Supporting Information for

Pd-Catalyzed Asymmetric Etherification of 2*H*-chromenes: Enantioselective Construction of Chiral 4-Alkoxy-4*H*-chromenes

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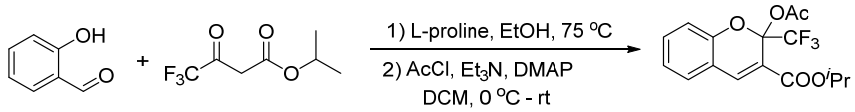
Table of Contents

1. General Information S2
2. General procedure for the synthesis of 2-trifluoromethyl 2*H*-chromenes S2
3. General procedure for the stereoselective etherification of 2*H*-chromene S2
4. General procedure for the transformation S3
5. Crystal data and structure refinement for **4rv** S4
6. Experimental characterization data for new products S5
7. Reference S20
8. Copy of NMR spectra for the products S21
9. Copy of HPLC spectra for the products S110

1. General Information

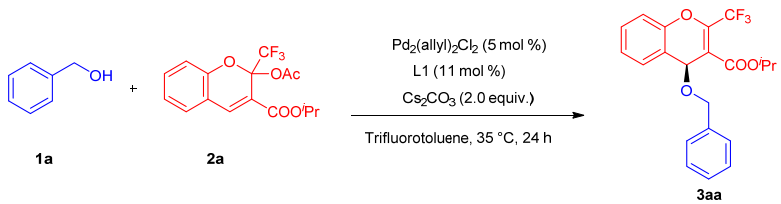
Unless otherwise noted, all reactions were performed under an argon atmosphere in glassware with magnetic stirring. Reagents were purchased from commercial sources and used without further purification. All solvents were treated with 4Å molecular sieve. Column chromatography was performed on silica gel (200 - 300 mesh) using petroleum ether/ethyl acetate as eluent. All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on Bruker AVANCE II-400 or Bruker AVANCE III-500 spectrometers with chemical shifts reported as ppm (in $CDCl_3$ with TMS as internal standard). Melting points were recorded on a Novel X-4 spectrometer. HRMS (ESI) were recorded on a Thermo LTQ Orbitrap XL spectrometer. The enantiomeric excess was determined by chiral HPLC with *n*-hexane and *i*-propanol as eluents. Optical rotations were measured on a Rudolph AUTOPOL IV polarimeter. X-ray analysis wa performed on a Bruker SMART APEX CCD diffractometer.

2. General procedure for the synthesis of 2-trifluoromethyl 2*H*-chromenes



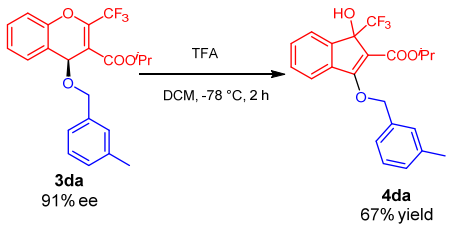
α-Trifluoromethyl alkenyl esters were prepared following similar reported literures.[1] Salicylaldehyde (10 mmol), Isopropyl 4,4,4-Trifluoroacetoacetate (12 mmol), L-proline (30 mol%) in EtOH (30 mL) were placed in a 50 mL round-bottomed flask and stirred at 75 °C for 12 h. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure, extracted with ethylacetate and water dried over Na_2SO_4 and the solvent was removed under reduced pressure and the crude product was used for next step without purification. Dissolve the crude product in dry DCM, add triethylamine (20 mmol), DMAP (1 mmol), the reaction solution was cooled to 0 °C. Acetyl chloride (AcCl, 20 mmol) was added slowly into the reaction mixture and return to room temperature. After the reaction was complete (12 h, monitored by TLC), the reaction was quenched with saturated potassium carbonate solution. The aqueous layer was separated and extracted with DCM. The combined organic extracts were washed with brine, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the products.[1]

3. General procedure for the stereoselective etherification of 2*H*-chromene

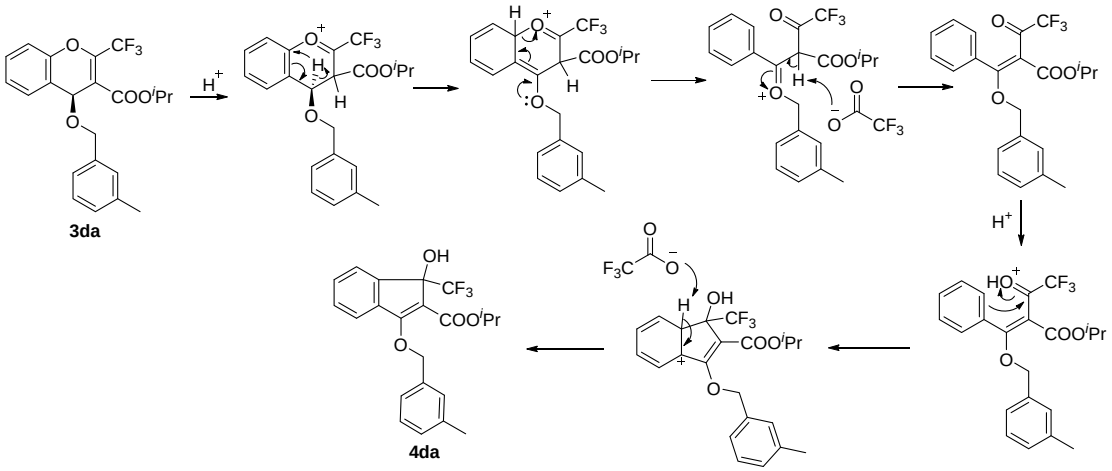


To a mixture of isopropyl 2-acetoxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (0.45 mmol), benzyl alcohol (0.3 mmol), $Pd_2(allyl)_2Cl_2$ (5 mol%), *R*-BINAP (11 mol%), Cs_2CO_3 (0.6 mmol) was added trifluorotoluene (3 mL) at room temperature under an argon atmosphere. After stirring for 24 h at 35 °C, the mixture was quenched with water and diluted with DCM. The organic layer was washed with brine, and dried over Na_2SO_4. The solvent was concentrated with a rotary evaporator and purified by column chromatography on silica gel to afford the products **3aa**.

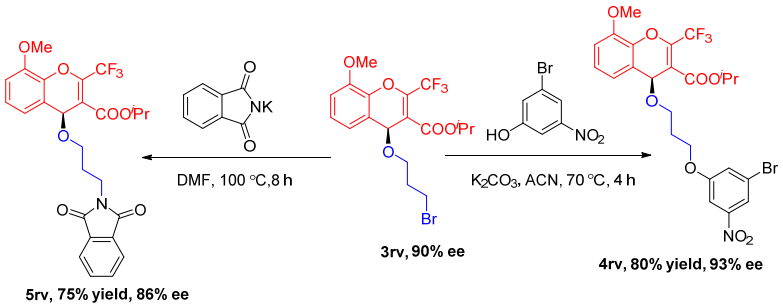
4. General procedure for the transformation



3da (81.3 mg, 0.2 mmol) was dissolved in DCM (3 mL) and trifluoroacetic acid (91.2 mg, 0.8 mmol) was added at -78 °C, then the mixture was stirred for 2 h. The mixture was diluted with DCM and slowly added into an aqueous solution of Na_2CO_3 (3 N) at 0°C and the pH of the aqueous solution was adjusted to base. The combined organic layer was concentrated under reduced pressure and the crude was directly purified by column chromatography on silica gel to afford the desired product **4da** 54.1 mg, 67% yield.[2] At the same time, we have proposed a possible mechanism (Scheme S1).



Scheme S1 Possible reaction mechanism for transformation of **3da** to **4da**



A mixture of **3rv** (90.7 mg, 0.2 mmol), 3-bromo-5-nitrophenol (87.2 mg, 0.4 mmol), K_2CO_3 (60 mg, 0.6 mmol) in anhydrous acetonitrile (10 mL) was stirred at 70 °C for 4 h in oil bath. Then, the reaction mixture was concentrated under reduced pressure and purified by column chromatography to afford the corresponding product **4rv** 91.7 mg, 80% yield, 93% ee**.**[3]

A mixture of **3rv** (90.7 mg, 0.2 mmol), potassium phthalimide (74.1 mg, 0.4 mmol) in DMF (3 mL) was stirred at 100 °C for 8 h in oil bath. The aqueous layer was separated and extracted with EA. The combined organic was washed with brine, dried over Na_2SO_4, and the solvent was

removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the product **5rv** 77.8 mg, 75% yield, 86% ee.

5. Crystal data and structure refinement for 4rv

4rv were obtained by slow evaporation of the solution (in *n*-hexane) at room temperature.

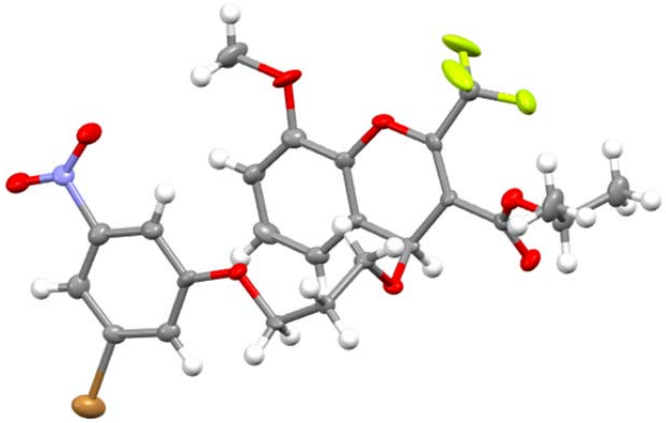
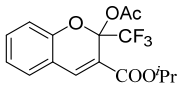


Figure S1. X-ray crystal structure of **4rv** with thermal ellipsoids 50% probability level

Formula	$C_{24}H_{23}BrF_3NO_8$
Formula weight	590.34
Crystal dimensions (mm^3)	0.3 × 0.15 × 0.1
Crystal system	monoclinic
Space group	P1211
a (Å)	11.7404(11)
b (Å)	8.3449(8)
c (Å)	13.0752(12)
α (º)	90
β (º)	94.168(3)
γ (º)	90
Volume ($Å^3$)	1277.6(2)
Z	2
T (K)	120
D_{calcd} ($g\ cm^{-3}$)	1.535
F (000)	600
No. of rflns. collected	30400
No. of indep. rflns. /R_{int}	4505 / 0.0790
No. of obsd. rflns. [$I_0 > 2\sigma(I_0)$]	3504
Data / restraints / parameters	4505 / 115 / 365
R_1 / wR_2 [$I_0 > 2\sigma(I_0)$]	0.0536 / 0.1208
R_1 / wR_2 (all data)	0.0788 / 0.1336
GOF (on F^2)	1.091
Largest diff. peak and hole (e $Å^{-3}$)	0.627 / -0.414

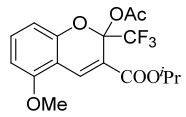
6. Experimental characterization data for new products

Isopropyl 2-acetoxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2a**)



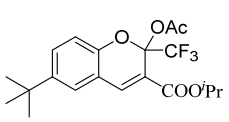
White solid, mp 101 – 102 °C, 2.2 g, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.37 (td, *J* = 7.8, 1.7 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 5.16 (heptet, *J* = 6.3 Hz, 1H), 2.21 (s, 3H), 1.32 – 1.34 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.7, 152.1, 139.2, 133.2, 129.4, 122.9, 121.1 (q, *J* = 289.9 Hz), 117.0, 116.2, 115.2, 96.3 (q, *J* = 35.4 Hz), 69.1, 21.8, 21.6, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.98. HRMS (ESI) *m/z*: calcd for $C_{16}H_{15}F_3NaO_5$ $[M + Na]^+$ 367.0769, found: 367.0767.

Isopropyl 2-acetoxy-5-methoxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2b**)



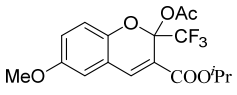
White solid, mp 95 – 96 °C, 2.4 g, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.29 – 7.25 (m, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 6.52 (d, *J* = 8.3 Hz, 1H), 5.13 (heptet, *J* = 6.3 Hz, 1H), 3.87 (s, 3H), 2.19 (s, 3H), 1.32 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 162.8, 157.0, 152.7, 134.1, 133.6, 121.3 (q, *J* = 289.9 Hz), 114.1, 107.6, 107.0, 104.5, 96.3 (q, *J* = 35.4 Hz), 68.8, 55.7, 21.6, 21.5, 21.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.10. HRMS (ESI) *m/z*: calcd for $C_{17}H_{17}F_3NaO_6$ $[M + Na]^+$ 397.0875, found: 397.0871.

Isopropyl 2-acetoxy-6-(tert-butyl)-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2c**)



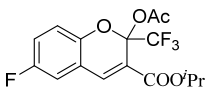
White solid, mp 130 – 131 °C, 2.2 g, 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.39 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 5.14 (heptet, *J* = 6.2 Hz, 1H), 2.19 (s, 3H), 1.32 – 1.30 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 162.8, 149.9, 145.7, 139.8, 130.5, 126.2, 121.2 (q, *J* = 289.8 Hz), 116.2, 115.8, 114.6, 96.5 (q, *J* = 35.3 Hz), 68.9, 34.2, 31.3, 21.8, 21.6, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.99. HRMS (ESI) *m/z*: calcd for $C_{20}H_{23}F_3NaO_5$ $[M + Na]^+$ 423.1395, found: 423.1392.

Isopropyl 2-acetoxy-6-methoxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2d**)



White solid, mp 111 – 112 °C, 2.2 g, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 6.97 – 6.84 (m, 2H), 6.78 (d, *J* = 2.8 Hz, 1H), 5.13 (heptet, *J* = 6.2 Hz, 1H), 3.78 (s, 3H), 2.19 (s, 3H), 1.32 – 1.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.7, 154.9, 146.2, 139.2, 121.2 (q, *J* = 290.9 Hz), 119.5, 117.1, 116.7, 116.0, 112.9, 96.4 (q, *J* = 35.4 Hz), 69.1, 55.8, 21.8, 21.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -84.92. HRMS (ESI) *m/z*: calcd for $C_{17}H_{17}F_3NaO_6$ $[M + Na]^+$ 397.0875, found: 397.0869.

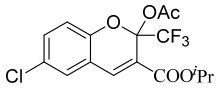
Isopropyl 2-acetoxy-6-fluoro-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2e**)



White solid, mp 101 – 102 °C, 1.7 g, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.07 (ddd, *J* = 8.9, 8.1, 3.0 Hz, 1H), 7.01 (dd, *J* = 7.8, 3.0 Hz, 1H), 6.94 (dd, *J* = 8.9, 4.3 Hz, 1H), 5.16 (heptet, *J* = 6.3 Hz, 1H), 2.22 (s, 3H), 1.34 – 1.32 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.4, 157.8 (d, *J* = 242.4 Hz), 148.0 (d, *J* = 2.0 Hz), 138.0 (d, *J* = 3.0 Hz), 121.0 (q, *J* = 289.9 Hz), 119.6 (d, *J* = 24.2 Hz), 117.65 (d, *J*

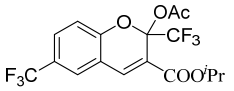
= 9.1 Hz), 117.64, 116.4 (d, *J* = 8.1 Hz), 115.0 (d, *J* = 24.2 Hz), 96.3 (q, *J* = 35.4 Hz), 69.4, 21.7, 21.5, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.85 (3F), -120.65 – -120.69 (m, 1F). HRMS (ESI) *m/z*: calcd for $C_{16}H_{14}F_4NaO_5$ $[M + Na]^+$ 385.0675, found: 385.0669.

Isopropyl 2-acetoxy-6-chloro-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2f**)



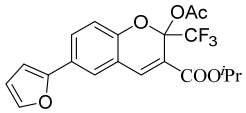
White solid, mp 118 – 119 °C, 2.9 g, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.29 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.25 (s, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 5.13 (heptet, *J* = 6.3 Hz, 1H), 2.19 (s, 3H), 1.31 – 29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.3, 150.4, 137.8, 132.7, 128.6, 127.8, 121.0 (q, *J* = 289.9 Hz), 118.2, 117.6, 116.6, 96.2 (q, *J* = 35.4 Hz), 69.4, 21.7, 21.6, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.82. HRMS (ESI) *m/z*: calcd for $C_{16}H_{14}ClF_3NaO_5$ $[M + Na]^+$ 401.0380, found: 401.0374.

Isopropyl 2-acetoxy-2,6-bis(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2g**)



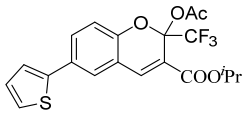
White solid, mp 99 – 100 °C, 2.5 g, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.64 – 7.59 (m, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 5.15 (heptet, *J* = 6.3 Hz, 1H), 2.21 (s, 3H), 1.33 – 1.31 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.1, 154.1, 137.6, 129.8 (q, *J* = 4.0 Hz), 126.6 (q, *J* = 4.0 Hz), 125.5 (q, *J* = 34.3 Hz), 123.6 (q, *J* = 272.7 Hz), 120.9 (q, *J* = 289.9 Hz), 117.9, 117.2, 115.9, 96.3 (q, *J* = 35.4 Hz), 69.5, 21.6, 21.5, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.21 (3F), δ -84.82 (3F). HRMS (ESI) *m/z*: calcd for $C_{17}H_{14}F_6NaO_5$ $[M + Na]^+$ 435.0643, found: 435.0634.

Isopropyl 2-acetoxy-6-(furan-2-yl)-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2h**)



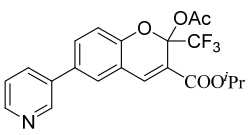
White solid, mp 124 – 125 °C, 1.0 g, 24% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.64 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.39 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.56 (d, *J* = 3.5 Hz, 1H), 6.46 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.15 (heptet, *J* = 6.2 Hz, 1H), 2.21 (s, 3H), 1.33 – 1.31 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.6, 152.6, 151.2, 142.1, 139.0, 128.6, 126.3, 124.5, 121.1 (q, *J* = 288.9 Hz), 117.2, 116.9, 115.6, 111.7, 104.7, 96.4 (q, *J* = 35.4 Hz), 69.2, 21.8, 21.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -84.86. HRMS (ESI) *m/z*: calcd for $C_{20}H_{17}F_3NaO_6$ $[M + Na]^+$ 433.0875, found: 433.0873.

Isopropyl 2-acetoxy-6-(thiophen-2-yl)-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2i**)



Yellow solid, mp 134 – 135 °C, 0.8 g, 19% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.54 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.23 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.19 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 5.19 (heptet, *J* = 6.2 Hz, 1H), 2.22 (s, 3H), 1.35 – 1.33 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 162.5, 151.3, 142.7, 138.9, 130.6, 129.7, 128.1, 126.5, 124.8, 123.1, 121.2 (q, *J* = 289.9 Hz), 117.30, 116.9, 115.7, 96.4 (q, *J* = 35.4 Hz), 69.2, 21.7, 21.6, 21.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -84.71. HRMS (ESI) *m/z*: calcd for $C_{20}H_{17}F_3NaO_5S$ $[M + Na]^+$ 449.0647, found: 449.0639.

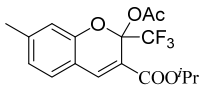
Isopropyl 2-acetoxy-6-(pyridin-3-yl)-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2j**)



Yellow solid, mp 136 – 137 °C, 0.7 g, 17% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.54 (d, *J* = 5.4 Hz, 1H), 7.88 (s, 1H), 7.73 (dt, *J*

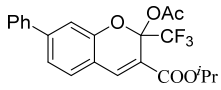
= 8.1, 2.0 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.28 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 5.14 (heptet, *J* = 6.3 Hz, 1H), 2.19 (s, 3H), 1.31 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 162.3, 151.8, 148.4, 147.6, 138.6, 134.8, 133.8, 132.5, 131.5, 127.7, 123.5, 121.0 (q, *J* = 289.9 Hz), 117.4, 116.9, 115.8, 96.2 (q, *J* = 35.4 Hz), 69.1, 21.5, 21.4, 21.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -84.89. HRMS (ESI) *m/z*: calcd for $C_{21}H_{19}F_3NO_5$ $[M + H]^+$ 422.1215, found: 422.1207.

Isopropyl 2-acetoxy-7-methyl-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2k**)



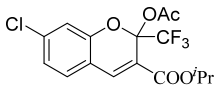
White solid, mp 98 – 99 °C, 1.8 g, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.79 (s, 1H), 5.13 (heptet, *J* = 6.2 Hz, 1H), 2.34 (s, 3H), 2.19 (s, 3H), 1.31 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 162.8, 152.0, 144.5, 139.3, 129.2, 123.8, 121.2 (q, *J* = 289.9 Hz), 115.7, 115.0, 114.5, 96.5 (q, *J* = 35.4 Hz), 68.9, 21.8, 21.6, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.02. HRMS (ESI) *m/z*: calcd for $C_{17}H_{17}F_3NaO_5$ $[M + Na]^+$ 381.0926, found: 381.0925.

Isopropyl 2-acetoxy-7-phenyl-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2l**)



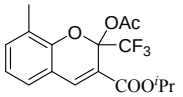
White solid, mp 123 – 124 °C, 1.6 g, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.44 (m, 2H), 7.41 – 7.33 (m, 2H), 7.32 – 7.23 (m, 2H), 5.22 (heptet, *J* = 6.2 Hz, 1H), 2.26 (s, 3H), 1.38 – 1.36 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.8, 152.5, 146.4, 139.5, 139.0, 129.8, 128.9, 128.4, 127.1, 121.7, 121.3 (q, *J* = 289.9 Hz), 116.0, 113.6, 96.6 (q, *J* = 35.4 Hz), 69.1, 21.8, 21.6, 21.2. (one aromatic carbon missing). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.88. HRMS (ESI) *m/z*: calcd for $C_{22}H_{19}F_3NaO_5$ $[M + Na]^+$ 443.1082, found: 443.1077.

Isopropyl 2-acetoxy-7-chloro-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2m**)



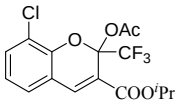
White solid, mp 112 – 113 °C, 2.3 g, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.03 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.00 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.13 (heptet, *J* = 6.2 Hz, 1H), 2.20 (s, 3H), 1.32 – 1.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.4, 152.3, 138.5, 138.1, 130.1, 123.4, 121.0 (q, *J* = 289.9 Hz), 116.4, 115.9, 115.6, 96.2 (q, *J* = 35.4 Hz), 69.3, 21.7, 21.6, 21.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -84.86. HRMS (ESI) *m/z*: calcd for $C_{16}H_{14}ClF_3NaO_5$ $[M + Na]^+$ 401.0380, found: 401.0375.

Isopropyl 2-acetoxy-8-methyl-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2n**)



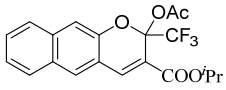
White solid, mp 61 – 62 °C, 1.1 g, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.20 (ddd, *J* = 7.5, 1.9, 0.9 Hz, 1H), 7.11 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 5.13 (heptet, *J* = 6.2 Hz, 1H), 2.23 (s, 3H), 2.20 (s, 3H), 1.32 – 1.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 162.8, 150.2, 139.7, 134.7, 127.1, 124.7, 122.3, 121.2 (q, *J* = 289.9 Hz), 116.6, 115.9, 96.6 (q, *J* = 35.4 Hz), 69.0, 21.8, 21.6, 21.3, 15.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.22. HRMS (ESI) *m/z*: calcd for $C_{17}H_{17}F_3NaO_5$ $[M + Na]^+$ 381.0926, found: 381.0923.

Isopropyl 2-acetoxy-8-chloro-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2o**)



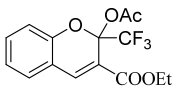
White solid, mp 102 – 103 °C, 2.1 g, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.40 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.19 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 5.15 (heptet, *J* = 6.3 Hz, 1H), 2.22 (s, 3H), 1.33 – 1.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 162.2, 147.7, 138.4, 133.4, 127.7, 123.1, 121.0 (q, *J* = 289.9 Hz), 120.5, 118.5, 117.3, 96.6 (q, *J* = 35.4 Hz), 69.3, 21.6, 21.4, 21.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -84.95. HRMS (ESI) *m/z*: calcd for $C_{16}H_{14}ClF_3NaO_5$ $[M + Na]^+$ 401.0380, found: 401.0370.

Isopropyl 2-acetoxy-2-(trifluoromethyl)-2*H*-benzo[g]chromene-3-carboxylate (**2p**)



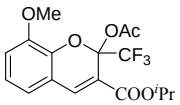
White solid, mp 164 – 165 °C, 1.8 g, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.79 (d, *J* = 11.0 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.48 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.36 – 7.40 (m, 1H), 7.34 (s, 1H), 5.19 (heptet, *J* = 6.3 Hz, 1H), 2.24 (s, 3H), 1.36 – 1.34 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.6, 148.8, 139.3, 136.1, 130.4, 129.7, 128.6, 128.4, 127.1, 125.2, 121.3 (q, *J* = 289.9 Hz), 118.4, 118.1, 110.8, 95.9 (q, *J* = 35.4 Hz), 69.2, 21.8, 21.7, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.42. HRMS (ESI) *m/z*: calcd for $C_{20}H_{17}F_3NaO_5$ $[M + Na]^+$ 417.0926, found: 417.0921.

Ethyl 2-acetoxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2q**)



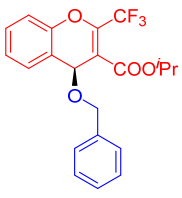
White solid, mp 58 – 59 °C, 1.6 g, 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.35 (td, *J* = 7.8, 1.6 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 163.0, 152.1, 139.4, 133.3, 129.5, 122.9, 121.1 (q, *J* = 289.8 Hz), 116.9, 115.7, 115.3, 96.3 (q, *J* = 35.3 Hz), 61.4, 21.3, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -85.08. HRMS (ESI) *m/z*: calcd for $C_{15}H_{13}F_3NaO_5$ $[M + Na]^+$ 353.0613, found: 353.0607.

Isopropyl 2-acetoxy-8-methoxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**2r**)



White solid, mp 135 – 136 °C, 1.5 g, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.02 – 6.96 (m, 2H), 6.89 (dd, *J* = 8.8, 4.4 Hz, 1H), 5.14 (heptet, *J* = 6.3 Hz, 1H), 3.87 (s, 3H), 2.20 (s, 3H), 1.32 – 1.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 162.7, 146.9, 141.3, 139.4, 122.6, 121.2, 121.3 (q, *J* = 290.8 Hz), 117.6, 116.3, 116.2, 96.4 (q, *J* = 35.4 Hz), 69.1, 56.3, 21.8, 21.6, 21.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.00. HRMS (ESI) *m/z*: calcd for $C_{17}H_{17}F_3NaO_6$ $[M + Na]^+$ 397.0875, found: 397.0871.

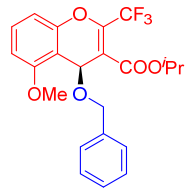
Isopropyl (*S*)-4-(benzyloxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3aa**)



Colorless liquid, 86.1 mg, 73% yield, 92% ee. $[\alpha]_D^{20}$ = -52.00 (c 0.20, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.31 – 7.21 (m, 6H), 7.19 (d, *J* = 8.3 Hz, 1H), 5.84 (s, 1H), 5.20 (heptet, *J* = 6.2 Hz, 1H), 4.47 (d, *J* = 10.7 Hz, 1H), 4.16 (d, *J* = 10.6 Hz, 1H), 1.33 – 1.29 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 150.0, 142.8 (q, *J* = 37.8 Hz), 137.7, 130.1, 129.3, 128.3, 128.0, 127.8, 125.6, 119.1 (q, *J* = 275.9 Hz), 118.6, 116.8, 111.1 (q, *J* = 1.9 Hz), 70.1, 68.7, 67.6, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.67. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.32 min, t_{minor} =

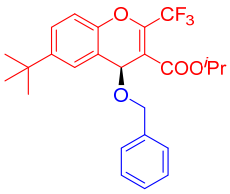
8.67 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{19}F_3NaO_4$ $[M + Na]^+$ 415.1133, found: 415.1128.

Isopropyl (*S*)-4-(benzyloxy)-5-methoxy-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ab**)



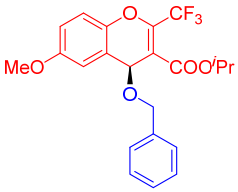
Colorless liquid, 75.7 mg, 60% yield, 80% ee. $[\alpha]_D^{20}$ = -97.50 (c 0.28, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.3 Hz, 1H), 7.28 – 7.18 (m, 5H), 6.80 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.72 (dd, *J* = 8.3, 0.9 Hz, 1H), 5.93 (s, 1H), 5.19 (heptet, *J* = 6.3 Hz, 1H), 4.61 (d, *J* = 10.9 Hz, 1H), 4.39 (d, *J* = 10.9 Hz, 1H), 3.87 (s, 3H), 1.33 – 1.31 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 158.1, 151.2, 143.0 (q, *J* = 39.1 Hz), 138.4, 130.1, 128.1, 127.9, 127.5, 119.2 (q, *J* = 275.9 Hz), 111.4 (q, *J* = 1.9 Hz), 109.0, 106.4, 70.00, 69.95, 65.3, 55.8, 21.6, 21.4. one aromatic carbon missing. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.38. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.54 min, t_{minor} = 10.08 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_5$ $[M + Na]^+$ 445.1239, found: 445.1233.

Isopropyl (*S*)-4-(benzyloxy)-6-(tert-butyl)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ac**)



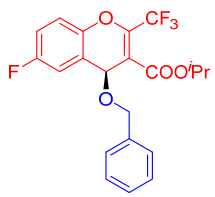
Colorless liquid, 87.6 mg, 65% yield, 85% ee.$[\alpha]_D^{20}$ = -72.85 (c 0.28, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.22 – 7.14 (m, 5H), 7.08 – 7.02 (m, 1H), 5.76 (s, 1H), 5.13 (heptet, *J* = 6.2 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 4.09 (d, *J* = 10.8 Hz, 1H), 1.27 – 1.22 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 147.8, 147.0, 141.9 (q, *J* = 37.8 Hz), 136.9, 127.3, 127.1, 126.7, 126.3, 124.7, 118.1 (q, *J* = 275.9 Hz), 116.8, 115.2, 109.9 (q, *J* = 1.9 Hz), 68.9, 67.8, 66.5, 33.6, 30.3, 20.6, 20.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.68. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 4.61 min, t_{minor} = 6.39 min. HRMS (ESI) *m/z*: calcd for $C_{25}H_{27}F_3NaO_4$ $[M + Na]^+$ 471.1759, found: 471.1754.

Isopropyl (*S*)-4-(benzyloxy)-6-methoxy-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ad**)



Colorless liquid, 77.3 mg, 61% yield, 88% ee. $[\alpha]_D^{20}$ = -91.76 (c 0.51, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.27 – 7.22 (m, 3H), 7.12 (d, *J* = 9.0 Hz, 1H), 6.94 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.87 (d, *J* = 3.0 Hz, 1H), 5.84 (s, 1H), 5.20 (heptet, *J* = 6.3 Hz, 1H), 4.46 (d, *J* = 10.8 Hz, 1H), 4.16 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.30 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 157.1, 144.2, 143.0 (q, *J* = 37.8 Hz), 137.8, 128.3, 128.0, 127.7, 119.2, 119.1 (q, *J* = 274.7 Hz), 117.9, 117.4, 111.8, 109.9 (q, *J* = 2.5 Hz), 70.0, 69.0, 67.5, 55.8, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.58. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.33 min, t_{minor} = 16.69 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_5$ $[M + Na]^+$ 445.1239, found: 445.1233.

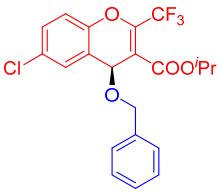
Isopropyl (*S*)-4-(benzyloxy)-6-fluoro-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ae**)



Colorless liquid, 92.6 mg, 75% yield, 92% ee. $[\alpha]_D^{20}$ = -56.89 (c 0.29, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 5H), 7.21 – 7.15 (m, 1H), 7.14 – 7.06 (m, 2H), 5.81 (s, 1H), 5.20 (heptet, *J* = 6.2 Hz, 1H), 4.49 (d, *J* = 10.6 Hz, 1H), 4.20 (d, *J* = 10.7 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.30 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 159.6 (d, *J* = 245.7 Hz), 146.0 (d, *J* = 2.4

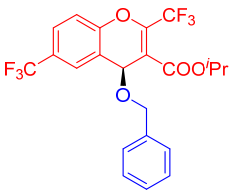
Hz), 142.8 (q, J = 39.1 Hz), 137.3, 128.4, 128.0, 127.9, 120.1 (d, J = 7.6 Hz), 118.9 (q, J = 275.9 Hz), 118.5 (d, J = 7.6 Hz), 117.6 (d, J = 23.9 Hz), 114.9 (d, J = 23.9 Hz), 110.2, 70.2, 68.5, 68.1, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.64 (s, 3F), -115.79 – -115.83 (m, 1F). HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.91 min, t_{minor} = 10.10 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{18}F_4NaO_4$ $[M + Na]^+$ 433.1039, found: 433.1033.

Isopropyl (*S*)-4-(benzyloxy)-6-chloro-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3af**)



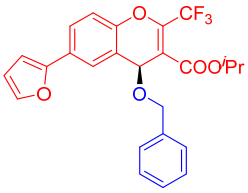
Colorless liquid, 99.6 mg, 78% yield, 90% ee. $[\alpha]_D^{20}$ = -116.44 (c 0.45, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 2.5 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.21 – 7.15 (m, 3H), 7.06 (d, J = 8.8 Hz, 1H), 5.69 (s, 1H), 5.12 (heptet, J = 6.3 Hz, 1H), 4.42 (d, J = 10.6 Hz, 1H), 4.15 (d, J = 10.7 Hz, 1H), 1.25 (d, J = 6.3 Hz, 3H), 1.22 (d, J = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 148.4, 142.7 (q, J = 37.8 Hz), 137.3, 130.6, 130.3, 128.8, 128.4, 128.0, 127.9, 120.2, 118.9 (q, J = 275.9 Hz), 118.3, 111.0 (q, J = 2.5 Hz), 70.3, 68.24, 68.22, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.60. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.65 min, t_{minor} = 8.87 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{18}ClF_3NaO_4$ $[M + Na]^+$ 449.0743, found: 449.0738.

Isopropyl (*S*)-4-(benzyloxy)-2,6-bis(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ag**)



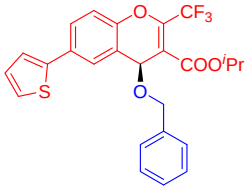
Yellow liquid , 97.7 mg, 71% yield, 87% ee. $[\alpha]_D^{20}$ = -53.53 (c 51, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.26 – 7.19 (m, 4H), 7.17 – 7.15 (m, 2H), 5.73 (s, 1H), 5.14 (heptet, J = 6.3 Hz, 1H), 4.45 (d, J = 10.7 Hz, 1H), 4.18 (d, J = 10.8 Hz, 1H), 1.26 (d, J = 6.2 Hz, 3H), 1.24 (d, J = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 151.8, 142.5 (q, J = 39.1 Hz), 137.1, 128.5, 128.1, 128.0, 127.9 (q, J = 34.0 Hz), 127.1 (q, J = 3.8 Hz), 127.0 (q, J = 3.8 Hz), 123.5 (q, J = 272.2 Hz), 119.4 , 118.8 (q, J = 274.7 Hz), 117.6, 111.7, 70.4, 68.8, 68.0, 21.5, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.20 (s, 3F), -66.65 (s, 3F). HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.24 min, t_{minor} = 6.76 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{18}ClF_3NaO_4$ $[M + Na]^+$ 483.1007, found:483.1002.

Isopropyl (*S*)-4-(benzyloxy)-6-(furan-2-yl)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ah**)



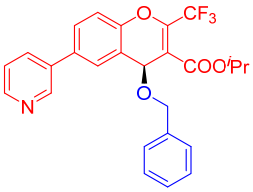
Colorless liquid, 88.4 mg, 64% yield, 85% ee. $[\alpha]_D^{20}$ = -125.00 (c 0.38, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 2.1 Hz, 1H), 7.68 (dd, J = 8.6, 2.2 Hz, 1H), 7.47 (d, J = 1.7 Hz, 1H), 7.31 – 7.23 (m, 5H), 7.21 (d, J = 8.6 Hz, 1H), 6.62 (d, J = 3.4 Hz, 1H), 6.48 (dd, J = 3.5, 1.8 Hz, 1H), 5.86 (s, 1H), 5.22 (heptet, J = 6.3 Hz, 1H), 4.50 (d, J = 10.7 Hz, 1H), 4.23 (d, J = 10.7 Hz, 1H), 1.33 (d, J = 6.3 Hz, 3H), 1.31 (d, J = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 152.6, 149.1, 142.8 (q, J = 37.8 Hz), 142.4, 137.6, 128.7, 128.4, 128.1, 127.8, 125.7, 124.3, 118.95, 119.03 (q, J = 274.7 Hz), 117.3, 111.9, 111.0 (q, J = 2.1 Hz), 105.4, 70.1, 68.5, 67.8, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.58. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 9/1, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.91 min, t_{minor} = 11.08 min. HRMS (ESI) *m/z*: calcd for $C_{25}H_{21}F_3NaO_5$ $[M + Na]^+$ 481.1239, found: 481.1233.

Isopropyl (*S*)-4-(benzyloxy)-6-(thiophen-2-yl)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ai**)



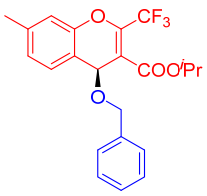
Colorless liquid, 99.2 mg, 70% yield, 81% ee. $[\alpha]_D^{20}$ = -184.26 (c 0.61, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.56 (m, 2H), 7.34 – 7.22 (m, 7H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.07 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.85 (s, 1H), 5.22 (hept, *J* = 6.3 Hz, 1H), 4.50 (d, *J* = 10.8 Hz, 1H), 4.24 (d, *J* = 10.8 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.31 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 149.3, 142.80 (q, *J* = 37.8 Hz), 142.76, 137.6, 132.2, 128.4, 128.2, 128.1, 127.9, 127.7, 126.3, 125.3, 123.5, 119.11, 119.06 (q, *J* = 275.9 Hz), 117.4, 111.1 (q, *J* = 2.1 Hz), 70.2, 68.5, 67.9, 21.7, 21.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.55. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 7.23 min, t_{minor} = 15.70 min. HRMS (ESI) *m/z*: calcd for $C_{25}H_{21}F_3NaO_4S$ $[M + Na]^+$ 497.1010, found: 497.1005.

Isopropyl (*S*)-4-(benzyloxy)-6-(pyridin-3-yl)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3aj**)



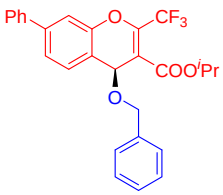
White solid, mp 80 – 81 °C, 104.8 mg, 74% yield, 85% ee. $[\alpha]_D^{20}$ = -159.84 (c 0.62, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.3 Hz, 1H), 8.61 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.81 – 7.79 (m, 1H), 7.66 – 7.55 (m, 2H), 7.37 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.33 – 7.22 (m, 6H), 5.90 (s, 1H), 5.23 (heptet, *J* = 6.3 Hz, 1H), 4.55 (d, *J* = 10.9 Hz, 1H), 4.29 (d, *J* = 10.9 Hz, 1H), 1.35 (d, *J* = 6.2 Hz, 3H), 1.32 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 149.9, 148.9, 148.1, 142.7 (q, *J* = 39.1 Hz), 137.6, 135.4, 135.1, 134.2, 128.8, 128.4, 128.1, 127.9, 127.8, 123.6, 119.4, 119.0 (q, *J* = 275.9 Hz), 117.6, 111.3 (q, *J* = 2.5 Hz), 70.2, 68.6, 68.3, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.57. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 8/2, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 8.03 min, t_{minor} = 23.04 min. HRMS (ESI) *m/z*: calcd for $C_{26}H_{22}F_3NNaO_4$ $[M + Na]^+$ 492.1399, found: 492.1393.

Isopropyl (*S*)-4-(benzyloxy)-7-methyl-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ak**)



Colorless liquid, 74.2 mg, 61% yield, 72% ee. $[\alpha]_D^{20}$ = -39.29 (c 0.14, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.26 – 7.22 (m, 3H), 7.07 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.02 (d, *J* = 1.1 Hz, 1H), 5.82 (s, 1H), 5.20 (heptet, *J* = 6.3 Hz, 1H), 4.43 (d, *J* = 10.6 Hz, 1H), 4.13 (d, *J* = 10.6 Hz, 1H), 2.39 (s, 3H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.30 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 150.0, 142.8 (q, *J* = 37.8 Hz), 140.6, 137.8, 128.9, 128.3, 128.0, 127.7, 126.7, 119.1 (q, *J* = 275.9 Hz), 116.9, 115.6, 111.1 (q, *J* = 2.5 Hz), 70.0, 68.5, 67.3, 21.6, 21.3, 21.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.74. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.81 min, t_{minor} = 8.86 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_4$ $[M + Na]^+$ 429.1290, found: 429.1284.

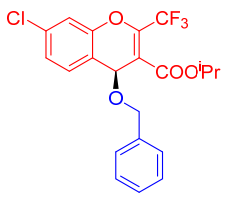
Isopropyl (*S*)-4-(benzyloxy)-7-phenyl-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3al**)



Colorless liquid, 81.6 mg, 58% yield, 83% ee. $[\alpha]_D^{20}$ = -36.67 (c 0.18, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.51 – 7.38 (m, 6H), 7.33 – 7.25 (m, 5H), 5.88 (s, 1H), 5.22 (heptet, *J* = 6.2 Hz, 1H), 4.50 (d, *J* = 10.7 Hz, 1H), 4.23 (d, *J* = 10.6 Hz, 1H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.31 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 150.4, 143.5, 142.9 (q, *J* = 37.8 Hz), 139.4, 137.7, 129.6, 129.0, 128.3, 128.2, 128.0, 127.7, 127.1, 124.4, 119.1 (q, *J*

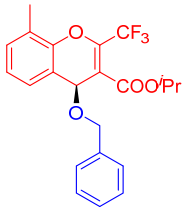
= 275.9 Hz), 117.4, 115.1, 111.3, 70.1, 68.5, 67.7, 21.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.66. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 7.92 min, t_{minor} = 9.75 min. HRMS (ESI) *m/z*: calcd for $C_{27}H_{23}F_3NaO_4$ $[M + Na]^+$ 491.1446, found: 491.1441.

Isopropyl (*S*)-4-(benzyloxy)-7-chloro-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3am**)



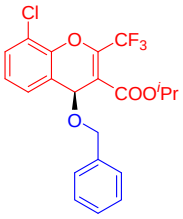
Colorless liquid, 86.7 mg, 68% yield, 89% ee. $[\alpha]_D^{20}$ = -51.67 (c 0.42, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.25 – 7.21 (m, 4H), 5.79 (s, 1H), 5.20 (heptet, *J* = 6.3 Hz, 1H), 4.46 (d, *J* = 10.7 Hz, 1H), 4.17 (d, *J* = 10.7 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.30 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 150.2, 142.5 (q, *J* = 37.8 Hz), 137.4, 135.6, 130.3, 128.4, 128.0, 127.9, 126.1, 118.9 (q, *J* = 274.7 Hz), 117.2, 117.1, 111.5 (q, *J* = 2.5 Hz), 70.3, 68.0, 67.9, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.69. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 7.13 min, t_{minor} = 9.24 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{18}ClF_3NaO_4$ $[M + Na]^+$ 449.0743, found: 449.0738.

Isopropyl (*S*)-4-(benzyloxy)-8-methyl-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3an**)



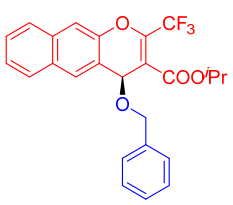
Colorless liquid, 85.0 mg, 70% yield, 89% ee. $[\alpha]_D^{20}$ = -47.41 (c 0.27, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 3H), 7.25 – 7.21 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H), 5.82 (s, 1H), 5.20 (heptet, *J* = 6.3 Hz, 1H), 4.46 (d, *J* = 10.7 Hz, 1H), 4.18 (d, *J* = 10.7 Hz, 1H), 2.36 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.31 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 148.4, 143.2 (q, *J* = 37.8 Hz), 137.7, 131.2, 128.3, 128.0, 127.7, 126.7, 126.3, 125.0, 119.2 (q, *J* = 274.7 Hz), 118.3, 110.8 (q, *J* = 2.1 Hz), 69.9, 68.8, 67.6, 21.6, 21.3, 15.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.54. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.08 min, t_{minor} = 7.88 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_4$ $[M + Na]^+$ 429.1290, found: 429.1284.

Isopropyl (*S*)-4-(benzyloxy)-8-chloro-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ao**)



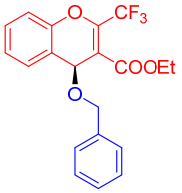
Colorless liquid, 92.1 mg, 72% yield, 88% ee. $[\alpha]_D^{20}$ = -32.55 (c 0.47, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.35 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.32 – 7.28(m, 2H), 7.26 – 7.21 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 5.83 (s, 1H), 5.21 (heptet, *J* = 6.2 Hz, 1H), 4.48 (d, *J* = 10.7 Hz, 1H), 4.19 (d, *J* = 10.7 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.31 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 146.0, 142.8 (q, *J* = 39.1 Hz), 137.4, 130.8, 128.4, 128.0, 127.9, 127.6, 125.7, 122.3, 120.5, 118.9 (q, *J* = 263.3 Hz), 111.7 (q, *J* = 2.5 Hz), 70.3, 68.6, 68.0, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.42. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.54 min, t_{minor} = 9.51 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{18}ClF_3NaO_4$ $[M + Na]^+$ 449.0743, found: 449.0738.

Isopropyl (*S*)-4-(benzyloxy)-2-(trifluoromethyl)-4*H*-benzo[g]chromene-3-carboxylate (**3ap**)



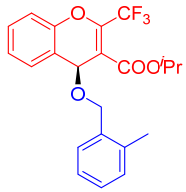
Colorless liquid, 86.1 mg, 65% yield, 87% ee. $[\alpha]_D^{20}$ = -157.78 (c 0.27, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.76 (dd, *J* = 11.6, 8.3 Hz, 2H), 7.57 (s, 1H), 7.46 – 7.43 (m, 1H), 7.40 – 7.37 (m, 1H), 7.22 – 7.15 (m, 5H), 5.91 (s, 1H), 5.15 (heptet, *J* = 6.3 Hz, 1H), 4.45 (d, *J* = 10.7 Hz, 1H), 4.14 (d, *J* = 10.8 Hz, 1H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 147.7, 143.3 (q, *J* = 37.8 Hz), 137.6, 133.9, 131.1, 129.2, 128.3, 128.1, 128.0, 127.7, 127.5, 127.3, 125.7, 119.3, 119.1 (q, *J* = 274.7 Hz), 112.9, 111.1 (q, *J* = 2.5 Hz), 70.1, 68.7, 67.8, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.61. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 9.14 min, t_{minor} = 19.50min. HRMS (ESI) *m/z*: calcd for $C_{25}H_{21}F_3NaO_4$ $[M + Na]^+$ 465.1290, found: 465.1284.

Ethyl (*S*)-4-(benzyloxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3aq**)



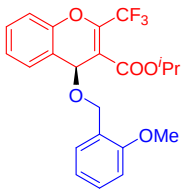
Colorless liquid, 76.3 mg, 67% yield, 82% ee. $[\alpha]_D^{20}$ = -70.67 (c 0.30, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 (ddd, *J* = 8.6, 7.5, 1.7 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.25 – 7.19 (m, 4H), 5.84 (s, 1H), 4.47 (d, *J* = 10.7 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.16 (d, *J* = 10.7 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 150.0, 143.1 (q, *J* = 38.4 Hz),137.6, 130.1, 129.2, 128.3, 128.0, 127.7, 125.7, 119.0 (q, *J* = 275.7 Hz),118.5, 116.8, 110.7 (q, *J* = 2.5 Hz), 68.4, 67.6, 62.1, 13.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.93. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.62 min, t_{minor} = 10.74min. HRMS (ESI) *m/z*: calcd for $C_{20}H_{17}F_3NaO_4$ $[M + Na]^+$ 401.0977, found: 401.0971.

Isopropyl (*S*)-4-((2-methylbenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ba**)



Colorless liquid, 97.1 mg, 80% yield, 87% ee. $[\alpha]_D^{20}$ = -61.48 (c 0.27, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.36 (m, 2H), 7.24 – 7.22 (m, 1H), 7.20 – 7.17 (m, 2H), 7.16 -7.14 (m, 1H), 7.13 – 7.09 (m, 2H), 5.82 (s, 1H), 5.19 (heptet, *J* = 6.3 Hz, 1H), 4.44 (d, *J* = 10.5 Hz, 1H), 4.18 (d, *J* = 10.5 Hz, 1H), 2.19 (s, 3H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.30 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 150.1, 143.1 (q, *J* = 37.8 Hz), 136.9, 135.6, 130.2, 130.1, 129.3, 128.1, 125.9, 125.6, 119.2 (q, *J* = 274.7 Hz), 118.8, 116.8, 111.2, 70.1, 68.6, 66.0, 21.6, 21.3, 18.7. aromatic carbon missing . ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.43. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.67 min, t_{minor} = 8.74 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_4$ $[M + Na]^+$ 429.1290, found: 429.1284.

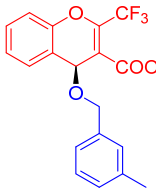
Isopropyl (*S*)-4-((2-methoxybenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ca**)



Colorless liquid, 96.8 mg, 76% yield, 92% ee. $[\alpha]_D^{20}$ = -27.13 (c 0.60, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.33 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.29 – 7.19 (m, 3H), 7.01 – 6.91 (m, 1H), 6.88 – 6.81 (m, 1H), 5.88 (s, 1H), 5.22 (heptet, *J* = 6.3 Hz, 1H), 4.58 (d, *J* = 11.3 Hz, 1H), 4.40 (d, *J* = 11.3 Hz, 1H), 3.79 (s, 3H), 1.36 (d, *J* = 6.3 Hz, 3H), 1.32 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 157.0, 149.9, 142.5 (q, *J* = 37.8 Hz), 129.9, 129.46, 129.45, 128.9, 126.2, 125.3, 120.4, 119.1 (q, *J* = 275.9 Hz), 119.0, 116.6, 111.5 (q, *J* = 1.9 Hz), 110.2, 69.9, 68.7, 63.3, 55.2, 21.6, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.64. HPLC analysis: Daicel

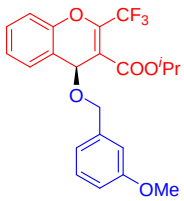
CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 9/1, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.29 min, t_{minor} = 9.83 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_5$ $[M + Na]^+$ 445.1239, found: 445.1233.

Isopropyl (*S*)-4-((3-methylbenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3da**)



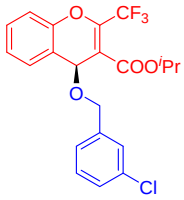
Colorless liquid, 93.7 mg, 77% yield, 92% ee. $[\alpha]_D^{20}$ = -55.26 (c 0.19, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.27 – 7.23 (m, 1H), 7.21 – 7.14 (m, 2H), 7.10 – 6.99 (m, 3H), 5.84 (s, 1H), 5.21 (heptet, *J* = 6.3 Hz, 1H), 4.43 (d, *J* = 10.5 Hz, 1H), 4.12 (d, *J* = 10.5 Hz, 1H), 2.30 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.31 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 150.0, 142.8 (q, *J* = 39.1 Hz), 138.0, 137.6, 130.1, 129.3, 128.8, 128.5, 128.3, 125.6, 125.1, 119.1 (q, *J* = 275.9 Hz), 118.7, 116.8, 111.1, 70.1, 68.5, 67.7, 21.6, 21.3, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.66. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.63 min, t_{minor} = 8.73 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_4$ $[M + Na]^+$ 429.1290, found: 429.1284.

Isopropyl (*S*)-4-((3-methoxybenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ea**)



Colorless liquid, 94.5 mg, 75% yield, 91% ee. $[\alpha]_D^{20}$ = -43.33 (c 0.18, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.26 – 7.23 (m, 1H), 7.20 (t, *J* = 8.0 Hz, 2H), 6.91 – 6.75 (m, 3H), 5.84 (s, 1H), 5.20 (heptet, *J* = 6.2 Hz, 1H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.15 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.30 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 159.7, 150.0, 142.9 (q, *J* = 37.8 Hz), 139.3, 130.1, 129.34, 129.30, 125.6, 120.2, 119.1 (q, *J* = 275.9 Hz), 118.6, 116.8, 113.41, 113.36, 111.1 (q, *J* = 2.0 Hz), 70.1, 68.5, 67.5, 55.2, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.66. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 7.31 min, t_{minor} = 14.81 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_5$ $[M + Na]^+$ 445.1239, found: 445.1233.

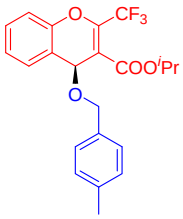
Isopropyl (*S*)-4-((3-chlorobenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3fa**)



Colorless liquid, 94.9 mg, 74% yield, 89% ee. $[\alpha]_D^{20}$ = -57.00 (c 0.20, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.30 – 7.17 (m, 5H), 7.12 – 7.07 (m, 1H), 5.85 (s, 1H), 5.21 (heptet, *J* = 6.3 Hz, 1H), 4.42 (d, *J* = 11.0 Hz, 1H), 4.11 (d, *J* = 11.0 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.30 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 150.0, 143.0 (q, *J* = 37.8 Hz), 139.8, 134.2, 130.3, 129.6, 129.2, 127.9, 127.8, 125.8, 125.7, 119.0 (q, *J* = 275.9 Hz), 118.3, 116.8, 110.9 (q, *J* = 2.5 Hz), 70.2, 68.8, 66.6, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.68. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.00 min, t_{minor} = 9.93 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{18}ClF_3NaO_4$ $[M + Na]^+$ 449.0743, found: 449.0738.

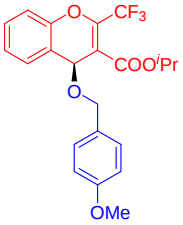
Isopropyl (*S*)-4-((4-methylbenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ga**)

Colorless liquid, 92.3 mg, 76% yield, 89% ee. $[\alpha]_D^{20}$ = +43.20 (c 0.25, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.25 – 7.22 (m, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.13 – 7.09 (m, 4H), 5.81 (s, 1H), 5.20 (heptet, *J* = 6.2 Hz, 1H), 4.42 (d, *J* =



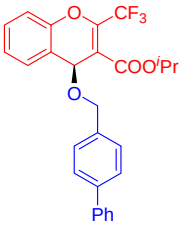
10.5 Hz, 1H), 4.12 (d, J = 10.5 Hz, 1H), 2.30 (s, 3H), 1.33 – 1.31 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 150.0, 142.7 (q, J = 39.1 Hz), 137.5, 134.7, 130.1, 129.3, 129.0, 128.1, 125.6, 119.1 (q, J = 275.9 Hz), 118.7, 116.8, 111.2 (q, J = 2.0 Hz), 70.1, 68.4, 67.6, 21.6, 21.3, 21.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.66. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.90 min, t_{minor} = 12.50 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_4$ $[M + Na]^+$ 429.1290, found: 429.1284.

Isopropyl (*S*)-4-((4-methoxybenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ha**)



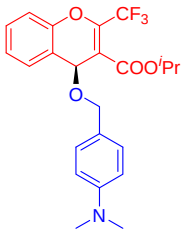
Colorless liquid, 97.3 mg, 77% yield, 90% ee. $[\alpha]_D^{20}$ = -49.55 (c 0.22, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.7 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.26 – 7.21 (m, 1H), 7.19 – 7.15 (m, 3H), 6.83 (d, J = 8.2 Hz, 2H), 5.81 (s, 1H), 5.21 (heptet, J = 6.2 Hz, 1H), 4.40 (d, J = 10.3 Hz, 1H), 4.10 (d, J = 10.3 Hz, 1H), 3.77 (s, 3H), 1.34 – 1.32 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 159.4, 150.0, 142.7 (q, J = 37.8 Hz), 130.1, 129.8, 129.6, 129.3, 125.6, 119.1 (q, J = 275.9 Hz), 118.8, 116.8, 113.8, 111.2 (q, J = 1.9 Hz), 70.0, 68.3, 67.4, 55.3, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.68. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 7.65 min, t_{minor} = 23.50 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_5$ $[M + Na]^+$ 445.1239, found: 445.1233.

Isopropyl (*S*)-4-([1,1'-biphenyl]-4-ylmethoxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ia**)



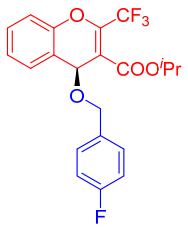
Colorless liquid, 97.9 mg, 70% yield, 88% ee. $[\alpha]_D^{20}$ = -41.93 (c 0.57, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 4H), 7.48 (dd, J = 7.7, 1.7 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.34 – 7.30 (m, 3H), 7.25 (td, J = 7.5, 1.2 Hz, 1H), 7.22 – 7.16 (m, 1H), 5.86 (s, 1H), 5.28 – 5.16 (m, 1H), 4.51 (d, J = 10.6 Hz, 1H), 4.20 (d, J = 10.7 Hz, 1H), 1.34 – 1.31 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 150.1, 142.9 (q, J = 37.4 Hz), 140.9, 140.8, 136.8, 130.2, 129.3, 128.8, 128.5, 127.3, 127.2, 127.1, 125.7, 119.1 (q, J = 275.7 Hz), 118.6, 116.8, 111.1 (q, J = 2.0 Hz), 70.2, 68.6, 67.3, 21.7, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.59. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.58 min, t_{minor} = 16.88 min. HRMS (ESI) *m/z*: calcd for $C_{27}H_{23}F_3NaO_4$ $[M + Na]^+$ 491.1446, found: 491.1441.

Isopropyl (*S*)-4-((4-(dimethylamino)benzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ja**)



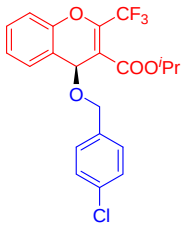
Colorless liquid, 91.0 mg, 70% yield, 79% ee. $[\alpha]_D^{20}$ = -26.25 (c 0.16, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.7, 1.7 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.25 – 7.22 (m, 1H), 7.16 (dd, J = 8.3, 1.0 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.69 – 6.63 (m, 2H), 5.77 (s, 1H), 5.21 (heptet, J = 6.4 Hz, 1H), 4.38 (d, J = 10.1 Hz, 1H), 4.09 (d, J = 10.2 Hz, 1H), 2.90 (s, 6H), 1.34 – 1.33 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 150.5, 150.0, 142.5 (q, J = 37.8 Hz), 129.9, 129.6, 129.4, 125.5, 125.4, 119.2 (q, J = 275.9 Hz), 119.1, 116.7, 112.5, 111.5 (q, J = 2.5 Hz), 70.0, 68.1, 68.0, 40.6, 21.7, 21.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.64. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.12 min, t_{minor} = 24.05 min. HRMS (ESI) *m/z*: calcd for $C_{23}H_{24}F_3NNaO_4$ $[M + Na]^+$ 458.1555, found: 458.1550.

Isopropyl (*S*)-4-((4-fluorobenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ka**)



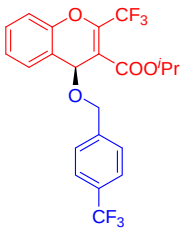
Colorless liquid, 91.5 mg, 74% yield, 84% ee. $[\alpha]_D^{20}$ = -56.58 (c 0.38, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.31 – 7.24 (m, 1H), 7.24 – 7.17 (m, 3H), 7.02 – 6.93 (m, 2H), 5.83 (s, 1H), 5.20 (heptet, *J* = 6.2 Hz, 1H), 4.42 (d, *J* = 10.6 Hz, 1H), 4.11 (d, *J* = 10.6 Hz, 1H), 1.33 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 162.4 (d, *J* = 246.4 Hz), 150.0, 142.9 (q, *J* = 38.4 Hz), 133.5 (d, *J* = 4.0 Hz), 130.2, 129.8 (d, *J* = 8.1 Hz), 129.2, 125.7, 119.0 (q, *J* = 276.7 Hz), 118.5, 117.7, , 115.2 (d, *J* = 21.2 Hz), 110.9 (q, *J* = 2.0 Hz), 70.1, 68.6, 66.7, 21.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.70 (s, 3F), -114.57 – -114.72 (m, 1F). HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.00 min, t_{minor} = 11.68 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{18}F_4NaO_4$ $[M + Na]^+$ 433.1039, found: 433.1033.

Isopropyl (*S*)-4-((4-chlorobenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3la**)



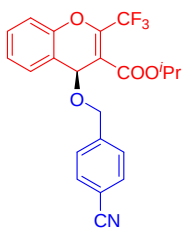
Colorless liquid, 99.0 mg, 77% yield, 90% ee. $[\alpha]_D^{20}$ = -53.68 (c 0.19, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.28 – 7.22 (m, 3H), 7.22 – 7.13 (m, 3H), 5.84 (s, 1H), 5.20 (heptet, *J* = 6.3 Hz, 1H), 4.42 (d, *J* = 10.9 Hz, 1H), 4.11 (d, *J* = 10.9 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.29 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 150.0, 143.0 (q, *J* = 39.1 Hz), 136.3, 133.5, 130.2, 129.24, 129.20, 128.5, 125.7, 119.0 (q, *J* = 275.9 Hz), 118.4, 116.8, 110.9 (q, *J* = 1.7 Hz), 70.1, 68.7, 66.6, 21.6, 21.3. ^{19}F NMR (370 MHz, $CDCl_3$) δ -66.68. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.24 min, t_{minor} = 13.01 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{18}ClF_3NaO_4$ $[M + Na]^+$ 449.0743, found: 449.0738.

Isopropyl (*S*)-2-(trifluoromethyl)-4-((4-(trifluoromethyl)benzyl)oxy)-4*H*-chromene-3-carboxylate (**3ma**)



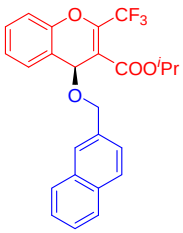
Colorless liquid, 99.9 mg, 72% yield, 85% ee. $[\alpha]_D^{20}$ = -52.96 (c 0.44, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.38 – 7.32 (m, 2H), 7.28 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.21 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.88 (s, 1H), 5.19 (heptet, *J* = 6.3 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 4.20 (d, *J* = 11.4 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.28 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 150.0, 143.1 (q, *J* = 37.4 Hz), 141.8 (q, *J* = 2.0 Hz), 130.3, 129.9 (q, *J* = 32.3 Hz), 129.2, 127.8, 125.8, 125.2 (q, *J* = 3.0 Hz), 124.1 (q, *J* = 273.7 Hz), 119.0 (q, *J* = 275.7 Hz), 118.2, 116.9, 110.7 (q, *J* = 2.0 Hz), 70.2, 68.9, 66.4, 21.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.58 (s, 3F), -66.71 (s, 3F). HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 4.59 min, t_{minor} = 6.48 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{18}F_6NaO_4$ $[M + Na]^+$ 483.1007, found: 483.1002.

Isopropyl (*S*)-4-((4-cyanobenzyl)oxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3na**)



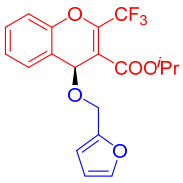
Colorless liquid, 63.4 mg, 51% yield, 83% ee. $[\alpha]_D^{20}$ = -32.31 (c 0.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.50 – 7.38 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 7.25 – 7.20 (m, 1H), 5.89 (s, 1H), 5.19 (heptet, *J* = 6.2 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 4.19 (d, *J* = 11.9 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 150.0, 143.28, 143.26 (q, *J* = 37.8 Hz), 132.1, 130.4, 129.1, 128.0, 125.8, 119.0 (q, *J* = 274.7 Hz), 118.8, 118.0, 116.9, 111.4, 110.6 (q, *J* = 2.5 Hz), 70.2, 69.0, 66.2, 21.6, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.68. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 12.06 min, t_{minor} = 27.60 min. HRMS (ESI) *m/z*: calcd for $C_{22}H_{18}F_3NNaO_4$ $[M + Na]^+$ 440.1086, found: 440.1080.

Isopropyl (*S*)-4-(naphthalen-2-ylmethoxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3oa**)



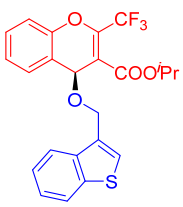
Colorless liquid, 103.8 mg, 78% yield, 90% ee. $[\alpha]_D^{20}$ = -49.49 (c 0.59, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 3H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.40 – 7.34 (m, 2H), 7.29 – 7.16 (m, 2H), 5.89 (s, 1H), 5.25 – 5.16 (m, 1H), 4.63 (d, *J* = 10.9 Hz, 1H), 4.33 (d, *J* = 10.9 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.29 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 150.1, 142.9 (q, *J* = 38.4 Hz), 135.2, 133.3, 133.0, 130.2, 129.3, 128.1, 127.9, 127.7, 126.7, 126.1, 126.0, 125.9, 125.7, 119.1 (q, *J* = 276.7 Hz), 118.6, 116.8, 111.2 (q, *J* = 1.9 Hz), 70.1, 68.7, 67.8, 21.7, 21.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.59. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.45 min, t_{minor} = 13.96 min. HRMS (ESI) *m/z*: calcd for $C_{25}H_{21}F_3NaO_4$ $[M + Na]^+$ 465.1290, found: 465.1284.

Isopropyl (*S*)-4-(furan-2-ylmethoxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3pa**)



Colorless liquid, 83.8 mg, 73% yield, 90% ee. $[\alpha]_D^{20}$ = -42.50 (c 0.12, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 3H), 7.26 – 7.22 (m, 1H), 7.19 – 7.17 (m, 1H), 6.31 – 6.30 (m, 1H), 6.28 – 6.21 (m, 1H), 5.79 (s, 1H), 5.21 (heptet, *J* = 6.3 Hz, 1H), 4.46 (d, *J* = 12.2 Hz, 1H), 4.23 (d, *J* = 12.1 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.33 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 151.3, 149.9, 142.93 (q, *J* = 39.1 Hz), 142.85, 130.1, 129.3, 125.7, 119.0 (q, *J* = 275.9 Hz), 118.6, 116.8, 111.0 (q, *J* = 2.5 Hz), 110.4, 109.5, 70.1, 68.2, 60.3, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.66. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.48 min, t_{minor} = 15.21 min. HRMS (ESI) *m/z*: calcd for $C_{19}H_{17}F_3NaO_5$ $[M + Na]^+$ 405.0926, found: 405.0920.

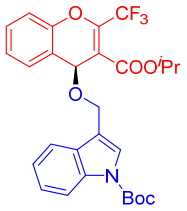
Isopropyl (*S*)-4-(benzo[b]thiophen-3-ylmethoxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3qa**)



Colorless liquid, 85.1 mg, 63% yield, 87% ee. $[\alpha]_D^{20}$ = -34.67 (c 0.15, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.33 – 7.22 (m, 3H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.12 (s, 1H), 5.88 (s, 1H), 5.22 (heptet, *J* = 6.3 Hz, 1H), 4.74 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 1.34 – 1.32 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 150.0, 143.1 (q, *J* = 37.8 Hz), 141.4, 140.3, 139.4, 130.3, 129.4,

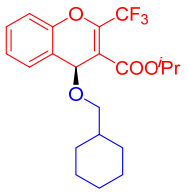
125.8, 124.3, 124.2, 123.5, 122.7, 122.4, 119.1 (q, J = 275.9 Hz), 118.3, 116.8, 110.9 (q, J = 2.1 Hz), 70.3, 68.6, 63.0, 21.7, 21.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.62. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 5.68 min, t_{minor} = 22.81 min. HRMS (ESI) *m/z*: calcd for $C_{23}H_{19}F_3NaO_4S$ $[M + Na]^+$ 471.0854, found: 471.0848.

Tert-butyl (*S*)-3-(((3-(isopropoxycarbonyl)-2-(trifluoromethyl)-4*H*-chromen-4-yl)oxy)methyl)-1*H*-indole-1-carboxylate (**3ra**)



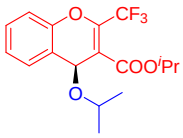
Colorless liquid, 98.6 mg, 62% yield, 93% ee. $[\alpha]_D^{20}$ = -14.15 (c 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.41 – 7.37 (m, 1H), 7.32 – 7.23 (m, 2H), 7.23 – 7.16 (m, 2H), 5.85 (s, 1H), 5.20 (heptet, J = 6.3 Hz, 1H), 4.62 (dd, J = 11.0, 0.8 Hz, 1H), 4.36 (dd, J = 11.1, 1.0 Hz, 1H), 1.65 (s, 9H), 1.33 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 150.1, 149.5, 143.1 (q, J = 38.4 Hz), 135.6, 130.1, 129.5, 129.3, 125.6, 124.8, 124.5, 122.6, 119.4, 118.60, 118.55 (q, J = 275.7 Hz), 117.1, 116.7, 115.2, 111.0 (q, J = 2.0 Hz), 83.6, 70.1, 68.3, 59.4, 28.1, 21.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.50. HPLC analysis: Daicel CHIRALPAK OD-H, n-hexane/i-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.53 min, t_{minor} = 5.55 min. HRMS (ESI) m/z: calcd for $C_{28}H_{28}F_3NNaO_6$ $[M + Na]^+$ 554.1766, found: 554.1758.

Isopropyl (*S*)-4-(cyclohexylmethoxy)-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3sa**)



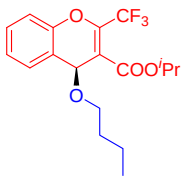
Colorless liquid, 89.9 mg, 75% yield, 87% ee. $[\alpha]_D^{20}$ = -56.07 (c 0.28, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 7.7, 1.7 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.29 – 7.21 (m, 1H), 7.15 (dd, J = 8.3, 1.2 Hz, 1H), 5.69 (s, 1H), 5.19 (heptet, J = 6.3 Hz, 1H), 3.22 (dd, J = 8.4, 6.2 Hz, 1H), 2.90 (dd, J = 8.4, 6.4 Hz, 1H), 1.74 – 1.57 (m, 5H), 1.50 – 1.42 (m, 1H), 1.34 – 1.33 (m, 6H), 1.27 – 1.02 (m, 3H), 0.99 – 0.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 149.8, 142.3 (q, J = 37.4 Hz), 129.8, 129.1, 125.4, 119.1 (q, J = 275.7 Hz), 119.0, 116.6, 111.3 (q, J = 2.0 Hz), 71.3, 69.9, 68.5, 38.1, 30.03, 30.02, 26.5, 25.82, 25.79, 21.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.66. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 4.90 min, t_{minor} = 7.68 min. HRMS (ESI) *m/z*: calcd for $C_{21}H_{25}F_3NaO_4$ $[M + Na]^+$ 421.1603, found: 421.1597.

Isopropyl (*S*)-4-isopropoxy-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ta**)



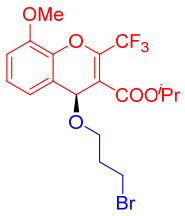
Colorless liquid, 54.8 mg, 53% yield, 92% ee. $[\alpha]_D^{20}$ = -48.95 (c 0.19, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.7, 1.6 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.25 – 7.22 (m, 1H), 7.17 (dd, J = 8.3, 1.2 Hz, 1H), 5.60 (s, 1H), 5.20 (heptet, J = 6.3 Hz, 1H), 3.85 (heptet, J = 6.1 Hz, 1H), 1.35 (d, J = 6.3 Hz, 3H), 1.34 (d, J = 6.3 Hz, 3H), 1.17 (d, J = 6.1 Hz, 3H), 1.03 (d, J = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 149.7, 142.5 (q, J = 37.8 Hz), 129.7, 129.3, 125.3, 120.2, 119.2 (q, J = 275.9 Hz), 116.8, 112.1 (q, J = 2.0 Hz), 70.0, 69.9, 67.3, 23.3, 23.0, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.42. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.32 min, t_{minor} = 8.67 min. HRMS (ESI) *m/z*: calcd for $C_{17}H_{19}F_3NaO_4$ $[M + Na]^+$ 367.1133, found: 367.1128.

Isopropyl (*S*)-4-butoxy-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3ua**)



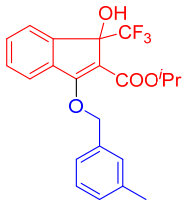
Colorless liquid, 64.7 mg, 60% yield, 88% ee. $[\alpha]_D^{20}$ = -51.52 (c 0.33, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.26 – 7.22 (m, 1H), 7.16 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.69 (s, 1H), 5.20 (heptet, *J* = 6.3 Hz, 1H), 3.44 – 3.39 (m, 1H), 3.12 – 3.08 (m, 1H), 1.50 – 1.41 (m, 2H), 1.34 – 1.33 (m, 6H), 1.30 – 1.26 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 149.9, 142.4 (q, *J* = 37.8 Hz), 129.8, 129.1, 125.4, 119.1 (q, *J* = 275.9 Hz), 119.0, 116.6, 111.3 (q, *J* = 2.0 Hz), 69.8, 68.5, 65.3, 31.9, 21.6, 21.3, 19.2, 13.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.74. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 4.82 min, t_{minor} = 9.03 min. HRMS (ESI) *m/z*: calcd for $C_{18}H_{21}F_3NaO_4$ $[M + Na]^+$ 381.1290, found: 381.1284.

Isopropyl (*S*)-4-(3-bromopropoxy)-8-methoxy-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**3rv**)



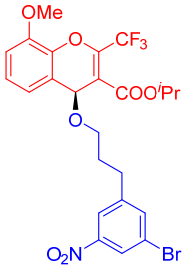
Colorless liquid, 85.4 mg, 63% yield, 90% ee. $[\alpha]_D^{20}$ = -50.67 (c 0.63, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.92 (dd, *J* = 8.1, 1.4 Hz, 1H), 5.67 (s, 1H), 5.19 (heptet, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.54 – 3.47 (m, 1H), 3.41 – 3.36 (m, 2H), 3.25 – 3.20 (m, 1H), 2.06 – 1.91 (m, 2H), 1.33 (d, *J* = 1.6 Hz, 3H), 1.32 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 147.9, 142.9 (q, *J* = 38.4 Hz), 139.8, 125.4, 120.0, 119.4, 119.1 (q, *J* = 275.7 MHz), 112.0, 110.6 (q, *J* = 2.0 Hz), 70.0, 68.6, 62.8, 56.2, 32.9, 30.3, 21.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.23. HPLC analysis: Daicel CHIRALPAK AD-H, n-hexane/i-PrOH = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: tmajor = 11.30 min, tminor = 6.84 min. HRMS (ESI) m/z: calcd for C18H20BrF3NaO5 $[M + Na]^+$ 475.0344, found: 475.0331.

Isopropyl 1-hydroxy-3-((3-methylbenzyl)oxy)-1-(trifluoromethyl)-1*H*-indene-2-carboxylate (**4da**)



Colorless liquid, 54.1 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.35 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 – 7.13 (m, 3H), 7.11 – 6.94 (m, 3H), 5.19 (heptet, *J* = 6.3 Hz, 1H), 4.64 (s, 2H), 2.32 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.27 (d, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 153.0, 141.5, 137.9, 136.4, 133.2, 129.2, 128.6, 128.5, 128.2, 124.8, 122.5, 121.6 (*J* = 289.9 Hz) 117.5, 116.8, 115.6, 99.8 (*J* = 33.3 Hz), 69.3, 66.6, 21.7, 21.6, 21.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -82.25. HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_3NaO_4$ $[M + Na]^+$ 429.1290, found: 429.1284.

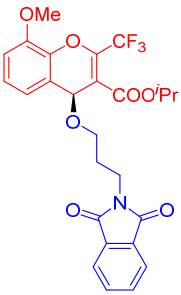
Isopropyl (*S*)-4-(3-(3-bromo-5-nitrophenyl)propoxy)-8-methoxy-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**4rv**)



White solid, mp 91 – 92 °C, 91.7 mg, 80% yield, 93% ee. $[\alpha]_D^{20}$ = -62.07 (c 0.64, CH_2Cl_2).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (t, *J* = 1.9 Hz, 1H), 7.56 (t, *J* = 2.2 Hz, 1H), 7.25 (t, *J* = 2.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.88 (dd, *J* = 8.2, 1.5 Hz, 1H), 5.70 (s, 1H), 5.19 (heptet, *J* = 6.3 Hz, 1H), 4.03 – 3.96 (m, 2H), 3.91 (s, 3H), 3.57 – 3.53 (m, 1H), 3.28 – 3.24 (m, 1H), 1.97 – 1.93 (m, 2H), 1.33 – 1.31 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 159.9, 149.4, 147.9, 143.1 (q, *J* = 37.8 Hz), 140.0, 125.3, 124.2, 122.8, 119.9, 119.3, 119.0 (q, *J* = 275.9 Hz), 118.7, 111.9, 110.5 (q, *J* = 2.5 Hz), 108.3, 70.0, 68.6, 65.7, 60.6, 56.2, 29.1, 21.6, 21.3. ^{19}F NMR

(470 MHz, $CDCl_3$) δ -66.25. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 6.30 min, t_{minor} = 8.44 min. HRMS (ESI) *m/z*: calcd for $C_{24}H_{23}BrF_3NNaO_7$ $[M + Na]^+$ 590.0637, found: 590.0624.

Isopropyl (*S*)-4-(3-(1,3-dioxoisoindolin-2-yl)propoxy)-8-methoxy-2-(trifluoromethyl)-4*H*-chromene-3-carboxylate (**5rv**)

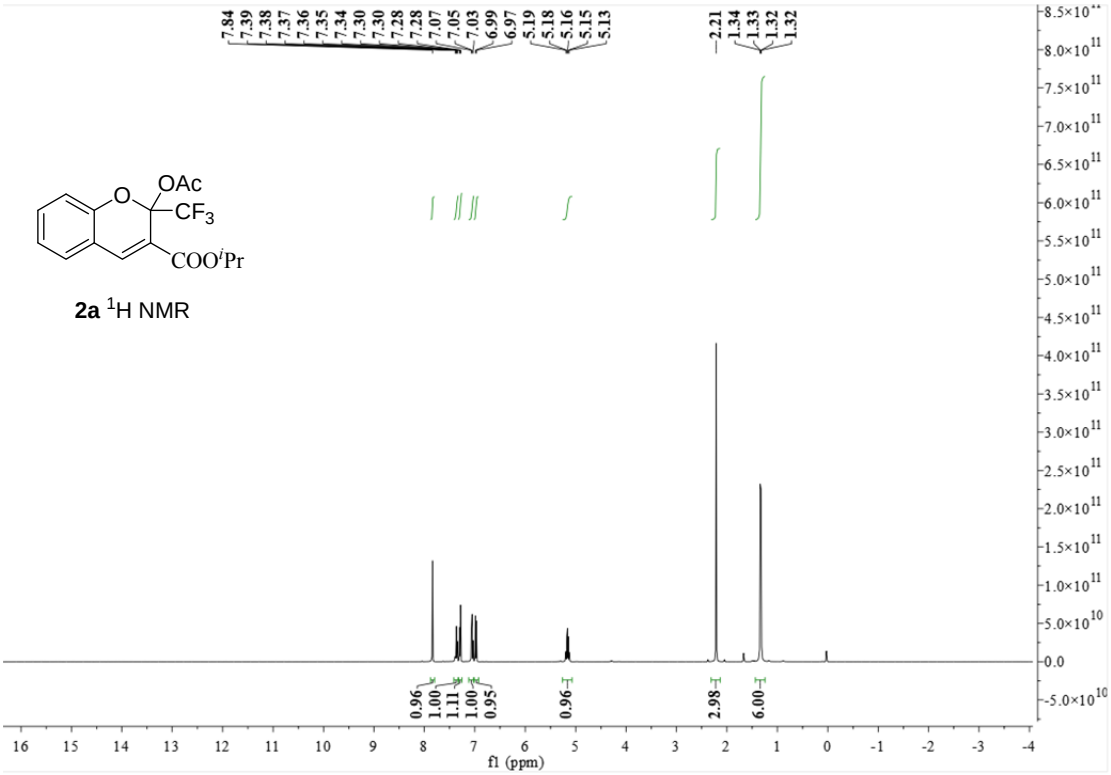


Colorless liquid, 77.8 mg, 75% yield, 86% ee. $[\alpha]_D^{20}$ = -37.45 (c 0.41, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.69 – 7.67 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.90 (dd, *J* = 8.1, 1.4 Hz, 1H), 5.67 (s, 1H), 5.17 (heptet, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.75 – 3.62 (m, 2H), 3.48 – 3.44 (m, 1H), 3.19 – 3.14 (m, 1H), 1.87 – 1.82 (m, 2H), 1.33 (d, *J* = 1.6 Hz, 3H), 1.32 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 164.6, 147.8, 142.8 (q, *J* = 37.8 Hz), 139.9, 133.8, 132.2, 125.3, 123.1, 120.3, 119.4, 119.1 (q, *J* = 274.7 Hz), 111.9, 110.7 (q, *J* = 2.5 Hz), 69.9, 68.6, 62.8, 56.2, 35.6, 28.7, 21.6, 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.30. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 254 nm, retention time: t_{major} = 12.32 min, t_{minor} = 8.76 min. HRMS (ESI) *m/z*: calcd for $C_{26}H_{24}F_3NNaO_5$ $[M + Na]^+$ 542.1403, found: 542.1396.

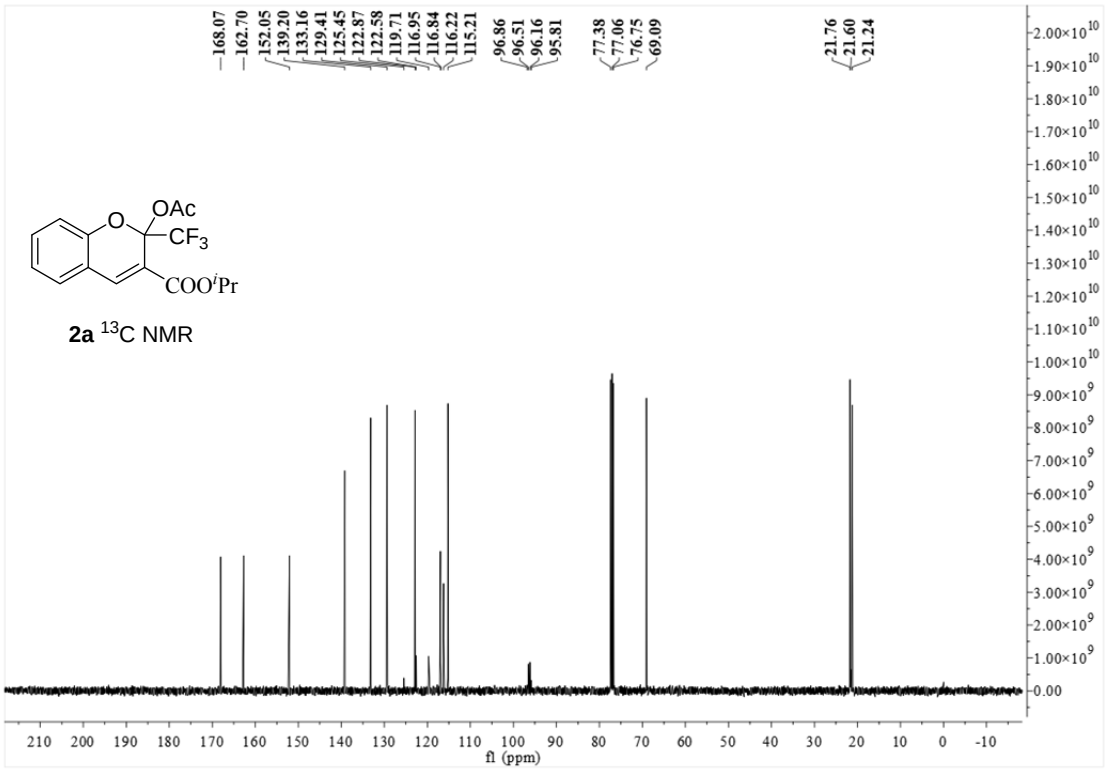
7. Reference

1. L. C. Rao, N. S. Kumar, N. J. Babu, H. M. Meshram, *New J. Chem*., 2015, **39**, 7164-7171.
2. I. Gorokhovik, L. Neuville, J. Zhu, *Org. Lett.,* 2011, **13**, 5536-5539.
3. Y.-W. Wang, Q. Wang, L. Wu, K.-P. Jia, M.-Y. Wang, Y.-A. Qiu, *Nat. Commun.,* 2014, **15**, 2780

8. Copy of NMR spectra for the products



2a ^{1}H NMR



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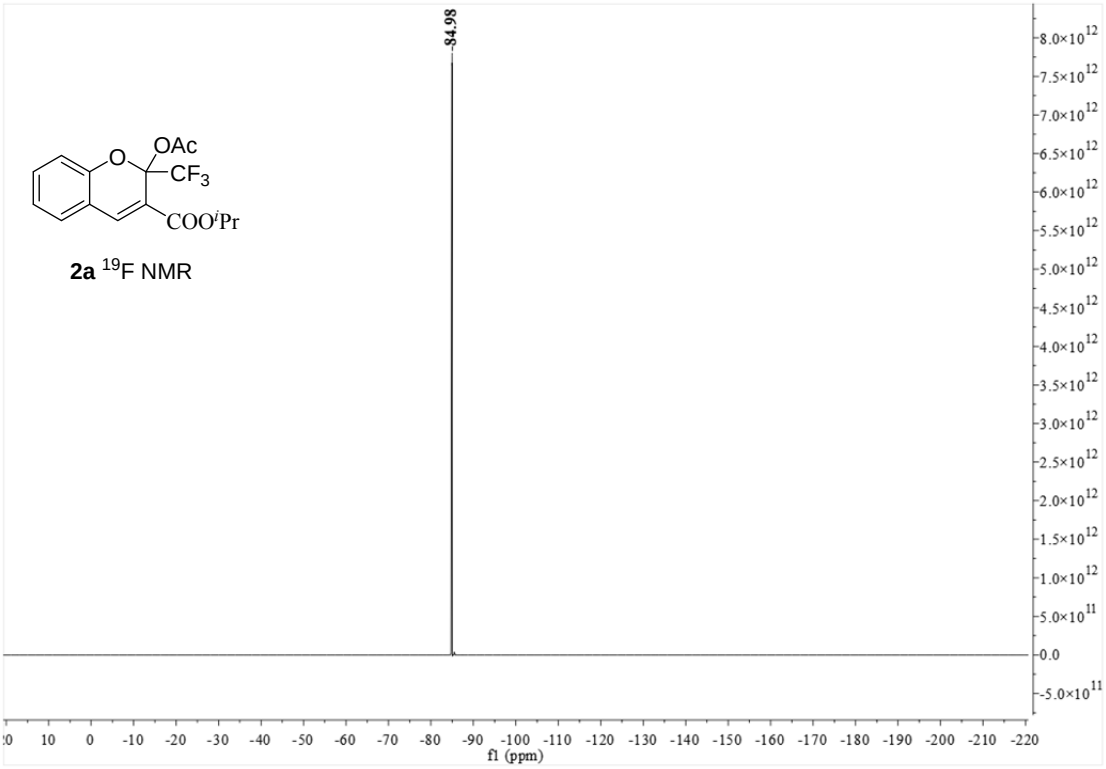

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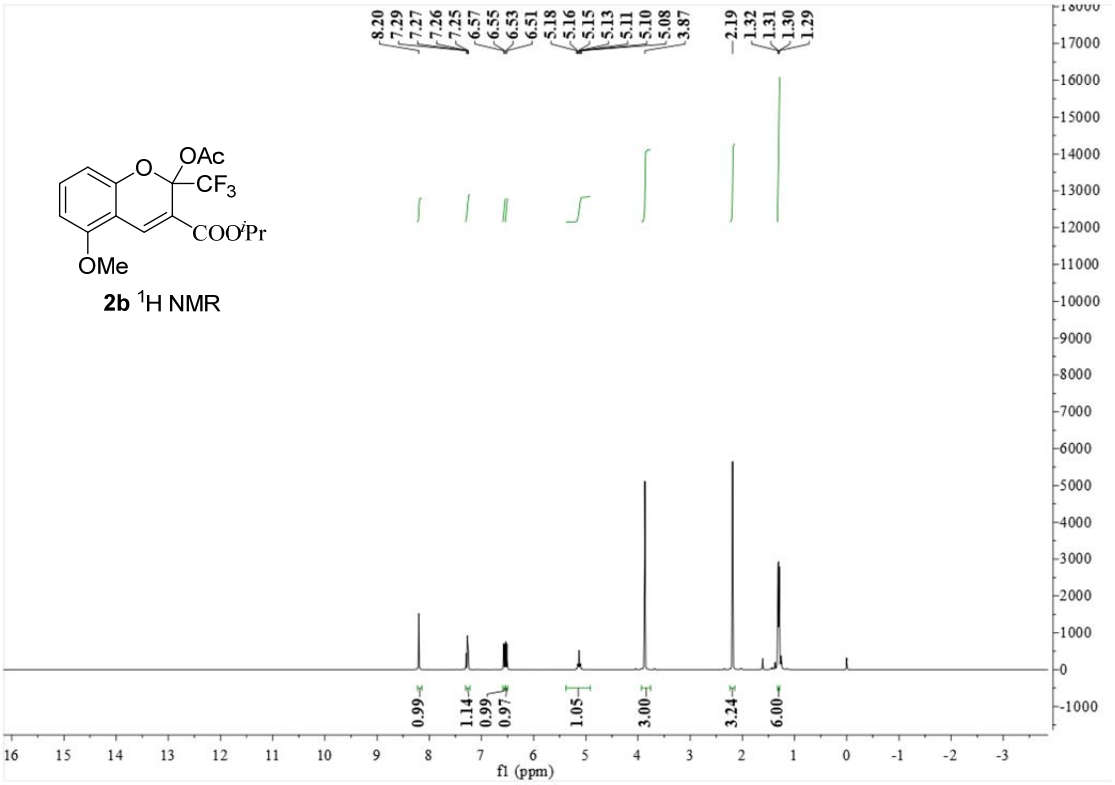

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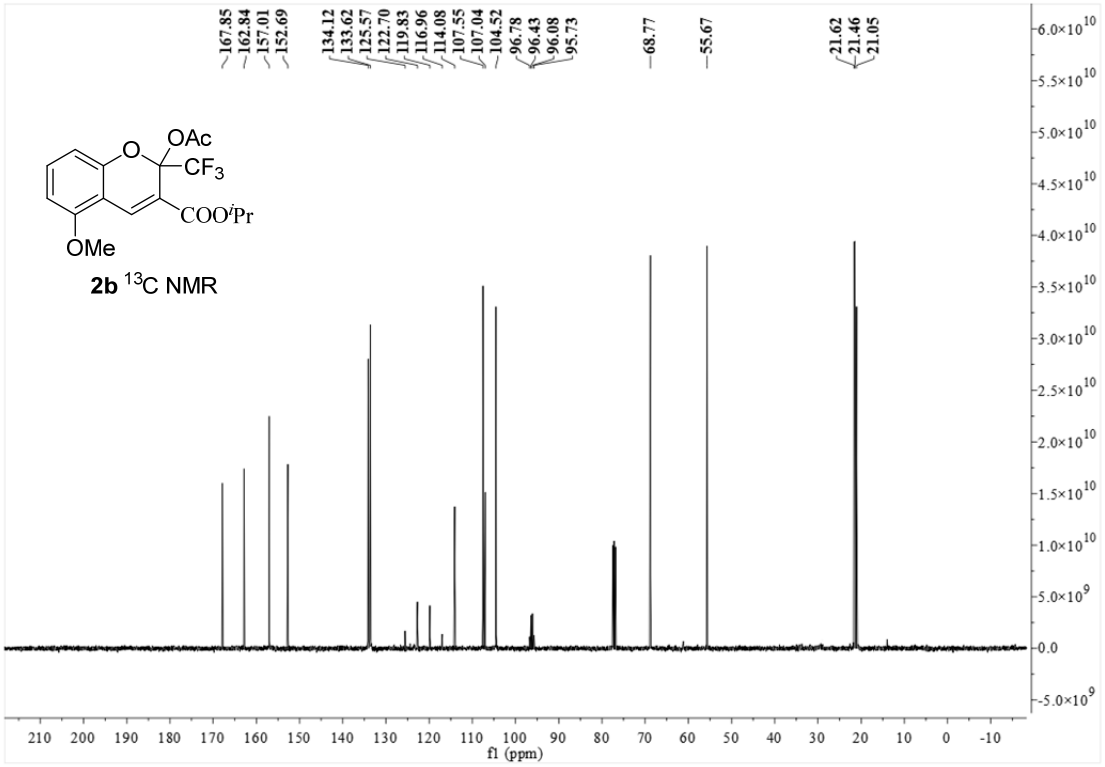
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125.57
122.70
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116.96
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107.55
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104.52
96.78
96.43
96.08
95.73
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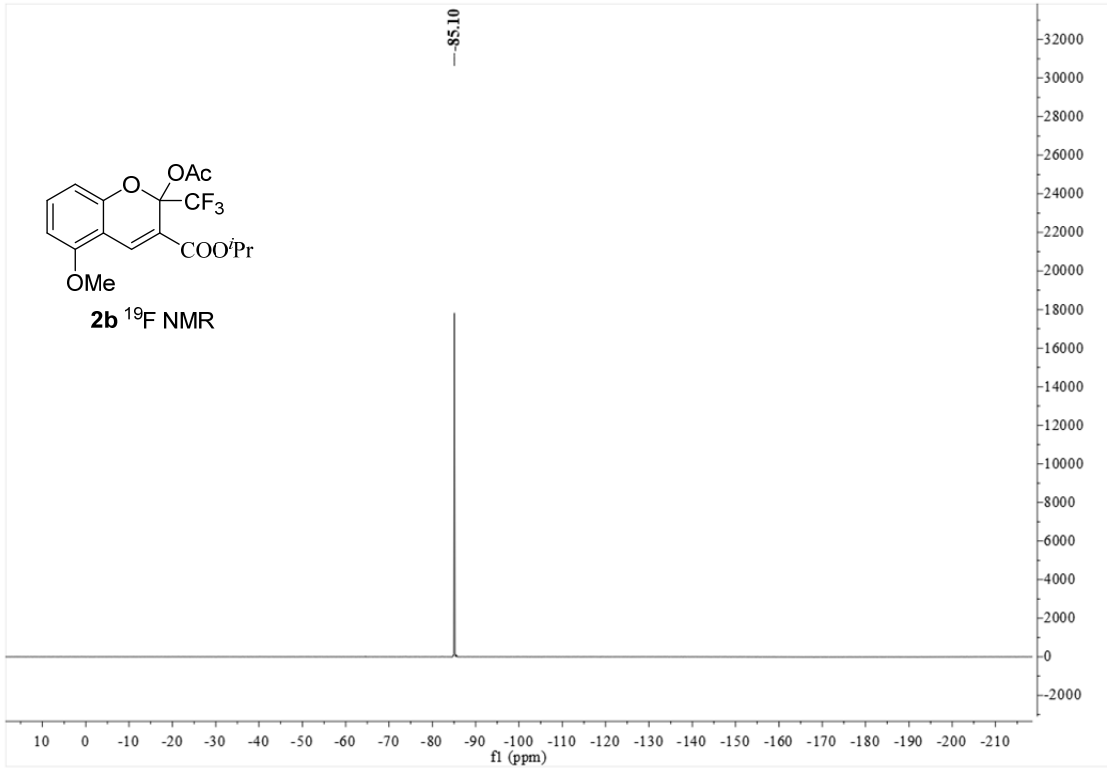
21.62
21.46
21.05
OAc
CF3
O
COO'Pr
OMe
2b 13C NMR
f1 (ppm)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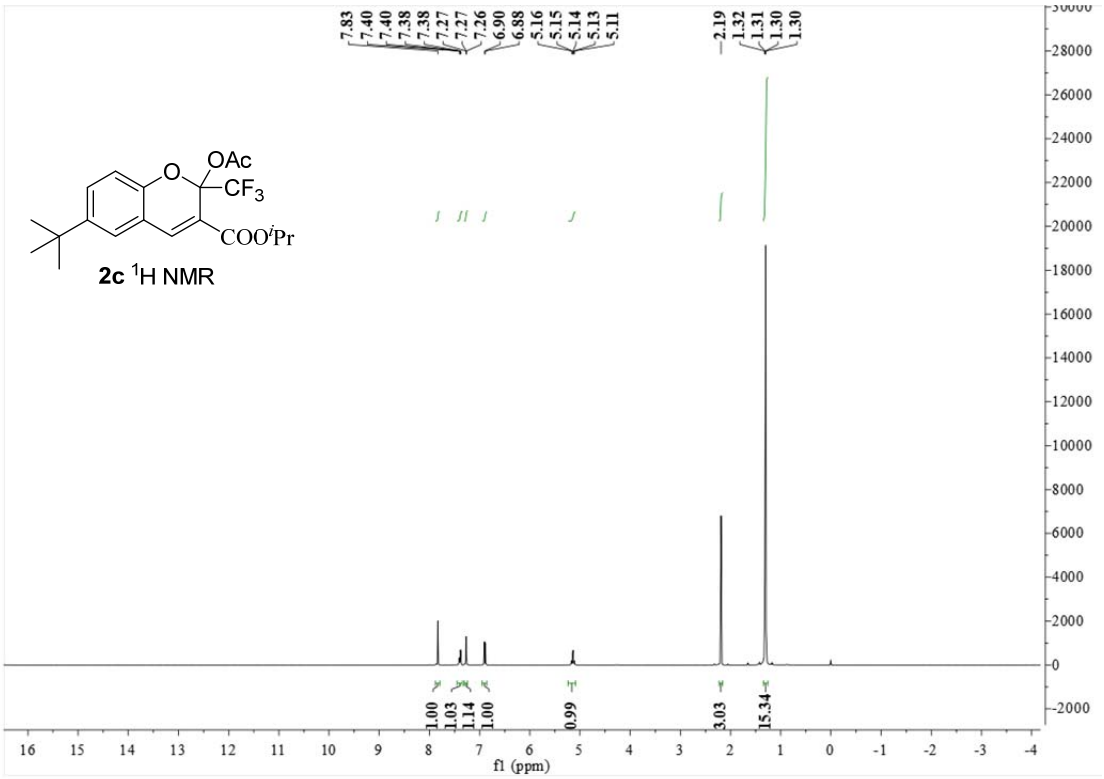
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6.88
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5.15
5.14
5.13
5.11
2.19
1.32
1.31
1.30
1.30
OAc
O
CF3
COOiPr
2c 1H NMR
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1.14
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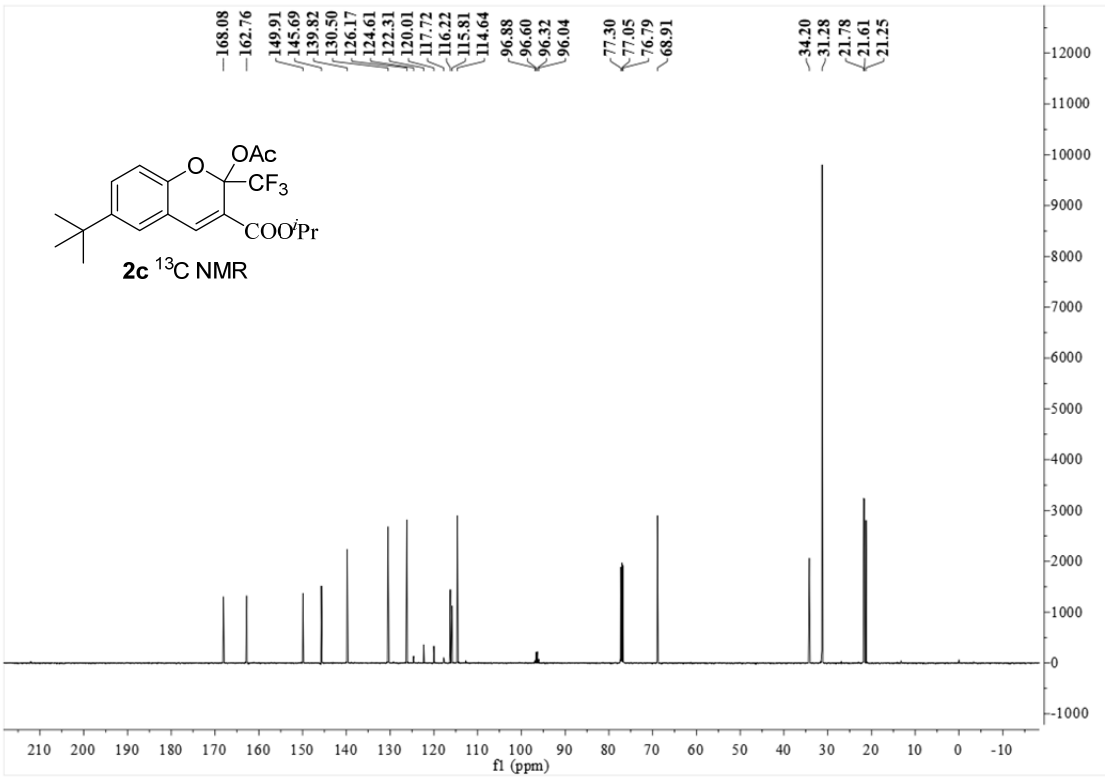
f1 (ppm)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96.60
96.32
96.04
77.30
77.05
76.79
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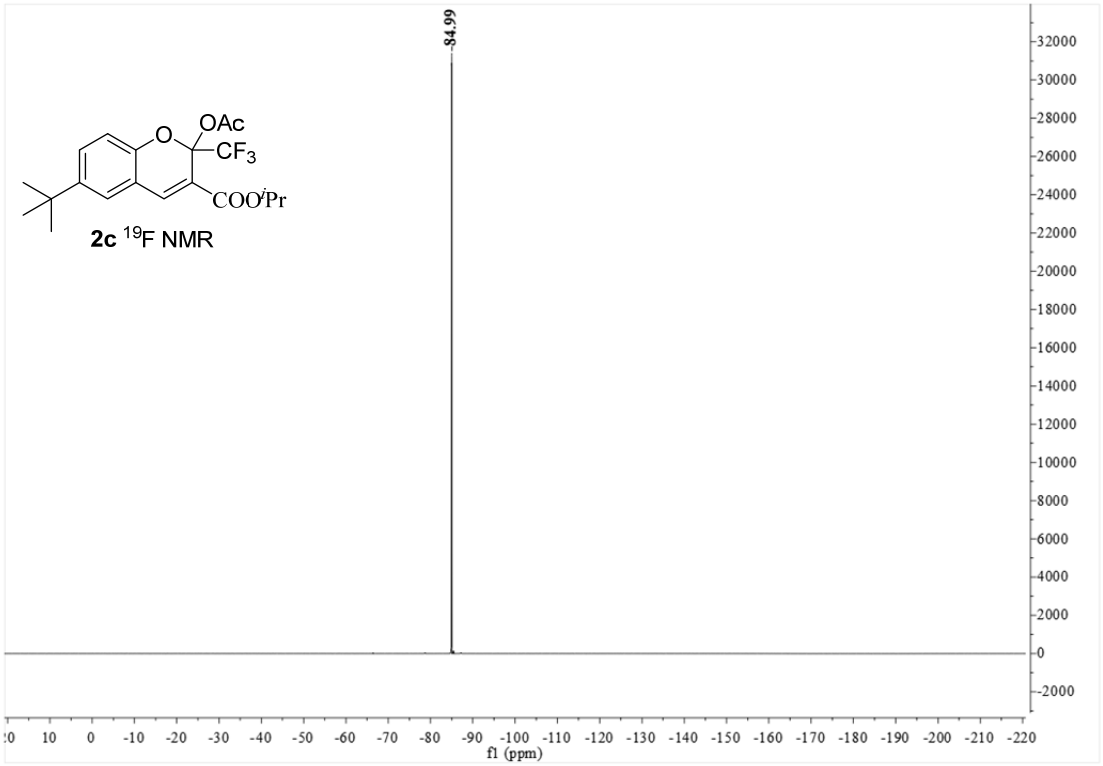
21.25
OAc
O
CF3
COOiPr
2c 13C NMR
f1 (ppm)



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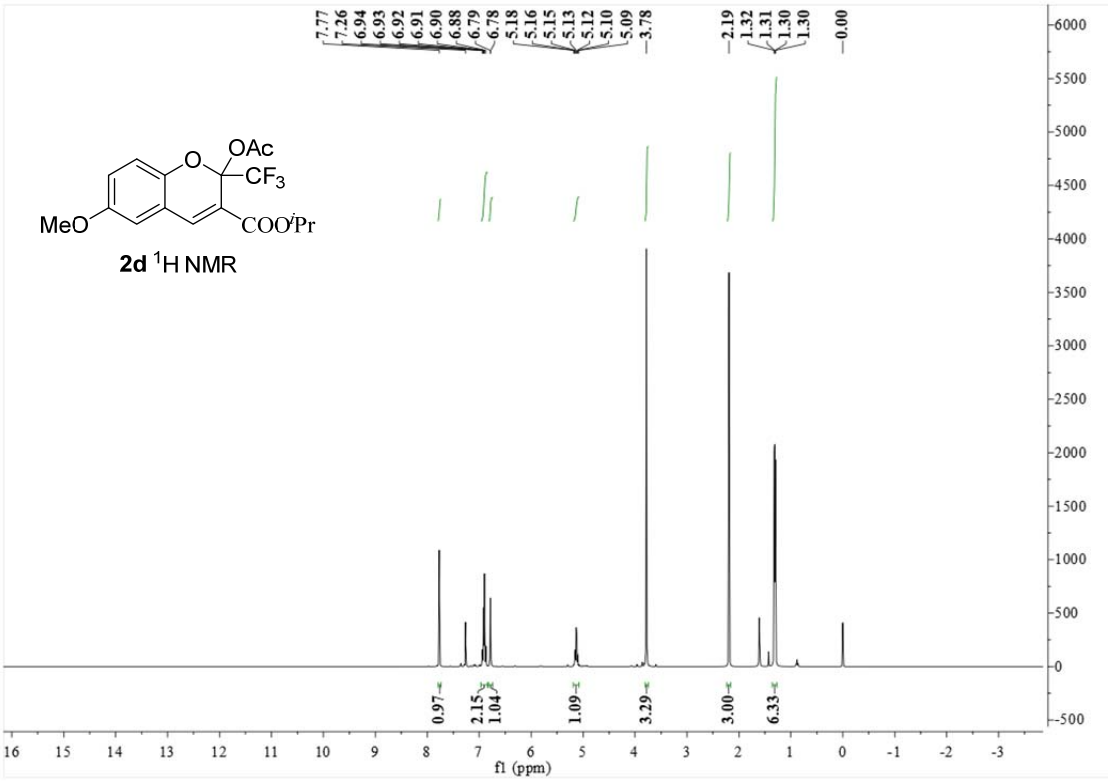

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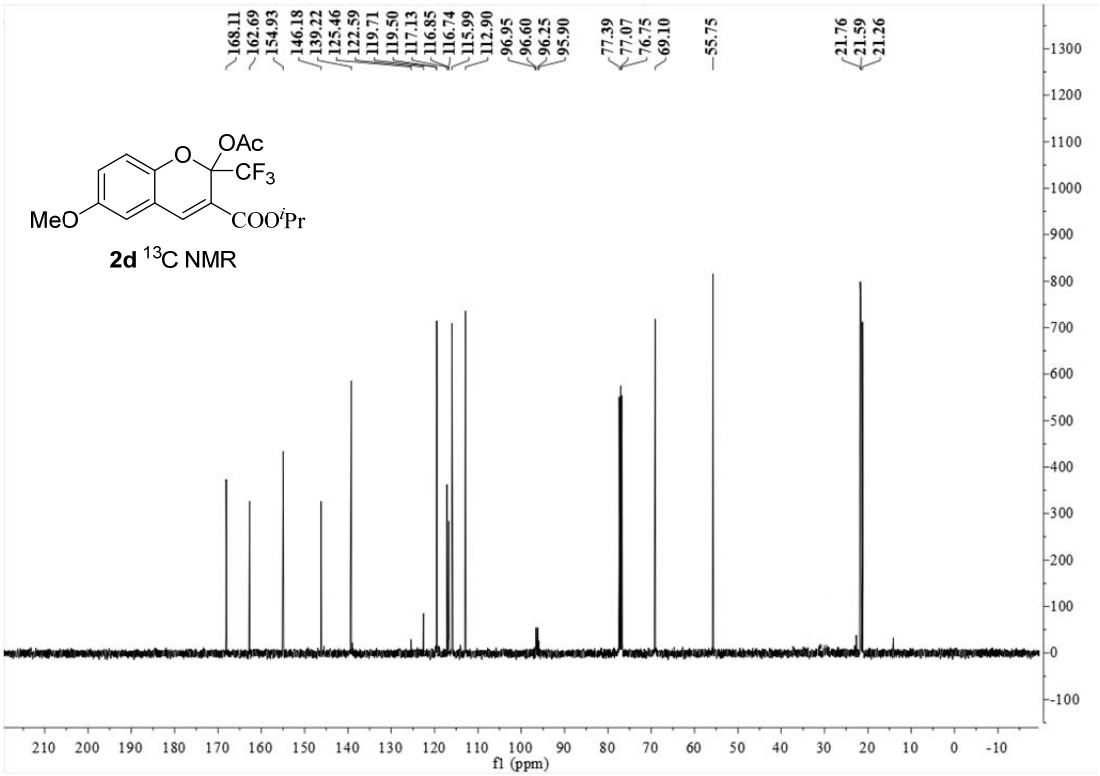

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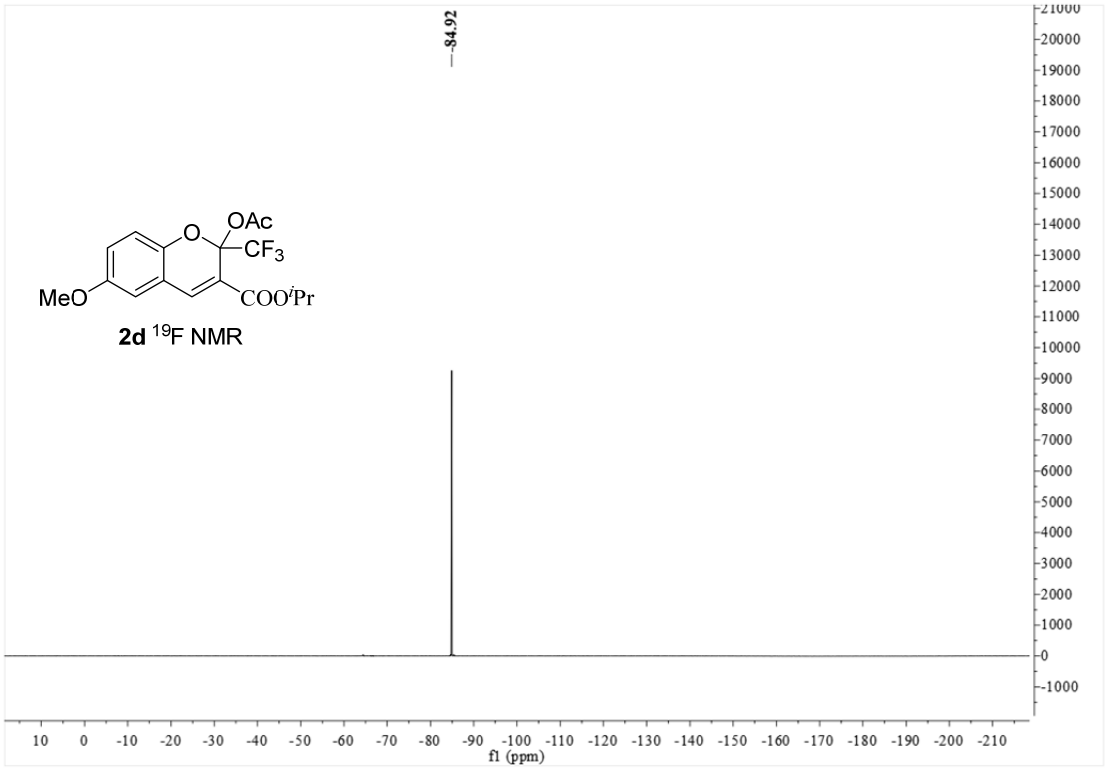

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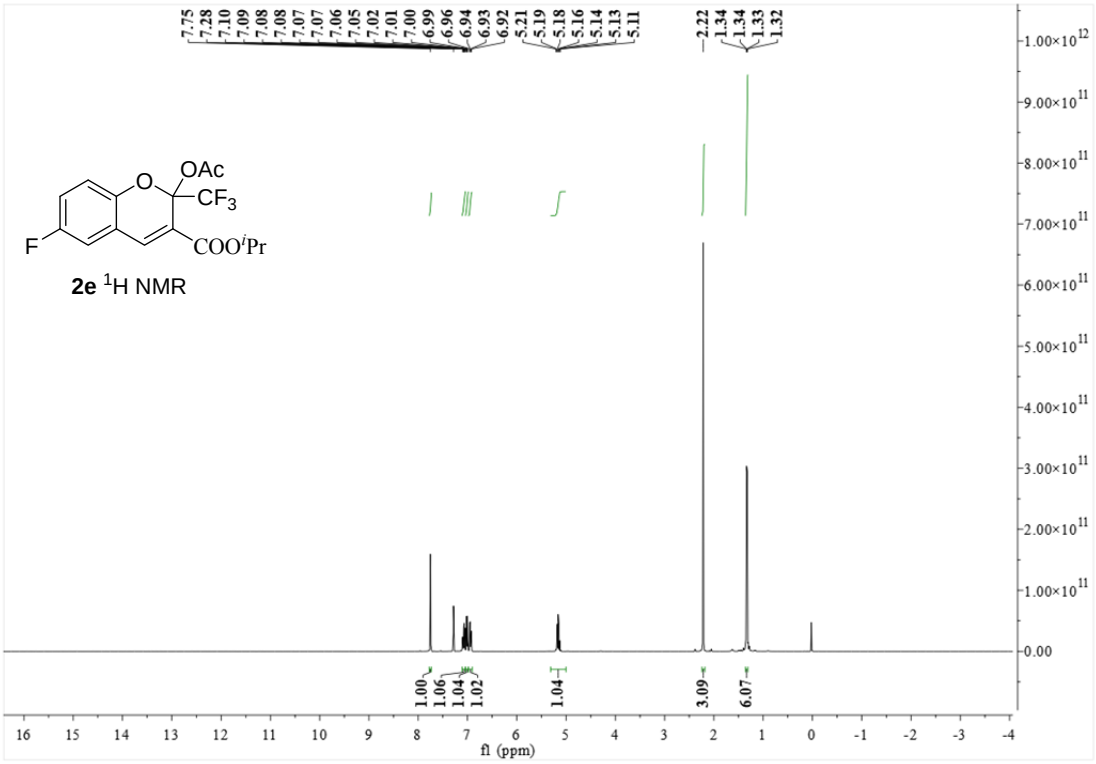

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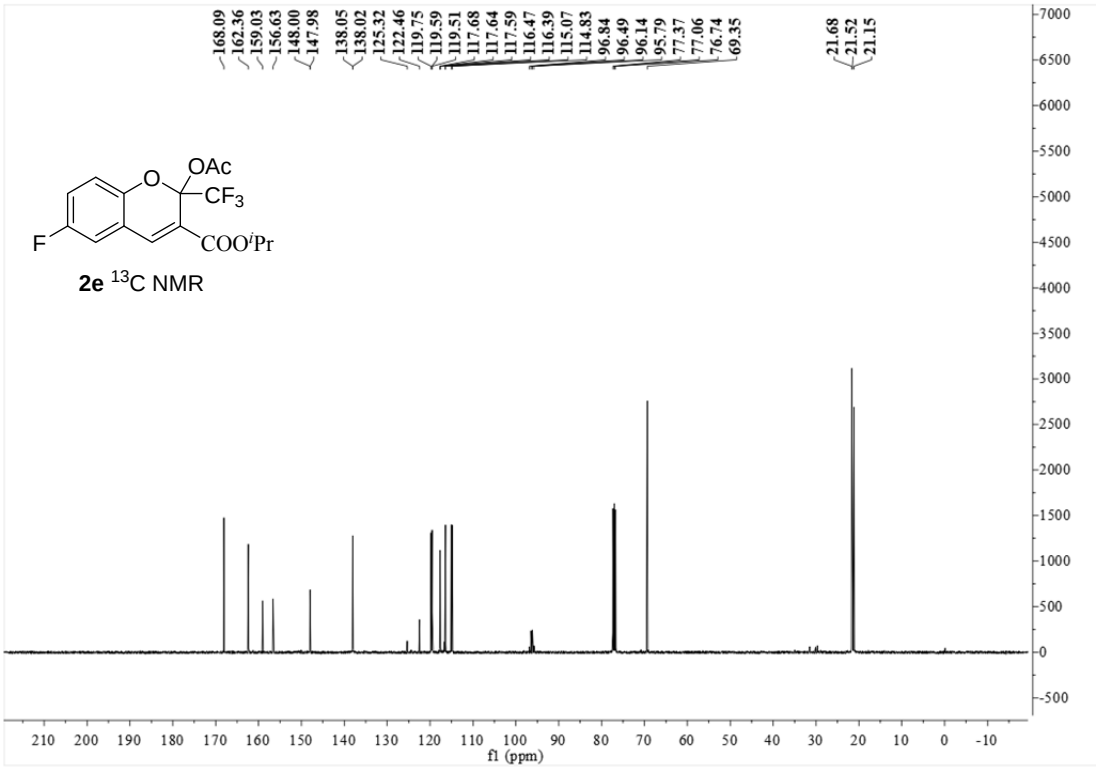

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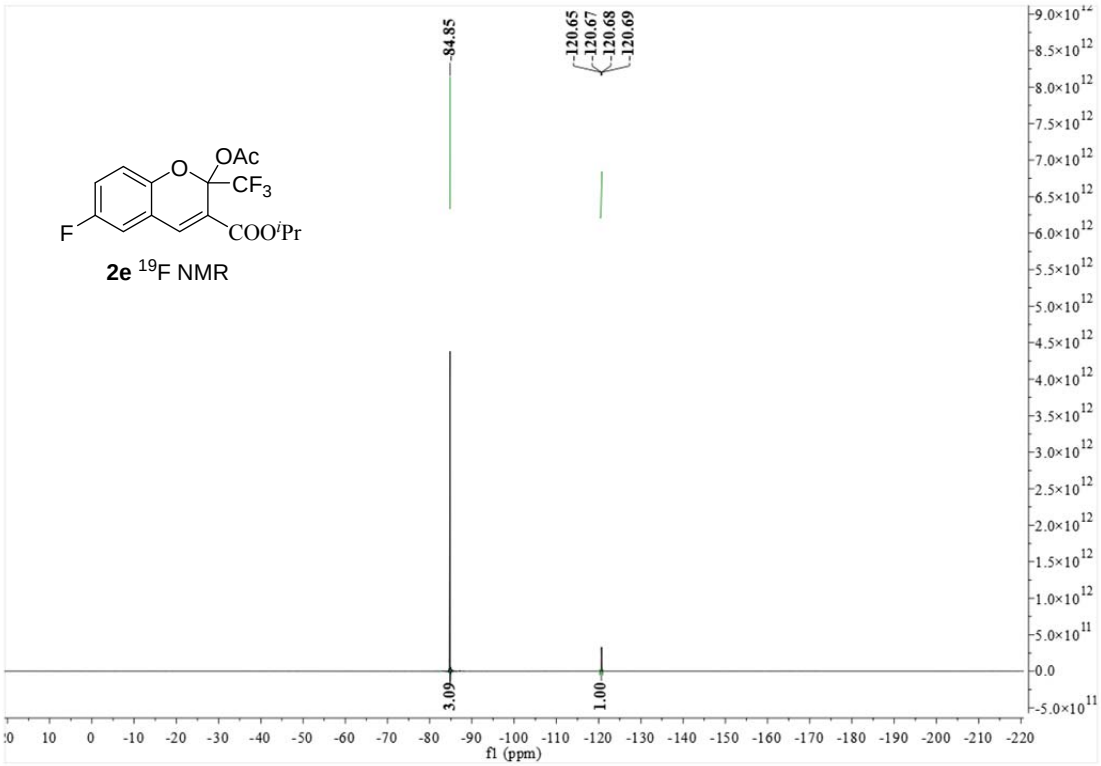
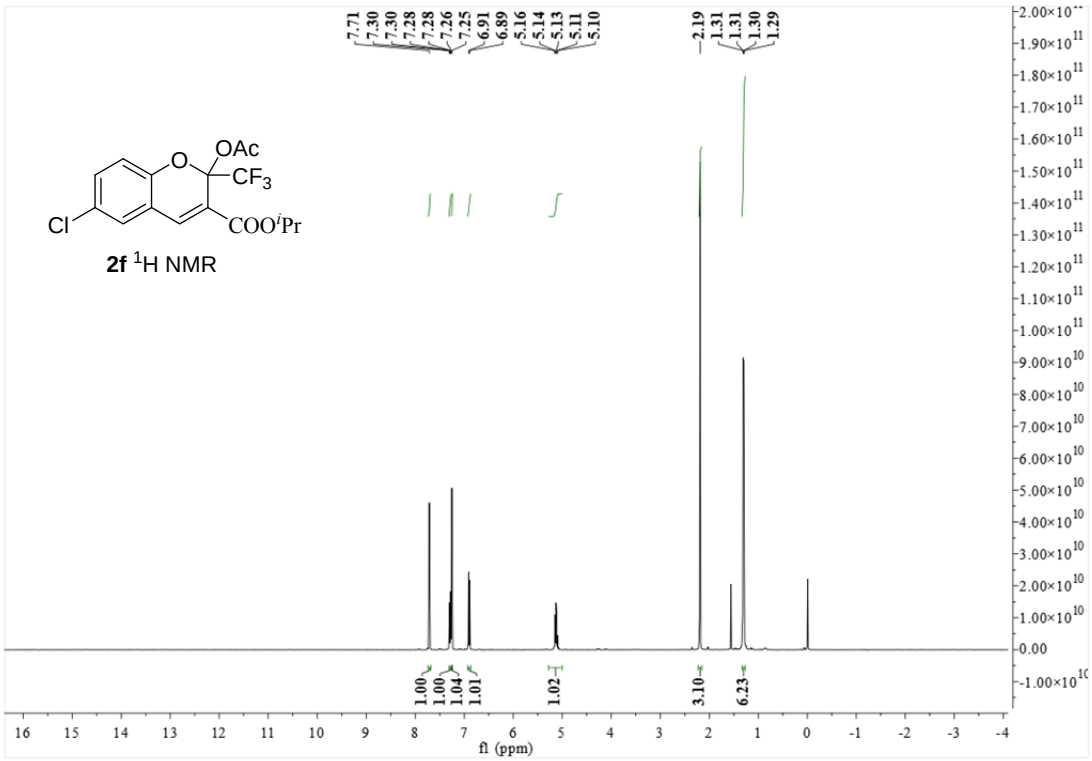


2e ^{19}F NMR



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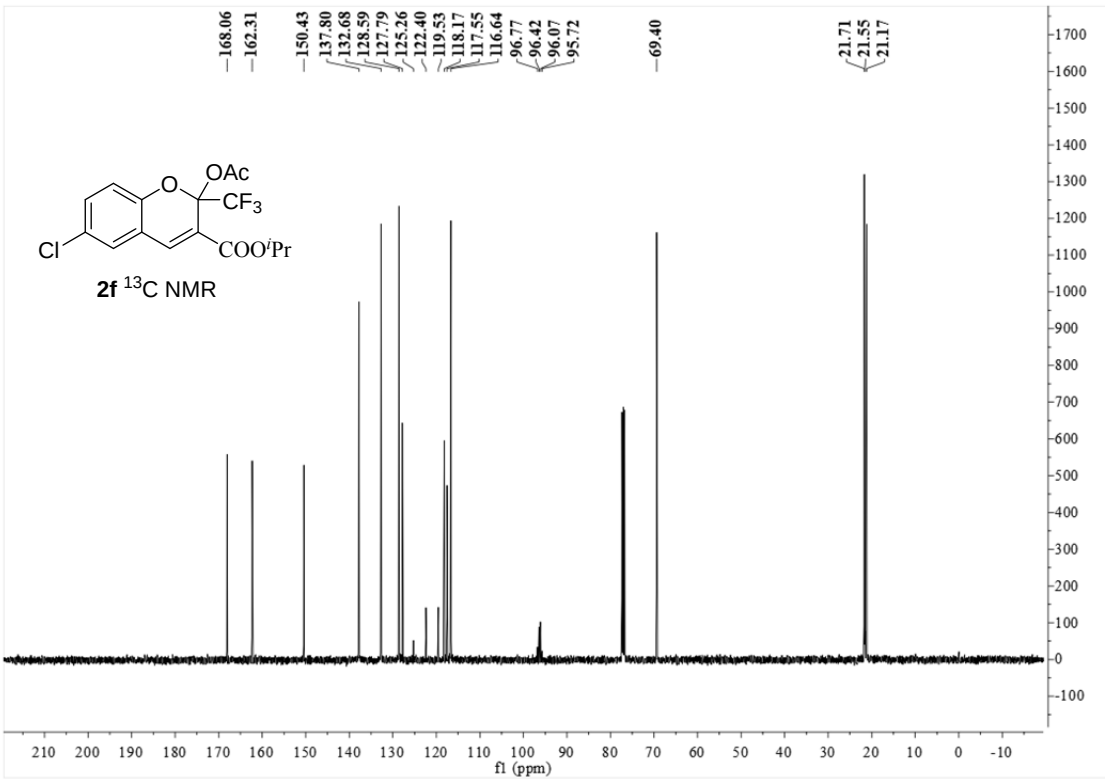
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119.53
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117.55
116.64
96.77
96.42
96.07
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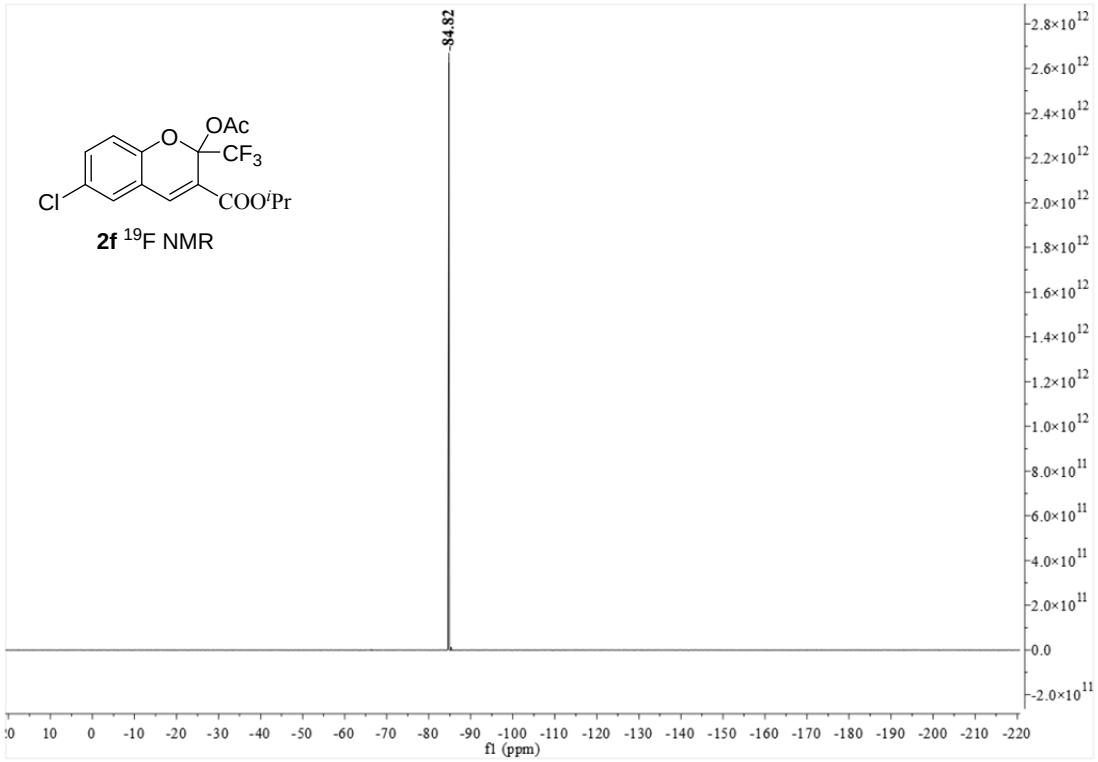
21.71
21.55
21.17
OAc
O
CF3
Cl
COOiPr
2f 13C NMR
f1 (ppm)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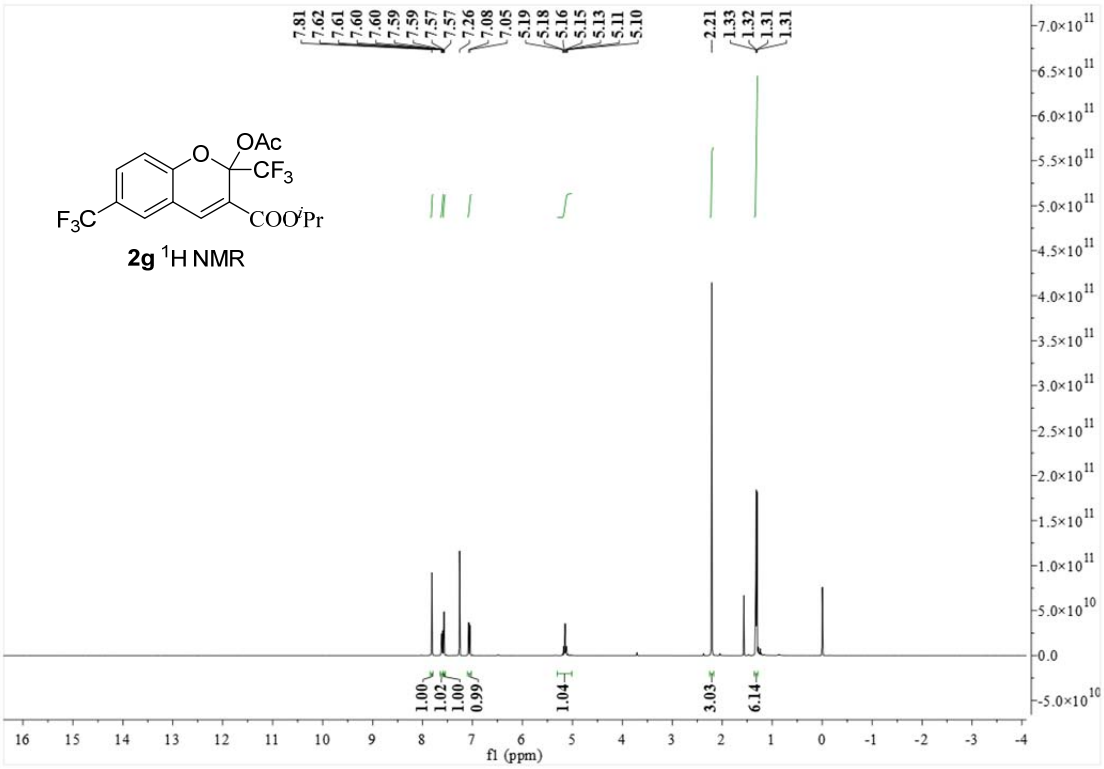
CF3
Cl
COOiPr
2f 19F NMR
f1 (ppm)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5.18
5.16
5.15
5.13
5.11
5.10
2.21
1.33
1.32
1.31
1.31
OAc
O
CF3
F3C
COOiPr
2g 1H NMR
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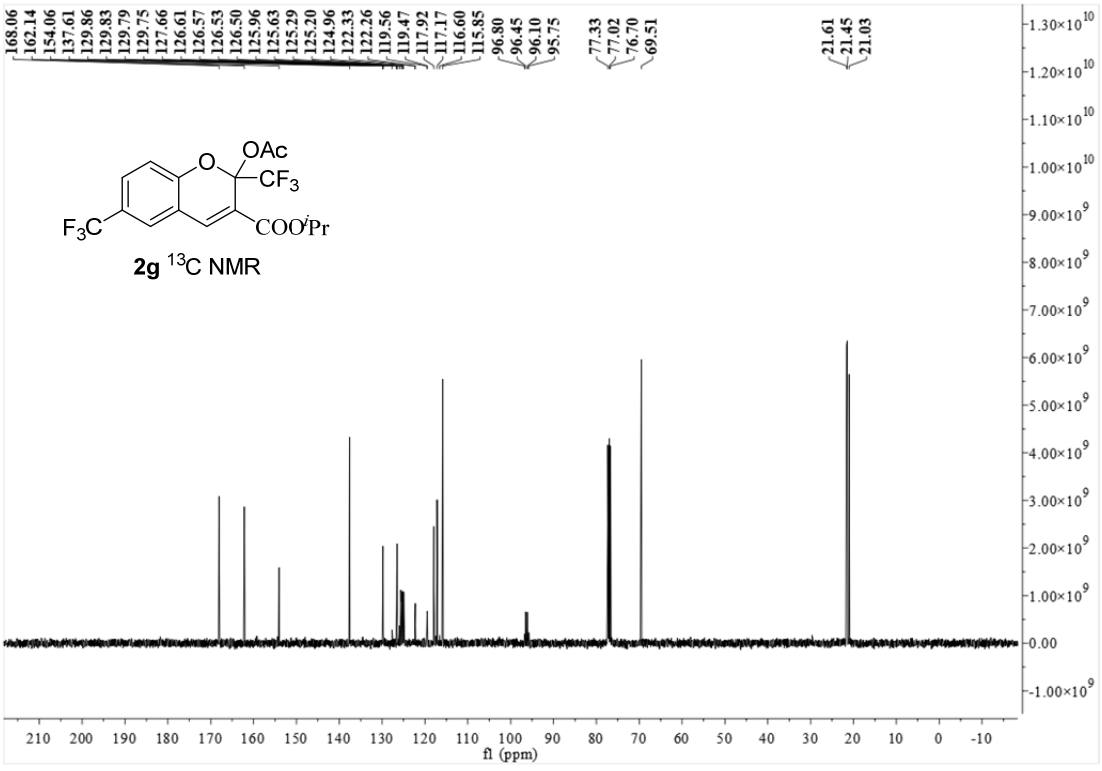
1.00
0.99
1.04
3.03
6.14
fl (ppm)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125.63
125.29
125.20
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122.33
122.26
119.56
119.47
117.92
117.17
116.60
115.85
96.80
96.45
96.10
95.75
77.33
77.02
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F3C
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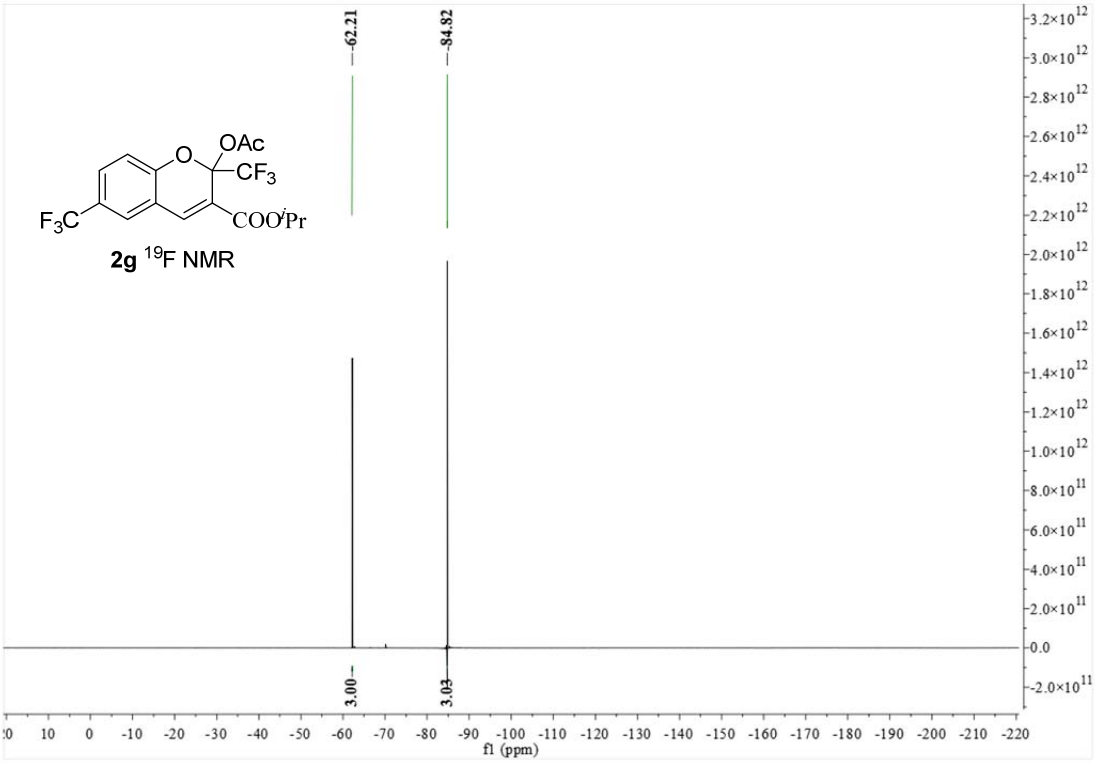
2g 13C NMR
fl (ppm)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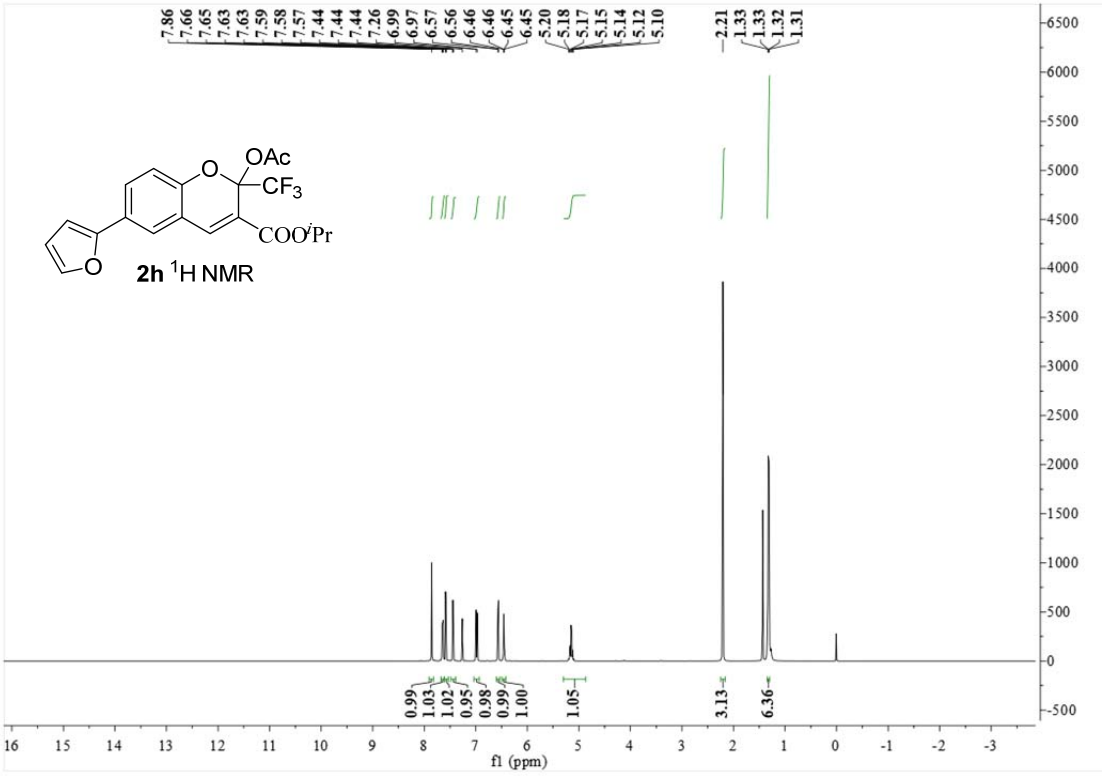
COOiPr
2g 19F NMR
3.00
3.03
f1 (ppm)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6.97
6.57
6.56
6.46
6.46
6.45
6.45
5.20
5.18
5.17
5.15
5.14
5.12
5.10
2.21
1.33
1.33
1.32
1.31
OAc
CF3
COOiPr
2h 1H NMR
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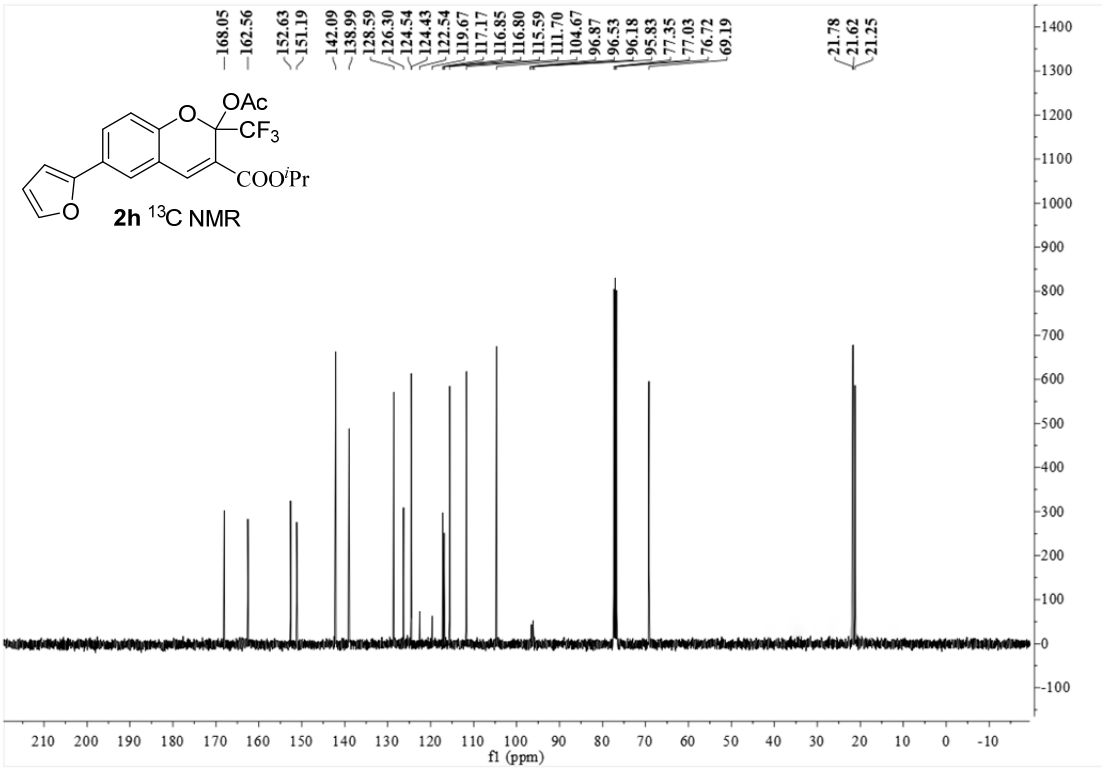
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77.35
77.03
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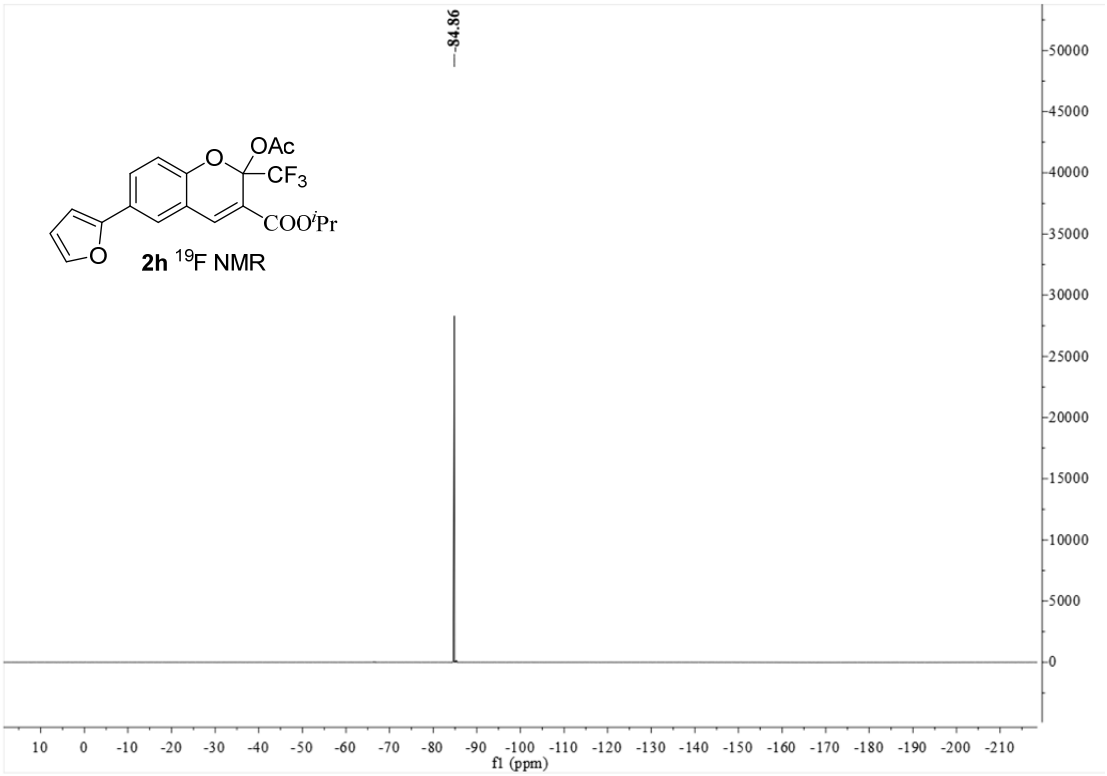
CF3
COO'Pr
O
O
2h 13C NMR
f1 (ppm)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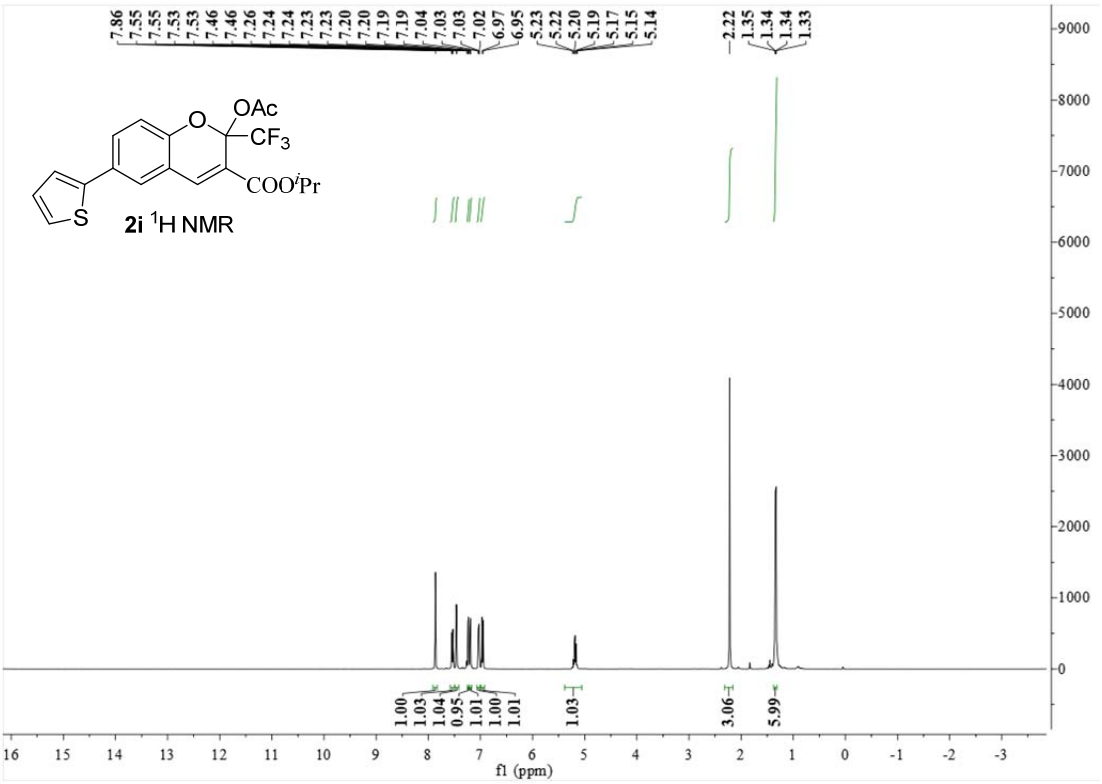
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7.19
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7.03
7.03
7.02
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5.23
5.22
5.20
5.19
5.17
5.15
5.14
2.22
1.35
1.34
1.34
1.33
OAc
CF3
COOiPr
S
2i 1H NMR
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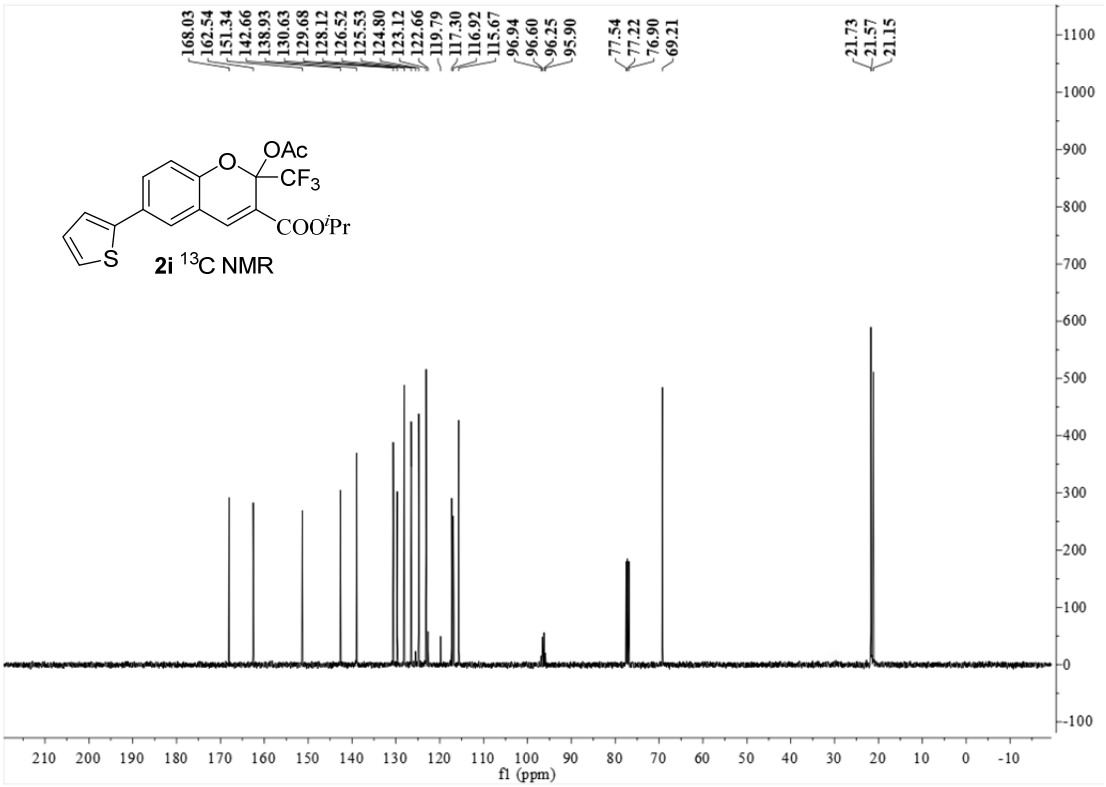
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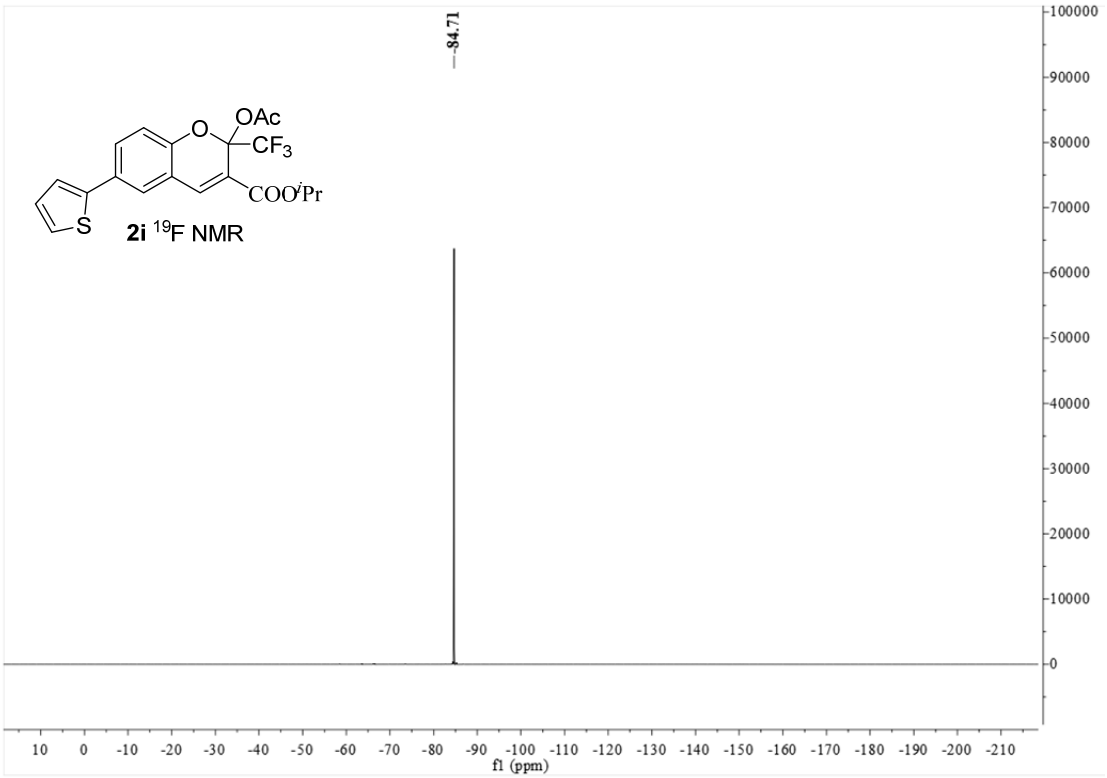
f1 (ppm)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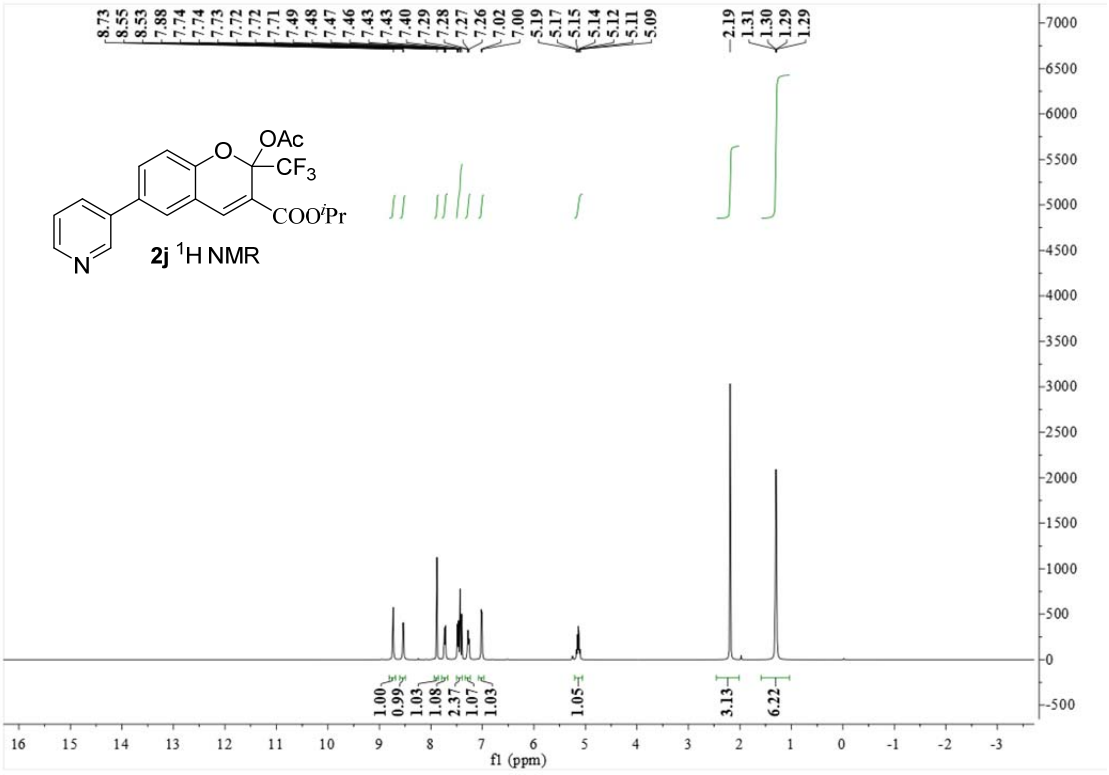
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7.72
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7.48
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7.46
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7.43
7.40
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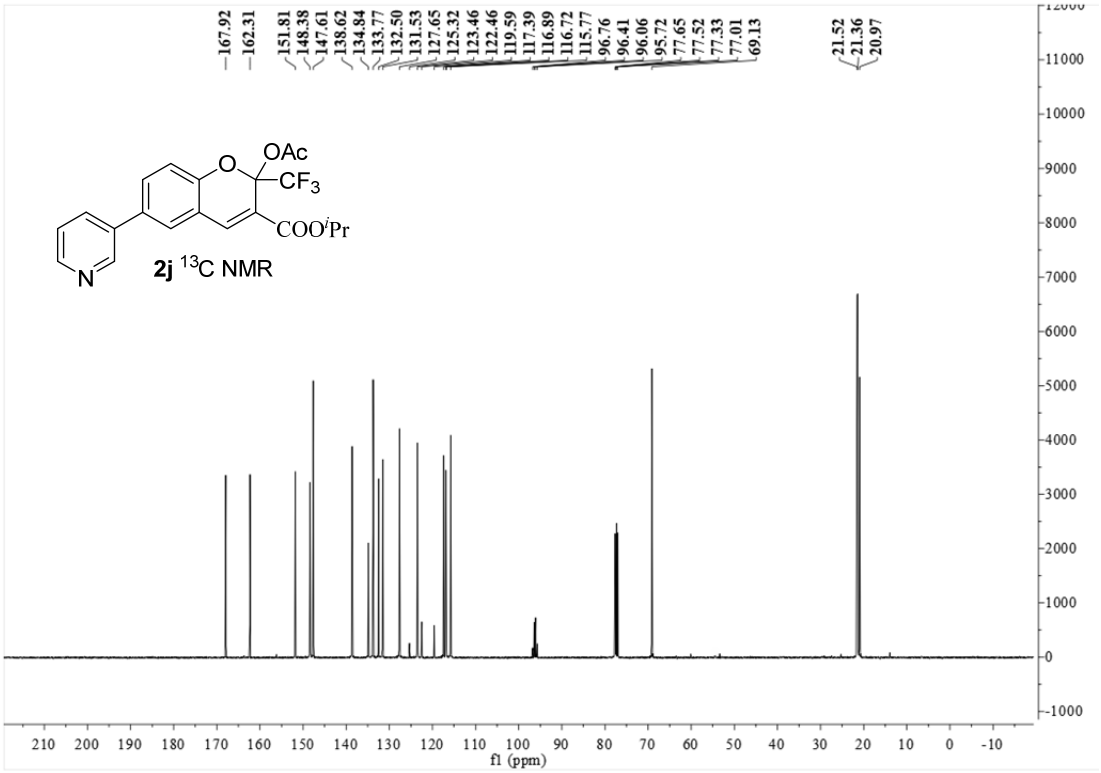
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CF3
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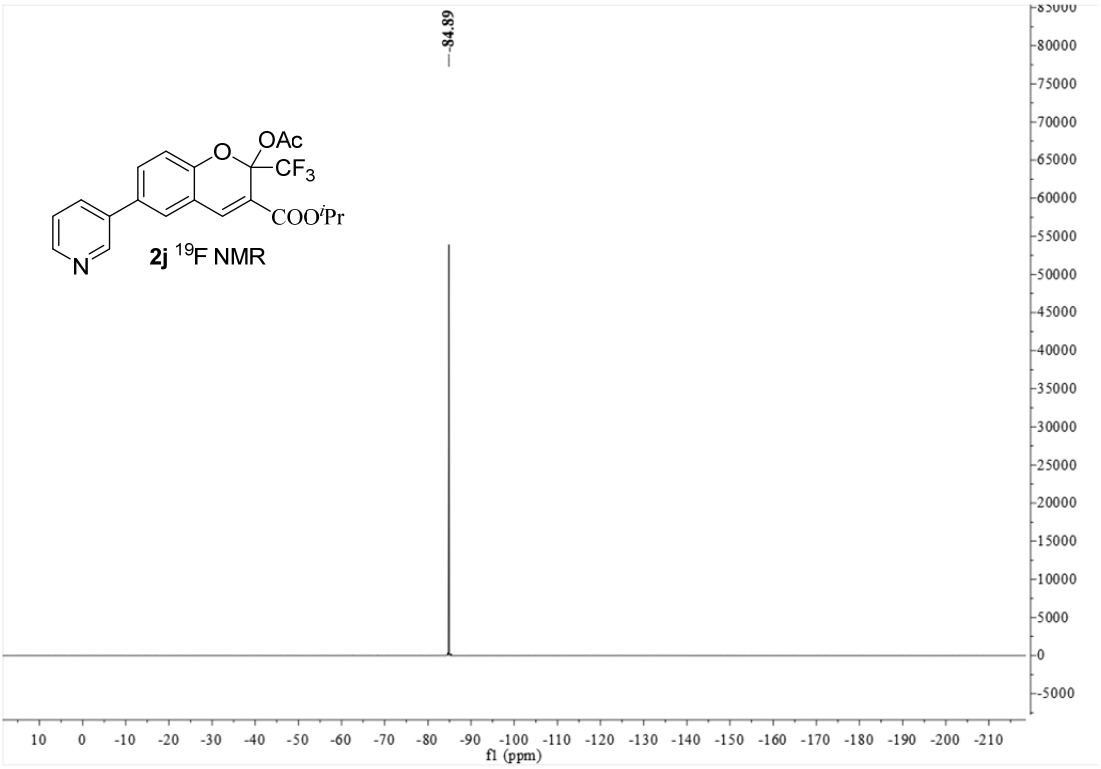
fl (ppm)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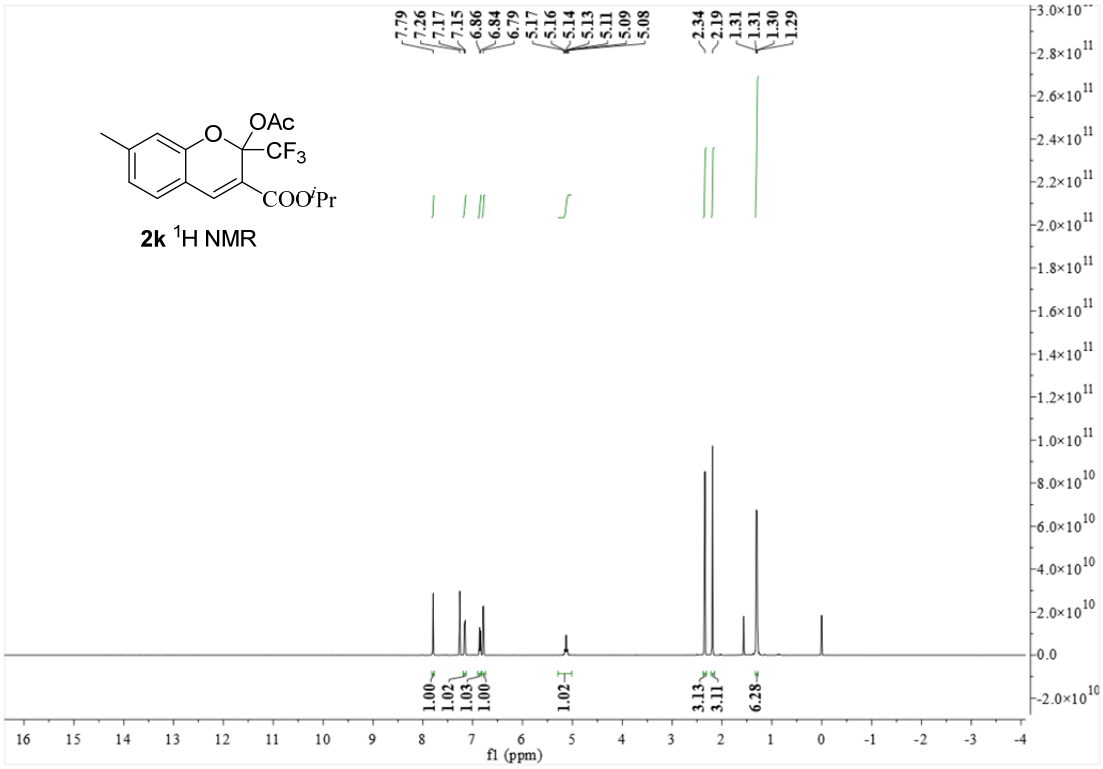
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2.19
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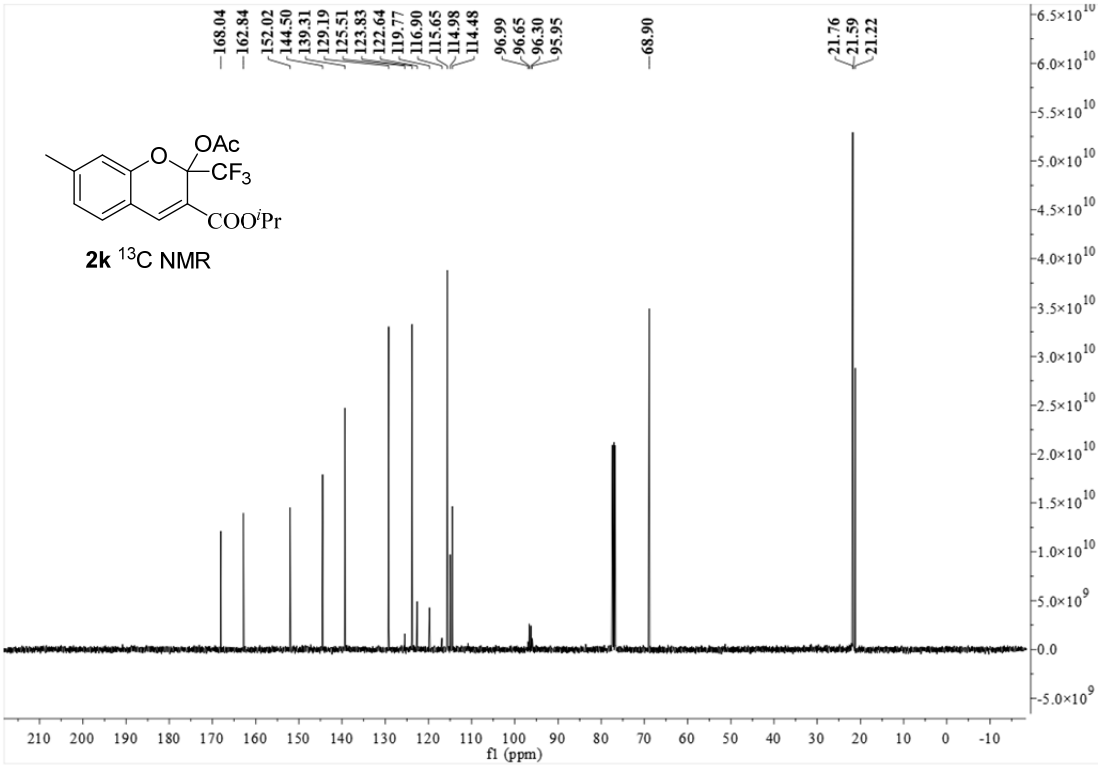
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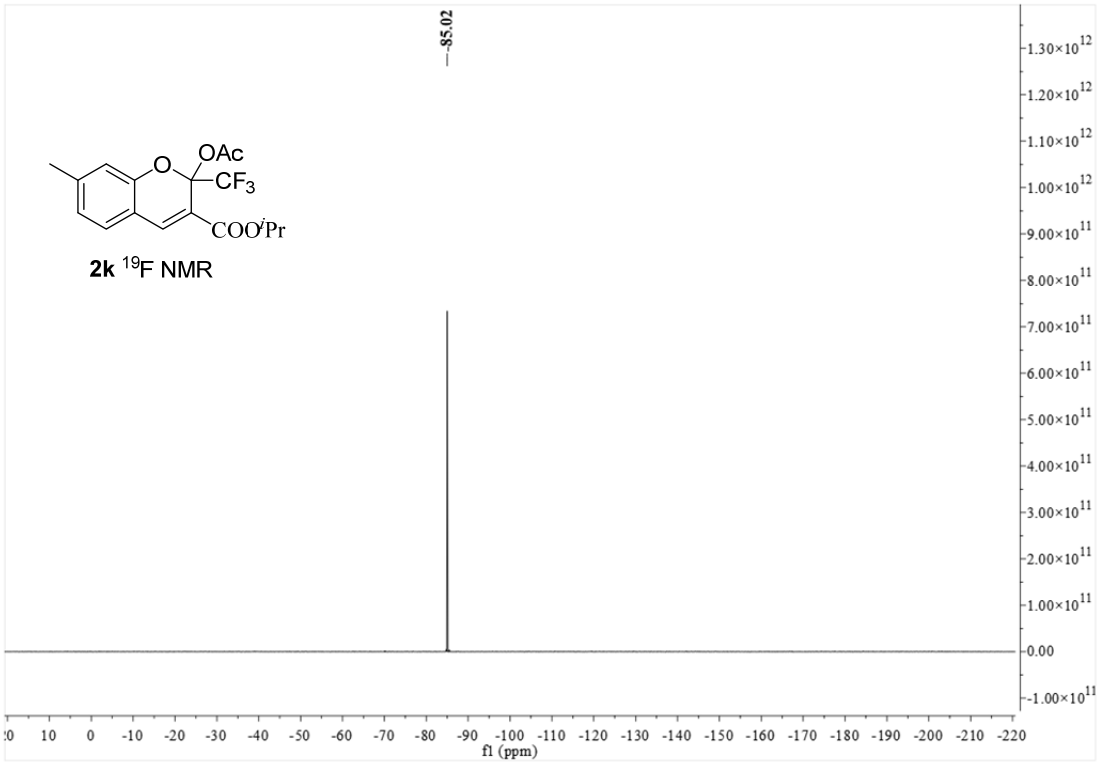

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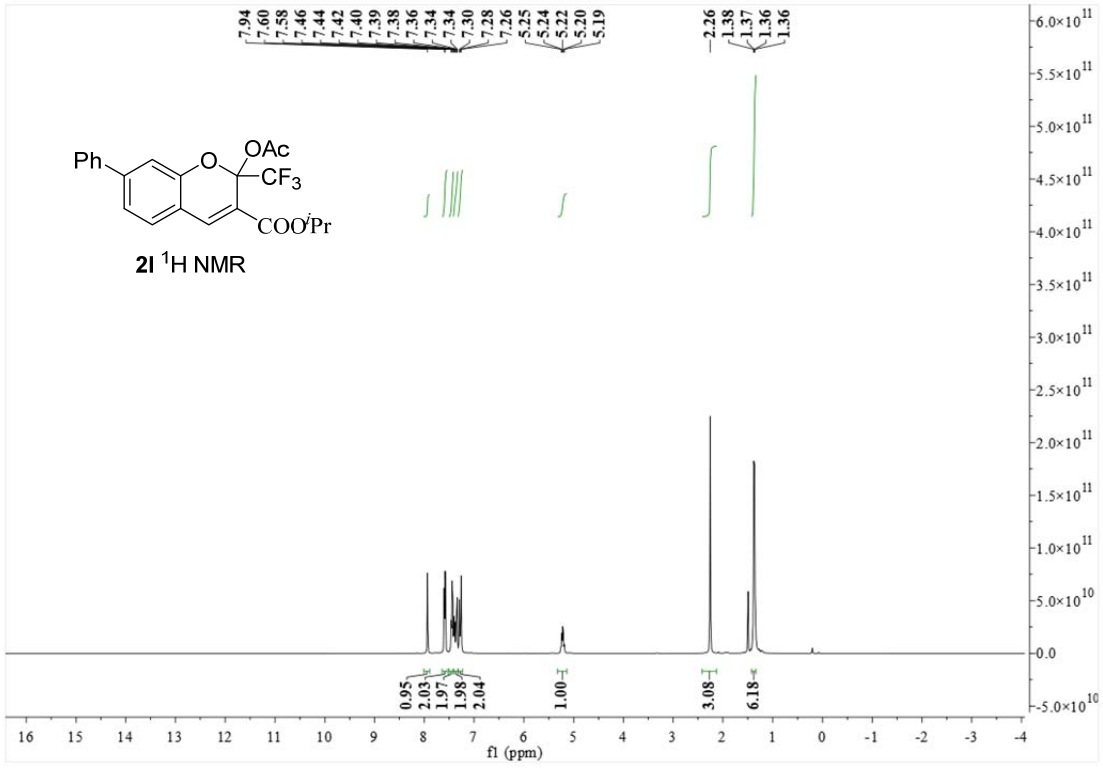

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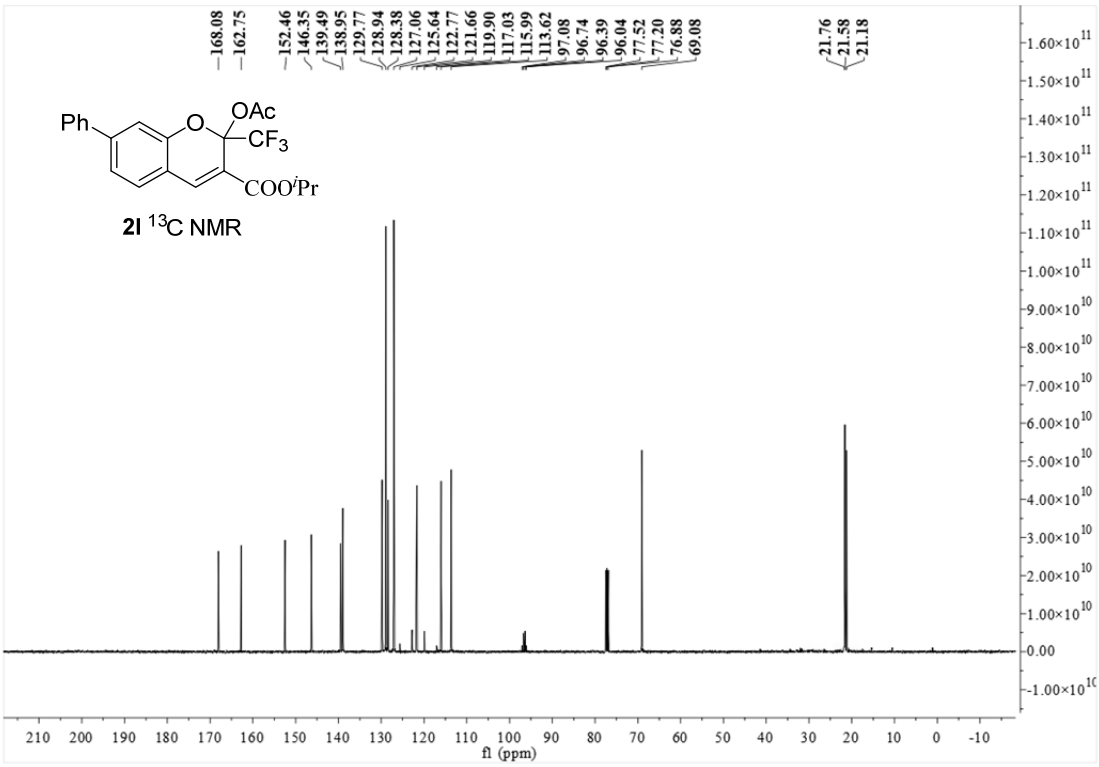
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77.52
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Ph
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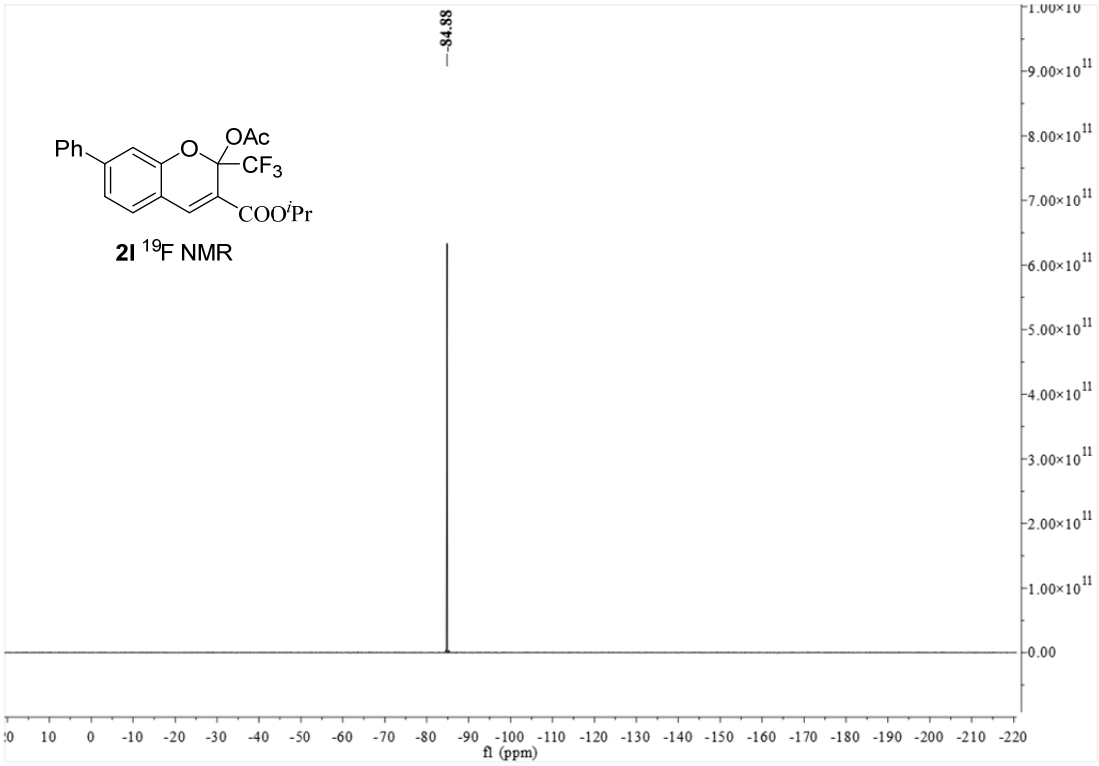
CF3
COO'Pr
2l 13C NMR
f1 (ppm)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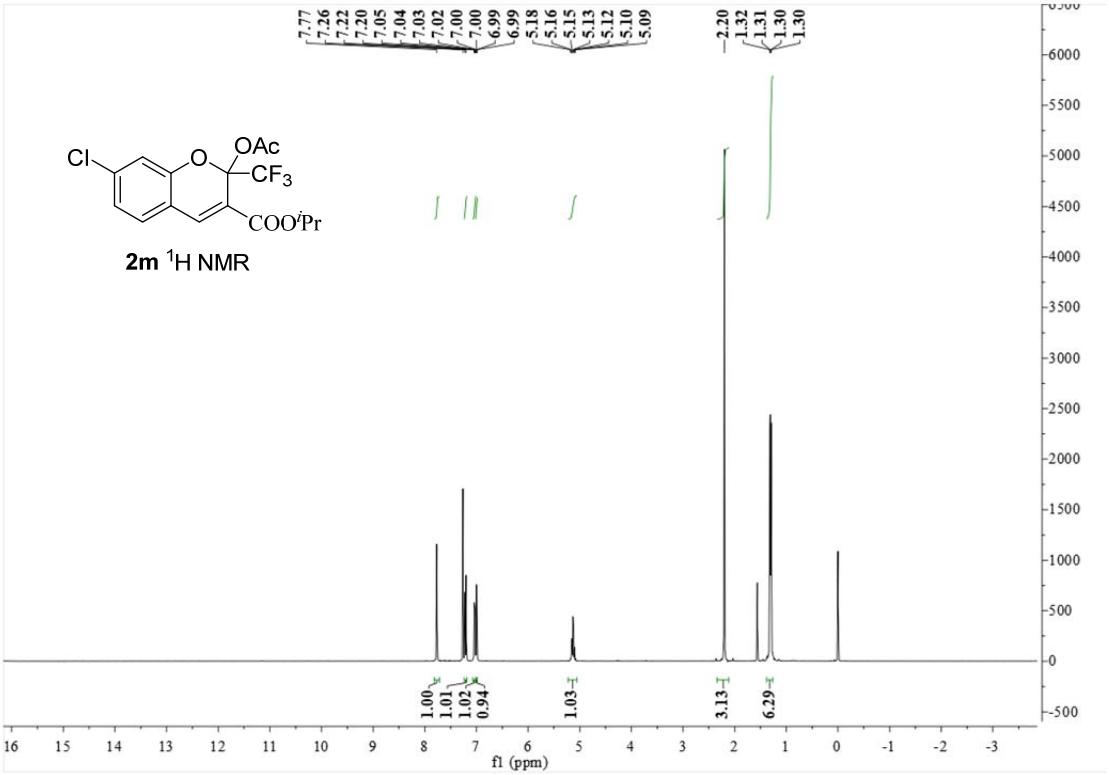
f1 (ppm)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CF3
COOiPr
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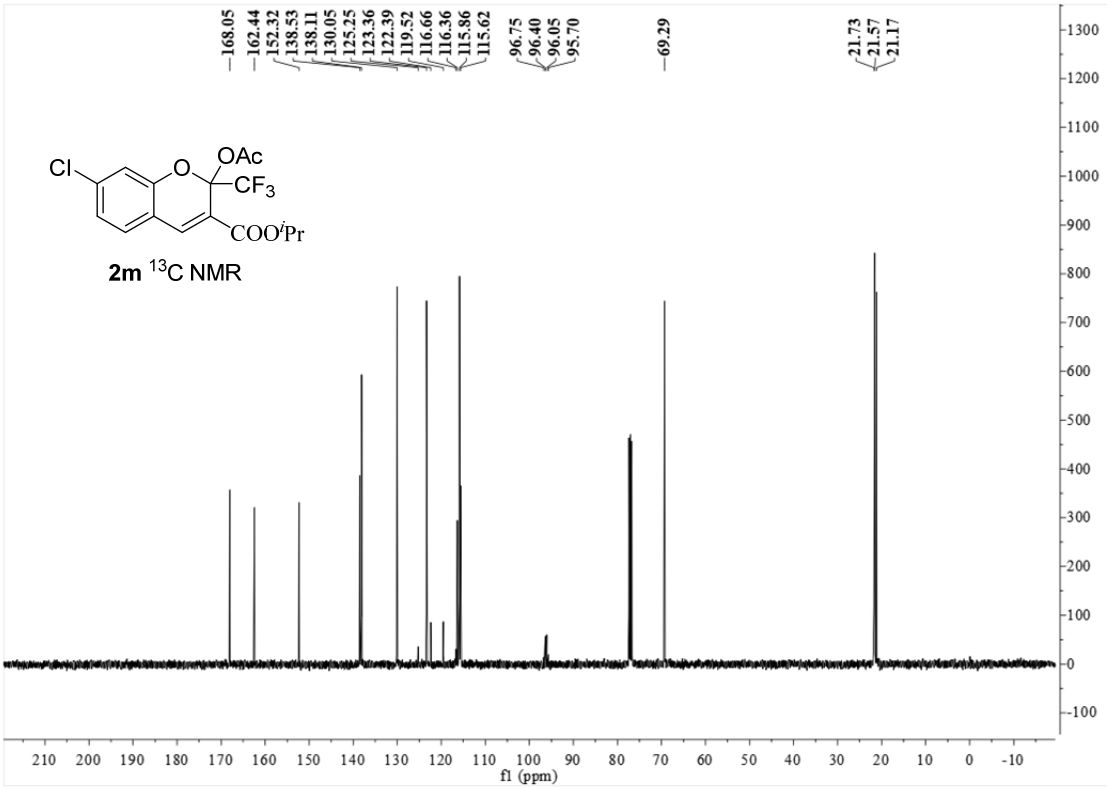
1.00
1.01
1.02
0.94
1.03
3.13
6.29
f1 (ppm)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115.86
115.62
96.75
96.40
96.05
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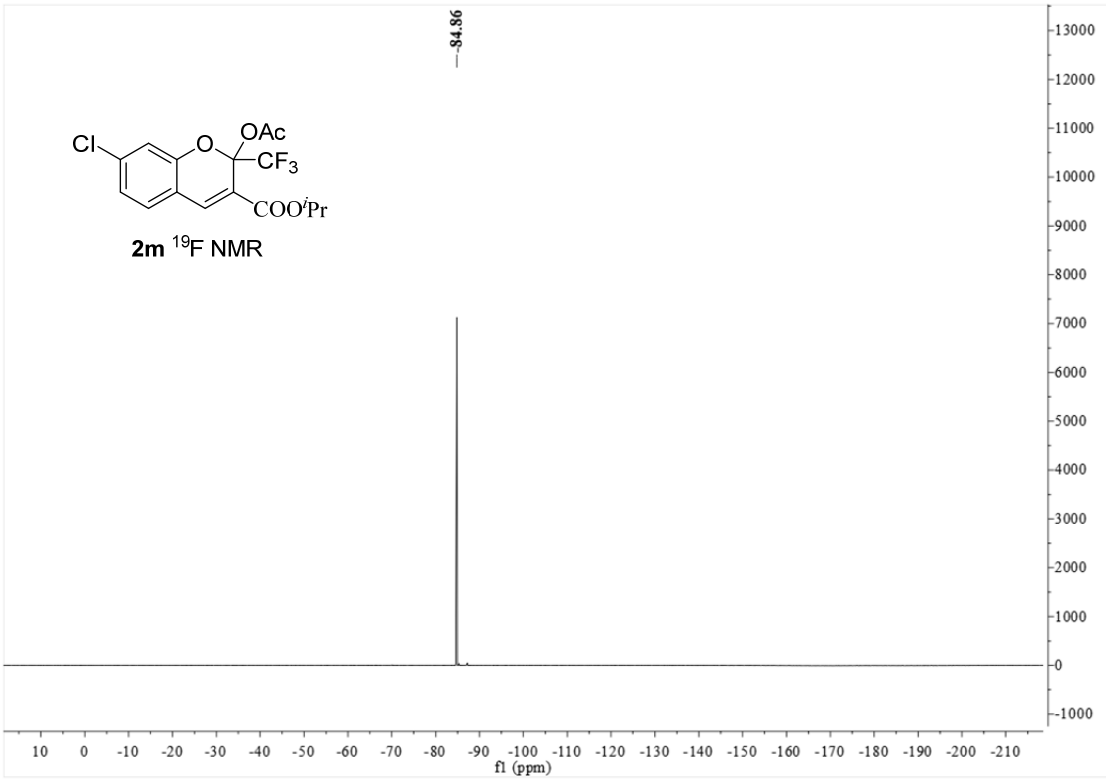
21.73
21.57
21.17
Cl
O
OAc
CF3
COOiPr
2m 13C NMR
f1 (ppm)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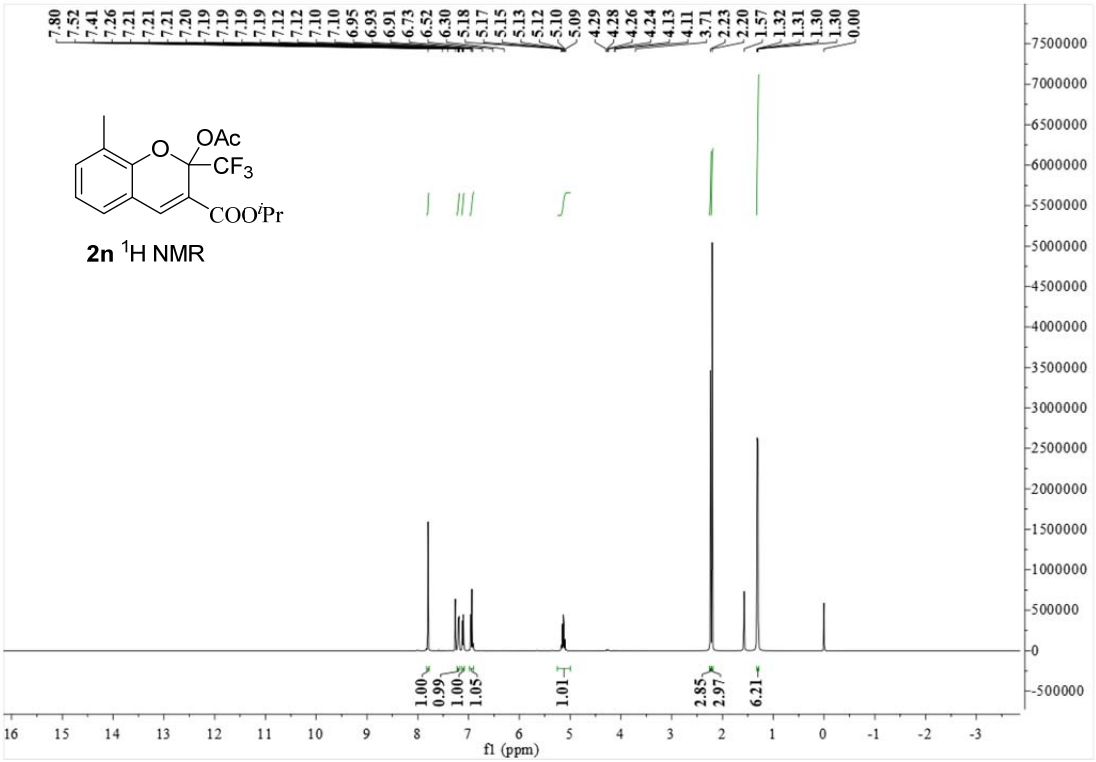
fl (ppm)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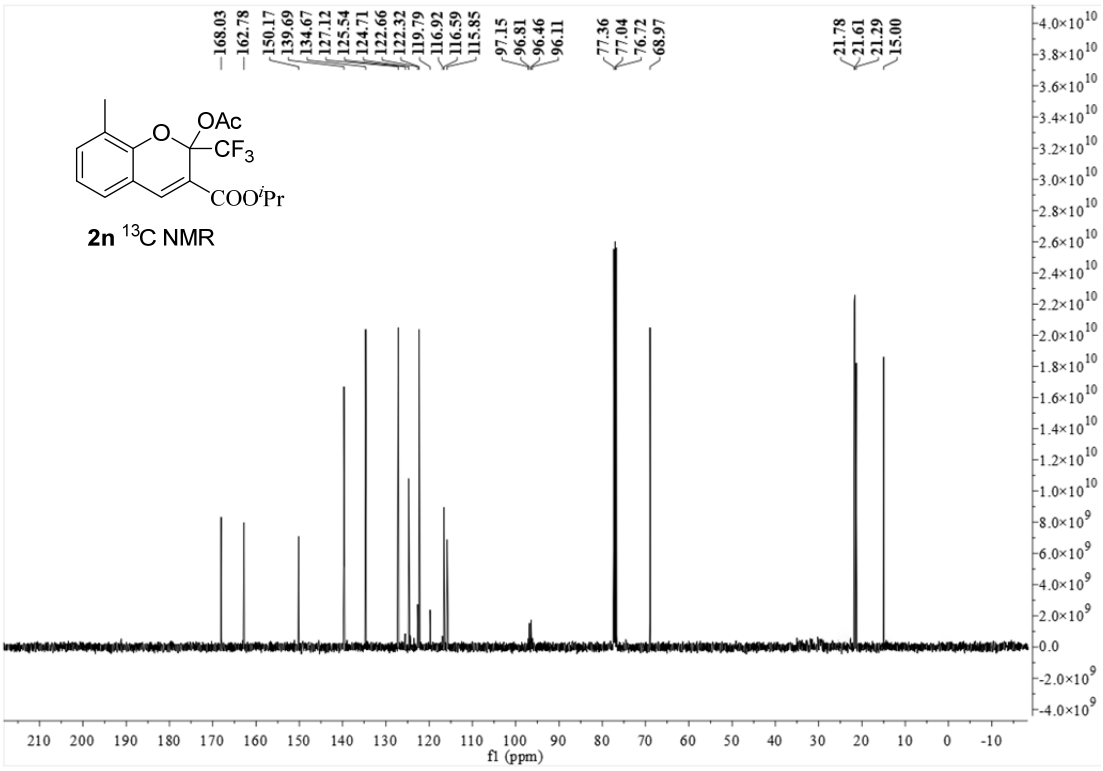
7.12
7.10
7.10
6.95
6.93
6.91
6.73
6.52
6.30
5.18
5.17
5.15
5.13
5.12
5.10
5.09
4.29
4.28
4.26
4.24
4.13
4.11
3.71
2.23
2.20
1.57
1.32
1.31
1.30
1.30
0.00
O
OAc
CF3
COOiPr
2n 1H NMR
1.00
0.99
1.00
1.05
1.01
2.85
2.97
6.21
fl (ppm)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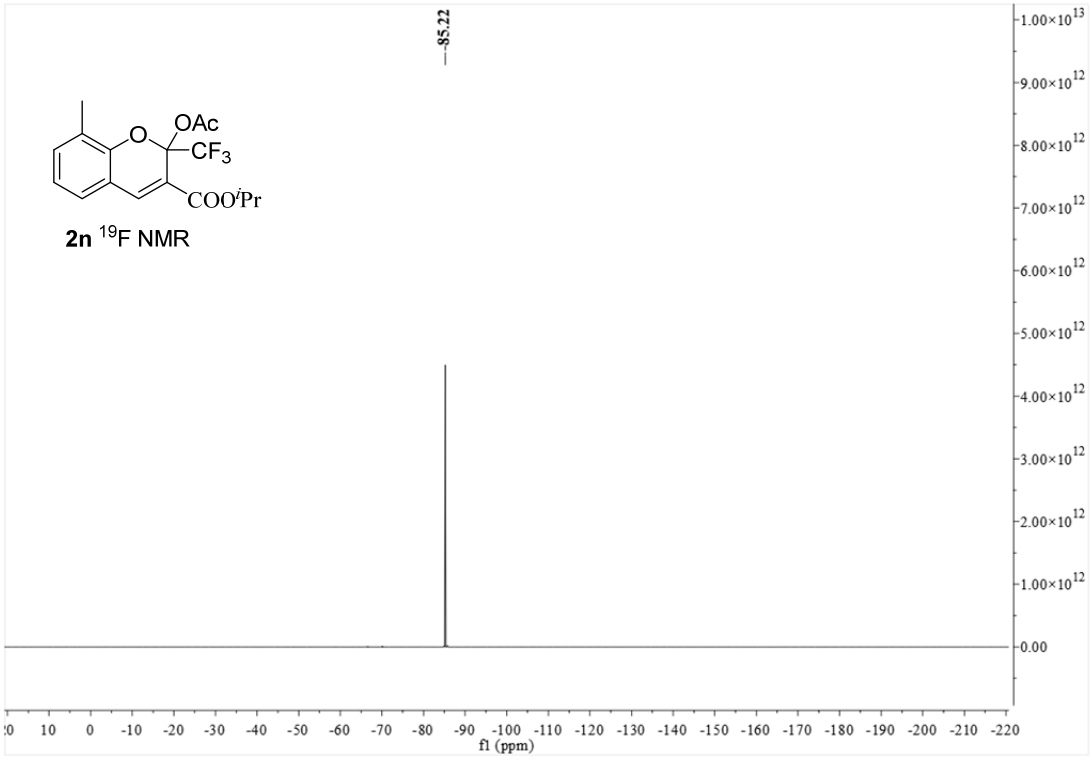
CF3
COOiPr
2n 13C NMR
f1 (ppm)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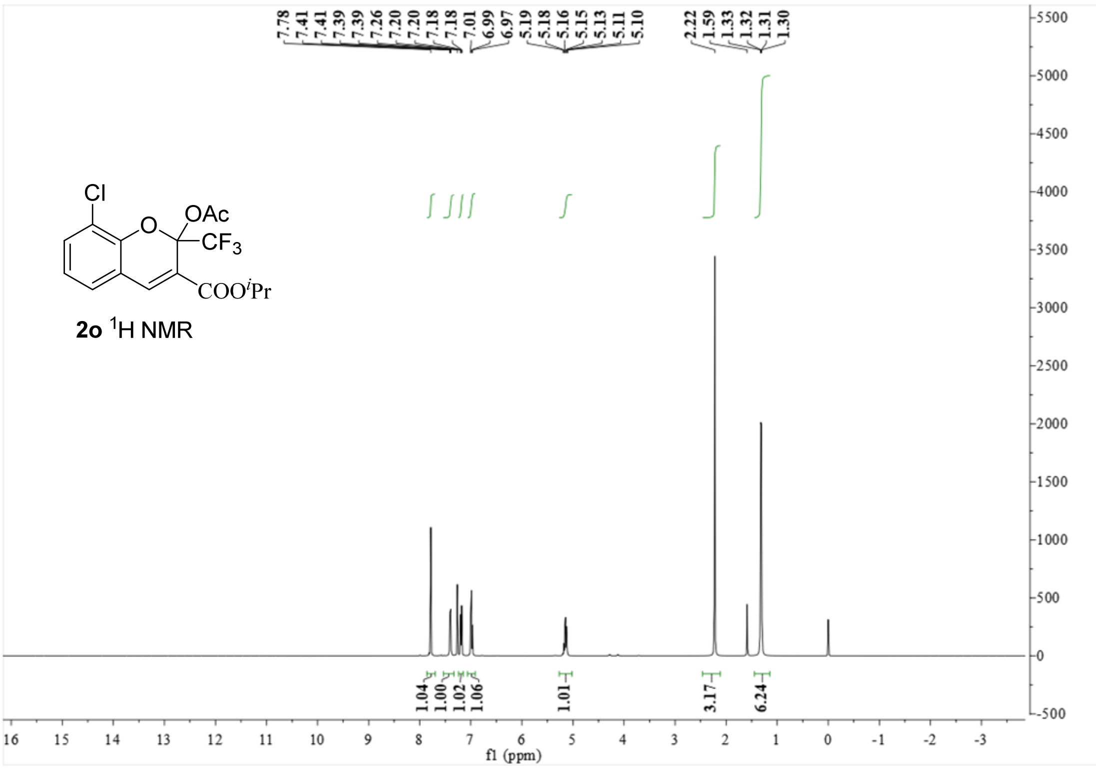
f1 (ppm)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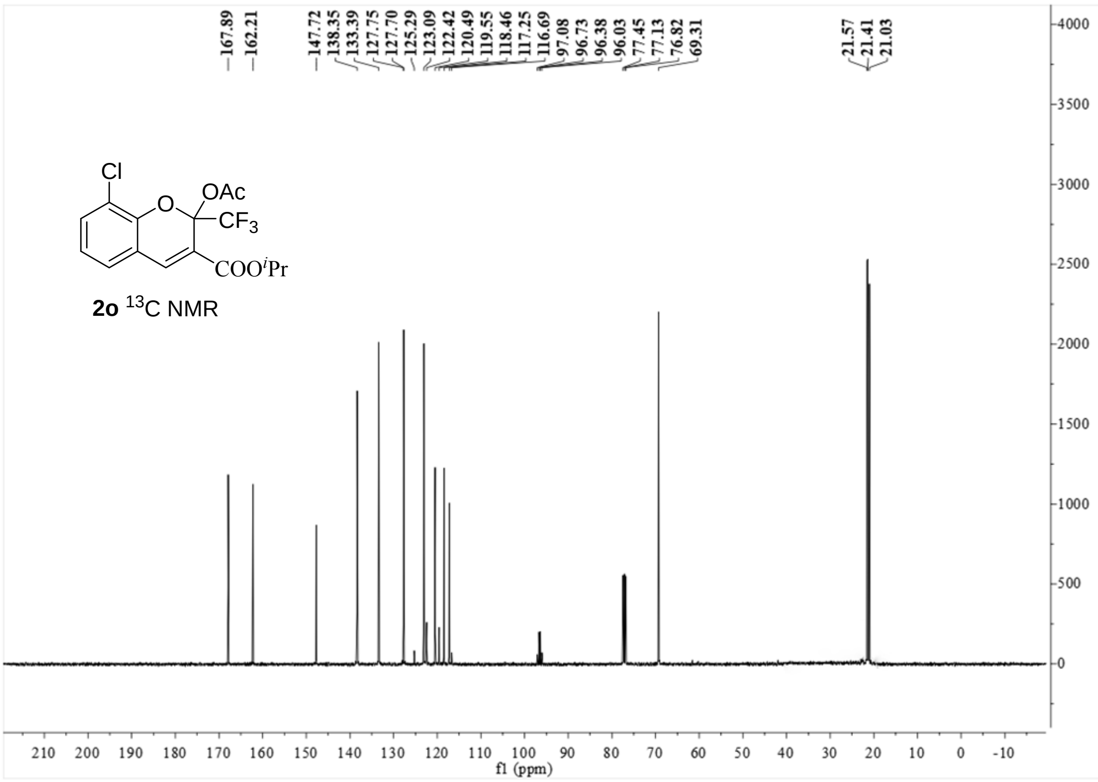
O
OAc
CF3
COOiPr
2o 1H NMR
1.04 1.00 1.02 1.06 1.01 3.17 6.24
f1 (ppm)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Cl
O
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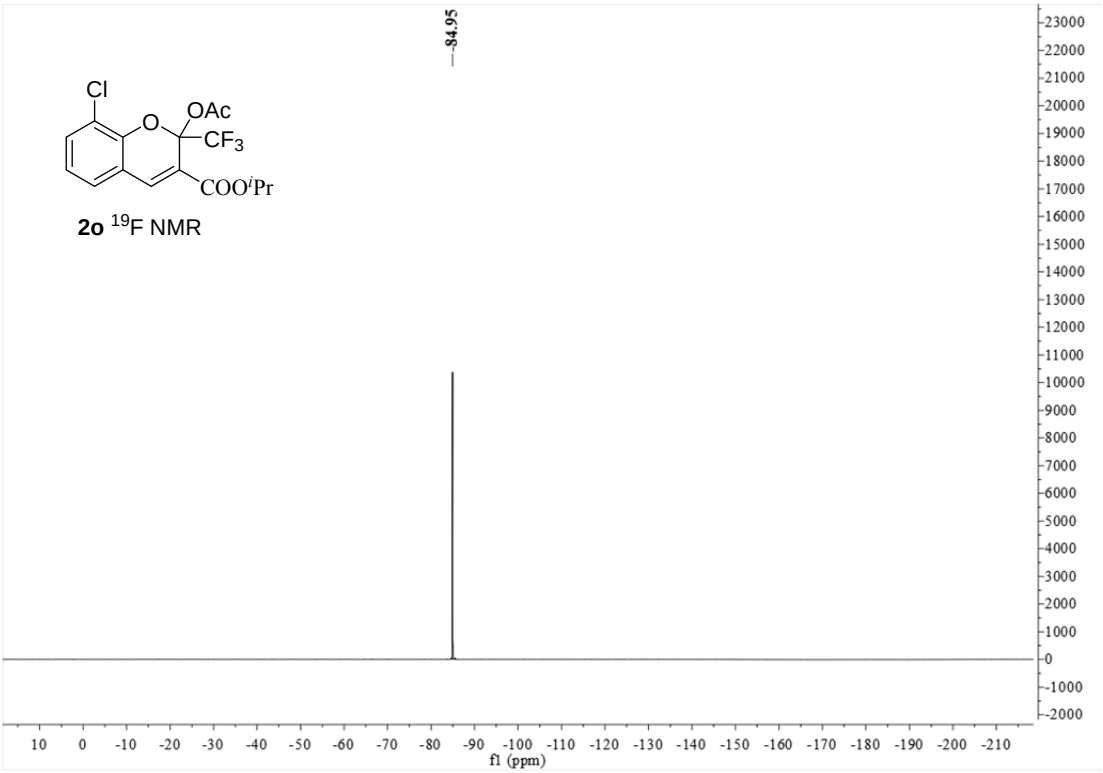
CF3
COOiPr
2o 13C NMR
f1 (ppm)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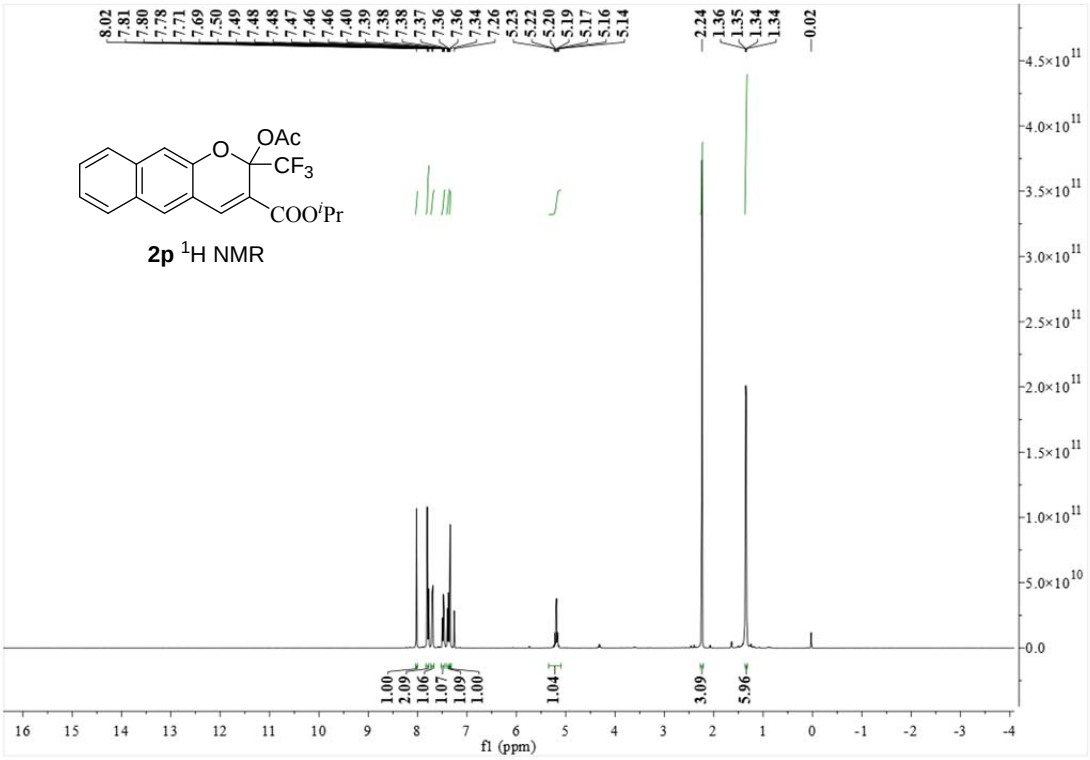
fl (ppm)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7.80
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7.71
7.69
7.50
7.49
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7.48
7.47
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7.46
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.34
7.26
5.23
5.22
5.20
5.19
5.17
5.16
5.14
2.24
1.36
1.35
1.34
1.34
0.02
OAc
O
CF3
COOiPr
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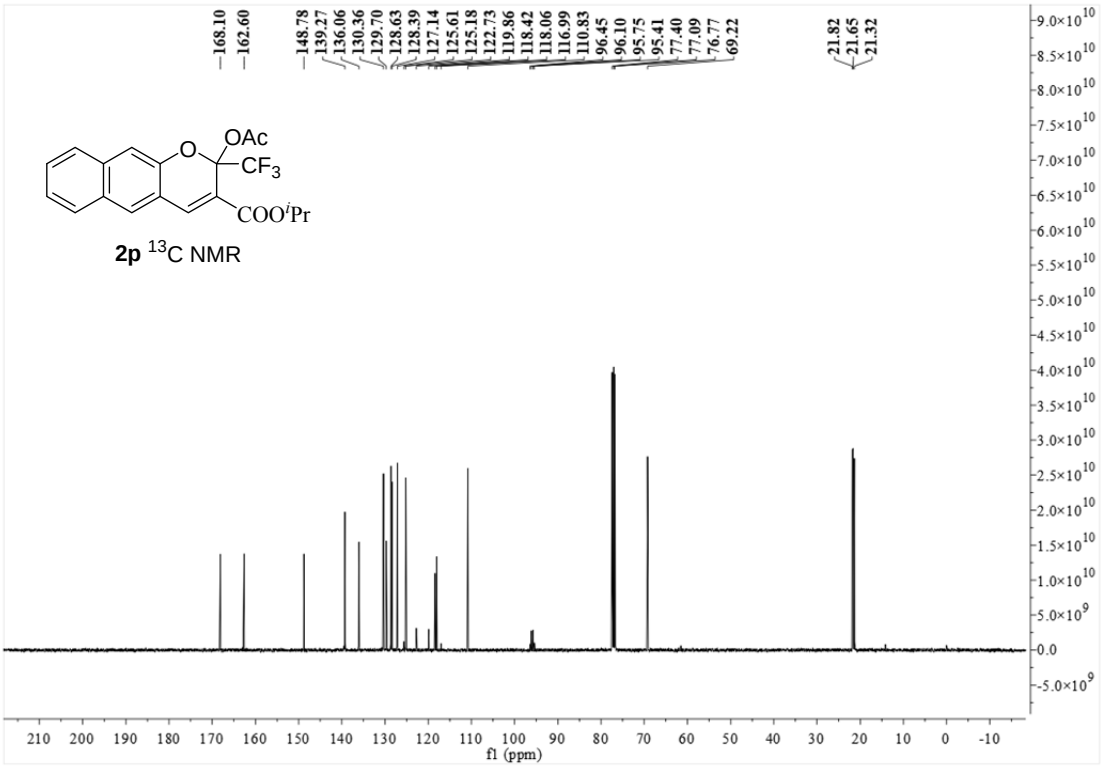
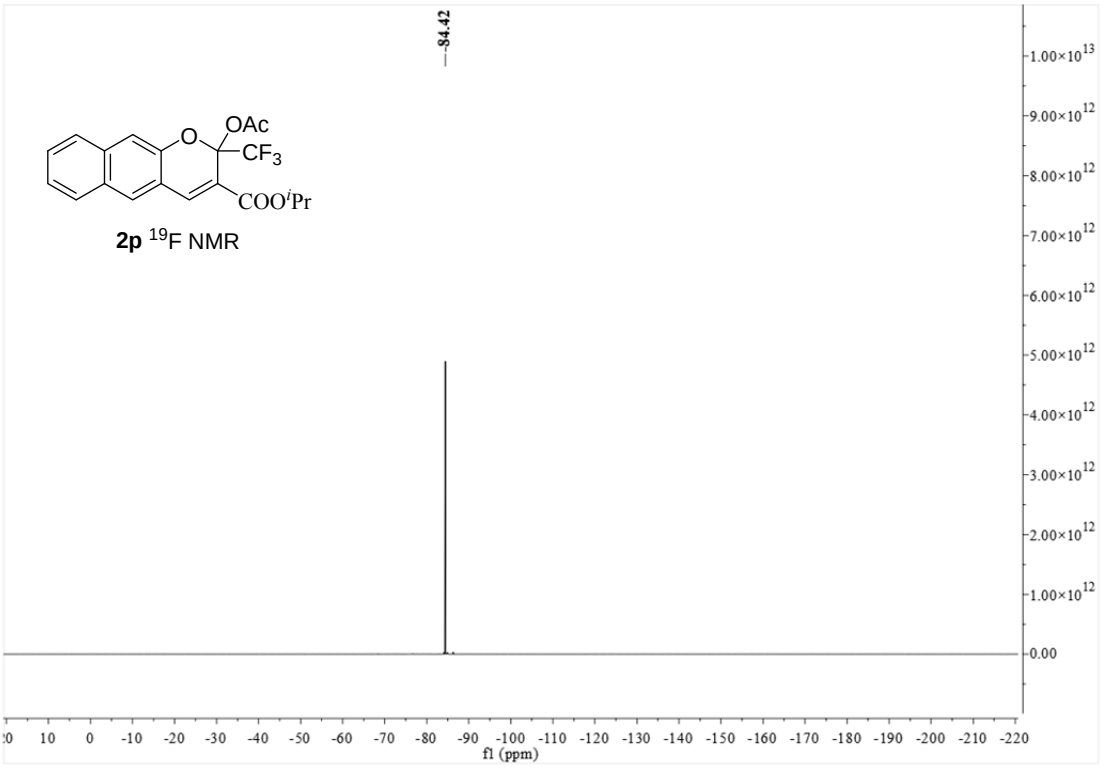
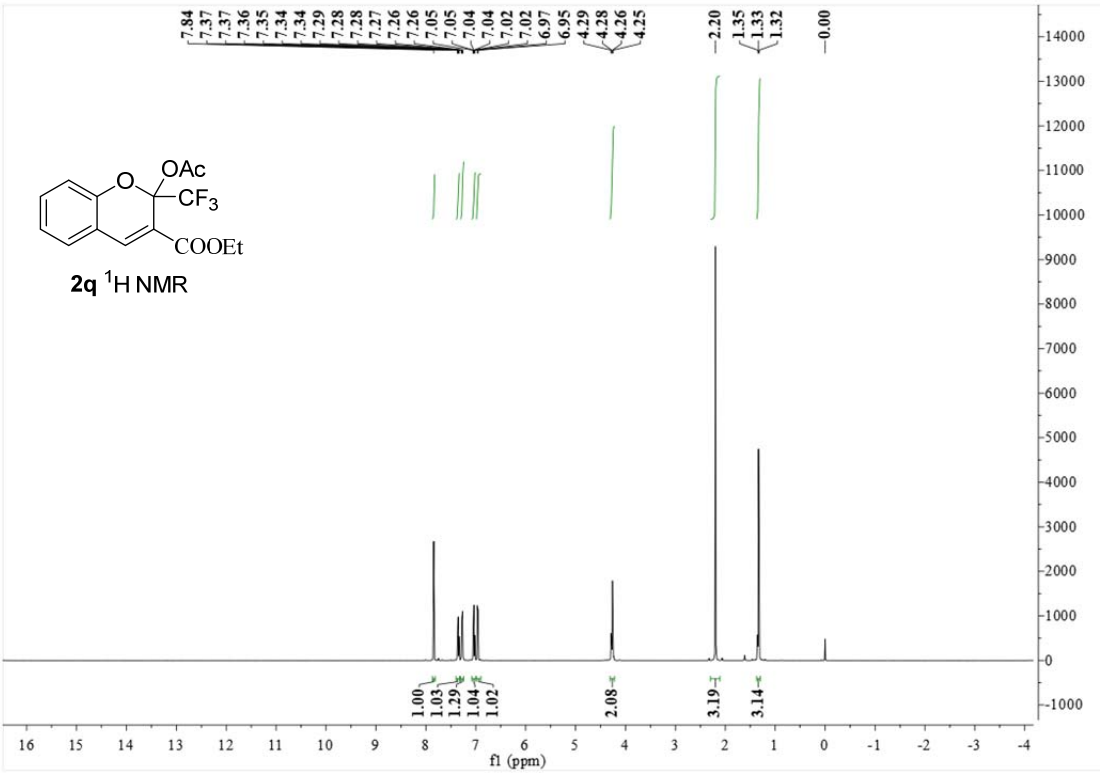
1.00
1.04
3.09
5.96
fl (ppm)



2p ^{13}C NMR



2p ^{19}F NMR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7.04
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7.02
7.02
6.97
6.95
4.29
4.28
4.26
4.25
2.20
1.35
1.33
1.32
0.00
OAc
CF3
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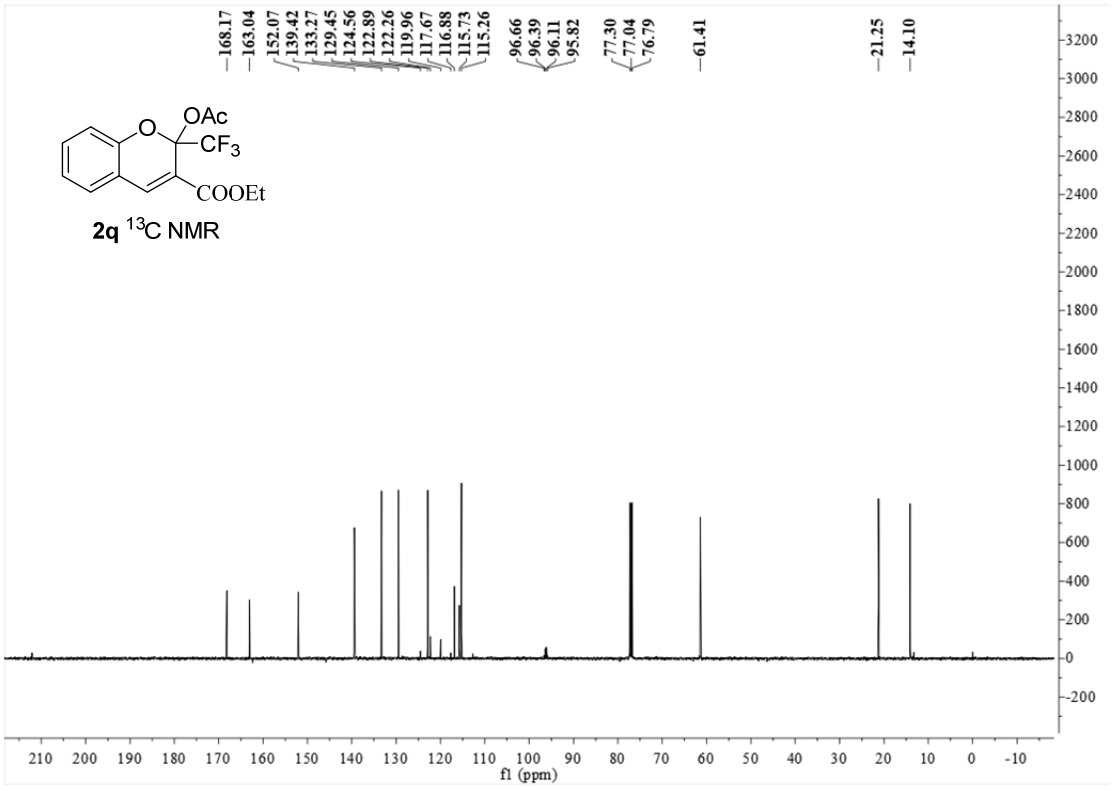
2q 1H NMR
1.00
1.03
1.29
1.04
1.02
2.08
3.19
3.14
f1 (ppm)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115.73
115.26
96.66
96.39
96.11
95.82
77.30
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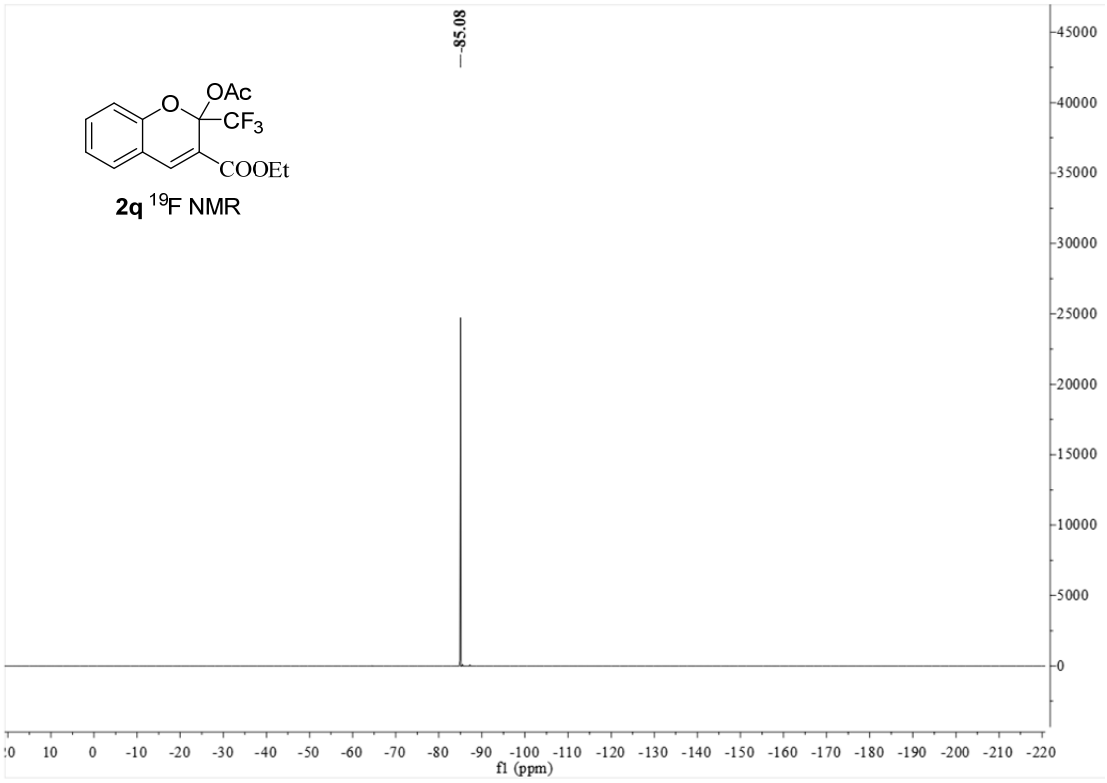
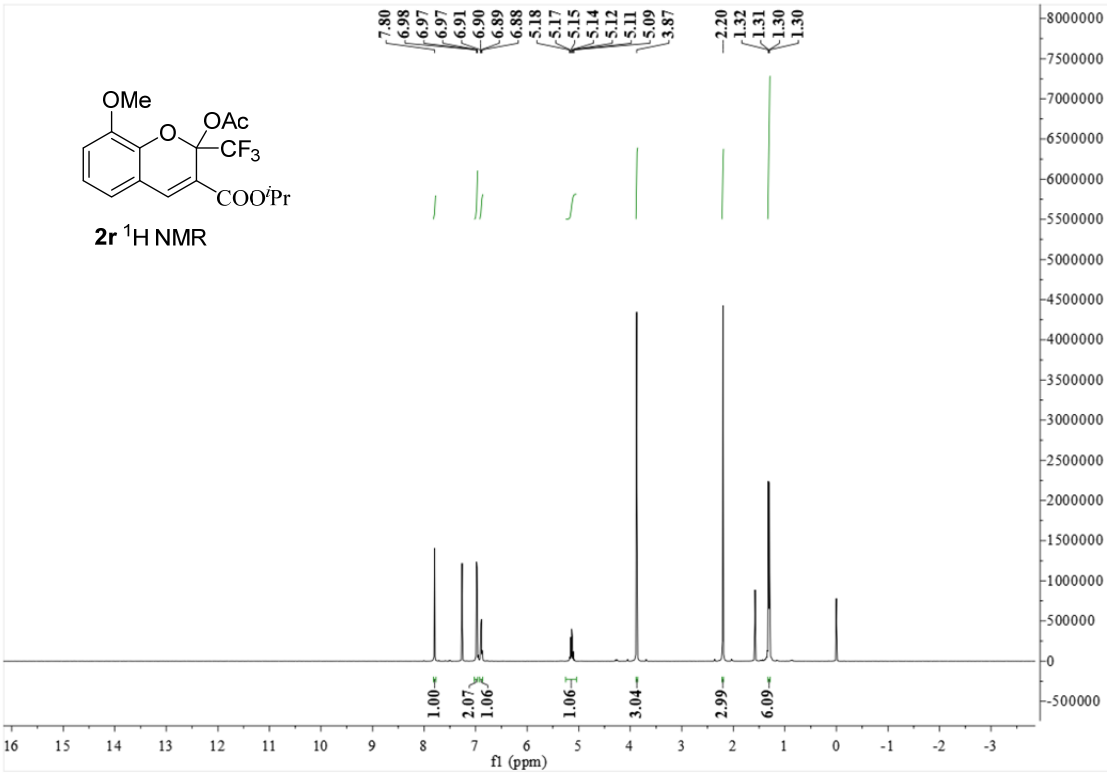
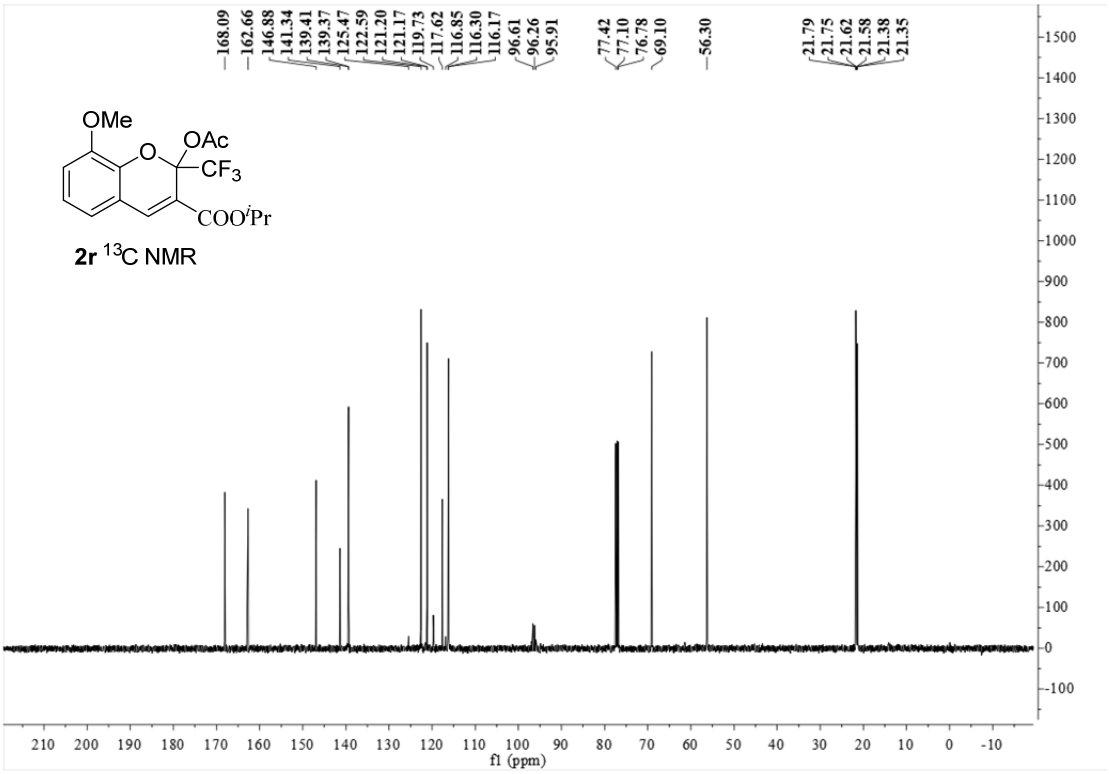
76.79
61.41
21.25
14.10
OAc
CF3
COOEt
2q 13C NMR
f1 (ppm)



2q ^{19}F NMR



2r ^{1}H NMR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122.59
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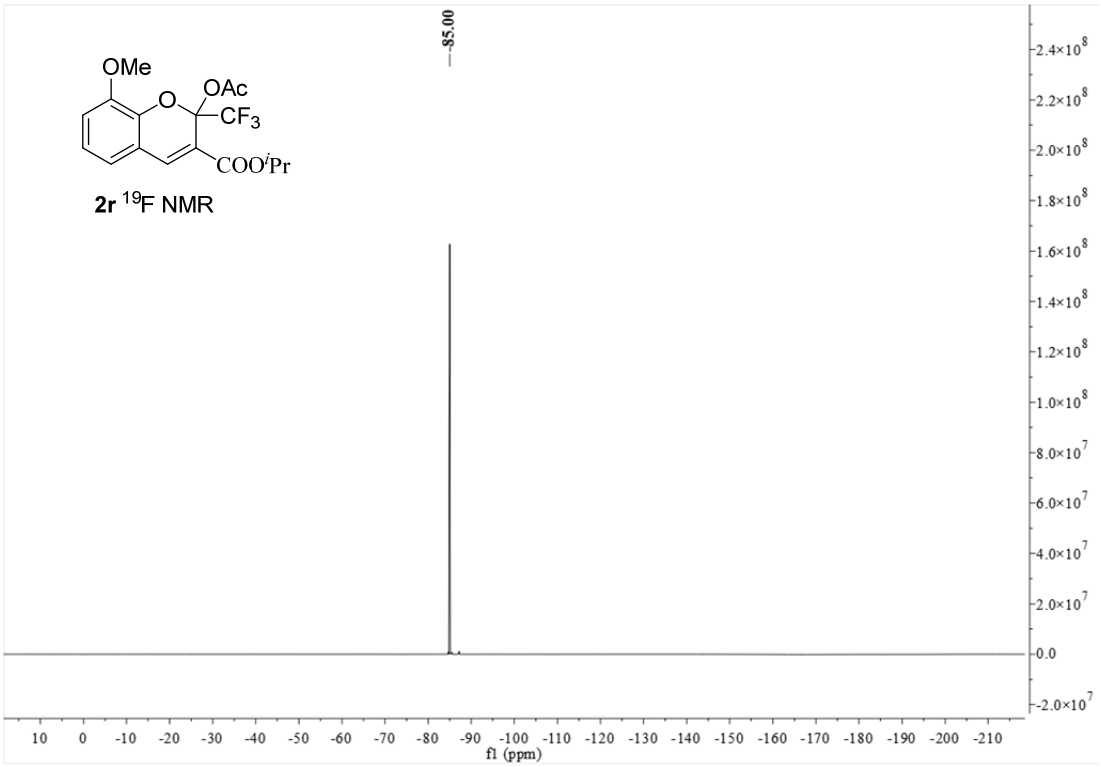
116.30
116.17
96.61
96.26
95.91
77.42
77.10
76.78
69.10
56.30
21.79
21.75
21.62
21.58
21.38
21.35
OMe
OAc
O
CF3
COOiPr
2r 13C NMR
f1 (ppm)


85.00
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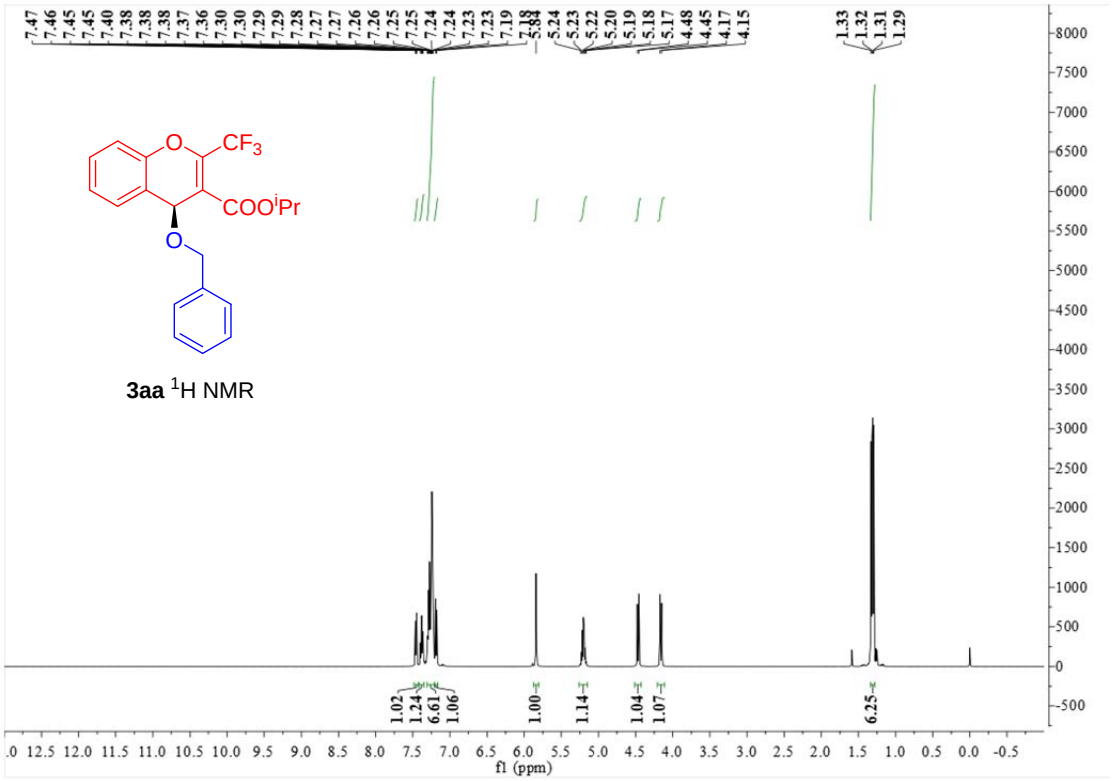
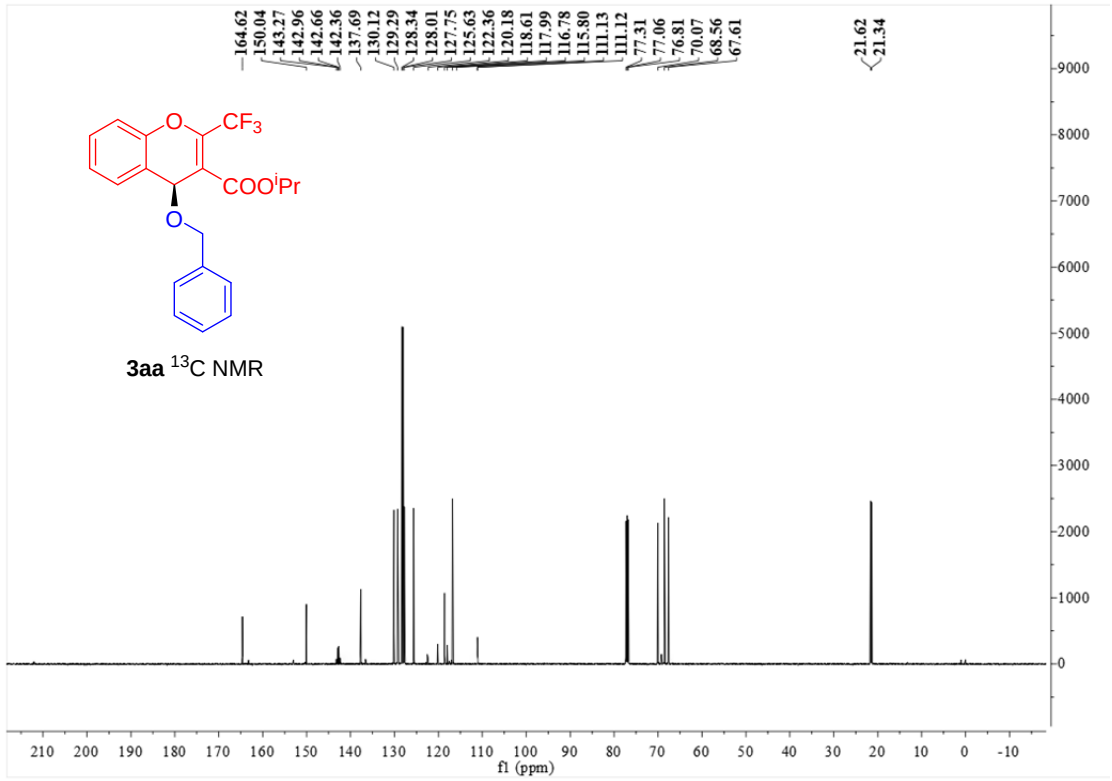
O
CF3
COOiPr
2r 19F NMR
f1 (ppm)



3aa ^{1}H NMR



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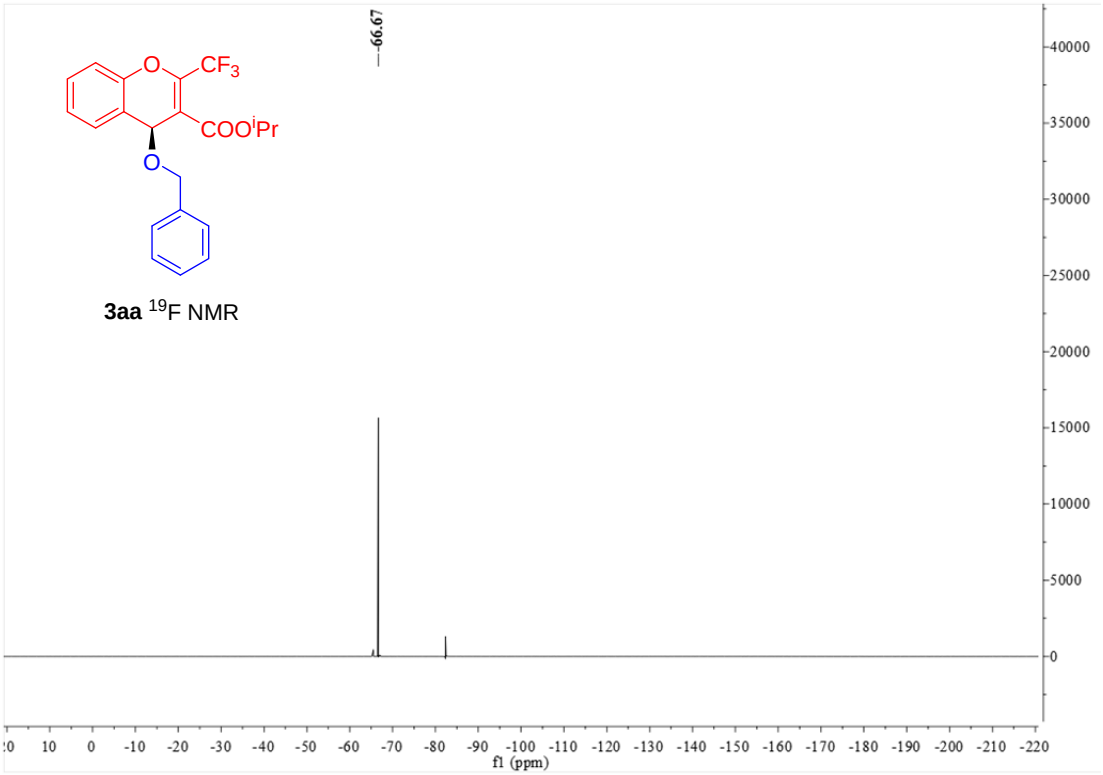

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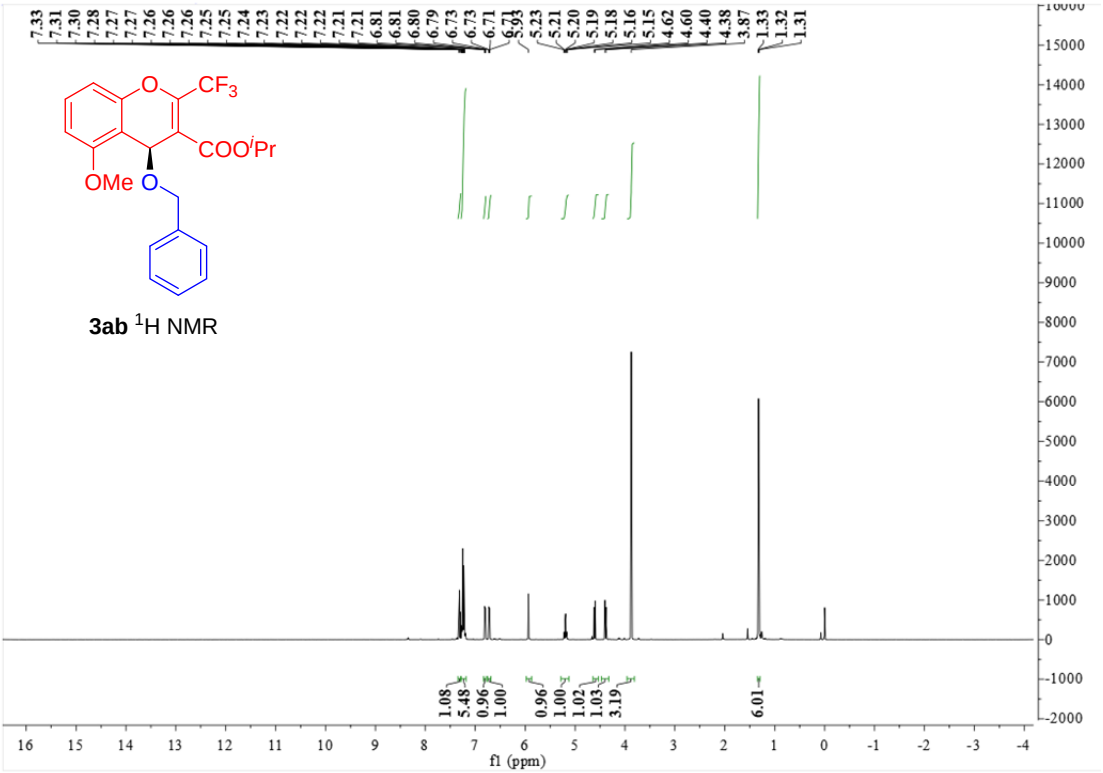
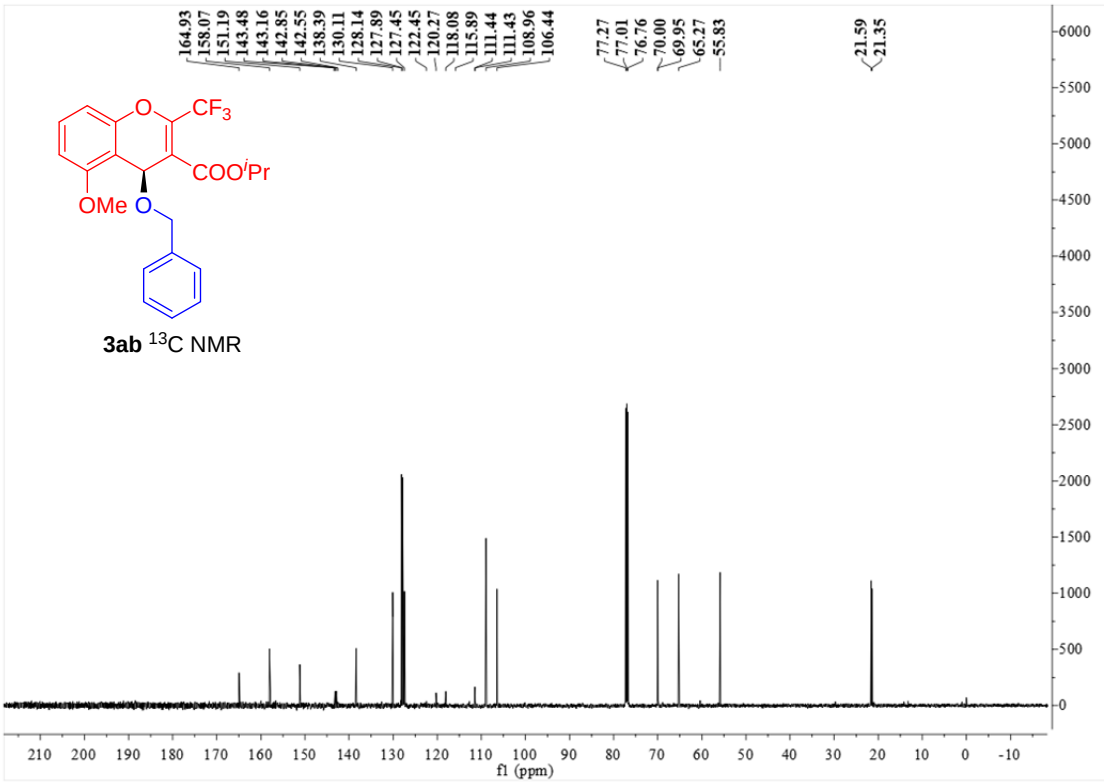
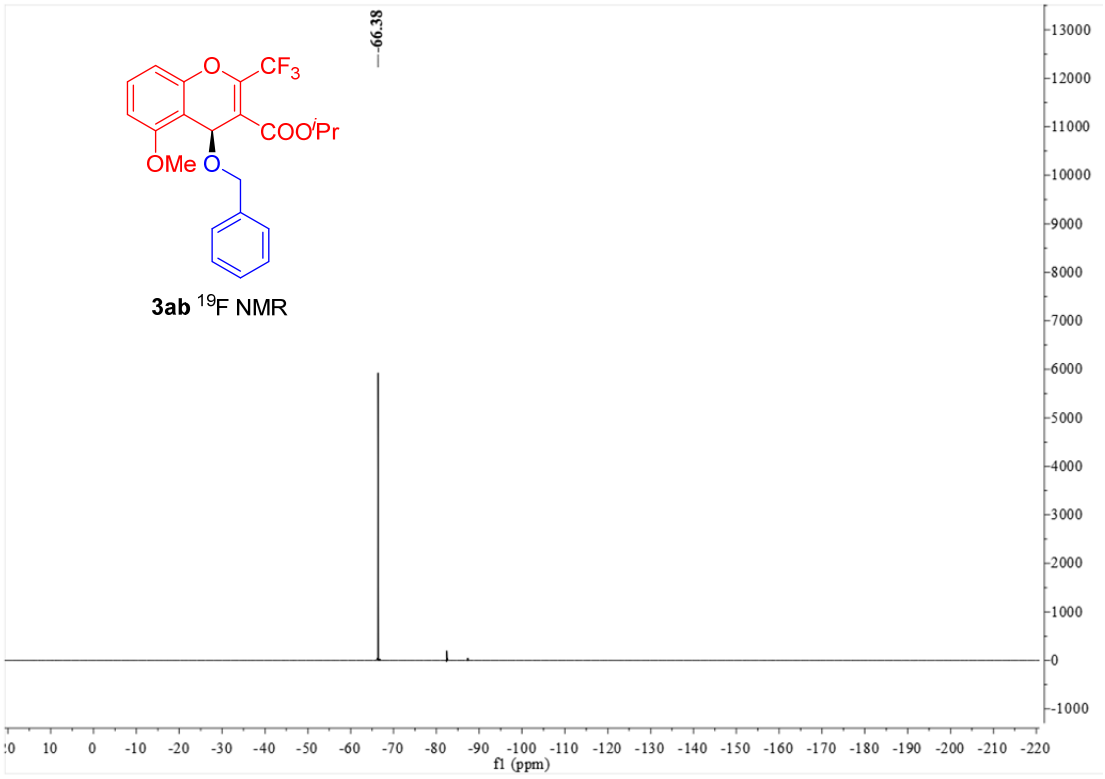


3ab ^{1}H NMR



3ab ^{13}C NMR



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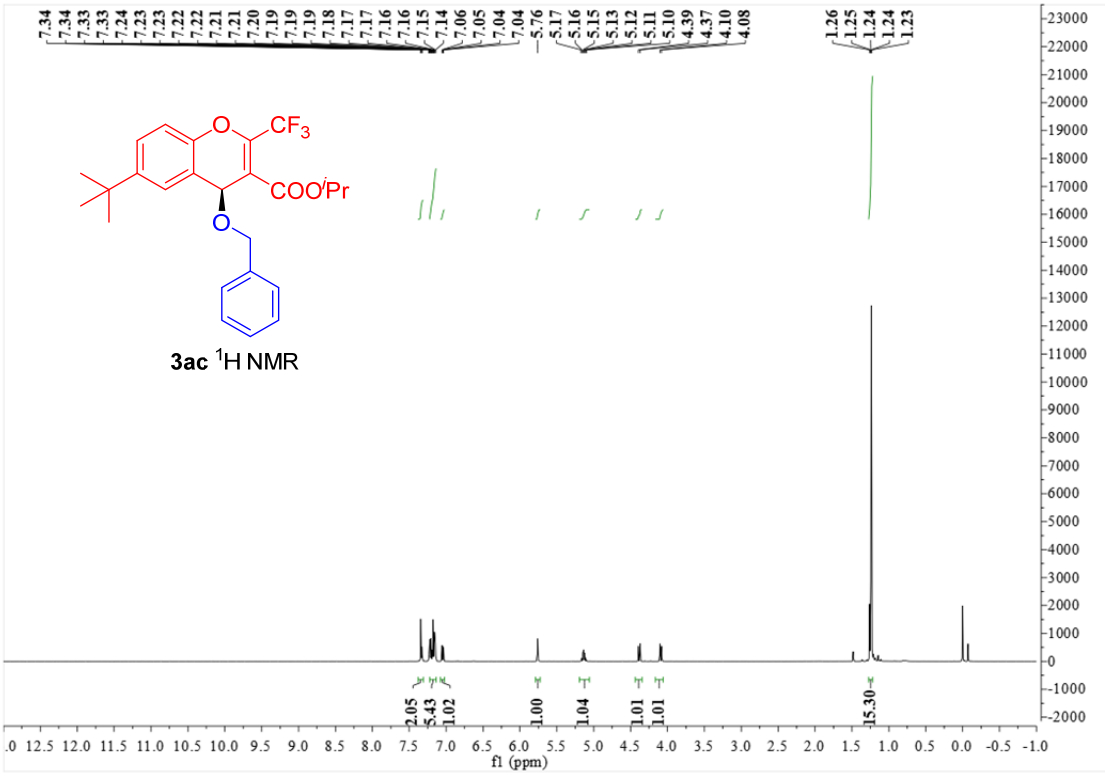

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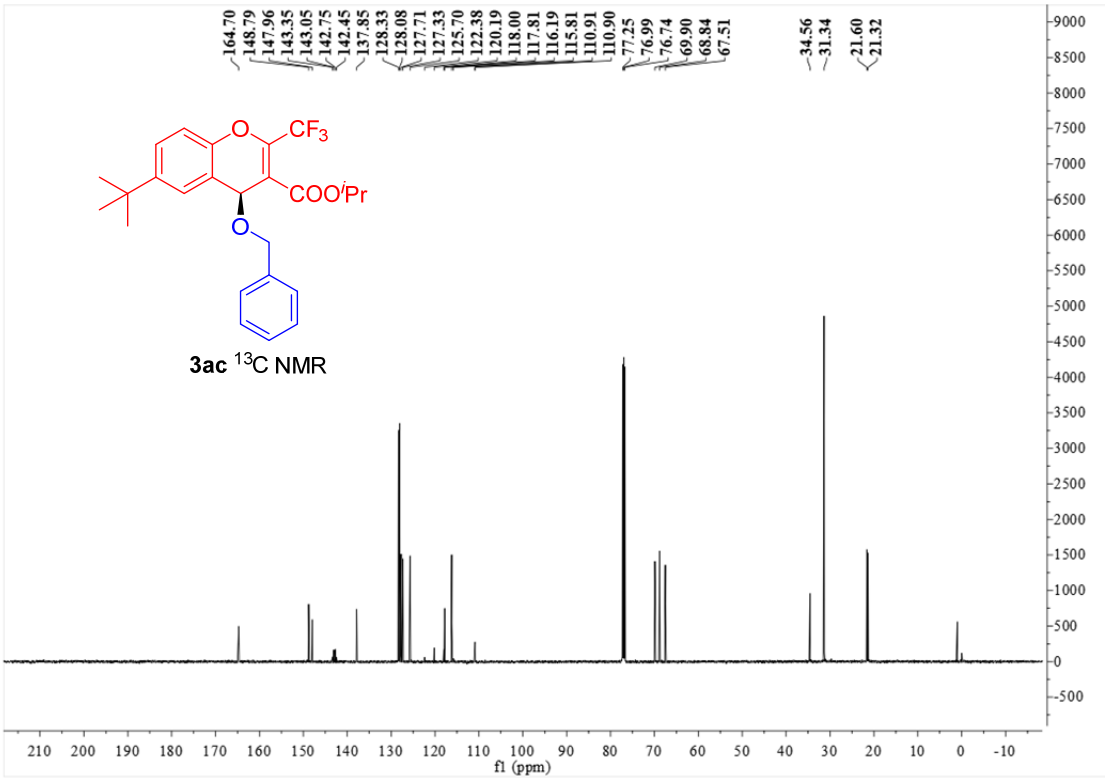
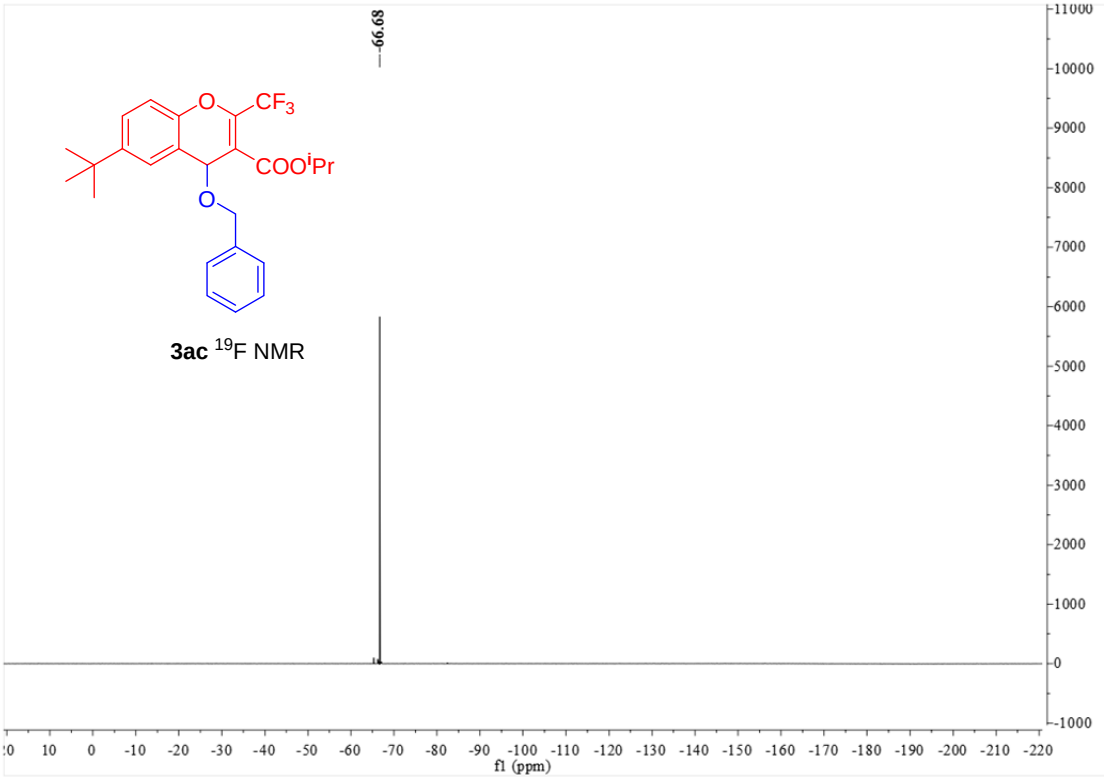


3ac ^{13}C NMR



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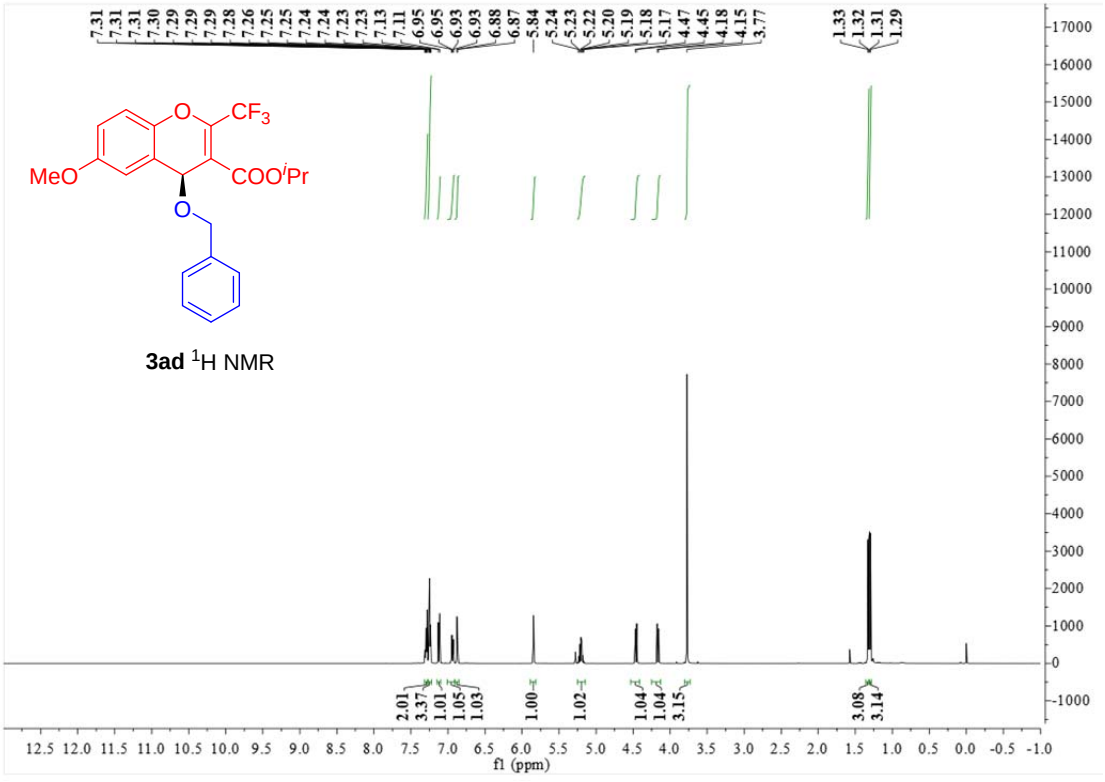

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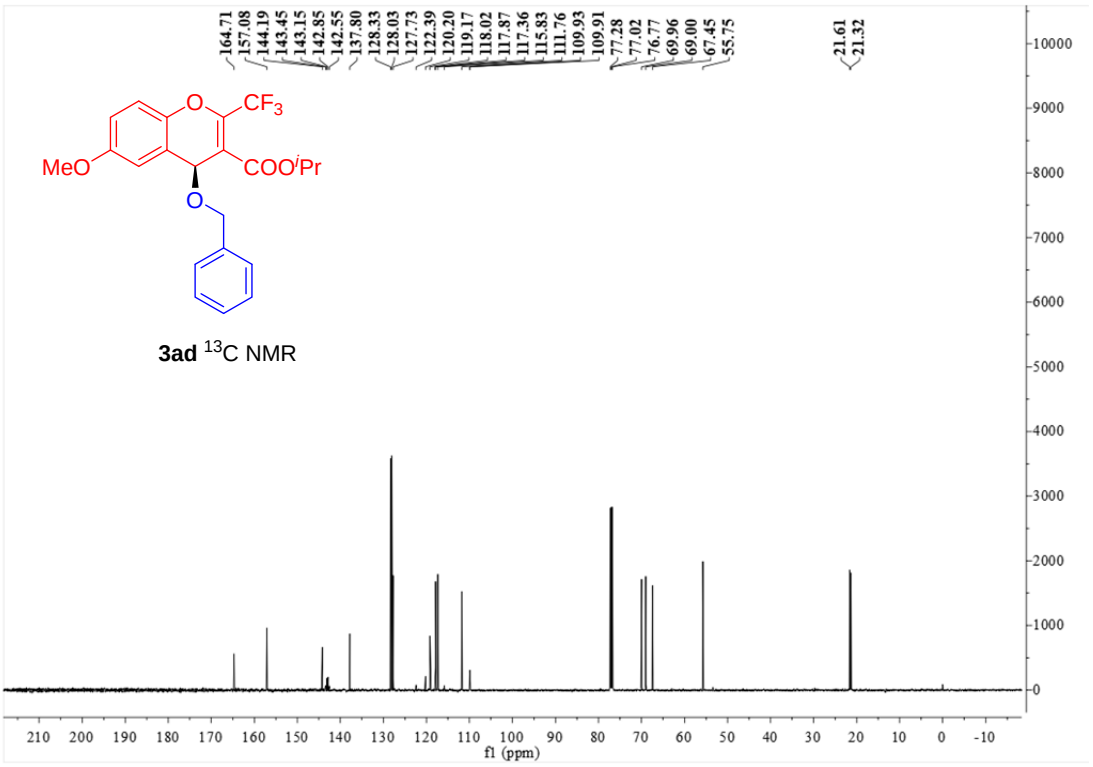
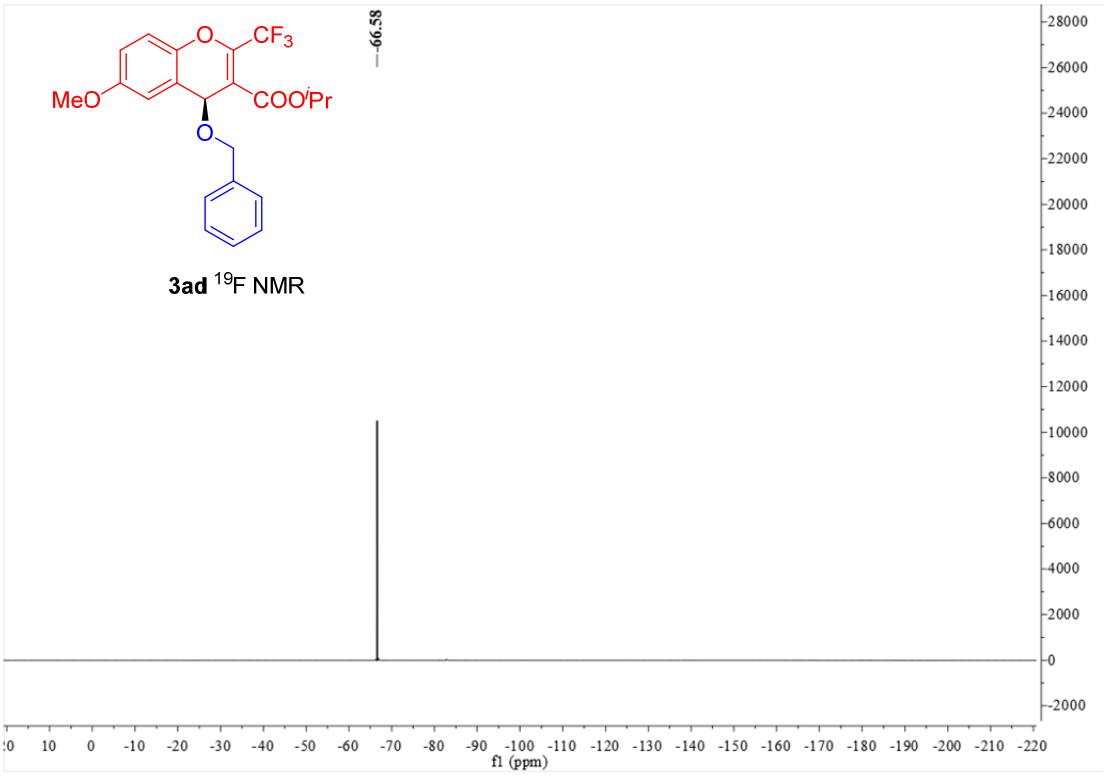
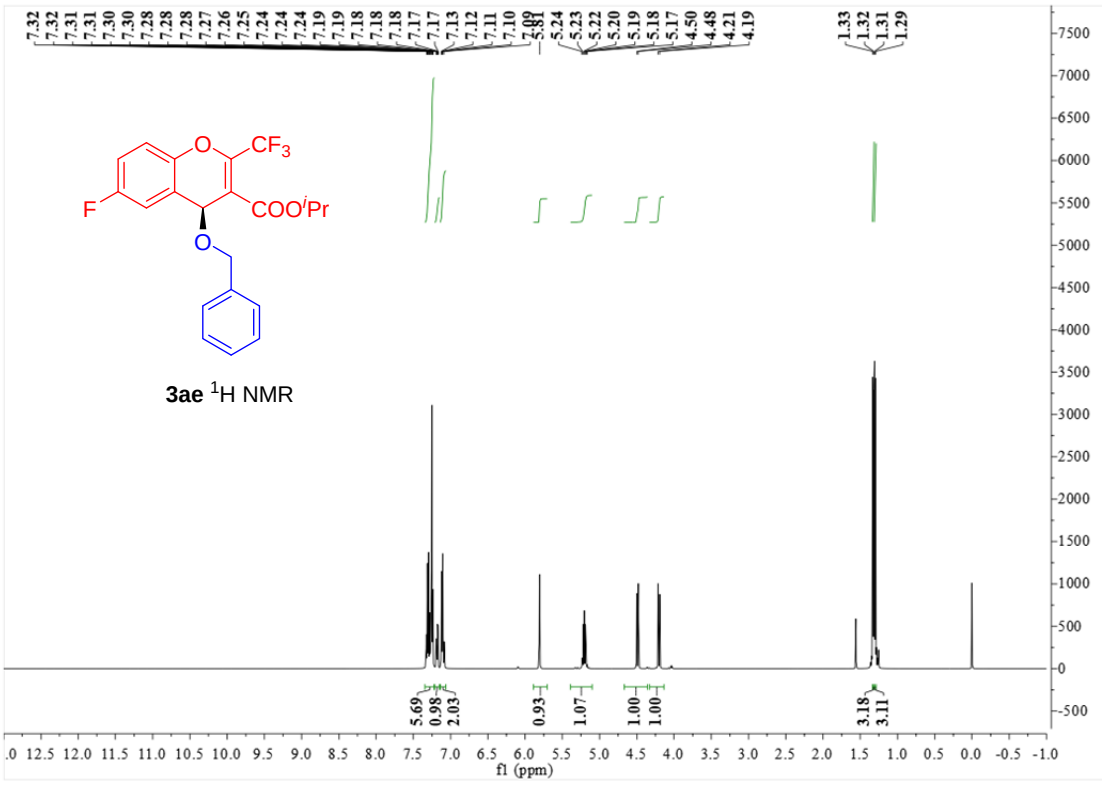
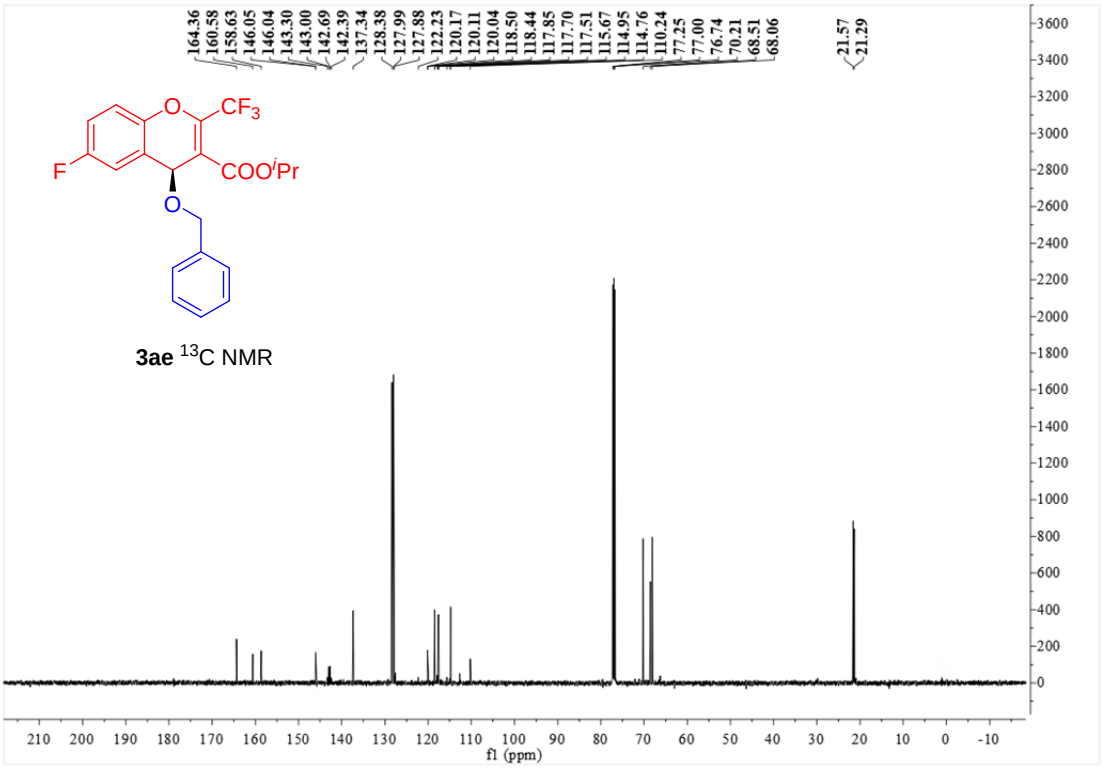


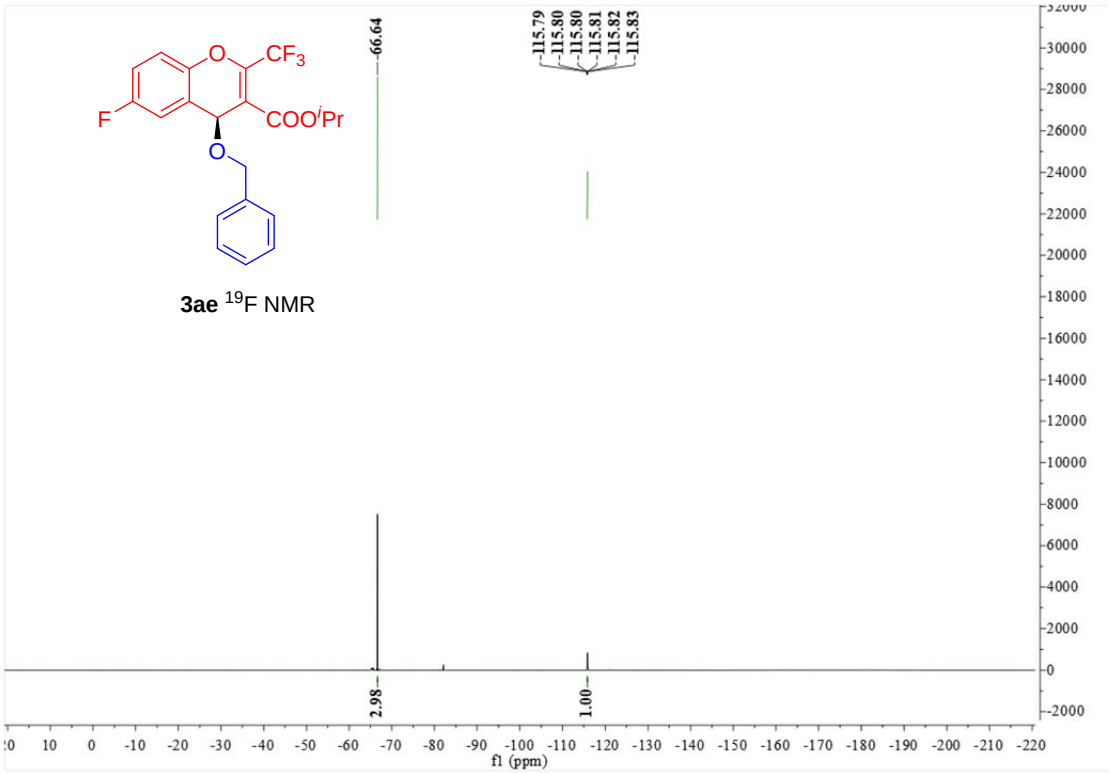
3ad ^{13}C NMR



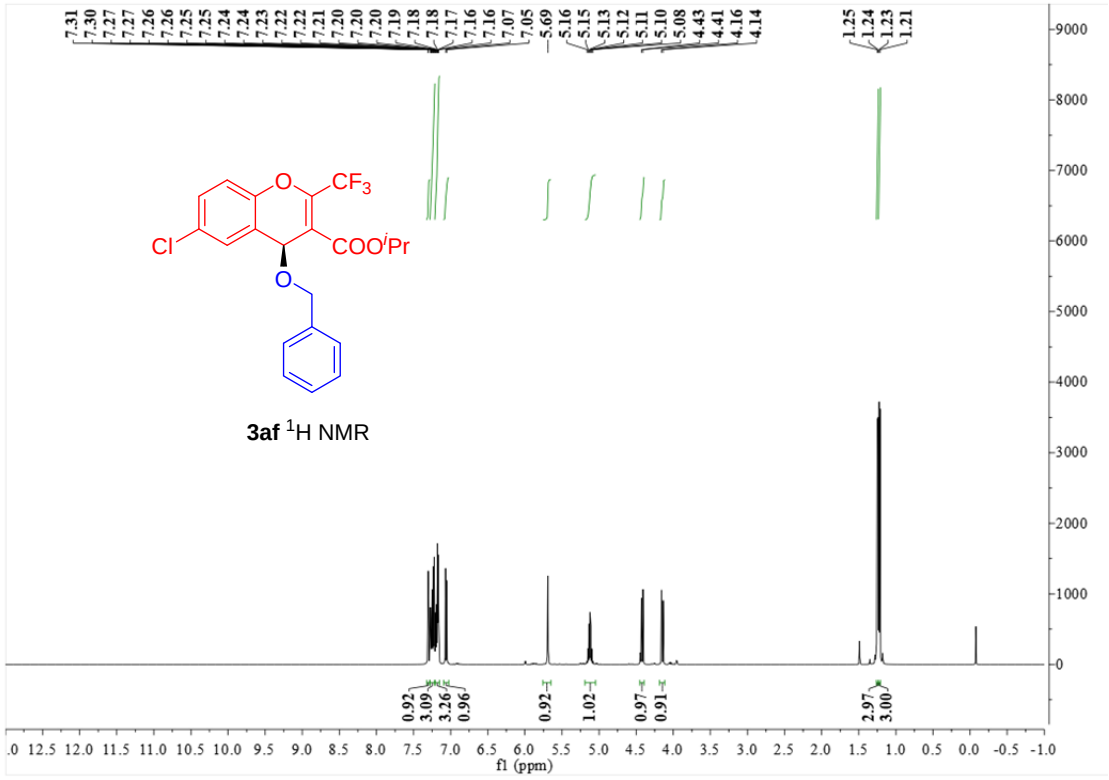
3ad ^{19}F NMR


F
O
CF3
COOiPr
O
3ae 1H NMR
fl (ppm)


F
O
CF3
COOiPr
O
3ae 13C NMR
fl (ppm)



3ae ^{19}F NMR



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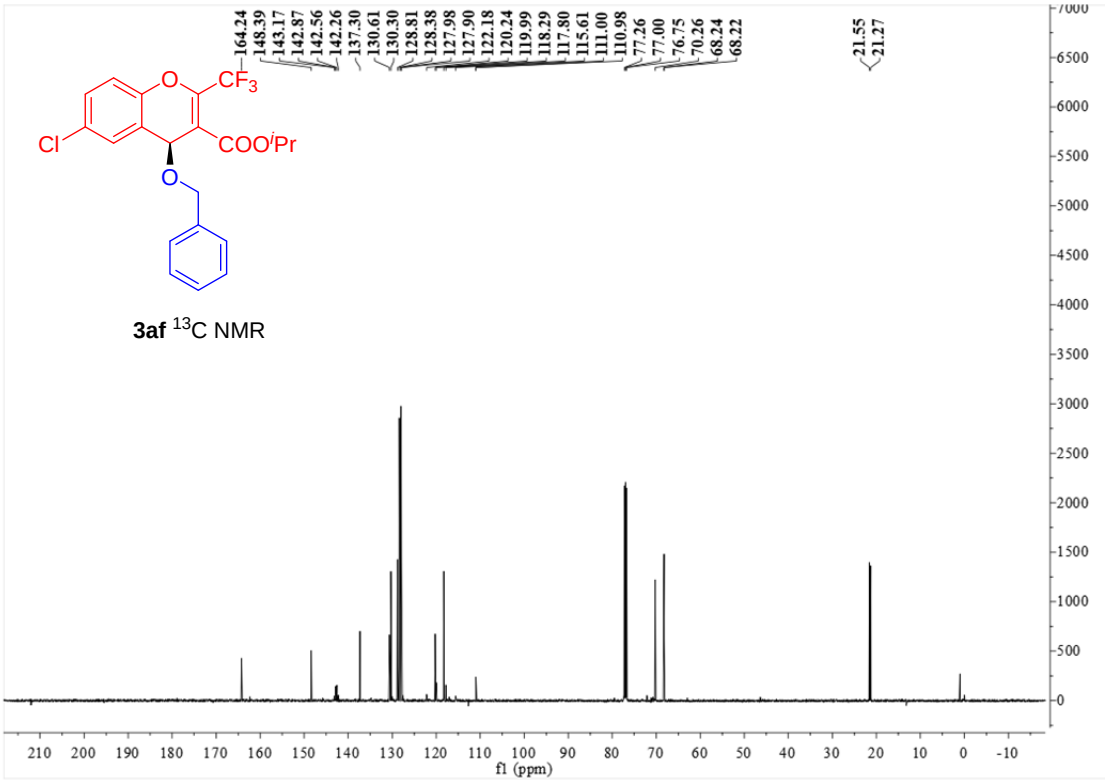

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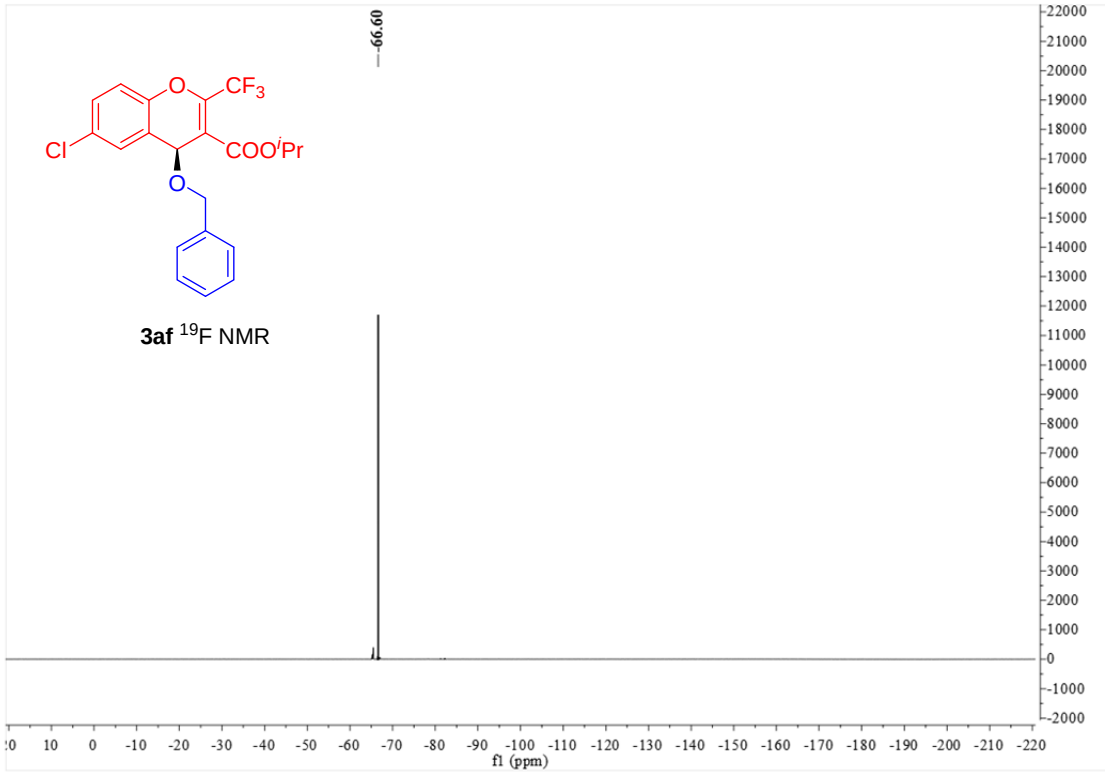
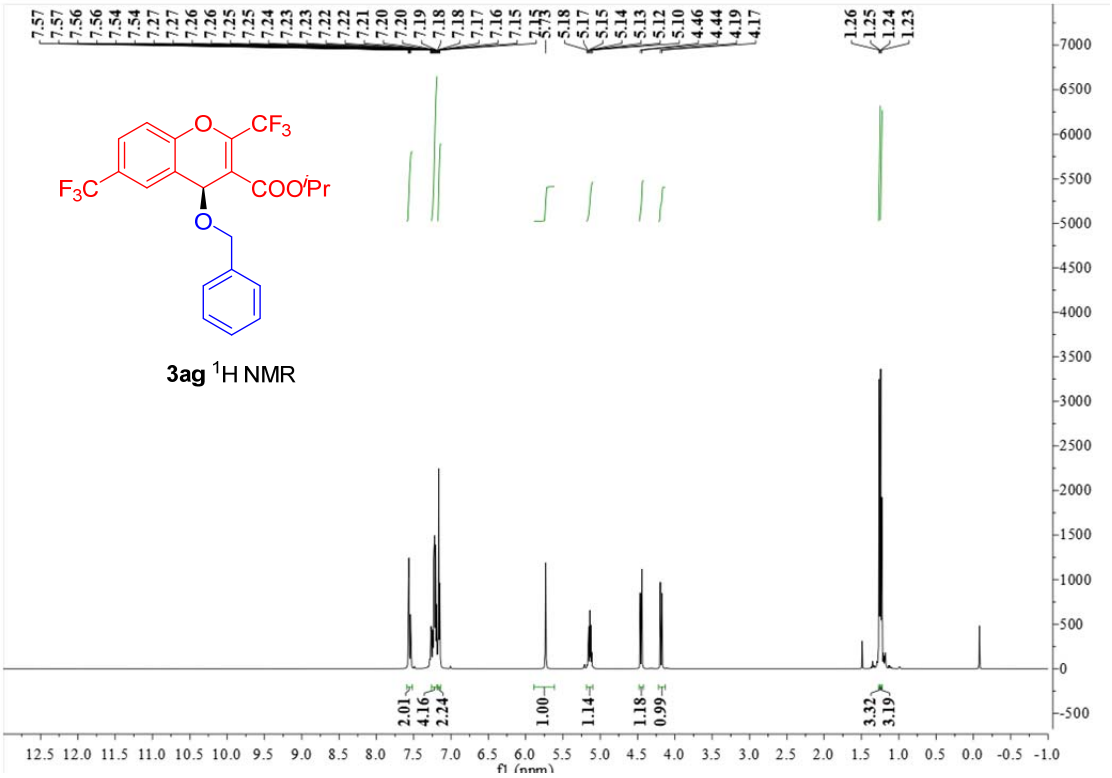


3af ^{19}F NMR



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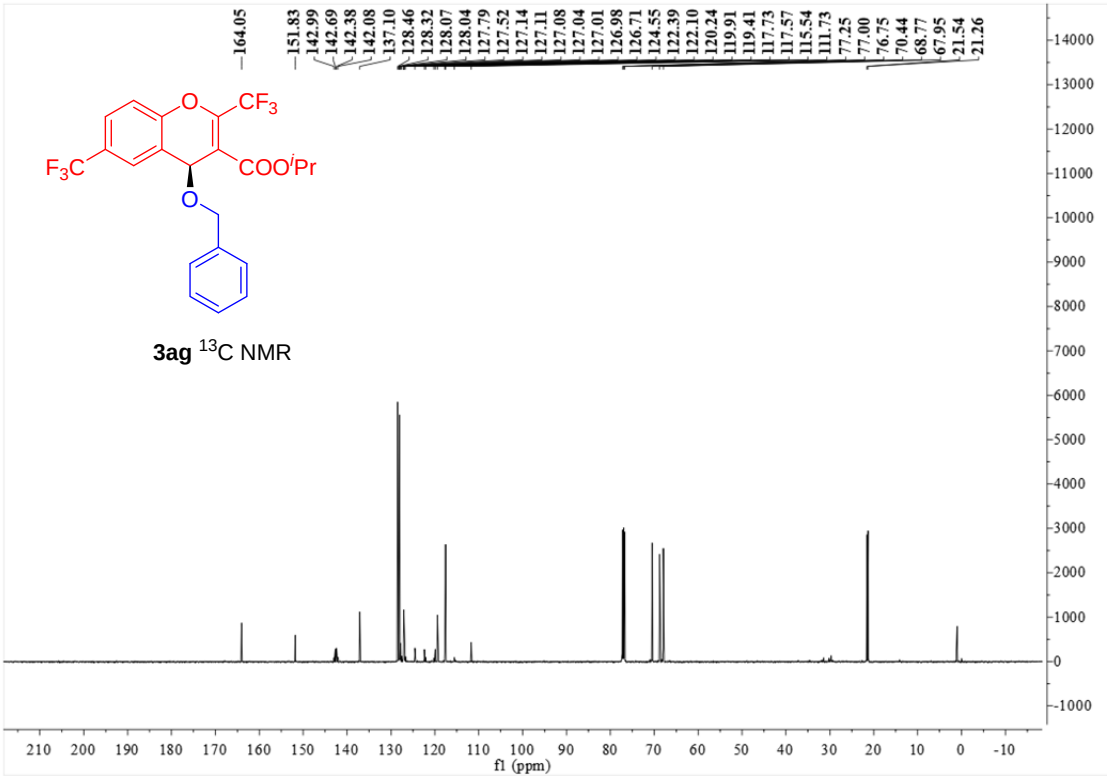

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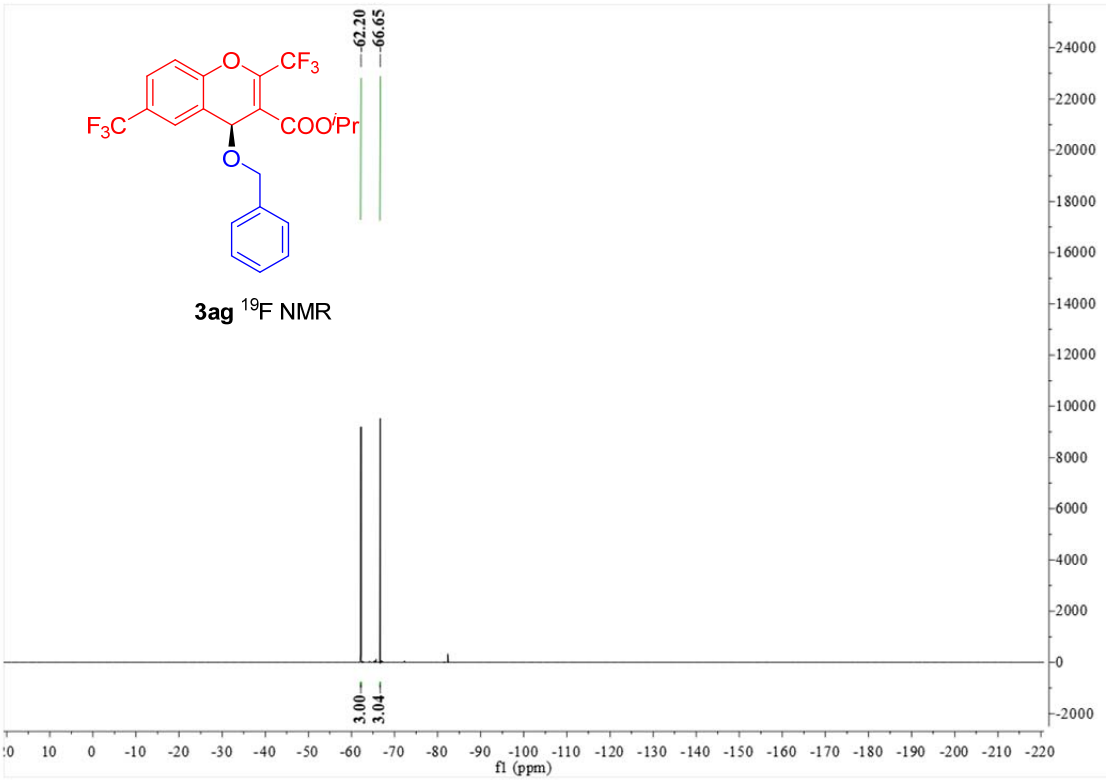
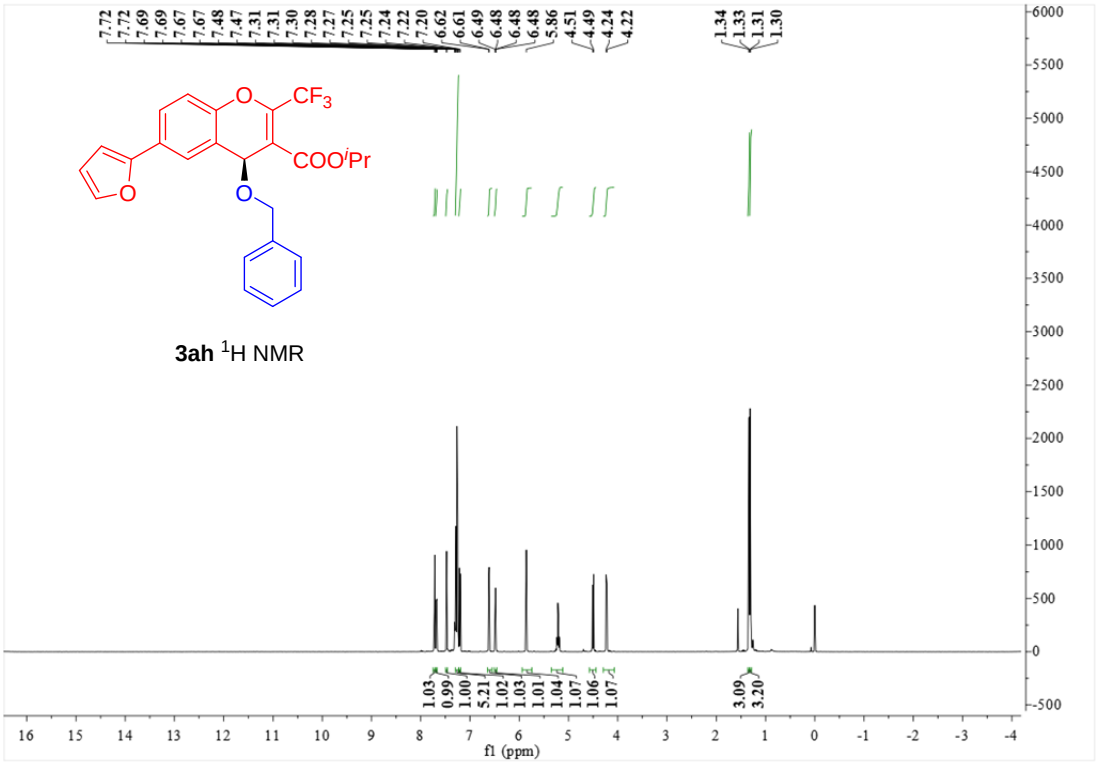
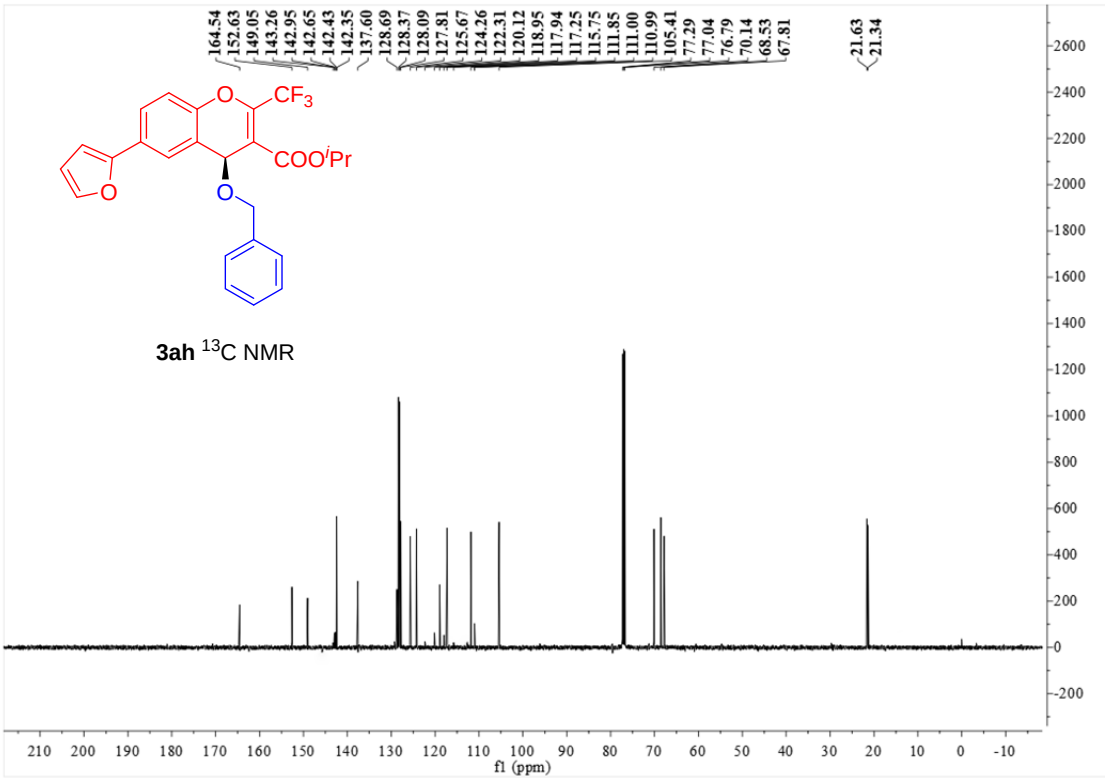


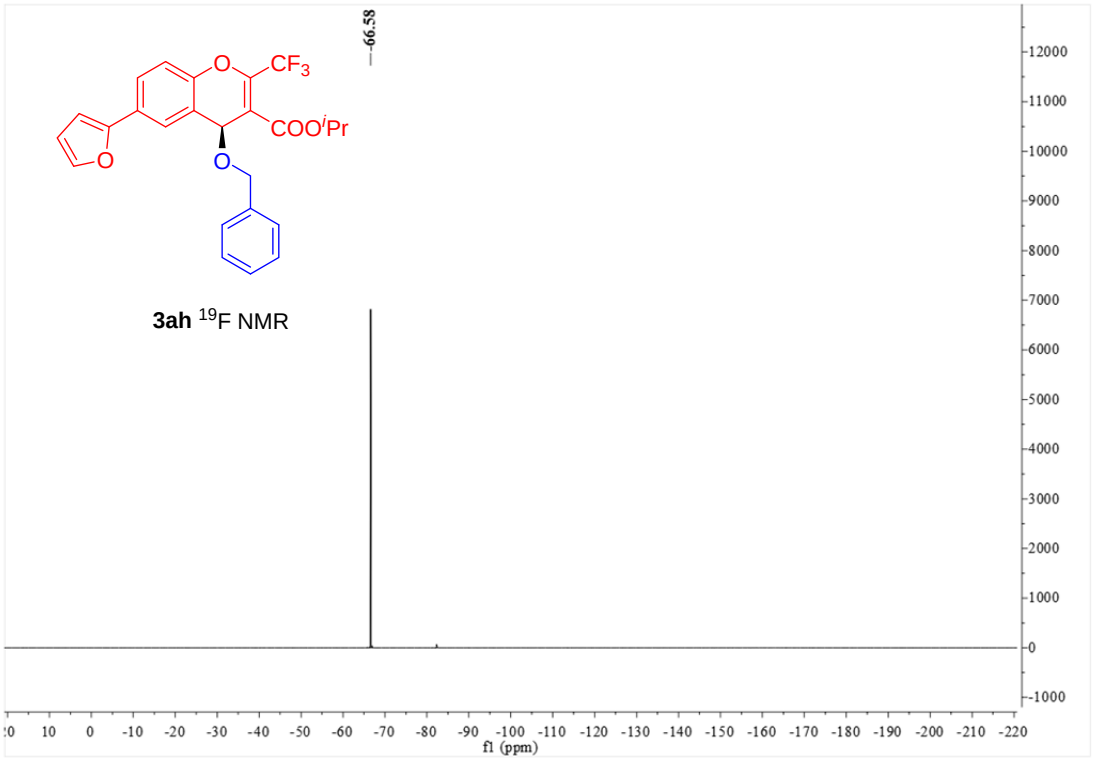
3ag ^{19}F NMR



3ah ^{1}H NMR



3ah ^{13}C NMR



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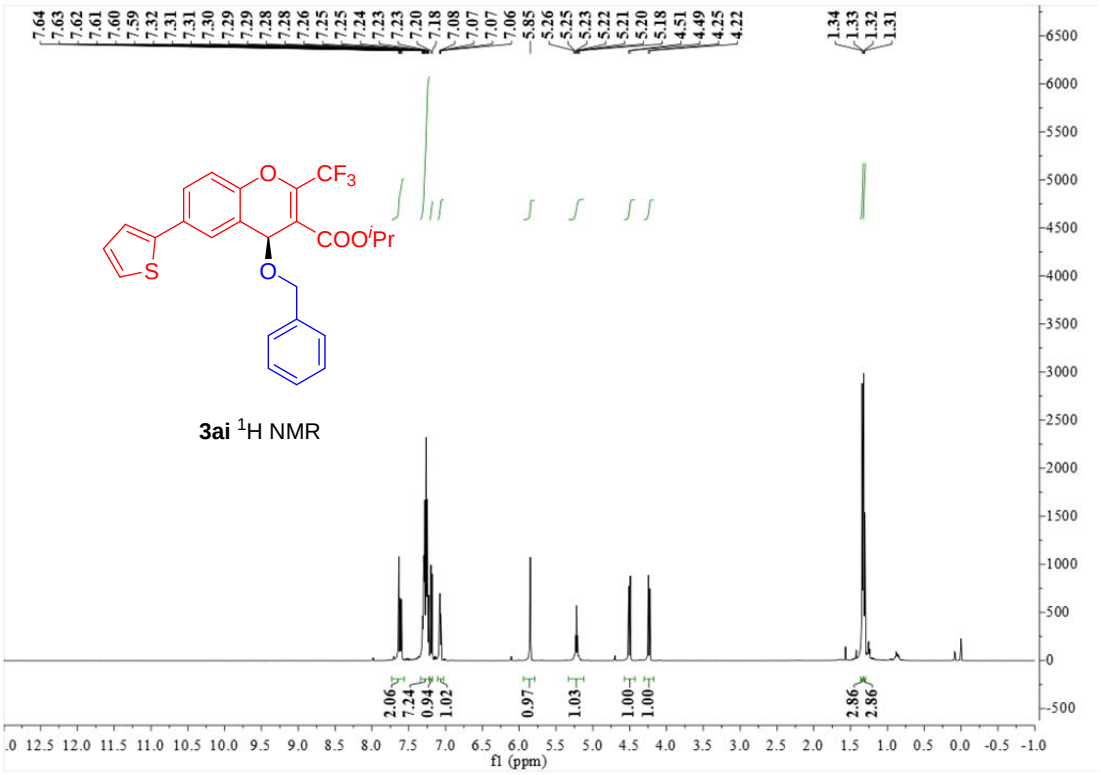

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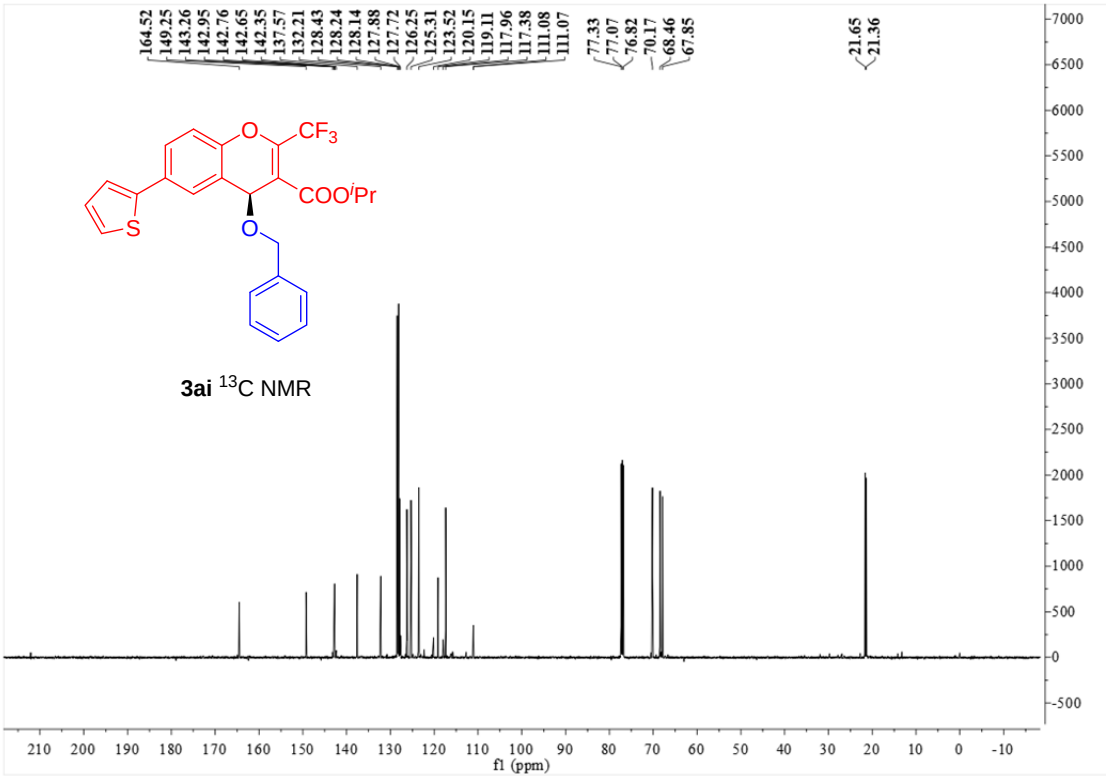

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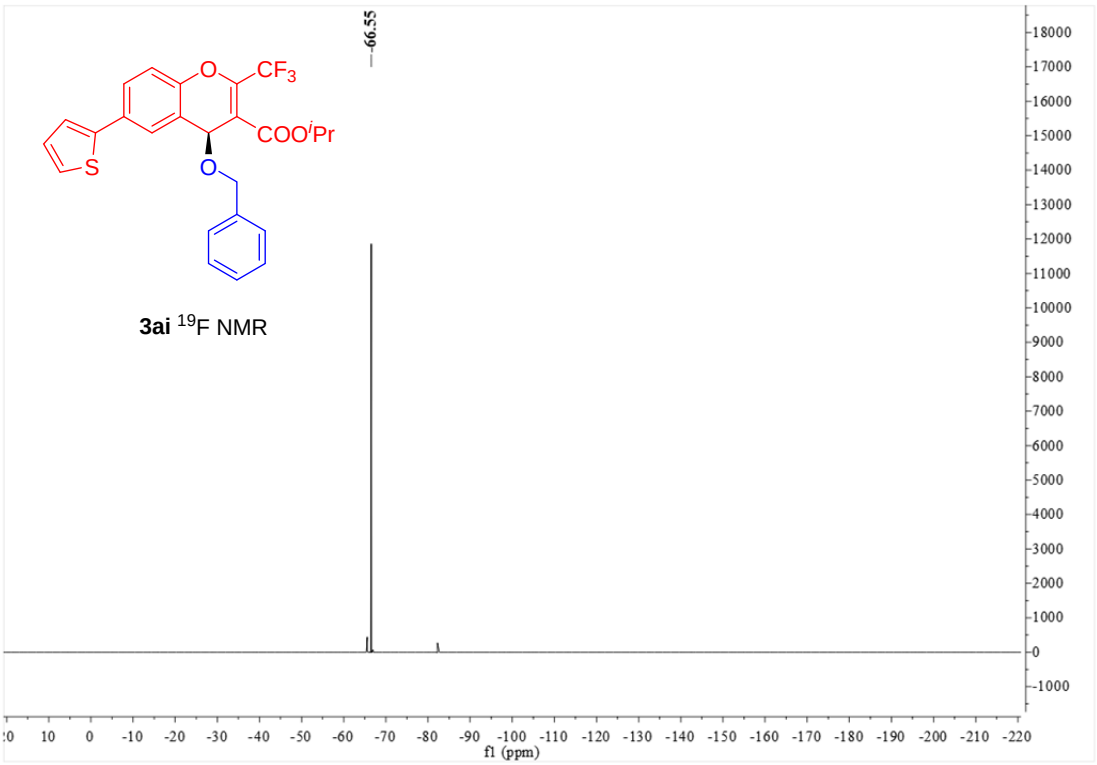

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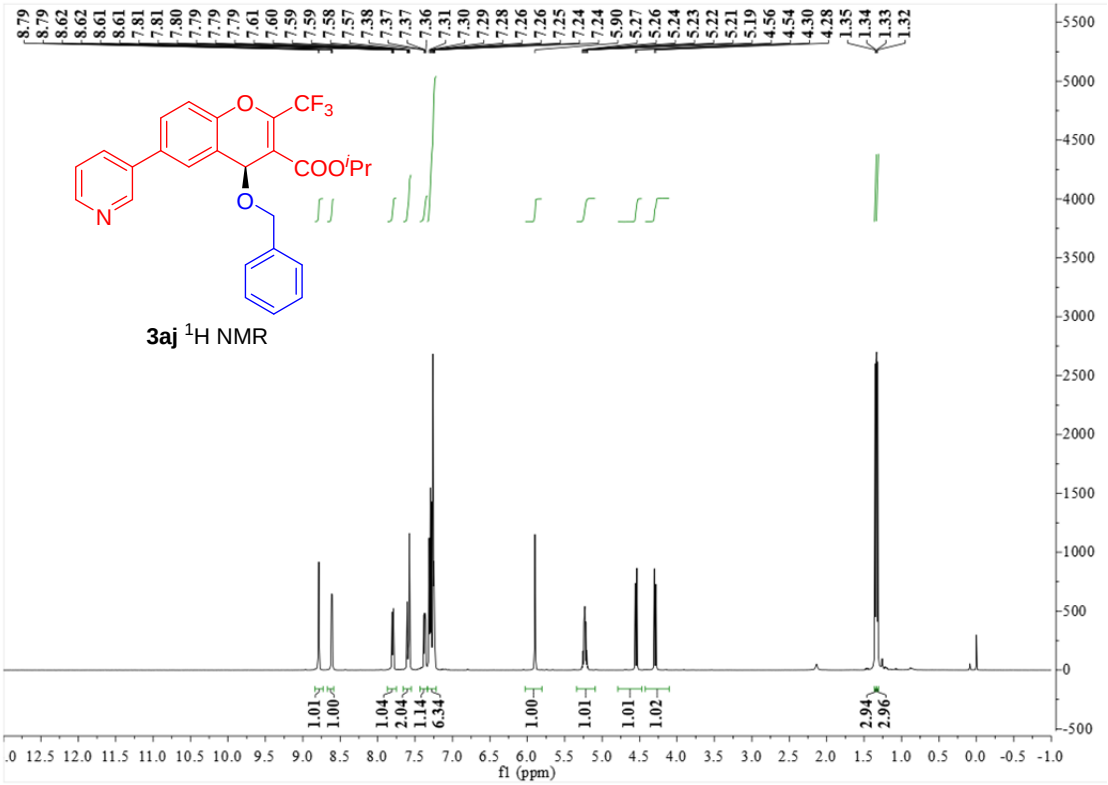

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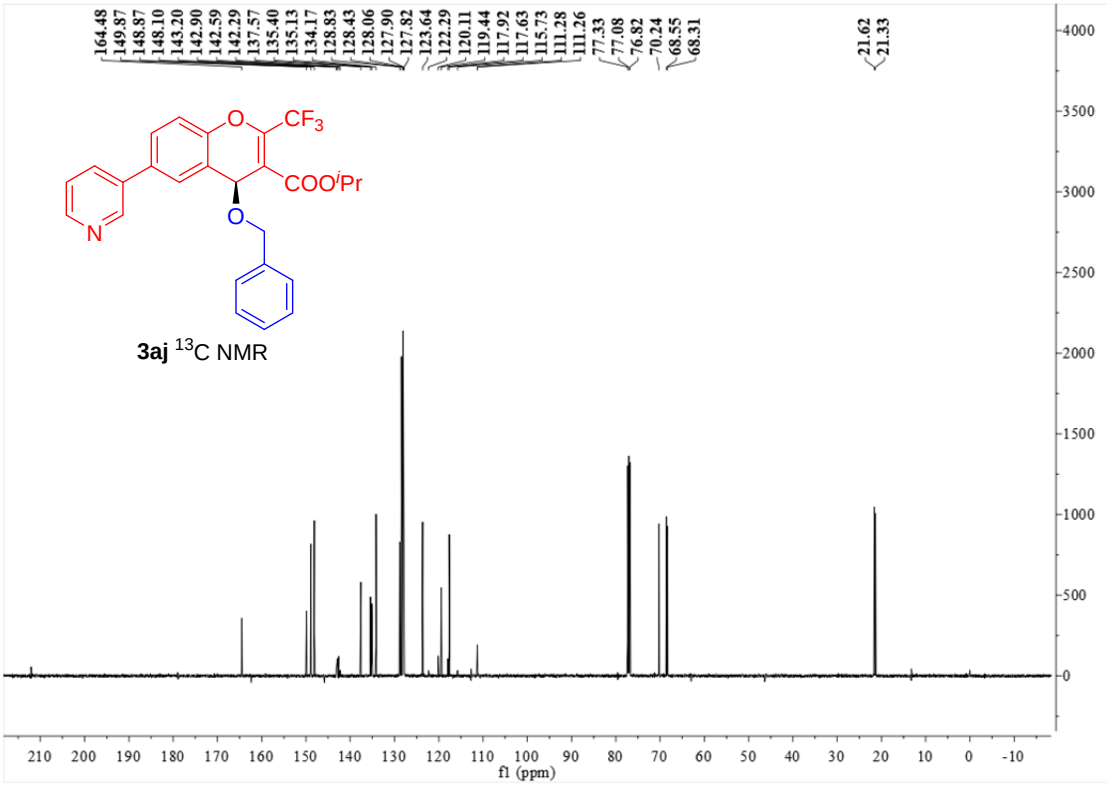

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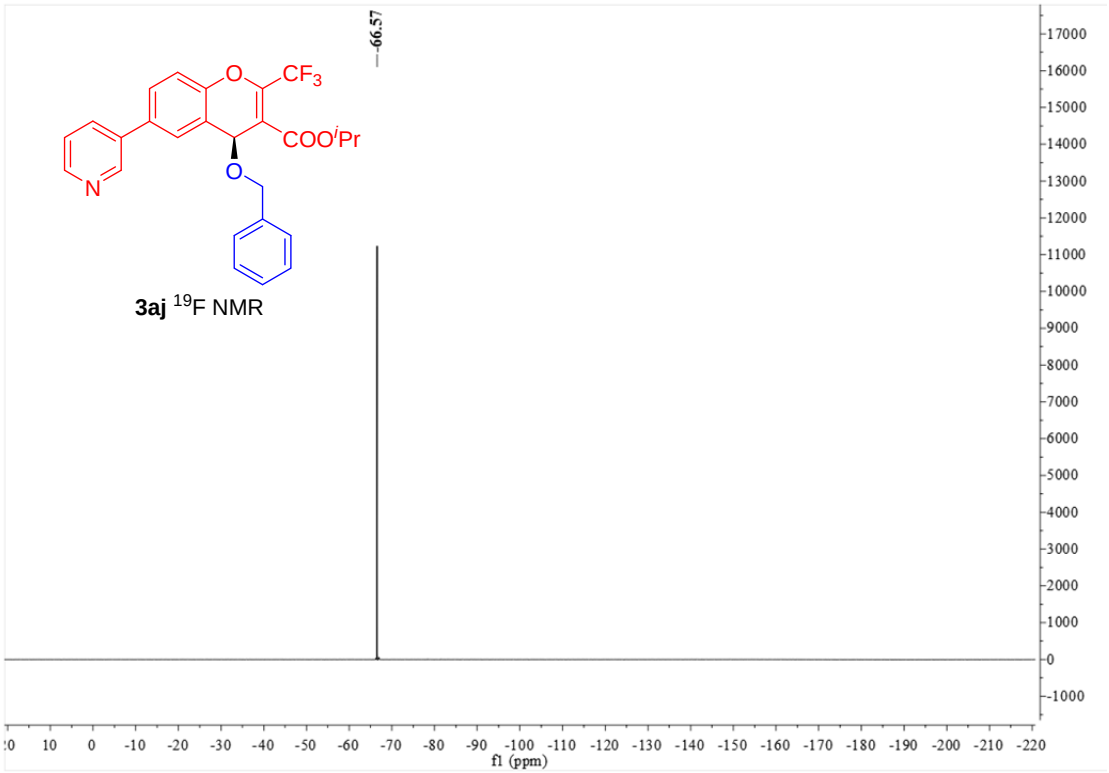
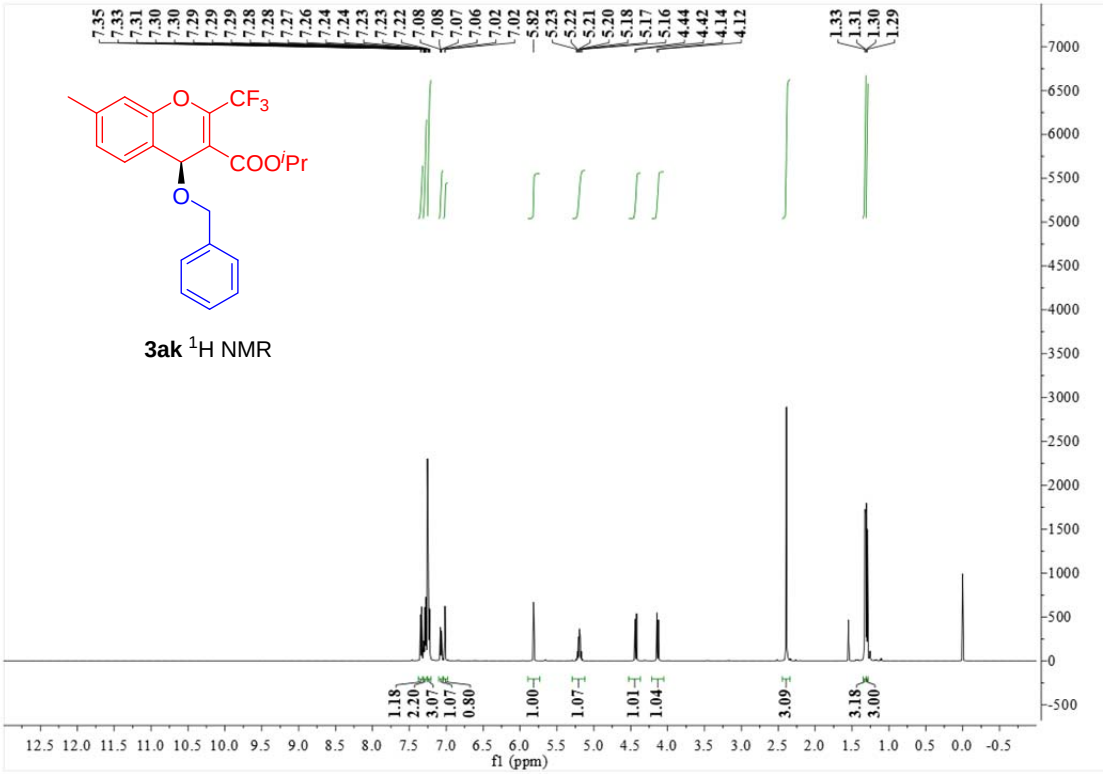
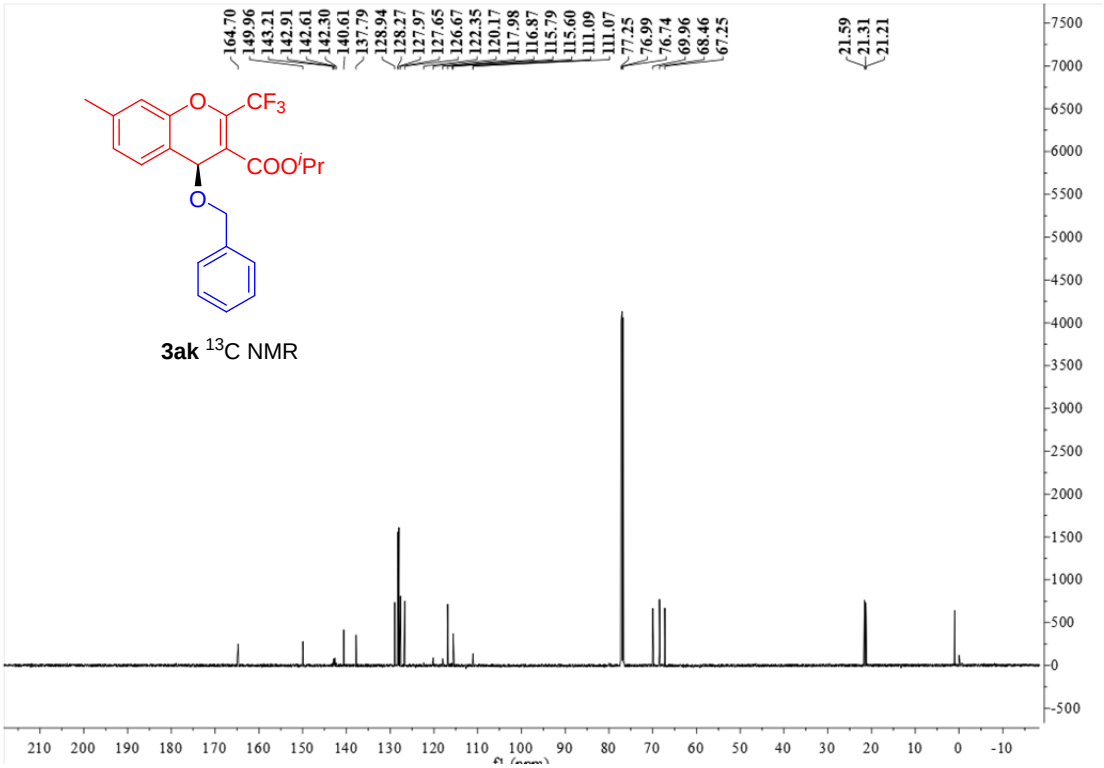


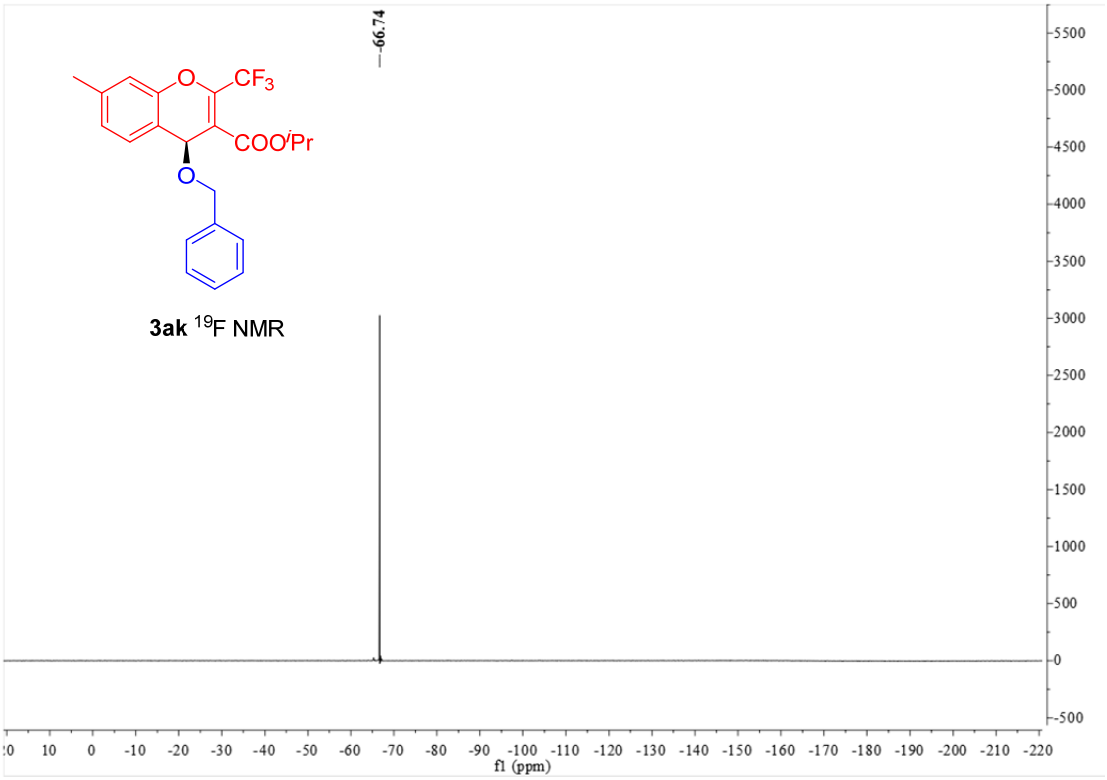
3aj ^{19}F NMR



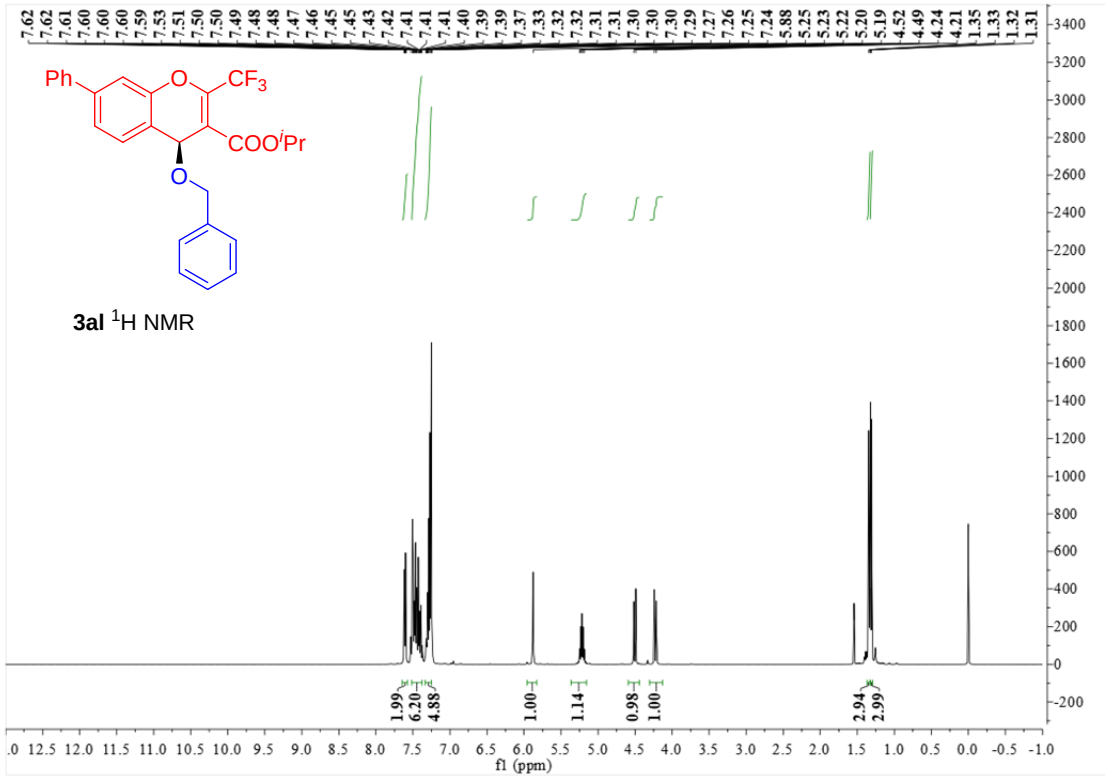
3ak ^{1}H NMR



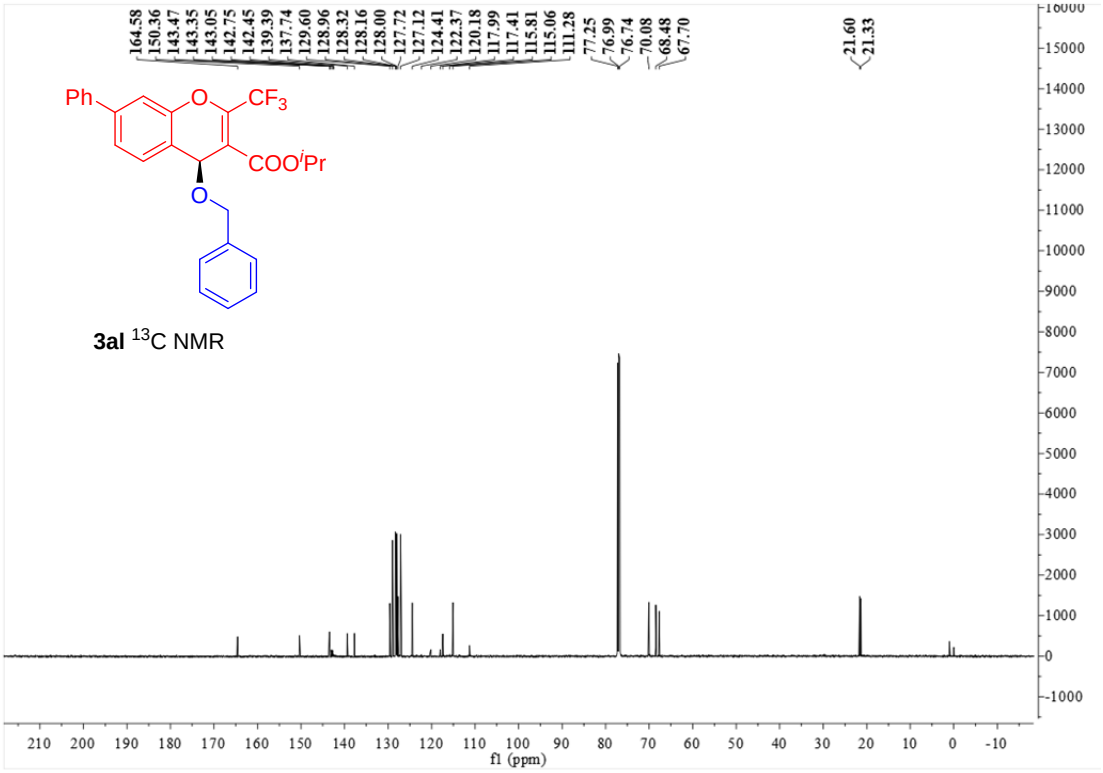
3ak ^{13}C NMR



3ak ^{19}F NMR



3al ^{1}H NMR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117.41
115.81
115.06
111.28
77.25
76.99
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67.70
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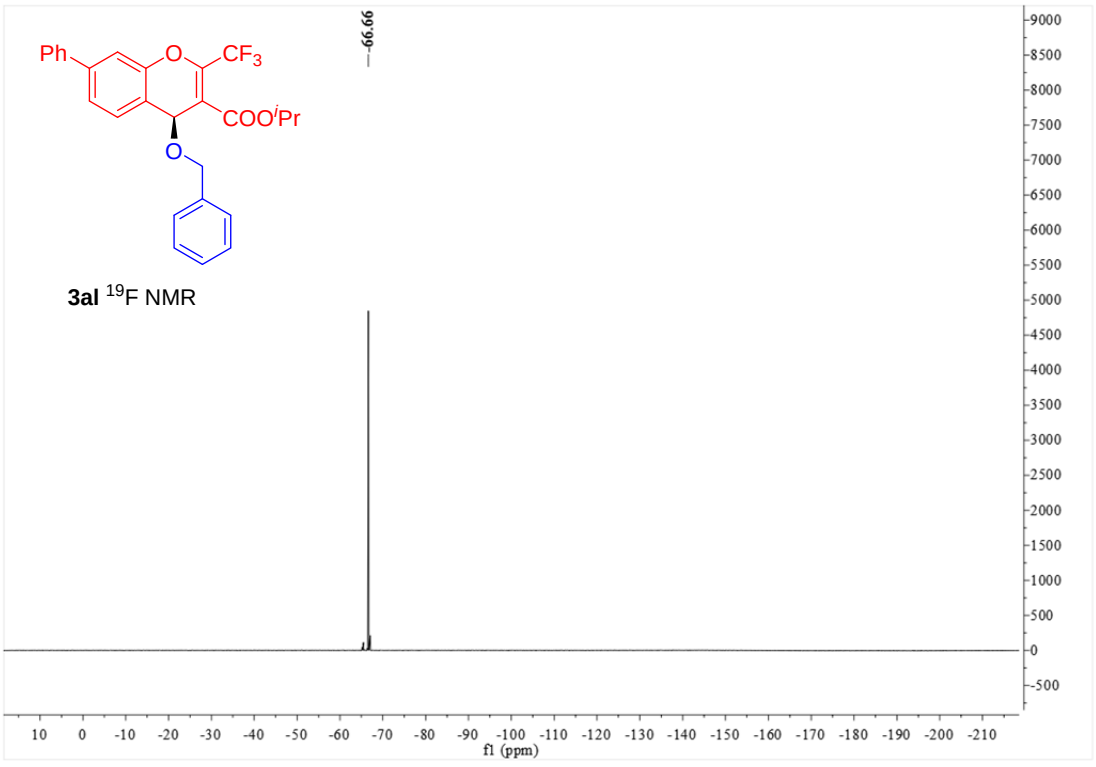
O
CF3
COOiPr
O
3al 13C NMR
fl (ppm)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Ph
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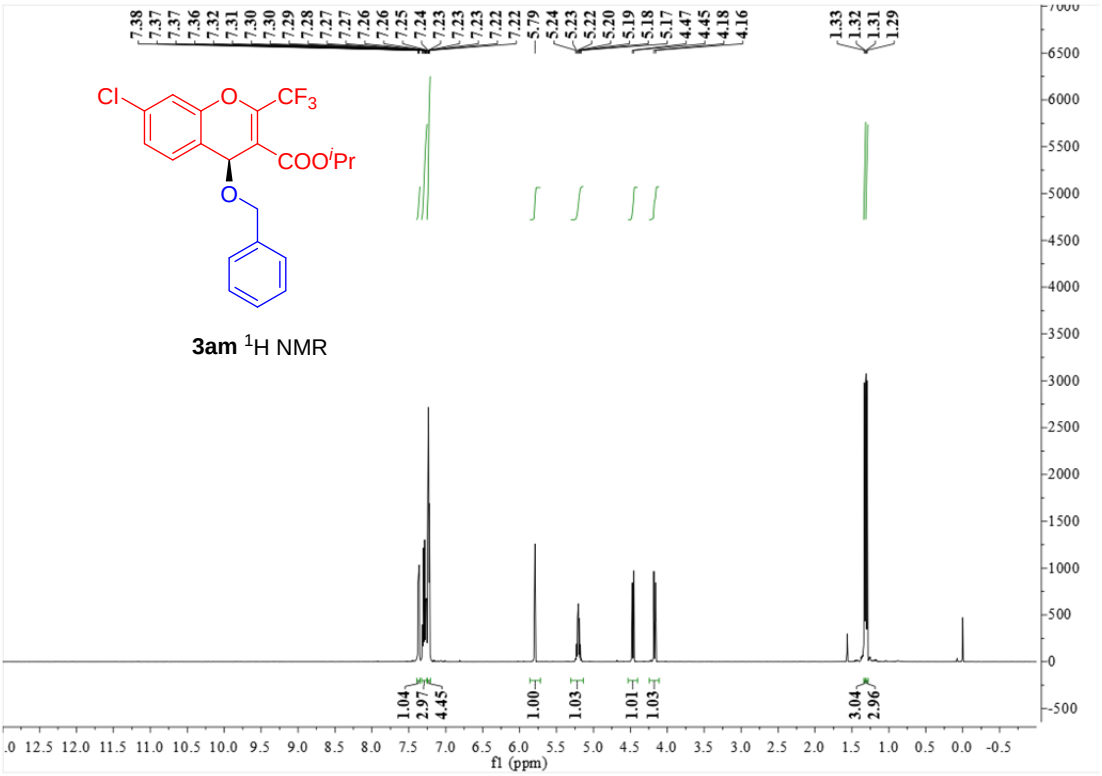
COOiPr
O
3al 19F NMR
fl (ppm)



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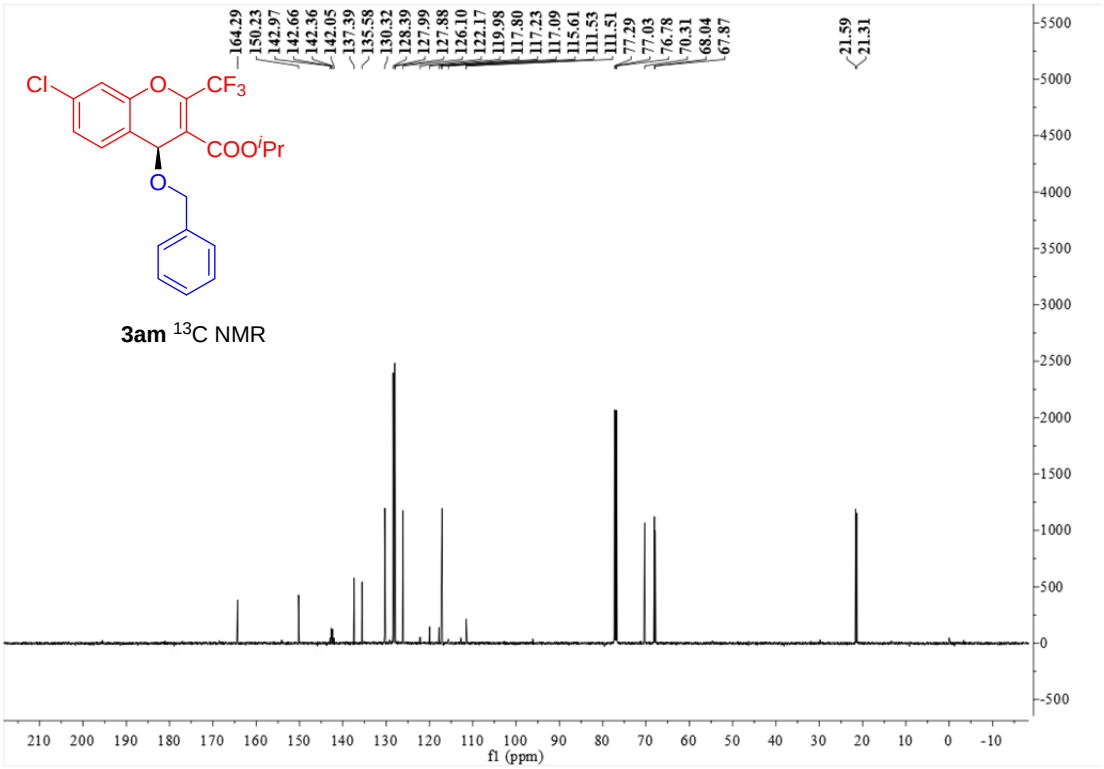
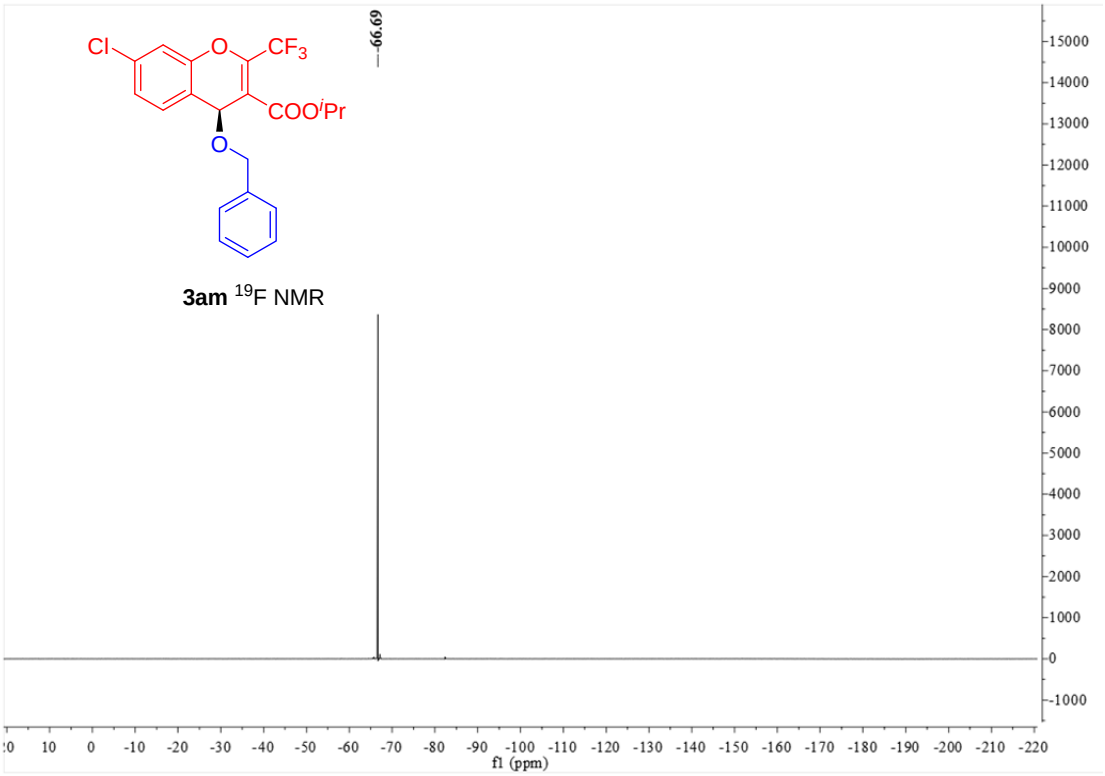
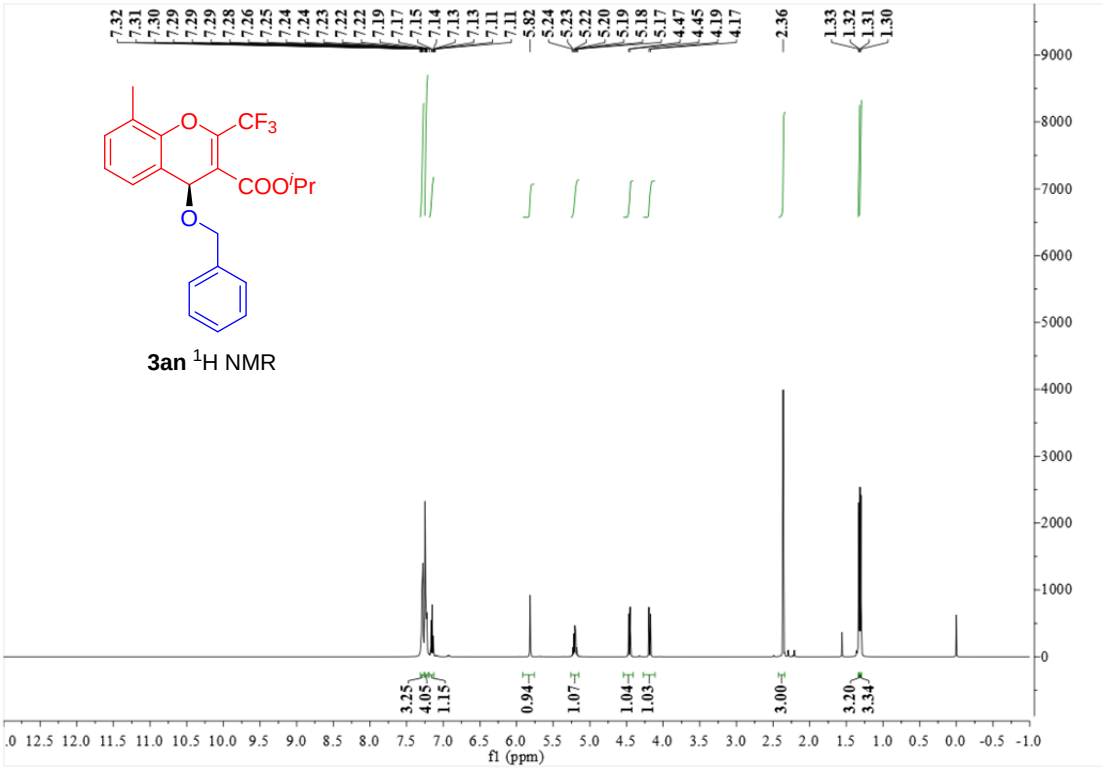


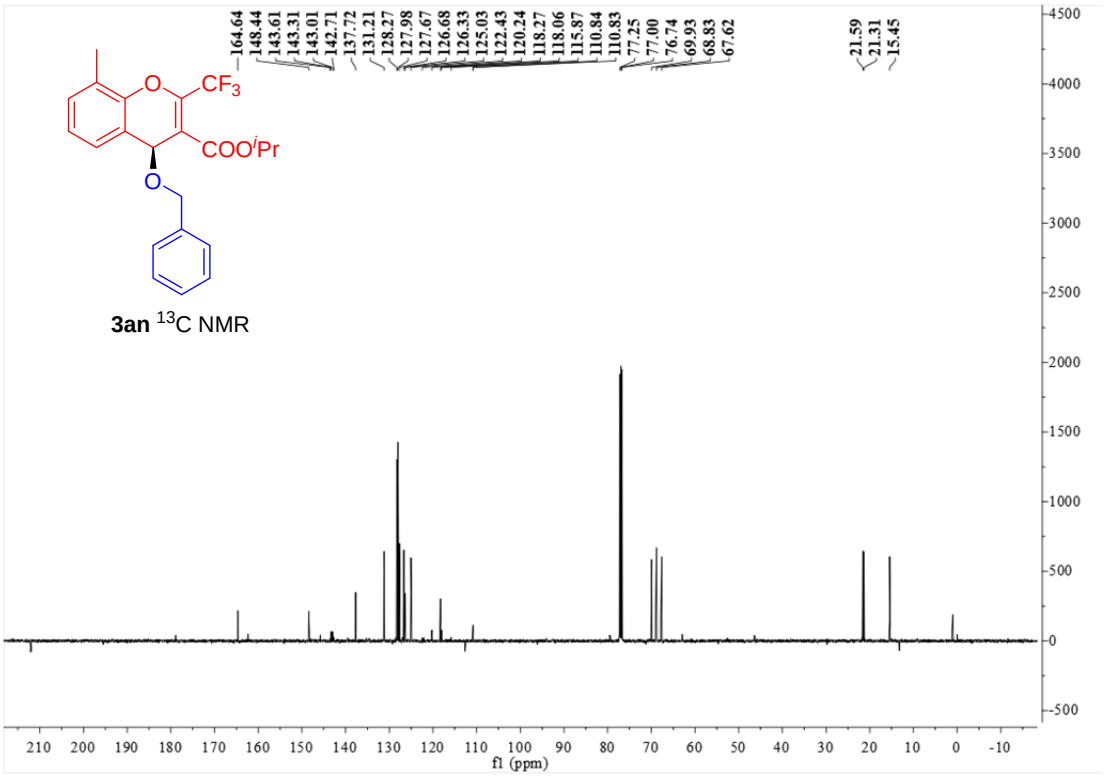
3am ^{13}C NMR



3am ^{19}F NMR



3an ^{1}H NMR



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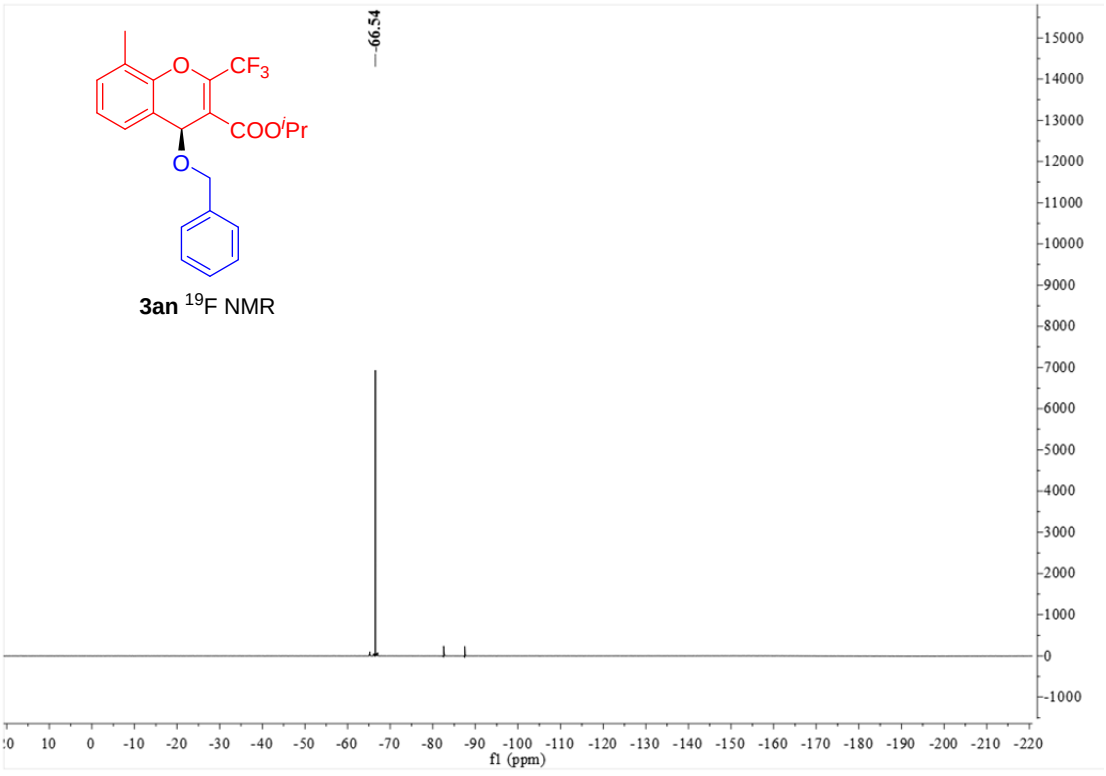
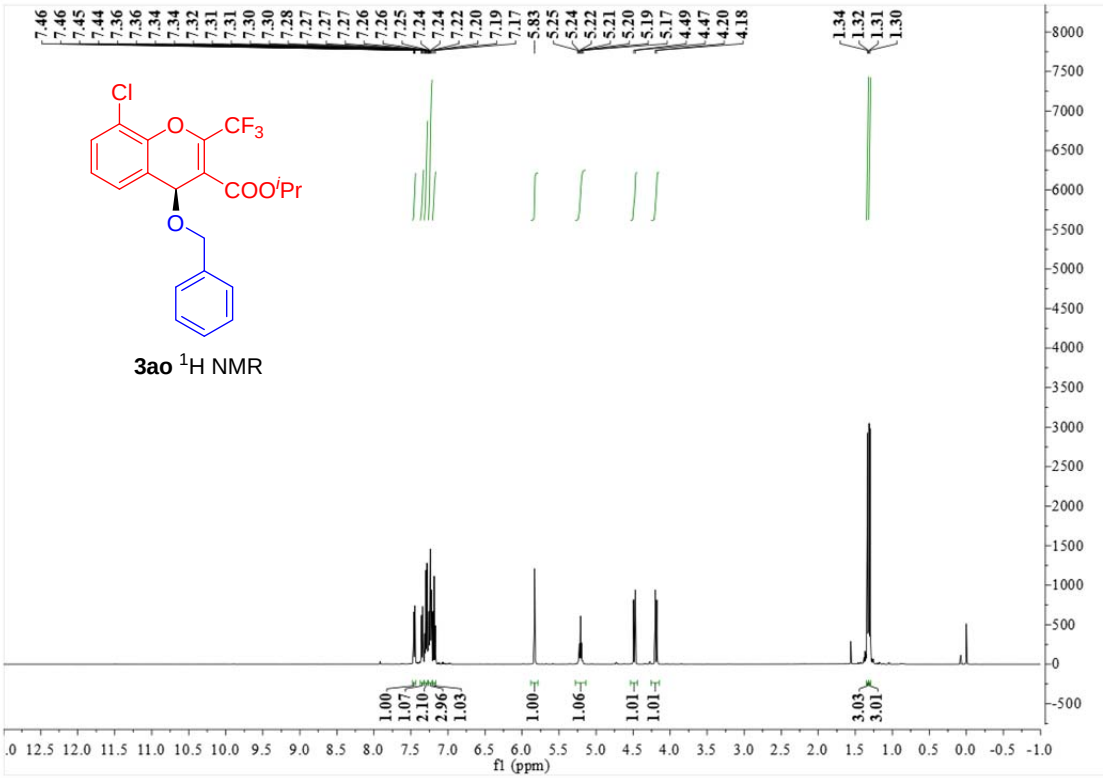


3an ^{19}F NMR



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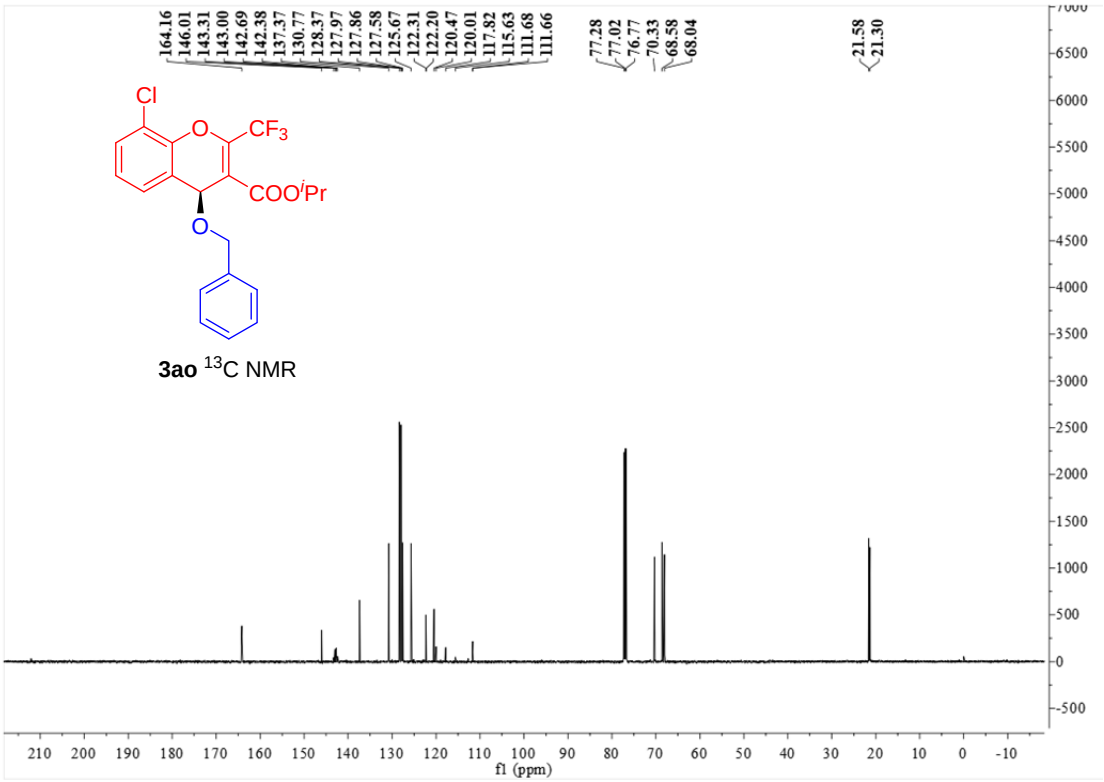

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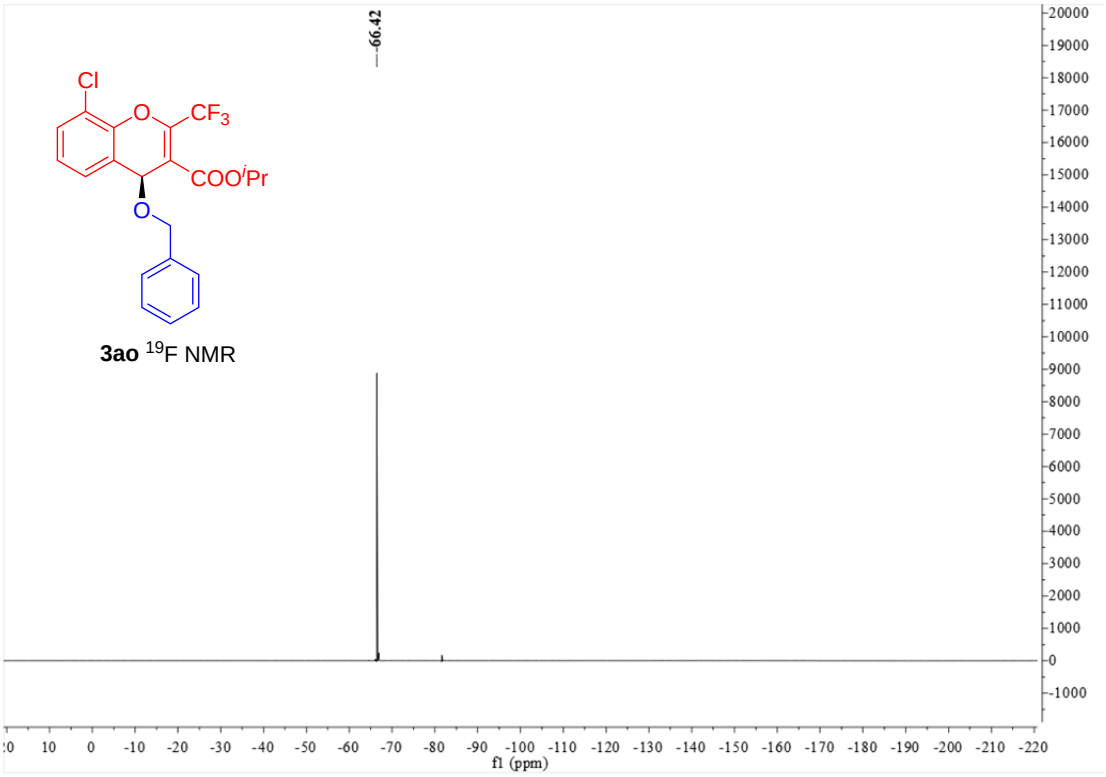
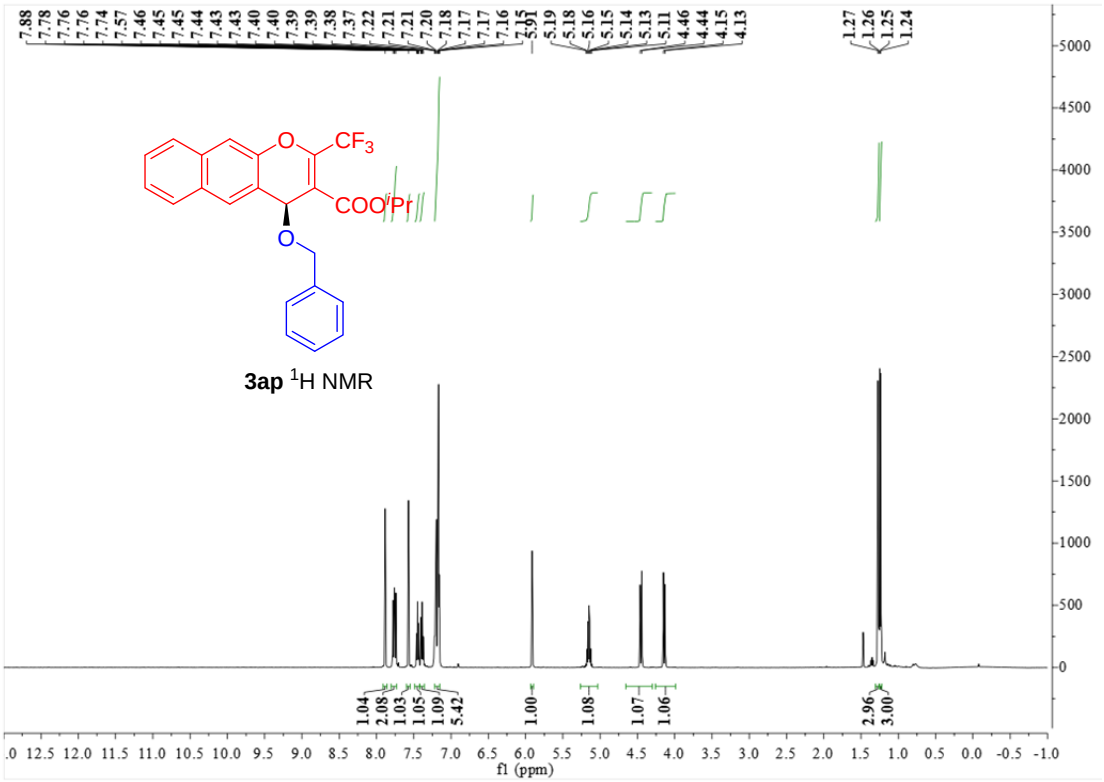
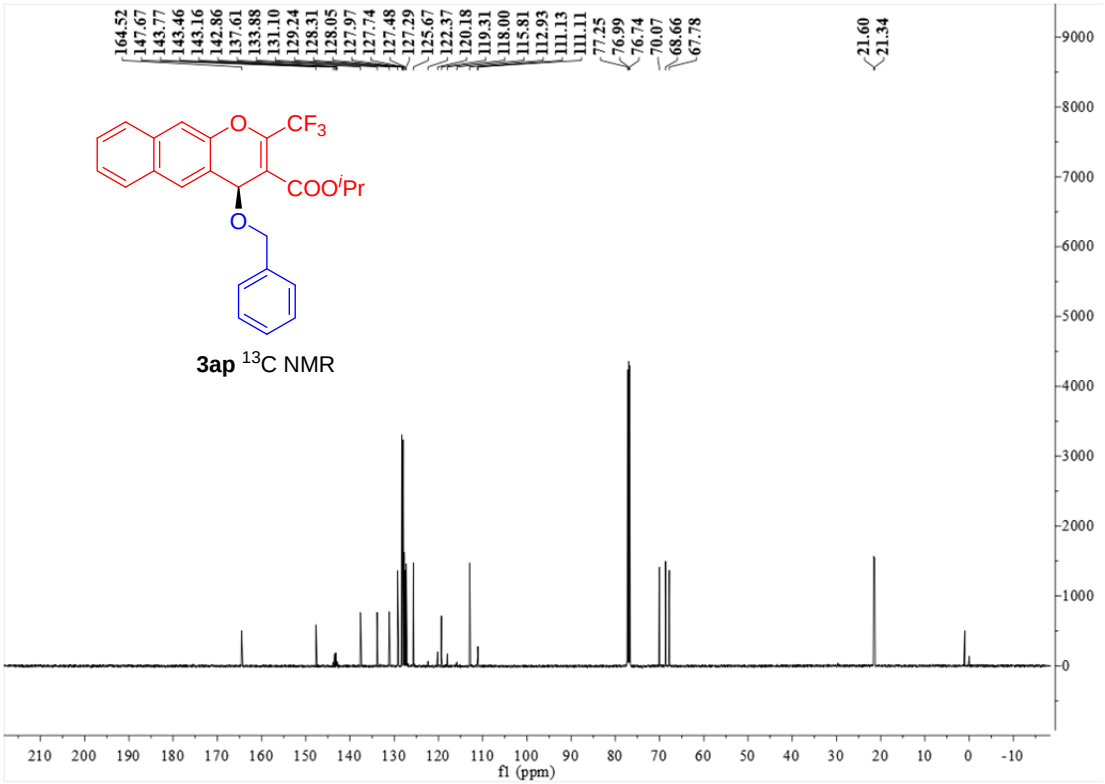


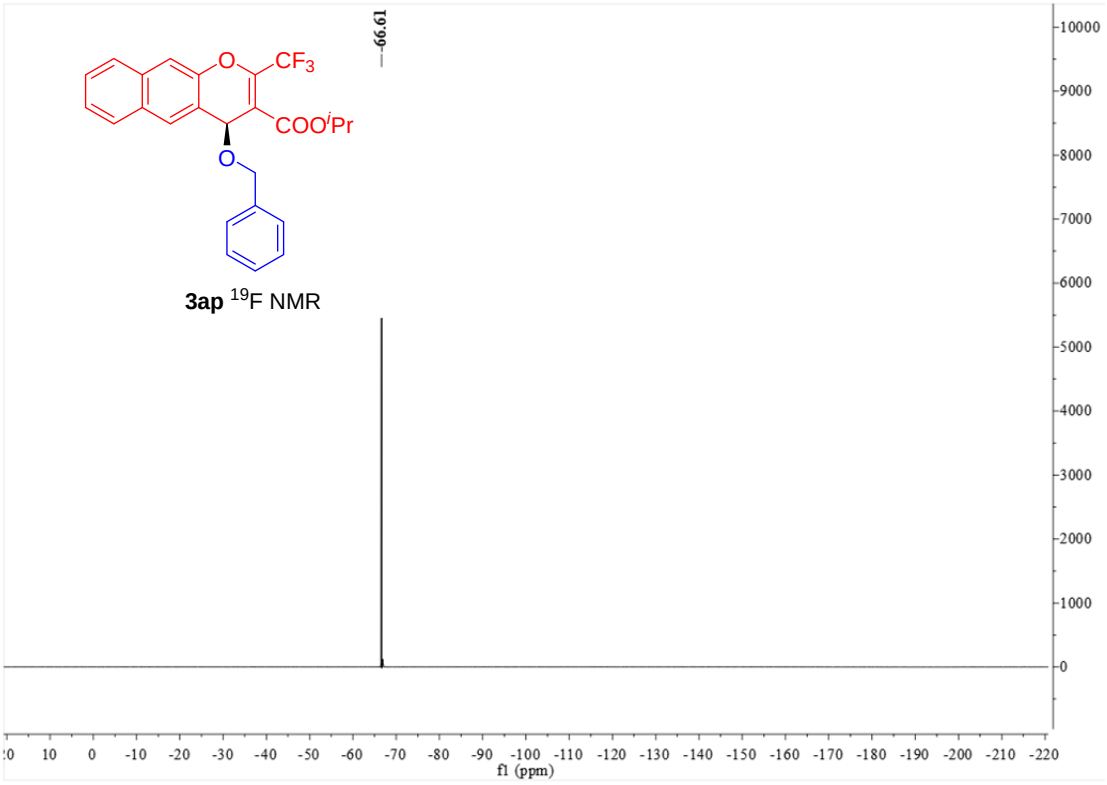
3ao ^{19}F NMR



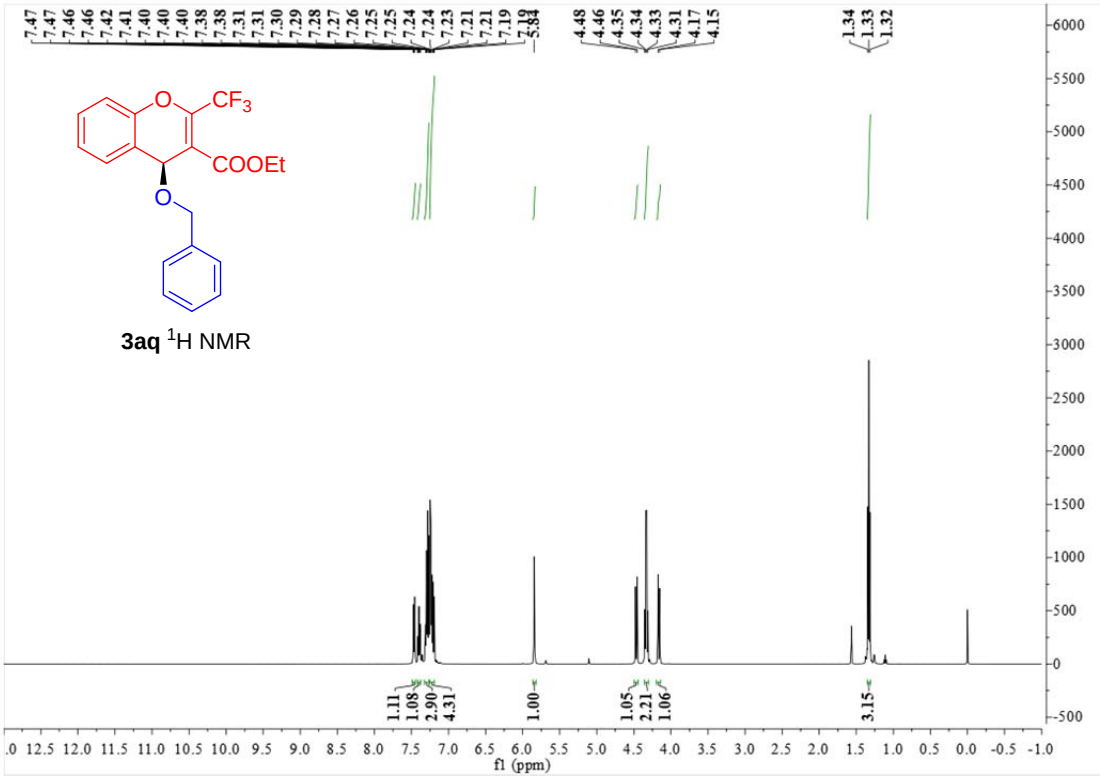
3ap ^{1}H NMR



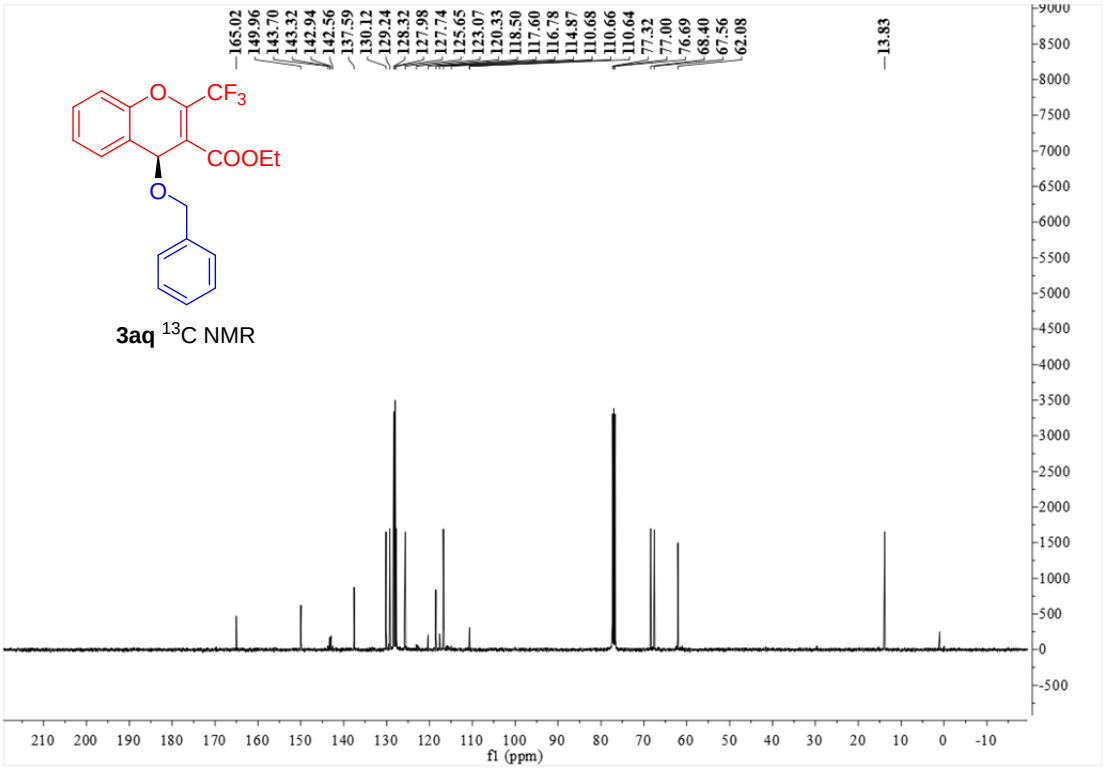
3ap ^{13}C NMR



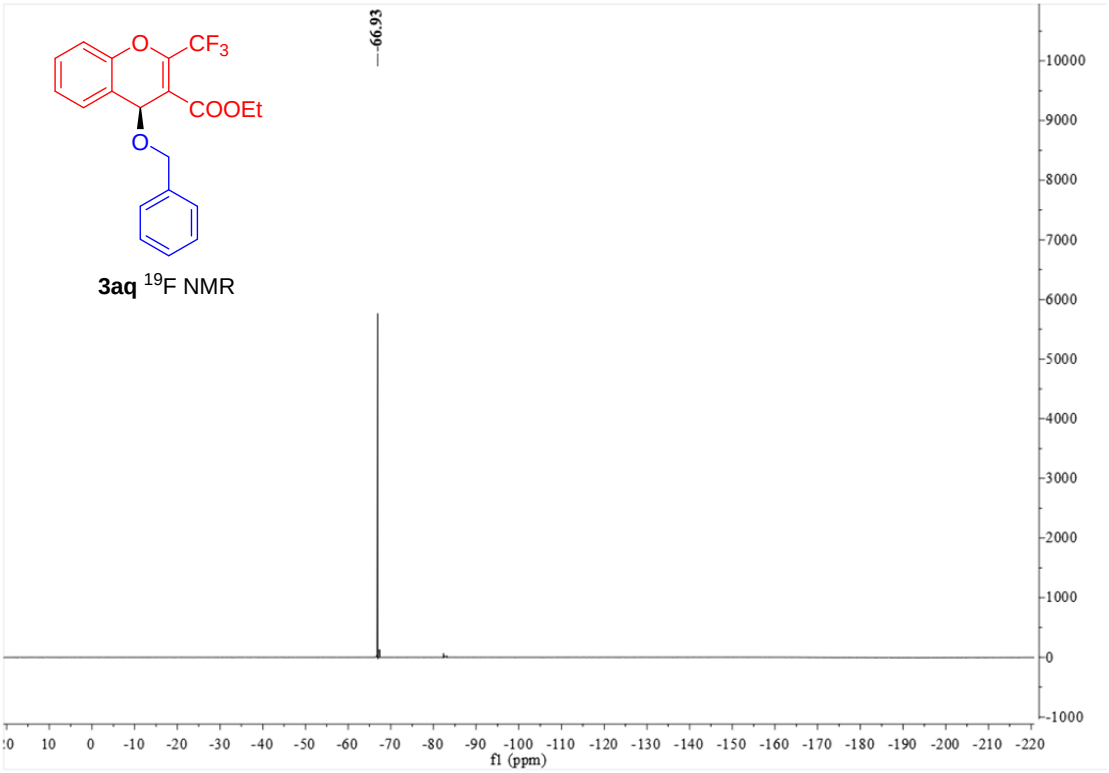
3ap ^{19}F NMR



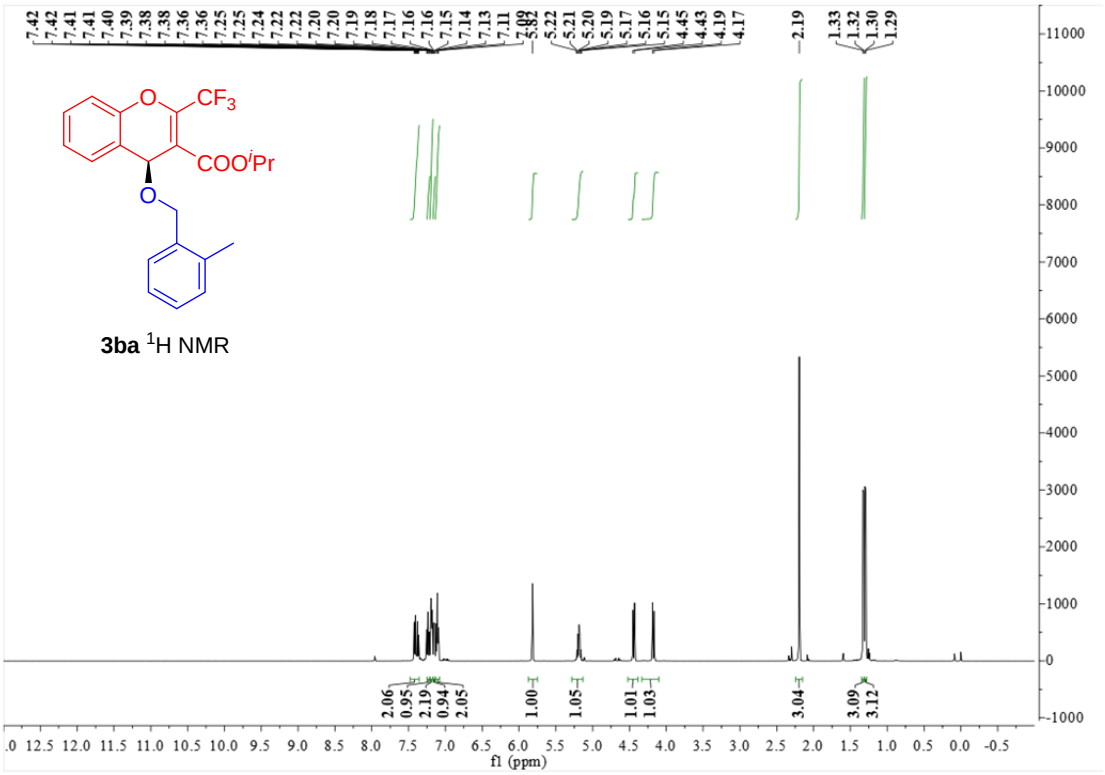
3aq ^{1}H NMR



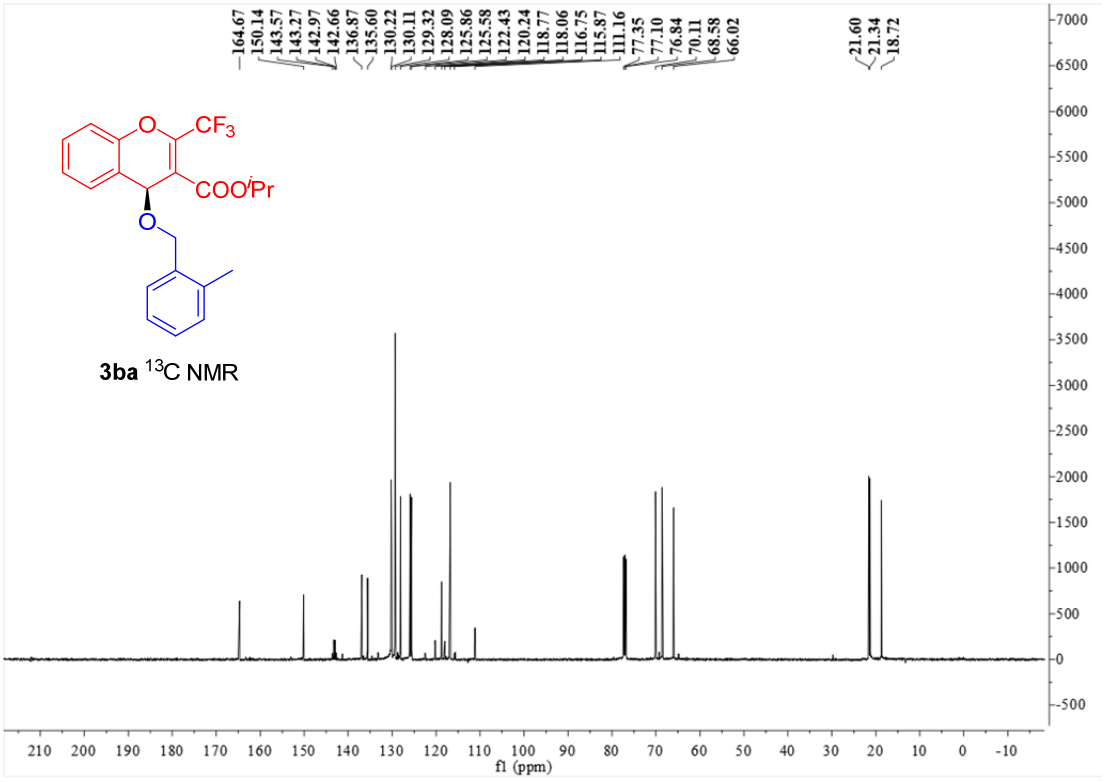
3aq ^{13}C NMR



3aq ^{19}F NMR



3ba ^{1}H NMR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142.66
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125.86
125.58
122.43
120.24
118.77
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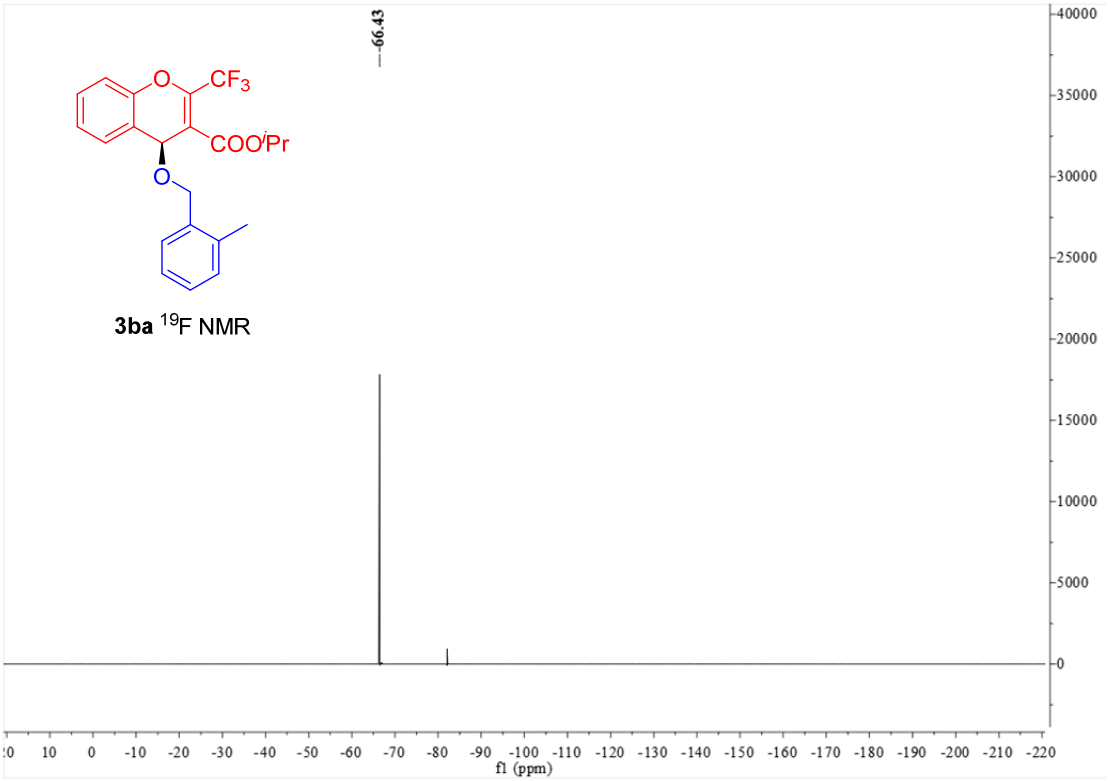
116.75
115.87
111.16
77.35
77.10
76.84
70.11
68.58
66.02
21.60
21.34
18.72
CF3
COO'Pr
O
O
3ba 13C NMR
fl (ppm)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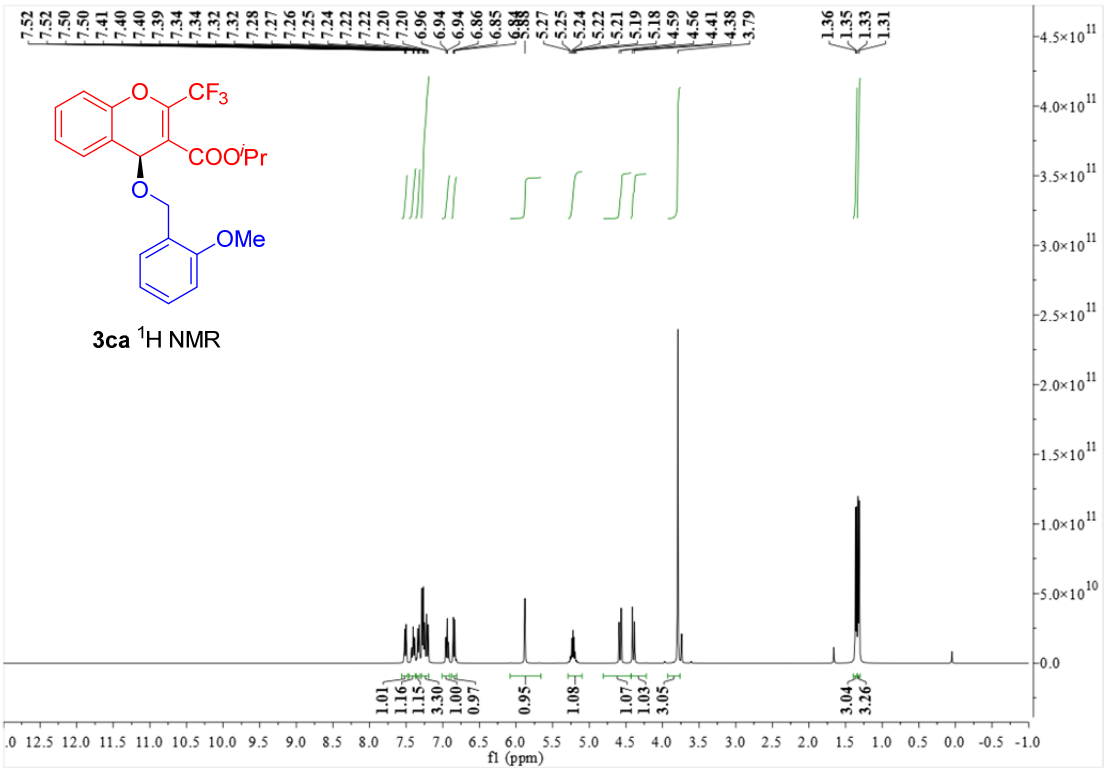
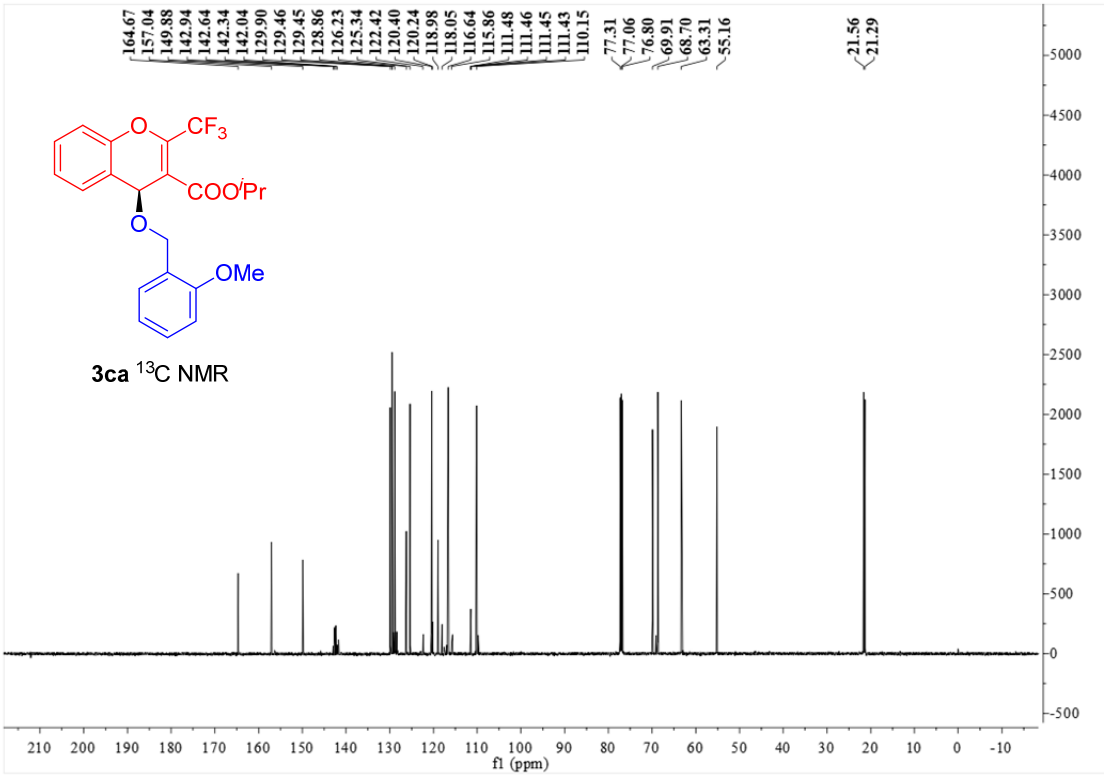
fl (ppm)


7.52 7.52 7.50 7.50 7.41 7.40 7.40 7.39 7.34 7.34 7.32 7.32 7.28 7.27 7.26 7.25 7.24 7.22 7.22 7.20 7.20 6.96 6.94 6.94 6.86 6.85 5.27 5.25 5.24 5.22 5.21 5.19 5.18 4.59 4.56 4.41 4.38 3.79 1.36 1.35 1.33 1.31
CF3
COO'Pr
O
OMe
3ca 1H NMR
1.01 1.16 1.15 3.30 1.00 0.97 0.95 1.08 1.07 1.03 3.05 3.04 3.26
f1 (ppm)


164.67 157.04 149.88 142.94 142.64 142.34 142.04 129.90 129.46 129.45 128.86 126.23 125.34 122.42 120.40 120.24 118.98 118.05 116.64 115.86 111.48 111.46 111.45 111.43 110.15 77.31 77.06 76.80 69.91 68.70 63.31 55.16 21.56 21.29
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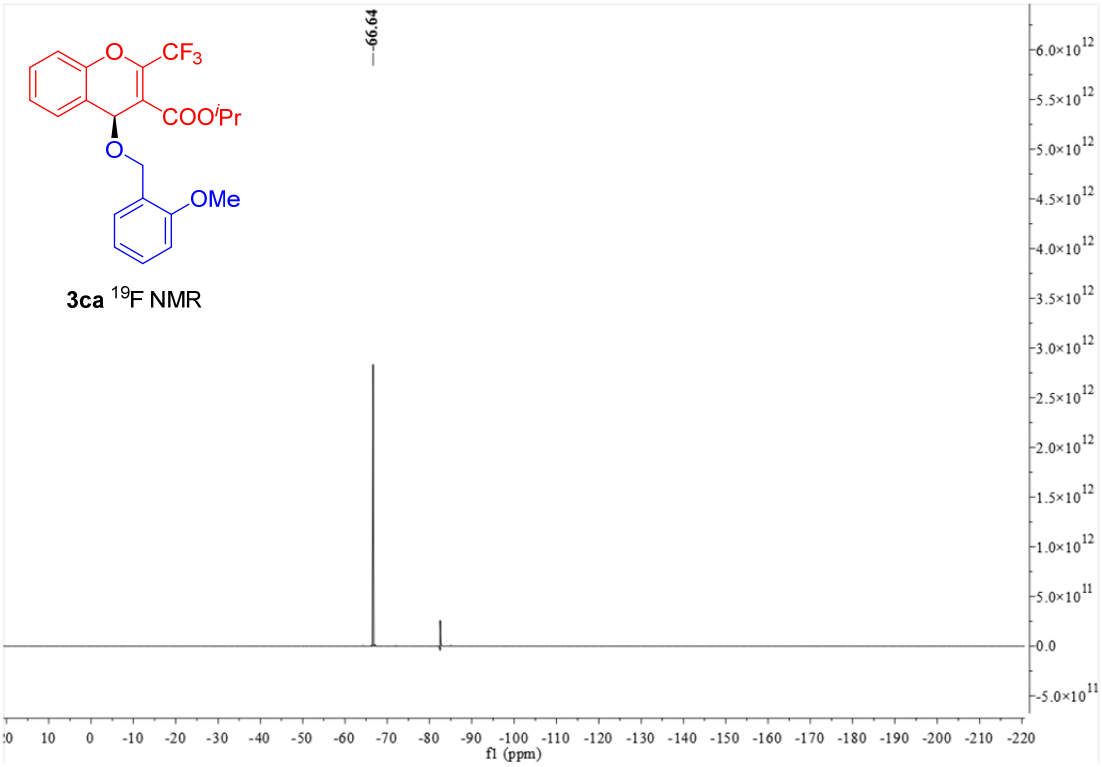
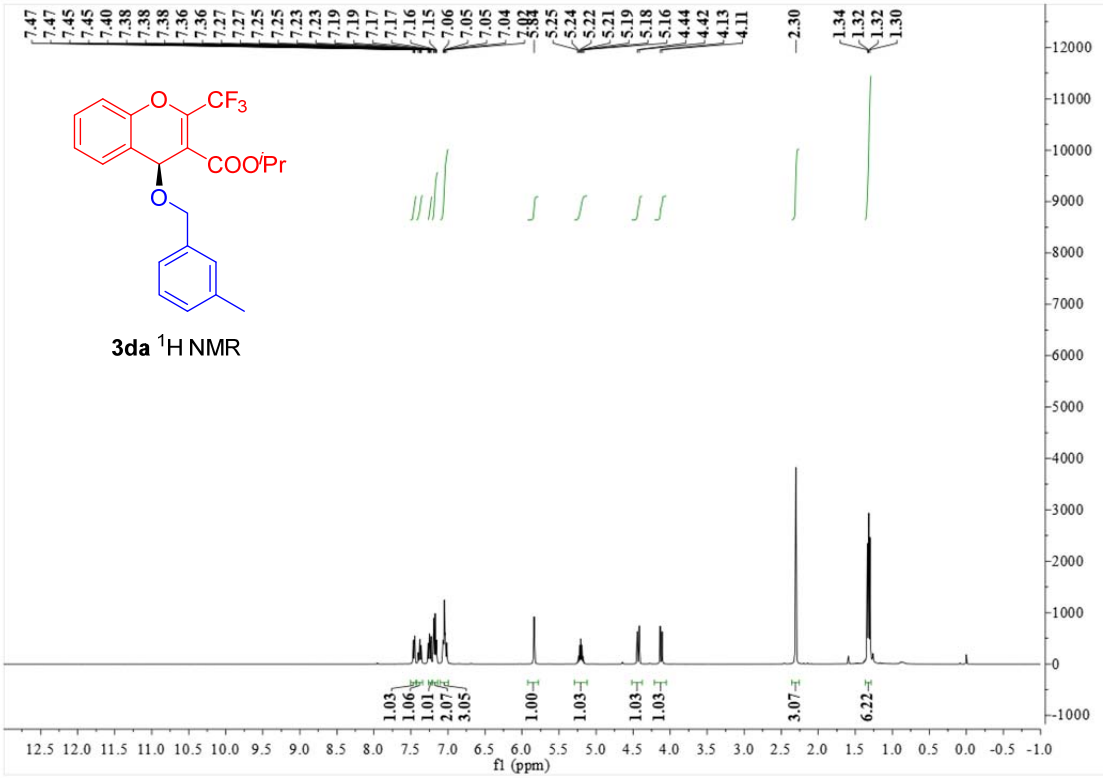
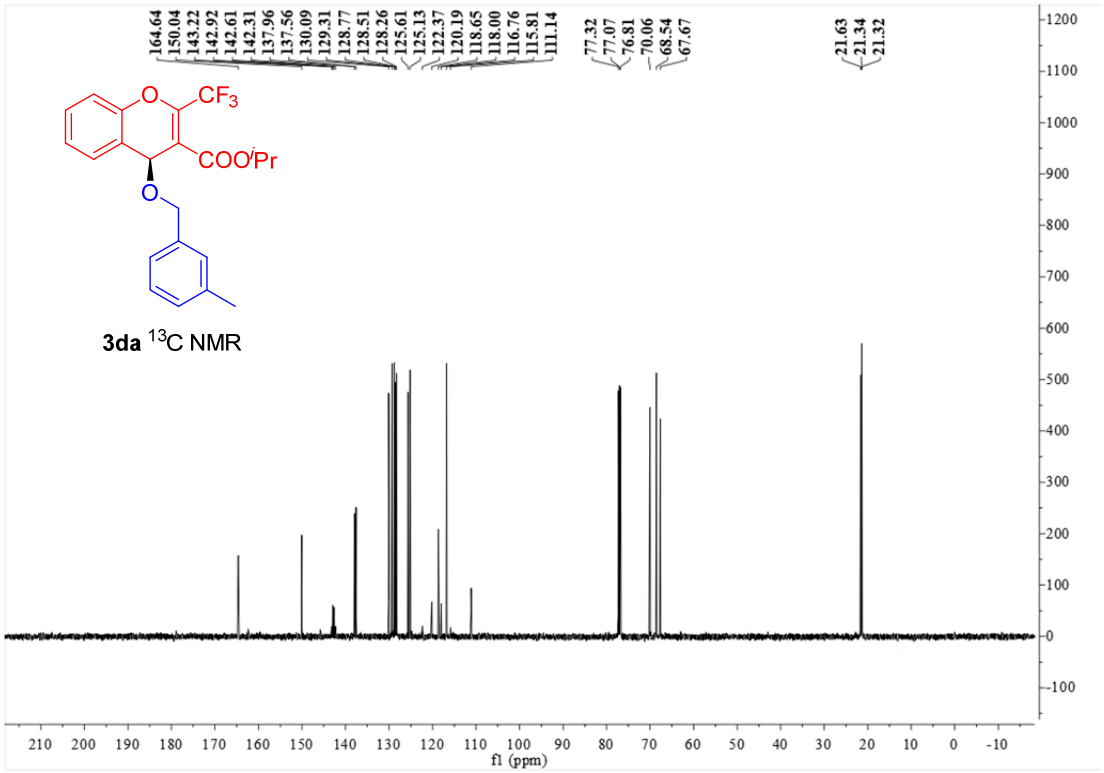
COO'Pr
O
OMe
3ca 13C NMR
f1 (ppm)



3ca ^{19}F NMR



3da ^{1}H NMR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111.14
77.32
77.07
76.81
70.06
68.54
67.67
21.63
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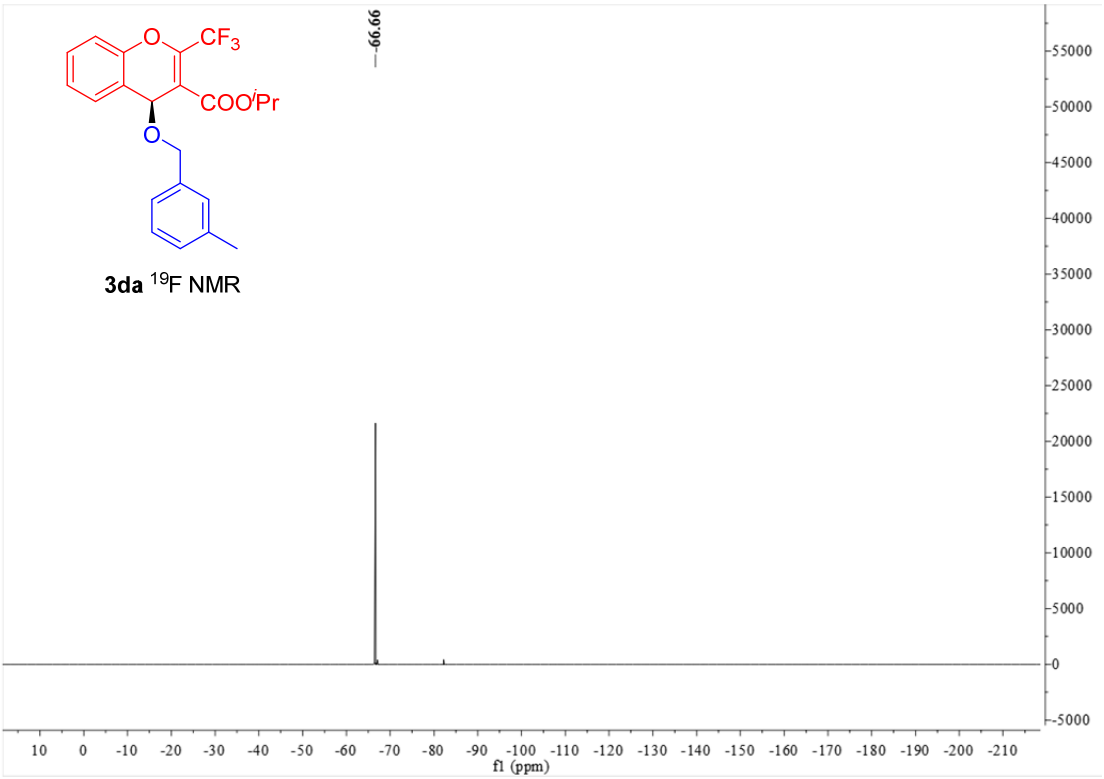
21.32
O
CF3
COO'Pr
O
3da 13C NMR
f1 (ppm)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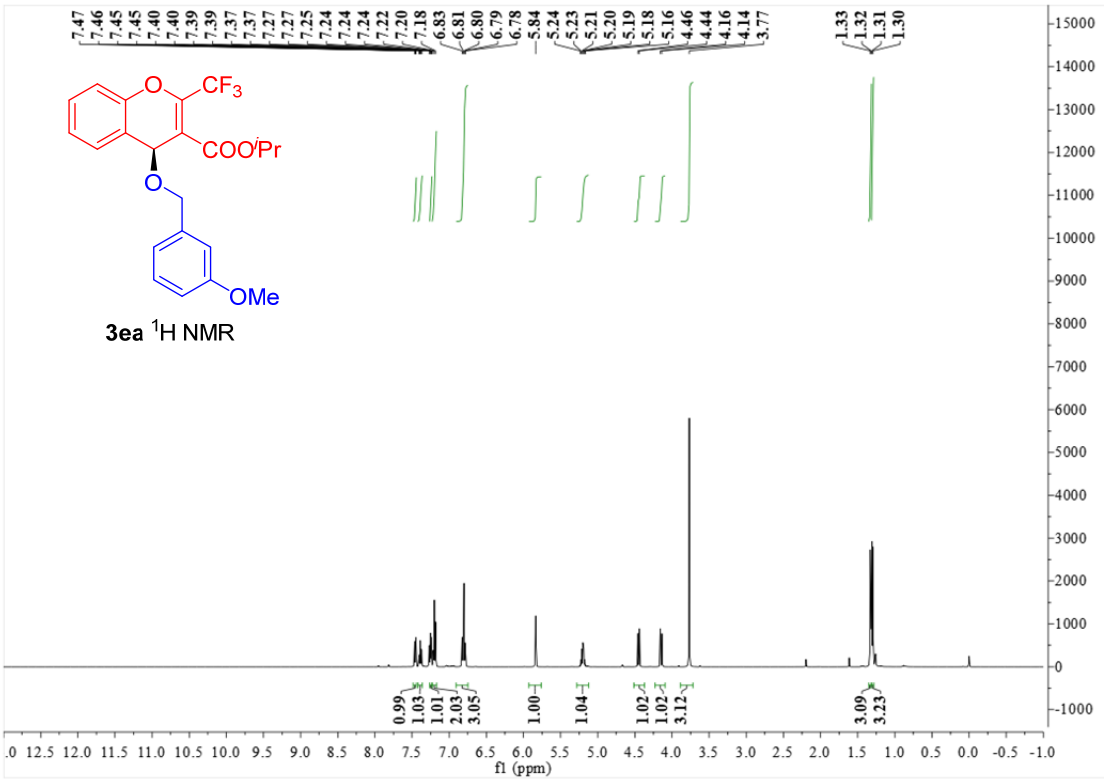
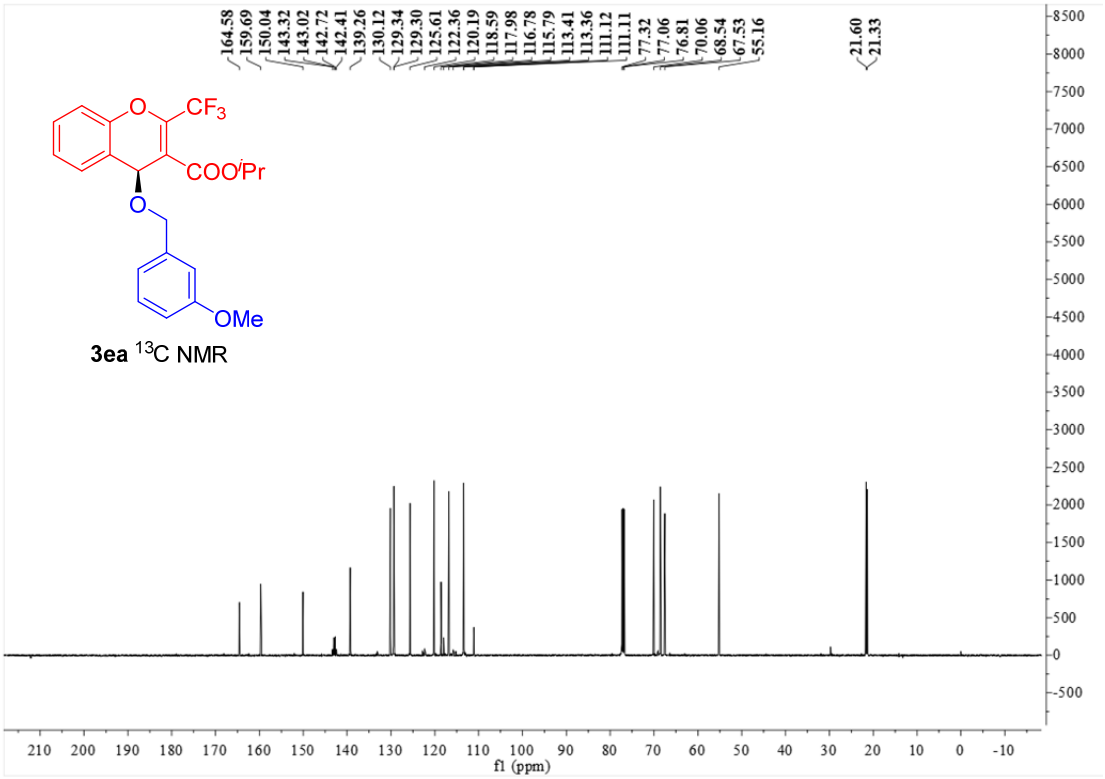
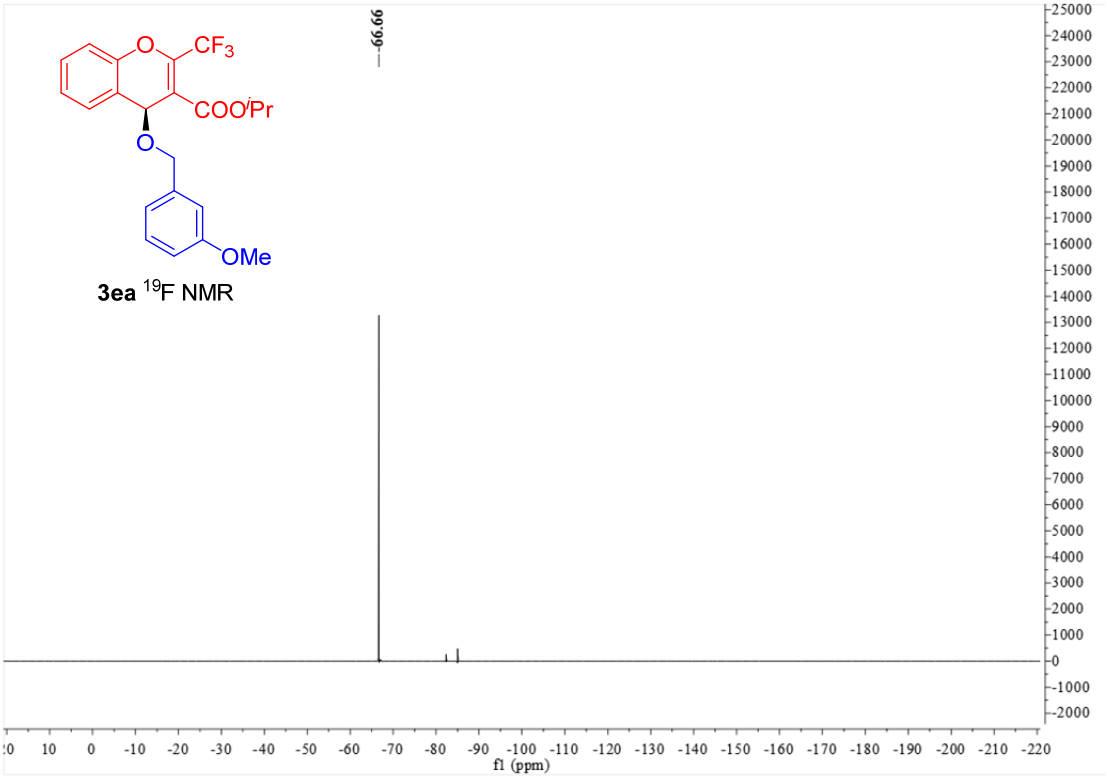
O
CF3
COO'Pr
O
3da 19F NMR
f1 (ppm)



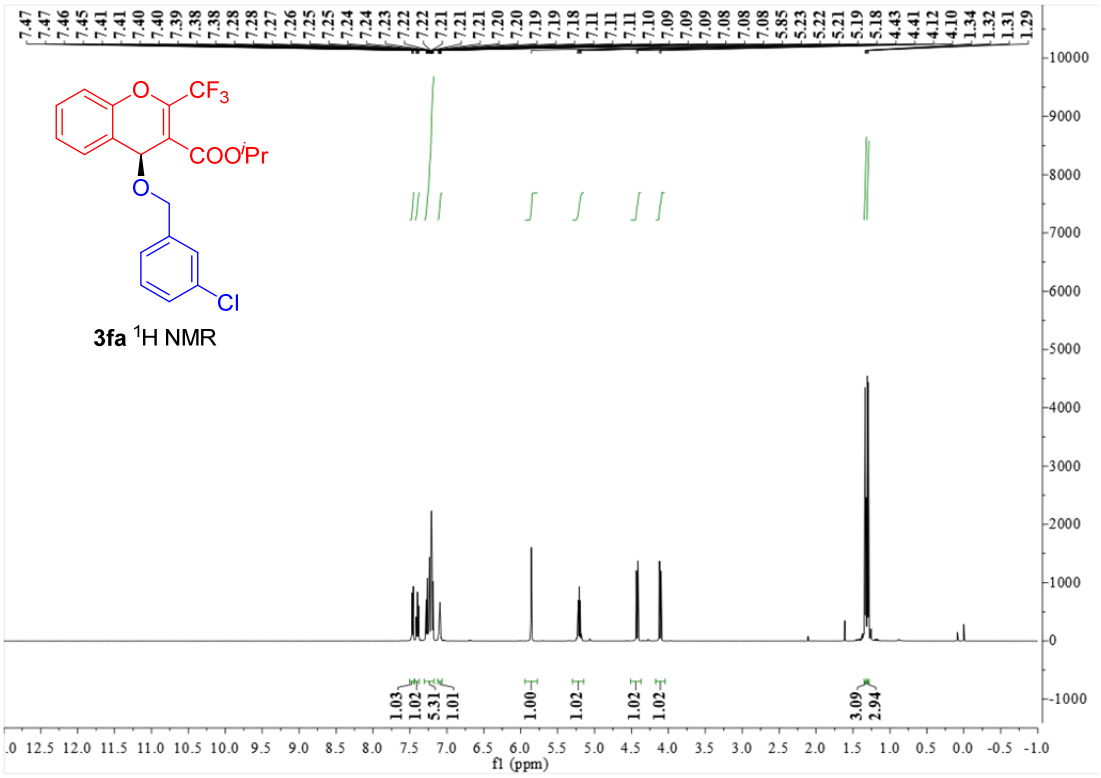
3ea ^{1}H NMR



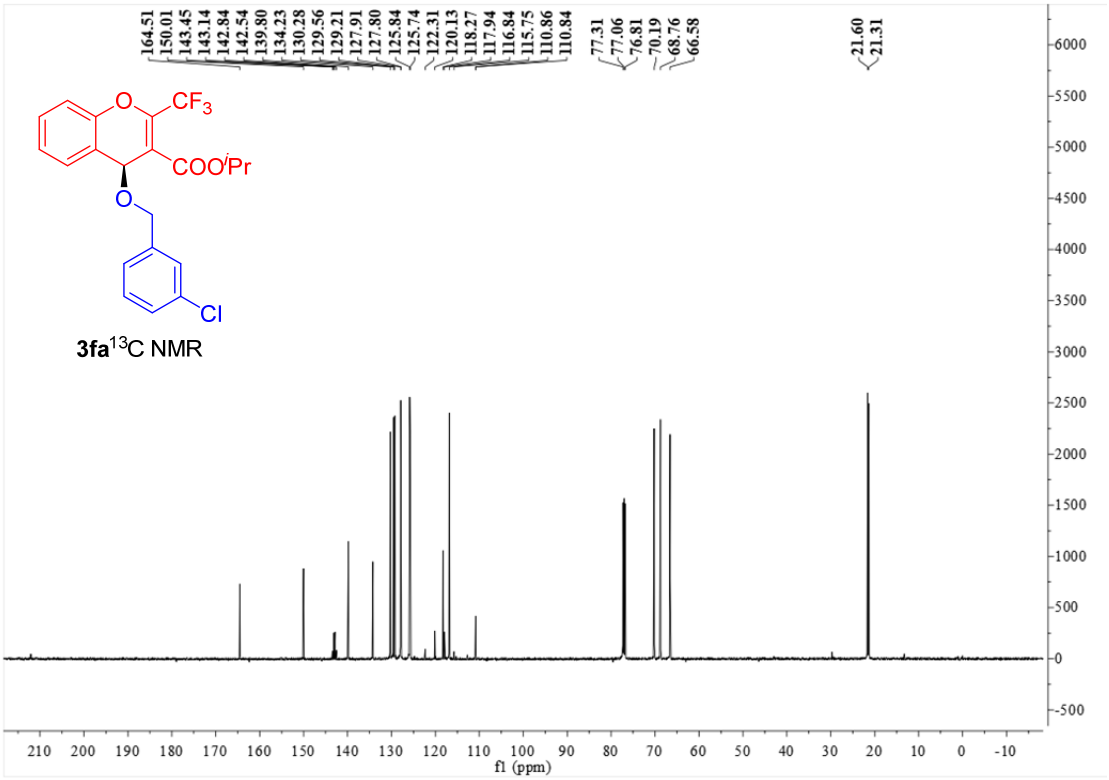
3ea ^{13}C NMR



3ea ^{19}F NMR



3fa ^{1}H NMR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77.31
77.06
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COOiPr
O
Cl
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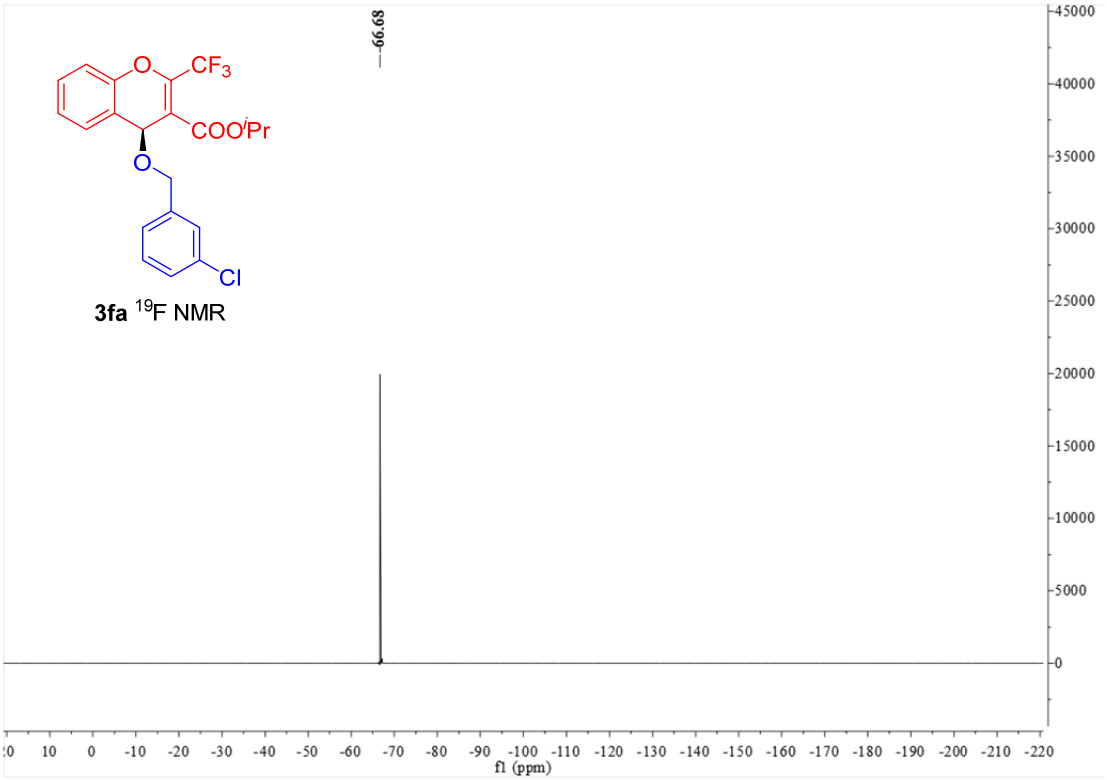
fl (ppm)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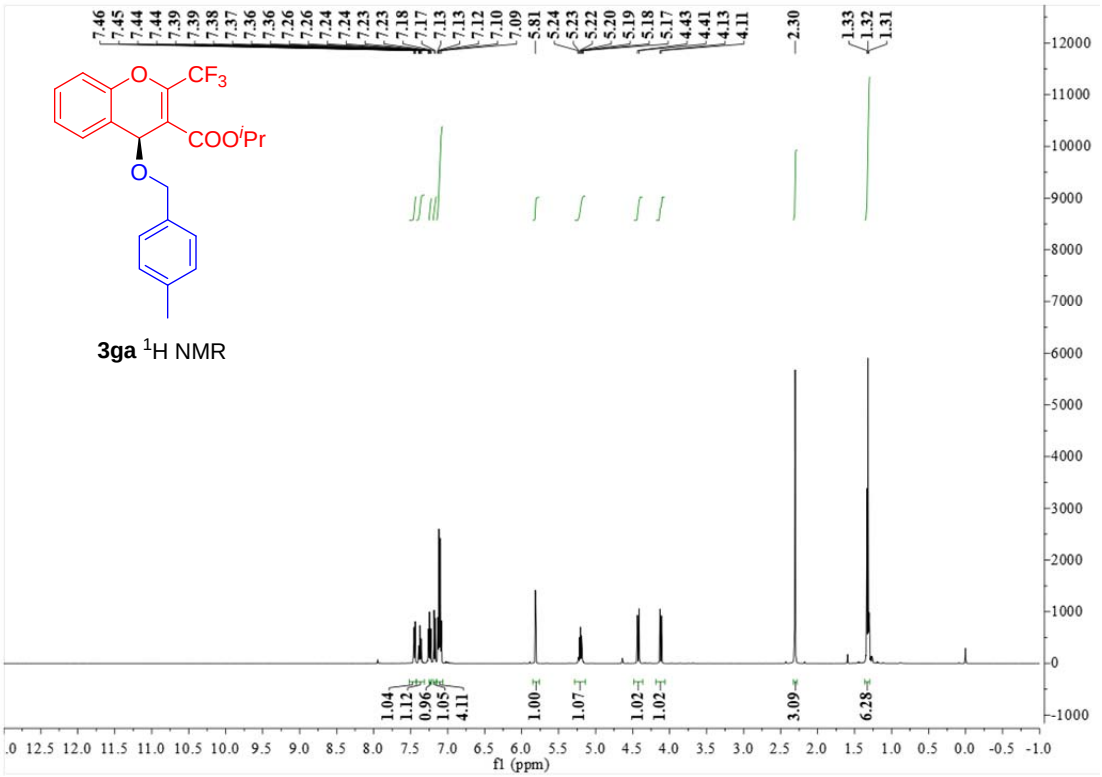
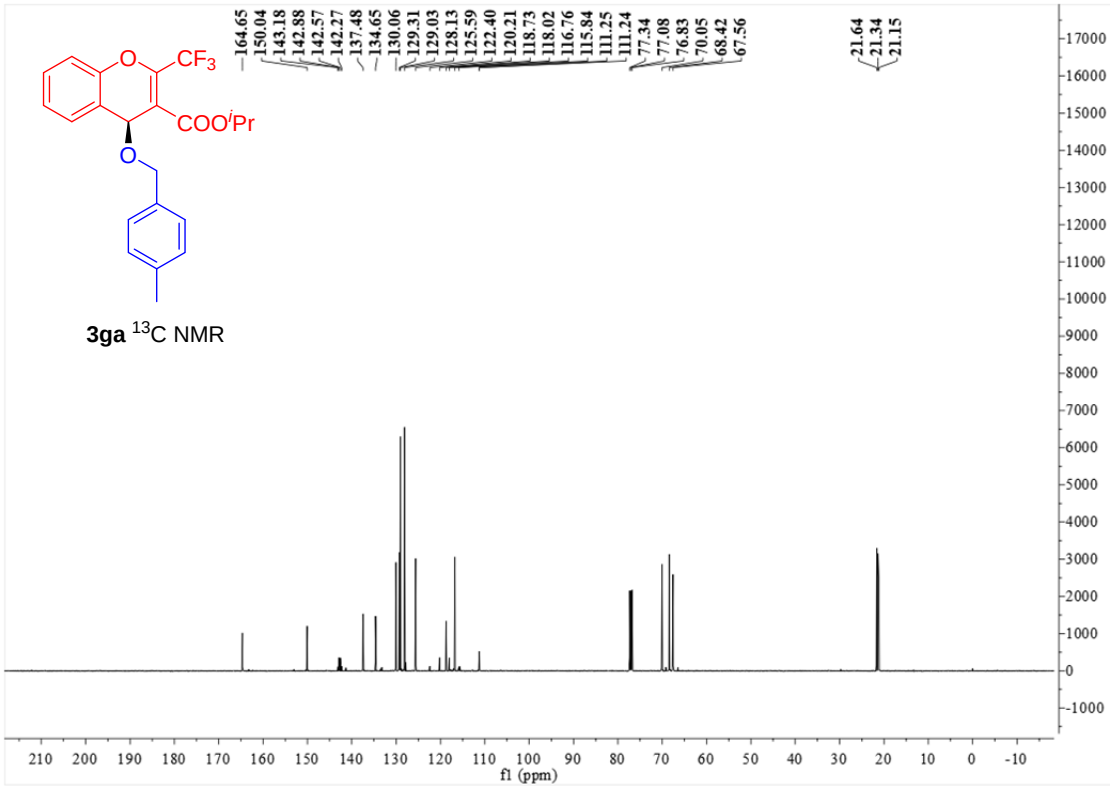
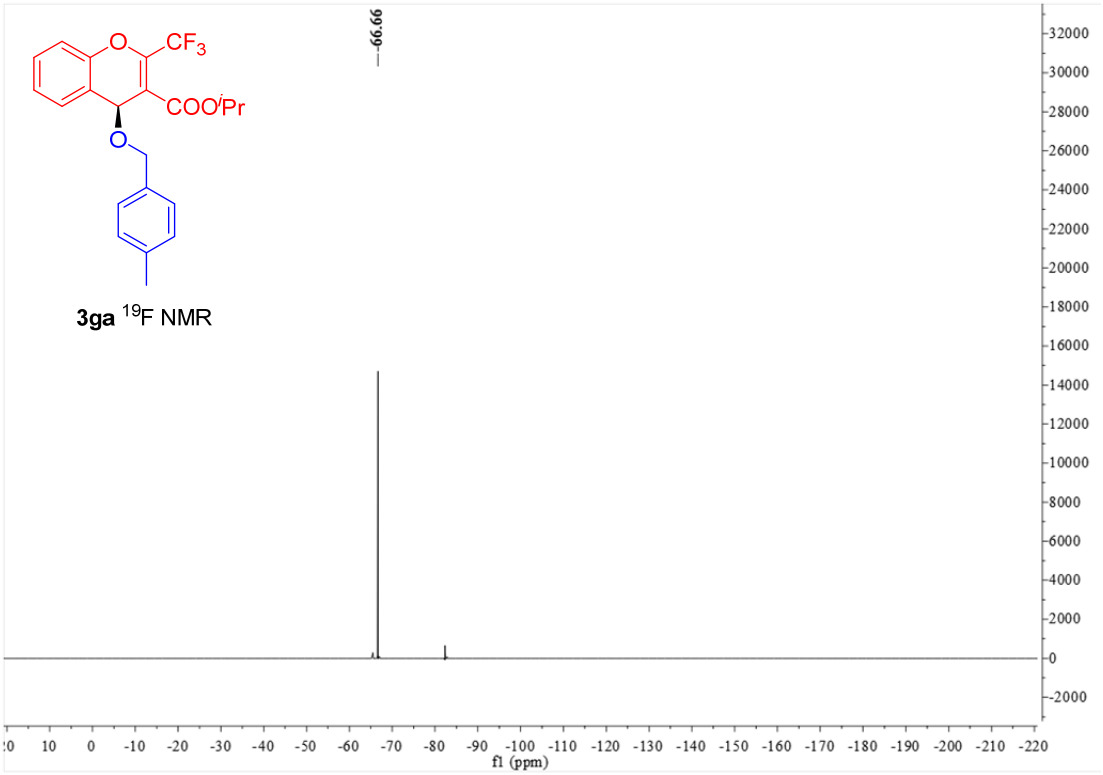
fl (ppm)



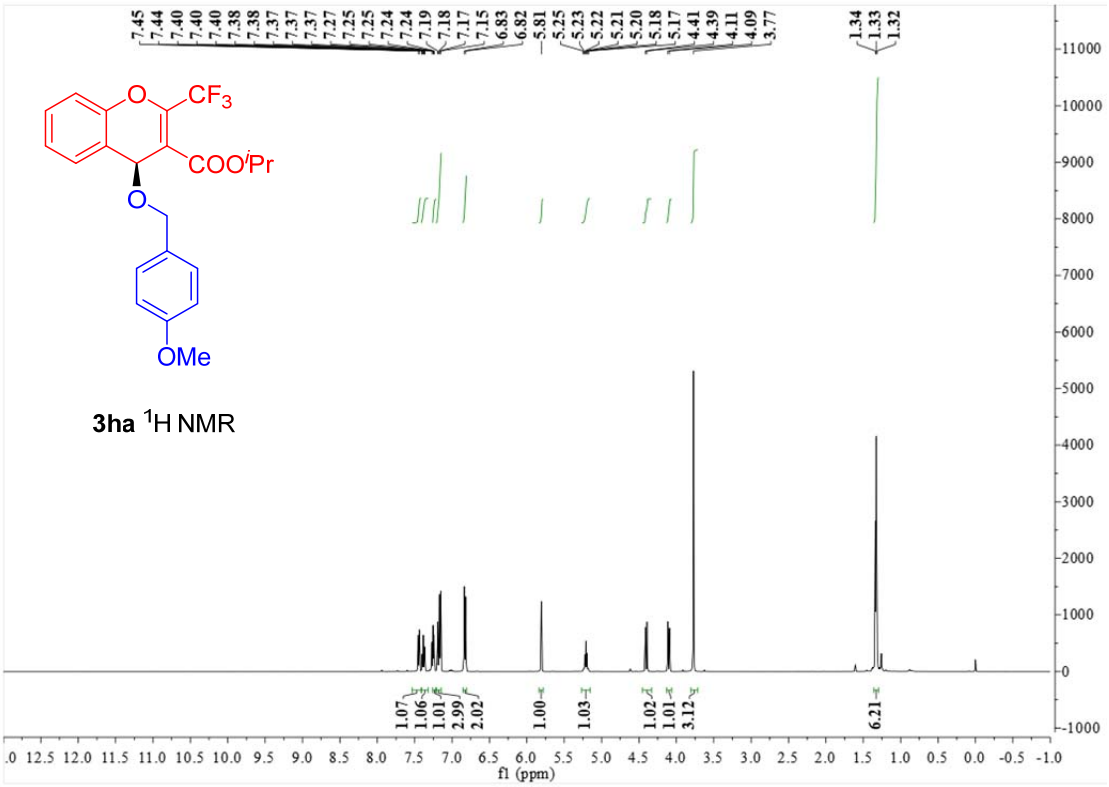
3ga ^{1}H NMR



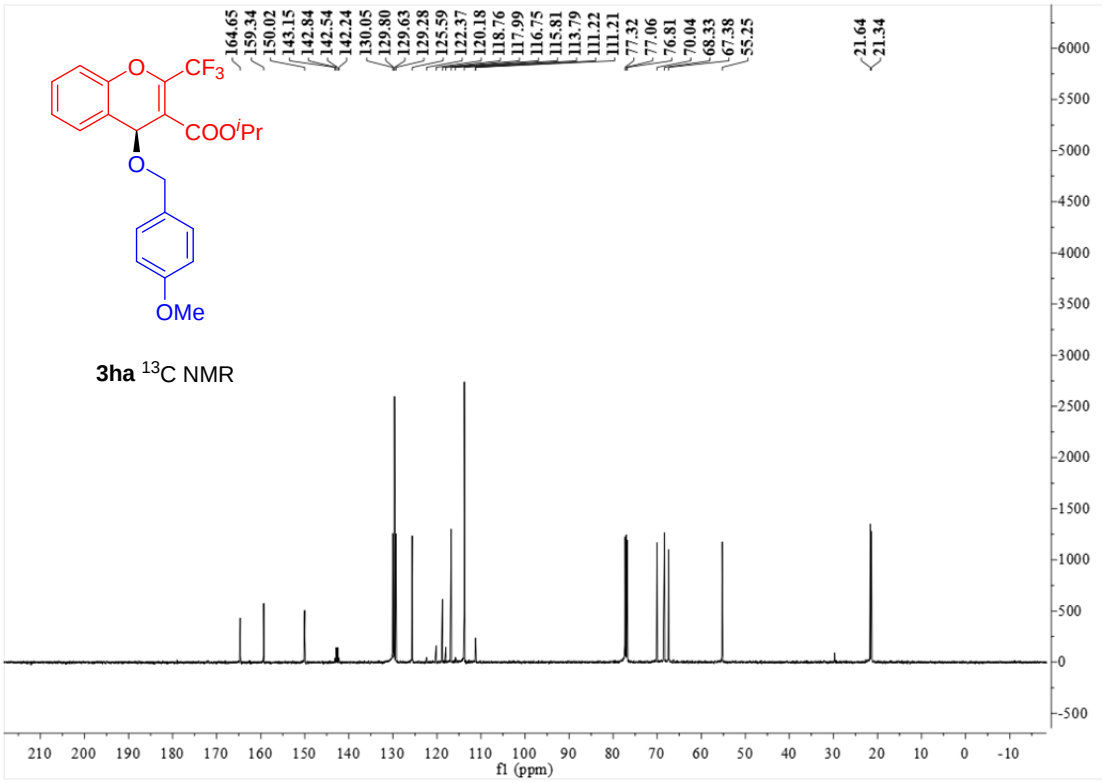
3ga ^{13}C NMR



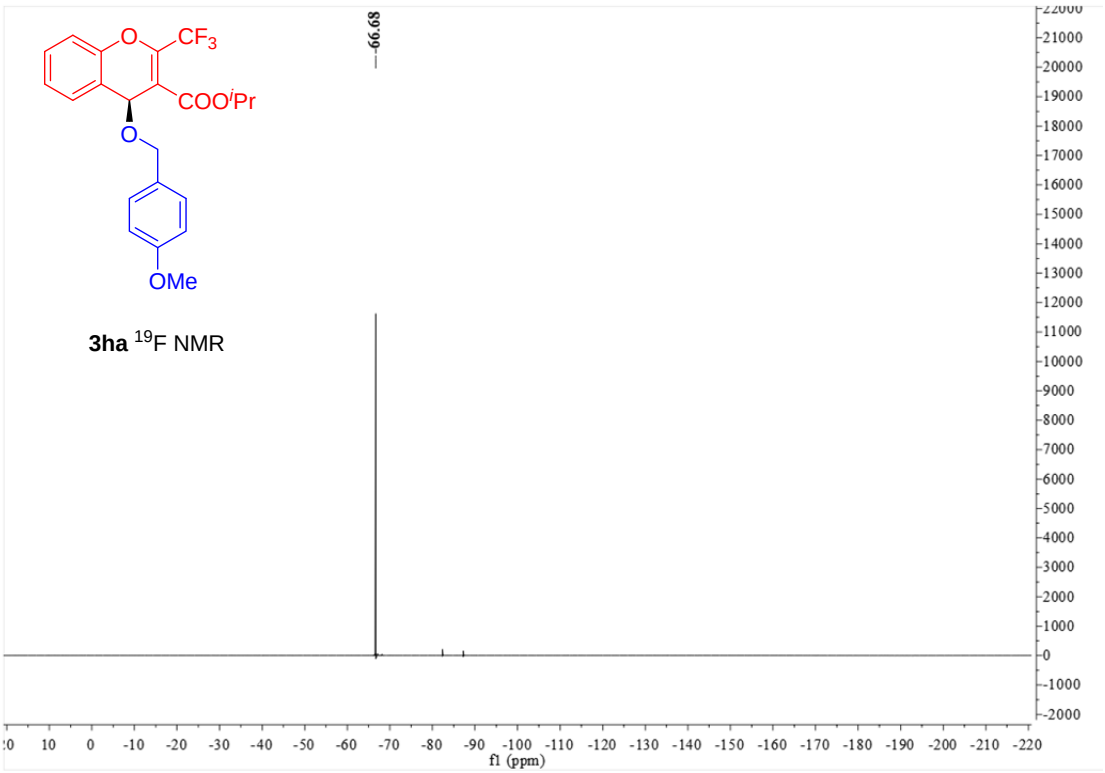
3ga ^{19}F NMR



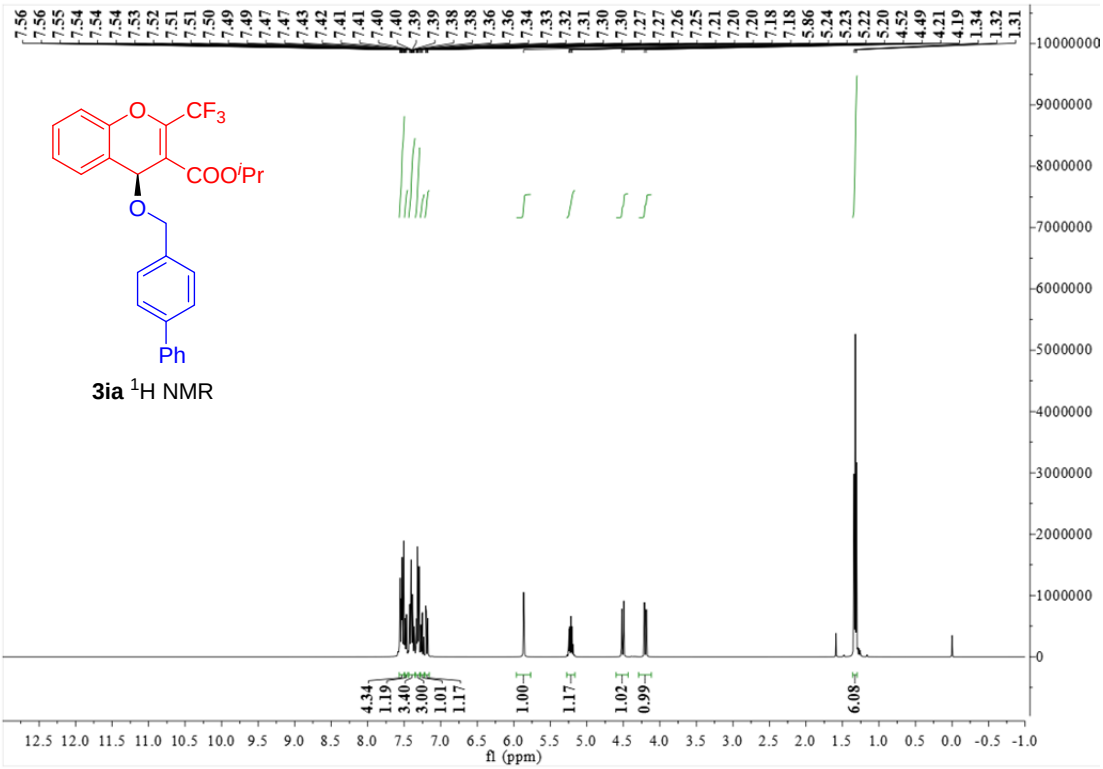
3ha ^{1}H NMR



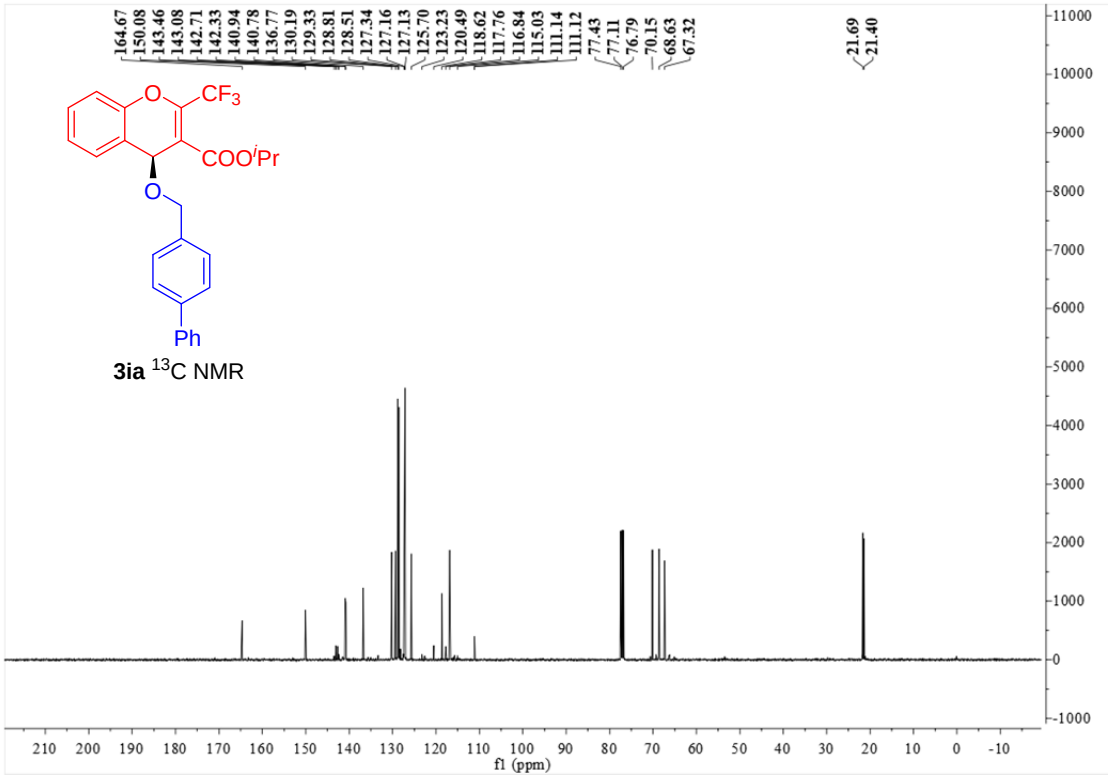
3ha ^{13}C NMR



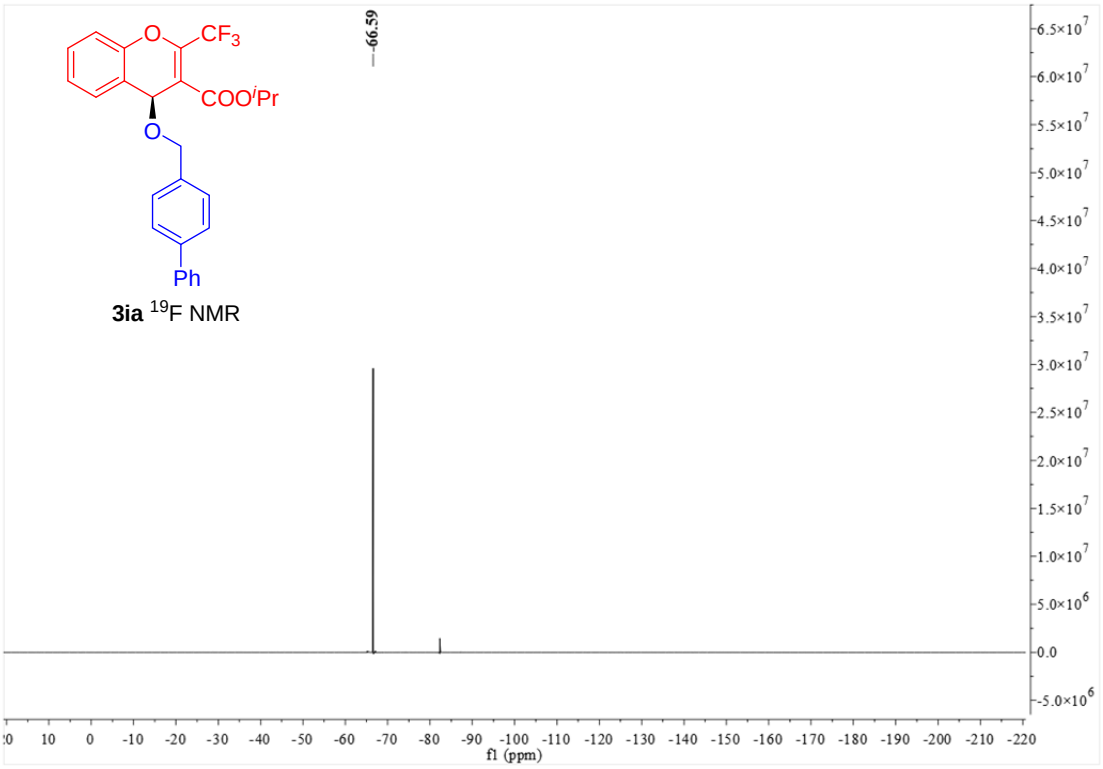
3ha ^{19}F NMR



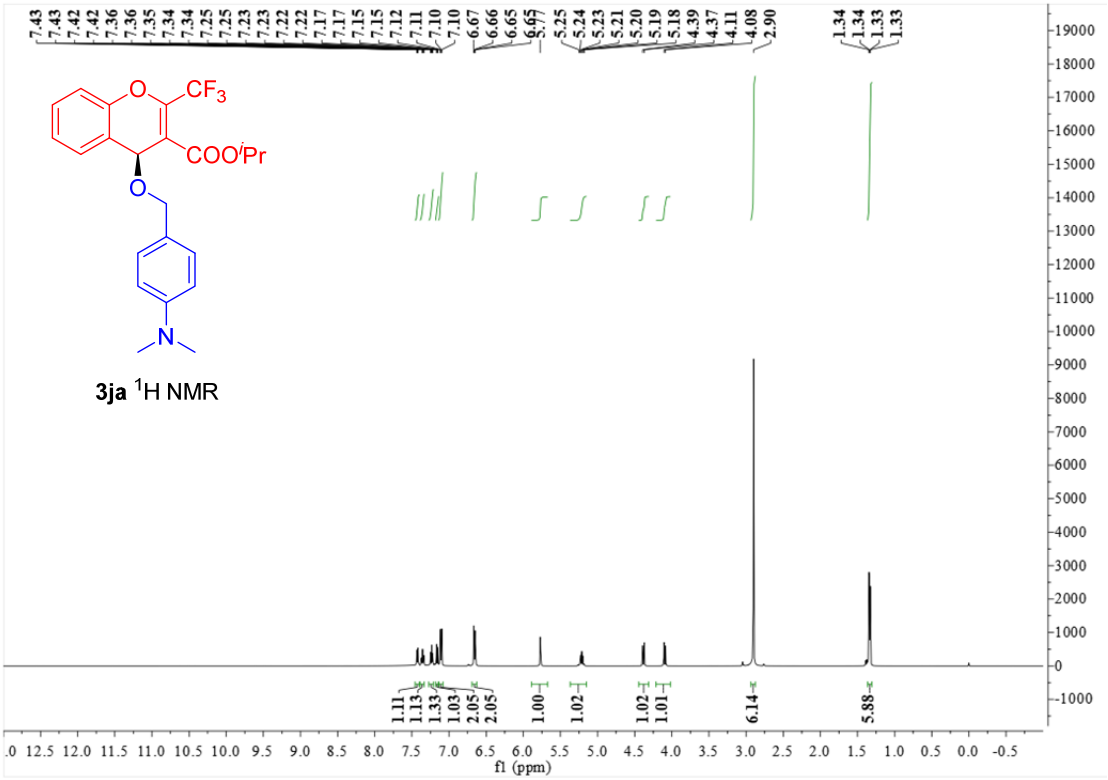
3ia ^{1}H NMR



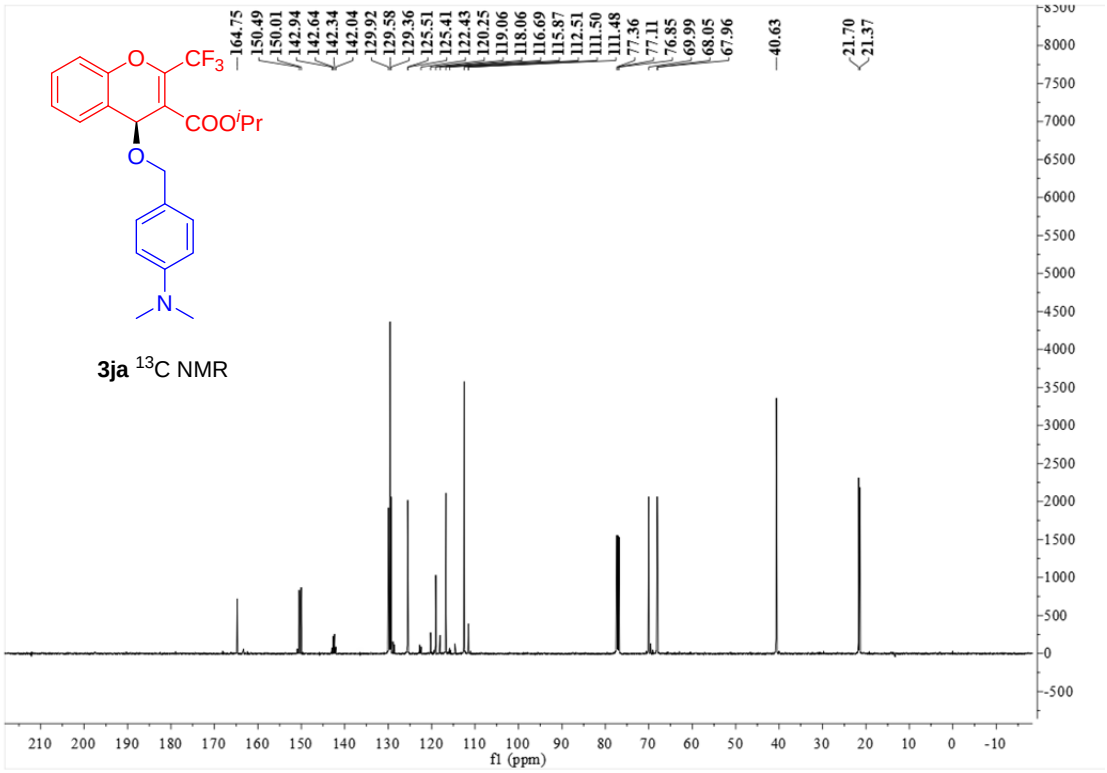
3ia ^{13}C NMR



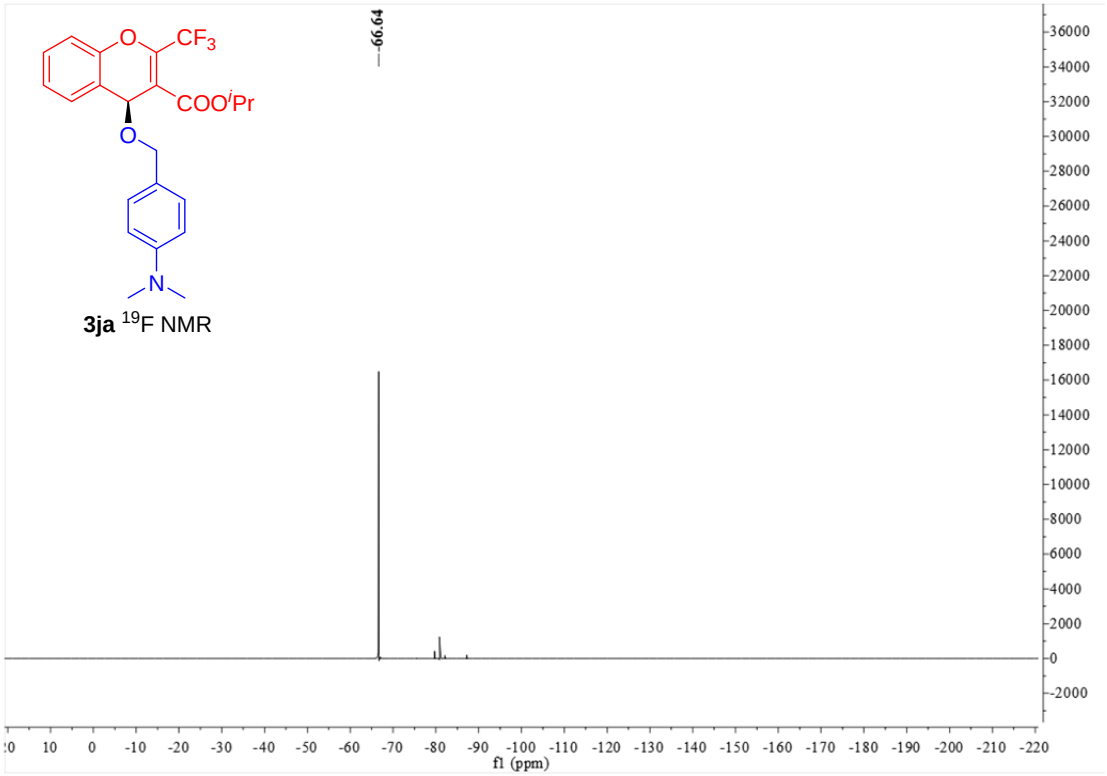
3ia ^{19}F NMR



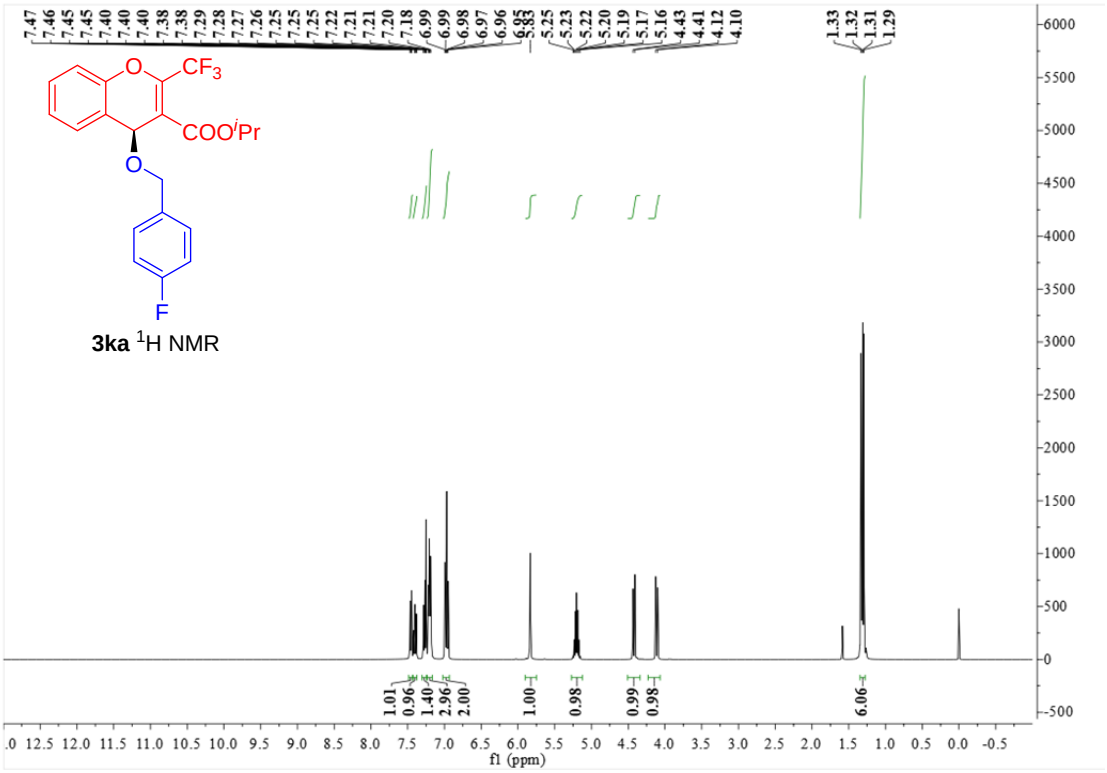
3ja ^{1}H NMR



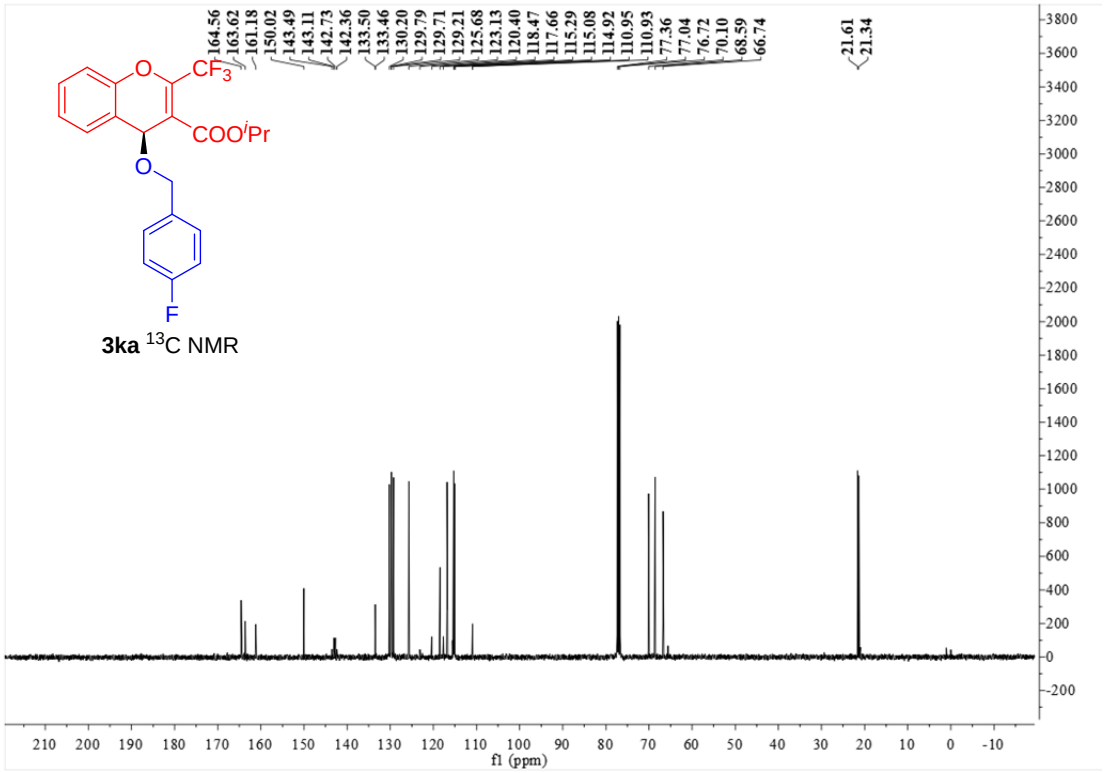
3ja ^{13}C NMR



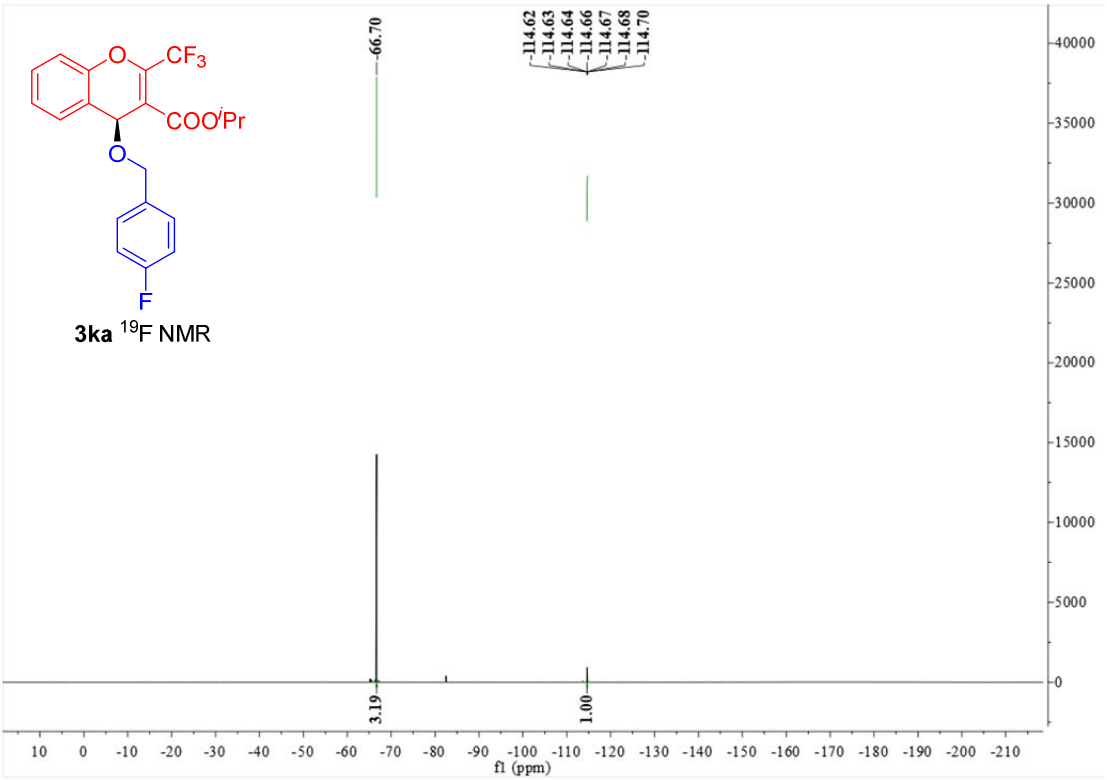
3ja ^{19}F NMR



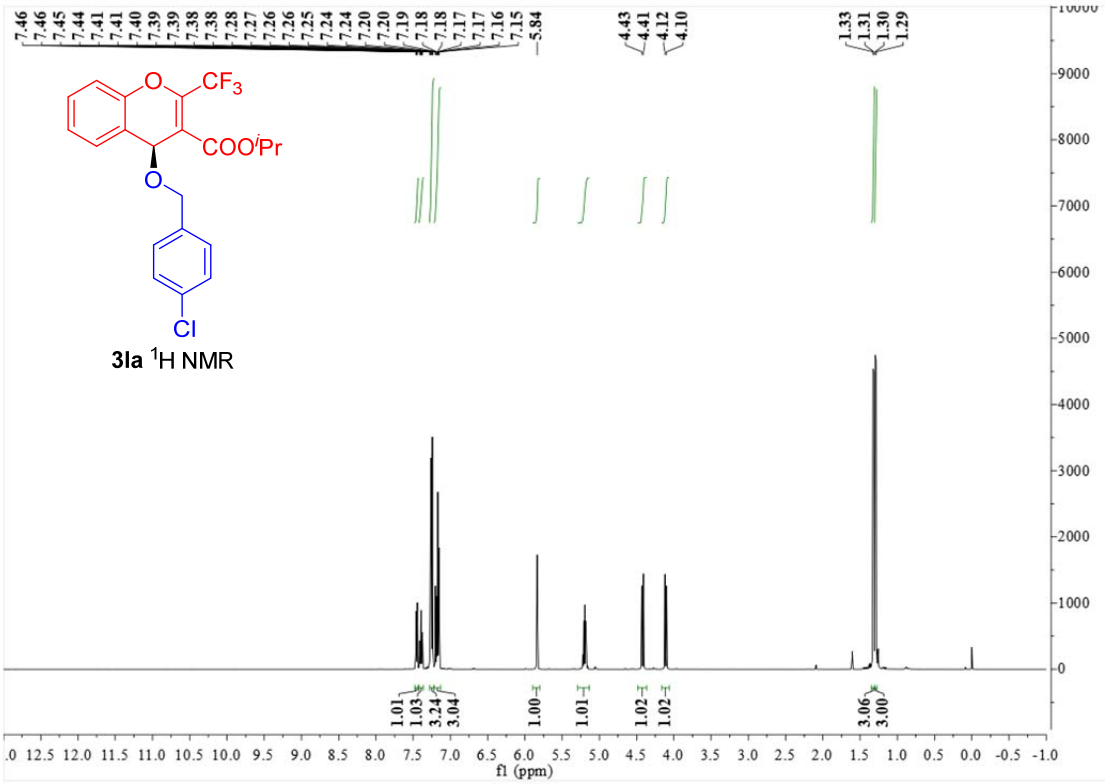
3ka ^{1}H NMR



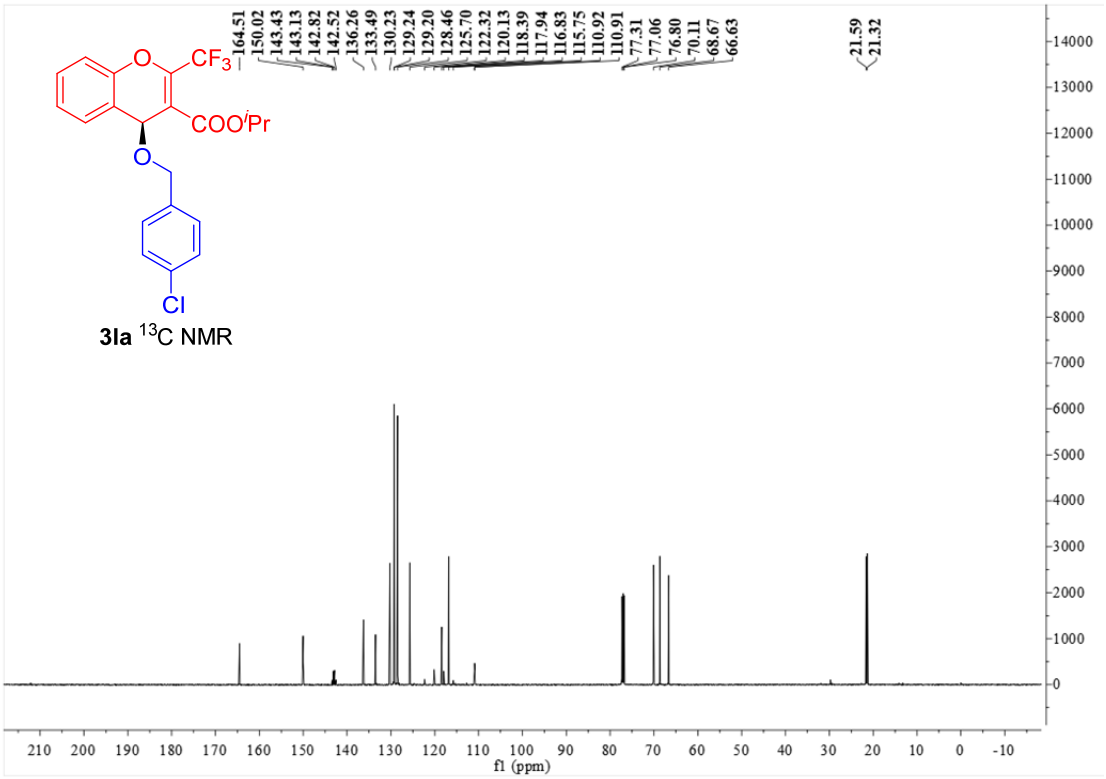
3ka ^{13}C NMR

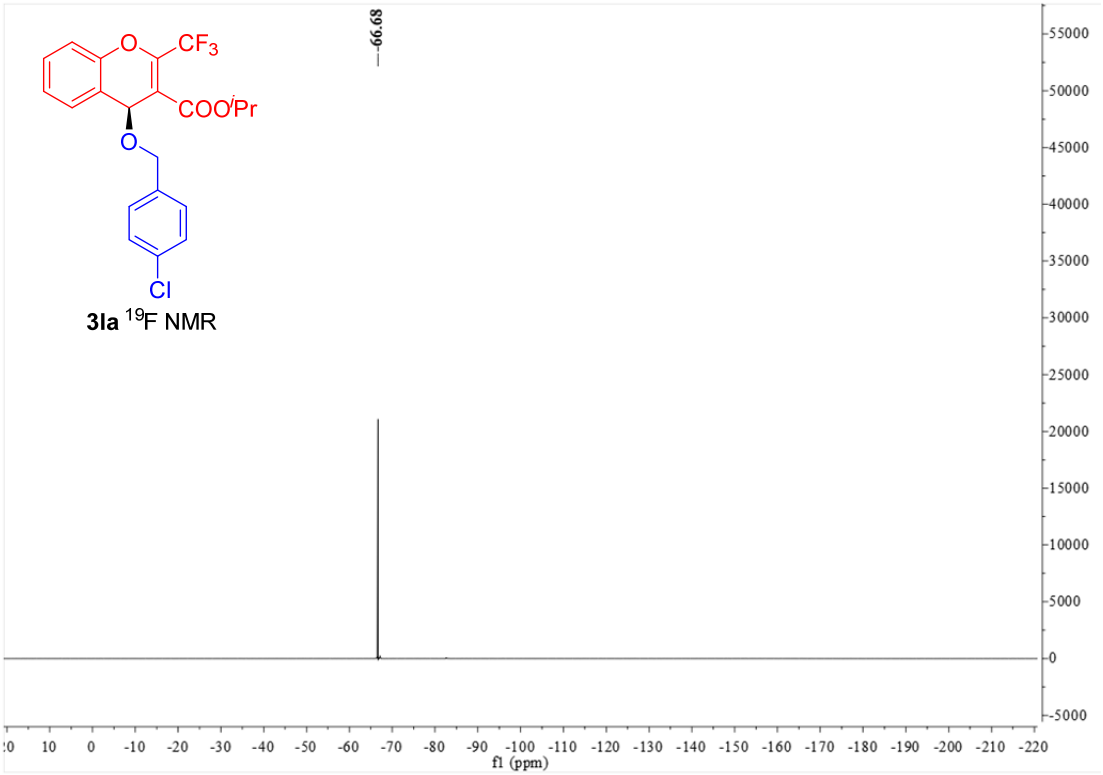


3ka ^{19}F NMR



3la ^{1}H NMR


164.51
150.02
143.43
143.13
142.82
142.52
136.26
133.49
130.23
129.24
129.20
128.46
125.70
122.32
120.13
118.39
117.94
116.83
115.75
110.92
110.91
77.31
77.06
76.80
70.11
68.67
66.63
21.59
21.32
O
CF3
COOiPr
O
Cl
3la 13C NMR
f1 (ppm)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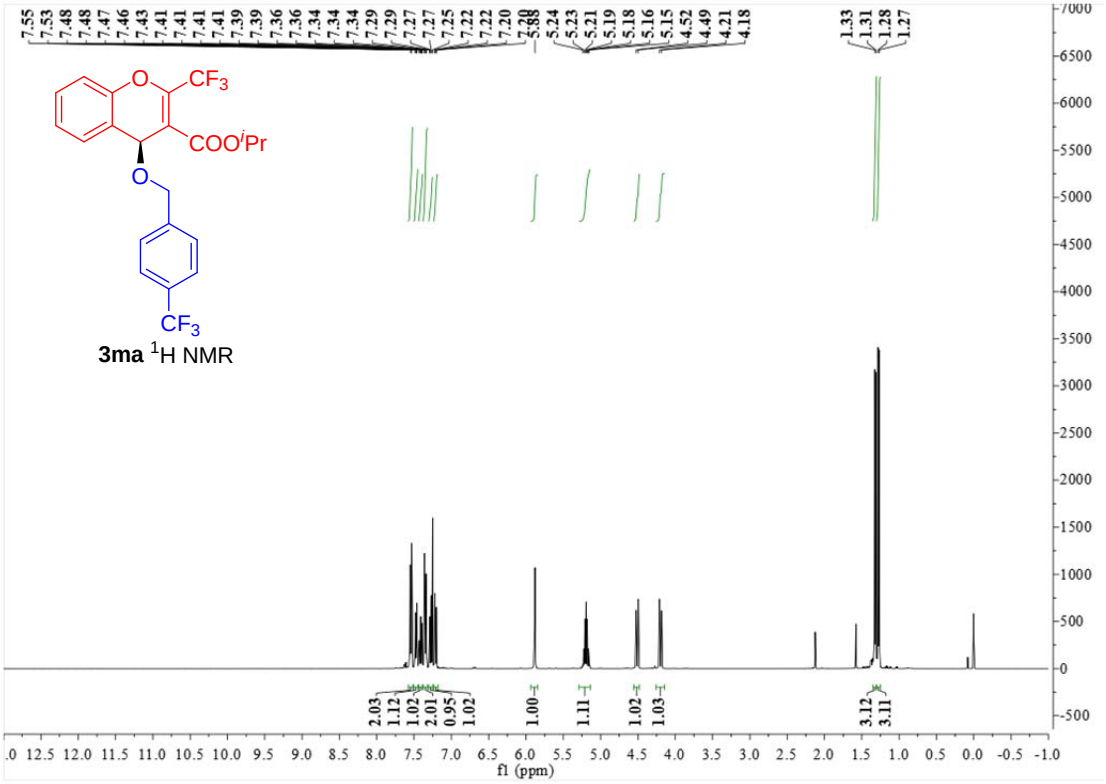
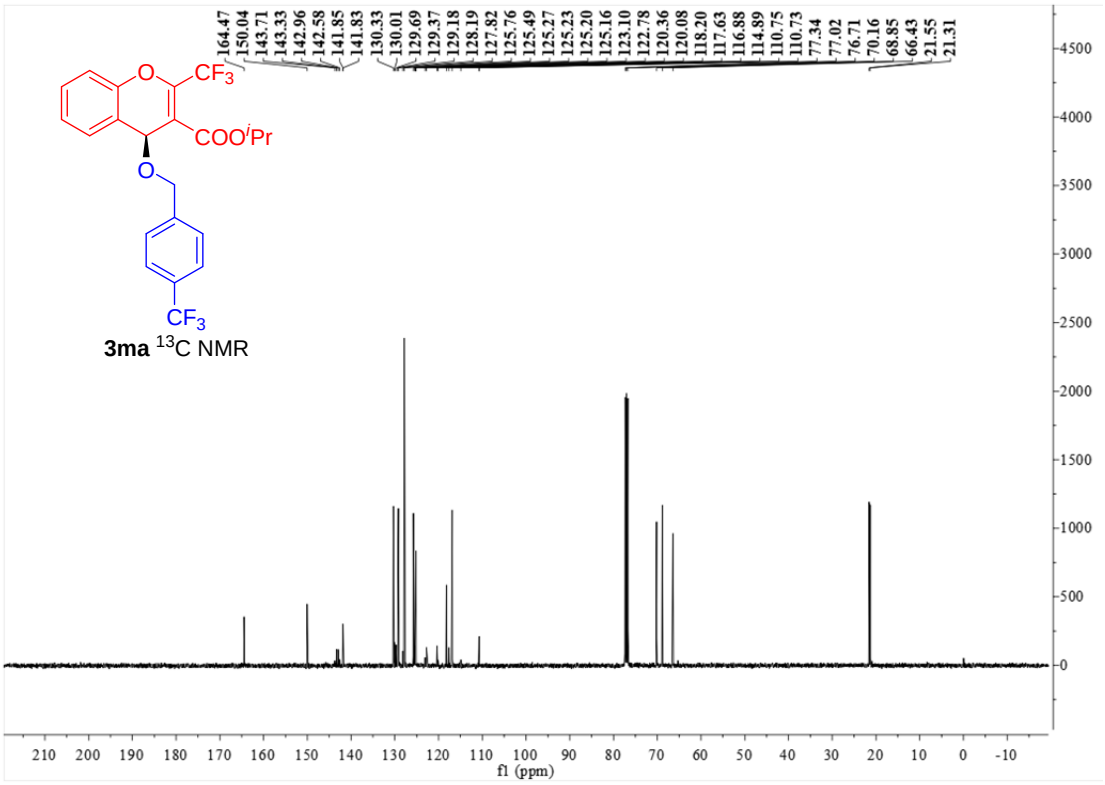
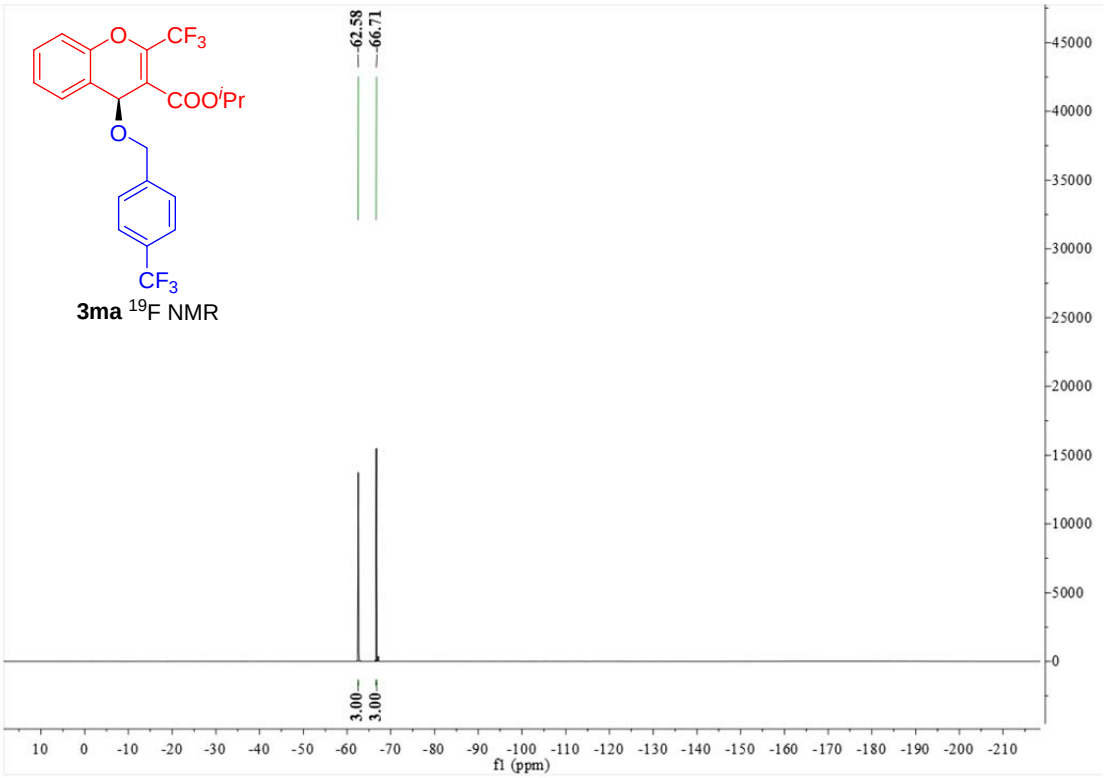
COOiPr
O
Cl
3la 19F NMR
f1 (ppm)



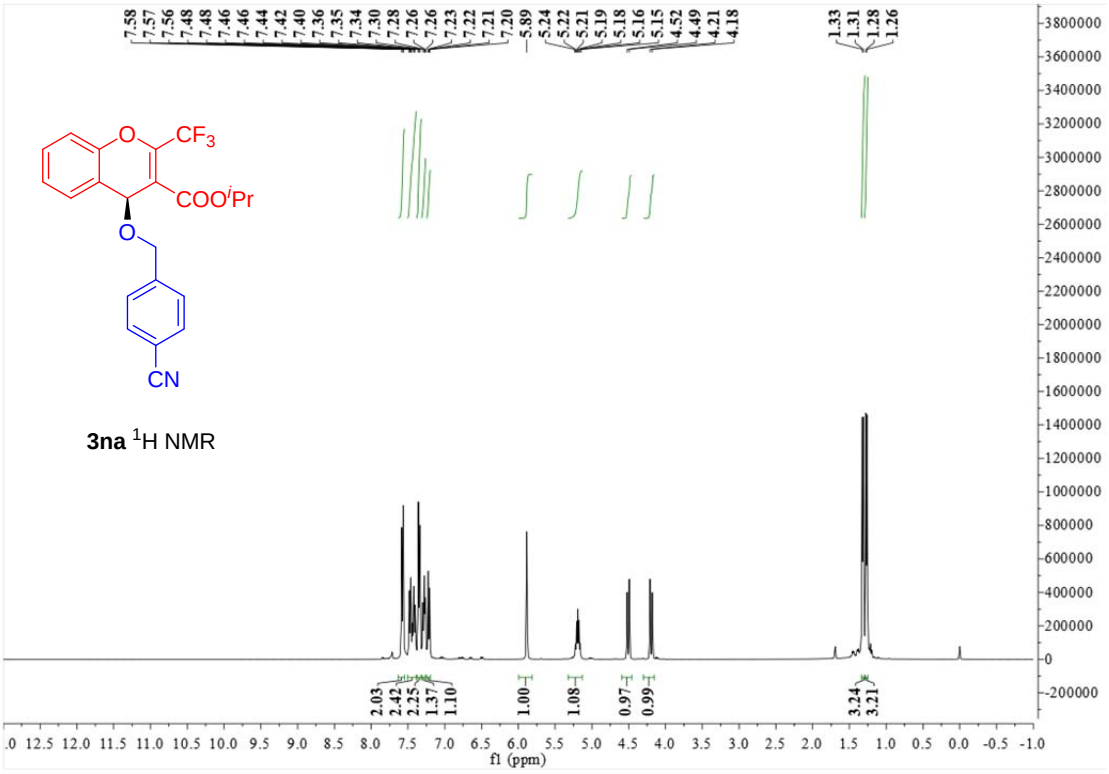
3ma ^{1}H NMR



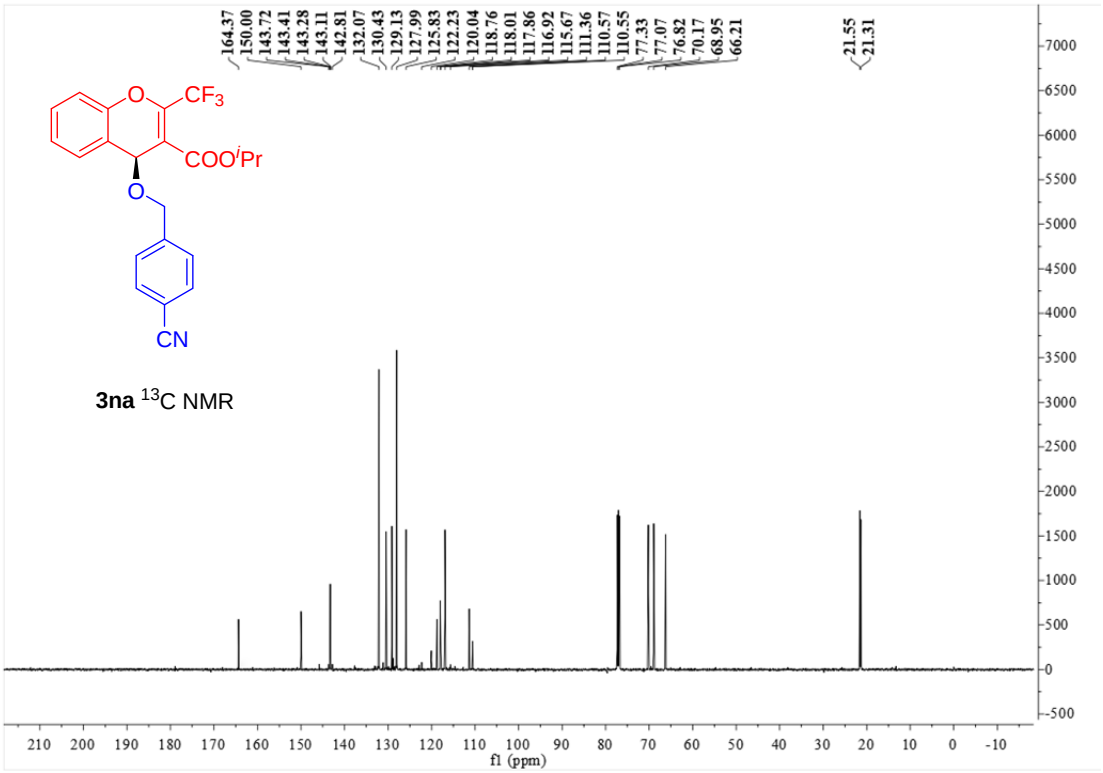
3ma ^{13}C NMR



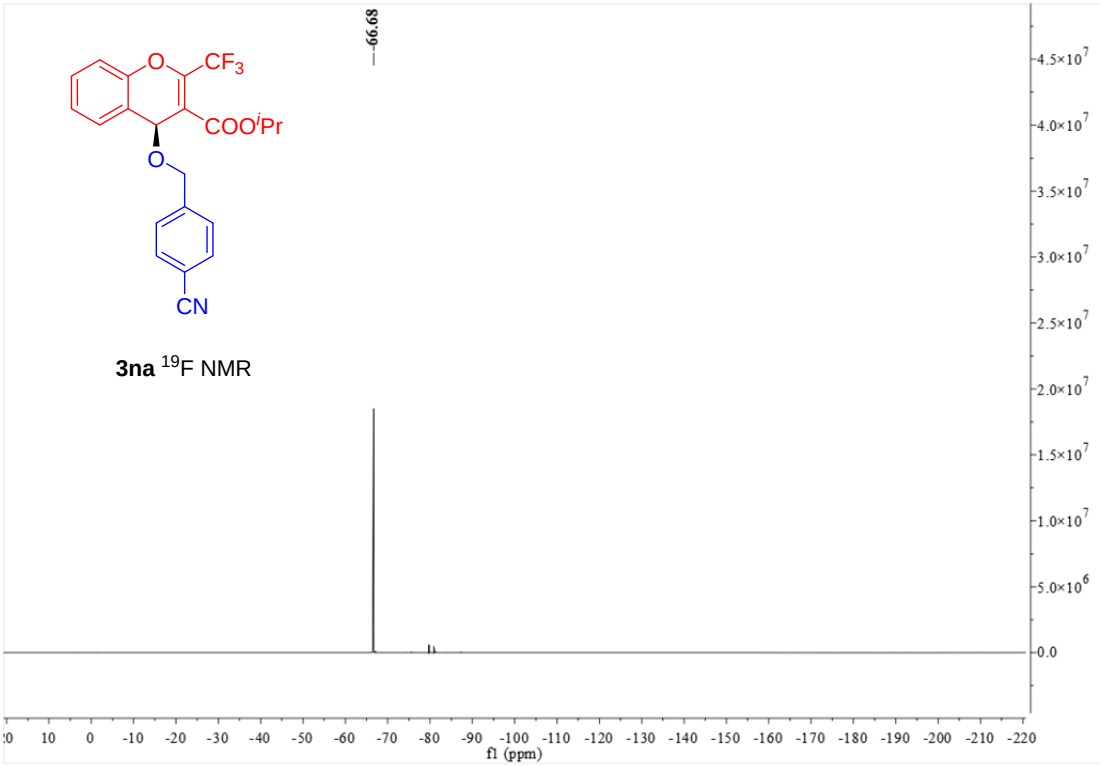
3ma ^{19}F NMR



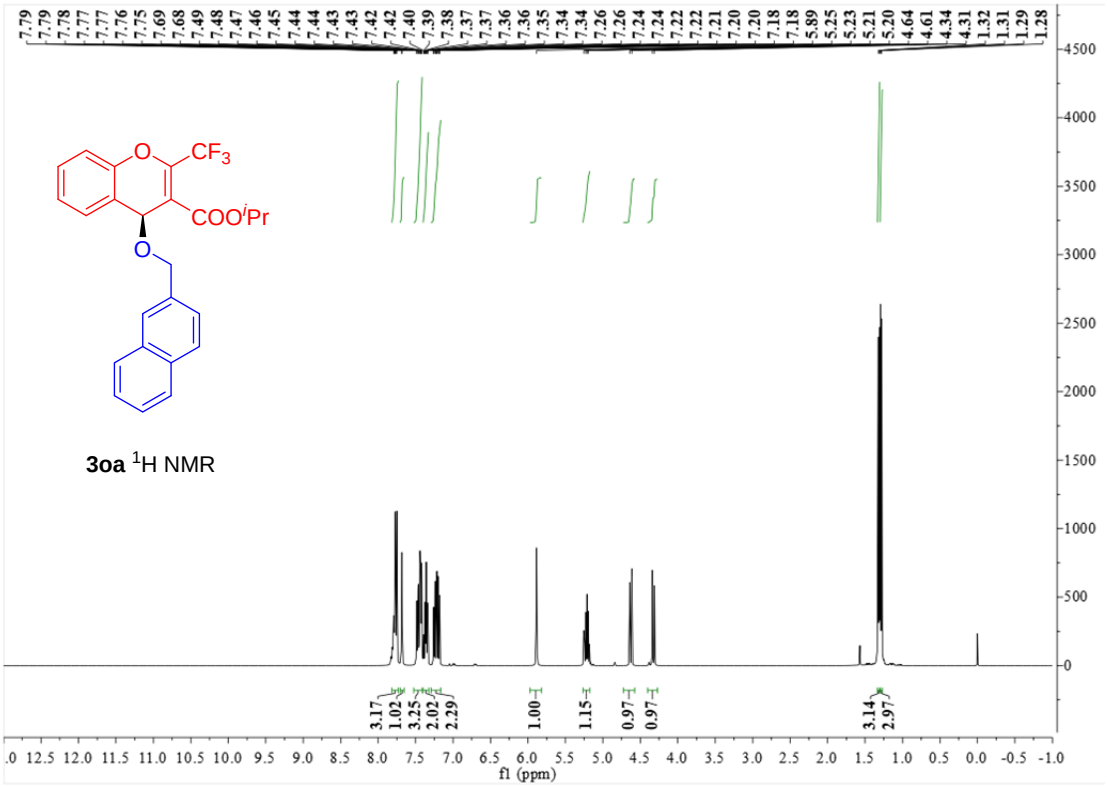
3na ^{1}H NMR

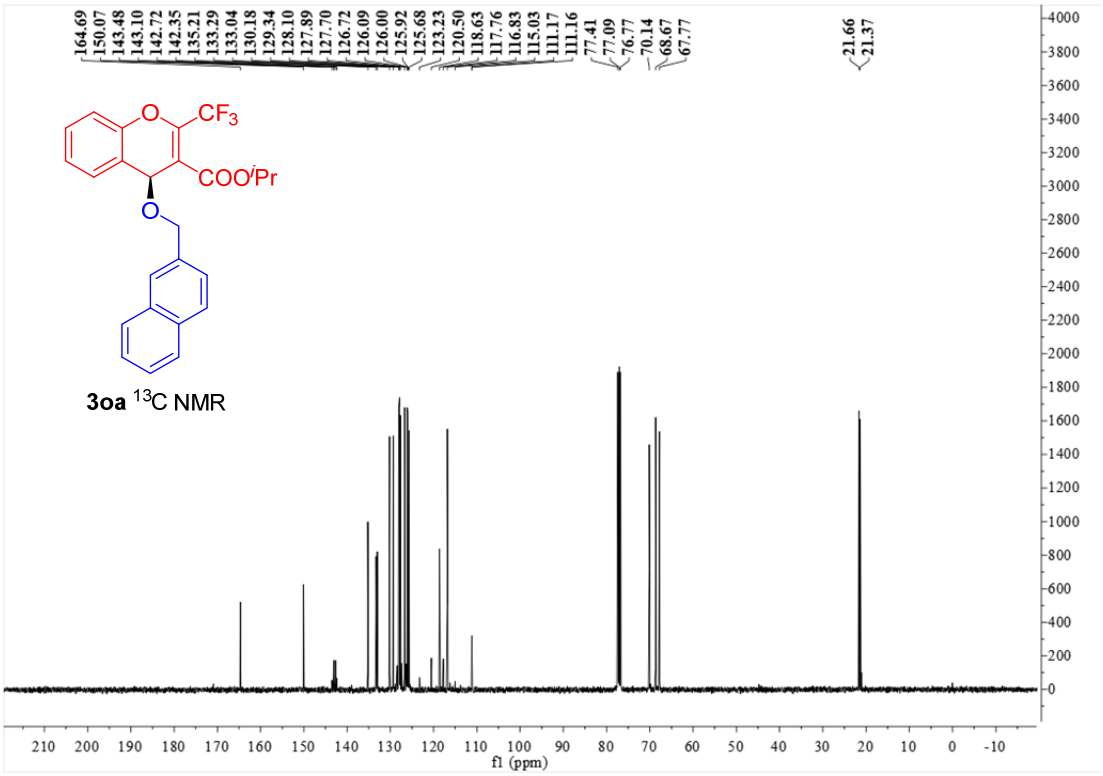


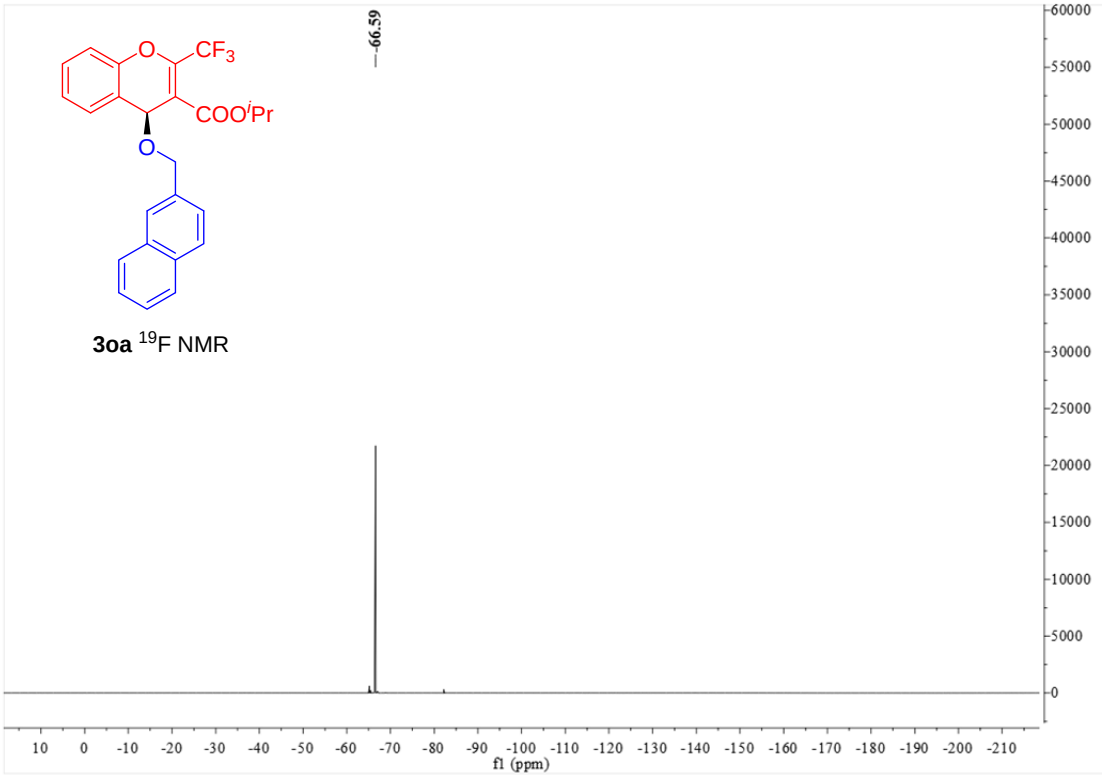
3na ^{13}C NMR



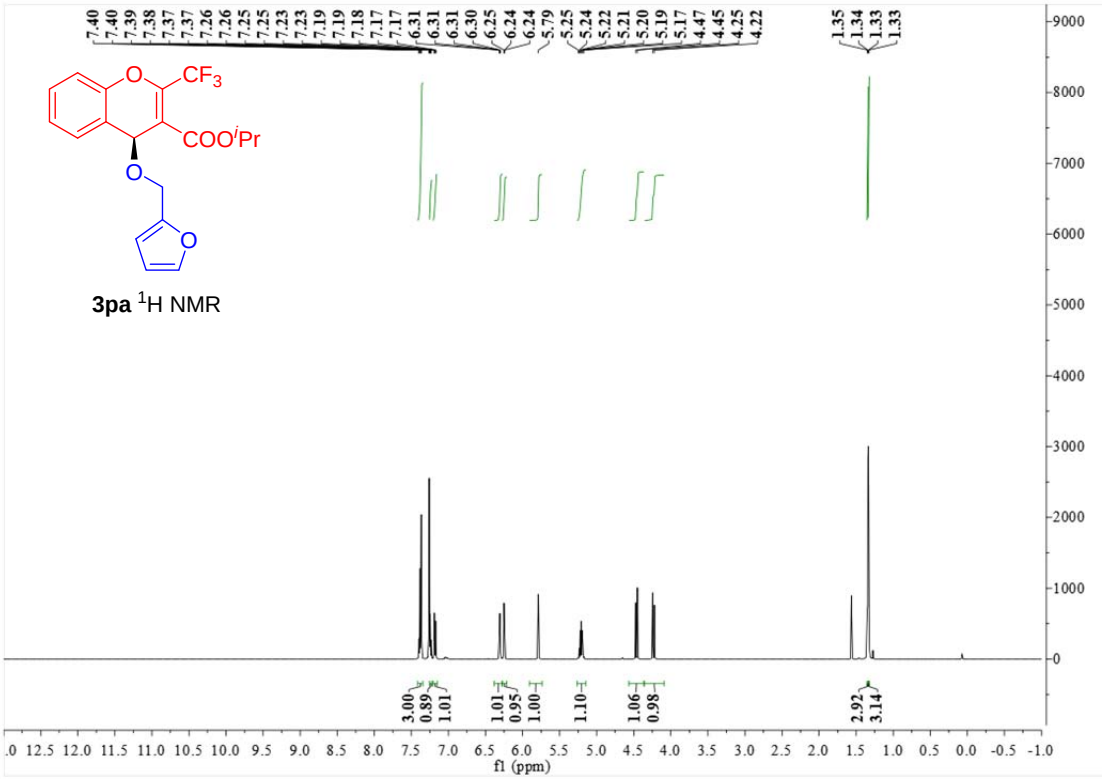
3na ^{19}F NMR


7.79 7.79 7.78 7.77 7.77 7.76 7.75 7.69 7.68 7.49 7.48 7.47 7.46 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.40 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.26 7.26 7.24 7.24 7.22 7.22 7.21 7.20 7.20 7.18 7.18 5.89 5.25 5.23 5.21 5.20 4.64 4.61 4.34 4.31 1.32 1.31 1.29 1.28
O
CF3
COO'Pr
O
3oa 1H NMR
3.17 1.02 3.25 2.02 2.29 1.00 1.15 0.97 0.97 3.14 2.97
fl (ppm)

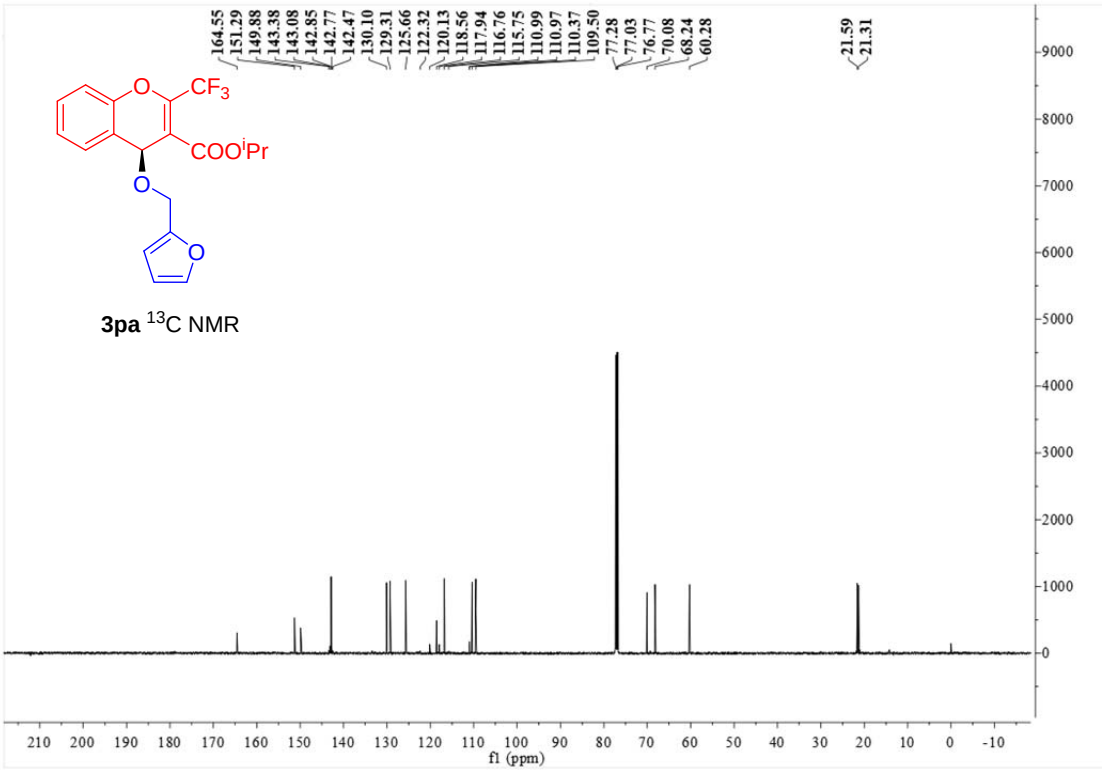

164.69 150.07 143.48 143.10 142.72 142.35 135.21 133.29 133.04 130.18 129.34 128.10 127.89 127.70 126.72 126.09 126.00 125.92 125.68 123.23 120.50 118.63 117.76 116.83 115.03 111.17 111.16 77.41 77.09 76.77 70.14 68.67 67.77 21.66 21.37
O
CF3
COO'Pr
O
3oa 13C NMR
fl (ppm)



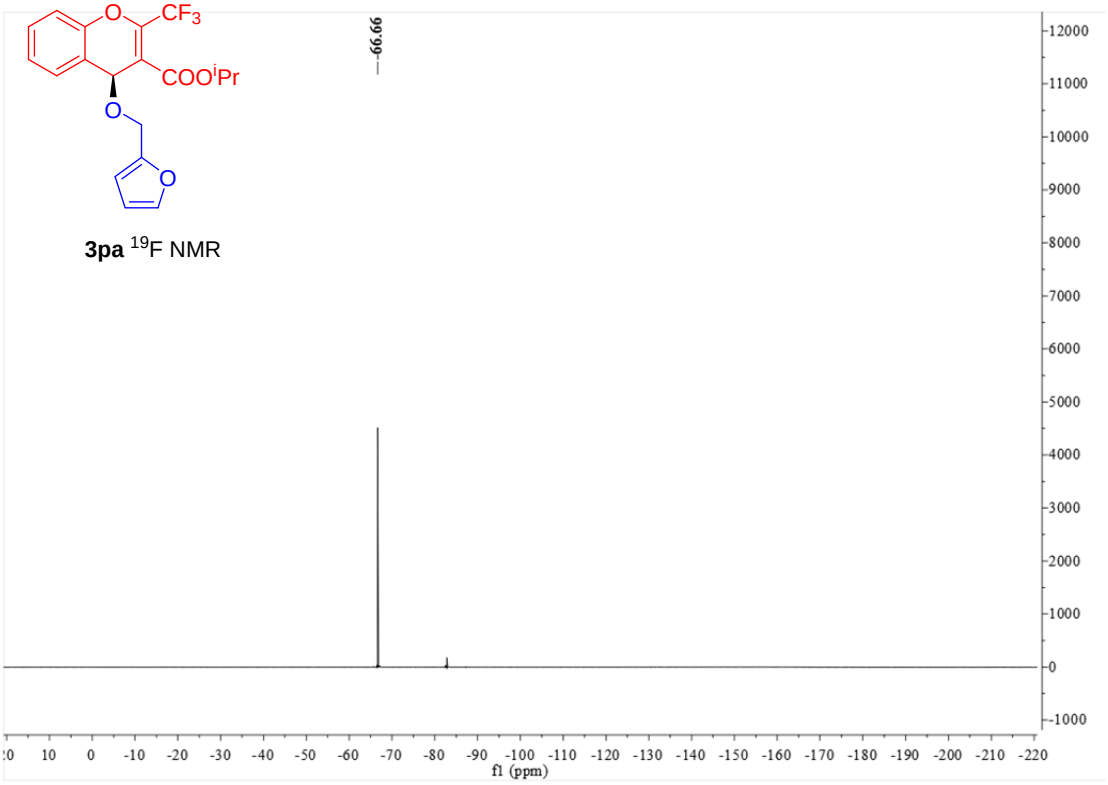
3oa ^{19}F NMR



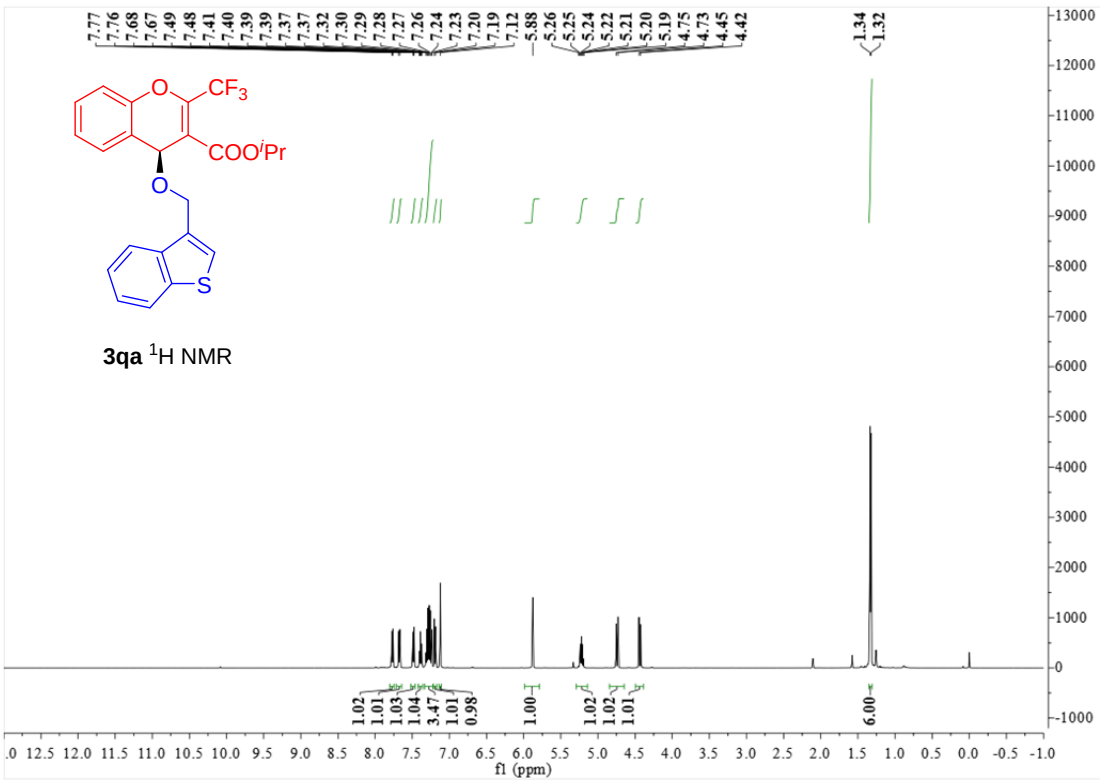
3pa ^{1}H NMR



3pa ^{13}C NMR



3pa ^{19}F NMR



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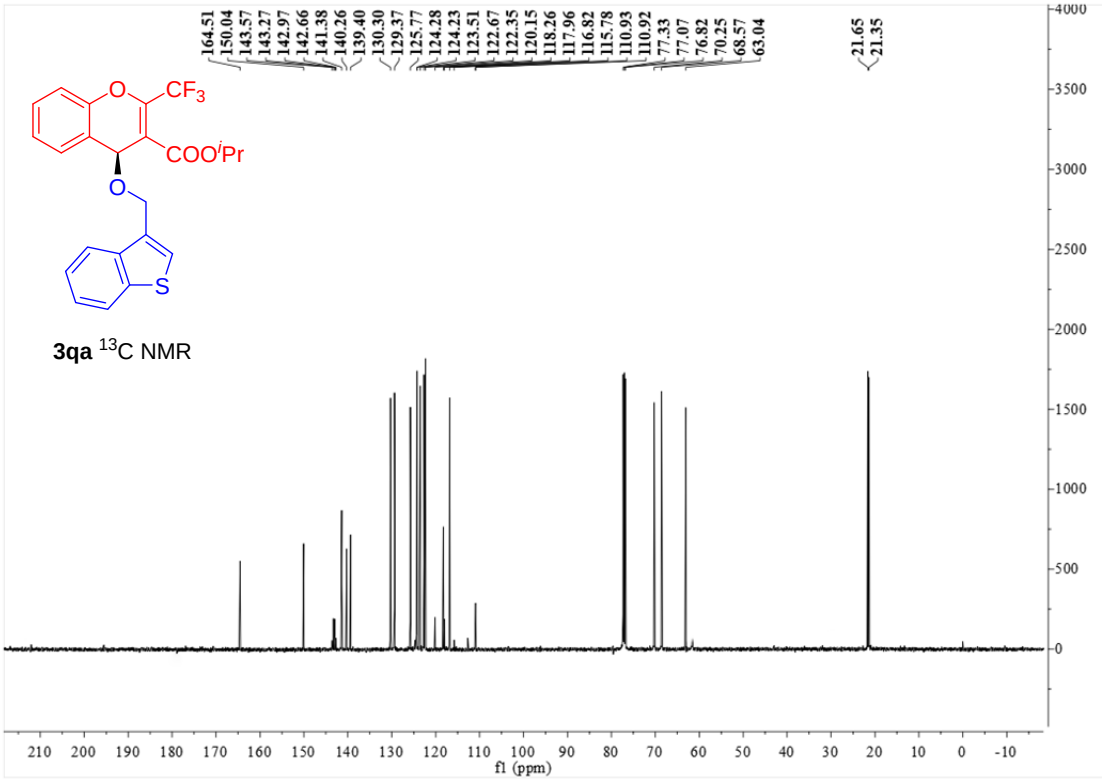
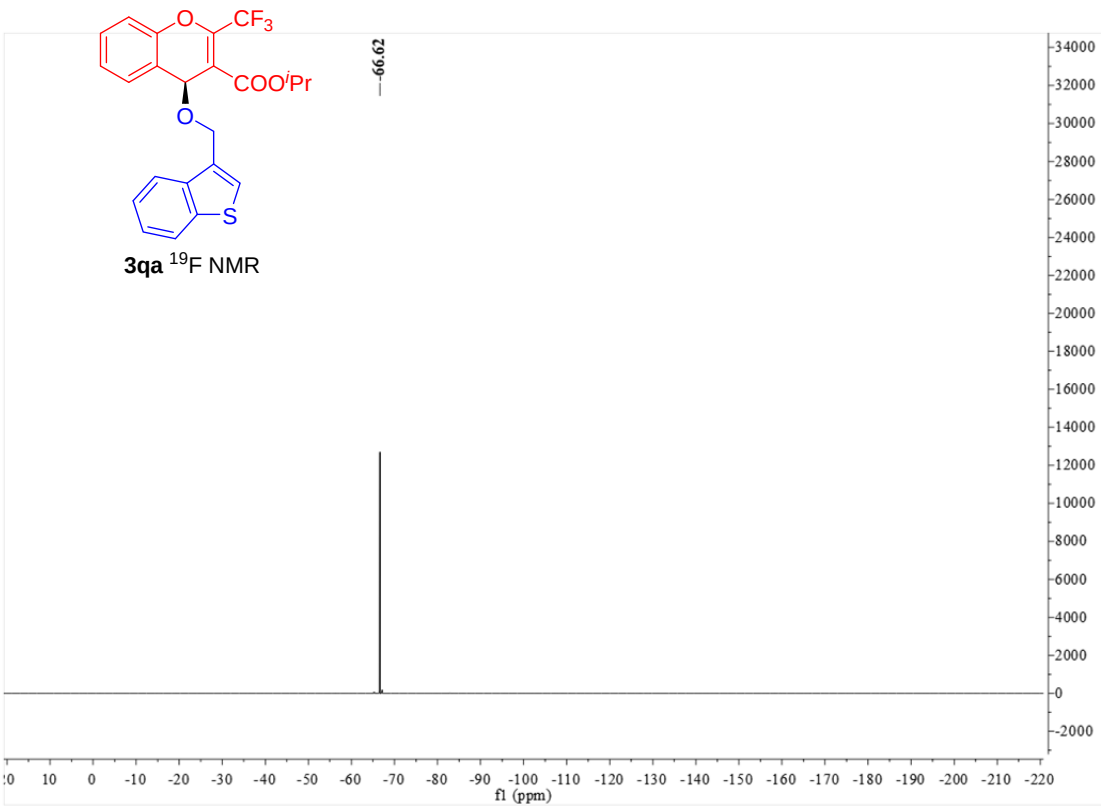
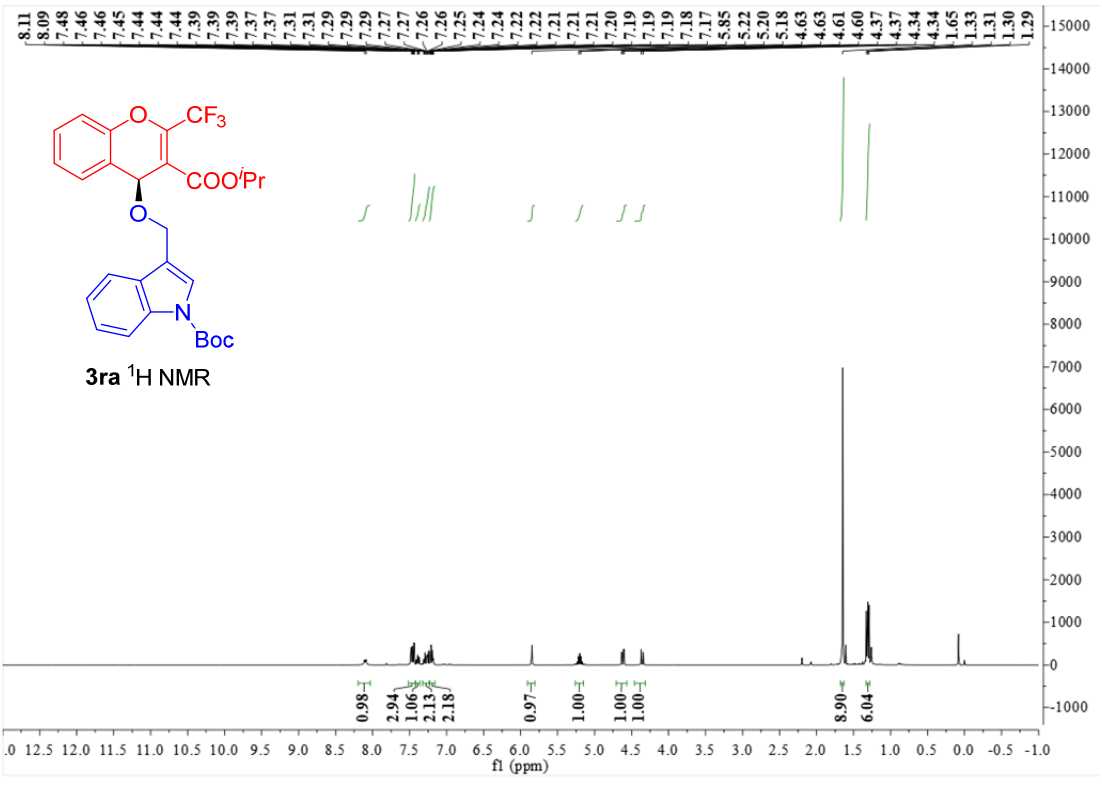


3qa ^{13}C NMR



3qa ^{19}F NMR



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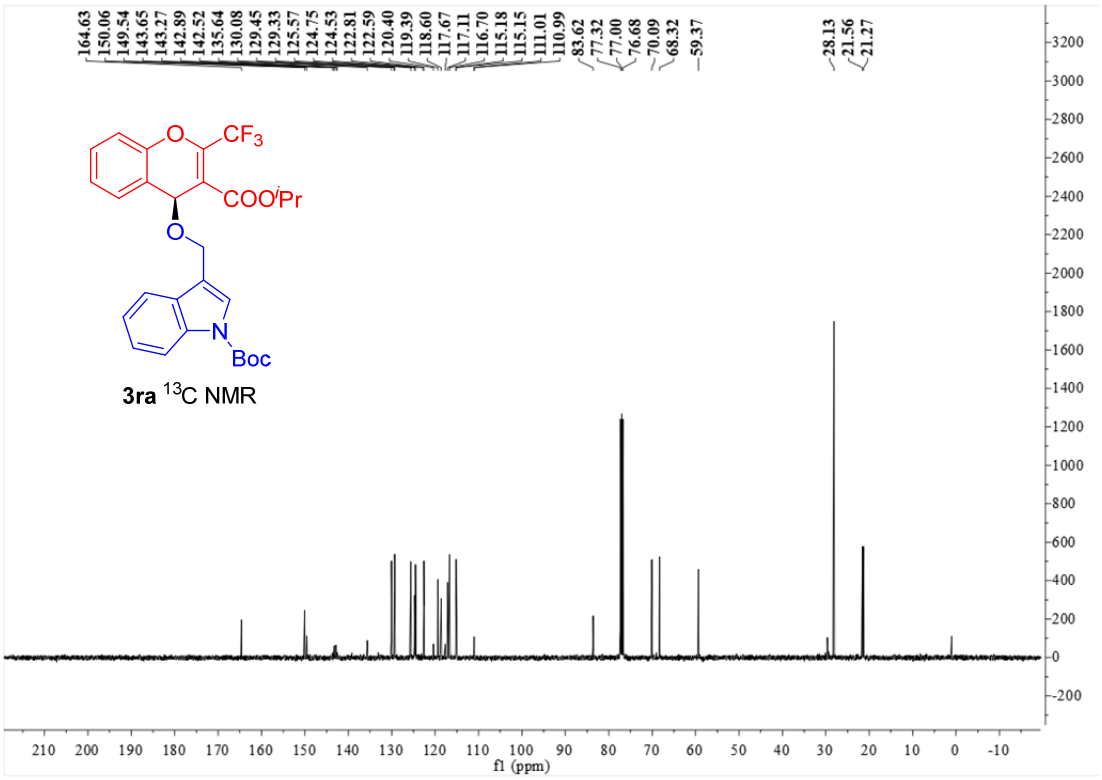

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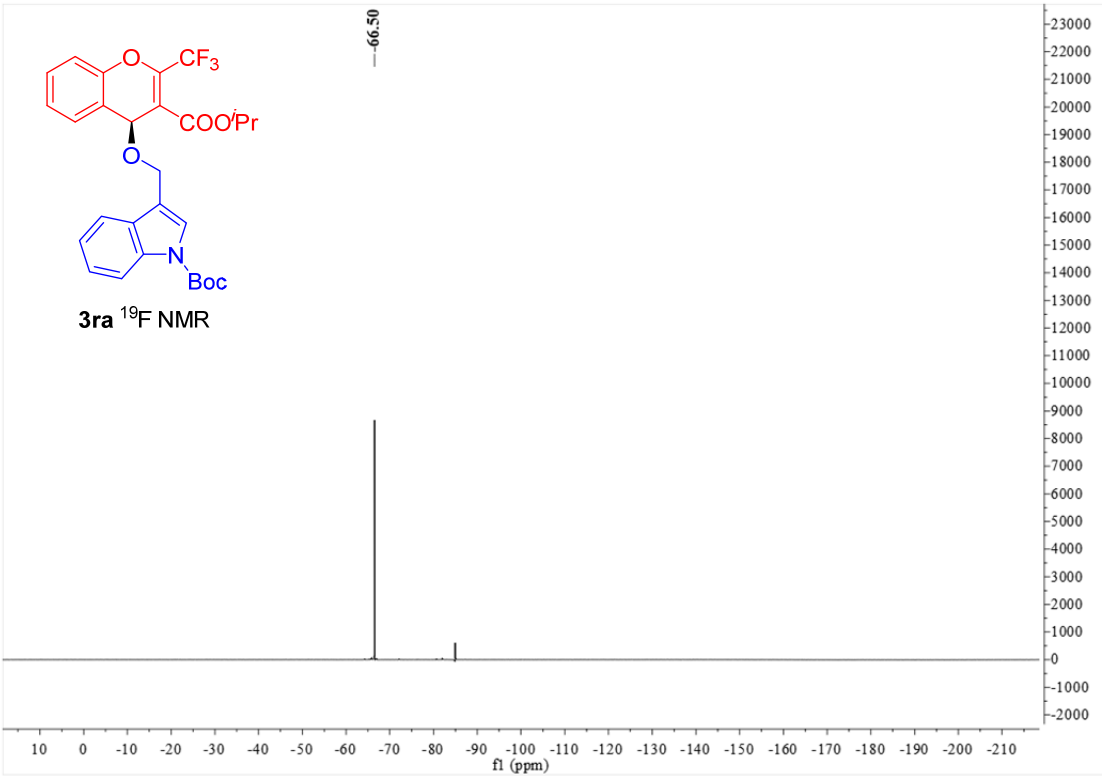
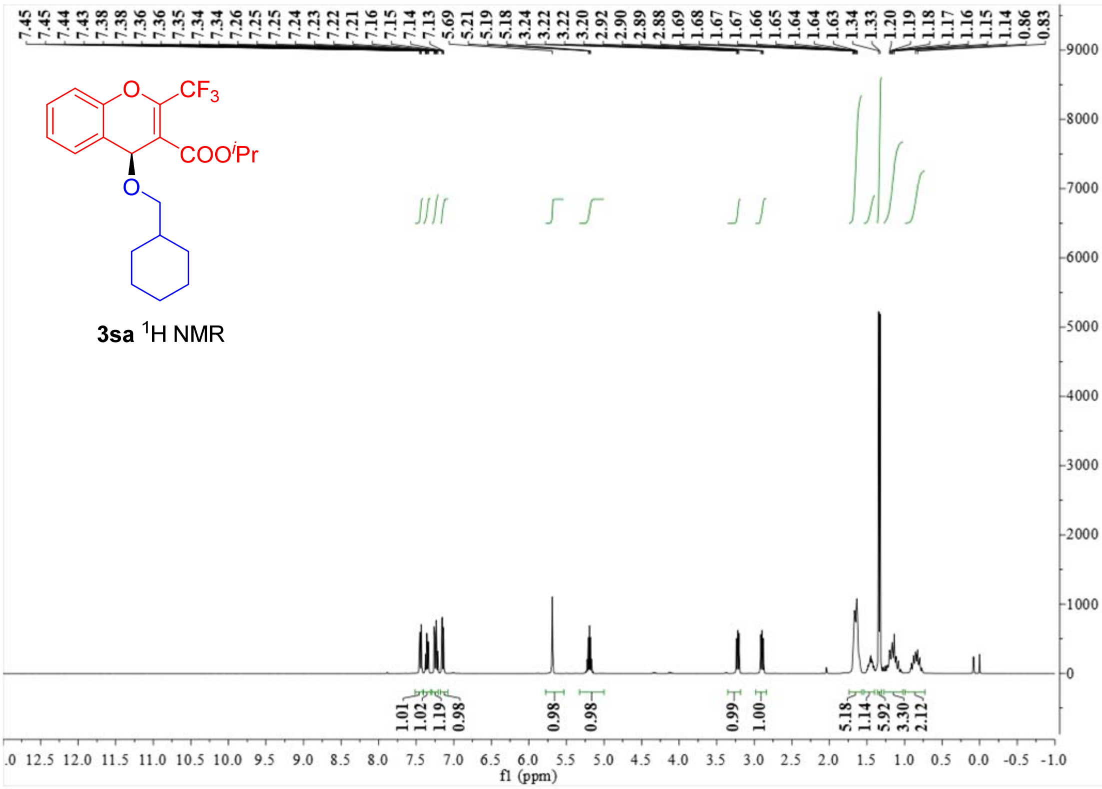
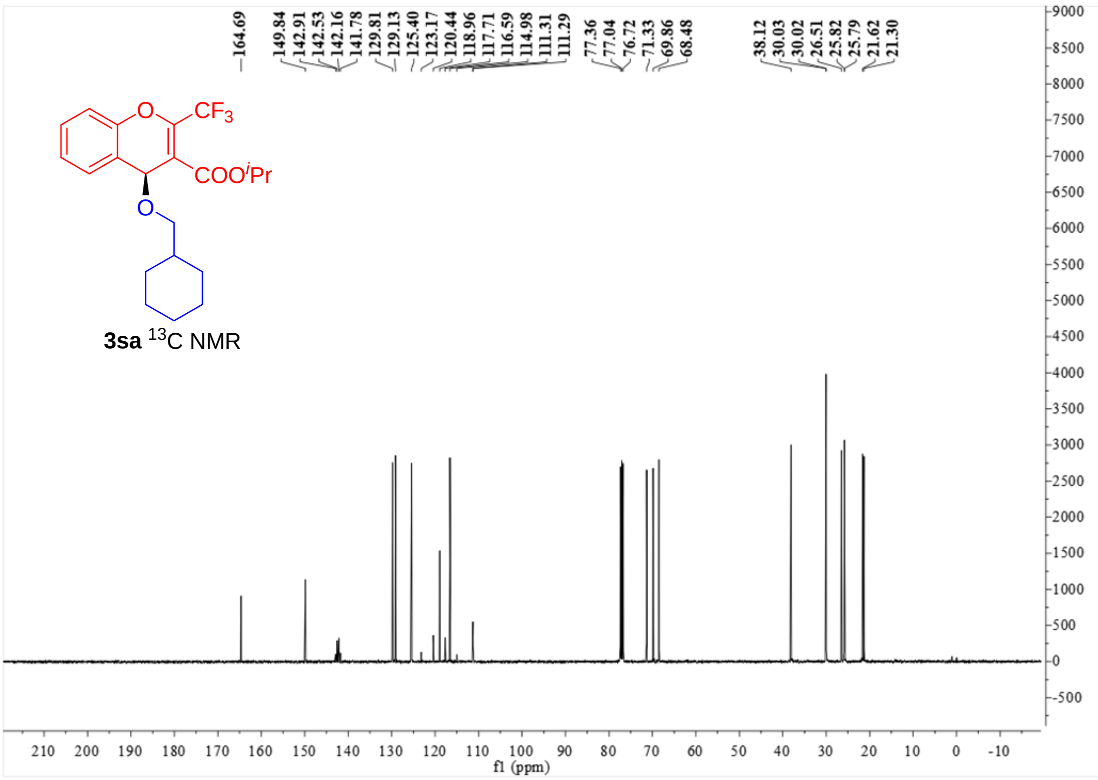
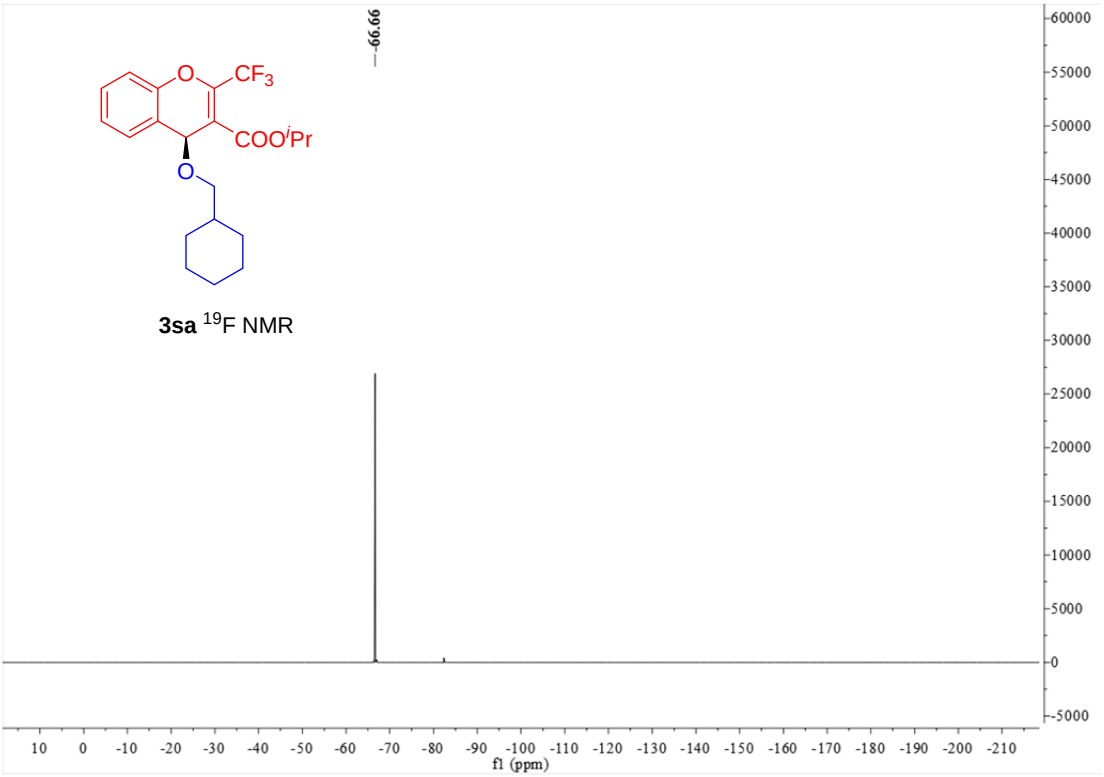


3ra ^{19}F NMR


CF3
COOⁱPr
3sa 1H NMR
f1 (ppm)


CF3
COOiPr
3sa 13C NMR
f1 (ppm)



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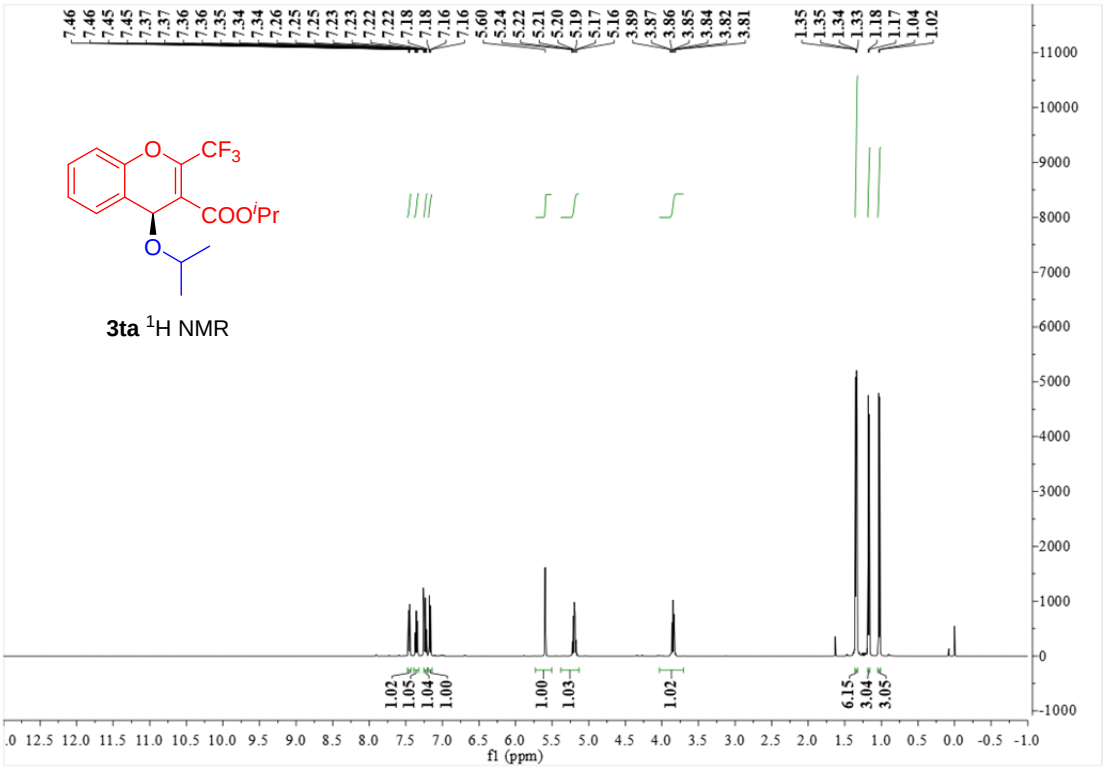
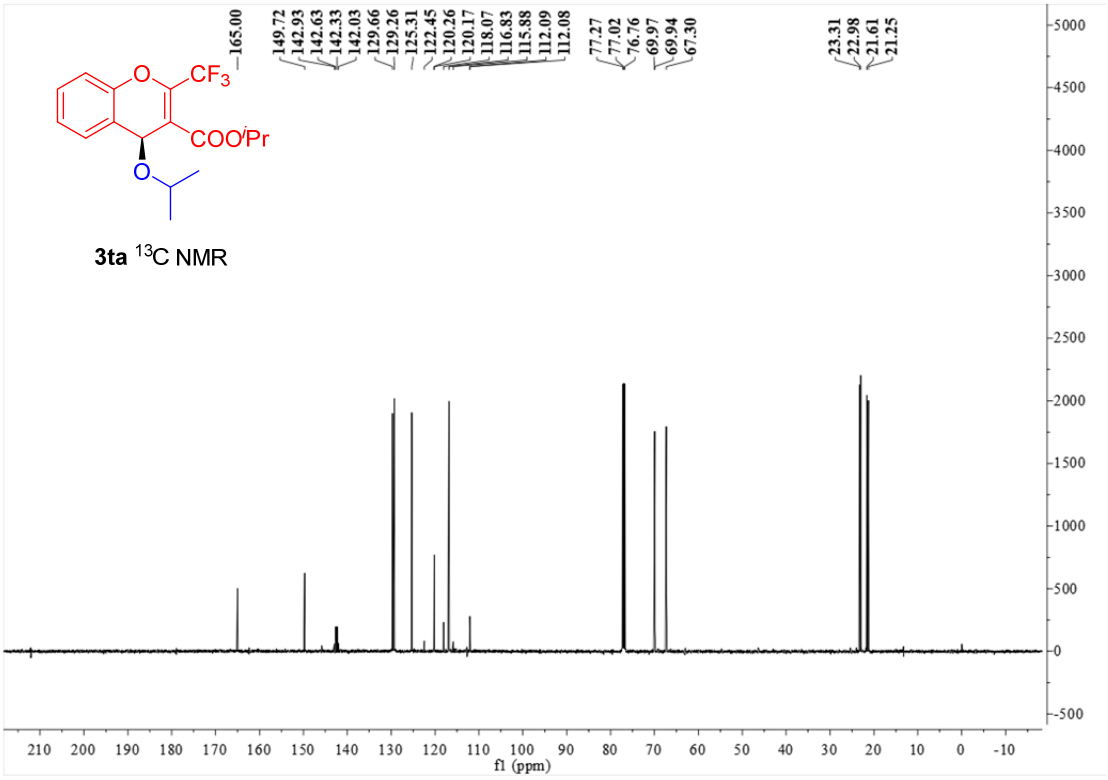


3ta ^{1}H NMR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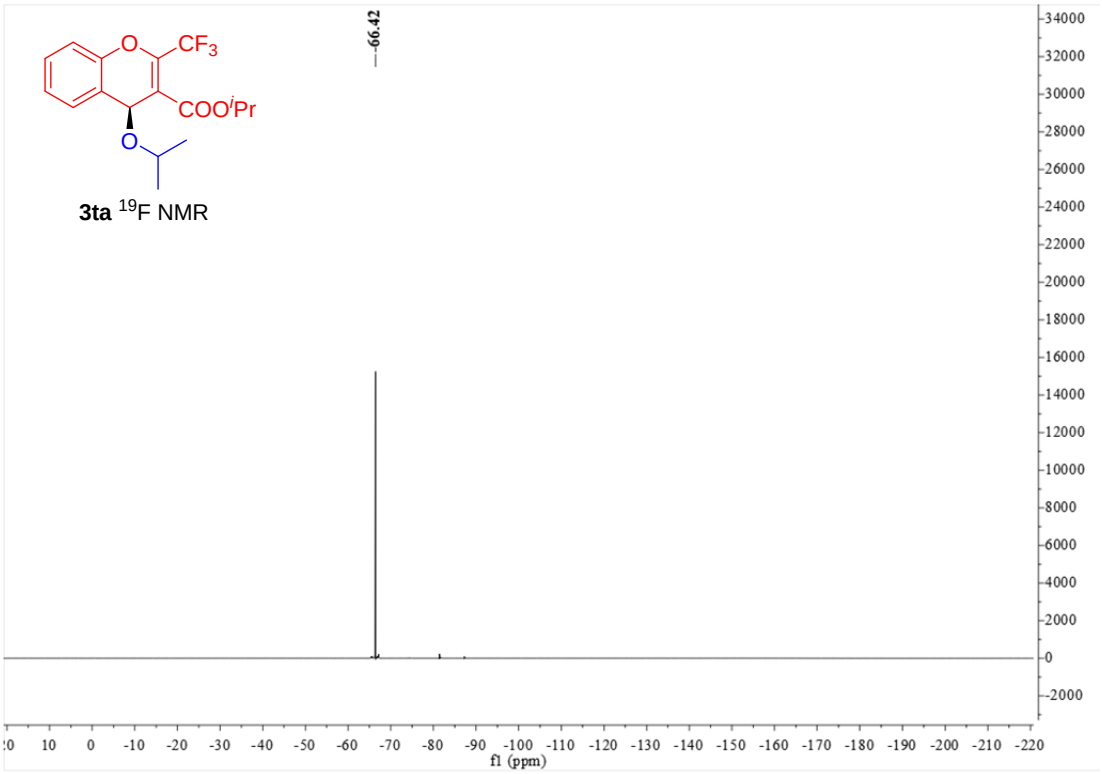
142.63
142.33
142.03
129.66
129.26
125.31
122.45
120.26
120.17
118.07
116.83
115.88
112.09
112.08
77.27
77.02
76.76
69.97
69.94
67.30
23.31
22.98
21.61
21.25
O
CF3
COOiPr
O
3ta 13C NMR
f1 (ppm)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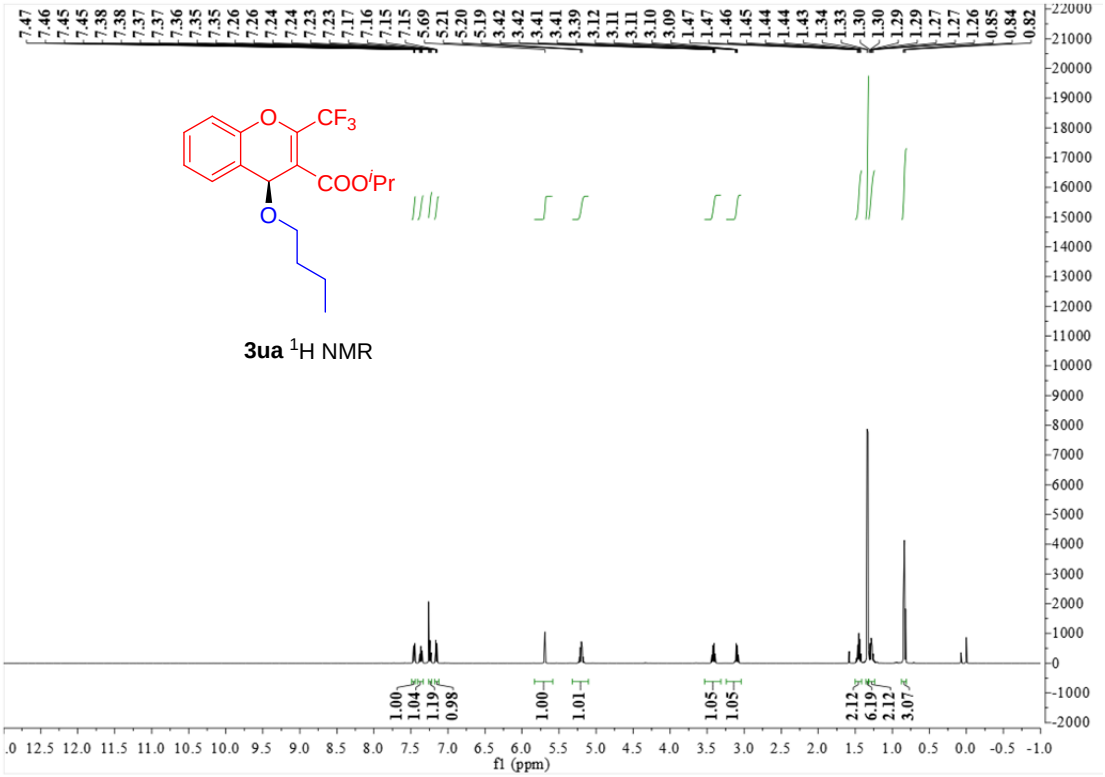
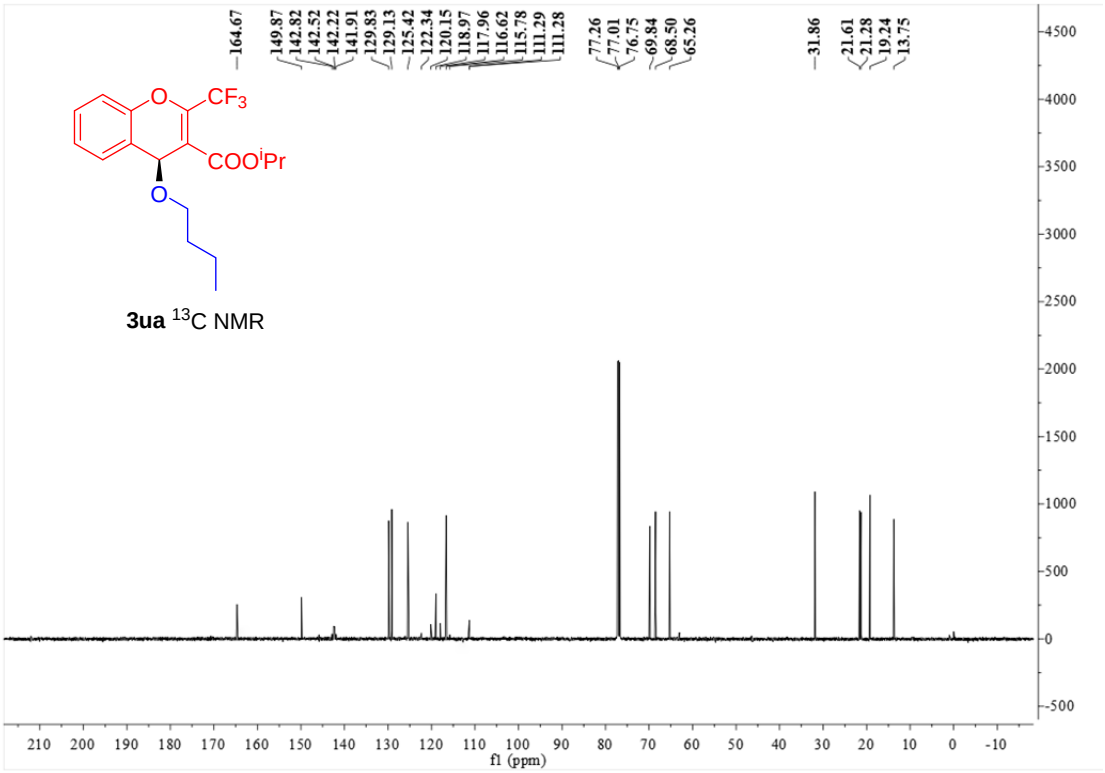
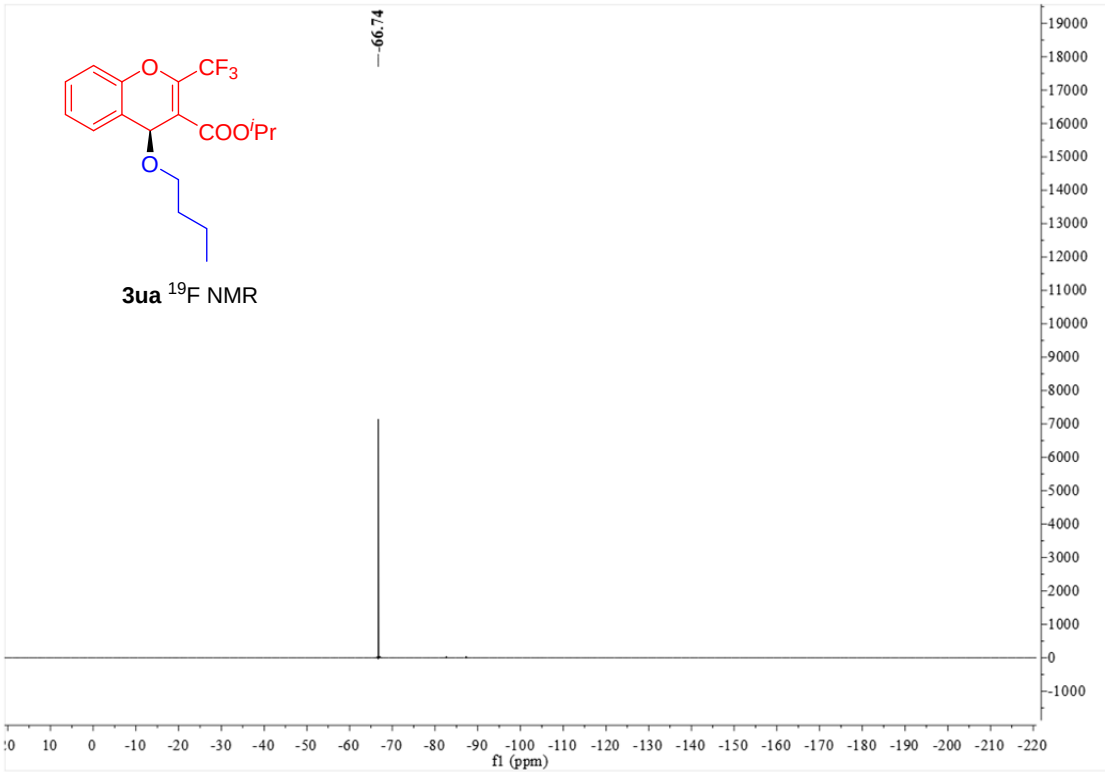
COOiPr
O
3ta 19F NMR
f1 (ppm)



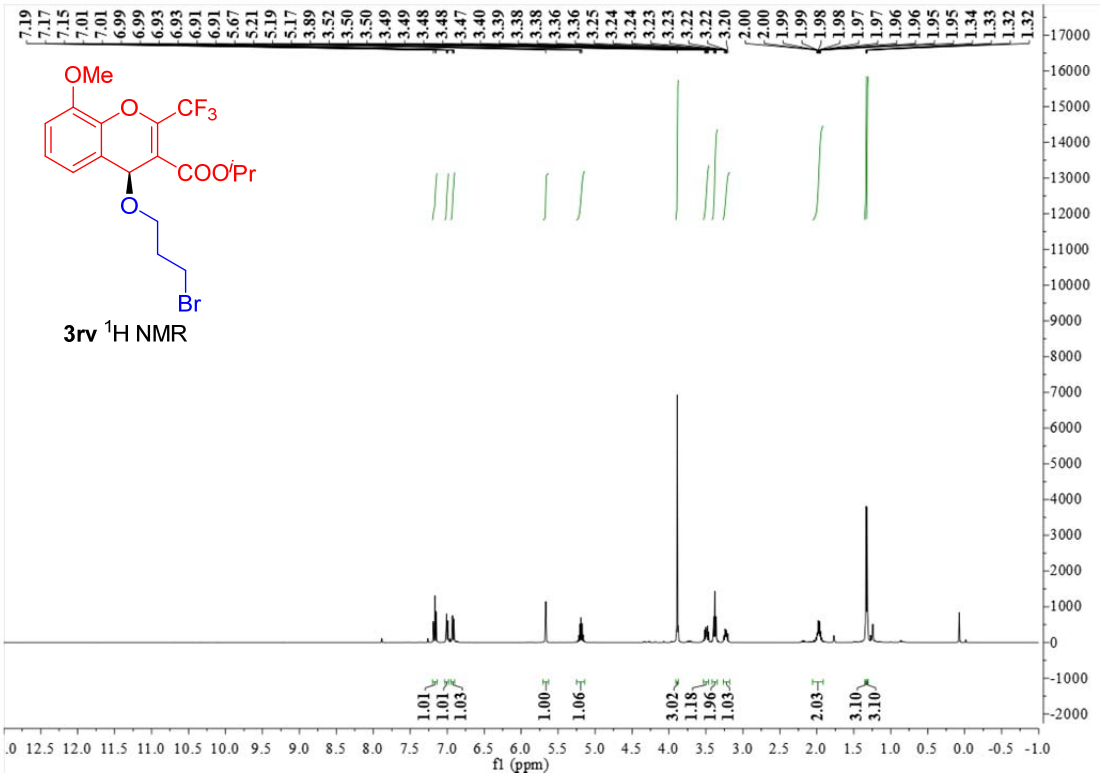
3ua ^{1}H NMR



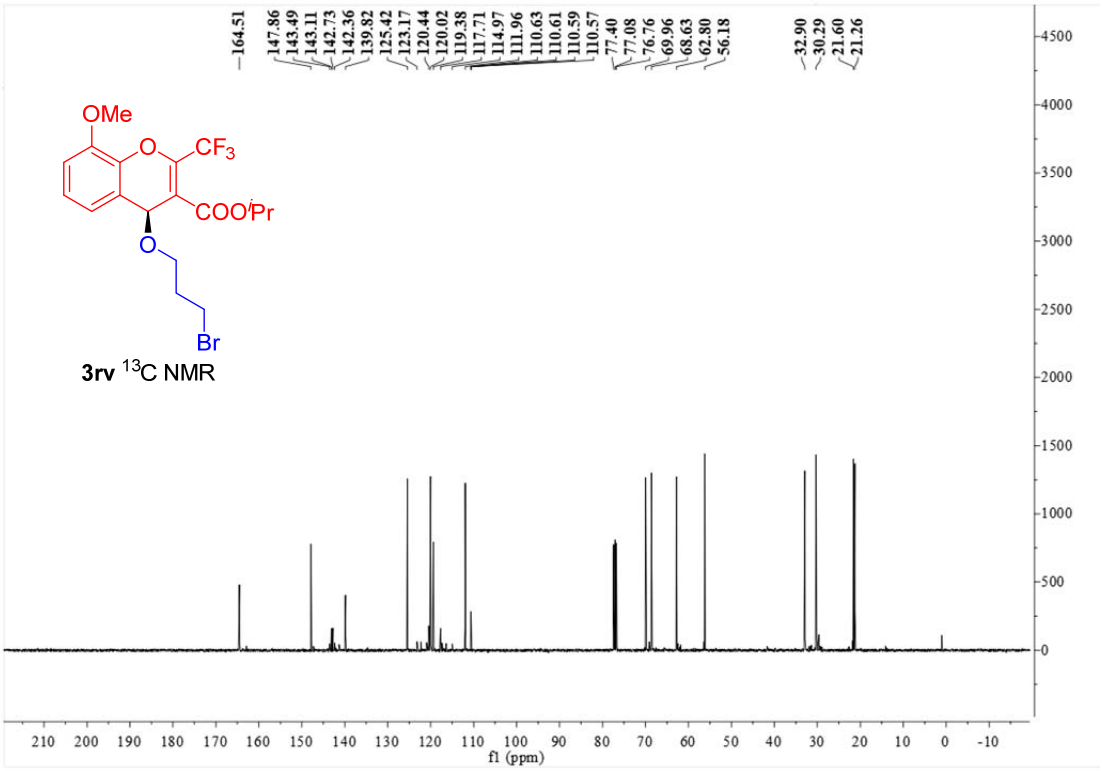
3ua ^{13}C NMR



3ua ^{19}F NMR



3rv ^{1}H NMR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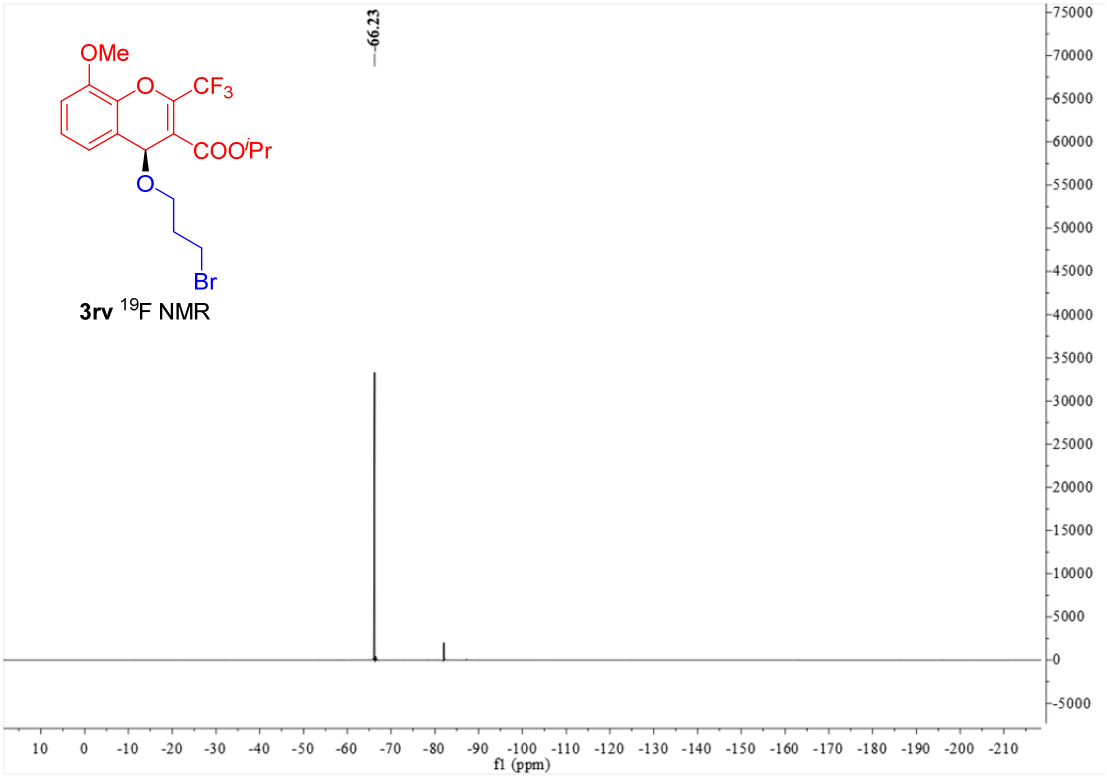
147.86
143.49
143.11
142.73
142.36
139.82
125.42
123.17
120.44
120.02
119.38
117.71
114.97
111.96
110.63
110.61
110.59
110.57
77.40
77.08
76.76
69.96
68.63
62.80
56.18
32.90
30.29
21.60
21.26
OMe
O
CF3
COOiPr
O
Br
3rv 13C NMR
fl (ppm)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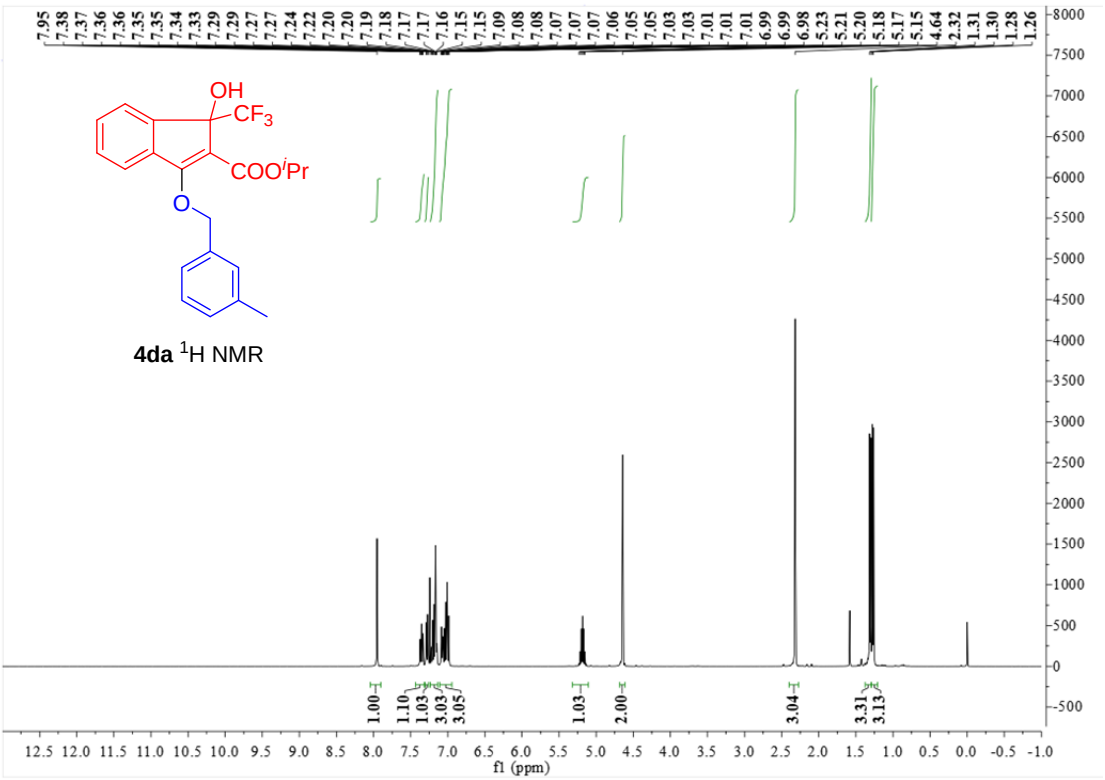
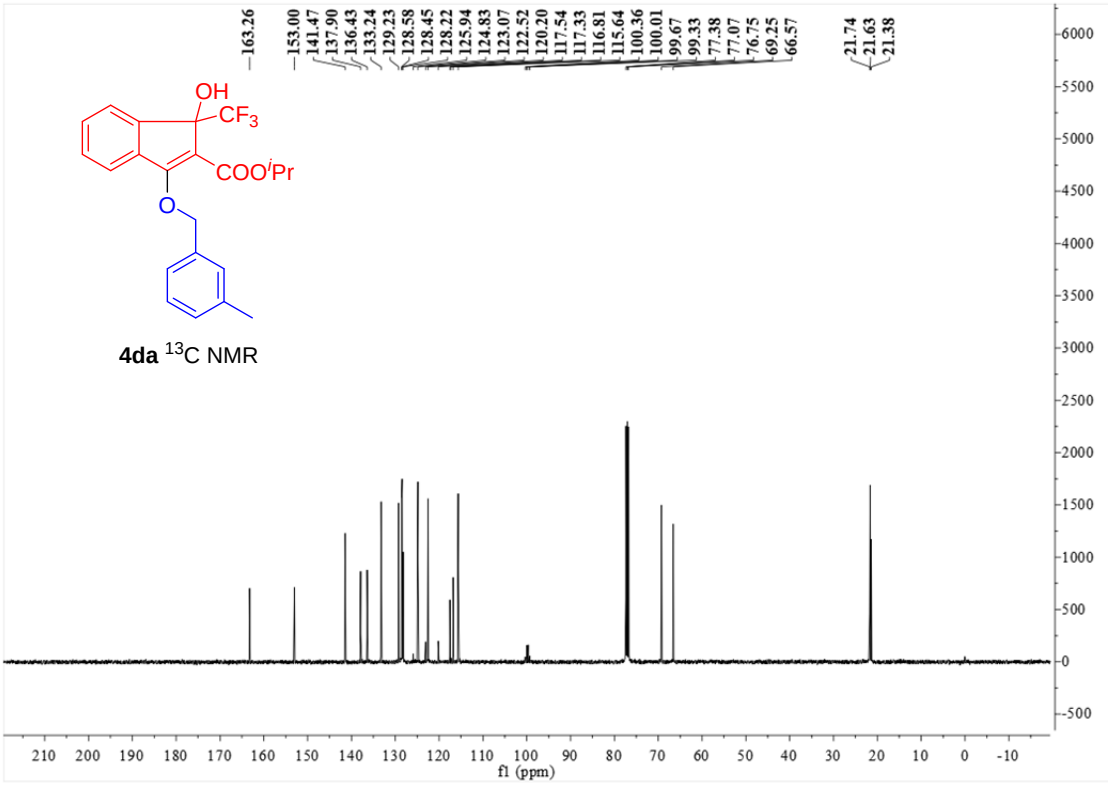
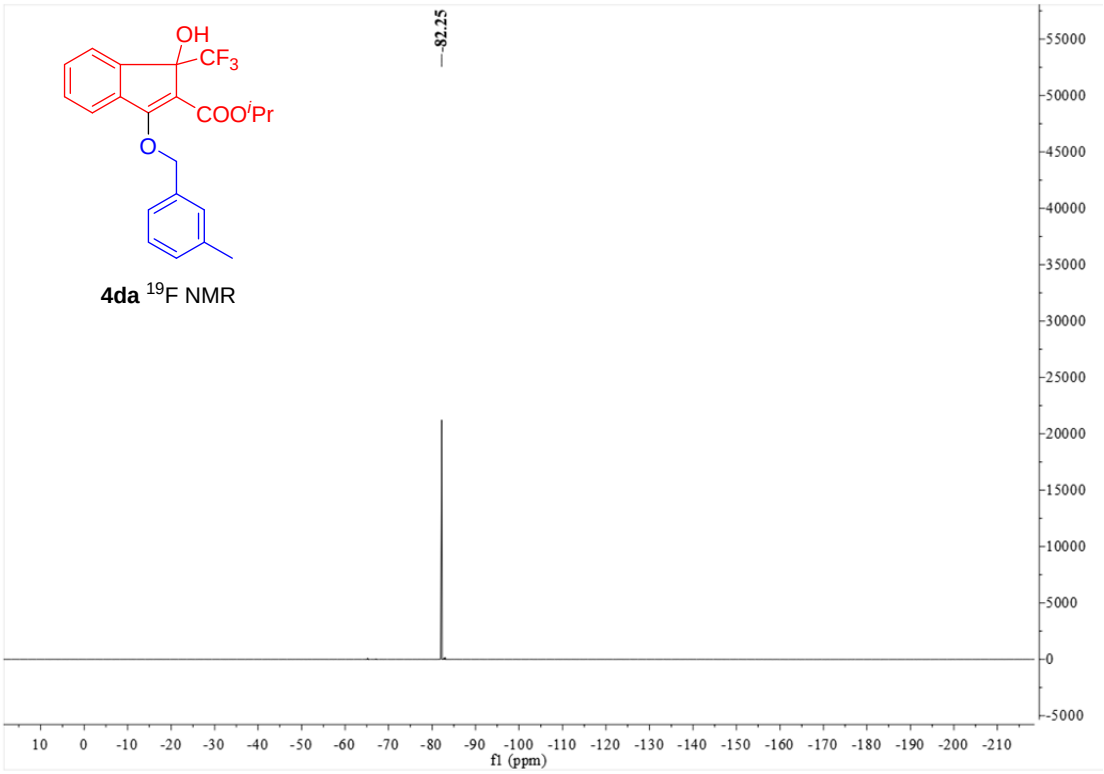
O
CF3
COOiPr
O
Br
3rv 19F NMR
fl (ppm)



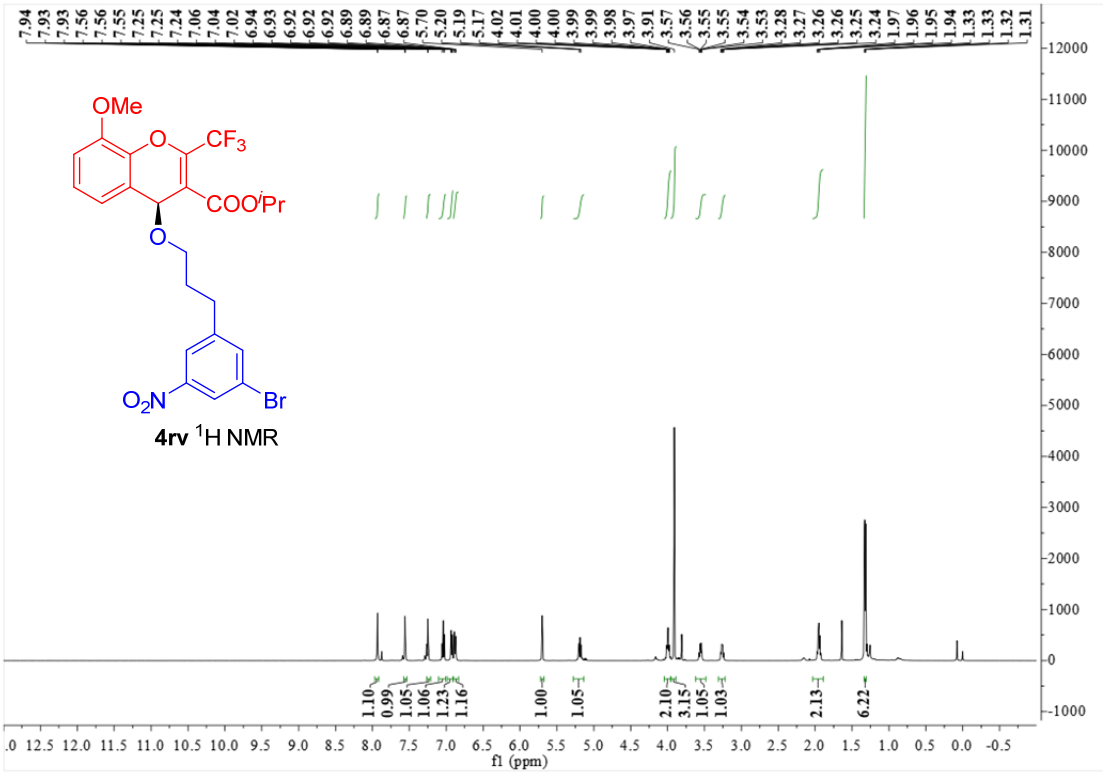
4da ^{1}H NMR



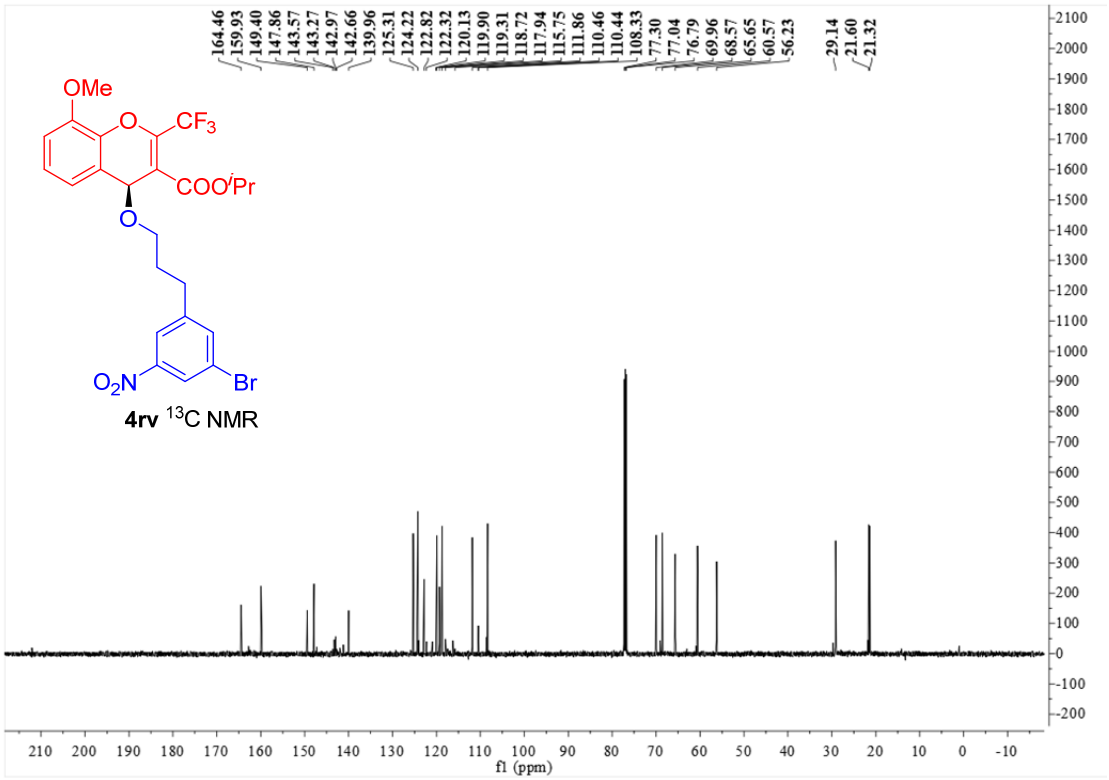
4da ^{13}C NMR



4da ^{19}F NMR



4rv ^{1}H NMR


164.46
159.93
149.40
147.86
143.57
143.27
142.97
142.66
139.96
125.31
124.22
122.82
122.32
120.13
119.90
119.31
118.72
117.94
115.75
111.86
110.46
110.44
108.33
77.30
77.04
76.79
69.96
68.57
65.65
60.57
56.23
29.14
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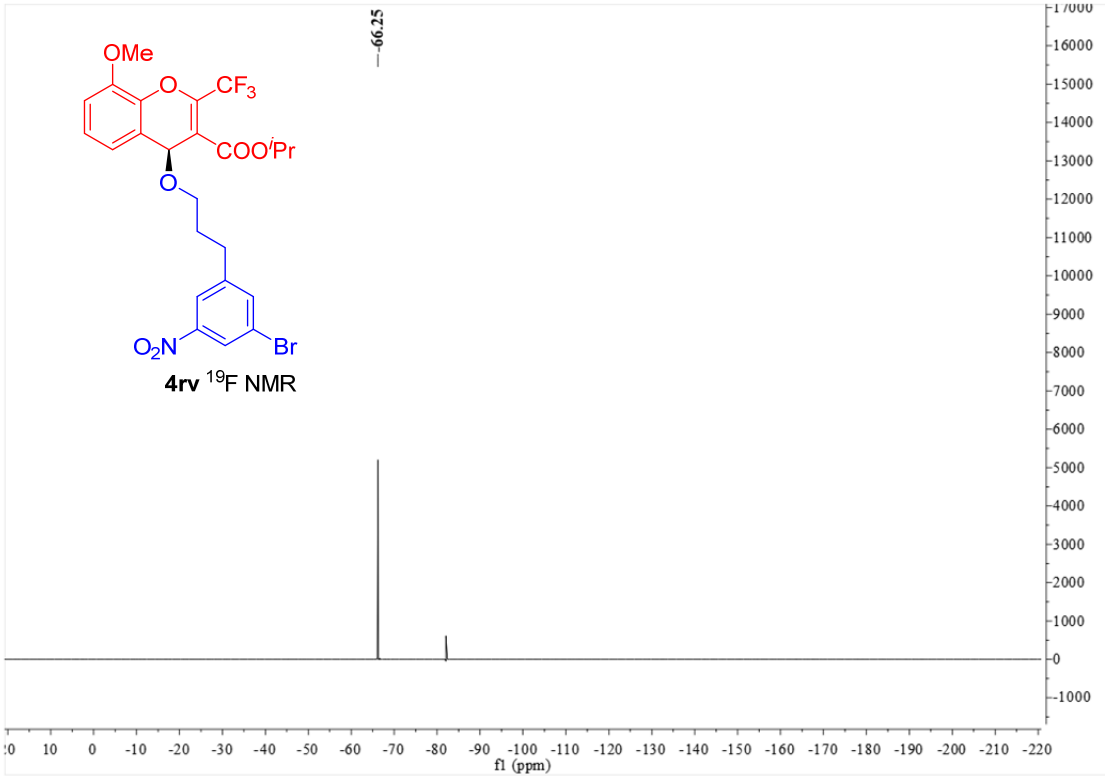
21.32
OMe
O
CF3
COO'Pr
O
O2N
Br
4rv 13C NMR
f1 (ppm)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CF3
COO'Pr
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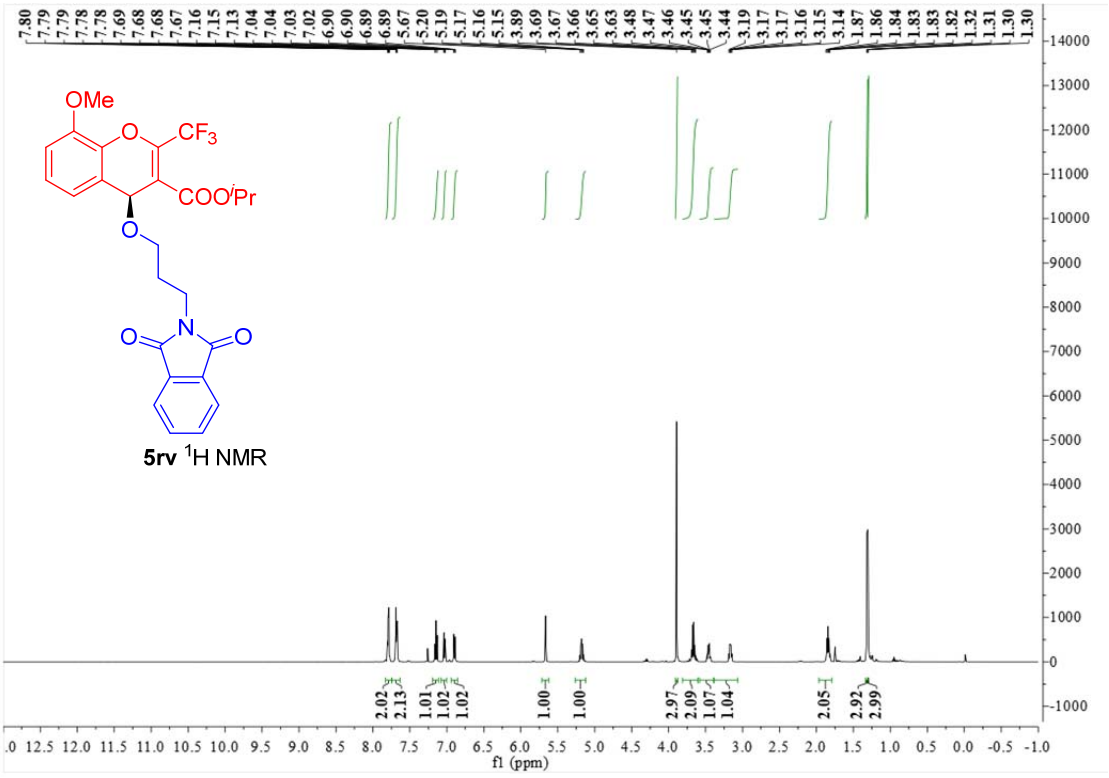
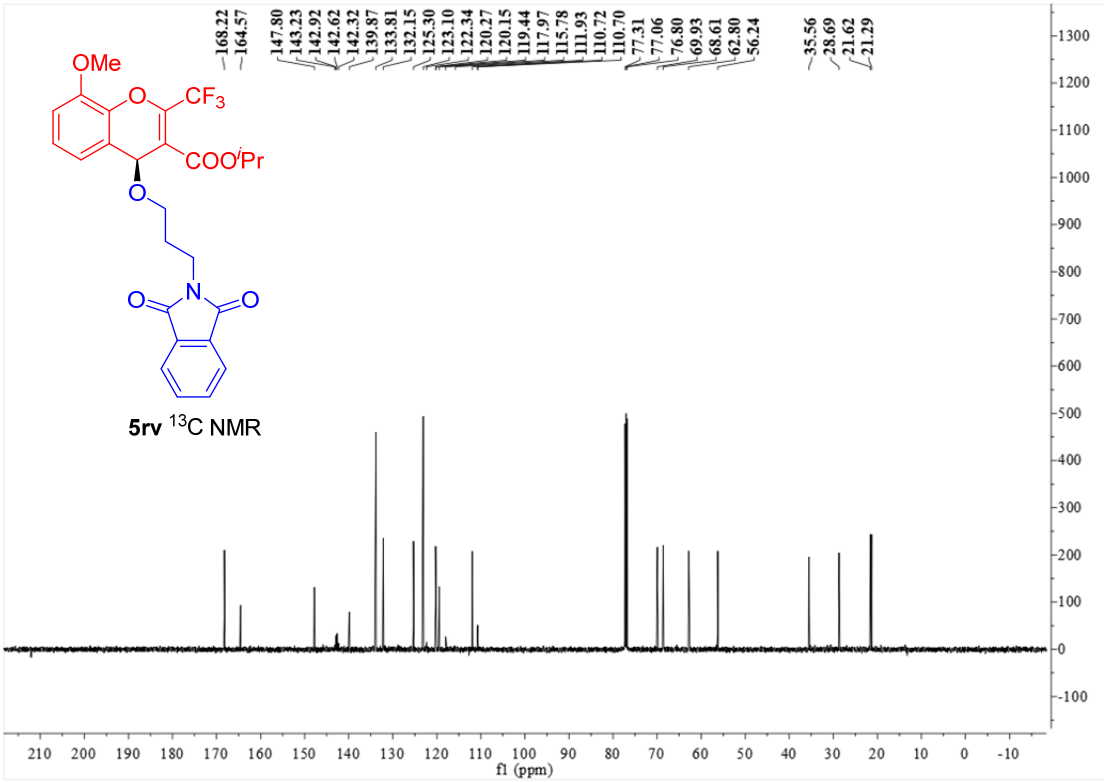
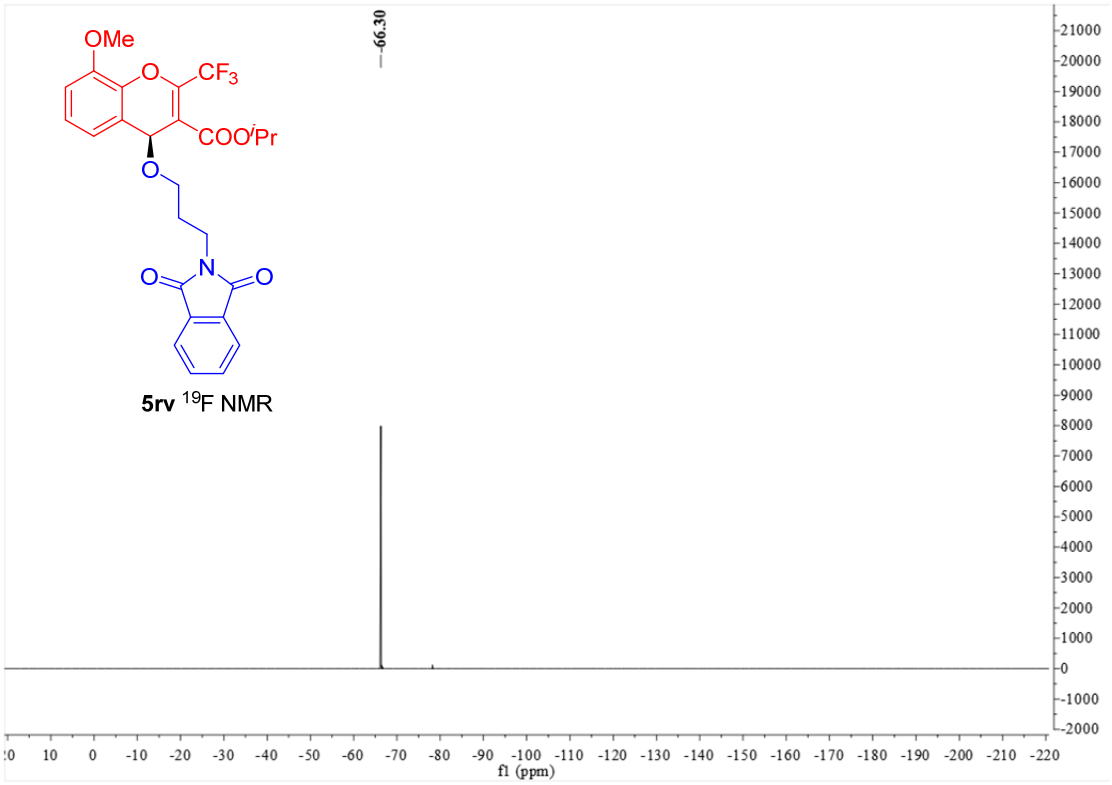
O2N
Br
4rv 19F NMR
f1 (ppm)

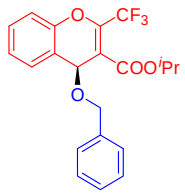

OMe
O
CF3
COO'Pr
O
N
O
O
5rv 1H NMR
f1 (ppm)


OMe
O
CF3
COO'Pr
O
N
O
O
5rv 13C NMR
f1 (ppm)

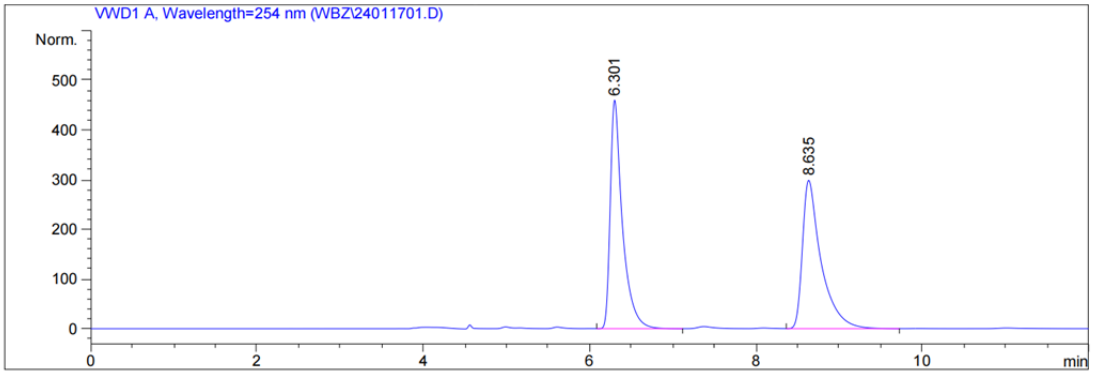

OMe
O
CF3
COOiPr
O
N
O
O
-66.30
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

5rv ^{19}F NMR

9. Copy of HPLC spectra for the products



3aa



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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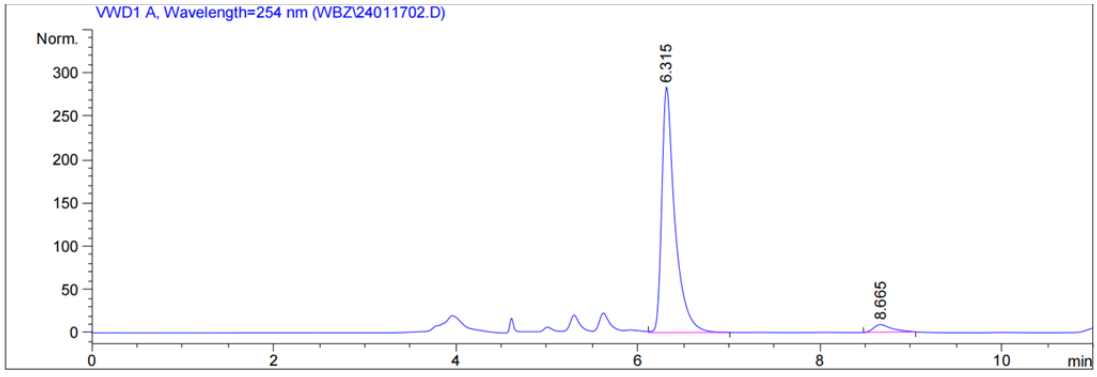
2	8.635	VB	0.2258	4666.25000	298.84241	49.8827



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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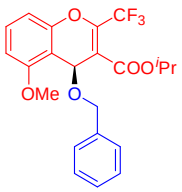
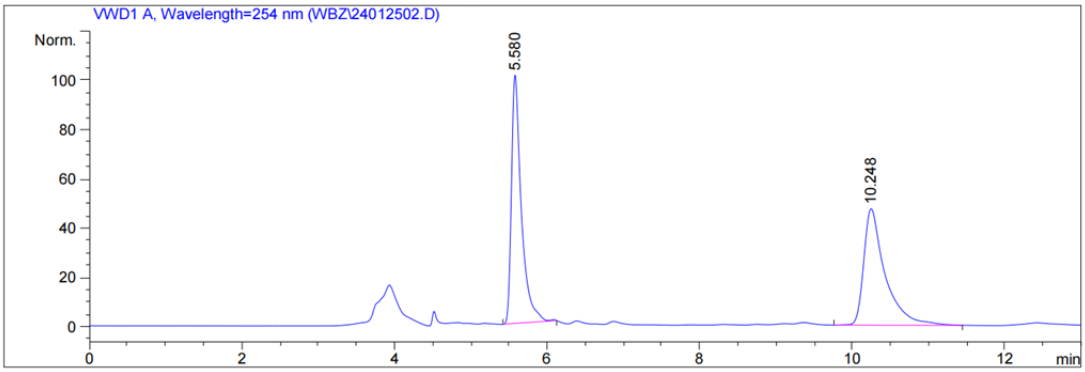
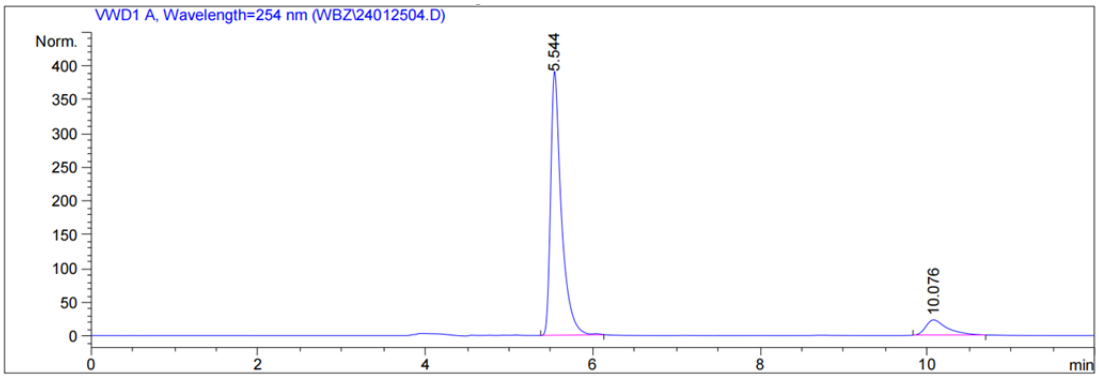
2	8.665	MM R	0.2326	123.95605	8.88308	4.1857



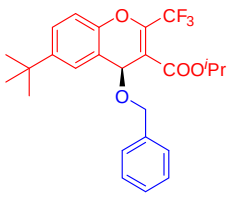
3ab



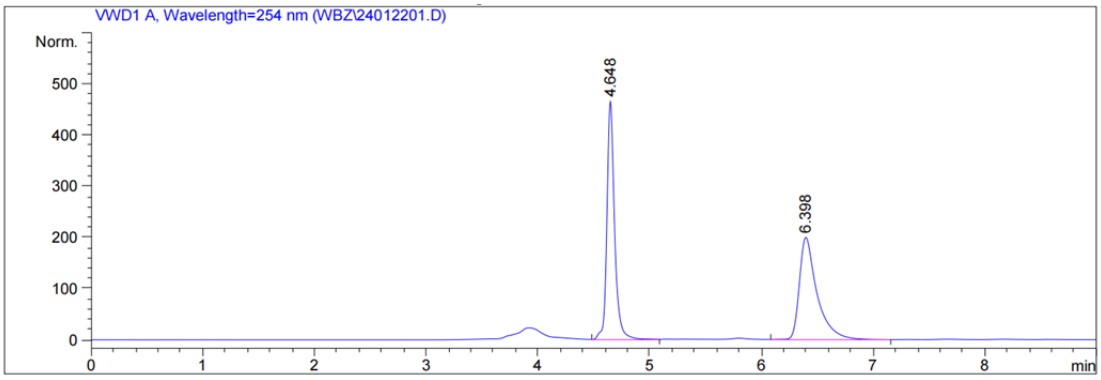
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.580	MM R	0.1505	910.55225	100.82197	49.6622
2	10.248	VB	0.2800	922.93933	47.31876	50.3378



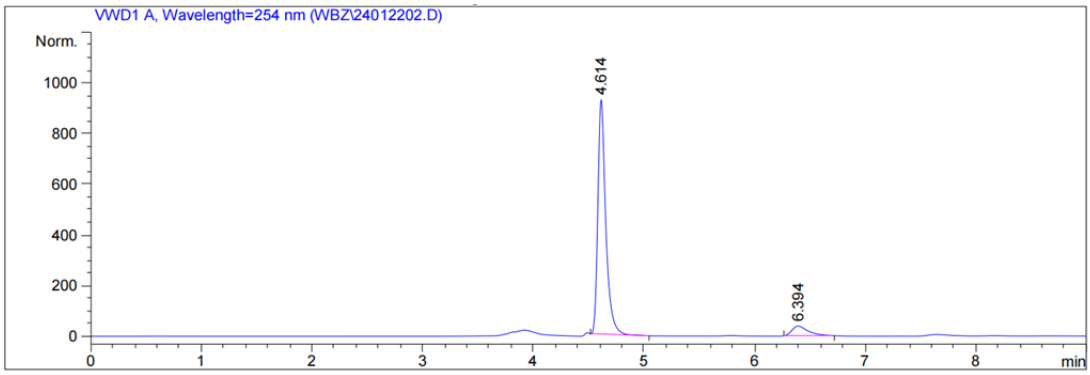
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.544	MM R	0.1493	3500.31274	390.83667	89.7282
2	10.076	MM R	0.2953	400.70493	22.61741	10.2718



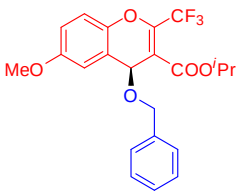
3ac



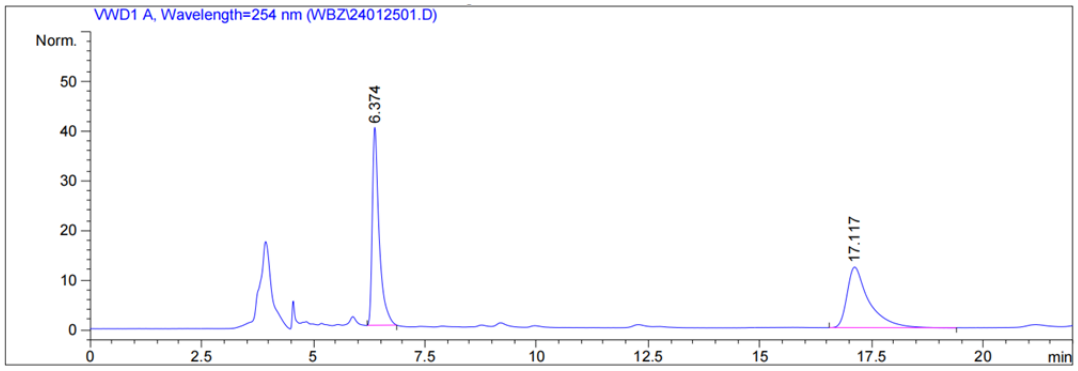
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.648	VV	0.0705	2233.10474	465.43930	50.3032
2	6.398	VB	0.1606	2206.18433	200.12021	49.6968



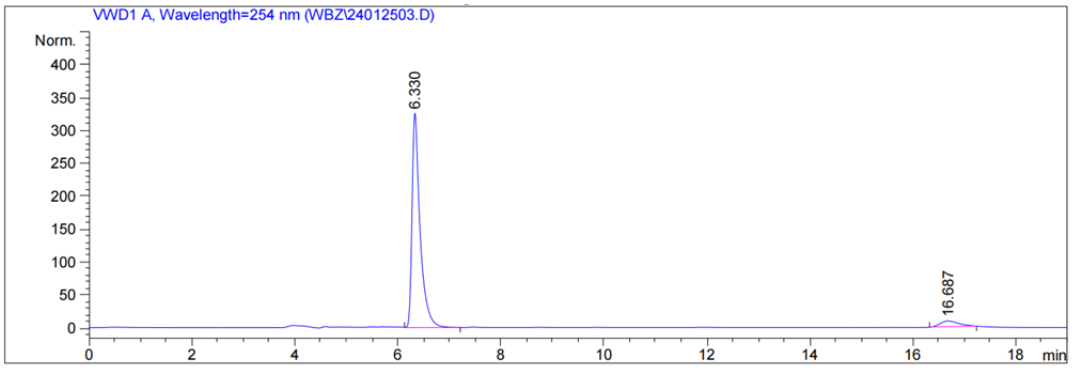
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.614	MM R	0.0829	4602.47949	925.78638	92.2511
2	6.394	MM R	0.1682	386.59634	38.30271	7.7489



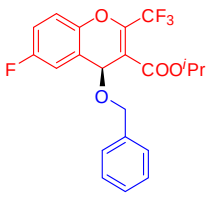
3ad



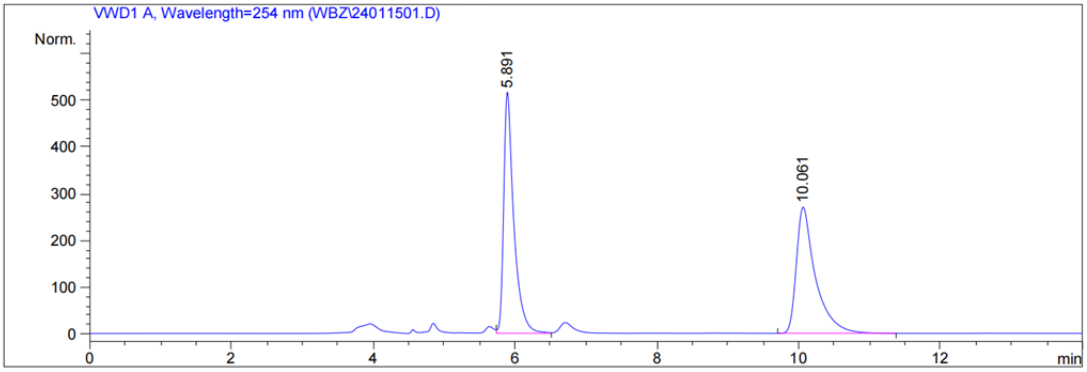
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.374	MM R	0.1786	426.94040	39.84053	50.6349
2	17.117	MM R	0.5685	416.23367	12.20318	49.3651



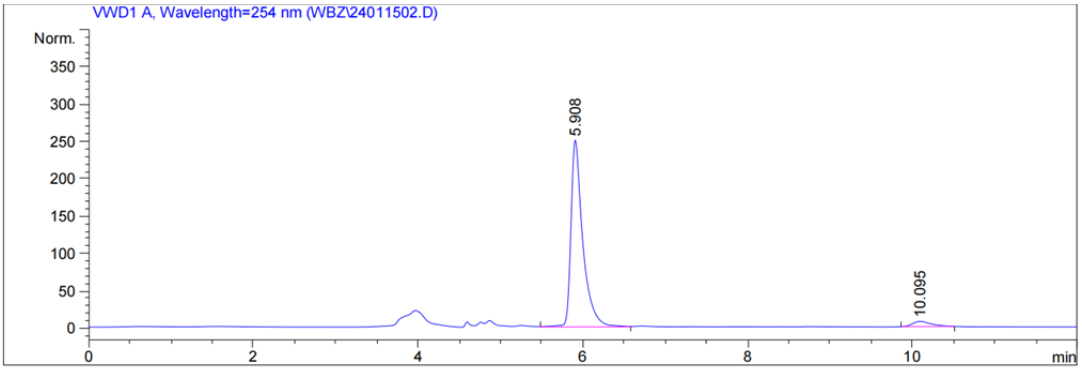
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.330	VB	0.1572	3533.96167	325.60712	94.1898
2	16.687	MM R	0.4150	217.99615	8.75397	5.8102



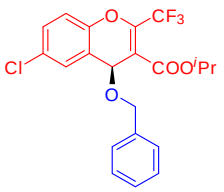
3ae



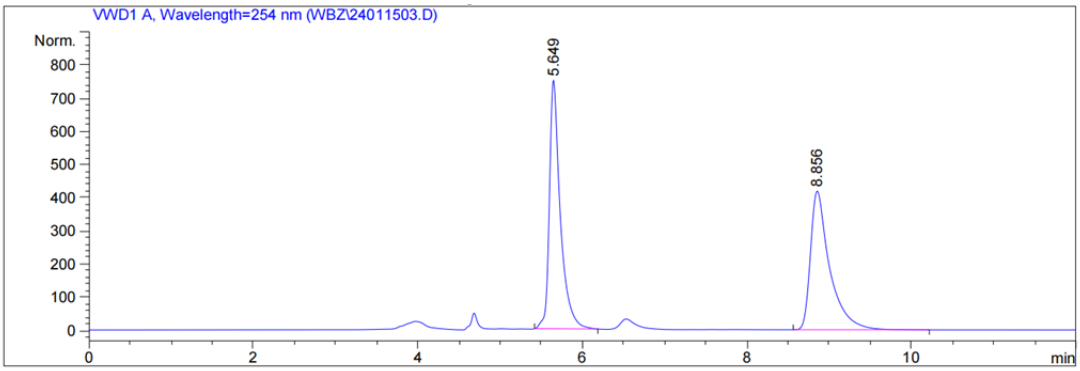
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.891	VV	0.1451	5123.75391	515.37366	50.3493
2	10.061	BB	0.2693	5052.66016	269.92380	49.6507



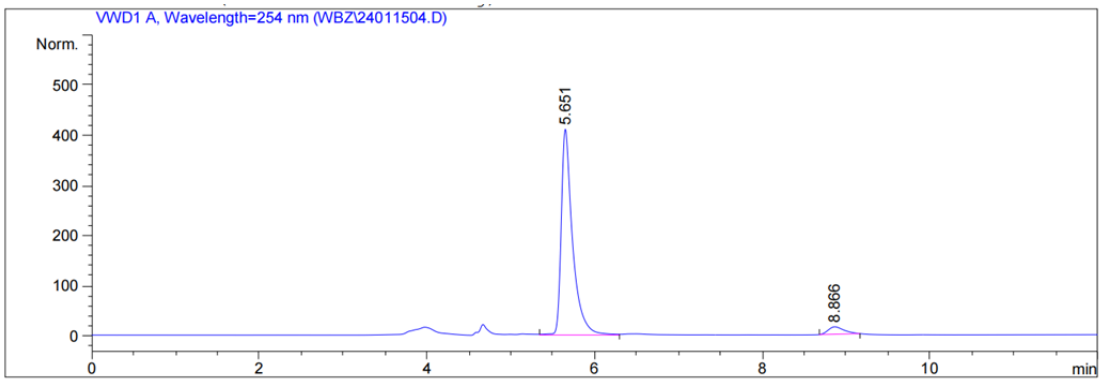
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.908	VV	0.1449	2512.83789	250.16330	95.7337
2	10.095	MM R	0.2676	111.98293	6.97436	4.2663



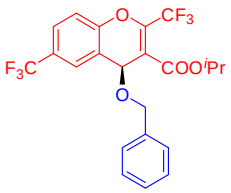
3af



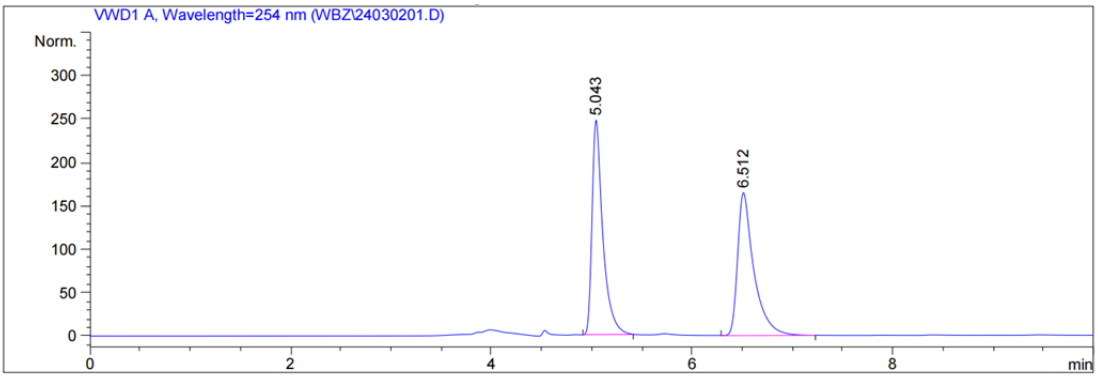
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.649	MM R	0.1539	6911.89014	748.36700	50.5571
2	8.856	PB	0.2325	6759.55713	417.57654	49.4429



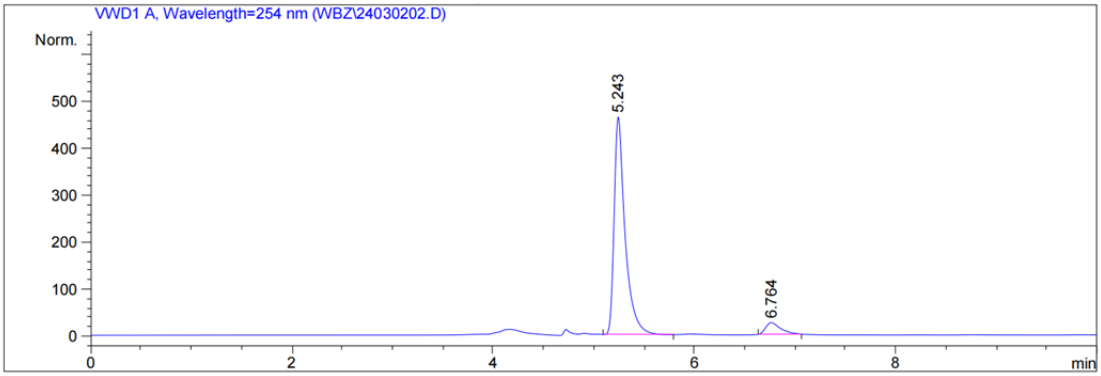
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.651	VV	0.1362	3867.82861	410.32492	95.0996
2	8.866	MM R	0.2224	199.30539	14.93906	4.9004



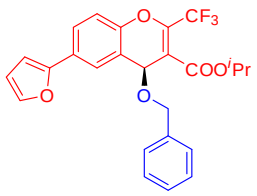
3ag



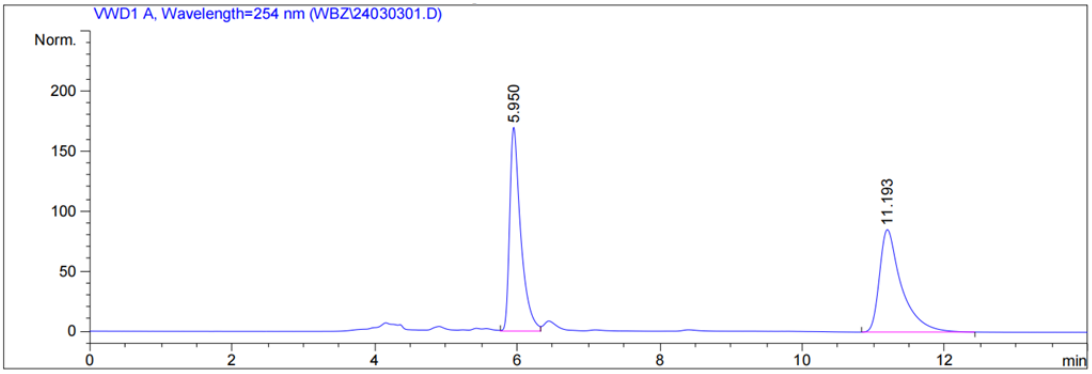
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.043	MM R	0.1243	1843.95947	247.26576	49.8806
2	6.512	BB	0.1634	1852.78699	164.50726	50.1194



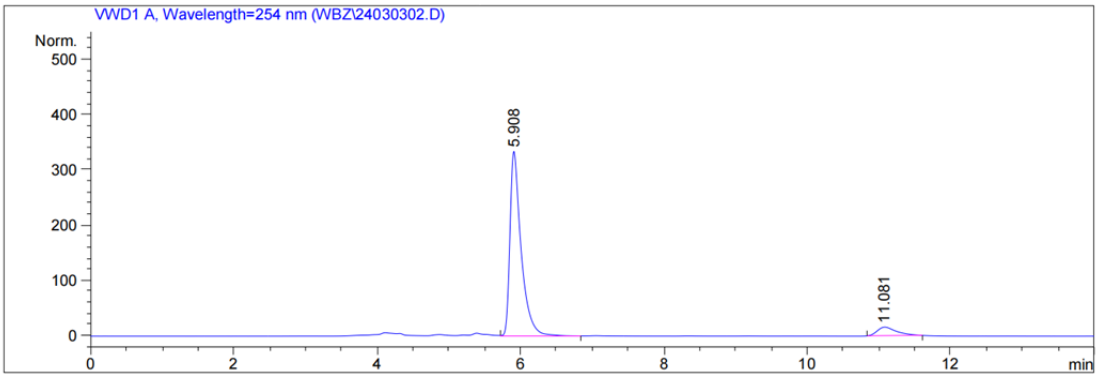
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.243	MM R	0.1261	3505.50586	463.23880	93.2174
2	6.764	MM R	0.1713	255.06351	24.80926	6.7826



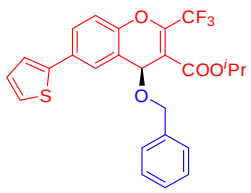
3ah



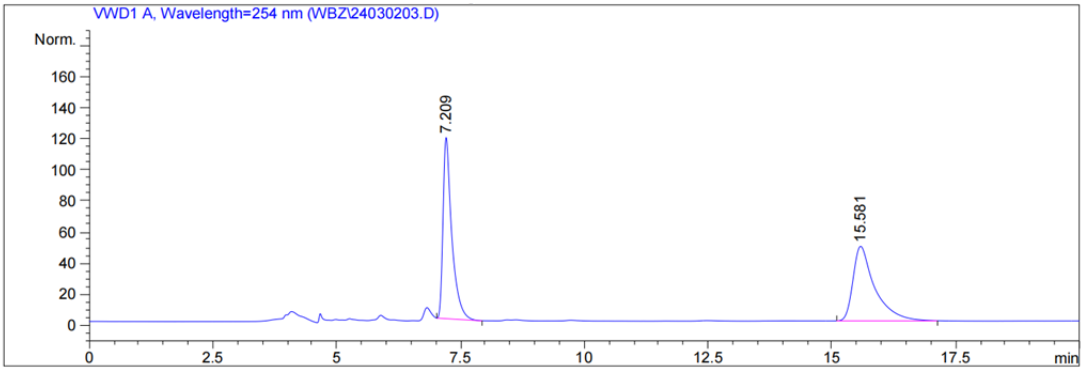
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.950	VV	0.1583	1836.66357	169.73415	50.0826
2	11.193	PB	0.3099	1830.60315	85.35184	49.9174



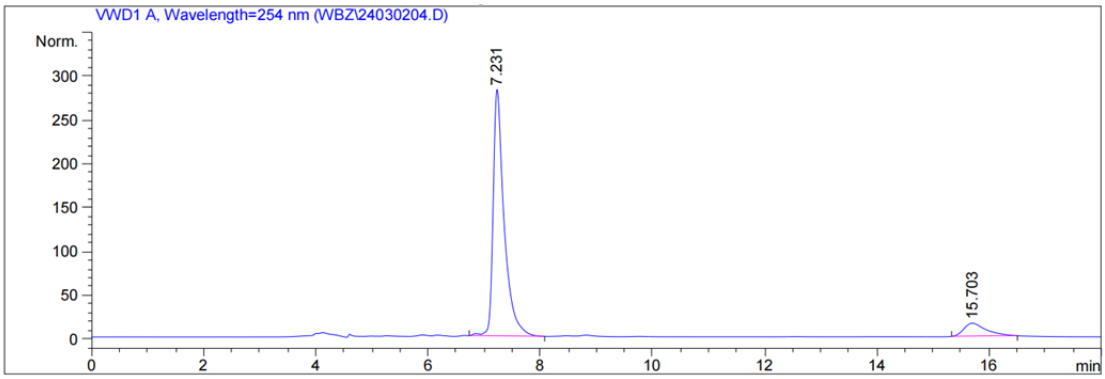
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.908	VB	0.1569	3618.79785	334.25531	92.4130
2	11.081	MM R	0.3151	297.09863	15.71359	7.5870



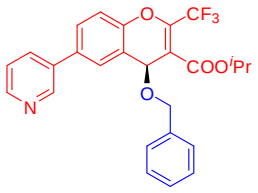
3ai



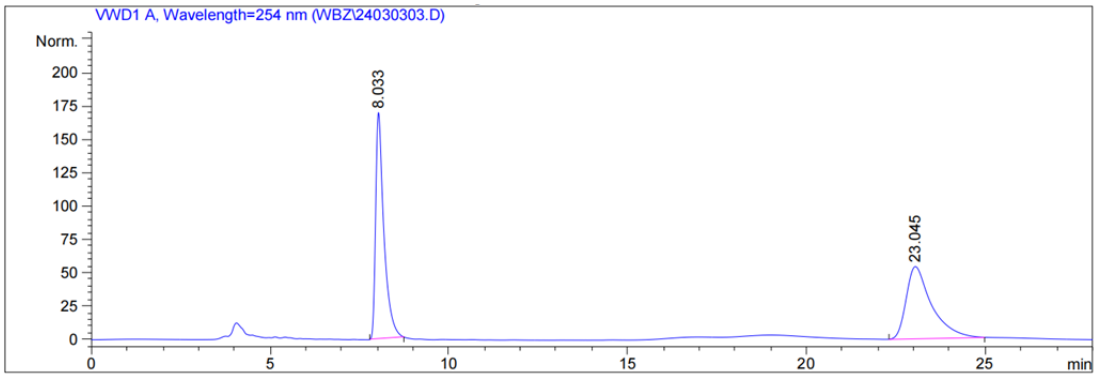
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.209	MM R	0.2063	1447.24927	116.94082	49.5759
2	15.581	BB	0.4398	1472.00916	48.12419	50.4241



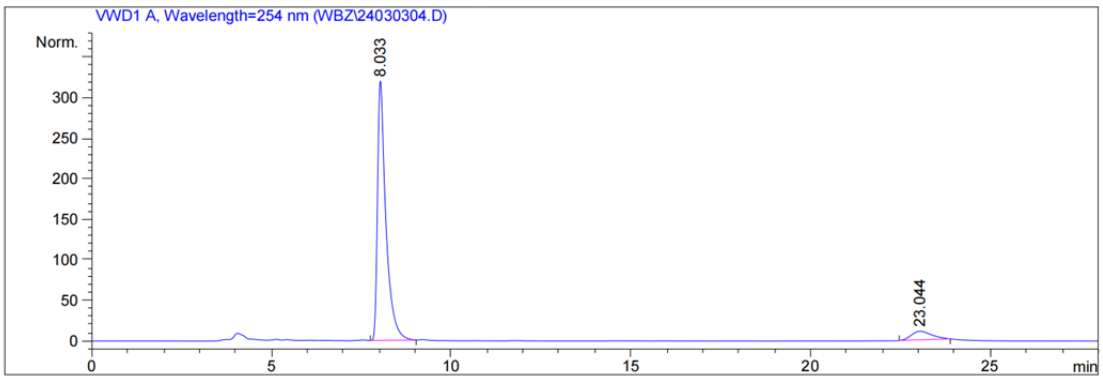
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.231	MM R	0.2284	3848.96216	280.90808	90.3597
2	15.703	MM R	0.4621	410.63733	14.81078	9.6403



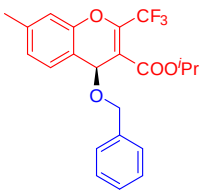
3aj



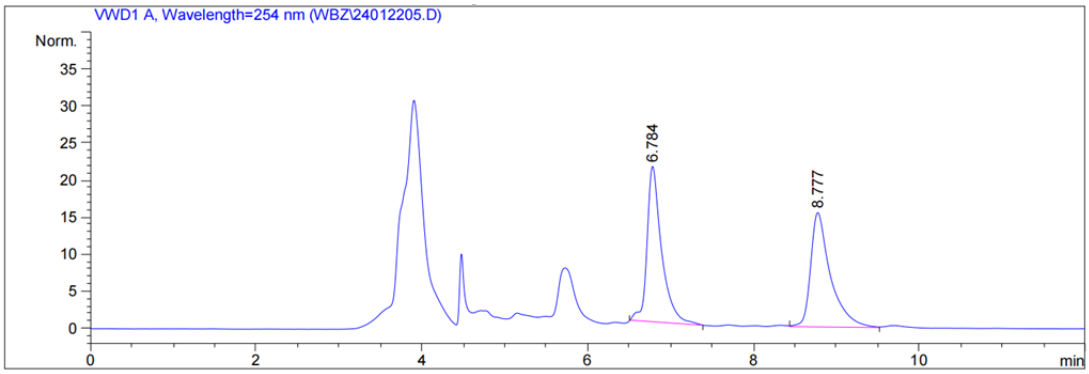
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.033	MM R	0.2682	2721.06616	169.12376	50.2772
2	23.045	MM R	0.8279	2691.06470	54.17568	49.7228



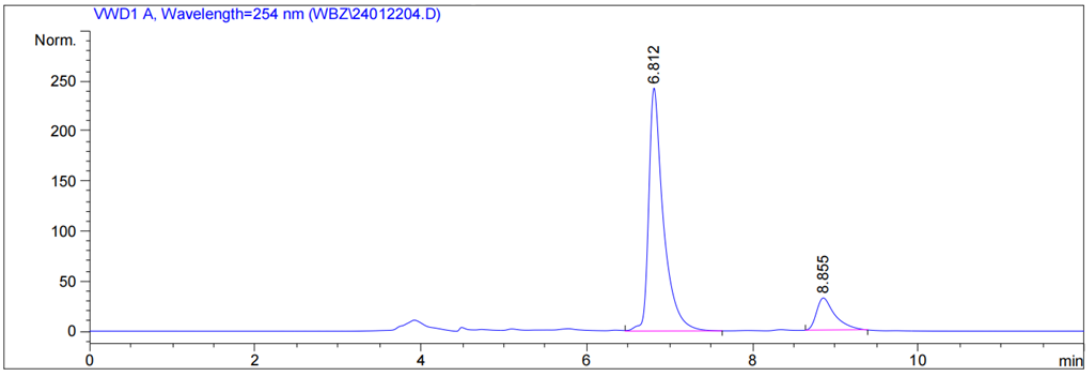
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.033	MM R	0.2704	5197.87207	320.35306	92.3657
2	23.044	MM R	0.6641	429.61859	10.78249	7.6343



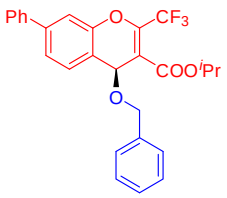
3ak



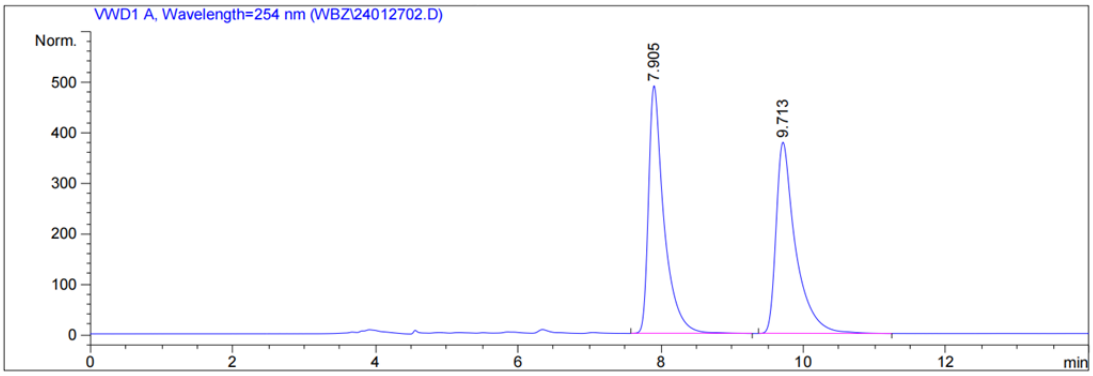
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.784	MM R	0.2037	256.24374	20.96994	49.9376
2	8.777	VB	0.2393	256.88370	15.43896	50.0624



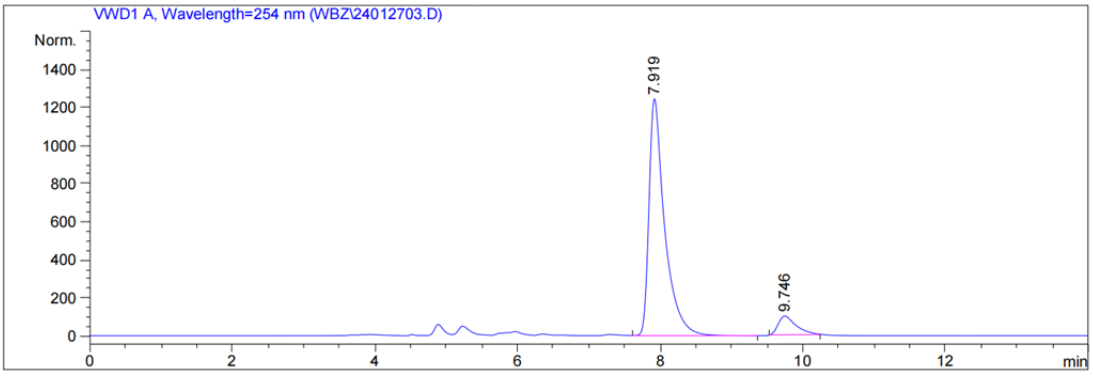
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.812	VB	0.1770	2989.45581	243.00635	85.7591
2	8.855	MM R	0.2576	496.42157	32.11656	14.2409



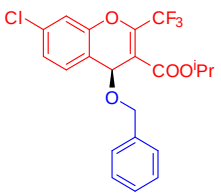
3al



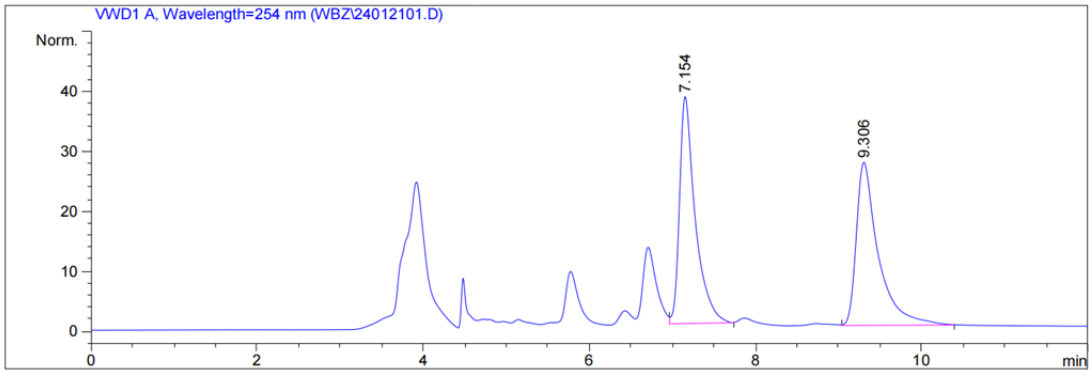
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.905	PB	0.2178	7380.58203	490.37415	50.5577
2	9.713	PB	0.2762	7217.74072	378.66901	49.4423



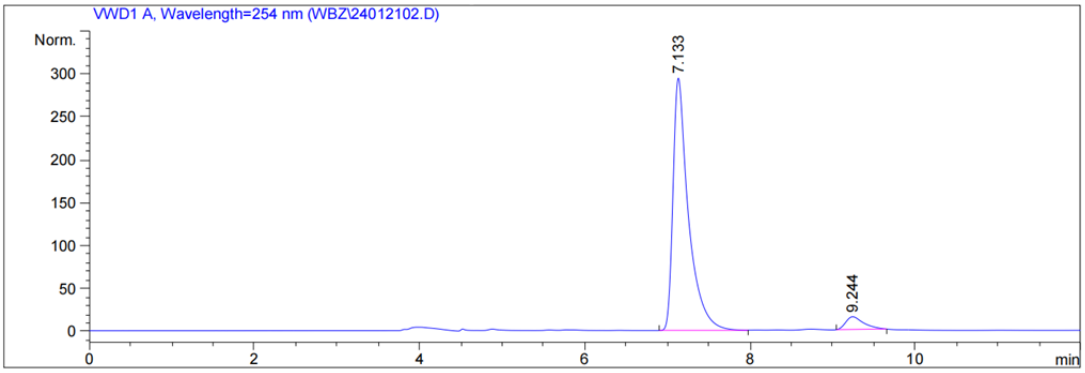
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.919	VB	0.2204	1.89773e4	1242.44702	91.6725
2	9.746	MM R	0.2903	1723.89343	98.98708	8.3275



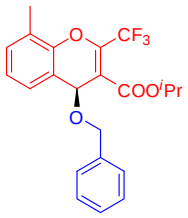
3am



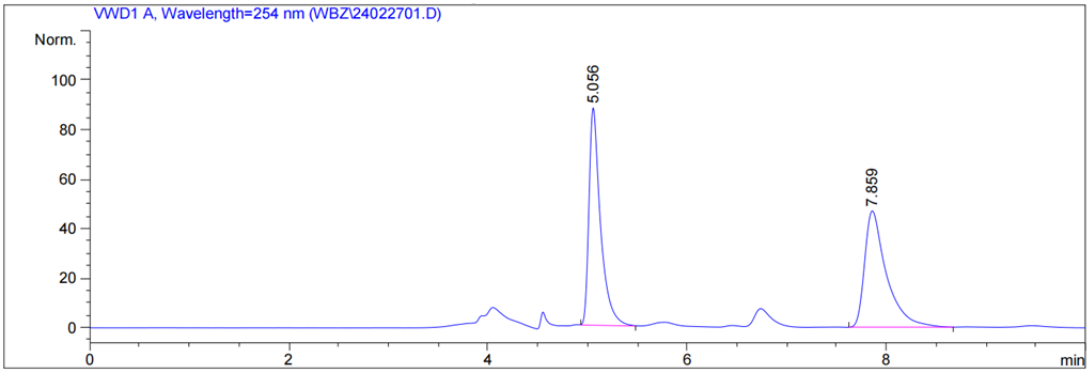
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.154	FM R	0.2191	497.36267	37.83823	49.8137
2	9.306	BB	0.2645	501.08292	27.19263	50.1863



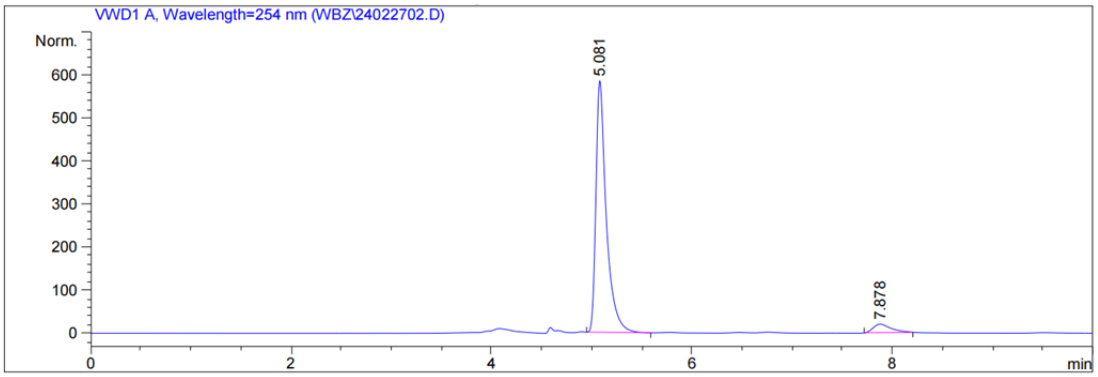
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.133	BB	0.1880	3817.10986	293.78690	94.4526
2	9.244	MM R	0.2513	224.18900	14.86820	5.5474



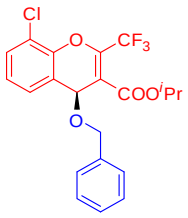
3an



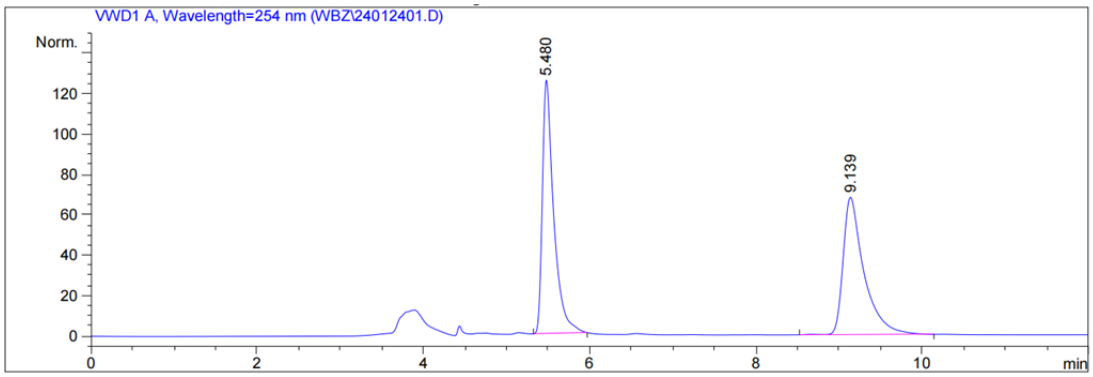
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.056	MM R	0.1341	707.42218	87.88947	49.7106
2	7.859	PB	0.2212	715.65961	47.03289	50.2894



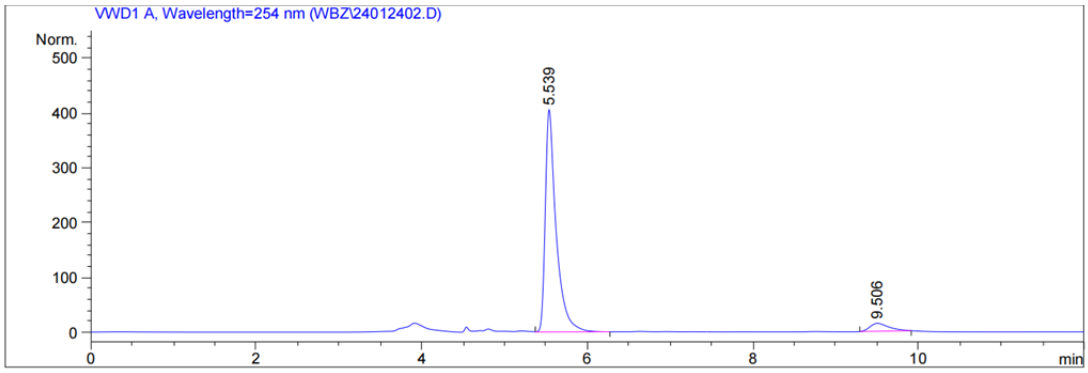
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.081	MM R	0.1198	4200.94873	584.22009	94.5108
2	7.878	MM R	0.2058	243.99355	19.76310	5.4892



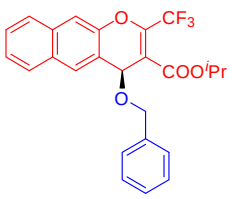
3ao



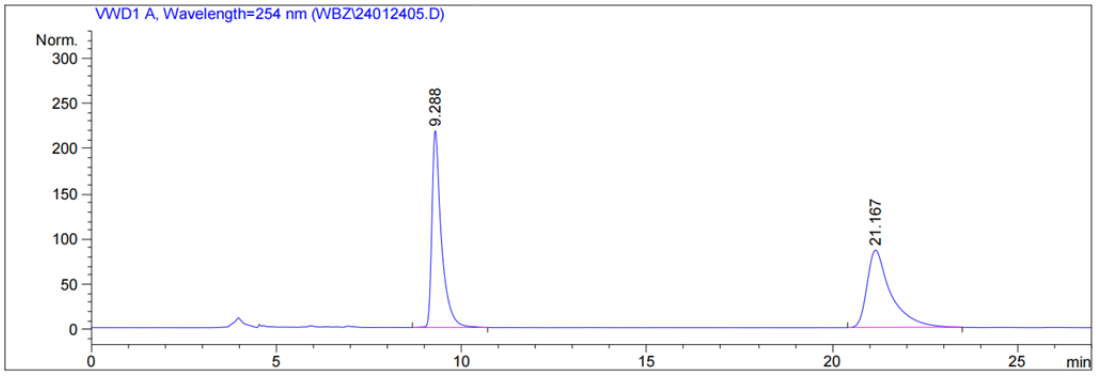
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.480	MM R	0.1578	1188.44006	125.48363	50.0792
2	9.139	BP	0.2512	1184.67871	68.03505	49.9208



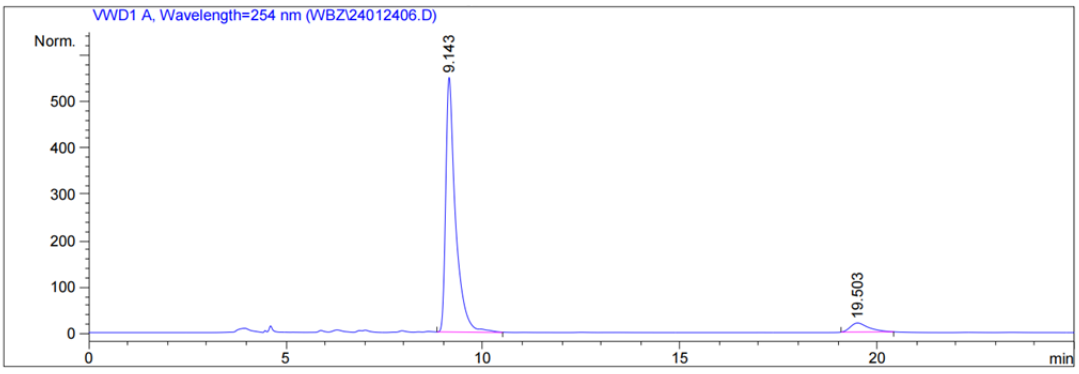
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.539	VB	0.1328	3695.54565	404.65500	94.0544
2	9.506	MM R	0.2670	233.61334	14.58184	5.9456



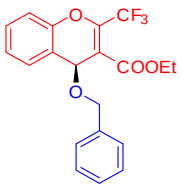
3ap



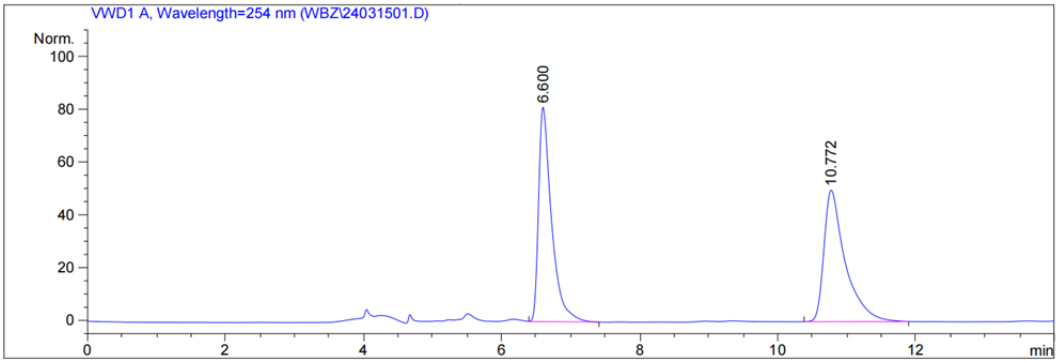
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.288	BB	0.2575	3876.02954	217.40881	50.3192
2	21.167	BB	0.6443	3826.85718	85.53328	49.6808



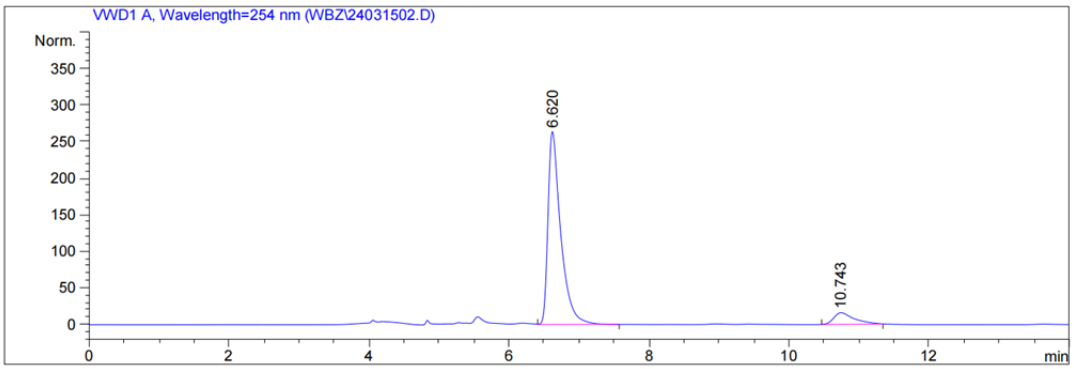
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.143	MM R	0.2893	9531.76172	549.20441	93.6528
2	19.503	MM R	0.5461	646.00775	19.71704	6.3472



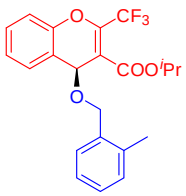
3aq



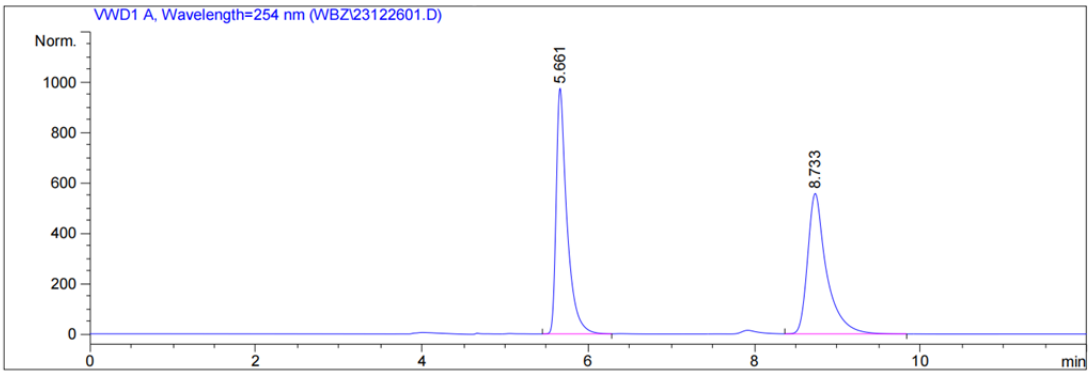
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.600	VB	0.1902	1061.00732	81.27670	49.8015
2	10.772	BB	0.3069	1069.46729	49.87541	50.1985



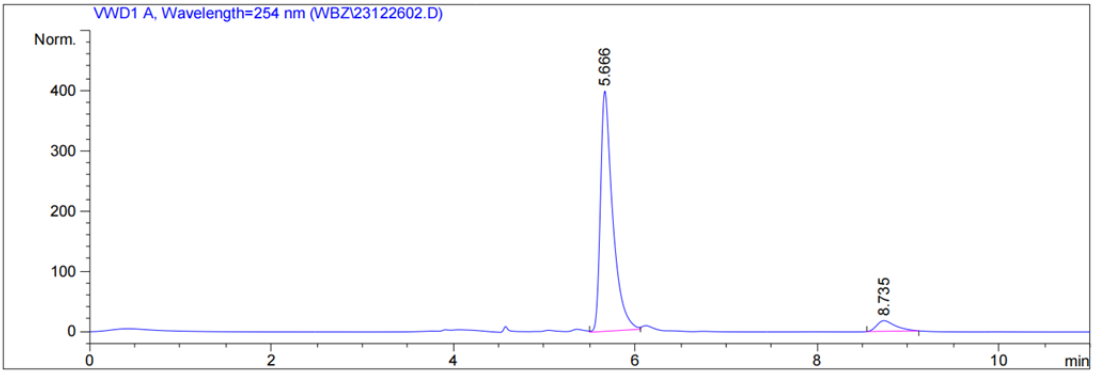
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.620	VB	0.1839	3337.38672	263.96118	91.1193
2	10.743	MM R	0.3389	325.26981	15.99680	8.8807



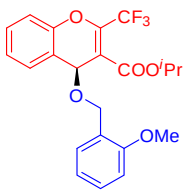
3ba



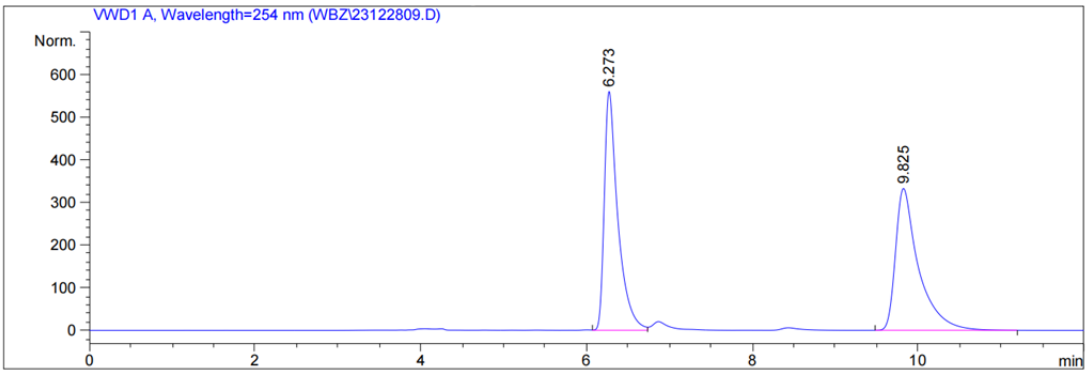
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.661	VV	0.1297	8792.74707	977.30933	49.8751
2	8.733	VP	0.2283	8836.78320	558.48853	50.1249



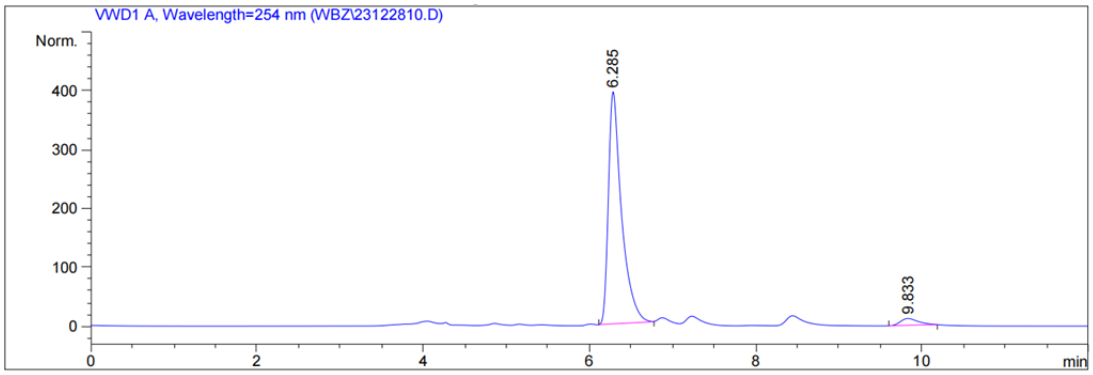
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.666	MM R	0.1562	3748.26538	399.94614	93.4375
2	8.735	MM R	0.2432	263.25797	18.03808	6.5625



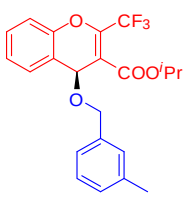
3ca



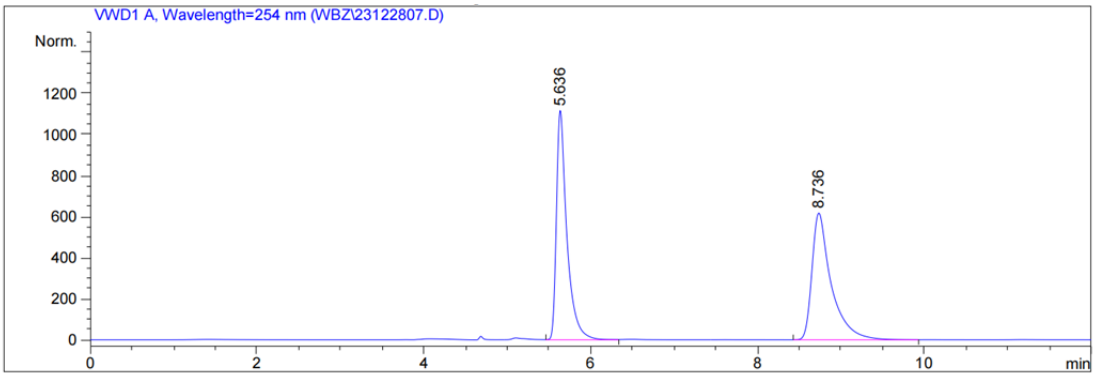
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.273	VV	0.1662	6374.05566	560.15680	49.8270
2	9.825	BB	0.2775	6418.32031	332.65454	50.1730



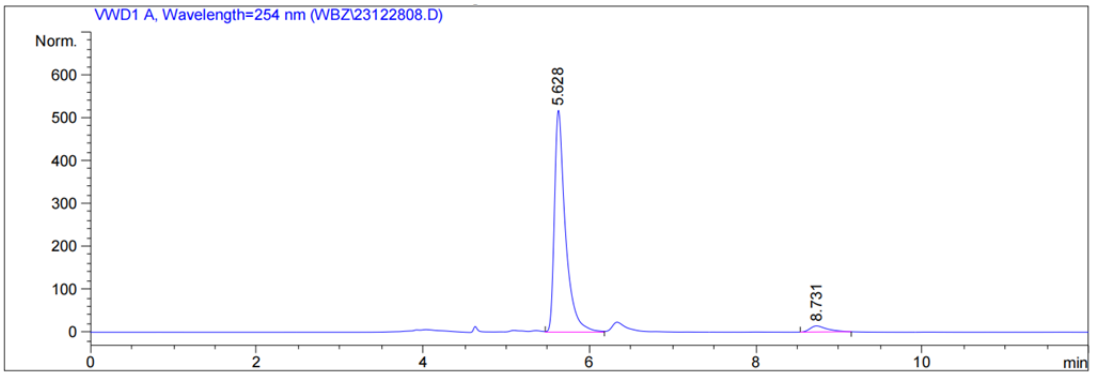
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.285	MM R	0.1838	4349.93262	394.37482	96.0853
2	9.833	MM R	0.2525	177.22696	11.69882	3.9147



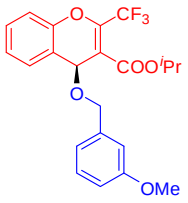
3da



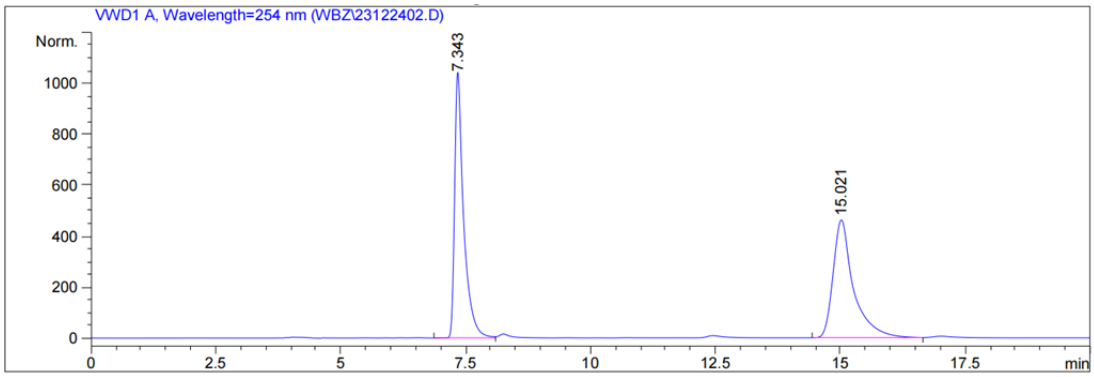
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.636	VV	0.1264	9734.04590	1117.57825	49.5992
2	8.736	BV	0.2304	9891.37305	617.97528	50.4008



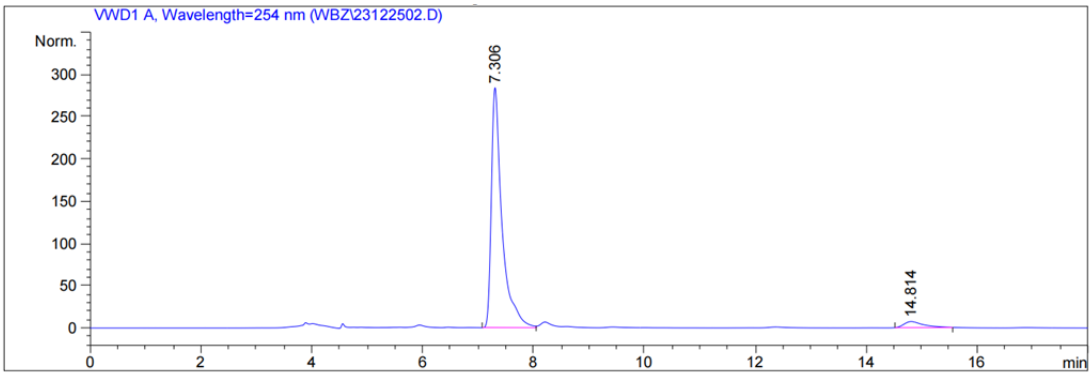
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.628	VV	0.1336	4769.25879	518.03925	95.7939
2	8.731	MM R	0.2451	209.40974	14.23832	4.2061



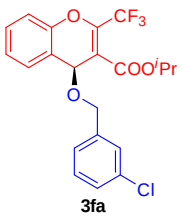
3ea



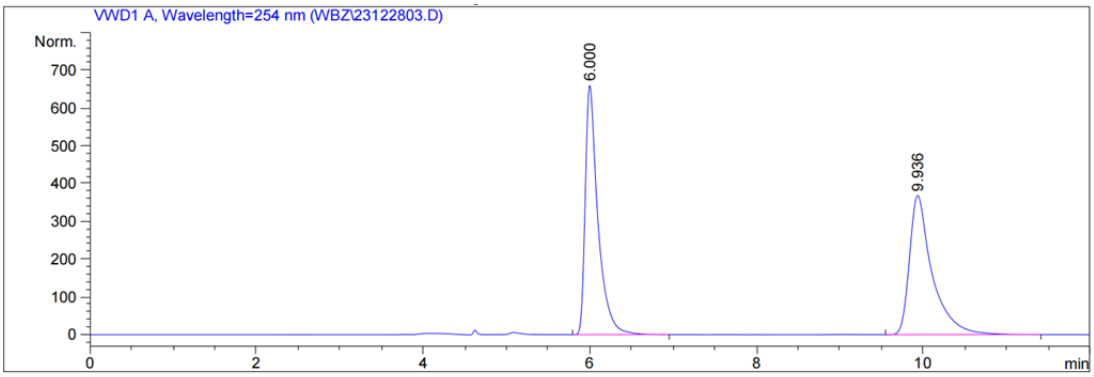
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.343	VV	0.1817	1.31033e4	1041.90698	49.8940
2	15.021	BV	0.4119	1.31590e4	462.63416	50.1060



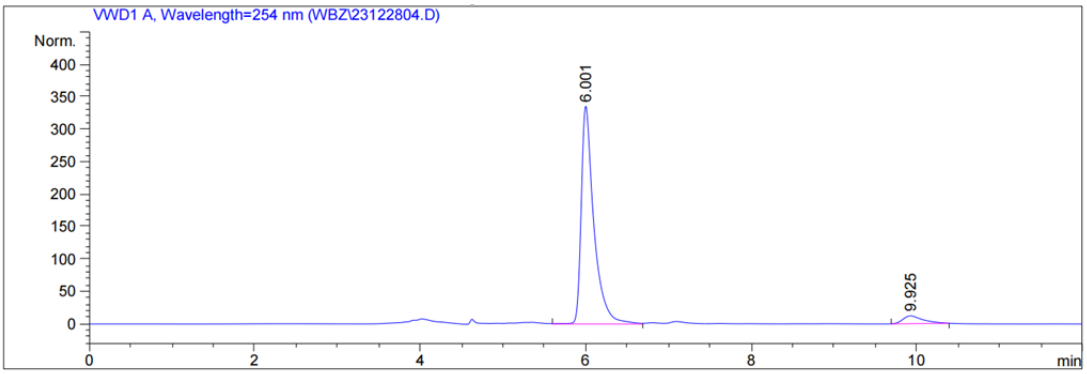
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.306	PV	0.1926	3800.48999	283.89047	95.3372
2	14.814	MM R	0.4230	185.87465	7.32393	4.6628



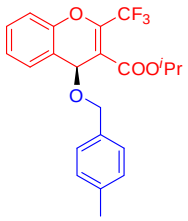
3fa



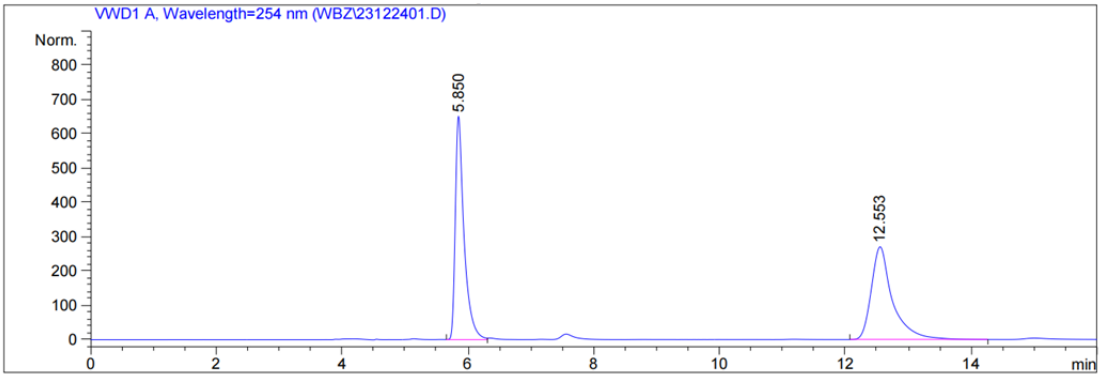
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.000	VP	0.1539	6978.11865	660.24500	50.0578
2	9.936	VB	0.2728	6962.00000	368.54605	49.9422



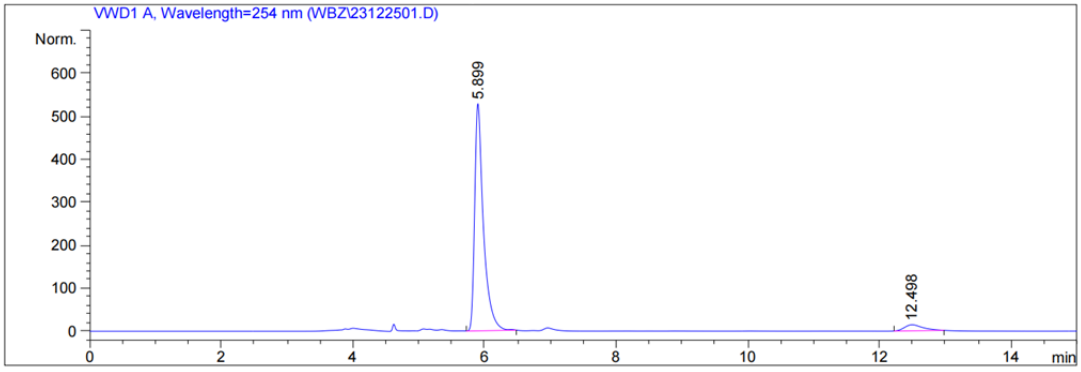
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.001	VV	0.1544	3566.49976	335.90515	94.4589
2	9.925	MM R	0.2861	209.21632	12.18929	5.5411



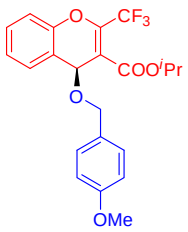
3ga



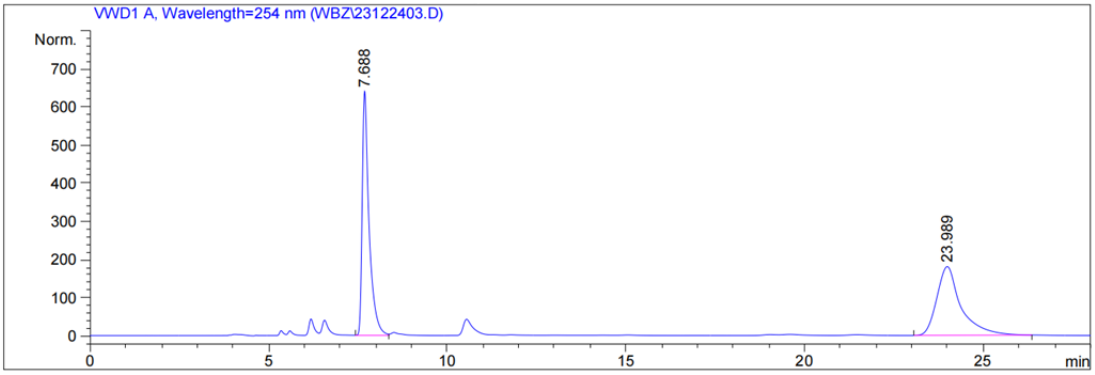
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.850	VV	0.1406	6308.75635	651.79138	49.8728
2	12.553	BB	0.3404	6340.94727	270.52322	50.1272



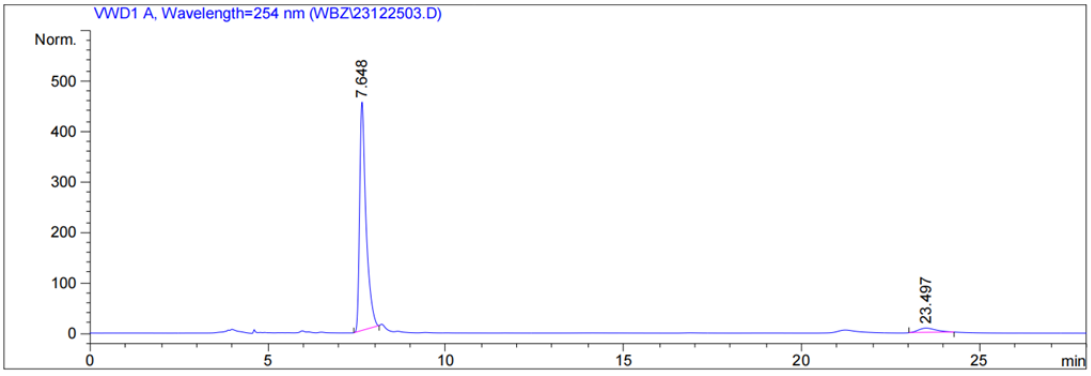
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.899	MM R	0.1544	4900.06885	528.80475	94.5085
2	12.498	MM R	0.3324	284.72202	14.27646	5.4915



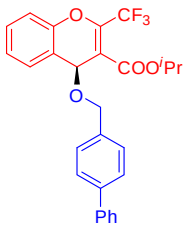
3ha



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.688	VV	0.1925	8554.56934	639.36078	50.2877
2	23.989	BB	0.6845	8456.68164	180.14378	49.7123



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.648	MM R	0.2096	5694.61230	452.89276	94.8594
2	23.497	MM R	0.5914	308.59827	8.69693	5.1406



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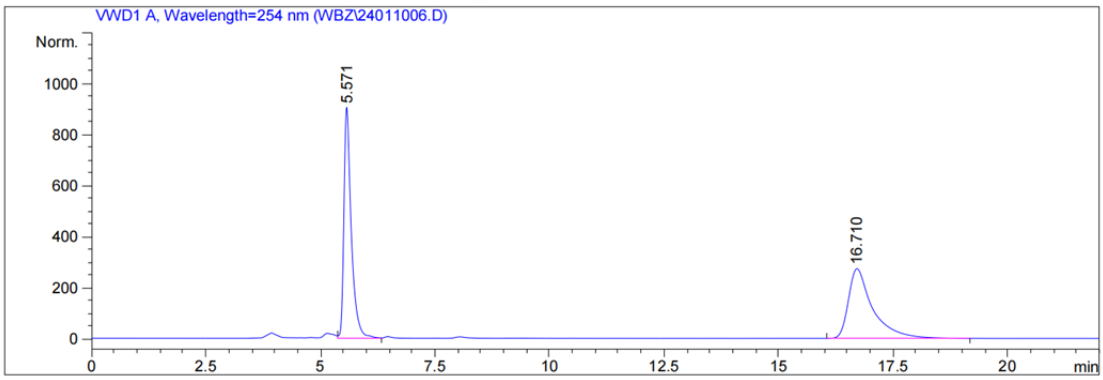
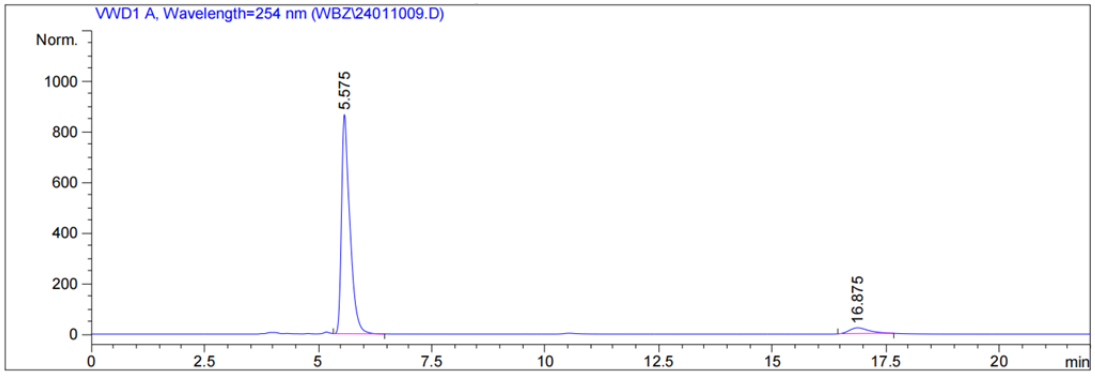
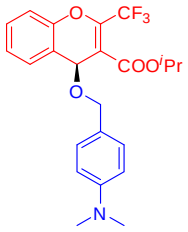


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.571	VV	0.1638	1.01136e4	905.24158	50.1799
2	16.710	BB	0.5289	1.00410e4	273.45135	49.8201



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.575	MM R	0.2128	1.10696e4	867.00549	94.0977
2	16.875	MM R	0.5042	694.34528	22.95144	5.9023



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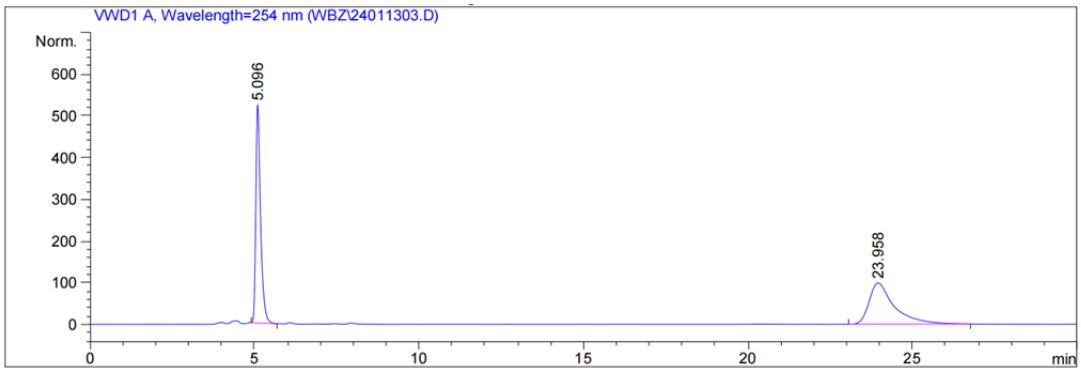
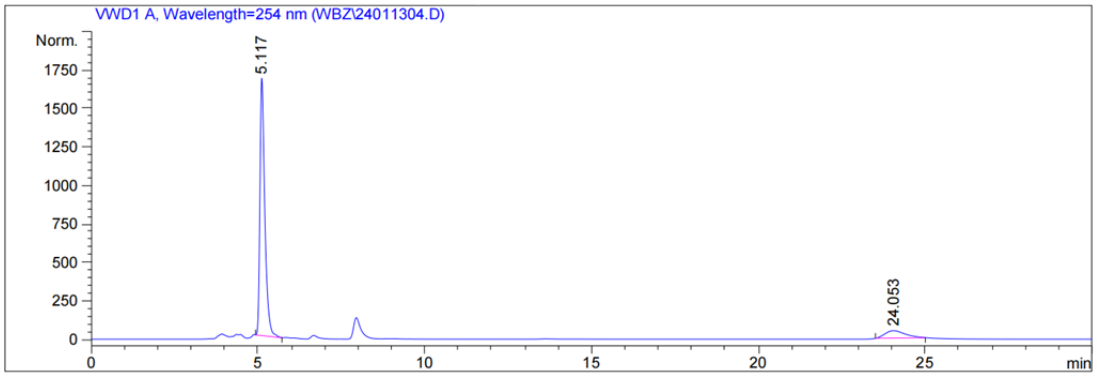
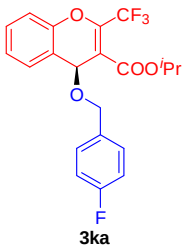


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.096	MM R	0.1670	5229.82373	521.86536	49.7793
2	23.958	BB	0.7733	5276.19873	98.75851	50.2207



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.117	MM R	0.1688	1.69161e4	1670.21289	89.2715
2	24.053	MM R	0.7023	2032.94788	48.24398	10.7285



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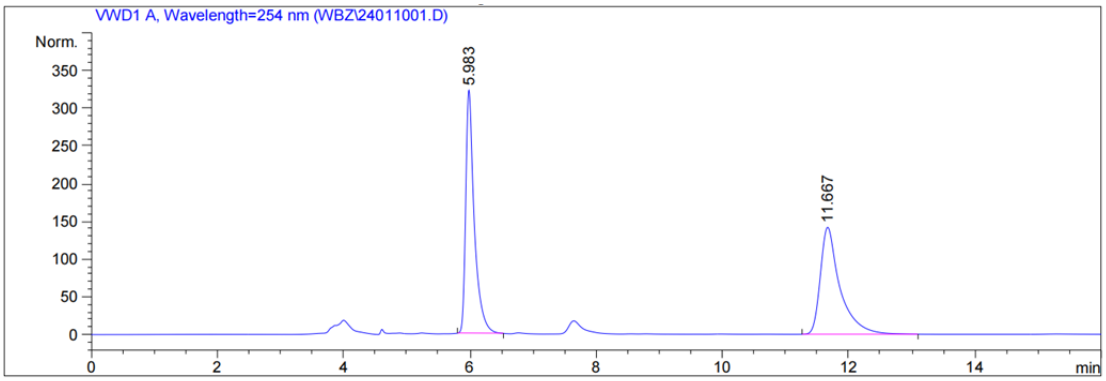
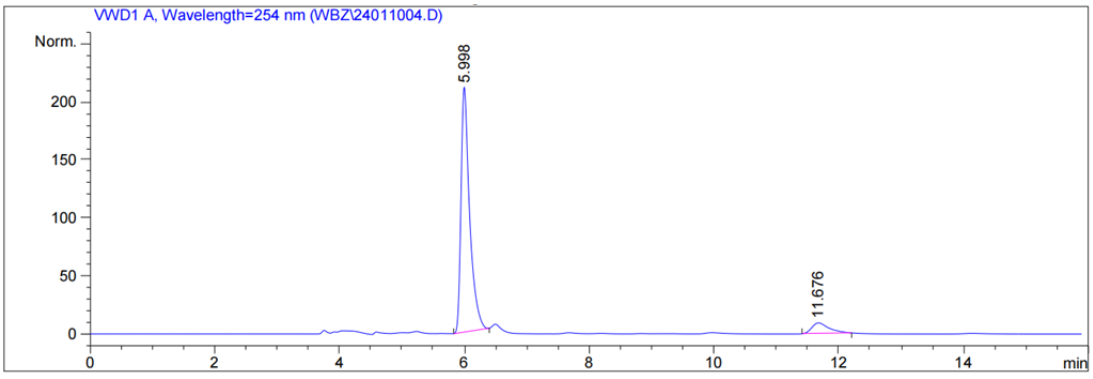
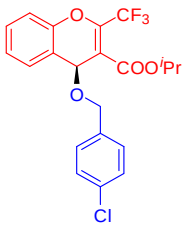


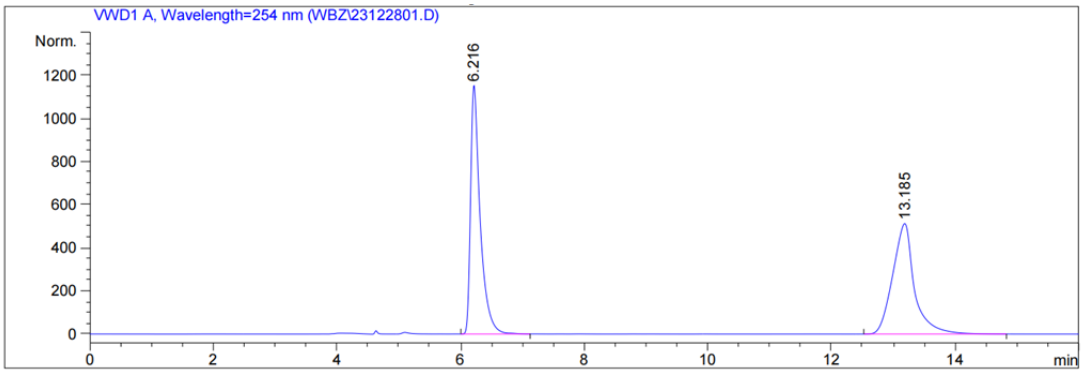
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.983	MM R	0.1573	3040.26587	322.12549	49.8128
2	11.667	BB	0.3118	3063.11963	141.76378	50.1872



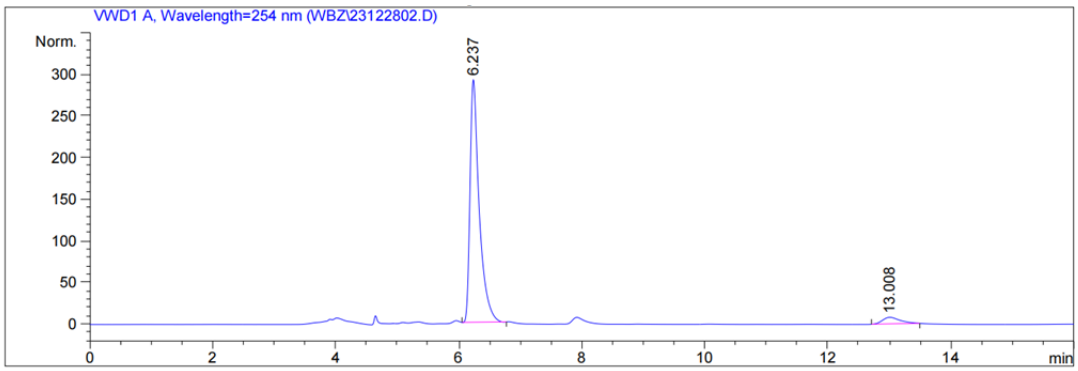
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.998	MM R	0.1598	2026.38391	211.29723	92.1092
2	11.676	MM R	0.3182	173.59537	9.09216	7.8908



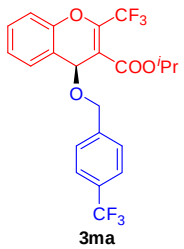
3la



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.216	VV	0.1563	1.24156e4	1152.14575	49.8348
2	13.185	BB	0.3602	1.24979e4	512.56653	50.1652



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.237	MM R	0.1728	3020.39429	291.32285	94.9661
2	13.008	MM R	0.3337	160.10402	7.99738	5.0339



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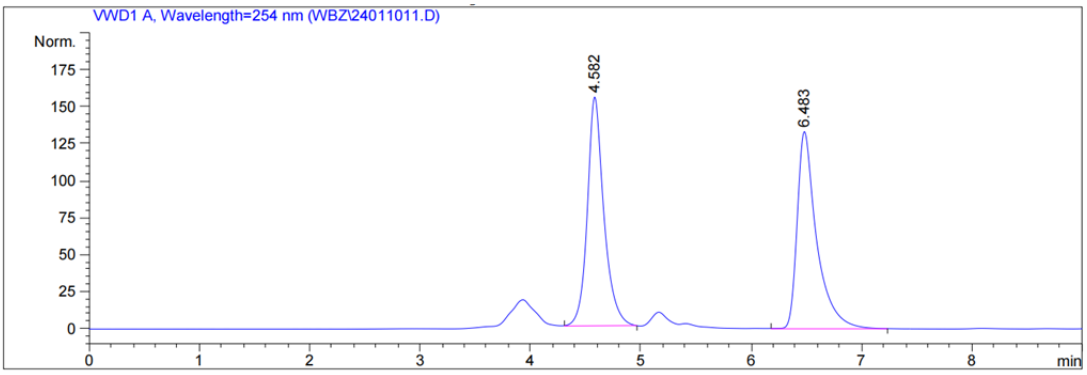
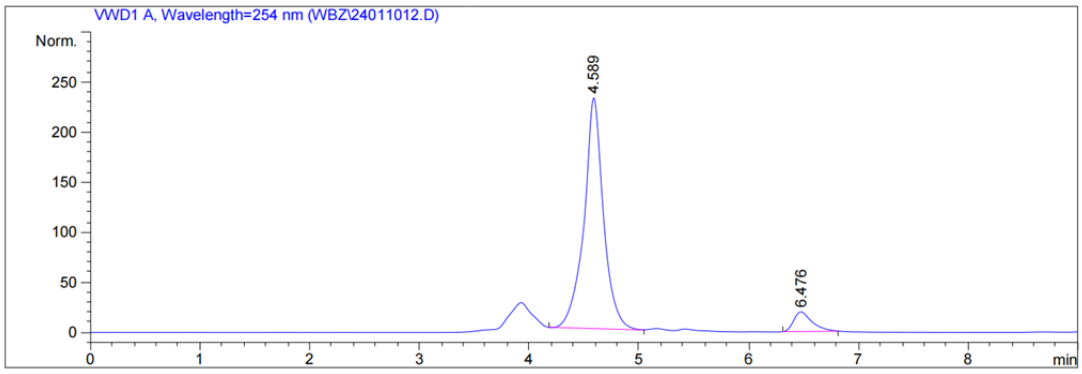
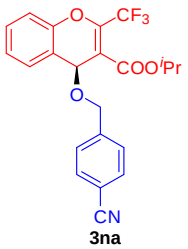


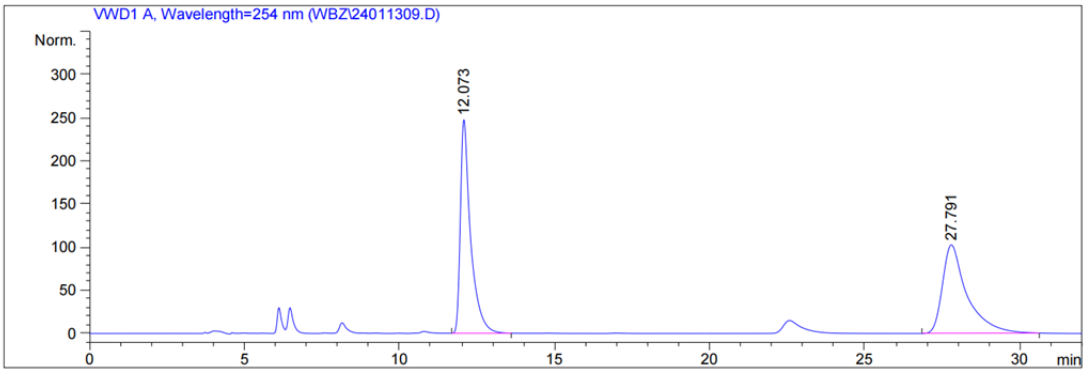
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.582	MM R	0.1740	1615.20215	154.73595	49.6488
2	6.483	BB	0.1783	1638.05200	133.27328	50.3512



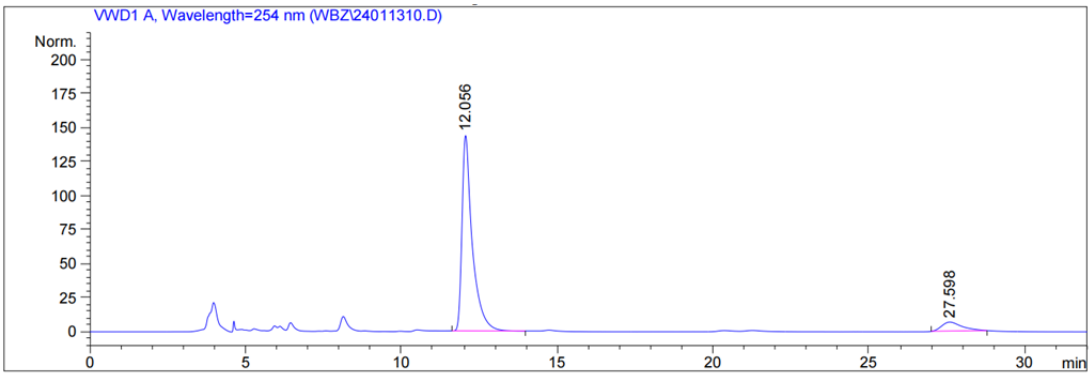
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.589	MM R	0.2059	2852.36597	230.83858	92.4763
2	6.476	MM R	0.1954	232.06458	19.79100	7.5237



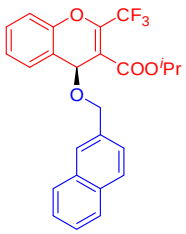
3na



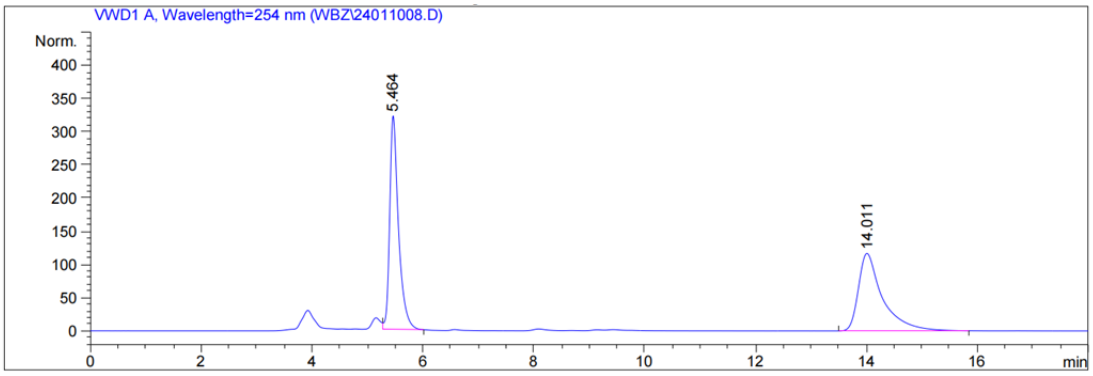
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.073	BB	0.3308	5685.16846	247.28731	50.1395
2	27.791	BB	0.7947	5653.52441	102.54185	49.8605



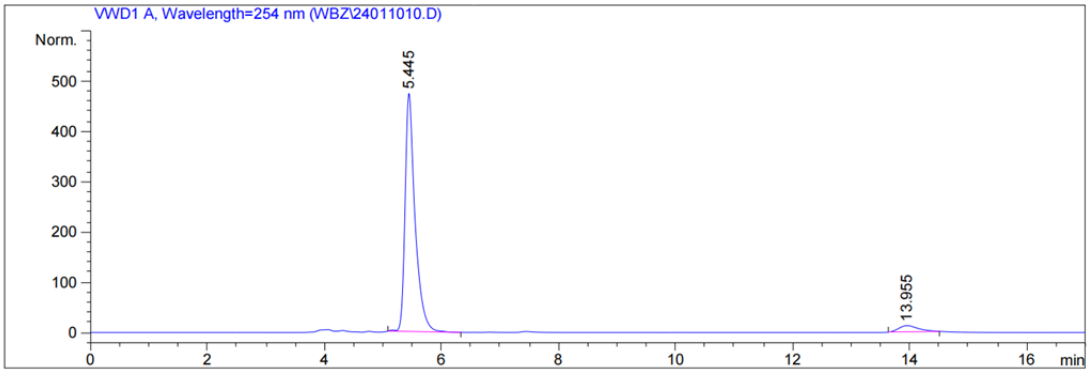
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.056	MM R	0.3828	3299.84106	143.65373	91.6286
2	27.598	MM R	0.7571	301.47964	6.63698	8.3714



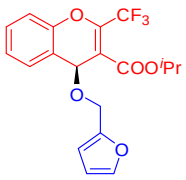
3oa



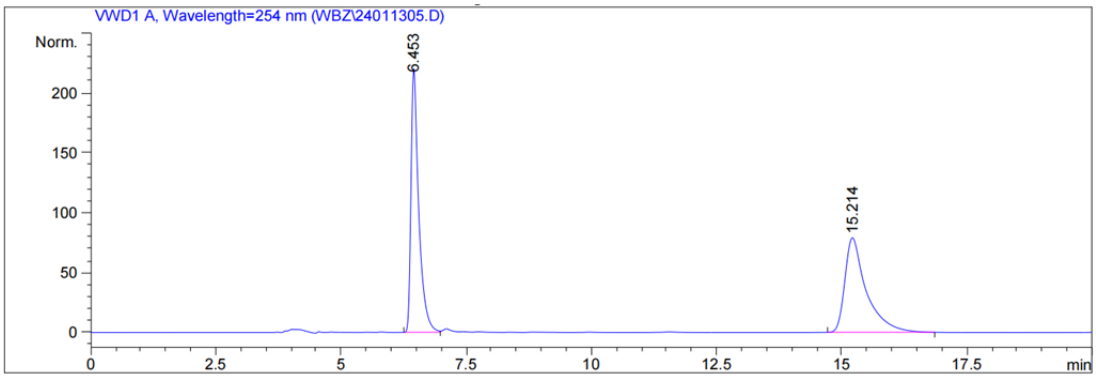
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	5.464	FM R	0.1845	3557.46313	321.44165	50.3148	
2	14.011	BB	0.4343	3512.94678	116.67551	49.6852	



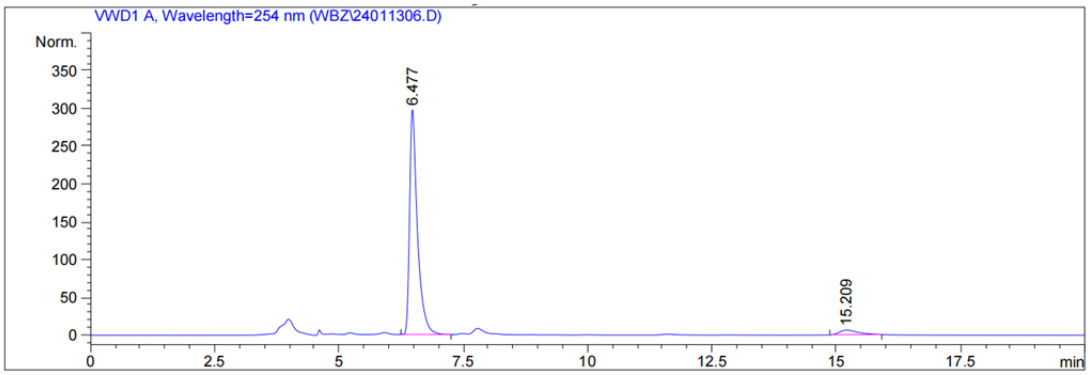
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	5.445	MM R	0.1978	5621.93701	473.60916	95.0497	
2	13.955	MM R	0.3920	292.79523	12.44768	4.9503	



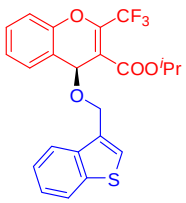
3pa



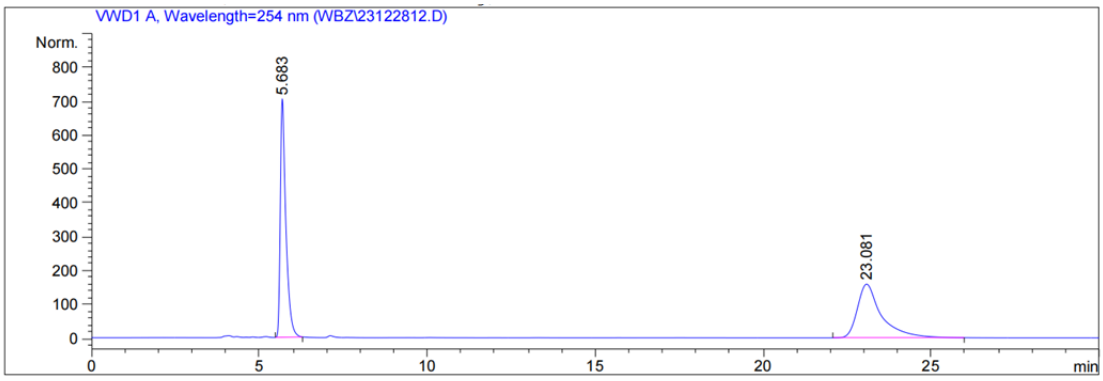
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.453	BV	0.1560	2364.80298	219.92555	50.1661
2	15.214	BB	0.4275	2349.14453	78.88789	49.8339



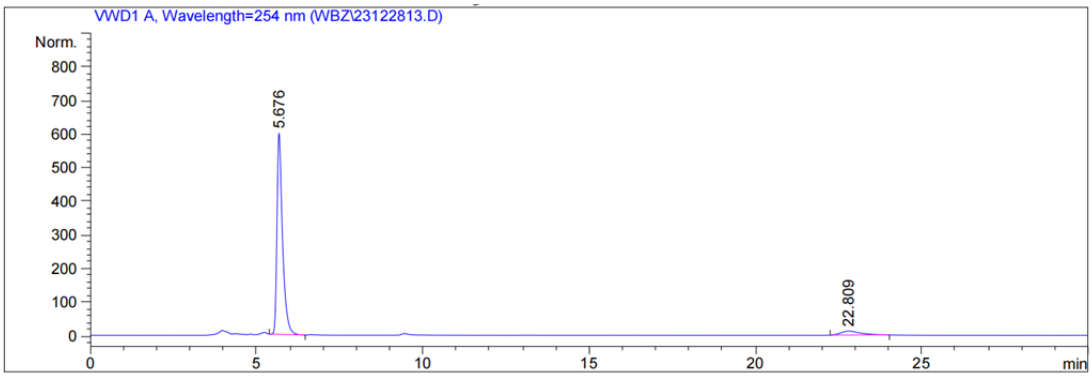
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.477	MM R	0.1821	3249.64917	297.39435	95.1920
2	15.209	MM R	0.4393	164.13358	6.22720	4.8080



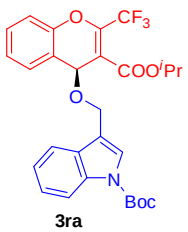
3qa



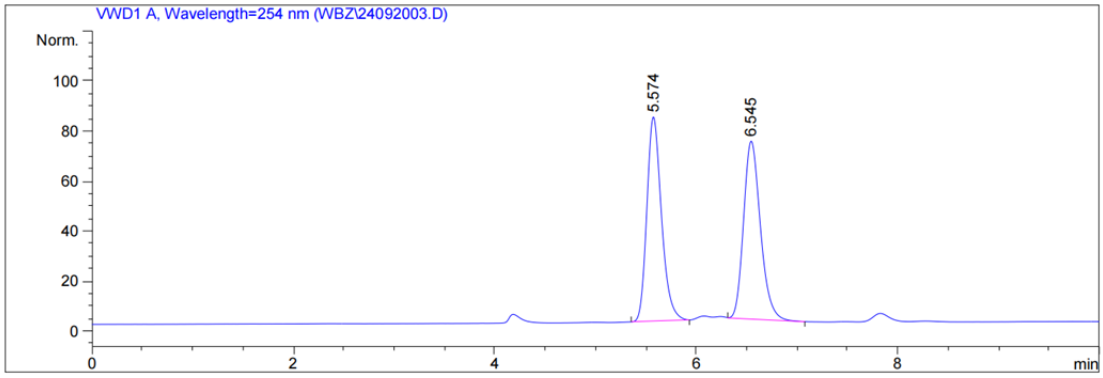
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.683	MM R	0.1920	8085.52832	701.92187	50.6471
2	23.081	BB	0.7220	7878.92090	158.27081	49.3529



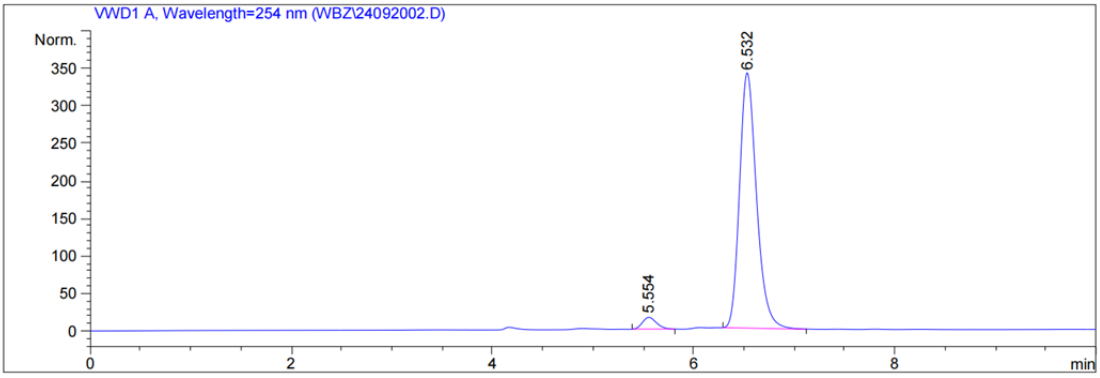
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.676	MM R	0.1936	6948.01855	598.21924	93.4093
2	22.809	MM R	0.6936	490.23538	11.77938	6.5907



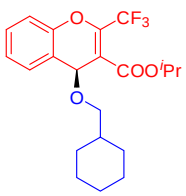
3ra



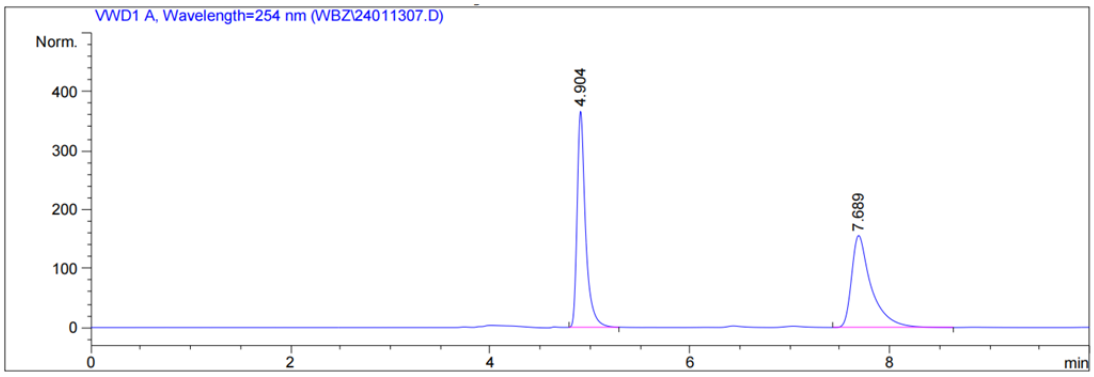
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.574	MM R	0.1678	822.14893	81.64303	49.7698
2	6.545	MM R	0.1942	829.75293	71.20930	50.2302



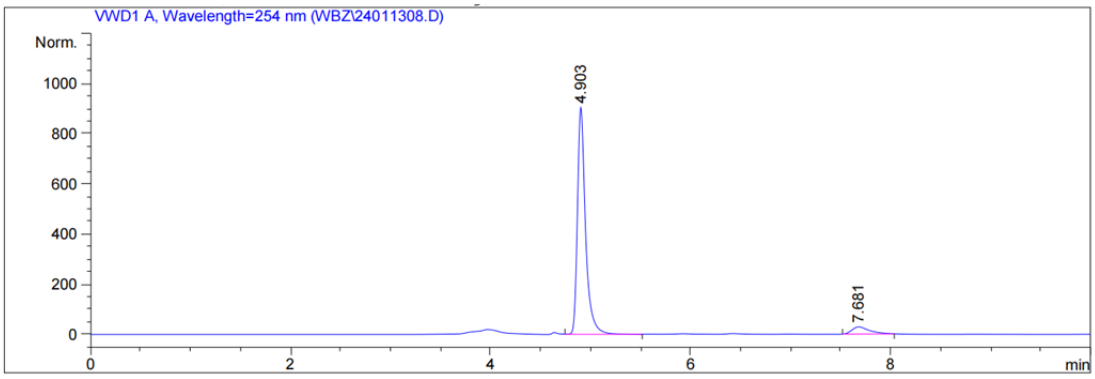
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.554	MM R	0.1650	156.93306	15.85119	3.7740
2	6.532	MM R	0.1962	4001.31787	339.94284	96.2260



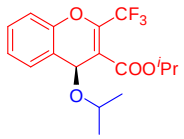
3sa



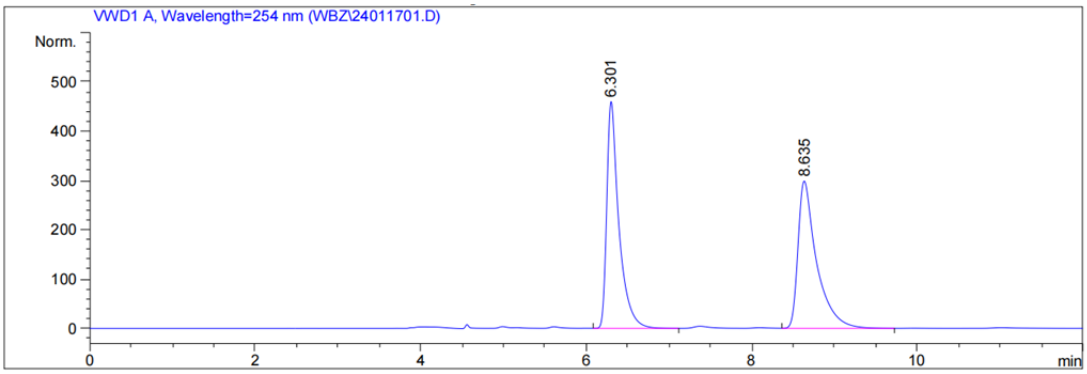
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	4.904	MM R	0.0977	2153.50269		367.30240	50.2774
2	7.689	VB	0.1971	2129.73657		156.04413	49.7226



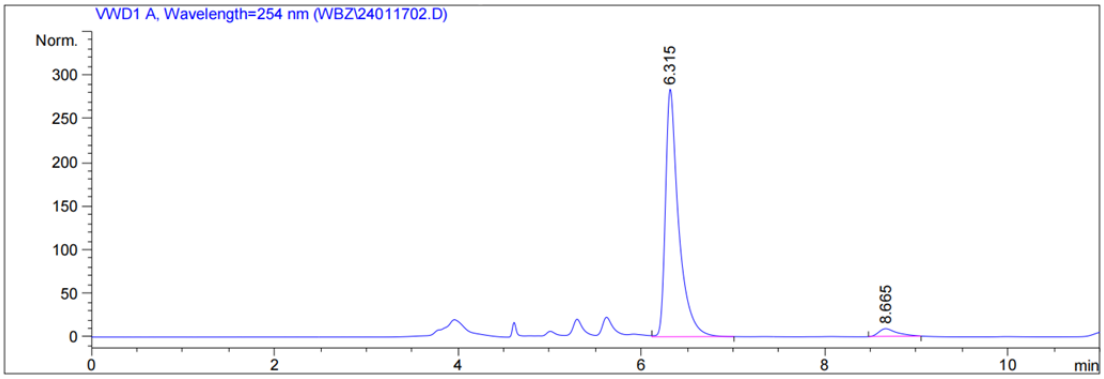
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	4.903	VV	0.0851	5128.43311		904.17926	93.5574
2	7.681	MM R	0.2041	353.15952		28.83405	6.4426



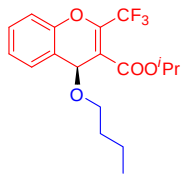
3ta



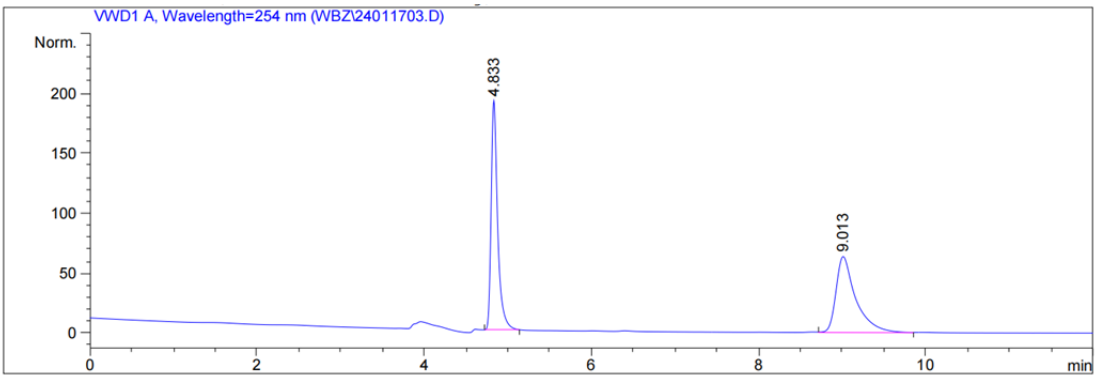
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.301	VB	0.1479	4688.20117	460.29327	50.1173
2	8.635	VB	0.2258	4666.25000	298.84241	49.8827



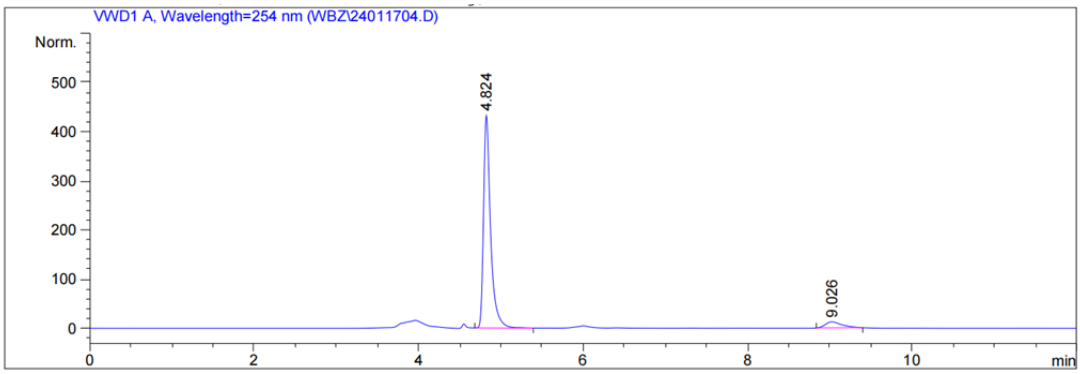
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.315	VB	0.1459	2837.42822	283.37958	95.8143
2	8.665	MM R	0.2326	123.95605	8.88308	4.1857



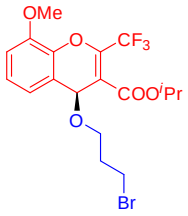
3ua



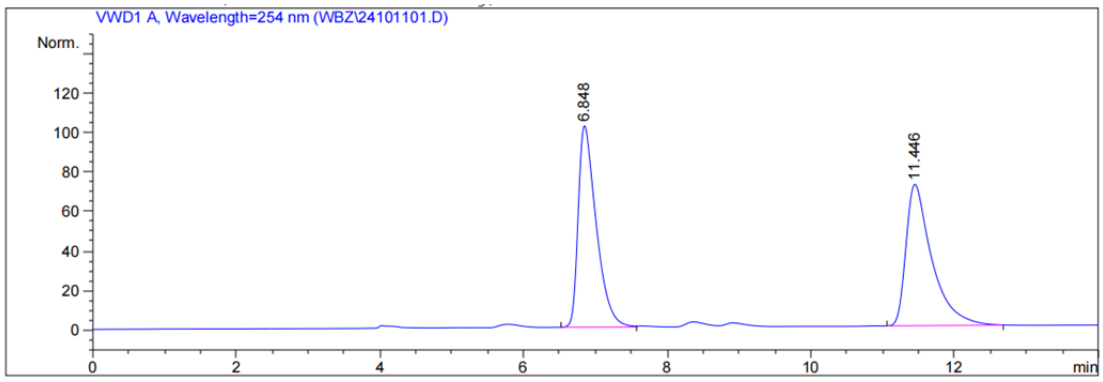
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.833	MM R	0.0903	1035.12305	191.14220	49.8053
2	9.013	VB	0.2373	1043.21460	63.33968	50.1947



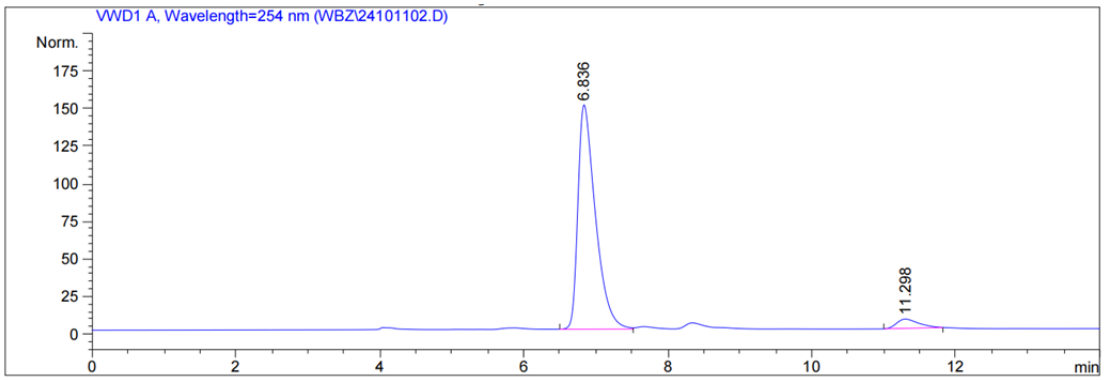
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.824	MM R	0.0989	2563.28394	431.85959	93.7508
2	9.026	MM R	0.2328	170.86346	12.23267	6.2492



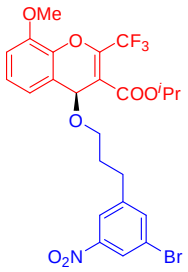
3rv



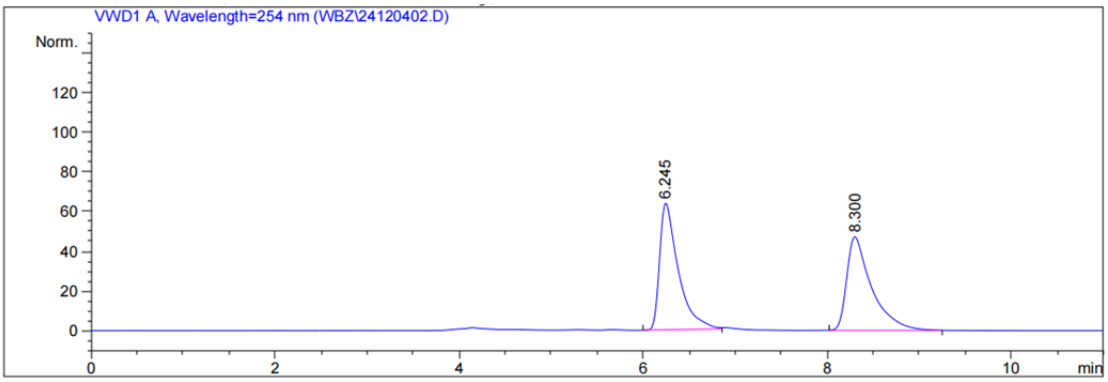
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.848	BB	0.2601	1780.89844	102.18798	49.7553
2	11.446	BB	0.3650	1798.41321	71.79414	50.2447



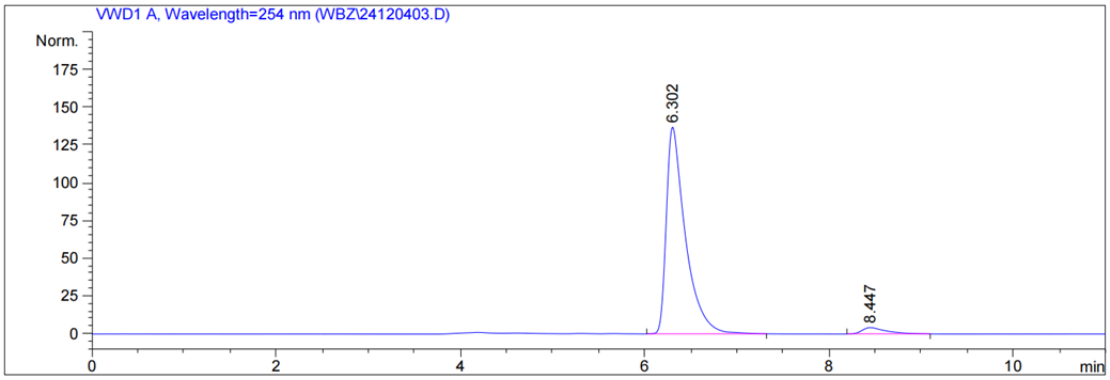
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.836	BV	0.2528	2524.33105	149.16432	94.9656
2	11.298	MM R	0.3589	133.82205	6.21401	5.0344



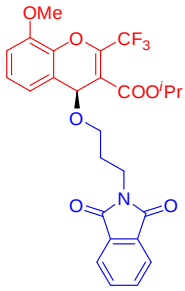
4rv



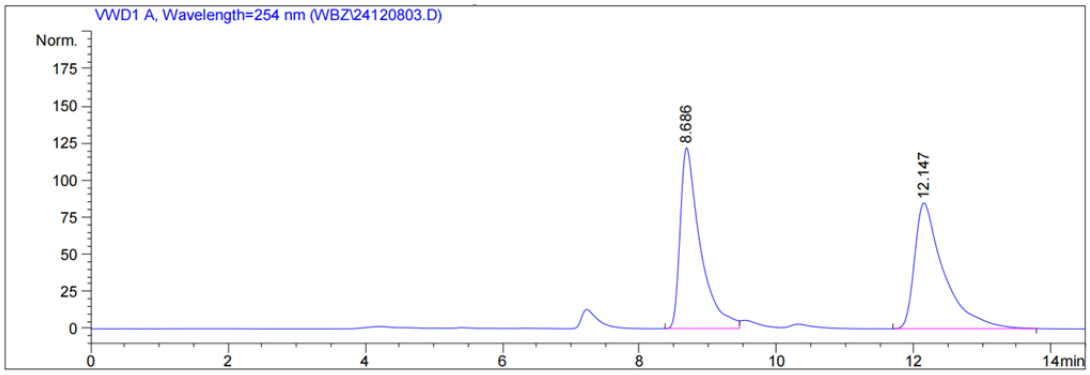
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.245	PB	0.2043	902.48907	63.83571	50.4820
2	8.300	BB	0.2671	885.25647	47.15247	49.5180



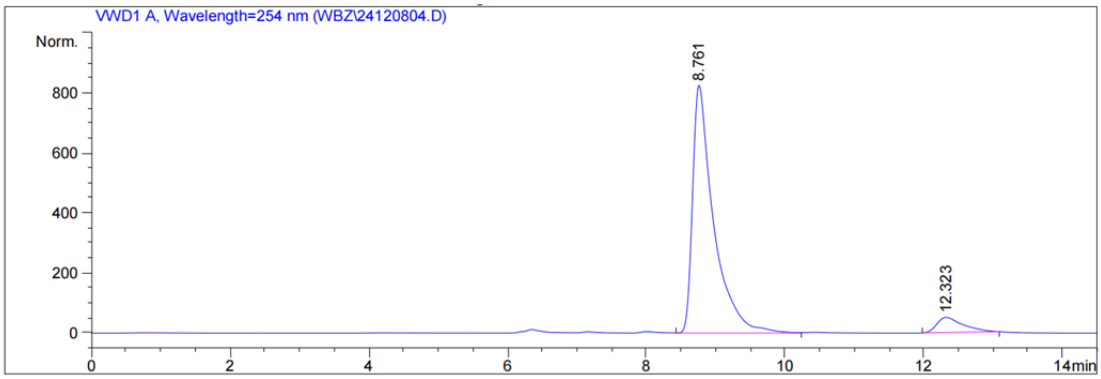
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.302	BB	0.2071	1969.92114	136.93571	96.2053
2	8.447	BB	0.2613	77.70206	4.22185	3.7947



5rv



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.686	BV	0.2907	2485.79272	121.72027	49.7368
2	12.147	PB	0.4205	2512.10303	84.64992	50.2632



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.761	VV	0.2985	1.73978e4	824.72845	92.9476
2	12.323	MM R	0.4363	1320.06433	50.42972	7.0524