Supporting Information

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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 ($\delta$) relative to internal tetramethylsilane (TMS, $\delta$ 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 $\alpha$-fluorinated gem-diols 1

\[
\text{To a stirred solution of sodium methoxide (100 mmol) in diethyl ether (50 mL) was added dropwise the solution of trifluoromethyl ethyl acetate (52.5 mmol) and cyclic ketones (50 mmol) in diethyl ether (50 mL), the mixture was stirred for 24 h at room temperature. Then the resulting mixture was diluted with 1 M HCl solution (pH = 3) and extracted with ether, the combined organics were dried over MgSO}_4 and concentrated under reduced pressure to afford intermediate di-ketone which was used in the next step without further purification. A solution of intermediate di-ketone (50 mmol) in acetonitrile (100 mL) was treated with Selectfluor (60 mmol) at room temperature. After 24 h, the reaction was diluted with ethyl acetate}
\]
(500 mL) and filtered through Celite. The residue was washed with H₂O (2 × 200 mL) and brine solution (1 × 200 mL) and dried with anhydrous Na₂SO₄, 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)

\[
\text{R}^1 = CF_2, CF_2C\equiv, CF_2Br
\]

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 Et₃N (40.5 mg, 0.4 mmol) dropwise. After 5 min, the reaction was quenched with saturated aqueous NH₄Cl (2 mL) followed by H₂O (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 H₂O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na₂SO₄, 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)

\[
\text{R}_F = CF_3CF_2, CF_2CF_2CF_3
\]

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 MgSO₄ (120.4 mg, 1.0 mmol) and heated at 40 °C for 4 h. After cooled to room temperature, MgSO₄ 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 °C was added Et₃N (40.5 mg, 0.4 mmol) dropwise. After 5 min, the reaction was quenched with saturated aqueous NH₄Cl (2 mL) followed by H₂O (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 H₂O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na₂SO₄, 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)

![Chemical reaction diagram]

Ethyl nonafluorovalerate (2.0 mmol) was dissolved in Et₂O (1 mL) and then this solution was added slowly to a solution of LiAlH₄ (22.8 mg, 0.6 mmol) in Et₂O (3 mL) at -78 °C for 5 min. After addition, the reaction mixture was stirred for 12 h at -78 °C. Then, concentrated sulfuric acid (0.1 mL) and ice water (3 mL) was added successively after the reaction mixture was warmed to 0 °C. The resulting mixture was extracted with ether (3 × 5 mL), then the combined organic layer was washed with H₂O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na₂SO₄, 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$_3$N (40.5 mg, 0.4 mmol) dropwise. After 5 min, the reaction was quenched with saturated aqueous NH$_4$Cl (2 mL) followed by H$_2$O (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$_2$O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na$_2$SO$_4$, 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

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$_2$Cl$_2$ (10 mL) and Et$_3$N (1.52 g, 15 mmol) was added. The mixture was stirred at 20 °C for 1 h, then H$_2$O (10 mL) was added. The organic layer was taken, washed with H$_2$O (2 × 10 mL), dried with anhydrous Na$_2$SO$_4$, 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

![Chemical structure](image)

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

White solid, 11.02 g (83% yield), m.p. 106–107 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 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) $\delta$ -78.04 (d, $J = 11.9$ Hz, 3F), -168.95 (q, $J = 11.8$ Hz, 1F); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 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).

![Chemical structure](image)

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

Yellow solid, 12.32 g (72% yield), m.p. 96–97 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 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) $\delta$ -77.84 (d, $J = 12.1$ Hz, 3F), -169.79 (q, $J = 12.1$ Hz, 1F); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 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).

![Chemical structure](image)

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

Yellow solid, 11.06 g (75% yield), m.p. 103–104 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 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) $\delta$ -78.25 (d, $J = 11.7$ Hz, 3F),
-167.21 (q, J = 11.7 Hz, 1F); ¹³C 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-1H-inden-1-one (1d)

Yellow solid, 12.08 g (86% yield), m.p. 115–116 °C. ¹H 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);

¹⁹F 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);

¹³C 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-1H-inden-1-one (1e)

White solid, 12.45 g (83% yield), m.p. 119–120 °C. ¹H 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);

¹⁹F NMR (376 MHz, DMSO) δ -78.02 (d, J = 12.0 Hz, 3F), -169.04 (q, J = 11.9 Hz, 1F);

¹³C 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-1H-inden-1-one (1f)

Yellow solid, 13.88 g (81% yield), m.p. 113–114 °C. ¹H 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);

¹⁹F NMR (376 MHz, DMSO) δ -77.95 (d, J = 12.0 Hz, 3F), -169.25 (q, J = 11.9 Hz, 1F);
NMR (101 MHz, DMSO) $\delta$ 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-1H-inden-1-one (1g)
White solid, 10.63 g (76% yield), m.p. 95–96 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 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) $\delta$ -78.10 (d, $J = 11.7$ Hz, 3F), -168.54 (q, $J = 11.7$ Hz, 1F); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 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-1H-inden-1-one (1h)
White solid, 10.98 g (78% yield), m.p. 91–92 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 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), 3.91 (dd, $J = 18.0$, 8.6 Hz, 1H); $^{19}$F NMR (376 MHz, DMSO) $\delta$ -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) $\delta$ 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-1H-inden-1-one (1i)
White solid, 12.71 g (85% yield), m.p. 95–96 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 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).
Hz, 1H), 3.21 (dd, \( J = 24.5, 18.0 \) Hz, 1H); \(^{19}\)F NMR (376 MHz, DMSO) \( \delta = -77.97 \) (d, \( J = 12.0 \) Hz, 3F), -169.18 (q, \( J = 12.0 \) Hz, 1F); \(^{13}\)C NMR (101 MHz, DMSO) \( \delta = 196.4 \) (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).

Yellow solid, 14.10 g (82% yield), m.p. 96–97 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta = 7.93 \) (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) \( \delta = -77.96 \) (d, \( J = 12.0 \) Hz, 3F), -169.24 (q, \( J = 11.9 \) Hz, 1F); \(^{13}\)C NMR (101 MHz, DMSO) \( \delta = 196.3 \) (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).

White solid, 11.71 g (72% yield), m.p. 120–121 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta = 7.81 \) (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) \( \delta = -78.30 \) (d, \( J = 11.8 \) Hz, 3F), -167.06 (q, \( J = 11.6 \) Hz, 1F); \(^{13}\)C NMR (101 MHz, DMSO) \( \delta = 195.9 \) (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).

White solid, 9.93 g (71% yield), m.p. 82–83 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta = 7.88–7.78 \) (m, 2H), \( \delta = 3.83–3.73 \) (m, 4H), 3.09 (dd, \( J = 24.5, 17.9 \) Hz, 1H); \(^{19}\)F NMR (376 MHz, DMSO) \( \delta = -78.80 \) (d, \( J = 11.8 \) Hz, 3F), -167.06 (q, \( J = 11.6 \) Hz, 1F); \(^{13}\)C NMR (101 MHz, DMSO) \( \delta = 195.9 \) (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).
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) \( \delta -78.48 \) (d, \( J = 14.3 \) Hz, 3F), -162.12 (q, \( J = 14.2 \) Hz, 1F); \(^{13}\)C NMR (101 MHz, DMSO) \( \delta 192.4 \) (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).

![Image of the molecule](attachment:image.png)

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

White solid, 10.44 g (68% yield), m.p. 75–76 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta 7.84 \) (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) \( \delta -78.45 \) (d, \( J = 14.4 \) Hz, 3F), -162.09 (q, \( J = 14.4 \) Hz, 1F); \(^{13}\)C NMR (101 MHz, DMSO) \( \delta 192.1 \) (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).

![Image of the molecule](attachment:image.png)

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

White solid, 13.59 g (76% yield), m.p. 87–88 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta 7.94 \) (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) \( \delta -78.55 \) (d, \( J = 14.5 \) Hz, 3F), -162.93 (q, \( J = 14.5 \) Hz, 1F); \(^{13}\)C NMR (101 MHz, DMSO) \( \delta 191.3 \) (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\textit{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) $\delta$ 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) $\delta$ -77.96 (d, $J = 14.5$ Hz, 3F), -159.52 (q, $J = 14.3$ Hz, 1F); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 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) $\delta$ 8.12 (s, 1H), 7.78–7.72 (m, 1H), 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) $\delta$ -78.60 (d, $J = 13.2$ Hz, 3F), -178.68 (q, $J = 13.1$ Hz, 1F); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 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\textit{H}-inden-2-yl)ethyl)propane-2-sulfinamide (3aa)

White solid, 68.4 mg (97% yield), m.p. 93–94 °C, $[\alpha]_{20}$ D = +94.1 (c = 0.20, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -69.01 (d, $J = 7.2$ Hz, 3F), -156.36 (q, $J$
= 7.2 Hz, 1F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 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$_4$NO$_2$SNa$^+$ [M+Na]$^+$ 374.0808, found 374.0810.

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

White solid, 74.2 mg (86% yield), m.p. 140–141 $^\circ$C, $[\alpha]_{D}^20 = +70.5$ (c = 0.86, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -68.80 (d, $J = 7.5$ Hz, 3F), -157.11 (q, $J = 7.4$ Hz, 1F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 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$_4$NO$_2$SNa$^+$ [M+Na]$^+$ 451.9913, found 451.9912.

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

White solid, 59.4 mg (78% yield), m.p. 126–127 $^\circ$C, $[\alpha]_{D}^20 = +76.6$ (c = 0.80, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -69.05 (d, $J = 7.4$ Hz, 3F), -156.06 (q, $J = 7.3$ Hz, 1F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.8 (d, $J = 17.4$ 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, $J = 283.6, 9.7$ Hz), 12.5. 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$_{4}$NO$_{3}$SNa$^{+}$ [M+Na]$^{+}$ 404.0914, found 404.0916.

![Chemical Structure](image)

(S)-N-((S)-2,5-difluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfonamide (3a)

White solid, 73.0 mg (99% yield), m.p. 90–91 °C, [α]$_{20}$D = +93.8 (c = 0.42, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -68.82 (d, $J = 7.5$ Hz, 3F), -97.82 (s, 1F), -156.87 (q, $J = 7.5$ Hz, 1F);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.2 (d, $J = 17.5$ 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, $J = 24.3$ 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$_{5}$NO$_{2}$SNa$^{+}$ [M+Na]$^{+}$ 392.0714, found 392.0714.

![Chemical Structure](image)

(S)-N-((S)-5-chloro-2-fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfonamide (3a)

White solid, 74.3 mg (96% yield), m.p. 110–111 °C, [α]$_{20}$D = +85.0 (c = 0.96, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 8.1$ Hz, 1H), 7.48–7.42 (m, 2H), 4.48 (d, $J = 14.5, 9.4, 7.2$ 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$_3$) $\delta$ -68.76 (d, $J = 7.5$ Hz, 3F), -157.33 (q, $J = 7.5$ Hz, 1F);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 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, $J = 24.3$ 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$_4$NO$_2$SNa$^+$ [M+Na]$^+$ 408.0419, found 408.0422.

(S)-N-((S)-5-bromo-2-fluoro-1-oxo-2,3-dihydro-1H-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$_2$Cl$_2$). $^1$H 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$_4$NO$_2$SNa$^+$ [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-1H-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$_2$Cl$_2$). $^1$H 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 (d, $J$ = 24.2, 1.7 Hz), 22.4, 21.1. IR (cm$^{-1}$): 3315, 1728, 1263, 1206, 1159, 1139, 1124, 1085. HRMS (TOF MS ESI): calcd for C$_{16}$H$_{19}$F$_4$NO$_2$SNa$^+$ [M+Na]$^+$ 388.0965, found 388.0966.
(S)-N-((S)-1-((S)-2,6-difluoro-1-oxo-2,3-dihydro-1H-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, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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); 19F NMR (376 MHz, CDCl3) δ -68.75 (d, J = 7.7 Hz, 3F), -111.45 (s, 1F), -157.88 (q, J = 7.6 Hz, 1F); 13C NMR (101 MHz, CDCl3) 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 C15H16F5NO2SNa⁺ [M+Na]⁺ 392.0714, found 392.0718.

(S)-N-((S)-1-((S)-6-chloro-2-fluoro-1-oxo-2,3-dihydro-1H-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, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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); 19F NMR (376 MHz, CDCl3) δ -68.72 (d, J = 7.6 Hz, 3F), -157.67 (q, J = 7.5 Hz, 1F); 13C NMR (101 MHz, CDCl3) 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 (d, 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 C15H16ClF3NO2SNa⁺ [M+Na]⁺ 408.0419, found 408.0422.
(S)-N-((S)-1-((S)-6-bromo-2-fluoro-1-oxo-2,3-dihydro-1H-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, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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 = 14.5 Hz, 1H), 3.33 (dd, J = 24.4, 18.2 Hz, 1H), 1.24 (s, 9H); 19F NMR (376 MHz, CDCl3) δ -68.83 (d, J = 7.2 Hz, 3F), -156.31 (q, J = 6.9 Hz, 1F); 13C NMR (101 MHz, CDCl3) 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, 1183, 1155, 1083, 824. HRMS (TOF MS ESI): calcd for C15H16BrF4NO2SNa⁺ [M+Na⁺] 451.9913, found 451.9916.

(3ka)

White solid, 64.3 mg (78% yield), m.p. 173–174 °C, [α]20 D = +78.8 (c = 0.62, CH2Cl2). 1H NMR (400 MHz, CDCl3) δ 7.21 (s, 1H), 6.85 (s, 1H), 4.53–4.40 (m, 1H), 4.02–3.89 (m, 1H), 3.56 (dd, J = 17.8, 13.5 Hz, 1H), 3.28 (dd, J = 23.7, 17.8 Hz, 1H), 1.25 (s, 9H); 19F NMR (376 MHz, CDCl3) δ -69.01 (d, J = 7.7 Hz, 3F), -157.06 (q, J = 7.5 Hz, 1F); 13C NMR (101 MHz, CDCl3) 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 (d, 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 C13H16BrF3NO3SNa⁺ [M+Na⁺] 434.1020, found 434.1022.

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

(3la)
Colorless oil, 72.3 mg (99% yield), [α]20 D = +26.7 (c = 0.26, CH2Cl2). 1H NMR (400 MHz, CDCl3): 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); 19F NMR (376 MHz, CDCl3) δ -68.24 (d, J = 8.9 Hz, 3F), -170.26 (q, J = 8.2 Hz, 1F); 13C NMR (101 MHz, CDCl3) 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 = 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): 1695, 1603, 1458, 1263, 1200, 1146, 1121, 1074, 915, 744, 707. HRMS (TOF MS ESI): calcd for C16H19F4NO2SNa⁺ [M+Na⁺] 388.0965, found 388.0970.

![Chemical structure](image)

**OCTF**

(3(S)-2-methyl-N-(3(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, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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); 19F NMR (376 MHz, CDCl3) δ -68.25 (d, J = 8.9 Hz, 3F), -170.29 (q, J = 8.2 Hz, 1F); 13C NMR (101 MHz, CDCl3) 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 C17H19F4NO3SNa⁺ [M+Na⁺] 418.1070, found 418.1073.

![Chemical structure](image)

**OCTB**

(3(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, CH2Cl2). 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, 1064, 1047, 931, 862. HRMS (TOF MS ESI): calcd for C$_{16}$H$_{18}$BrF$_4$NO$_2$SNa$^+$ [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-5H-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$_2$Cl$_2$). $^1$H 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, 1086, 646. HRMS (TOF MS ESI): calcd for C$_{17}$H$_{21}$F$_3$NO$_2$SNa$^+$ [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$_2$Cl$_2$). $^1$H 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 =
$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.21 (d, $J = 10.7$ Hz, 3F), -187.44 (q, $J = 10.2$ Hz, 1F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 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$_4$NO$_3$SNa$^+$ [M+Na]$^+$ 390.0757, found 390.0762.

White solid, 69.2 mg (94% yield), m.p. 45–46 °C, $[\alpha]_{20}^D = +95.2$ (c = 1.05, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -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$_3$) $\delta$ 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), 122.4. IR (cm$^{-1}$): 3200, 2961, 1732, 1608, 1469, 1211, 1105, 1069, 967, 734. HRMS (TOF MS ESI): calcd for C$_{15}$H$_{17}$ClF$_3$NO$_2$SNa$^+$ [M+Na]$^+$ 390.0513, found 390.0514.

White solid, 70.2 mg (85% yield), m.p. 47–48 °C, $[\alpha]_{20}^D = +79.7$ (c = 0.73, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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)-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, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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); 19F NMR (376 MHz, CDCl3) δ -51.74 (d, J = 172.8 Hz, 1F), -56.62 (d, J = 172.7 Hz, 1F), -165.98 (s, 1F); 13C NMR (101 MHz, CDCl3) 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 C16H19ClF3NO2SNa⁺ [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, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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 (dtdd, 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$_3$) $\delta$ -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$_3$) $\delta$ 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$_3$NO$_2$SNa$^+$ [M+Na]$^+$ 448.0164, found 448.0167.

![Structure of (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 ºC, $\lbrack \alpha \rbrack_{20}^D = +15.1$ (c = 0.53, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -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$_3$) $\delta$ 189.1 (d, $J = 184.0$ Hz, 1F), 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$_6$NO$_2$SNa$^+$ [M+Na]$^+$ 438.0933, found 438.0932.

![Structure of (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 ºC, $\lbrack \alpha \rbrack_{20}^D = +8.7$ (c = 0.37, CH$_2$Cl$_2$). $^1$H NMR
(400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -80.29 (dd, $J = 12.1$, 9.6 Hz, 3F), -109.45--110.42 (m, 1F), -115.73--116.83 (m, 1F), -124.66--124.63 (m, 1F), -124.85--125.80 (m, 1F), -163.09 (s, 1F); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 189.0 (d, $J = 18.6$ Hz), 143.0, 134.8, 130.0, 128.9, 128.8, 127.6, 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$_{8}$NO$_{2}$SNa$^+$ [M+Na]$^+$ 488.0901, found 488.0904.

White solid, 44.1 mg (43% yield), m.p. 167–168 °C, [a]$_{20}^D = +5.0$ (c = 1.19, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -80.78 (tt, $J = 9.8$, 2.3 Hz, 3F), -109.03--110.02 (m, 1F), -115.03--116.07 (m, 1F), -121.18--121.41 (m, 2F), -125.04 (dtd, $J = 30.5$, 24.1, 5.7 Hz, 1F), -126.22--127.16 (m, 1F), -162.84 (s, 1F); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 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$_{2}$SNa$^+$ [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-5H-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, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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); 19F NMR (376 MHz, CDCl3) 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); 13C NMR (101 MHz, CDCl3) 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 C17H21ClF3NO2SNa+ [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, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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); 19F NMR (376 MHz, CDCl3) 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); 13C NMR (101 MHz, CDCl3) 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_{3}NO_{3}SNa^{+} [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_{2}Cl_{2}). \textsuperscript{1}H 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); \textsuperscript{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); \textsuperscript{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_{3}NO_{3}SNa^{+} [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_{2}Cl_{2}). \textsuperscript{1}H 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); \textsuperscript{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); \textsuperscript{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,
(S)-2-((S)-1-amino-2,2,2-trifluoroethyl)-2-fluoro-3,4-dihyronaphthalen-1(2H)-one (5)

Slightly green solid, m.p. 61–62 °C, [α]20 D = +5.1 (c = 0.43, CH2Cl2). 1H NMR (400 MHz, CDCl3) 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); 19F NMR (376 MHz, CDCl3) δ -71.26 (d, J = 8.9 Hz, 3F), -173.45 (q, J = 8.8 Hz, 1F); 13C NMR (101 MHz, CDCl3) 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 C12H12F4NO+ [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
\(^{19}\text{F} \text{NMR (376 MHz, DMSO)} \text{ spectrum of } \mathbf{1b}\)

\(^{13}\text{C} \text{NMR (101 MHz, DMSO)} \text{ spectrum of } \mathbf{1b}\)
$^1$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 \textbf{1i}

$^{19}$F NMR (376 MHz, DMSO) spectrum of \textbf{1i}
$^{13}$C NMR (101 MHz, DMSO) spectrum of 1i

$^1$H NMR (400 MHz, DMSO) spectrum of 1j
$^{19}\text{F NMR (376 MHz, DMSO) spectrum of Ij}$

$^{13}\text{C NMR (101 MHz, DMSO) spectrum of Ij}$
$^1$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 II

$^{13}$C NMR (101 MHz, DMSO) spectrum of II
$^1$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 \textbf{In}

$^{13}$C NMR (101 MHz, DMSO) spectrum of \textbf{In}
$^1$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

![H NMR spectrum](image)

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3ba

![C NMR spectrum](image)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3ba

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of the crude reaction mixture

94.6% dr ($^{19}$F NMR integration of 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
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of 3ea

$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ 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
$^{19}\text{F} \text{ NMR (376 MHz, CDCl}_3\text{) spectrum of 3fa}$

$^{19}\text{F} \text{ NMR (376 MHz, CDCl}_3\text{) spectrum of the crude reaction mixture}$
$^1$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
\[^{19}\text{F} \text{NMR} (376 \text{ MHz, CDCl}_3)\] spectrum of 3ha

\[^{19}\text{F} \text{NMR} (376 \text{ MHz, CDCl}_3)\] 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

>98:2 dr ($^{19}$F NMR integration of crude reaction mixture)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of $3\text{ma}$

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of $3\text{ma}$
$^{19}$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

$>$98:2 dr ($^{19}$F NMR integration of 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
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of 3pa

$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of the crude reaction mixture

>98:2 dr ($^{19}\text{F NMR integration of crude reaction mixture}$)
$^{1}$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 $3\text{ac}$

$^{19}$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 $3le$

$^{19}$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

$^{19}$F NMR integration of 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 $3\text{ob}$

$^{19}$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
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of $3\text{pe}$

$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ 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

>98:2 dr ($^{19}$F NMR integration of 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

HPLC spectrum of deprotection product 5