
Rf = 0.31 (hexane:Et_2O = 25:1).

^{1}H NMR ($CDCl_3$) δ 7.16 (2H, d, *J* = 8.3 Hz), 6.87 (2H, d, *J* = 8.3 Hz), 3.80 (3H, s), 2.77-2.66 (1H, m), 1.85-1.72 (1H, m), 1.61-1.50 (1H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 158.7, 129.2, 125.6, 113.9, 112.7 (dd, *J* = 286.3, 283.2 Hz), 55.2, 26.4 (t, *J* = 11.2 Hz), 16.9 (dd, *J* = 10.8, 10.2 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −127.30 ~ −127.93 (1F, m), −141.66 ~ −142.25 (1F, m) ppm.

1-(2,2-Difluorocyclopropyl)-3-methoxybenzene (**1b**) [2641779-74-8][2]



Method B, 1.73 g (9.39 mmol, 91%).

Pale yellow oil.

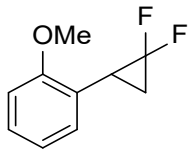
Rf = 0.30 (hexane:Et_2O = 50:1).

^{1}H NMR ($CDCl_3$) δ 7.24 (1H, t, *J* = 7.8 Hz), 6.83-6.76 (3H, m), 3.80 (3H, s), 2.73 (1H, ddd, *J* = 13.2, 11.7, 8.1 Hz), 1.80 (1H, dddd, *J* = 12.6, 11.7, 7.8, 4.8 Hz), 1.61 (1H, dddd, *J* = 12.6, 11.7, 7.8, 3.9 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 159.6, 135.1, 129.4, 120.3, 113.1, 112.53 (dd, *J* = 286.0, 282.2 Hz), 112.46, 55.1, 27.2 (t, *J* = 11.8, 10.6 Hz), 16.9 (t, *J* = 11.1, 10.3 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –127.93 ~ –128.56 (1F, m), –143.17 ~ –143.76 (1F, m) ppm.

1-(2,2-Difluorocyclopropyl)-2-methoxybenzene (**1c**) [1910105-56-4][3]



Method B, 1.80 g (9.77 mmol, 84%).

Colorless oil.

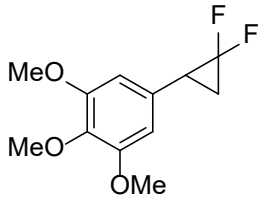
Rf = 0.30 (hexane:Et_2O = 50:1).

^{1}H NMR ($CDCl_3$) δ 7.26 (1H, td, *J* = 7.8, 1.7 Hz), 7.09 (1H, d, *J* = 7.5 Hz), 6.93 (1H, d, *J* = 7.5 Hz), 6.89 (1H, d, *J* = 7.8 Hz), 3.87 (3H, s), 2.86 (1H, ddd, *J* = 13.2, 12.3, 8.4 Hz), 1.84-1.72 (1H, m), 1.63-1.52 (1H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 158.7 (d, *J* = 0.6 Hz), 128.4, 127.8 (dd, *J* = 3.1, 1.8 Hz), 122.0, 120.3 (d, *J* = 0.7 Hz), 113.1 (dd, *J* = 286.0, 282.2 Hz), 110.2, 55.4, 22.5 (dd, *J* = 11.8, 10.6 Hz), 15.8 (dd, *J* = 11.1, 10.3 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –127.93 ~ –128.56 (1F, m), –143.17 ~ –143.76 (1F, m) ppm.

5-(2,2-Difluorocyclopropyl)-1,2,3-trimethoxybenzene (**1d**) [3026542-50-4][2]



Method B, 2.20 g (9.00 mmol, 90%).

White solid.

m.p.: 47.3 - 48.1 °C.

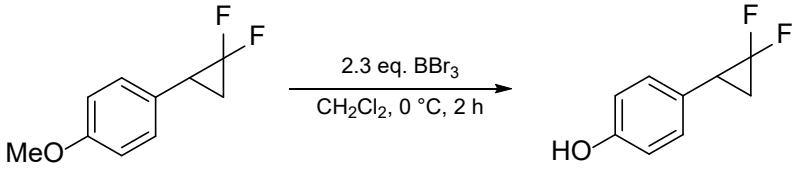
Rf = 0.27 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 6.45 (2H, s), 3.86 (6H, s), 3.84 (3H, s), 2.72 (1H, ddd, *J* = 13.2, 11.4, 8.4 Hz), 1.80 (1H, dddd, *J* = 16.5, 12.6, 8.1, 4.8 Hz), 1.64-1.53 (1H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 153.2, 137.2, 129.2, 112.5 (dd, *J* = 286.0, 283.4 Hz), 105.2, 60.8, 56.0, 27.3 (t, *J* = 11.1 Hz), 17.1 (t, *J* = 10.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −126.64 ~ −127.30 (1F, m), −142.73 ~ −143.33 (1F, m) ppm.

Preparation of 4-(2,2-difluorocyclopropyl)phenol (**1e**) [52178-86-6][4]



To a mixture of 1-(2,2-difluorocyclopropyl)-4-methoxybenzene 0.5524 g (3.00 mmol) and CH_2Cl_2 17 mL under argon atmosphere was added 1 M BBr_3 in CH_2Cl_2, 6.9 mL at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, after warming to room temperature, water (20 mL) was added to the residue, which was extracted by CH_2Cl_2 three times. The combined extract was washed with water, and brine. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography (hexane:AcOEt = 4:1) to obtain 4-(2,2-difluorocyclopropyl)phenol 0.44 g (2.60 mmol, 87%).

White solid.

m.p.: 56.5 - 57.8 °C.

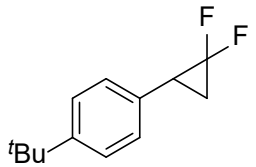
Rf = 0.31 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.07 (2H, d, *J* = 8.4 Hz), 6.78 (2H, d, *J* = 8.4 Hz), 5.64 (1H, br s), 2.72-2.61 (1H, m), 1.81-1.69 (1H, m), 1.57-1.46 (1H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 154.4, 129.4, 126.0, 115.4, 112.7 (dd, *J* = 286.6, 283.5 Hz), 26.4 (t, *J* = 11.8 Hz), 16.8 (t, *J* = 10.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −127.22 ~ −127.86 (1F, m), −143.34 ~ −143.94 (1F, m) ppm.

1-(2,2-Difluorocyclopropyl)-4-*tert*-butylbenzene (**1f**) [1241957-35-6][3]



Method B, 1.04 g (4.95 mmol, 99%).

Colorless oil.

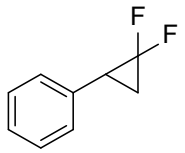
Rf = 0.50 (hexane).

^{1}H NMR ($CDCl_3$) δ 7.35 (2H, d, *J* = 8.4 Hz), 7.16 (2H, d, *J* = 7.8 Hz), 2.72 (1H, m), 1.79 (1H, ddd, *J* = 12.0, 7.2, 4.5 Hz), 1.60 (1H, ddd, *J* = 12.3, 8.1, 3.9 Hz), 1.31 (9H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 150.1, 130.7, 127.7, 125.4, 112.7 (t, *J* = 286.6 Hz), 34.5, 31.3, 26.8 (t, *J* = 11.2 Hz), 17.0 (d, *J* = 10.6 Hz) ppm.

^{19}F NMR $CDCl_3$) δ −127.16 (1F, dtd, *J* = 152.9, 13.8, 4.8 Hz), −143.53 (1F, ddd, *J* = 152.6, 12.8, 4.5 Hz) ppm.

(2,2-Difluorocyclopropyl)benzene (**1g**) [13343-40-3][1]



Method B, 1.36 g (8.81 mmol, 88%, Purity 90 wt% in THF). This compound **1g** is high volatility, so without further evaporation it was used at the next step.

Pale yellow oil.

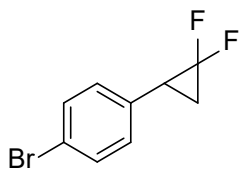
Rf = 0.75 (hexane).

^{1}H NMR ($CDCl_3$) δ 7.34-7.20 (5H, m), 2.79-2.68 (1H, m), 1.86-1.73 (1H, m), 1.66-1.55 (1H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 133.7, 128.4, 128.0 (dd, *J* = 1.9, 1.2 Hz), 127.1, 112.6 (dd, *J* = 285.9, 283.4 Hz), 27.2 (t, *J* = 11.2 Hz), 17.0 (t, *J* = 10.1 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −126.84 ~ −127.47 (1F, m), −143.39 ~ −144.00 (1F, m) ppm.

1-Bromo-4-(2,2-difluorocyclopropyl)benzene (**1h**) [1275621-14-1][1]



Method A, 1.85 g (7.93 mmol, 82%).

Colorless oil.

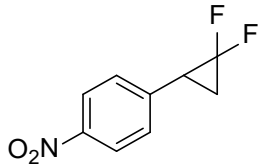
Rf = 0.57 (hexane).

^{1}H NMR ($CDCl_3$) δ 7.44 (2H, d, *J* = 8.1 Hz), 7.09 (2H, d, *J* = 8.4 Hz), 2.75-2.64 (1H, m), 1.90-1.76 (1H, m), 1.64-1.35 (1H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 132.7, 131.6, 129.7, 121.0, 112.2 (dd, *J* = 286.6, 283.4 Hz), 26.6 (dd, *J* = 11.7, 11.2 Hz), 17.1 (dd, *J* = 10.6, 10.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −127.09 ~ −127.72 (1F, m), −143.27 ~ −143.89 (1F, m) ppm.

1-(2,2-Difluorocyclopropyl)-4-nitrobenzene (**1i**) [35694-66-7][5]



Method B, 0.88 g (4.42 mmol, 88%).

Yellow oil.

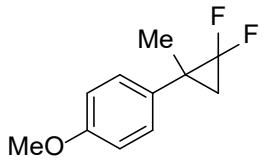
Rf = 0.28 (hexane:AcOEt = 10:1).

^{1}H NMR ($CDCl_3$) δ 8.18 (2H, d, *J* = 8.7 Hz), 7.38 (2H, d, *J* = 8.7 Hz), 2.91-2.80 (1H, m), 2.05-1.93 (1H, m), 1.80-1.69 (1H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 147.0, 141.4, 128.7 (t, *J* = 1.9 Hz), 123.6, 111.9 (dd, *J* = 287.7, 283.5 Hz), 27.0 (dd, *J* = 12.4, 11.2 Hz), 17.9 (t, *J* = 10.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −126.40 ~ −127.04 (1F, m), −142.83 ~ −143.44 (1F, m) ppm.

1-(2,2-Difluoro-1-methylcyclopropyl)-4-methoxybenzene (**1j**) [52178-70-8][5]



Method A, 2.35 g (11.85 mmol, 99%).

Pale yellow oil.

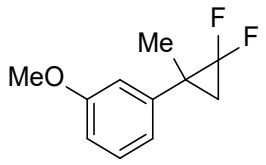
Rf = 0.57 (hexane:CH_2Cl_2 = 1:1).

^{1}H NMR ($CDCl_3$) δ 7.26-7.22 (2H, m), 6.90-6.85 (2H, m), 3.80 (3H, s), 1.63 (1H, ddd, *J* = 13.5, 7.5, 3.6 Hz), 1.49 (3H, dd, *J* = 2.7, 1.8 Hz), 1.36 (1H, ddd, *J* = 12.3, 7.5, 4.2 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 158.6, 131.2, 129.4, 114.8 (dd, *J* = 288.7, 286.3 Hz), 113.9, 55.2, 30.5 (dd, *J* = 10.6, 10.0 Hz), 22.5 (dd, *J* = 10.0, 9.9 Hz), 21.5 (d, *J* = 6.2 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −133.72 ~ −134.29 (1F, m), −138.67 ~ −139.25 (1F, m) ppm.

1-(2,2-Difluoro-1-methylcycloprop-1-yl)-3-methoxybenzene (**1k**)



Method A, 0.84 g (4.23 mmol, 72%).

Colorless oil.

Rf = 0.60 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.27 (1H, t, *J* = 7.8 Hz), 6.91 (1H, d, *J* = 7.8 Hz), 6.86-6.85 (1H, m), 6.83-6.80 (1H, m), 3.81 (3H, s), 1.67 (1H, ddd, *J* = 13.8, 7.8, 3.6 Hz), 1.52 (3H, s), 1.39 (1H, ddd, *J* = 12.3, 7.5, 4.5 Hz) ppm.

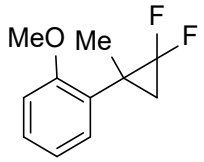
^{13}C NMR ($CDCl_3$) δ 159.6, 140.6, 129.5, 120.6 (d, *J* =1.9 Hz), 114.5 (dd, *J* = 289.4, 286.9 Hz), 114.3 (d, *J* = 2.5 Hz), 55.1, 31.2 (t, *J* = 10.3 Hz), 22.4 (t, *J* = 10.0 Hz), 21.3 (dd, *J* = 6.1, 1.9 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −133.87 (1F, dd, *J* = 150.7, 13.7 Hz), −138.73 (1F, dd, *J* = 150.4, 12.6 Hz) ppm.

IR ($CHCl_3$) ν 2966, 2937, 2838, 1603, 1470, 1238, 1204, 1048, 1007, 699 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{11}H_{12}F_2O$ 198.0856; found, 198.0873.

1-(2,2-Difluoro-1-methylcyclopropyl)-2-methoxybenzene (**1l**) [2366981-51-1][5]



Method A, 1.54 g (7.77 mmol, 78%)

Colorless oil.

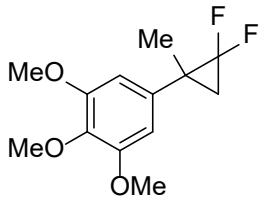
Rf = 0.71 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.20−7.26 (2H, m), 6.91 (1H, dt, *J* = 7.2, 1.2 Hz), 6.89 (1H, d, *J* = 8.1 Hz), 3.87 (3H, s), 1.53(1H, ddd, *J* = 13.5, 7.8, 3.9 Hz), 1.44 (3H, dd, *J* = 2.7, 1.8 Hz), 1.36 (1H, ddd, *J* = 12.3, 7.8, 4.8 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 158.5, 129.7, 128.7, 127.5, 120.4, 114.9 (t, *J* = 286.0 Hz), 110.7, 55.4, 28.4 (t, *J* = 10.6 Hz), 22.4 (t, *J* = 10.0 Hz), 19.4 (d, *J* = 5.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −134.78 (1F, dd, *J* = 150.7, 11.6 Hz), −140.3 (1F, dd, *J* = 150.7, 11.6 Hz) ppm.

1-(2,2-Difluoro-1-methylcycloprop-1-yl)-3,4,5-trimethoxybenzene (**1m**)



Method B, 0.97 g (3.76 mmol, 94%).

Colorless oil.

Rf = 0.38 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 6.51 (2H, s), 3.87 (6H, s), 3.84 (3H. s), 1.65 (1H, ddd, *J* = 13.8, 7.5, 3.5 Hz), 1.51 (3H, m), 1.39 (1H, ddd, *J* = 12.0, 7.5, 4.5 Hz) ppm.

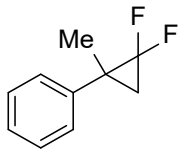
^{13}C NMR ($CDCl_3$) δ 153.1, 137.1, 134.7, 114.5 (t, *J* =286.6 Hz), 105.4, 60.6, 56.0, 31.4 (t, *J* = 9.9 Hz), 22.7 (t, *J* = 10.0 Hz), 21.4 (d, *J* = 6.2 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –133.56 (1F, dd, *J* = 150.4, 13.6 Hz), –138.54 (1F, dd, *J* = 150.7, 13.8 Hz) ppm.

IR ($CHCl_3$) ν 2940, 2841, 1589, 1466, 1261, 1238, 1173, 1129, 1007, 493 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{13}H_{17}F_2O_3$ 259.1146; found, 259.1149.

(2,2-Difluoro-1-methylcyclopropyl)benzene (**1n**) [59164-24-8][1]



Method A, 5.31 g (31.60 mmol, 79%).

Colorless oil.

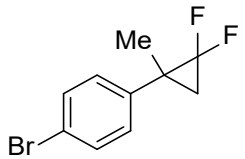
Rf = 0.42 (hexane).

^{1}H NMR ($CDCl_3$) δ 7.37-7.26 (5H, m), 1.68 (1H, ddd, *J* = 13.7, 7.7, 3.6 Hz), 1.52 (3H, dd, *J* = 2.7, 1.8 Hz), 1.40 (1H, ddd, *J* = 12.3, 7.7, 4.5 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 139.1 (t, *J* = 2.5 Hz), 128.5, 128.3 (d, *J* = 2.4 Hz), 127.2, 114.5 (dd, *J* = 288.7, 286.9 Hz), 31.2 (dd, *J* = 11.2, 9.3 Hz), 22.5 (t, *J* = 9.9 Hz), 21.4 (dd, *J* = 6.2, 1.8 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –133.49 ~ –134.06 (1F, m), –138.50 ~ –139.08 (1F, m) ppm.

1-(2,2-Difluoro-1-methylcyclopropyl)-4-bromobenzene (**1o**) [2138083-44-8][5]



Method A, 1.15 g (4.66 mmol, 93%).

Colorless oil.

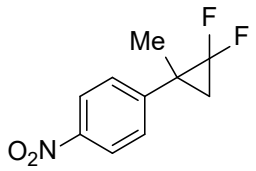
Rf = 0.26 (hexane).

^{1}H NMR ($CDCl_3$) δ 7.51-7.45 (2H, m), 7.26-7.17 (2H, m), 1.64 (1H, ddd, *J* = 13.5, 7.8, 3.6 Hz), 1.49 (3H, dd, *J* = 3.0, 2.1 Hz), 1.42 (1H, ddd, *J* = 12.3, 7.5, 4.5 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 138.1 (t, *J* = 1.9 Hz), 131.7, 130.1 (d, *J* = 2.5 Hz), 121.2, 114.1 (dd, *J* = 289.0, 285.4 Hz), 30.6 (dd, *J* = 11.2, 9.3 Hz), 22.5 (t, *J* = 9.9 Hz), 21.1 (dd, *J* = 6.2, 2.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −133.70 (1F, dd, *J* = 150.5, 11.4 Hz), −138.87 (1F, dd, *J* = 150.5, 11.4 Hz) ppm.

1-(2,2-Difluoro-1-methylcyclopropyl)-4-nitrobenzene (**1p**) [113664-78-1][5]



Method A, 0.47 g (2.22 mmol, 89%).

White solid.

m.p.: 53.6 - 53.9 °C.

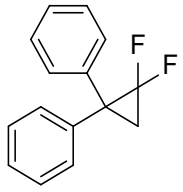
Rf = 0.20 (hexane:Et_2O = 25:1).

^{1}H NMR ($CDCl_3$) δ 8.11 (2H, d, *J* = 8.7 Hz), 7.41 (2H, d, *J* = 8.7 Hz), 1.70-1.62 (1H, m), 1.50-1.42 (4H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 147.0, 146.4 (dd, *J* = 2.5, 1.9 Hz), 129.4 (dd, *J* = 1.9, 0.6 Hz), 123.8, 113.6 (dd, *J* = 290.3, 286.6 Hz), 30.8 (dd, *J* = 11.5, 9.6 Hz), 22.8 (t, *J* = 9.9 Hz), 20.8 (dd, *J* = 6.2, 1.8 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −133.07 ~ −138.81 (1F, m), −138.24 ~ −138.81 (1F, m) ppm.

1,1-Difluoro-2,2-diphenylcyclopropane (**1q**) [51954-17-7][1]



Method A, 2.53 g (11.01 mmol, 93%).

White solid.

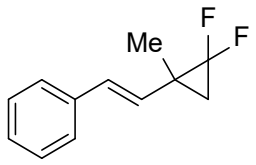
Rf = 0.43 (hexane:Et_2O = 20:1).

^{1}H NMR ($CDCl_3$) δ 7.43-7.24 (10H, m), 2.08 (1H, t, *J* = 8.6 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 138.6, 128.8 (t, *J* = 1.2 Hz), 128.6, 127.3, 112.9 (t, *J* = 288.1 Hz), 40.0 (t, *J* = 10.6 Hz), 23.6 (t, *J* = 9.9 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −131.19 (t, *J* = 9.0 Hz) ppm.

(E)-[2-(2,2-Difluoro-1-methylcyclopropyl)ethen-1-yl]benzene (**1r**) [1323437-19-9][1]



Method B, 1.18 g (6.08 mmol, 61%).

Colorless oil.

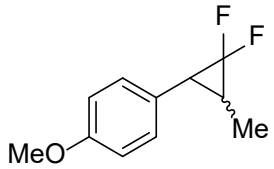
Rf = 0.43 (hexane).

^{1}H NMR ($CDCl_3$) δ 7.36-7.21 (5H, m), 6.34 (1H, d, *J* = 16.2 Hz), 6.06 (1H, d, *J* = 16.2 Hz), 1.51-1.30 (m, 5H) ppm.

^{13}C NMR ($CDCl_3$) δ 136.8, 129.8, 128.6, 127.9 (dd, *J* = 6.3, 2.5 Hz), 127.4, 126.1, 115.9 (dd, *J* = 292.7, 288.4 Hz), 28.6 (dd, *J* = 11.8, 10.0 Hz), 24.1 (dd, *J* = 10.6, 8.7 Hz), 15.3 (dd, *J* = 6.2, 1.2 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –136.51 (1F, dd, *J* = 152.9, 13.6 Hz), –137.76 (1F, dd, *J* = 152.9, 11.3 Hz) ppm.

(2,2-Difluoro-3-methylcyclopropyl)-4-methoxybenzene (**1s**) [1809584-73-3][6]



*The data in literatures were all for the trans isomer. Although **1s** in this study was the cis and trans mixture, the NMR data could be divided into respective data based on reference data and ratio. So, they are listed separately. See also NMR spectra (page S62-63).*

Method B, 0.93 g (4.73 mmol, 95%, *cis:trans* = 73:27).

Colorless oil.

Rf = 0.32 (hexane:AcOEt = 20:1).

***cis* isomer**

^{1}H NMR ($CDCl_3$) δ 7.18 (2H, d, *J* = 8.4 Hz), 6.84 (2H, d, *J* = 8.7 Hz), 3.79 (3H, s), 2.70 (1H, dd, *J* = 15.3, 12.0 Hz), 1.94-1.79 (1H, m), 0.94 – 0.91 (3H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 158.6, 131.2 (t, *J* = 1.9 Hz), 123.6 (d, *J* = 1.2 Hz), 115.1 (dd, *J* = 288.4, 285.9 Hz), 113.8, 55.1, 27.8 (dd, *J* = 12.4, 9.3 Hz), 21.8 (t, *J* = 9.8 Hz), 6.7 (m) ppm.

^{19}F NMR ($CDCl_3$) δ –122.98 (1F, dm, *J* = 155.2 Hz), –150.76 (1F, d, *J* = 155.2 Hz) ppm.

***trans* isomer**

^{1}H NMR ($CDCl_3$) δ 7.12 (2H, d, J = 8.7 Hz), 6.84 (2H, d, J = 8.7 Hz), 3.79 (3H, s), 2.23 (1H, ddd, J = 10.8, 7.5, 4.2 Hz), 1.82-1.68 (1H, m), 1.34 – 1.31 (3H, m) ppm.

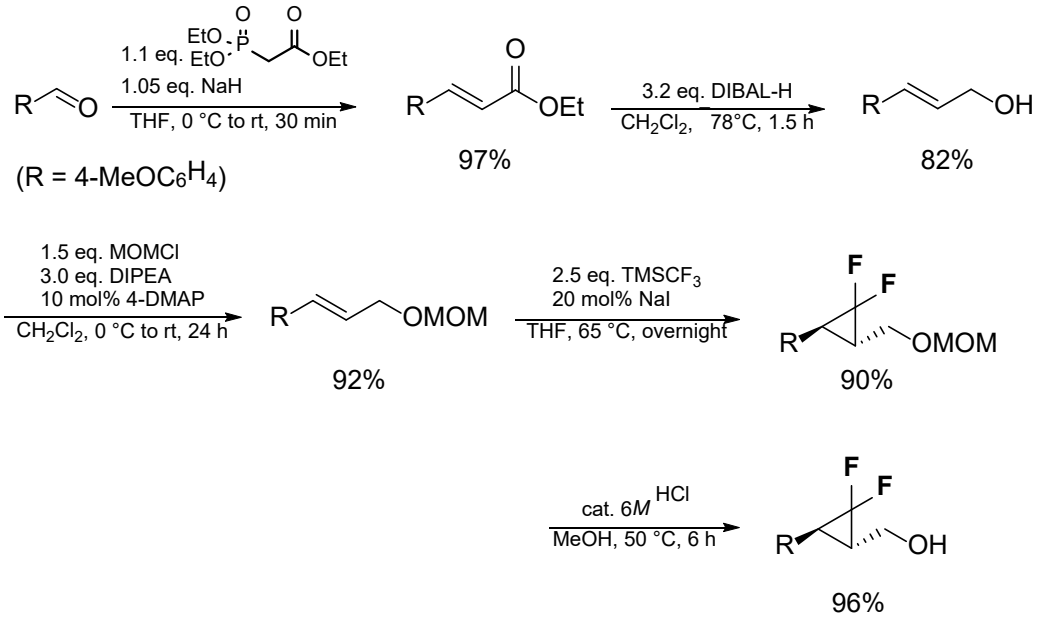
^{13}C NMR ($CDCl_3$) δ 158.6, 128.9 (t, J = 1.5 Hz), 126.2, 114.8 (t, J = 289.7 Hz), 113.8, 55.2, 33.2 (t, J = 10.9 Hz), 24.1 (t, J = 9.9 Hz), 11.4 (d, J = 3.1 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −138.74 ~ −139.92 (2F, m) ppm.

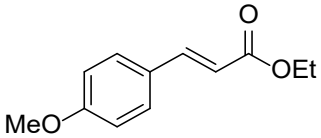
IR ($CHCl_3$) ν 3007, 2964, 2936, 2837, 1613, 1517, 1475, 1290, 1250, 1180 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ calcd for $C_{11}H_{13}F_2O^+$, 199.0929; found, 199.0957.

Preparation of 2,2-difluoro-3-(4-methoxyphenyl)cycloprop-1-yl)methanol (1t)



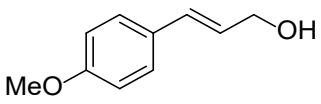
(E)-Ethyl 3-(4-methoxyphenyl)prop-1-enoate [24393-56-4][7]



To a mixture of NaH (55% oil dispersion) 0.9165 g (21.0 mmol) in THF 25 mL was added ethyl diethylphosphonoacetate 4.40 mL (22.0 mmol) at 0 °C under argon atmosphere. After stirring at 0 °C for 20 min, the solution of 4-methoxybenzaldehyde 2.7232 g (20.0 mmol) in THF 16.7 mL was dropwised into the mixture. The mixture was stirred at 0 °C to room temperature for 30 min. After quenching by brine (20 mL), the residue was evaporated to dryness under reduced pressure, which was extracted by CH_2Cl_2 three times. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography (hexane:AcOEt = 10:1) to obtain *(E)*-ethyl 3-(4-methoxyphenyl)prop-2-enoate 4.0173 g (19.48 mmol, 97%) as a white solid.

^{1}H NMR ($CDCl_3$) δ 7.64 (1H, d, J = 15.9 Hz), 7.47 (2H, d, J = 8.4 Hz), 6.89 (2H, d, J = 8.4 Hz), 6.30 (1H, d, J = 15.9 Hz), 4.25 (2H, q, J = 6.9 Hz), 3.82 (3H, s), 1.33 (3H, t, J = 6.9 Hz) ppm.
^{13}C NMR ($CDCl_3$) δ 167.2, 161.2, 144.2, 129.6, 127.1, 115.6, 114.2, 60.2, 55.3, 14.3 ppm.

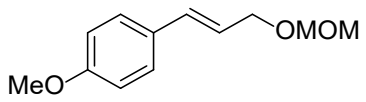
(E)-3-(4-Methoxyphenyl)prop-2-en-1-ol [53484-50-7][8]



To a mixture of *(E)*-ethyl 2-(4-methoxyphenyl)prop-1-enoate 2.0624 g (10.0 mmol) in CH_2Cl_2 20 mL was dropwised DIBAL-H (1.04 M hexane solution) 21.2 mL (22.0 mmol) at −78 °C under argon atmosphere. After stirring at −78 °C for 1 h, the additional DIBAL-H (1.04 M hexane solution) 10.0 mL (10.0 mmol) was dropwised and the reaction mixture was stirred at −78 °C to room temperature for 1 h. After quenching by 10% NaOH aq. (20 mL) at −78 °C, the residue was warmed up to room temperature and stirred for 1 h, then the residue was extracted by CH_2Cl_2 three times. After drying over anhydrous Na_2SO_4 and concentration, a white solid was precipitated, which was filtered and washed by hexane to obtain *(E)*-3-(4-methoxyphenyl)prop-2-en-1-ol 3.1986 g (19.48 mmol, 97%).

^{1}H NMR ($CDCl_3$) δ 7.35-7.30 (2H, m), 6.88-6.84 (2H, m), 6.56 (1H, d, *J* = 15.9 Hz), 6.24 (1H, dt, *J* = 15.9, 6.0 Hz), 4.32-4.28 (2H, m), 3.81 (3H, s), 1.50 (1H, t, *J* = 5.4 Hz) ppm.
^{13}C NMR ($CDCl_3$) δ 159.3, 130.9, 129.3, 127.6, 126.2, 114.0, 63.9, 55.3 ppm.

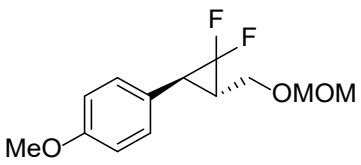
(E)-1-Methoxy-4-(3-(methoxymethoxy)prop-1-en-1-yl)benzene [2268814-11-3][9]



To a mixture of (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol 0.8211 g (5.0 mmol) in CH_2Cl_2 10 mL were added DIPEA 2.60 mL (15.0 mmol) and DMAP 0.0608 g (0.50 mmol) at room temperature. Chloromethyl methyl ether 0.60 mL (7.5 mmol) was dropwised to the mixuture at 0 °C, which was stirred at 0 °C to room temperature for 24 h. After quenching by water (20 mL), the residue was was extracted by Et_2O three times. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by column chromatography (hexane:AcOEt = 4:1) to obtain (*E*)-1-methoxy-4-(3-(methoxymethoxy)prop-1-en-1-yl)benzene 0.9590 g (4.60 mmol, 92%) as a colorless oil.

^{1}H NMR ($CDCl_3$) δ 7.36-7.31 (2H, m), 6.88-6.83 (2H, m), 6.58 (1H, dd, *J* = 16.2, 1.2 Hz), 6.16 (1H, dt, *J* = 16.2, 6.3 Hz), 4.70 (2H, s), 3.81 (3H, s), 3.40 (3H, s) ppm.
^{13}C NMR ($CDCl_3$) δ 159.3, 132.4, 129.4, 127.7, 123.2, 113.9, 95.5, 68.0, 55.2 ppm.

trans-1-{2,2-Difluoro-3-[(methoxymethoxy)methyl]cycloprop-1-yl}-4-methoxybenzene (pre-**1t**)



This compound was synthesized by **Method B** from *(E)*-1-methoxy-4-(3-(methoxymethoxy)prop-1-en-1-yl) benzene 0.8335 g (4.0 mmol).

Method B: 0.9250 g (3.58 mmol, 90%).

Yellow oil.

Rf = 0.44 (hexane:AcOEt = 3:1).

^{1}H NMR ($CDCl_3$) δ 7.14 (2H, d, *J* = 8.7 Hz), 6.84 (2H, d, *J* = 8.7 Hz), 4.65 (2H, s), 3.79-3.60 (2H, m), 3.75 (3H, s), 3.36 (3H, s), 2.53 (1H, dd, *J* = 14.1, 7.5 Hz), 2.18-2.07 (1H, m) ppm.

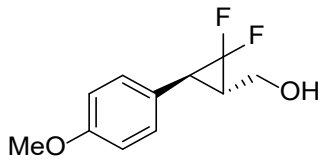
^{13}C NMR ($CDCl_3$) vδ 158.7, 129.0 (dd, *J* = 1.9, 1.2 Hz), 124.9, 113.8, 113.4 (dd, *J* = 289.0, 288.4 Hz), 96.0, 64.0 (d, *J* = 5.1 Hz), 55.0 (dd, *J* = 4.3, 1.2 Hz), 30.8 (t, *J* = 11.2 Hz), 28.8 (t, *J* = 9.9 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –137.06 (1F, dd, *J* = 155.2, 13.8 Hz), –138.54 (1F, dd, *J* = 155.2, 13.8 Hz) ppm.

IR ($CHCl_3$) ν 3101, 2937, 2889, 2839, 1614, 1519, 1466, 1251, 1181, 1037 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{13}H_{17}F_2O_3^+$, 259.1140; found, 259.1158.

trans-[2,2-Difluoro-3-(4-methoxyphenyl)cyclopropyl]methanol (**1t**)



To a mixture of *trans*-1-(2,2-difluoro-3-((methoxymethoxy)methyl)cyclopropyl)-4-methoxybenzene in MeOH 6.0 mLwas added 6 M HCl aq. (4 drops) at room temperature. After stirring at 50 °C for 6 h, the residue was evaporated to remove MeOH. Water 20 mL was added to the residue, which was extracted by Et_2O two times. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by column chromatography (hexane:AcOEt = 2:1) to obtain *trans*-(2,2-difluoro-3-(4-methoxyphenyl)cyclopropyl)methanol 0.3779 g (1.77 mmol, 89%).

Pale yellow oil.

Rf = 0.27 (hexane:AcOEt = 2:1).

^{1}H NMR ($CDCl_3$) δ 7.13 (2H, d, *J* = 8.7 Hz), 6.85 (2H, d, *J* = 8.7 Hz), 4.02-3.66 (2H, m), 3.75 (3H, s), 2.54 (1H, ddd, *J* = 10.8, 7.5, 3.6 Hz), 2.39 (1H, br s), 2.17-2.05 (1H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 158.7, 129.1, 124.8, 113.9, 113.7 (t, *J* = 288.4 Hz), 59.6 (d, *J* = 3.7 Hz), 55.2, 31.0 (t, *J* = 9.6 Hz), 30.6 (t, *J* = 10.8 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –137.70 (1F, dd, *J* = 155.2, 8.8 Hz), –136.87 (1F, dd, *J* = 155.2, 11.6 Hz) ppm.

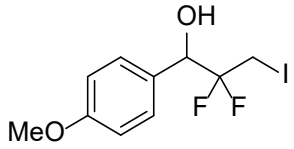
IR ($CHCl_3$) ν 3369, 3007, 2938, 2838, 1614, 1519, 1465, 1250, 1614, 833 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{11}H_{12}F_2O_2^+$, 214.0800; found, 214.0804.

General Procedure of Iodohydroxylation

2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)propan-1-ol (**2a**) [2366981-43-1][5]

A mixture of 0.0916 g (0.50 mmol) of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene, 0.254 g (1.00 mmol) of I_2 in 0.75 mL of MeCN and 0.75 mL of water in a pressure tight glass tube was stirred at 80 °C (oil bath temperature) for 18 h, and the reaction mixture was extracted with CH_2Cl_2 three times. After dried over anhydrous Na_2SO_4, the crude product was evaporated and purified by silica gel column chromatography by hexane:AcOEt = 20:1-10:1 as an eluent to yield 0.149 g (0.453 mmol) of 2,2-difluoro-3-iodo-1-(4-methoxyphenyl)propan-1-ol as a colorless oil in 91% yield.



Colorless oil.

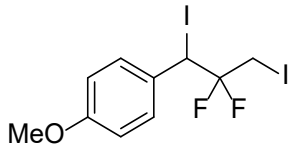
Rf = 0.32 (hexane:CH_2Cl_2 = 1:2).

^{1}H NMR ($CDCl_3$) δ 7.37 (2H, d, *J* = 8.4 Hz), 6.91 (2H, d, *J* = 9.0 Hz), 5.05 (1H, ddd, *J* = 9.9, 8.1, 3.6 Hz), 3.81 (3H, s), 3.56 (1H, ddd, *J* = 23.7, 12.0, 9.0 Hz), 3.28 (1H, ddd, *J* = 23.1, 12.0, 7.8 Hz), 2.64 (1H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 160.1, 128.6, 127.8, 119.3 (dd, *J* = 253.7, 249.4 Hz), 73.4 (t, *J* = 27.9 Hz), 55.3, 1.4 (t, *J* = 28.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −104.56 (1F, ddt, *J* = 244.2, 22.9, 9.0 Hz), −106.53 (1F, ddt, *J* = 243.9, 22.8, 9.0 Hz) ppm.

1-(2,2-Difluoro-1,3-diiodoprop-1-yl)-4-methoxybenzene (**3a**) [2244675-09-8][10]



White solid.

m.p.: 81.5 - 82.9 °C.

Rf = 0.21 (hexane:CH_2Cl_2 = 4:1).

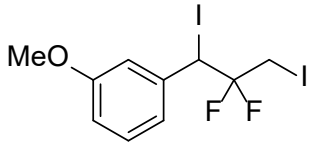
^{1}H NMR ($CDCl_3$) δ 7.46-7.41 (2H, m), 6.87-6.82 (2H, m), 5.55 (1H, dd, *J* = 20.6, 7.4 Hz), 3.80 (3H, s), 3.47 (1H, ddd, *J* = 16.5, 11.7, 8.7 Hz), 3.33 (1H, td, *J* = 15.6, 8.7 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 160.0, 130.3 (dd, *J* = 2.5, 1.3 Hz), 128.7 (d, *J* = 5.0 Hz), 118.0 (t, *J* = 246.9 Hz), 114.3, 55.3, 27.9 (dd, *J* = 27.8, 24.7 Hz), 0.6 (dd, *J* = 32.3, 31.1 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –87.33 ~ –88.32 (1F, m), –94.41 ~ –95.41 (1F, m) ppm.

(2,2-Difluoro-1,3-diiodoprop-1-yl)-3-methoxybenzene (**3b**)

It was difficult to isolate this compound from the substrate **1b**, so only NMR data was shown below.

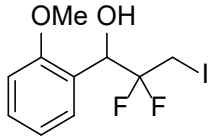


^{1}H NMR ($CDCl_3$) δ 7.27-7.22 (1H, m), 7.09-7.05 (1H, m), 6.88-6.77 (2H, m), 5.51 (1H, dd, *J* = 20.4, 7.2 Hz), 3.73 (3H, s), 3.55-3.28 (2H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 159.7, 138.1 (d, *J* = 5.6 Hz), 130.0, 129.4, 121.3, 117.9 (t, *J* = 246.9 Hz), 114.8, 55.3, 27.4 (t, *J* = 25.4 Hz) 0.4 (t, *J* = 30.4 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −87.71 (1F, dm, *J* = 239.7 Hz), −94.52 (1F, dm *J* = 239.4 Hz) ppm.

2,2-Difluoro-3-iodo-1-(2-methoxyphenyl)propan-1-ol (**2c**)



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0917 g (0.5 mmol) of 1-(2,2-difluorocycloprop-1-yl)-2-methoxybenzene (**1c**) was employed to afford 0.120 g of the title compound (0.366 mmol) in 73% yield.

White solid.

m.p.: 63.5 - 64.5 °C.

Rf = 0.32 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.40-7.32 (2H, m), 7.15 (1H, t, *J* = 6.8 Hz), 6.94 (1H, d, *J* = 8.1 Hz), 5.33 (1H, ddd, *J* = 12.8, 9.5, 7.1 Hz), 3.88 (3H, s), 3.65-3.49 (3H, m) ppm.

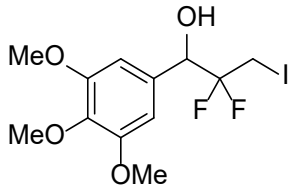
^{13}C NMR ($CDCl_3$) δ 157.3, 130.1, 129.3, 123.6, 121.0, 119.4 (t, *J* = 247.1 Hz), 111.2, 70.5 (t, *J* = 27.6 Hz), 55.7, 2.4 (t, *J* = 28.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −105.24 ~ −106.24 (1F, m), −106.56 ~ -107.57 (1F, m) ppm.

IR (KBr) ν 3449, 3012, 2941, 2841, 1603, 1494, 1465, 1248, 1011, 757 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{10}H_{11}F_2IO_2^+$, 327.9766; found: 327.9764.

2,2-Difluoro-3-iodo-1-(3,4,5-trimethoxyphenyl)propan-1-ol (**2d**)



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.122 g (0.5 mmol) of 1-(2,2-difluorocycloprop-1-yl)-3,4,5-trimethoxybenzene (**1d**) was employed to afford 0.157 g of the title compound (0.404 mmol) in 81% yield.

White solid.

m.p.: 121.0 - 123.0 °C.

Rf = 0.20 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 6.67 (2H, s), 5.06 (1H, td, *J* = 9.5, 3.9 Hz), 3.87 (6H, s), 3.85 (3H, s), 3.52 (1H, ddd, *J* = 23.1, 12.0, 9.6 Hz), 3.30 (1H, ddd, *J* = 22.7, 11.9, 8.4 Hz), 2.70 (1H, br s) ppm.

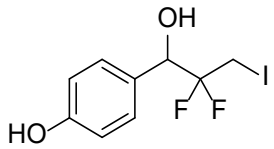
^{13}C NMR ($CDCl_3$) δ 153.2, 138.2, 131.4, 119.2 (dd, *J* = 248.7, 245.0 Hz), 104.2, 73.7 (t, *J* = 28.5 Hz), 60.8, 56.1, 1.3 (dd, *J* = 29.4, 27.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −103.58 ~ −104.52 (1F, m), −105.61 ~ -106.59 (1F, m) ppm.

IR (KBr) ν 3610, 3423, 3019, 1595, 1464, 1421, 1216, 1131, 761, 670 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{12}H_{15}F_2IO_4^+$, 387.9978; found, 387.9986.

2,2-Difluoro-3-iodo-1-(4-hydroxyphenyl)propan-1-ol (**2e**)



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0851 g (0.5 mmol) of 4-(2,2-difluorocycloprop-1-yl)phenol (**1e**) was employed to afford 0.131 g of the title compound (0.416 mmol) in 83% yield.

White solid.

m.p.: 118.0 - 121.0 °C.

Rf = 0.24 (hexane:AcOEt = 2:1).

^{1}H NMR (acetone-d_6) δ 8.28 (1H, s), 7.18 (2H, d, *J* = 8.4 Hz), 6.72 (2H, d, *J* = 8.4 Hz), 5.20 (1H, d, *J* = 5.1 Hz), 4.89 (1H, ddd, *J* = 12.8, 7.7, 5.0 Hz), 3.68-3.35 (2H, m) ppm.

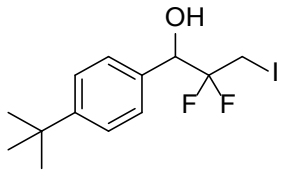
^{13}C NMR (acetone-d_6) δ 158.3, 129.7, 129.2, 120.4 (dd, *J* = 245.9, 244.0 Hz), 115.6, 73.5 (dd, *J* = 29.1, 27.3 Hz), 3.2 (t, *J* = 28.2 Hz) ppm.

^{19}F NMR (acetone-d_6) δ −103.43 (1F, ddd, *J* = 241.7, 27.3, 7.9 Hz), −107.66 (1F, ddd, *J* = 240.5, 26.1, 12.4 Hz) ppm.

IR (KBr) ν 3257, 3027, 1905, 1685, 1612, 1516, 1444, 1180, 1000, 820 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_9H_9F_2IO_2^+$, 313.9610; found, 313.9635.

1-(4-*tert*-Butylphenyl)-2,2-difluoro-3-iodopropan-1-ol (**2f**) [2366981-46-4][5]



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.105 g (0.5 mmol) of 1-(*tert*-butyl)-4-(2,2-difluorocycloprop-1-yl)benzene (**1f**) was employed to afford 0.080 g of the title compound (0.225 mmol) in 45% yield.

White solid.

m.p.: 83.0 - 84.0 °C.

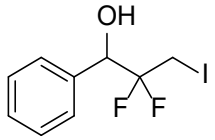
Rf = 0.46 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.42 – 7.35 (4H, m), 5.09 (1H, td, *J* = 9.0, 3.9 Hz), 3.59 (1H, ddd, *J* = 24.0, 11.7, 8.4 Hz), 3.29 (1H, ddd, *J* = 23.6, 11.7, 7.5 Hz), 2.46 (1H, br d, *J* = 4.2 Hz), 1.32 (9H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 152.2, 132.7 (d, *J* = 1.9 Hz), 126.9, 125.5, 119.3 (t, *J* = 246.3 Hz), 73.6 (t, *J* = 28.5 Hz), 34.6, 31.2, 1.44 (t, *J* = 28.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −104.20 (1F, ddt, *J* = 244.2, 18.4, 9.0 Hz), −106.25 (1F, ddt, *J* = 243.9, 18.4, 9.0 Hz) ppm.

2,2-Difluoro-3-iodo-1-phenylpropan-1-ol (**2g**)



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0855 g (0.5 mmol, Purity 90 wt% in THF) of 2,2-difluorocycloprop-1-ylbenzene (**1g**) was employed to afford 0.057 g of the title compound (0.193 mmol) in 39% yield with the corresponding iodide in 22% and ketone 6% in ^{19}F NMR yield.

White solid.

m.p.: 56.2 - 57.0 °C.

Rf = 0.32 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.46-7.38 (5H, m), 5.10 (1H, t, *J* = 9.3 Hz), 3.59 (1H, ddd, *J* = 24.3, 12.0, 8.9 Hz), 3.27 (1H, ddd, *J* = 23.7, 12.0, 7.2 Hz), 2.61 (1H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 135.6, 129.1, 128.5, 127.2, 119.2 (t, *J* = 246.5 Hz), 73.7 (t, *J* = 28.5 Hz), 1.2 (t, *J* = 28.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −104.08 (1F, ddt, *J* = 244.1, 22.8, 9.2 Hz), −106.35 (1F, dddd, *J* = 246.3, 25.2,

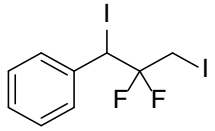
11.4, 6.8 Hz) ppm.

IR (KBr) ν 3585, 3430, 3035, 1455, 1417, 1216, 1059, 1013, 757, 705 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_9H_9F_2IO^+$, 297.9661, found, 297.9679.

(2,2-Difluoro-1,3-diiodoprop-1-yl)benzene (**3g**)

Data for the crude product were included, because it was difficult to isolate from the byproduct.



22% in ^{19}F NMR yield.

Rf = 0.56 (hexane:AcOEt = 4:1).

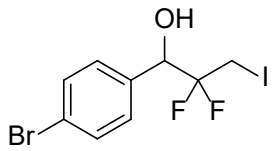
^1H NMR ($CDCl_3$) δ 7.57-7.501 (2H, m), 7.39-7.31 (3H, m), 5.55 (1H, dd, *J* = 20.1, 7.5 Hz), 3.55-3.26 (2H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 136.7 (d, *J* = 5.0 Hz), 130.2 (t, *J* = 3.1 Hz), 129.3, 129.1, 129.0, 118.0 (t, *J* = 246.9 Hz), 27.6 (dd, *J* = 27.9, 25.4 Hz), 0.5 (dd, *J* = 32.3, 31.0 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –87.66 ~ –88.64 (1F, m), –94.25 ~ –95.25 (1F, m) ppm.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_9H_8F_2I_2^+$, 407.8678, found, 407.8680.

1-(4-Bromophenyl)-2,2-difluoro-3-iodopropan-1-ol (**2h**)



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0937 g (0.25 mmol) of 1-bromo-4-(2,2-difluorocycloprop-1-yl)benzene (**1h**) and instead of MeCN, DMSO as solvent were employed to afford 0.0492 g of the title compound (0.130 mmol) in 52% yield.

White solid.

m.p.: 88.5 - 89.4 °C.

Rf = 0.41 (hexane:AcOEt = 4:1).

^1H NMR ($CDCl_3$) δ 7.55-7.52 (2H, m), 7.36-7.33 (2H, m), 5.11 (1H, ddd, *J* = 11.7, 7.8, 4.2 Hz), 3.59 (1H, ddd, *J* = 23.4, 11.7, 9.6 Hz), 3.25 (1H, ddd, *J* = 23.0, 11.7, 7.2 Hz), 2.56 (1H, br m) ppm.

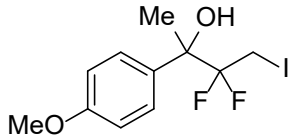
^{13}C NMR ($CDCl_3$) δ 134.7, 131.7, 128.9, 123.3, 119.0 (t, *J* = 247.2 Hz), 73.1 (t, *J* = 28.5 Hz), 0.7 (t, *J* = 29.1 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –103.71 (1F, dm, *J* = 246.5 Hz), –106.58 (1F, dm, *J* = 246.5 Hz) ppm.

IR (KBr) ν 3595, 3048, 2909, 1912, 1593, 1486, 1186, 999, 793, 583 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_9H_8BrF_2IO^+$, 375.8766; found, 375.8778.

3,3-Difluoro-4-iodo-2-(4-methoxyphenyl)butan-2-ol (**2j**) [2366981-41-9][5]



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0989 g (0.5 mmol) of 1-(2,2-difluoro-1-methylcycloprop-2-yl)-4-methoxybenzene (**1j**) was employed to afford 0.139 g of the title compound (0.407 mmol) in 81% yield.

White solid.

m.p.: 63.5 - 64.0 °C.

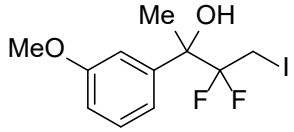
Rf = 0.20 (hexane:CH_2Cl_2 = 1:1).

^{1}H NMR ($CDCl_3$) δ 7.48−7.42 (2H, m), 6.92−6.87 (2H, m), 3.81 (3H, s), 3.65 (1H, ddd, *J* = 32.7, 12.0, 2.4 Hz), 3.03 (1H, ddd, *J* = 31.2, 12.0, 3.2 Hz), 2.34 (1H, s), 1.74 (3H, dd, *J* = 1.5, 1.2 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 159.3, 132.2 (dd, *J* =3.7, 1.2 Hz), 127.0 (dd, *J* = 2.5, 1.3 Hz), 120.2 (t, *J* = 250.3 Hz), 113.6, 75.0 (dd, *J* = 27.9, 26.7 Hz), 55.2, 24.3 (t, *J* = 2.5 Hz), 2.9 (t, *J* = 28.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −105.97 (1F, dd, *J* = 239.4, 31.9 Hz), −108.35 (1F, dd, *J* = 239.4, 31.7 Hz) ppm.

3,3-Difluoro-4-iodo-2-(3-methoxyphenyl)butan-2-ol (**2k**)



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0929 g (0.47 mmol) of 1-(2,2-difluoro-1-methylcycloprop-1-yl)-3-methoxybenzene (**1k**) was employed to afford 0.119 g of the title compound (0.348 mmol) in 74% yield.

Colorless oil.

Rf = 0.46 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.31 (1H, d, *J* = 7.5 Hz), 7.12-7.09 (2H, m), 6.89-6.86 (1H, m), 3.83 (3H, s), 3.66 (1H, ddd, *J* = 32.7, 12.3, 2.1 Hz), 3.02 (1H, ddd, *J* = 31.5, 12.3, 3.3 Hz), 2.26 (1H, d, *J* = 0.9 Hz), 1.76 (3H, s) ppm.

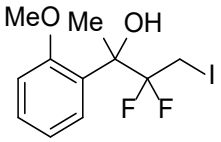
^{13}C NMR ($CDCl_3$) δ 159.5, 141.8 (d, *J* = 4.4 Hz), 129.5, 120.0 (dd, *J* = 251.8, 250.0 Hz), 118.1 (d, *J* = 1.8 Hz), 113.1, 111.9, 75.2 (dd, *J* = 27.3, 26.1 Hz), 55.2, 24.3, 2.8 (d, *J* = 27.9 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −105.72 (1F, dd, *J* = 241.9, 31.9 Hz), −108.20 (1F, dd, *J* = 241.9, 30.7 Hz) ppm.

IR ($CHCl_3$) ν 3470, 3003, 2837, 1584, 1489, 1435, 1249, 1011, 757, 704 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{11}H_{14}F_2O_2I^+$, 343.0001; found, 343.0010.

3,3-Difluoro-4-iodo-2-(2-methoxyphenyl)butan-2-ol (**2l**) [2366981-49-7][5]



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0991 g (0.5 mmol) of 1-(2,2-difluoro-1-methylcycloprop-2-yl)-2-methoxybenzene (**1l**) was employed to afford 0.132 g of the title compound (0.384 mmol) in 77% yield.

White solid.

m.p.: 60.5 - 61.0 °C.

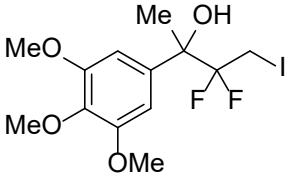
Rf = 0.46 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.36−7.28 (2H, m), 7.04−6.96 (2H, m), 3.93 (3H, s), 3.78−3.57 (2H,m), 1.73 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 157.7, 129.8, 129.7, 127.3, 121.5, 120.4 (t, J = 251.9 Hz), 112.4, 77.2 (t, J = 26.0 Hz), 56.2, 23.9, 3.1 (t, J = 28.6 Hz) ppm.

^{19}F NMR: δ −104.87 (1F, dm, J = 239.4 Hz), −106.14 (1F, dm, J = 239.4 Hz) ppm.

3,3-Difluoro-4-iodo-2-(3,4,5-trimethoxyphenyl)butan-2-ol (**2m**)



Instead of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.1290 g (0.5 mmol) of 1-(2,2-difluoro-1-methylcycloprop-2-yl)-3,4,5-methoxybenzene (**1m**) was employed to afford 0.143 g of the title compound (0.356 mmol) in 71% yield.

White solid.

m.p.: 192.0 - 193.4 °C.

Rf = 0.24 (hexane:AcOEt = 4:1).

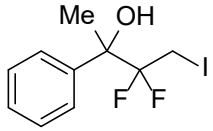
^{1}H NMR ($CDCl_3$) δ 6.76 (2H, d, J = 1.5 Hz), 3.88 (6H, s), 3.86 (3H. s), 3.66 (1H, ddd, J = 32.4, 12.4, 2.4 Hz), 3.04 (1H, ddd, J = 30.6, 12.0, 3.3 Hz), 2.29 (1H, br s), 1.76 (3H, s) ppm.

^{13}C NMR (acetone-d_6) δ 153.6, 138.5 (d, J = 3.2 Hz), 138.4, 121.3 (t, J = 250.6 Hz), 104.8, 75.2 (t, J = 26.7 Hz), 60.3, 56.3, 23.9, 4.4 (t, J = 27.9 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −105.58 (1F, dd, J = 239.4, 31.9 Hz), −107.87 (1F, dd, J = 241.7, 31.9 Hz) ppm.

IR (KBr) ν 3437, 2998, 2944, 2840, 1596, 1454, 1419, 1248, 1133, 1007 cm^{-1}.
HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{13}H_{17}F_2O_4I^+$, 402.0134; found, 402.0118.

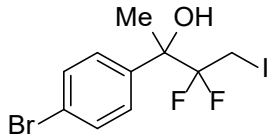
3,3-Difluoro-4-iodo-2-phenylbutan-2-ol (**2n**)



Instead of 0.5 mmol of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0843 g (0.5 mmol) of (2,2-difluoro-1-methylcycloprop-1-yl)benzene (**1n**) was employed to afford 0.127 g of the title compound (0.407 mmol) in 81% yield.

Colorless oil.
Rf = 0.49 (hexane:AcOEt = 4:1).
^{1}H NMR ($CDCl_3$) δ 7.56-7.53 (2H, m), 7.41-7.26 (3H, m), 3.66 (1H, ddd, *J* = 32.7, 12.3, 2.7 Hz), 3.01 (1H, ddd, *J* = 31.1, 12.3, 3.3 Hz), 2.31 (1H, s), 1.78 (3H, s) ppm.
^{13}C NMR ($CDCl_3$) δ 140.2 (d, *J* = 3.7 Hz), 128.4, 128.1, 125.7, 120.1 (dd, *J* = 250.9, 249.7 Hz), 75.3 (dd, *J* = 27.6, 26.4 Hz), 24.4, 2.6 (t, *J* = 27.9 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ −105.84 (1F, dd, *J* = 241.7, 31.9 Hz), −108.24 (1F, dd, *J* = 241.7, 31.9 Hz) ppm.
IR ($CHCl_3$) ν 3470, 2984, 2926, 1711, 1448, 1193, 1029, 1011, 763, 702 cm^{-1}.
HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{10}H_{11}F_2IO^+$, 311.9817; found, 311.9847.

2-(4-Bromophenyl)-3,3-difluoro-4-iodobutan-2-ol (**2o**)

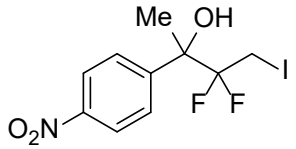


Data for **2o**: 0.120 g (0.384 mmol, 77% isolated yield).
Instead of 0.5 mmol of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0988 g (0.4 mmol) of 1-bromo-4-(2,2-difluorocycloprop-1-yl)benzene (**1o**) was employed to afford 0.120 g of the title compound (0.301 mmol) in 75% yield.

Colorless oil.
Rf = 0.49 (hexane:AcOEt = 4:1).
^{1}H NMR ($CDCl_3$) δ 7.51 (2H, d, *J* = 8.6 Hz), 7.42 (2H, d, *J* = 8.6 Hz), 3.64 (1H, ddd, *J* = 32.7, 12.0, 2.1 Hz), 2.97 (1H, ddd, *J* = 31.2, 12.3, 3.3 Hz), 2.31 (1H, s), 1.75 (3H, s) ppm.
^{13}C NMR ($CDCl_3$) δ 139.2 (d, *J* = 3.1 Hz), 134.5, 127.6 (d, *J* = 1.3 Hz), 122.5, 119.8 (t, *J* = 249.4 Hz), 75.1 (t, *J* = 27.9 Hz), 23.2 (t, *J* = 2.5 Hz), 2.2 (t, *J* = 27.9 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −105.76 (1F, dd, *J* = 241.7, 31.9 Hz), −108.28 (1F, dd, *J* = 241.7, 31.9 Hz) ppm.
IR ($CHCl_3$) ν 3581, 2984, 1488, 1398, 1209, 1101, 1010, 926, 813, 460 cm^{-1}.
HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{10}H_{10}{}^{79}BrF_2OI^+$, 389.8922; found, 389.8901.

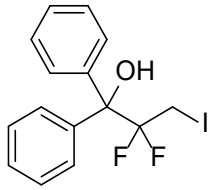
3,3-Difluoro-4-iodo-2-(4-nitrophenyl)butan-2-ol (**2p**)



Instead of 0.5 mmol of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0847 g (0.4 mmol) of 1-(2,2-difluorocycloprop-1-yl)-4-nitrobenzene (**1p**) was employed to afford 0.064 g of the title compound (0.180 mmol) in 45% yield.

White solid.
m.p.: 100.3 - 101.3 °C.
Rf = 0.33 (hexane:AcOEt = 4:1).
^{1}H NMR ($CDCl_3$) δ 8.27-8.22 (2H, m), 7.80-7.75 (2H, m), 3.67 (1H, ddd, *J* = 32.4, 12.3, 2.4 Hz), 2.95 (1H, ddd, *J* = 30.9, 12.0, 3.2 Hz), 2.46 (1H, s), 1.82 (3H, s) ppm.
^{13}C NMR ($CDCl_3$) δ 147.6, 147.3 (d, *J* = 3.7 Hz), 127.1 (d, *J* = 1.9 Hz), 123.5, 119.6 (dd, *J* = 251.2, 250.0 Hz), 75.3 (t, *J* = 27.8 Hz), 24.4 (t, *J* = 2.5 Hz), 1.4 (t, *J* = 27.9 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ −105.14 (1F, dd, *J* = 244.2, 31.9 Hz), −107.78 (1F, dd, *J* = 243.9, 29.6 Hz) ppm.
IR (KBr) ν 3496, 3048, 2991, 1602, 1521, 1352, 1030, 1013, 857, 702 cm^{-1}.
HRMS (FAB−, m/z): $[M]^-$ calcd for $C_{10}H_{10}F_2NO_3I^-$, 356.9679; found, 356.9675.

2,2-Difluoro-3-iodo-1,1-diphenylpropan-1-ol (**2q**)



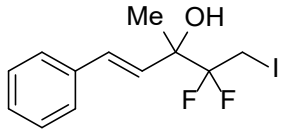
Instead of 0.5 mmol of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0922 g (0.4 mmol) of 1,1-difluoro-2,2-diphenylcyclopropane (**1q**) was employed to afford 0.121 g of the title compound (0.349 mmol) in 81% yield.
Colorless oil.
Rf = 0.50 (hexane:AcOEt = 4:1).
^{1}H NMR ($CDCl_3$) δ 7.55-7.52 (4H, m), 7.37-7.30 (6H, m), 3.51 (2H, t, *J* = 17.3 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ −102.18 (t, *J* = 17.1 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 141.0, 128.22, 128.16, 127.3, 121.2 (t, *J* = 253.7 Hz), 78.9 (t, *J* = 25.7 Hz), 4.2 (t, *J* = 27.6 Hz) ppm.

IR ($CHCl_3$) ν 3584, 3061, 3012, 1494, 1449, 1342, 1216, 1019, 900, 757 cm^{-1}.

HRMS (FAB+, m/z): $[M+Na]^+$ calcd for $C_{15}H_{13}F_2IONa^+$, 396.9871; found, 396.9854.

(E)-4,4-Difluoro-5-iodo-3-methyl-1-phenylpent-1-en-3-ol (**2r**)



Instead of 0.5 mmol of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0966 g (0.5 mmol) of (*E*)-(2-(2,2-difluoro-1-methylcyclopropyl)ethen-1-yl)benzene (**1r**) was employed to afford 0.127 g of the title compound (0.374 mmol) in 75% yield.

Colorless oil.

Rf = 0.52 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.43-7.28 (5H, m), 6.84 (1H, d, *J* = 15.9 Hz), 6.26 (1H, dd, *J* = 15.9, 1.7 Hz), 3.73 (1H, ddd, *J* = 31.7, 12.3, 2.9 Hz), 3.54 (1H, ddd, *J* = 31.2, 12.3, 3.2 Hz), 2.10 (1H, s), 1.57 (3H, s) ppm.

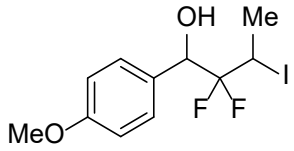
^{13}C NMR ($CDCl_3$) δ 135.7, 131.0, 128.6, 128.2, 128.0 (d, *J* = 3.7 Hz), 126.6, 121.4 (dd, *J* = 251.2, 249.3 Hz), 74.6 (t, *J* = 27.6 Hz), 23.0 (dd, *J* = 2.5, 1.9 Hz), 2.5 (t, *J* = 27.9 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −106.15 (1F, dd, *J* = 241.7, 31.9 Hz), −109.65 (1F, dd, *J* = 240.8, 30.8 Hz) ppm.

IR ($CHCl_3$) ν 3564, 3458, 3029, 2986, 1417, 1205, 1028, 1011, 749, 693 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{12}H_{13}F_2IO^+$, 337.9974; found, 337.9983.

2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)butan-1-ol (**2s**)



Instead of 0.5 mmol of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0933 g (0.5 mmol) of 1-(2,2-difluoro-3-methylcycloprop-1-yl)-4-methoxybenzene (**1s**, *cis*:*trans* = 77:23) was employed to afford 0.121 g of the title compound (0.385 mmol, *d.r.*=60:40) in 77% yield.

major

(1*R**,3*S**)-2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)butan-1-ol (major-**2s**, **60**:40)

White solid.

m.p.: 94.2 - 95.0 °C.

Rf = 0.35 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.43 (2H, d, *J* = 8.7 Hz), 6.91 (2H, d, *J* = 8.7 Hz), 5.25 (1H, td, *J* = 15.0, 3.8 Hz), 4.12 (1H, tq, *J* = 14.1, 7.2 Hz), 3.82 (3H, s), 2.40 (1H, br s), 2.00 (3H, d, *J* = 7.2 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 160.1, 129.0, 127.9 (d, *J* = 3.1 Hz), 120.2 (dd, *J* = 250.3, 248.4 Hz), 113.9, 73.0 (dd, *J* = 28.2, 25.7 Hz), 55.3, 21.6 (d, *J* = 3.8 Hz), 21.5 (dd, *J* = 29.1, 24.8 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –109.45 (1F, dm, *J* = 244.2 Hz), –117.44 (1F, dm, *J* = 244.2 Hz) ppm.

IR (KBr) ν 3495, 2940, 2844, 2017, 1899, 1609, 1510, 1010, 796, 577 cm^{-1}.

HRMS (FAB+, *m/z*): $[M]^+$ calcd for $C_{11}H_{13}F_2IO_2^+$, 341.9923; found, 341.9916.

minor

(1*R**,3*R**)-2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)butan-1-ol (minor-**2s**, 60:**40**)

Colorless oil.

Rf = 0.40 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d, *J* = 8.4 Hz), 6.92 (2H, d, *J* = 8.7 Hz), 5.29 (1H, dt, *J* = 17.9, 5.1 Hz), 4.49 (1H, ddq, *J* = 19.4, 8.4, 7.1 Hz), 3.82 (3H, s), 2.33 (1H, br s), 1.95 (3H, d, *J* = 6.9 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 160.0 (d, *J* = 1.8 Hz), 129.0, 128.2 (t, *J* = 2.2 Hz), 120.1 (dd, *J* = 251.2, 248.1 Hz), 113.8, 73.5 (dd, *J* = 30.7, 25.7 Hz), 55.3, 20.9 (t, *J* = 3.7 Hz), 20.7 (td, *J* = 27.9, 3.1 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –113.02 (1F, dd, *J* = 248.6, 18.2 Hz), –119.98 (1F, ddd, *J* = 248.6, 18.2, 9.0 Hz) ppm.

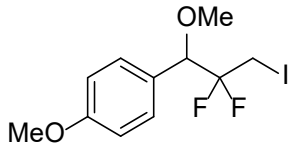
IR ($CHCl_3$) ν 3448, 2935, 2838, 1613, 1514, 1452, 1254, 1036, 799, 761 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{11}H_{14}F_2IO_2^+$, 343.0001; found, 342.9990.

General Procedure of Iodoalkoxylation

1-(2,2-Difluoro-3-iodo-1-methoxyprop-1-yl)-4-methoxybenzene (**5aa**)

A mixture of 0.0920 g (0.50 mmol) of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.254 g (1.00 mmol) of I_2 in 0.75 mL of MeOH in a pressure tight glass tube was stirred at 60 °C (oil bath temperature) for 6 h, and the reaction mixture was quenched by sat. $NaHCO_3$ aq. (2 mL). To the mixture was added sat. $Na_2S_2O_3$ aq. (2 mL), then extracted with CH_2Cl_2 three times. After the usual workup yielded 0.1594 g (0.466 mmol, yield 93%) of 1-(2,2-difluoro-3-iodo-1-methoxyprop-1-yl)-4-methoxybenzene (**5aa**) [2244675-10-1][10] as a colorless oil which was found to be virtually pure without purification.



Colorless oil.

Rf = 0.26 (hexane:AcOEt = 10:1).

^{1}H NMR ($CDCl_3$) δ 7.31 (2H, d, *J* = 8.4 Hz), 6.92 (2H, d, *J* = 8.4 Hz), 4.56 (1H, dd, *J* = 12.9, 6.9 Hz), 3.81 (3H, s), 3.63 (1H, dt, *J* = 21.9, 11.7 Hz), 3.46-3.28 (1H, m), 3.34 (3H, s) ppm.

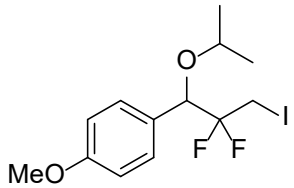
^{13}C NMR ($CDCl_3$) δ 160.1, 129.4, 125.5, 118.7 (t, *J* = 246.9 Hz), 113.8, 81.9 (t, *J* = 27.3 Hz), 57.7, 55.2, 2.0 (t, *J* = 28.4 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −102.35 ~ −103.33 (1F, m), −105.91 ~ −106.83 (1F, m) ppm.

IR ($CHCl_3$) ν 3006, 2936, 2837, 1612, 1514, 1464, 1253, 1174, 1083, 1017 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{11}H_{13}F_2IO_2^+$, 341.9923; found, 341.9911.

1-(2,2-Difluoro-3-iodo-1-isopropoxyprop-1-yl)-4-methoxybenzene (**5ab**)



Instead of MeOH (0.75 mL), 2-propanol (0.75 mL) was employed as solvent, and the reaction was continued for 24 h instead of 6 h, 0.178 g (0.480 mmol) of the title compound was obtained in 96% yield.

Yellow oil.

Rf = 0.33 (hexane:AcOEt = 10:1).

^{1}H NMR ($CDCl_3$) δ 7.33 (2H, d, *J* = 8.4 Hz), 6.90 (2H, d, *J* = 8.4 Hz), 4.74 (1H, dd, *J* = 13.2, 6.6 Hz), 3.82 (3H, s), 3.70-3.58 (2H, m), 3.40 (1H, ddd, *J* = 22.5, 11.7, 5.7 Hz), 1.20 (3H, d, *J* = 6.0 Hz), 1.12 (3H, d, *J* = 6.0 Hz) ppm.

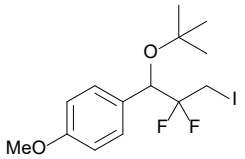
^{13}C NMR ($CDCl_3$) δ 159.9, 129.3, 127.0, 118.6 (dd, *J* = 246.9, 245.0 Hz), 113.7, 77.7 (dd, *J* = 29.8, 26.6 Hz), 70.7, 55.2, 23.1, 21.1, 2.3 (dd, *J* = 30.5, 28.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −101.98 ~ −102.99 (1F, m), −105.94 ~ −106.93 (1F, m) ppm.

IR ($CHCl_3$) ν 2975, 2934, 2839, 1612, 1513, 1252, 1173, 1084, 1013, 837 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{13}H_{18}F_2IO_2^+$, 371.0314; found, 371.0315.

1-(2,2-Difluoro-3-iodo-1-*tert*-butoxyprop-1-yl)-4-methoxybenzene (**5ac**)



Instead of MeOH (0.75 mL), *tert*-butanol (0.75 mL) was employed as solvent with 2.0 eq. of K_2CO_3 as an additive to afford 0.059 g (0.153 mmol) of the title compound was obtained in 61% yield.

White solid.

m.p.: 120.7 - 121.3 °C

Rf = 0.69 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.35 (2H, d, *J* = 8.4 Hz), 6.87 (2H, d, *J* = 8.7 Hz), 4.81 (1H, t, *J* = 8.7 Hz), 3.81 (3H, s), 3.63 (1H, ddd, *J* = 27.3, 11.7, 6.0 Hz), 3.27 (1H, ddd, *J* = 26.7, 12.0, 5.1 Hz), 1.15 (9H, s) ppm.

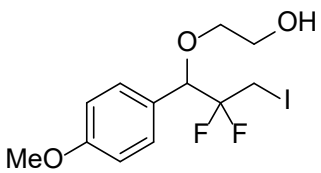
^{13}C NMR ($CDCl_3$) δ 159.6, 129.9 (d, *J* = 4.3 Hz), 128.8, 118.9 (t, *J* = 245.6 Hz), 113.5, 76.0, 73.4 (t, *J* = 28.5 Hz), 55.2, 28.4, 2.7 (t, *J* = 28.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −101.41 (1F, ddt, *J* = 239.4, 27.4, 9.0 Hz), −104.61 (1F, dddd, *J* = 239.7, 27.4, 9.0, 4.5 Hz) ppm.

IR ($CHCl_3$) ν 2973, 2933, 1612, 1584, 1512, 1250, 1085, 893, 573, 537 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{14}H_{19}F_2IO_2^+$, 384.0392; found, 384.0382.

2-{2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)propyloxy}ethan-1-ol (**5ad**) [2244675-11-2][10]



Instead of MeOH (0.75 mL), ethylene glycol (0.75 mL) was employed as solvent to afford 0.184 g

(0.495 mmol) of the title compound was obtained in 99% yield.

Colorless oil.

Rf = 0.40 (hexane:AcOEt = 2:1).

^{1}H NMR ($CDCl_3$) δ 7.34-7.26 (2H, m), 6.95-6.90 (2H, m), 4.75 (1H, dd, *J* = 12.3, 7.5 Hz), 3.82 (3H, s), 3.80-3.72 (2H, m), 3.68-3.51 (3H, m), 3.38 (1H, ddd, *J* = 18.6, 11.7, 6.9 Hz), 1.92 (1H, t, *J* = 6.0 Hz) ppm.

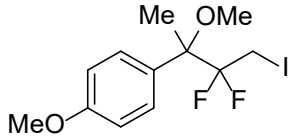
^{13}C NMR ($CDCl_3$) δ 160.1, 129.3, 125.6, 118.6 (t, *J* = 245.0 Hz), 113.9, 80.7 (dd, *J* = 29.8, 27.3 Hz), 71.3, 61.6, 55.2, 1.9 (t, *J* = 29.2 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −102.97 (1F, dddd, *J* = 248.7, 20.3, 11.3, 6.8 Hz), −105.77 (1F, dddd, *J* = 248.7, 18.1, 11.3, 6.8 Hz) ppm.

IR ($CHCl_3$) ν 2935, 2881, 2834, 1613, 1515, 1462, 1253, 1174, 1123, 1013 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{12}H_{16}F_2IO_3^+$, 373.0107; found, 373.0129.

1-(3,3-Difluoro-4-iodo-2-methoxybut-2-yl)-4-methoxybenzene (**5ja**)



Instead of 0.5 mmol of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene, 0.0992 g (0.5 mmol) of 1-(2,2-difluoro-1-methylcycloprop-1-yl)-4-methoxybenzene was employed to afford 0.165 g of the title compound (0.464 mmol) in 93% yield.

Colorless oil.

Rf = 0.39 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.34-7.30 (2H, m), 6.92-6.87 (2H, m), 3.81 (3H, s), 3.79-3.65 (1H, m), 3.38-3.65 (1H, m), 3.23 (3H, s), 1.73 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 159.4, 129.7, 128.9, 119.4 (dd, *J* = 251.2, 246.2 Hz), 113.6, 80.4 (dd, *J* = 27.9, 26.0 Hz), 55.2, 50.7, 17.7 (t, *J* =3.1 Hz), 1.9 (t, *J* = 27.9 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −104.33 (1F, dd, *J* = 239.4, 34.2 Hz), −107.14 (1F, dd, *J* = 239.4, 31.9 Hz) ppm.

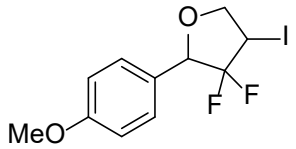
IR ($CHCl_3$) ν 2995, 2955, 2837, 1733, 1611, 1512, 1464, 1302, 1254, 1180 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{12}H_{16}F_2IO_2^+$, 357.0158; found, 357.0133.

3,3-Difluoro-4-iodo-2-(4-methoxyphenyl)tetrahydrofuran (**6**)

Instead of 0.5 mmol of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene, 0.1072 g (0.5 mmol) of *trans*-{2,2-difluoro-3-(4-methoxyphenyl)cycloprop-1-yl}methanol was employed was employed and the reaction was continued for 48 h instead of 6 h, 0.112 g (0.328 mmol) of the title compound was

obtained in 66% combined yield whose diastereomer ratio was 65:35.



major isomer

White solid.

m.p.: 45.0 - 46.3 °C

Rf = 0.29 (hexane:AcOEt = 10:1).

^{1}H NMR ($CDCl_3$) δ 7.30 (2H, d, *J* = 8.1 Hz), 6.93 (2H, d, *J* = 8.1 Hz), 4.92 (1H, dd, *J* = 13.2, 11.1 Hz), 4.54 (1H, dd, *J* = 16.2, 7.8 Hz), 4.47-4.36 (1H, m), 4.11 (1H, t, *J* = 9.3 Hz), 3.82 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 160.1, 128.3, 125.3 (dd, *J* = 3.1, 1.9 Hz), 124.2 (dd, *J* = 258.6, 254.2 Hz), 113.8, 81.5 (dd, *J* = 34.1, 25.4 Hz), 73.5 (dd, *J* = 5.7, 1.9 Hz), 55.2, 19.8 (dd, *J* = 29.8, 23.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –94.67 (1F, ddd, *J* = 225.8, 13.7, 11.3 Hz), –109.93 (1F, ddd, *J* = 225.8, 13.6, 11.3 Hz) ppm.

IR ($CHCl_3$) ν 2969, 2938, 2863, 1610, 1516, 1464, 1347, 1304, 1253, 1042 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{11}H_{12}F_2IO_2^+$, 340.9845; found, 340.9829.

minor isomer

White solid.

m.p.: 75.6 - 77.2 °C

Rf = 0.26 (hexane:AcOEt = 10:1).

^{1}H NMR ($CDCl_3$) δ 7.35-7.31 (2H, m), 6.95-6.90 (2H, m), 5.00 (1H, dd, *J* = 16.8, 8.4 Hz), 4.67-4.47 (2H, m), 4.31 (1H, ddd, *J* = 9.6, 8.7, 1.2 Hz), 3.82 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 160.1, 128.4, 125.0 (d, *J* = 1.8 Hz), 122.7 (dd, *J* = 256.8, 254.3 Hz), 113.8, 80.2 (dd, *J* = 31.0, 26.0 Hz), 73.9 (d, *J* = 7.5 Hz), 55.2, 19.2 (dd, *J* = 26.0, 24.8 Hz) ppm.

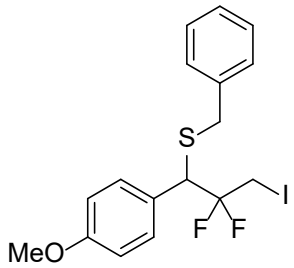
^{19}F NMR ($CDCl_3$) δ –102.57 (1F, dt, *J* = 223.6, 16.0 Hz), –116.01 (1F, dt, *J* = 223.6, 7.9 Hz) ppm.

IR ($CHCl_3$) ν 3013, 2936, 2839, 1611, 1584, 1514, 1453, 1327, 1253, 1027 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{11}H_{12}F_2IO_2^+$, 340.9845; found, 340.9846.

General Procedure of Iodosulfenylation

A mixture of 0.0923 g (0.50 mmol) of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0678 g (0.275 mmol) of dibenzyl disulfide and 0.254 g (1.00 mmol) of I_2 in 0.75 mL of 1,2-dichloroethane in a pressure tight glass tube was stirred at 60 °C (oil bath temperature) for 6 h, and the reaction mixture was quenched by sat. $Na_2S_2O_3$ aq. (5 mL). The crude mixture was then extracted with CH_2Cl_2 three times and washed by sat. $Na_2S_2O_3$ aq. (5 mL). After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography yielded 0.1594 g (0.466 mmol, yield 93%) of 1-[(1-benzylsulfenyl-2,2-difluoro-3-iodo)prop-1-yl]-4-methoxybenzene (**7aa**) [2244675-00-9][10] as a colorless oil.



White solid.

m.p.:47.5 - 49.8 °C.

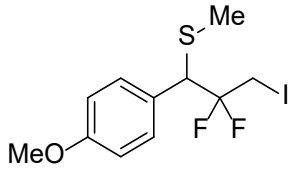
Rf = 0.24 (hexane:Et_2O = 20:1).

^{1}H NMR ($CDCl_3$) δ 7.34-7.24 (7H, m), 6.86 (2H, d, *J* = 8.7 Hz), 4.16 (1H, t, *J* = 13.8 Hz), 3.81 (3H, s), 3.78 (1H, d, *J* = 13.2 Hz), 3.57 (1H, d, *J* = 13.2 Hz), 3.51 (1H, ddd, *J* = 25.8, 12.0, 11.7 Hz), 3.33 (1H, ddd, *J* = 16.8, 12.9, 11.7 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 159.5, 136.8, 130.4, 129.1, 128.5, 127.3, 126.8 (dd, *J* = 3.1, 1.9 Hz), 120.2 (t, *J* = 246.9 Hz), 114.0, 55.2, 51.4 (t, *J* = 25.4 Hz), 36.2, 3.7 (t, *J* = 30.4 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –95.23 ~ –96.24 (1F, m), –96.26 ~ –97.31 (1F, m) ppm.

1-[(2,2-Difluoro-3-iodo-1-methylsulfenyl)prop-1-yl]-4-methoxybenzene (**7ab**) [2244675-12-3][10]



Instead of 0.275 mmol of dibenzyl disulfide, 0.0259 g (0.275 mmol) of dimethyl disulfide was employed to afford 0.170 g of the title compound (0.474 mmol) in 95% yield.

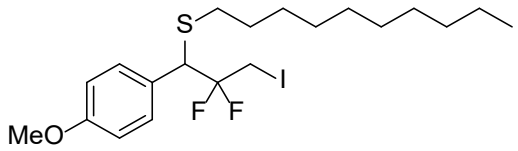
Yellow oil.

Rf = 0.24 (hexane:Et_2O = 20:1).

^{1}H NMR ($CDCl_3$) δ 7.34 (2H, d, *J* = 8.7 Hz), 6.88 (2H, d, *J* = 8.7 Hz), 4.31 (1H, dd, *J* = 14.4, 12.3 Hz), 3.80 (3H, s), 3.66-3.53 (1H, m), 3.44-3.30 (1H, m), 2.08 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 159.5, 130.3, 126.7 (dd, *J* = 3.1, 1.2 Hz), 120.4 (t, *J* = 246.9 Hz), 114.0, 55.2, 54.5 (t, *J* = 25.1 Hz), 15.8 (dd, *J* = 1.8, 1.2 Hz), 3.7 (t, *J* = 30.7 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ –95.29 ~ –96.29 (1F, m), –96.72 ~ –97.73 (1F, m) ppm.

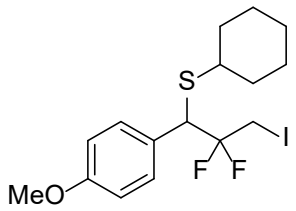
1-[(1-Decylsulfenyl-2,2-difluoro-3-iodo)prop-1-yl]-4-methoxybenzene (**7ac**) [2244675-13-4][10]



Instead of 0.275 mmol of dibenzyl disulfide, 0.0953 g (0.275 mmol) of didecyl disulfide was employed to afford 0.215 g of the title compound (0.443 mmol) in 89% yield.

Yellow oil.
Rf = 0.50 (hexane:AcOEt = 10:1).
^{1}H NMR ($CDCl_3$) δ 7.38-7.32 (2H, m), 6.90-6.86 (2H, m), 4.38 (1H, t, *J* = 13.5 Hz), 3.80 (3H, s), 3.62 (1H, ddd, *J* = 16.2, 12.6, 11.7 Hz), 3.38 (1H, ddd, *J* = 16.2, 12.9, 11.4 Hz), 2.50 (2H, t, *J* = 7.4 Hz), 1.58-1.48 (2H, m), 1.32-1.24 (14H, m), 0.88 (3H, t, *J* = 6.8 Hz) ppm.
^{13}C NMR ($CDCl_3$) δ 159.5, 130.3, 127.3 (dd, *J* = 2.5, 1.9 Hz), 120.3 (t, *J* = 246.9 Hz), 113.9, 55.2, 52.8 (t, *J* = 24.7 Hz), 32.5, 31.8, 29.5, 29.4, 29.3, 29.1, 29.0, 28.6, 22.6, 14.1, 3.8 (t, *J* = 31.0 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ –96.64 ~ –96.93 (m) ppm.

1-[(1-Cyclohexylsulfenyl-2,2-difluoro-3-iodo)propyl]-4-methoxybenzene (**7ad**) [2244675-14-5][10]

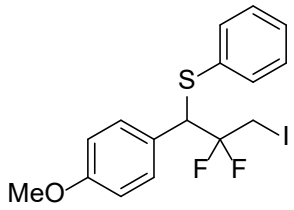


Instead of 0.275 mmol of dibenzyl disulfide, 0.0637 g (0.275 mmol) of dicyclohexyl disulfide was employed to afford 0.178 g of the title compound (0.417 mmol) in 83% yield.

Pale yellow oil.
Rf = 0.34 (hexane:AcOEt = 10:1).
^{1}H NMR ($CDCl_3$) δ 7.34 (2H, d, *J* = 8.7 Hz), 6.89-6.85 (2H, m), 4.46 (1H, t, *J* = 13.5 Hz), 3.81 (3H, s), 3.64 (1H, td, *J* = 14.4, 11.3 Hz), 3.40 (1H, td, *J* = 14.4, 11.4 Hz), 2.70-2.61 (1H, m), 1.98-1.93 (1H, m), 1.88-1.84 (1H, m), 1.75-1.67 (2H, m), 1.36-1.22 (6H, m) ppm.
^{13}C NMR ($CDCl_3$) δ 159.4, 130.3, 128.0 (dd, *J* = 2.5, 1.9 Hz), 120.1 (t, *J* = 246.9 Hz), 113.9, 55.2,

51.0 (t, J = 25.5 Hz), 44.0, 33.2 (d, J = 2.5 Hz), 25.7 (d, J = 6.7 Hz), 25.6, 3.9 (t, J = 31.0 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ –96.53 ~ –96.68 (m) ppm.

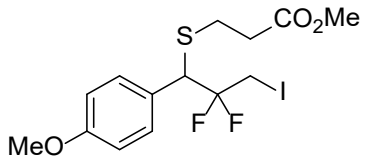
1-[(2,2-Difluoro-3-iodo-1-phenylsulfenyl)prop-1-yl]-4-methoxybenzene (**7ae**) [2244675-01-0][10]



Instead of 0.275 mmol of dibenzyl disulfide, 0.0604 g (0.275 mmol) of diphenyl disulfide was employed to afford 0.199 g of the title compound (0.473 mmol) in 95% yield.

Colorless oil.
Rf = 0.28 (hexane:AcOEt = 10:1).
^{1}H NMR ($CDCl_3$) δ 7.37-7.32 (2H, m), 7.30 (1H, s), 7.27 (1H, s), 7.25-7.22 (3H, m), 6.86-6.81 (2H, m), 4.66 (1H, dd, J = 15.0, 13.2 Hz), 3.78 (3H, s), 3.59 (1H, td, J = 17.1, 11.7 Hz), 3.40 (1H, td, J = 17.1, 12.0 Hz) ppm.
^{13}C NMR ($CDCl_3$) δ 160.0, 135.4. 132.9, 130.3 (dd, J =1.8, 1.2 Hz), 129.0, 128.0, 127.4 (dd, J = 2.5, 1.3 Hz), 119.9 (t, J = 247.5 Hz), 114.0, 57.4 (t, J = 24.8 Hz), 55.2, 3.7 (t, J = 30.4 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ –95.50 ~ –97.89 (2F, m) ppm.

Methyl 3-{1-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]sulfenyl}propanoate (**7af**) [2244675-15-6][10]

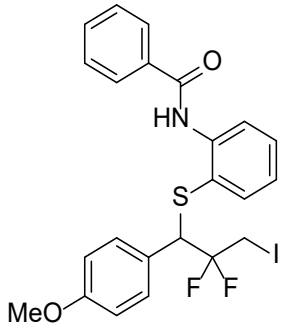


Instead of 0.275 mmol of dibenzyl disulfide, 0.0655 g (0.275 mmol) of dimethyl 3,3'-disulfanediyldipropionate was employed to afford 0.167 g of the title compound (0.388 mmol) in 78% yield.
Colorless oil.
Rf = 0.40 (toluene:CH_2Cl_2 = 1:1).
^{1}H NMR ($CDCl_3$) δ 7.35 (2H, d, J = 8.7 Hz), 6.90-6.86 (2H, m), 4.47 (1H, dd, J = 14.7, 12.3 Hz), 3.81 (3H, s), 3.67 (3H, s), 3.58 (1H, ddd, J = 17.4, 11.4, 10.8 Hz), 3.35 (1H, ddd, J = 17.4, 12.3, 11.7 Hz), 2.88-2.72 (2H, m), 2.56 (t, J = 7.2 Hz) ppm.
^{13}C NMR ($CDCl_3$) δ 171.8, 159.6, 130.2, 126.8 (dd, J = 3.1, 1.2 Hz), 120.0 (t, J = 246.9 Hz), 114.0,

55.2, 53.1 (t, J = 25.5 Hz), 51.7, 34.2, 27.2, 3.5 (t, J = 31.1 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –95.55 ~ –96.55 (1F, m), –97.09 ~ –98.10 (1F, m) ppm.

N-{2-[2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]sulfenyl}phenyl]benzamide (**7ag**)



Instead of 0.275 mmol of dibenzyl disulfide, 0.126 g (0.275 mmol) of bis(2-benzamidophenyl) disulfide was employed and the reaction was conducted in 0.50 mL of 1,2-dichloroethane and 0.25 mL of MeCN to afford 0.143 g of the title compound (0.265 mmol) in 53% yield.

White solid.

m.p.: 105.3 - 106.9 °C.

Rf = 0.34 (hexane:CH_2Cl_2 = 2:1).

^{1}H NMR ($CDCl_3$) δ 9.21 (1H, br s) 8.59 (1H, dd, J = 8.1, 1.1 Hz), 7.77-7.73 (2H, m), 7.57-7.51 (1H, m), 7.47-7.39 (4H, m), 7.16-7.39 (2H, m), 7.01 (1H, td, J = 6.3, 1.2 Hz), 6.70-6.65 (2H, m), 4.34 (1H, dd, J = 21.0, 8.7 Hz), 3.71 (3H, s), 3.43 (1H, ddd, J = 17.7, 11.7, 8.7 Hz), 3.21 (1H, ddd, J = 17.4, 14.7, 11.7 Hz) ppm.

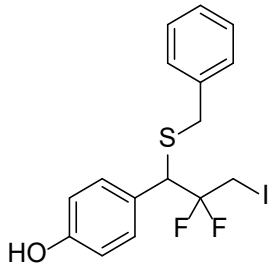
^{13}C NMR ($CDCl_3$) δ 164.9, 159.7, 140.6, 137.3, 134.3, 131.8, 131.3, 129.8, 127.1, 127.0, 124.0, 120.9, 120.1, 120.0 (t, J = 246.9 Hz), 114.2, 58.8 (dd, J = 26.0, 24.1 Hz), 55.1, 2.9 (t, J = 30.3 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –93.46 ~ –98.98 (1F, m), –98.98 ~ –100.00 (1F, m) ppm.

IR (KBr) ν 3330, 3034, 2963, 2835, 1671, 1512, 1306, 1254, 1184, 1006 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{23}H_{21}F_2INO_2S^+$, 540.0300; found, 540.0282.

4-{1-(Benzylsulfenyl-2,2-difluoro-3-iodo)prop-1-yl}phenol (**7da**)

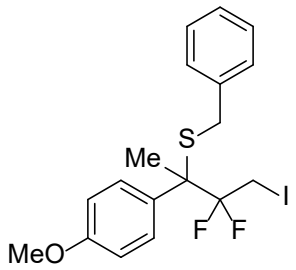


Instead of 0.5 mmol of **1a**, 0.0851 g (0.5 mmol) of 1-(2,2-difluorocycloprop-1-yl)phenol (**1d**) was

employed to afford 0.2018 g of the title compound (0.480 mmol) in 96% yield.

White solid.
m.p.: 91.8 - 93.2 °C.
Rf = 0.19 (hexane:AcOEt = 4:1).
^{1}H NMR ($CDCl_3$) δ 7.34-7.09 (7H, m), 6.82-6.77 (2H, m), 4.89 (1H, s), 4.15 (1H, t, *J* = 13.7 Hz), 3.80 (1H, d, *J* = 13.7 Hz), 3.58 (1H, d, *J* = 13.5 Hz), 3.58 (1H, ddd, *J* = 16.2, 12.9, 11.7 Hz), 3.49 (1H, ddd, *J* = 16.5, 13.5, 11.7 Hz) ppm.
^{13}C NMR ($CDCl_3$) δ 155.5, 136.7, 130.6, 129.1, 128.5, 127.3, 127.0 (dd, *J* = 3.1, 1.2 Hz), 120.2 (t, *J* = 246.8 Hz), 115.5, 51.4 (t, *J* = 25.1 Hz), 36.2, 3.6 (t, *J* = 30.3 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ –95.35 ~ –97.29 (m) ppm.
IR ($CHCl_3$) ν 3011, 1611, 1512, 1254, 1216, 1179, 1077, 1034, 1002, 758 cm^{-1}.
HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{16}H_{16}F_2IOS^+$, 420.9929; found, 420.9953.

1-{(2-Benzylsulfenyl-3,3-difluoro-4-iodo)but-2-yl}-4-methoxybenzene (**7ja**)

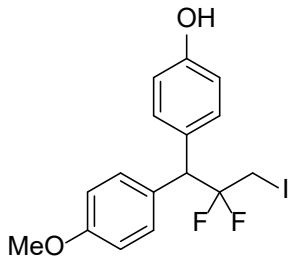


Instead of 0.5 mmol of **1a**, 0.0991 g (0.5 mmol) of 1-(2,2-difluoro-1-methylcycloprop-1-yl)-4-methoxybenzene (**1j**) was employed and the reaction was conducted at 25 °C to afford 0.1753 g of the title compound (0.391 mmol) in 96% yield.

Yellow oil.
Rf = 0.50 (hexane:AcOEt = 4:1).
^{1}H NMR ($CDCl_3$) δ 7.61 (2H, d, *J* = 9.0 Hz), 7.29-7.23 (5H, m), 6.92-6.89 (2H, m), 3.83 (3H, s), 3.78-3.47 (4H, m), 1.97 (3H, s) ppm.
^{13}C NMR ($CDCl_3$) δ 159.2, 136.6, 130.2, 129.6, 129.1, 127.2, 121.4 (t, *J* = 250.6 Hz), 113.7, 56.5, 55.2, 34.8, 22.7 (d, *J* = 3.1 Hz), 4.1 (t, *J* = 29.2 Hz) ppm.
^{19}F NMR ($CDCl_3$) δ –95.92 ~ –97.84 (m) ppm.
IR ($CHCl_3$) ν 3019, 1609, 1543, 1509, 1458, 1256, 1216, 1031, 757, 670 cm^{-1}.
HRMS (FAB+, m/z): $[M]^+$ calcd. for $C_{18}H_{19}F_2IOS^+$, 448.0164; found, 448.0159.

General Procedure of Iodoarylation

A mixture of 0.0922 g (0.50 mmol) of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**), 0.0941 g (1.00 mmol) of phenol, 0.254 g (1.00 mmol) of I_2 and 0.1382 g (1.00 mmol) of K_2CO_3 in 0.75 mL of 1,2-dichloroethane in a pressure tight glass tube was stirred at 80 °C (oil bath temperature) for 6 h, and the reaction mixture was quenched by sat. $Na_2S_2O_3$ aq. (5 mL). The resultant mixture was then extracted with CH_2Cl_2 three times and washed by sat. $Na_2S_2O_3$ aq. (5 mL). After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography to obtain 0.153 g (0.379 mmol, yield 76%) of 4-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]phenol (**8aa**) as a colorless oil.



Colorless oil.

Rf = 0.30 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.34 (2H, d, *J* = 8.7 Hz), 7.29 (2H, d, *J* = 8.4 Hz), 6.86 (2H, d, *J* = 9.0 Hz), 6.78 (2H, d, *J* = 9.0 Hz), 4.92 (1H, s), 4.62 (1H, t, *J* = 17.0 Hz), 3.78 (3H, s), 3.40 (2H, t, *J* = 14.4 Hz) ppm.

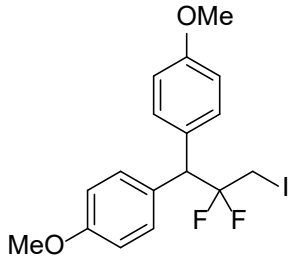
^{13}C NMR ($CDCl_3$) δ 158.8, 154.9, 130.5, 130.3, 129.5, 129.4, 120.9 (t, *J* = 247.4 Hz), 115.5, 114.1, 55.3, 54.4 (t, *J* = 23.2 Hz), 4.7 (t, *J* = 29.5 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –97.51 ~ –97.73 (m) ppm.

IR ($CHCl_3$) ν 3585, 3402, 3018, 1612, 1513, 1253, 1216, 1177, 1001, 754 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{16}H_{15}F_2IO_2^+$, 404.0079; found, 404.0090.

2,2-Difluoro-3-iodo-1,1-bis(4-methoxyphenyl)propane (**8ab**)



Instead of 1.0 mmol of phenol, 0.1084 g (1.0 mmol) of anisole was employed to afford 0.161 g of the title compound (0.386 mmol) in 77% yield.

Colorless oil.

Rf = 0.54 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.34 (4H, d, *J* = 8.7 Hz), 6.86 (4H, d, *J* = 8.7 Hz), 4.63 (1H, t, *J* = 16.8 Hz), 3.78 (6H, s), 3.40 (1H, t, *J* = 14.4 Hz) ppm.

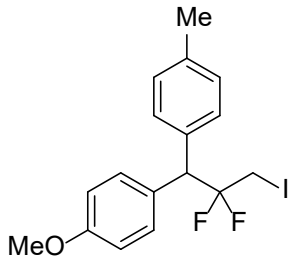
^{13}C NMR ($CDCl_3$) δ 158.8, 130.3, 129.3, 120.8 (t, *J* = 247.5 Hz), 114.0, 55.1, 54.4 (t, *J* = 23.2 Hz), 4.8 (t, *J* = 30.7 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –97.57 (q, *J* = 14.8 Hz) ppm.

IR ($CHCl_3$) ν 3585, 3402, 3018, 1612, 1513, 1253, 1216, 1177, 1001, 754 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{17}H_{18}F_2IO_2^+$, 419.0314; found, 419.0321.

1-[2,2-Difluoro-3-iodo-1-(4-methylphenyl)prop-1-yl]-4-methoxybenzene (**8ac**)



Instead of of 1.0 mmol of K_2CO_3, 0.1226 g (1.0 mmol) of nitrobenzene was employed. Instead of 1.0 mmol of phenol, 0.75 mL of toluene was used as reagent and solvent to afford 0.141 g of the title compound (0.350 mmol) in 70% yield.

Colorless oil.

Rf = 0.59 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.36-7.30 (2H, m), 7.14-7.12 (2H, m), 6.88-6.82 (2H, m), 4.63 (1H, t, *J* = 17.1 Hz), 3.78 (3H, s), 3.41 (2H, t, *J* = 14.4 Hz), 2.31 (3H, s) ppm.

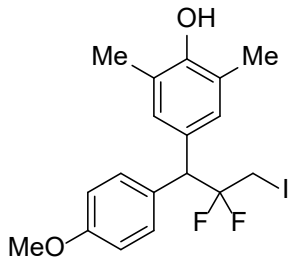
^{13}C NMR ($CDCl_3$) δ 158.8, 137.2, 134.2, 131.0 (d, *J* = 2.5 Hz), 130.3, 129.4, 129.1, 120.8 (t, *J* = 247.5 Hz), 114.0, 55.2, 54.9 (t, *J* = 22.9 Hz), 21.0, 4.8 (t, *J* = 31.0 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –97.53 (q, *J* = 15.3 Hz) ppm.

IR ($CHCl_3$) ν 3007, 2932, 2837, 1610, 1513, 1253, 1181, 1001, 810, 758 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{17}H_{17}F_2IO^+$, 41402.0287; found, 402.0289.

4-[2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]-2,6-dimethylphenol (**8ad**)



Instead of 1.0 mmol of phenol, 0.1223 g (1.0 mmol) of 2,6-dimethylphenol was employed to afford 0.171 g of the title compound (0.396 mmol) in 79% yield.

Orange high viscose oil.

Rf = 0.31 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.34 (2H, d, *J* = 8.4 Hz), 7.02 (2H, s), 6.85 (2H, d, *J* = 8.4 Hz), 4.57 (1H, s), 4.52 (1H, t, *J* = 17.4 Hz), 3.78 (3H, s), 3.41 (2H, t, *J* = 14.6 Hz), 2.22 (6H, s) ppm.

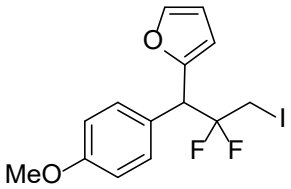
^{13}C NMR ($CDCl_3$) δ 158.7, 151.6, 130.2, 129.5 (d, *J* = 3.1 Hz), 129.3, 128.8 (d, *J* = 3.8 Hz), 123.2, 120.8 (t, *J* = 247.5 Hz), 113.9, 53.1, 54.5 (t, *J* = 23.3 Hz), 16.0, 5.0 (t, *J* = 30.7 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –96.88 (1F, dq, *J* = 243.0, 13.6 Hz), –98.00 (1F, dq, *J* = 243.0, 16.0 Hz) ppm.

IR ($CHCl_3$) ν 3599, 3493, 3009, 2916, 2838, 1610, 1512, 1253, 1000, 757 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{18}H_{19}F_2IO_2^+$, 432.0392; found, 432.0377.

2-[2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]furan (**8ae**)



Instead of 1.0 mmol of phenol, 0.2045 g (3.0 mmol) of furan and 0.0782 g (1.0 mmol) of DMSO was employed and the reaction was conducted at 40 °C for 9 h to afford 0.154 g of the title compound (0.408 mmol) in 82% yield.

Pale yellow oil.

Rf = 0.51 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.39-7.38 (1H, m), 7.37 (2H, d, *J* = 8.7 Hz), 6.88 (2H, d, *J* = 8.7 Hz), 6.36 (2H, d, *J* = 1.5 Hz), 4.79 (1H, t, *J* = 15.0 Hz), 3.80 (3H, s), 3.54-3.29 (2H, m) ppm.

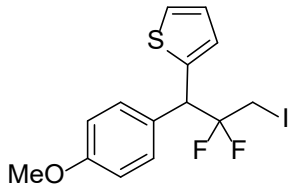
^{13}C NMR ($CDCl_3$) δ 159.4, 150.2, 142.4, 130.6, 126.6, 119.7 (t, *J* = 248.1 Hz), 114.1, 110.5, 108.9, 55.2, 49.5 (t, *J* = 24.8 Hz), 3.8 (t, *J* = 30.1 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –97.33 (1F, ddt, *J* = 241.8, 18.2, 13.7 Hz), –98.62 (1F, dtd, *J* = 242.9, 17.1, 11.4 Hz) ppm.

IR ($CHCl_3$) ν 3009, 2838, 1609, 1514, 1300, 1258, 1187, 1031, 1005, 754 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{14}H_{13}F_2IO_2^+$, 377.9928; found, 377.9954.

2-[2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]thiophene (**8af**)



Instead of 1.0 mmol of phenol, 0.2525 g (3.0 mmol) of thiophene and 0.1383g (2.0 mmol) of K_2CO_3 was employed and the reaction was conducted at 30 °C for 6 h to afford 0.137 g of the title compound (0.347 mmol) in 69% yield.

Pale yellow oil.

Rf = 0.55 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.41-7.38 (2H, m), 7.24 (1H, d, *J* = 6.6 Hz), 7.08 (1H, d, *J* = 3.3 Hz), 6.98-6.95 (1H, m), 6.90-6.87 (2H, m), 4.96 (1H, dd, *J* = 17.1, 15.0 Hz), 3.80 (3H, s), 3.50-3.28 (2H, m) ppm.

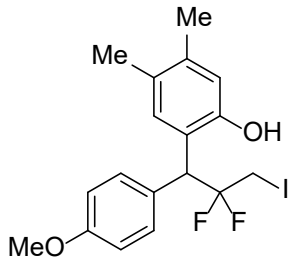
^{13}C NMR ($CDCl_3$) δ 159.3, 139.2 (d, *J* = 3.7 Hz), 130.3, 128.5 (d, *J* = 5.0 Hz), 127.2, 126.7, 125.4, 120.2 (t, *J* = 248.7 Hz), 114.1, 55.2, 50.8 (t, *J* = 24.1 Hz), 4.0 (t, *J* = 31.0 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –97.46 (1F, dq, *J* = 241.9, 14.8 Hz), –99.62 (1F, dtd, *J* = 241.7, 14.8 Hz) ppm.

IR ($CHCl_3$) ν 3010, 2838, 1611, 1513, 1254, 1217, 1181, 1002, 757, 467 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{14}H_{13}F_2IOS^+$, 393.9694; found, 393.9709.

2-[2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)propyl]-4,5-dimethylphenol (**8ag**)



Instead of 1.0 mmol of phenol, 0.1223 g (1.0 mmol) of 3,4-dimethylphenol was employed to afford 0.165 g of the title compound (0.395 mmol) in 76% yield.

Pale yellow oil.

Rf = 0.31 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.37 (2H, d, *J* = 8.4 Hz), 7.25 (1H, s), 6.84 (2H, d, *J* = 8.4 Hz), 6.53 (1H, s), 5.13 (1H, t, *J* = 17.4 Hz), 4.84 (1H, br s), 3.77 (3H, s), 3.54-3.42 (2H, m), 2.18 (3H, s), 2.15 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 158.6, 150.9, 136.9, 130.6, 130.2, 129.3 (d, *J* = 3.8 Hz), 128.9, 121.4 (d, *J* = 5.0 Hz), 121.0 (t, *J* = 247.2 Hz), 117.1, 113.9, 55.2, 46.4 (t, *J* = 23.6 Hz), 19.4, 19.1, 5.3 (t, *J* = 29.8 Hz) ppm.

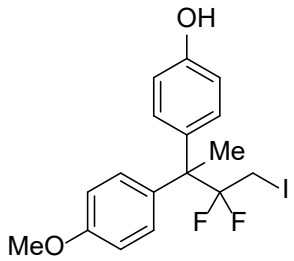
^{19}F NMR ($CDCl_3$) δ –95.03 (1F, ddt, *J* = 241.8, 17.1, 11.4 Hz), –97.81 (1F, dtd, *J* = 241.8, 18.2, 11.4 Hz) ppm.

IR ($CHCl_3$) ν 3412, 2924, 1610, 1512, 1456, 1413, 1251, 1181, 1000, 758 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{18}H_{19}F_2IO_2^+$, 432.0392; found, 432.0404.

4-[3,3-Difluoro-4-iodo-2-(4-methoxyphenyl)but-2-yl]phenol (**8ja**)

Instead of 0.5 mmol of **1a**, 0.0991 g (0.5 mmol) of 1-(2,2-difluoro-1-methylcycloprop-1-yl)-4-methoxybenzene (**1j**) was employed to afford 0.148 g of the title compound (0.354 mmol) in 71% yield.



Colorless oil.

Rf = 0.31 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.22 (2H, d, *J* = 8.4 Hz), 7.18 (2H, d, *J* = 9.0 Hz), 6.82 (2H, d, *J* = 8.7 Hz), 6.75 (2H, d, *J* = 8.7 Hz), 4.90 (1H, br s), 3.81 (3H, s), 3.41 (2H, t, *J* = 16.8 Hz), 1.80 (3H, s) ppm.

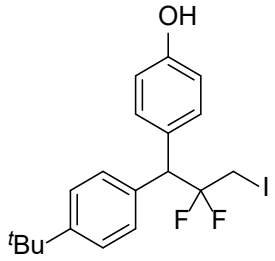
^{13}C NMR ($CDCl_3$) δ 158.1, 154.4, 138.2, 135.5, 130.0, 129.7 (d, *J* = 6.8 Hz), 122.0 (t, *J* = 251.5 Hz), 114.9, 113.4, 55.2, 52.9 (t, *J* = 22.0 Hz), 25.5 (t, *J* = 4.0 Hz), 5.6 (t, *J* = 29.2 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ –95.70 (t, *J* = 16.0 Hz) ppm.

IR ($CHCl_3$) ν 3400, 3008, 2838, 1611, 1513, 1182, 1027, 999, 832, 735 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{17}H_{18}F_2IO_2^+$, 419.0314; found, 419.0321.

4-{[1-(4-*tert*-Butylphenyl)-2,2-difluoro-3-iodo]prop-1-yl}phenol (**8fa**)



Instead of 0.5 mmol of **1a**, 0.1051 g (0.5 mmol) of 1-*tert*-butyl-4-(2,2-difluorocycloprop-1-yl)benzene (**1f**) was employed to afford 0.152 g of the title compound (0.352 mmol) in 70% yield.

Pale yellow solid.

m.p.: 70.0 - 71.0 °C.

Rf = 0.40 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.35-7.30 (2H, m), 6.81-6.76 (2H, m), 4.74 (1H, br s), 4.62 (1H, t, *J* = 17.1 Hz), 3.41 (2H, t, *J* = 14.4 Hz), 1.29 (9H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 154.5, 150.3, 134.1 (d, *J* = 2.5 Hz), 130.6, 129.5 (d, *J* = 2.5 Hz), 128.8, 125.6, 120.8 (t, *J* = 247.5 Hz), 115.5, 54.8 (t, *J* = 23.5 Hz), 34.4, 31.2, 4.9 (t, *J* = 31.0 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −96.40 – 98.38 (m) ppm.

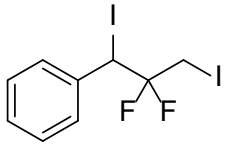
IR ($CHCl_3$) ν 3248, 2965, 2245, 1889, 1560, 1513, 1249, 1000, 819, 733 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{19}H_{21}F_2IO^+$, 430.0600; found, 430.0586.

(2,2-Difluoro-1,3-diiodoprop-1-yl)benzene (**3g**)

Instead of 0.5 mmol of **1a**, 0.1051 g (0.5 mmol) of (2,2-difluorocycloprop-1-yl)benzene (**1g**) was employed to afford the byproduct **3g** (0.230 mmol) in 46% in ^{19}F NMR yield with the substrate **1g**.

Data for the crude product were included, because it was difficult to isolate from the byproducts.



Brown oil.

Rf = 0.80 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.55-7.48 (2H, m), 7.36-7.31 (3H, m), 5.55 (1H, dd, *J* = 19.8, 7.8 Hz), 3.56-3.27 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$) δ 136.7 (d, *J* = 5.6 Hz), 129.3, 129.1, 129.0, 118.0 (t, *J* = 247.5 Hz), 27.6 (dd, *J* = 27.9, 24.8 Hz), 0.6 (t, *J* = 31.6 Hz) ppm.

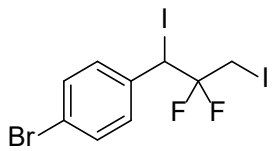
^{19}F NMR ($CDCl_3$) δ −87.67 ~ −87.80 (1F, m), −88.50 ~ −88.64 (1F, m) ppm.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_9H_8F_2I_2^+$, 407.8678; found, 407.8680.

1-Bromo-4-(2,2-difluoro-1,3-diiodoprop-1-yl)benzene (**3h**)

Instead of 0.5 mmol of **1a**, 0.1051 g (0.5 mmol) of 1-bromo-4-(2,2-difluorocycloprop-1-yl)benzene (**1h**) was employed to afford the byproduct **3h** (0.252 mmol) in 50% in ^{19}F NMR yield with other byproducts.

Data for the crude product were included, because it was difficult to isolate from the byproducts.



Colorless oil.

Rf = 0.63 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.50-7.46 (2H, m), 7.41-738 (2H, m), 5.52 (1H, dd, *J* = 18.9, 8.4 Hz), 3.58-3.27 (2H, m) ppm.

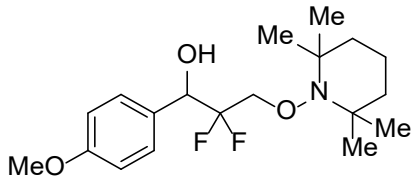
^{13}C NMR ($CDCl_3$) δ 135.6, 132.1, 130.6, 123.3, 117.9 (t, *J* = 247.1 Hz), 26.4 (t, *J* = 27.3 Hz), 0.6 (t, *J* = 31.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −88.68 ~ −89.74 (1F, m), −94.51 ~ −95.50 (1F, m) ppm.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_9H_8BrF_2I_2O^+$, 486.7861; found, 486.7888.

Control experiment

2,2-Difluoro-1-(4-methoxyphenyl)-3-[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]propan-1-ol (Scheme 5 (eq. 4), **2a-TEMPO**)



To a mixture of 0.0920 g (0.50 mmol) of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene (**1a**) and 0.1716 g (1.10 mmol) of 2,2,6,6-tetrameethylpiperidine 1-oxyl radical in 0.75 mL of 1,2-dichloroethane and 0.75 mL of water in a pressure tight glass tube, 0.1400 g (0.55 mmol) of iodine was added and stirred for 18 h at 25 °C. The reaction mixture was extracted with CH_2Cl_2 three times. After dried over anhydrous Na_2SO_4, the crude product was evaporated and purified by silica gel column chromatography by hexane/AcOEt = 20:1-10:1 as an eluent to yield 0.462 g (0.160 mmol) of the title compound as a colorless oil in 32% yield.

White solid.

m.p.: 92.5 - 93.5 °C.

Rf = 0.49 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.42-7.39 (2H, m), 7.18 (1H, br s), 6.92-6.87 (2H, m), 5.01 (1H, dd, *J* = 24.3, 2.3 Hz), 3.80 (3H, s), 3.35-3.10 (2H, m), 1.70-1.07 (18H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 159.4, 129.2, 128.4, 118.4 (dd, *J* = 256.8, 240.6 Hz), 113.1, 75.5 (dd, *J* = 29.8, 25.4 Hz), 56.7-55.8 (m), 55.1, 50.9 (dd, *J* = 35.3, 27.8 Hz), 40.7, 33.1, 21.1, 20.6, 17.2 ppm.

^{19}F NMR ($CDCl_3$) δ −100.91 ~ −101.83 (1F, m), −106.50 ~ −107.67 (1F, m) ppm.

IR (KBr) ν 3630, 3224, 2929, 1887, 1612, 1514, 1466, 1249, 984, 817 cm^{-1}.

HRMS (FAB−, m/z): $[M-H]^-$ calcd for $C_{19}H_{28}F_2NO_3^-$, 356.2043; found, 356.2062.

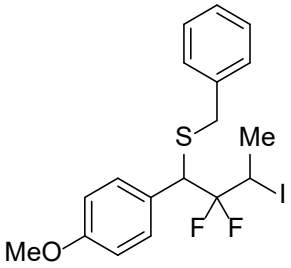
2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)propan-1-ol (Scheme 5 (eq. 5), **2a**)

A mixture of 0.0459 g (0.25 mmol) of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene, 0.0986 g (0.55 mmol) of 1,1-diphenylethene, 0.0698 g (0.275 mmol) of I_2 in 0.75 mL of MeCN and 0.75 mL of water in a pressure tight glass tube was stirred at 80 °C (oil bath temperature) for 18 h, and the reaction mixture was extracted with CH_2Cl_2 three times. After dried over anhydrous Na_2SO_4, the crude product was evaporated and purified by silica gel column chromatography by hexane:AcOEt = 20:1-10:1 as an eluent to yield 0.0487 g (0.11 mmol) of 2,2-difluoro-3-iodo-1-(4-methoxyphenyl)-propan-1-ol as a colorless oil in 44% yield.

(Scheme 5 (eq. 6), **2a**)

A mixture of 0.0457 g (0.25 mmol) of 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene, 0.0626 g (0.275 mmol) of *N*-iodosuccinimide in 0.75 mL of MeCN and 0.75 mL of water in a pressure tight glass tube was stirred at 80 °C (oil bath temperature) for 18 h, and the reaction mixture was extracted with CH_2Cl_2 three times. After dried over anhydrous Na_2SO_4, the crude product was evaporated and purified by silica gel column chromatography by hexane:AcOEt = 20:1-10:1 as an eluent to yield 0.0508 g (0.12 mmol) of 2,2-difluoro-3-iodo-1-(4-methoxyphenyl)-propan-1-ol as a colorless oil in 46% yield.

1-{(1-Benzylsulfenyl-2,2-difluoro-3-iodo)but-1-yl}-4-methoxybenzene (**7sa**)



Instead of 0.5 mmol of **1a**, 0.0992 g (0.5 mmol) of 1-(2,2-difluoro-3-methylcycloprop-1-yl)-4-methoxybenzene (**1s**, *d.r.* = 77:23) was employed to afford 0.1149 g of the title compound (0.256 mmol) in 51% yield as a diastereomer mixture.

diastereomer ratio = 55:45.

Pale yellow oil.

Rf = 0.46 (hexane:AcOEt = 10:1).

^{1}H NMR ($CDCl_3$) δ 7.35-7.22 (14H, m), 6.91-6.82 (4H, m), 4.49-4.33 (1H, m), 4.34 (1H, d, *J* = 10.4 Hz), 4.29 (1H, d, *J* = 10.4 Hz), 4.08-3.91 (1H, m), 3.82 (3H, s), 3.81 (3H, s), 3.86-3.73 (m, 2H), 3.56 (1H, d, *J* = 9.5 Hz), 3.52 (1H, d, *J* = 9.5 Hz), 1.85 (3H, d, *J* = 7.2 Hz), 1.79 (3H, d, *J* = 7.2 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 159.5 and 159.4, 137.1 and 136.8, 130.64 and 130.58, 129.3 and 129.2, 128.5 (C*2), 127.3 (C*2), 126.83 and 126.77, 121.4 (t, *J* = 249.4 Hz, C*2), 113.94 and 113.88, 55.2 (C*2), 51.2 (t, *J* = 25.4 Hz) and 51.0 (t, *J* = 24.7 Hz), 36.2 (d, *J* = 1.9 Hz) and 36.0 (s), 23.1 (t, *J* = 27.9 Hz) and 22.7 (t, *J* = 27.9 Hz), 21.2 (t, *J* = 3.8 Hz) and 21.0 (t, *J* = 3.7 Hz)) ppm.

^{19}F NMR ($CDCl_3$) δ −100.45 (minor 1F, dt, *J* = 243.9, 13.6 Hz)) and −103.09 (major 1F, ddd, *J* = 244.2, 16.1, 9.3 Hz), −107.63 ~ −108.67 (2F, m) ppm.

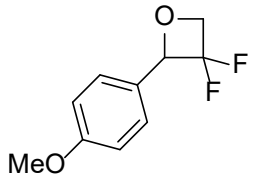
IR ($CHCl_3$) ν 3009, 2958, 2936, 2839, 1611, 1512, 1454, 1253, 1179, 1035 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{18}H_{19}F_2IOS^+$, 448.0164; found, 448.0177.

Transformation of the ring-opening products

3,3-Difluoro-2-(4-methoxyphenyl)oxetane (**9a**) [1777805-21-6][11]

A mixture of 0.1643 g (0.50 mmol) of **2a** and 0.2076 g (1.50 mmol) of K_2CO_3 in 1.0 mL of DMF in a 30 mL round-bottomed flask was stirred at 90 °C for 4 h, and the reaction mixture was quenched by water. The resultant mixture was then extracted with hexane:AcOEt (v:v=4:1) three times and successively washed by brine. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography to furnish 0.088 g (0.44 mmol, yield 88%) of the title compound as a colorless oil.



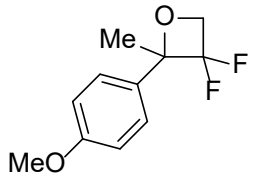
^{1}H NMR ($CDCl_3$) δ 7.37-7.33 (2H, m), 6.98-6.93 (2H, m), 5.80 (1H, t, *J* = 10.8 Hz), 4.99-4.77 (2H, m), 3.82 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 160.4, 128.5, 125.4 (d, *J* = 3.2 Hz), 117.8 (t, *J* = 281.0 Hz), 113.9, 91.5 (dd, *J* = 25.4, 23.5 Hz), 78.5 (t, *J* = 24.8 Hz), 55.2 ppm.

^{19}F NMR ($CDCl_3$) δ −112.93 (1F, ddt, *J* = 191.4, 15.8, 11.3 Hz), −100.04 (1F, dq, *J* = 192.4, 11.3 Hz) ppm.

3,3-Difluoro-2-(4-methoxyphenyl)-2-methyloxetane (**9j**) [1777805-22-7][11]

Instead of 0.5 mmol of **2a**, 0.1706 g (0.5 mmol) of 3,3-difluoro-4-iodo-2-(4-methoxyphenyl)butan-2-ol (**2j**) was employed to afford 0.0944 g of the title compound (0.44 mmol) in 88% yield as a colorless oil.



^{1}H NMR ($CDCl_3$) δ 7.35-7.31 (2H, m), 6.96-6.91 (2H, m), 4.87-4.65 (2H, m), 3.83 (3H, s), 1.74 (3H, d, *J* = 2.1 Hz) ppm.

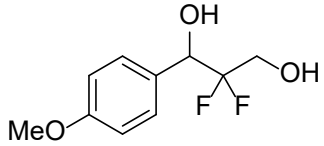
^{13}C NMR ($CDCl_3$) δ 159.4, 131.0, 126.2, 118.4 (t, *J* = 282.9 Hz), 113.7, 95.0 (t, *J* = 22.9 Hz), 76.3 (t, *J* = 26.0 Hz), 55.1, 23.0 (d, *J* = 5.6 Hz) ppm.

^{19}F NMR ($CDCl_3$) δ −105.86 ~ −106.61 (1F, m), −111.02 ~ −111.77 (1F, m) ppm.

2,2-Difluoro-1-(4-methoxyphenyl)propane-1,3-diol (**10a**)

A mixture of 0.0405 g (0.30 mmol) of **9a** and 0.0040 g (0.02 mmol) of *p*-TsOH·H_2O in 1.0 mL of

water in a 10 mL round-bottom flask was stirred at 50 °C for 24 h, and the reaction mixture was extracted with CH_2Cl_2 three times and washed by sat. $Na_2S_2O_3$ aq. and brine. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography yielded 0.0367 g (0.168 mmol, yield 84%) of the title compound as a white solid.



White solid.

m.p.: 71.0 - 72.4 °C.

Rf = 0.36 (hexane:AcOEt = 1:1).

^{1}H NMR ($CDCl_3$) δ 7.39-7.36 (2H, m), 6.94-6.89 (2H, m), 5.00 (1H, ddd, *J* = 13.2, 8.7, 3.9 Hz), 3.97-3.72 (2H, m), 3.82 (3H, s), 2.77 (1H, br s), 2.25 (1H, br s) ppm.

^{13}C NMR ($CDCl_3$) δ 159.9, 128.7, 128.0, 120.4 (dd, *J* = 248.7, 246.2 Hz), 113.9, 73.0 (t, *J* = 26.0 Hz), 62.1 (t, *J* = 31.0 Hz), 55.3 ppm.

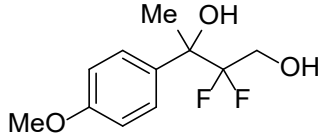
^{19}F NMR ($CDCl_3$) δ −104.01 (1F, ddt, *J* = 244.2, 24.9, 7.1 Hz), −105.93 (1F, dm, *J* = 245.1 Hz) ppm.

IR ($CHCl_3$) ν 3609, 3411, 3020, 1613, 1514, 1252, 1216, 1070, 757, 500 cm^{-1}.

HRMS (FAB−, m/z): $[M-H]^-$ calcd for $C_{10}H_{11}F_2O_3^-$, 217.0682; found, 217.0698.

2,2-Difluoro-3-(4-methoxyphenyl)butan-1,3-diol (**10j**)

Instead of 0.2 mmol of **9a**, 0.0425 g (0.20 mmol) of 3,3-difluoro-2-(4-methoxyphenyl)-2-methyloxetane (**9j**) was employed to afford 0.0425 g of the title compound (0.18 mmol) in 92% yield as a white solid.



White solid.

m.p.: 84.0 - 85.0 °C.

Rf = 0.48 (hexane:AcOEt = 1:1).

^{1}H NMR ($CDCl_3$) δ 7.48-7.44 (2H, m), 6.92-6.87 (2H, m), 3.91-3.57 (2H, m), 3.81 (3H, s), 2.94 (1H, br s), 2.26 (1H, t, *J* = 6.8 Hz), 1.71-1.70 (3H, m) ppm.

^{13}C NMR ($CDCl_3$) δ 159.2, 132.8, 127.0, 120.6 (t, *J* = 251.9 Hz), 113.6, 76.6 (t, *J* = 26.1 Hz), 62.0 (dd, *J* = 31.0, 28.6 Hz), 55.2, 23.7 (t, *J* = 2.8 Hz) ppm.

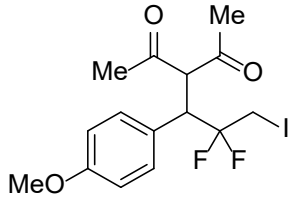
^{19}F NMR ($CDCl_3$) δ −118.74 (1F, dt, *J* = 255.5, 11.6 Hz), −122.89 (1F, dt, *J* = 255.5, 15.8 Hz) ppm

IR ($CHCl_3$) ν 3452, 3369, 1615, 1512, 1460, 1303, 1215, 1023, 917, 756, 500 cm^{-1}.

HRMS (FAB−, m/z): $[M-H]^-$ calcd for $C_{11}H_{13}F_2O_3^-$, 231.0838; found, 231.0811.

3-[2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]pentan-2,4-dione (**11**)

A mixture of 0.0686 g (0.20 mmol) of 1-(2,2-difluoro-3-iodo-1-methoxyprop-1-yl)-4-methoxybenzene (**5aa**), 0.0200 g (0.20 mmol) of acetylacetone and0.0108 g (0.04 mmol) of $FeCl_3 \cdot 6H_2O$ in 1.0 mL of 1,2-dichloroethane in a pressure tight glass tube was stirred 80 °C for 24 h, and the reaction mixture was quenched by sat. $NaHCO_3$ aq. The resultant mixture was then extracted with CH_2Cl_2 three times and washed by sat. $Na_2S_2O_3$ aq. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by recrystallization yielded 0.0607 g (0.148 mmol, yield 74%) of 3-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)propyl]pentan-2,4-dione (**11**) as white solid.



White solid.

m.p.: 118.1 - 121.3 °C.

Rf = 0.19 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.27-7.23 (2H, m), 6.88-6.83 (2H, m), 4.61 (1H, d, *J* = 11.4 Hz), 4.41 (1H, ddd, *J* = 25.8, 11.4, 1.2 Hz), 3.79 (3H, s), 3.27-3.01 (2H, m), 2,33 (3H, s), 1.84 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 201.5 (d, *J* = 1.2 Hz), 201.1, 159.7, 130.6, 125.5 (d, *J* = 8.0 Hz), 121.1 (dd, *J* = 248.7, 248.1 Hz), 114.5, 69.0, 55.2, 49.0 (dd, *J* = 22.3, 21.1 Hz), 29.7 (d, *J* = 3.7 Hz), 28.7, 3.1 (dd, *J* = 31.0, 29.8 Hz) ppm.

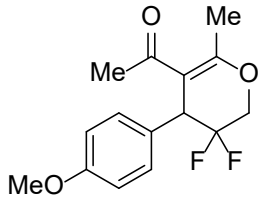
^{19}F NMR ($CDCl_3$) δ –92.25 ~ –93.24 (1F, m), –103.73 ~ –104.72 (1F, m) ppm.

IR (KBr) ν 3025, 2937, 2844, 1741, 1704, 1517, 1360, 1267, 1170, 999 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{15}H_{17}F_2IO_3^+$, 410.0185; found, 410.0155.

1-[3,3-Difluoro-4-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2*H*-pyran-5-yl]ethan-1-one (**12**)

A mixture of 0.124 g (0.30 mmol) of **11** and 0.124 g (0.90 mmol) of K_2CO_3 in 6.5 mL of DMF in a 30 mL round-bottom flask was stirred at 90 °C for 4 h, and the reaction mixture was quenched by water. The resultant mixture was then extracted with CH_2Cl_2 three times and successively washed by sat. $Na_2S_2O_3$ aq. and brine. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography yielded 0.069 g (0.246 mmol, yield 82%) of 1-[3,3-difluoro-4-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2*H*-pyran-5-yl]ethan-1-one (**12**) as a white solid.



White solid.

m.p.: 93.2 - 94.5 °C.

Rf = 0.25 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.17 (2H, d, *J* = 8.4 Hz), 6.88 (2H, d, *J* = 8.4 Hz), 4.19-4.13 (1H, m), 4.06-3.85 (2H, m), 3.80 (3H, s), 2.35 (3H, s), 2.01 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 197.8, 163.9, 159.4, 130.5, 128.5 (dd, *J* = 7.3, 2.5 Hz), 117.4 (t, *J* = 245.6 Hz), 114.1, 110.0 (dd, *J* = 4.4, 1.3 Hz), 63.3 (dd, *J* = 38.1, 27.2 Hz), 55.2, 46.3 (dd, *J* = 25.3, 12.1 Hz), 29.2, 20.2 ppm.

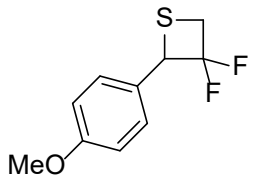
^{19}F NMR ($CDCl_3$) δ −103.88 (1F, dm, *J* = 246.2 Hz), −116.23 (1F, d, *J* = 246.2 Hz) ppm.

IR (KBr) ν 3001, 2959, 2933, 2838, 1676, 1581, 1512, 1279, 1076, 960 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{15}H_{16}F_2O_3$, 282.1062; found, 282.1060.

3,3-Difluoro-2-(4-methoxyphenyl)thietane (**13**)

A mixture of 1.291 g (3.00 mmol) of Methyl 3-{1-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]sulfenyl}-propanoate (**7af**) and 0.90 mL (6.00 mmol) of DBU in 6 mL of toluene in a 50 mL round-bottom flask was stirred at 120 °C (oil bath temperature) for 1 h, and the reaction mixture was quenched by water. The resultant mixture was then extracted with AcOEt three times. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography yielded 0.575 g (2.66 mmol, yield 89%) of 3,3-difluoro-2-(4-methoxyphenyl)thietane (**13**) as a colorless oil.



Rf = 0.38 (hexane:AcOEt = 10:1).

^{1}H NMR ($CDCl_3$) δ 7.40 (2H, d, *J* = 8.4 Hz), 6.94-6.89 (2H, m), 5.14 (1H, t, *J* = 12.6 Hz), 3.81 (3H, s), 3.76 (1H, dt, *J* = 15.9, 10.8 Hz), 3.59 (1H, dddd, *J* = 16.8, 10.8, 6.3, 2.1 Hz) ppm.

^{13}C NMR ($CDCl_3$) δ 160.0, 130.5, 125.1, 119.4 (dd, *J* = 283.5, 275.4 Hz), 113.8, 57.6 (t, *J* = 26.7 Hz), 55.2, 37.0 (t, *J* = 27.9 Hz) ppm.

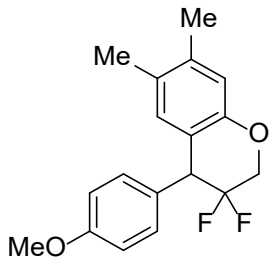
^{19}F NMR ($CDCl_3$) δ −70.88 (1F, dddd, *J* = 186.8, 13.8, 11.6, 6.8 Hz), −102.32 (1F, dtd, *J* = 186.8, 16.1, 11.6 Hz) ppm.

IR ($CHCl_3$) ν 3010, 2958, 2935, 2839, 1611, 1514, 1254, 1177, 1034, 990 cm^{-1}.

HRMS (FAB+, m/z): $[M]^+$ calcd. for $C_{10}H_{10}F_2OS^+$, 216.0415; found, 216.0440.

3,3-Diluoro-4-(4-methoxyphenyl)-6,7-dimethylchromane (**14**)

A mixture of 0.173 g (0.40 mmol) of 2-(2,2-difluoro-3-iodo-1-(4-methoxyphenyl)propyl)-4,5-dimethylphenol **(8ag)** and 0.166 g (1.20 mmol) of K_2CO_3 in 1.0 mL of DMF in a 30mL round-bottom flask was stirred at 30 °C for 16 h, and the reaction mixture was quenched by water, then extracted with hexane:AcOEt (v:v=1:1) three times and washed by brine. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography yielded 0.071 g (0.231 mmol, yield 58%) of 3,3-difluoro-4-(4-methoxyphenyl)-6,7-dimethylchromane (**15**) as a white solid.



White solid.

m.p.: 103.5 - 104.5 °C.

Rf = 0.62 (hexane:AcOEt = 4:1).

^{1}H NMR ($CDCl_3$) δ 7.11-7.09 (2H, m), 6.89-6.84 (2H, m), 6.77 (1H, s), 6.63 (1H, s), 4.39 (1H, t, *J* = 13.2 Hz), 4.23-4.01 (2H, m), 3.80 (3H, s), 2.22 (3H, s), 2.09 (3H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 159.2, 150.7, 131.5, 130.9, 130.2, 129.1 (d, *J* = 1.9 Hz), 129.0 (d, *J* = 1.9 Hz), 118.4 (t, *J* = 3.4 Hz), 117.4, 117.3 (t, *J* = 245.9 Hz), 113.7, 73.0 (t, *J* = 26.0 Hz), 62.1 (t, *J* = 31.0 Hz), 55.3 ppm.

^{19}F NMR ($CDCl_3$) δ −104.01 (1F, ddt, *J* = 244.2, 24.9, 7.1 Hz), −105.93 (1F, dm, *J* = 245.1 Hz) ppm.

IR ($CHCl_3$) ν 2939, 2842, 1894, 1612, 1511, 1458, 1301, 1104, 866, 757 cm^{-1}.

HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{18}H_{19}F_2O_2^+$, 305.1348; found, 305.1350.

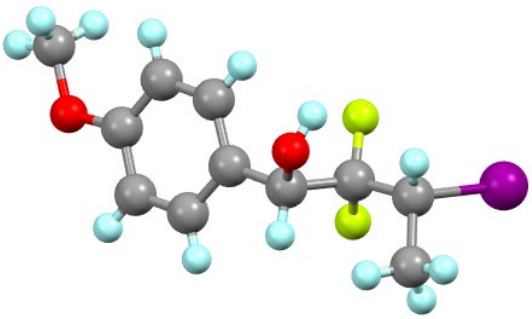
X-Ray Crystallographic Data for the Compound 2s.

Table S1. Crystal data and structure refinement for the compound **2s**.

Identification code	**2s**	
Empirical formula	C11 H13 F2 I O2	
Formula weight	342.11	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Pn	
Unit cell dimensions	a = 8.0439(15) Å	a= 90°.
	b = 6.9280(13) Å	b= 100.98(2)°.
	c = 11.632(3) Å	g = 90°.
Volume	636.4(2) $Å^3$	
Z	2	
Density (calculated)	1.785 Mg/m^3	
Absorption coefficient	2.525 mm^{-1}	
F(000)	332	
Crystal size	0.250 x 0.250 x 0.230 mm^3	
Theta range for data collection	2.843 to 25.470°.	
Index ranges	-7<=h<=9, -8<=k<=8, -11<=l<=14	
Reflections collected	2098	
Independent reflections	1346 [R(int) = 0.0265]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.14899	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1346 / 2 / 148	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1472	
R indices (all data)	R1 = 0.0568, wR2 = 0.1579	
Absolute structure parameter	-0.10(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.036 and -1.176 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for the compound **2s**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4760(20)	2449(18)	4599(11)	49(3)
C(2)	4673(17)	680(18)	5164(12)	60(3)
C(3)	6028(18)	-60(20)	5917(16)	69(4)
C(4)	7553(16)	944(19)	6165(11)	52(3)
C(5)	7688(18)	2690(20)	5610(13)	53(3)
C(6)	6320(30)	3400(30)	4894(17)	53(4)
C(7)	3270(30)	3230(20)	3803(15)	50(4)
C(8)	2361(14)	4867(17)	4258(10)	50(3)
C(9)	926(16)	5790(20)	3411(11)	57(3)
C(10)	-460(20)	4360(20)	2855(14)	72(4)
C(11)	10415(19)	1110(20)	7283(14)	67(4)
O(1)	8835(12)	99(15)	6937(9)	62(2)
O(2)	3666(13)	3935(13)	2692(8)	58(2)
F(1)	3512(10)	6244(11)	4720(8)	64(2)
F(2)	1784(10)	4118(12)	5208(6)	62(2)
I(1)	-215(1)	8029(1)	4314(1)	78(1)



2s

Table S3. Bond lengths [Å] and angles [°] for the compound **2s**.

C(1)-C(2)	1.399(18)
C(1)-C(6)	1.40(2)
C(1)-C(7)	1.47(3)
C(2)-C(3)	1.361(19)
C(2)-H(8)	0.9500
C(3)-C(4)	1.391(18)
C(3)-H(9)	0.9500
C(4)-O(1)	1.364(15)
C(4)-C(5)	1.39(2)
C(5)-C(6)	1.34(3)
C(5)-H(10)	0.9500
C(6)-H(11)	0.9500
C(7)-O(2)	1.47(2)
C(7)-C(8)	1.50(2)
C(7)-H(7)	1.0000
C(8)-F(1)	1.366(13)
C(8)-F(2)	1.379(14)
C(8)-C(9)	1.511(18)
C(9)-C(10)	1.54(2)
C(9)-I(1)	2.171(14)
C(9)-H(13)	1.0000
C(10)-H(1)	0.9800
C(10)-H(2)	0.9800
C(10)-H(3)	0.9800
C(11)-O(1)	1.439(17)
C(11)-H(4)	0.9800
C(11)-H(5)	0.9800
C(11)-H(6)	0.9800
O(2)-H(12)	0.8400
C(2)-C(1)-C(6)	114.9(14)
C(2)-C(1)-C(7)	120.7(13)
C(6)-C(1)-C(7)	124.4(12)
C(3)-C(2)-C(1)	121.7(13)

C(3)-C(2)-H(8)	119.1
C(1)-C(2)-H(8)	119.1
C(2)-C(3)-C(4)	120.8(13)
C(2)-C(3)-H(9)	119.6
C(4)-C(3)-H(9)	119.6
O(1)-C(4)-C(5)	124.4(11)
O(1)-C(4)-C(3)	116.7(11)
C(5)-C(4)-C(3)	118.9(12)
C(6)-C(5)-C(4)	119.0(14)
C(6)-C(5)-H(10)	120.5
C(4)-C(5)-H(10)	120.5
C(5)-C(6)-C(1)	124.6(17)
C(5)-C(6)-H(11)	117.7
C(1)-C(6)-H(11)	117.7
O(2)-C(7)-C(1)	112.7(16)
O(2)-C(7)-C(8)	105.2(11)
C(1)-C(7)-C(8)	116.8(14)
O(2)-C(7)-H(7)	107.2
C(1)-C(7)-H(7)	107.2
C(8)-C(7)-H(7)	107.2
F(1)-C(8)-F(2)	104.7(9)
F(1)-C(8)-C(7)	109.1(12)
F(2)-C(8)-C(7)	105.1(11)
F(1)-C(8)-C(9)	109.6(10)
F(2)-C(8)-C(9)	110.5(9)
C(7)-C(8)-C(9)	117.0(12)
C(8)-C(9)-C(10)	113.7(11)
C(8)-C(9)-I(1)	109.2(8)
C(10)-C(9)-I(1)	109.0(9)
C(8)-C(9)-H(13)	108.3
C(10)-C(9)-H(13)	108.3
I(1)-C(9)-H(13)	108.3
C(9)-C(10)-H(1)	109.5
C(9)-C(10)-H(2)	109.5
H(1)-C(10)-H(2)	109.5
C(9)-C(10)-H(3)	109.5

H(1)-C(10)-H(3)	109.5
H(2)-C(10)-H(3)	109.5
O(1)-C(11)-H(4)	109.5
O(1)-C(11)-H(5)	109.5
H(4)-C(11)-H(5)	109.5
O(1)-C(11)-H(6)	109.5
H(4)-C(11)-H(6)	109.5
H(5)-C(11)-H(6)	109.5
C(4)-O(1)-C(11)	119.5(11)
C(7)-O(2)-H(12)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for the compound **2s**. The anisotropic

displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	43(6)	45(5)	60(8)	-2(5)	17(7)	-3(6)
C(2)	41(6)	50(6)	77(8)	5(6)	-14(6)	-17(5)
C(3)	52(8)	57(7)	93(10)	26(8)	3(8)	-11(7)
C(4)	41(6)	55(7)	59(6)	3(6)	8(5)	-6(5)
C(5)	39(6)	51(6)	75(8)	3(6)	22(6)	-6(5)
C(6)	40(10)	48(7)	71(10)	-7(7)	12(8)	-4(7)
C(7)	43(10)	50(8)	54(9)	3(6)	4(8)	0(6)
C(8)	39(6)	54(6)	56(6)	0(6)	8(5)	-14(5)
C(9)	42(6)	73(8)	59(6)	9(6)	15(5)	8(6)
C(10)	53(8)	79(9)	78(9)	-14(8)	-5(7)	15(7)
C(11)	41(7)	74(8)	79(8)	11(8)	-9(6)	-5(7)
O(1)	43(5)	59(5)	77(6)	14(5)	-1(4)	-1(4)
O(2)	69(6)	45(4)	65(5)	7(4)	23(5)	2(4)
F(1)	44(4)	49(4)	97(5)	-13(4)	7(4)	-1(3)
F(2)	54(4)	72(5)	62(4)	6(4)	17(4)	2(4)
I(1)	49(1)	70(1)	112(1)	-16(1)	11(1)	10(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for the compound **2s.**

	x	y	z	U(eq)
H(8)	3641	-24	5019	72
H(9)	5930	-1272	6278	83
H(10)	8732	3372	5736	64
H(11)	6422	4641	4562	63
H(7)	2438	2152	3609	59
H(13)	1406	6412	2769	69
H(1)	72	3201	2602	108
H(2)	-1181	4963	2177	108
H(3)	-1146	4001	3432	108
H(4)	10969	1242	6606	101
H(5)	11152	381	7901	101
H(6)	10199	2393	7577	101
H(12)	3986	5090	2770	87

Table S6. Torsion angles [°] for the compound **2s**.

C(6)-C(1)-C(2)-C(3)	-2(2)
C(7)-C(1)-C(2)-C(3)	-178.9(16)
C(1)-C(2)-C(3)-C(4)	1(3)
C(2)-C(3)-C(4)-O(1)	179.5(15)
C(2)-C(3)-C(4)-C(5)	-2(2)
O(1)-C(4)-C(5)-C(6)	-178.1(15)
C(3)-C(4)-C(5)-C(6)	3(2)
C(4)-C(5)-C(6)-C(1)	-4(3)
C(2)-C(1)-C(6)-C(5)	3(3)
C(7)-C(1)-C(6)-C(5)	-179.5(14)
C(2)-C(1)-C(7)-O(2)	-133.3(13)
C(6)-C(1)-C(7)-O(2)	50(2)
C(2)-C(1)-C(7)-C(8)	104.7(16)
C(6)-C(1)-C(7)-C(8)	-72(2)
O(2)-C(7)-C(8)-F(1)	-76.3(15)
C(1)-C(7)-C(8)-F(1)	49.5(17)
O(2)-C(7)-C(8)-F(2)	171.9(11)
C(1)-C(7)-C(8)-F(2)	-62.3(17)
O(2)-C(7)-C(8)-C(9)	48.9(17)
C(1)-C(7)-C(8)-C(9)	174.7(13)
F(1)-C(8)-C(9)-C(10)	-179.1(11)
F(2)-C(8)-C(9)-C(10)	-64.2(14)
C(7)-C(8)-C(9)-C(10)	56.0(16)
F(1)-C(8)-C(9)-I(1)	-57.2(11)
F(2)-C(8)-C(9)-I(1)	57.7(11)
C(7)-C(8)-C(9)-I(1)	177.9(11)
C(5)-C(4)-O(1)-C(11)	5(2)
C(3)-C(4)-O(1)-C(11)	-176.5(15)

Symmetry transformations used to generate equivalent atoms:

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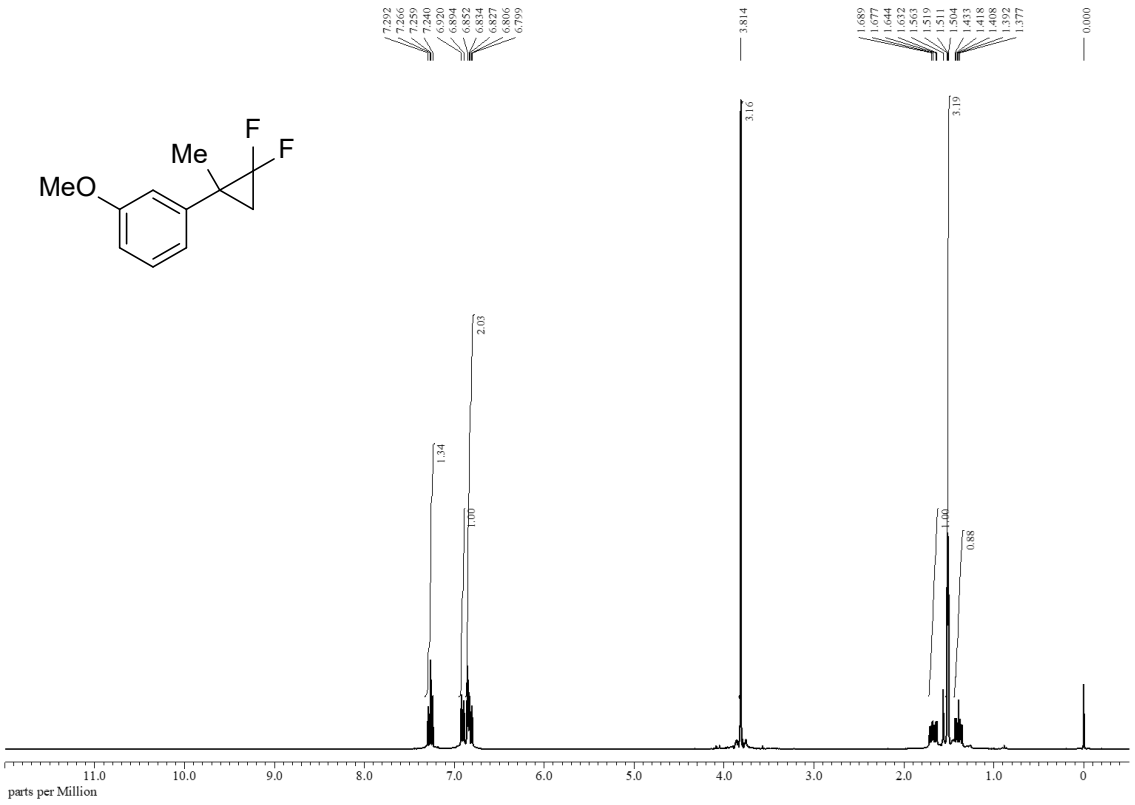
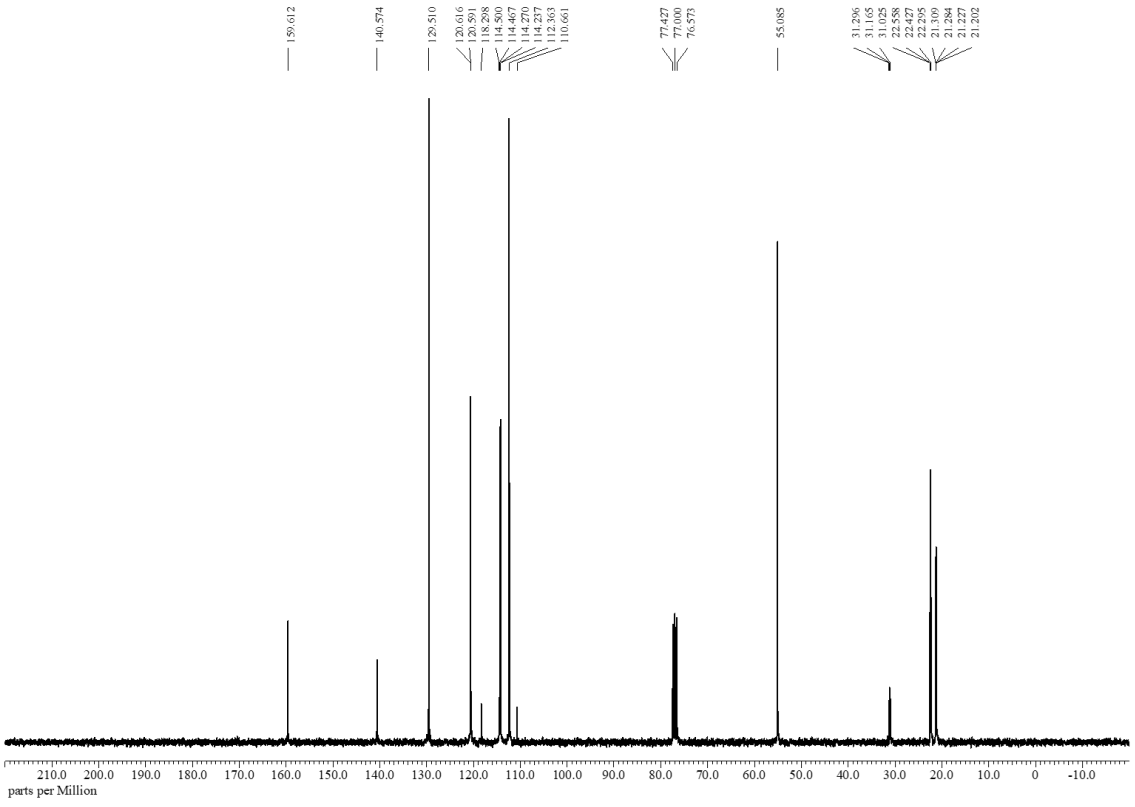
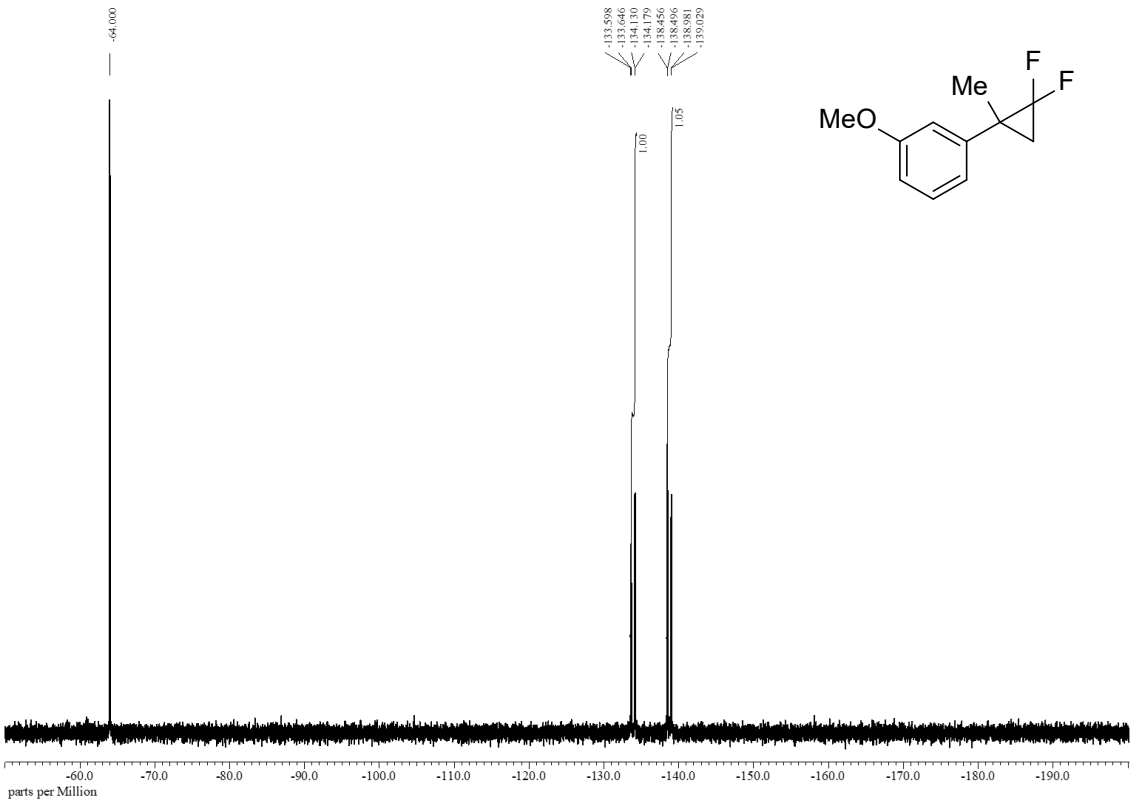
NMR spectra of the substrates.

^{1}H and ^{13}C NMR spectra of 1-(2,2-difluoro-1-methylcycloprop-1-yl)-3-methoxybenzene (**1k**)

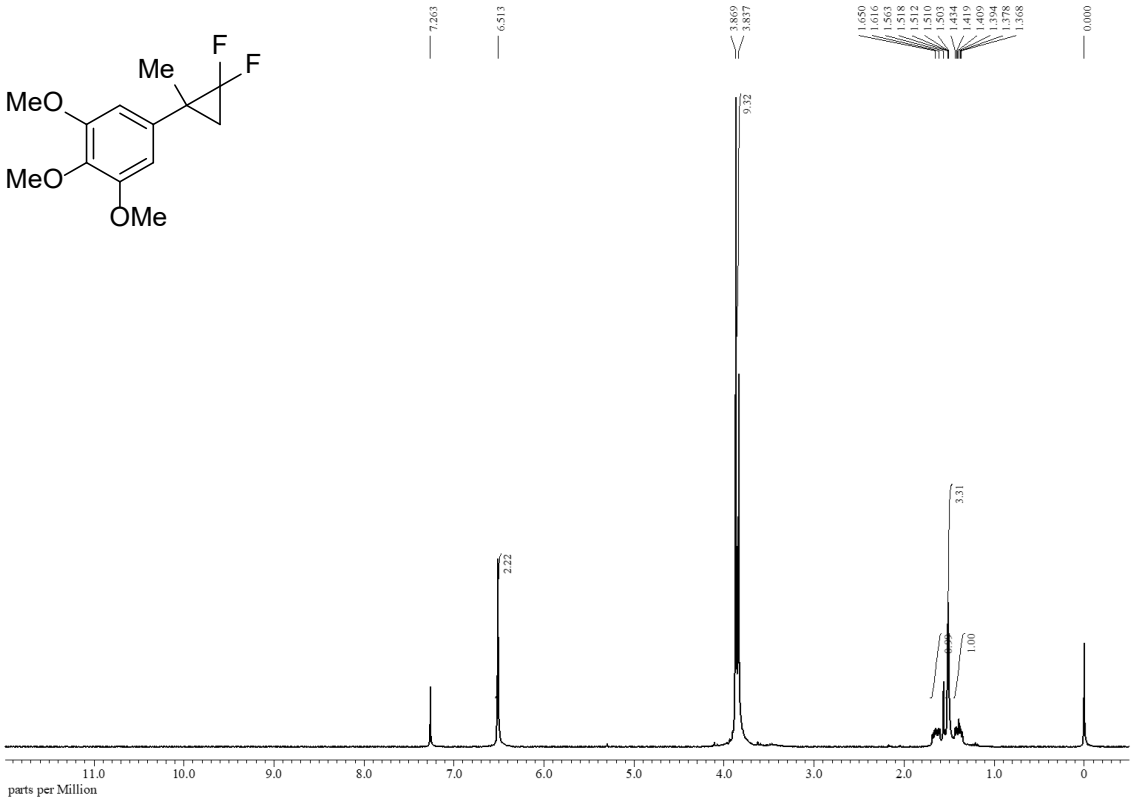


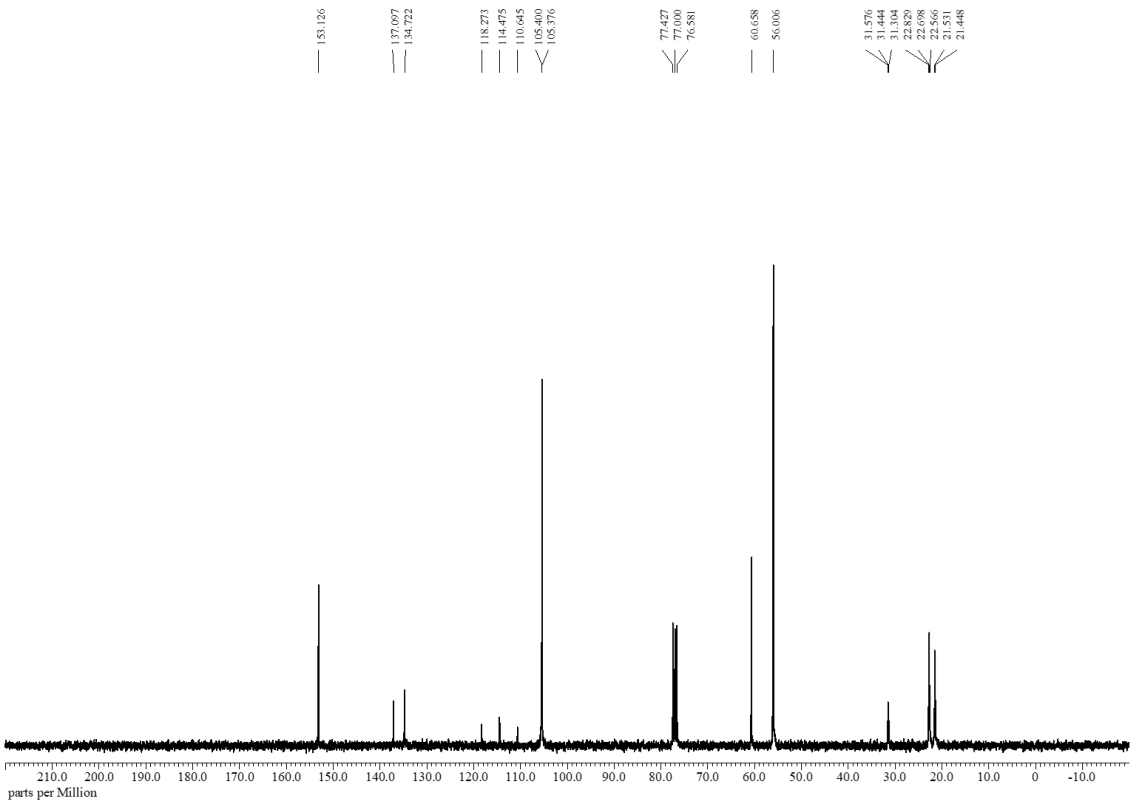


^{19}F NMR spectrum of 1-(2,2-difluoro-1-methylcycloprop-1-yl)-3-methoxybenzene (**1k**)

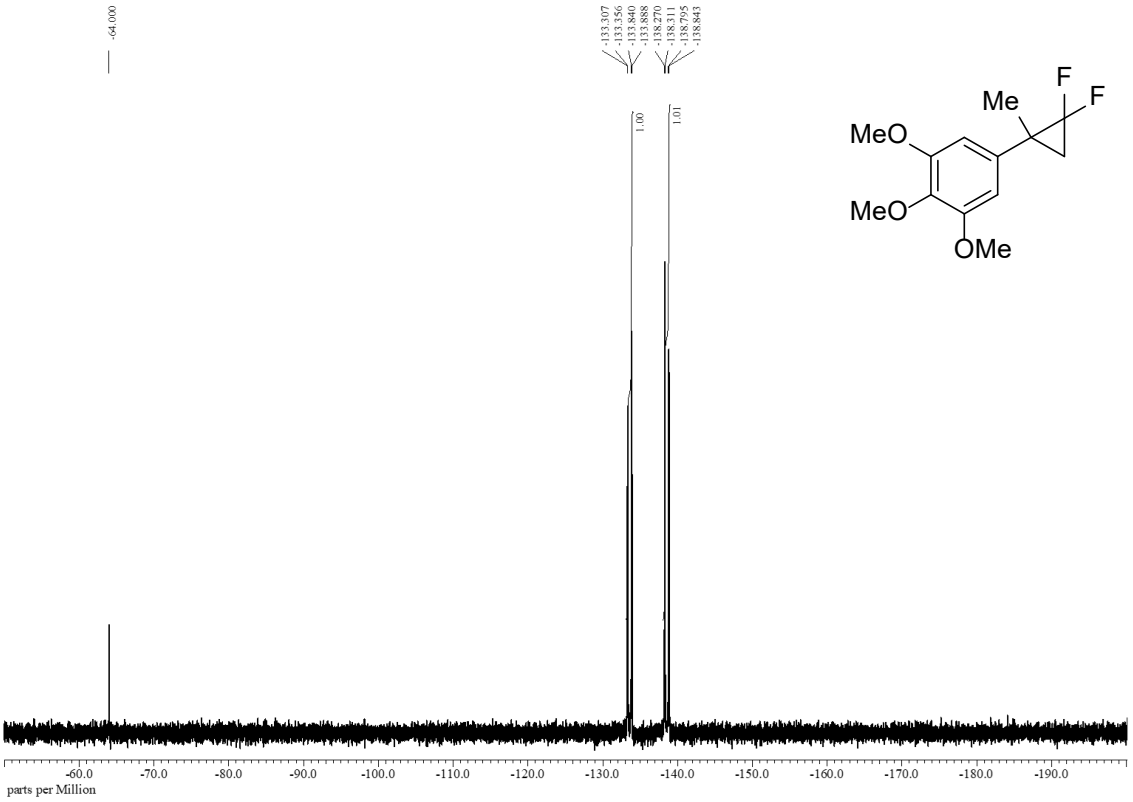


^{1}H and ^{13}C NMR spectra of 1-(2,2-difluoro-1-methylcycloprop-1-yl)-3,4,5-trimethoxybenzene (**1m**)

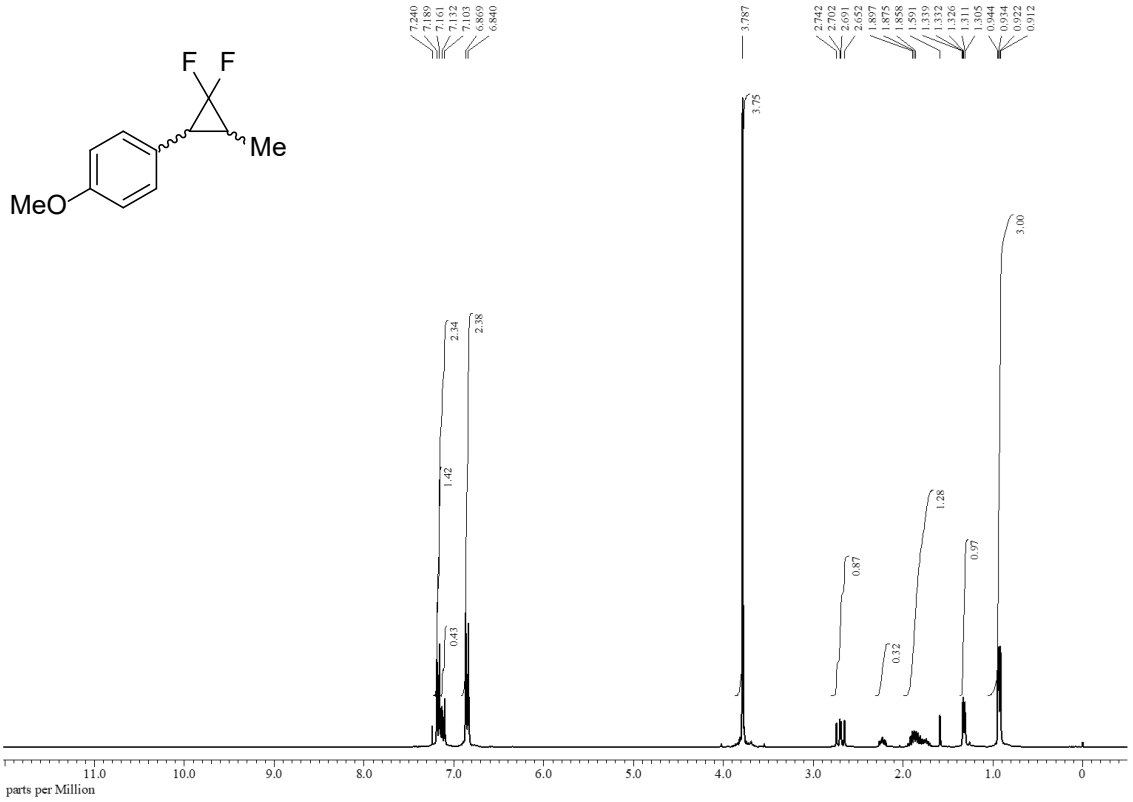


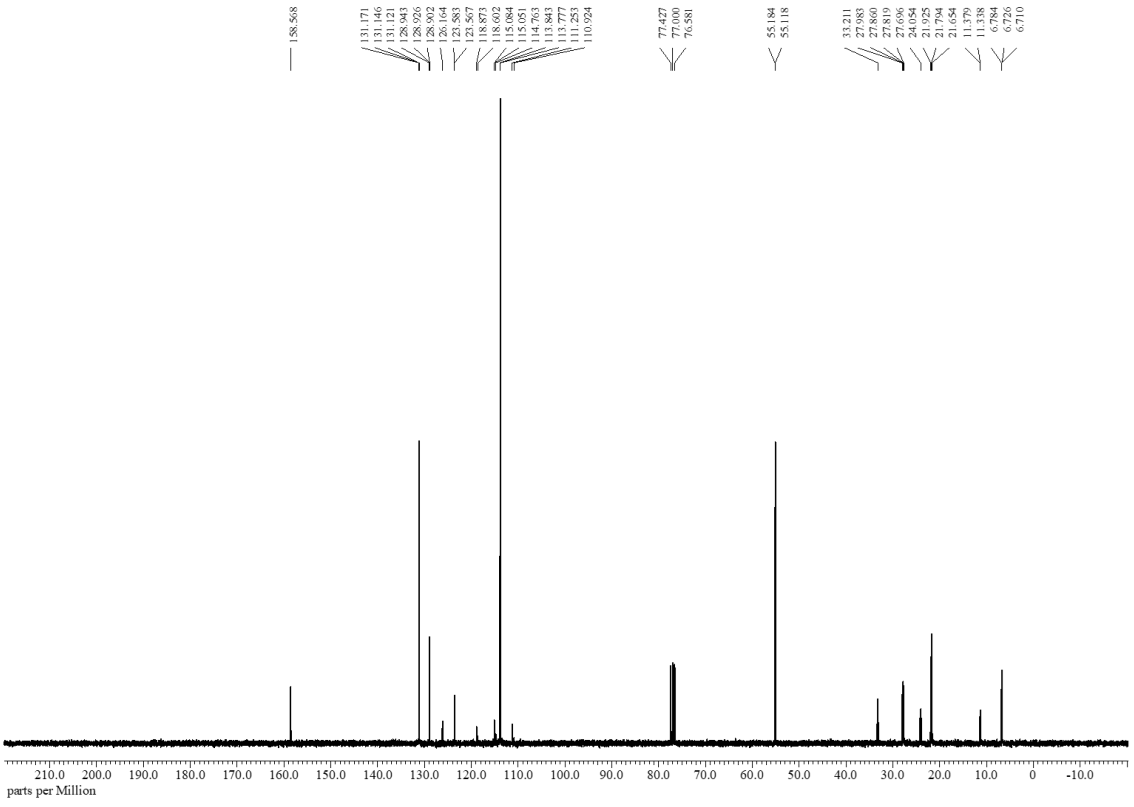


^{19}F NMR spectrum of 1-(2,2-difluoro-1-methylcycloprop-1-yl)-3,4,5-trimethoxybenzene (**1m**)

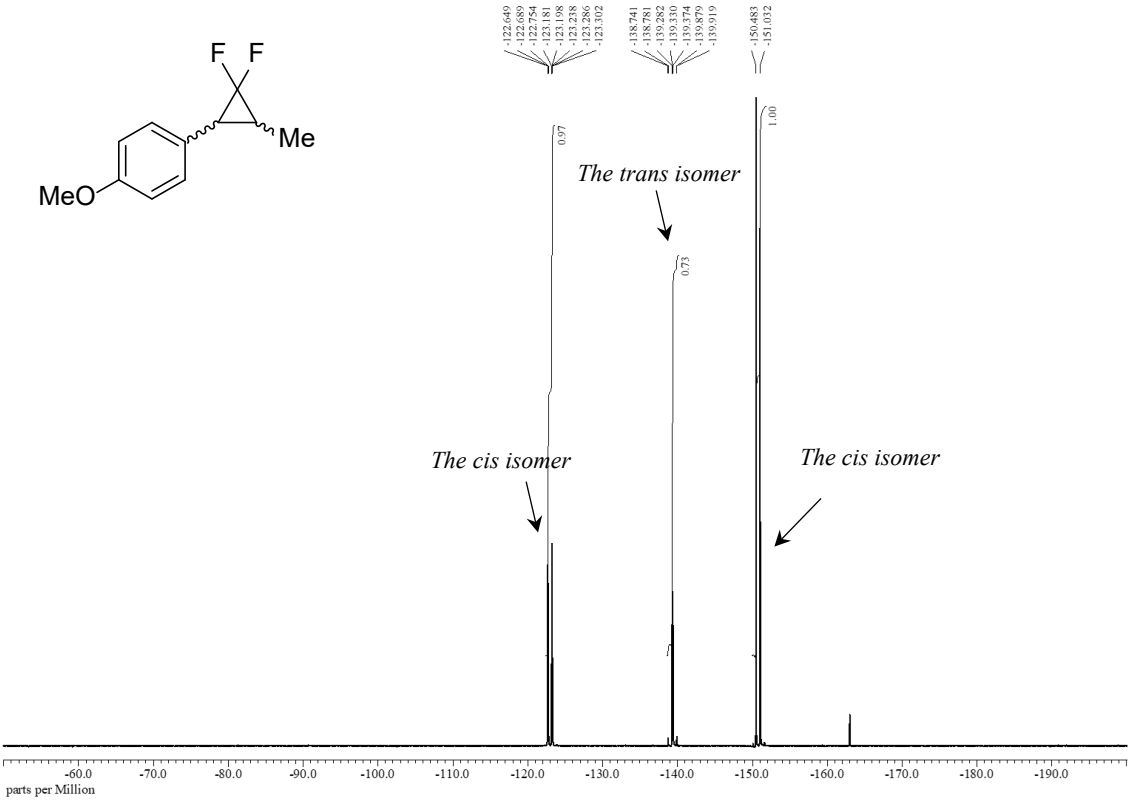


^{1}H and ^{13}C NMR spectra of (2,2-difluoro-3-methylcyclopropyl)-4-methoxybenzene (**1s**)

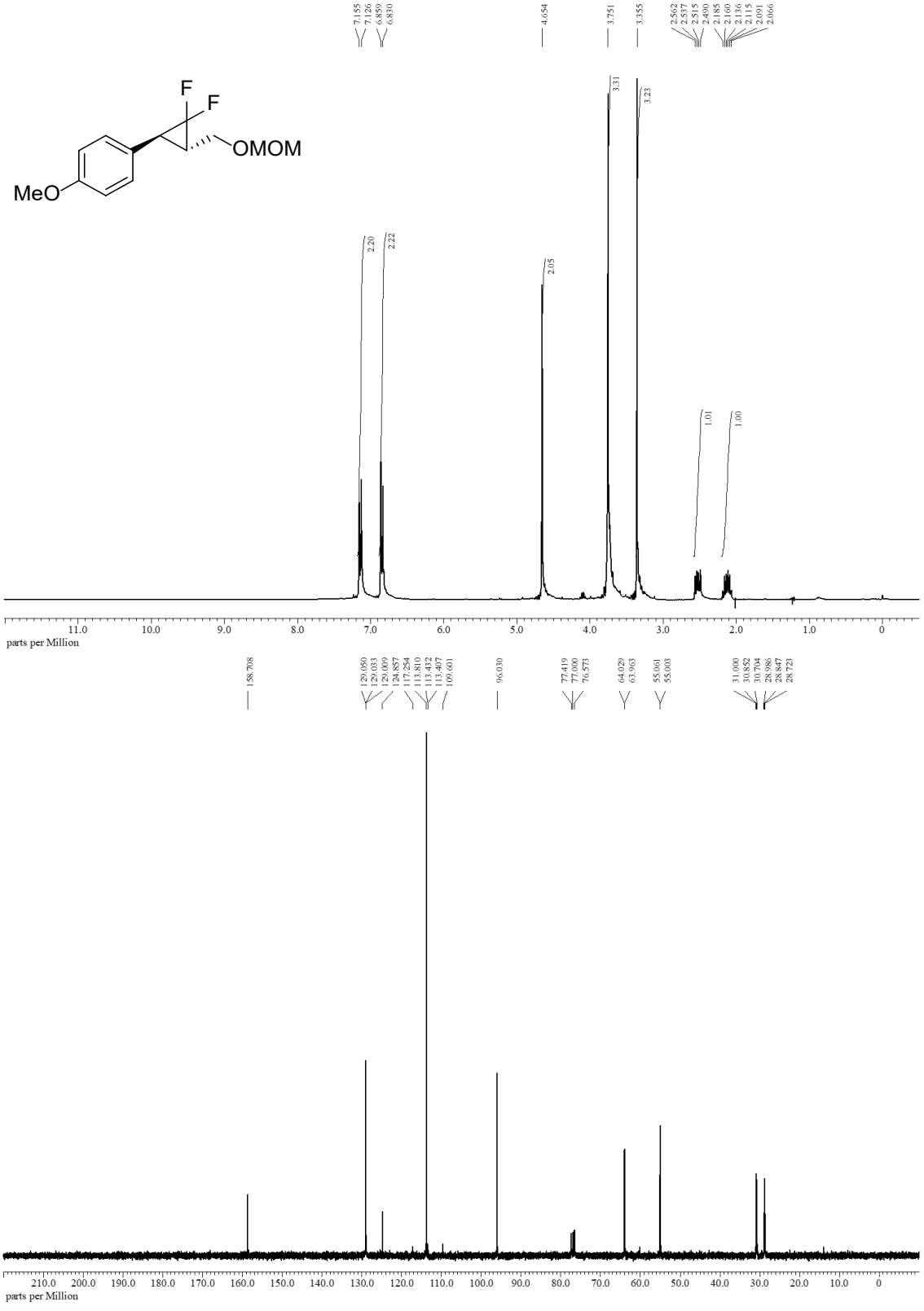




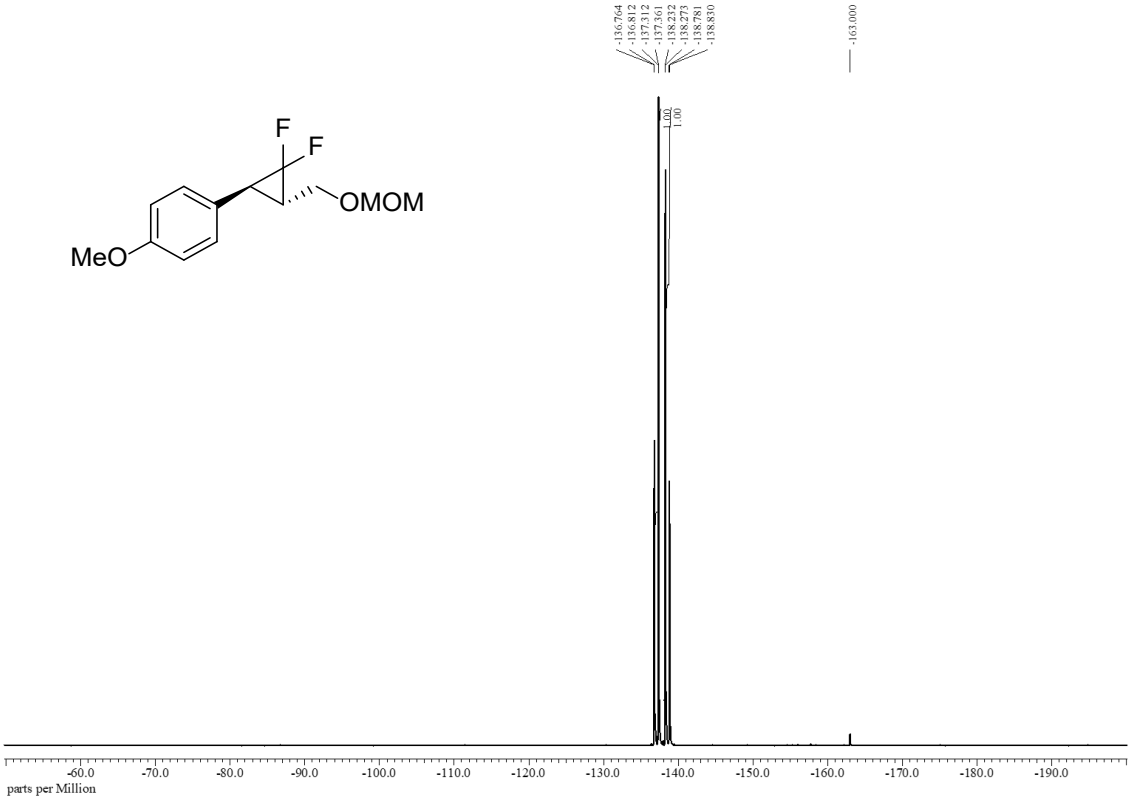
^{19}F NMR spectrum of (2,2-difluoro-3-methylcyclopropyl)-4-methoxybenzene (**1s**)



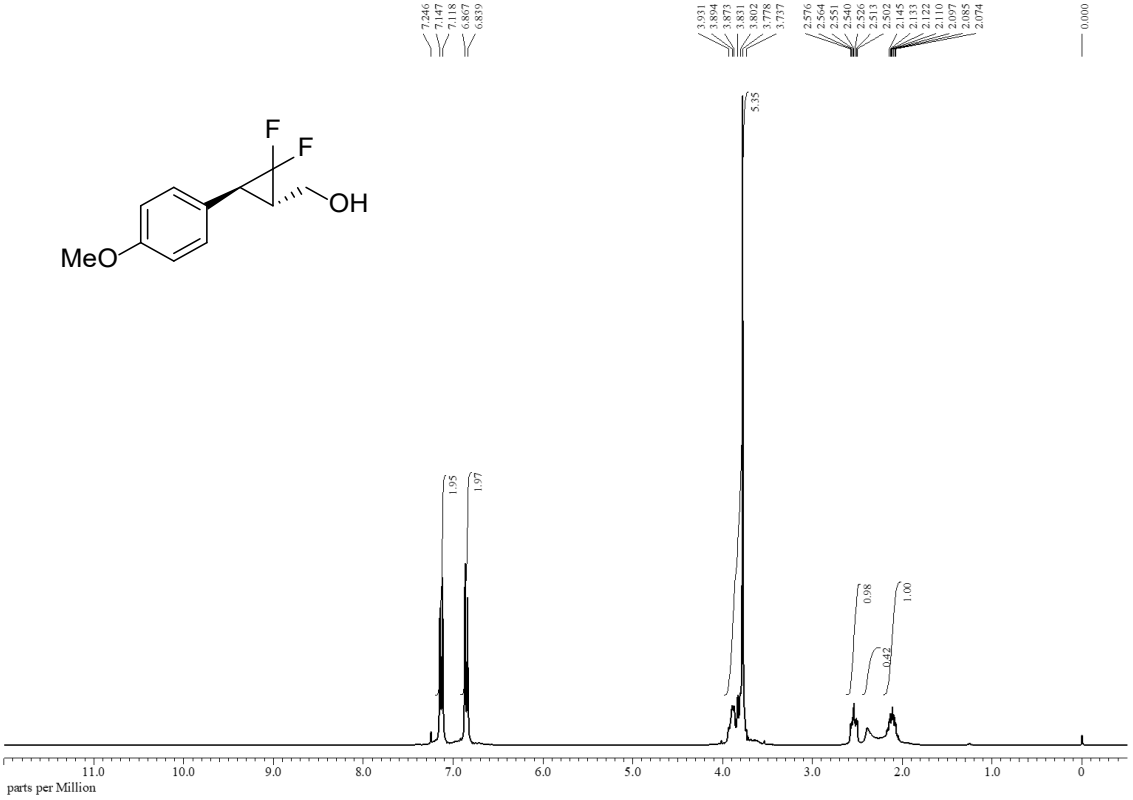
^{1}H and ^{13}C NMR spectra of *trans*-1-{2,2-difluoro-3-[(methoxymethoxy)methyl]cycloprop-1-yl}-4-methoxybenzene (pre-**1t**)

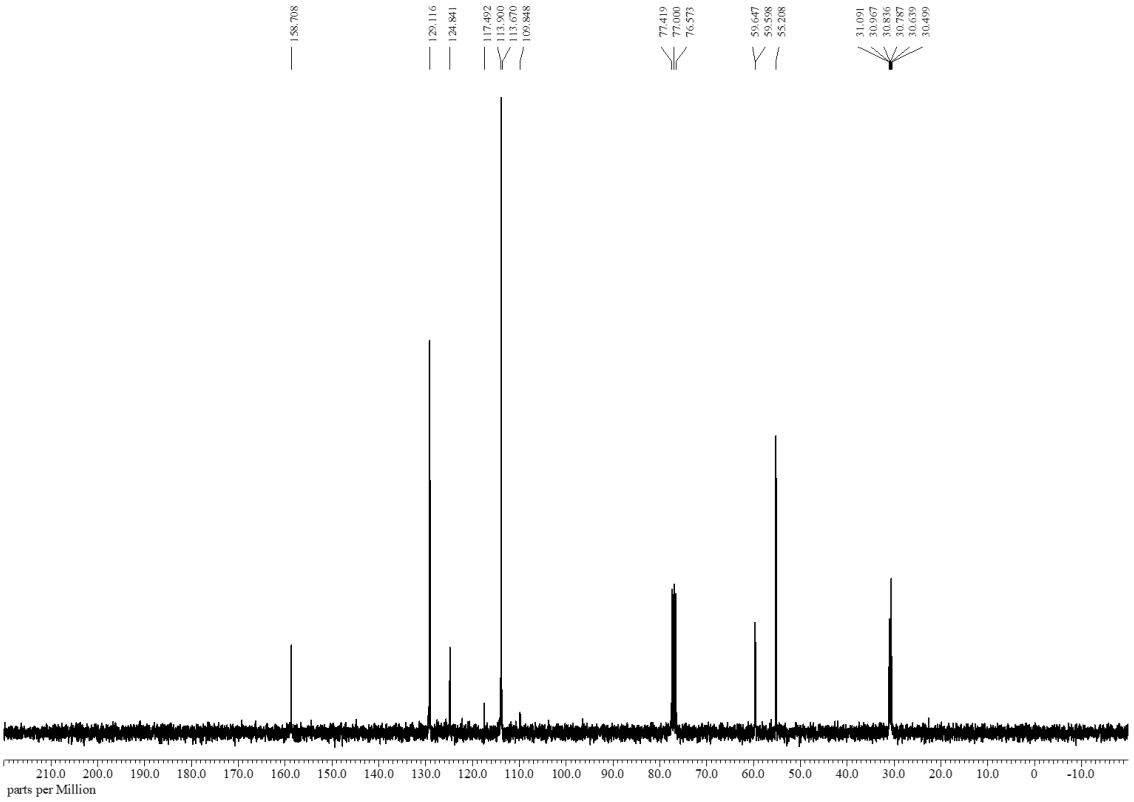


^{19}F NMR spectrum of *trans*-1-{2,2-difluoro-3-[(methoxymethoxy)methyl]cyclopropyl}-4-methoxybenzene (pre-**1t**)

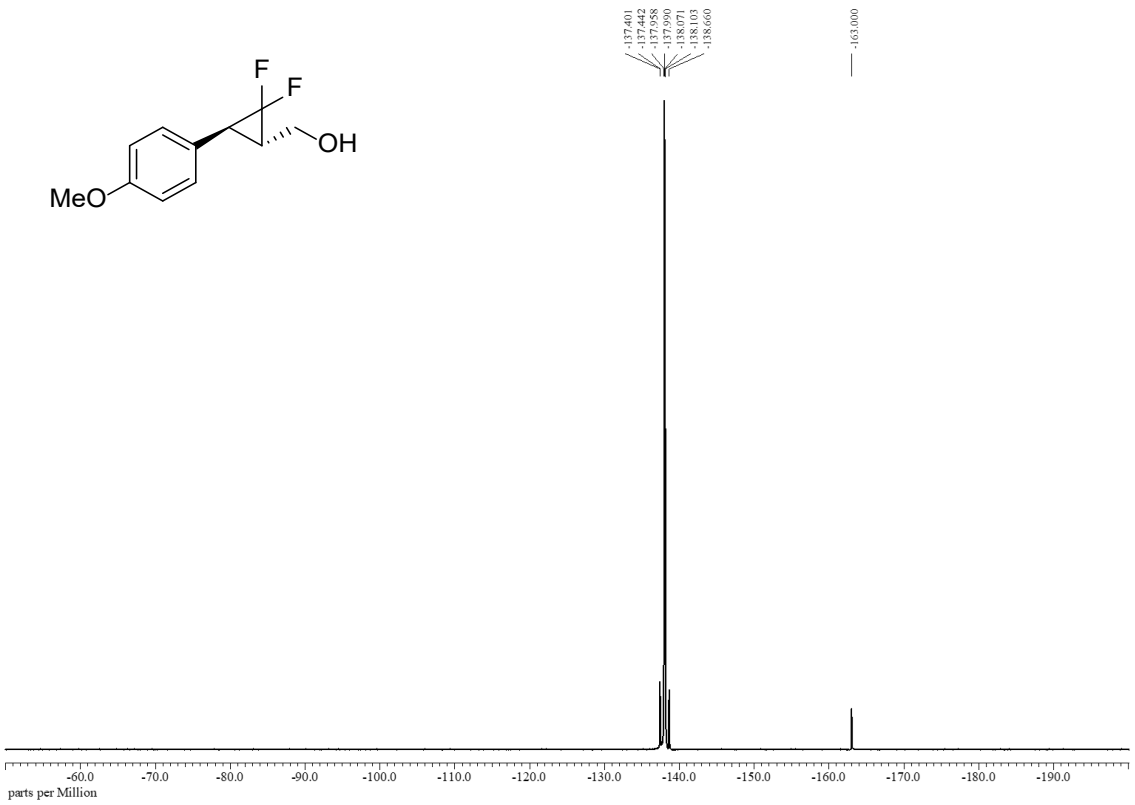


^{1}H and ^{13}C NMR spectra of *trans*-(2,2-difluoro-3-(4-methoxyphenyl)cyclopropyl)methanol (**1t**)



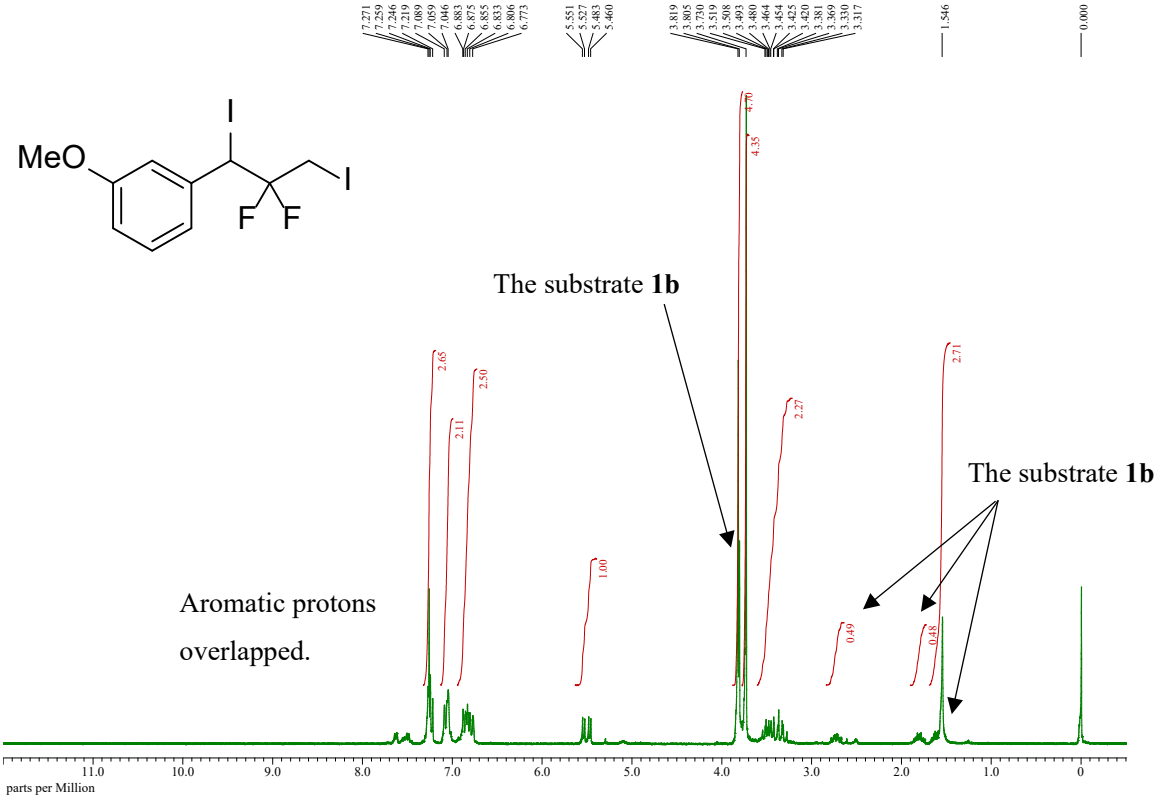


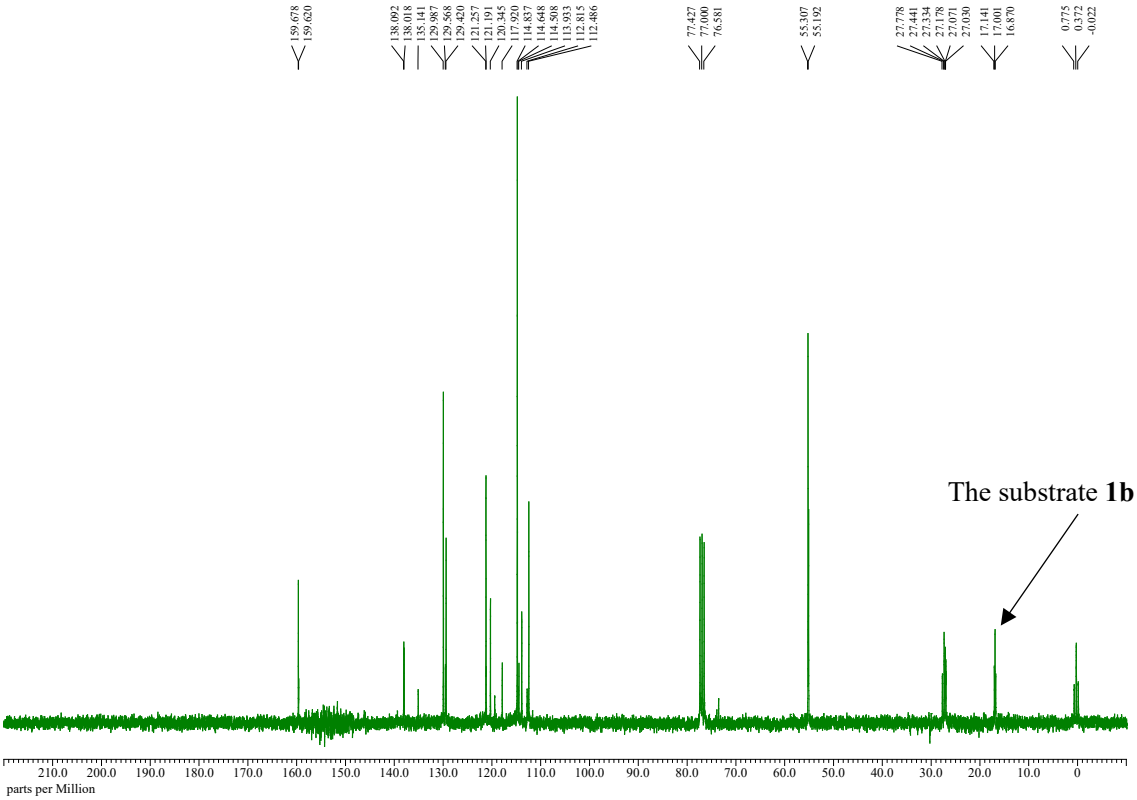
^{19}F NMR spectrum of *trans*-(2,2-difluoro-3-(4-methoxyphenyl)cyclopropyl)methanol (**1t**)



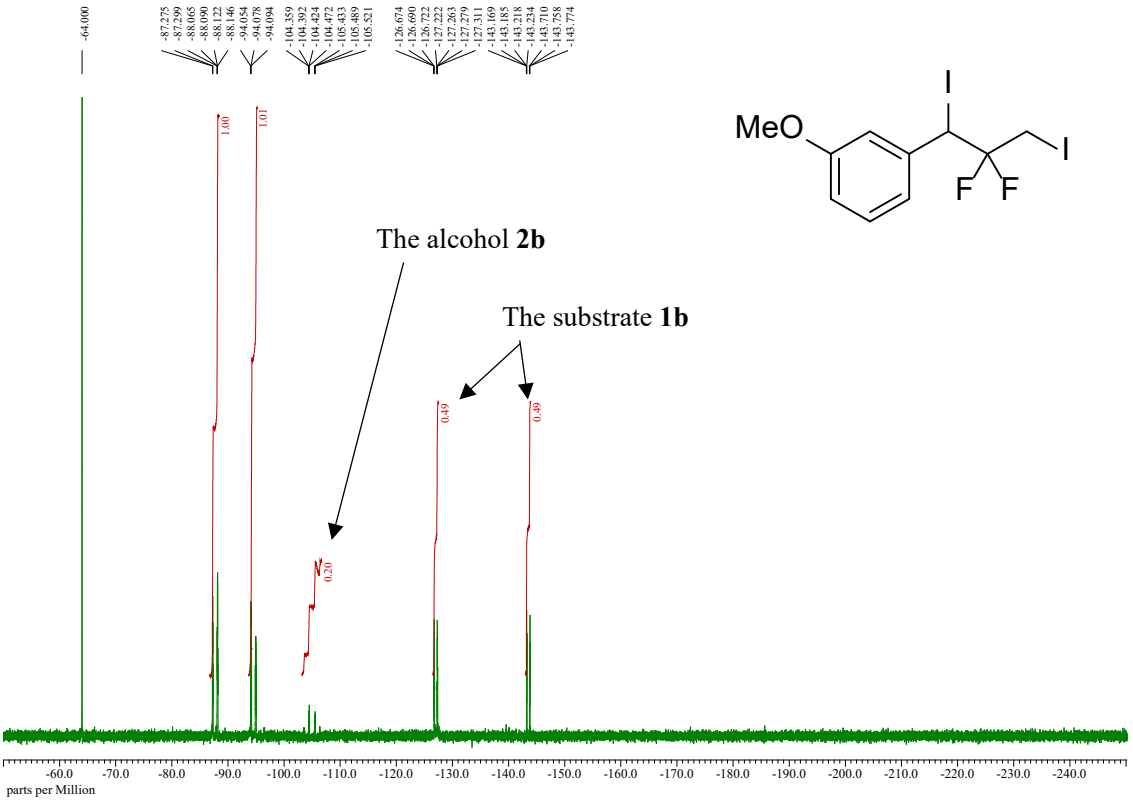
NMR spectra of the products.

^{1}H and ^{13}C NMR spectra of (2,2-difluoro-1,3-diiodoprop-1-yl)-3-methoxybenzene (**3b**)

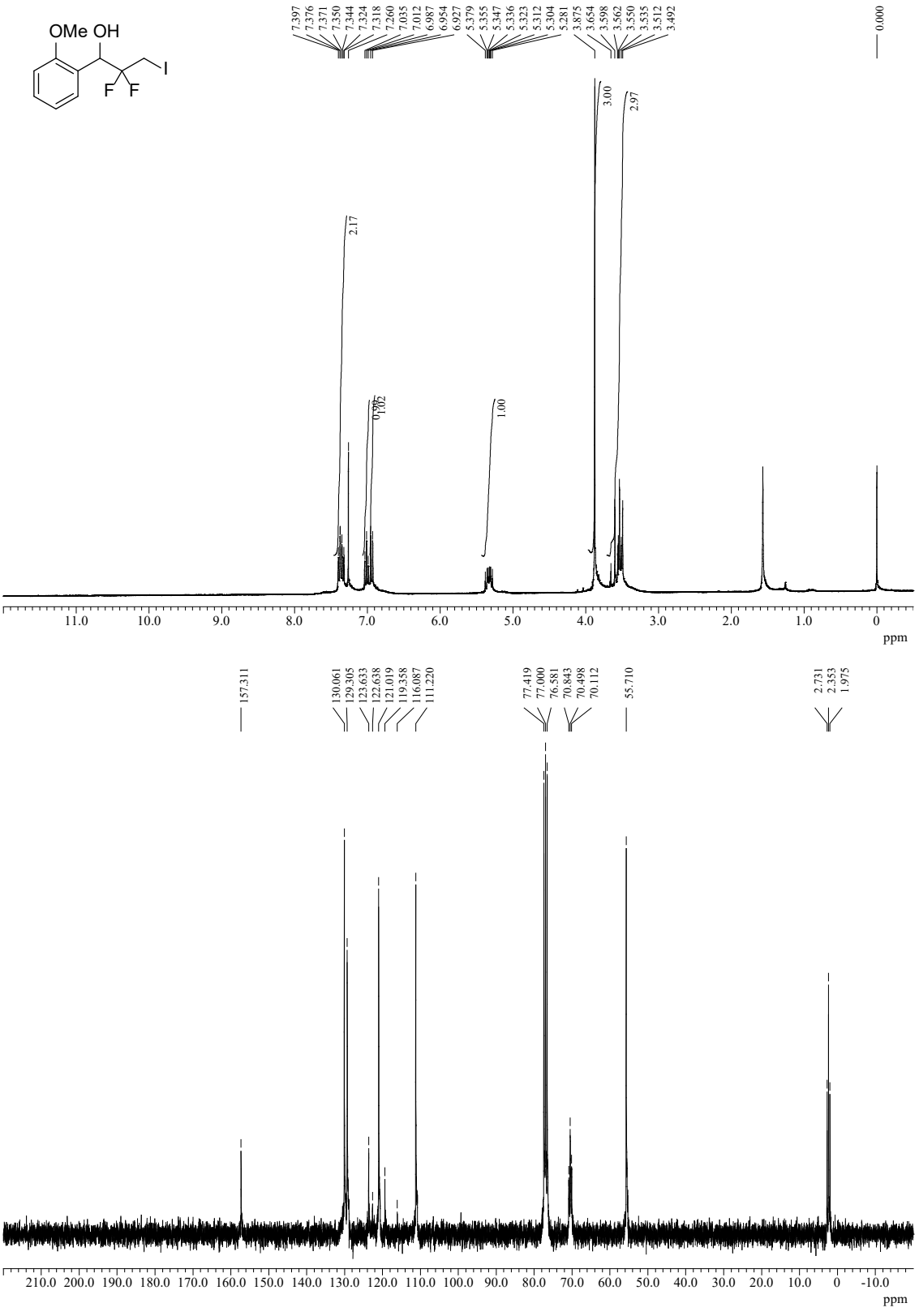




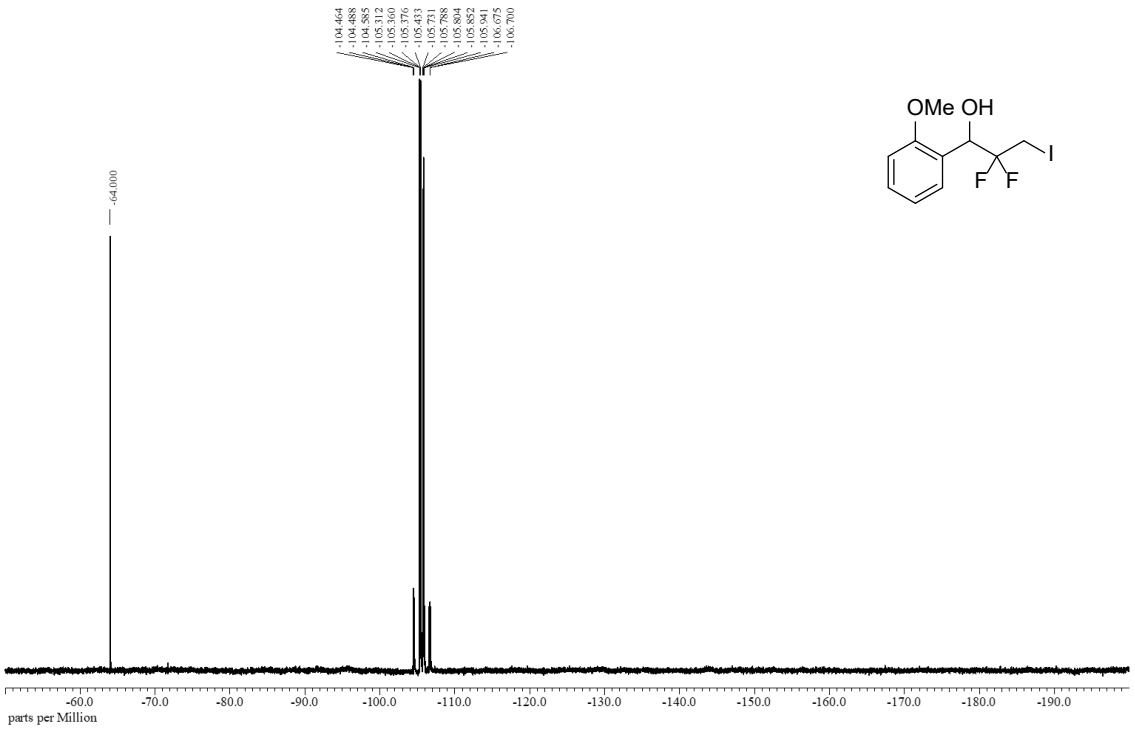
^{19}F NMR spectrum of (2,2-difluoro-1,3-diiodoprop-1-yl)-3-methoxybenzene (**3b**)



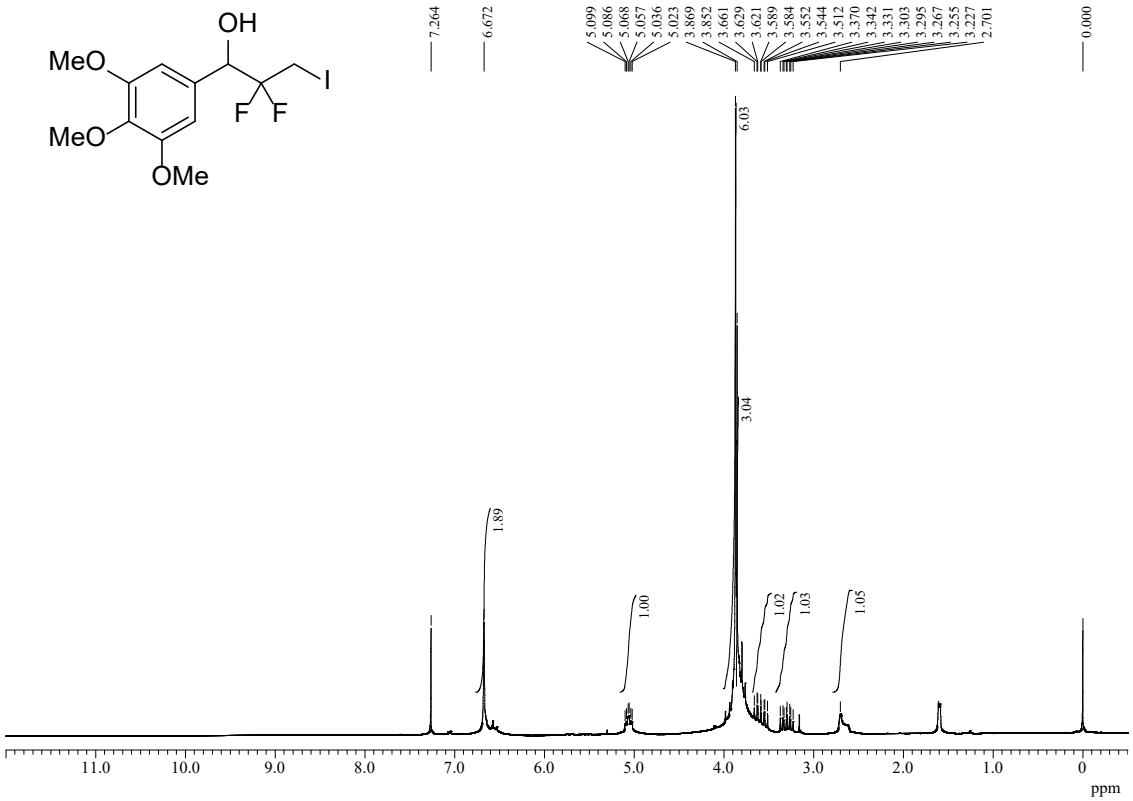
^{1}H and ^{13}C NMR spectra of 2,2-difluoro-3-iodo-1-(2-methoxyphenyl)propan-1-ol (**2c**)

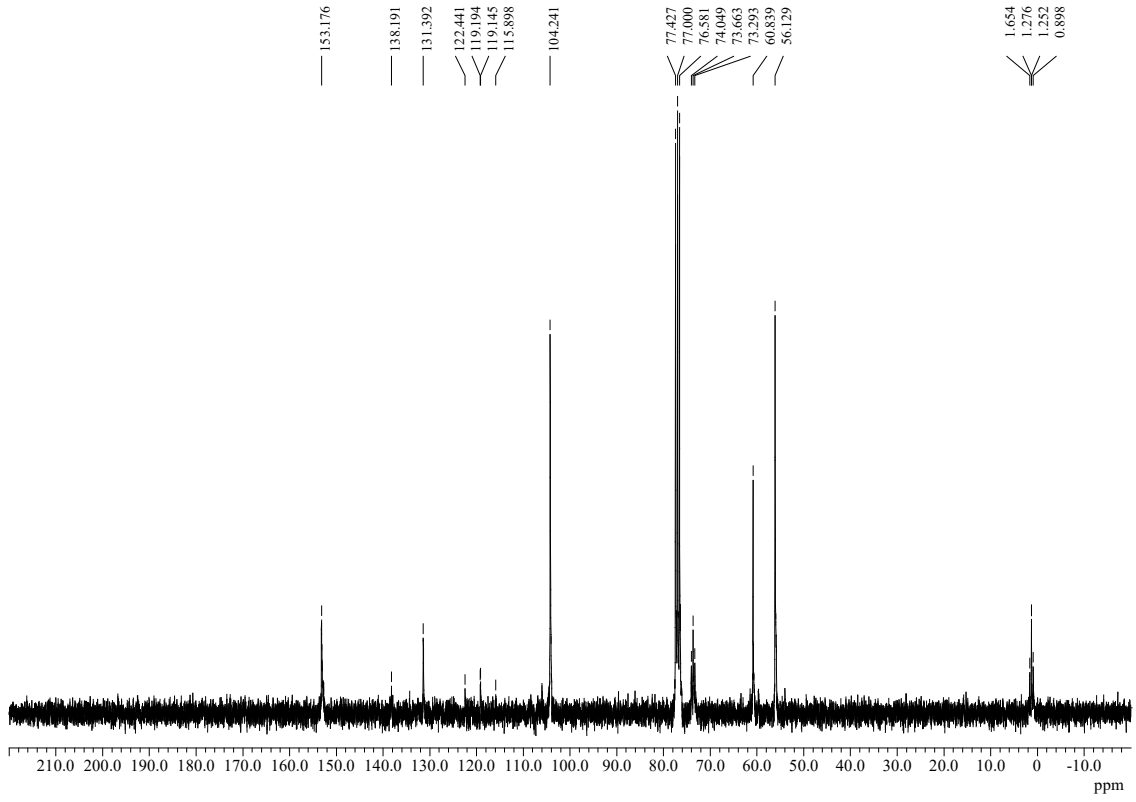


^{19}F NMR spectrum of 2,2-difluoro-3-iodo-1-(2-methoxyphenyl)propan-1-ol (**2c**)

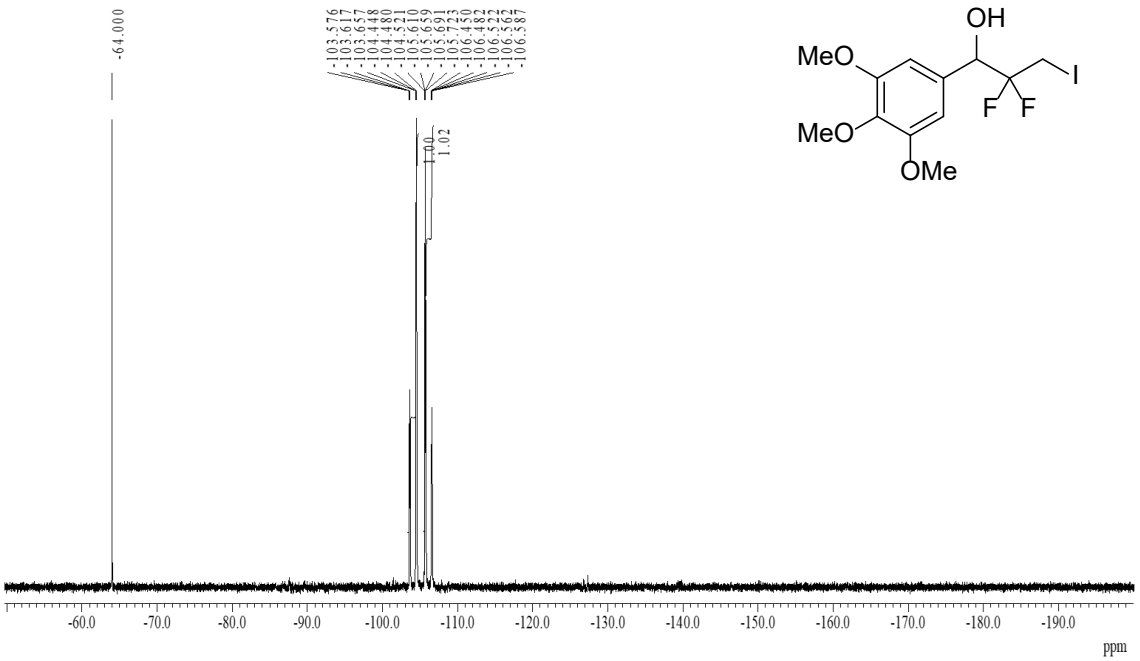


^{1}H and ^{13}C NMR spectra of 2,2-difluoro-3-iodo-1-(3,4,5-trimethoxyphenyl)propan-1-ol (**2d**)

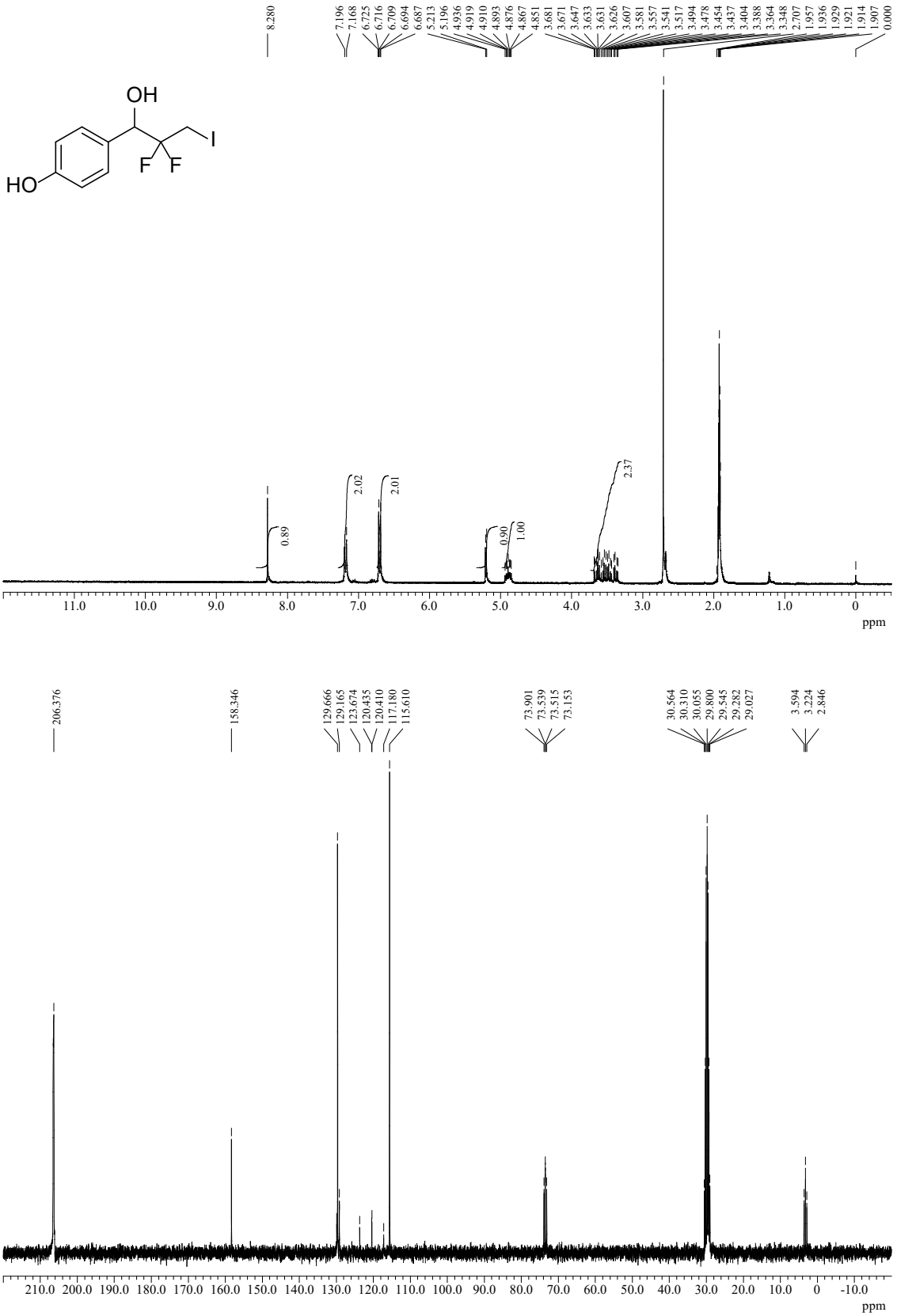




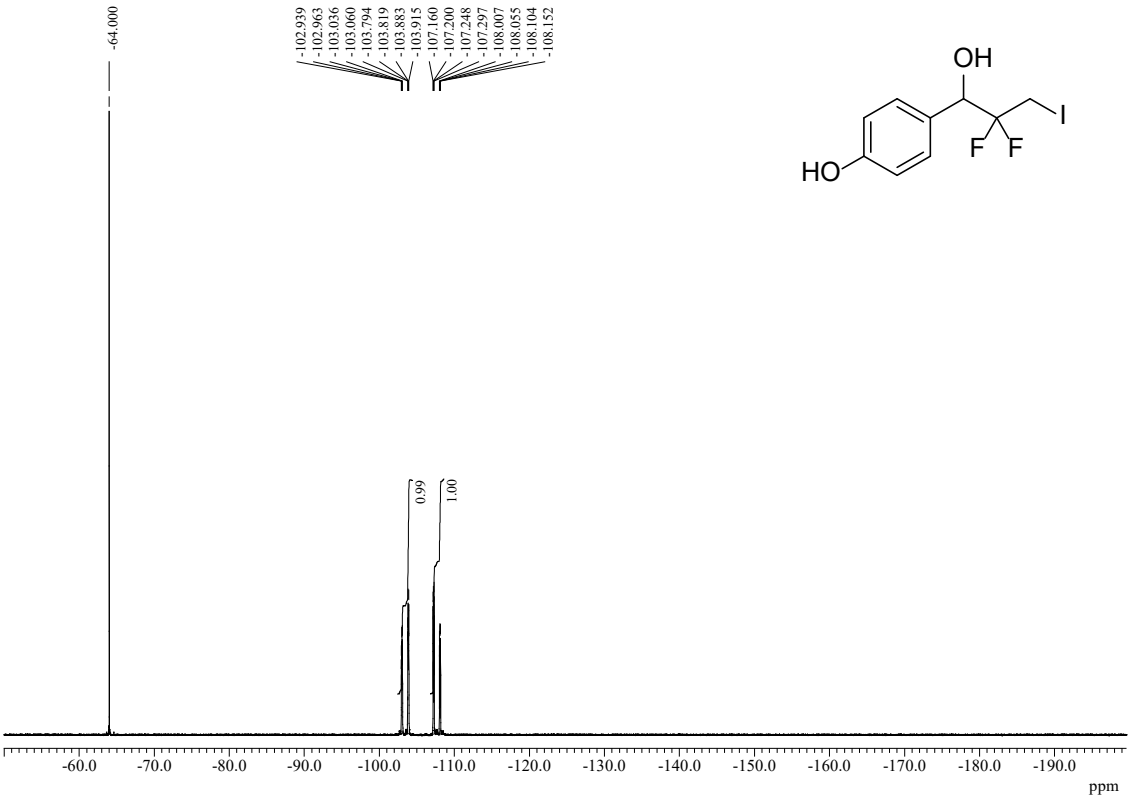
^{19}F NMR spectrum of 2,2-difluoro-3-iodo-1-(3,4,5-trimethoxyphenyl)propan-1-ol (**2d**)



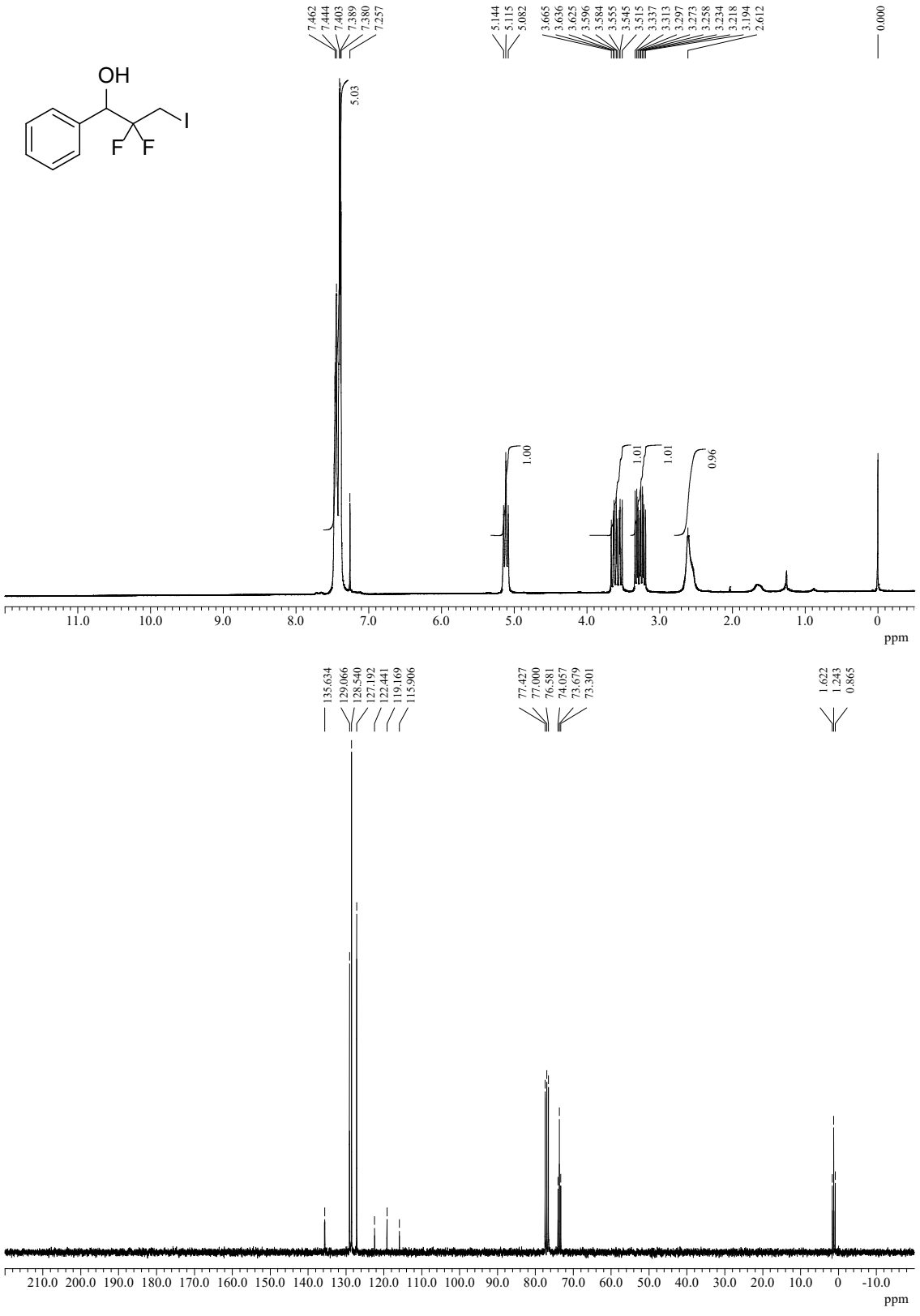
^{1}H and ^{13}C NMR spectra of 2,2-difluoro-3-iodo-1-(4-hydroxyphenyl)propan-1-ol (**2e**)



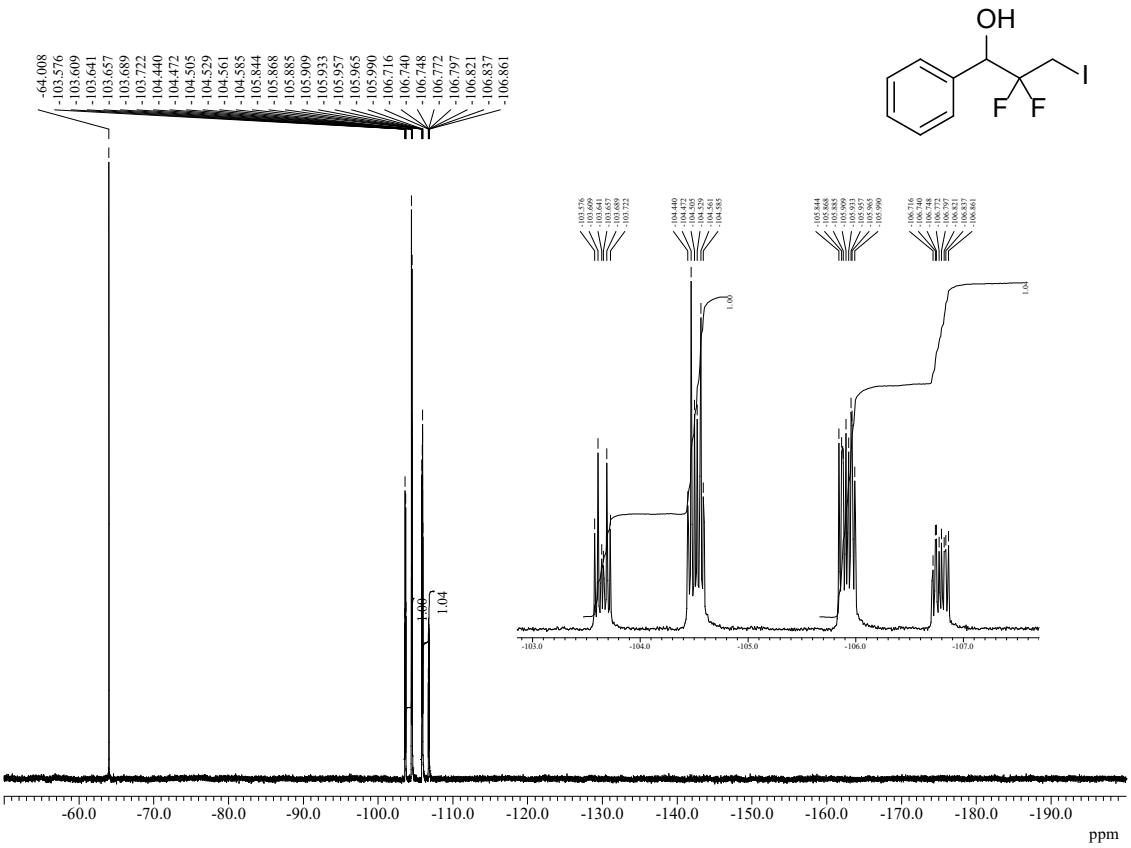
^{19}F NMR spectrum of 2,2-difluoro-3-iodo-1-(4-hydroxyphenyl)propan-1-ol (**2e**)



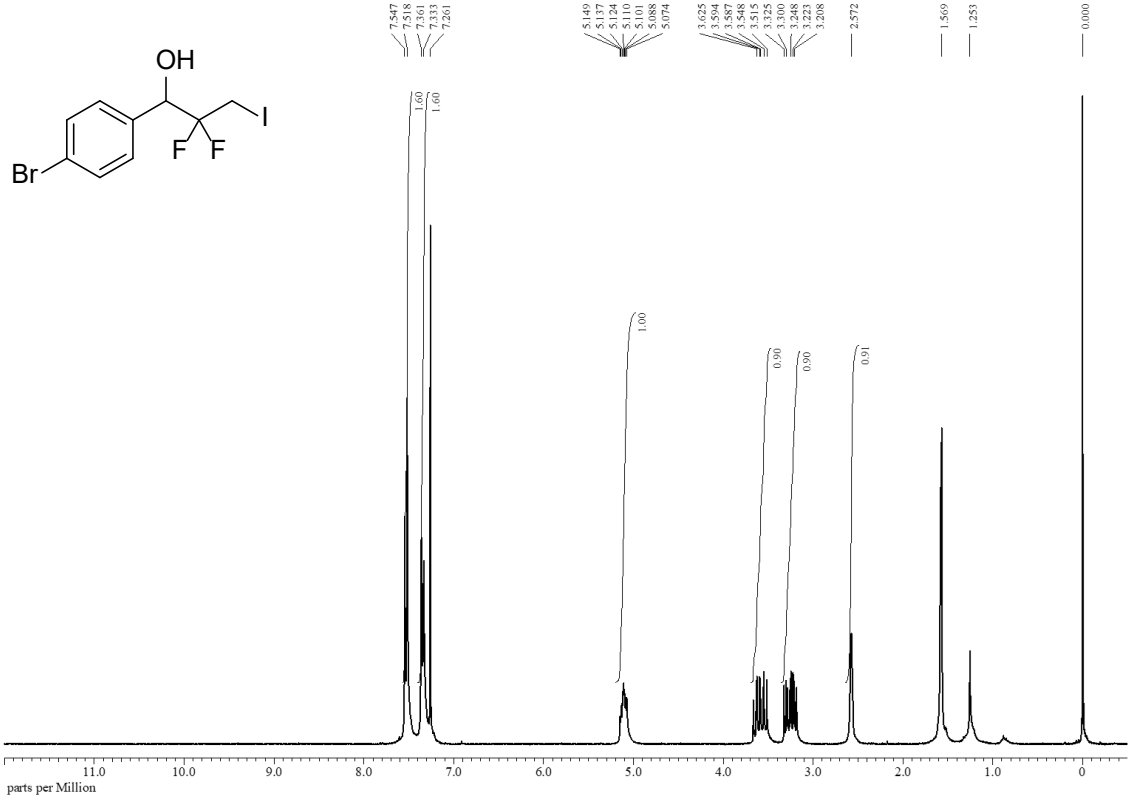
^{1}H and ^{13}C NMR spectra of 2,2-difluoro-3-iodo-1-phenylpropan-1-ol (**2g**)

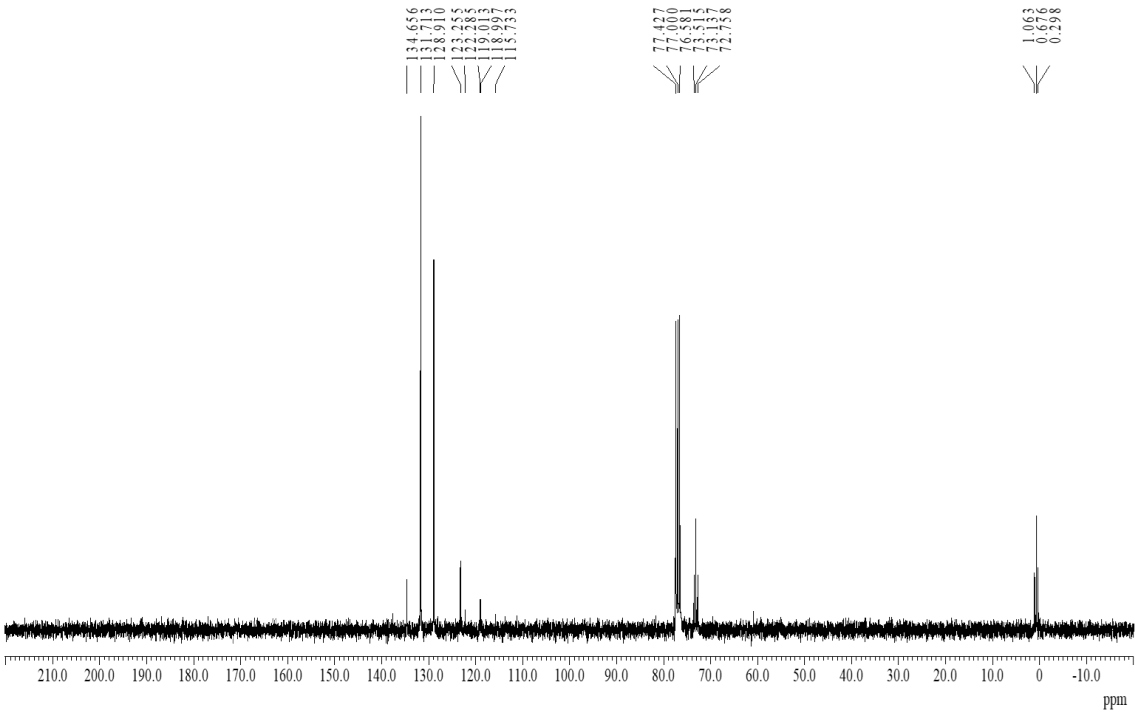


^{19}F NMR spectrum of 2,2-difluoro-3-iodo-1-phenylpropan-1-ol (**2g**)

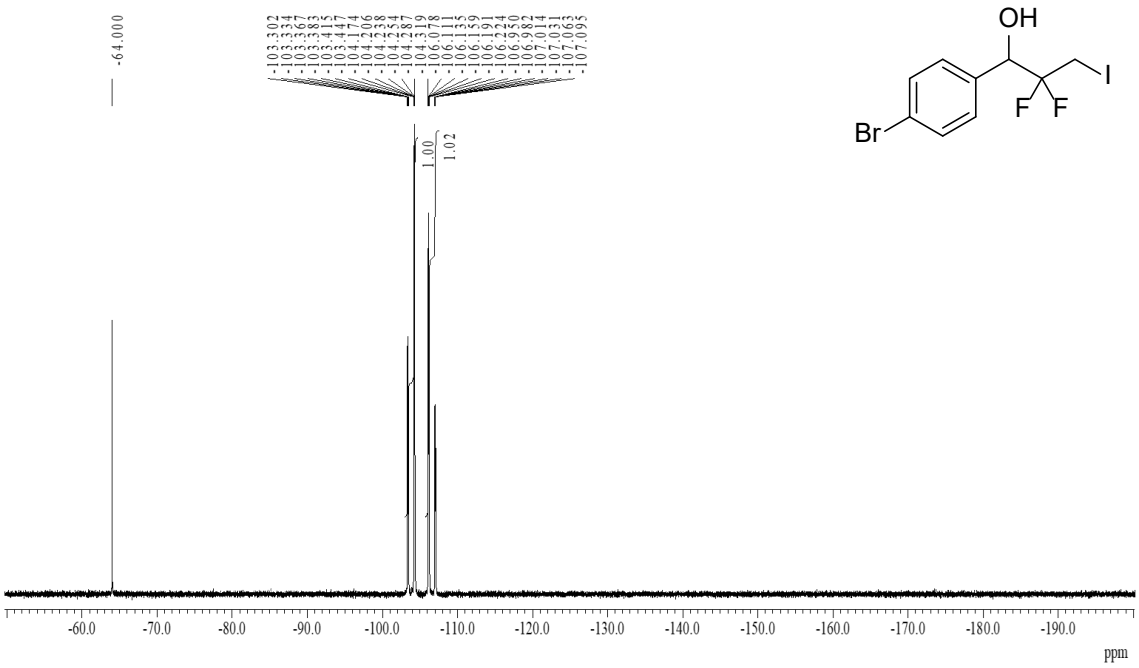


^{1}H and ^{13}C NMR spectra of 1-(4-bromophenyl)-2,2-difluoro-3-iodopropan-2-ol (**2h**)

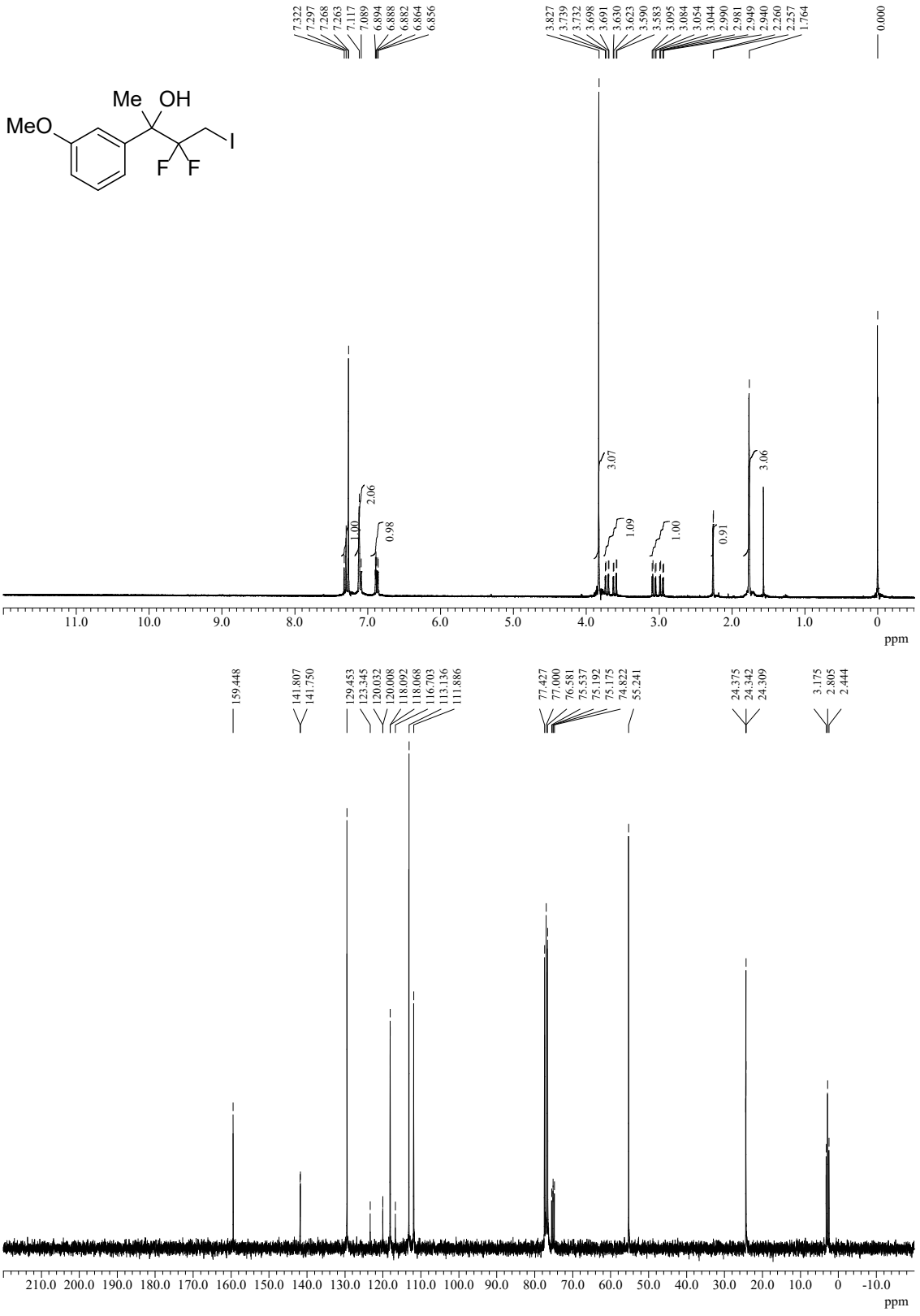




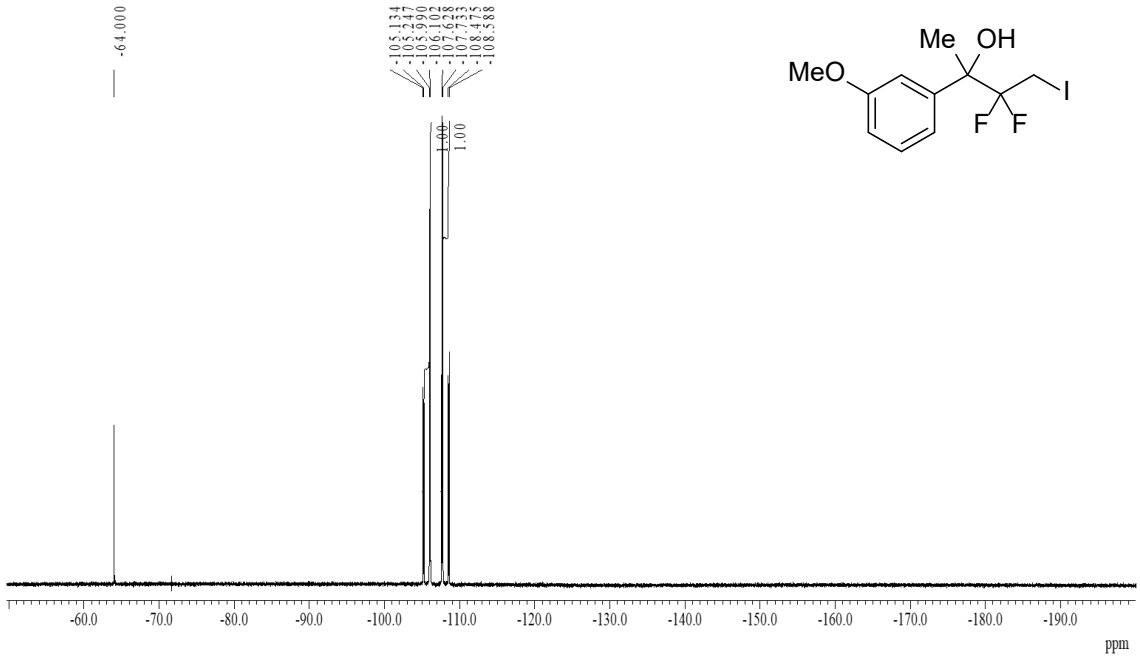
^{19}F NMR spectrum of 1-(4-bromophenyl)-2,2-difluoro-3-iodopropan-2-ol (**2h**)



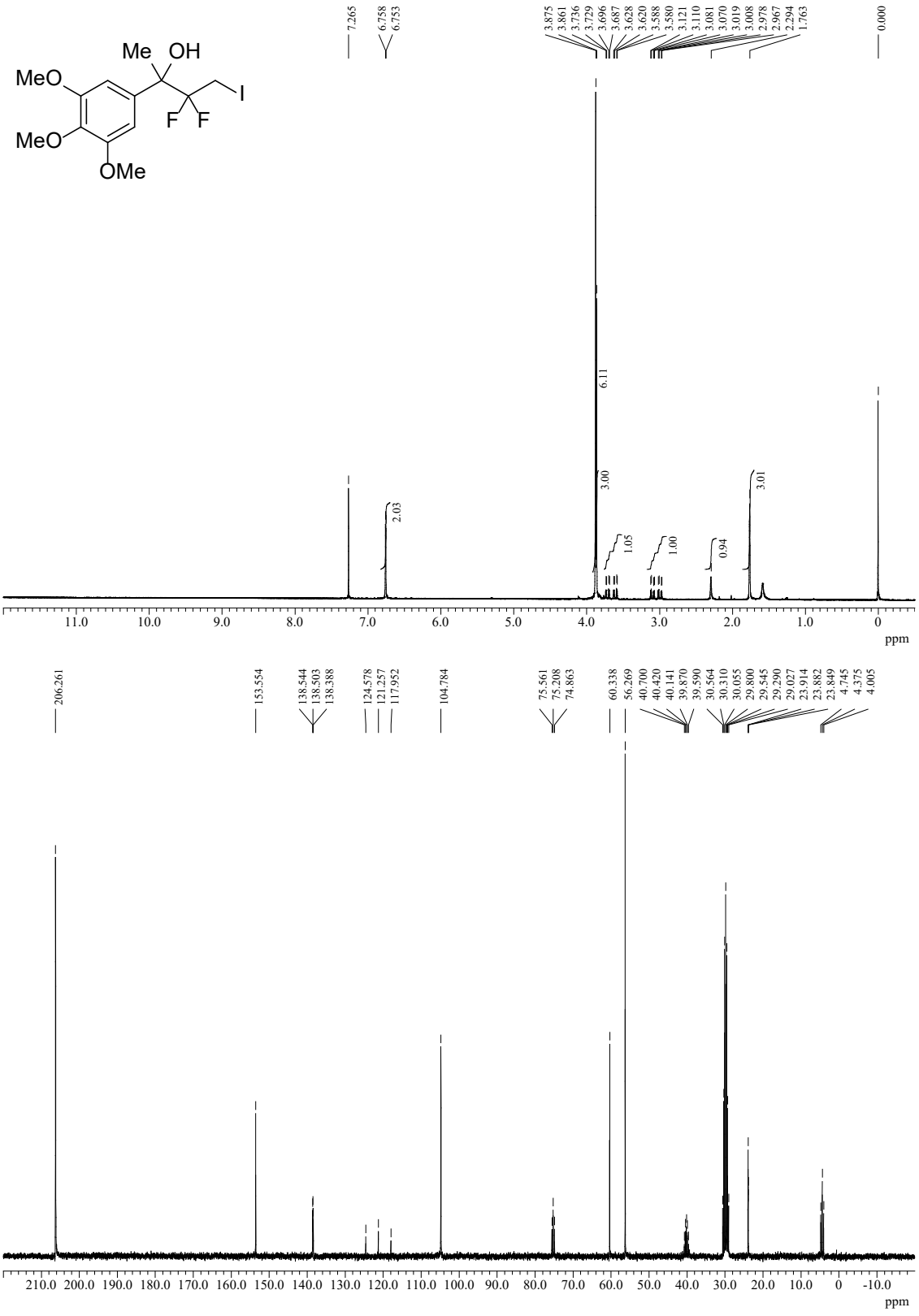
^{1}H and ^{13}C NMR spectra of 3,3-difluoro-4-iodo-2-(3-methoxyphenyl)butan-2-ol (**2k**)



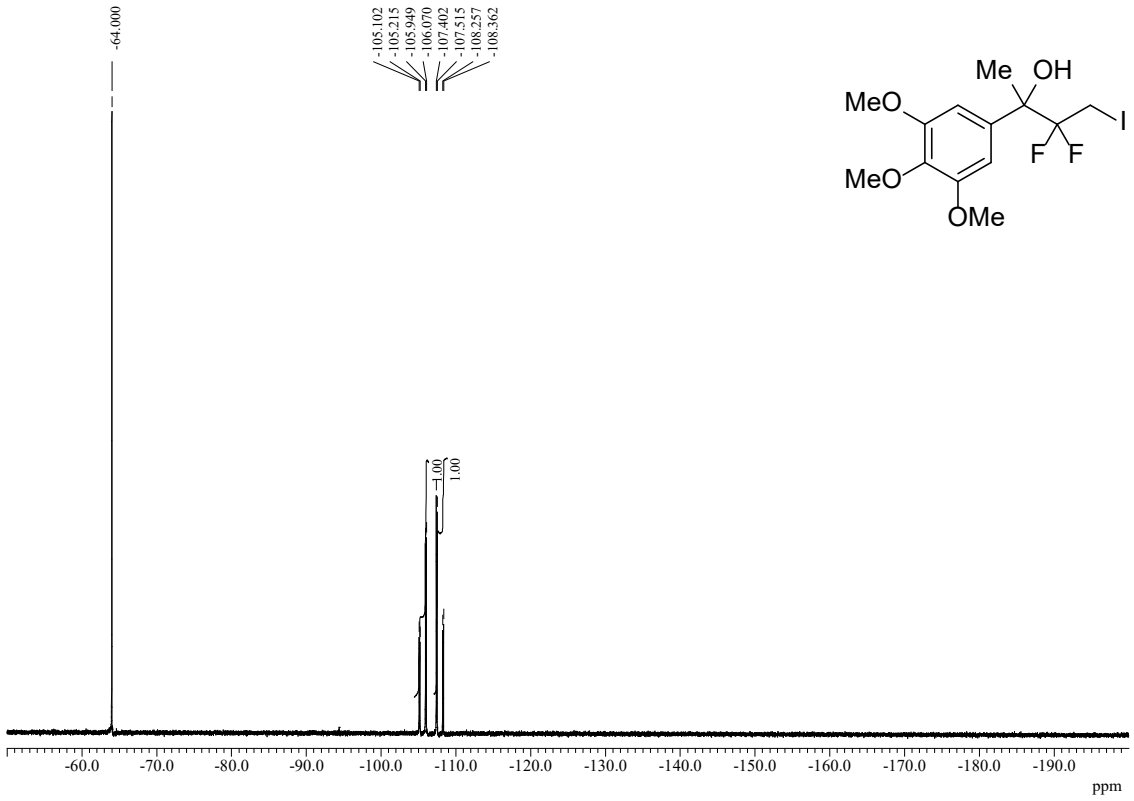
^{19}F NMR spectrum of 3,3-difluoro-4-iodo-2-(3-methoxyphenyl)butan-2-ol (**2k**)



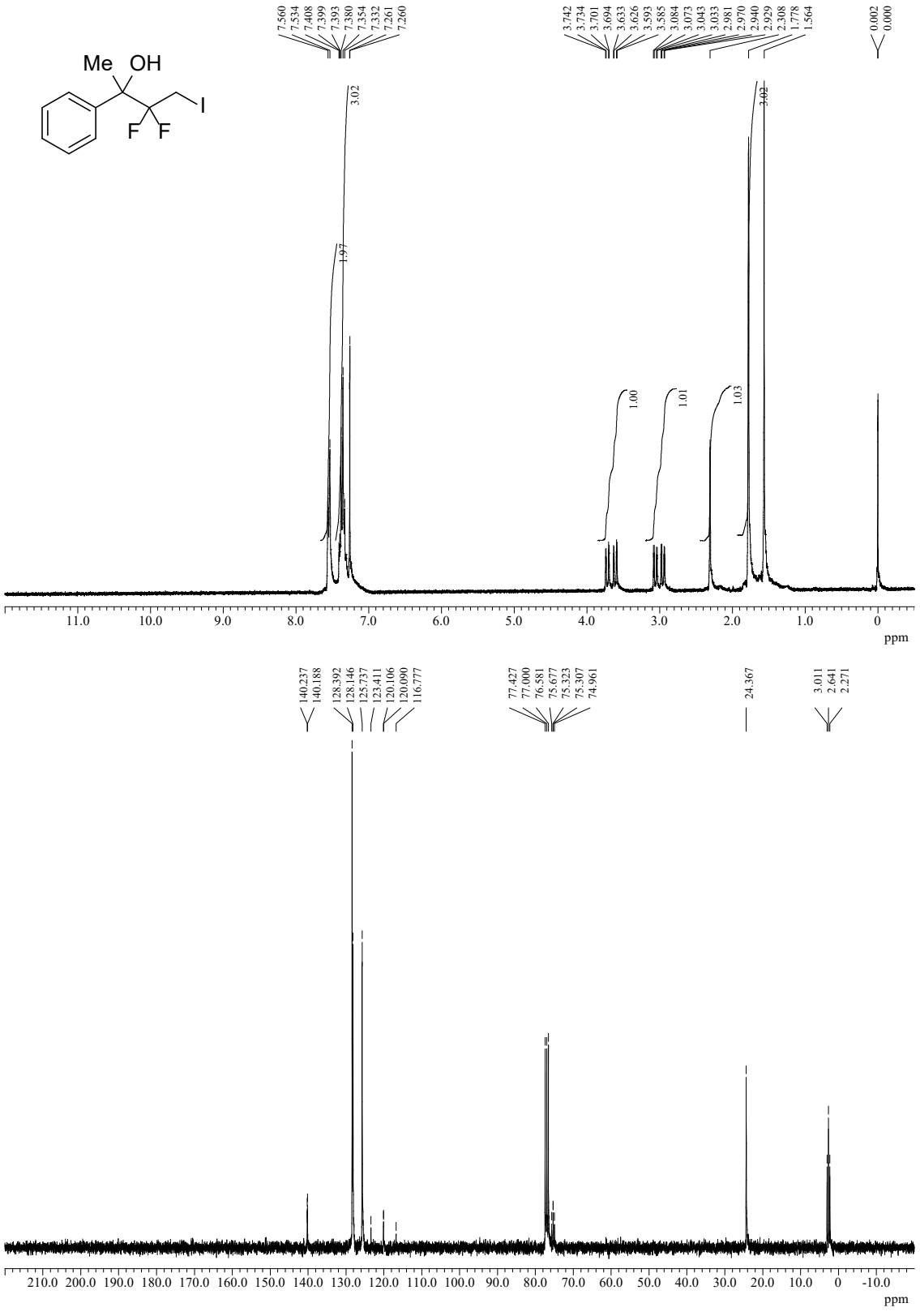
^{1}H and ^{13}C NMR spectra of 3,3-difluoro-4-iodo-2-(3,4,5-trimethoxyphenyl)butan-2-ol (**2m**)



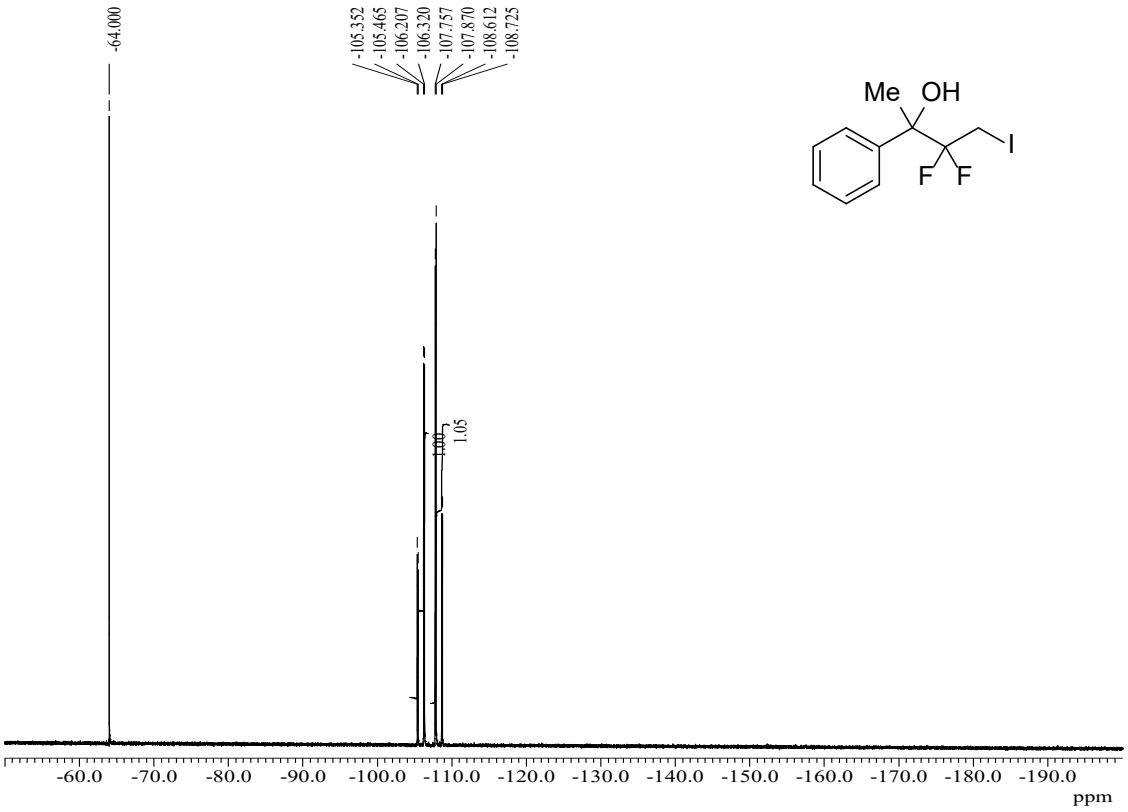
^{19}F NMR spectrum of 3,3-difluoro-4-iodo-2-(3,4,5-trimethoxyphenyl)butan-2-ol (**2m**)



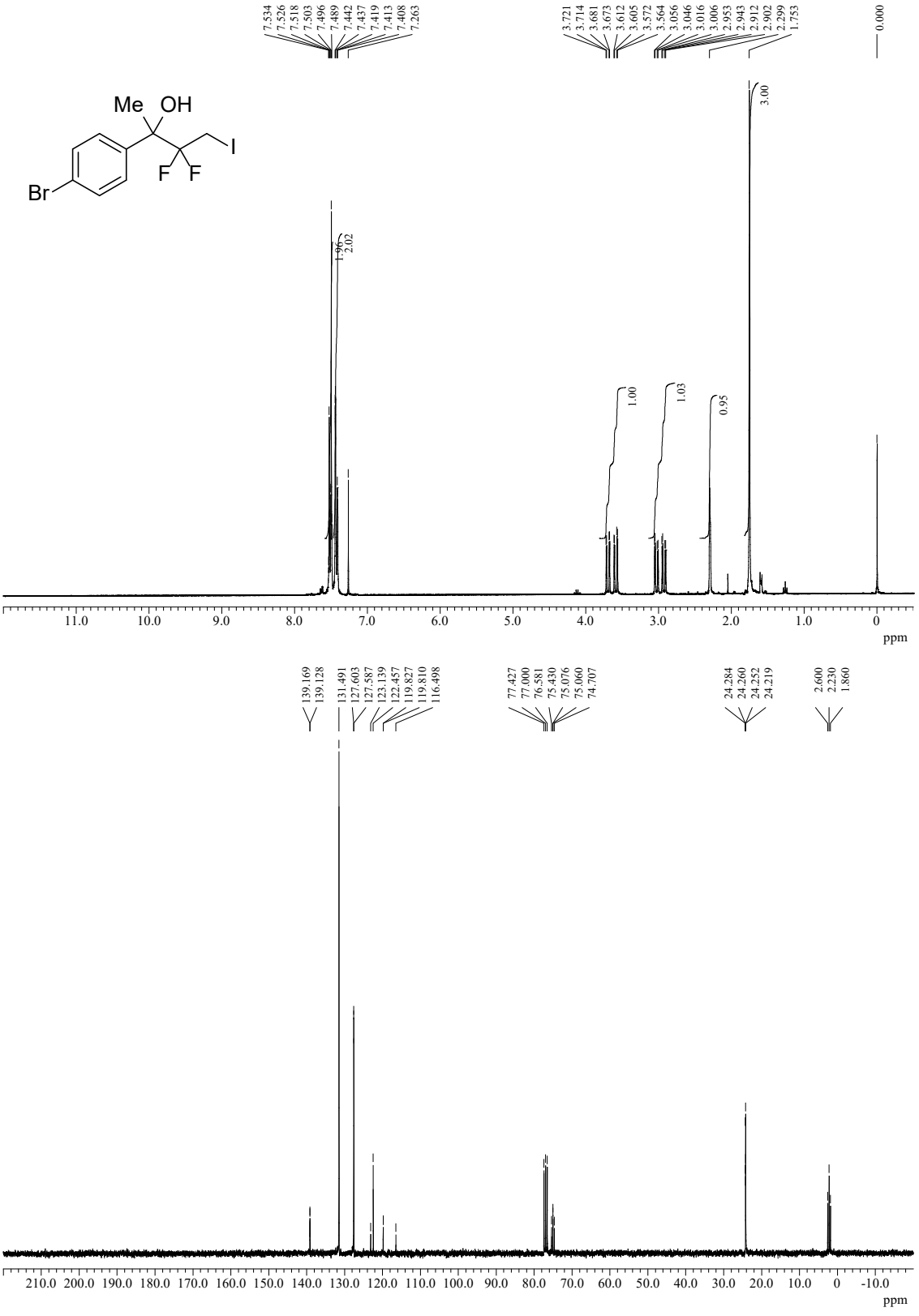
^{1}H and ^{13}C NMR spectra of 3,3-difluoro-4-iodo-2-phenylbutan-2-ol (**2n**)



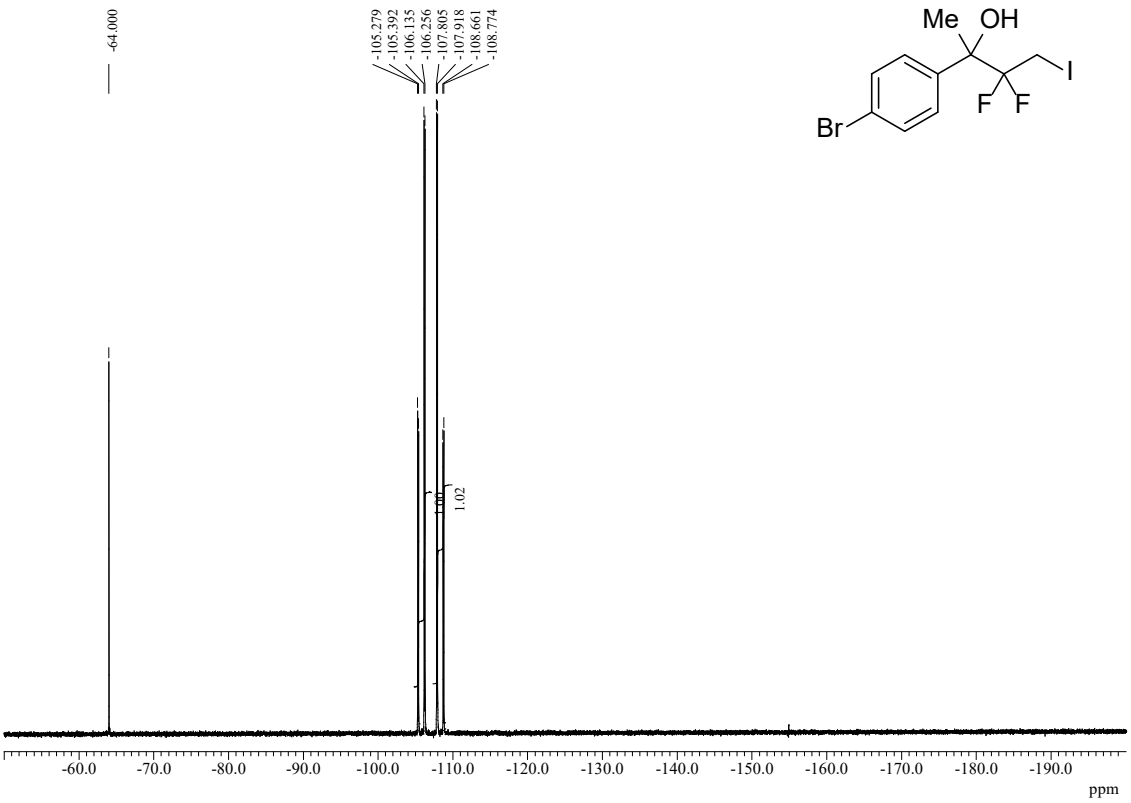
^{19}F NMR spectrum of 3,3-difluoro-4-iodo-2-phenylbutan-2-ol (**2n**)



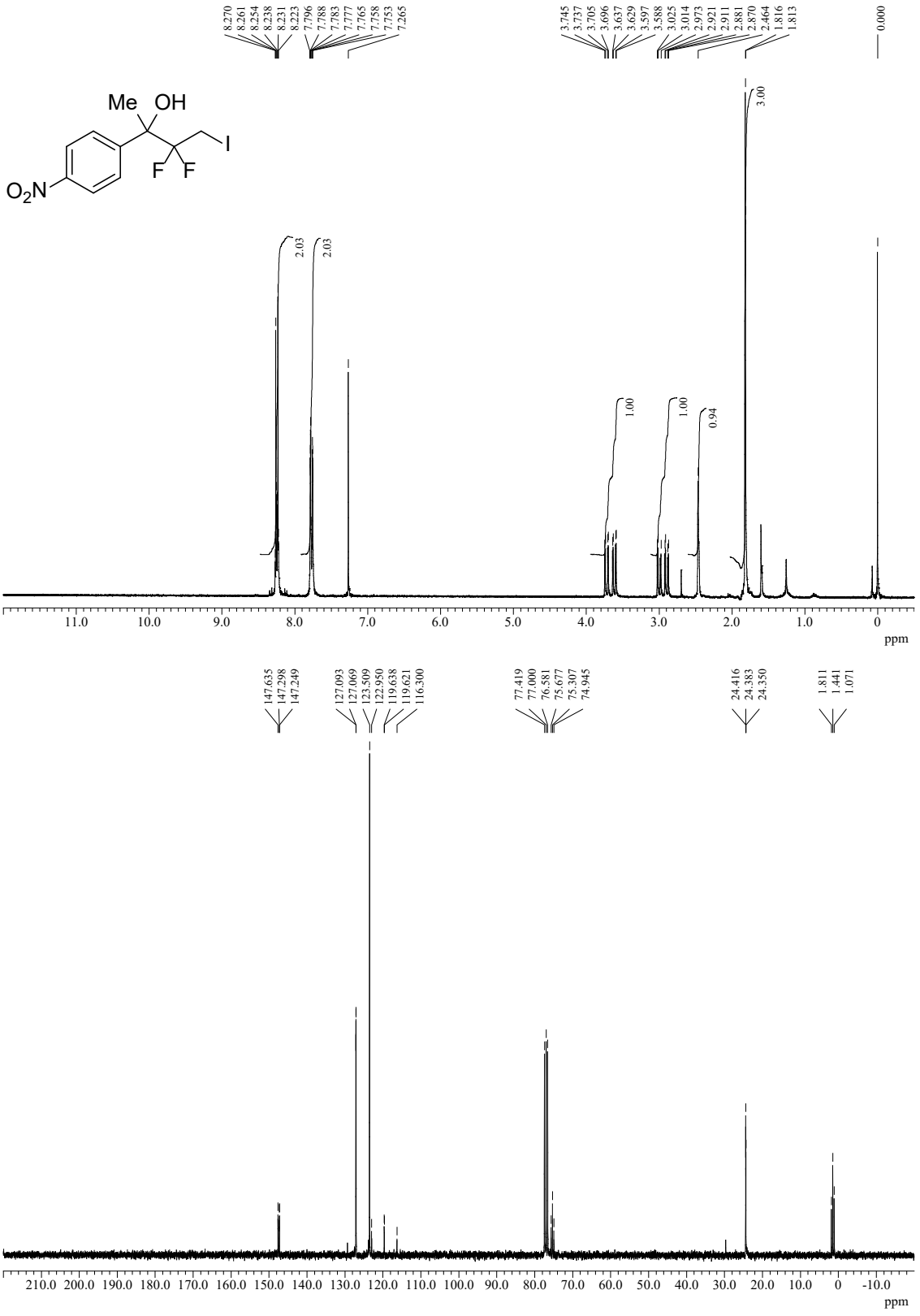
^{1}H and ^{13}C NMR spectra of 2-(4-bromophenyl)-3,3-difluoro-4-iodobutan-2-ol (**2o**)



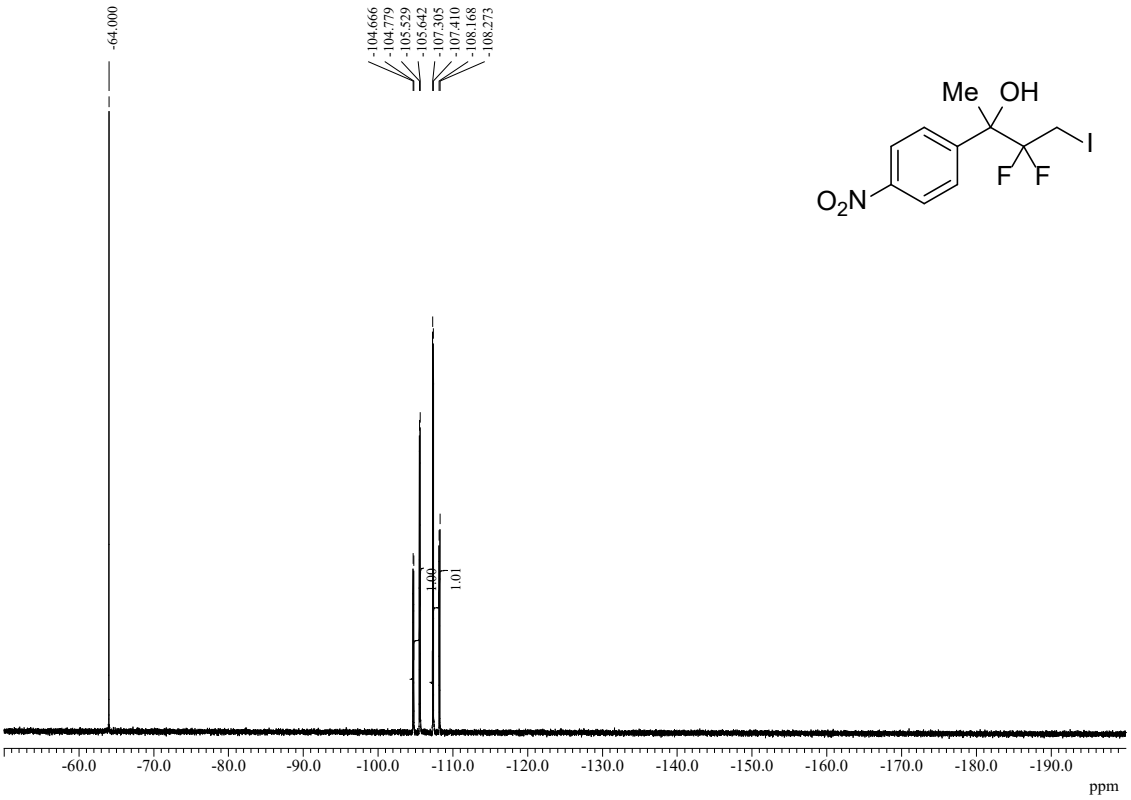
^{19}F NMR spectrum of 2-(4-bromophenyl)-3,3-difluoro-4-iodobutan-2-ol (**2o**)



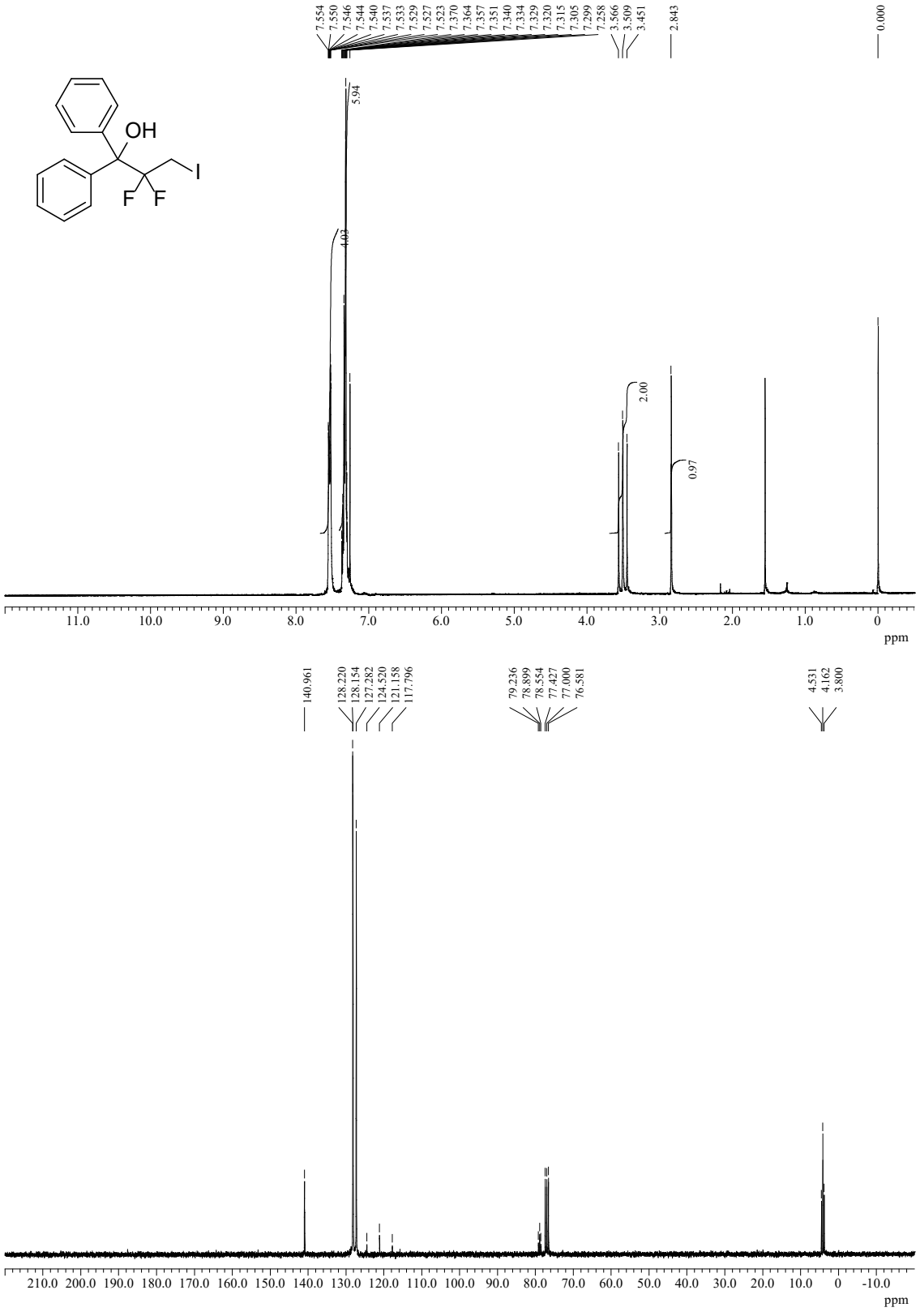
^{1}H and ^{13}C NMR spectra of 3,3-difluoro-4-iodo-2-(4-nitrophenyl)-butan-2-ol (**2p**)



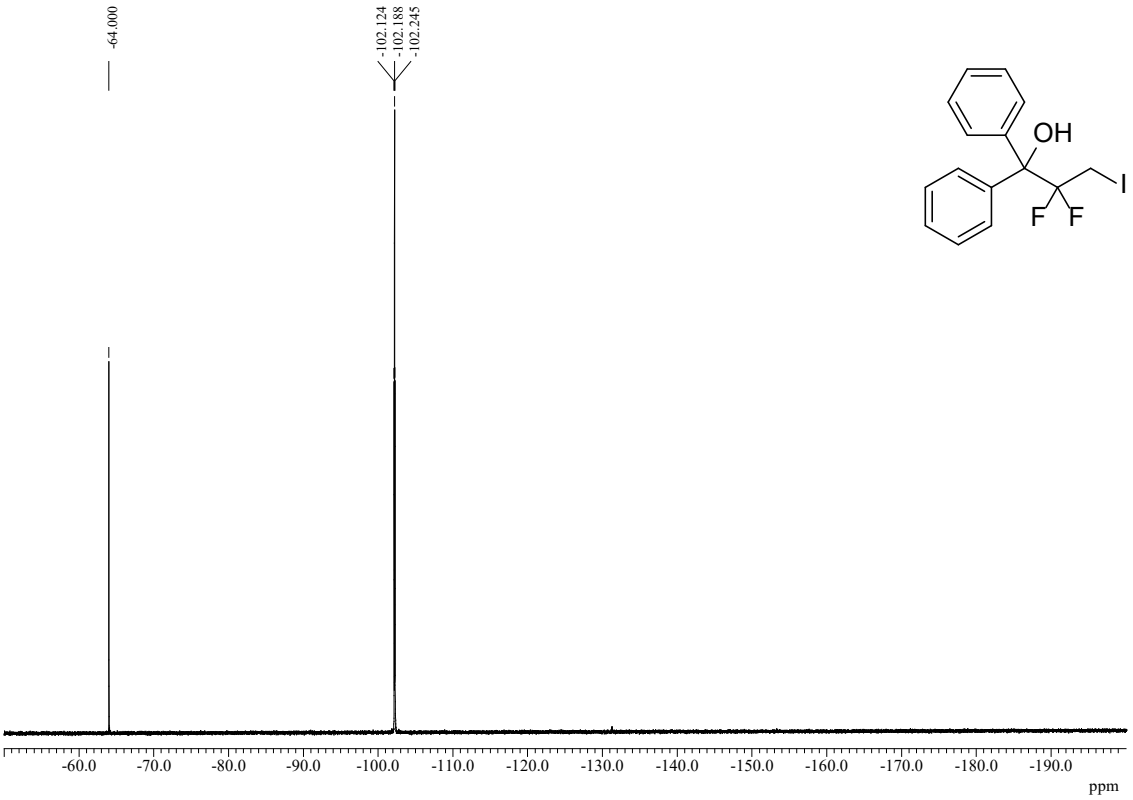
^{19}F NMR spectrum of 3,3-difluoro-4-iodo-2-(4-nitrophenyl)-butan-2-ol (**2p**)



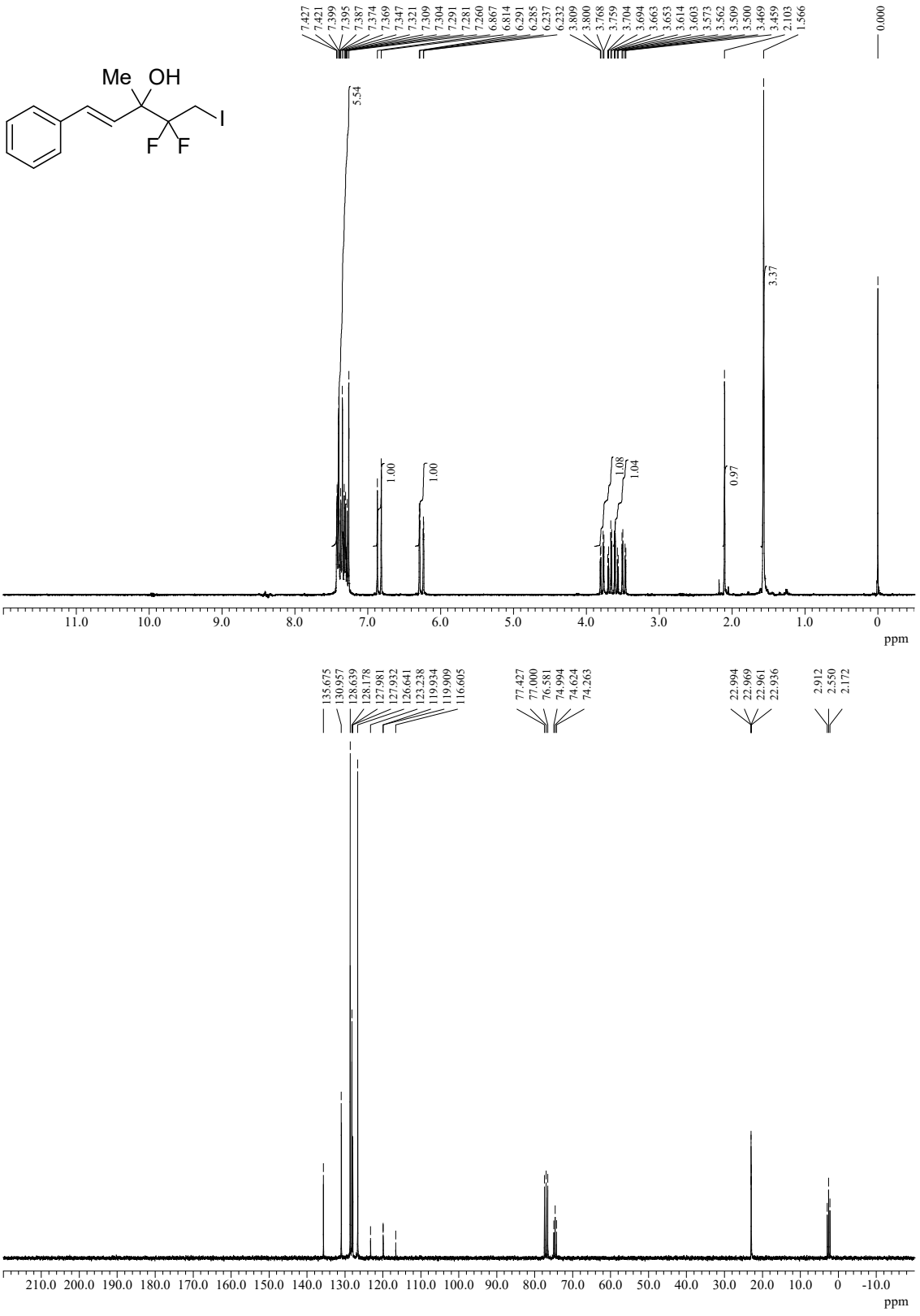
^{1}H and ^{13}C NMR spectra of 2,2-difluoro-3-iodo-1,1-diphenylpropan-1-ol (**2q**)



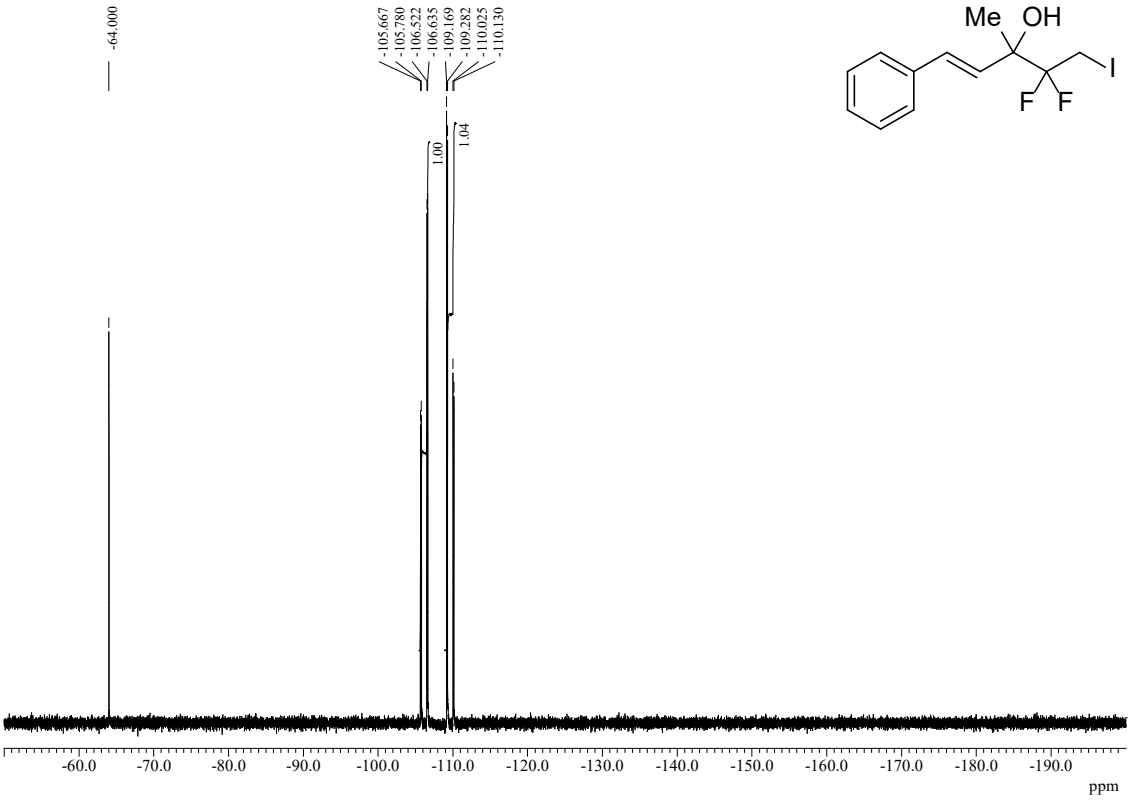
^{19}F NMR spectrum of 2,2-difluoro-3-iodo-1,1-diphenylpropan-1-ol (**2q**)



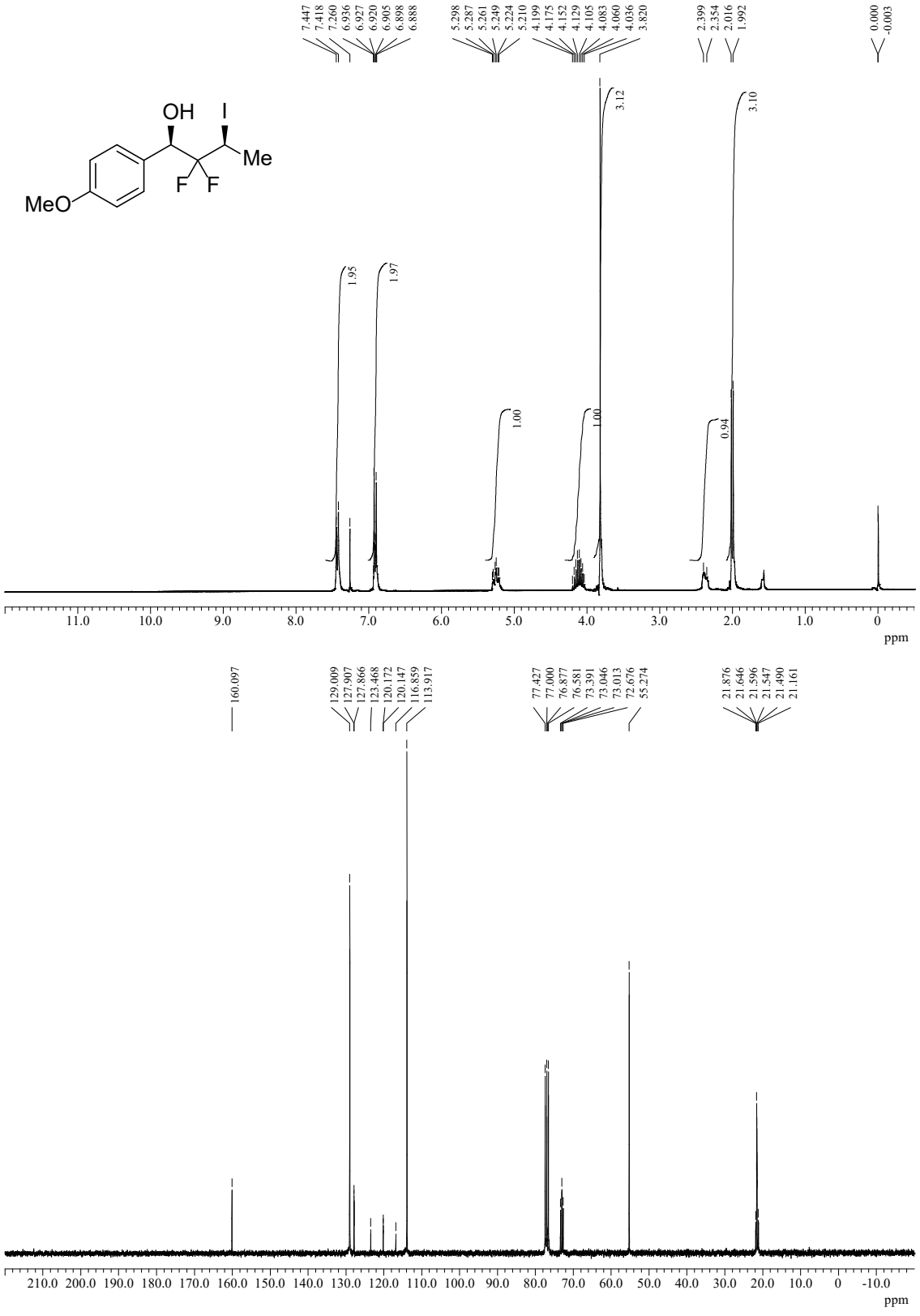
^{1}H and ^{13}C NMR spectra of *(E)*-4,4-difluoro-5-iodo-3-methyl-1-phenylpent-1-en-3-ol (**2r**)



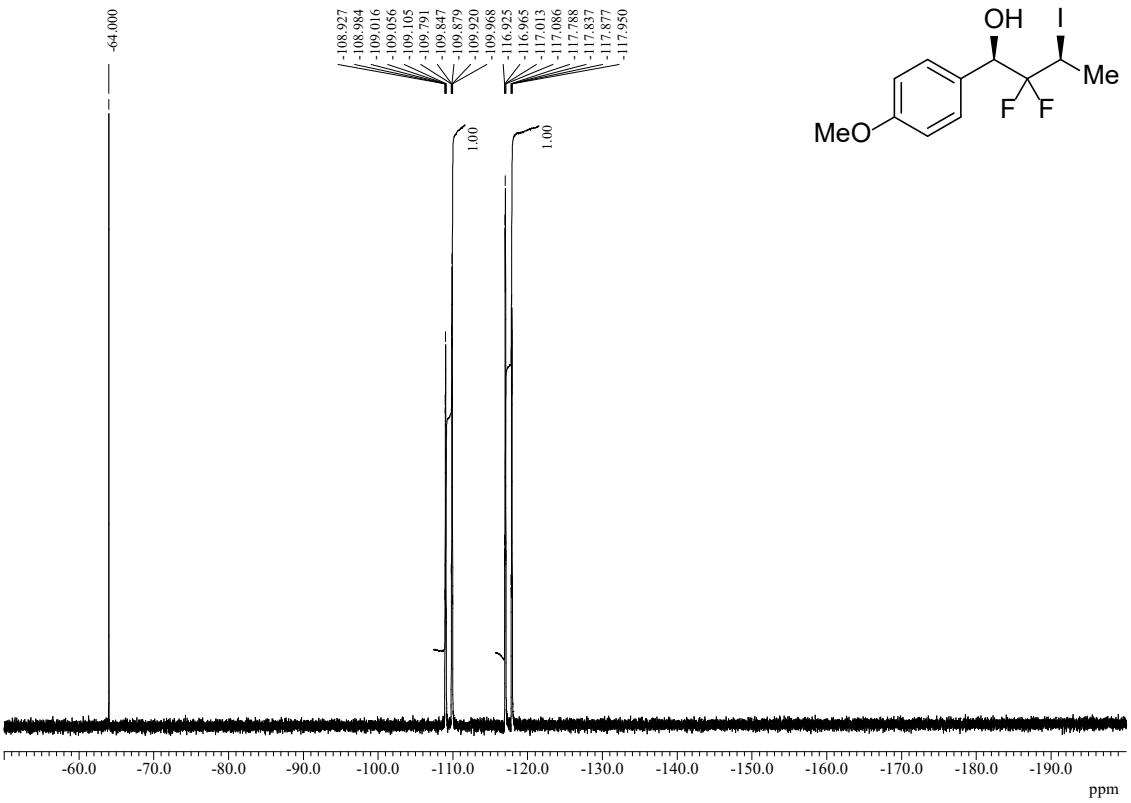
^{19}F NMR spectrum of *(E)*-4,4-difluoro-5-iodo-3-methyl-1-phenylpent-1-en-3-ol (**2r**)



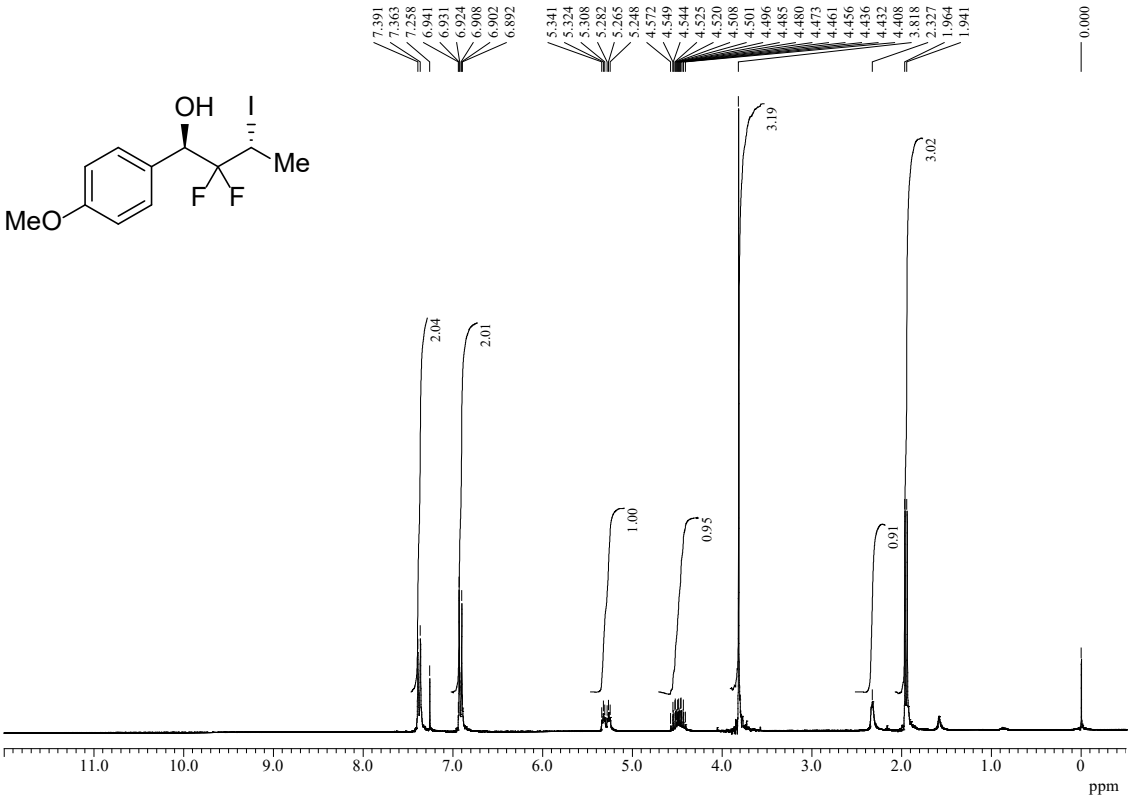
^{1}H and ^{13}C NMR spectra of 2,2-difluoro-3-iodo-1-(4-methoxyphenyl)butan-1-ol (major-**2s**)

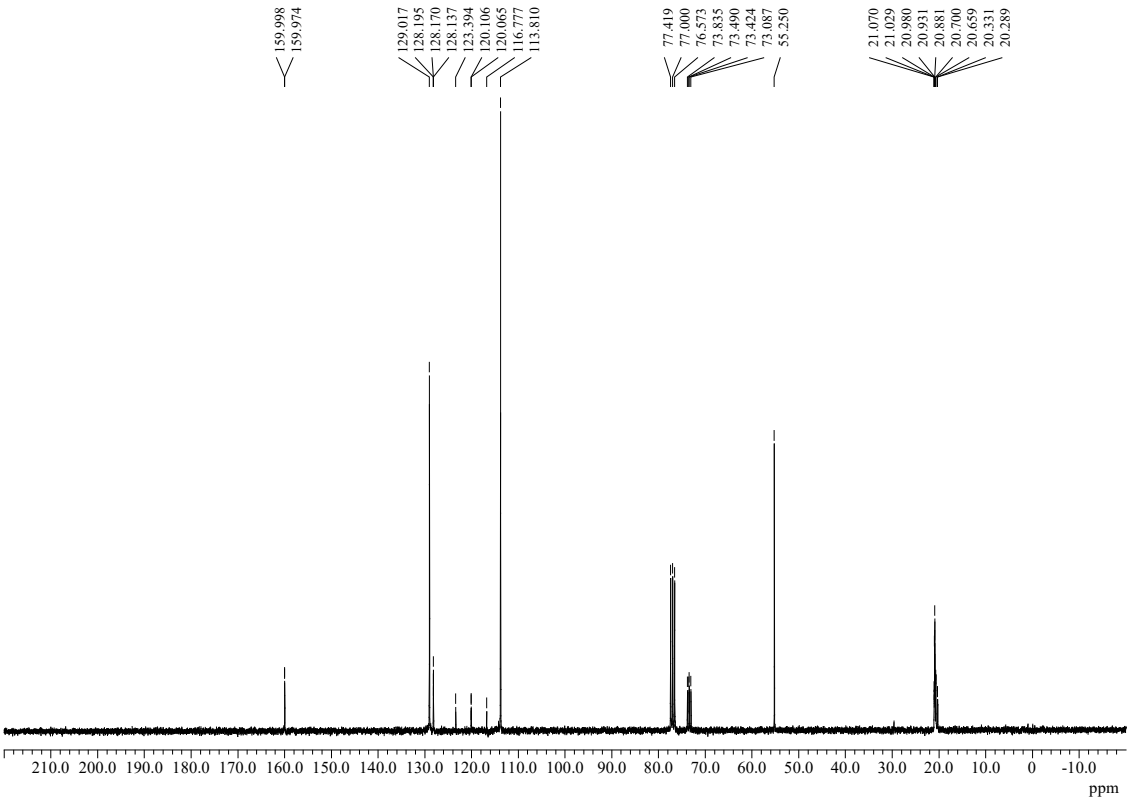


^{19}F NMR spectrum of 2,2-difluoro-3-iodo-1-(4-methoxyphenyl)butan-1-ol (major-**2s**)

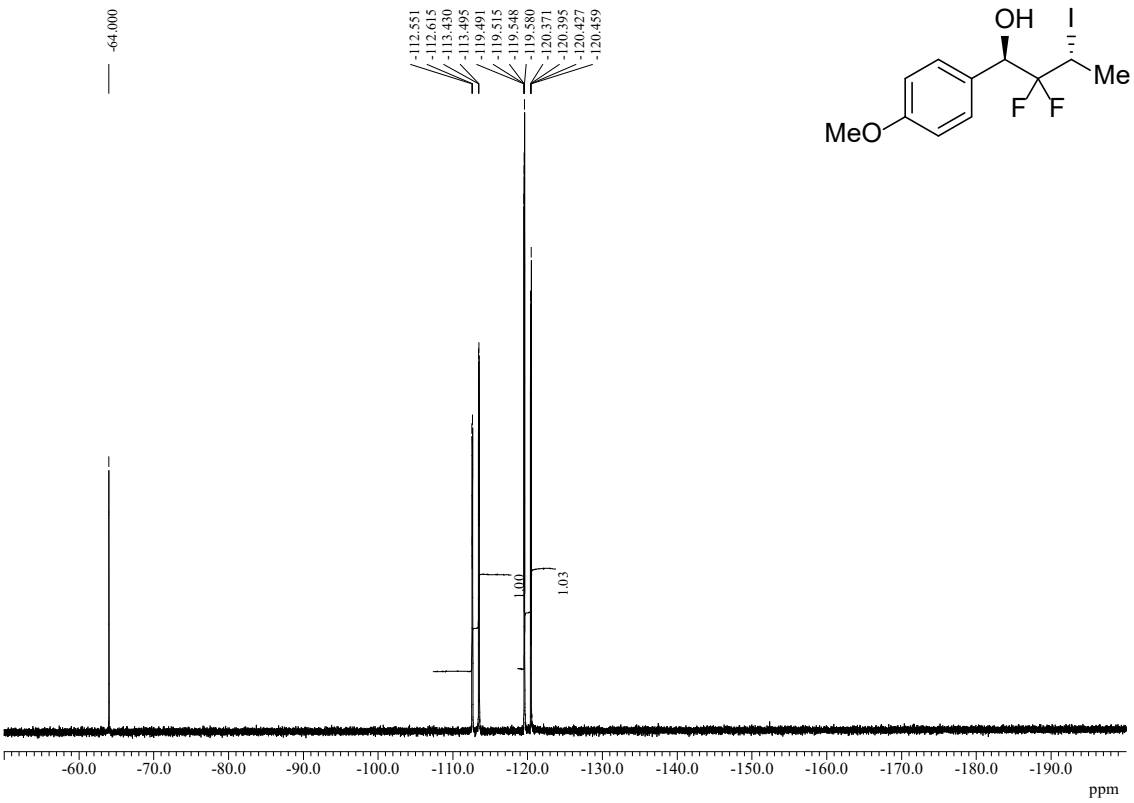


^{1}H and ^{13}C NMR spectra of (1*R**,3*R**)-2,2-difluoro-3-iodo-1-(4-methoxyphenyl)butan-1-ol (minor-**2s**

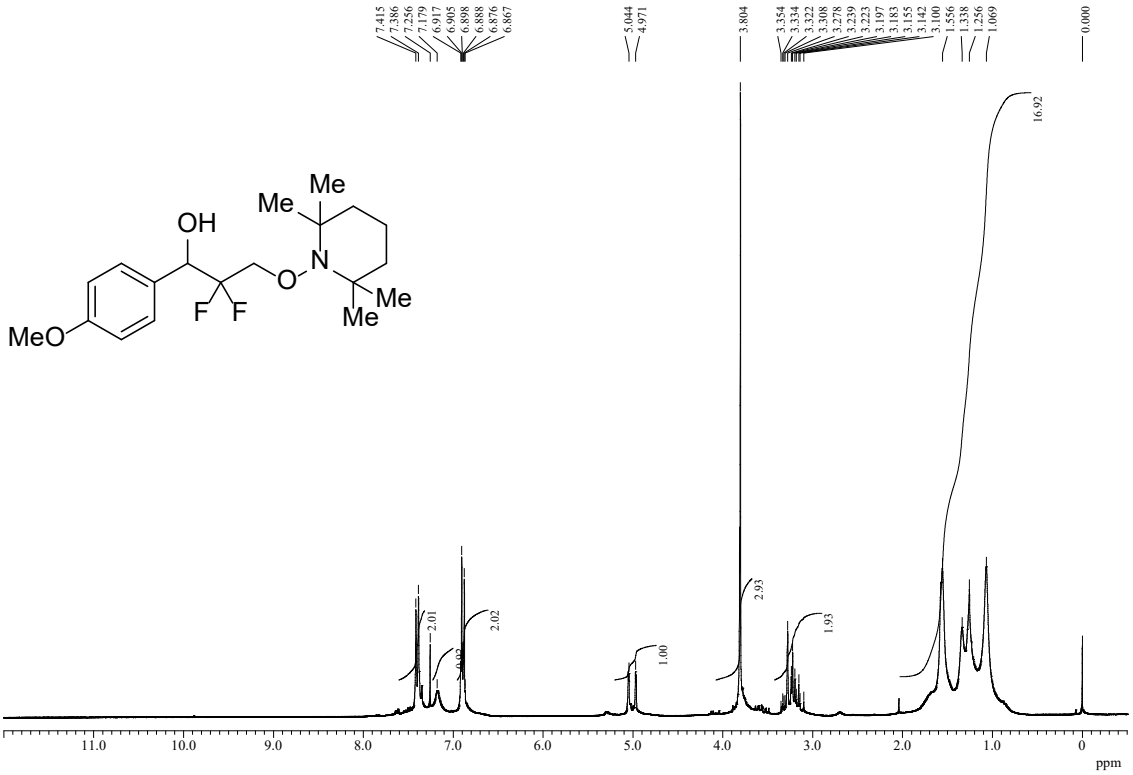


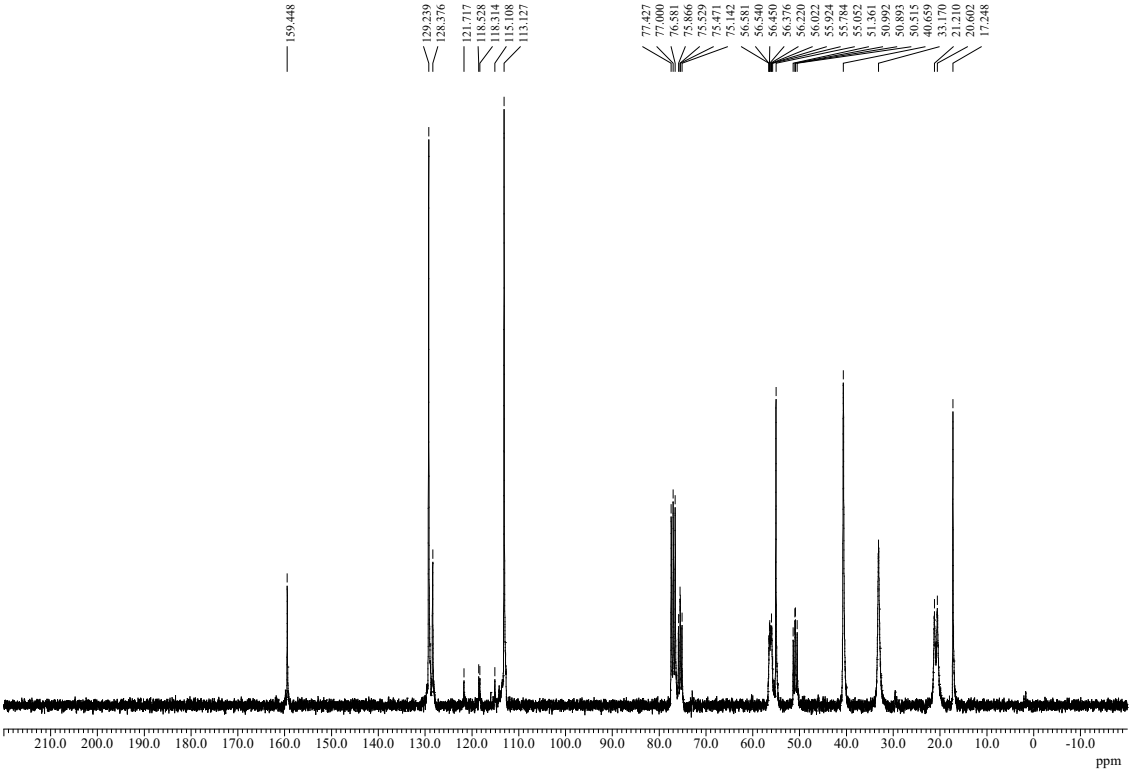


^{19}F NMR spectrum of (1*R**,3*R**)-2,2-difluoro-3-iodo-1-(4-methoxyphenyl)butan-1-ol (minor-**2s**)

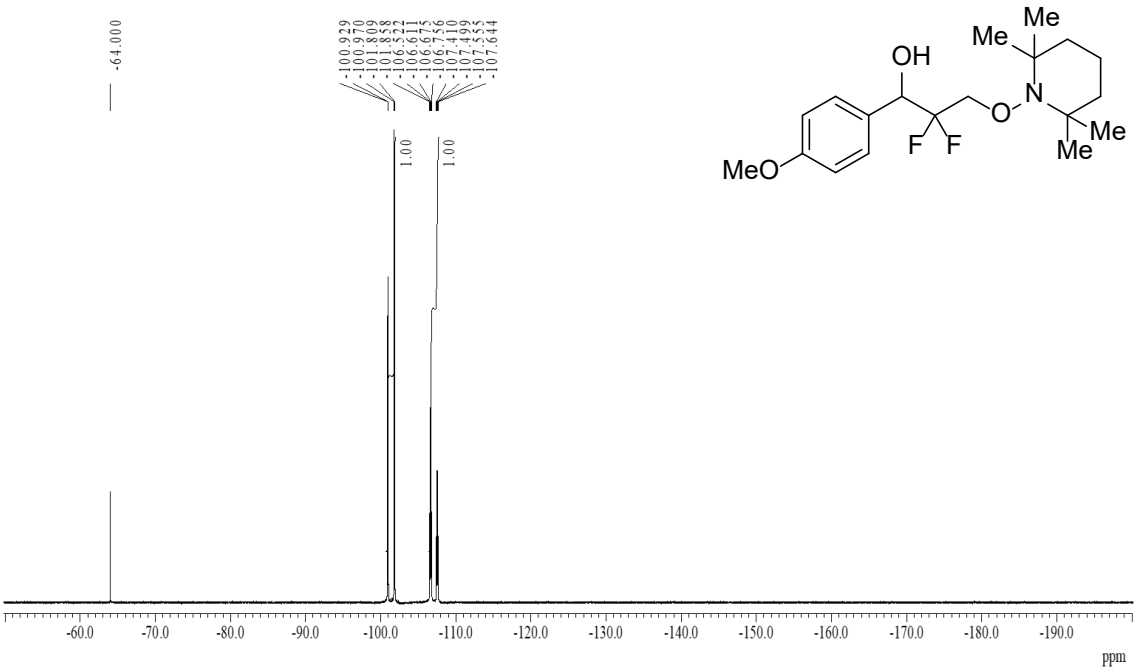


^{1}H and ^{13}C NMR spectra of 2,2-difluoro-1-(4-methoxyphenyl)-3-[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]propan-1-ol (**2a-TEMPO**)

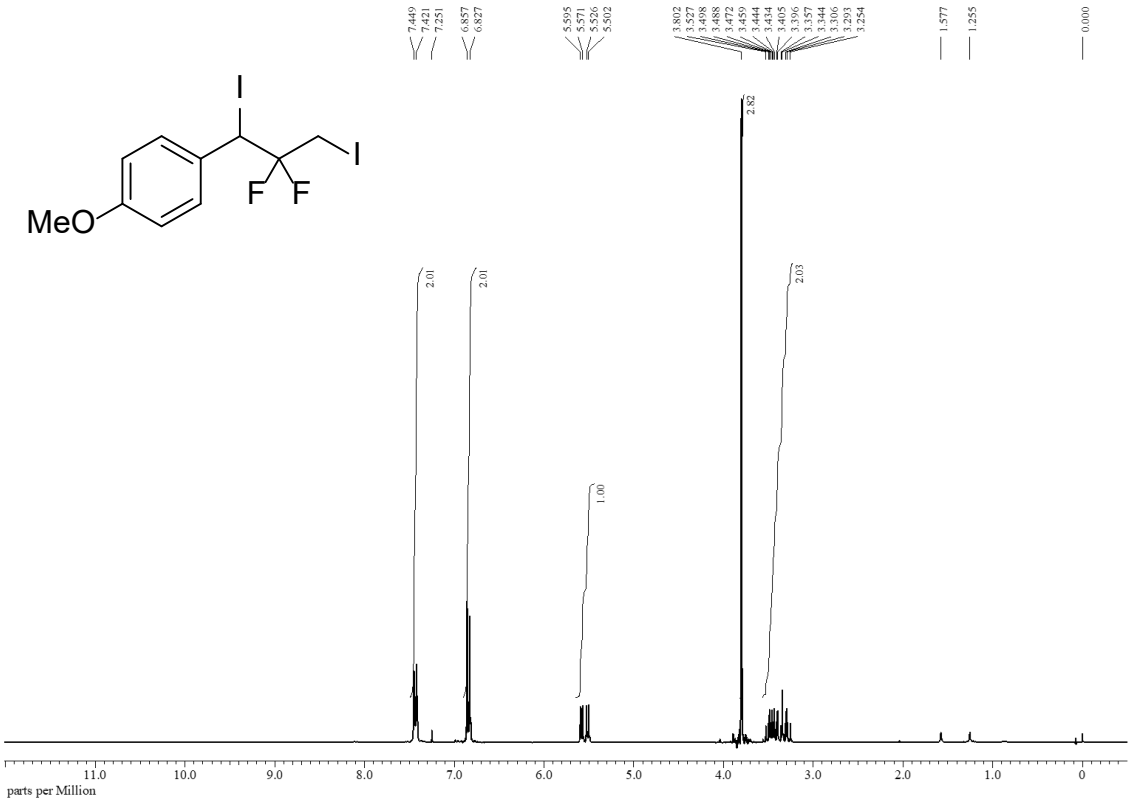


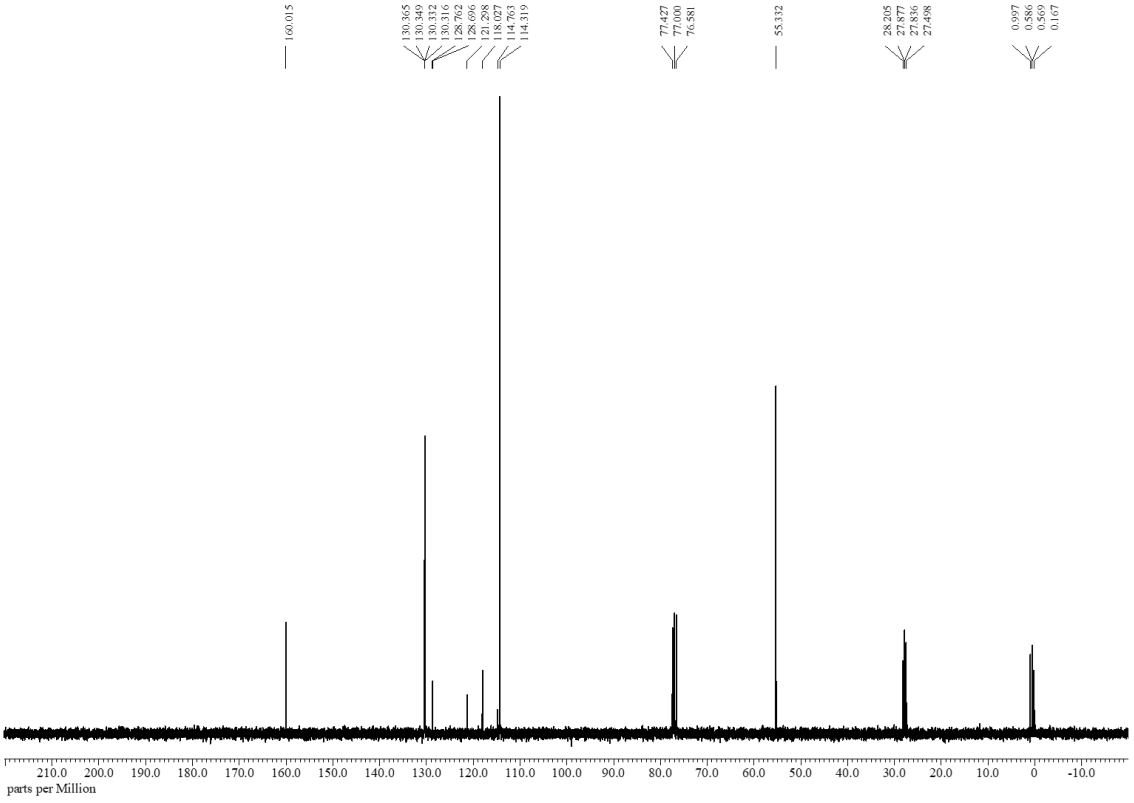


^{19}F NMR spectrum of 2,2-difluoro-1-(4-methoxyphenyl)-3-[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]propan-1-ol (**2a-TEMPO**)

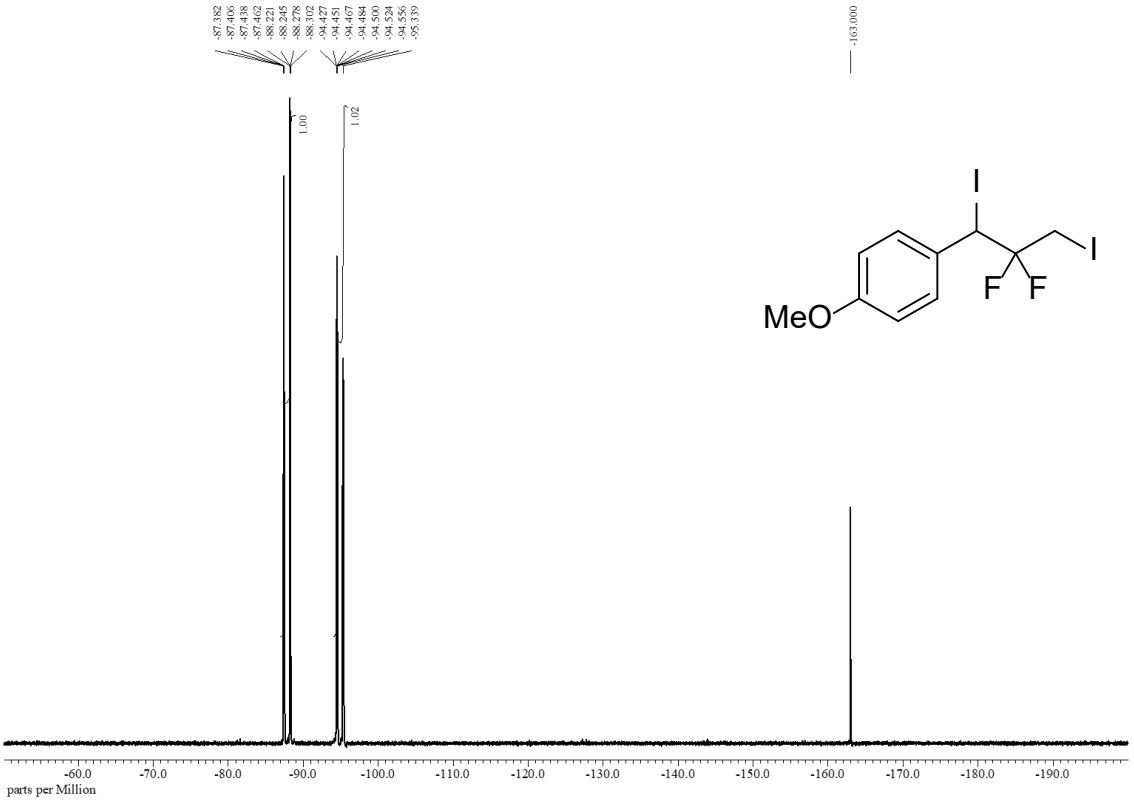


^{1}H and ^{13}C NMR spectra of 1-(2,2-difluoro-1,3-diiodoprop-1-yl)-4-methoxybenzene (**3a**)

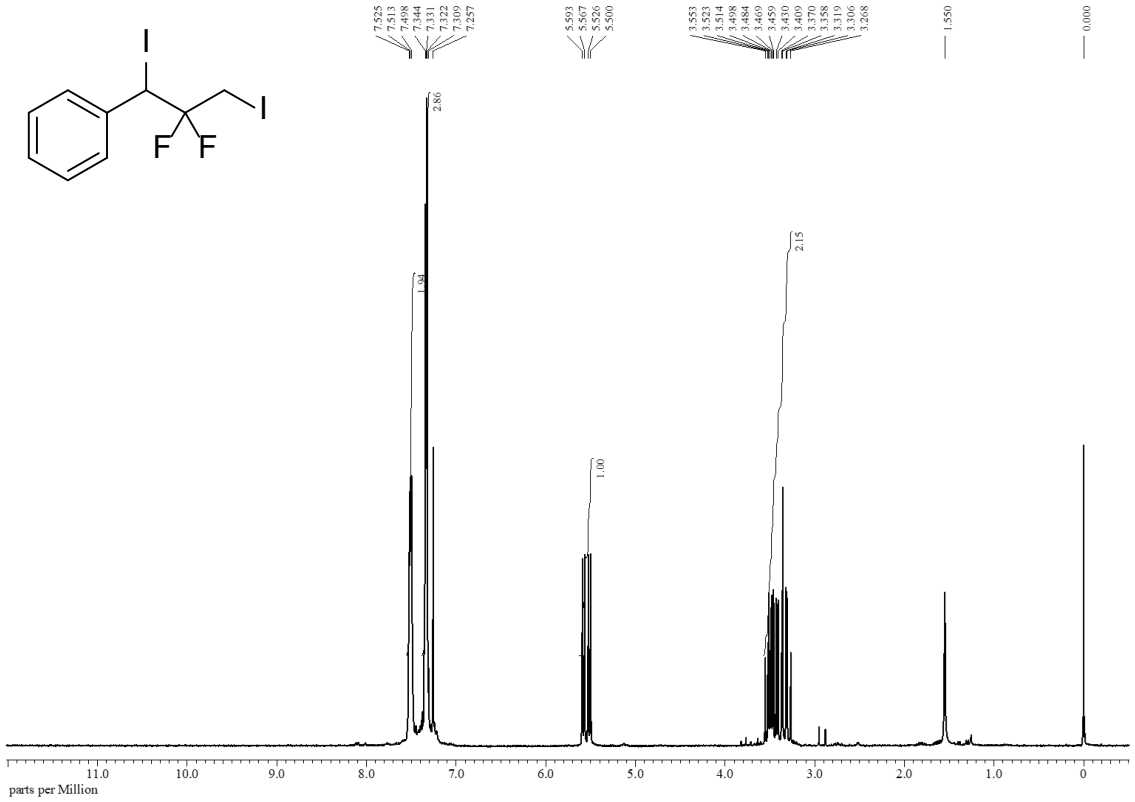


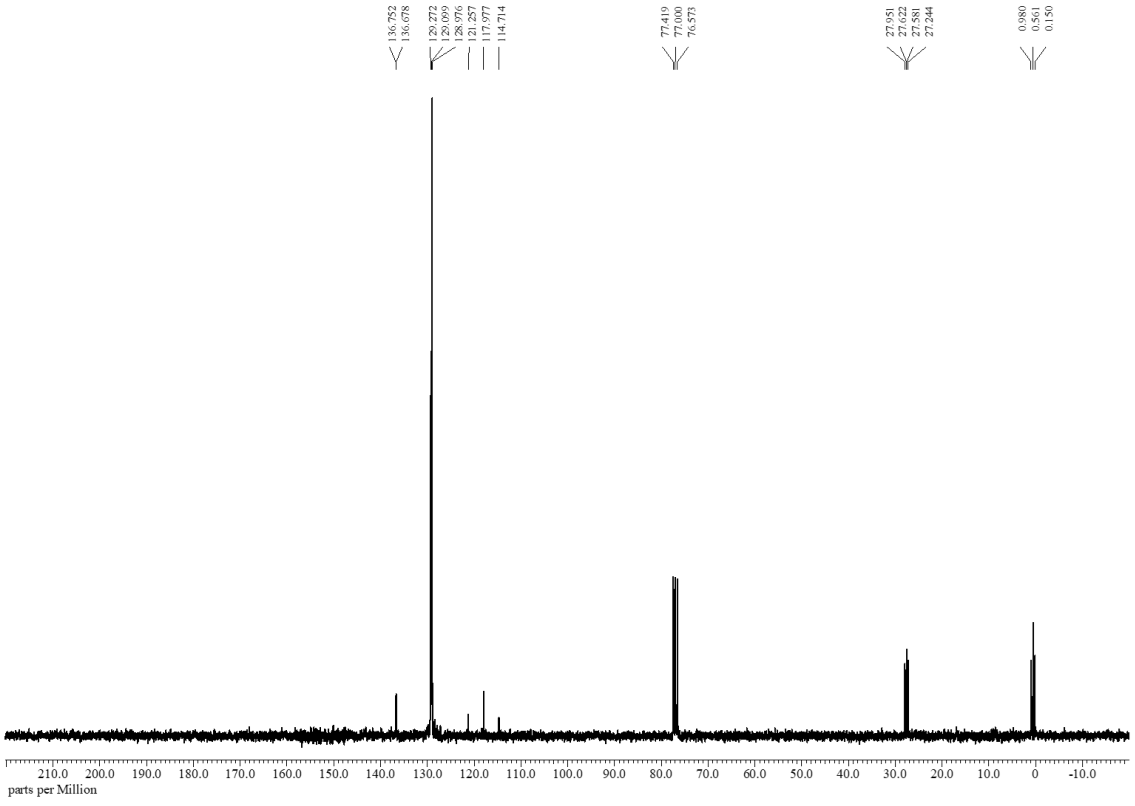


^{19}F NMR spectrum of 1-(2,2-difluoro-1,3-diiodoprop-1-yl)-4-methoxybenzene (**3a**)

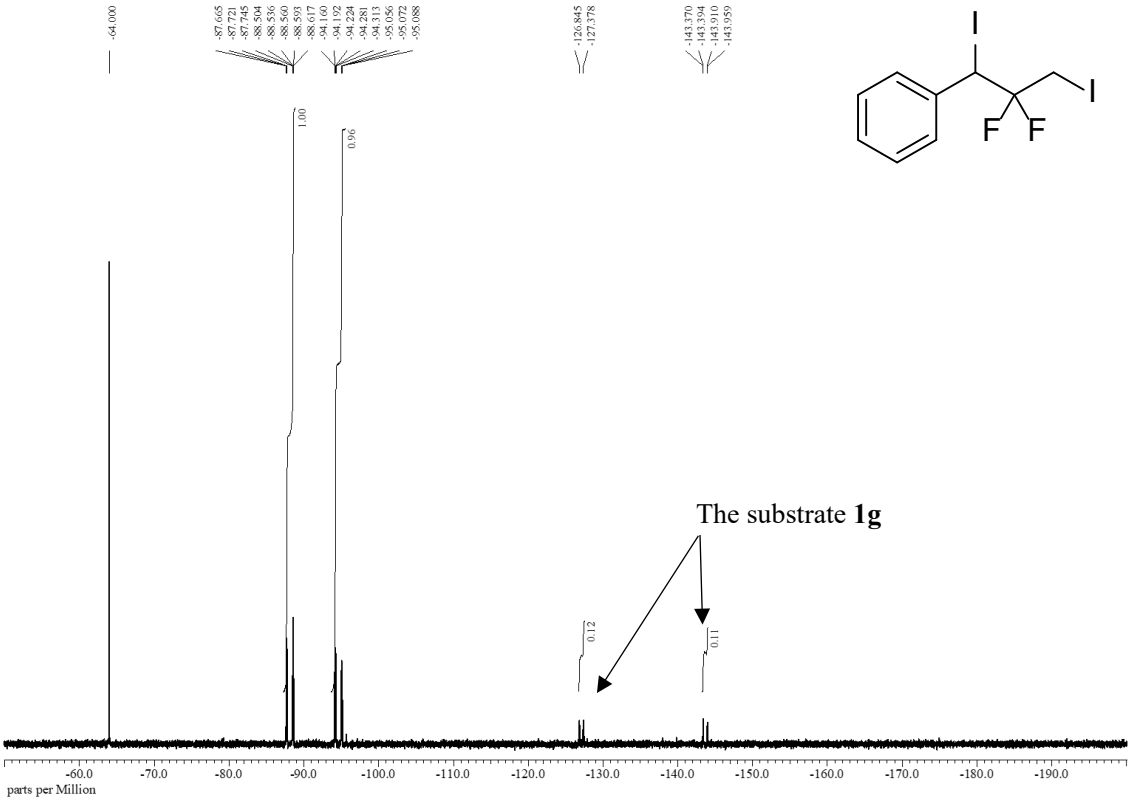


^{1}H and ^{13}C NMR spectra of (2,2-difluoro-1,3-diiodoprop-1-yl)benzene (**3g**)

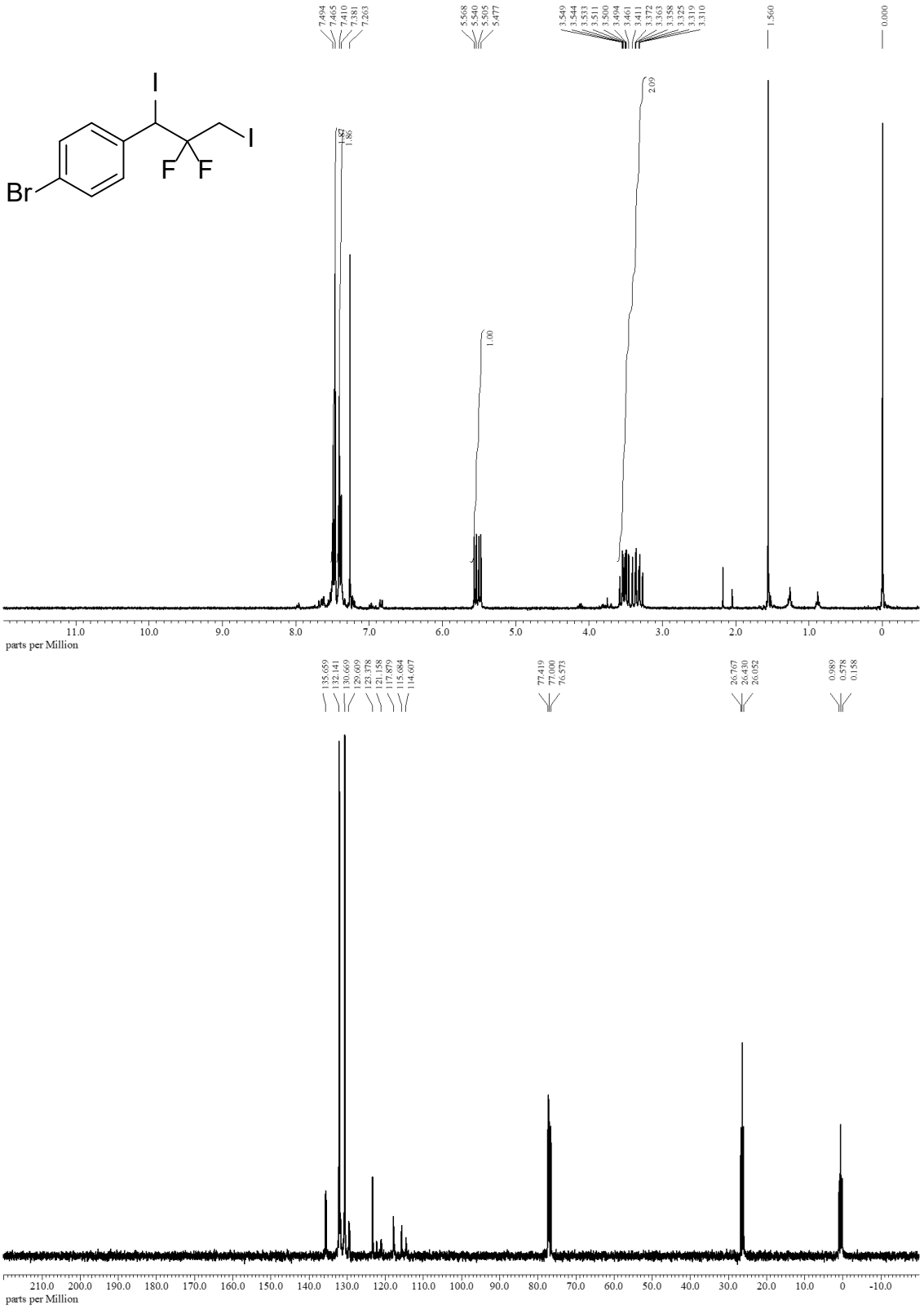




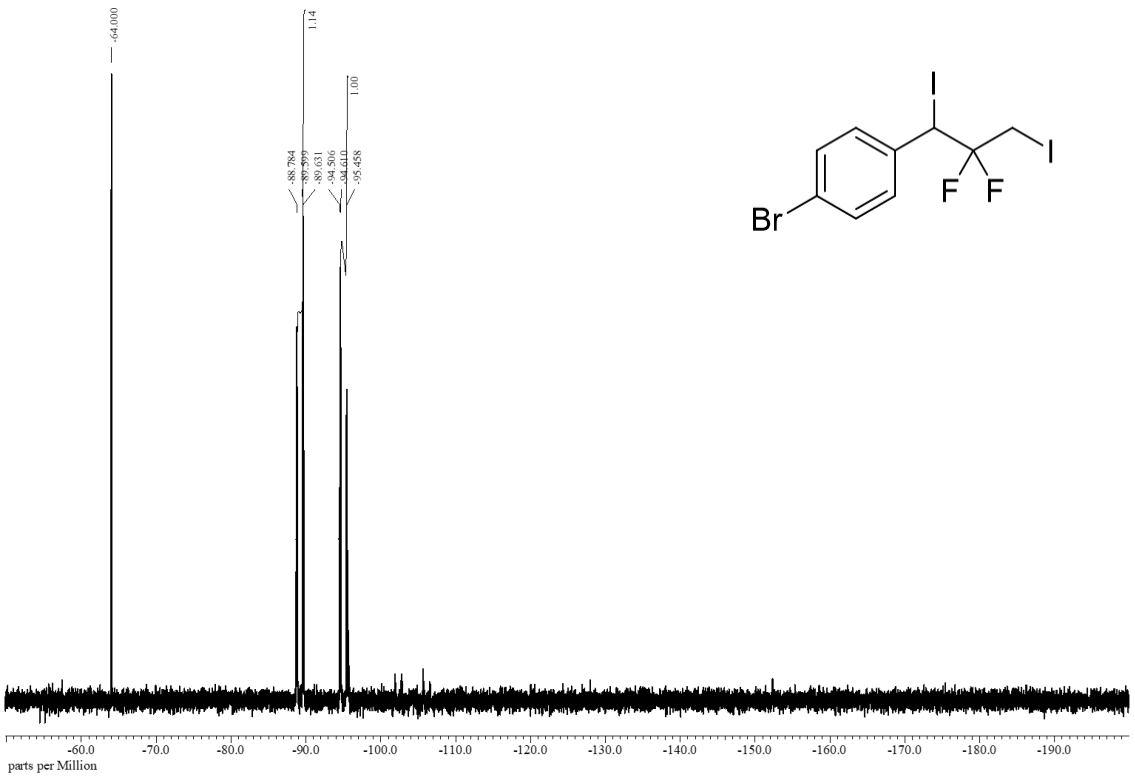
^{19}F NMR spectrum of (2,2-difluoro-1,3-diiodoprop-1-yl)benzene (**3g**)



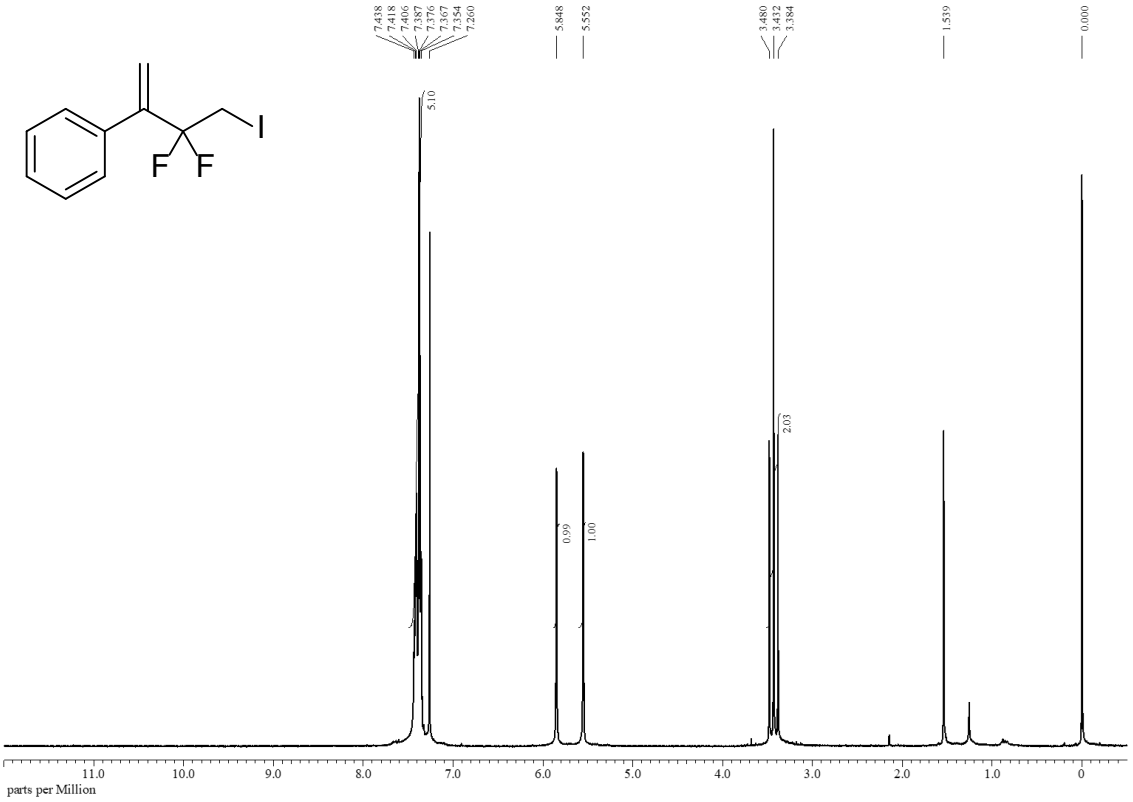
^{1}H and ^{13}C NMR spectra of 1-bromo-4-(2,2-difluoro-1,3-diiodoprop-1-yl)benzene (**3h**)

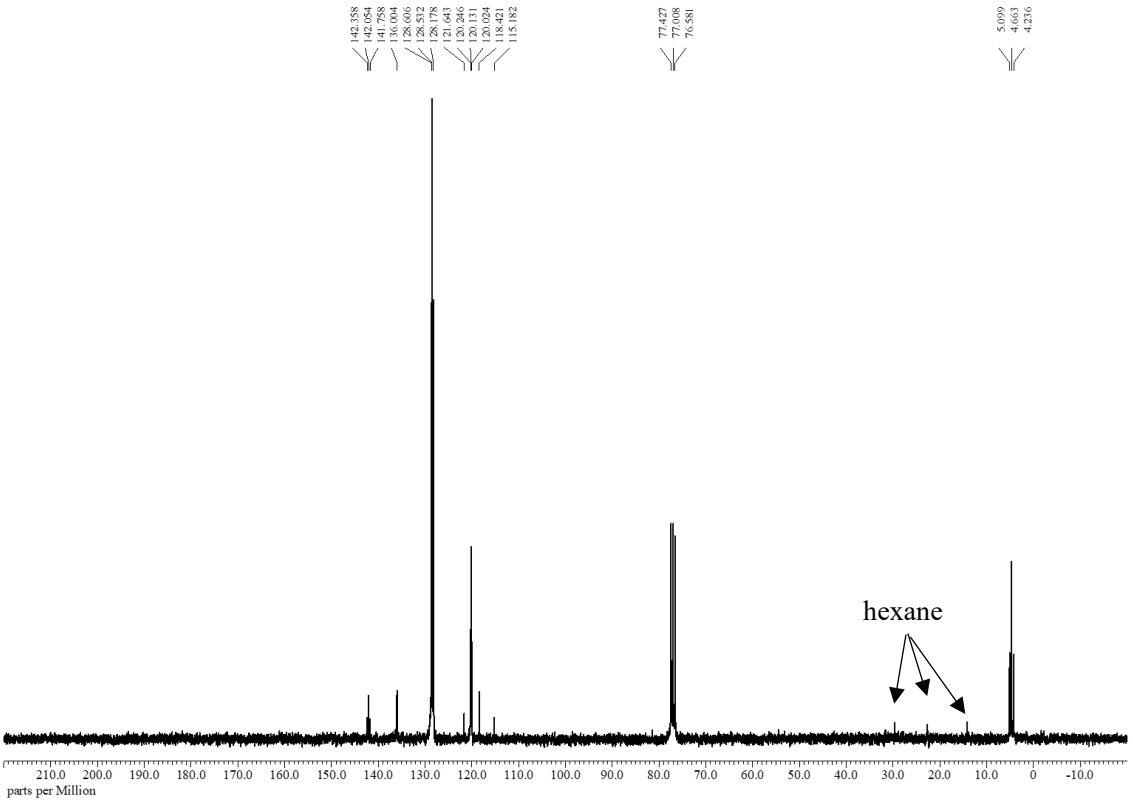


^{19}F NMR spectrum of 1-bromo-4-(2,2-difluoro-1,3-diiodoprop-1-yl)benzene (**3h**)

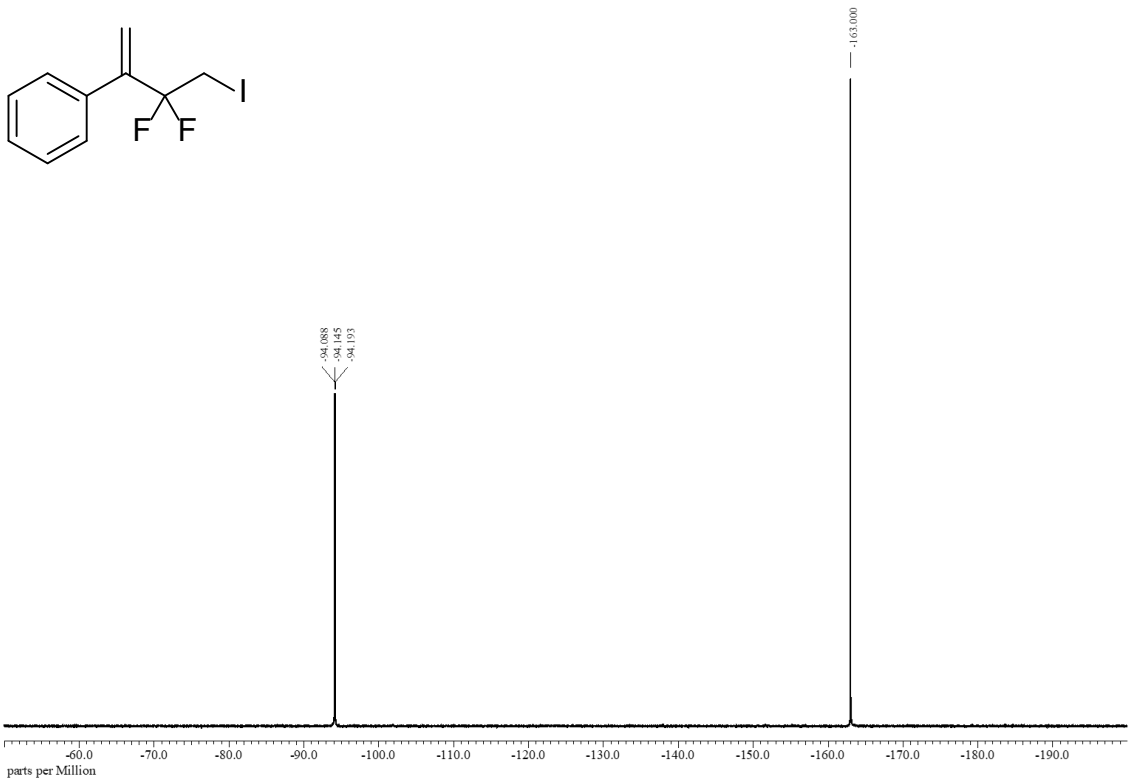


^{1}H and ^{13}C NMR spectra of (3,3-difluoro-4-iodobut-1-en-2-yl)benzene (**4n**)

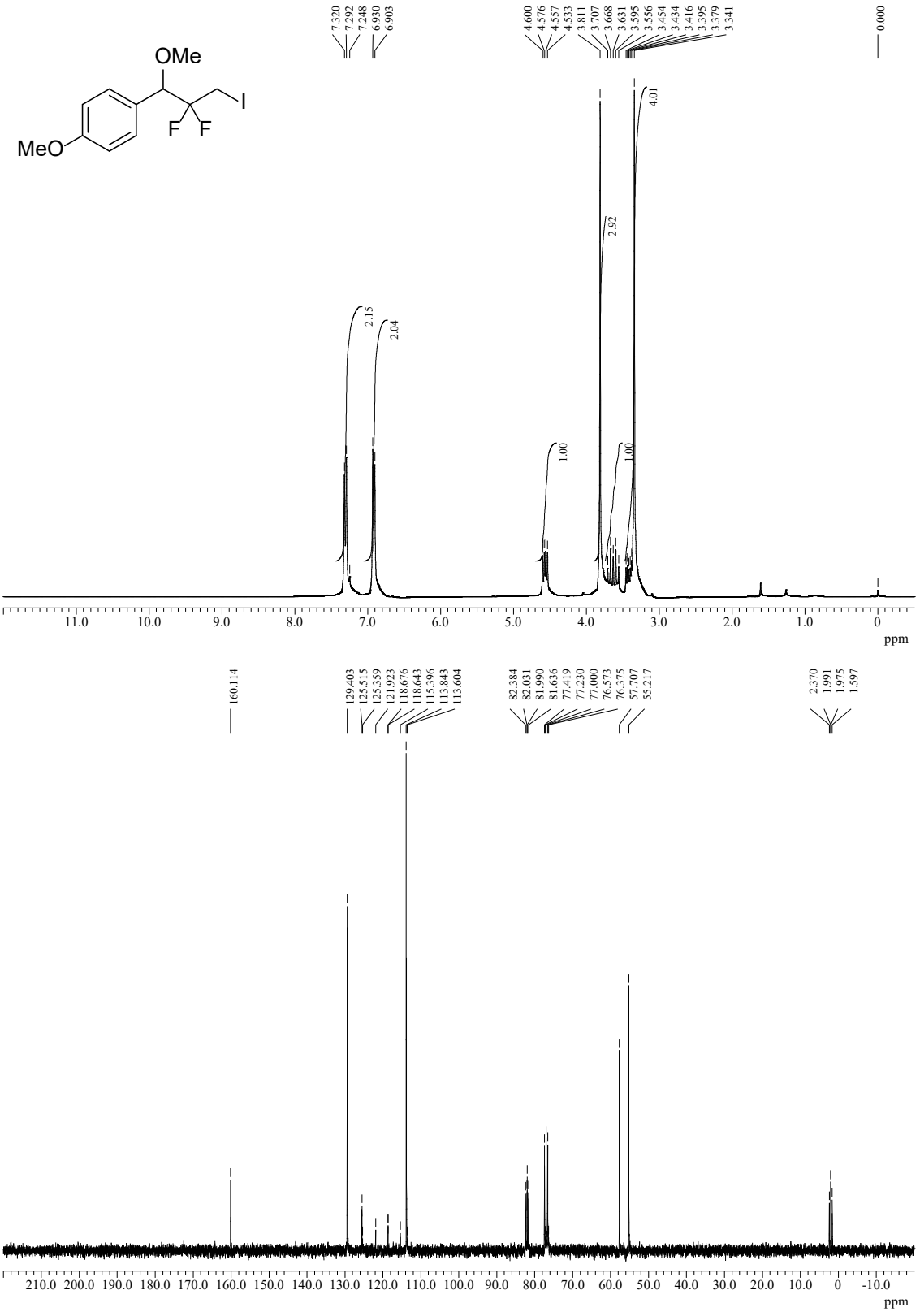




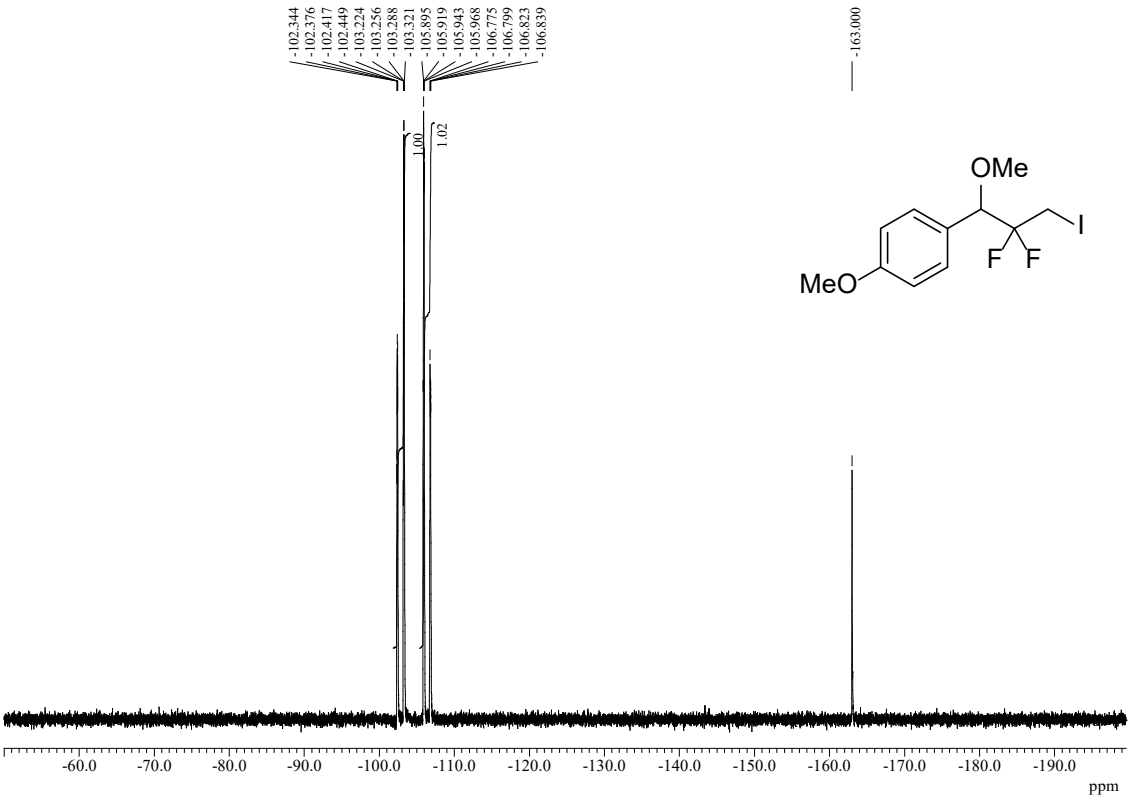
^{19}F NMR spectrum of (3,3-difluoro-4-iodobut-1-en-2-yl)benzene (**4n**)



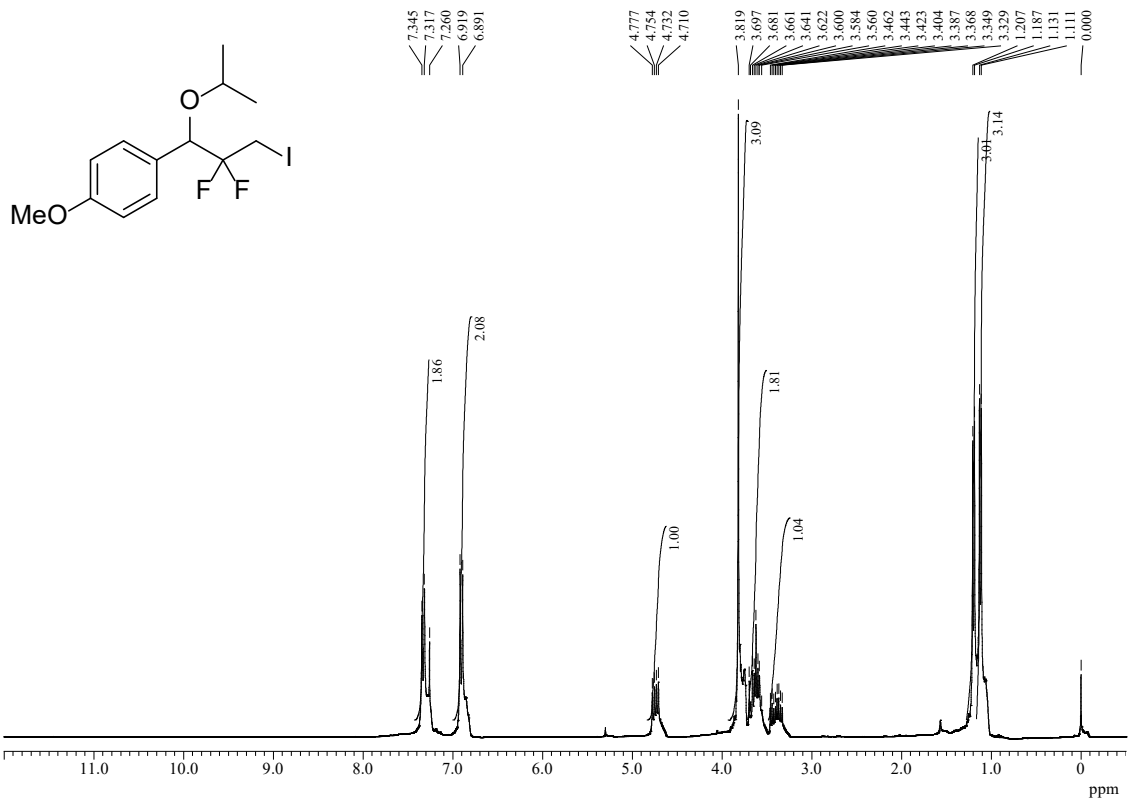
^{1}H and ^{13}C NMR spectra of 1-(2,2-difluoro-3-iodo-1-methoxyprop-1-yl)-4-methoxybenzene (**5aa**)

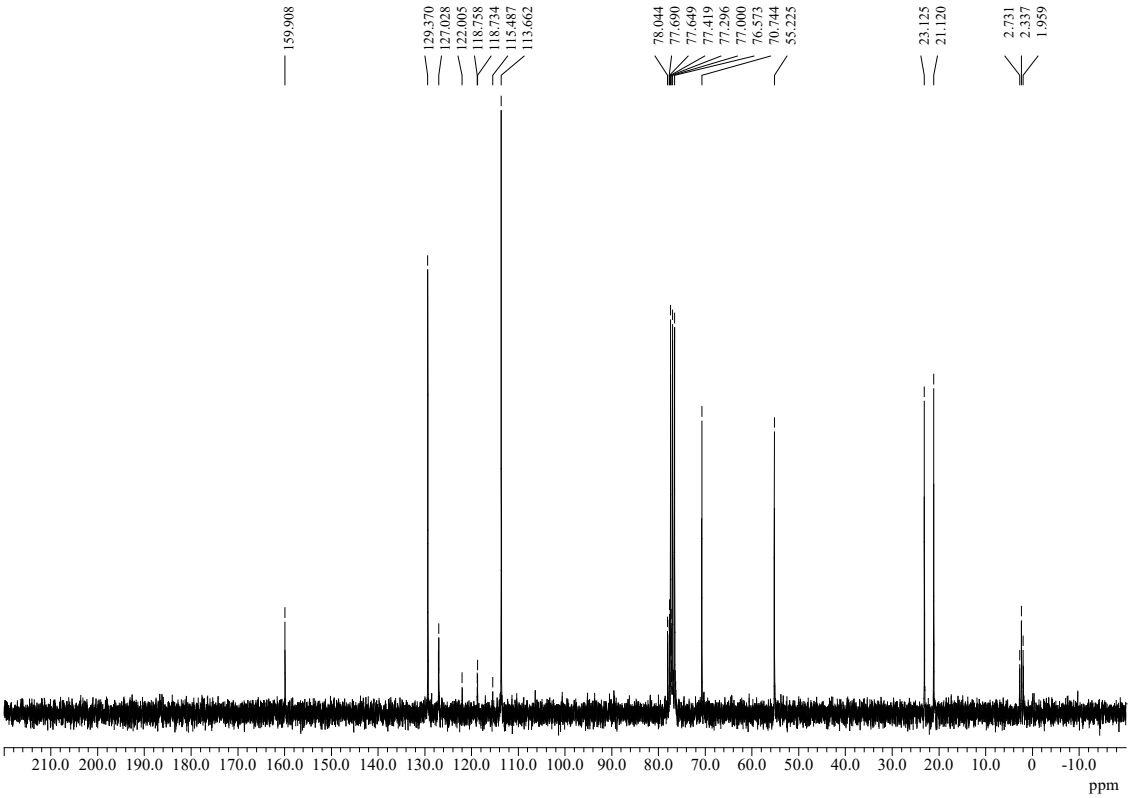


^{19}F NMR spectrum of 1-(2,2-difluoro-3-iodo-1-methoxyprop-1-yl)-4-methoxybenzene (**5aa**)

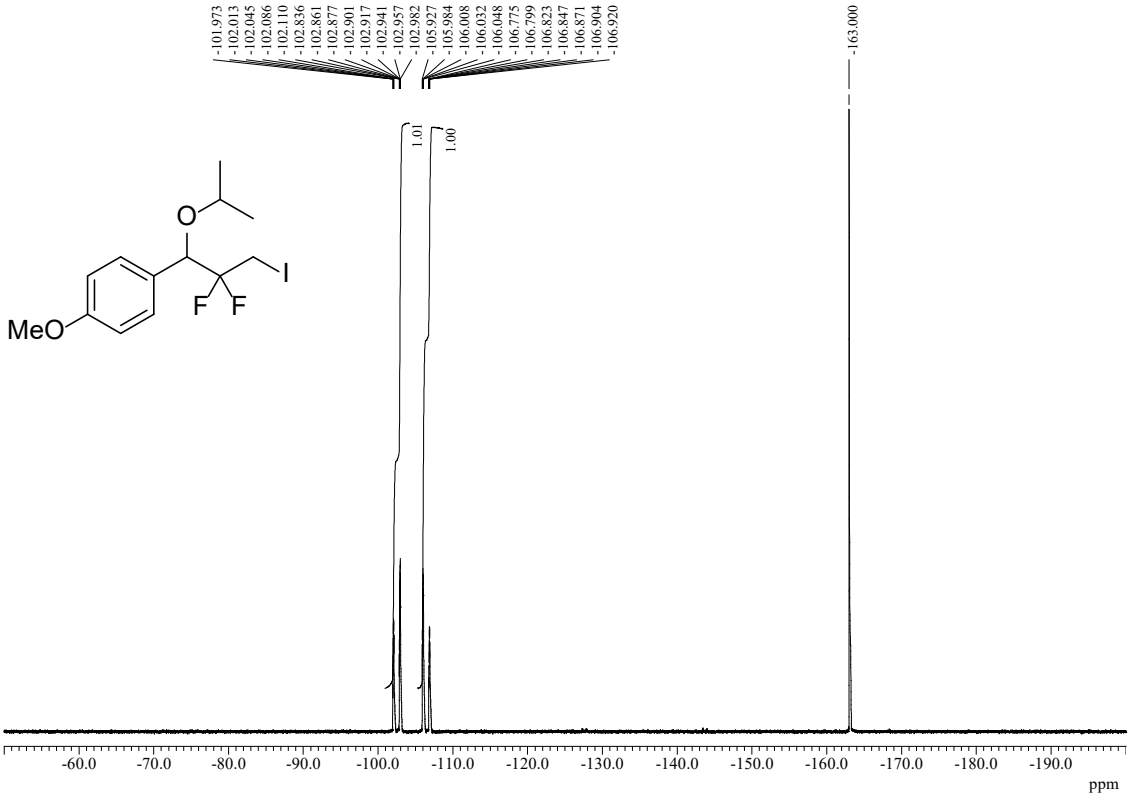


^{1}H and ^{13}C NMR spectra of 1-(2,2-difluoro-3-iodo-1-isopropoxyprop-1-yl)-4-methoxybenzene (**5ab**)

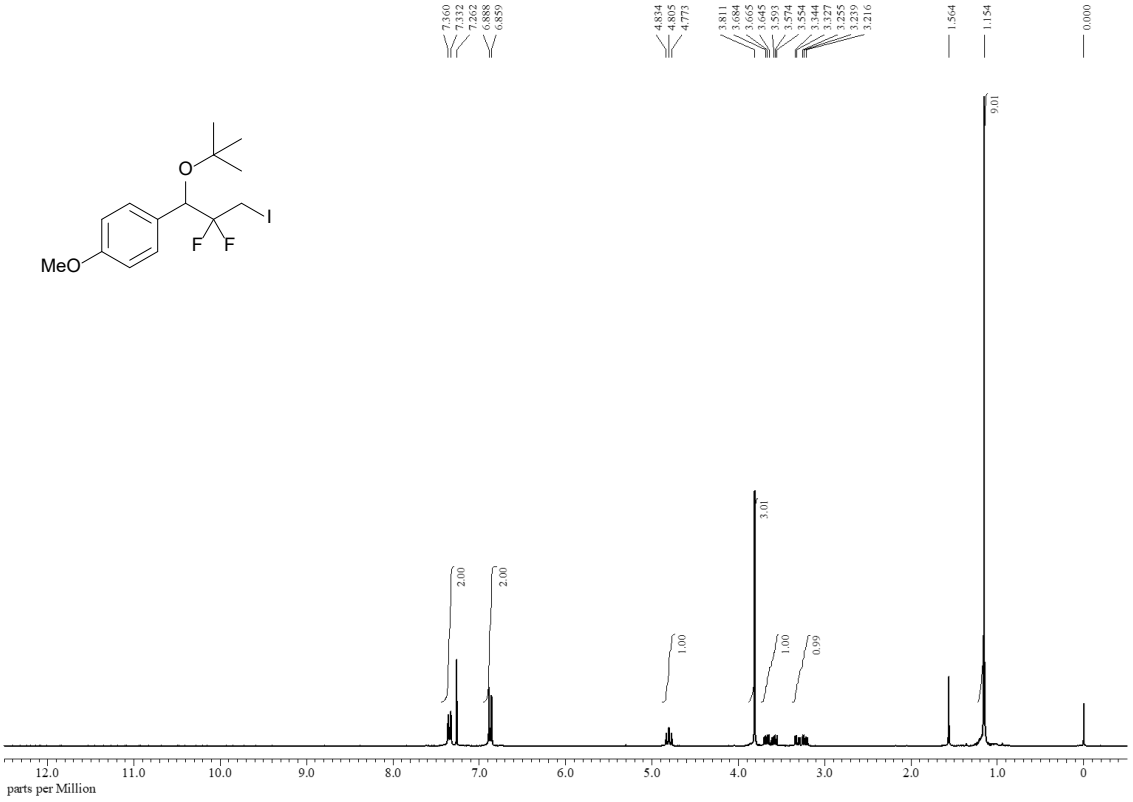


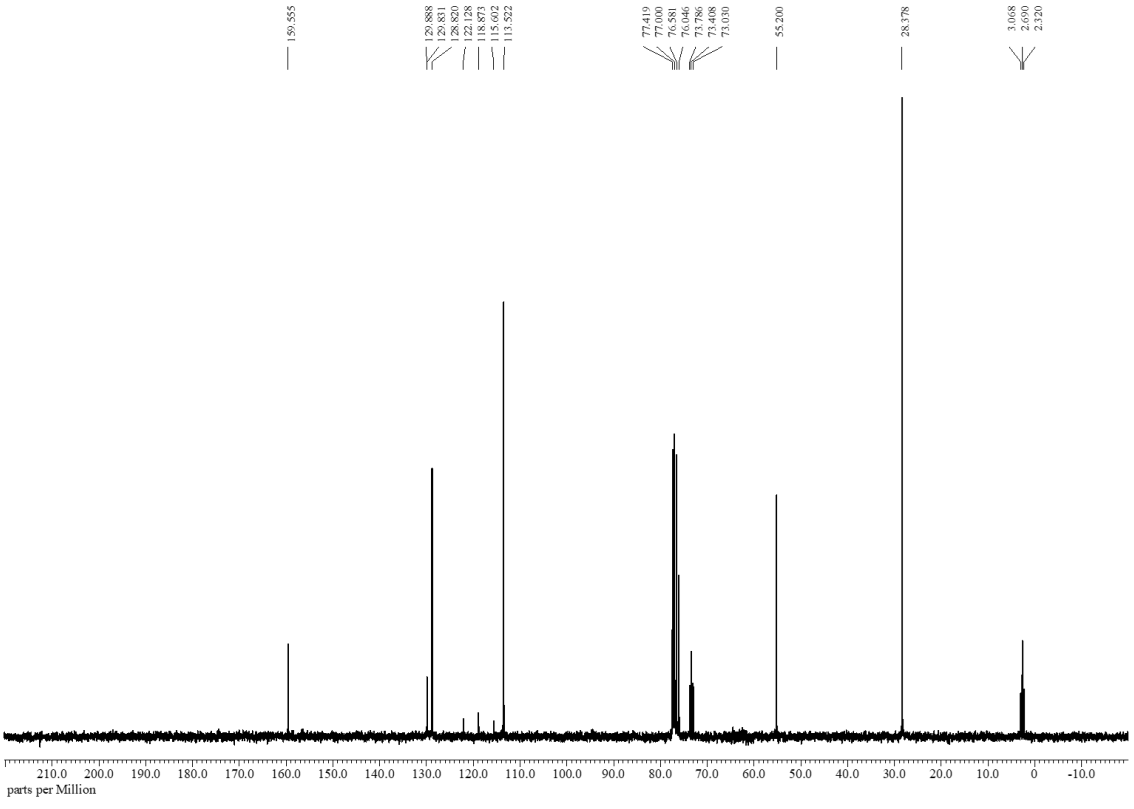


^{19}F NMR spectrum of 1-(2,2-difluoro-3-iodo-1-isopropoxyprop-1-yl)-4-methoxybenzene (**5ab**)

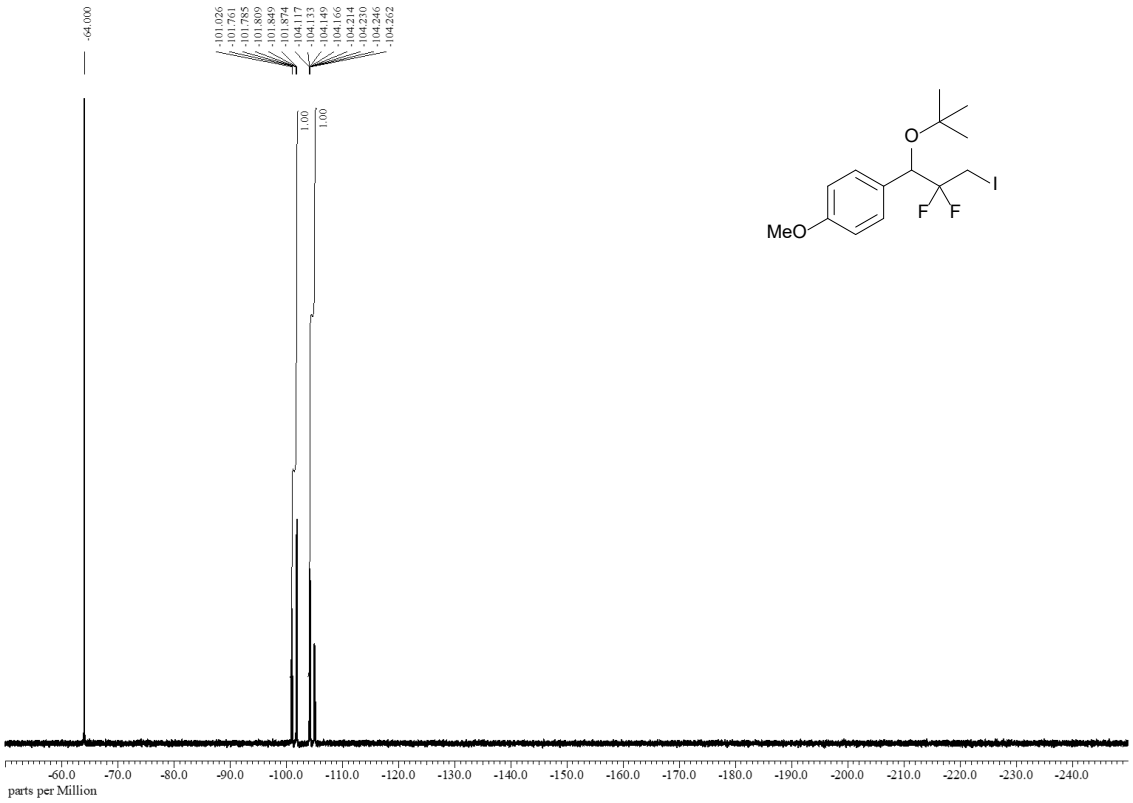


^{1}H and ^{13}C NMR spectra of 1-(2,2-difluoro-3-iodo-1-*tert*-butoxyprop-1-yl)-4-methoxybenzene (**5ac**)

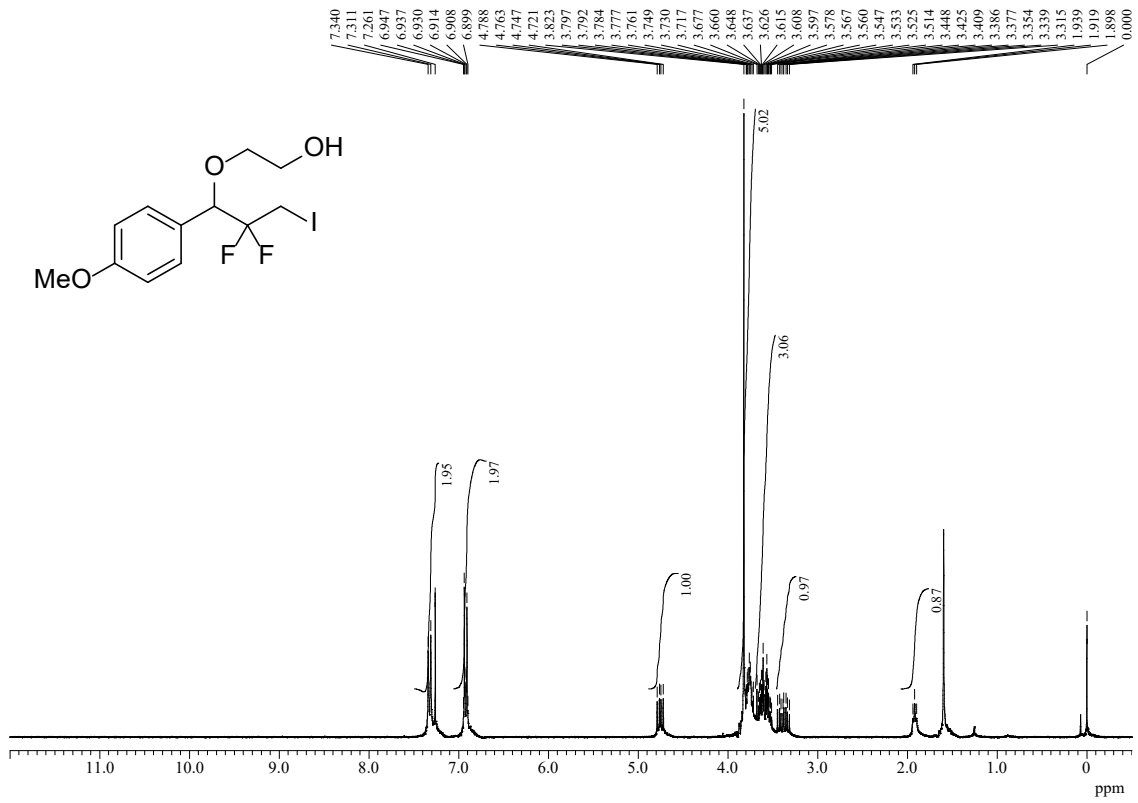


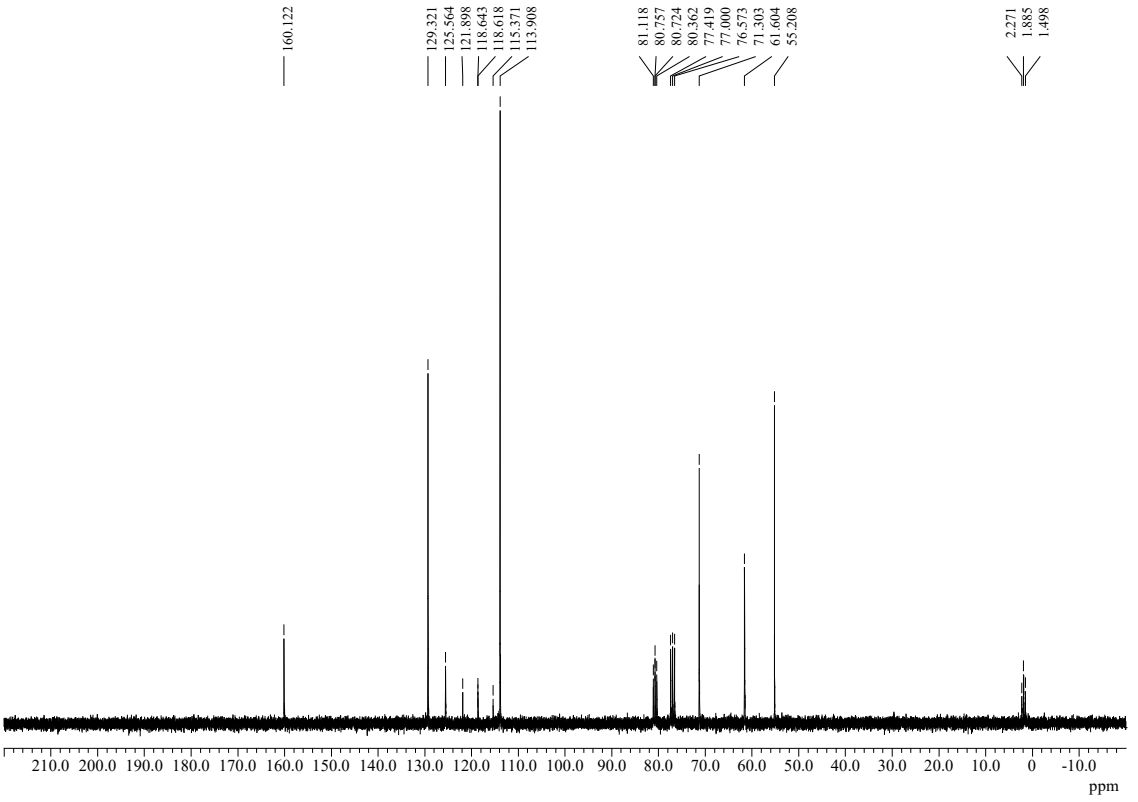


^{19}F NMR spectrum of 1-(2,2-difluoro-3-iodo-1-*tert*-butoxyprop-1-yl)-4-methoxybenzene (**5ac**)

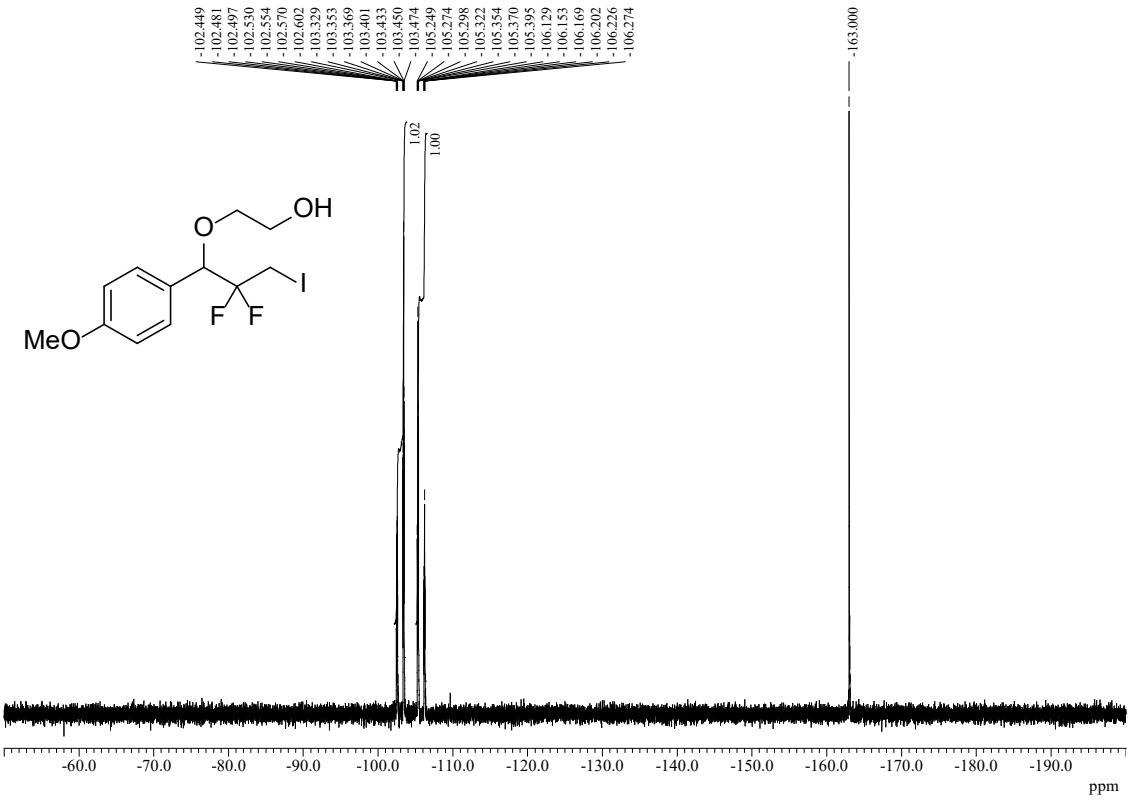


^{1}H and ^{13}C NMR spectra of 2-{2,2-difluoro-3-iodo-1-(4-methoxyphenyl)propyloxy}ethan-1-ol (**5ad**)

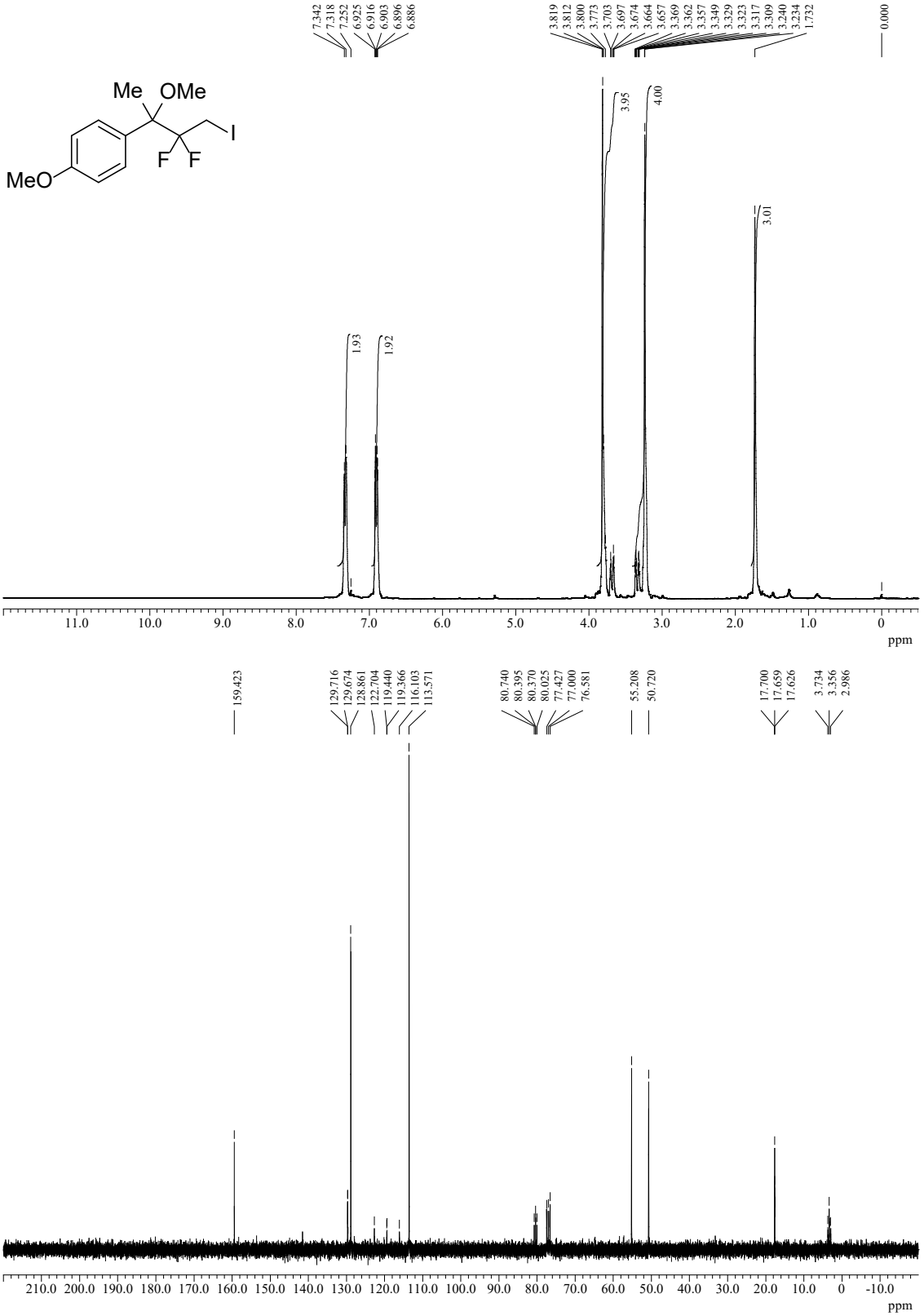




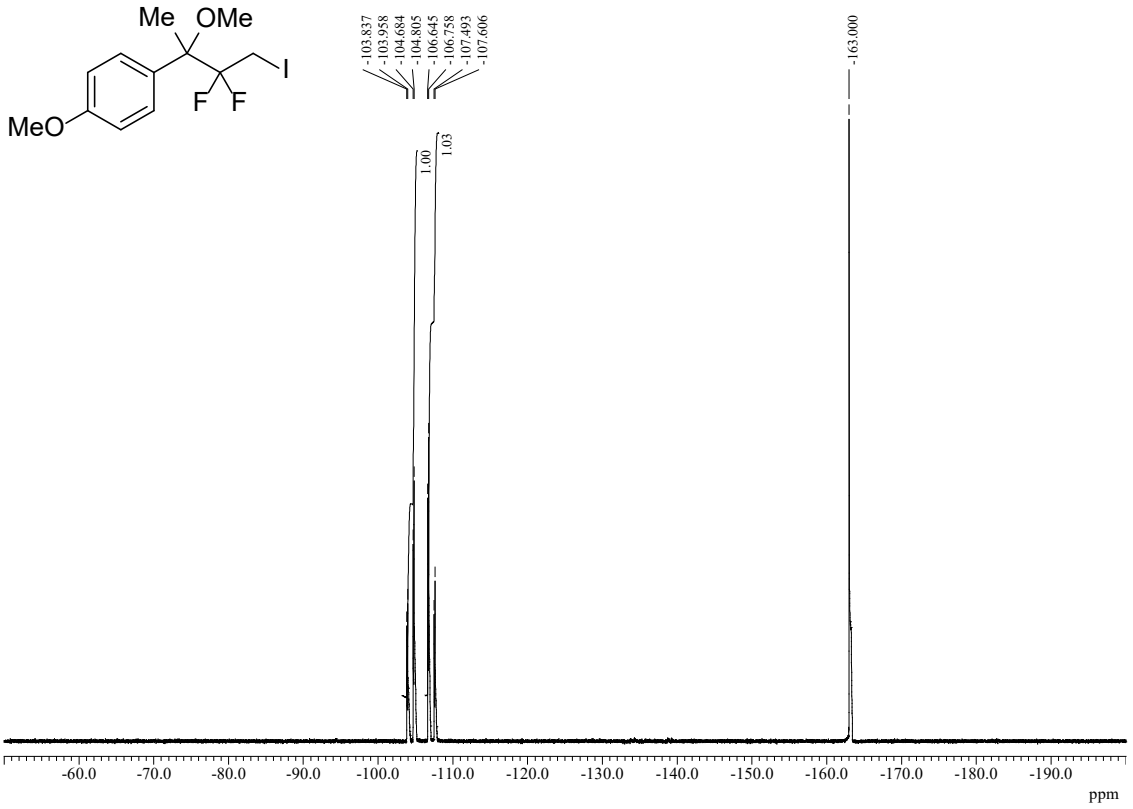
^{19}F NMR spectrum of 2-{2,2-difluoro-3-iodo-1-(4-methoxyphenyl)propyloxy}ethan-1-ol (**5ad**)



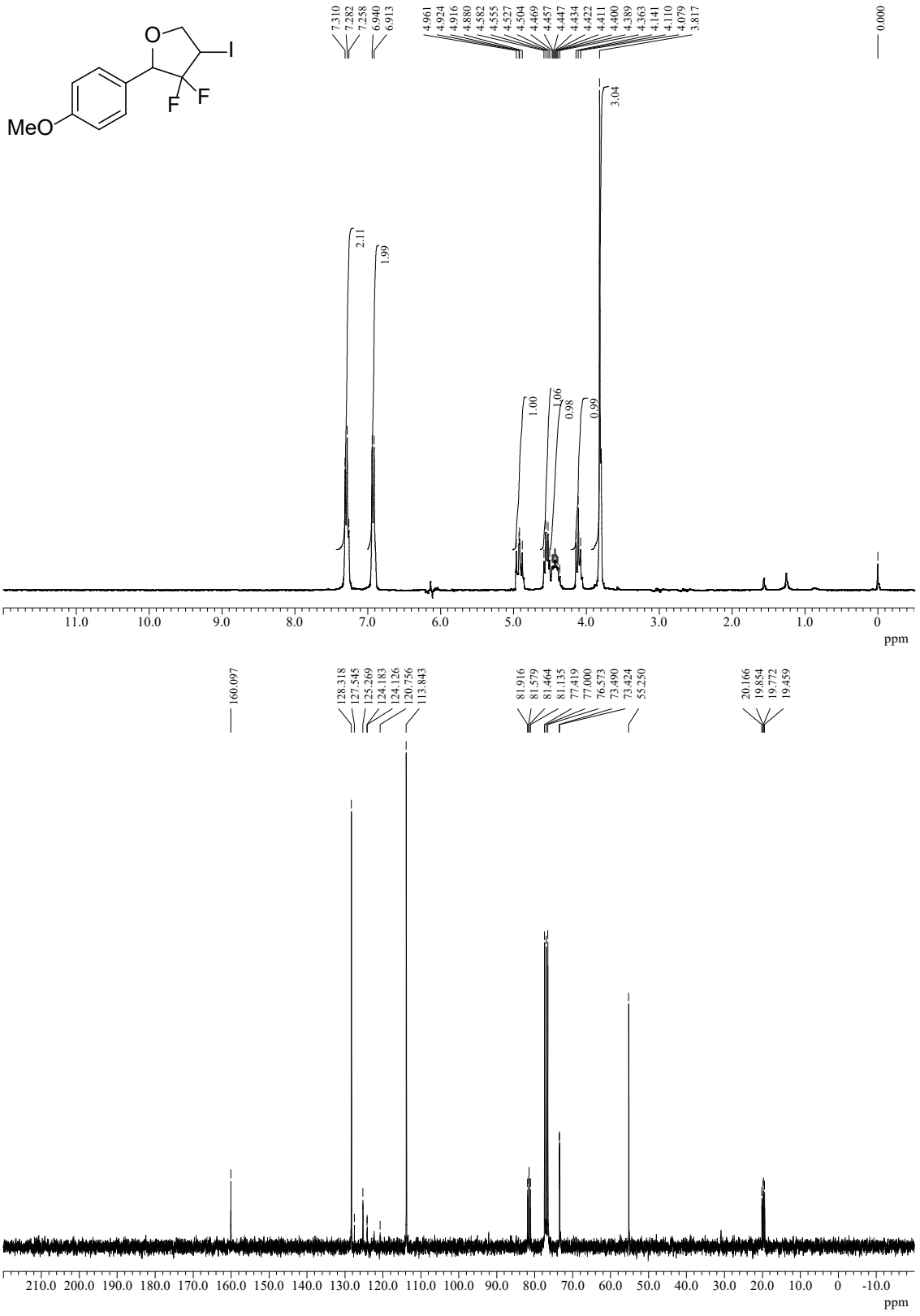
^{1}H and ^{13}C NMR spectra of 1-(3,3-difluoro-4-iodo-2-methoxybut-2-yl)-4-methoxybenzene (**5ja**)



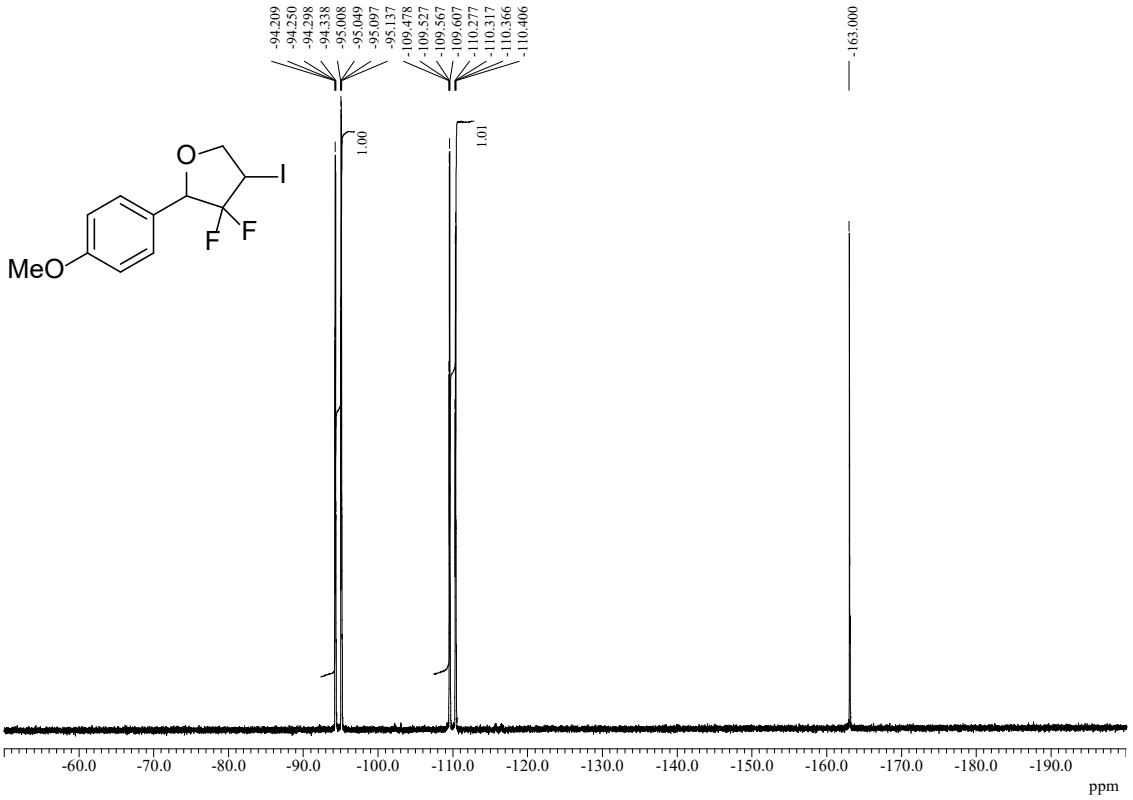
^{19}F NMR spectra of 1-(3,3-difluoro-4-iodo-2-methoxybut-2-yl)-4-methoxybenzene (**5ja**)



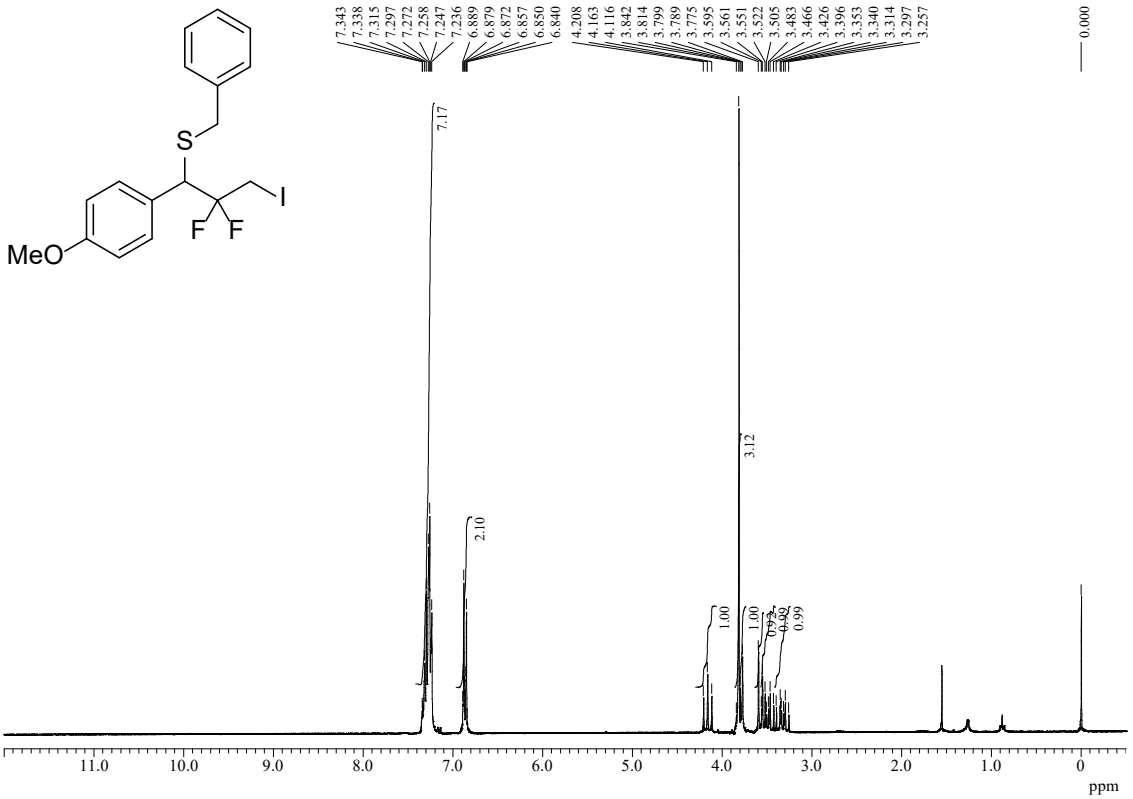
^{1}H and ^{13}C NMR spectra of 3,3-difluoro-4-iodo-2-(4-methoxyphenyl)tetrahydrofuran (**6**)

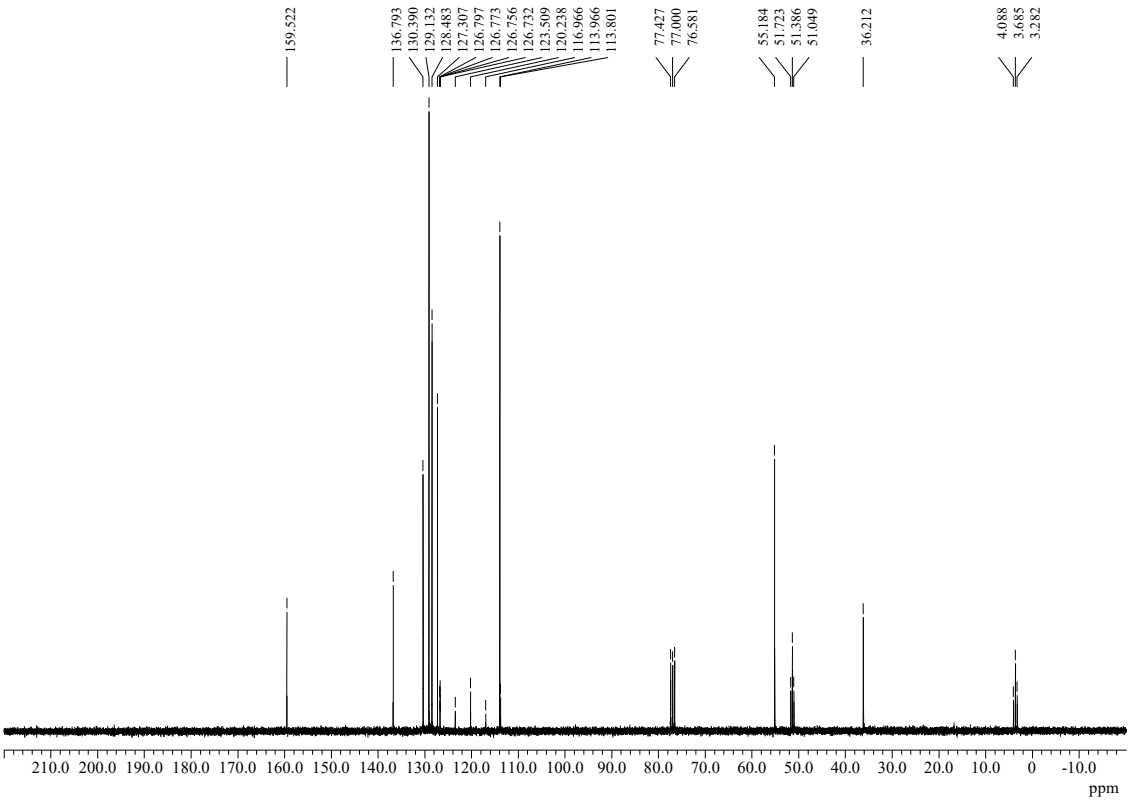


^{19}F NMR spectrum of 3,3-difluoro-4-iodo-2-(4-methoxyphenyl)tetrahydrofuran (major-**6**, **65**:35)

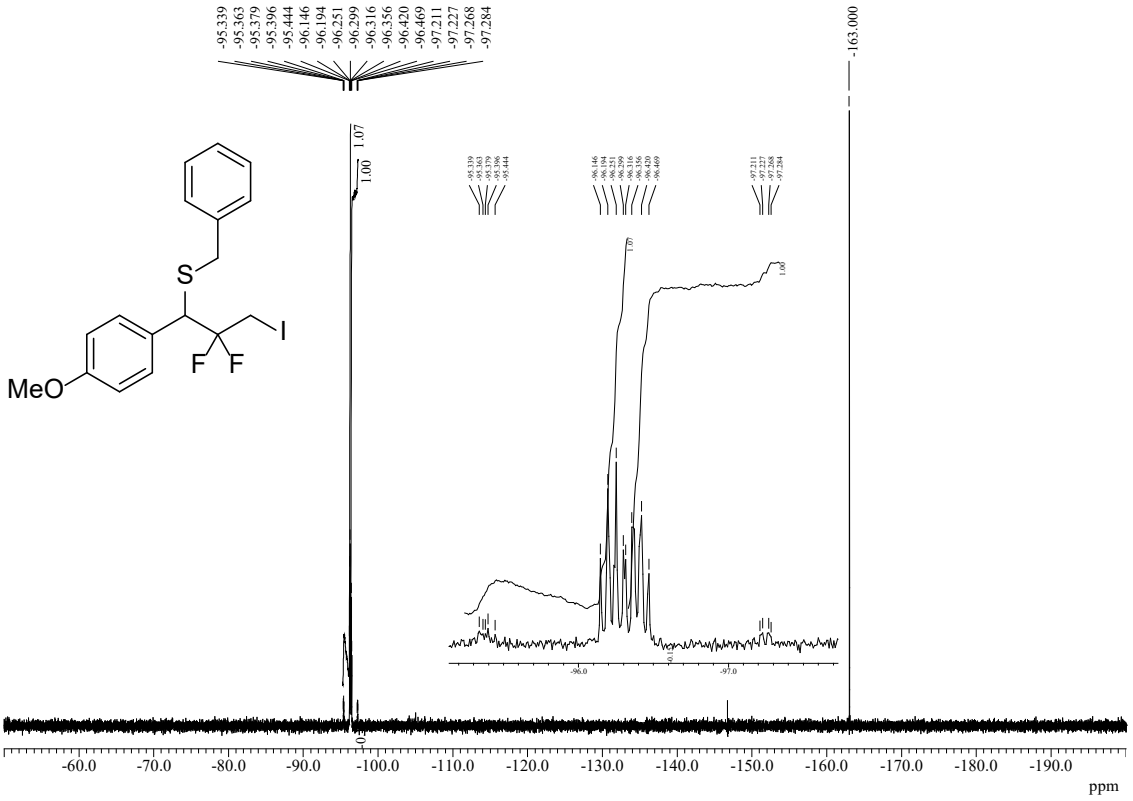


^{1}H and ^{13}C NMR spectra of 1-(1-benzylsulfenyl-2,2-difluoro-3-iodoprop-1-yl)-4-methoxybenzene (**7aa**)

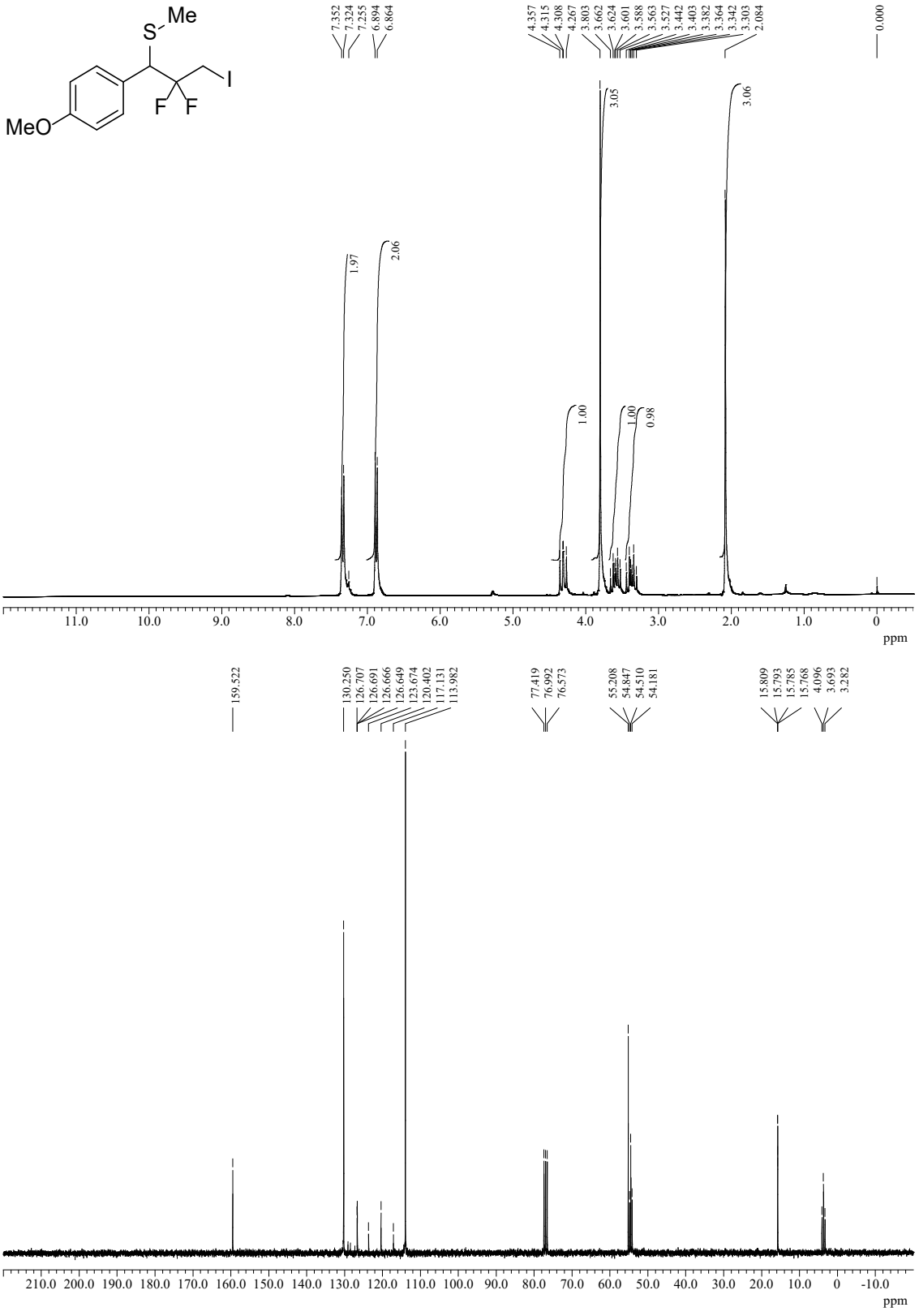




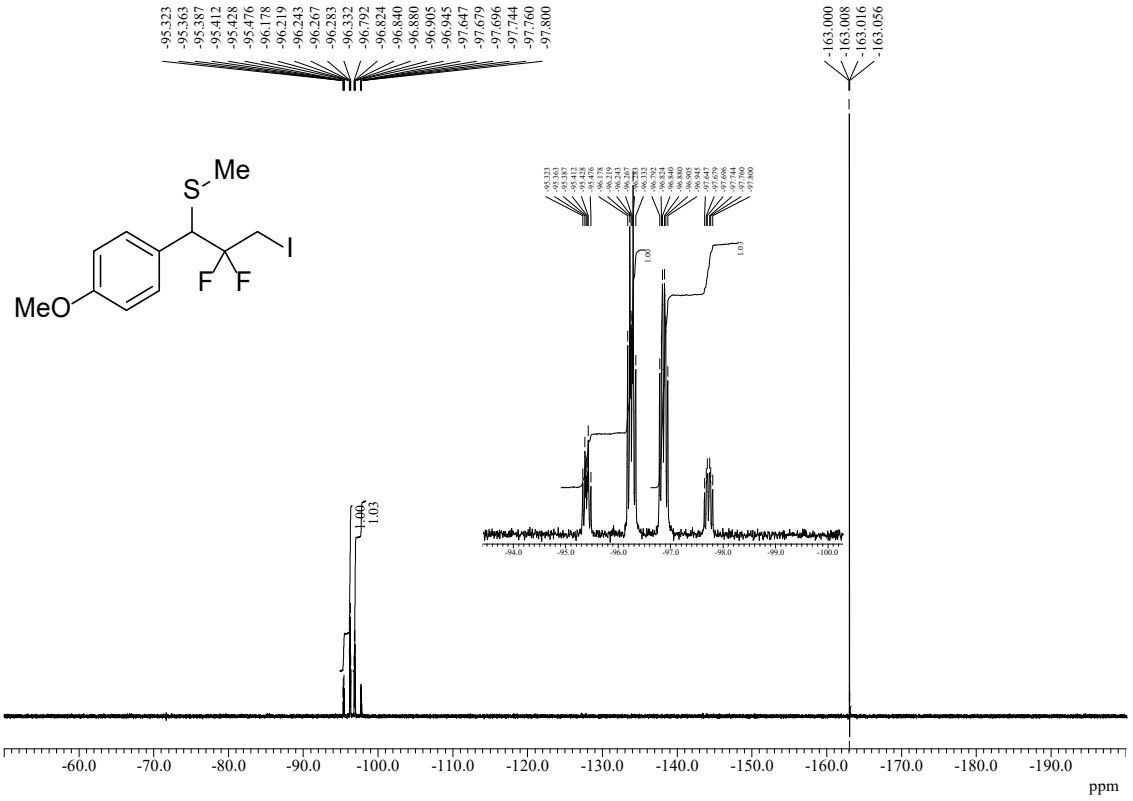
^{19}F NMR spectrum of 1-(1-benzylsulfenyl-2,2-difluoro-3-iodoprop-1-yl)-4-methoxybenzene (**7aa**)



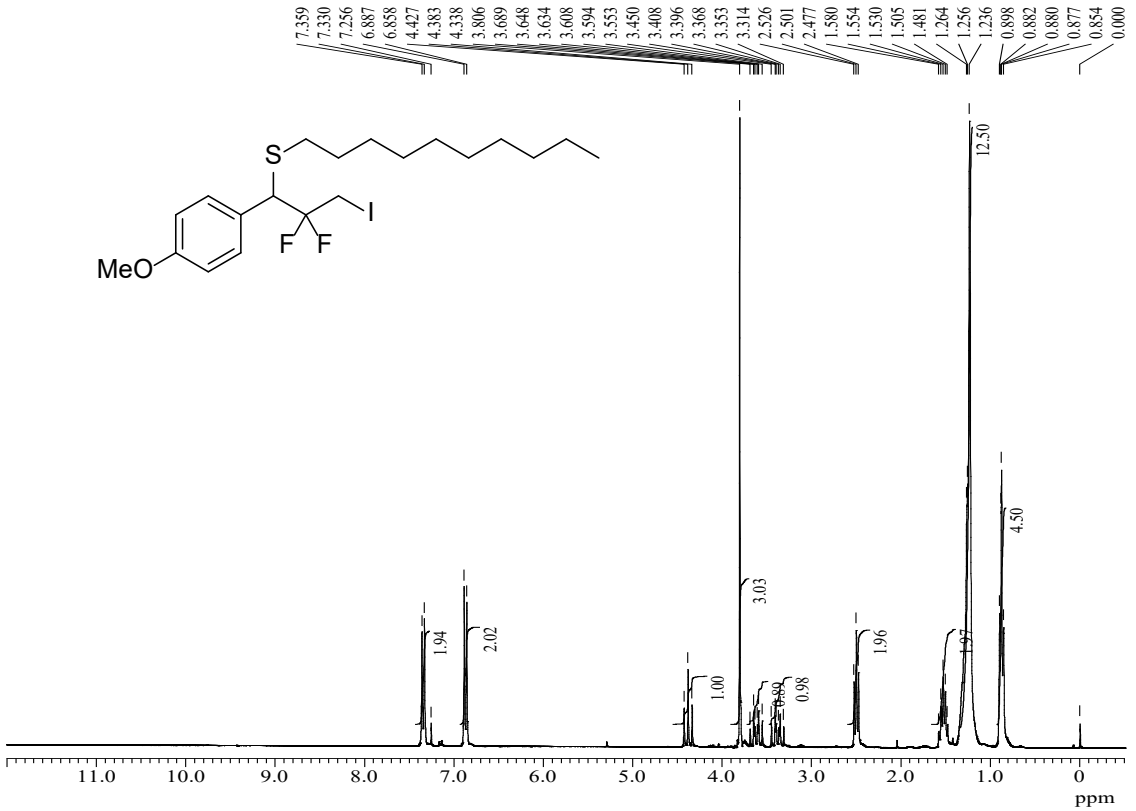
^{1}H and ^{13}C NMR spectra of 1-(2,2-difluoro-3-iodo-1-methylsulfenylprop-1-yl)-4-methoxybenzene (**7ab**)

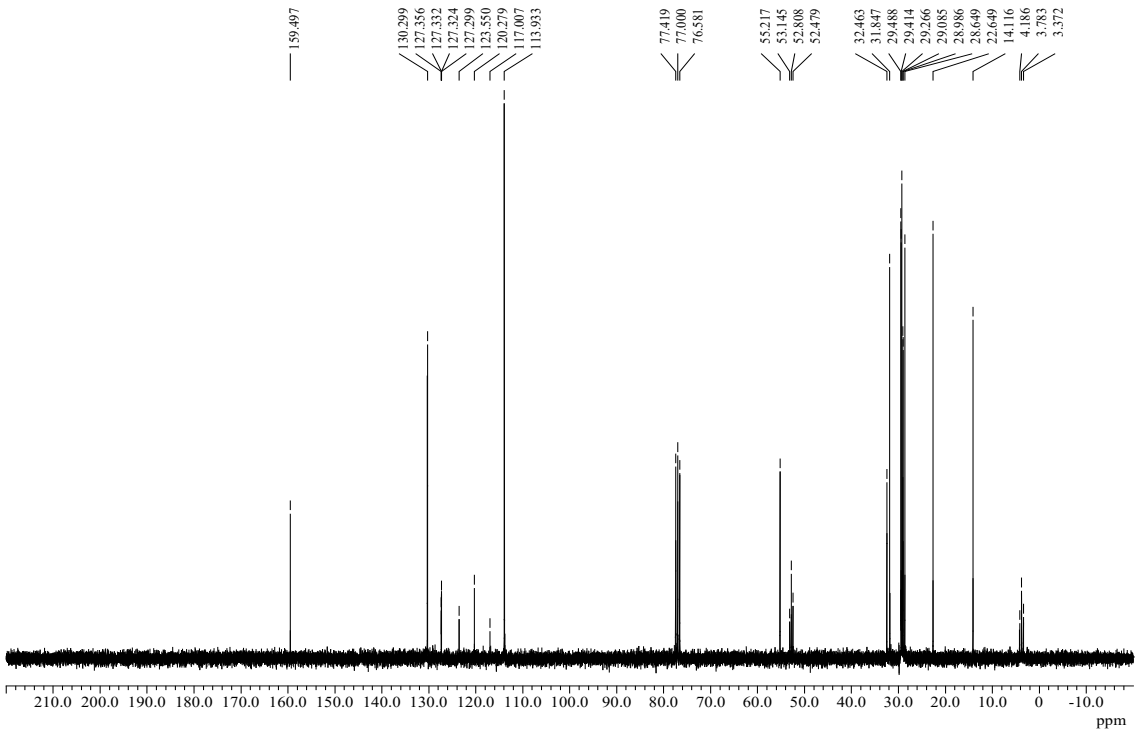


^{19}F NMR spectrum of 1-(2,2-difluoro-3-iodo-1-methylsulfenylprop-1-yl)-4-methoxybenzene (**7ab**)

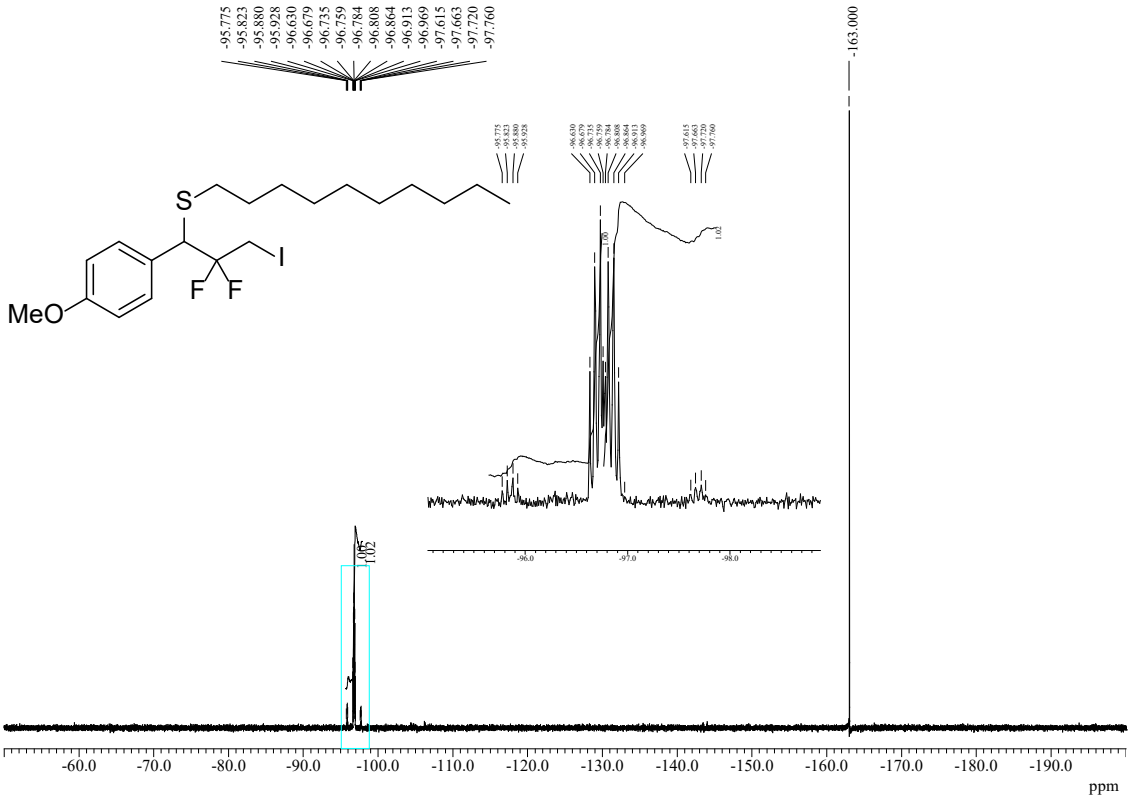


^{1}H and ^{13}C NMR spectra of 1-(1-decylsulfenyl-2,2-difluoro-3-iodoprop-1-yl)-4-methoxybenzene (**7ac**)

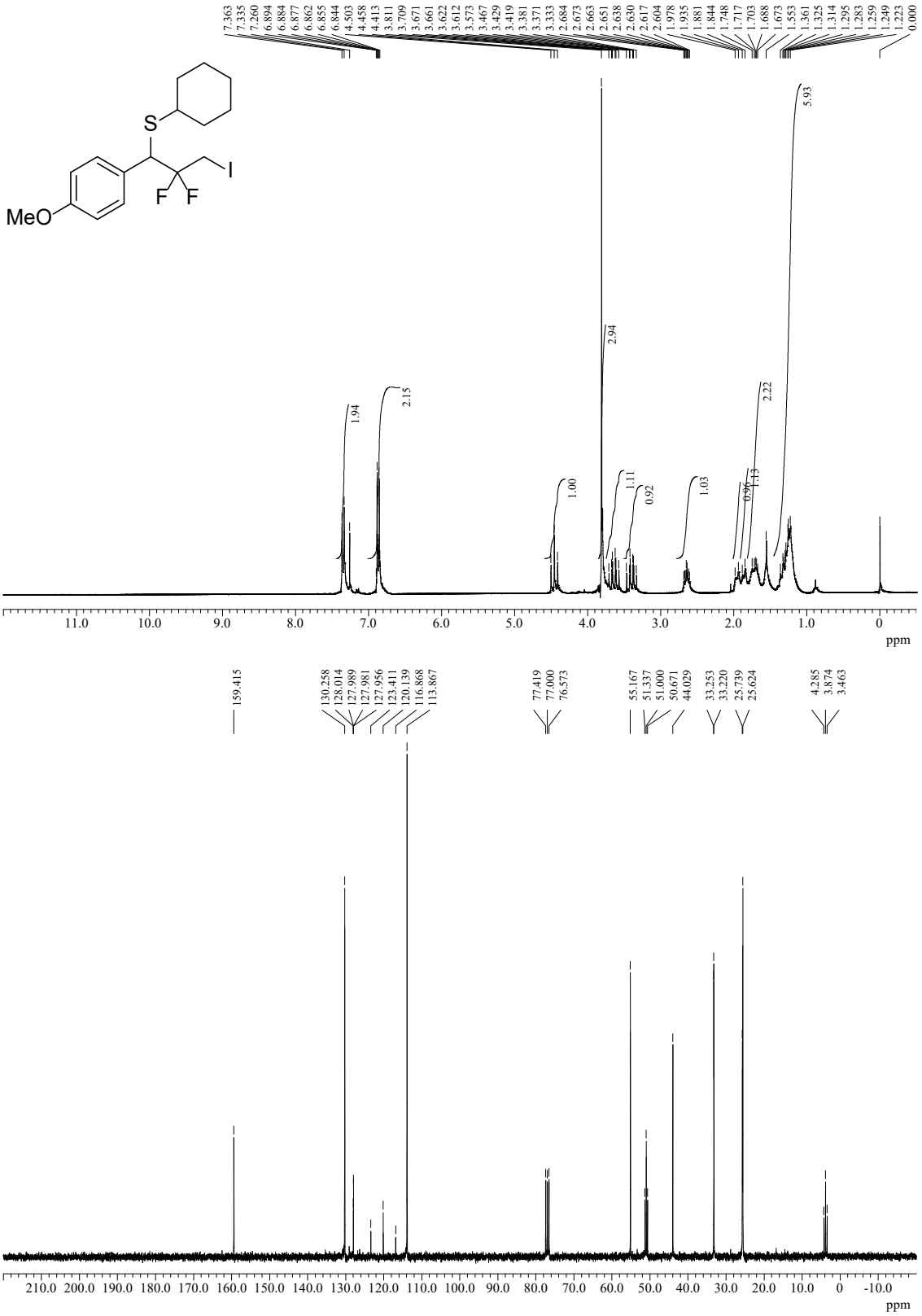




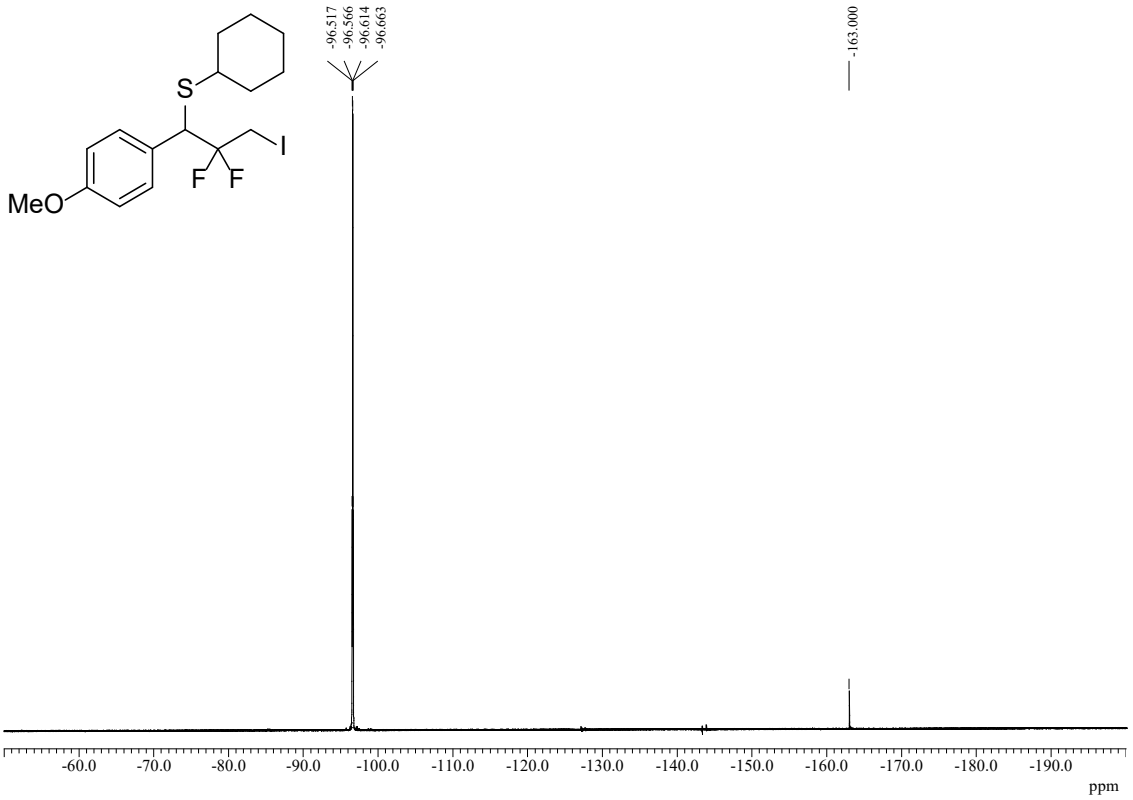
^{19}F NMR spectrum of 1-(1-decylsulfenyl-2,2-difluoro-3-iodoprop-1-yl)-4-methoxybenzene (**7ac**)



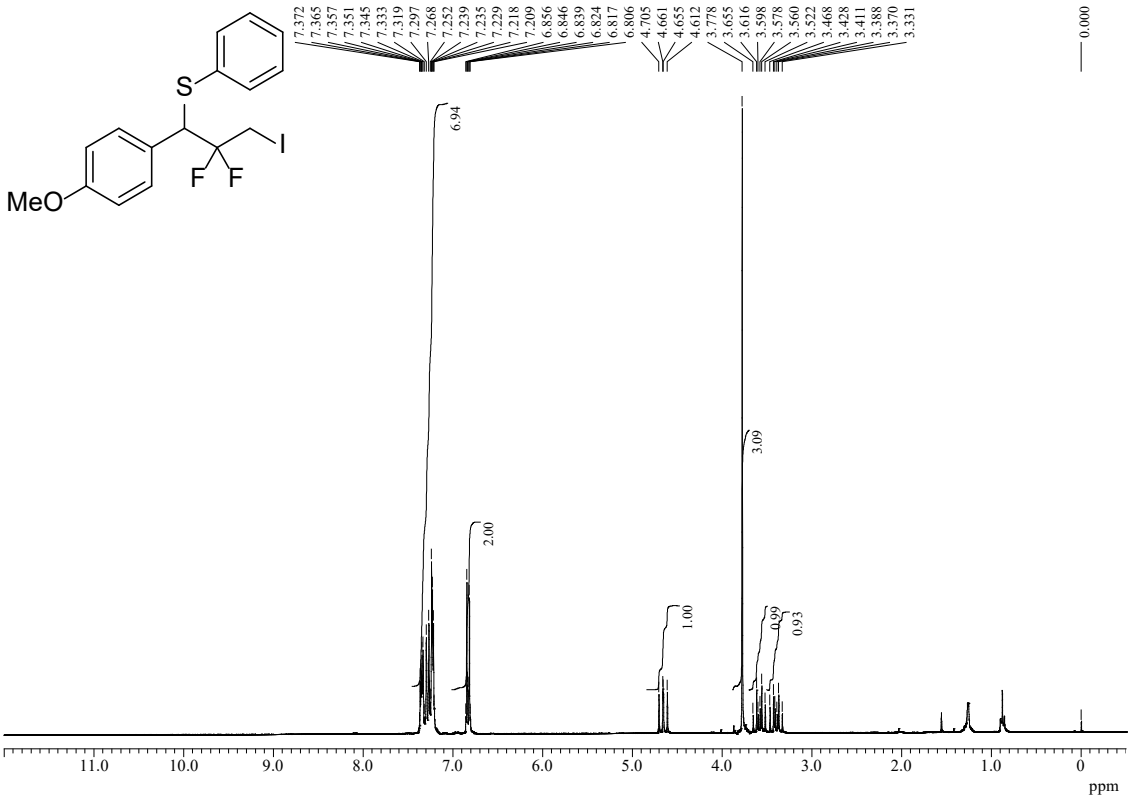
^{1}H and ^{13}C NMR spectra of 1-(1-cyclohexylsulfenyl-2,2-difluoro-3-iodoprop-1-yl)-4-methoxybenzene (**7ad**)

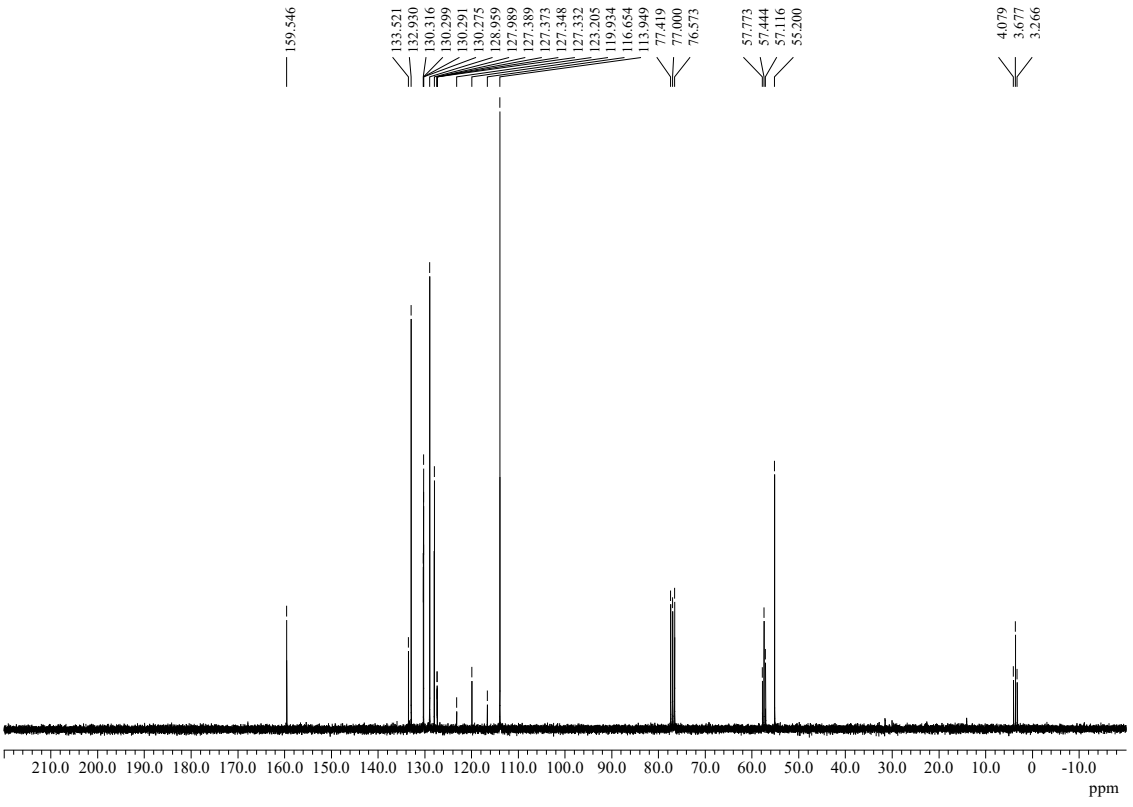


^{19}F NMR spectrum of 1-(1-cyclohexylsulfenyl-2,2-difluoro-3-iodoprop-1-yl)-4-methoxybenzene (**7ad**)

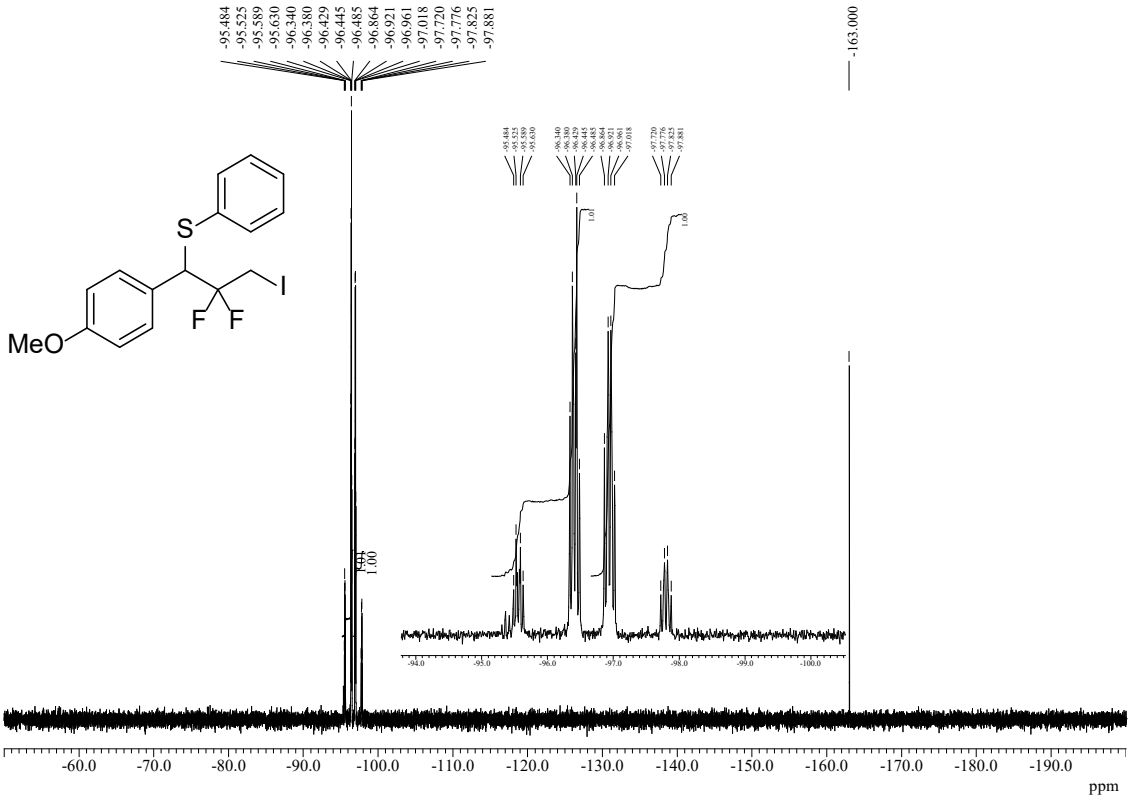


^{1}H and ^{13}C NMR spectra of 1-(2,2-difluoro-3-iodo-1-phenylsulfenylprop-1-yl)-4-methoxybenzene (**7ae**)

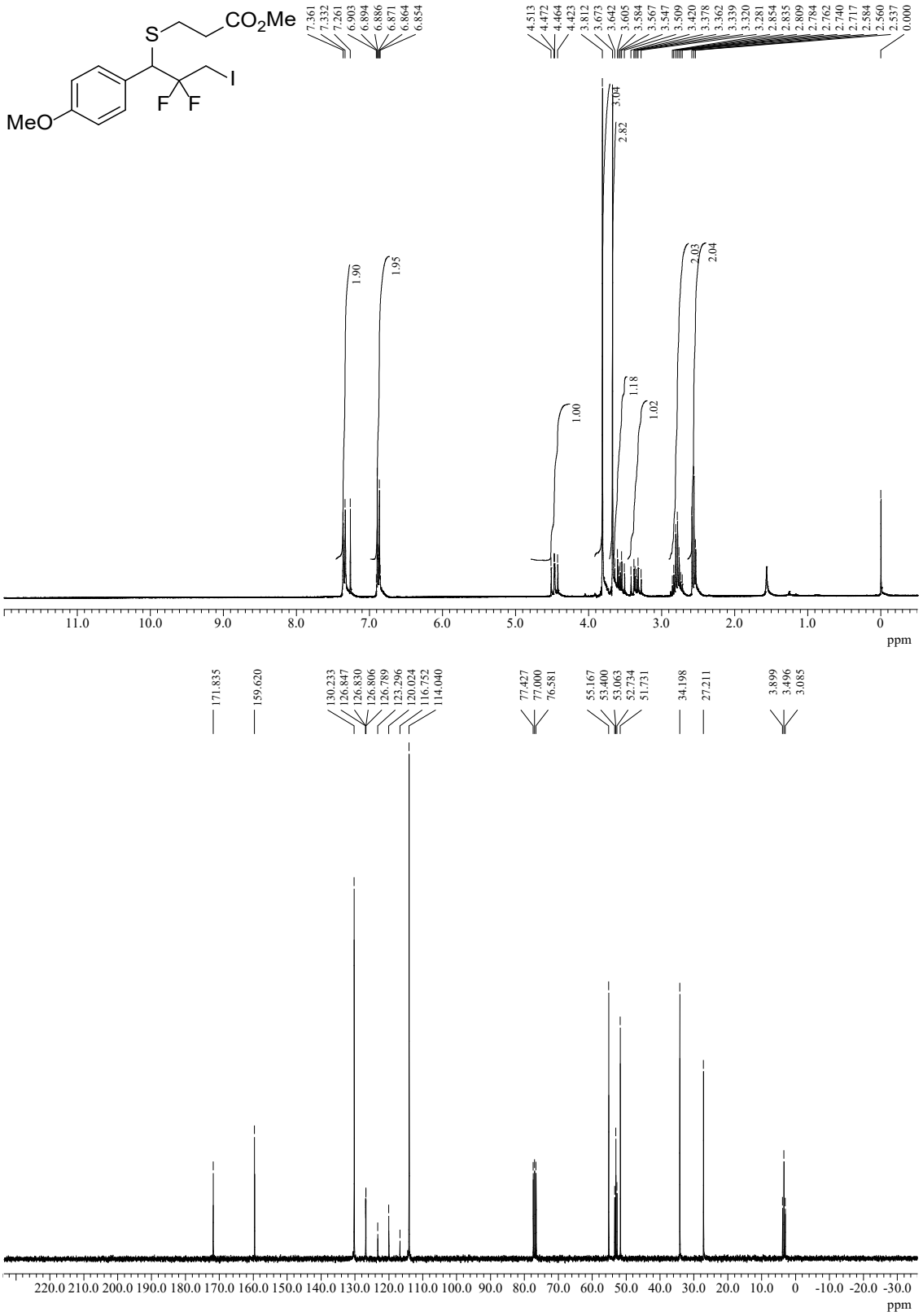




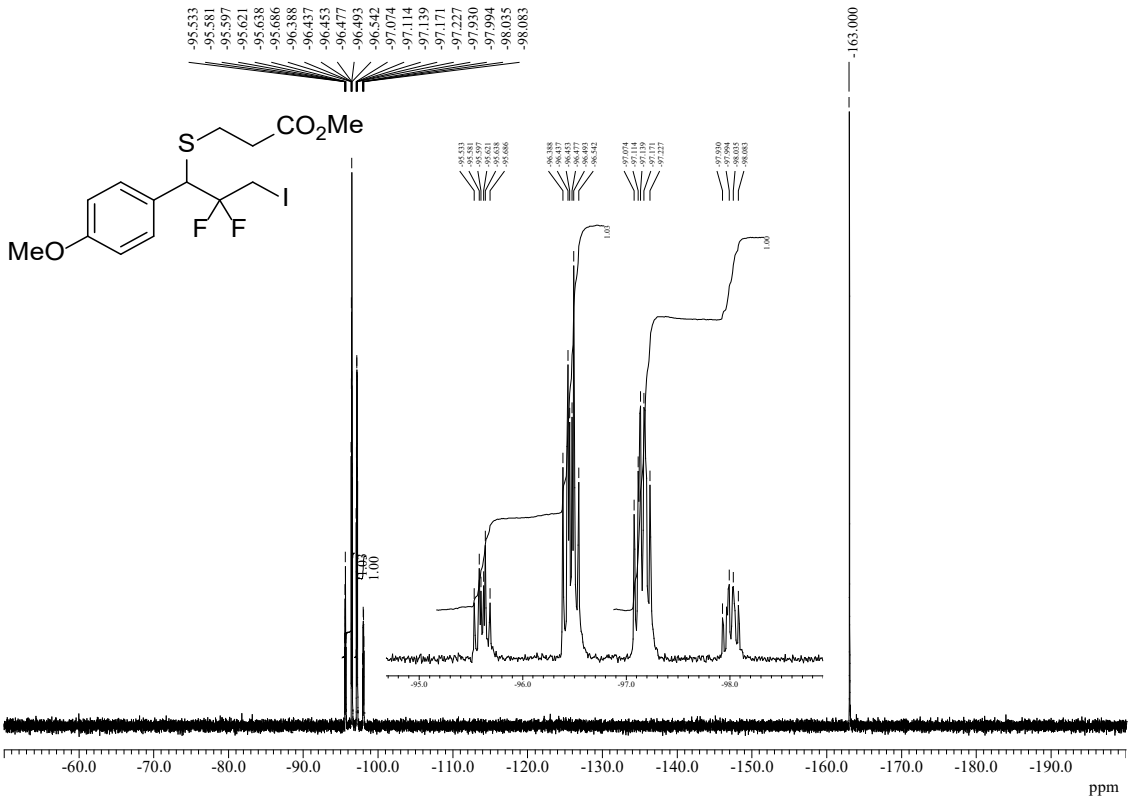
^{19}F NMR spectrum of 1-{(2,2-difluoro-3-iodo-1-phenylsulfenyl)propyl}-4-methoxybenzene (**7ae**)



^{1}H and ^{13}C NMR spectra of methyl 3-{1-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]-sulfenyl}propanoate (**7af**)

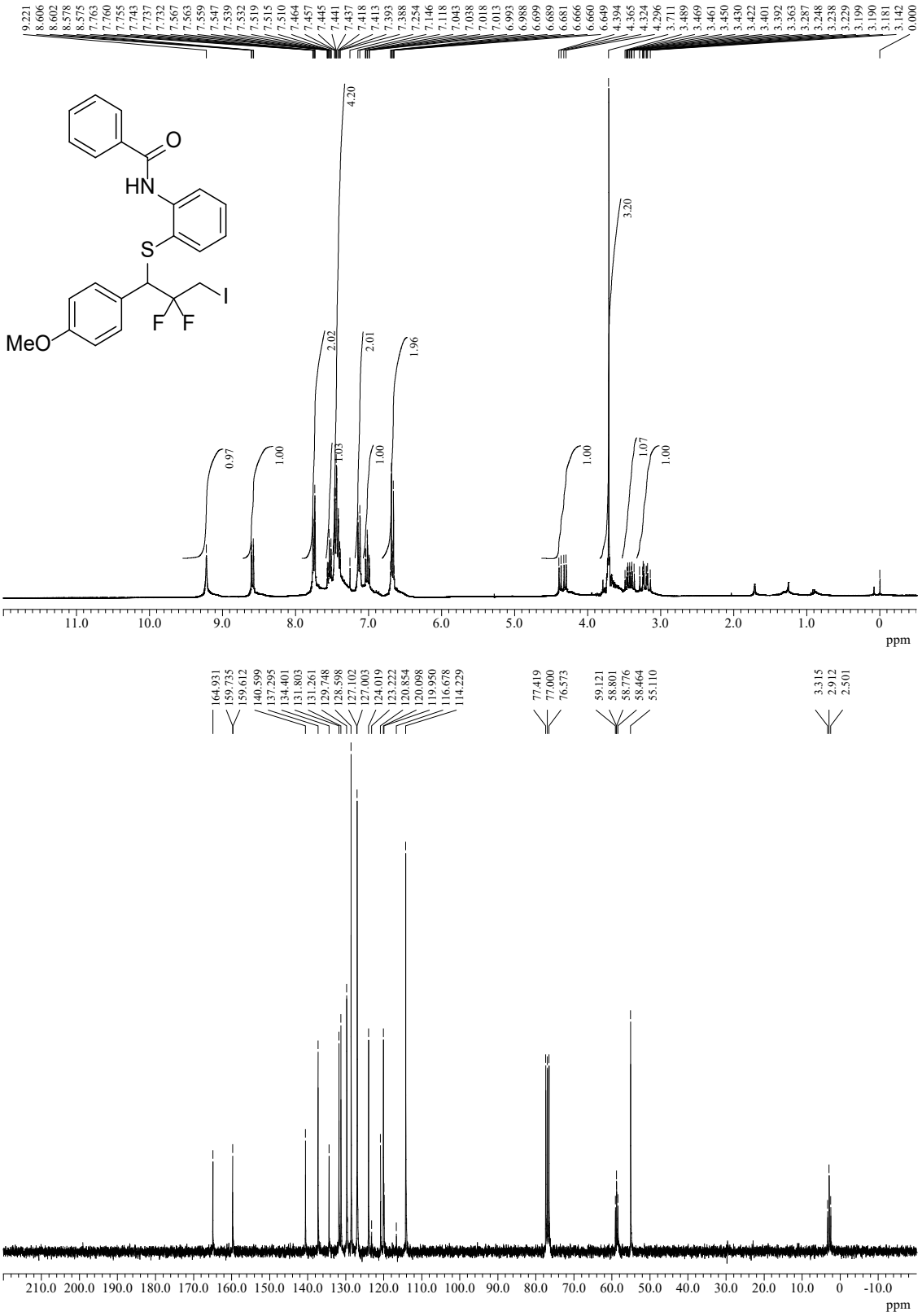


^{19}F NMR spectrum of methyl 3-{1-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]sulfenyl}-propanoate (**7af**)



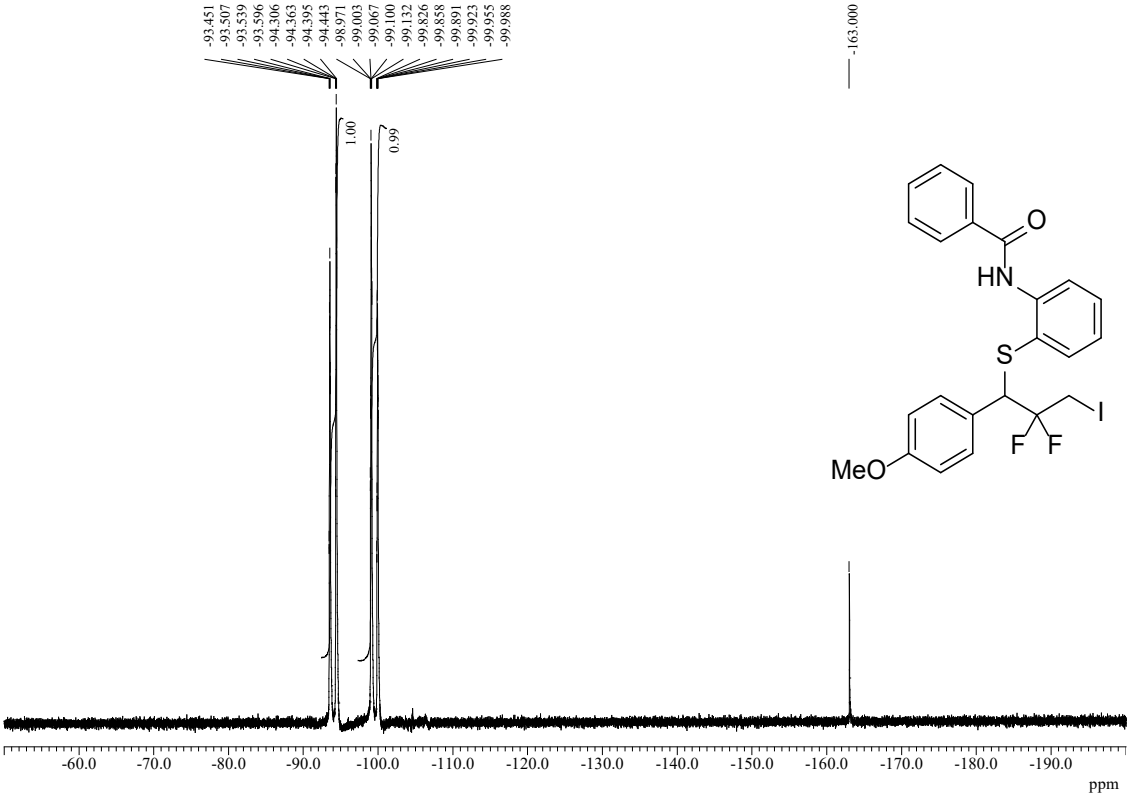
^{1}H and ^{13}C NMR spectra of

N-{2-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]sulfenyl}phenyl]benzamide (**7ag**)

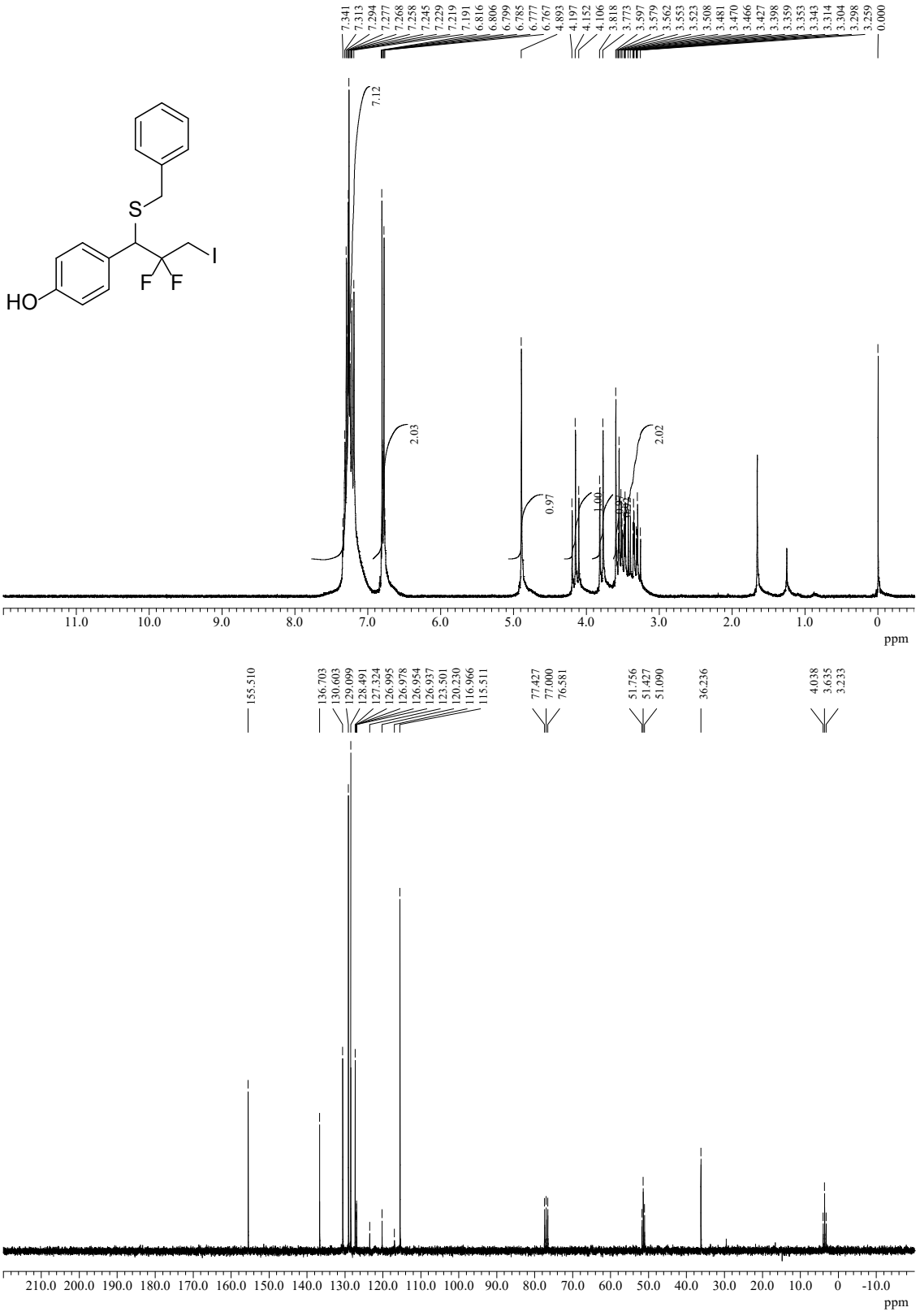


^{19}F NMR spectrum of

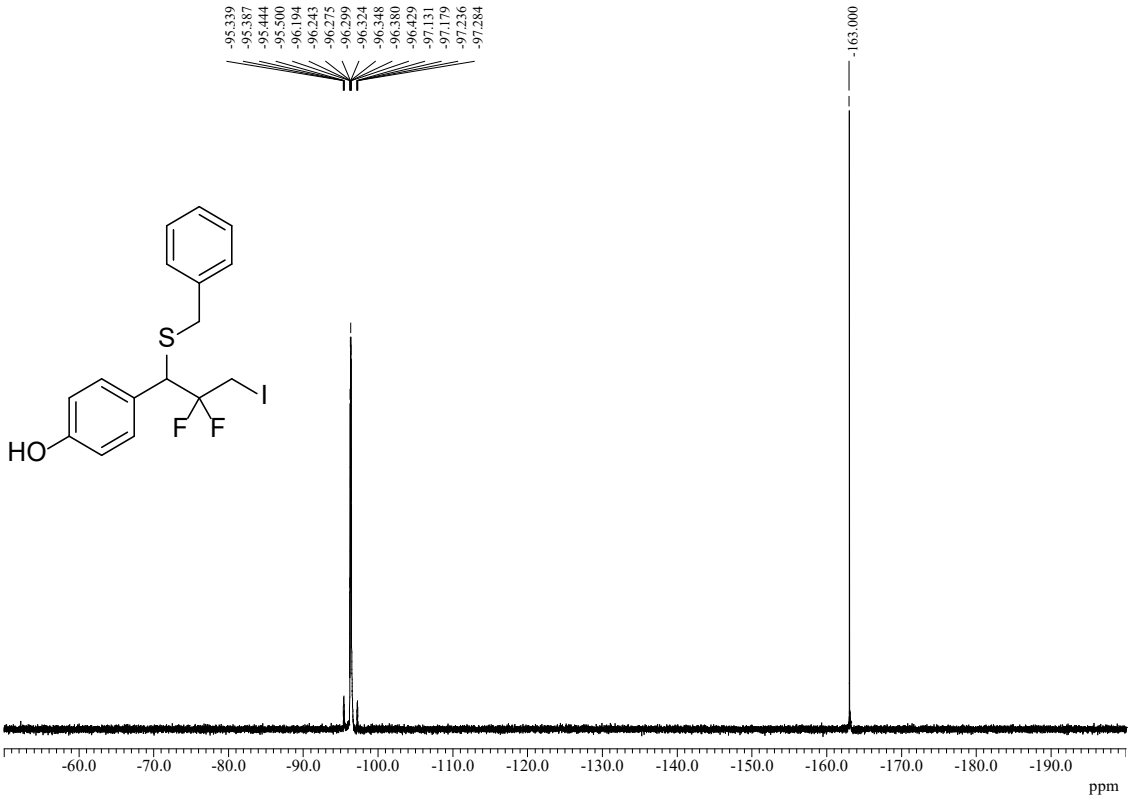
N-{2-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]sulfenyl}phenyl]benzamide (**7ag**)



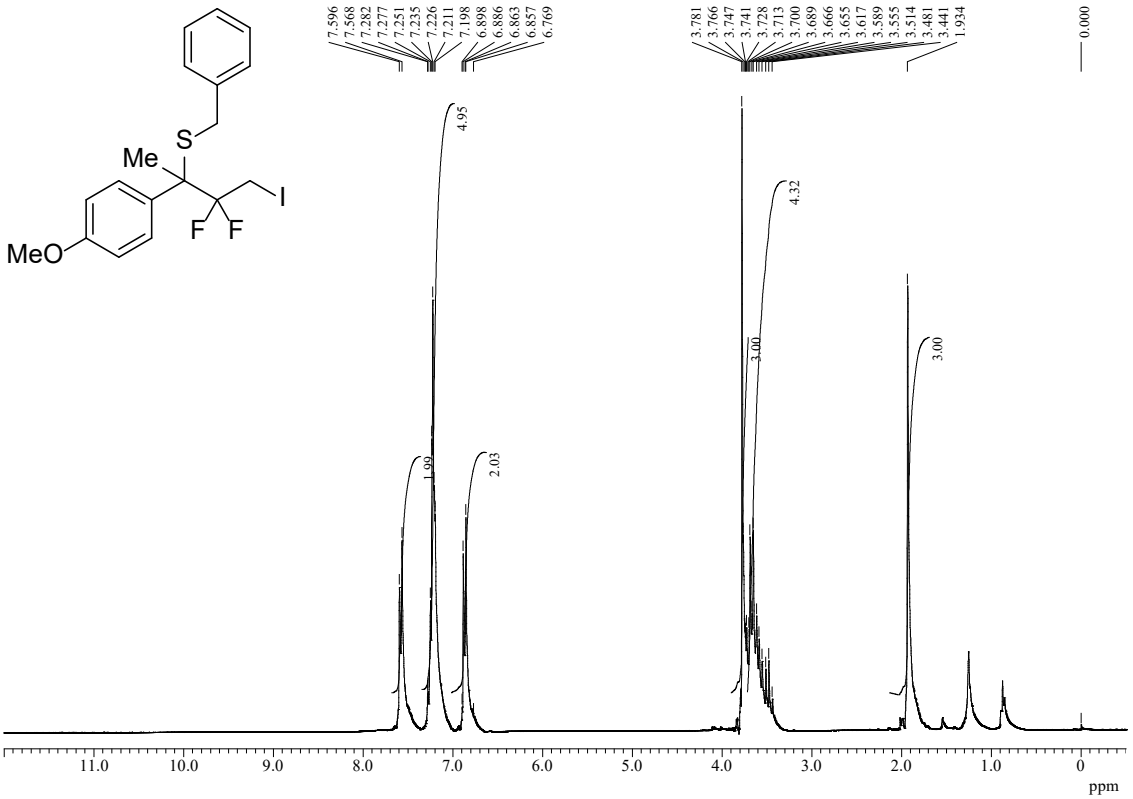
^{1}H and ^{13}C NMR spectra of 4-[1-(benzylsulfenyl-2,2-difluoro-3-iodo)propyl]phenol (**7ea**)

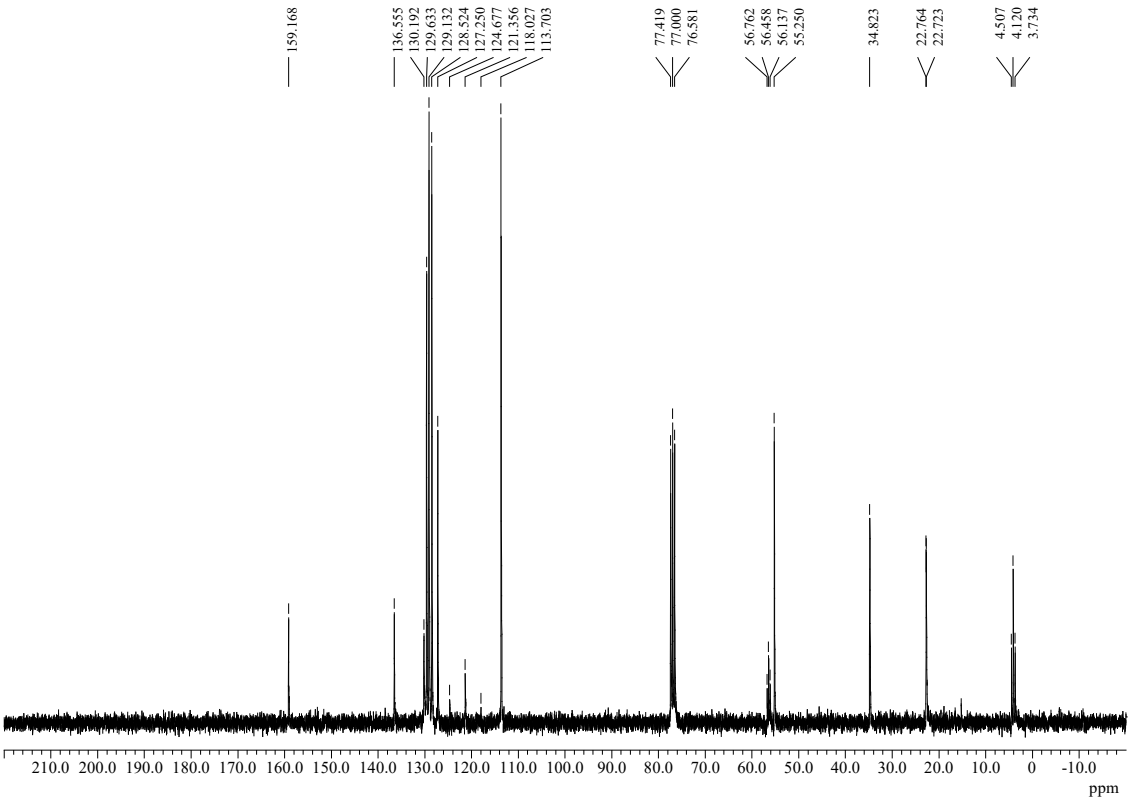


^{19}F NMR spectrum of 4-[1-(benzylsulfenyl-2,2-difluoro-3-iodo)propyl]phenol (**7ea**)

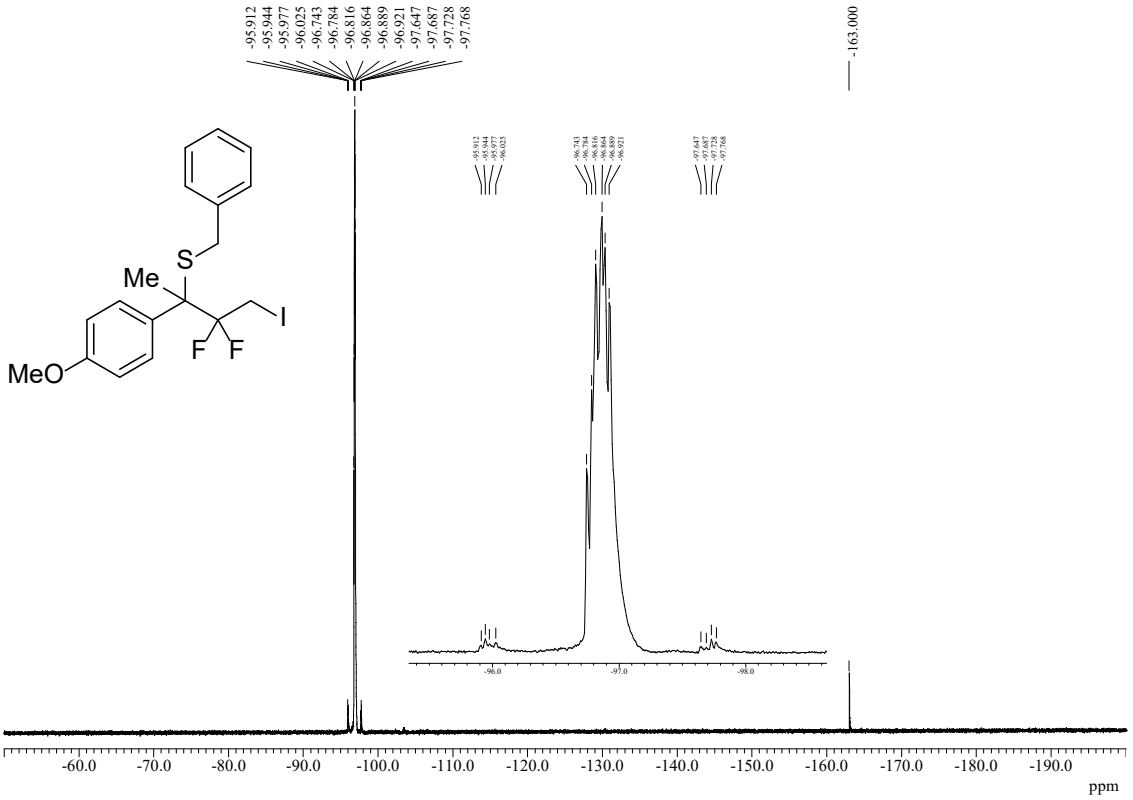


^{1}H and ^{13}C NMR spectra of 1-(2-benzylsulfenyl-3,3-difluoro-4-iodobut-2-yl)-4-methoxybenzene (**7ja**)

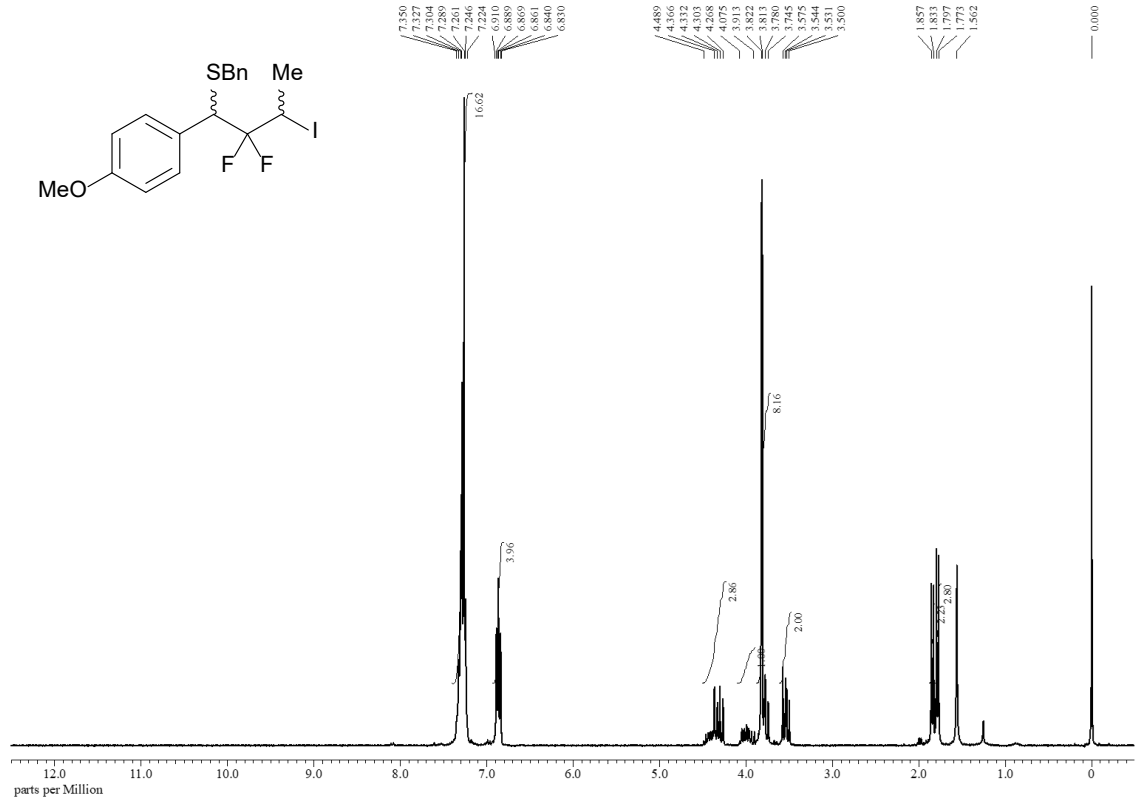


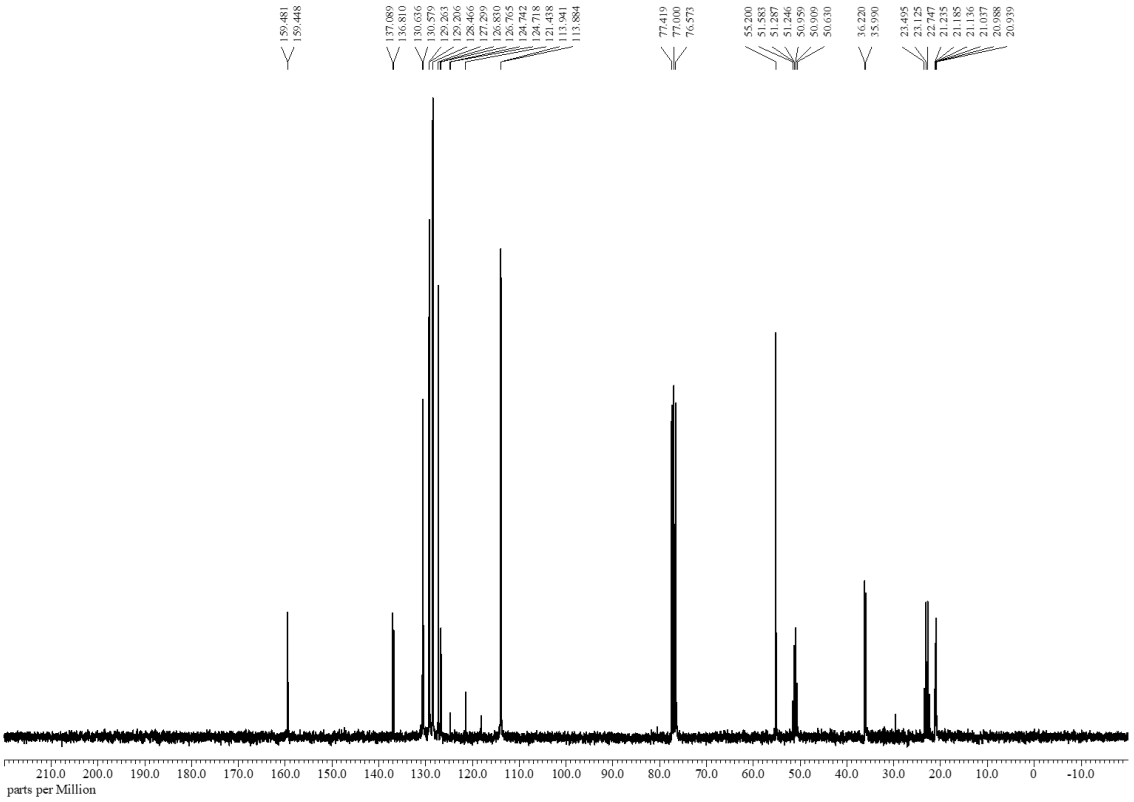


^{19}F NMR spectrum of 1-(2-benzylsulfenyl-3,3-difluoro-4-iodobut-2-yl)-4-methoxybenzene (**7ja**)

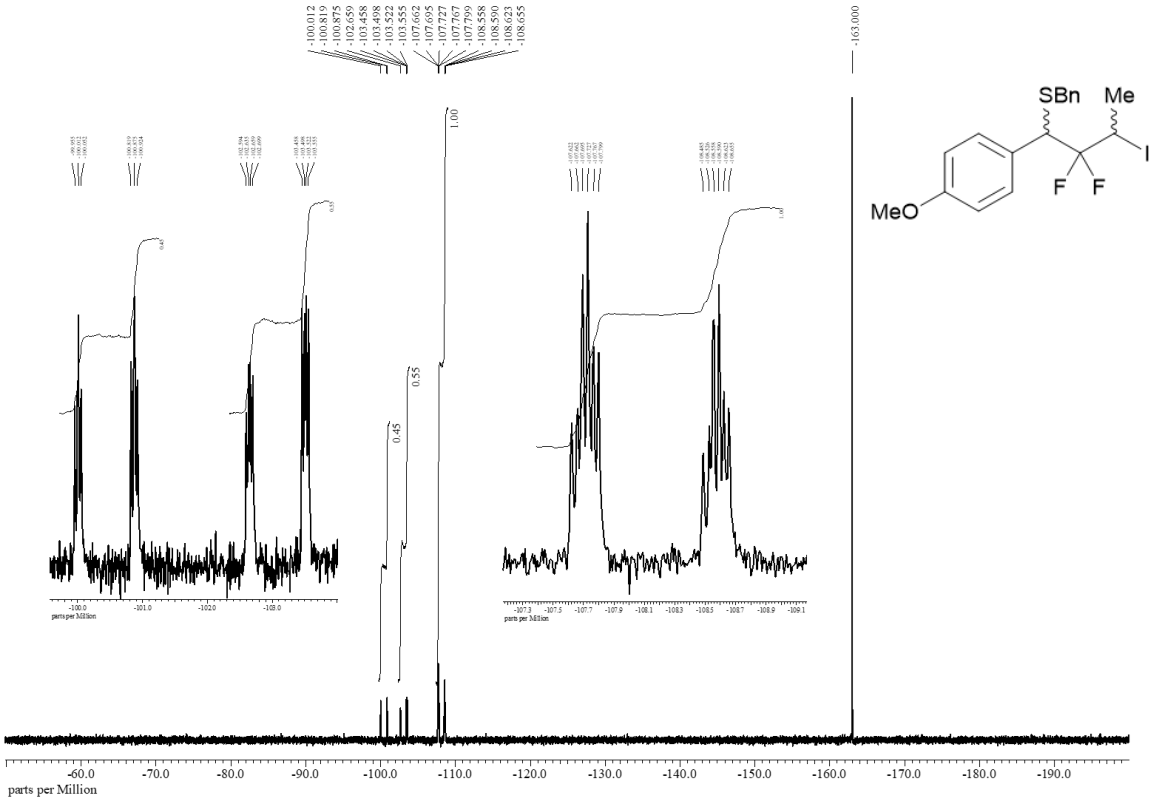


^{1}H and ^{13}C NMR spectra of 1-{(1-Benzylsulfenyl-2,2-difluoro-3-iodo)but-1-yl}-4-methoxybenzene (**7sa**)

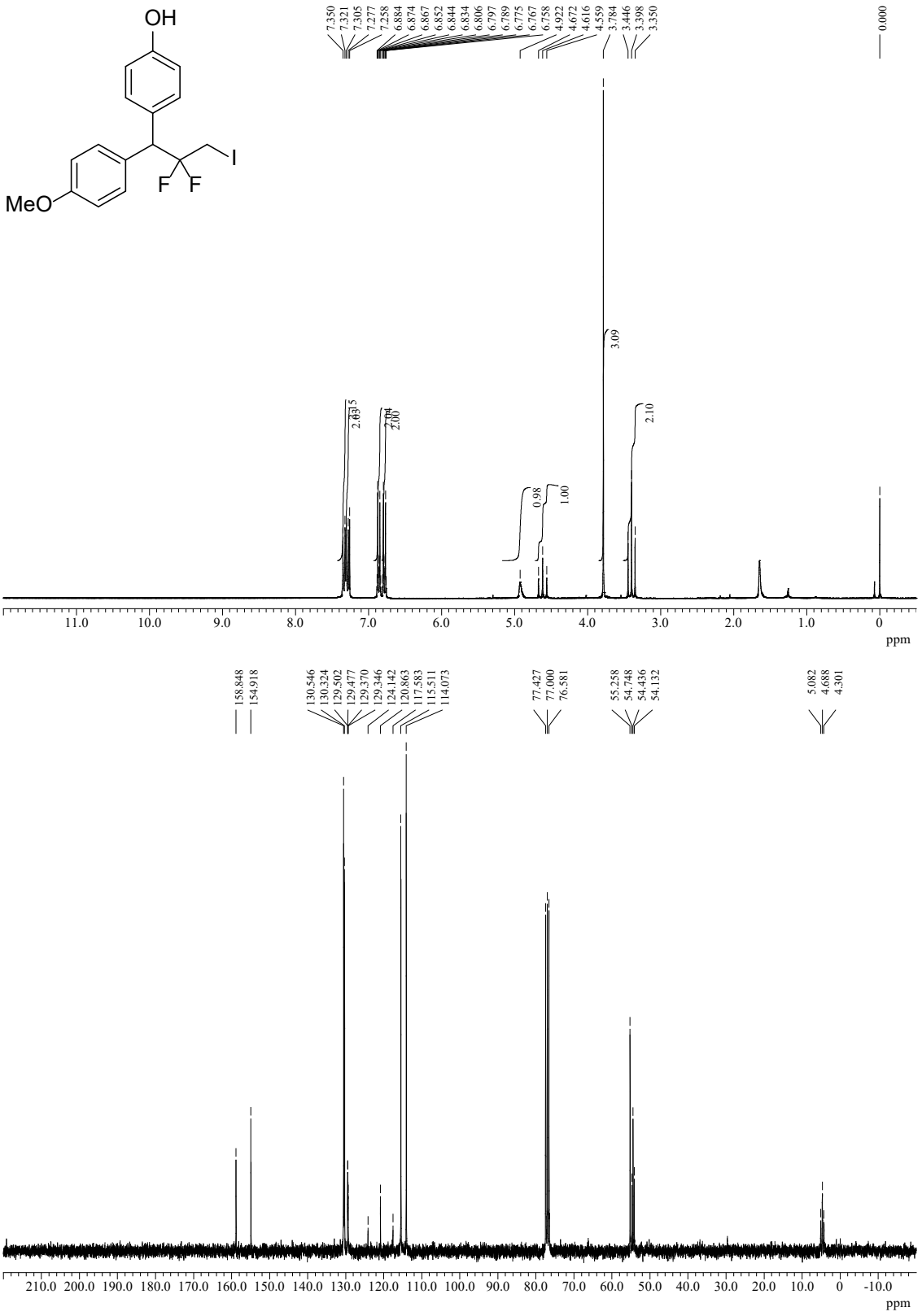




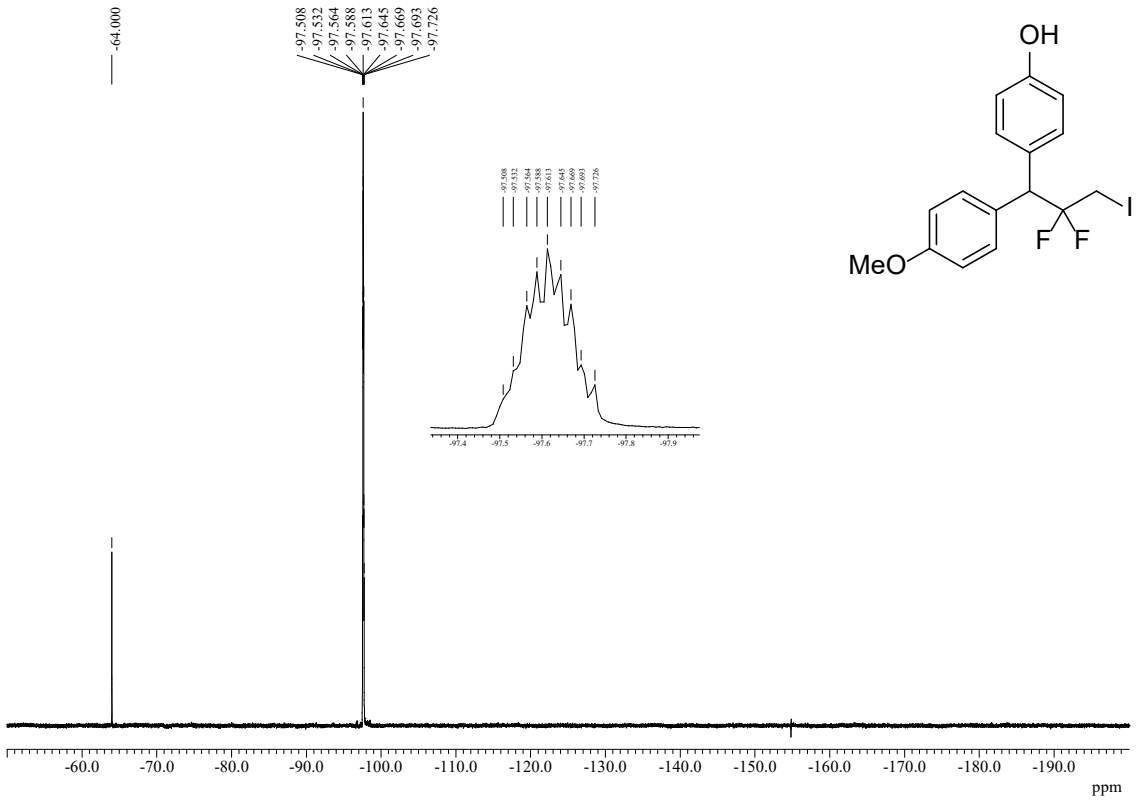
^{19}F NMR spectrum of 1-{(1-Benzylsulfenyl-2,2-difluoro-3-iodo)but-1-yl}-4-methoxybenzene (**7sa**)



^{1}H and ^{13}C NMR spectra of 4-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]phenol (**8aa**)



^{19}F NMR spectrum of 4-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]phenol (**8aa**)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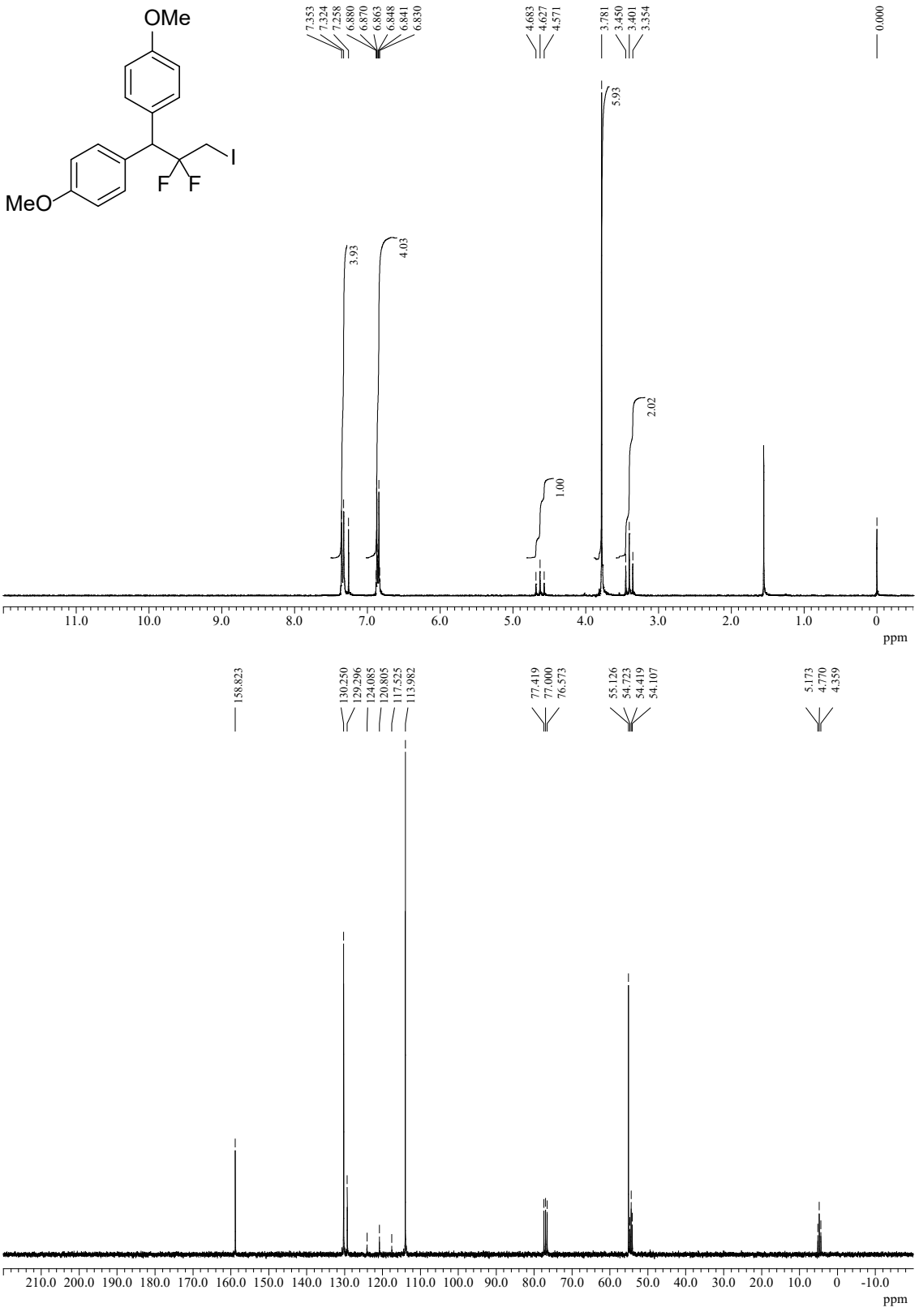
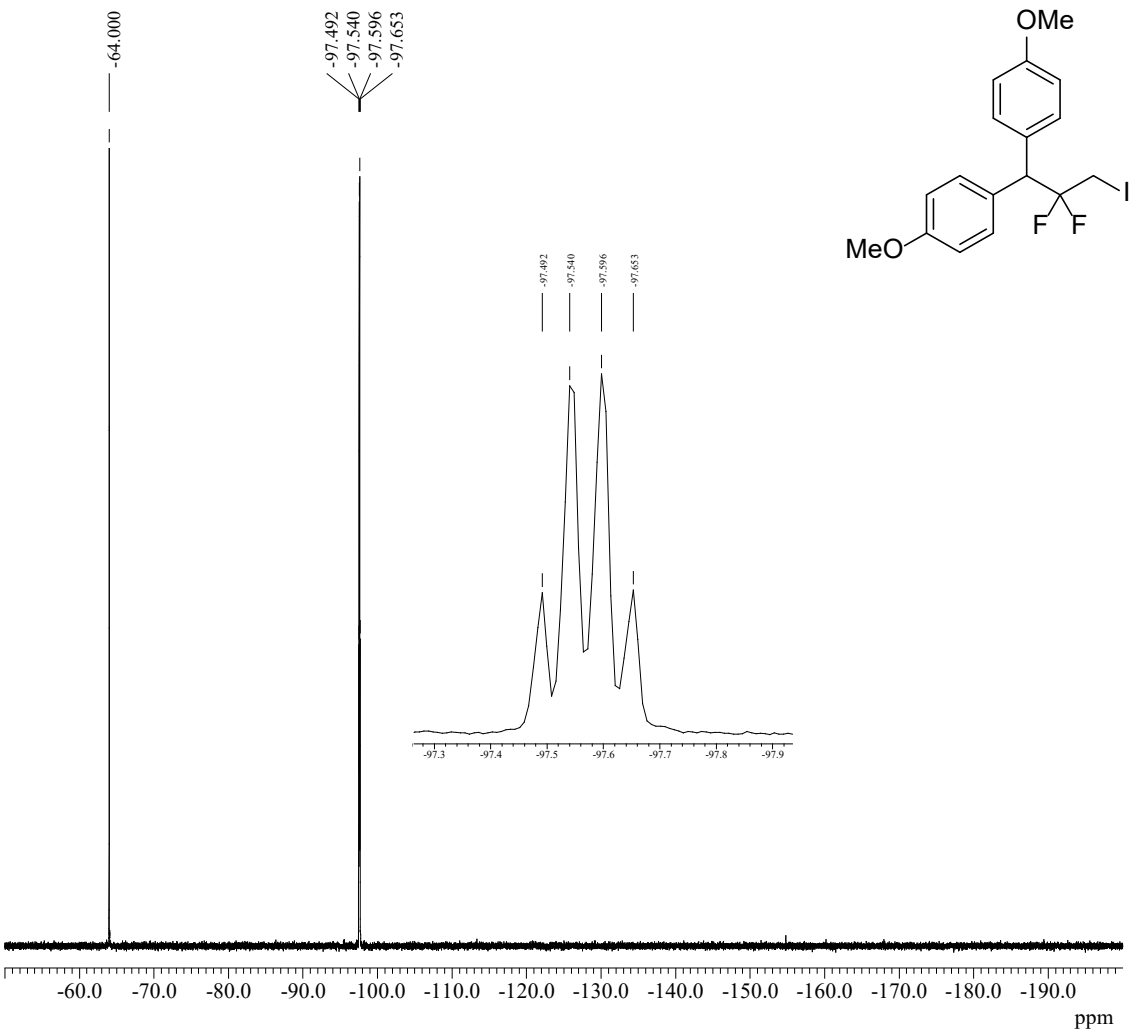
-97.508
-97.532
-97.564
-97.588
-97.613
-97.645
-97.669
-97.693
-97.726
OH
I
F
F
MeO
-60.0
-70.0
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
-190.0
ppm

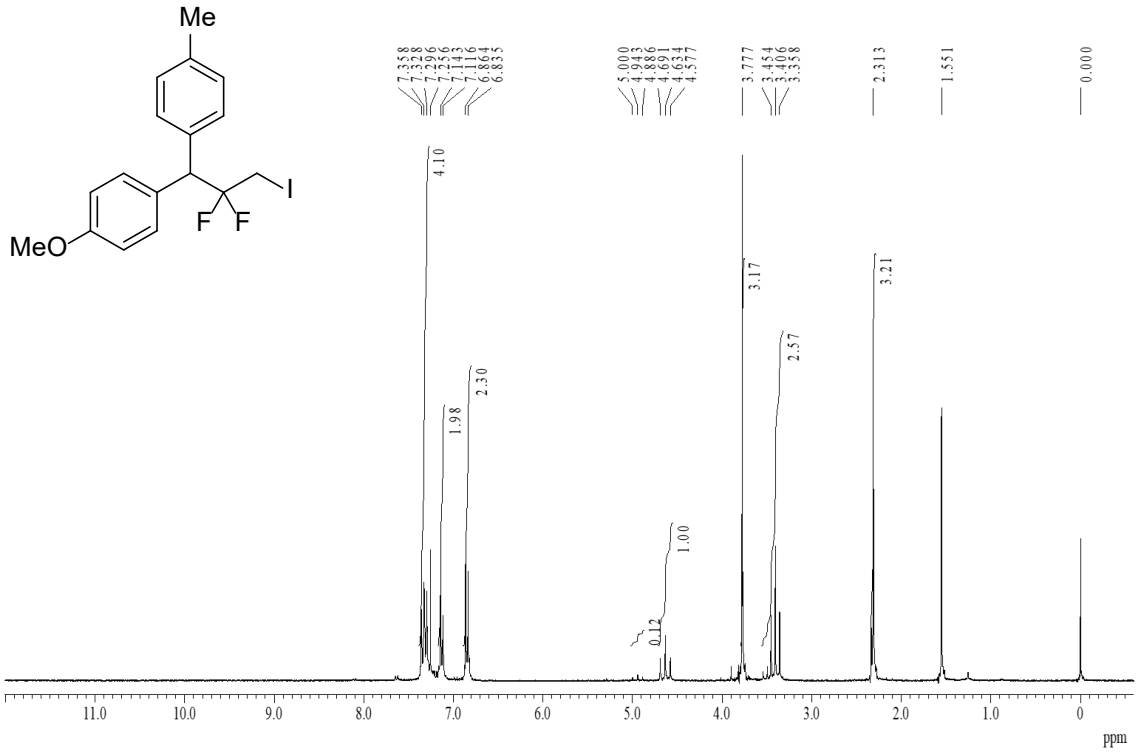
^{1}H and ^{13}C NMR spectra of 2,2-difluoro-3-iodo-1,1-bis(4-methoxyphenyl)propane (**8ab**)

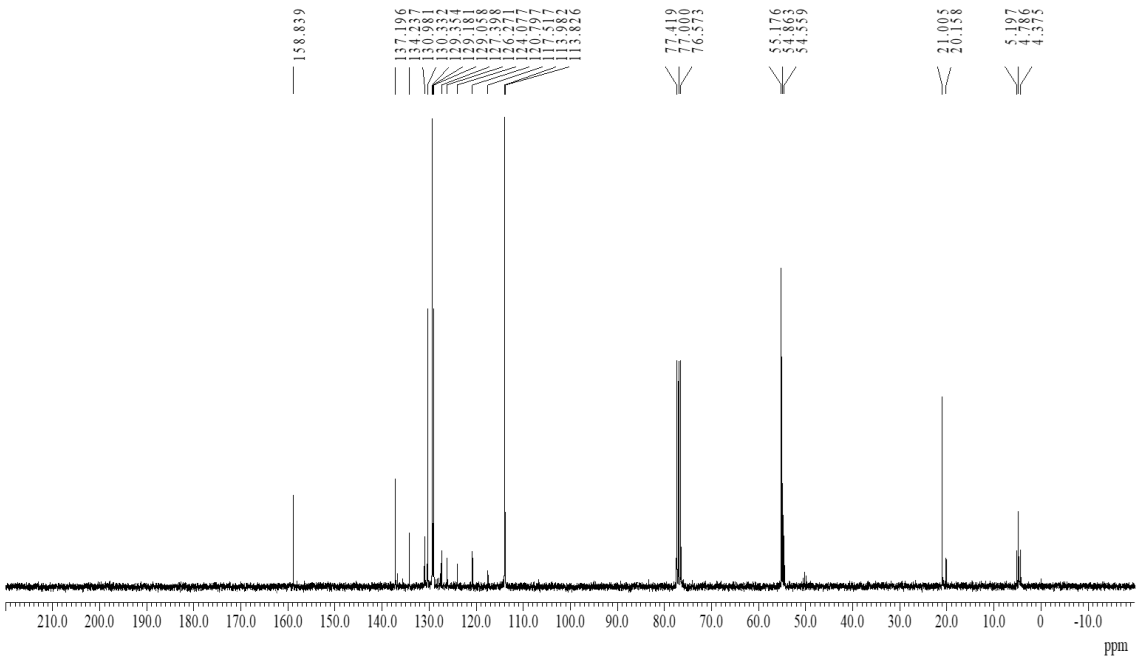


^{19}F NMR spectrum of 2,2-difluoro-3-iodo-1,1-bis(4-methoxyphenyl)propane (**8ab**)

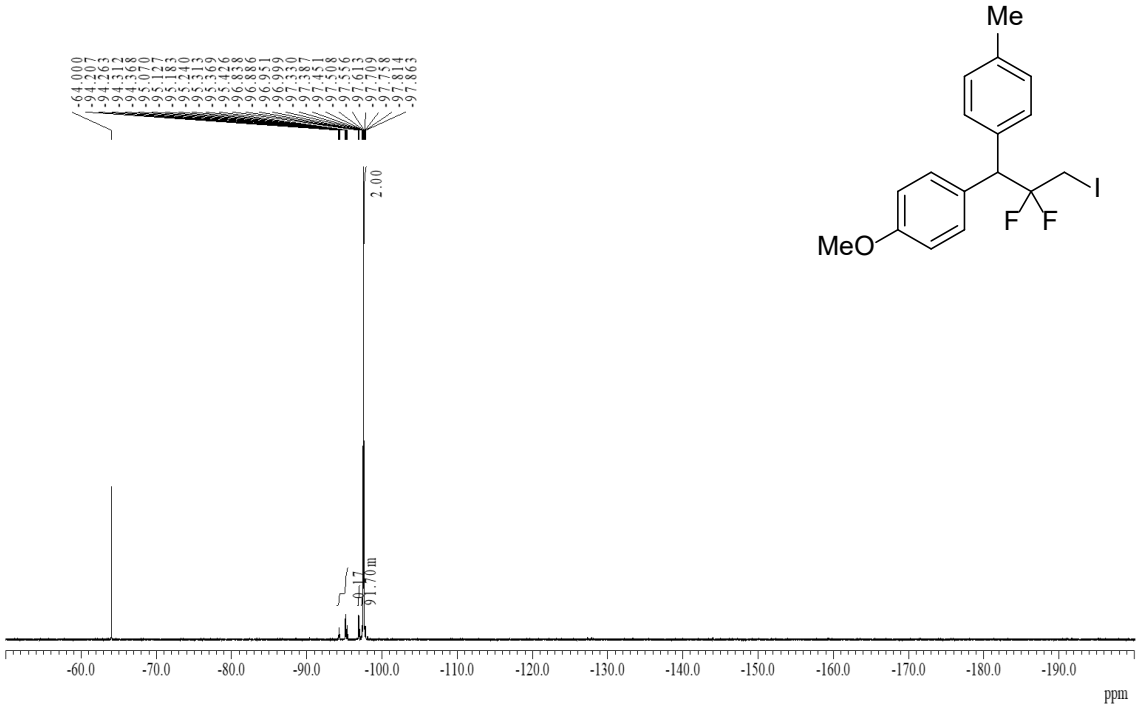


^{1}H and ^{13}C NMR spectra of 1-[2,2-difluoro-3-iodo-1-(4-methylphenyl)prop-1-yl]-4-methoxybenzene (**8ac**)

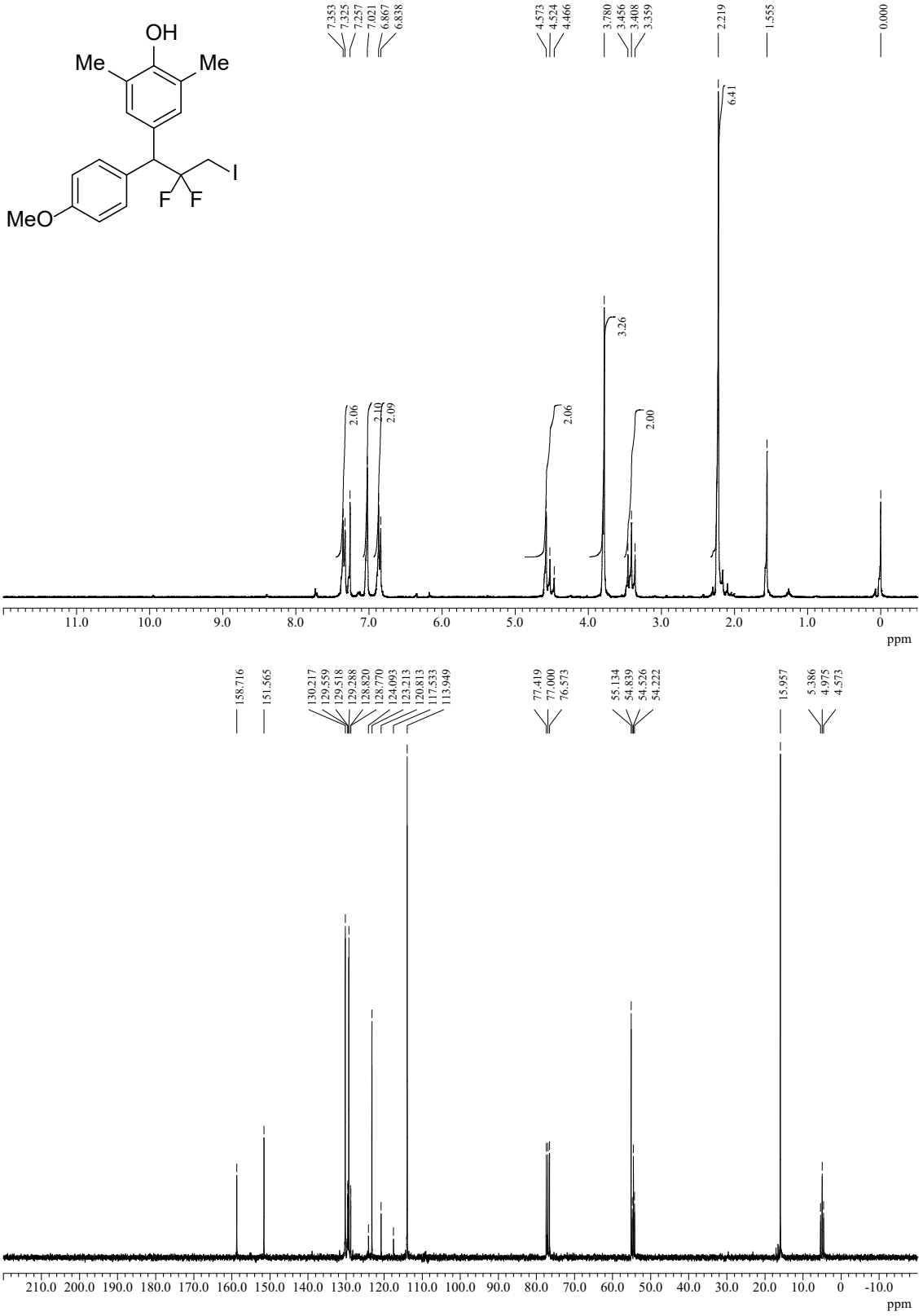




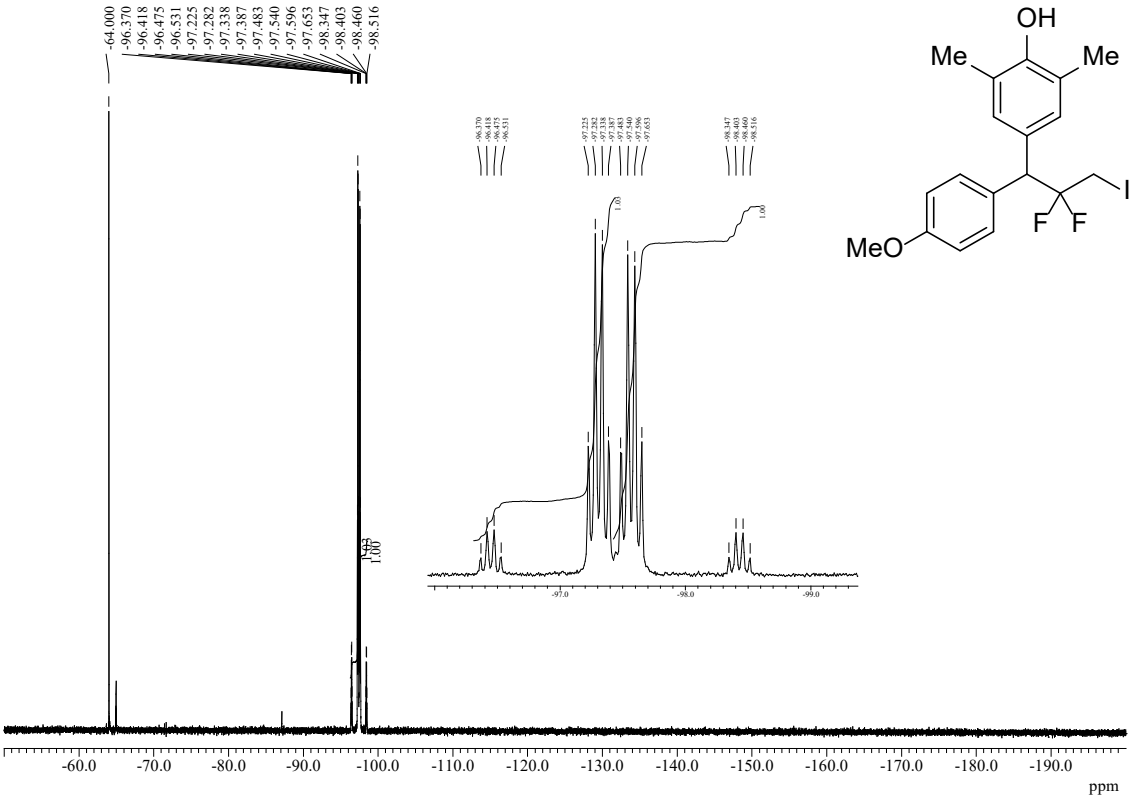
^{19}F NMR spectrum of 1-[2,2-difluoro-3-iodo-1-(4-methylphenyl)prop-1-yl]-4-methoxybenzene (**8ac**)



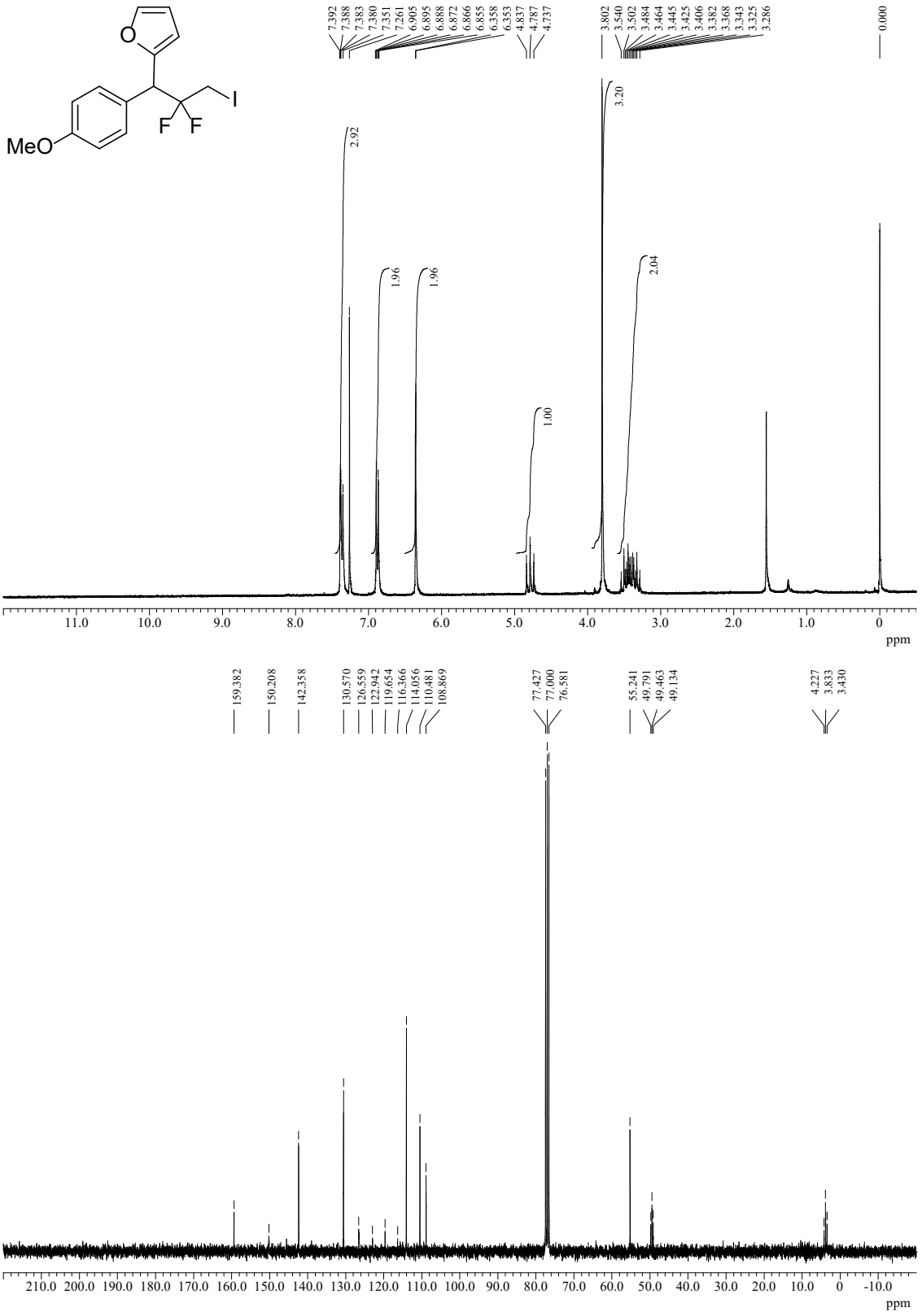
^{1}H and ^{13}C NMR spectra of 4-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]-2,6-dimethylphenol (**8ad**)



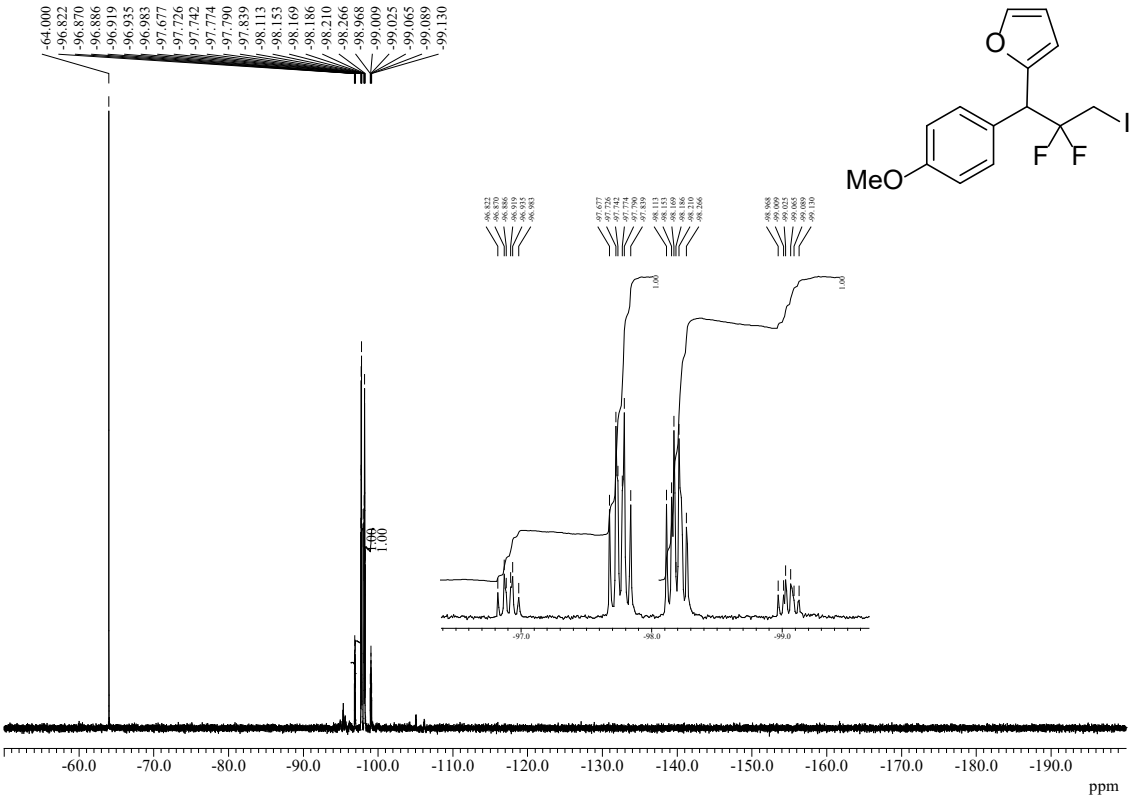
^{19}F NMR spectrum of 4-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]-2,6-dimethylphenol (**8ad**)



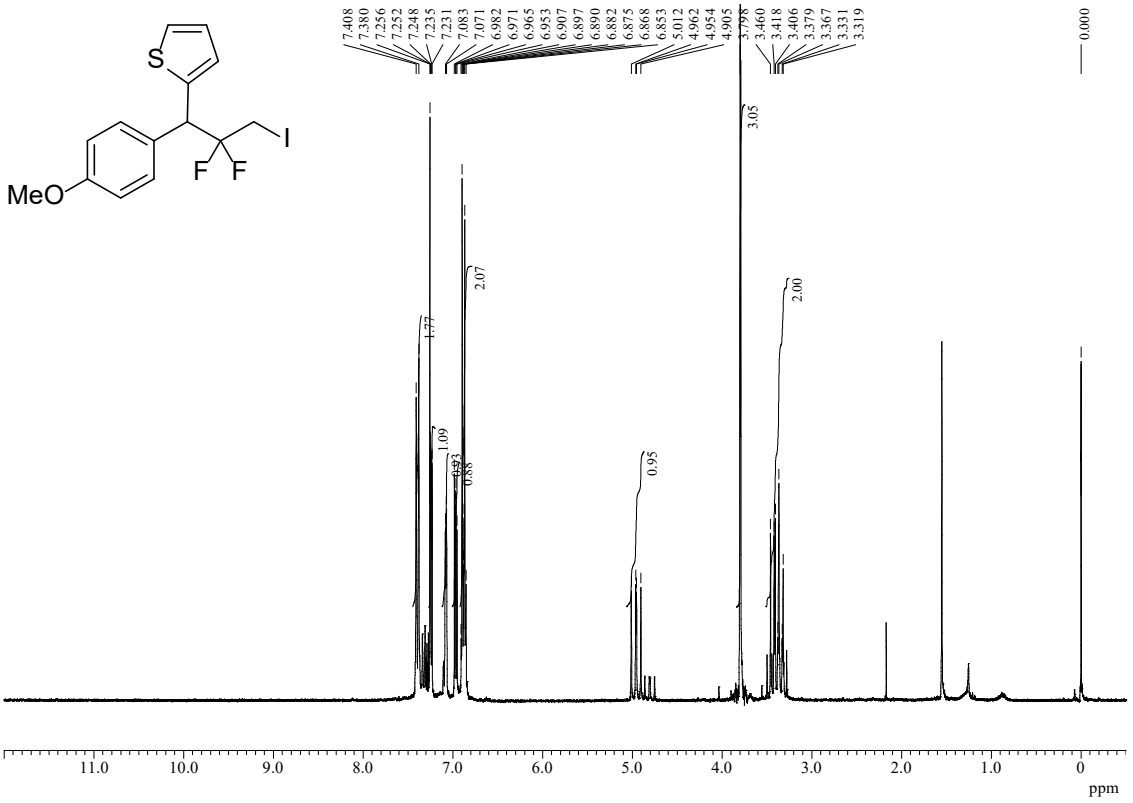
^{1}H and ^{13}C NMR spectra of 2-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]furan (**8ae**)

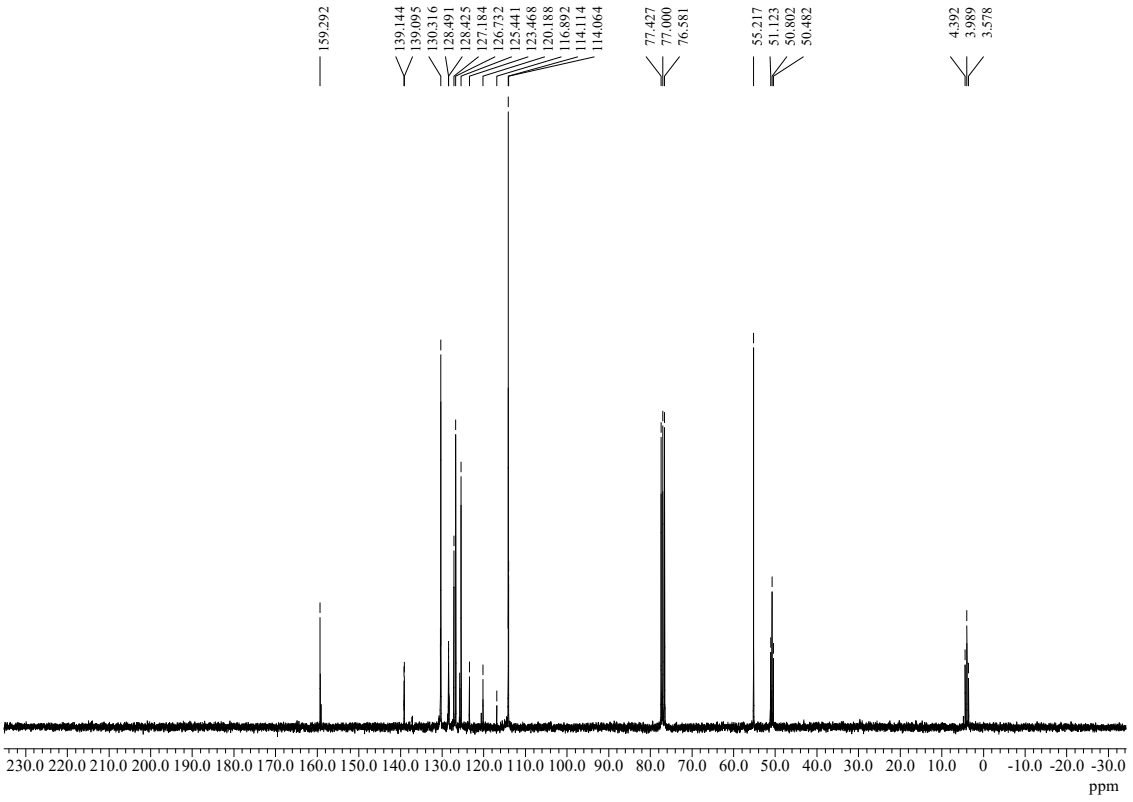


^{19}F NMR spectrum of 2-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]furan (**8ae**)

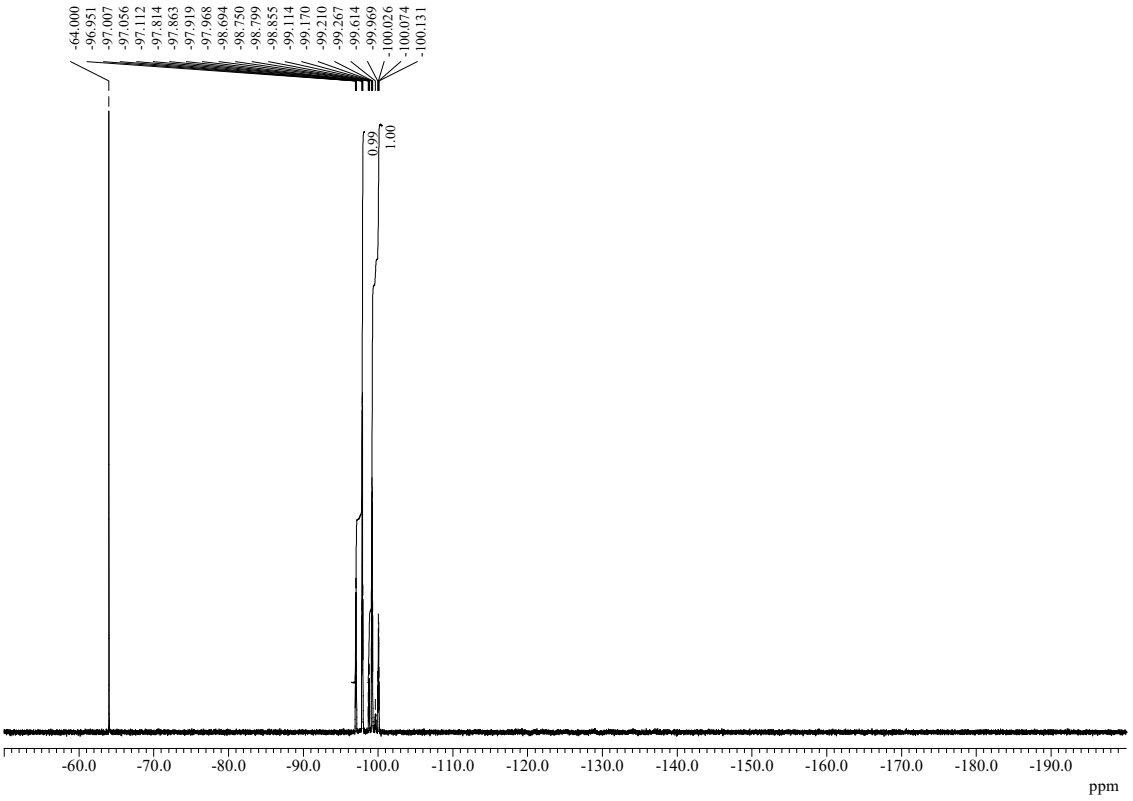


^{1}H and ^{13}C NMR spectra of 2-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]thiophene (**8af**)

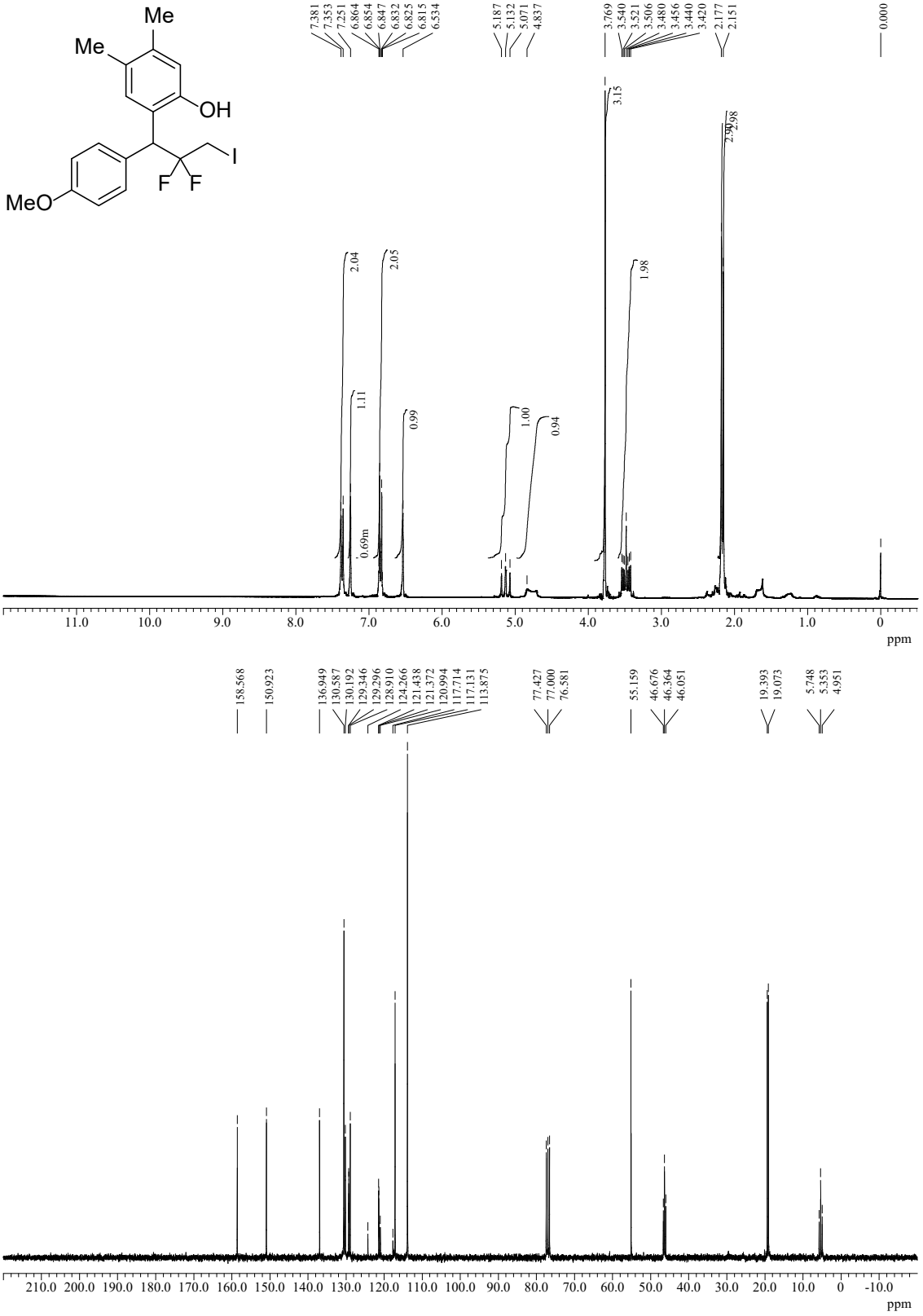




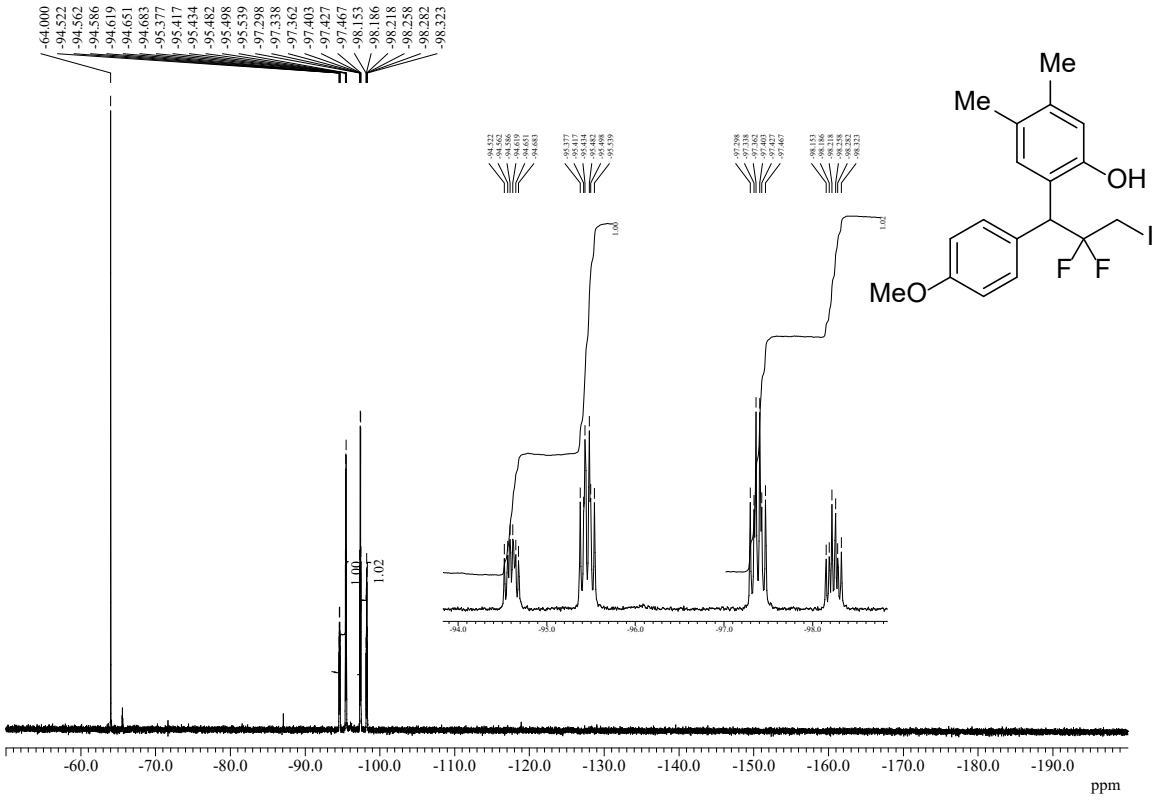
^{19}F NMR spectrum of 2-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]thiophene (**8af**)



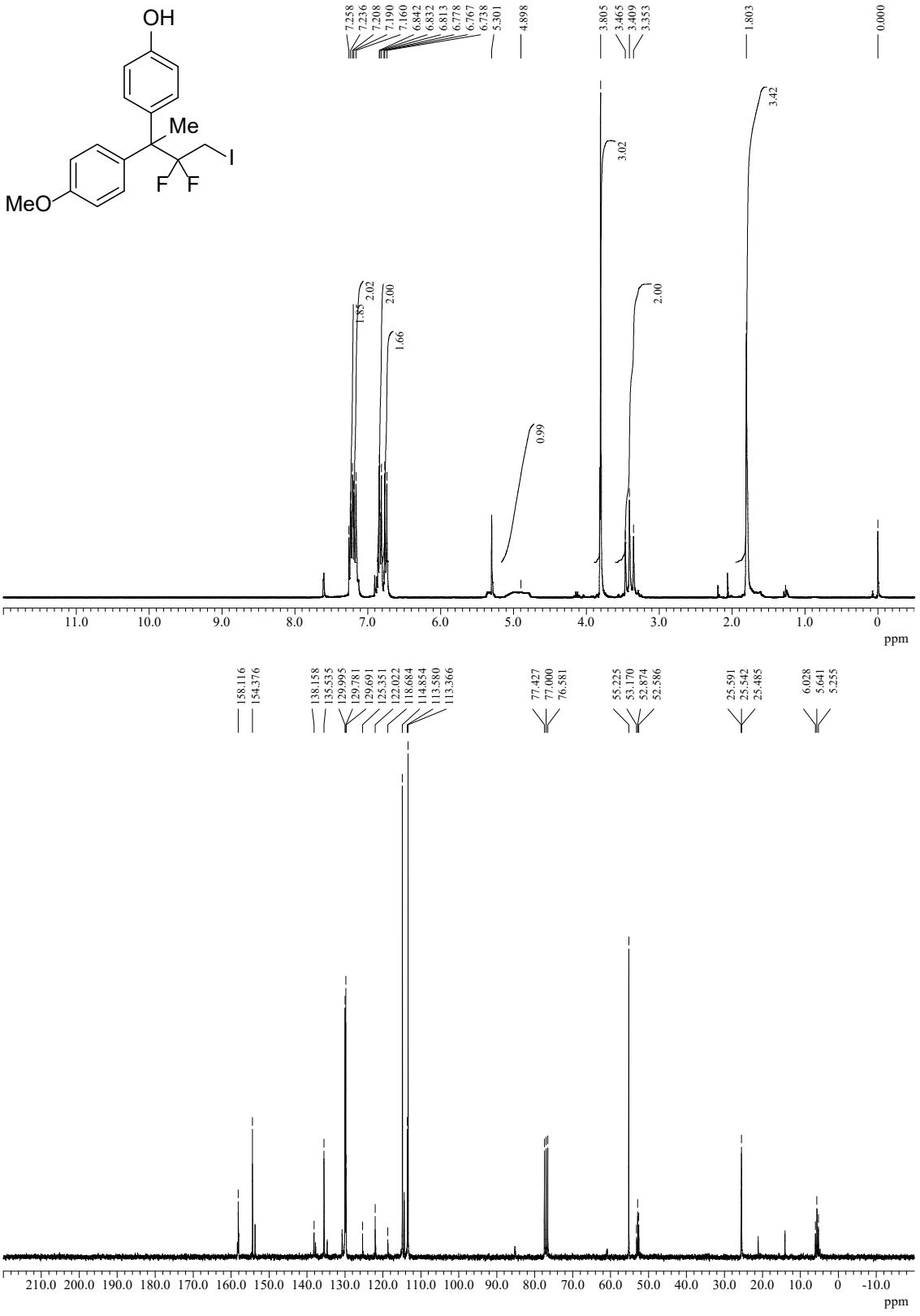
^{1}H and ^{13}C NMR spectra of 2-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]-4,5-dimethylphenol (**8ag**)



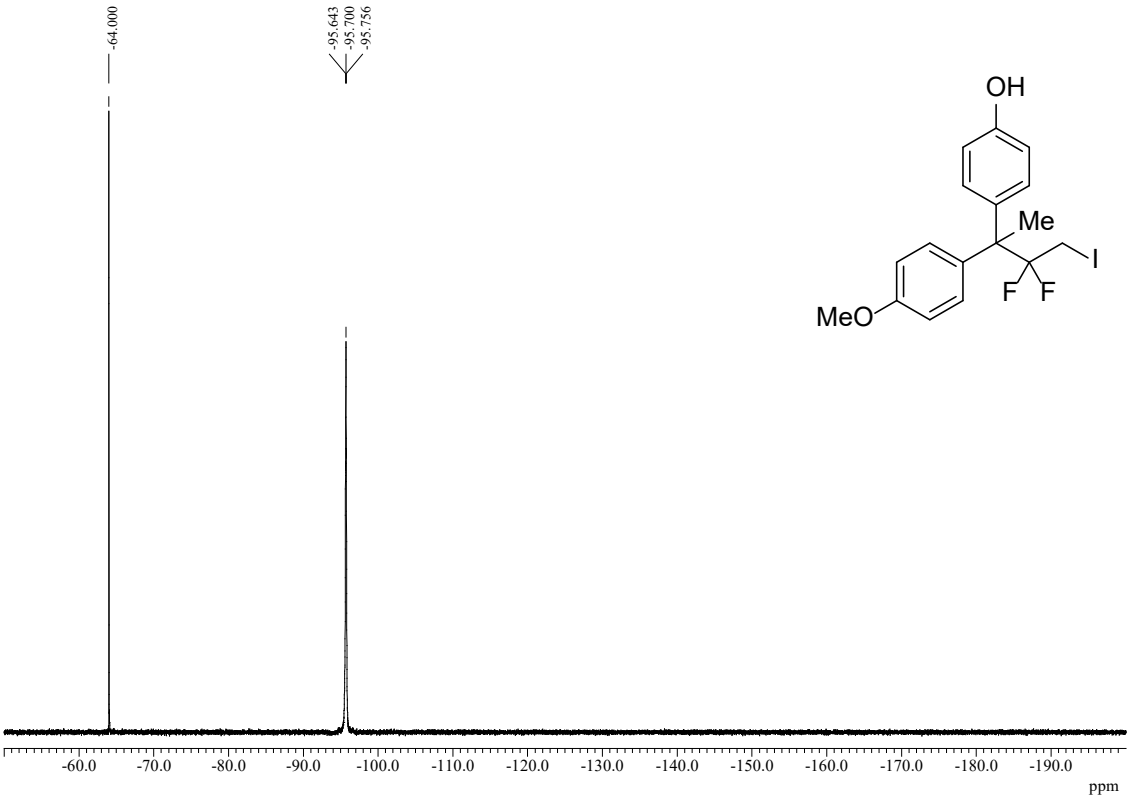
^{19}F NMR spectrum of 2-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]-4,5-dimethylphenol (**8ag**)



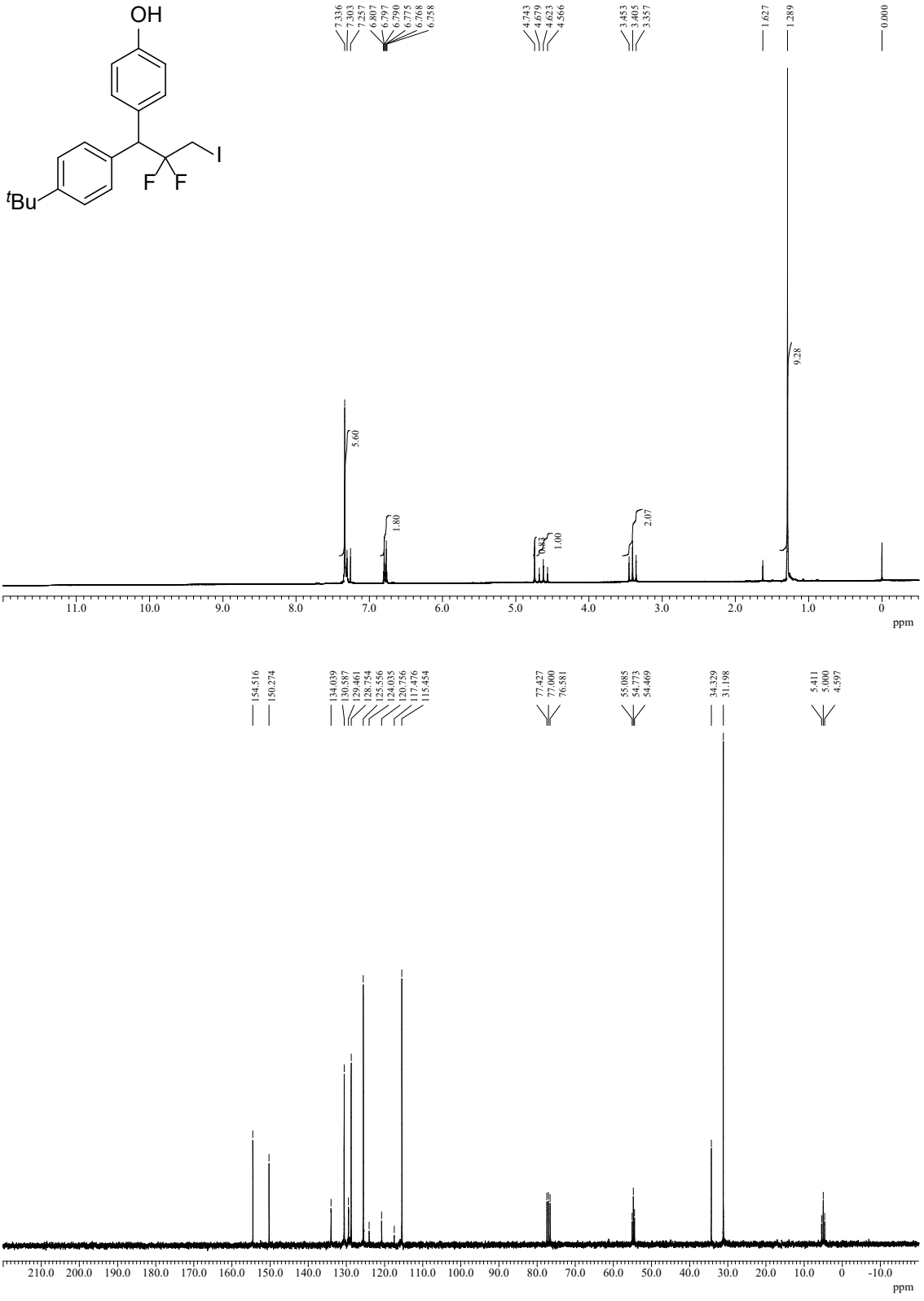
^{1}H and ^{13}C NMR spectra of 4-[3,3-difluoro-4-iodo-2-(4-methoxyphenyl)butan-2-yl]phenol (**8ja**)



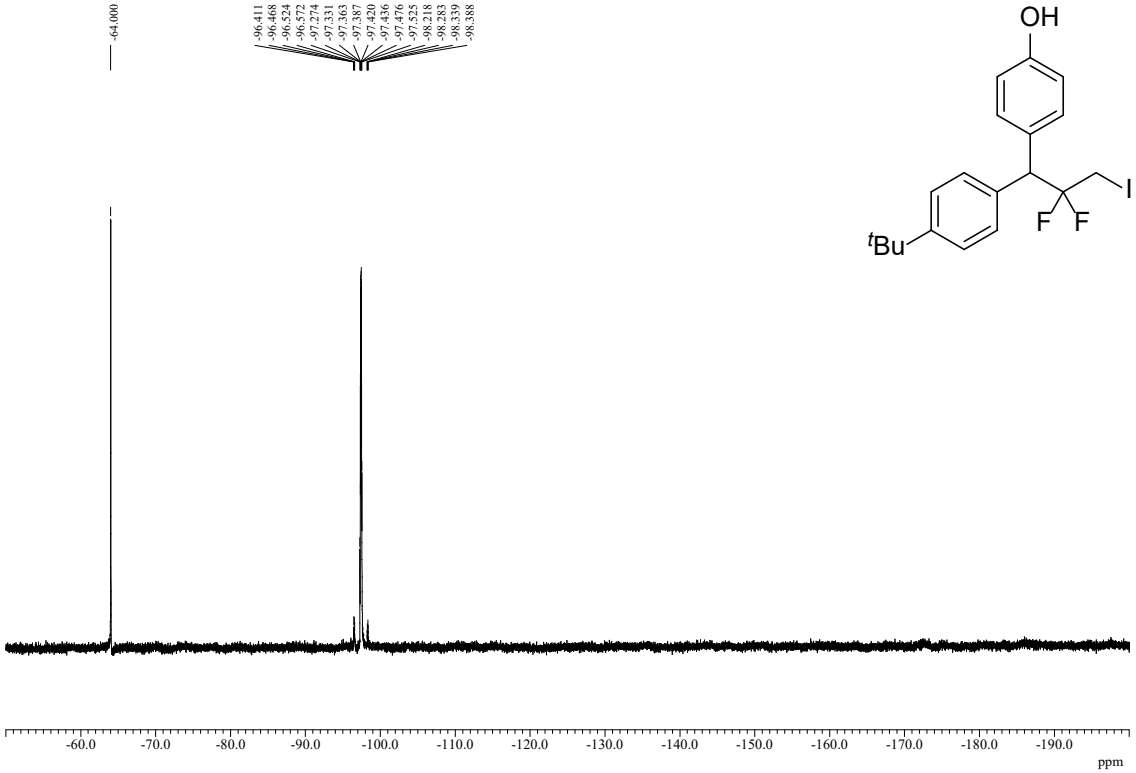
^{19}F NMR spectrum of 4-[3,3-difluoro-4-iodo-2-(4-methoxyphenyl)butan-2-yl]phenol (**8ja**)



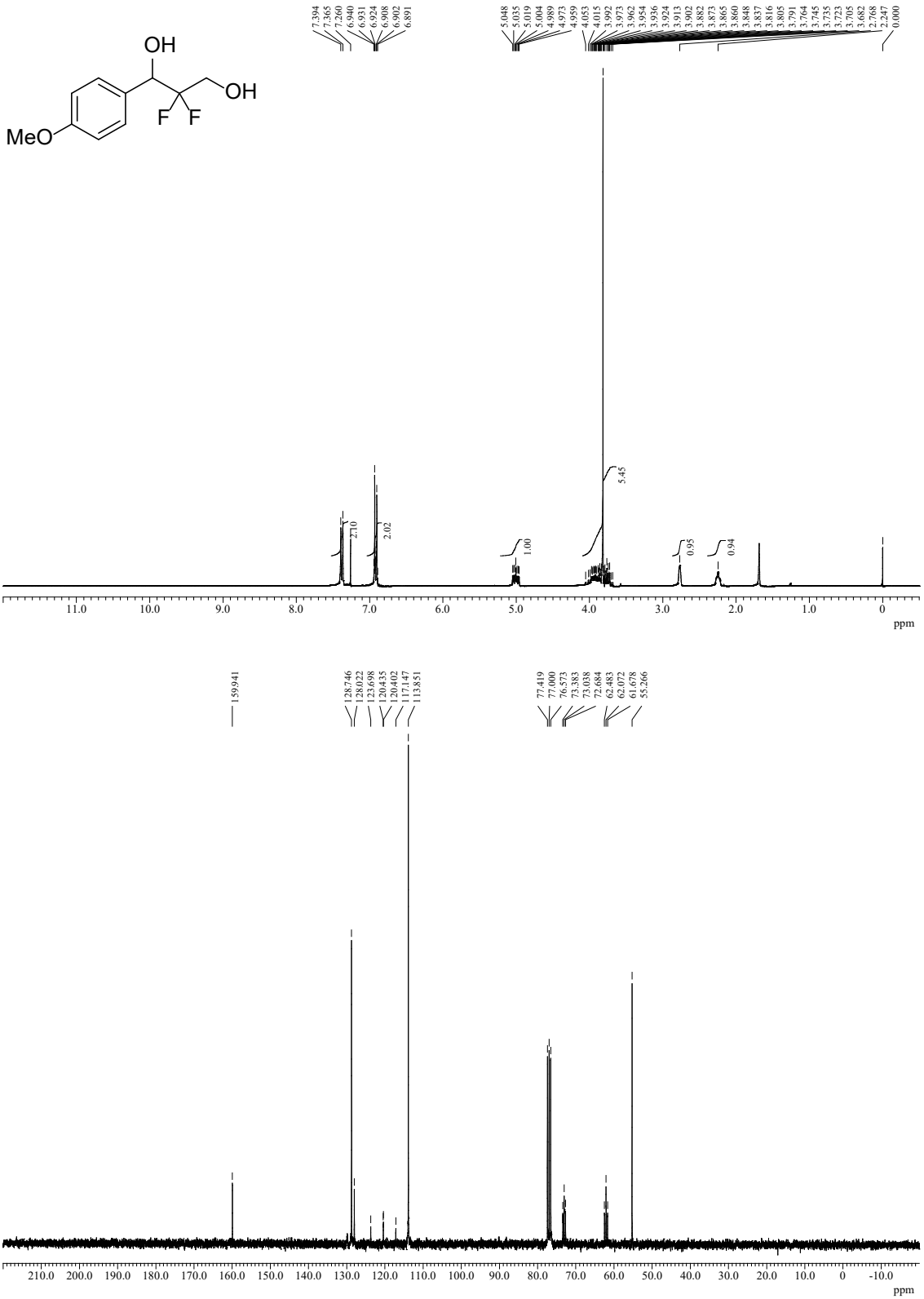
^{1}H and ^{13}C NMR spectra of 4-{[1-(4-*tert*-butylphenyl)-2,2-difluoro-3-iodo]prop-1-yl}phenol (**8fa**)



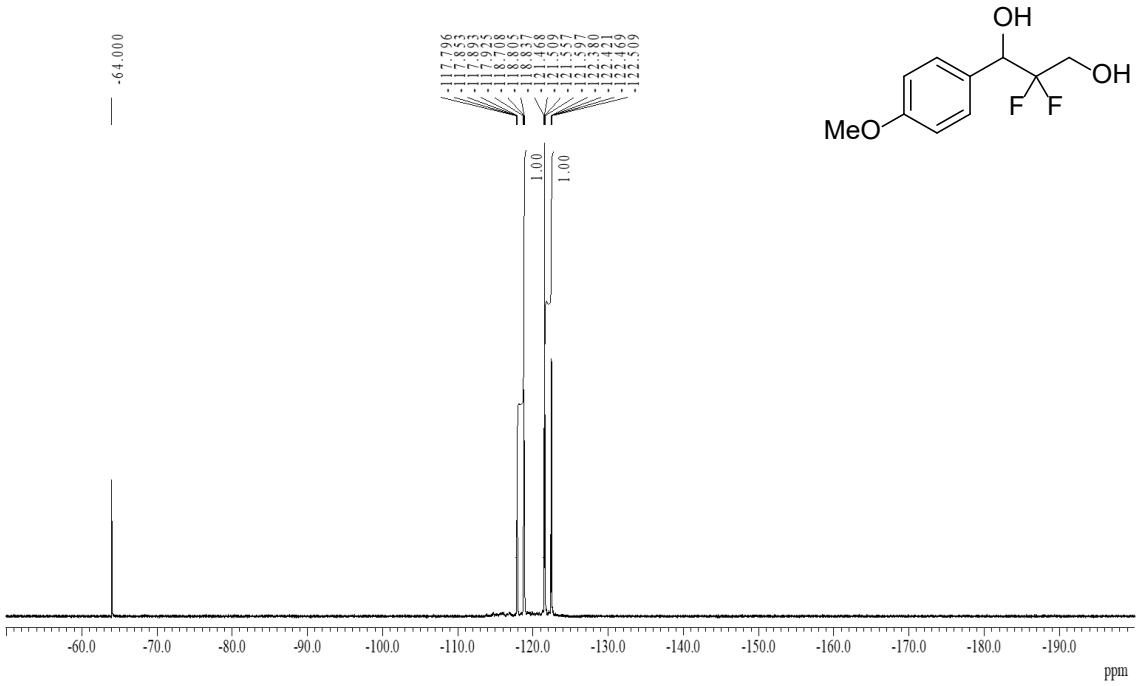
^{19}F NMR spectrum of 4-{[1-(4-*tert*-butylphenyl)-2,2-difluoro-3-iodo]prop-1-yl}phenol (**8fa**)



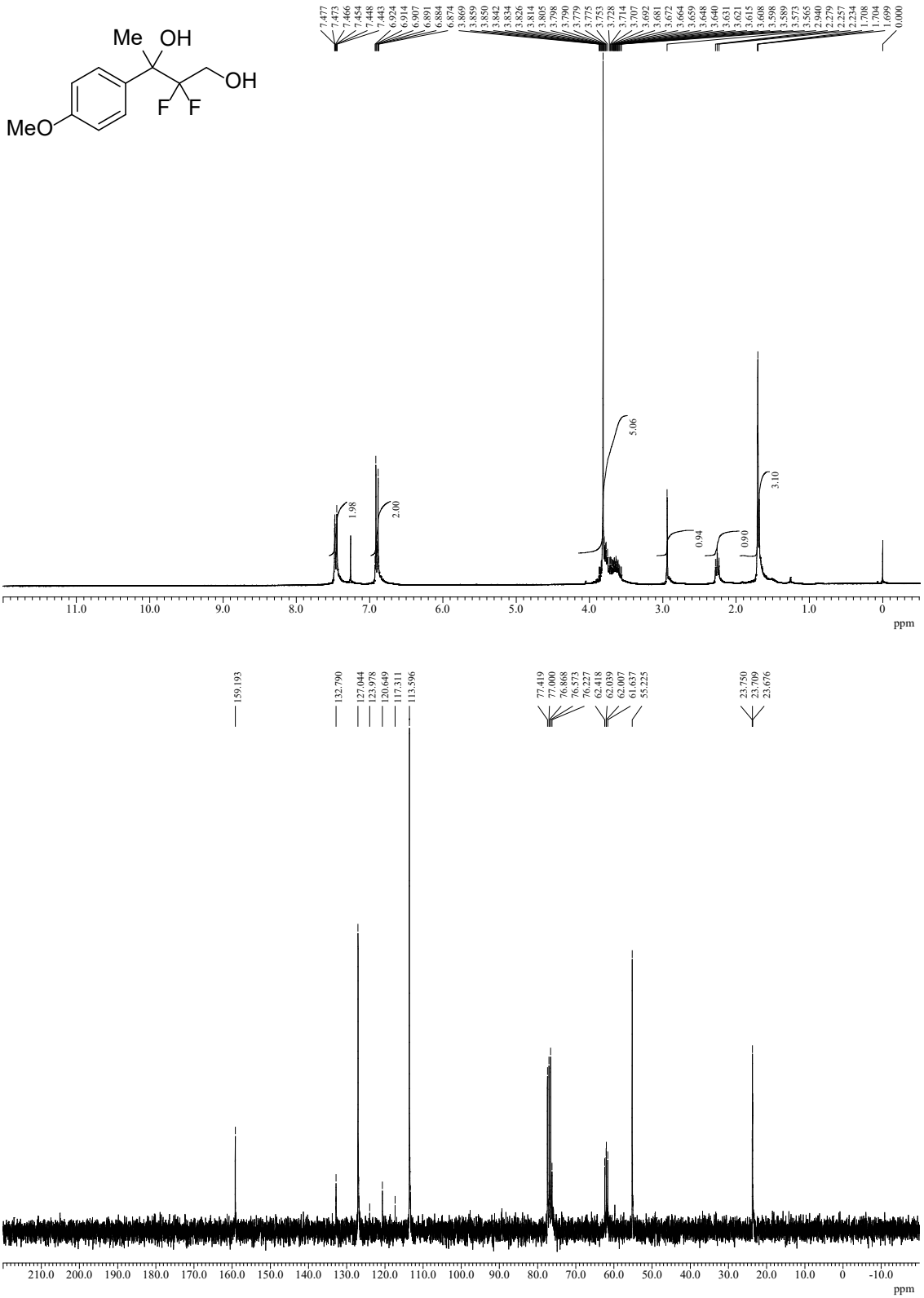
^{1}H and ^{13}C NMR spectra of 2,2-difluoro-1-(4-methoxyphenyl)propane-1,3-diol (**10a**)



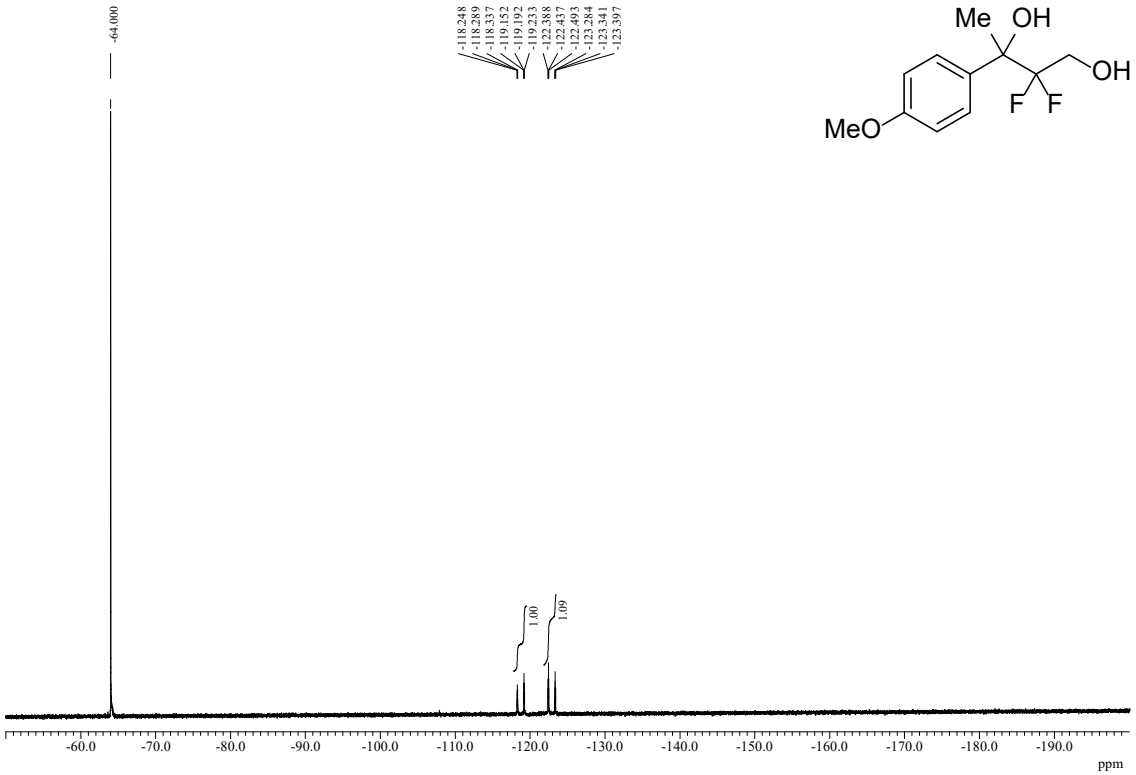
^{19}F NMR spectrum of 2,2-difluoro-1-(4-methoxyphenyl)propan-1,3-diol (**10a**)



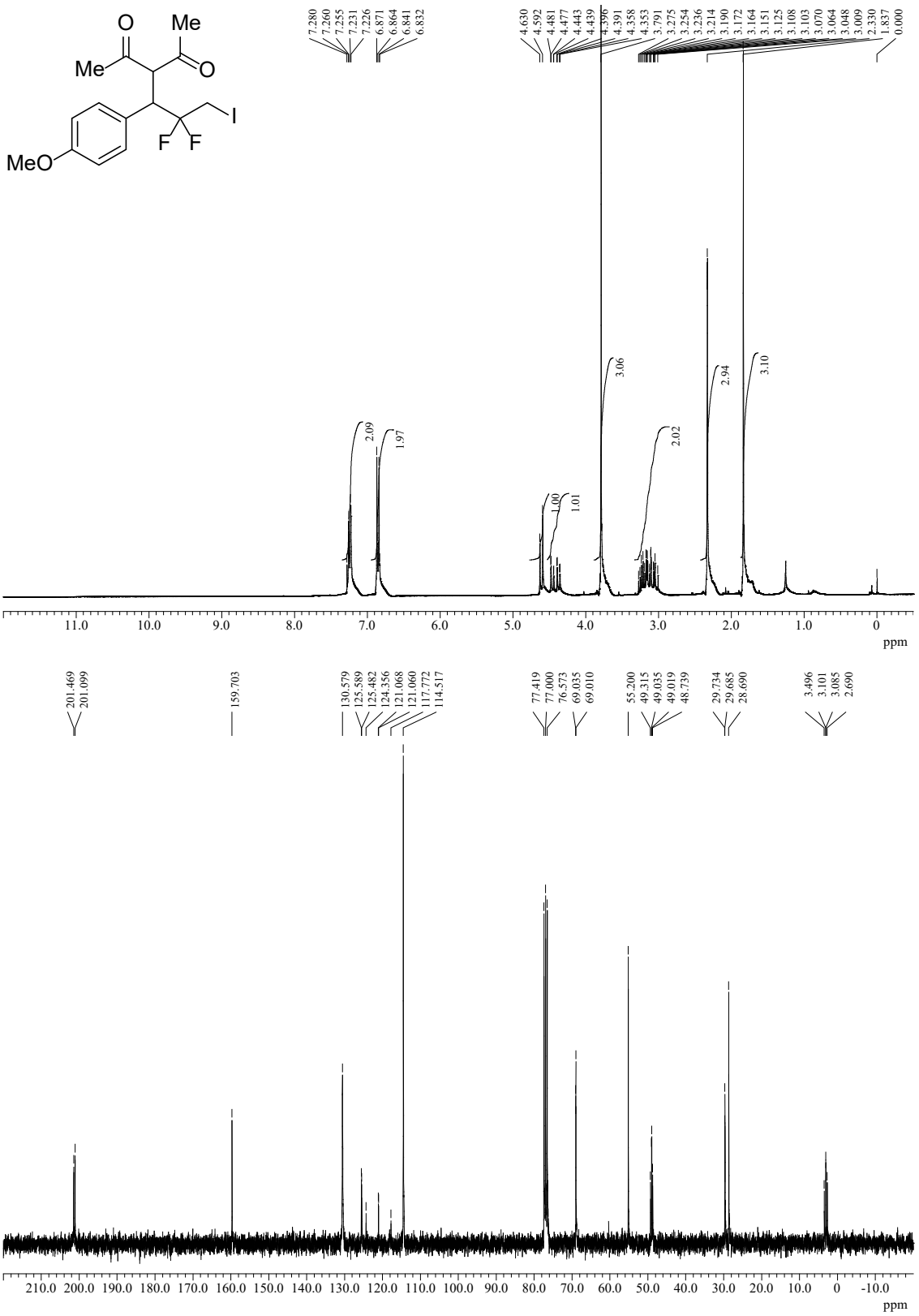
^{1}H and ^{13}C NMR spectra of 2,2-difluoro-3-(4-methoxyphenyl)butan-1,3-diol (**10j**)



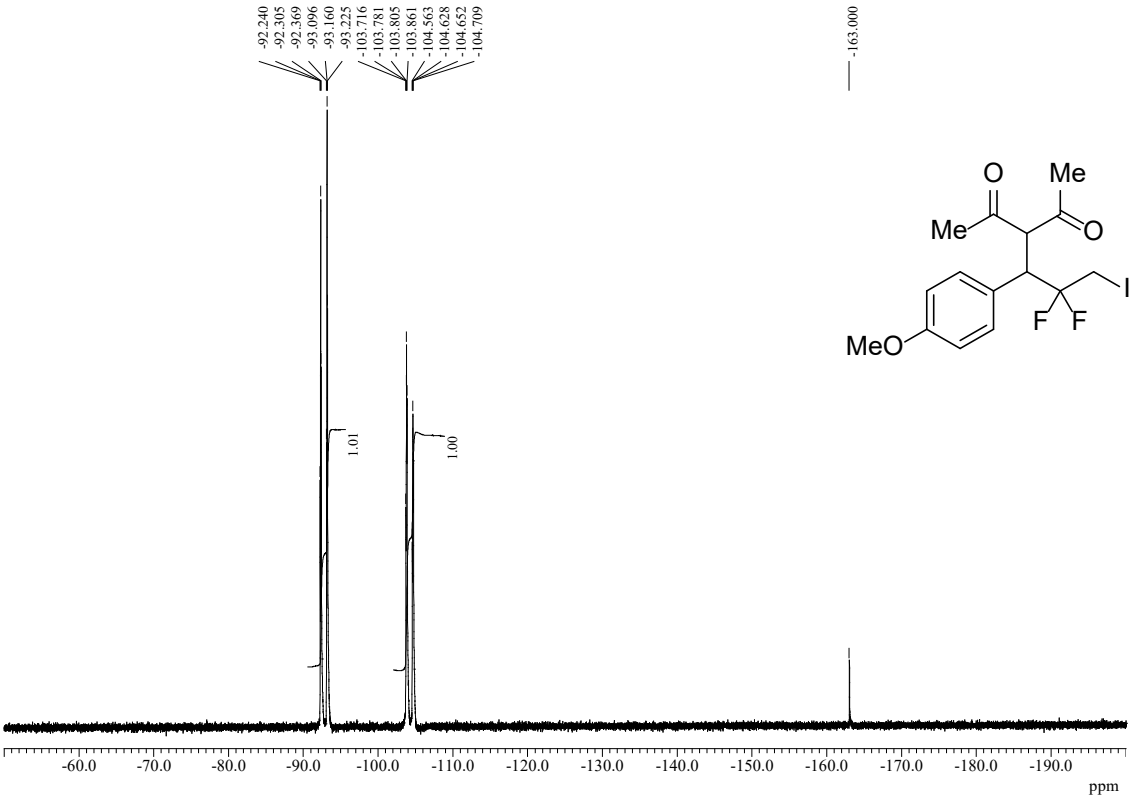
^{19}F NMR spectrum of 2,2-difluoro-3-(4-methoxyphenyl)butan-1,3-diol (**10j**)



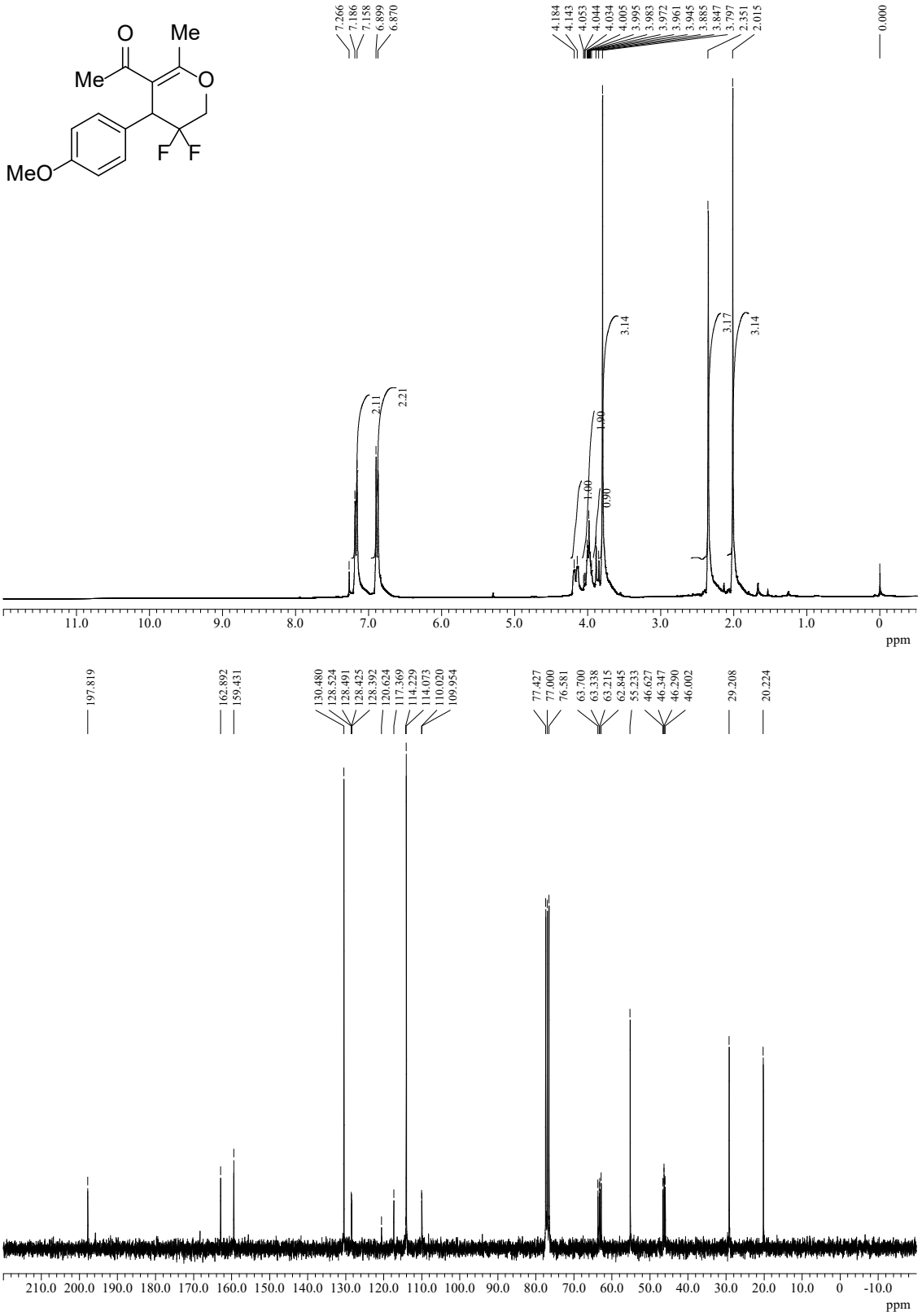
^{1}H and ^{13}C NMR spectra of 3-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]pentan-2,4-dione (**11**)



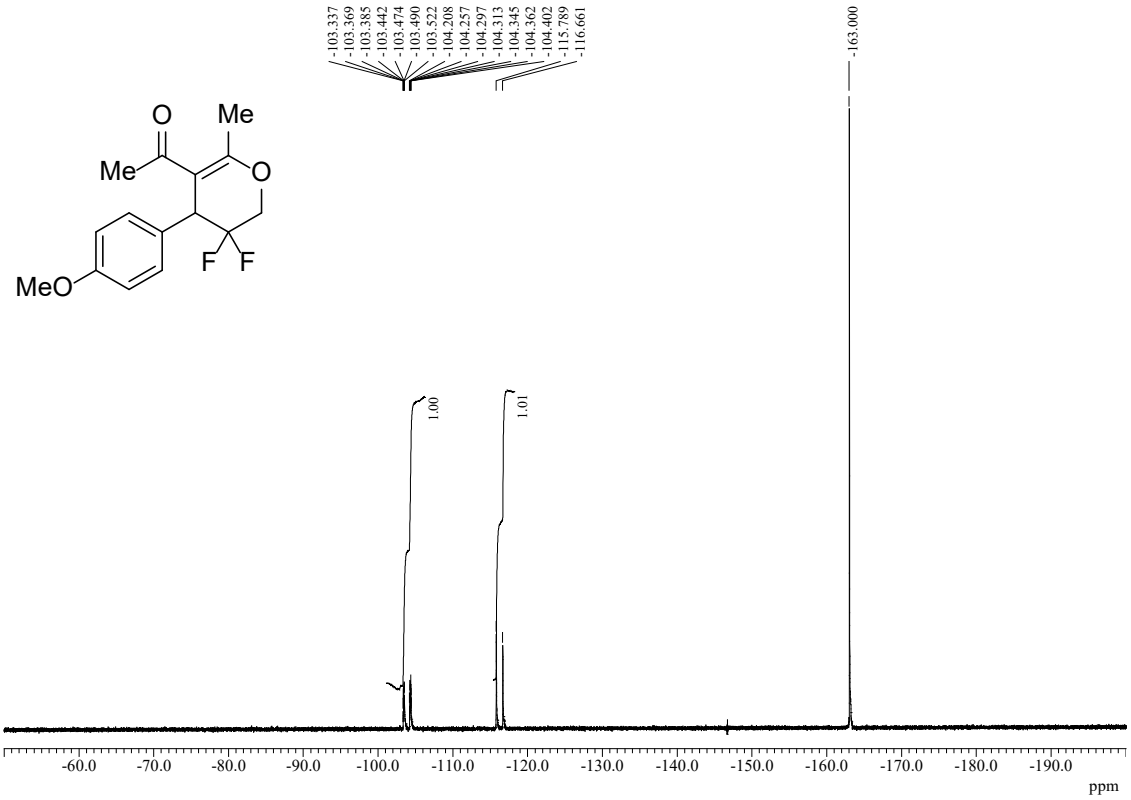
^{19}F NMR spectrum of 3-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]pentan-2,4-dione (**11**)



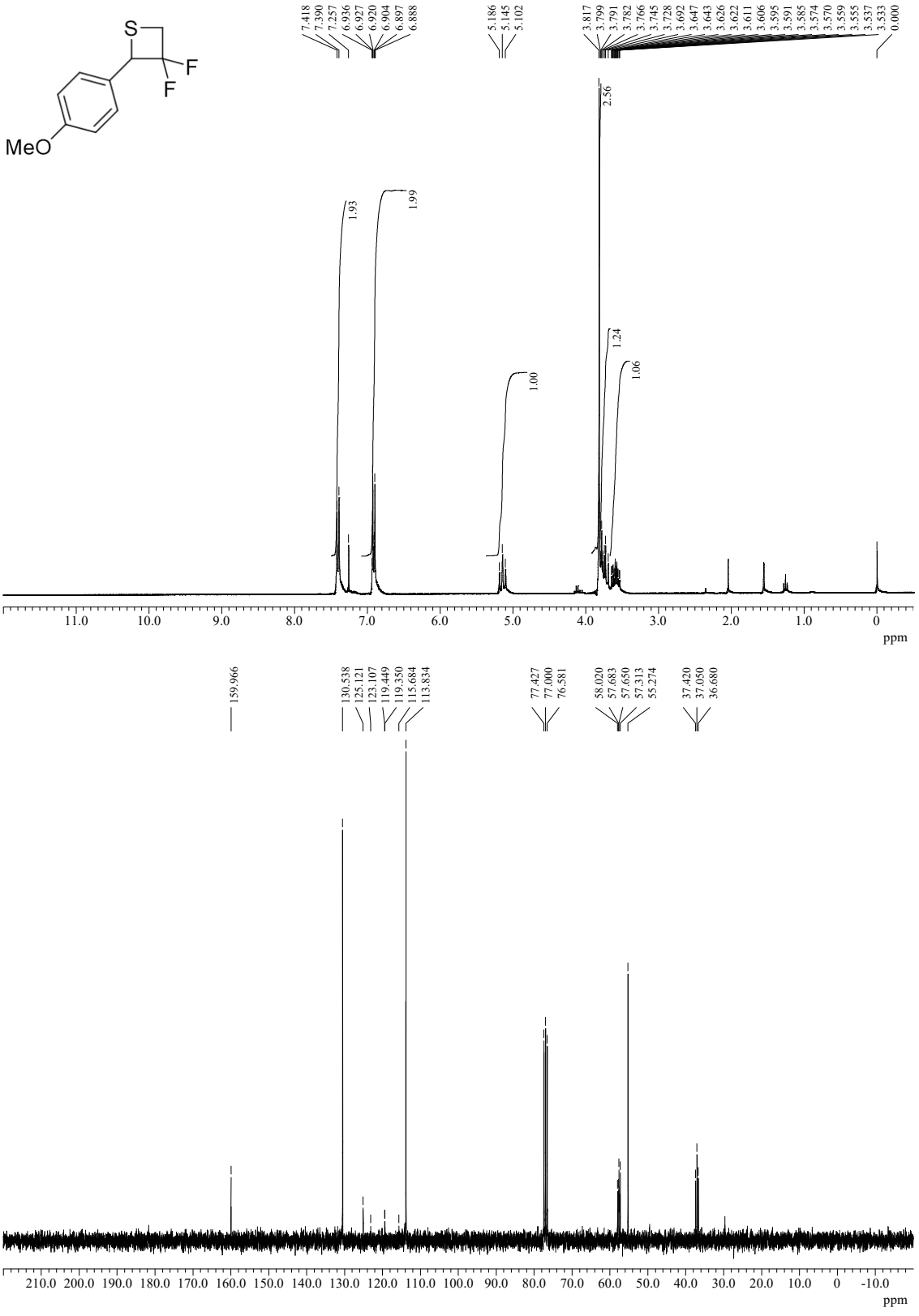
^{1}H and ^{13}C NMR spectra of 1-[3,3-difluoro-4-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2*H*-pyran-5-yl]ethan-1-one (**12**)



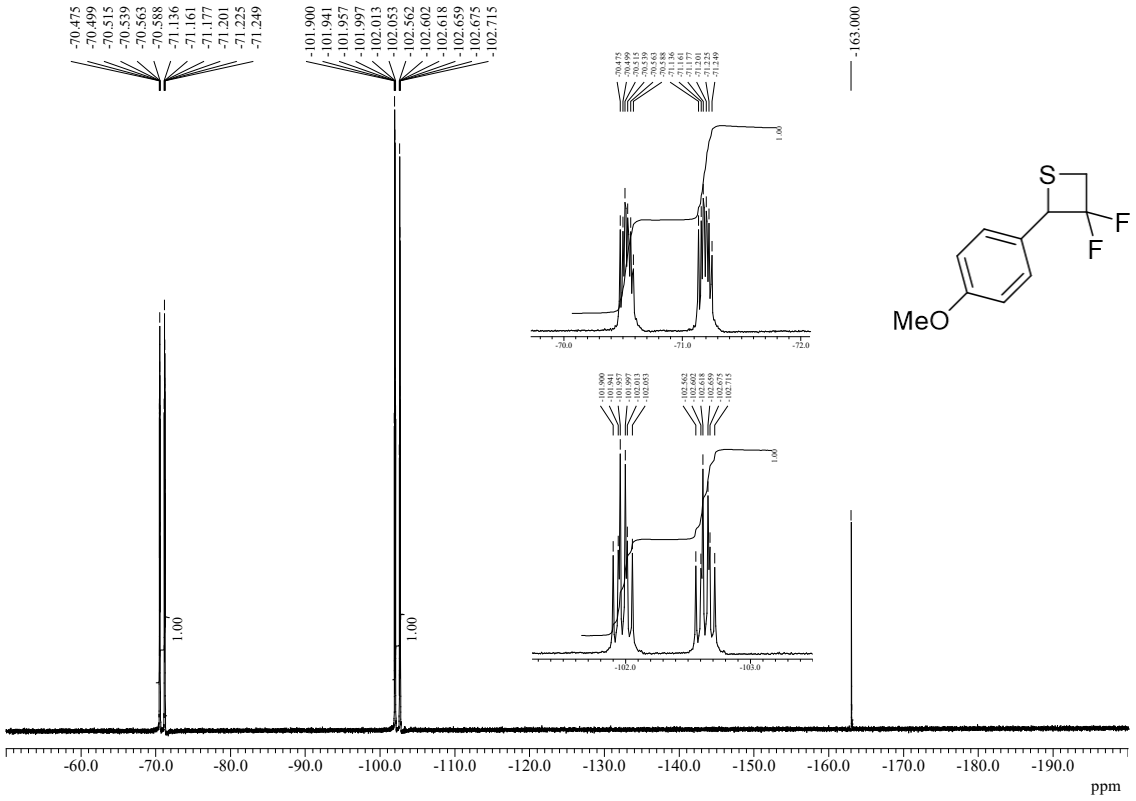
^{19}F NMR spectrum of 1-[3,3-difluoro-4-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2*H*-pyran-5-yl]ethan-1-one (**12**)



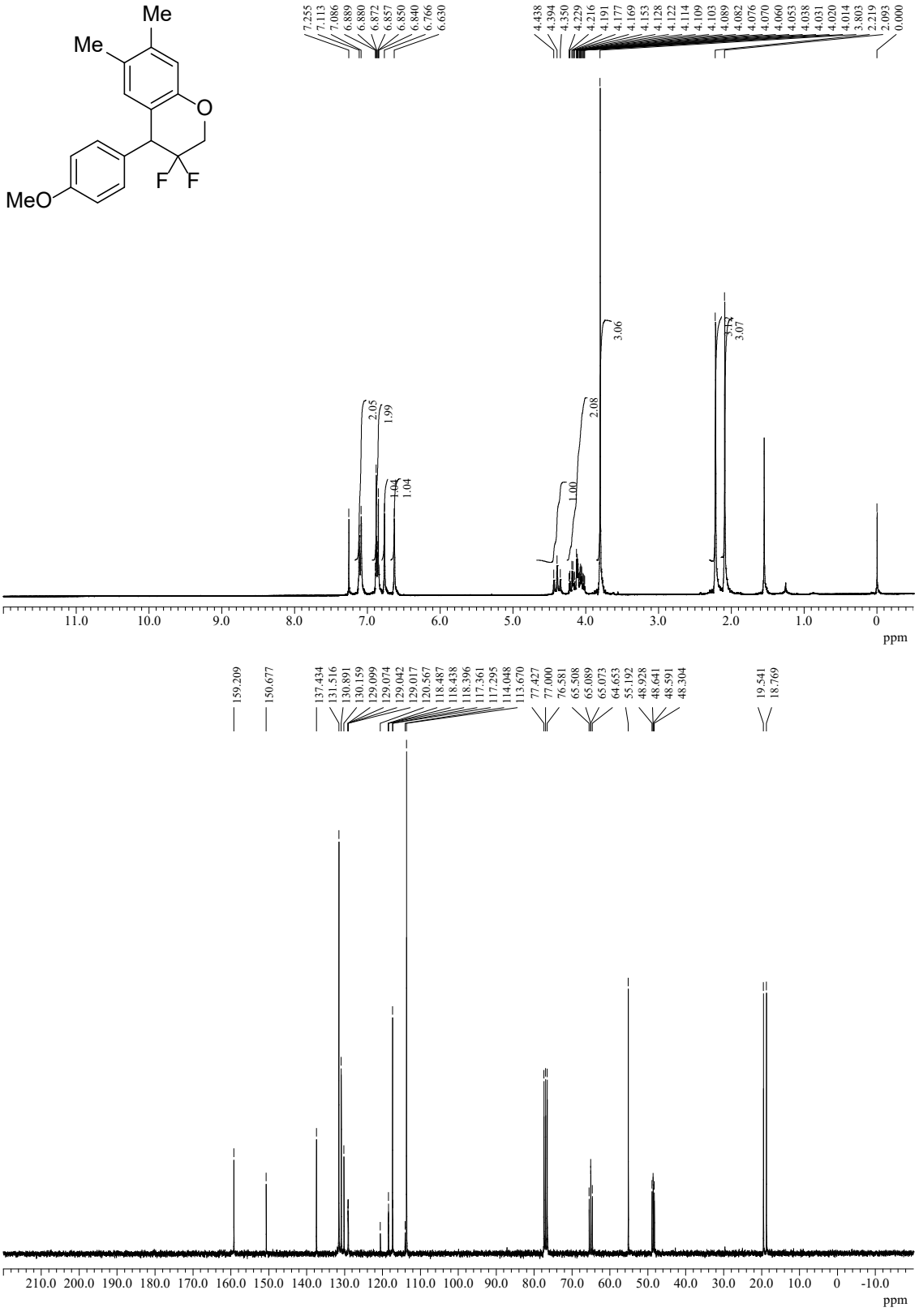
^{1}H and ^{13}C NMR spectra of 3,3-difluoro-2-(4-methoxyphenyl)thietane (**13**)



^{19}F NMR spectrum of 3,3-difluoro-2-(4-methoxyphenyl)thietane (**13**)



^{1}H and ^{13}C NMR spectra of 3,3-diluoro-4-(4-methoxyphenyl)-6,7-dimethylchromane (**14**)



^{19}F NMR spectrum of 3,3-diluoro-4-(4-methoxyphenyl)-6,7-dimethylchromane (**14**)