Supporting Information

Total Synthesis of γ-Tocopherol via Asymmetric 1,4-Conjugate Addition of Alkyl Grignard Reagents to 2-Methyl Chromone

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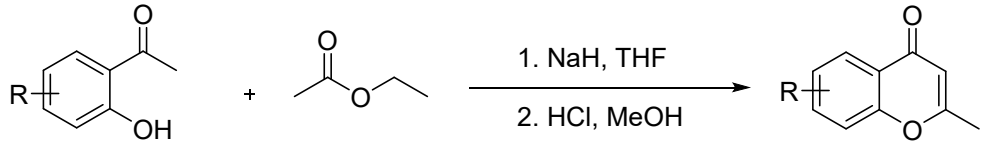
1. General Information

Dichloromethane and diethyl ether were freshly distilled from CaH_2 under N_2. Tetrahydrofuran was freshly distilled from sodium chips and indicated by benzophenone under N_2. Substituted chromones **1a-1p** were used as received or prepared according to literature[1], CuX was used as received and stored in a desiccator under ambient lab conditions. $BF_3{\cdot}OEt_2$ were purchased from Aladdin. Unless otherwise specified, all reagents and solvents were purchased from commercial sources and used as received. All new compounds were characterized by NMR spectroscopy, high resolution mass spectrometry (HRMS). ^1H (400 MHz) and ^{13}C (100 MHz) NMR were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standards. Reference values for residual solvent were taken as δ = 7.26 ($CDCl_3$) ppm for ^1H NMR and δ = 77.16 ($CDCl_3$) ppm for ^{13}C NMR. Coupling constant (*J*) values are given in Hz. Multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. Products were purified by flash column chromatography on silica gel purchased from Qingdao Haiyang Chemical Co., Ltd. Optical rotations were measured by a Rudolph AUTOPOL I Automatic Polarimeter. HRMS were recorded on a Bruker microTOF spectrometer. HPLC analysis was performed with Daicel Chiralpak IC column (25 cm×4.6 mm×5 μm).

2. Experimental Procedures

2.1 General procedure for the synthesis of 2-methylchromone substrates (1a-1p)[1]

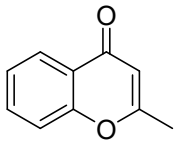


1a-1p

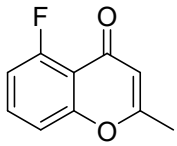
Under an argon atmosphere, sodium hydride (1.6 g, 40 mmol, 60 wt% in mineral oil) was added to an oven-dried round-bottom flask, followed by anhydrous THF (4 mL). At 0 °C, a THF solution (3 mL) of o-hydroxyacetophenone (1.36 g, 10.0 mmol) and ethyl acetate (24.5 mL, 25 mmol) was added dropwise to the resulting suspension. After the addition was complete, the reaction mixture was heated to reflux and stirred overnight, and the progress was monitored by TLC. The reaction was quenched with ice water, and the pH was adjusted to 6 with 6 M HCl. The mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product.

Methanol (28 mL) and concentrated HCl (1.0 mL) were added to the crude product, and the mixture was stirred at room temperature for 12 h, with the reaction monitored by TLC. After removal of methanol under reduced pressure, the residue was extracted with ethyl acetate. The combined organic layers were washed successively with saturated $NaHCO_3$ solution, water, and brine, then dried over anhydrous

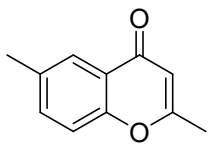
Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the desired products 141a–141p.The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 15:1) to give the desired products **1a**-**1p**.



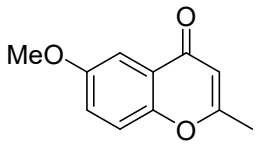
2-methyl-4H-chromen-4-one (**1a**): White solid, 1.35 g, 84% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.63 (m 1H), 7.43 – 7.33 (m, 2H), 6.16 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 166.3, 156.6, 133.5, 125.8, 125.0, 123.7, 117.9, 110.7, 20.7. HRMS (ESI) m/z calcd for $C_{10}H_9O_2$ $[M + H]^+$:161.0597, found: 161.0596.



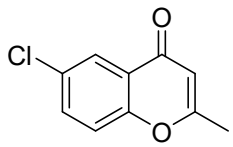
5-fluoro-2-methyl-4H-chromen-4-one (1b): Pale yellow solid, 1.25 g, 70% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.03 – 6.95 (m, 1H), 6.08 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 165.2, 160.8, 157.6, 133.5, 114.1, 113.9, 111.9, 111.8, 20.3. HRMS (ESI) m/z calcd for $C_{10}H_8FO_2$ $[M + H]^+$: 179.0503, found: 179.0501.



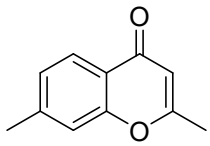
2,6-dimethyl-4H-chromen-4-one (1c): Pale yellow solid, 1.43 g, 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 2.1, 1.1 Hz, 1H), 7.43 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 6.14 (s, 1H), 2.43 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 166.1, 154.9, 134.9, 134.7, 125.1, 123.3, 117.6, 110.5, 21.0, 20.7. HRMS (ESI) m/z calcd for $C_{11}H_{11}O_2$ $[M + H]^+$: 175.0754, found: 175.0752.



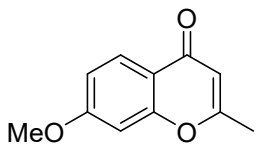
6-methoxy-2-methyl-4H-chromen-4-one (1d): Pale yellow solid, 1.62 g, 85% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 3.2, 1.7 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.25 – 7.18 (m, 1H), 6.21 – 6.08 (m, 1H), 3.87 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 166.0, 156.9, 151.5, 124.3, 123.5, 119.3, 110.0, 105.1, 56.0, 20.7. HRMS (ESI) m/z calcd for $C_{11}H_{11}O_3$ $[M + H]^+$: 191.0703, found: 191.0706.



6-chloro-2-methyl-4H-chromen-4-one (1e): Pale yellow solid, 1.48 g, 76% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.7 Hz, 1H), 7.51 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 6.11 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 166.6, 154.8, 133.6, 130.9, 125.1, 124.6, 119.6, 110.5, 20.6. HRMS (ESI) m/z calcd for $C_{10}H_8ClO_2$ $[M + H]^+$: 195.0208, found: 195.0213.

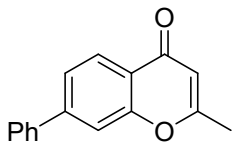


2,7-dimethyl-4H-chromen-4-one (1f): Pale yellow solid, 1.39 g, 80% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.17 (dd, *J* = 11.0, 2.7 Hz, 2H), 6.12 (s, 1H), 2.46 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 165.9, 156.8, 144.8, 126.5, 125.5, 121.5, 117.7, 110.6, 21.9, 20.7. HRMS (ESI) m/z calcd for $C_{11}H_{11}O_2$ $[M + H]^+$: 175.0754, found: 175.0752.

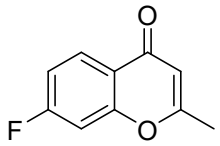


7-methoxy-2-methyl-4H-chromen-4-one (1g): Pale yellow solid, 1.58 g, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.92 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.79 (s, 1H), 6.08 (d, *J* = 2.2 Hz, 1H), 3.87 (s, 3H), 2.33

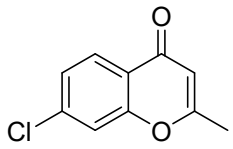
(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 165.7, 164.0, 158.3, 127.1, 117.6, 114.1, 110.5, 100.3, 55.9, 20.5. HRMS (ESI) m/z calcd for $C_{11}H_{11}O_3$ $[M + H]^+$: 191.0703, found: 191.0699.



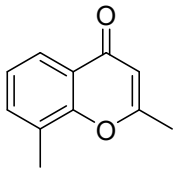
2-methyl-7-phenyl-4H-chromen-4-one (1h): Pale yellow solid, 852.0 mg, 36% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.6 Hz, 1H), 7.68 – 7.59 (m, 4H), 7.52 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H), 6.20 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 166.5, 157.0, 146.8, 139.3, 129.2, 128.7, 127.5, 126.3, 124.2, 122.4, 116.0, 110.8, 20.8. HRMS (ESI) m/z calcd for $C_{16}H_{13}O_2$ $[M + H]^+$: 237.0910, found: 237.0908.



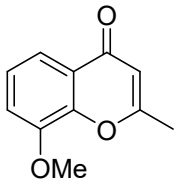
7-fluoro-2-methyl-4H-chromen-4-one (1i): Pale yellow solid, 1.25 g, 70% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.14 (m, 1H), 7.10 (m, 2H), 6.14 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 166.5, 165.6, 157.6, 128.3, 120.6, 113.8, 110.8, 104.6, 20.6. HRMS (ESI) m/z calcd for $C_{10}H_8FO_2$ $[M + H]^+$: 179.0503, found: 179.0503.



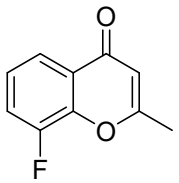
7-chloro-2-methyl-4H-chromen-4-one (1j): Pale yellow solid, 1.44 g, 74% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.8, 2.2 Hz, 1H), 7.43 (s, 1H), 7.34 (dd, J = 8.6, 2.6 Hz, 1H), 6.15 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 166.5, 156.7, 139.6, 127.2, 125.9, 122.3, 118.0, 111.0, 20.7. HRMS (ESI) m/z calcd for $C_{10}H_8ClO_2$ $[M + H]^+$: 195.0208, found: 195.0207.



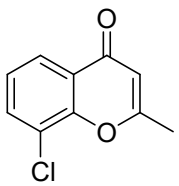
2,8-dimethyl-4H-chromen-4-one (1k): Pale yellow solid, 1.43 g, 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 7.3 Hz, 1H), 7.26 (t, J = 5.7 Hz, 1H), 6.18 (s, 1H), 2.47 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 165.9, 155.1, 134.5, 127.2, 124.6, 123.6, 123.4, 110.6, 20.7, 15.7. HRMS (ESI) m/z calcd for $C_{11}H_{11}O_2$ $[M + H]^+$: 175.0754, found: 175.0752.



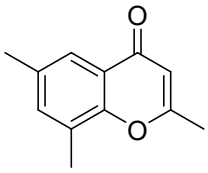
8-methoxy-2-methyl-4H-chromen-4-one (1l): Pale yellow solid, 1.5 g, 79% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.1, 1.5 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.11 (dd, J = 8.0, 1.5 Hz, 1H), 6.15 (s, 1H), 3.95 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 166.0, 148.6, 147.0, 124.7, 124.6, 116.6, 114.2, 110.7, 56.4, 20.7. HRMS (ESI) m/z calcd for $C_{11}H_{11}O_3$ $[M + H]^+$: 191.0703, found: 191.0701.



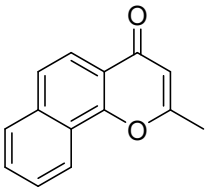
8-fluoro-2-methyl-4H-chromen-4-one (1m): Pale yellow solid, 1.33 g, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.45 – 7.37 (m, 1H), 7.30 (m, 1H), 6.20 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 166.1, 152.3, 149.8, 145.2, 125.6, 124.5, 120.7, 119.3, 111.0, 20.5. HRMS (ESI) m/z calcd for $C_{10}H_8FO_2$ $[M + H]^+$: 179.0503, found: 179.0504.



8-chloro-2-methyl-4H-chromen-4-one (1n): Pale yellow solid, 1.5 g, 77% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.0, 1.6 Hz, 1H), 7.68 (dd, J = 7.7, 1.6 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 6.20 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 166.4, 152.2, 133.8, 125.0, 124.3, 122.9, 110.8, 20.6. HRMS (ESI) m/z calcd for $C_{10}H_8ClO_2$ $[M + H]^+$: 195.0208, found: 195.0208.

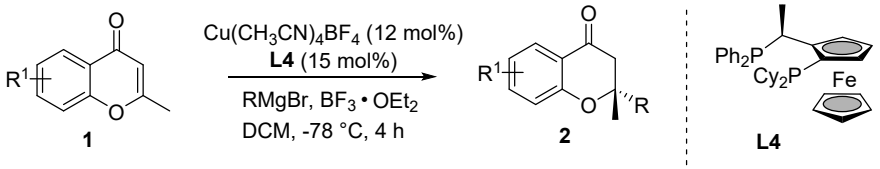


2,6,8-trimethyl-4H-chromen-4-one (1o): Pale yellow solid, 1.28 g, 68% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.28 (s, 1H), 6.14 (s, 1H), 2.42 (s, 3H), 2.39 (d, *J* = 0.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 165.7, 153.4, 135.8, 134.3, 126.9, 123.2, 122.7, 110.3, 20.9, 20.6, 15.6. HRMS (ESI) m/z calcd for $C_{12}H_{13}O_2$ $[M + H]^+$: 189.0910, found: 189.0906.



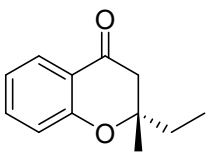
2-methyl-4H-benzo[h]chromen-4-one (1p): Pale yellow solid, 1.56 g, 74% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.69 – 7.58 (m, 3H), 6.29 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 165.4, 153.9, 135.8, 129.2, 128.1, 127.0, 125.1, 123.9, 122.3, 120.8, 119.8, 111.9, 20.5. HRMS (ESI) m/z calcd for $C_{14}H_{11}O_2$ $[M + H]^+$: 211.0754, found: 211.0751.

2.2 General procedure for the enantioselective catalytic addition of Grignard reagents to 2-methylchromones



To a mixture of $Cu(CH_3CN)_4BF_4$ (3.8 mg, 0.012 mmol), **L4** (8.9 mg, 0.015 mmol) and 2-methyl chromone **1** (0.1 mmol), dry DCM (2.0 mL) was added under N_2 atmosphere and the mixture was stirred at room temperature for 20 mins. Then, $BF_3{\cdot}OEt_2$ (0.2 mmol, 2.0 equiv.) was added via syringe under -78 °C and the mixture was allowed to stir at -78 ºC for 20 mins. Then, RMgBr (0.2 mmol, 2.0 equiv.) was added dropwise in about 1 min. The reaction mixture was stirred for 4 hours and quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with DCM. The combined organic layers were dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 30:1) to give the desired products.

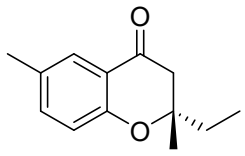
(*S*)-2-ethyl-2-methylchroman-4-one (**2a**): Colorless oil, 18.1 mg, 95% yield, $[\alpha]_D^{20}$: +1.45 (c = 0.18 in $CHCl_3$), 95% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 20.8 min, t (minor) = 19.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.00 – 6.89 (m, 2H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.65 (d, *J* = 16.0 Hz, 1H), 1.88 – 1.68 (m, 2H), 1.39 (s, 3H), 0.98 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 160.1, 136.3, 126.6, 120.7, 120.6, 118.5, 81.5, 47.2, 32.3, 23.5, 8.1. HRMS (ESI) m/z calcd for $C_{12}H_{15}O_2$ $[M + H]^+$: 191.1067, found: 191.1066.



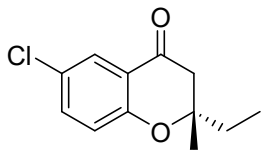
(*S*)-2-ethyl-5-fluoro-2-methylchroman-4-one (**2b**):Colorless oil, 15.0 mg, 72% yield, $[\alpha]_D^{20}$: +0.61 (c = 0.34 in $CHCl_3$), 80% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 68.3 min, t (minor) = 57.9 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (td, *J* = 8.4, 6.0 Hz, 1H), 6.73 (dt, *J* = 8.5, 1.1 Hz, 1H), 6.68 – 6.60 (m, 1H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.63 (d, *J* = 16.0 Hz, 1H), 1.86 – 1.69 (m, 2H), 1.39 (s, 3H), 0.97 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 190.6, 161.5, 161.0, 136.1, 136.0, 114.2, 110.6, 108.2, 81.9, 48.0, 32.2, 23.3, 8.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.83. HRMS (ESI) m/z calcd for $C_{12}H_{14}FO_2$ $[M + H]^+$: 209.0973, found: 209.0973.

(*S*)-2-ethyl-2,6-dimethylchroman-4-one (**2c**): Colorless oil, 18.8 mg, 92% yield, $[\alpha]_D^{20}$: +3.66 (c = 0.74 in $CHCl_3$), 94% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 19.8 min, t (minor) = 18.7 min; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 4.0 Hz, 1H), 7.29 – 7.25 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 2.74 (d, *J* = 16.0 Hz, 1H), 2.62 (d, *J* = 16.0 Hz, 1H), 2.29 (s, 3H), 1.83 – 1.68 (m, 2H), 1.37 (s, 3H), 0.96 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 158.1, 137.3, 130.1, 126.2, 120.2, 118.3, 81.3, 47.3, 32.2, 23.5, 20.5, 8.1. HRMS (ESI) m/z calcd for $C_{13}H_{17}O_2$ $[M + H]^+$: 205.1223, found: 205.1220.

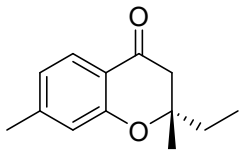


(*S*)-2-ethyl-6-methoxy-2-methylchroman-4-one (**2d**): Colorless oil, 18.5 mg, 84% yield, $[\alpha]_D^{20}$: -1.11 (c = 0.33 in $CHCl_3$), 86% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 27.3 min, t (minor) = 26.4 min; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 4.0 Hz, 1H), 7.07 (dd, *J* = 12.0, 3.2 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 2.74 (d, *J* = 16.0 Hz, 1H), 2.62 (d, *J* = 16.0 Hz, 1H), 1.82 – 1.67 (m, 2H), 1.36 (s, 3H), 0.96 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 154.7, 153.7, 125.4, 120.3, 119.7, 107.1, 81.3, 55.9, 47.1, 32.1, 23.4, 8.1. HRMS (ESI) m/z calcd for $C_{13}H_{17}O_3$ $[M + H]^+$: 221.1172, found: 221.1168.



(*S*)-6-chloro-2-ethyl-2-methylchroman-4-one (**2e**): Colorless oil, 19.9 mg, 89% yield, $[\alpha]_D^{20}$: +0.68 (c = 0.26 in $CHCl_3$), 90% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 16.7 min, t (minor) = 16.0 min; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 8.0, 2.7 Hz, 1H), 6.89 (d, *J* = 12.0 Hz, 1H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 1.86 – 1.66 (m, 2H), 1.38 (s, 3H), 0.97 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 158.5, 136.1, 126.3, 126.0, 121.3, 120.2, 82.1, 46.9, 32.2, 23.4, 8.0. HRMS (ESI) m/z calcd for $C_{12}H_{14}ClO_2$ $[M + H]^+$: 225.0677, found: 225.0681.

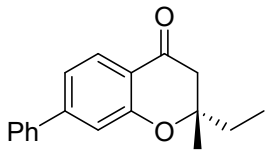
(*S*)-2-ethyl-2,7-dimethylchroman-4-one (**2f**): Colorless oil, 18.6 mg, 91% yield, $[\alpha]_D^{20}$: +4.10 (c = 0.16 in $CHCl_3$), 90% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 26.3 min, t (minor) = 24.9 min; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 6.81 – 6.71 (m, 2H), 2.74 (d, *J* = 16.0 Hz, 1H), 2.61 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H), 1.86 – 1.66 (m, 2H), 1.37 (s, 3H), 0.97 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 160.1, 147.7, 126.5, 122.1, 118.5, 118.4, 81.5, 47.2, 32.3, 23.6, 22.1, 8.1. HRMS (ESI) m/z calcd for $C_{13}H_{17}O_2$ $[M + H]^+$: 205.1223, found: 205.1225.



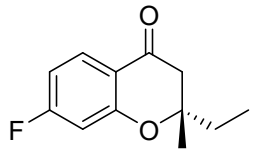
(*S*)-2-ethyl-7-methoxy-2-methylchroman-4-one (**2g**): Colorless oil, 20.9 mg, 95% yield, $[\alpha]_D^{20}$: +1.40 (c = 0.36 in $CHCl_3$), 80% ee, determined by chiral HPLC (Chiralpak OJ-H), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 26.8

min, t (minor) = 23.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 6.53 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 3.83 (s, 3H), 2.72 (d, *J* = 16.0 Hz, 1H), 2.59 (d, *J* = 16.0 Hz, 1H), 1.87 – 1.68 (m, 2H), 1.38 (s, 3H), 0.98 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 166.4, 162.1, 128.3, 114.5, 109.3, 101.3, 82.0, 55.7, 46.9, 32.4, 23.6, 8.1. HRMS (ESI) m/z calcd for $C_{13}H_{17}O_3$ $[M + H]^+$: 221.1172, found: 221.1174.

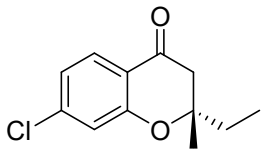
(*S*)-2-ethyl-2-methyl-7-phenylchroman-4-one (**2h**): Colorless oil, 5.3 mg, 20% yield, $[\alpha]_D^{20}$: +6.19 (c = 0.24 in $CHCl_3$), 90% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 254 nm; t (major) = 19.4 min, t (minor) = 18.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.48 – 7.36 (m, 3H), 7.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 2.81 (d, *J* = 16.0 Hz, 1H), 2.67 (d, *J* = 16.0 Hz, 1H), 1.91 – 1.71 (m, 2H), 1.42 (s, 3H), 1.01 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 160.3, 149.2, 139.8, 129.0, 128.6, 127.3, 127.1, 119.8, 119.4, 116.7, 81.7, 47.2, 32.3, 23.6, 8.1. HRMS (ESI) m/z calcd for $C_{18}H_{19}O_2$ $[M + H]^+$: 267.1380, found: 267.1379.



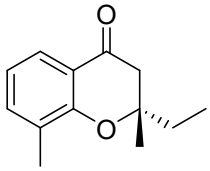
(*S*)-2-ethyl-7-fluoro-2-methylchroman-4-one (**2i**): Colorless oil, 19.6 mg, 94% yield, $[\alpha]_D^{20}$: +0.50 (c = 0.20 in $CHCl_3$), 87% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 18.0 min, t (minor) = 17.0 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 6.7 Hz, 1H), 6.73 – 6.56 (m, 2H), 2.75 (d, *J* = 16.0 Hz, 1H), 2.62 (d, *J* = 16.0 Hz, 1H), 1.85 – 1.68 (m, 2H), 1.38 (s, 3H), 0.98 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 167.9, 161.8, 129.1, 117.5, 109.1, 105.1, 82.5, 46.9, 32.28, 23.5, 8.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.01. HRMS (ESI) m/z calcd for $C_{12}H_{14}FO_2$ $[M + H]^+$: 209.0973, found: 209.0971.



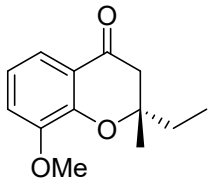
(*S*)-7-chloro-2-ethyl-2-methylchroman-4-one (**2j**): Colorless oil, 22.0 mg, 98% yield, $[\alpha]_D^{20}$: +2.59 (c = 0.54 in $CHCl_3$), 93% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99.5/0.5, 0.25 mL/min, λ = 254 nm; t (major) = 59.3 min, t (minor) = 55.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 6.99 – 6.90 (m, 2H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.62 (d, *J* = 16.0 Hz, 1H), 1.85 – 1.68 (m, 2H), 1.37 (s, 3H), 0.97 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 160.5, 142.0, 127.8, 121.5, 119.1, 118.6, 82.4, 47.0, 32.3, 23.5, 8.0. HRMS (ESI) m/z calcd for $C_{12}H_{14}ClO_2$ $[M + H]^+$: 225.0677, found: 225.0680.



(*S*)-2-ethyl-2,8-dimethylchroman-4-one (**2k**): Colorless oil, 18.0 mg, 88% yield, $[\alpha]_D^{20}$: +4.70 (c = 0.25 in $CHCl_3$), 84% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 23.9 min, t (minor) = 22.5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.34 – 7.30 (m 1H), 6.85 (t, *J* = 8.0 Hz, 1H), 2.75 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 2.22 (s,

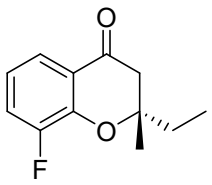


3H), 1.87 – 1.67 (m, 2H), 1.38 (s, 3H), 0.98 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 158.2, 137.0, 127.6, 124.1, 120.2, 120.0, 81.1, 47.4, 32.2, 23.5, 15.8, 8.0. HRMS (ESI) m/z calcd for $C_{13}H_{17}O_2$ $[M + H]^+$: 205.1223, found: 205.1224.

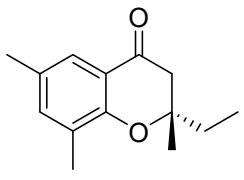


(*S*)-2-ethyl-8-methoxy-2-methylchroman-4-one (**2l**): Colorless oil, 20.0 mg, 91% yield, $[\alpha]_D^{20}$: +4.30 (c = 0.15 in $CHCl_3$), 90% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 43.5 min, t (minor) = 41.9 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.0, 1.5 Hz, 1H), 7.04 (dd, J = 8.0, 1.5 Hz, 1H), 6.89 (t, J = 8.0 Hz, 1H), 3.88 (s, 3H), 2.77 (d, J = 16.0 Hz, 1H), 2.67 (d, J = 16.0 Hz, 1H), 1.91 – 1.74 (m, 2H), 1.44 (s, 3H), 0.98 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 150.2, 149.6, 121.3, 120.1, 117.9, 117.5, 82.2, 56.5, 47.1, 32.0, 23.6, 8.2. HRMS (ESI) m/z calcd for $C_{13}H_{17}O_3$ $[M + H]^+$: 221.1172, found: 221.1174.

(*S*)-2-ethyl-8-fluoro-2-methylchroman-4-one (**2m**): Colorless oil, 19.1 mg, 92% yield, $[\alpha]_D^{20}$: +1.93 (c = 0.15 in $CHCl_3$), 86% ee, determined by chiral HPLC (Chiralpak OJ-H), *n*-hexane/*i*-PrOH = 99.5/0.5, 0.25 mL/min, λ = 254 nm; t (major) = 51.6 min, t (minor) = 45.8 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dt, J = 8.0, 1.5 Hz, 1H), 7.32 – 7.22 (m, 1H), 6.89 (m, 1H), 2.81 (d, J = 16.0 Hz, 1H), 2.69 (d, J = 16.0 Hz, 1H), 1.91 – 1.73 (m, 2H), 1.43 (s, 3H), 1.00 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 152.3, 148.4, 122.6, 122.0, 121.6, 112.0, 82.9, 47.2, 32.1, 23.5, 8.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.36. HRMS (ESI) m/z calcd for $C_{12}H_{14}FO_2$ $[M + H]^+$: 209.0973, found: 209.0975.

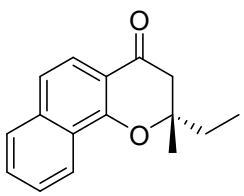


(*S*)-8-chloro-2-ethyl-2-methylchroman-4-one (**2n**): Colorless oil, 21.7 mg, 97% yield, $[\alpha]_D^{20}$: +3.02 (c = 0.46 in $CHCl_3$), 88% ee, determined by chiral HPLC (Chiralpak OJ-H), *n*-hexane/*i*-PrOH = 99.5/0.5, 0.25 mL/min, λ = 254 nm; t (major) = 46.2 min, t (minor) = 41.6 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.0, 1.7 Hz, 1H), 7.54 (dd, J = 8.0, 1.7 Hz, 1H), 6.91 (t, J = 8.0 Hz, 1H), 2.79 (d, J = 16.0 Hz, 1H), 2.70 (d, J = 16.0 Hz, 1H), 1.91 – 1.69 (m, 2H), 1.43 (s, 3H), 1.01 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 155.6, 136.3, 125.1, 123.3, 121.8, 120.8, 82.8, 47.2, 32.0, 23.4, 8.0. HRMS (ESI) m/z calcd for $C_{12}H_{14}ClO_2$ $[M + H]^+$: 225.0677, found: 225.0677.



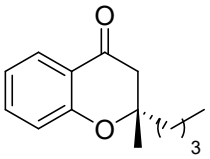
(*S*)-2-ethyl-2,6,8-trimethylchroman-4-one (**2o**): Colorless oil, 4.2 mg, 19% yield, $[\alpha]_D^{20}$: +0.89 (c = 0.06 in $CHCl_3$), 75% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 254 nm; t (major) = 13.2 min, t (minor) = 112.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 2.3 Hz, 1H), 7.22 – 7.07 (m, 1H), 2.72 (d, J = 16.0 Hz, 1H), 2.62 (d, J = 16.0 Hz, 1H), 2.25 (s, 3H), 2.18 (s, 3H), 1.85 – 1.64 (m, 2H), 1.36 (s, 3H), 0.97 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 156.2, 138.2, 129.3, 127.4, 123.7, 119.8, 80.9, 47.4, 32.1, 23.5, 20.4, 15.7, 8.0. HRMS (ESI) m/z calcd for $C_{14}H_{19}O_2$ $[M + H]^+$: 219.1380, found: 219.1378.

(*S*)-2-ethyl-2-methyl-2,3-dihydro-4H-benzo[h]chromen-4-one (**2p**): Colorless oil, 5.8 mg, 24% yield, $[\alpha]_D^{20}$: +1.19 (c = 0.11 in $CHCl_3$), 97% ee, determined by chiral HPLC

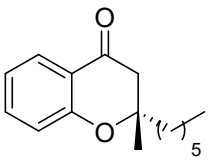


(Chiralpak IC), *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, λ = 254 nm; t (major) = 13.4 min, t (minor) = 12.9 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 2.88 (d, *J* = 16.0 Hz, 1H), 2.75 (d, *J* = 16.0 Hz, 1H), 2.01 – 1.79 (m, 2H), 1.51 (s, 3H), 1.06 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (1010 MHz, $CDCl_3$) δ 192.5, 158.1, 137.9, 129.5, 128.0, 126.1, 125.5, 123.7, 121.6, 120.3, 114.8, 82.7, 46.9, 32.4, 23.4, 8.2. HRMS (ESI) m/z calcd for $C_{16}H_{17}O_2$ $[M + H]^+$: 241.1223, found: 241.1219.

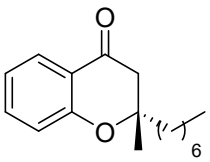
(*S*)-2-butyl-2-methylchroman-4-one (**3a**): Colorless oil, 19.2 mg, 88% yield, $[\alpha]_D^{20}$: +3.02 (c = 0.39 in $CHCl_3$), 90% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 17.5 min, t (minor) = 14.9 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.49 – 7.41 (m, 1H), 6.99 – 6.89 (m, 2H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 1.79 – 1.65 (m, 2H), 1.43 – 1.30 (m, 7H), 0.90 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 160.1, 136.2, 126.6, 120.7, 120.6, 118.5, 81.4, 47.6, 39.3, 25.9, 24.1, 23.1, 14.1. HRMS (ESI) m/z calcd for $C_{14}H_{19}O_2$ $[M + H]^+$: 219.1380, found: 219.1382.



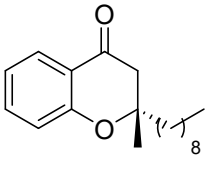
(*S*)-2-hexyl-2-methylchroman-4-one (**3b**): Colorless oil, 17.5 mg, 71% yield, $[\alpha]_D^{20}$: -3.58 (c = 0.10 in $CHCl_3$), 89% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 17.0 min, t (minor) = 14.2 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.50 – 7.42 (m, 1H), 6.99 – 6.90 (m, 2H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 1.79 – 1.64 (m, 2H), 1.40 (s, 3H), 1.36 – 1.19 (m, 8H), 0.90 – 0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 160.1, 136.3, 126.6, 120.7, 120.6, 118.5, 81.4, 47.6, 39.6, 31.8, 29.6, 24.1, 23.7, 22.7, 14.2. HRMS (ESI) m/z calcd for $C_{16}H_{23}O_2$ $[M + H]^+$: 247.1693, found: 247.1695.



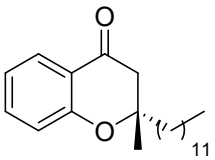
(*S*)-2-heptyl-2-methylchroman-4-one (**3c**): Colorless oil, 16.7 mg, 64% yield, $[\alpha]_D^{20}$: +4.39 (c = 0.17 in $CHCl_3$), 81% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 254 nm; t (major) = 17.0 min, t (minor) = 14.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.50 – 7.41 (m, 1H) (m, 1H), 7.01 – 6.84 (m, 2H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 1.81 – 1.65 (m, 2H), 1.39 (s, 5H), 1.29 – 1.23 (m, 8H), 0.87 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 160.1, 136.3, 126.6, 120.7, 120.6, 118.5, 81.4, 47.6, 39.6, 31.9, 29.9, 29.3, 24.1, 23.7, 22.8, 14.2. HRMS (ESI) m/z calcd for $C_{17}H_{25}O_2$ $[M + H]^+$: 261.1849, found: 261.1852.



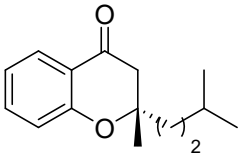
(*S*)-2-methyl-2-nonylchroman-4-one (**3d**): Colorless oil, 15.9 mg, 55% yield, $[\alpha]_D^{20}$: +2.20 (c = 0.09 in $CHCl_3$), 81% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 15.3 min, t (minor) = 13.0 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.51 – 7.40 (m, 1H), 6.98 – 6.88 (m, 2H), 2.77 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 1.78 – 1.63 (m, 2H), 1.39 (s, 5H), 1.26 (d, *J* = 8.0 Hz, 12H), 0.87 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 160.1, 136.2, 126.6, 120.7, 120.7, 120.6, 118.4, 81.4, 47.6, 39.6, 32.0, 29.9, 29.6, 29.4, 24.1, 23.7, 22.8, 14.2. HRMS (ESI) m/z calcd for $C_{18}H_{29}O_2$ $[M + H]^+$: 289.2162, found: 289.2161.



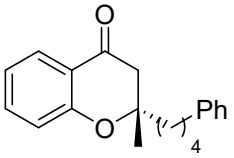
(*S*)-2-dodecyl-2-methylchroman-4-one (**3e**): Colorless oil, 25.8 mg, 78% yield, $[\alpha]_D^{20}$: +3.24 (c = 0.16 in $CHCl_3$), 92% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 14.2 min, t (minor) = 12.0 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.50 – 7.40 (m, 1H), 6.99 – 6.89 (m, 2H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 1.80 – 1.62 (m, 2H), 1.39 (s, 3H), 1.26 (d, *J* = 7.5 Hz, 20H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 160.1, 136.2, 126.6, 120.7, 120.6, 118.5, 81.4, 47.6, 39.6, 32.1, 30.0, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 24.1, 23.7, 22.8, 14.2. HRMS (ESI) m/z calcd for $C_{22}H_{35}O_2$ $[M + H]^+$: 331.2632, found: 331.2630.



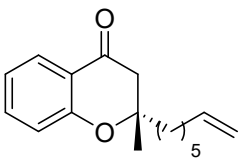
(*S*)-2-isopentyl-2-methylchroman-4-one (**3f**): Colorless oil, 15.3 mg, 66% yield, $[\alpha]_D^{20}$: +0.09 (c = 0.28 in $CHCl_3$), 95% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, λ = 254 nm; t (major) = 16.3 min, t (minor) = 13.5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.52 – 7.38 (m 1H), 6.98 – 6.90 (m, 2H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 1.79 – 1.65 (m, 2H), 1.53 – 1.46 (m, 1H), 1.39 (s, 3H), 1.34 – 1.24 (m, 2H), 0.87 (dd, *J* = 6.0, 4.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 160.1, 136.2, 126.6, 120.7, 120.6, 118.5, 81.5, 77.48, 77.2, 76.8, 47.6, 37.4, 32.6, 28.4, 24.0, 22.6. HRMS (ESI) m/z calcd for $C_{15}H_{21}O_2$ $[M + H]^+$: 233.1536, found: 233.1536.



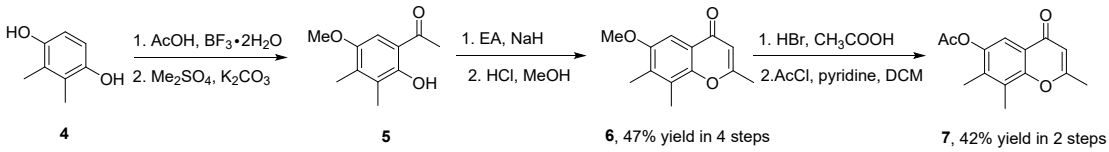
(*S*)-2-methyl-2-(4-phenylbutyl)chroman-4-one (**3g**): Colorless oil, 14.7 mg, 50% yield, $[\alpha]_D^{20}$: +4.01 (c = 0.15 in $CHCl_3$), 74% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 254 nm; t (major) = 29.0 min, t (minor) = 23.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.25 (d, *J* = 4.0 Hz, 1H), 7.20 – 7.13 (m, 3H), 7.00 – 6.89 (m, 2H), 2.77 (d, *J* = 16.0 Hz, 1H), 2.67 – 2.58 (m, 3H), 1.84 – 1.61 (m, 4H), 1.52 – 1.43 (m, 2H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 160.0, 142.4, 136.3, 128.5, 128.5, 126.6, 125.9, 120.8, 120.5, 118.5, 81.3, 47.6, 39.4, 35.9, 31.7, 24.1, 23.3. HRMS (ESI) m/z calcd for $C_{20}H_{23}O_2$ $[M + H]^+$: 295.1693, found: 295.1696.



(*S*)-2-(hept-6-en-1-yl)-2-methylchroman-4-one (**3h**): Colorless oil, 15.0 mg, 58% yield, $[\alpha]_D^{20}$: -2.03 (c = 0.22 in $CHCl_3$), 75% ee, determined by chiral HPLC (Chiralpak IC), *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 254 nm; t (major) = 19.1 min, t (minor) = 15.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.46 (m, 1H), 7.06 – 6.78 (m, 2H), 5.87 – 5.71 (m, 1H), 5.13 – 4.75 (m, 2H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 2.11 – 1.94 (m, 2H), 1.79 – 1.63 (m, 2H), 1.48 – 1.27 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 160.1, 139.0, 136.3, 126.6, 120.7, 120.6, 118.5, 114.5, 81.4, 47.6, 39.5, 33.8, 29.4, 28.9, 24.1, 23.6. HRMS (ESI) m/z calcd for $C_{17}H_{23}O_2$ $[M + H]^+$: 259.1693, found: 259.1689.



2.3 Synthetic strategy of chromone derivatives 7



4 **5** **6**, 47% yield in 4 steps **7**, 42% yield in 2 steps

Under an argon atmosphere, 2,3-dimethylhydroquinone **4** (5.0 mL, 36.2 mmol), glacial acetic acid (4.2 mL, 72.4 mmol), and boron trifluoride dihydrate (6.9 mL, 108.6 mmol) were added sequentially to a pressure-resistant sealed tube. The mixture was then refluxed at 120 ºC for 20 hours, and the reaction progress was monitored by TLC. Upon completion, the reaction was quenched with ice water and extracted with ethyl acetate. The combined organic layers were washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The resulting crude product was used directly in the next step without further purification.

Under an argon atmosphere, the crude product from the previous step (4.7 g, 26.0 mmol), acetone (30 mL), potassium carbonate (10.8 g, 78.0 mmol), and dimethyl sulfate (7.4 mL, 78.0 mmol) were added to a dried round-bottom flask. The mixture was refluxed for 40 hours, and the reaction was monitored by TLC. The reaction mixture was then diluted with water and extracted with diethyl ether. The combined organic layers were washed with saturated ammonium chloride solution and saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The resulting crude product **5** was used directly in the next step without purification.

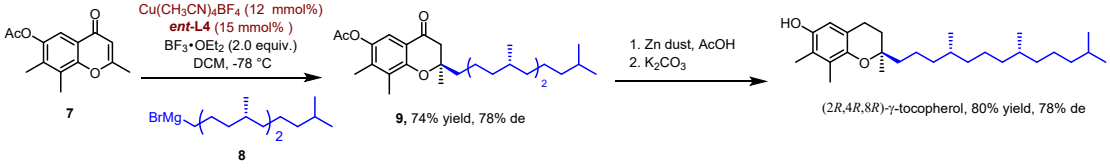
Under an argon atmosphere, sodium hydride (1.7 g, 41.2 mmol; 60 wt% in mineral oil) and anhydrous tetrahydrofuran (THF, 4 mL) were added to a dried round-bottom flask. A solution of crude product 145 (2.0 g, 10.3 mmol) and ethyl acetate (25.2 mL, 25.8 mmol) in THF (3 mL) was added dropwise at 0 ºC. The mixture was then refluxed overnight, with the reaction monitored by TLC. The reaction was quenched with ice water and adjusted to pH = 6 using 6 M HCl, then extracted with ethyl acetate. The combined organic layers were washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give a crude product. Methanol (28 mL) and concentrated hydrochloric acid (1.0 mL) were added to the crude product, and the mixture was stirred at room temperature for 12 hours while monitoring by TLC. Methanol was removed by concentration, and the residue was extracted with ethyl acetate. The combined organic layers were washed with saturated $NaHCO_3$ solution, water, and saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc = 15:1) to afford the desired product **6**, Pale yellow solid, 3.7 g, 47% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.12 (s, 1H), 3.88 (s, 3H), 2.39 – 2.32 (m, 6H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 165.4, 155.0, 150.0, 133.0, 126.6, 121.6, 109.6, 100.8, 55.9, 20.6, 12.7, 12.1. HRMS (ESI) m/z calcd for $C_{13}H_{15}O_3$ $[M + H]^+$: 219.1016, found: 219.1012.

Under an argon atmosphere, compound **6** (872.4 mg, 4.0 mmol), glacial acetic acid (3.0 mL), and hydrobromic acid (30.0 mL) were added to a 15 mL pressure-resistant sealed tube. The mixture was heated at 120 ºC for 2 hours, and the reaction was monitored by TLC. The reaction was quenched with saturated $NaHCO_3$ and extracted with ethyl acetate. The combined organic layers were washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography and used directly in the next step without further purification.

Under an argon atmosphere, the crude product from the previous step, dichloromethane (20.0 mL), and pyridine (388.2 μL, 4.8 mmol) were added to a reaction tube. The mixture was cooled in an ice bath, and acetyl chloride (342.5 μL, 4.8 mmol) was added dropwise. After the addition was complete, the

reaction mixture was stirred at room temperature overnight, and the progress was monitored by TLC. The reaction was quenched with 2 M HCl and extracted with dichloromethane. The combined organic layers were washed with saturated sodium bicarbonate and saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc = 15:1) to afford the target compound **7**, pale yellow solid, 866.2 mg, 42% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 6.13 (s, 1H), 2.40 (d, J = 1.2 Hz, 6H), 2.34 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 169.4, 166.0, 152.7, 146.4, 135.9, 127.5, 122.1, 115.3, 110.0, 20.8, 20.7, 13.6, 12.3. HRMS (ESI) m/z calcd for $C_{14}H_{15}O_4$ $[M + H]^+$: 247.0965, found: 247.0965.

2.4 Synthesis of γ-tocopherol

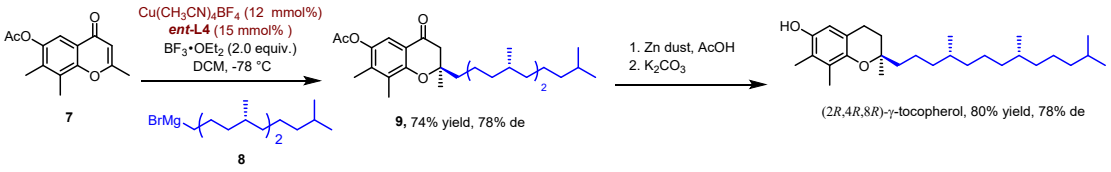


To a mixture of $Cu(CH_3CN)_4BF_4$ (7.6 mg, 0.024 mmol), **L4** (17.8 mg, 0.03 mmol) and **7** (49.2mg, 0.2 mmol), dry DCM (4.0 mL) was added under N_2 atmosphere and the mixture was stirred at room temperature for 20 mins. Then, $BF_3{\cdot}OEt_2$ (0.4 mmol, 2.0 equiv.) was added via syringe under -78 °C and the mixture was allowed to stir at -78 ºC for 20 mins. Then, Grignard reagent **8** (0.4 mmol, 2.0 equiv.)[2] was added dropwise in about 1 min. The reaction mixture was stirred for 4 hours and quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with DCM. The combined organic layers were dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 30:1) to give the desired product **9**, Colorless oil, 69.9 mg, 74% yield, $[\alpha]_D^{20}$: -1.02 (c = 0.23 in $CHCl_3$), 78% de, determined by chiral HPLC (Chiralpak AS-H), *n*-hexane/*i*-PrOH = 99/1, 0.17 mL/min, λ = 254 nm; t (major) = 50.3 min, t (minor) = 67.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 2.74 (d, J = 16.4 Hz, 1H), 2.60 (d, J = 16.4 Hz, 1H), 2.31 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 1.71 – 1.08 (m, 24H), 0.89 – 0.81 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 169.8, 155.6, 142.9, 138.0, 127.6, 118.2, 116.0, 81.2, 47.4, 39.9, 39.5, 37.6, 37.5, 37.4, 37.2, 32.9, 32.7, 28.1, 24.9, 24.6, 24.1, 22.9, 22.8, 21.2, 20.9, 19.9, 19.7, 13.8, 12.2. HRMS (ESI) m/z calcd for $C_{30}H_{49}O_4$ $[M + H]^+$: 473.3625, found: 473.3628.

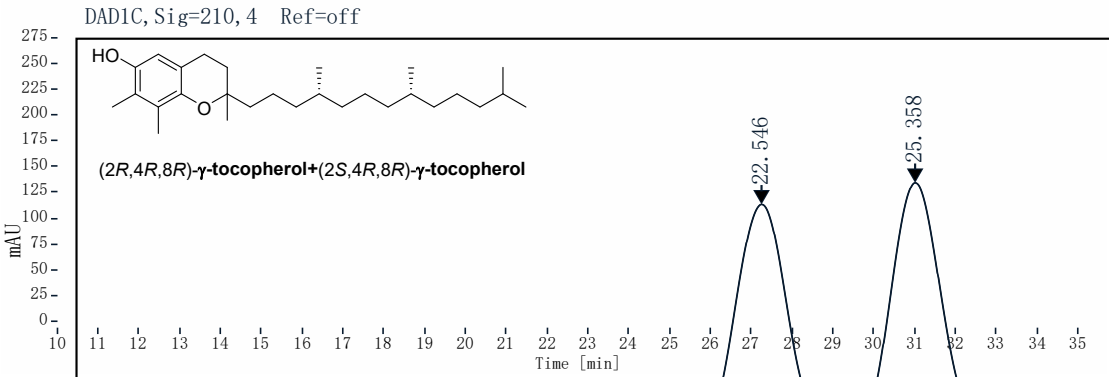
Under an argon atmosphere, glacial acetic acid (1.0 mL) and activated zinc powder (241.9 mg, 3.7 mmol) were added to a 15 mL pressure-resistant sealed tube. A solution of intermediate **9** (69.9 mg, 0.15 mmol) in glacial acetic acid (0.2 mL) was then added to the resulting suspension. The reaction mixture was stirred at 100 ºC for 12 hours, and the reaction progress was monitored by TLC. After completion, the reaction was quenched with saturated K_2CO_3 solution and filtered through diatomaceous earth, followed by concentration. The residue was extracted with ethyl acetate. The combined organic layers were washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford the crude product. Under an argon atmosphere, the crude product (59.8 mg, 0.13 mmol), methanol (3.0 mL), and potassium carbonate (54.0 mg, 0.39 mmol) were added sequentially to a 15 mL reaction tube. The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion, the reaction mixture was filtered through diatomaceous earth and concentrated. The residue was diluted with ethyl acetate and washed with 1 M HCl. The combined organic layers were

washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc = 60:1) to afford the colorless oily product, (2*S*,4*R*,8*R*)-γ-tocopherol, Colorless oil, 49.8 mg, 80% yield, $[\alpha]_D^{20}$: +0.99 (c = 0.33 in $CHCl_3$), 78% de, determined by chiral HPLC (Chiralpak IA-H), *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 210 nm; t (major) = 24.8 min, t (minor) = 22.1 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H), 4.21 (s, 1H), 2.67 (m, 2H), 2.13 (d, *J* = 9.1 Hz, 6H), 1.82 – 1.67 (m, 2H), 1.58 – 1.05 (m, 24H), 0.92 – 0.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 145.9, 126.0, 121.7, 118.5, 112.3, 75.6, 40.2, 39.5, 37.6, 37.6, 37.6, 37.4, 33.0, 32.8, 31.6, 28.1, 25.0, 24.6, 24.2, 22.9, 22.8, 22.5, 21.2, 19.9, 19.8, 12.1, 12.0. HRMS (ESI) m/z calcd for $C_{28}H_{49}O_2$ $[M + H]^+$: 417.3727, found: 417.3728.

3. The determination of absolute configuration



Product (2*R*,4*R*,8*R*)-γ-**tocopherol** was obtained using *ent*-**L4** as the chiral ligand, which is consistent with commercially available (2*R*,4*R*,8*R*)-γ-tocopherol (CAS:54-28-4). This result indicated that the catalytic system produced the *S* configuration product.



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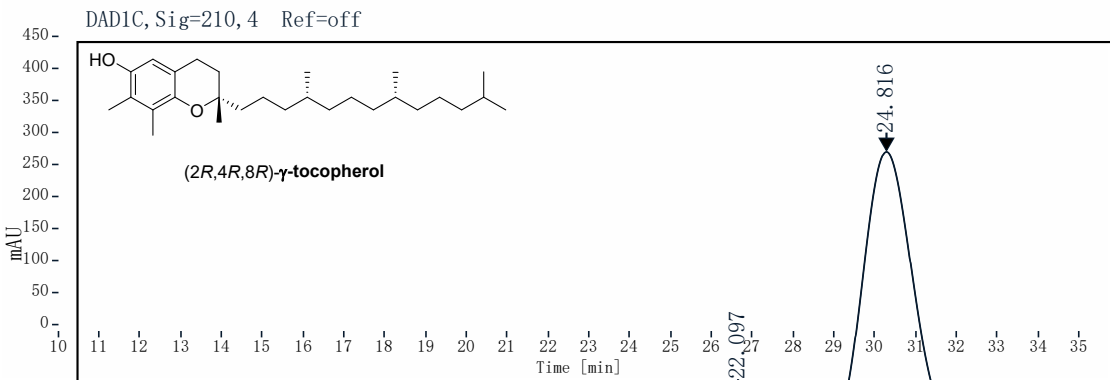
25.358	MM m	0.95	10931.97	177.78	50.96



Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
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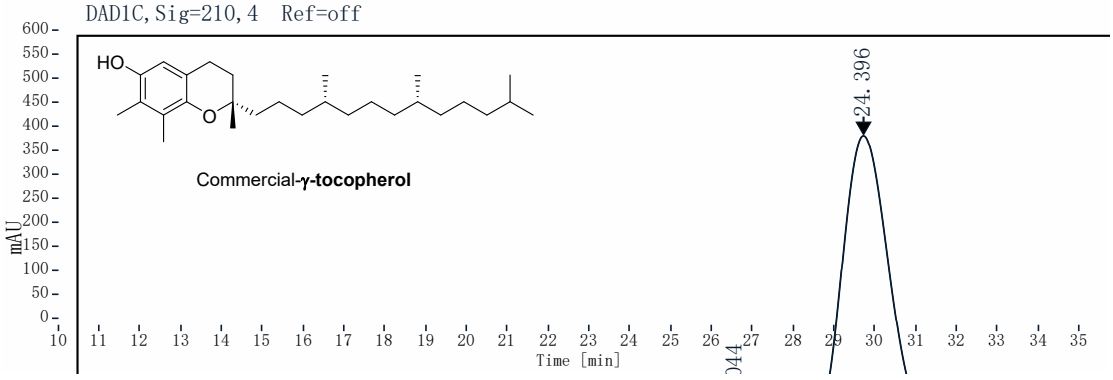
24.816	MM m	0.98	20424.28	328.94	88.85

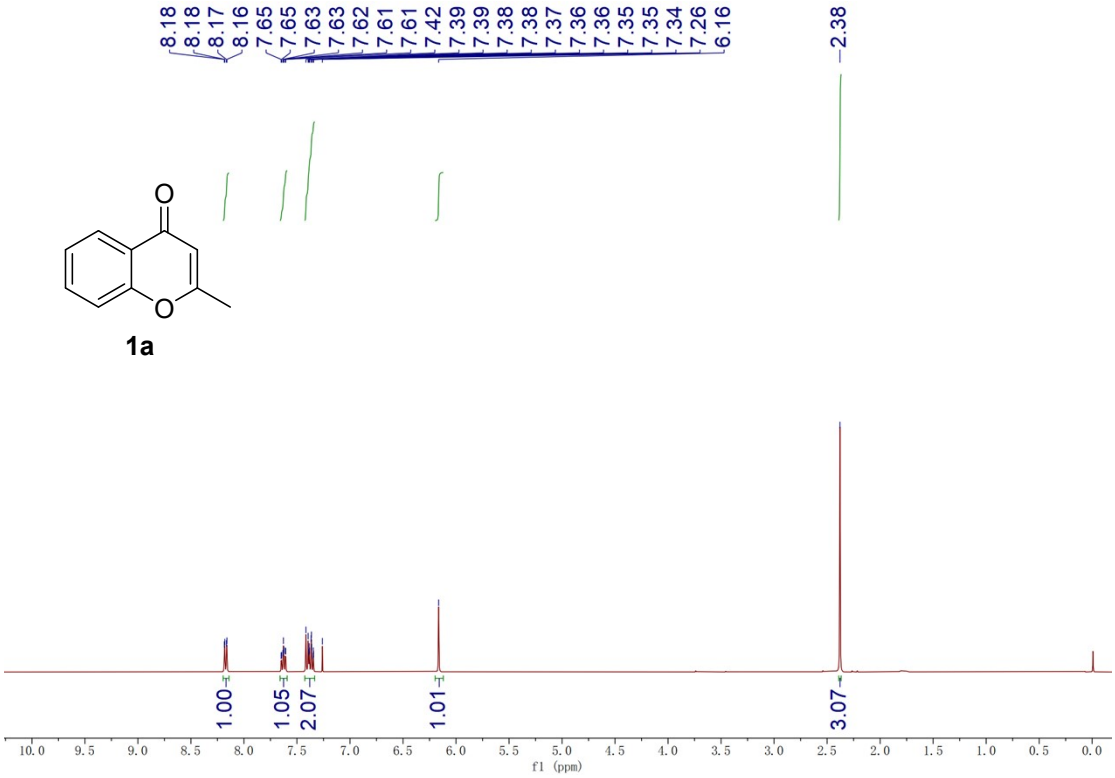


Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
22.044	MM m	0.57	30.43	0.63	0.11
24.396	MM m	0.92	26603.38	456.59	99.89

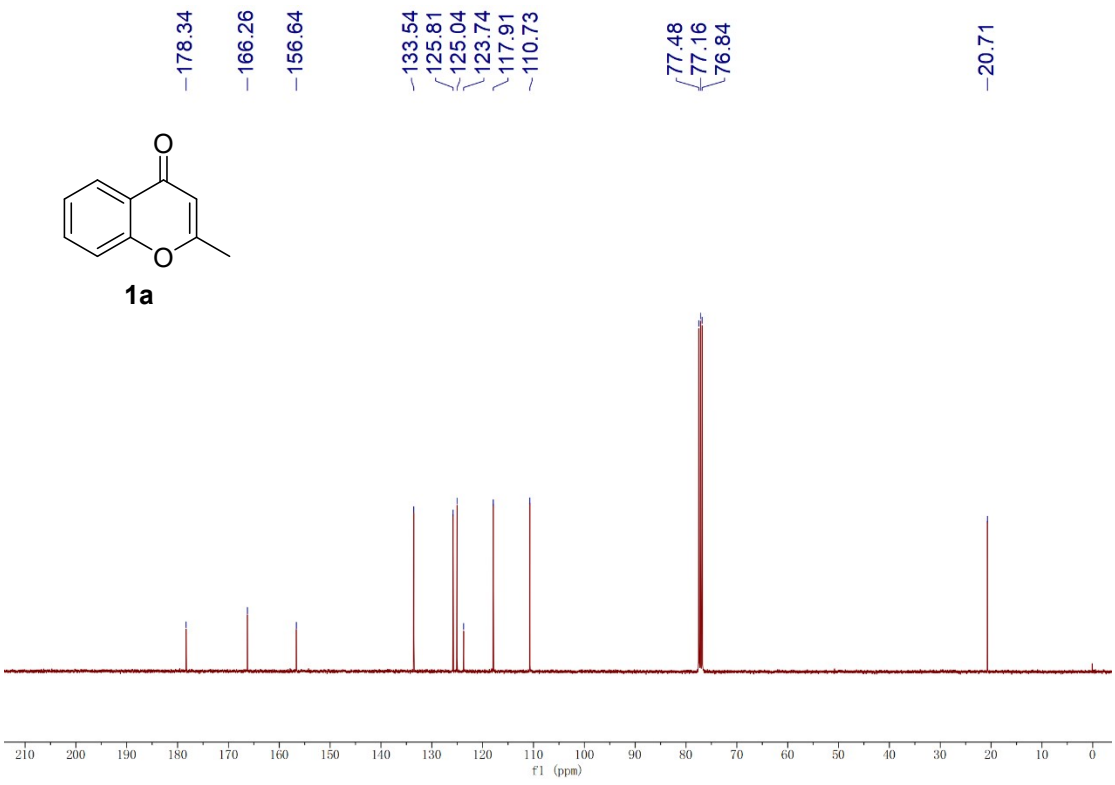
4. References

1. D. Zhao, B. Beiring, F. Glorius, Ruthenium-NHC-catalyzed asymmetric hydrogenation of flavones and chromones: General access to enantiomerically enriched flavanones, flavanols, chromanones, and chromanols, *Angew. Chem. Int. Ed.* **2013**, *52*, 8454−8458.
2. Z. Wu, S. R. Harutyunyan, A. J. Minnaard, Total synthesis of (R,R,R)-γ-tocopherol through Cu-catalyzed asymmetric 1,2-addition, *Chem. Eur. J.*, **2014**, *20*, 14250−14255.

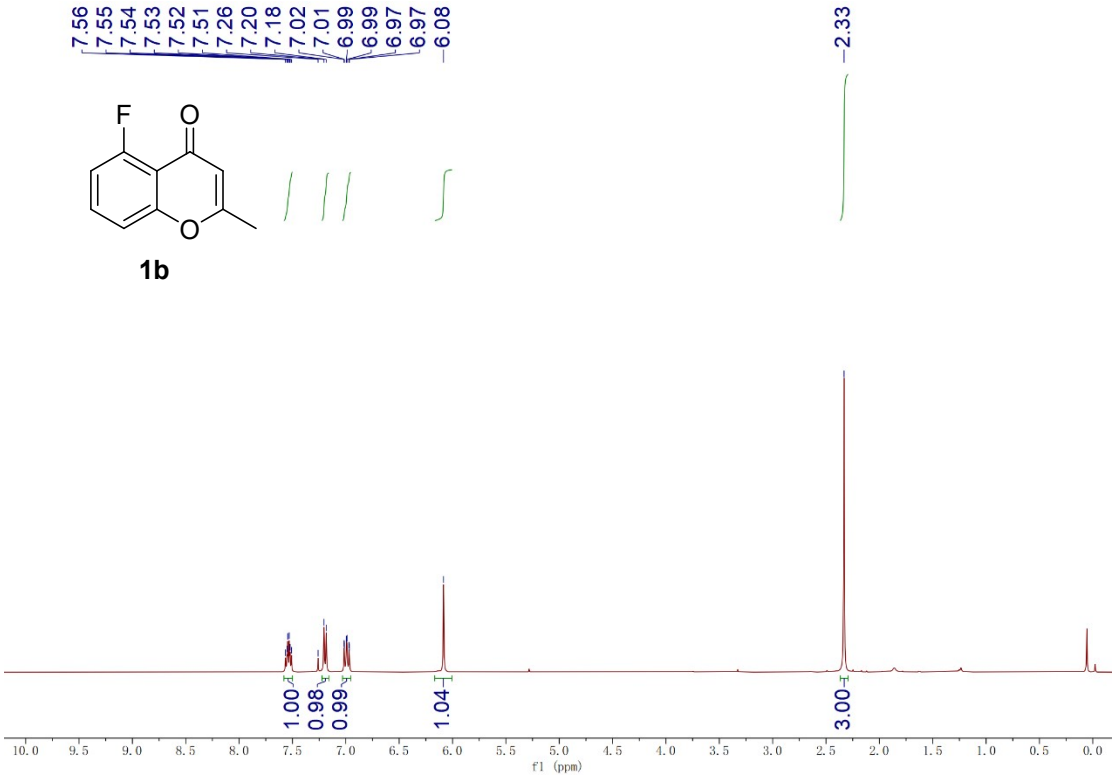
5. NMR Spectrum



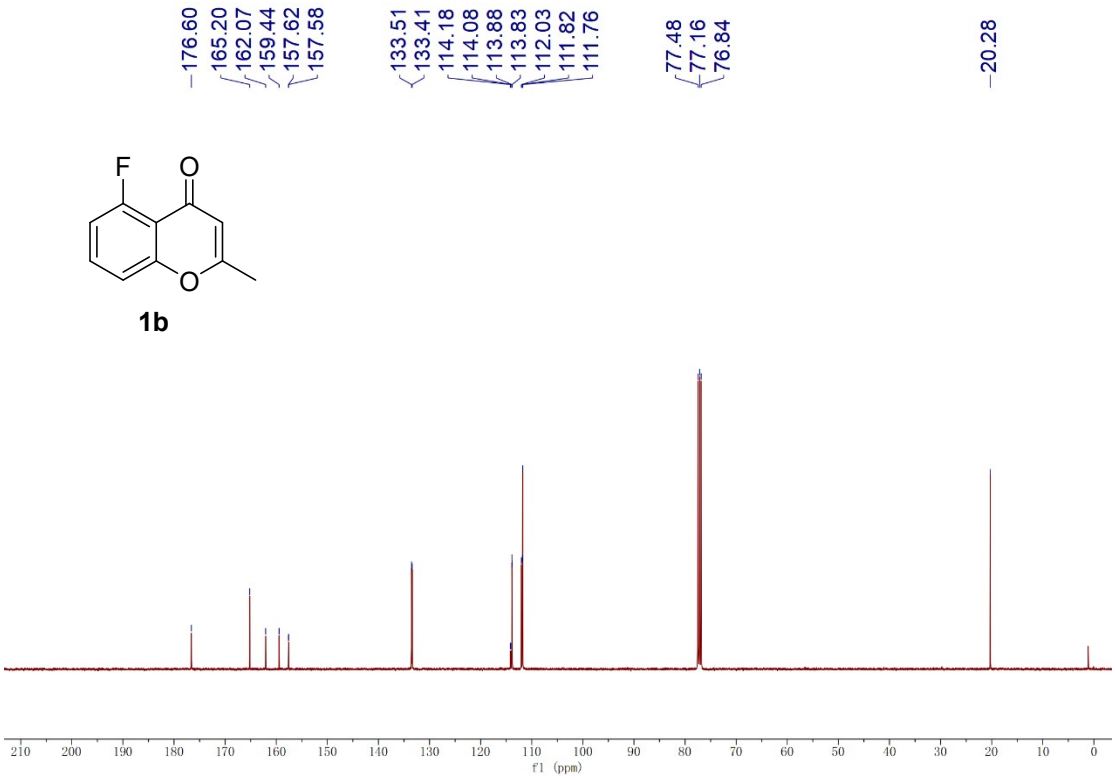
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1a



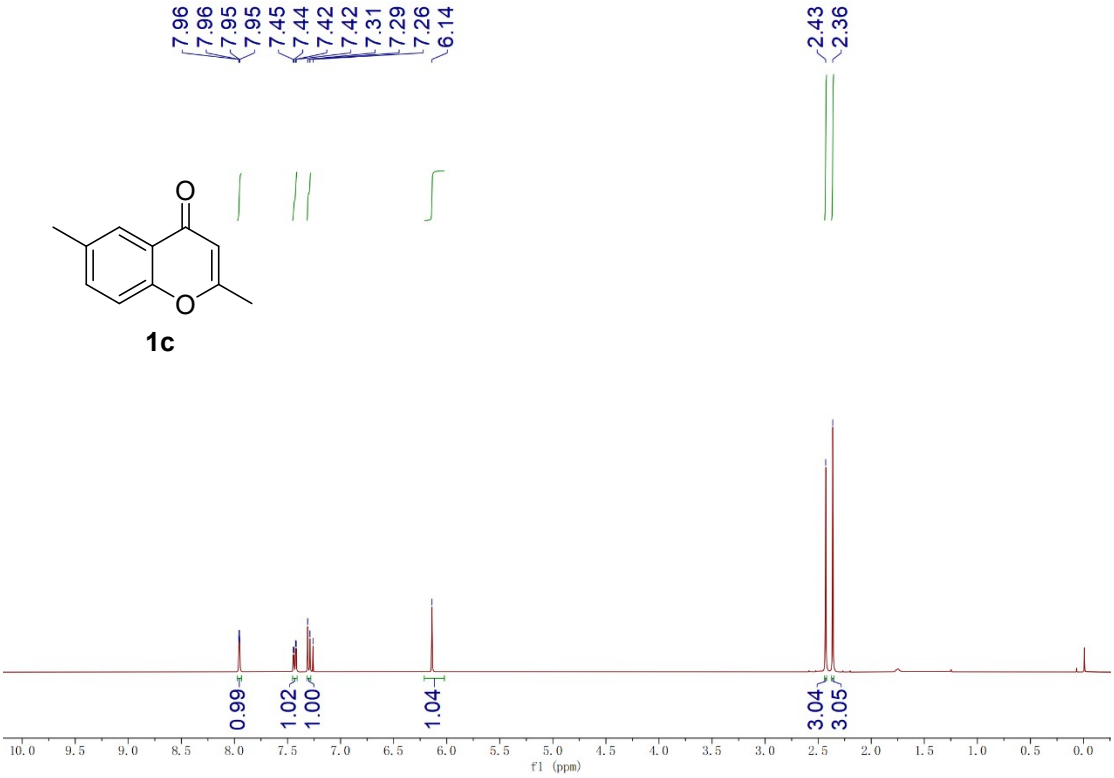
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1a



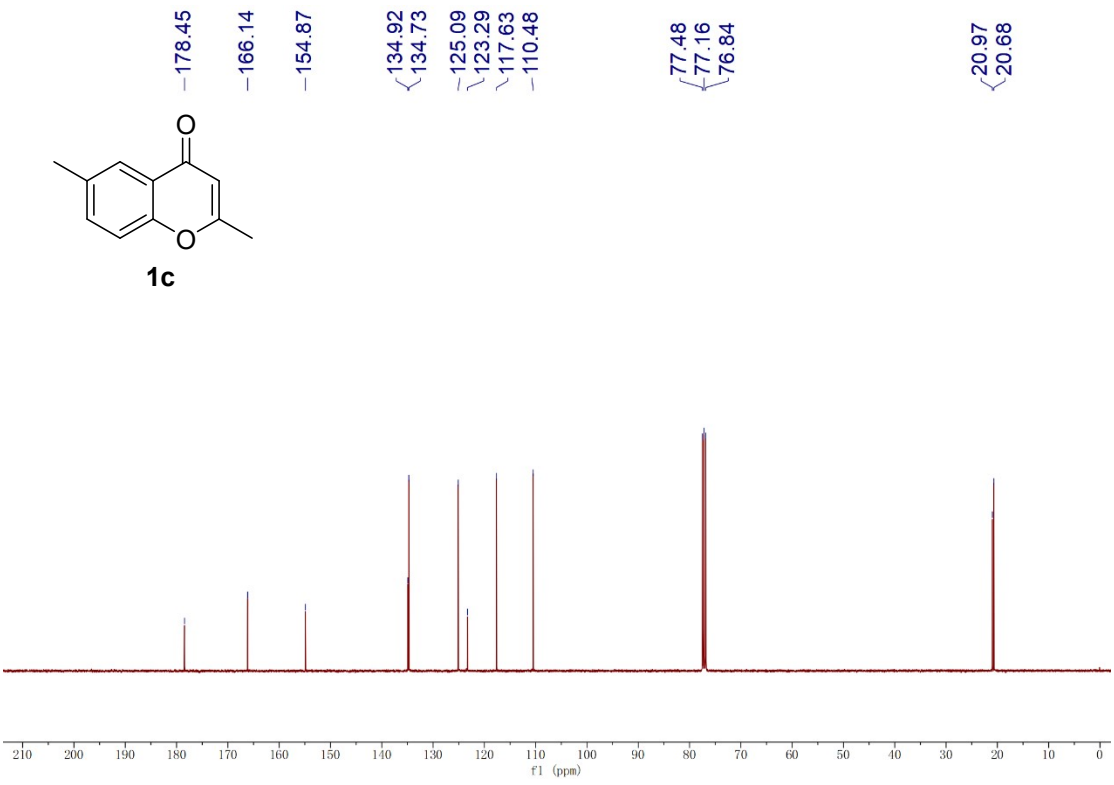
[1]H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1b



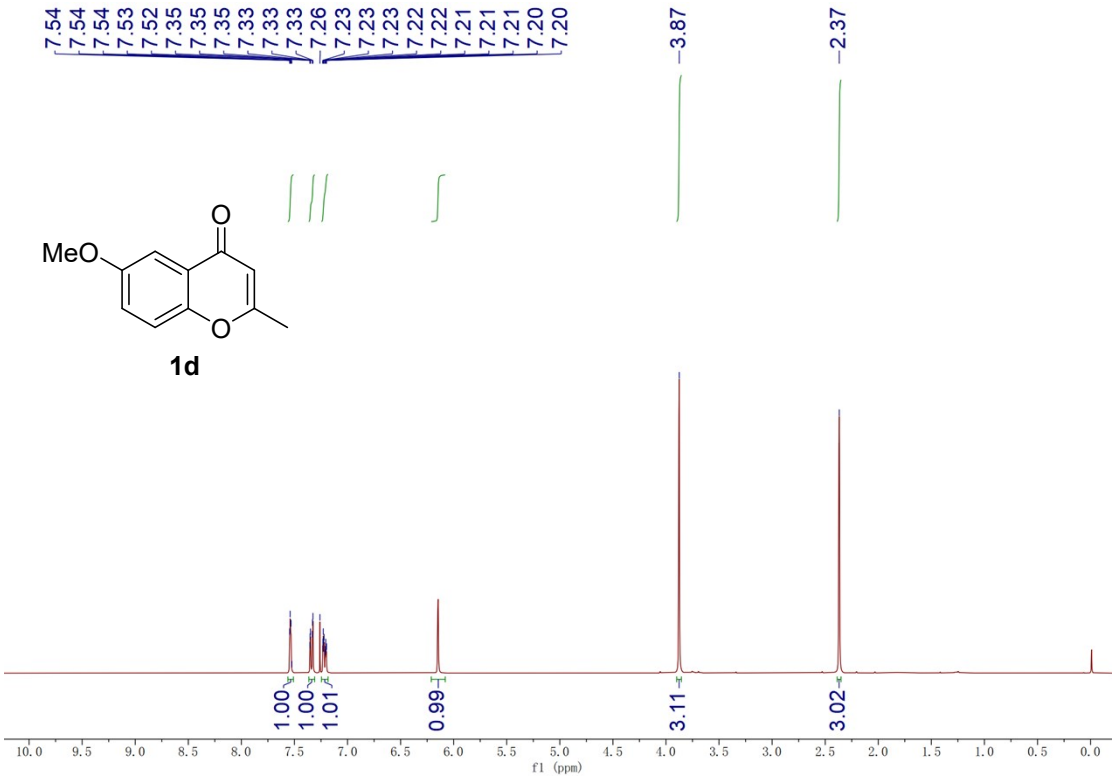
[13]C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1b



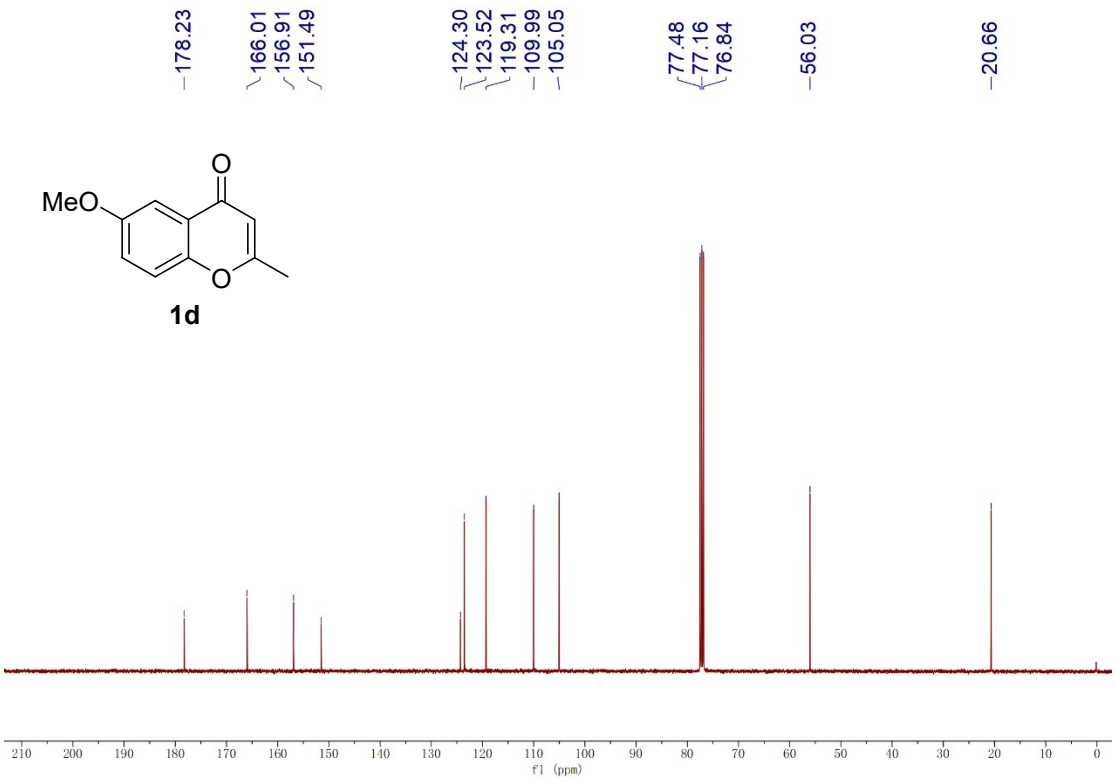
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1c



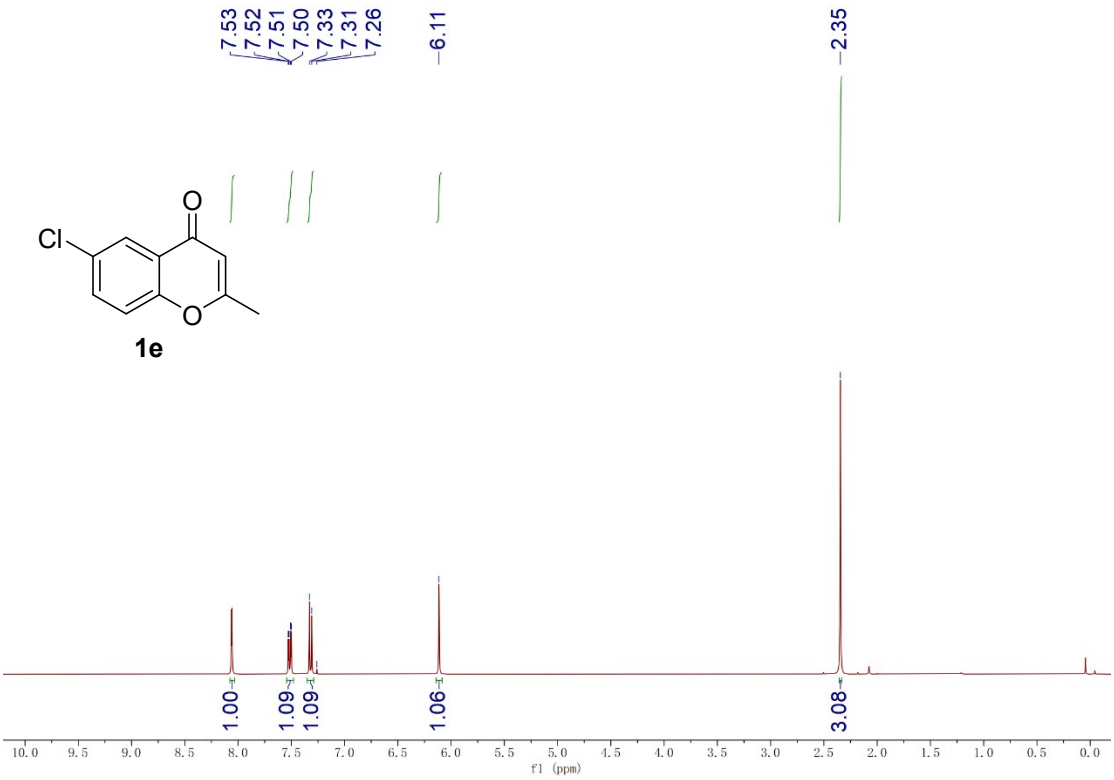
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1c



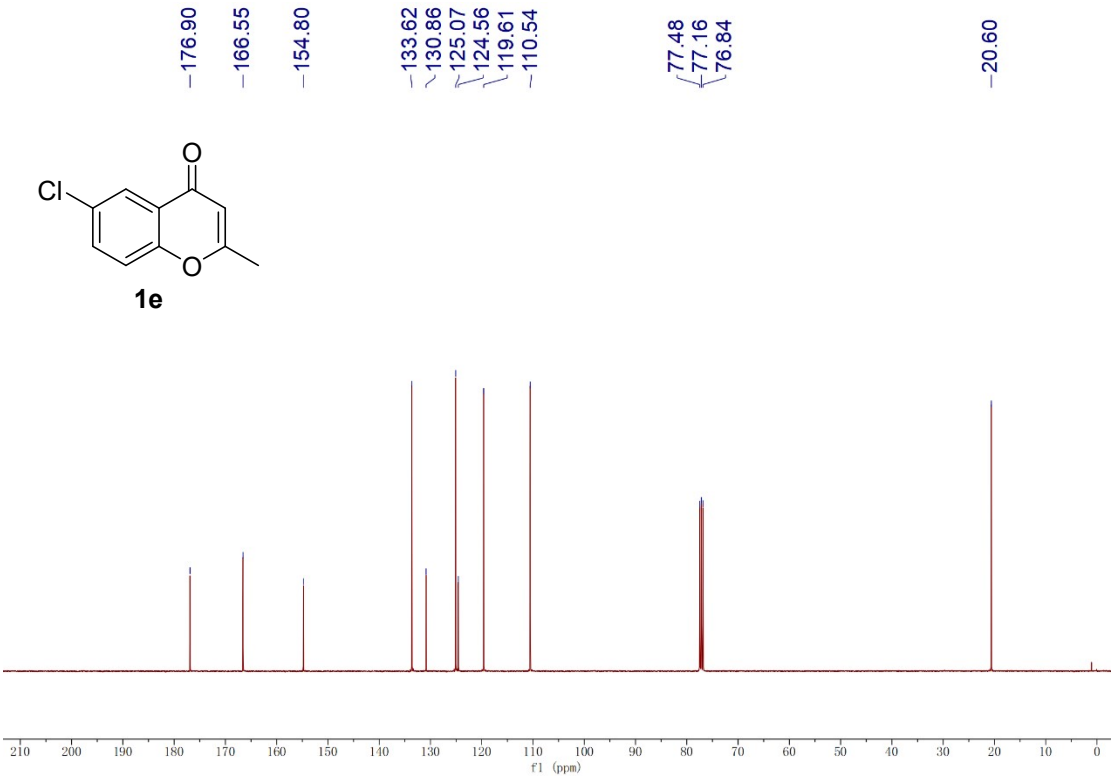
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1d



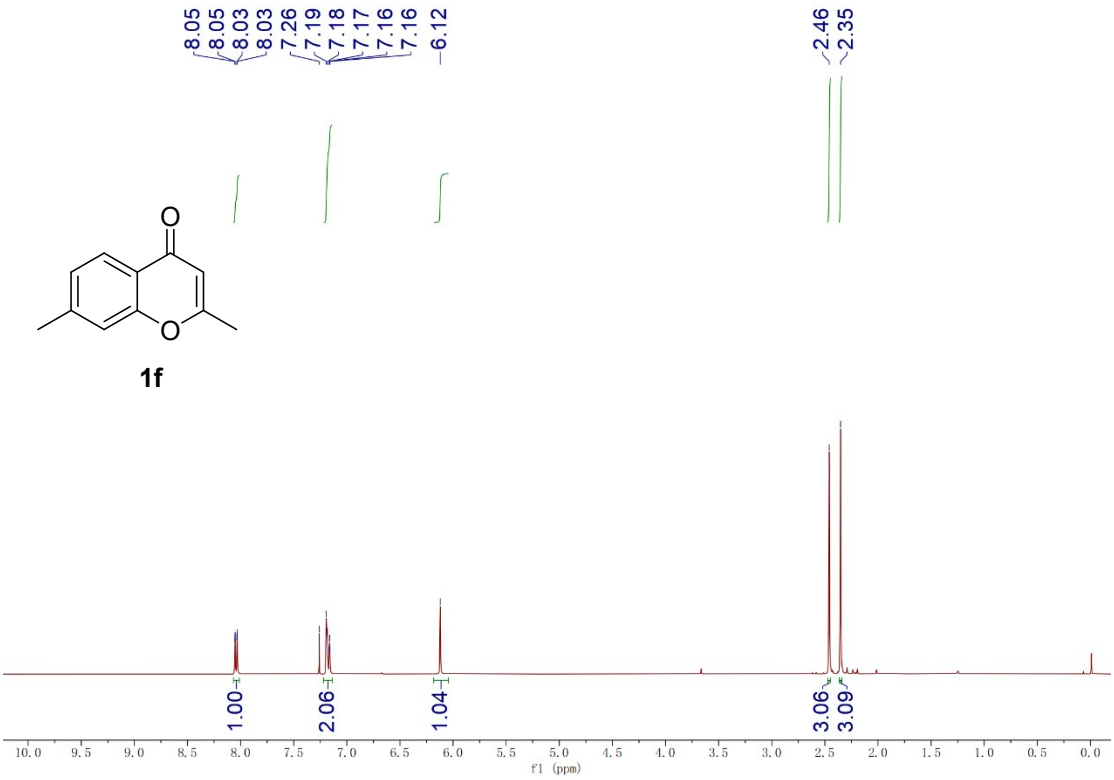
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1d



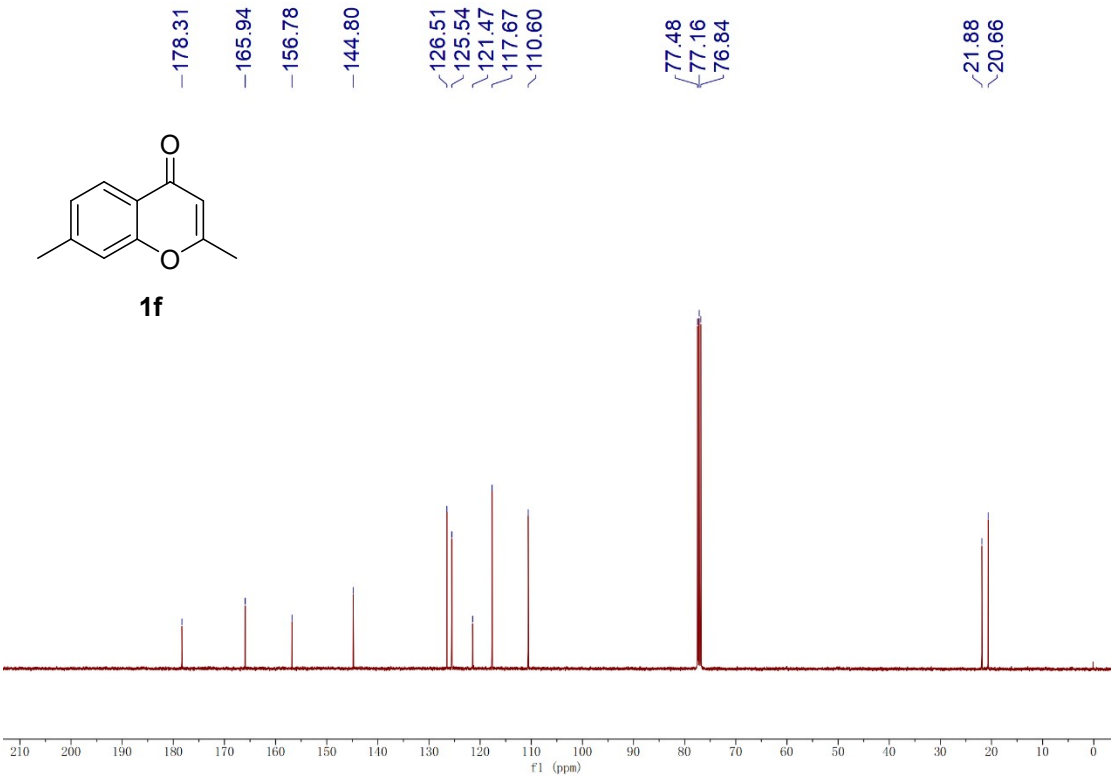
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1e



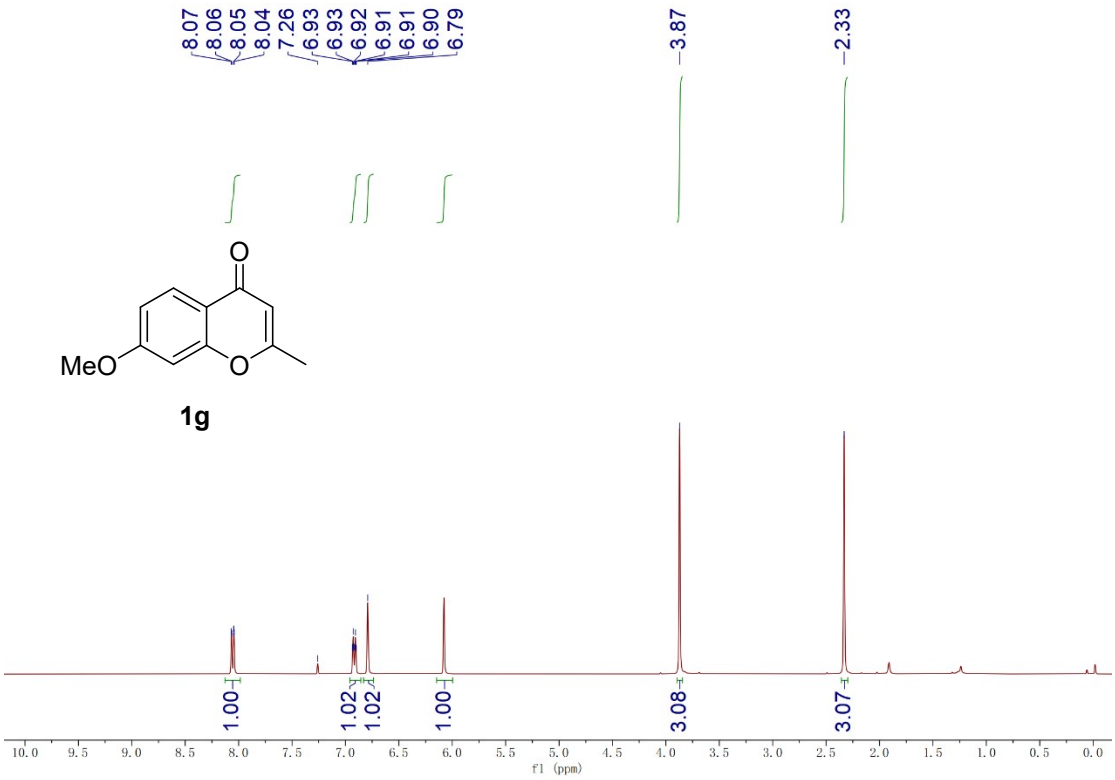
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1e



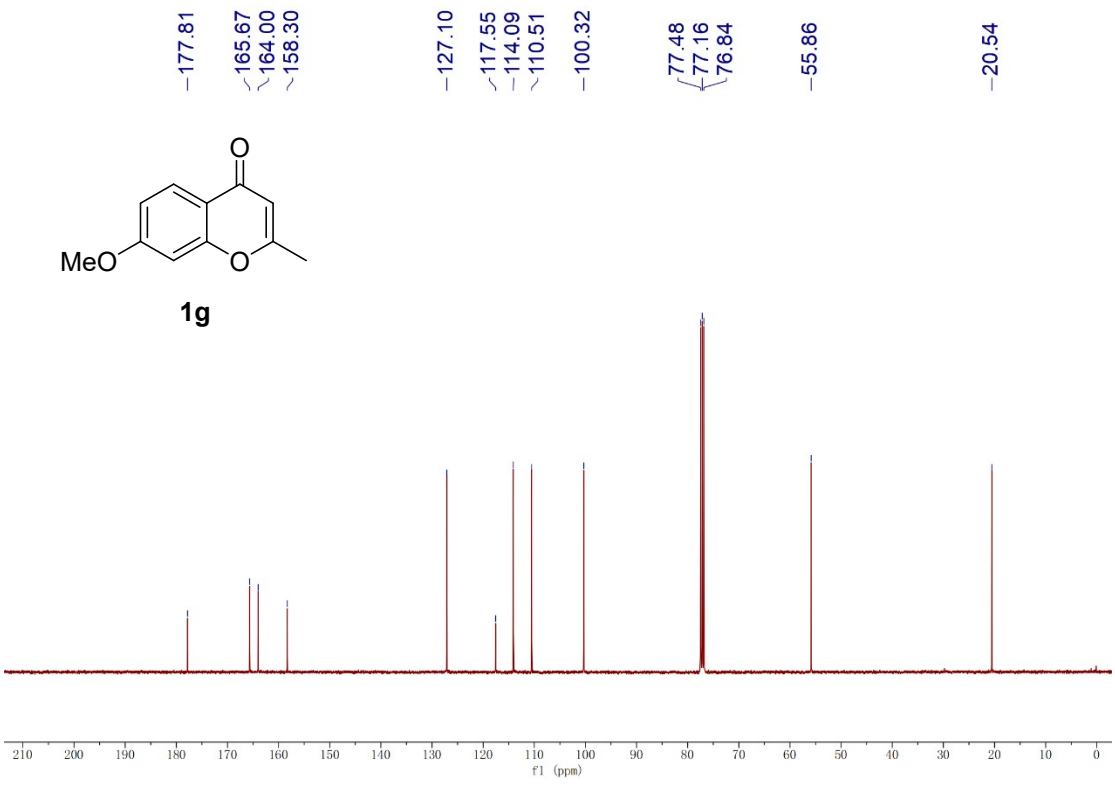
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1f



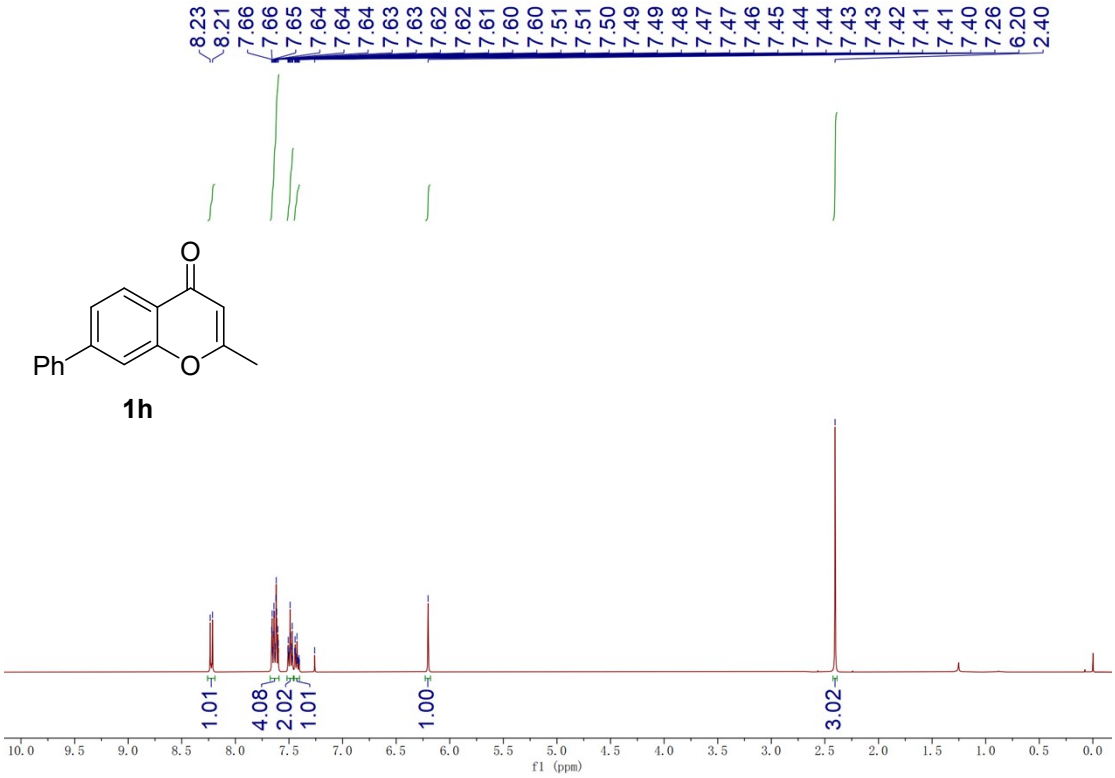
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1f



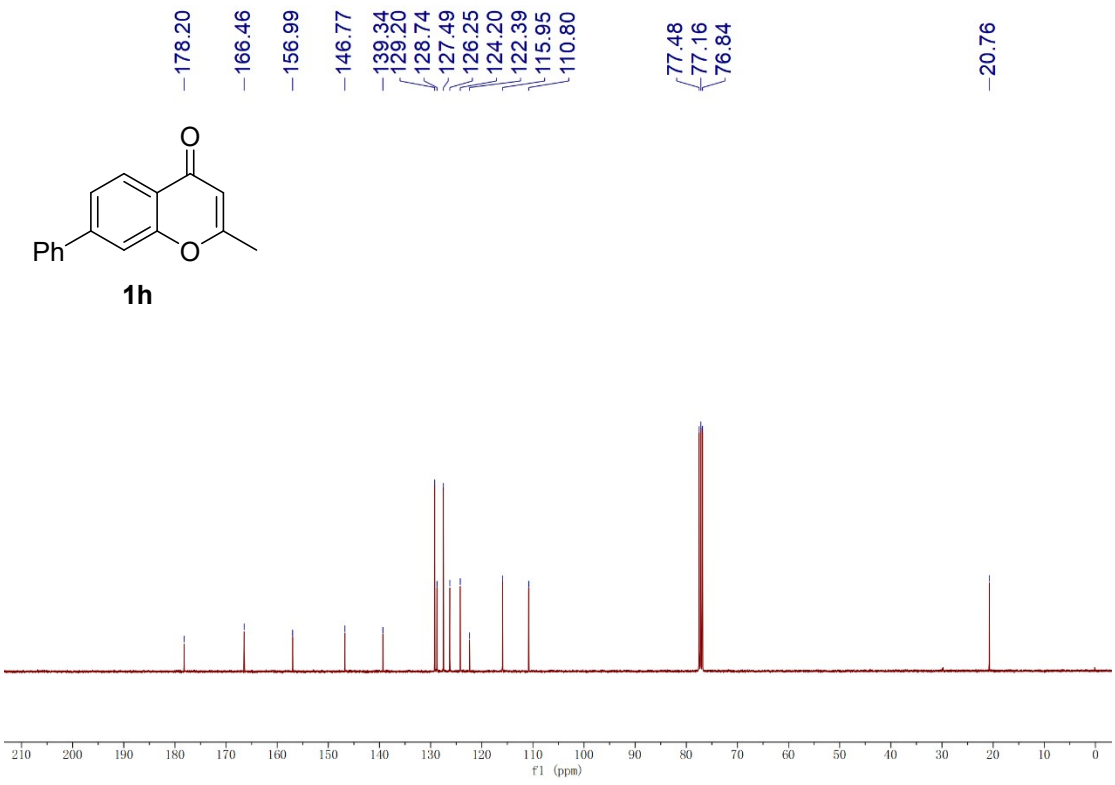
[1]H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1g



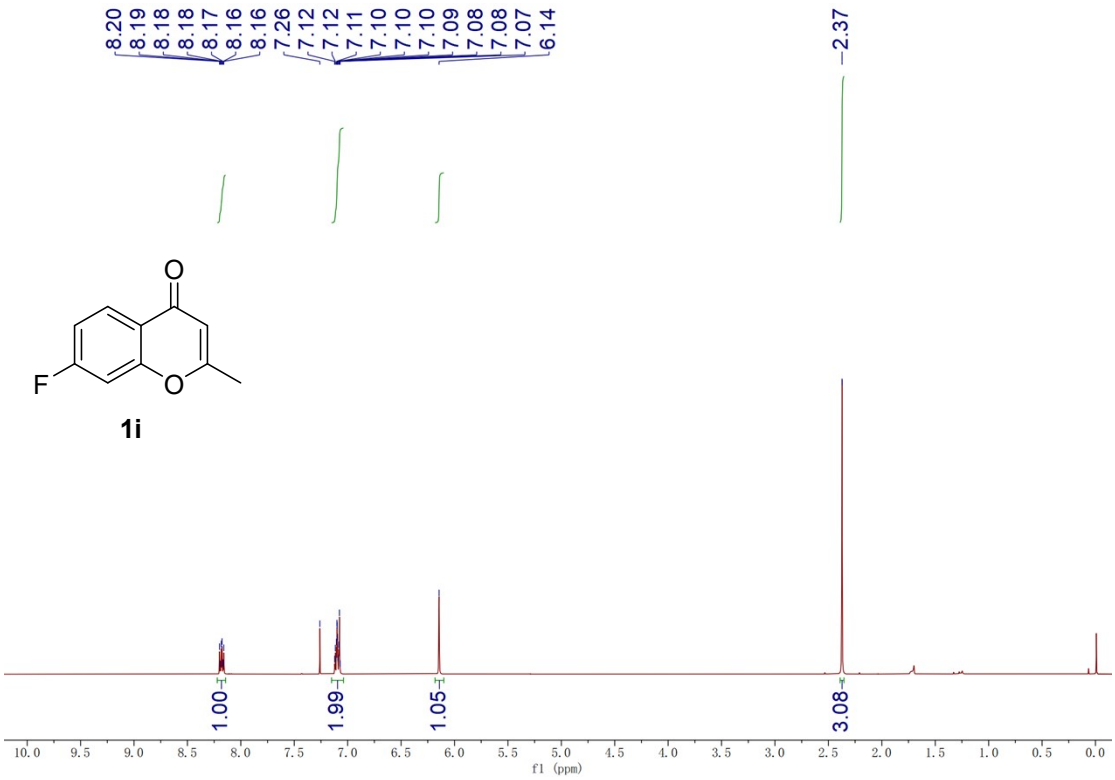
[13]C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1g



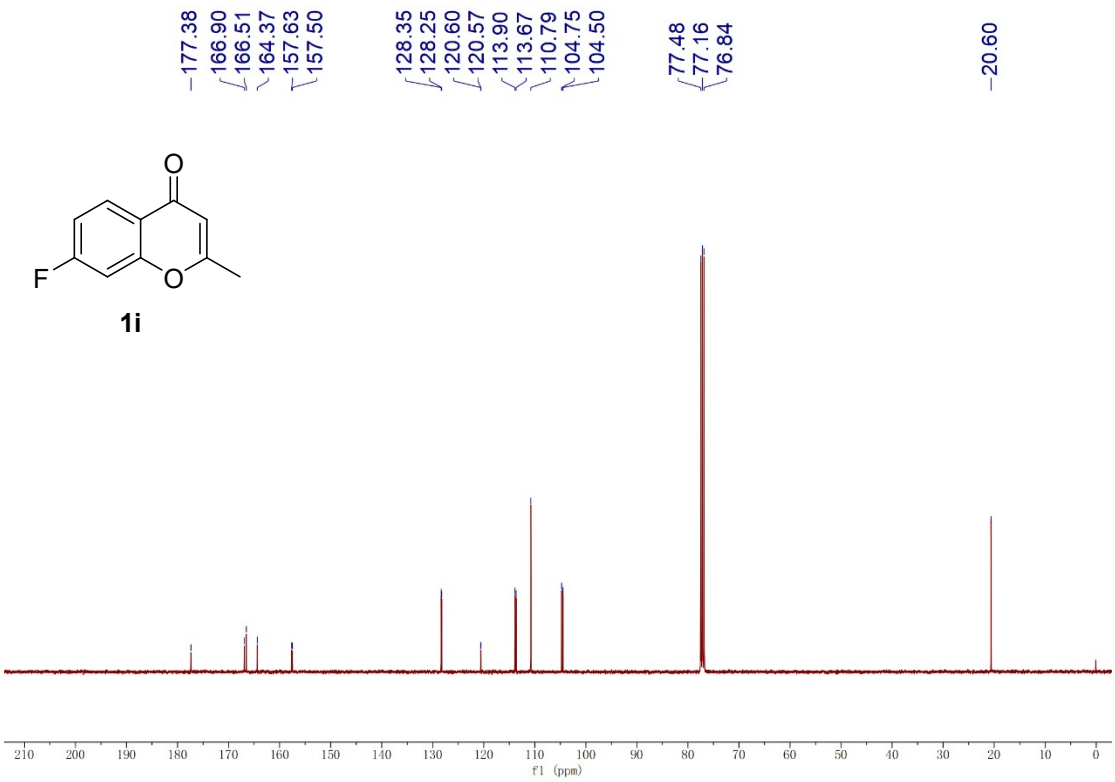
[1]H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1h



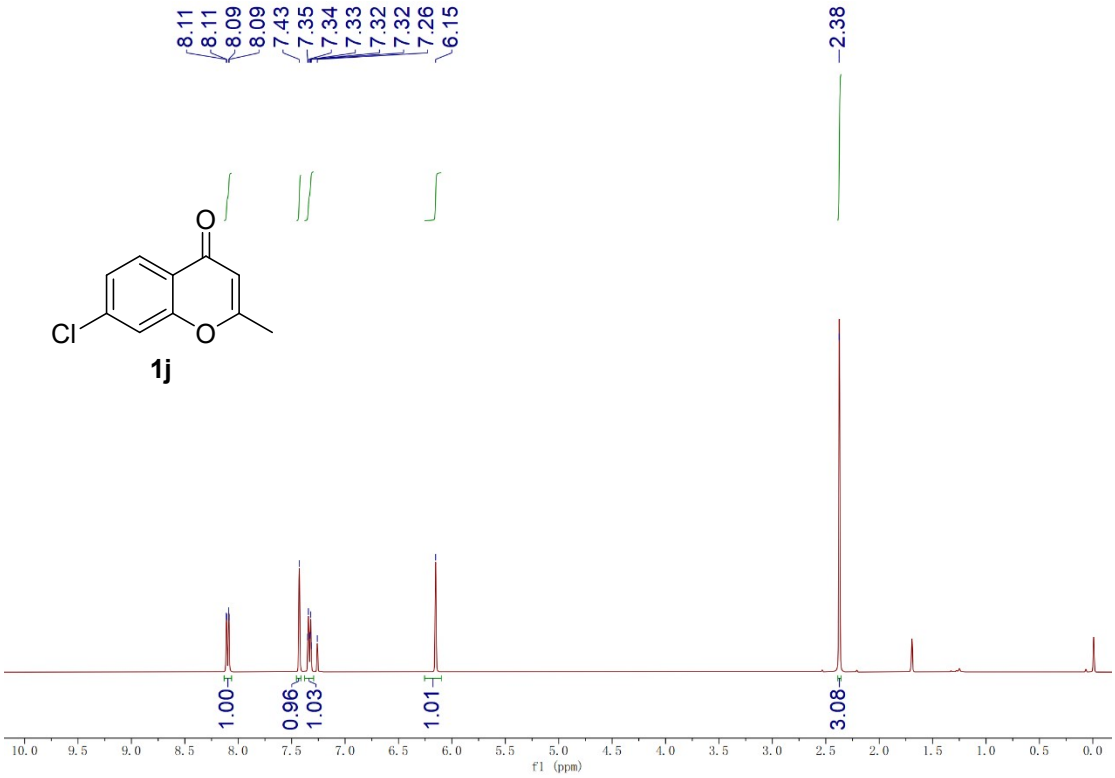
[13]C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 和 1h



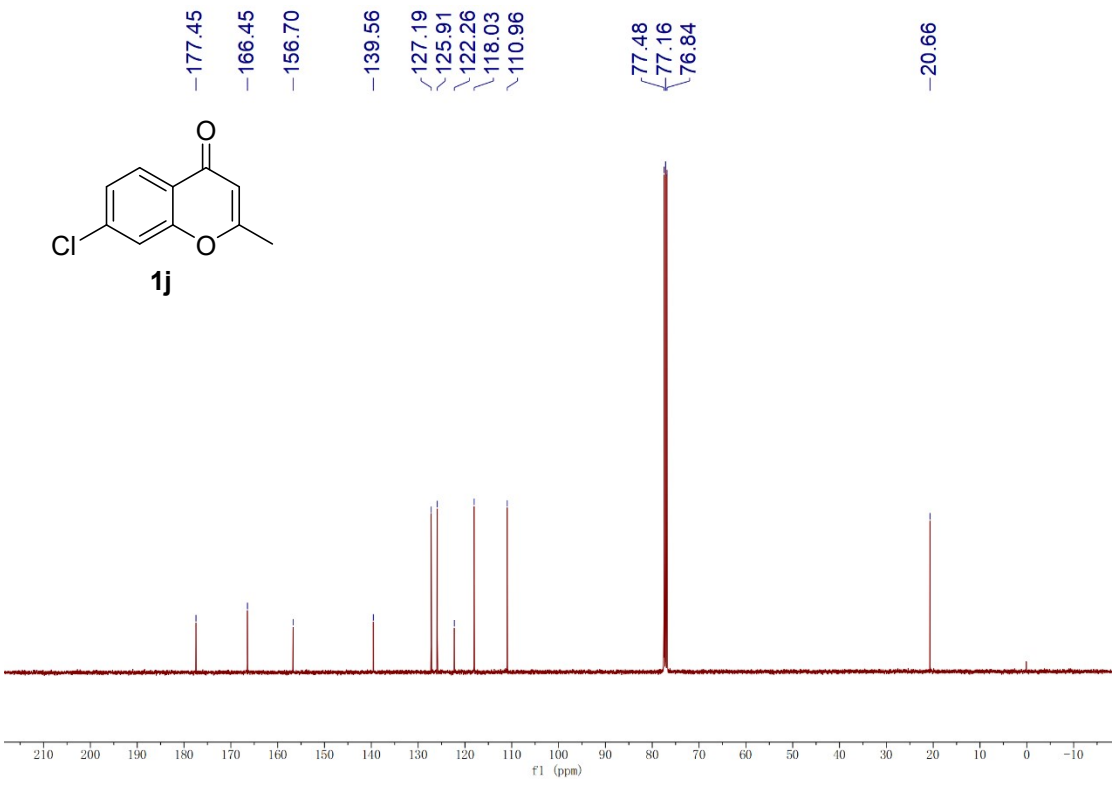
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1i



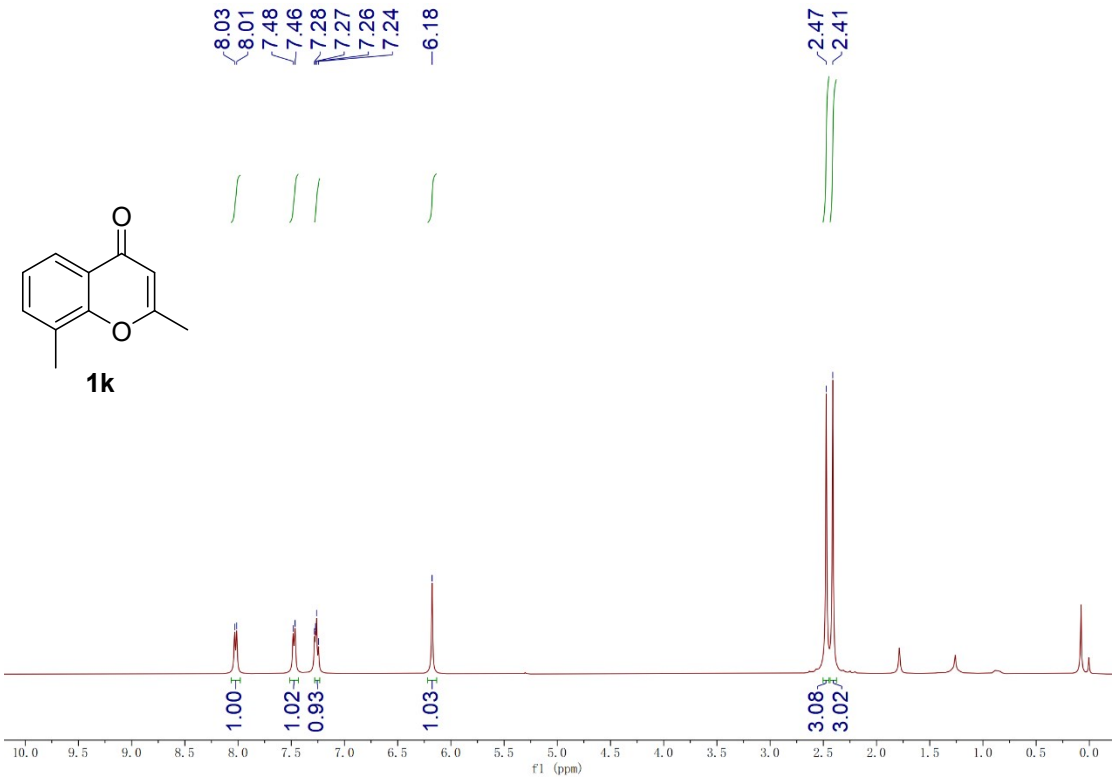
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1i



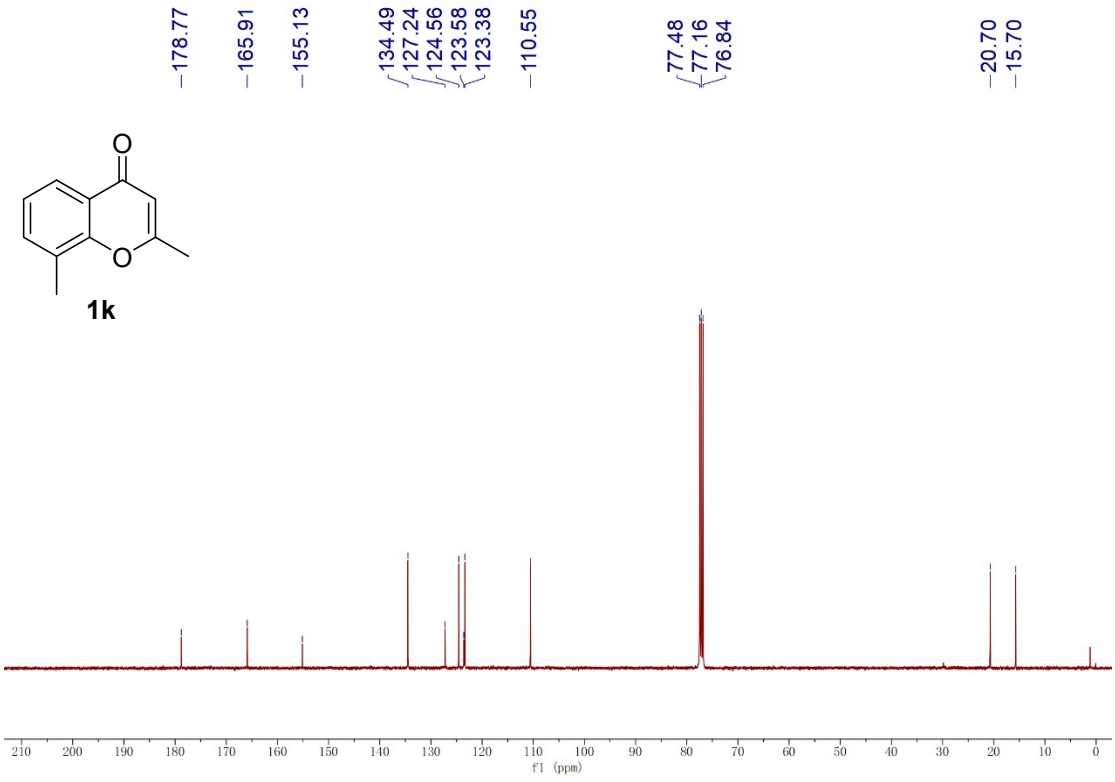
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1j



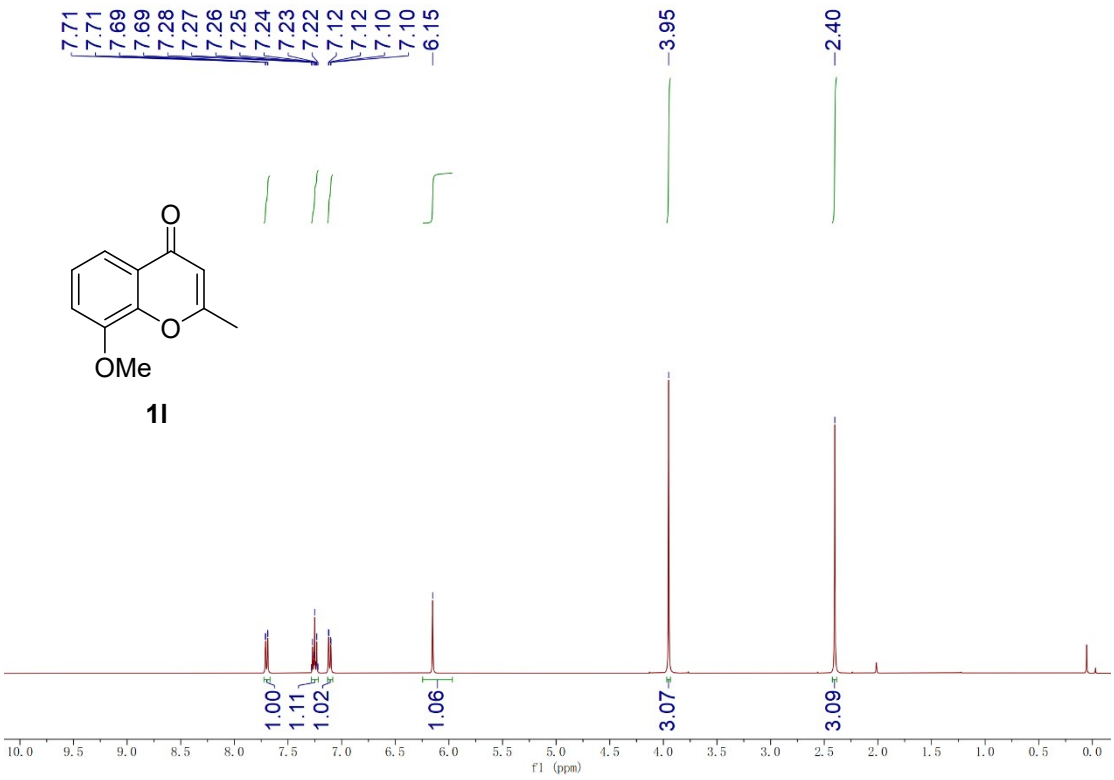
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1j



^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1k

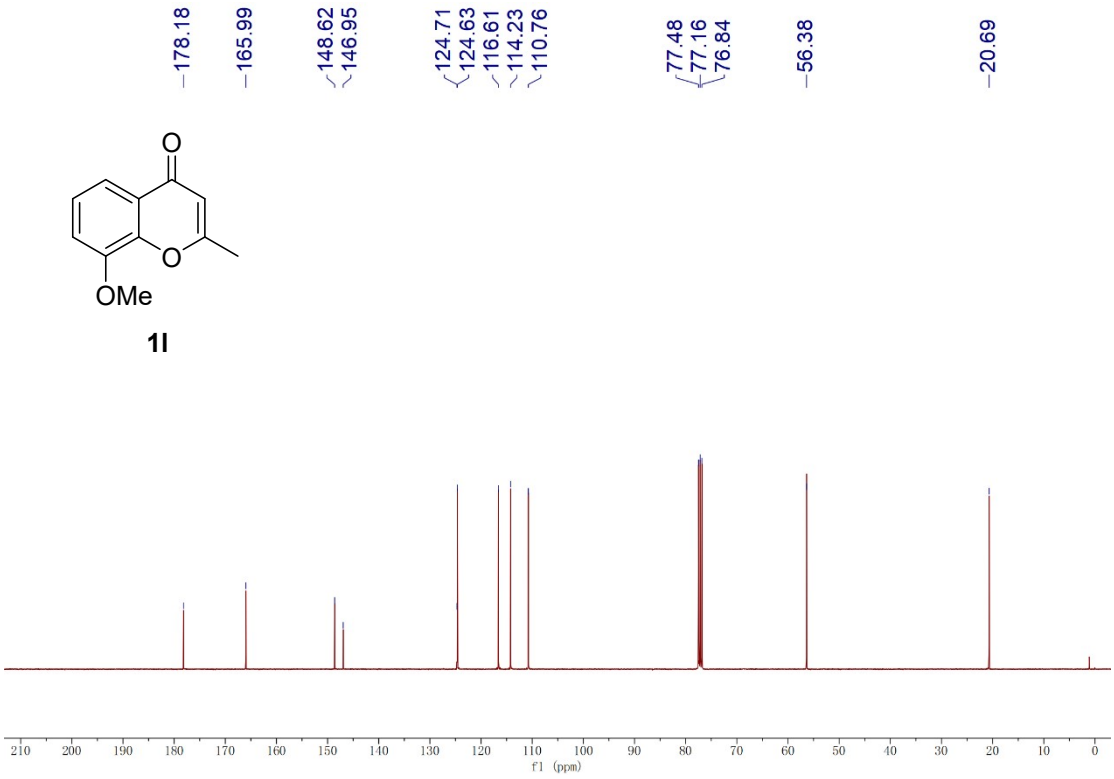


^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1k



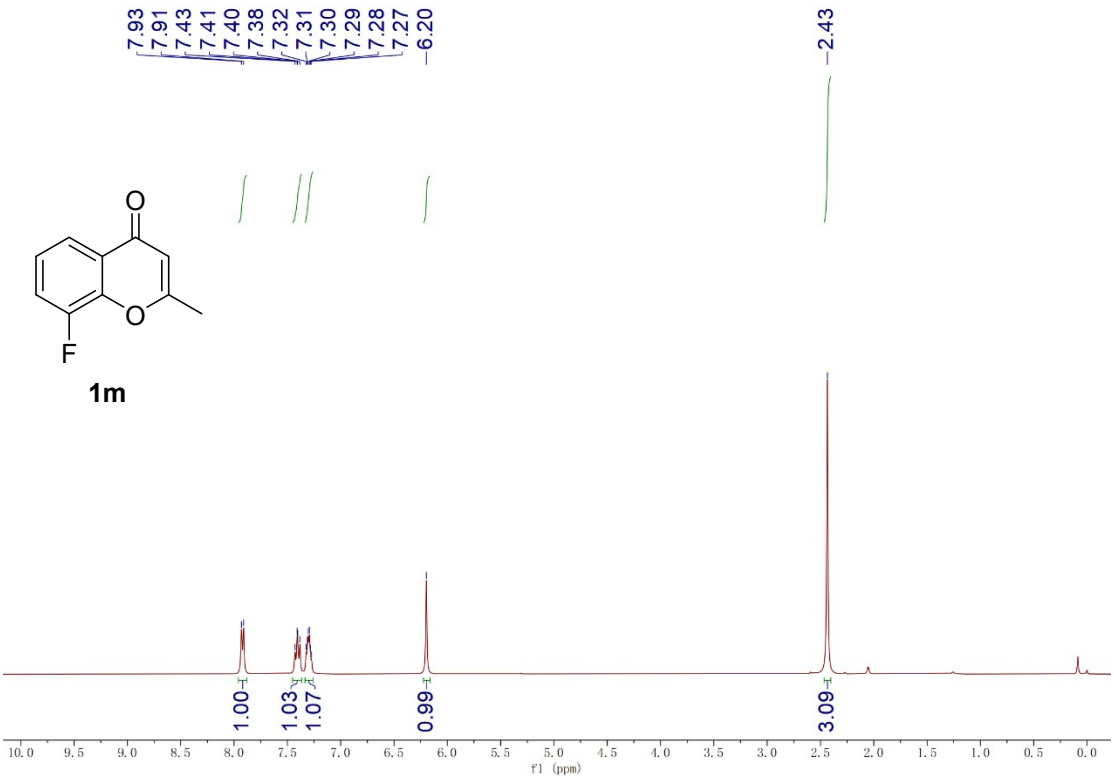
1l

^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1l



1l

^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1l



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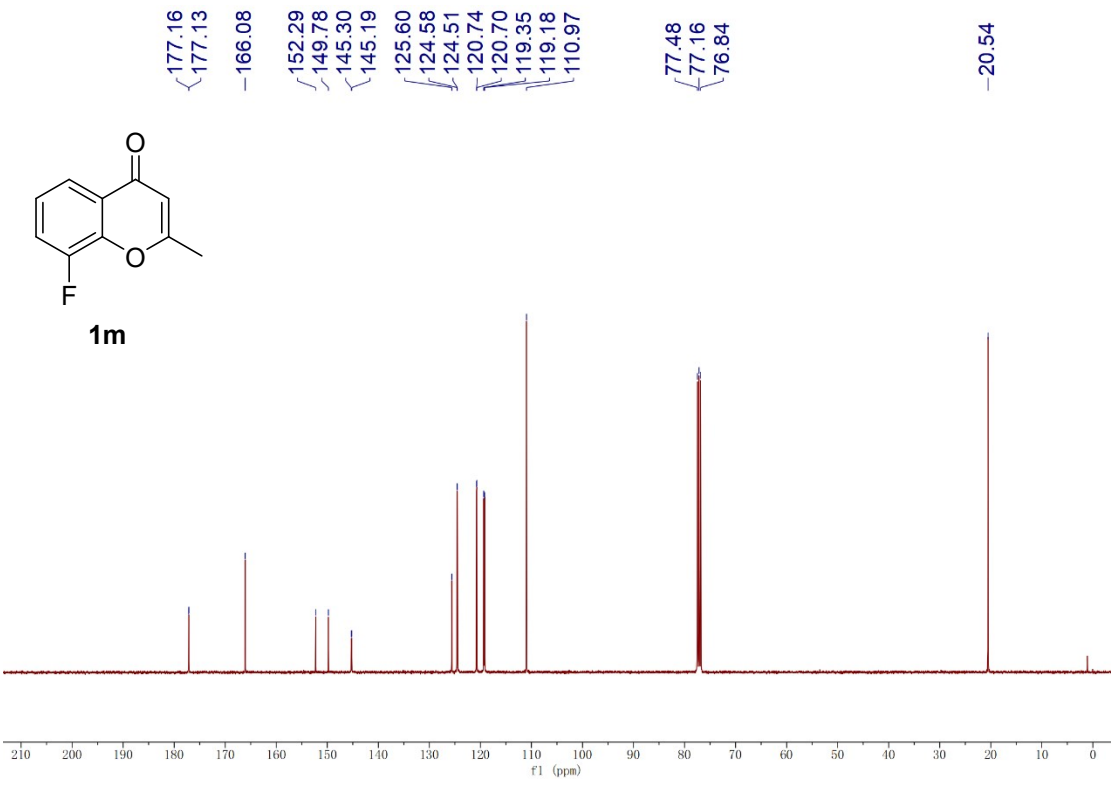
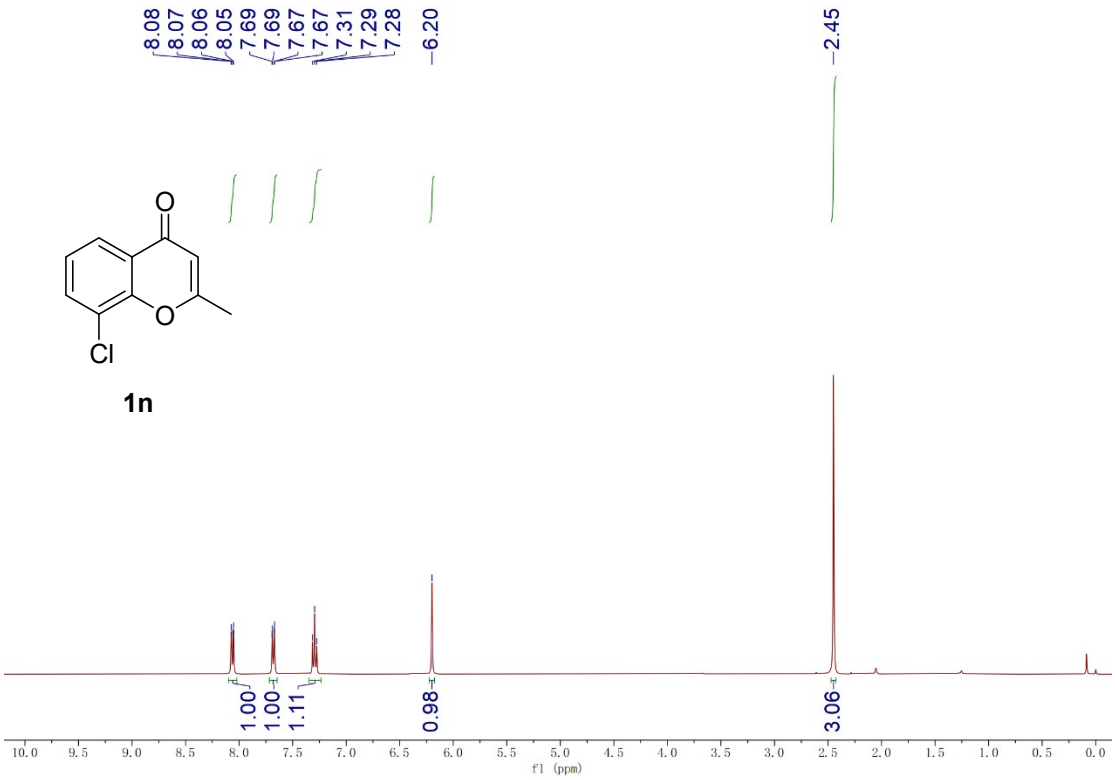


^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1m



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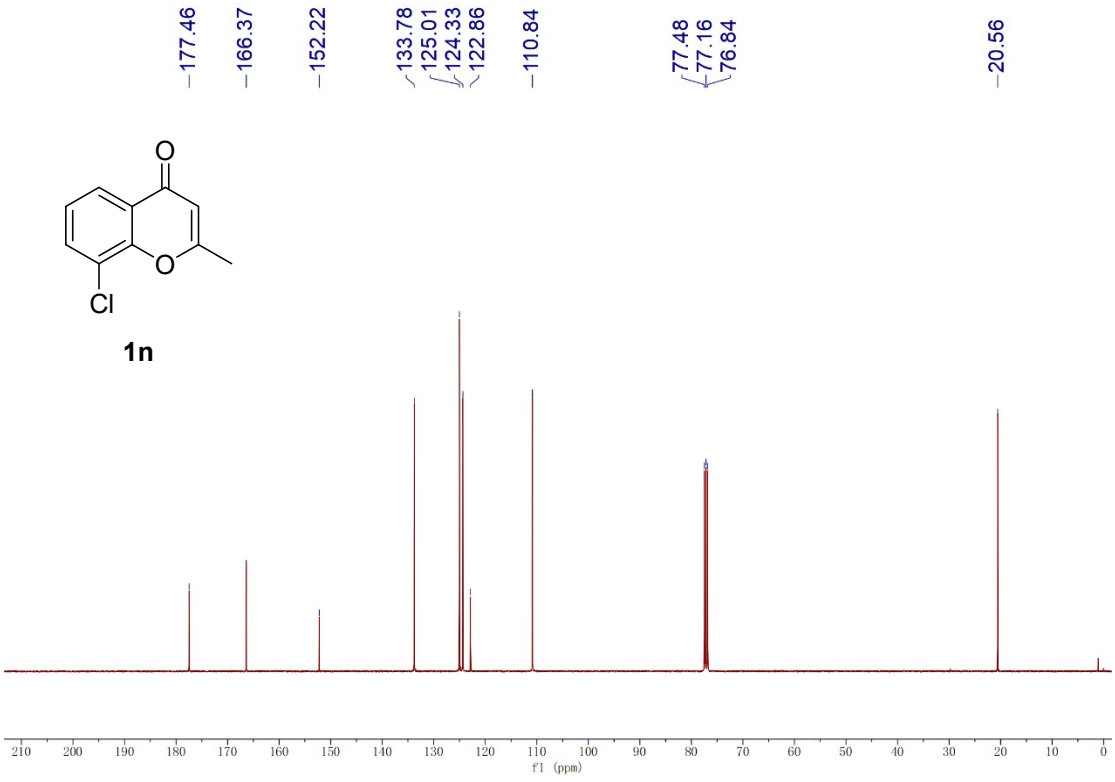
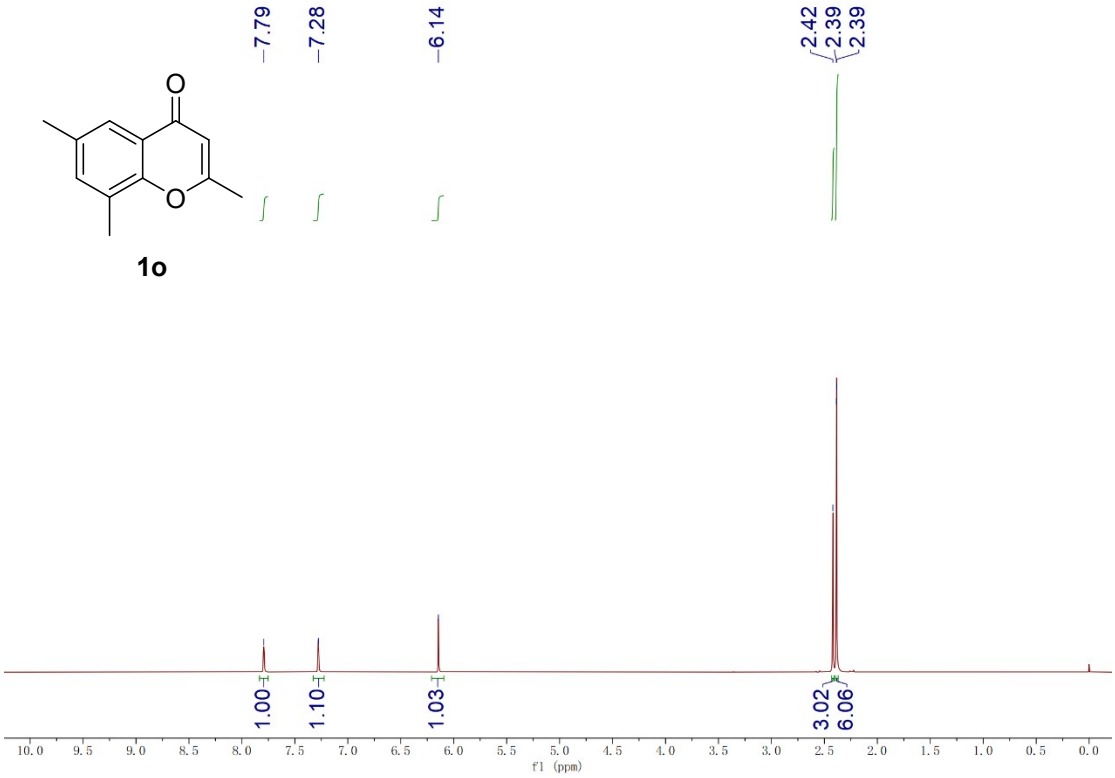
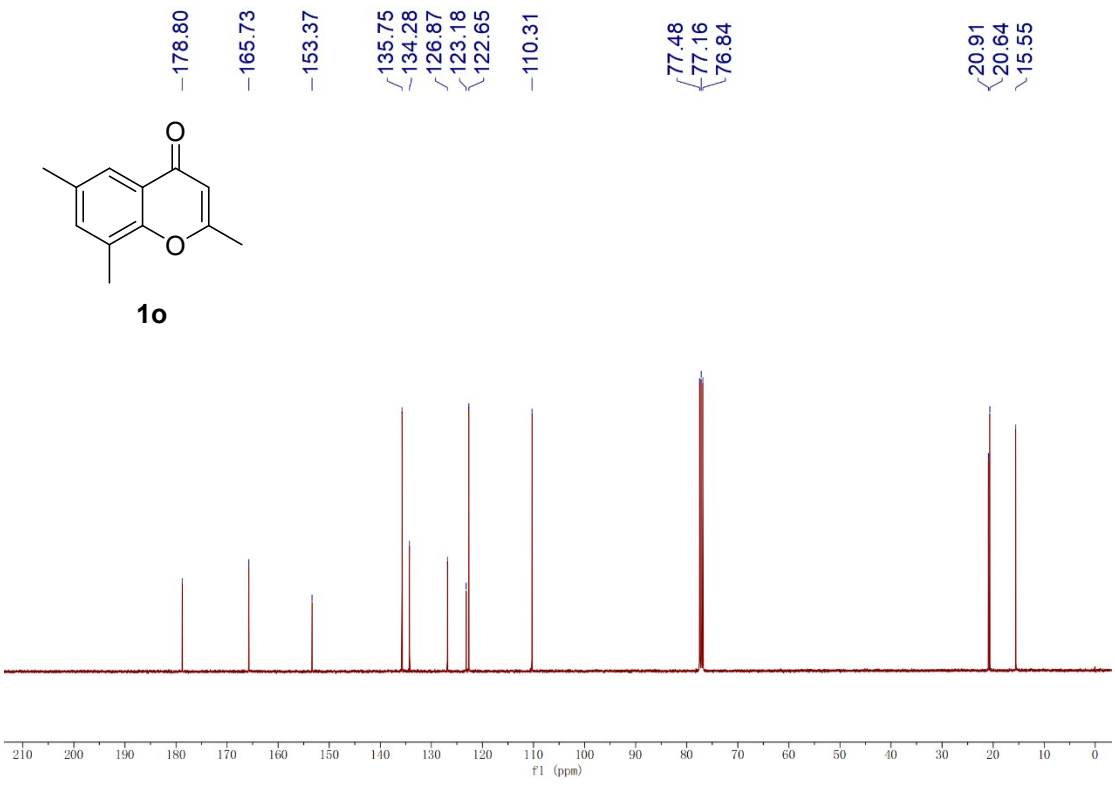


^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1n



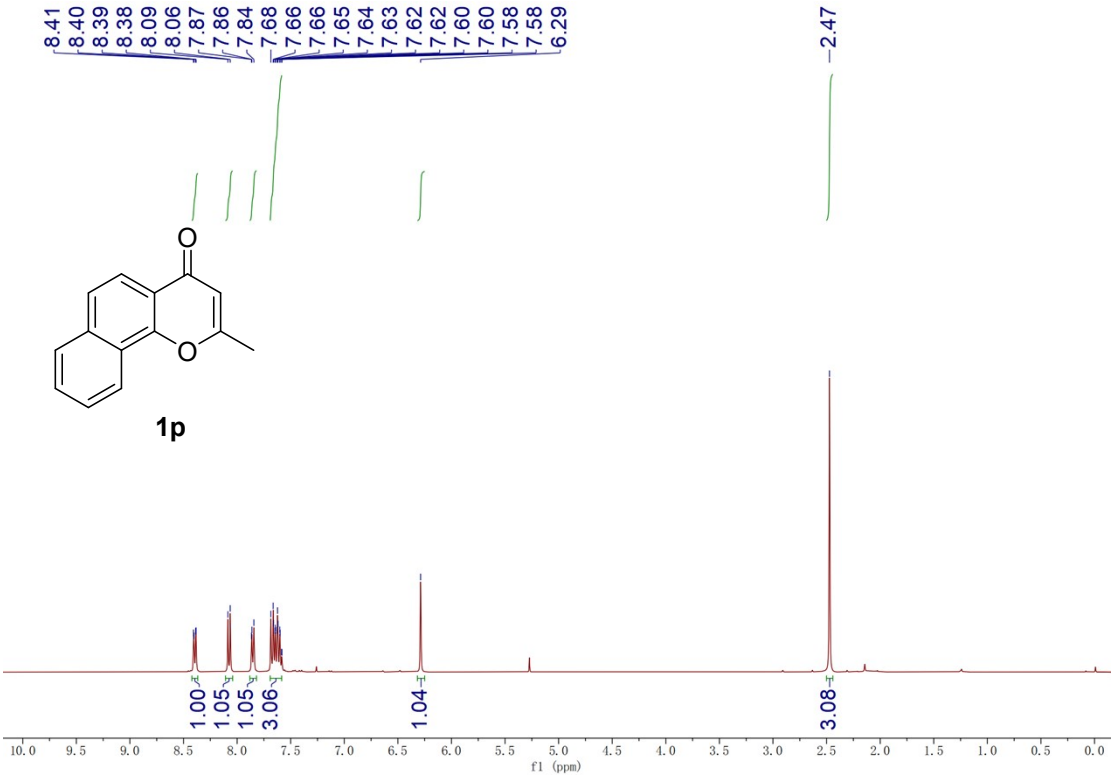
1o

^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 1o



1o

^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 1o



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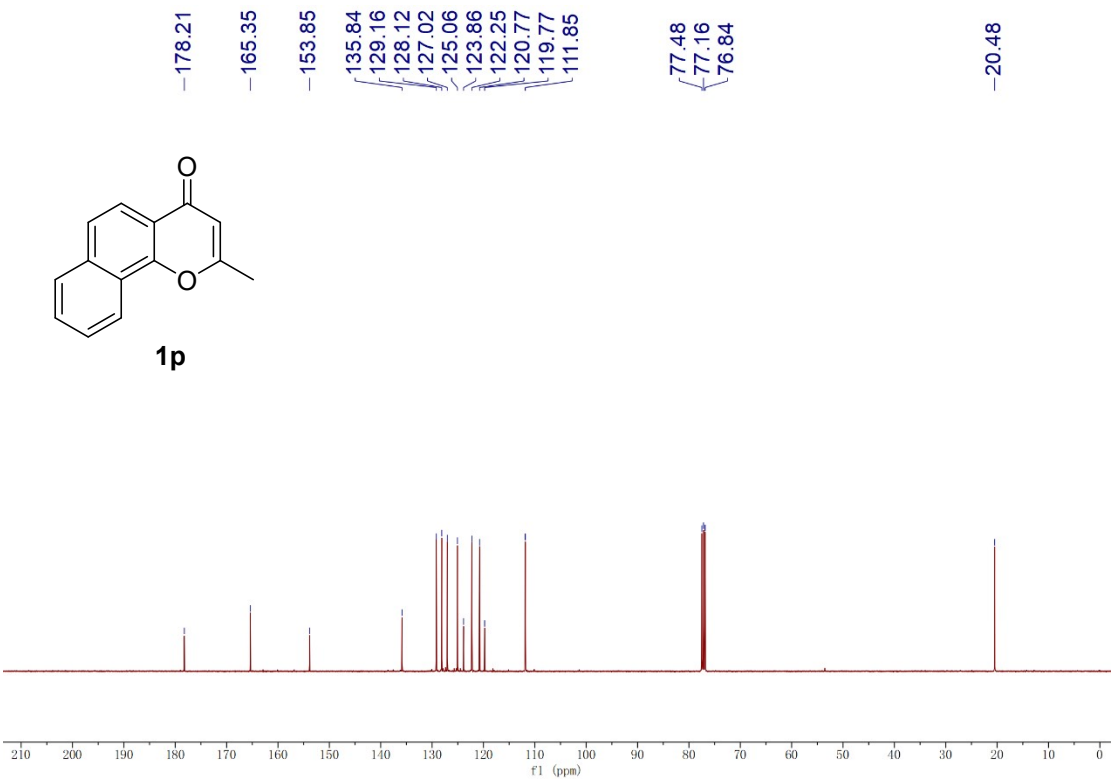

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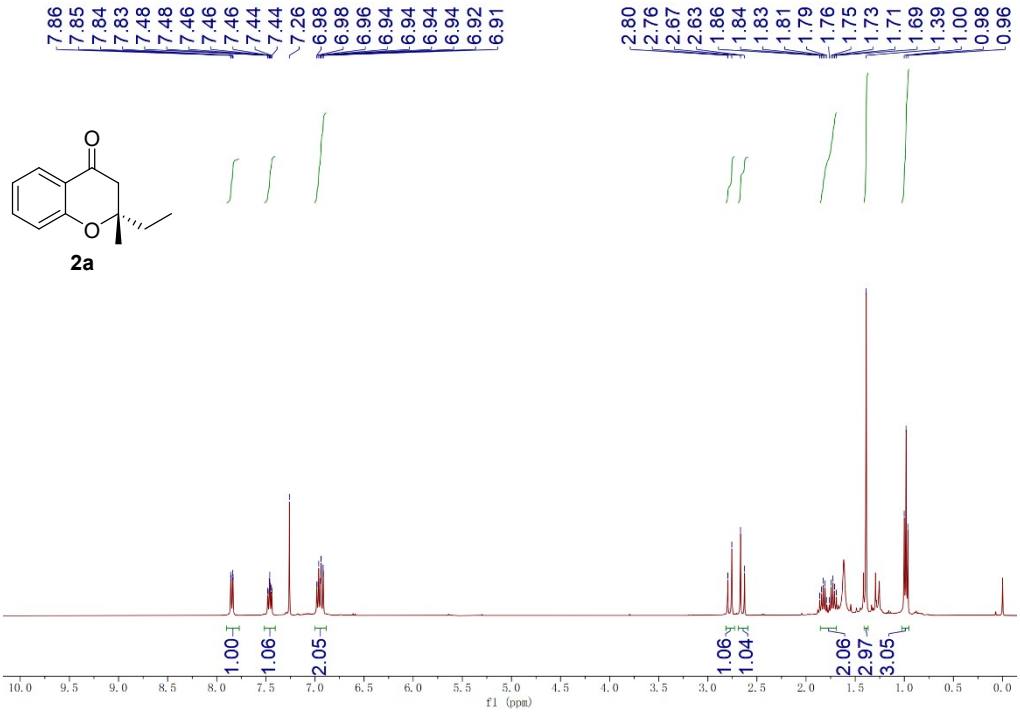
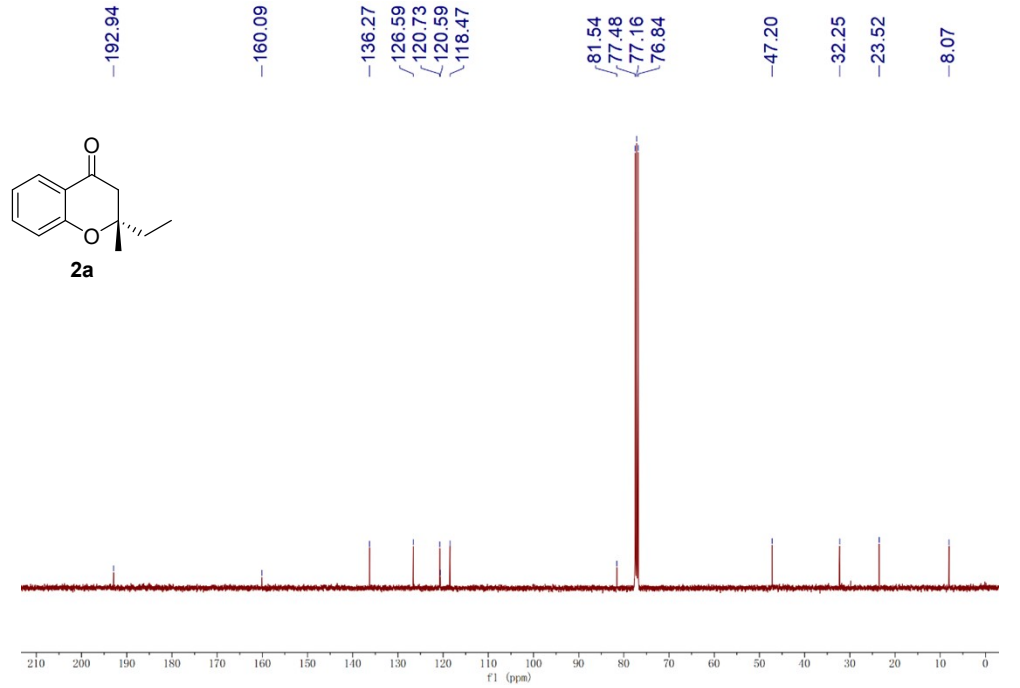
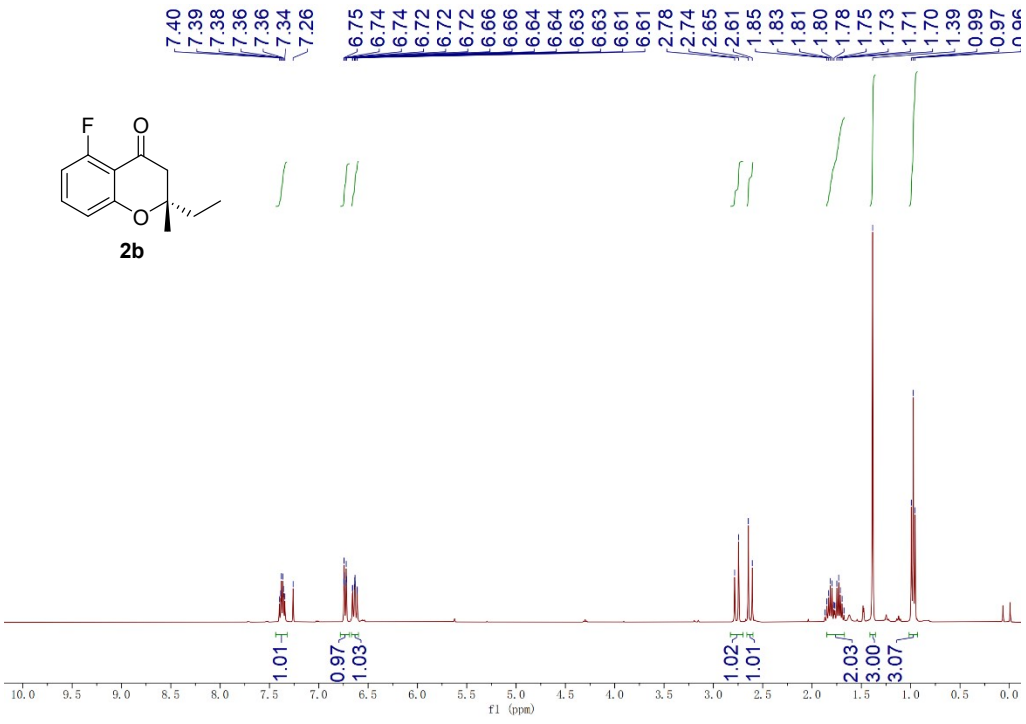


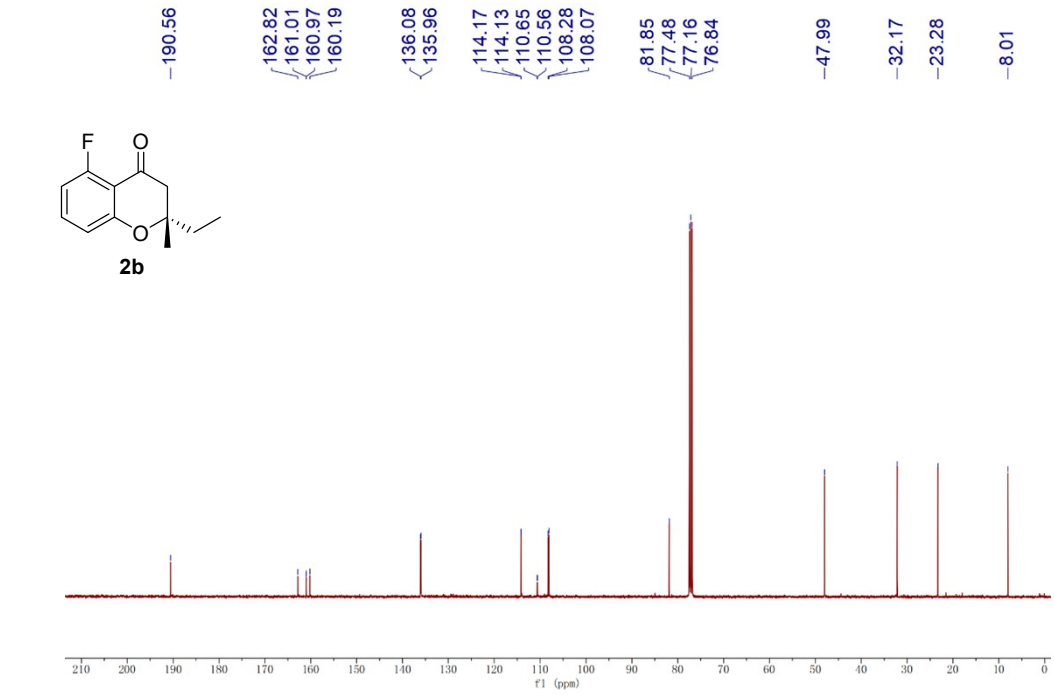
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2a



^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2a



^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2b



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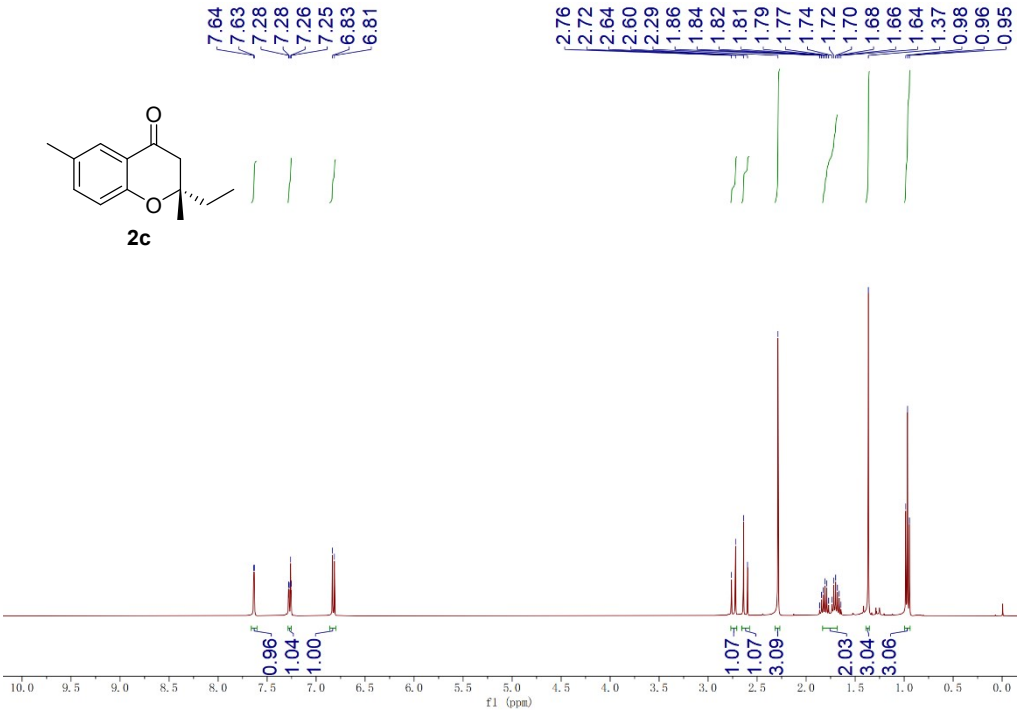

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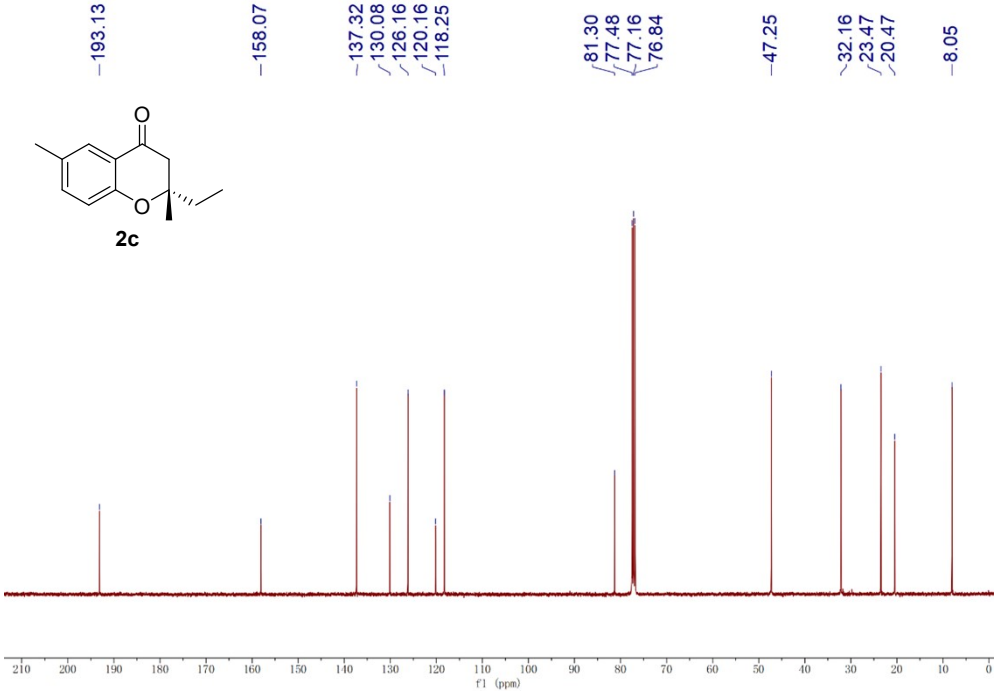

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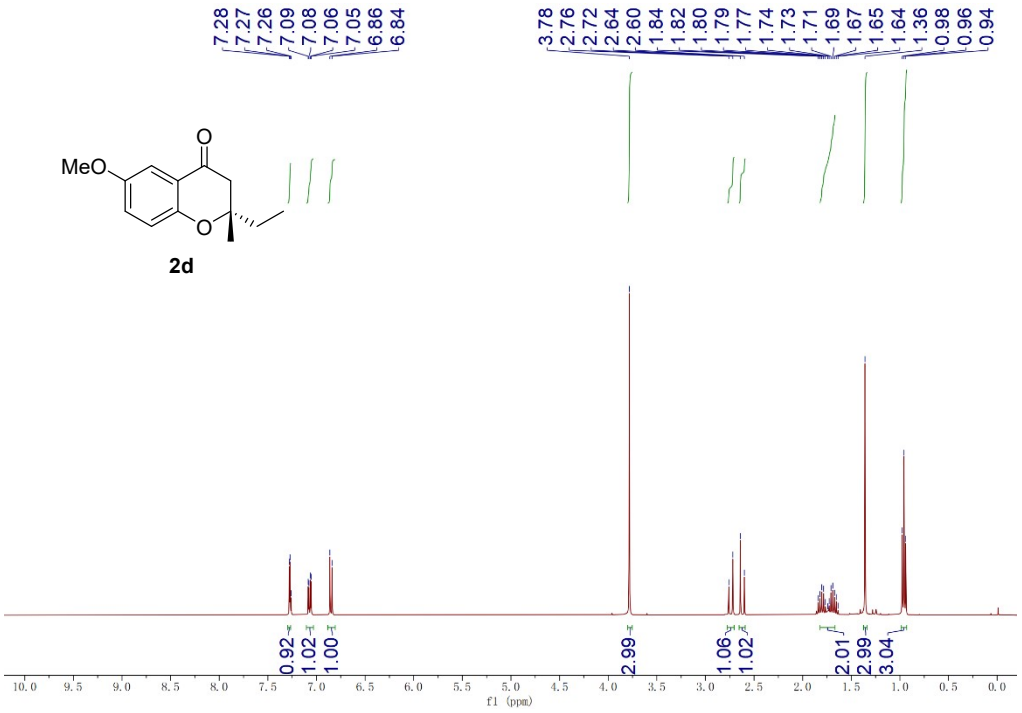

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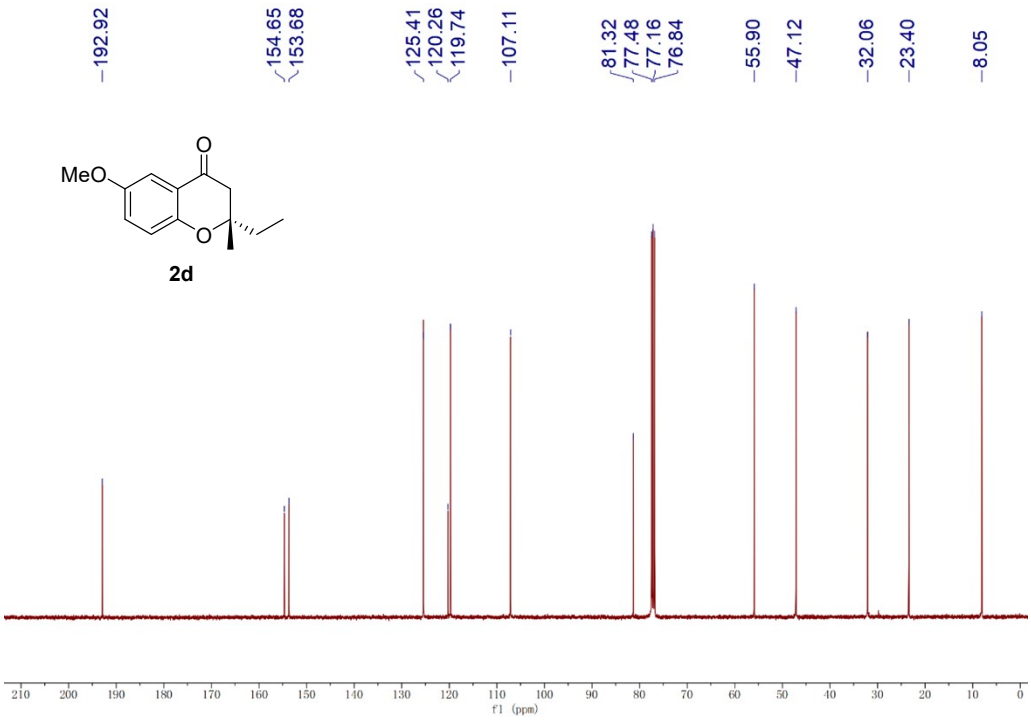

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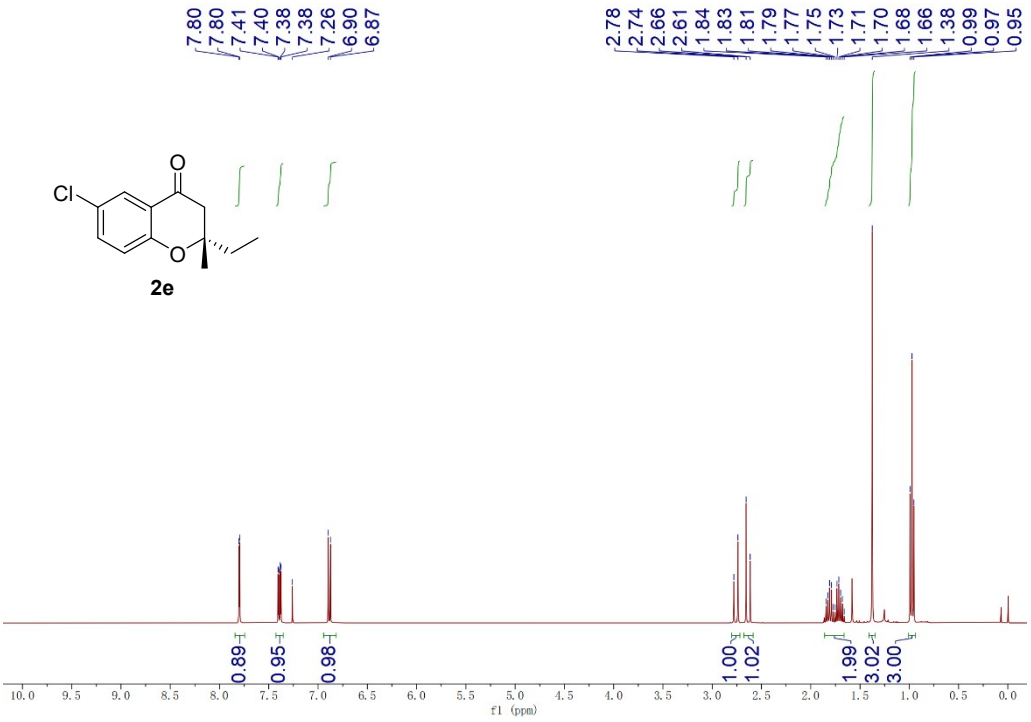

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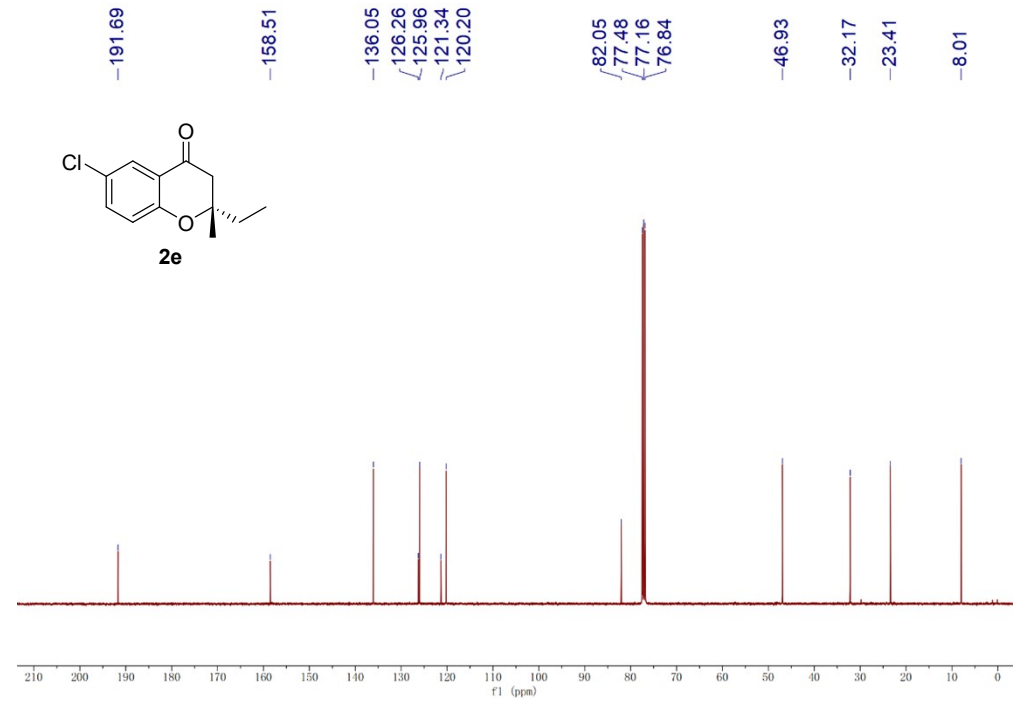

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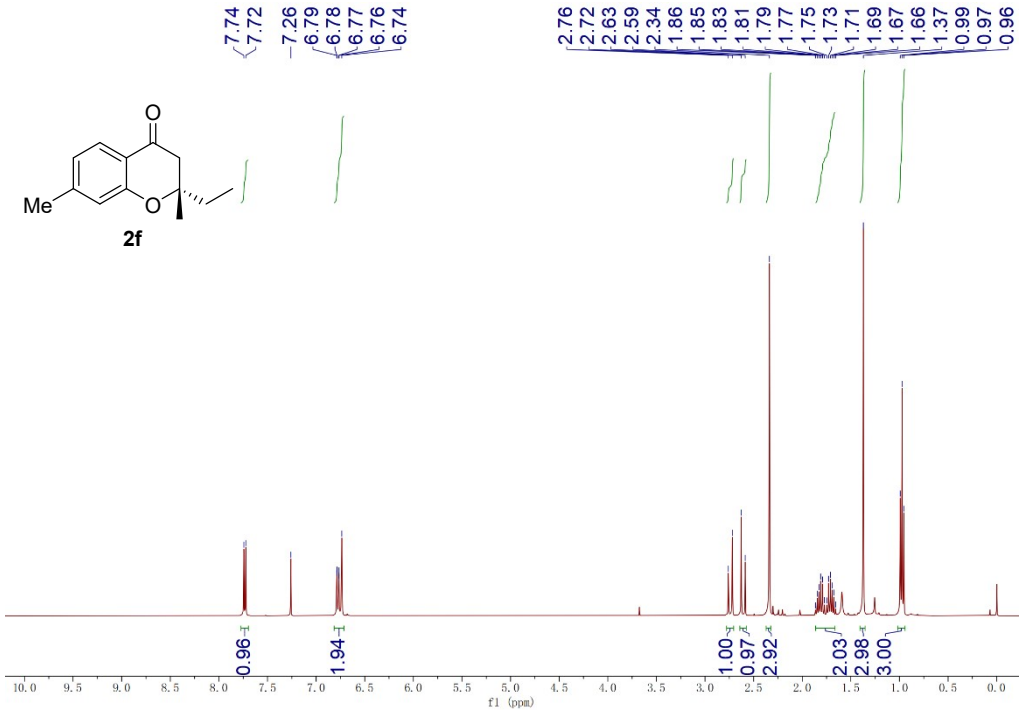
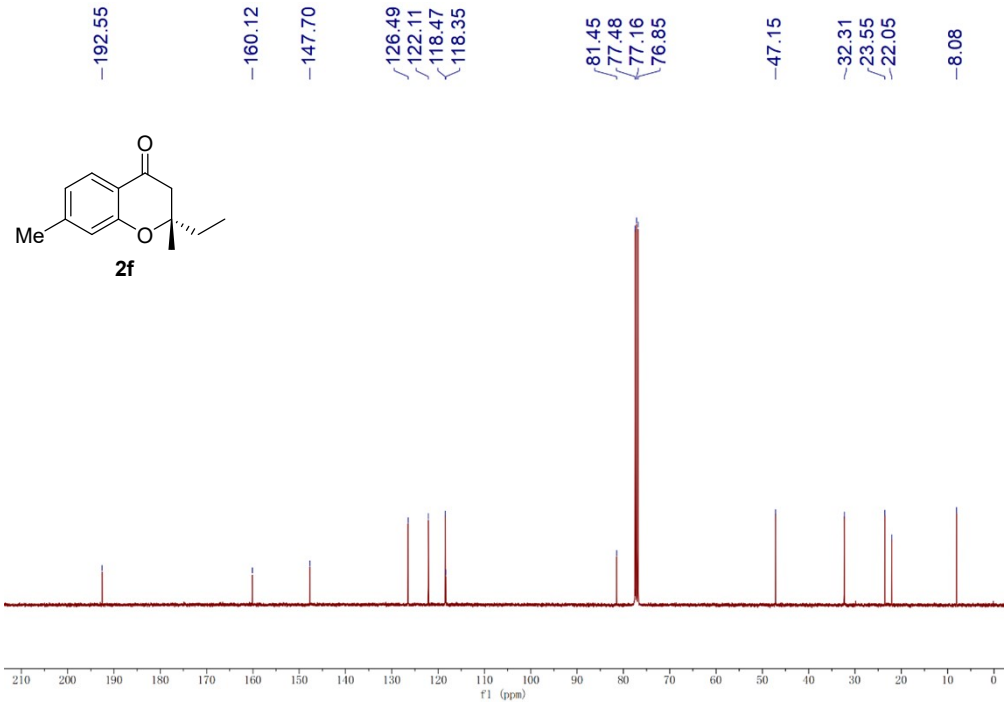


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2f



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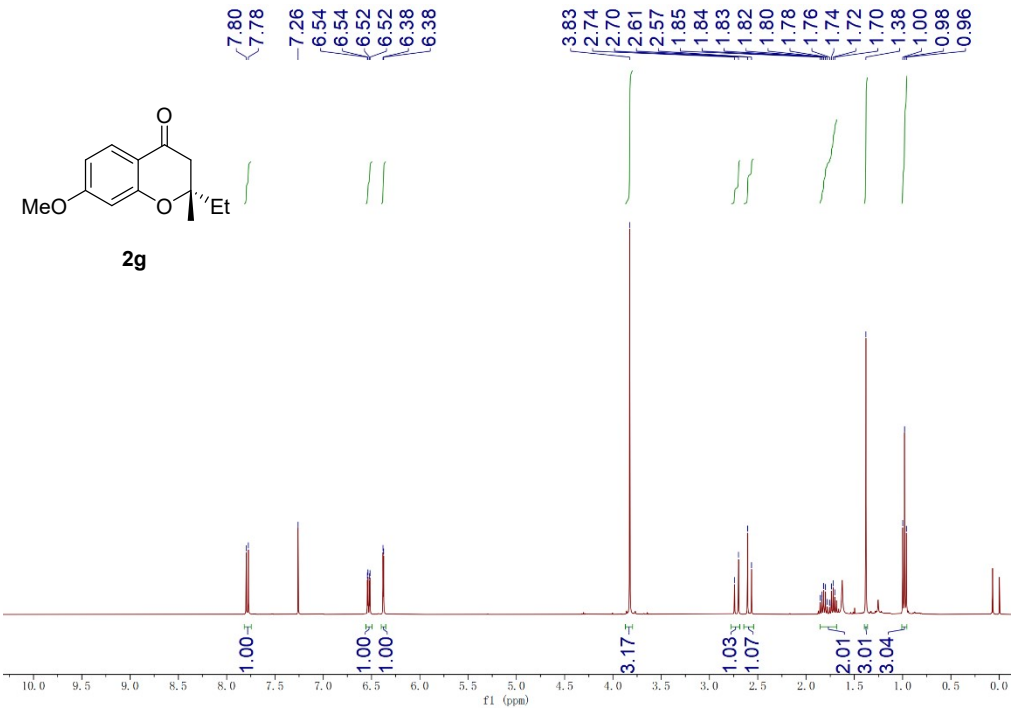
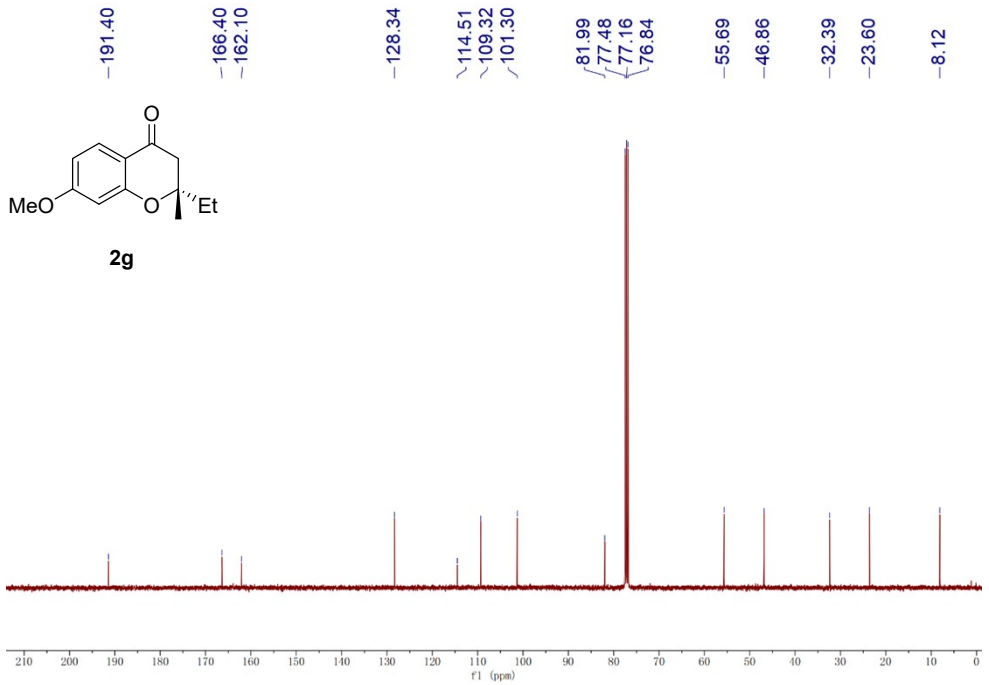


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2g



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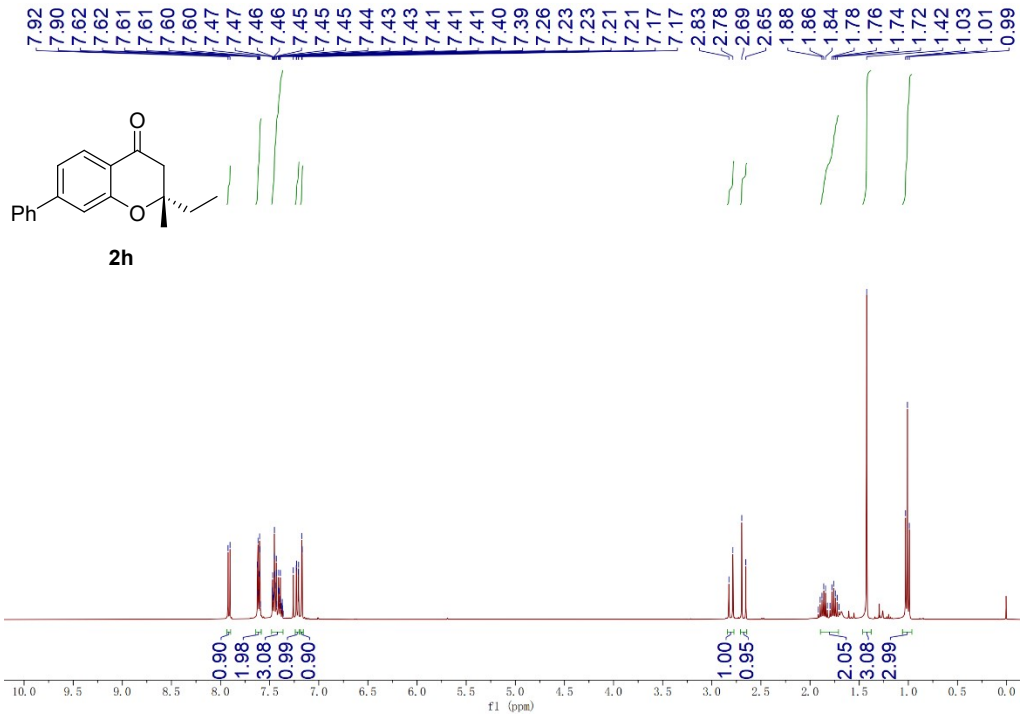

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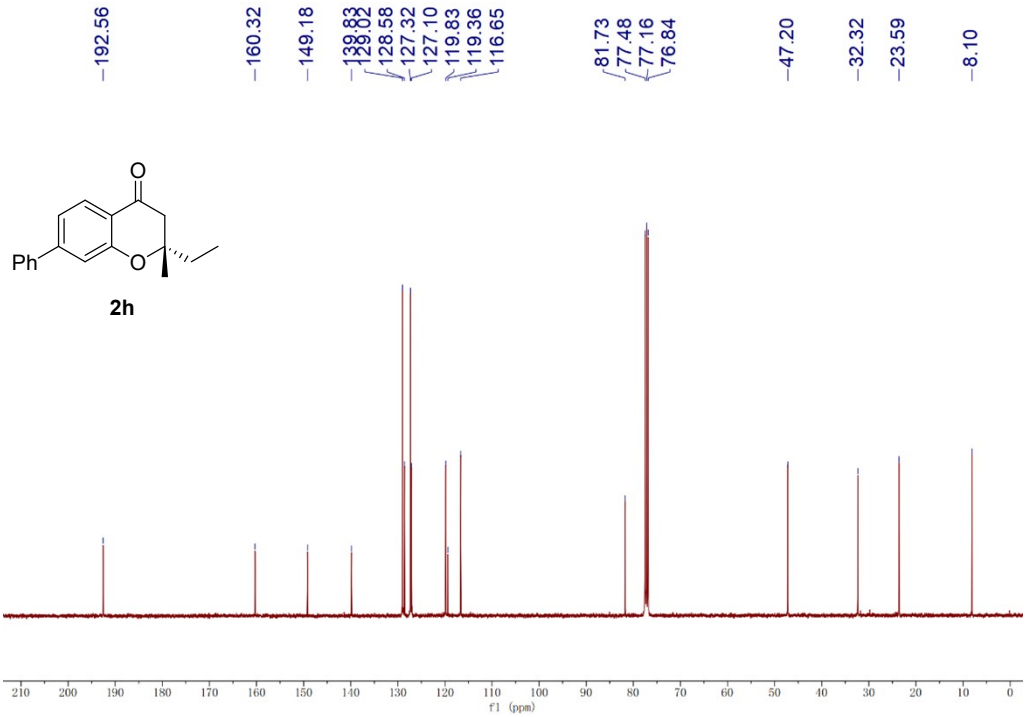

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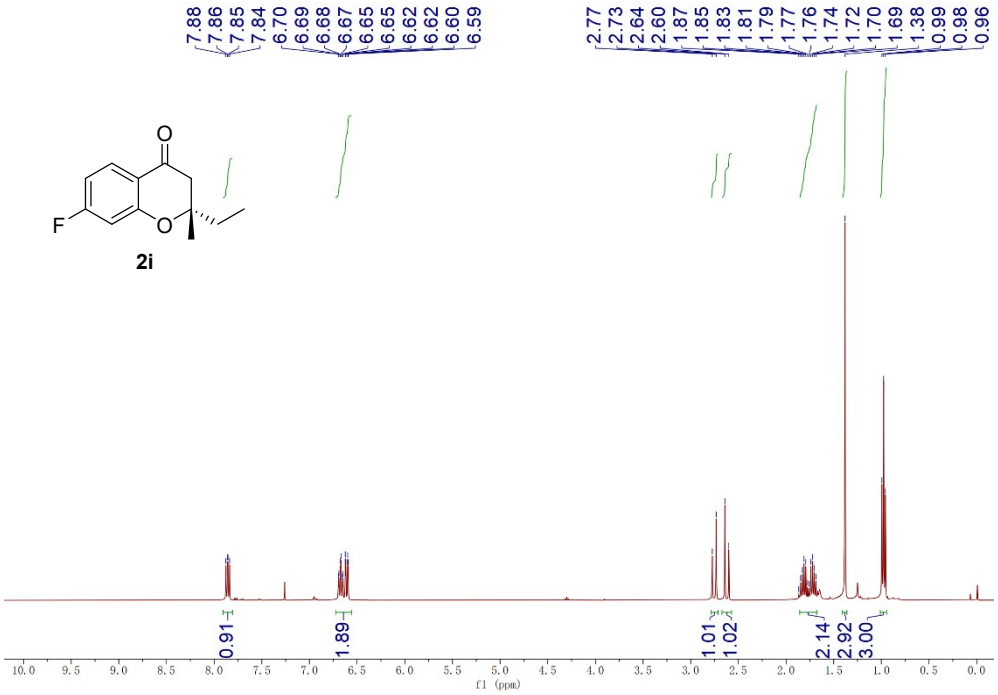
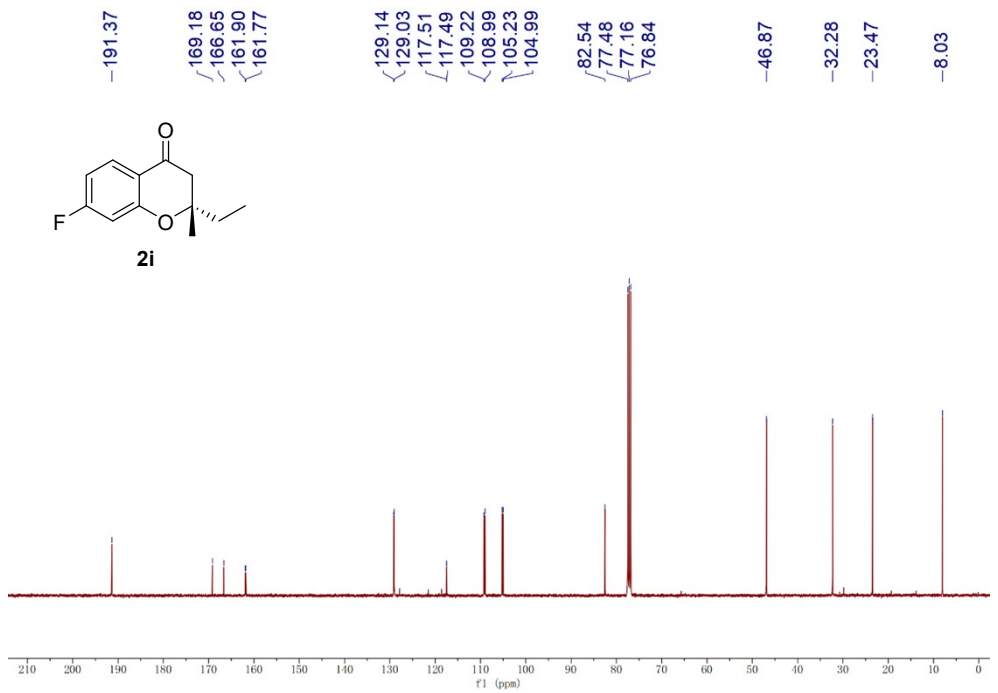
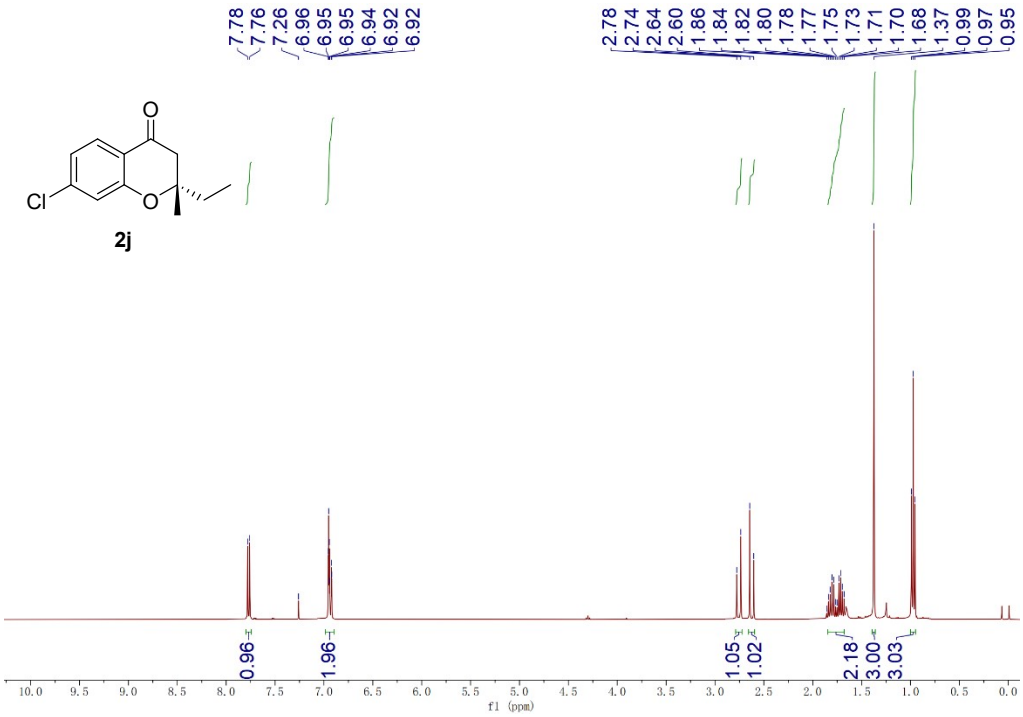


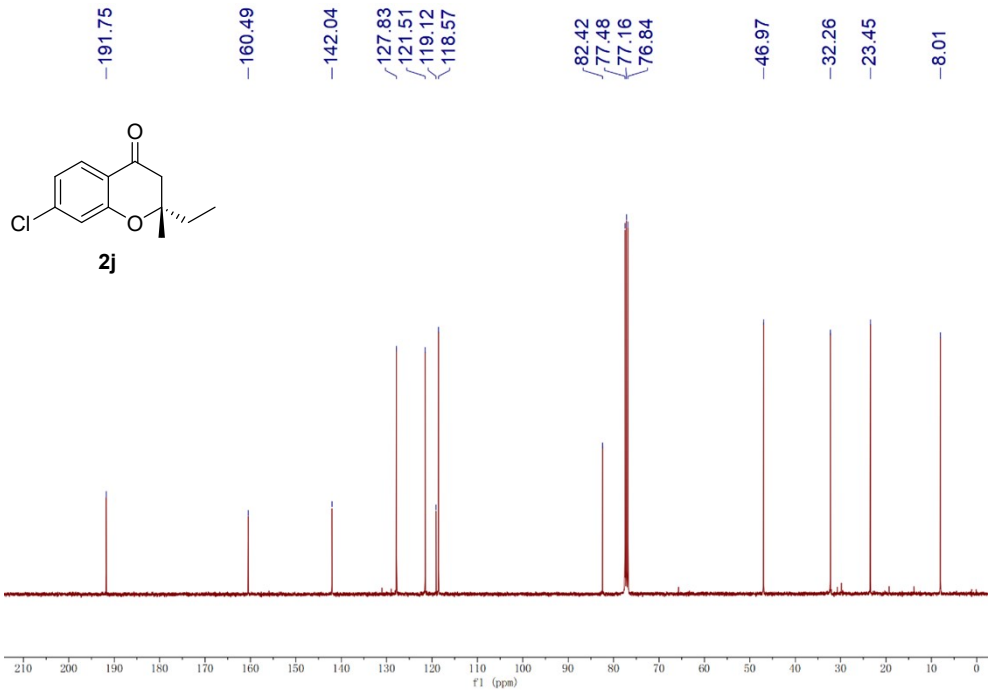
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2i



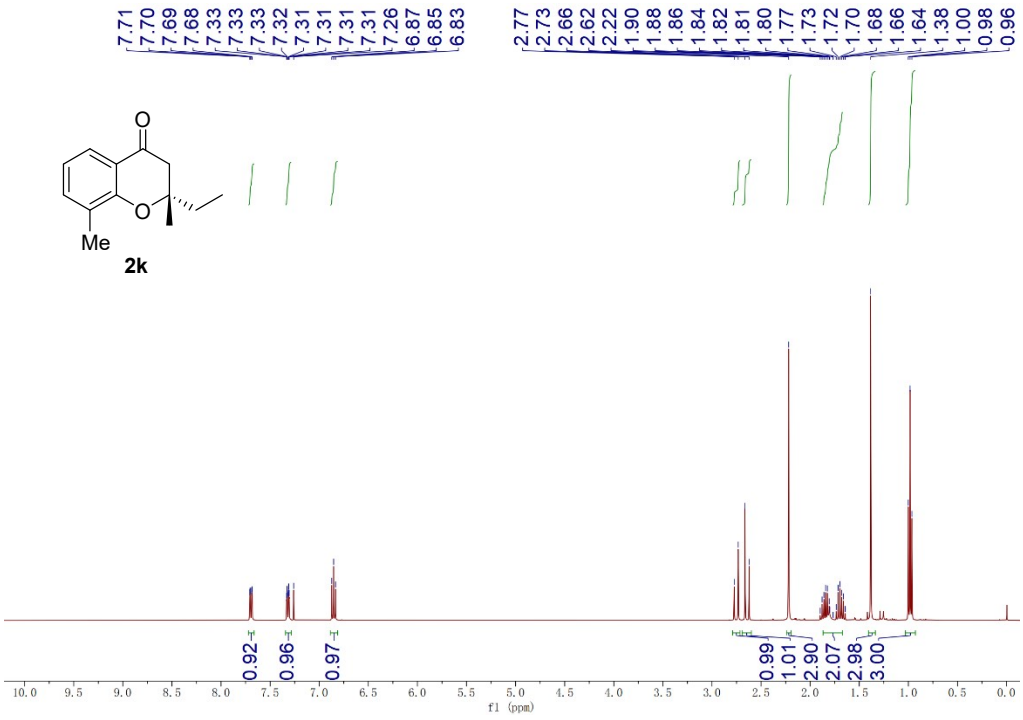
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2i



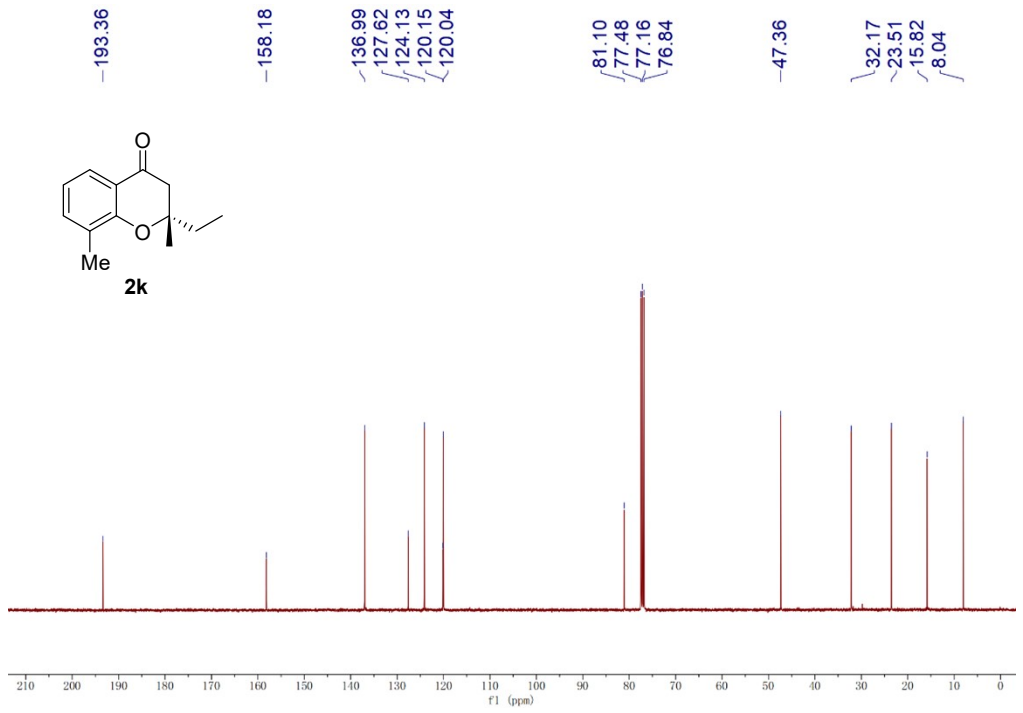
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2j



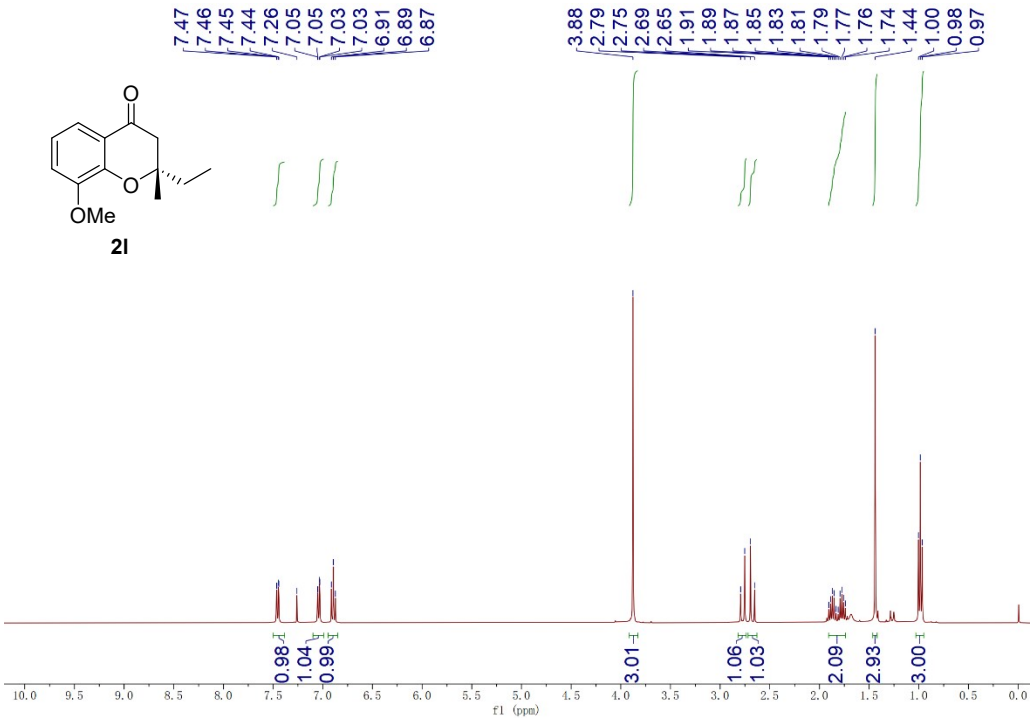
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2j



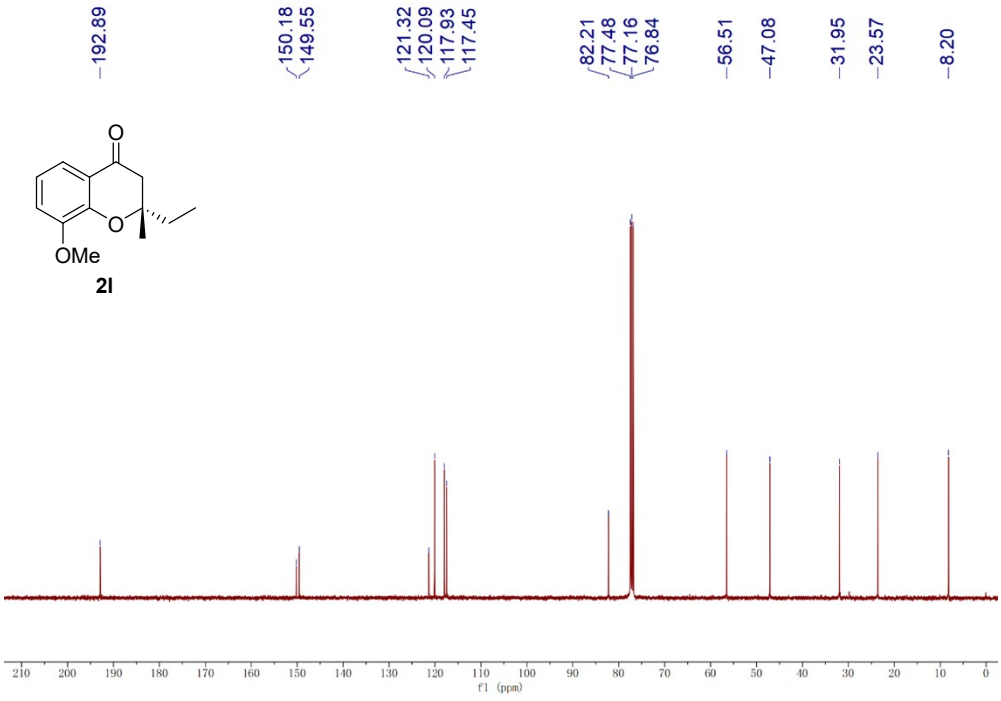
[1]H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2k



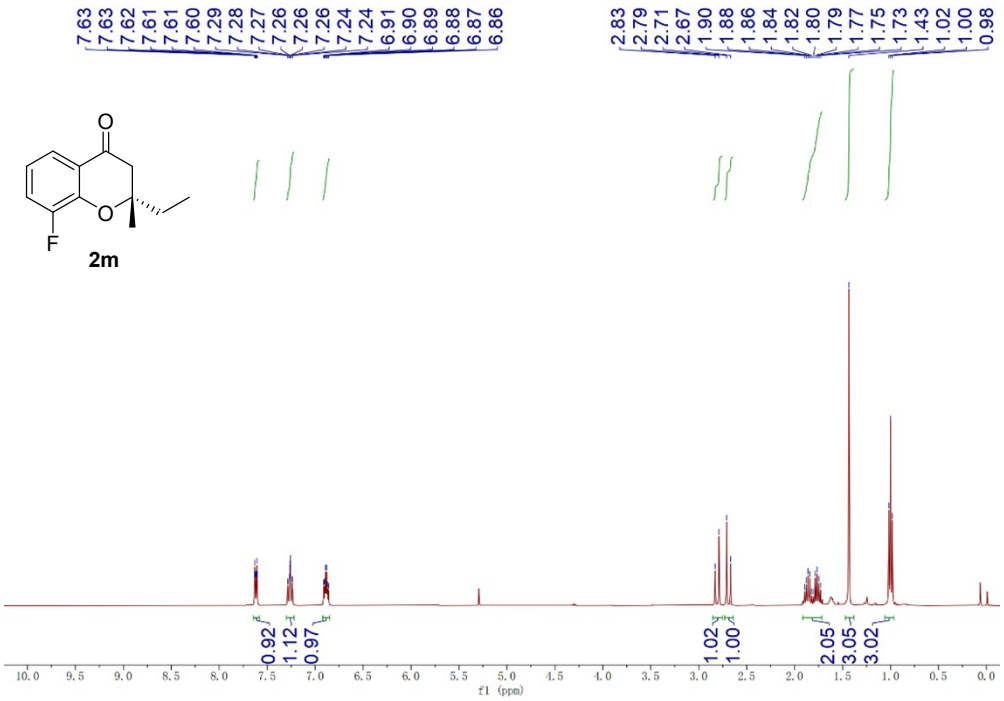
[13]C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2k



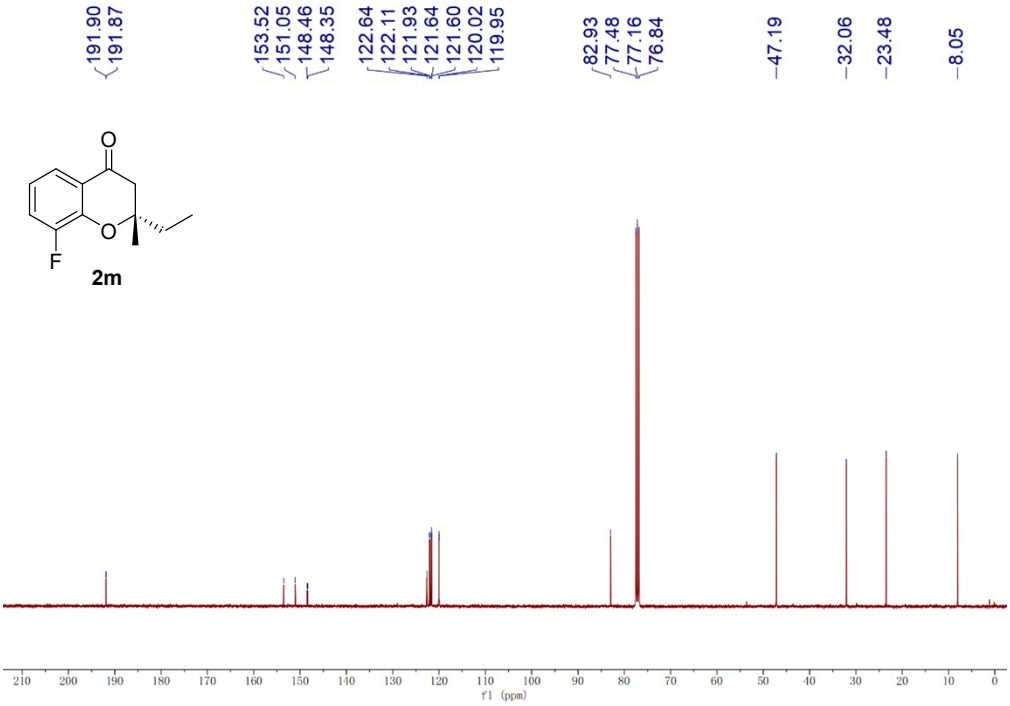
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2l



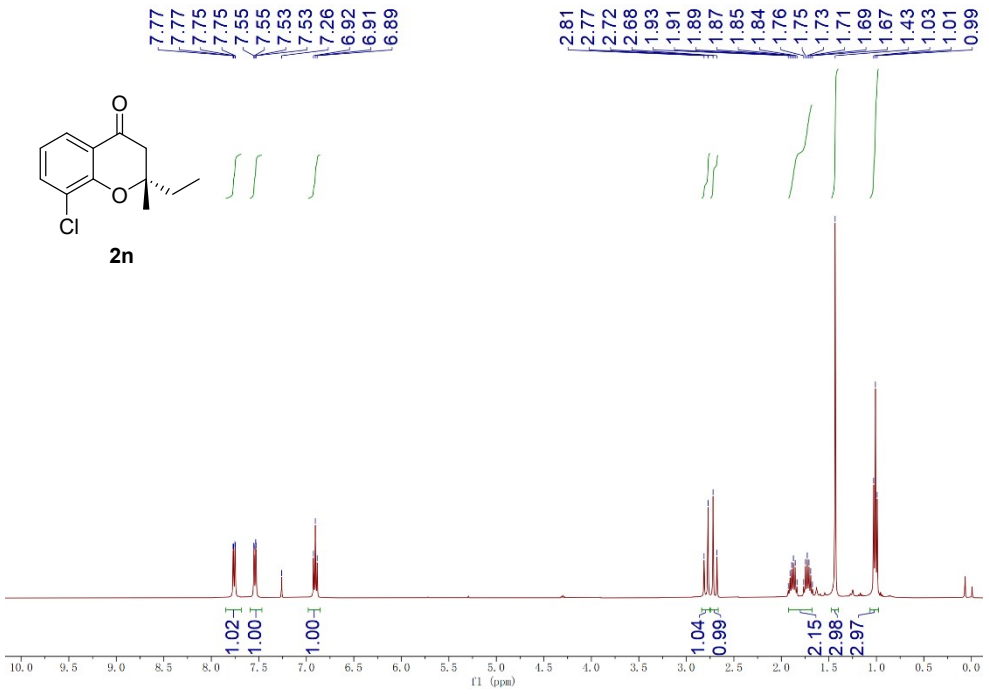
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2l



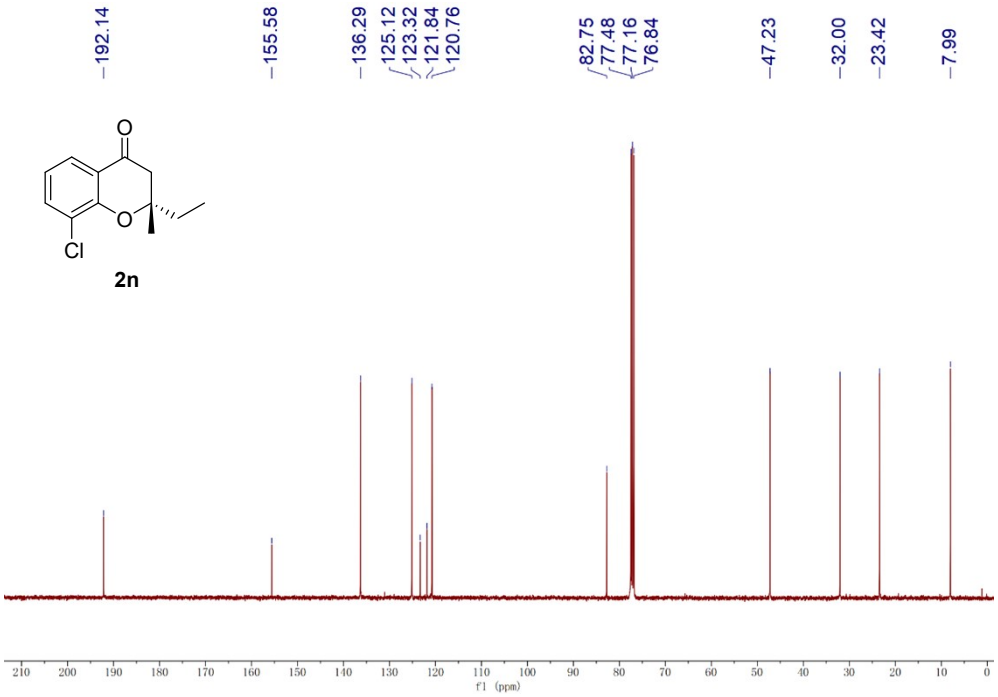
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2m



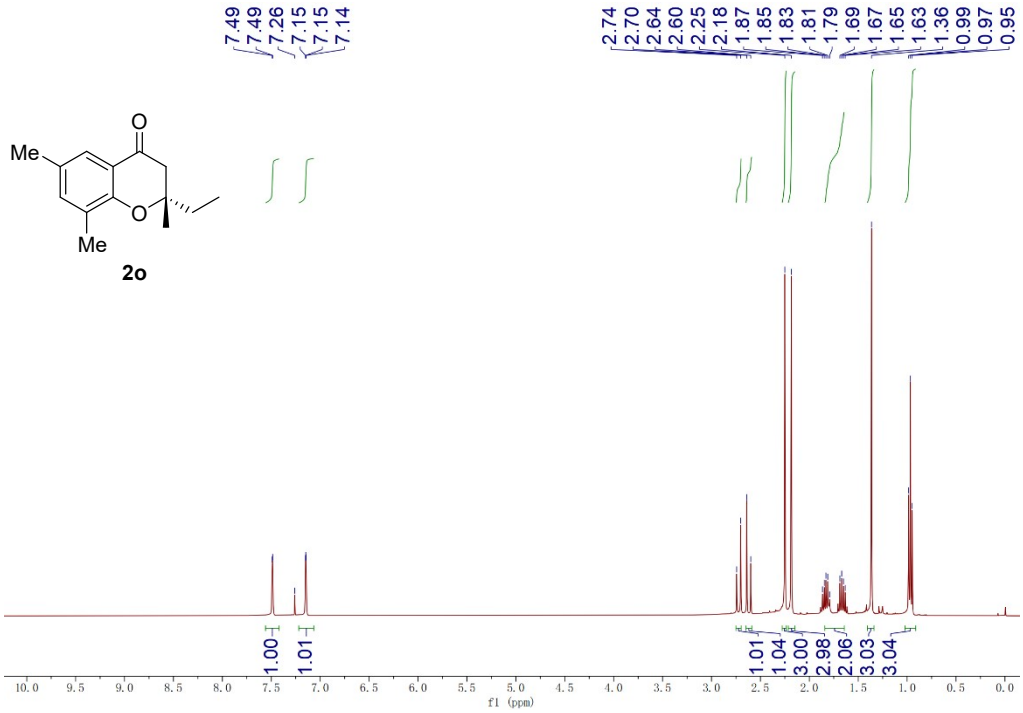
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2m



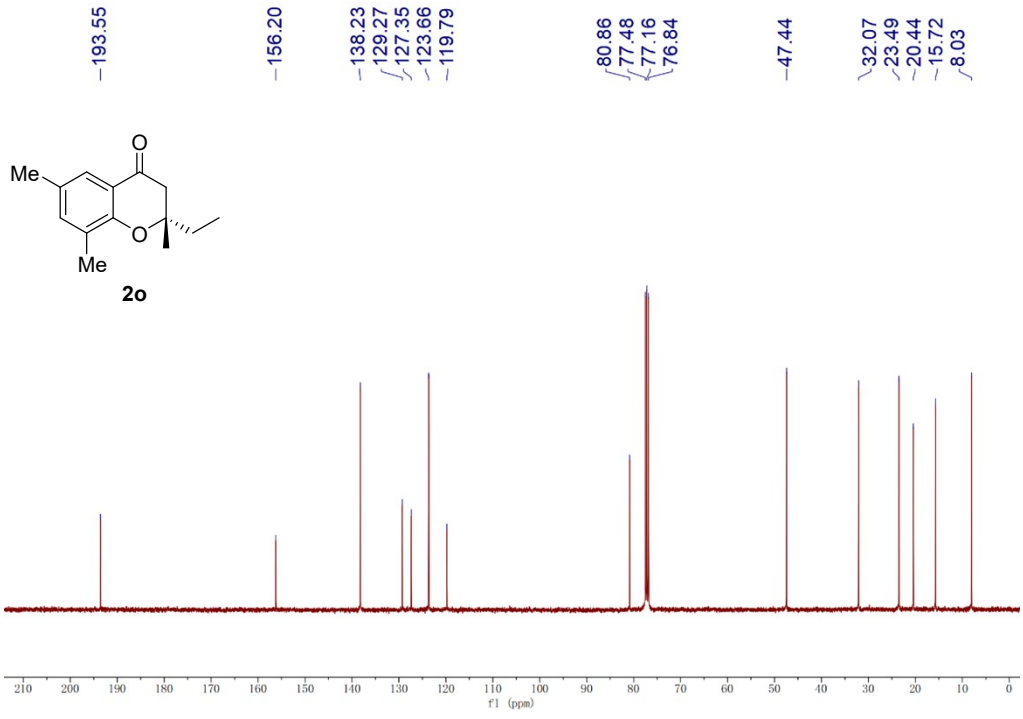
[1]H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2n



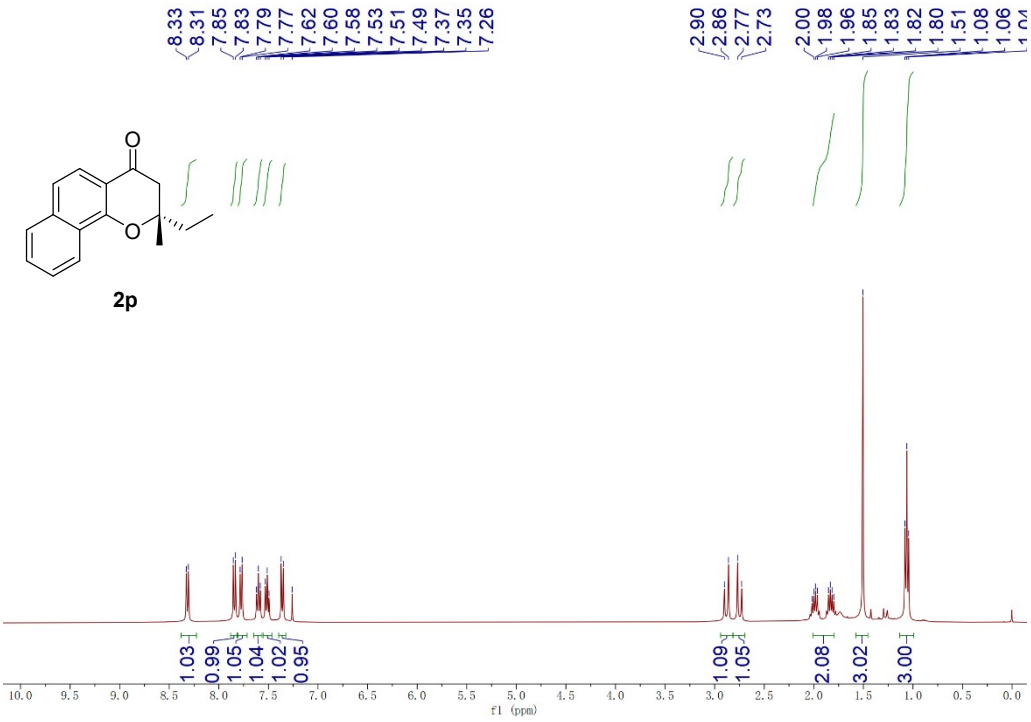
[13]C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2n



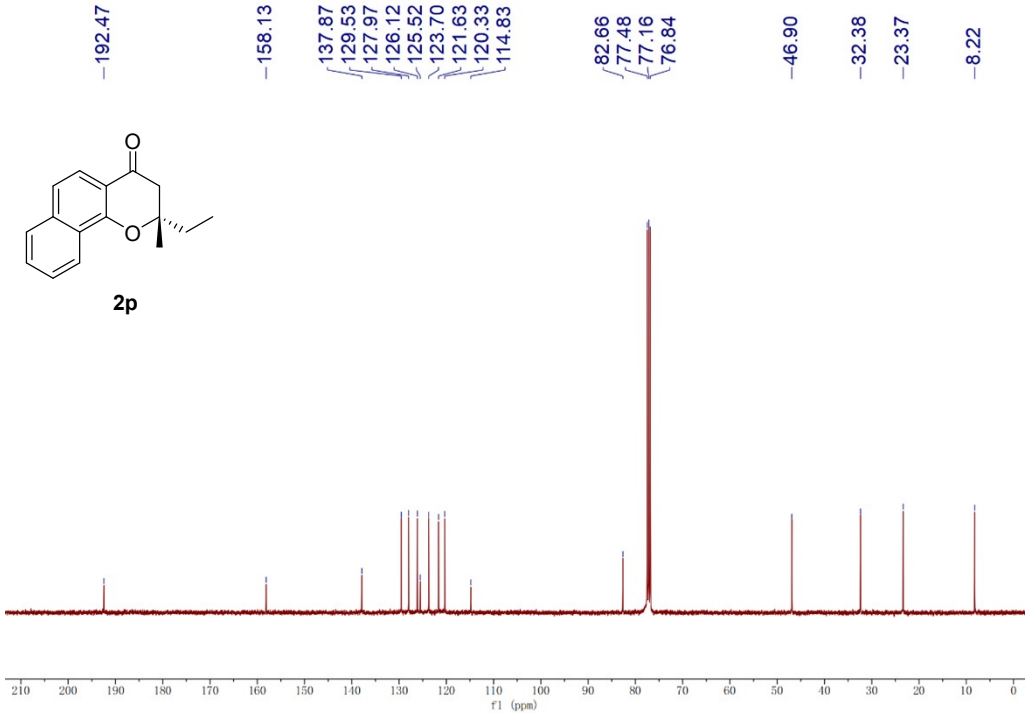
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2o



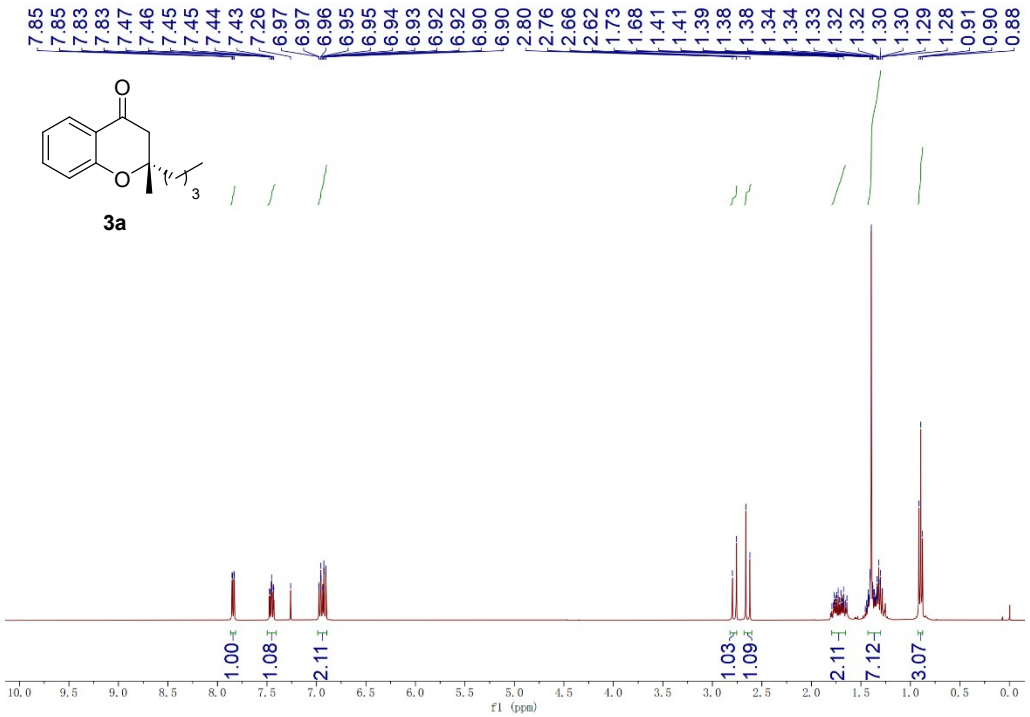
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2o



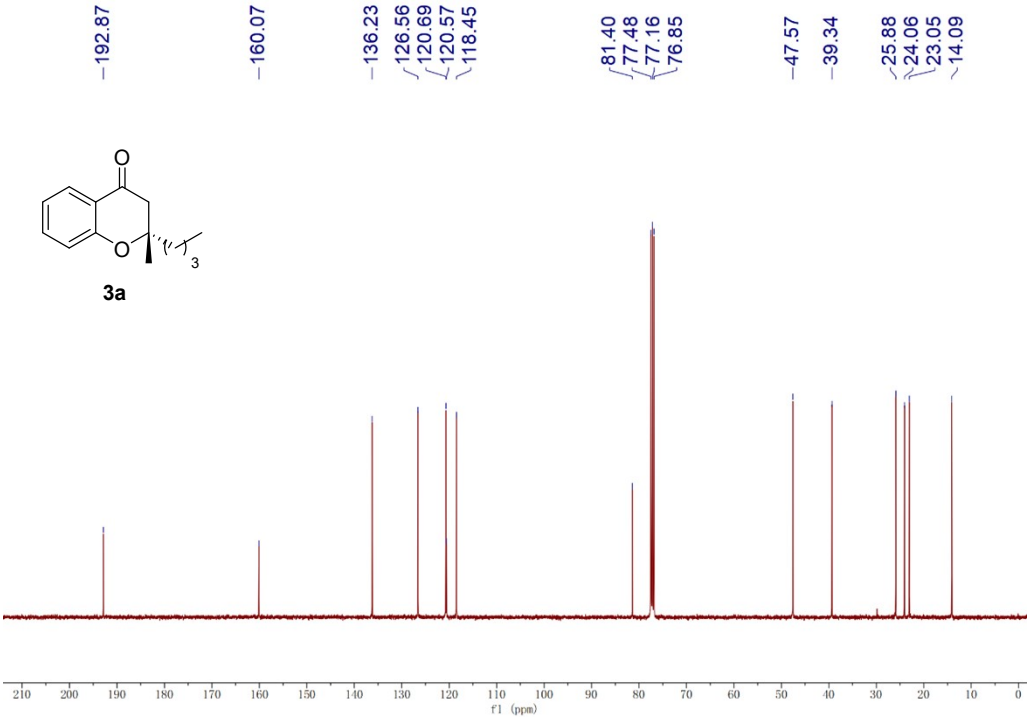
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 2p



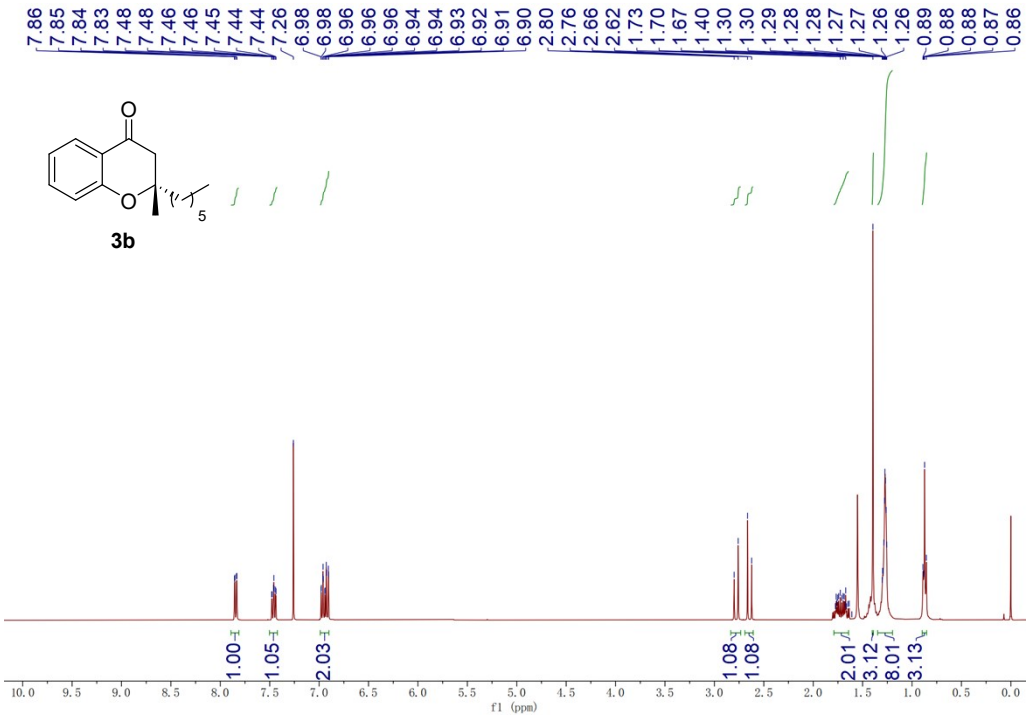
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 2p



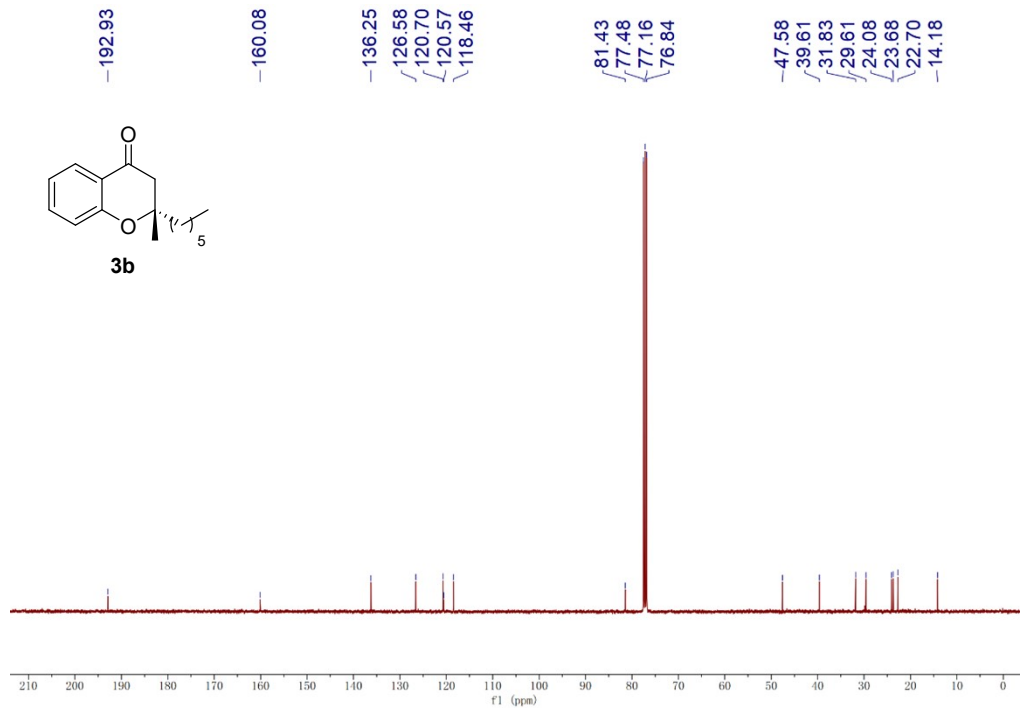
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 3a



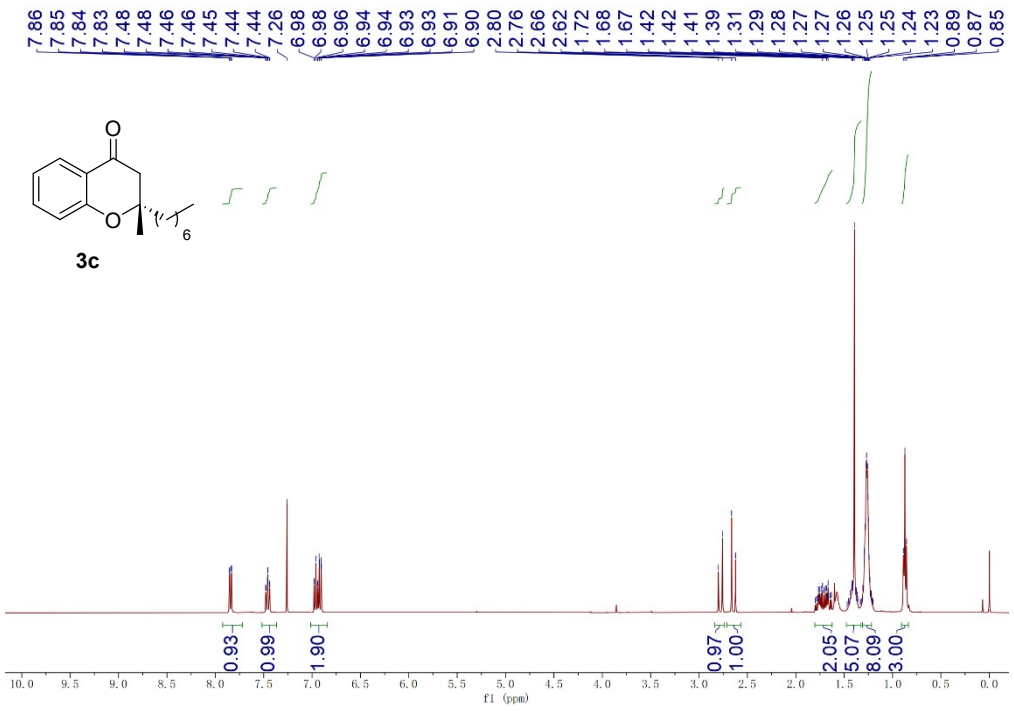
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3a



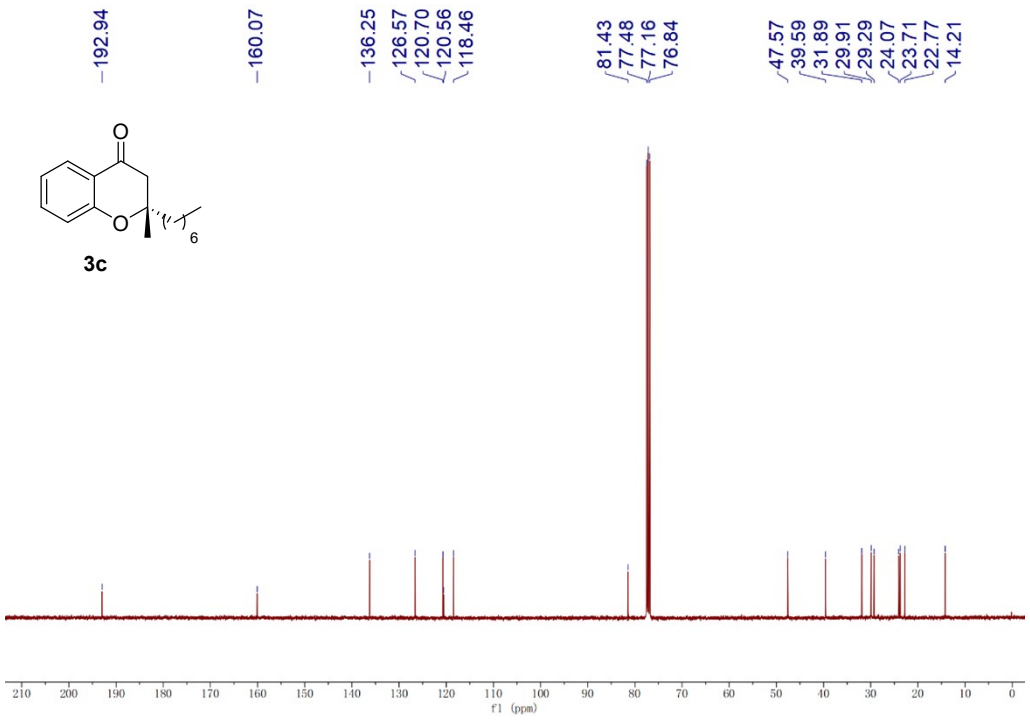
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 3b



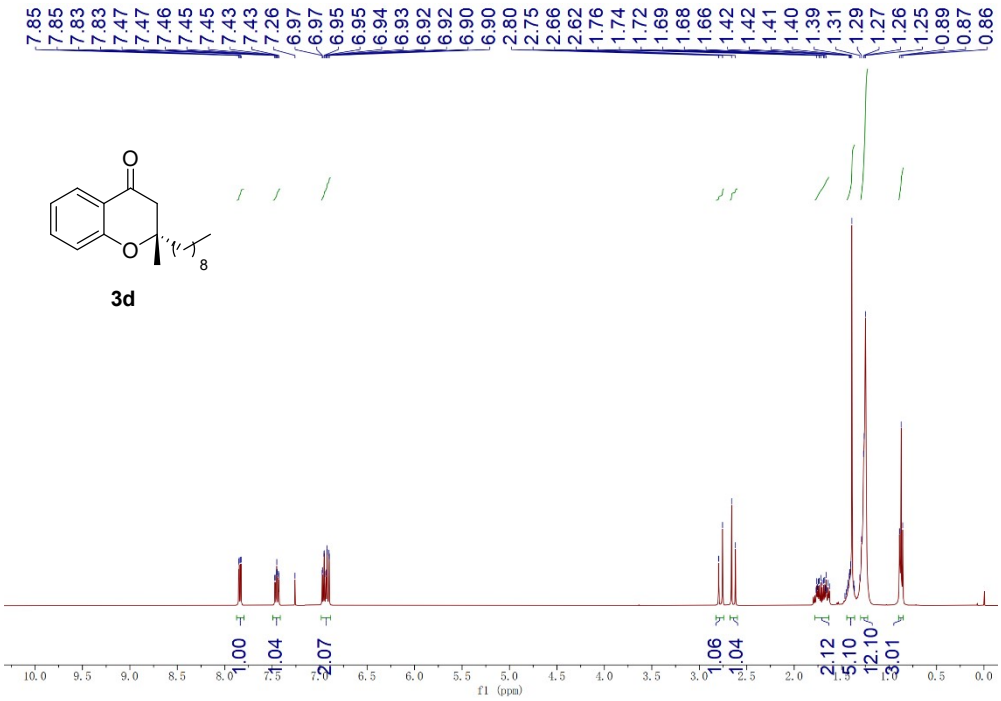
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3b



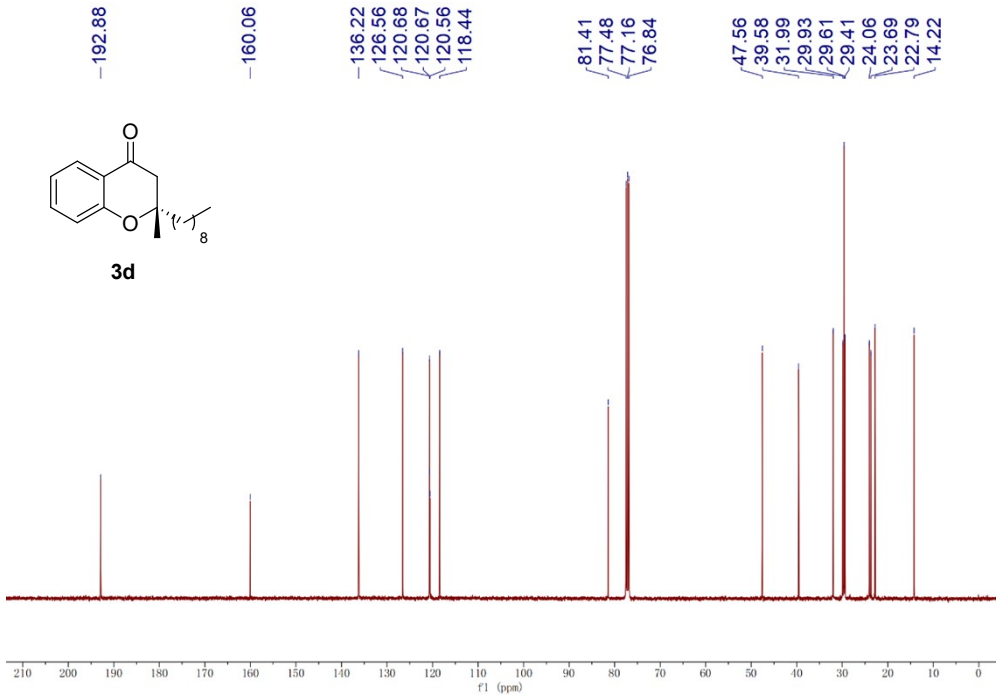
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 3c



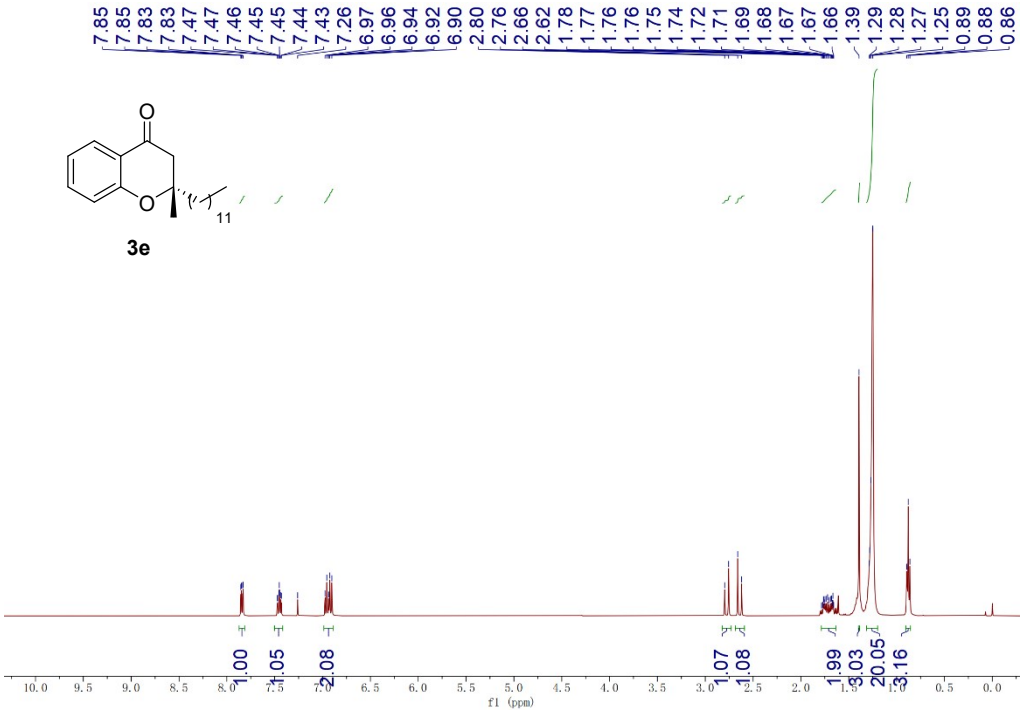
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3c



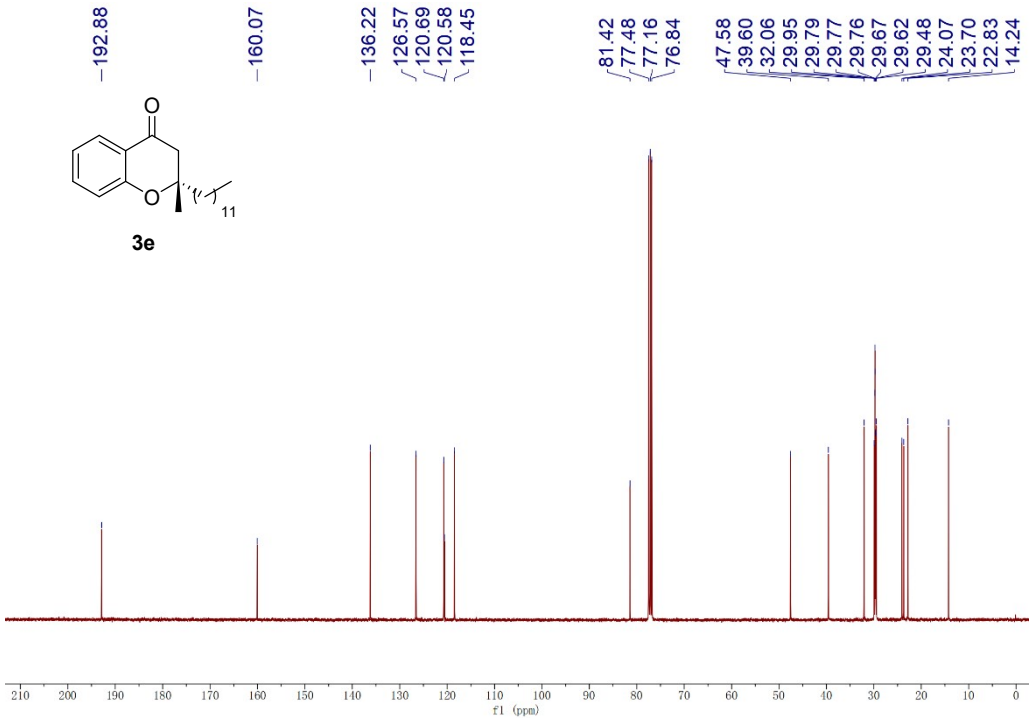
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 3d



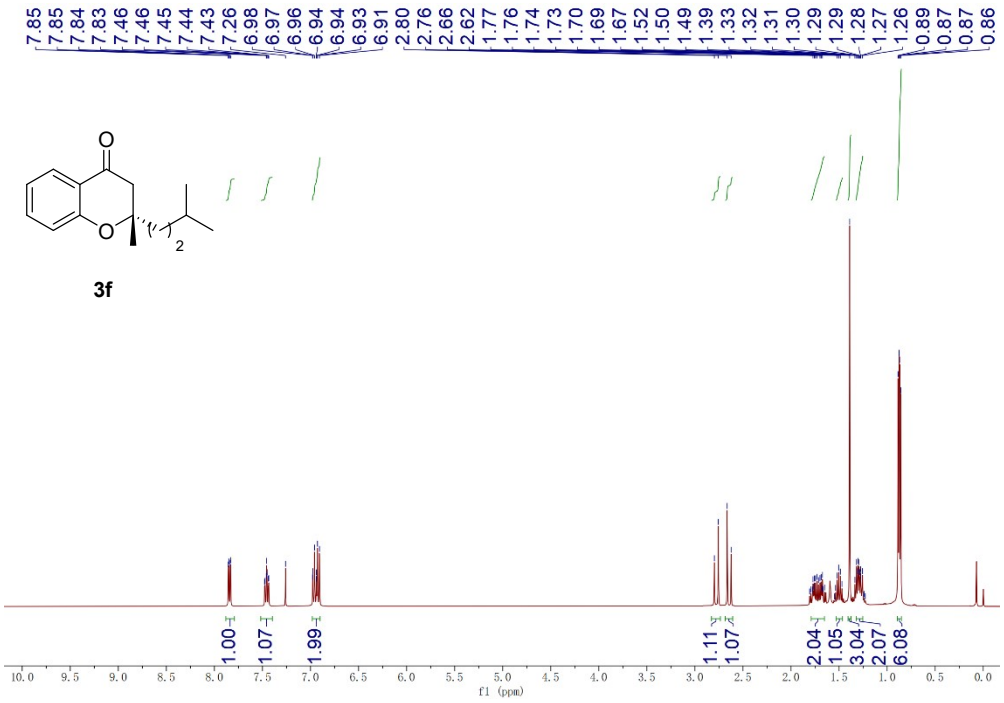
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3d



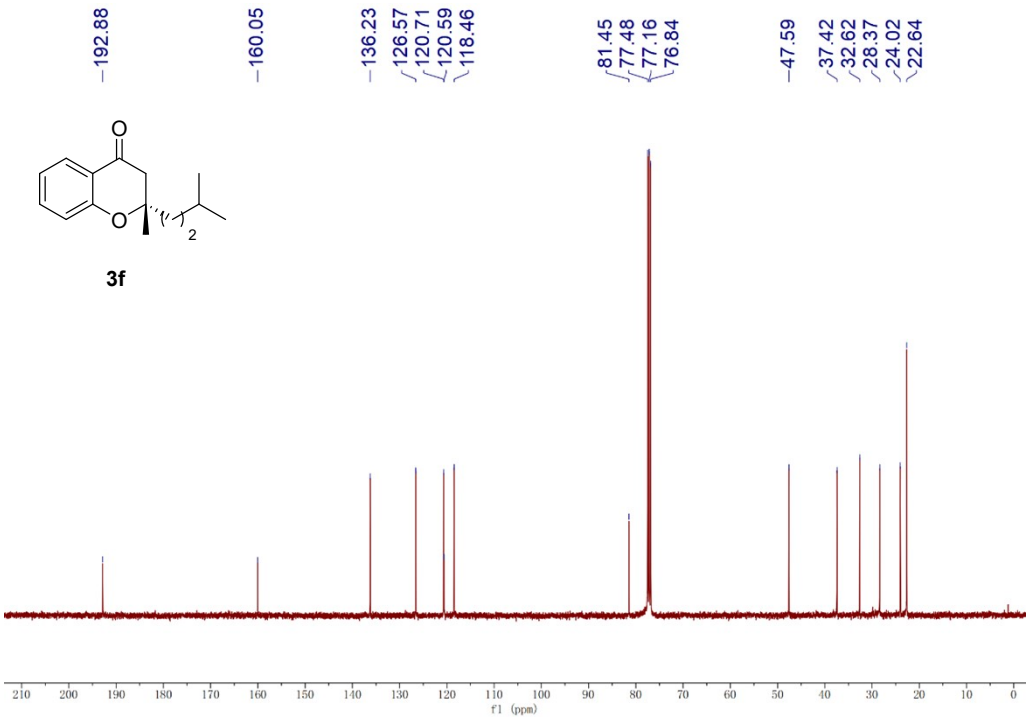
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 3e



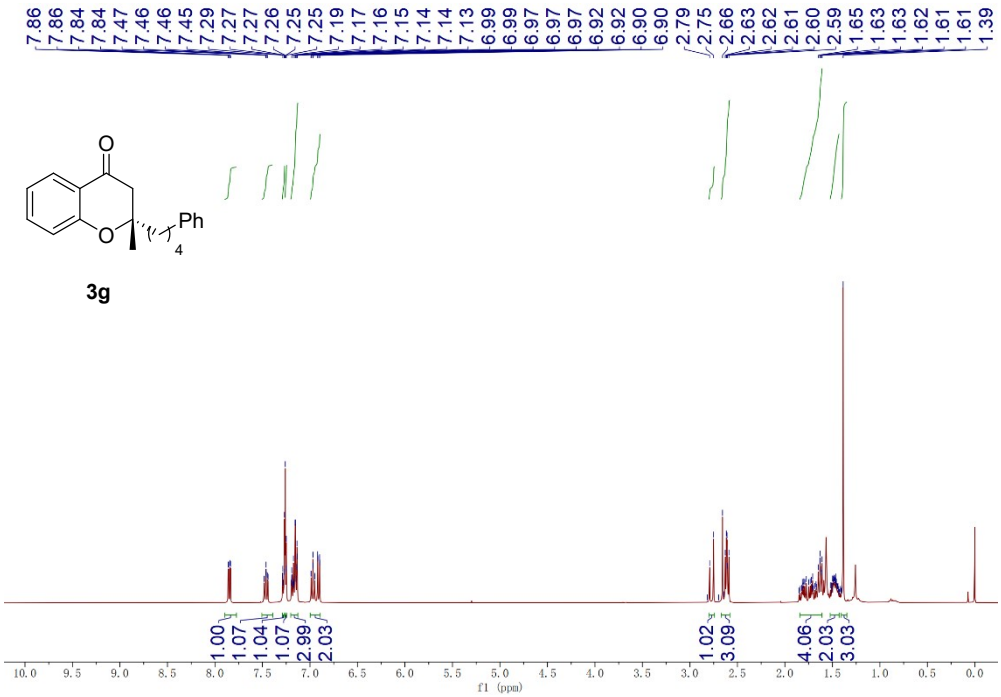
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3e



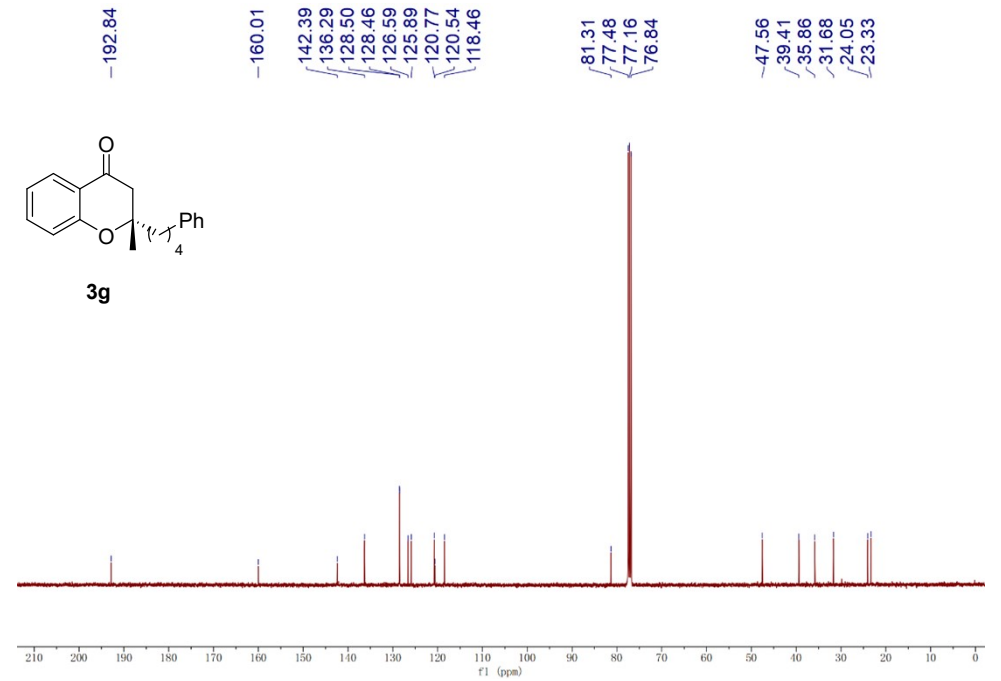
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 3f



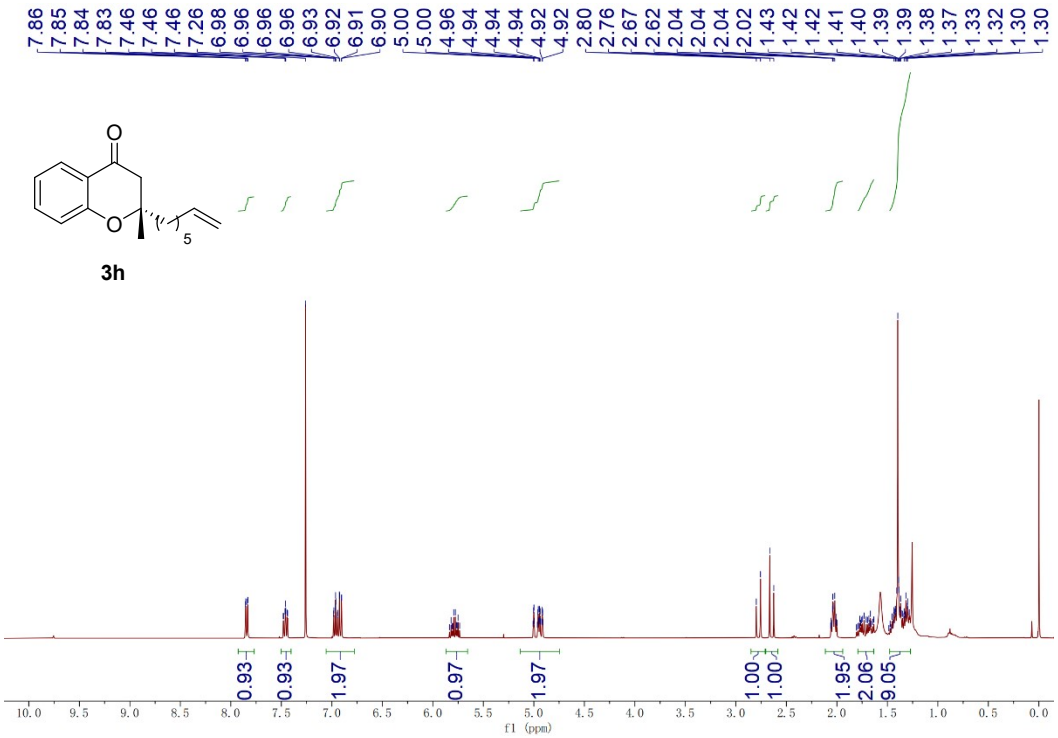
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3f



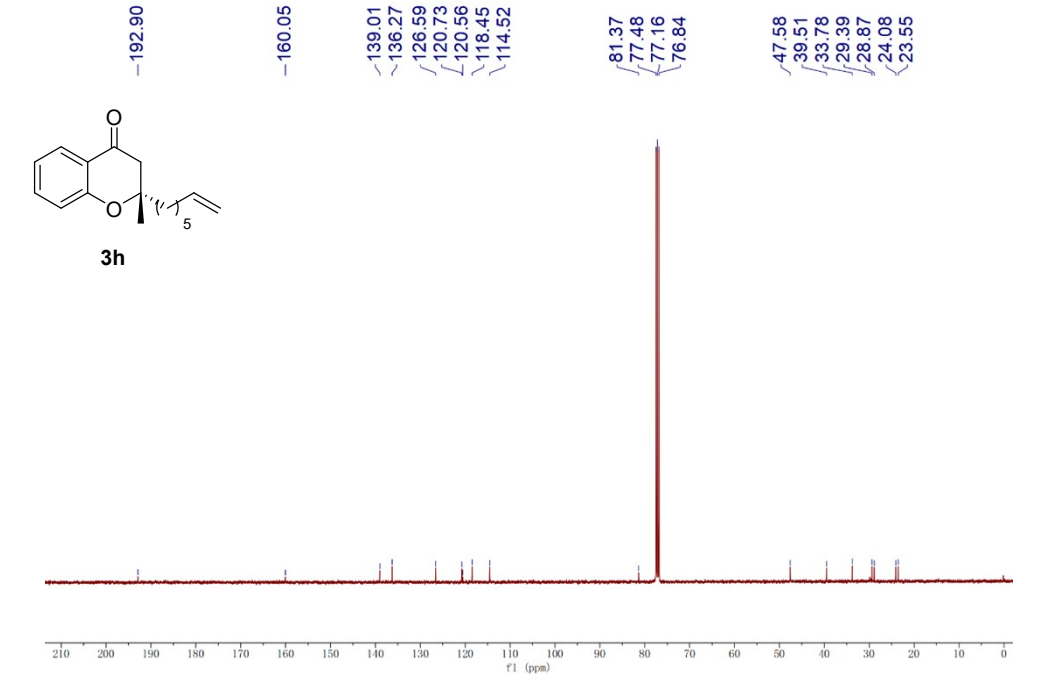
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 3g



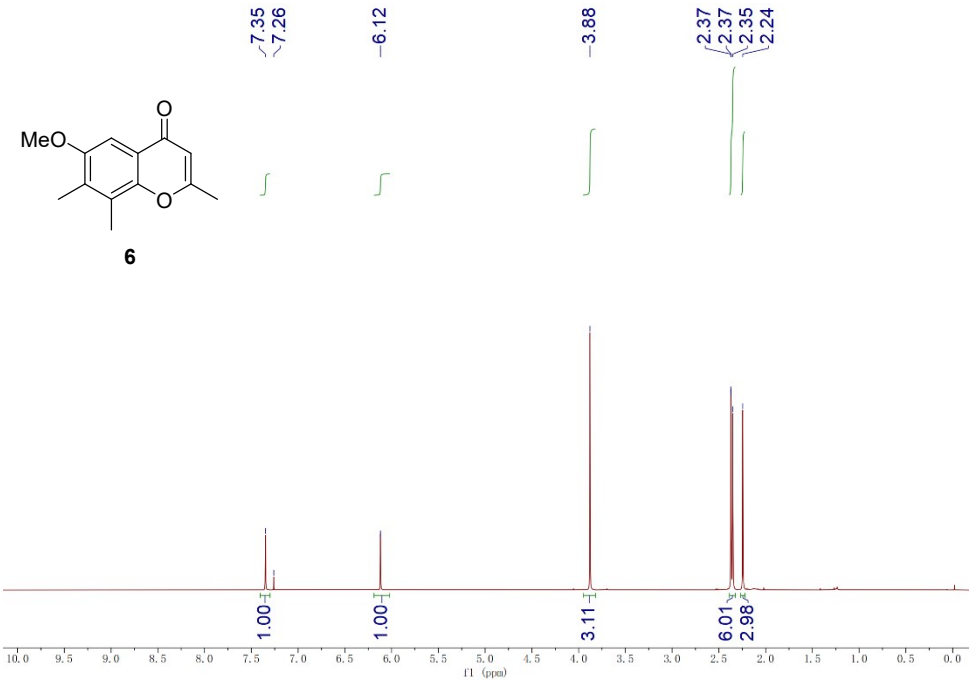
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3g



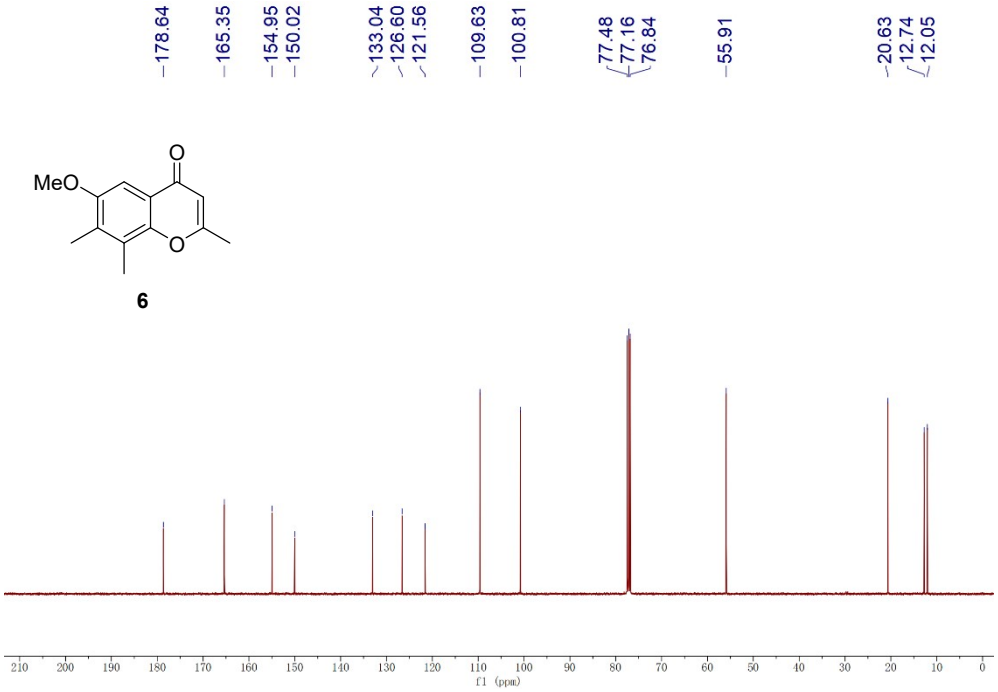
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 3h



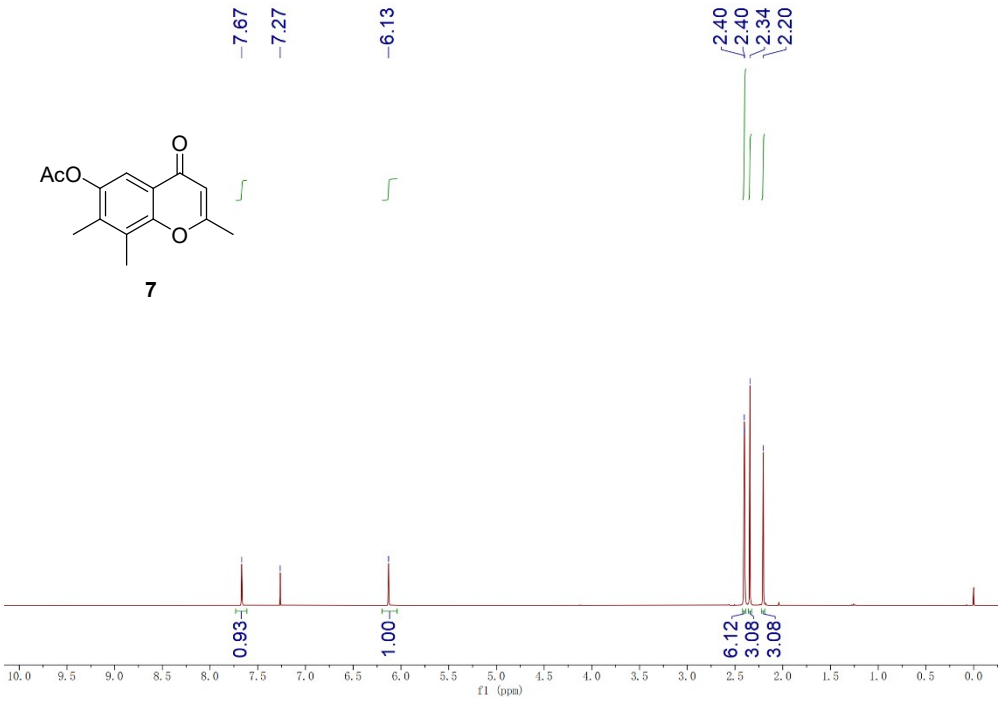
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3h



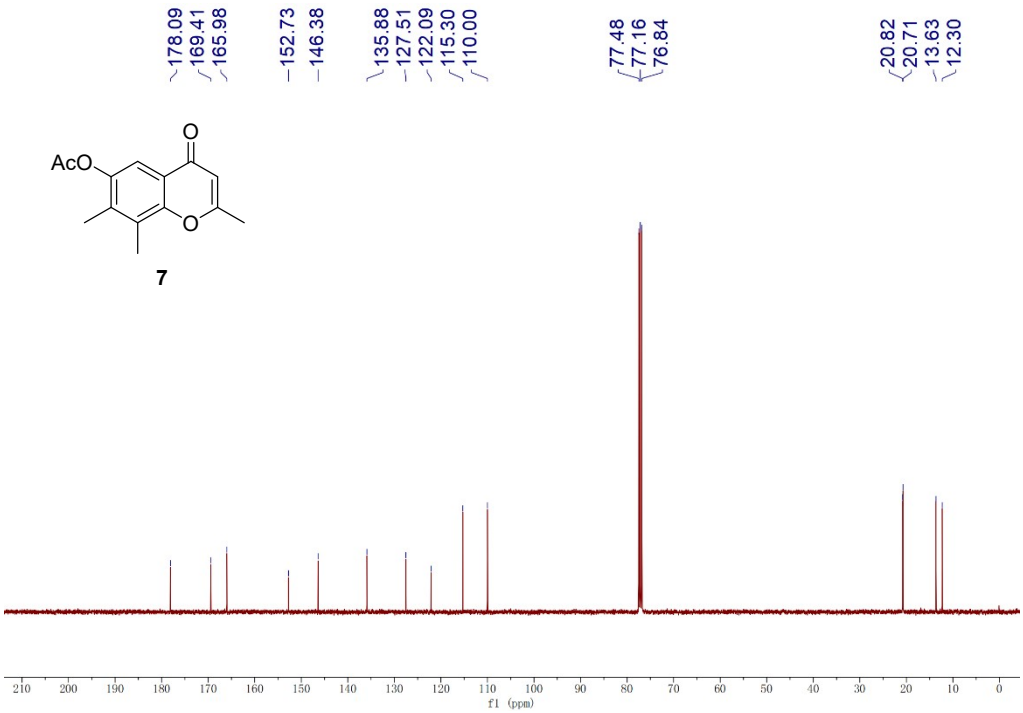
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 6



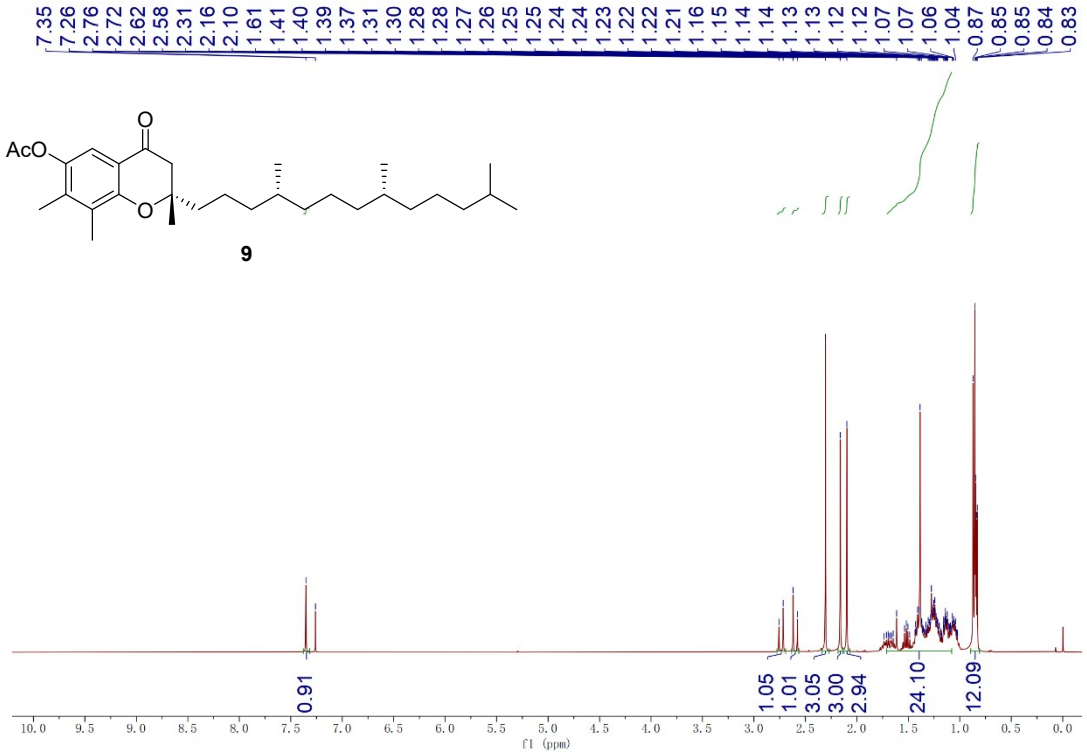
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 6



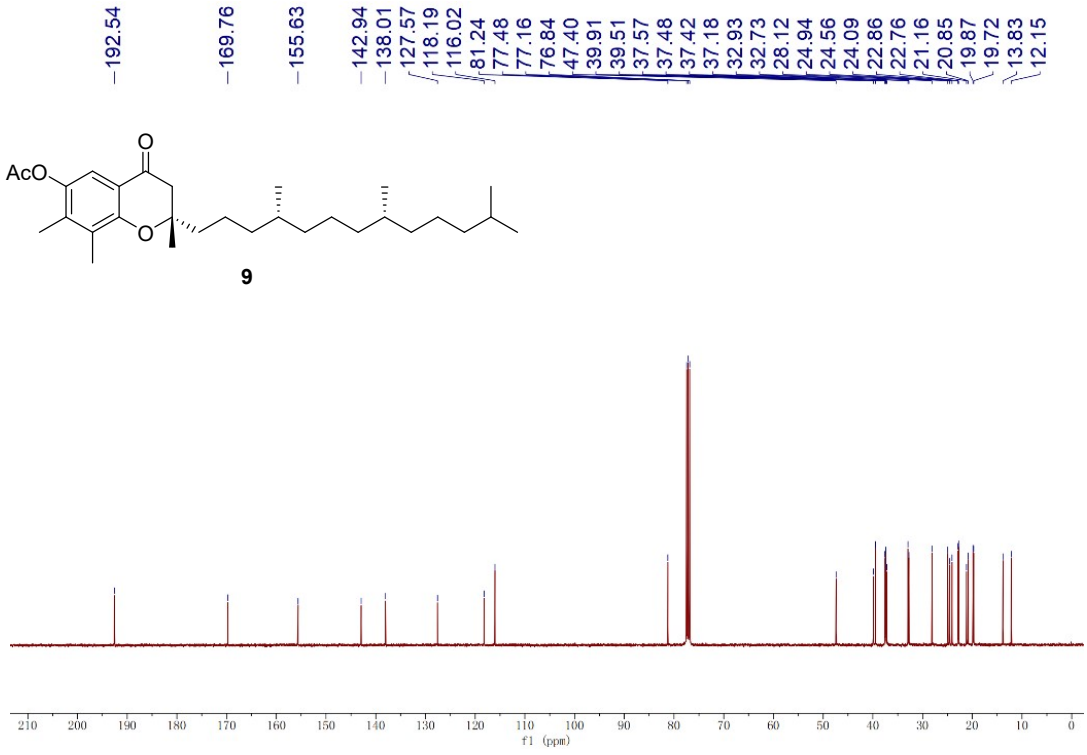
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 7



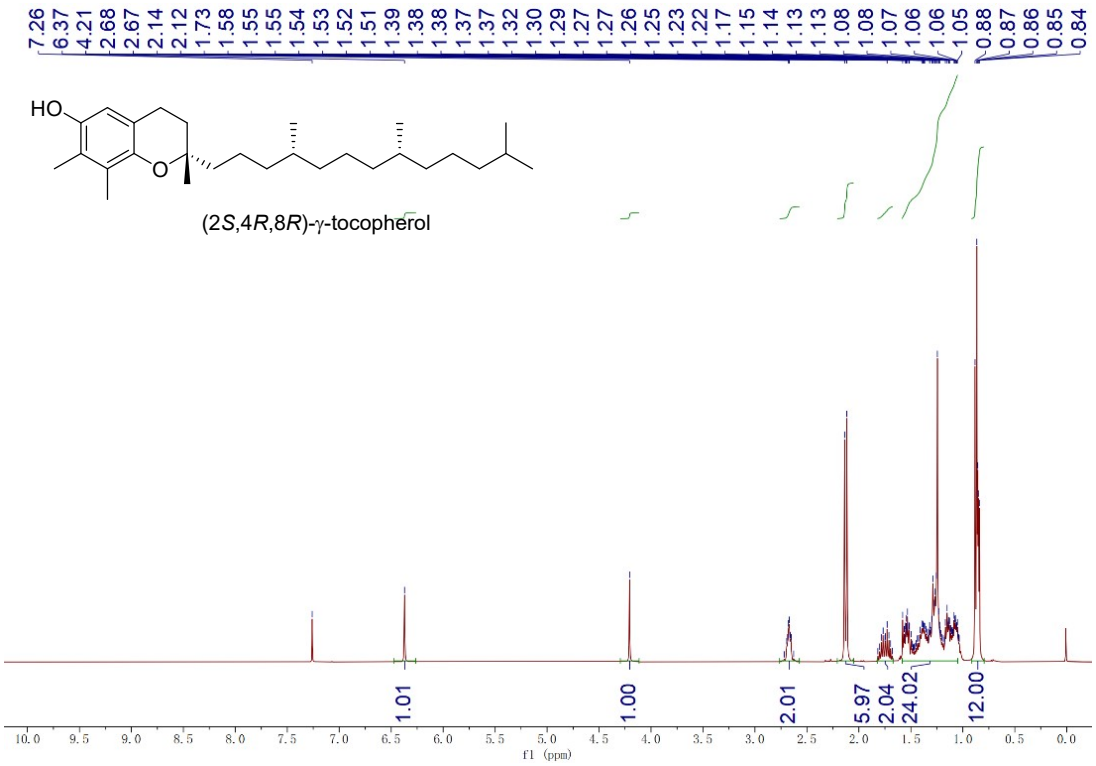
^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 7



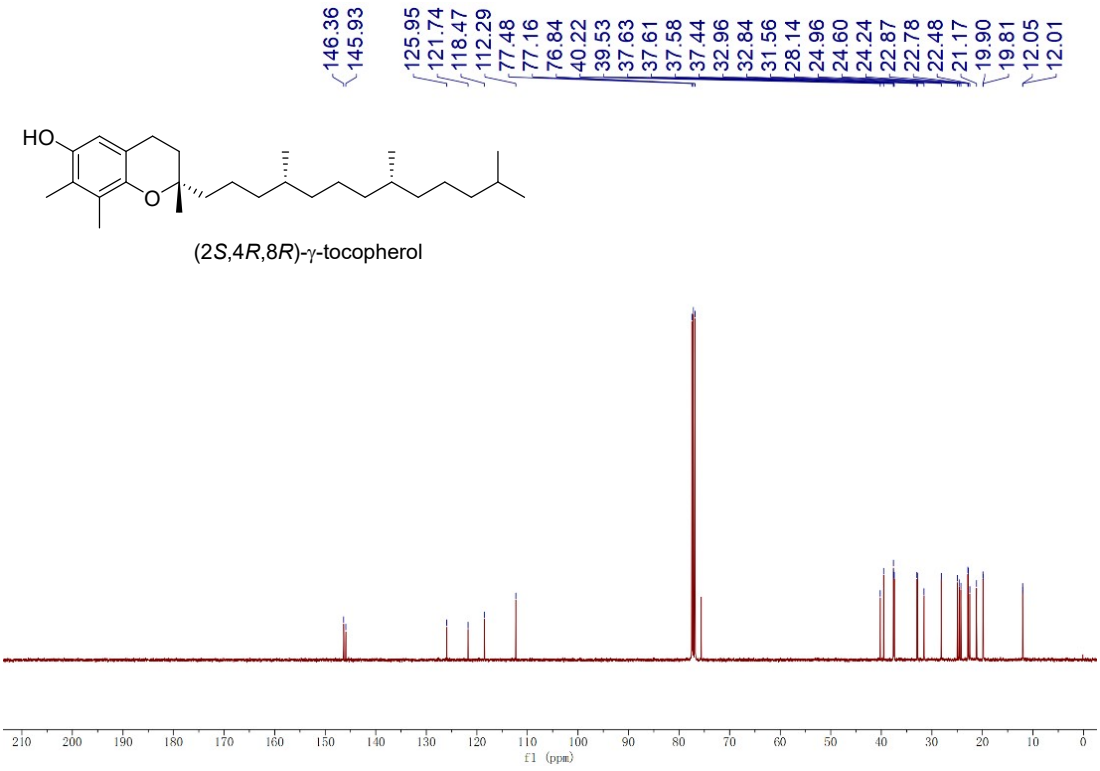
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound 9



^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound 9

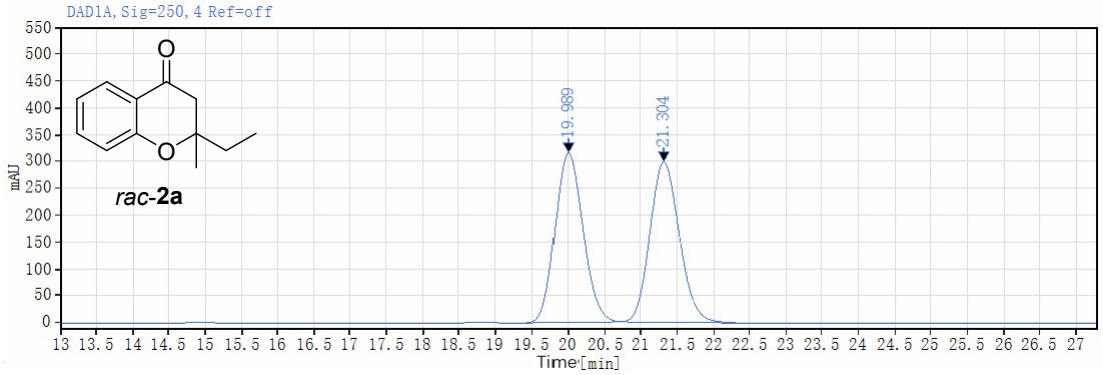


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of Compound (2*S*,4*R*,8*R*)-tocopherol

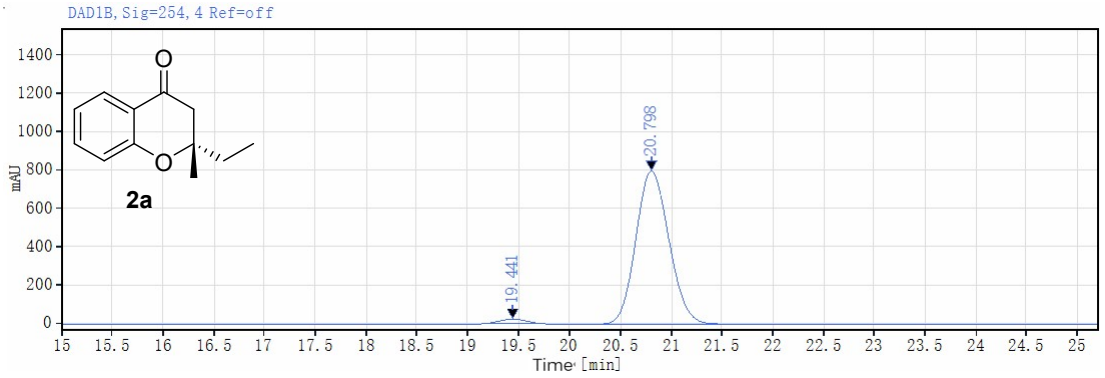


^{13}C-NMR Spectrum (100 MHz, $CDCl_3$) of Compound (2*S*,4*R*,8*R*)-tocopherol

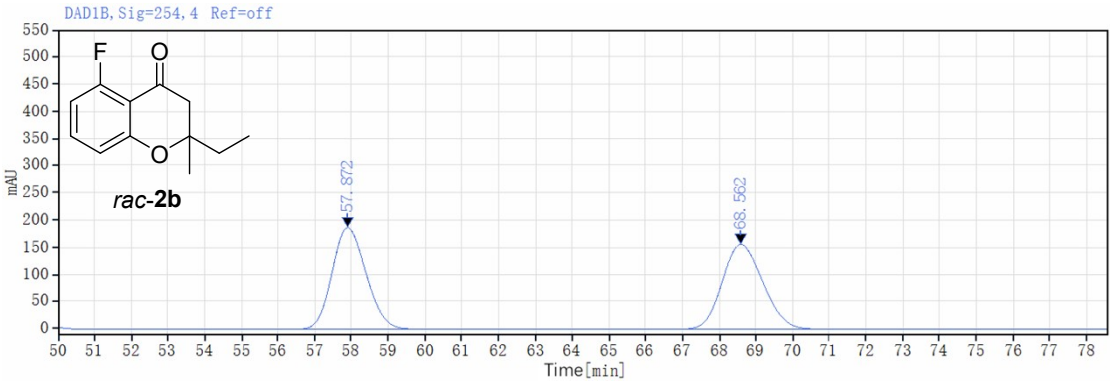
6. HPLC Spectra



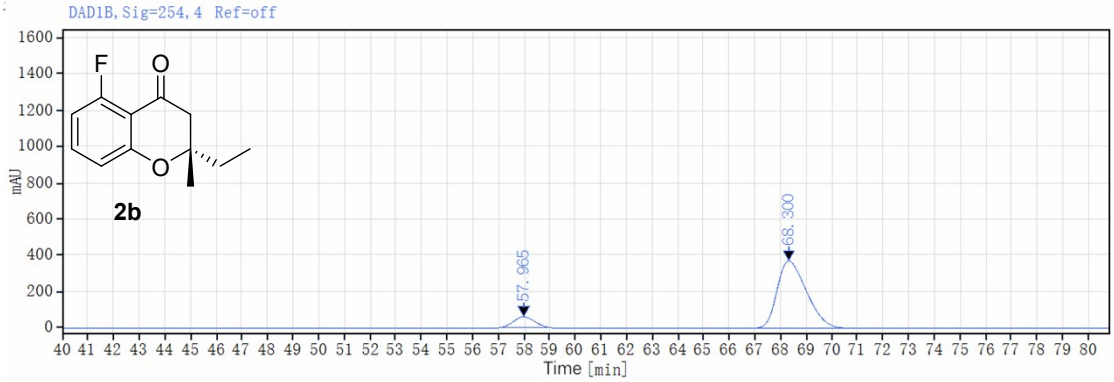
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
19.989	MM m	0.42	8367.18	315.67	49.82
21.304	MM m	0.44	8428.02	298.61	50.18



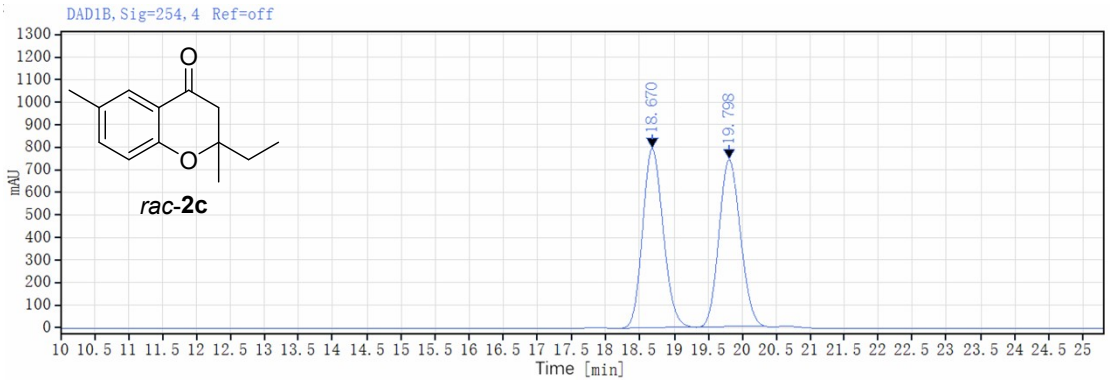
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
19.441	MM m	0.29	433.15	23.68	2.33
20.798	MM m	0.35	18161.44	800.34	97.67



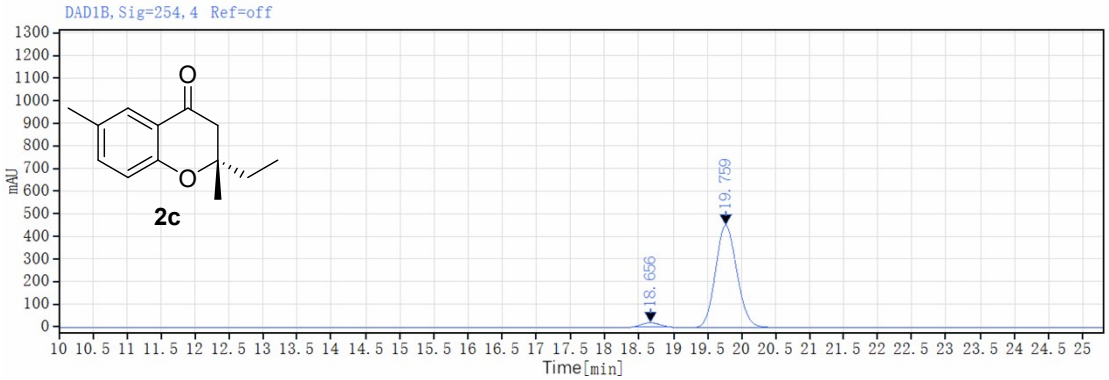
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
57.872	MM m	0.98	12036.34	187.01	50.01
68.562	MM m	1.18	12032.24	156.07	49.99



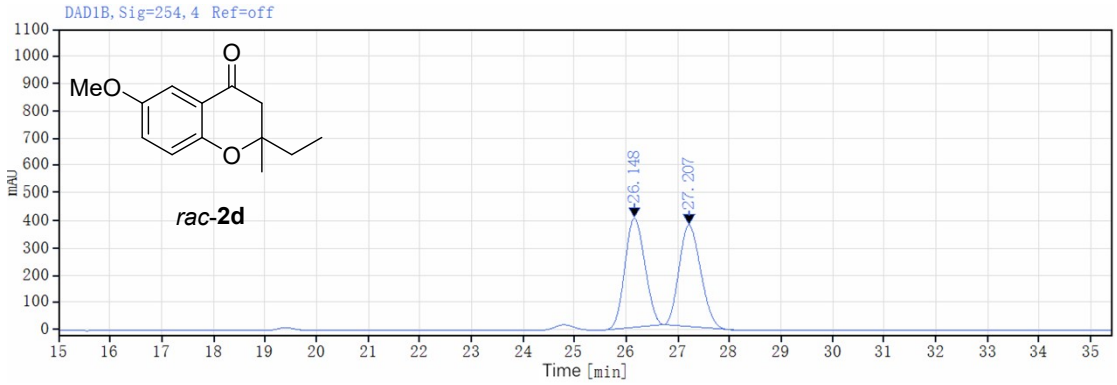
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
57.965	MM m	0.88	3364.30	59.02	10.19
68.300	MM m	1.22	29665.36	372.47	89.81



Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
18.670	MM m	0.33	16644.19	794.70	50.74
19.798	MM m	0.34	16161.42	741.10	49.26



Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
18.656	MM m	0.29	341.51	19.10	3.33
19.759	MM m	0.34	9900.52	452.71	96.67



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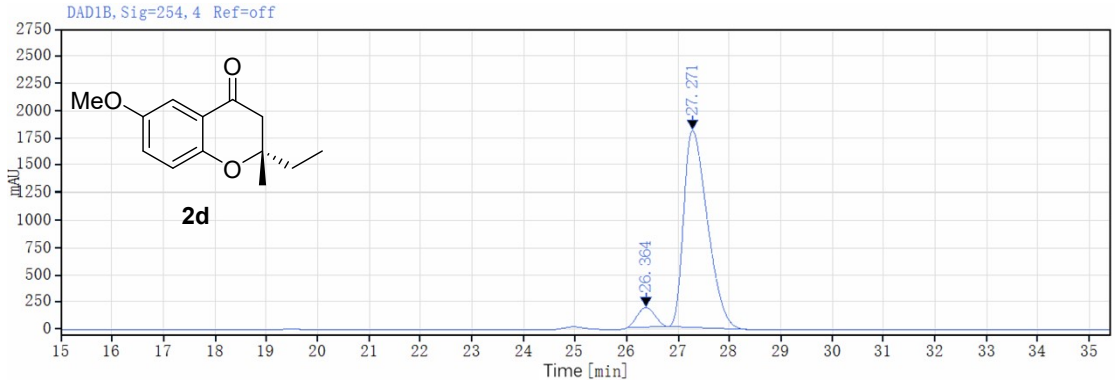
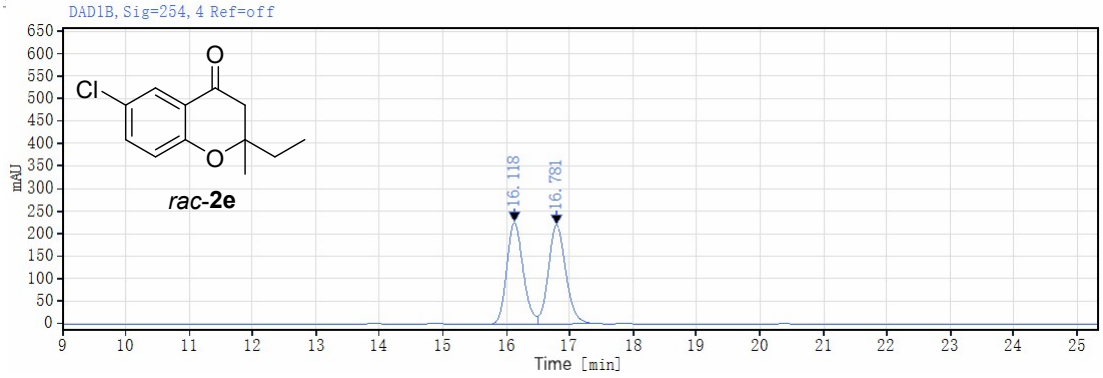
26.148	MM m	0.42	10798.40	400.78	50.01
27.207	MM m	0.46	10793.70	371.78	49.99



Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
26.364	MM m	0.39	4259.24	179.17	6.84
27.271	MM m	0.50	57977.53	1802.70	93.16



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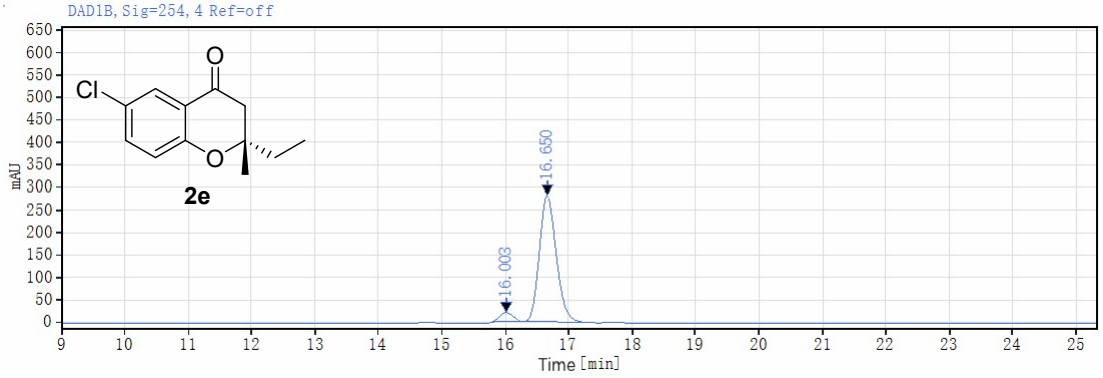
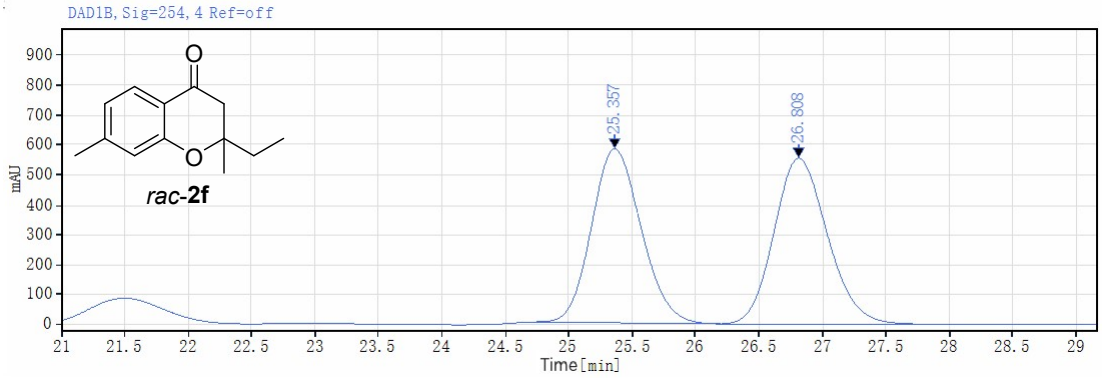
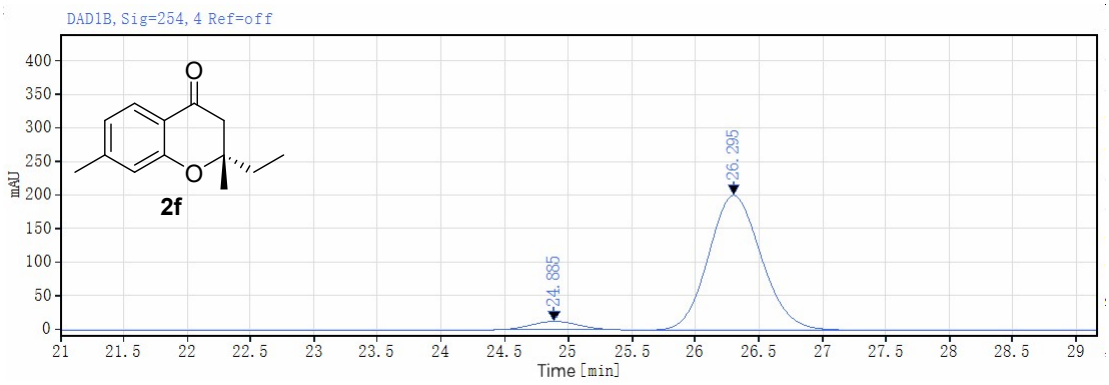
16.118	MM m	0.28	4100.82	227.69	49.35
16.781	MM m	0.29	4208.99	221.32	50.65



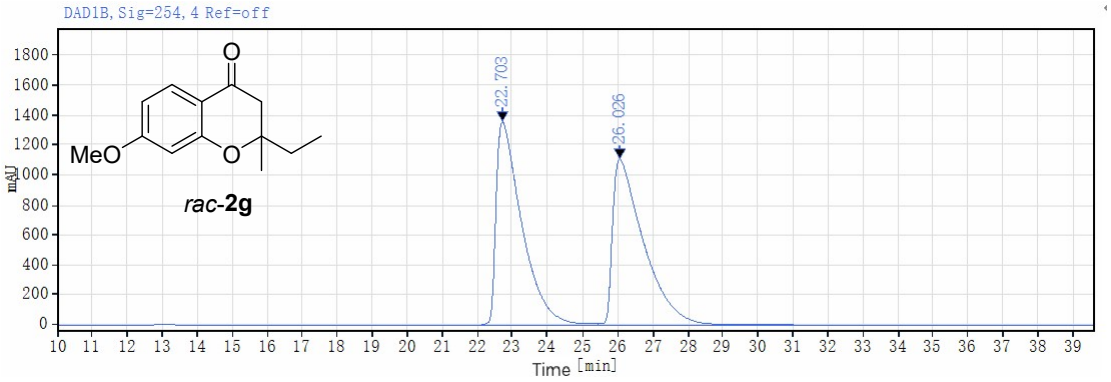
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
16.003	MM m	0.23	278.86	19.68	5.10
16.650	MM m	0.29	5192.63	280.79	94.90



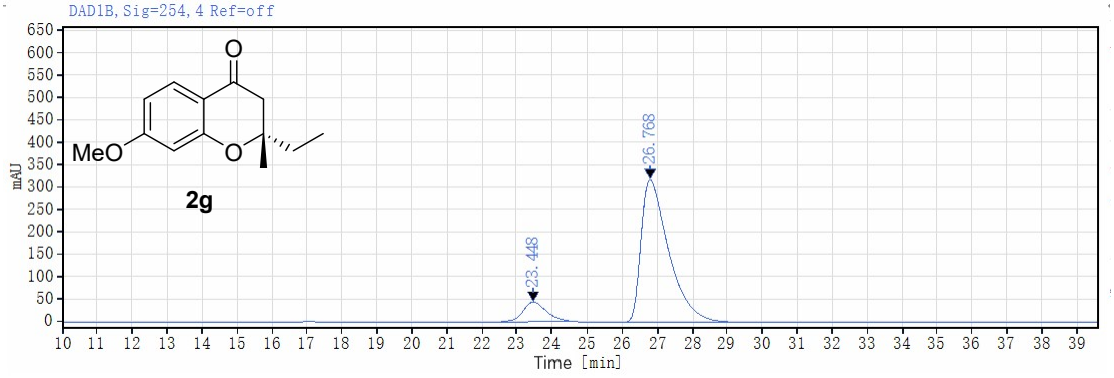
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
25.357	MM m	0.42	15790.26	580.15	49.34
26.808	MM m	0.46	16211.78	552.56	50.66



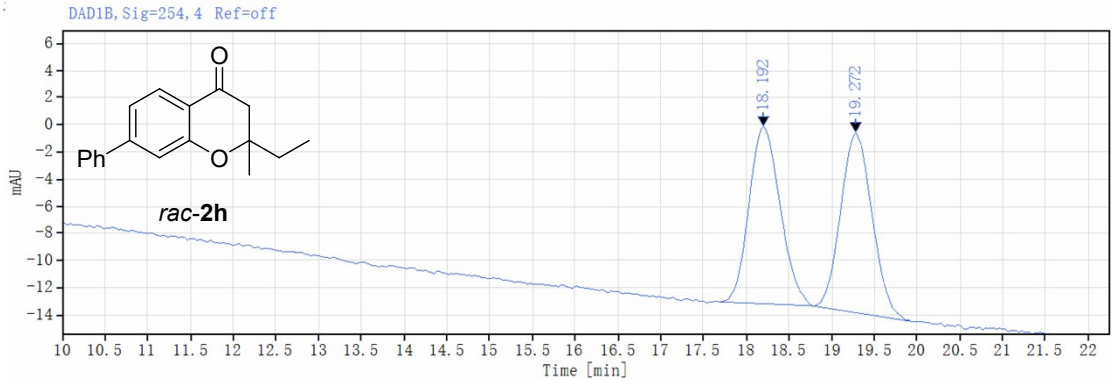
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
24.885	MM m	0.40	304.52	12.08	4.97
26.295	MM m	0.45	5819.81	200.96	95.03



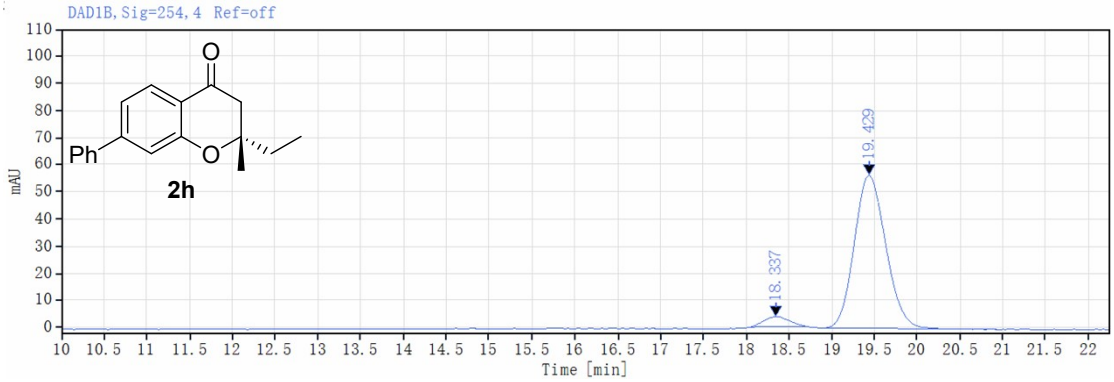
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
22.703	BV	3.79	69399.56	1356.69	50.35
26.026	VV	5.95	68429.02	1105.72	49.65



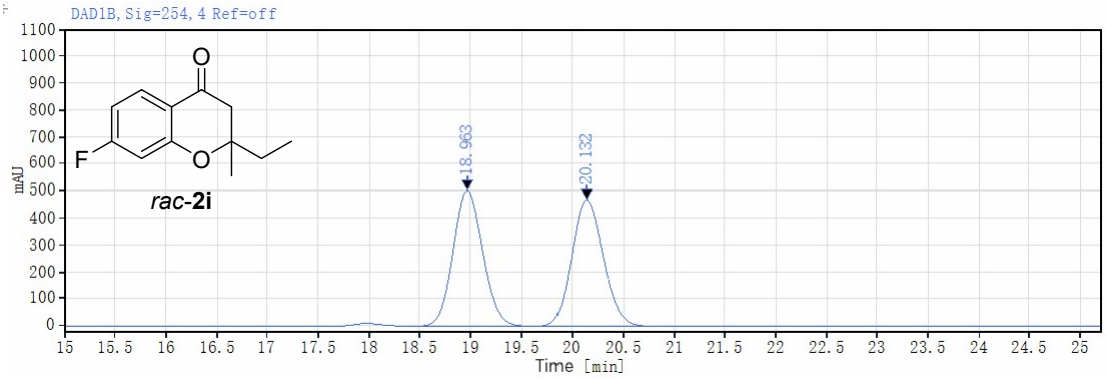
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
23.448	MM m	0.68	2026.89	43.72	10.34
26.768	MM m	0.82	17568.14	319.78	89.66



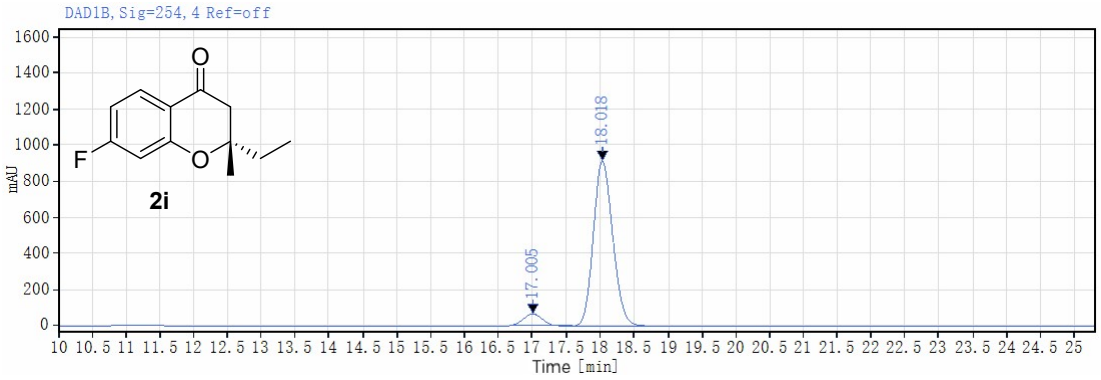
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
18.192	MM m	0.37	331.18	13.05	49.41
19.272	MM m	0.31	339.08	13.24	50.59



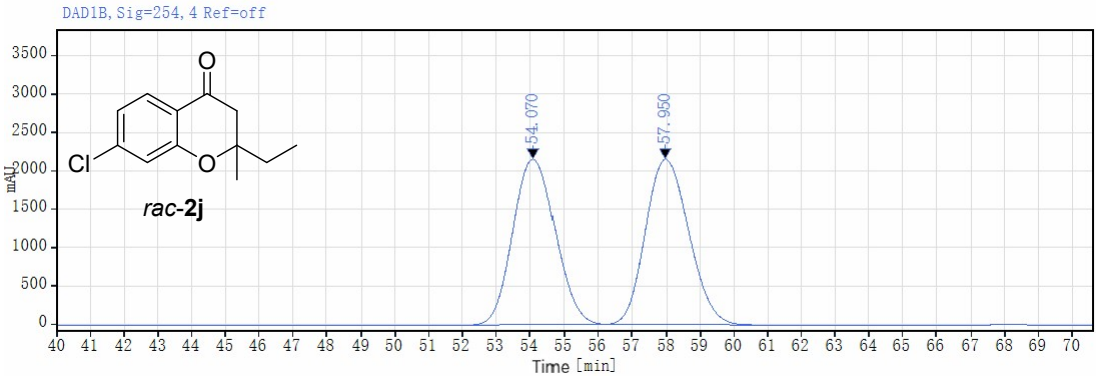
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
18.337	MM m	0.25	75.56	3.63	4.99
19.429	MM m	0.40	1439.17	56.41	95.01



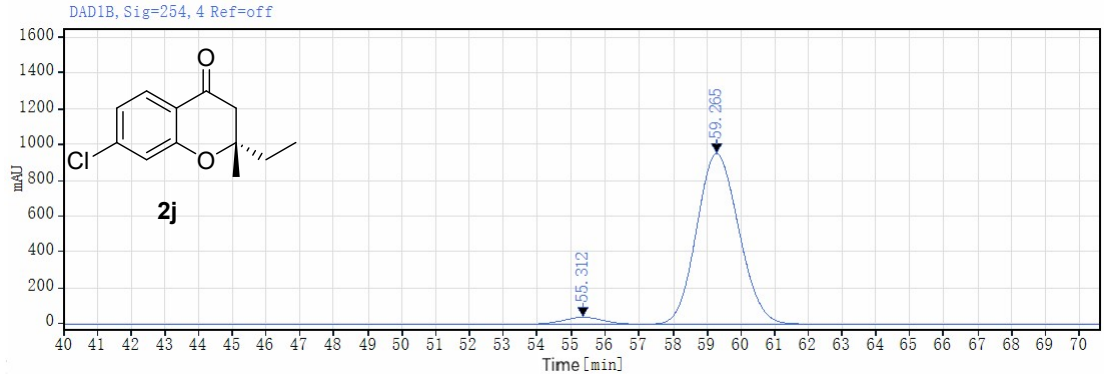
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
18.963	MM m	0.32	10259.84	503.87	50.33
20.132	MM m	0.34	10127.02	470.42	49.67



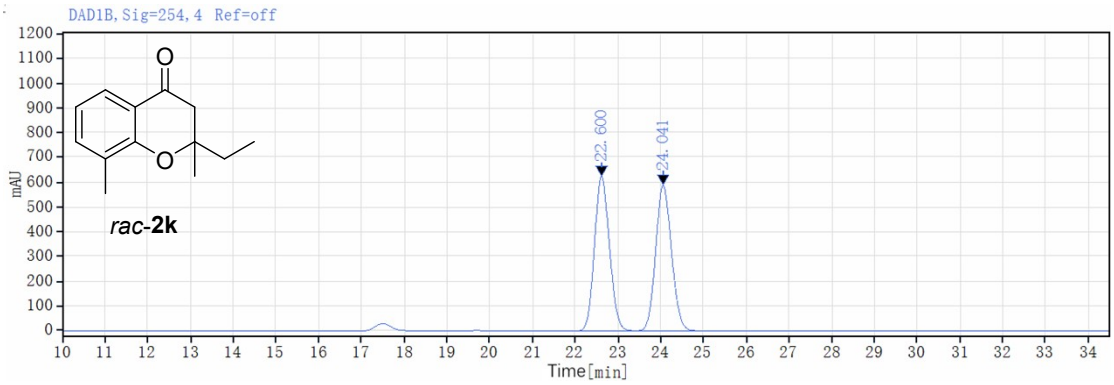
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
17.005	MM m	0.30	1232.58	64.28	6.36
18.018	MM m	0.31	18151.07	912.80	93.64



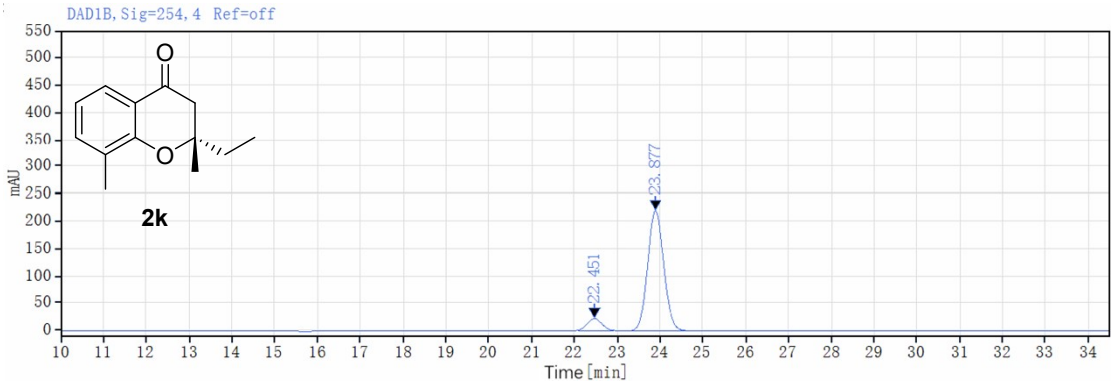
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
54.070	MM m	1.03	185583.85	2155.56	49.12
57.950	BB	4.67	192199.95	2155.84	50.88



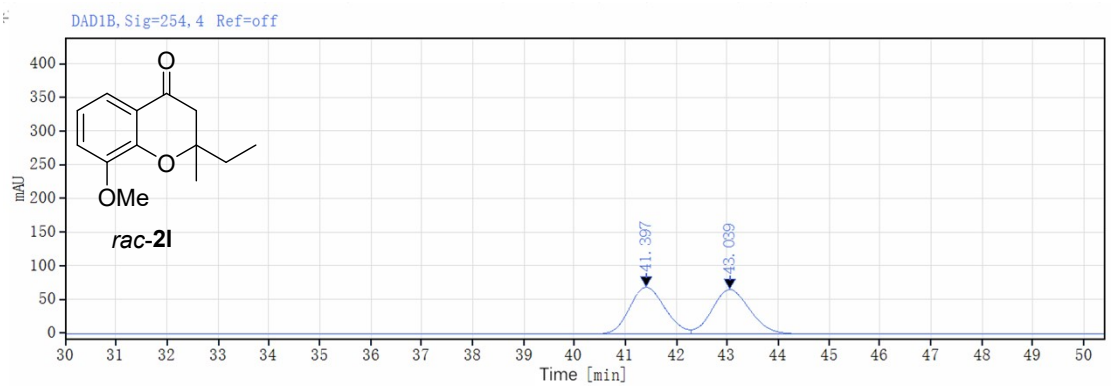
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
55.312	MM m	1.08	2989.02	37.72	3.49
59.265	MM m	1.34	82542.04	952.34	96.51



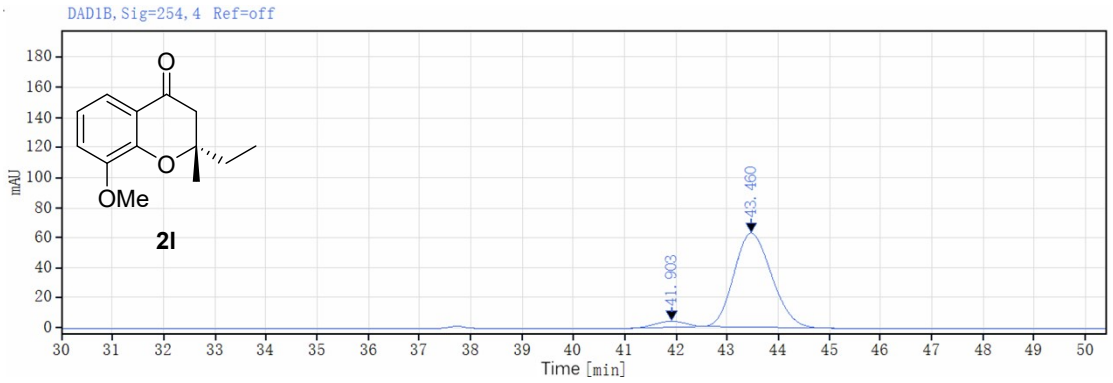
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
22.600	MM m	0.38	15201.30	622.27	50.00
24.041	MM m	0.41	15201.62	586.36	50.00



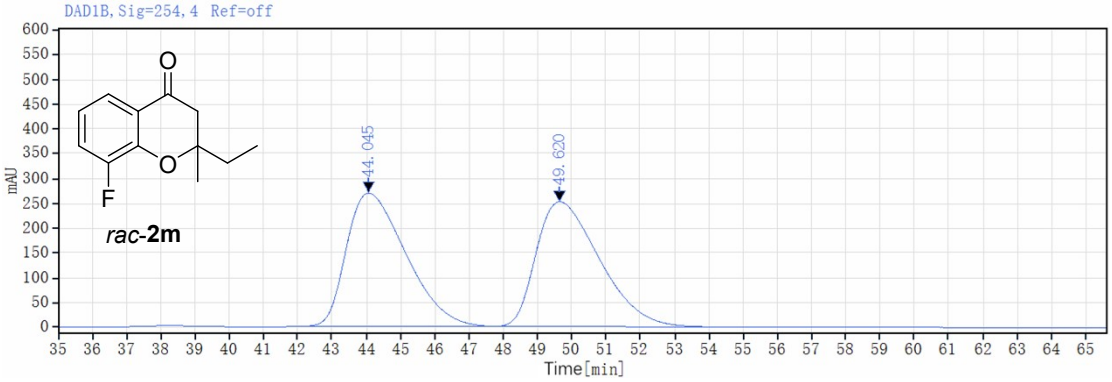
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
22.451	MM m	0.36	512.79	21.92	8.17
23.877	MM m	0.41	5765.26	220.68	91.83



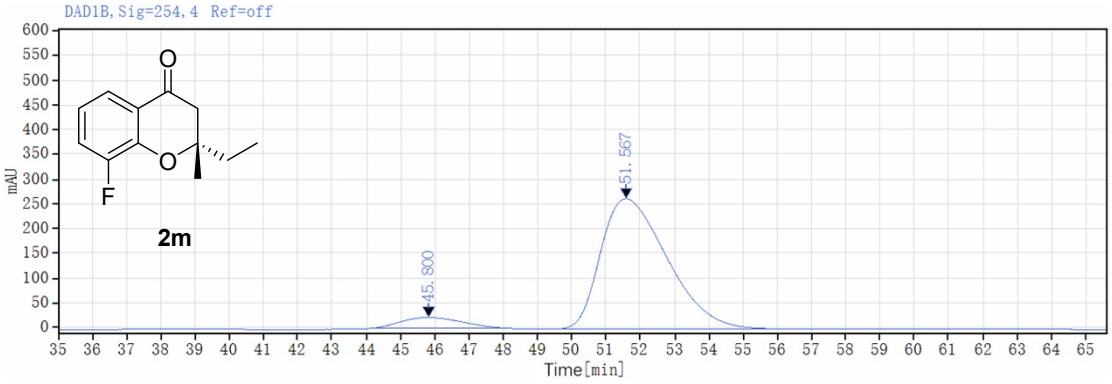
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
41.397	VV	1.93	3366.09	69.55	49.78
43.039	VB	2.39	3396.01	66.06	50.22



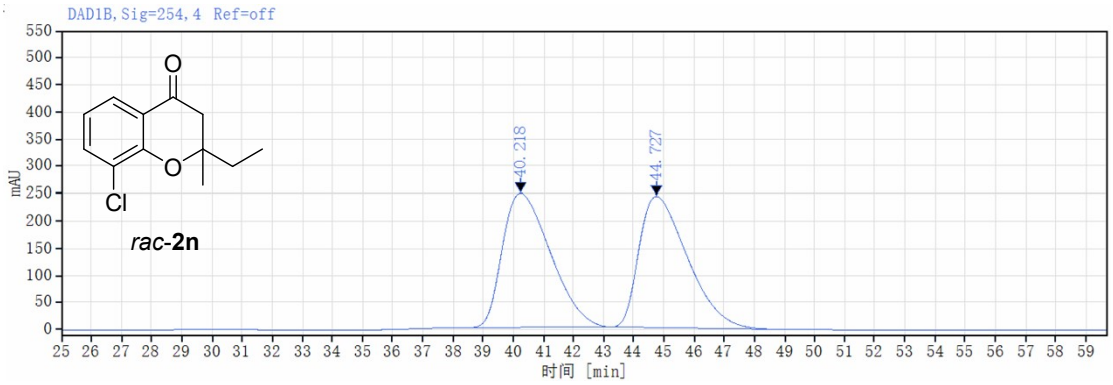
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
41.903	MM m	0.48	157.40	3.91	4.70
43.460	MM m	0.78	3190.53	62.43	95.30



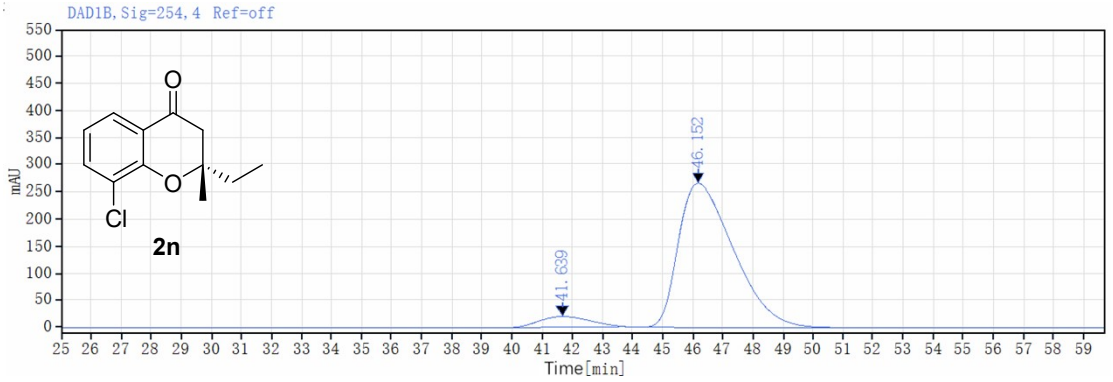
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
44.045	MM m	1.58	32350.14	269.38	50.00
49.620	MM m	1.59	32351.16	252.20	50.00



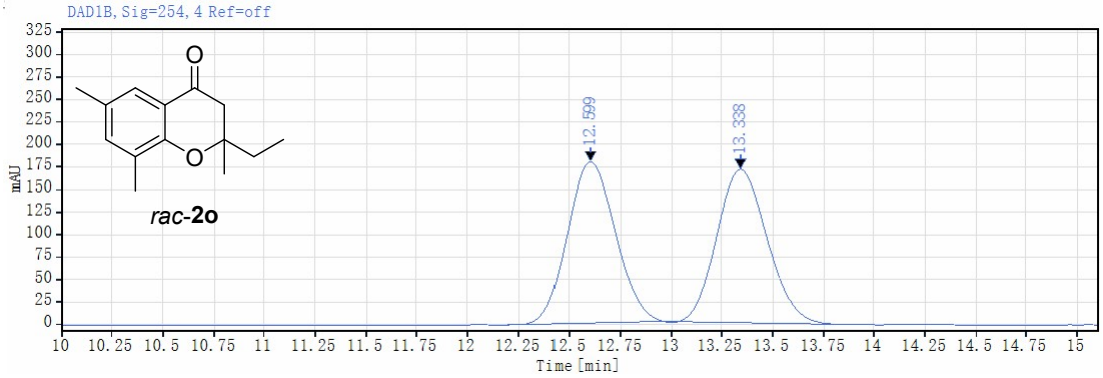
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
45.800	MM m	1.45	2661.59	21.55	6.96
51.567	MM m	1.69	35603.06	263.53	93.04



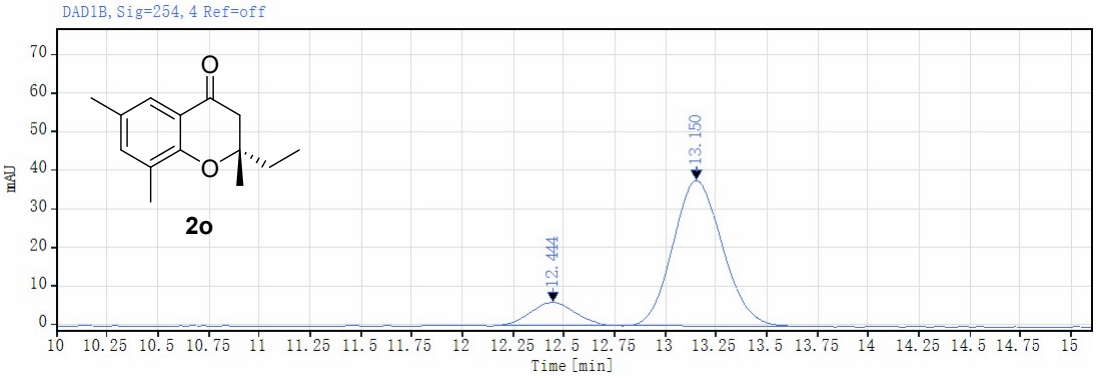
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
40.218	MM m	1.62	27291.46	246.80	50.29
44.727	MM m	1.61	26975.83	241.51	49.71



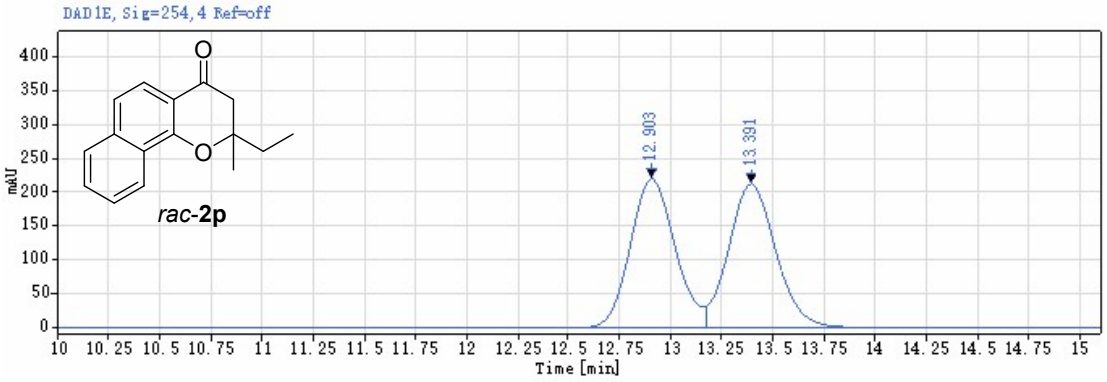
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
41.639	MM m	1.37	2261.32	19.57	6.26
46.152	MM m	1.69	33877.98	265.36	93.74



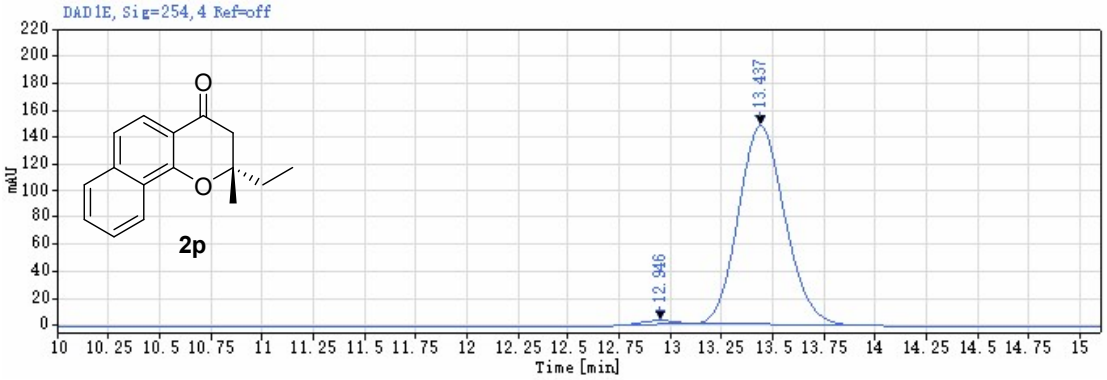
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
12.599	MM m	0.26	2937.26	179.27	49.93
13.338	MM m	0.27	2945.19	170.43	50.07



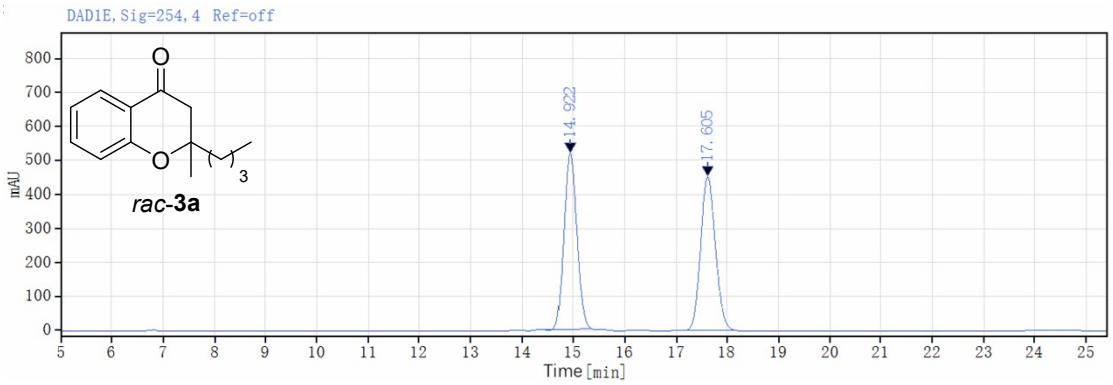
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
12.444	MM m	0.23	91.44	5.98	12.46
13.150	MM m	0.27	642.61	37.64	87.54



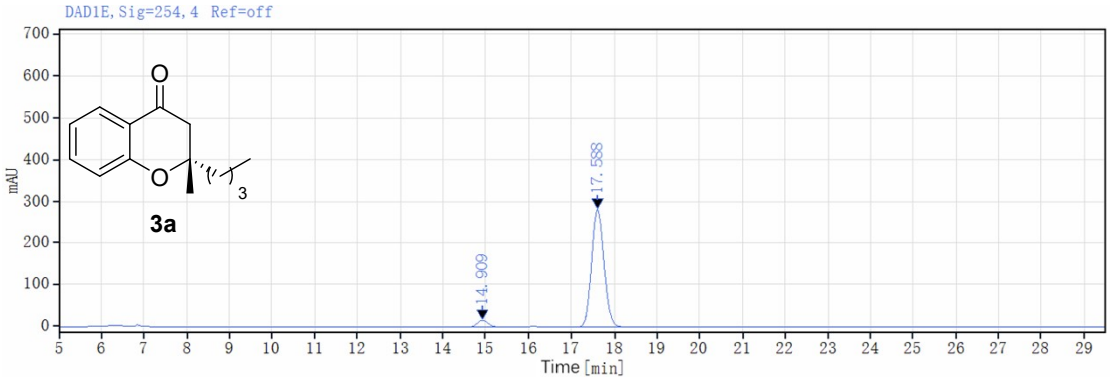
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
12.903	MM m	0.23	3343.98	220.54	49.64
13.391	MM m	0.25	3392.78	212.82	50.36



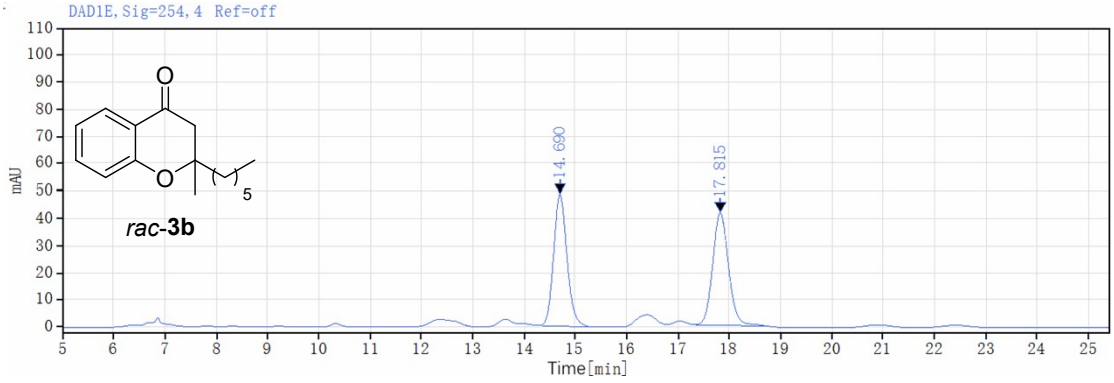
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
12.946	MM m	0.17	27.03	2.63	1.15
13.437	MM m	0.25	2329.52	147.70	98.85



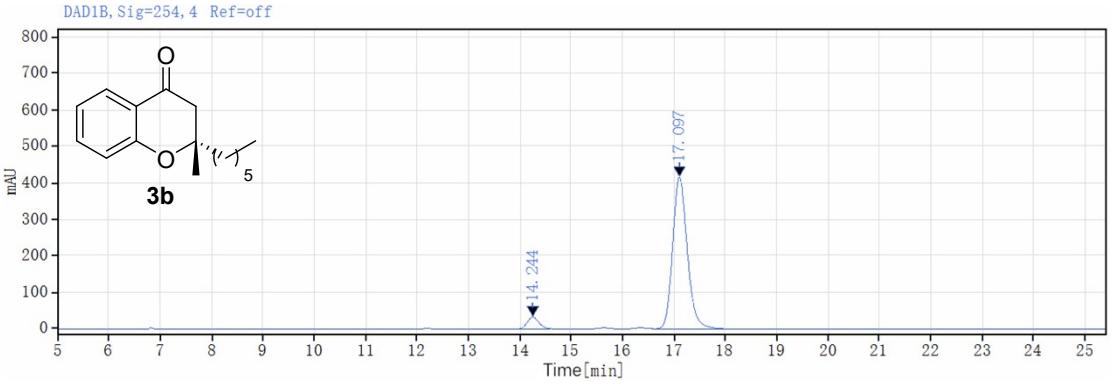
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
14.922	MM m	0.27	8923.64	517.21	49.45
17.605	MM m	0.32	9120.99	452.33	50.55



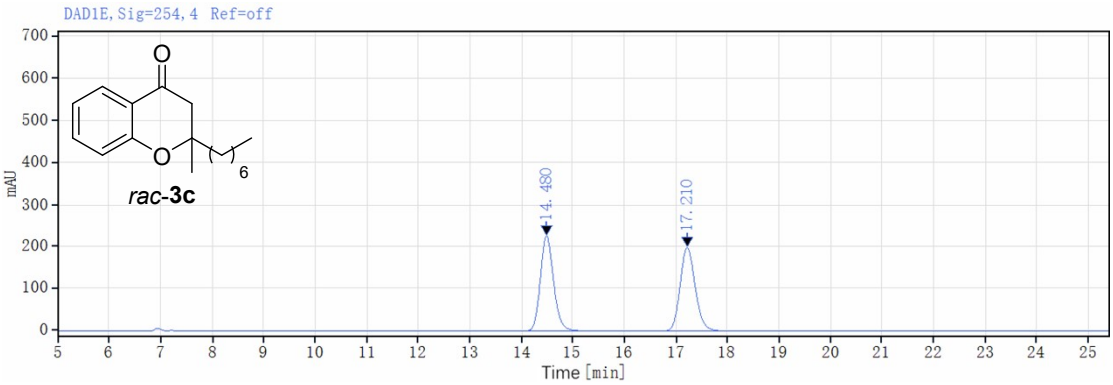
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
14.909	MM m	0.27	290.84	16.71	4.84
17.588	MM m	0.31	5719.18	282.18	95.16



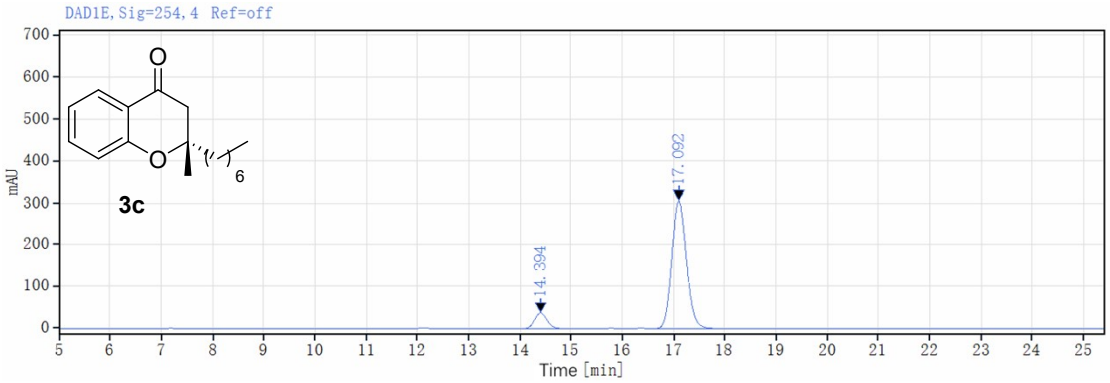
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
14.690	BB	1.09	880.42	48.48	49.83
17.815	MM m	0.33	886.28	41.41	50.17



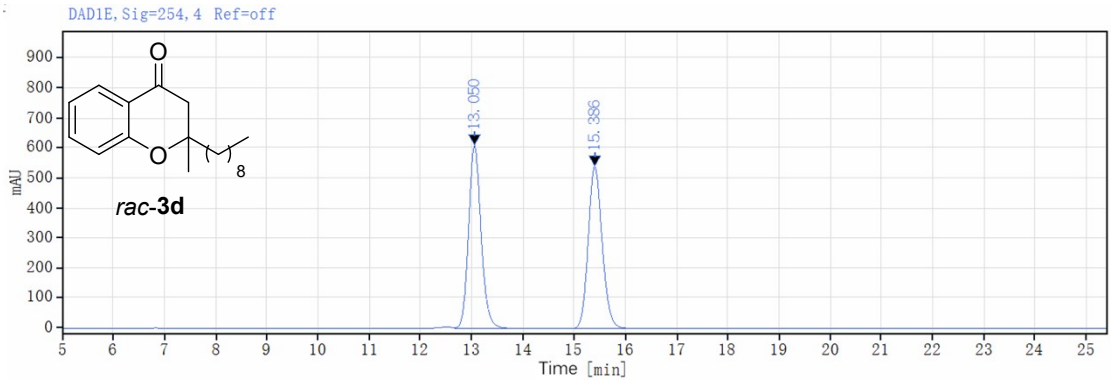
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
14.244	MM m	0.24	500.08	32.46	5.66
17.097	VM m	0.31	8334.43	416.67	94.34



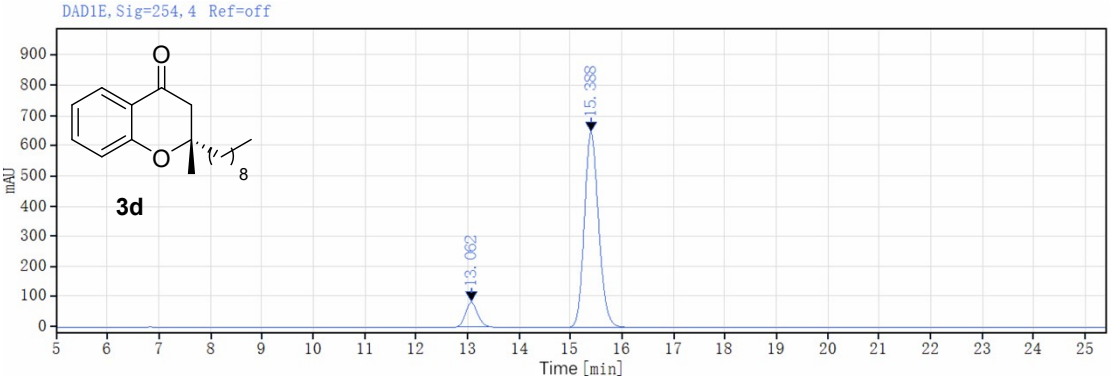
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
14.480	BB	1.59	4087.17	227.54	50.08
17.210	BB	1.79	4074.46	200.27	49.92



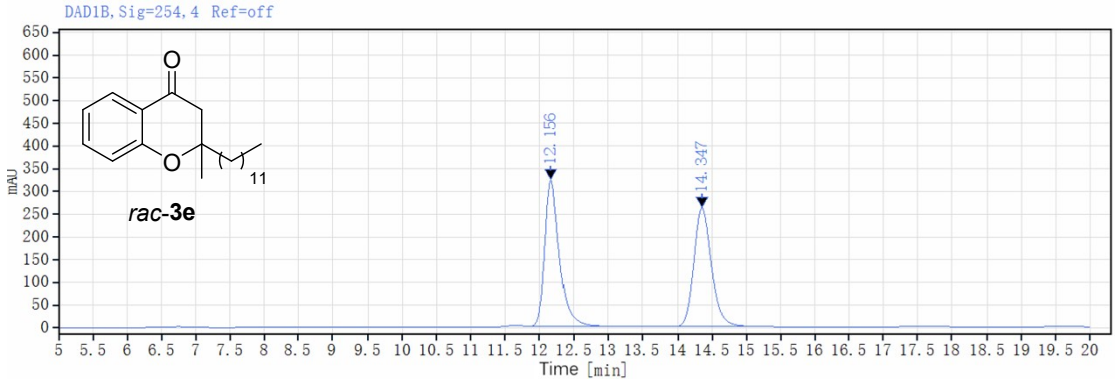
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
14.394	MM m	0.26	632.94	37.89	9.42
17.092	MM m	0.31	6087.11	306.34	90.58



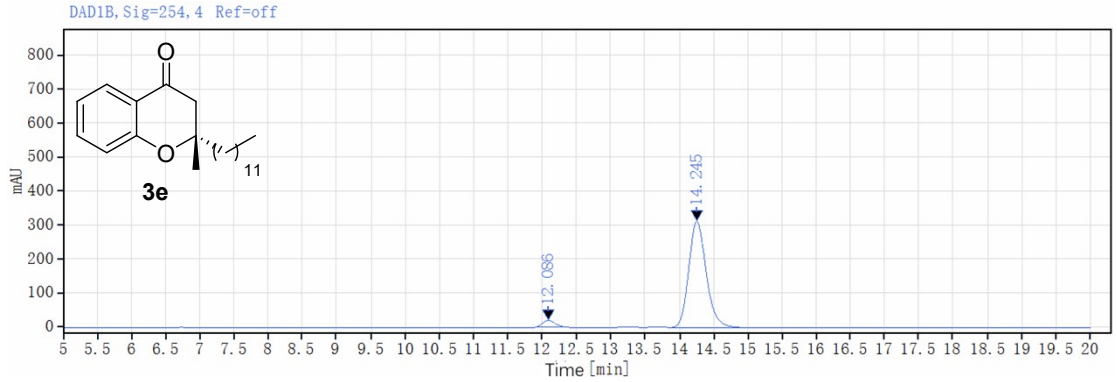
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
13.050	VB	1.36	10388.89	609.42	50.33
15.386	BB	1.54	10254.70	538.84	49.67



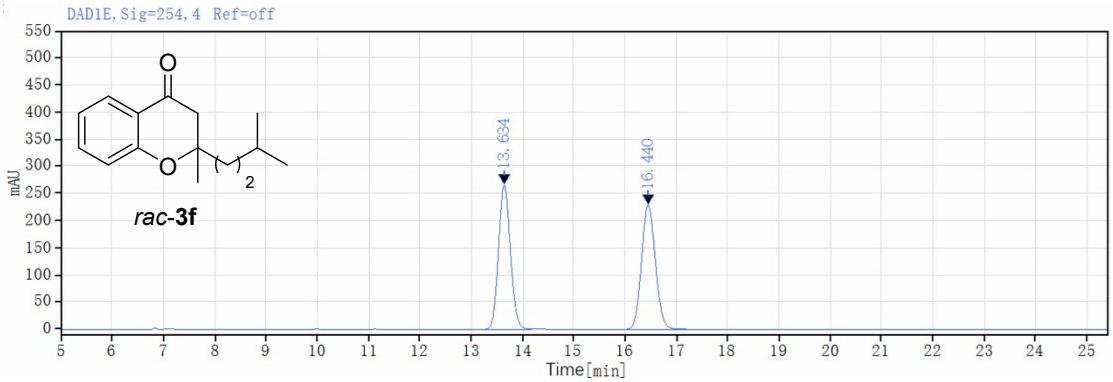
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
13.062	MM m	0.25	1332.49	81.62	9.66
15.388	VB	1.57	12458.32	645.47	90.34



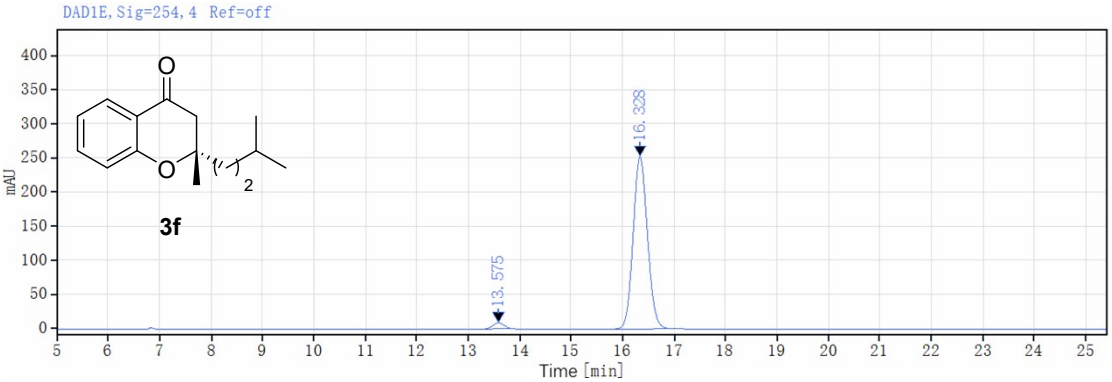
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
12.156	MM m	0.22	4694.84	321.72	50.50
14.347	MM m	0.27	4600.97	260.51	49.50



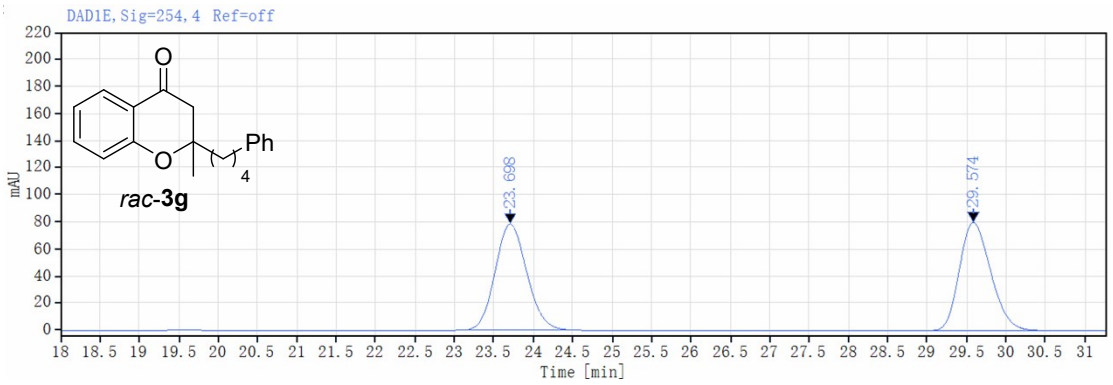
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
12.086	MM m	0.20	245.89	19.41	4.24
14.245	MM m	0.27	5553.94	312.95	95.76



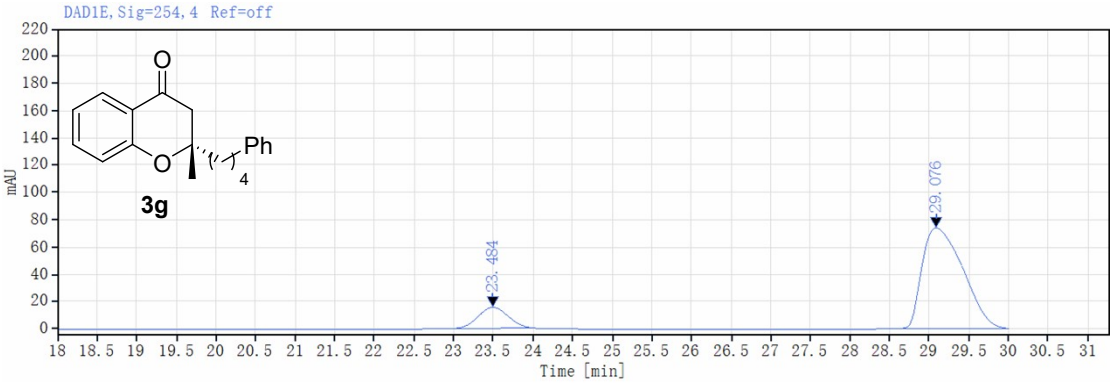
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
13.634	BV	1.04	4316.04	266.27	49.91
16.440	MM m	0.29	4331.19	229.39	50.09



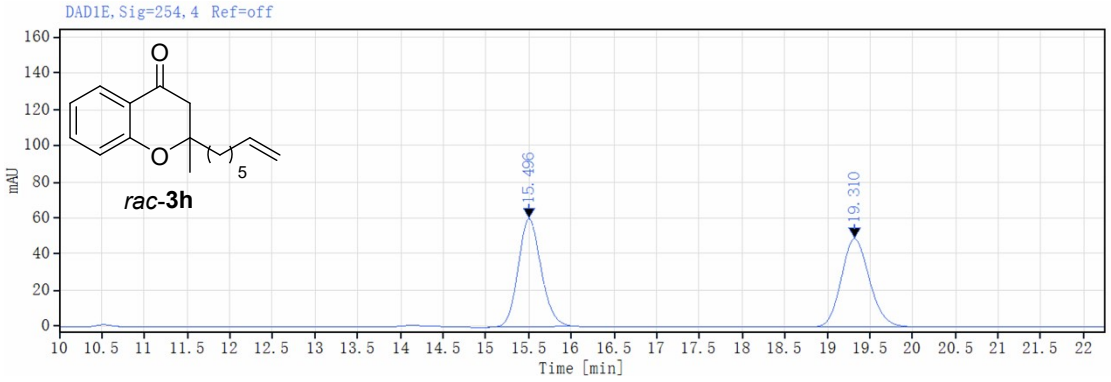
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
13.575	MM m	0.24	133.77	8.66	2.66
16.328	MM m	0.30	4898.89	253.02	97.34



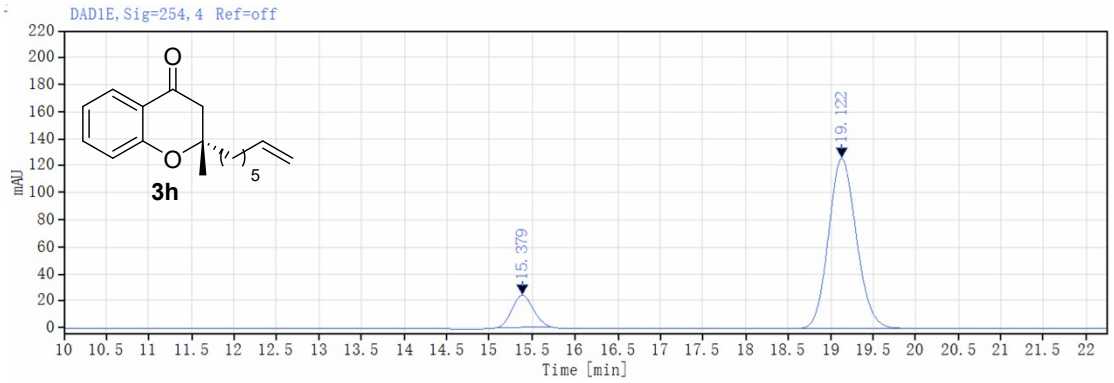
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
23.698	MM m	0.43	2201.37	78.61	50.00
29.574	MM m	0.43	2201.41	79.64	50.00



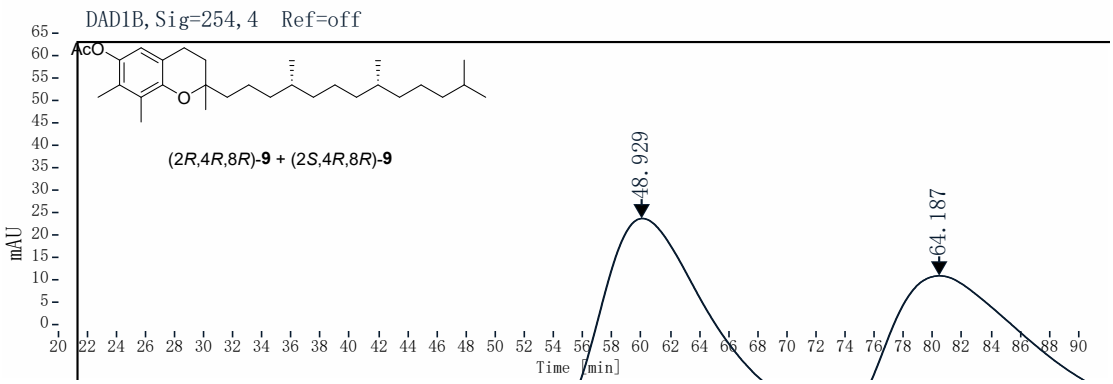
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
23.484	MM m	0.41	403.75	15.40	13.21
29.076	MM m	0.60	2653.49	73.92	86.79



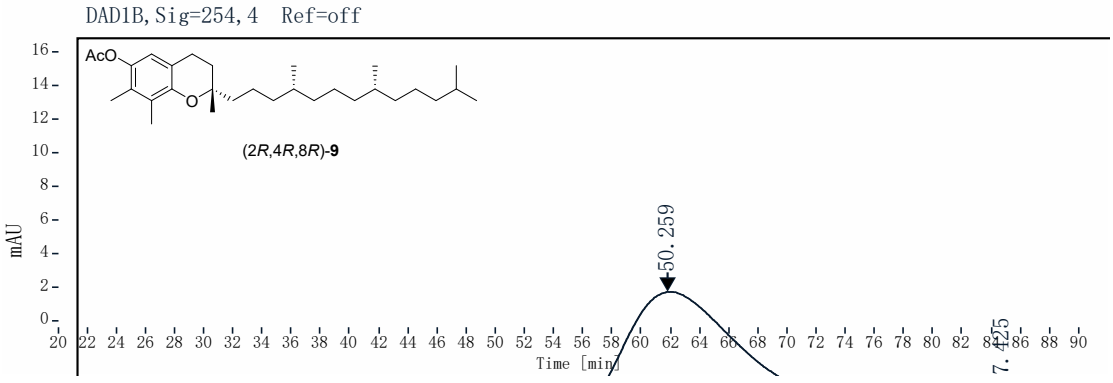
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
15.496	MM m	0.29	1119.39	59.84	50.11
19.310	MM m	0.35	1114.32	48.85	49.89



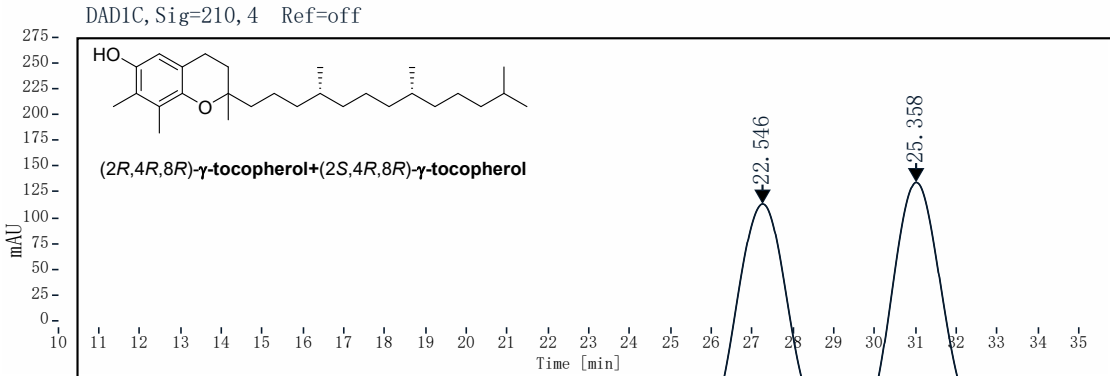
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
15.379	MM m	0.27	409.77	23.65	12.51
19.122	MM m	0.35	2866.45	125.95	87.49



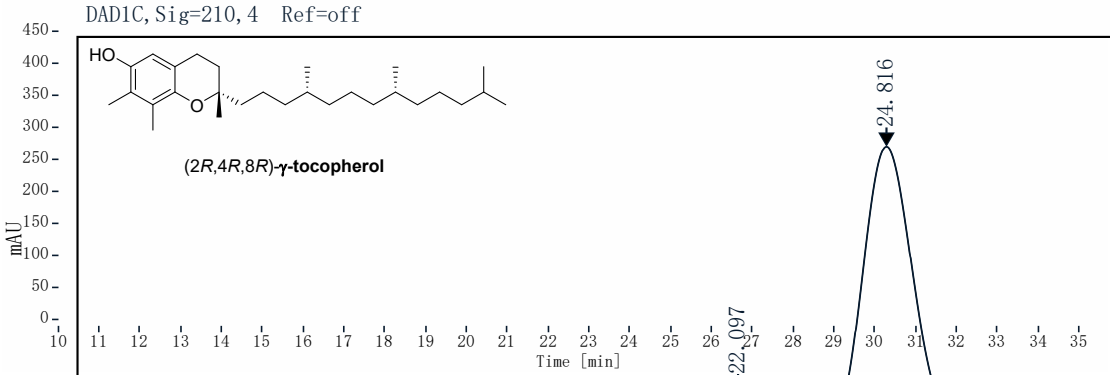
Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
48.929	MM m	4.87	15074.98	36.17	50.43
64.187	MM m	6.54	14816.17	26.47	49.57



Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
50.259	MM m	5.51	2829.21	6.00	89.09
67.425	MM m	5.37	346.60	0.75	10.91



Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
22.546	MM m	0.96	10521.12	164.88	49.04
25.358	MM m	0.95	10931.97	177.78	50.96



Ret Time [min]	Type	Width [min]	Area [mAU * s]	Height [mAU]	Area%
22.097	MM m	0.79	2562.89	43.70	11.15
24.816	MM m	0.98	20424.28	328.94	88.85