

# Highly Efficient Synthesis of Enantioenriched Vicinal Halohydrins via Ir-Catalyzed Asymmetric Hydrogenation Using Dynamic Kinetic Resolution

Bin He<sup>b</sup>, Gen-Qiang Chen<sup>c,\*</sup>, Xumu Zhang<sup>a,\*</sup>

<sup>a</sup>Medi-X Pingshan and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518000, People's Republic of China;

<sup>b</sup>Institute of Zhejiang University-Quzhou, Quzhou, 324000, China;

<sup>c</sup>Academy for Advanced Interdisciplinary Studies and Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, People's Republic of China;

\*Email: chengq@sustech.edu.cn; zhangxm@sustech.edu.cn

## Content

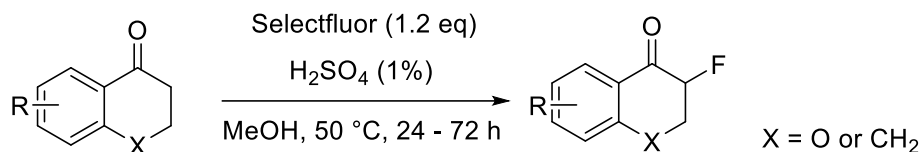
1. General remarks.....	S2
2. General procedure for the preparation of substrate compounds .....	S3
3. NMR spectra of substrate 1a-1x. ....	S12
4. General procedure for Asymmetric hydrogenation of cyclic $\alpha$ -halogenated ketones .....	S34
5. NMR spectra of compounds 2a-2y.....	S45
6. HPLC chromatograms.....	S71
7. Crystallographic Information .....	S122
8. References .....	S124

## 1. General remarks

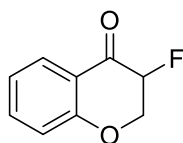
All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glove box or using standard Schlenk techniques. Anhydrous *i*PrOH, EtOH, CH<sub>2</sub>Cl<sub>2</sub>, THF, dioxane, EtOAc, hexane and toluene purchased from J&K were treated with bubbled argon before used; anhydrous toluene was prepared by treating the commercially available toluene with Na and distillation. K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, NaOH, NaO<sup>t</sup>Bu, KO<sup>t</sup>Bu and LiO<sup>t</sup>Bu was purchased from Sinopharm Chemical Reagent Co., Ltd. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded with a Bruker ADVANCE III (400 MHz) spectrometer with CDCl<sub>3</sub> or D<sub>2</sub>O as the solvent. NMR chemical shifts are listed in ppm relative to CHCl<sub>3</sub> (7.26 ppm for <sup>1</sup>H, and 77.0 ppm for <sup>13</sup>C) or H<sub>2</sub>O (4.79 ppm for <sup>1</sup>H). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. <sup>13</sup>C NMR analyses were run with decoupling. HPLC analyses were performed by Agilent 1290 UPLC using Daicel chiral column, the racemates of products were prepared by reduction of the substrates with NaBH<sub>4</sub>.

## 2. General procedure for the preparation of substrate compounds

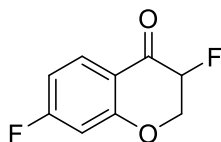
Synthesis of Compounds **1a–1q**.



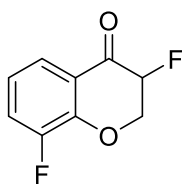
According to the reported procedure,<sup>[1]</sup> to a 50 mL-round-bottom flask fitted with a stirrer and a condenser and set under argon were added ketone (4.0 mmol, 1.0 equiv), SelectFluor (1.70 g, 4.8 mmol, 1.2 equiv), MeOH (7 mL), and conc. H<sub>2</sub>SO<sub>4</sub> (20  $\mu$ L, 0.4 mmol, 0.1 equiv). The resulting suspension was heated at 50 °C (oil bath) for 24–72 h (completion of the reaction was monitored by TLC; petroleum ether/ ethyl acetate 80:20). After the reaction mixture was cooled, the slurry was diluted with 3 mL of methanol and filtered. The obtained solid was washed with MeOH (2  $\times$  3 mL), and the filtrate was concentrated under reduced pressure. The resulting mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate from 95:5 to 85:15) to yield **1a–1r** as a white crystalline solid.



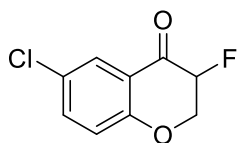
3-Fluorochroman-4-one (**1a**):<sup>[1a]</sup> White solid, 7.5 g, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.91 (dd,  $J = 7.9, 1.8$  Hz, 1H), 7.53 (ddd,  $J = 8.7, 7.2, 1.8$  Hz, 1H), 7.08 (t,  $J = 7.5$  Hz, 1H), 7.00 (d,  $J = 8.4$  Hz, 1H), 5.16 (ddd,  $J = 47.0, 9.2, 4.7$  Hz, 1H), 4.70-4.47 (m, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -204.05 (ddd,  $J = 47.0, 15.9, 7.5$  Hz).



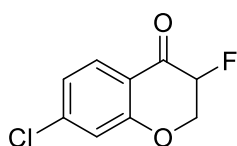
3,7-Difluorochroman-4-one (**1b**):<sup>[1b]</sup> White solid, 200 mg, 72% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.95 (dd, *J* = 8.8, 6.5 Hz, 1H), 6.82 (ddd, *J* = 8.8, 8.0, 2.4 Hz, 1H), 6.71 (dd, *J* = 9.6, 2.4 Hz, 1H), 5.13 (ddd, *J* = 46.9, 8.5, 4.7 Hz, 1H), 4.75-4.40 (m, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -98.49 (m), -203.59 (ddd, *J* = 46.9, 17.3, 8.5 Hz).



3,8-Difluorochroman-4-one (**1c**):<sup>[2]</sup> White solid, 193 mg, 70% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.71 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.35 (ddd, *J* = 10.5, 8.0, 1.6 Hz, 1H), 7.04 (td, *J* = 8.0, 4.3 Hz, 1H), 5.19 (ddd, *J* = 46.8, 8.9, 4.6 Hz, 1H), 4.93-4.45 (m, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -134.31 (dd, *J* = 10.1, 4.5 Hz), -203.63 (ddd, *J* = 47.2, 17.1, 7.9 Hz).

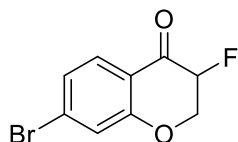


6-Chloro-3-fluorochroman-4-one (**1d**):<sup>[1b]</sup> White solid, 480 mg, 80% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.87 (d, *J* = 2.7 Hz, 1H), 7.47 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 5.14 (ddd, *J* = 46.9, 8.8, 4.7 Hz, 1H), 4.77-4.48 (m, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -203.73 (ddd, *J* = 47.2, 17.4, 8.4 Hz).

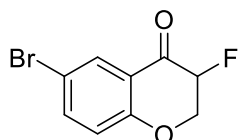


7-Chloro-3-fluorochroman-4-one (**1e**):<sup>[2]</sup> White solid, 213 mg, 76% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.10-6.93 (m, 2H), 5.13 (ddd, *J* = 46.9,

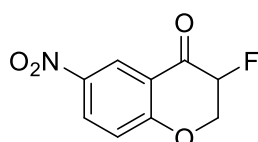
8.7, 4.6 Hz, 1H), 4.70-4.42 (m, 2H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -203.50 (ddd,  $J = 46.6, 16.9, 8.3$  Hz).



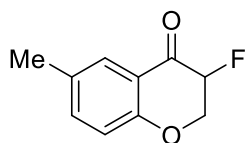
7-Bromo-3-fluorochroman-4-one (**1f**):<sup>[3]</sup> White solid, 200 mg, 75% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77 (d,  $J = 8.9$  Hz, 1H), 7.25-7.20 (m, 2H), 5.13 (ddd,  $J = 46.9, 8.7, 4.7$  Hz, 1H), 4.75-4.47 (m, 2H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -203.50 (ddd,  $J = 46.4, 17.5, 7.9$  Hz).



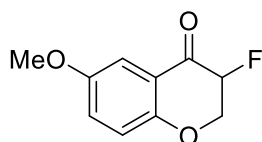
6-Bromo-3-fluorochroman-4-one (**1g**):<sup>[2]</sup> White solid, 430 mg, 68% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.20-7.89 (m, 1H), 7.70-7.46 (m, 1H), 6.99-6.85 (m, 1H), 5.26-4.92 (m, 1H), 4.76-4.44 (m, 2H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -203.71 (m).



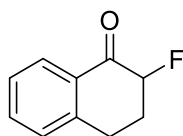
3-Fluoro-7-nitrochroman-4-one (**1h**):<sup>[3]</sup> White solid, 430 mg, 78% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.80 (d,  $J = 2.8$  Hz, 1H), 8.39 (dd,  $J = 9.2, 2.8$  Hz, 1H), 7.18 (d,  $J = 9.2$  Hz, 1H), 5.30-5.03 (m, 1H), 4.80-4.71 (m, 2H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -202.73 (ddd,  $J = 46.0, 16.4, 11.9$  Hz).



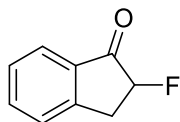
3-Fluoro-6-methylchroman-4-one (**1i**):<sup>[1b]</sup> White solid, 405 mg, 75% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.70 (s, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 5.14 (dddd, *J* = 47.1, 9.3, 4.7, 2.5 Hz, 1H), 4.72-4.34 (m, 2H), 2.32 (s, 3H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -204.07 (ddd, *J* = 47.2, 16.5, 7.4 Hz).



3-Fluoro-6-methoxychroman-4-one (**1j**):<sup>[3]</sup> White solid, 178 mg, 65% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31 (d, *J* = 3.2 Hz, 1H), 7.14 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.95 (d, *J* = 9.1 Hz, 1H), 5.14 (ddd, *J* = 47.0, 9.1, 4.7 Hz, 1H), 4.74-4.41 (m, 2H), 3.81 (s, 3H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -203.86 (ddd, *J* = 47.2, 16.8, 8.1 Hz).

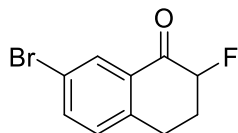


2-Fluoro-3,4-dihydronaphthalen-1(2H)-one (**1k**):<sup>[1b]</sup> Colourless crystal, 697 mg, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.07 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.53 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 5.15 (ddd, *J* = 47.9, 12.7, 5.1 Hz, 1H), 3.13 (dd, *J* = 9.5, 4.1 Hz, 2H), 2.58 (dddt, *J* = 12.5, 10.3, 5.1, 4.2 Hz, 1H), 2.36 (tddd, *J* = 12.6, 9.3, 7.8, 6.7 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -190.32 (dt, *J* = 48.1, 9.1 Hz).

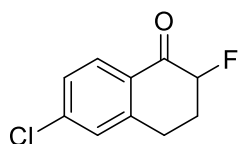


2-Fluoro-2,3-dihydro-1H-inden-1-one (**1l**):<sup>[1b]</sup> Colourless crystal, 2.8 g, 92% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 5.27 (ddd, *J* = 51.1, 7.8, 4.4 Hz, 1H), 3.63 (dt,

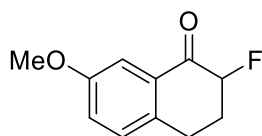
$J = 16.9, 7.5$  Hz, 1H), 3.23 (ddd,  $J = 22.2, 16.9, 4.4$  Hz, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -193.99 (ddd,  $J = 51.1, 23.9, 7.2$  Hz).



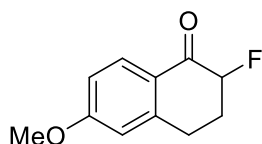
7-Bromo-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (**1m**):<sup>[1b]</sup> Colourless crystal, 968 mg, 80% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18 (dt,  $J = 5.5, 2.3$  Hz, 1H), 7.63 (ddd,  $J = 8.2, 3.0, 1.7$  Hz, 1H), 7.16 (d,  $J = 8.2$  Hz, 1H), 5.14 (dddt,  $J = 47.7, 12.6, 5.1, 1.2$  Hz, 1H), 3.21-3.03 (m, 2H), 2.67-2.49 (m, 1H), 2.42-2.22 (m, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -190.70 (ddd,  $J = 48.3, 11.2, 6.9$  Hz).



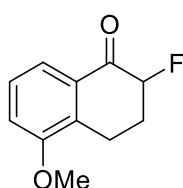
6-Chloro-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (**1n**):<sup>[4]</sup> Colourless crystal, 842 mg, 85% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (d,  $J = 8.4$  Hz, 1H), 7.33 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.28 (br, 1H), 5.12 (ddd,  $J = 47.7, 12.5, 5.1$  Hz, 1H), 3.21-2.99 (m, 2H), 2.66-2.49 (m, 1H), 2.44-2.24 (m, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -190.70 (ddd,  $J = 48.3, 11.2, 6.9$  Hz).



2-Fluoro-7-methoxy-3,4-dihydronaphthalen-1(2H)-one (**1o**):<sup>[5]</sup> Colourless crystal, 737 mg, 76% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.52 (d,  $J = 2.8$  Hz, 1H), 7.18 (d,  $J = 8.5$  Hz, 1H), 7.10 (dd,  $J = 8.5, 2.8$  Hz, 1H), 5.13 (ddd,  $J = 47.9, 12.8, 5.1$  Hz, 1H), 3.85 (s, 3H), 3.06 (dd,  $J = 9.4, 4.2$  Hz, 2H), 2.63-2.49 (m, 1H), 2.43-2.26 (m, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -190.41 (m).

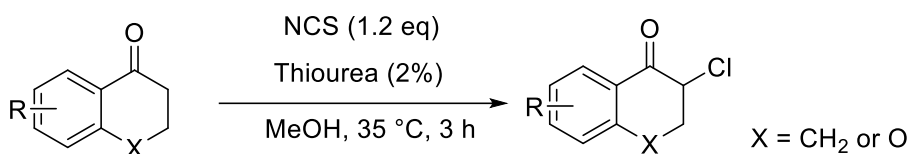


2-Fluoro-6-methoxy-3,4-dihydronaphthalen-1(2H)-one (**1p**):<sup>[5]</sup> Colourless crystal, 819 mg, 84% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.04 (d, *J* = 8.8 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 5.09 (ddd, *J* = 48.0, 12.4, 5.1 Hz, 1H), 3.86 (s, 3H), 3.08 (dd, *J* = 9.2, 4.2 Hz, 2H), 2.61-2.47 (m, 1H), 2.41-2.24 (m, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -190.37 (ddd, *J* = 47.7, 10.2, 6.7 Hz).



2-Fluoro-5-methoxy-3,4-dihydronaphthalen-1(2H)-one (**1q**):<sup>[1a]</sup> Colourless crystal, 719 mg, 74% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.65 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 8.1, 1.0 Hz, 1H), 5.15 (ddd, *J* = 48.3, 13.1, 5.2 Hz, 1H), 3.87 (s, 3H), 3.27 (dtd, *J* = 18.0, 4.9, 3.3 Hz, 1H), 2.95-2.70 (m, 1H), 2.65-2.50 (m, 1H), 2.39-2.18 (m, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -191.03 (ddt, *J* = 47.3, 10.2, 5.4 Hz).

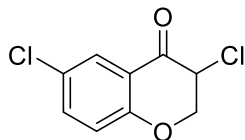
#### Synthesis of Compounds **1r–1x**.



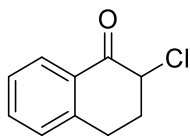
According to the reported procedure,<sup>[6]</sup> a MeOH solution (100 mL) containing ketone (10 mmol), thiourea (15 mg, 0.2 mmol), and N-chlorosuccinimide (1.60 g, 12 mmol) was heated by oil bath under N<sub>2</sub> atmosphere at 35 °C, for 3 h. The solution was concentrated under a reduced pressure, then AcOEt (50 mL) and H<sub>2</sub>O (20 mL) were added and stirred for 10 min. The organic layer was separated, and the aqueous phase was extracted with AcOEt (2 × 50 mL). The combined organic portions were dried over



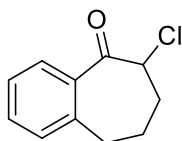
MgSO<sub>4</sub> and concentrated to give a crude product. Purification by silica gel column chromatography (eluent: Hexane/AcOEt = 5/1) gave the product **1r-1x**.



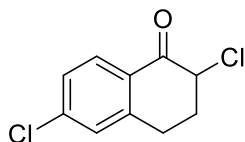
3,6-Dichlorochroman-4-one (**1r**): White solid, 480 mg, 45% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 (d, *J* = 2.6 Hz, 1H), 7.48 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 4.67 (dd, *J* = 11.4, 3.1 Hz, 1H), 4.61-4.50 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 184.5, 159.4, 136.8, 128.0, 127.4, 119.9, 119.8, 71.2, 54.8. HRMS (ESI/ion trap): *m/z* [M + H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>7</sub>Cl<sub>2</sub>O<sub>2</sub> 216.9823, found 216.9814.



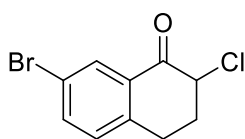
2-Chloro-3,4-dihydronaphthalen-1(2H)-one (**1s**):<sup>[6]</sup> Light yellow liquid, 5.8 g, 95% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (td, *J* = 7.6, 1.1 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 4.62 (dd, *J* = 7.8, 3.9 Hz, 1H), 3.27 (ddd, *J* = 17.1, 8.0, 4.6 Hz, 1H), 2.98 (ddd, *J* = 17.1, 7.0, 4.7 Hz, 1H), 2.63-2.51 (m, 1H), 2.50-2.39 (m, 1H).



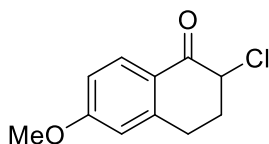
6-Chloro-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (**1t**):<sup>[7]</sup> Light yellow liquid, 834 g, 86% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.64 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.5, 1.1 Hz, 1H), 4.80 (dd, *J* = 8.7, 4.7 Hz, 1H), 3.02 (ddd, *J* = 15.8, 7.7, 3.4 Hz, 1H), 2.92 (ddd, *J* = 15.8, 9.6, 3.4 Hz, 1H), 2.39 (dddd, *J* = 14.3, 9.7, 6.1, 4.7 Hz, 1H), 2.20 (ddt, *J* = 14.0, 8.7, 5.3 Hz, 1H), 2.11-1.87 (m, 2H).



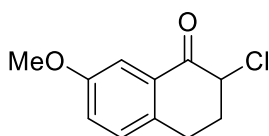
2,6-Dichloro-3,4-dihydronaphthalen-1(2H)-one (**1u**): White solid, 952 mg, 89% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (d,  $J = 8.4$  Hz, 1H), 7.51-7.09 (m, 2H), 4.61 (dd,  $J = 7.3, 3.8$  Hz, 1H), 3.27 (ddd,  $J = 17.3, 8.4, 4.6$  Hz, 1H), 2.95 (ddd,  $J = 17.0, 6.6, 5.0$  Hz, 1H), 2.63-2.50 (m, 1H), 2.52-2.39 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.9, 144.8, 140.8, 130.3, 129.0, 128.8, 127.9, 59.3, 32.1, 26.1.



7-Bromo-2-chloro-3,4-dihydronaphthalen-1(2H)-one (**1v**):<sup>[7]</sup> White solid, 908 mg, 88% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.19 (d,  $J = 2.2$  Hz, 1H), 7.62 (dd,  $J = 8.2, 2.2$  Hz, 1H), 7.17 (d,  $J = 8.2$  Hz, 1H), 4.61 (dd,  $J = 7.3, 3.8$  Hz, 1H), 3.24 (ddd,  $J = 17.3, 8.3, 4.6$  Hz, 1H), 2.94 (ddd,  $J = 17.3, 6.5, 4.7$  Hz, 1H), 2.63-2.50 (m, 1H), 2.52-2.39 (m, 1H).



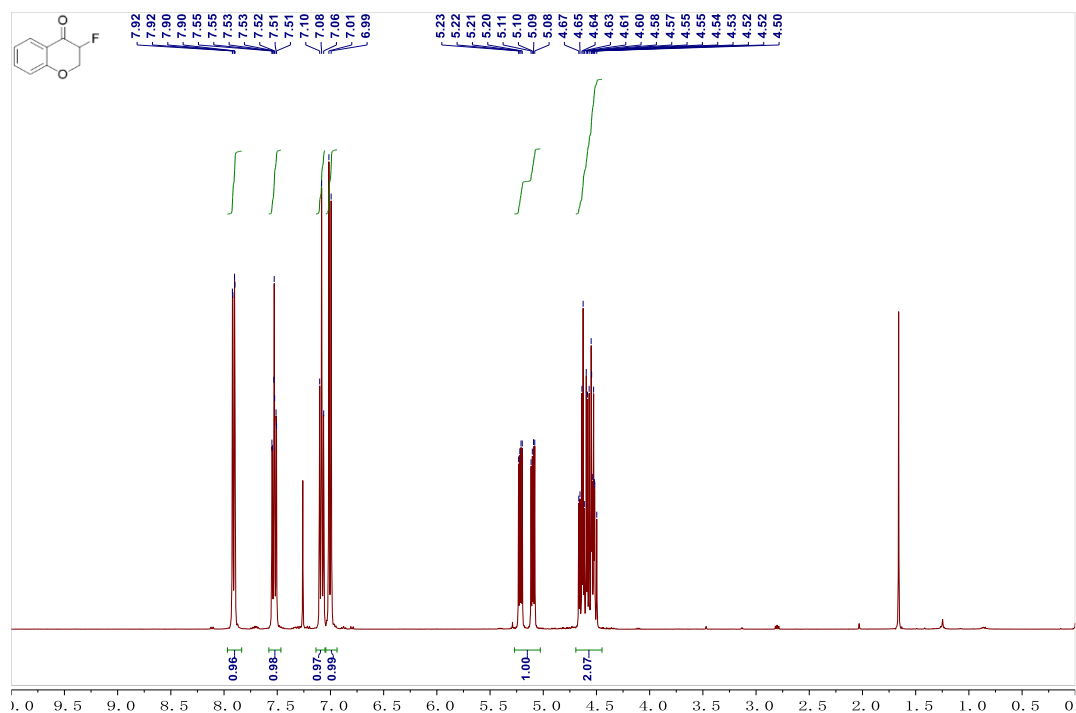
2-Chloro-6-methoxy-3,4-dihydronaphthalen-1(2H)-one (**1w**):<sup>[6]</sup> White solid, 952 mg, 89% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (d,  $J = 8.8$  Hz, 1H), 6.86 (dd,  $J = 8.8, 2.5$  Hz, 1H), 6.70 (dd,  $J = 2.4, 1.1$  Hz, 1H), 4.58 (dd,  $J = 7.4, 3.9$  Hz, 1H), 3.86 (s, 3H), 3.25 (ddd,  $J = 17.1, 8.4, 4.5$  Hz, 1H), 2.93 (ddd,  $J = 17.0, 6.7, 4.6$  Hz, 1H), 2.61-2.48 (m, 1H), 2.49-2.33 (m, 1H).



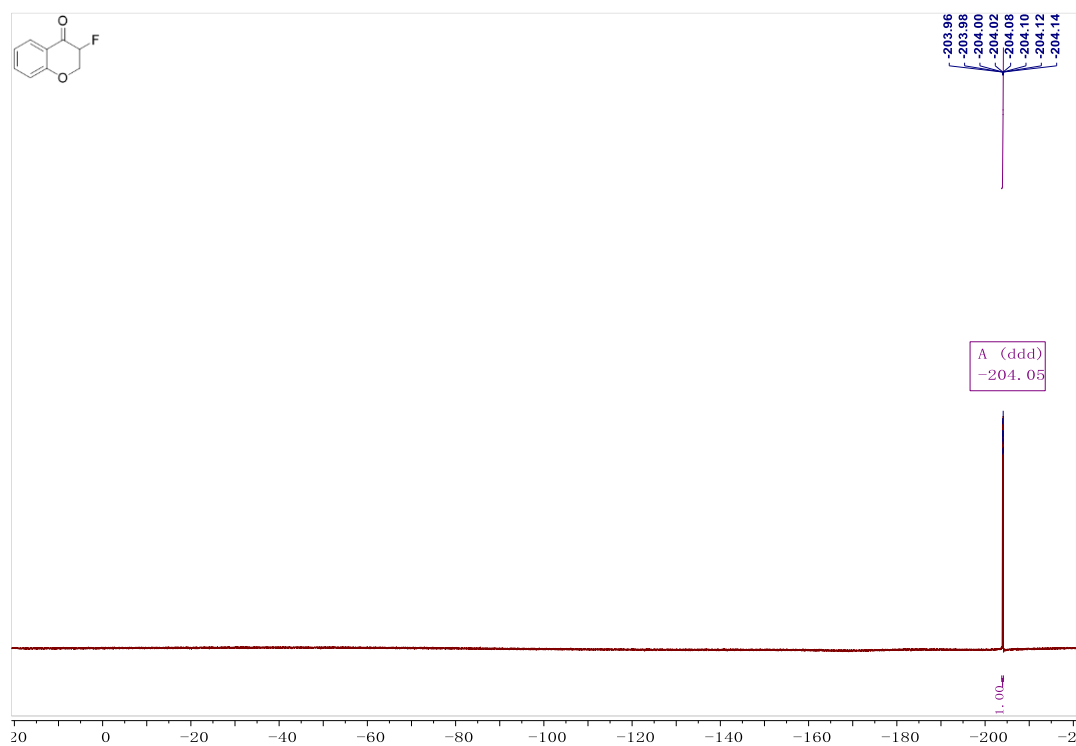
2-Chloro-7-methoxy-3,4-dihydronaphthalen-1(2H)-one (**1x**):<sup>[7]</sup> White solid, 1.5 g, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.53 (d, *J* = 2.8 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.61 (dd, *J* = 7.6, 3.8 Hz, 1H), 3.83 (s, 3H), 3.20 (ddd, *J* = 16.9, 8.0, 4.5 Hz, 1H), 2.92 (ddd, *J* = 16.9, 6.8, 4.6 Hz, 1H), 2.63-2.49 (m, 1H), 2.49-2.32 (m, 1H).

### 3. NMR spectra of substrates 1a-1x.

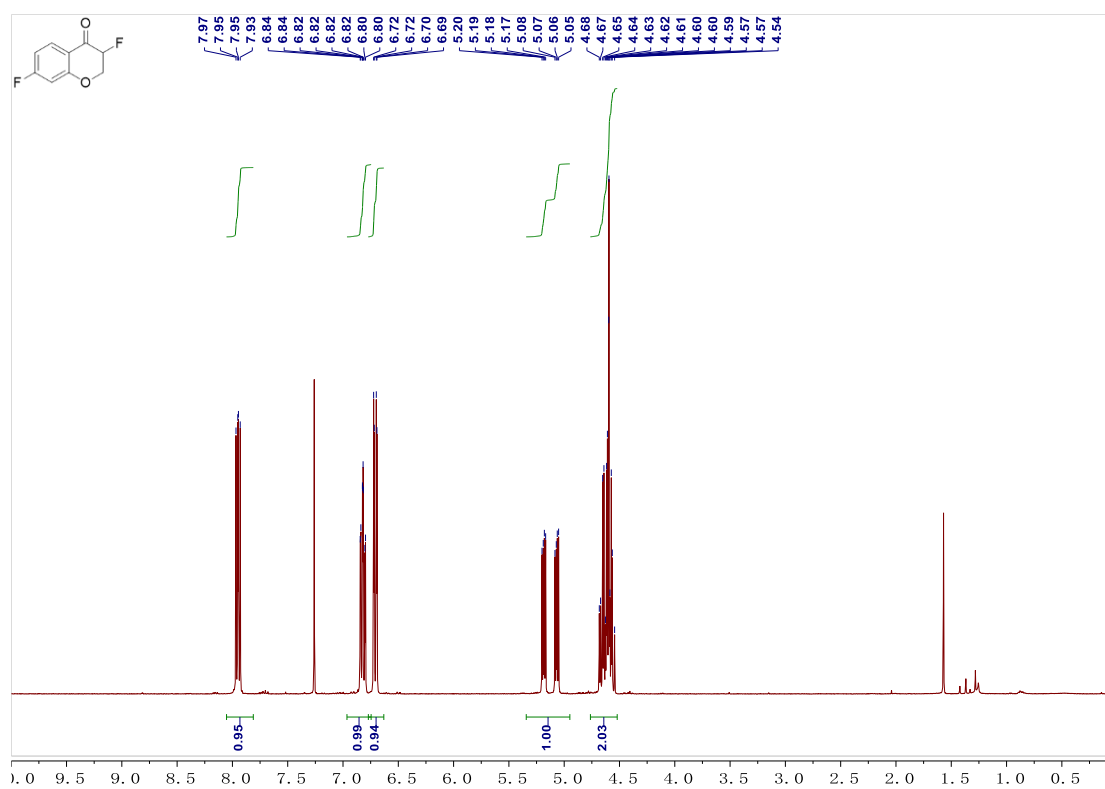
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1a**



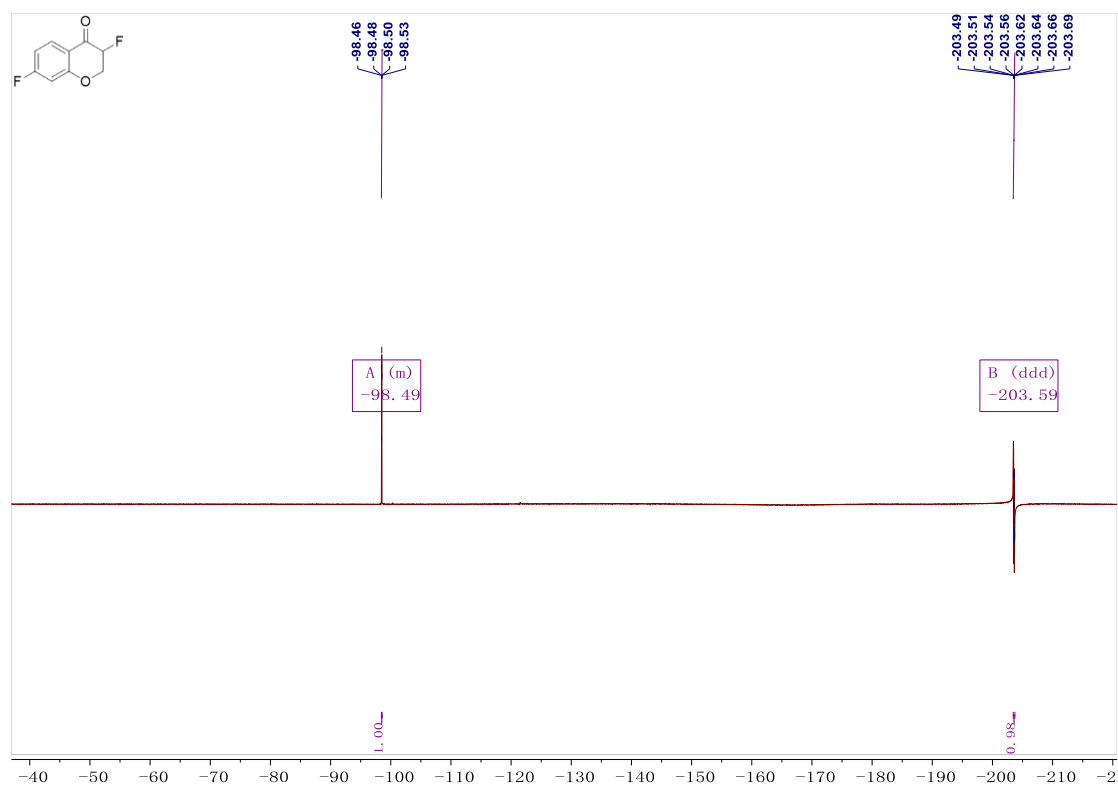
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1a**



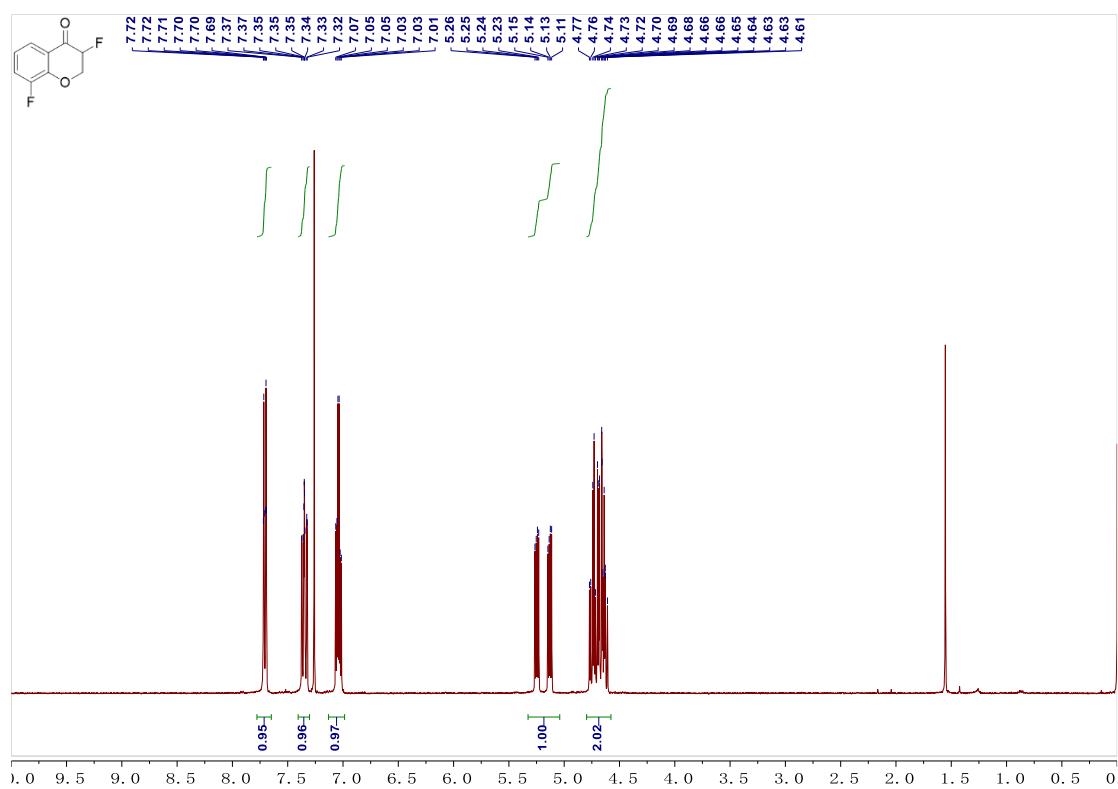
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1b**



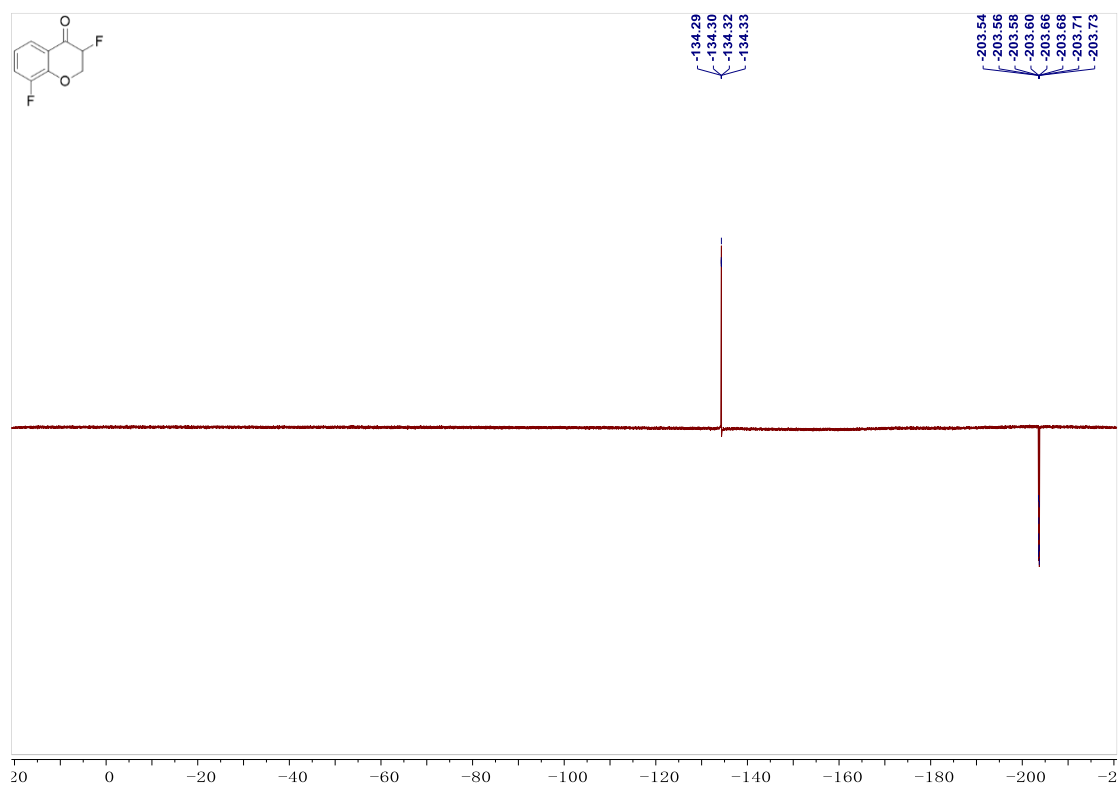
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1b**



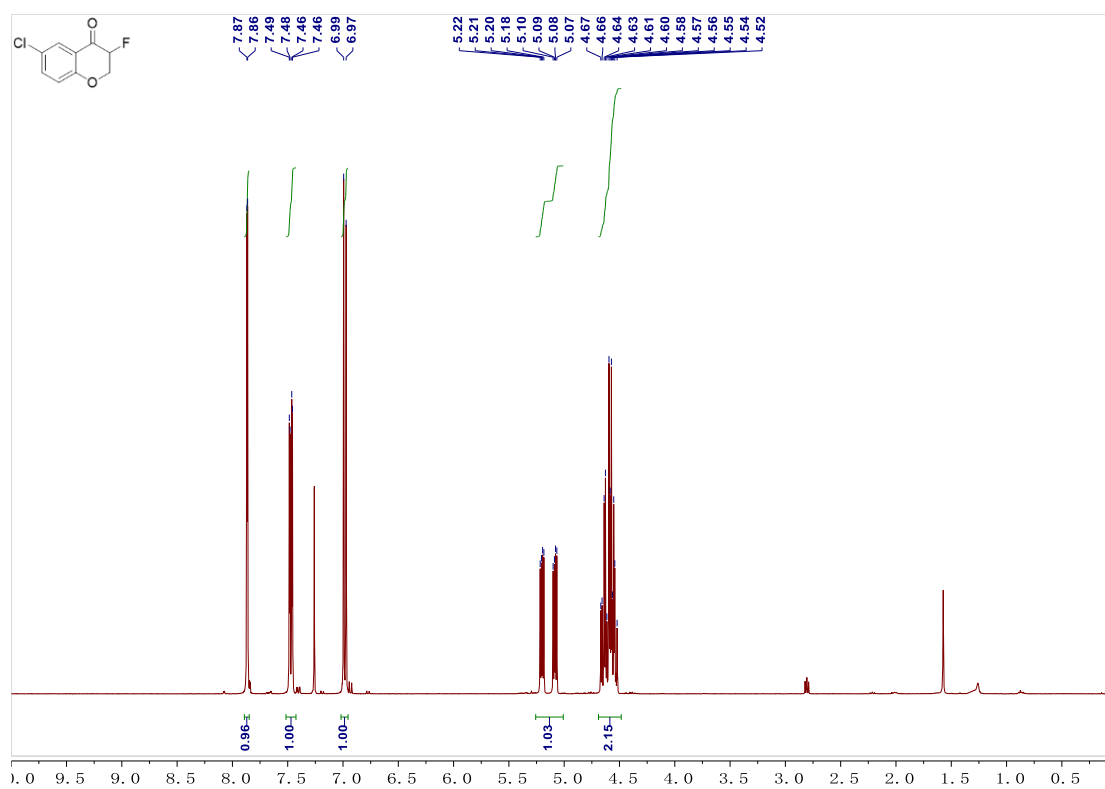
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1c**



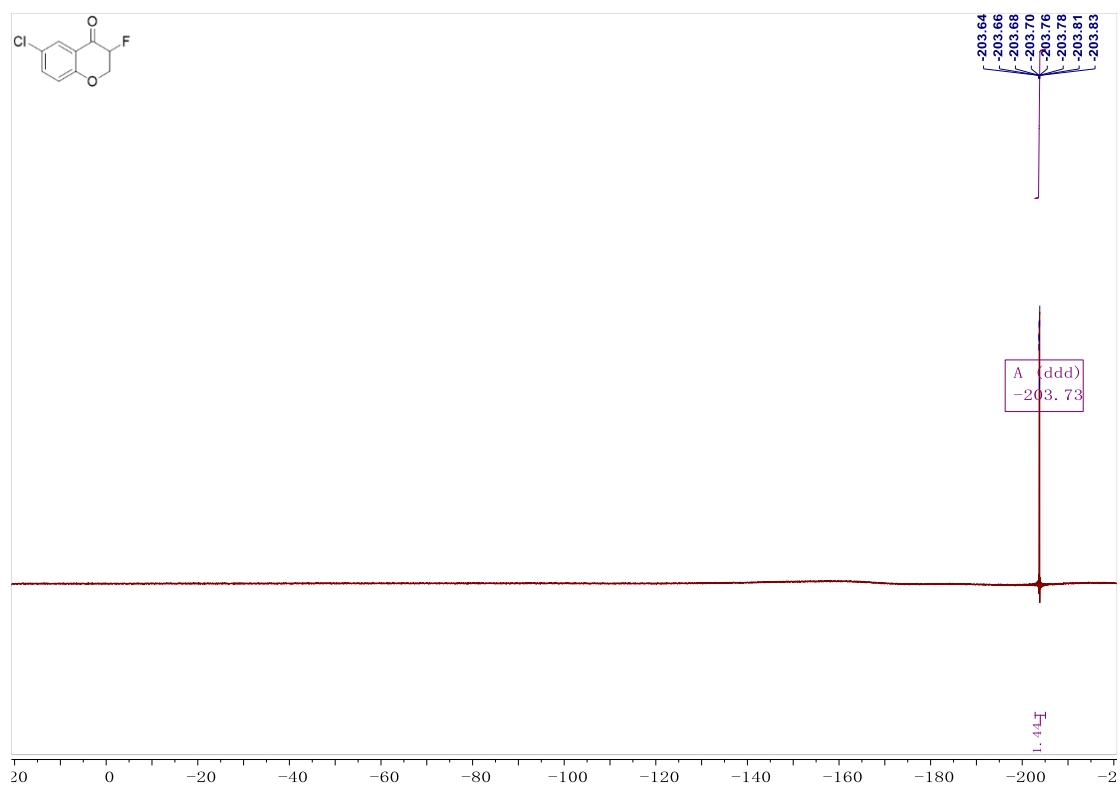
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1c**



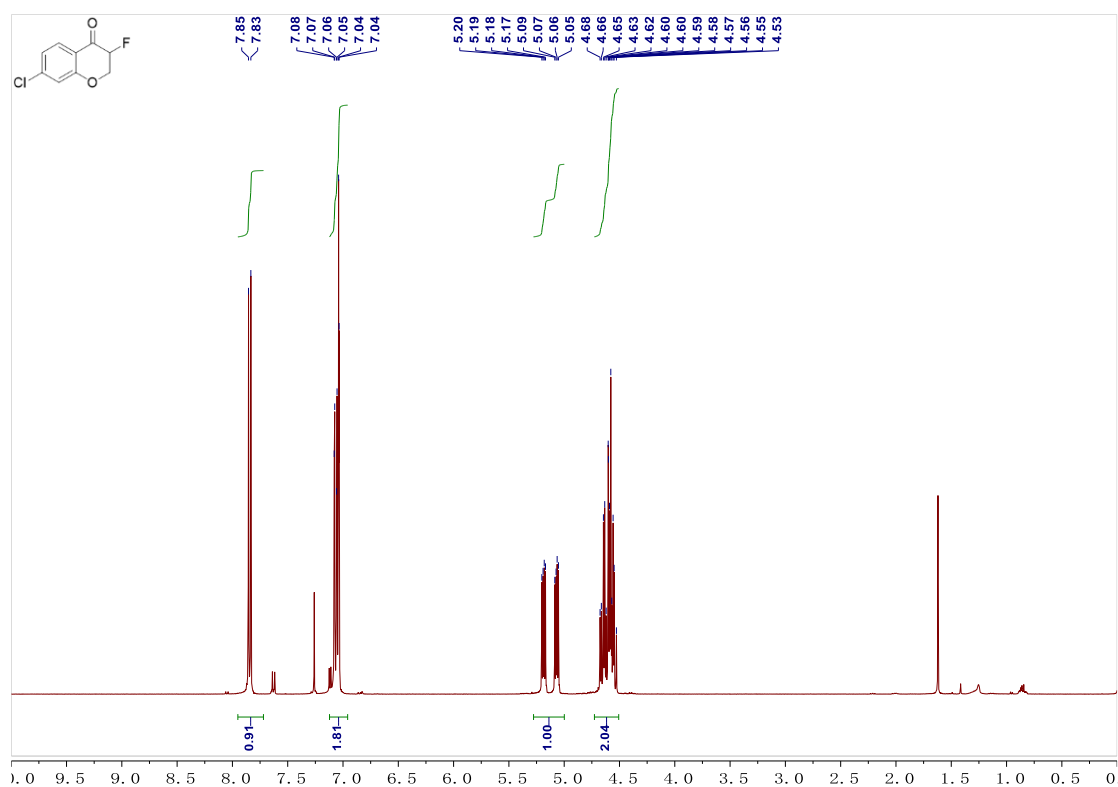
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1d**



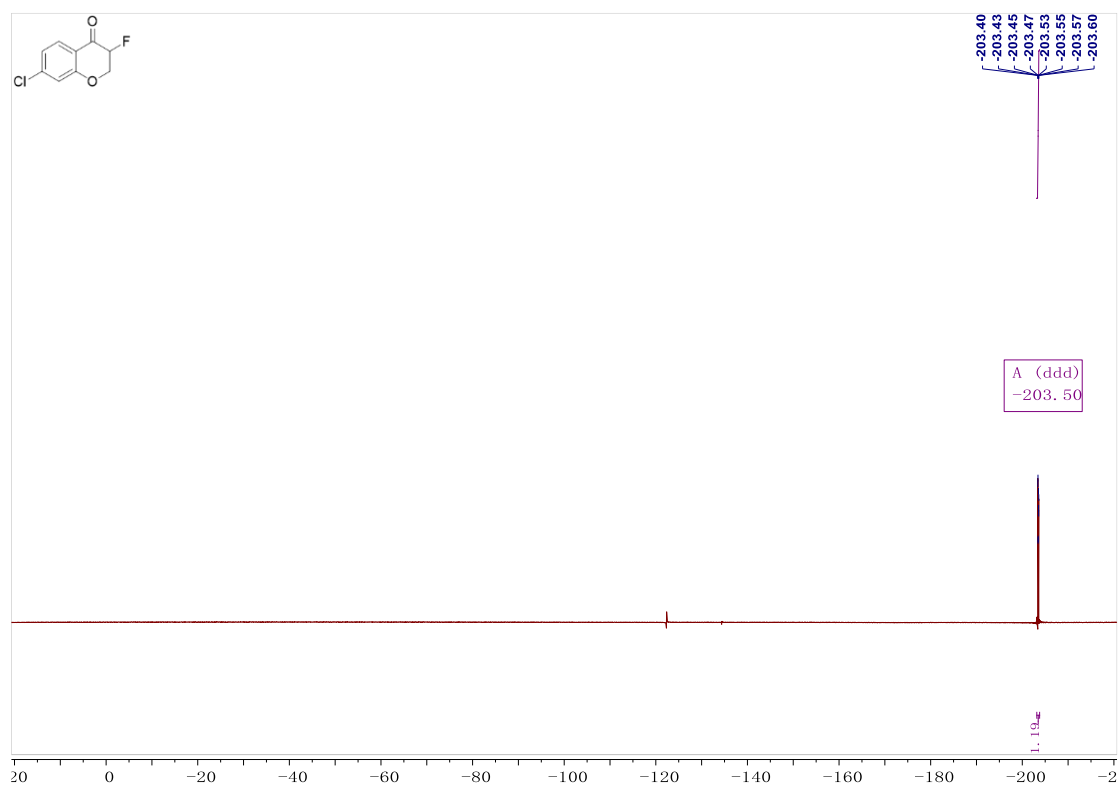
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1d**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1e**

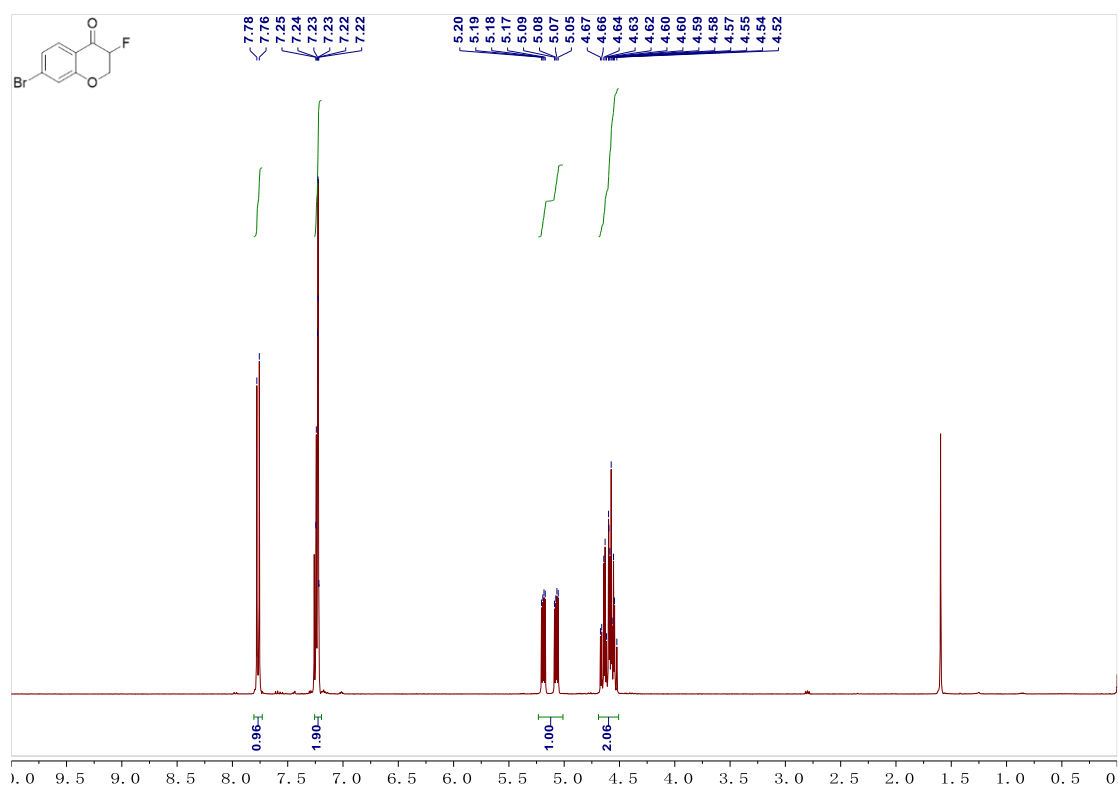


<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1e**

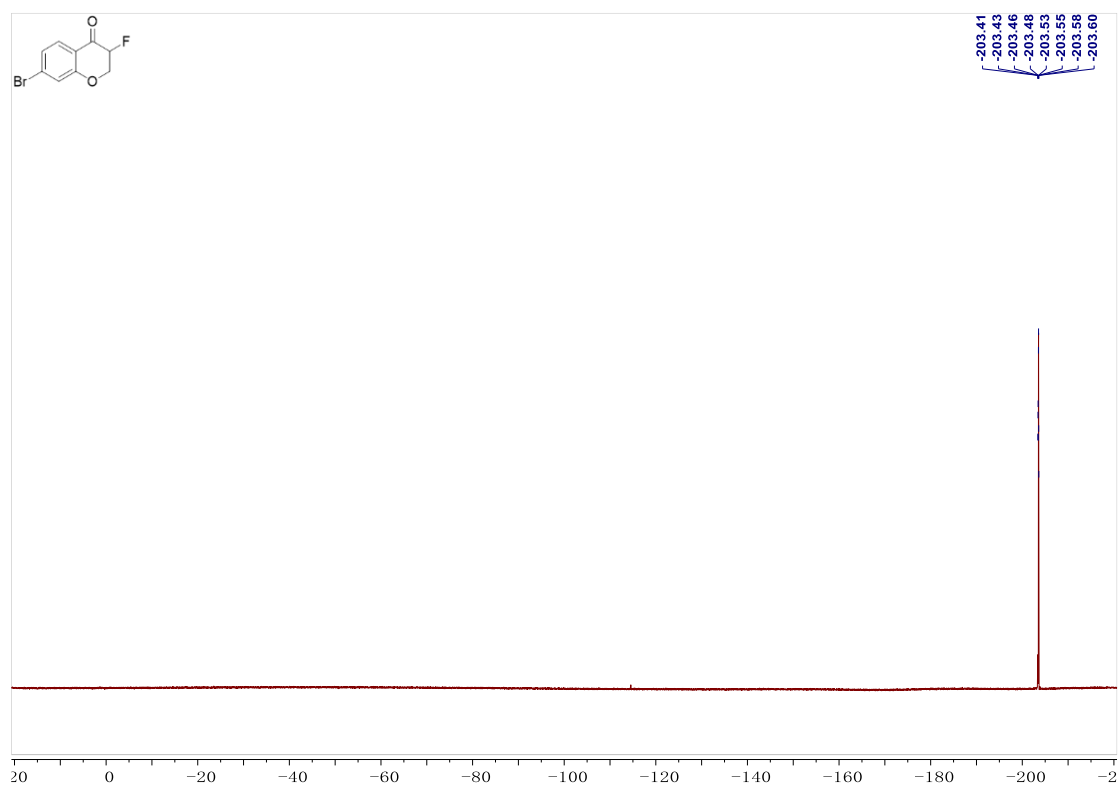




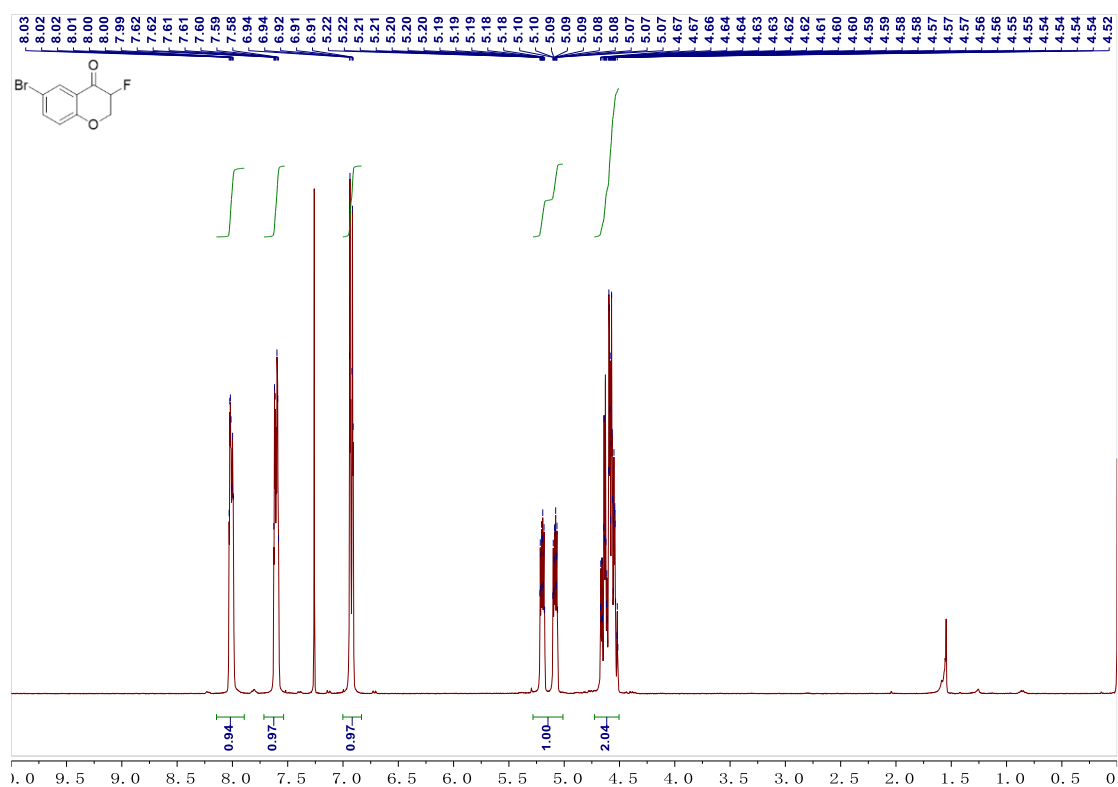
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1f**



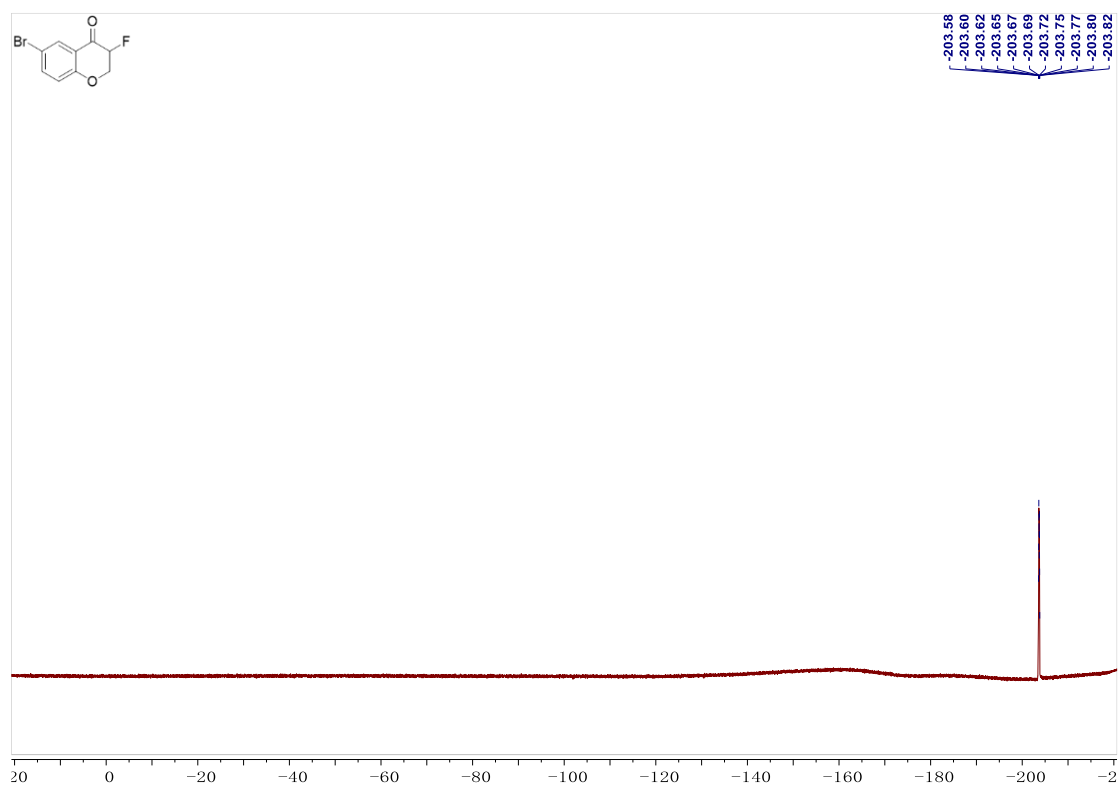
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1f**



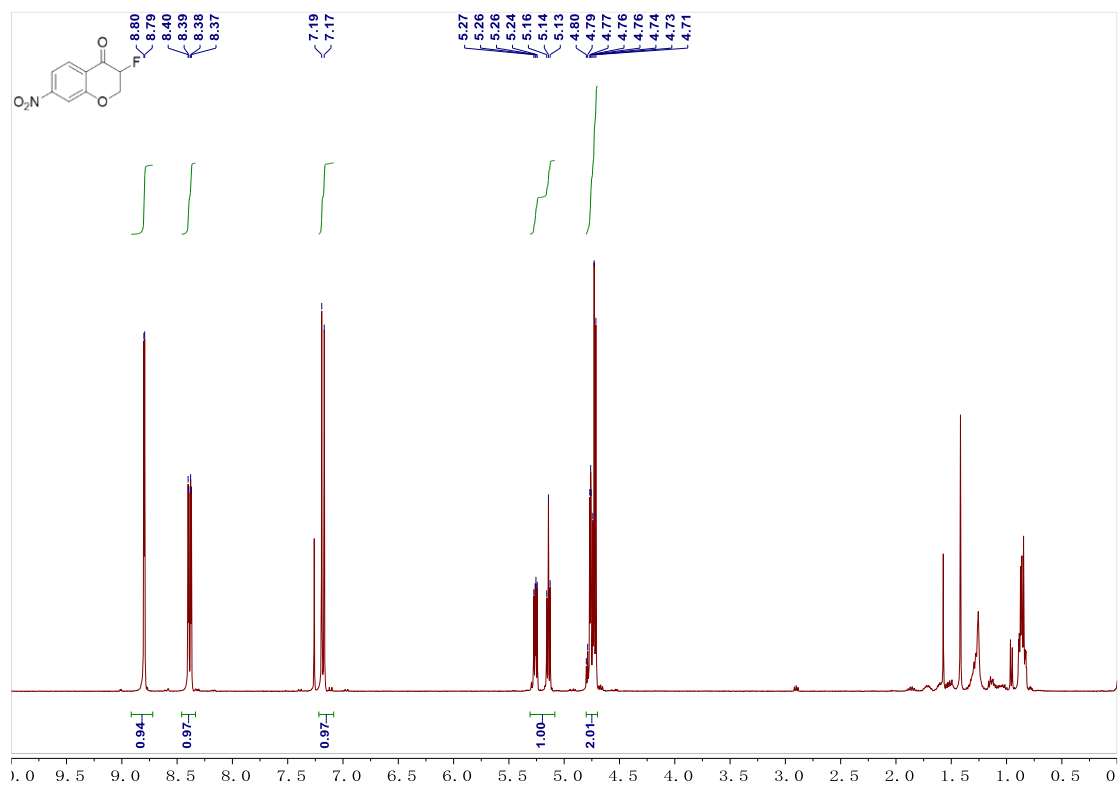
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1g**



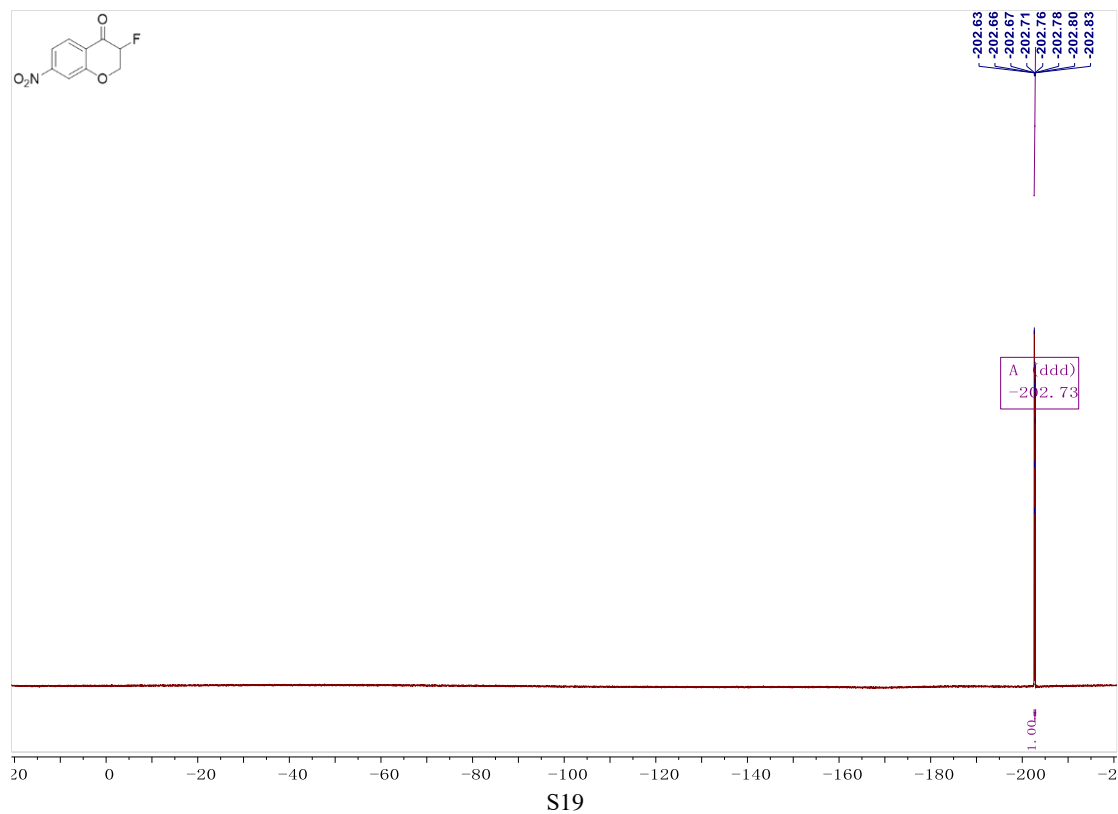
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1g**



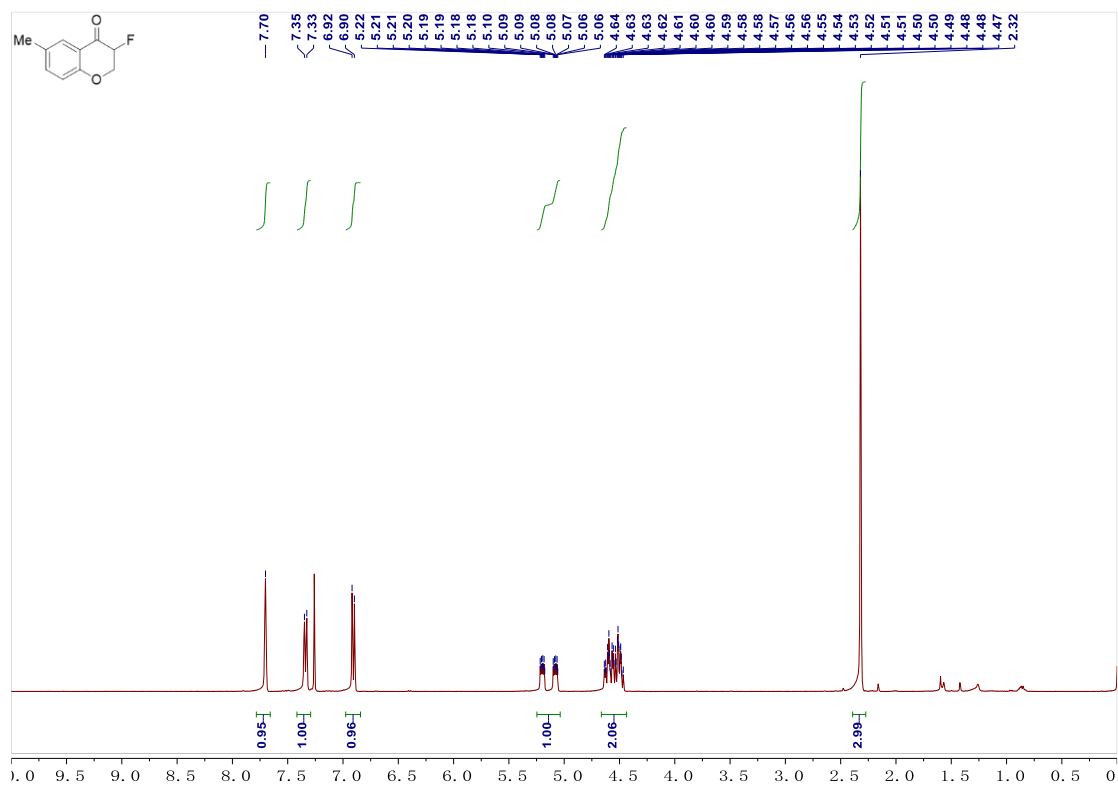
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1h**



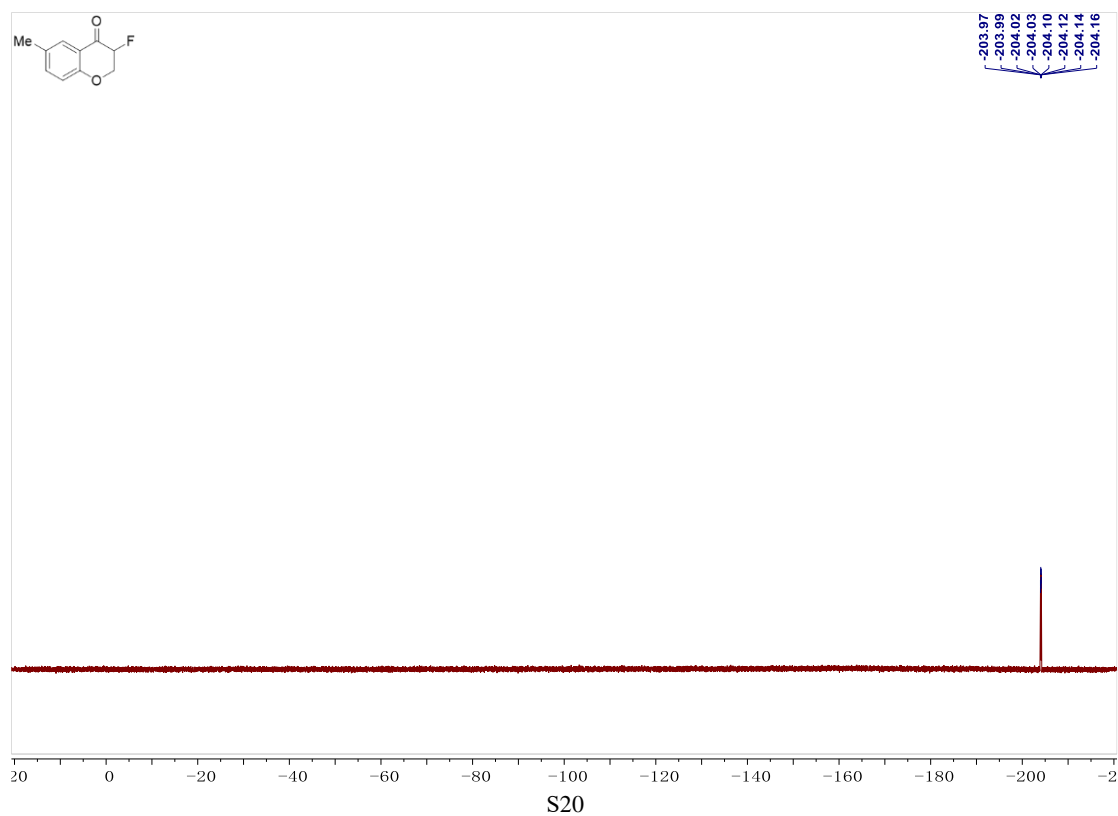
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1h**



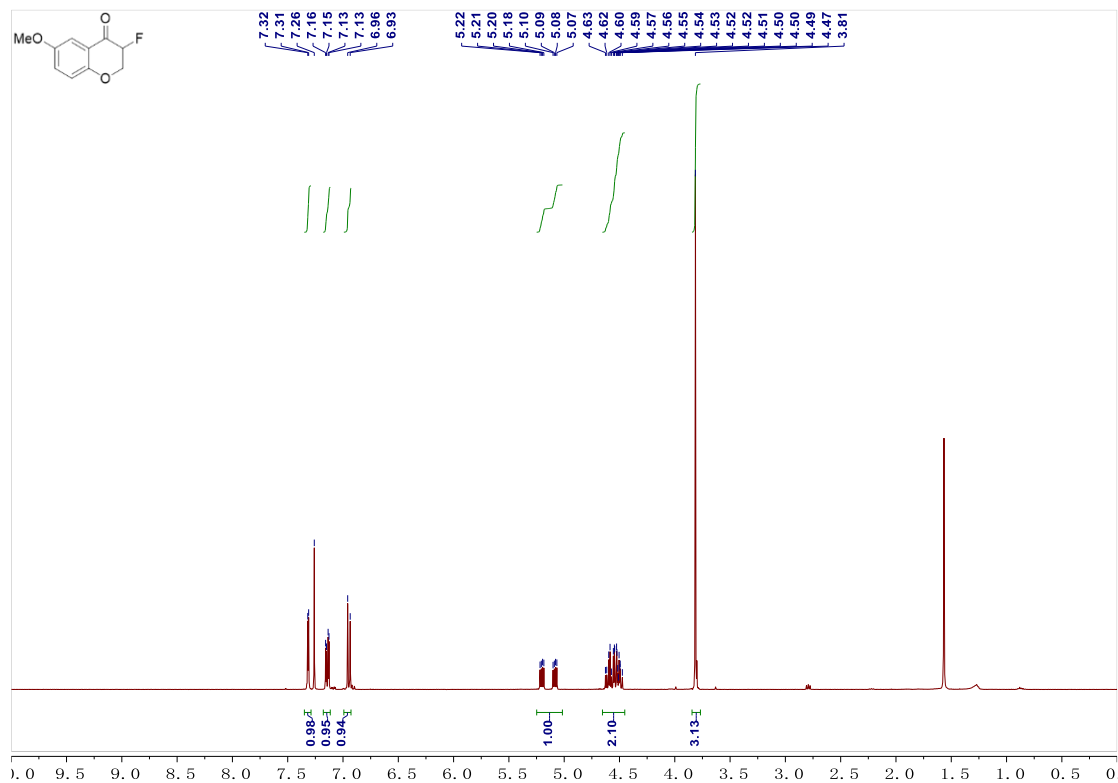
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1i**



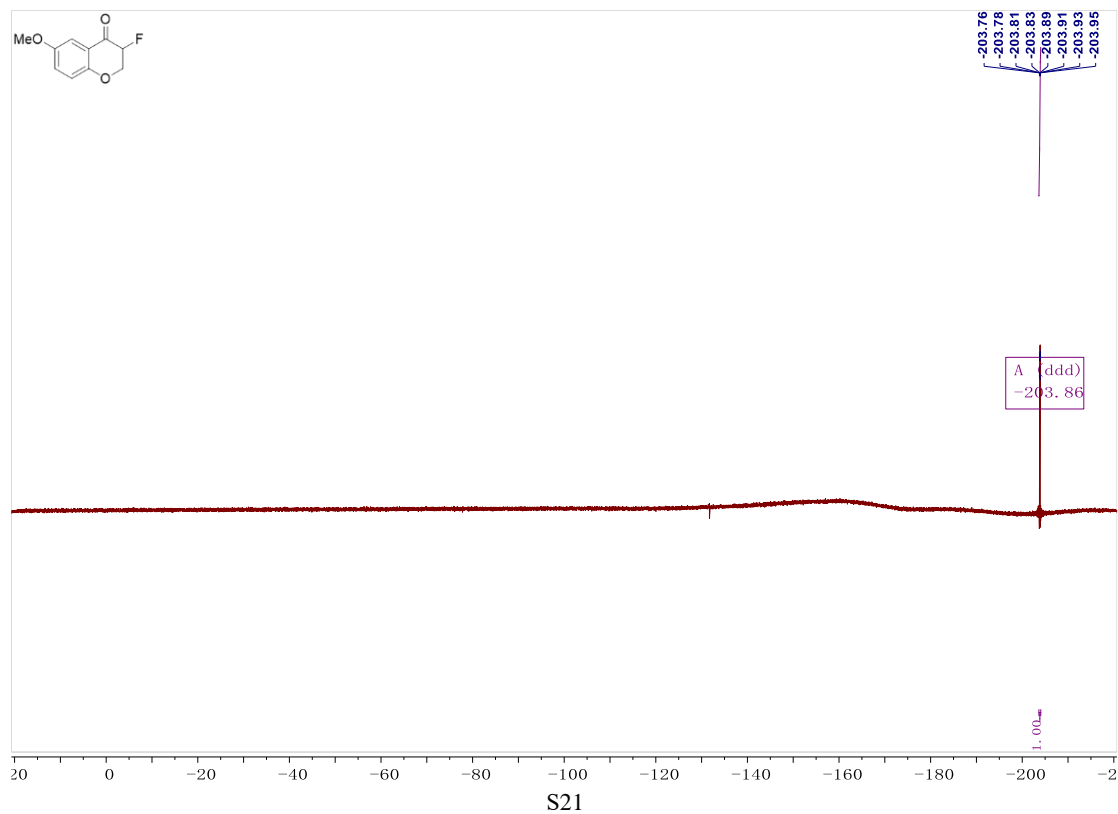
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1i**



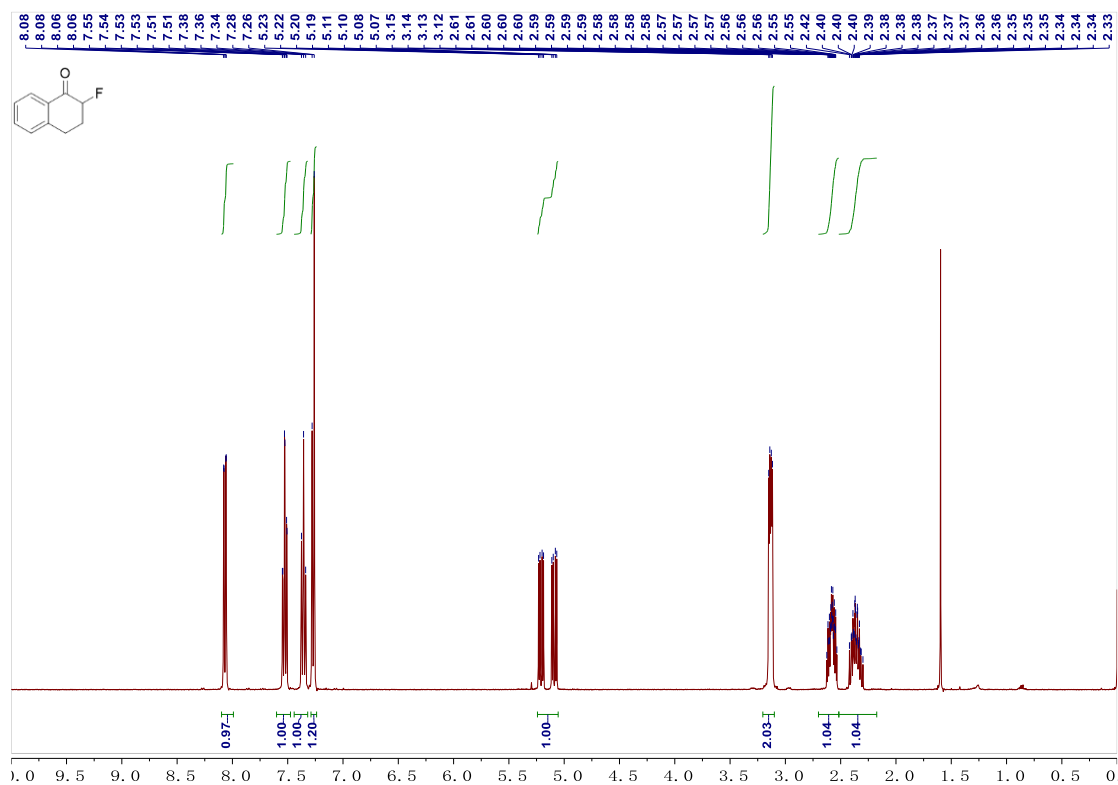
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1j**



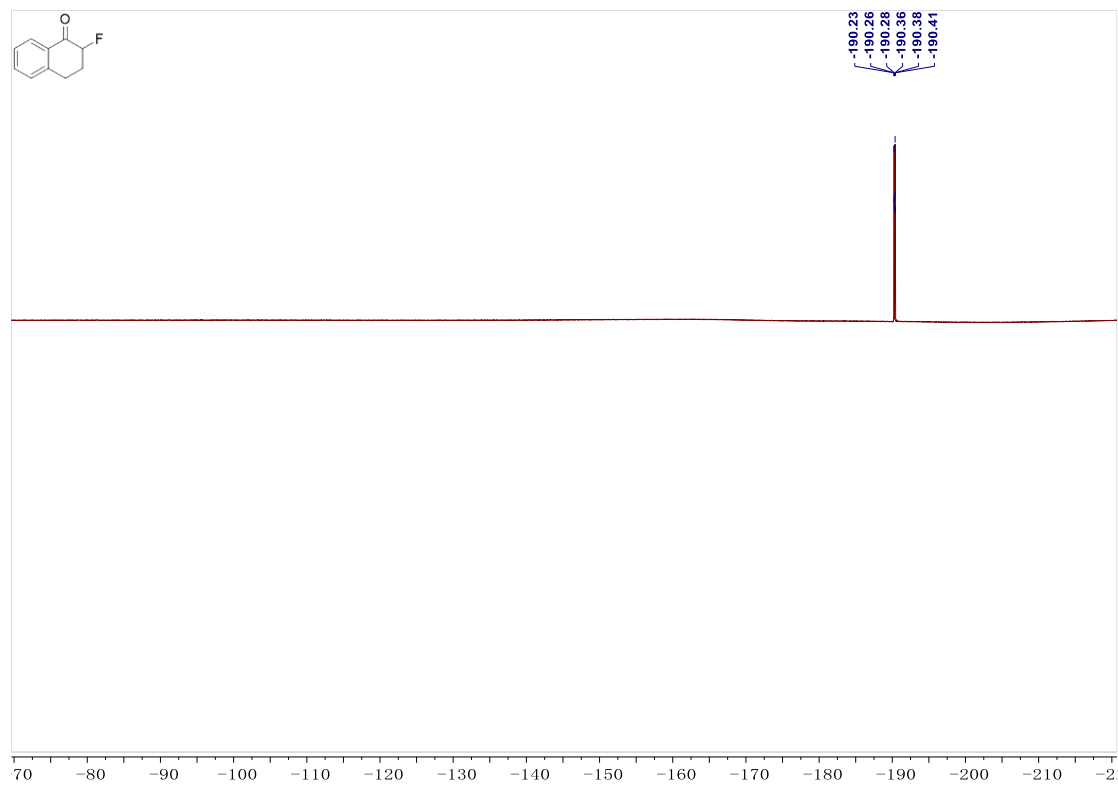
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1j**



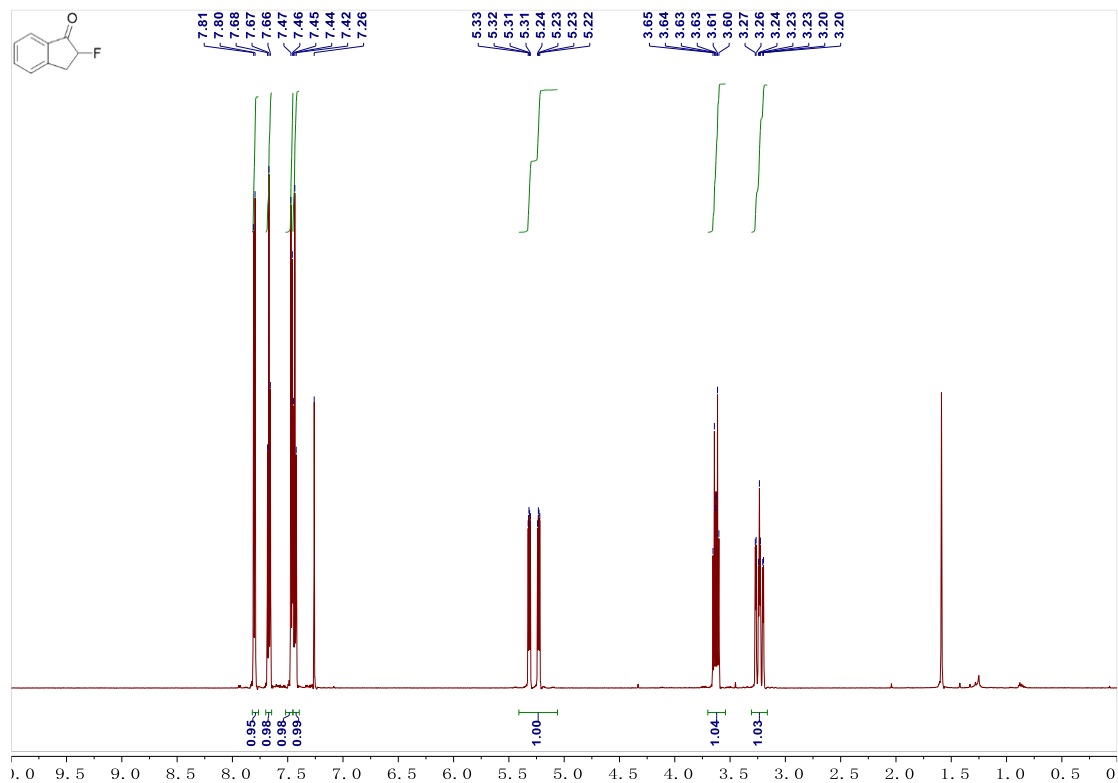
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1k**



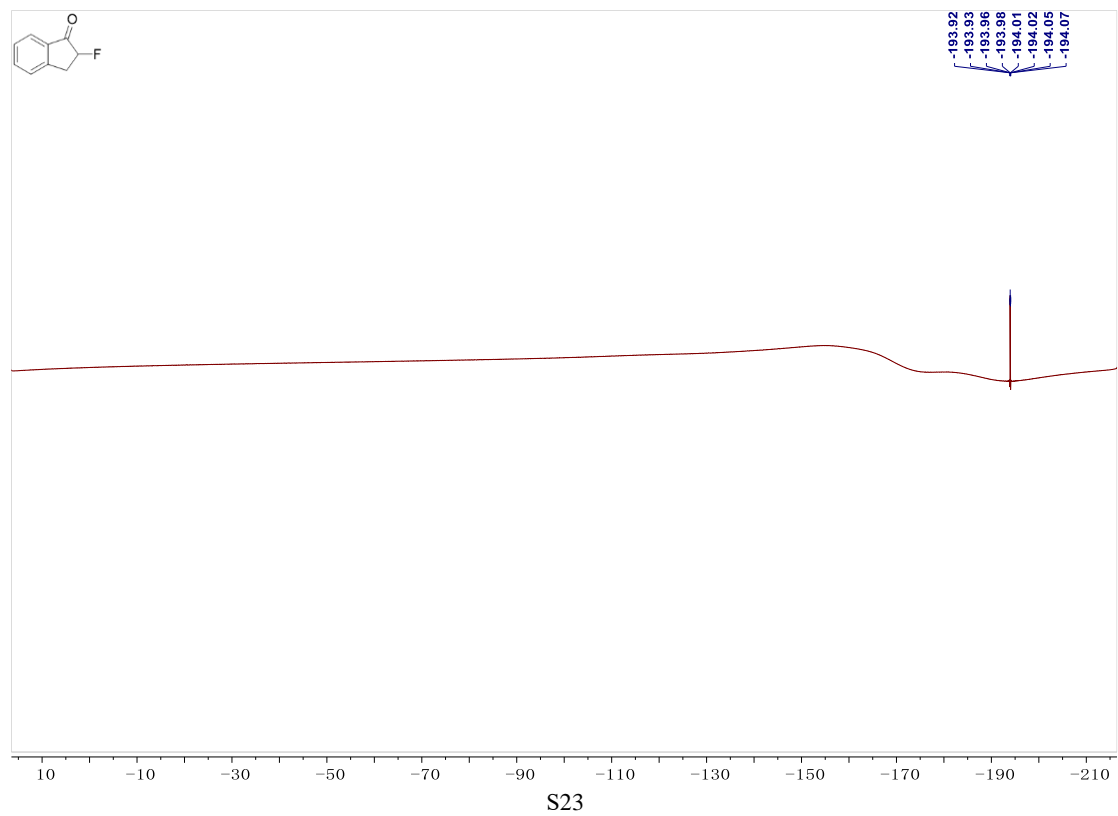
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1k**



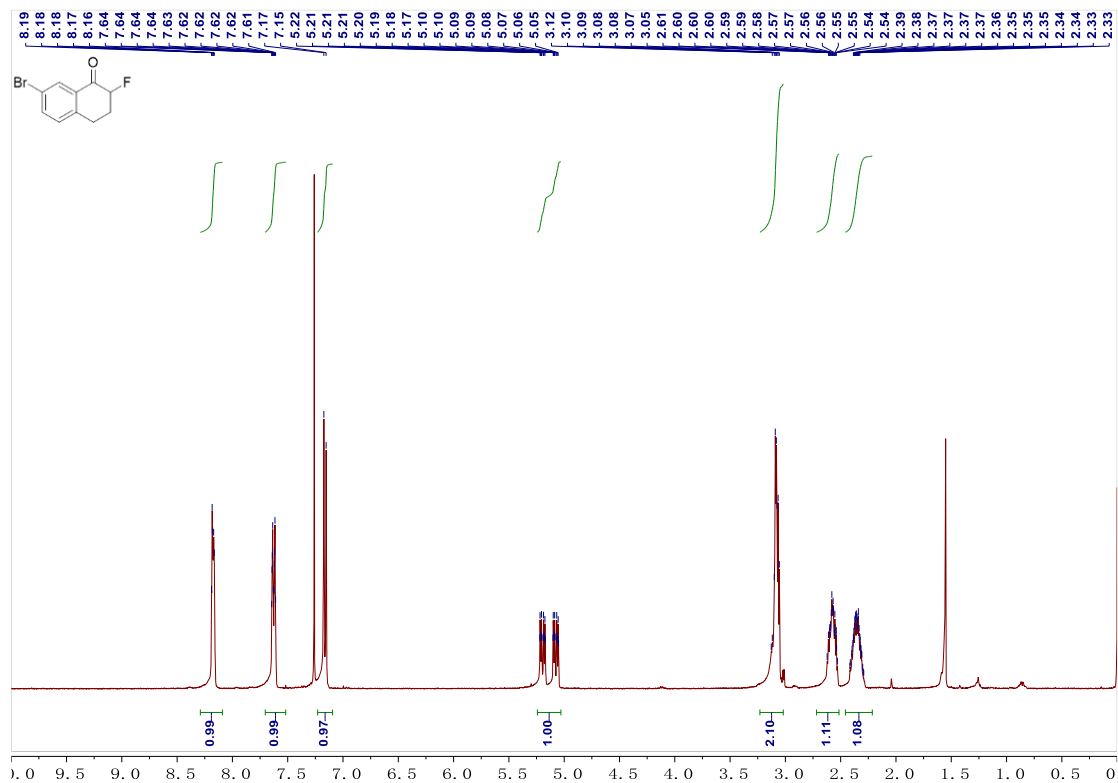
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **11**



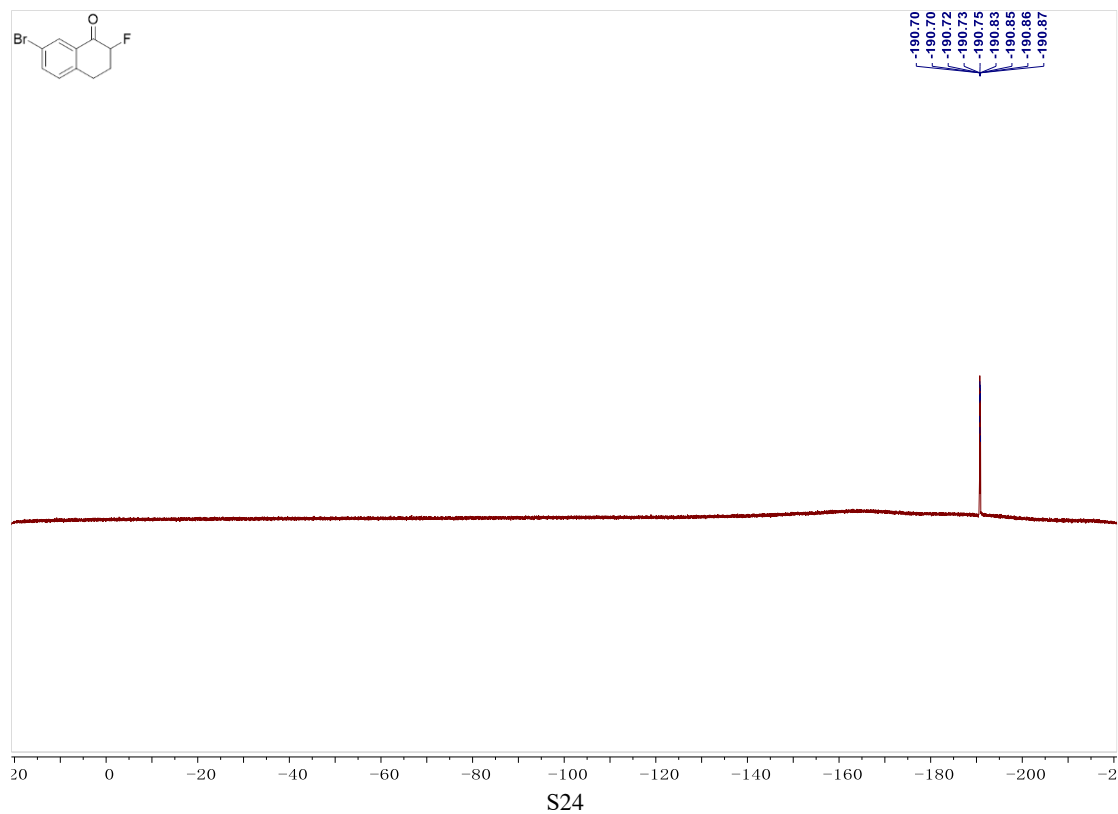
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **11**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1m**

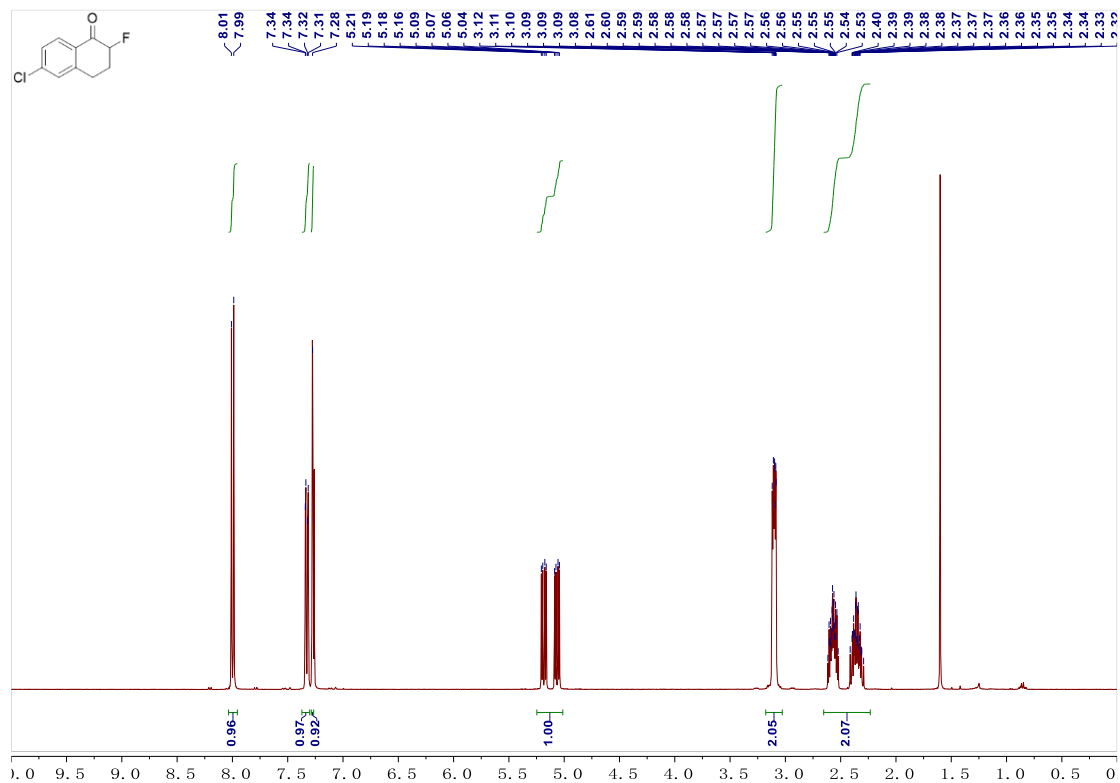


<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1m**

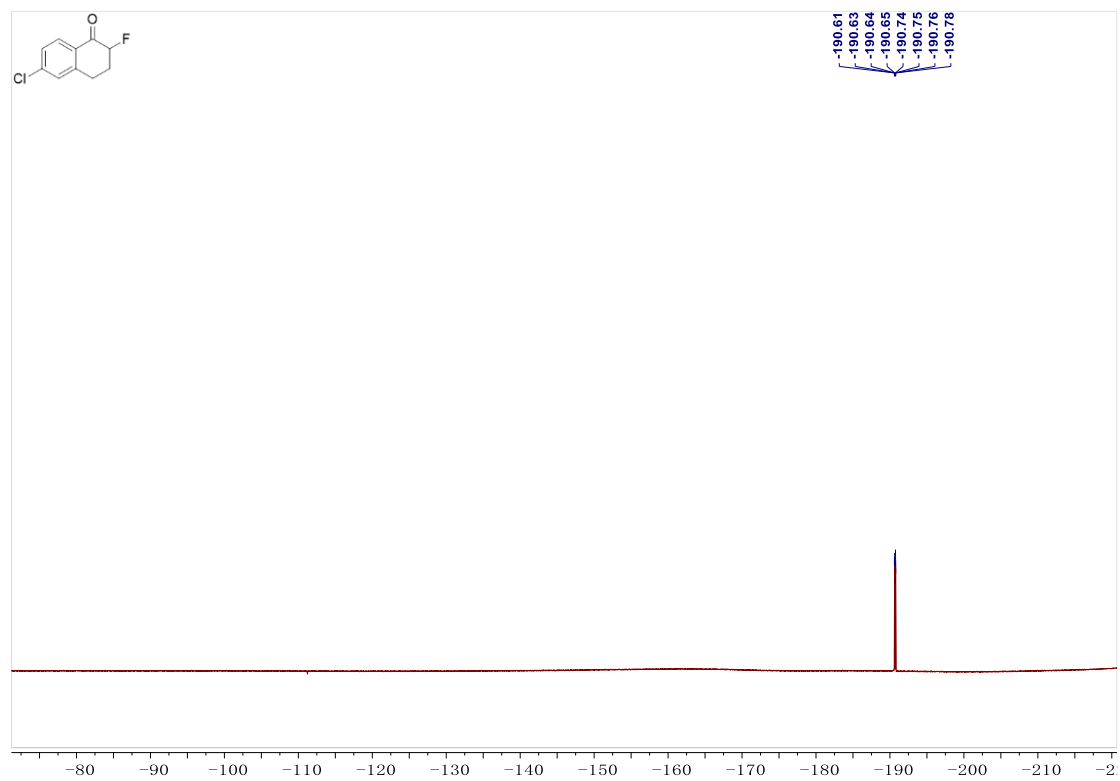




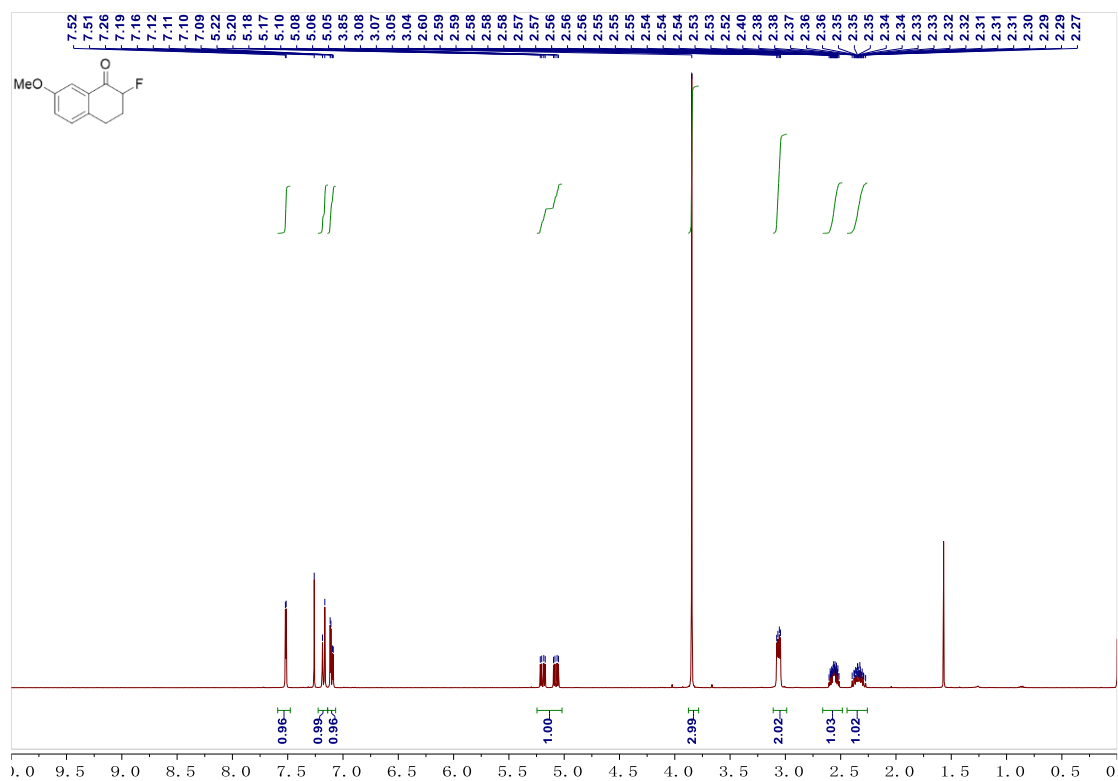
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1n**



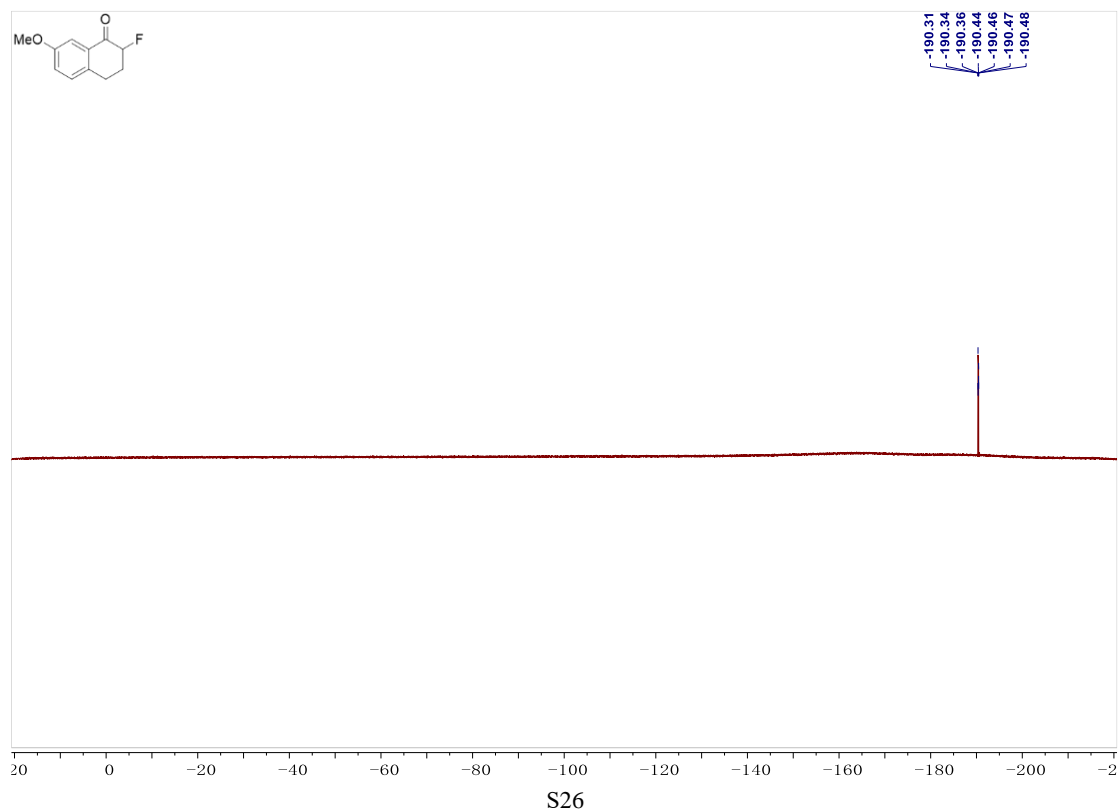
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1n**



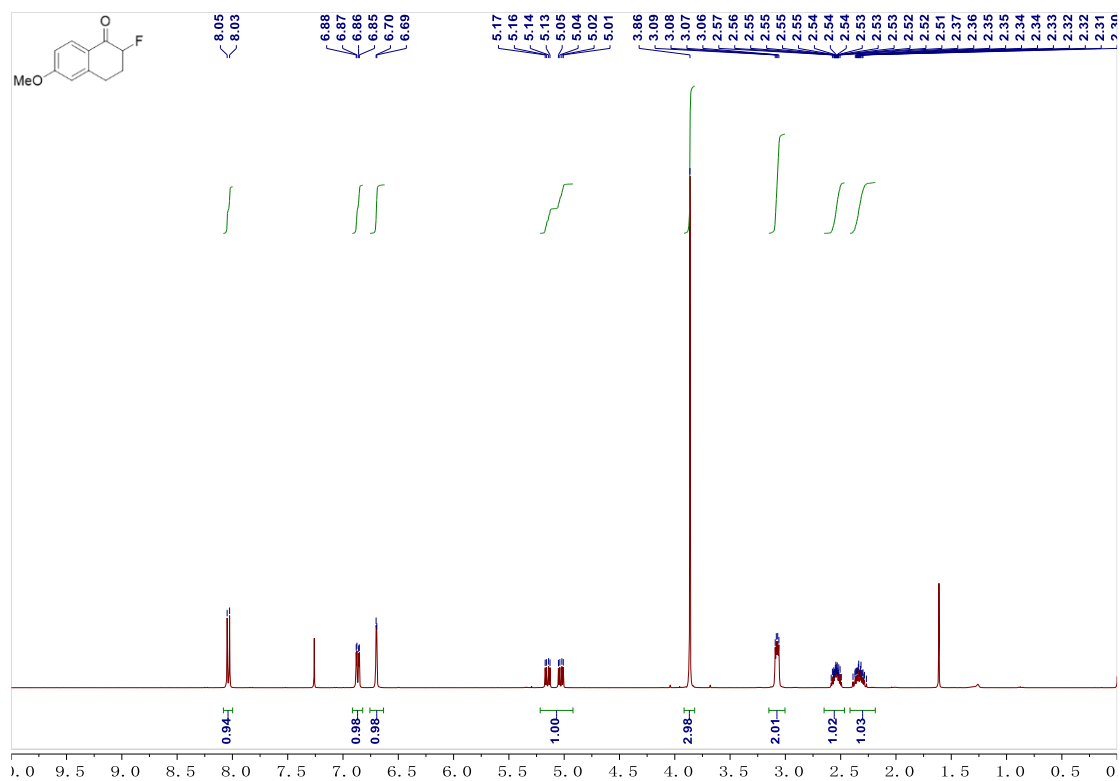
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1o**



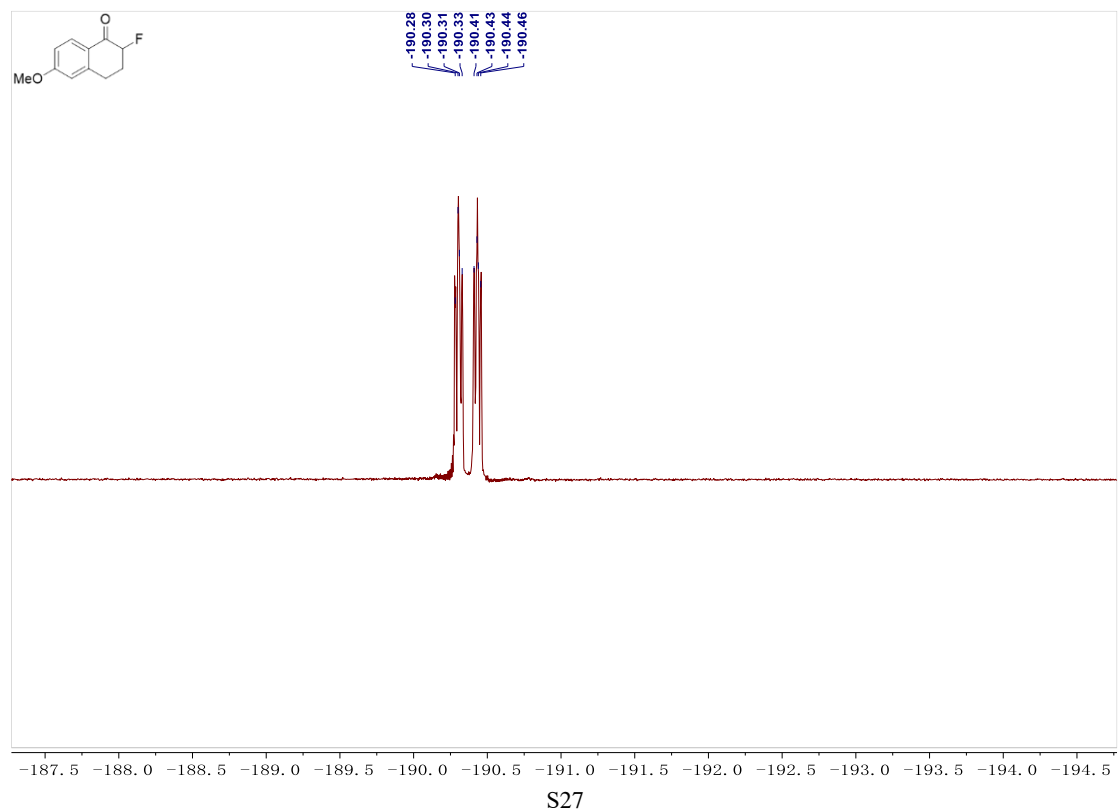
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1o**



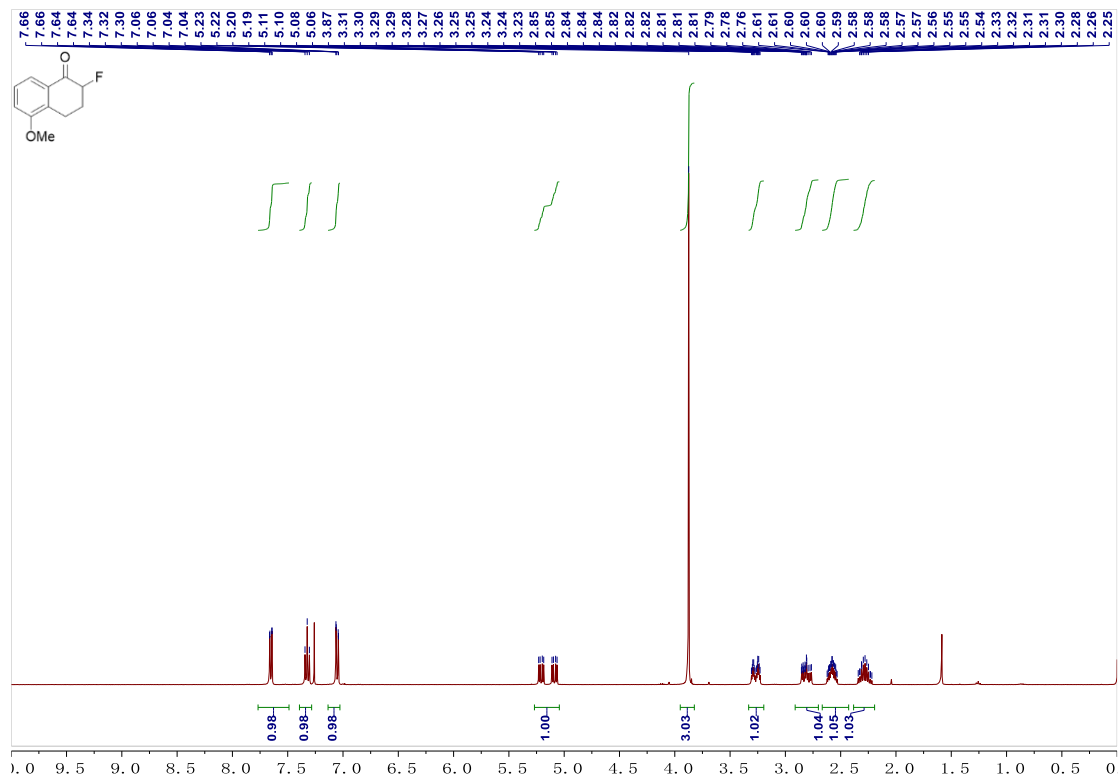
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1p**



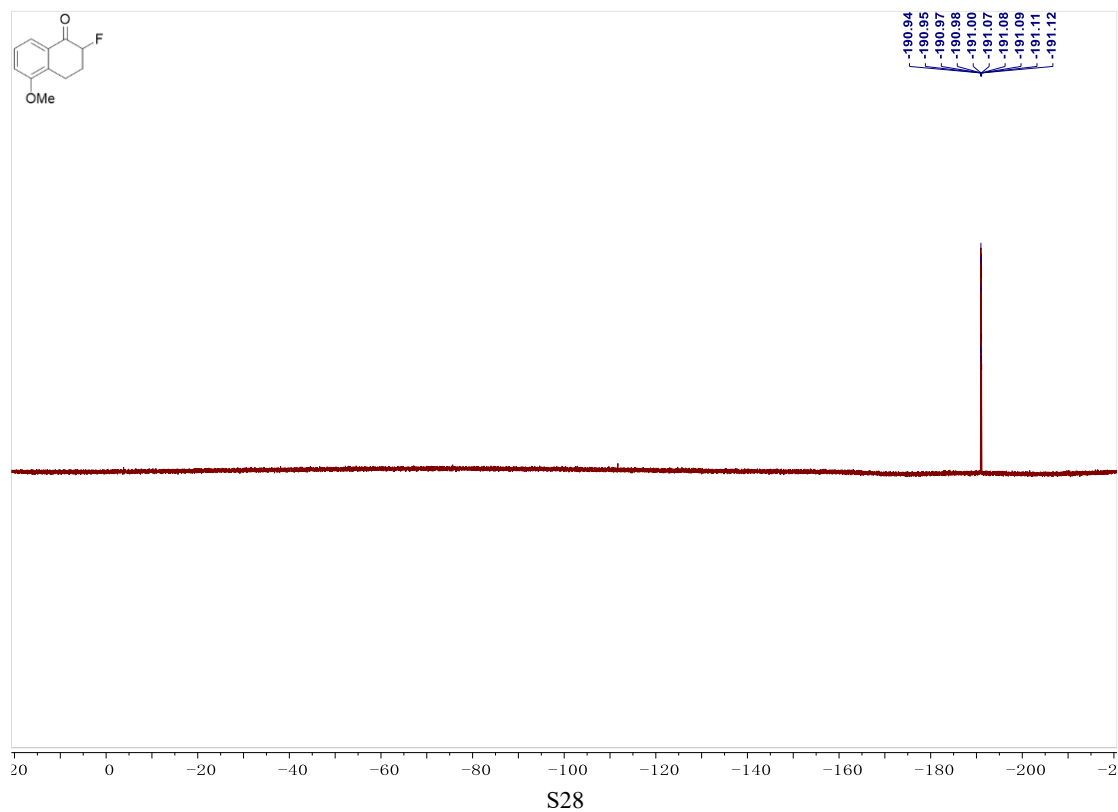
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1p**



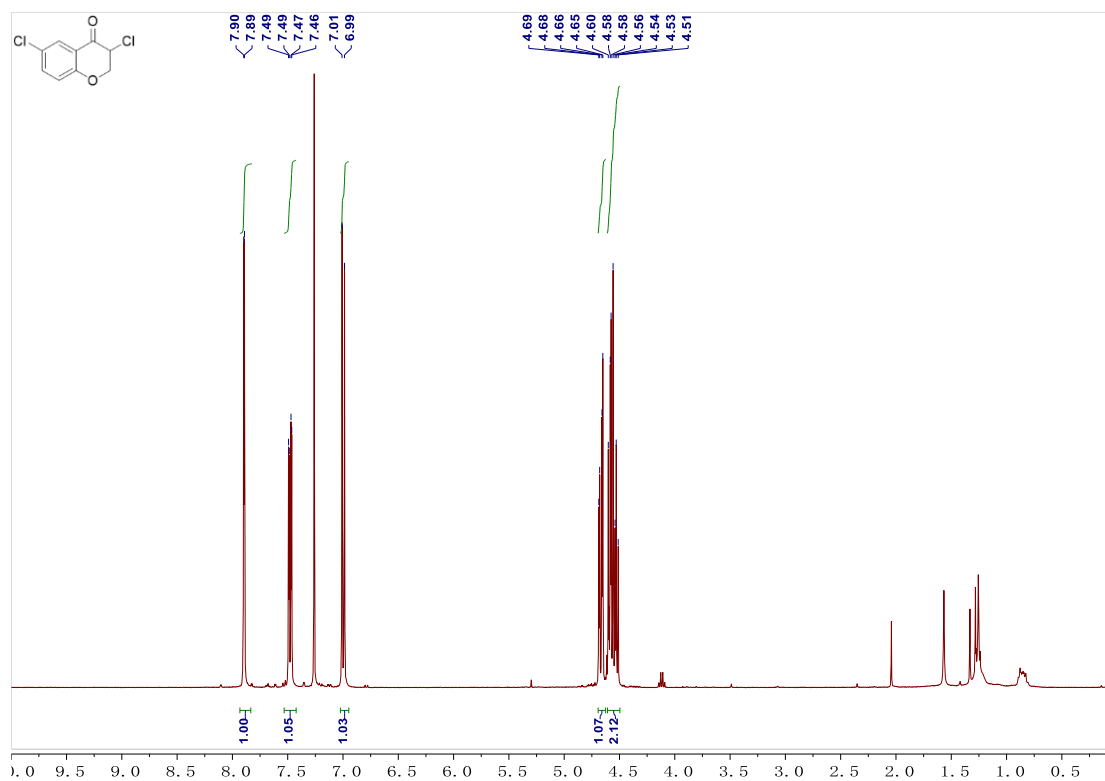
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1q**



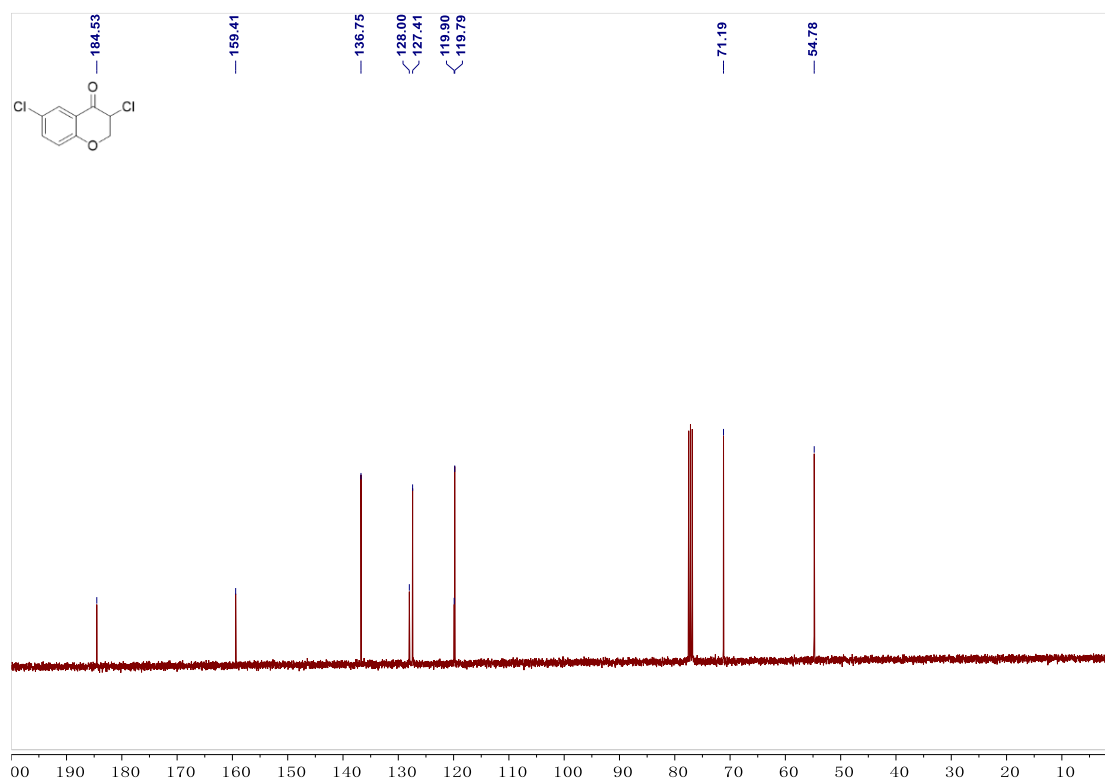
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **1q**



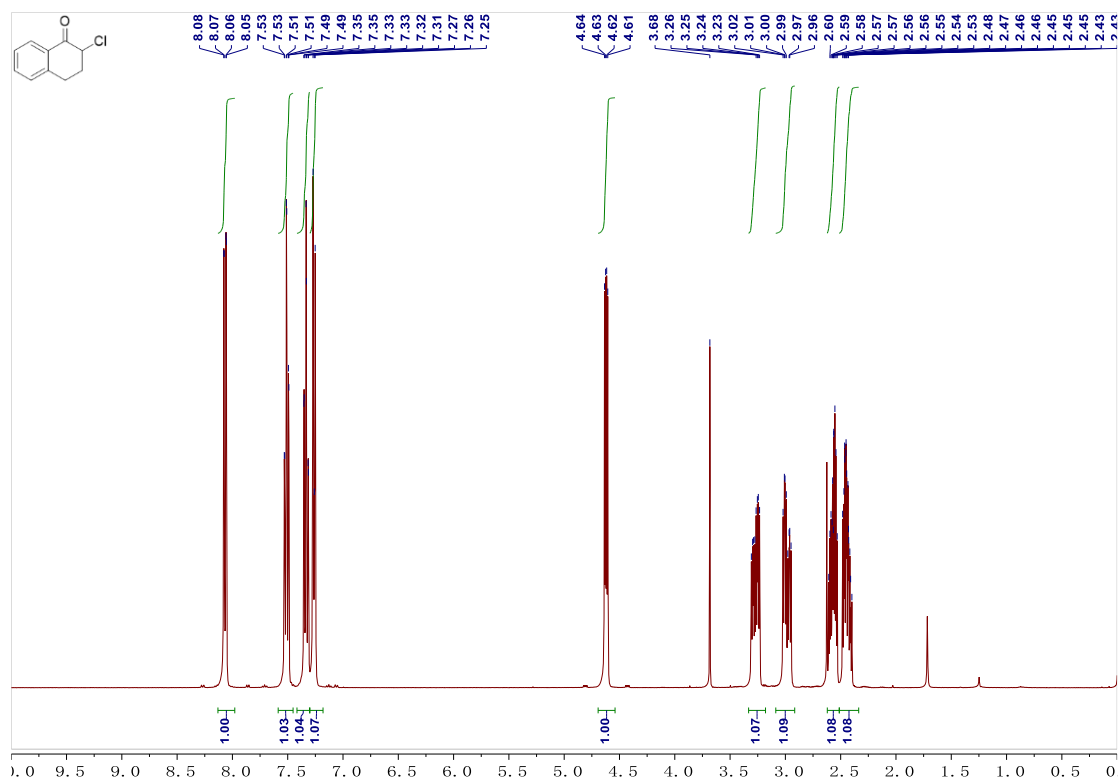
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **1r**



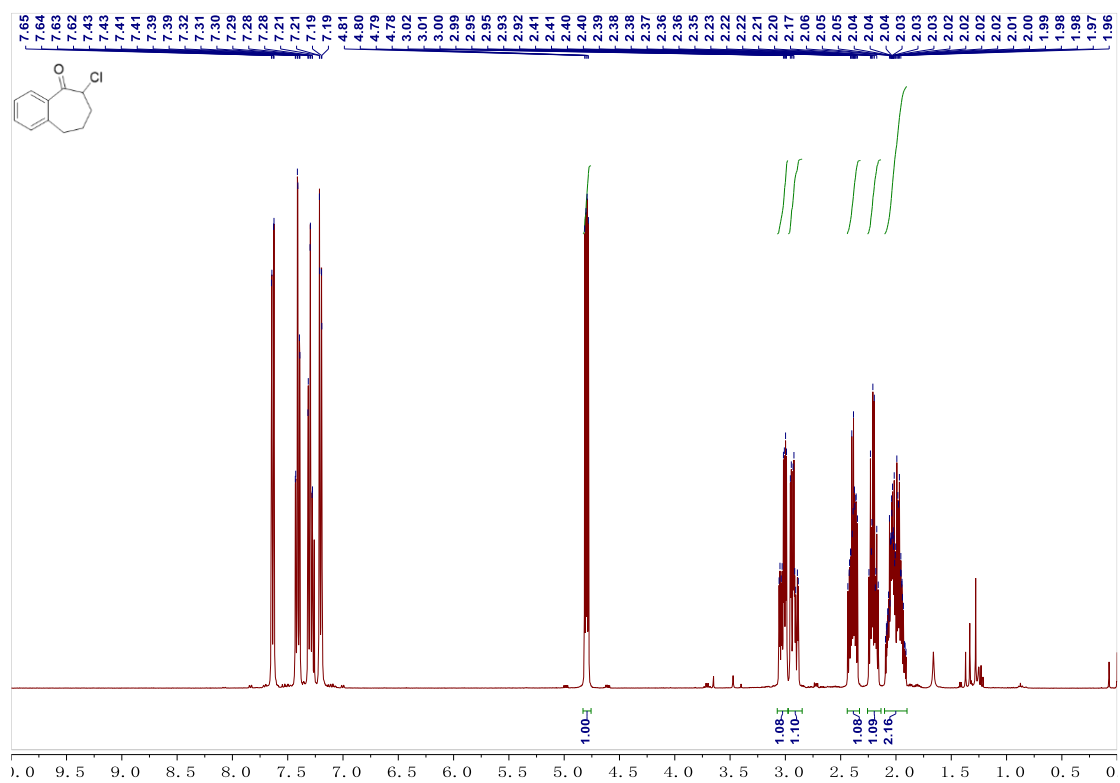
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **1r**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1s**

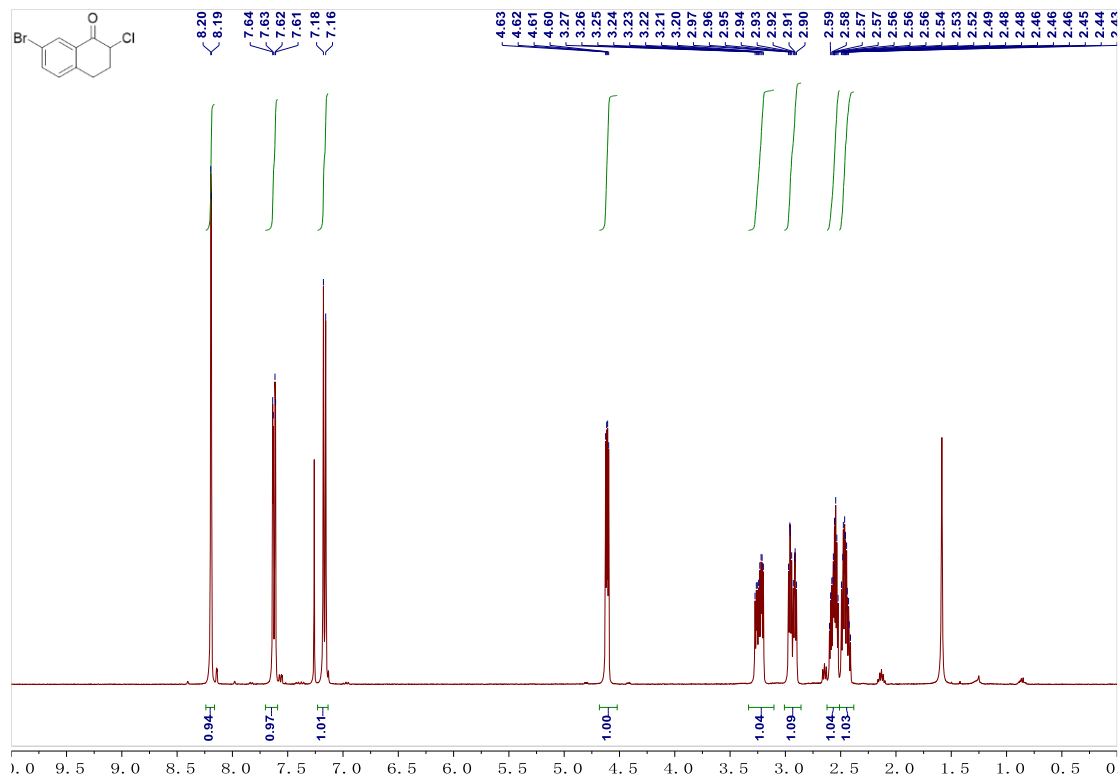


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1t**

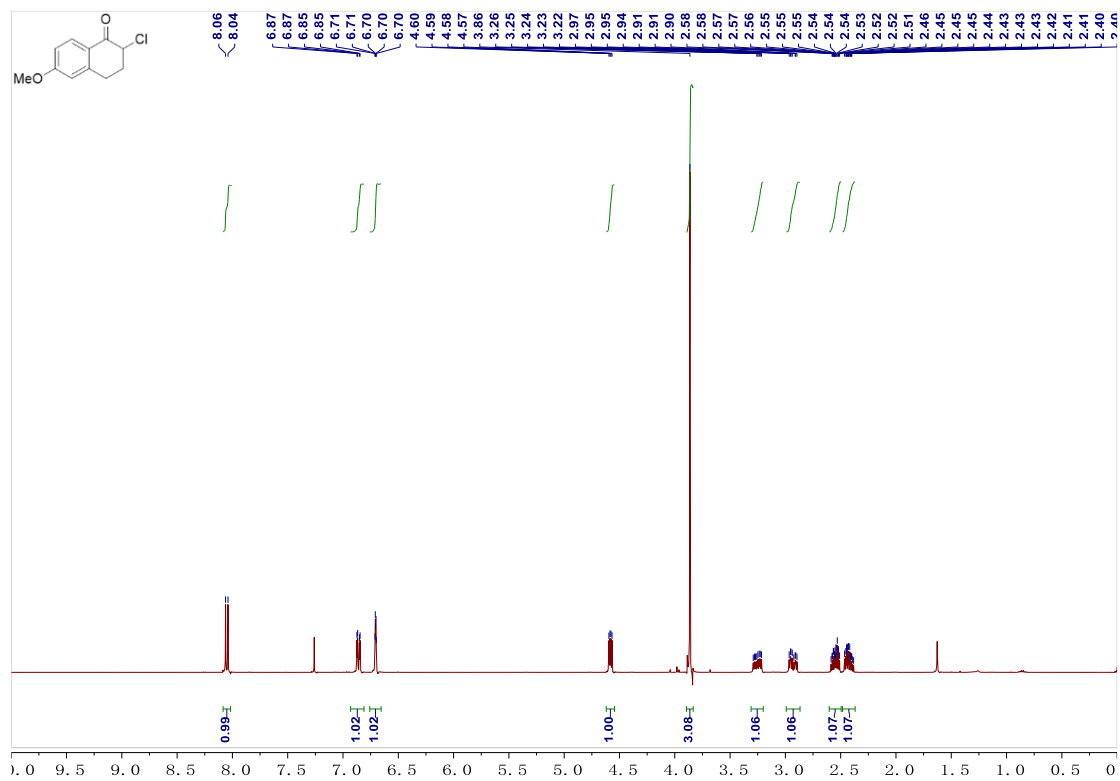




<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1v**

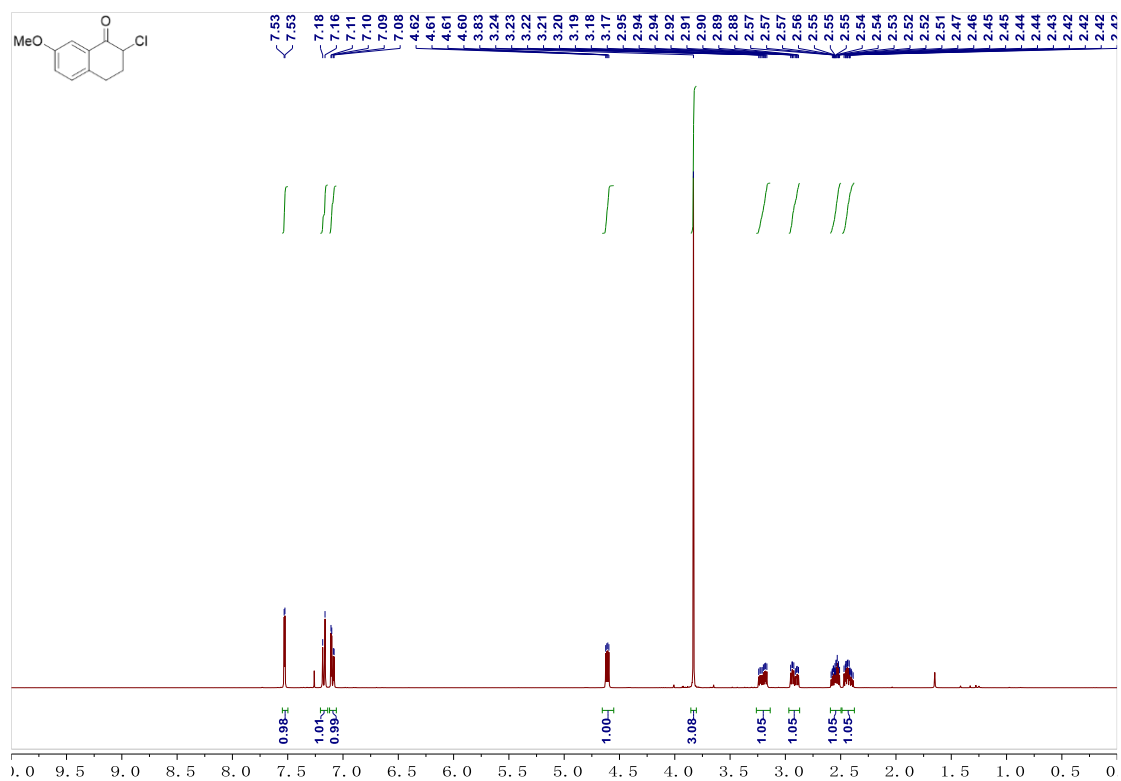


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1w**





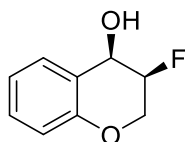
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **1x**



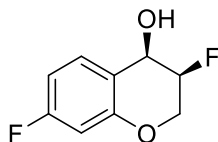
## 4. General procedure for Asymmetric hydrogenation of cyclic $\alpha$ -halogenated ketones

Prepared the [Ir-f-phamidol] solution: in a 5 ml vial was charged with [Ir-f phamidol] complexes 19.6 mg and anhydrous toluene 2 ml to make a 0.0125M [Ir-f- phamidol] solution.

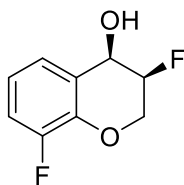
General procedure for S/C = 1000: In an argon-filled glove box, the prepared [Ir-f-phamidol] solution (32  $\mu$ L), KOH (2.2 mg, 0.04 mmol) and ketones (0.4 mmol) in were charged in a 5 ml vial in 1.0 mL anhydrous toluene. The vial was transferred to an autoclave, which was then pressurized with 5 atm of H<sub>2</sub> and stirred at room temperature for 16 h. The hydrogen gas was released slowly in a well-ventilated hood and the crude reaction mixture was evaporated under reduced pressure. The dr values were measured by <sup>1</sup>H NMR from the crude product, after that, purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (80:20, v/v) afforded the reduced product, then the product was analyzed by chiral HPLC for ee.



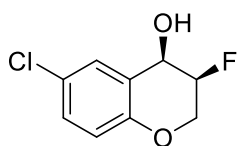
(3*S*,4*R*)-3-Fluorochroman-4-ol (**2a**):<sup>[31]</sup> Colourless crystal, 67 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 99%, [ $\alpha$ ]<sub>D</sub><sup>23</sup> = 42.7 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 7.6 Hz, 1H), 7.23 (dddd, *J* = 8.0, 7.3, 1.7, 0.6 Hz, 1H), 6.99 (td, *J* = 7.5, 1.2 Hz, 1H), 6.85 (dd, *J* = 8.2, 0.9 Hz, 1H), 5.00 (dddd, *J* = 48.3, 5.6, 3.6, 2.0 Hz, 1H), 4.90 (dd, *J* = 20.0, 4.0 Hz, 1H), 4.48 (ddd, *J* = 12.2, 7.8, 5.6 Hz, 1H), 4.21 (dddd, *J* = 28.5, 12.2, 2.0, 1.2 Hz, 1H), 2.37 (d, *J* = 7.8 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -209.40 (dddd, *J* = 48.1, 28.4, 20.0, 7.9 Hz).



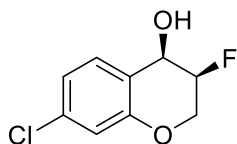
(3*S*,4*R*)-3,7-Difluorochroman-4-ol (**2b**):<sup>[3]</sup> Colourless crystal, 72 mg, 97% yield, dr (*cis/trans*) > 20:1,  $ee_{cis}$  = 96%,  $[\alpha]_D^{23}$  = 46.8 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 (dd,  $J$  = 8.6, 6.4 Hz, 1H), 6.71 (td,  $J$  = 8.4, 2.5 Hz, 1H), 6.57 (dd,  $J$  = 10.0, 2.5 Hz, 1H), 4.99 (dddd,  $J$  = 48.1, 5.6, 3.6, 2.0 Hz, 1H), 4.86 (ddd,  $J$  = 19.6, 8.9, 3.5 Hz, 1H), 4.48 (ddd,  $J$  = 12.3, 7.9, 5.6 Hz, 1H), 4.22 (ddt,  $J$  = 28.2, 12.2, 1.6 Hz, 1H), 2.34 (dd,  $J$  = 8.9, 2.3 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -111.52 (q,  $J$  = 8.2 Hz), -209.63 (dddd,  $J$  = 48.0, 28.1, 19.5, 8.1 Hz).



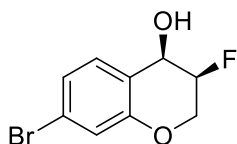
(3*S*,4*R*)-3,8-Difluorochroman-4-ol (**2c**): Colourless crystal, 73 mg, 98% yield, dr (*cis/trans*) > 20:1,  $ee_{cis}$  = 93%,  $[\alpha]_D^{23}$  = 33.6 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.25 (d,  $J$  = 8.4 Hz, 1H), 7.03 (ddd,  $J$  = 10.5, 8.2, 1.6 Hz, 1H), 6.91 (td,  $J$  = 8.0, 4.7 Hz, 1H), 5.02 (dddd,  $J$  = 48.0, 5.4, 3.6, 1.9 Hz, 1H), 4.90 (dd,  $J$  = 20.6, 3.6 Hz, 1H), 4.57 (ddd,  $J$  = 12.4, 8.3, 5.2 Hz, 1H), 4.28 (ddt,  $J$  = 29.9, 12.5, 1.5 Hz, 1H), 2.45 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.9 (d,  $J$  = 246.1 Hz), 141.8 (d,  $J$  = 11.6 Hz), 124.3, 123.7 (d,  $J$  = 3.6 Hz), 121.2 (d,  $J$  = 7.1 Hz), 116.4 (d,  $J$  = 17.6 Hz), 85.9 (d,  $J$  = 178.2 Hz), 65.1 (d,  $J$  = 22.3 Hz), 64.9 (dd,  $J$  = 19.7 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -136.26 (dd,  $J$  = 10.7, 4.5 Hz), -209.43 (dddd,  $J$  = 48.7, 29.5, 20.8, 8.3 Hz). HRMS (ESI/ion trap):  $m/z$  [M + H - H<sub>2</sub>O]<sup>+</sup> calcd for C<sub>9</sub>H<sub>7</sub>F<sub>2</sub>O 169.0465, found 169.0456.



(3*S*,4*R*)-6-Chloro-3-fluorochroman-4-ol (**2d**): Colourless crystal, 80 mg, 99% yield, dr (*cis/trans*) > 20:1,  $ee_{cis} = 96\%$ ,  $[\alpha]_D^{23} = 58.3$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 (s, 1H), 7.17 (dd,  $J = 8.6, 2.4$  Hz, 1H), 6.78 (d,  $J = 8.6$  Hz, 1H), 4.99 (d,  $J = 48.3$  Hz, 1H), 4.84 (dd,  $J = 21.4, 3.5$  Hz, 1H), 4.49 (ddd,  $J = 13.1, 8.6, 4.8$  Hz, 1H), 4.20 (dd,  $J = 31.6, 12.6$  Hz, 1H), 2.40 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.0, 129.9, 128.4, 126.5, 123.5, 117.9, 85.8 (d,  $J = 178.1$  Hz), 65.1 (d,  $J = 21.7$  Hz), 65.0 (d,  $J = 19.8$  Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -209.50 (dddd,  $J = 48.5, 30.7, 21.3, 8.5$  Hz). HRMS (ESI/ion trap):  $m/z$  [M + H - H<sub>2</sub>O]<sup>+</sup> calcd for C<sub>9</sub>H<sub>7</sub>ClFO 185.0169, found 185.0161.

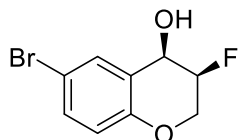


(3*S*,4*R*)-7-Chloro-3-fluorochroman-4-ol (**2e**): Colourless crystal, 80 mg, 99% yield, dr (*cis/trans*) > 20:1,  $ee_{cis} = 93\%$ ,  $[\alpha]_D^{23} = 45.9$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.40 (d,  $J = 8.3$  Hz, 1H), 6.97 (dd,  $J = 8.3, 2.1$  Hz, 1H), 6.87 (d,  $J = 2.1$  Hz, 1H), 4.99 (dddd,  $J = 48.2, 5.4, 3.6, 1.9$  Hz, 1H), 4.85 (d,  $J = 20.3$  Hz, 1H), 4.49 (ddd,  $J = 12.4, 8.3, 5.3$  Hz, 1H), 4.21 (ddt,  $J = 29.8, 12.4, 1.5$  Hz, 1H), 2.34 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.0, 135.2, 129.8, 121.9, 120.4, 116.6, 86.0 (d,  $J = 178.6$  Hz), 65.0 (d,  $J = 22.3$  Hz), 64.9 (d,  $J = 19.8$  Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -209.56 (dddd,  $J = 56.4, 30.1, 21.0, 7.5$  Hz). HRMS (ESI/ion trap):  $m/z$  [M + H - H<sub>2</sub>O]<sup>+</sup> calcd for C<sub>9</sub>H<sub>7</sub>ClFO 185.0169, found 185.0161.

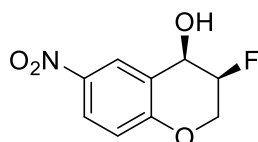


(3*S*,4*R*)-7-Bromo-3-fluorochroman-4-ol (**2f**):<sup>[31]</sup> Colourless crystal, 96 mg, 98% yield, dr (*cis/trans*) > 20:1,  $ee_{cis} = 98\%$ ,  $[\alpha]_D^{23} = 38.6$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.33 (d,  $J = 8.2$  Hz, 1H), 7.11 (dd,  $J = 8.2, 1.6$  Hz, 1H), 7.03 (d,  $J = 1.6$  Hz, 1H), 4.99 (d,  $J = 48.4$  Hz, 1H), 4.83 (d,  $J = 20.5$  Hz, 1H), 4.48 (ddd,  $J = 13.1, 8.3, 5.1$

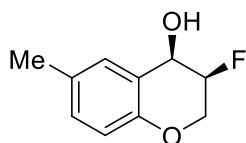
Hz, 1H), 4.21 (dd,  $J = 30.1, 12.4$  Hz, 1H), 2.41 (br, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -209.50 (dddd,  $J = 49.8, 30.0, 20.7, 8.3$  Hz).



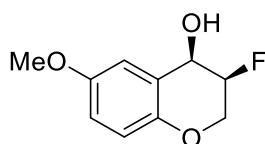
(3*S*,4*R*)-6-Bromo-3-fluorochroman-4-ol (**2g**): Colourless crystal, 96 mg, 98% yield, dr (*cis/trans*) > 20:1,  $ee_{cis} = 99\%$ ,  $[\alpha]_D^{23} = 27.3$  (c 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.61 (d,  $J = 2.5$  Hz, 1H), 7.30 (dd,  $J = 8.7, 2.4$  Hz, 1H), 6.73 (d,  $J = 8.7$  Hz, 1H), 4.99 (d,  $J = 48.3$  Hz, 1H), 4.85 (d,  $J = 21.1$  Hz, 1H), 4.49 (ddd,  $J = 13.1, 8.6, 4.8$  Hz, 1H), 4.20 (dd,  $J = 31.6, 12.6$  Hz, 1H), 2.43 (br, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.5, 132.8, 131.3, 124.0, 118.3, 113.7, 85.8 (d,  $J = 178.5$  Hz), 65.1 (d,  $J = 21.8$  Hz), 65.0 (d,  $J = 19.8$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -209.61 (dddd,  $J = 47.6, 30.6, 21.4, 8.5$  Hz). HRMS (ESI/ion trap):  $m/z$   $[\text{M} + \text{H} - \text{H}_2\text{O}]^+$  calcd for  $\text{C}_9\text{H}_7\text{BrFO}$  228.9664, found 228.9654.



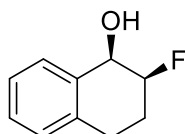
(3*S*,4*R*)-3-Fluoro-6-nitrochroman-4-ol (**2h**):<sup>[3]</sup> Colourless crystal, 79 mg, 93% yield, dr (*cis/trans*) > 20:1,  $ee_{cis} = \%$ ,  $[\alpha]_D^{23} = 195.5$  (c 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.46 (d,  $J = 2.7$  Hz, 1H), 8.10 (dd,  $J = 9.1, 2.7$  Hz, 1H), 6.93 (d,  $J = 9.1$  Hz, 1H), 5.09 (dt,  $J = 48.3, 3.9$  Hz, 1H), 4.93 (dd,  $J = 23.0, 6.9$  Hz, 1H), 4.63 (ddd,  $J = 13.5, 9.5, 4.3$  Hz, 1H), 4.34 (dd,  $J = 33.7, 13.0$  Hz, 1H), 2.62 (d,  $J = 9.2$  Hz, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -209.30 (dddd,  $J = 48.3, 33.1, 23.1, 9.6$  Hz).



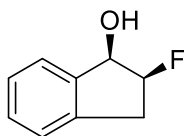
(3*S*,4*R*)-3-Fluoro-6-methylchroman-4-ol (**2i**):<sup>[31]</sup> Colourless crystal, 71 mg, 98% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 94%, [α]<sub>D</sub><sup>23</sup> = 31.0 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.26 (br, 1H), 7.03 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 4.99 (dddd, *J* = 48.2, 5.8, 3.6, 2.1 Hz, 1H), 4.87 (d, *J* = 18.8, 1H), 4.44 (ddd, *J* = 12.1, 7.6, 5.8 Hz, 1H), 4.16 (ddt, *J* = 27.7, 12.1, 1.5 Hz, 1H), 2.32 (br, 1H), 2.29 (s, 3H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -209.72 (m).



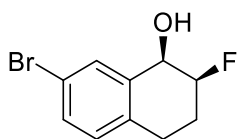
(3*S*,4*R*)-3-Fluoro-6-methoxychroman-4-ol (**2j**):<sup>[31]</sup> Colourless crystal, 78 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 91%, [α]<sub>D</sub><sup>23</sup> = 44.3 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.01 (d, *J* = 2.3 Hz, 1H), 6.86-6.73 (m, 2H), 4.99 (dddd, *J* = 48.3, 5.3, 3.7, 1.8 Hz, 1H), 4.87 (dd, *J* = 20.8, 3.7 Hz, 1H), 4.45 (ddd, *J* = 12.4, 8.1, 5.2 Hz, 1H), 4.16 (ddt, *J* = 30.3, 12.4, 1.5 Hz, 1H), 3.77 (s, 3H), 2.38 (br, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -209.44 (dddd, *J* = 48.7, 29.7, 20.8, 8.3 Hz).



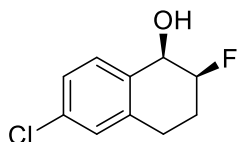
(1*R*,2*S*)-2-Fluoro-1,2,3,4-tetrahydronaphthalen-1-ol (**2k**):<sup>[81]</sup> Colourless crystal, 66 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 99%, [α]<sub>D</sub><sup>23</sup> = 21.2 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.52 (dd, *J* = 5.5, 3.7 Hz, 1H), 7.30-.21 (m, 2H), 7.17-7.09 (m, 1H), 5.00 (ddt, *J* = 49.7, 8.7, 3.0 Hz, 1H), 4.81 (ddd, *J* = 17.8, 7.2, 3.3 Hz, 1H), 3.04 (ddd, *J* = 15.9, 9.7, 3.8 Hz, 1H), 2.80 (dt, *J* = 17.1, 6.7 Hz, 1H), 2.49-2.29 (m, 2H), 2.02 (ddtd, *J* = 27.1, 13.6, 6.9, 2.6 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -197.58 (dddd, *J* = 50.1, 25.1, 17.6, 5.9 Hz).



(1*R*,2*S*)-2-Fluoro-2,3-dihydro-1*H*-inden-1-ol (**2l**):<sup>[8]</sup> Colourless crystal, 60 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 96%, [α]<sub>D</sub><sup>23</sup> = 53 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.48 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.34-7.22 (m, 3H), 5.32 (dtd, *J* = 53.8, 4.3, 1.5 Hz, 1H), 5.13 (ddd, *J* = 18.2, 10.4, 4.2 Hz, 1H), 3.33-3.02 (m, 2H), 2.39 (dd, *J* = 10.4, 4.4 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -201.51 (m).



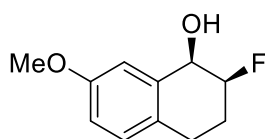
(1*R*,2*S*)-7-Bromo-2-fluoro-1,2,3,4-tetrahydronaphthalen-1-ol (**2m**): Colourless crystal, 96 mg, 98% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 99%, [α]<sub>D</sub><sup>23</sup> = 43.4 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.68 (d, *J* = 2.1 Hz, 1H), 7.34 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 5.00 (ddt, *J* = 49.9, 7.8, 2.7 Hz, 1H), 4.72 (ddd, *J* = 20.1, 8.3, 3.3 Hz, 1H), 2.97 (dt, *J* = 17.4, 7.2 Hz, 1H), 2.72 (dt, *J* = 17.2, 6.2 Hz, 1H), 2.45 (dd, *J* = 8.2, 2.6 Hz, 1H), 2.44-2.29 (m, 1H), 2.10-1.85 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 138.0 (d, *J* = 3.6 Hz), 134.6, 131.8, 131.2, 130.1, 120.2, 90.6 (d, *J* = 173.6 Hz), 68.8 (d, *J* = 19.6 Hz), 24.8 (d, *J* = 6.6 Hz), 24.7 (d, *J* = 18.8 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -200.28 (dddd, *J* = 50.2, 30.3, 20.4, 6.4 Hz). HRMS (ESI/ion trap): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>10</sub>H<sub>10</sub>BrFNaO 266.9797, found 266.9786.



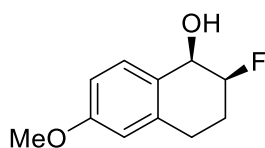
(1*R*,2*S*)-6-Chloro-2-fluoro-1,2,3,4-tetrahydronaphthalen-1-ol (**2n**): Colourless crystal, 79 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 99%, [α]<sub>D</sub><sup>23</sup> = 58.4 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.44 (d, *J* = 8.3 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.11 (d, *J* = 2.1 Hz, 1H), 4.98 (ddt, *J* = 49.8, 8.2, 2.9 Hz, 1H), 4.73 (ddd, *J* = 18.9, 7.7,

3.3 Hz, 1H), 3.00 (dt,  $J = 15.5, 7.1$  Hz, 1H), 2.75 (dt,  $J = 17.3, 6.4$  Hz, 1H), 2.45 (dd,  $J = 7.7, 2.7$  Hz, 1H), 2.41-2.30 (m, 1H), 2.07-1.90 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.6, 134.2 (d,  $J = 4.2$  Hz), 133.9, 130.6, 128.2, 127.0, 90.8 (d,  $J = 173.7$  Hz), 68.7 (d,  $J = 19.5$  Hz), 25.4 (d,  $J = 8.7$  Hz), 24.5 (d,  $J = 20.2$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -199.05 (m).

HRMS (ESI/ion trap):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{10}\text{H}_{10}\text{ClFNaO}$  223.0302, found 223.0292.



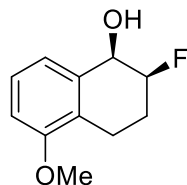
(1*R*,2*S*)-2-Fluoro-7-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (**2o**):<sup>[9]</sup> Colourless crystal, 78 mg, 99% yield, dr (*cis/trans*) > 20:1,  $ee_{cis} = 99\%$ ,  $[\alpha]_{\text{D}}^{23} = 43.6$  (c 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.06 (d,  $J = 2.8$  Hz, 1H), 7.04 (d,  $J = 8.4$  Hz, 1H), 6.81 (dd,  $J = 8.4, 2.8$  Hz, 1H), 4.99 (ddt,  $J = 49.9, 8.3, 2.9$  Hz, 1H), 4.75 (dd,  $J = 18.9, 3.3$  Hz, 1H), 3.80 (s, 3H), 2.96 (dt,  $J = 15.3, 7.0$  Hz, 1H), 2.72 (dt,  $J = 16.7, 7.0$  Hz, 1H), 2.42-2.30 (m, 1H), 2.27 (br, 1H), 2.09-1.89 (m, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -198.97 (dddd,  $J = 48.5, 28.0, 18.6, 6.0$  Hz).



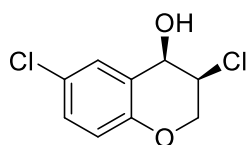
(1*R*,2*S*)-2-Fluoro-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (**2p**):<sup>[9]</sup> Colourless crystal, 78 mg, 99% yield, dr (*cis/trans*) > 20:1,  $ee_{cis} = 99\%$ ,  $[\alpha]_{\text{D}}^{23} = 18.3$  (c 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (d,  $J = 8.5$  Hz, 1H), 6.81 (dd,  $J = 8.6, 2.7$  Hz, 1H), 6.64 (d,  $J = 2.7$  Hz, 1H), 4.94 (ddt,  $J = 49.4, 9.2, 3.1$  Hz, 1H), 4.78 (ddd,  $J = 16.1, 6.7, 3.4$  Hz, 1H), 3.79 (s, 3H), 3.08-2.91 (m, 1H), 2.78 (dt,  $J = 17.1, 7.1$  Hz, 1H), 2.43-2.33 (m, 1H), 2.31 (dd,  $J = 6.6, 2.8$  Hz, 1H), 2.10-1.91 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.6, 137.2, 130.9, 127.9 (d,  $J = 4.9$  Hz), 113.1, 113.0, 91.4 (d,  $J = 174.3$  Hz), 68.7 (d,  $J = 19.0$  Hz), 55.4, 26.4 (d,  $J = 9.5$  Hz), 24.2 (d,  $J = 19.7$  Hz).  $^{19}\text{F}$  NMR (376 MHz,



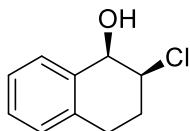
CDCl<sub>3</sub>):  $\delta$  -195.87 (m). HRMS (ESI/ion trap):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>11</sub>H<sub>13</sub>FNaO<sub>2</sub> 219.0797, found 219.0787.



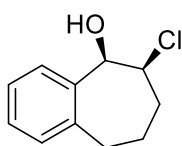
(1*R*,2*S*)-2-Fluoro-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (**2q**): Colourless crystal, 78 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>*cis*</sub> = 99%, [ $\alpha$ ]<sub>D</sub><sup>23</sup> = 10.4 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 (t,  $J$  = 8.4 Hz, 1H), 7.12 (d,  $J$  = 7.7 Hz, 1H), 6.79 (d,  $J$  = 8.1 Hz, 1H), 4.96 (ddt,  $J$  = 49.7, 8.9, 3.0 Hz, 1H), 4.79 (ddd,  $J$  = 17.3, 7.1, 3.3 Hz, 1H), 3.83 (s, 3H), 2.91 (dtd,  $J$  = 18.0, 6.6, 2.1 Hz, 1H), 2.68 (dt,  $J$  = 18.0, 6.9 Hz, 1H), 2.49-2.23 (m, 2H), 1.99 (ddtd,  $J$  = 26.9, 13.6, 6.8, 2.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.8, 136.8 (d,  $J$  = 4.3 Hz), 127.3, 124.9, 121.1, 109.3, 91.2 (d,  $J$  = 173.6 Hz), 69.0 (d,  $J$  = 19.1 Hz), 55.50, 23.69 (d,  $J$  = 19.7 Hz), 20.24 (d,  $J$  = 8.8 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -197.72 (m). HRMS (ESI/ion trap):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>11</sub>H<sub>13</sub>FNaO<sub>2</sub> 219.0797, found 219.0787.



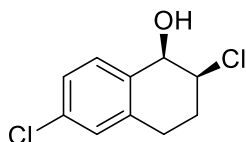
(3*S*,4*R*)-3,6-Dichlorochroman-4-ol (**2r**): Colourless crystal, 83 mg, 95% yield, dr (*cis/trans*) > 20:1, ee<sub>*cis*</sub> = 99%, [ $\alpha$ ]<sub>D</sub><sup>23</sup> = 45.9 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.38 (d,  $J$  = 2.5 Hz, 1H), 7.19 (dd,  $J$  = 8.8, 2.6 Hz, 1H), 6.80 (d,  $J$  = 8.8 Hz, 1H), 4.88 (dd,  $J$  = 7.2, 3.7 Hz, 1H), 4.46 (dt,  $J$  = 6.9, 3.4 Hz, 1H), 4.41-4.26 (m, 2H), 2.49 (d,  $J$  = 7.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  151.8, 130.3, 129.2, 126.4, 123.3, 118.2, 66.1, 66.0, 57.3. HRMS (ESI/ion trap):  $m/z$  [M + H - H<sub>2</sub>O]<sup>+</sup> calcd for C<sub>9</sub>H<sub>7</sub>ClO<sub>2</sub> 200.9874, found 200.9865.



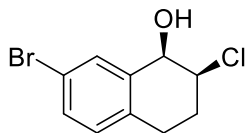
(1*R*,2*S*)-2-Chloro-1,2,3,4-tetrahydronaphthalen-1-ol (**2s**):<sup>[7]</sup> Colourless crystal, 70 mg, 96% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 97%, [α]<sub>D</sub><sup>23</sup> = 22.2 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.55-7.44 (m, 1H), 7.30-7.19 (m, 2H), 7.17-7.06 (m, 1H), 4.86 (dd, *J* = 7.5, 3.4 Hz, 1H), 4.55 (dt, *J* = 8.7, 3.1 Hz, 1H), 3.12 (dt, *J* = 17.3, 6.5 Hz, 1H), 2.85 (dt, *J* = 17.3, 6.6 Hz, 1H), 2.56-2.33 (m, 2H), 2.26-2.14 (m, 1H).



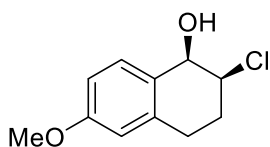
(5*R*,6*S*)-6-Chloro-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol (**2t**):<sup>[7]</sup> Colourless crystal, 78 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = %, [α]<sub>D</sub><sup>23</sup> = -170.0 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.33-7.27 (m, 1H), 7.25-7.17 (m, 2H), 7.13-7.07 (m, 1H), 5.08 (s, 1H), 4.40 (dd, *J* = 9.2, 3.0 Hz, 1H), 3.27-3.00 (m, 1H), 2.64 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.57-2.43 (m, 2H), 2.25 (ddt, *J* = 14.2, 7.3, 3.4 Hz, 1H), 1.97-1.83 (m, 1H), 1.71-1.54 (m, 1H).



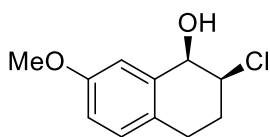
(1*R*,2*S*)-2,6-Dichloro-1,2,3,4-tetrahydronaphthalen-1-ol (**2u**):<sup>[10]</sup> Colourless crystal, 85 mg, 98% yield, dr (*cis/trans*) > 20:1, ee<sub>cis</sub> = 99%, [α]<sub>D</sub><sup>23</sup> = 14.6 (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43 (d, *J* = 8.3 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 4.81 (dd, *J* = 8.0, 3.4 Hz, 1H), 4.53 (dt, *J* = 8.2, 3.0 Hz, 1H), 3.09 (dt, *J* = 17.4, 6.9 Hz, 1H), 2.80 (dt, *J* = 17.4, 6.3 Hz, 1H), 2.49 (d, *J* = 8.0 Hz, 1H), 2.39 (ddt, *J* = 14.2, 8.1, 6.1 Hz, 1H), 2.19 (dddd, *J* = 13.9, 8.3, 6.4, 2.7 Hz, 1H).



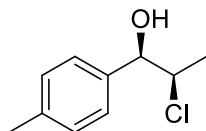
(1*R*,2*S*)-7-Bromo-2-chloro-1,2,3,4-tetrahydronaphthalen-1-ol (**2v**):<sup>[7]</sup> Colourless crystal, 103 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>*cis*</sub> = 99%,  $[\alpha]_{\text{D}}^{23} = 21.2$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.67 (d, *J* = 2.1 Hz, 1H), 7.35 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 4.81 (dd, *J* = 8.6, 3.5 Hz, 1H), 4.56 (dt, *J* = 7.6, 3.0 Hz, 1H), 3.14-2.98 (m, 1H), 2.76 (dt, *J* = 17.4, 6.0 Hz, 1H), 2.48 (d, *J* = 8.5 Hz, 1H), 2.39 (ddt, *J* = 13.52, 7.4, 5.8 Hz, 1H), 2.20 (dddd, *J* = 14.3, 8.6, 6.3, 2.6 Hz, 1H).



(1*R*,2*S*)-2-Chloro-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (**2w**):<sup>[10]</sup> Colourless crystal, 84 mg, 99% yield, dr (*cis/trans*) > 20:1, ee<sub>*cis*</sub> = 99%,  $[\alpha]_{\text{D}}^{23} = 21.5$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.38 (d, *J* = 8.5 Hz, 1H), 6.80 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 4.80 (dd, *J* = 7.0, 3.3 Hz, 1H), 4.49 (dt, *J* = 9.1, 3.1 Hz, 1H), 3.79 (s, 3H), 3.07 (dt, *J* = 17.3, 6.3 Hz, 1H), 2.81 (dt, *J* = 17.3, 6.9 Hz, 1H), 2.45 (d, *J* = 6.9 Hz, 1H), 2.43-2.36 (m, 1H), 2.16 (dtd, *J* = 13.3, 6.4, 2.8 Hz, 1H).



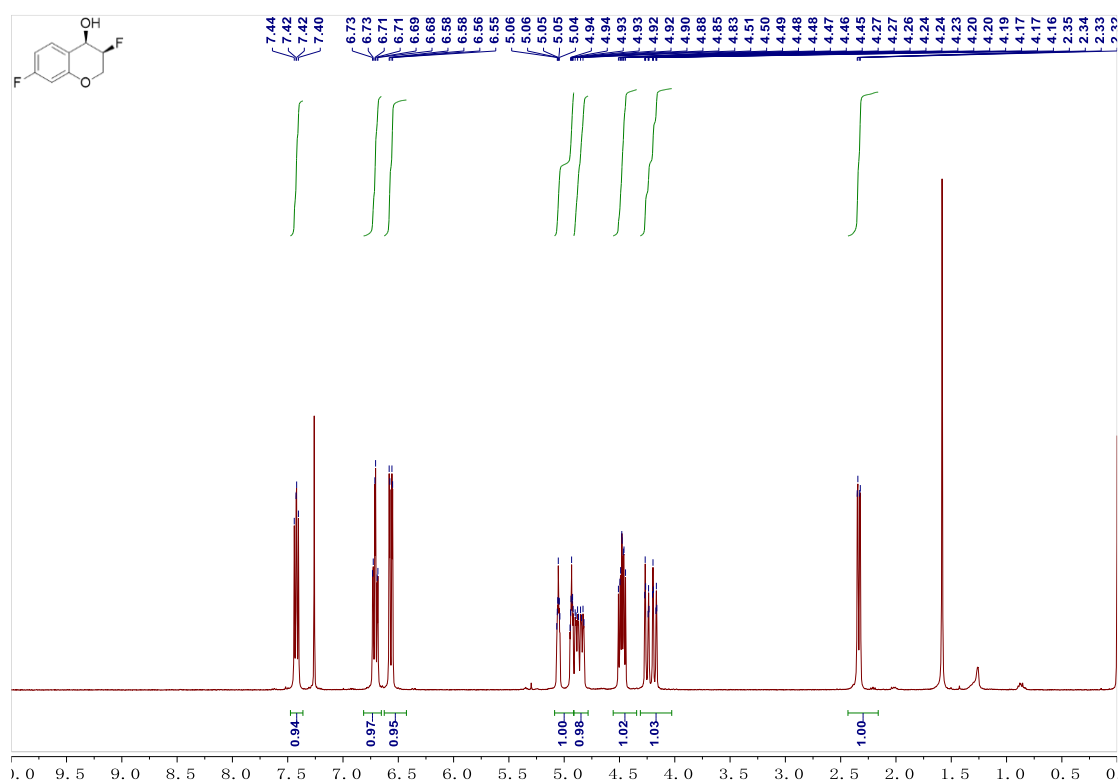
(1*R*,2*S*)-2-Chloro-7-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (**2x**):<sup>[10]</sup> Colourless crystal, 83 mg, 98% yield, dr (*cis/trans*) > 20:1, ee<sub>*cis*</sub> = 99%,  $[\alpha]_{\text{D}}^{23} = 31.4$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.07-6.98 (m, 2H), 6.82 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.82 (dd, *J* = 8.2, 3.4 Hz, 1H), 4.56 (dt, *J* = 8.1, 3.0 Hz, 1H), 3.80 (s, 3H), 3.02 (dt, *J* = 17.0, 6.9 Hz, 1H), 2.76 (dt, *J* = 16.9, 6.2 Hz, 1H), 2.44 (d, *J* = 8.1 Hz, 1H), 2.46-2.33 (m, 1H), 2.18 (dddd, *J* = 13.9, 8.4, 6.3, 2.6 Hz, 1H).



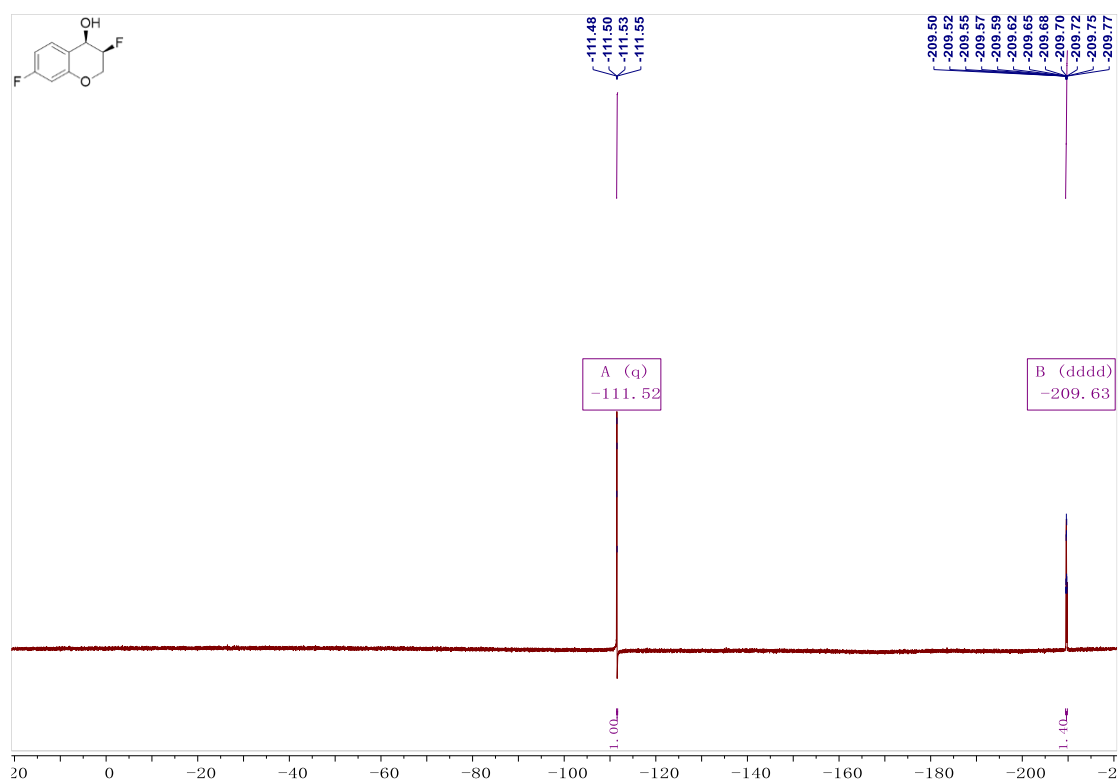
(1*R*,2*R*)-2-Chloro-1-(*p*-tolyl)propan-1-ol (**2y**):<sup>[11]</sup> Colourless oil, 83 mg, 80% yield, dr (*cis/trans*) = 15:1,  $ee_{cis} = 98\%$ ,  $[\alpha]_D^{23} = -29.8$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.24-7.22 (m, 2H), 7.17-7.16 (m, 2H), 4.54 (d,  $J = 7.6$  Hz, 1H), 4.19 (m, 1H), 2.79 (s, 1H), 2.34 (s, 3H), 1.35 (d,  $J = 6.7$  Hz, 3H).



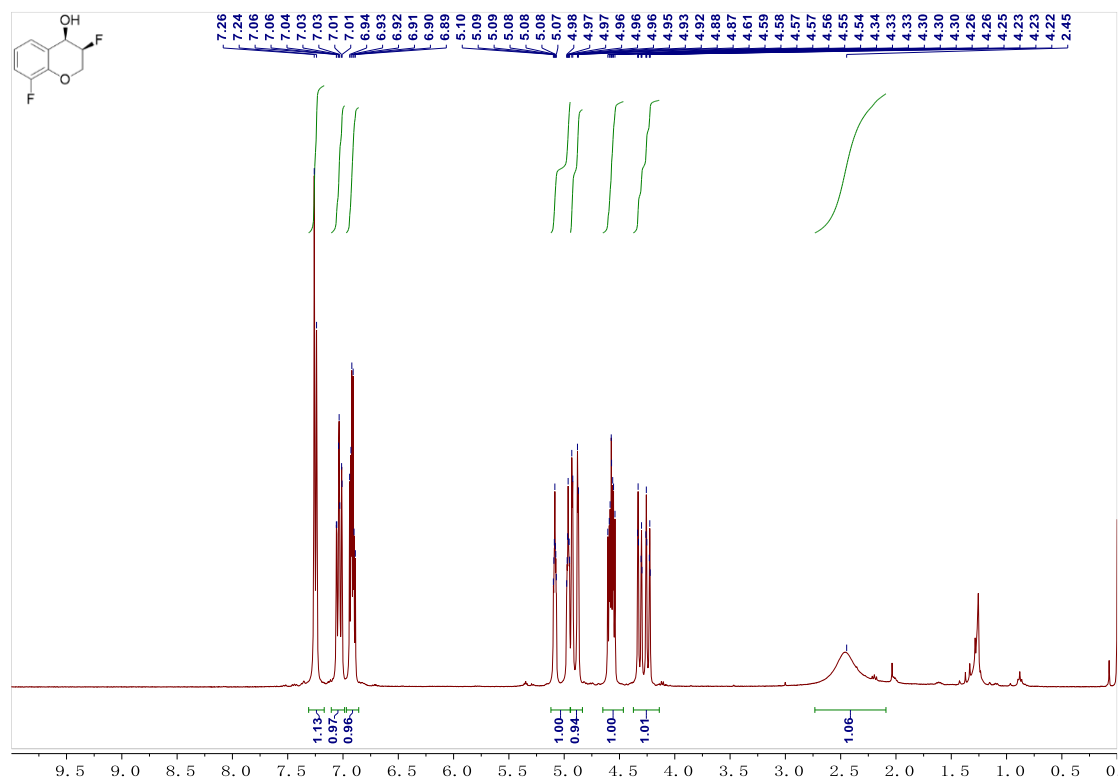
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **2b**



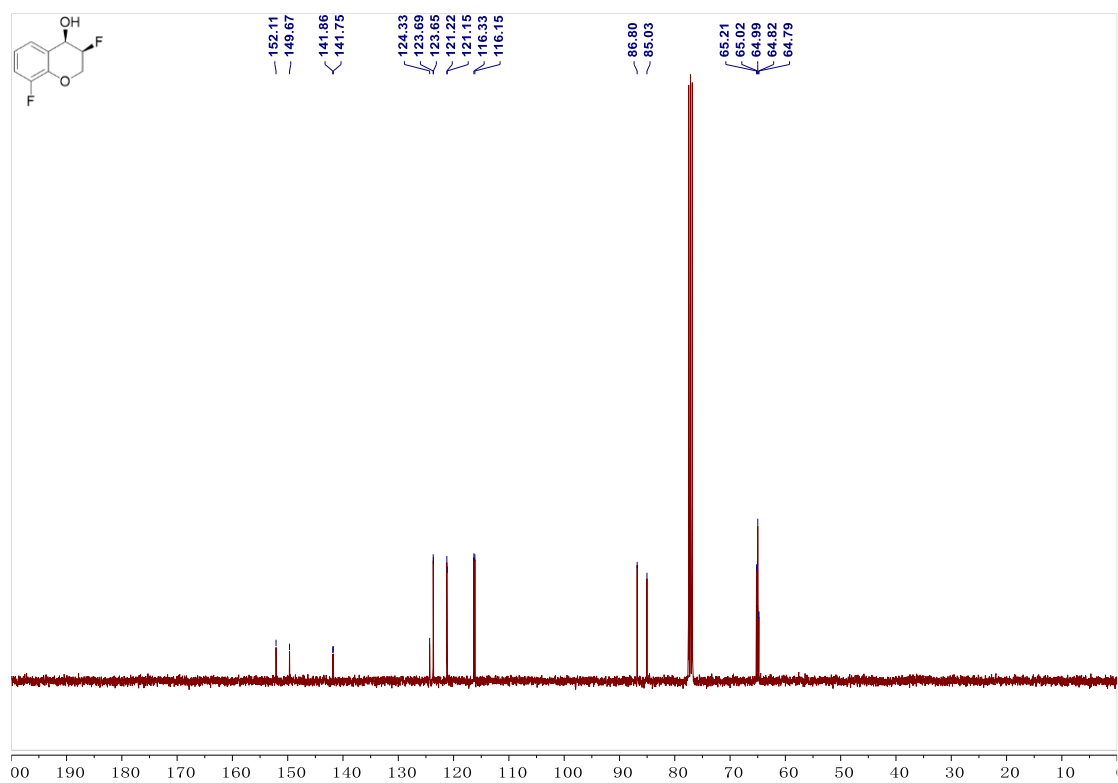
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **2b**



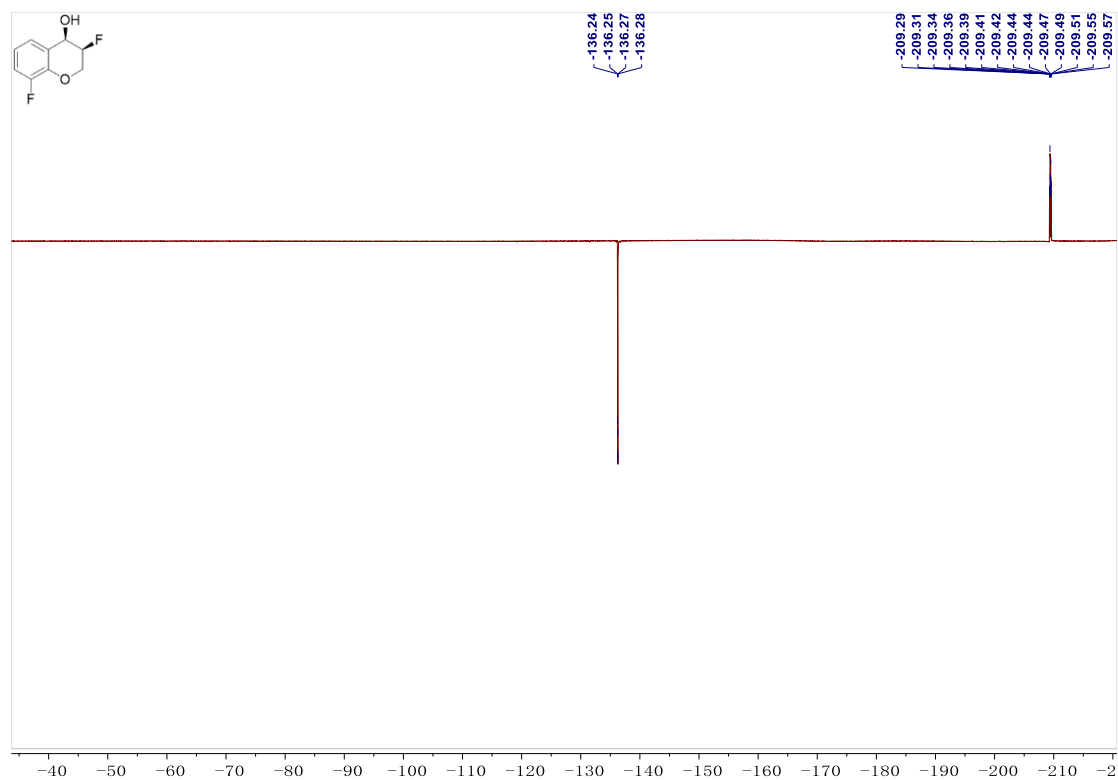
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **2c**



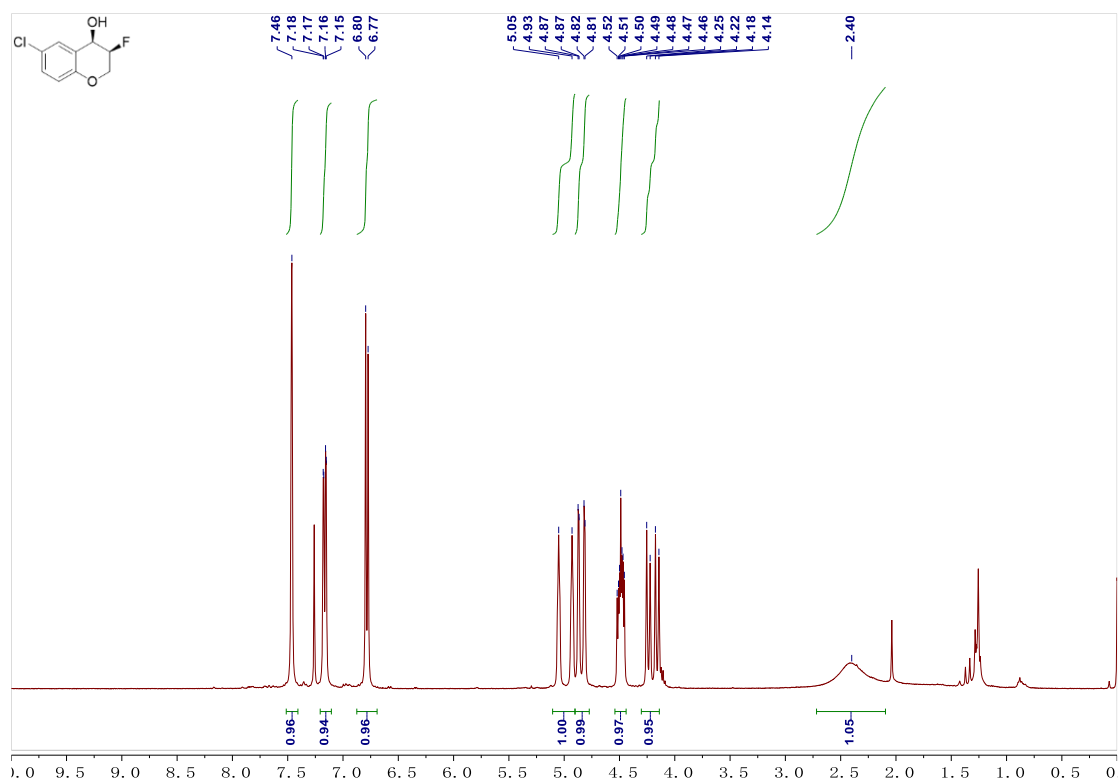
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **2c**



$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2c**

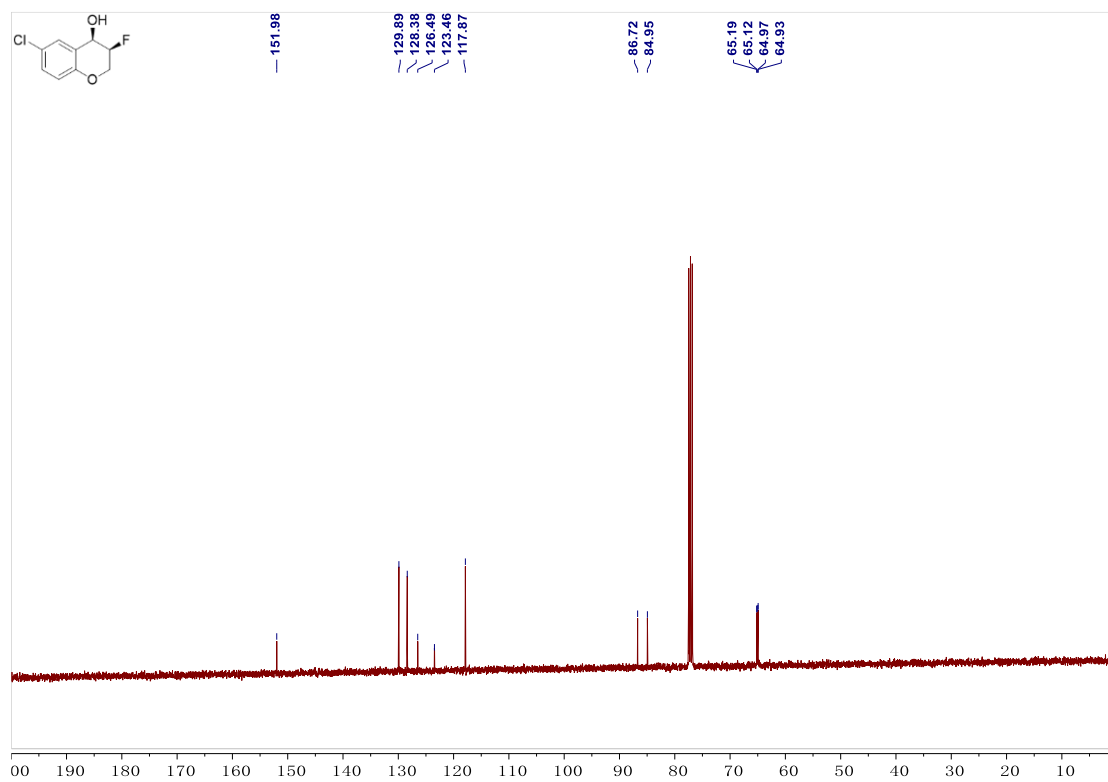


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2d**

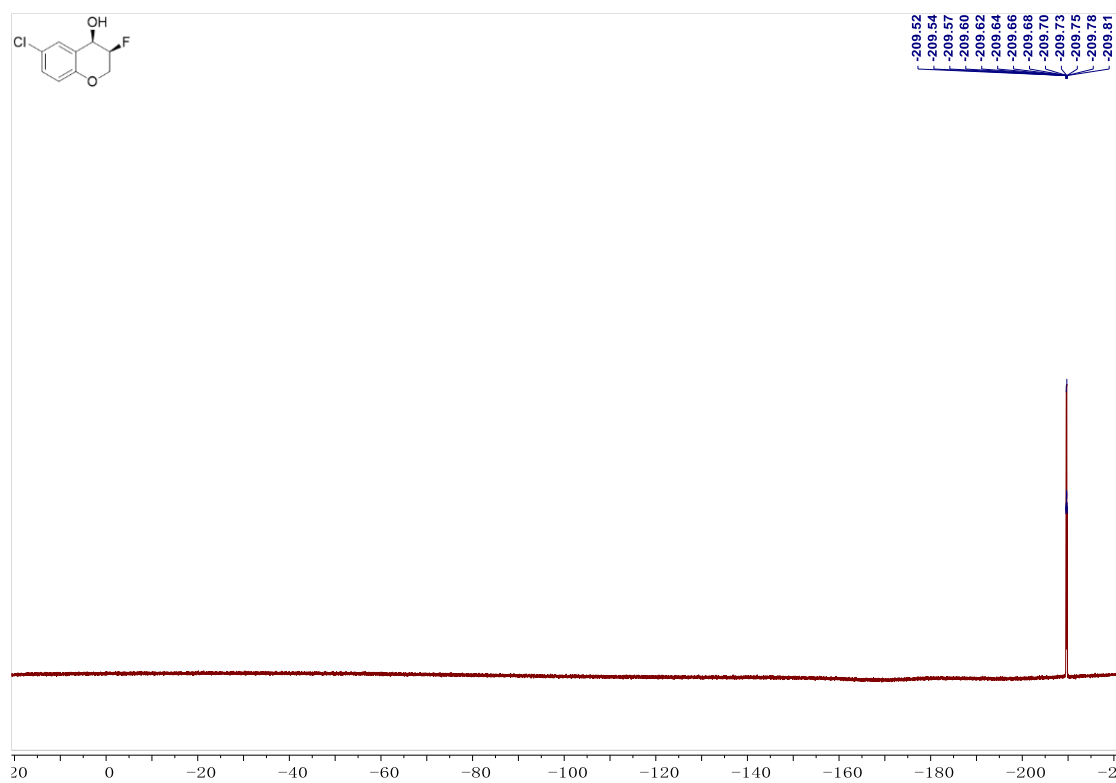




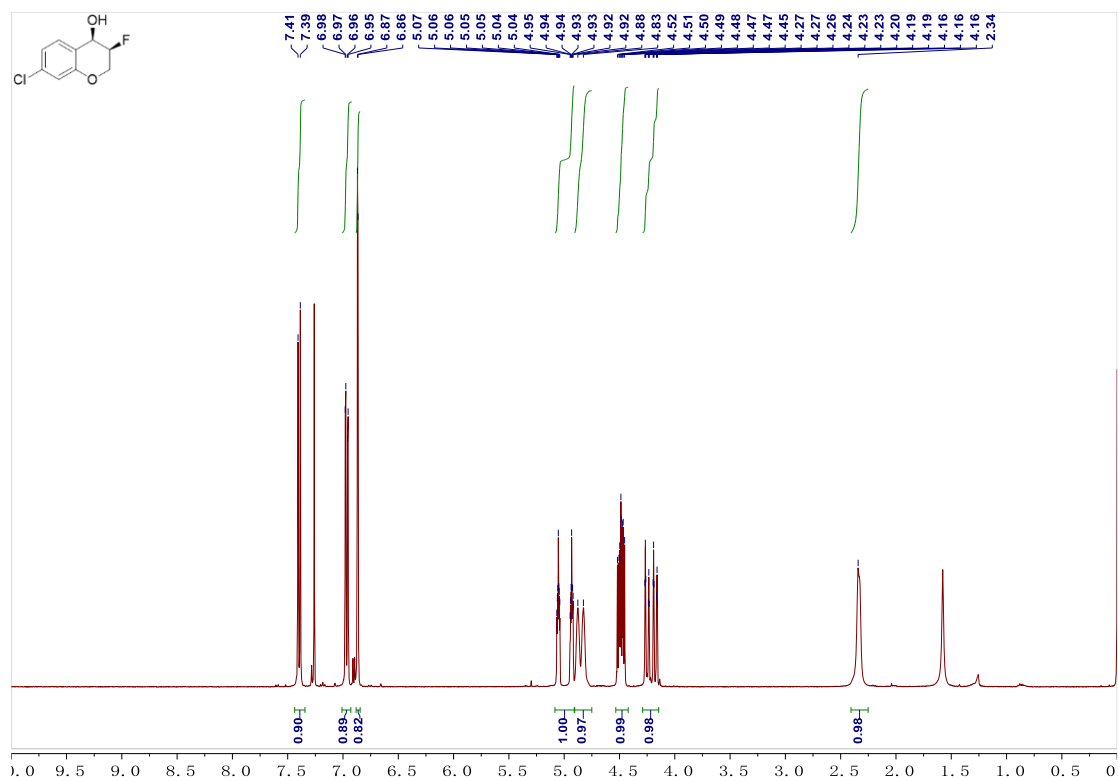
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **2d**



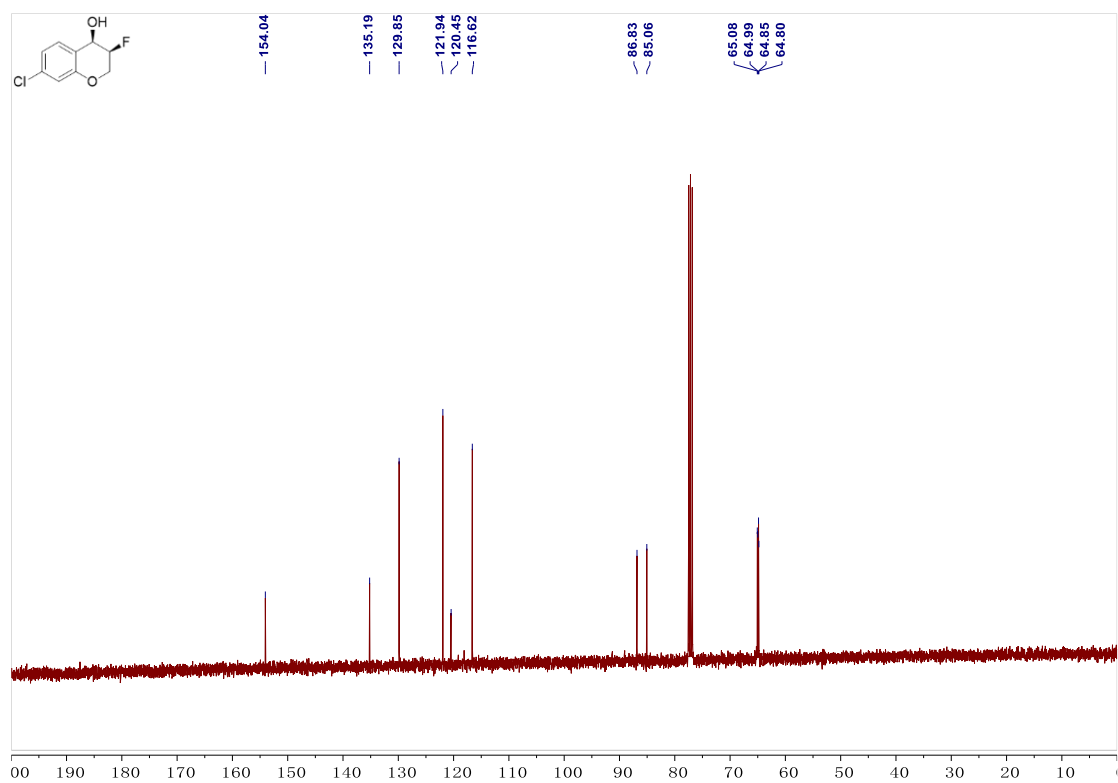
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2d**



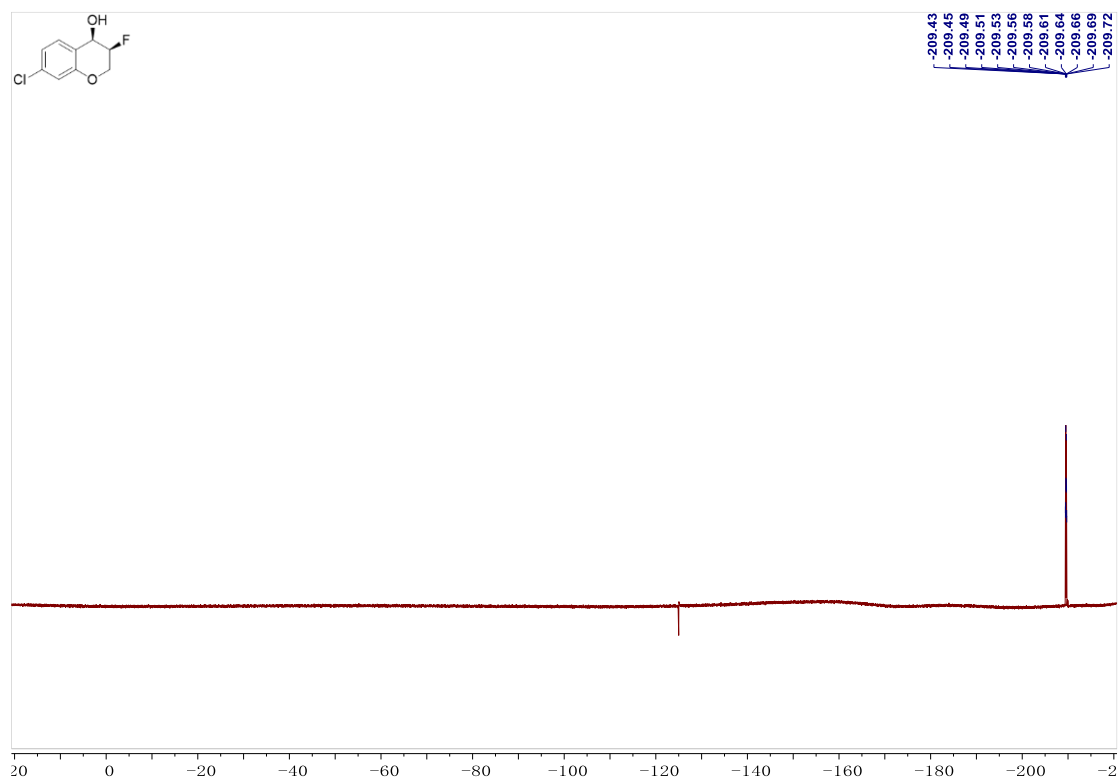
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **2e**



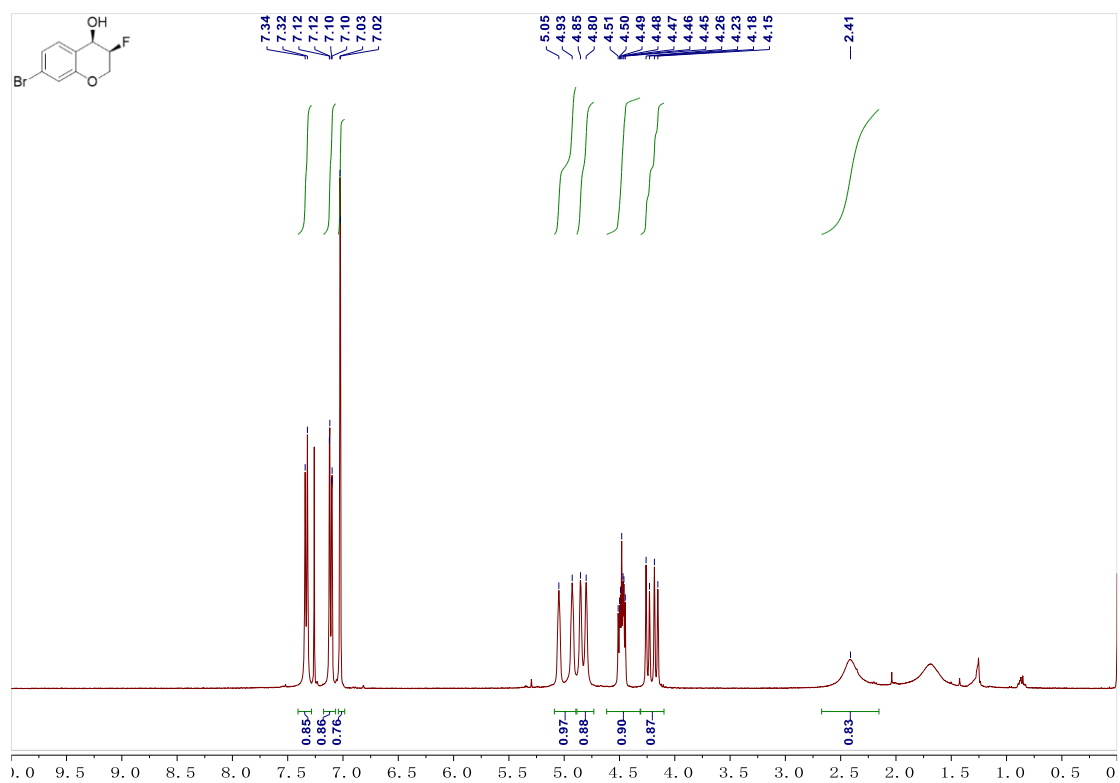
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **2e**



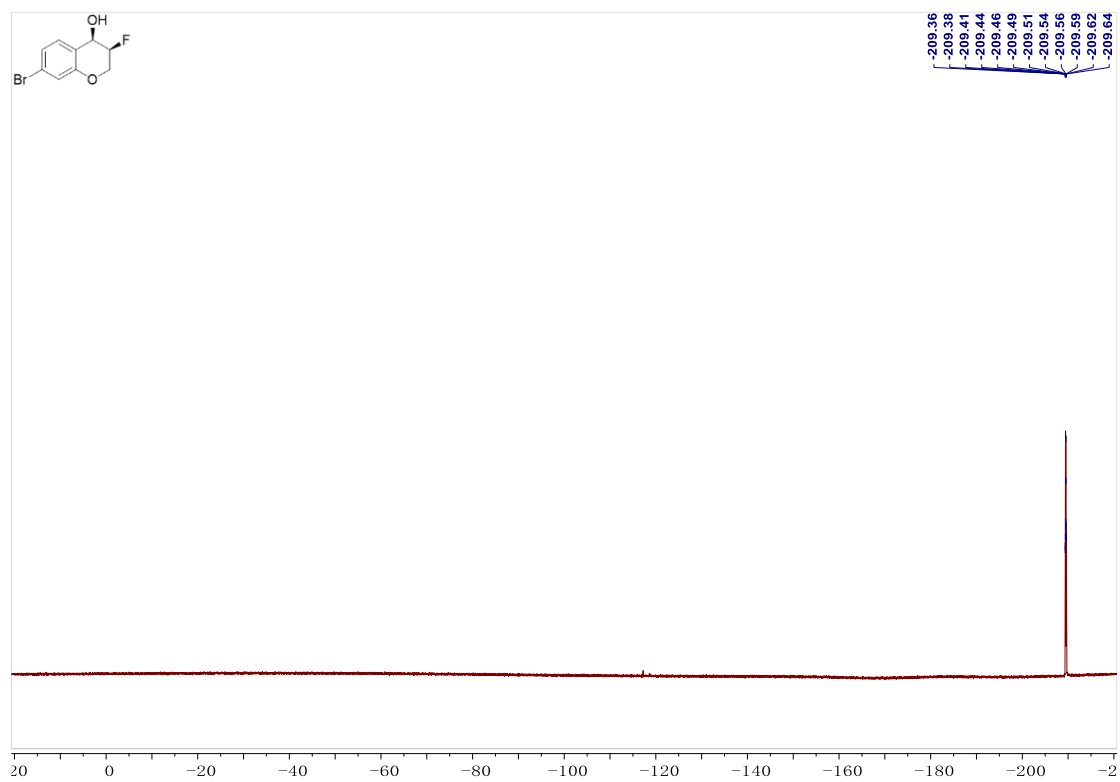
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2e**



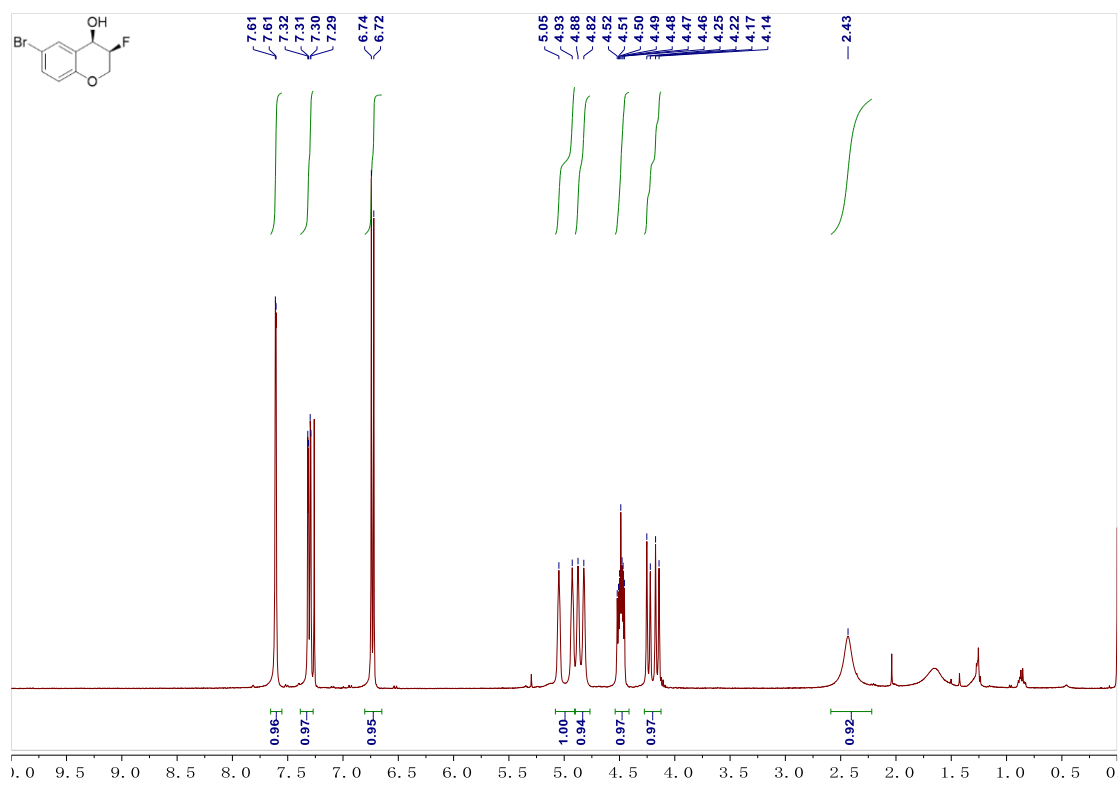
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2f**



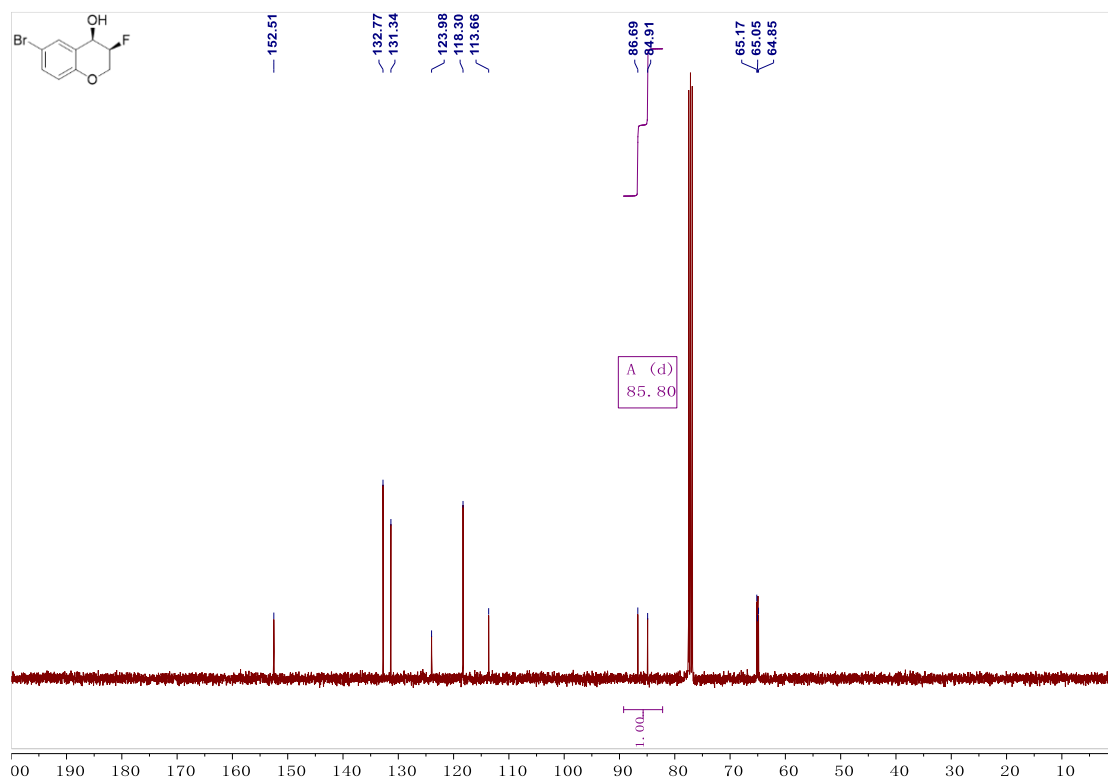
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2f**



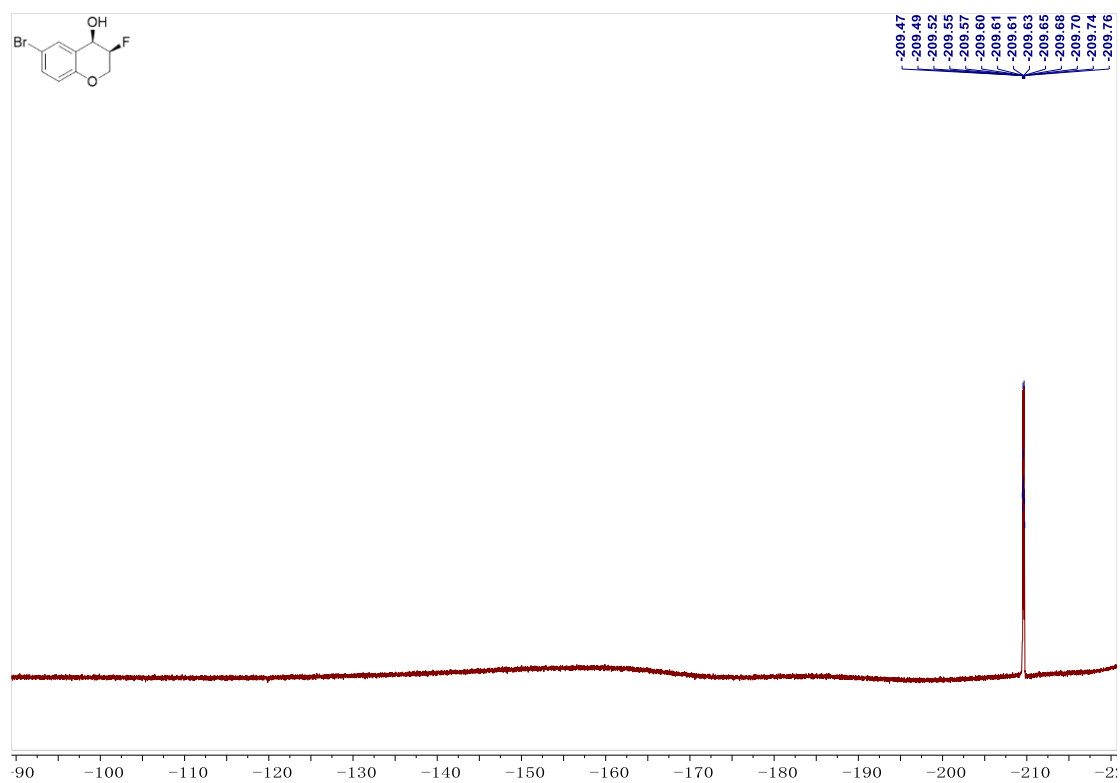
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2g**



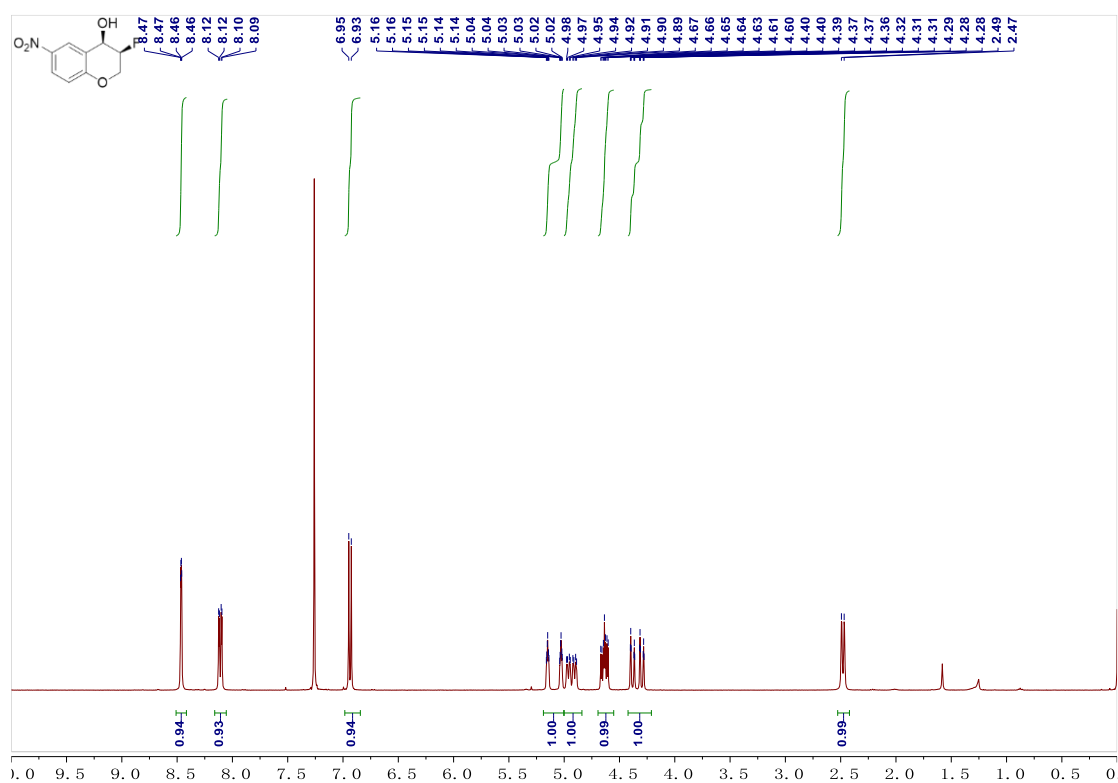
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **2g**



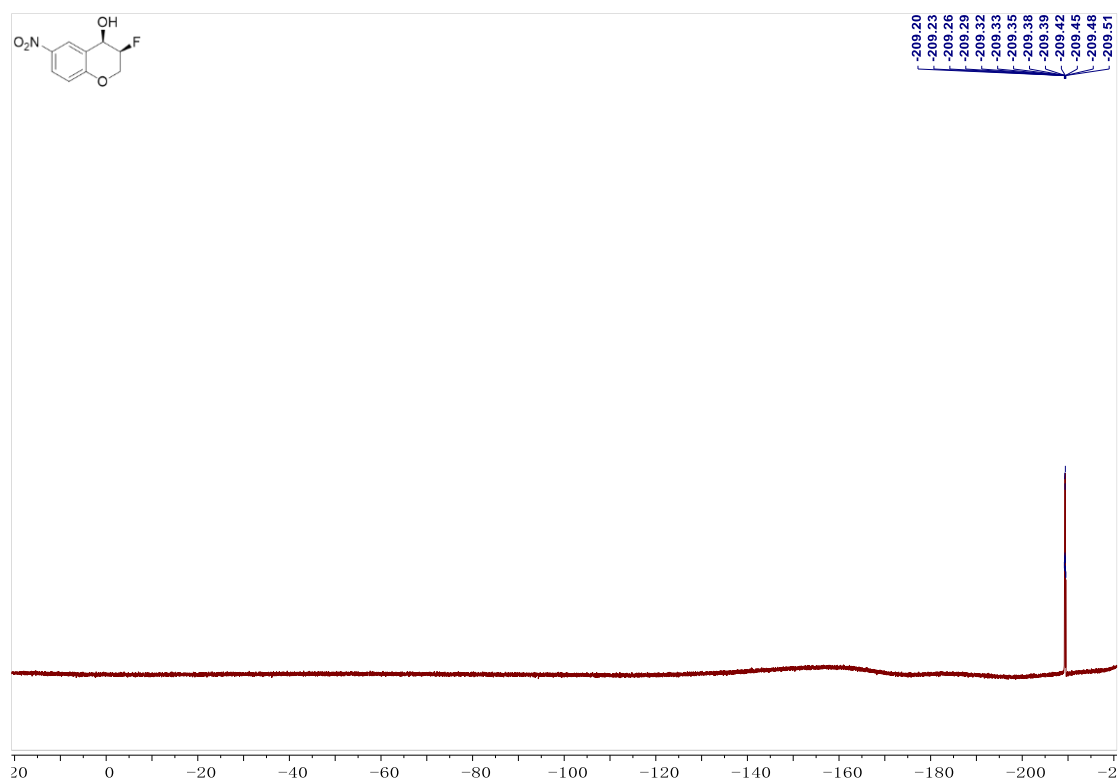
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **2g**



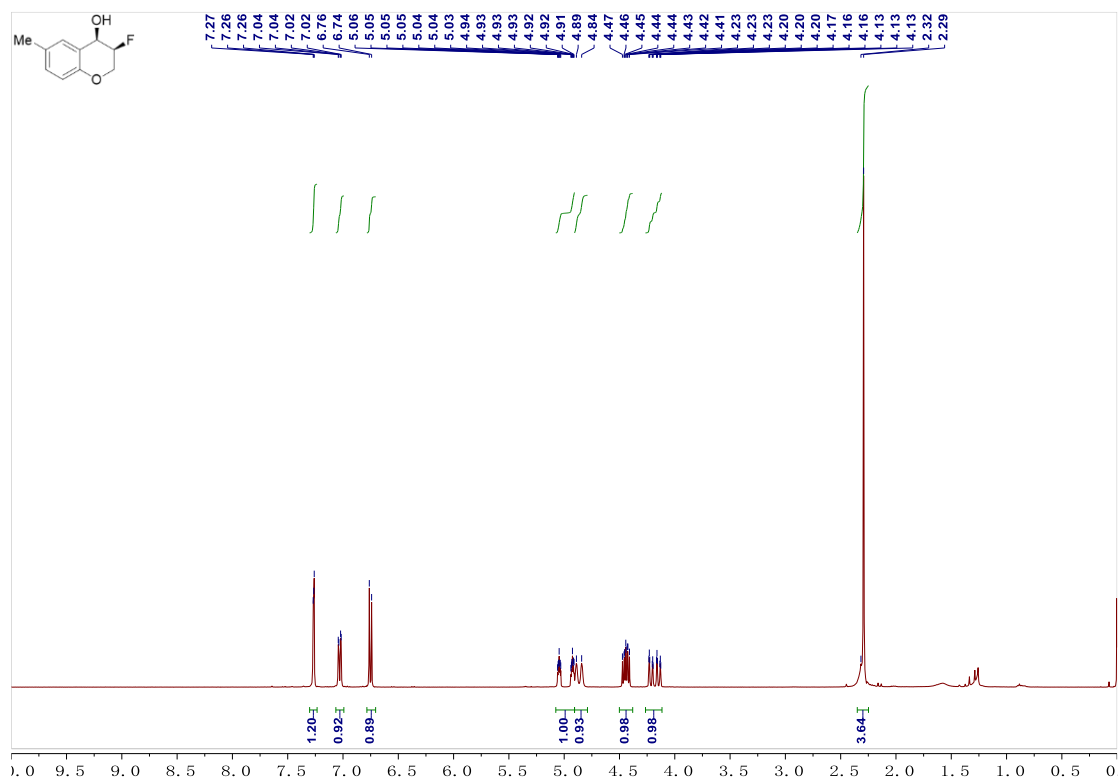
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2h**



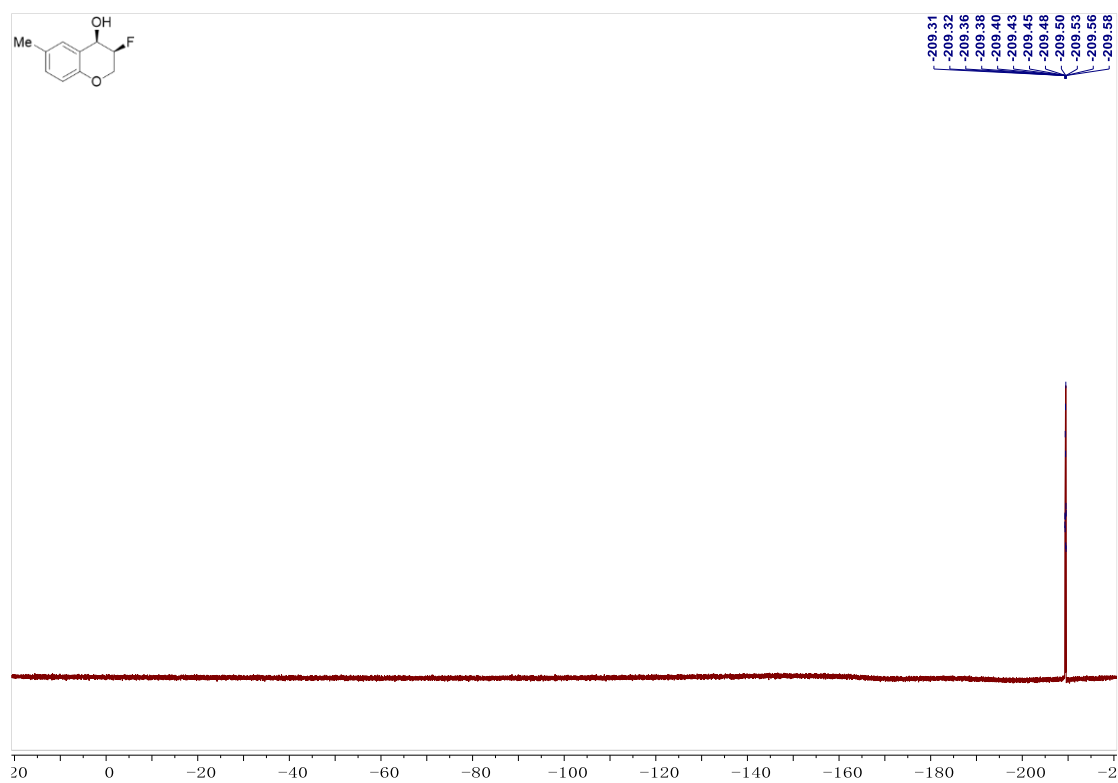
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2h**



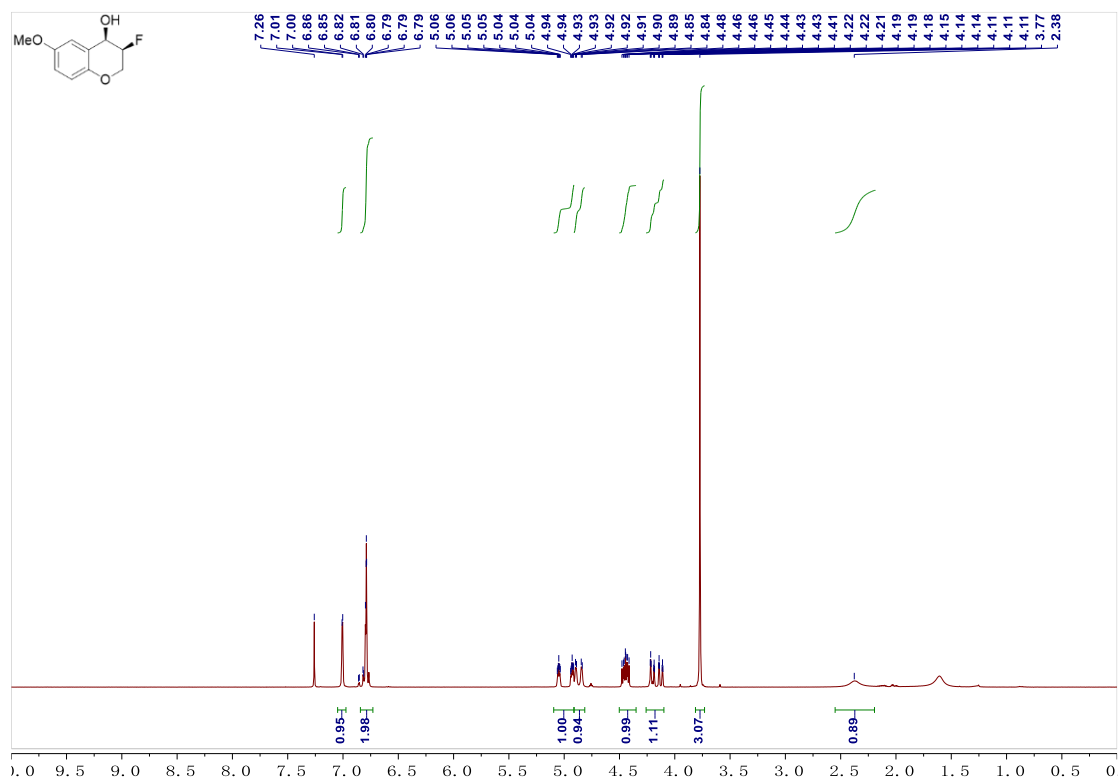
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2i**



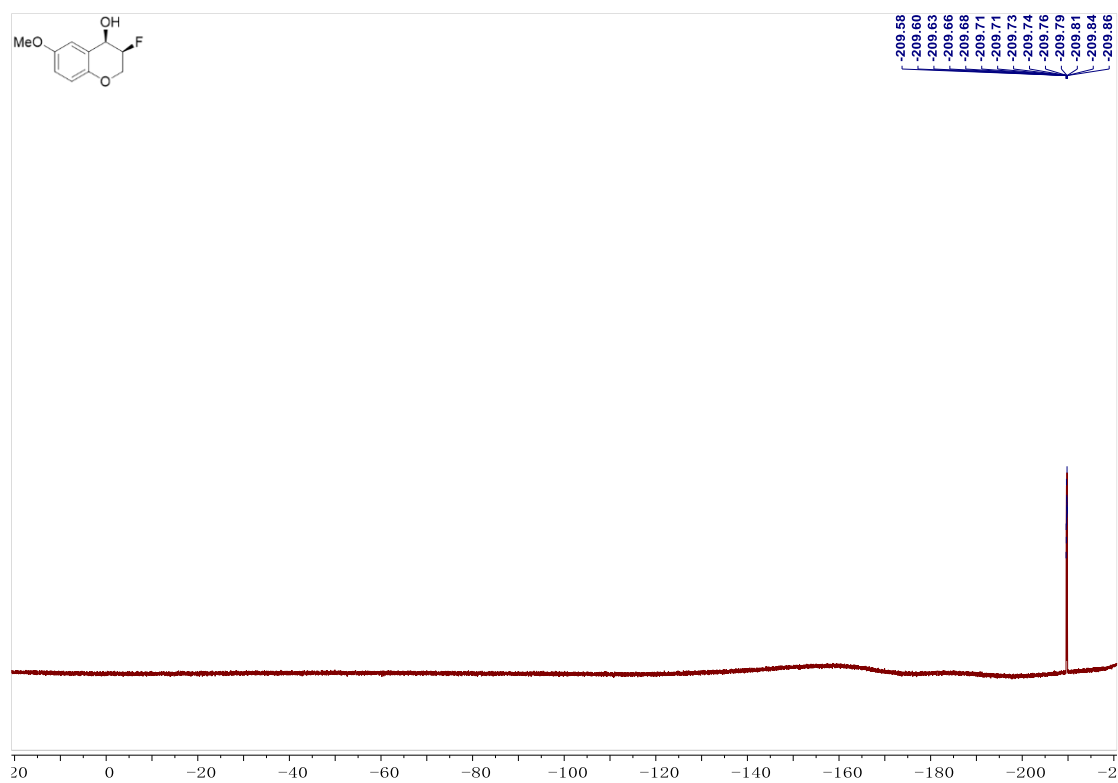
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2i**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **2j**

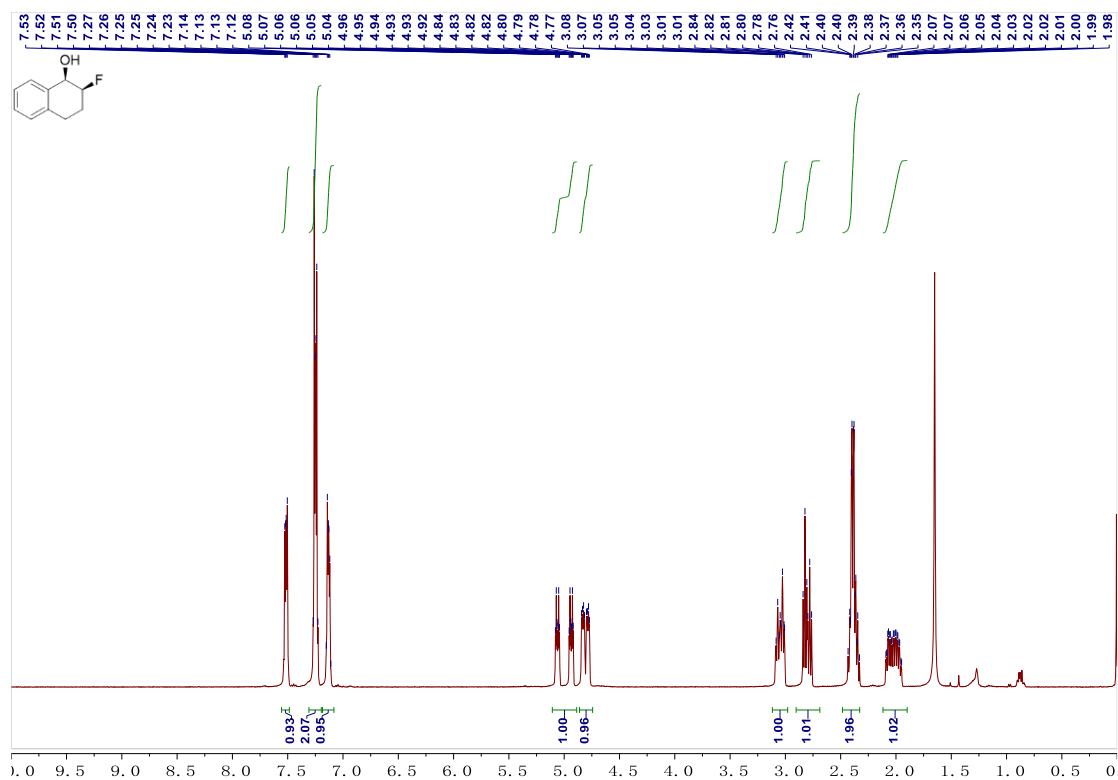


<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **2j**

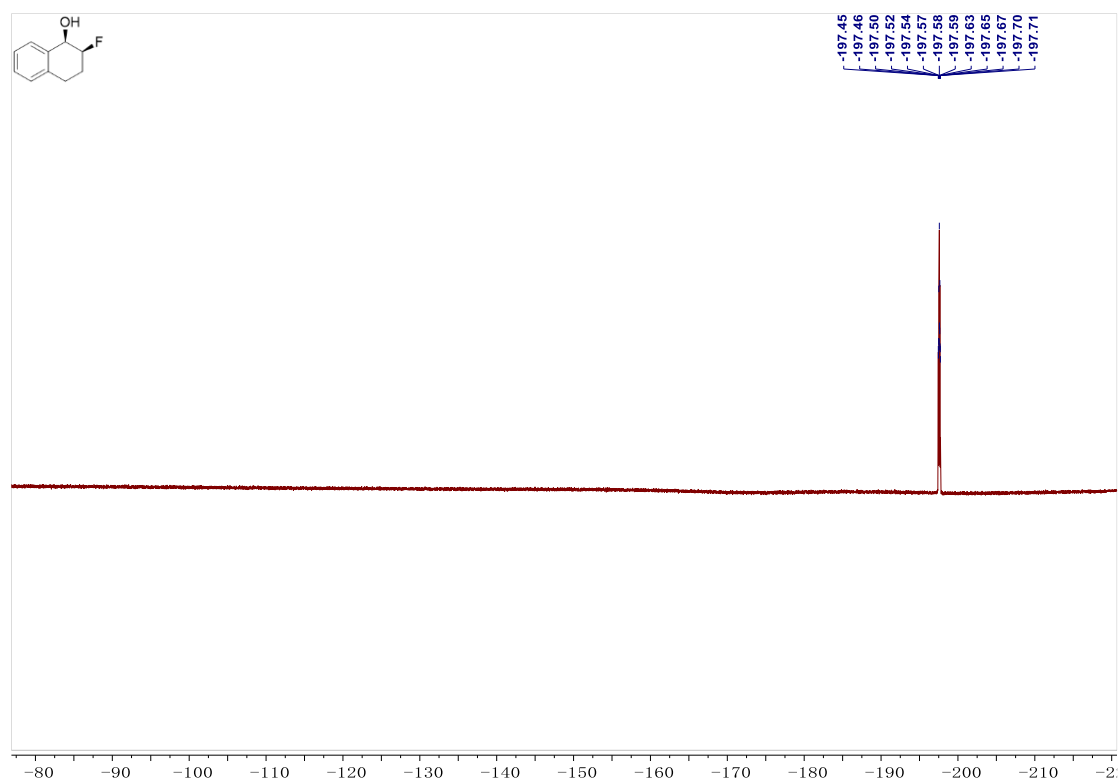




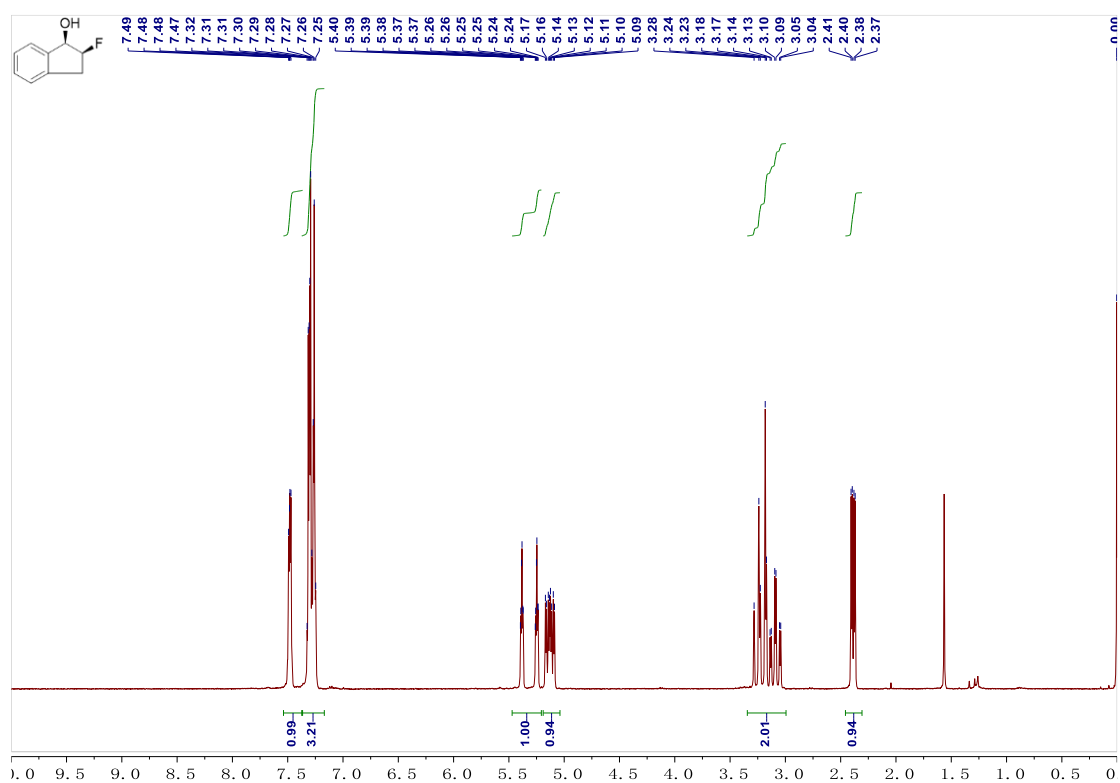
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **2k**



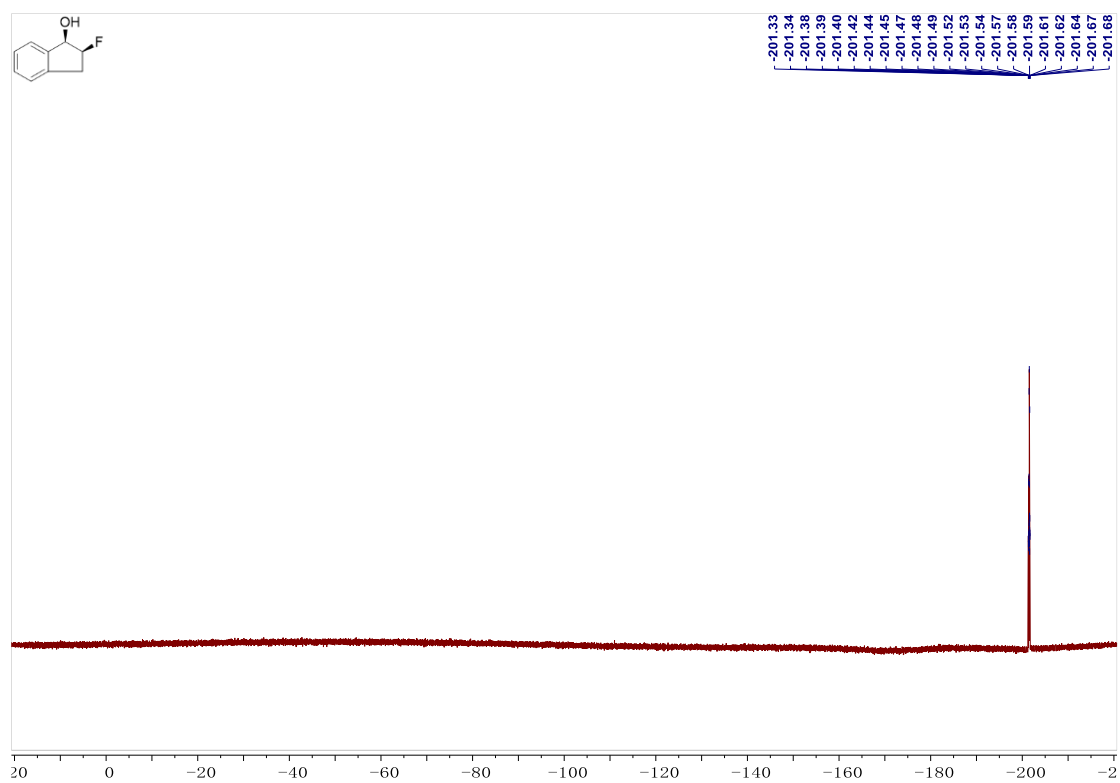
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **2k**



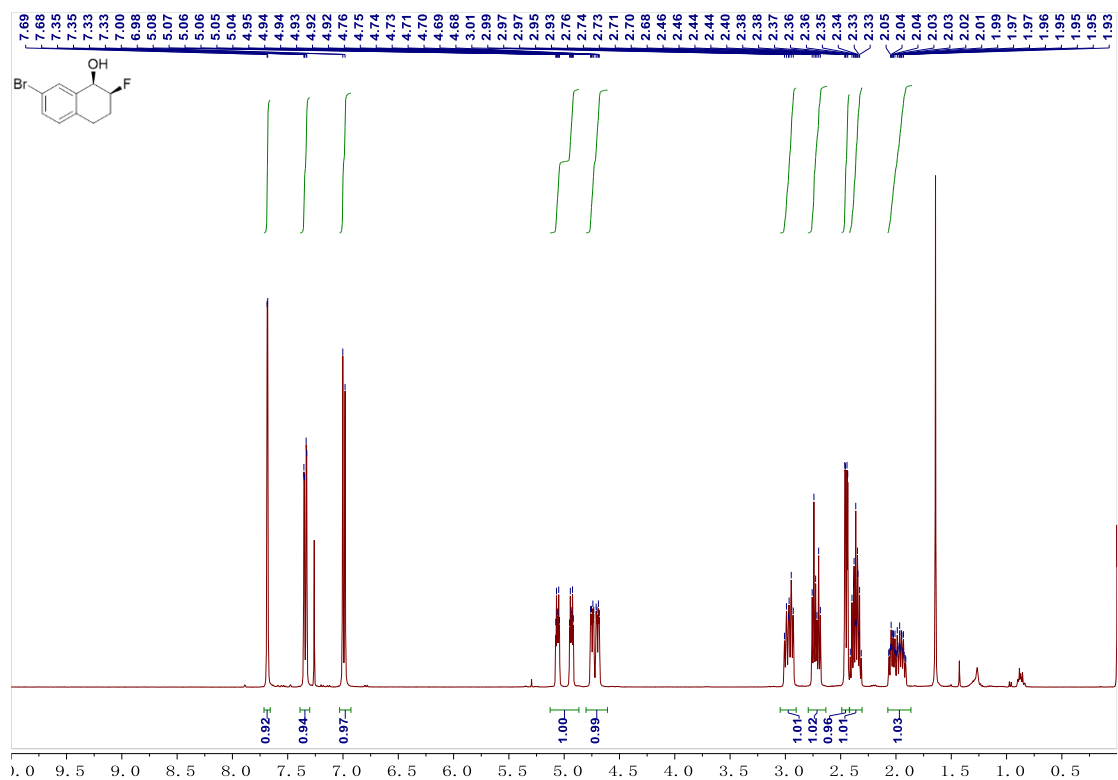
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **21**



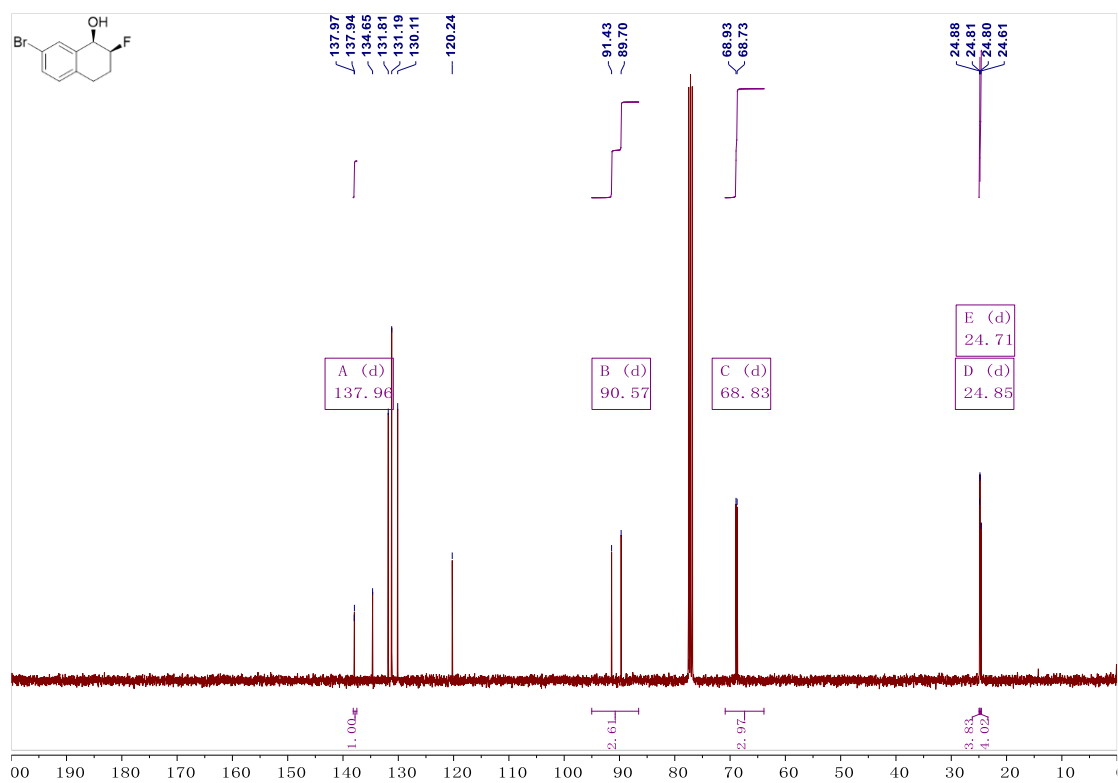
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **21**



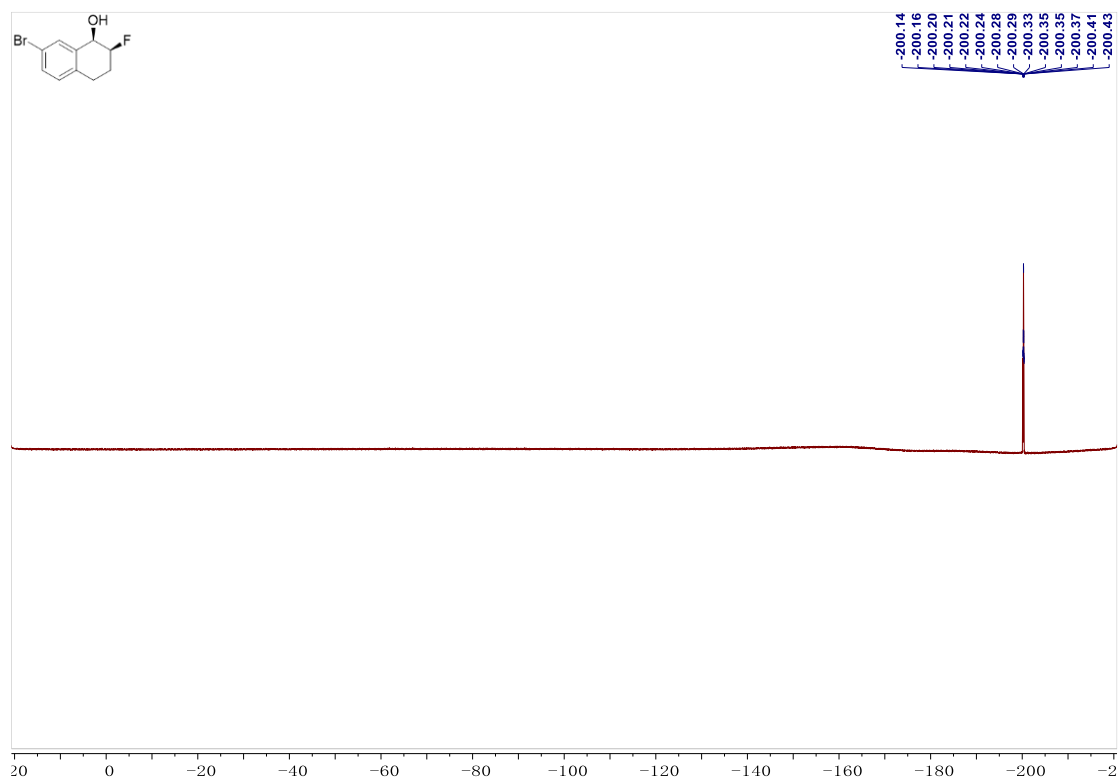
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2m**



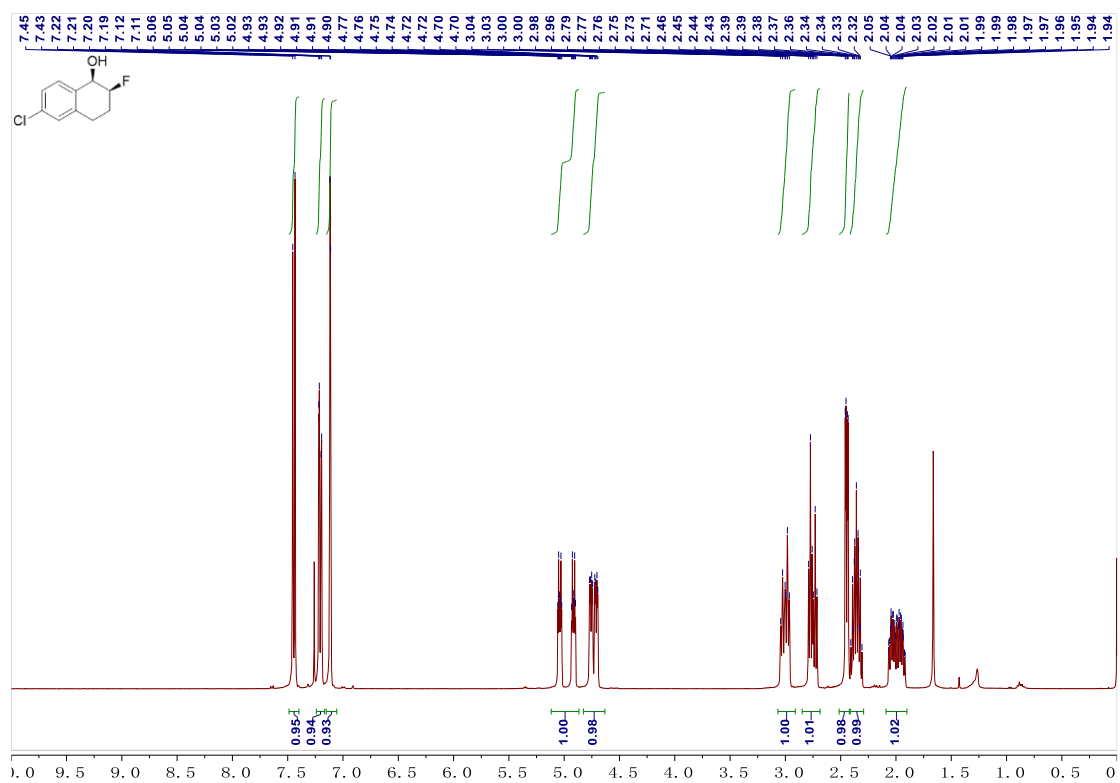
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **2m**



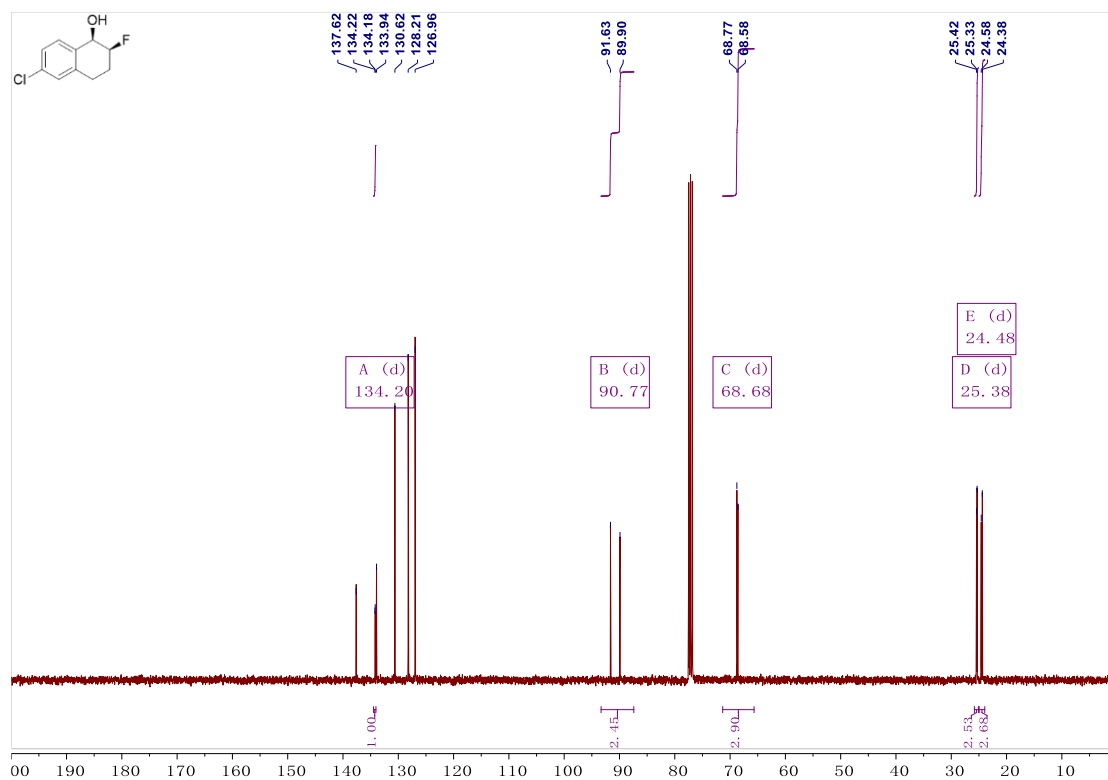
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2m**



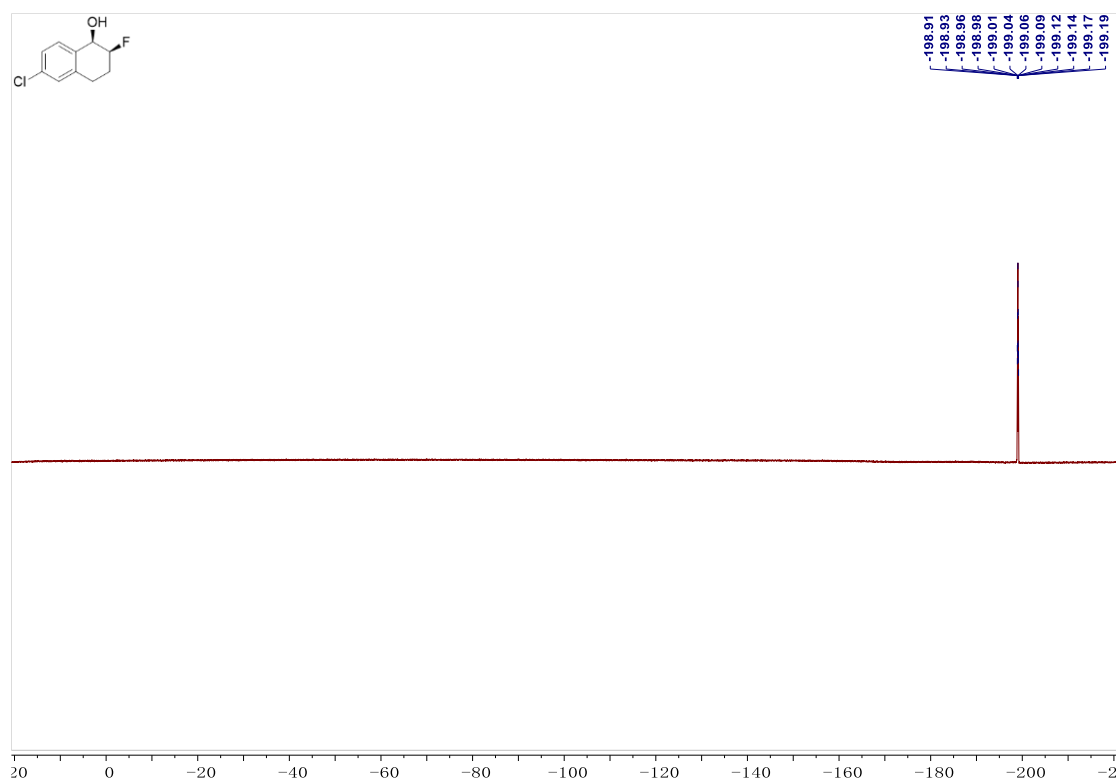
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2n**



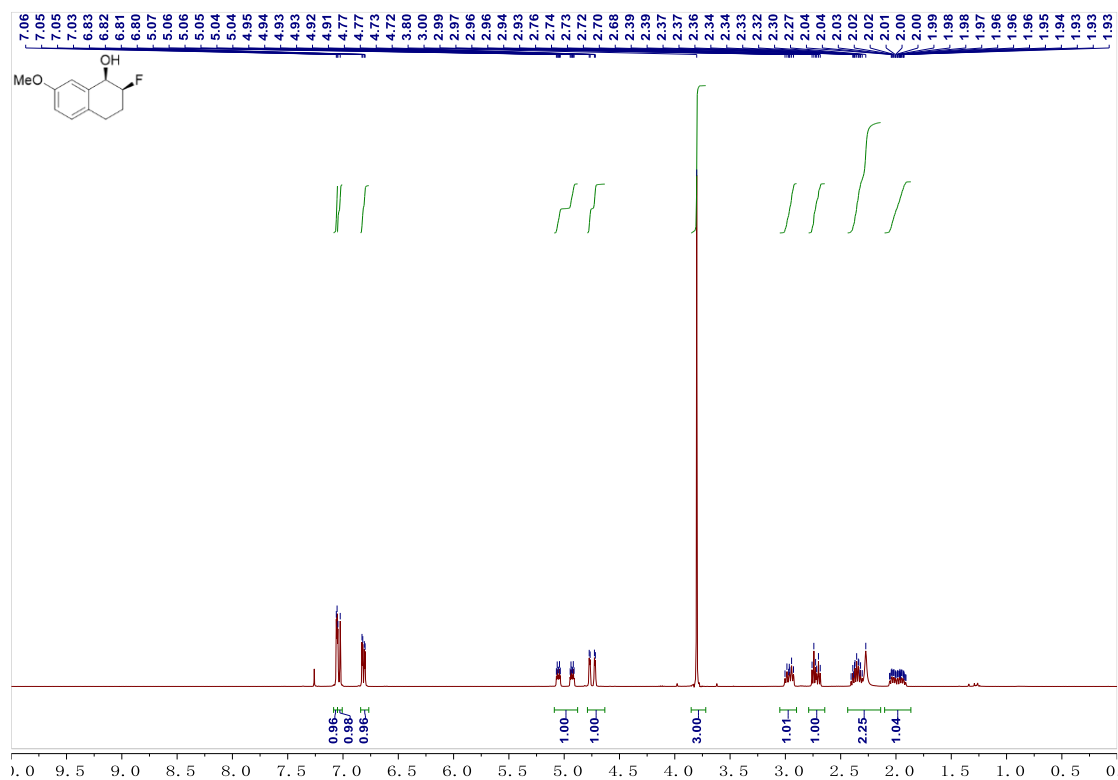
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **2n**



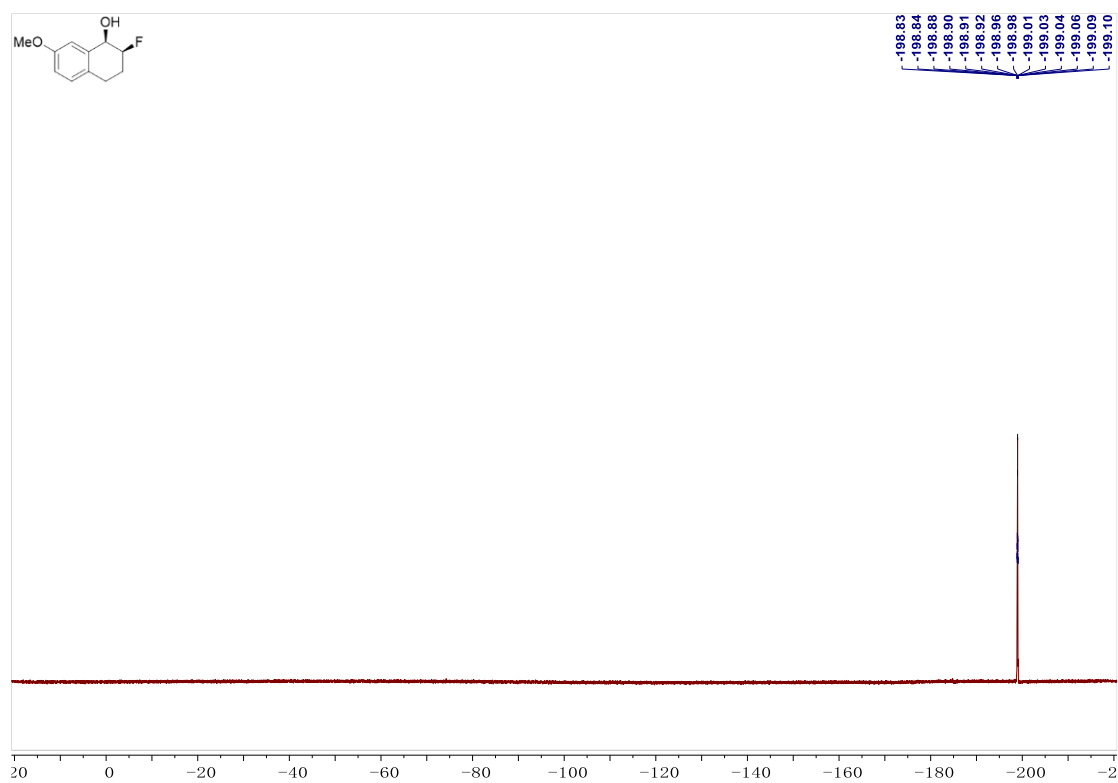
$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2n**



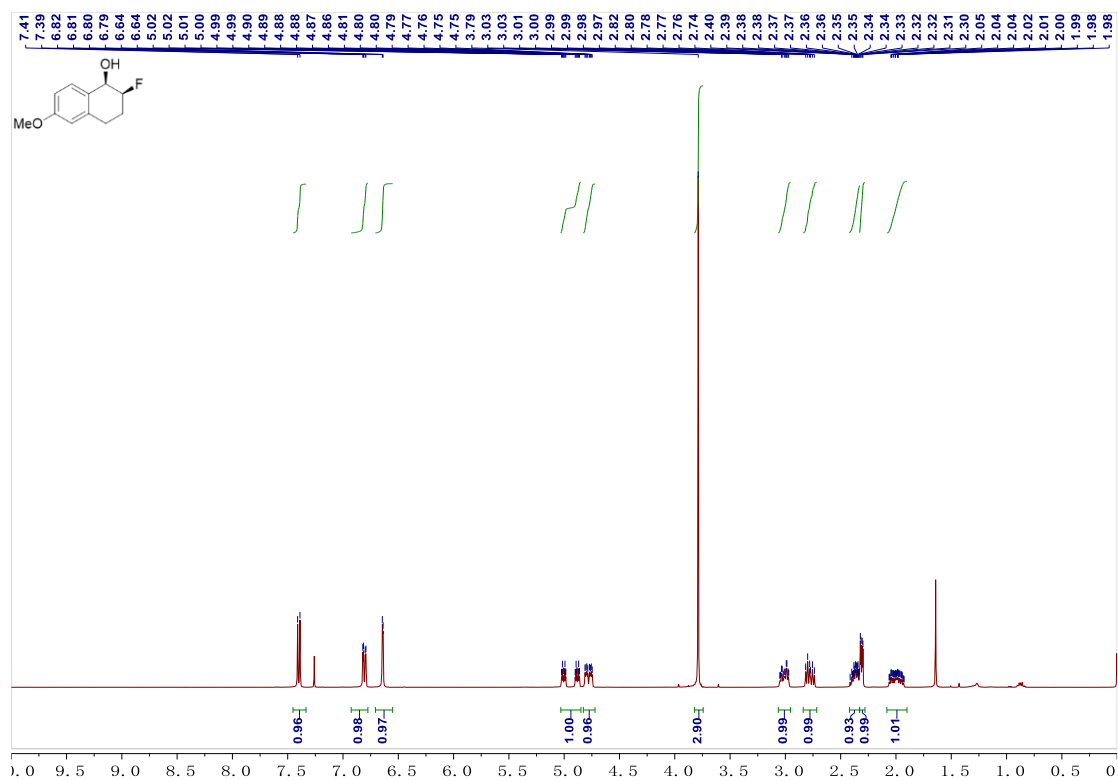
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound **2o**



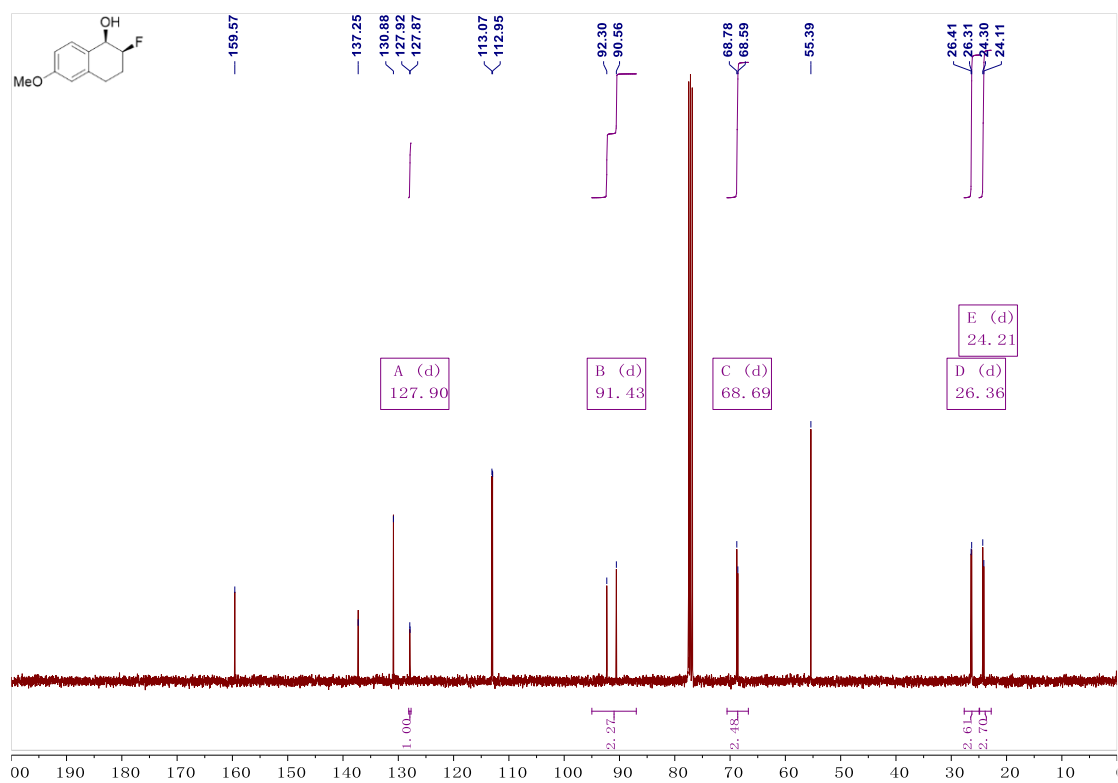
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **2o**



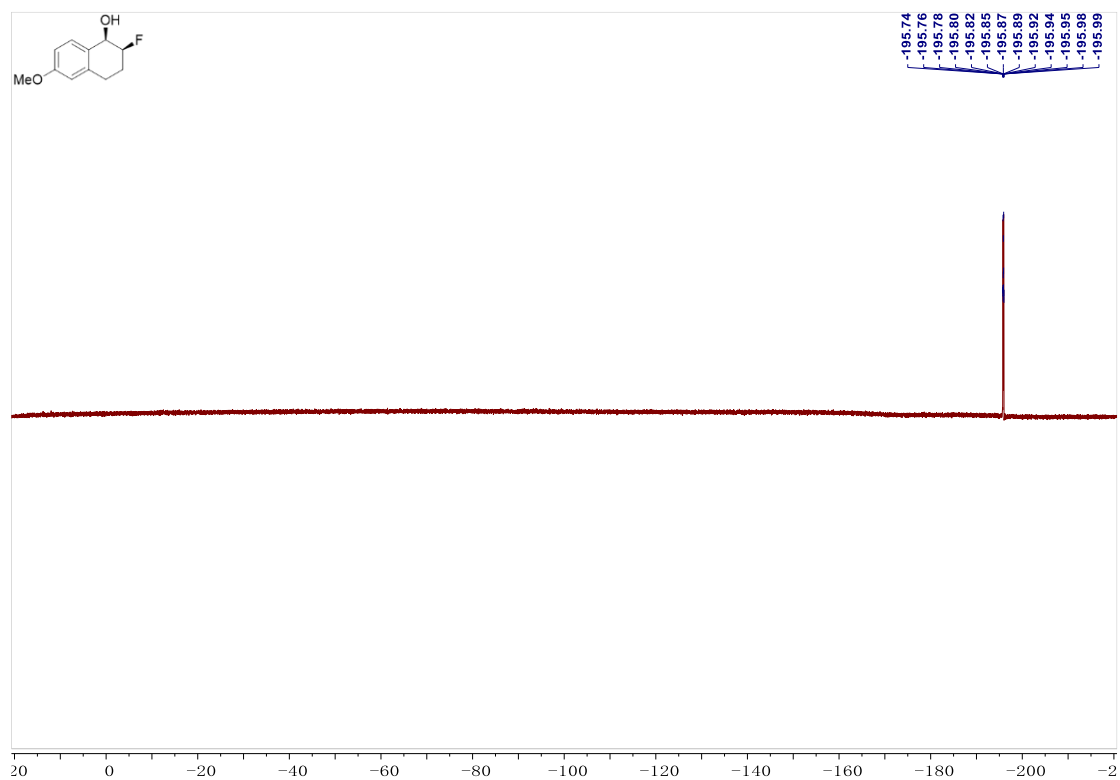
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2p**



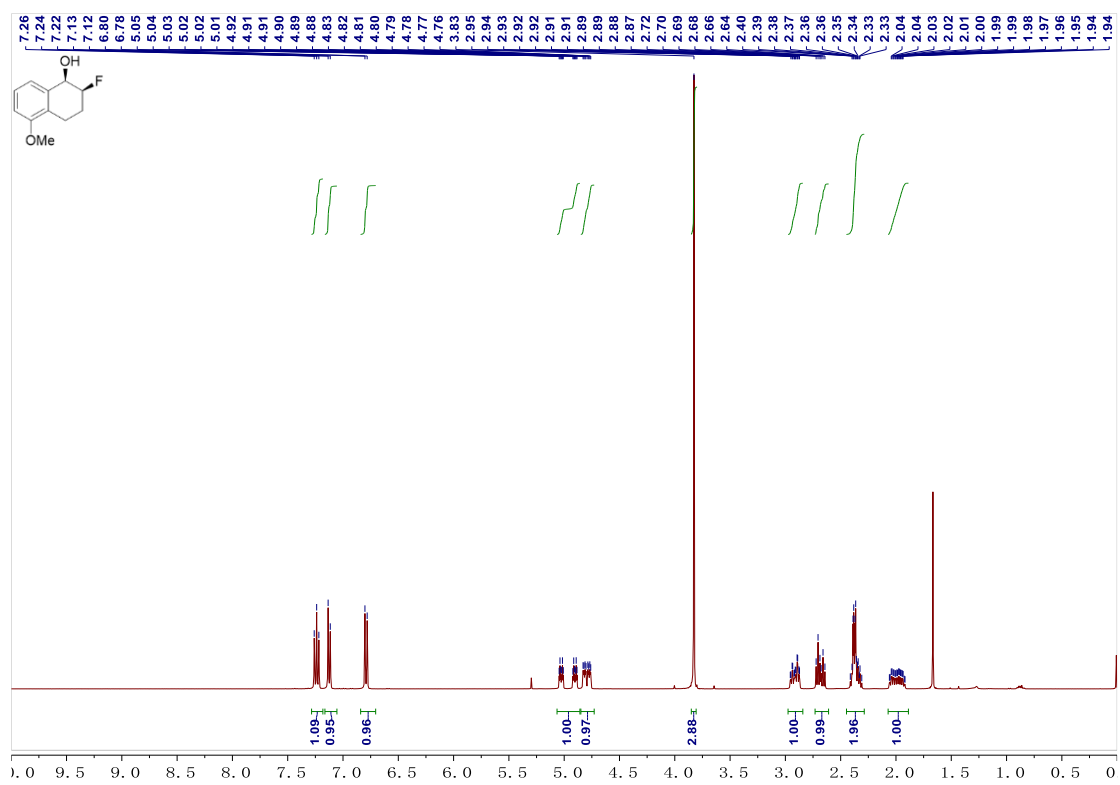
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **2p**



$^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2p**

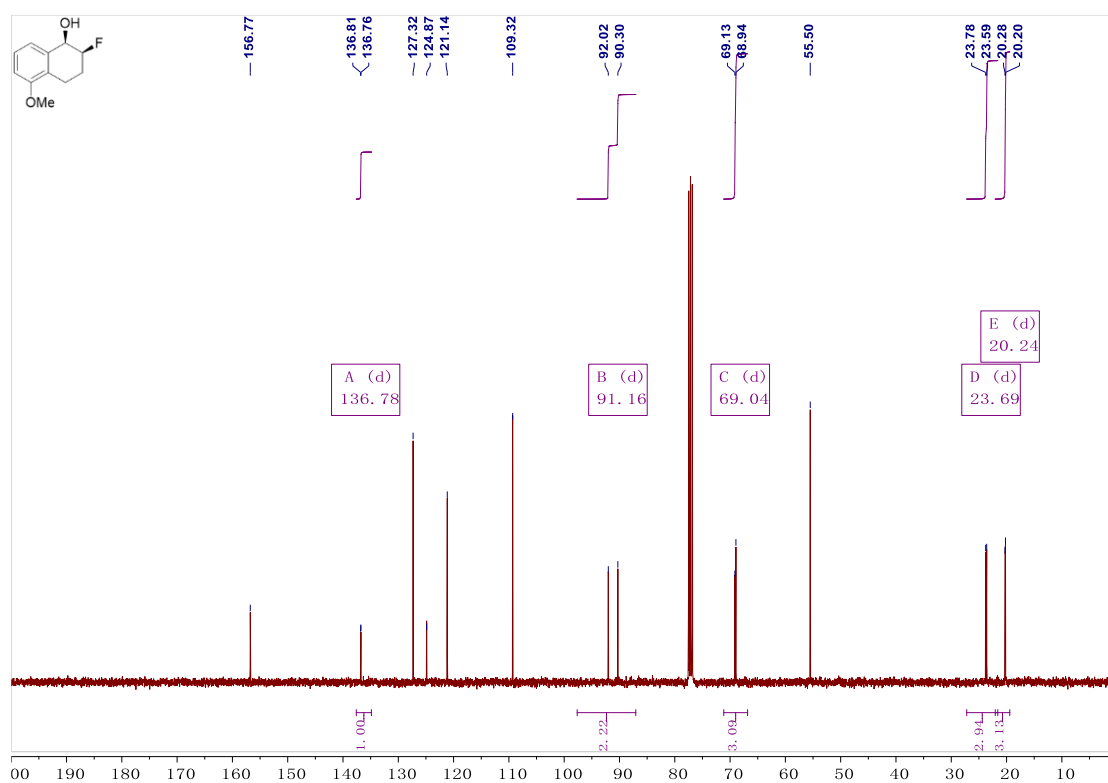


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2q**

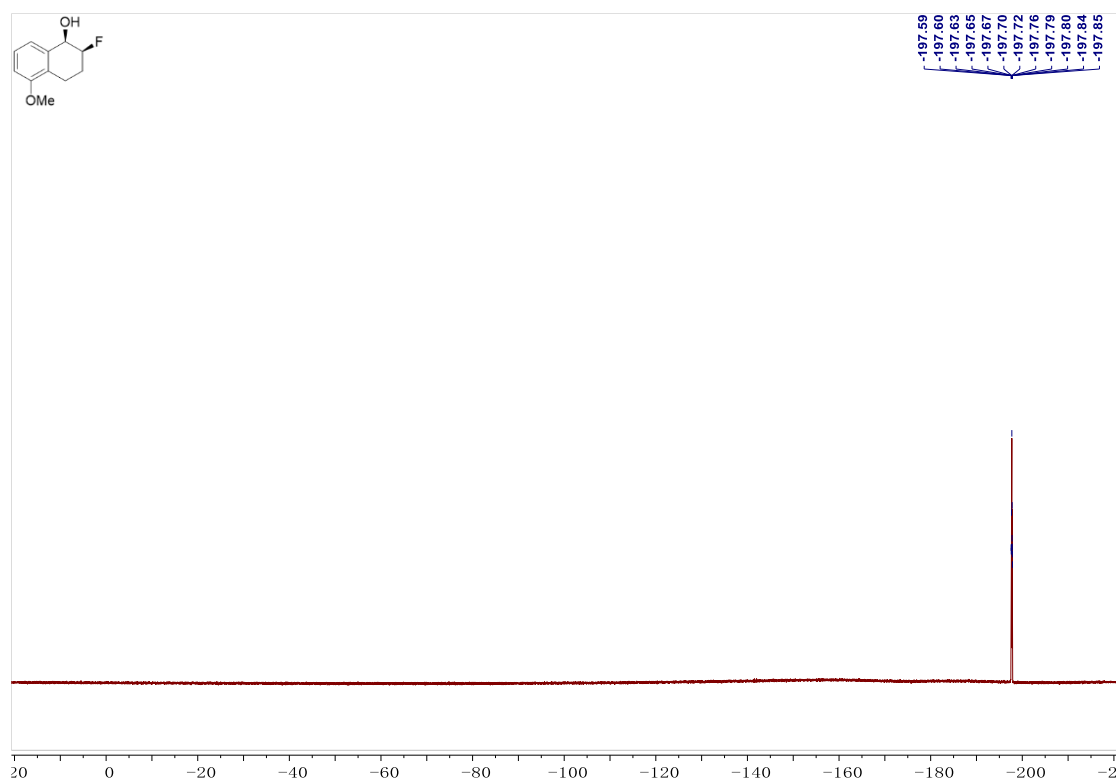




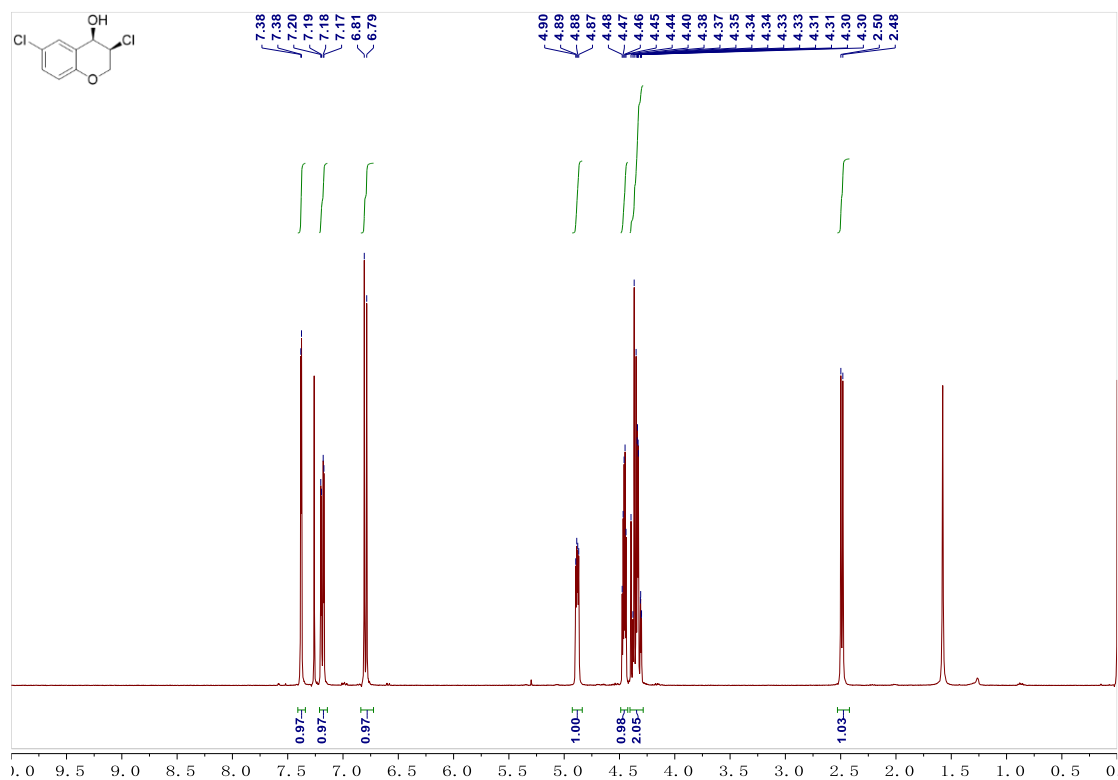
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **2q**



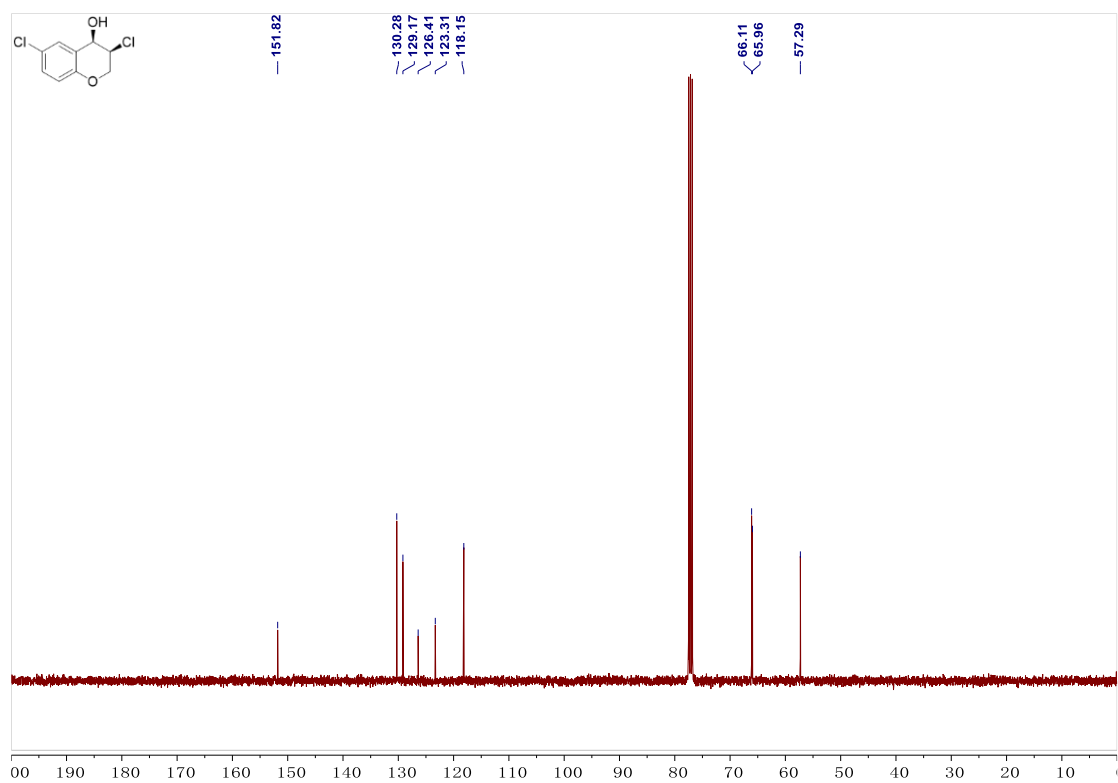
<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) of compound **2q**



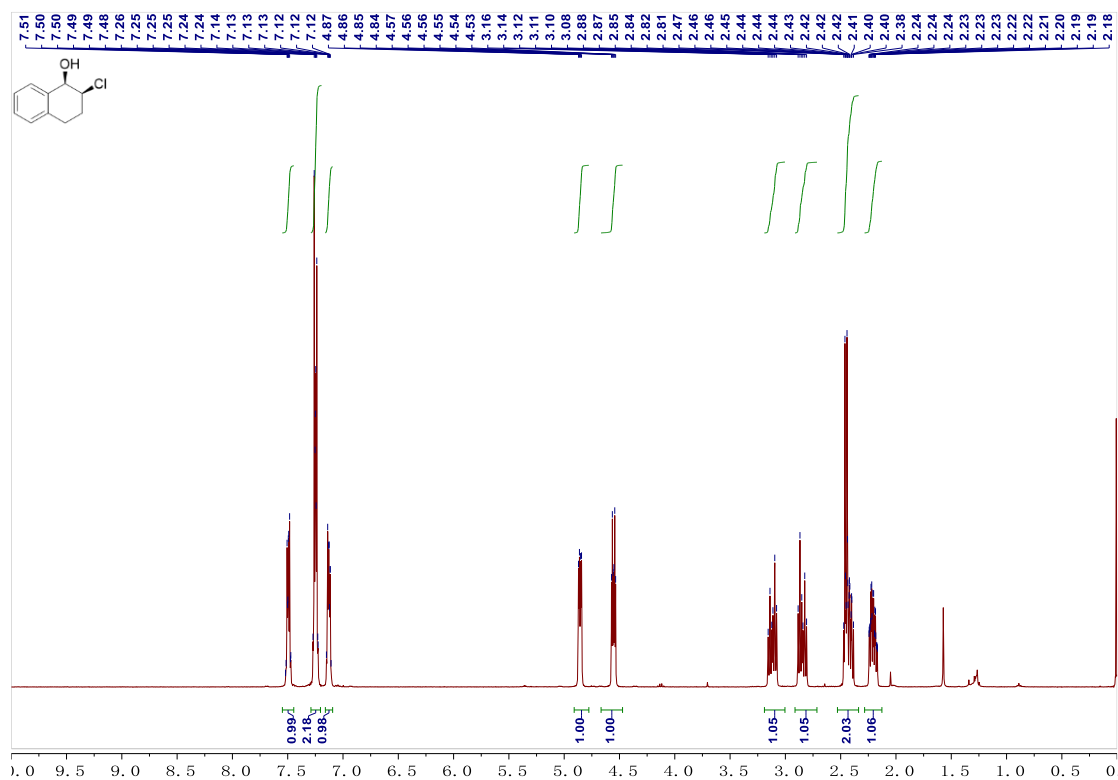
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2r**



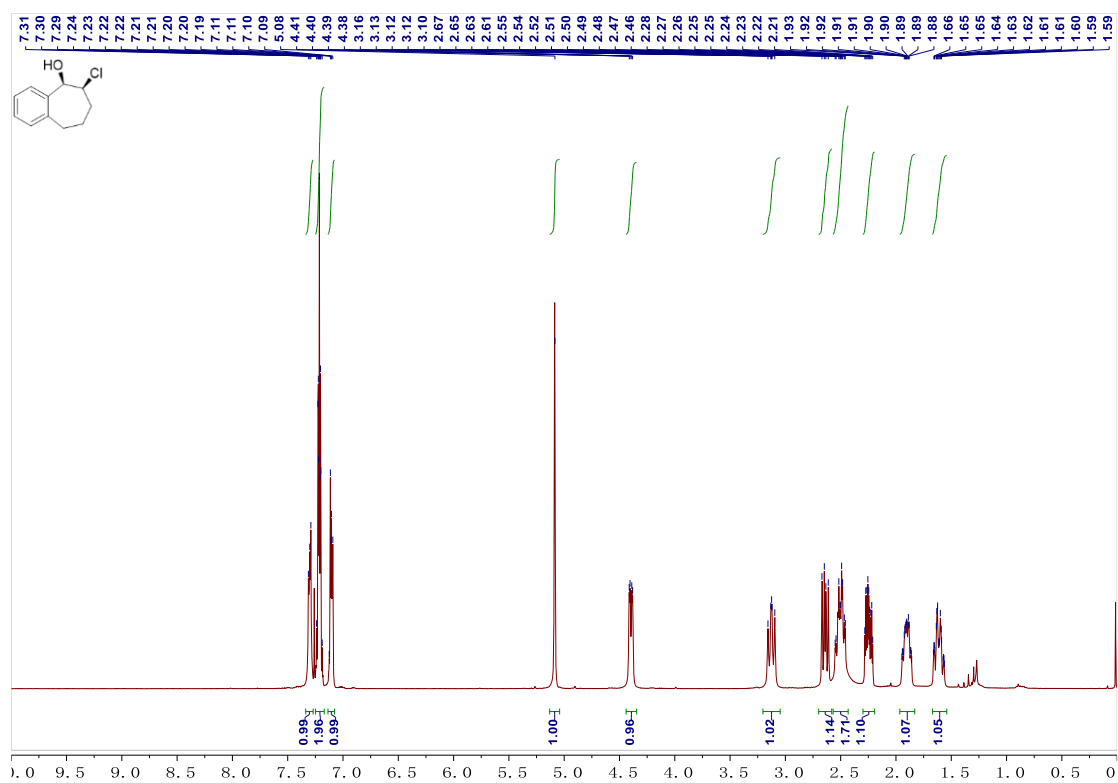
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **2r**



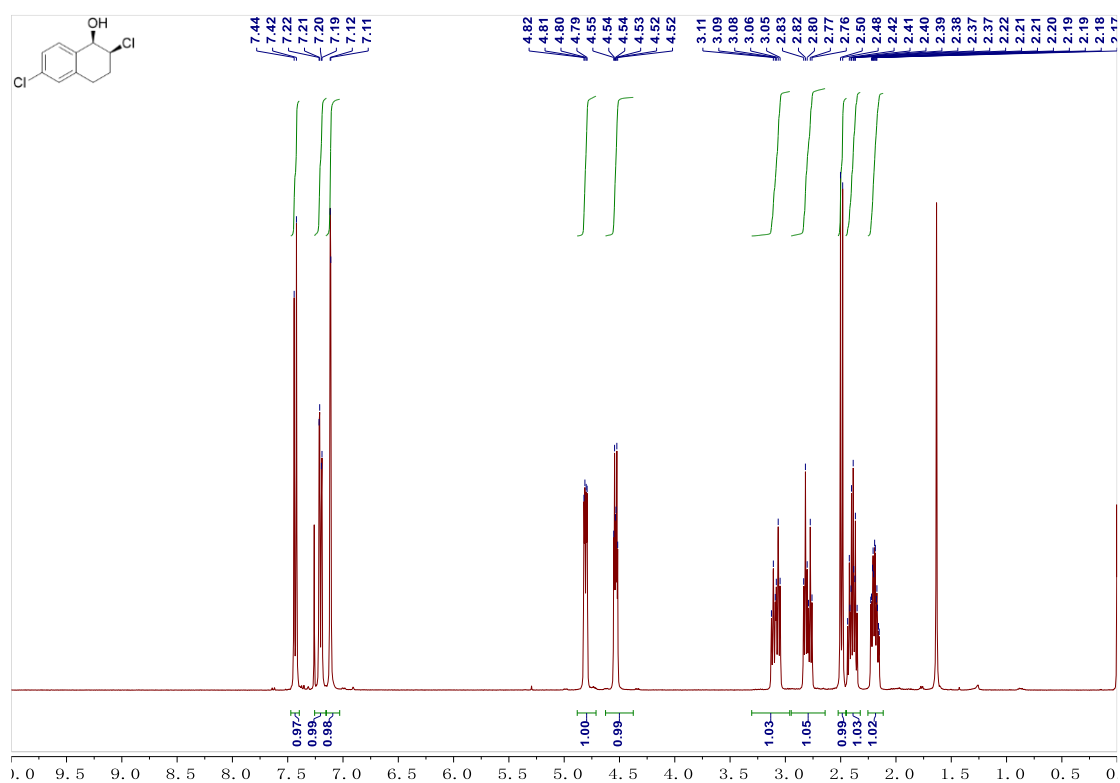
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound 2s



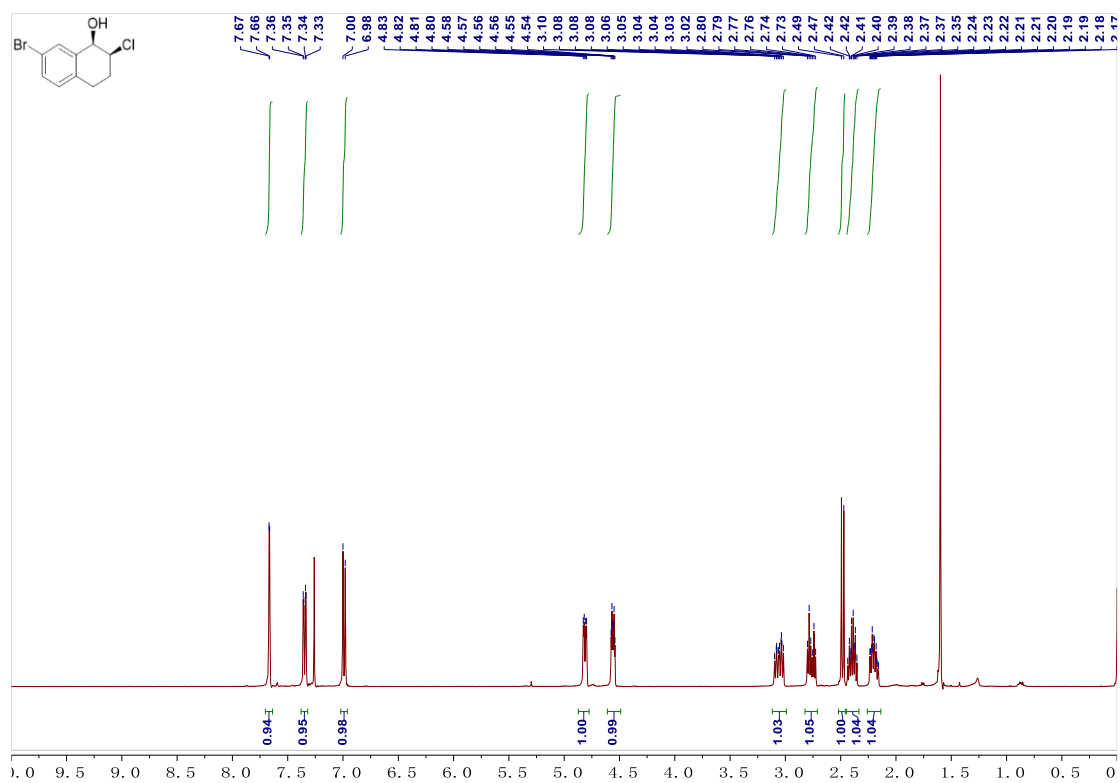
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound 2t



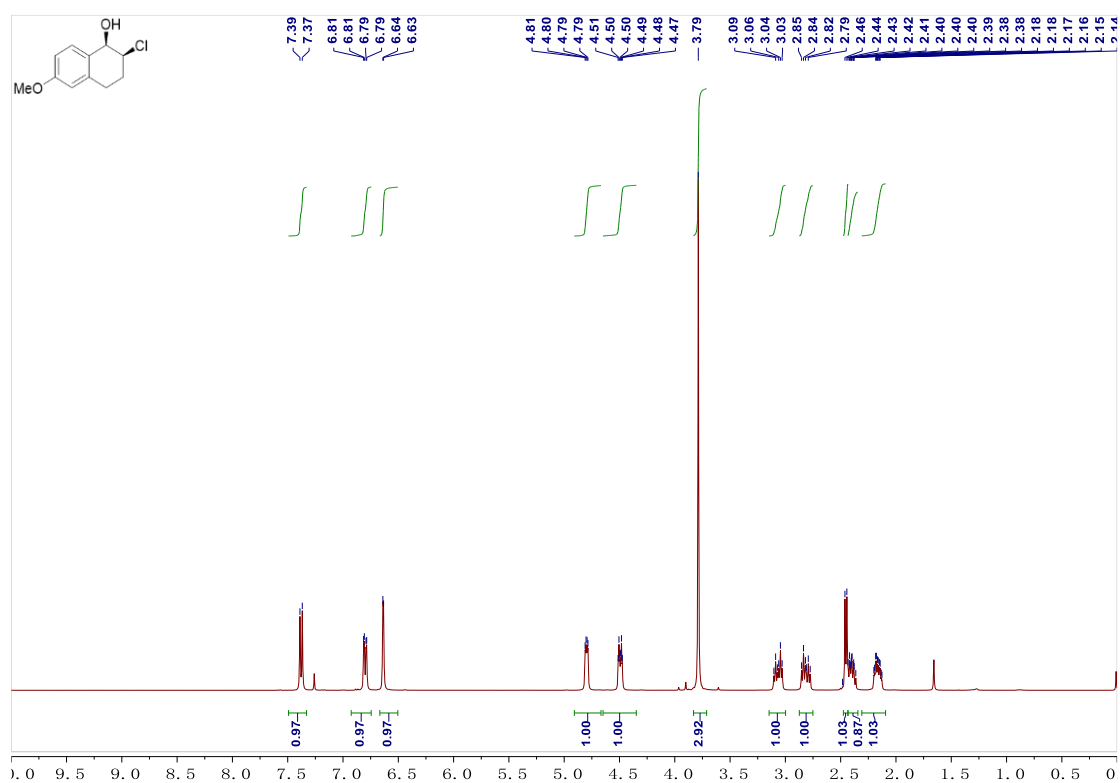
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2u**



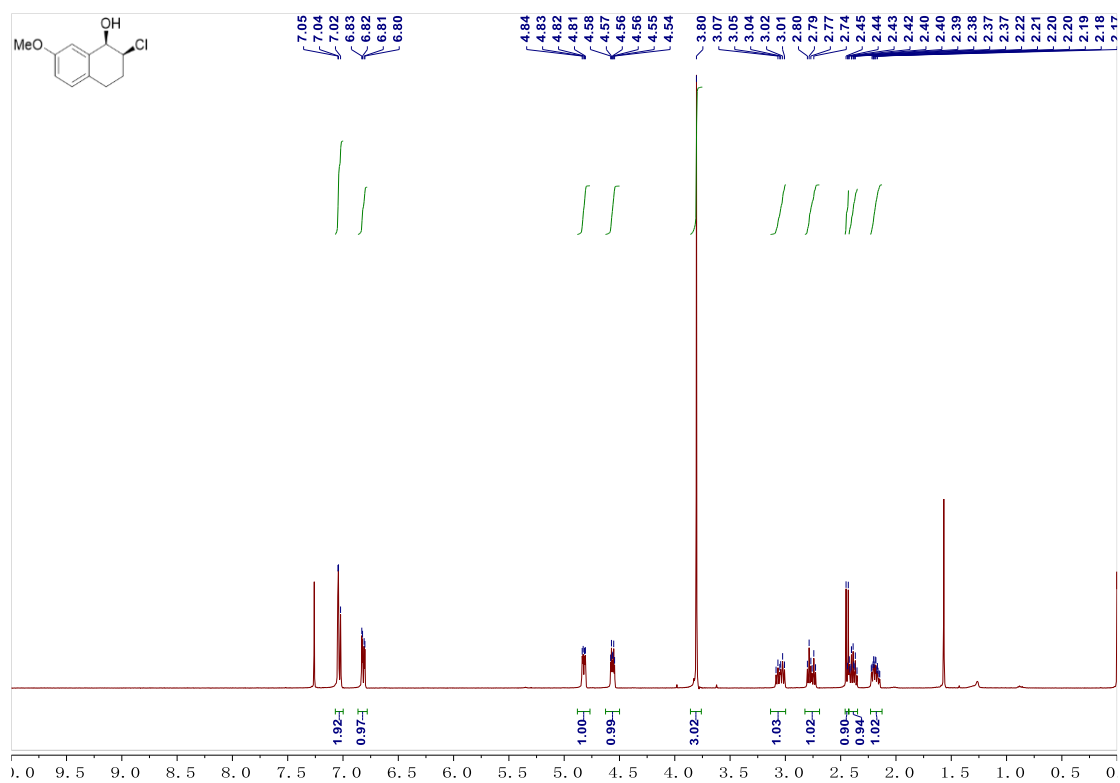
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2v**



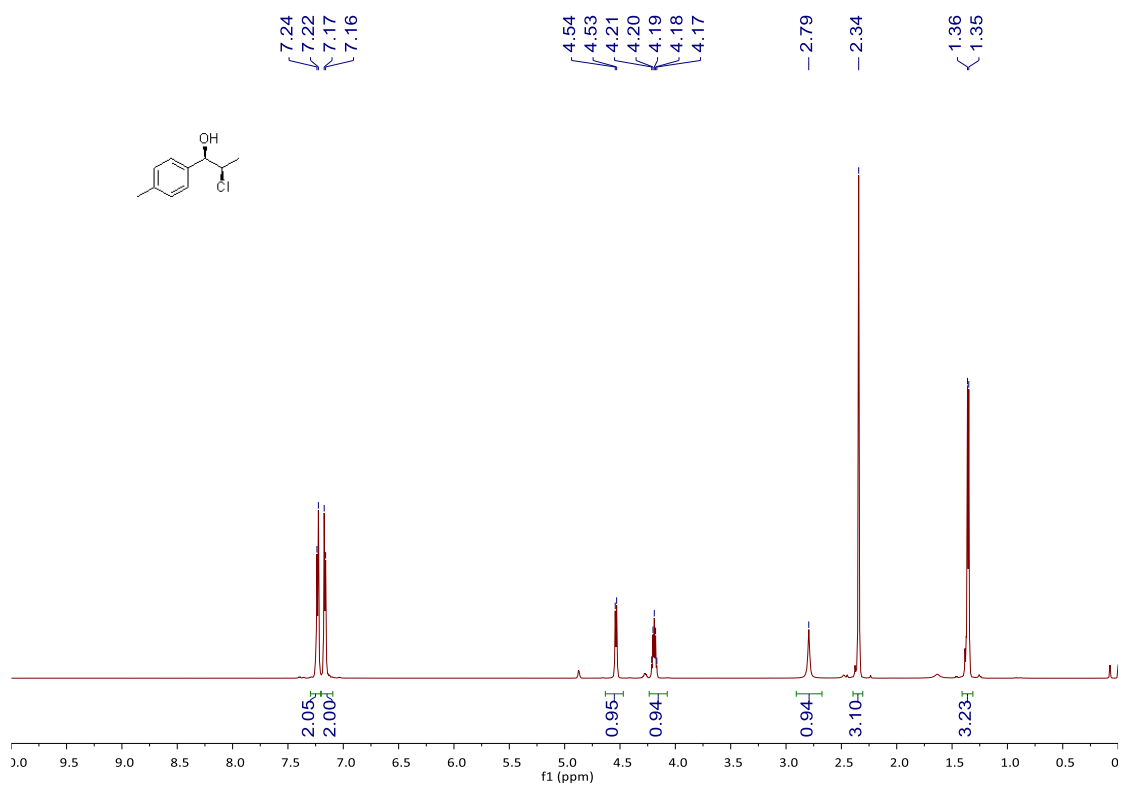
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2w**



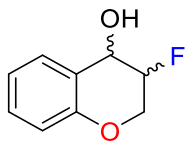
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2x**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2y**



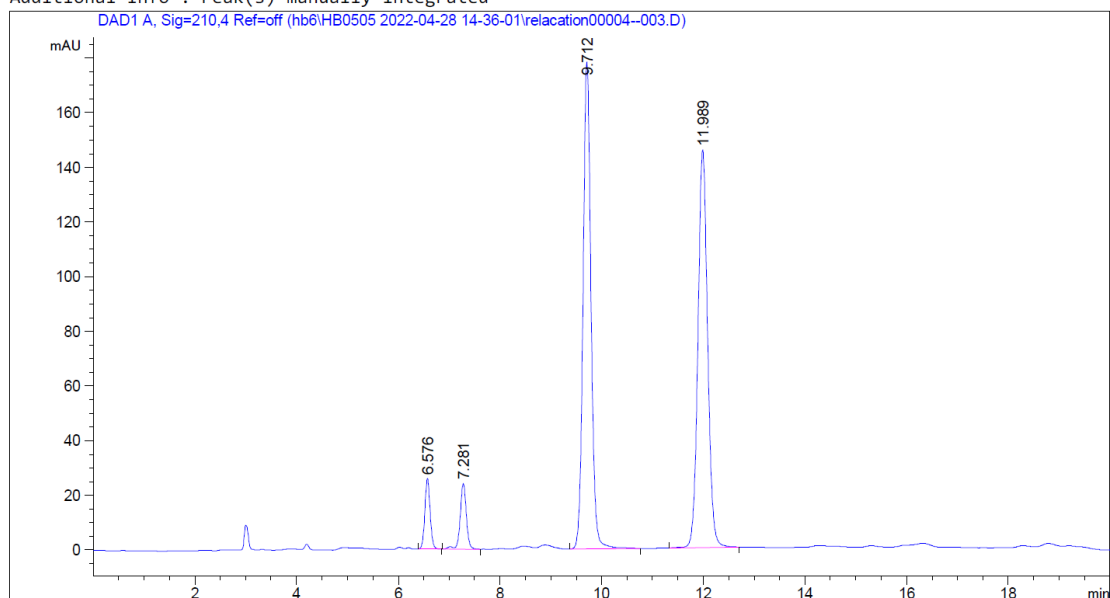
## 6. HPLC chromatograms



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P1-F-05
Injection Date  : 4/28/2022 3:12:47 PM      Inj       :    1
                                           Inj Volume: 1.000 µl

Acq. Method     : D:\ChemStation\1\Data\hb6\HB0505 2022-04-28 14-36-01\hb6_IF-3-90-10-1ML-
                  13min.M
Last changed    : 4/28/2022 2:53:43 PM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\HB0505 2022-04-28 14-36-01\hb6_IF-3-90-10-1ML-
                  13min.M (Sequence Method)
Last changed    : 4/28/2022 3:34:10 PM by SYSTEM
Additional Info  : Peak(s) manually integrated
    
```



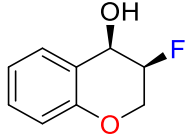
### Area Percent Report

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
    
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

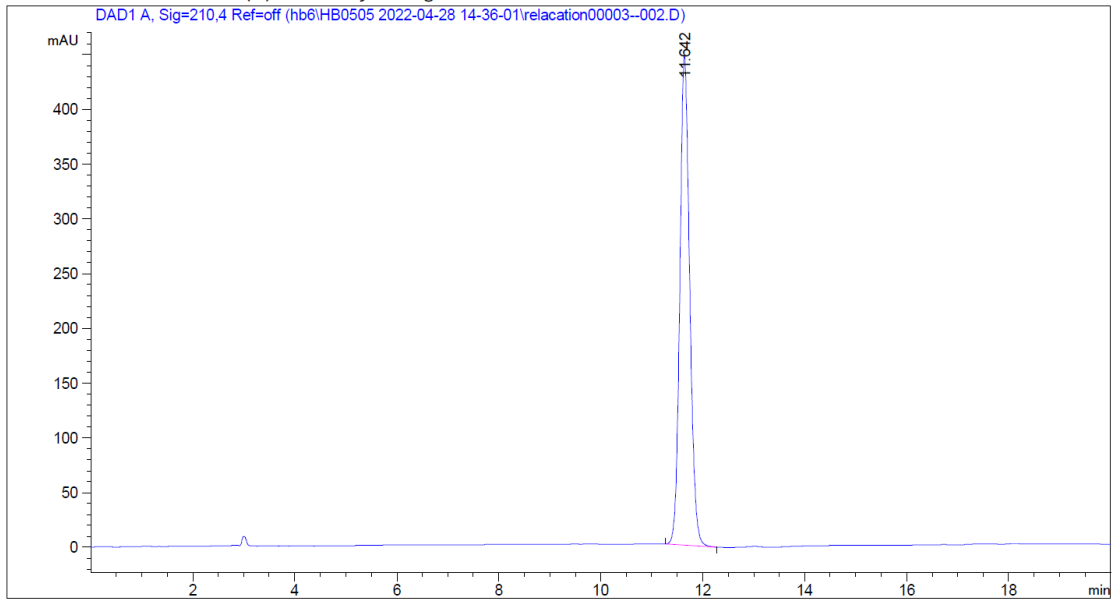
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.576	BB	0.1101	185.82097	25.78374	4.3882
2	7.281	VB R	0.1313	204.27399	23.99939	4.8240
3	9.712	BB	0.1664	1931.38953	178.29167	45.6103
4	11.989	BB	0.2036	1913.06653	145.33151	45.1776



**2a**

```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P1-F-04
Injection Date  : 4/28/2022 2:51:53 PM      Inj       :    1
                                           Inj Volume: 1.000 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0505 2022-04-28 14-36-01\hb6_IF-3-90-10-1ML-
                                           13min.M
Last changed    : 4/28/2022 2:53:43 PM by SYSTEM
                                           (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0505 2022-04-28 14-36-01\hb6_IF-3-90-10-1ML-
                                           13min.M (Sequence Method)
Last changed    : 4/28/2022 3:31:17 PM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

```

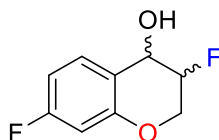
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.642	BB	0.2066	5992.00977	446.31683	100.0000

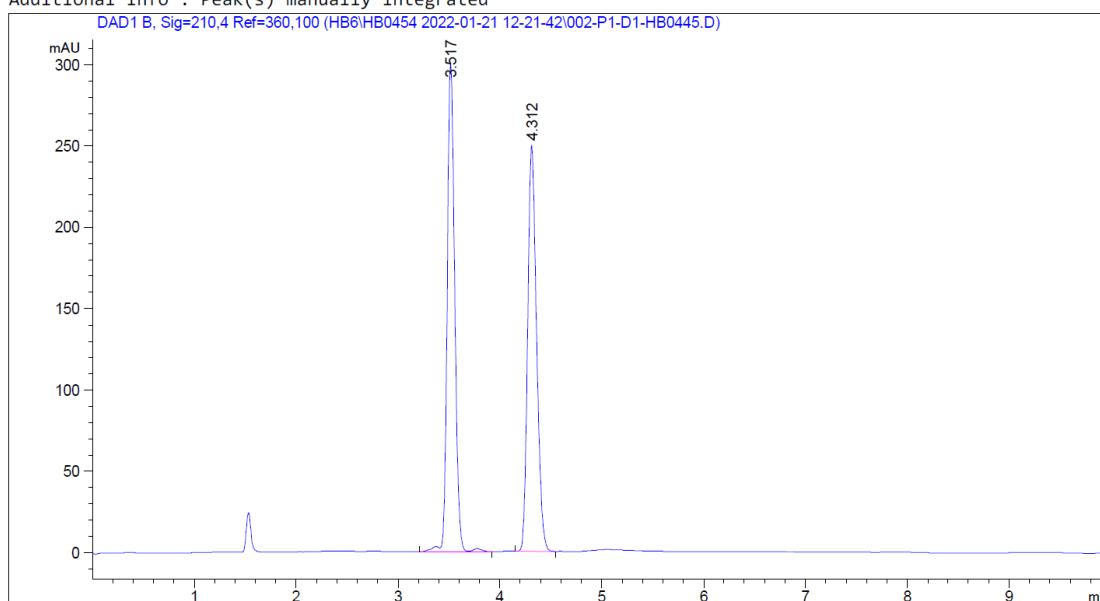
Totals :                                    5992.00977 446.31683





```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : 1290-DAD                   Location  : P1-D-01
Injection Date  : 1/21/2022 12:33:02 PM      Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0454 2022-01-21 12-21-42\IE-3-90-10-0.45-0.5UL-10MIN
                                           .M
Last changed    : 1/21/2022 11:27:03 AM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0454 2022-01-21 12-21-42\IE-3-90-10-0.45-0.5UL-10MIN
                                           .M (Sequence Method)
Last changed    : 4/15/2022 2:17:23 PM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

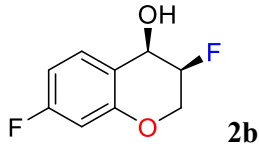
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

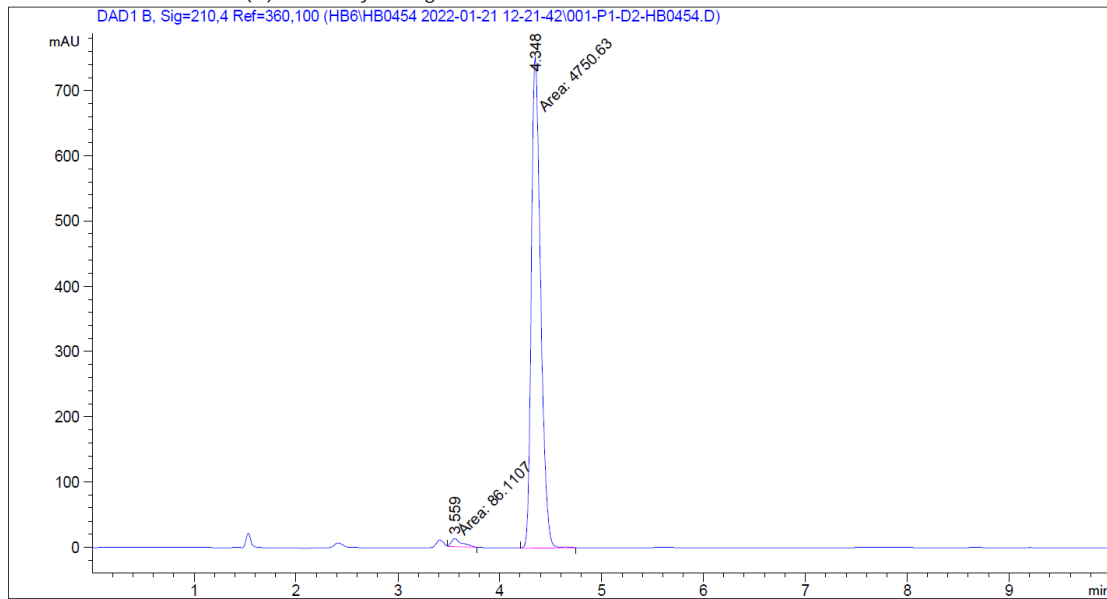
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.517	VV R	0.0786	1542.66687	300.86826	50.4892
2	4.312	BB	0.0946	1512.77258	250.03011	49.5108

Totals :                    3055.43945   550.89836



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Acq. Instrument : 1290-DAD                   Location  : P1-D-02
Injection Date  : 1/21/2022 12:22:36 PM      Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0454 2022-01-21 12-21-42\IE-3-90-10-0.45-0.5UL-10MIN
                                           .M
Last changed    : 1/21/2022 11:27:03 AM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0454 2022-01-21 12-21-42\IE-3-90-10-0.45-0.5UL-10MIN
                                           .M (Sequence Method)
Last changed    : 4/15/2022 2:17:23 PM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

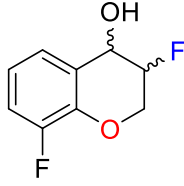
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.559	MM	0.1177	86.11067	12.19253	1.7803
2	4.348	MM	0.1052	4750.62891	752.53674	98.2197

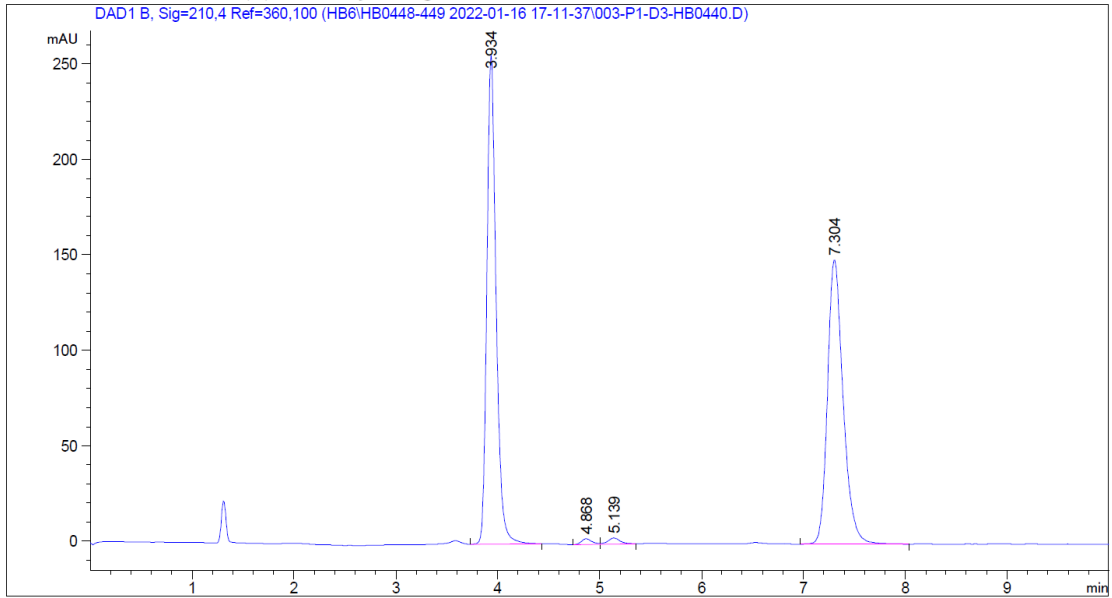
Totals :                    4836.73958   764.72928



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Acq. Instrument : 1290-DAD                    Location  : P1-D-03
Injection Date  : 1/16/2022 5:33:22 PM       Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0448-449 2022-01-16 17-11-37\IF-3-90-10-0.5-0.5UL-
                                           10MIN.M
Last changed    : 1/16/2022 4:48:35 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0448-449 2022-01-16 17-11-37\IF-3-90-10-0.5-0.5UL-
                                           10MIN.M (Sequence Method)
Last changed    : 4/15/2022 1:09:22 PM by SYSTEM
                                           (modified after loading)
Additional Info : Peak(s) manually integrated
DAD1 B, Sig=210,4 Ref=360,100 (HB6\HB0448-449 2022-01-16 17-11-37\003-P1-D3-HB0440.D)

```



```

=====
                          Area Percent Report
=====

```

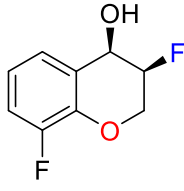
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

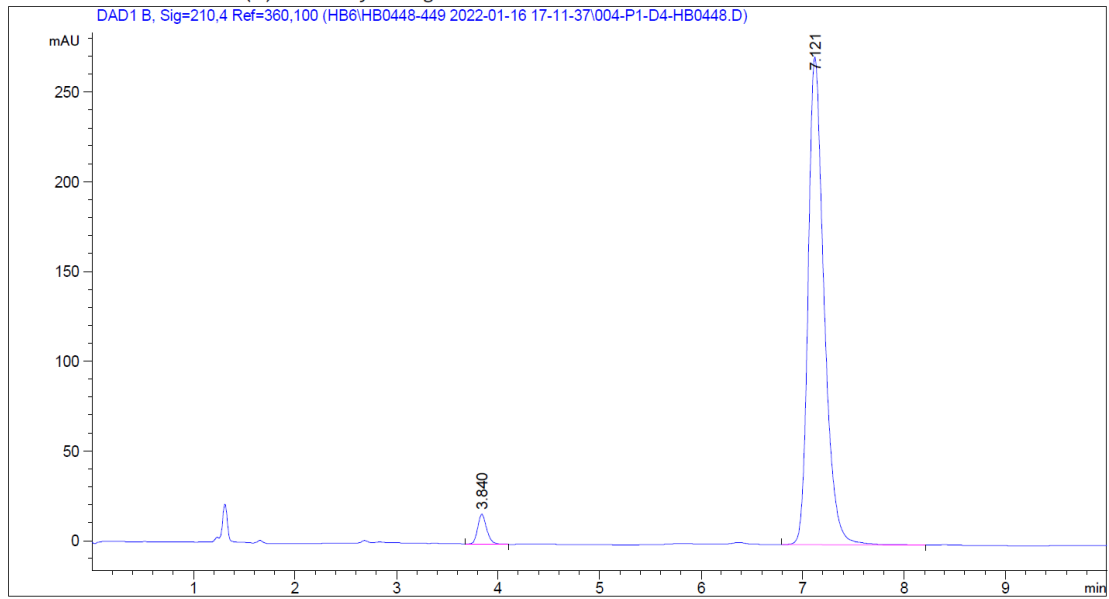
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.934	VB	0.0954	1610.66064	256.16379	49.6485
2	4.868	BV	0.1063	21.01318	2.97911	0.6477
3	5.139	VB	0.1232	25.90921	3.17523	0.7986
4	7.304	BB	0.1603	1586.54370	148.95432	48.9051



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    4
Acq. Instrument : 1290-DAD                    Location  : P1-D-04
Injection Date  : 1/16/2022 5:43:48 PM       Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0448-449 2022-01-16 17-11-37\IF-3-90-10-0.5-0.5UL-
                  10MIN.M
Last changed    : 1/16/2022 4:48:35 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0448-449 2022-01-16 17-11-37\IF-3-90-10-0.5-0.5UL-
                  10MIN.M (Sequence Method)
Last changed    : 4/15/2022 1:09:22 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====
  
```



=====  
 Area Percent Report  
 =====

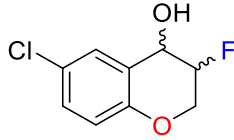
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

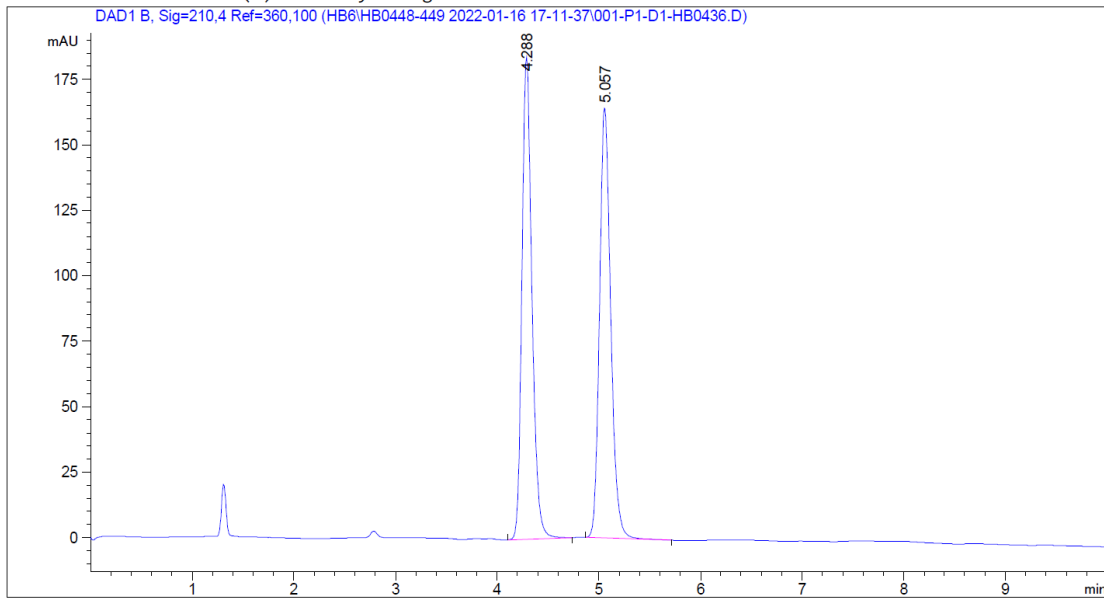
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.840	BB	0.0937	102.69276	16.69804	3.3677
2	7.121	BB	0.1645	2946.64453	271.72641	96.6323

Totals :                                    3049.33730   288.42445



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Acq. Instrument : 1290-DAD                    Location  : P1-D-01
Injection Date  : 1/16/2022 5:12:30 PM       Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0448-449 2022-01-16 17-11-37\IF-3-90-10-0.5-0.5UL-
                  10MIN.M
Last changed    : 1/16/2022 4:48:35 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0448-449 2022-01-16 17-11-37\IF-3-90-10-0.5-0.5UL-
                  10MIN.M (Sequence Method)
Last changed    : 4/15/2022 1:09:22 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

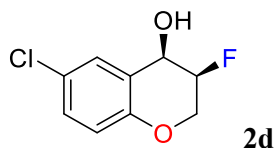
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

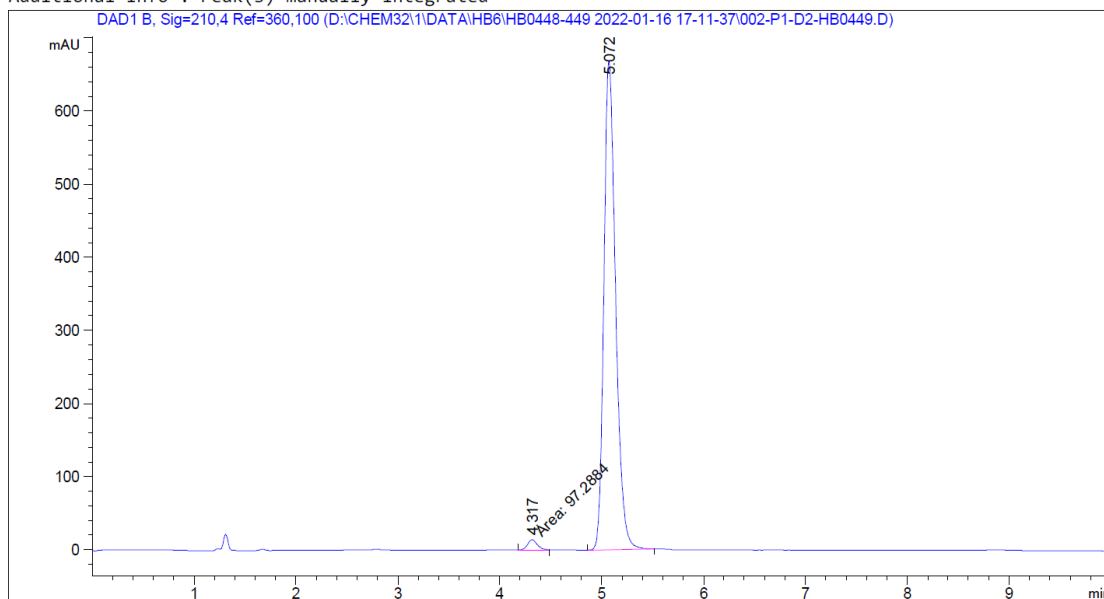
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.288	BB	0.1057	1255.98950	183.95157	50.0653
2	5.057	BB	0.1169	1252.71411	164.35622	49.9347

Totals :                    2508.70361  348.30779



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : 1290-DAD                   Location  : P1-D-02
Injection Date  : 1/16/2022 5:22:56 PM      Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0448-449 2022-01-16 17-11-37\IF-3-90-10-0.5-0.5UL-
                  10MIN.M
Last changed    : 1/16/2022 4:48:35 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0448-449 2022-01-16 17-11-37\IF-3-90-10-0.5-0.5UL-
                  10MIN.M (Sequence Method)
Last changed    : 4/15/2022 1:09:22 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

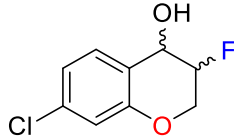
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.317	MM	0.1132	97.28838	14.32150	1.7920
2	5.072	BB	0.1210	5331.71826	669.17145	98.2080

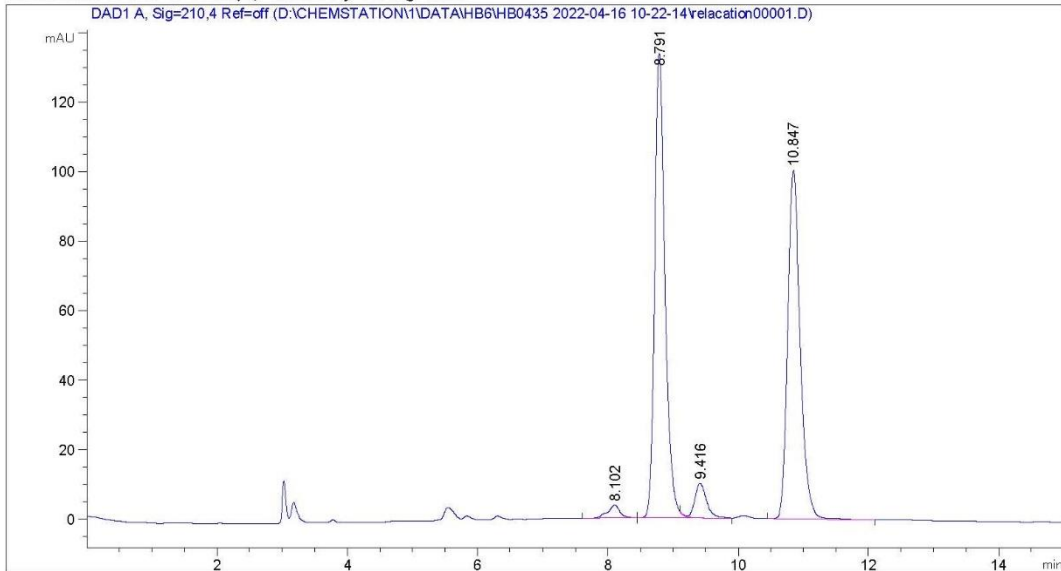
Totals :                                    5429.00665    683.49295



Data File D:\CHEMSTATION\1\DATA\HB6\HB0435 2022-04-16 10-22-14\relacation00001.D  
 Sample Name: HB0435

```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-09
Injection Date  : 4/16/2022 10:23:03 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0435 2022-04-16 10-22-14\hb6_IE-3-90-10-1ML-
                  10min.M
Last changed    : 4/16/2022 10:22:53 AM by SYSTEM
                  (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\hb0435 2022-04-16 10-22-14\hb6_IE-3-90-10-1ML-
                  10min.M (Sequence Method)
Last changed    : 4/16/2022 10:58:03 AM by SYSTEM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



Area Percent Report

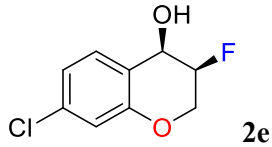
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.102	BB	0.1901	49.39766	3.74002	1.6609
2	8.791	BV R	0.1664	1472.49548	133.76942	49.5103
3	9.416	VB E	0.1846	121.44904	9.93720	4.0835
4	10.847	BB	0.2027	1330.77722	100.38687	44.7453

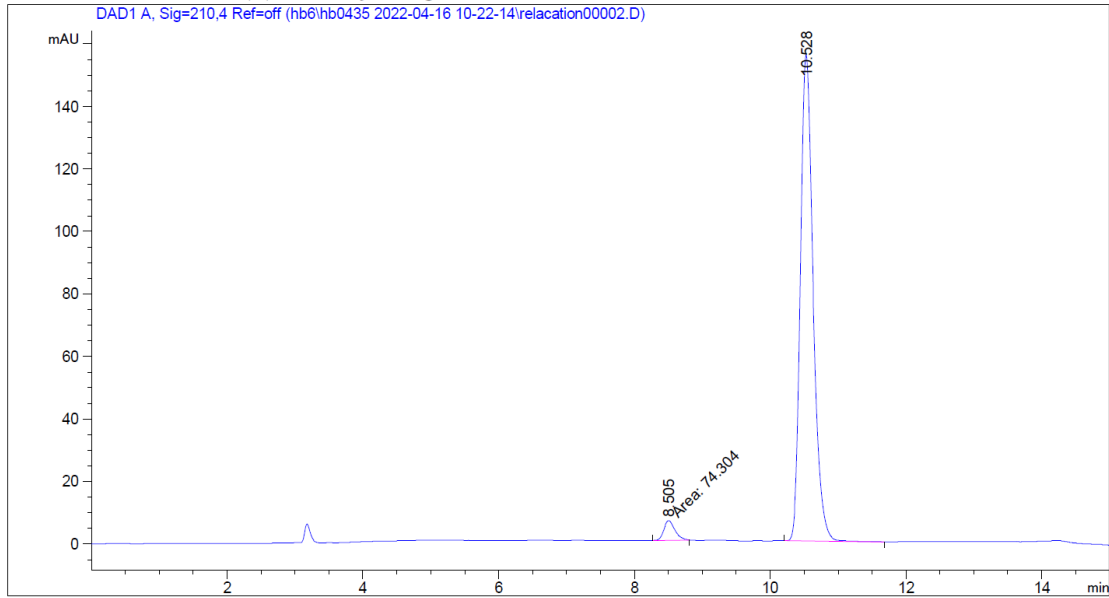
Totals : 2974.11941 247.83352



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-10
Injection Date  : 4/16/2022 10:38:53 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0435 2022-04-16 10-22-14\hb6_IE-3-90-10-1ML-
                  10min.M
Last changed    : 4/16/2022 10:22:53 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0435 2022-04-16 10-22-14\hb6_IE-3-90-10-1ML-
                  10min.M (Sequence Method)
Last changed    : 4/16/2022 10:58:03 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
DAD1 A, Sig=210,4 Ref=off (hb6\hb0435 2022-04-16 10-22-14\relacation00002.D)

```



```

=====
                          Area Percent Report
=====

```

```

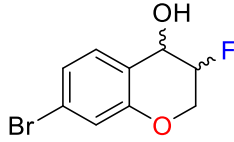
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

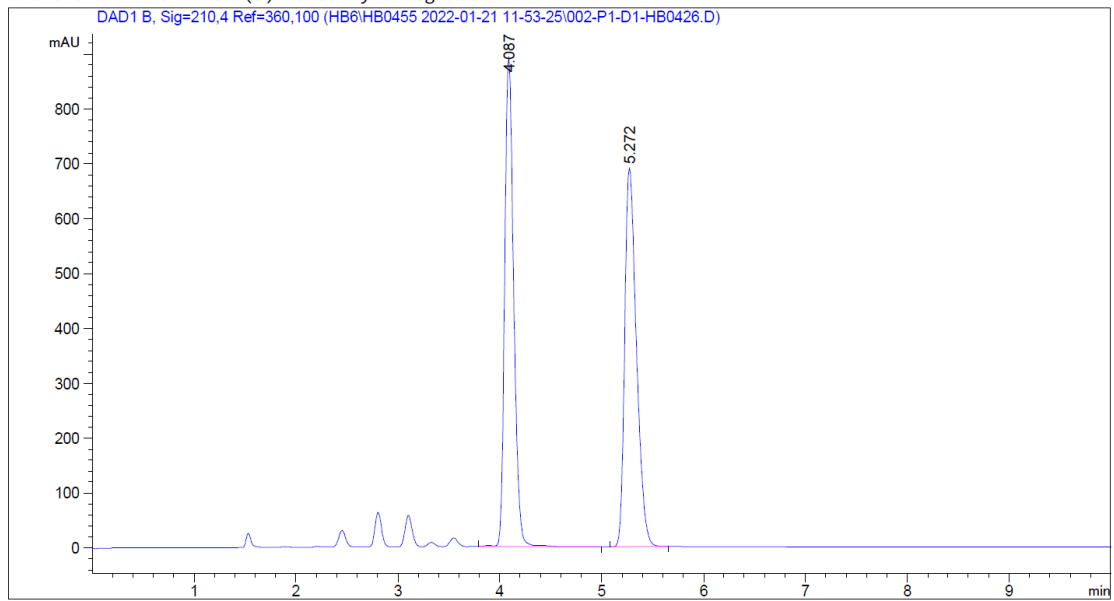
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.505	MM	0.1935	74.30401	6.40093	3.5543
2	10.528	BB	0.1992	2016.22791	155.59818	96.4457





```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : 1290-DAD                    Location  : P1-D-01
Injection Date  : 1/21/2022 12:04:46 PM      Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0455 2022-01-21 11-53-25\IE-3-90-10-0.45-0.5UL-10MIN
                                           .M
Last changed    : 1/21/2022 11:27:03 AM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0455 2022-01-21 11-53-25\IE-3-90-10-0.45-0.5UL-10MIN
                                           .M (Sequence Method)
Last changed    : 4/15/2022 1:17:13 PM by SYSTEM
                                           (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



```

=====
                          Area Percent Report
=====
  
```

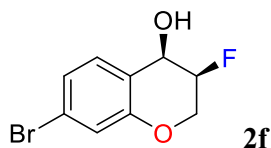
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

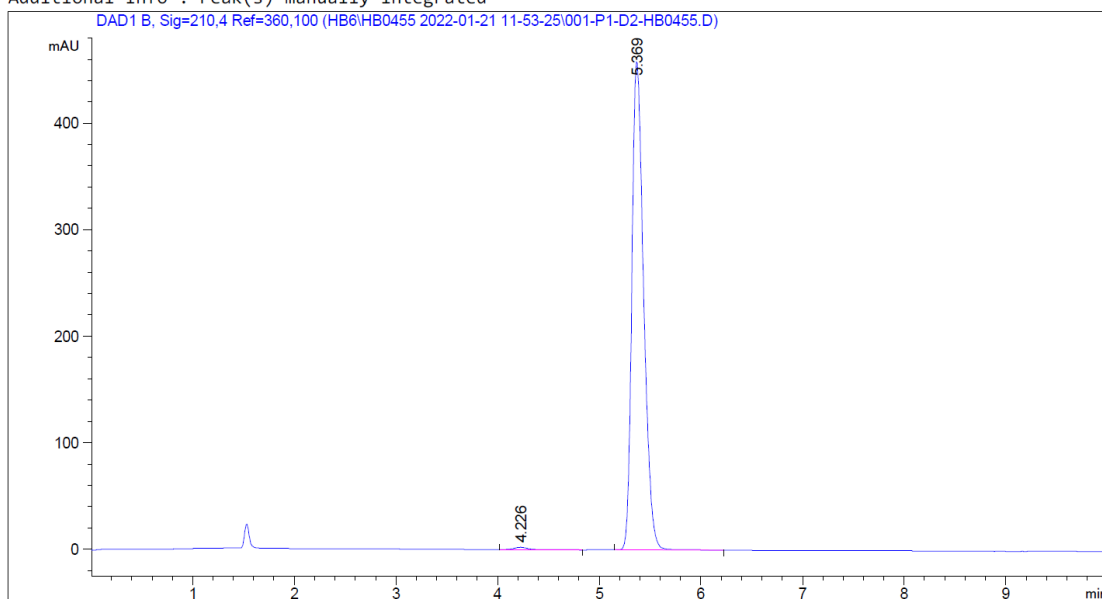
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.087	VV R	0.0933	5463.86475	889.47711	49.8246
2	5.272	BB	0.1230	5502.33984	690.20117	50.1754

Totals : 1.09662e4 1579.67828



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Acq. Instrument : 1290-DAD                    Location  : P1-D-02
Injection Date  : 1/21/2022 11:54:20 AM      Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0455 2022-01-21 11-53-25\IE-3-90-10-0.45-0.SUL-10MIN
                                           .M
Last changed    : 1/21/2022 11:27:03 AM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0455 2022-01-21 11-53-25\IE-3-90-10-0.45-0.SUL-10MIN
                                           .M (Sequence Method)
Last changed    : 4/15/2022 1:17:13 PM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
=====
  
```



```

=====
                          Area Percent Report
=====
  
```

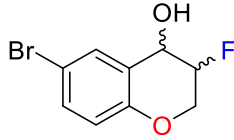
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

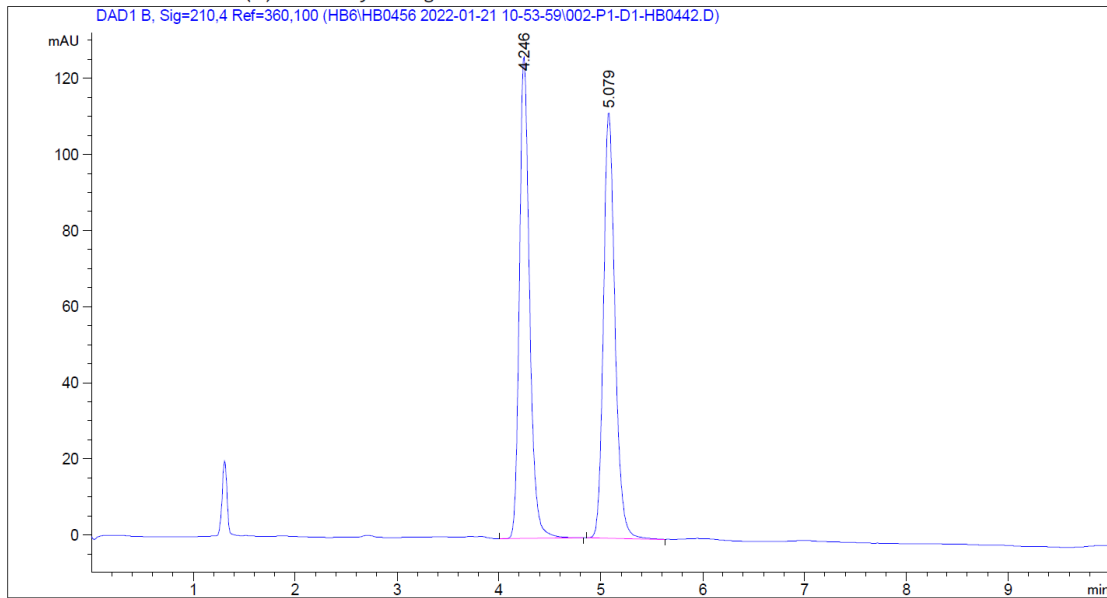
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.226	BB	0.1483	24.88840	2.41460	0.6706
2	5.369	BB	0.1238	3686.73096	458.62585	99.3294

Totals :                                    3711.61935    461.04045



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : 1290-DAD                   Location  : P1-D-01
Injection Date  : 1/21/2022 11:05:19 AM      Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0456 2022-01-21 10-53-59\IF-3-90-10-0.5-0.5UL-10MIN.
                                           M
Last changed    : 1/16/2022 4:48:35 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0456 2022-01-21 10-53-59\IF-3-90-10-0.5-0.5UL-10MIN.
                                           M (Sequence Method)
Last changed    : 4/15/2022 1:15:18 PM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



```

=====
                          Area Percent Report
=====
  
```

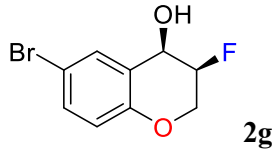
```

Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

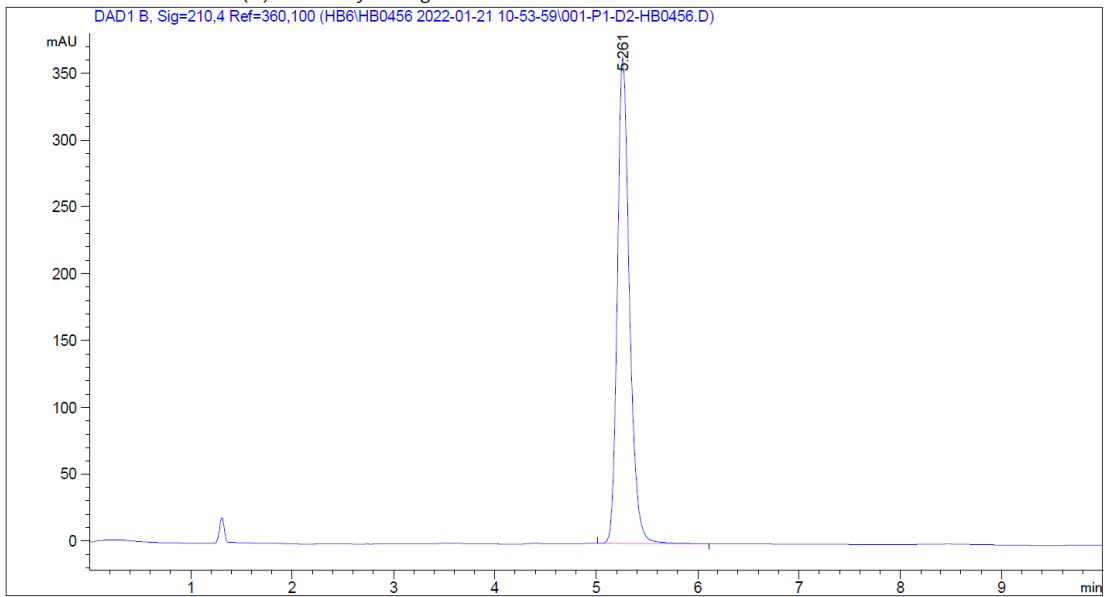
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.246	BB	0.1049	878.08563	126.65380	49.9226
2	5.079	BB	0.1198	880.80896	111.95924	50.0774

Totals :                    1758.89459   238.61304



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Acq. Instrument : 1290-DAD                    Location  : P1-D-02
Injection Date  : 1/21/2022 10:54:53 AM      Inj       :    1
                                           Inj Volume: 0.500 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0456 2022-01-21 10-53-59\IF-3-90-10-0.5-0.5UL-10MIN.
                                           M
Last changed    : 1/16/2022 4:48:35 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0456 2022-01-21 10-53-59\IF-3-90-10-0.5-0.5UL-10MIN.
                                           M (Sequence Method)
Last changed    : 4/15/2022 1:15:18 PM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

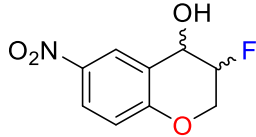
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

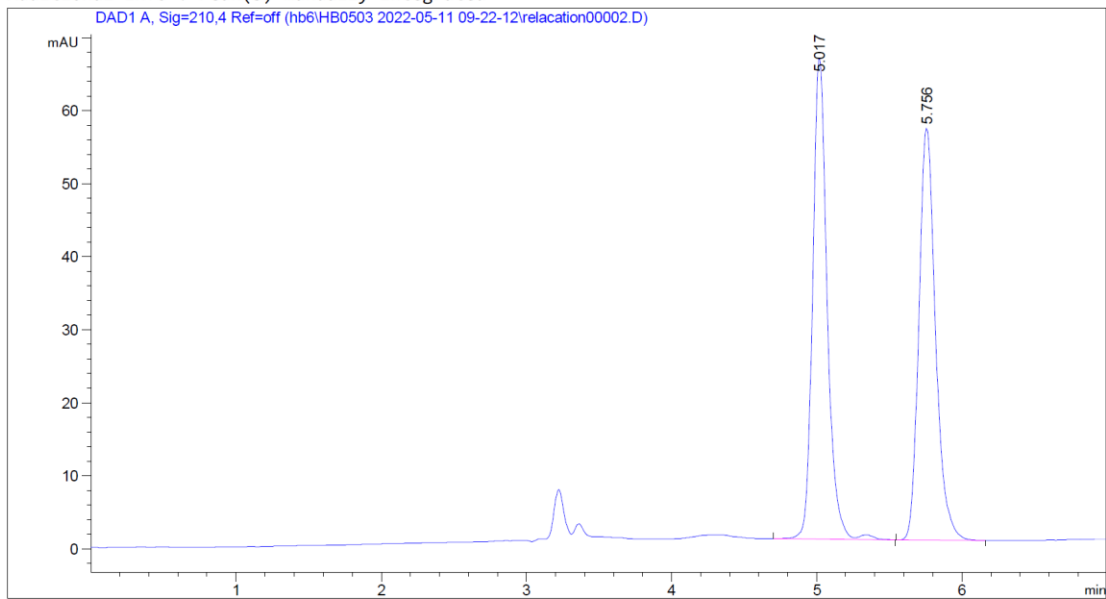
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.261	BB	0.1274	3033.09717	363.48572	100.0000

Totals :                                    3033.09717  363.48572



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-A-02
Injection Date  : 5/11/2022 9:30:54 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0503 2022-05-11 09-22-12\hb6_IE-3-50-50-1ML-
                 30min.M
Last changed    : 5/11/2022 9:22:21 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\HB0503 2022-05-11 09-22-12\hb6_IE-3-50-50-1ML-
                 30min.M (Sequence Method)
Last changed    : 5/11/2022 9:43:57 AM by SYSTEM
Additional Info  : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

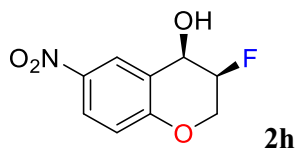
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

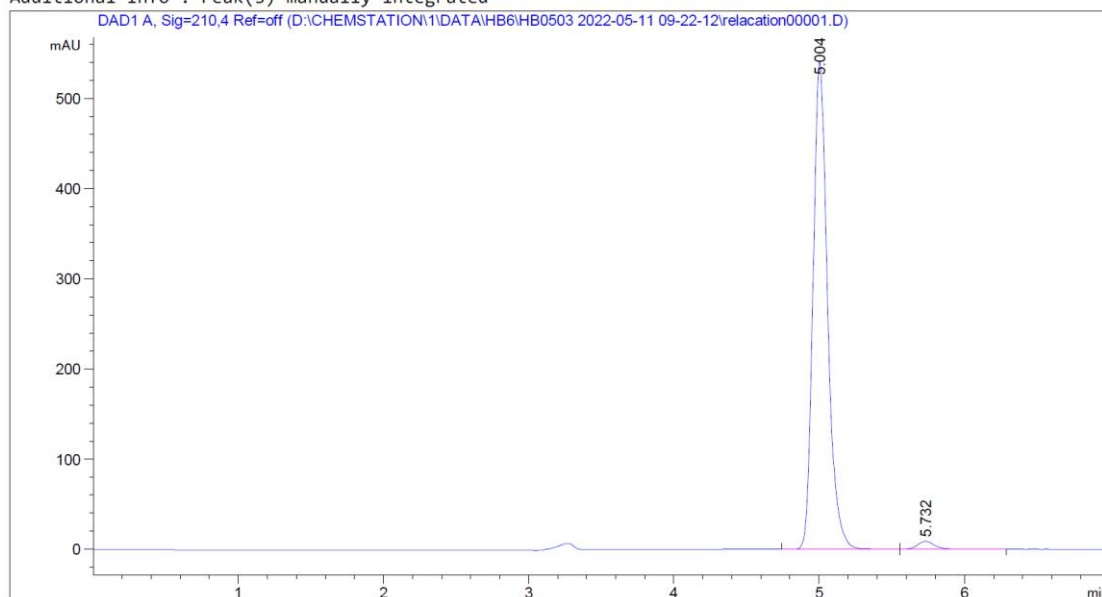
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.017	BV R	0.1050	457.99380	66.00484	50.4161
2	5.756	BB	0.1231	450.43417	56.44759	49.5839

Totals :                    908.42798 122.45243



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-A-01
Injection Date  : 5/11/2022 9:23:03 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 5.000 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0503 2022-05-11 09-22-12\hb6_IE-3-50-50-1ML-
30min.M
Last changed    : 5/11/2022 9:22:21 AM by SYSTEM
                 (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0503 2022-05-11 09-22-12\hb6_IE-3-50-50-1ML-
30min.M (Sequence Method)
Last changed    : 5/11/2022 9:42:58 AM by SYSTEM
                 (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



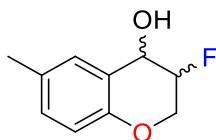
=====  
Area Percent Report  
=====

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

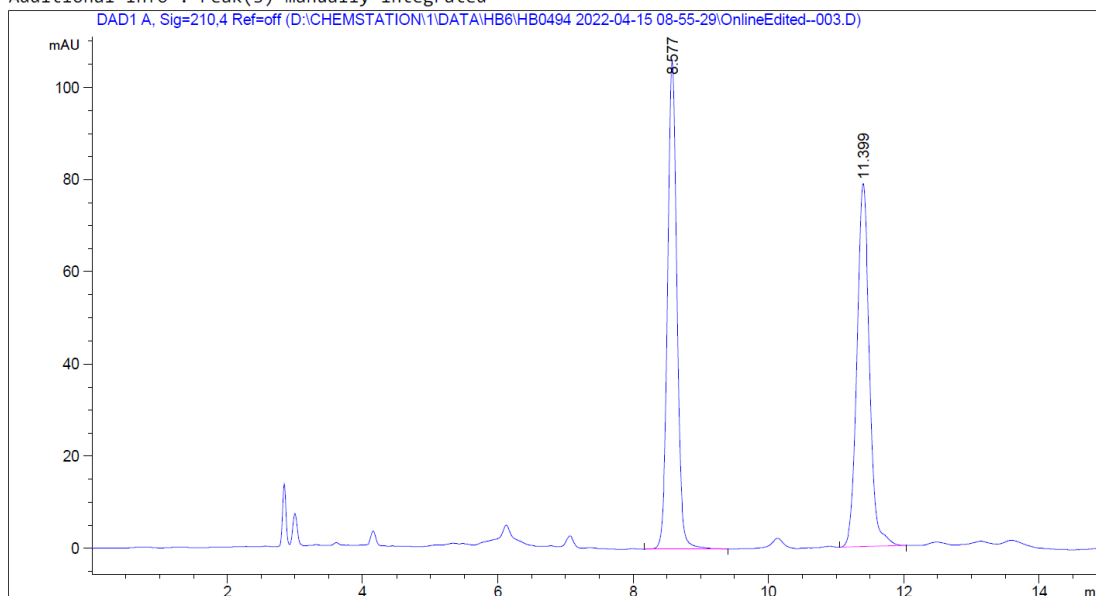
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.004	BV	0.1067	3738.42480	540.69000	98.0800
2	5.732	VB	0.1274	73.18188	8.76197	1.9200



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-09
Injection Date  : 4/15/2022 9:32:58 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0494 2022-04-15 08-55-29\hb6_IF-3-90-10-1ML-
                 30min.M
Last changed    : 4/15/2022 9:33:34 AM by SYSTEM
                 (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0494 2022-04-15 08-55-29\hb6_IF-3-90-10-1ML-
                 30min.M (Sequence Method)
Last changed    : 4/15/2022 9:51:51 AM by SYSTEM
                 (modified after loading)
Additional Info : Peak(s) manually integrated
=====

```



```

=====
                          Area Percent Report
=====

```

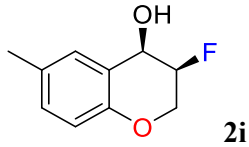
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

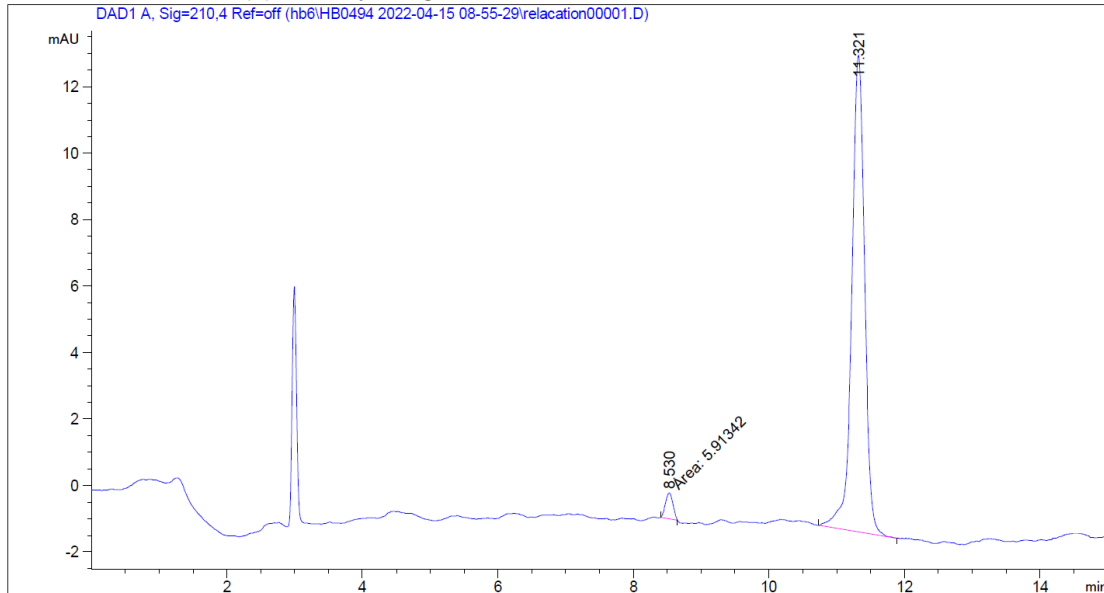
Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.577	BB	0.1454	1010.66382	105.88894	50.0347
2	11.399	BB	0.1974	1009.26031	78.83788	49.9653



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                          Location  : P2-D-06
Injection Date  : 4/15/2022 8:56:18 AM       Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0494 2022-04-15 08-55-29\hb6_IF-3-90-10-1ML-
                 30min.M
Last changed    : 4/15/2022 8:56:40 AM by SYSTEM
                 (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0494 2022-04-15 08-55-29\hb6_IF-3-90-10-1ML-
                 30min.M (Sequence Method)
Last changed    : 4/15/2022 9:51:51 AM by SYSTEM
                 (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

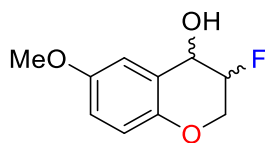
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

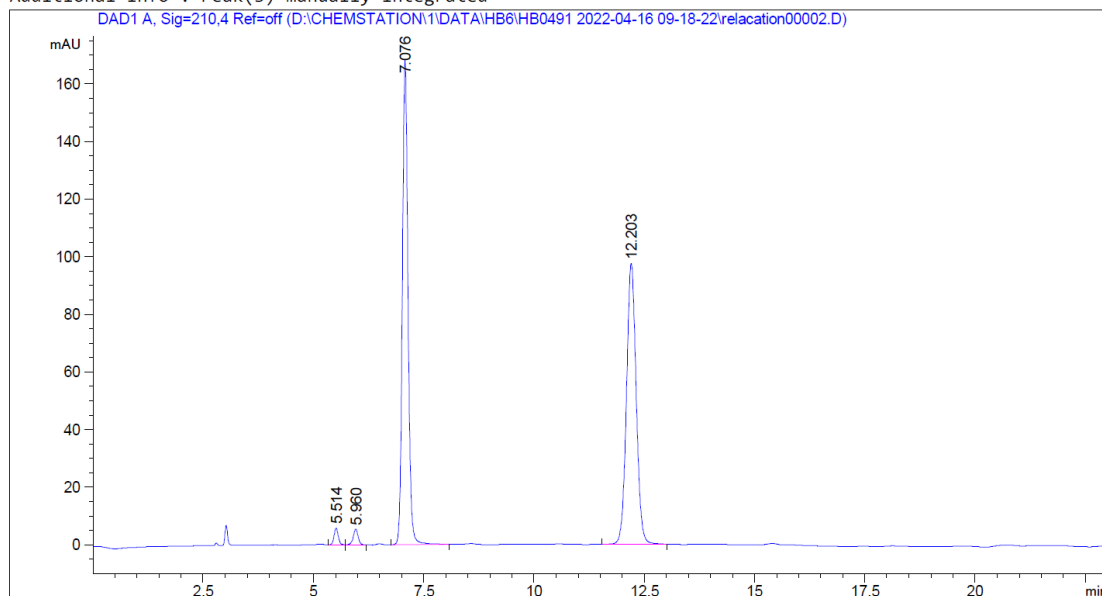
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.530	MM	0.1260	5.91342	7.82083e-1	3.0564
2	11.321	BB	0.2005	187.56075	14.34489	96.9436





```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-08
Injection Date  : 4/16/2022 9:43:01 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0491 2022-04-16 09-18-22\hb6_IF-3-70-30-1ML-
                 30min.M
Last changed    : 4/16/2022 9:41:34 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0491 2022-04-16 09-18-22\hb6_IF-3-70-30-1ML-
                 30min.M (Sequence Method)
Last changed    : 4/16/2022 10:12:12 AM by SYSTEM
                 (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



Area Percent Report

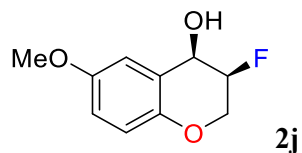
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

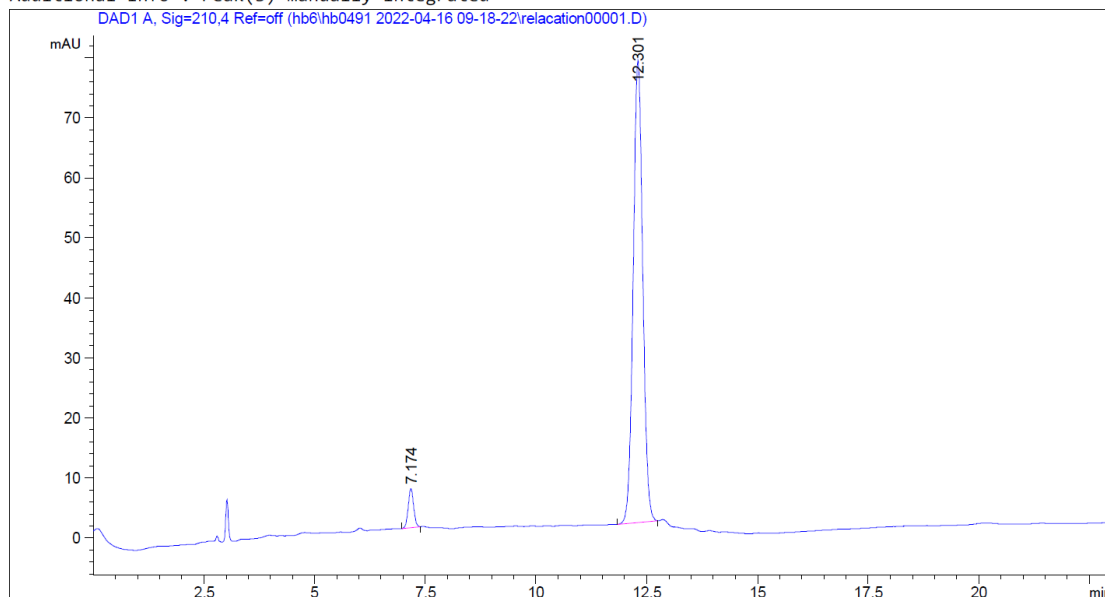
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.514	BB	0.1000	37.78038	5.80128	1.2369
2	5.960	BB	0.1128	40.48632	5.44117	1.3254
3	7.076	BB	0.1351	1488.45520	168.39778	48.7289
4	12.203	BB	0.2361	1487.83911	97.46669	48.7088

Totals : 3054.56101 277.10693



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-07
Injection Date  : 4/16/2022 9:19:12 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0491 2022-04-16 09-18-22\hb6_IF-3-70-30-1ML-
                 30min.M
Last changed    : 4/16/2022 9:41:34 AM by SYSTEM
                 (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\hb0491 2022-04-16 09-18-22\hb6_IF-3-70-30-1ML-
                 30min.M (Sequence Method)
Last changed    : 4/16/2022 10:12:12 AM by SYSTEM
                 (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



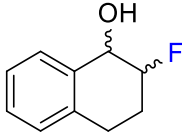
Area Percent Report

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

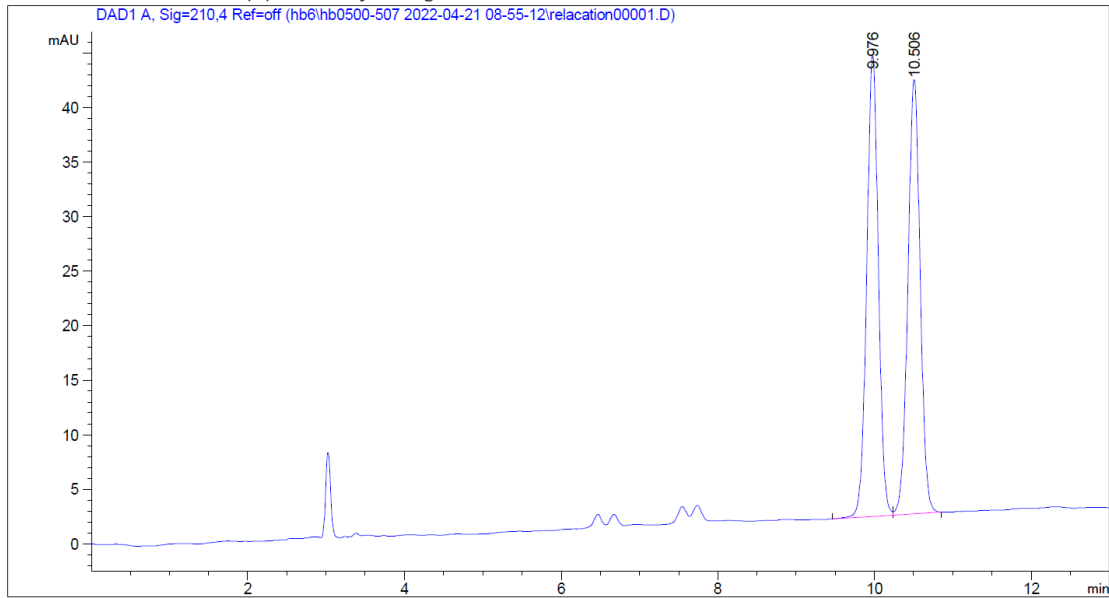
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.174	BB	0.1309	54.90629	6.47710	4.5483
2	12.301	BB	0.2325	1152.27161	77.02238	95.4517



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-01
Injection Date  : 4/21/2022 8:56:04 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M
Last changed    : 1/12/2022 9:06:58 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:09:25 AM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
DAD1 A, Sig=210,4 Ref=off (hb6\hb0500-507 2022-04-21 08-55-12\relacation00001.D)

```



```

=====
                          Area Percent Report
=====

```

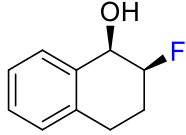
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.976	BV	0.1606	436.86185	42.25964	50.1593
2	10.506	VB	0.1692	434.08661	39.80902	49.8407

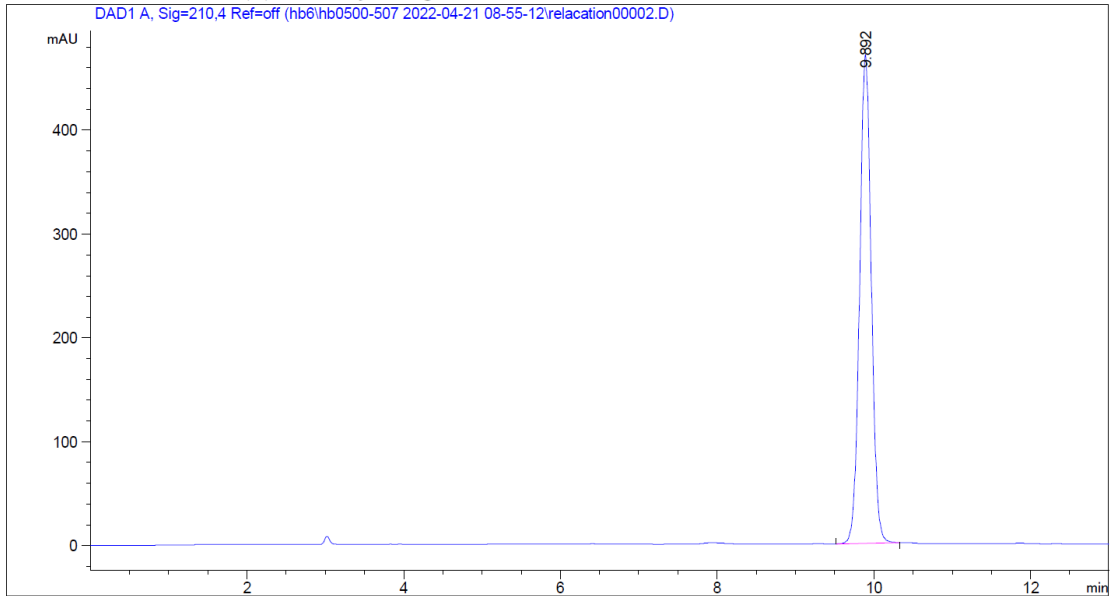


**2k**

```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-02
Injection Date  : 4/21/2022 9:09:54 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 1/12/2022 9:06:58 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:09:25 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
DAD1 A, Sig=210,4 Ref=off (hb6\hb0500-507 2022-04-21 08-55-12\relacation00002.D)

```



=====  
Area Percent Report  
=====

```

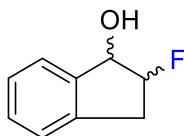
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

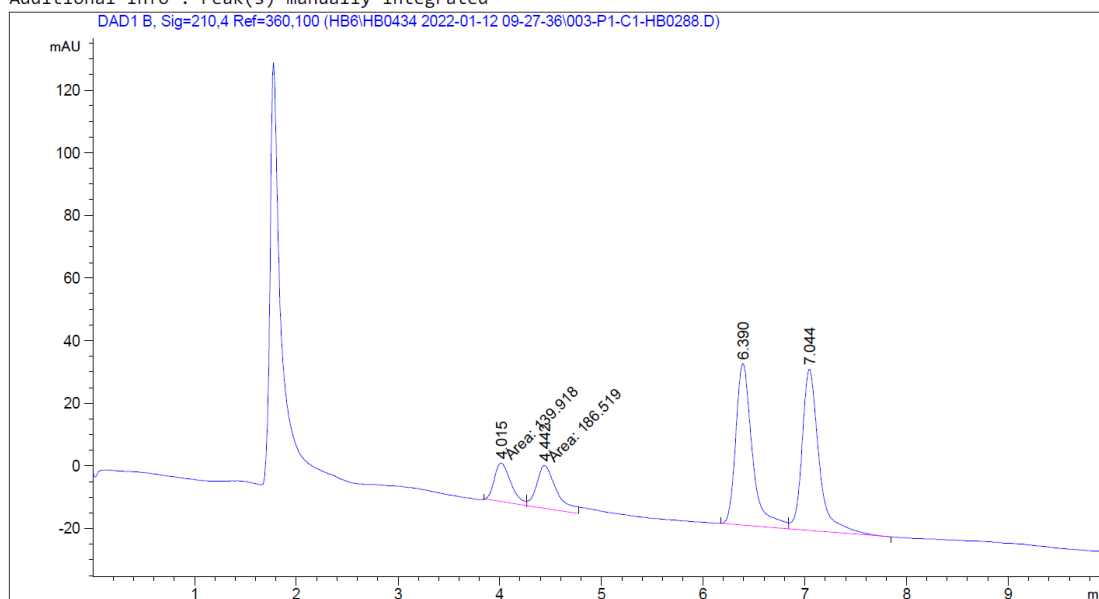
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.892	BB	0.1587	4864.91992	470.38858	100.0000

Totals :                                    4864.91992  470.38858



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Acq. Instrument : 1290-DAD                    Location  : P1-C-01
Injection Date  : 1/12/2022 9:47:35 AM       Inj       :    1
                                           Inj Volume: 0.500 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0434 2022-01-12 09-27-36\IE-3-95-5-0.4-0.5UL-8MIN.M
Last changed    : 1/12/2022 9:38:12 AM by SYSTEM
Analysis Method : d:\Chem32\1\Data\HB6\HB0434 2022-01-12 09-27-36\IE-3-95-5-0.4-0.5UL-8MIN.M
                 (Sequence Method)
Last changed    : 4/15/2022 2:22:07 PM by SYSTEM
                 (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



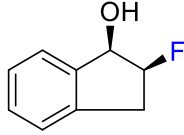
Area Percent Report

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

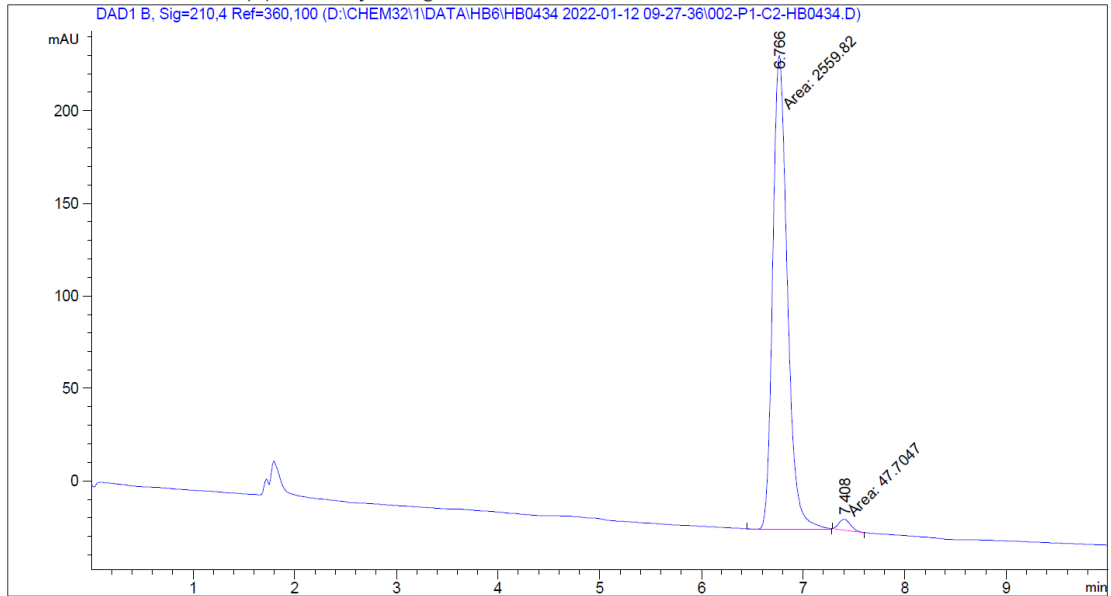
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.015	MF	0.1895	139.91812	12.30830	9.3194
2	4.442	FM	0.2277	186.51871	13.65295	12.4233
3	6.390	BV	0.1699	582.71686	51.55563	38.8127
4	7.044	VB	0.1720	592.20355	51.54663	39.4445



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : 1290-DAD                   Location  : P1-C-02
Injection Date  : 1/12/2022 9:36:48 AM      Inj       :    1
                                           Inj Volume: 0.500 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\HB6\HB0434 2022-01-12 09-27-36\IE-3-95-5-0.4-0.5UL-8MIN.M
Last changed    : 1/12/2022 9:38:12 AM by SYSTEM
                (modified after loading)
Analysis Method : d:\Chem32\1\Data\HB6\HB0434 2022-01-12 09-27-36\IE-3-95-5-0.4-0.5UL-8MIN.M
                (Sequence Method)
Last changed    : 4/15/2022 2:22:07 PM by SYSTEM
                (modified after loading)
Additional Info  : Peak(s) manually integrated
DAD1 B, Sig=210,4 Ref=360,100 (D:\CHEM32\1\DATA\HB6\HB0434 2022-01-12 09-27-36\002-P1-C2-HB0434.D)
  
```



Area Percent Report

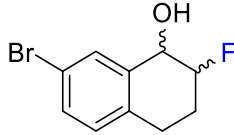
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

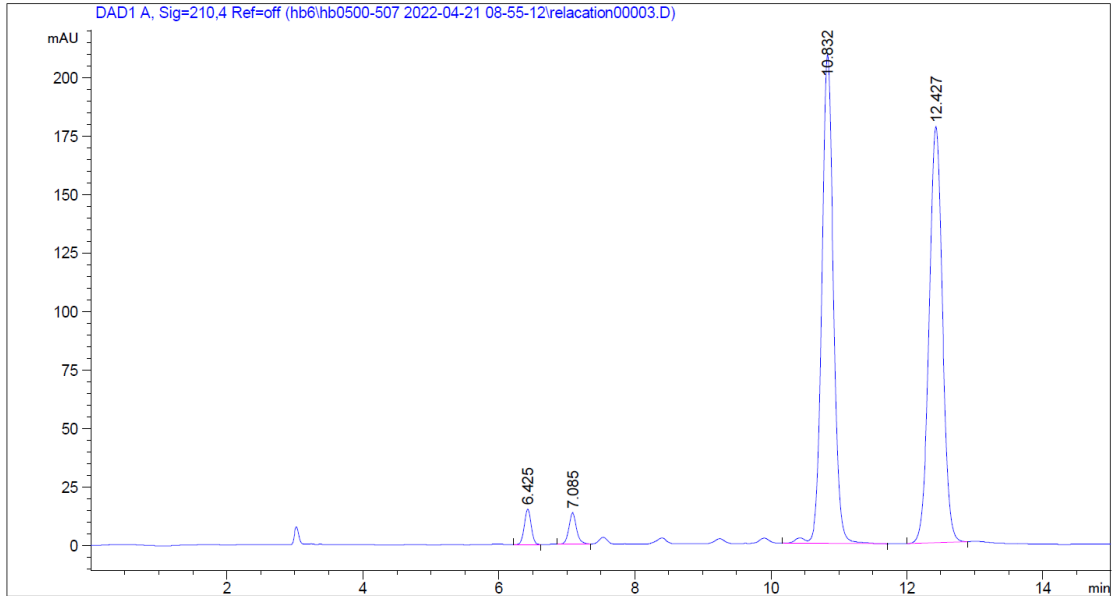
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.766	MM	0.1667	2559.81787	255.96498	98.1705
2	7.408	MM	0.1339	47.70472	5.93678	1.8295

Totals : 2607.52259 261.90176



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-03
Injection Date  : 4/21/2022 9:23:42 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M
Last changed    : 4/21/2022 9:24:16 AM by SYSTEM
                                           (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:09:25 AM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



=====  
Area Percent Report  
=====

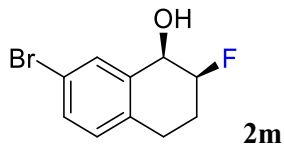
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

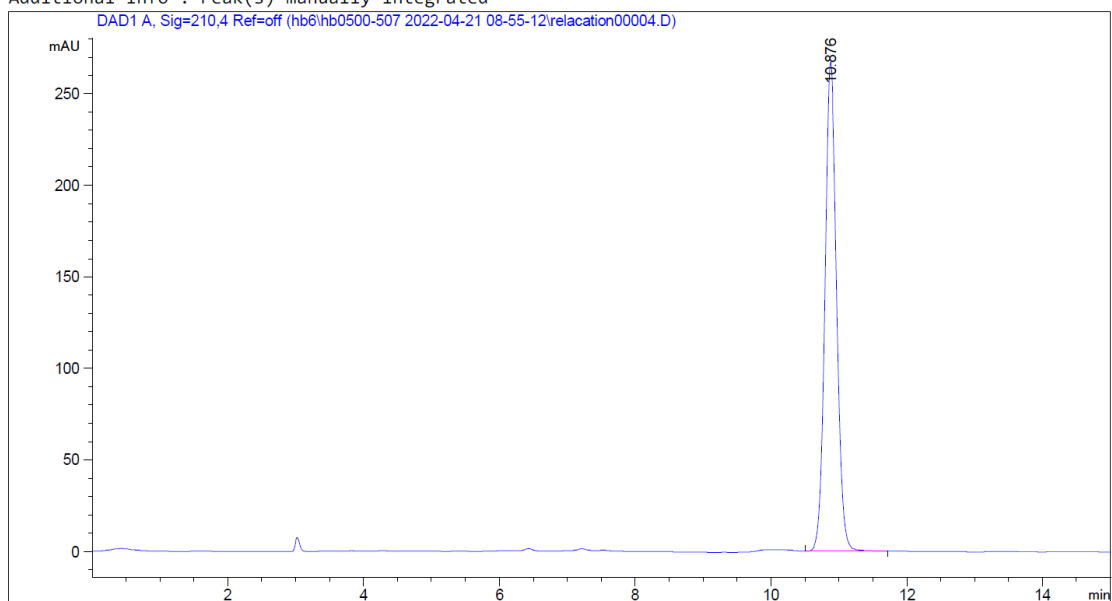
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.425	BB	0.1057	103.16124	15.10779	2.0211
2	7.085	BB	0.1200	106.25610	13.47160	2.0818
3	10.832	VB R	0.1810	2477.78882	209.00507	48.5447
4	12.427	BB	0.2106	2416.93628	177.82518	47.3524

Totals :                    5104.14244   415.40964



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    4
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-04
Injection Date  : 4/21/2022 9:39:31 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M
Last changed    : 4/21/2022 9:24:16 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:09:25 AM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



=====  
 Area Percent Report  
 =====

```

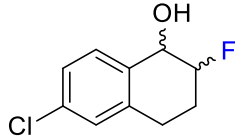
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.876	BB	0.1825	3174.99268	267.35388	100.0000

Totals :                                    3174.99268   267.35388

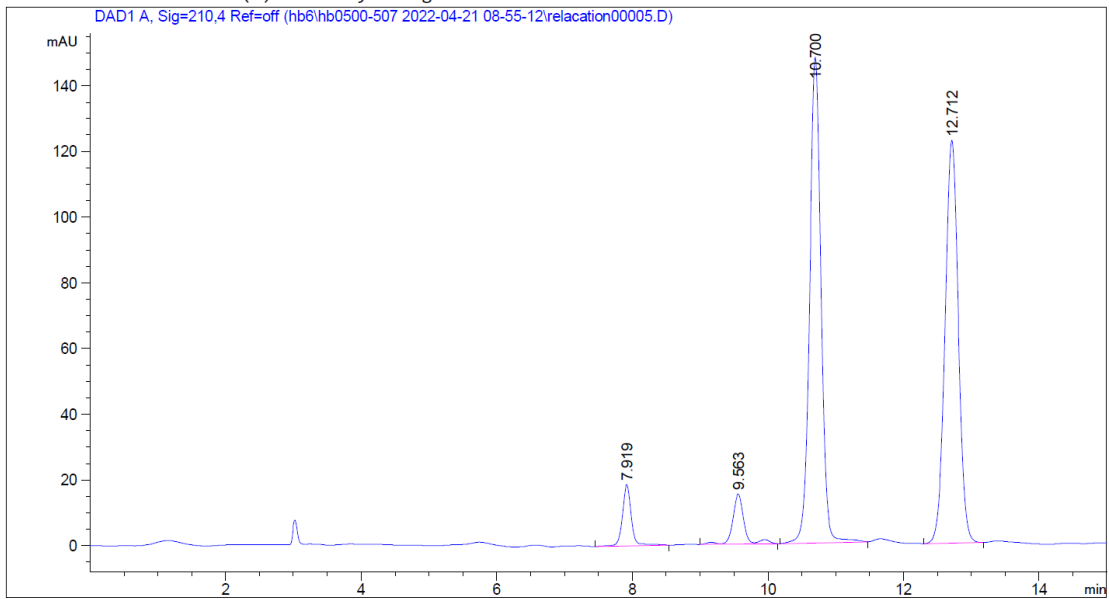




```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    5
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-05
Injection Date  : 4/21/2022 9:55:20 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M
Last changed    : 4/21/2022 9:24:16 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:09:25 AM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
DAD1 A, Sig=210,4 Ref=off (hb6\hb0500-507 2022-04-21 08-55-12\relacation00005.D)

```



Area Percent Report

```

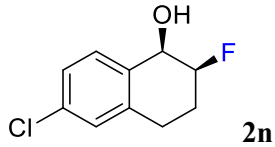
Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.919	BB	0.1396	172.13202	18.66072	4.6121
2	9.563	VV R	0.1662	178.40820	15.26559	4.7803
3	10.700	BB	0.1776	1716.37402	147.72502	45.9888
4	12.712	BB	0.2105	1665.24536	122.61124	44.6188

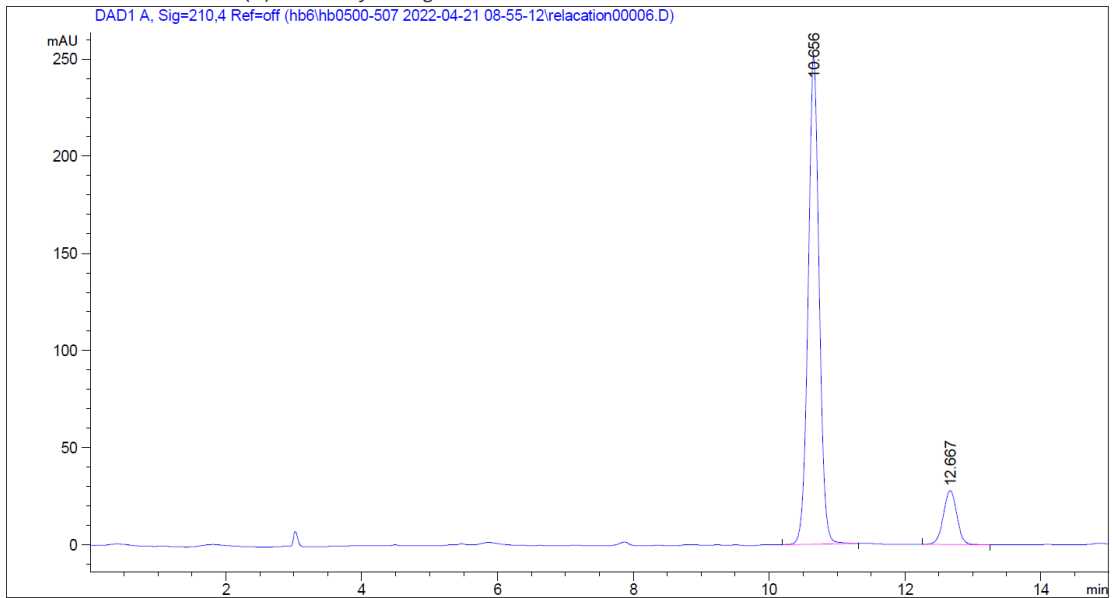
Totals : 3732.15961 304.26257



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    6
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-06
Injection Date  : 4/21/2022 10:11:09 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/21/2022 9:24:16 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:09:25 AM by SYSTEM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
                  DAD1 A, Sig=210.4 Ref=off (hb6\hb0500-507 2022-04-21 08-55-12\relacation00006.D)
=====

```



=====  
Area Percent Report  
=====

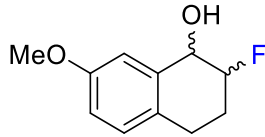
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

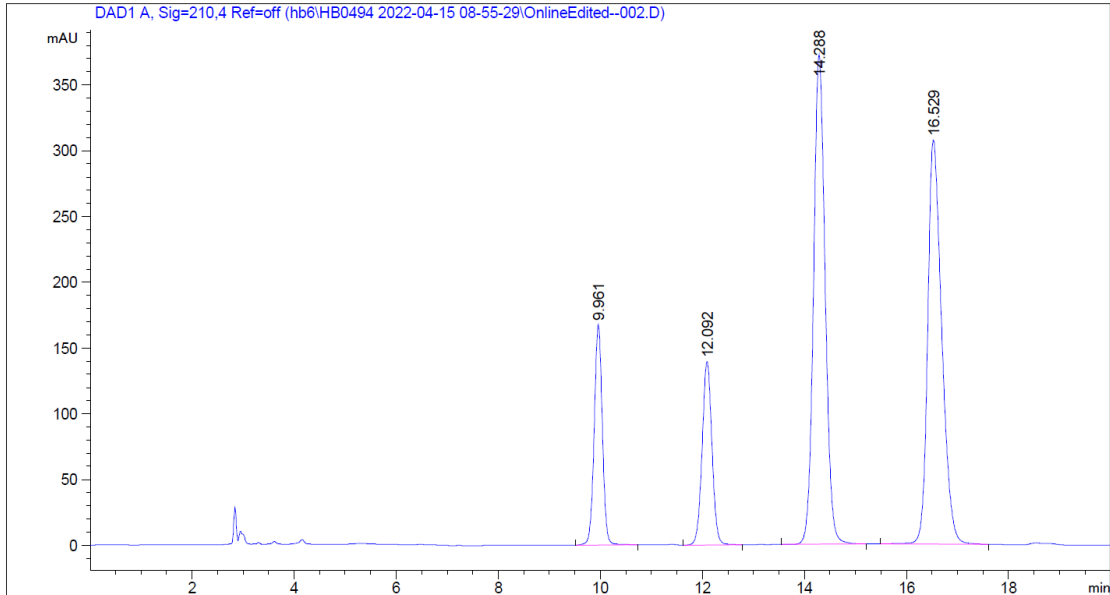
Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.656	BB	0.1743	2843.49219	250.78300	88.2430
2	12.667	BB	0.2110	378.85104	27.80083	11.7570



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-05
Injection Date  : 4/15/2022 9:12:08 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0494 2022-04-15 08-55-29\hb6_IF-3-90-10-1ML-
                 30min.M
Last changed    : 4/15/2022 9:24:17 AM by SYSTEM
                 (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0494 2022-04-15 08-55-29\hb6_IF-3-90-10-1ML-
                 30min.M (Sequence Method)
Last changed    : 4/15/2022 9:51:51 AM by SYSTEM
                 (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



Area Percent Report

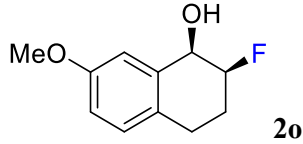
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

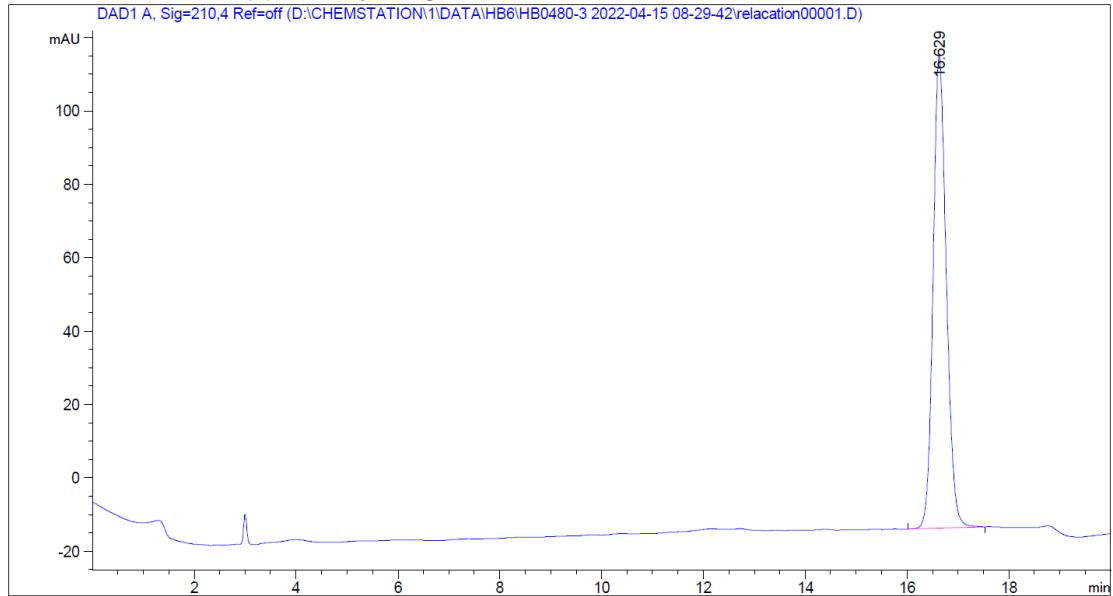
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.961	BB	0.1709	1853.91919	167.73854	11.9943
2	12.092	BB	0.2062	1868.16284	139.51624	12.0865
3	14.288	BB	0.2419	5870.72070	372.39542	37.9819
4	16.529	BB	0.2906	5863.83984	307.29147	37.9373

Totals : 1.54566e4 986.94167



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-05
Injection Date  : 4/15/2022 8:30:32 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0480-3 2022-04-15 08-29-42\hb6_IF-3-90-10-1ML-
                 30min.M
Last changed    : 4/15/2022 8:29:53 AM by SYSTEM
                 (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0480-3 2022-04-15 08-29-42\hb6_IF-3-90-10-1ML-
                 30min.M (Sequence Method)
Last changed    : 4/15/2022 9:57:44 AM by SYSTEM
                 (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



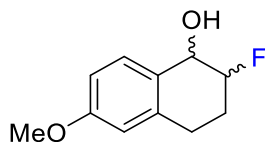
=====  
 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

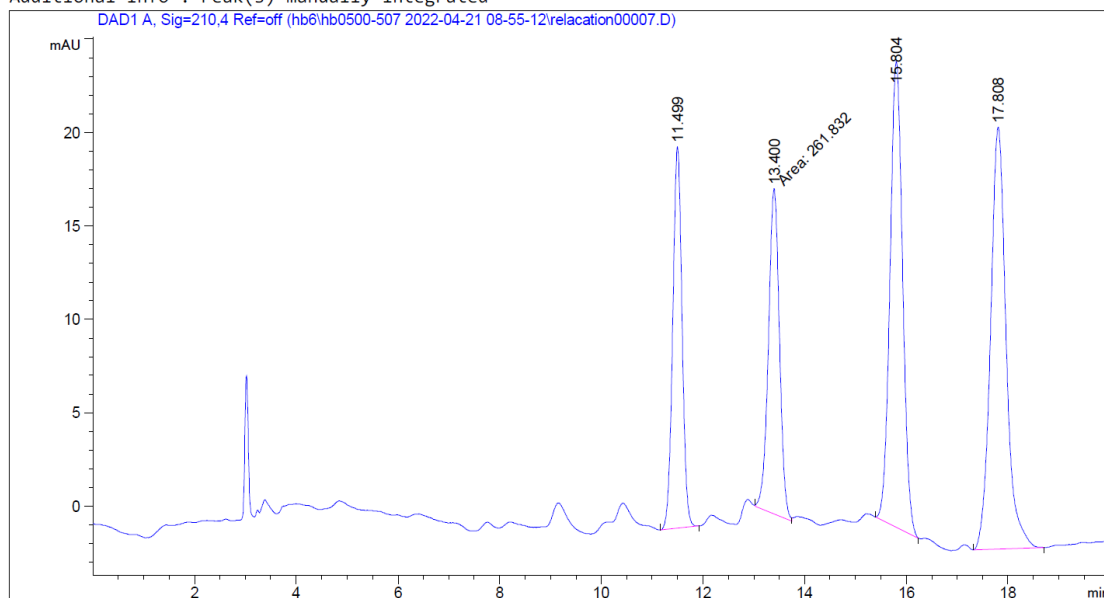
Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.629	BB	0.2765	2322.59009	128.73792	100.0000



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    7
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-07
Injection Date  : 4/21/2022 10:26:58 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/21/2022 10:26:59 AM by SYSTEM
                  (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:09:25 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



Area Percent Report

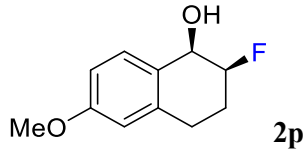
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.499	BB	0.1956	258.59717	20.43511	18.1188
2	13.400	MM	0.2506	261.83215	17.41634	18.3455
3	15.804	BB	0.2662	427.71014	24.92516	29.9679
4	17.808	BB	0.3195	479.09048	22.57970	33.5679

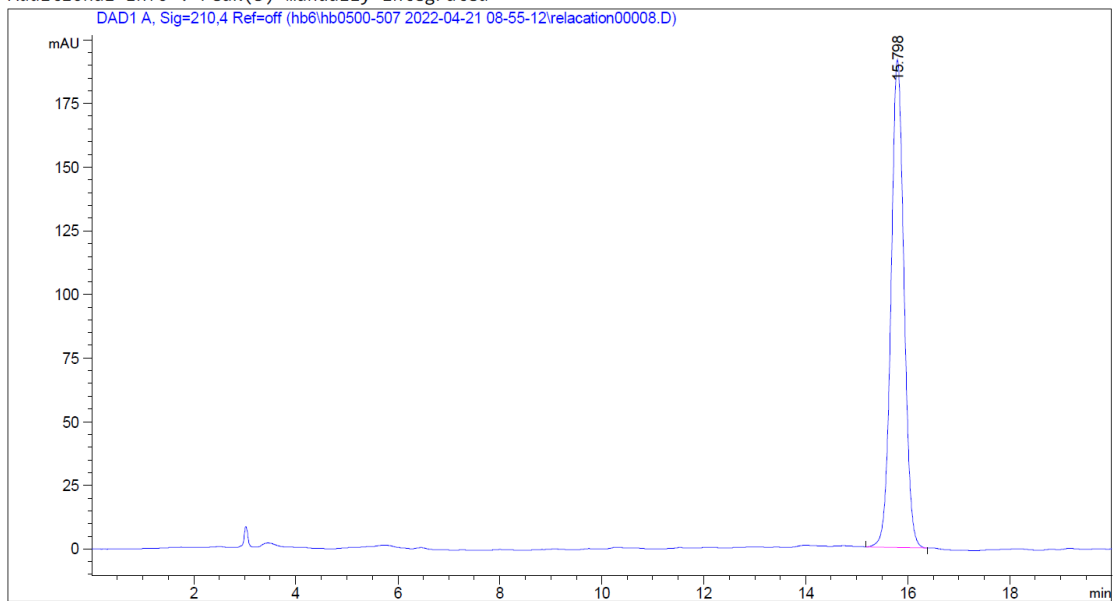
Totals : 1427.22995 85.35631



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    8
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-08
Injection Date  : 4/21/2022 10:47:48 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M
Last changed    : 4/21/2022 10:26:59 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:09:25 AM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated
=====

```



=====  
Area Percent Report  
=====

```

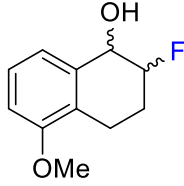
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.798	BB	0.2714	3376.19116	191.74646	100.0000

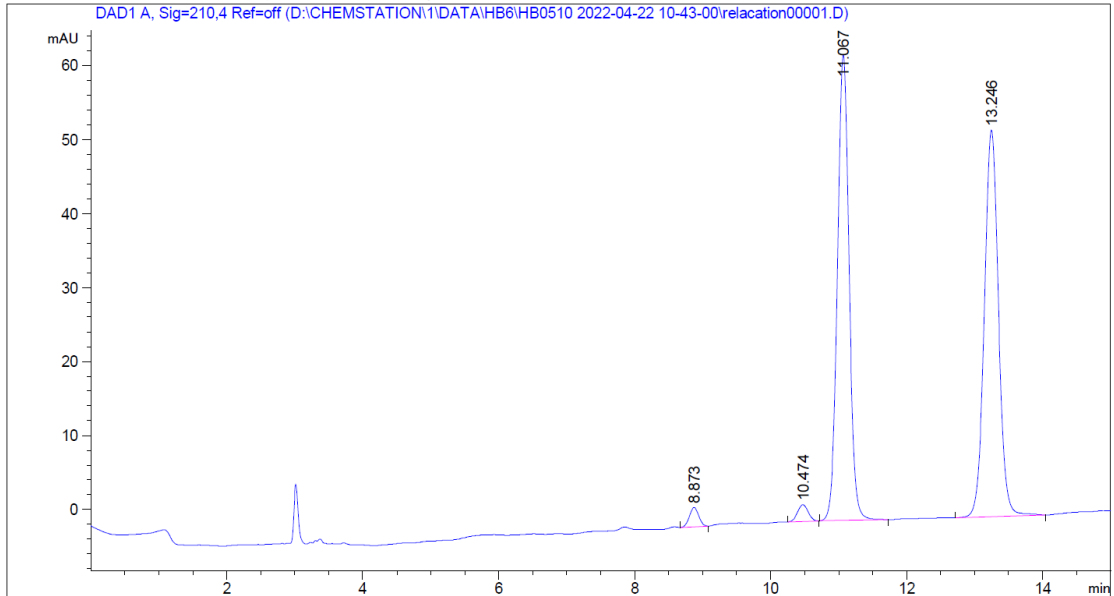
Totals :                    3376.19116  191.74646



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                          Location  : P2-D-06
Injection Date  : 4/22/2022 10:43:49 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0510 2022-04-22 10-43-00\hb6_IF-3-90-10-1ML-
                  13min.M
Last changed    : 4/22/2022 10:43:37 AM by SYSTEM
                  (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0510 2022-04-22 10-43-00\hb6_IF-3-90-10-1ML-
                  13min.M (Sequence Method)
Last changed    : 4/22/2022 11:45:29 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
=====

```



```

=====
                          Area Percent Report
=====

```

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

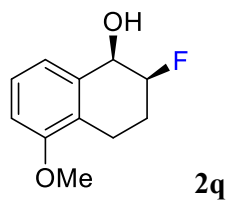
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.873	BB	0.1448	24.19081	2.59424	1.5681
2	10.474	BB	0.1685	24.03299	2.25277	1.5579

3	11.067	BB	0.1816	743.15253	62.99266	48.1724
4	13.246	BB	0.2197	751.31750	52.26147	48.7017

Totals : 1542.69382 120.10114

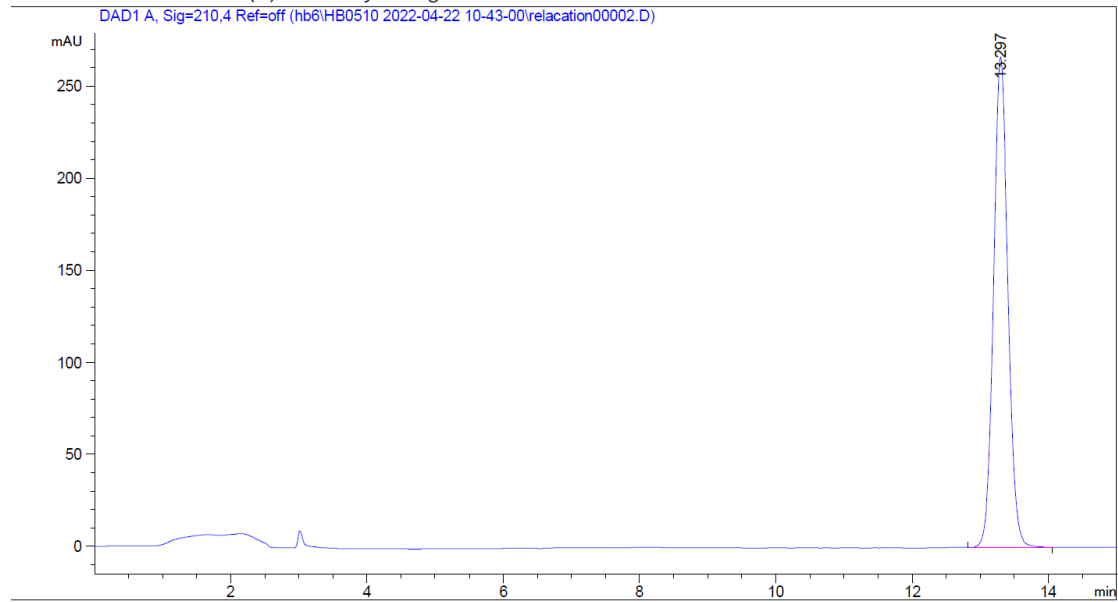




```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-07
Injection Date  : 4/22/2022 10:59:38 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0510 2022-04-22 10-43-00\hb6_IF-3-90-10-1ML-
                  13min.M
Last changed    : 4/22/2022 10:43:37 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\HB0510 2022-04-22 10-43-00\hb6_IF-3-90-10-1ML-
                  13min.M (Sequence Method)
Last changed    : 4/22/2022 11:45:29 AM by SYSTEM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated

```



=====  
Area Percent Report  
=====

```

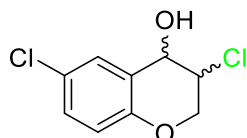
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.297	BB	0.2244	3886.76196	266.11545	100.0000

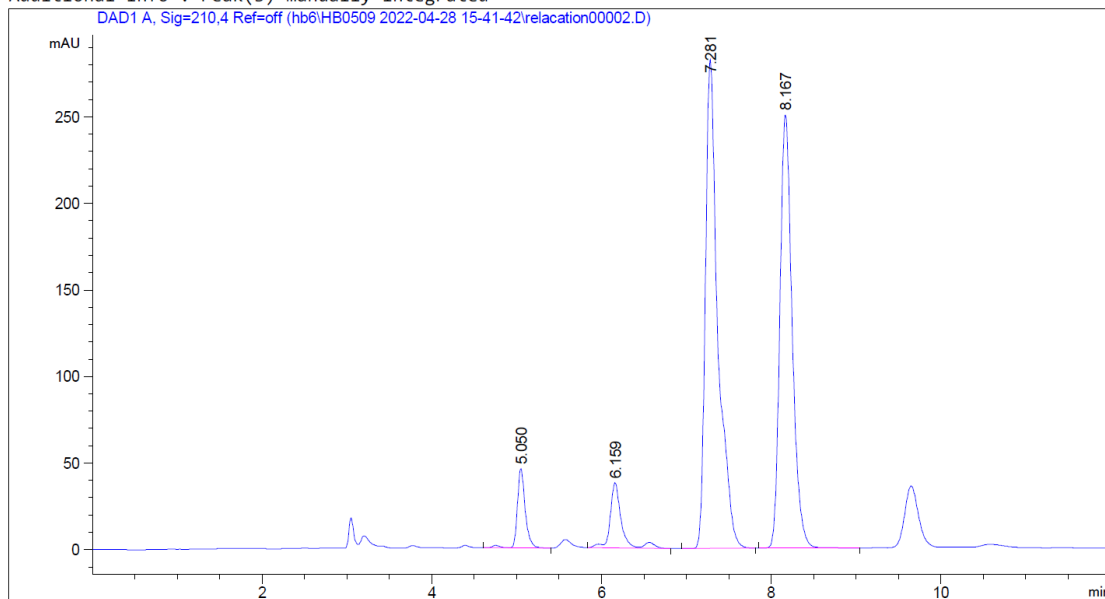
Totals :                    3886.76196   266.11545



```

=====
Acq. Operator   : SYSTEM                               Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                                 Location  : P1-F-03
Injection Date  : 4/28/2022 3:55:29 PM              Inj       :    1
                                                    Inj Volume: 1.000 µl
Acq. Method    : D:\ChemStation\1\Data\hb6\HB0509 2022-04-28 15-41-42\hb6_IE-3-90-10-1ML-
10min.M
Last changed   : 4/28/2022 3:41:56 PM by SYSTEM
Analysis Method: D:\ChemStation\1\Data\hb6\HB0509 2022-04-28 15-41-42\hb6_IE-3-90-10-1ML-
10min.M (Sequence Method)
Last changed   : 4/28/2022 4:09:10 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated

```



```

=====
                          Area Percent Report
=====

```

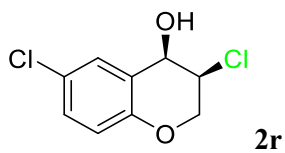
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.050	VB R	0.0957	297.97076	45.73538	4.9404
2	6.159	VV R	0.1221	352.60867	37.67241	5.8463
3	7.281	BB	0.1490	2881.44800	282.57953	47.7751
4	8.167	BB	0.1524	2499.24805	250.47849	41.4381

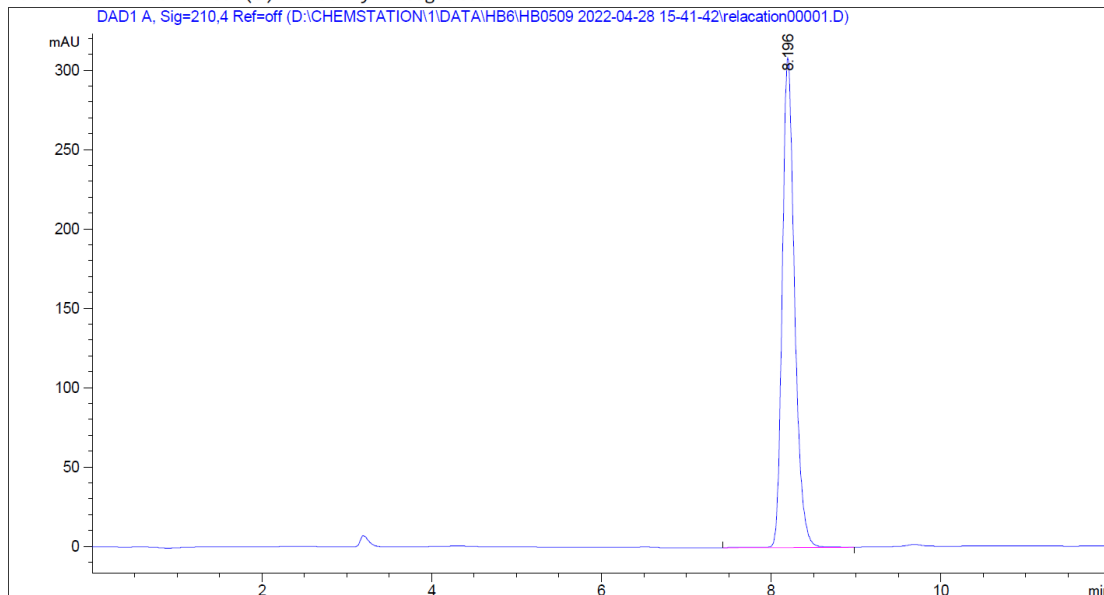


```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                          Location  : P1-F-02
Injection Date  : 4/28/2022 3:42:35 PM       Inj       :    1
                                           Inj Volume: 1.000 µl

Acq. Method     : D:\ChemStation\1\Data\hb6\HB0509 2022-04-28 15-41-42\hb6_IE-3-90-10-1ML-
10min.M
Last changed    : 4/28/2022 3:41:56 PM by SYSTEM
(modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0509 2022-04-28 15-41-42\hb6_IE-3-90-10-1ML-
10min.M (Sequence Method)
Last changed    : 4/28/2022 4:09:10 PM by SYSTEM
(modified after loading)
Additional Info  : Peak(s) manually integrated

```



```

=====
                          Area Percent Report
=====

```

```

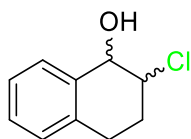
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.196	BB	0.1533	3099.71191	308.38446	100.0000

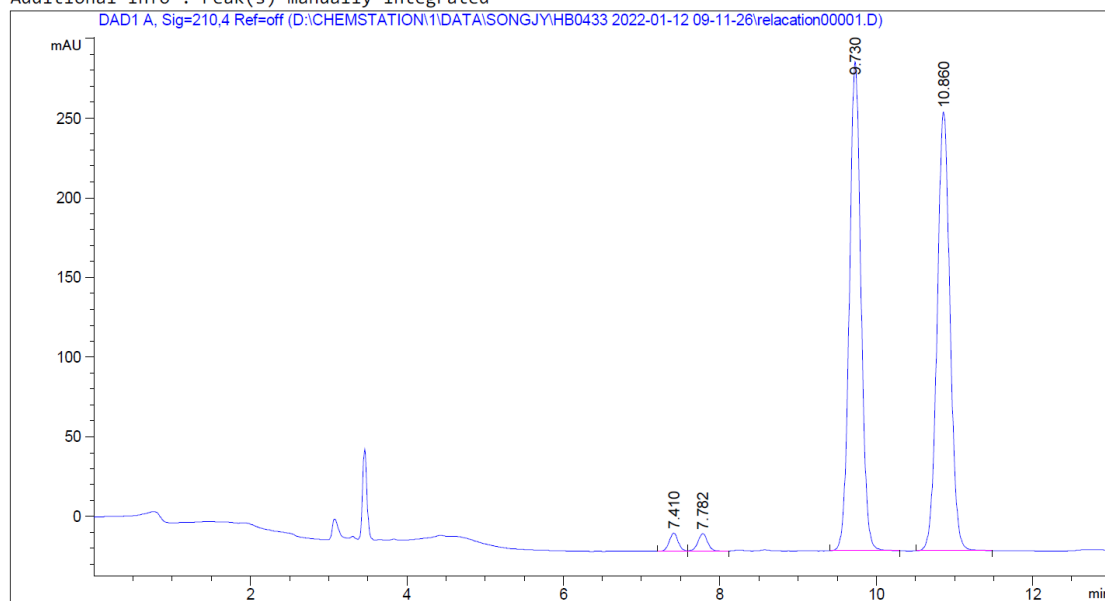
```
Totals :                3099.71191  308.38446
```



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P1-A-01
Injection Date  : 1/12/2022 9:12:18 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Acq. Method     : D:\ChemStation\1\Data\SongJY\HB0433 2022-01-12 09-11-26\hb6_IF-3-90-10-1ML-
                  13min.M
Last changed    : 1/12/2022 9:06:58 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\SongJY\HB0433 2022-01-12 09-11-26\hb6_IF-3-90-10-1ML-
                  13min.M (Sequence Method)
Last changed    : 4/15/2022 12:03:38 PM by SYSTEM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated

```



```

=====
                          Area Percent Report
=====

```

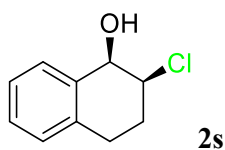
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

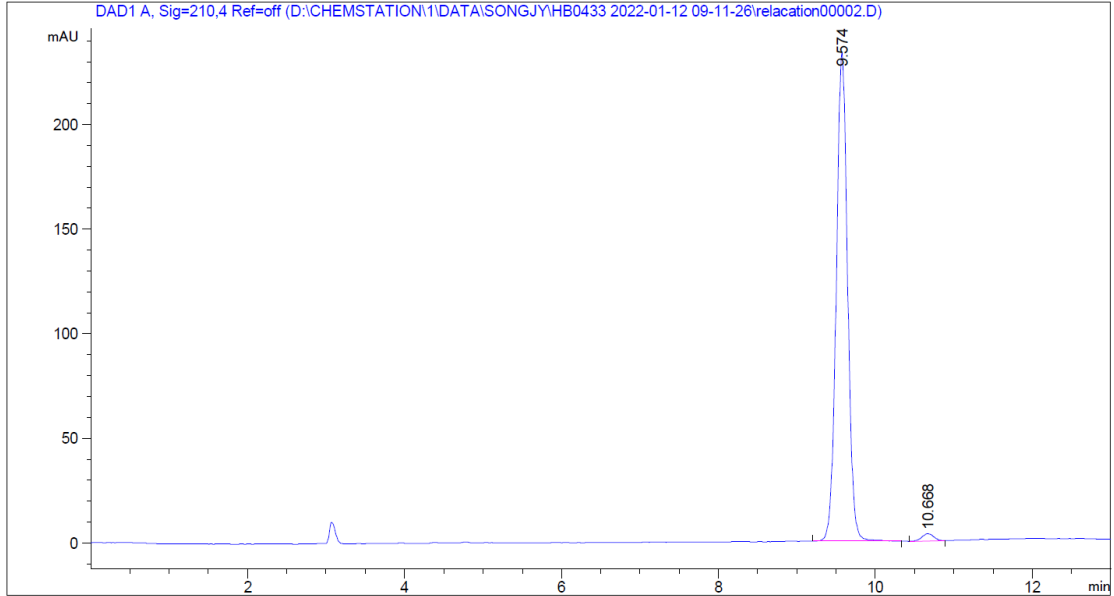
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.410	BV	0.1256	91.02695	11.34294	1.4042
2	7.782	VV	0.1324	94.88305	11.02155	1.4637
3	9.730	BB	0.1596	3148.05786	307.07074	48.5631
4	10.860	BB	0.1753	3148.43286	275.60364	48.5689



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P1-A-02
Injection Date  : 1/12/2022 9:26:09 AM      Inj       :    1
                                           Inj Volume: 1.000 µl

Acq. Method    : D:\ChemStation\1\Data\SongJY\HB0433 2022-01-12 09-11-26\hb6_IF-3-90-10-1ML-
                13min.M
Last changed   : 1/12/2022 9:06:58 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\SongJY\HB0433 2022-01-12 09-11-26\hb6_IF-3-90-10-1ML-
                13min.M (Sequence Method)
Last changed   : 4/15/2022 12:01:16 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



=====  
Area Percent Report  
=====

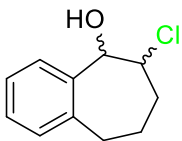
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.574	BB	0.1546	2335.41016	233.63559	98.4418
2	10.668	BB	0.1607	36.96539	3.51414	1.5582

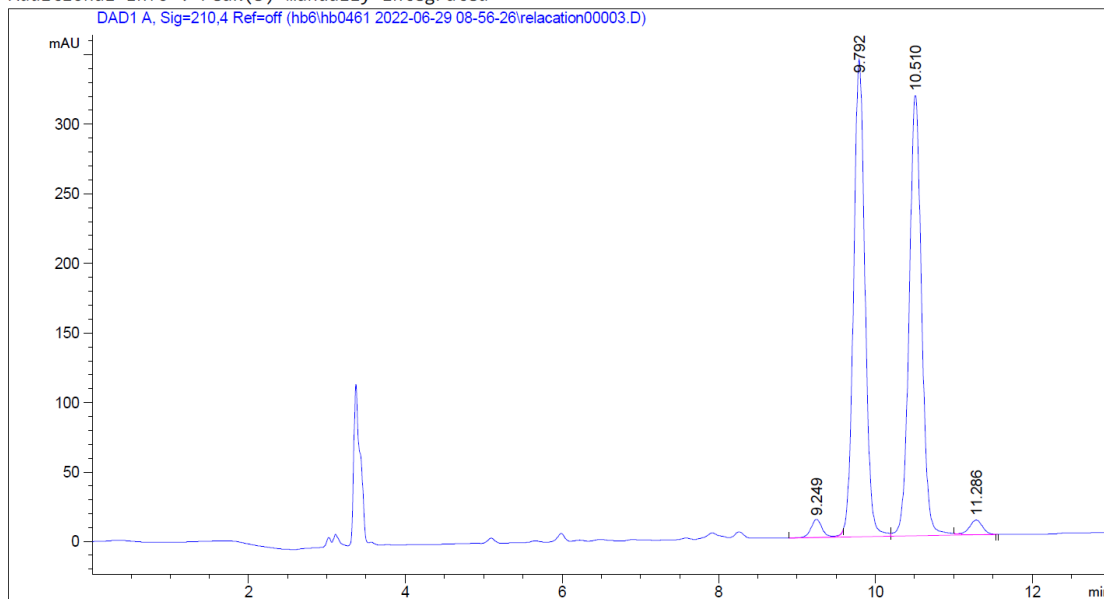
Totals :                                    2372.37554   237.14973



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P1-F-02
Injection Date  : 6/29/2022 9:27:14 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0461 2022-06-29 08-56-26\hb6_IF-3-95-5-1ML-
                                           20min.M
Last changed    : 6/29/2022 9:24:07 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0461 2022-06-29 08-56-26\hb6_IF-3-95-5-1ML-
                                           20min.M (Sequence Method)
Last changed    : 6/29/2022 11:24:12 AM by SYSTEM
Additional Info  : Peak(s) manually integrated

```



```

=====
                          Area Percent Report
=====

```

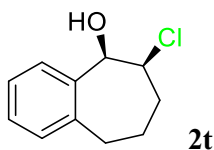
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

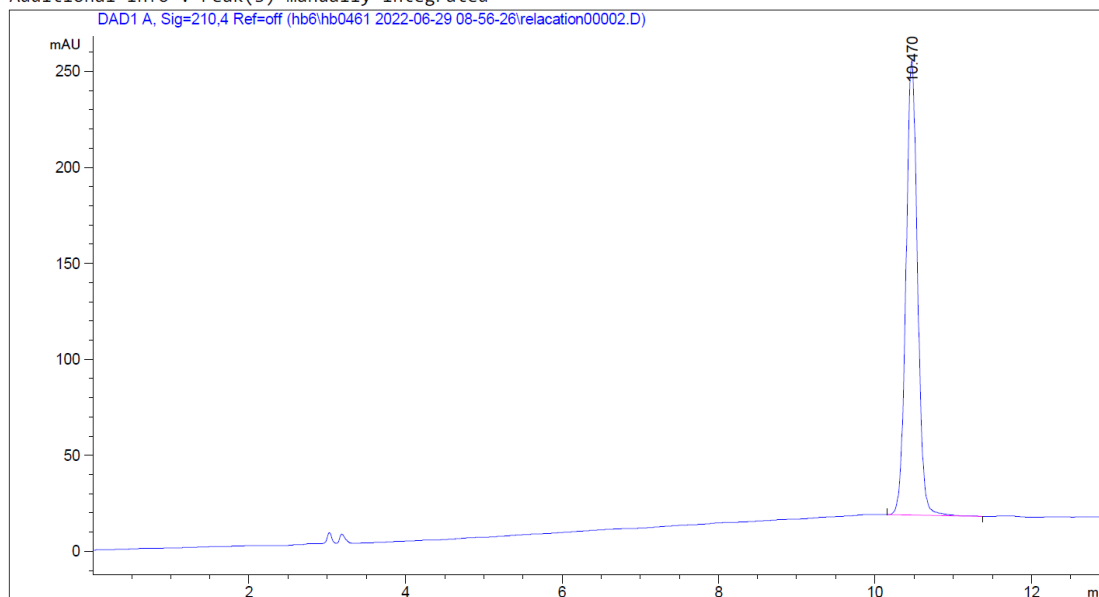
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.249	BV E	0.1549	133.74602	13.11970	1.8528
2	9.792	VV R	0.1559	3470.34570	343.31000	48.0744
3	10.510	VV R	0.1688	3497.50146	316.83517	48.4506
4	11.286	VB E	0.1742	117.10435	10.33564	1.6222



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P1-F-01
Injection Date  : 6/29/2022 9:13:21 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0461 2022-06-29 08-56-26\hb6_IF-3-95-5-1ML-
                20min.M
Last changed    : 6/29/2022 9:24:07 AM by SYSTEM
                (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\hb0461 2022-06-29 08-56-26\hb6_IF-3-95-5-1ML-
                20min.M (Sequence Method)
Last changed    : 6/29/2022 10:04:20 AM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated

```



```

=====
                          Area Percent Report
=====

```

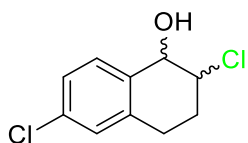
```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.470	BB	0.1581	2437.30005	236.78580	100.0000

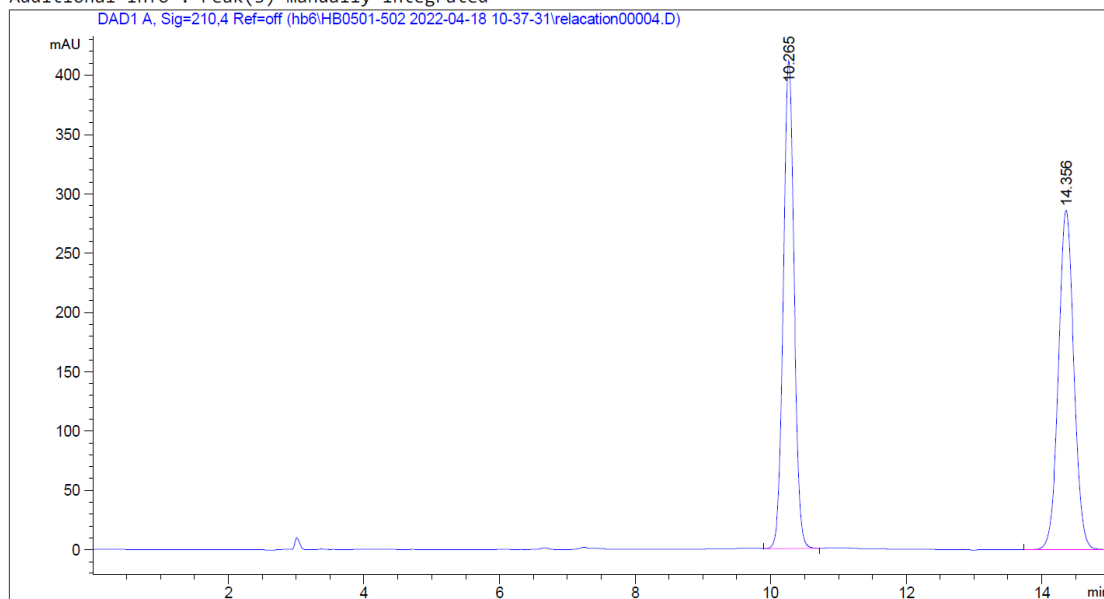


```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    4
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-10
Injection Date  : 4/18/2022 11:35:50 AM     Inj       :    1
                                           Inj Volume: 1.000 µl

Acq. Method     : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/18/2022 11:21:39 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/18/2022 11:51:59 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated

```



=====  
Area Percent Report  
=====

```

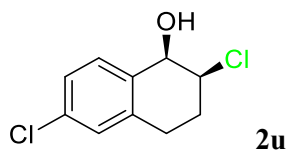
Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.265	BB	0.1681	4514.69922	411.14957	49.9390
2	14.356	BBA	0.2444	4525.73145	286.30136	50.0610

Totals :                    9040.43066   697.45093



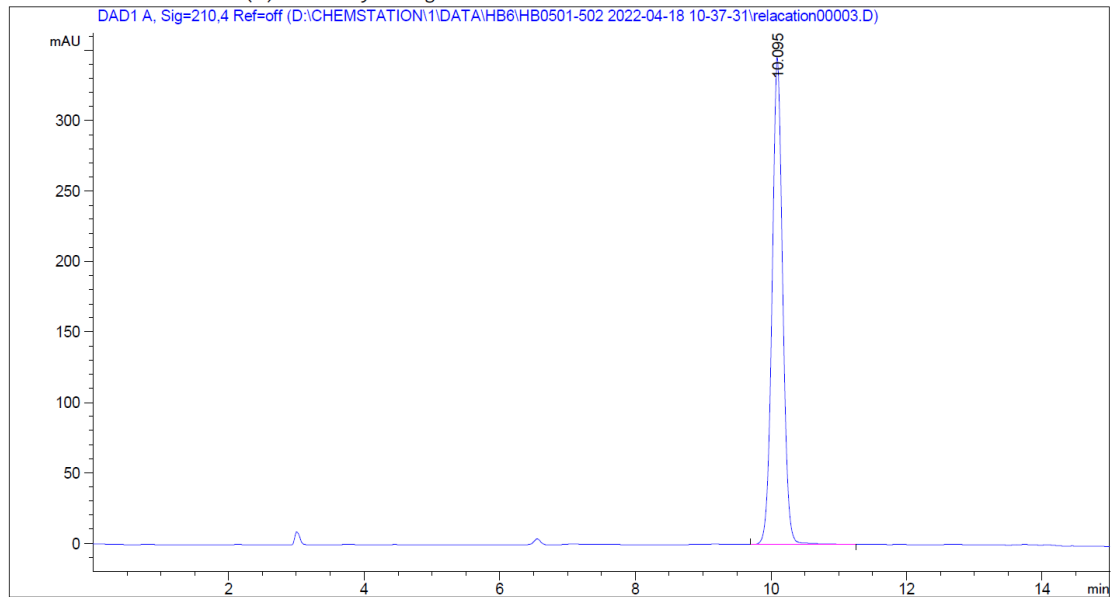


```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-09
Injection Date  : 4/18/2022 11:19:59 AM      Inj       :    1
                                           Inj Volume: 1.000 µl

Acq. Method     : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/18/2022 11:21:39 AM by SYSTEM
                  (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/18/2022 11:51:59 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated

```



```

=====
                          Area Percent Report
=====

```

```

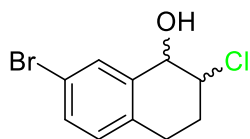
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.095	BB	0.1699	3791.14063	345.81458	100.0000

Totals :                    3791.14063   345.81458

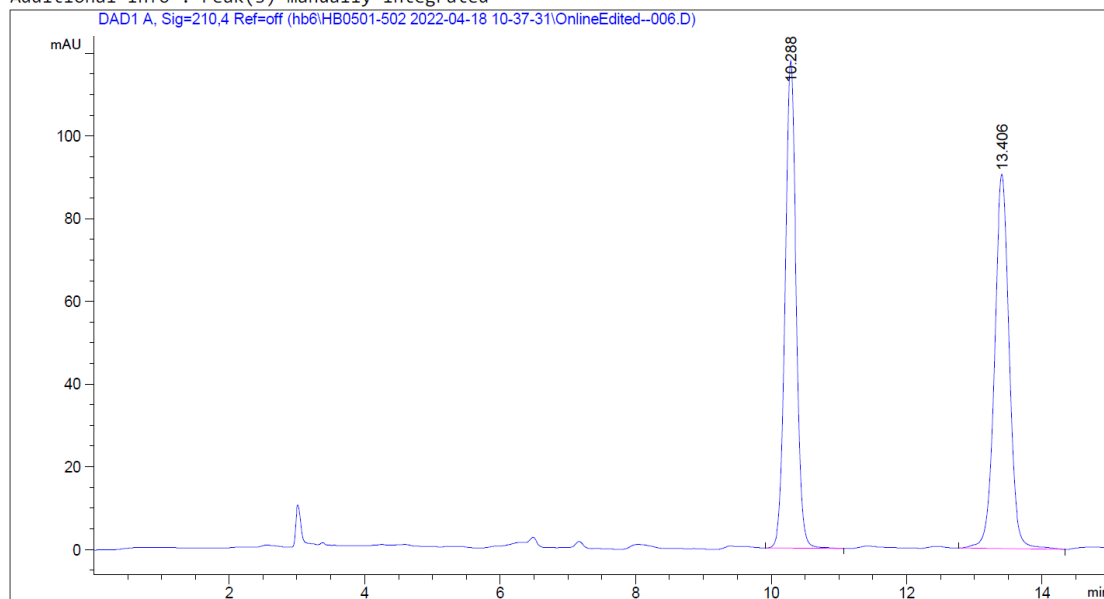


```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    6
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-E-01
Injection Date  : 4/18/2022 12:07:33 PM      Inj       :    1
                                                Inj Volume: 1.000 µl

Acq. Method     : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/18/2022 11:21:39 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/18/2022 12:29:43 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated

```



Area Percent Report

```

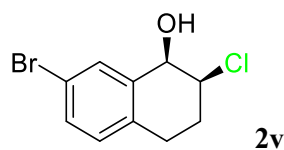
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.288	BB	0.1737	1329.18738	117.76014	49.3727
2	13.406	BB	0.2298	1362.96106	90.44734	50.6273

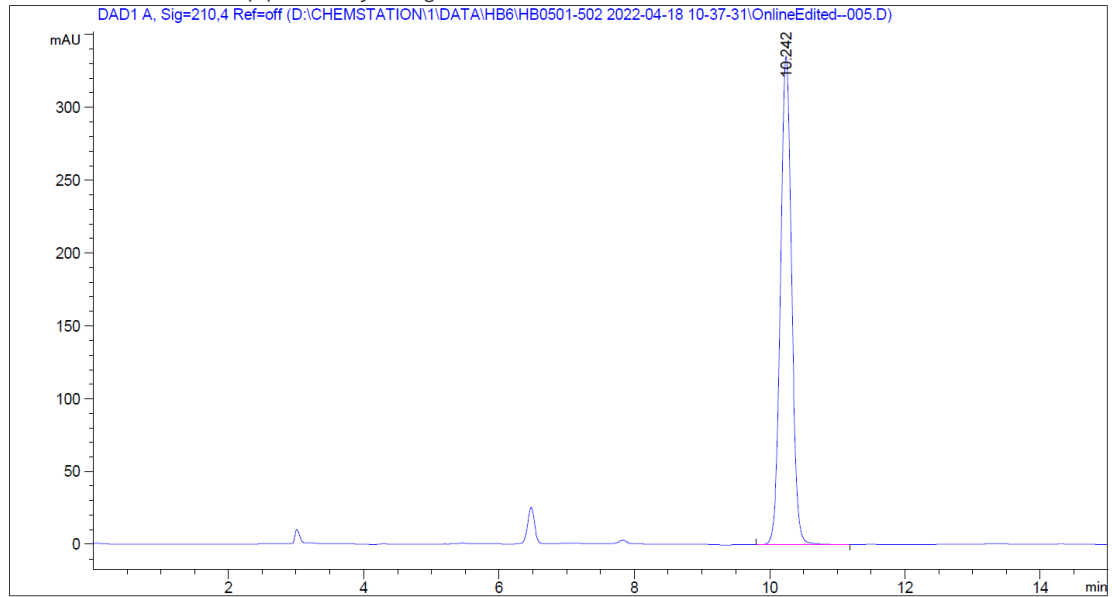
Totals : 2692.14844 208.20748



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    5
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-11
Injection Date  : 4/18/2022 11:51:41 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/18/2022 11:21:39 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/18/2022 12:29:43 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated

```



```

=====
                          Area Percent Report
=====

```

```

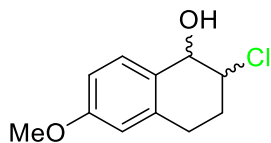
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.242	BB	0.1744	3807.09180	335.41757	100.0000

```
Totals :                3807.09180  335.41757
```

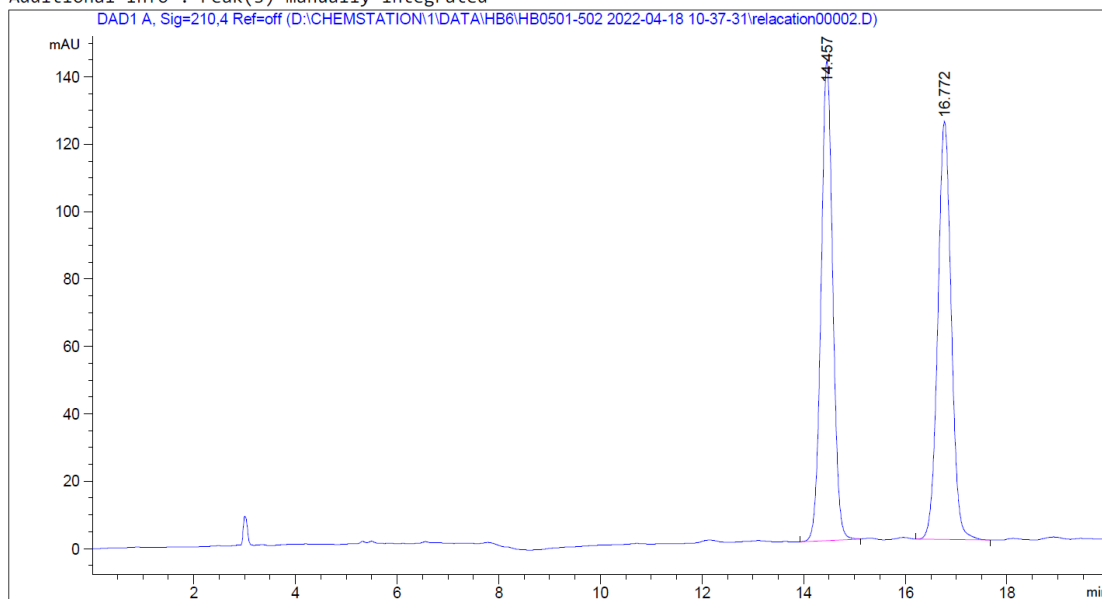


```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-08
Injection Date  : 4/18/2022 10:59:10 AM      Inj       :    1
                                           Inj Volume: 1.000 µl

Acq. Method     : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/18/2022 10:38:11 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/18/2022 11:20:02 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated

```



=====  
Area Percent Report  
=====

```

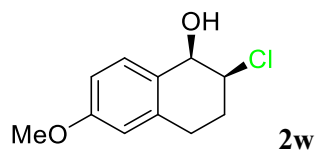
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.457	BB	0.2451	2257.44897	142.31580	49.7195
2	16.772	BB	0.2848	2282.92114	124.00315	50.2805

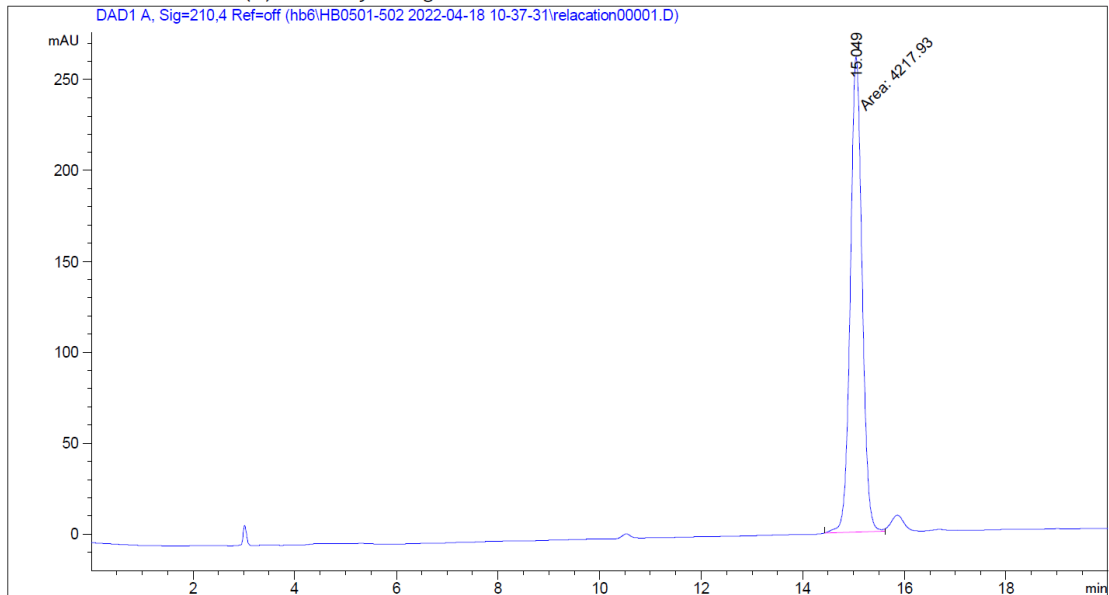
Totals :                    4540.37012  266.31895



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    1
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-07
Injection Date  : 4/18/2022 10:38:21 AM      Inj       :    1
                                           Inj Volume: 1.000 µl

Acq. Method     : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/18/2022 10:38:11 AM by SYSTEM
                  (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\HB0501-502 2022-04-18 10-37-31\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/18/2022 11:20:02 AM by SYSTEM
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
  
```



=====  
Area Percent Report  
=====

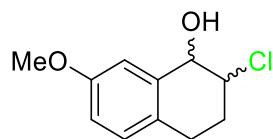
```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.049	MM	0.2687	4217.93457	261.65979	100.0000

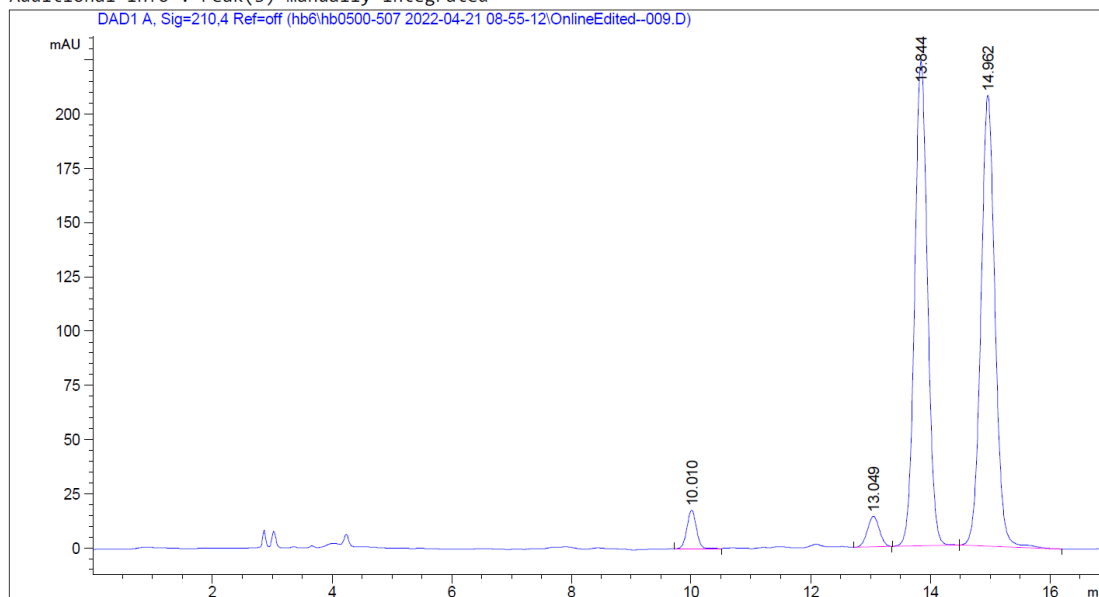
Totals :                    4217.93457  261.65979



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    9
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-09
Injection Date  : 4/21/2022 11:08:36 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M
Last changed    : 4/21/2022 11:25:25 AM by SYSTEM
                                           (modified after loading)
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                                           -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:49:00 AM by SYSTEM
                                           (modified after loading)
Additional Info  : Peak(s) manually integrated

```



Area Percent Report

```

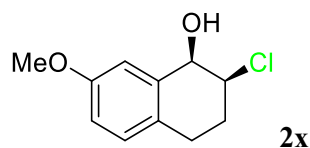
Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.010	BB	0.1689	193.66286	17.80045	2.7251
2	13.049	BB	0.2161	195.89513	14.09885	2.7565
3	13.844	BB	0.2294	3323.16797	223.61839	46.7612
4	14.962	BB	0.2505	3393.94580	207.81985	47.7572

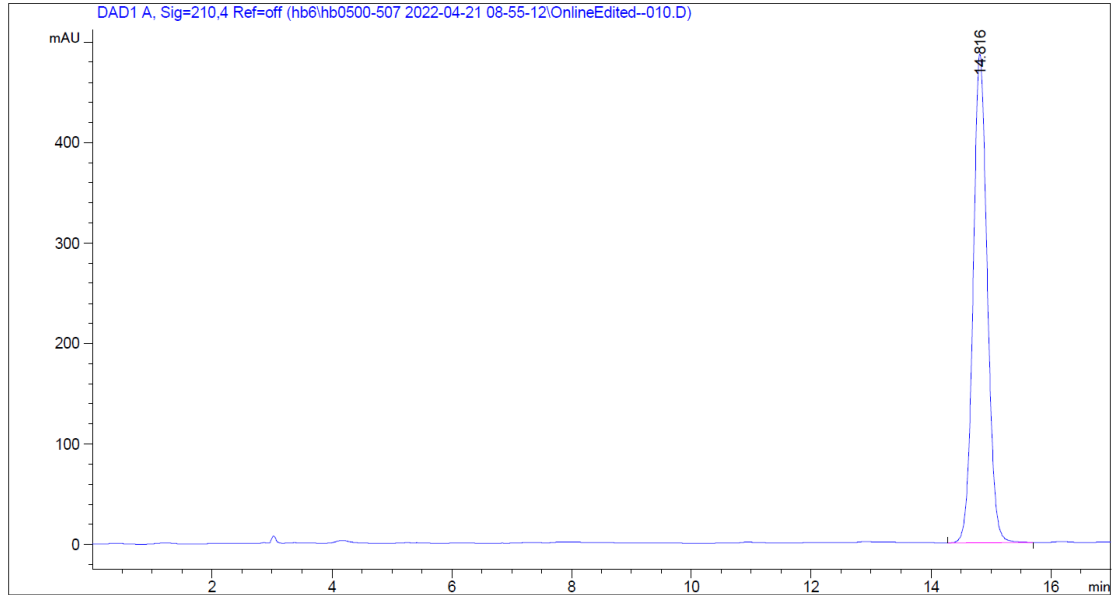
Totals : 7106.67175 463.33755



```

=====
Acq. Operator   : SYSTEM                      Seq. Line :   10
Sample Operator : SYSTEM
Acq. Instrument : LC                        Location  : P2-D-02
Injection Date  : 4/21/2022 11:26:26 AM      Inj       :    1
                                           Inj Volume: 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.500 µl
Acq. Method     : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                  -13min.M
Last changed    : 4/21/2022 11:25:25 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\hb6\hb0500-507 2022-04-21 08-55-12\hb6_IF-3-90-10-1ML
                  -13min.M (Sequence Method)
Last changed    : 4/21/2022 11:49:00 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated

```



=====  
Area Percent Report  
=====

```

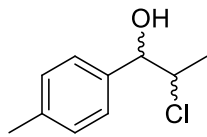
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.816	BB	0.2508	7959.64355	486.61734	100.0000

Totals :                    7959.64355  486.61734



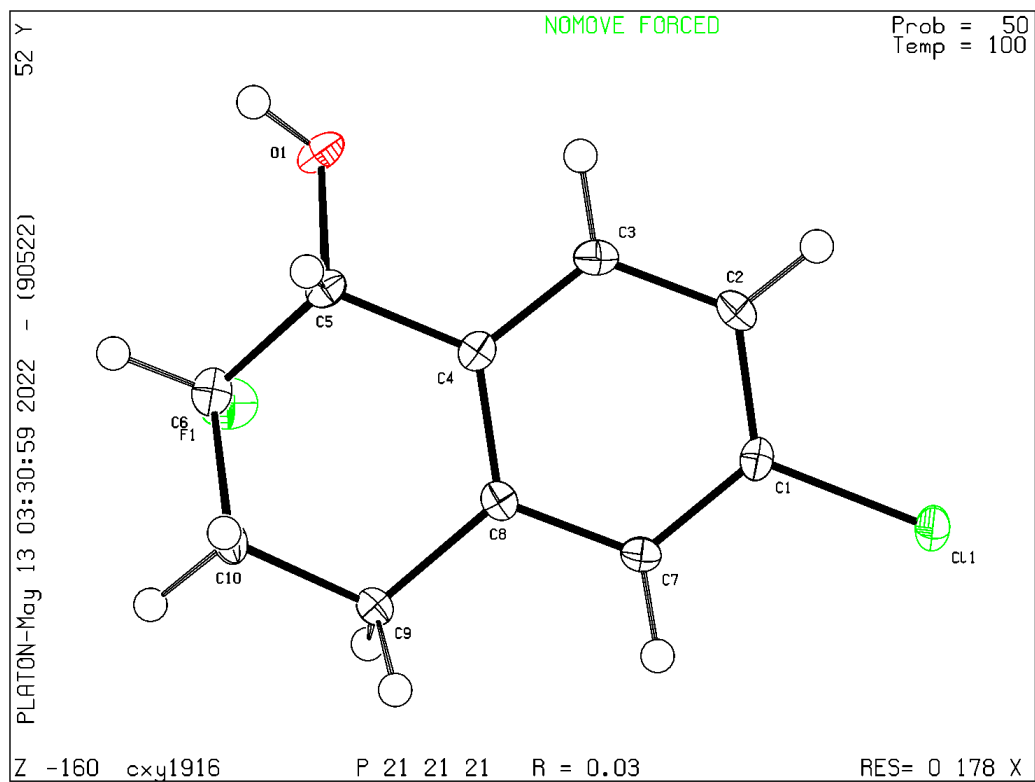




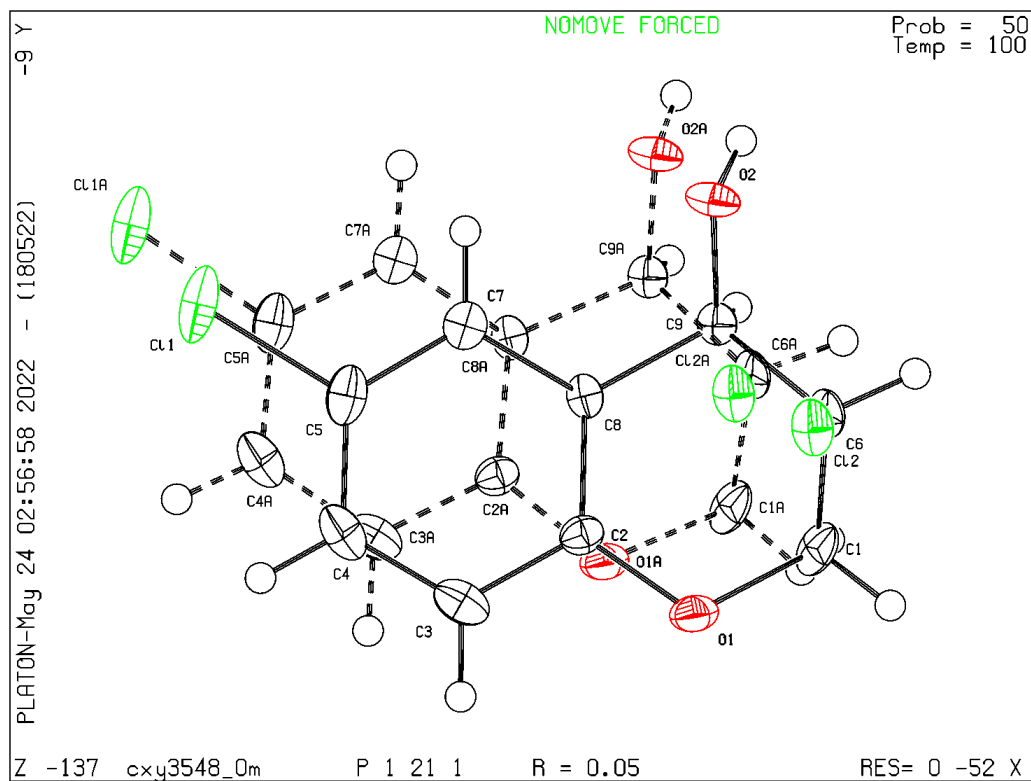


## 7. Crystallographic Information

The Crystallographic data of compound **2n** has been deposited in CCDC with number 2175167 and has been displayed at 50% ellipsoid contour probability level.



The Crystallographic data of compound **2r** has been deposited in CCDC with number 2175166 and has been displayed at 50% ellipsoid contour probability level.



## 8. References

1. (a) Stavber, S.; Jereb, M.; Zupan, M. Direct  $\alpha$ -Fluorination of Ketones Using N-F Reagents. *Synthesis* **2002**, 2609. (b) Zhao, Y.; Pan, Y.; Liu, H.; Yang, Y.; Jiang, Z.; Tan, C.-H. Fluorinated Aromatic Ketones as Nucleophiles in the Asymmetric Organocatalytic Formation of C-C and C-N Bonds: A Facile Route to the Construction of Fluorinated Quaternary Stereogenic Centers. *Chem. - Eur. J.* **2011**, *17*, 3571.
2. Dai, Y.; Meng, W.; Feng, X.; Du, H. Chiral FLP-catalyzed asymmetric hydrogenation of 3-fluorinated chromones. *Chem. Commun.*, **2022**, *58*, 1558.
3. Molina-Betancourt, R.; Phansavath, P.; Ratovelomanana-Vidal, V. Ru(II)-Catalyzed Asymmetric Transfer Hydrogenation of 3-Fluorochromanone Derivatives to Access Enantioenriched cis-3-Fluorochroman-4-ols through Dynamic Kinetic Resolution. *J. Org. Chem.* **2021**, *86*, 12054.
4. Wood, S. H.; Etridge, S.; Kennedy, A. R.; Percy, J. M.; Nelson, D. J. The Electrophilic Fluorination of Enol Esters Using SelectFluor: A Polar Two-Electron Process. *Chem. Eur. J.* **2019**, *25*, 5574.
5. Bacheley, L.; Molina-Betancourt, R.; Ravindra, R.; Guillamot, G.; Phansavath, P.; Ratovelomanana-Vidal, V. Asymmetric Synthesis of Monofluorinated Carbocyclic Alcohols and Vicinal Difluorinated Heterocycles and Carbocycles.
6. Mei, Y.; Bentley, P. A.; Du, J. Thiourea catalysis of NCS in the synthesis of  $\alpha$ -chloroketones. *Tetrahedron Lett.* **2008**, *49*, 3802.
7. Touge, T.; Nara, H.; Kida, M.; Matsumura, K.; Kayaki, Y. Convincing Catalytic Performance of Oxo-Tethered Ruthenium Complexes for Asymmetric Transfer Hydrogenation of Cyclic  $\alpha$ -Halogenated Ketones through Dynamic Kinetic Resolution. *Org. Lett.* **2021**, *23*, 3070.
8. Ros, A.; Magriz, A.; Dietrich, H.; Fernández, R.; Alvarez, E.; Lassaletta, J. M. Enantioselective Synthesis of Vicinal Halohydrins via Dynamic Kinetic Resolution. *Org. Lett.* **2006**, *8*, 127.
9. Bacheley, L.; Molina-Betancourt, R.; Ravindra, R.; Guillamot, G.; Phansavath, P;

Ratovelomanana-Vidal, V. Asymmetric Synthesis of Monofluorinated Carbocyclic Alcohols and Vicinal Difluorinated Heterocycles and Carbocycles. *Eur. J. Org. Chem.* **2023**, 26, e2023003.

10. Hou, M.; Lin, L.; Chai, X.; Zhao, X.; Qiao, B.; Jiang, Z. Enantioselective photoredox dehalogenative protonation. *Chem. Sci.*, **2019**, 10, 6629.

11. Li, Z.; Wang, B.; Zhang, C.; Lo, W. Y.; Yang, L; Sun, J. Catalytic Enantioselective Nucleophilic  $\alpha$ -Chlorination of Ketones with NaCl. *J. Am. Chem. Soc.* **2024**, 146, 2779.