

Supporting Information

Iridium-Catalyzed Asymmetric Hydrogenation of 2*H*-Chromenes: A Highly Enantioselective Approach to Isoflavan Derivatives

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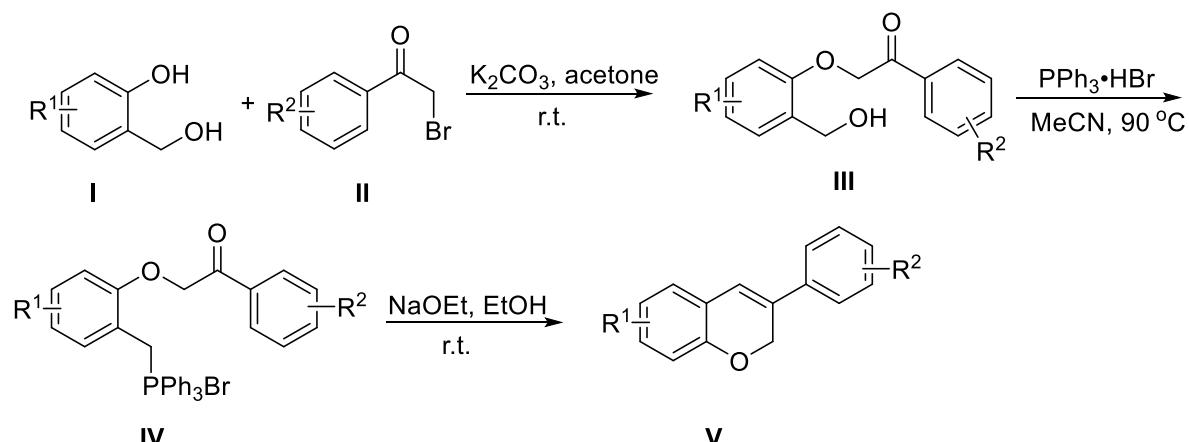
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1. General Details

All reactions were performed in flame-dried glassware under an atmosphere of dried Nitrogen, and the workup was carried out in air. Solvents were dried and distilled through standard procedures. The solvent of dried *o*-xylene was purchased from Energy Chemical without further purification. Commercially available materials purchased from Adamas-beta, TCI or Energy Chemical and were used as received. The NMR spectra were recorded on a Varian Mercury Plus-400 (400 MHz, ¹H; 100 MHz, ¹³C) spectrometer. HRMS of substrates were performed on a Fourier-transform mass spectrometry at the Instrumental Analysis Center of Shanghai Jiao Tong University. The ee values were determined by HPLC using a Daicel chiral column or purchased from Guangzhou Research & Creativity Biotechnology Co., Ltd. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. The absolute configuration of hydrogenated products was determined by X-ray analysis of the single crystal of **2e** and **4e**.

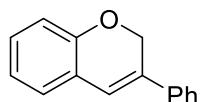
2. Preparation of 3-Substituted-2H-chromene¹



To a suspension of substituted 2-hydroxybenzyl alcohol (**I**) (6.3 mmol, 1.0 equiv.), K_2CO_3 (7.6 mmol, 1.2 equiv.) in acetone (20.0 mL), substituted 2-bromo-1-phenylethan-1-one (**II**) (6.3 mmol, 1.0 equiv.) was added dropwise. After stirring at room temperature for a complete reaction, the acetone was removed under reduced pressure, water (20.0 mL) was added, and extracted with EtOAc (10.0 mL \times 3). The organic layers were combined, washed with brine (10.0 mL), dried by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue was purified with 200-300 mesh silica gel column chromatography (15:1 petroleum ether : EtOAc) to give the corresponding products (**III**).

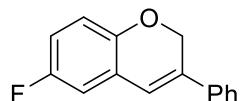
$\text{PPh}_3\text{•HBr}$ (8.3 mmol, 1.0 equiv.) was added into **III** (8.3 mmol, 1.0 equiv.) in MeCN (20.0 mL), the reaction system was warmed up to 90 °C. After cooling, the crystalline precipitate (**IV**) was filtered and washed with ether.

The crude triphenylphosphonium salts (**IV**) (8.0 mmol, 1.0 equiv.), EtONa (8.0 mmol, 1.0 equiv.) were suspended in absolute ethanol (15.0 mL) dropwise at room temperature. After 24 h, water was added to the suspension in such amounts so as to have an ethanol-water mixture of 3:2 and extracted with EtOAc (10.0 mL \times 3). The organic layers were combined, washed with brine (15.0 mL), dried by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue was purified with 200-300 mesh silica gel column chromatography (20:1 petroleum ether : EtOAc) to give the 3-substituted-2H-chromene (**V**).



1a

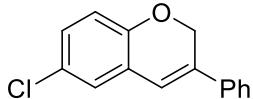
3-Phenyl-2H-chromene (1a). White crystal, m.p. = 82.1 – 83.0 °C. 86% overall yield, 1.4 g. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.36 (m, 4H), 7.35 – 7.29 (m, 1H), 7.17 – 7.07 (m, 2H), 6.95 – 6.89 (m, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.82 (s, 1H), 5.18 (d, J = 1.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.3, 136.8, 131.8, 129.1, 128.8, 128.1, 127.0, 124.8, 123.0, 121.6, 120.2, 115.5, 67.2. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{13}\text{O}$ ($\text{M}+\text{H}$) $^+$: 209.0966; found: 209.0960.



1b

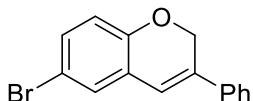
¹ Burali, C.; Desideri, N.; Stein, M. L.; Conti, C.; Orsi, N. *Eur. J. Med. Chem.* **1987**, 22, 119-123.

6-Fluoro-3-phenyl-2H-chromene (1b). White crystal, m.p. = 106.2 – 107.1 °C. 84% overall yield, 1.5 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 4H), 7.36 – 7.31 (m, 1H), 6.80 (m, 3H), 6.74 (s, 1H), 5.13 (d, *J* = 1.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 157.8 (d, *J*_{C-F} = 236.6), 149.1, 136.4, 133.5, 128.8, 128.4, 124.9, 124.1 (d, *J*_{C-F} = 8.4), 119.5, 116.3 (d, *J*_{C-F} = 8.1), 115.0 (d, *J*_{C-F} = 23.3), 113.0 (d, *J*_{C-F} = 23.5), 67.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -122.8. HRMS (ESI) calcd for C₁₅H₁₂FO (M+H)⁺: 227.0872; found: 227.0874.



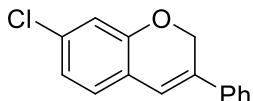
1c

6-Chloro-3-phenyl-2H-chromene (1c). White crystal, m.p. = 45.2 – 46.1 °C. 87% overall yield, 1.7 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.38 (m, 4H), 7.37 – 7.30 (m, 1H), 7.09 – 7.04 (m, 2H), 6.80 – 6.76 (m, 1H), 6.73 (s, 1H), 5.17 (d, *J* = 1.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 136.3, 133.1, 128.8, 128.54, 128.46, 126.4, 126.3, 124.9, 124.3, 119.1, 116.7, 67.3. HRMS (ESI) calcd for C₁₅H₁₂ClO (M+H)⁺: 243.0577; found: 243.0579.



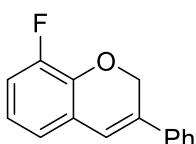
1d

6-Bromo-3-phenyl-2H-chromene (1d). White crystal, m.p. = 109.4 – 110.1 °C. 84% overall yield, 1.9 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (m, 4H), 7.34 (m, 1H), 7.23 – 7.18 (m, 2H), 6.75 – 6.72 (m, 1H), 6.72 (s, 1H), 5.17 (d, *J* = 1.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 136.2, 133.1, 131.5, 129.3, 128.8, 128.5, 124.87, 124.86, 118.9, 117.2, 113.6, 67.3. HRMS (ESI) calcd for C₁₅H₁₂BrO (M+H)⁺: 287.0072; found: 287.0070.



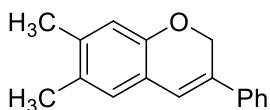
1e

7-Chloro-3-phenyl-2H-chromene (1e). White crystal, m.p. = 112.3 – 113.0 °C. 89% overall yield, 1.7 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.36 (m, 4H), 7.35 – 7.29 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.90 – 6.84 (m, 2H), 6.77 (s, 1H), 5.17 (d, *J* = 1.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 136.4, 133.8, 131.8, 128.8, 128.3, 127.6, 124.8, 121.7, 121.5, 119.2, 116.0, 67.3. HRMS (ESI) calcd for C₁₅H₁₂ClO (M+H)⁺: 243.0577; found: 243.0573.



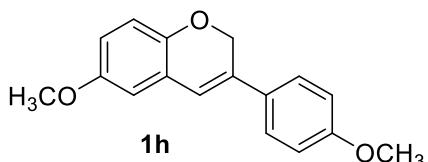
1f

8-Fluoro-3-phenyl-2H-chromene (1f). White crystal, m.p. = 52.8 – 53.9 °C. 87% overall yield, 1.5 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.37 (m, 4H), 7.38 – 7.30 (m, 1H), 6.98 – 6.92 (m, 1H), 6.90 – 6.80 (m, 3H), 5.24 (d, *J* = 1.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.9 (d, *J*_{C-F} = 243.4), 140.6 (d, *J*_{C-F} = 11.0), 136.4, 132.7, 128.8, 128.4, 125.3 (d, *J*_{C-F} = 2.5), 124.9, 122.2 (d, *J*_{C-F} = 3.2), 121.2 (d, *J*_{C-F} = 7.1), 119.5 (d, *J*_{C-F} = 3.8), 116.1 (d, *J*_{C-F} = 18.2), 67.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.2. HRMS (ESI) calcd for C₁₅H₁₂FO (M+H)⁺: 227.0872; found: 227.0870.

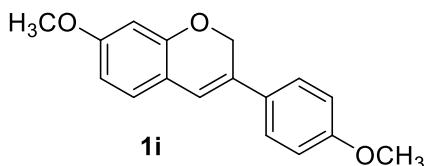


1g

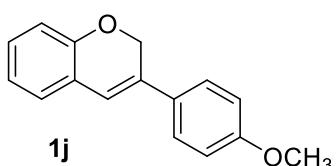
6,7-Dimethyl-3-phenyl-2H-chromene (1g). White crystal, m.p. = 82.5 – 83.0 °C. 85% overall yield, 1.6 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 4H), 7.32 – 7.27 (m, 1H), 6.86 (s, 1H), 6.77 (s, 1H), 6.67 (s, 1H), 5.11 (d, *J* = 1.2 Hz, 2H), 2.22 (s, 3H), 2.19 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 137.8, 137.1, 130.7, 129.4, 128.7, 127.9, 127.7, 124.7, 120.6, 120.2, 116.5, 67.18, 19.9, 18.9. HRMS (ESI) calcd for C₁₇H₁₇O (M+H)⁺: 237.3220; found: 237.3220.



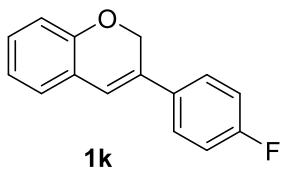
6-Methoxy-3-(4-methoxyphenyl)-2H-chromene (1h). White crystal, m.p. = 109.5 – 110.4 °C. 86% overall yield, 1.8 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 6.96 – 6.89 (m, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.70 – 6.63 (m, 3H), 5.08 (d, *J* = 1.2 Hz, 2H), 3.83 (s, 3H), 3.78 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 154.3, 147.0, 132.6, 129.2, 126.1, 124.0, 118.5, 115.9, 114.2, 113.7, 111.8, 67.2, 55.8, 55.4. HRMS (ESI) calcd for C₁₇H₁₇O₃ (M+H)⁺: 269.1178; found: 269.1174.



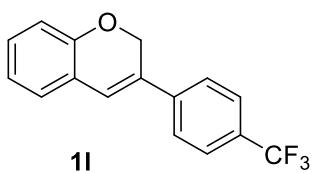
7-Methoxy-3-(4-methoxyphenyl)-2H-chromene (1i). White crystal, m.p. = 160.1 – 160.8 °C. 86% overall yield, 1.8 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.93 – 6.89 (m, 2H), 6.68 (s, 1H), 6.51 – 6.43 (m, 2H), 5.11 (d, *J* = 1.2 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 159.2, 154.3, 129.5, 128.4, 127.4, 125.8, 118.1, 116.4, 114.1, 107.3, 101.4, 67.3, 55.4, 55.3. HRMS (ESI) calcd for C₁₇H₁₇O₃ (M+H)⁺: 269.1178; found: 269.1179.



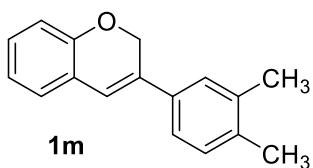
3-(4-Methoxyphenyl)-2H-chromene (1j). White crystal, m.p. = 95.2 – 96.0 °C. 88% overall yield, 1.6 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.31 (m, 2H), 7.15 – 7.05 (m, 2H), 6.96 – 6.88 (m, 3H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.72 (s, 1H), 5.15 (d, *J* = 1.2 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 153.0, 131.4, 129.3, 128.7, 126.7, 126.0, 123.2, 121.6, 118.3, 115.4, 114.2, 67.2, 55.4. HRMS (ESI) calcd for C₁₆H₁₅O₂ (M+H)⁺: 239.1072; found: 239.1077.



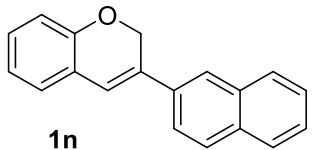
3-(4-Fluorophenyl)-2H-chromene (1k). White crystal, m.p. = 86.7 – 87.2 °C. 81% overall yield, 1.4 g. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.18 – 7.14 (m, 1H), 7.14 – 7.07 (m, 3H), 6.96 – 6.92 (m, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.77 (s, 1H), 5.16 (d, J = 1.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.5 (d, $J_{\text{C-F}}$ = 246.6 Hz), 153.1, 133.0, 130.8, 129.1, 127.0, 126.5 (d, $J_{\text{C-F}}$ = 8.0 Hz), 122.8, 121.7, 120.0 (d, $J_{\text{C-F}}$ = 1.9 Hz), 115.8, 115.6 (d, $J_{\text{C-F}}$ = 11.7 Hz), 67.1. ^{19}F NMR (376 MHz, CDCl_3) δ -113.4. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{12}\text{FO}$ ($\text{M}+\text{H}$) $^+$: 227.0872; found: 227.0871.



3-(4-(Trifluoromethyl)phenyl)-2H-chromene (1l). White crystal, m.p. = 116.2 – 116.9 °C. 84% overall yield, 1.5 g. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.12 (dd, J = 7.6, 1.6 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.90 (s, 1H), 6.88 (d, J = 8.0 Hz, 1H), 5.17 (d, J = 1.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 140.2 (q, $J_{\text{C-F}}$ = 1.1 Hz), 130.2, 129.8, 129.8 (q, $J_{\text{C-F}}$ = 32.4 Hz), 127.4, 125.7 (q, $J_{\text{C-F}}$ = 3.8 Hz), 124.9, 124.1 (q, $J_{\text{C-F}}$ = 270.2 Hz), 122.4, 122.3, 121.8, 115.7, 66.9. ^{19}F NMR (376 MHz, CDCl_3) δ -62.6. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{O}$ ($\text{M}+\text{H}$) $^+$: 277.0840; found: 277.0838.

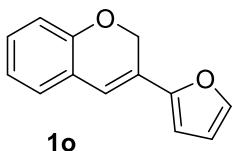


3-(3,4-Dimethylphenyl)-2H-chromene (1m). White crystal, m.p. = 66.8 – 67.2 °C. 82% overall yield, 1.5 g. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.23 (s, 1H), 7.20 – 7.05 (m, 4H), 6.93 – 6.89 (m, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.77 (s, 1H), 5.16 (d, J = 1.4 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 136.9, 136.8, 134.3, 131.9, 130.0, 128.8, 126.9, 126.0, 123.2, 122.2, 121.6, 119.1, 115.4, 67.3, 19.9, 19.6. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}$ ($\text{M}+\text{H}$) $^+$: 237.3220; found: 237.3223.

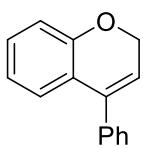


3-(Naphthalen-2-yl)-2H-chromene (1n). White crystal, m.p. = 145.5 – 146.0 °C. 87% overall yield, 1.8 g. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.79 (m, 3H), 7.76 (s, 1H), 7.69 (dd, J = 8.6, 2.0 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.20 – 7.10 (m, 2H), 7.01 – 6.85 (m, 3H), 5.31 (d, J = 1.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 134.0, 133.6, 133.2, 131.6, 129.4, 128.6, 128.4, 127.9, 127.4, 126.8, 126.5, 123.6, 123.2, 123.1, 122.0, 120.8, 115.8, 67.4. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{O}$ ($\text{M}+\text{H}$) $^+$:

259.1123; found: 259.1120.

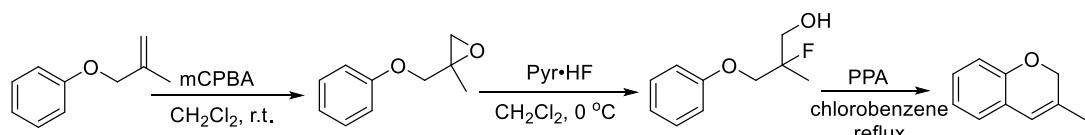


3-(Furan-2-yl)-2H-chromene (1o). White crystal, m.p. = 48.6 – 49.2 °C. 83% overall yield, 1.3 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.15 – 7.07 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.88 – 6.81 (m, 2H), 6.45 (m, 1H), 6.33 (d, *J* = 3.4 Hz, 1H), 5.00 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 150.6, 142.6, 128.9, 127.1, 122.7, 122.2, 121.8, 117.1, 115.6, 111.5, 106.6, 64.9. HRMS (ESI) calcd for C₁₃H₁₁O₂ (M+H)⁺: 199.0759; found: 199.0760.



4-Phenyl-2H-chromene (3a) **3a** was prepared according the reported literature.² Colorless liquid, 86% yield, 1.4 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.32 (m, 5H), 7.18 – 7.14 (m, 1H), 7.01 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.92 – 6.83 (m, 2H), 5.80 (t, *J* = 4.0 Hz, 1H), 4.86 (d, *J* = 4.0 Hz, 2H).

Preparation of 3-Methyl-2H-chromene³



Into a mixture of 1.5 g (10.1 mmol) of ((2-Methylallyl)oxy)benzene in 15.0 ml of CH₂Cl₂, *m*-chloroperbenzoic acid (2.1 g, 12.2 mmol) was dropped under stirring at 0 °C for 1.0 hour. Then the precipitated *m*-chlorobenzoic acid was filtered. The organic layer was extracted with CH₂Cl₂ (5.0 mL×3). The organic layers were combined, washed with brine (10.0 mL), dried by anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure. The residue was purified with 200-300 mesh silica gel column chromatography (50:1 petroleum ether : EtOAc) to give the corresponding product.

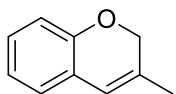
3.2 g (22.9 mmol) of Olah's reagent were added to a solution of 0.5 g (3.0 mmol) of 2-Methyl-2-(phenoxyethyl)oxirane in 10.0 ml of CH₂Cl₂ with stirring at 0 °C. After continuous stirring for 45 min at 0 °C, the mixture was neutralized with 2 N NaOH. The organic layer was separated and the aqueous layer extracted with CH₂Cl₂ (5.0 mL×3). The organic layers were combined, washed with brine (10.0 mL), dried by anhydrous Na₂SO₄ and filtered. The residue was purified with 200-300 mesh silica gel column chromatography (25:1 petroleum ether : EtOAc) to give the corresponding product.

To a boiling solution consisting of 0.75 g of polyphosphoric acid in 15.0 ml of chlorobenzene was

² Qu, B.; Samankumara, L. P.; Ma, S.; Frick, K. R.; Desrosiers, J.-N.; Rodriguez, S.; Li, Z.; Haddad, N.; Han, Z. S.; McKellop, K.; Pennino, S.; Grinberg, N.; Gonnella, N. C.; Song, J. J.; Senanayake, C. H. *Angew. Chem., Int. Ed.* **2014**, *53*, 14428–14432.

³ Haufe, G.; Weßel, U.; Schulze, K.; Alvernhe, G. *J. Fluorine Chem.* **1995**, *74*, 283-291.

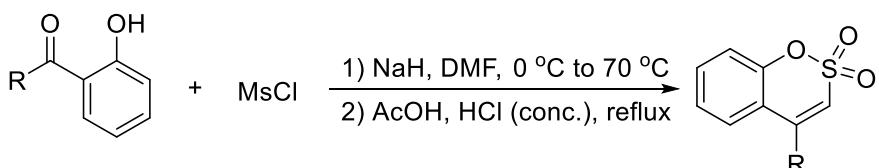
added 0.55 g of 2-Fluoro-2-methyl-3-phenoxypropan-1-ol and the mixture refluxed for a full conversion. After cooling, the mixture separated and washed with EtOAc (5 mL×3) and water. The organic layers were combined, washed with brine (10.0 mL), dried by anhydrous Na₂SO₄ and filtered. The residue was purified with 200-300 mesh silica gel column chromatography (petroleum ether) to give 3-Methyl-2*H*-chromene.



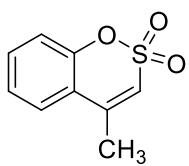
1p

3-Methyl-2*H*-chromene (**1p**). Colorless liquid, 71% overall yield, 0.4 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.04 (t, *J* = 7.6 Hz, 1H), 6.92 – 6.72 (m, 3H), 6.15 (s, 1H), 4.68 (s, 2H), 1.79 (s, 3H). These data are consistent with literature values.^[4]

3. Preparation of 4-Substituted-benzo[e][1,2]oxathiine 2,2-Dioxide



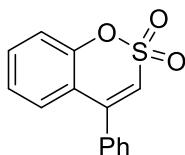
To a suspension of NaH (10.0 mmol, 2.0 equiv.), substituted phenol (5.0 mmol, 1.0 equiv.) was slowly added in DMF (10.0 mL) at 0 °C, then heated to 70 °C for 45 min. MsCl (5.0 mmol, 1.0 equiv.) was added into the reaction system after it was cooled to room temperature. Stirring at room temperature until a full conversion, water (20.0 mL) was added carefully, and extracted with EtOAc (10.0 mL×3). The organic layers were combined, washed with brine (10.0 mL), dried by anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure. The crude product was taken into next step without purification. To a solution of AcOH (20.0 mL), concentrated HCl (0.5 mL) was added above product, heated to reflux for 20 h for a full reaction. Water (25.0 mL) was added, and extracted with EtOAc (5.0 mL×3). The organic layers were combined, washed with brine (10.0 mL), dried by anhydrous Na₂SO₄ and filtered. The residue was purified with 200-300 mesh silica gel column chromatography (5:1 petroleum ether : EtOAc) to give the corresponding products.



3b

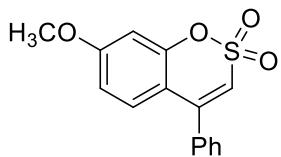
4-Methylbenzo[e][1,2]oxathiine 2,2-dioxide (3b). White crystal, m.p. = 58.3 – 59.0 °C. 74% yield, 0.72 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.36 – 7.32 (m, 1H), 7.29 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.65 (d, *J* = 1.4 Hz, 1H), 2.38 (d, *J* = 1.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 144.7, 132.3, 126.3, 125.9, 120.9, 119.2, 119.2, 19.8. HRMS (ESI) calcd for C₉H₉O₃S (M+H)⁺: 197.0272; found: 197.0270.

⁴ Clausen, D. J.; Floreancig, P. E. *J. Org. Chem.* **2012**, 77, 6574–6582.



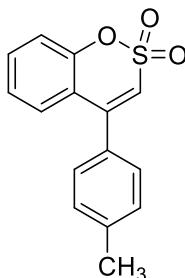
3c

4-Phenylbenzo[e][1,2]oxathiine 2,2-dioxide (3c). White crystal, m.p. = 113.4 – 114.3 °C. 76% yield, 0.98 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.47 (m, 4H), 7.43 – 7.34 (m, 3H), 7.32 – 7.26 (m, 2H), 6.74 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 149.0, 134.8, 132.5, 130.3, 129.4, 129.0, 128.9, 125.8, 120.9, 119.4, 119.1. HRMS (ESI) calcd for C₁₄H₁₁O₃S (M+H)⁺: 259.0429; found: 259.0434.



3d

7-Methoxy-4-phenylbenzo[e][1,2]oxathiine 2,2-dioxide (3d). White crystal, m.p. = 112.0 – 112.9 °C. 78% yield, 1.1 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.46 (m, 3H), 7.43 – 7.38 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 2.6 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.59 (s, 1H), 3.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.8, 152.8, 149.2, 135.1, 130.5, 130.2, 129.0, 128.9, 116.0, 113.8, 112.5, 104.3, 55.9. HRMS (ESI) calcd for C₁₅H₁₃O₄S (M+H)⁺: 289.0535; found: 289.0530.



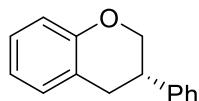
3e

4-(*p*-Tolyl)benzo[e][1,2]oxathiine 2,2-dioxide (3e). White crystal, m.p. = 135.6 – 136.2 °C. 74% yield, 1.0 g. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 1H), 7.42 – 7.29 (m, 7H), 6.74 (s, 1H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 149.0, 140.7, 132.4, 131.9, 129.7, 129.4, 128.9, 125.7, 120.9, 119.3, 118.6, 21.4. HRMS (ESI) calcd for C₁₅H₁₃O₃S (M+H)⁺: 273.0585; found: 273.0593.

4. General Procedure for Hydrogenation of 2*H*-Chromenes

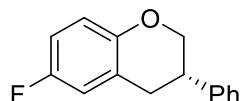
The catalyst (4.0 mg, 0.0024 mmol, 0.01 equiv.) and substrate (0.24 mmol, 1.0 equiv.) were placed in a 5.0 mL tube equipped with a magnetic stirrer bar. This tube was then put into a nitrogen-filled autoclave. Solvent (2.0 mL) was added to the mixture under nitrogen atmosphere. The autoclave was then closed, purged three times with hydrogen (less than the pressure needed), and finally

pressurized to 10 bar. The reaction mixture was stirred at r.t. for 24 h, and the hydrogen gas was slowly released. The conversion of the product was determined by ^1H NMR spectroscopic analysis of the crude reaction mixture and isolated by chromatography (15:1 petroleum ether : EtOAc). The *ee* was determined by chiral HPLC.



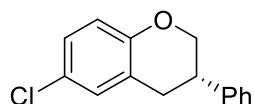
2a

(S)-3-Phenylchromane (2a). White solid, m.p. = 30.1 – 30.8 °C. 98% yield, 49.4 mg. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.33 – 7.24 (m, 3H), 7.18 – 7.09 (m, 2H), 6.93 – 6.86 (m, 2H), 4.40 – 4.36 (m, 1H), 4.06 (t, J = 10.6 Hz, 1H), 3.33 – 3.23 (m, 1H), 3.15 – 2.99 (m, 2H). ^{13}C NMR (100 MHz, CDCl₃) δ 154.3, 141.3, 129.8, 128.8, 127.5, 127.4, 127.1, 122.0, 120.4, 116.6, 70.9, 38.6, 32.4. HRMS (ESI) calcd for C₁₅H₁₅O (M+H)⁺: 211.1123; found: 211.1120; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 0.5 mL/min. t_{R1} = 21.1 min (major), t_{R2} = 26.9 min (minor)]; *ee* = 98%. $[\alpha]^{25}\text{D}$ = –9.96 (c = 0.63, CHCl₃).



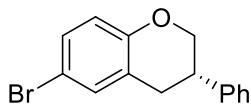
2b

(S)-6-Fluoro-3-phenylchromane (2b). Colorless liquid. 99% yield, 54.2 mg. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.21 (m, 2H), 6.88 – 6.75 (m, 3H), 4.36 – 4.32 (m, 1H), 4.01 (t, J = 10.6 Hz, 1H), 3.27 – 3.19 (m, 1H), 3.10 – 2.94 (m, 2H). ^{13}C NMR (100 MHz, CDCl₃) δ 156.8 (d, $J_{\text{C-F}}$ = 236.7 Hz), 150.3 (d, $J_{\text{C-F}}$ = 1.9 Hz), 141.0, 128.9, 127.3, 127.2, 123.1 (d, $J_{\text{C-F}}$ = 7.4 Hz), 117.4 (d, $J_{\text{C-F}}$ = 8.1 Hz), 115.5 (d, $J_{\text{C-F}}$ = 22.4 Hz), 114.2 (d, $J_{\text{C-F}}$ = 23.0 Hz), 70.9, 38.3, 32.5 (d, $J_{\text{C-F}}$ = 1.3 Hz). ^{19}F NMR (376 MHz, CDCl₃) δ -124.3. HRMS (ESI) calcd for C₁₅H₁₄FO (M+H)⁺: 229.1029; found: 229.1032; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 0.5 mL/min, 25 °C. t_{R1} = 25.9 min (major), t_{R2} = 31.0 min (minor)]; *ee* = 98%. $[\alpha]^{25}\text{D}$ = –9.16 (c = 0.68, CHCl₃).



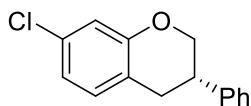
2c

(S)-6-Chloro-3-phenylchromane (2c). Colorless liquid. 97% yield, 56.8 mg. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.26 (m, 1H), 7.26 – 7.23 (m, 2H), 7.11 – 7.06 (m, 2H), 6.82 – 6.78 (m, 1H), 4.38 – 4.34 (m, 1H), 4.03 (t, J = 10.6 Hz, 1H), 3.27 – 3.19 (m, 1H), 3.10 – 2.94 (m, 2H). ^{13}C NMR (100 MHz, CDCl₃) δ 152.9, 140.8, 129.3, 128.9, 127.4, 127.35, 127.3, 125.1, 123.6, 117.9, 70.9, 38.2, 32.2. HRMS (ESI) calcd for C₁₅H₁₄ClO (M+H)⁺: 245.0733; found: 245.0733; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 97/3, 210 nm, 1.0 mL/min, 25 °C. t_{R1} = 10.9 min (major), t_{R2} = 12.0 min (minor)]; *ee* = 98%. $[\alpha]^{25}\text{D}$ = –0.67 (c = 0.40, CHCl₃).



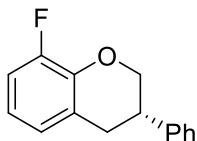
2d

(S)-6-Bromo-3-phenylchromane (2d). Colorless liquid. 98% yield, 67.7 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 2H), 7.33 – 7.20 (m, 5H), 6.79 – 6.73 (m, 1H), 4.38 – 4.34 (m, 1H), 4.03 (t, *J* = 10.6 Hz, 1H), 3.27 – 3.19 (m, 1H), 3.11 – 2.95 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 153.5, 140.8, 132.2, 130.3, 128.9, 127.3, 127.27, 124.2, 118.4, 112.4, 70.9, 38.2, 32.1. HRMS (ESI) calcd for C₁₅H₁₄BrO (M+H)⁺: 289.0228; found: 289.0225; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 1.0 mL/min, 25 °C. t_{R1} = 11.3 min (major), t_{R2} = 12.5 min (minor)]; ee = 97%. $[\alpha]^{25}_D = -1.44$ (c = 0.61, CHCl₃).



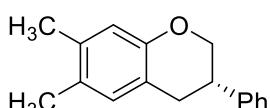
2e

(S)-7-Chloro-3-phenylchromane (2e). White solid, m.p. = 32.2 – 32.9 °C. 98% yield, 57.9 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 7.26 – 7.20 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.90 – 6.83 (m, 2H), 4.39 – 4.33 (m, 1H), 4.03 (t, *J* = 10.6 Hz, 1H), 3.26 – 3.19 (m, 1H), 3.04 – 2.95 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 154.9, 140.9, 132.4, 130.6, 128.9, 127.3, 127.2, 120.6, 120.5, 116.7, 70.9, 38.3, 31.9. HRMS (ESI) calcd for C₁₅H₁₄ClO (M+H)⁺: 245.0733; found: 245.0736; HPLC [DAICEL CHIRALPAK OD-H, hexane/iPrOH = 99.9/0.1, 210 nm, 0.5 mL/min. t_{R1} = 57.0 min (minor), t_{R2} = 60.1 min (minor)]; ee = 99%. $[\alpha]^{25}_D = -9.80$ (c = 0.73, CHCl₃).



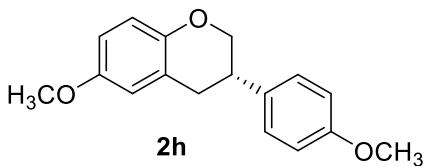
2f

(S)-8-Fluoro-3-phenylchromane (2f). White solid, m.p. = 55.3 – 56.2 °C. 98% yield, 53.6 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 7.31 – 7.21 (m, 3H), 6.96 – 6.88 (m, 1H), 6.88 – 6.84 (m, 1H), 6.81 – 6.75 (m, 1H), 4.78 – 4.43 (m, 1H), 4.06 (t, *J* = 10.6 Hz, 1H), 3.29 – 3.21 (m, 1H), 3.12 – 2.97 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 151.7 (d, *J*_{C-F} = 243.1 Hz), 142.6 (d, *J*_{C-F} = 10.9 Hz), 140.8, 128.9, 127.4, 127.3, 124.7, 124.6 (d, *J*_{C-F} = 1.6 Hz), 119.8 (d, *J*_{C-F} = 7.2 Hz), 113.9 (d, *J*_{C-F} = 17.8 Hz), 71.1, 38.3, 32.1 (d, *J*_{C-F} = 2.6 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -137.3. HRMS (ESI) calcd for C₁₅H₁₄FO (M+H)⁺: 229.1029; found: 229.1032; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 0.5 mL/min, 25 °C. t_{R1} = 22.9 min (major), t_{R2} = 25.2 min (minor)]; ee = 98%. $[\alpha]^{25}_D = -7.99$ (c = 0.68, CHCl₃).

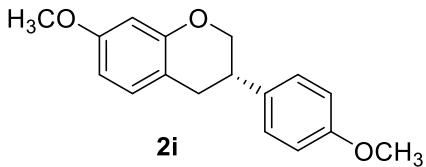


2g

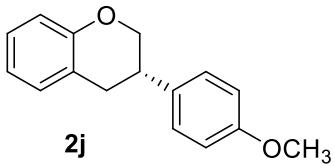
(S)-6,7-Dimethyl-3-phenylchromane (2g). White solid, m.p. = 63.2 – 64.0 °C. 99% yield, 56.5 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 2H), 7.30 – 7.21 (m, 3H), 6.85 (s, 1H), 6.67 (s, 1H), 4.34 – 4.29 (m, 1H), 3.99 (t, *J* = 10.6 Hz, 1H), 3.26 – 3.17 (m, 1H), 3.06 – 2.90 (m, 2H), 2.21 (s, 3H), 2.18 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 141.6, 135.8, 130.5, 128.8, 128.4, 127.4, 127.0, 118.9, 117.4, 70.8, 38.9, 32.0, 19.6, 18.8. HRMS (ESI) calcd for C₁₇H₁₉O (M+H)⁺: 239.1436; found: 239.1439; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 0.5 mL/min, 25 °C. t_{R1} = 22.3 min (major), t_{R2} = 32.1 min (minor)]; *ee* = 98%. [α]²⁵_D = –12.12 (c = 0.42, CHCl₃).



(S)-6-Methoxy-3-(4-methoxyphenyl)chromane (2h). Colorless liquid. 99% yield, 64.1 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.14 (m, 2H), 6.92 – 6.86 (m, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.71 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 4.30 – 4.26 (m, 1H), 3.95 (t, *J* = 10.6 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.23 – 3.15 (m, 1H), 3.07 – 2.92 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.6, 153.4, 148.4, 133.4, 128.3, 122.6, 117.1, 114.2, 114.18, 113.5, 71.1, 55.8, 55.3, 37.8, 32.8. HRMS (ESI) calcd for C₁₇H₁₉O₃ (M+H)⁺: 271.1334; found: 271.1329; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 1.0 mL/min. t_{R1} = 32.8 min (major), t_{R2} = 39.5 min (minor)]; *ee* = 99%. [α]²⁵_D = +1.23 (c = 0.81, CHCl₃).

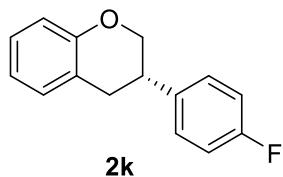


(S)-7-Methoxy-3-(4-methoxyphenyl)chromane (2i). White solid, m.p. = 81.5 – 82.4 °C. 99% yield, 64.1 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.13 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.48 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 4.32 – 4.28 (m, 1H), 3.97 (t, *J* = 10.6 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.22 – 3.12 (m, 1H), 3.02 – 2.88 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 158.6, 155.0, 133.4, 130.2, 128.3, 114.17, 114.16, 107.3, 101.4, 71.1, 55.33, 55.3, 37.9, 31.9. HRMS (ESI) calcd for C₁₇H₁₉O₃ (M+H)⁺: 271.1334; found: 271.1332; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 1.0 mL/min, 25 °C. t_{R1} = 27.8 min (major), t_{R2} = 34.8 min (minor)]; *ee* = 98%. [α]²⁵_D = –7.94 (c = 0.81, CHCl₃).

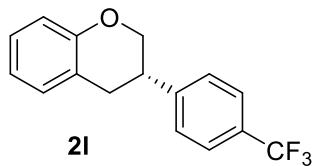


(S)-3-(4-Methoxyphenyl)chromane (2j). Colorless liquid. 98% yield, 56.4 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.05 (m, 4H), 6.94 – 6.84 (m, 4H), 4.34 – 4.30 (m, 1H), 3.99 (t, *J* = 10.6 Hz, 1H), 3.80 (s, 3H), 3.24 – 3.17 (m, 1H), 3.08 – 2.98 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.6, 154.3, 133.4, 129.8, 128.3, 127.4, 122.1, 120.4, 116.5, 114.2, 71.1, 55.3, 37.7, 32.6. HRMS (ESI) calcd for C₁₆H₁₇O₂ (M+H)⁺: 241.1229; found: 241.1232; HPLC [DAICEL CHIRALPAK OJ-

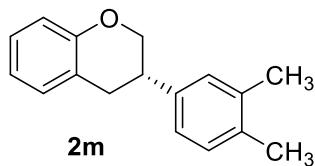
H, hexane/iPrOH = 95/5, 210 nm, 0.5 mL/min, 25 °C. $t_{R1} = 24.9$ min (major), $t_{R2} = 29.1$ min (minor)]; $ee = 98\%$. $[\alpha]^{25}_D = -1.39$ ($c = 0.72$, CHCl_3).



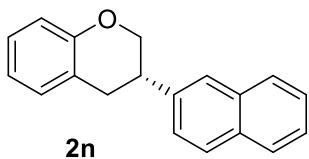
(S)-3-(4-Fluorophenyl)chromane (2k). White solid, m.p. = 30.1 – 30.6 °C. 97% yield, 53.0 mg. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.19 (m, 2H), 7.18 – 6.98 (m, 4H), 6.93 – 6.82 (m, 2H), 4.37 – 4.29 (m, 1H), 4.01 (t, $J = 10.6$ Hz, 1H), 3.29 – 3.22 (m, 1H), 3.03 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.9 (d, $J_{C-F} = 243.8$ Hz), 154.2, 137.1 (d, $J_{C-F} = 3.3$ Hz), 129.8, 128.8 (d, $J_{C-F} = 8.0$ Hz), 127.5, 121.7, 120.5, 116.6, 115.6 (d, $J_{C-F} = 21.0$ Hz), 70.8, 37.9, 32.5. ^{19}F NMR (376 MHz, CDCl_3) δ -115.7. HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 97/3, 210 nm, 0.5 mL/min, 25 °C. $t_{R1} = 10.4$ min (major), $t_{R2} = 11.4$ min (minor)]; $ee = 97\%$. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{FO}$ ($\text{M}+\text{H}$) $^+$: 229.1029; found: 229.1035. $[\alpha]^{25}_D = -11.98$ ($c = 0.10$, CHCl_3).



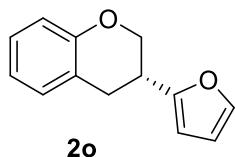
(S)-3-(4-(Trifluoromethyl)phenyl)chromane (2l). White solid, m.p. = 58.3 – 59.1 °C. 99% yield, 66.0 mg. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.19 – 7.06 (m, 2H), 6.93 – 6.84 (m, 2H), 4.36 (dd, $J = 10.6, 3.6$ Hz, 1H), 4.07 (t, $J = 10.6$ Hz, 1H), 3.38 – 3.29 (m, 1H), 3.07 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.2, 145.5, 129.7, 129.4 (q, $J_{C-F} = 32.3$ Hz), 127.8, 127.6, 125.7 (q, $J_{C-F} = 3.8$ Hz), 124.1 (q, $J_{C-F} = 271.2$ Hz), 121.3, 120.6, 116.7, 70.3, 38.5, 32.1. ^{19}F NMR (376 MHz, CDCl_3) δ -62.5. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{O}$ ($\text{M}+\text{H}$) $^+$: 279.0997; found: 279.0993; HPLC [Enantiopak OD-H, hexane/iPrOH = 99/1, 210 nm, 0.5 mL/min, 25 °C. $t_{R1} = 31.9$ min (major), $t_{R2} = 34.1$ min (minor)]; $ee = 99\%$. $[\alpha]^{25}_D = +0.48$ ($c = 0.83$, CHCl_3).



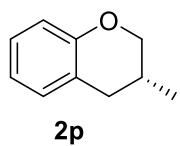
(S)-3-(3,4-Dimethylphenyl)chromane (2m). Colorless liquid. 99% yield, 56.5 mg. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.06 (m, 3H), 7.02 (s, 1H), 6.98 (dd, $J = 7.6, 1.8$ Hz, 1H), 6.89 – 6.85 (m, 2H), 4.36 – 4.31 (m, 1H), 4.00 (t, $J = 10.6$ Hz, 1H), 3.23 – 3.15 (m, 1H), 3.10 – 2.93 (m, 2H), 2.27 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 138.8, 137.0, 135.4, 130.0, 129.8, 128.7, 127.4, 124.6, 122.2, 120.3, 116.5, 71.1, 38.2, 32.5, 19.9, 19.4. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}$ ($\text{M}+\text{H}$) $^+$: 239.1436; found: 239.1439; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 0.5 mL/min, 25 °C. $t_{R1} = 16.3$ min (major), $t_{R2} = 17.4$ min (minor)]; $ee = 98\%$. $[\alpha]^{25}_D = -6.70$ ($c = 0.71$, CHCl_3).



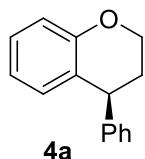
(S)-3-(Naphthalen-2-yl)chromane (2n). White solid, m.p. = 97.3 – 98.0 °C. 98% yield, 61.1 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.79 (m, 3H), 7.70 (s, 1H), 7.52 – 7.43 (m, 2H), 7.39 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.18 – 7.11 (m, 2H), 6.92 – 6.88 (m, 2H), 4.47 – 4.43 (m, 1H), 4.15 (t, *J* = 10.6 Hz, 1H), 3.47 – 3.38 (m, 1H), 3.24 – 3.17 (m, 1H), 3.13 – 3.07 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.3, 138.7, 133.6, 132.6, 129.8, 128.5, 127.7, 127.6, 127.5, 126.3, 125.8, 125.79, 125.75, 121.9, 120.5, 116.6, 70.9, 38.7, 32.4. HRMS (ESI) calcd for C₁₉H₁₇O (M+H)⁺: 261.1279; found: 261.1283; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 0.5 mL/min, 25 °C. t_{R1} = 42.2 min (major), t_{R2} = 46.8 min (minor)]; ee = 98%. $[\alpha]^{25}_D$ = +11.52 (c = 0.78, CHCl₃).



(R)-3-(Furan-2-yl)chromane (2o). Colorless liquid. 99% yield, 47.5 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.18 – 7.09 (m, 2H), 6.94 – 6.85 (m, 2H), 6.36 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 4.51 – 4.47 (m, 1H), 4.08 (dd, *J* = 10.6, 9.4 Hz, 1H), 3.46 – 3.39 (m, 1H), 3.16 – 3.04 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 154.7, 154.2, 141.7, 129.8, 127.5, 120.9, 120.5, 116.6, 110.2, 105.3, 68.7, 32.6, 29.7. HRMS (ESI) calcd for C₁₃H₁₃O₂ (M+H)⁺: 201.0916; found: 201.0919; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 95/5, 210 nm, 1.0 mL/min, 25 °C. t_{R1} = 7.8 min (major), t_{R2} = 8.7 min (minor)]; ee = 99.7%. $[\alpha]^{25}_D$ = -6.99 (c = 0.40, CHCl₃).



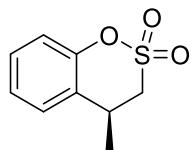
(R)-3-Methylchromane (2p)⁵. Colorless liquid. 93% yield, 33.0 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.11 – 7.00 (m, 2H), 6.85 – 6.75 (m, 2H), 4.20 – 4.14 (m, 1H), 3.68 (t, *J* = 10.0 Hz, 1H), 2.83 (dd, *J* = 15.2, 4.2 Hz, 1H), 2.44 (dd, *J* = 16.0, 9.6 Hz, 1H), 2.19 – 2.10 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H). HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 98/2, 200 nm, 0.5 mL/min, 25 °C. t_{R1} = 11.8 min (major), t_{R2} = 12.4 min (minor)]; ee = 93%. $[\alpha]^{25}_D$ = -19.97 (c = 0.10, CHCl₃).



(S)-4-Phenylchromane (4a). Colorless liquid. 99% yield, 49.8 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 7.17 – 7.10 (m, 3H), 6.90 – 6.76 (m, 3H), 4.21 – 4.17 (m, 3H), 2.38 – 2.27 (m, 1H), 2.15 – 2.05 (m, 1H). HPLC [DAICEL CHIRALPAK OJ-

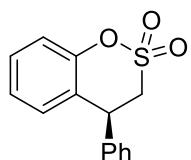
⁵ Wipf, P.; Ribe, S. *Org. Lett.*, **2001**, 3, 1503-1505.

H, hexane/iPrOH = 95/5, 210 nm, 1.0 mL/min, 25 °C. $t_{R1} = 8.8$ min (major), $t_{R2} = 17.6$ min (minor)]; $ee = 13\%$. $[\alpha]^{25}_D = +1.97$ ($c = 0.29$, CHCl₃).



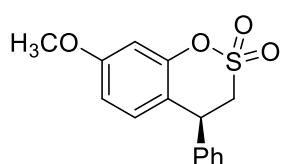
4b

(S)-4-Methyl-3,4-dihydrobenzo[e][1,2]oxathiine 2,2-dioxide (4b). Colorless liquid. 99% yield, 47.0 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.05 (dd, *J* = 8.0, 1.4 Hz, 1H), 3.73 – 3.65 (m, 1H), 3.63 – 3.57 (m, 1H), 3.24 (dd, *J* = 13.6, 9.8 Hz, 1H), 1.57 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 129.0, 127.9, 126.0, 125.9, 119.2, 51.6, 32.2, 19.9. HRMS (ESI) calcd for C₉H₁₁O₃S (M+H)⁺: 199.0429; found: 199.0432; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 80/20, 210 nm, 1.0 mL/min, 25 °C. $t_{R1} = 18.8$ min (major), $t_{R2} = 20.3$ min (minor)]; $ee = 27\%$. $[\alpha]^{25}_D = -7.72$ ($c = 0.59$, CHCl₃).



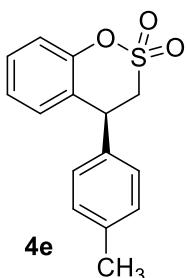
4c

(S)-4-Phenyl-3,4-dihydrobenzo[e][1,2]oxathiine 2,2-dioxide (4c). Colorless liquid. 99% yield, 61.7 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 3H), 7.34 – 7.30 (m, 1H), 7.28 – 7.23 (m, 2H), 7.17 – 7.07 (m, 2H), 6.90 – 6.87 (m, 1H), 4.81 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.74 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.61 (dd, *J* = 14.0, 12.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 151.2, 139.8, 130.2, 129.4, 129.3, 128.7, 128.3, 125.6, 124.6, 119.1, 51.7, 44.4. HRMS (ESI) calcd for C₁₄H₁₃O₃S (M+H)⁺: 261.0585; found: 261.0587; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 80/20, 210 nm, 1.0 mL/min, 25 °C. $t_{R1} = 39.3$ min (minor), $t_{R2} = 41.8$ min (major)]; $ee = 94\%$. $[\alpha]^{25}_D = +2.82$ ($c = 0.78$, CHCl₃).



4d

(S)-7-Methoxy-4-phenyl-3,4-dihydrobenzo[e][1,2]oxathiine 2,2-dioxide (4d). Colorless liquid. 98% yield, 68.2 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.32 (m, 3H), 7.24 – 7.22 (m, 2H), 6.74 (d, *J* = 8.6 Hz, 1H), 6.66 – 6.60 (m, 2H), 4.71 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.79 (s, 3H), 3.67 (dd, *J* = 13.8, 6.0 Hz, 1H), 3.53 (dd, *J* = 13.8, 12.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 151.8, 140.1, 130.8, 129.4, 128.64, 128.3, 116.3, 112.6, 103.6, 55.6, 51.7, 43.8. HRMS (ESI) calcd for C₁₅H₁₅O₄S (M+H)⁺: 291.0691; found: 291.0687; HPLC [DAICEL CHIRALPAK OD-H, hexane/iPrOH = 80/20, 210 nm, 1.0 mL/min, 25 °C. $t_{R1} = 10.4$ min (minor), $t_{R2} = 11.1$ min (major)]; $ee = 91\%$. $[\alpha]^{25}_D = -2.99$ ($c = 0.87$, CHCl₃).

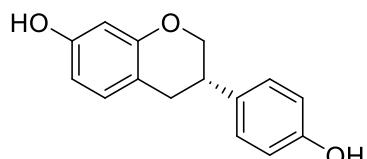


(S)-4-(p-Tolyl)-3,4-dihydrobenzo[e][1,2]oxathiine 2,2-dioxide (4e). White solid, m.p. = 136.8 – 137.6 °C. 98% yield, 64.4 mg. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.05 (m, 4H), 6.90 – 6.85 (m, 1H), 4.76 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.69 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.57 (dd, *J* = 14.0, 12.6 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.2, 138.2, 136.8, 130.2, 130.1, 129.2, 128.6, 125.6, 124.8, 119.0, 51.7, 44.0, 21.1. HRMS (ESI) calcd for C₁₅H₁₅O₃S (M+H)⁺: 275.0742; found: 275.0741; HPLC [DAICEL CHIRALPAK OJ-H, hexane/iPrOH = 80/20, 210 nm, 1.0 mL/min, 25 °C. t_{R1} = 21.5 min (major), t_{R2} = 23.9 min (minor)]; *ee* = 91%. [α]²⁵_D = +10.47 (c = 0.82, CHCl₃).

5. Larger Scale Synthesis of (S)-Equol by Asymmetric Hydrogenation

Larger scale of hydrogenation: The catalyst (2.0 mg, 0.0012mmol, 0.001 equiv.) and 7-methoxy-3-(4-methoxyphenyl)-2*H*-chromene (323.0 mg, 1.2 mmol, 1.0 equiv.) were placed in a 10.0 mL tube equipped with a magnetic stirrer bar. This tube was then put into a nitrogen-filled autoclave. CH₂Cl₂ (4.0 mL) was added to the mixture under nitrogen atmosphere. The autoclave was then closed, purged three times with hydrogen (less than the pressure needed), and finally pressurized to 60 bar. The reaction mixture was stirred at 40 °C for 72 h, and the hydrogen gas was slowly released. The conversion of the product was determined by ¹H NMR spectroscopic analysis of the crude reaction mixture and isolated by chromatography (15:1 petroleum ether : EtOAc) to give the desired product in 98% yield (319 mg). The *ee* was determined to be 98% by chiral HPLC.

Synthesis of (S)-Equol: A 50 mL round bottom flask was charged with (S)-7-methoxy-3-(4-methoxyphenyl)chromane (319 mg, 1.2 mmol, 1.0 equiv.) and pyridine hydrochloride (3.5 g, 30.0 mmol, 25 equiv.) then sealed with a septum equipped with a drying tube. The mixture was heated to a melt in an oil bath at 150 °C with stirring for 48 h, then cooled to room temperature. Water (10.0 mL) and EtOAc (10.0 mL) were added, the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 5.0 mL). The combined organic phase was dried over Na₂SO₄, filtered, which was purified by silica gel chromatography (3:1 to 1:1 petroleum ether : EtOAc) to provide 209 mg of white solid.

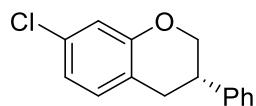


(S)-Equol

(S)-Equol. White solid, m.p. = 187.8– 188.6 °C. 82% yield, 209.0 mg. ¹H NMR (400 MHz, Methanol-*d*₄) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.31 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.22 (d, *J* = 2.4 Hz, 1H), 4.21 – 4.17 (m, 1H), 3.91 (t, *J* = 10.6 Hz, 1H), 3.09 – 3.01 (m, 1H), 2.91 – 2.80 (m, 2H). ¹³C NMR (100 MHz, Methanol-*d*₄) δ 156.2, 155.9, 154.9, 132.4,

129.8, 127.9, 115.0, 113.2, 107.7, 102.4, 70.8, 38.1, 31.7. HRMS (ESI) calcd for $C_{15}H_{15}O_3 (M+H)^+$: 243.1021; found: 243.1024; HPLC [DAICEL CHIRALPAK IA, hexane/*i*PrOH = 90/10, 200 nm, 1.0 mL/min, 25 °C. $t_{R1} = 42.0$ min (major), $t_{R2} = 33.5$ min (minor)]; *ee* = 95%. $[\alpha]^{25}_D = -20.21$ ($c = 0.81$, EtOH).

6. X-ray Analysis Data



Bond precision: C-C = 0.0032 Å Wavelength=1.54178
 Cell: a=5.7624 (1) b=22.9736 (6) c=9.5587 (2)
 alpha=90 beta=106.003 (1) gamma=90
 Temperature: 173 K

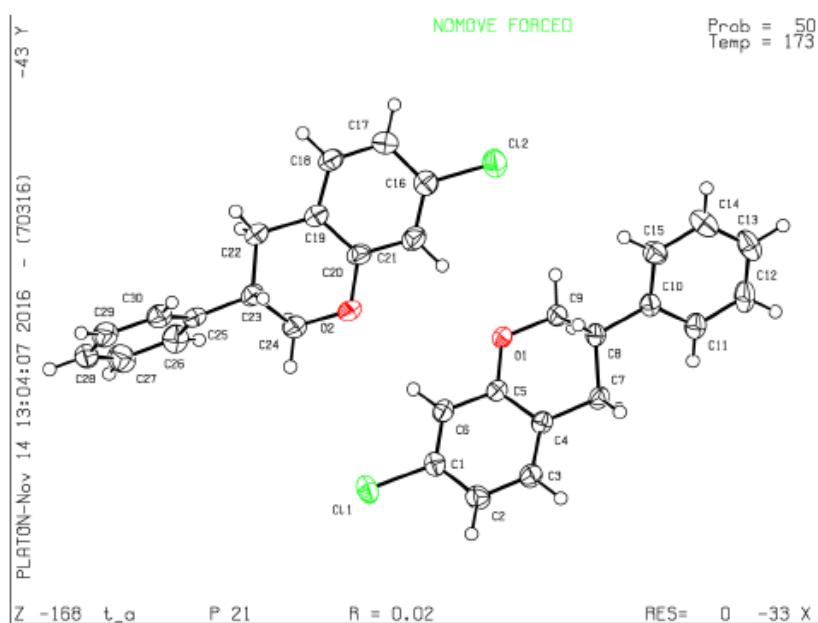
	Calculated	Reported
Volume	1216.37(5)	1216.37(5)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C15 H13 Cl O	C15 H13 Cl O
Sum formula	C15 H13 Cl O	C15 H13 Cl O
Mr	244.70	244.70
Dx, g cm ⁻³	1.336	1.336
Z	4	4
Mu (mm ⁻¹)	2.598	2.598
F000	512.0	512.0
F000'	514.70	
h,k,lmax	6,27,11	6,27,11
Nref	4450 [2284]	4315
Tmin,Tmax	0.624, 0.595	
Tmin'	0.566	

Correction method= Not given

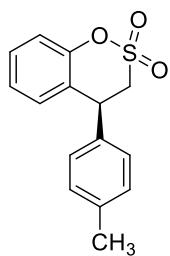
Data completeness= 1.89/0.97 Theta(max) = 68.292

R(reflections) = 0.0244 (4220) wR2(reflections) = 0.0749 (4315)

S = 0.661 Npar= 307



Note: These data (CCDC 1562372) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

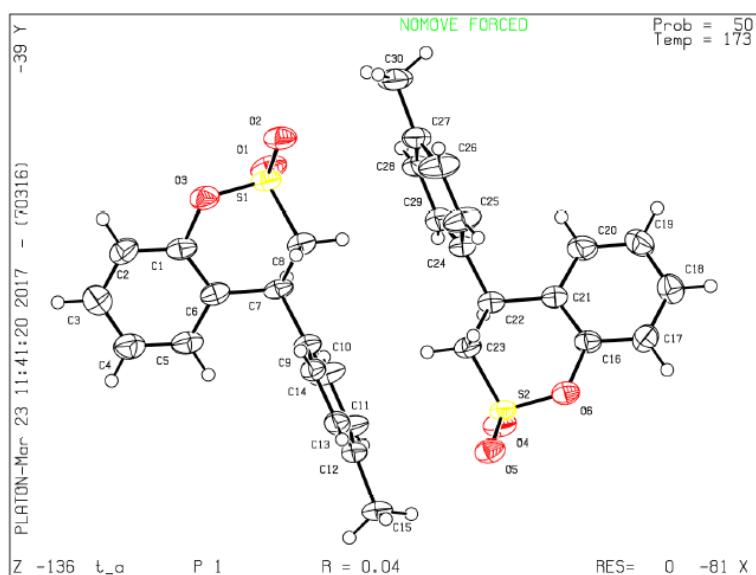


Bond precision: C-C = 0.0072 Å Wavelength=1.54178
 Cell: a=7.8451(4) b=8.3042(4) c=11.0600(6)
 alpha=76.583(2) beta=88.533(2) gamma=75.925(2)
 Temperature: 173 K

	Calculated	Reported
Volume	679.46(6)	679.46(6)
Space group	P 1	P 1
Hall group	P 1	P 1
Moity formula	C15 H14 O3 S	C15 H14 O3 S
Sum formula	C15 H14 O3 S	C15 H14 O3 S
Mr	274.32	274.32
Dx,g cm-3	1.341	1.341
Z	2	2
Mu (mm-1)	2.131	2.131
F000	288.0	288.0
F000'	289.48	
h,k,lmax	9,10,13	9,9,13
Nref	4990 [2495]	4652
Tmin,Tmax	0.686,0.653	
Tmin'	0.622	

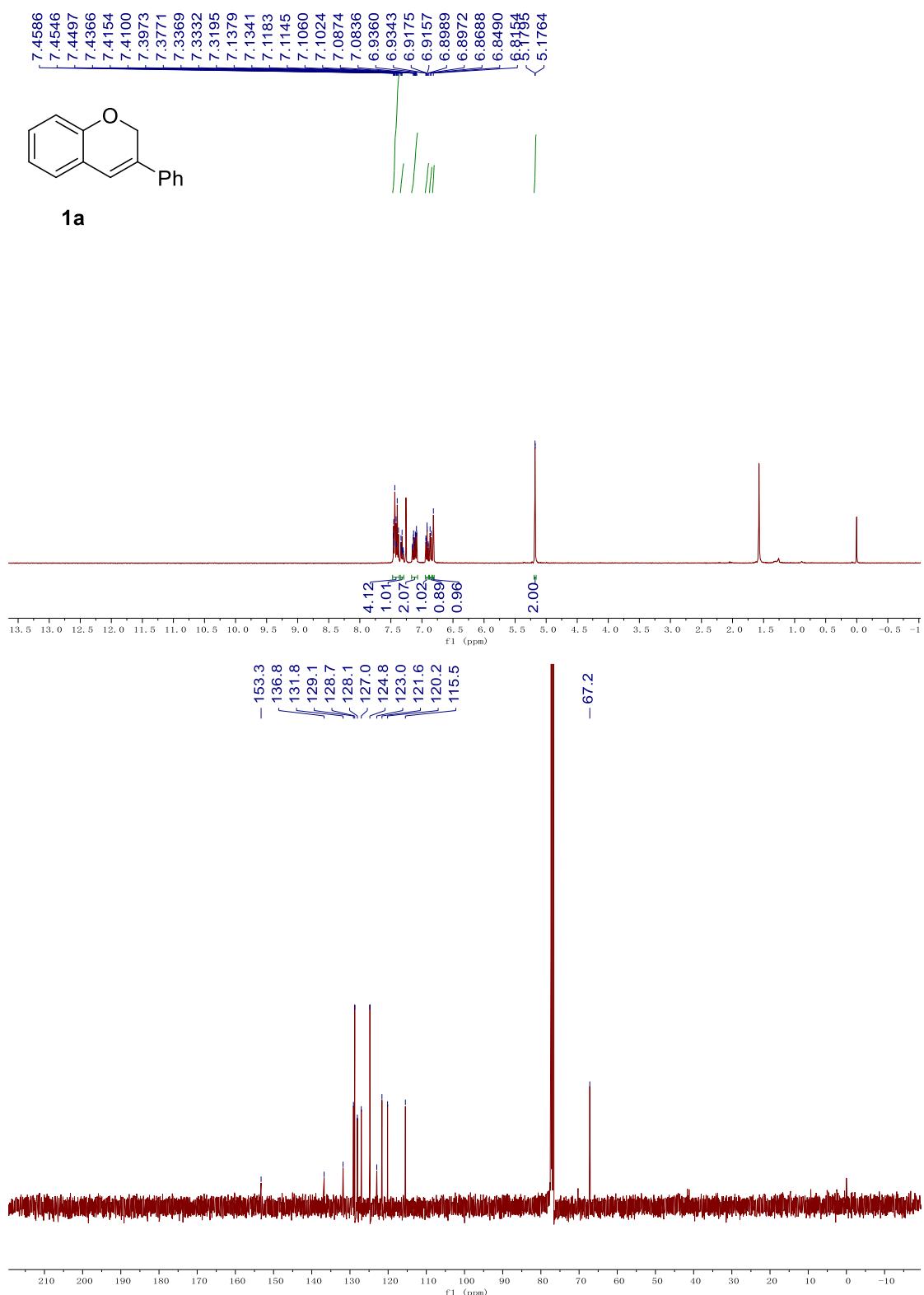
Correction method= Not given

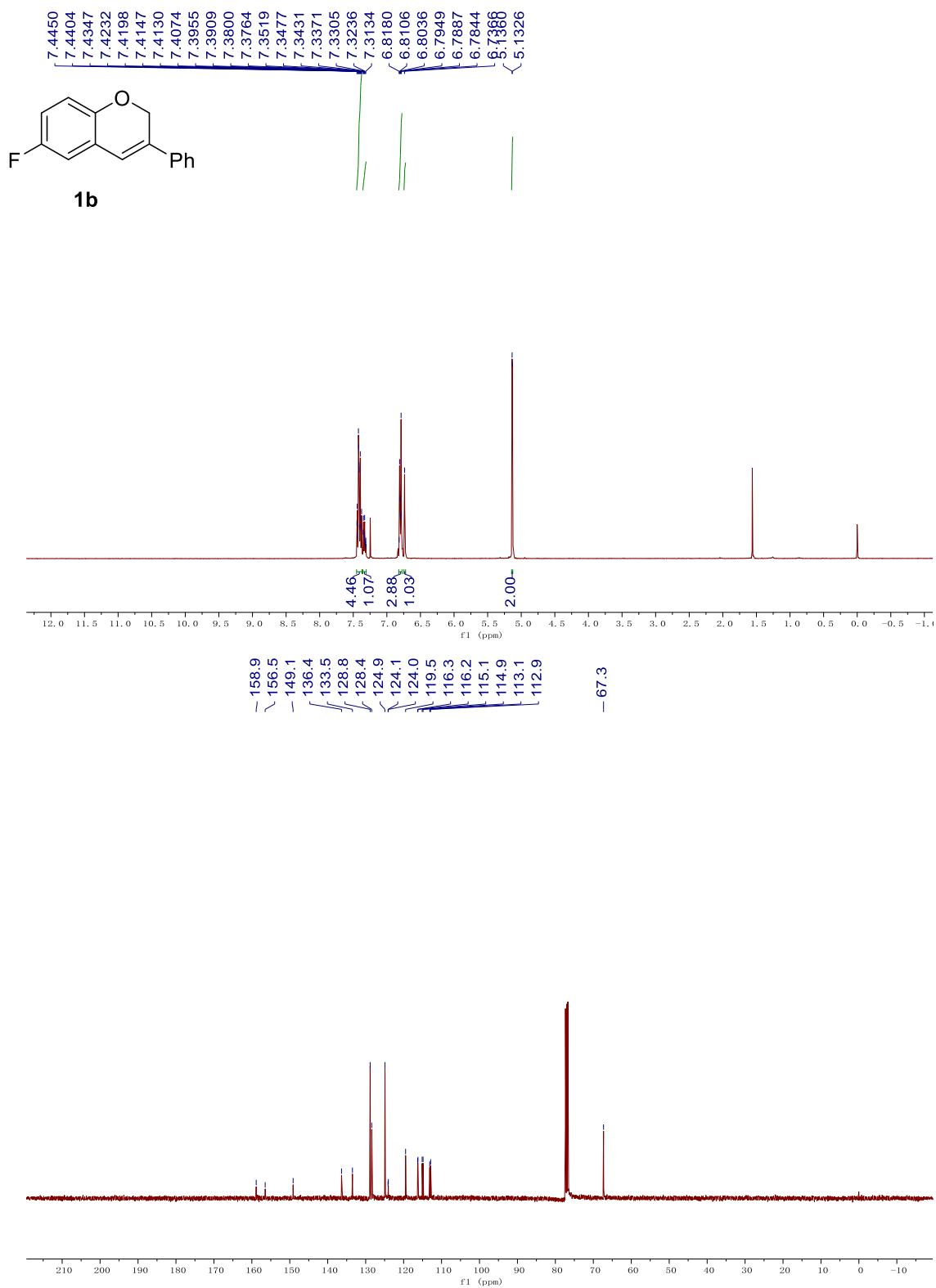
Data completeness= 1.86/0.93 Theta (max)= 68.373
 R(reflections)= 0.0414(4353) wR2 (reflections)= 0.1269(4652)
 S = 1.032 Npar= 346

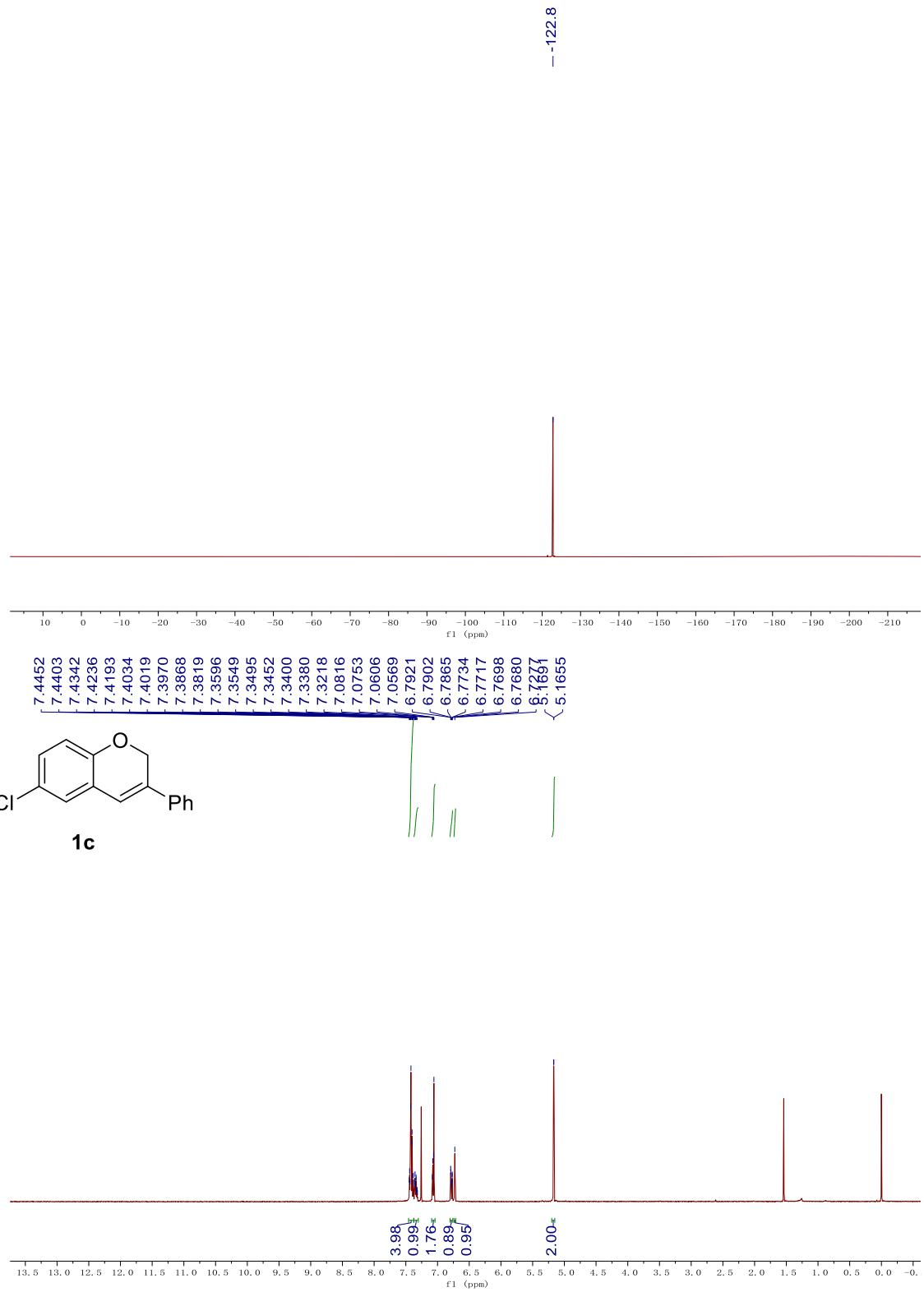


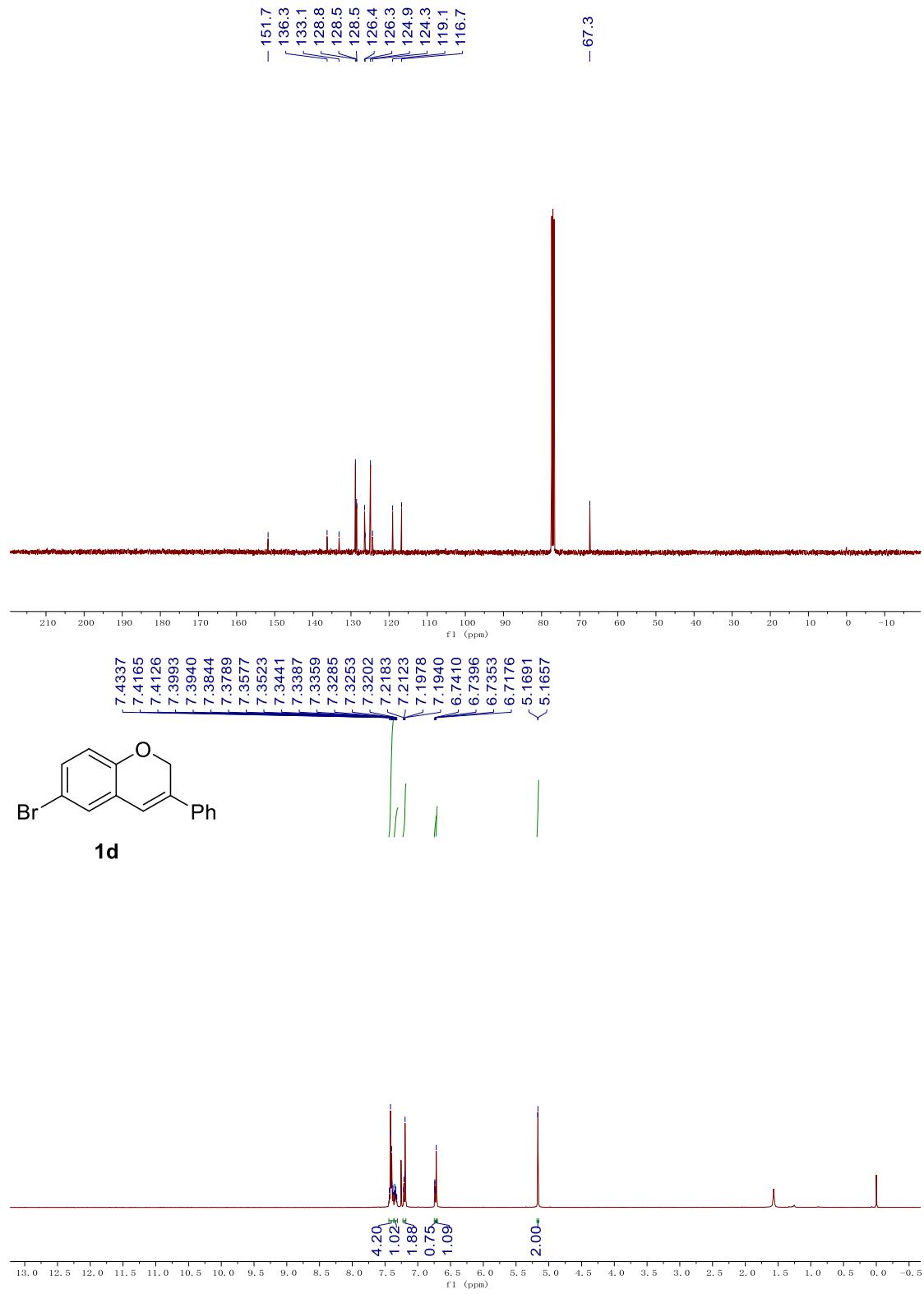
Note: These data (CCDC 1562373) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

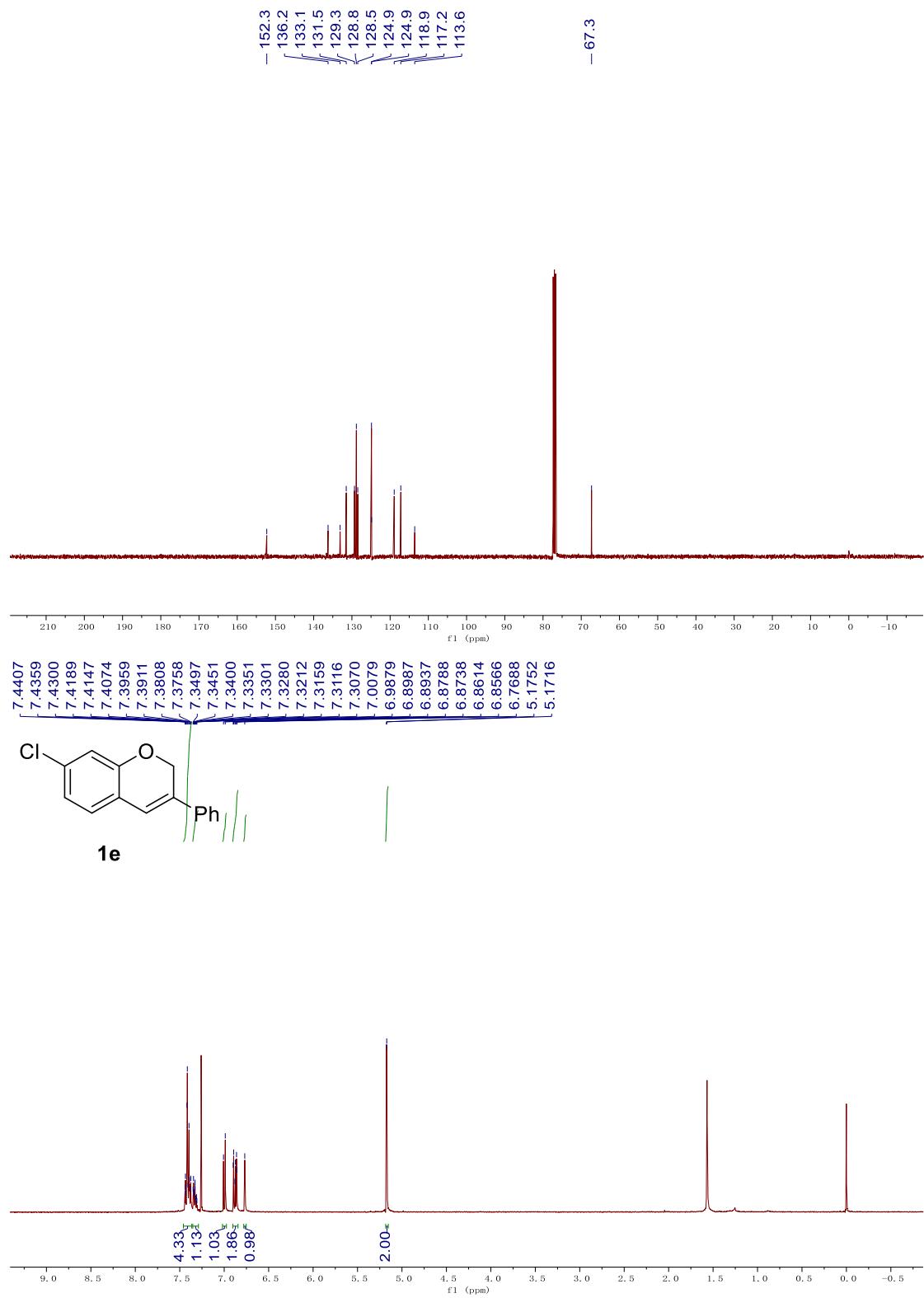
7. NMR Spectra and HPLC Charts

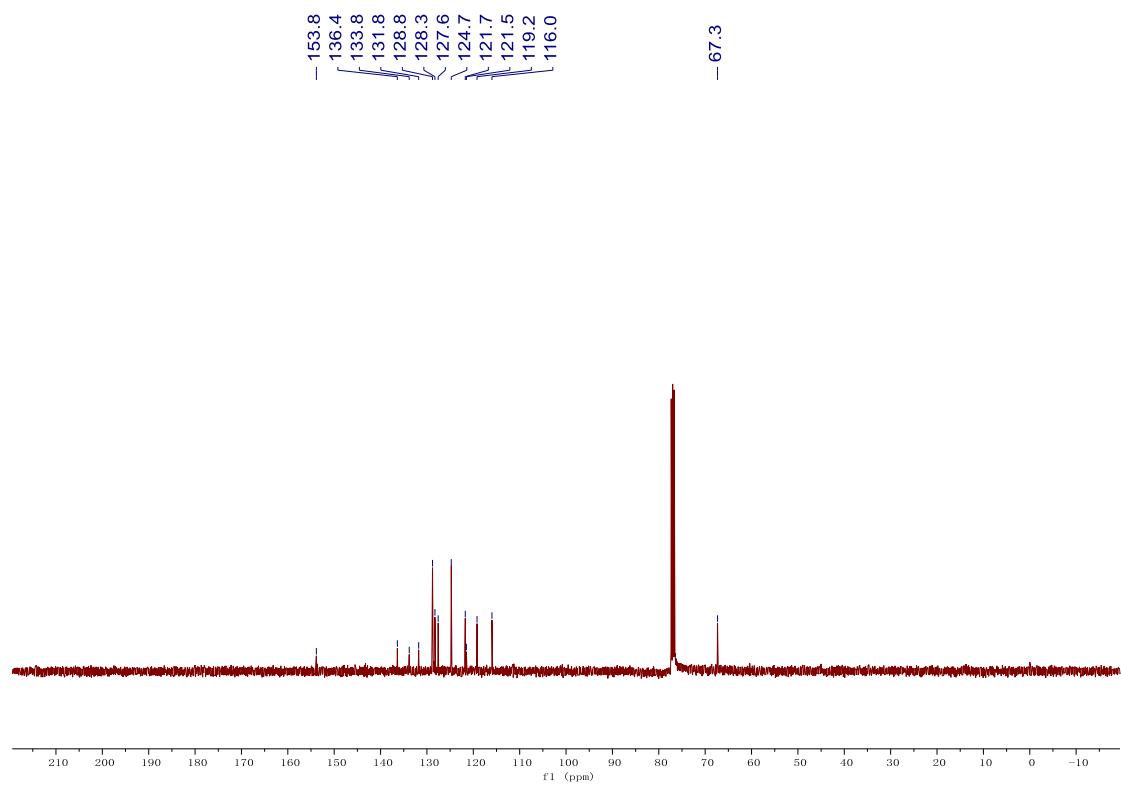




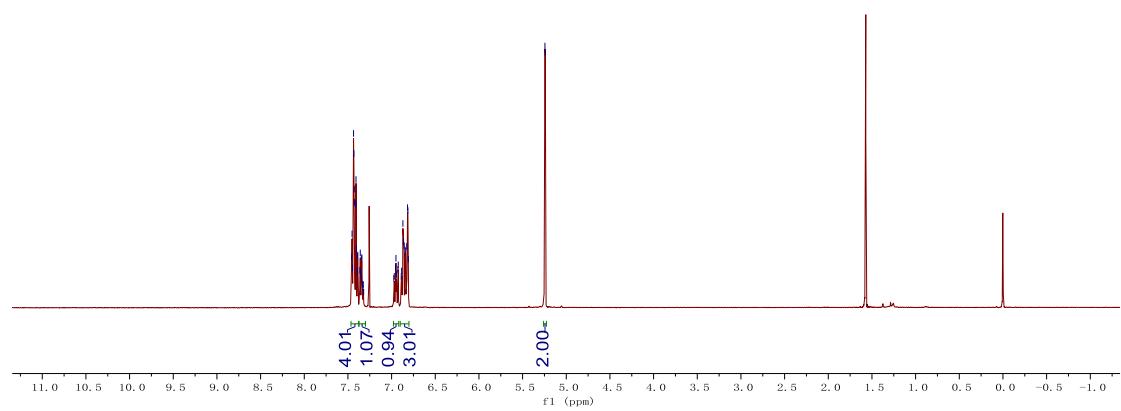


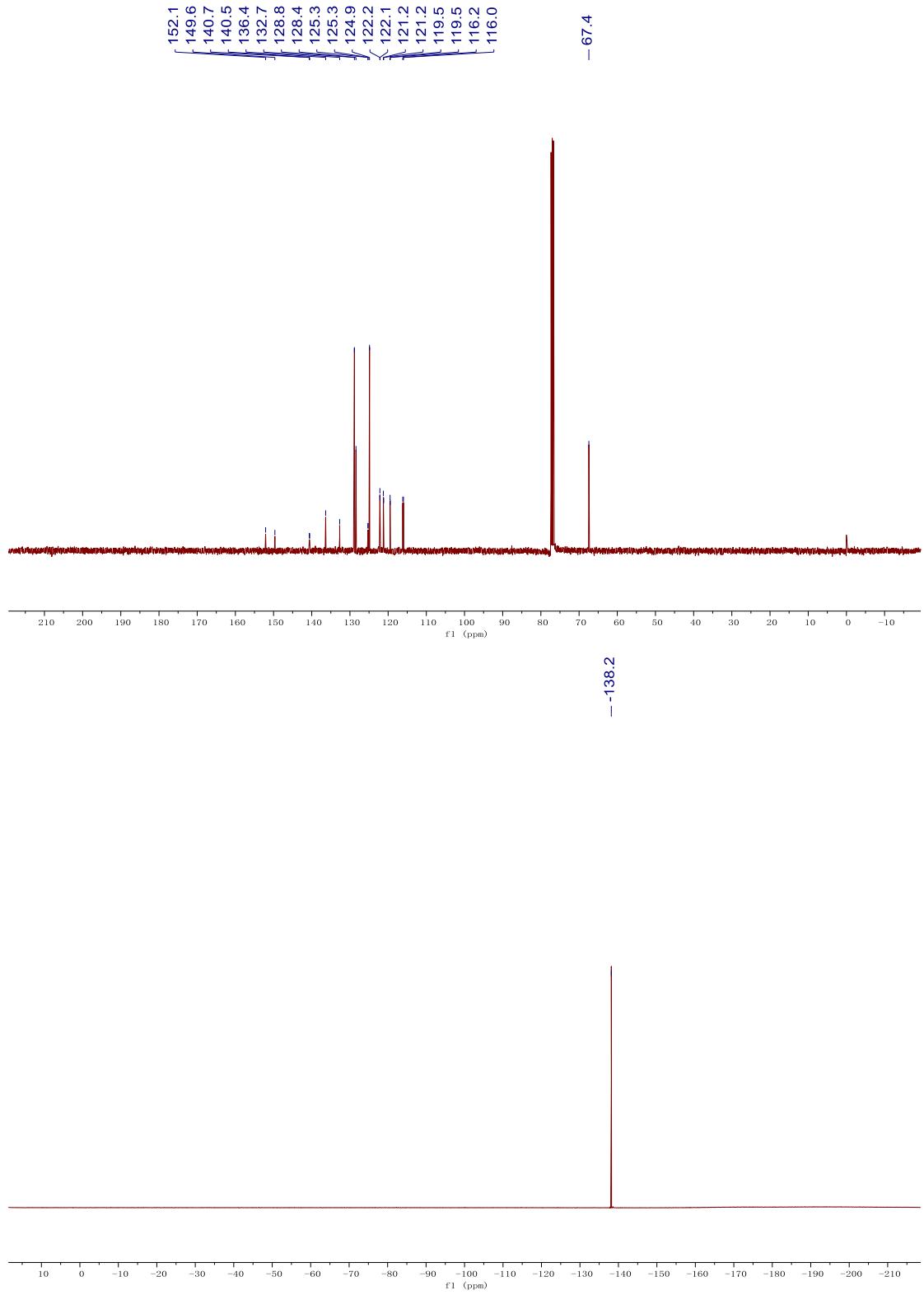


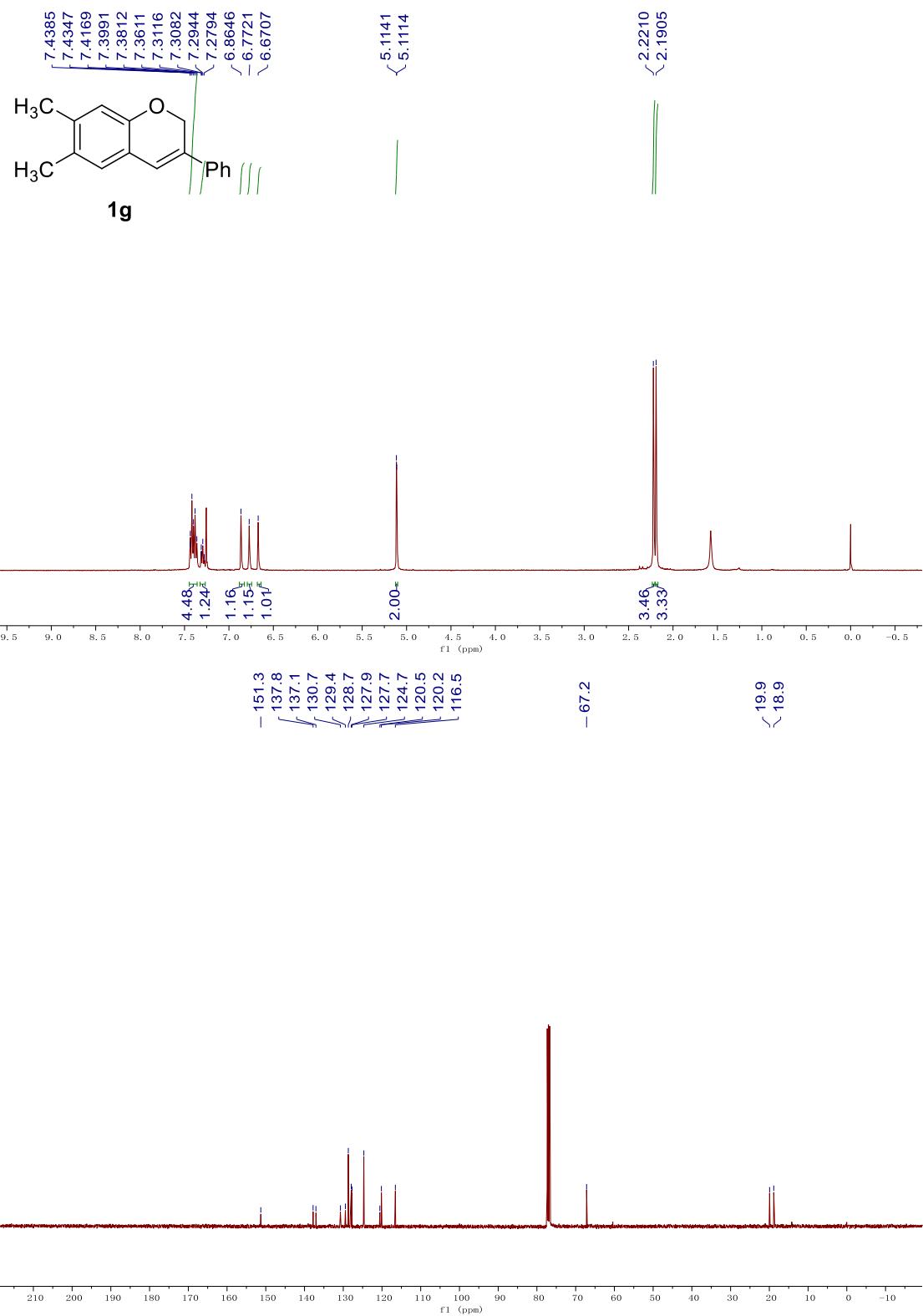


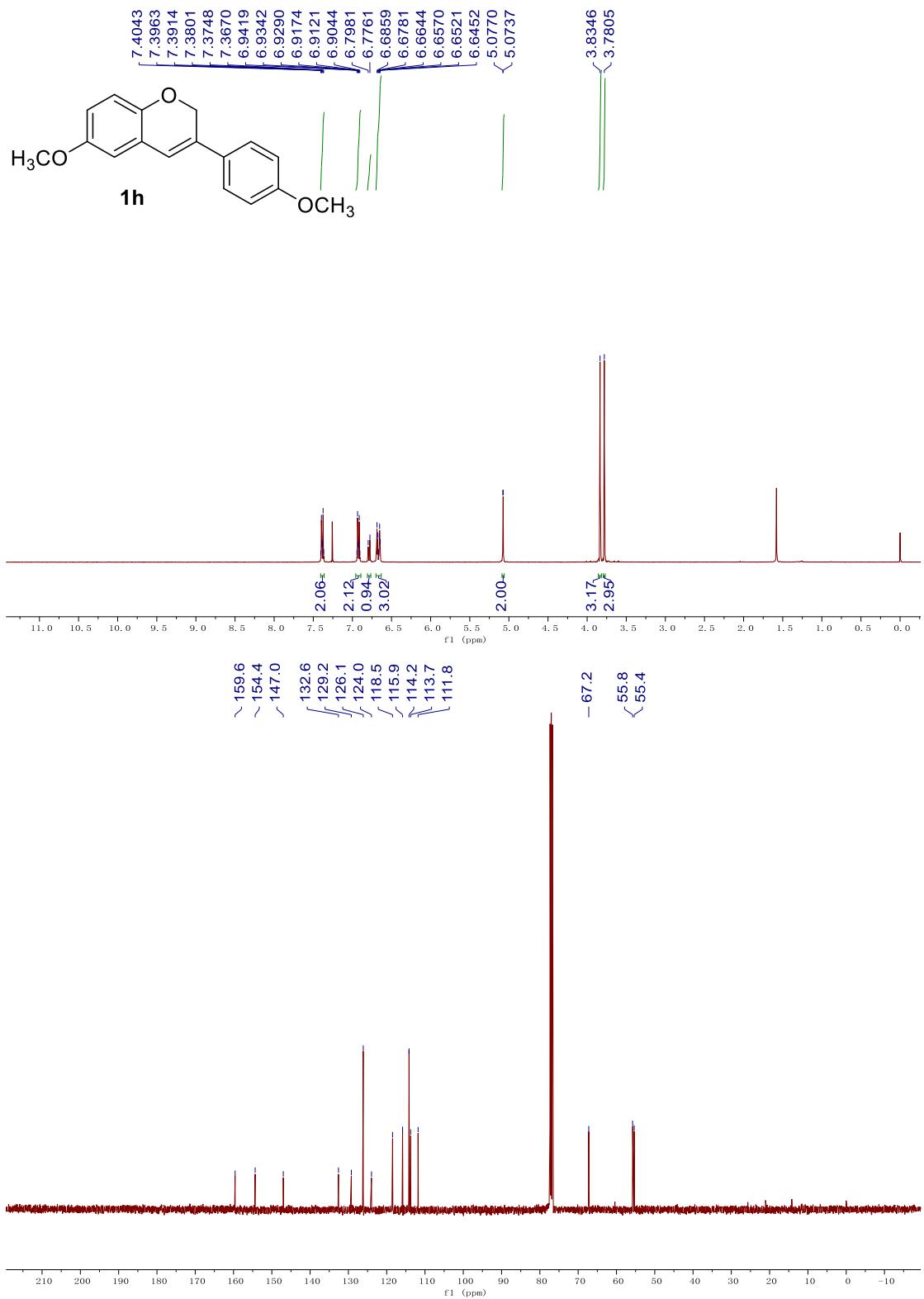


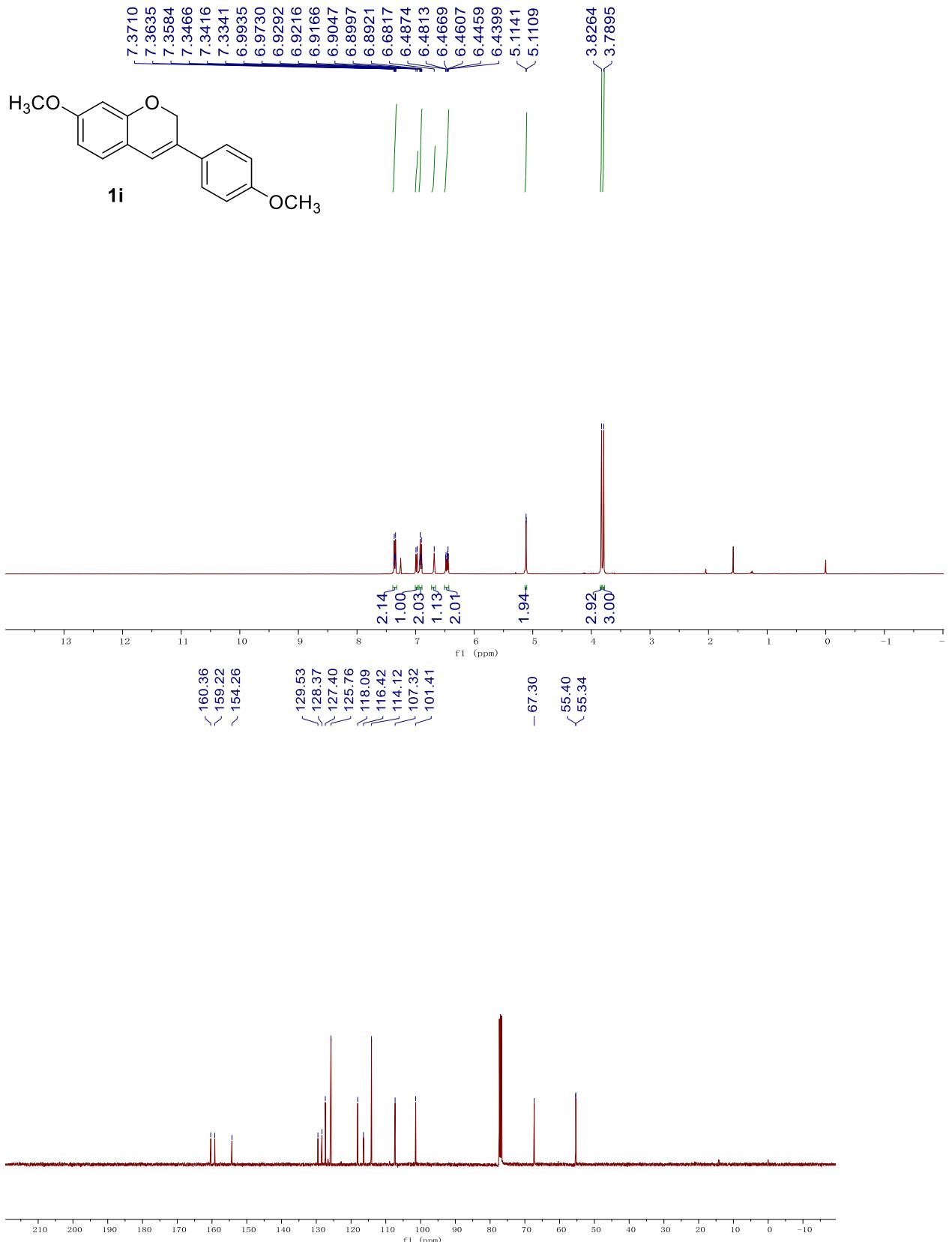
1f

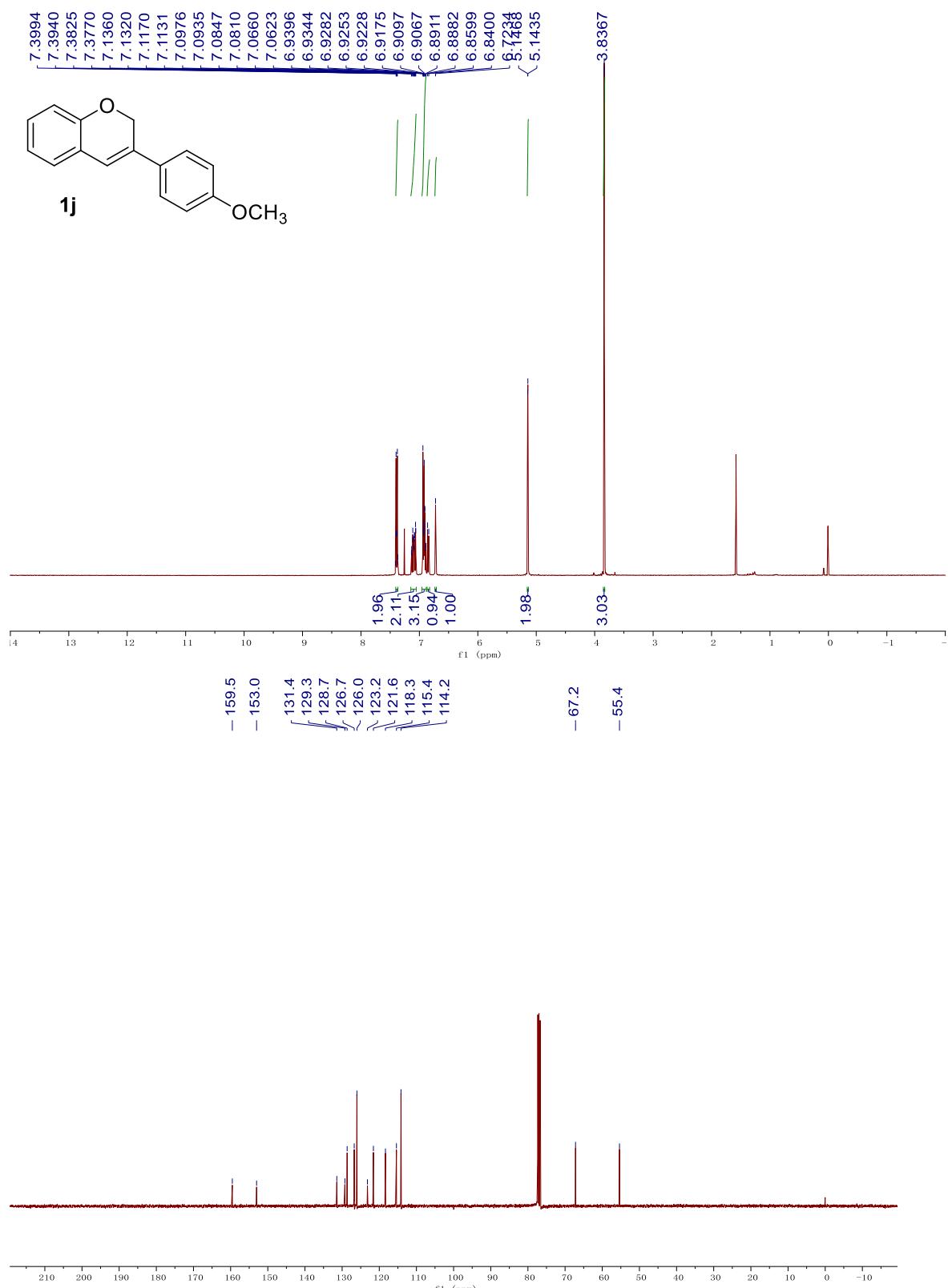


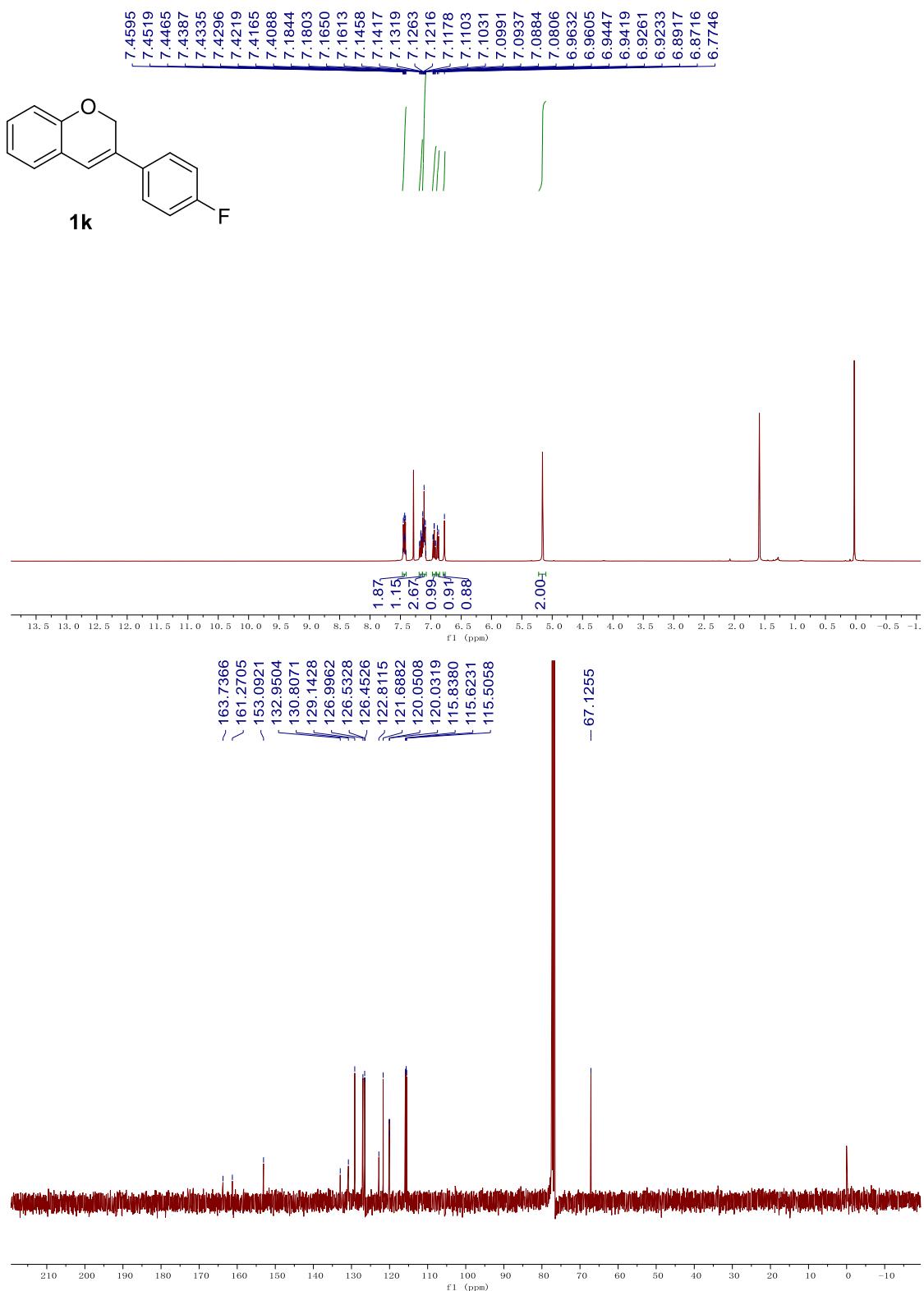


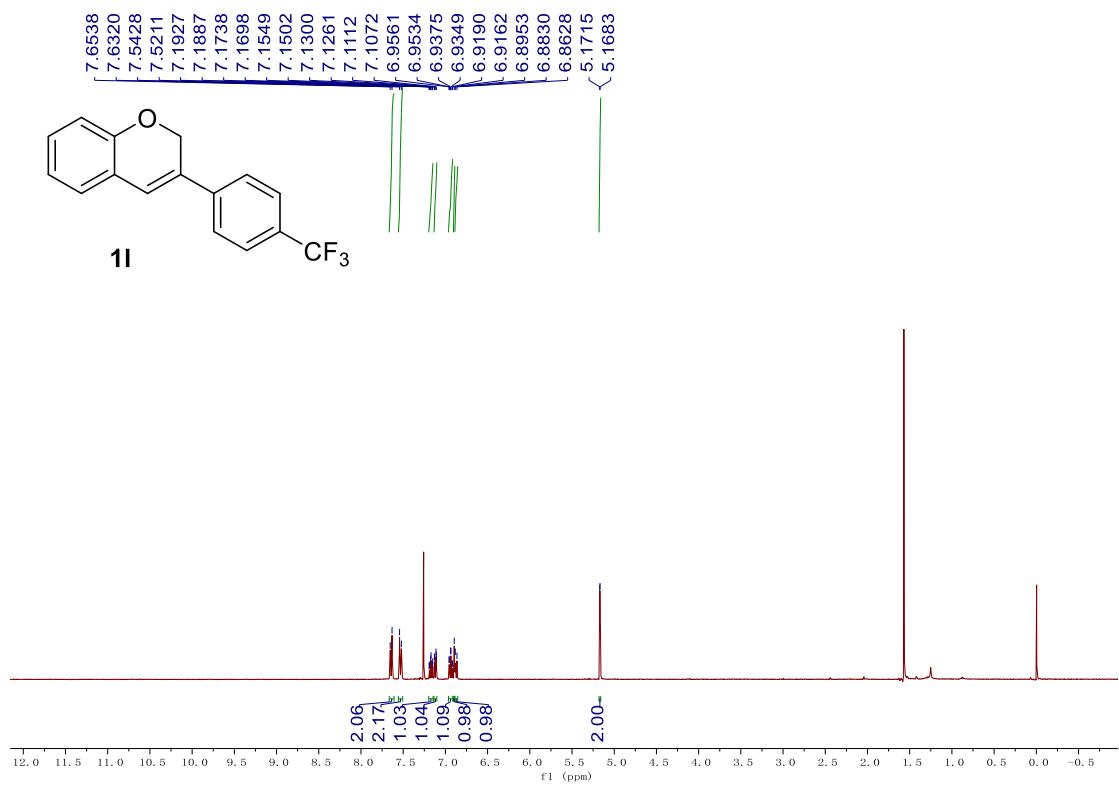
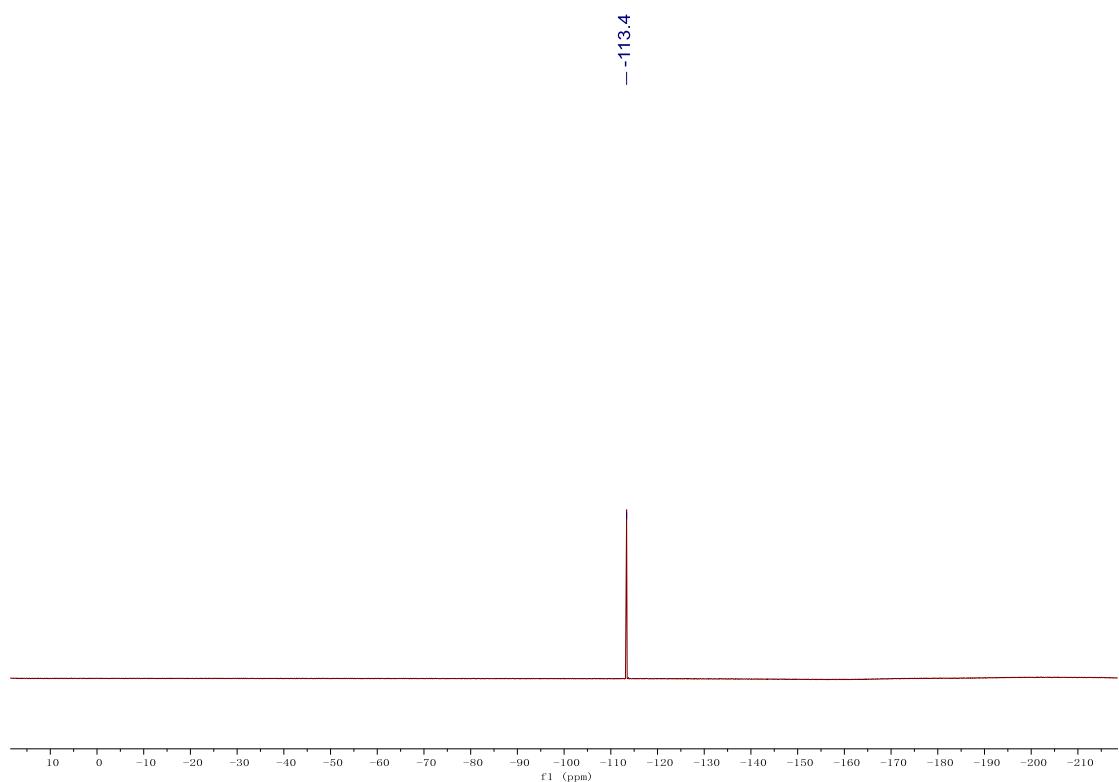


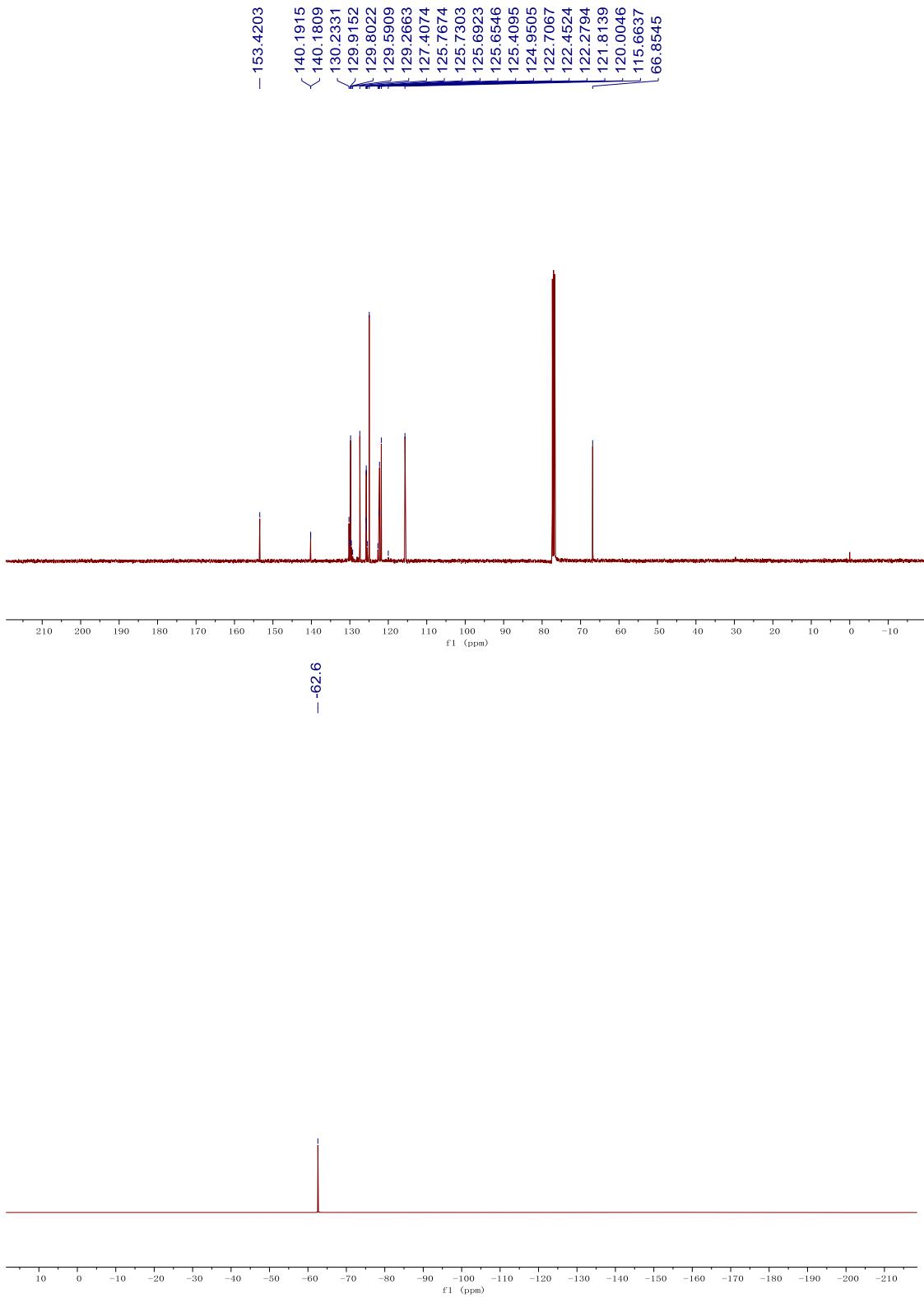


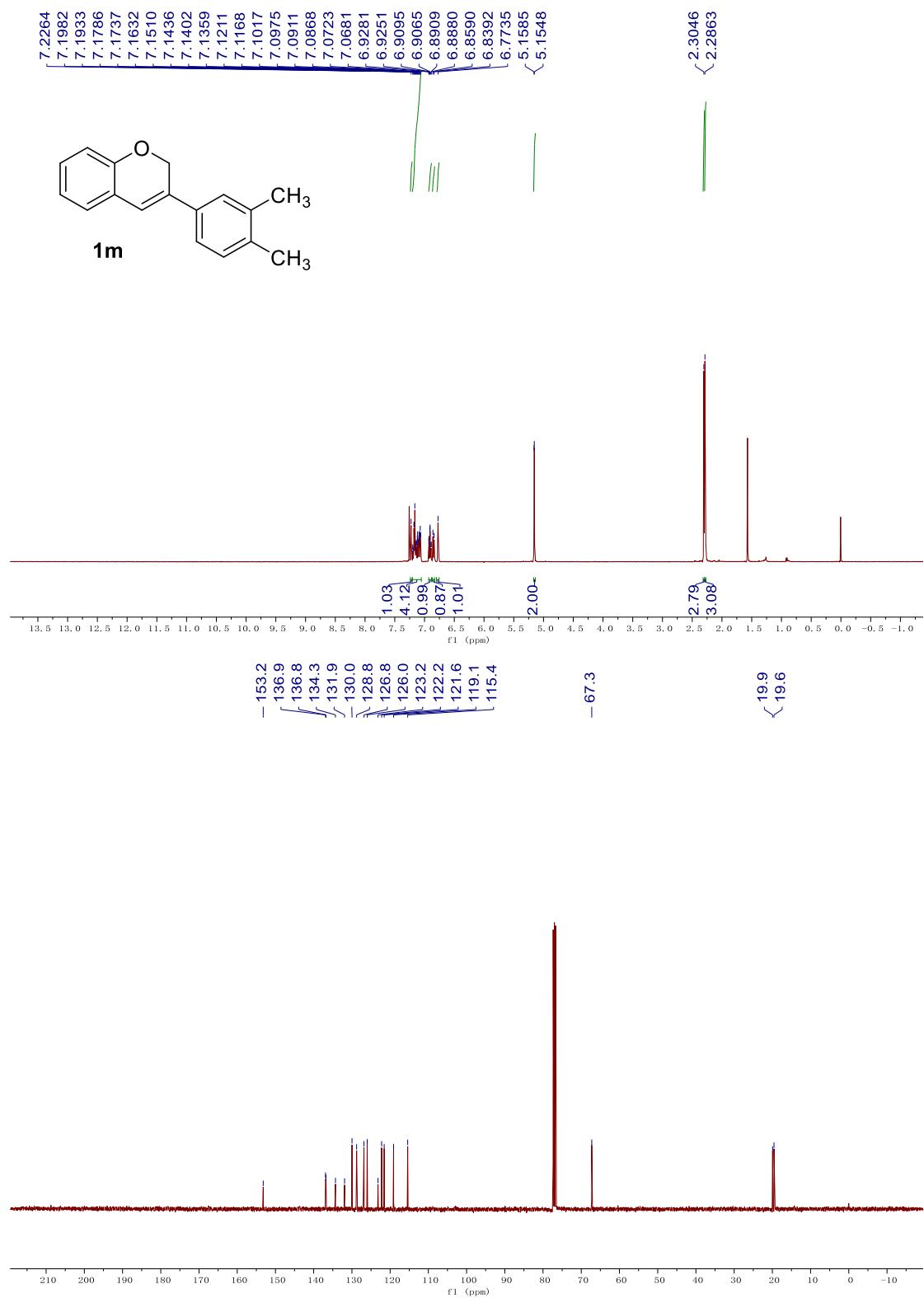


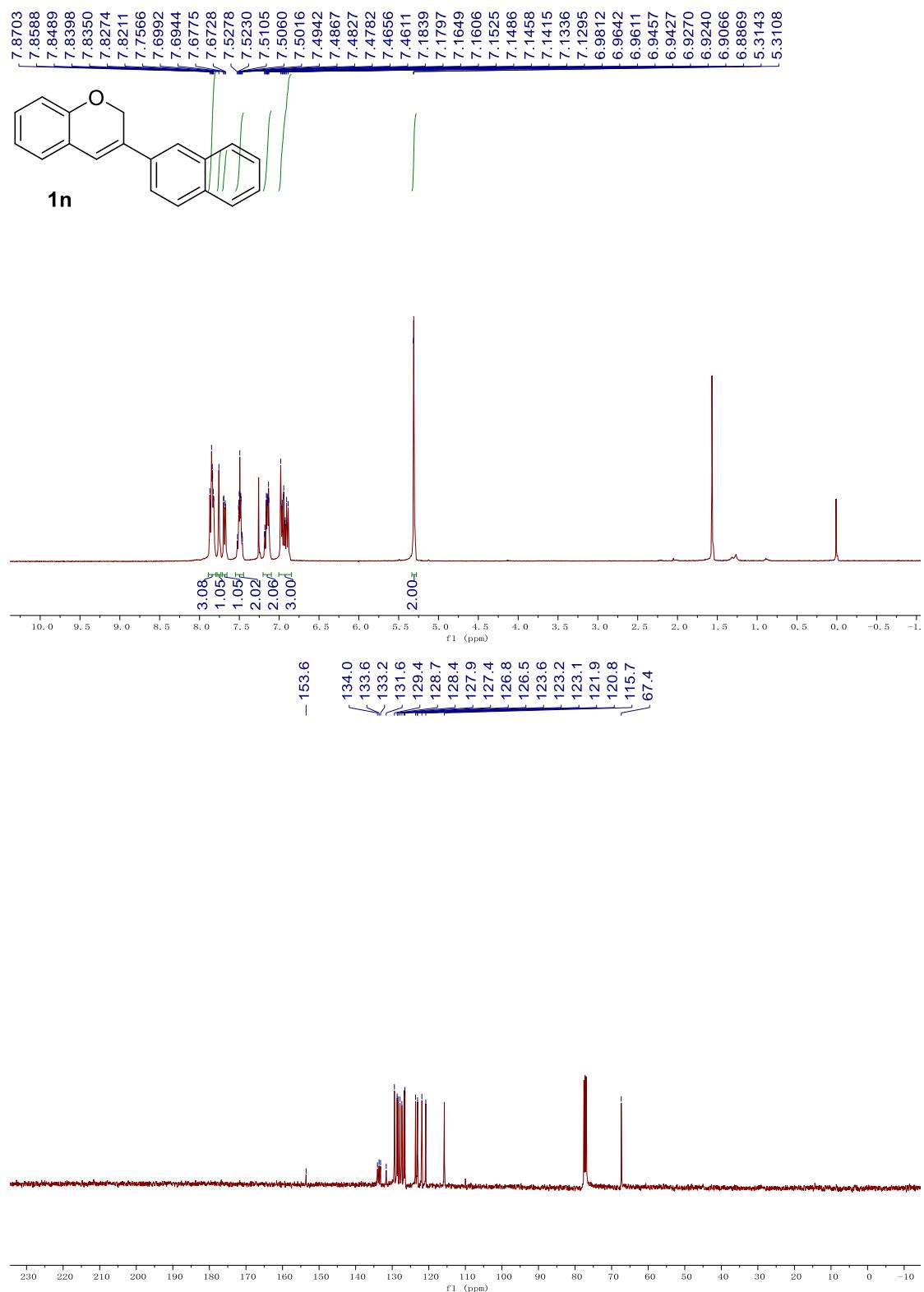


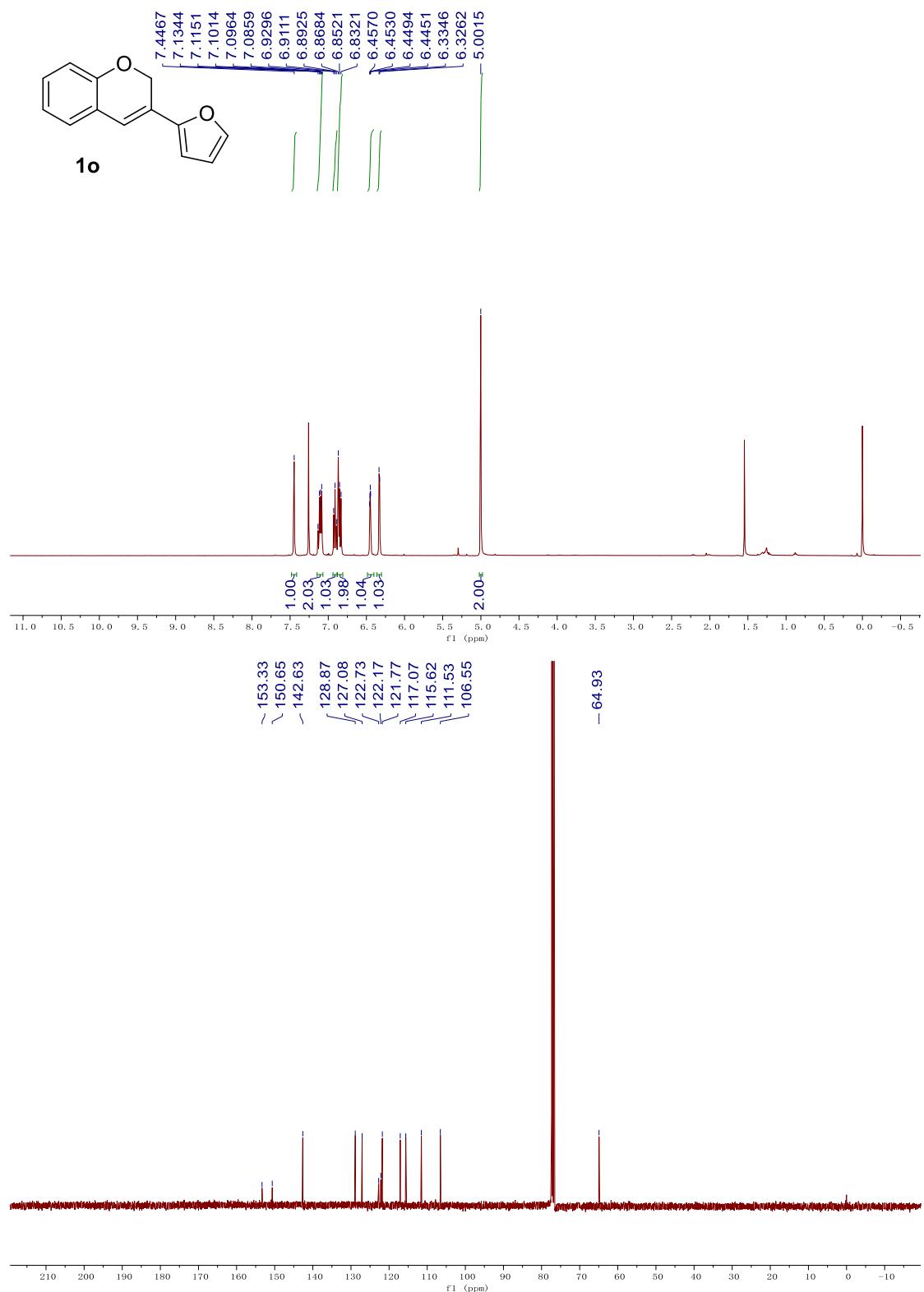


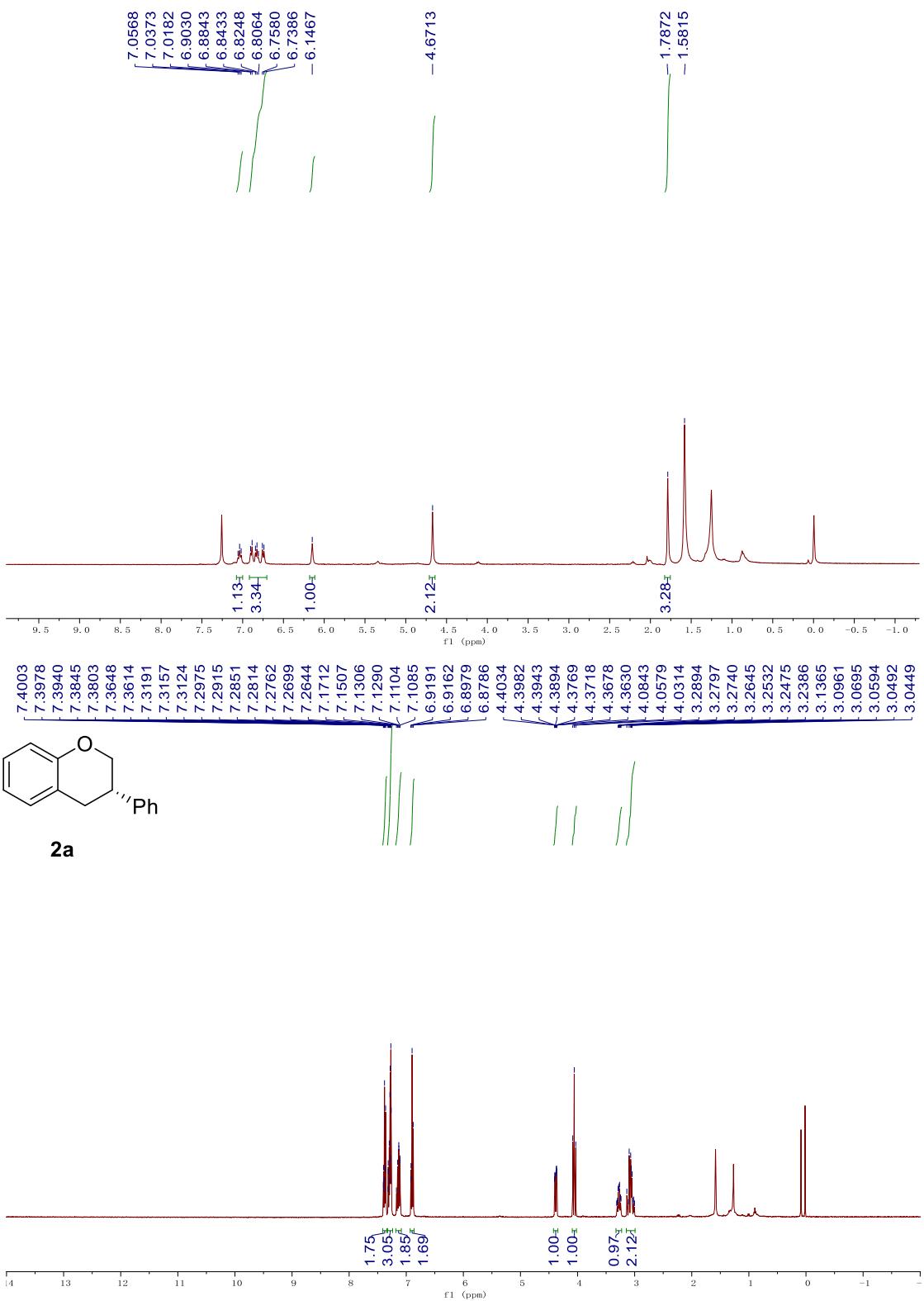


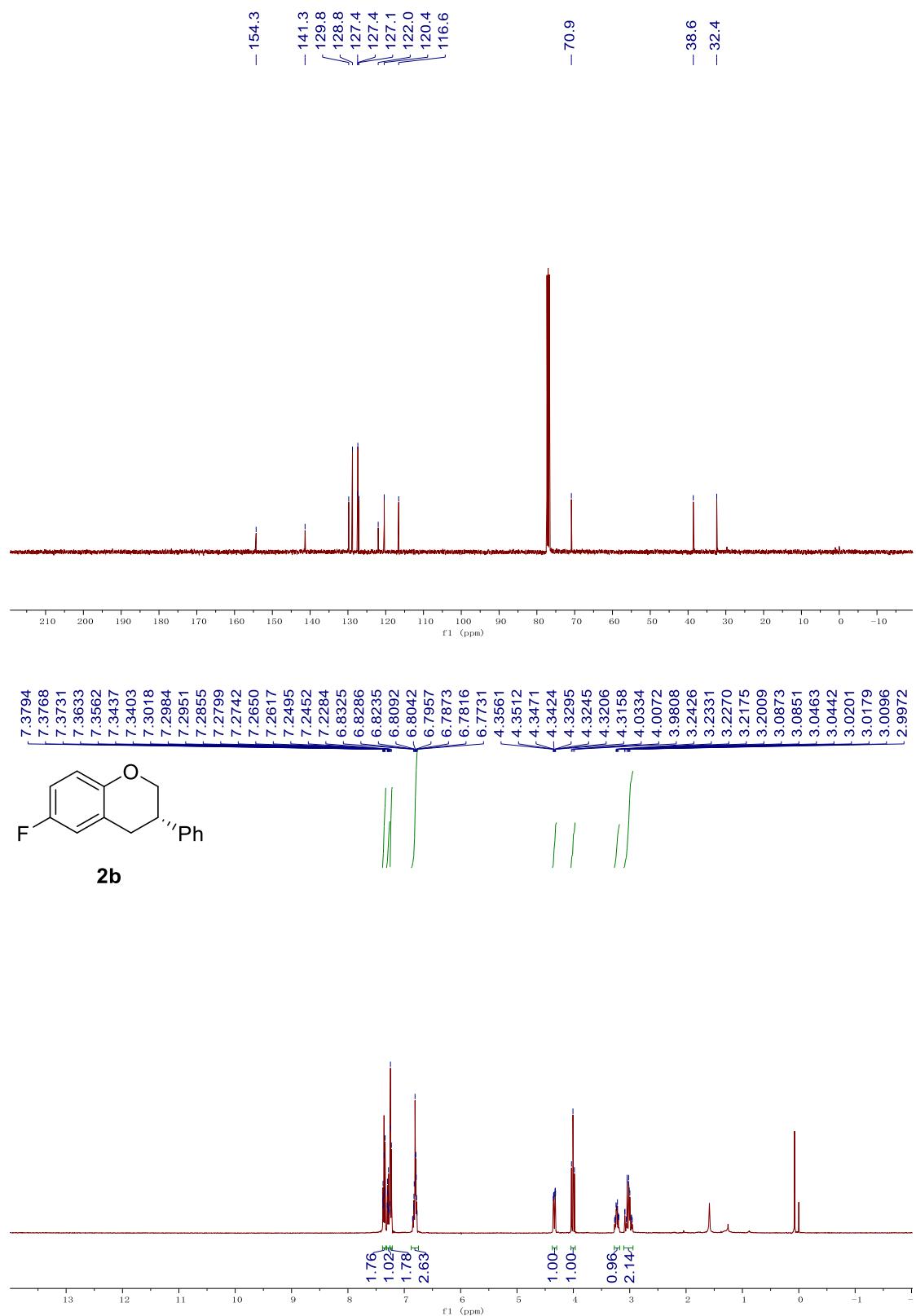


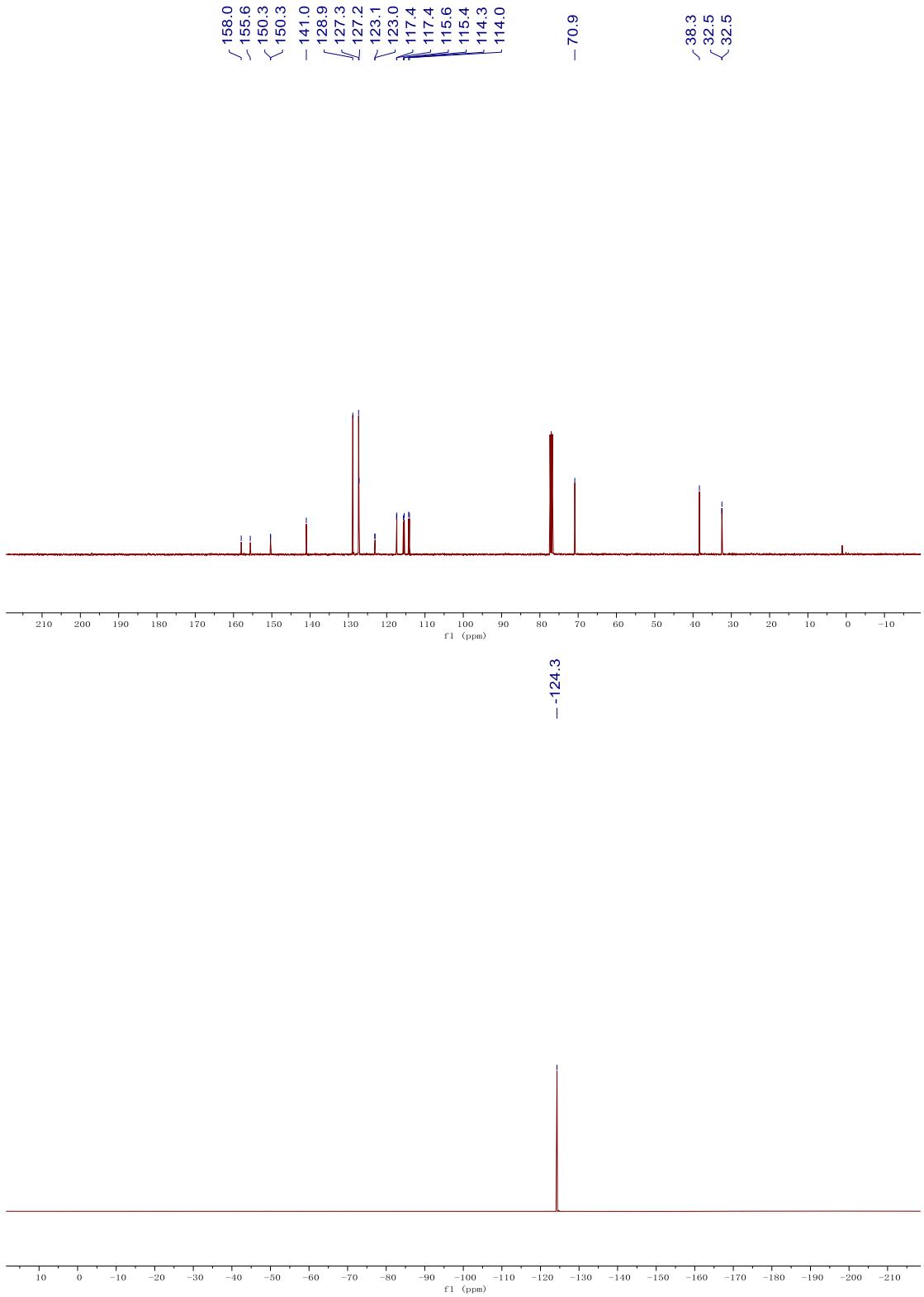


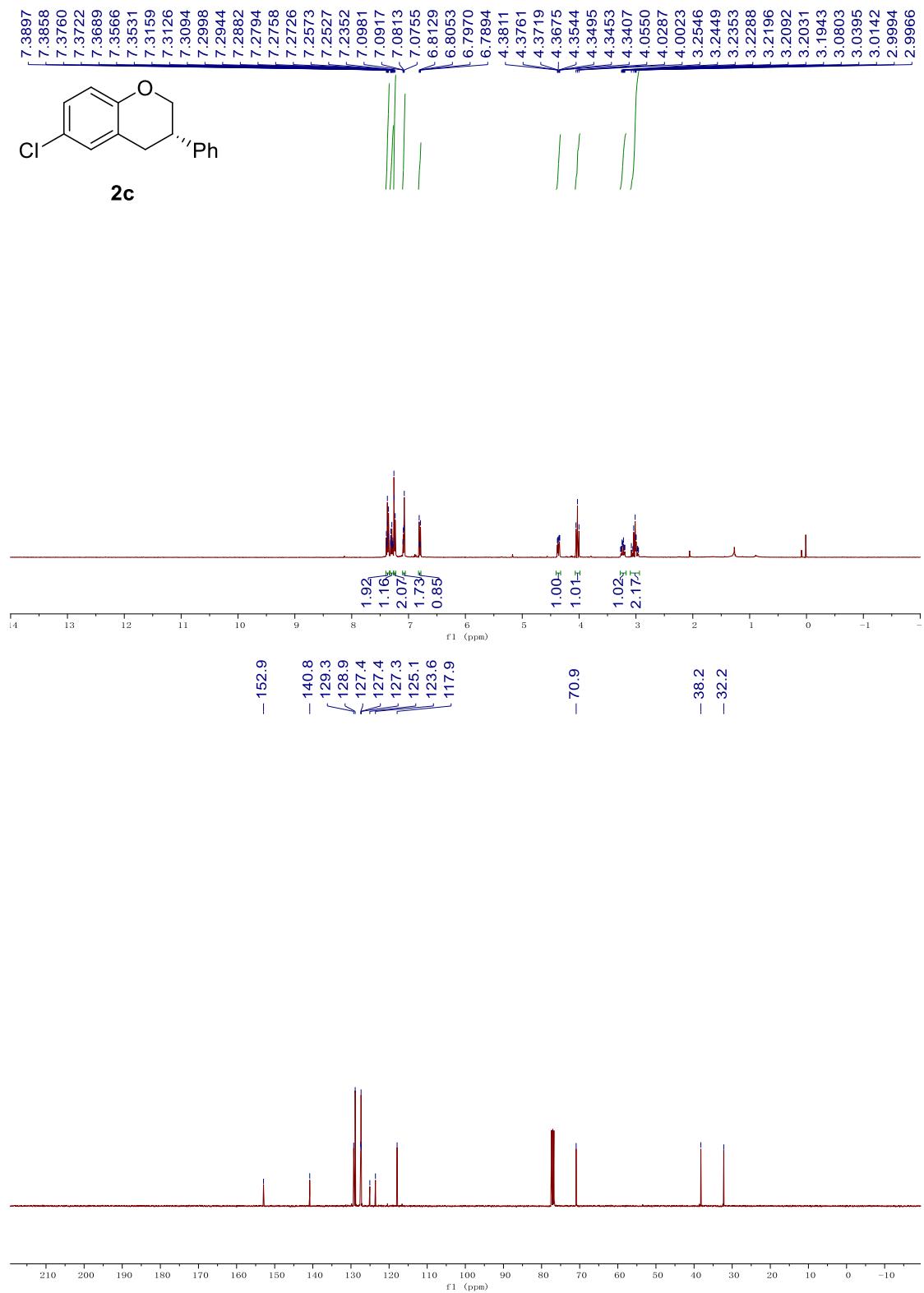


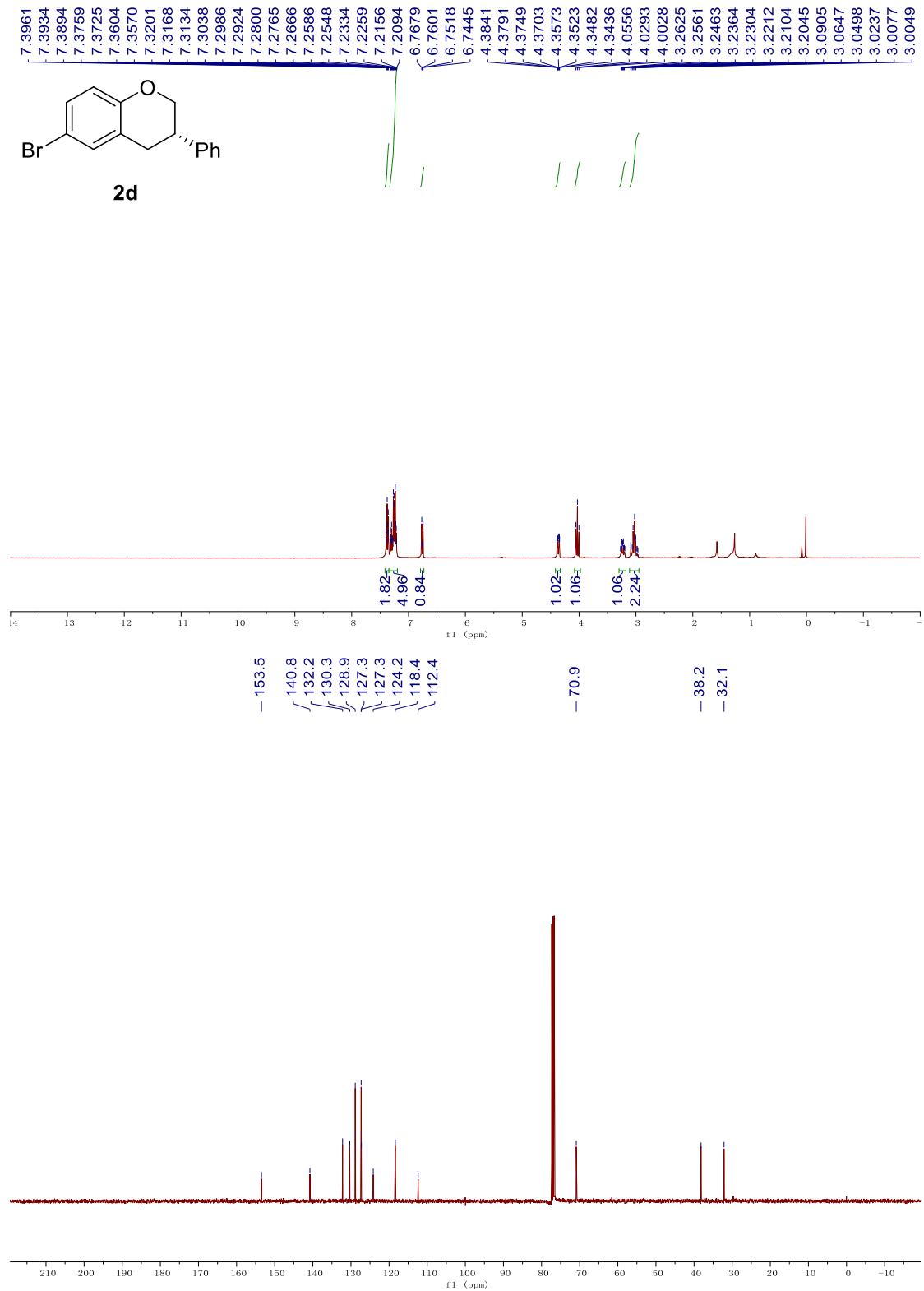


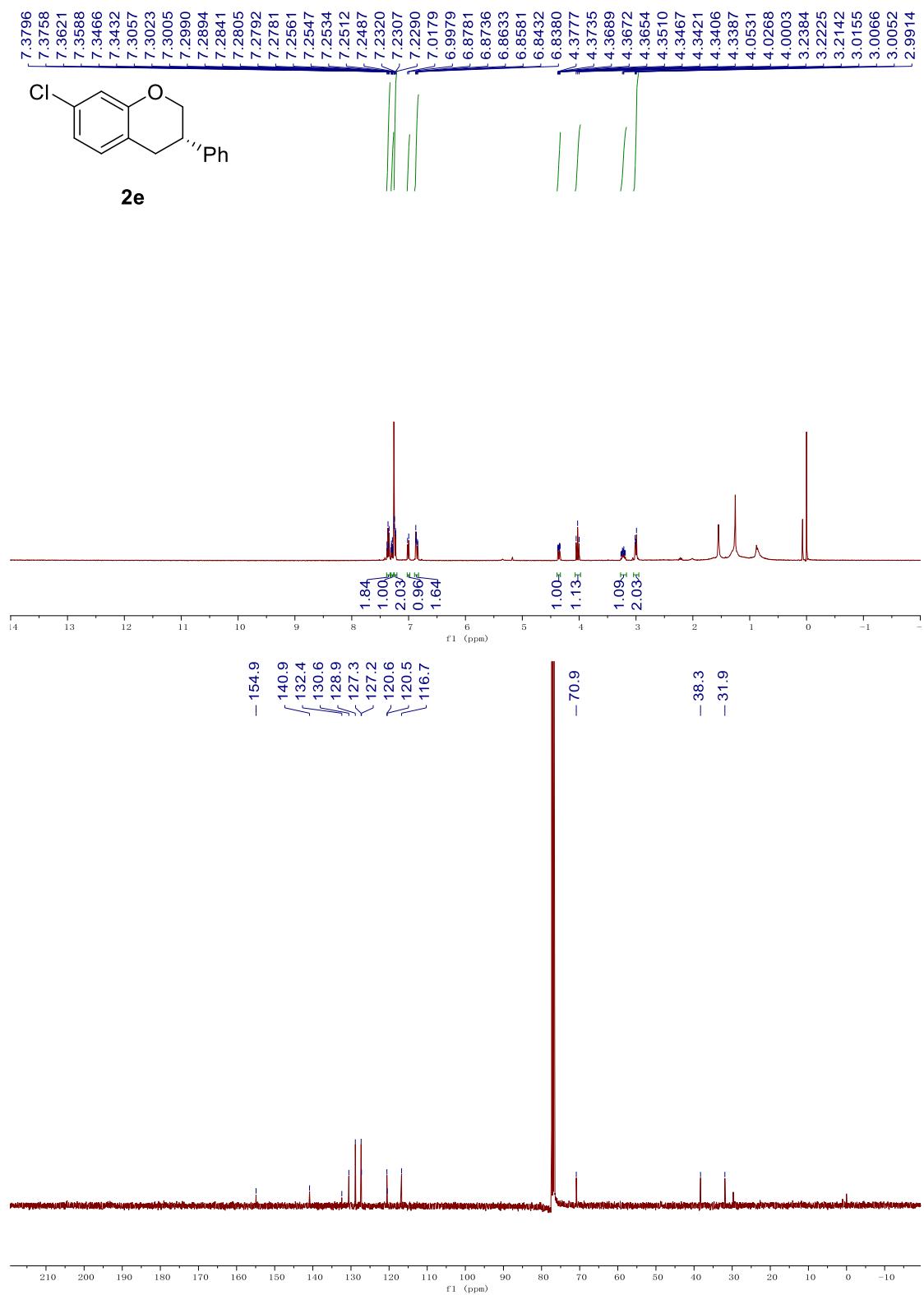


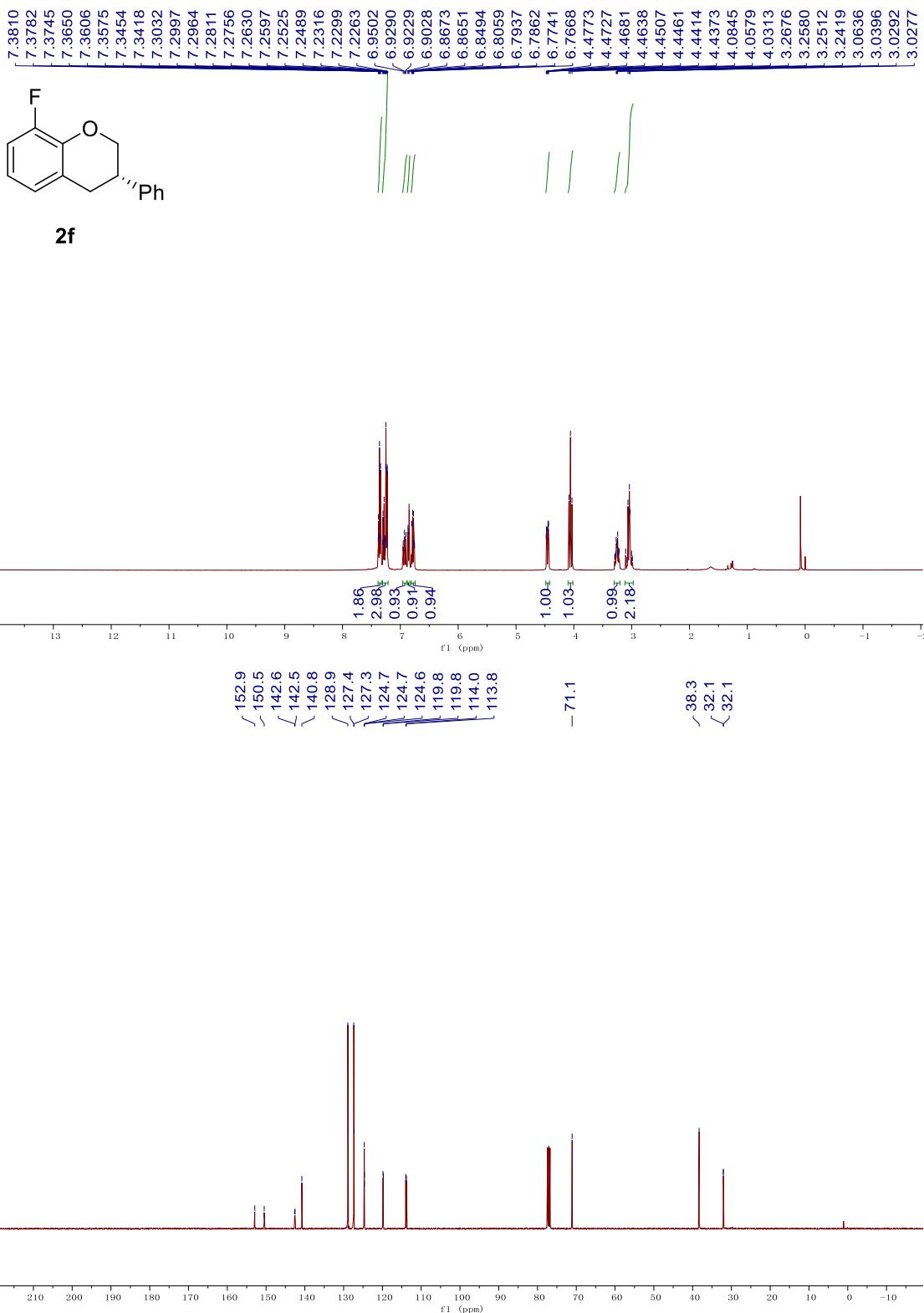


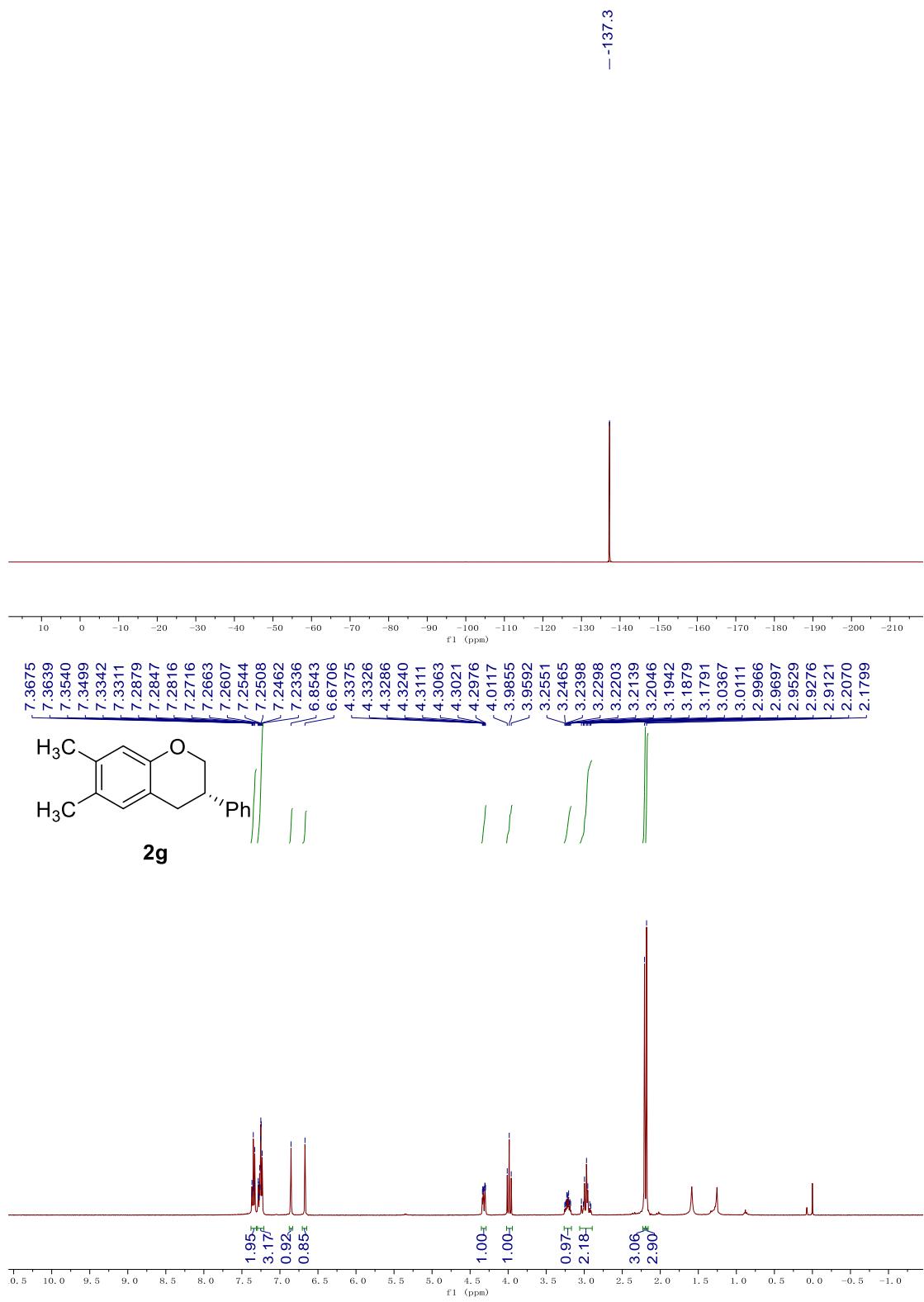


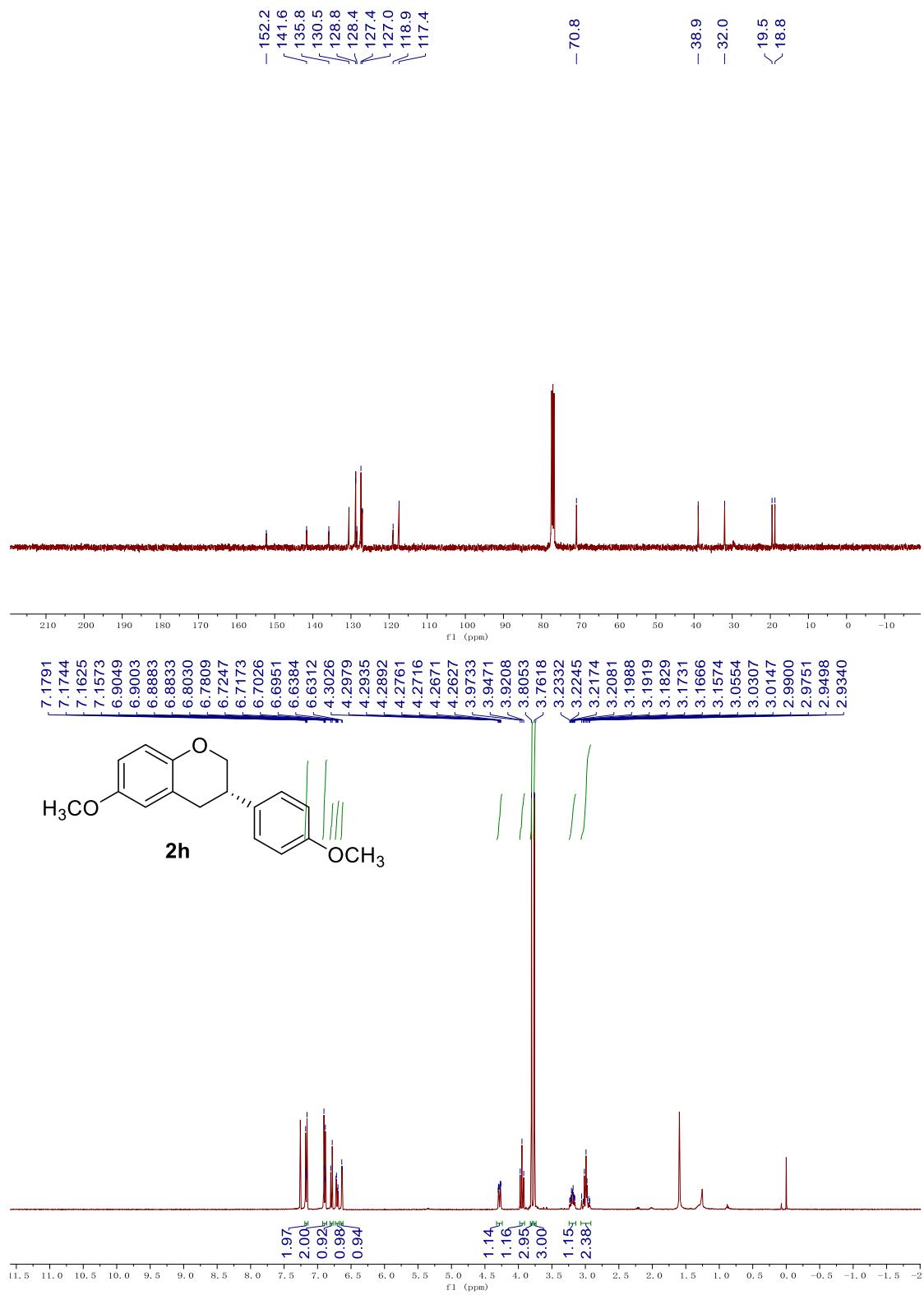


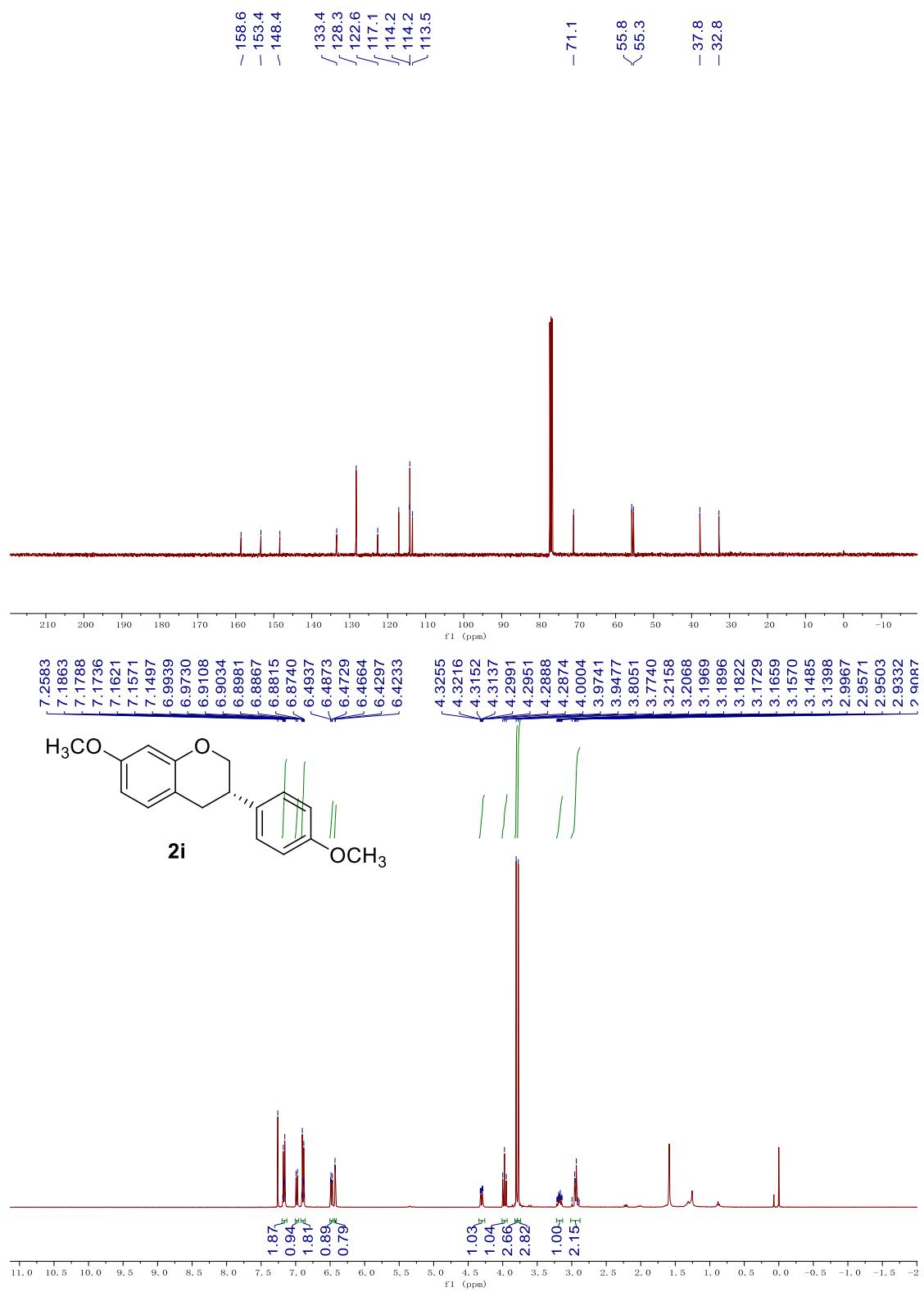


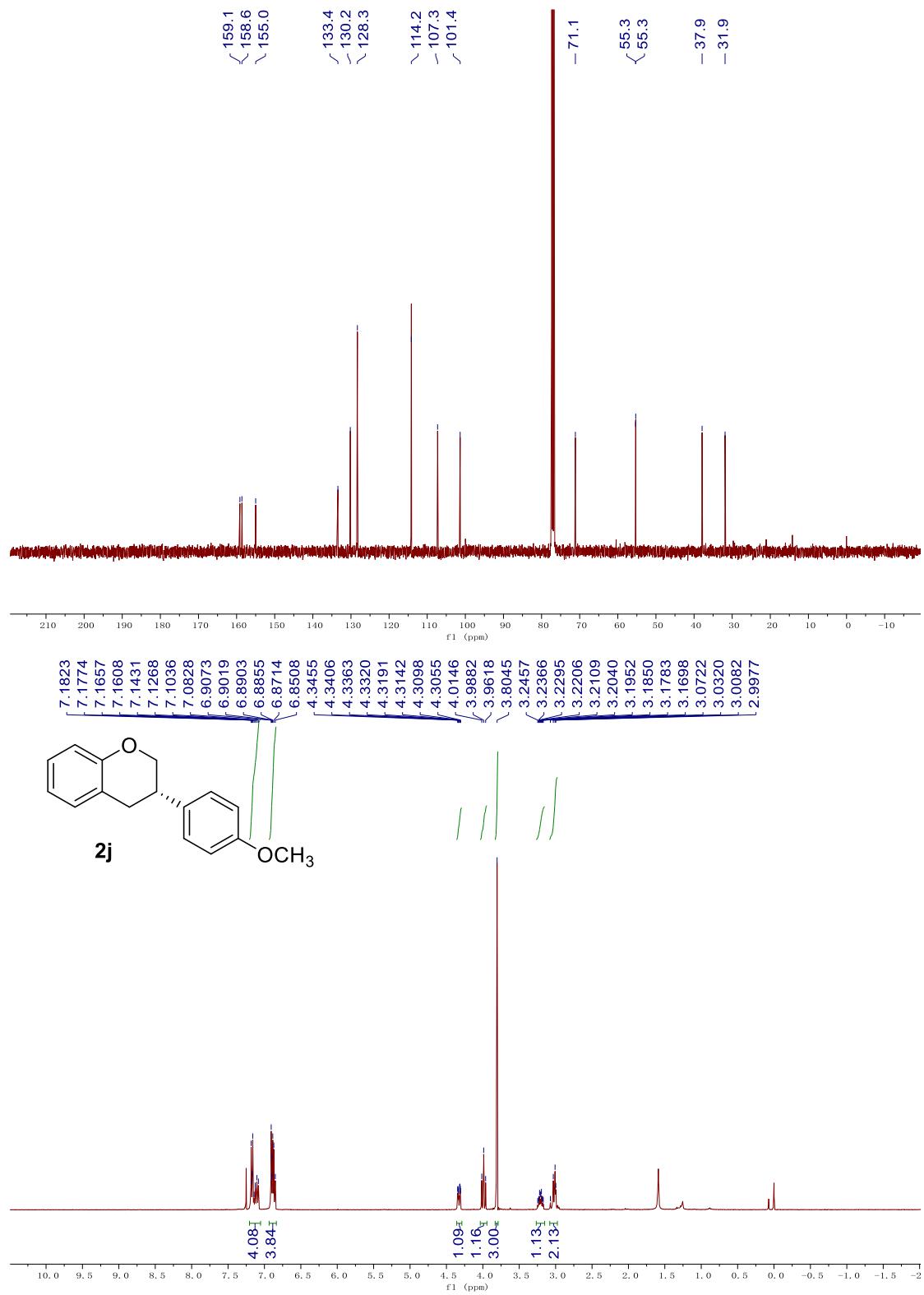


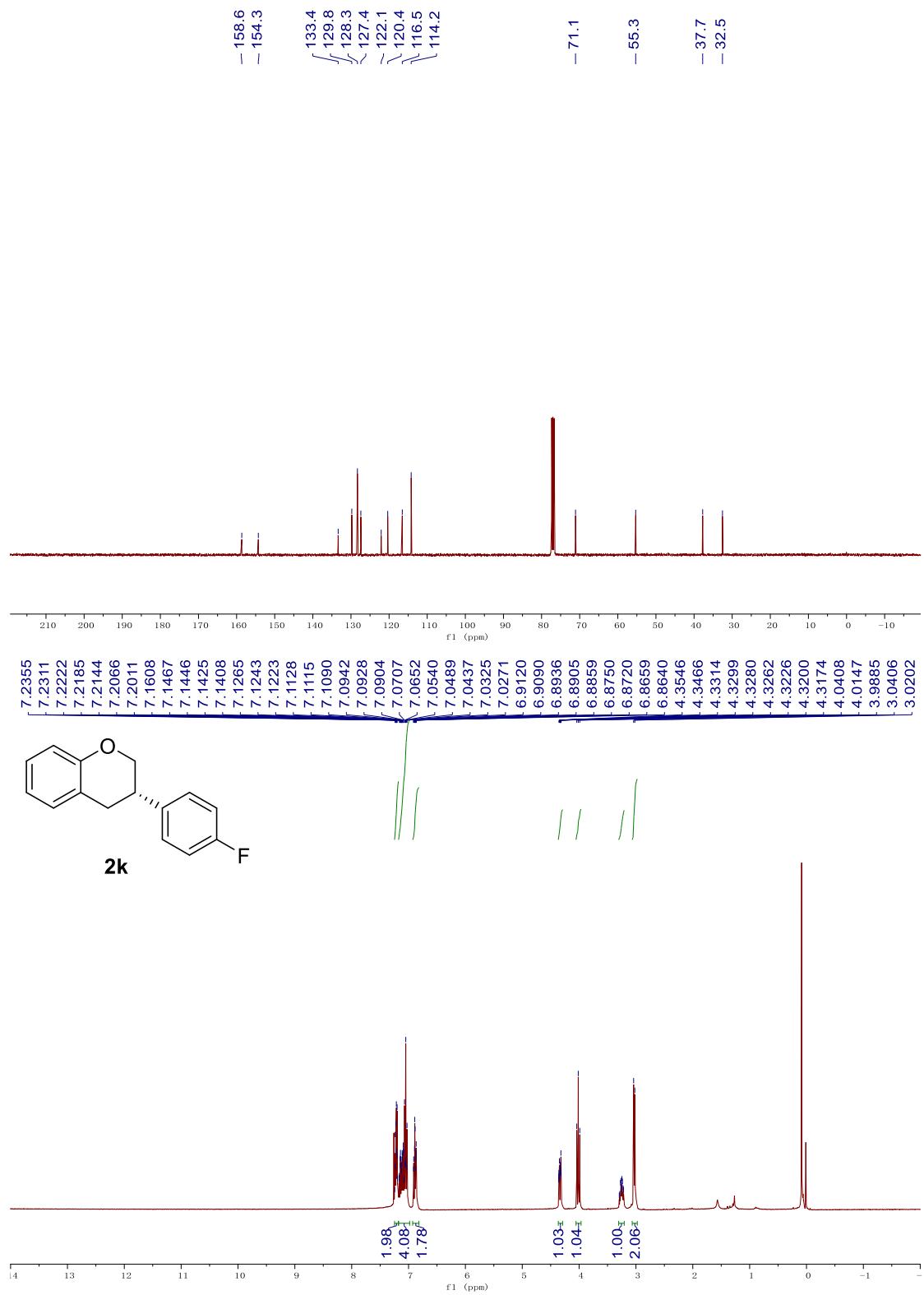


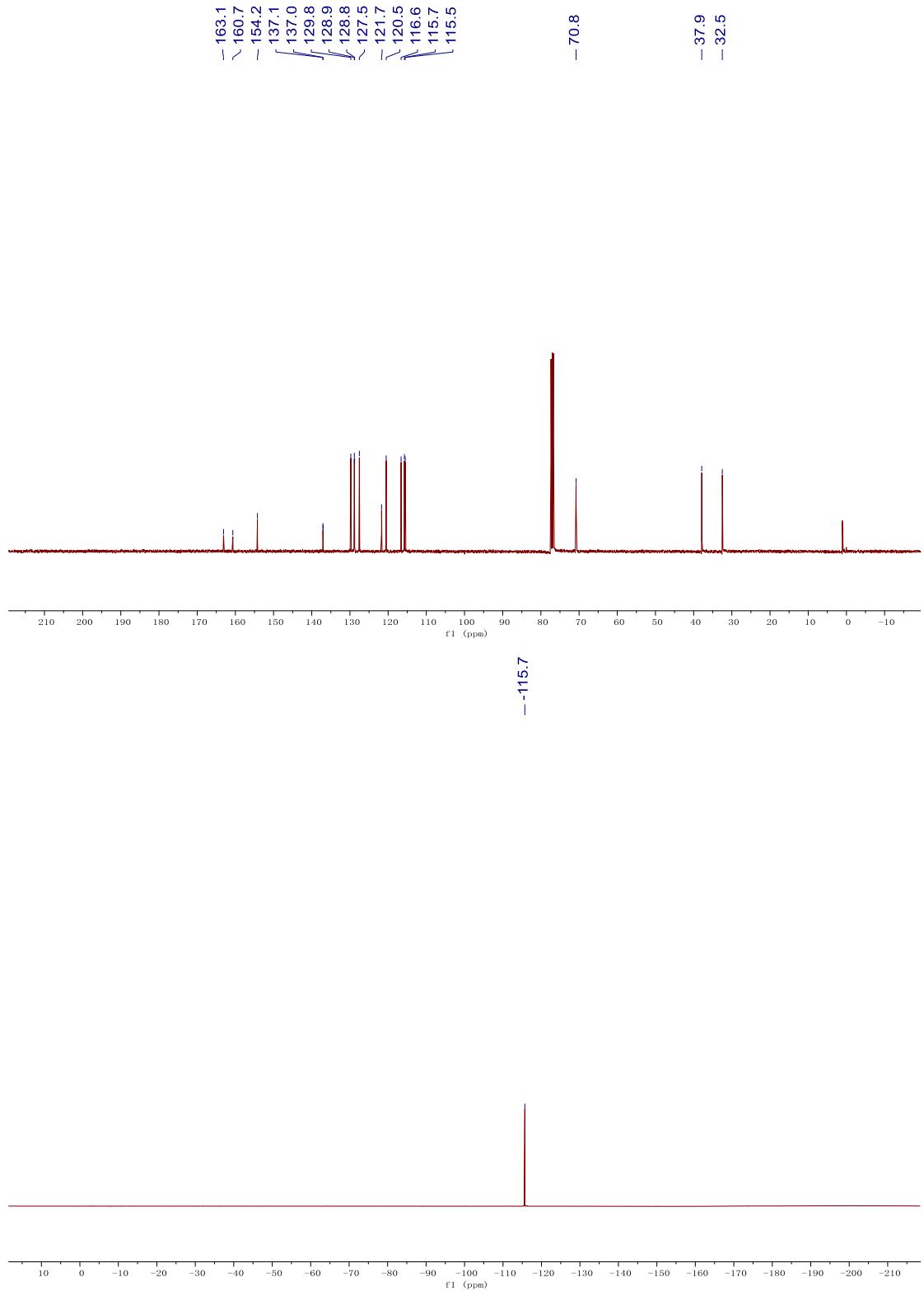


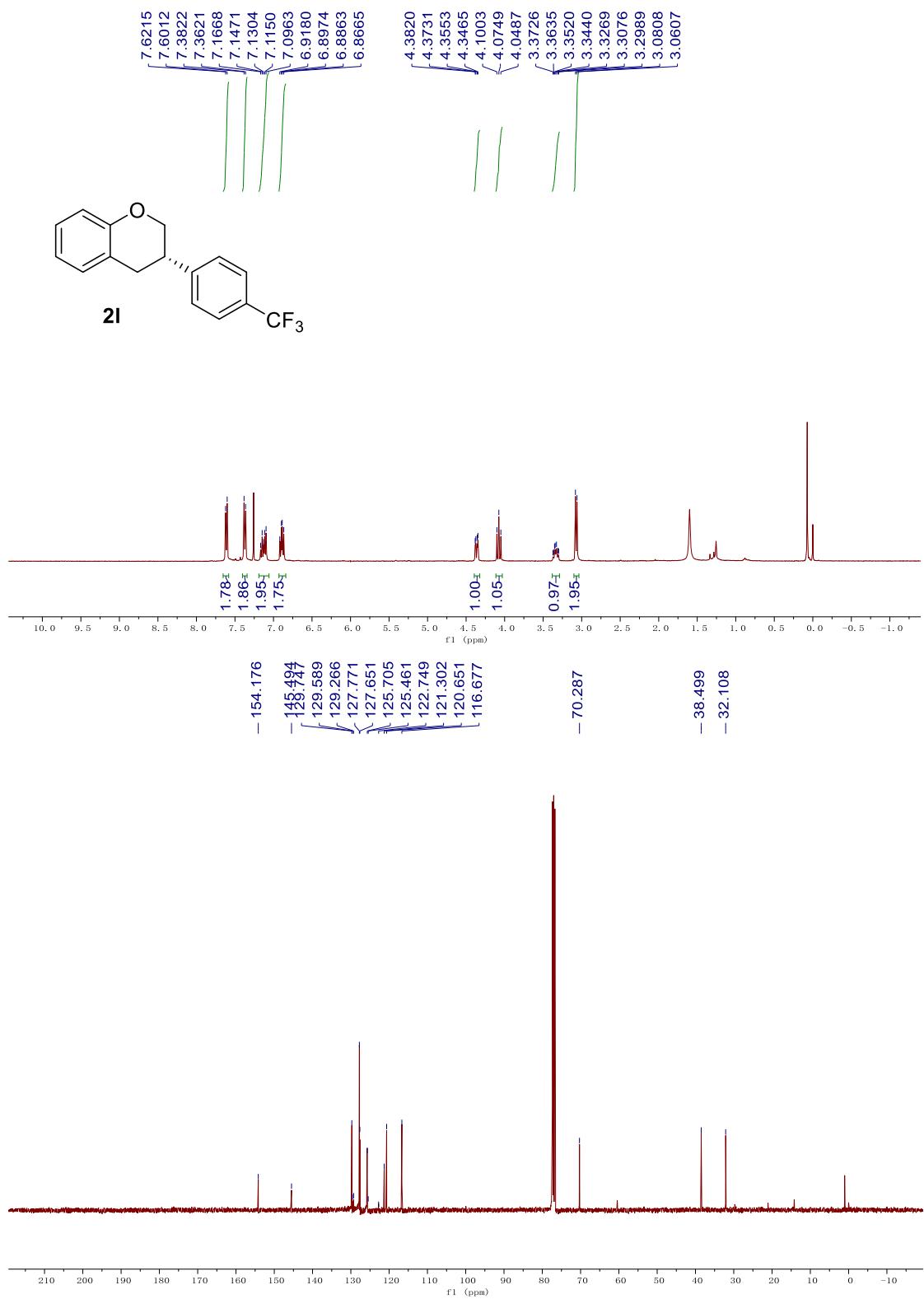


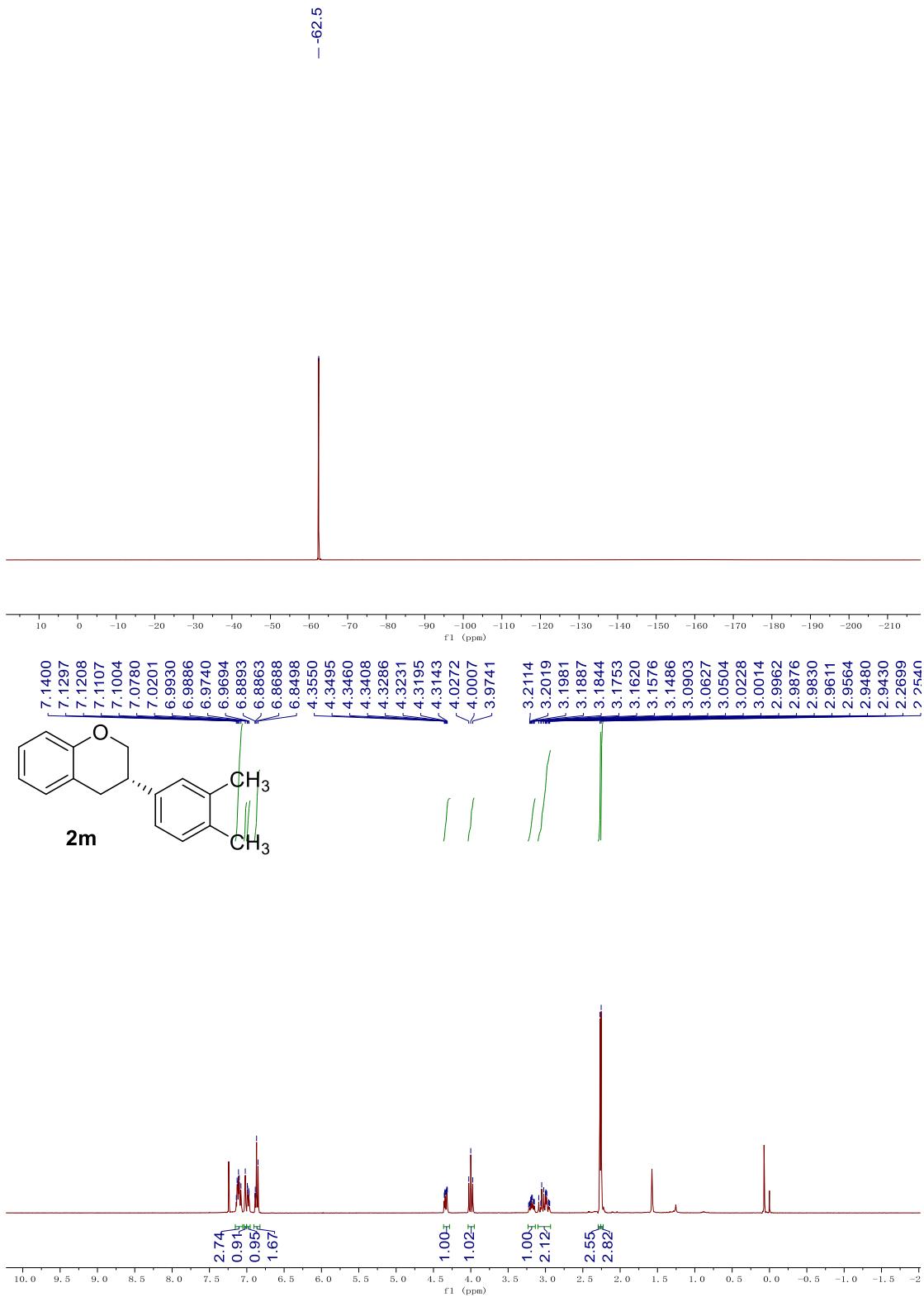


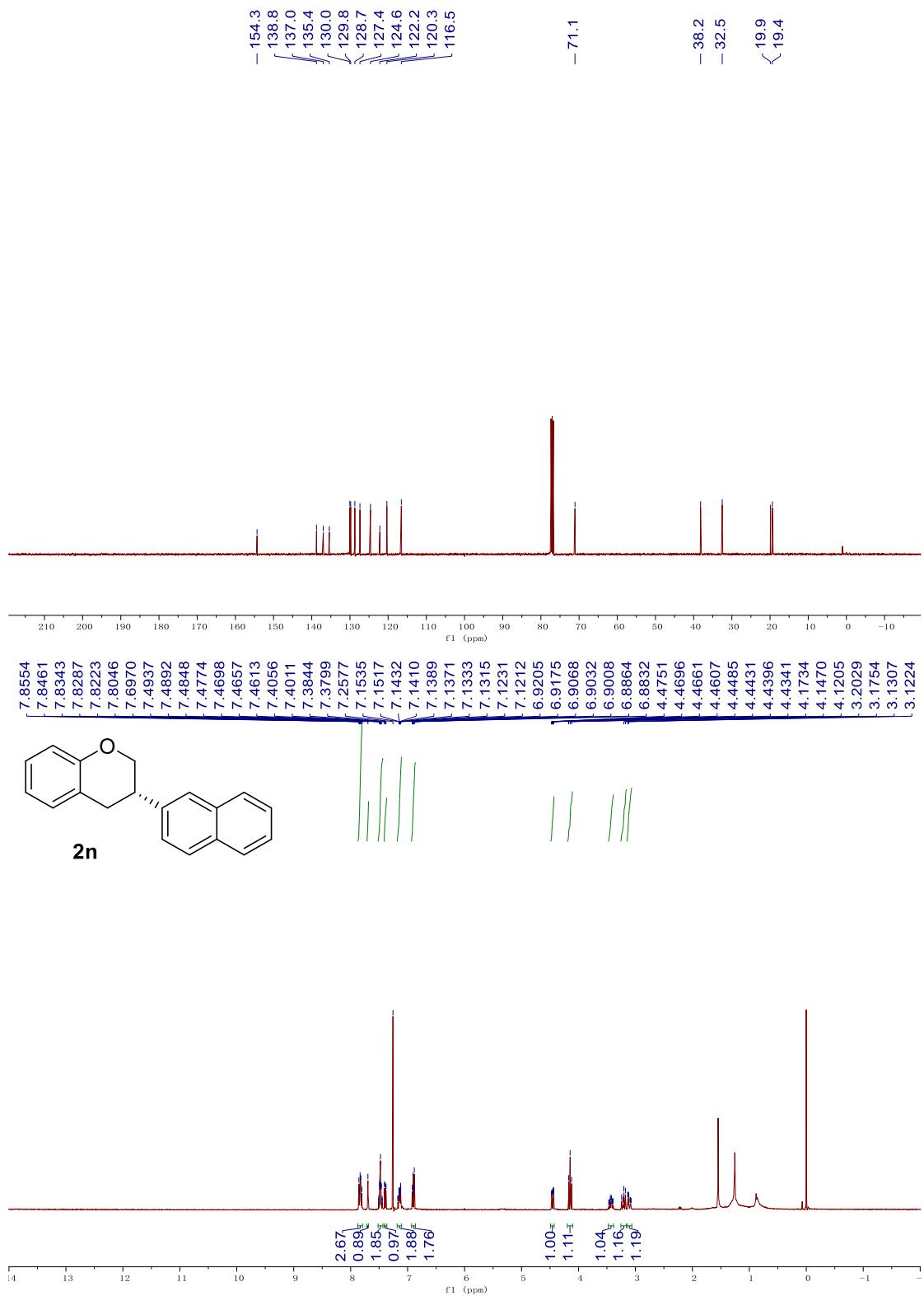


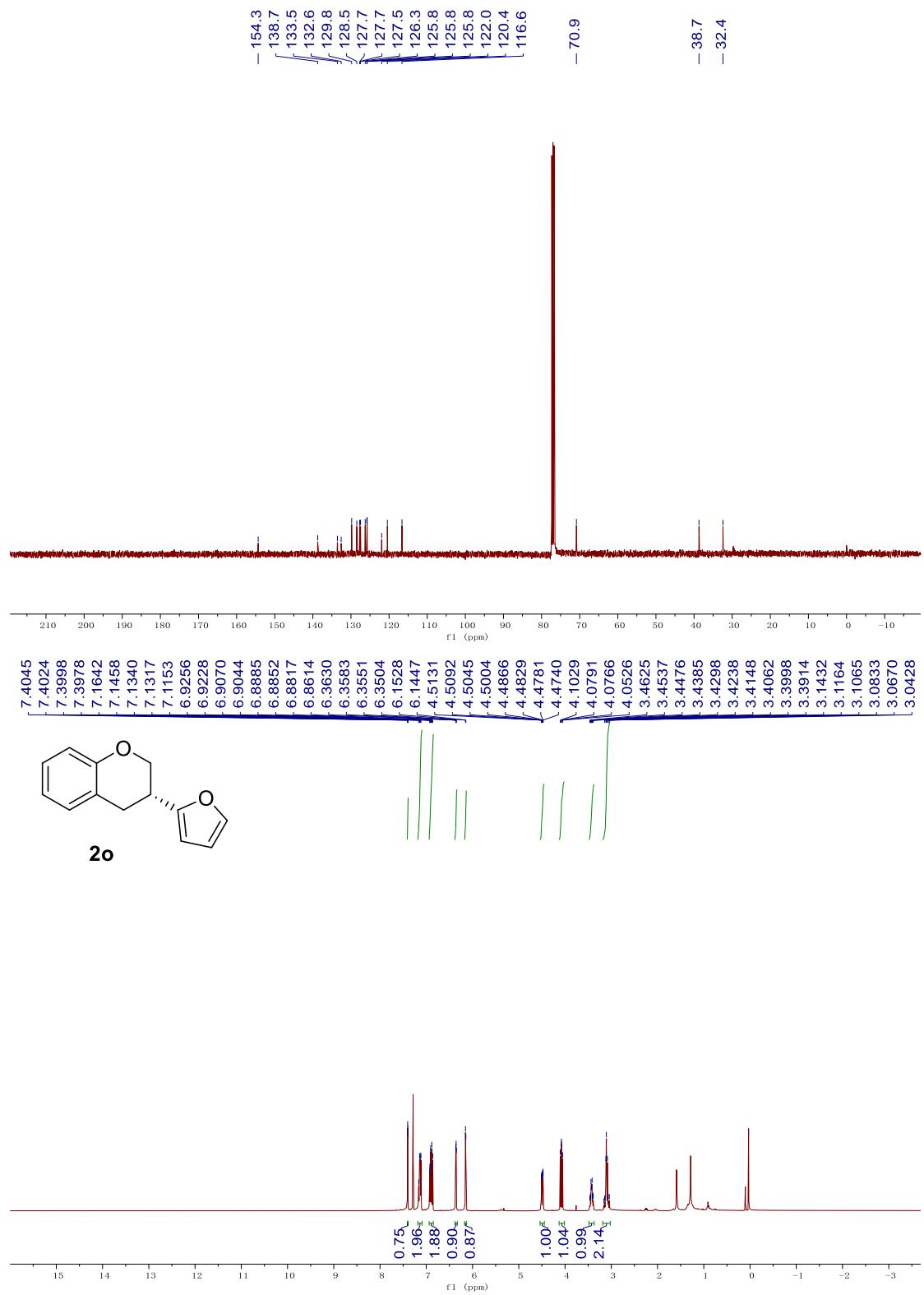


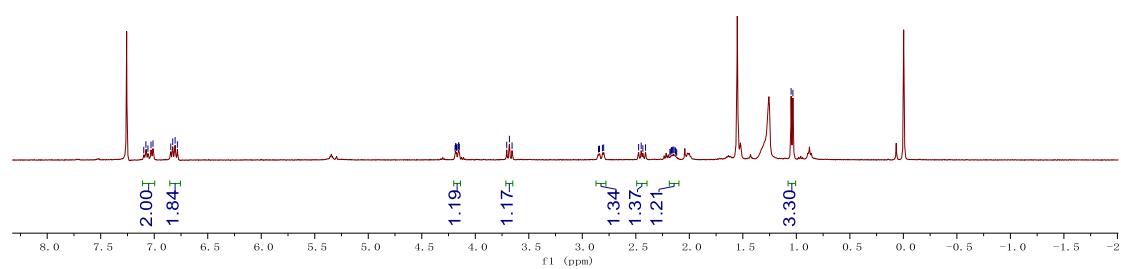
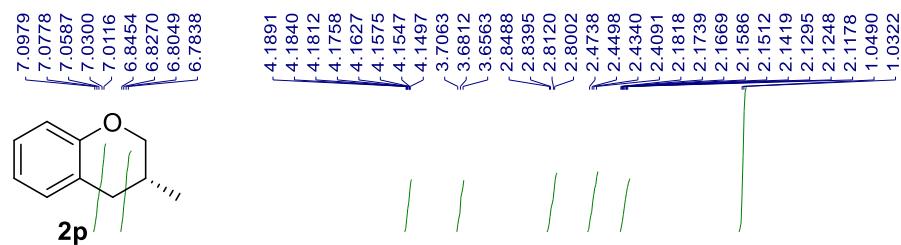
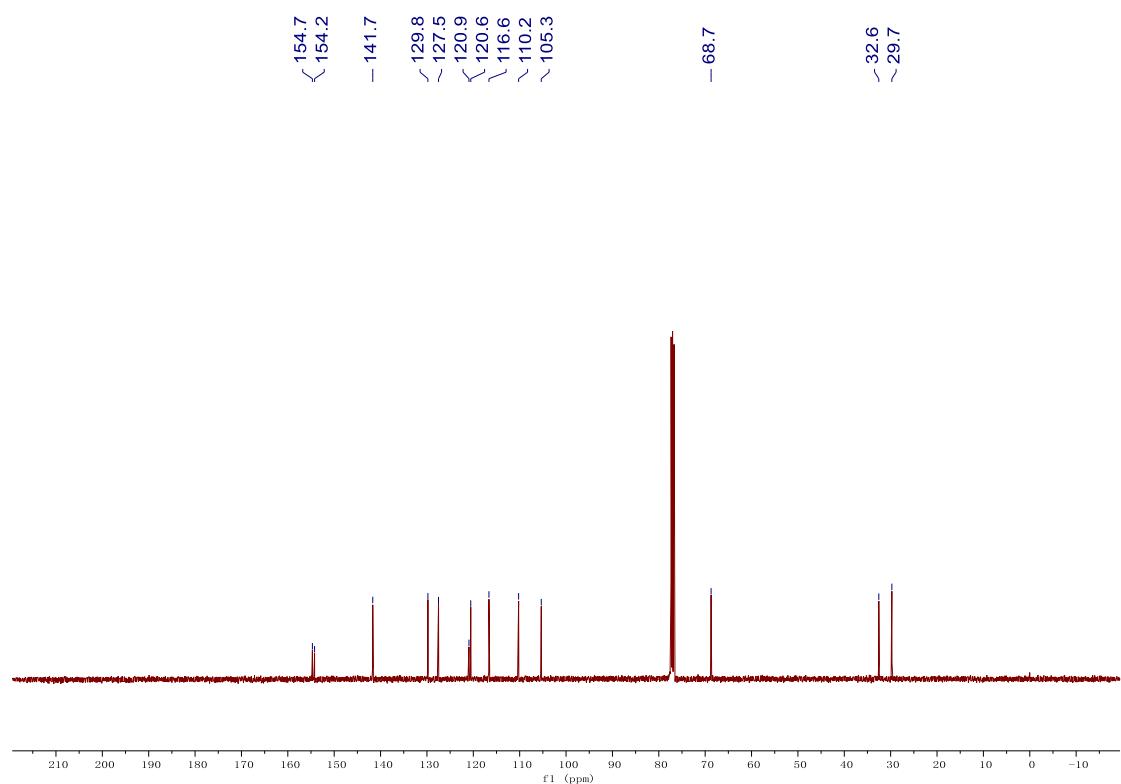


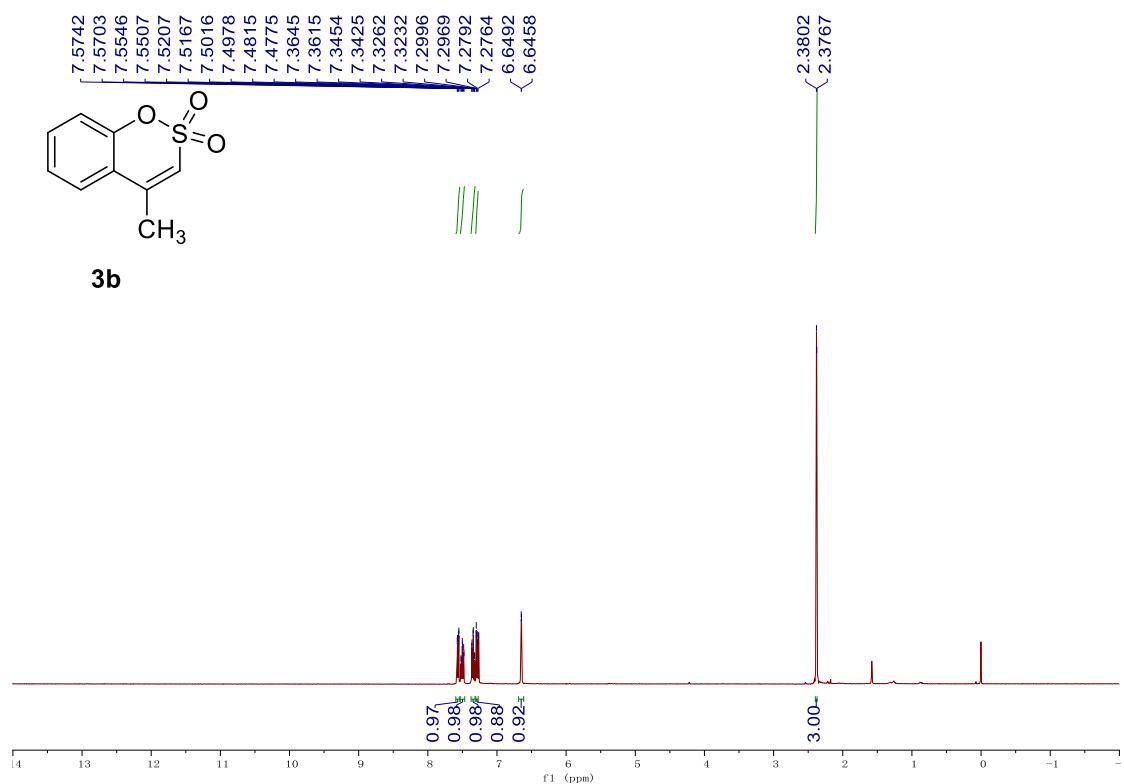
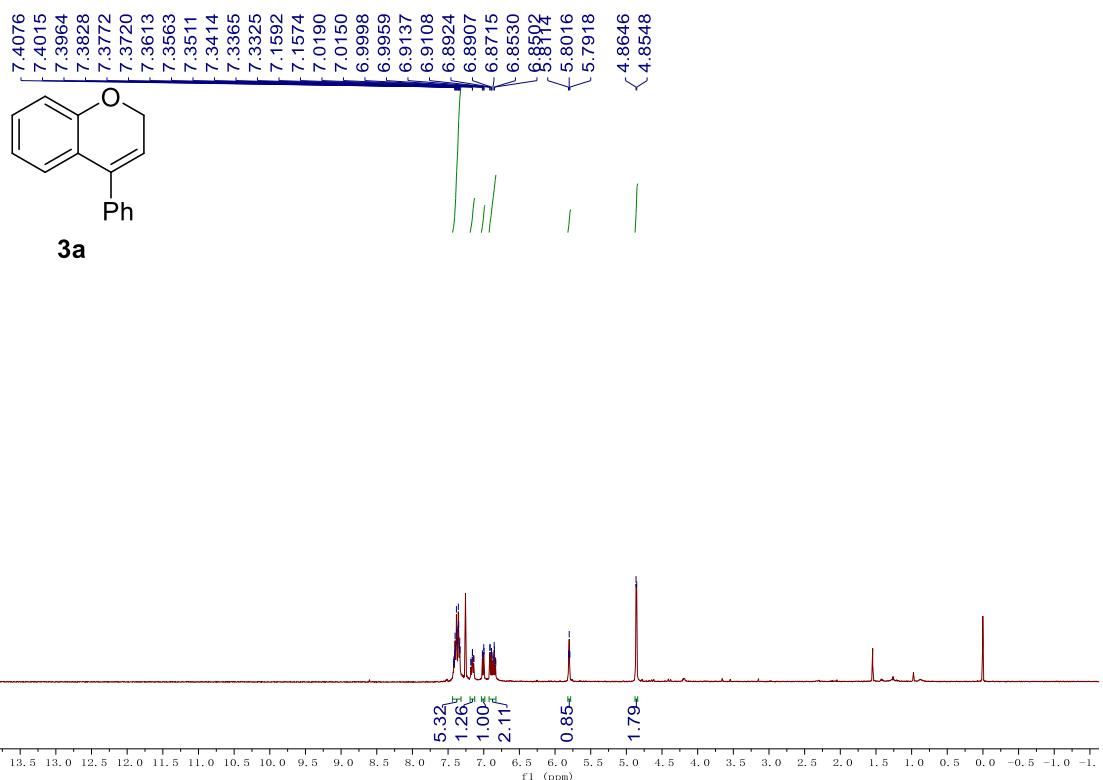


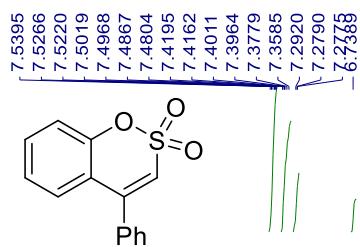
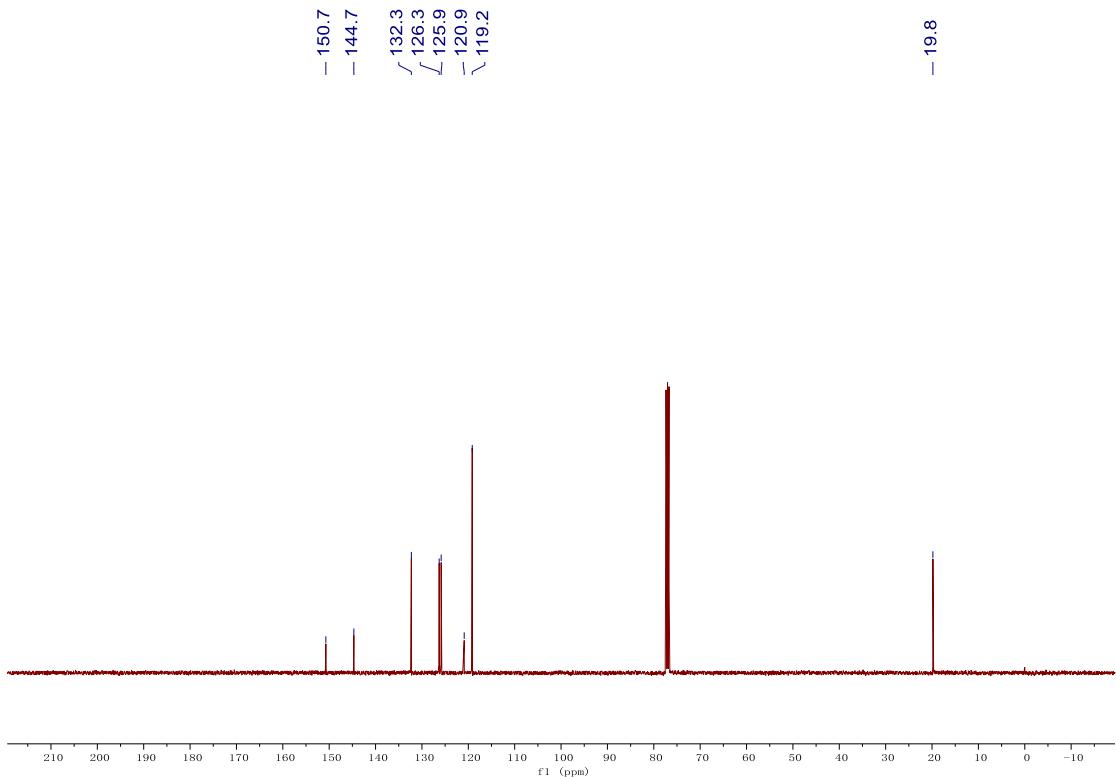




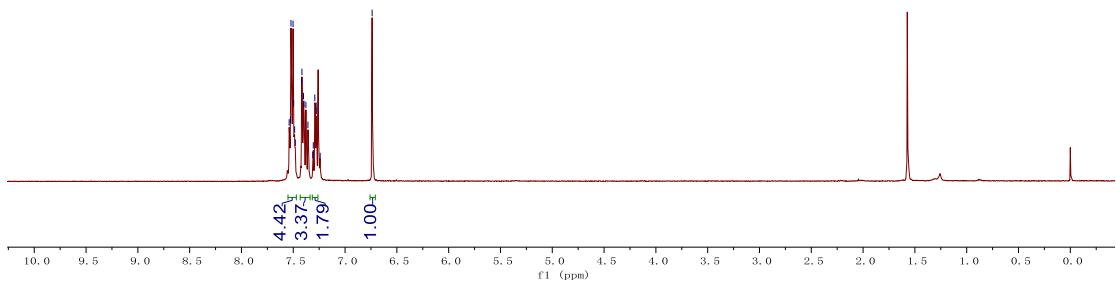


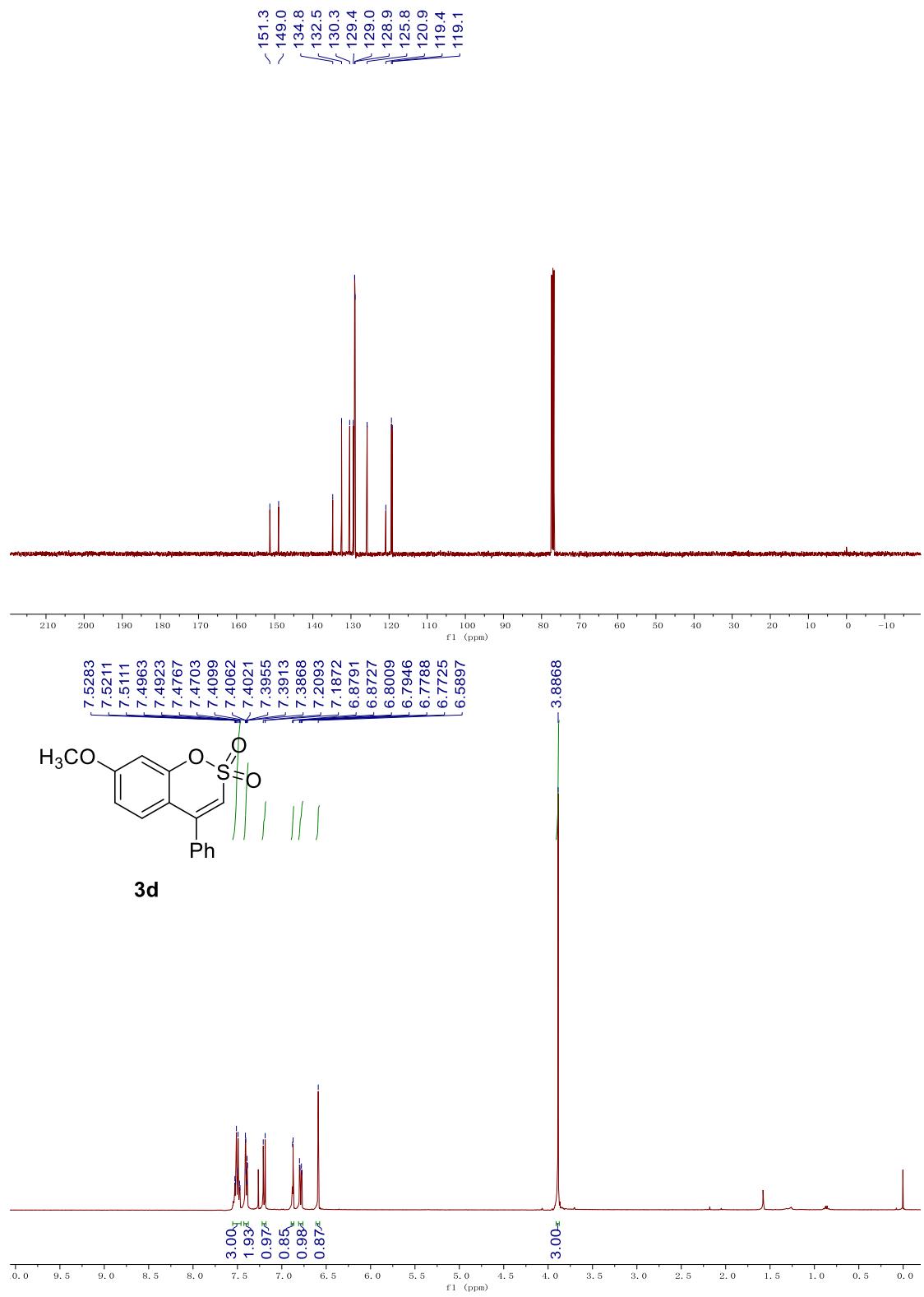


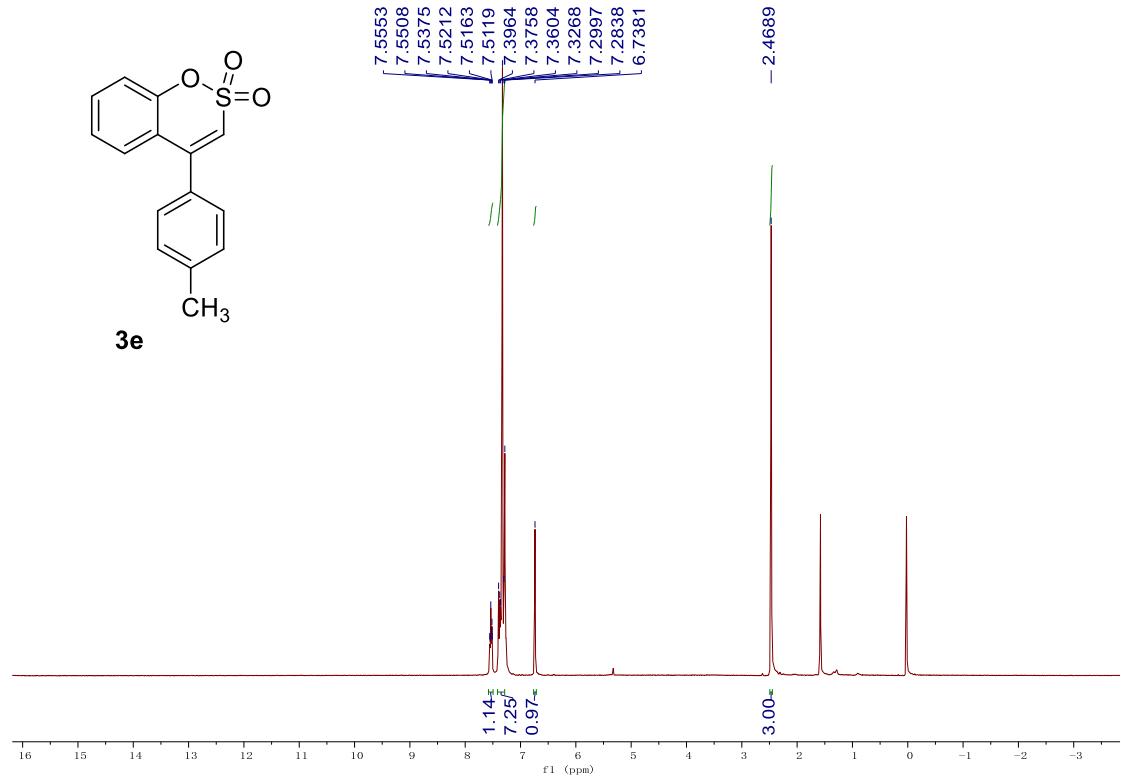
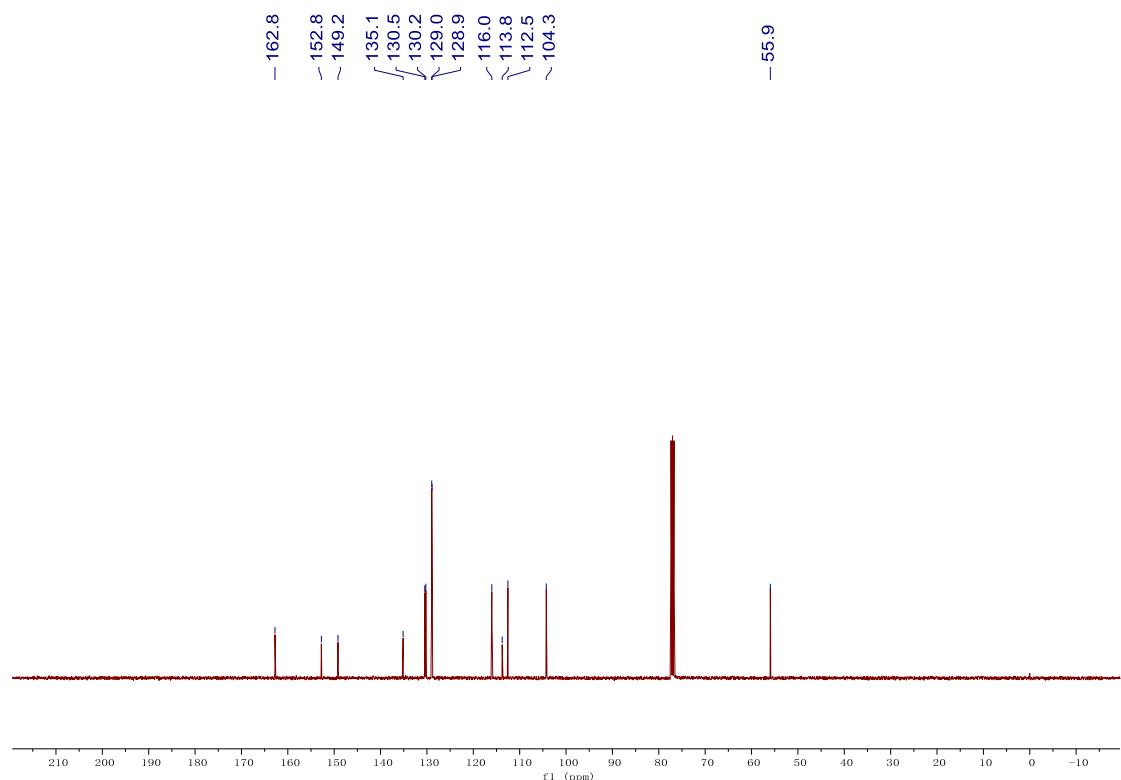




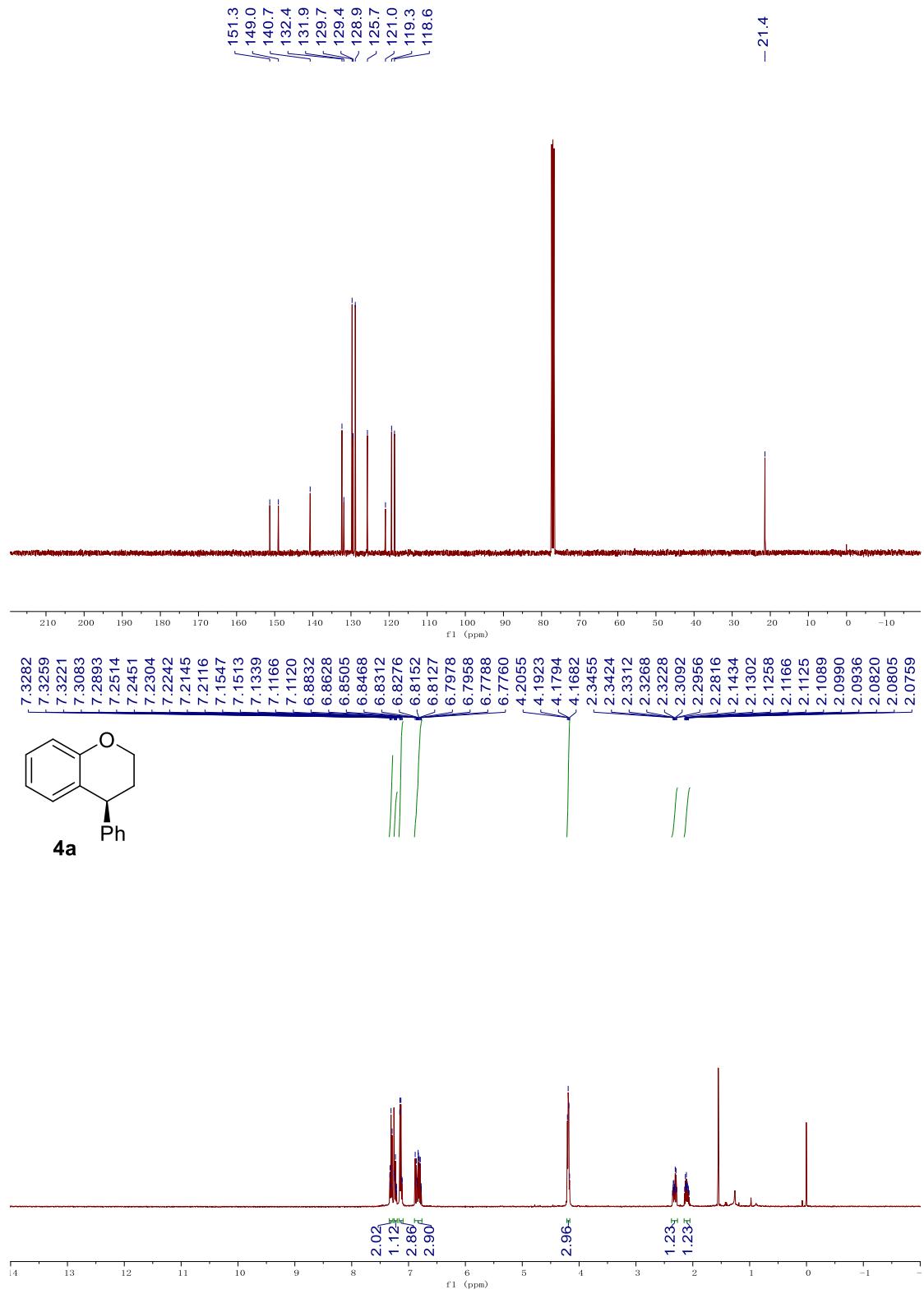
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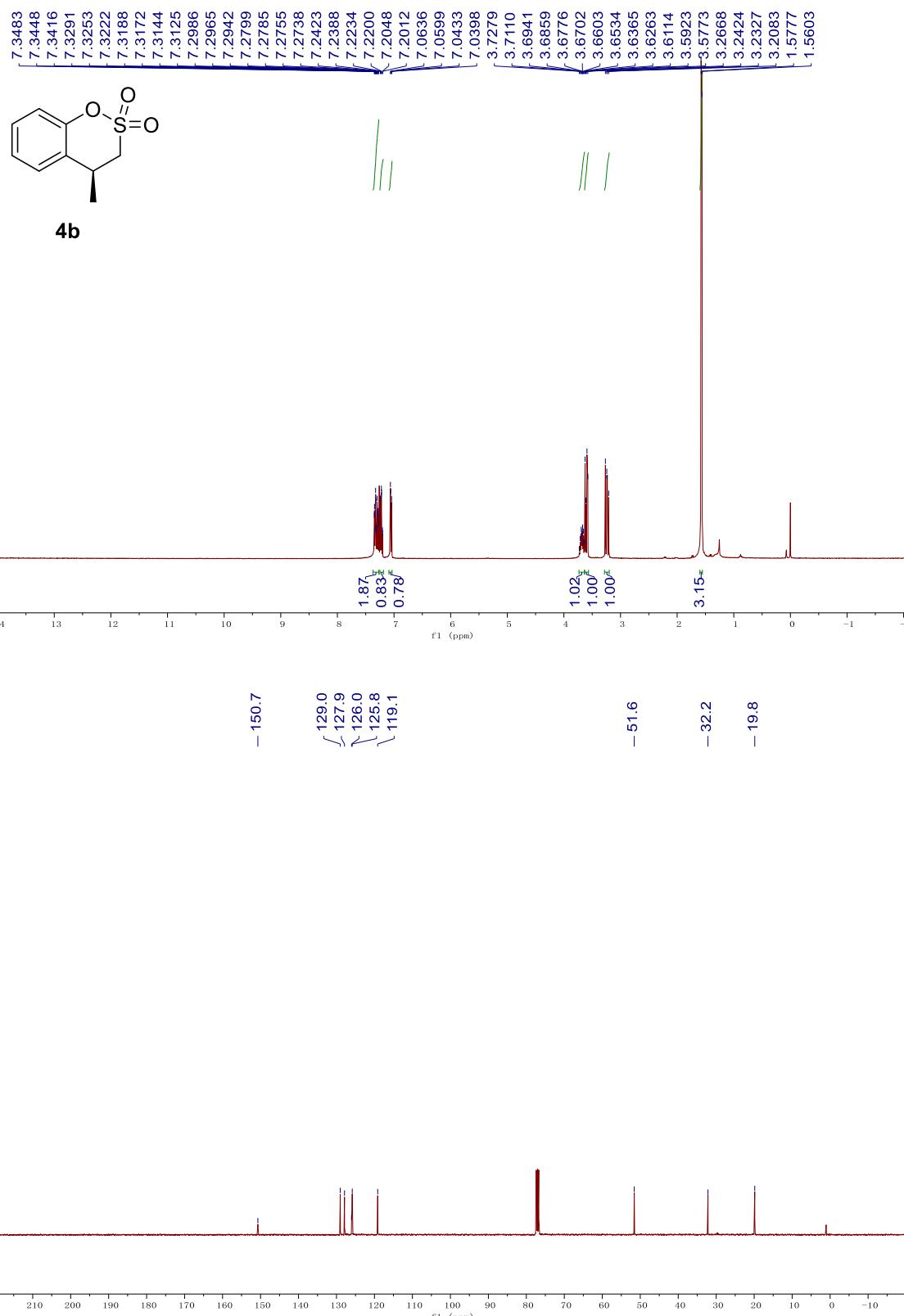


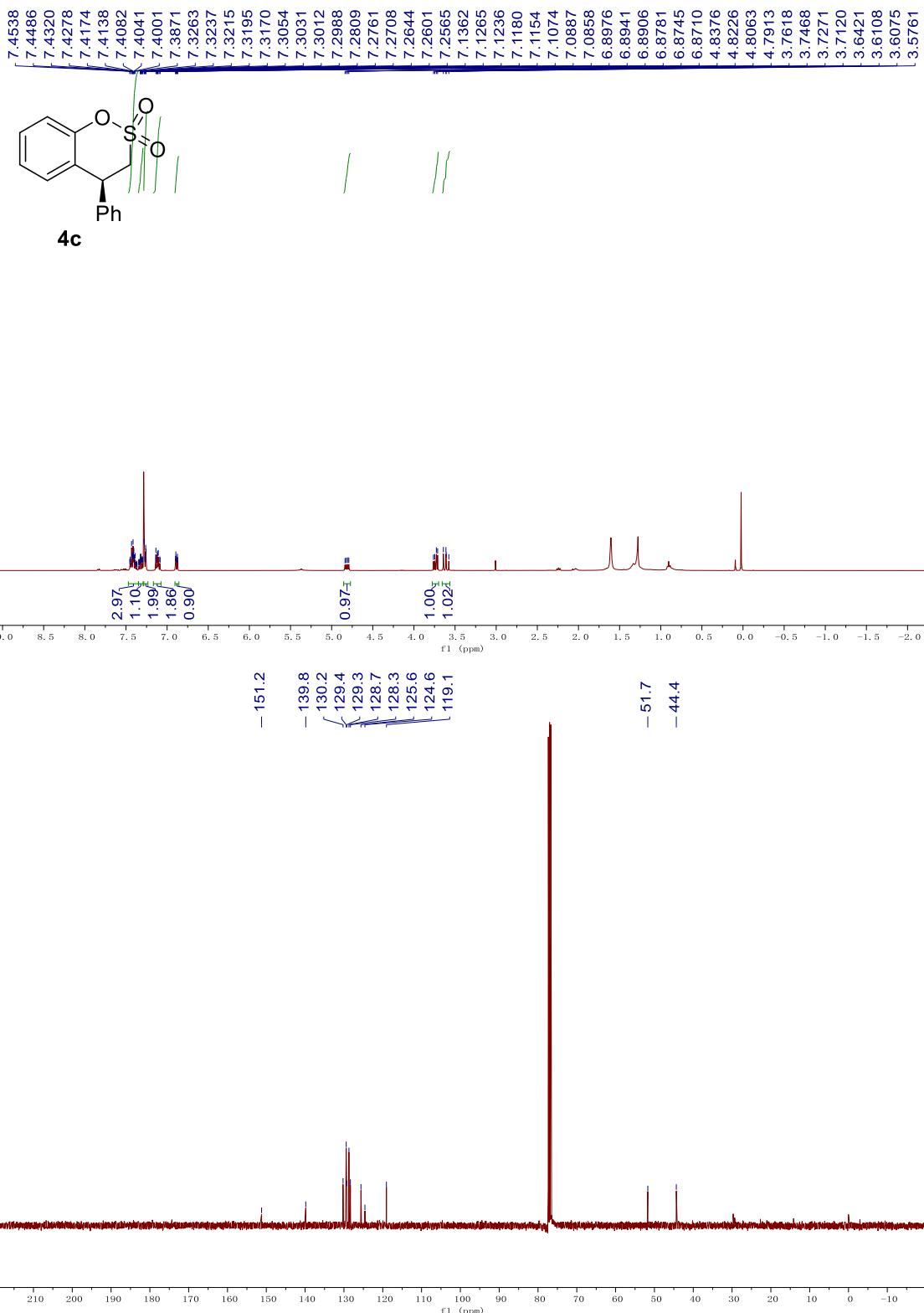


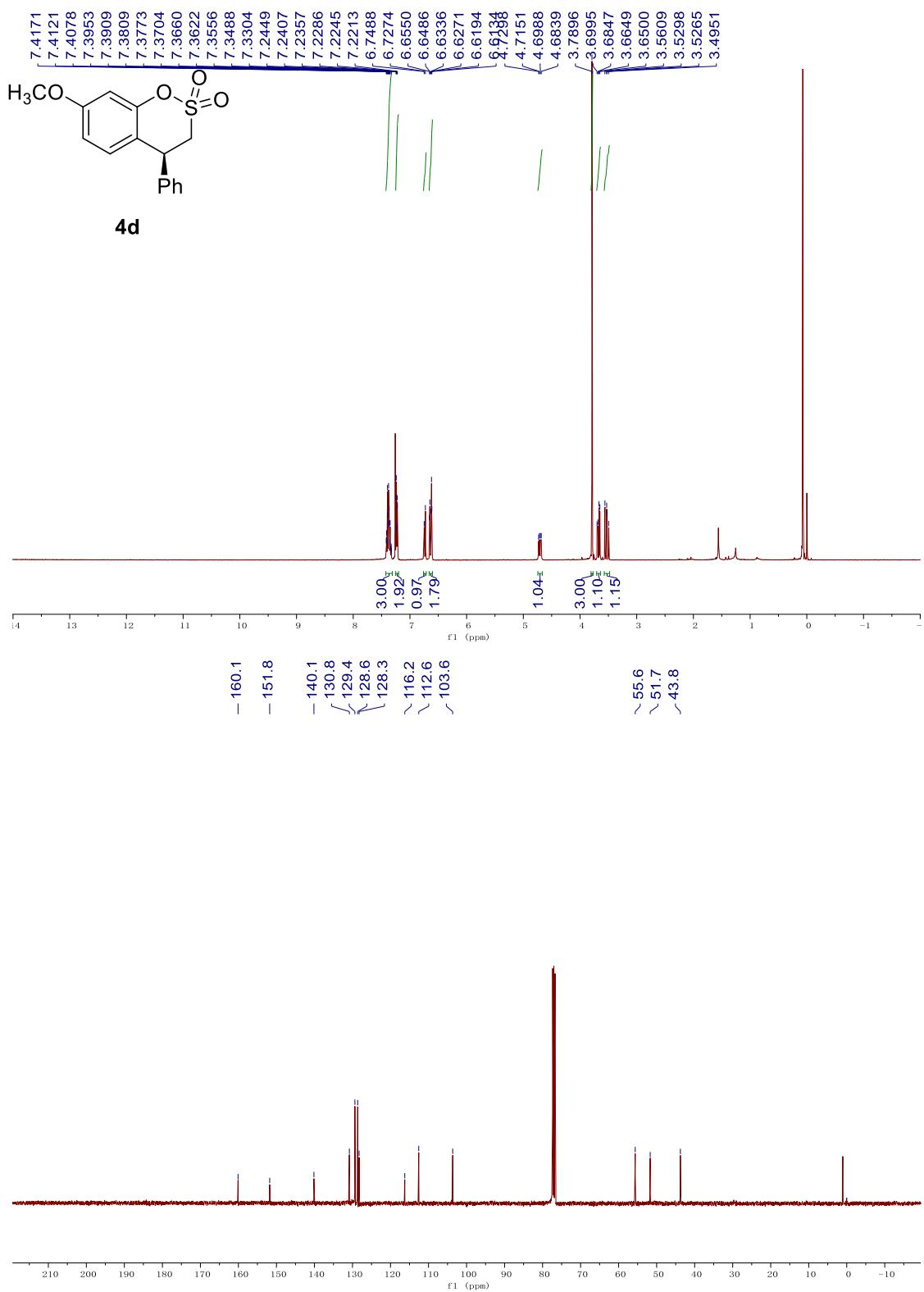


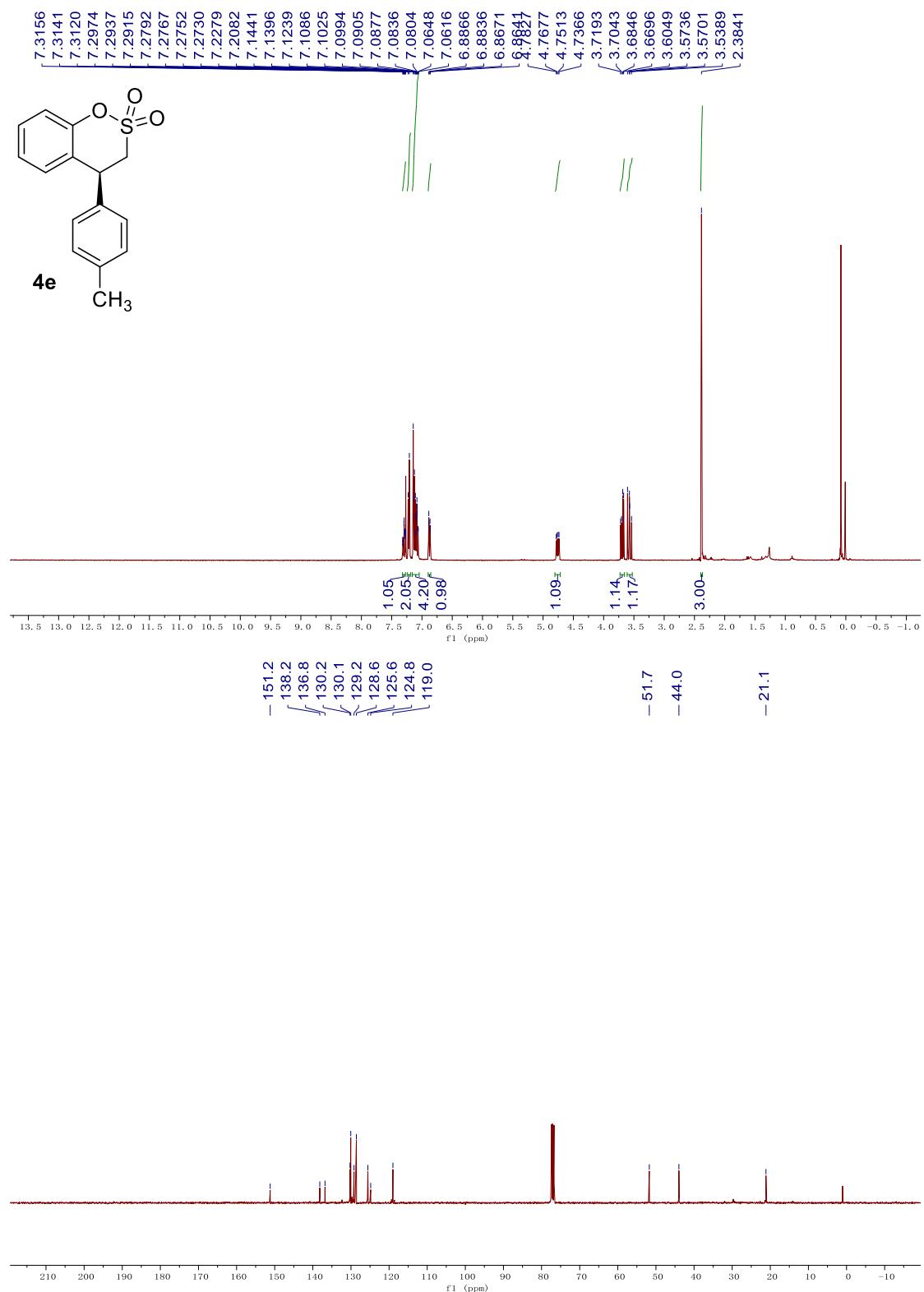
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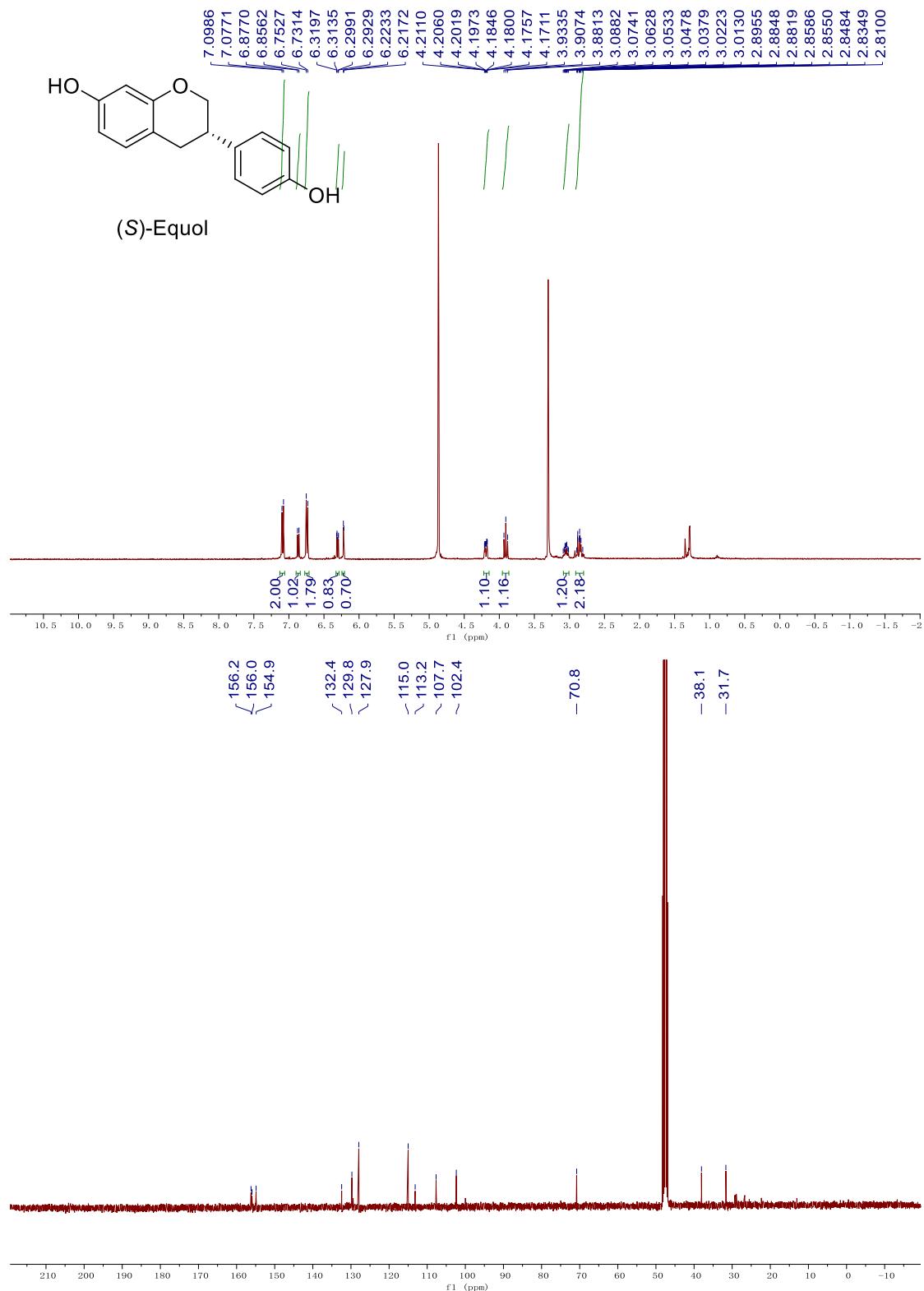


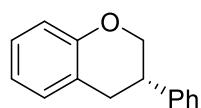




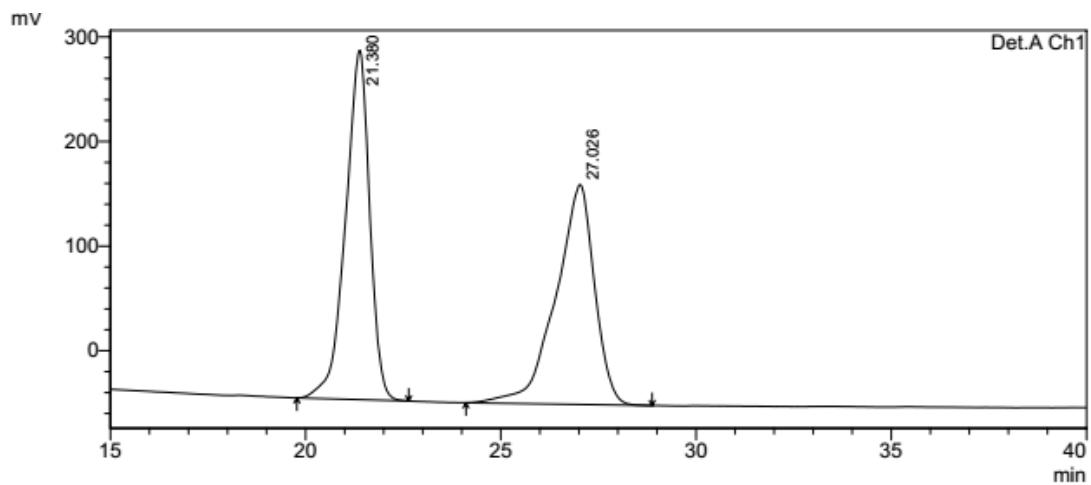








2a

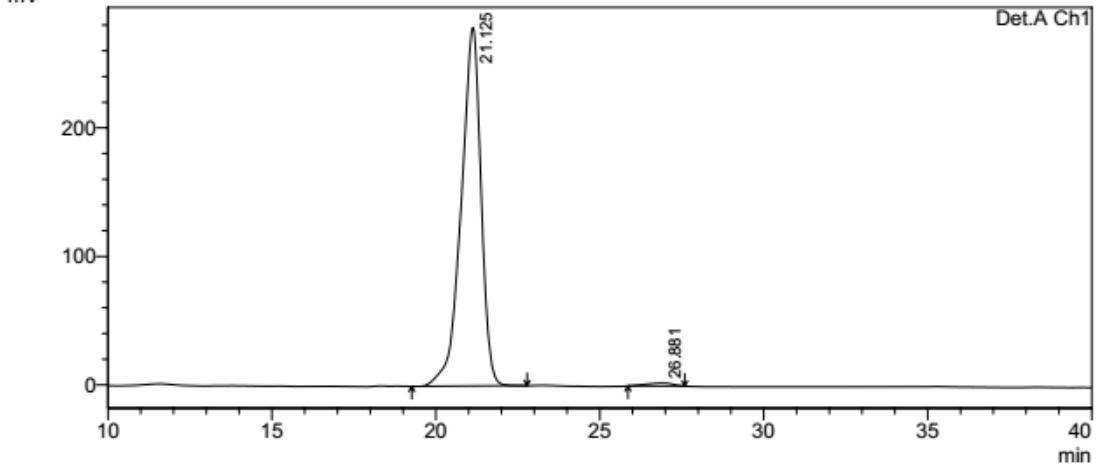


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.380	14371286	333812	49.869	61.378
2	27.026	14446741	210053	50.131	38.622
Total		28818027	543865	100.000	100.000

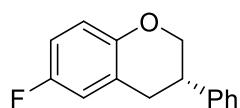
mV



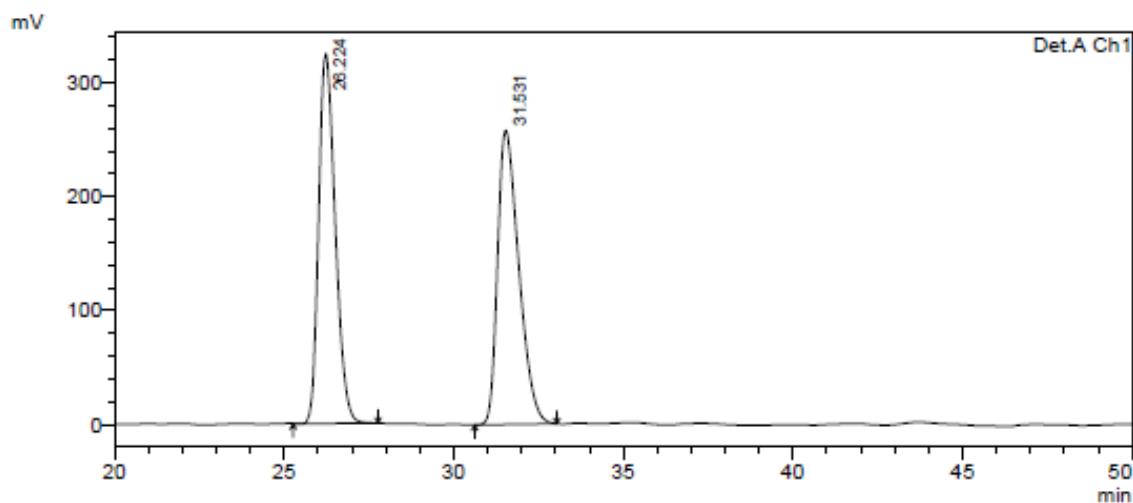
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.125	11713364	278887	98.889	99.170
2	26.881	131542	2333	1.111	0.830
Total		11844906	281220	100.000	100.000



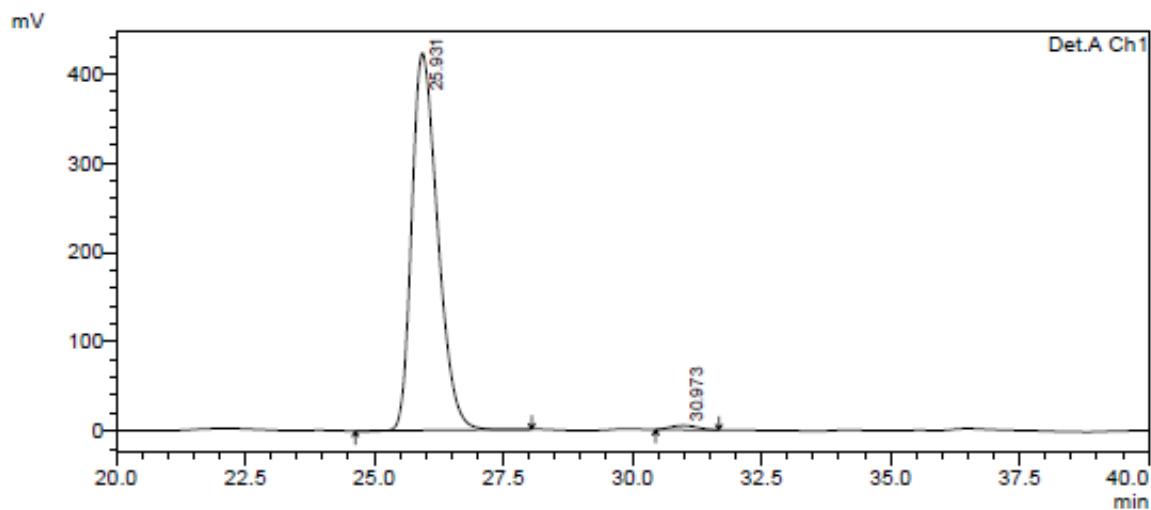
2b



PeakTable

Detector A Ch1 210nm

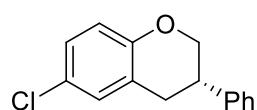
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.224	11055938	324883	49.628	55.711
2	31.531	11221771	258279	50.372	44.289
Total		22277709	583161	100.000	100.000



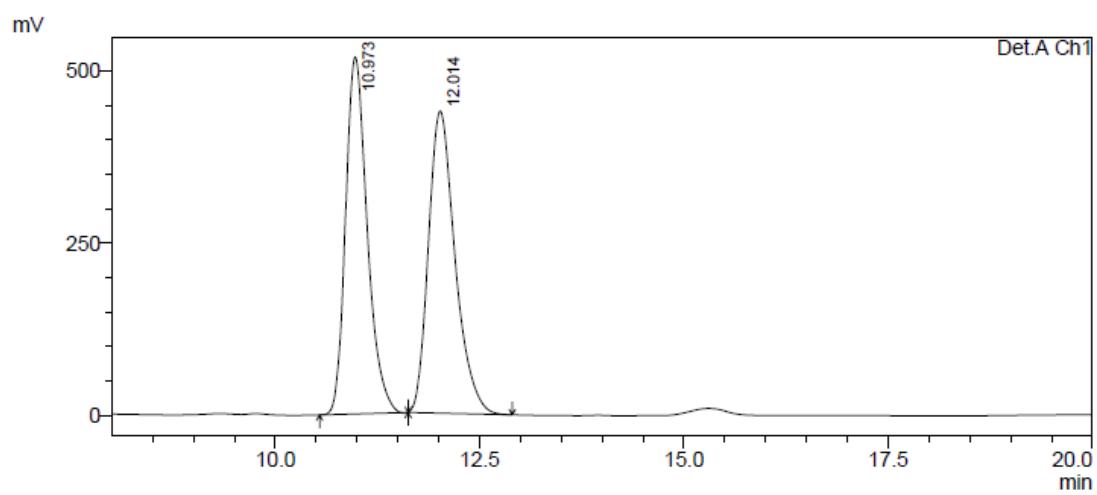
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.931	14711179	422545	98.854	98.883
2	30.973	170608	4774	1.146	1.117
Total		14881787	427319	100.000	100.000



2c

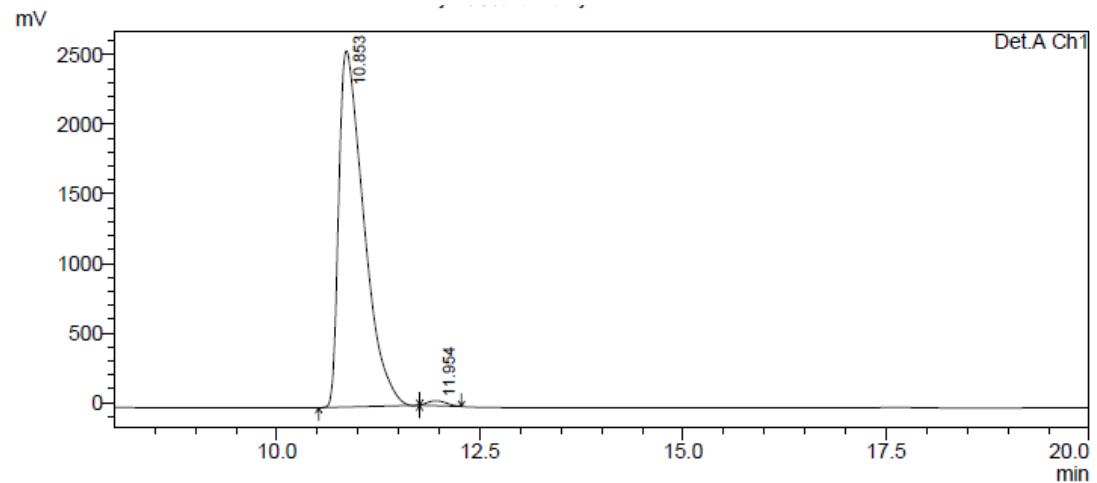


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.973	9551721	518227	49.021	54.149
2	12.014	9933178	438809	50.979	45.851
Total		19484899	957036	100.000	100.000

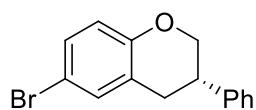


1 Det.A Ch1/210nm

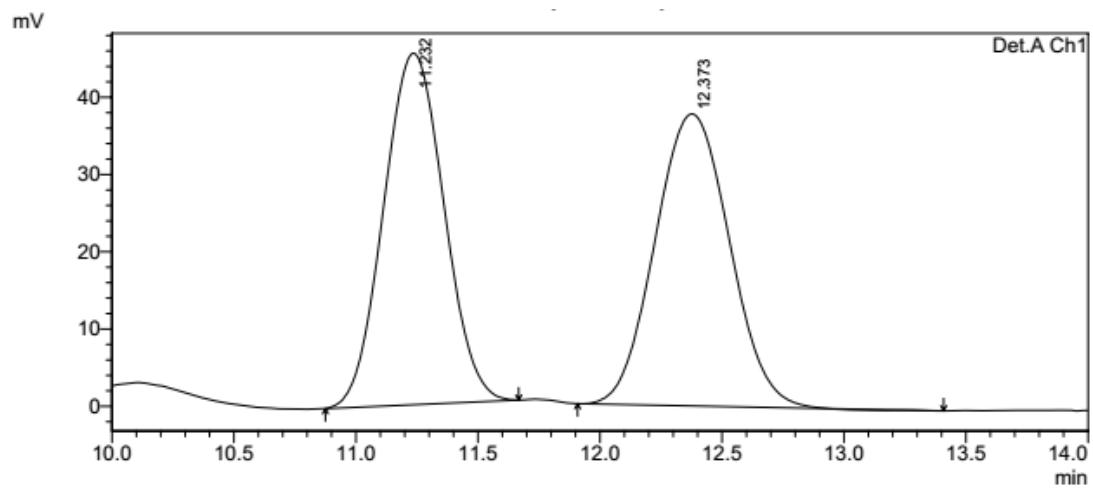
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.853	54877402	2559888	98.983	98.648
2	11.954	564041	35079	1.017	1.352
Total		55441443	2594968	100.000	100.000



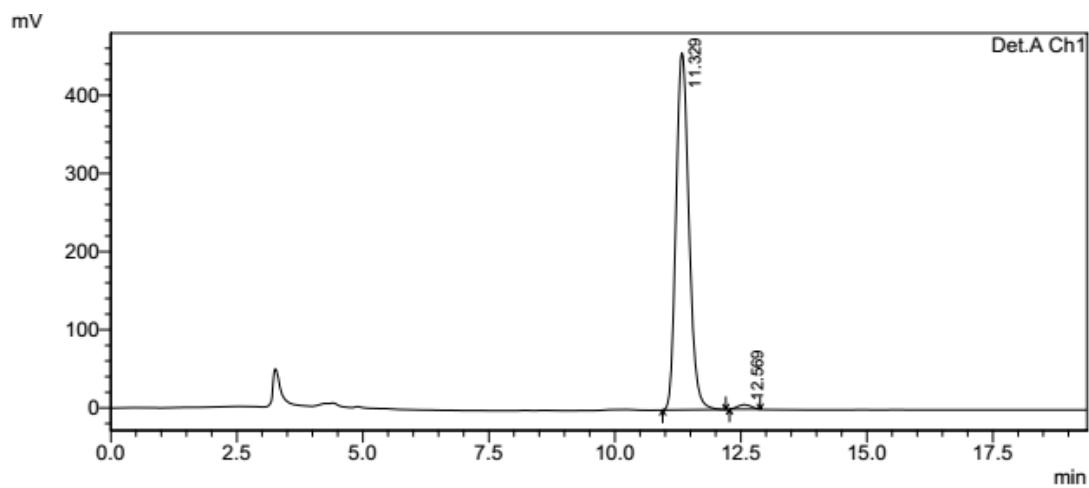
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PeakTable

Detector A Ch1 210nm

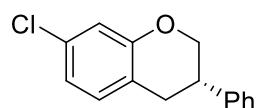
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.232	783600	45519	49.455	54.630
2	12.373	800885	37803	50.545	45.370
Total		1584485	83322	100.000	100.000



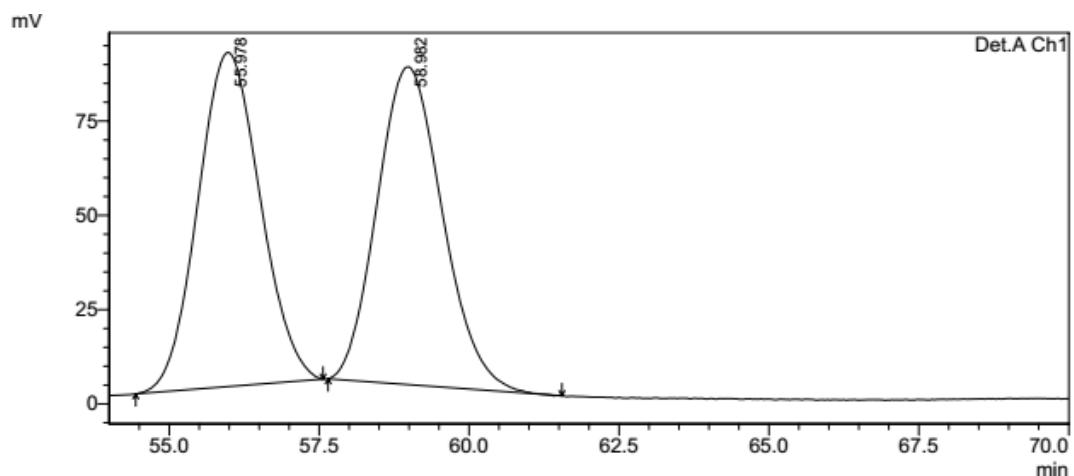
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.329	8113291	456583	98.685	98.742
2	12.569	108144	5819	1.315	1.258
Total		8221435	462402	100.000	100.000



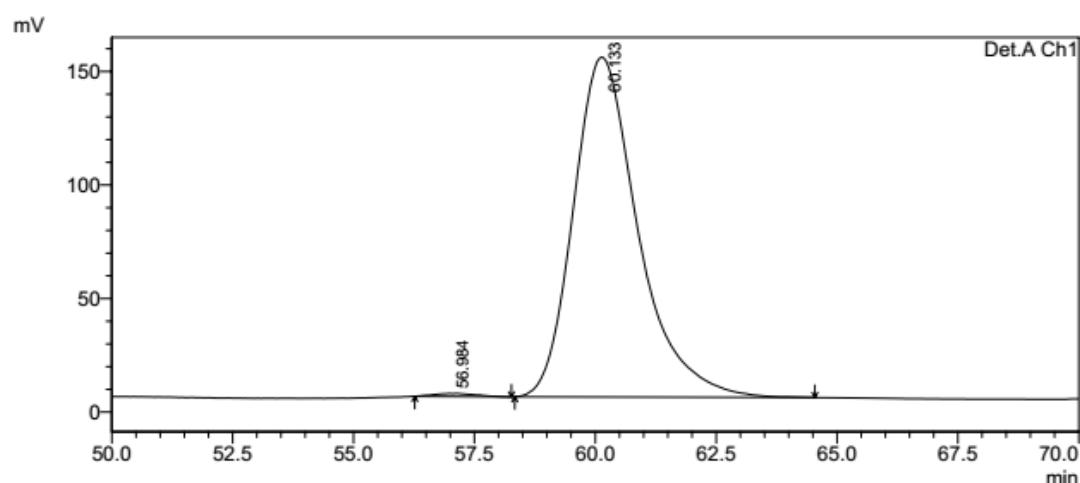
2e



PeakTable

Detector A Ch1 210nm

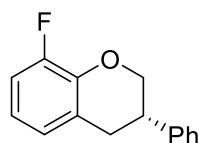
Peak#	Ret. Time	Area	Height	Area %	Height %
1	55.978	6402306	88652	50.016	51.264
2	58.982	6398279	84279	49.984	48.736
Total		12800585	172931	100.000	100.000



PeakTable

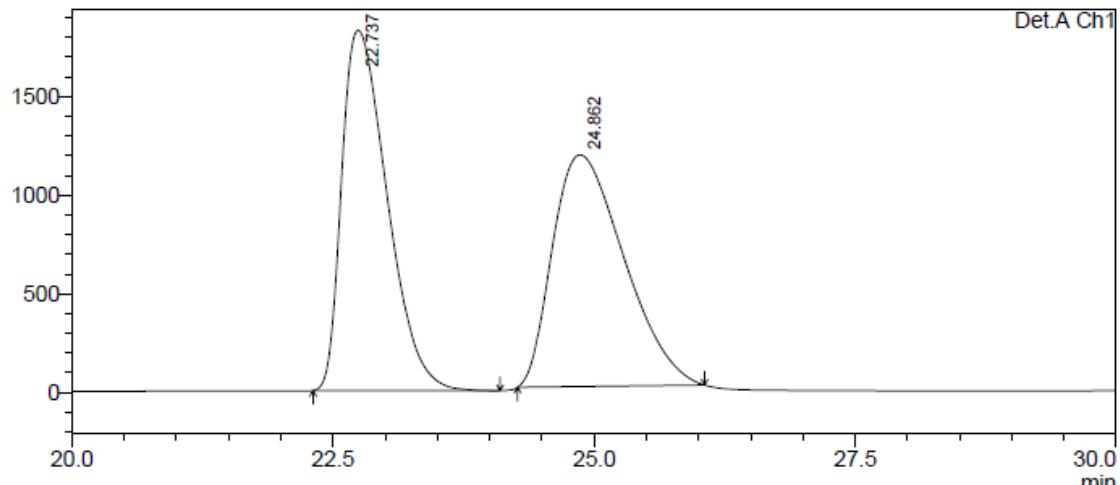
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	56.984	83112	1349	0.593	0.894
2	60.133	13924699	149658	99.407	99.106
Total		14007812	151007	100.000	100.000



2f

mV



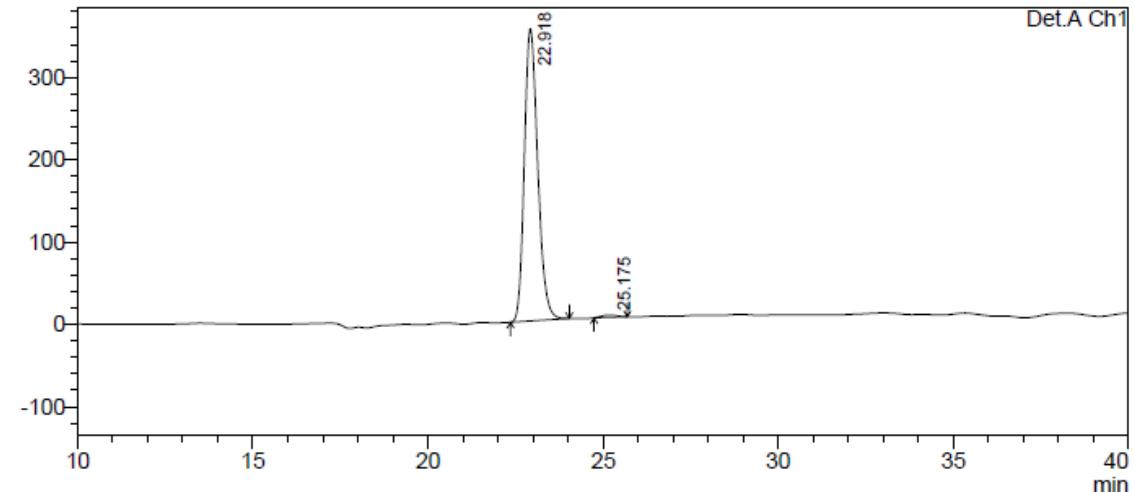
1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.737	55270748	1828171	49.670	60.868
2	24.862	56005387	1175317	50.330	39.132
Total		111276135	3003488	100.000	100.000

mv

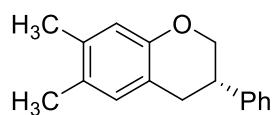


1 Det.A Ch1/210nm

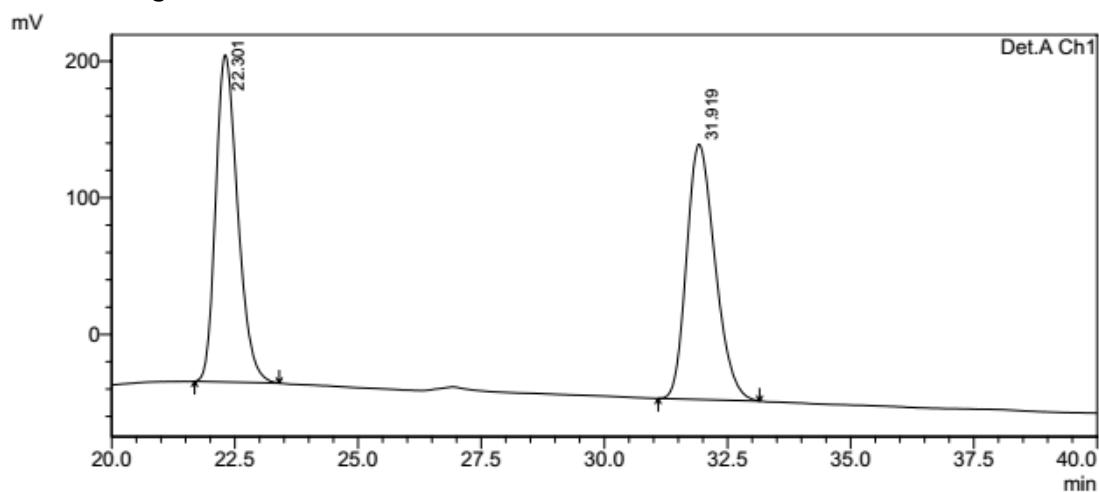
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.918	9432944	355031	99.123	99.250
2	25.175	83457	2681	0.877	0.750
Total		9516401	357712	100.000	100.000



2g

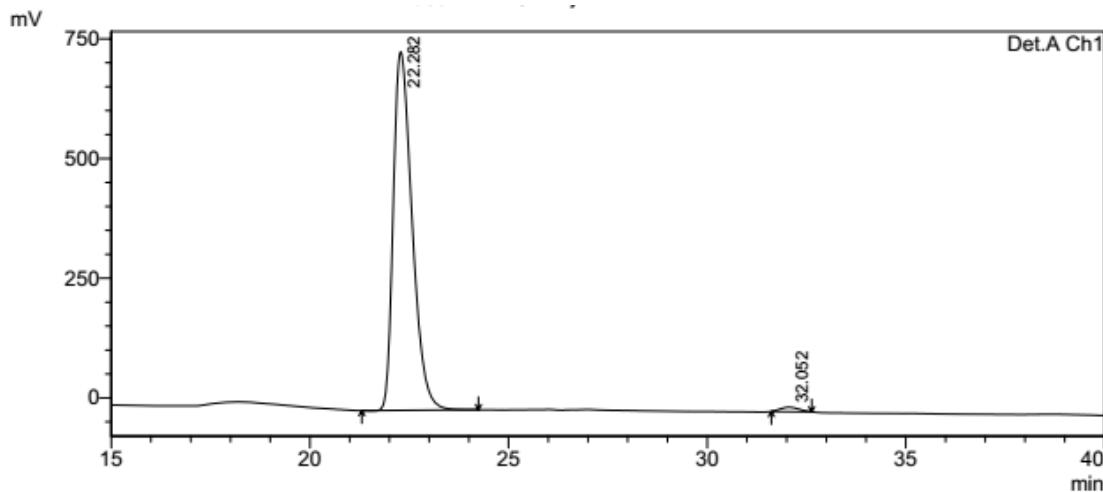


1 Det.A Ch1/210nm

PeakTable

检测器 A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.301	7437629	239309	49.727	56.171
2	31.919	7519356	186724	50.273	43.829
Total		14956984	426033	100.000	100.000

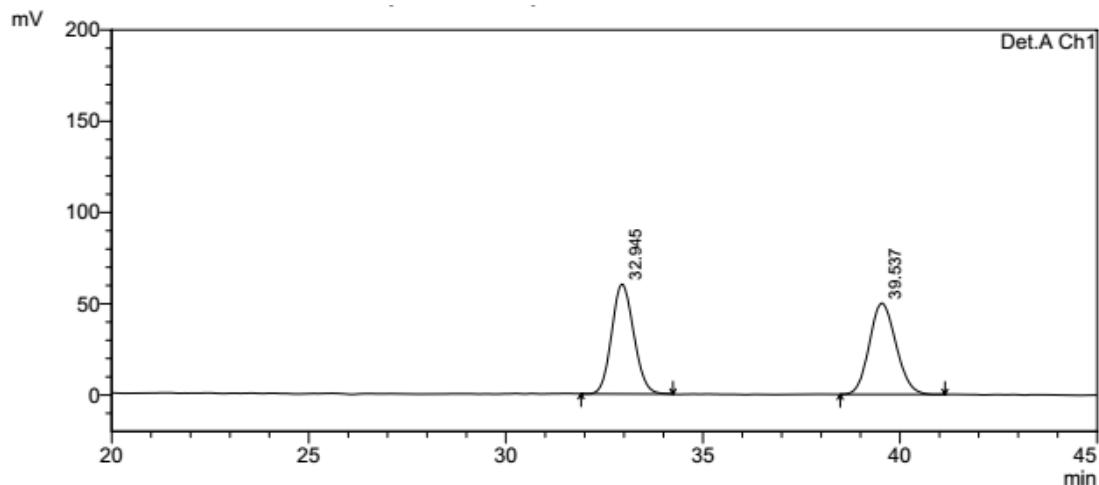
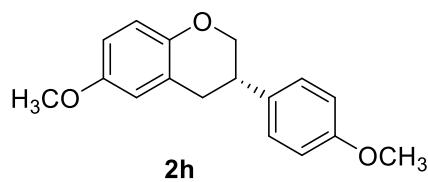


1 Det.A Ch1/210nm

PeakTable

检测器 A Ch1 210nm

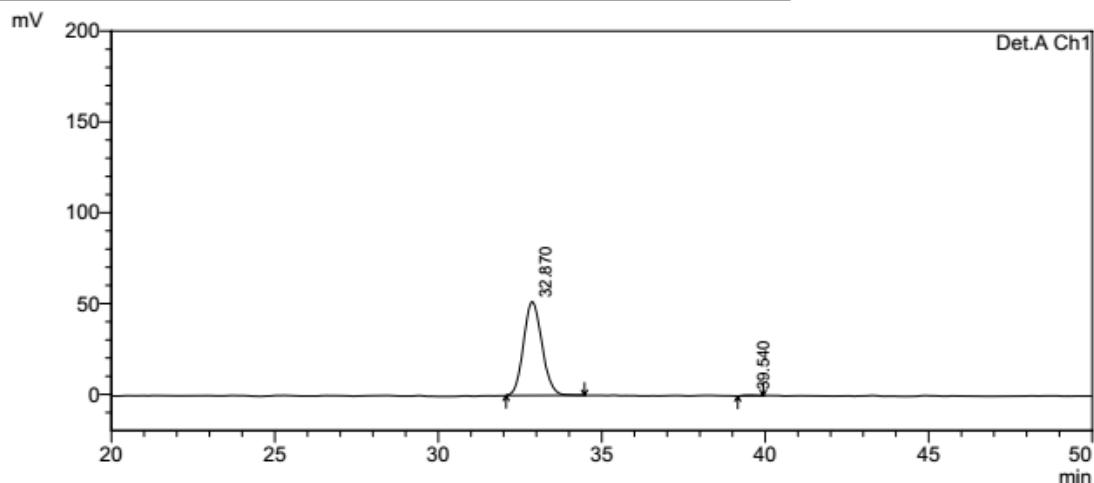
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.282	24657510	748967	98.810	98.796
2	32.052	296959	9125	1.190	1.204
Total		24954469	758093	100.000	100.000



PeakTable

Detector A Ch1 210nm

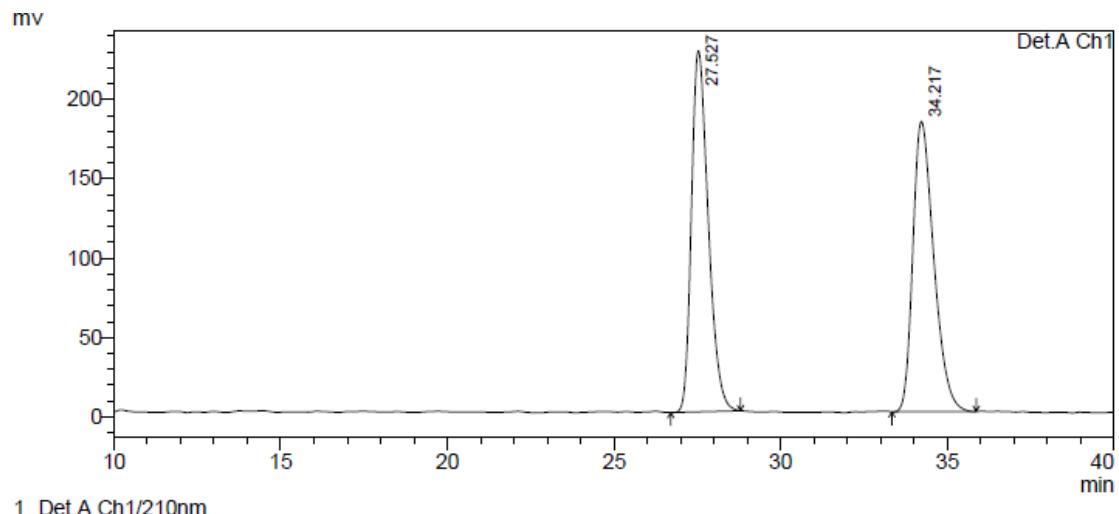
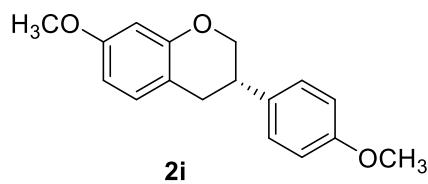
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.945	2350780	60095	50.048	54.633
2	39.537	2346290	49902	49.952	45.367
Total		4697071	109997	100.000	100.000



PeakTable

Detector A Ch1 210nm

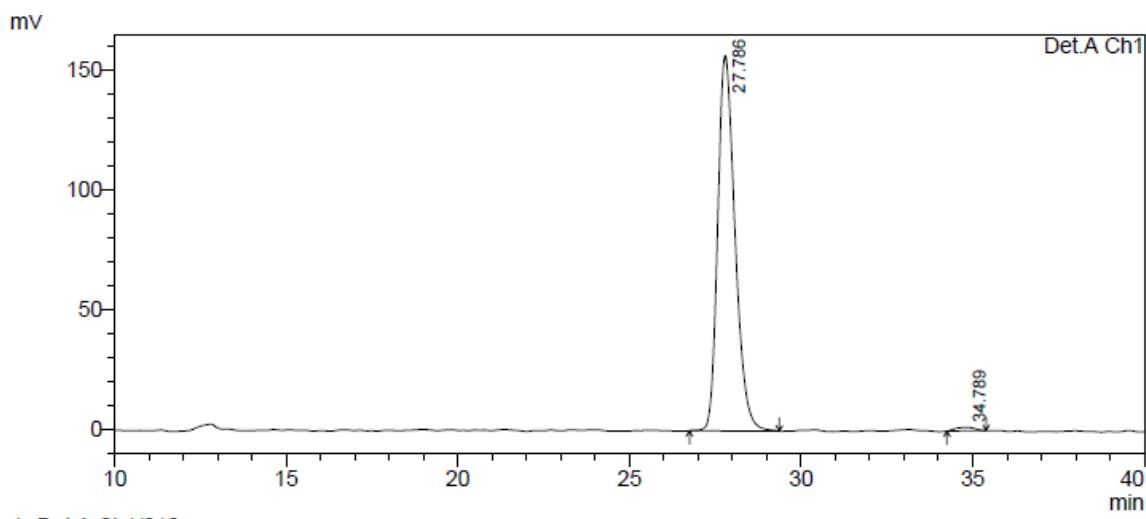
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.870	2021006	51537	99.575	99.325
2	39.540	8618	350	0.425	0.675
Total		2029624	51887	100.000	100.000



PeakTable

Detector A Ch1 210nm

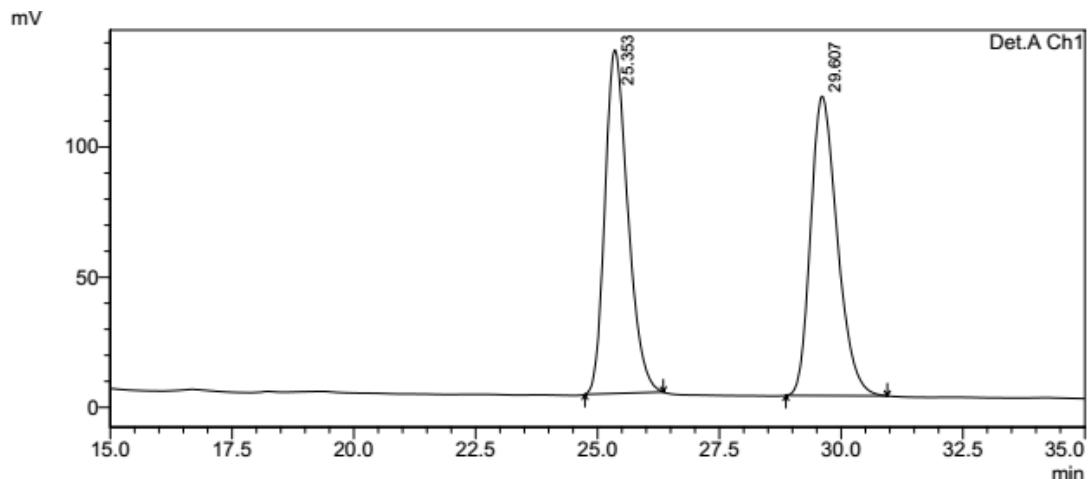
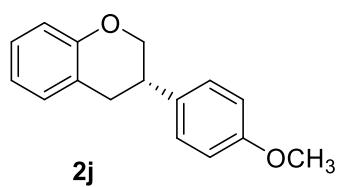
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.527	7984634	227477	49.967	55.429
2	34.217	7995177	182914	50.033	44.571
Total		15979811	410391	100.000	100.000



PeakTable

Detector A Ch1 210nm

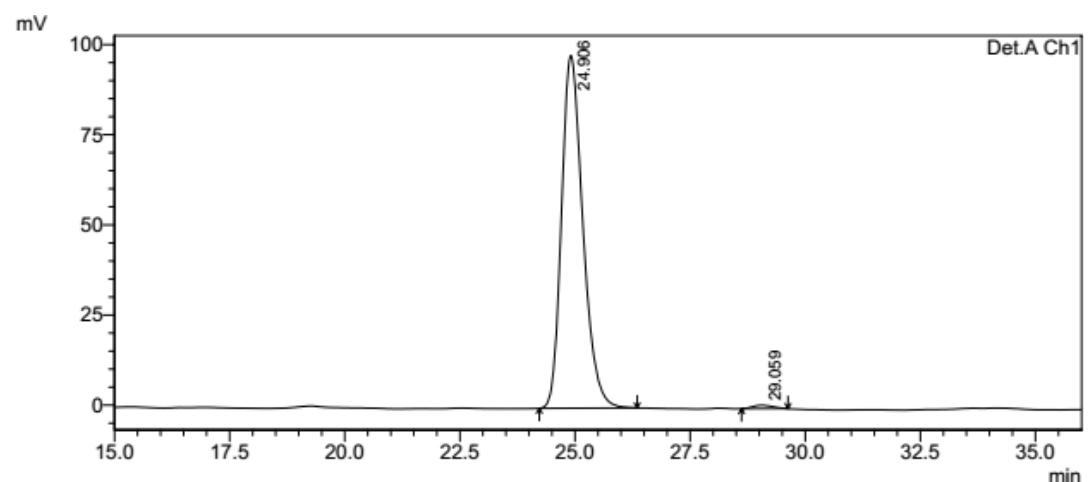
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.786	5503199	156993	98.985	99.109
2	34.789	56437	1412	1.015	0.891
Total		5559636	158405	100.000	100.000



PeakTable

Detector A Ch1 210nm

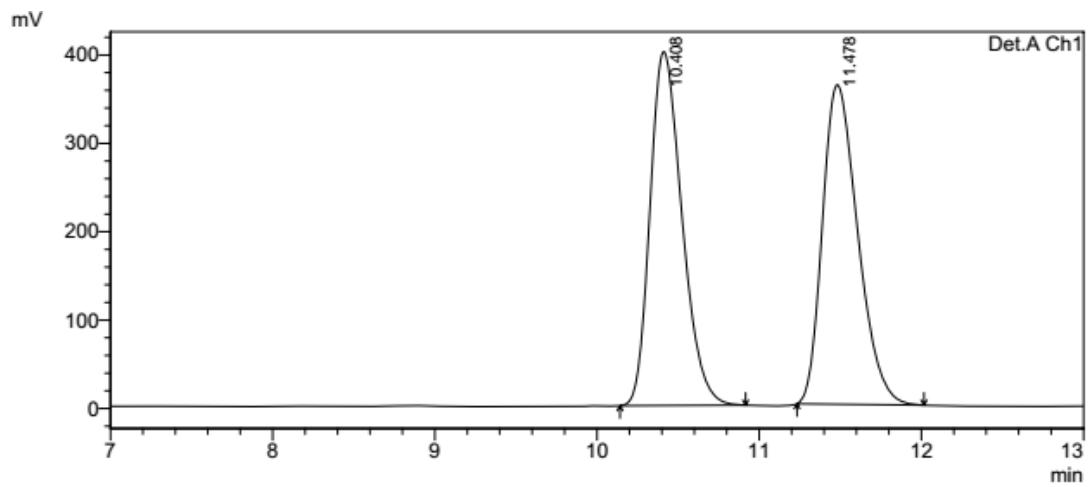
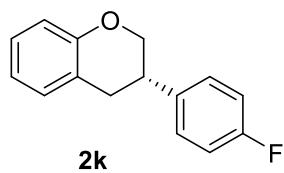
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.353	4332763	131895	49.728	53.434
2	29.607	4380114	114942	50.272	46.566
Total		8712877	246837	100.000	100.000



PeakTable

Detector A Ch1 210nm

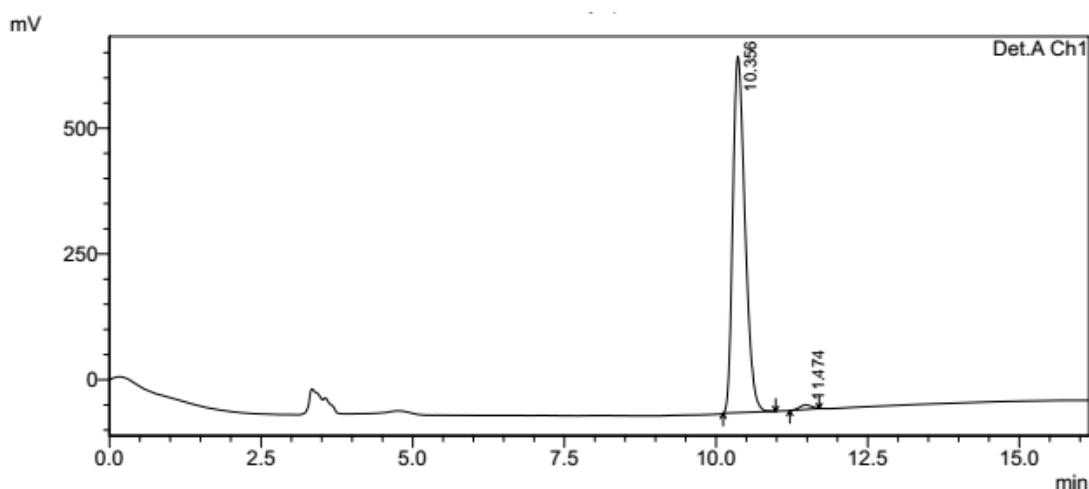
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.906	3143317	97805	99.069	99.027
2	29.059	29542	961	0.931	0.973
Total		3172859	98767	100.000	100.000



检测器 A Ch1 210nm

PeakTable

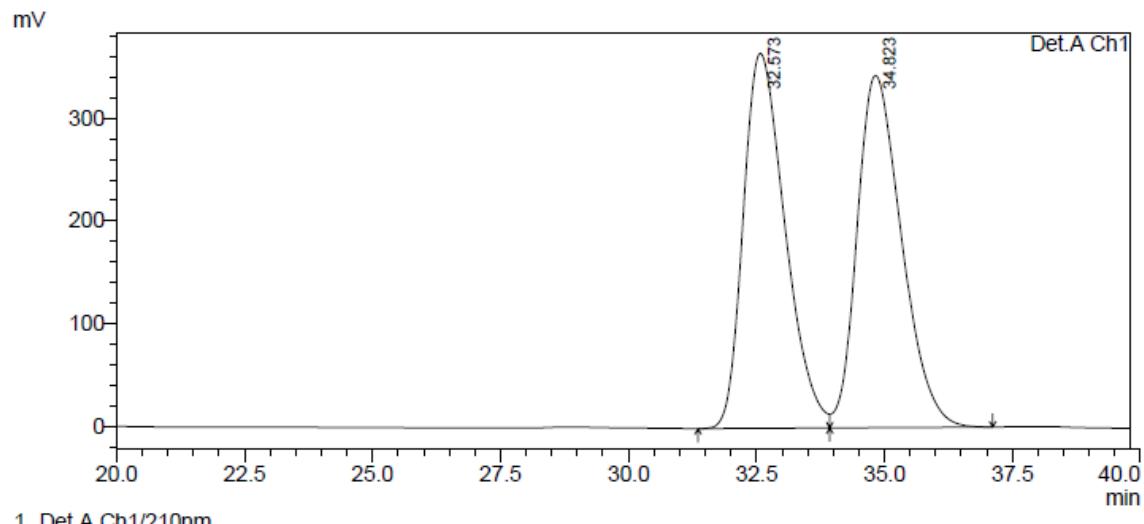
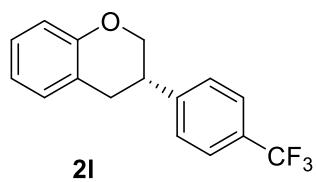
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.408	5489370	400402	50.069	52.550
2	11.478	5474219	361543	49.931	47.450
Total		10963590	761945	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

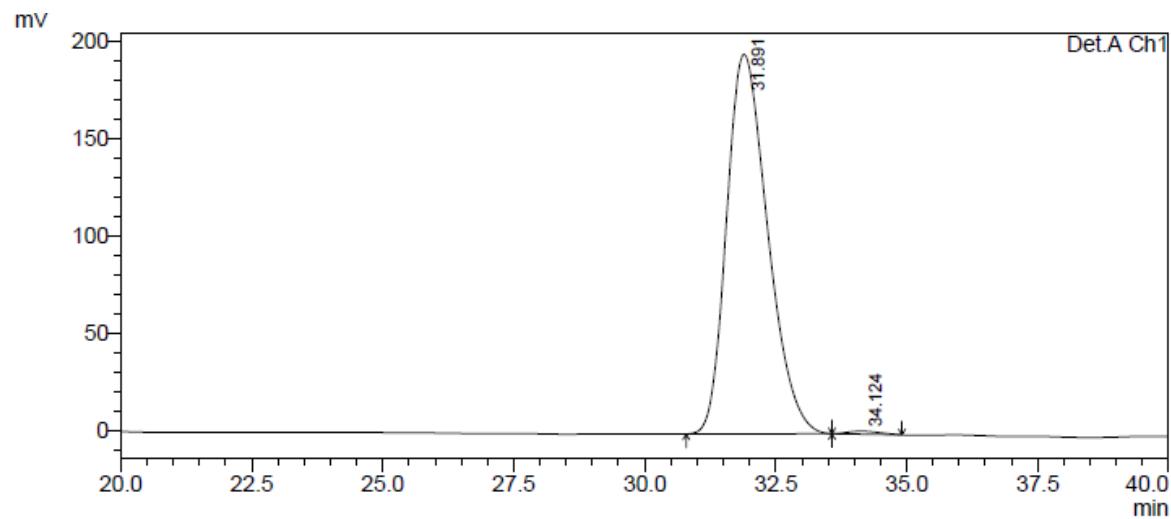
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.356	9907296	708013	98.767	98.734
2	11.474	123711	9075	1.233	1.266
Total		10031007	717088	100.000	100.000



PeakTable

Detector A Ch1 210nm

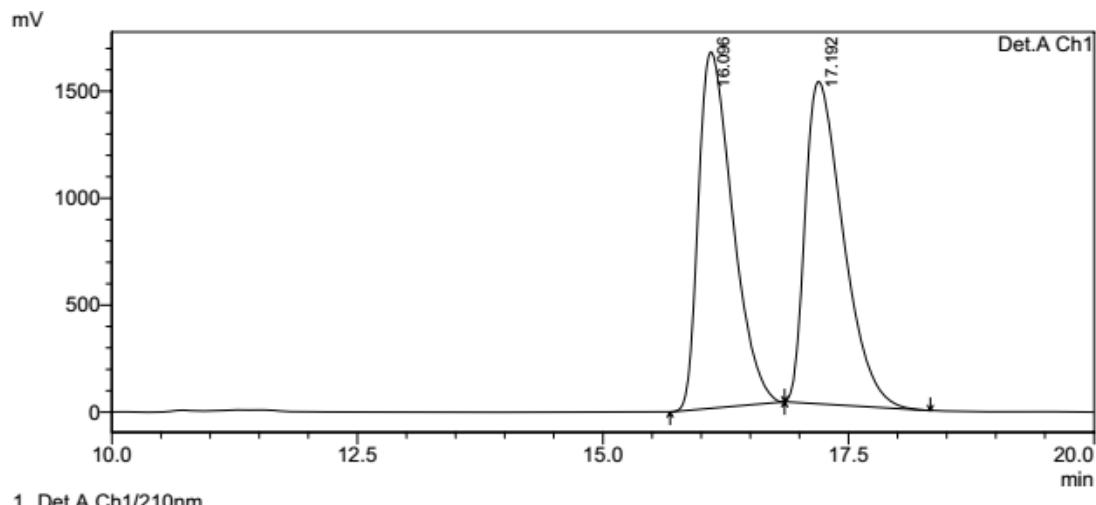
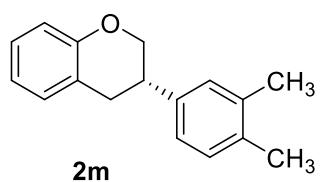
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.573	20728138	365598	49.934	51.571
2	34.823	20782715	343327	50.066	48.429
Total		41510853	708925	100.000	100.000



PeakTable

Detector A Ch1 210nm

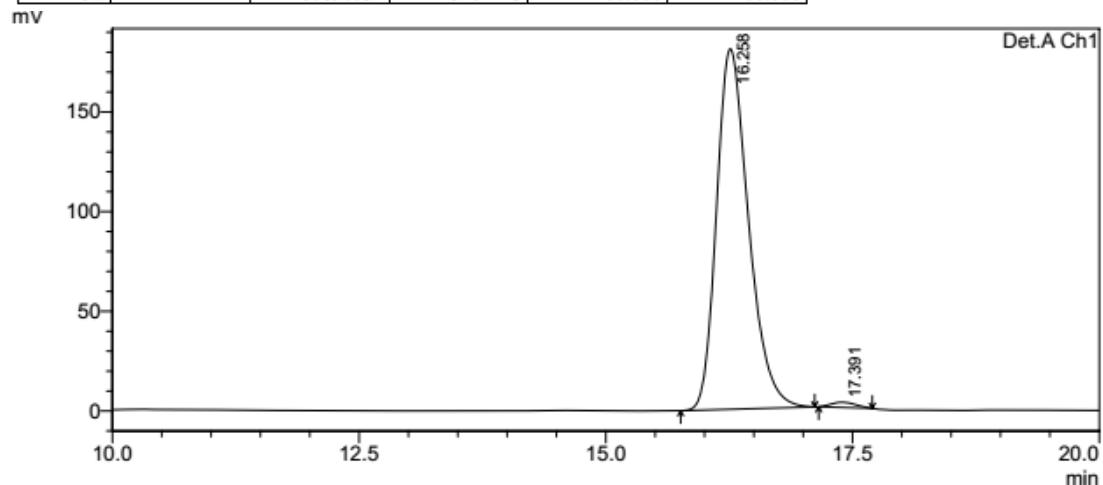
Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.891	10637178	195264	99.392	99.230
2	34.124	65052	1516	0.608	0.770
Total		10702230	196779	100.000	100.000



PeakTable

Detector A Ch1 210nm

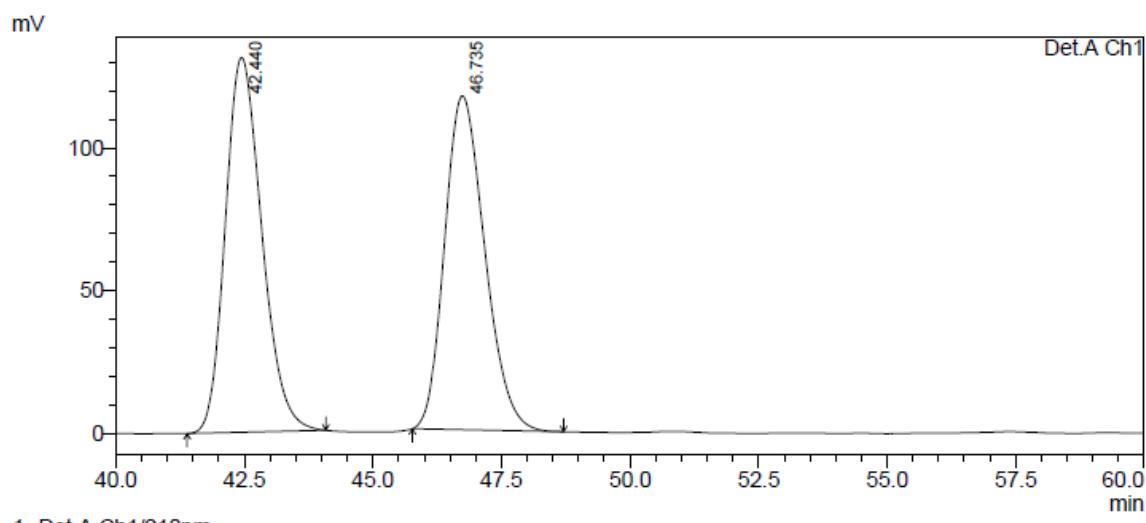
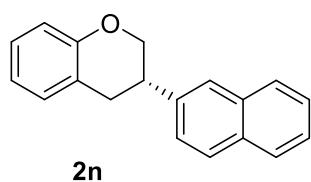
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.096	40277021	1665671	49.792	52.510
2	17.192	40613710	1506452	50.208	47.490
Total		80890731	3172123	100.000	100.000



PeakTable

Detector A Ch1 210nm

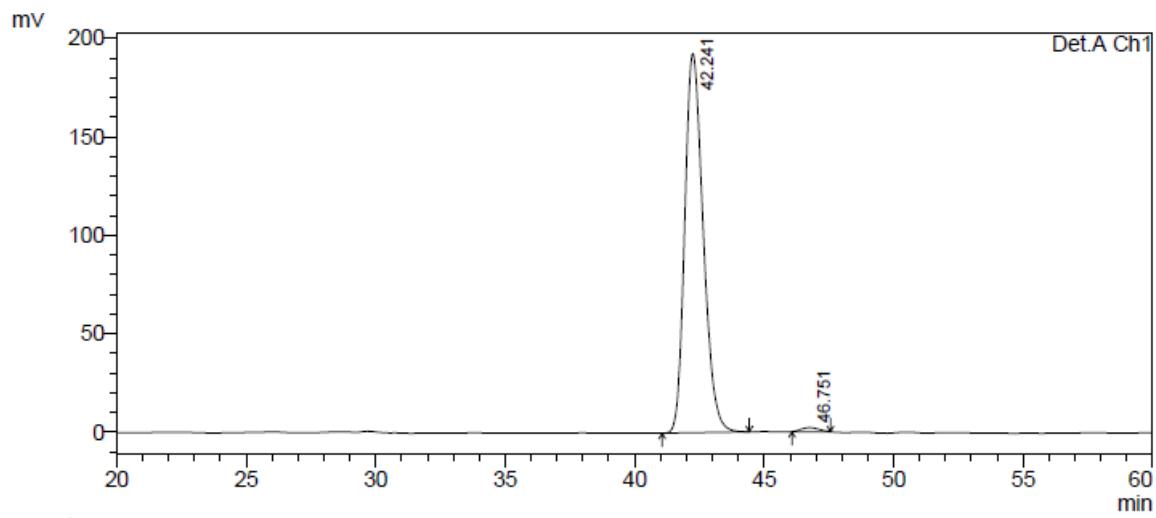
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.258	4076020	180885	98.881	98.579
2	17.391	46124	2607	1.119	1.421
Total		4122144	183492	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

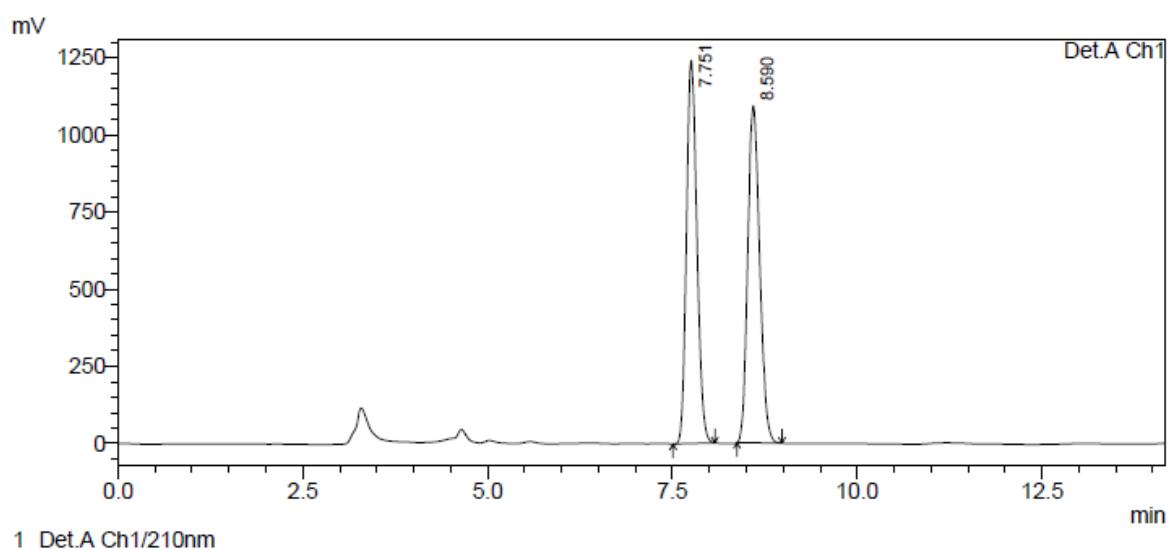
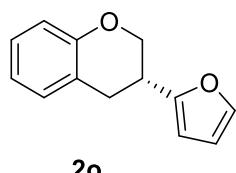
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.440	6489392	131348	50.506	52.890
2	46.735	6359268	116995	49.494	47.110
Total		12848661	248344	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

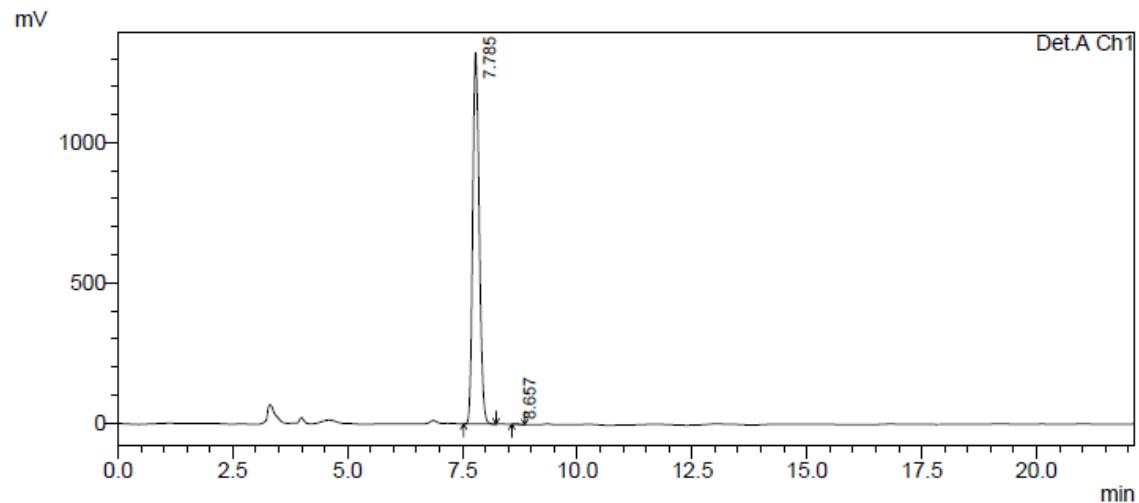
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.241	9534823	192543	98.978	98.929
2	46.751	98415	2085	1.022	1.071
Total		9633238	194628	100.000	100.000



PeakTable

Detector A Ch1 210nm

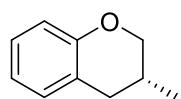
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.751	12212138	1241716	49.895	53.193
2	8.590	12263478	1092652	50.105	46.807
Total		24475615	2334368	100.000	100.000



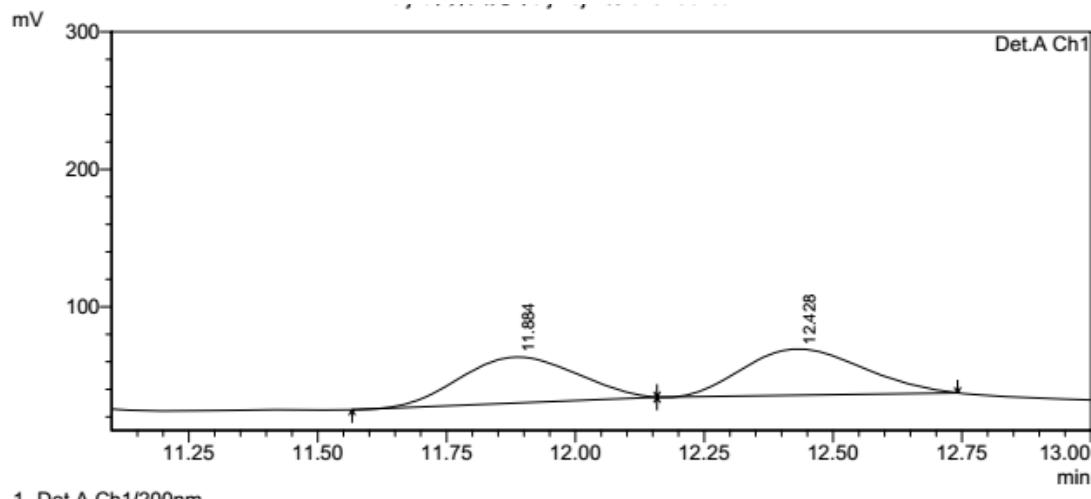
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.785	13096983	1324187	99.883	99.862
2	8.657	15394	1832	0.117	0.138
Total		13112377	1326020	100.000	100.000



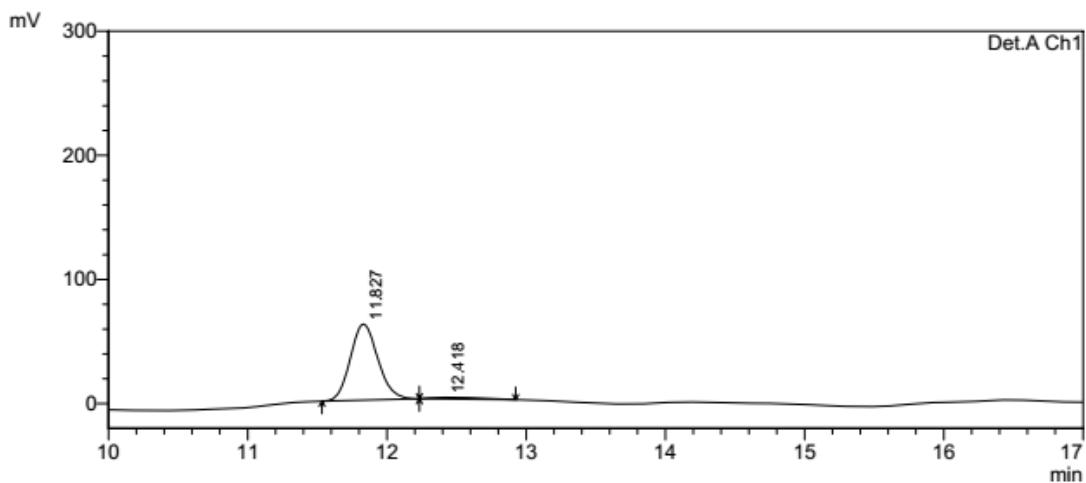
2p



PeakTable

Detector A Ch1 200nm

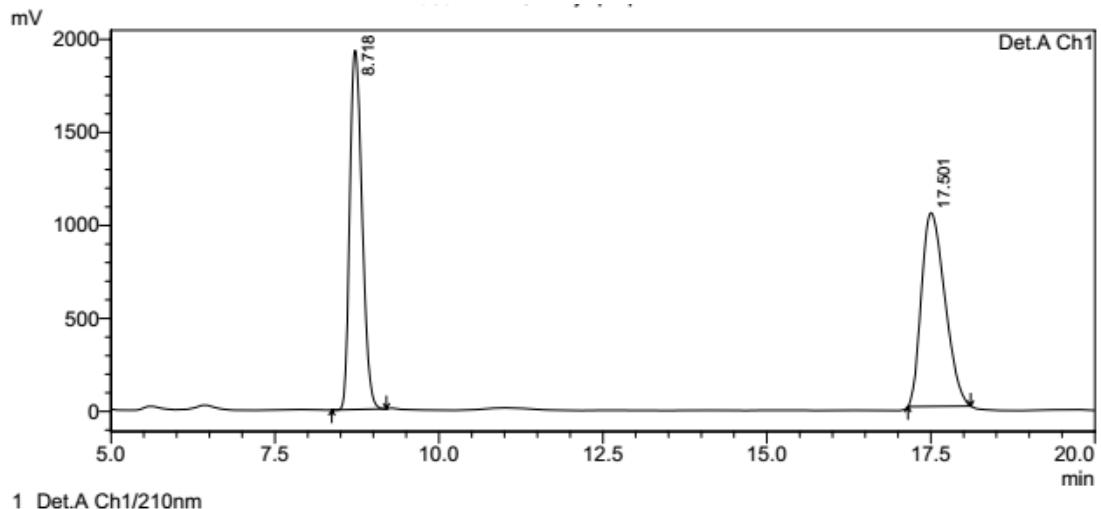
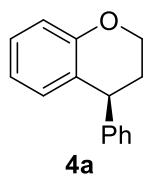
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.884	528844	33418	49.309	49.845
2	12.428	543673	33625	50.691	50.155
Total		1072517	67043	100.000	100.000



PeakTable

Detector A Ch1 200nm

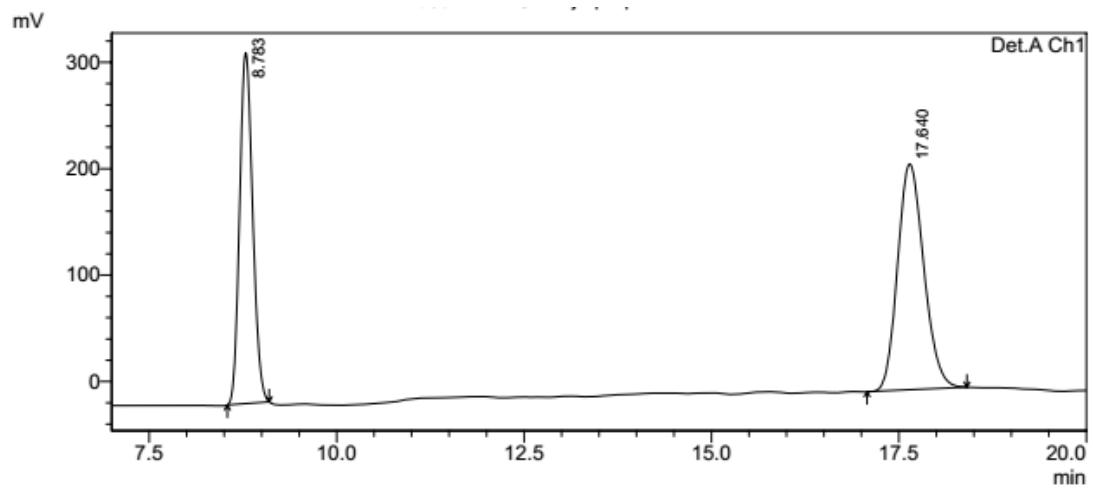
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.827	840224	61210	96.251	97.875
2	12.418	32731	1329	3.749	2.125
Total		872954	62538	100.000	100.000



PeakTable

检测器 A Ch1 210nm

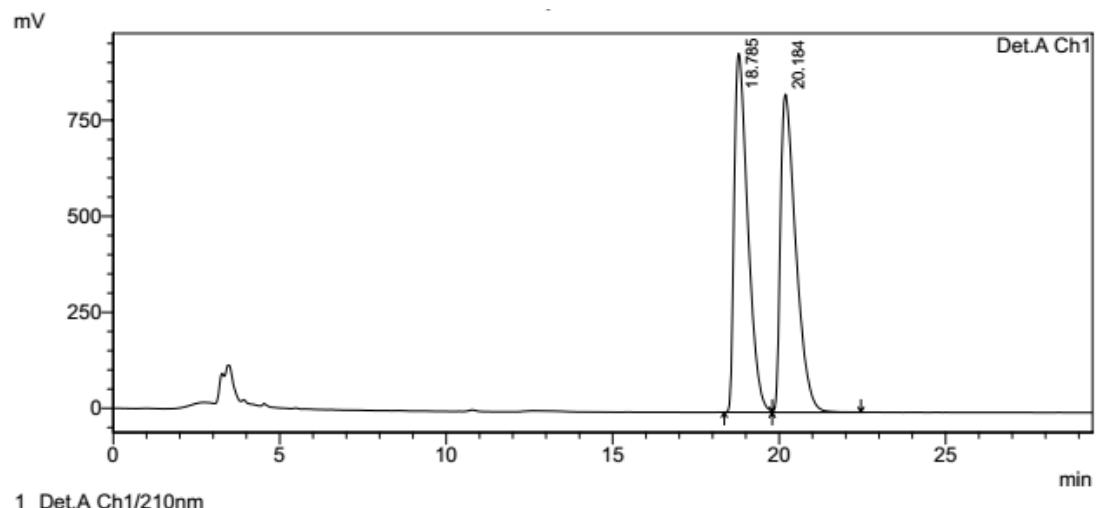
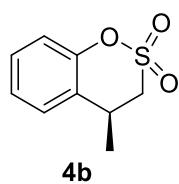
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.718	25222531	1930864	49.310	64.981
2	17.501	25927985	1040565	50.690	35.019
Total		51150516	2971430	100.000	100.000



PeakTable

检测器 A Ch1 210nm

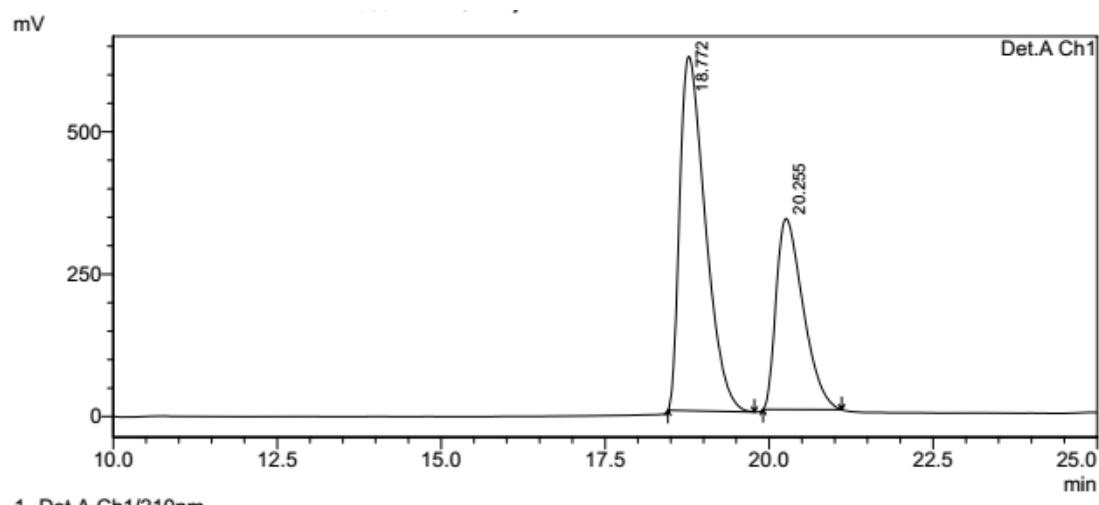
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.783	3994934	329593	43.657	60.835
2	17.640	5155786	212188	56.343	39.165
Total		9150720	541781	100.000	100.000



检测器 A Ch1 210nm

PeakTable

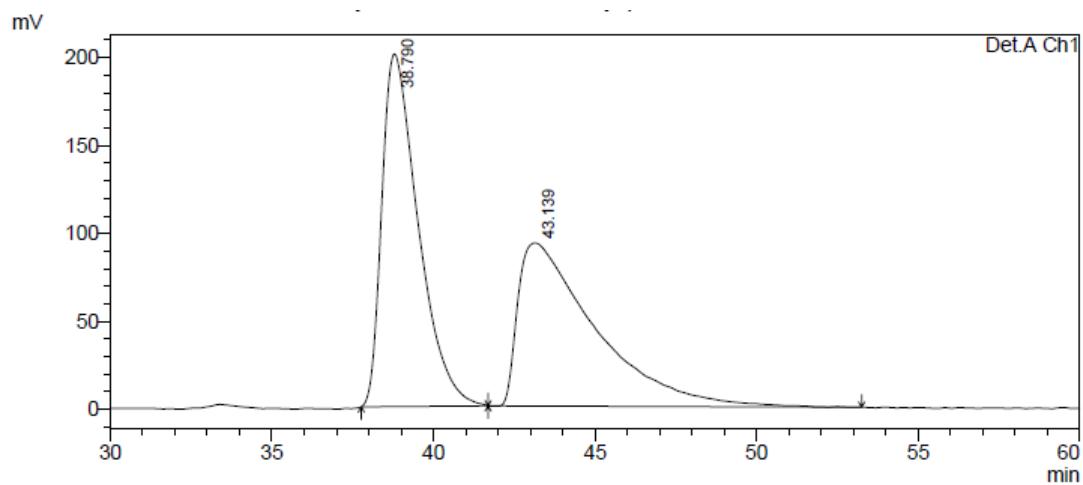
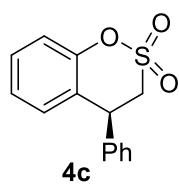
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.785	26530899	934395	49.809	53.010
2	20.184	26734745	828272	50.191	46.990
Total		53265644	1762667	100.000	100.000



检测器 A Ch1 210nm

PeakTable

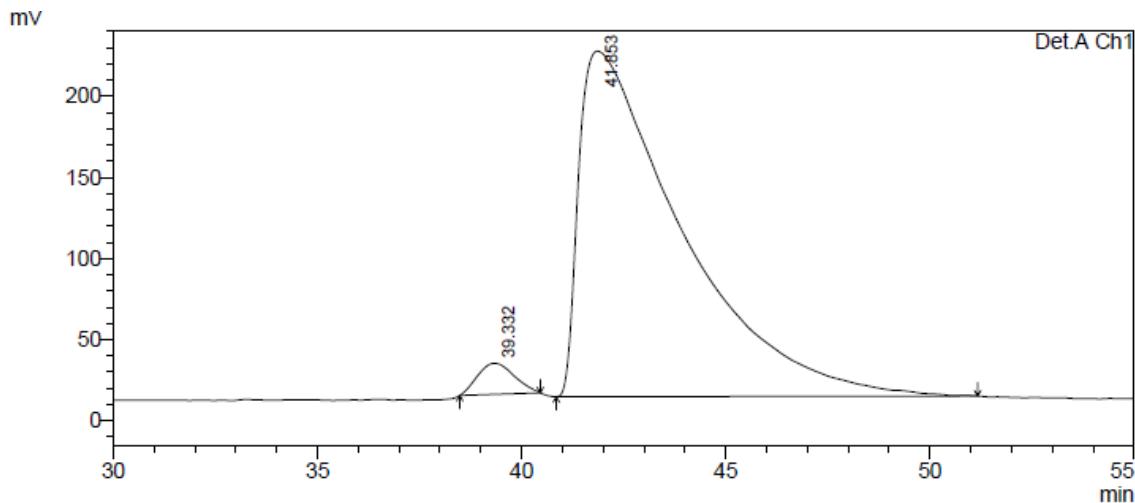
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.772	16878973	621991	63.780	64.992
2	20.255	9585465	335042	36.220	35.008
Total		26464439	957033	100.000	100.000



PeakTable

Detector A Ch1 210nm

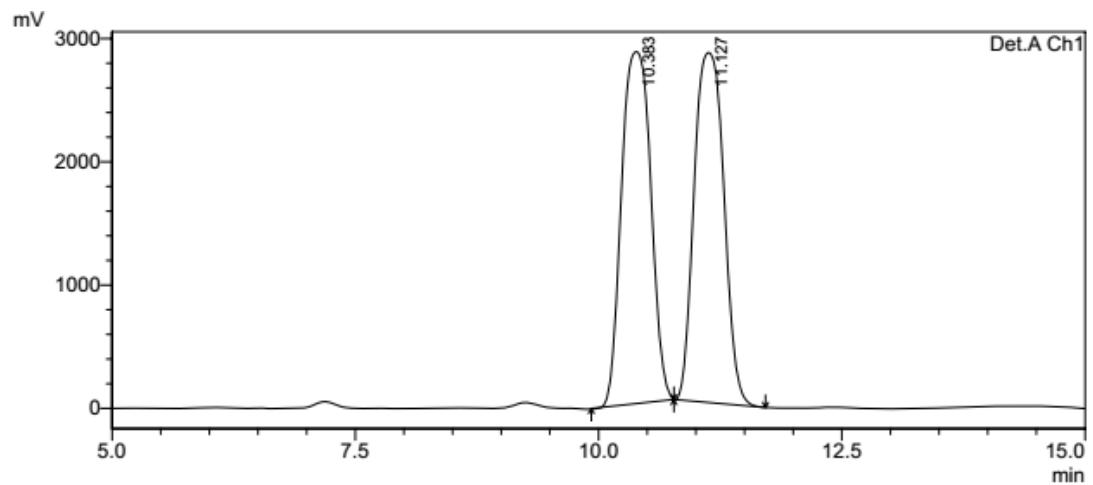
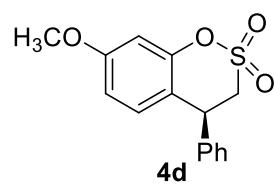
Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.790	15668478	200385	50.417	68.380
2	43.139	15409096	92660	49.583	31.620
Total		31077574	293045	100.000	100.000



PeakTable

Detector A Ch1 210nm

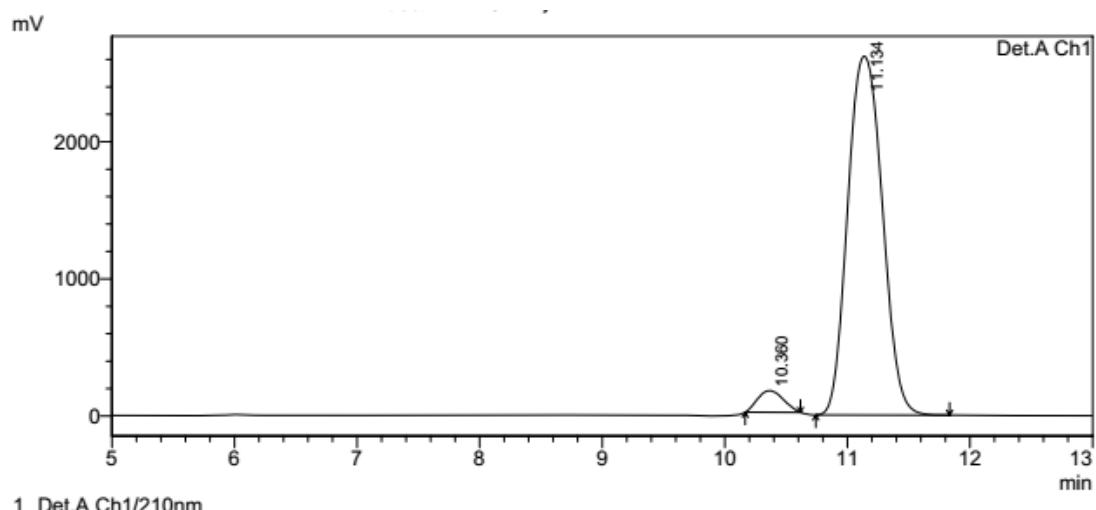
Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.332	1201320	19185	3.118	8.257
2	41.853	37329037	213162	96.882	91.743
Total		38530356	232346	100.000	100.000



PeakTable

检测器 A Ch1 210nm

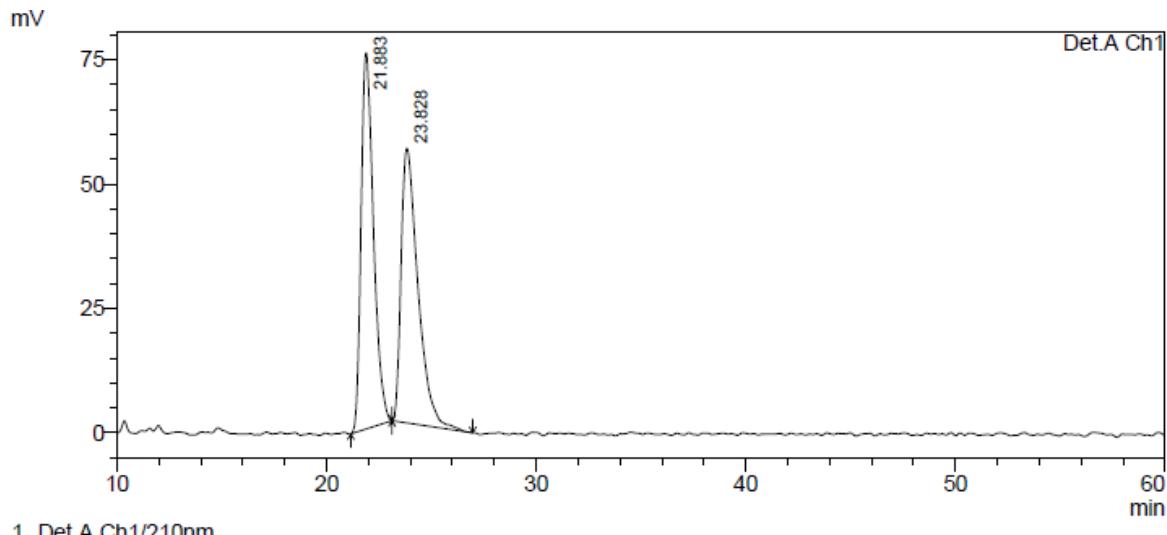
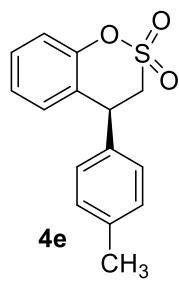
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.383	59744571	2855788	49.790	50.152
2	11.127	60247526	2838435	50.210	49.848
Total		119992097	5694223	100.000	100.000



PeakTable

检测器 A Ch1 210nm

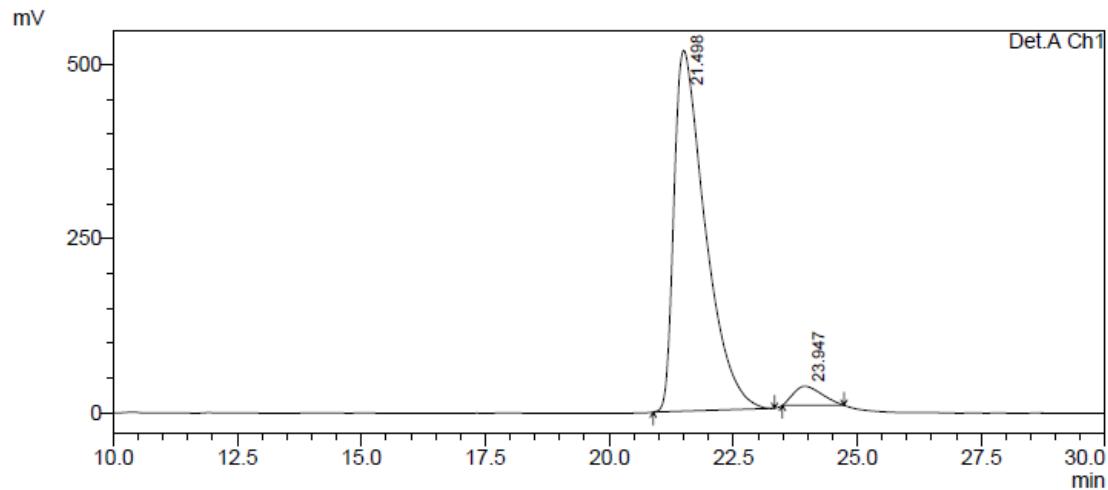
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.360	2302550	158300	4.283	5.705
2	11.134	51459394	2616468	95.717	94.295
Total		53761945	2774768	100.000	100.000



PeakTable

Detector A Ch1 210nm

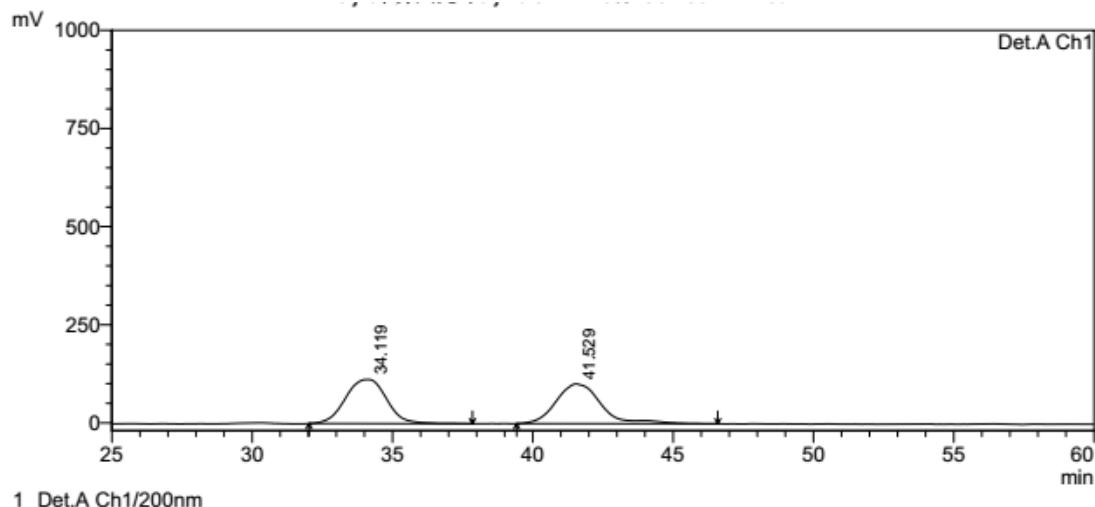
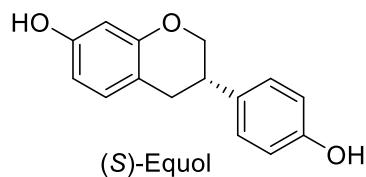
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.883	3107497	75622	50.247	57.807
2	23.828	3076929	55195	49.753	42.193
Total		6184426	130817	100.000	100.000



PeakTable

Detector A Ch1 210nm

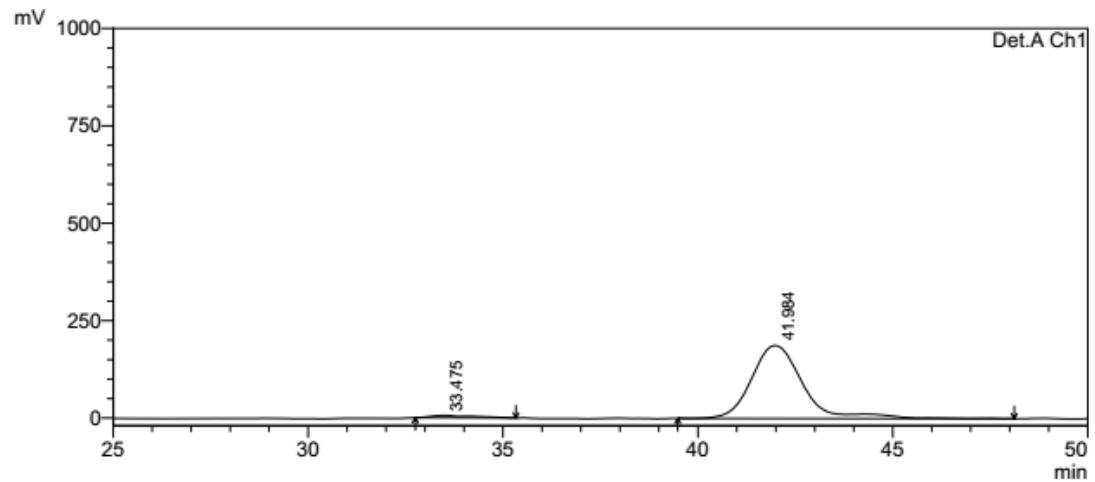
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.498	22685278	517423	95.434	95.000
2	23.947	1085436	27232	4.566	5.000
Total		23770714	544655	100.000	100.000



PeakTable

Detector A Ch1 200nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.119	11412044	112155	50.320	52.597
2	41.529	11267114	101078	49.680	47.403
Total		22679158	213233	100.000	100.000



PeakTable

Detector A Ch1 200nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.475	468109	5768	2.677	2.995
2	41.984	17018886	186834	97.323	97.005
Total		17486996	192602	100.000	100.000