Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Table of Content

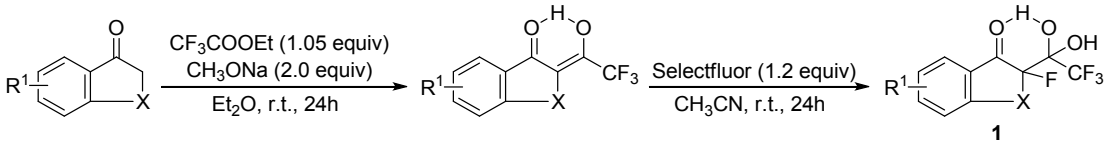
1. General information

All commercial reagents were used without additional purification unless otherwise specified. Solvents were purified and dried according to standard methods prior to use. All experiments were monitored by thin layer chromatography (TLC) using UV light as visualizing agent. TLC was performed on pre-coated silica gel plated. Column chromatography was performed using silica gel 60 (300-400 mesh).

^{1}H NMR, ^{13}C NMR and ^{19}F NMR were measured on Bruker AVANCE III-400 and III-600 spectrometers. Chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0 ppm) or with the solvent reference relative to TMS employed as the internal standard. Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad (br) and multiplet (m)], coupling constants [Hz], integration). Melting points are uncorrected. Values of optical rotation were measured on Rudolph Automatic Polarimeter A21101 at the wavelength of the sodium D-line (589 nm). Infrared spectra were obtained on Bruker Vector 22 in KBr pellets. HRMS were recorded on a LTQ-Orbitrap XL (Thermofisher, U. S. A.). HPLC analysis was performed on Shimadzu SPD-20A using Daicel Chiralpak IC Column.

2. General synthetic procedures

2.1. General procedures for the synthesis of α-fluorinated *gem*-diols 1



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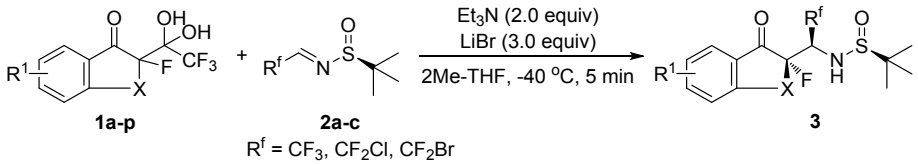
To a stirred solution of sodium methoxide (100 mmol) in diethyl ether (50 mL) was added dropwise the solution of trifluoromethyl ethyl acetate (52.5 mmol) and cyclic ketones (50 mmol) in diethyl ether (50 mL), the mixture was stirred for 24 h at room temperature. Then the resulting mixture was diluted with 1 M HCl solution (pH = 3) and extracted with ether, the combined organics were dried over $MgSO_4$ and concentrated under reduced pressure to afford intermediate di-ketone which was used in the next step without further purification.

A solution of intermediate di-ketone (50 mmol) in acetonitrile (100 mL) was treated with Selectfluor (60 mmol) at room temperature. After 24 h, the reaction was diluted with ethyl acetate

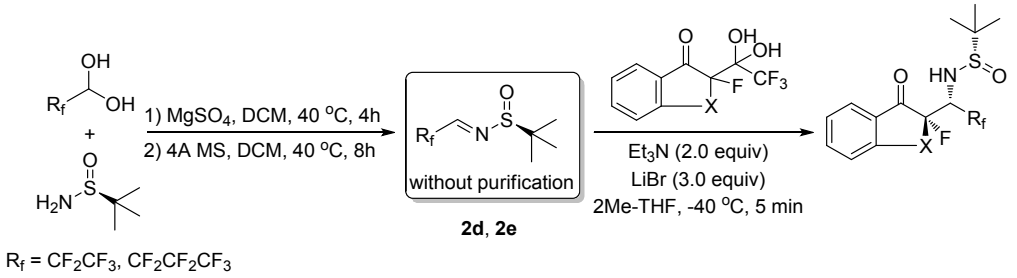
(500 mL) and filtered through Celite. The residue was washed with H_2O (2 × 200 mL) and brine solution (1 × 200 mL) and dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by recrystallization or column chromatography to afford *α*-fluorinated *gem*-diols **1**.

2.2. General procedures for asymmetric detrifluoroacetylative Mannich reaction (Method A)



To a solution of *α*-fluorinated *gem*-diols **1a-p** (0.2 mmol), fluorinated sulfinylimine **2a-c** (0.24 mmol), and LiBr (52.1 mg, 0.6 mmol) in 2-Me-THF (10 mL) at -40 °C was added Et_3N (40.5 mg, 0.4 mmol) dropwise. After 5 min, the reaction was quenched with saturated aqueous NH_4Cl (2 mL) followed by H_2O (10 mL) and the mixture was brought to room temperature. The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layer was washed with H_2O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by column chromatography to afford the corresponding product **3**.

2.3. General procedures for asymmetric detrifluoroacetylative Mannich reaction (Method B)

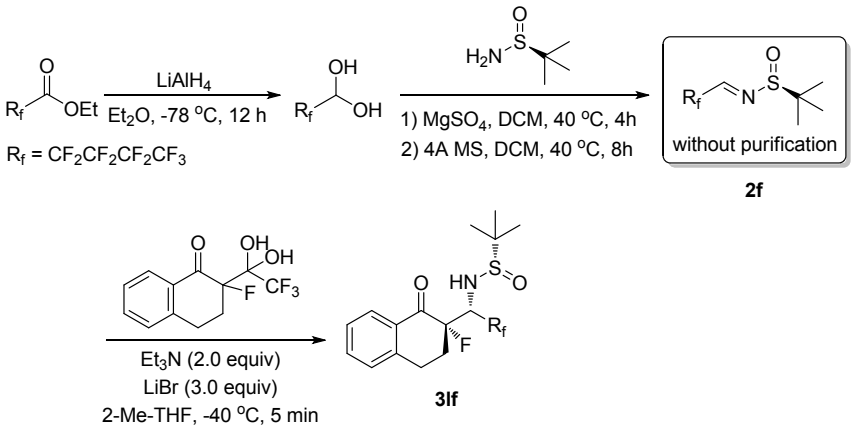


A round-bottom flask equipped with a magnetic stirrer bar and a condenser connected to a nitrogen source was charged with 20 mL of anhydrous DCM, (*S*)-*tert*-butane sulfinamide (1.2 mmol), pentafluoropropionaldehyde hydrate or heptafluorobutyraldehyde hydrate (1.0 mmol) and $MgSO_4$ (120.4 mg, 1.0 mmol) and heated at 40 °C for 4 h. After cooled to room temperature, $MgSO_4$ was removed by filtration. To the filtrate, molecular sieves 4A (1.0 g) were added and the

mixture was heated again for 8 h. After that, molecular sieves were removed by filtration and washed with anhydrous DCM (10 mL). The solvent was removed to give the crude fluorinated sulfinylimine **2d** or **2e**, which was used in the next step without further purification.

To a solution of *α*-fluorinated *gem*-diols (0.2 mmol), the crude fluorinated sulfinylimine **2d** or **2e** obtained in the last step, and LiBr (52.1 mg, 0.6 mmol) in 2Me-THF (10 mL) at -40 ^{o}C was added Et_3N (40.5 mg, 0.4 mmol) dropwise. After 5 min, the reaction was quenched with saturated aqueous NH_4Cl (2 mL) followed by H_2O (10 mL) and the mixture was brought to room temperature. The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layer was washed with H_2O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by column chromatography to afford the corresponding product **3**.

2.4. General procedures for asymmetric detrifluoroacetylative Mannich reaction (Method C)



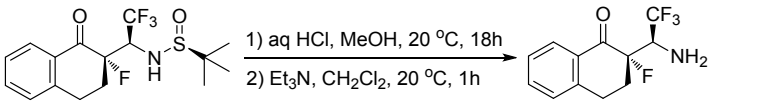
Ethyl nonafluorovalerate (2.0 mmol) was dissolved in Et_2O (1 mL) and then this solution was added slowly to a solution of $LiAlH_4$ (22.8 mg, 0.6 mmol) in Et_2O (3 mL) at -78 ^{o}C for 5 min. After addition, the reaction mixture was stirred for 12 h at -78 ^{o}C. Then, concentrated sulfuric acid (0.1 mL) and ice water (3 mL) was added successively after the reaction mixture was warmed to 0 ^{o}C. The resulting mixture was extracted with ether (3 × 5 mL), then the combined organic layer was washed with H_2O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude reduction product.

A round-bottom flask equipped with a magnetic stirrer bar and a condenser connected to a nitrogen source was charged with 20 mL of anhydrous DCM, (*S*)-*tert*-butane sulfinamide (1.2

mmol), the crude reduction product obtained in the last step and $MgSO_4$ (120.4 mg, 1.0 mmol) and heated at 40 °C for 4 h. After cooled to room temperature, $MgSO_4$ was removed by filtration. To the filtrate, molecular sieves 4 Å (1.0 g) were added and the mixture was heated again for 8 h. After that, molecular sieves were removed by filtration and washed with anhydrous DCM (10 mL). The solvent was removed to give the crude fluorinated sulfinylimine **2f**, which was used in the next step without further purification.

To a solution of *α*-fluorinated *gem*-diols (0.2 mmol), the crude fluorinated sulfinylimine **2f** obtained in the last step, and LiBr (52.1 mg, 0.6 mmol) in 2-Me-THF (10 mL) at -40 °C was added Et_3N (40.5 mg, 0.4 mmol) dropwise. After 5 min, the reaction was quenched with saturated aqueous NH_4Cl (2 mL) followed by H_2O (10 mL) and the mixture was brought to room temperature. The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layer was washed with H_2O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by column chromatography to afford the corresponding product **3**.

2.5. Procedures for the deprotection of 3la to affording the free amine 5

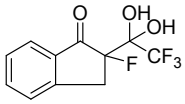


92% yield, >99.5% ee

3la (73.1 mg, 0.2 mmol) and MeOH (5 mL) were placed in a 25 mL round-bottom flask and aq HCl (36%, 1 mL) was added dropwise. The reaction was stirred at 20 °C for 18 h, during which the cleavage was monitored by TLC. Volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL) and Et_3N (1.52 g, 15 mmol) was added. The mixture was stirred at 20 °C for 1 h, then H_2O (10 mL) was added. The organic layer was taken, washed with H_2O (2 × 10 mL), dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by column chromatography to afford the corresponding deprotection product **5** as a slightly green solid in 92% isolated yield.

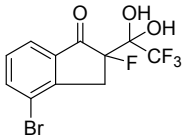
3. Characterization data of compounds

3.1. Characterization data of compounds α-fluorinated *gem*-diols 1



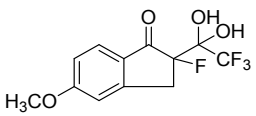
2-fluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1a)

White solid, 11.02 g (83% yield), m.p. 106–107 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.87 (d, *J* = 0.9 Hz, 1H), 7.77–7.68 (m, 2H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 3.92 (dd, *J* = 17.9, 9.9 Hz, 1H), 3.23 (dd, *J* = 25.0, 17.9 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.04 (d, *J* = 11.9 Hz, 3F), -168.95 (q, *J* = 11.8 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 197.7 (d, *J* = 18.2 Hz), 151.0 (d, *J* = 4.7 Hz), 136.5, 134.4 (d, *J* = 1.4 Hz), 128.2, 126.6 (d, *J* = 0.8 Hz), 124.1, 123.1 (q, *J* = 291.0 Hz), 97.8 (d, *J* = 197.5 Hz), 93.2 (qd, *J* = 31.1, 26.5 Hz), 36.0 (d, *J* = 22.9 Hz).



4-bromo-2-fluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1b)

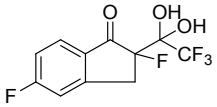
Yellow solid, 12.32 g (72% yield), m.p. 96–97 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.06–7.92 (m, 2H), 7.79–7.65 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 3.88 (dd, *J* = 17.9, 8.2 Hz, 1H), 3.14 (dd, *J* = 24.1, 18.0 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -77.84 (d, *J* = 12.1 Hz, 3F), -169.79 (q, *J* = 12.1 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 196.7 (d, *J* = 18.4 Hz), 150.0 (d, *J* = 5.7 Hz), 138.8, 136.6 (d, *J* = 1.6 Hz), 130.4, 123.3, 123.0 (q, *J* = 290.9 Hz), 120.8 (d, *J* = 1.1 Hz), 98.2 (d, *J* = 200.1 Hz), 93.0 (qd, *J* = 31.2, 26.6 Hz), 36.8 (d, *J* = 23.6 Hz).



2-fluoro-5-methoxy-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1c)

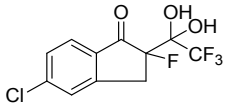
Yellow solid, 11.06 g (75% yield), m.p. 103–104 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.83 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.37 (s, 1H), 7.12 (s, 1H), 7.01 (dd, *J* = 8.5, 1.6 Hz, 1H), 3.92–3.78 (m, 4H), 3.17 (dd, *J* = 24.9, 18.1 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.25 (d, *J* = 11.7 Hz, 3F),

-167.21 (q, *J* = 11.7 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 195.6 (d, *J* = 18.1 Hz), 166.3, 154.4 (d, *J* = 4.3 Hz), 127.2 (d, *J* = 0.9 Hz), 126.2, 123.0 (q, *J* = 290.9 Hz), 116.4, 109.9, 97.1 (d, *J* = 195.9 Hz), 93.2 (qd, *J* = 31.0, 26.6 Hz), 56.0, 36.1 (d, *J* = 23.4 Hz).



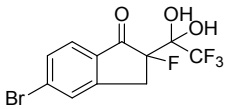
2,5-difluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1d)

Yellow solid, 12.08 g (86% yield), m.p. 115–116 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.91 (s, 1H), 7.79 (dd, *J* = 8.5, 5.4 Hz, 1H), 7.57 (s, 1H), 7.46 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.31 (td, *J* = 9.1, 2.3 Hz, 1H), 3.92 (dd, *J* = 18.1, 9.3 Hz, 1H), 3.24 (dd, *J* = 24.5, 18.2 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.02 (d, *J* = 12.0 Hz, 3F), -100.88 (s, 1F), -168.56 (q, *J* = 11.8 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 195.9 (d, *J* = 18.3 Hz), 167.3 (d, *J* = 255.4 Hz), 154.2 (dd, *J* = 11.0, 5.1 Hz), 131.1, 127.0 (d, *J* = 10.8 Hz), 123.1 (q, *J* = 291.0 Hz), 116.5 (d, *J* = 24.0 Hz), 113.4 (d, *J* = 23.0 Hz), 98.0 (d, *J* = 198.3 Hz), 93.1 (qd, *J* = 31.0, 26.8 Hz), 36.0 (d, *J* = 23.2 Hz).



5-chloro-2-fluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1e)

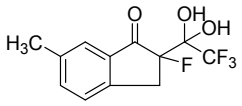
White solid, 12.45 g (83% yield), m.p. 119–120 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.94 (s, 1H), 7.74–7.67 (m, 2H), 7.61 (d, *J* = 1.2 Hz, 1H), 7.49 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.93 (dd, *J* = 18.1, 9.0 Hz, 1H), 3.24 (dd, *J* = 24.5, 18.1 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.02 (d, *J* = 12.0 Hz, 3F), -169.04 (q, *J* = 11.9 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 196.3 (d, *J* = 18.4 Hz), 152.7 (d, *J* = 5.2 Hz), 141.3, 133.2 (d, *J* = 1.6 Hz), 128.7, 126.6 (d, *J* = 0.8 Hz), 125.7, 123.1 (q, *J* = 291.0 Hz), 98.1 (d, *J* = 198.9 Hz), 93.1 (qd, *J* = 31.1, 26.4 Hz), 35.7 (d, *J* = 23.2 Hz).



5-bromo-2-fluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1f)

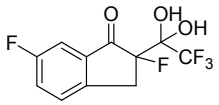
Yellow solid, 13.88 g (81% yield), m.p. 113–114 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.92 (s, 1H), 7.88 (s, 1H), 7.70–7.55 (m, 3H), 3.91 (dd, *J* = 18.0, 8.8 Hz, 1H), 3.24 (dd, *J* = 24.4, 18.2 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -77.95 (d, *J* = 12.0 Hz, 3F), -169.25 (q, *J* = 11.9 Hz, 1F); ^{13}C

NMR (101 MHz, DMSO) δ 196.6 (d, *J* = 18.4 Hz), 152.7 (d, *J* = 5.0 Hz), 133.4, 131.5, 130.6, 129.6, 125.7, 123.0 (q, *J* = 291.1 Hz), 98.1 (d, *J* = 199.2 Hz), 93.0 (qd, *J* = 31.1, 26.5 Hz), 35.6 (d, *J* = 23.3 Hz).



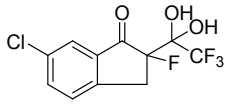
2-fluoro-6-methyl-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1g)

White solid, 10.63 g (76% yield), m.p. 95–96 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.85 (s, 1H), 7.60–7.42 (m, 4H), 3.87 (dd, *J* = 17.7, 10.1 Hz, 1H), 3.15 (dd, *J* = 24.9, 17.9 Hz, 1H), 2.36 (s, 3H); ^{19}F NMR (376 MHz, DMSO) δ -78.10 (d, *J* = 11.7 Hz, 3F), -168.54 (q, *J* = 11.7 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 197.5 (d, *J* = 18.2 Hz), 148.3 (d, *J* = 4.8 Hz), 137.8, 137.5, 134.4 (d, *J* = 1.2 Hz), 126.2, 123.8, 123.0 (q, *J* = 290.8 Hz), 97.9 (d, *J* = 197.2 Hz), 93.1 (qd, *J* = 31.0, 26.5 Hz), 35.6 (d, *J* = 22.8 Hz), 20.6.



2,6-difluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1h)

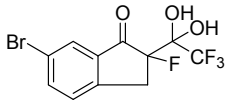
White solid, 10.98 g (78% yield), m.p. 91–92 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.96 (s, 1H), 7.65–7.54 (m, 2H), 7.50 (td, *J* = 8.8, 2.5 Hz, 1H), 7.43 (dd, *J* = 7.5, 2.4 Hz, 1H), 3.94 (dd, *J* = 17.7, 9.4 Hz, 1H), 3.18 (dd, *J* = 24.6, 17.7 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.25 (d, *J* = 11.9 Hz, 3F), -113.70 (s, 1F), -168.53 (q, *J* = 11.7 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 197.3 (dd, *J* = 18.5, 3.0 Hz), 162.3 (d, *J* = 246.7 Hz), 147.2 (dd, *J* = 4.9, 1.6 Hz), 136.3 (dd, *J* = 7.6, 1.4 Hz), 128.9 (d, *J* = 7.9 Hz), 124.2 (d, *J* = 23.6 Hz), 123.4 (q, *J* = 291.0 Hz), 110.0 (d, *J* = 22.3 Hz), 98.8 (d, *J* = 198.5 Hz), 93.5 (qd, *J* = 31.1, 26.4 Hz), 35.7 (d, *J* = 23.0 Hz).



6-chloro-2-fluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1i)

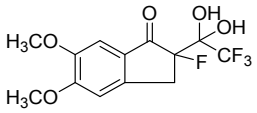
White solid, 12.71 g (85% yield), m.p. 95–96 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.93 (s, 1H), 7.77 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.67–7.58 (m, 2H), 3.91 (dd, *J* = 18.0, 8.6

Hz, 1H), 3.21 (dd, *J* = 24.5, 18.0 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -77.97 (d, *J* = 12.0 Hz, 3F), -169.18 (q, *J* = 12.0 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 196.4 (d, *J* = 18.5 Hz), 149.4 (d, *J* = 5.3 Hz), 136.0, 136.0, 133.1, 128.4 (d, *J* = 1.1 Hz), 123.3, 123.0 (q, *J* = 291.9 Hz), 98.6 (d, *J* = 199.5 Hz), 93.0 (qd, *J* = 31.1, 26.4 Hz), 35.5 (d, *J* = 23.1 Hz).



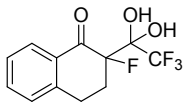
6-bromo-2-fluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1j)

Yellow solid, 14.10 g (82% yield), m.p. 96–97 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.93 (s, 1H), 7.91–7.81 (m, 2H), 7.64 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 3.89 (dd, *J* = 17.9, 8.5 Hz, 1H), 3.19 (dd, *J* = 24.4, 18.0 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -77.96 (d, *J* = 12.0 Hz, 3F), -169.24 (q, *J* = 11.9 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 196.3 (d, *J* = 18.5 Hz), 149.8 (d, *J* = 5.3 Hz), 138.7, 136.3 (d, *J* = 1.6 Hz), 128.7 (d, *J* = 0.6 Hz), 126.3, 123.0 (d, *J* = 291.3 Hz), 121.3, 98.5 (d, *J* = 199.5 Hz), 93.0 (qd, *J* = 31.2, 26.6 Hz), 35.6 (d, *J* = 22.9 Hz).



2-fluoro-5,6-dimethoxy-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2,3-dihydro-1*H*-inden-1-one (1k)

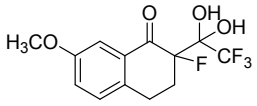
White solid, 11.71 g (72% yield), m.p. 120–121 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.81 (s, 1H), 7.33 (s, 1H), 7.15 (s, 1H), 7.13 (s, 1H), 3.90 (s, 3H), 3.84–3.73 (m, 4H), 3.10 (dd, *J* = 24.5, 17.9 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.30 (d, *J* = 11.8 Hz, 3F), -167.06 (q, *J* = 11.6 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 195.9 (d, *J* = 18.3 Hz), 156.8, 149.7, 147.2 (d, *J* = 4.1 Hz), 126.5, 123.0 (q, *J* = 291.0 Hz), 108.0, 104.6, 96.9 (d, *J* = 195.3 Hz), 93.2 (qd, *J* = 30.8, 26.5 Hz), 56.3, 55.8, 35.7 (d, *J* = 23.5 Hz).



2-fluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-3,4-dihydronaphthalen-1(2*H*)-one (1l)

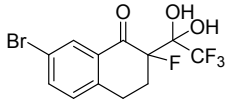
White solid, 9.93 g (71% yield), m.p. 82–83 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.88–7.78 (m, 2H),

7.59–7.49 (m, 2H), 7.38–7.28 (m, 2H), 3.50–3.34 (m, 1H), 2.93 (dd, *J* = 17.2, 5.1 Hz, 1H), 2.84–2.73 (m, 1H), 2.31–2.15 (m, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.48 (d, *J* = 14.3 Hz, 3F), -162.12 (q, *J* = 14.2 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 192.4 (d, *J* = 16.4 Hz), 144.0, 133.6, 133.0, 128.7, 126.8 (d, *J* = 1.0 Hz), 126.4, 123.1 (q, *J* = 291.8 Hz), 95.4 (d, *J* = 191.5 Hz), 94.1 (qd, *J* = 30.6, 28.6 Hz), 30.4 (d, *J* = 21.3 Hz), 26.0 (d, *J* = 11.9 Hz).



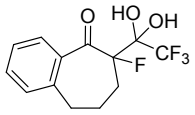
2-fluoro-7-methoxy-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-3,4-dihydronaphthalen-1(2*H*)-one (1m)

White solid, 10.44 g (68% yield), m.p. 75–76 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.84 (s, 1H), 7.51 (d, *J* = 2.2 Hz, 1H), 7.29 (d, *J* = 2.7 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.14 (dd, *J* = 8.5, 2.8 Hz, 1H), 3.78 (s, 3H), 3.37 (ddd, *J* = 16.9, 12.6, 4.7 Hz, 1H), 2.93–2.72 (m, 2H), 2.29–2.14 (m, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.45 (d, *J* = 14.4 Hz, 3F), -162.09 (q, *J* = 14.4 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 192.1 (d, *J* = 16.5 Hz), 157.8, 136.4 (d, *J* = 0.8 Hz), 133.7, 130.0, 123.0 (qd, *J* = 292.0, 1.4 Hz), 121.3, 109.2 (d, *J* = 1.6 Hz), 95.4 (d, *J* = 191.3 Hz), 94.1 (qd, *J* = 30.7, 28.5 Hz), 55.3, 30.7 (d, *J* = 21.2 Hz), 25.2 (d, *J* = 12.0 Hz).



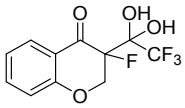
7-bromo-2-fluoro-2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-3,4-dihydronaphthalen-1(2*H*)-one (1n)

White solid, 13.59 g (76% yield), m.p. 87–88 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.94 (s, 1H), 7.88 (d, *J* = 2.1 Hz, 1H), 7.70 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.64 (s, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 3.39 (ddd, *J* = 17.4, 12.7, 4.9 Hz, 1H), 2.98–2.75 (m, 2H), 2.34–2.17 (m, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.55 (d, *J* = 14.5 Hz, 3F), -162.93 (q, *J* = 14.5 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 191.3 (d, *J* = 16.7 Hz), 143.2, 136.0, 134.9 (d, *J* = 0.7 Hz), 131.2, 128.9 (d, *J* = 1.5 Hz), 123.0 (qd, *J* = 292.0, 1.0 Hz), 119.5, 95.5 (d, *J* = 192.9 Hz), 94.1 (qd, *J* = 30.9, 28.3 Hz), 30.1 (d, *J* = 21.5 Hz), 25.7 (d, *J* = 12.1 Hz).



6-fluoro-6-(2,2,2-trifluoro-1,1-dihydroxyethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (1o)

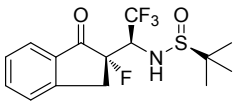
White solid, 8.55 g (59% yield), m.p. 85–86 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.51 (s, 1H), 7.47 (s, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.31–7.18 (m, 3H), 3.10–2.87 (m, 2H), 2.57–2.36 (m, 1H), 2.23–2.04 (m, 1H), 2.00–1.77 (m, 2H); ^{19}F NMR (376 MHz, DMSO) δ -77.96 (d, *J* = 14.5 Hz, 3F), -159.52 (q, *J* = 14.3 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 201.5 (d, *J* = 24.4 Hz), 139.2 (d, *J* = 1.0 Hz), 139.0, 130.6, 129.3, 128.2, 125.9, 123.1 (qd, *J* = 291.9, 1.7 Hz), 102.3 (d, *J* = 192.8 Hz), 93.6 (qd, *J* = 30.4, 26.5 Hz), 33.9, 30.9 (d, *J* = 22.4 Hz), 21.5 (d, *J* = 1.3 Hz).



3-fluoro-3-(2,2,2-trifluoro-1,1-dihydroxyethyl)chroman-4-one (1p)

White solid, 9.41 g (67% yield), m.p. 119–120 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.12 (s, 1H), 7.78–7.72 (m, 2H), 7.62–7.56 (m, 1H), 7.12–7.06 (m, 1H), 7.03 (dd, *J* = 8.4, 0.5 Hz, 1H), 4.98 (dd, *J* = 12.1, 1.7 Hz, 1H), 4.46 (dd, *J* = 11.8, 10.4 Hz, 1H); ^{19}F NMR (376 MHz, DMSO) δ -78.60 (d, *J* = 13.2 Hz, 3F), -178.68 (q, *J* = 13.1 Hz, 1F); ^{13}C NMR (101 MHz, DMSO) δ 186.8 (d, *J* = 16.4 Hz), 160.7, 136.6, 126.8 (d, *J* = 1.2 Hz), 122.8 (qd, *J* = 291.5, 1.1 Hz), 121.7, 120.9 (d, *J* = 0.5 Hz), 117.6, 93.3 (qd, *J* = 31.5, 26.1 Hz), 90.1 (d, *J* = 193.7 Hz), 67.6 (d, *J* = 33.8 Hz).

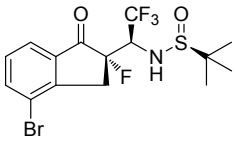
3.2. Characterization data of products 3



(*S*)-2-methyl-*N*-((*S*)-2,2,2-trifluoro-1-((*S*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)ethyl)propane-2-sulfinamide (3aa)

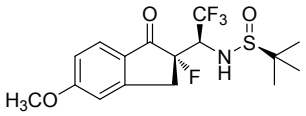
White solid, 68.4 mg (97% yield), m.p. 93–94 °C, [α]20 D = +94.1 (c = 0.20, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.4 Hz, 1H), 7.69 (td, *J* = 7.5, 1.1 Hz, 1H), 7.50–7.42 (m, 2H), 4.53–4.41 (m, 1H), 3.99 (d, *J* = 9.2 Hz, 1H), 3.66 (dd, *J* = 18.1, 14.5 Hz, 1H), 3.38 (dd, *J* = 24.6, 18.1 Hz, 1H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.01 (d, *J* = 7.2 Hz, 3F), -156.36 (q, *J*

= 7.2 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 (d, *J* = 17.4 Hz), 149.6 (d, *J* = 2.2 Hz), 136.9, 133.3, 128.7, 126.7, 125.3, 123.3 (qd, *J* = 283.7, 10.0 Hz), 95.0 (d, *J* = 190.6 Hz), 60.7 (qd, *J* = 29.4, 26.5 Hz), 57.7, 35.6 (d, *J* = 24.2 Hz), 22.3. IR (cm^{-1}): 3195, 1728, 1307, 1271, 1215, 1160, 1080, 1066, 875, 736, 683. HRMS (TOF MS ESI): calcd for $C_{15}H_{17}F_4NO_2SNa^+$ $[M+Na]^+$ 374.0808, found 374.0810.



(*S*)-*N*-((*S*)-1-((*S*)-4-bromo-2-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3ba)

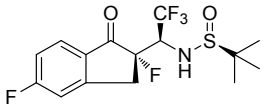
White solid, 74.2 mg (86% yield), m.p. 140–141 °C, [α]20 D = +70.5 (c = 0.86, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 4.57–4.45 (m, 1H), 4.03 (d, *J* = 9.7 Hz, 1H), 3.56 (dd, *J* = 18.6, 15.1 Hz, 1H), 3.29 (dd, *J* = 24.6, 18.6 Hz, 1H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.80 (d, *J* = 7.5 Hz, 3F), -157.11 (q, *J* = 7.4 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4 (d, *J* = 17.4 Hz), 149.3 (d, *J* = 3.3 Hz), 139.6, 135.5, 130.7, 124.3, 123.4 (qd, *J* = 283.6, 9.3 Hz), 122.1, 94.7 (d, *J* = 191.5 Hz), 60.3 (qd, *J* = 29.7, 25.6 Hz), 57.9, 37.1 (d, *J* = 25.2 Hz), 22.4. IR (cm^{-1}): 1733, 1275, 1264, 1207, 1126, 1058, 936, 762. HRMS (TOF MS ESI): calcd for $C_{15}H_{16}BrF_4NO_2SNa^+$ $[M+Na]^+$ 451.9913, found 451.9912.



(*S*)-2-methyl-*N*-((*S*)-2,2,2-trifluoro-1-((*S*)-2-fluoro-5-methoxy-1-oxo-2,3-dihydro-1*H*-inden-2-yl)ethyl)propane-2-sulfinamide (3ca)

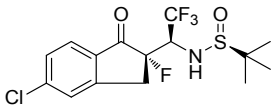
White solid, 59.4 mg (78% yield), m.p. 126–127 °C, [α]20 D = +76.6 (c = 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 1H), 6.97 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 4.52–4.40 (m, 1H), 4.22 (d, *J* = 9.6 Hz, 1H), 3.90 (s, 3H), 3.61 (dd, *J* = 18.1, 14.3 Hz, 1H), 3.31 (dd, *J* = 24.4, 18.2 Hz, 1H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.05 (d, *J* = 7.4 Hz, 3F), -156.06 (q, *J* = 7.3 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8 (d, *J* = 17.5 Hz), 167.1,

152.7 (d, *J* = 3.4 Hz), 127.4, 126.5, 123.4 (qd, *J* = 283.7, 10.2 Hz), 116.8, 109.9, 95.5 (d, *J* = 190.4 Hz), 60.8 (qd, *J* = 29.5, 26.2 Hz), 57.9, 55.9, 35.8 (d, *J* = 24.5 Hz), 22.5. IR (cm^{-1}): 3188, 1724, 1609, 1345, 1271, 1202, 1166, 1117, 1065, 901, 852, 707. HRMS (TOF MS ESI): calcd for $C_{16}H_{19}F_4NO_3SNa^+$ $[M+Na]^+$ 404.0914, found 404.0916.



(*S*)-*N*-((*S*)-1-((*S*)-2,5-difluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3da)

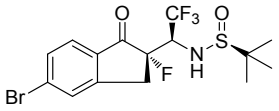
White solid, 73.0 mg (99% yield), m.p. 90–91 °C, [α]20 D = +93.8 (c = 0.42, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.20–7.12 (m, 2H), 4.55–4.42 (m, 1H), 3.99 (d, *J* = 9.5 Hz, 1H), 3.65 (dd, *J* = 18.2, 14.7 Hz, 1H), 3.38 (dd, *J* = 24.3, 18.4 Hz, 1H), 1.25 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.82 (d, *J* = 7.5 Hz, 3F), -97.82 (s, 1F), -156.87 (q, *J* = 7.3 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2 (d, *J* = 17.4 Hz), 168.2 (d, *J* = 260.2 Hz), 152.8 (d, *J* = 10.6 Hz), 129.7, 128.0 (d, *J* = 10.8 Hz), 123.2 (qd, *J* = 283.6, 10.5 Hz), 117.2 (d, *J* = 23.9 Hz), 113.6 (d, *J* = 22.9 Hz), 95.0 (d, *J* = 190.4 Hz), 61.3–60.0 (m), 57.8, 35.5 (d, *J* = 24.8 Hz), 22.3. IR (cm^{-1}): 3186, 1730, 1618, 1595, 1271, 1261, 1146, 1108, 1067, 943, 859. HRMS (TOF MS ESI): calcd for $C_{15}H_{16}F_5NO_2SNa^+$ $[M+Na]^+$ 392.0714, found 392.0714.



(*S*)-*N*-((*S*)-1-((*S*)-5-chloro-2-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3ea)

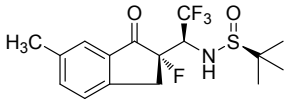
White solid, 74.3 mg (96% yield), m.p. 110–111 °C, [α]20 D = +85.0 (c = 0.96, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.48–7.42 (m, 2H), 4.48 (ddq, *J* = 14.5, 9.4, 7.2 Hz, 1H), 3.96 (d, *J* = 9.5 Hz, 1H), 3.64 (dd, *J* = 18.3, 14.6 Hz, 1H), 3.36 (dd, *J* = 24.4, 18.3 Hz, 1H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.76 (d, *J* = 7.5 Hz, 3F), -157.33 (q, *J* = 7.5 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6 (d, *J* = 17.5 Hz), 150.9 (d, *J* = 3.2 Hz), 143.7, 131.9, 129.8, 127.0, 126.6, 123.4 (qd, *J* = 283.5, 9.7 Hz), 95.0 (d, *J* = 191.3 Hz), 60.3 (qd, *J* = 29.6, 25.7 Hz), 57.9, 35.6 (d, *J* = 24.8 Hz), 22.4. IR (cm^{-1}): 1741, 1602, 1265, 1209, 1159, 1120, 1071, 910.

HRMS (TOF MS ESI): calcd for $C_{15}H_{16}ClF_4NO_2SNa^+$ $[M+Na]^+$ 408.0419, found 408.0422.



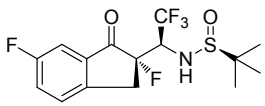
(*S*)-*N*-((*S*)-1-((*S*)-5-bromo-2-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3fa)

Yellow solid, 75.0 mg (87% yield), m.p. 126–127 °C, [α]20 D = +73.5 (c = 0.78, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.65 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 4.48 (ddq, *J* = 14.4, 9.3, 7.2 Hz, 1H), 3.96 (d, *J* = 9.5 Hz, 1H), 3.64 (dd, *J* = 18.3, 14.6 Hz, 1H), 3.37 (dd, *J* = 24.3, 18.3 Hz, 1H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.75 (d, *J* = 7.6 Hz, 3F), -157.54 (q, *J* = 7.5 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8 (d, *J* = 17.5 Hz), 150.9 (d, *J* = 3.2 Hz), 132.6, 132.6, 132.2, 130.1 (d, *J* = 0.5 Hz), 126.6, 123.3 (qd, *J* = 283.6, 9.7 Hz), 94.9 (d, *J* = 191.3 Hz), 60.3 (qd, *J* = 29.6, 25.8 Hz), 57.9, 35.5 (d, *J* = 23.0 Hz), 22.4. IR (cm^{-1}): 3215, 1739, 1598, 1263, 1208, 1159, 1121, 1070, 1061, 909. HRMS (TOF MS ESI): calcd for $C_{15}H_{16}BrF_4NO_2SNa^+$ $[M+Na]^+$ 451.9913, found 451.9915.



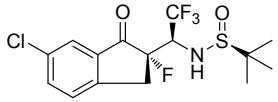
(*S*)-2-methyl-*N*-((*S*)-2,2,2-trifluoro-1-((*S*)-2-fluoro-6-methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl)ethyl)propane-2-sulfinamide (3ga)

White solid, 64.1 mg (88% yield), m.p. 131–132 °C, [α]20 D = +98.4 (c = 0.49, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 4.45 (ddq, *J* = 14.4, 9.6, 7.2 Hz, 1H), 3.94 (d, *J* = 9.6 Hz, 1H), 3.60 (dd, *J* = 17.9, 14.2 Hz, 1H), 3.32 (dd, *J* = 24.5, 18.0 Hz, 1H), 2.42 (s, 3H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.92 (d, *J* = 7.7 Hz, 3F), -158.07 (q, *J* = 7.6 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 (d, *J* = 17.5 Hz), 146.9 (d, *J* = 3.4 Hz), 139.1, 138.3, 133.6, 126.4, 125.3, 123.4 (qd, *J* = 283.7, 9.6 Hz), 95.4 (d, *J* = 191.0 Hz), 60.6 (qd, *J* = 29.5, 25.8 Hz), 57.8, 35.5 (dd, *J* = 24.2, 1.7 Hz), 22.4, 21.1. IR (cm^{-1}): 3317, 1728, 1263, 1206, 1159, 1139, 1124, 1085. HRMS (TOF MS ESI): calcd for $C_{16}H_{19}F_4NO_2SNa^+$ $[M+Na]^+$ 388.0965, found 388.0966.



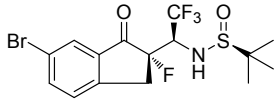
(*S*)-*N*-((*S*)-1-((*S*)-2,6-difluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3ha)

White solid, 70.8 mg (96% yield), m.p. 91–92 °C, [α]20 D = +91.3 (c = 0.67, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.39 (m, 3H), 4.47 (ddq, *J* = 14.4, 9.5, 7.2 Hz, 1H), 3.98 (d, *J* = 9.6 Hz, 1H), 3.63 (dd, *J* = 17.8, 14.2 Hz, 1H), 3.36 (dd, *J* = 24.4, 18.1 Hz, 1H), 1.25 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.75 (d, *J* = 7.7 Hz, 3F), -111.45 (s, 1F), -157.88 (q, *J* = 7.6 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3 (dd, *J* = 17.6, 2.7 Hz), 162.7 (d, *J* = 250.4 Hz), 145.2, 134.9 (d, *J* = 7.7 Hz), 128.4 (d, *J* = 7.9 Hz), 124.7 (d, *J* = 23.8 Hz), 123.2 (qd, *J* = 283.6, 10.1 Hz), 111.0 (d, *J* = 22.3 Hz), 95.6 (d, *J* = 191.0 Hz), 60.6 (qd, *J* = 29.6, 26.1 Hz), 57.8, 35.1 (d, *J* = 24.4 Hz), 22.3. IR (cm^{-1}): 3182, 1736, 1486, 1271, 1217, 1138, 1109, 1073, 767. HRMS (TOF MS ESI): calcd for $C_{15}H_{16}F_5NO_2SNa^+$ $[M+Na]^+$ 392.0714, found 392.0718.



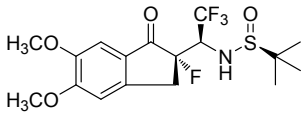
(*S*)-*N*-((*S*)-1-((*S*)-6-chloro-2-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3ia)

White solid, 76.5 mg (99% yield), m.p. 62–63 °C, [α]20 D = +93.0 (c = 0.88, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.9 Hz, 1H), 7.65 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 4.47 (ddq, *J* = 14.4, 9.4, 7.2 Hz, 1H), 3.99 (d, *J* = 9.6 Hz, 1H), 3.63 (dd, *J* = 18.2, 14.5 Hz, 1H), 3.35 (dd, *J* = 24.4, 18.3 Hz, 1H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.72 (d, *J* = 7.6 Hz, 3F), -157.67 (q, *J* = 7.5 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9 (d, *J* = 17.6 Hz), 147.6 (d, *J* = 3.2 Hz), 137.0, 135.3, 134.9, 128.0, 125.1, 123.3 (qd, *J* = 283.6, 9.5 Hz), 95.3 (d, *J* = 191.5 Hz), 60.3 (qd, *J* = 29.6, 25.8 Hz), 57.9, 35.5 (dd, *J* = 24.6, 1.9 Hz), 22.4. IR (cm^{-1}): 1737, 1471, 1264, 1209, 1183, 1158, 1121, 1067. HRMS (TOF MS ESI): calcd for $C_{15}H_{16}ClF_4NO_2SNa^+$ $[M+Na]^+$ 408.0419, found 408.0422.



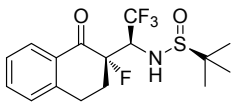
(*S*)-*N*-((*S*)-1-((*S*)-6-bromo-2-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3ja)

Yellow solid, 69.8 mg (81% yield), m.p. 114–115 °C, [α]20 D = +84.7 (c = 0.46, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.7 Hz, 1H), 7.80 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 4.47 (ddq, *J* = 14.4, 9.5, 7.3 Hz, 1H), 3.95 (d, *J* = 9.5 Hz, 1H), 3.61 (dd, *J* = 18.2, 14.5 Hz, 1H), 3.33 (dd, *J* = 24.4, 18.2 Hz, 1H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.83 (d, *J* = 7.2 Hz, 3F), -156.31 (q, *J* = 6.9 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7 (d, *J* = 17.5 Hz), 148.1 (d, *J* = 3.1 Hz), 139.7, 135.1, 128.3, 128.2, 123.3 (qd, *J* = 283.6, 9.7 Hz), 122.9, 95.1 (d, *J* = 191.3 Hz), 60.4 (qd, *J* = 29.6, 25.9 Hz), 57.9, 35.5 (d, *J* = 24.6 Hz), 22.4. IR (cm^{-1}): 3316, 1732, 1263, 1210, 1183, 1155, 1083, 824. HRMS (TOF MS ESI): calcd for $C_{15}H_{16}BrF_4NO_2SNa^+$ $[M+Na]^+$ 451.9913, found 451.9916.



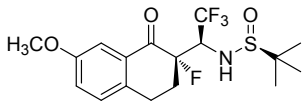
(*S*)-2-methyl-*N*-((*S*)-2,2,2-trifluoro-1-((*S*)-2-fluoro-5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-inden-2-yl)ethyl)propane-2-sulfinamide (3ka)

White solid, 64.3 mg (78% yield), m.p. 173–174 °C, [α]20 D = +78.8 (c = 0.62, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.85 (s, 1H), 4.53–4.40 (m, 1H), 4.02–3.89 (m, 7H), 3.56 (dd, *J* = 17.8, 13.5 Hz, 1H), 3.28 (dd, *J* = 23.7, 17.8 Hz, 1H), 1.25 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.01 (d, *J* = 7.7 Hz, 3F), -157.06 (q, *J* = 7.5 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2 (d, *J* = 17.8 Hz), 157.5, 150.6, 145.4 (d, *J* = 3.6 Hz), 126.3, 123.5 (qd, *J* = 283.7, 9.8 Hz), 107.4, 105.3, 95.5 (d, *J* = 190.7 Hz), 60.5 (qd, *J* = 29.4, 26.3 Hz), 57.8, 56.6, 56.3, 35.7 (dd, *J* = 24.5, 1.4 Hz), 22.4. IR (cm^{-1}): 3245, 1714, 1603, 1586, 1506, 1333, 1283, 1224, 1200, 1123, 1067, 1051, 1030, 996, 777. HRMS (TOF MS ESI): calcd for $C_{17}H_{21}F_4NO_4SNa^+$ $[M+Na]^+$ 434.1020, found 434.1022.



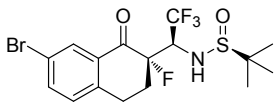
(*S*)-2-methyl-*N*-((*S*)-2,2,2-trifluoro-1-((*S*)-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)ethyl)propane-2-sulfinamide (3la)

Colorless oil, 72.3 mg (99% yield), [α]20 D = +26.7 (c = 0.26, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.57 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 4.48 (ddq, *J* = 17.6, 10.5, 7.1 Hz, 1H), 3.91 (d, *J* = 10.5 Hz, 1H), 3.24 (dt, *J* = 17.5, 5.6 Hz, 1H), 3.10 (ddd, *J* = 17.7, 8.6, 5.0 Hz, 1H), 2.66–2.42 (m, 2H), 1.19 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.24 (d, *J* = 8.9 Hz, 3F), -170.26 (q, *J* = 8.6 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1 (d, *J* = 17.9 Hz), 142.2, 134.7, 130.2, 128.9, 128.6 (d, *J* = 0.7 Hz), 127.4, 123.6 (qd, *J* = 284.9, 3.7 Hz), 93.7 (d, *J* = 190.2 Hz), 58.7 (qd, *J* = 30.0, 22.0 Hz), 57.7, 29.5 (dd, *J* = 21.6, 1.7 Hz), 25.1 (d, *J* = 8.5 Hz), 22.3. IR (cm^{-1}): 1695, 1603, 1458, 1263, 1200, 1146, 1121, 1074, 915, 744, 707. HRMS (TOF MS ESI): calcd for $C_{16}H_{19}F_4NO_2SNa^+$ $[M+Na]^+$ 388.0965, found 388.0970.



(*S*)-2-methyl-*N*-((*S*)-2,2,2-trifluoro-1-((*S*)-2-fluoro-7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)ethyl)propane-2-sulfinamide (3ma)

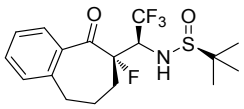
White solid, 68.2 mg (86% yield), m.p. 64–65 °C, [α]20 D = +48.5 (c = 0.59, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.7 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.15 (dd, *J* = 8.5, 2.7 Hz, 1H), 4.48 (ddq, *J* = 17.7, 10.6, 7.2 Hz, 1H), 3.89 (d, *J* = 10.6 Hz, 1H), 3.83 (s, 3H), 3.16 (dt, *J* = 17.5, 5.6 Hz, 1H), 3.03 (ddd, *J* = 17.5, 8.5, 5.0 Hz, 1H), 2.63–2.40 (m, 2H), 1.20 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.25 (d, *J* = 8.9 Hz, 3F), -170.29 (q, *J* = 8.2 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9 (d, *J* = 18.0 Hz), 158.7, 134.7, 130.9, 130.0, 123.6 (qd, *J* = 285.0, 3.8 Hz), 122.9, 110.3, 93.6 (d, *J* = 190.0 Hz), 58.7 (qd, *J* = 29.8, 22.1 Hz), 57.5, 55.3, 29.6 (d, *J* = 20.5 Hz), 24.2 (d, *J* = 8.4 Hz), 22.2. IR (cm^{-1}): 3461, 1688, 1500, 1348, 1262, 1198, 1143, 1120, 1041. HRMS (TOF MS ESI): calcd for $C_{17}H_{21}F_4NO_3SNa^+$ $[M+Na]^+$ 418.1070, found 418.1073.



(*S*)-*N*-((*S*)-1-((*S*)-7-bromo-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3na)

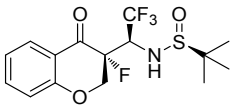
White solid, 81.9 mg (92% yield), m.p. 68–69 °C, [α]20 D = +34.4 (c = 0.48, CH_2Cl_2). ^1H NMR

(400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.1 Hz, 1H), 7.68 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 4.59–4.45 (m, 1H), 3.88 (d, *J* = 10.4 Hz, 1H), 3.18 (dt, *J* = 17.6, 5.9 Hz, 1H), 3.09–2.97 (m, 1H), 2.62–2.42 (m, 2H), 1.20 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.15 (d, *J* = 8.4 Hz, 3F), -169.72 (q, *J* = 8.0 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6 (d, *J* = 18.5 Hz), 141.1, 137.3, 131.5, 131.0, 130.6, 123.5 (qd, *J* = 284.7, 4.5 Hz), 121.2, 93.0 (d, *J* = 189.2 Hz), 58.5 (qd, *J* = 29.9, 22.2 Hz), 57.6, 29.0 (d, *J* = 21.9 Hz), 24.3 (d, *J* = 7.8 Hz), 22.2. IR (cm^{-1}): 3473, 1697, 1479, 1350, 1268, 1234, 1200, 1145, 1123, 1064, 1047, 931, 862. HRMS (TOF MS ESI): calcd for $C_{16}H_{18}BrF_4NO_2SNa^+$ $[M+Na]^+$ 466.0070, found 466.0071.



(*S*)-2-methyl-*N*-((*S*)-2,2,2-trifluoro-1-((*S*)-6-fluoro-5-oxo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-6-yl)ethyl)propane-2-sulfinamide (3oa)

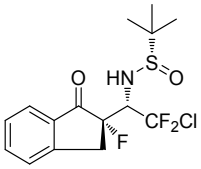
Colorless oil, 62.3 mg (82% yield), [α]20 D = +50.7 (c = 0.14, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 4.62 (ddq, *J* = 26.2, 10.9, 7.6 Hz, 1H), 3.89 (d, *J* = 10.9 Hz, 1H), 3.29 (dd, *J* = 16.8, 12.0 Hz, 1H), 3.02–2.91 (m, 1H), 2.34–2.14 (m, 3H), 1.83–1.68 (m, 1H), 1.20 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.19 (d, *J* = 8.6 Hz, 3F), -166.60 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2 (d, *J* = 30.5 Hz), 142.9 (d, *J* = 3.0 Hz), 135.6 (d, *J* = 1.3 Hz), 131.9, 129.7, 128.9, 126.2, 124.3 (q, *J* = 285.1 Hz), 102.4 (d, *J* = 191.6 Hz), 61.4 (qd, *J* = 30.1, 20.6 Hz), 57.4, 32.9 (d, *J* = 3.8 Hz), 32.6 (dd, *J* = 21.4, 2.5 Hz), 24.0, 22.5. IR (cm^{-1}): 1696, 1282, 1264, 1175, 1142, 1121, 1086, 646. HRMS (TOF MS ESI): calcd for $C_{17}H_{21}F_4NO_2SNa^+$ $[M+Na]^+$ 402.1121, found 402.1125.



(*S*)-2-methyl-*N*-((*S*)-2,2,2-trifluoro-1-((*R*)-3-fluoro-4-oxochroman-3-yl)ethyl)propane-2-sulfinamide (3pa)

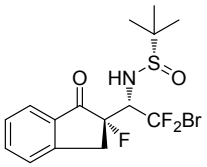
White solid, 68.5 mg (93% yield), m.p. 127–128 °C, [α]20 D = +45.4 (c = 0.39, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.09–7.03 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.67 (dd, *J* = 12.2, 9.6 Hz, 1H), 4.53–4.37 (m, 2H), 4.03 (d, *J* =

11.0 Hz, 1H), 1.06 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.21 (d, *J* = 10.7 Hz, 3F), -187.44 (q, *J* = 10.2 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.5 (d, *J* = 17.8 Hz), 160.6, 137.3, 128.2 (d, *J* = 1.1 Hz), 123.5 (qd, *J* = 285.3, 2.1 Hz), 122.9, 118.7, 118.1, 90.5 (d, *J* = 197.3 Hz), 68.7 (dd, *J* = 29.5, 3.1 Hz), 57.7, 57.2 (qd, *J* = 30.6, 21.0 Hz), 22.2. IR (cm^{-1}): 3334, 2951, 1699, 1611, 1483, 1471, 1335, 1309, 1253, 1206, 1172, 1138, 1069, 894, 851, 764, 714. HRMS (TOF MS ESI): calcd for $C_{15}H_{17}F_4NO_3SNa^+$ $[M+Na]^+$ 390.0757, found 390.0762.



(*S*)-*N*-((*S*)-2-chloro-2,2-difluoro-1-((*S*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)ethyl)-2-methylpropane-2-sulfinamide (3ab)

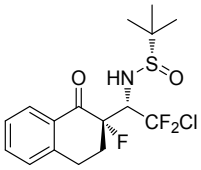
White solid, 69.2 mg (94% yield), m.p. 45–46 °C, [α]20 D = +95.2 (c = 1.05, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 1H), 7.69 (td, *J* = 7.6, 1.1 Hz, 1H), 7.49–7.42 (m, 2H), 4.63 (tdd, *J* = 11.3, 9.8, 5.6 Hz, 1H), 3.99 (d, *J* = 9.5 Hz, 1H), 3.76–3.64 (m, 1H), 3.34 (dd, *J* = 25.2, 18.2 Hz, 1H), 1.27 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.72 (dd, *J* = 172.5, 2.2 Hz, 1F), -57.86 (dd, *J* = 172.6, 4.8 Hz, 1F), -152.53 (dd, *J* = 4.8, 2.2 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 (d, *J* = 17.5 Hz), 149.5 (d, *J* = 2.9 Hz), 136.8, 133.3, 128.6, 126.9 (td, *J* = 297.8, 9.4 Hz), 126.6, 125.3, 95.4 (d, *J* = 189.5 Hz), 66.1 (td, *J* = 25.7, 25.3 Hz), 57.8, 35.4 (dd, *J* = 24.4, 2.3 Hz), 22.4. IR (cm^{-1}): 3200, 2961, 1732, 1608, 1469, 1211, 1105, 1069, 967, 734. HRMS (TOF MS ESI): calcd for $C_{15}H_{17}ClF_3NO_2SNa^+$ $[M+Na]^+$ 390.0513, found 390.0514.



(*S*)-*N*-((*S*)-2-bromo-2,2-difluoro-1-((*S*)-2-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)ethyl)-2-methylpropane-2-sulfinamide (3ac)

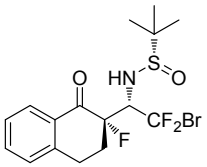
White solid, 70.2 mg (85% yield), m.p. 47–48 °C, [α]20 D = +79.7 (c = 0.73, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 1H), 7.69 (td, *J* = 7.6, 1.2 Hz, 1H), 7.48–7.43 (m, 2H), 4.72–4.60 (m, 1H), 4.00 (d, *J* = 9.3 Hz, 1H), 3.78–3.65 (m, 1H), 3.34 (dd, *J* = 25.2, 18.2 Hz, 1H), 1.28

(s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -47.62 (d, *J* = 172.4 Hz), -52.88 (dd, *J* = 172.4, 3.8 Hz), -151.91 (d, *J* = 3.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 (dd, *J* = 17.4, 0.9 Hz), 149.5 (d, *J* = 2.9 Hz), 136.8, 133.4, 128.7, 126.7, 125.3, 120.2 (td, *J* = 311.3, 8.7 Hz), 95.4 (d, *J* = 190.0 Hz), 67.5 (td, *J* = 25.1, 22.0 Hz), 57.9, 35.5 (dd, *J* = 24.3, 3.2 Hz), 22.5. IR (cm^{-1}): 1731, 1608, 1469, 1209, 1098, 1070, 951, 734. HRMS (TOF MS ESI): calcd for $C_{15}H_{17}BrF_3NO_2SNa^+$ $[M+Na]^+$ 434.0008, found 434.0010.



(*S*)-*N*-((*S*)-2-chloro-2,2-difluoro-1-((*S*)-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)ethyl)-2-methylpropane-2-sulfinamide (3lb)

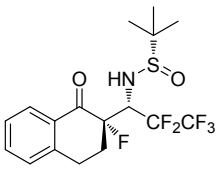
White solid, 74.3 mg (97% yield), m.p. 56–57 °C, [α]20 D = +19.0 (c = 1.28, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.57 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 4.78–4.65 (m, 1H), 3.95 (d, *J* = 10.4 Hz, 1H), 3.28–3.17 (m, 1H), 3.07 (ddd, *J* = 17.5, 7.1, 5.2 Hz, 1H), 2.64–2.41 (m, 2H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.74 (d, *J* = 172.8 Hz, 1F), -56.62 (d, *J* = 172.7 Hz, 1F), -165.98 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5 (d, *J* = 18.3 Hz), 142.4, 134.5, 130.0, 128.7, 128.5, 127.3 (dd, *J* = 298.5, 4.0 Hz), 127.3, 93.2 (d, *J* = 188.0 Hz), 63.8 (td, *J* = 25.9, 21.7 Hz), 57.6, 29.0 (dd, *J* = 21.8, 3.0 Hz), 24.5 (d, *J* = 7.3 Hz), 22.2. IR (cm^{-1}): 3448, 3199, 2961, 1693, 1602, 1458, 1200, 1105, 1071, 959, 743. HRMS (TOF MS ESI): calcd for $C_{16}H_{19}ClF_3NO_2SNa^+$ $[M+Na]^+$ 404.0669, found 404.0672.



(*S*)-*N*-((*S*)-2-bromo-2,2-difluoro-1-((*S*)-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)ethyl)-2-methylpropane-2-sulfinamide (3lc)

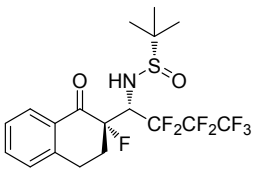
White solid, 75.2 mg (88% yield), m.p. 54–55 °C, [α]20 D = +16.5 (c = 0.23, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.53 (td, *J* = 7.6, 1.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 4.72 (dtd, *J* = 13.4, 10.3, 6.0 Hz, 1H), 3.96 (d, *J* = 10.3 Hz, 1H),

3.19 (dt, *J* = 17.3, 6.4 Hz, 1H), 3.02 (dt, *J* = 17.4, 5.9 Hz, 1H), 2.58–2.41 (m, 2H), 1.20 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.58 (d, *J* = 173.3 Hz, 1F), -51.41 (dd, *J* = 173.3, 3.3 Hz, 1F), -166.16 (1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8 (d, *J* = 18.8 Hz), 142.5, 134.7, 130.3, 128.9, 128.8, 127.6, 120.71 (td, *J* = 311.9, 3.2 Hz), 93.6 (dt, *J* = 188.9, 2.1 Hz), 65.0 (td, *J* = 23.5, 21.6 Hz), 57.9, 29.4 (dd, *J* = 21.8, 3.8 Hz), 24.9 (dd, *J* = 7.6, 1.4 Hz), 22.5. IR (cm^{-1}): 3209, 2960, 1694, 1601, 1458, 1183, 1103, 1077, 943, 744. HRMS (TOF MS ESI): calcd for $C_{16}H_{19}BrF_3NO_2SNa^+$ $[M+Na]^+$ 448.0164, found 448.0167.



(*S*)-2-methyl-*N*-((*S*)-2,2,3,3,3-pentafluoro-1-((*S*)-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propyl)propane-2-sulfinamide (3ld)

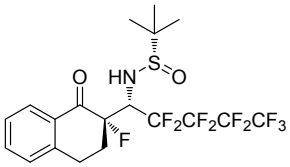
White solid, 67.9 mg (82% yield), m.p. 163–164 °C, [α]20 D = +15.1 (c = 0.53, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.55 (td, *J* = 7.6, 1.1 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 5.00 (ddd, *J* = 19.7, 11.9, 3.6 Hz, 1H), 3.87 (d, *J* = 9.0 Hz, 1H), 3.31–3.16 (m, 1H), 2.98 (dt, *J* = 17.0, 4.7 Hz, 1H), 2.60–2.30 (m, 2H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.03 (d, *J* = 4.4 Hz, 3F), -112.29 (d, *J* = 281.2 Hz, 1F), -120.03 (d, *J* = 281.2 Hz, 1F), -163.91 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1 (dd, *J* = 18.6, 0.9 Hz), 142.9, 134.8, 130.0, 128.8, 128.8, 127.5, 118.4 (qt, *J* = 287.4, 35.7 Hz), 113.2 (tqd, *J* = 260.9, 37.5, 5.3 Hz), 92.7 (d, *J* = 184.0 Hz), 57.7, 56.9 (td, *J* = 23.6, 20.8 Hz), 28.8 (d, *J* = 21.9 Hz), 24.3 (d, *J* = 5.9 Hz), 22.6. IR (cm^{-1}): 3351, 1686, 1602, 1309, 1227, 1191, 1086, 1014, 910, 748. HRMS (TOF MS ESI): calcd for $C_{17}H_{19}F_6NO_2SNa^+$ $[M+Na]^+$ 438.0933, found 438.0932.



(*S*)-*N*-((*S*)-2,2,3,3,4,4,4-heptafluoro-1-((*S*)-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)butyl)-2-methylpropane-2-sulfinamide (3le)

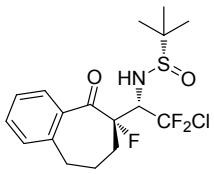
White solid, 71.8 mg (77% yield), m.p. 171–172 °C, [α]20 D = +8.7 (c = 0.37, CH_2Cl_2). ^{1}H NMR

(400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 5.16 (dtd, *J* = 12.8, 9.6, 3.5 Hz, 1H), 3.87 (d, *J* = 8.6 Hz, 1H), 3.26 (ddd, *J* = 15.8, 11.0, 4.4 Hz, 1H), 2.97 (dt, *J* = 16.9, 4.3 Hz, 1H), 2.63–2.29 (m, 2H), 1.26 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.29 (dd, *J* = 12.1, 9.6 Hz, 3F), -109.45–-110.42 (m, 1F), -115.73–-116.83 (m, 1F), -123.66–-124.63 (m, 1F), -124.85–-125.80 (m, 1F), -163.09 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.0 (d, *J* = 18.6 Hz), 143.0, 134.8, 130.0, 128.9, 128.8, 127.5, 117.6 (qt, *J* = 288.4, 33.7 Hz), 115.2 (ttd, *J* = 261.7, 32.0, 4.9 Hz), 108.7 (tsext, *J* = 267.2, 37.5 Hz), 92.7 (d, *J* = 183.5 Hz), 57.8, 57.1 (dd, *J* = 44.6, 23.1 Hz), 28.9 (d, *J* = 21.9 Hz), 24.2 (d, *J* = 5.0 Hz), 22.7. IR (cm^{-1}): 3355, 1686, 1602, 1229, 1194, 1117, 1109, 1087, 935, 744. HRMS (TOF MS ESI): calcd for $C_{18}H_{19}F_8NO_2SNa^+$ $[M+Na]^+$ 488.0901, found 488.0904.



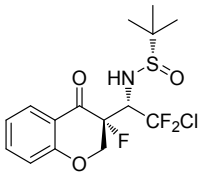
(*S*)-2-methyl-*N*-((*S*)-2,2,3,3,4,4,5,5,5-nonafluoro-1-((*S*)-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)pentyl)propane-2-sulfinamide (3lf)

White solid, 44.1 mg (43% yield), m.p. 167–168 °C, [α]20 D = +5.0 (c = 1.19, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.57 (td, *J* = 7.5, 1.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 5.20 (dtd, *J* = 12.7, 9.3, 3.4 Hz, 1H), 3.88 (dd, *J* = 9.0, 0.8 Hz, 1H), 3.32–3.20 (m, 1H), 2.97 (dt, *J* = 16.9, 4.4 Hz, 1H), 2.61–2.30 (m, 2H), 1.26 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.78 (tt, *J* = 9.8, 2.3 Hz, 3F), -109.03–-110.02 (m, 1F), -115.02–-116.07 (m, 1F), -121.18–-121.41 (m, 2F), -125.04 (ddt, *J* = 30.5, 24.1, 5.7 Hz, 1F), -126.22–-127.16 (m, 1F), -162.84 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.9 (d, *J* = 18.7 Hz), 143.1, 134.9, 130.0, 129.0, 128.8, 127.6, 117.4 (qt, *J* = 288.5, 33.2 Hz), 115.8 (ttd, *J* = 263.1, 32.8, 4.9 Hz), 112.8–106.5 (m, 2C), 92.7 (d, *J* = 183.4 Hz), 57.9, 57.3 (dd, *J* = 44.3, 23.4 Hz), 28.9 (d, *J* = 22.0 Hz), 24.2 (d, *J* = 5.2 Hz), 22.7. IR (cm^{-1}): 1688, 1246, 1218, 1136, 1081, 915, 743. HRMS (TOF MS ESI): calcd for $C_{19}H_{19}F_{10}NO_2SNa^+$ $[M+Na]^+$ 538.0869, found 538.0871.



(*S*)-*N*-((*S*)-2-chloro-2,2-difluoro-1-((*S*)-6-fluoro-5-oxo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-6-yl)ethyl)-2-methylpropane-2-sulfinamide (3ob)

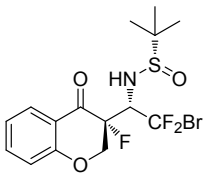
Colorless oil, 64.0 mg (81% yield), [α]20 D = +24.1 (c = 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 2H), 7.31–7.22 (m, 2H), 4.82–4.69 (m, 1H), 3.92 (d, *J* = 10.8 Hz, 1H), 3.27 (dd, *J* = 16.8, 12.2 Hz, 1H), 3.00–2.88 (m, 1H), 2.40–2.13 (m, 3H), 1.81–1.66 (m, 1H), 1.18 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -47.93 (dd, *J* = 173.2, 4.6 Hz, 1F), -52.90 (dd, *J* = 173.3, 5.7 Hz, 1F), -166.92 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4 (dd, *J* = 30.5, 0.6 Hz), 143.1 (d, *J* = 3.1 Hz), 135.9 (d, *J* = 1.4 Hz), 132.1, 129.8, 129.2, 128.1 (t, *J* = 298.9 Hz), 126.4, 102.6 (ddd, *J* = 192.5, 4.6, 1.6 Hz), 65.9 (td, *J* = 26.7, 19.8 Hz), 57.6, 33.1 (d, *J* = 4.1 Hz), 32.7 (dd, *J* = 21.2, 6.9 Hz), 24.2 (d, *J* = 1.9 Hz), 22.8. IR (cm^{-1}): 2960, 2932, 1698, 1608, 1479, 1466, 1459, 1282, 1261, 1177, 1098, 1025. HRMS (TOF MS ESI): calcd for $C_{17}H_{21}ClF_3NO_2SNa^+$ $[M+Na]^+$ 418.0826, found 418.0825.



(*S*)-*N*-((*S*)-2-chloro-2,2-difluoro-1-((*R*)-3-fluoro-4-oxochroman-3-yl)ethyl)-2-methylpropane-2-sulfinamide (3pb)

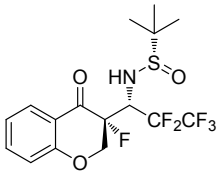
Colorless oil, 69.7 mg (91% yield), [α]20 D = +32.7 (c = 1.56, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.59–7.52 (m, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 4.74 (t, *J* = 12.1 Hz, 1H), 4.68–4.54 (m, 1H), 4.47 (dd, *J* = 12.4, 5.8 Hz, 1H), 4.01 (d, *J* = 10.7 Hz, 1H), 1.12 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.76 (dd, *J* = 174.1, 4.6 Hz, 1F), -56.55 (dd, *J* = 174.1, 7.7 Hz, 1F), -182.82 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.4 (d, *J* = 18.0 Hz), 160.7, 137.4, 128.3 (d, *J* = 0.9 Hz), 127.4 (t, *J* = 299.9 Hz), 123.0, 118.9, 118.2, 90.6 (dt, *J* = 197.1, 2.0 Hz), 69.0 (ddd, *J* = 29.0, 6.3, 2.5 Hz), 62.1 (td, *J* = 27.1, 20.4 Hz), 57.9, 22.4. IR (cm^{-1}): 3169, 2959, 2929, 2877, 1705, 1690, 1609, 1479, 1468, 1113, 1064, 1045, 760, 754.

HRMS (TOF MS ESI): calcd for $C_{15}H_{17}ClF_3NO_3SNa^+$ $[M+Na]^+$ 406.0462, found 406.0462.



(*S*)-*N*-((*S*)-2-bromo-2,2-difluoro-1-((*R*)-3-fluoro-4-oxochroman-3-yl)ethyl)-2-methylpropane-2-sulfinamide (3pc)

Colorless oil, 68.7 mg (80% yield), [α]20 D = +26.3 (c = 1.29, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.57 (ddd, *J* = 8.7, 7.4, 1.7 Hz, 1H), 7.14–7.08 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 4.76 (t, *J* = 12.3 Hz, 1H), 4.67–4.53 (m, 1H), 4.47 (dd, *J* = 12.4, 5.8 Hz, 1H), 4.01 (d, *J* = 10.6 Hz, 1H), 1.15 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.82 (dd, *J* = 174.3, 3.3 Hz, 1F), -51.15 (dd, *J* = 174.3, 6.6 Hz, 1F), -182.30 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.4 (d, *J* = 18.1 Hz), 160.8, 137.4, 128.4 (d, *J* = 1.0 Hz), 123.0, 120.6 (t, *J* = 313.3 Hz), 118.9, 118.2, 90.6 (ddd, *J* = 197.4, 3.2, 2.0 Hz), 69.0 (ddd, *J* = 28.9, 6.8, 2.0 Hz), 63.1 (td, *J* = 24.9, 20.3 Hz), 58.0, 22.4. IR (cm^{-1}): 2963, 2928, 1699, 1609, 1479, 1467, 1318, 1224, 1139, 1110, 1047, 760. HRMS (TOF MS ESI): calcd for $C_{15}H_{17}BrF_3NO_3SNa^+$ $[M+Na]^+$ 449.9957, found 449.9961.

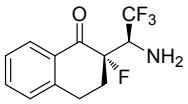


(*S*)-2-methyl-*N*-((*S*)-2,2,3,3,3-pentafluoro-1-((*R*)-3-fluoro-4-oxochroman-3-yl)propyl)propane-2-sulfinamide (3pd)

White solid, 61.1 mg (73% yield), m.p. 160–161 °C, [α]20 D = +66.4 (c = 1.71, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.16–7.10 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 4.98–4.83 (m, 1H), 4.73–4.54 (m, 2H), 3.84 (d, *J* = 9.0 Hz, 1H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.36 (d, *J* = 6.4 Hz, 3F), -111.35 (d, *J* = 281.6 Hz, 1F), -118.57 (dd, *J* = 281.7, 5.4 Hz, 1F), -174.74 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3 (d, *J* = 18.6 Hz), 160.9, 137.4, 128.3, 122.9, 118.7, 118.3 (qt, *J* = 287.2, 35.5 Hz), 118.2, 113.2 (tqd, *J* = 262.0, 38.1, 4.1 Hz), 90.1 (d, *J* = 192.3 Hz), 68.8 (dt, *J* = 25.6, 3.0 Hz), 57.8, 55.6 (dt, *J* = 24.2,

22.1 Hz), 22.5. IR (cm^{-1}): 3345, 1694, 1611, 1480, 1468, 1322, 1279, 1228, 1200, 1137, 1084, 1053, 1004, 891, 762, 708. HRMS (TOF MS ESI): calcd for $C_{16}H_{17}F_6NO_3SNa^+$ $[M+Na]^+$ 440.0726, found 440.0725.

3.3. Characterization data of the deprotection product 5



(*S*)-2-((*S*)-1-amino-2,2,2-trifluoroethyl)-2-fluoro-3,4-dihydronaphthalen-1(2*H*)-one (5)

Slightly green solid, m.p. 61–62 °C, [α]20 D = +5.1 (c = 0.43, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.53 (td, *J* = 7.6, 1.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 3.95 (dq, *J* = 17.3, 7.6 Hz, 1H), 3.19 (dt, *J* = 17.6, 5.8 Hz, 1H), 3.07 (dt, *J* = 17.7, 6.8 Hz, 1H), 2.55–2.44 (m, 2H), 1.68 (br, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.26 (d, *J* = 8.9 Hz, 3F), -173.45 (q, *J* = 8.8 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2 (d, *J* = 18.1 Hz), 142.2, 134.4, 130.8, 128.8, 128.6 (d, *J* = 1.2 Hz), 127.4, 125.0 (qd, *J* = 282.9, 3.3 Hz), 94.1 (d, *J* = 187.7 Hz), 54.3 (qd, *J* = 28.8, 22.9 Hz), 29.4 (dq, *J* = 21.9, 2.0 Hz), 25.4 (d, *J* = 9.0 Hz). IR (cm^{-1}): 1713, 1605, 1263, 1225, 1172, 1145, 1116, 945, 780, 736. HRMS (TOF MS ESI): calcd for $C_{12}H_{12}F_4NO^+$ $[M+H]^+$ 262.0850, found 262.0850. The ee values were determined by chiral stationary phase HPLC analysis using a Daicel Chiralpak IC column (90:10 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm).

4. X-ray crystallography for 3ka

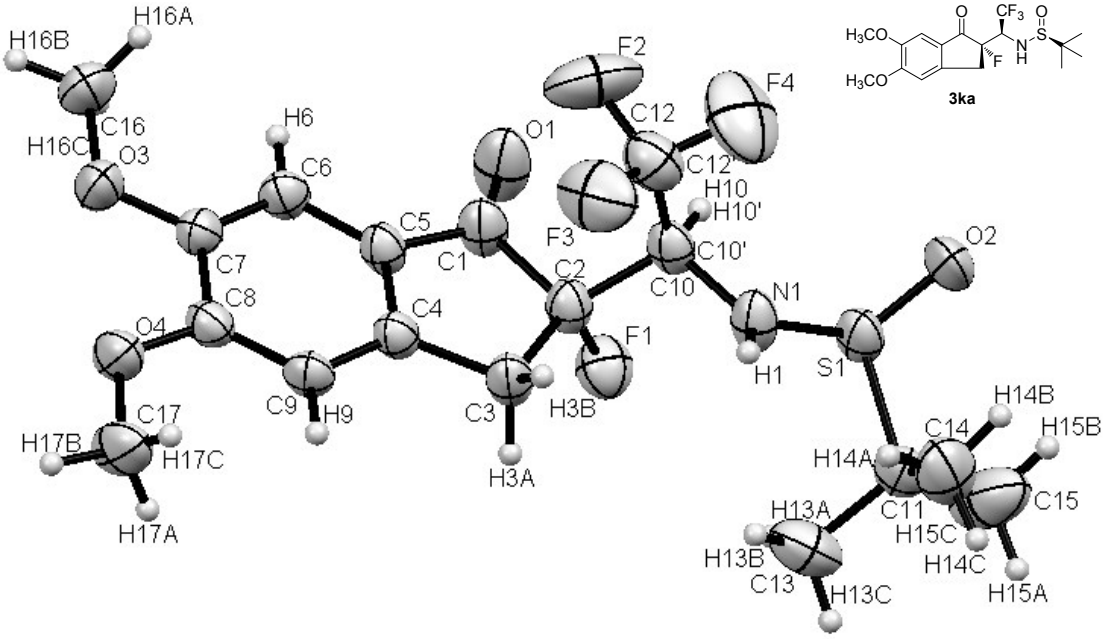
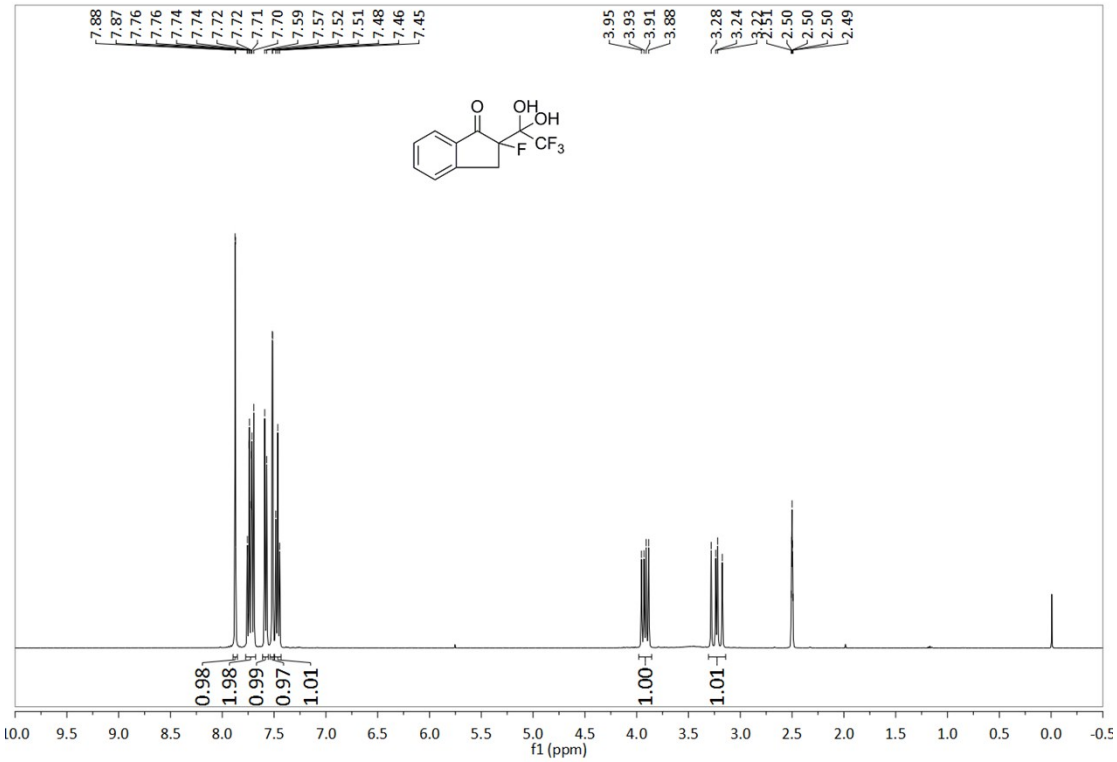


Figure 1 ORTEP structure of compound **3ka** (CCDC number 1048606)

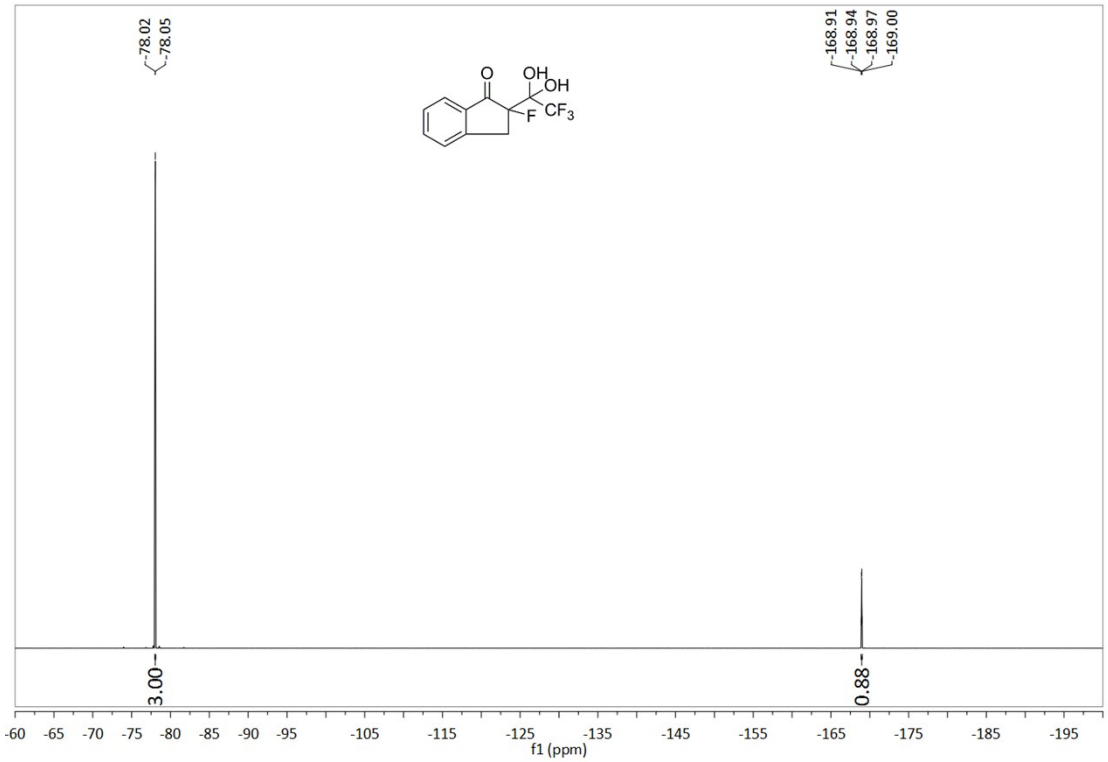
5. NMR spectra for compound 1, 3 and 5

5.1. NMR spectra of compounds α-fluorinated *gem*-diols 1

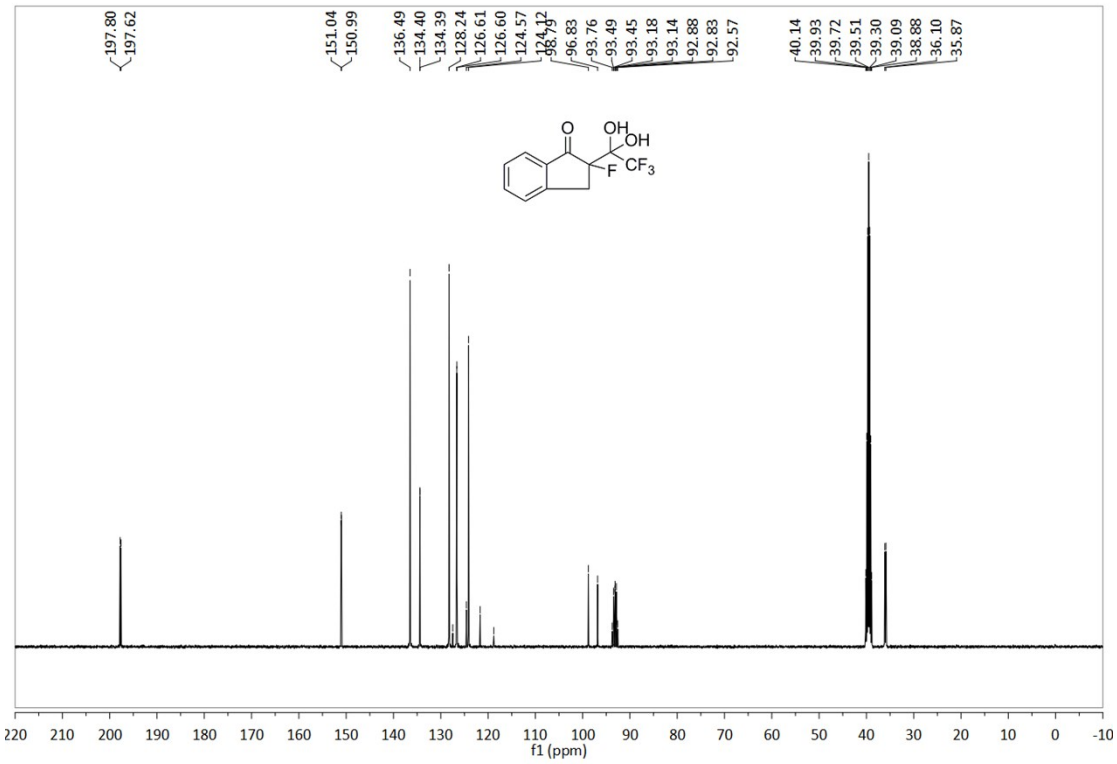
^{1}H NMR (400 MHz, DMSO) spectrum of **1a**



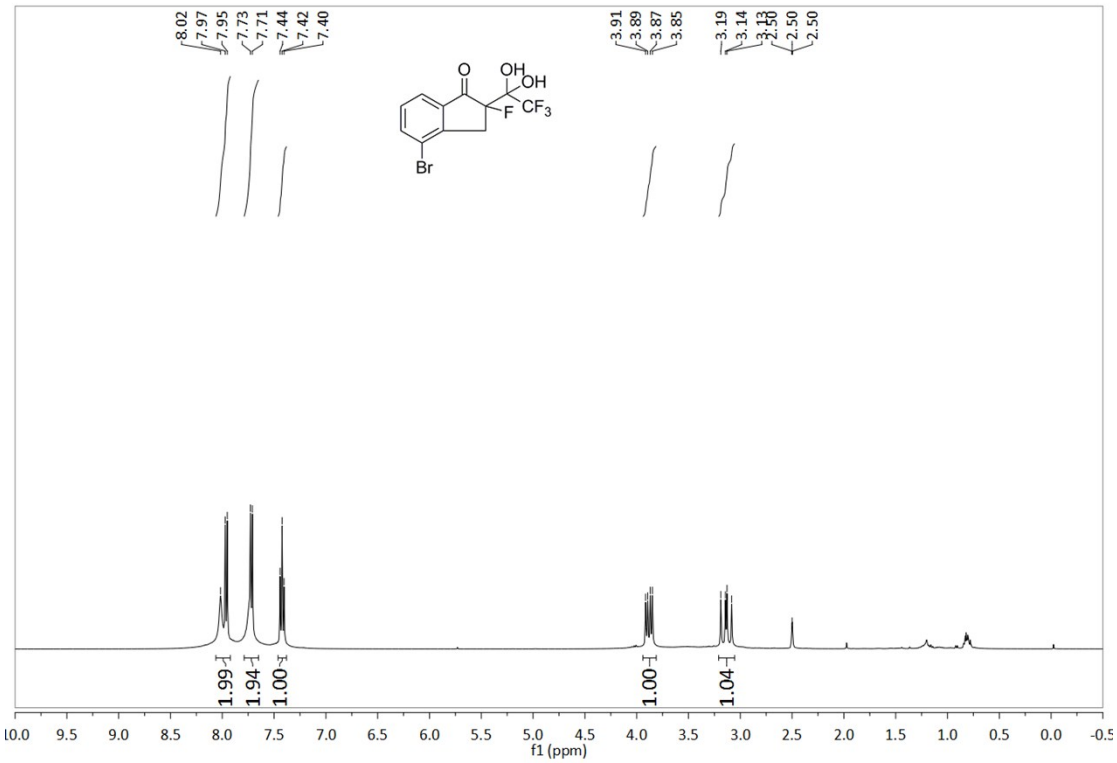
^{19}F NMR (376 MHz, DMSO) spectrum of **1a**



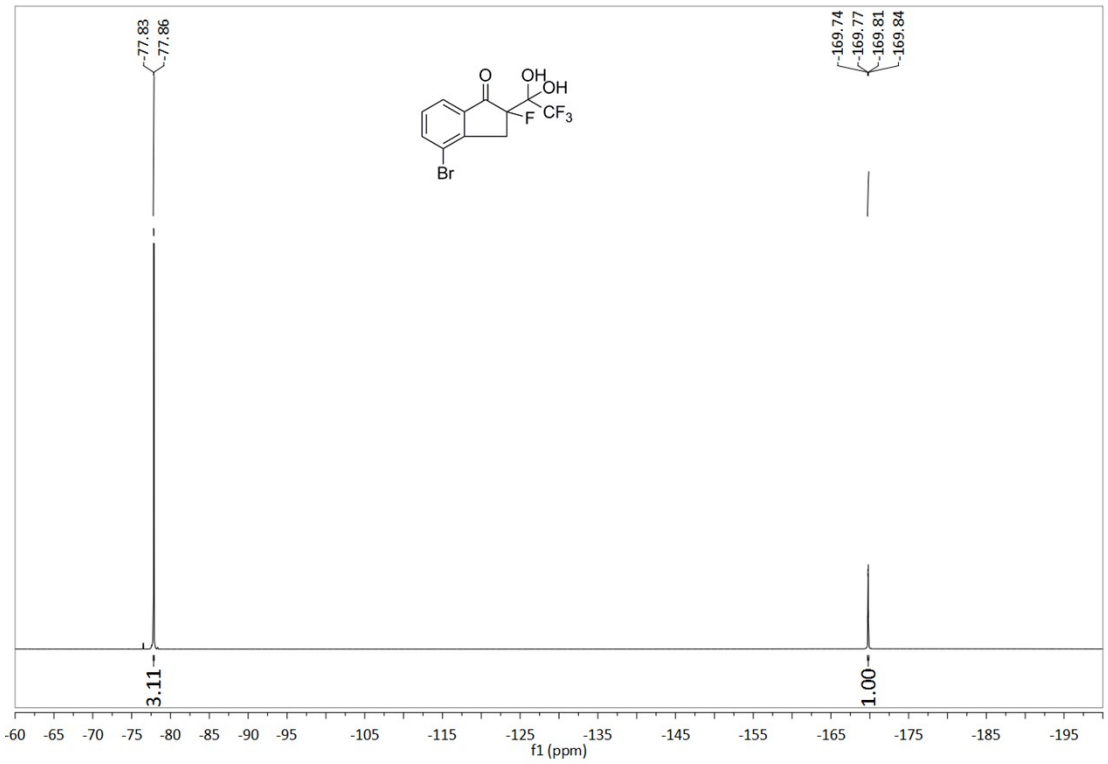
^{13}C NMR (101 MHz, DMSO) spectrum of **1a**



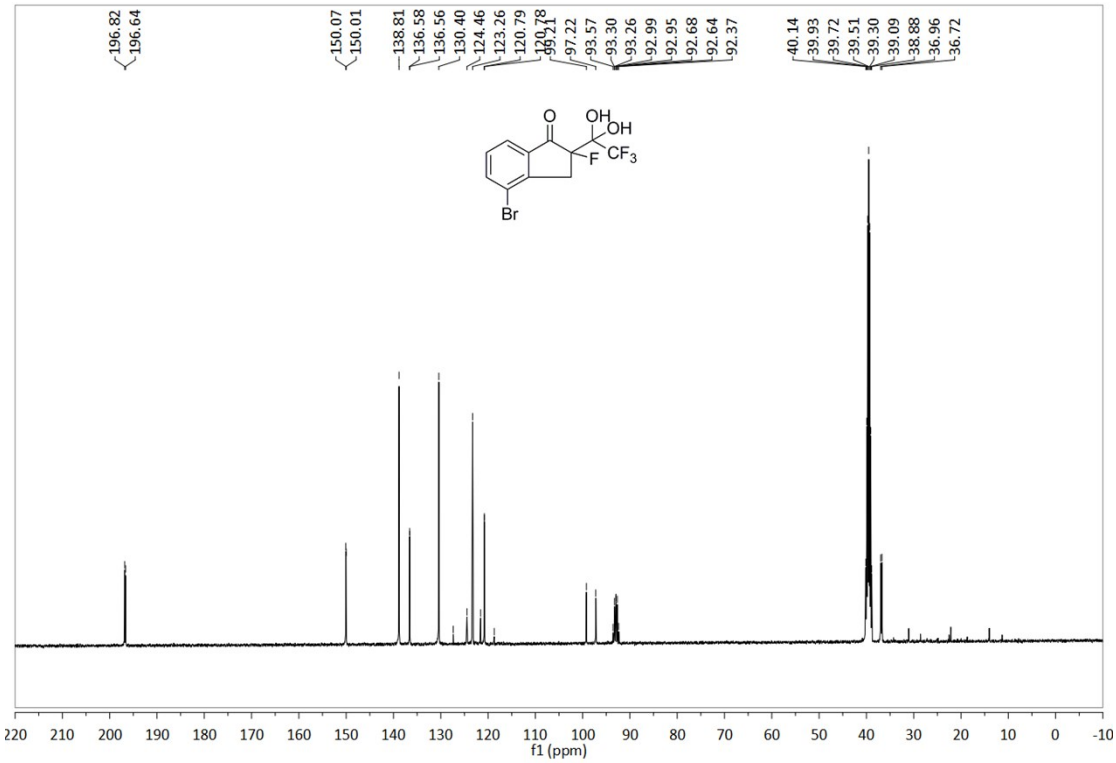
^{1}H NMR (400 MHz, DMSO) spectrum of **1b**



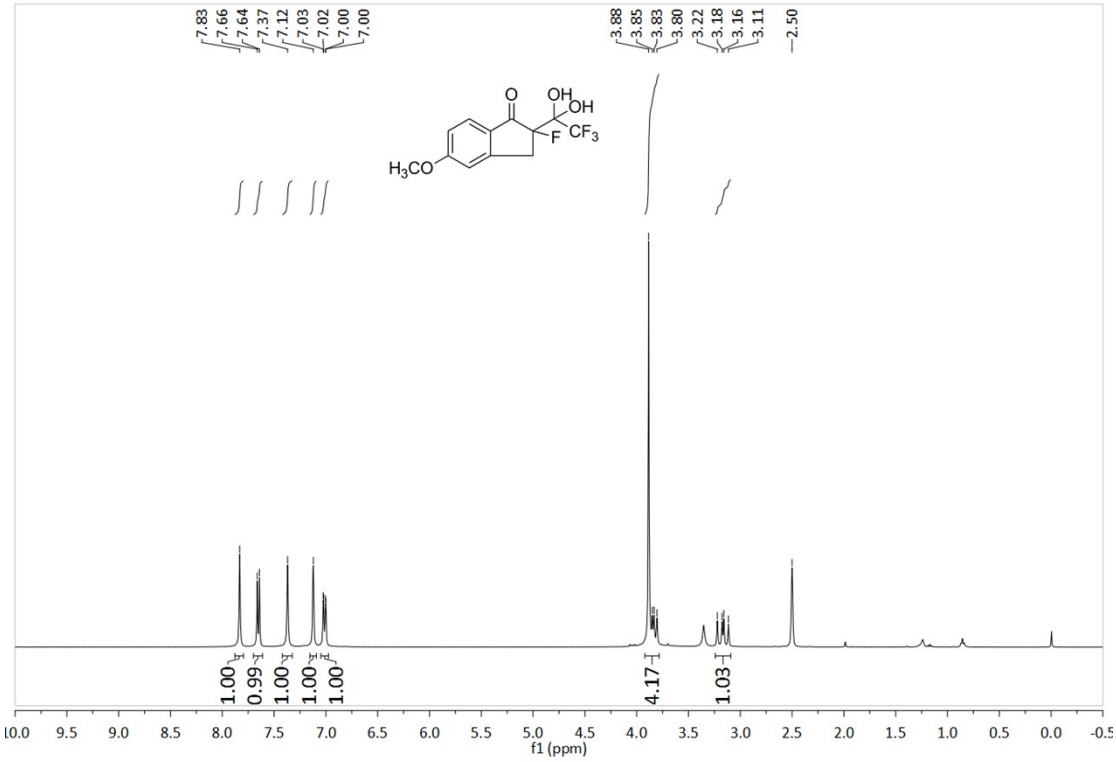
^{19}F NMR (376 MHz, DMSO) spectrum of **1b**



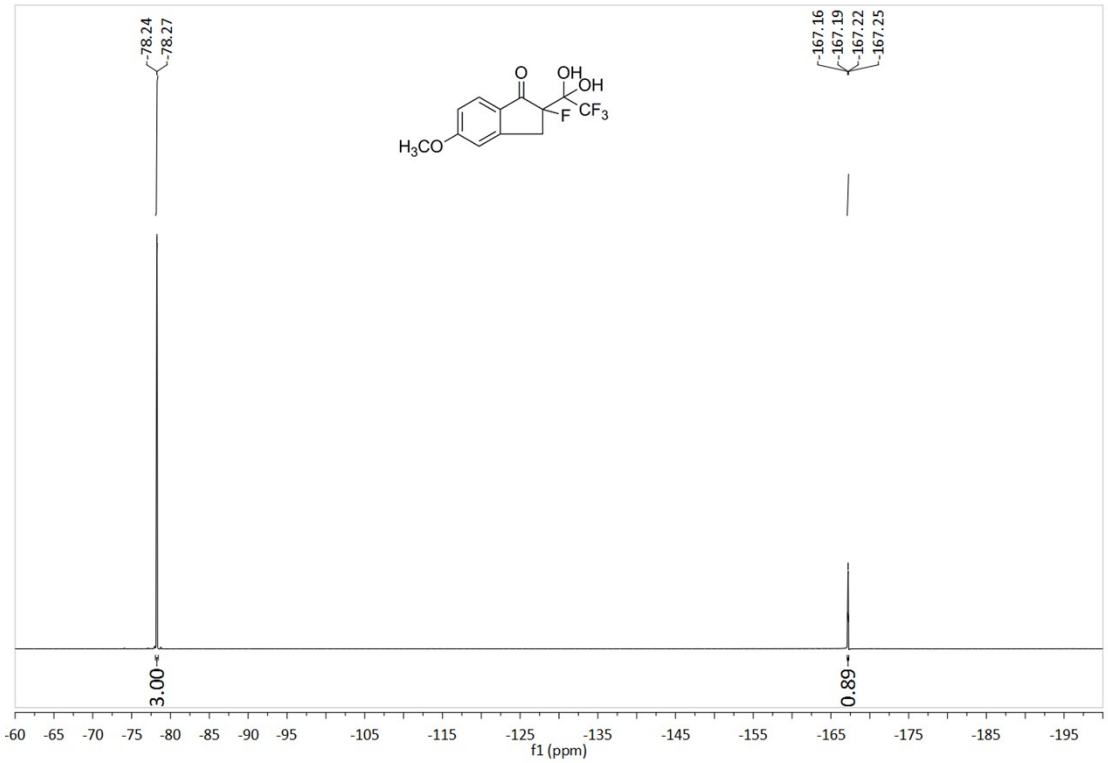
^{13}C NMR (101 MHz, DMSO) spectrum of **1b**



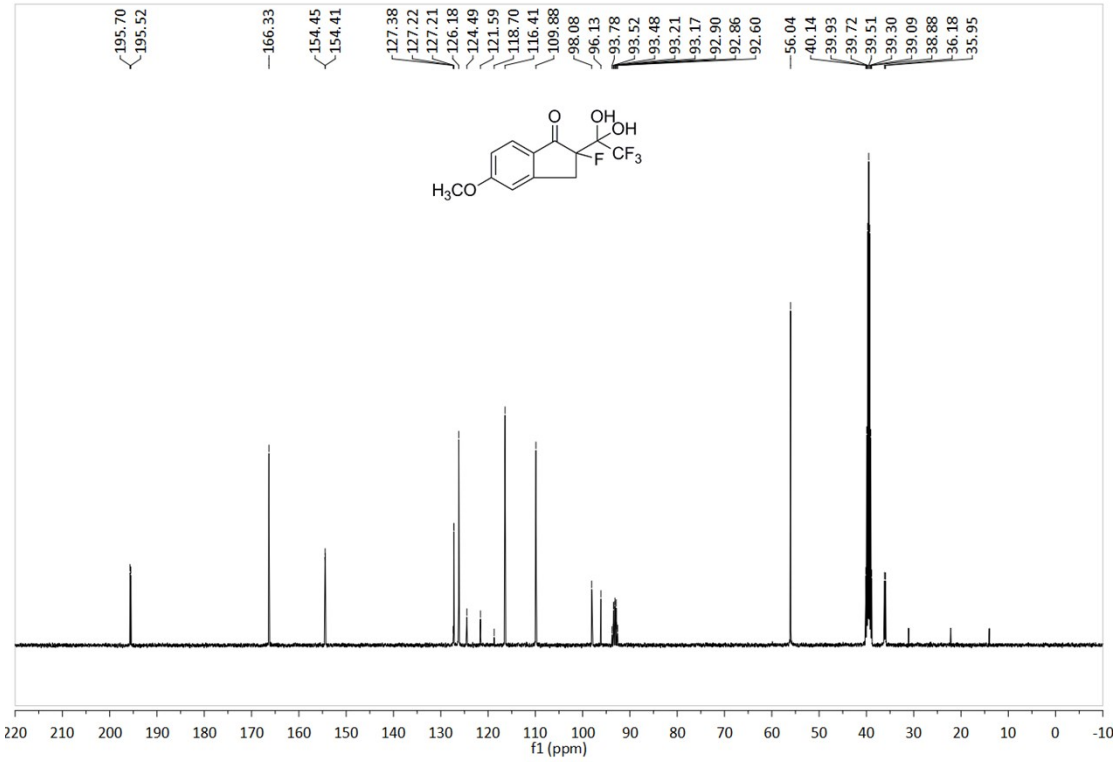
^{1}H NMR (400 MHz, DMSO) spectrum of **1c**



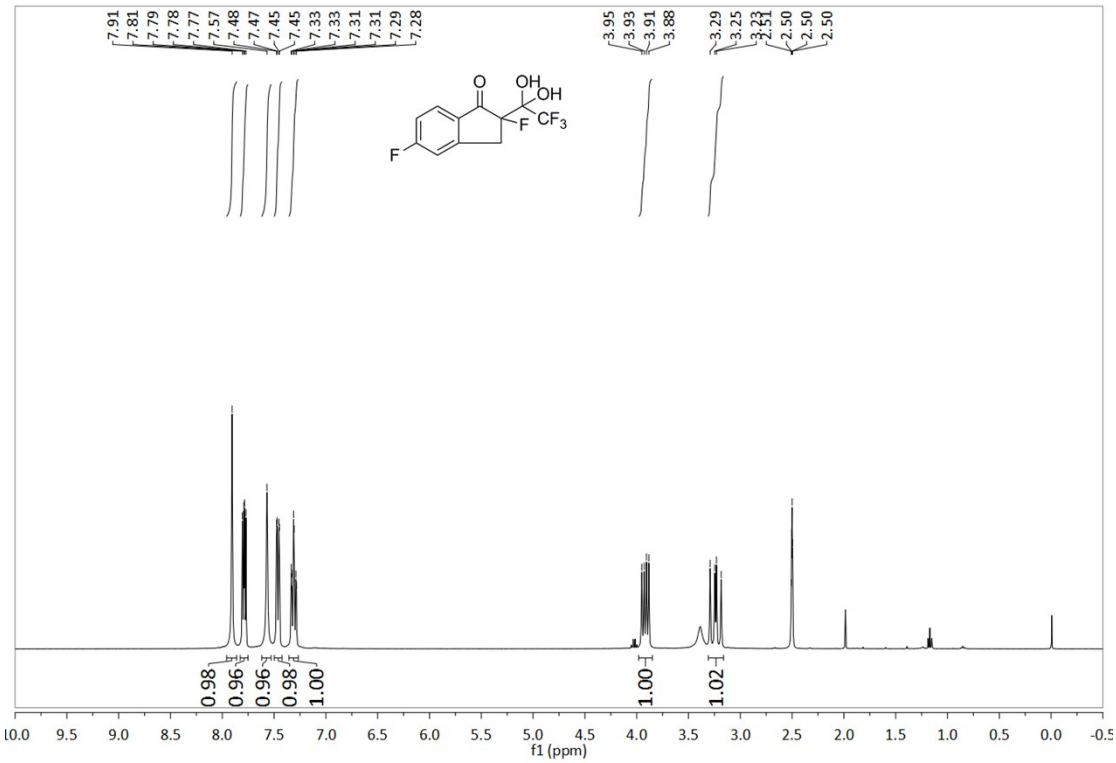
^{19}F NMR (376 MHz, DMSO) spectrum of **1c**



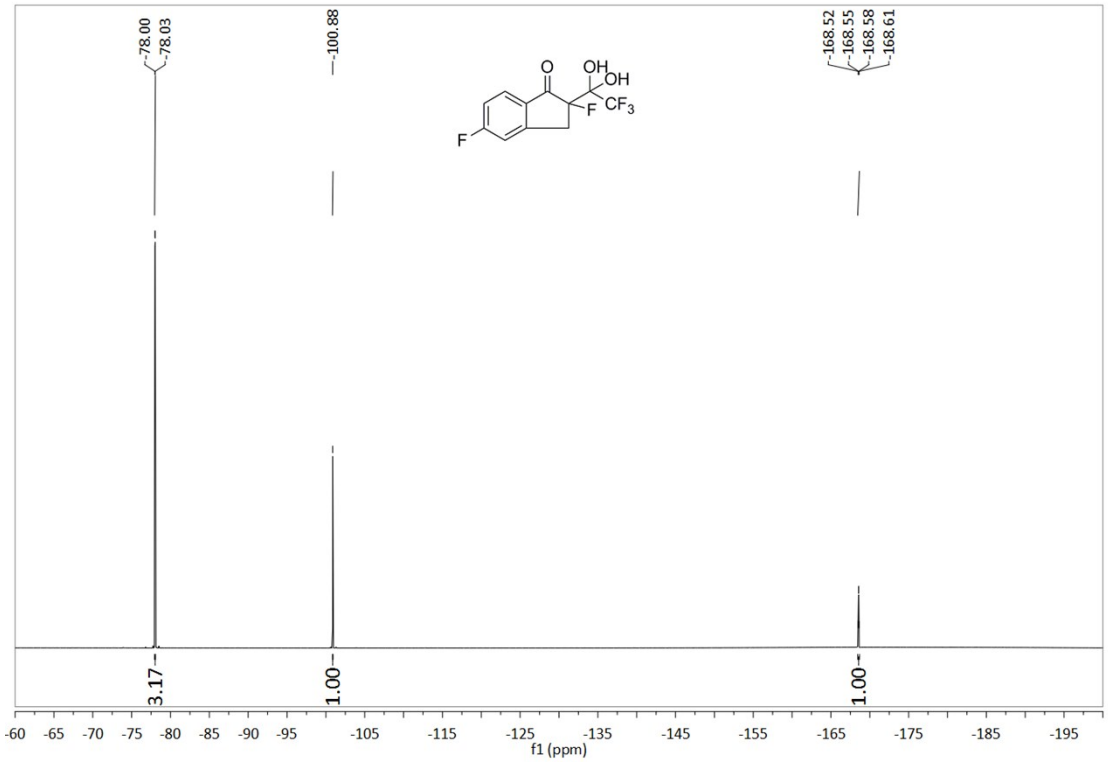
^{13}C NMR (101 MHz, DMSO) spectrum of **1c**



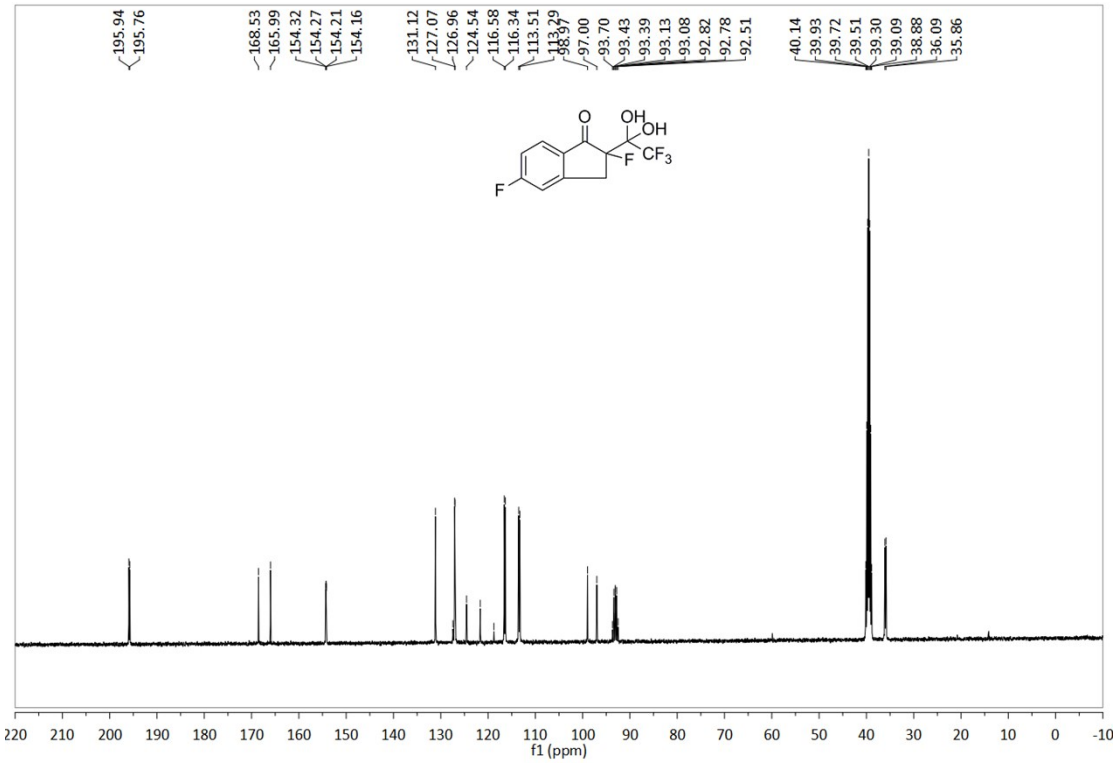
^{1}H NMR (400 MHz, DMSO) spectrum of **1d**



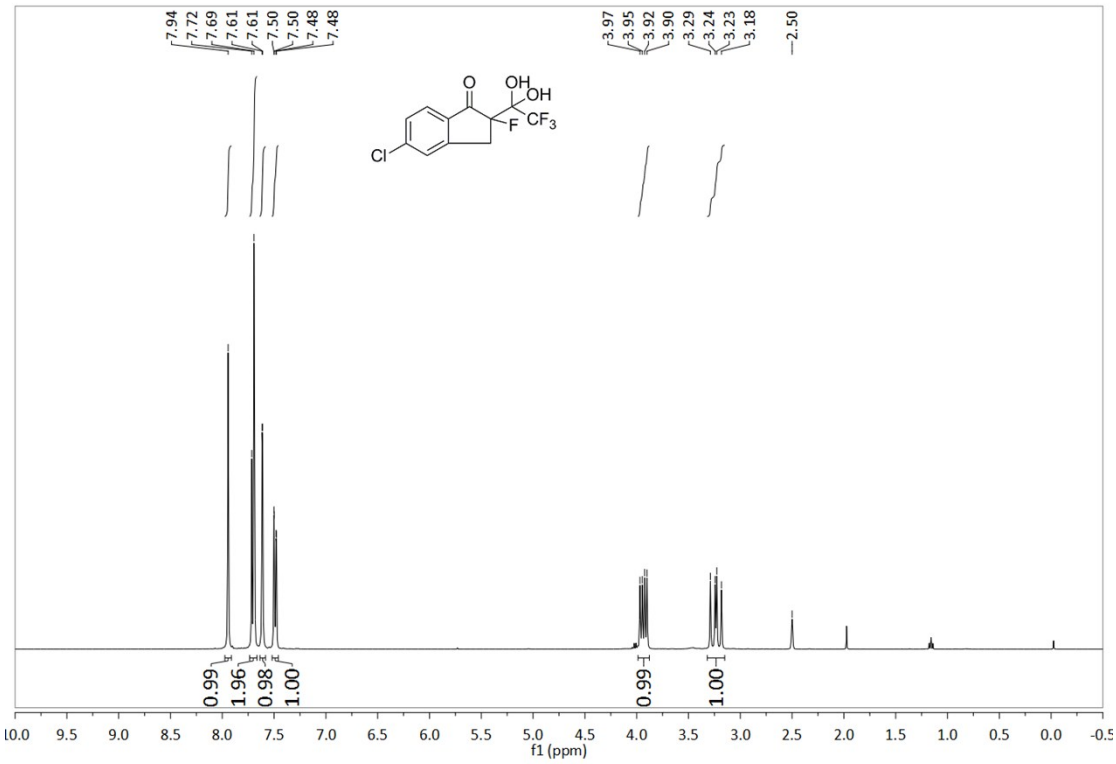
^{19}F NMR (376 MHz, DMSO) spectrum of **1d**



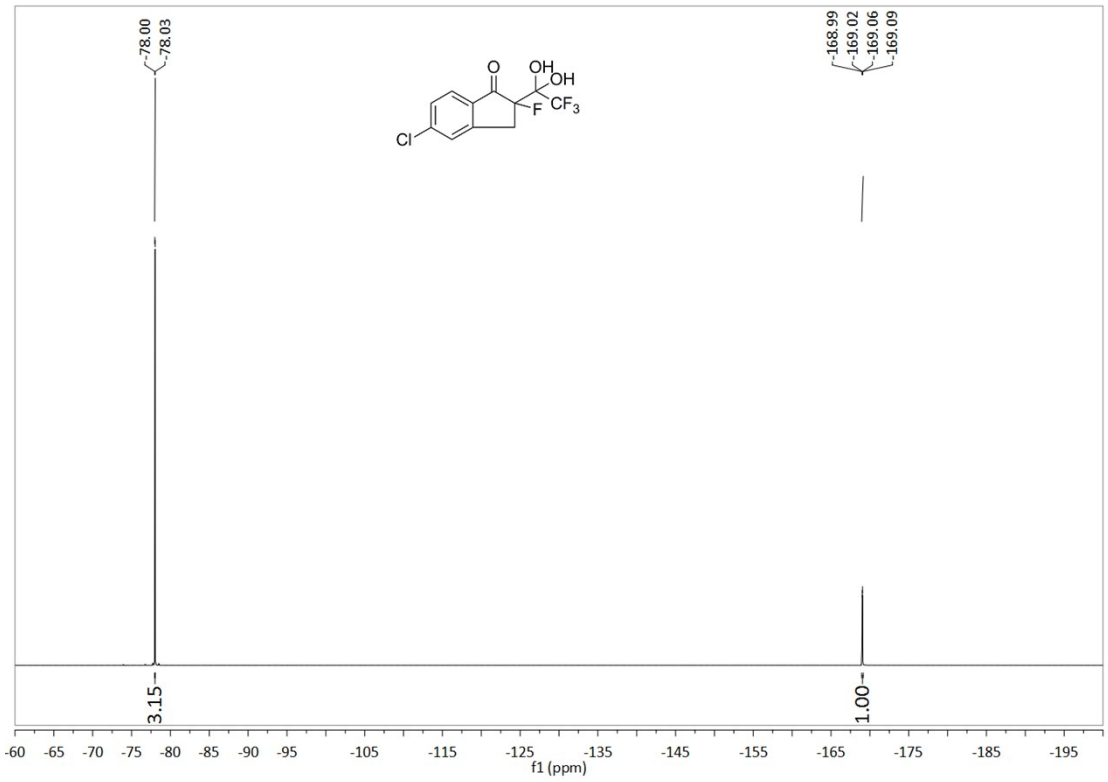
^{13}C NMR (101 MHz, DMSO) spectrum of **1d**



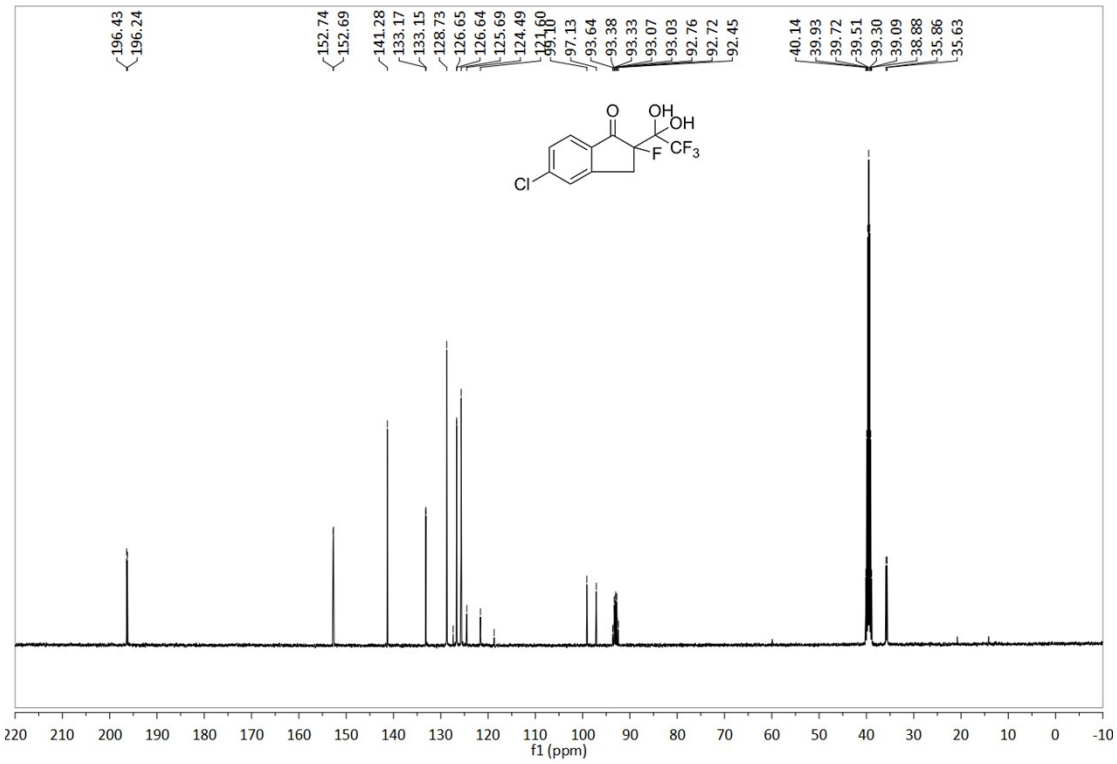
^{1}H NMR (400 MHz, DMSO) spectrum of **1e**



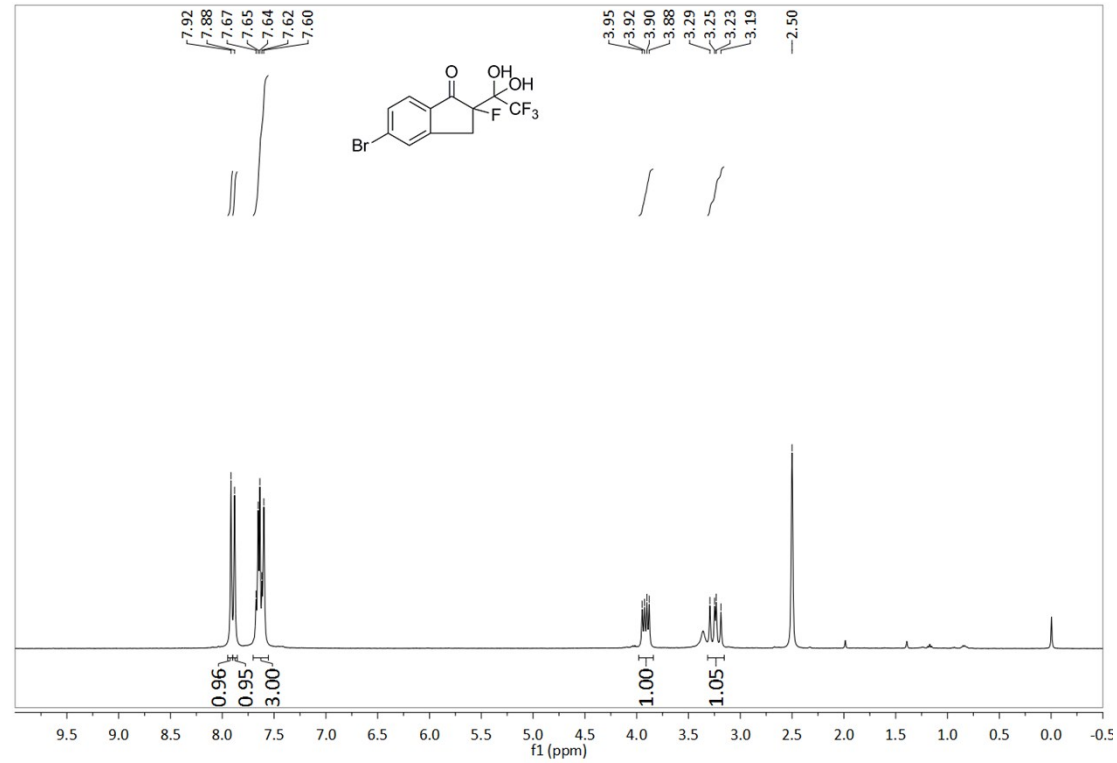
^{19}F NMR (376 MHz, DMSO) spectrum of **1e**



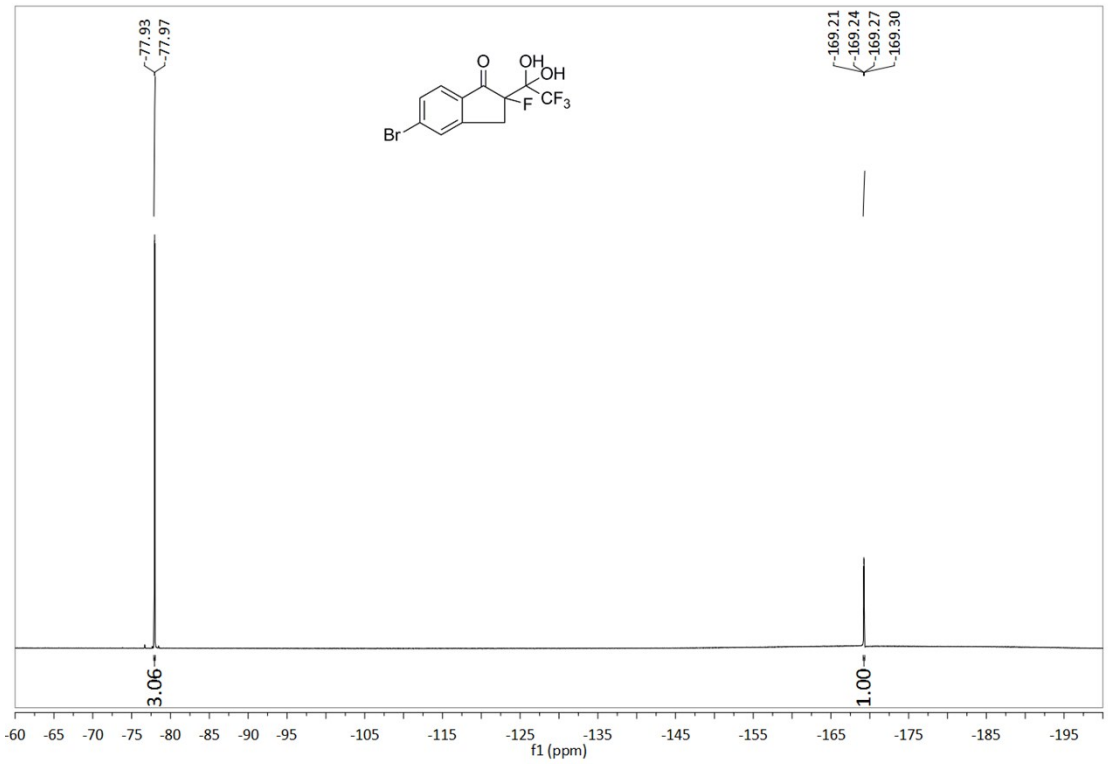
^{13}C NMR (101 MHz, DMSO) spectrum of **1e**



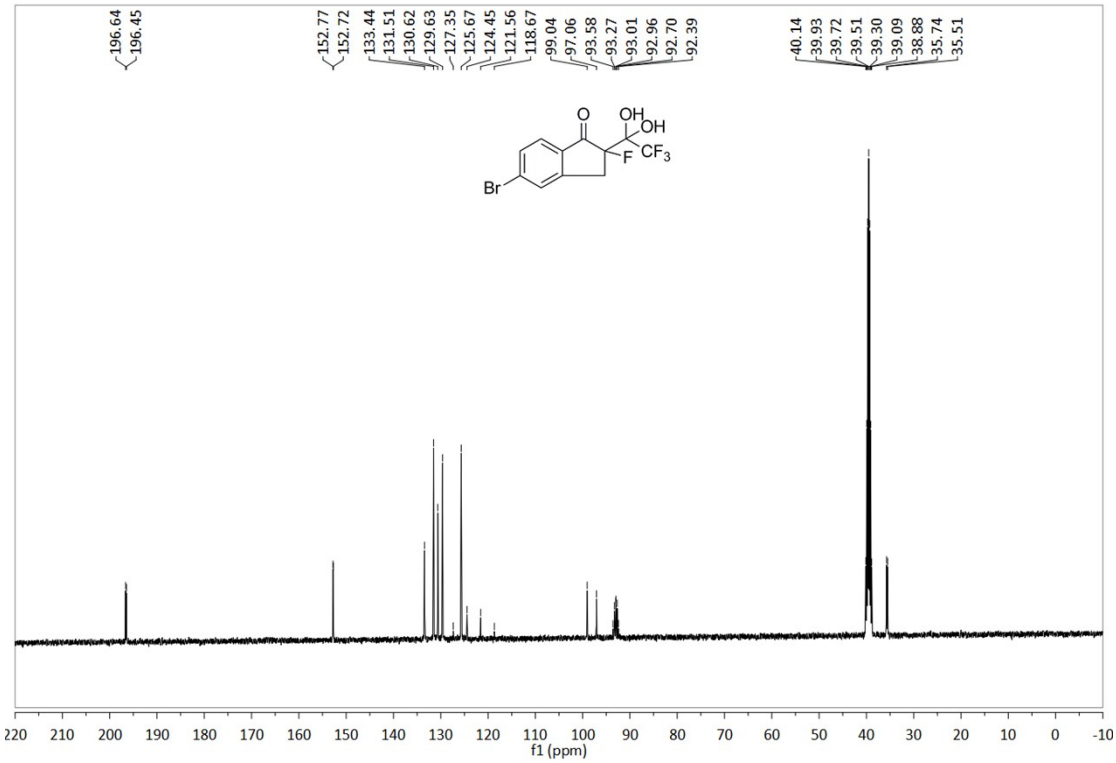
^{1}H NMR (400 MHz, DMSO) spectrum of **1f**



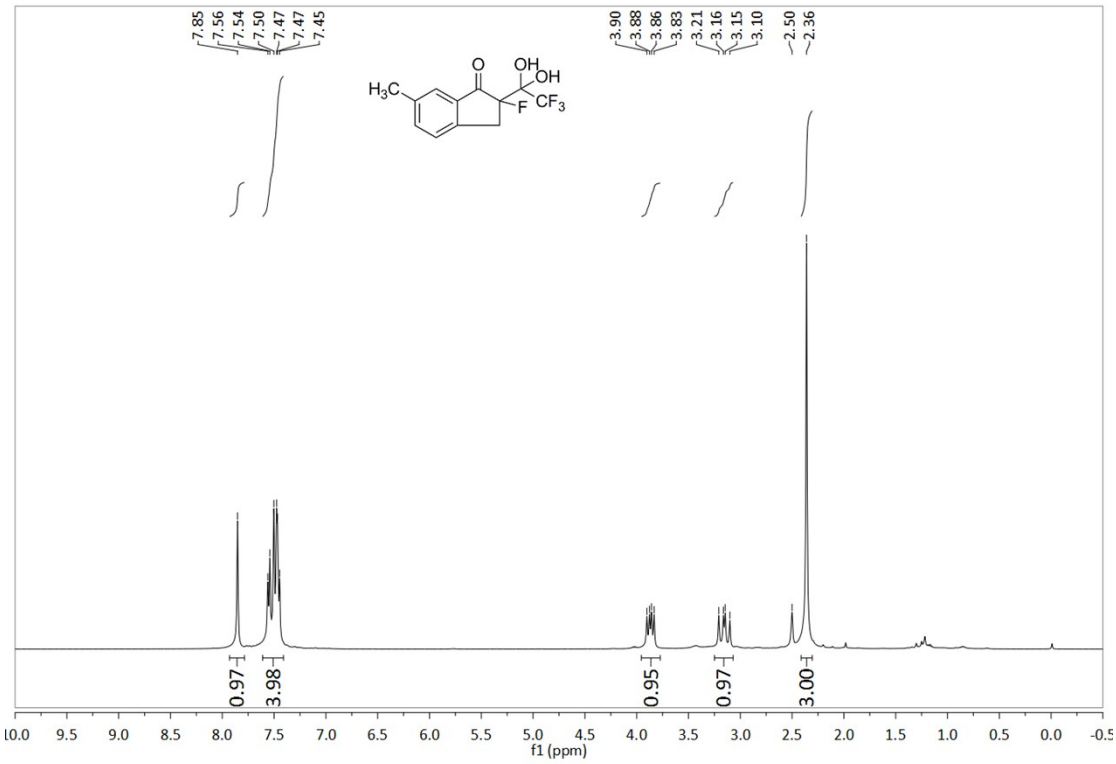
^{19}F NMR (376 MHz, DMSO) spectrum of **1f**



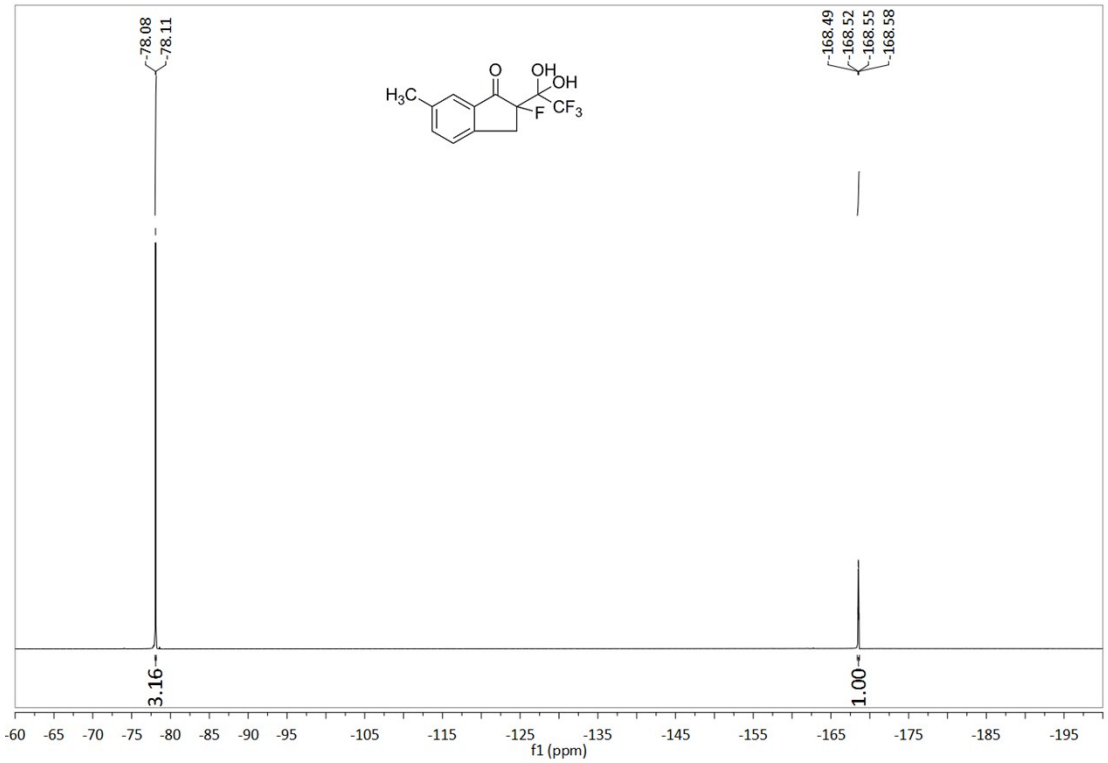
^{13}C NMR (101 MHz, DMSO) spectrum of **1f**



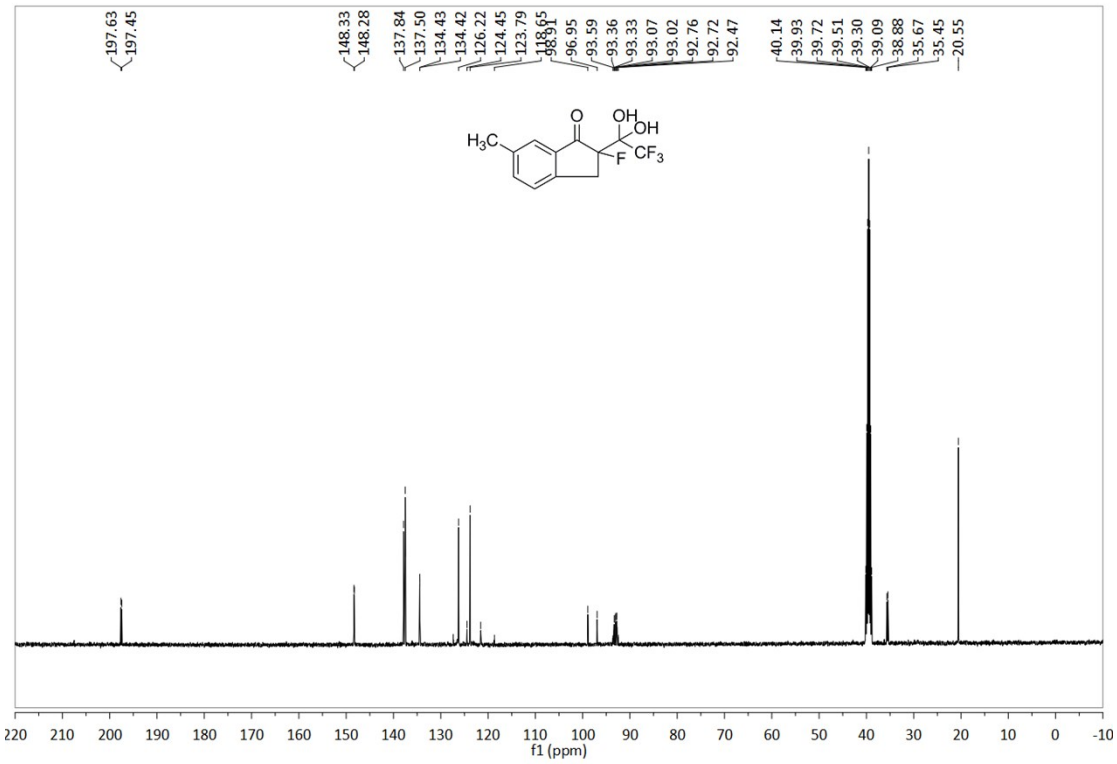
^{1}H NMR (400 MHz, DMSO) spectrum of **1g**



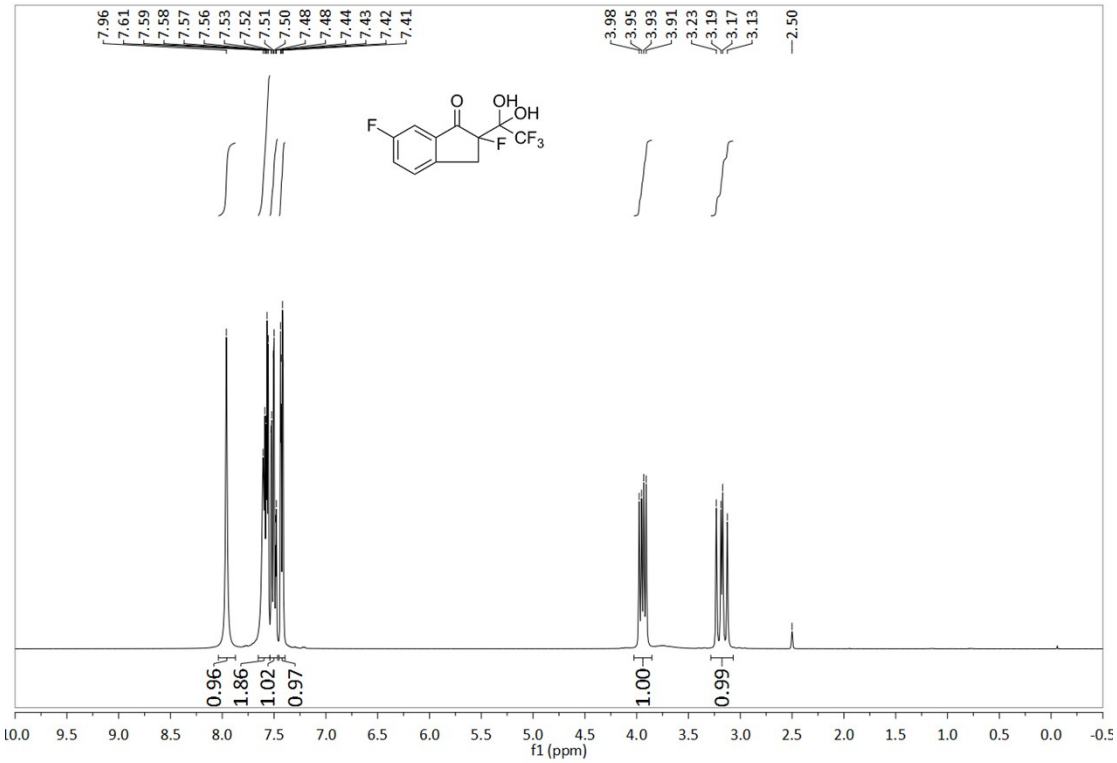
^{19}F NMR (376 MHz, DMSO) spectrum of **1g**



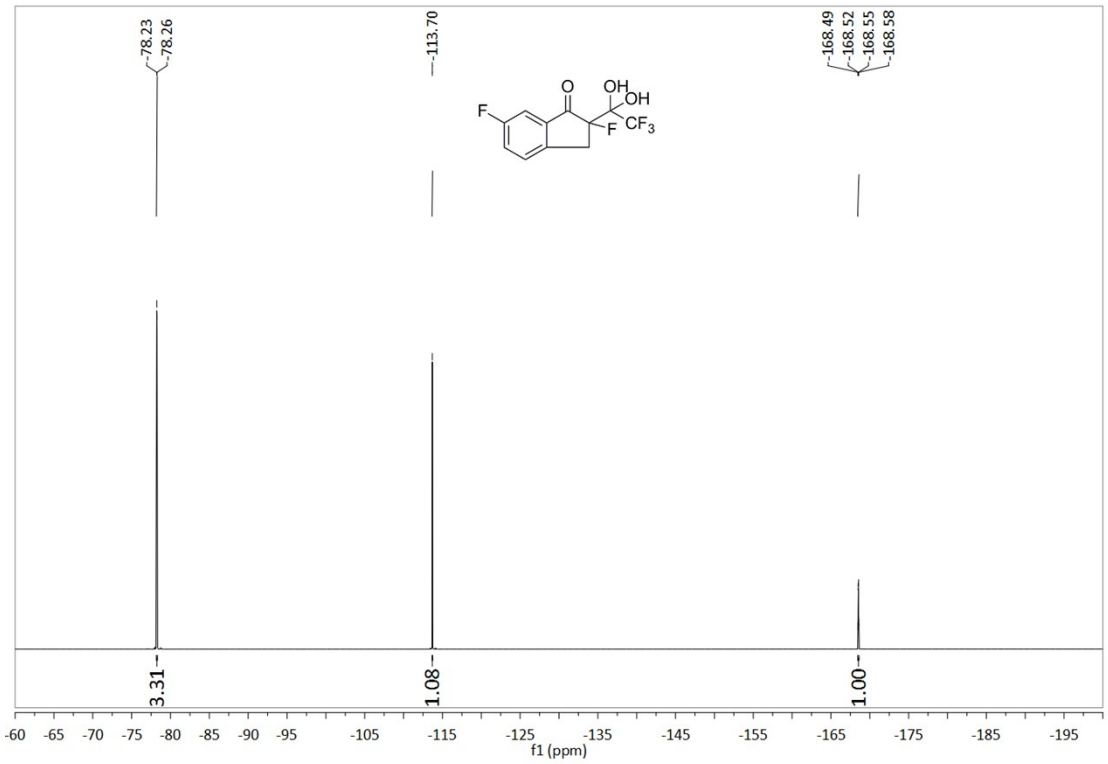
^{13}C NMR (101 MHz, DMSO) spectrum of **1g**



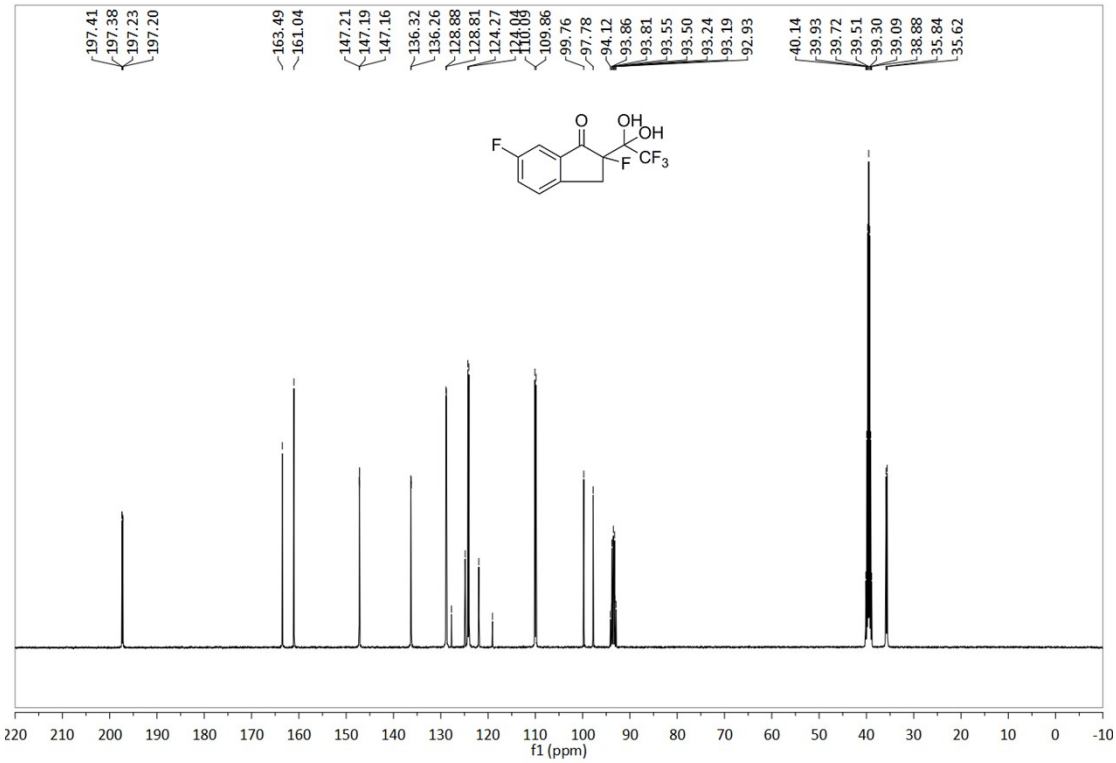
^{1}H NMR (400 MHz, DMSO) spectrum of **1h**



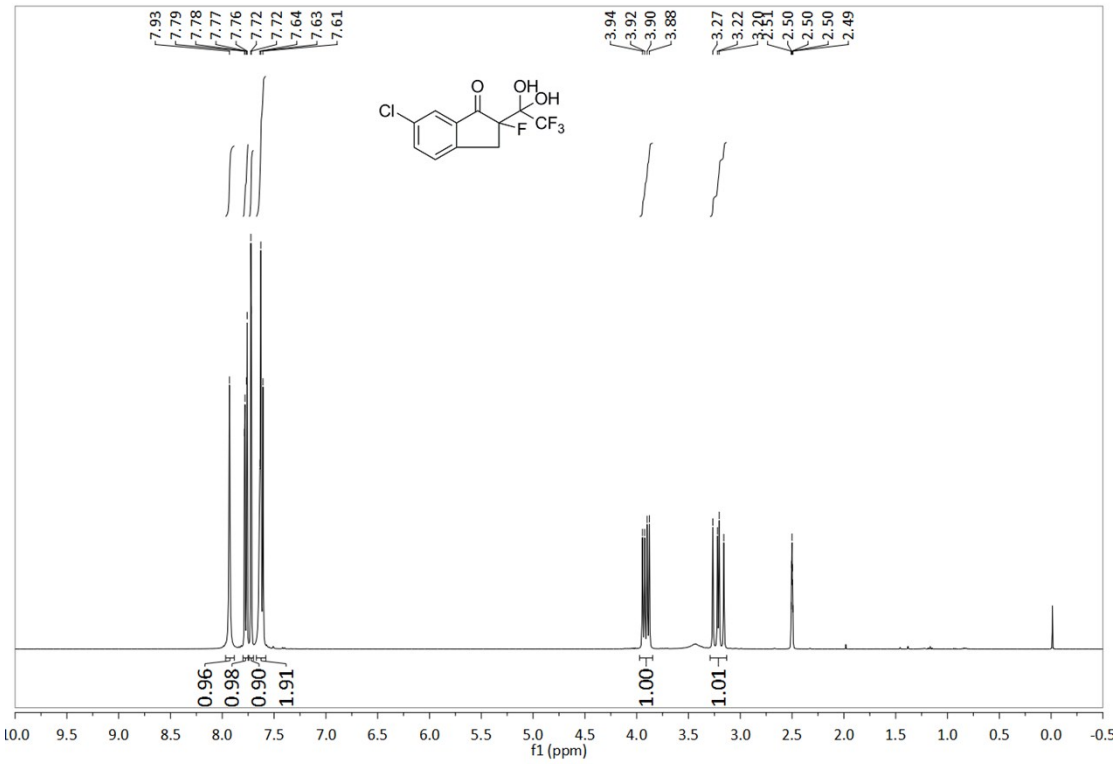
^{19}F NMR (376 MHz, DMSO) spectrum of **1h**



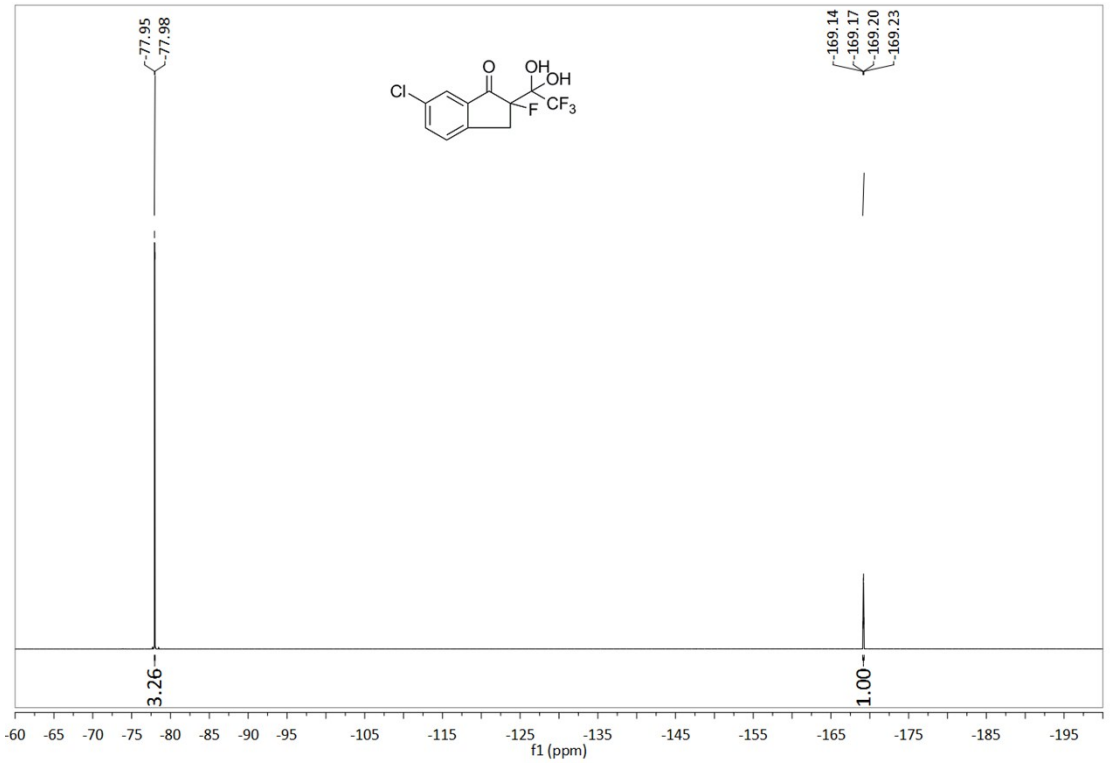
^{13}C NMR (101 MHz, DMSO) spectrum of **1h**



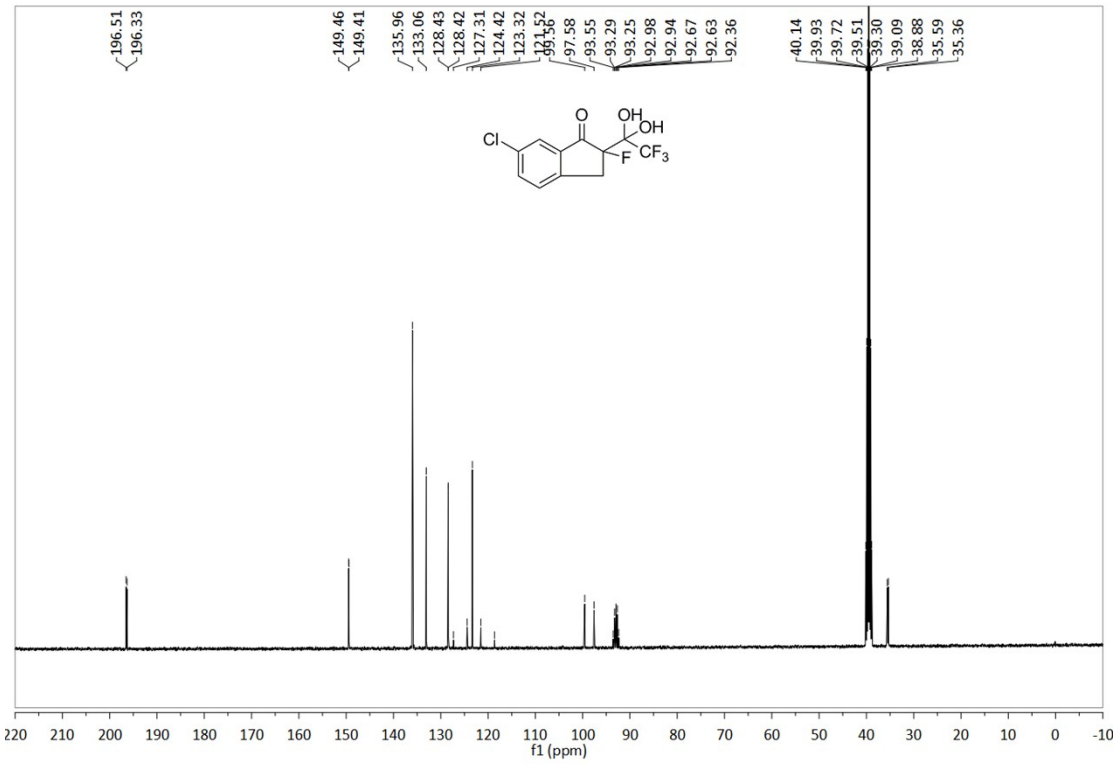
^{1}H NMR (400 MHz, DMSO) spectrum of **1i**



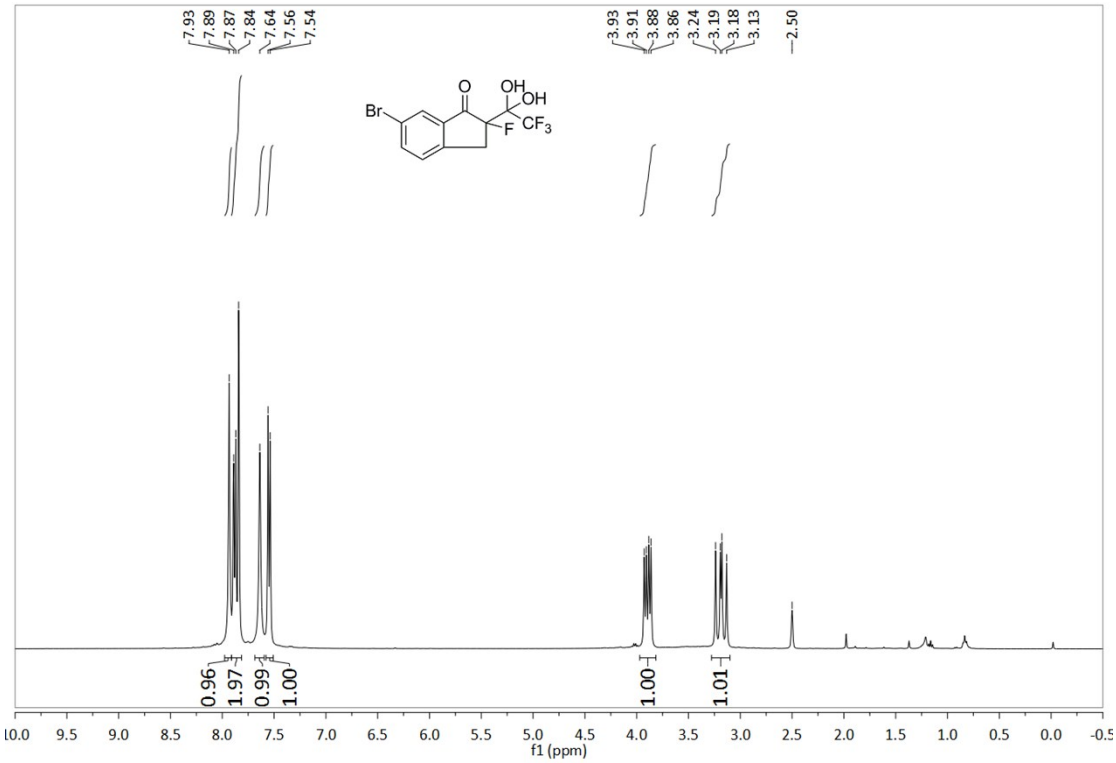
^{19}F NMR (376 MHz, DMSO) spectrum of **1i**



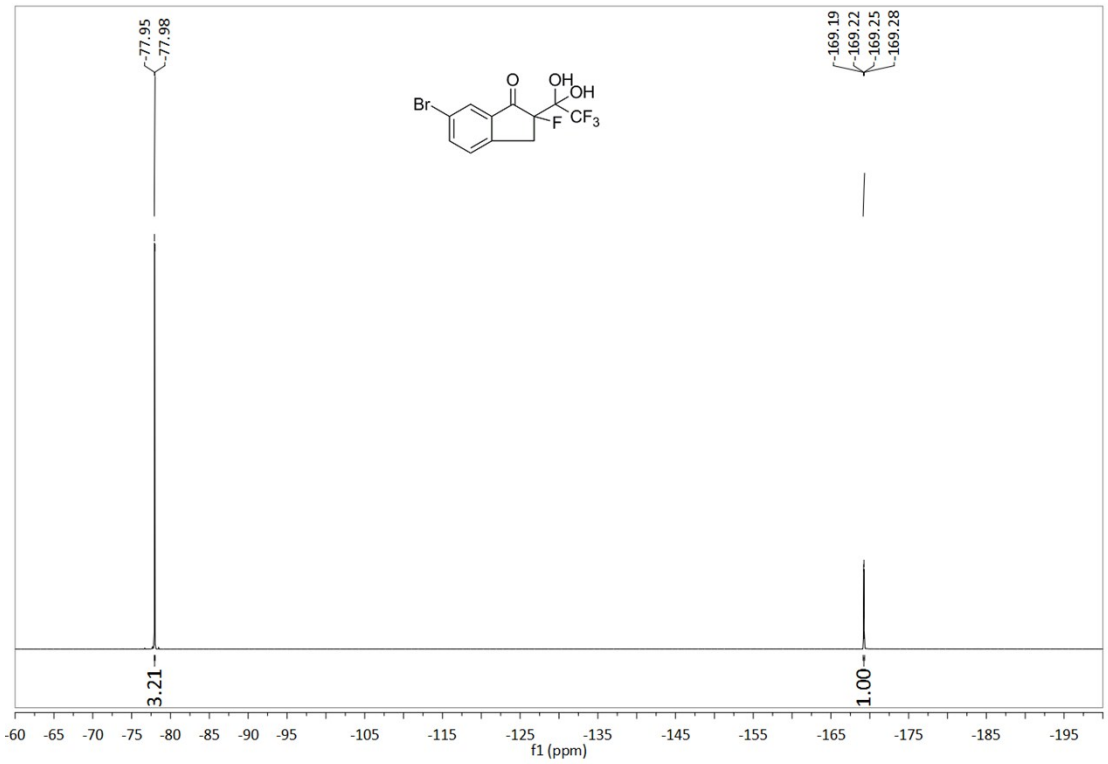
^{13}C NMR (101 MHz, DMSO) spectrum of **1i**



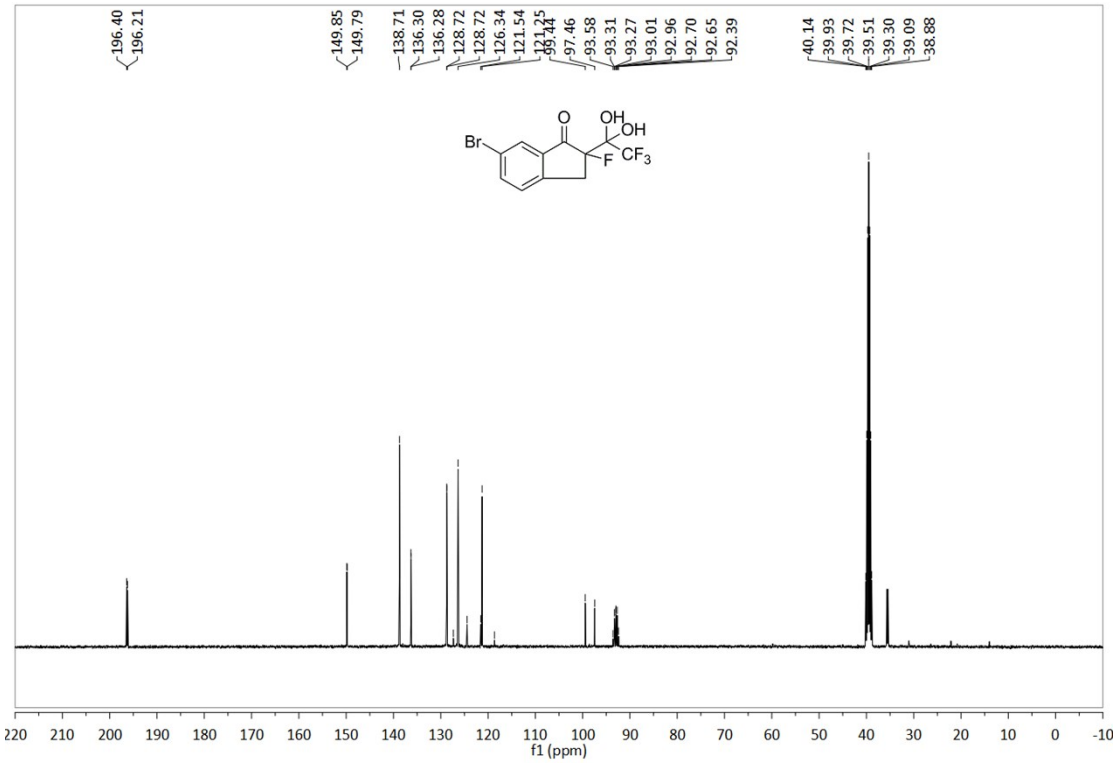
^{1}H NMR (400 MHz, DMSO) spectrum of **1j**



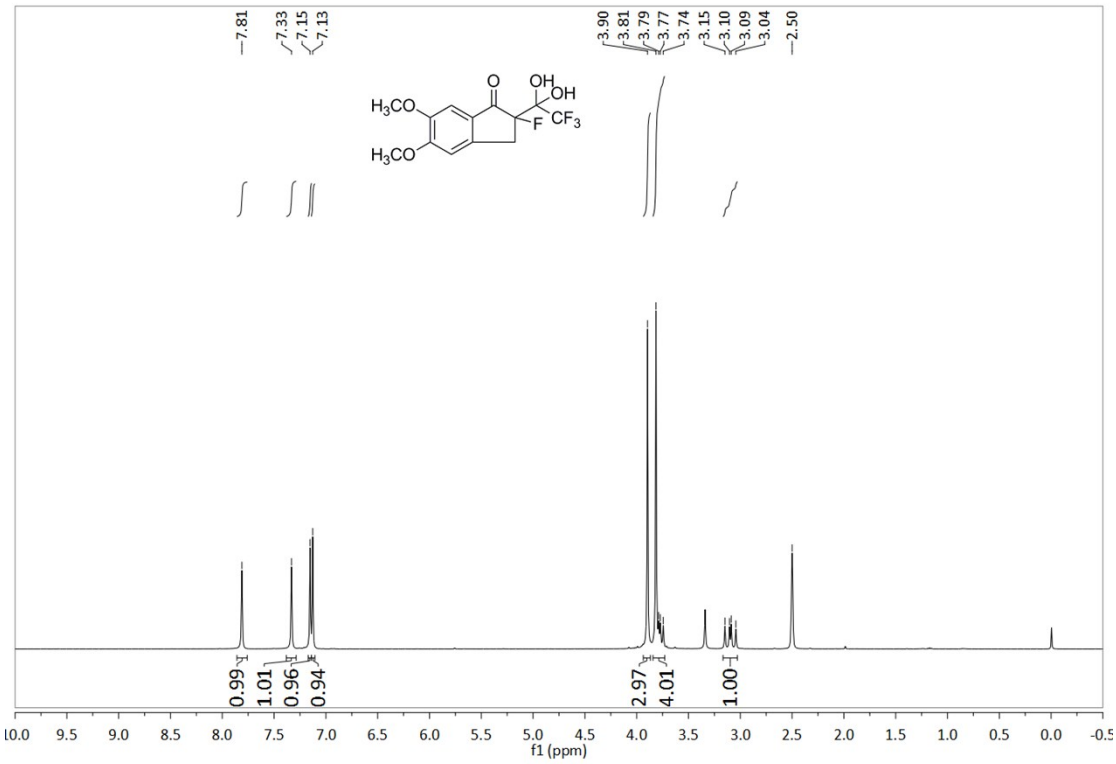
^{19}F NMR (376 MHz, DMSO) spectrum of **1j**



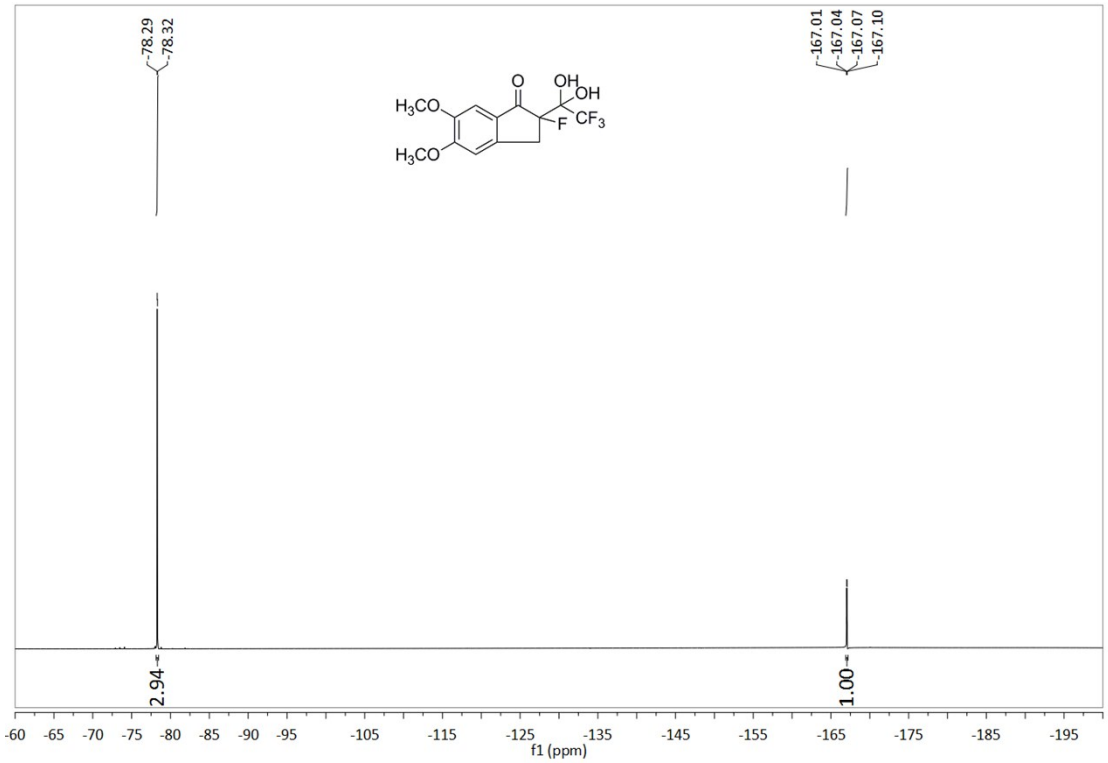
^{13}C NMR (101 MHz, DMSO) spectrum of **1j**



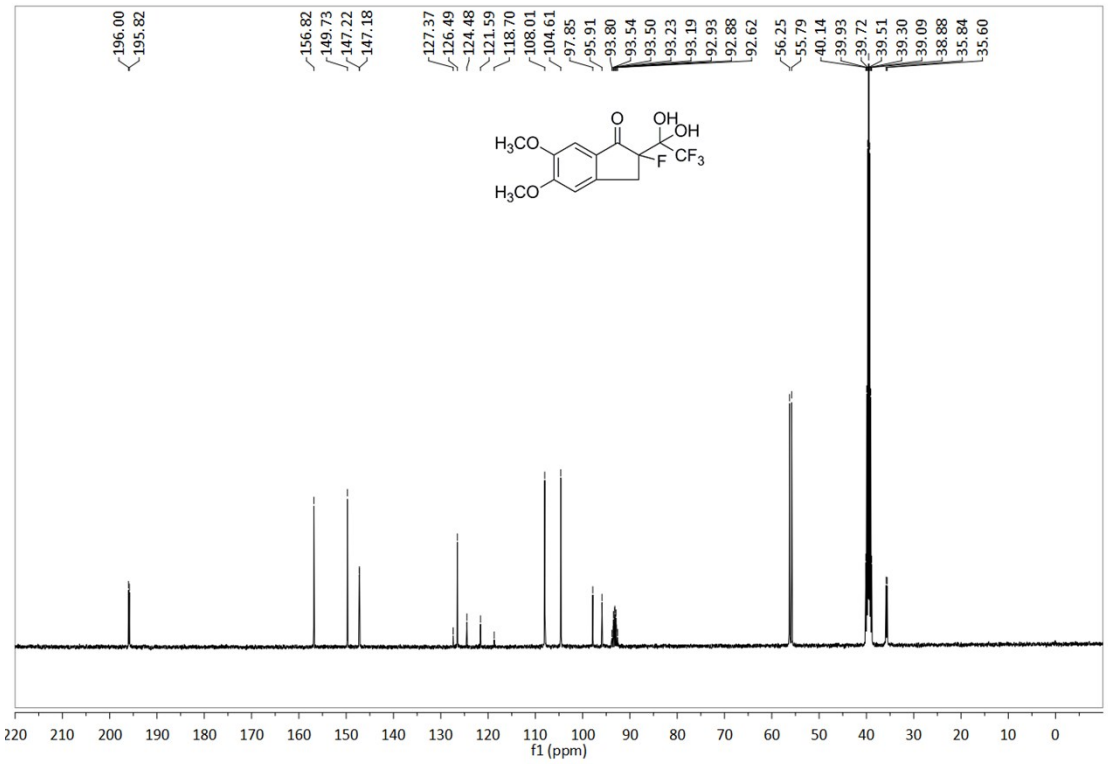
^{1}H NMR (400 MHz, DMSO) spectrum of **1k**



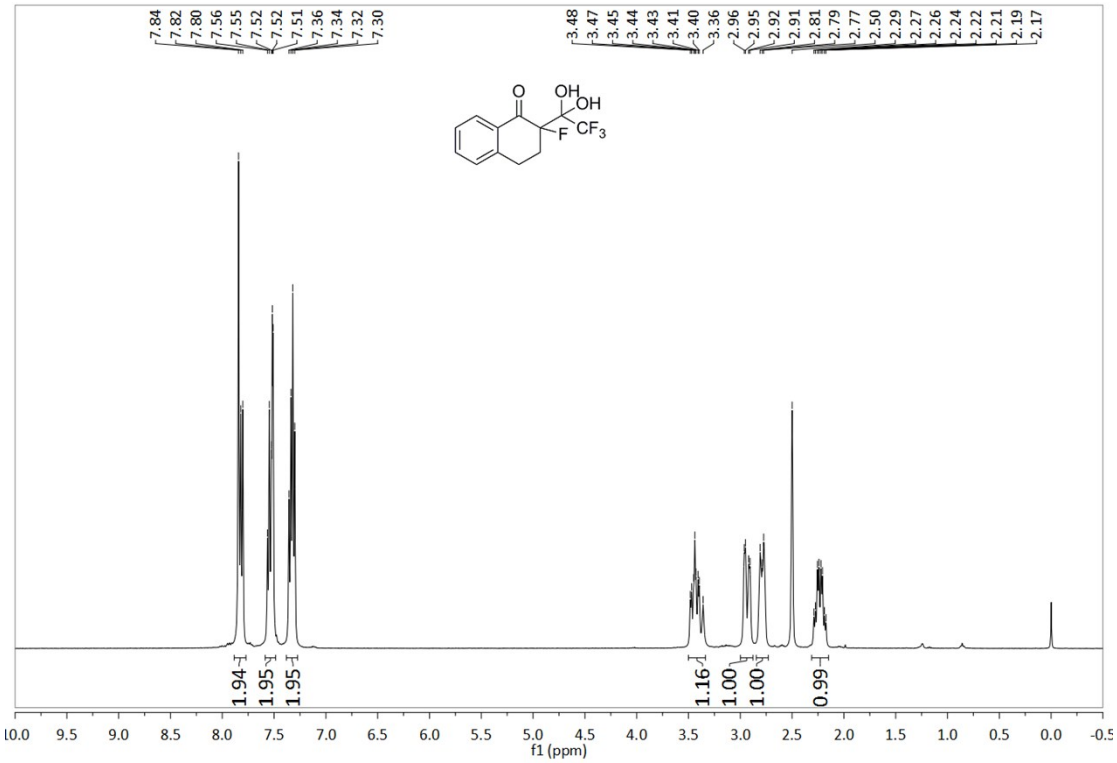
^{19}F NMR (376 MHz, DMSO) spectrum of **1k**



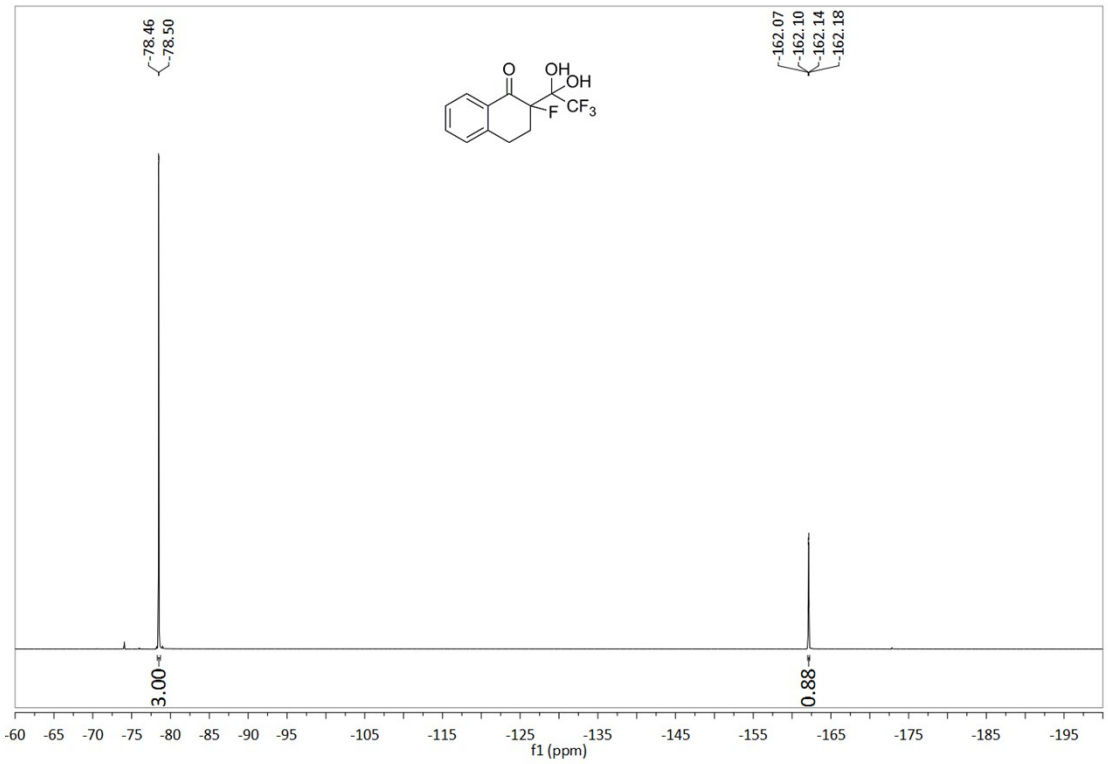
^{13}C NMR (101 MHz, DMSO) spectrum of **1k**



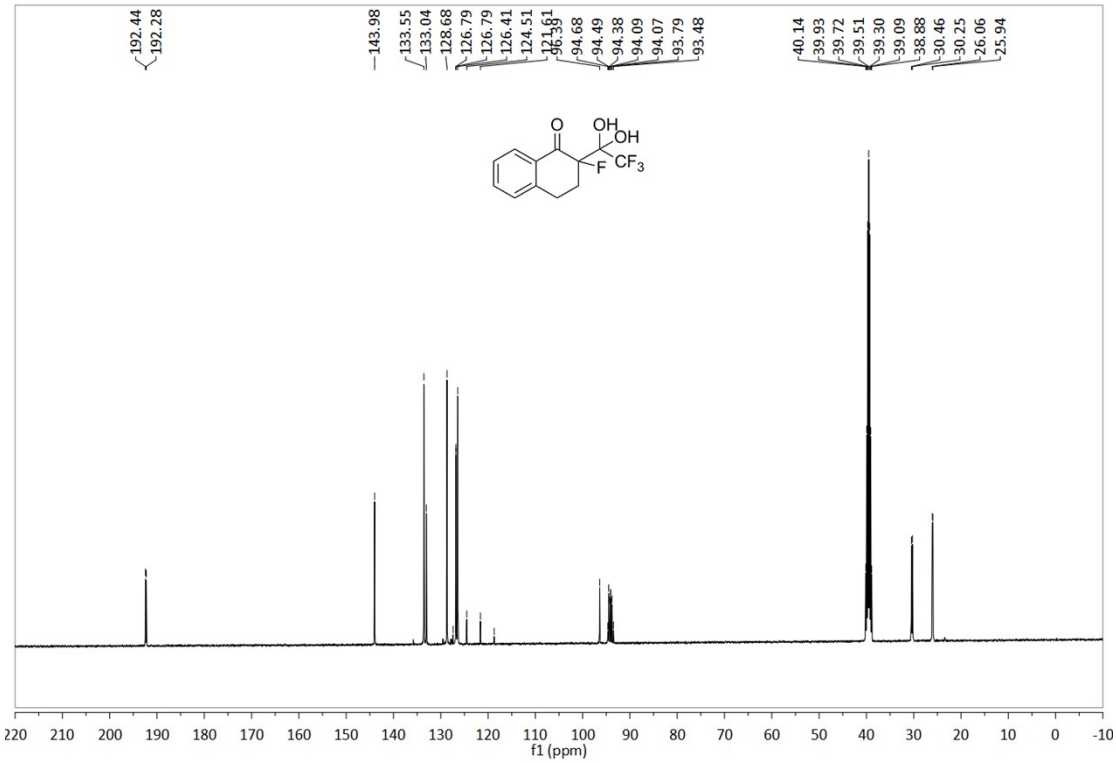
^{1}H NMR (400 MHz, DMSO) spectrum of **1l**



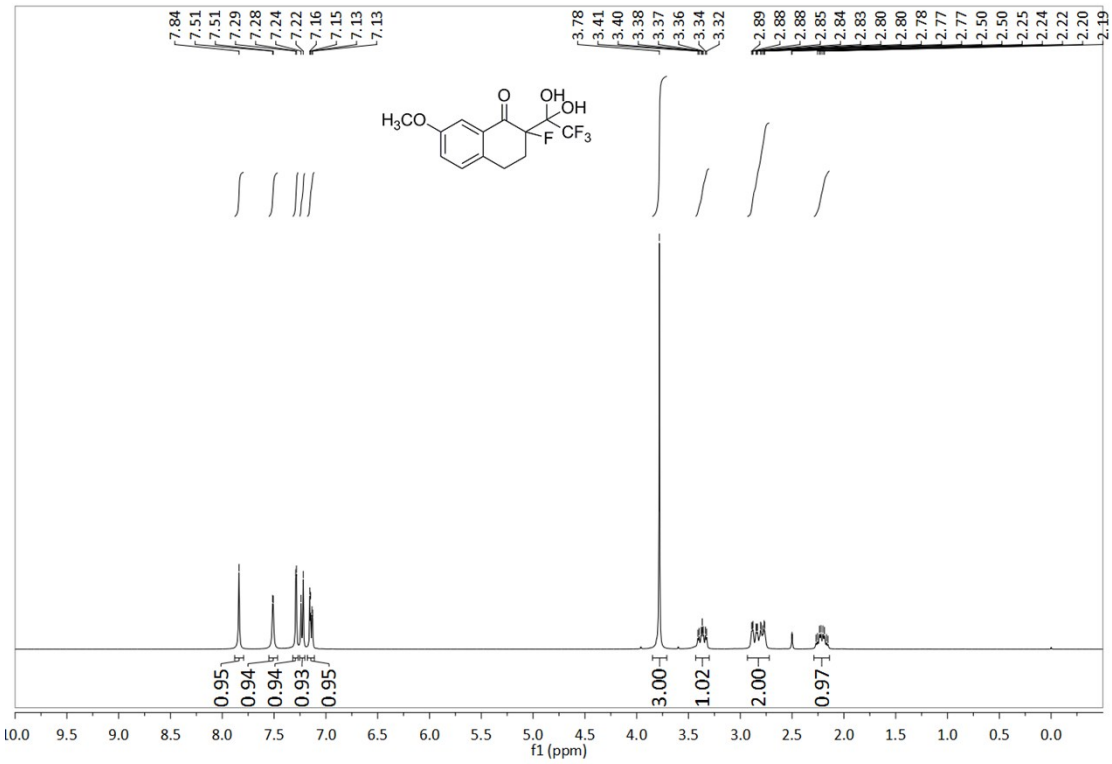
^{19}F NMR (376 MHz, DMSO) spectrum of **1l**



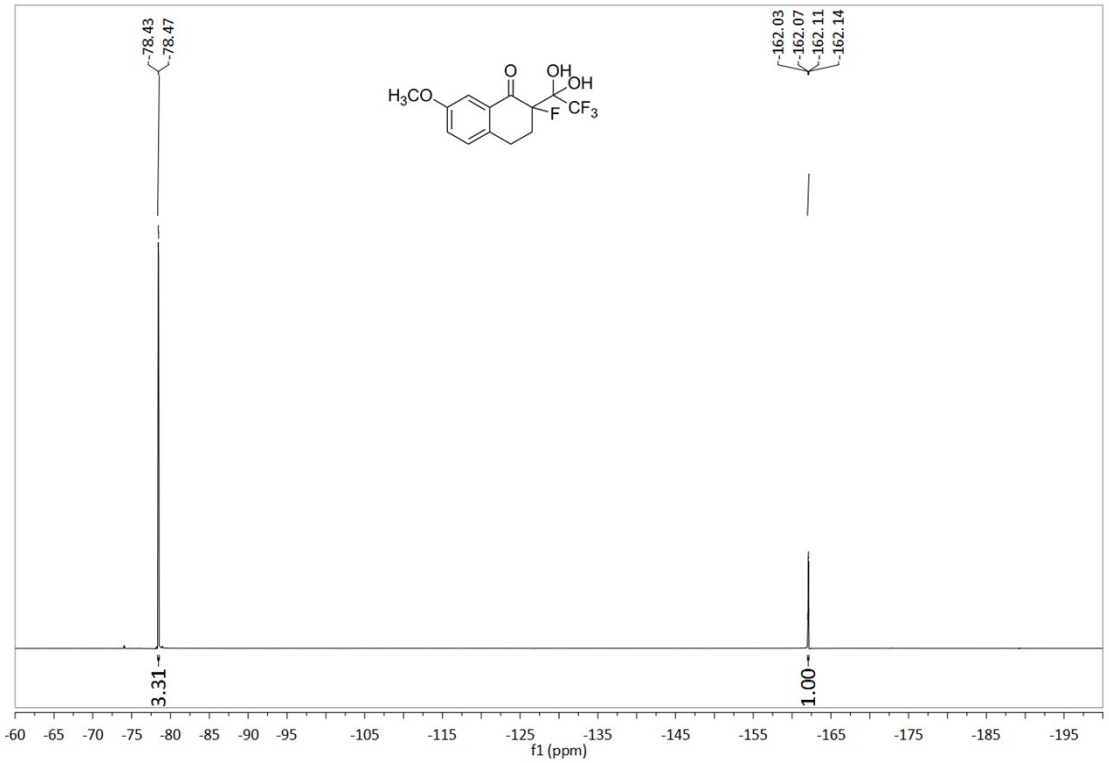
^{13}C NMR (101 MHz, DMSO) spectrum of **1l**



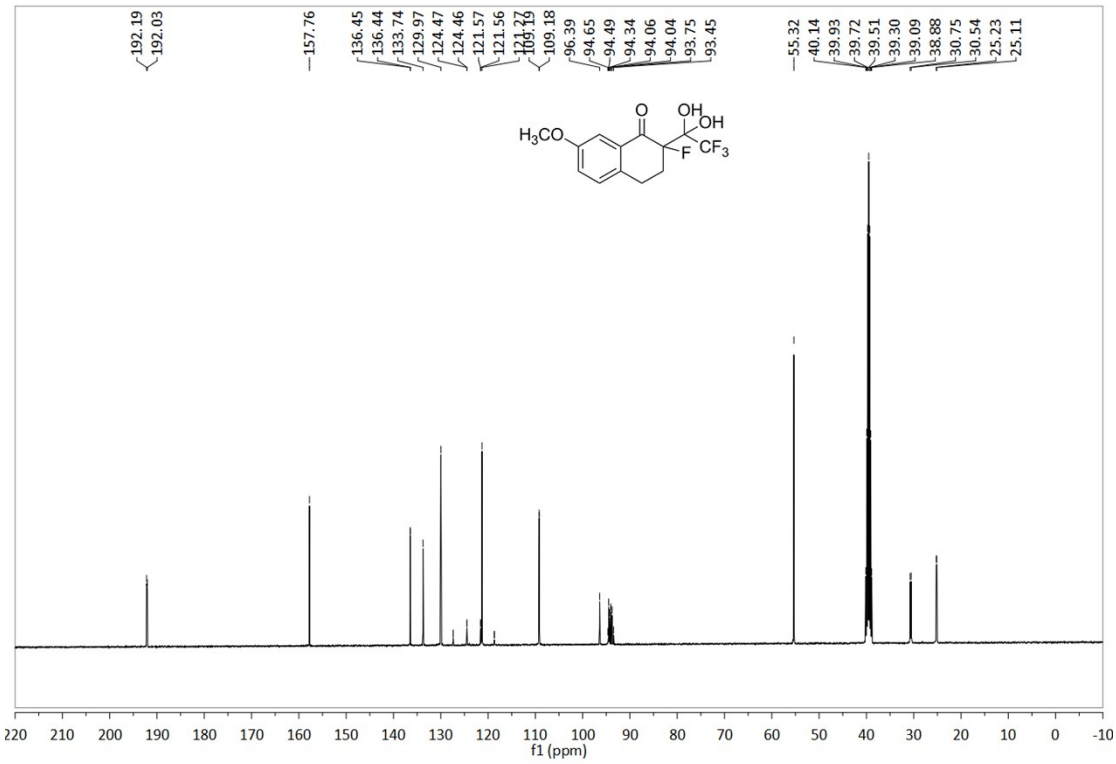
^{1}H NMR (400 MHz, DMSO) spectrum of **1m**



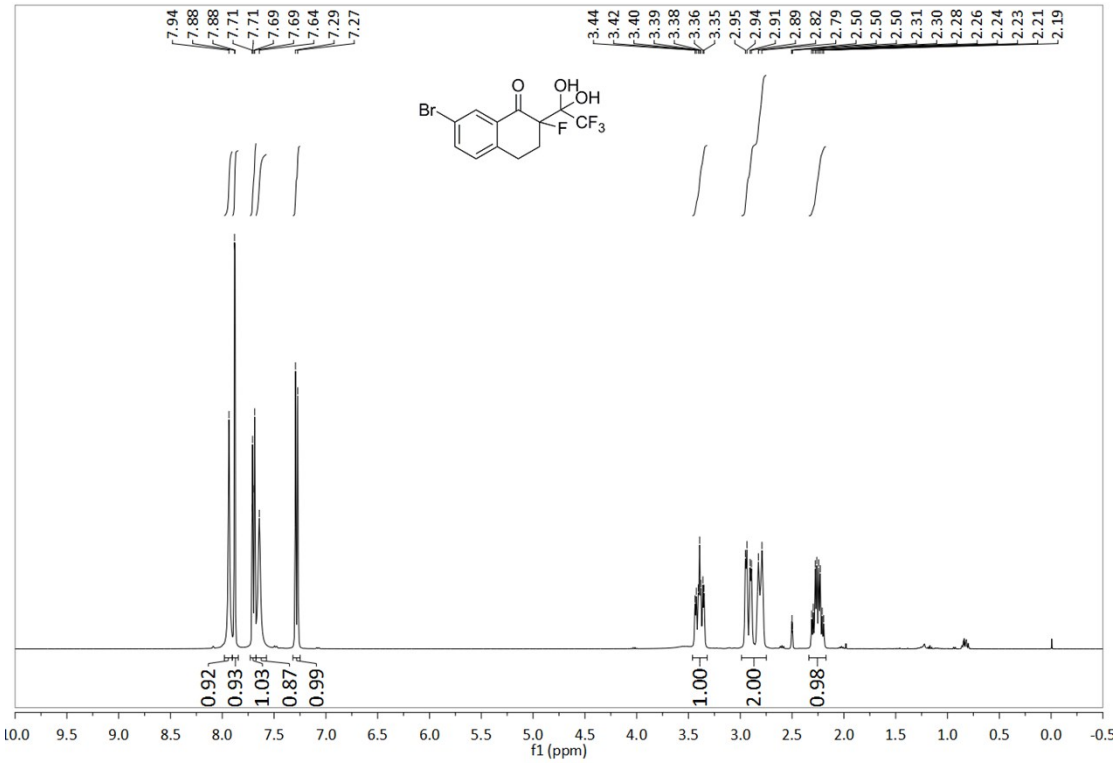
^{19}F NMR (376 MHz, DMSO) spectrum of **1m**



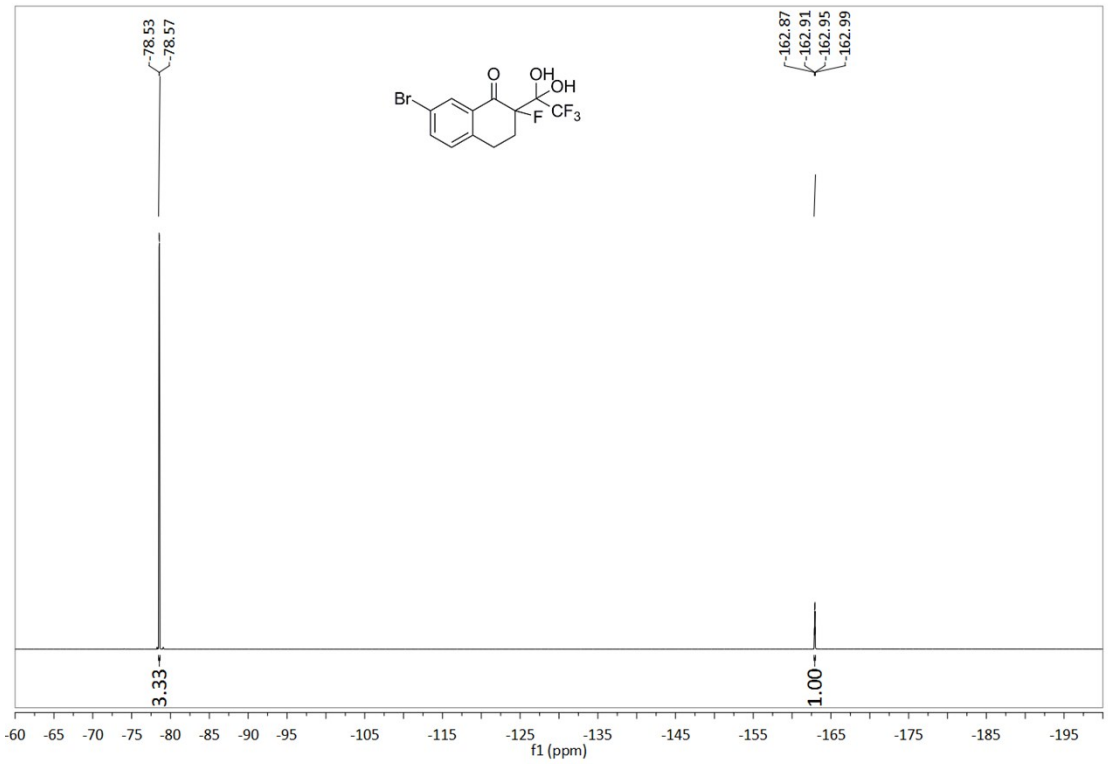
^{13}C NMR (101 MHz, DMSO) spectrum of **1m**



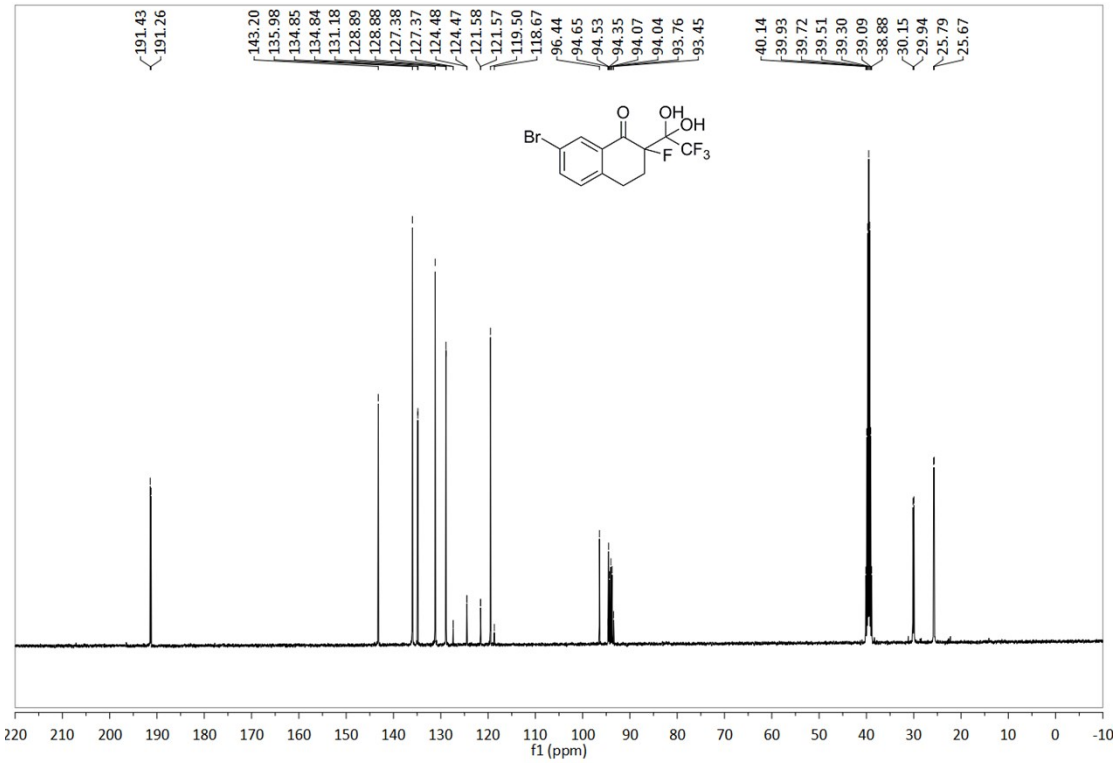
^{1}H NMR (400 MHz, DMSO) spectrum of **1n**



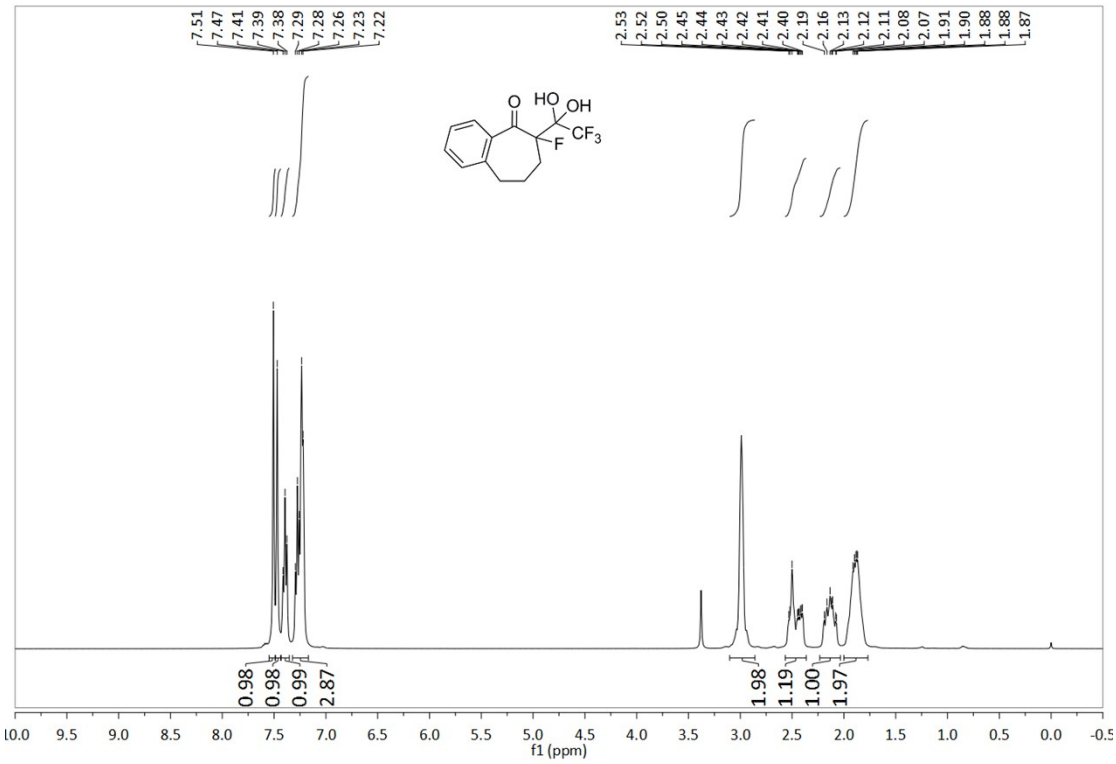
^{19}F NMR (376 MHz, DMSO) spectrum of **1n**



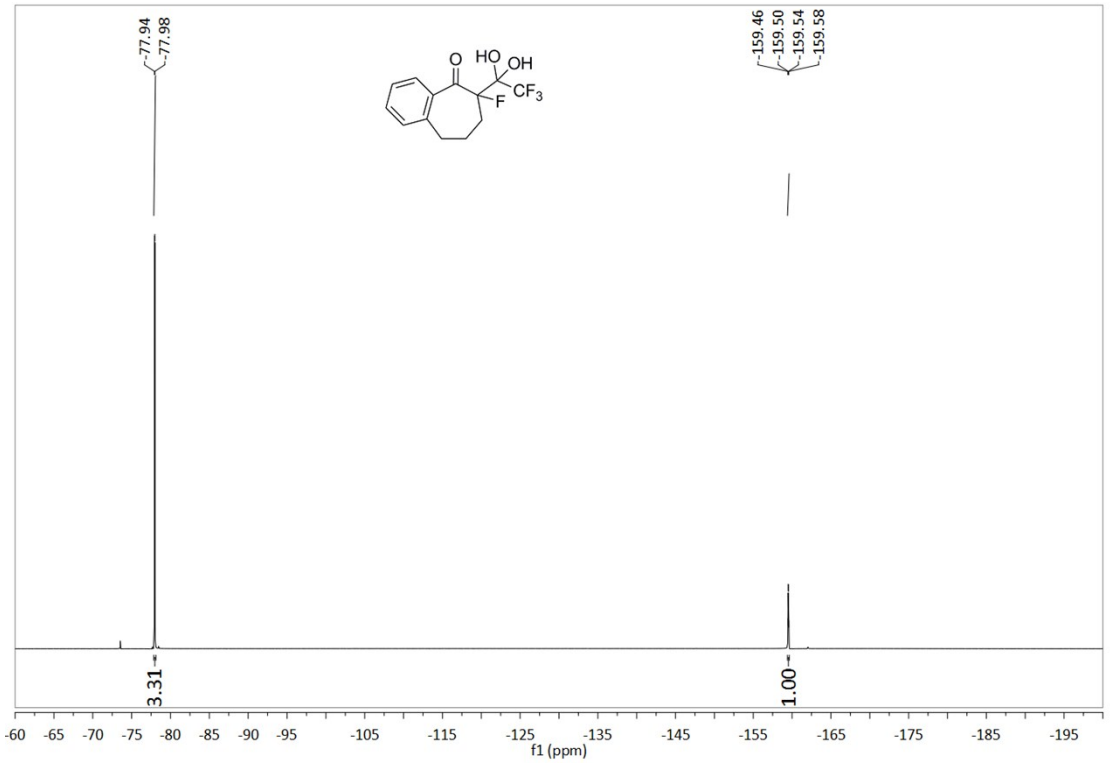
^{13}C NMR (101 MHz, DMSO) spectrum of **1n**



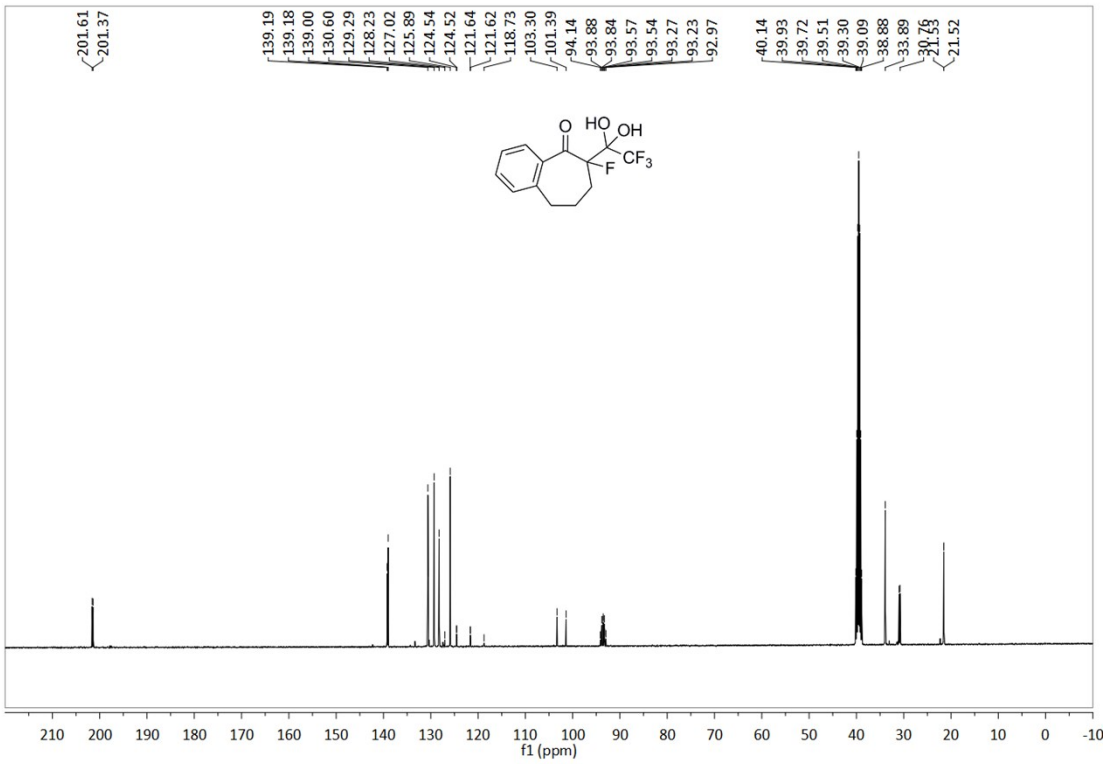
^{1}H NMR (400 MHz, DMSO) spectrum of **1o**



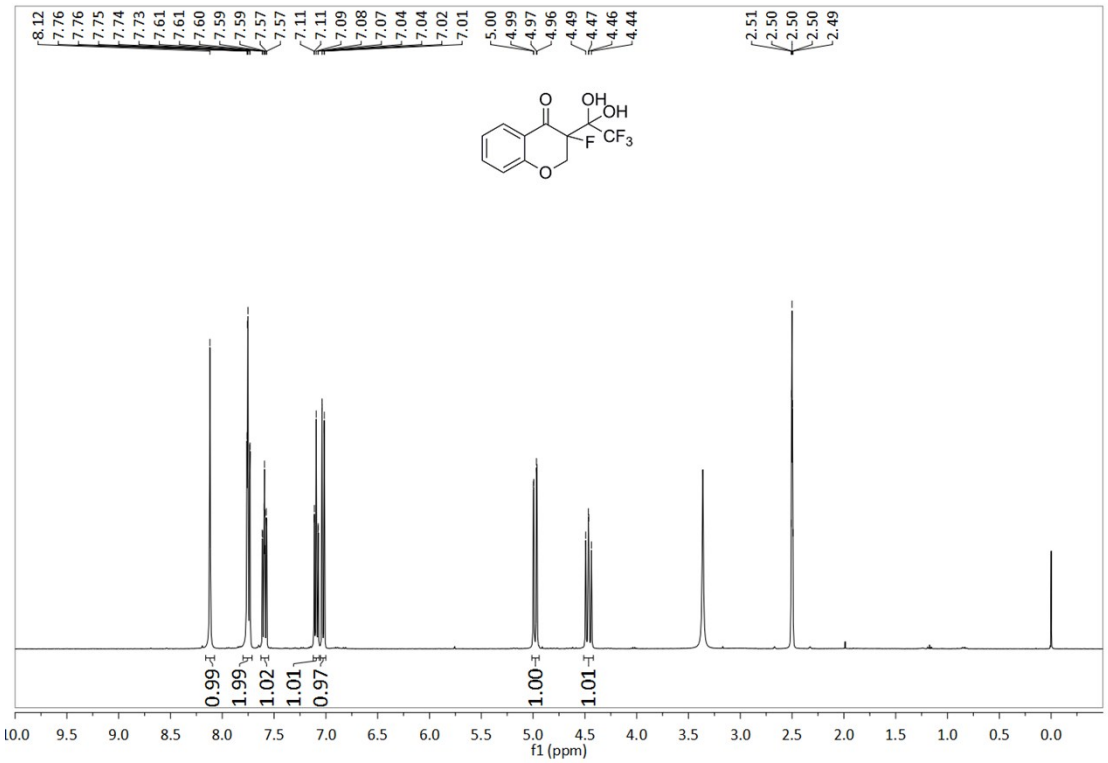
^{19}F NMR (376 MHz, DMSO) spectrum of **1o**



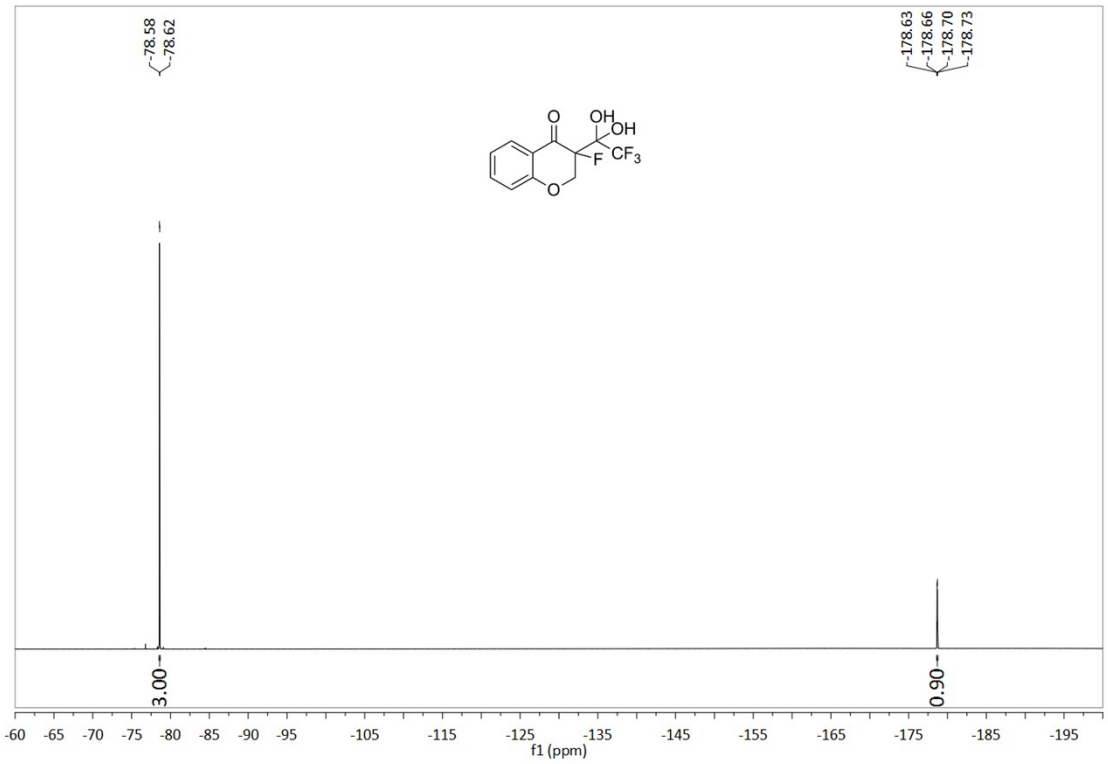
^{13}C NMR (101 MHz, DMSO) spectrum of **1o**



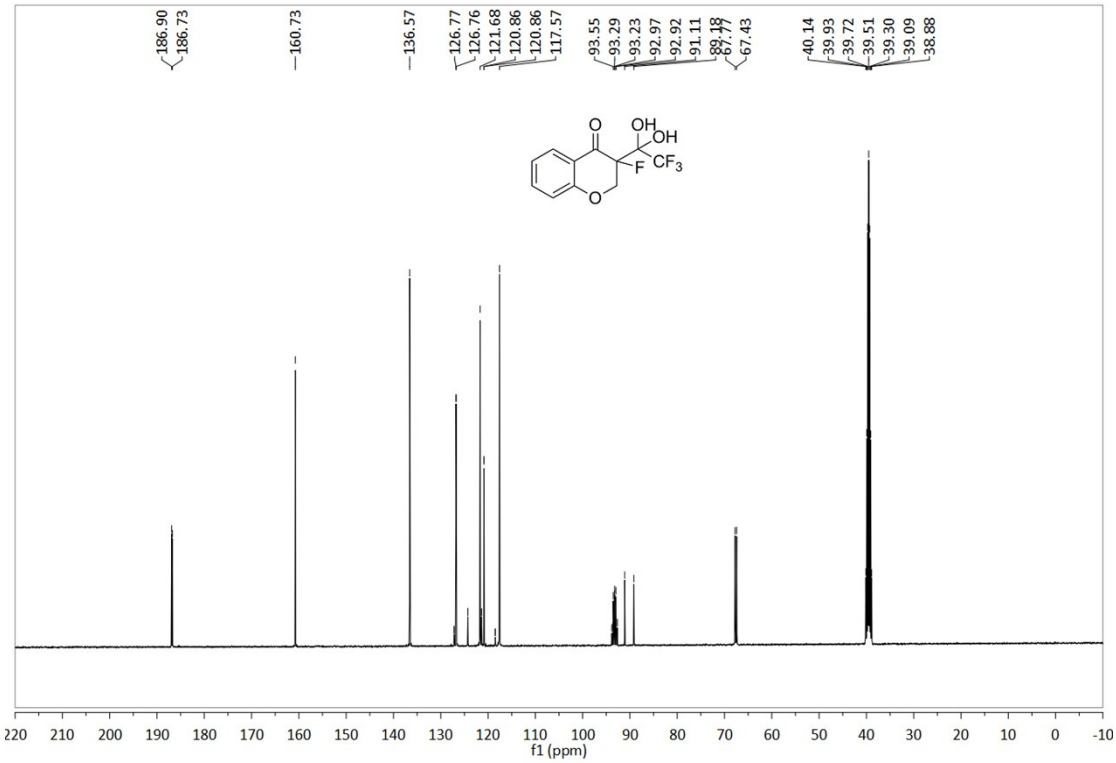
^{1}H NMR (400 MHz, DMSO) spectrum of **1p**



^{19}F NMR (376 MHz, DMSO) spectrum of **1p**

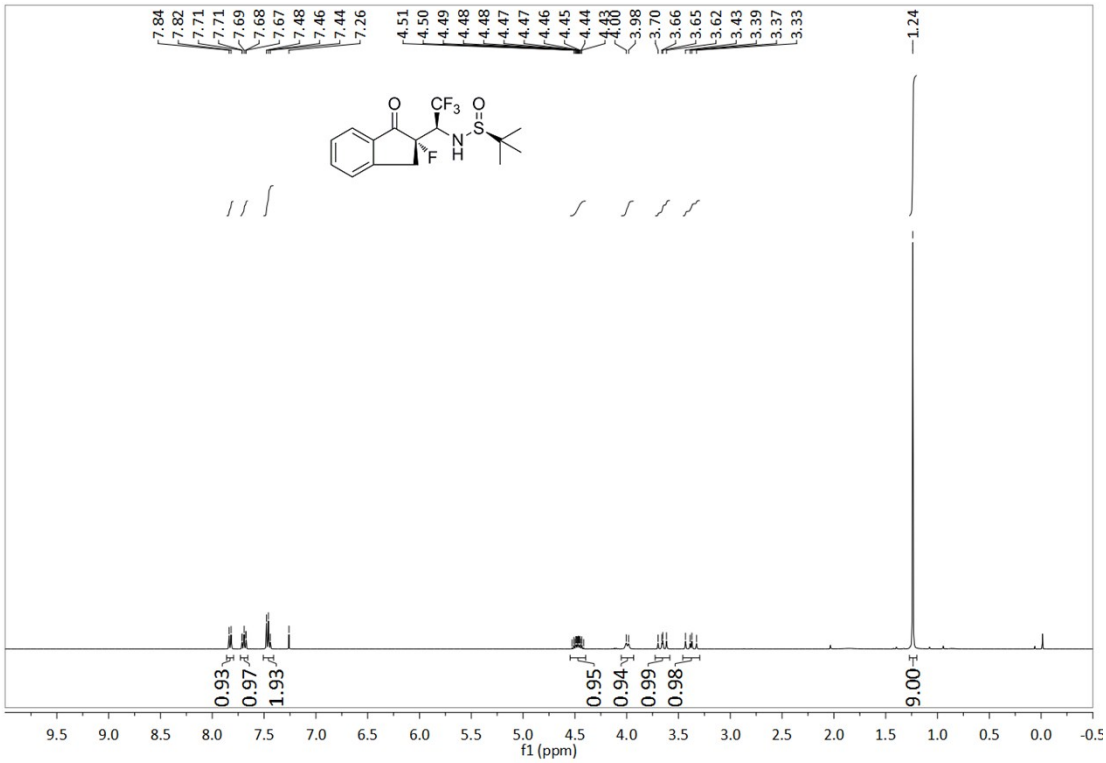


^{13}C NMR (101 MHz, DMSO) spectrum of **1p**

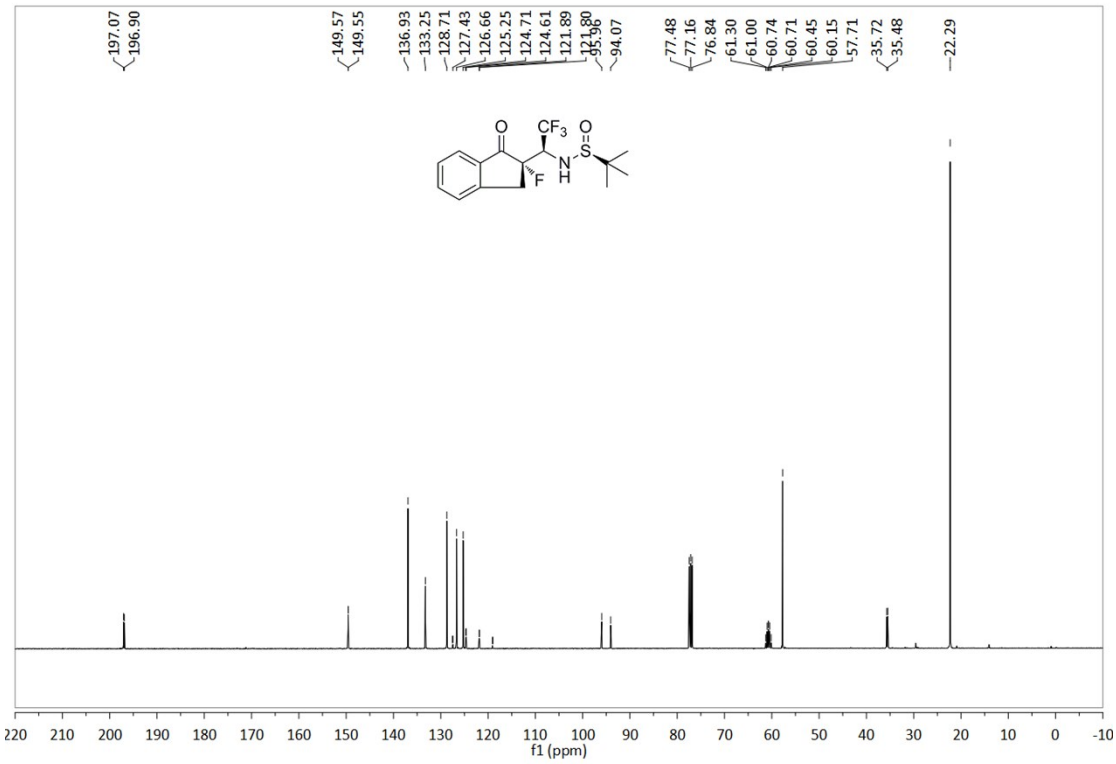


5.2. NMR spectra of products 3

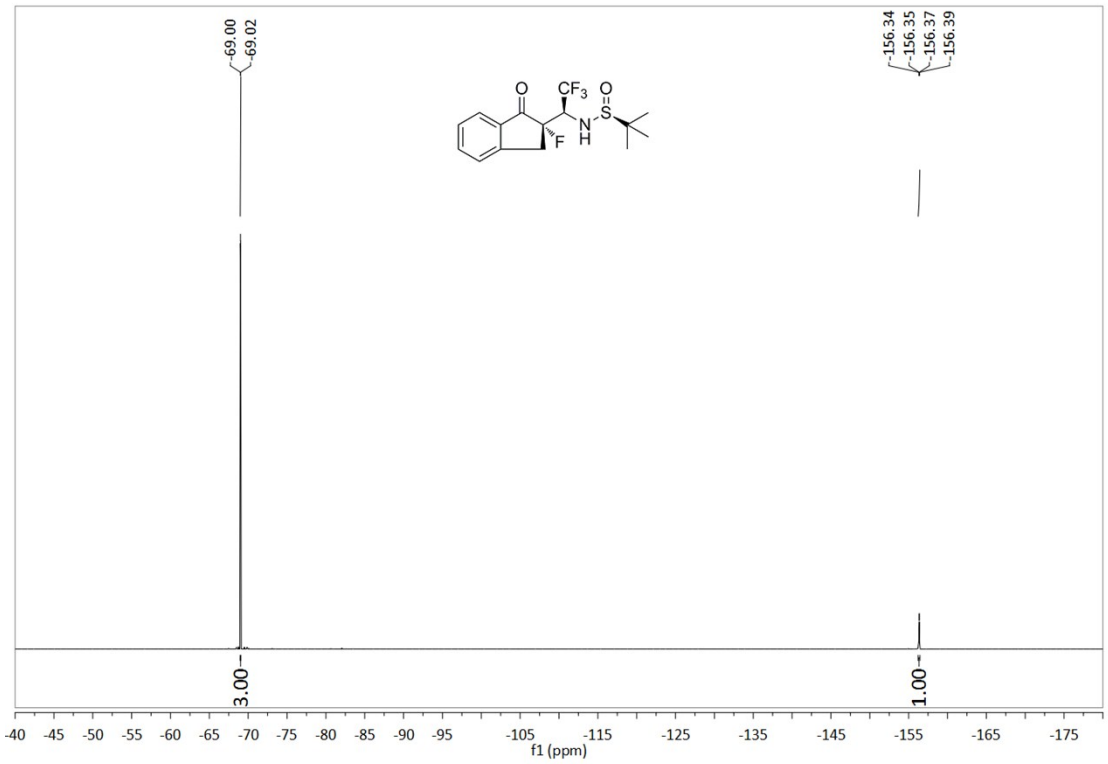
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



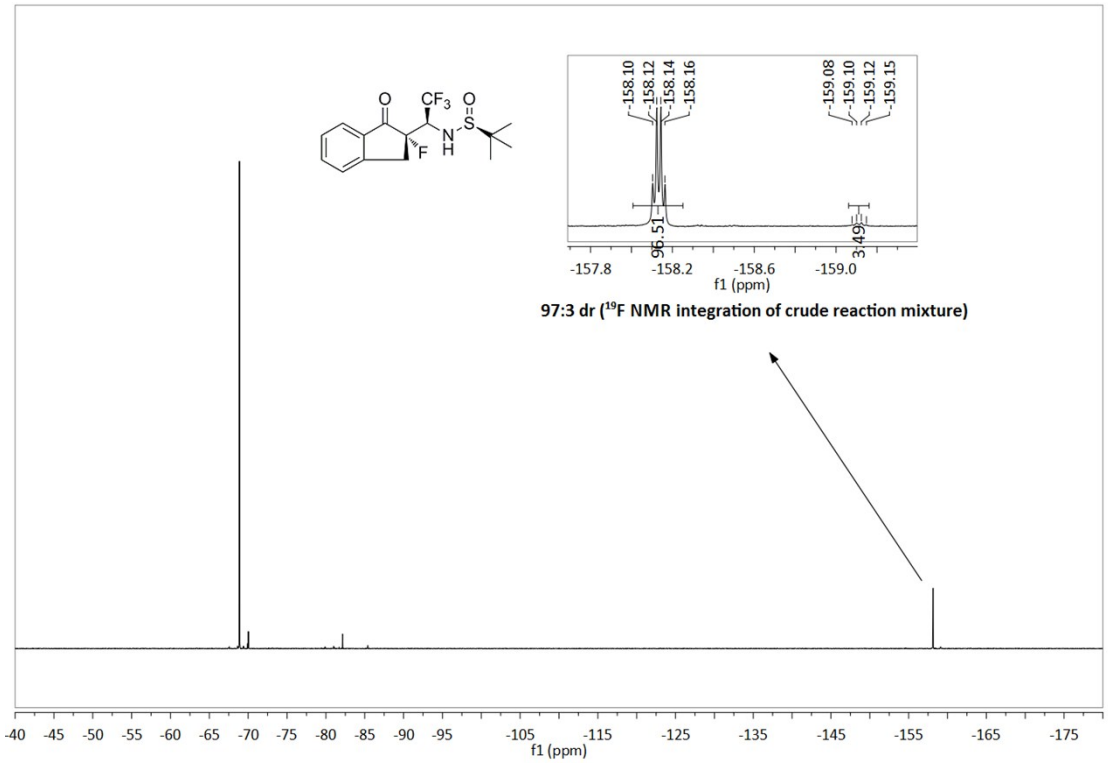
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3aa**



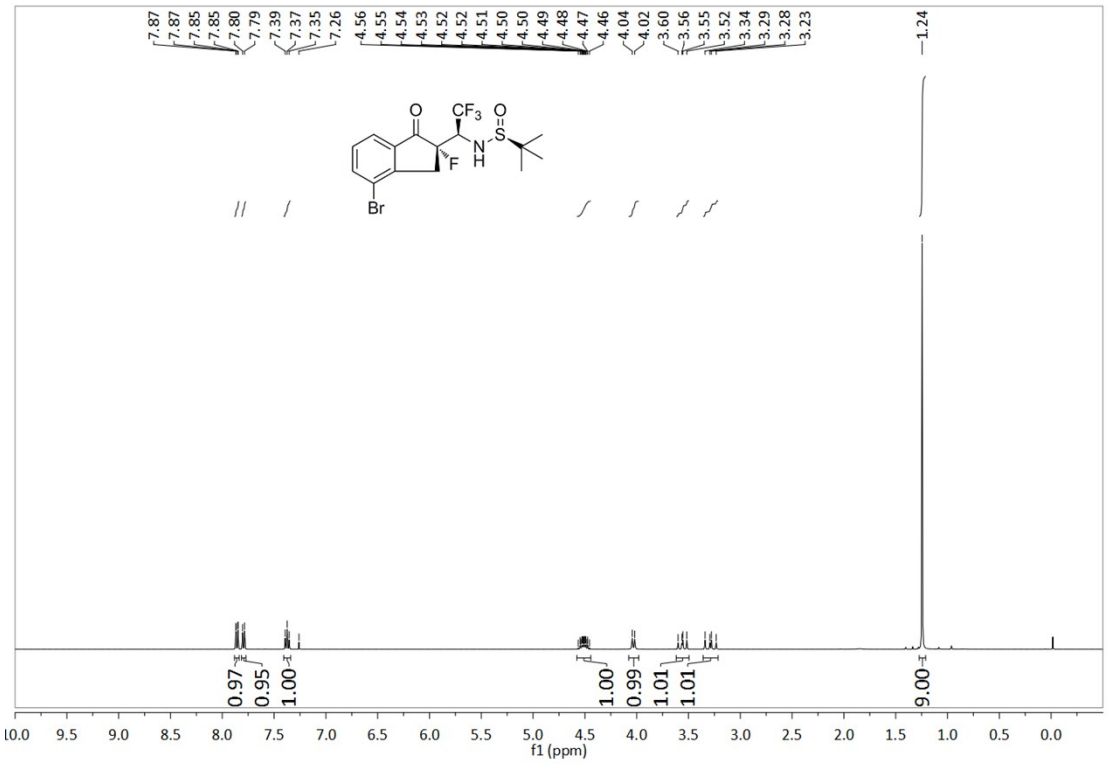
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3aa**



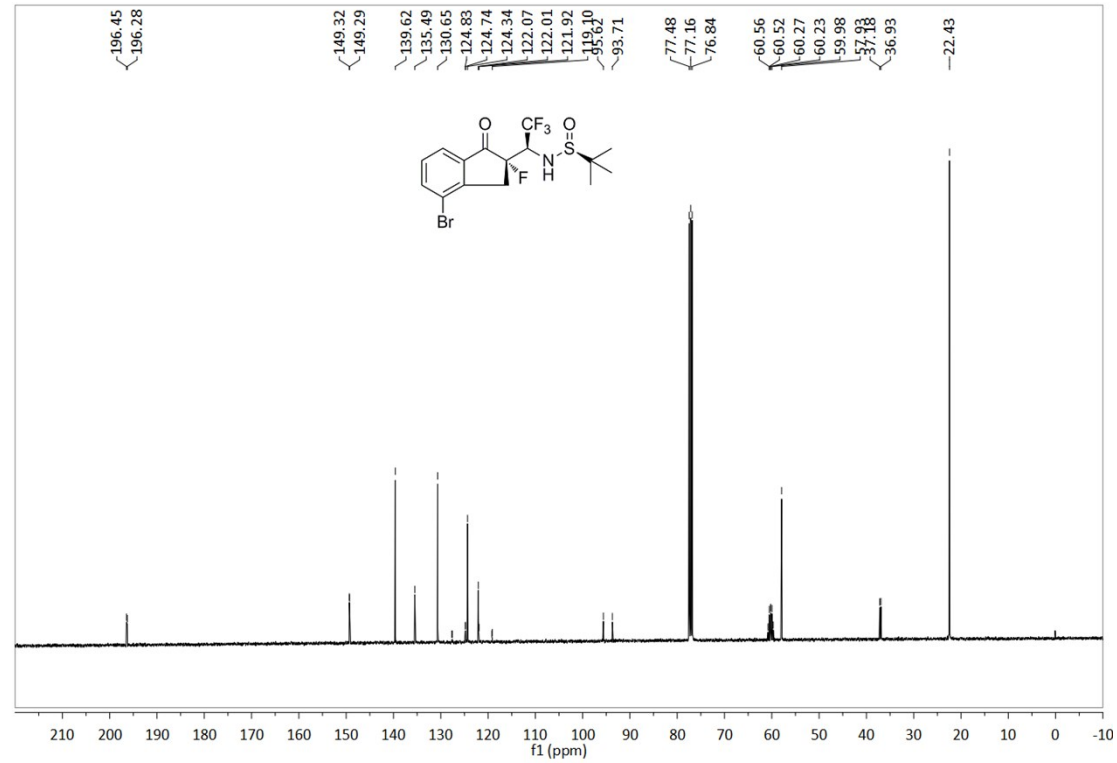
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



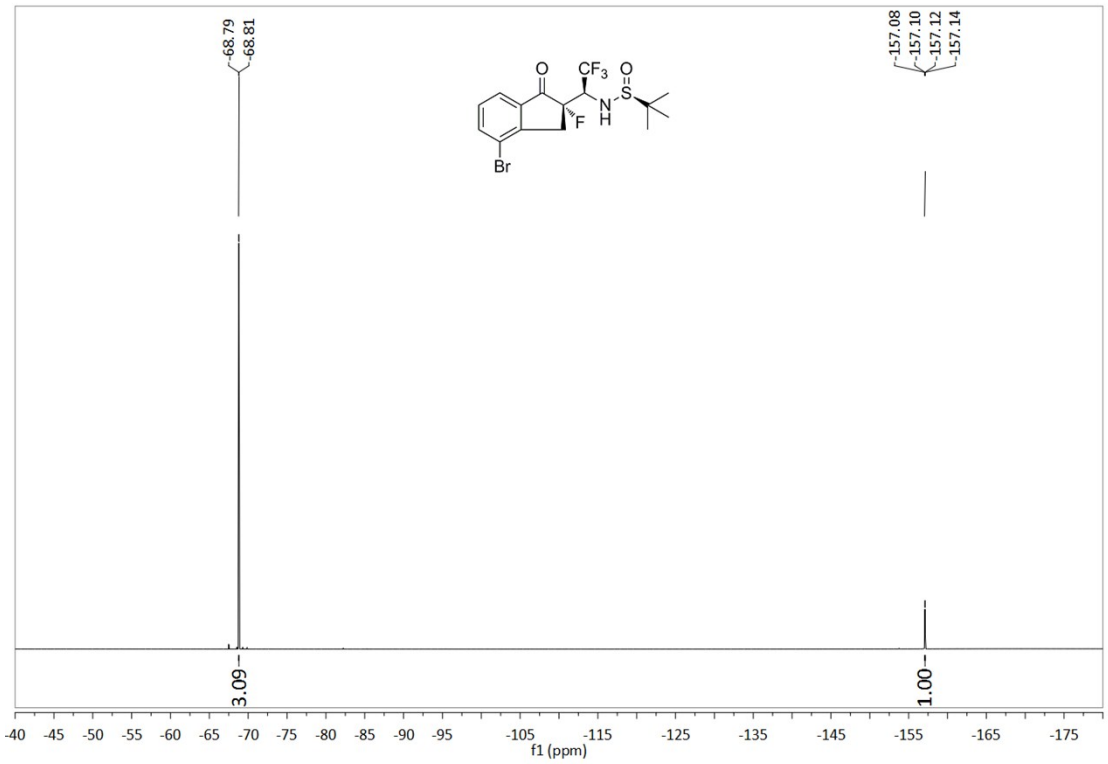
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ba**



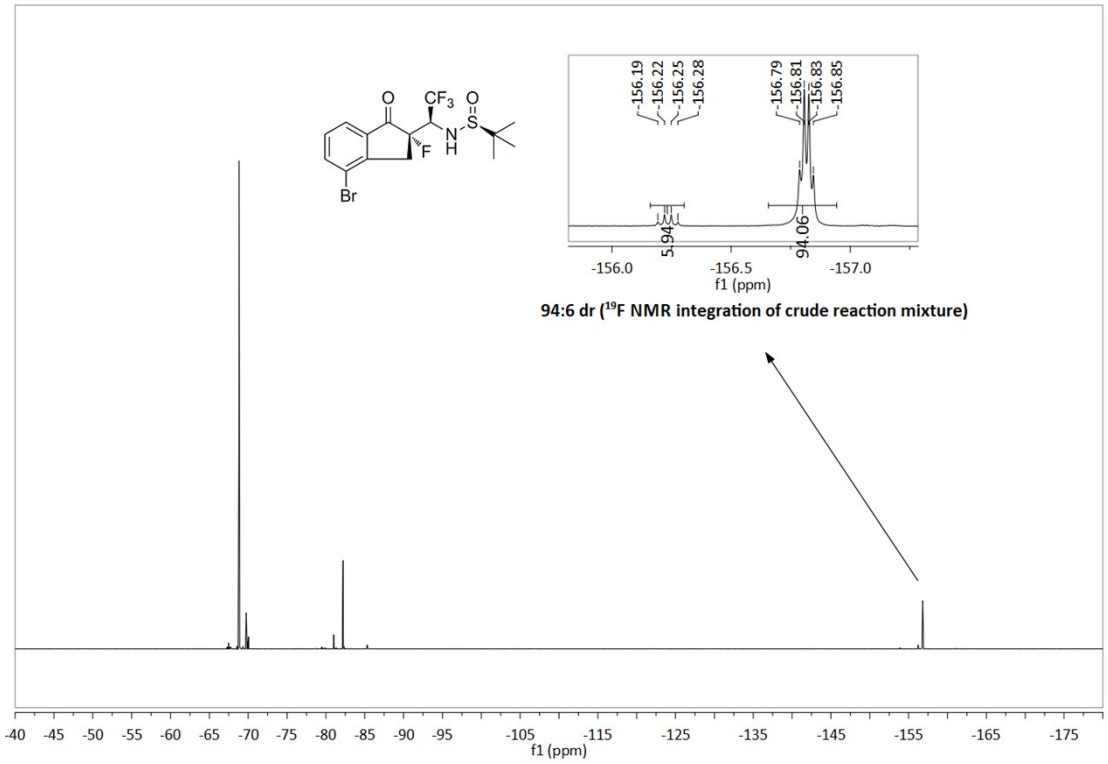
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ba**



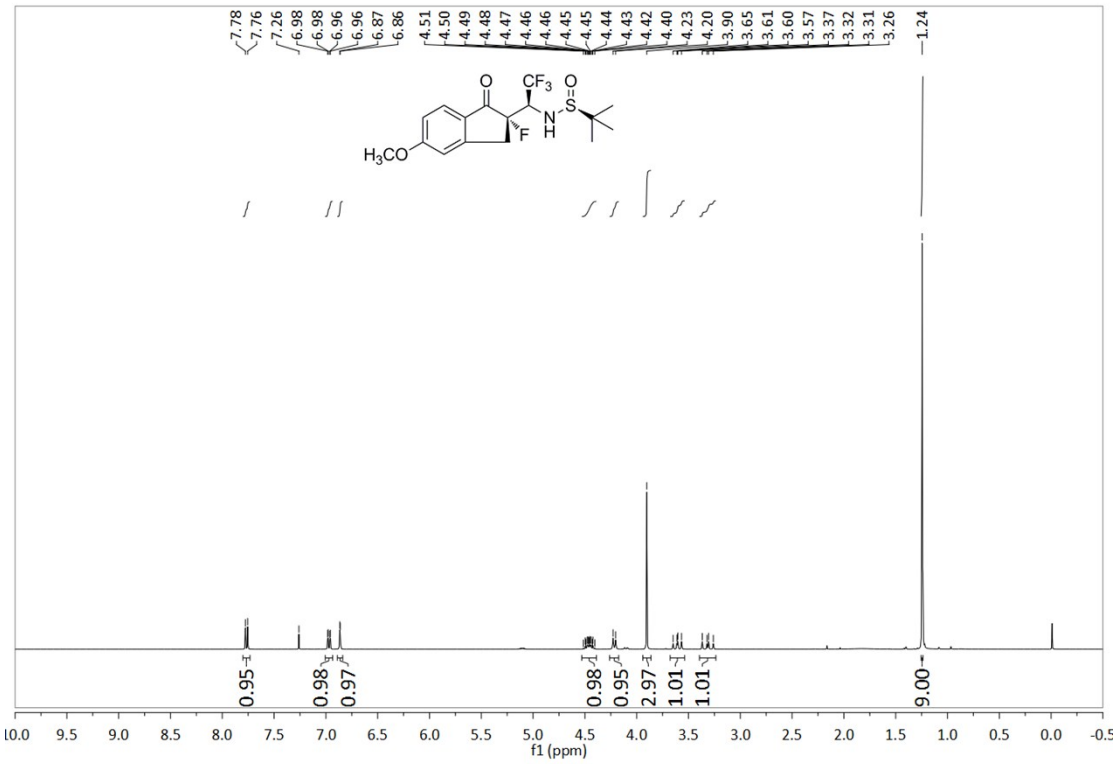
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ba**



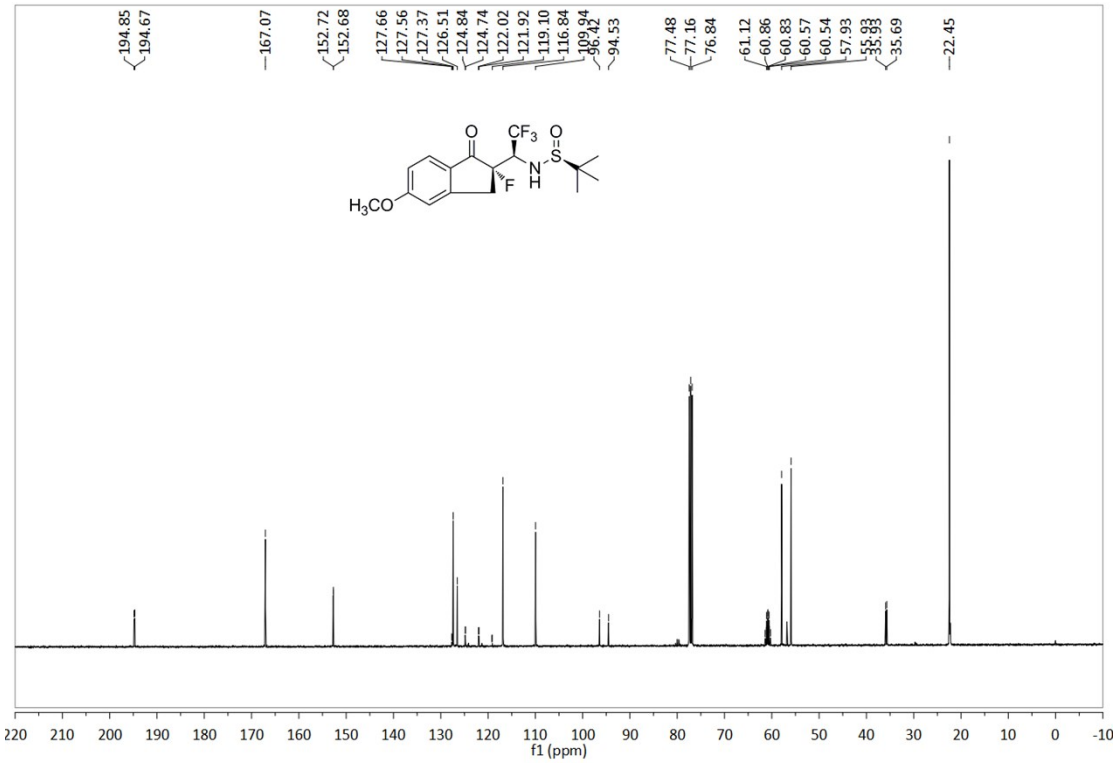
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



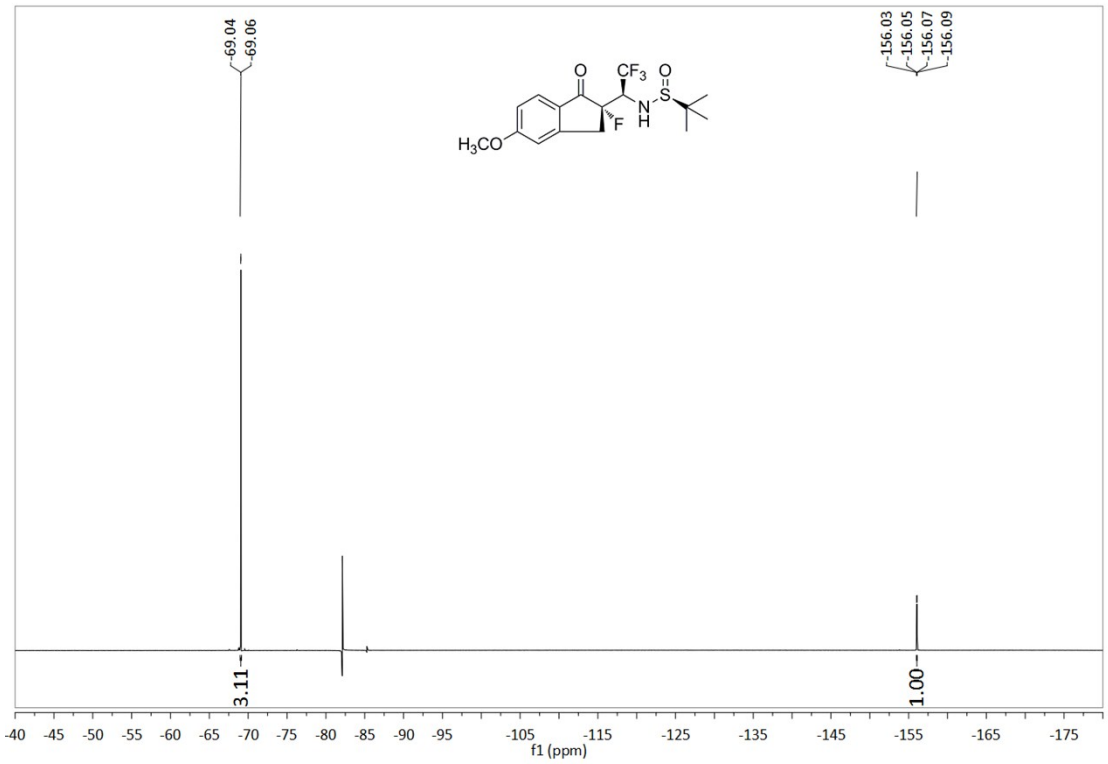
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ca**



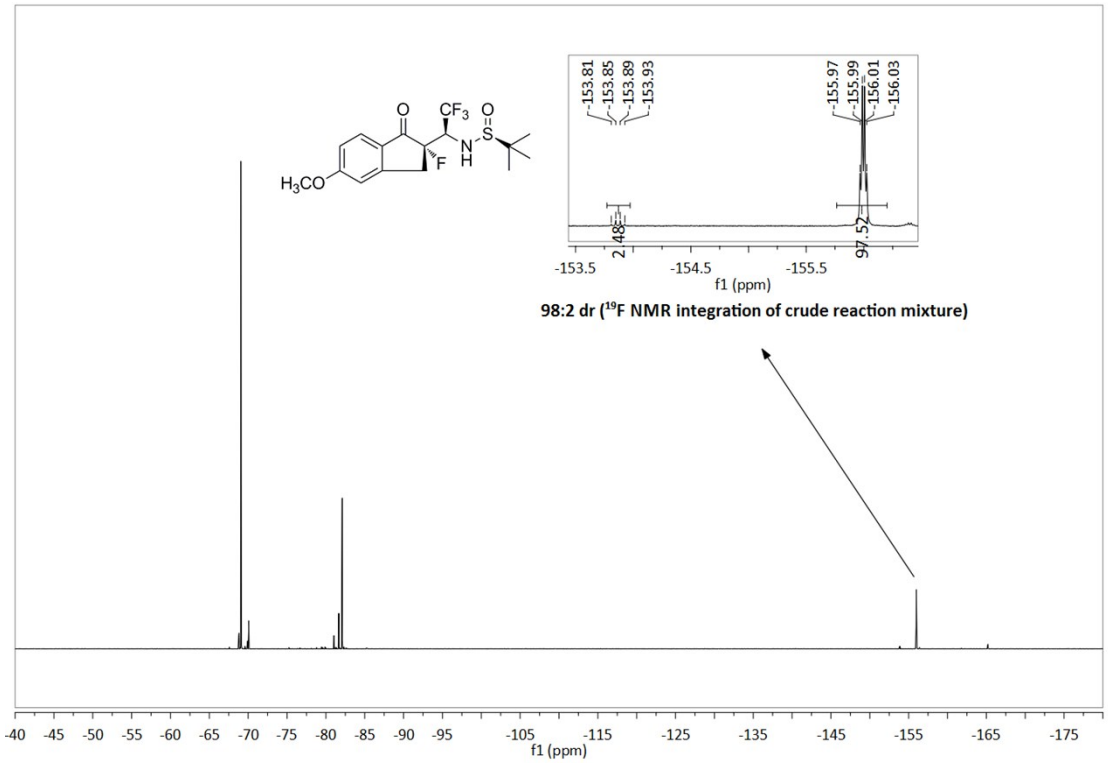
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ca**



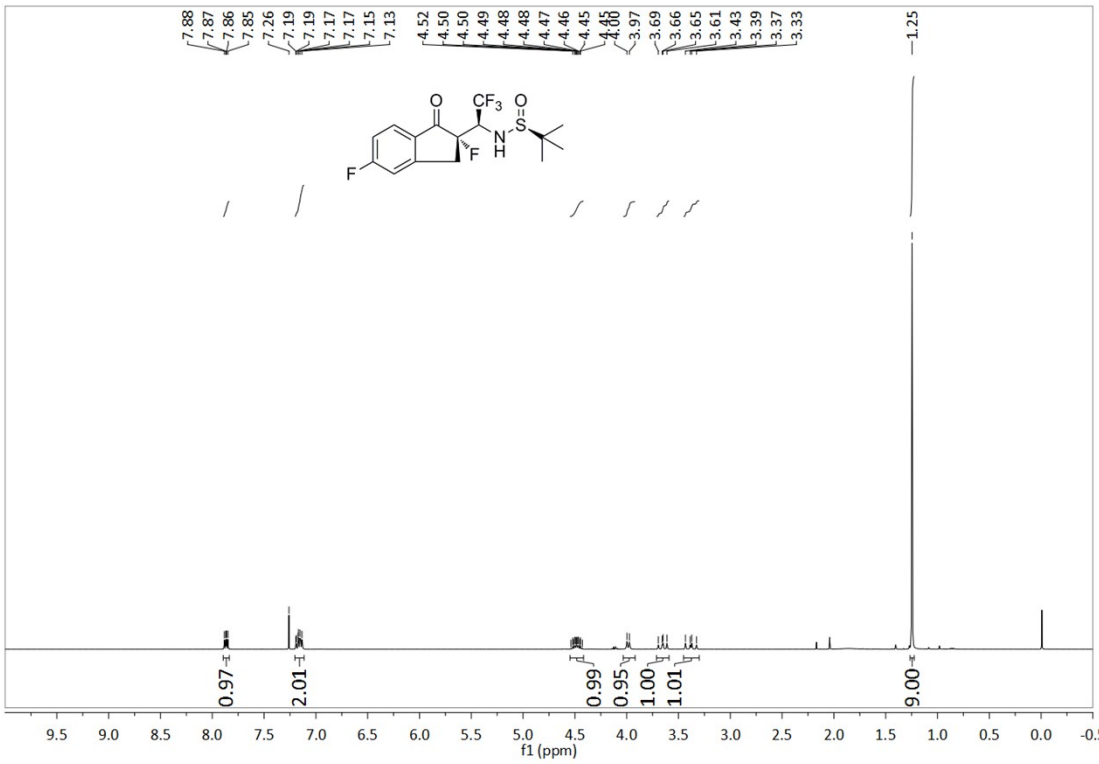
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ca**



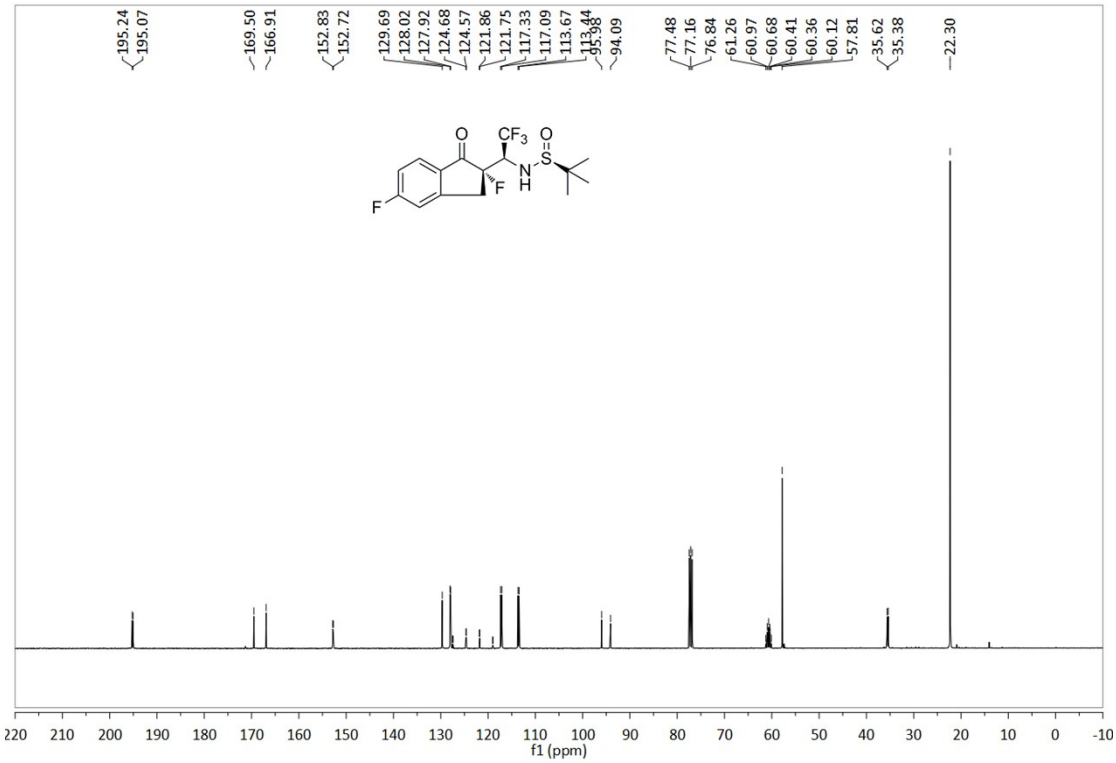
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



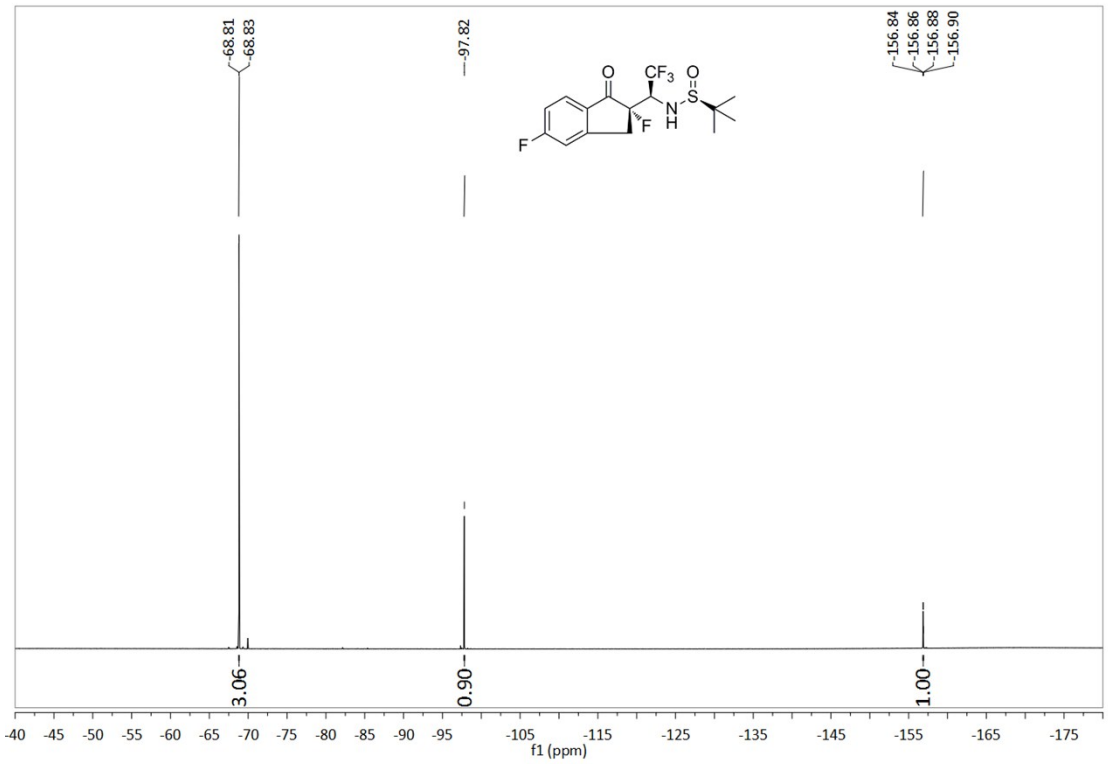
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3da**



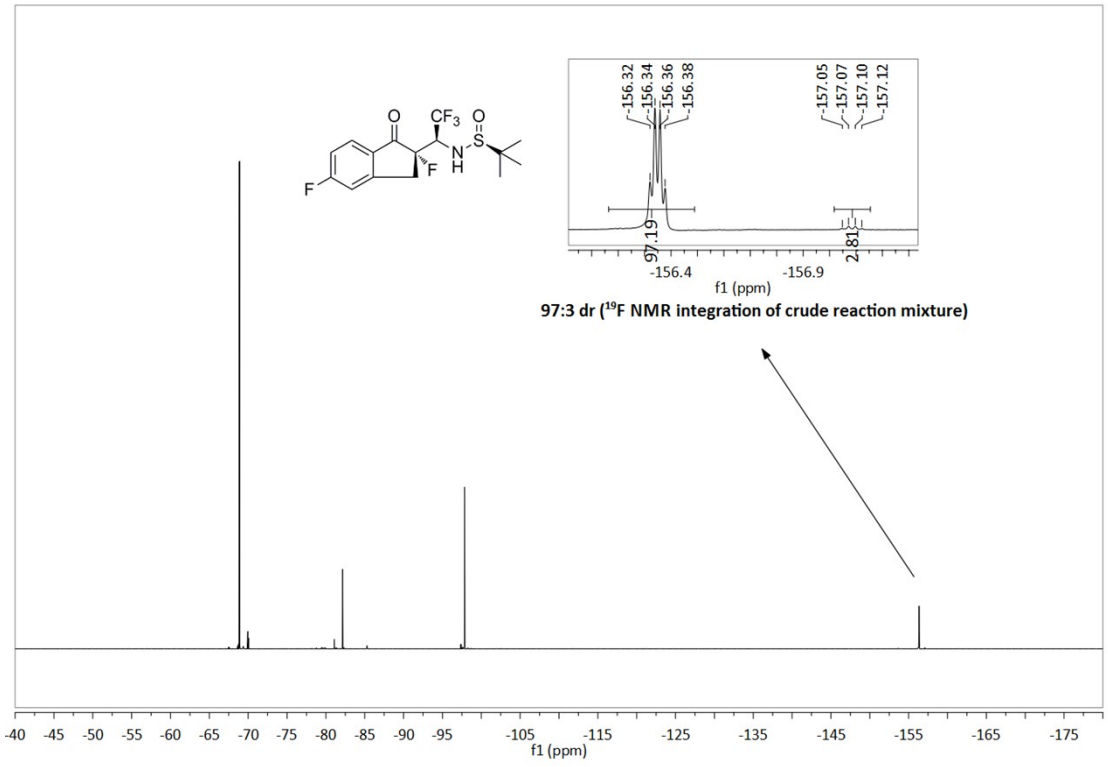
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3da**



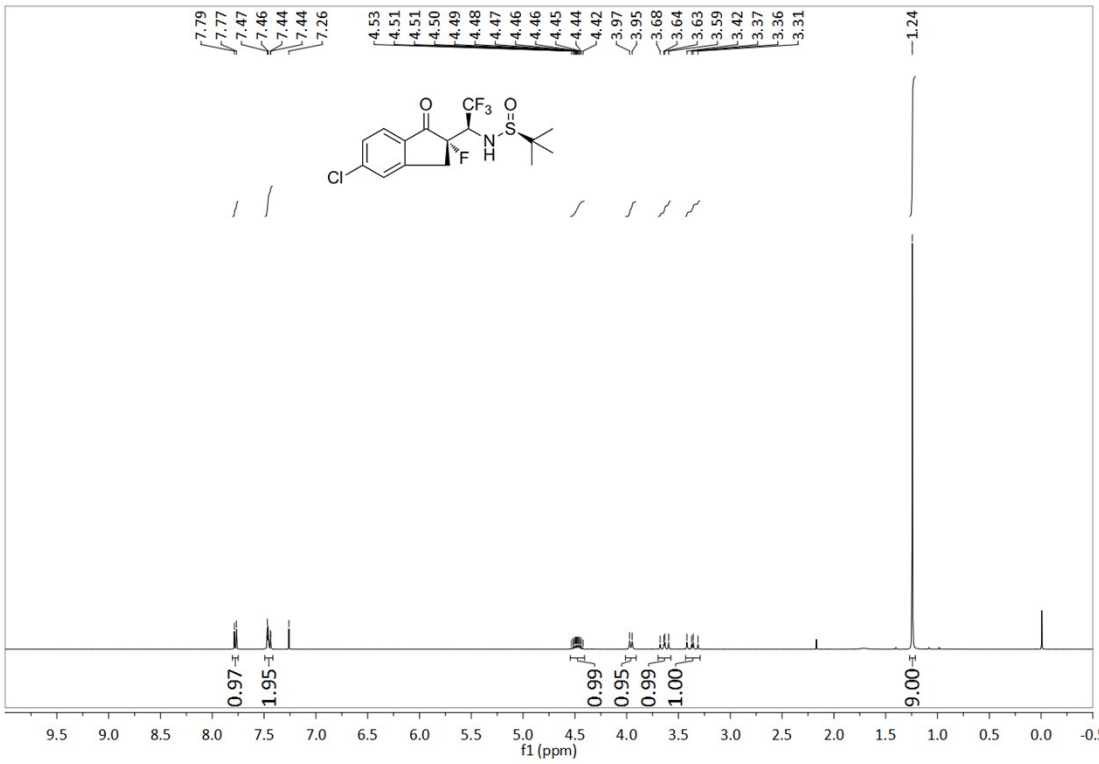
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3da**



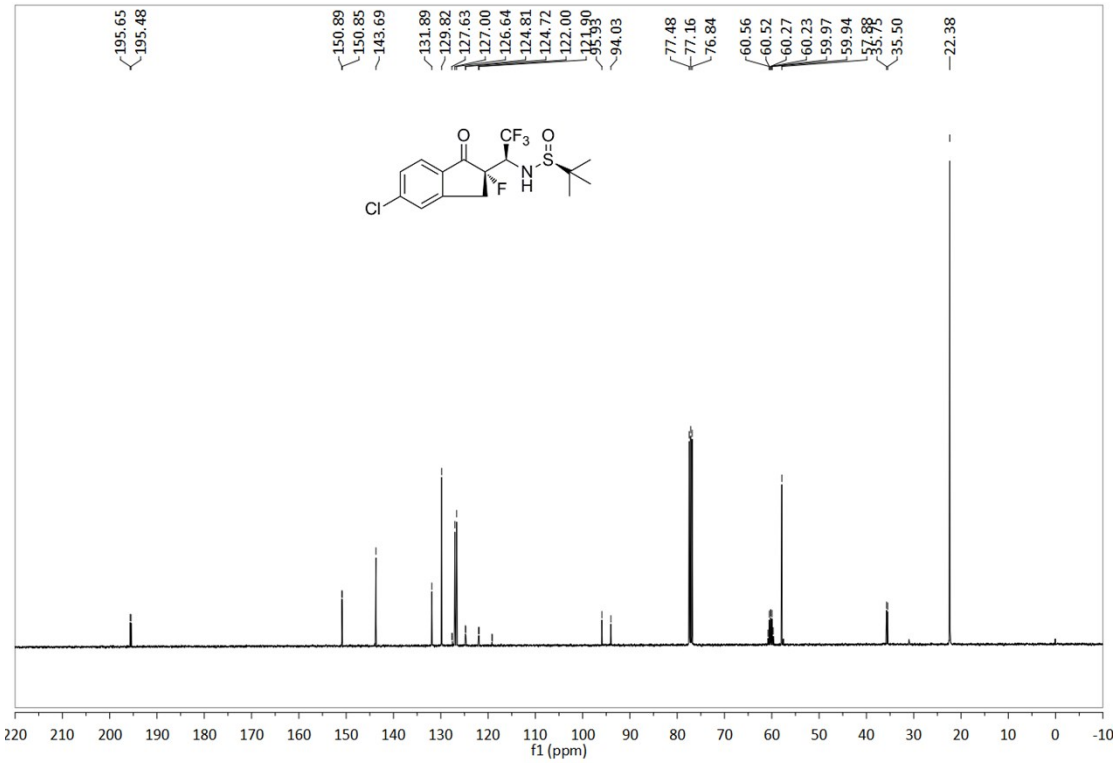
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



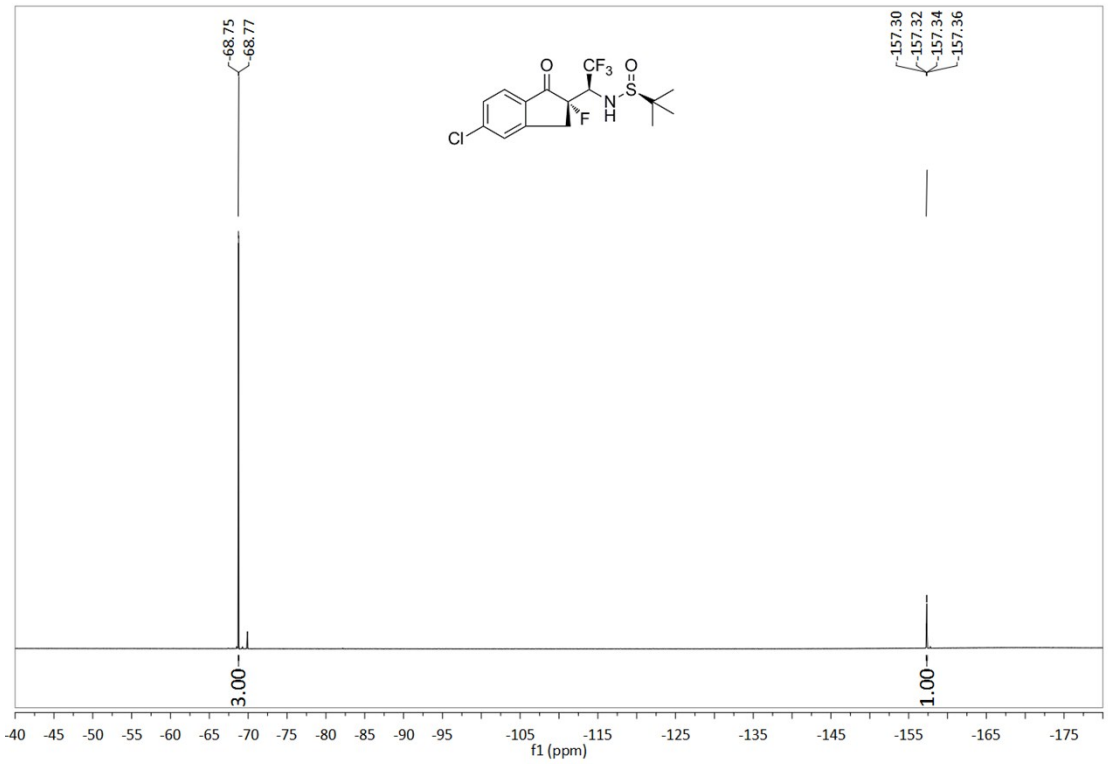
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ea**



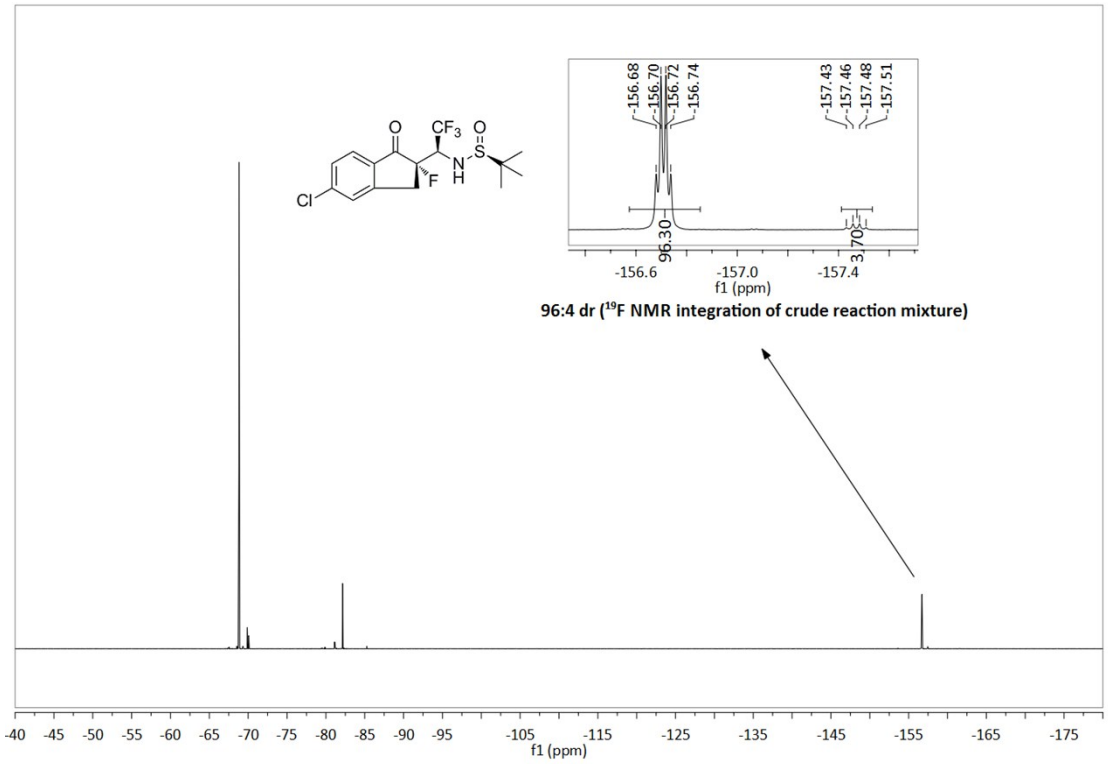
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ea**



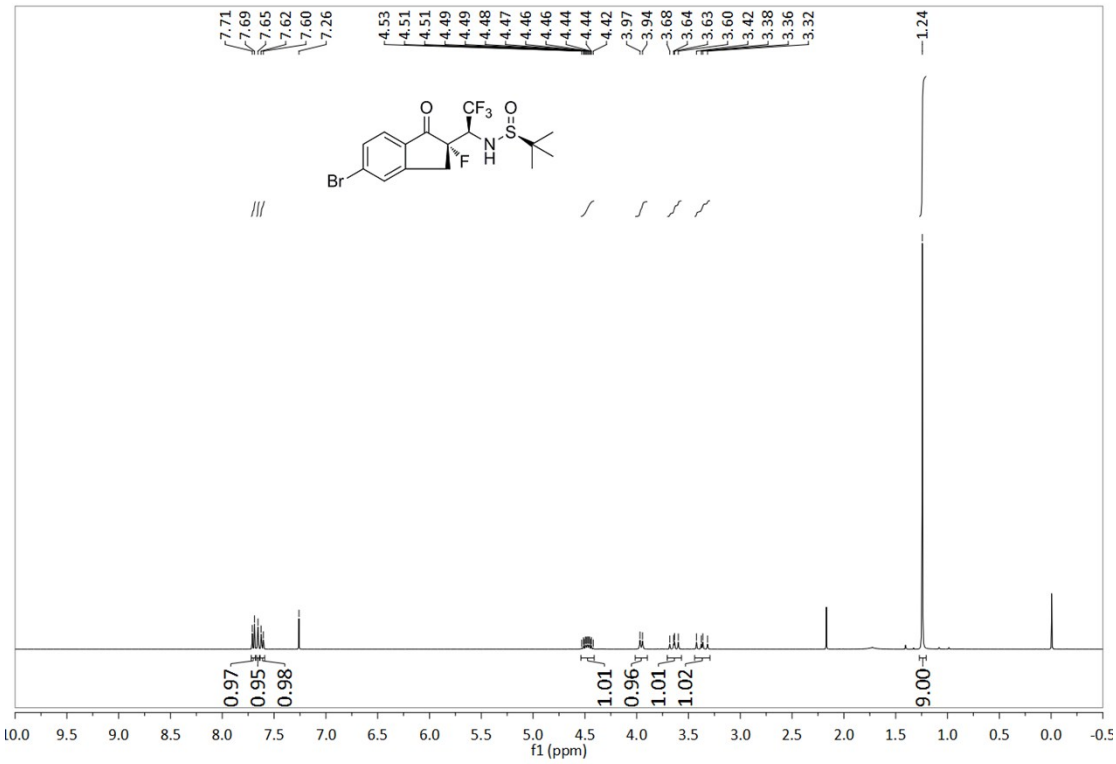
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ea**



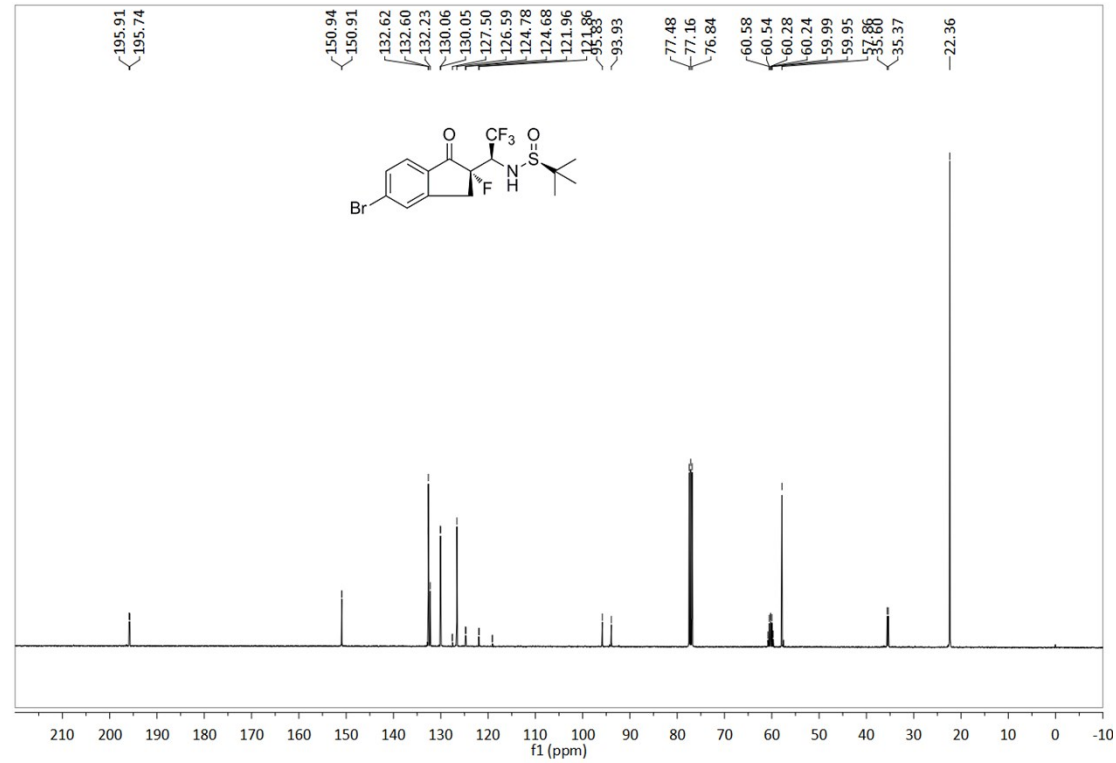
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



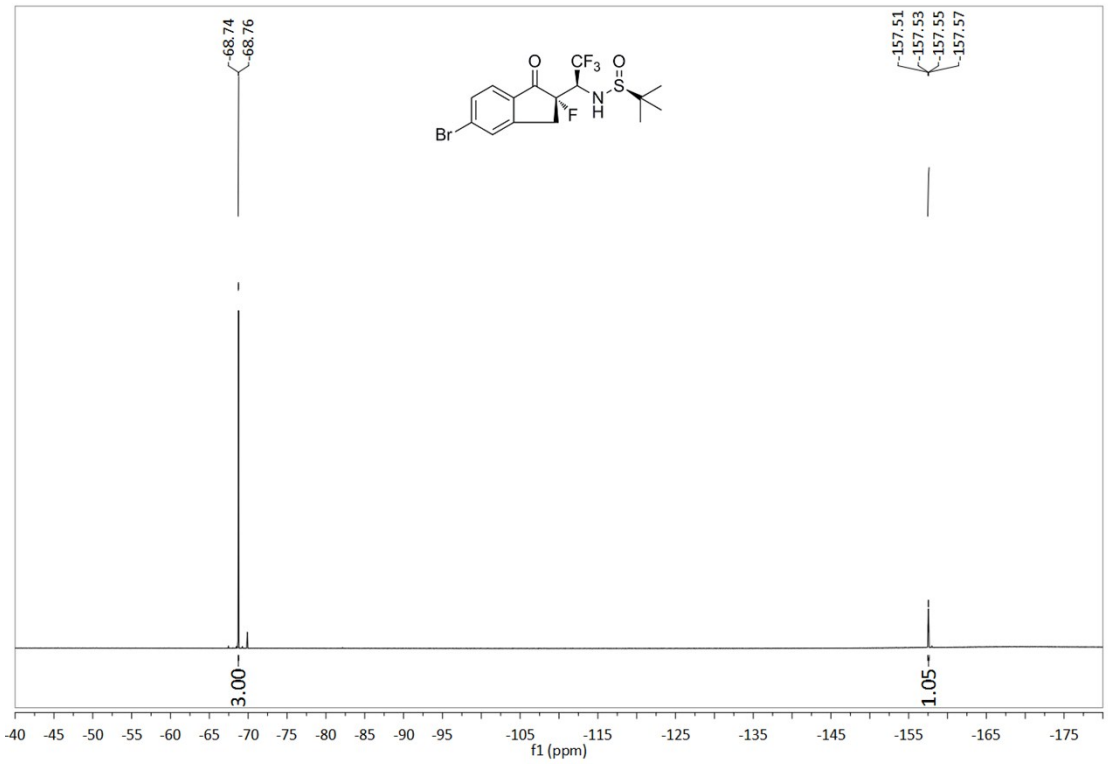
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3fa**



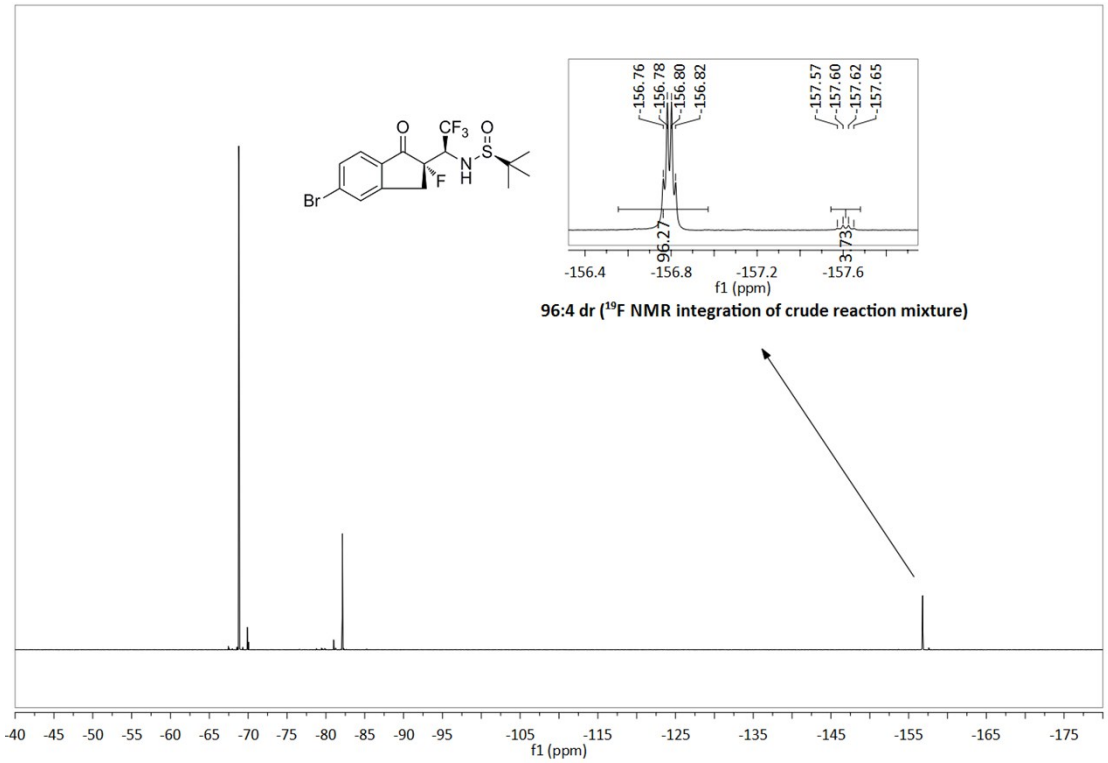
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3fa**



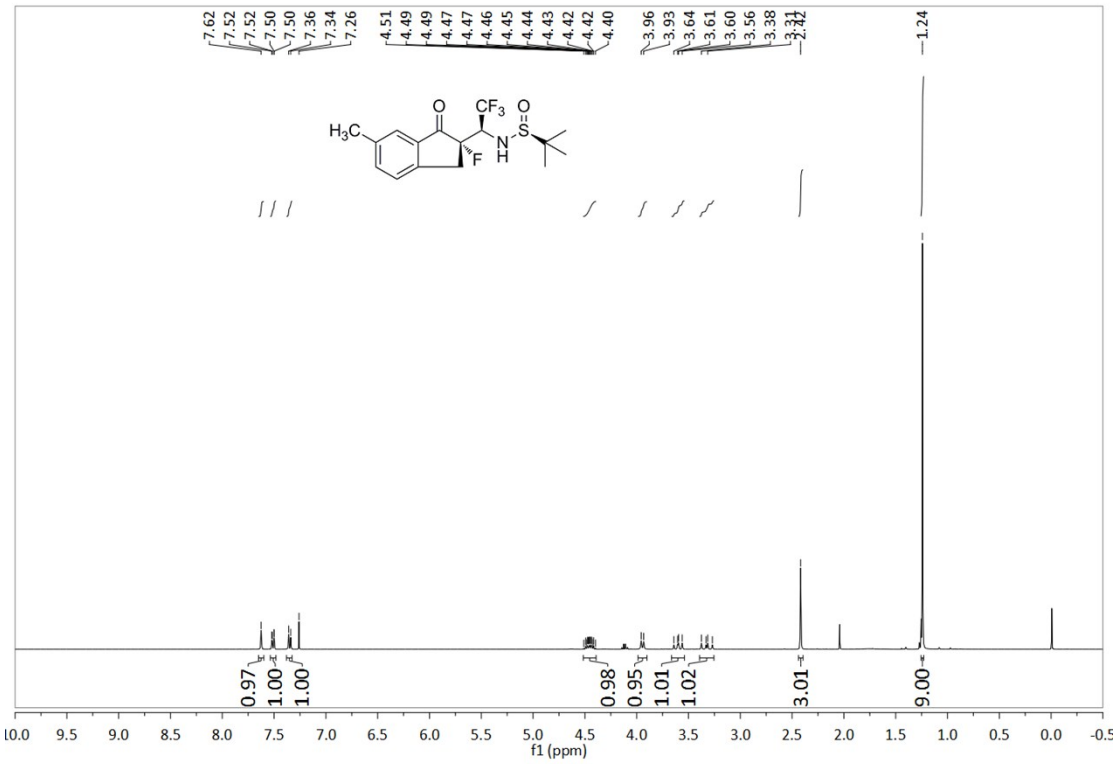
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3fa**



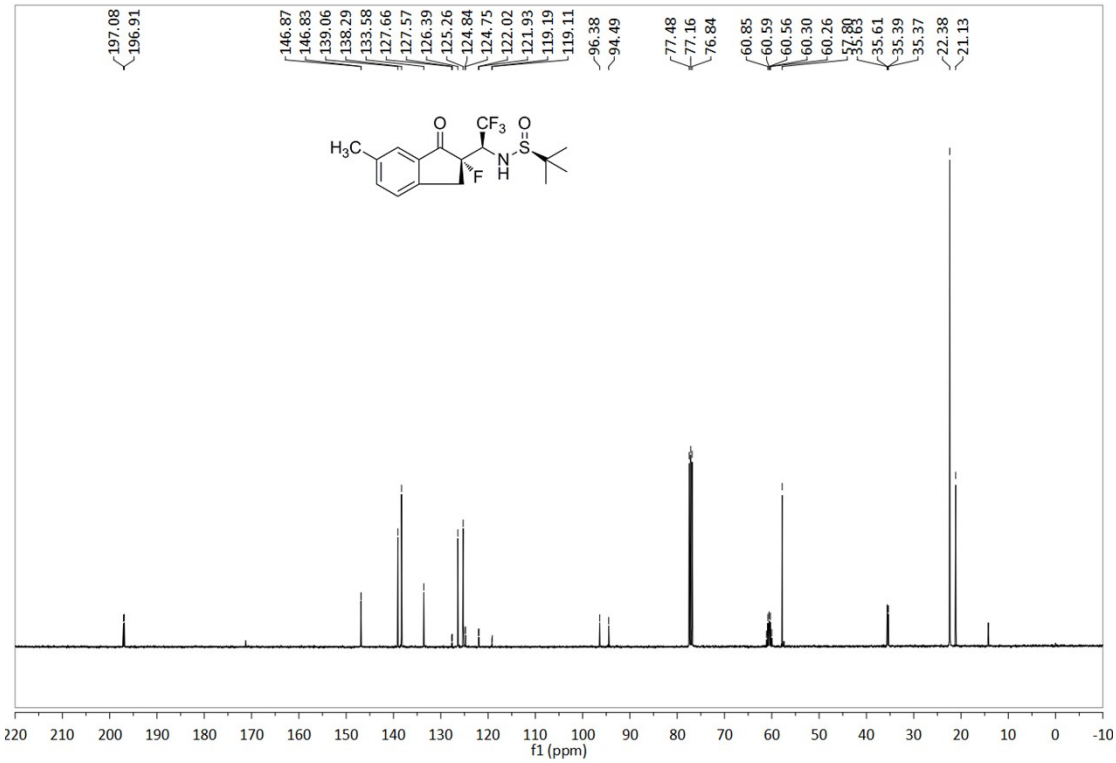
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



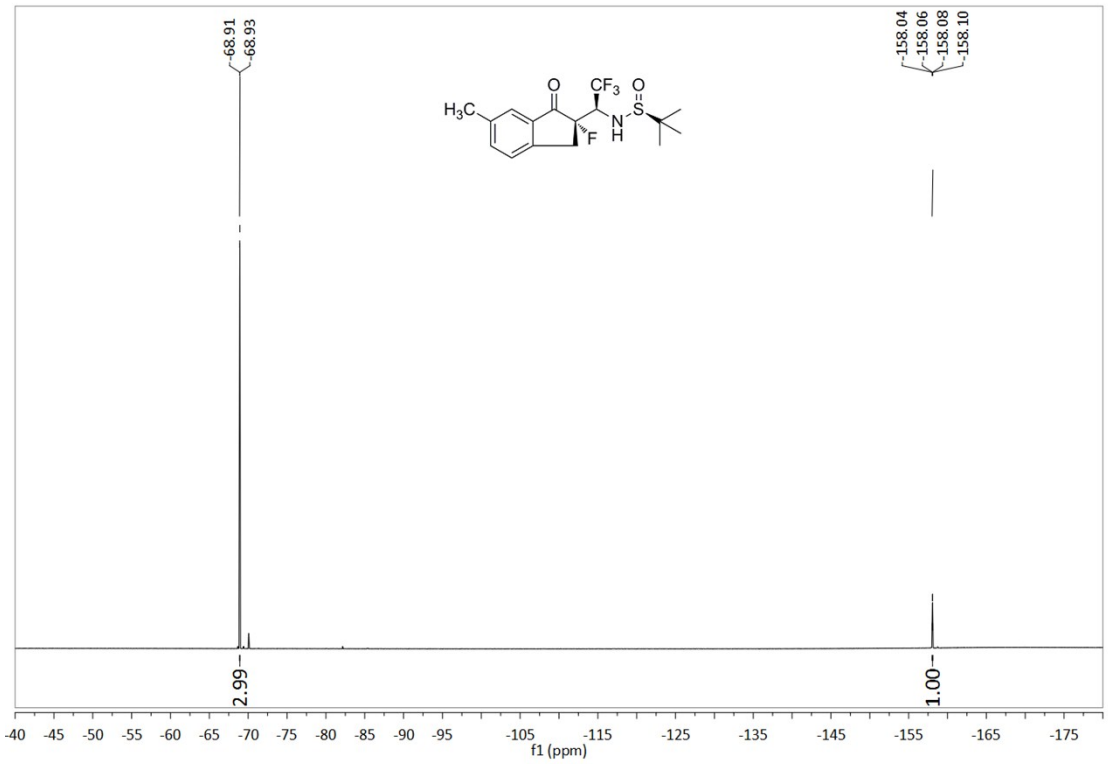
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ga**



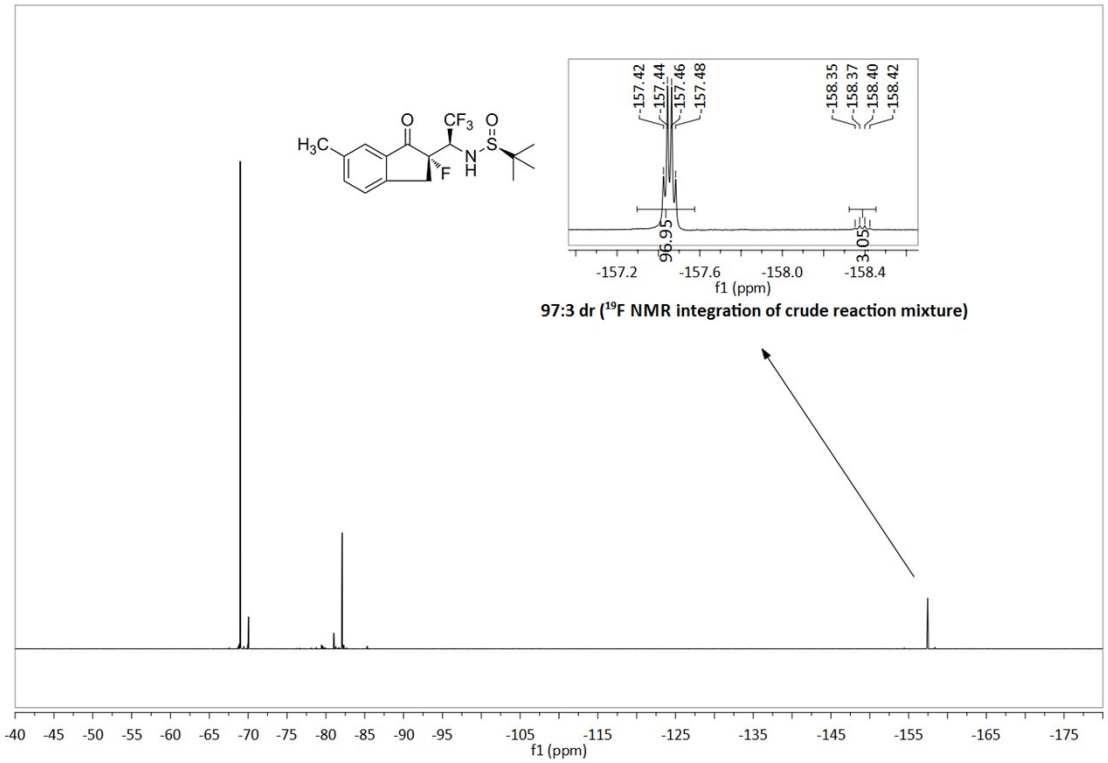
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ga**



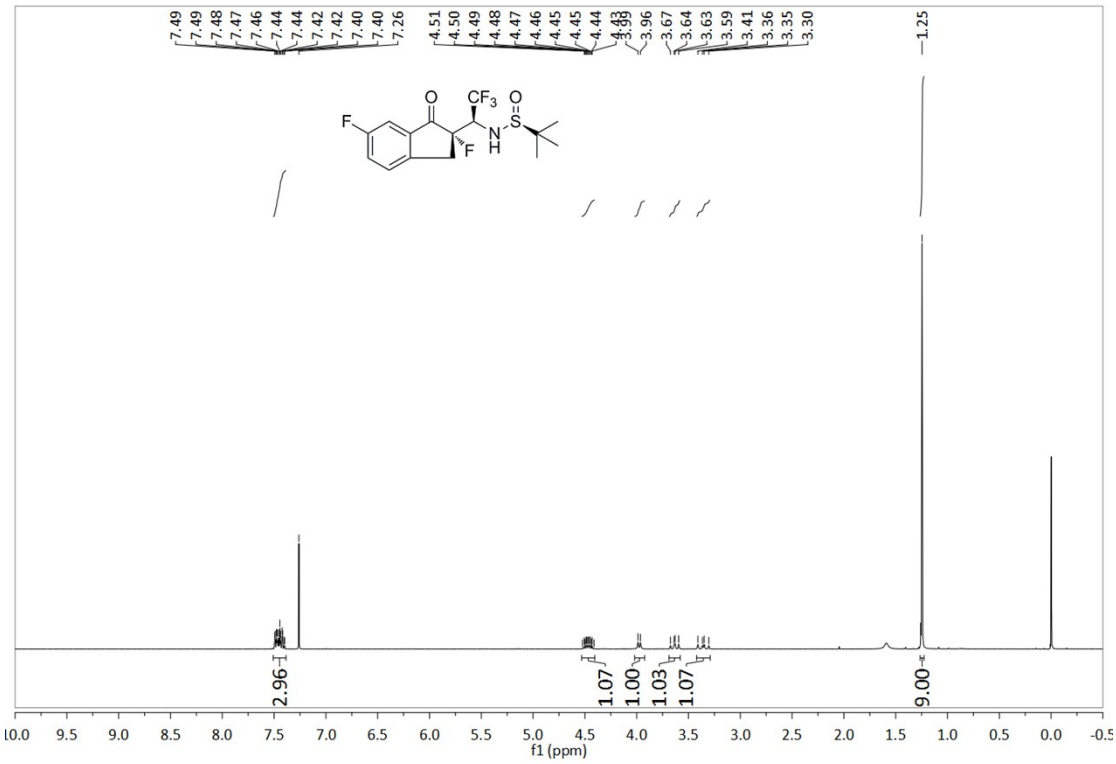
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ga**



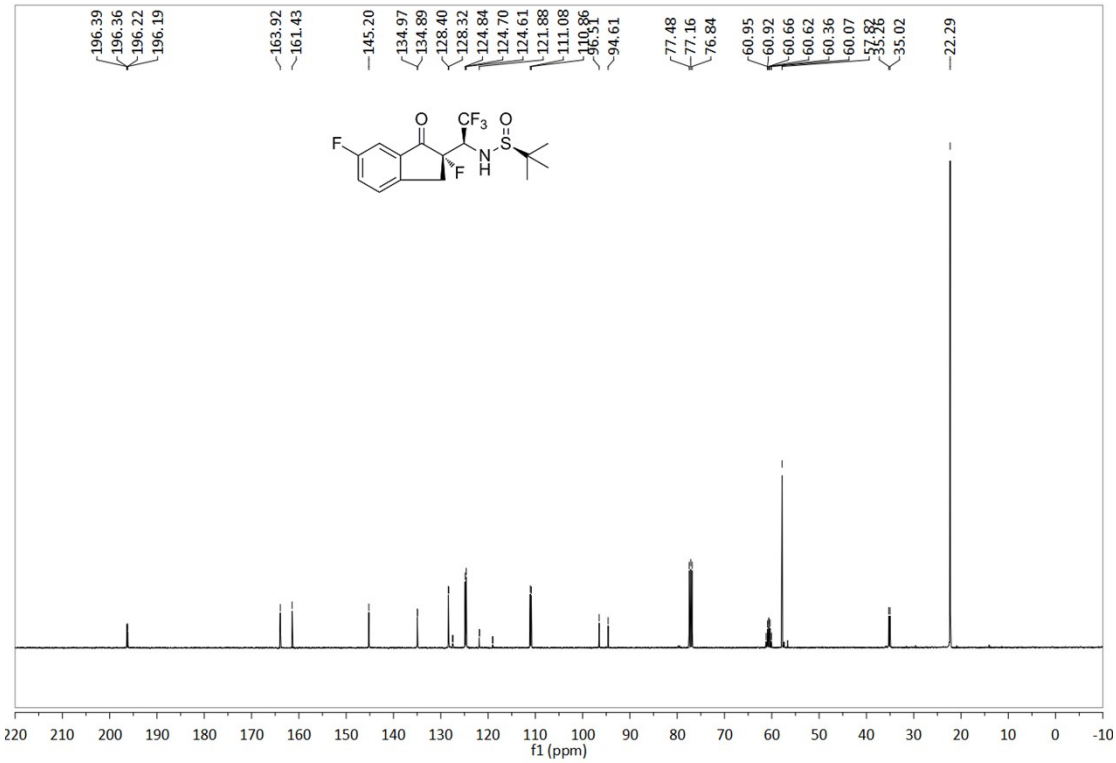
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



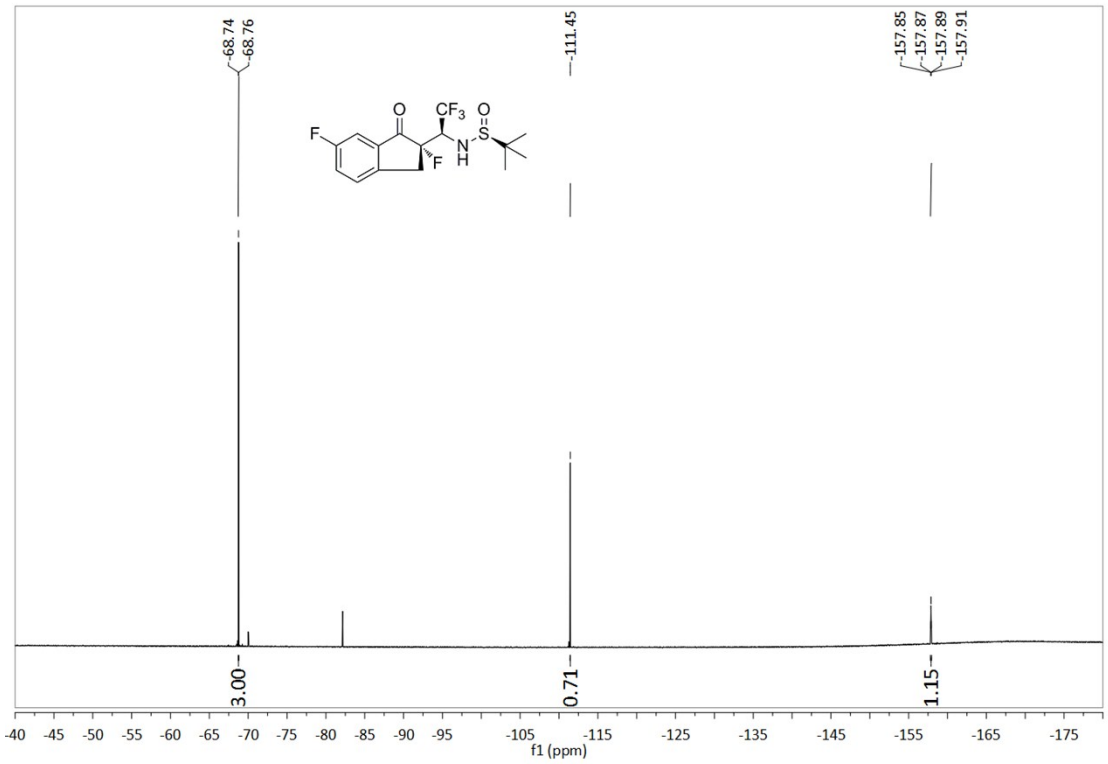
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ha**



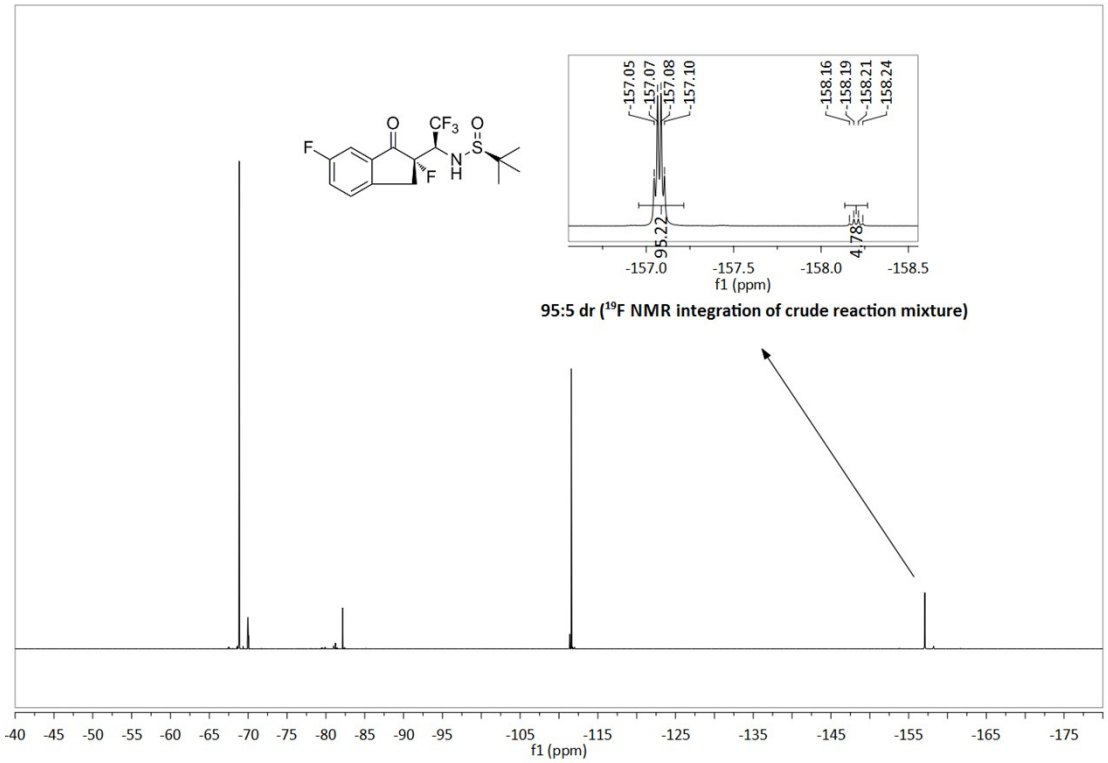
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ha**



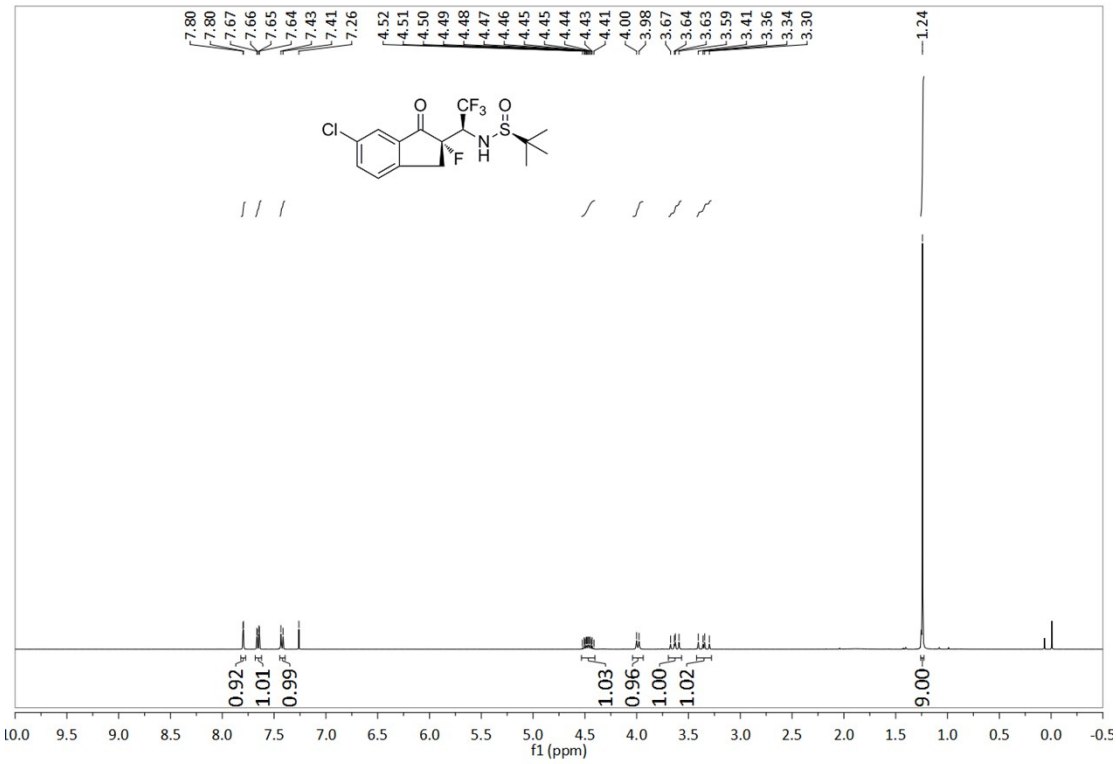
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ha**



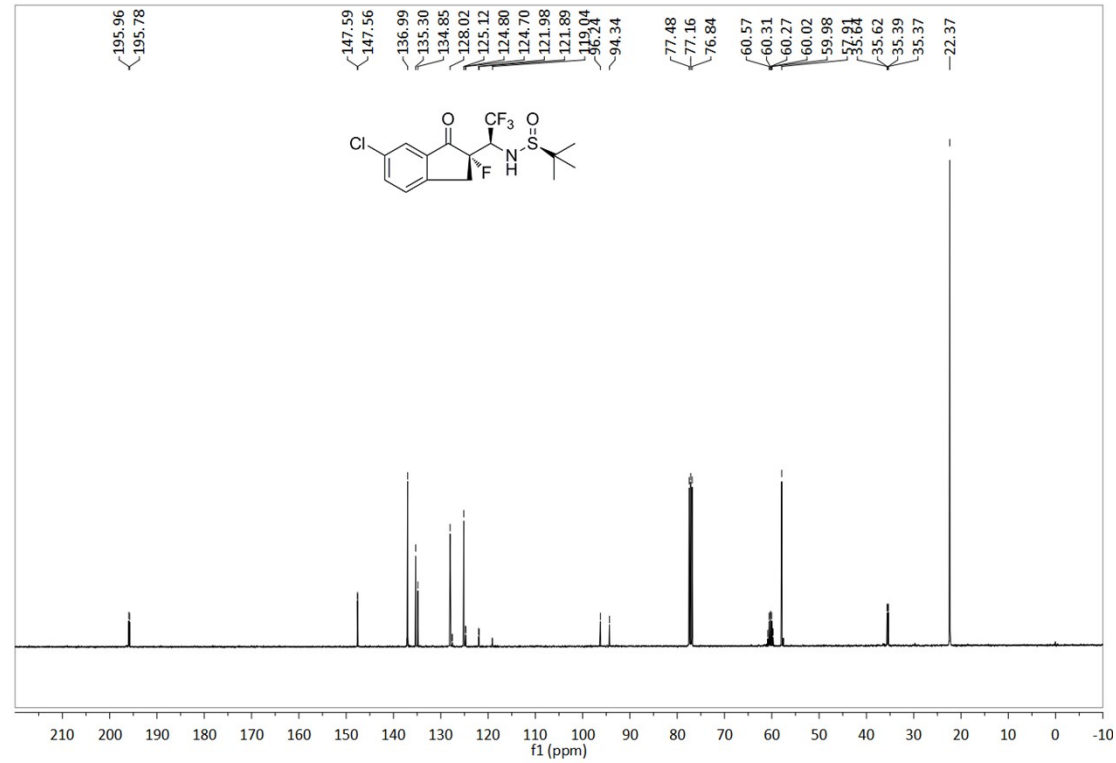
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



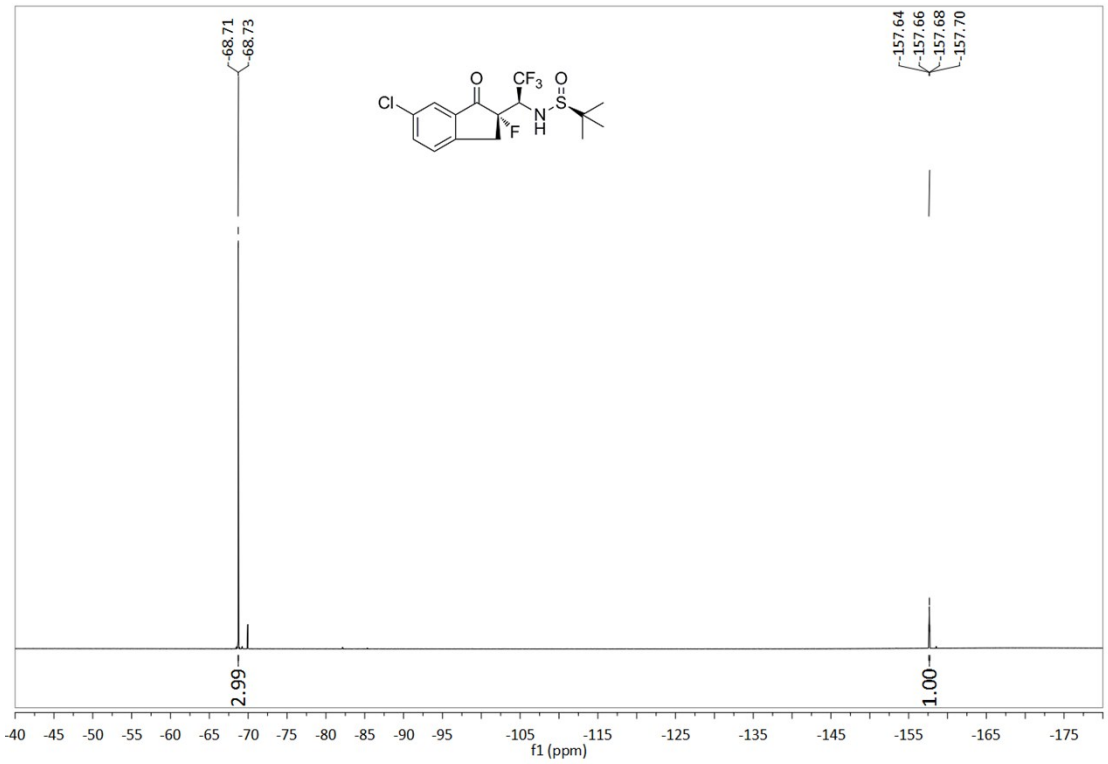
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ia**



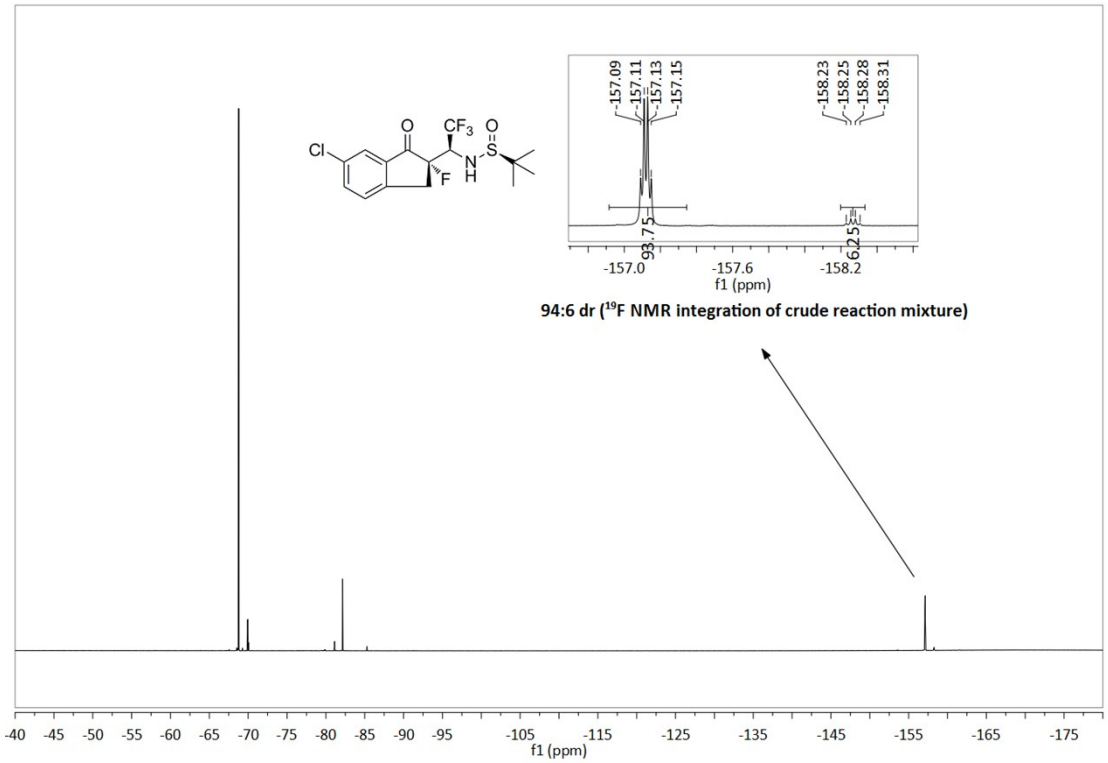
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ia**



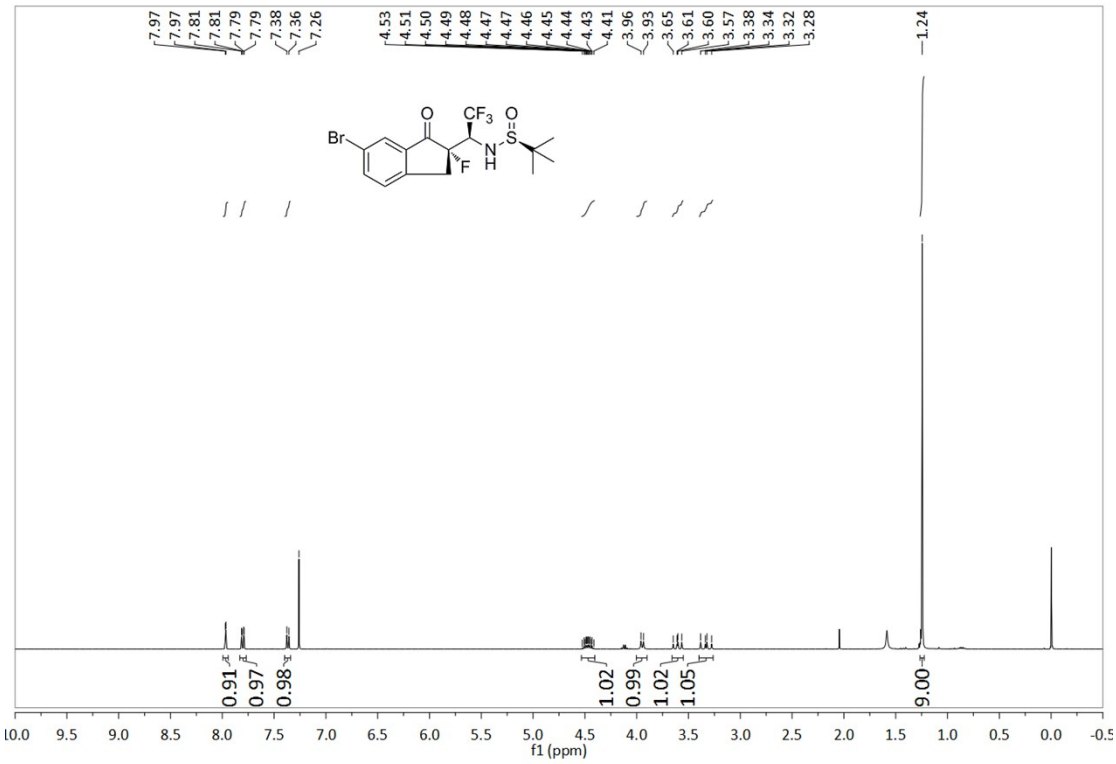
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ia**



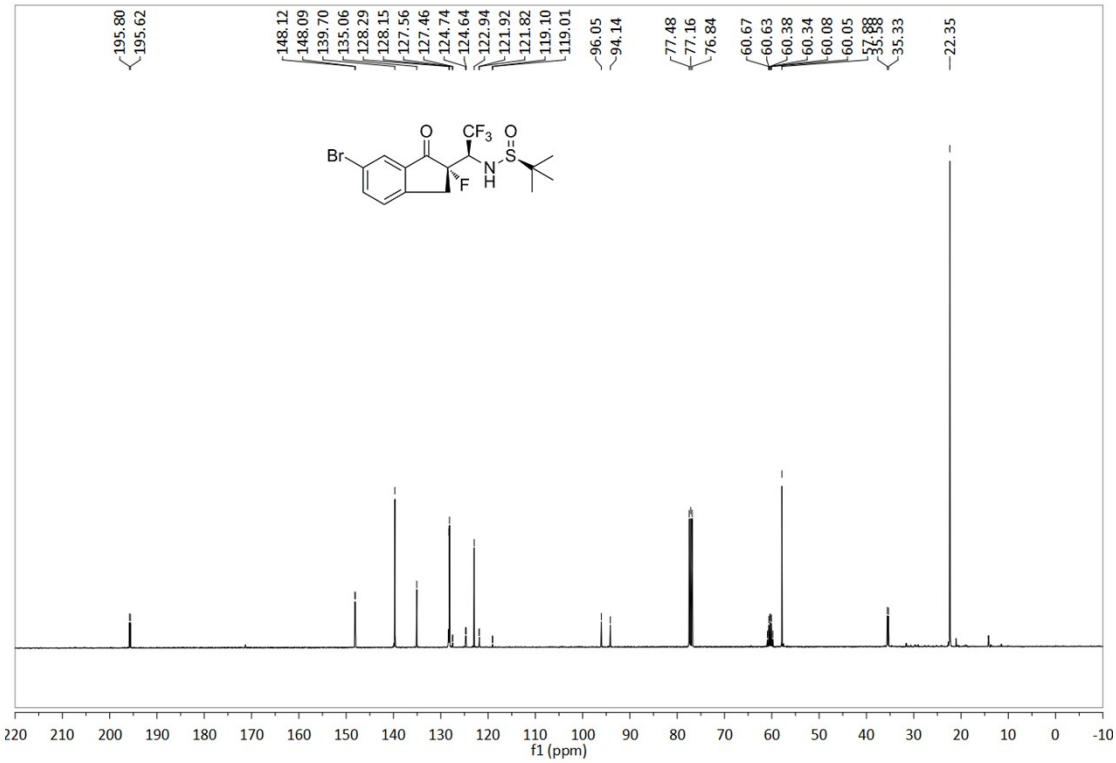
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



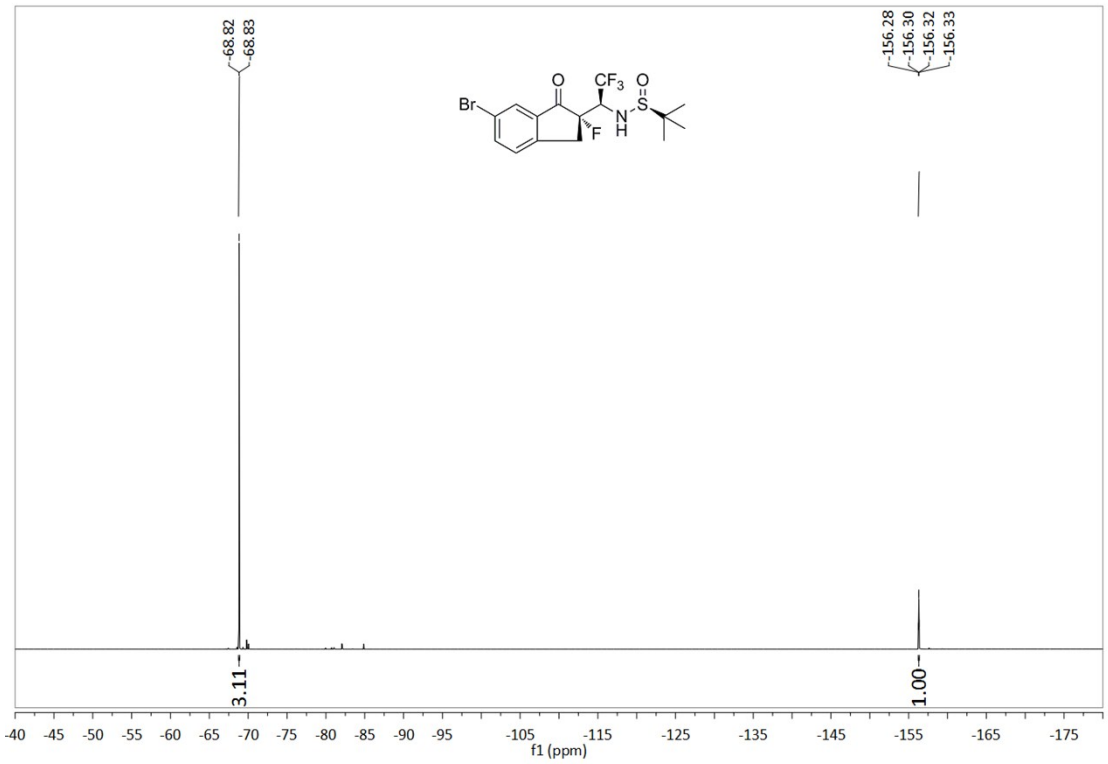
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ja**



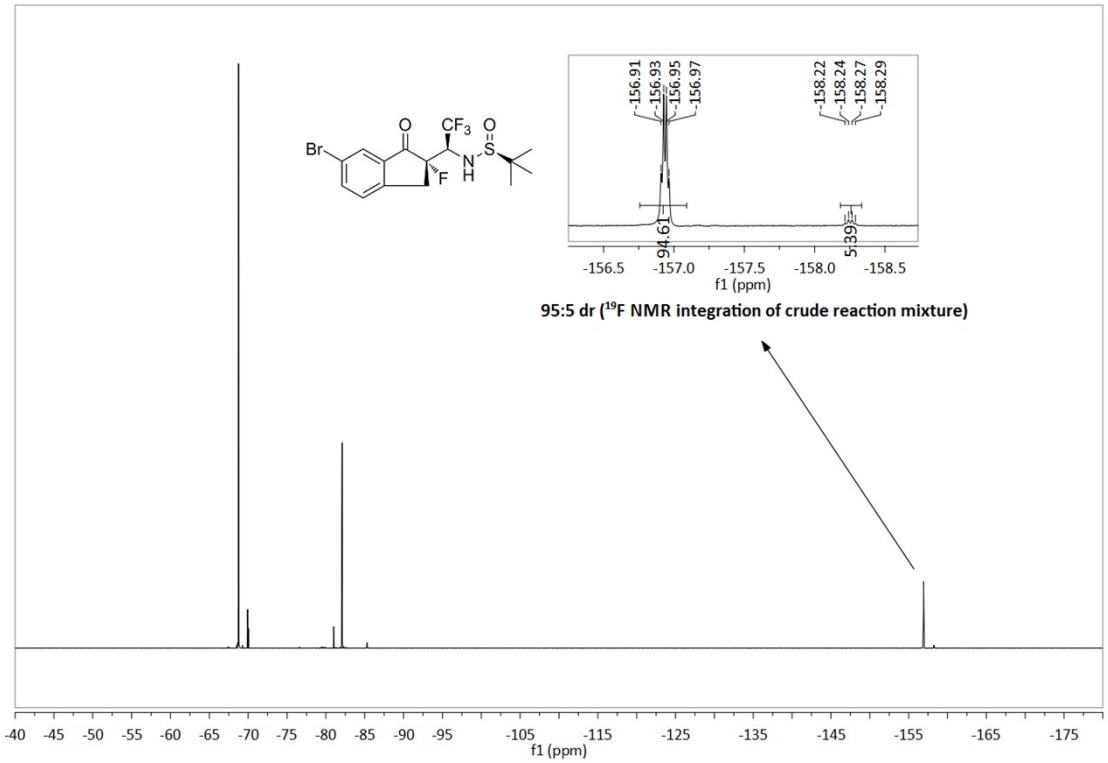
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ja**



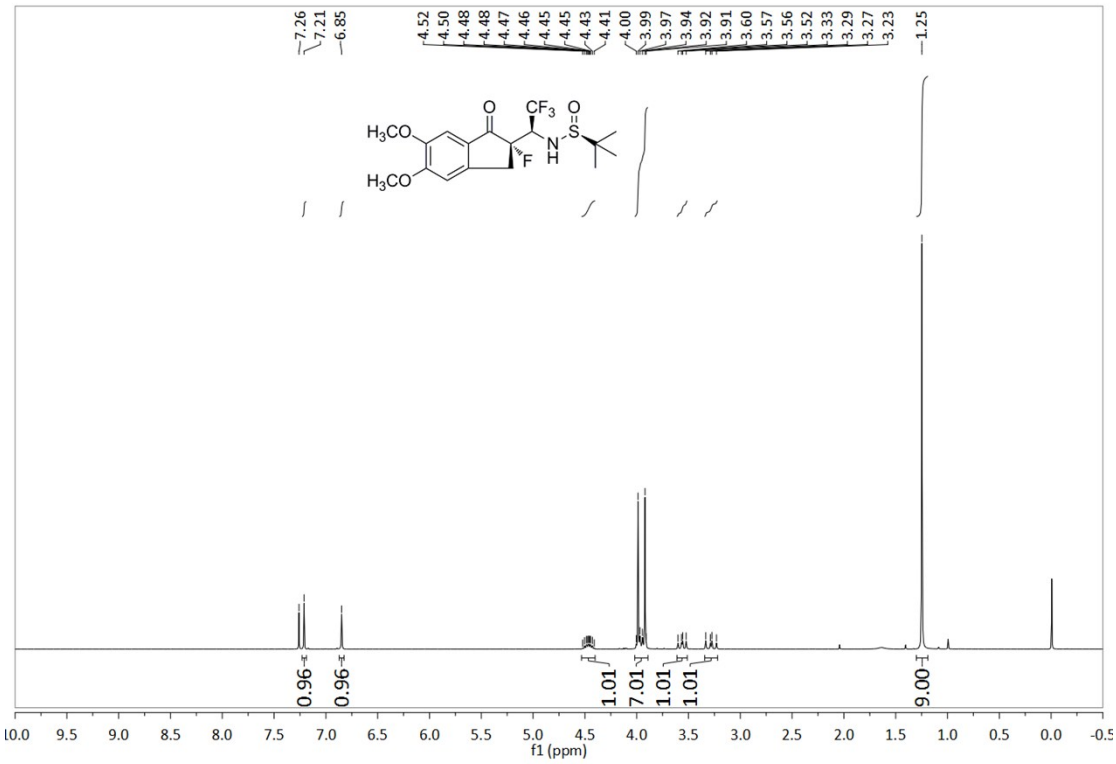
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ja**



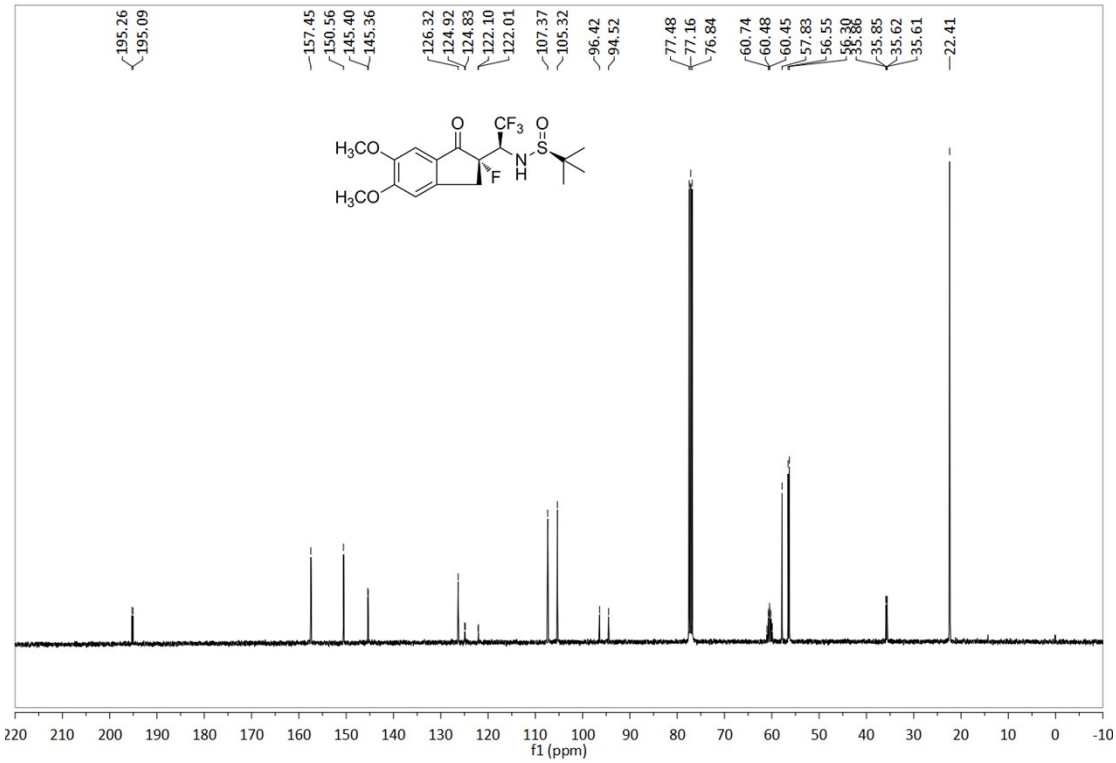
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



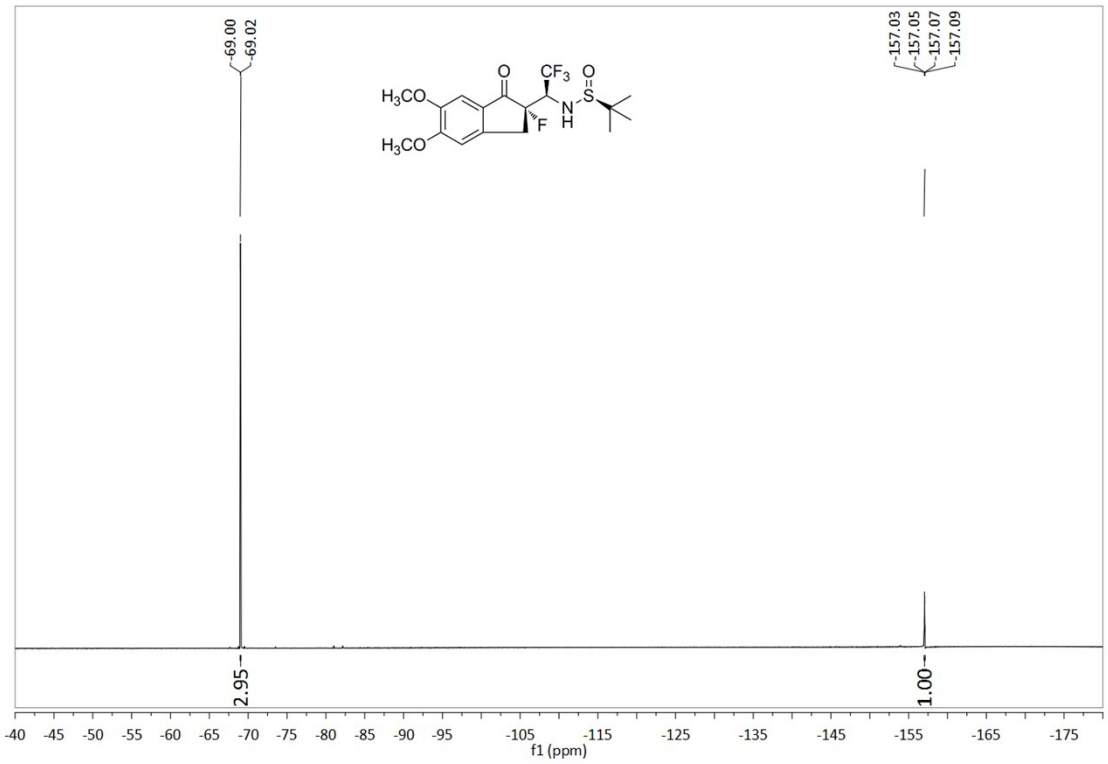
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ka**



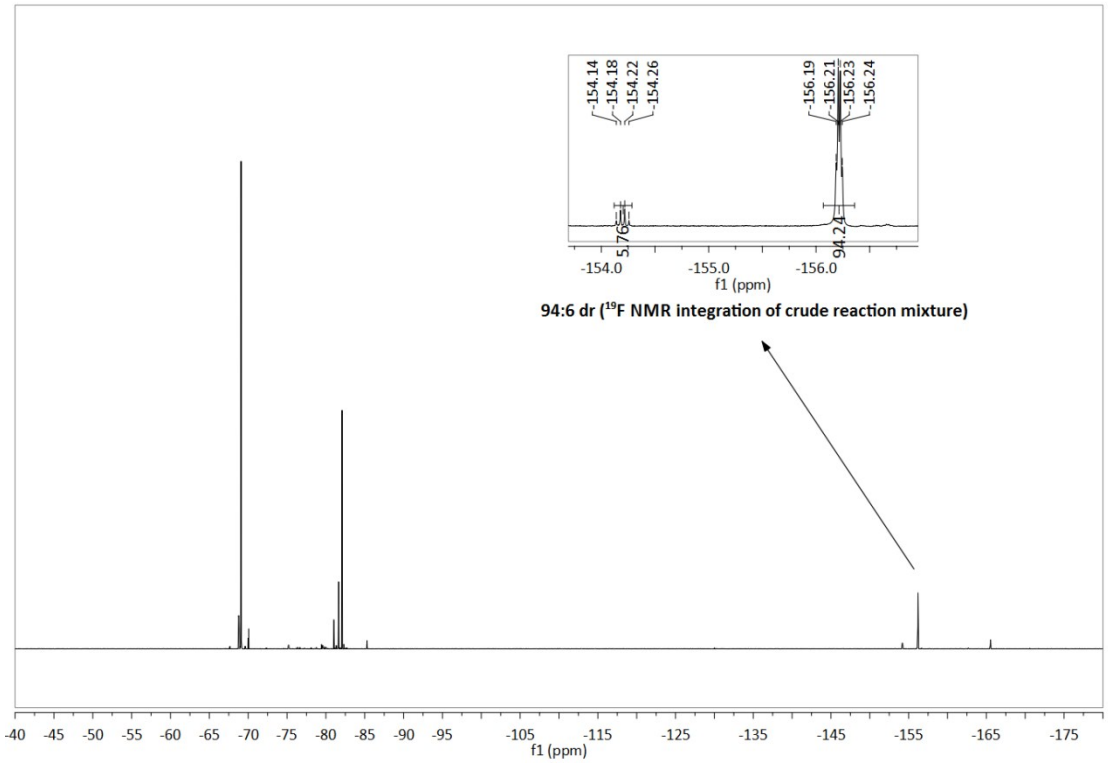
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ka**



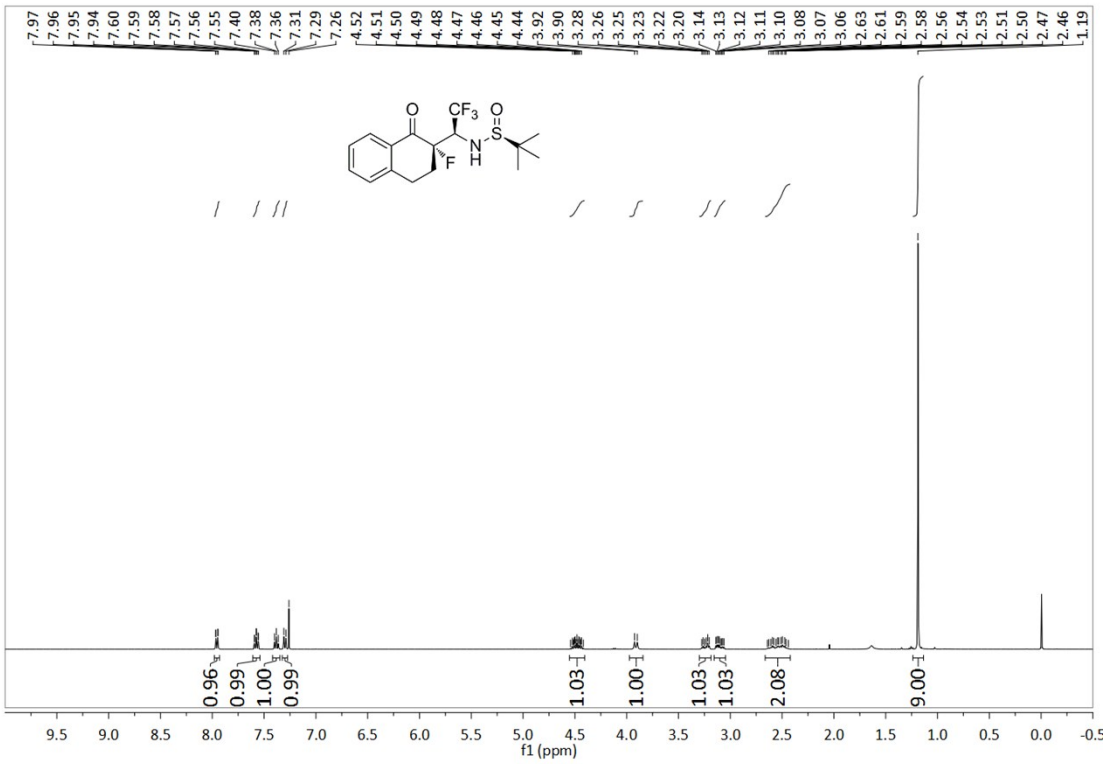
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ka**



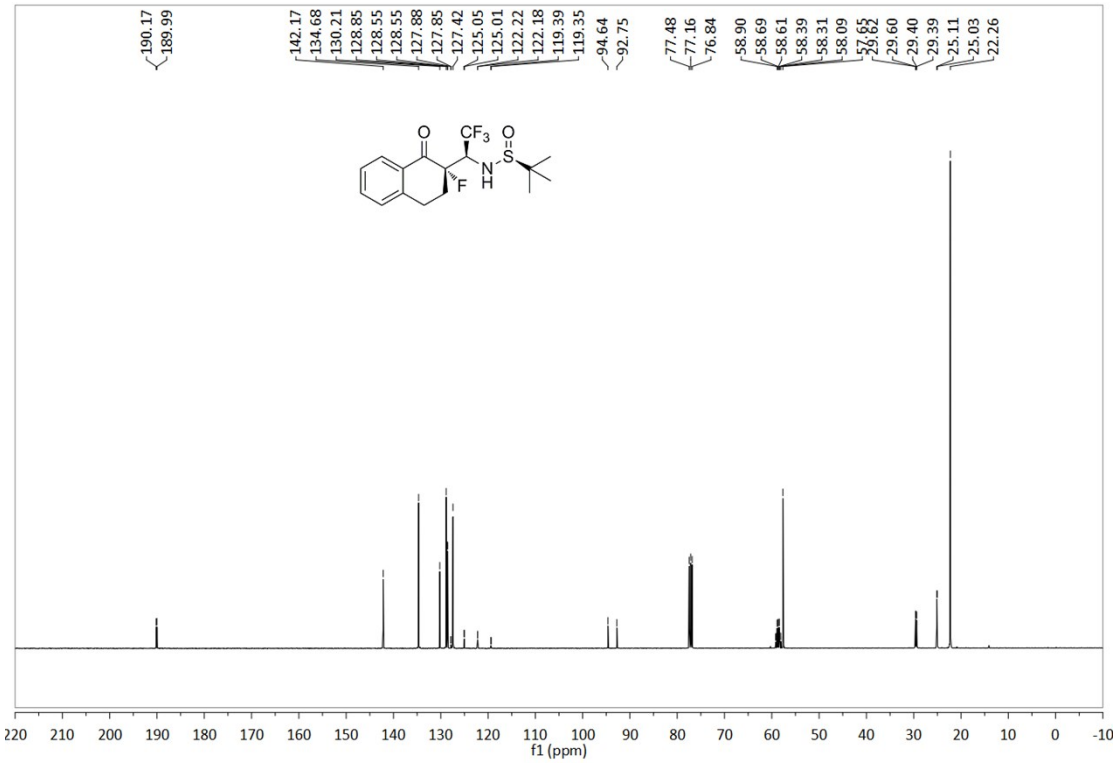
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



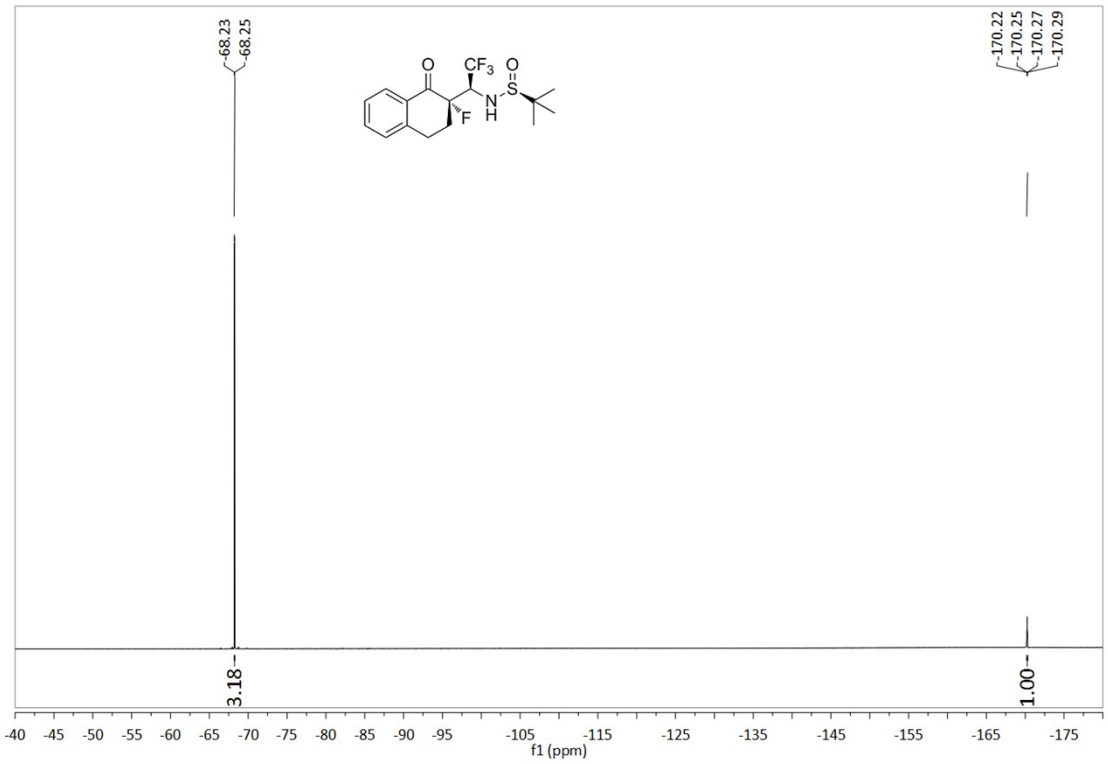
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3la**



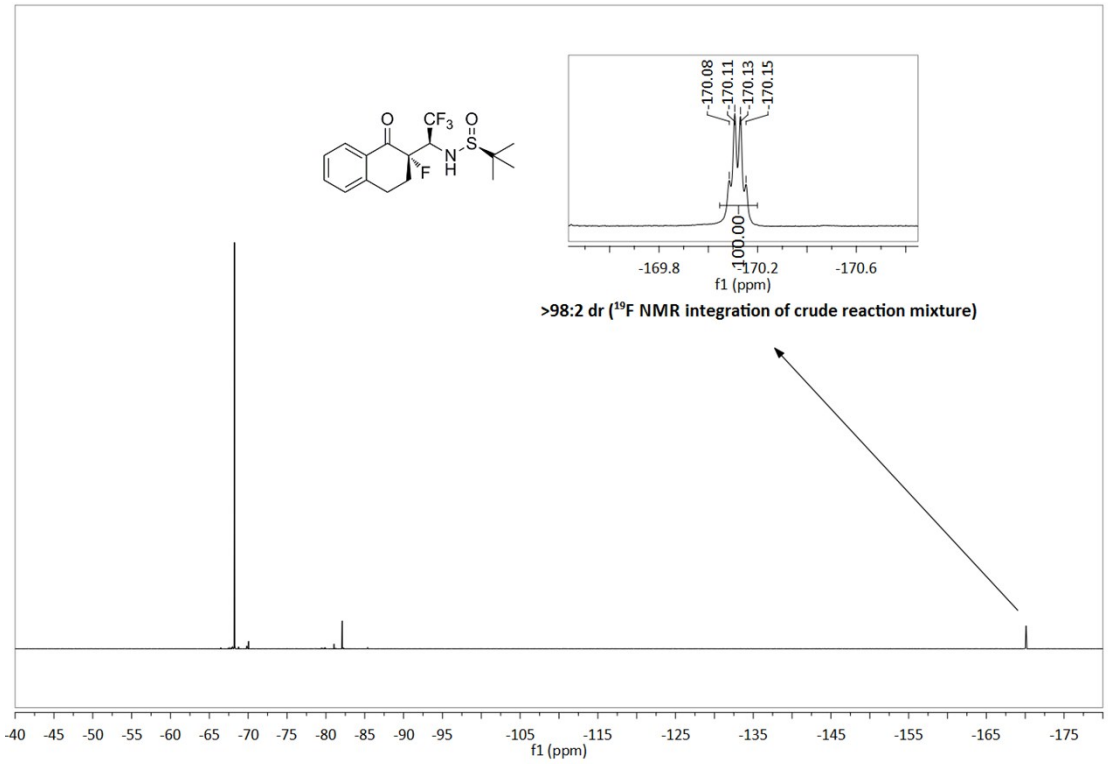
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3la**



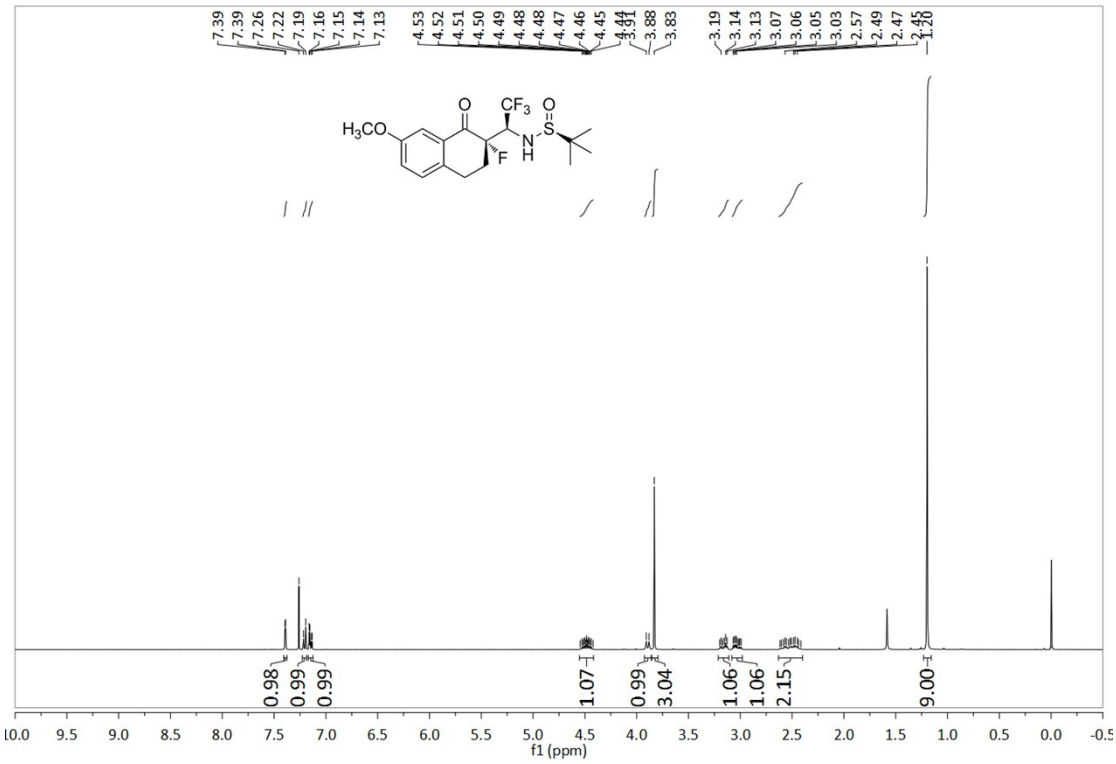
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3la**



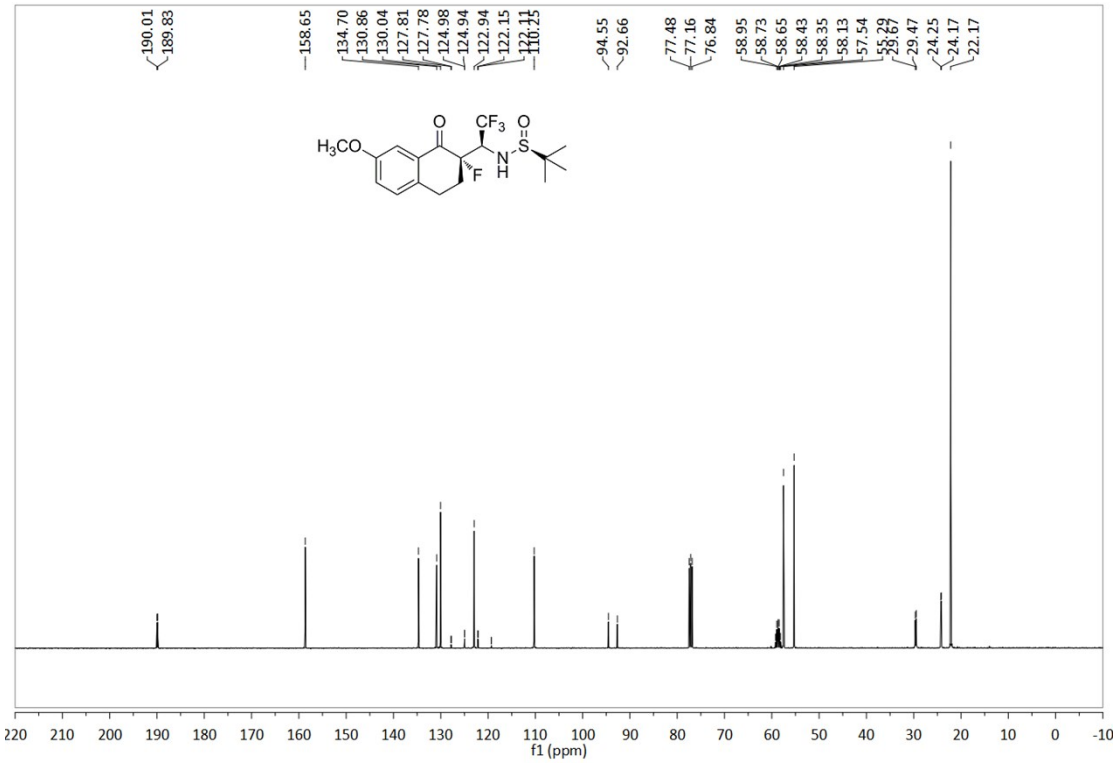
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



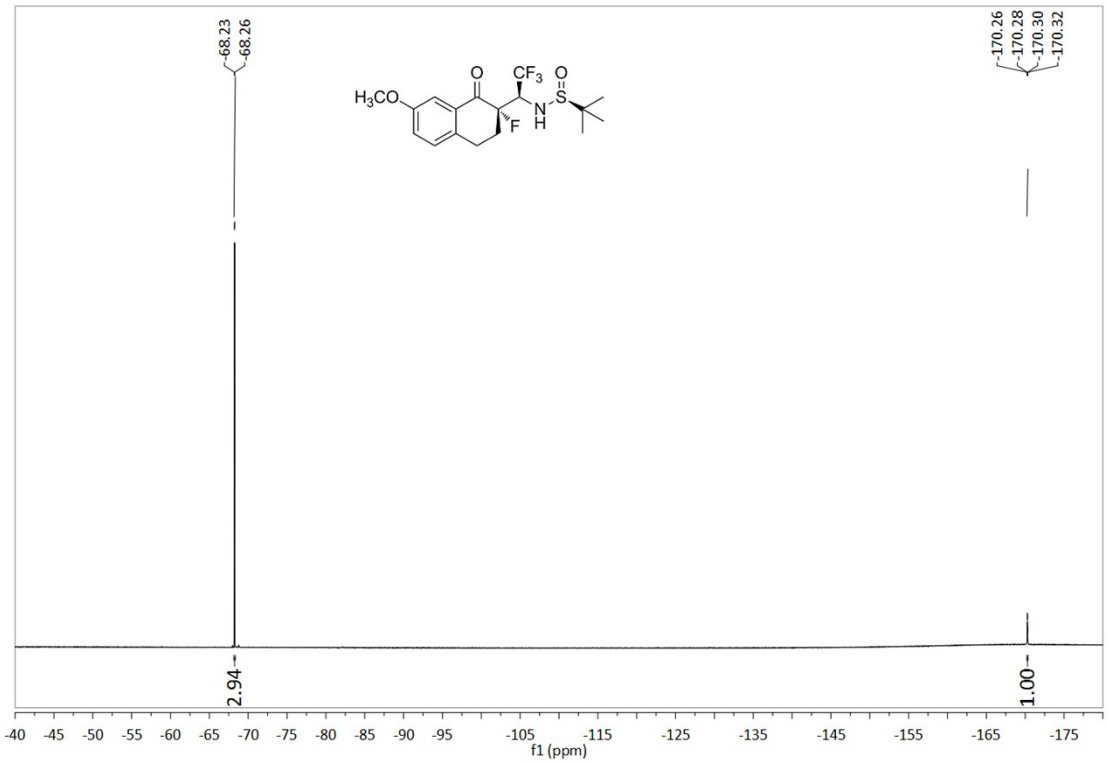
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ma**



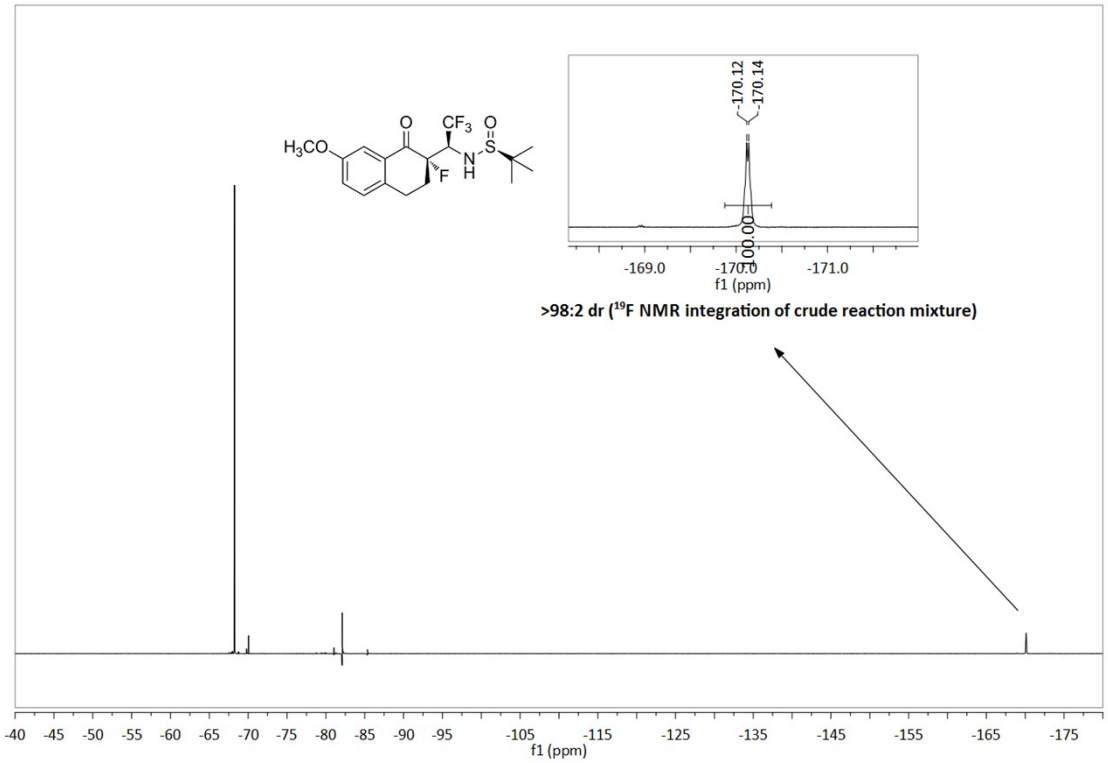
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ma**



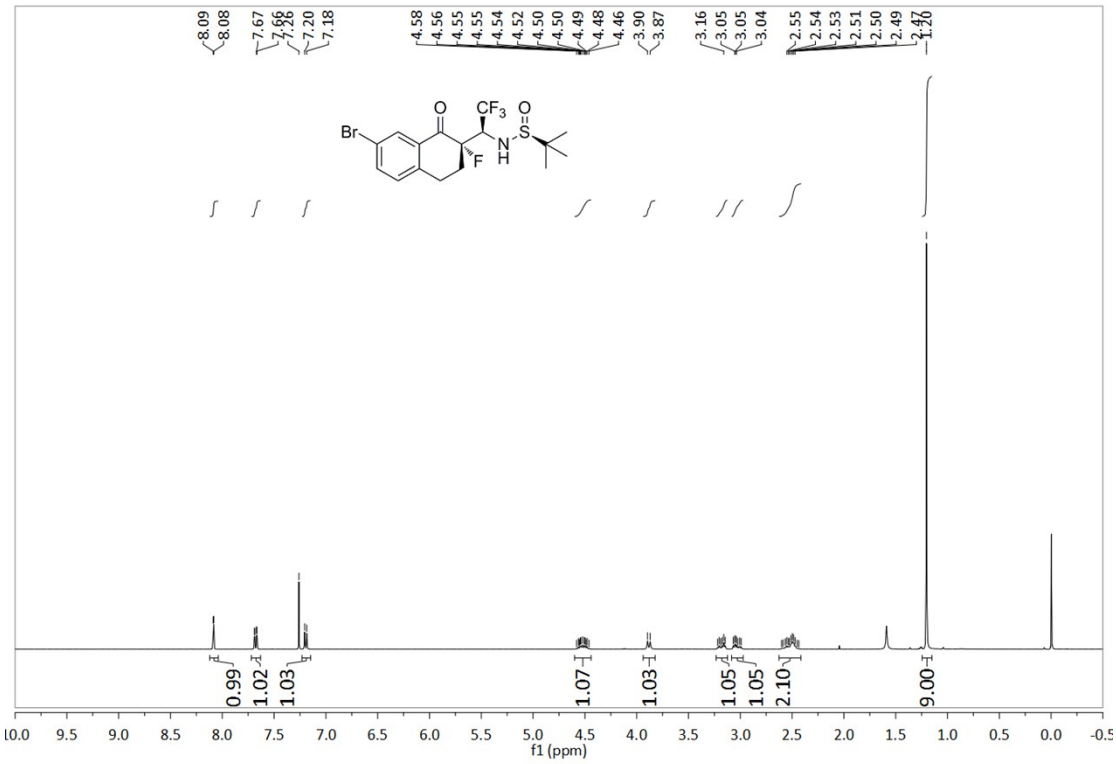
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ma**



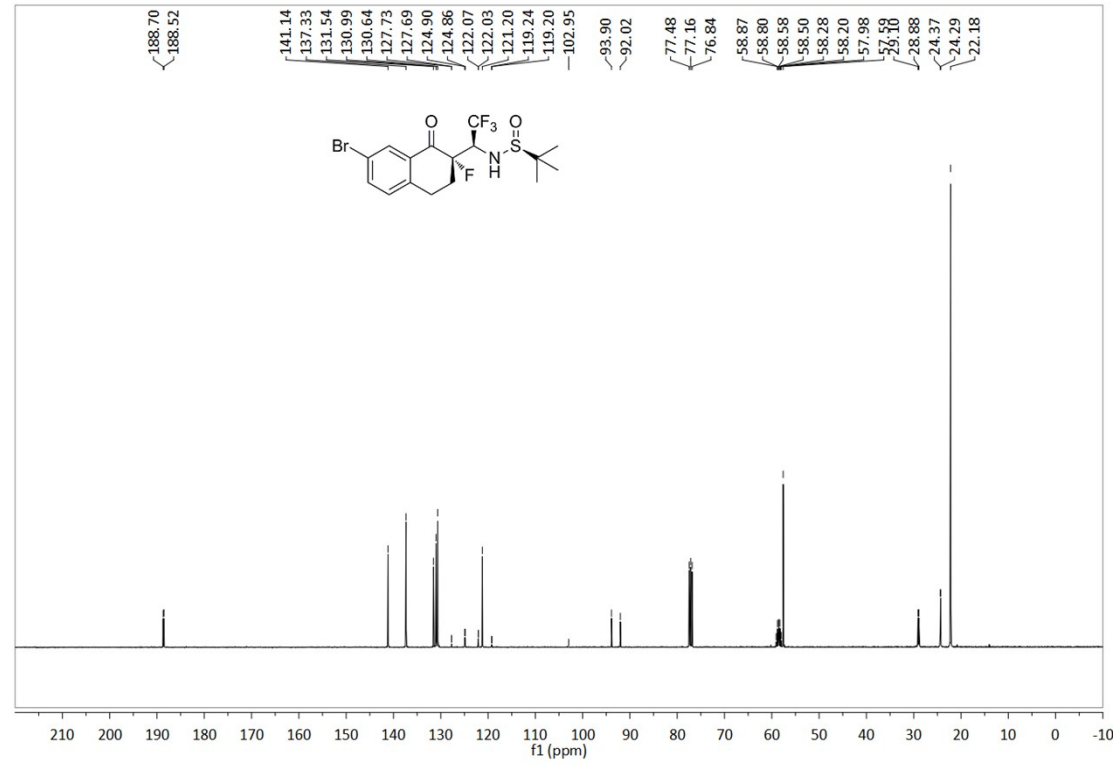
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



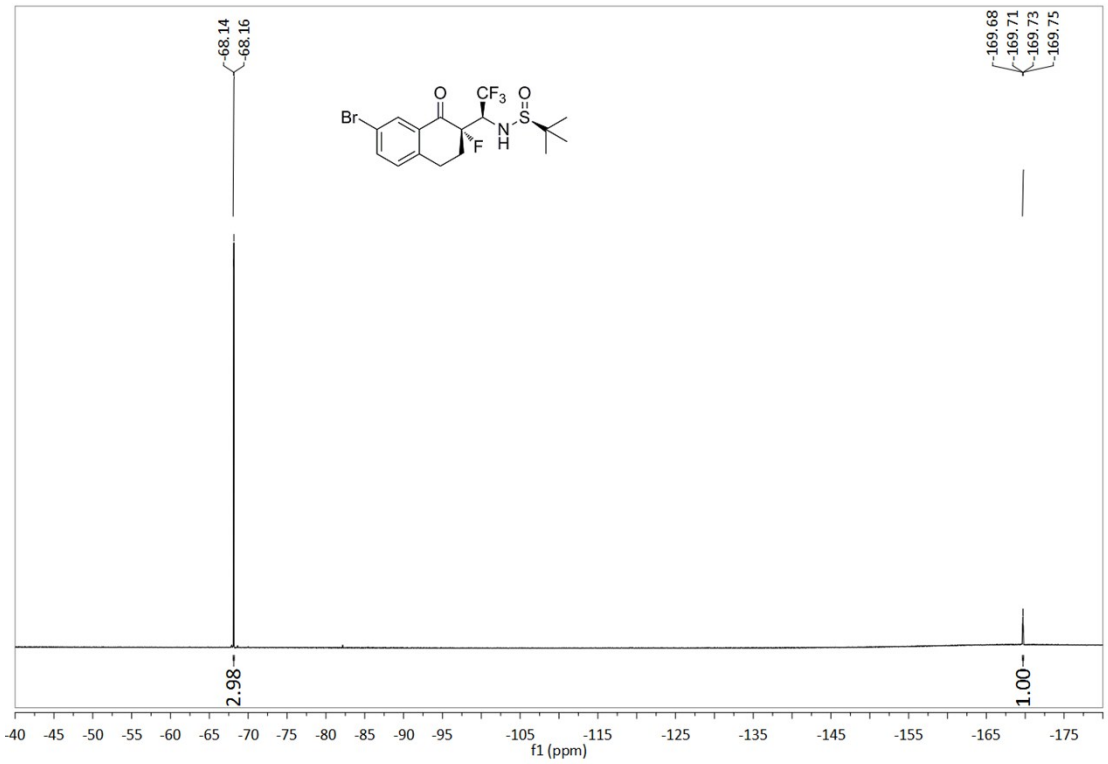
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3na**



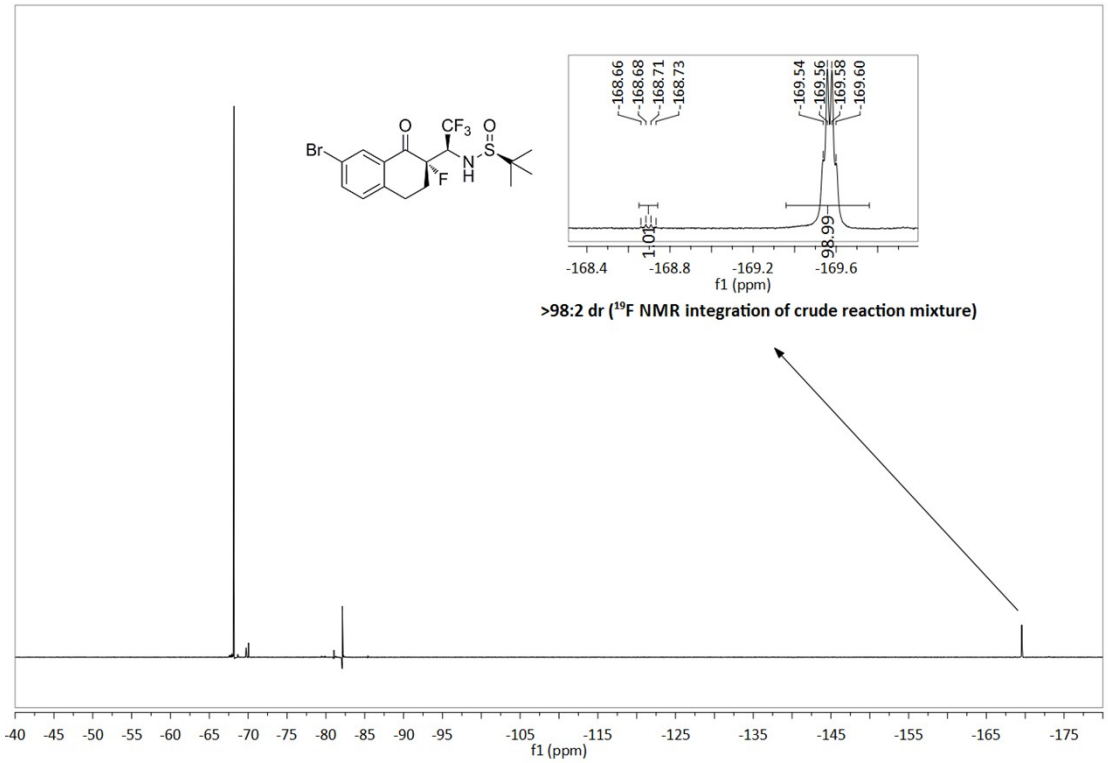
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3na**



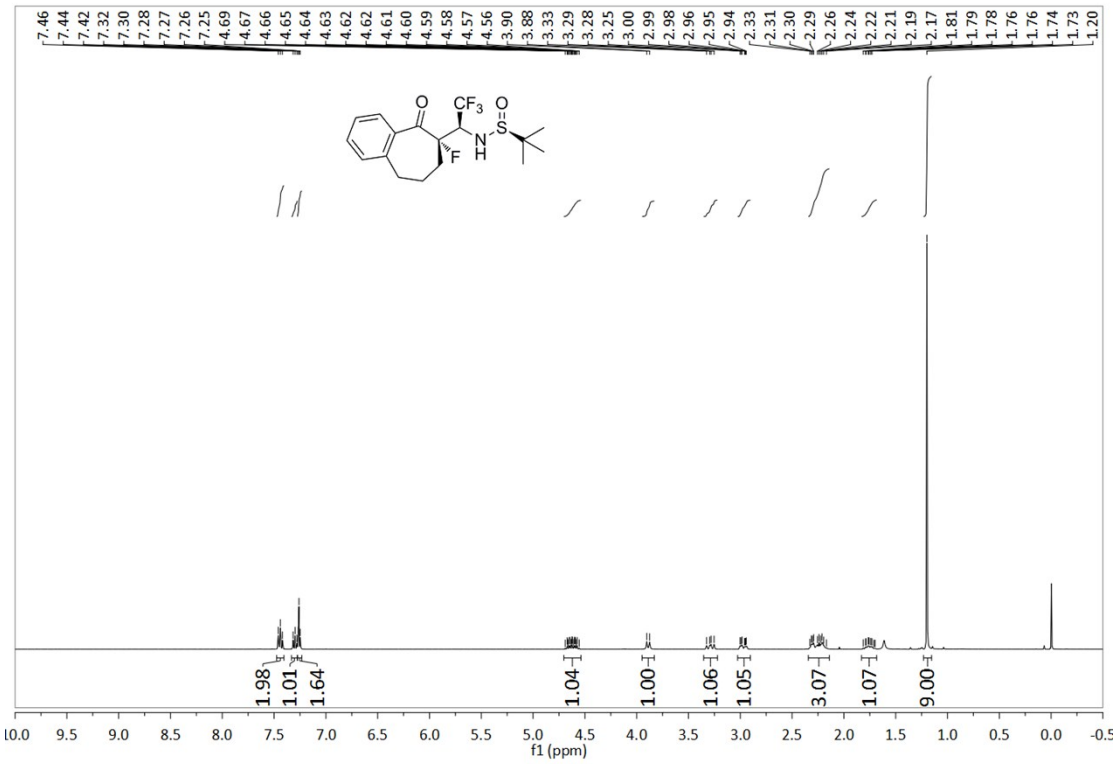
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3na**



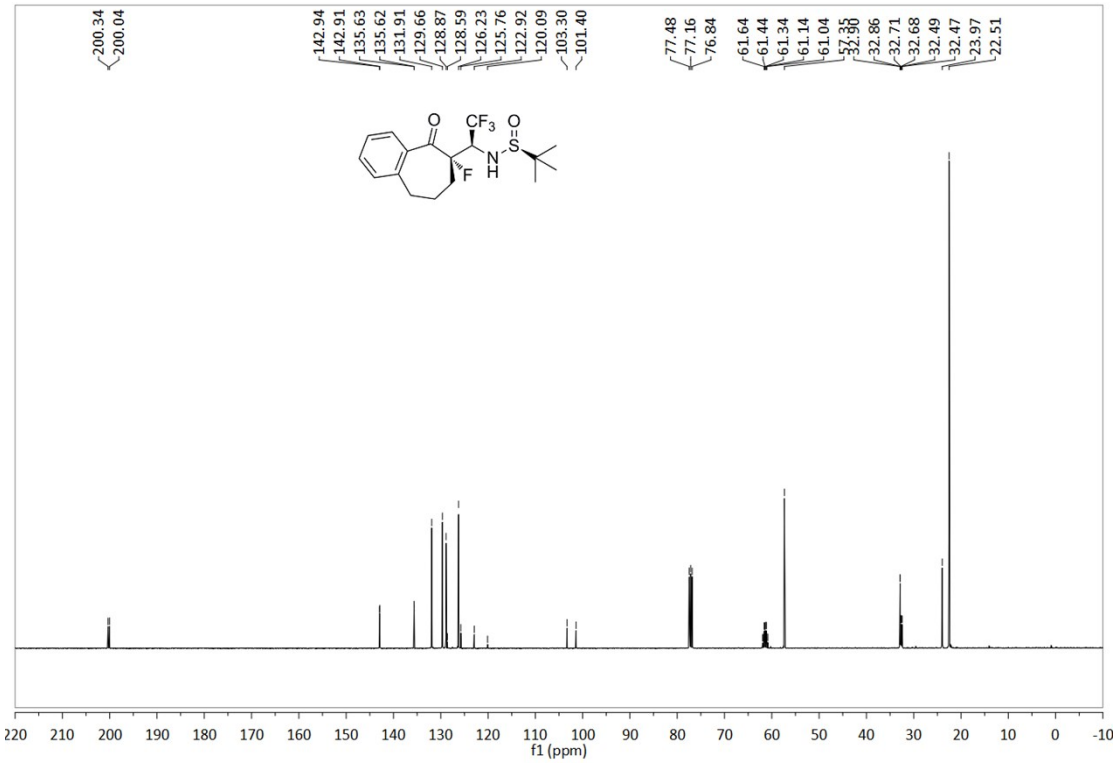
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



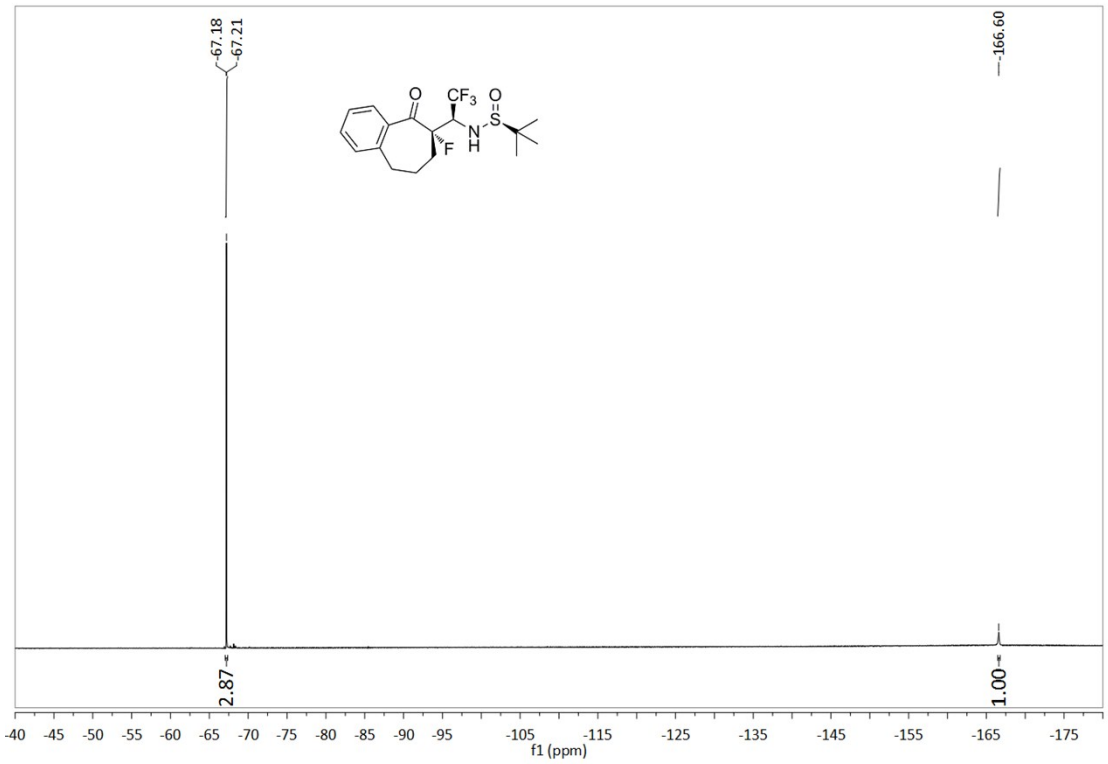
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3oa**



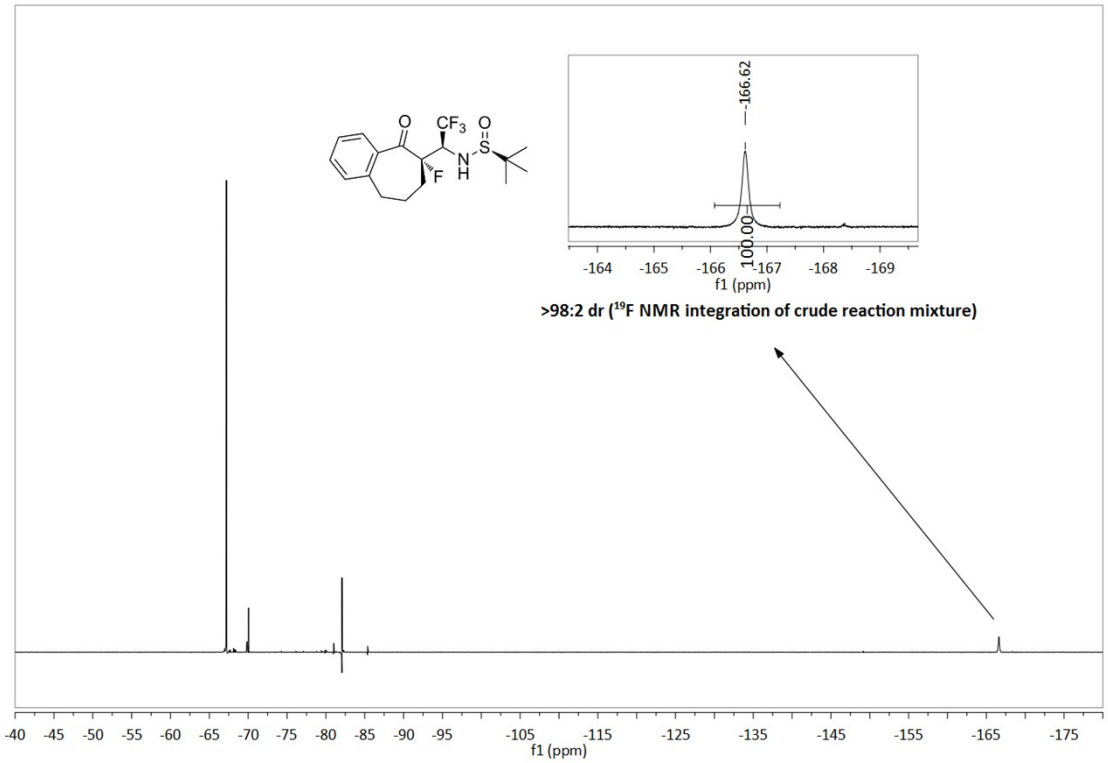
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3oa**



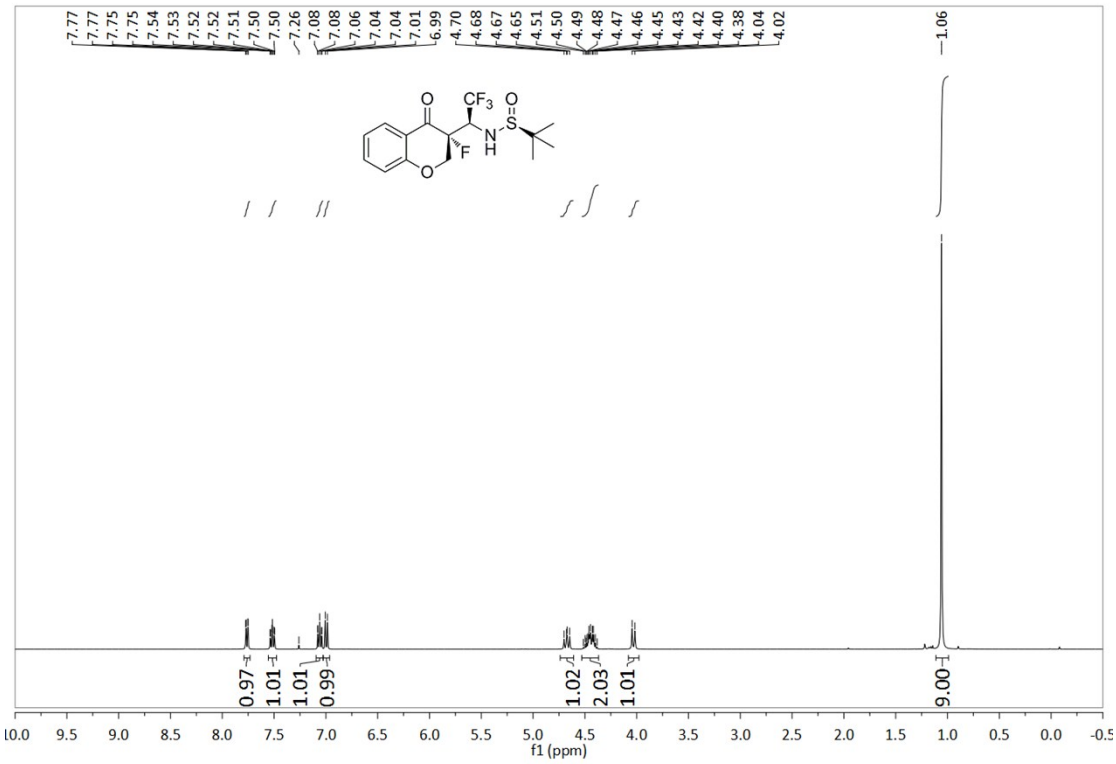
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3oa**



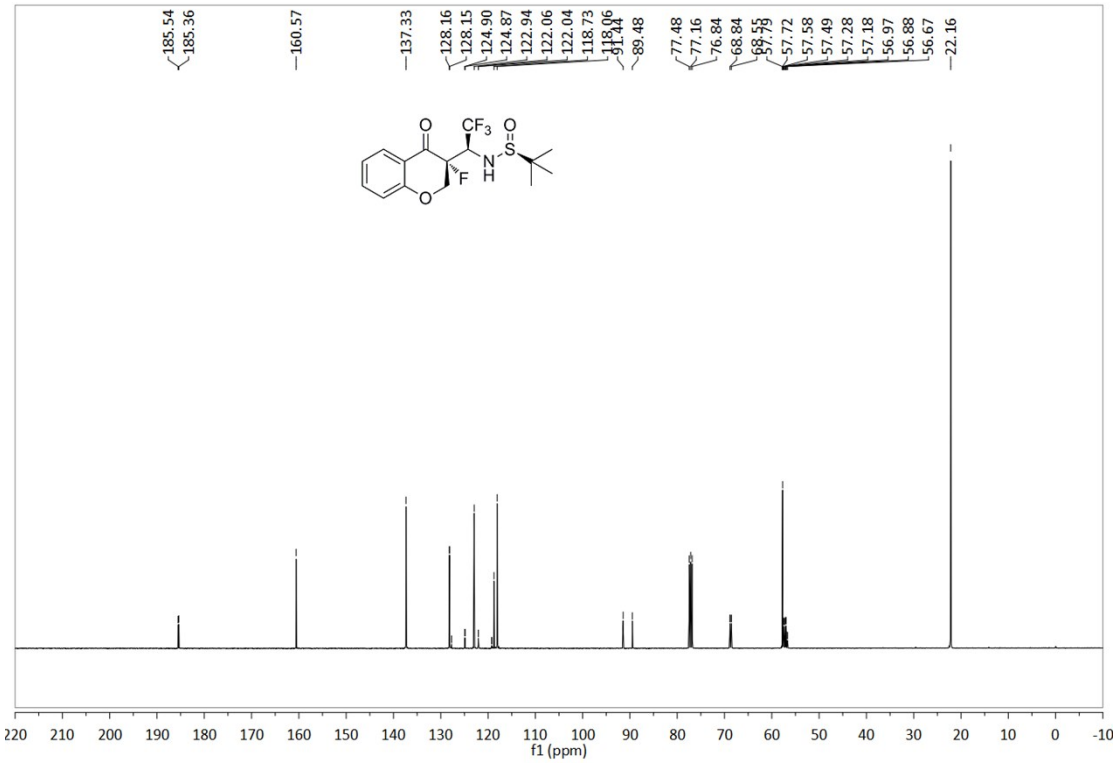
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



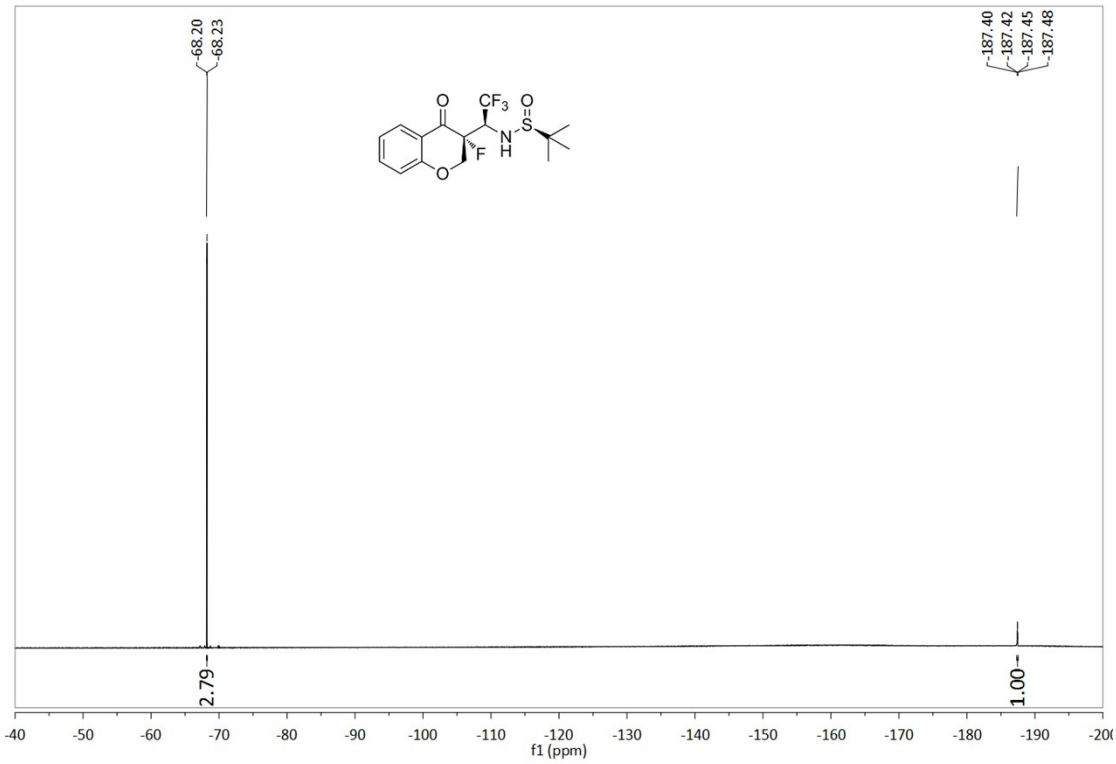
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3pa**



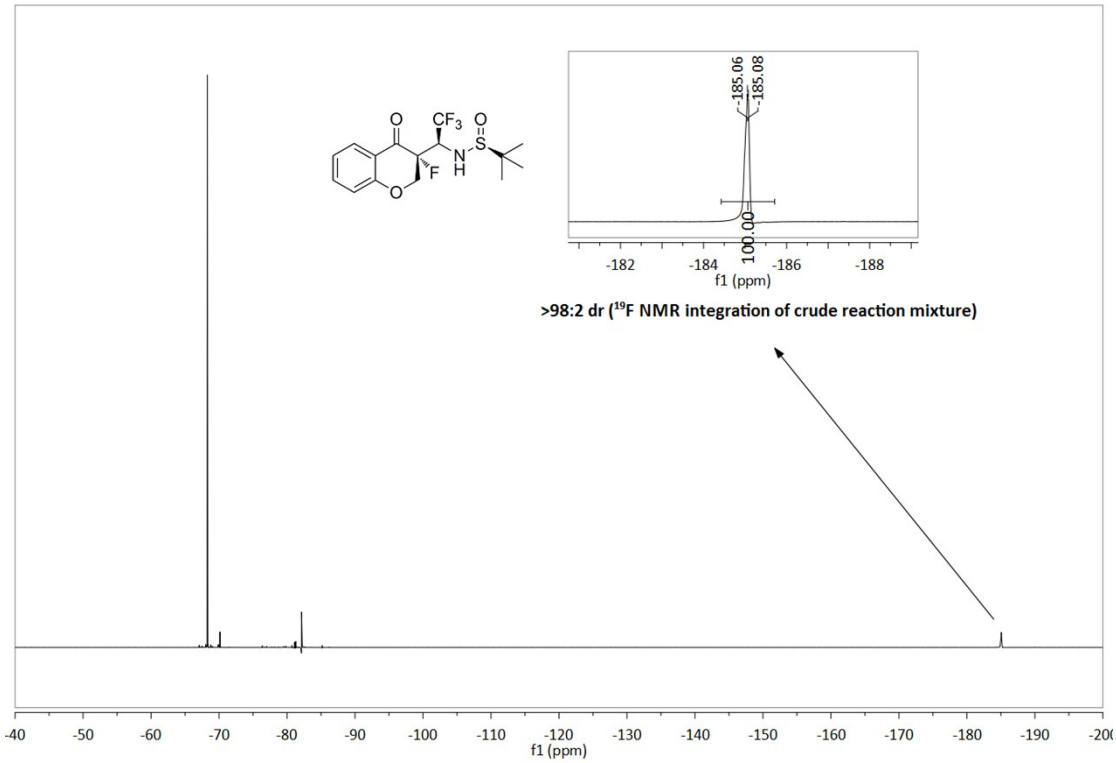
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3pa**



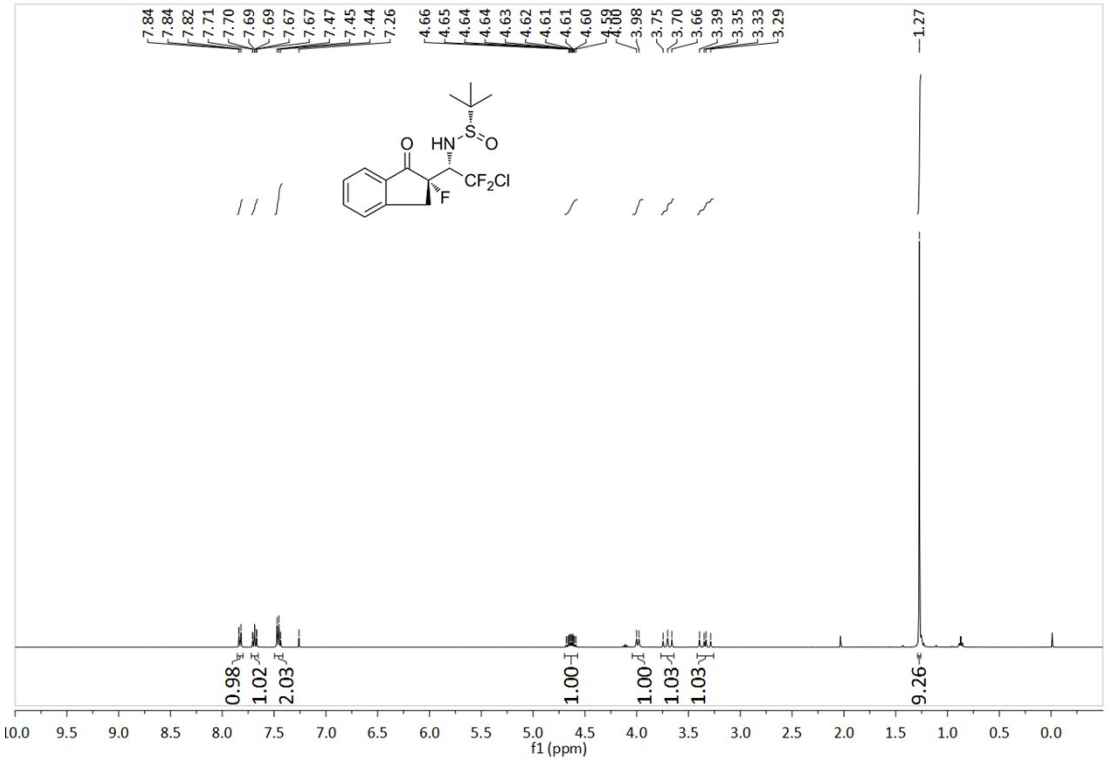
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3pa**



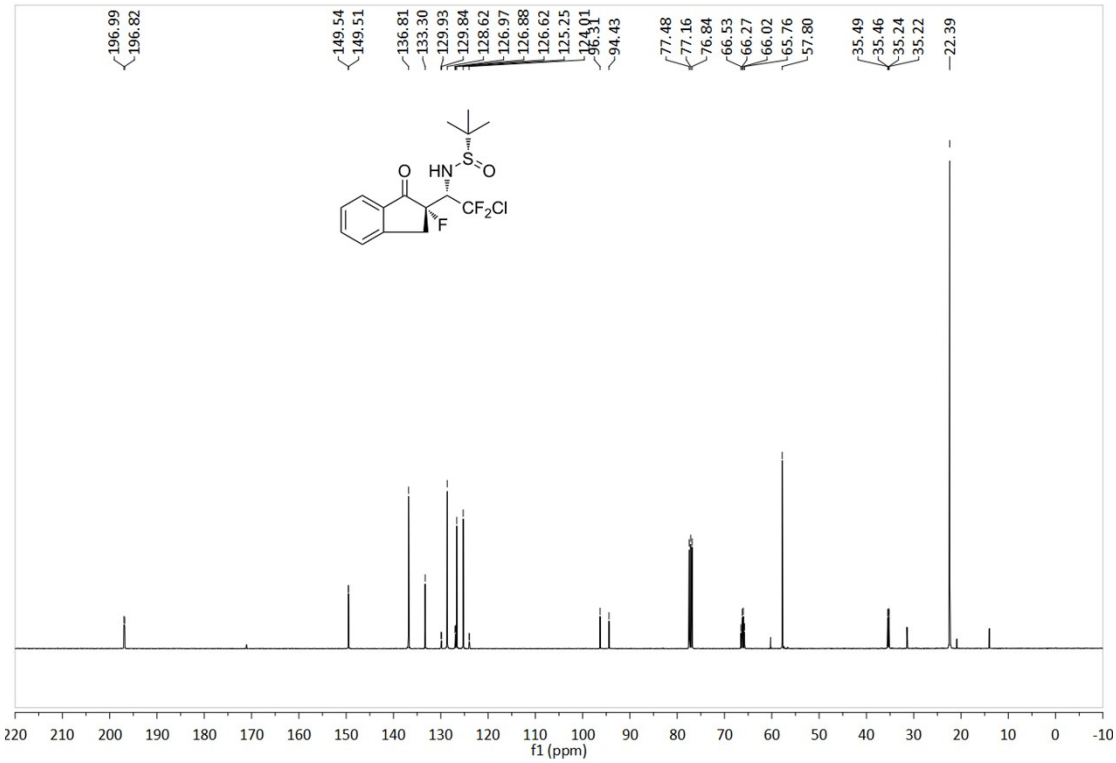
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



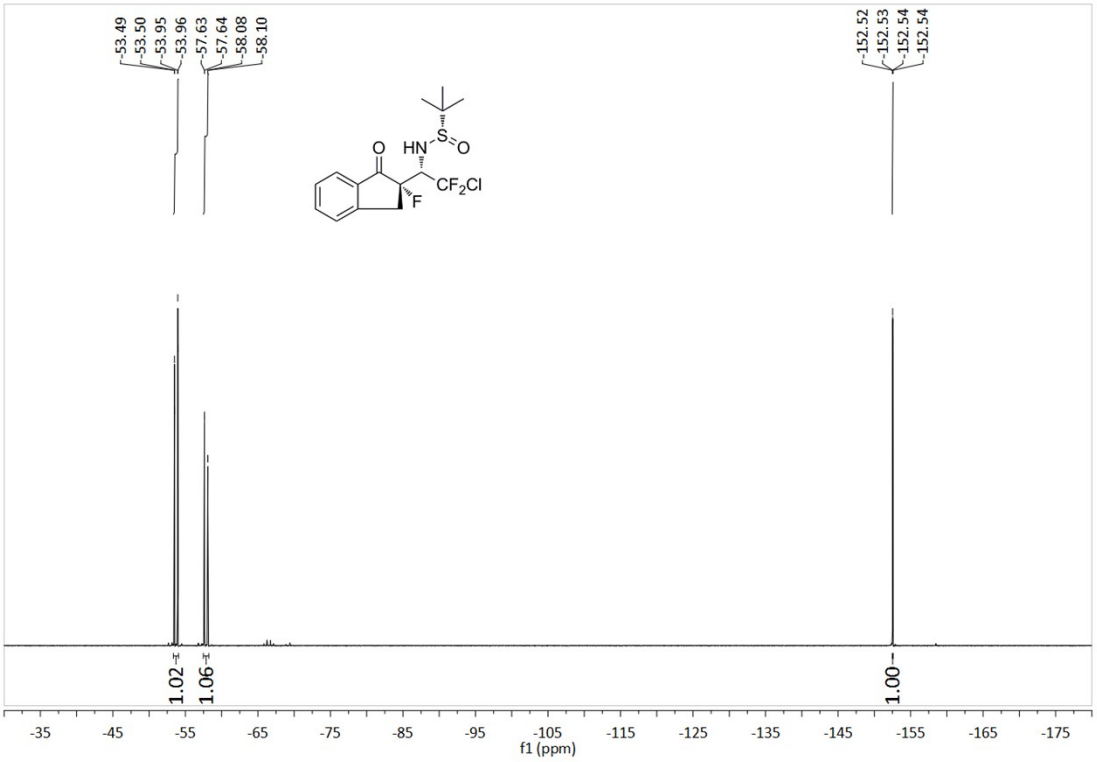
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



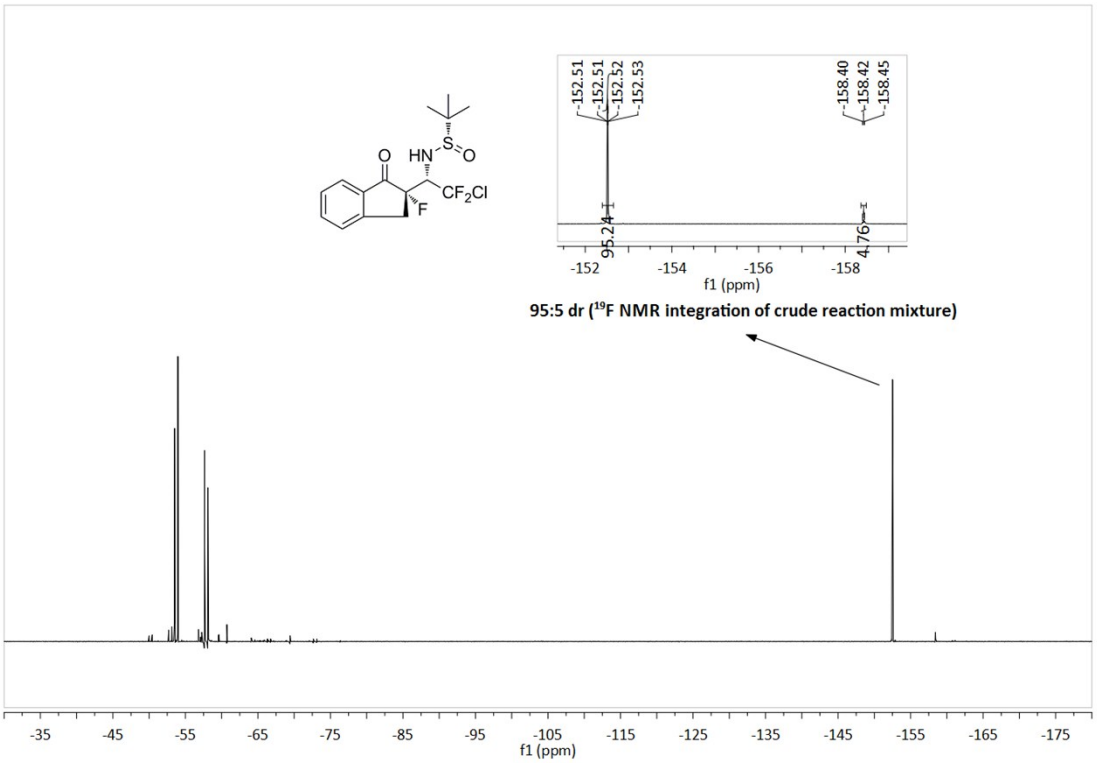
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ab**



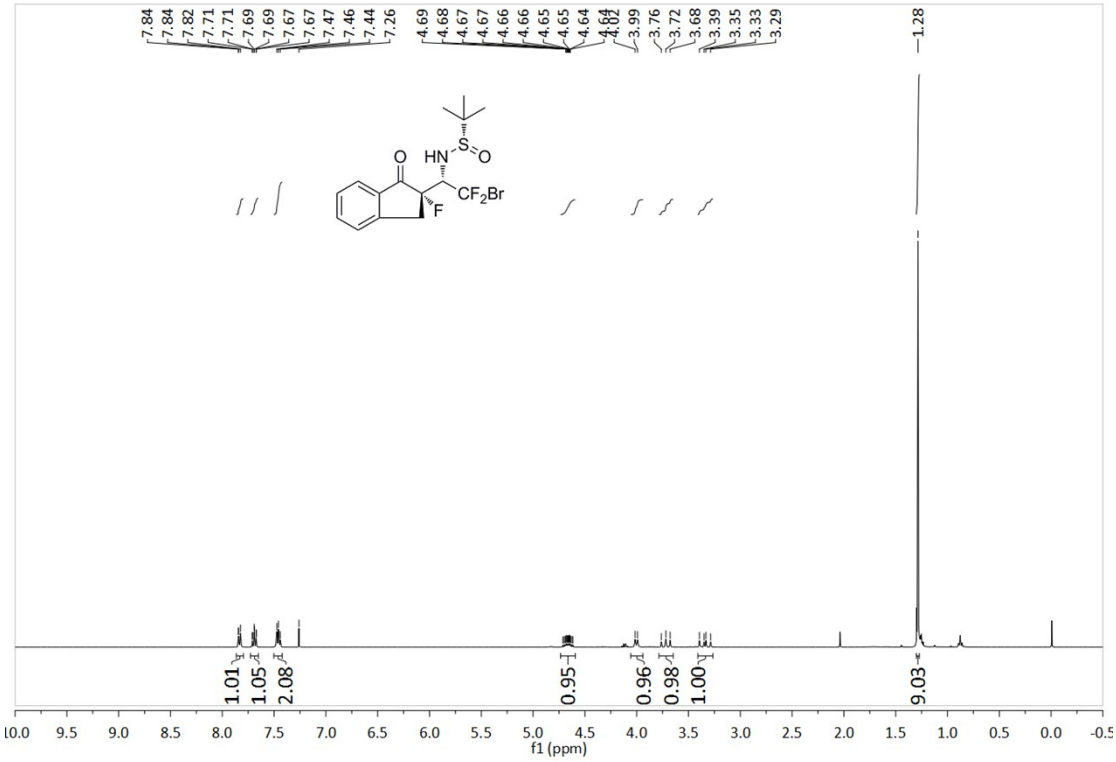
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ab**



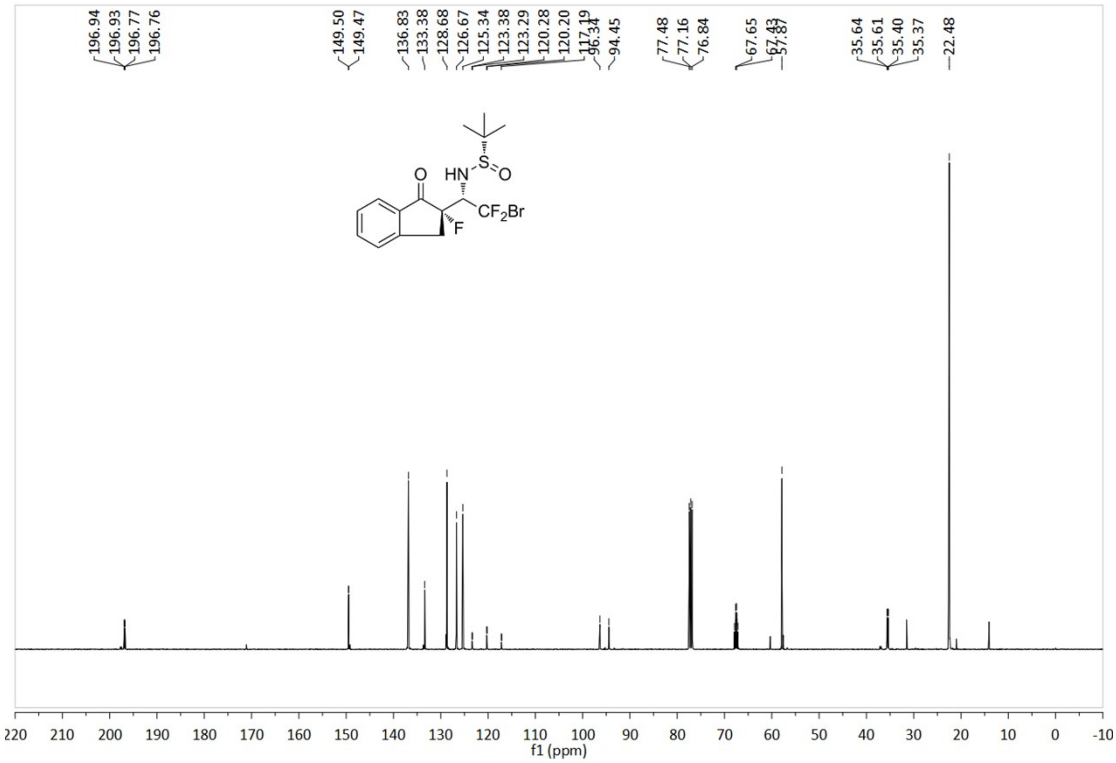
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



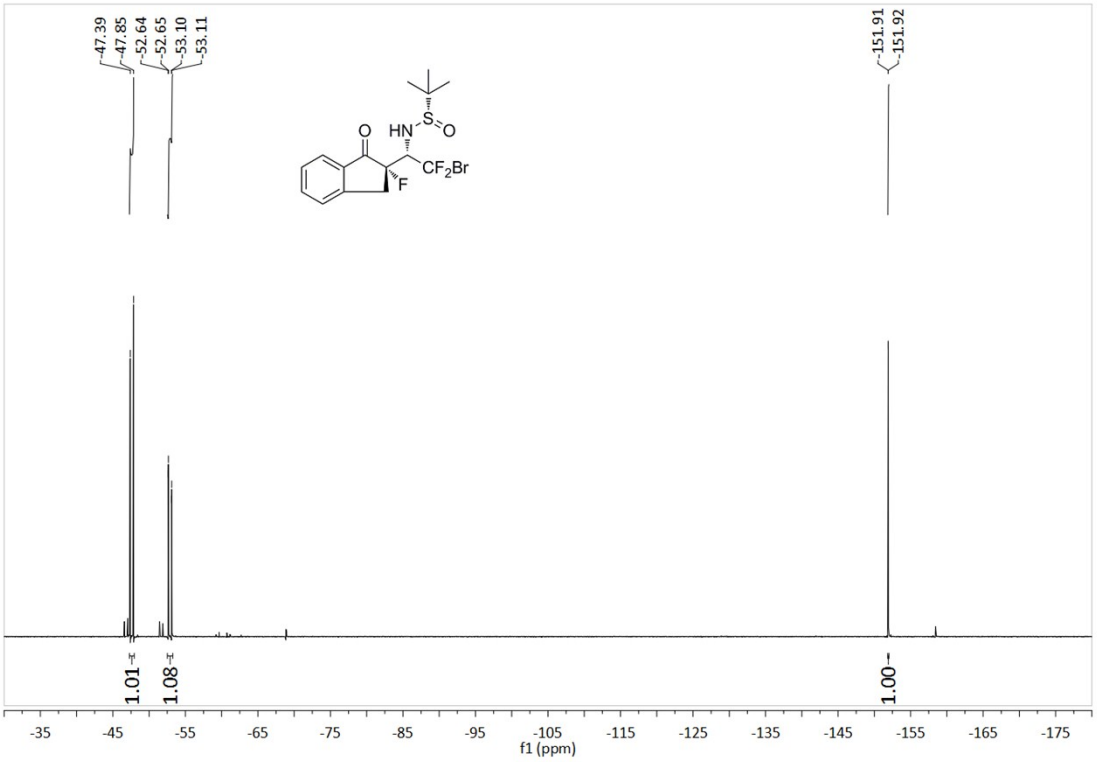
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



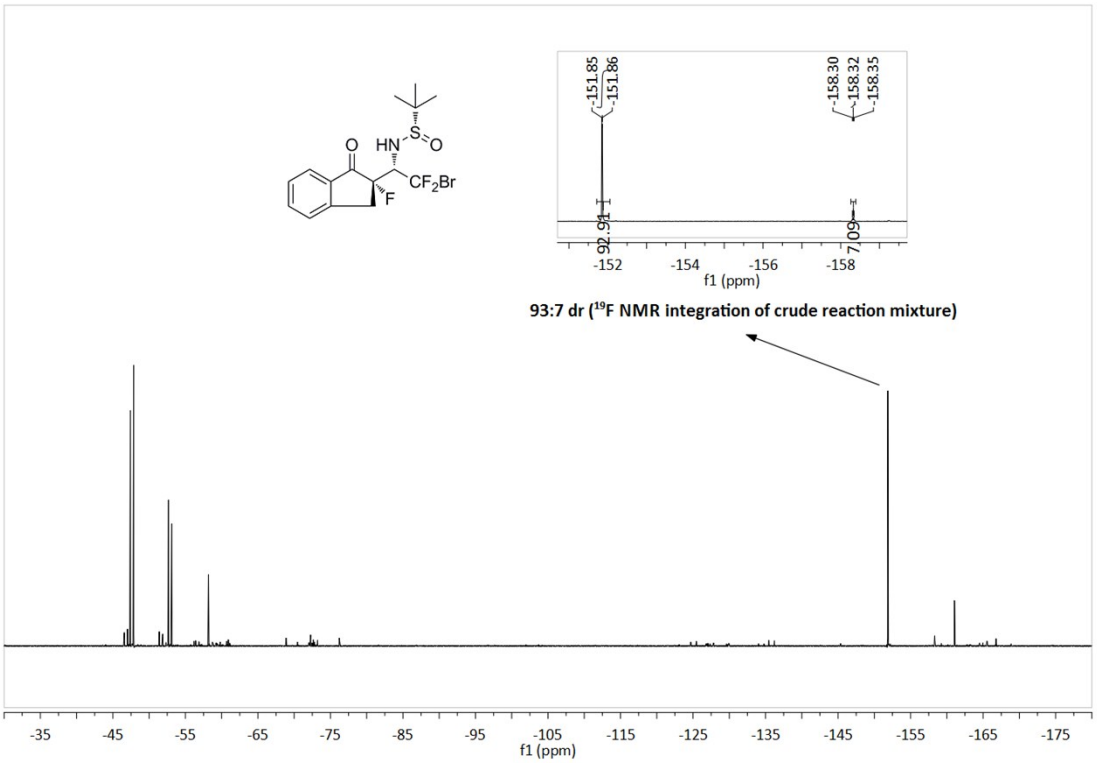
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ac**



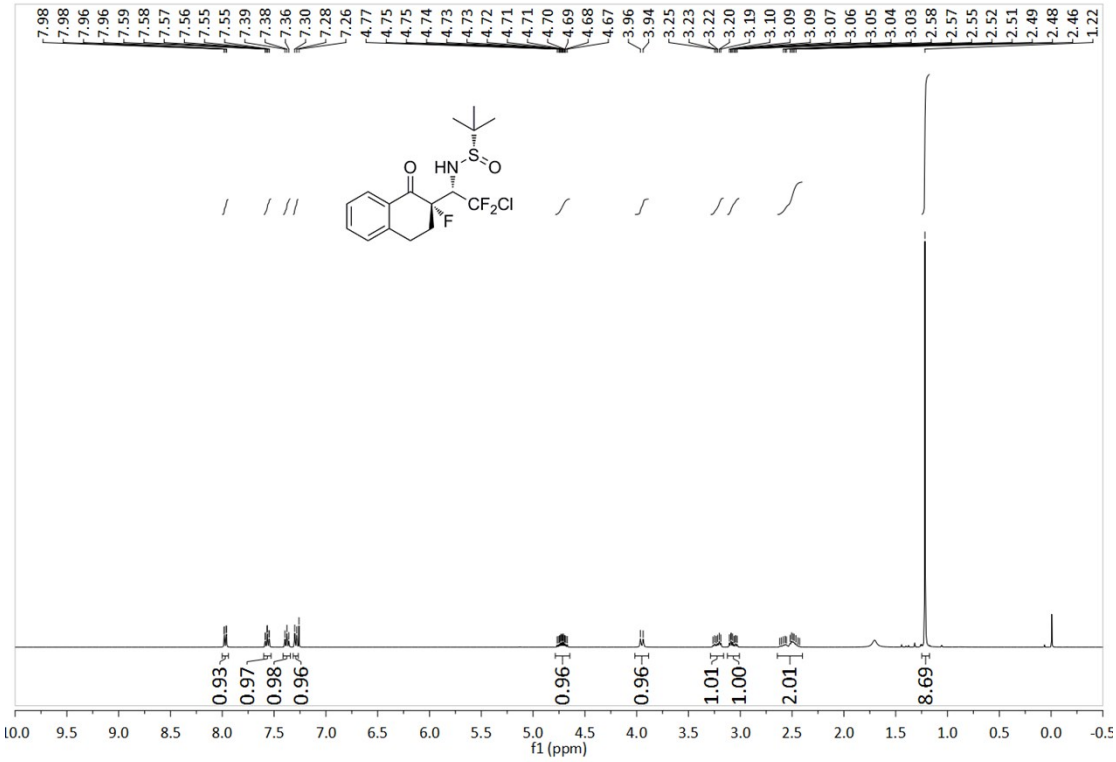
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ac**



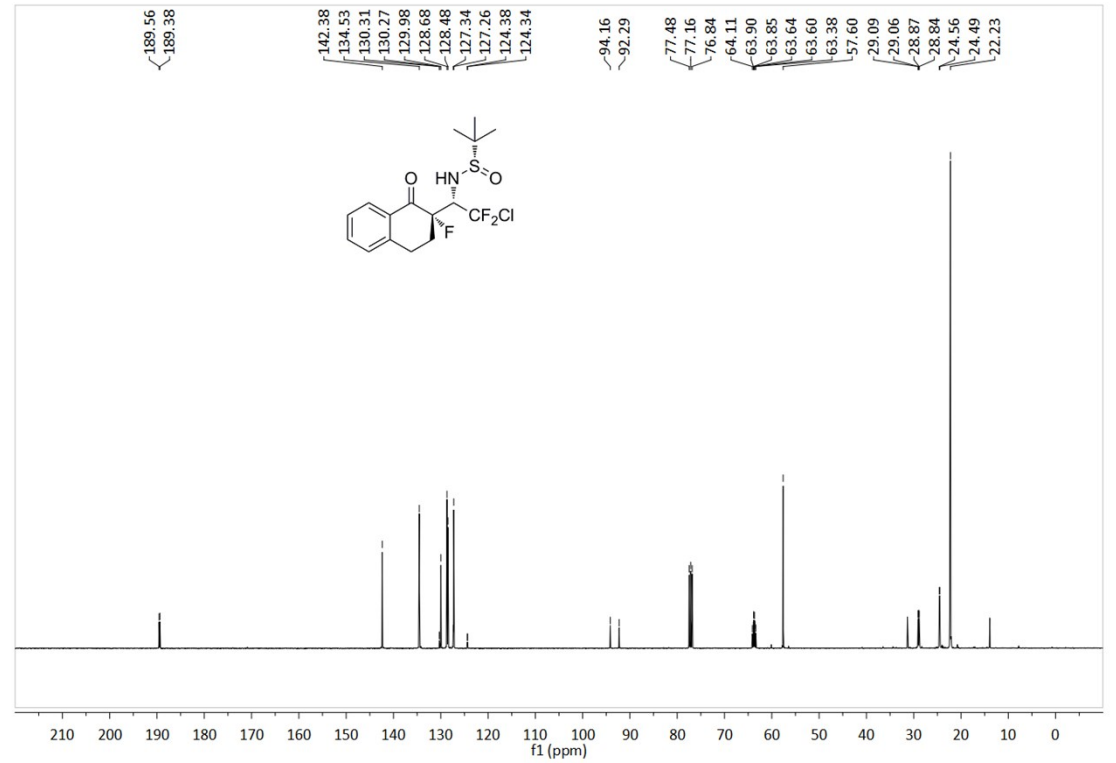
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



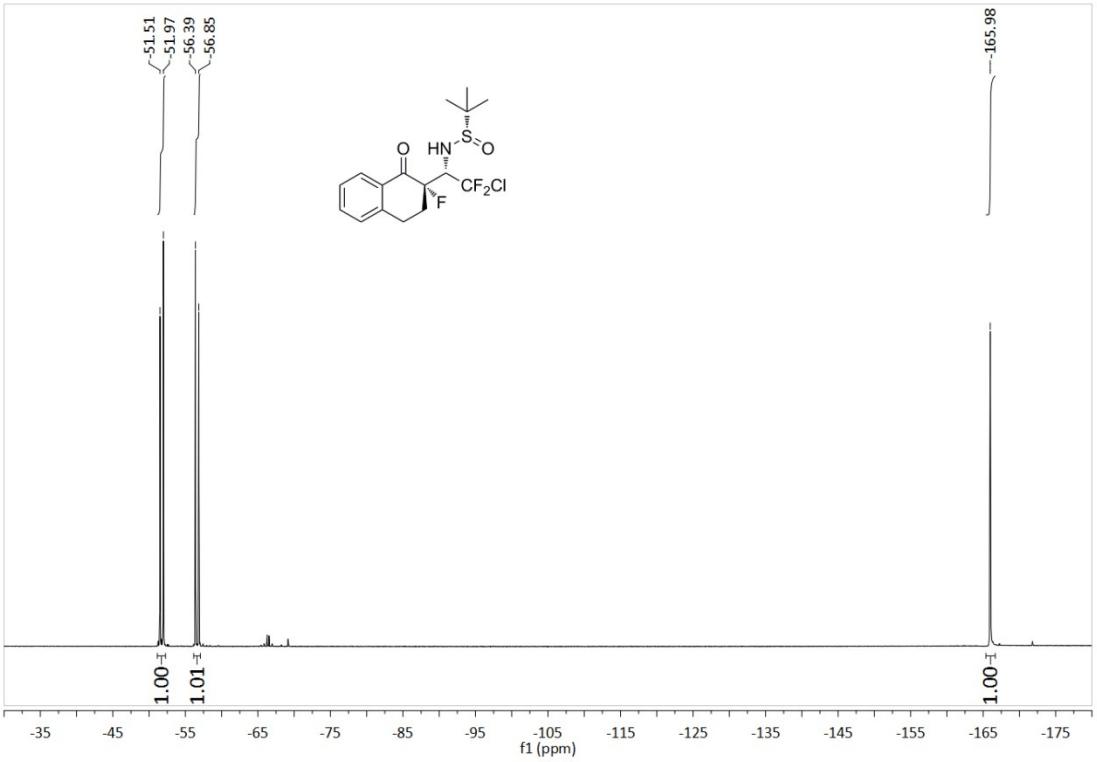
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3lb**



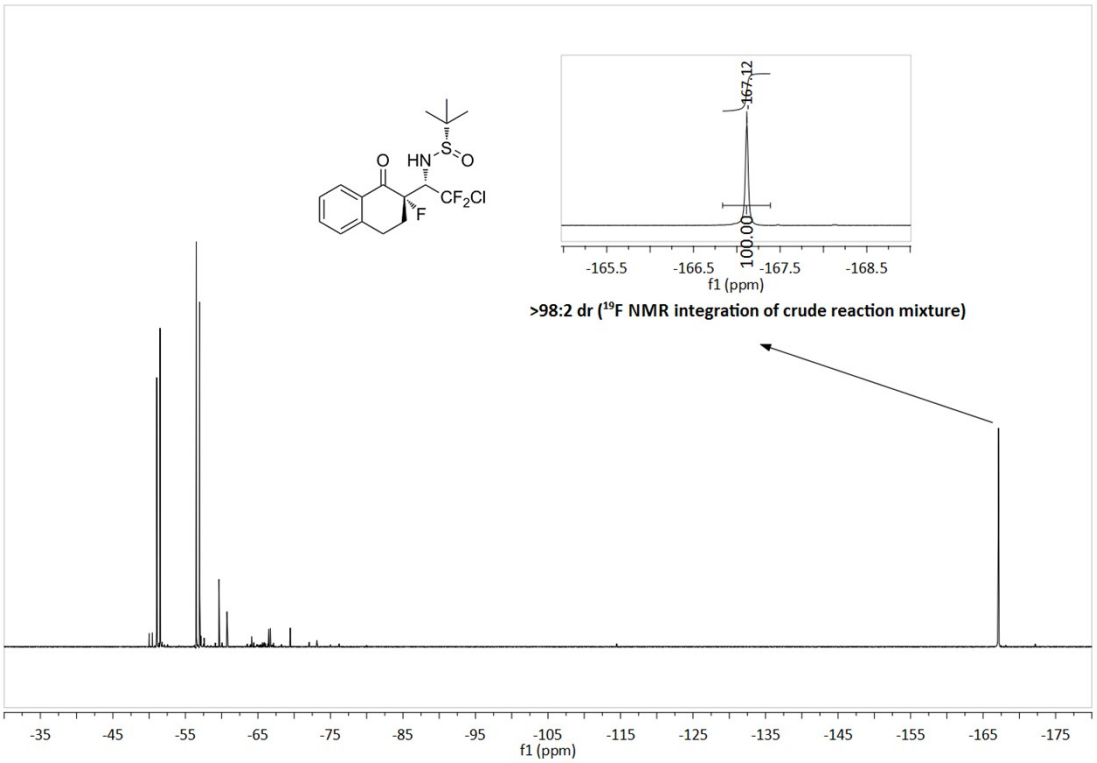
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3lb**



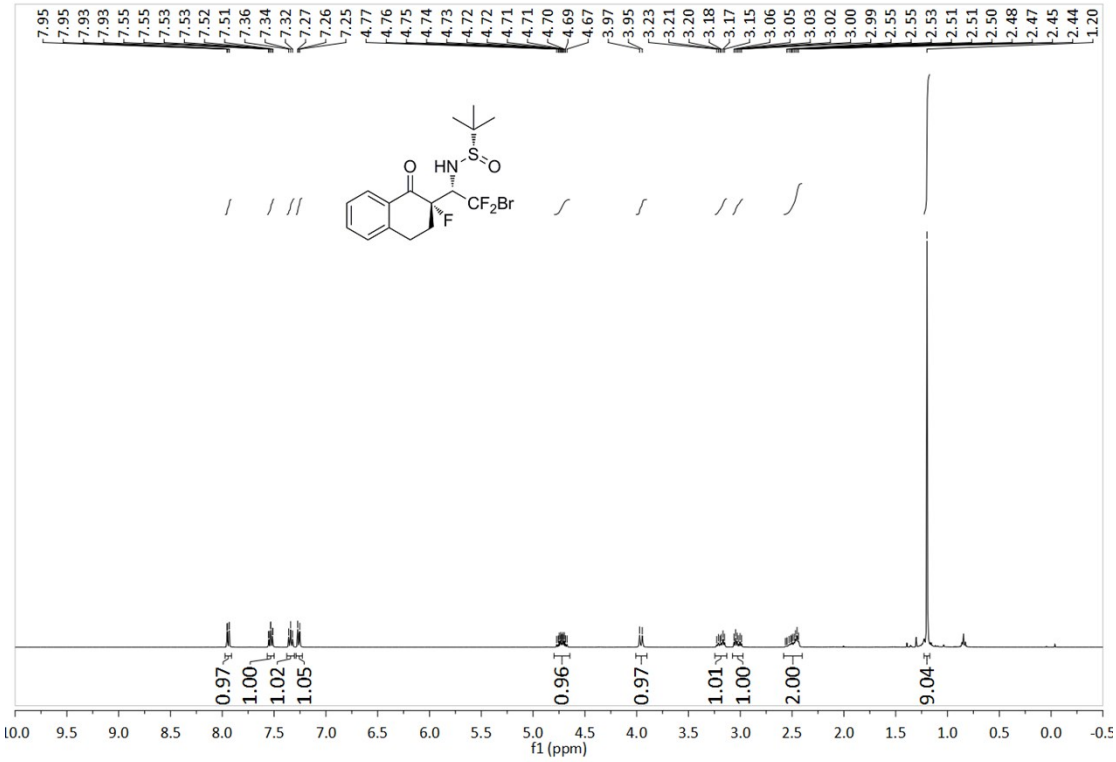
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3lb**



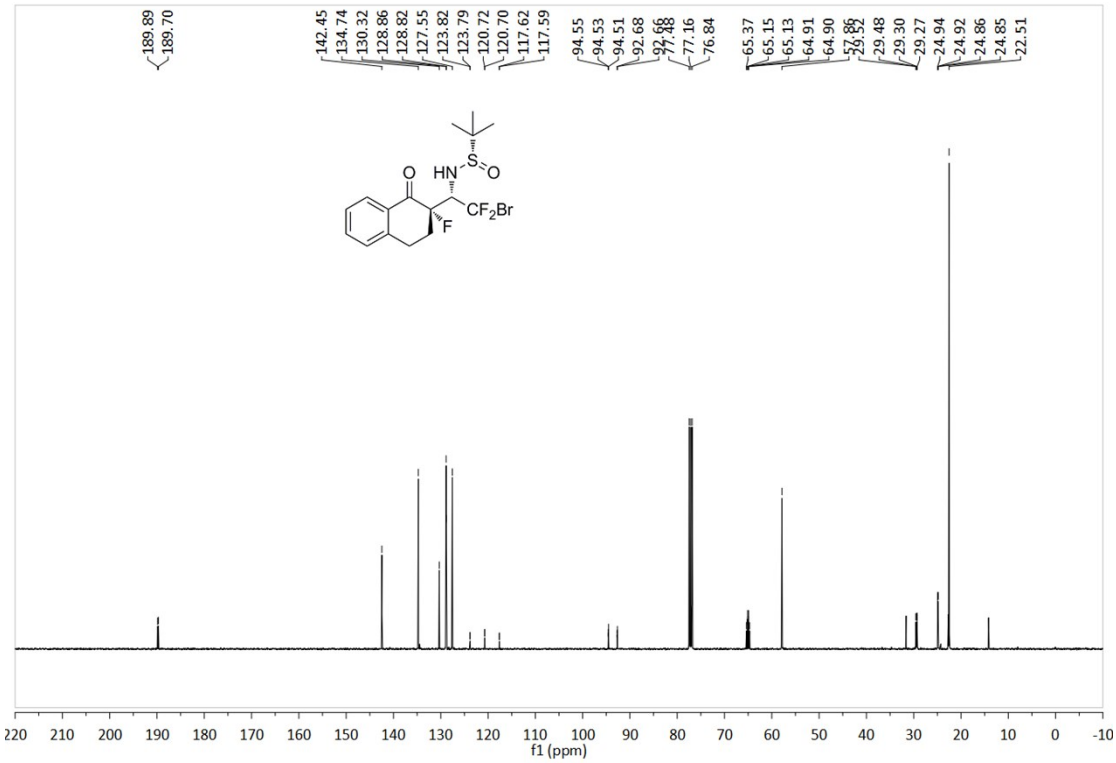
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



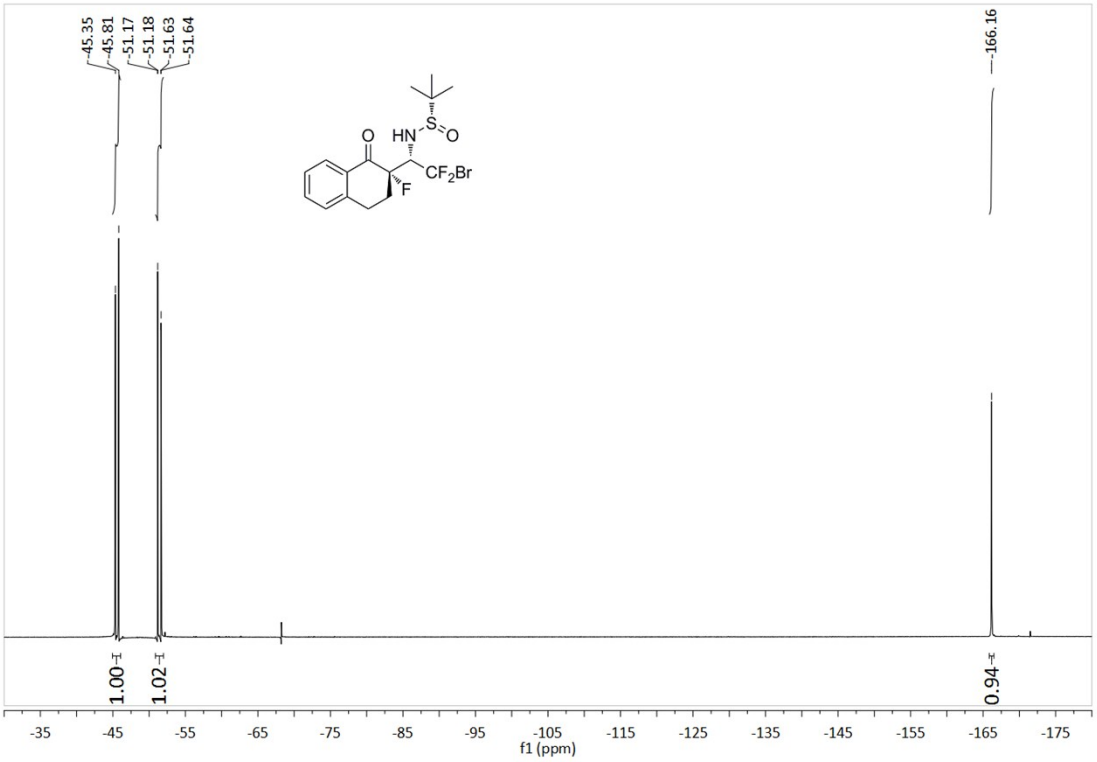
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3lc**



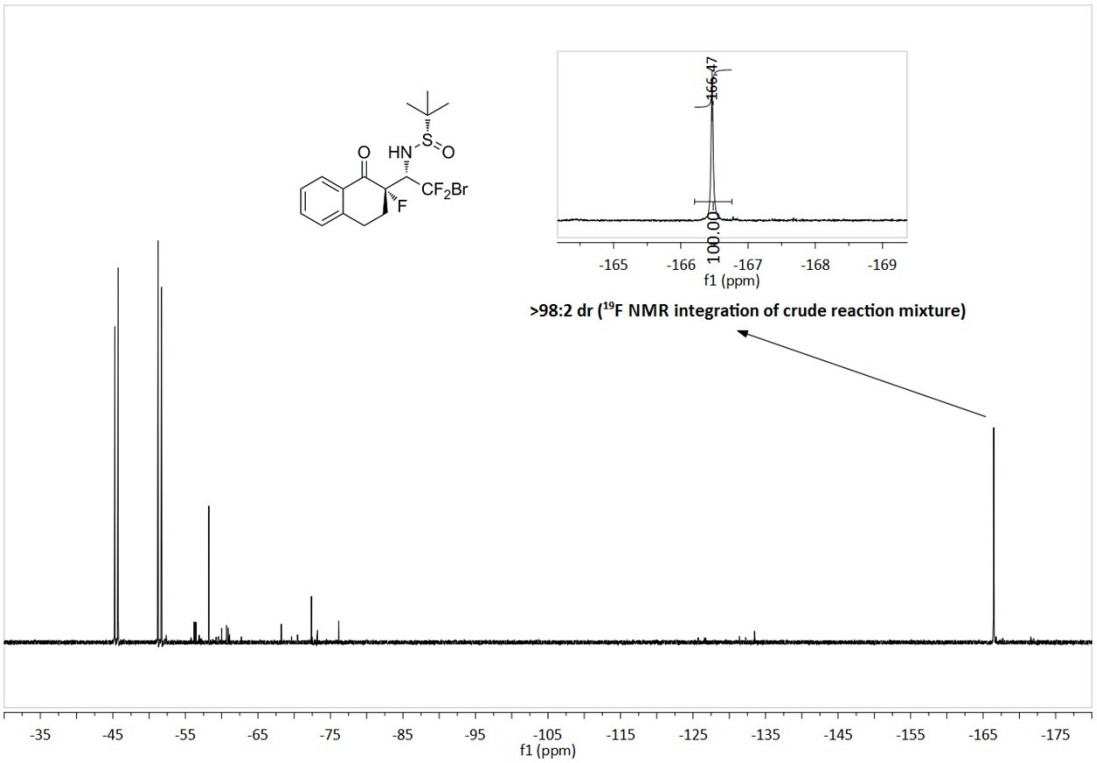
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3lc**



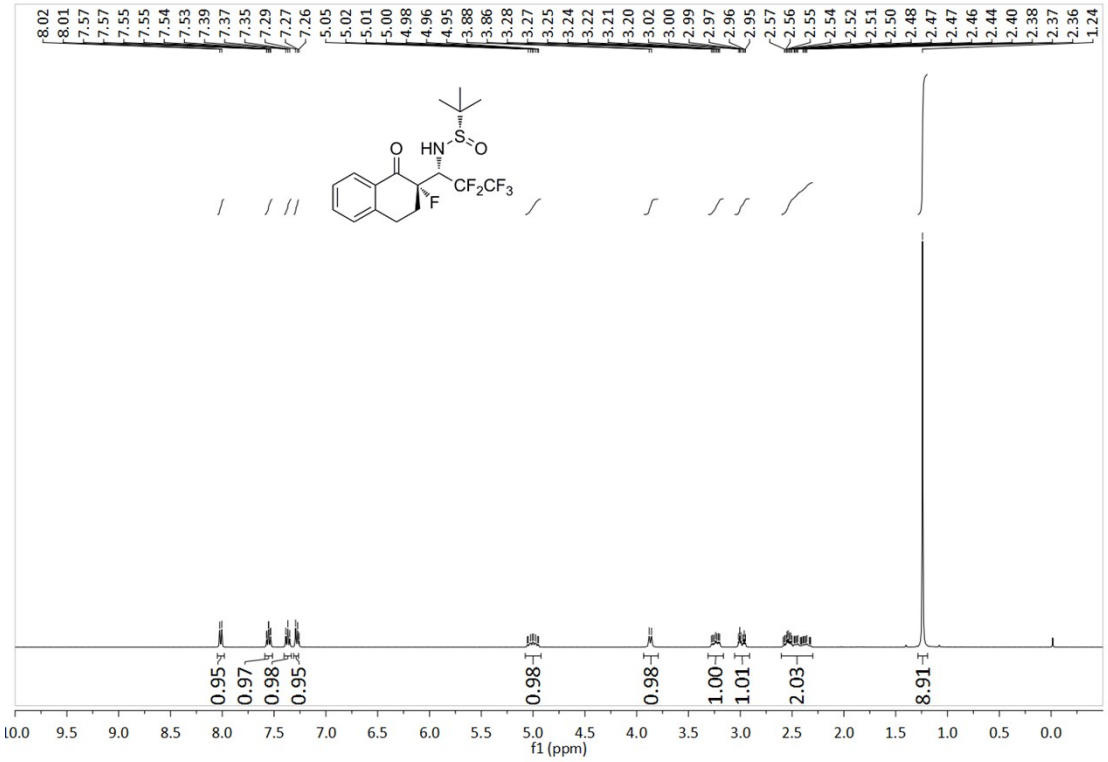
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3lc**



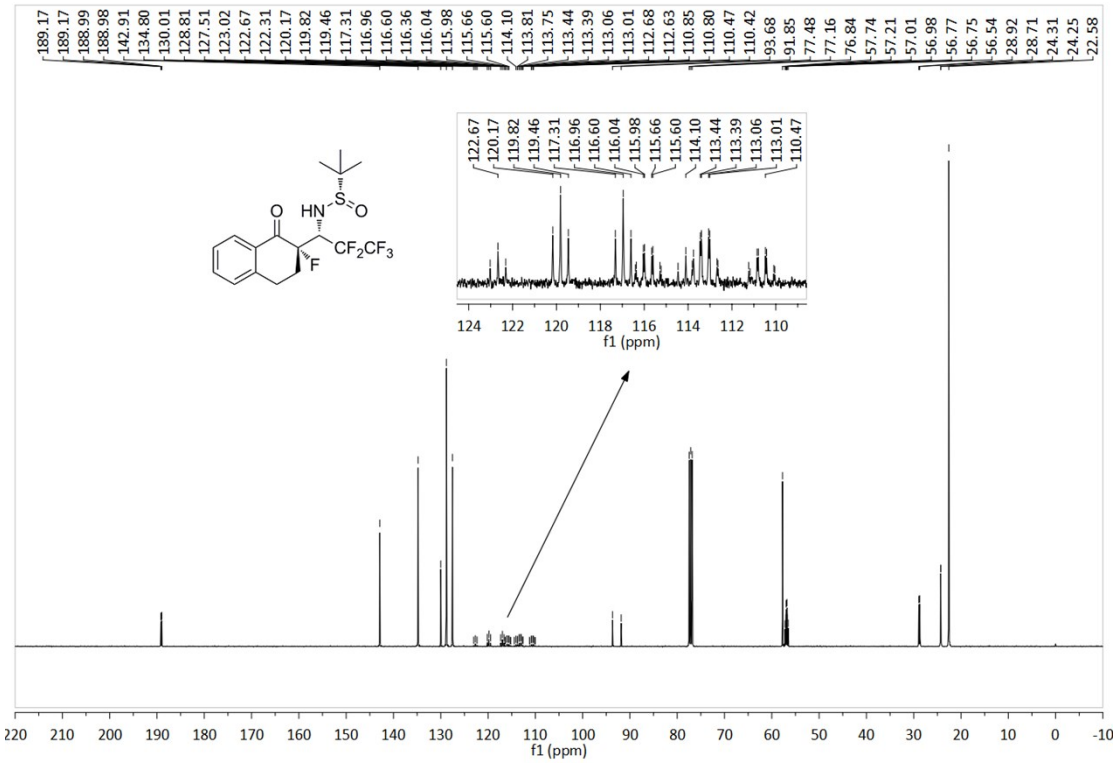
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



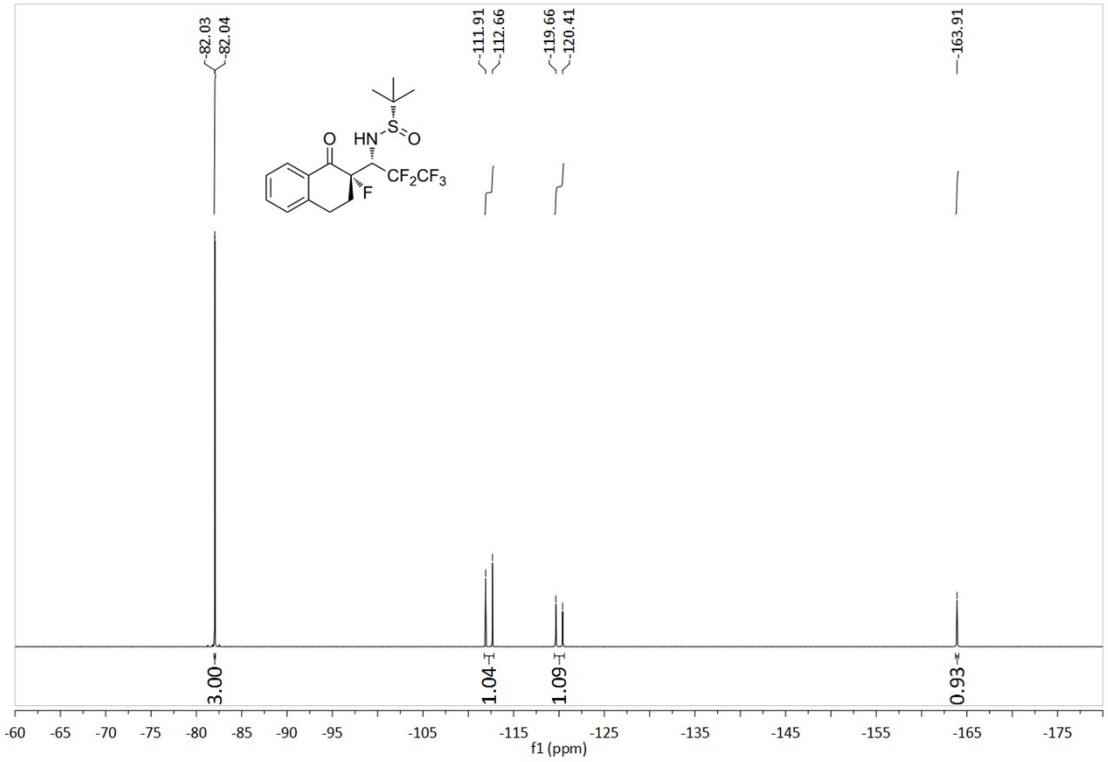
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ld**



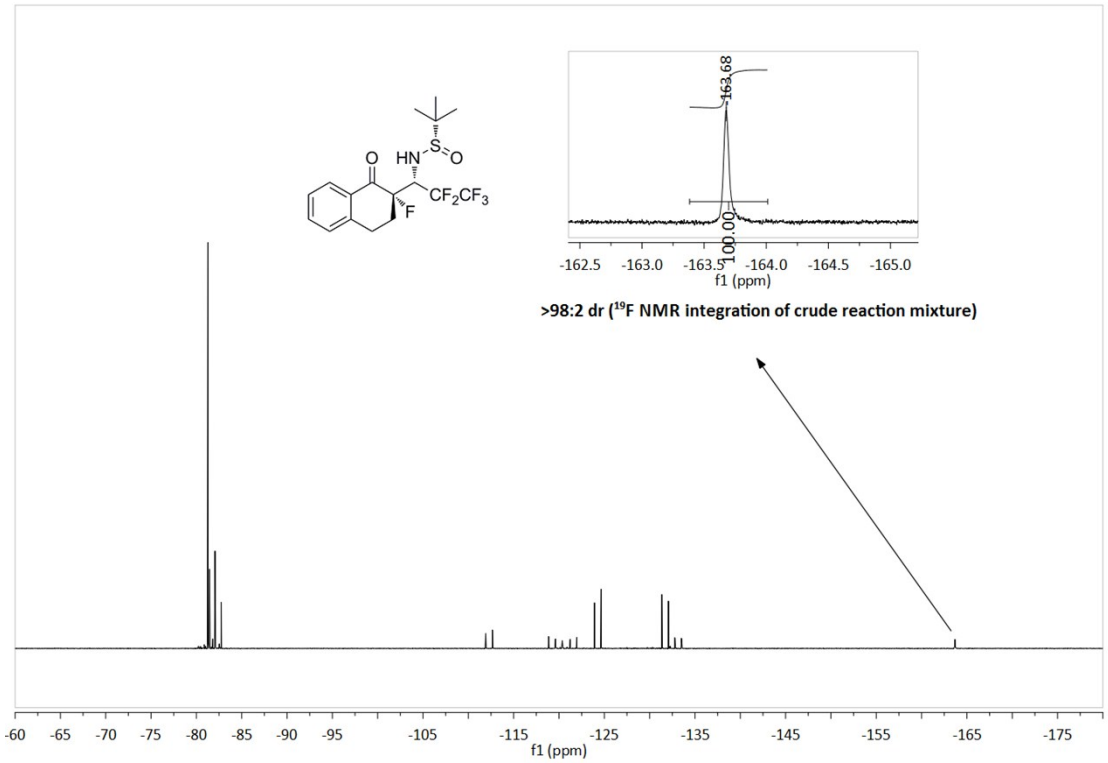
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ld**



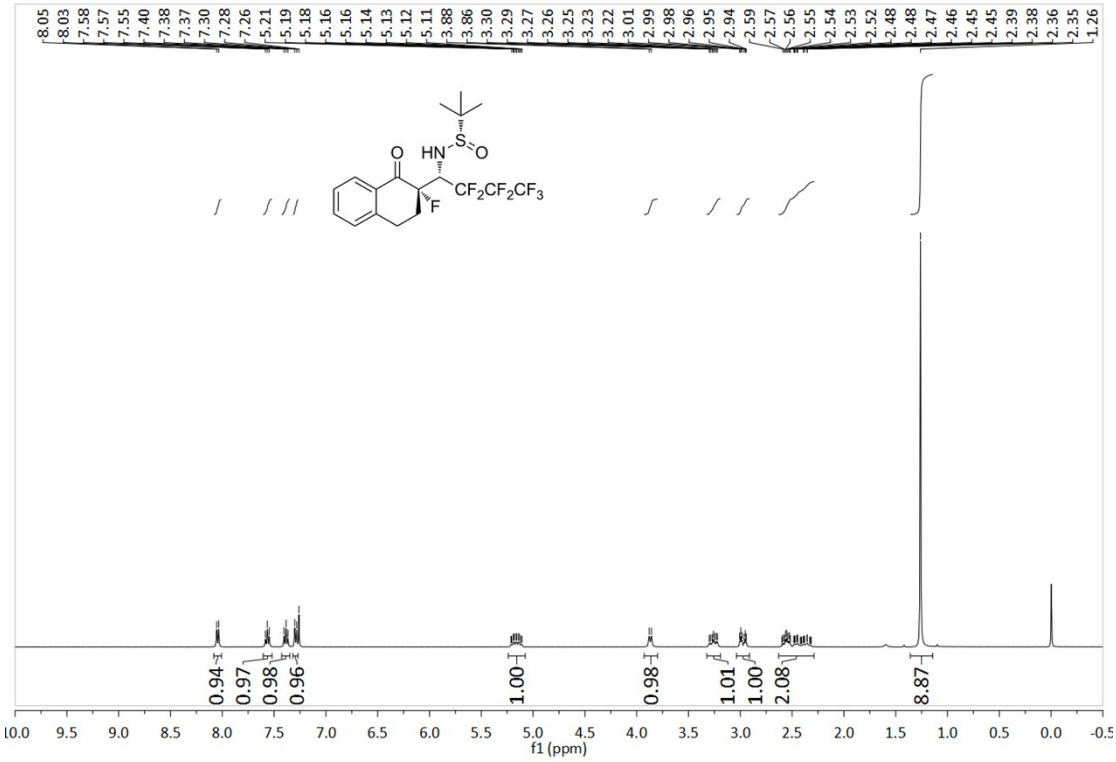
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ld**



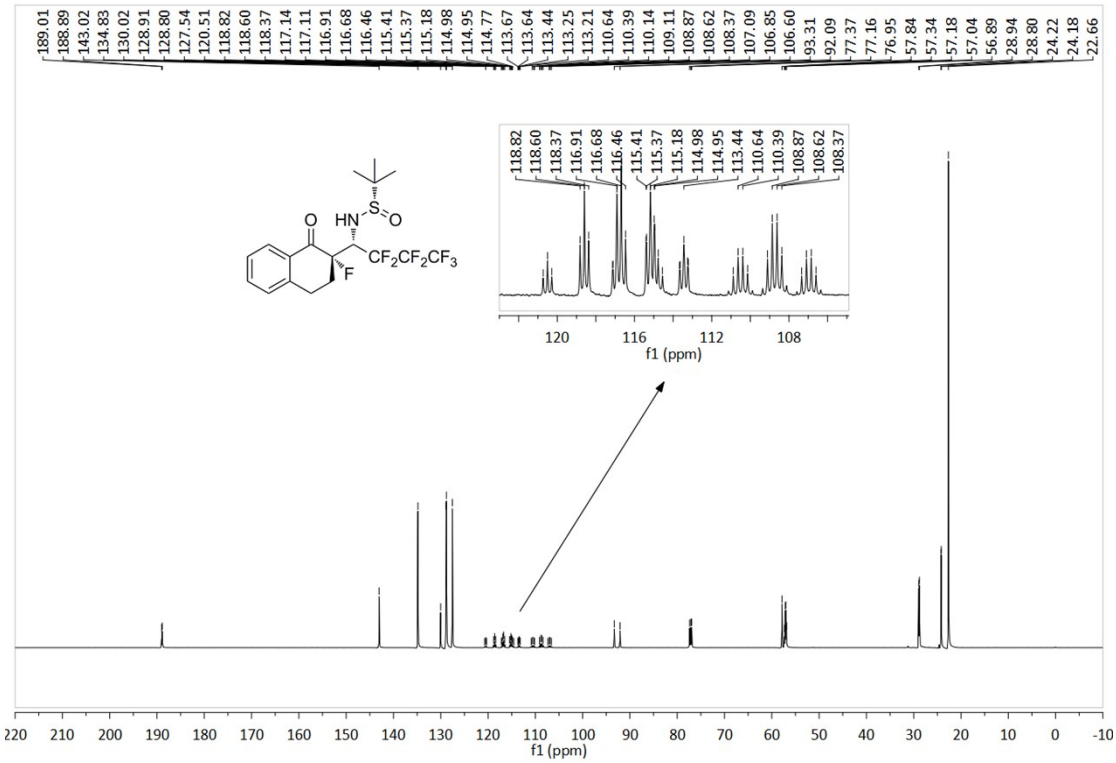
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



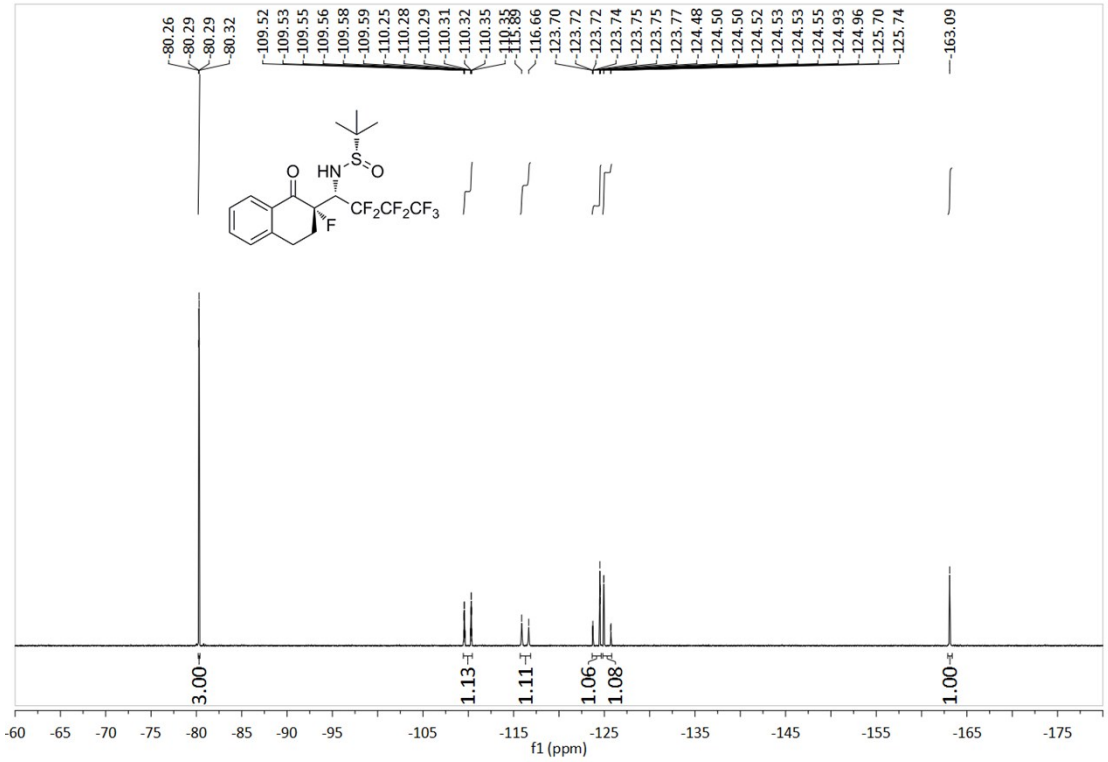
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3le**



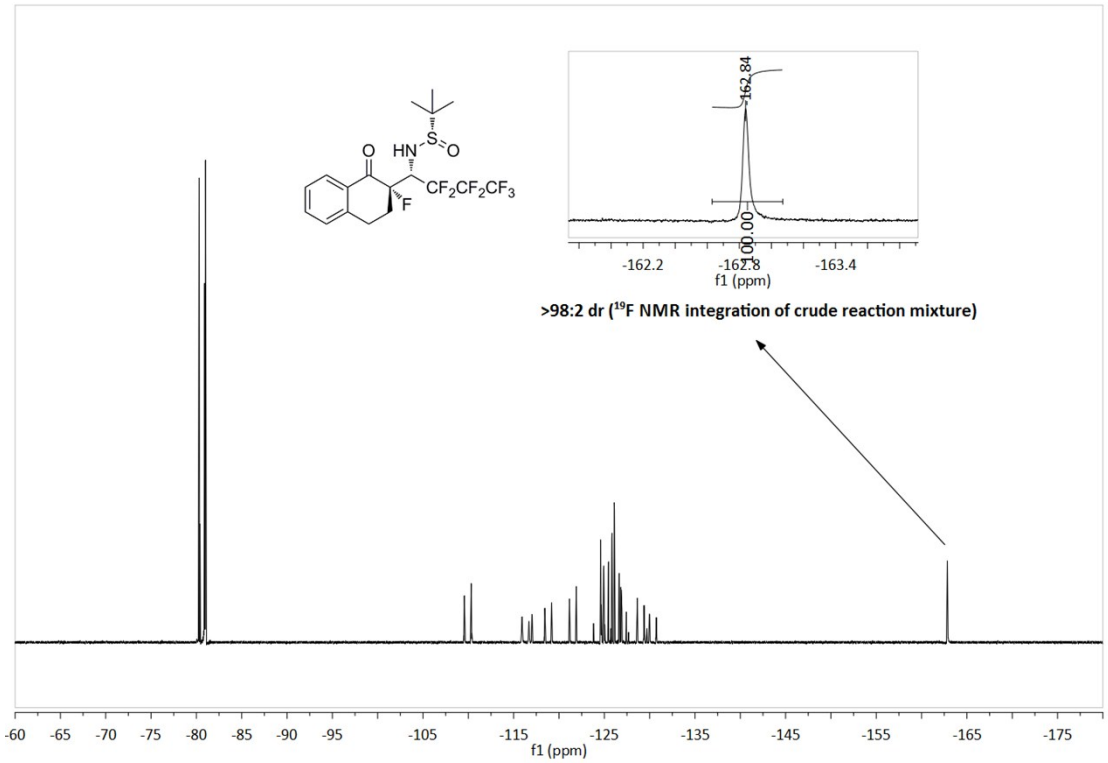
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3le**



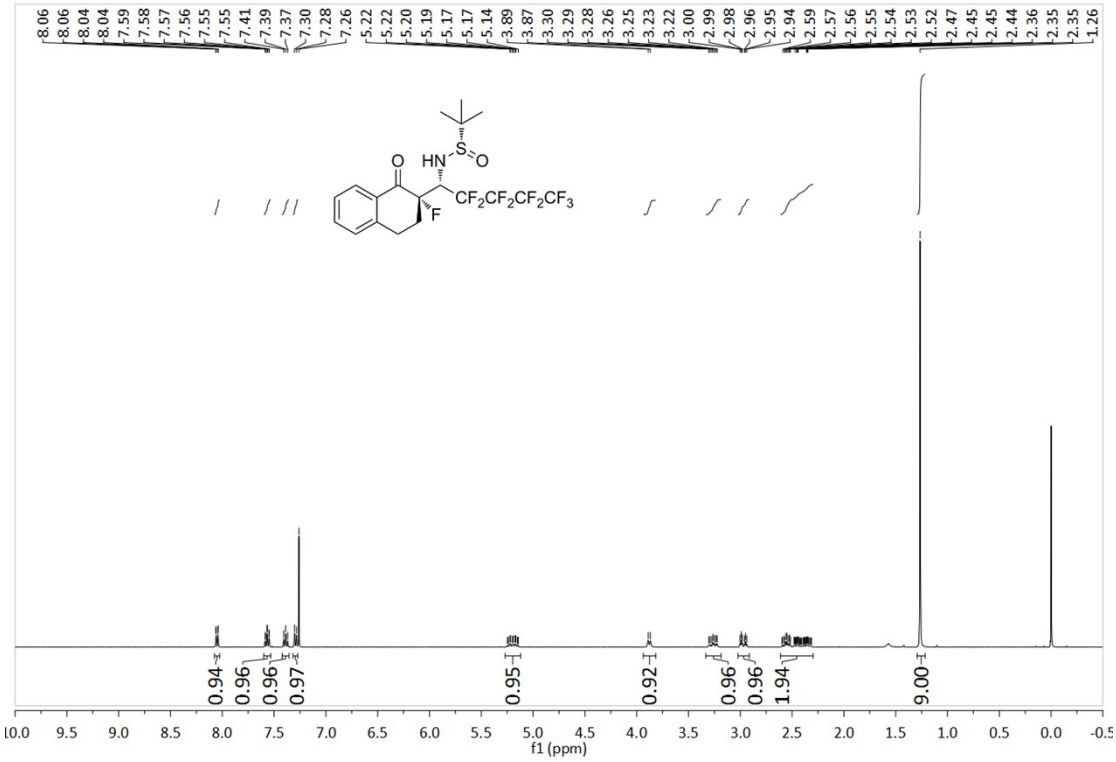
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3le**



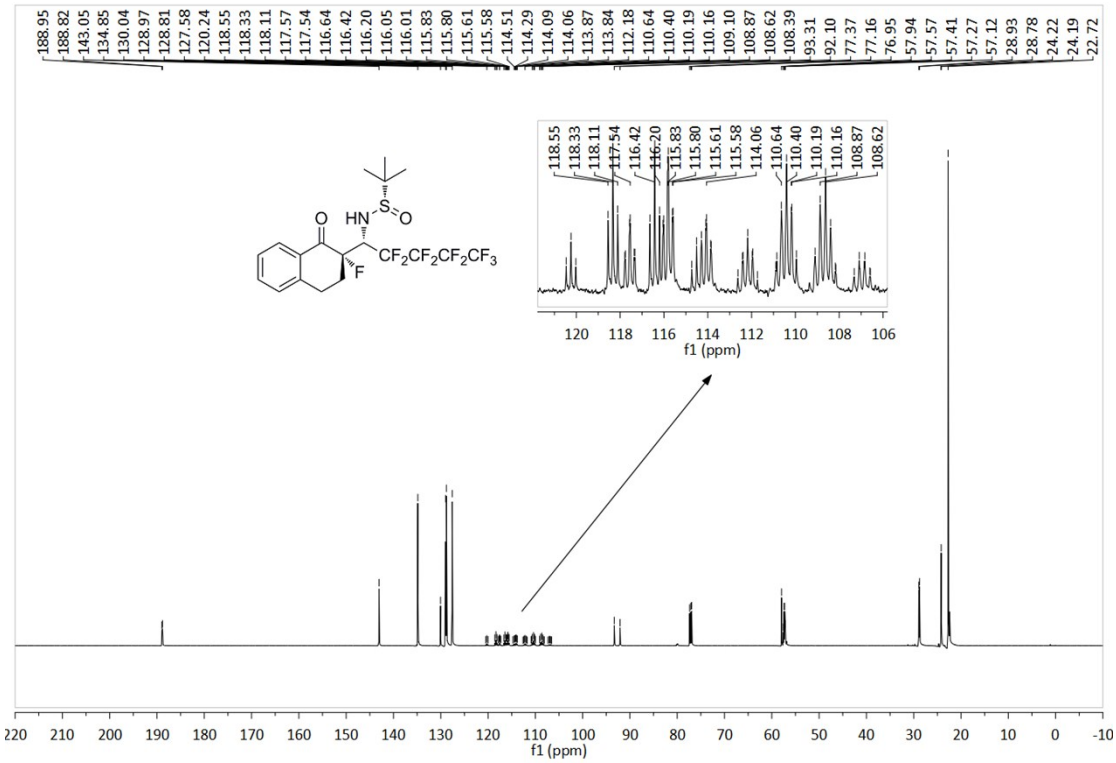
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



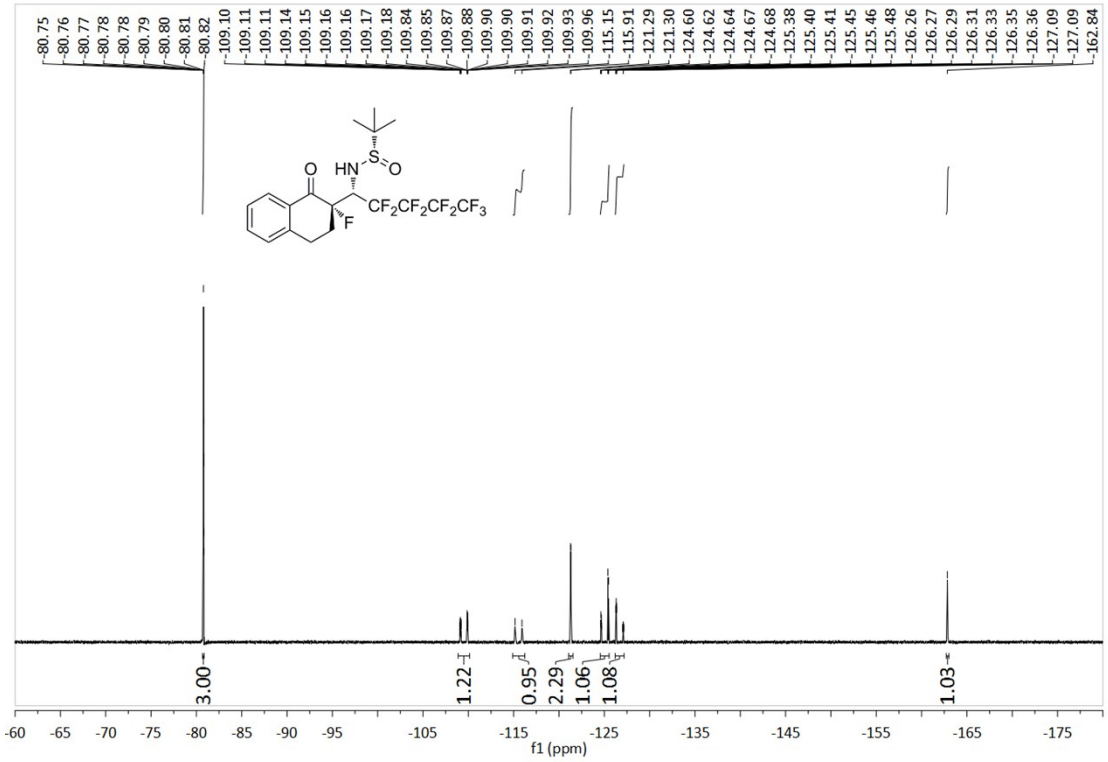
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3lf**



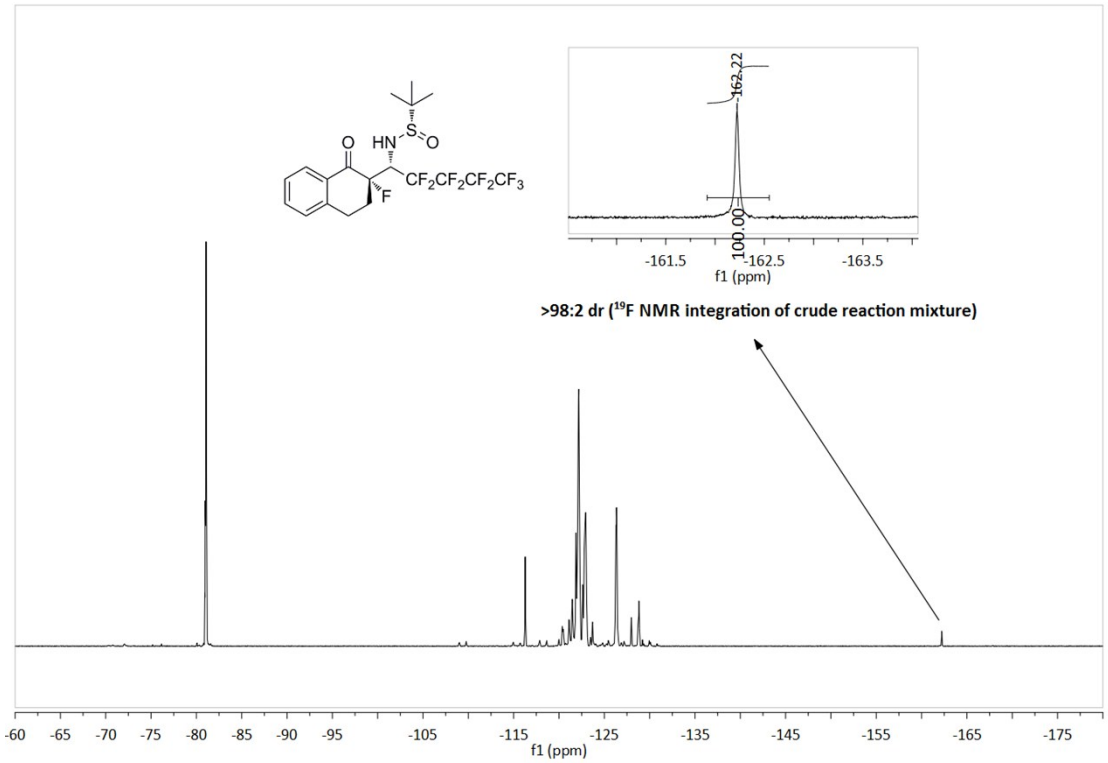
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3lf**



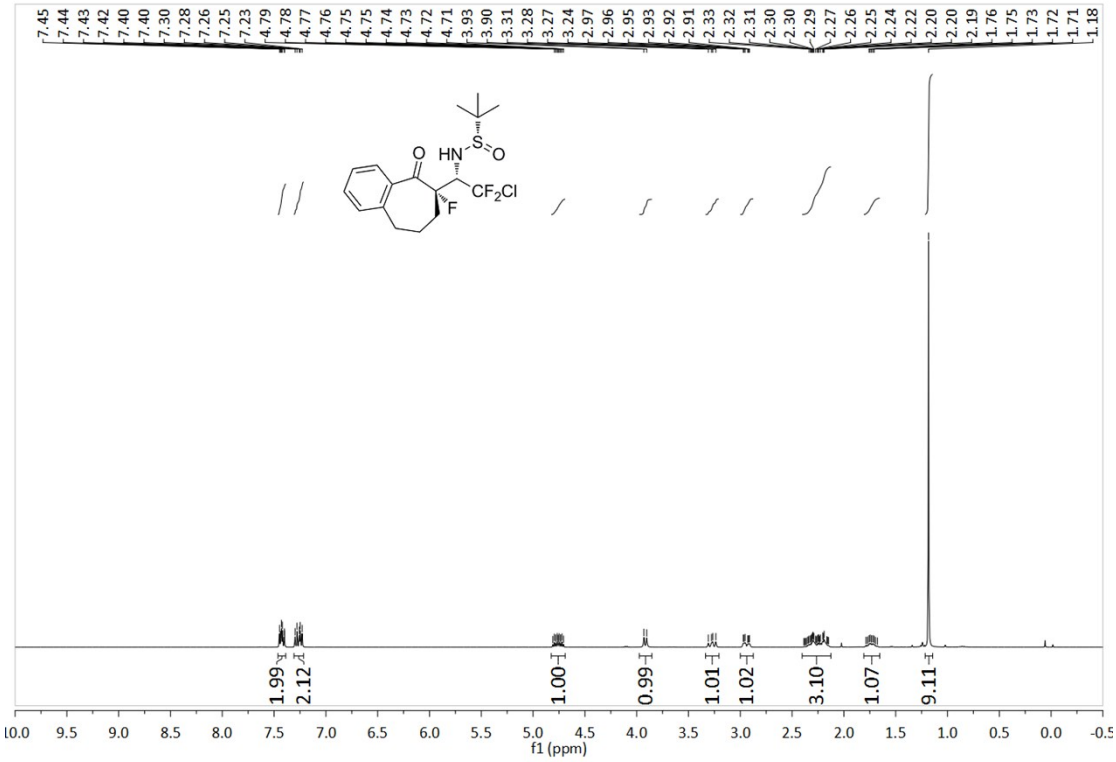
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3lf**



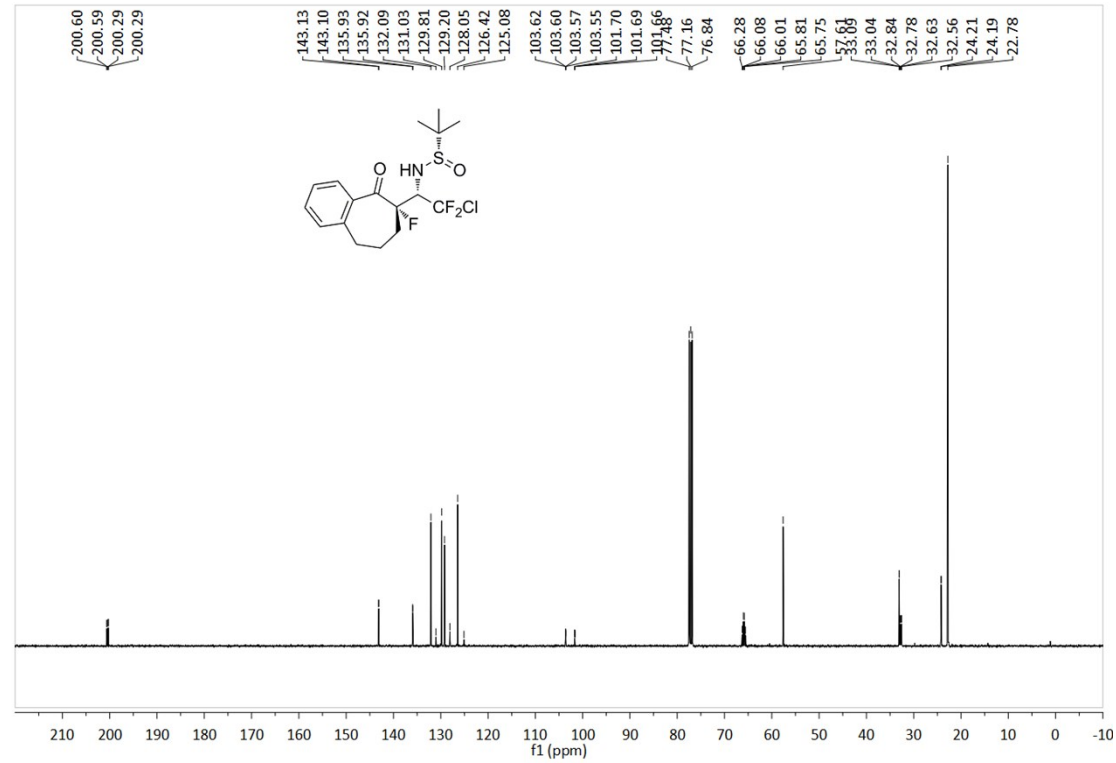
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



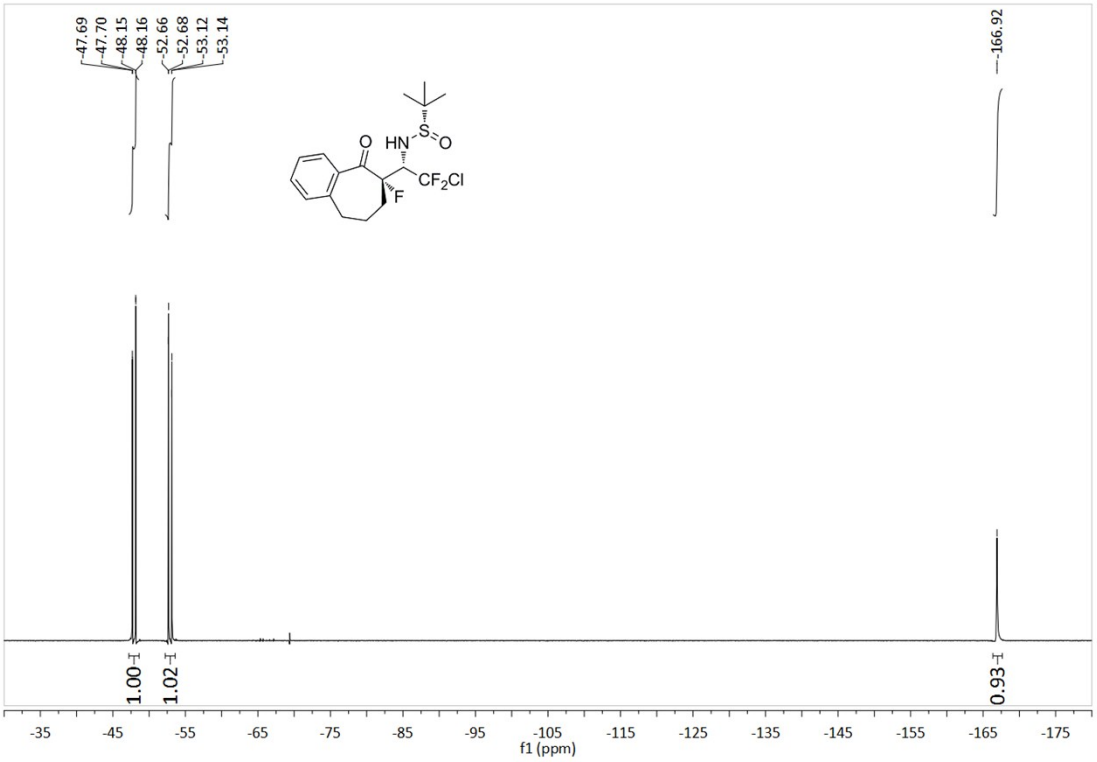
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ob**



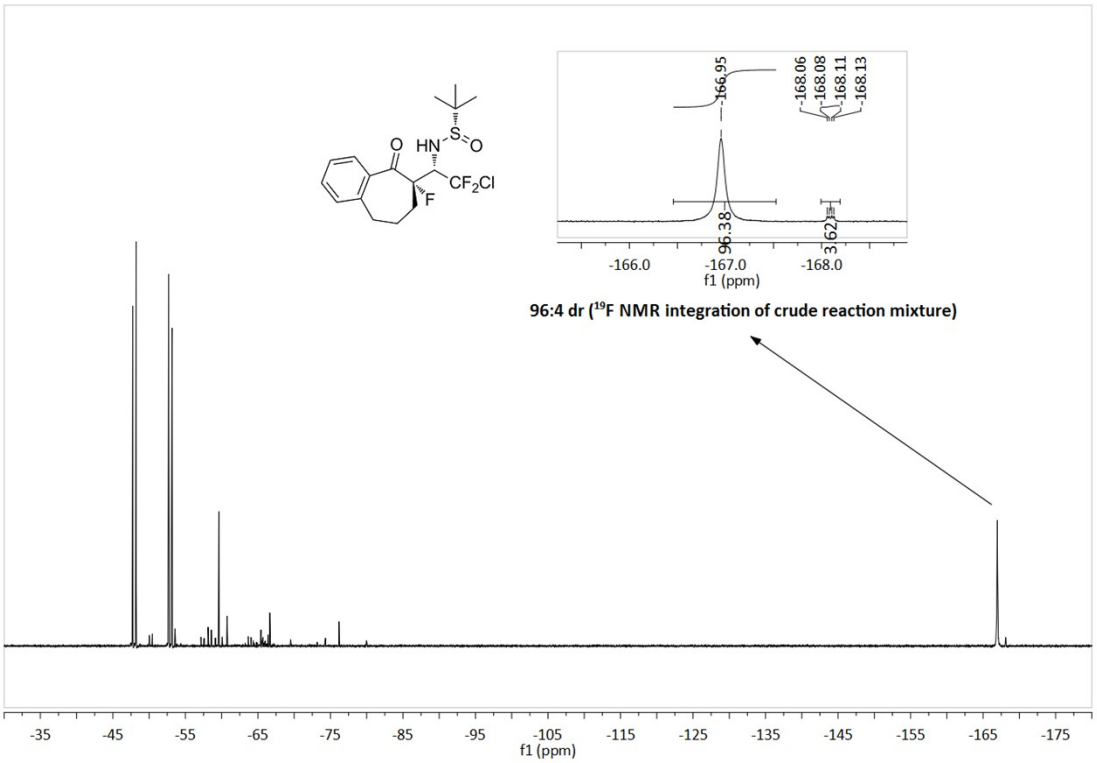
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ob**



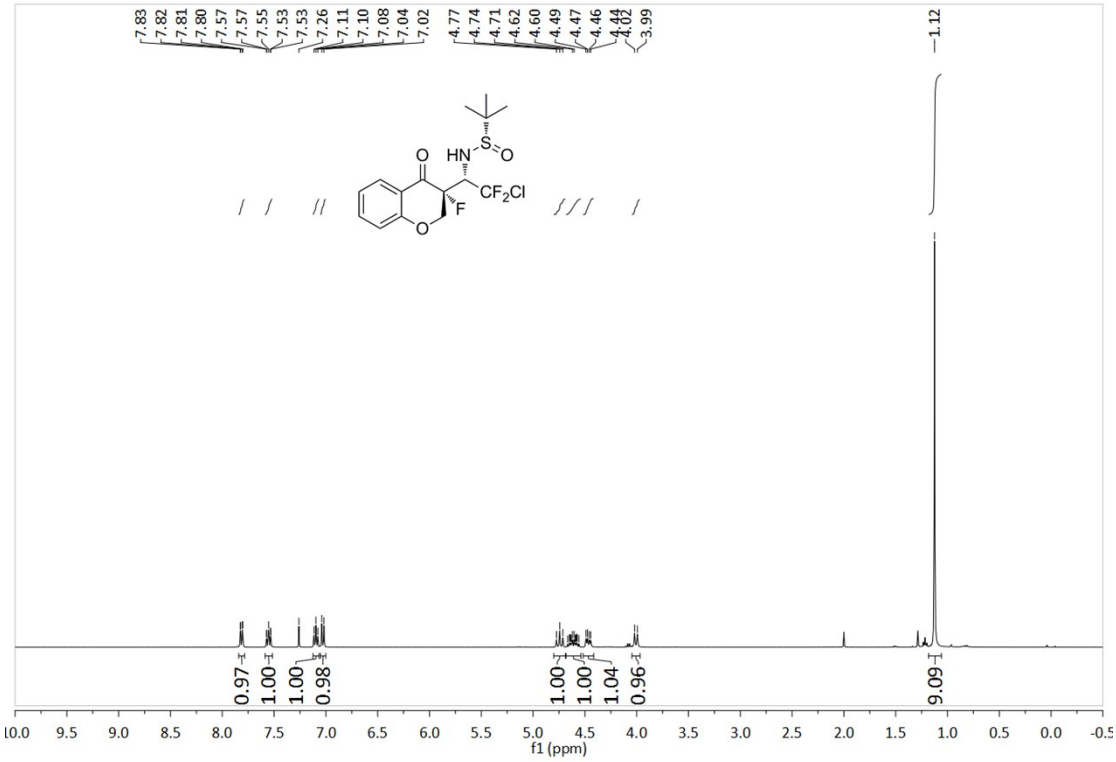
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ob**



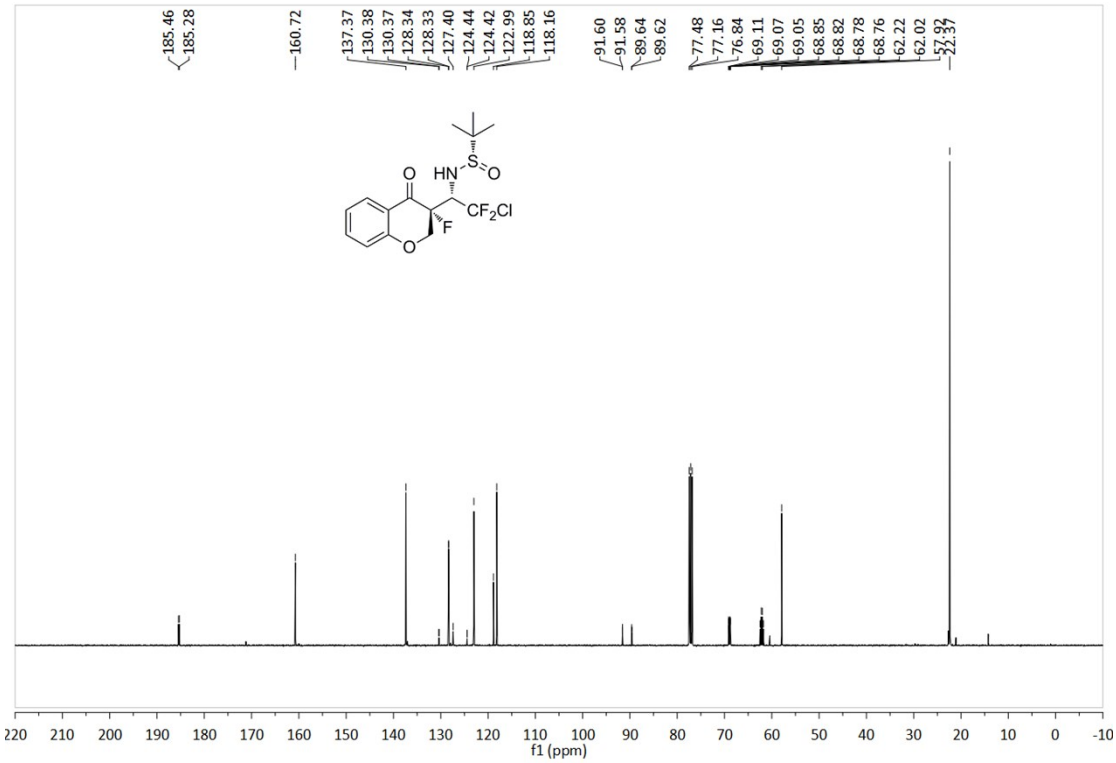
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



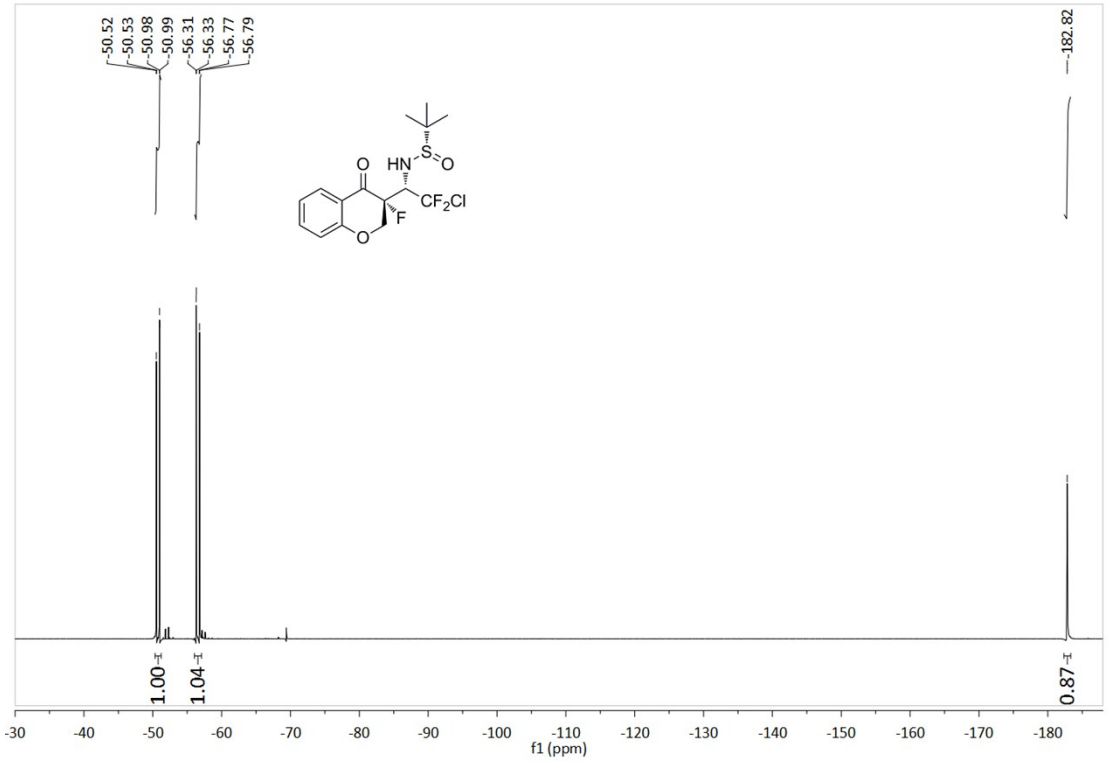
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3pb**



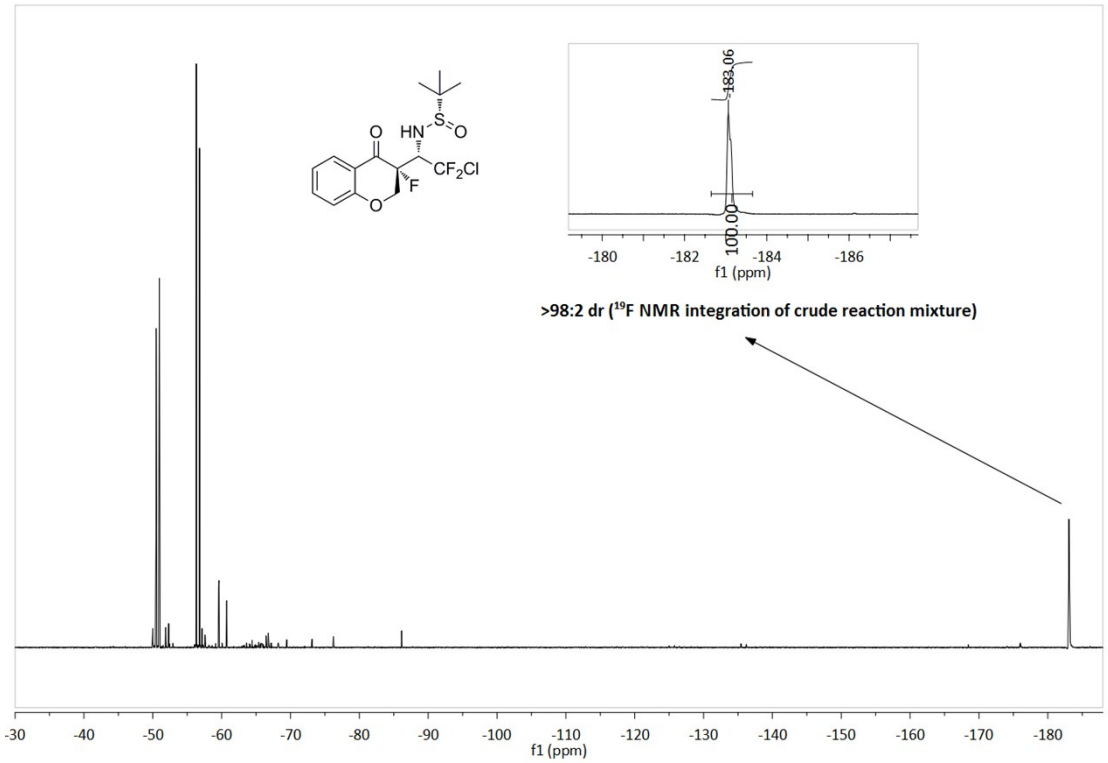
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3pb**



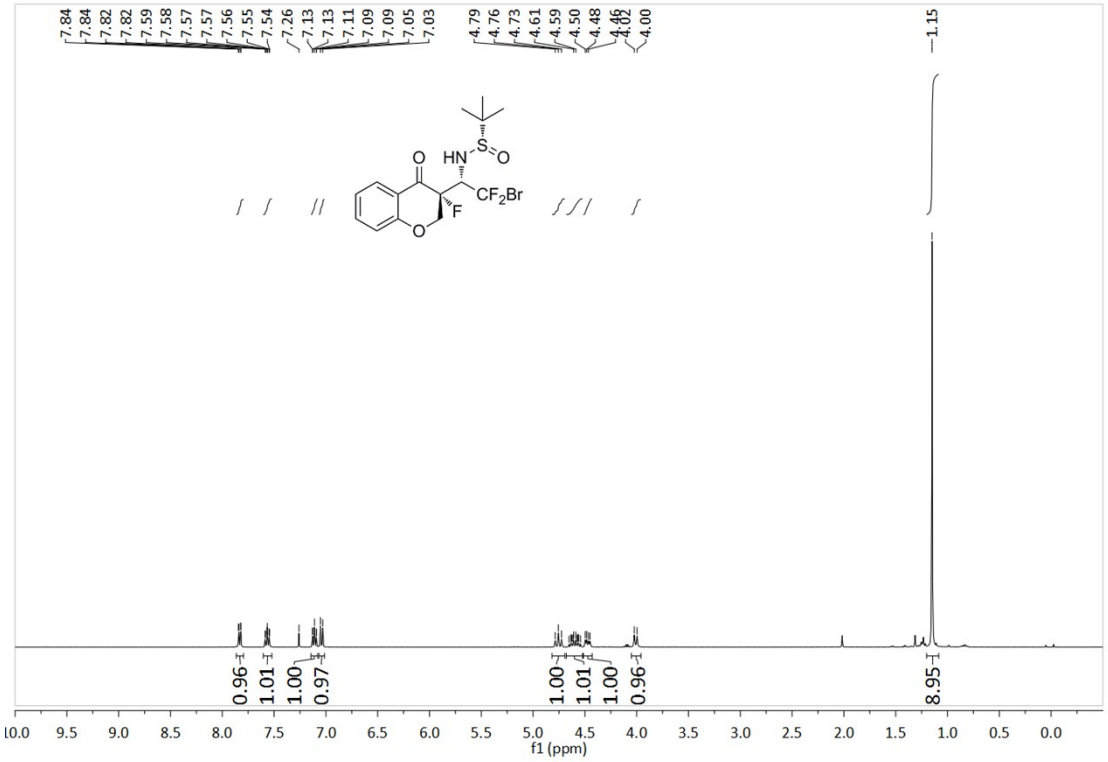
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3pb**



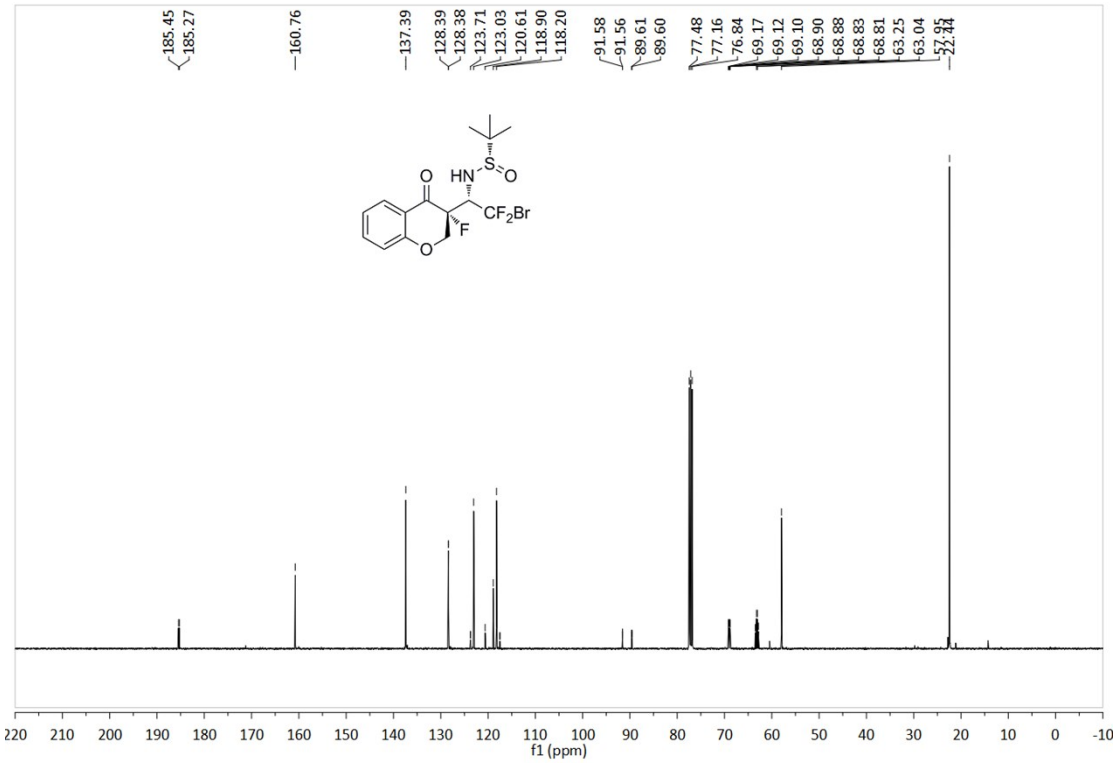
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



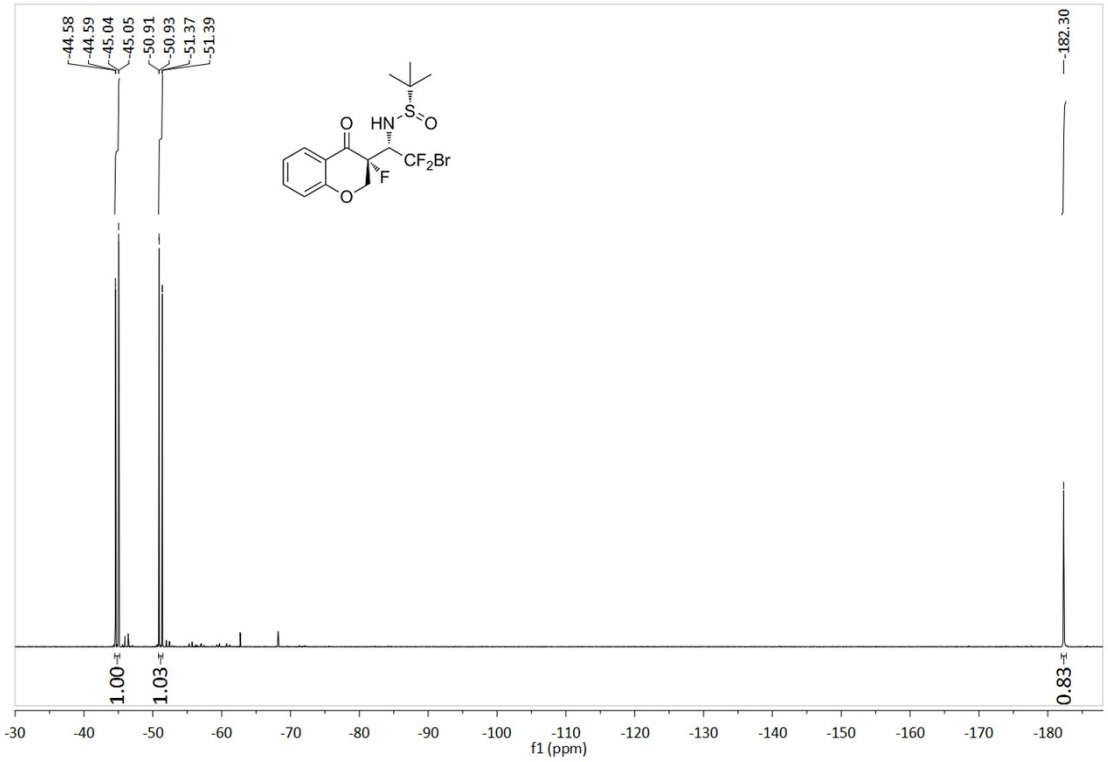
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3pc**



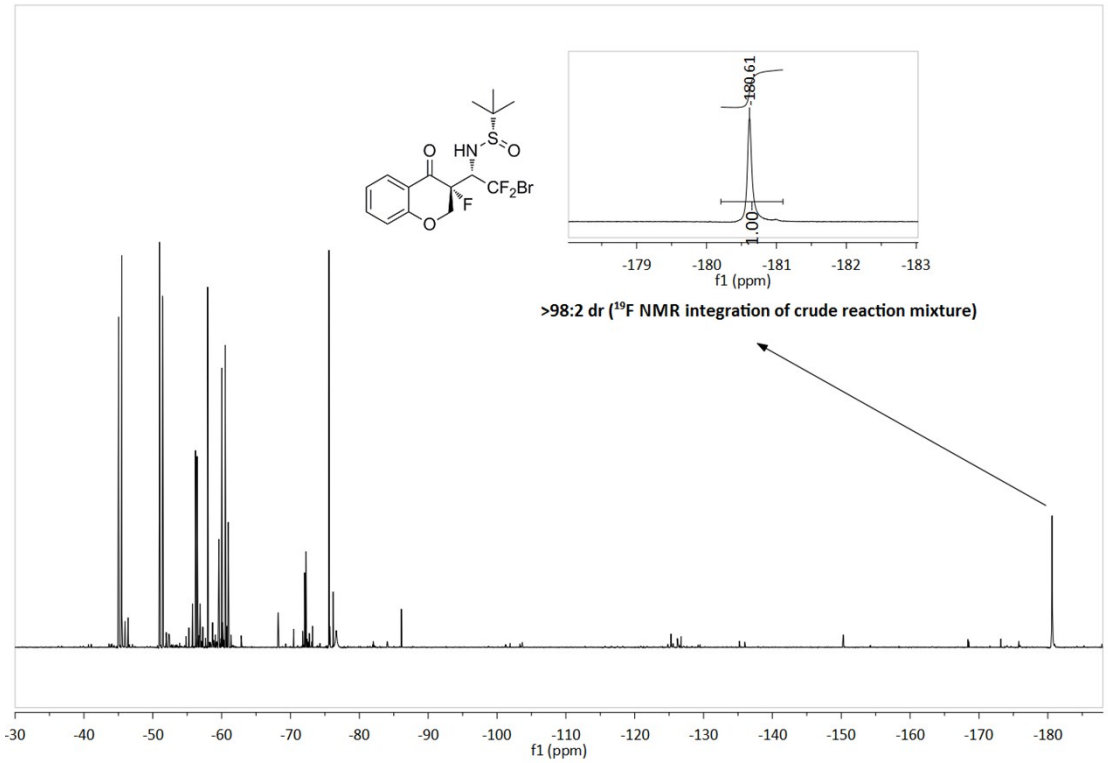
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3pc**



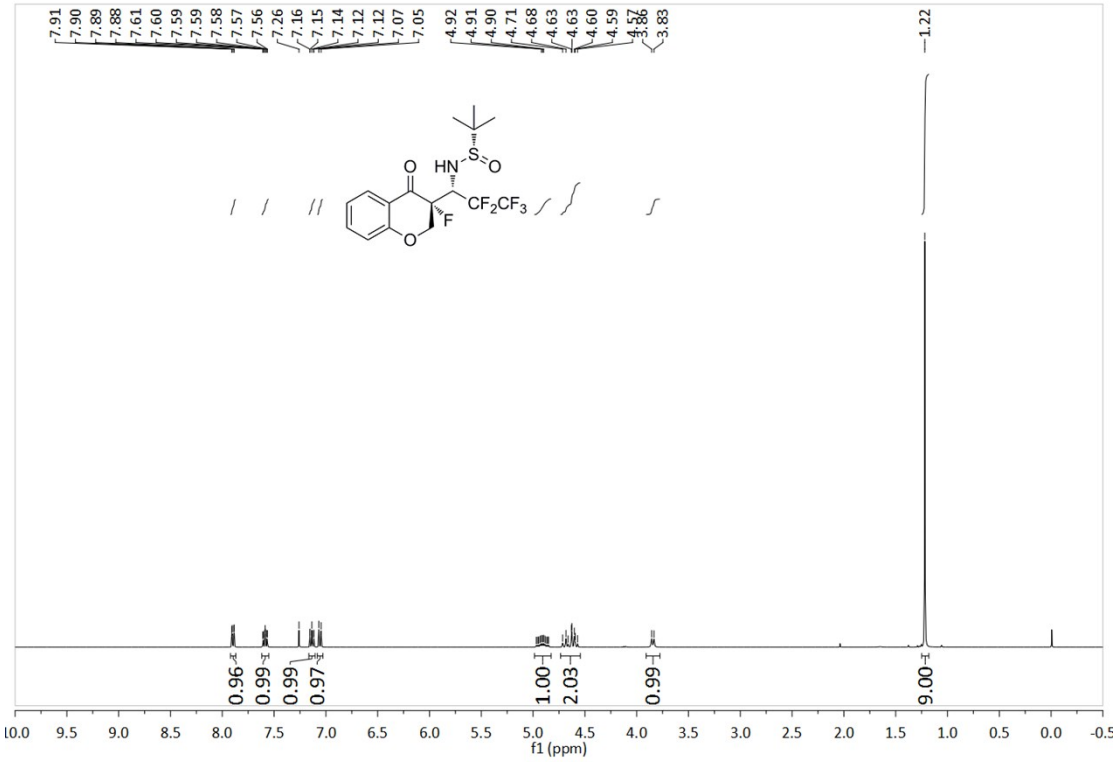
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3pc**



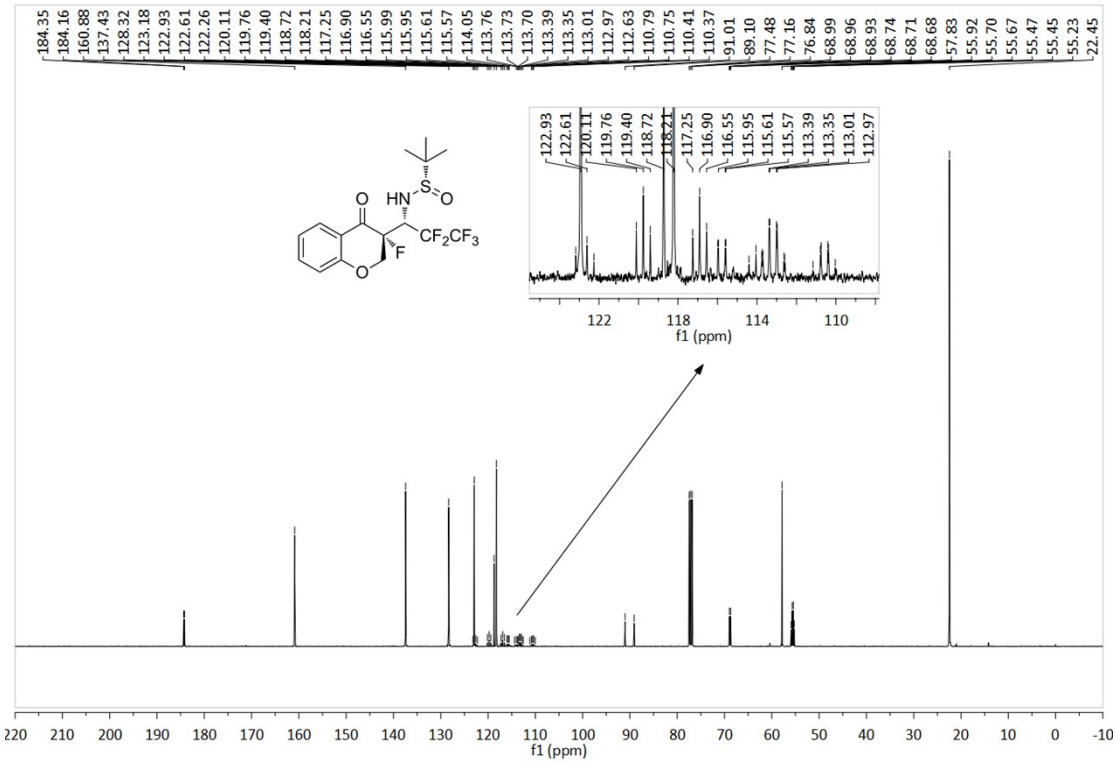
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture



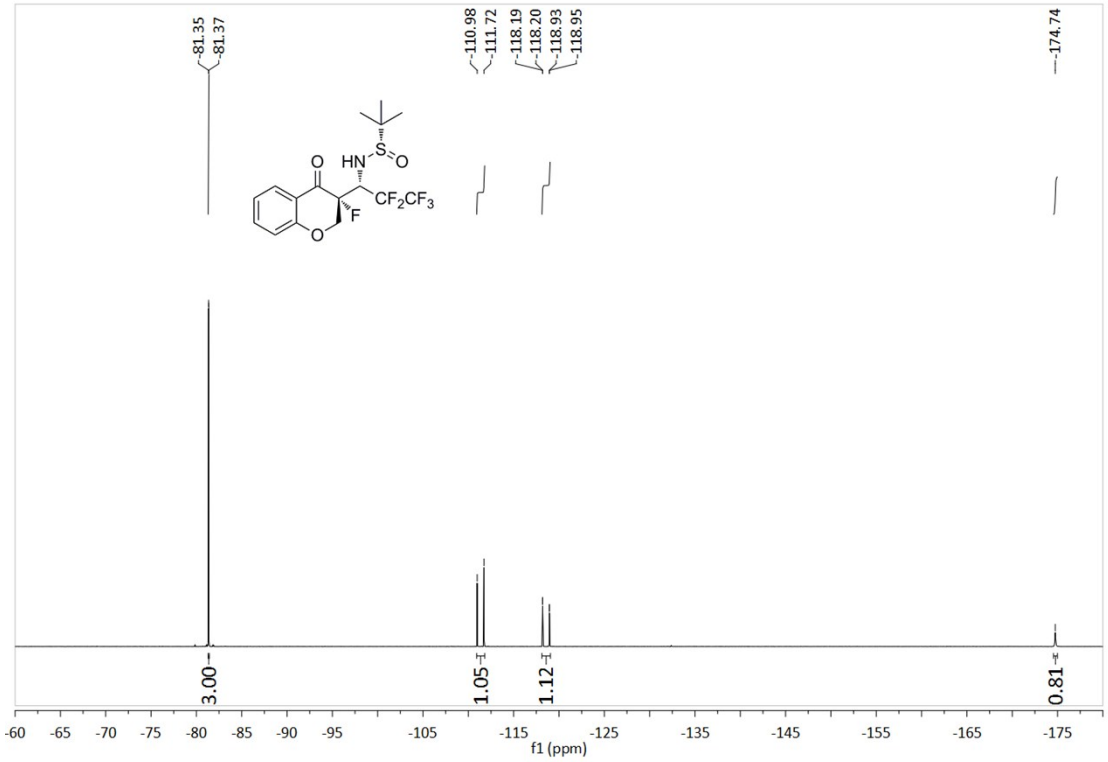
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3pd**



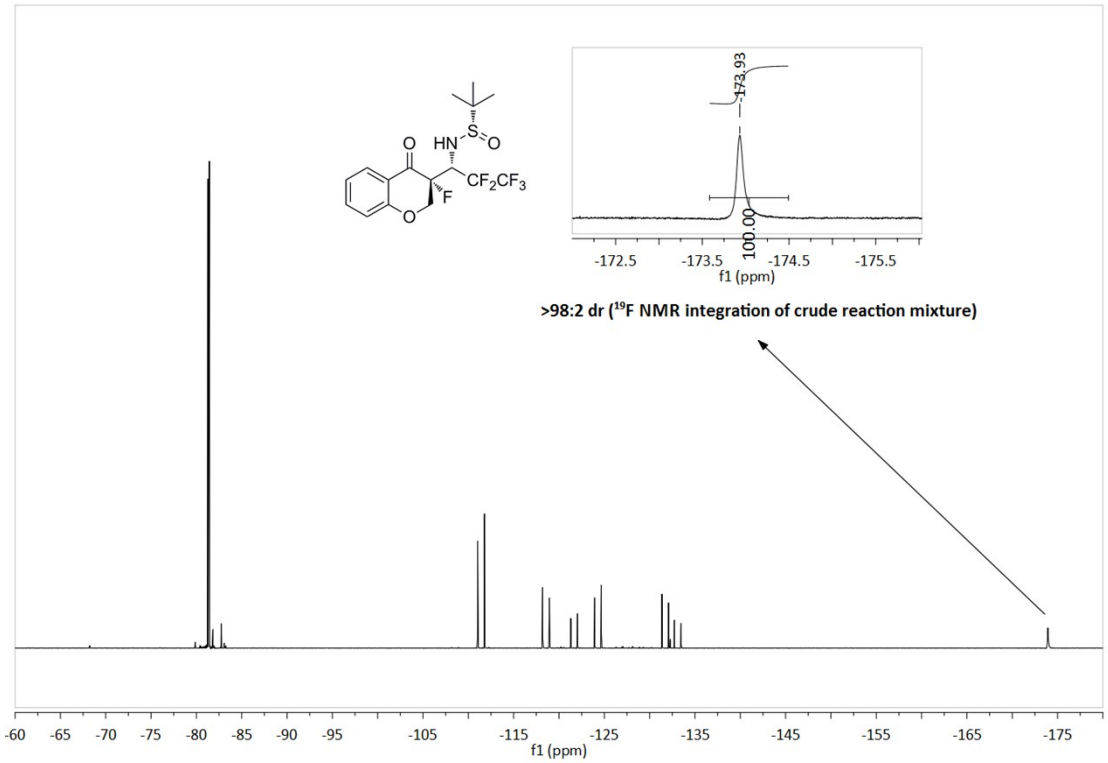
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3pd**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3pd**

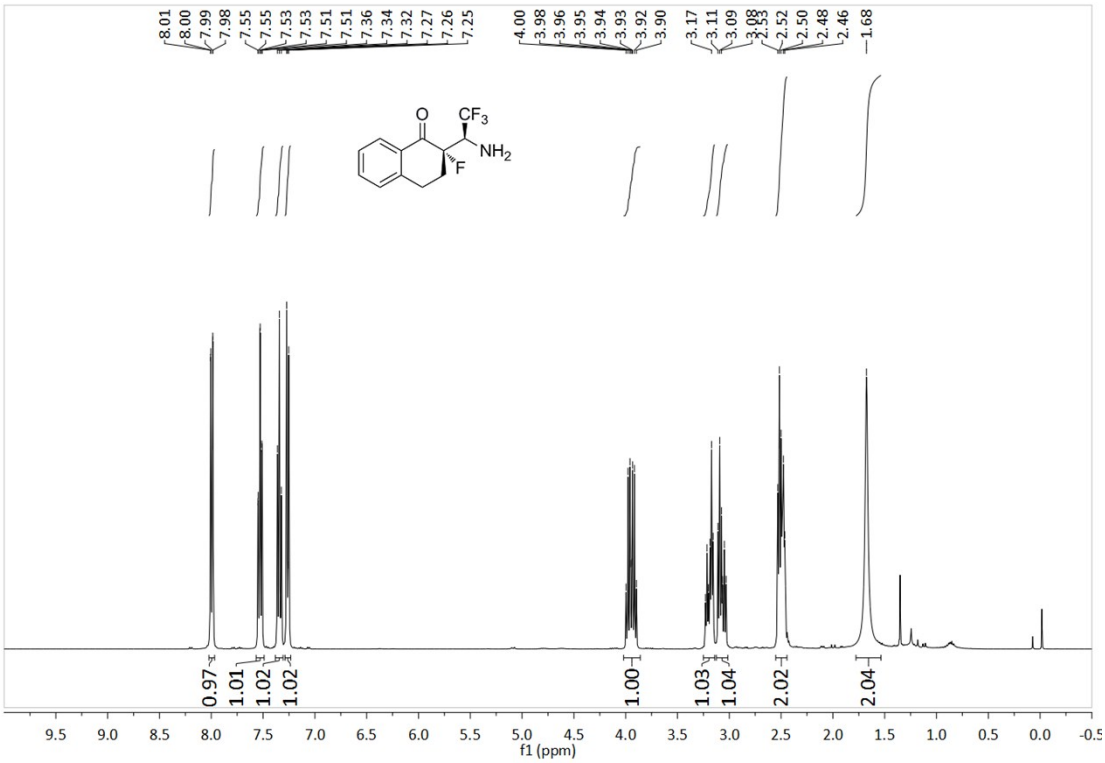


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the crude reaction mixture

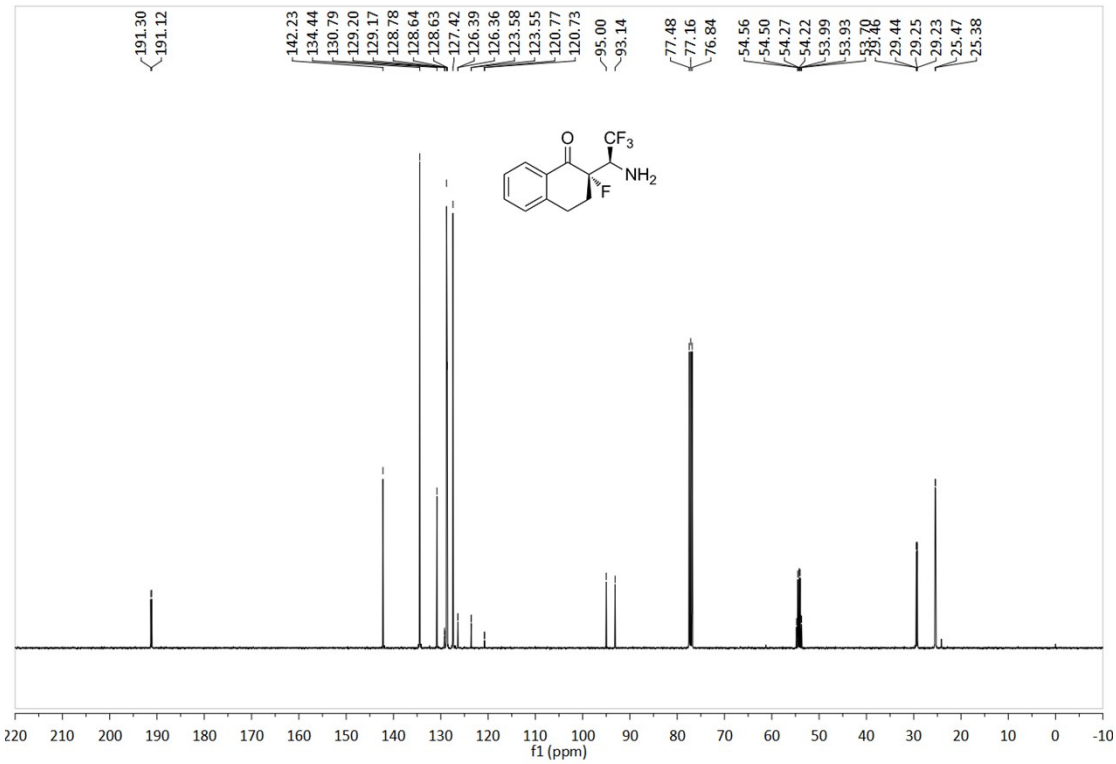


5.3. NMR spectra of the deprotection product 5

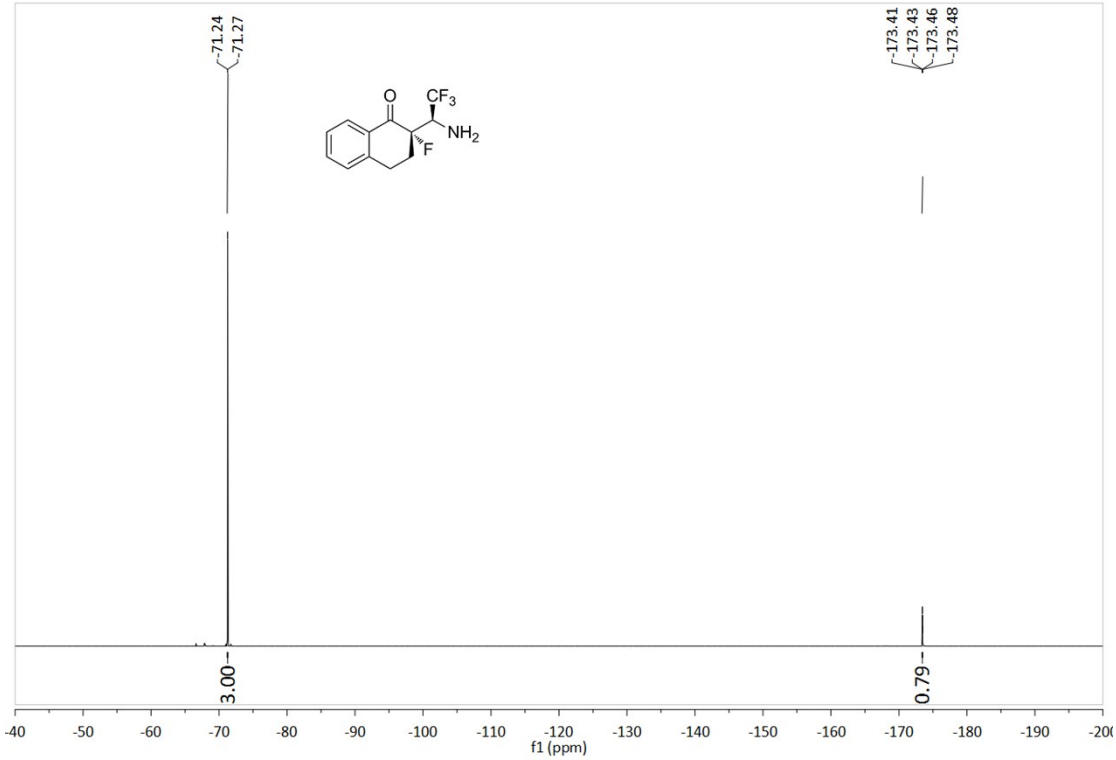
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5**

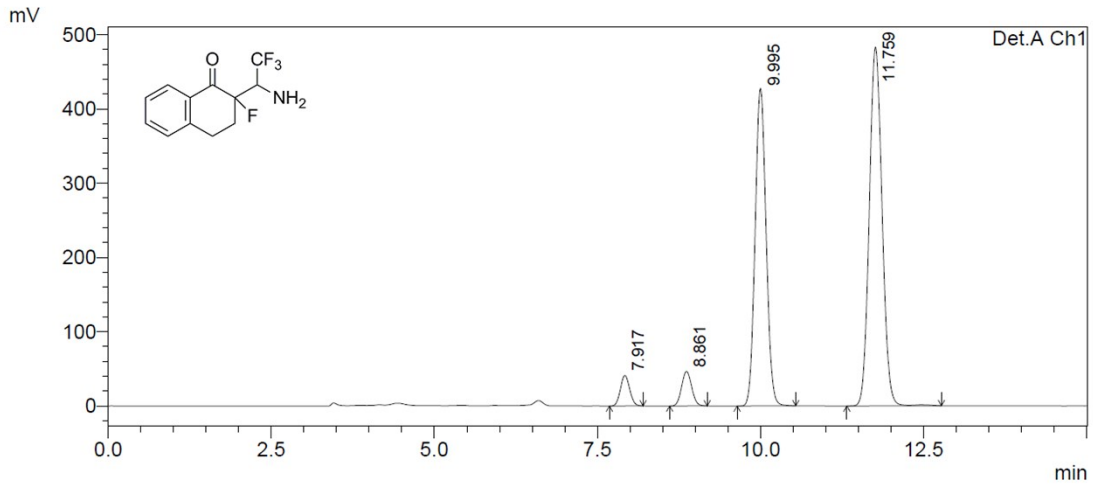


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5**



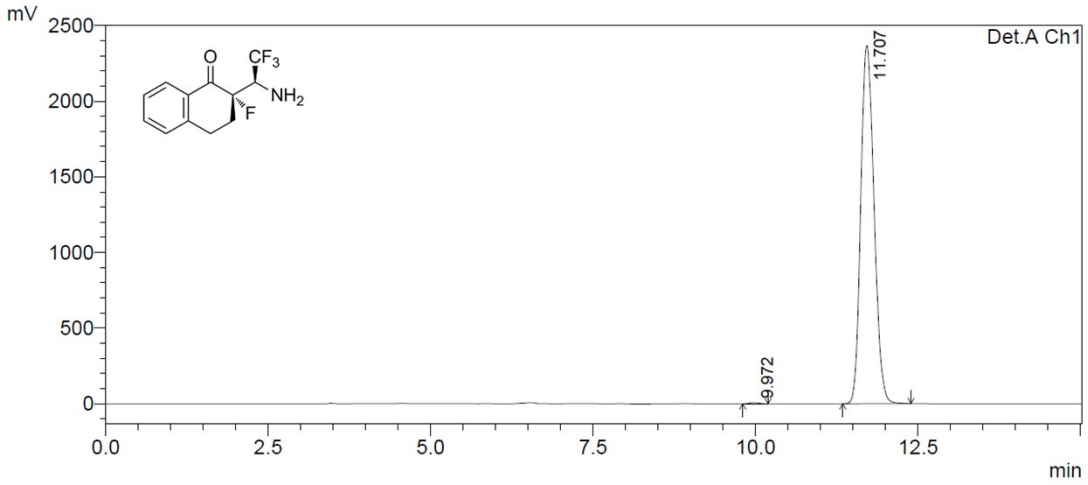
6. HPLC spectra of the deprotection product 5

HPLC spectrum of **racemic-5**



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.917	406957	41027	3.250	4.109
2	8.861	500260	46647	3.995	4.672
3	9.995	4996534	427849	39.899	42.848
4	11.759	6619258	483007	52.857	48.372
Total		12523009	998531	100.000	100.000

HPLC spectrum of deprotection product **5**



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.972	78201	7103	0.231	0.299
2	11.707	33820220	2367362	99.769	99.701
Total		33898421	2374465	100.000	100.000