

Supporting Information

Iridium-Catalyzed Enantio- and Diastereoselective Allylation of Dioxindoles: A One-step Synthesis of 3-Allyl-3-hydroxyoxindoles

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1. General Experimental Details

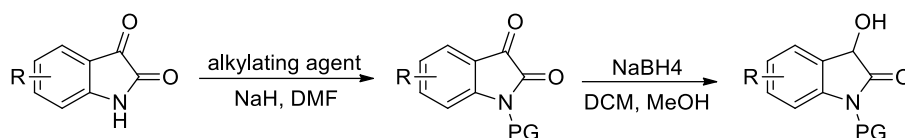
Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All solvents were purified and dried according to standard methods prior to use.

The NMR spectra were recorded on the Varian MERCURY plus-400 (400 MHz, ^1H ; 101 MHz, ^{13}C), Bruker AscendTM 400 (400 MHz, ^1H ; 101 MHz, ^{13}C) and Bruker AscendTM 500 (500 MHz, ^1H ; 126 MHz, ^{13}C) spectrometers with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane. ^{19}F NMR spectra were recorded on the Bruker AscendTM 400 (376 MHz, ^{19}F) and Bruker AscendTM 500 (470 MHz, ^{19}F), and referenced relative to PhCF_3 . Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). The ee values were determined by HPLC using the Daicel and Enantiocol chiral columns. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm.

2. Preparation of Starting Materials

Reagents were purchased from Sigma-Aldrich, TCI, or Alfa Aesar and used as received unless otherwise stated. **L1** was purchased from Daicel chiral reagents. **L2**,¹ allylic acetates,² and 3-hydroxyoxindoles³ were prepared according to literature procedures. The racemic samples were prepared by running reactions with a racemic catalyst.

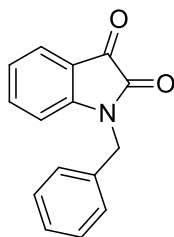
General Procedure for the Synthesis of Substituted 3-Hydroxyoxindoles:



A solution of the isatin (10 mmol) in 15 mL of dry DMF was slowly added to a suspension of sodium hydride (15 mmol, 1.5 eq) in 10 mL of dry DMF at 0 °C. The suspension was stirred for 15 min at 25 °C. Then 1.5 equivalent of the alkylating agent (1-naphthylmethyl bromide, 2-naphthylmethyl bromide, benzyl bromide, etc.) was added at 0 °C. The mixture was stirred for 1 h at room temperature and water was added until precipitation of the N-protected isatin. Crystallization from hexane/ethyl acetate afforded the pure product.

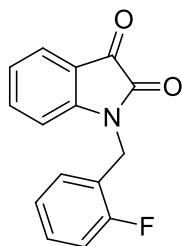
Sodium borohydride (7.5 mmol, 1.5 eq) was added in small portions to a stirred suspension of the pure N-protected isatin (5 mmol) in 30 mL of a 1:1 dichloromethane/ethanol mixture at 0 °C. The mixture was vigorously stirred at 0 °C until the suspension became colorless (about 10 min). Then water (5 mL) was added and the reaction mixture was stirred until bubbling stop. The mixture was extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried (MgSO₄) and the solvent evaporated under reduced pressure below 30 °C. The residue was purified by chromatography on silica gel quickly using a 1:1 mixture of hexane/diethyl ether, or crystallized by ethyl acetate/hexane to separate the 3-hydroxy-2-oxindole derivative from the pigments formed during the extraction and evaporation procedures. The isatin reductions generally proceed smoothly providing the corresponding dioxindoles in good overall yield after chromatography or crystallization.

1-Benzylindoline-2,3-dione



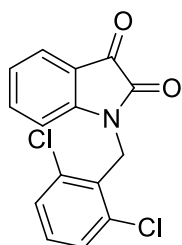
Orange solid (1.99 g, 84% yield). m.p. = 127 – 129 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.39 – 7.24 (m, 5H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.93 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 183.3, 158.3, 150.7, 138.3, 134.5, 129.1, 128.2, 127.4, 125.4, 123.9, 117.7, 111.0, 44.1. HRMS (Q-TOF Premier) calcd for C₁₅H₁₂NO₂ (M+H)⁺: 238.0863; found: 238.0870.

1-(2-Fluorobenzyl)indoline-2,3-dione



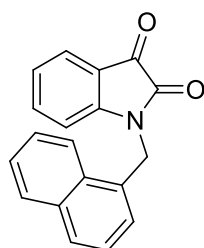
Orange solid (1.91 g, 75% yield). m.p. = 153 – 155 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 6.8 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.39 – 7.27 (m, 2H), 7.14 – 7.08 (m, 3H), 6.90 (d, J = 7.8 Hz, 1H), 4.99 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 183.0, 160.6(d, J = 247.5 Hz), 158.4, 150.4, 138.5, 130.1 (d, J = 8.1 Hz), 129.9(d, J = 3.0 Hz), 125.4, 124.8(d, J = 3.0 Hz), 124.0, 121.7(d, J = 14.1 Hz), 117.7, 115.7(d, J = 31.3 Hz), 110.7(d, J = 3.0 Hz), 37.3(d, J = 5.1 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -118.1. HRMS (Q–TOF Premier) calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_2\text{F}$ ($\text{M}+\text{H}$) $^+$: 256.0774; found: 256.0776.

1-(2,6-Dichlorobenzyl)indoline-2,3-dione



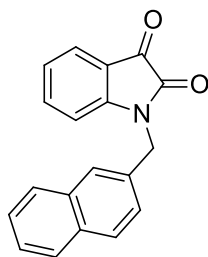
Orange solid (2.41 g, 79% yield). m.p. = 180 – 182 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 7.4 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.26 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 182.9, 157.8, 150.5, 138.4, 136.3, 130.3, 129.1, 125.4, 123.7, 117.9, 111.2, 100.0, 40.2. HRMS (Q–TOF Premier) calcd for $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 306.0083; found: 306.0088.

1-(Naphthalen-1-ylmethyl)indoline-2,3-dione



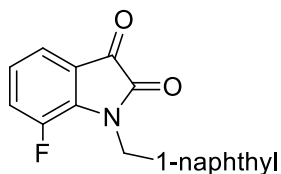
Orange solid (2.35 g, 82% yield). m.p. = 191 – 193 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.82 (dd, J = 7.0 Hz, 1.6Hz, 1H), 7.63 – 7.51 (m, 3H), 7.43 – 7.36 (m, 3H), 7.06 (t, J = 7.6 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 5.39 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 183.1, 158.4, 151.1, 138.4, 133.9, 130.9, 129.3, 129.1, 128.9, 126.9, 126.3, 125.4, 125.2, 125.0, 123.9, 122.7, 117.8, 111.5, 42.4. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{14}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 288.1019; found: 288.1021.

1-(Naphthalen-2-ylmethyl)indoline-2,3-dione



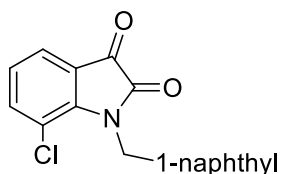
Orange solid (2.30 g, 80% yield). m.p. = 155 – 157 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.78 (m, 4H), 7.60 (d, J = 7.4 Hz, 1H), 7.52 – 7.37 (m, 4H), 7.06 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 5.07 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 183.3, 158.4, 150.7, 138.4, 133.3, 133.0, 131.9, 129.1, 127.8, 127.8, 126.6, 126.4, 126.4, 125.4, 125.0, 123.9, 117.7, 111.1, 44.3. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{14}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 288.1019; found: 288.1016.

7-Fluoro-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



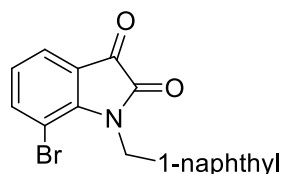
Orange solid (2.29 g, 75% yield). m.p. = 140 – 142 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.48 (d, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.20 (dd, J = 10.8, 8.4 Hz, 1H), 7.06 (td, J = 7.8, 3.8 Hz, 1H), 5.55 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 182.2 (d, J = 3.4 Hz), 158.2, 148.0 (d, J = 250.0 Hz), 137.0 (d, J = 9.1 Hz), 133.8, 130.6, 130.5, 129.0, 128.4, 126.8, 126.7 (d, J = 19.8 Hz), 126.6, 125.3, 124.9 (d, J = 5.8 Hz), 122.9 (d, J = 2.0 Hz), 122.6, 121.5 (d, J = 3.3 Hz), 120.4 (d, J = 2.5 Hz), 43.6 (d, J = 4.7 Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -131.5. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{13}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 306.0925; found: 306.0923.

7-Chloro-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



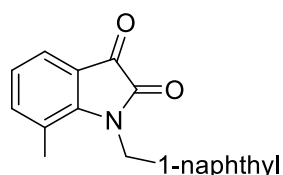
Orange solid (2.44 g, 76% yield). m.p. = 150 – 152 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.69 (dd, J = 7.4, 1.2 Hz, 1H), 7.66 – 7.49 (m, 3H), 7.37 (t, J = 7.8 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 7.03 (dd, J = 8.0, 7.6 Hz, 1H), 5.87 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 182.3, 158.9, 147.9, 144.2, 133.8, 131.1, 130.0, 129.0, 128.0, 126.6, 126.1, 125.4, 125.3, 124.8, 122.2, 121.5, 120.8, 104.8, 42.9. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{13}\text{ClNO}_2$ ($\text{M}+\text{H}$) $^+$: 322.0629; found: 322.0632.

7-Bromo-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



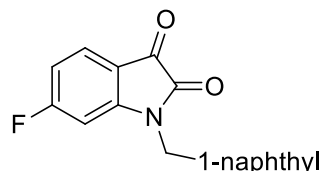
Orange solid (2.81 g, 77% yield). m.p. = 123 – 125 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.65 (dd, J = 7.2, 1.2 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.45 (dd, J = 8.2, 1.2 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.20 – 7.03 (m, 2H), 5.83 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 182.3, 158.8, 146.4, 140.8, 133.8, 131.1, 130.1, 129.0, 128.0, 126.6, 126.1, 125.4, 125.0, 124.3, 122.2, 121.4, 120.4, 117.9, 43.2. HRMS (Q-TOF Premier) calcd for $\text{C}_{19}\text{H}_{13}\text{BrNO}_2$ ($\text{M}+\text{H}$) $^+$: 366.0124; found: 366.0120.

7-Methyl-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



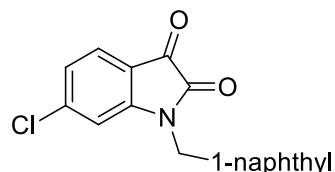
Orange solid (2.47 g, 82% yield). m.p. = 94 – 96 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.70 – 7.48 (m, 3H), 7.38 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 4.8 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 5.63 (s, 2H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 183.6, 159.5, 148.6, 142.6, 133.9, 130.9, 129.9, 129.1, 128.2, 126.8, 126.2, 125.5, 124.1, 123.7, 122.2, 122.0, 121.7, 118.9, 43.4, 17.9. HRMS (Q-TOF Premier) calcd for $\text{C}_{20}\text{H}_{16}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 302.1176; found: 302.1180.

6-Fluoro-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



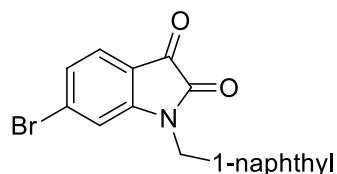
Orange solid (2.35 g, 77% yield). m.p. = 146 – 148 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 8.2, 5.6 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.47 – 7.37 (m, 2H), 6.73 (td, J = 8.8, 2.2 Hz, 1H), 6.47 (dd, J = 8.8, 2.2 Hz, 1H), 5.39 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 180.9, 169.0 (d, J = 261.7 Hz), 158.6, 153.7 (d, J = 12.6 Hz), 134.0, 130.9, 129.2, 129.1, 128.9, 128.2, 128.1, 127.1, 126.4, 125.3, 122.7, 114.3 (d, J = 2.5 Hz), 110.9 (d, J = 22.7 Hz), 100.4 (d, J = 27.7 Hz), 42.7. ^{19}F NMR (471 MHz, CDCl_3) δ -92.7. HRMS (Q-TOF Premier) calcd for $\text{C}_{19}\text{H}_{13}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 306.0925; found: 306.0927.

6-Chloro-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



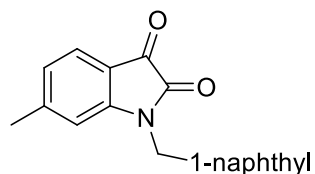
Orange solid (2.50 g, 78% yield). m.p. = 158 – 160 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.44 – 7.37 (t, 10Hz, 1H), 7.35 (d, J = 7.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.73 (s, 1H), 5.34 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 181.6, 158.3, 152.0, 144.8, 133.8, 130.8, 129.2, 129.1, 128.8, 127.1, 126.4, 126.3, 125.3, 124.9, 124.2, 122.7, 116.1, 112.2, 42.6. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{13}\text{ClNO}_2$ ($\text{M}+\text{H}$) $^+$: 322.0629; found: 322.0628.

6-Bromo-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



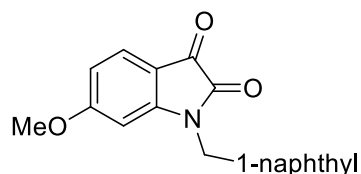
Orange solid (2.92 g, 80% yield). m.p. = 156 – 158 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.4 Hz, 1H), 7.87 (dd, J = 26.0, 8.2 Hz, 2H), 7.57 (ddd, J = 15.0, 14.0, 6.8 Hz, 2H), 7.43 (dd, J = 13.8, 8.0 Hz, 2H), 7.35 (d, J = 7.0 Hz, 1H), 7.21 (dd, J = 8.0, 1.4 Hz, 1H), 6.92 (d, J = 1.0 Hz, 1H), 5.37 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 181.8, 158.2, 151.8, 134.0, 133.6, 130.8, 129.2, 129.1, 128.7, 127.2, 127.0, 126.4, 126.3, 125.3, 124.9, 122.6, 116.5, 115.0, 42.6. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{13}\text{BrNO}_2$ ($\text{M}+\text{H}$) $^+$: 366.0124; found: 366.0117.

6-Methyl-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



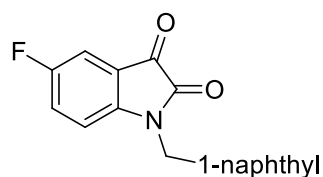
Orange solid (2.47 g, 82% yield). m.p. = 168 – 170 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.0 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.54 (s, 1H), 5.38 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 182.4, 159.1, 151.5, 150.9, 133.9, 130.8, 129.4, 129.1, 128.8, 126.9, 126.2, 125.4, 125.3, 124.7, 124.5, 122.7, 115.7, 112.1, 42.2, 22.9. HRMS (Q–TOF Premier) calcd for $\text{C}_{20}\text{H}_{16}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 302.1176; found: 302.1178.

6-Methoxy-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



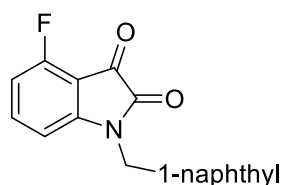
Orange solid (2.63 g, 83% yield). m.p. = 136 – 138 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.44 – 7.35 (m, 2H), 6.49 (dd, J = 8.6, 2.2 Hz, 1H), 6.23 (d, J = 2.2 Hz, 1H), 5.36 (s, 2H), 3.71 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 180.4, 168.2, 159.8, 153.7, 133.9, 130.9, 129.6, 129.1, 128.9, 127.9, 126.9, 126.3, 125.2, 125.1, 122.7, 111.4, 108.3, 98.5, 56.0, 42.3. HRMS (Q–TOF Premier) calcd for $\text{C}_{20}\text{H}_{16}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 318.1125; found: 318.1129.

5-Fluoro-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



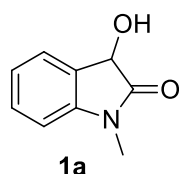
Orange solid (2.44 g, 80% yield). m.p. = 150 – 152 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.44 – 7.36 (m, 2H), 7.31 (dd, J = 6.4, 2.8 Hz, 1H), 7.11 (td, J = 8.6, 2.8 Hz, 1H), 6.70 (dd, J = 8.8, 3.6 Hz, 1H), 5.39 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 182.5, 159.3 (d, J = 246.7 Hz), 158.2 (d, J = 1.3 Hz), 147.1, 134.0, 130.9, 129.1 (d, J = 1.3 Hz), 129.0, 127.1, 126.4, 125.2, 125.1, 124.8, 124.6, 122.7, 118.4 (d, J = 7.6 Hz), 112.7 (d, J = 7.6 Hz), 112.4 (d, J = 25.2 Hz), 42.6. ^{19}F NMR (471 MHz, CDCl_3) δ -117.8. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{13}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 306.0925; found: 306.0927.

4-Fluoro-1-(naphthalen-1-ylmethyl)indoline-2,3-dione



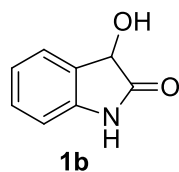
Orange solid (2.47 g, 81% yield). m.p. = 136 – 138 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.45 – 7.34 (m, 3H), 6.71 (t, J = 8.4 Hz, 1H), 6.54 (d, J = 7.8 Hz, 1H), 5.39 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 178.7, 158.8 (d, J = 268.6 Hz), 157.8, 151.4 (d, J = 6.3 Hz), 140.6 (d, J = 10.1 Hz), 133.93, 130.81, 129.12, 129.08, 129.02, 127.04, 126.34, 125.2, 125.0, 122.62, 111.9 (d, J = 20.2 Hz), 107.6 (d, J = 3.8 Hz), 106.0 (d, J = 18.9 Hz), 42.82. ^{19}F NMR (471 MHz, CDCl_3) δ -105.9. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{13}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 306.0925; found: 306.0922.

3-Hydroxy-1-methylindolin-2-one



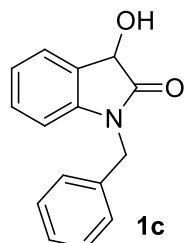
White solid (0.60 g, 73% yield). m.p. = 151 – 153 °C. ^1H NMR (400 MHz, DMSO) δ 7.37 – 7.27 (m, 2H), 7.07 – 7.01 (m, 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.24 (d, J = 7.4 Hz, 1H), 4.90 (d, J = 7.4 Hz, 1H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 176.5, 144.1, 129.5, 129.0, 124.9, 122.6, 108.8, 69.2, 26.2. HRMS (Q–TOF Premier) calcd for $\text{C}_9\text{H}_9\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 186.0531; found: 186.0525.

3-Hydroxyindolin-2-one



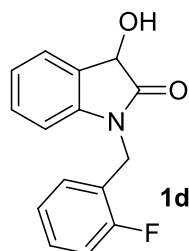
White solid (0.55 g, 74% yield). m.p. = 166 – 168 °C. ^1H NMR (400 MHz, DMSO) δ 10.22 (s, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 6.96 (td, J = 7.6, 0.8 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.15 (d, J = 7.6 Hz, 1H), 4.83 (d, J = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 178.4, 142.6, 129.8, 129.4, 125.2, 121.9, 109.9, 69.6. HRMS (Q–TOF Premier) calcd for $\text{C}_8\text{H}_8\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 150.0550; found: 150.0547.

1-Benzyl-3-hydroxyindolin-2-one



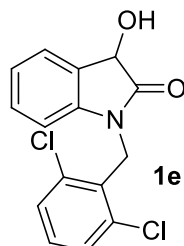
White solid (0.85 g, 71% yield). m.p. = 138 – 140 °C. ^1H NMR (500 MHz, DMSO) δ 7.38 – 7.30 (m, 5H), 7.26 (ddd, J = 10.8, 5.6, 2.8 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.52 – 6.24 (s, 1H), 5.05 (s, 1H), 4.85 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 176.7, 143.1, 136.8, 129.4, 129.1, 129.0, 127.8, 127.7, 125.1, 122.8, 109.5, 69.3, 42.9. HRMS (Q–TOF Premier) calcd for $\text{C}_{15}\text{H}_{13}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 262.0838; found: 262.0840.

1-(2-Fluorobenzyl)-3-hydroxyindolin-2-one



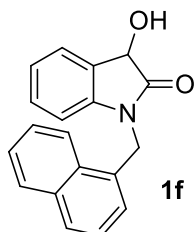
White solid (0.86 g, 67% yield). m.p. = 96 – 98 °C. ^1H NMR (400 MHz, DMSO) δ 7.38 – 7.31 (m, 2H), 7.30 – 7.19 (m, 3H), 7.14 (td, J = 7.4, 1.2 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 5.05 (d, J = 7.8 Hz, 1H), 4.93 (d, J = 16.2 Hz, 1H), 4.86 (d, J = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 176.65, 160.6 (d, J = 245.4 Hz), 142.93, 130.0 (d, J = 8.1 Hz), 129.6 (d, J = 4.0 Hz), 129.5, 129.1, 125.2, 125.1 (d, J = 3.0 Hz), 123.4 (d, J = 15.2 Hz), 122.86, 115.9 (d, J = 21.2 Hz), 109.1, 69.2, 37.1 (d, J = 5.1 Hz). ^{19}F NMR (376 MHz, DMSO) δ -117.8. HRMS (Q–TOF Premier) calcd for $\text{C}_{15}\text{H}_{12}\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 280.0744; found: 280.0751.

1-(2,6-Dichlorobenzyl)-3-hydroxyindolin-2-one



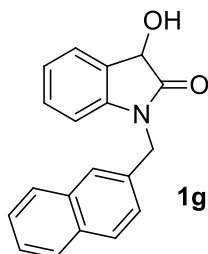
Light pink solid (1.04 g, 68% yield). m.p. = 150 – 152 °C. ^1H NMR (400 MHz, DMSO) δ 7.52 – 7.44 (m, 2H), 7.38 (dd, J = 8.6, 7.6 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.35 (d, J = 6.6 Hz, 1H), 5.14 (d, J = 15.2 Hz, 1H), 5.00 (d, J = 15.2 Hz, 1H), 4.96 (d, J = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 176.2, 142.9, 135.9, 131.0, 130.8, 129.5, 129.4, 129.1, 125.2, 122.7, 109.0, 68.8, 40.2. HRMS (Q–TOF Premier) calcd for $\text{C}_{15}\text{H}_{11}\text{Cl}_2\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 330.0059; found: 330.0057.

3-Hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one



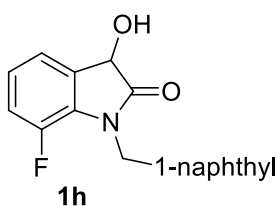
White solid (1.01 g, 70% yield). m.p. = 156 – 158 °C. ^1H NMR (500 MHz, DMSO) δ 8.25 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.60 (dt, J = 14.6, 7.0 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.31 (d, J = 6.8 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 5.39 (d, J = 16.6 Hz, 1H), 5.29 (d, J = 16.6 Hz, 1H), 5.14 (d, J = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 176.9, 143.4, 133.9, 131.5, 131.1, 129.5, 129.2, 129.1, 128.3, 126.9, 126.5, 125.8, 125.1, 124.4, 123.7, 122.8, 109.7, 69.3, 41.3. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 290.1181; found: 290.1178.

3-Hydroxy-1-(naphthalen-2-ylmethyl)indolin-2-one



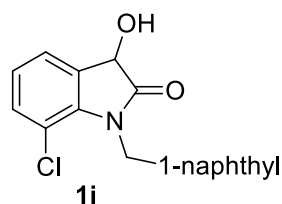
White solid (0.98 g, 68% yield). m.p. = 142 – 144 °C. ^1H NMR (400 MHz, DMSO) δ 7.93 – 7.82 (m, 4H), 7.55 – 7.44 (m, 3H), 7.38 (d, J = 7.2 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.01 (td, J = 7.7, 0.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 5.10 (d, J = 7.8 Hz, 1H), 5.04 (d, J = 16.4 Hz, 1H), 5.00 (d, J = 16.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 176.8, 143.2, 134.4, 133.3, 132.8, 129.4, 129.2, 128.8, 128.1, 128.0, 126.8, 126.5, 126.3, 125.9, 125.1, 122.8, 109.5, 69.3, 43.2. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{15}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 312.0995; found: 312.0996.

7-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one



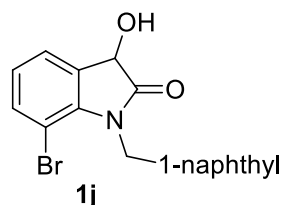
White solid (0.98 g, 64% yield). m.p. = 153 – 155 °C. ^1H NMR (400 MHz, DMSO) δ 8.18 (d, J = 8.2 Hz, 1H), 8.03 – 7.97 (m, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.44 – 7.37 (m, 1H), 7.33 – 7.28 (m, 1H), 7.16 (d, J = 6.8 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.61 (d, J = 7.8 Hz, 1H), 5.47 (d, J = 17.4 Hz, 1H), 5.41 (d, J = 17.4 Hz, 1H), 5.26 (d, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 176.7, 147.1 (d, J = 243.4 Hz), 133.7, 132.5, 132.4 (d, J = 3.0 Hz), 130.5, 129.7 (d, J = 8.1 Hz), 129.1, 127.9, 126.9, 126.5, 125.9, 124.0 (d, J = 7.1 Hz), 123.3, 122.1, 121.5 (d, J = 3.0 Hz), 117.4 (d, J = 19.3 Hz), 69.4 (d, J = 3.0 Hz), 42.7 (d, J = 5.1 Hz). ^{19}F NMR (376 MHz, DMSO) δ -136.4. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{14}\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 330.0901; found: 330.0905.

7-Chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one



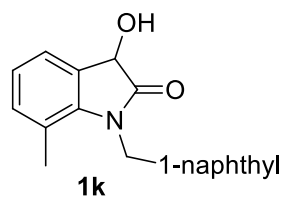
White solid (0.98 g, 65% yield). m.p. = 114 – 116 °C. ^1H NMR (400 MHz, DMSO) δ 8.17 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.47 (dt, J = 7.2, 1.2 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.08 – 7.01 (m, 2H), 6.59 (d, J = 7.8 Hz, 1H), 5.70 (d, J = 17.8 Hz, 1H), 5.64 (d, J = 17.8 Hz, 1H), 5.24 (d, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 177.5, 140.5, 134.9, 133.8, 133.1, 133.0, 130.2, 129.1, 127.7, 127.0, 126.5, 125.9, 124.8, 124.7, 123.2, 121.9, 102.1, 68.9, 42.6. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{15}\text{ClNO}_2$ ($\text{M}+\text{H}$) $^+$: 324.0786; found: 324.0788.

7-Bromo-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one



White solid (1.23 g, 67% yield). m.p. = 149 – 151 °C. ^1H NMR (400 MHz, DMSO) δ 8.18 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.44 (dt, J = 7.3, 1.0 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H), 7.23 (d, J = 8.2 Hz, 1H), 7.16 – 7.05 (m, 2H), 6.60 (d, J = 7.8 Hz, 1H), 5.67 (d, J = 17.8 Hz, 1H), 5.62 (d, J = 17.8 Hz, 1H), 5.25 (d, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 177.3, 139.1, 133.7, 133.2, 132.6, 131.5, 130.2, 129.1, 127.7, 126.9, 126.5, 125.9, 124.4, 124.3, 123.2, 121.8, 114.7, 68.9, 42.7. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{15}\text{BrNO}_2$ ($\text{M}+\text{H}$) $^+$: 368.0281; found: 368.0285.

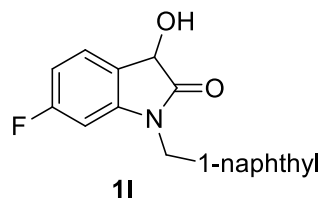
3-Hydroxy-7-methyl-1-(naphthalen-1-ylmethyl)indolin-2-one



White solid (1.06 g, 70% yield). m.p. = 120 – 122 °C. ^1H NMR (400 MHz, DMSO) δ 8.19 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.46 – 7.36 (m, 1H),

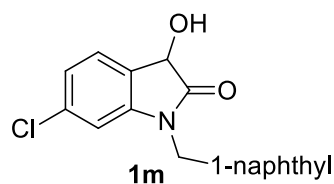
7.36 – 7.26 (m, 1H), 7.10 (d, $J = 6.8$ Hz, 1H), 7.06 – 6.92 (m, 2H), 6.45 (d, $J = 7.6$ Hz, 1H), 5.56 (d, $J = 18.8$ Hz, 1H), 5.51 (d, $J = 18.8$ Hz, 1H), 5.15 (d, $J = 7.6$ Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 177.7, 141.1, 133.8, 133.4, 133.1, 130.1, 130.0, 129.2, 127.9, 127.1, 126.1, 126.0, 123.2, 123.2, 122.4, 122.4, 119.9, 68.9, 42.6, 17.8. HRMS (Q–TOF Premier) calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 304.1332; found: 304.1337.

6-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one



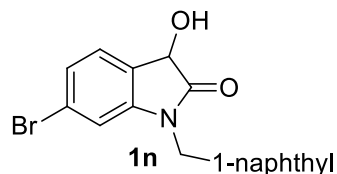
White solid (1.00 g, 65% yield). m.p. = 166 – 168 °C. ^1H NMR (400 MHz, DMSO) δ 8.22 (d, $J = 7.8$ Hz, 1H), 7.98 (d, $J = 7.6$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.65 – 7.56 (m, 2H), 7.46 – 7.39 (m, 2H), 7.31 (d, $J = 6.8$ Hz, 1H), 6.83 (t, $J = 8.8$ Hz, 1H), 6.74 (d, $J = 9.4$ Hz, 1H), 6.47 (d, $J = 7.6$ Hz, 1H), 5.40 (d, $J = 16.6$ Hz, 1H), 5.31 (d, $J = 16.6$ Hz, 1H), 5.12 (d, $J = 7.2$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 177.2, 163.2 (d, $J = 243.4$ Hz), 145.3 (d, $J = 12.1$ Hz), 133.9, 131.3, 131.0, 129.1, 128.4, 126.9, 126.7, 126.6, 125.8, 125.1 (d, $J = 3.0$ Hz), 124.3, 123.8, 108.7 (d, $J = 22.2$ Hz), 98.4 (d, $J = 18.2$ Hz), 68.8, 41.5. ^{19}F NMR (471 MHz, DMSO) δ -111.5. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{14}\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 330.0901; found: 330.0903.

6-Chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one



White solid (1.08 g, 67% yield). m.p. = 106 – 108 °C. ^1H NMR (400 MHz, DMSO) δ 8.22 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 7.68 – 7.56 (m, 2H), 7.46 – 7.40 (m, 2H), 7.28 (d, $J = 6.8$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.92 (s, 1H), 6.54 (d, $J = 7.6$ Hz, 1H), 5.42 (d, $J = 16.8$ Hz, 1H), 5.33 (d, $J = 16.8$ Hz, 1H), 5.16 (d, $J = 7.4$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 176.9, 145.0, 133.9, 133.9, 131.2, 131.0, 129.1, 128.4, 128.1, 126.9, 126.6, 126.6, 125.8, 124.0, 123.8, 122.5, 110.0, 68.9, 41.4. HRMS (Q–TOF Premier) calcd for $\text{C}_{19}\text{H}_{15}\text{ClNO}_2$ ($\text{M}+\text{H}$) $^+$: 324.0786; found: 324.0781.

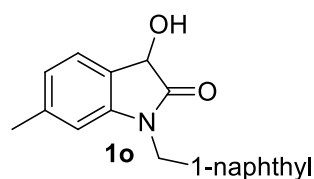
6-Bromo-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one



White solid (1.25 g, 68% yield). m.p. = 160 – 162 °C. ^1H NMR (400 MHz, DMSO) δ 8.21 (d, $J = 8.2$ Hz, 1H), 7.99 (d, $J = 8.8$ Hz, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 7.68 – 7.54 (m, 2H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 1H), 7.32 – 7.17 (m, 2H), 7.05 (d, $J = 1.6$ Hz, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 5.42 (d, $J = 16.8$ Hz, 1H), 5.33 (d, $J = 16.8$ Hz, 1H), 5.14 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 176.8, 145.1, 133.8, 131.2, 131.0, 129.1, 128.6, 128.3, 126.9, 126.6, 125.8, 125.4, 123.9,

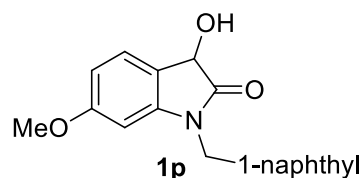
123.9, 123.8, 122.1, 112.7, 68.9, 41.3. HRMS (Q-TOF Premier) calcd for C₁₉H₁₅BrNO₂ (M+H)⁺: 368.0281; found: 368.0287.

3-Hydroxy-6-methyl-1-(naphthalen-1-ylmethyl)indolin-2-one



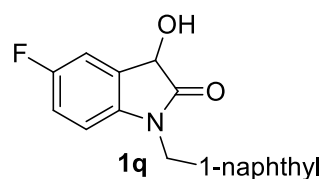
White solid (1.06 g, 70% yield). m.p. = 125 – 127 °C. ¹H NMR (400 MHz, DMSO) δ 8.23 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.0 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 6.36 (d, *J* = 7.4 Hz, 1H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.27 (d, *J* = 16.8 Hz, 1H), 5.08 (d, *J* = 7.4 Hz, 1H), 2.18 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 177.2, 143.6, 139.2, 133.8, 131.5, 131.0, 129.1, 128.2, 126.9, 126.5, 126.3, 125.8, 125.0, 123.9, 123.7, 123.3, 110.3, 69.2, 41.2, 21.8. HRMS (Q-TOF Premier) calcd for C₂₀H₁₈NO₂ (M+H)⁺: 304.1332; found: 304.1335.

3-Hydroxy-6-methoxy-1-(naphthalen-1-ylmethyl)indolin-2-one



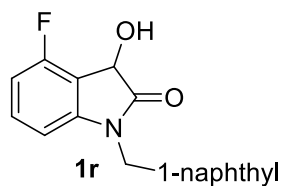
White solid (1.15 g, 72% yield). m.p. = 136 – 138 °C. ¹H NMR (500 MHz, DMSO) δ 8.23 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.57 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.40 (d, *J* = 1.8 Hz, 1H), 6.32 (d, *J* = 7.4 Hz, 1H), 5.37 (d, *J* = 16.6 Hz, 1H), 5.29 (d, *J* = 16.6 Hz, 1H), 5.03 (d, *J* = 7.4 Hz, 1H), 3.63 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 177.3, 160.8, 144.9, 133.8, 131.7, 131.1, 129.1, 128.3, 126.9, 126.5, 126.0, 125.8, 124.5, 123.8, 121.0, 106.8, 97.5, 68.9, 55.8, 41.3. HRMS (Q-TOF Premier) calcd for C₂₀H₁₇NNaO₃ (M+Na)⁺: 342.1101; found: 342.1102.

5-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one



White solid (1.03 g, 67% yield). m.p. = 162 – 164 °C. ¹H NMR (400 MHz, DMSO) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.72 – 7.53 (m, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.29 (dd, *J* = 12.8, 7.2 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 4.2 Hz, 1H), 6.57 (d, *J* = 7.2 Hz, 1H), 5.40 (d, *J* = 16.6 Hz, 1H), 5.29 (d, *J* = 16.6 Hz, 1H), 5.17 (d, *J* = 6.8 Hz, 1H). ¹³C NMR (101 MHz, DMSO) δ 176.7, 159.0 (d, *J* = 239.4 Hz), 139.6, 133.9, 131.3, 131.2 (d, *J* = 8.1 Hz), 131.0, 129.1, 128.4, 126.9, 126.5, 125.8, 124.4, 123.7, 115.5 (d, *J* = 23.2 Hz), 113.0 (d, *J* = 24.2 Hz), 110.6 (d, *J* = 8.1 Hz), 69.5, 41.4. ¹⁹F NMR (376 MHz, DMSO) δ -121.0. HRMS (Q-TOF Premier) calcd for C₁₉H₁₄FNNaO₂ (M+Na)⁺: 330.0901; found: 330.0903.

4-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

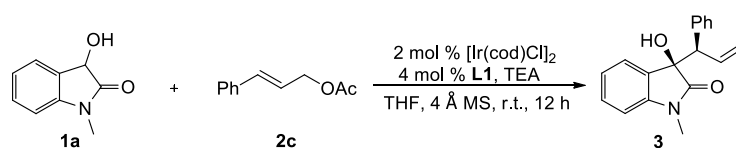


White solid (1.04 g, 68% yield). m.p. = 164 – 166 °C. ^1H NMR (400 MHz, DMSO) δ 8.23 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.0 Hz, 1H), 7.23 (dd, J = 13.8, 8.0 Hz, 1H), 6.84 (t, J = 8.8 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 6.58 (d, J = 8.2 Hz, 1H), 5.41 – 5.26 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 176.19, 159.5 (d, J = 248.5 Hz), 145.8 (d, J = 9.1 Hz), 133.8, 131.8 (d, J = 8.1 Hz), 131.2, 131.0, 129.1, 128.3, 126.9, 126.5, 125.8, 124.2, 123.7, 114.7 (d, J = 21.2 Hz), 110.4 (d, J = 20.2 Hz), 106.3 (d, J = 3.0 Hz), 67.7, 41.7. ^{19}F NMR (376 MHz, DMSO) δ -118.4. HRMS (Q-TOF Premier) calcd for $\text{C}_{19}\text{H}_{14}\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 330.0901; found: 330.0900.

3. General Procedure for Stereoselective α -Allylation of 3-Hydroxyoxindoles

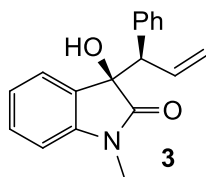
A flame dried Schlenk tube was cooled to rt and filled with N₂. To this flask were added [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol, 2 mol%), phosphoramidite ligand **L1** (5.4 mg, 0.010 mmol, 4 mol%), THF (0.5 mL) and *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a pale yellow solid. 3-Hydroxyoxindoles (0.25 mmol), allylic acetate (0.30 mmol), 4Å MS (100 mg), TEA (1 equiv) and THF (1.5 mL) were then added. The reaction mixture was stirred at rt for 24 h. The crude reaction mixture was concentrated by rotary evaporation. The residue was then purified by SiO₂ column chromatography (petroleum ether/ethyl acetate = 3:1) to give the desired product including both of the diastereoisomers and the overall yield was obtained. The dr value was determined by ¹H NMR analysis of the diastereoisomers. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5:1) to give the major diastereomer and the minor diastereomer respectively. The NMR was determined with both of them. The ee value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.

Table S1. Optimization of the Reaction Conditions^a



entry	solvent	yield (%) ^b	dr ^c	ee (%) ^d
1	toluene	16	2:1	91
2	MeOH	31	2:1	94
3	DCM	37	3:1	94
4	EA	42	3:1	95
5	NMP	34	2:1	95
6	MeCN	trace	ND	ND
7	DMF	55	3:1	95
8	1,4-dioxane	28	3:1	95
9	THF	60	3:1	95
10 ^e	THF	23	3:1	95

^aReaction conditions: **1a** (0.25 mmol, 1.0 equiv), **2c** (0.30 mmol, 1.2 equiv), [Ir(cod)Cl]₂ (2 mol %), **L1** (4 mol %), 1 equiv TEA, 100mg 4Å MS, THF (2 ml), 25 °C, 12 h. ^bOverall yield of the diastereoisomers. ND = not determined. ^cRatio of dr determined by ¹H NMR integration. ^dDetermined by HPLC analysis using an IC-3 column. ^eNone of 4Å MS.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (63.5 mg, 91% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

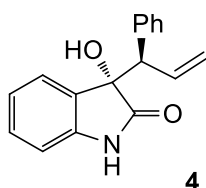
(R)-3-Hydroxy-1-methyl-3-((R)-1-phenylallyl)indolin-2-one (3)

Light yellow solid (47.4 mg, 68% yield). m.p. = 57 – 59 °C. 95% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/*i*-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 13.540 min (major), $t_{\text{R}2}$ = 17.908 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -40.8 (*c* 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.44 (dd, 7.6, 0.8 Hz, 1H), 7.30 (td, *J* = 7.8, 1.2 Hz, 1H), 7.14 – 7.03 (m, 4H), 6.78 (dd, 8.0, 1.0 Hz, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.47 (ddd, *J* = 17.0, 10.2, 8.4 Hz, 1H), 5.38 (d, *J* = 10.2 Hz, 1H), 5.28 (dt, *J* = 17.0, 1.2 Hz, 1H), 3.88 (d, *J* = 8.4 Hz, 1H), 2.93 (br, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.8, 143.8, 136.5, 134.3, 129.9, 128.8, 128.0, 127.7, 127.2, 124.7, 122.6, 120.1, 108.1, 78.8, 58.2, 25.7. HRMS (Q-TOF Premier) calcd for $\text{C}_{18}\text{H}_{17}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 302.1151; found: 302.1156.

Minor diastereomer:

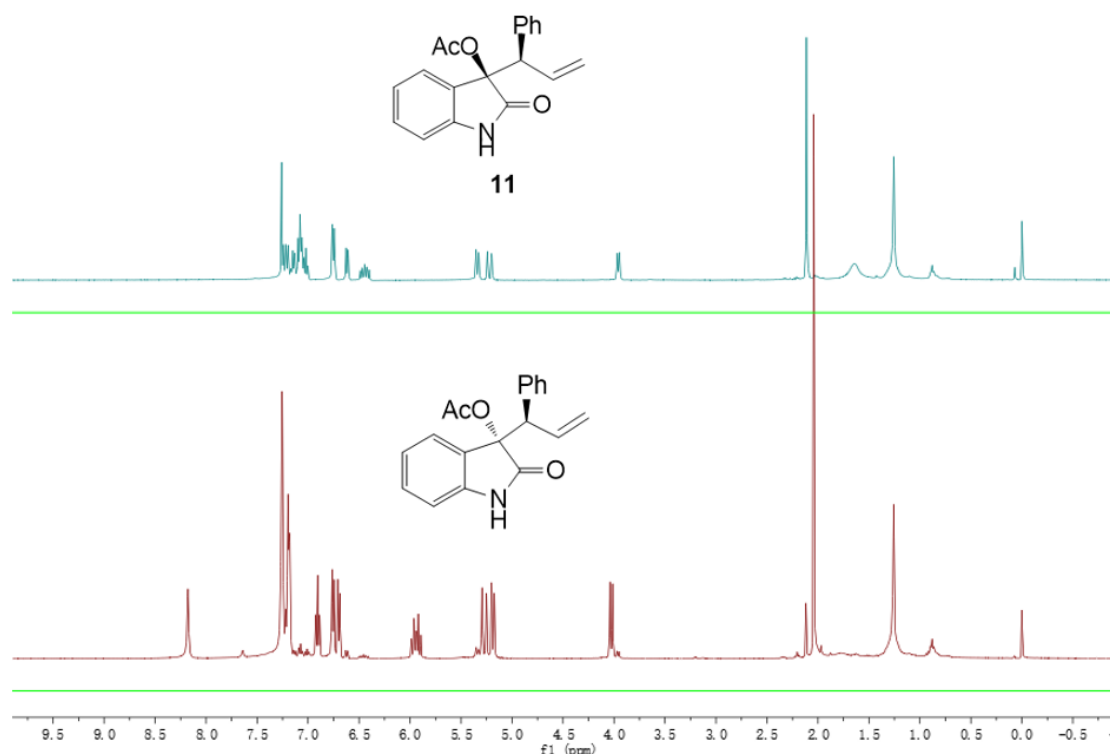
(S)-3-Hydroxy-1-methyl-3-((R)-1-phenylallyl)indolin-2-one

Light yellow solid (15.3 mg, 22% yield). m.p. = 88 – 90 °C. 89% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/*i*-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 15.139 min (minor), $t_{\text{R}2}$ = 20.718 min (major)]. $[\alpha]_{\text{D}}^{20}$ = -11.8 (*c* 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, *J* = 7.4 Hz, 2H), 7.14 – 7.11 (m, 3H), 7.10 – 6.98 (m, 3H), 6.56 (d, *J* = 7.6 Hz, 1H), 6.38 (dt, *J* = 16.8, 10.2 Hz, 1H), 5.40 (dd, *J* = 16.8, 1.4 Hz, 1H), 5.35 (dd, *J* = 10.2, 1.4 Hz, 1H), 3.83 (d, *J* = 10.2 Hz, 1H), 2.98 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.9, 143.5, 136.9, 133.9, 129.7, 128.8, 128.3, 127.8, 127.1, 124.3, 122.6, 120.7, 108.0, 78.2, 58.8, 25.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{18}\text{H}_{17}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 302.1151; found: 302.1159.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1) afforded the product including both of the diastereoisomers (62.3 mg, 94% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 2:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 3/1) to give the major diastereomer and the minor diastereomer respectively.

We achieved the acetylation of the hydroxyl group of **4**.⁴ Then the reaction product was compared with **11** to identify the absolute configuration.



Major diastereomer:

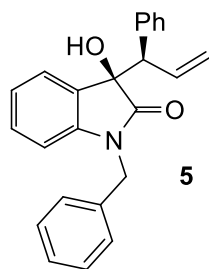
(S)-3-Hydroxy-3-((R)-1-phenylallyl)indolin-2-one

White solid (40.4 mg, 61% yield). m.p. = 146 – 148 °C. 98% ee, HPLC [DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 92/8, 220 nm, 1 mL/min; t_{R1} = 16.977 min (minor), t_{R2} = 18.374 min (major)]. $[\alpha]_D^{20}$ = -37.2 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.20 – 7.04 (m, 7H), 6.99 (td, *J* = 7.6, 0.8 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.30 (dt, *J* = 16.8, 10.2 Hz, 1H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.31 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.87 (d, *J* = 10.2 Hz, 1H), 3.43 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 179.4, 140.6, 137.0, 133.8, 129.7, 129.1, 128.8, 128.0, 127.2, 125.1, 122.6, 120.7, 110.0, 78.4, 58.1. HRMS (Q-TOF Premier) calcd for C₁₇H₁₅NNaO₂ (M+Na)⁺: 288.0905; found: 288.0908.

Minor diastereomer:

(R)-3-Hydroxy-3-((R)-1-phenylallyl)indolin-2-one

White solid (20.1 mg, 30% yield). m.p. = 162 – 164 °C. 97% ee, HPLC [DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 92/8, 220 nm, 1 mL/min; t_{R1} = 16.307 min (major), t_{R2} = 18.392 min (minor)]. $[\alpha]_D^{20}$ = -63.0 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, DMSO) δ 9.02 (s, 1H), 6.46 (d, *J* = 7.2 Hz, 1H), 6.34 (td, *J* = 7.8, 1.2 Hz, 1H), 6.20 (ddd, *J* = 15.8, 7.8, 3.6 Hz, 3H), 6.12 (td, *J* = 7.4, 0.8 Hz, 1H), 5.84 – 5.80 (m, 2H), 5.73 (d, *J* = 7.8 Hz, 1H), 5.66 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1H), 5.29 (s, 1H), 4.41 – 4.34 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.17 – 4.08 (dt, *J* = 17.4, 1.6 Hz, 1H), 2.94 (d, *J* = 7.2 Hz, 1H). ¹³C NMR (101 MHz, DMSO) δ 178.7, 142.7, 138.1, 136.8, 130.2, 129.7, 129.5, 128.0, 127.2, 125.7, 121.6, 118.4, 109.7, 78.4, 56.8. HRMS (Q-TOF Premier) calcd for C₁₇H₁₅NNaO₂ (M+Na)⁺: 288.0905; found: 288.0904.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (79.9 mg, 90% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 4:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

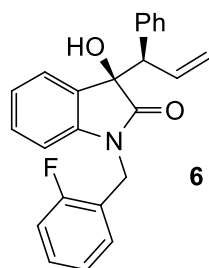
(R)-1-Benzyl-3-hydroxy-3-((R)-1-phenylallyl)indolin-2-one

Light yellow solid (62.9 mg, 71% yield). m.p. = 70 – 72 °C. 98% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 12.152 min (major), $t_{\text{R}2}$ = 14.811 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -33.2 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (dd, J = 7.2, 0.8 Hz, 1H), 7.25 – 7.05 (m, 8H), 6.83 (d, J = 7.2 Hz, 2H), 6.55 (ddd, J = 17.2, 10.2, 8.2 Hz, 1H), 6.48 (d, J = 7.2 Hz, 2H), 6.40 (d, J = 7.6 Hz, 1H), 5.41 (d, J = 10.2 Hz, 1H), 5.31 (d, J = 17.2 Hz, 1H), 4.94 (d, J = 16.0 Hz, 1H), 4.26 (d, J = 16.0 Hz, 1H), 4.05 (d, J = 8.2 Hz, 1H), 3.16 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.1, 143.3, 136.6, 134.9, 134.8, 129.9, 129.3, 128.6, 128.3, 128.1, 127.4, 127.2, 126.5, 125.0, 122.8, 120.0, 109.6, 78.4, 57.9, 43.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 356.1645; found: 356.1638.

Minor diastereomer:

(S)-1-Benzyl-3-hydroxy-3-((R)-1-phenylallyl)indolin-2-one

Light yellow solid (14.8 mg, 17% yield). m.p. = 65 – 67 °C. 85% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 9.945 min (major), $t_{\text{R}2}$ = 12.020 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -50.2 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.20 (m, 5H), 7.16 – 7.10 (m, 3H), 7.10 – 7.05 (m, 2H), 7.04 – 6.99 (m, 1H), 6.99 – 6.94 (m, 2H), 6.50 (dt, J = 17.0, 10.2 Hz, 1H), 6.44 (d, J = 7.8 Hz, 1H), 5.45 (dd, J = 17.0, 1.6 Hz, 1H), 5.38 (dd, J = 10.2, 1.6 Hz, 1H), 4.89 (d, J = 15.8 Hz, 1H), 4.54 (d, J = 15.8 Hz, 1H), 3.94 (d, J = 10.2 Hz, 1H), 3.20 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.1, 143.1, 137.0, 135.1, 134.0, 129.7, 129.1, 128.6, 128.4, 128.1, 127.4, 127.1, 127.1, 124.5, 122.7, 121.1, 109.3, 77.9, 58.3, 43.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 356.1645; found: 356.1642.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (79.3 mg, 85% overall yield). ^1H NMR analysis of the

diastereoisomers showed a dr of 4:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

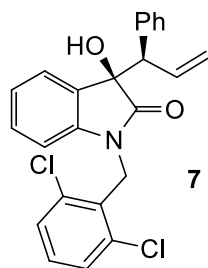
(R)-1-(2-Fluorobenzyl)-3-hydroxy-3-((R)-1-phenylallyl)indolin-2-one

Light yellow solid (62.8 mg, 67% yield). m.p. = 50 – 52 °C. 97% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 92/8, 220 nm, 1 mL/min; *t*_{R1} = 11.111 min (major), *t*_{R2} = 13.527 min (minor)]. [α]_D²⁰ = -41.7 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.11 (m, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 10.0 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.54 (ddd, *J* = 17.0, 10.2, 8.2 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.92 (t, *J* = 7.6 Hz, 1H), 5.41 (d, *J* = 10.2 Hz, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 4.85 (d, *J* = 16.4 Hz, 1H), 4.45 (d, *J* = 16.4 Hz, 1H), 4.01 (d, *J* = 8.2 Hz, 1H), 2.97 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.2, 160.2 (d, *J* = 245.7 Hz), 143.0, 136.5, 134.7, 130.1, 129.3, 128.9 (d, *J* = 8.8 Hz), 128.4 (d, *J* = 3.8 Hz), 128.3, 128.1, 127.4, 125.1, 124.5 (d, *J* = 2.5 Hz), 123.0, 121.9 (d, *J* = 13.9 Hz), 120.1, 115.0 (d, *J* = 21.4 Hz), 109.2, 78.4, 57.9, 37.1 (d, *J* = 6.3 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -119.0. HRMS (Q-TOF Premier) calcd for C₂₄H₂₁FNO₂ (M+H)⁺: 374.1551; found: 374.1546.

Minor diastereomer:

(S)-1-(2-Fluorobenzyl)-3-hydroxy-3-((R)-1-phenylallyl)indolin-2-one

Light yellow solid (15.1 mg, 16% yield). m.p. = 47 – 49 °C. 89% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; *t*_{R1} = 8.250 min (major), *t*_{R2} = 10.417 min (minor)]. [α]_D²⁰ = -14.1 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 7.28 (s, 1H), 7.23 – 7.19 (m, 1H), 7.16 – 7.09 (m, 4H), 7.06 – 7.01 (m, 4H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.56 – 6.44 (m, 2H), 5.45 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.38 (dd, *J* = 10.2, 1.6 Hz, 1H), 4.88 (d, *J* = 16.2 Hz, 1H), 4.65 (d, *J* = 16.2 Hz, 1H), 3.92 (d, *J* = 10.2 Hz, 1H), 3.18 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.3, 160.4 (d, *J* = 247.0 Hz), 142.8, 136.9, 133.9, 129.9, 129.3 (d, *J* = 3.8 Hz), 129.2 (d, *J* = 8.8 Hz), 129.0, 128.4, 128.1, 127.1, 124.4, 124.3 (d, *J* = 3.8 Hz), 122.9, 122.2 (d, *J* = 15.1 Hz), 121.2, 115.2 (d, *J* = 21.4 Hz), 109.0, 77.8, 58.4, 37.2 (d, *J* = 5.0 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -118.3. HRMS (Q-TOF Premier) calcd for C₂₄H₂₁FNO₂ (M+H)⁺: 374.1551; found: 374.1553.

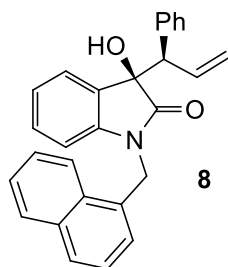


Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (93.1 mg, 88% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 6:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-1-(2,6-Dichlorobenzyl)-3-hydroxy-3-((R)-1-phenylallyl)indolin-2-one (7)

Light yellow solid (78.8 mg, 75% yield). m.p. = 55 – 57 °C. >99% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 92/8, 220 nm, 1 mL/min; t_{R1} = 16.228 min (major), t_{R2} = 21.879 min (minor)]. $[\alpha]_D^{20}$ = -1.1 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.25 (m, 3H), 7.22 – 7.06 (m, 5H), 7.00 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.2 Hz, 2H), 6.54 (d, J = 8.0 Hz, 1H), 6.48 (ddd, J = 17.0, 10.2, 8.2 Hz, 1H), 5.31 (d, J = 10.2 Hz, 1H), 5.16 (d, J = 17.0 Hz, 1H), 4.93 (d, J = 15.0 Hz, 1H), 4.77 (d, J = 15.0 Hz, 1H), 3.85 (d, J = 8.2 Hz, 1H), 2.81 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.4, 142.9, 136.8, 136.4, 134.6, 130.1, 129.7, 129.7, 129.4, 128.7, 128.5, 128.0, 127.4, 125.0, 122.4, 119.7, 109.3, 77.8, 57.9, 40.2. HRMS (Q-TOF Premier) calcd for C₂₄H₁₉Cl₂NNaO₂ (M+Na)⁺: 446.0685; found: 446.0695.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (94.2 mg, 93% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 6:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

(R)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8)

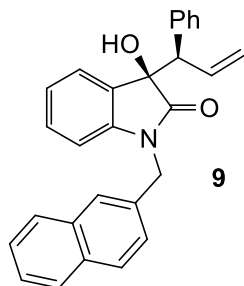
Light yellow solid (80.2 mg, 79% yield). m.p. = 66 – 68 °C. 99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 14.585 min (major), t_{R2} = 26.536 min (minor)]. $[\alpha]_D^{20}$ = -100.2 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.53 – 7.44 (m, 2H), 7.25 (dd, J = 15.4, 8.0 Hz, 1H), 7.16 – 7.06 (m, 4H), 6.99 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.6 Hz, 2H), 6.67 – 6.56 (ddd, J = 16.8, 10.2, 8.0 Hz, 1H), 6.31 (d, J = 6.8 Hz, 1H), 5.70 (d, J = 7.0 Hz, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.35 (d, J = 4.8 Hz, 1H), 5.32 (d, J = 4.8 Hz, 1H), 4.77 (d, J = 16.8 Hz, 1H), 4.13 (d, J = 8.0 Hz, 1H), 3.68 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.8, 143.6, 136.8, 134.9, 133.6, 130.5, 130.0, 129.6, 129.4, 128.9, 128.4, 128.4, 127.6, 127.5, 126.4, 125.8, 125.7, 125.1, 123.0, 122.8, 122.4, 120.0, 109.8, 78.8, 57.8, 41.7. HRMS (Q-TOF Premier) calcd for C₂₈H₂₄NO₂ (M+H)⁺: 406.1802; found: 406.1791.

Minor diastereomer:

(S)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one

Light yellow solid (12.5 mg, 12% yield). m.p. = 73 – 75 °C. 86% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 17.861 min (major), t_{R2} = 20.847 min (minor)]. $[\alpha]_D^{20}$ = -32.0 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.54 (dt, J = 14.8, 7.0 Hz, 2H), 7.35 (d, J = 6.8 Hz, 1H), 7.23 – 7.03 (m, 8H), 6.61 (dt, J = 17.0, 10.2 Hz, 1H), 6.45 (d, J = 7.2 Hz, 1H), 6.38 (d, J = 7.4 Hz, 1H), 5.49 (d, J = 17.0 Hz, 1H), 5.42 (d, J = 16.6 Hz, 1H), 5.41 (d, J = 10.2 Hz, 1H), 4.99 (d, J = 16.6 Hz, 1H), 3.98 (d, J = 10.2 Hz, 1H), 3.27 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.4, 143.4, 137.0, 134.0, 133.7, 130.7, 129.8, 129.7, 129.2, 128.9, 128.6, 128.2, 127.9, 127.2, 126.5, 125.9, 125.4, 124.4, 123.8,

122.9, 122.7, 121.4, 109.7, 78.0, 58.4, 41.9. HRMS (Q–TOF Premier) calcd for C₂₈H₂₄NO₂ (M+H)⁺: 406.1802; found: 406.1790.

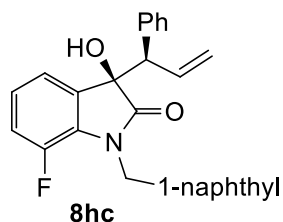


Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (90.1 mg, 89% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 5:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-3-Hydroxy-1-(naphthalen-2-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (9)

Light yellow solid (74.6 mg, 74% yield). m.p. = 47 – 49 °C. 98% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 14.126 min (major), t_{R2} = 17.798 min (minor)]. [α]_D²⁰ = -42.1 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 7.80 – 7.74 (m, 1H), 7.74 – 7.68 (m, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.44 (p, *J* = 7.0 Hz, 2H), 7.38 (s, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.16 – 7.06 (m, 4H), 6.86 (d, *J* = 7.4 Hz, 2H), 6.54 (ddd, *J* = 17.0, 10.2, 8.2 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 5.41 (d, *J* = 10.2 Hz, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 5.02 (d, *J* = 15.8 Hz, 1H), 4.48 (d, *J* = 15.8 Hz, 1H), 4.04 (d, *J* = 8.2 Hz, 1H), 2.93 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.1, 143.4, 136.6, 134.8, 133.1, 132.7, 132.6, 129.9, 129.2, 128.6, 128.2, 128.1, 127.7, 127.6, 127.5, 126.1, 125.9, 125.7, 125.0, 124.6, 122.8, 120.0, 109.7, 78.4, 58.0, 44.2. HRMS (Q–TOF Premier) calcd for C₂₈H₂₄NO₂ (M+H)⁺: 406.1802; found: 406.1793.



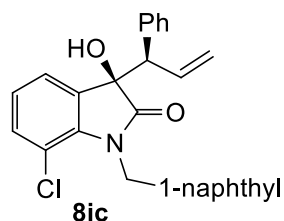
Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (97.3 mg, 92% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 6:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-7-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8hc)

Light yellow solid (82.7 mg, 78% yield). m.p. = 117 – 119 °C. 98% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 11.899 min (major), t_{R2} = 22.925 min (minor)]. [α]_D²⁰ = -110.8 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.78 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 2H), 7.09 – 7.02 (m, 1H), 7.02 – 6.98 (m, 1H), 6.94 – 6.85 (m, 3H), 6.59 (ddd, *J* = 17.2, 10.2, 7.8 Hz, 1H), 5.75 (d, *J* = 6.8

Hz, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.37 (d, J = 16.8 Hz, 1H), 5.31 (d, J = 17.2 Hz, 1H), 5.06 (d, J = 16.8 Hz, 1H), 4.13 (d, J = 7.8 Hz, 1H), 3.88 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -134.5. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 424.1707; found: 424.1694.

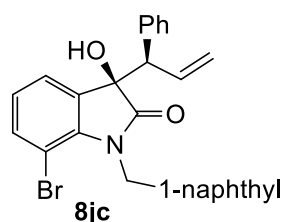


Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (98.8 mg, 90% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 11:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-7-Chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8ic)

Light yellow solid (89.5 mg, 82% yield). m.p. = 83 – 85 °C. >99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 13.442 min (major), $t_{\text{R}2}$ = 24.457 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -66.1 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.86 – 7.79 (m, 2H), 7.63 (d, J = 8.2 Hz, 1H), 7.58 (dd, J = 7.4, 0.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.38 – 7.32 (m, 2H), 7.22 (d, J = 18.0 Hz, 1H), 7.20 (d, J = 15.4 Hz, 1H), 7.07 – 6.95 (m, 2H), 6.89 (d, J = 7.4 Hz, 2H), 6.56 (ddd, J = 17.2, 10.4, 7.8 Hz, 1H), 5.66 (d, J = 7.0 Hz, 1H), 5.49 (d, J = 17.2 Hz, 1H), 5.43 (d, J = 10.4 Hz, 1H), 5.42 (d, J = 17.0 Hz, 1H), 5.30 (d, J = 17.0 Hz, 1H), 4.10 (d, J = 7.8 Hz, 1H), 3.45 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 178.1, 141.1, 136.2, 135.9, 134.5, 133.5, 132.0, 131.6, 129.9, 129.6, 128.8, 128.6, 127.8, 127.0, 126.1, 125.8, 125.7, 124.3, 124.2, 122.2, 121.5, 120.4, 103.0, 77.8, 57.9, 43.2. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 462.1231; found: 462.1239.



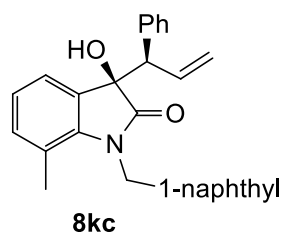
Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (100.2 mg, 83% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 8:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-7-Bromo-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8jc)

Light yellow solid (88.3 mg, 73% yield). m.p. = 82 – 84 °C. 98% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 12.850 min (major), $t_{\text{R}2}$ = 23.343 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -69.8 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 7.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.08 (t, J = 7.8 Hz, 1H), 7.00 (t, J = 7.8 Hz, 1H), 6.89 (d, J = 7.8 Hz, 2H), 6.57 (ddd, J = 17.0,

10.2, 7.8 Hz 1H), 5.67 (d, $J = 7.2$ Hz, 1H), 5.50 (d, $J = 17.0$ Hz, 1H), 5.43 (d, $J = 10.2$ Hz, 1H), 5.38 (d, $J = 17.0$ Hz, 1H), 5.31 (d, $J = 17.0$ Hz, 1H), 4.10 (d, $J = 7.8$ Hz, 1H), 3.46 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.9, 139.7, 136.2, 134.5, 133.5, 132.5, 131.9, 131.3, 129.9, 129.5, 128.8, 128.6, 127.8, 127.0, 126.1, 125.8, 125.7, 123.8, 123.8, 122.2, 121.3, 120.4, 116.1, 77.9, 57.9, 43.3. HRMS (Q–TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{BrNO}_2$ ($\text{M}+\text{H}$) $^+$: 484.0907; found: 484.0905.

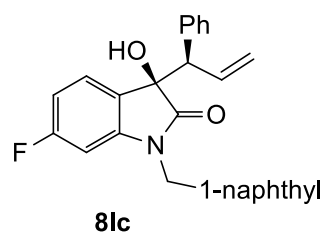


Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (97.4 mg, 93% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 8:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-3-Hydroxy-7-methyl-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8kc)

Light yellow solid (86.0 mg, 82% yield). m.p. = 88 – 90 °C. 98% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 15.456 min (major), $t_{\text{R}2}$ = 32.521 min (minor)]. $[\alpha]_{\text{D}}^{20} = -74.8$ (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 7.8$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 8.2$ Hz, 1H), 7.52 – 7.44 (m, 3H), 7.31 (t, $J = 7.4$ Hz, 1H), 7.17 (t, $J = 7.6$ Hz, 2H), 7.05 (t, $J = 7.6$ Hz, 1H), 7.01 – 6.94 (m, 2H), 6.88 (d, $J = 7.6$ Hz, 2H), 6.61 (ddd, $J = 17.2$, 10.2, 7.8 Hz, 1H), 5.62 (d, $J = 7.0$ Hz, 1H), 5.45 (d, $J = 17.4$ Hz, 1H), 5.41 (d, $J = 10.2$ Hz, 1H), 5.30 (d, $J = 17.2$ Hz, 1H), 5.05 (d, $J = 17.4$ Hz, 1H), 4.12 (d, $J = 7.8$ Hz, 1H), 3.61 (s, 1H), 1.82 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 178.5, 141.6, 136.9, 135.1, 134.0, 133.5, 131.9, 129.8, 129.7, 129.2, 128.9, 128.4, 127.5, 127.3, 126.3, 126.0, 125.8, 123.2, 123.0, 122.0, 121.7, 120.4, 119.9, 77.8, 57.9, 43.4, 17.8. HRMS (Q–TOF Premier) calcd for $\text{C}_{29}\text{H}_{25}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 442.1778; found: 442.1788.



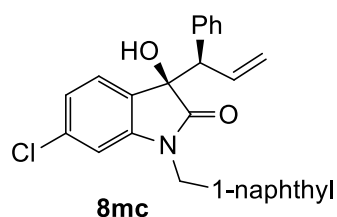
Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (100.5 mg, 95% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 5:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-6-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8lc)

Light yellow solid (82.1 mg, 78% yield). m.p. = 63 – 65 °C. 97% ee, HPLC [Enantiocol OX-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 12.786 min (major), $t_{\text{R}2}$ = 20.261 min (minor)]. $[\alpha]_{\text{D}}^{20} = -73.4$ (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.83 (t, $J = 6.6$ Hz, 2H), 7.66 (d, $J = 8.2$

Hz, 1H), 7.54 – 7.46 (m, 3H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 2H), 7.01 (t, $J = 7.8$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 2H), 6.81 – 6.75 (m, 1H), 6.58 (ddd, $J = 17.0, 10.2, 7.8$ Hz, 1H), 6.07 (dd, $J = 8.8, 1.8$ Hz, 1H), 5.71 (d, $J = 7.2$ Hz, 1H), 5.42 (d, $J = 10.2$ Hz, 1H), 5.32 (d, $J = 17.0$ Hz, 1H), 5.31 (d, $J = 16.8$ Hz, 1H), 4.74 (d, $J = 16.8$ Hz, 1H), 4.11 (d, $J = 7.8$ Hz, 1H), 3.76 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 178.1, 163.94 (d, $J = 248.2$ Hz), 145.3 (d, $J = 11.3$ Hz), 136.5, 134.6, 133.6, 130.4, 129.5, 128.9, 128.8, 128.5, 127.8, 127.6, 126.5, 126.4 (d, $J = 8.8$ Hz), 125.9, 125.6, 123.9 (d, $J = 3.8$ Hz), 122.8, 122.3, 120.3, 109.2 (d, $J = 21.4$ Hz), 98.6 (d, $J = 27.7$ Hz), 78.4, 57.6, 41.9. ^{19}F NMR (471 MHz, CDCl_3) δ -109.1. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{22}\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 446.1527; found: 446.1530.

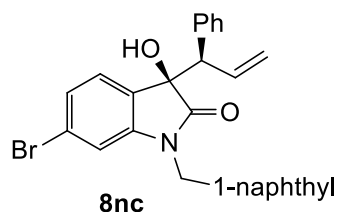


Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (96.6 mg, 88% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 5:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-6-Chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8mc)

Light yellow solid (79.5 mg, 72% yield). m.p. = 72 – 74 $^\circ\text{C}$. 94% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 12.462 min (major), $t_{\text{R}2}$ = 17.839 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -96.3 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.88 – 7.82 (m, 2H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.52 (ddd, $J = 15.4, 10.2, 4.7$ Hz, 3H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.17 (t, $J = 7.6$ Hz, 2H), 7.10 (dd, $J = 8.0, 1.8$ Hz, 1H), 7.06 – 7.00 (m, 1H), 6.91 (d, $J = 7.2$ Hz, 2H), 6.57 (ddd, $J = 17.0, 10.2, 8.0$ Hz, 1H), 6.36 (d, $J = 1.8$ Hz, 1H), 5.70 (d, $J = 6.8$ Hz, 1H), 5.43 (d, $J = 10.2$ Hz, 1H), 5.34 (d, $J = 17.0$ Hz, 1H), 5.33 (d, $J = 17.0$ Hz, 1H), 4.76 (d, $J = 17.0$ Hz, 1H), 4.08 (d, $J = 8.0$ Hz, 1H), 3.48 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.7, 144.9, 136.3, 135.8, 134.4, 133.6, 130.4, 129.5, 128.9, 128.8, 128.5, 127.8, 127.7, 126.8, 126.5, 126.0, 125.9, 125.6, 122.9, 122.5, 122.2, 120.4, 110.3, 78.3, 57.6, 41.9. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 462.1231; found: 462.1239.

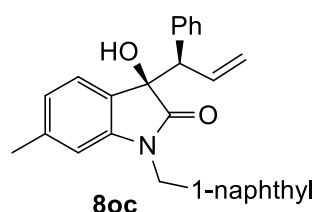


Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (105.1 mg, 87% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 6:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-6-Bromo-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8nc)

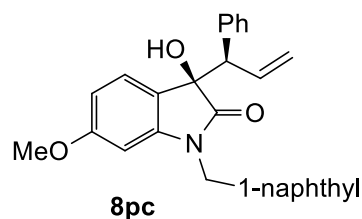
Light yellow solid (88.8 mg, 74% yield). m.p. = 85 – 87 °C. 98% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 12.815 min (major), t_{R2} = 18.553 min (minor)]. $[\alpha]_D^{20}$ = -95.2 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 7.82 (t, J = 7.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.6 Hz, 2H), 7.01 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 2H), 6.57 (ddd, 17.0, 10.2, 7.8 Hz, 1H), 6.49 (s, 1H), 5.66 (d, J = 7.2 Hz, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.32 (d, J = 17.0 Hz, 2H), 4.71 (d, J = 17.0 Hz, 1H), 4.10 (d, J = 7.8 Hz, 1H), 3.87 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.8, 144.9, 136.4, 134.5, 133.6, 130.4, 129.5, 128.9, 128.8, 128.6, 127.8, 127.7, 127.5, 126.5, 125.9, 125.7, 123.7, 122.5, 122.3, 120.4, 113.0, 78.5, 57.5, 41.9. HRMS (Q-TOF Premier) calcd for C₂₈H₂₃BrNO₂ (M+H)⁺: 484.0907; found: 484.0912.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (84.8 mg, 81% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 6:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:**(R)-3-Hydroxy-6-methyl-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8oc)**

Light yellow solid (71.7 mg, 68% yield). m.p. = 80 – 82 °C. 99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 11.976 min (major), t_{R2} = 26.233 min (minor)]. $[\alpha]_D^{20}$ = -106.3 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.0 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.30 – 7.23 (m, 1H), 7.14 (dd, J = 10.6, 4.8 Hz, 2H), 7.04 – 6.97 (m, 1H), 6.96 – 6.87 (m, 3H), 6.61 (ddd, J = 17.0, 10.2, 8.0 Hz, 1H), 6.17 (s, 1H), 5.67 (dd, J = 7.0, 0.8 Hz, 1H), 5.44 – 5.39 (dt, J = 10.2, 1.2 Hz, 1H), 5.39 (d, J = 16.8 Hz, 1H), 5.30 (d, J = 16.8 Hz, 1H), 4.76 (d, J = 17.0 Hz, 1H), 4.09 (d, J = 8.0 Hz, 1H), 3.40 (s, 1H), 2.18 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.0, 143.7, 140.4, 136.9, 135.0, 133.6, 130.4, 129.6, 129.5, 128.9, 128.4, 127.5, 127.4, 126.3, 125.8, 125.7, 125.4, 124.9, 123.6, 122.5, 122.3, 119.9, 110.4, 78.5, 57.7, 41.7, 21.8. HRMS (Q-TOF Premier) calcd for C₂₉H₂₆NO₂ (M+H)⁺: 420.1958; found: 420.1949.



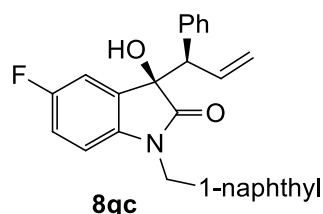
Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (86.0 mg, 79% overall yield). ¹H NMR analysis of the

diastereoisomers showed a dr of 6:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer.

Major diastereomer:

(R)-3-Hydroxy-6-methoxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8pc)

Light yellow solid (71.9 mg, 66% yield). m.p. = 59 – 61 °C. 99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 15.302 min (major), t_{R2} = 42.278 min (minor)]. $[\alpha]_D^{20}$ = -18.4 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.2 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.51 (m, 3H), 7.28 (s, 1H), 7.15 (t, J = 7.6 Hz, 2H), 7.05 – 6.99 (m, 1H), 6.92 (d, J = 7.2 Hz, 2H), 6.66 – 6.54 (m, 2H), 5.94 (d, J = 2.2 Hz, 1H), 5.75 (d, J = 6.8 Hz, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.34 (d, J = 16.8 Hz, 1H), 5.32 (d, J = 17.2 Hz, 1H), 4.79 (d, J = 16.8 Hz, 1H), 4.04 (d, J = 8.2 Hz, 1H), 3.64 (s, 3H), 3.08 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 178.0, 161.4, 145.1, 136.9, 135.0, 133.6, 130.5, 129.5, 129.4, 128.9, 128.4, 127.6, 127.4, 126.3, 125.9, 125.8, 125.6, 122.8, 122.3, 120.2, 119.9, 106.7, 97.6, 78.3, 57.8, 55.4, 41.7. HRMS (Q-TOF Premier) calcd for C₂₉H₂₆NO₃ (M+H)⁺: 436.1907; found: 436.1907.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (84.6 mg, 80% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 4:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

(R)-5-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8qc)

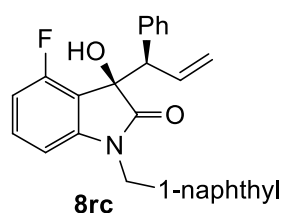
Light yellow solid (66.1 mg, 62% yield). m.p. = 81 – 83 °C. 99% ee, HPLC [Enantiocol OX-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 12.660 min (major), t_{R2} = 21.699 min (minor)]. $[\alpha]_D^{20}$ = -28.1 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, J = 8.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.33 (dd, J = 7.8, 2.6 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.16 (t, J = 7.8 Hz, 2H), 7.07 – 6.99 (m, 1H), 6.92 (d, J = 7.2 Hz, 2H), 6.85 (td, J = 8.8, 2.6 Hz, 1H), 6.57 (ddd, J = 17.2, 10.2, 8.0 Hz, 1H), 6.26 (dd, J = 8.6, 4.2 Hz, 1H), 5.74 (d, J = 6.8 Hz, 1H), 5.46 (d, J = 10.2 Hz, 1H), 5.36 (d, J = 17.2 Hz, 1H), 5.35 (d, J = 16.8 Hz, 1H), 4.80 (d, J = 16.8 Hz, 1H), 4.08 (d, J = 8.0 Hz, 1H), 3.31 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.4, 159.2 (d, J = 241.9 Hz), 139.5 (d, J = 2.6 Hz), 136.3, 134.2, 133.6, 130.4, 129.9 (d, J = 7.6 Hz), 129.5, 129.1, 128.9, 128.5, 127.7, 127.6, 126.4, 125.9, 125.6, 122.8, 122.3, 120.6, 116.2 (d, J = 23.9 Hz), 113.2 (d, J = 25.2 Hz), 110.4 (d, J = 8.8 Hz), 78.8 (d, J = 1.3 Hz), 57.7, 41.9. ¹⁹F NMR (471 MHz, CDCl₃) δ -119.5. HRMS (Q-TOF Premier) calcd for C₂₈H₂₂FNNO₂ (M+Na)⁺: 446.1527; found: 446.1532.

Minor diastereomer:

(S)-5-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one

Light yellow solid (15.1 mg, 14% yield). m.p. = 70 – 72 °C. 94% ee, HPLC [Enantiocol OX-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 13.317 min (minor), t_{R2} = 26.488 min (major)].

$[\alpha]_D^{20} = -11.2$ (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.61 – 7.54 (m, 2H), 7.23 (d, $J = 7.2$ Hz, 1H), 7.21 – 7.13 (m, 3H), 7.15 – 7.13 (m, 3H), 6.77 (td, $J = 8.8, 2.6$ Hz, 1H), 6.61 (dt, $J = 17.0, 10.2$ Hz, 1H), 6.44 (d, $J = 7.2$ Hz, 1H), 6.29 (dd, $J = 8.6, 4.2$ Hz, 1H), 5.50 (d, $J = 17.0$ Hz, 1H), 5.44 (d, $J = 10.2$ Hz, 1H), 5.38 (d, $J = 16.6$ Hz, 1H), 4.98 (d, $J = 16.6$ Hz, 1H), 3.93 (d, $J = 10.2$ Hz, 1H), 3.33 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.2, 159.2 (d, $J = 241.9$ Hz), 139.3 (d, $J = 2.6$ Hz), 136.6, 133.7, 133.6, 130.7, 130.2 (d, $J = 7.9$ Hz), 129.4, 129.0, 128.9, 128.4, 128.1, 127.4, 126.5, 126.0, 125.3, 123.8, 122.6, 121.7, 116.0 (d, $J = 23.9$ Hz), 112.4 (d, $J = 25.2$ Hz), 110.4 (d, $J = 7.6$ Hz), 78.1, 58.6, 42.0. ^{19}F NMR (471 MHz, CDCl_3) δ -119.6. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{22}\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 446.1527; found: 446.1530.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (87.8 mg, 83% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 2:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

(R)-4-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one (8rc)

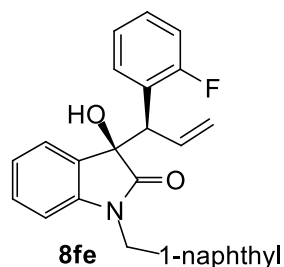
Light yellow solid (57.6 mg, 54% yield). m.p. = 110 – 112 °C. 95% ee, HPLC [Enantiocol OX-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 16.846 min (major), t_{R2} = 23.454 min (minor)]. $[\alpha]_D^{20} = -68.1$ (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.56 – 7.48 (m, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.17 (t, $J = 7.6$ Hz, 2H), 7.09 (td, $J = 8.2, 5.4$ Hz, 1H), 7.07 – 7.02 (m, 3H), 6.81 (t, $J = 8.8$ Hz, 1H), 6.55 (dt, $J = 17.0, 10.0$ Hz, 1H), 6.13 (d, $J = 7.8$ Hz, 1H), 5.84 (d, $J = 7.2$ Hz, 1H), 5.42 (d, $J = 10.0$ Hz, 1H), 5.41 (d, $J = 17.0$ Hz, 1H), 5.39 (d, $J = 16.8$ Hz, 1H), 4.85 (d, $J = 16.8$ Hz, 1H), 4.16 (d, $J = 10.0$ Hz, 1H), 3.27 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 176.5, 159.4 (d, $J = 249.5$ Hz), 145.5 (d, $J = 8.8$ Hz), 136.7, 135.6 (d, $J = 6.4$ Hz), 133.6, 131.8 (d, $J = 8.8$ Hz), 130.4, 129.2, 129.1, 128.9, 128.5, 127.8, 127.6, 126.5, 125.9, 125.5, 122.9, 122.3, 120.6, 114.4 (d, $J = 20.2$ Hz), 110.8 (d, $J = 21.4$ Hz), 105.9 (d, $J = 2.5$ Hz), 79.2 (d, $J = 2.3$ Hz), 58.7, 42.1. ^{19}F NMR (471 MHz, CDCl_3) δ -112.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 424.1707; found: 424.1699.

Minor diastereomer:

(S)-4-Fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-phenylallyl)indolin-2-one

Light yellow solid (28.2 mg, 27% yield). m.p. = 83 – 85 °C. 71% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 14.872 min (major), t_{R2} = 23.997 min (minor)]. $[\alpha]_D^{20} = -41.1$ (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 1H), 7.54 (dt, $J = 14.8, 7.2$ Hz, 2H), 7.19 (t, $J = 6.8$ Hz, 1H), 7.14 – 7.09 (m, 5H), 7.03 – 6.99 (m, 1H), 6.89 (dt, $J = 17.0, 10.2$ Hz, 1H), 6.74 (t, $J = 8.8$ Hz, 1H), 6.24 (d, $J = 7.2$ Hz, 1H), 6.09 (d, $J = 7.8$ Hz, 1H), 5.58 (d, $J = 17.0$ Hz, 1H), 5.53 (d, $J = 10.2$ Hz, 1H), 5.36 (d, $J = 16.8$ Hz, 1H), 4.96 (d, $J = 16.8$ Hz, 1H), 4.29 (d, $J = 10.2$ Hz, 1H), 3.45 (s, 1H). ^{13}C NMR (126

MHz, CDCl₃) δ 176.3, 159.4 (d, J = 250.7 Hz), 145.1 (d, J = 8.8 Hz), 137.0, 133.8, 133.6, 131.7 (d, J = 8.8 Hz), 130.6, 129.2, 128.9, 128.5, 128.4, 128.0, 127.3, 126.5, 125.9, 125.3, 123.5, 122.5, 121.9, 114.4 (d, J = 18.9 Hz), 110.7 (d, J = 21.4 Hz), 105.8 (d, J = 2.6 Hz), 78.4 (d, J = 1.3 Hz), 56.7, 42.0. ¹⁹F NMR (471 MHz, CDCl₃) δ -118.5. HRMS (Q-TOF Premier) calcd for C₂₈H₂₃FNO₂ (M+H)⁺: 424.1707; found: 424.1701.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (89.9 mg, 85% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 4:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

(R)-3-((R)-1-(2-Fluorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fe)

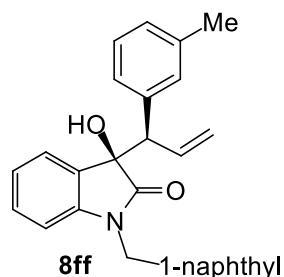
Light yellow solid (70.4 mg, 67% yield). m.p. = 70 – 72 °C. 97% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 16.291 min (major), t_{R2} = 19.877 min (minor)]. [α]_D²⁰ = -55.5 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, J = 8.2 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.56 – 7.48 (m, 3H), 7.25 – 7.20 (m, 1H), 7.17 (td, J = 7.8, 1.2 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.98 – 6.92 (m, 1H), 6.92 – 6.86 (m, 1H), 6.74 (td, J = 7.6, 1.6 Hz, 1H), 6.56 (ddd, J = 17.0, 10.2, 7.8 Hz, 1H), 6.45 (d, J = 7.8 Hz, 1H), 6.11 (d, J = 6.8 Hz, 1H), 5.45 (d, J = 16.6 Hz, 1H), 5.38 (d, J = 10.2 Hz, 1H), 5.26 (d, J = 17.0 Hz, 1H), 4.86 (d, J = 16.6 Hz, 1H), 4.56 (d, J = 7.8 Hz, 1H), 3.41 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.5, 160.9 (d, J = 248.2 Hz), 143.6, 134.0, 133.7, 130.6, 130.1 (d, J = 2.6 Hz), 130.0, 129.7, 128.9, 128.8, 128.4, 127.8, 126.5, 125.9, 125.4, 125.2, 124.2, 124.1, 123.6 (d, J = 2.6 Hz), 123.0 (d, J = 3.8 Hz), 122.5, 120.2, 115.9 (d, J = 23.9 Hz), 109.7, 78.2, 49.0, 41.9. ¹⁹F NMR (471 MHz, CDCl₃) δ -114.7. HRMS (Q-TOF Premier) calcd for C₂₈H₂₃FNO₂ (M+H)⁺: 424.1707; found: 424.1700.

Minor diastereomer:

(S)-3-((R)-1-(2-Fluorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (16.8 mg, 16% yield). m.p. = 58 – 60 °C. 83% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 16.676 min (major), t_{R2} = 24.375 min (minor)]. [α]_D²⁰ = -27.1 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.27 (d, J = 7.4 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.20 – 7.15 (m, 1H), 7.11 – 7.06 (m, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.98 – 6.89 (m, 2H), 6.83 (d, J = 7.2 Hz, 1H), 6.50 – 6.36 (m, 2H), 5.47 (d, J = 17.0 Hz, 1H), 5.45 (d, J = 16.4 Hz, 1H), 5.37 (dd, J = 10.0, 1.4 Hz, 1H), 5.08 (d, J = 16.4 Hz, 1H), 4.47 (d, J = 10.2 Hz, 1H), 3.31 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.5, 160.4 (d, J = 245.7 Hz), 143.3, 133.7, 133.4, 130.8, 129.9, 129.9, 129.4 (d, J = 3.9 Hz), 128.9, 128.7 (d, J = 8.9 Hz), 128.1, 127.7, 126.5, 126.0, 125.2, 125.1 (d, J = 1.9 Hz), 124.8, 124.7, 124.2, 123.9 (d, J = 2.6 Hz), 122.8 (d, J = 1.3

Hz), 121.5, 115.5 (d, $J = 23.9$ Hz), 109.5, 77.9, 49.5, 42.0. ^{19}F NMR (471 MHz, CDCl_3) δ -115.4. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 424.1707; found: 424.1709.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (85.9 mg, 82% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 2:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

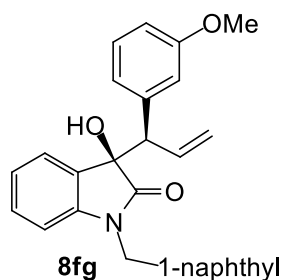
(*R*)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-3-((*R*)-1-(*m*-tolyl)allyl)indolin-2-one (8ff)

Light yellow solid (56.1 mg, 54% yield). m.p. = 58 – 60 °C. >99% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/*i*-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 16.077 min (major), $t_{\text{R}2}$ = 14.230 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -53.7 (*c* 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.61 – 7.58 (m, 1H), 7.55 – 7.47 (m, 2H), 7.17 – 7.08 (m, 3H), 7.01 (dt, $J = 10.0, 7.8$ Hz, 2H), 6.71 – 6.65 (m, 2H), 6.58 (ddd, $J = 17.2, 10.2, 8.4$ Hz, 1H), 6.38 – 6.31 (m, 1H), 5.68 (d, $J = 7.0$ Hz, 1H), 5.42 (d, $J = 10.2$ Hz, 1H), 5.41 (d, $J = 17.0$ Hz, 1H), 5.34 (d, $J = 17.0$ Hz, 1H), 4.80 (d, $J = 16.8$ Hz, 1H), 4.03 (d, $J = 8.4$ Hz, 1H), 3.19 (s, 1H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.6, 143.7, 138.0, 136.6, 134.9, 133.6, 130.5, 130.3, 129.9, 129.4, 128.9, 128.4, 128.2, 128.2, 127.6, 126.3, 126.3, 125.8, 125.6, 125.0, 122.9, 122.6, 122.3, 120.0, 109.7, 78.6, 57.9, 41.7, 21.4. HRMS (Q-TOF Premier) calcd for $\text{C}_{29}\text{H}_{26}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 420.1958; found: 420.1966.

Minor diastereomer:

(*S*)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-3-((*R*)-1-(*m*-tolyl)allyl)indolin-2-one

Light yellow solid (27.4 mg, 26% yield). m.p. = 51 – 53 °C. 92% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 15.837 min (major), $t_{\text{R}2}$ = 18.321 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -14.1 (*c* 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 7.59 – 7.48 (m, 2H), 7.41 – 7.34 (m, 1H), 7.17 – 7.13 (m, 1H), 7.11 – 7.02 (m, 4H), 6.94 (s, 1H), 6.89 – 6.83 (m, 1H), 6.62 (dt, $J = 17.0, 10.2$ Hz, 1H), 6.43 – 6.32 (m, 2H), 5.48 (d, $J = 17.0$ Hz, 1H), 5.45 (d, $J = 16.8$ Hz, 1H), 5.42 (d, $J = 10.2$ Hz, 1H), 4.97 (d, $J = 16.8$ Hz, 1H), 3.95 (d, $J = 10.2$ Hz, 1H), 3.27 (s, 1H), 2.17 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.4, 143.5, 137.9, 136.8, 134.1, 133.6, 130.7, 129.8, 129.8, 129.7, 128.9, 128.7, 128.1, 128.0, 127.8, 126.4, 126.3, 125.9, 125.4, 124.4, 123.5, 122.8, 122.6, 121.2, 109.7, 78.0, 58.4, 41.8, 21.4. HRMS (Q-TOF Premier) calcd for $\text{C}_{29}\text{H}_{26}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 420.1958; found: 420.1961.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (96.8 mg, 89% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 4:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

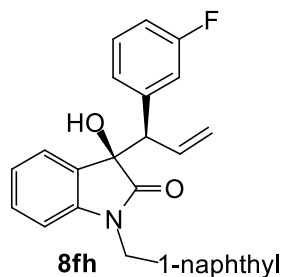
(R)-3-Hydroxy-3-((R)-1-(3-methoxyphenyl)allyl)-1-(naphthalen-1-ylmethyl)indolin-2-one (8fg)

Light yellow solid (76.6 mg, 70% yield). m.p. = 57 – 59 °C. >99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 16.950 min (major), $t_{\text{R}2}$ = 20.491 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -32.3 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 6.8 Hz, 1H), 7.52 (dt, J = 18.8, 7.2 Hz, 2H), 7.18 – 7.11 (m, 2H), 7.06 (td, J = 7.8, 3.6 Hz, 2H), 6.83 (dd, J = 8.2, 2.2 Hz, 1H), 6.62 – 6.55 (m, 2H), 6.40 – 6.31 (m, 2H), 5.81 (d, J = 7.2 Hz, 1H), 5.44 (d, J = 10.2 Hz, 1H), 5.42 (d, J = 17.0 Hz, 1H), 5.34 (d, J = 17.0 Hz, 1H), 4.83 (d, J = 16.8 Hz, 1H), 4.05 (d, J = 8.2 Hz, 1H), 3.46 (s, 3H), 3.10 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.4, 159.3, 143.8, 138.1, 134.8, 133.6, 130.5, 130.0, 129.4, 129.4, 128.9, 128.4, 127.7, 126.4, 125.8, 125.6, 125.0, 122.9, 122.7, 122.3, 122.1, 120.2, 114.3, 113.6, 109.8, 78.5, 57.9, 55.0, 41.7. HRMS (Q-TOF Premier) calcd for $\text{C}_{29}\text{H}_{25}\text{NNaO}_3$ ($\text{M}+\text{Na}$) $^+$: 458.1727; found: 458.1732.

Minor diastereomer:

(S)-3-Hydroxy-3-((R)-1-(3-methoxyphenyl)allyl)-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (17.8 mg, 16% yield). m.p. = 51 – 53 °C. 96% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 44.273 min (minor), $t_{\text{R}2}$ = 58.668 min (major)]. $[\alpha]_{\text{D}}^{20}$ = -100.2 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.38 (dd, J = 6.8, 1.6 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.11 – 7.04 (m, 3H), 6.78 (dd, J = 8.2, 1.8 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 6.65 – 6.55 (m, 2H), 6.45 (d, J = 7.0 Hz, 1H), 6.42 – 6.35 (m, 1H), 5.52 – 5.40 (m, 3H), 4.98 (d, J = 16.6 Hz, 1H), 3.97 (d, J = 10.2 Hz, 1H), 3.58 (s, 3H), 3.28 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.4, 159.2, 143.5, 138.4, 133.9, 133.7, 130.7, 129.8, 129.7, 129.2, 128.9, 128.7, 127.9, 126.4, 125.9, 125.4, 124.3, 123.6, 122.8, 122.6, 121.4, 121.4, 114.4, 113.4, 109.7, 77.9, 58.4, 55.1, 41.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{29}\text{H}_{25}\text{NNaO}_3$ ($\text{M}+\text{Na}$) $^+$: 458.1727; found: 458.1719.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (95.2 mg, 90% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

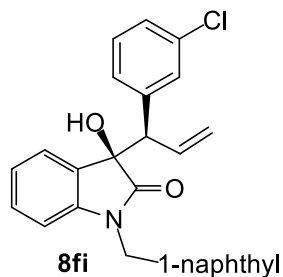
(R)-3-((R)-1-(3-Fluorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fh)

Light yellow solid (70.1 mg, 66% yield). m.p. = 60 – 62 °C. >99% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 11.716 min (major), $t_{\text{R}2}$ = 12.830 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -62.7 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.59 – 7.47 (m, 3H), 7.19 – 7.04 (m, 4H), 6.95 (td, J = 8.4, 2.0 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.61 – 6.52 (m, 2H), 6.40 (d, J = 7.2 Hz, 1H), 5.93 (d, J = 7.0 Hz, 1H), 5.44 (d, J = 10.2 Hz, 1H), 5.36 (d, J = 16.8 Hz, 1H), 5.32 (d, J = 17.6 Hz, 1H), 4.83 (d, J = 16.8 Hz, 1H), 4.10 (d, J = 7.8 Hz, 1H), 3.52 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.5, 162.4 (d, J = 246.4 Hz), 143.5, 139.4 (d, J = 7.1 Hz), 134.3, 133.6, 130.5, 130.2, 129.8, 129.7, 129.4, 128.9, 128.0, 127.8, 126.4, 125.9, 125.4, 125.1, 123.1, 122.8, 122.4, 120.4, 116.2 (d, J = 22.2 Hz), 114.4 (d, J = 21.2 Hz), 109.9, 78.4, 57.3, 41.8. ^{19}F NMR (376 MHz, CDCl_3) δ -112.6. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 424.1707; found: 424.1712.

Minor diastereomer:

(S)-3-((R)-1-(3-Fluorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (22.4 mg, 21% yield). m.p. = 65 – 67 °C. 97% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 30.786 min (minor), $t_{\text{R}2}$ = 32.885 min (major)]. $[\alpha]_{\text{D}}^{20}$ = -33.1 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.30 (dd, J = 7.2, 1.2 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.14 – 7.03 (m, 3H), 6.94 – 6.88 (m, 2H), 6.86 – 6.81 (m, 1H), 6.61 (d, J = 7.0 Hz, 1H), 6.50 (dt, J = 16.8, 10.2 Hz, 1H), 6.44 (d, J = 7.4 Hz, 1H), 5.48 (dd, J = 16.8, 1.2 Hz, 1H), 5.41 (d, J = 10.2 Hz, 1H), 5.41 (d, J = 16.4 Hz, 1H), 5.04 (d, J = 16.4 Hz, 1H), 3.97 (d, J = 10.2 Hz, 1H), 3.23 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.2, 162.4 (d, J = 247.0 Hz), 143.4, 139.7 (d, J = 7.6 Hz), 133.7, 133.5, 130.7, 130.0, 129.7, 129.5 (d, J = 7.6 Hz), 128.9, 128.2, 128.1, 126.5, 125.9, 125.3, 124.9 (d, J = 2.5 Hz), 124.4, 123.7, 123.0, 122.7, 121.7, 116.2 (d, J = 21.4 Hz), 114.1 (d, J = 21.4 Hz), 109.8, 77.8, 58.0, 41.9. ^{19}F NMR (471 MHz, CDCl_3) δ -112.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 424.1707; found: 424.1705.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (101.0 mg, 92% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

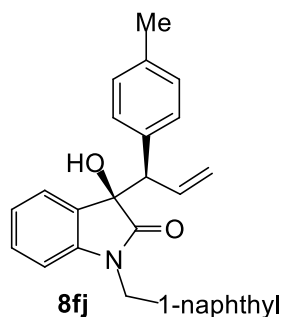
(R)-3-((R)-1-(3-Chlorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fi)

Light yellow solid (74.4 mg, 68% yield). m.p. = 73 – 75 °C. >99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 14.617 min (major), $t_{\text{R}2}$ = 32.144 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -72.4 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 7.8 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.57 (dd, J = 7.2, 1.1 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.24 – 7.21 (m, 1H), 7.17 – 7.01 (m, 4H), 6.80 (d, J = 7.4 Hz, 2H), 6.56 (ddd, J = 17.2, 10.2, 7.8 Hz, 1H), 6.41 (d, J = 7.6 Hz, 1H), 5.90 (d, J = 7.0 Hz, 1H), 5.44 (d, J = 10.2 Hz, 1H), 5.37 (d, J = 16.8 Hz, 1H), 5.30 (d, J = 17.2 Hz, 1H), 4.82 (d, J = 16.8 Hz, 1H), 4.07 (d, J = 7.8 Hz, 1H), 3.54 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.5, 143.5, 138.9, 134.2, 134.0, 133.6, 130.5, 130.2, 129.6, 129.4, 129.4, 128.9, 127.9, 127.8, 127.7, 126.4, 125.9, 125.5, 125.1, 123.1, 122.7, 122.4, 120.5, 109.9, 78.5, 57.3, 41.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 462.1231; found: 462.1237.

Minor diastereomer:

(S)-3-((R)-1-(3-Chlorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (23.8 mg, 22% yield). m.p. = 67 – 69 °C. 94% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 11.332 min (minor), $t_{\text{R}2}$ = 13.763 min (major)]. $[\alpha]_{\text{D}}^{20}$ = -14.2 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.18 (m, 2H), 7.13 – 7.04 (m, 4H), 6.99 (d, J = 7.8 Hz, 1H), 6.62 (d, J = 6.8 Hz, 1H), 6.48 (dt, J = 16.8, 10.2 Hz, 1H), 6.44 (d, J = 7.4 Hz, 1H), 5.47 (d, J = 16.8 Hz, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.40 (d, J = 16.4 Hz, 1H), 5.05 (d, J = 16.4 Hz, 1H), 3.95 (d, J = 10.2 Hz, 1H), 3.25 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.2, 143.3, 139.2, 134.0, 133.7, 133.3, 130.7, 130.1, 129.7, 129.3, 129.3, 128.9, 128.1, 128.1, 127.4, 127.4, 126.5, 125.9, 125.4, 124.4, 123.7, 123.0, 122.7, 121.8, 109.9, 77.8, 58.0, 41.9. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 462.1231; found: 462.1241.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (88.0 mg, 84% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

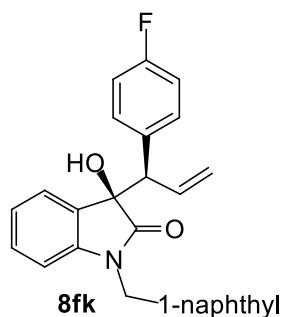
(R)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-(p-tolyl)allyl)indolin-2-one (8fj)

Light yellow solid (65.3 mg, 62% yield). m.p. = 68 – 70 °C. >99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 85/15, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 8.565 min (major), $t_{\text{R}2}$ = 21.535 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -69.8 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.2 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.55 – 7.47 (m, 2H), 7.17 – 7.09 (m, 2H), 6.96 (dd, J = 15.4, 7.8 Hz, 3H), 6.78 (d, J = 8.0 Hz, 2H), 6.59 (ddd, J = 17.2, 10.2, 8.2 Hz, 1H), 6.39 – 6.32 (m, 1H), 5.79 (d, J = 7.0 Hz, 1H), 5.44 (d, J = 17.2 Hz, 1H), 5.41 (d, J = 10.2 Hz, 1H), 5.33 (d, J = 17.0 Hz, 1H), 4.79 (d, J = 16.8 Hz, 1H), 4.06 (d, J = 8.2 Hz, 1H), 3.27 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.6, 143.6, 137.0, 135.0, 133.6, 133.5, 130.5, 129.9, 129.4, 129.3, 129.1, 129.0, 128.9, 128.4, 127.6, 126.4, 125.8, 125.2, 125.1, 122.9, 122.9, 122.4, 119.9, 109.8, 78.6, 57.5, 41.8, 21.3. HRMS (Q-TOF Premier) calcd for $\text{C}_{29}\text{H}_{25}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 442.1778; found: 442.1787.

Minor diastereomer:

(S)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-(p-tolyl)allyl)indolin-2-one

Light yellow solid (21.2 mg, 20% yield). m.p. = 59 – 61 °C. >99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 16.741 min (major), $t_{\text{R}2}$ = 19.142 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -32.3 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.40 – 7.33 (m, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.97 (q, J = 8.4 Hz, 4H), 6.59 (dt, J = 17.0, 10.2 Hz, 1H), 6.46 (d, J = 7.2 Hz, 1H), 6.39 (d, J = 7.0 Hz, 1H), 5.47 (d, J = 17.0 Hz, 2H), 5.41 (dd, J = 10.2, 1.2 Hz, 1H), 4.98 (d, J = 17.0 Hz, 1H), 3.95 (d, J = 10.2 Hz, 1H), 3.22 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.5, 143.5, 136.7, 134.2, 133.9, 133.7, 130.7, 129.7, 129.7, 129.0, 129.0, 128.9, 127.9, 126.5, 125.9, 125.1, 124.4, 123.8, 122.8, 122.7, 121.1, 109.7, 77.9, 58.0, 41.8, 21.1. HRMS (Q-TOF Premier) calcd for $\text{C}_{29}\text{H}_{25}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 442.1778; found: 442.1781.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (99.5 mg, 94% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 2:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

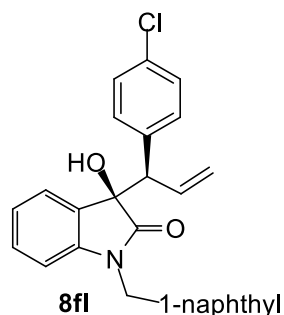
(R)-3-((R)-1-(4-Fluorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fk)

Light yellow solid (65.2 mg, 62% yield). m.p. = 66 – 68 °C. >99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 80/20, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 8.596 min (major), $t_{\text{R}2}$ = 19.036 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -54.5 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.18 – 7.07 (m, 3H), 6.88 – 6.78 (m, 4H), 6.59 (ddd, J = 17.6, 10.2, 7.8 Hz, 1H), 6.39 (d, J = 7.6 Hz, 1H), 5.79 (d, J = 7.2 Hz, 1H), 5.44 (d, J = 10.2 Hz, 1H), 5.40 (d, J = 16.8 Hz, 1H), 5.29 (d, J = 17.6 Hz, 1H), 4.80 (d, J = 16.8 Hz, 1H), 4.09 (d, J = 7.8 Hz, 1H), 3.35 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.5, 162.2 (d, J = 247.0 Hz), 143.6, 134.6, 133.6, 132.5 (d, J = 3.8 Hz), 131.2 (d, J = 8.8 Hz), 130.5, 130.1, 129.3, 128.9, 128.0, 127.9, 126.4, 125.9, 125.2, 125.1, 123.0, 122.7, 122.3, 120.2, 115.2 (d, J = 21.4 Hz), 109.8, 78.6, 56.8, 41.7. ^{19}F NMR (471 MHz, CDCl_3) δ -114.57. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 424.1707; found: 424.1717.

Minor diastereomer:

(S)-3-((R)-1-(4-Fluorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (31.9 mg, 30% yield). m.p. = 62 – 64 °C. 95% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 16.660 min (major), $t_{\text{R}2}$ = 19.045 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -15.8 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.35 (dd, J = 7.2, 1.2 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.13 – 6.99 (m, 4H), 6.86 – 6.79 (m, 2H), 6.59 (dt, J = 16.8, 10.2 Hz, 1H), 6.43 (t, J = 7.8 Hz, 2H), 5.49 (dd, J = 16.8, 1.2 Hz, 1H), 5.43 (d, J = 16.6 Hz, 1H), 5.44 (d, J = 10.2, 2.0 Hz, 1H), 4.98 (d, J = 16.6 Hz, 1H), 3.96 (d, J = 10.2 Hz, 1H), 3.22 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.2, 161.9 (d, J = 247.0 Hz), 143.4, 133.8, 133.7, 132.8 (d, J = 2.6 Hz), 130.7, 130.6, 130.0, 129.6, 128.9, 128.4, 128.1, 126.5, 125.9, 125.2, 124.2, 123.8, 123.0, 122.7, 121.6, 115.0 (d, J = 21.4 Hz), 109.8, 77.9, 57.6, 41.9. ^{19}F NMR (471 MHz, CDCl_3) δ -115.1. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$: 424.1707; found: 424.1711.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (102.1 mg, 93% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

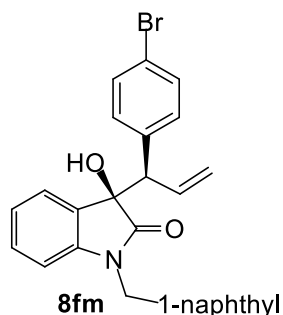
(R)-3-((R)-1-(4-Chlorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fl)

Light yellow solid (75.2 mg, 68% yield). m.p. = 66 – 68 °C. >99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 14.121 min (major), $t_{\text{R}2}$ = 29.391 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -87.2 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 7.8 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.56 – 7.49 (m, 2H), 7.19 – 7.09 (m, 5H), 6.81 (d, J = 8.4 Hz, 2H), 6.58 (ddd, J = 17.8, 10.2, 7.8 Hz, 1H), 6.39 (d, J = 7.6 Hz, 1H), 5.76 (d, J = 7.2 Hz, 1H), 5.46 – 5.41 (m, 2H), 5.30 (d, J = 17.0 Hz, 1H), 4.80 (d, J = 17.0 Hz, 1H), 4.08 (d, J = 7.8 Hz, 1H), 3.28 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.4, 143.6, 135.3, 134.4, 133.6, 133.4, 130.9, 130.4, 130.2, 129.2, 128.9, 128.6, 127.9, 126.4, 125.9, 125.4, 125.1, 123.1, 122.7, 122.3, 120.4, 109.9, 78.4, 56.9, 41.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 462.1231; found: 462.1235.

Minor diastereomer:

(S)-3-((R)-1-(4-Chlorophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (24.3 mg, 22% yield). m.p. = 62 – 64 °C. 98% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 11.591 min (minor), $t_{\text{R}2}$ = 14.550 min (major)]. $[\alpha]_{\text{D}}^{20}$ = -25.1 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.36 (d, J = 6.8 Hz, 1H), 7.29 – 7.21 (m, 1H), 7.16 – 7.05 (m, 4H), 7.01 (d, J = 8.4 Hz, 2H), 6.58 (dt, J = 16.0, 10.2 Hz, 1H), 6.42 (d, J = 7.6 Hz, 1H), 6.39 (d, J = 7.2 Hz, 1H), 5.59 (d, J = 16.8 Hz, 1H), 5.47 (d, J = 16.0 Hz, 1H), 5.44 (d, J = 10.2 Hz, 1H), 4.96 (d, J = 16.8 Hz, 1H), 3.96 (d, J = 10.2 Hz, 1H), 3.26 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.2, 143.4, 135.6, 133.7, 133.5, 133.1, 130.7, 130.5, 130.0, 129.5, 128.9, 128.4, 128.3, 128.1, 126.5, 125.9, 125.2, 124.2, 123.7, 123.0, 122.6, 121.8, 109.9, 77.8, 57.7, 41.9. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 462.1231; found: 462.1230.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (111.1 mg, 92% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 5:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

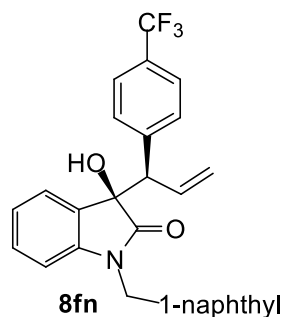
(R)-3-((R)-1-(4-Bromophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fm)

Light yellow solid (90.7 mg, 75% yield). m.p. = 70 – 72 °C. 98% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 80/20, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 8.516 min (major), $t_{\text{R}2}$ = 24.404 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -20.5 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 7.6 Hz, 1H), 7.88 – 7.80 (m, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.27 – 7.19 (m, 3H), 7.19 – 7.07 (m, 2H), 6.74 (d, J = 8.2 Hz, 2H), 6.58 (ddd, J = 17.8, 10.2, 7.8 Hz, 1H), 6.39 (d, J = 7.6 Hz, 1H), 5.81 (d, J = 7.0 Hz, 1H), 5.43 (d, J = 10.2 Hz, 1H), 5.42 (d, J = 17.0 Hz, 1H), 5.28 (d, J = 17.0 Hz, 1H), 4.79 (d, J = 17.8 Hz, 1H), 4.07 (d, J = 7.8 Hz, 1H), 3.44 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.5, 143.6, 135.8, 134.3, 133.6, 131.5, 131.3, 130.4, 130.2, 129.2, 128.9, 127.9, 127.9, 126.4, 125.9, 125.5, 125.1, 123.1, 122.7, 122.3, 121.6, 120.3, 109.9, 78.4, 57.0, 41.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{BrNO}_2$ ($\text{M}+\text{H}$) $^+$: 484.0907; found: 484.0911.

Minor diastereomer:

(S)-3-((R)-1-(4-Bromophenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (17.6 mg, 15% yield). m.p. = 62 – 64 °C. 91% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 15.347 min (minor), $t_{\text{R}2}$ = 20.825 min (major)]. $[\alpha]_{\text{D}}^{20}$ = -46.4 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.56 (dd, J = 18.0, 7.6 Hz, 2H), 7.35 (d, J = 6.8 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.14 – 7.04 (m, 2H), 6.95 (d, J = 8.2 Hz, 2H), 6.57 (dt, J = 17.0, 10.2 Hz, 1H), 6.48 – 6.36 (m, 2H), 5.48 (d, J = 17.0 Hz, 1H), 5.47 (d, J = 16.6 Hz, 1H), 5.46 (d, J = 10.2 Hz, 1H), 4.96 (d, J = 16.6 Hz, 1H), 3.94 (d, J = 10.2 Hz, 1H), 3.26 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.2, 143.4, 136.1, 133.7, 133.4, 131.3, 130.8, 130.7, 130.1, 129.5, 128.9, 128.3, 128.1, 126.5, 125.9, 125.3, 124.2, 123.7, 123.0, 122.6, 121.8, 121.3, 109.9, 77.7, 57.8, 41.9. HRMS (Q-TOF Premier) calcd for $\text{C}_{28}\text{H}_{23}\text{BrNO}_2$ ($\text{M}+\text{H}$) $^+$: 484.0907; found: 484.0915.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (106.4 mg, 90% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 4/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

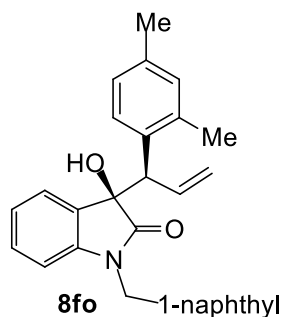
(R)-3-hydroxy-1-(Naphthalen-1-ylmethyl)-3-((R)-1-(4-(trifluoromethyl)phenyl)allyl)indolin-2-one (8fn)

Yellow solid (78.4 mg, 66% yield). m.p. = 63 – 65 °C. 98% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 7.575 min (major), t_{R2} = 9.791 min (minor)]. [α]_D²⁰ = -55.3 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.88 – 7.80 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.55 – 7.46 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.10 (m, 2H), 7.05 – 7.00 (m, 3H), 6.60 (ddd, *J* = 17.2, 10.2, 7.8 Hz, 1H), 6.42 (d, *J* = 7.2 Hz, 1H), 5.98 (d, *J* = 7.2 Hz, 1H), 5.45 (d, *J* = 10.2 Hz, 1H), 5.35 (d, *J* = 16.8 Hz, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 4.82 (d, *J* = 16.8 Hz, 1H), 4.16 (d, *J* = 7.8 Hz, 1H), 3.50 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 177.4, 143.5, 141.0, 134.1, 133.6, 130.5, 130.3, 129.9, 129.8, 129.5, 129.4, 129.2, 128.9, 128.0, 127.9, 126.4, 125.9, 125.4, 125.2 (q, *J* = 3.7 Hz), 125.1, 125.1, 123.2, 122.8, 122.4, 120.6, 110.1, 78.3, 57.4, 41.9. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.2. HRMS (Q-TOF Premier) calcd for C₂₉H₂₂F₃NNaO₂ (M+Na)⁺: 496.1495; found: 496.1498.

Minor diastereomer:

(S)-3-hydroxy-1-(Naphthalen-1-ylmethyl)-3-((R)-1-(4-(trifluoromethyl)phenyl)allyl)indolin-2-one

Yellow solid (25.4 mg, 21% yield). m.p. = 84 – 86 °C. 97% ee, HPLC [DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 7.747 min (major), t_{R2} = 10.366 min (minor)]. [α]_D²⁰ = -24.9 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.56 (dt, *J* = 14.8, 7.0 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 7.2 Hz, 1H), 6.53 (dt, *J* = 17.0, 10.2 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.49 (d, *J* = 17.0 Hz, 1H), 5.46 (d, *J* = 16.4 Hz, 1H), 5.43 (d, *J* = 10.2 Hz, 1H), 4.99 (d, *J* = 16.4 Hz, 1H), 4.03 (d, *J* = 10.2 Hz, 1H), 3.24 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.1, 143.3, 141.3, 133.7, 133.2, 130.7, 130.2, 129.7, 129.6, 129.5, 129.2, 128.9, 128.2, 128.0, 126.5, 126.0, 125.1, 125.0 (q, *J* = 3.8 Hz), 124.3, 123.8, 123.0, 122.7, 122.0, 109.9, 77.7, 58.1, 42.0. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.4. HRMS (Q-TOF Premier) calcd for C₂₉H₂₂F₃NNaO₂ (M+Na)⁺: 496.1495; found: 496.1496.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (83.4 mg, 77% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 8:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

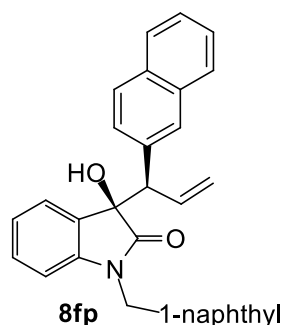
(R)-3-((R)-1-(2,4-Dimethylphenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fo)

Light yellow solid (72.7 mg, 67% yield). m.p. = 56 – 58 °C. 98% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 11.833 min (major), $t_{\text{R}2}$ = 26.739 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -27.7 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.2 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.51 (td, J = 13.6, 6.8 Hz, 2H), 7.18 – 7.10 (m, 2H), 6.91 (dd, J = 14.2, 7.4 Hz, 2H), 6.66 (s, 1H), 6.62 – 6.50 (m, 2H), 6.36 (d, J = 6.8 Hz, 1H), 5.77 (d, J = 6.8 Hz, 1H), 5.45 (d, J = 16.8 Hz, 1H), 5.39 (d, J = 10.2 Hz, 1H), 5.31 (d, J = 17.0 Hz, 1H), 4.80 (d, J = 16.8 Hz, 1H), 4.00 (d, J = 8.4 Hz, 1H), 3.27 (d, J = 8.4 Hz, 1H), 2.25 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.7, 143.7, 136.6, 135.5, 135.2, 134.1, 133.5, 130.8, 130.5, 129.9, 129.6, 129.5, 128.9, 128.6, 127.6, 126.6, 126.3, 125.8, 125.2, 125.0, 122.9, 122.8, 122.4, 119.8, 109.7, 78.5, 57.5, 41.8, 19.7, 19.6. HRMS (Q-TOF Premier) calcd for $\text{C}_{30}\text{H}_{27}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 456.1934; found: 456.1927.

Minor diastereomer:

(S)-3-((R)-1-(2,4-Dimethylphenyl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (8.6 mg, 8% yield). m.p. = 44 – 46 °C. 91% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 13.708 min (major), $t_{\text{R}2}$ = 15.835 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -7.7 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.54 (dt, J = 14.6, 6.8 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.13 – 7.04 (m, 3H), 6.94 – 6.89 (m, 2H), 6.81 (d, J = 7.8 Hz, 1H), 6.57 (dt, J = 17.0, 10.2 Hz, 1H), 6.43 (d, J = 7.0 Hz, 1H), 6.37 (d, J = 6.8 Hz, 1H), 5.48 (d, J = 14.4 Hz, 1H), 5.45 (d, J = 14.4 Hz, 1H), 5.38 (d, J = 10.2 Hz, 1H), 4.96 (d, J = 17.0 Hz, 1H), 3.93 (d, J = 10.2 Hz, 1H), 3.27 (s, 1H), 2.23 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.6, 143.5, 136.4, 135.4, 134.4, 134.4, 133.6, 130.7, 130.4, 129.7, 129.7, 129.5, 128.9, 128.8, 127.8, 126.6, 126.4, 125.9, 125.2, 124.4, 123.6, 122.7, 122.6, 121.0, 109.7, 78.0, 58.0, 41.8, 19.7, 19.5. HRMS (Q-TOF Premier) calcd for $\text{C}_{30}\text{H}_{27}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 456.1934; found: 456.1941.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (92.1 mg, 81% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

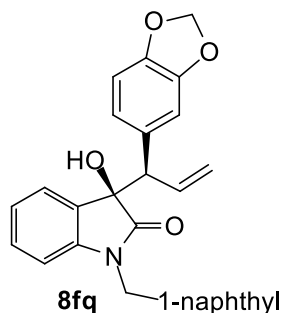
(R)-3-hydroxy-1-(Naphthalen-1-ylmethyl)-3-((R)-1-(naphthalen-2-yl)allyl)indolin-2-one (8fp)

Light yellow solid (67.8 mg, 60% yield). m.p. = 89 – 91 °C. >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 80/20, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 18.047 min (major), $t_{\text{R}2}$ = 32.285 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -82.6 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 8.0 Hz, 2H), 7.76 – 7.71 (m, 1H), 7.71 – 7.65 (m, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.53 – 7.37 (m, 6H), 7.22 – 7.12 (m, 2H), 6.94 (d, J = 8.4 Hz, 1H), 6.74 (ddd, J = 16.8, 10.2, 7.8 Hz, 1H), 6.33 – 6.23 (m, 1H), 5.84 (t, J = 7.8 Hz, 1H), 5.47 (d, J = 10.2 Hz, 1H), 5.39 (d, J = 16.8 Hz, 1H), 5.36 (d, J = 16.8 Hz, 1H), 5.22 (d, J = 7.2 Hz, 1H), 4.71 (d, J = 16.8 Hz, 1H), 4.29 (d, J = 7.8 Hz, 1H), 3.34 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.7, 143.7, 134.9, 134.3, 133.4, 133.4, 132.8, 130.2, 130.1, 128.9, 128.9, 128.8, 128.3, 128.2, 127.8, 127.6, 127.3, 127.1, 126.2, 126.1, 126.1, 125.6, 125.2, 124.9, 123.0, 122.4, 122.2, 120.3, 109.8, 78.7, 57.9, 41.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{32}\text{H}_{25}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 478.1778; found: 478.1783.

Minor diastereomer:

(S)-3-hydroxy-1-(Naphthalen-1-ylmethyl)-3-((R)-1-(naphthalen-2-yl)allyl)indolin-2-one

Light yellow solid (22.4 mg, 20% yield). m.p. = 126 – 128 °C. 94% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 85/15, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 27.613 min (minor), $t_{\text{R}2}$ = 39.235 min (major)]. $[\alpha]_{\text{D}}^{20}$ = -19.9 (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 8.2 Hz, 1H), 7.80 (t, J = 8.0 Hz, 2H), 7.62 (t, J = 10.2 Hz, 3H), 7.56 – 7.39 (m, 6H), 7.17 (d, J = 8.6 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.79 (dt, J = 17.0, 10.2 Hz, 1H), 6.43 (t, J = 7.8 Hz, 1H), 6.28 (d, J = 7.0 Hz, 1H), 6.05 (d, J = 7.0 Hz, 1H), 5.54 (d, J = 17.0 Hz, 1H), 5.48 (d, J = 10.2 Hz, 1H), 5.44 (d, J = 16.8 Hz, 1H), 4.92 (d, J = 16.8 Hz, 1H), 4.17 (d, J = 10.2 Hz, 1H), 3.34 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.4, 143.4, 134.6, 134.1, 133.6, 133.2, 132.5, 130.5, 129.9, 129.3, 128.8, 128.6, 128.1, 128.0, 127.6, 127.6, 127.5, 127.4, 126.3, 126.1, 126.0, 125.8, 125.1, 124.4, 123.3, 122.9, 122.5, 121.5, 109.8, 78.1, 58.5, 41.8. HRMS (Q-TOF Premier) calcd for $\text{C}_{32}\text{H}_{25}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$: 478.1778; found: 478.1777.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (98.8 mg, 88% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 4:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

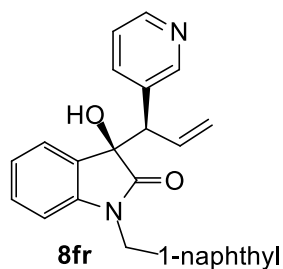
(R)-3-((R)-1-(Benzo[d][1,3]dioxol-5-yl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fq)

Light yellow solid (78.1 mg, 70% yield). m.p. = 73 – 75 °C. >99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 21.549 min (major), t_{R2} = 65.262 min (minor)]. [α]_D²⁰ = -70.5 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.46 (m, 3H), 7.20 – 7.07 (m, 3H), 6.60 (d, *J* = 8.2 Hz, 1H), 6.54 (ddd, *J* = 17.0, 10.2, 7.8 Hz, 1H), 6.47 – 6.38 (m, 2H), 6.30 (s, 1H), 5.93 (d, *J* = 7.0 Hz, 1H), 5.88 (d, *J* = 1.0 Hz, 1H), 5.83 (d, *J* = 1.0 Hz, 1H), 5.48 (d, *J* = 16.8 Hz, 1H), 5.41 (d, *J* = 10.2 Hz, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 4.81 (d, *J* = 16.8 Hz, 1H), 4.02 (d, *J* = 7.8 Hz, 1H), 3.38 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 177.6, 147.4, 146.9, 143.7, 134.9, 133.6, 130.6, 130.5, 130.1, 129.6, 128.9, 128.3, 127.8, 126.4, 125.8, 125.1, 125.0, 123.0, 123.0, 122.9, 122.4, 119.9, 109.8, 109.7, 108.2, 100.9, 78.5, 57.3, 41.7. HRMS (Q-TOF Premier) calcd for C₂₉H₂₃NNaO₄ (M+Na)⁺: 472.1519; found: 472.1526.

Minor diastereomer:

(S)-3-((R)-1-(Benzo[d][1,3]dioxol-5-yl)allyl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

Light yellow solid (17.9 mg, 16% yield). m.p. = 80 – 82 °C. 95% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 27.704 min (major), t_{R2} = 30.860 min (minor)]. [α]_D²⁰ = -19.5 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.13 – 7.04 (m, 2H), 6.63 – 6.42 (m, 6H), 5.89 (s, 2H), 5.48 (d, *J* = 16.6 Hz, 1H), 5.45 (d, *J* = 16.8 Hz, 1H), 5.40 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 16.6 Hz, 1H), 3.91 (d, *J* = 10.2 Hz, 1H), 3.21 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 177.4, 147.4, 146.7, 143.5, 134.1, 133.7, 130.8, 130.7, 129.9, 129.7, 128.9, 128.6, 128.0, 126.5, 125.9, 125.1, 124.3, 123.7, 122.9, 122.7, 122.5, 121.2, 109.8, 109.6, 108.0, 101.0, 77.9, 57.9, 41.8. HRMS (Q-TOF Premier) calcd for C₂₉H₂₃NNaO₄ (M+Na)⁺: 472.1519; found: 472.1530.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1) afforded the product including both of the diastereoisomers (84.2 mg, 83% overall yield). ^1H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO_2 column chromatography (petroleum ether/ethyl acetate = 2/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

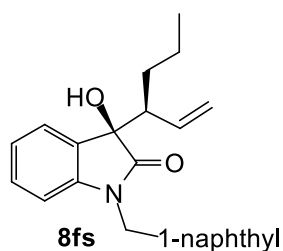
(R)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-(pyridin-3-yl)allyl)indolin-2-one (8fr)

Light yellow solid (62.4 mg, 61% yield). m.p. = 185 – 187 °C. >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 85/15, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 41.983 min (minor), $t_{\text{R}2}$ = 58.668 min (major)]. $[\alpha]_{\text{D}}^{20}$ = -49.6 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 8.42 (d, J = 4.6 Hz, 1H), 8.12 (s, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.58 – 7.45 (m, 3H), 7.19 – 7.06 (m, 4H), 6.99 (dd, J = 7.8, 4.8 Hz, 1H), 6.58 (ddd, J = 17.6, 10.2, 7.6 Hz, 1H), 6.41 (d, J = 7.8 Hz, 1H), 6.07 (d, J = 7.2 Hz, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.26 (d, J = 16.8 Hz, 1H), 5.22 (d, J = 17.6 Hz, 1H), 4.83 (d, J = 16.8 Hz, 1H), 4.07 (d, J = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.3, 150.5, 148.5, 143.3, 137.2, 133.8, 133.6, 132.8, 130.5, 130.3, 129.5, 128.9, 128.0, 127.9, 126.5, 125.9, 125.4, 125.1, 123.2, 123.1, 123.1, 122.4, 120.5, 109.9, 78.3, 55.1, 41.7. HRMS (Q-TOF Premier) calcd for $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 407.1754; found: 407.1749.

Minor diastereomer:

(S)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-3-((R)-1-(pyridin-3-yl)allyl)indolin-2-one

Light yellow solid (20.3 mg, 20% yield). m.p. = 99 – 101 °C. 99% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; $t_{\text{R}1}$ = 25.045 min (major), $t_{\text{R}2}$ = 38.781 min (minor)]. $[\alpha]_{\text{D}}^{20}$ = -26.4 (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 8.40 (d, J = 4.0 Hz, 1H), 8.28 (s, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.59 – 7.50 (m, 3H), 7.25 – 7.17 (m, 2H), 7.12 – 7.01 (m, 3H), 6.75 (d, J = 7.0 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 6.37 (dt, J = 17.0, 10.2 Hz, 1H), 5.46 (d, J = 17.0 Hz, 1H), 5.38 (d, J = 10.2 Hz, 1H), 5.38 (d, J = 16.6 Hz, 1H), 5.05 (d, J = 16.6 Hz, 1H), 4.01 (d, J = 10.2 Hz, 1H), 3.80 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.2, 150.5, 148.3, 143.2, 136.5, 133.7, 133.2, 132.8, 130.8, 130.1, 129.8, 128.9, 128.2, 128.0, 126.6, 126.0, 125.2, 124.6, 124.1, 123.1, 123.0, 122.8, 121.9, 109.9, 77.8, 55.6, 42.0. HRMS (Q-TOF Premier) calcd for $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 407.1754; found: 407.1758.



Purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product including both of the diastereoisomers (83.5 mg, 90% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 3:1. Then the diastereoisomers were further separated by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) to give the major diastereomer and the minor diastereomer respectively.

Major diastereomer:

(R)-3-((S)-Hex-1-en-3-yl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (8fs)

Light yellow oil (61.3 mg, 66% yield). 93% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 11.511 min (major), t_{R2} = 29.034 min (minor)]. [α]_D²⁰ = 22.8 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.58 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.40 – 7.35 (m, 2H), 7.34 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.17 (td, *J* = 7.8, 1.2 Hz, 1H), 7.04 (td, *J* = 7.6, 0.8 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.83 (dt, *J* = 17.0, 10.2 Hz, 1H), 5.63 (d, *J* = 16.2 Hz, 1H), 5.36 (dd, *J* = 10.2, 1.7 Hz, 1H), 5.32 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.15 (d, *J* = 16.2 Hz, 1H), 2.84 (s, 1H), 2.81 – 2.72 (m, 1H), 1.31 – 1.10 (m, 4H), 0.73 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 177.9, 143.5, 135.6, 133.9, 131.0, 130.4, 129.5, 129.1, 128.9, 128.5, 126.6, 126.1, 125.2, 125.1, 124.7, 123.1, 122.9, 120.8, 109.9, 77.6, 52.0, 42.4, 30.3, 20.6, 13.8. HRMS (Q–TOF Premier) calcd for C₂₅H₂₆NO₂ (M+H)⁺: 372.1958; found: 372.1957.

Minor diastereomer:

(S)-3-((S)-Hex-1-en-3-yl)-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

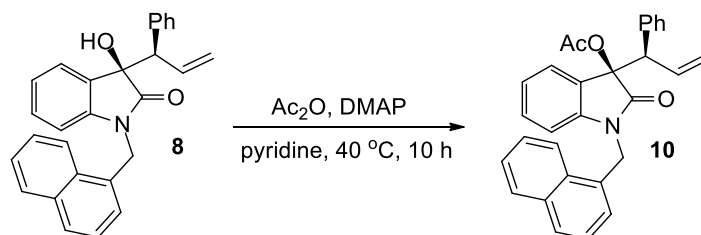
Light yellow oil (18.9 mg, 20% yield). 98% ee, HPLC [DAICEL CHIRALPAK OD-H, hexane/i-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 11.689 min (minor), t_{R2} = 28.521 min (major)]. [α]_D²⁰ = -23.0 (c 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 5.73 (dt, *J* = 17.2, 9.8 Hz, 1H), 5.54 (d, *J* = 16.2 Hz, 1H), 5.31 (d, *J* = 17.0 Hz, 1H), 5.29 (d, *J* = 9.8 Hz, 1H), 5.14 (d, *J* = 16.2 Hz, 1H), 3.00 (s, 1H), 2.65 (t, *J* = 10.4 Hz, 1H), 1.44 – 1.27 (m, 4H), 0.81 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 177.9, 143.8, 136.0, 133.8, 131.0, 130.3, 129.7, 129.0, 128.9, 128.3, 126.5, 126.0, 125.2, 124.6, 124.1, 123.1, 123.0, 121.1, 109.7, 77.5, 53.0, 42.1, 30.0, 20.6, 13.8. HRMS (Q–TOF Premier) calcd for C₂₅H₂₆NO₂ (M+H)⁺: 372.1958; found: 372.1962.

4. Procedure for the Scale-up Experiment

A flame dried Schlenk tube was cooled to rt and filled with N₂. To this flask were added [Ir(COD)Cl]₂ (17.0 mg, 0.025 mmol, 2 mol%), phosphoramidite ligand **L2** (29.5 mg, 0.050 mmol, 4 mol%), THF (2.5 mL) and *n*-propylamine (2.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a pale yellow solid. 3-Hydroxyoxindoles (1.25 mmol), allylic acetate (1.50 mmol), 4Å MS (500 mg), TEA (1 equiv) and THF (7.5 mL) were then added. The reaction mixture was stirred at rt for 24 h. The crude reaction mixture was concentrated by rotary evaporation. The residue was then purified by SiO₂ column chromatography (petroleum ether/ethyl acetate = 5/1) afforded the product including both of the diastereoisomers (458.4 mg, 90% overall yield). ¹H NMR analysis of the diastereoisomers showed a dr of 5:1. The ee values were determined by HPLC using the Daicel chiral column. The ee value of the major diastereomer is 98%.

5. Procedures for the Transformations of the 3-Allyl-3-hydroxyoxindoles

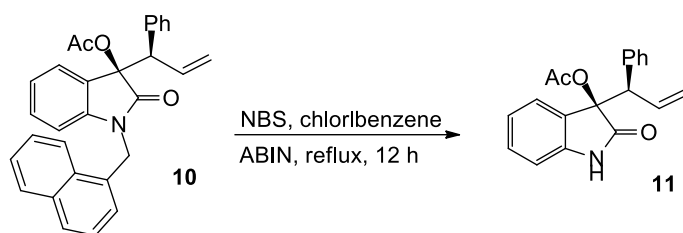
(*R*)-1-(Naphthalen-1-ylmethyl)-2-oxo-3-((*R*)-1-phenylallyl)indolin-3-yl acetate (**10**)⁵



DMAP (12.2 mg, 0.10 mmol) and acetic anhydride (0.045 mL, 0.40 mmol) were added to a stirred solution of **8** (91.0 mg, 0.20 mmol) in pyridine (2 mL). The resulting mixture was stirred at 40 °C for 10 h, after which time the reaction mixture was added to H₂O. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with H₂O, brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product purified by column chromatography (silica) to afford **10** (87.6 mg, 98% yield) as a light yellow oil.

ee = 99%, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 80/20, 220 nm, 1 mL/min; *t*_{R1} = 8.706 min (minor), *t*_{R2} = 35.632 min (major)]. [α]_D²⁰ = -64.7 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.41 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.20 – 7.03 (m, 5H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.54 (ddd, *J* = 17.2, 10.2, 7.8 Hz, 1H), 6.30 (d, *J* = 7.6 Hz, 1H), 6.10 – 5.99 (m, 1H), 5.39 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.30 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.18 (d, *J* = 17.0 Hz, 1H), 4.89 (d, *J* = 17.0 Hz, 1H), 4.15 (d, *J* = 7.8 Hz, 1H), 2.15 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 174.4, 168.9, 144.4, 135.5, 134.5, 133.6, 130.4, 130.1, 129.8, 129.8, 128.8, 128.2, 127.6, 127.4, 126.2, 125.7, 125.7, 125.5, 123.8, 122.9, 122.4, 122.3, 119.7, 109.6, 81.9, 55.3, 41.9, 20.8. HRMS (Q-TOF Premier) calcd for C₃₀H₂₅NNaO₃ (M+Na)⁺: 470.1727; found: 470.1721.

(*R*)-2-Oxo-3-((*R*)-1-phenylallyl)indolin-3-yl acetate (**11**)⁶

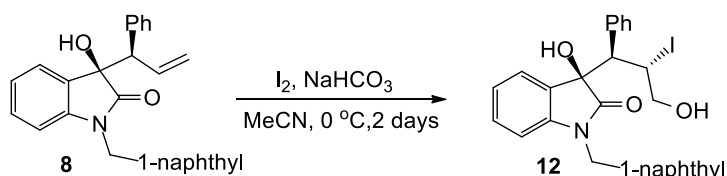


A solution of **10** (44.7 mg, 0.100 mmol) in chlorobenzene (3 mL) containing NBS (21.36 mg, 0.120 mmol) and AIBN (3.28 mg, 0.020 mmol) was heated to reflux under a nitrogen atmosphere. After 4 h further AIBN (0.1 equiv.) and NBS (0.2 equiv.) were added. The solution was heated overnight then cooled, filtered and concentrated. Diethyl ether (2 mL) and water (4 mL) were added to the residue which was stirred for 4 h, the organic layer separated, dried (MgSO₄), evaporated and the crude product purified by column chromatography (silica) to afford **11** (22.4 mg, 73% yield) as a white solid.

m.p. = 148 – 150 °C. ee = 99%, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 90/10, 220 nm, 1 mL/min; *t*_{R1} = 19.717 min (major), *t*_{R2} = 22.114 min (minor)]. [α]_D²⁰ = -38.7 (*c* 1.0, CHCl₃). ¹H

NMR (400 MHz, CDCl₃) δ 7.26 (s, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.14 (d, J = 7.1 Hz, 1H), 7.05 (m, 4H), 6.75 (d, J = 7.3 Hz, 2H), 6.62 (d, J = 7.8 Hz, 1H), 6.44 (ddd, J = 17.0, 10.2, 7.8 Hz, 1H), 5.34 (d, J = 10.2 Hz, 1H), 5.22 (d, J = 17.0 Hz, 1H), 3.96 (d, J = 7.8 Hz, 1H), 2.11 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 174.9, 168.8, 141.4, 135.4, 134.3, 129.9, 129.5, 127.9, 127.5, 125.9, 124.2, 122.2, 119.5, 109.8, 81.7, 55.3, 20.7 HRMS (Q-TOF Premier) calcd for C₁₉H₁₈NO₃ (M+H)⁺: 308.1281; found: 308.1276.

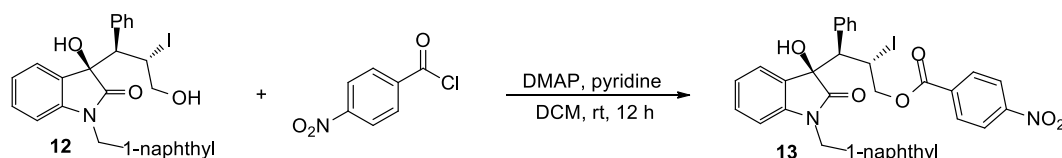
(R)-3-Hydroxy-3-((1R,2S)-3-hydroxy-2-iodo-1-phenylpropyl)-1-(naphthalen-1-ylmethyl)indolin-2-one (12)⁷



40.5 mg (0.100 mmol) of **8** was taken in 10 mL round bottom flask and it was dissolved in 3 mL of dry acetonitrile. Then 16.5 mg (0.13 mmol) of iodine and 25.2 mg (0.30 mmol) of sodium bicarbonate were added to the stirred solution of **8** under argon atm at 0 °C. The reaction was continued to stir for 2 days at 0 °C and quenched with ice cold sodium sulfite then extracted with ethyl acetate twice (20 mL). The organic fractions were combined and dried with anhydrous Na₂SO₄ followed by rotary evaporation yielded the crude product of **12**. Then it was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **12** as a white solid of a white solid (45.0 mg, 82% yield).

m.p. = 63 – 65 °C. ee = 98%, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 90/10, 220 nm, 1 mL/min; t_{R1} = 26.619 min (major), t_{R2} = 40.525 min (minor)]. $[\alpha]_D^{20}$ = -33.0 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, J = 5.6, 3.0 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.59 – 7.43 (m, 2H), 7.32 (d, J = 7.4 Hz, 1H), 7.25 – 7.07 (m, 4H), 6.99 (t, J = 7.6 Hz, 1H), 6.76 (s, 2H), 6.41 – 6.27 (m, 1H), 5.63 (d, J = 7.0 Hz, 1H), 5.15 (d, J = 16.8 Hz, 1H), 5.05 – 4.97 (m, 1H), 4.93 (s, 1H), 4.83 – 4.67 (m, 2H), 4.47 (dd, J = 12.6, 6.0 Hz, 1H), 4.34 (s, 1H), 3.99 (d, J = 11.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 177.1, 143.7, 139.5, 133.6, 130.5, 130.3, 129.0, 128.9, 128.2, 128.0, 127.7, 126.8, 126.4, 126.0, 125.8, 125.6, 123.5, 122.6, 122.2, 110.2, 79.2, 69.1, 58.8, 42.0, 41.8, 29.7. HRMS (Q-TOF Premier) calcd for C₂₈H₂₅INO₃ (M+H)⁺: 550.0874; found: 550.0869.

(2S,3R)-3-((R)-3-Hydroxy-1-(naphthalen-1-ylmethyl)-2-oxoindolin-3-yl)-2-iodo-3-phenylpropyl 4-nitrobenzoate (13)



(*R*)-3-Hydroxy-3-((1*R*,2*S*)-3-hydroxy-2-iodo-1-phenylpropyl)-1-(naphthalen-1-ylmethyl)indolin-2-one (**12**) (24.7 mg, 0.045 mmol) and DMAP (3 mg, 0.0246 mmol) was dissolved in dry pyridine (1.5 mL), cooled to 0 °C, then *p*-NO₂C₆H₄COCl (16.9 mg, 0.060 mmol) in CH₂Cl₂ (0.5 mL) was added

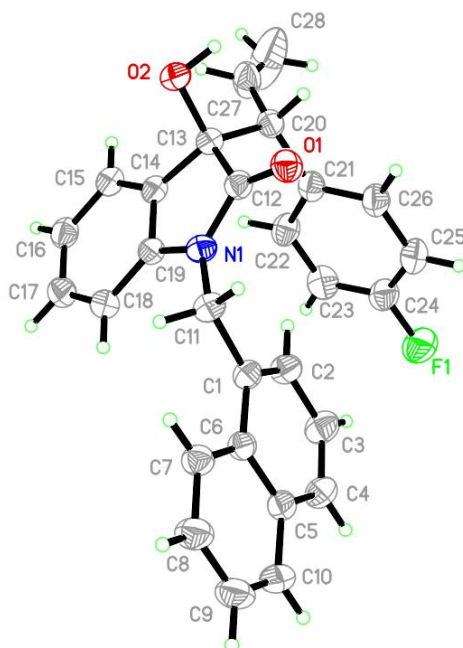
dropwise. The mixture was stirred at 25 °C for 12 h. The mixture was cooled to room temperature and EtOAc (10 mL) was added. The organic phase was washed with saturated sodium bicarbonate, brine, dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) to afford **13** as a white solid (29.8 mg, 95% yield).

m.p. = 90 – 92 °C. ee = 98%, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 80/20, 220 nm, 1 mL/min; *t*_{R1} = 31.828 min (minor), *t*_{R2} = 37.694 min (major)]. [α]_D²⁰ = -21.9 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.34 (m, 4H), 7.90 – 7.81 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.52 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.16 (t, *J* = 7.0 Hz, 2H), 7.02 (m, 1H), 6.82 (s, 2H), 6.40 (d, *J* = 8.2 Hz, 1H), 5.69 (m, 2H), 5.20 (m, 2H), 4.99 (t, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 16.6 Hz, 1H), 3.99 (d, *J* = 11.4 Hz, 1H), 3.60 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 164.5, 150.8, 143.7, 138.3, 135.3, 133.6, 131.1, 130.7, 130.4, 129.1, 128.9, 128.6, 128.5, 128.3, 128.3, 127.8, 126.6, 126.4, 125.9, 125.5, 125.4, 123.7, 122.7, 122.2, 110.3, 79.2, 70.1, 58.5, 41.8, 35.1. HRMS (Q-TOF Premier) calcd for C₃₅H₂₈IN₂O₆ (M+H)⁺: 699.0987; found: 699.0982.

6. ORTEP Representations of 8fk and 13

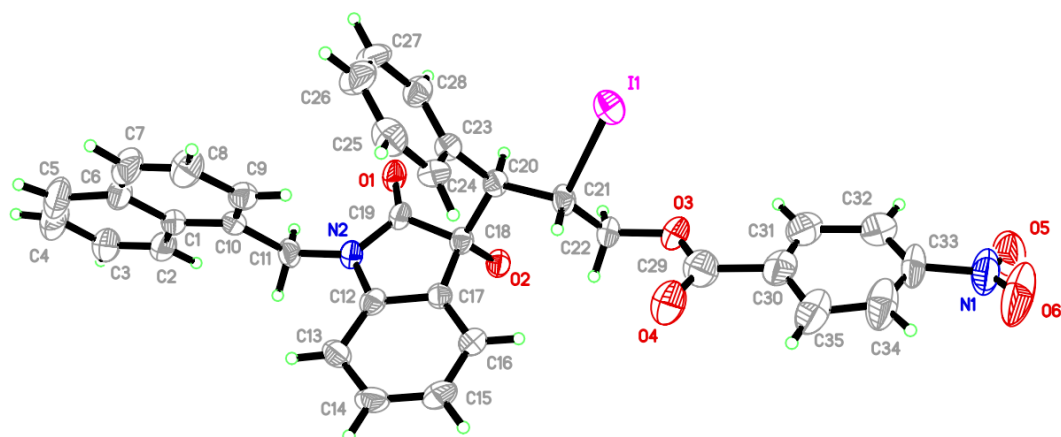
The data were collected on an Agilent Technologies Gemini Atlas Ultra diffractometer using a ultra Cu radiation ($\lambda=1.54184\text{\AA}$) with collimating mirror monochromators and at 293 K. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.35.11.1 The structure was solved by direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using Olex2/ SHELXTL program package. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to nitrogen were located in a ΔF map and refined with isotropic displacement parameters.

ORTEP Representation of 8fk



Bond precision:	C-C = 0.0106 Å		Wavelength=1.54178
Cell:	a=21.5078 (15)	b=9.2660 (6)	c=13.4784 (8)
	alpha=90	beta=90	gamma=90
Temperature:	297 K		
	Calculated	Reported	
Volume	2686.1 (3)	2686.1 (3)	
Space group	P 21 21 2	P 21 21 2	
Hall group	P 2 2ab	P 2 2ab	
Moiety formula	2(C28 H19 F N O2), 2(C3 H7 O), O	2(C28 H19 F N O2), 2(C3 H7 O), O	
Sum formula	C62 H52 F2 N2 O7	C62 H52 F2 N2 O7	
Mr	975.06	975.05	
Dx, g cm-3	1.206	1.206	
Z	2	2	
Mu (mm-1)	0.676	0.676	
F000	1024.0	1024.0	
F000'	1027.21		
h, k, lmax	23, 10, 14	23, 9, 14	
Nref	3857 [2217]	3779	
Tmin, Tmax	0.862, 0.885	0.055, 0.162	
Tmin'	0.862		
Correction method= # Reported T Limits: Tmin=0.055 Tmax=0.162			
AbsCorr = ?			
Data completeness=	1.70/0.98	Theta(max)= 58.920	
R(reflections)=	0.0565 (2402)	wR2(reflections)= 0.1522 (3779)	
S =	1.047	Npar= 337	

ORTEP Representation of 13



Bond precision: C-C = 0.0305 Å

Wavelength=1.54178

Cell: a=8.5130 (18) b=13.017 (3) c=14.940 (3)
 alpha=81.552 (9) beta=82.416 (10) gamma=71.669 (8)
 Temperature: 299 K

	Calculated	Reported
Volume	1548.0 (6)	1548.1 (6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C35 H26 I N2 O6	C35 H26 I N2 O6
Sum formula	C35 H26 I N2 O6	C35 H26 I N2 O6
Mr	697.48	697.48
Dx, g cm ⁻³	1.496	1.496
Z	2	2
Mu (mm ⁻¹)	8.531	8.531
F000	702.0	702.0
F000'	703.40	
h, k, lmax	9, 14, 16	9, 14, 16
Nref	4470	3922
Tmin, Tmax	0.227, 0.278	0.058, 0.167
Tmin'	0.145	

Correction method= # Reported T Limits: Tmin=0.058 Tmax=0.167
 AbsCorr = ?

Data completeness= 0.877

Theta(max)= 58.930

R(reflections)= 0.1564 (3145)

wR2(reflections)= 0.4492 (3922)

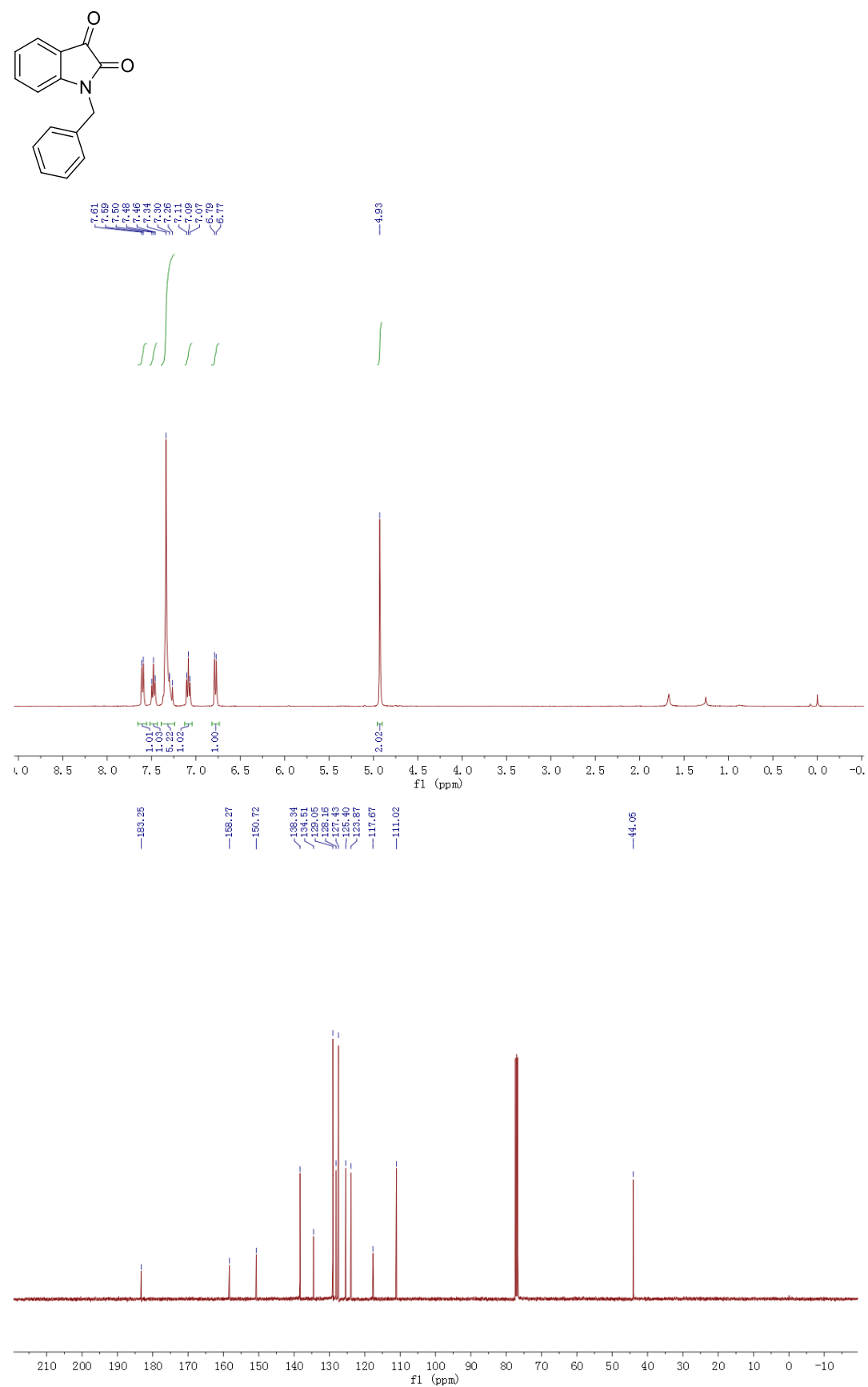
S = 1.535

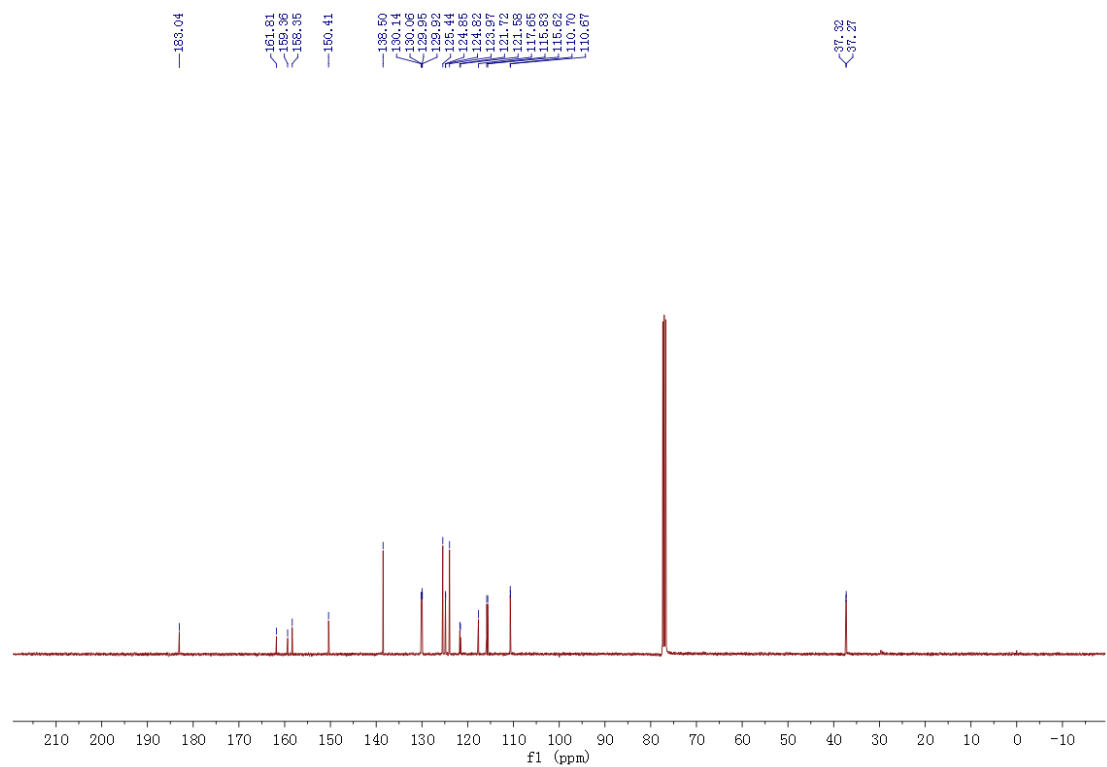
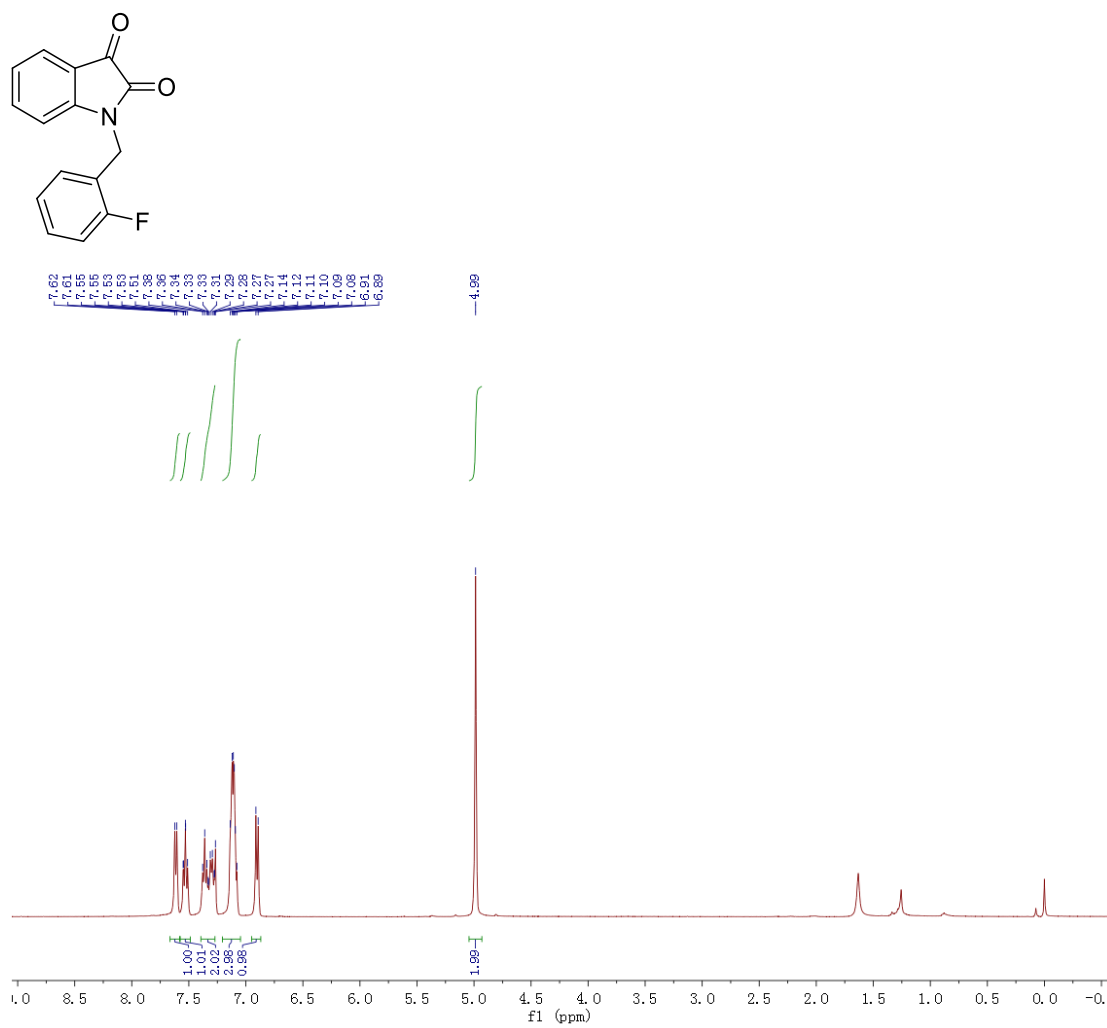
Npar= 397

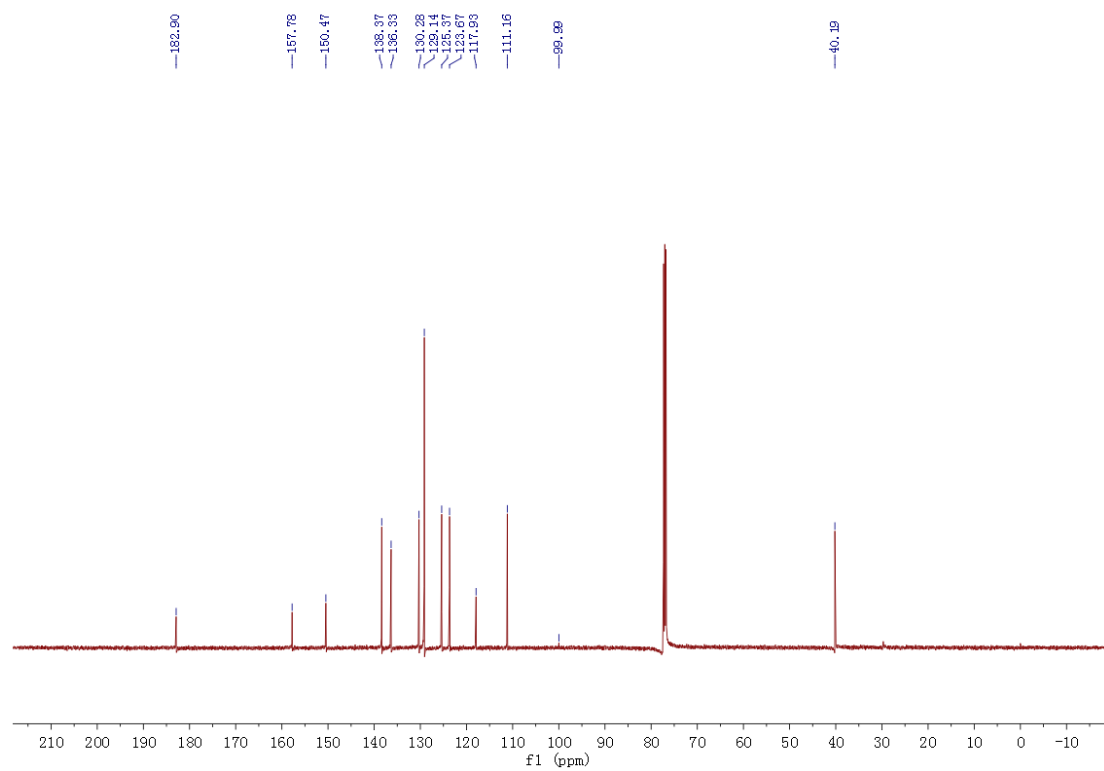
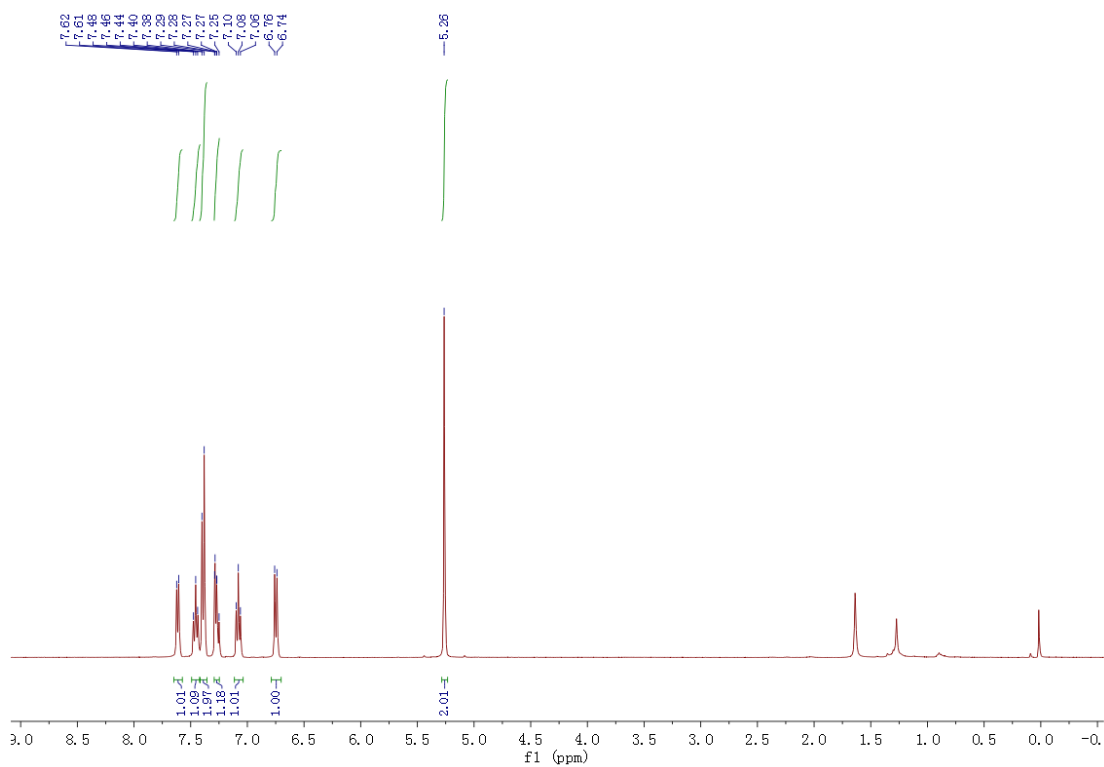
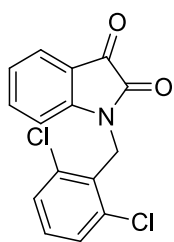
7. References

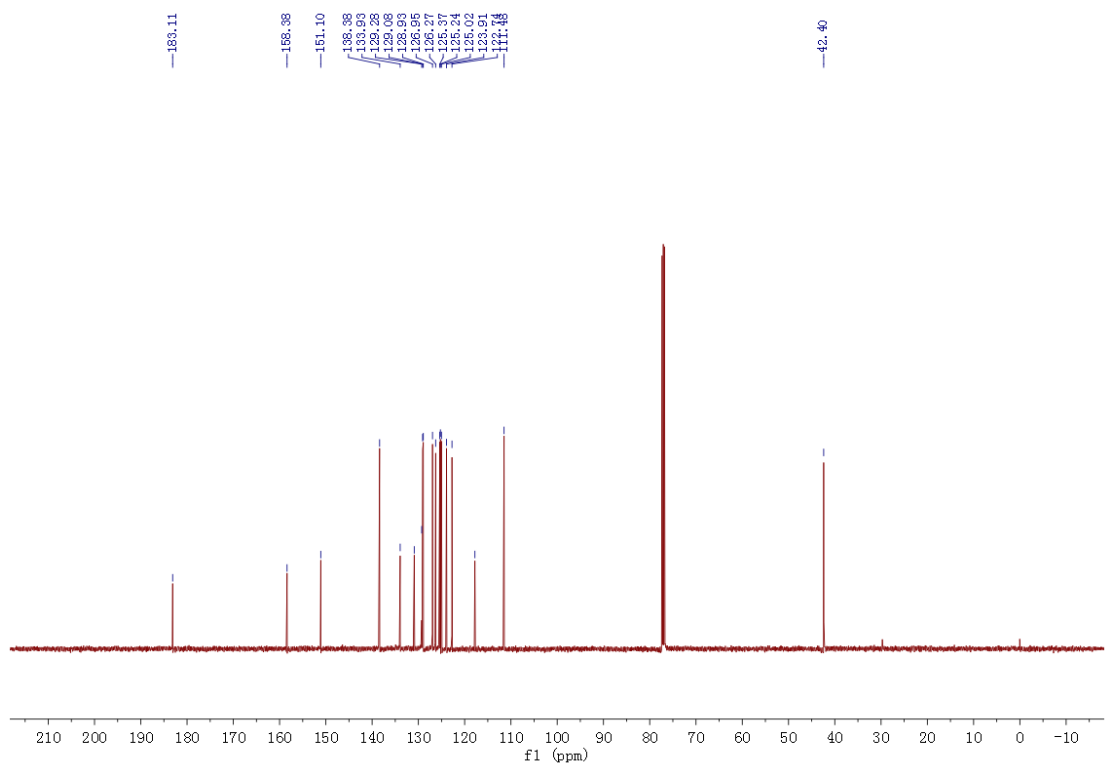
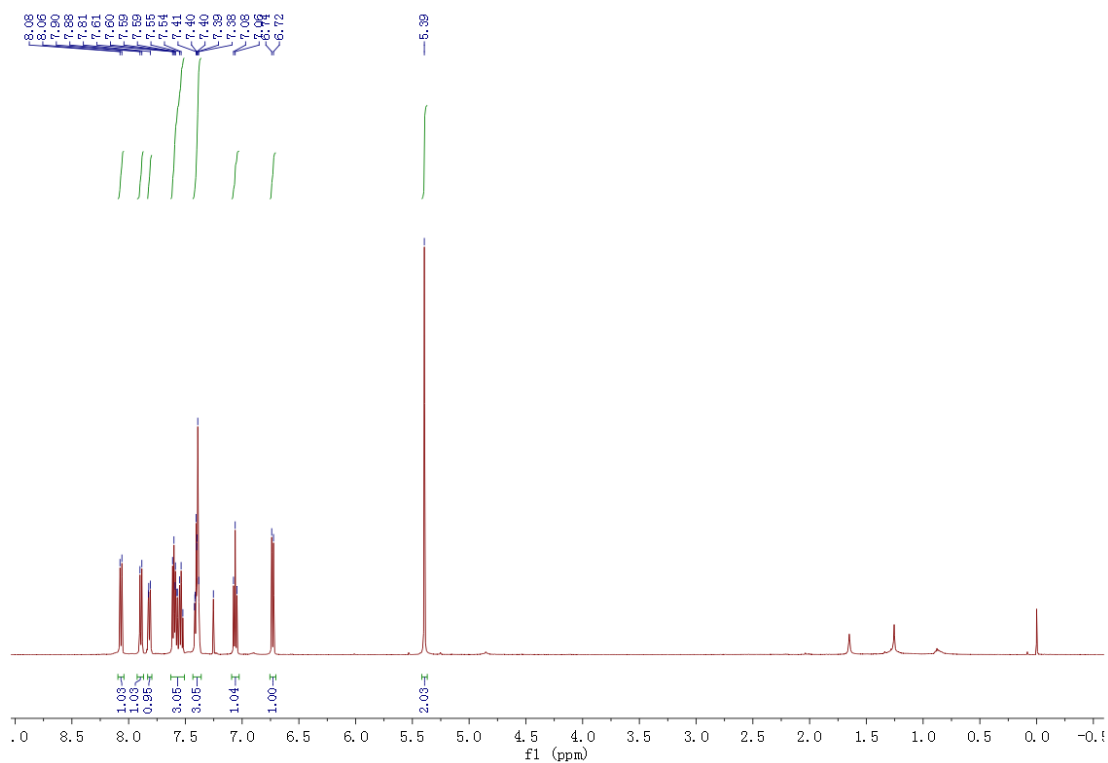
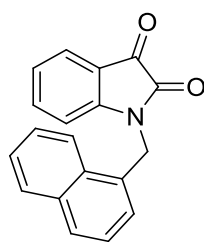
- (1) Polet, D.; Alexakis, A. *Org. Lett.* **2005**, *7*, 1621.
- (2) Huo, X.; He, R.; Fu, J.; Zhang, J.; Yang, G.; Zhang, W. *J. Am. Chem. Soc.* **2017**, *139*, 9819.
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- (6) Baker, S. R.; Parsons, A. F.; Wilson, M. *Tetrahedron Lett.* **1998**, *39*, 331.
- (7) Jayakumar, S.; Kumarswamyreddy, N.; Prakash, M.; Kesavan, V. *Org. Lett.* **2015**, *17*, 1066.

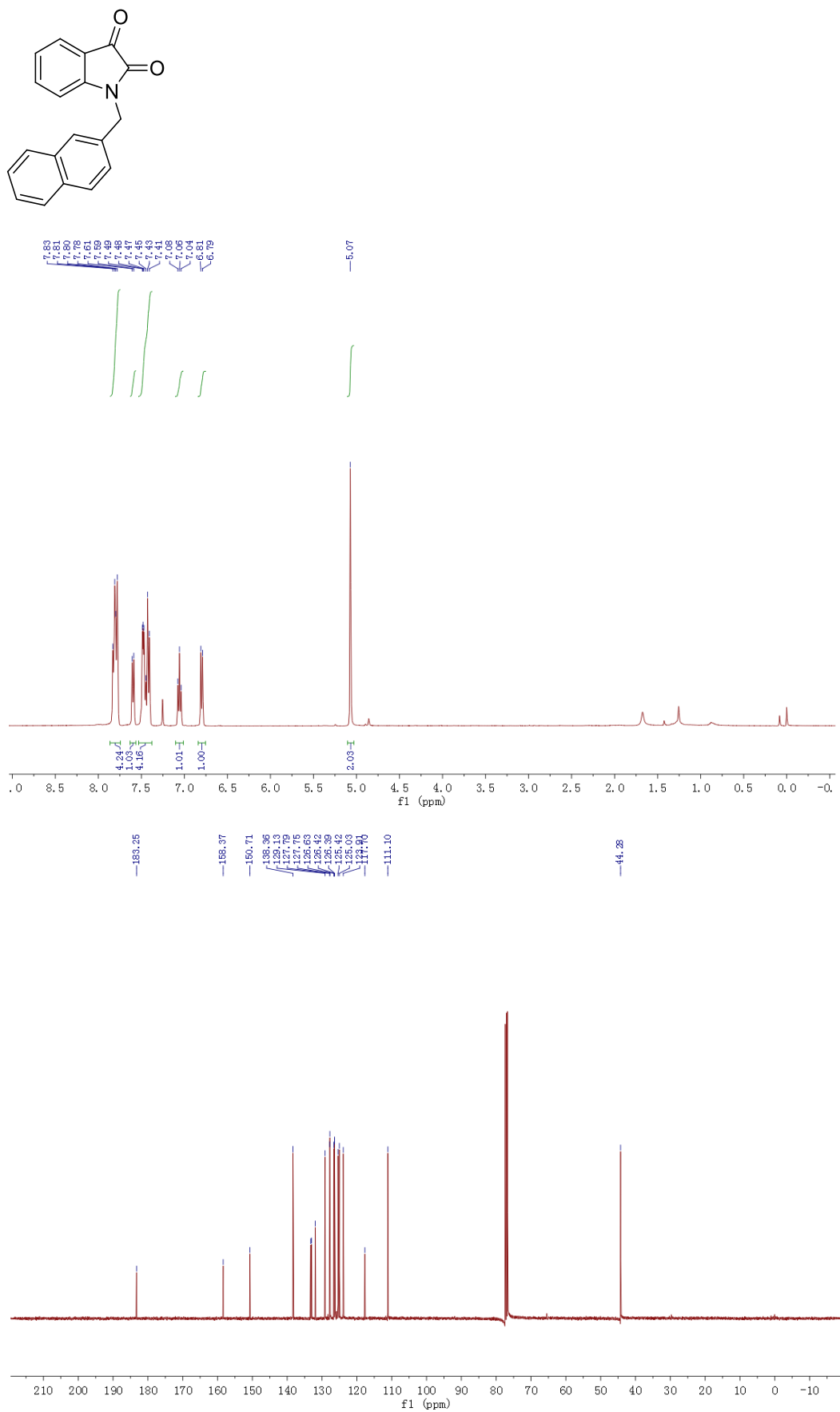
8. NMR and HPLC Spectra

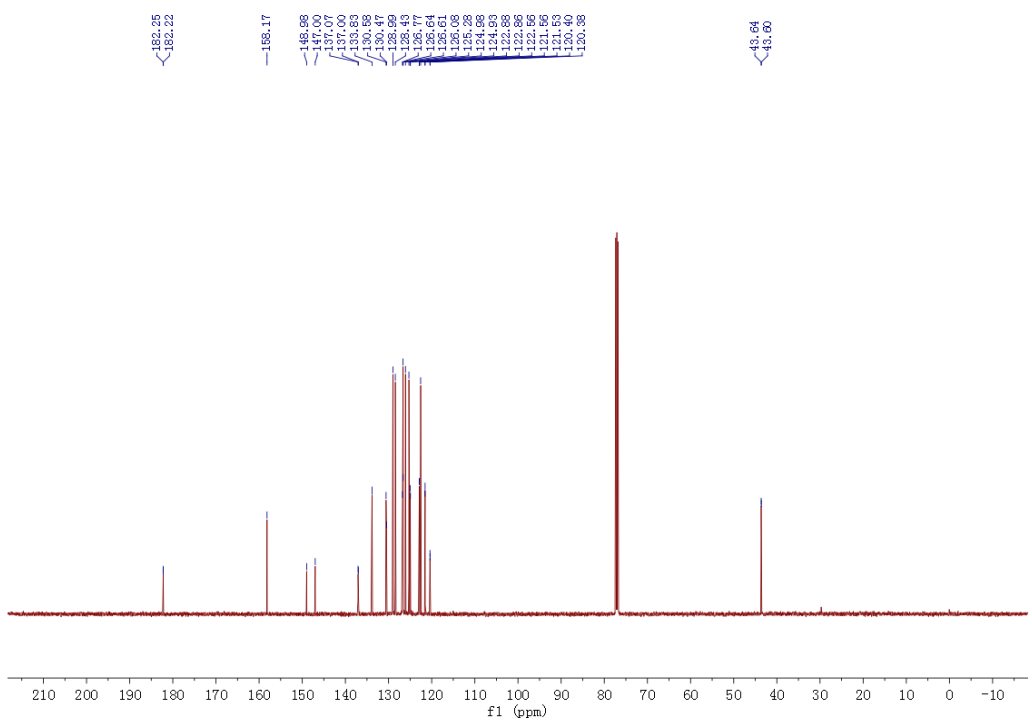
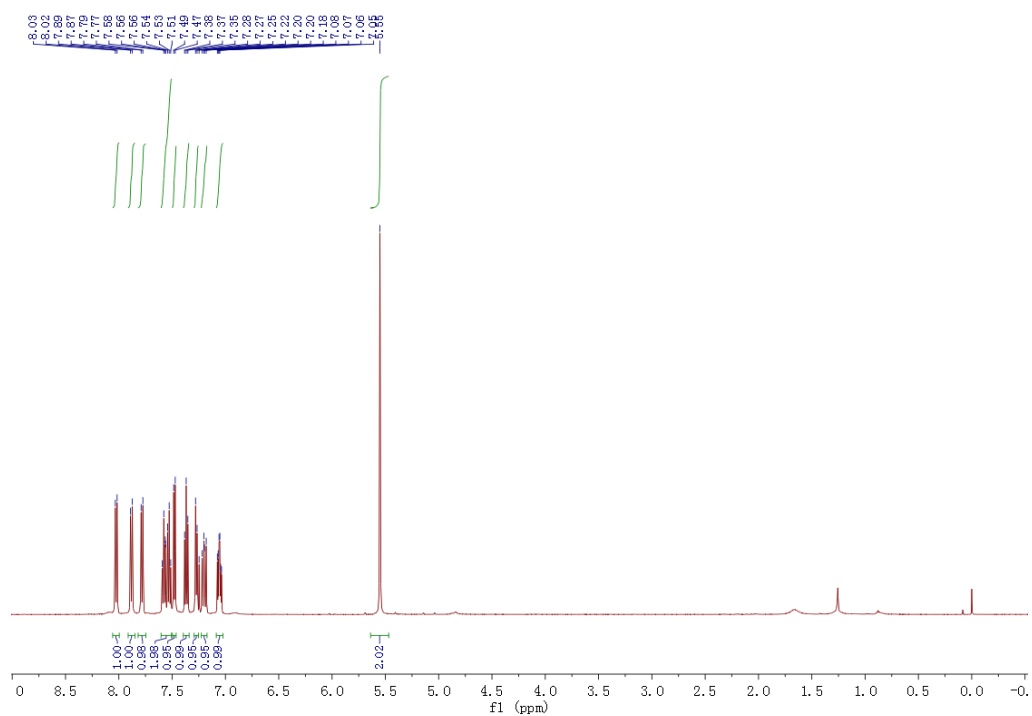
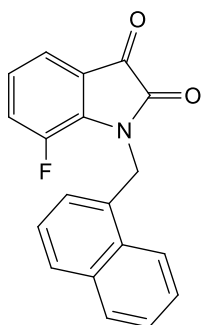


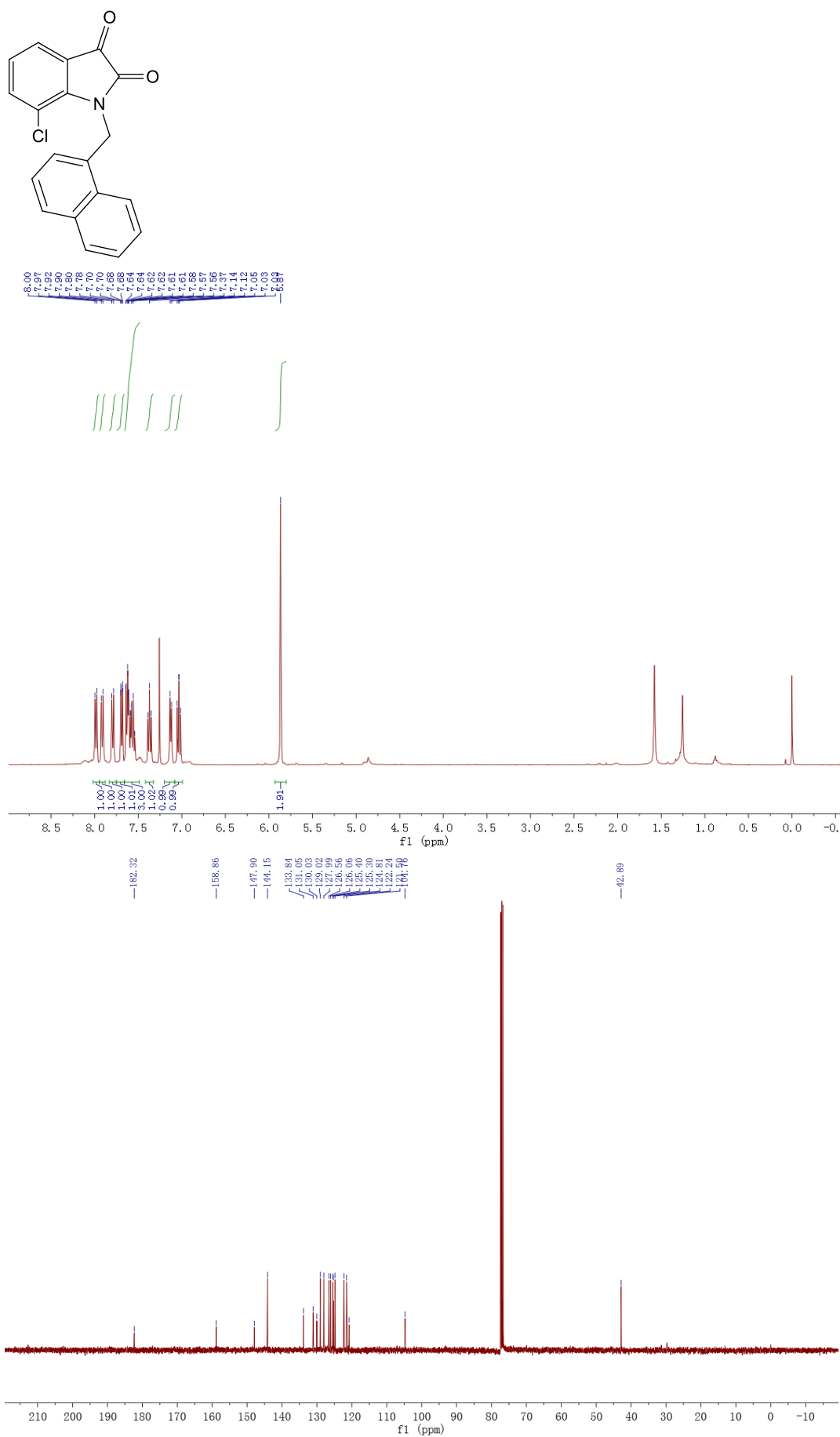


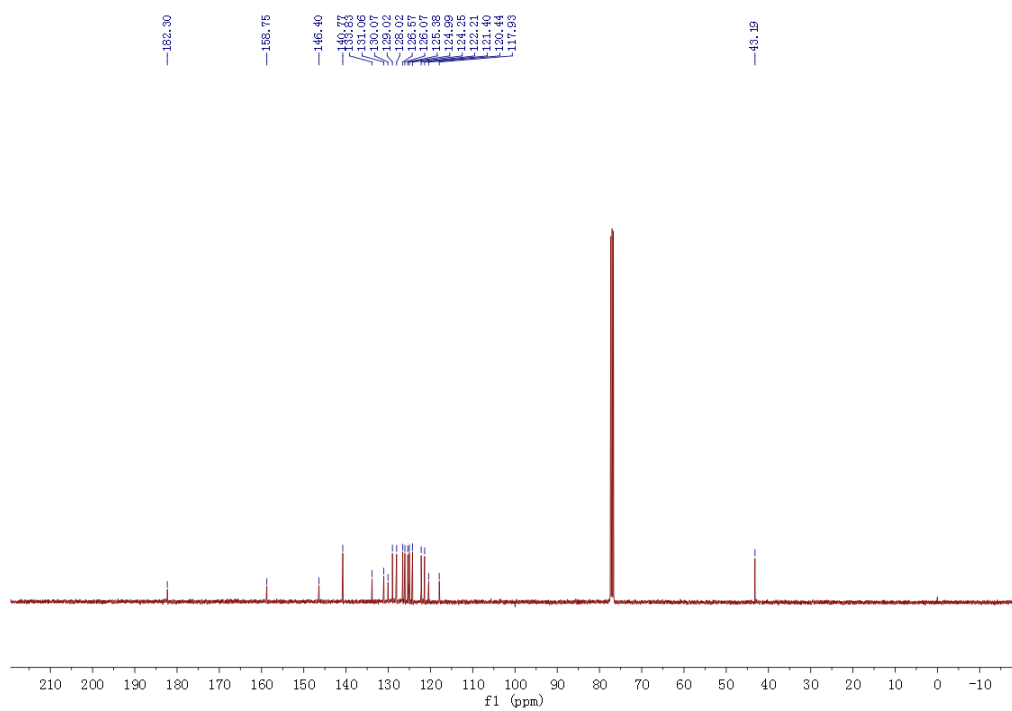
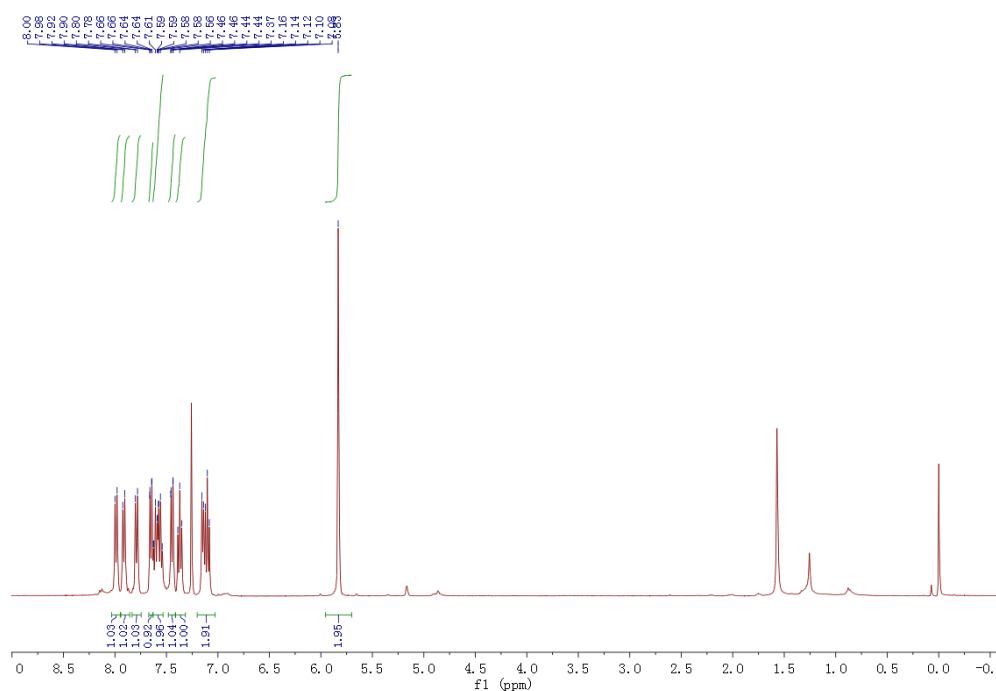
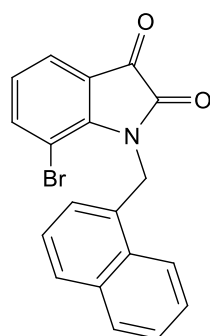


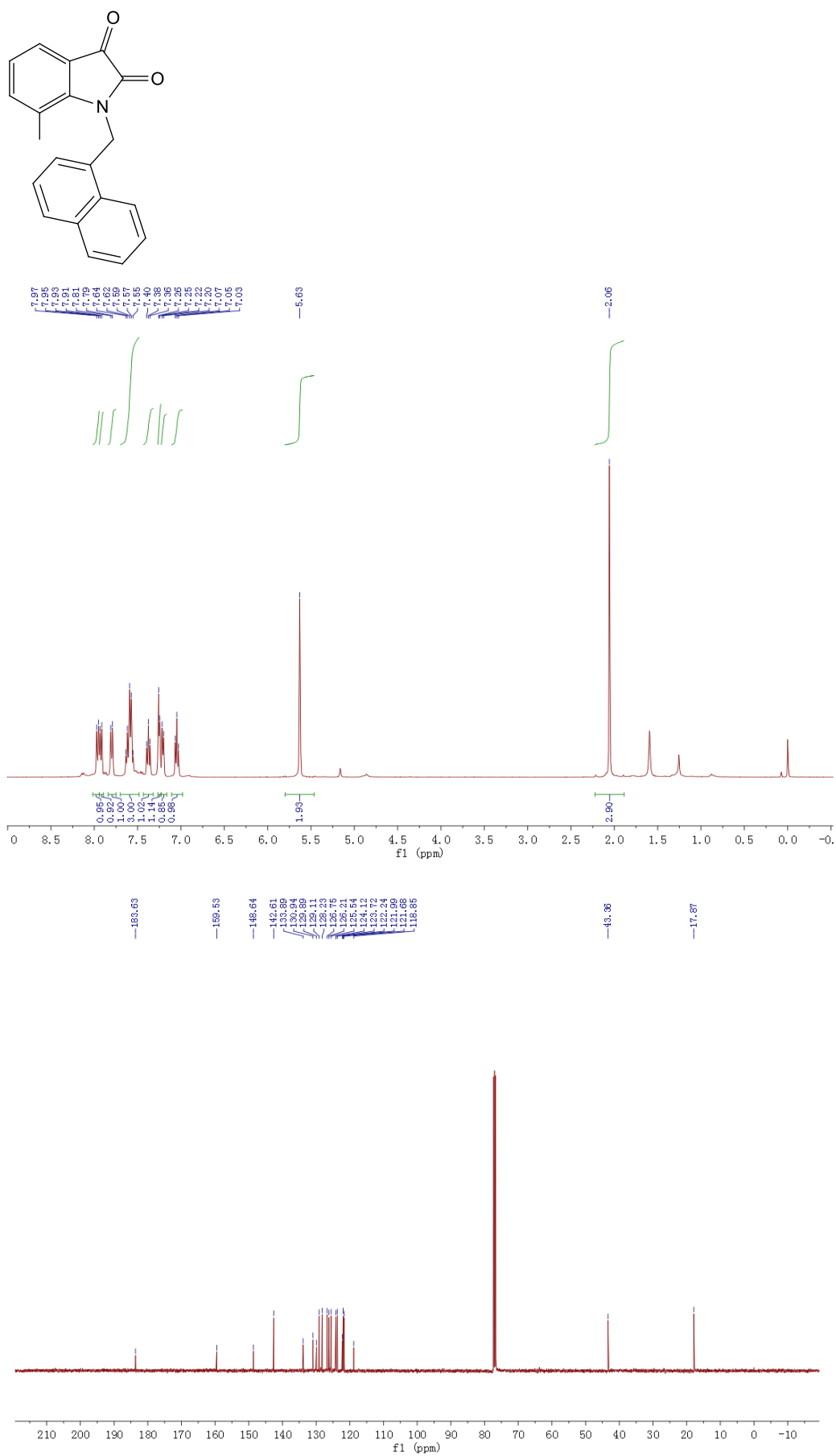


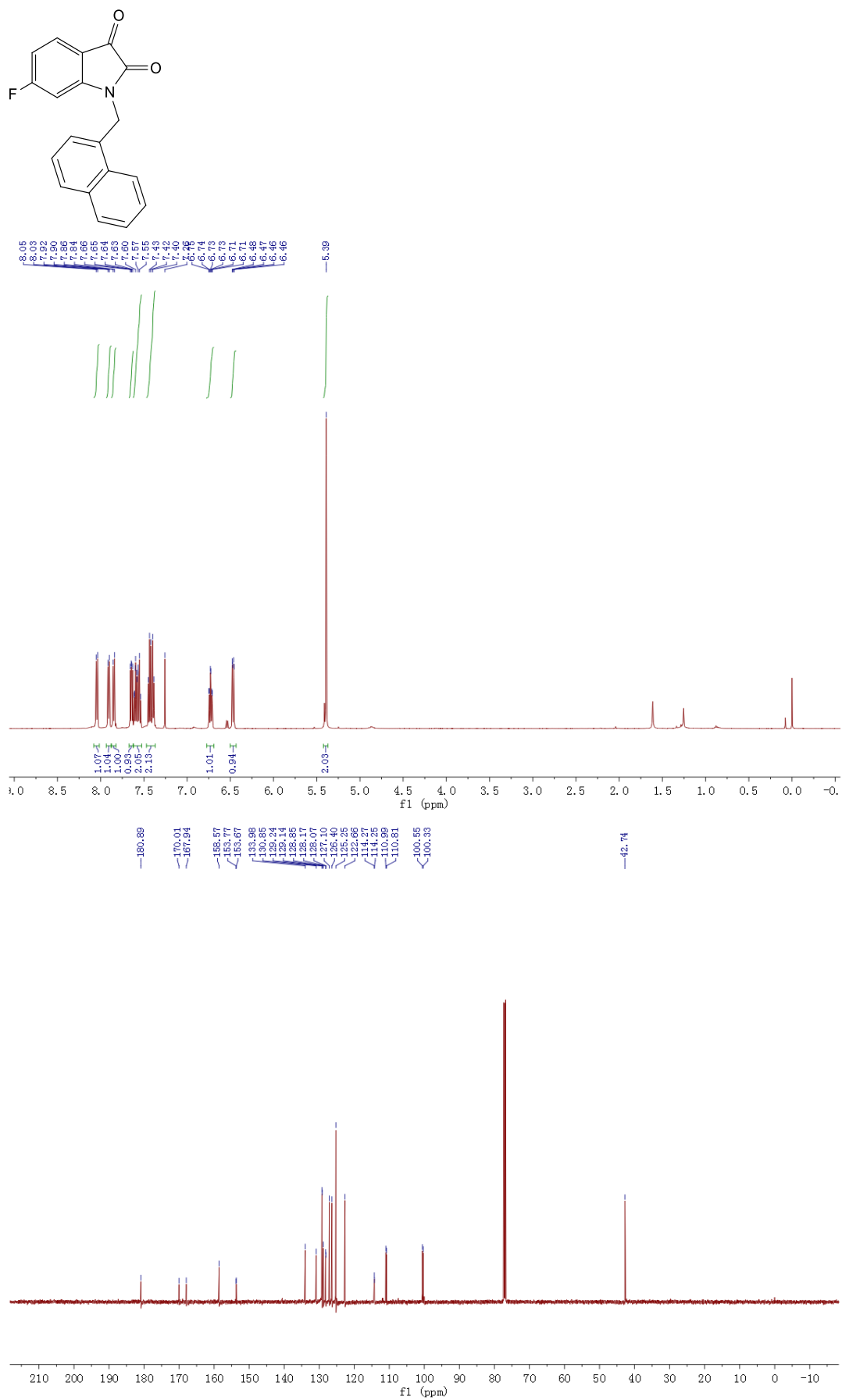


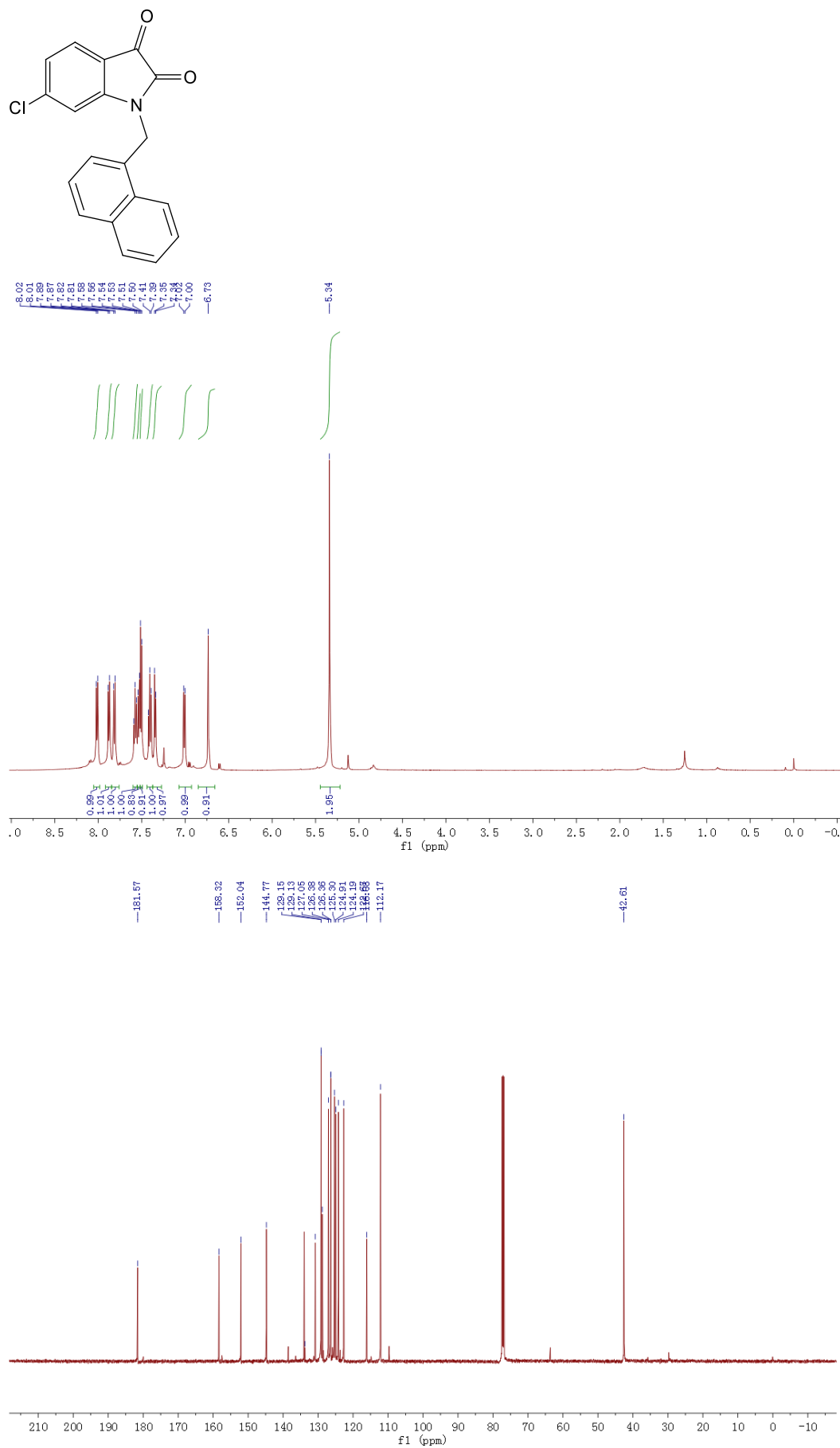


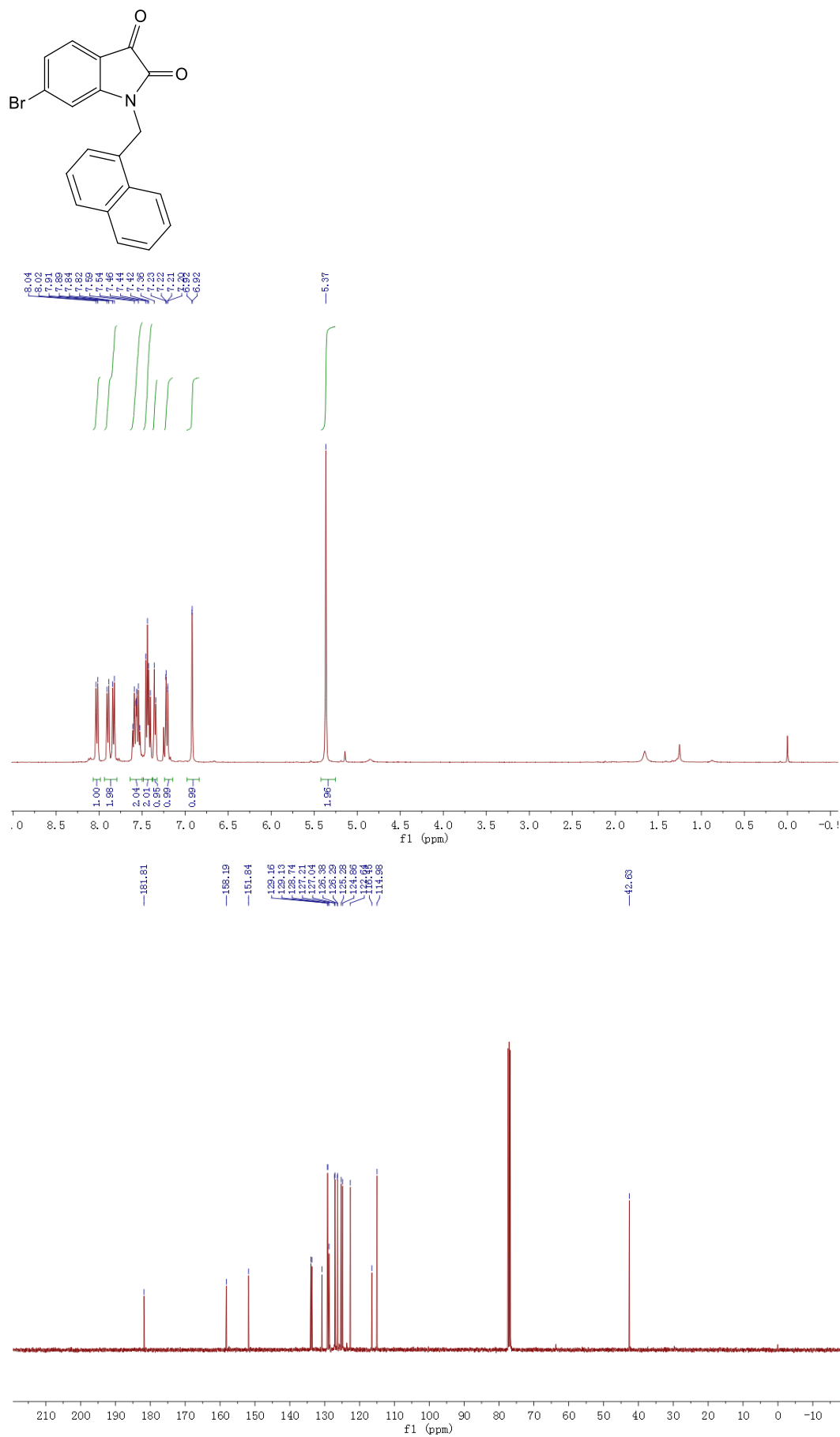


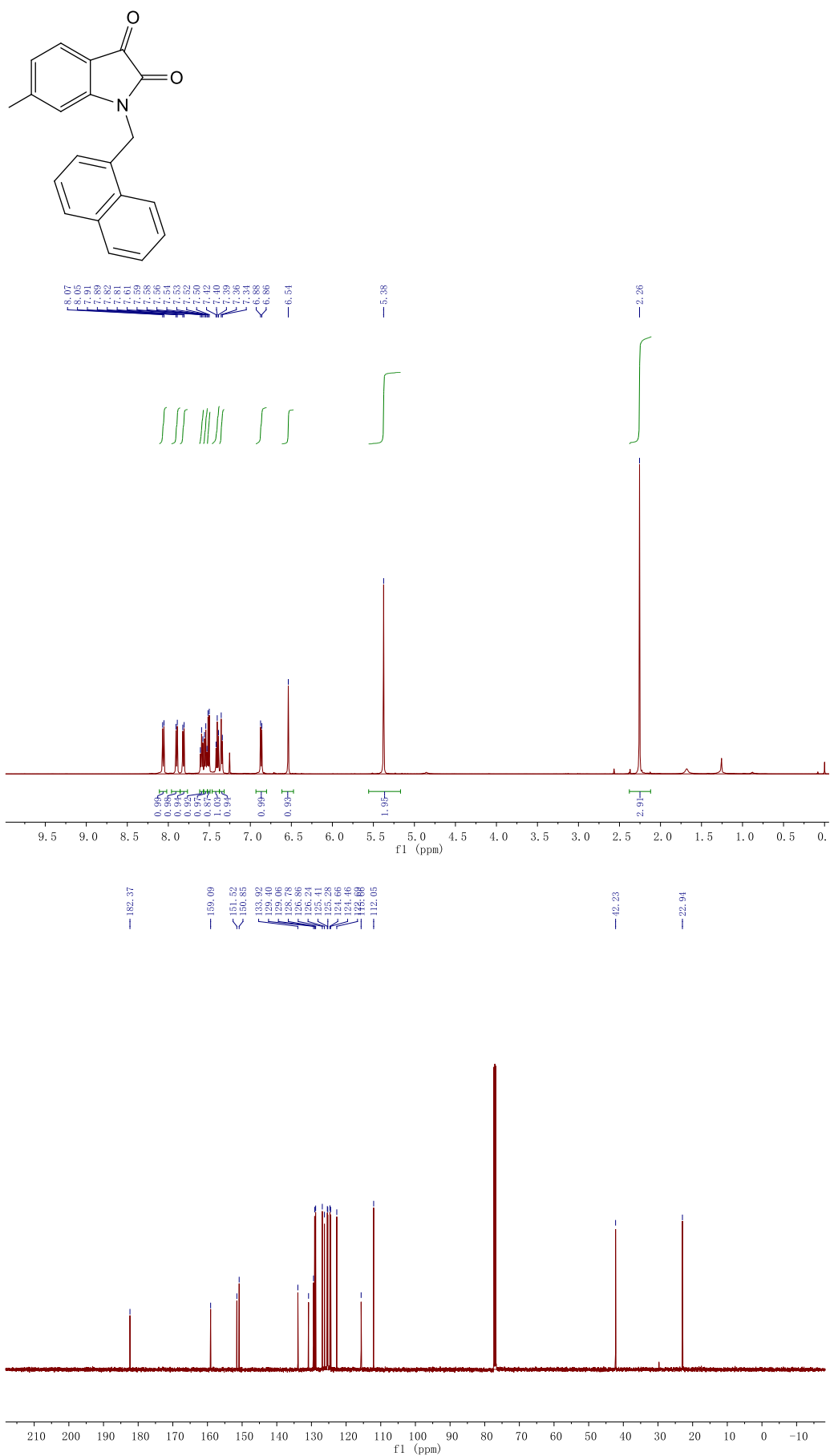


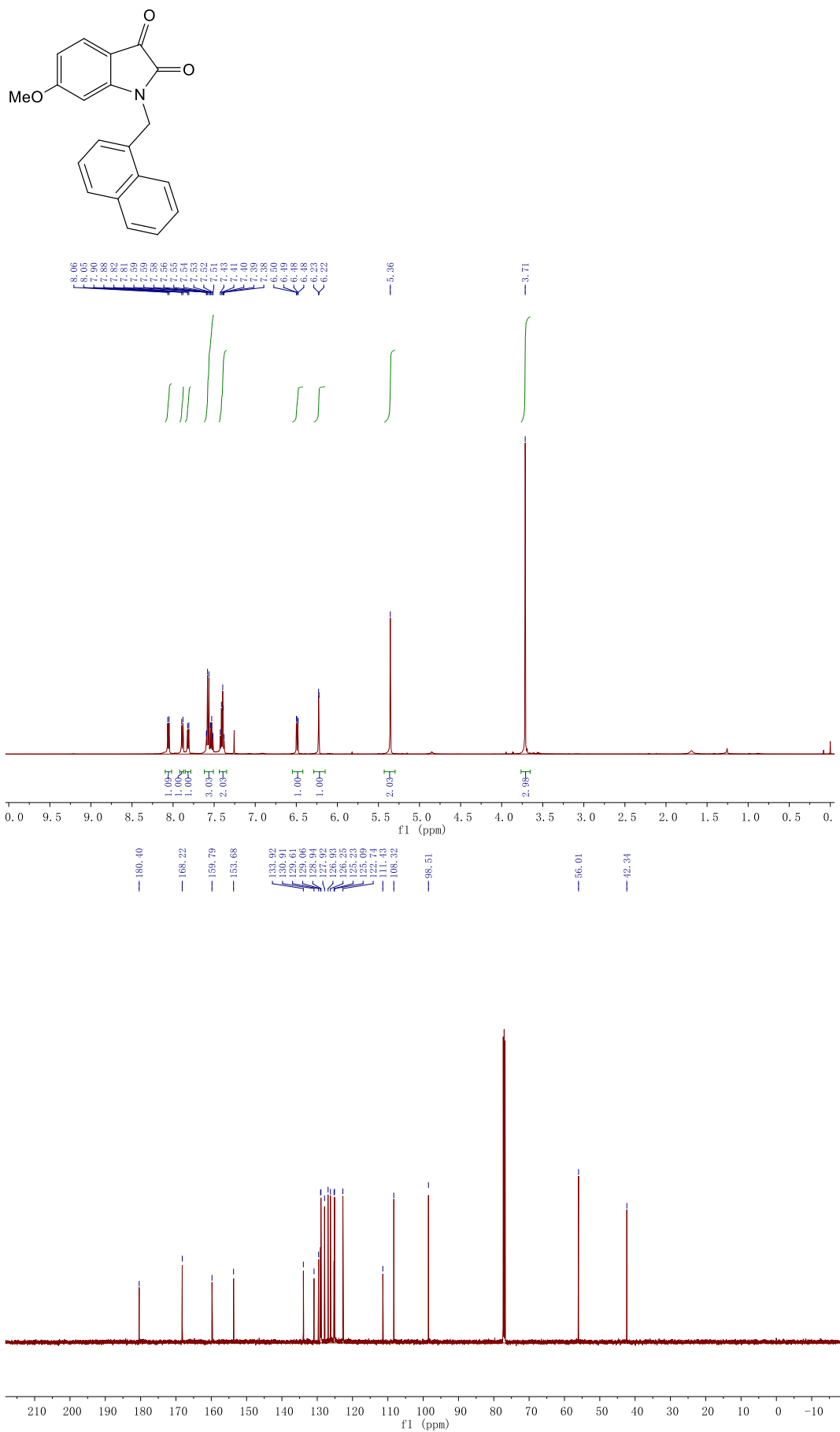


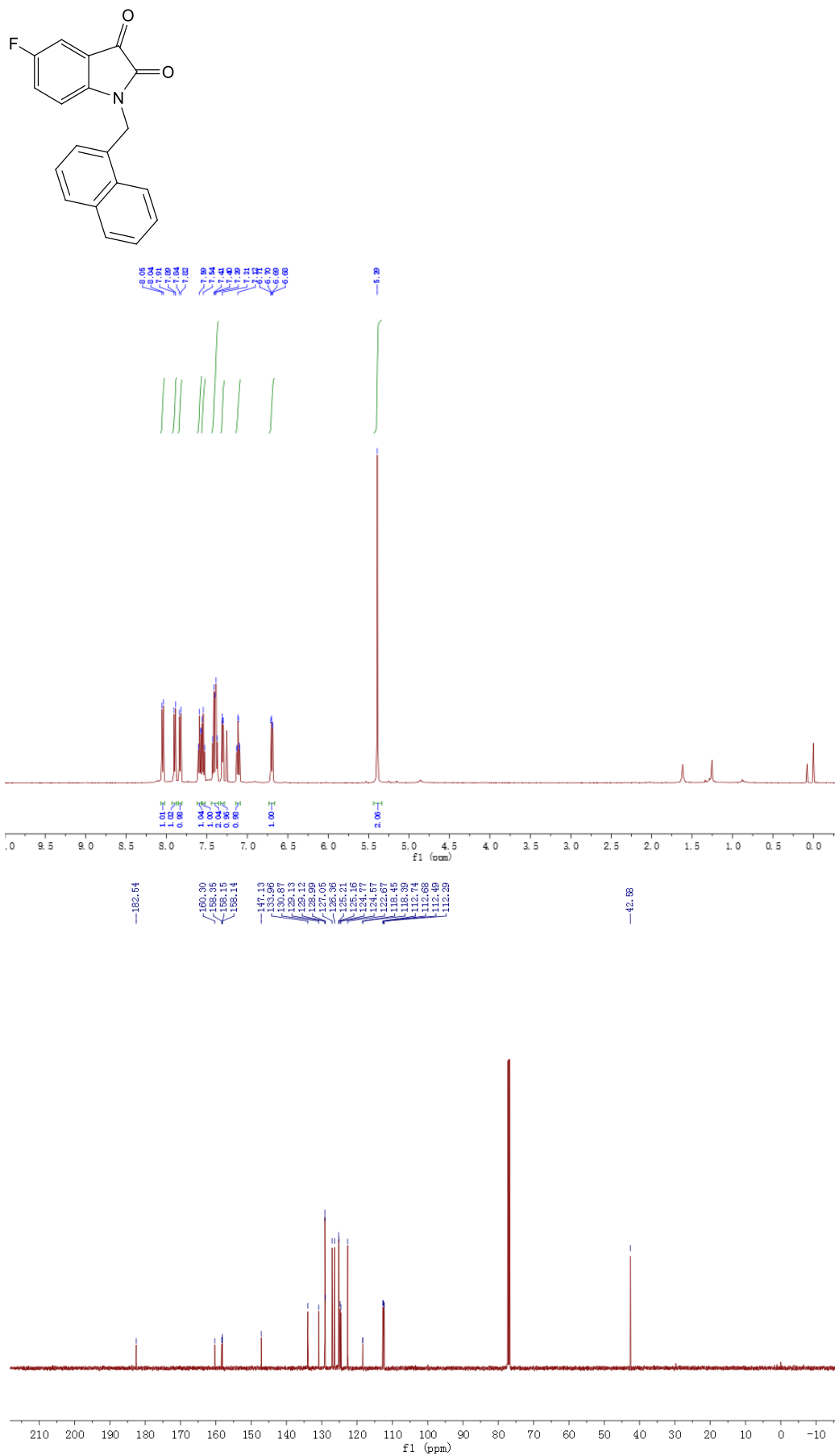


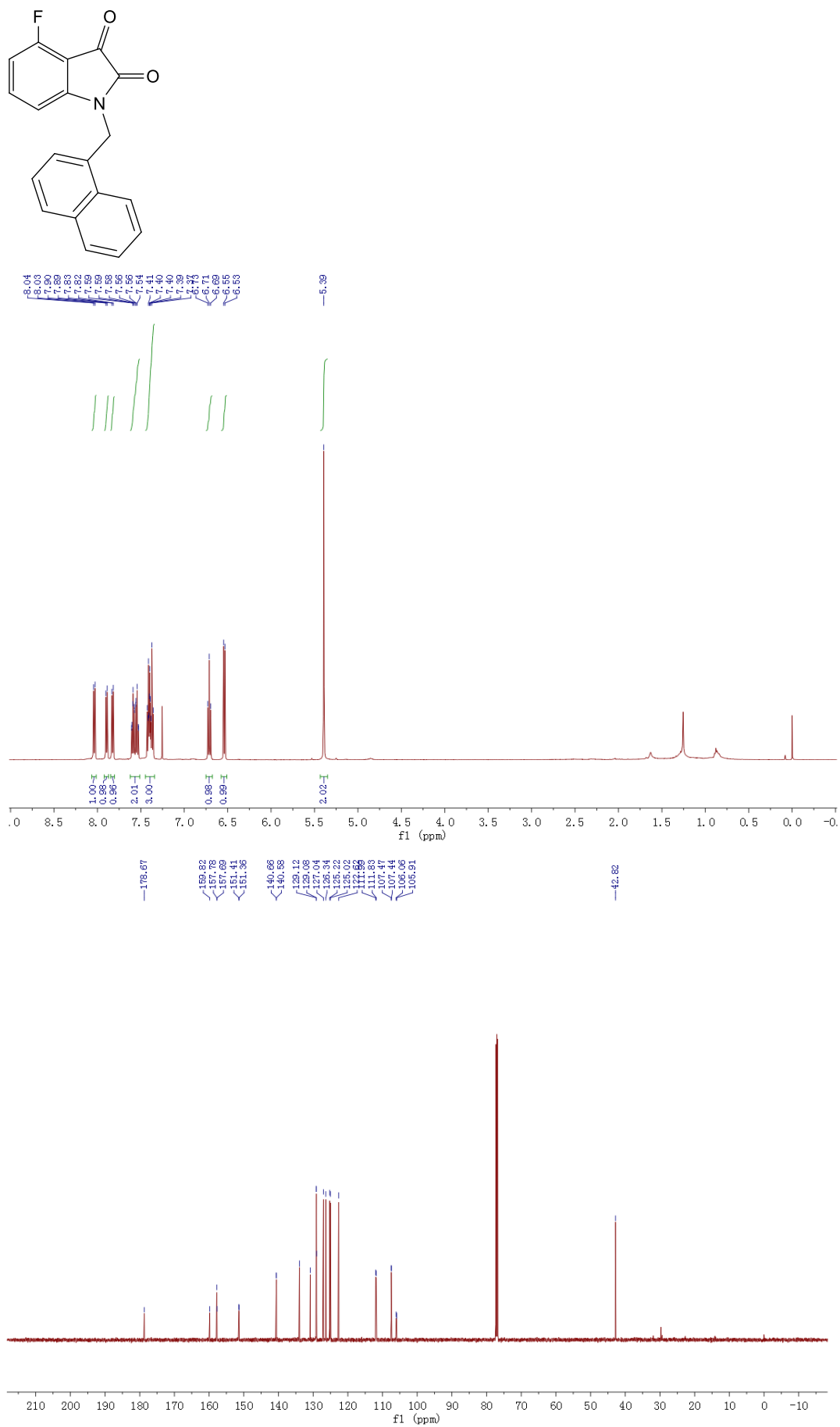


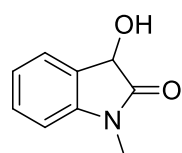






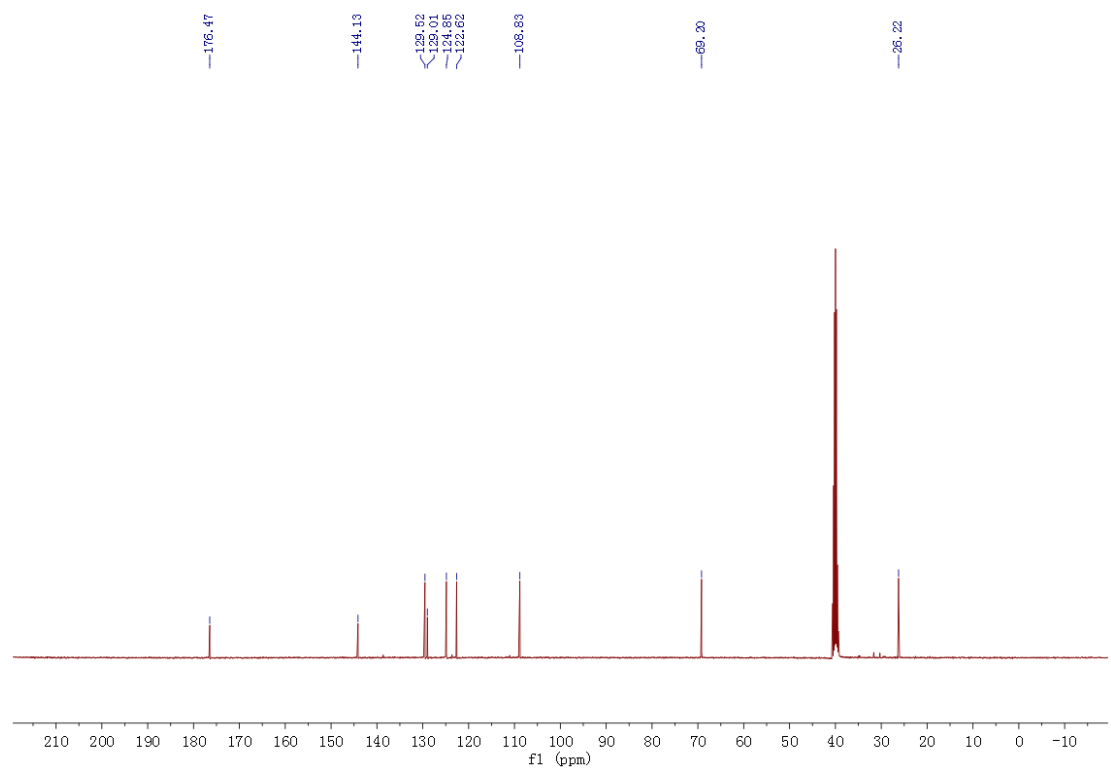
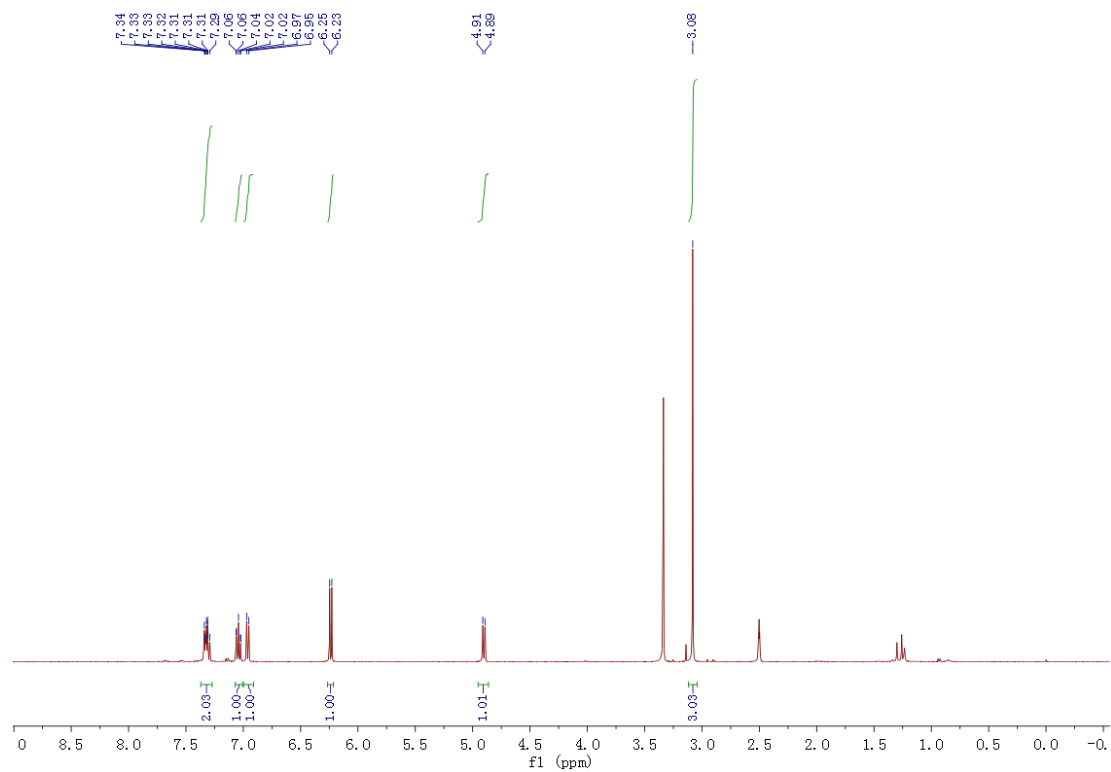


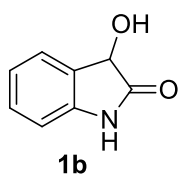




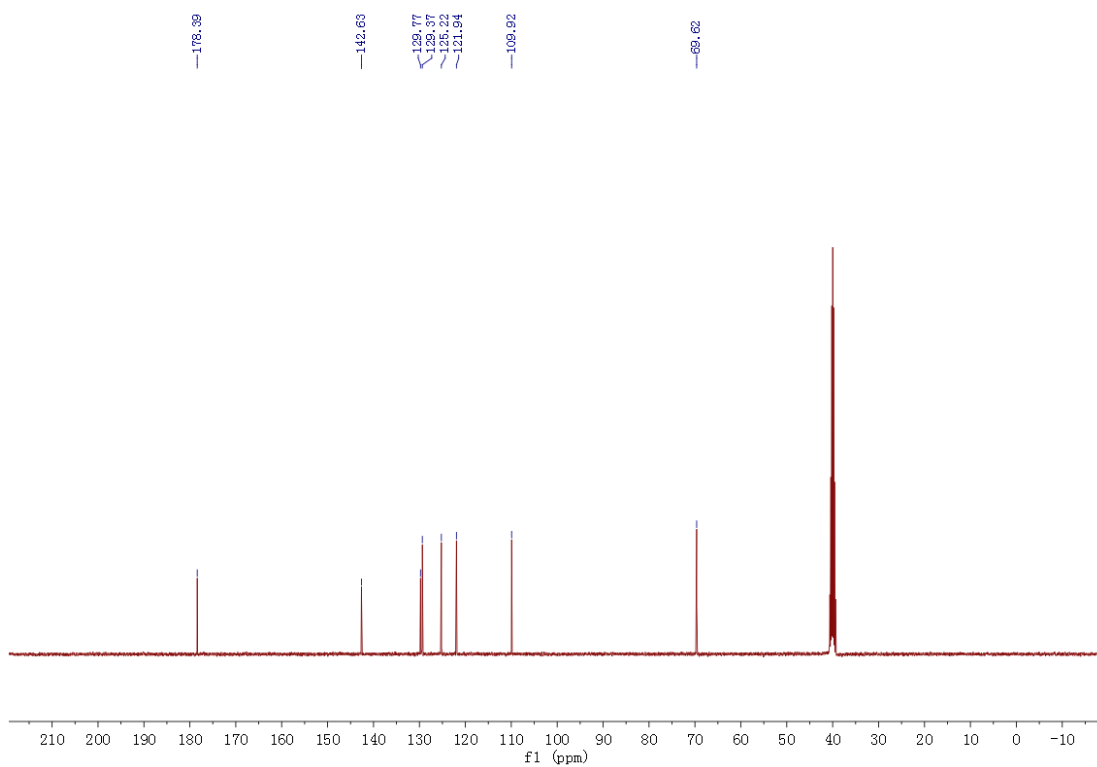
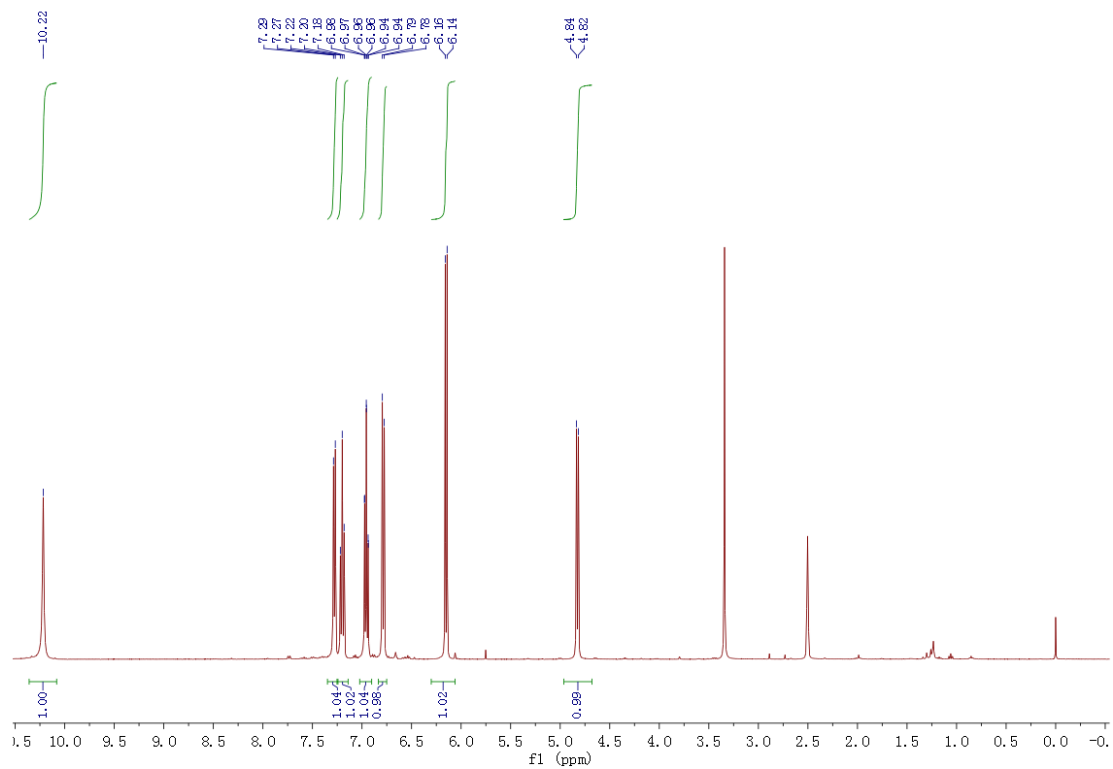
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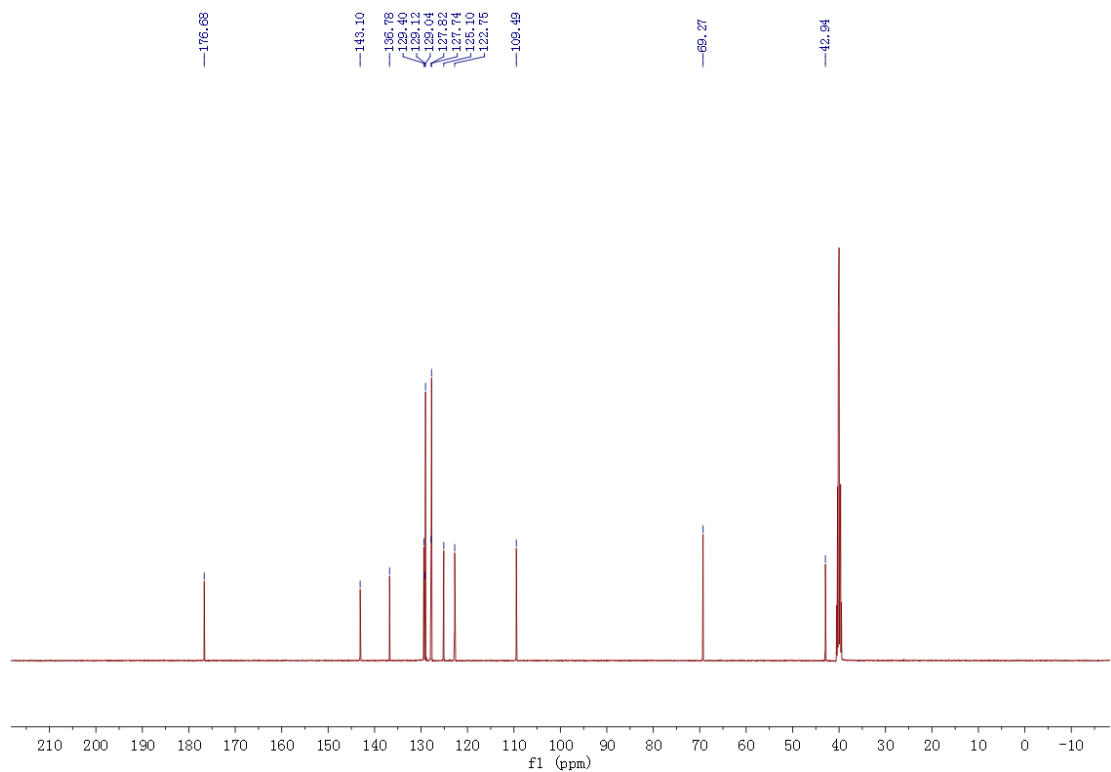
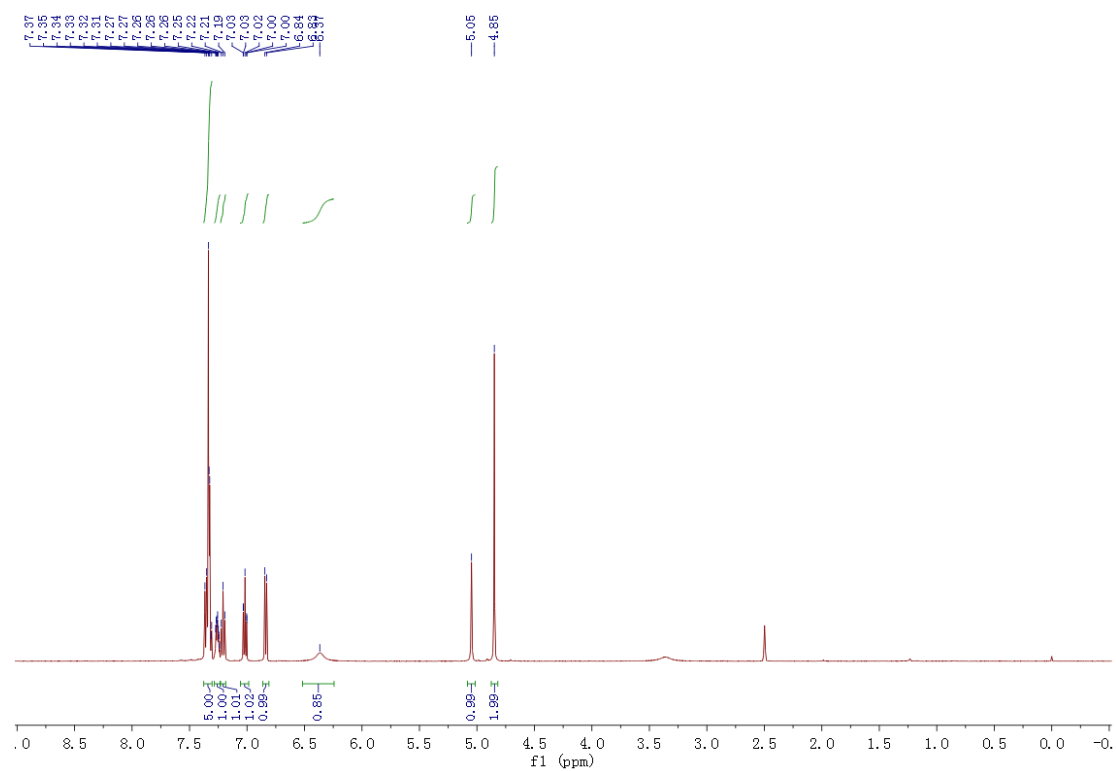
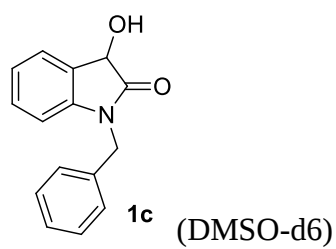
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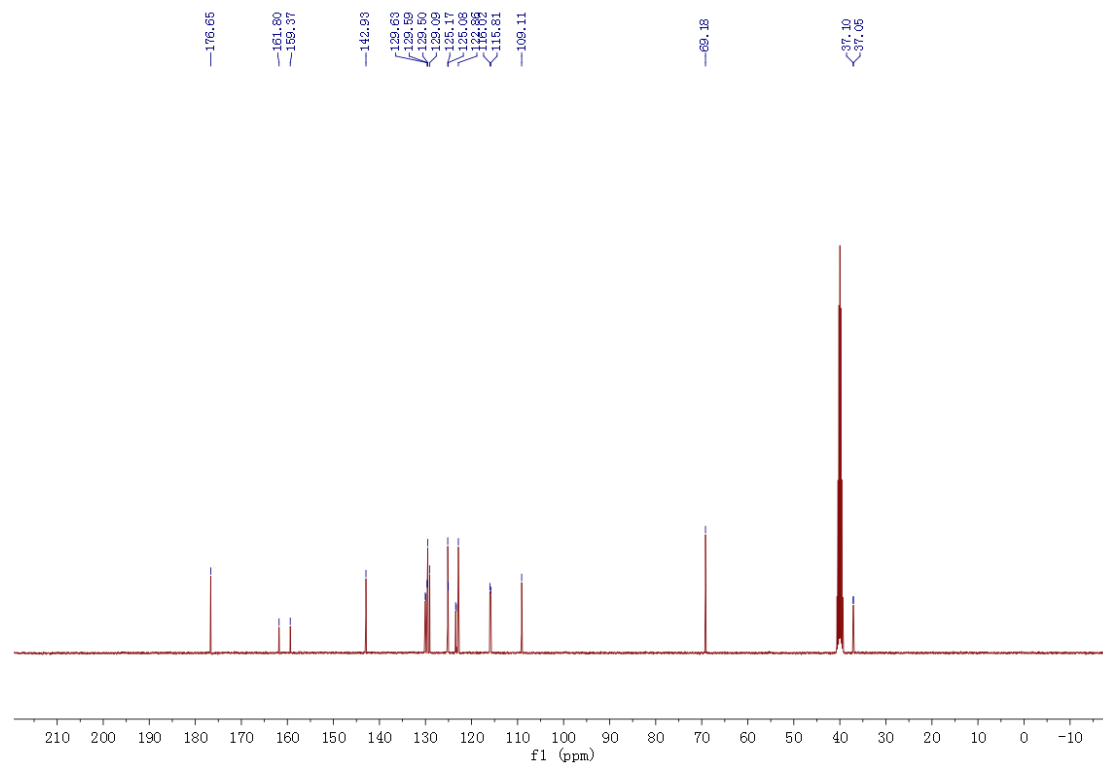
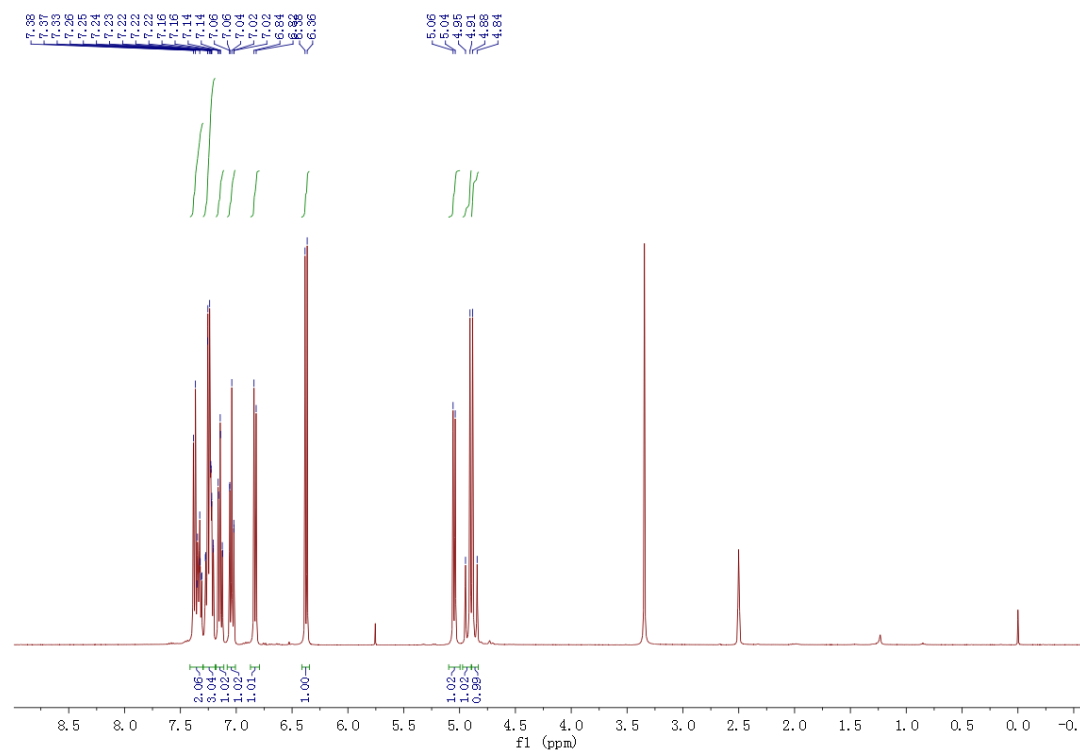
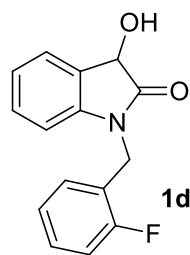


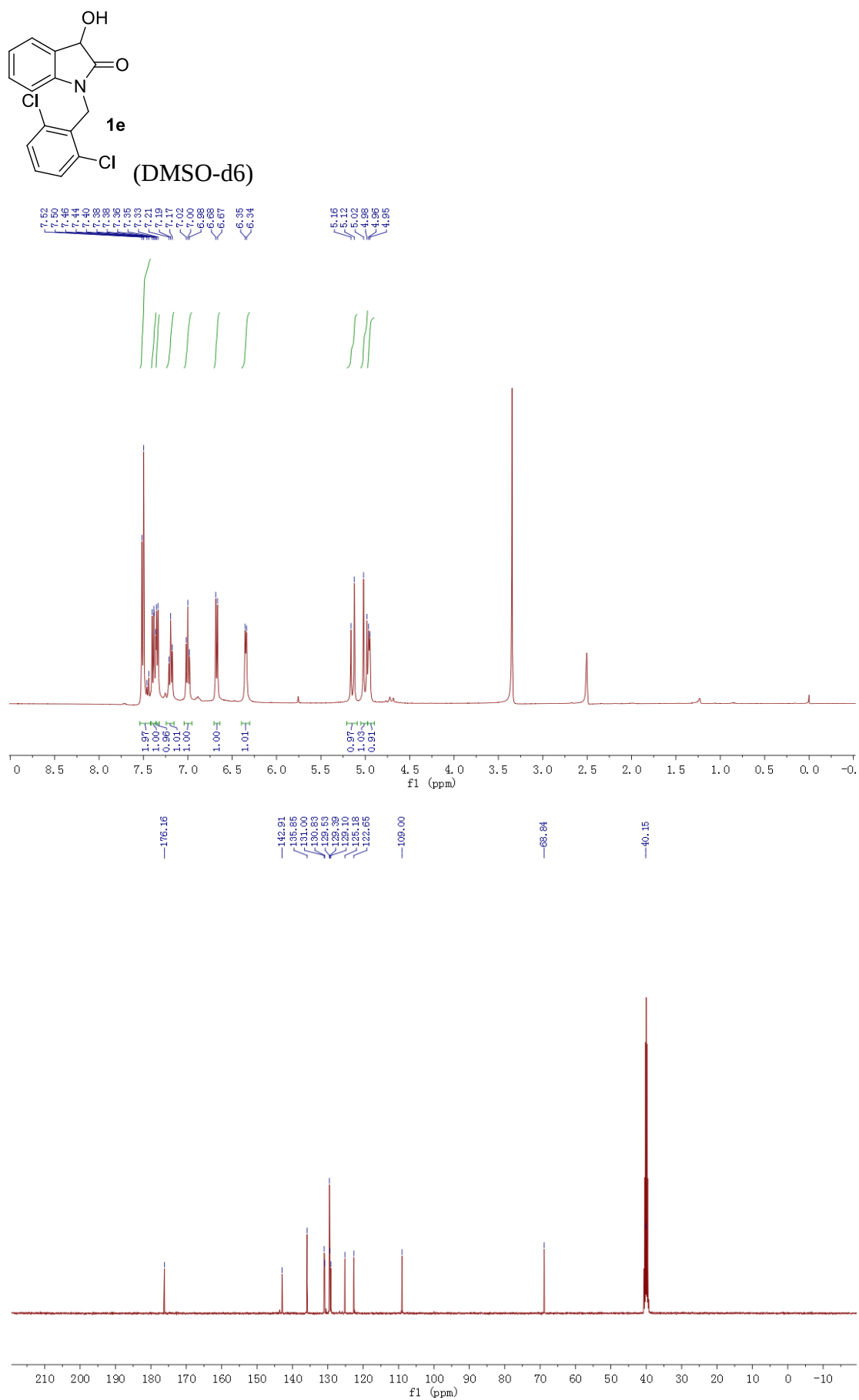


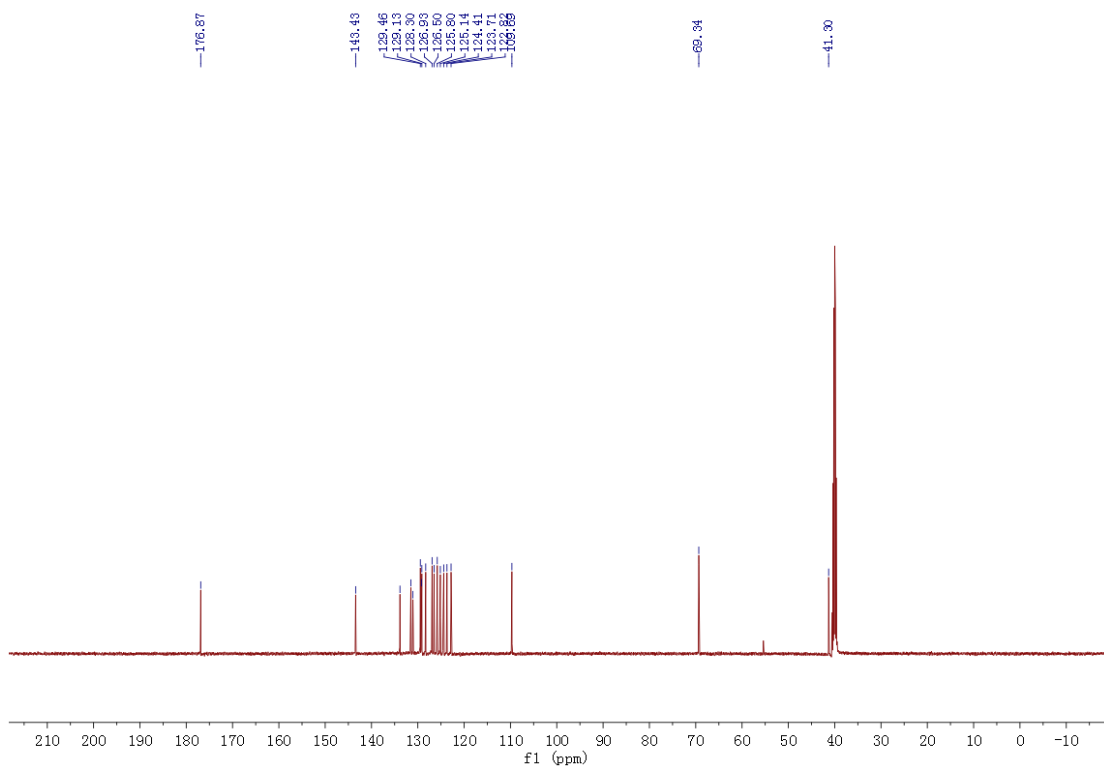
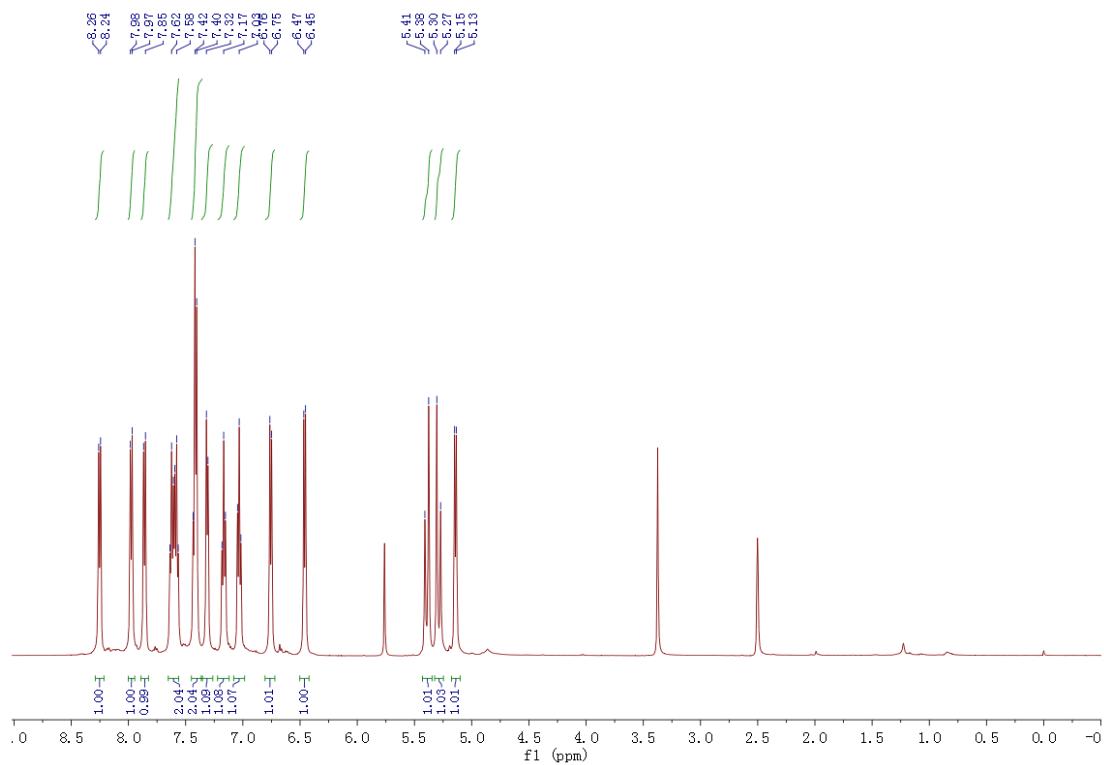
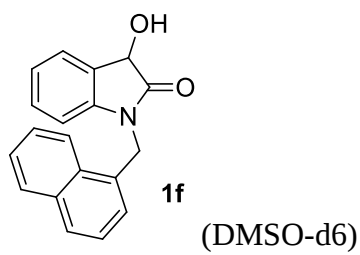
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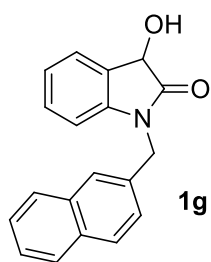






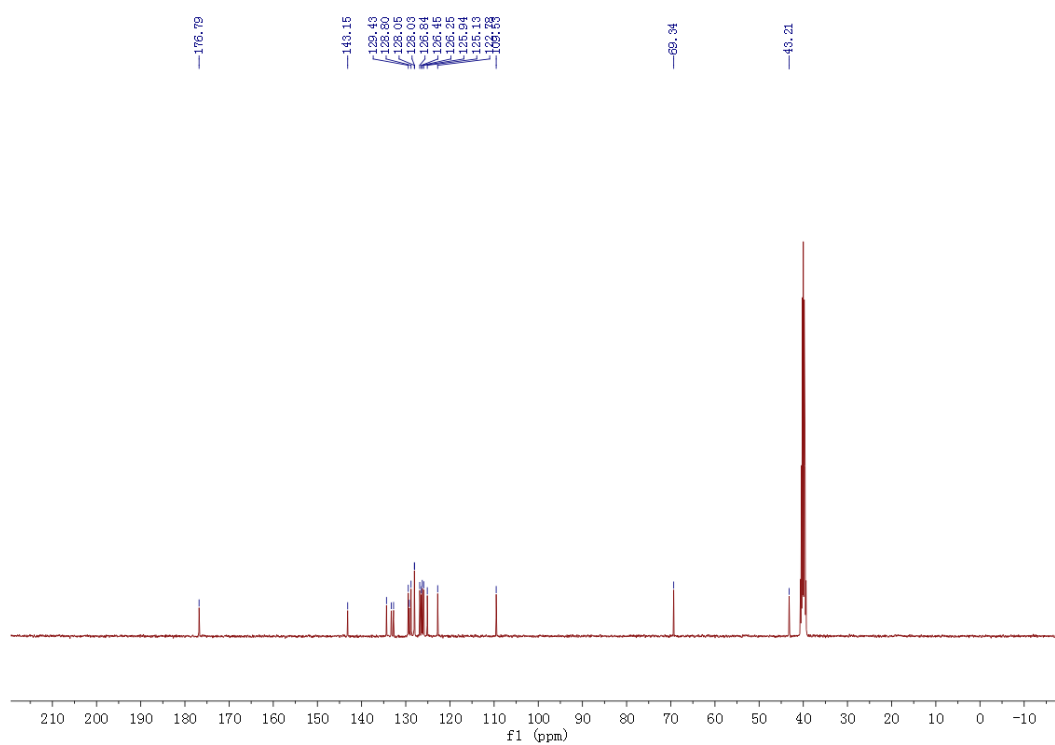
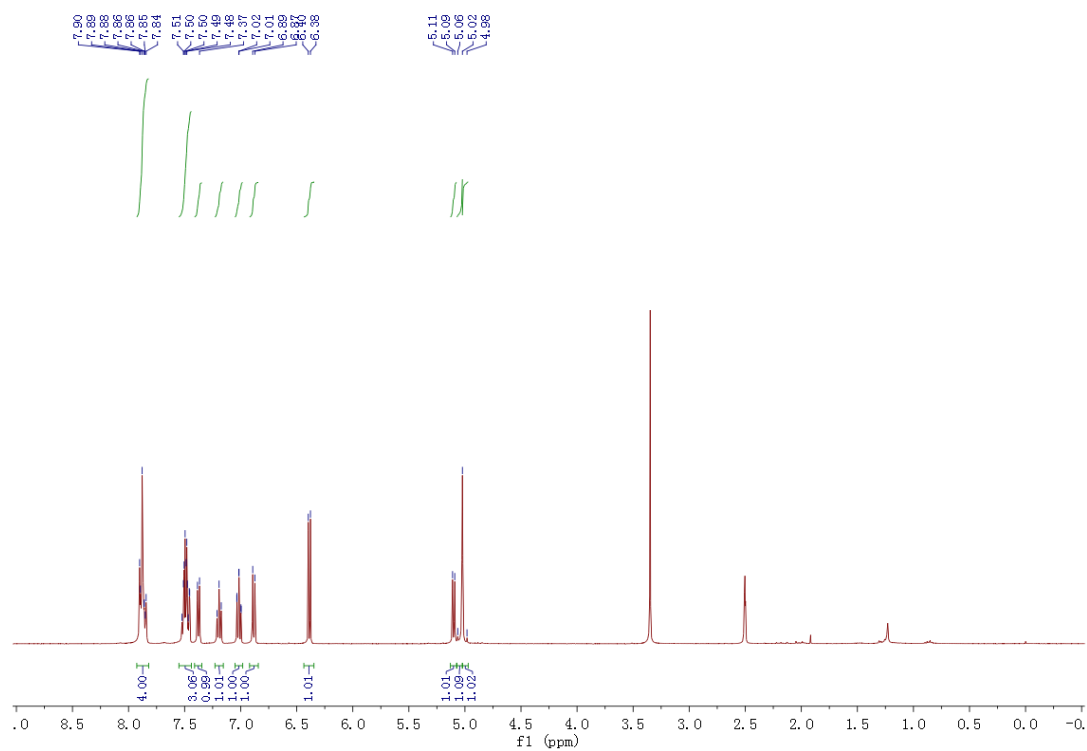


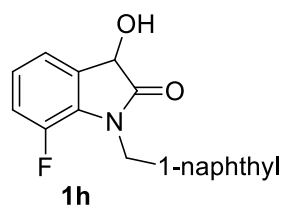




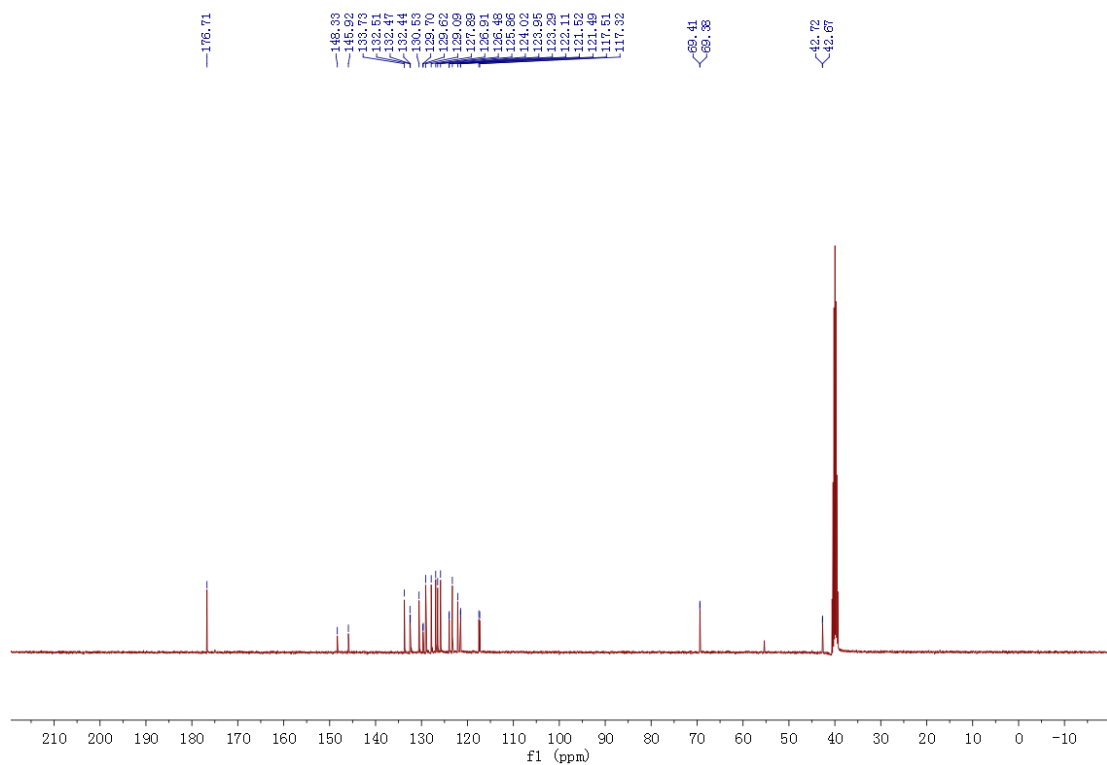
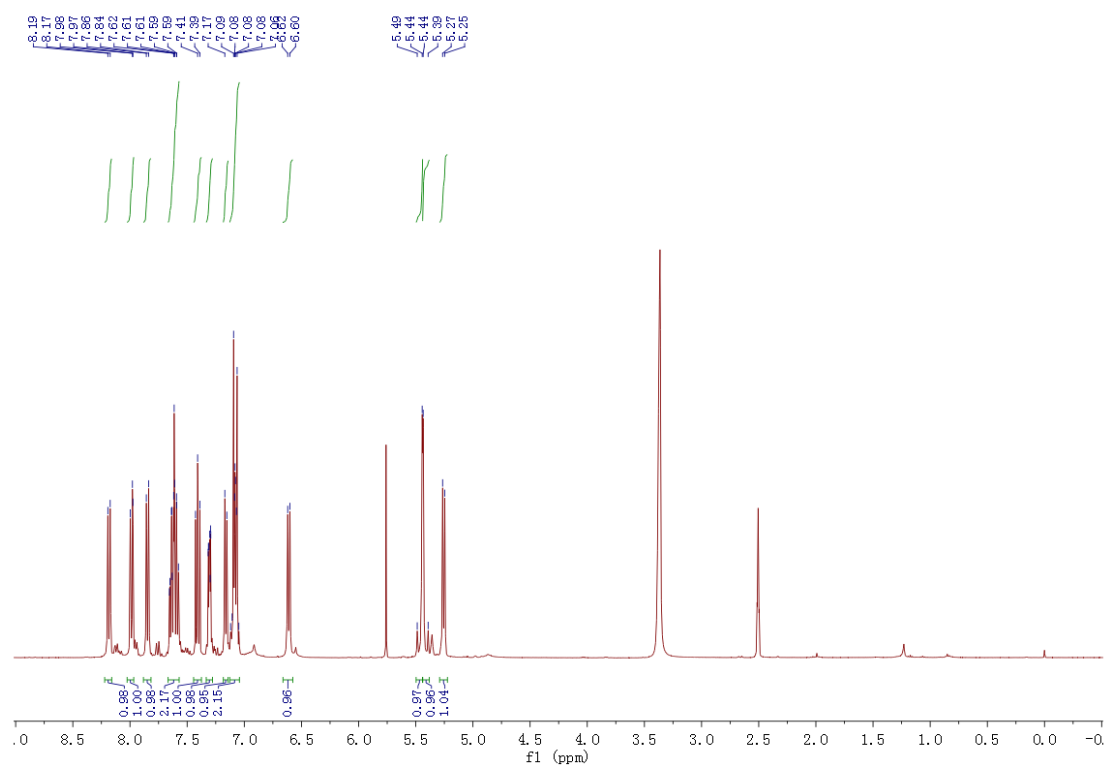
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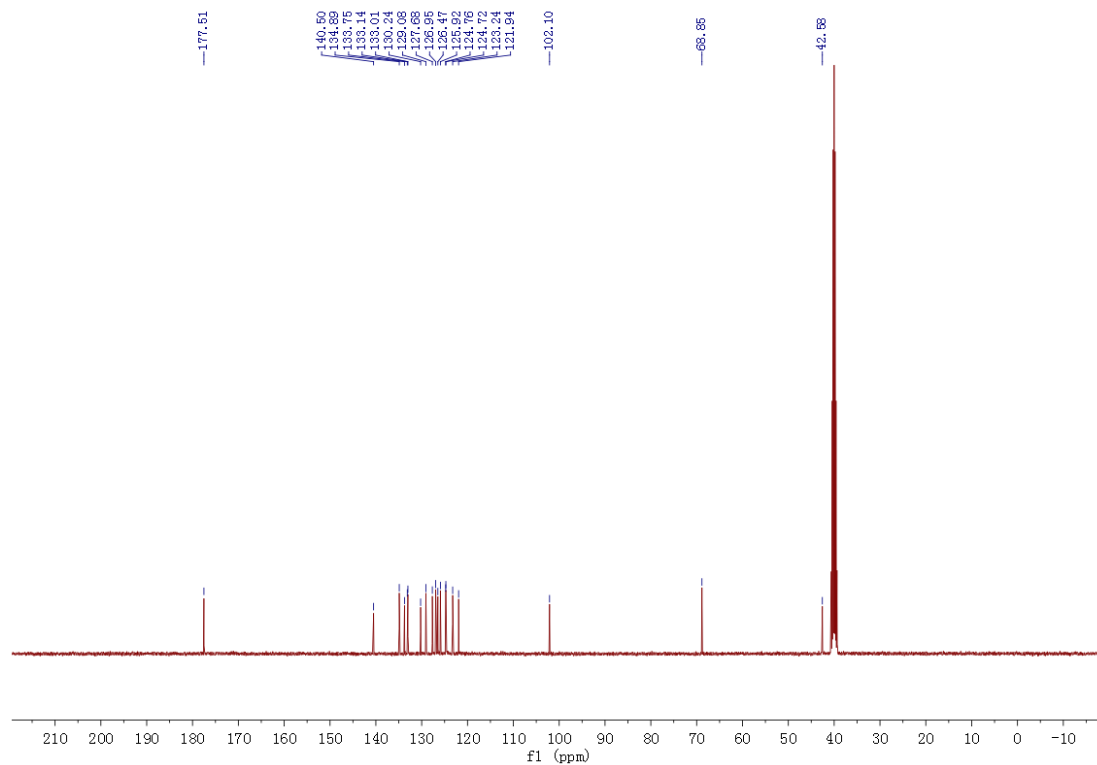
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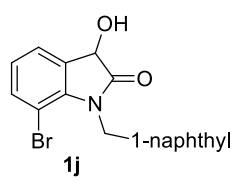




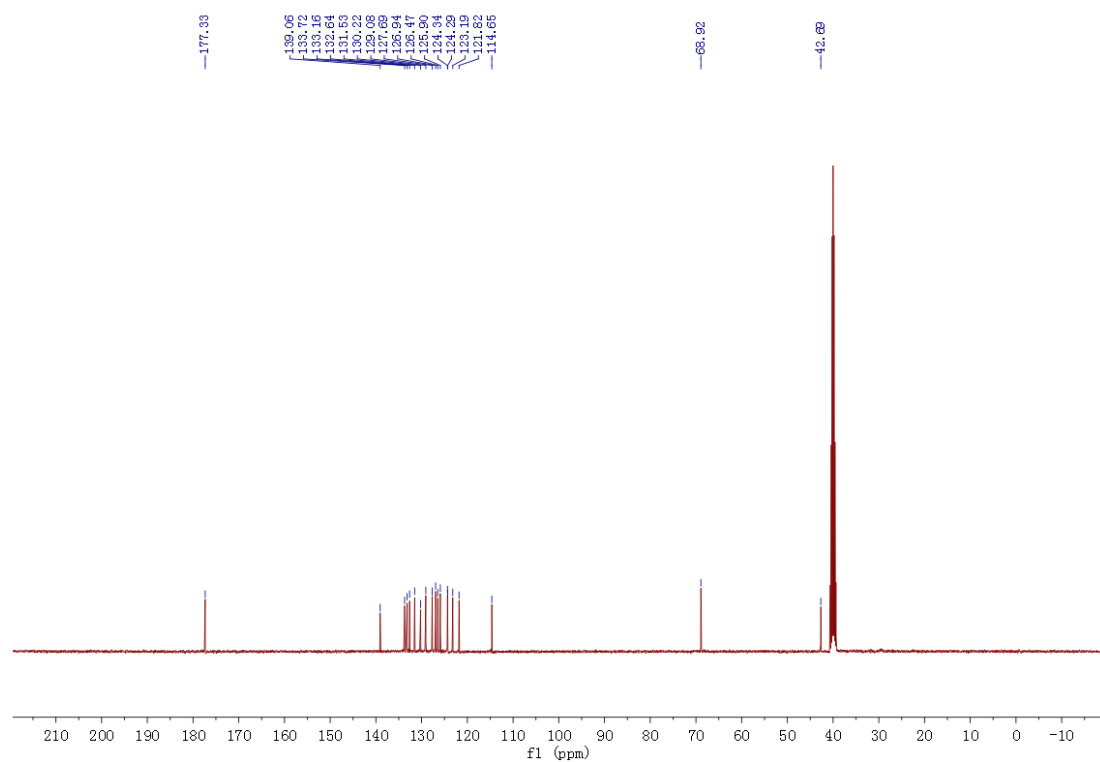
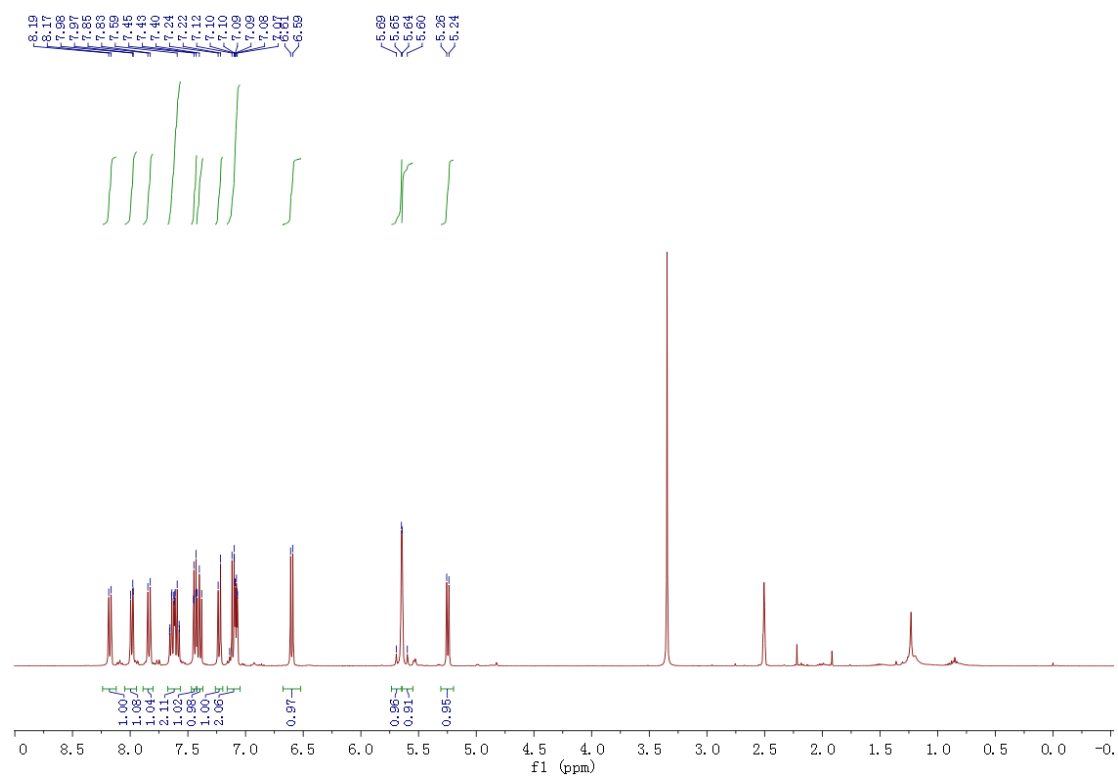
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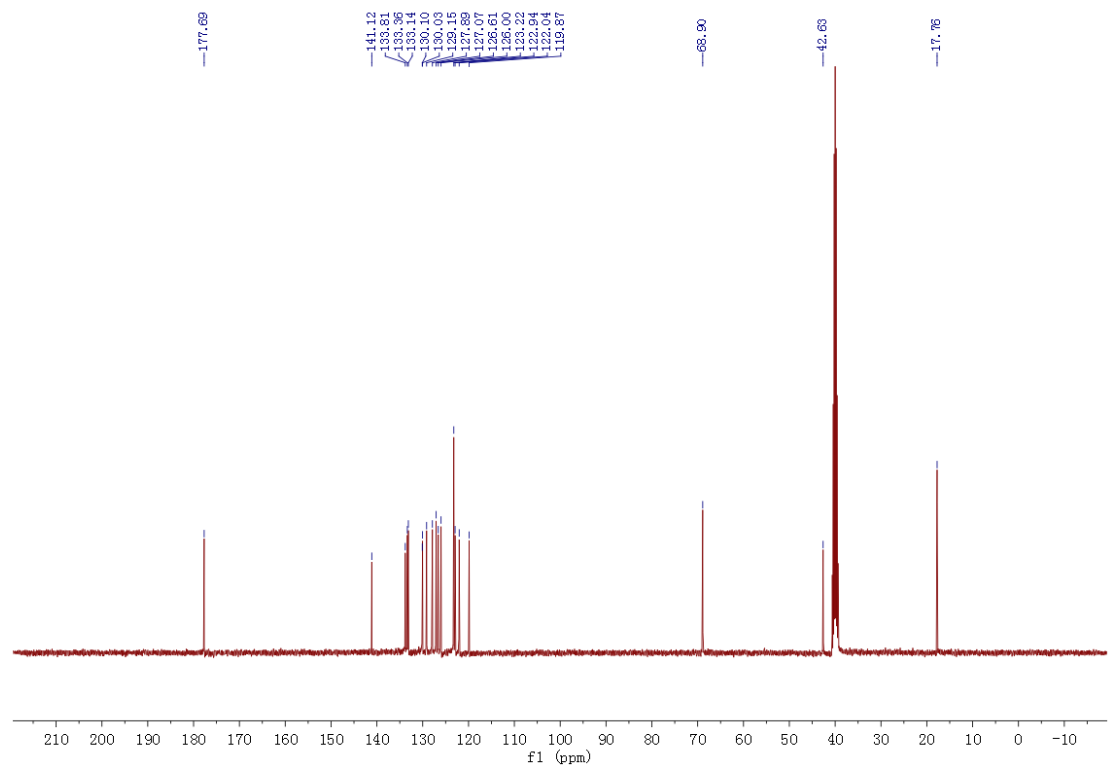
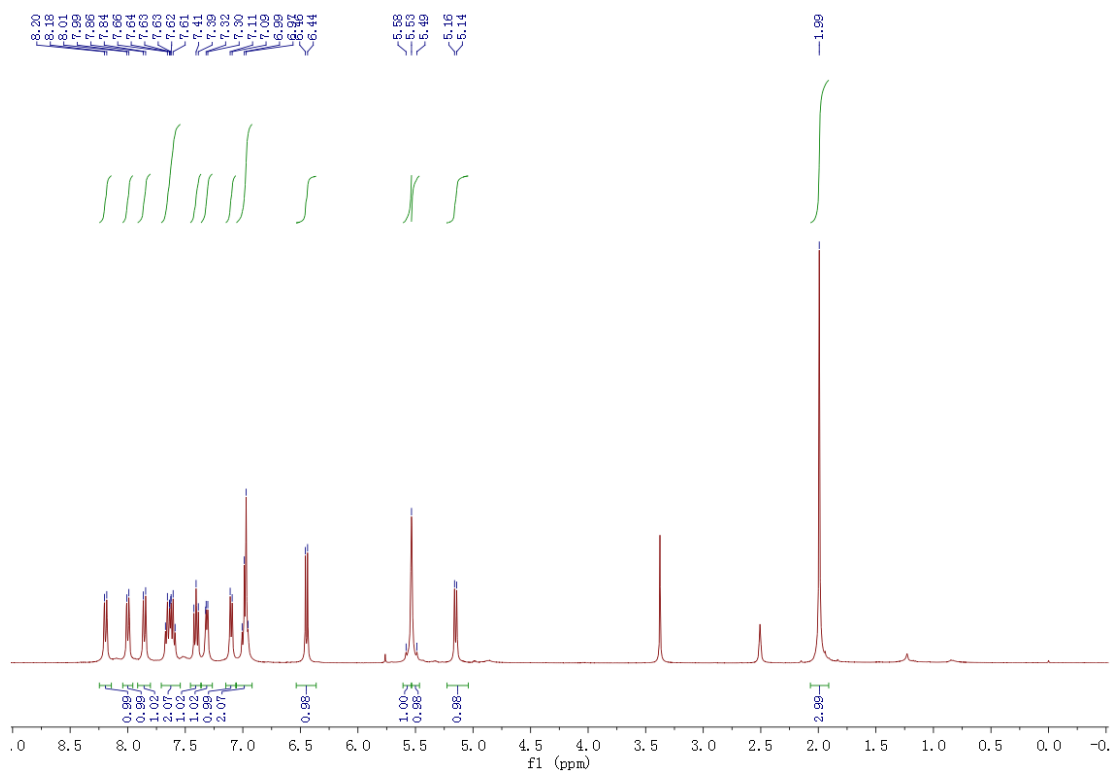
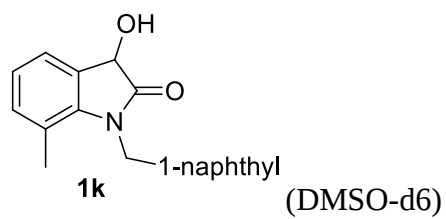


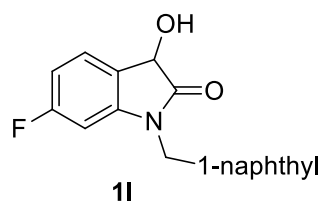




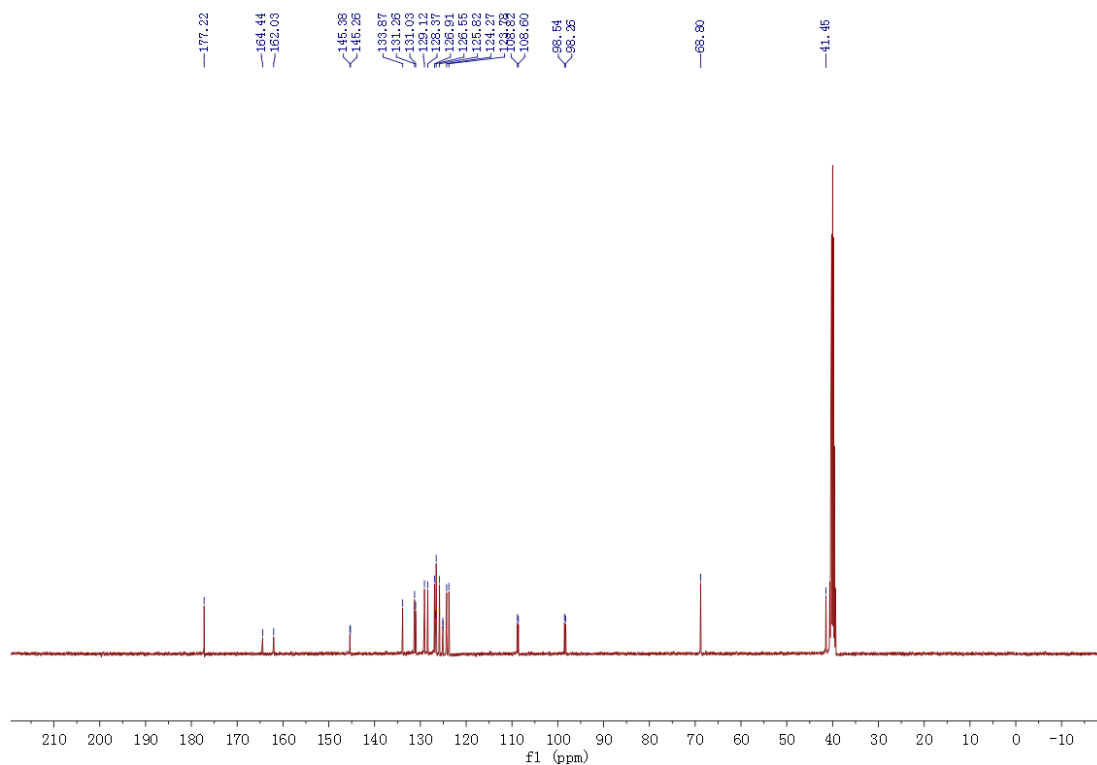
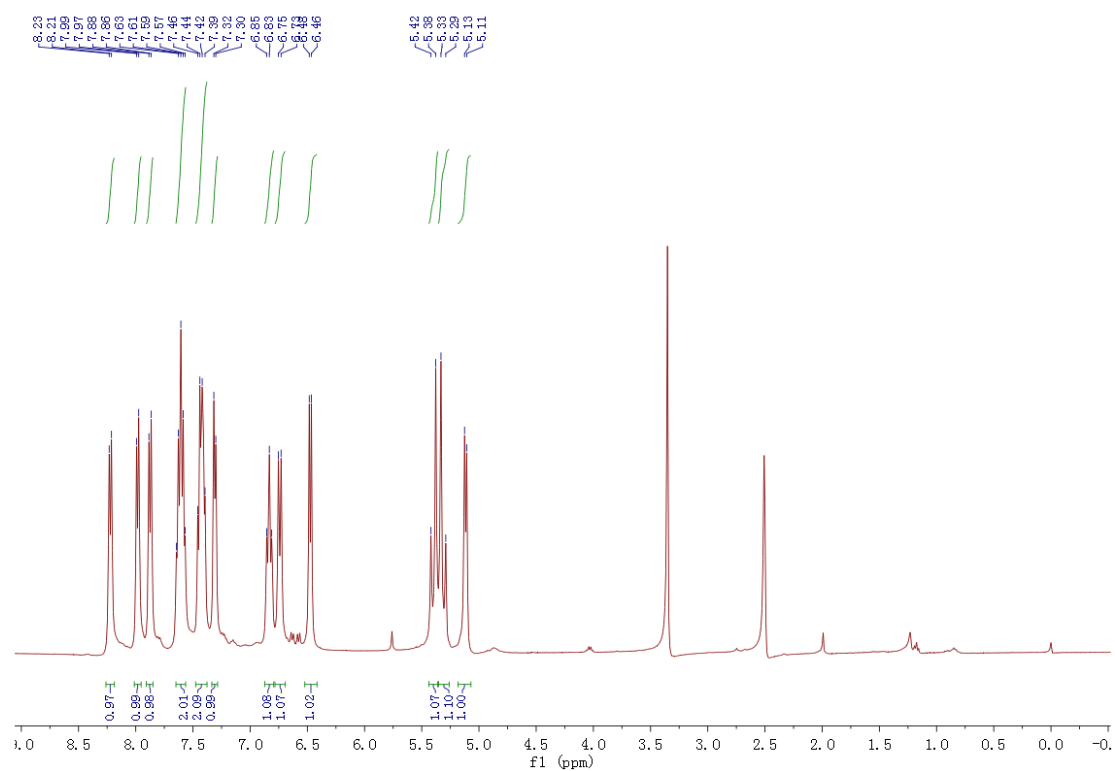
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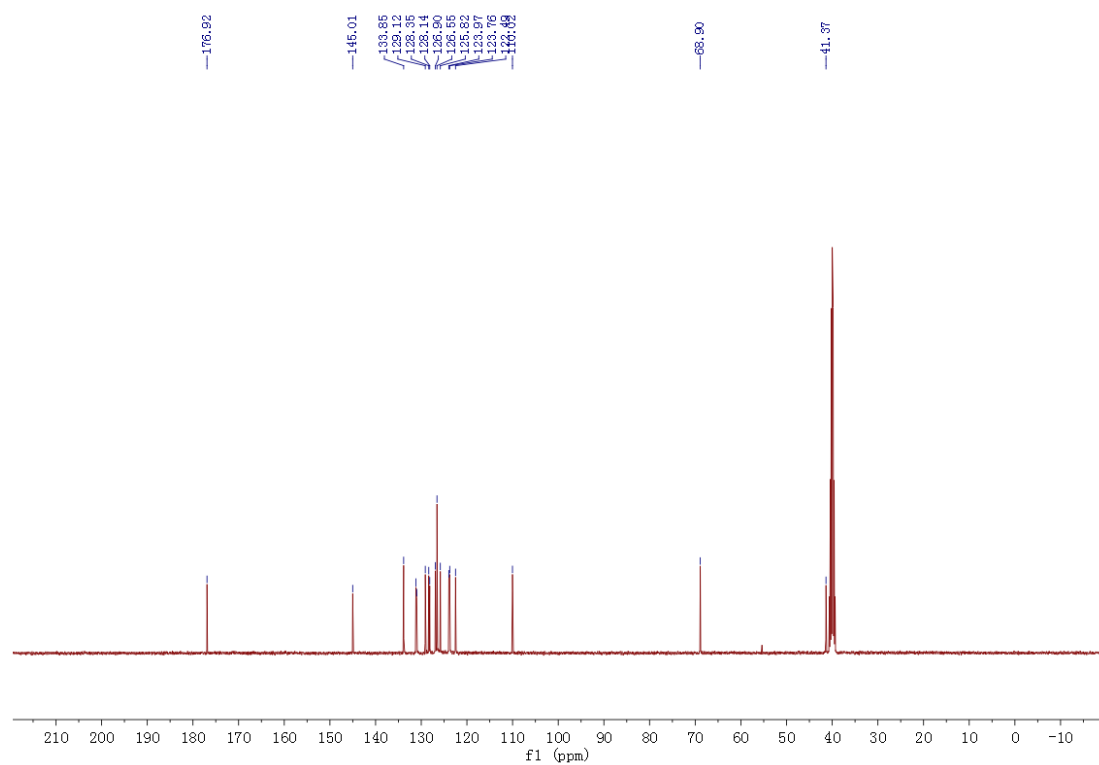
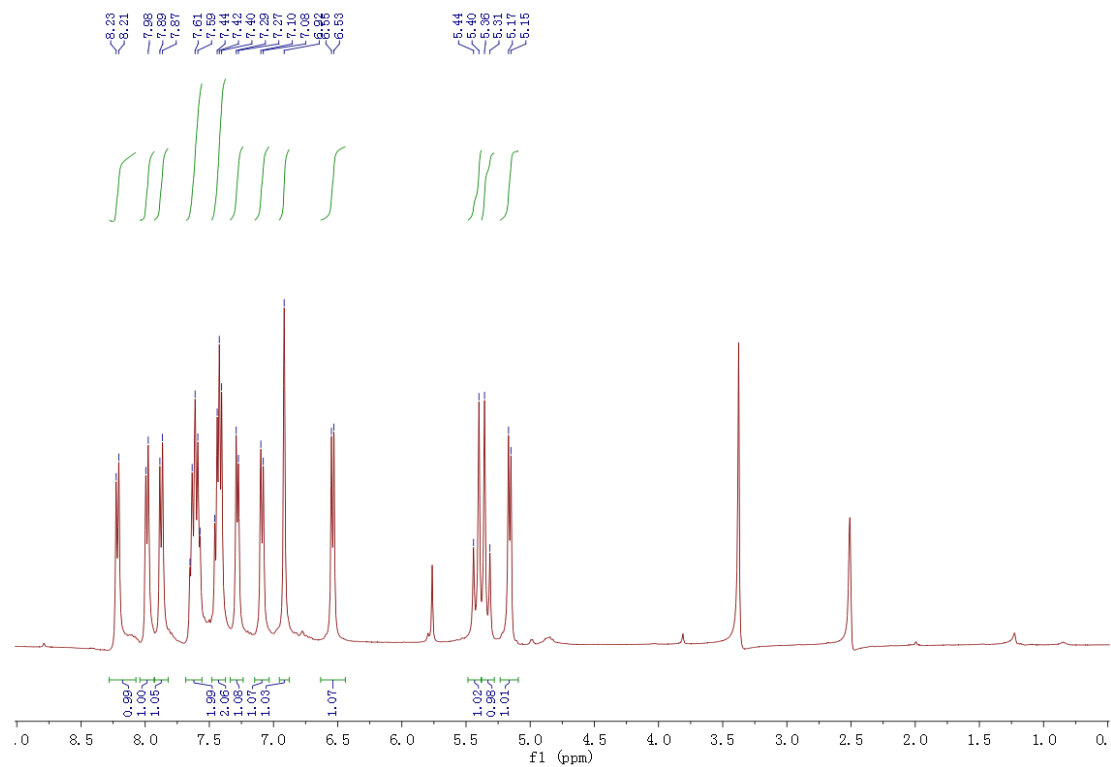
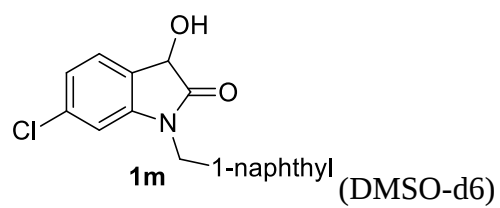


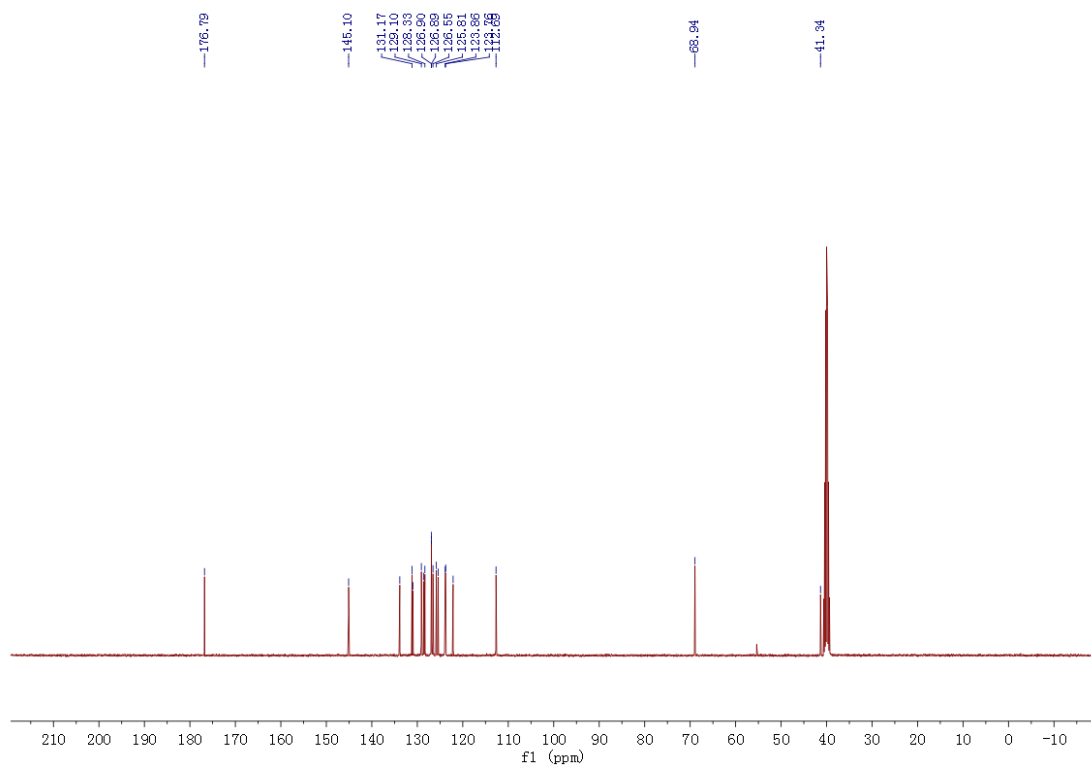
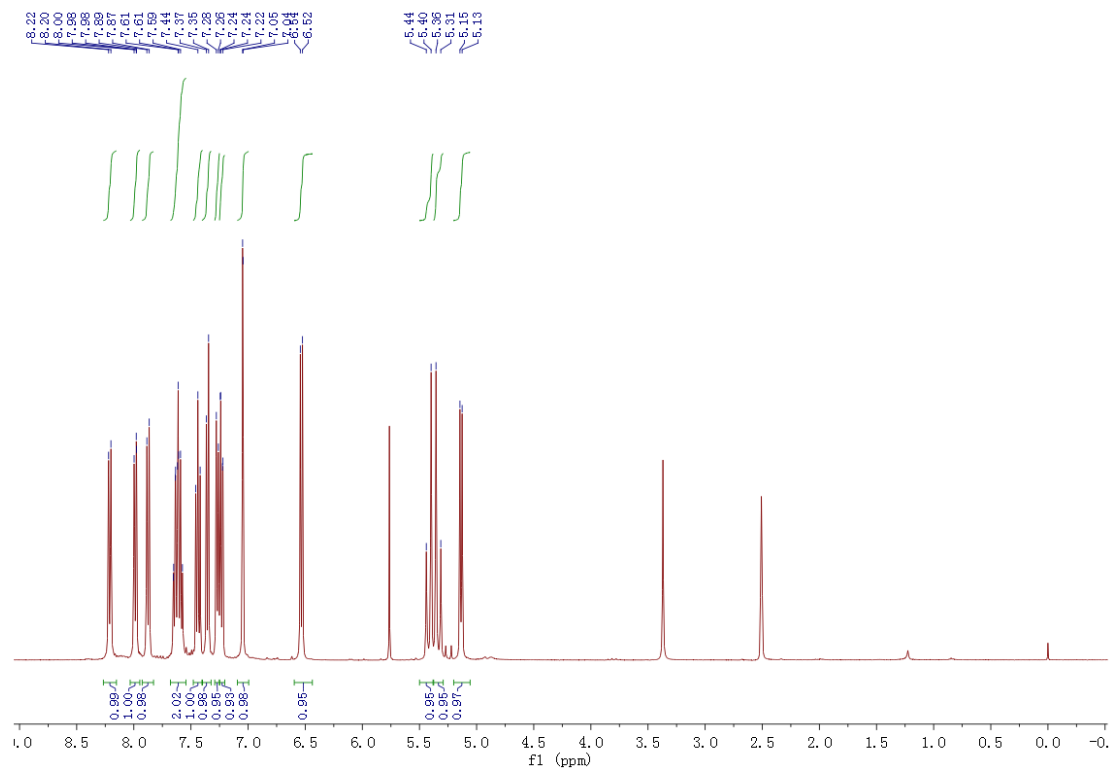
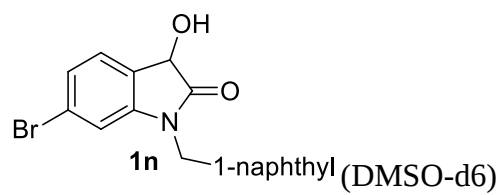


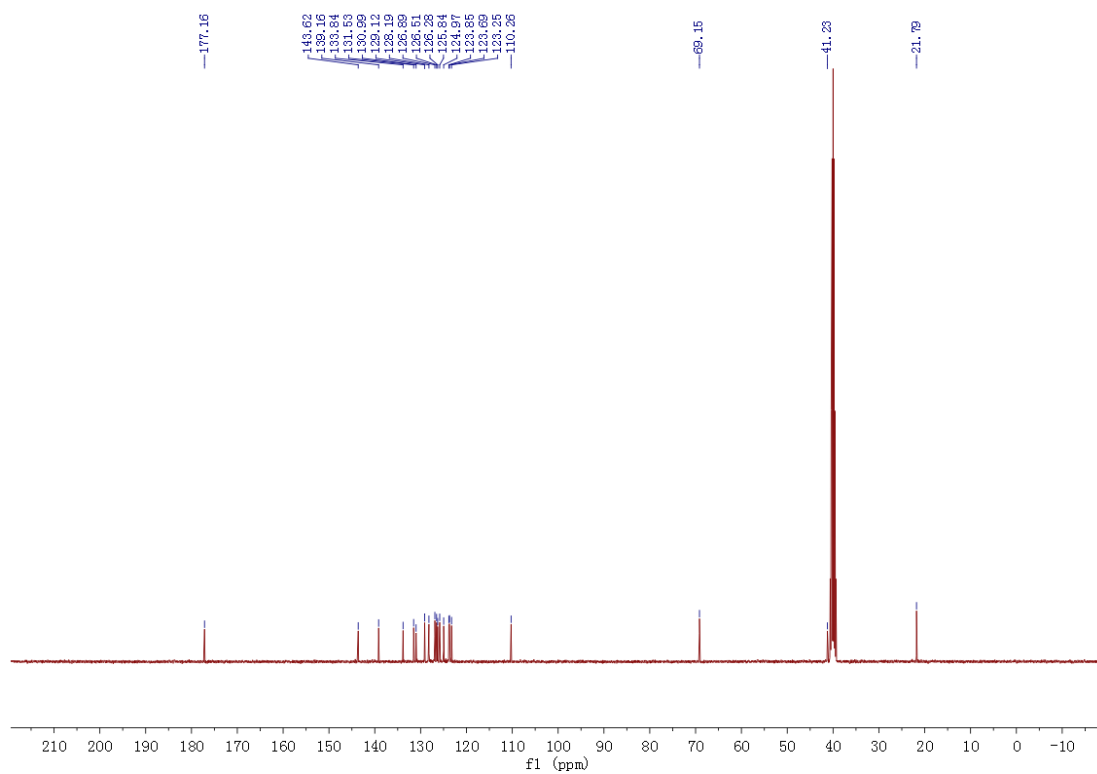
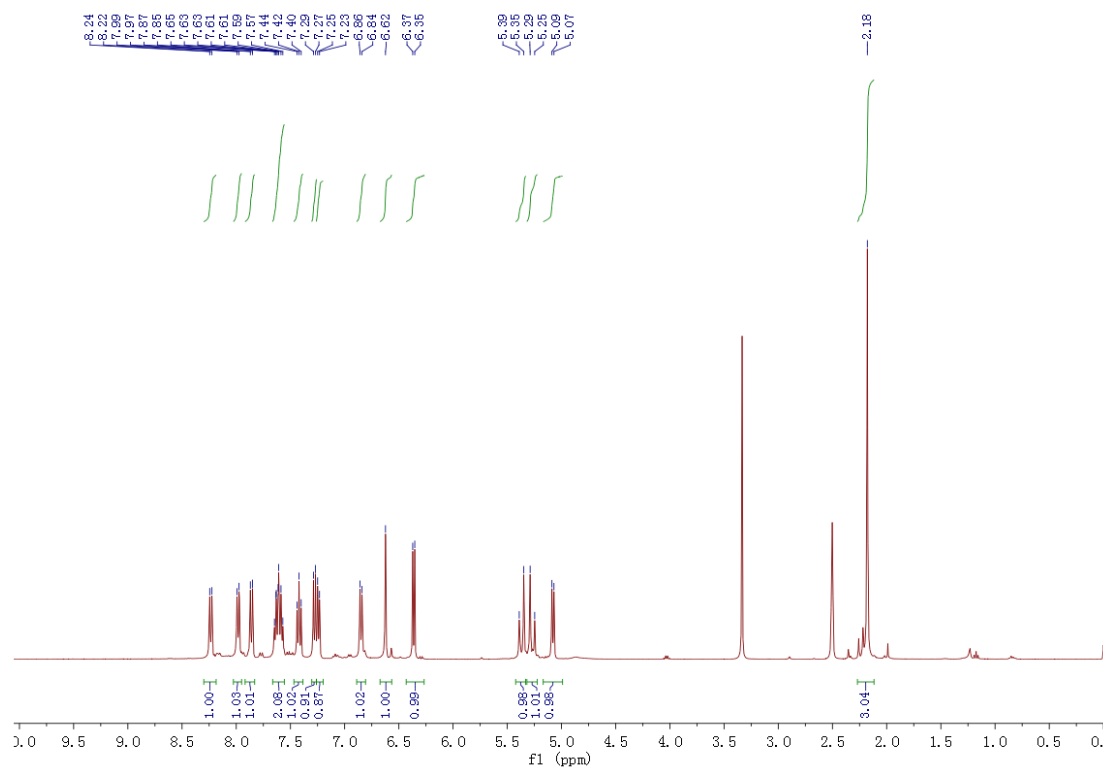
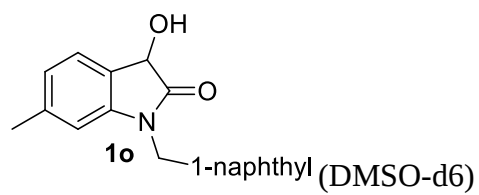


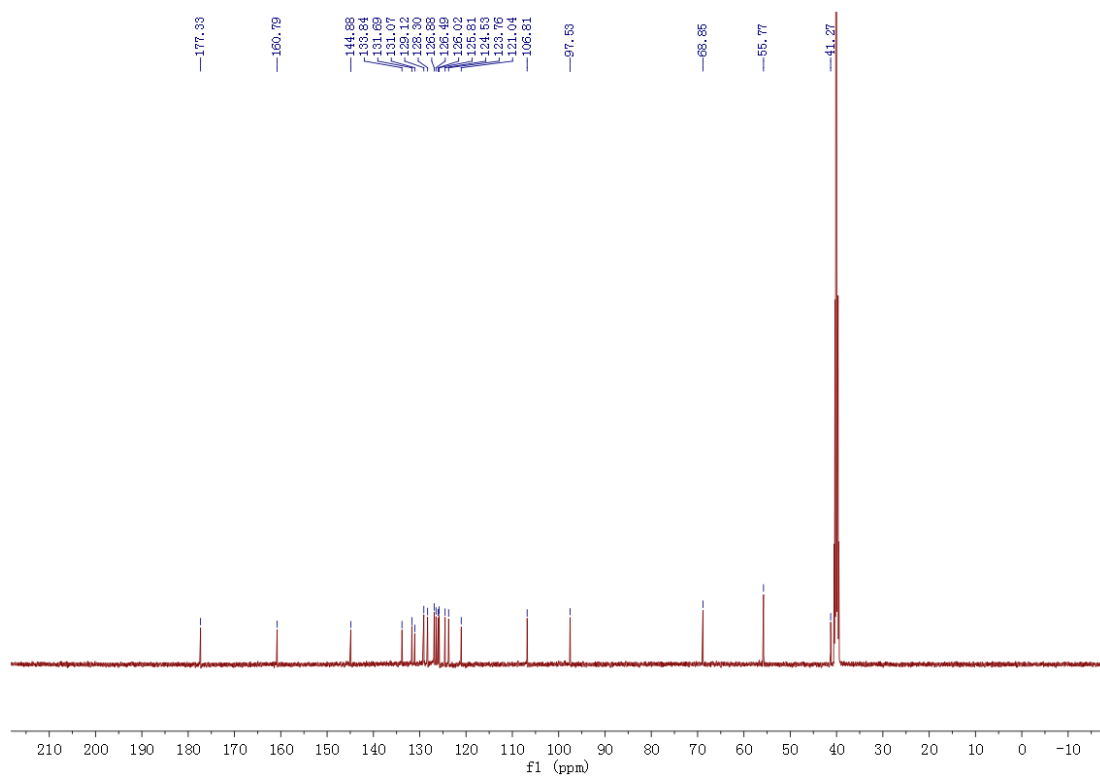
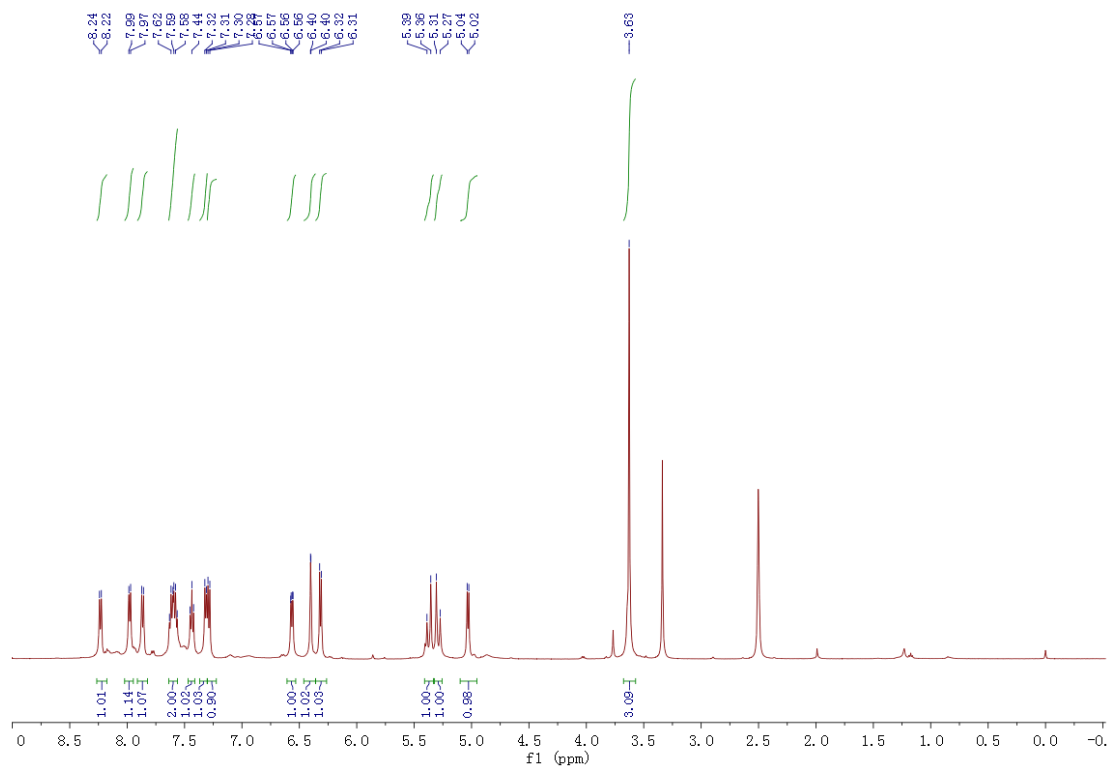
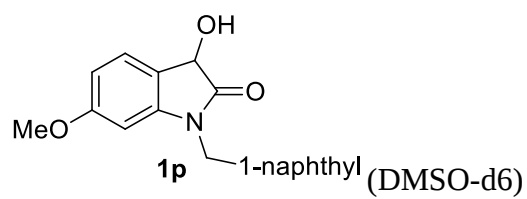
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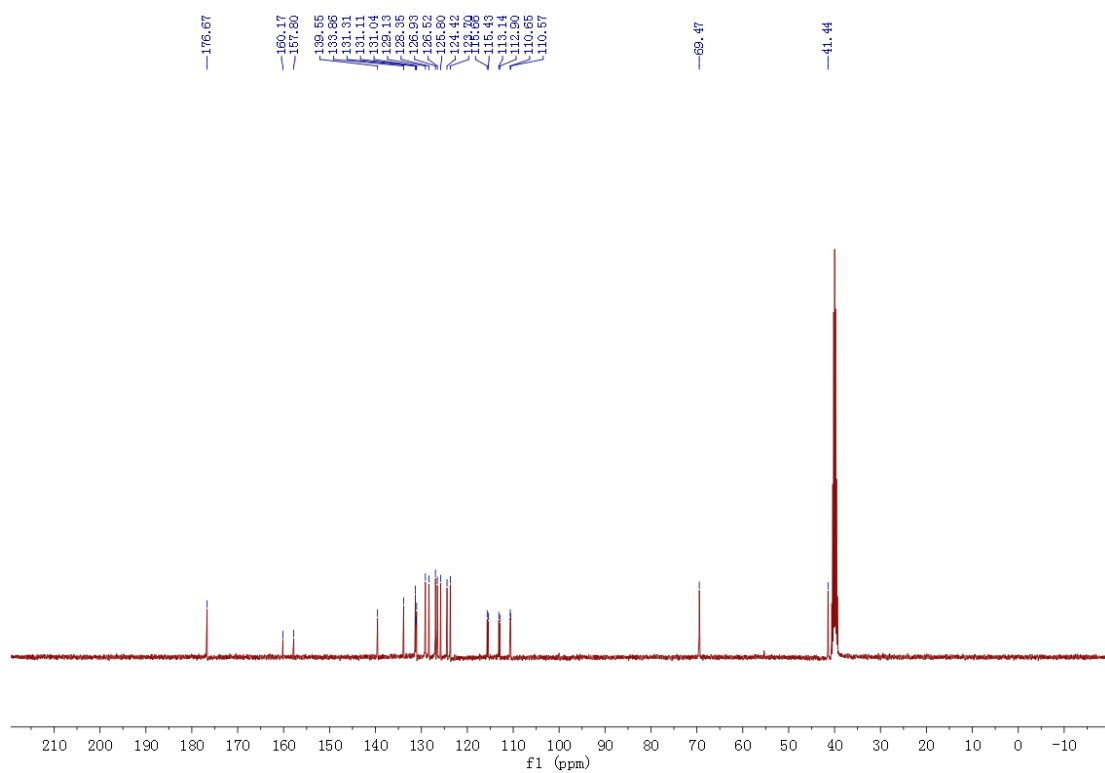
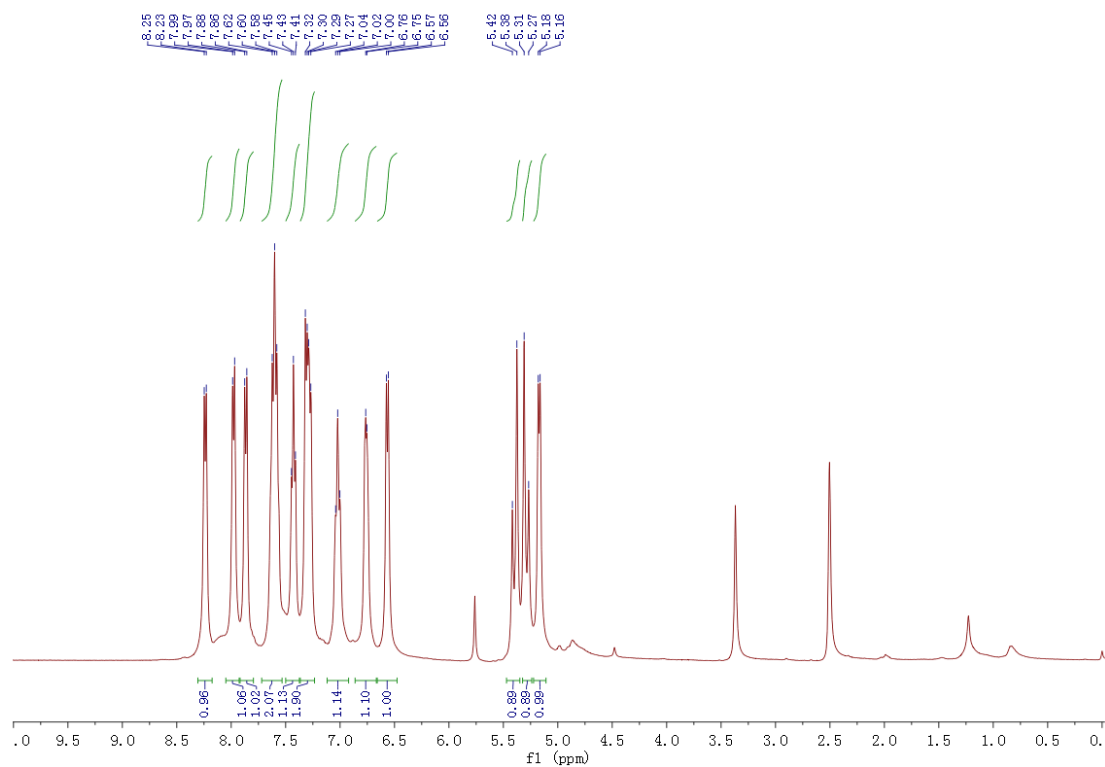
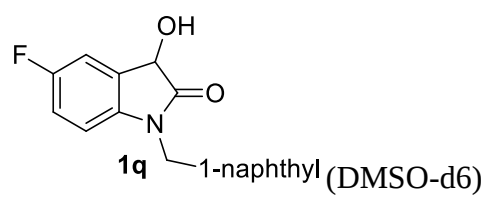


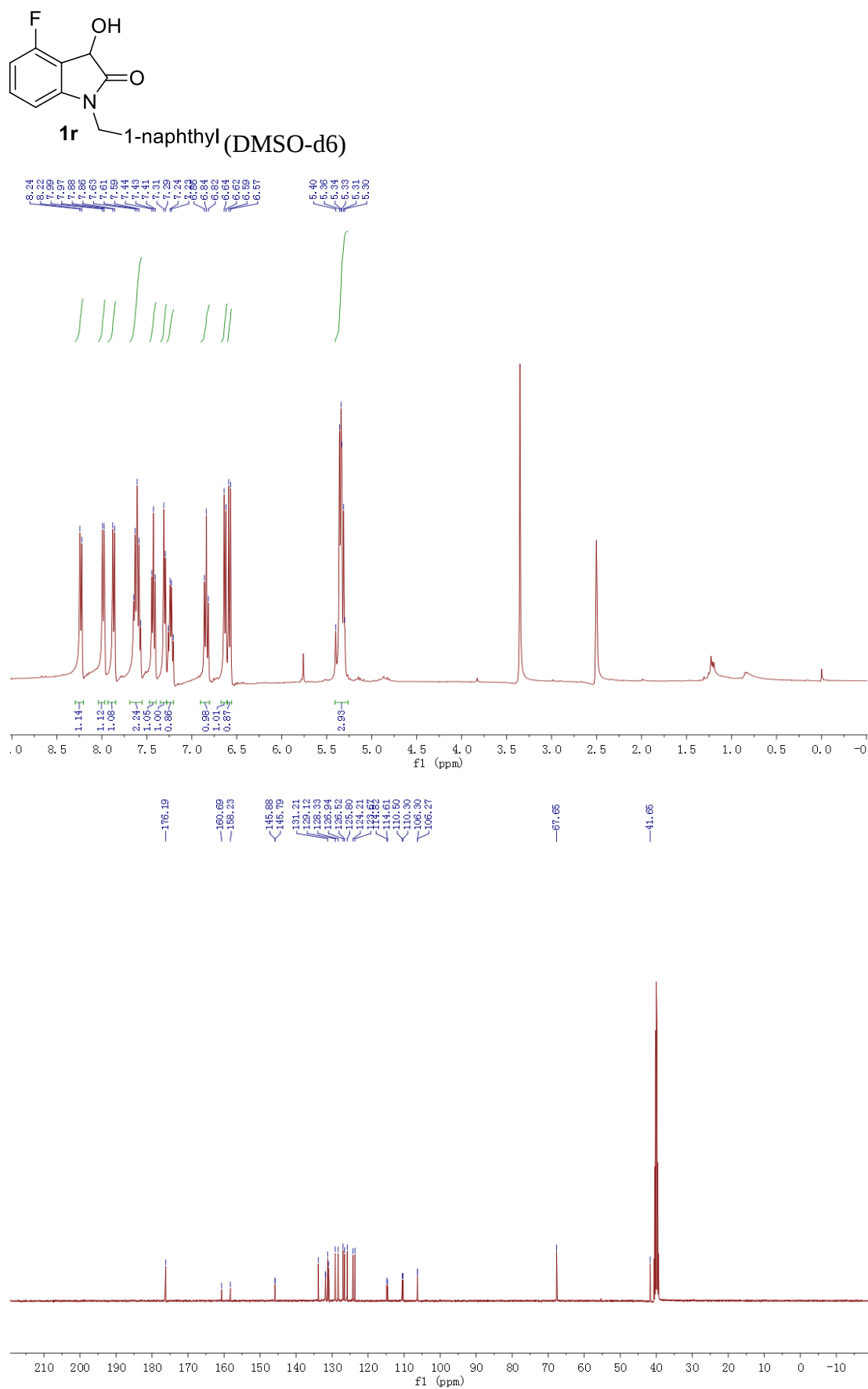


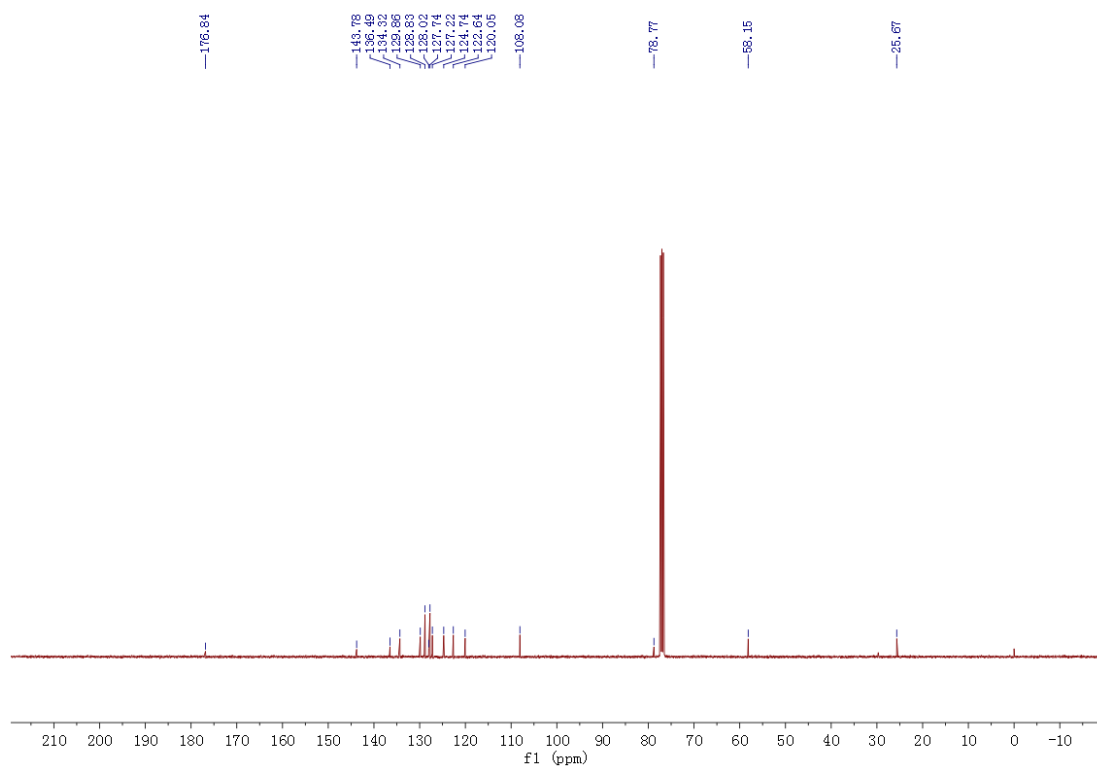
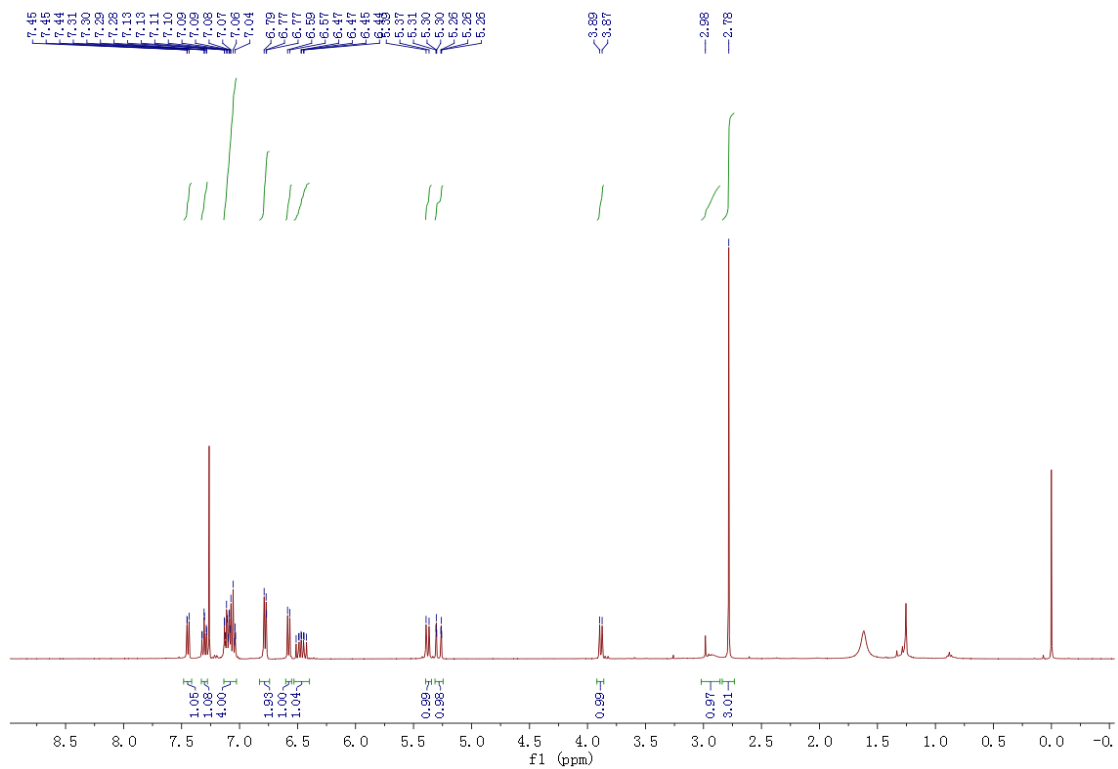
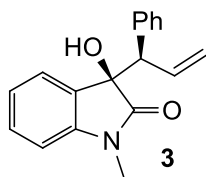


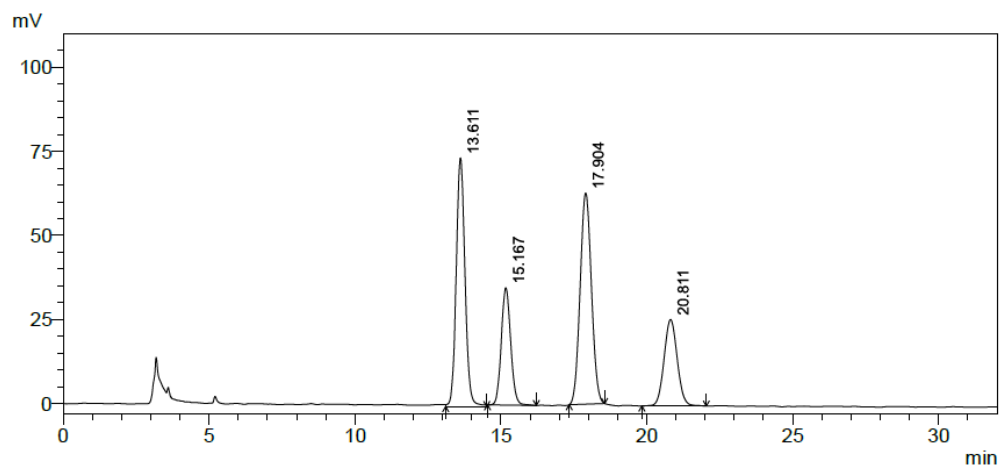
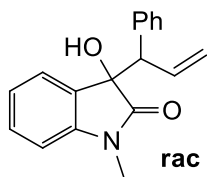






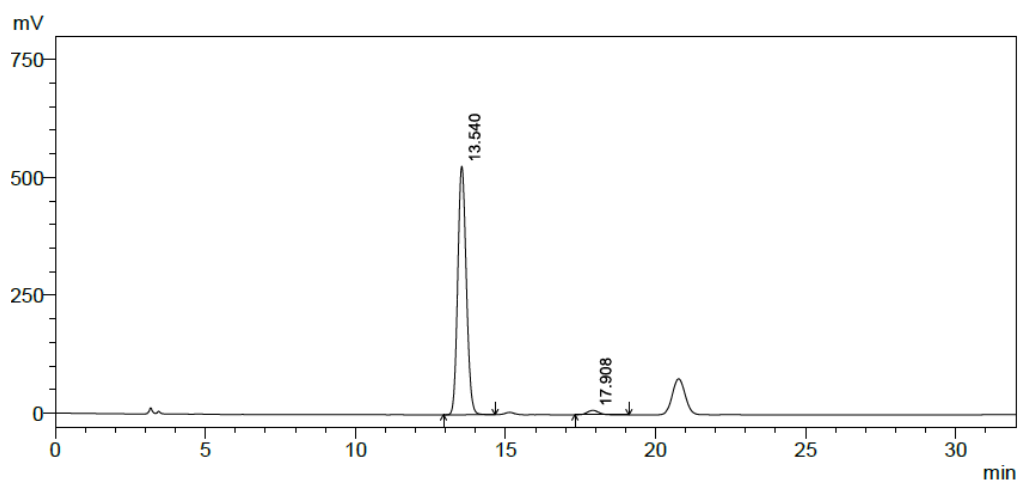
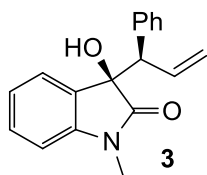






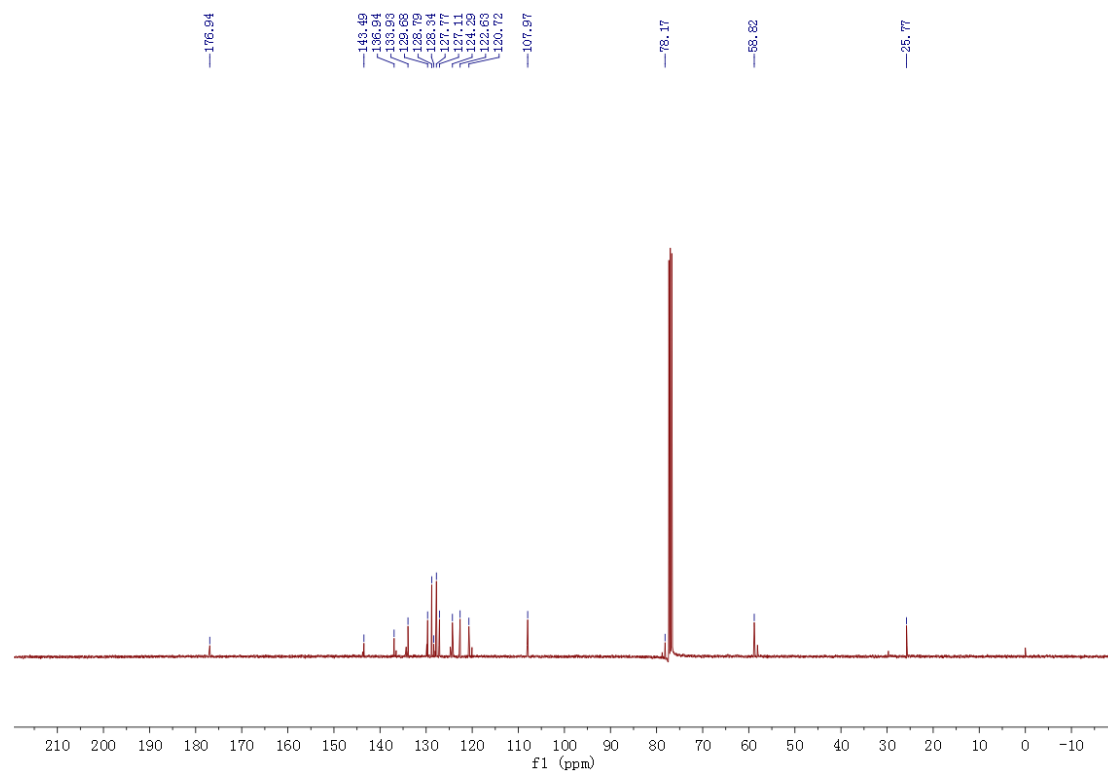
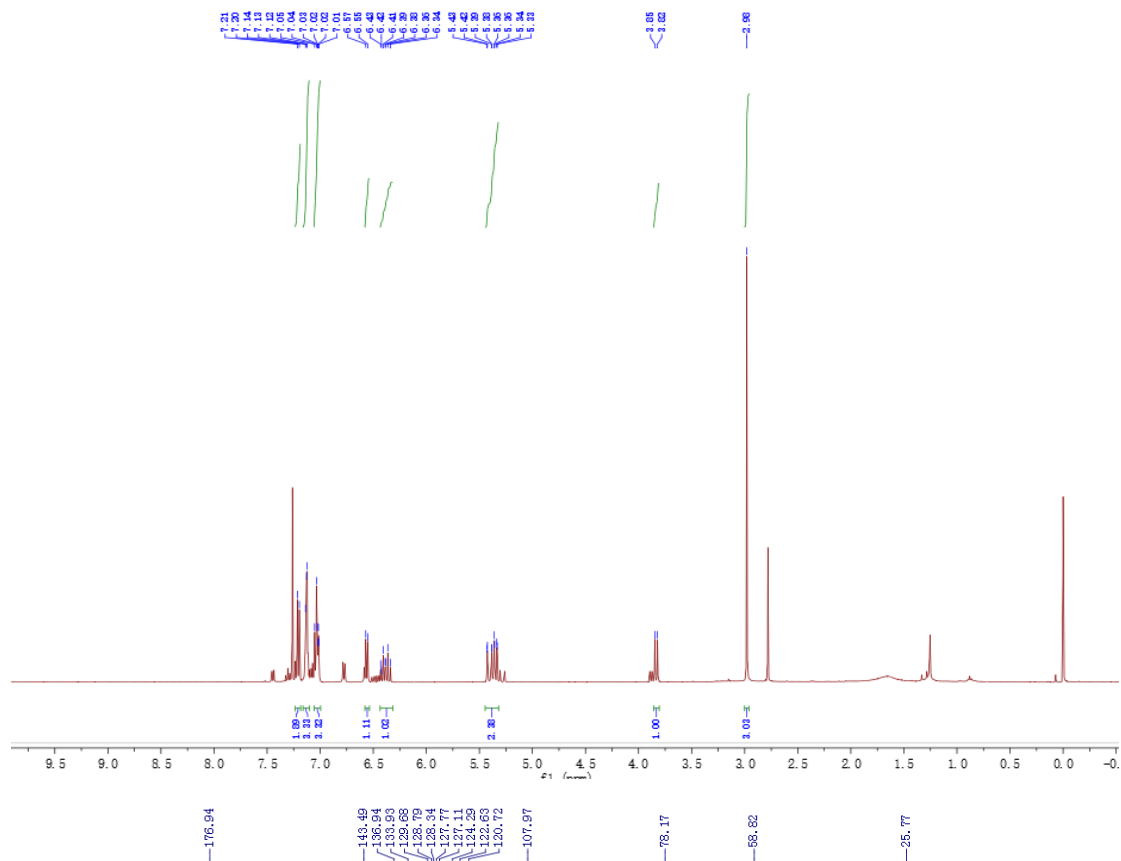
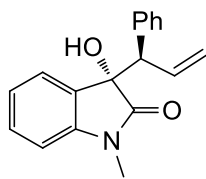
PeakTable

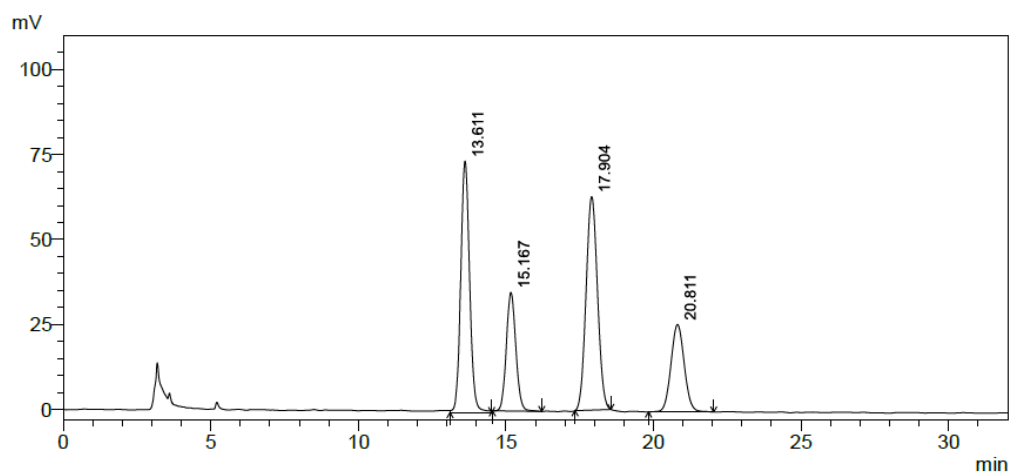
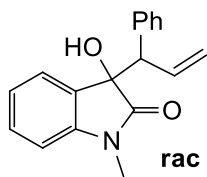
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.611	1545993	73879	32.036	37.461
2	15.167	783379	34846	16.233	17.669
3	17.904	1689072	62772	35.000	31.829
4	20.811	807410	25718	16.731	13.040
Total		4825855	197215	100.000	100.000



PeakTable

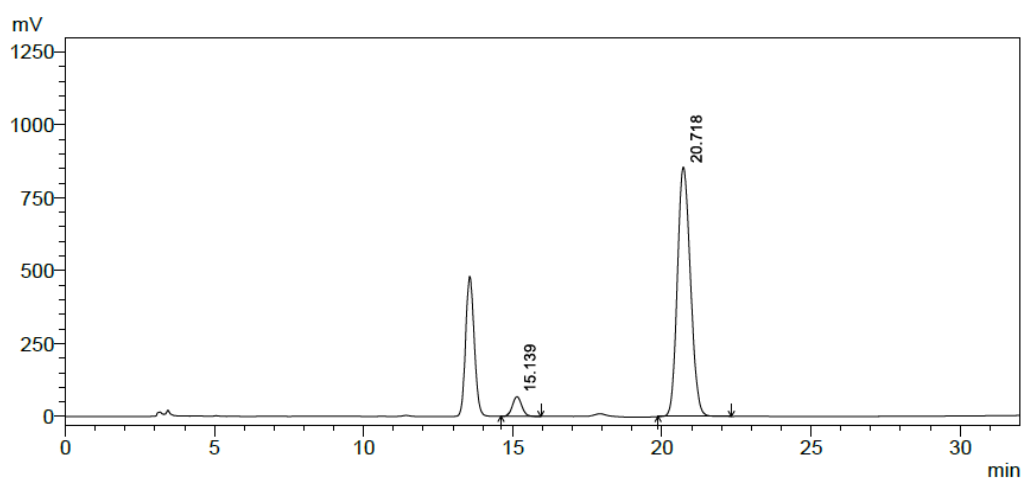
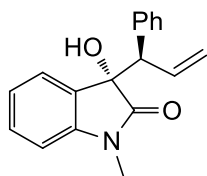
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.540	10454154	527286	97.667	98.239
2	17.908	249749	9452	2.333	1.761
Total		10703903	536738	100.000	100.000





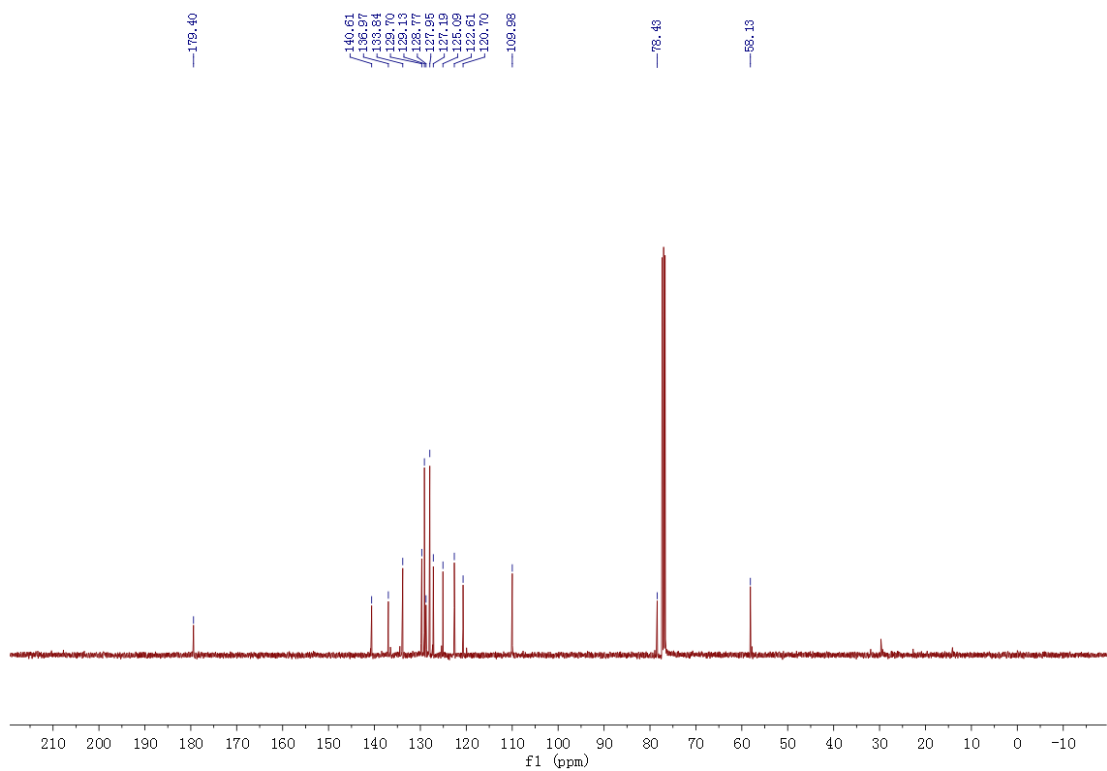
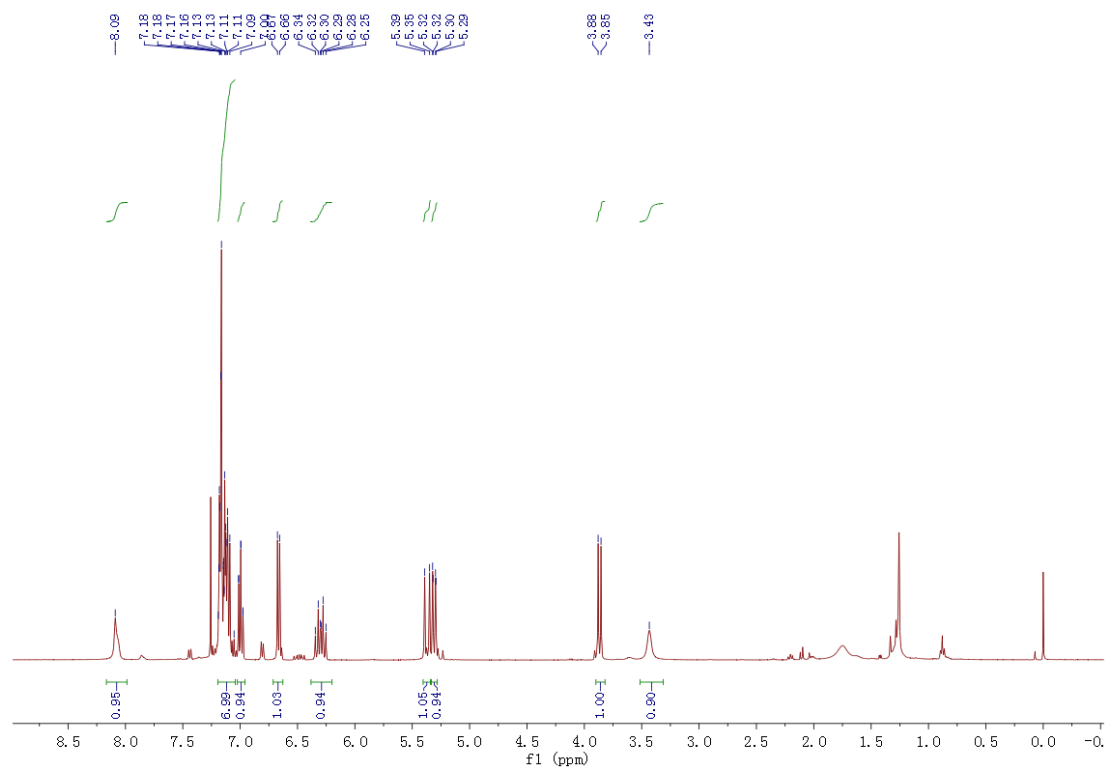
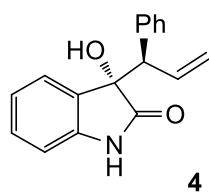
PeakTable

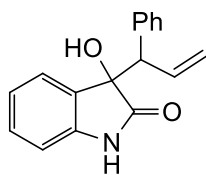
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.611	1545993	73879	32.036	37.461
2	15.167	783379	34846	16.233	17.669
3	17.904	1689072	62772	35.000	31.829
4	20.811	807410	25718	16.731	13.040
Total		4825855	197215	100.000	100.000



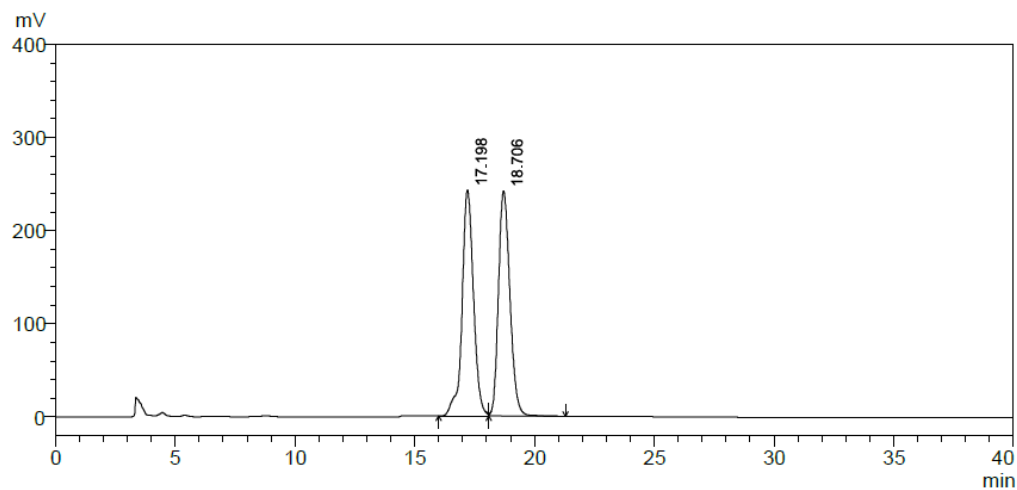
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.139	1460296	67490	5.314	7.315
2	20.718	26018976	855100	94.686	92.685
Total		27479272	922590	100.000	100.000



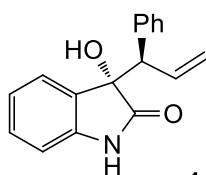


major rac

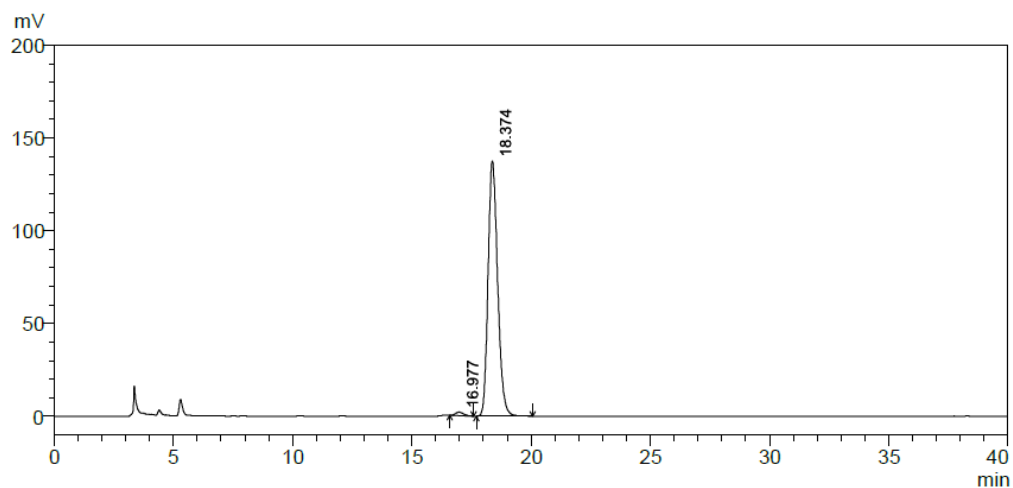


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.198	8073485	242681	49.991	50.095
2	18.706	8076442	241759	50.009	49.905
Total		16149927	484440	100.000	100.000

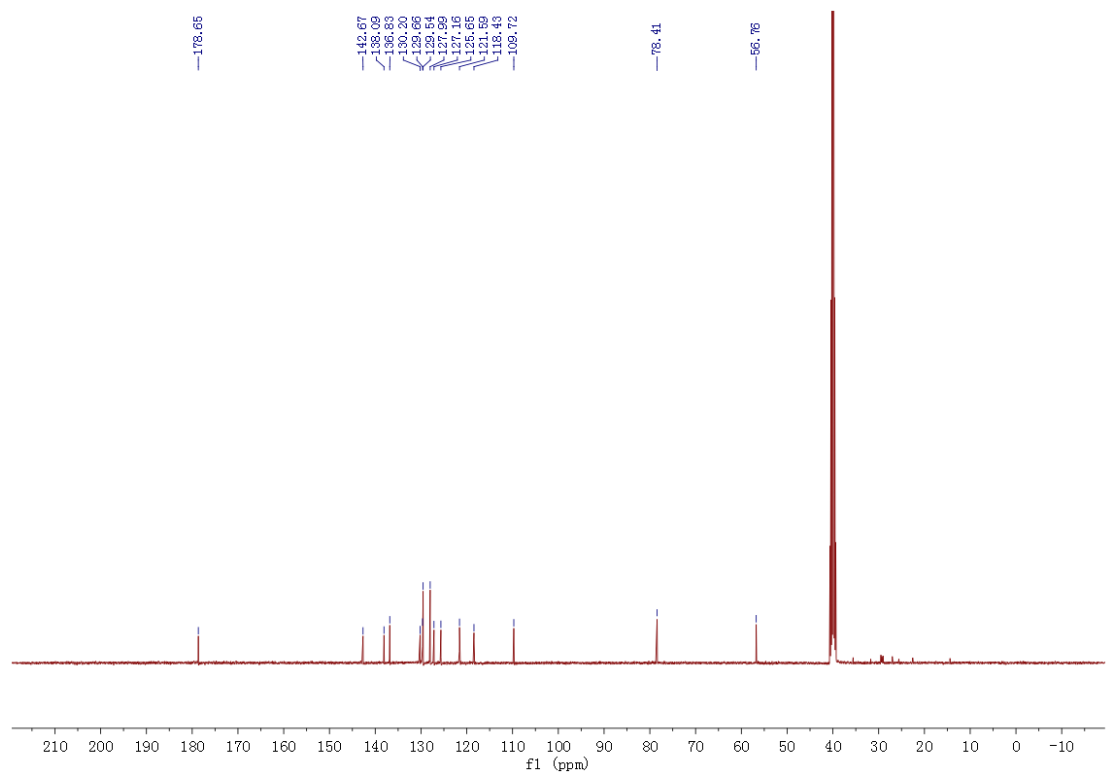
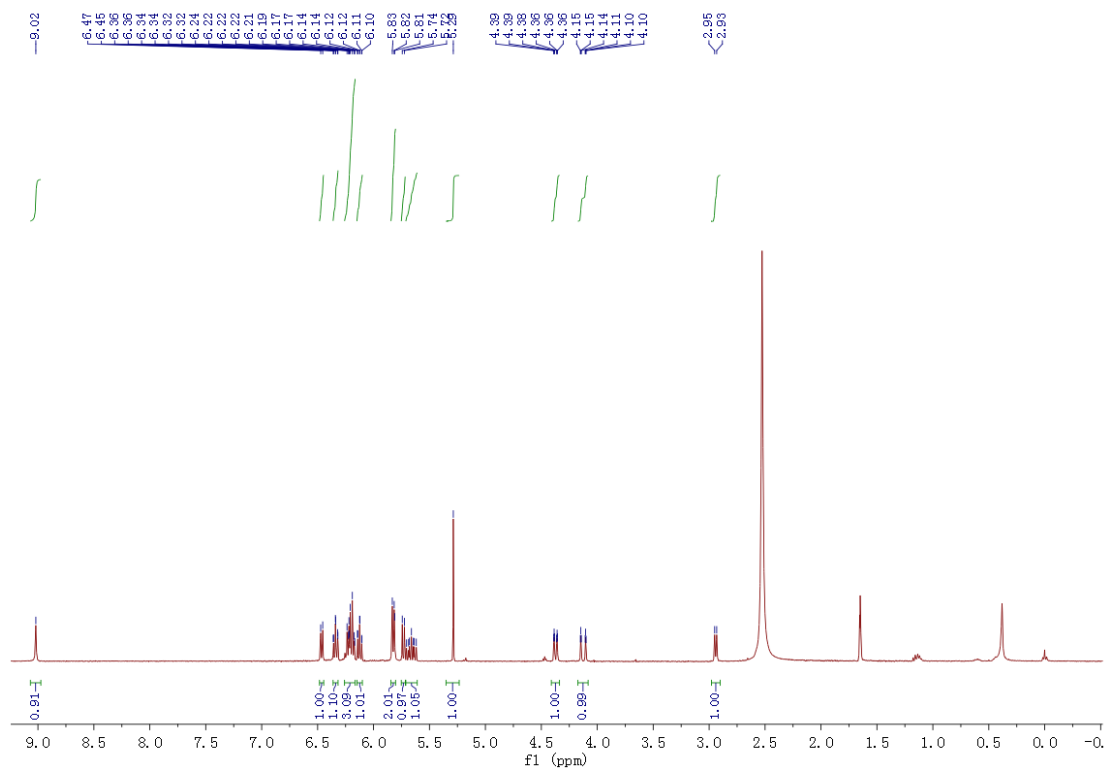
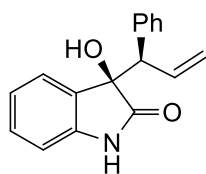


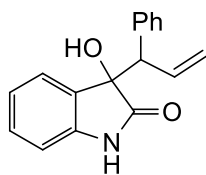
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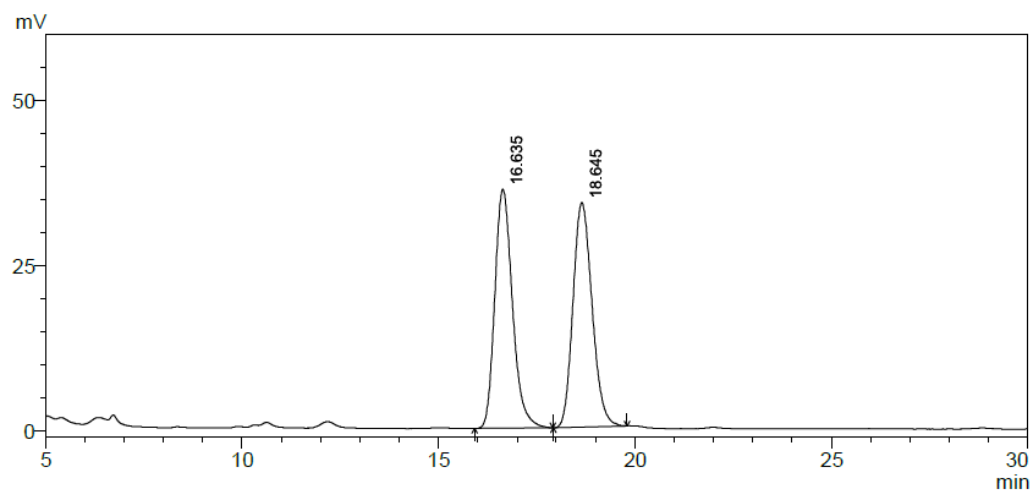
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.977	44733	1889	1.154	1.357
2	18.374	3832311	137345	98.846	98.643
Total		3877044	139235	100.000	100.000



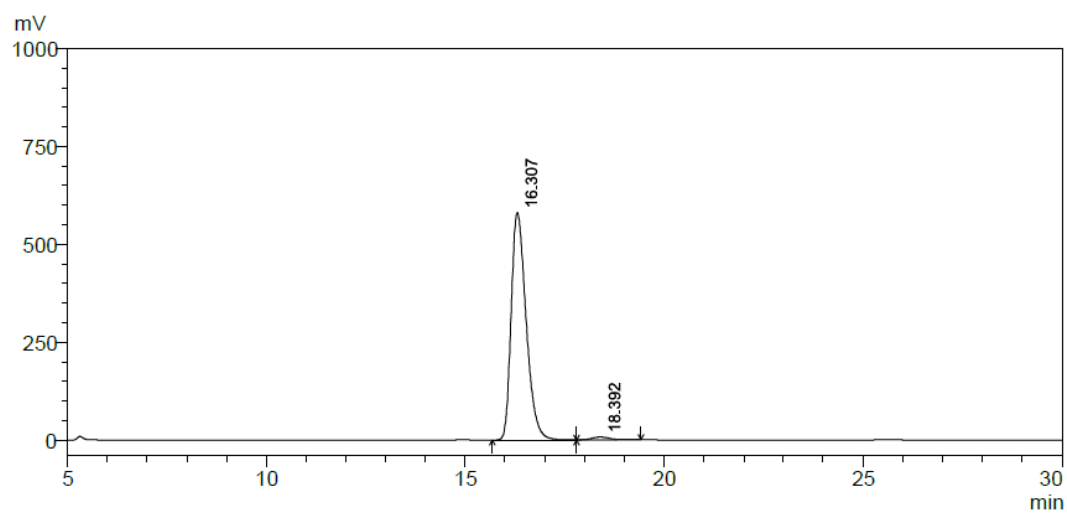
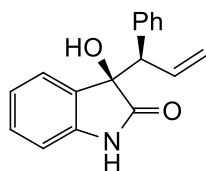


minor rac



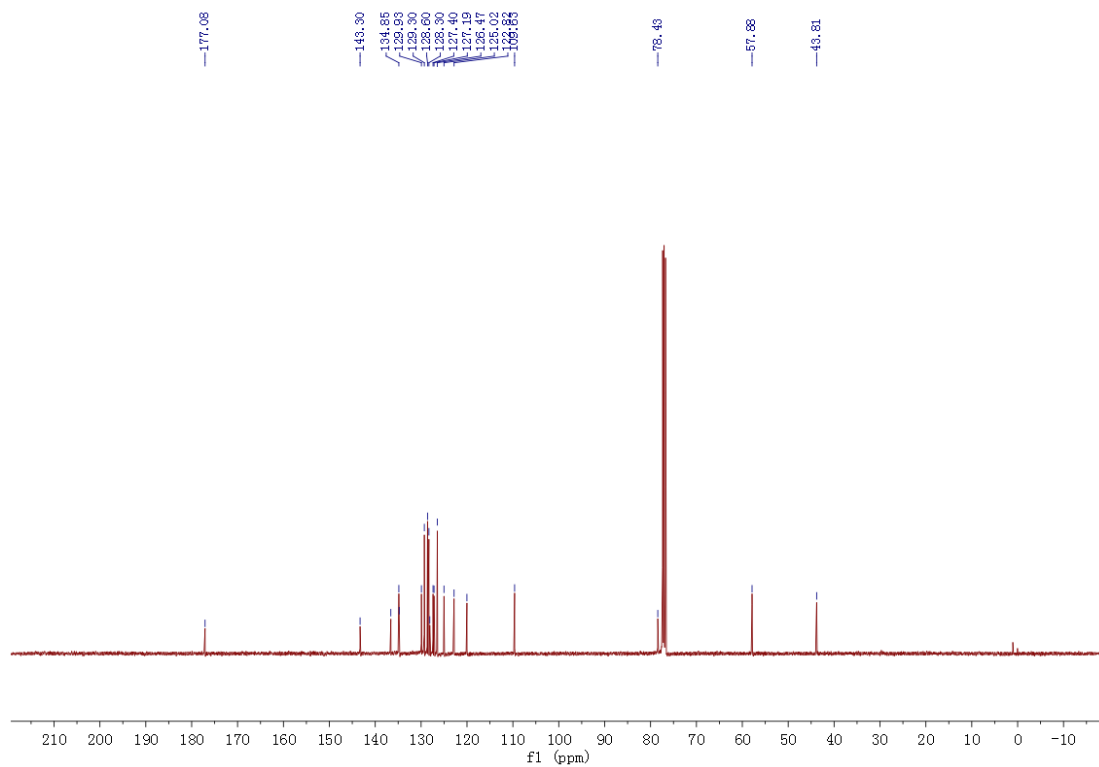
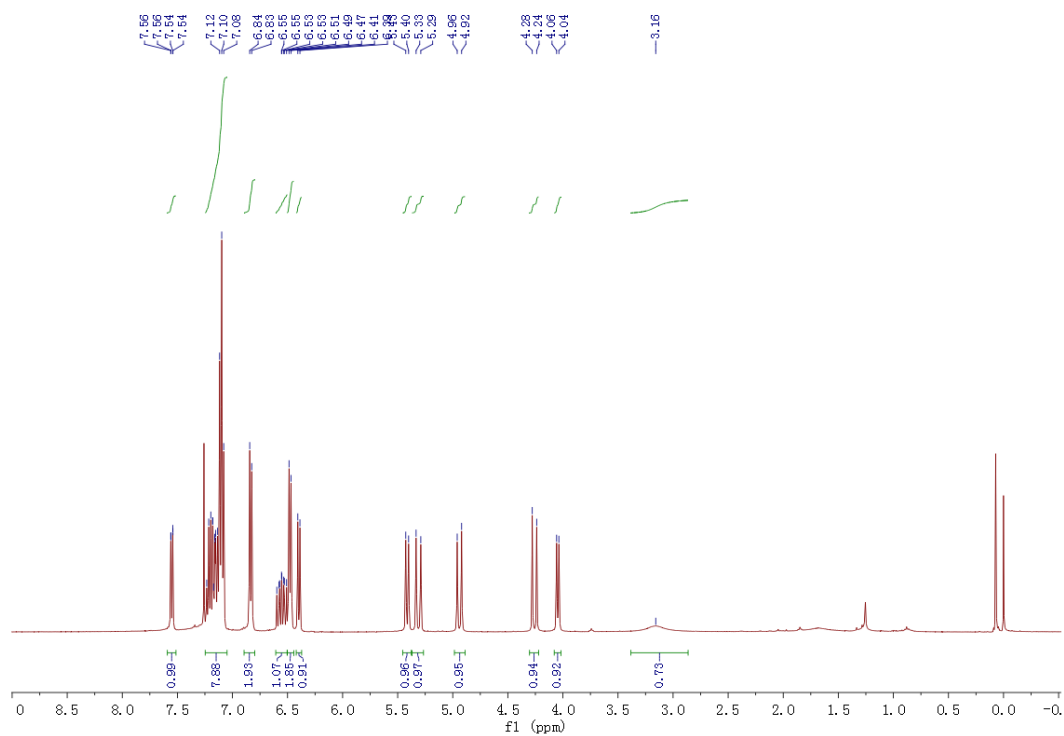
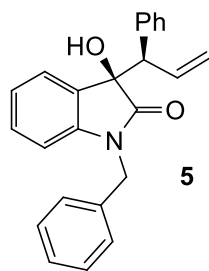
PeakTable

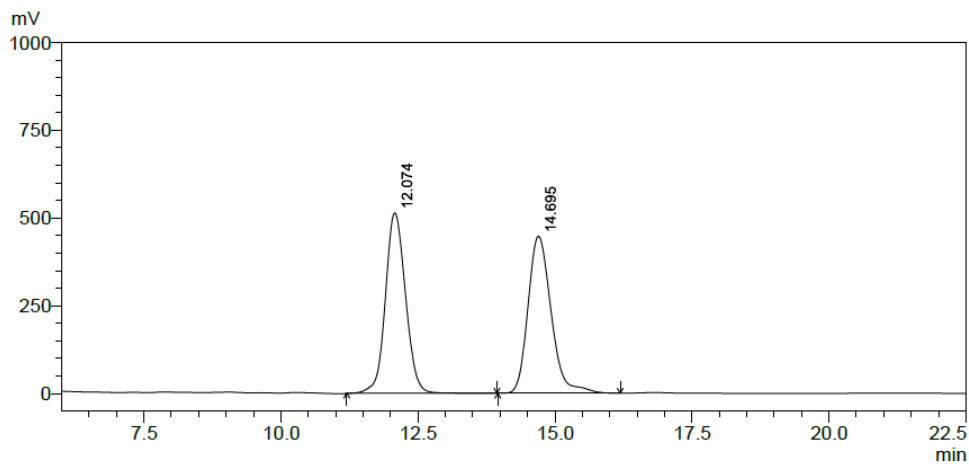
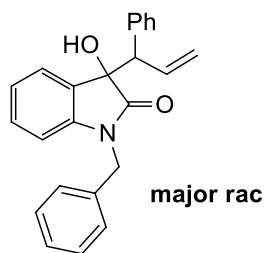
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.635	1134205	36300	49.673	51.582
2	18.645	1149149	34073	50.327	48.418
Total		2283355	70374	100.000	100.000



PeakTable

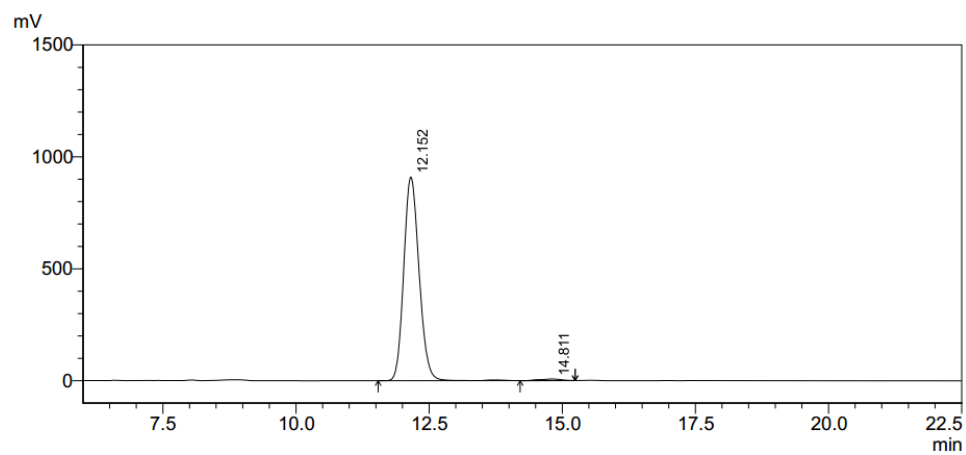
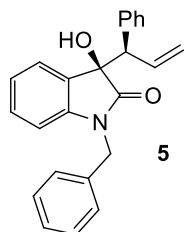
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.307	15145346	580673	98.557	98.698
2	18.392	221675	7658	1.443	1.302
Total		15367021	588331	100.000	100.000





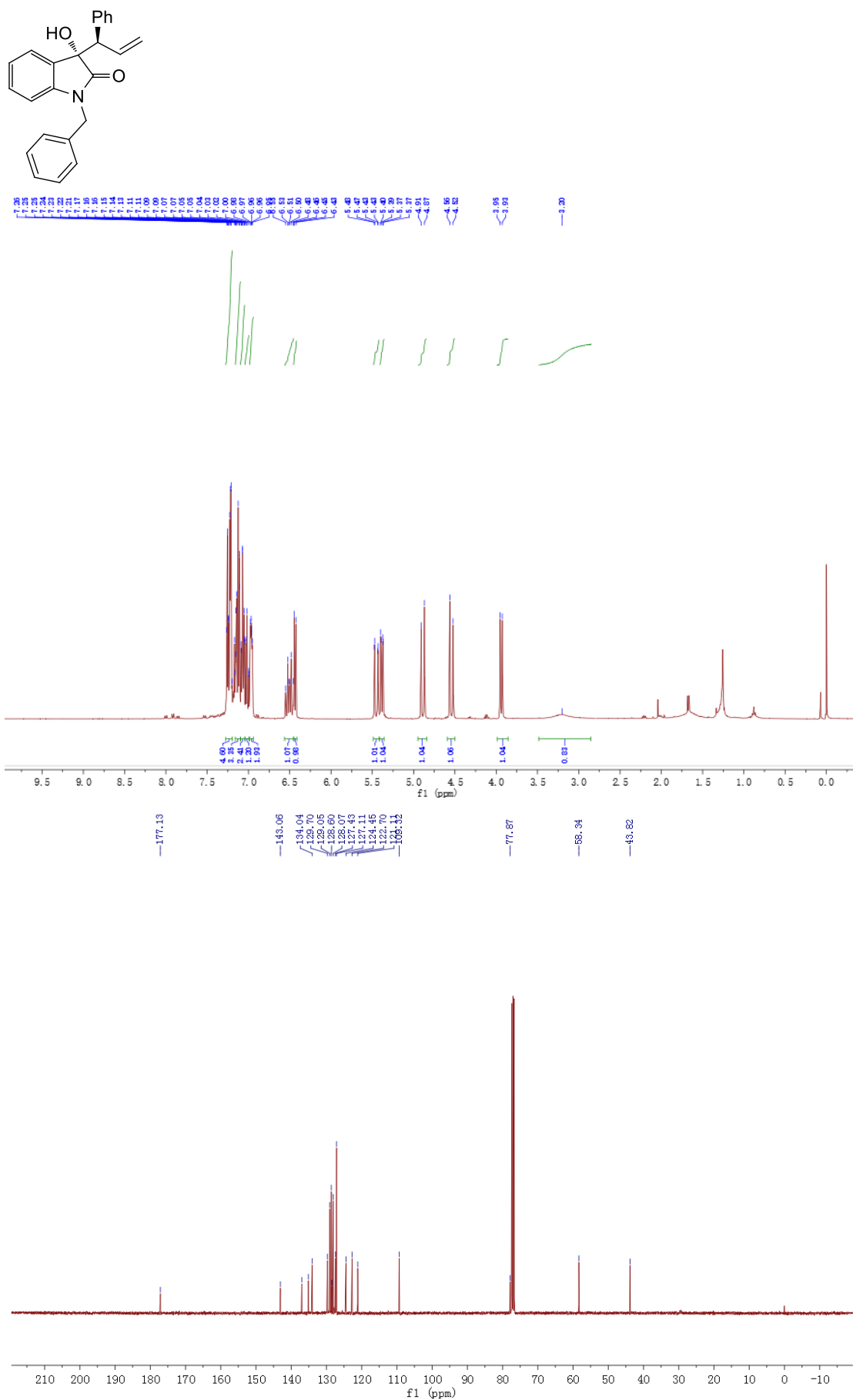
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PeakTable

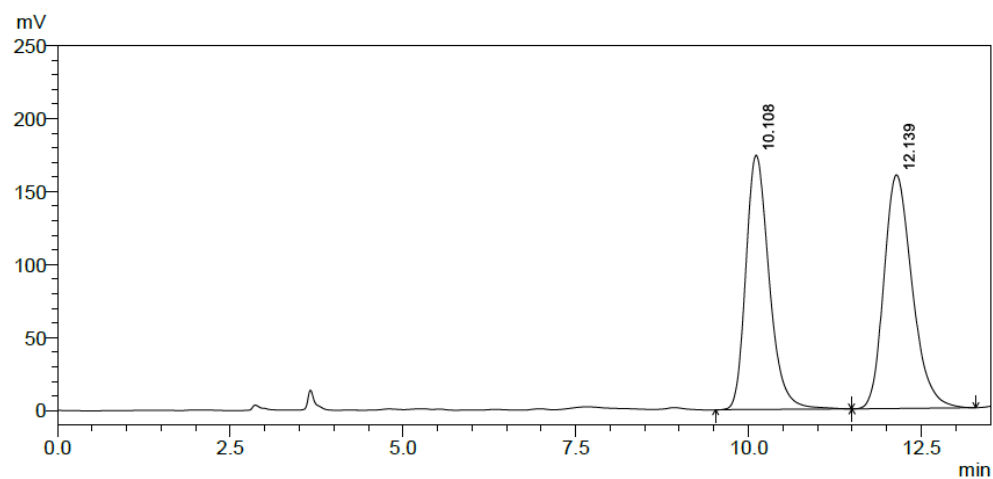
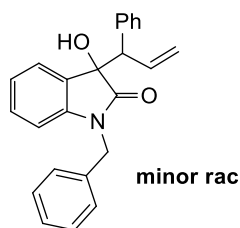
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.074	13075208	513611	49.879	53.452
2	14.695	13138517	447267	50.121	46.548
Total		26213725	960878	100.000	100.000



PeakTable

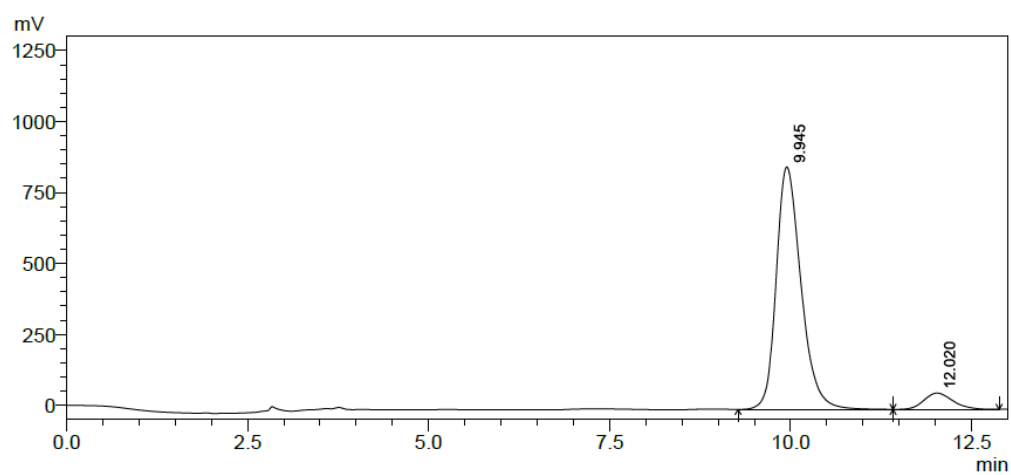
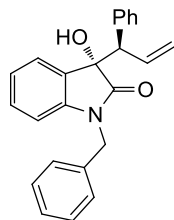
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.152	18135732	910244	98.874	99.205
2	14.811	206452	7296	1.126	0.795
Total		18342184	917540	100.000	100.000





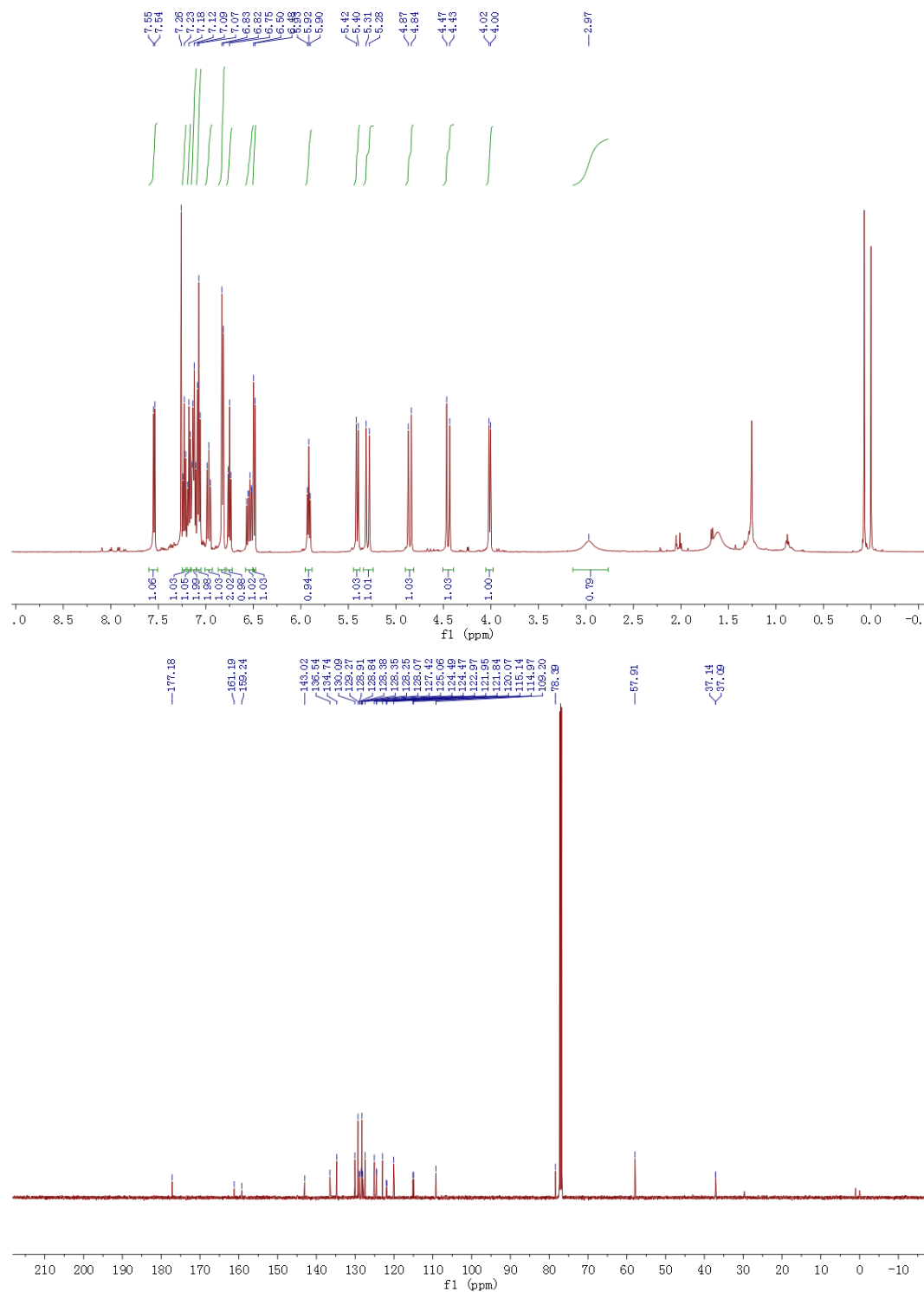
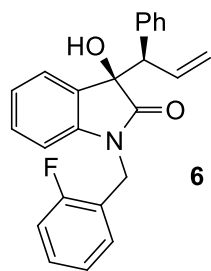
PeakTable

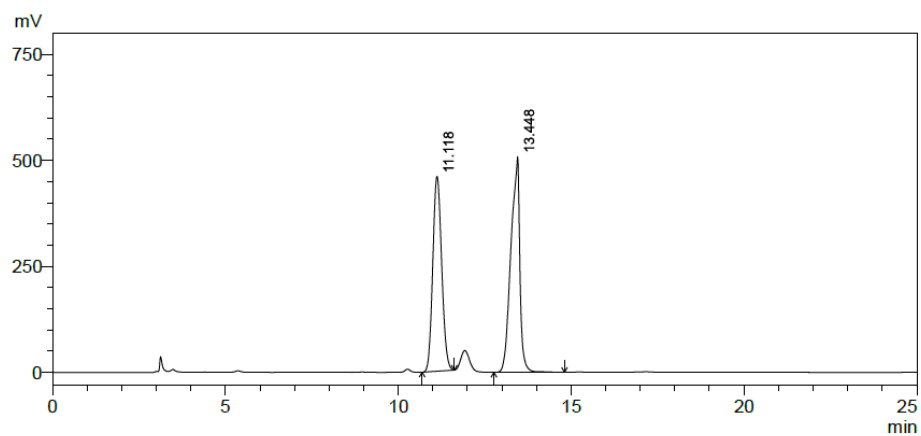
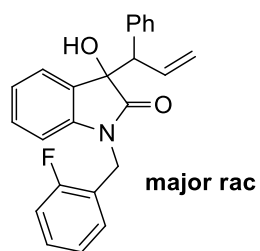
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.108	4095675	174245	47.315	52.118
2	12.139	4560477	160082	52.685	47.882
Total		8656152	334328	100.000	100.000



PeakTable

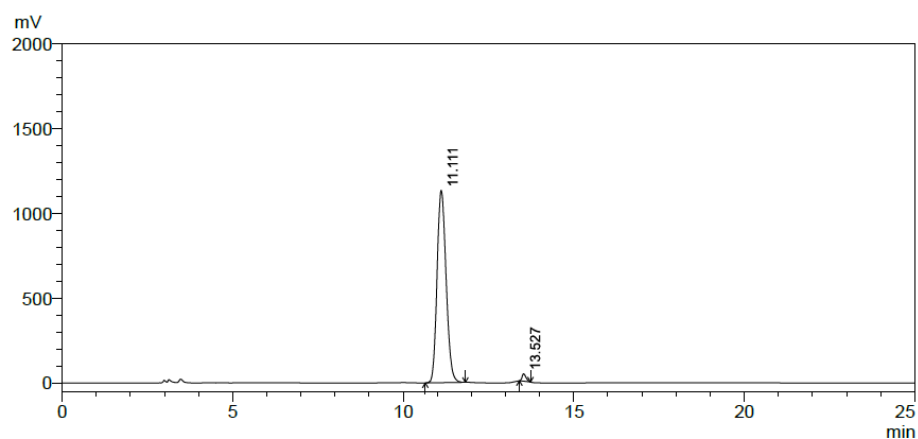
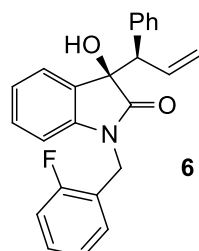
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.945	20346473	853883	92.733	93.705
2	12.020	1594443	57365	7.267	6.295
Total		21940916	911248	100.000	100.000





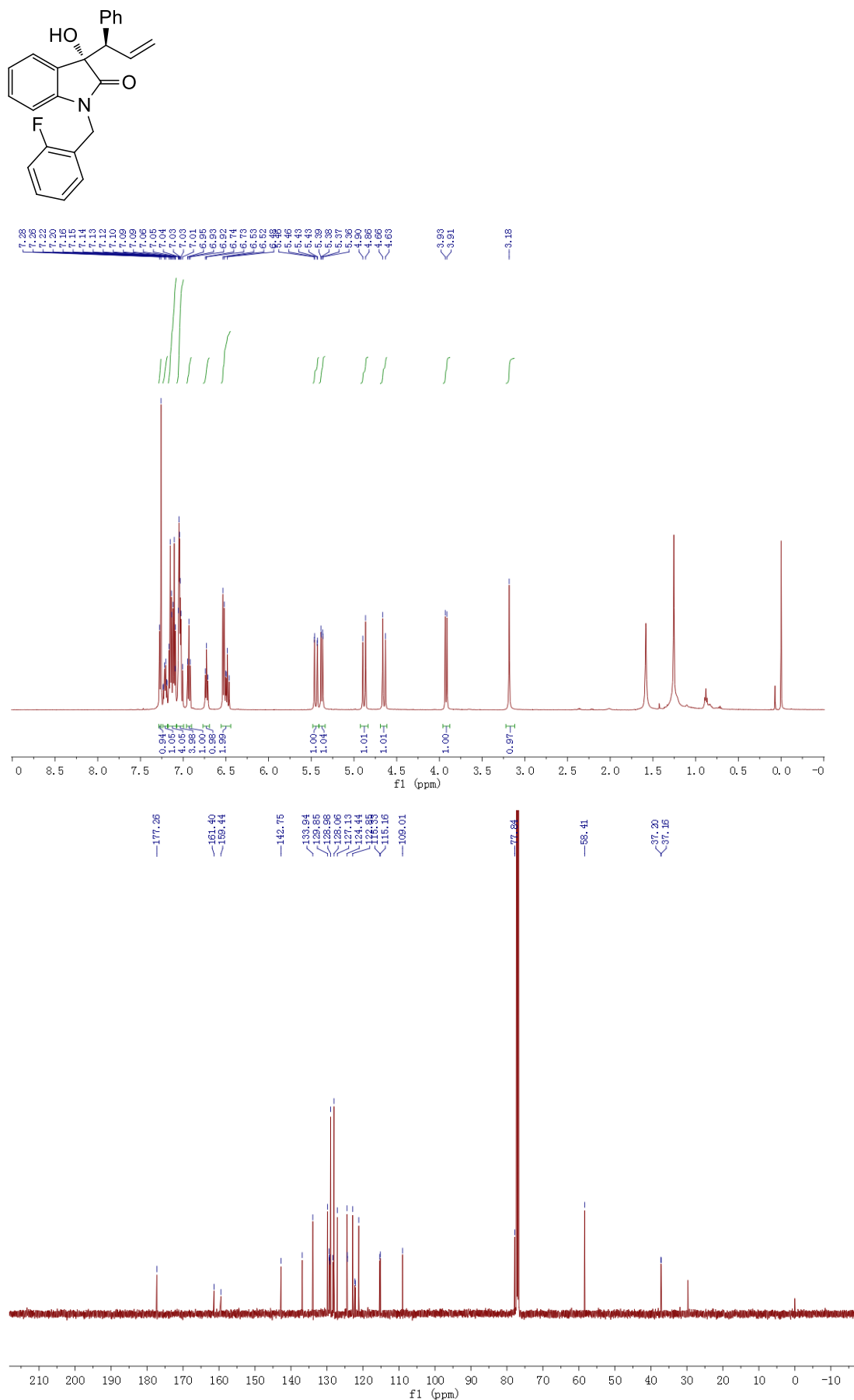
PeakTable

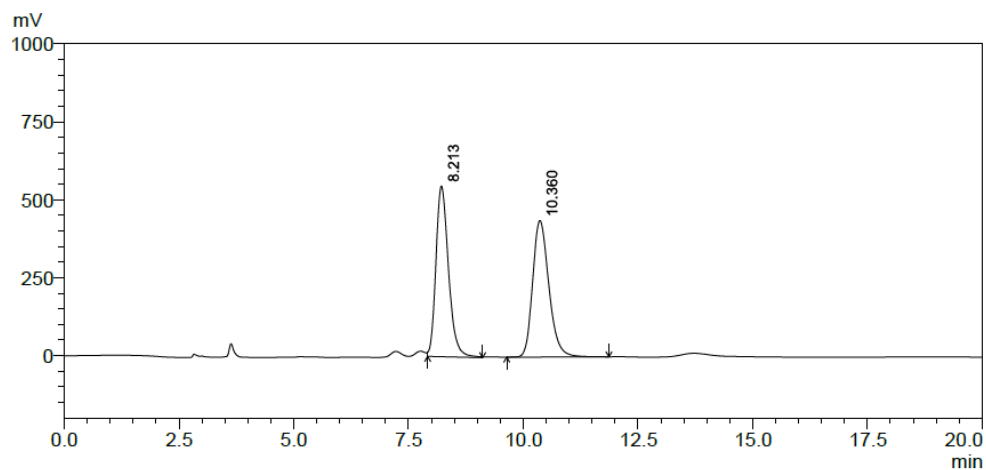
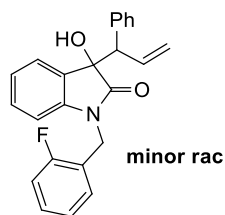
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.118	8221534	459270	47.371	47.458
2	13.448	9134176	508465	52.629	52.542
Total		17355710	967736	100.000	100.000



PeakTable

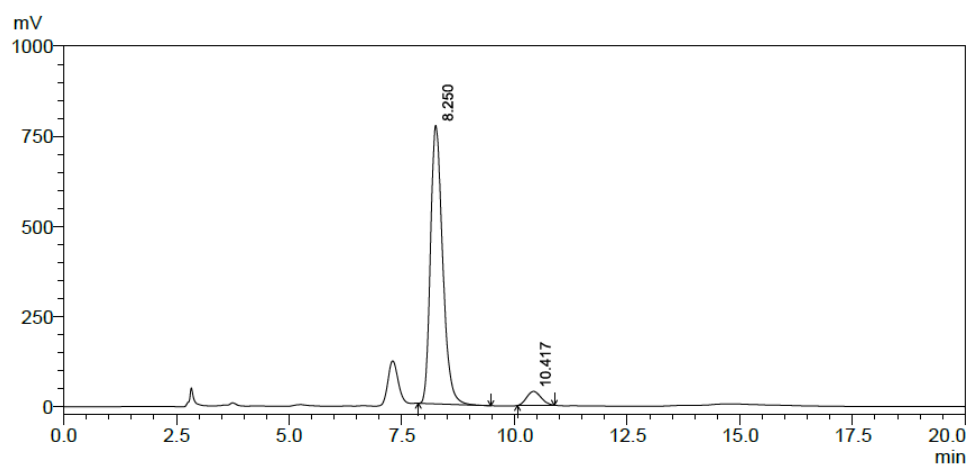
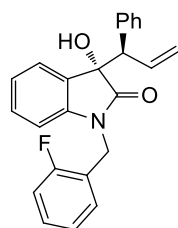
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.111	20979751	1135681	98.348	96.322
2	13.527	352375	43361	1.652	3.678
Total		21332126	1179042	100.000	100.000





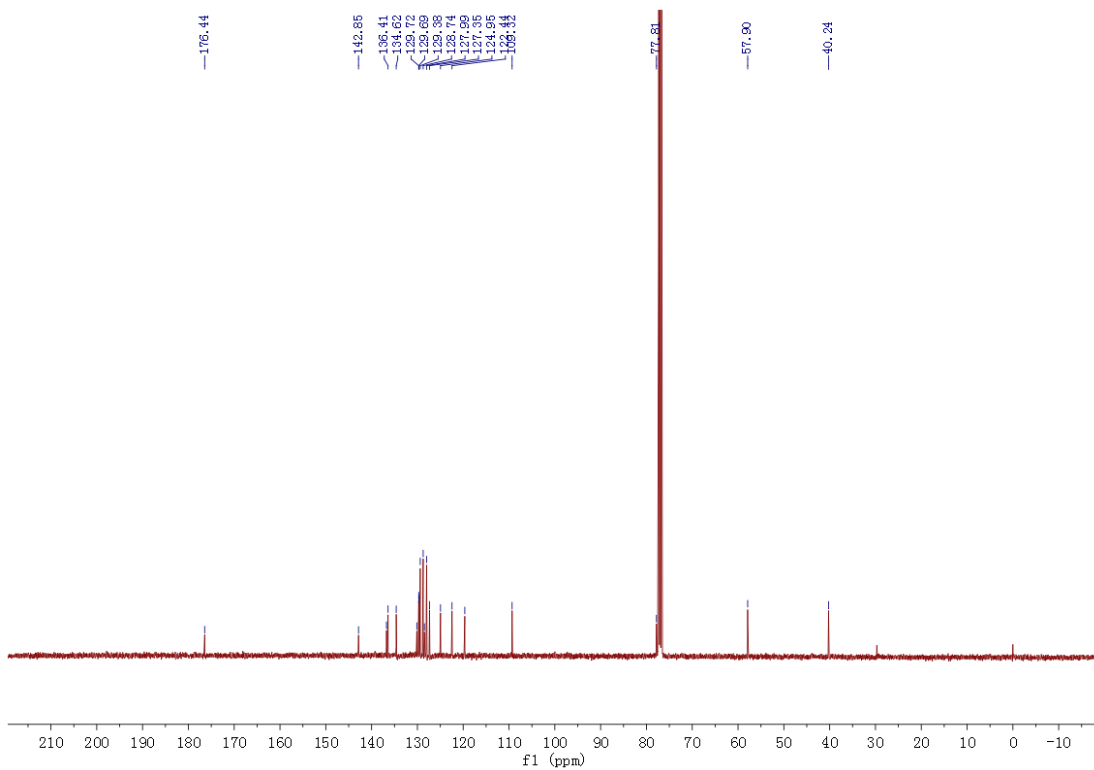
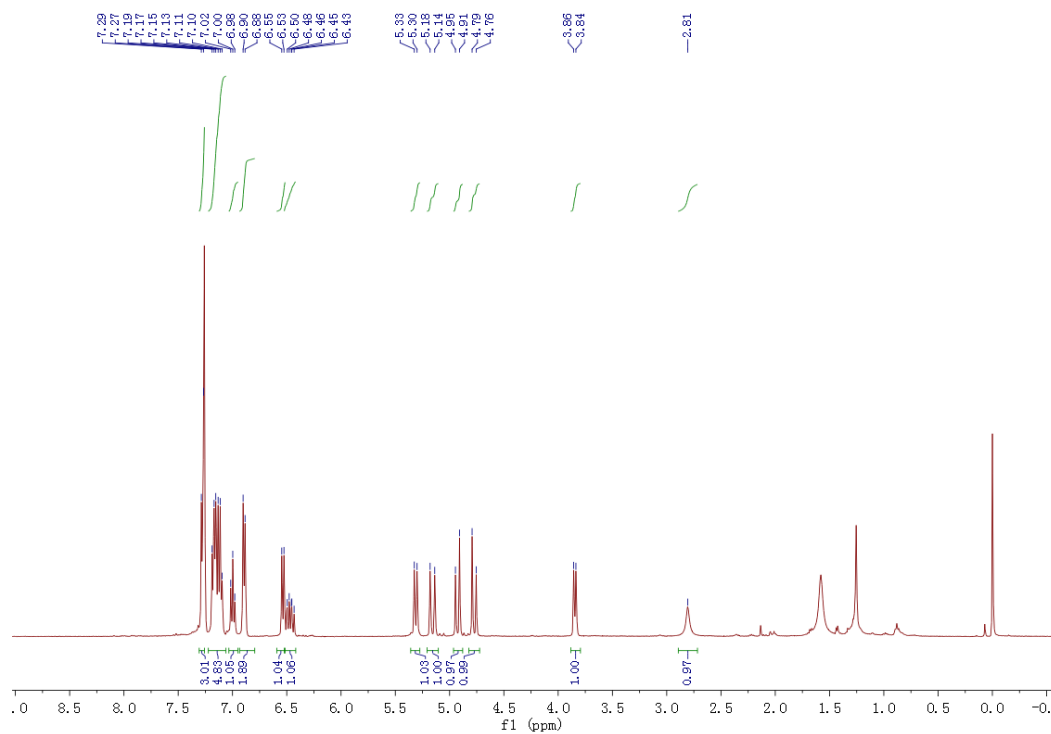
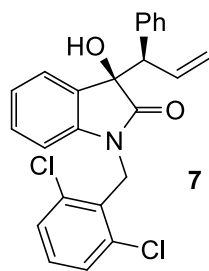
PeakTable

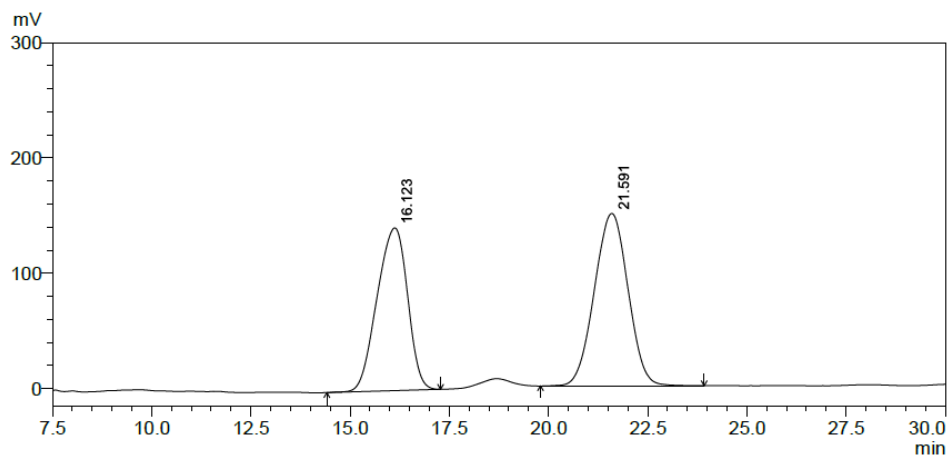
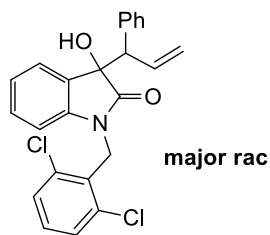
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.213	10453046	547727	49.238	55.560
2	10.360	10776795	438103	50.762	44.440
Total		21229841	985830	100.000	100.000



PeakTable

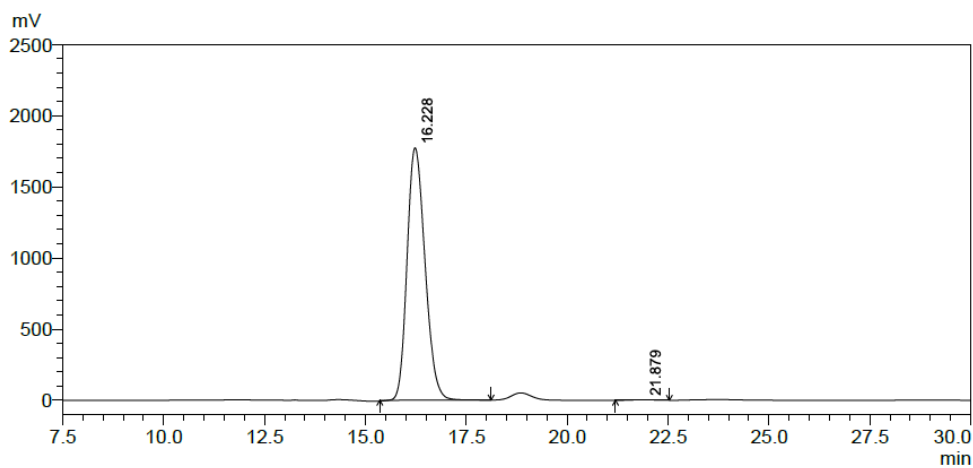
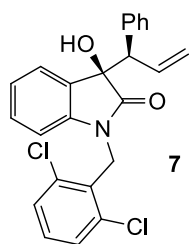
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.250	14537399	772149	94.458	95.228
2	10.417	852925	38696	5.542	4.772
Total		15390324	810845	100.000	100.000





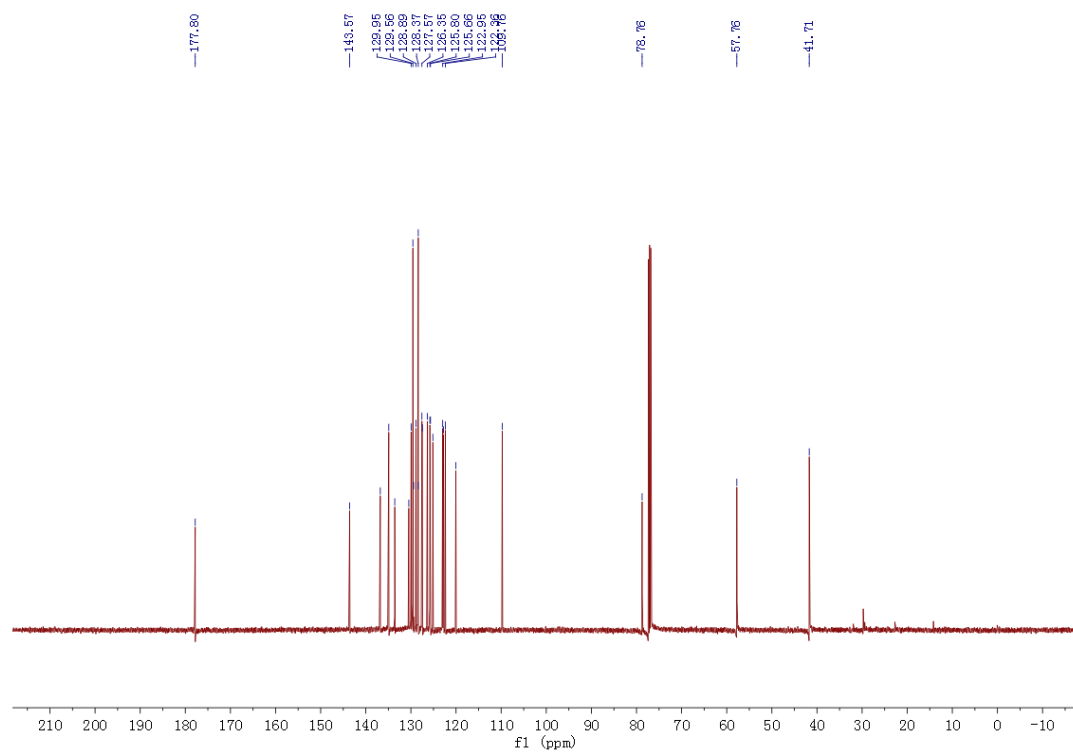
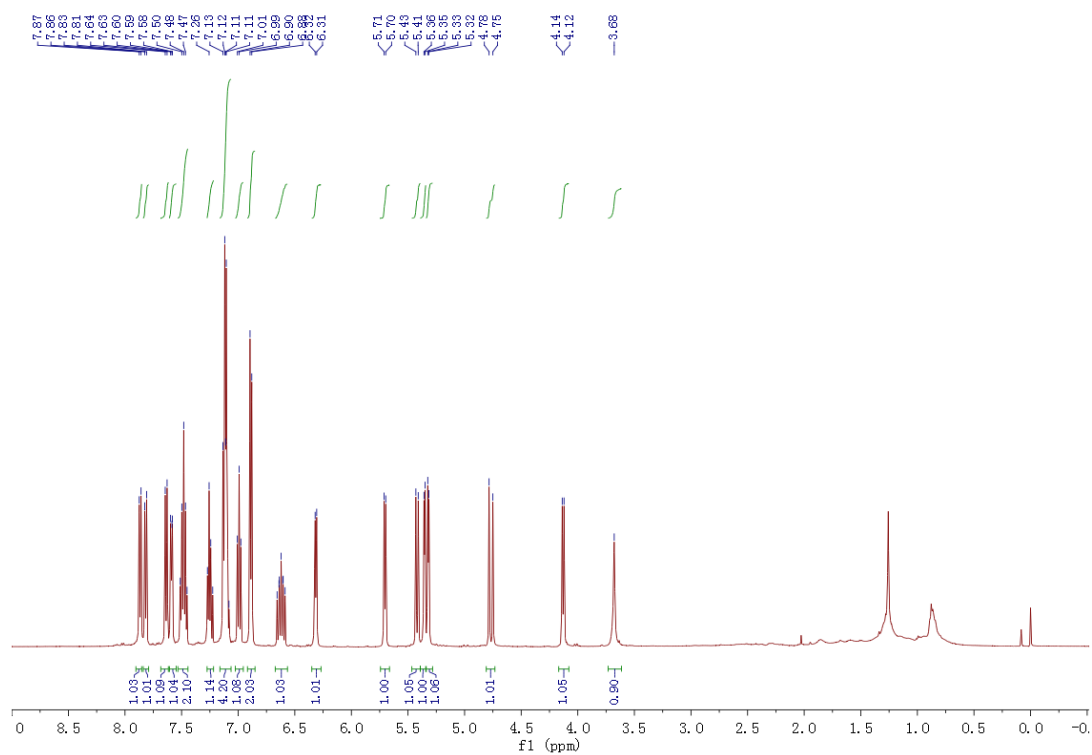
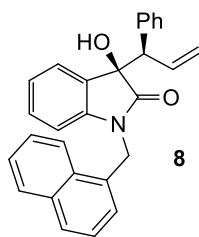
PeakTable

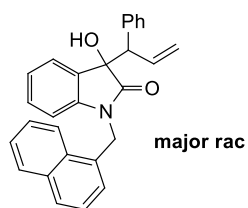
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.123	7543891	141158	46.125	48.589
2	21.591	8811490	149359	53.875	51.411
Total		16355381	290518	100.000	100.000



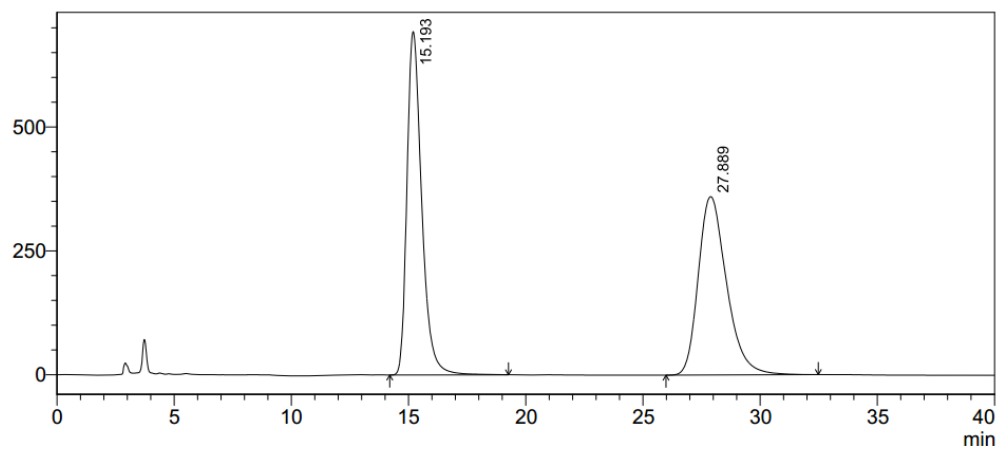
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.228	54976935	1774025	99.767	99.794
2	21.879	128395	3657	0.233	0.206
Total		55105330	1777682	100.000	100.000



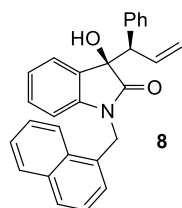


mV

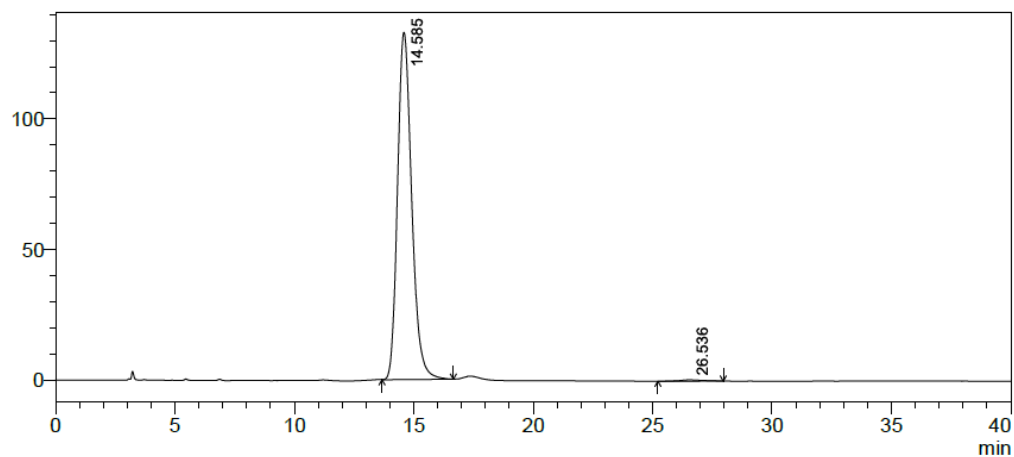


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.193	30286134	693015	50.051	65.815
2	27.889	30224089	359957	49.949	34.185
Total		60510224	1052972	100.000	100.000

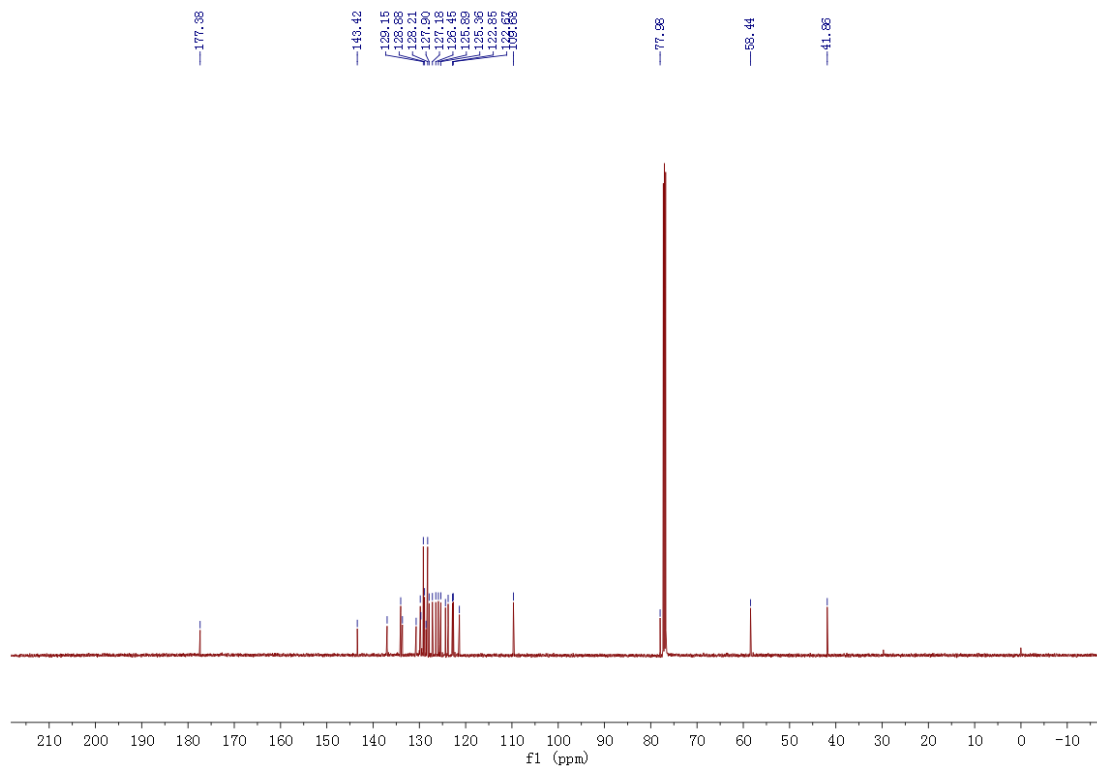
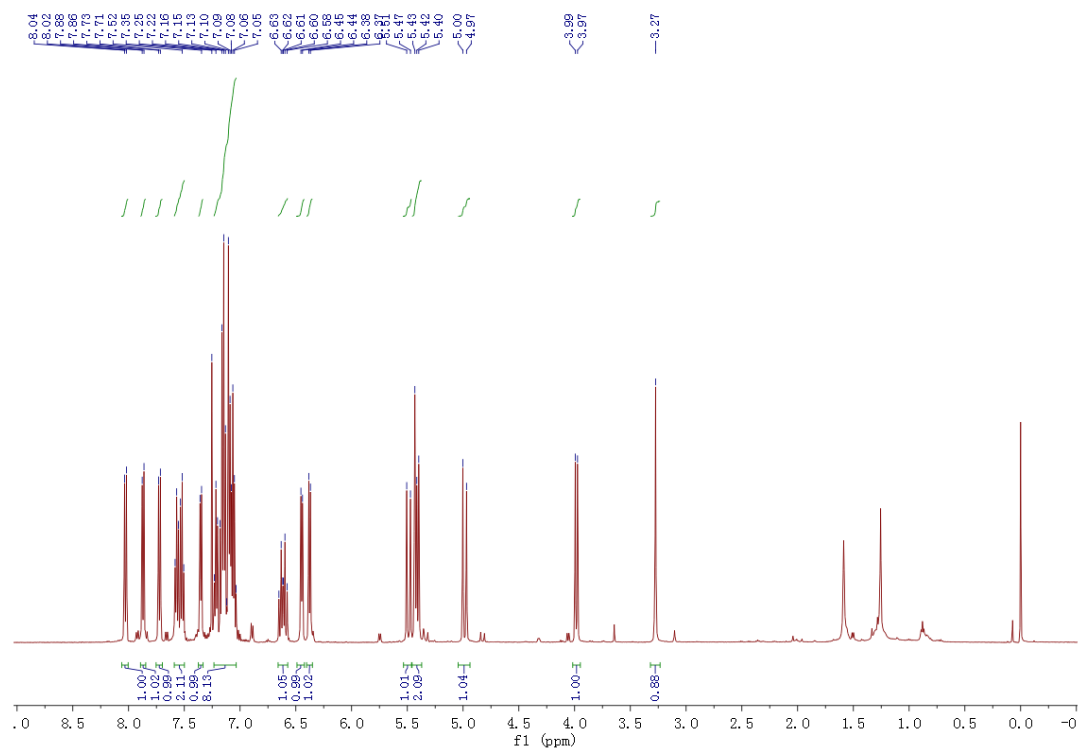
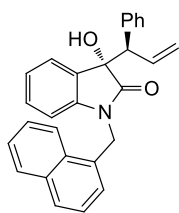


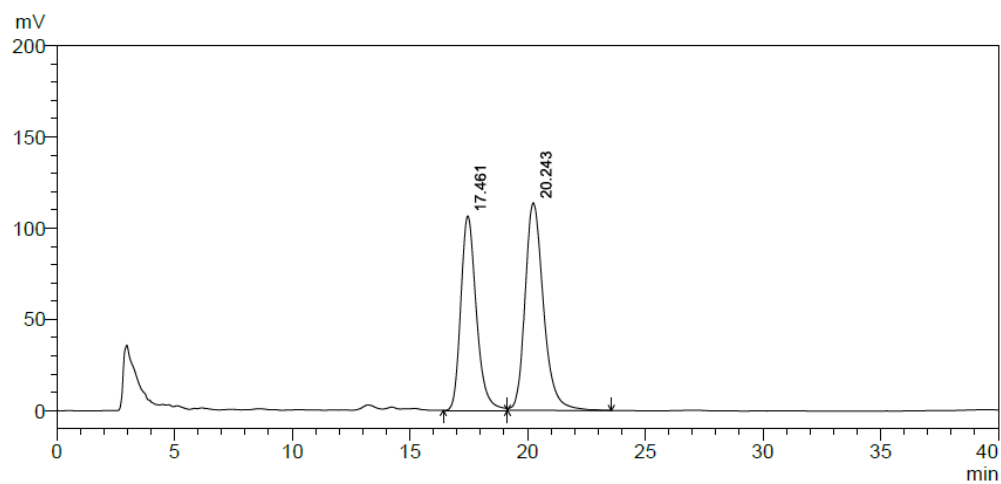
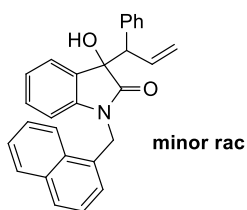
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PeakTable

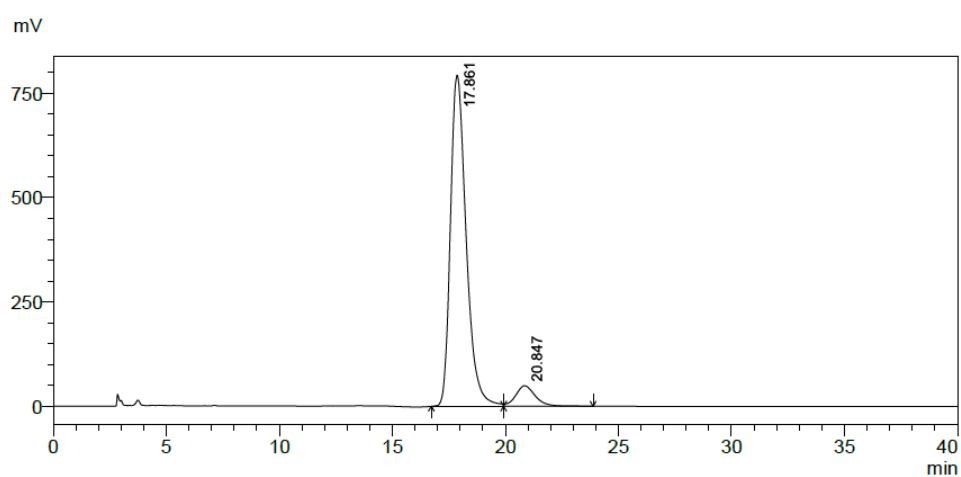
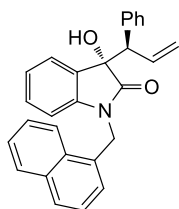
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.585	5476430	132966	99.320	99.611
2	26.536	37481	519	0.680	0.389
Total		5513911	133485	100.000	100.000





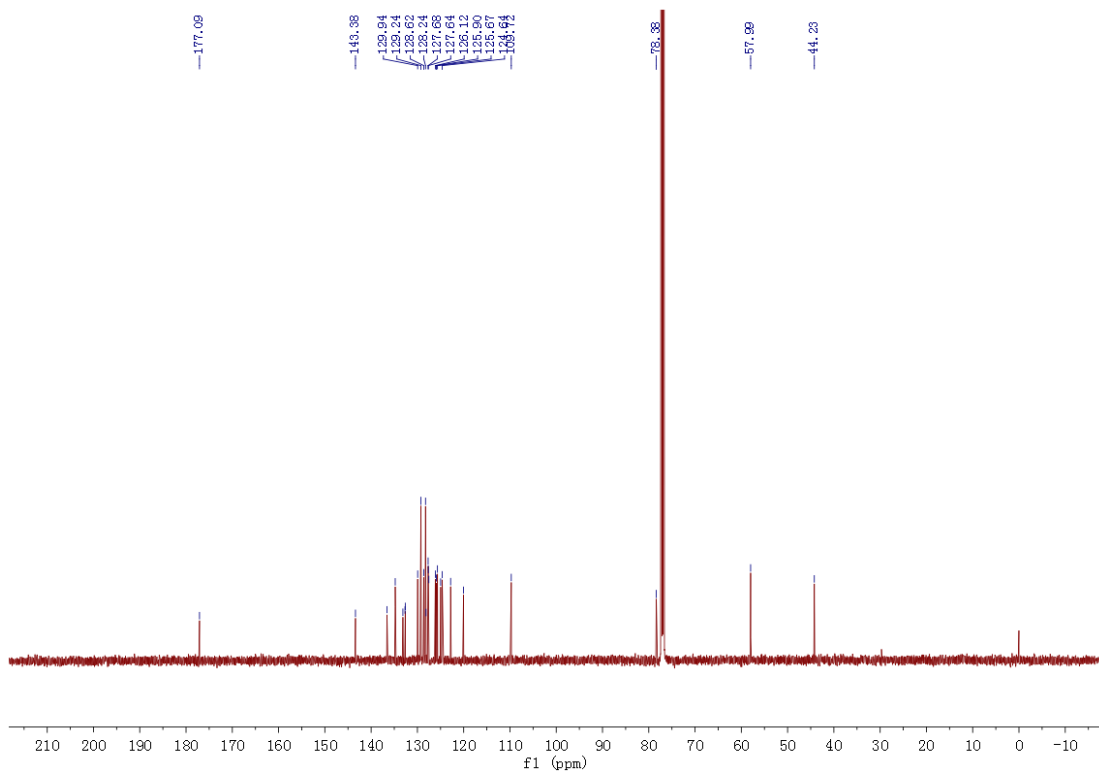
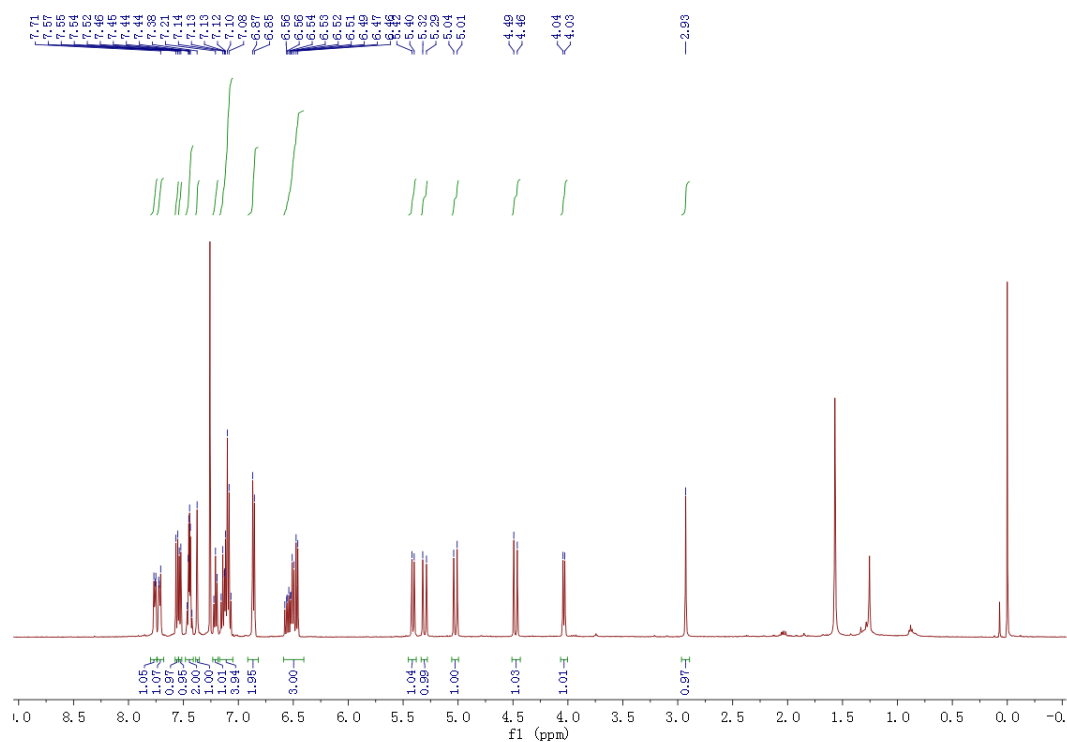
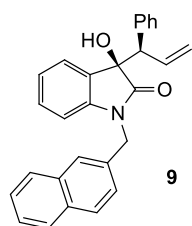
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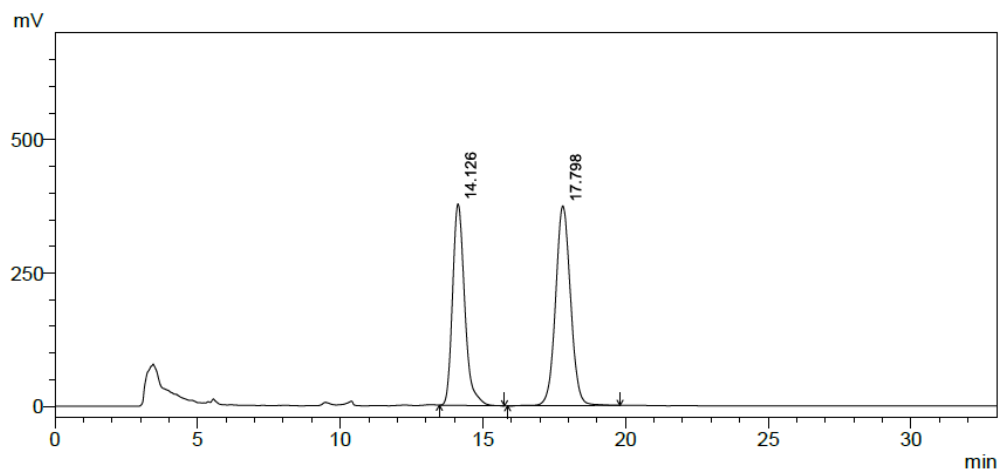
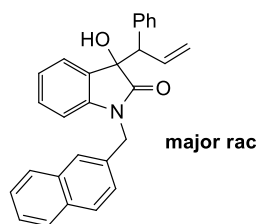
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.461	4906389	106579	44.135	48.351
2	20.243	6210464	113847	55.865	51.649
Total		11116853	220426	100.000	100.000



PeakTable

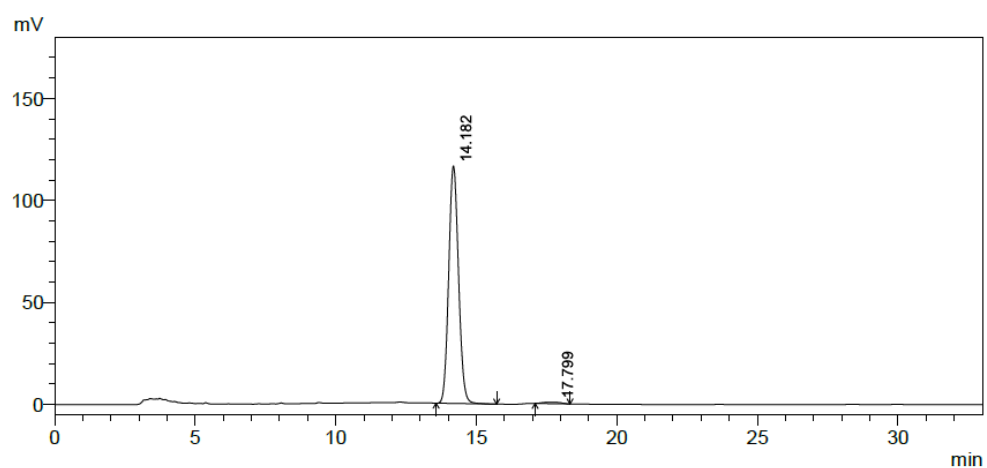
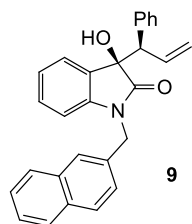
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.861	38267925	792936	92.815	94.191
2	20.847	2962236	48902	7.185	5.809
Total		41230161	841838	100.000	100.000





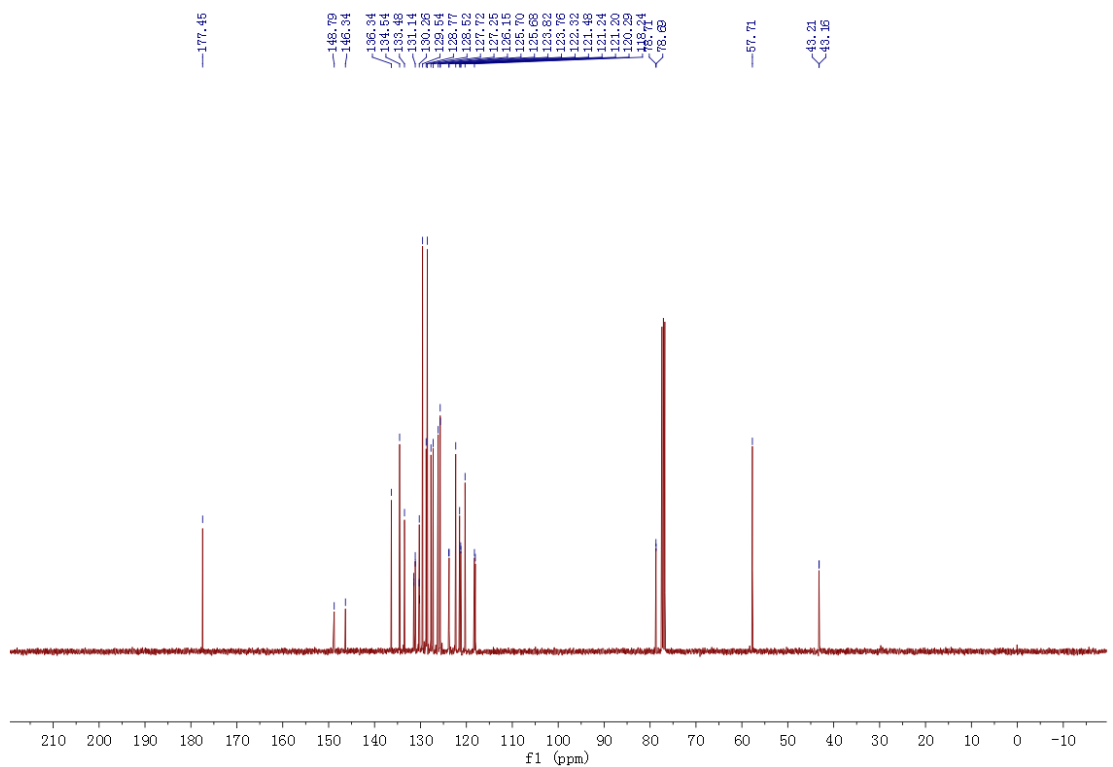
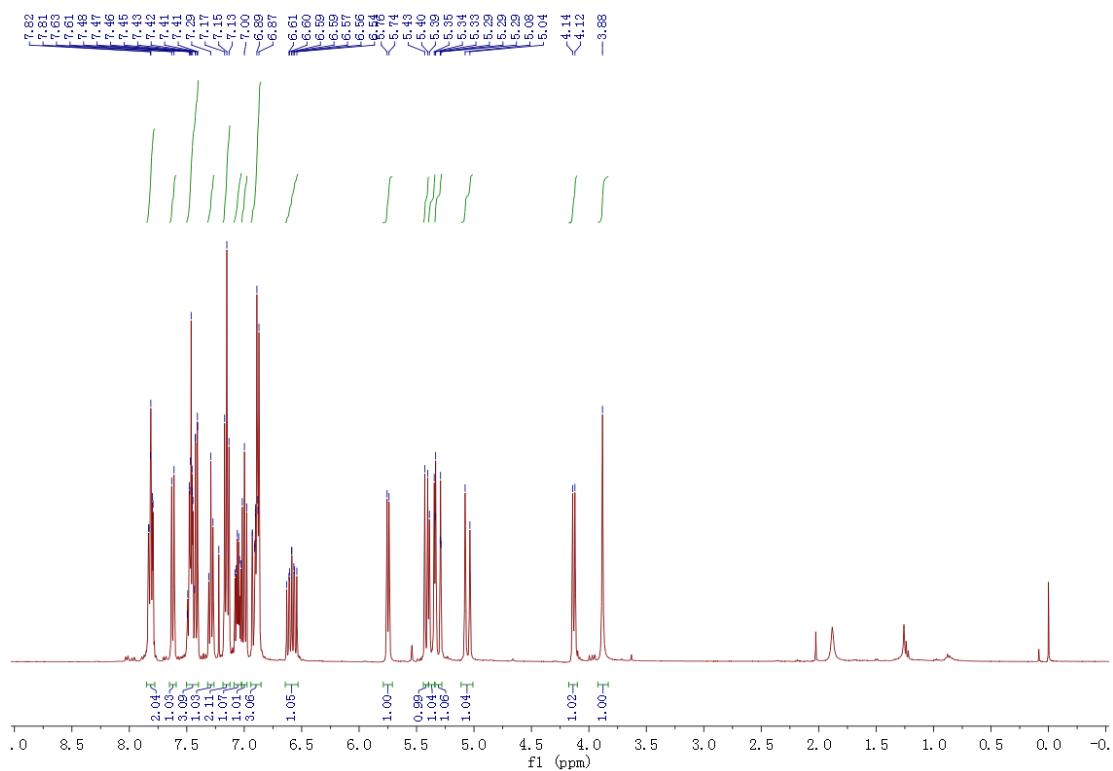
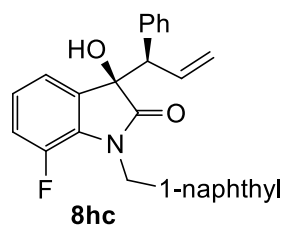
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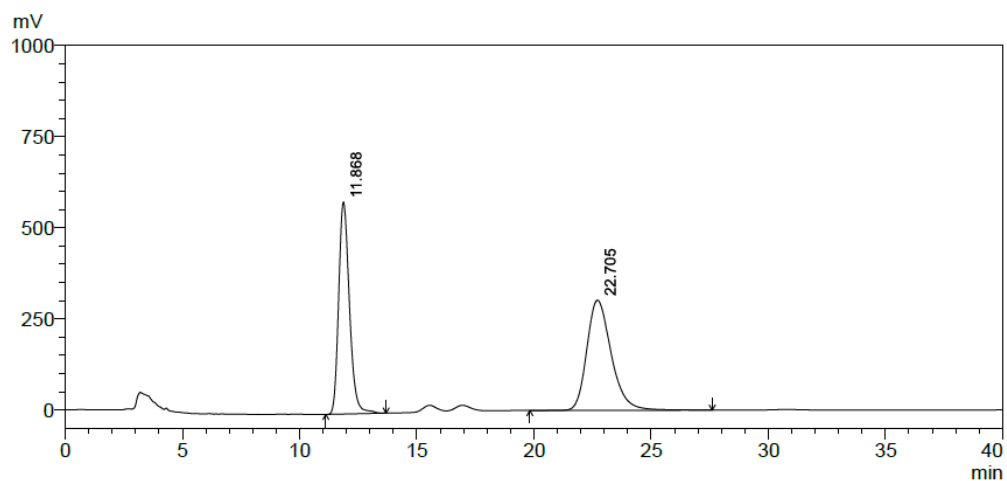
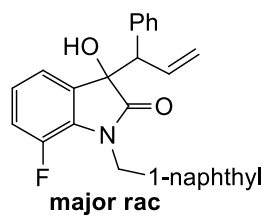
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.126	11187033	378084	45.019	50.220
2	17.798	13662555	374776	54.981	49.780
Total		24849587	752860	100.000	100.000



PeakTable

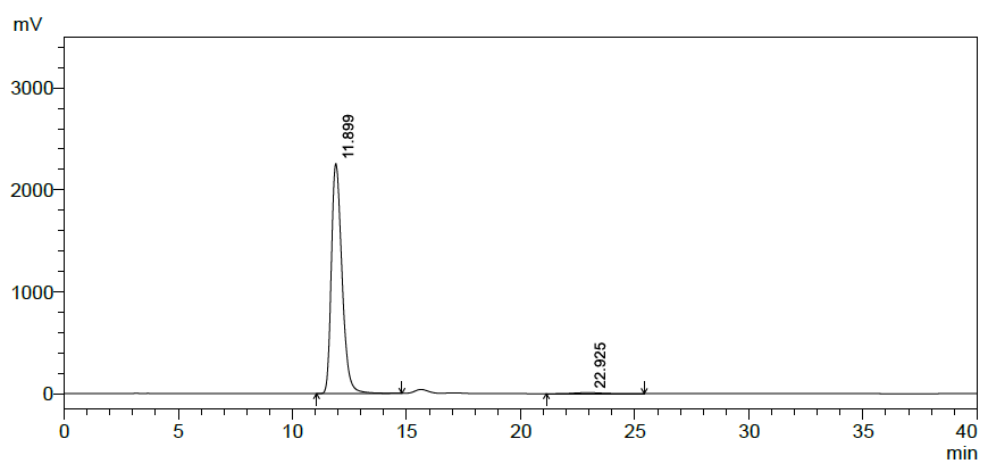
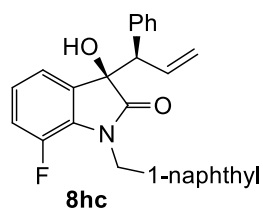
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.182	2824587	116421	98.940	99.425
2	17.799	30252	673	1.060	0.575
Total		2854839	117094	100.000	100.000





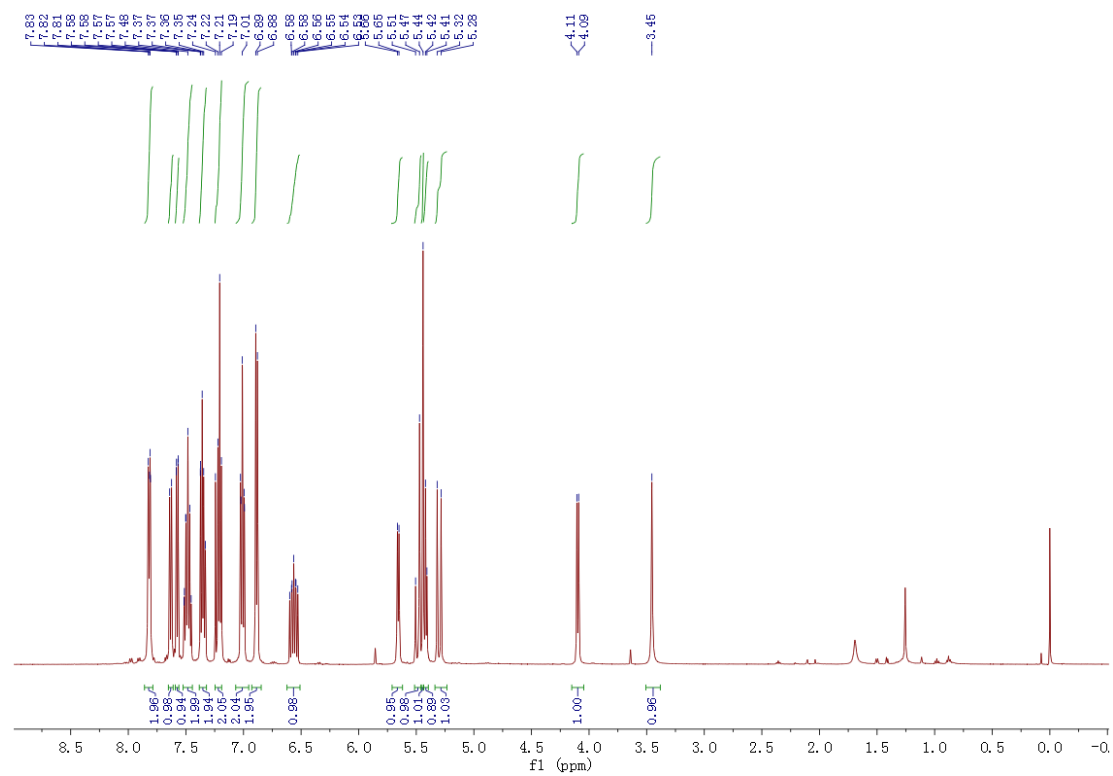
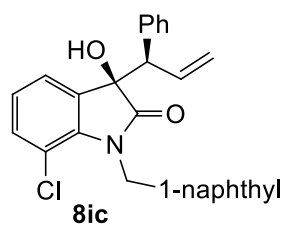
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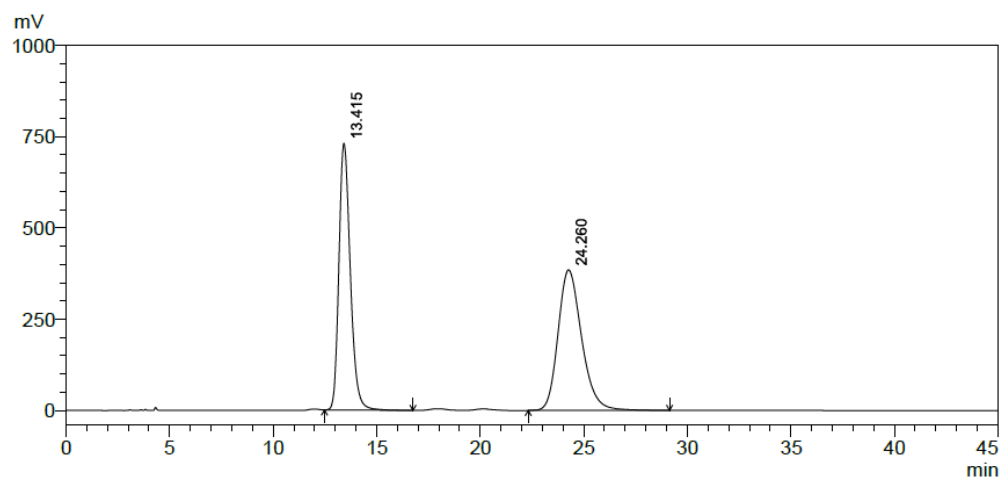
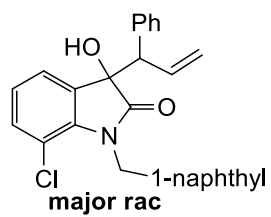
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.868	18577505	582551	45.828	65.779
2	22.705	21959613	303070	54.172	34.221
Total		40537119	885621	100.000	100.000



PeakTable

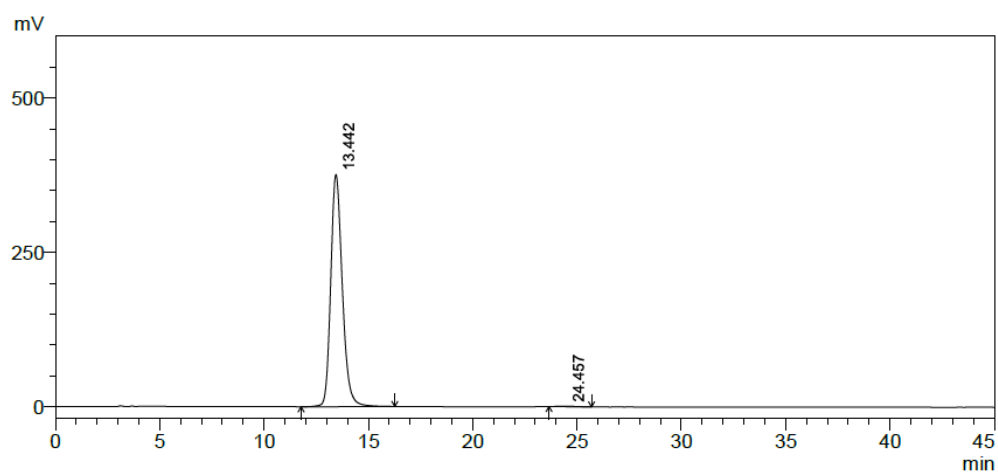
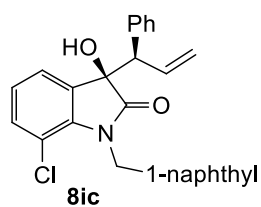
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.899	73107440	2258019	98.983	99.562
2	22.925	750830	9936	1.017	0.438
Total		73858270	2267955	100.000	100.000





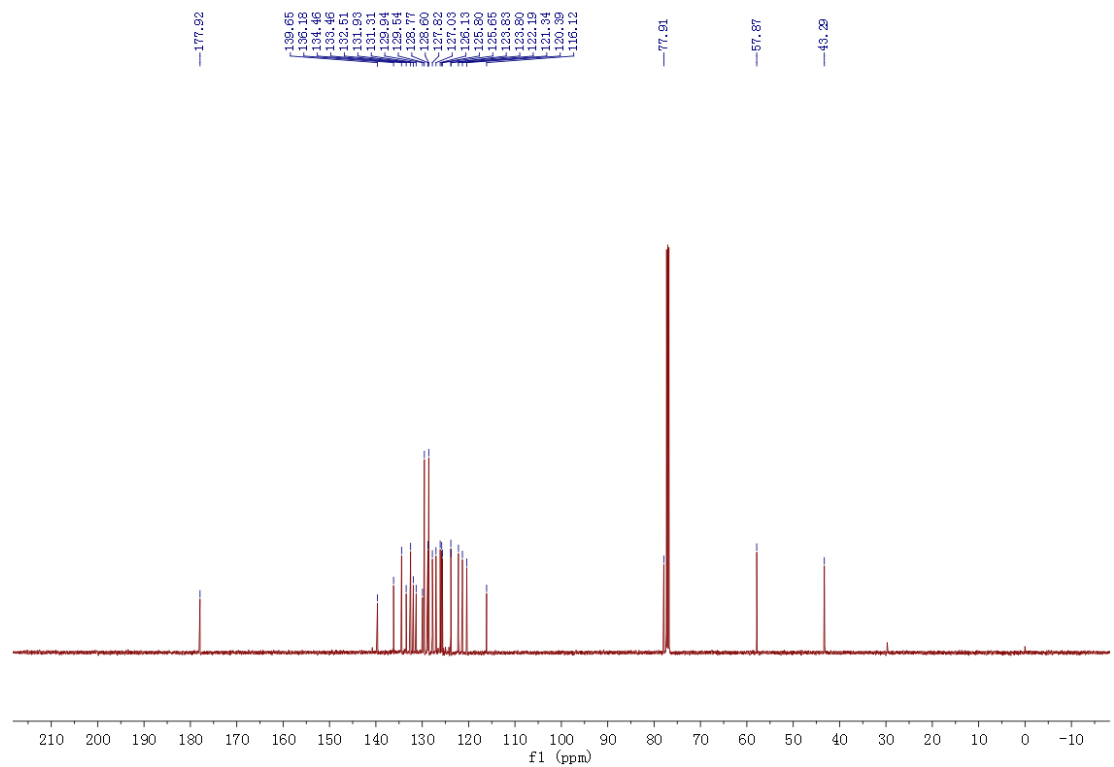
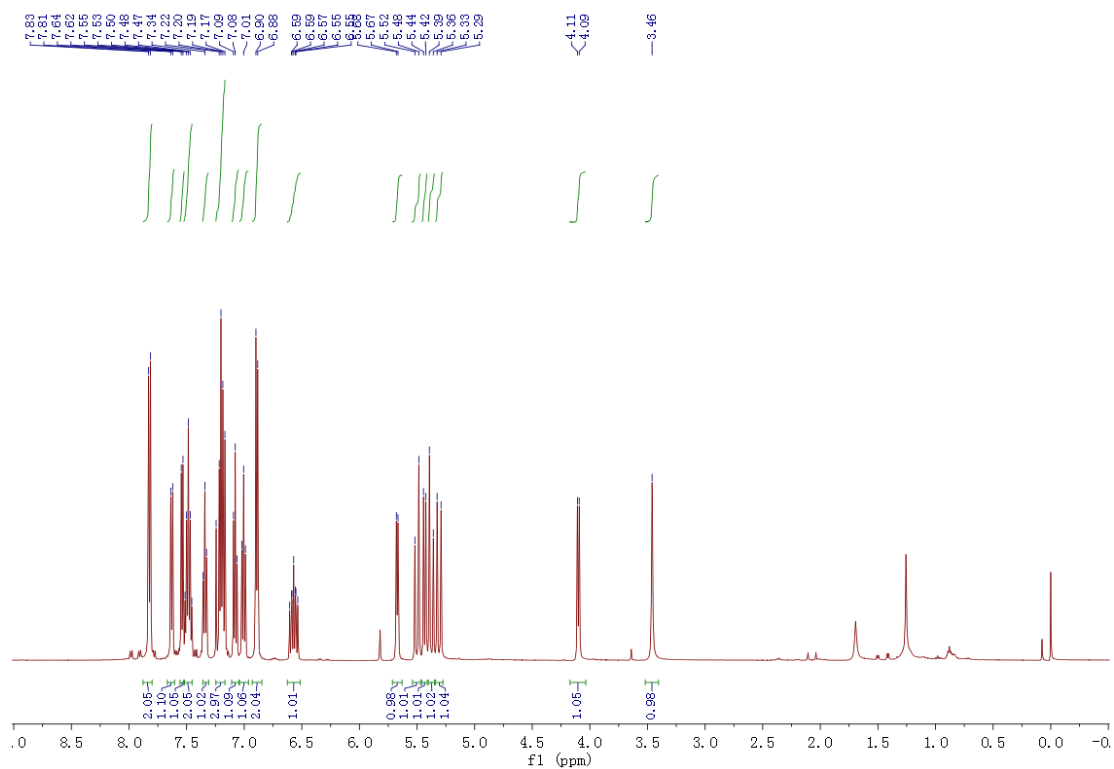
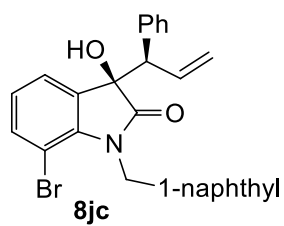
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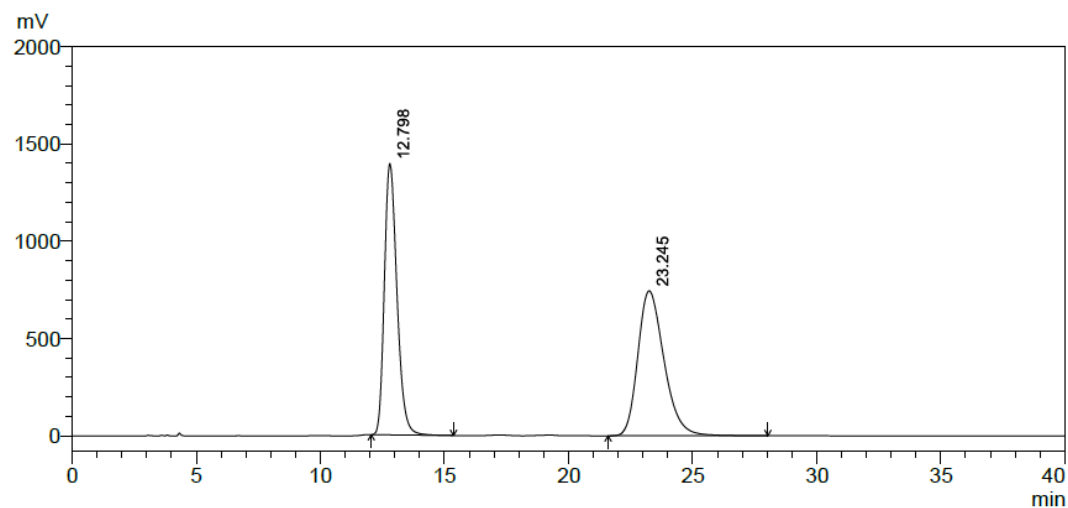
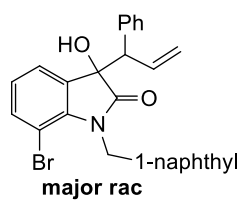
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.415	27893403	730112	47.825	65.478
2	24.260	30430695	384945	52.175	34.522
Total		58324098	1115057	100.000	100.000



PeakTable

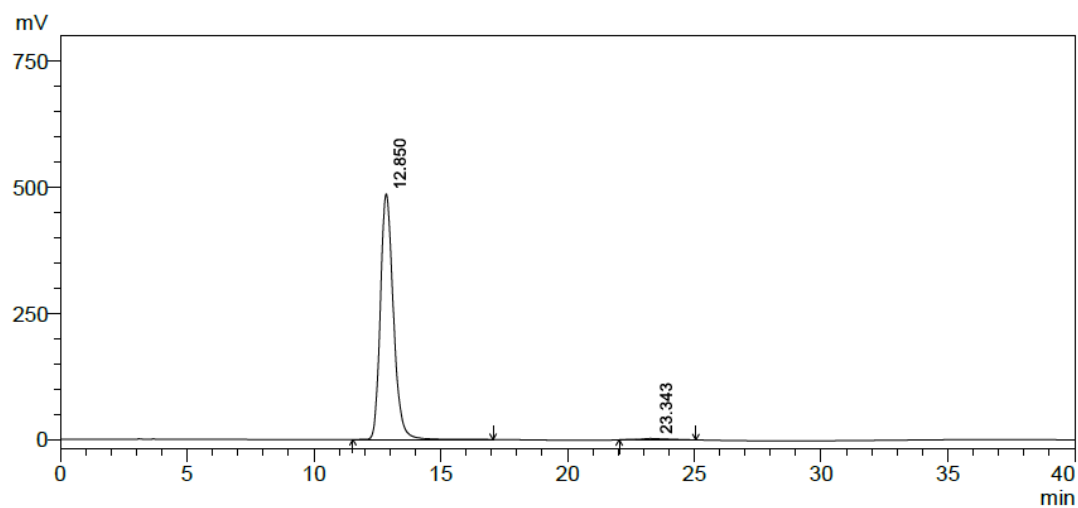
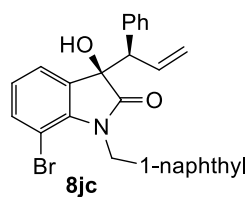
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.442	14507976	376301	99.655	99.769
2	24.457	50284	871	0.345	0.231
Total		14558260	377172	100.000	100.000





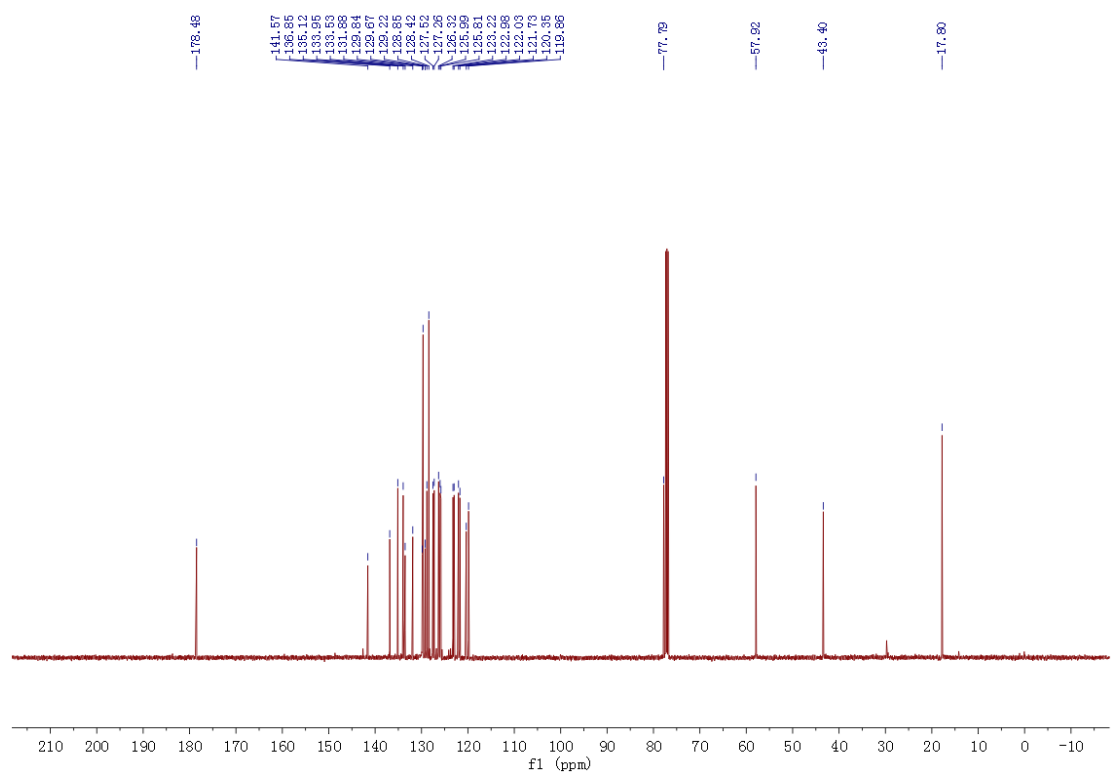
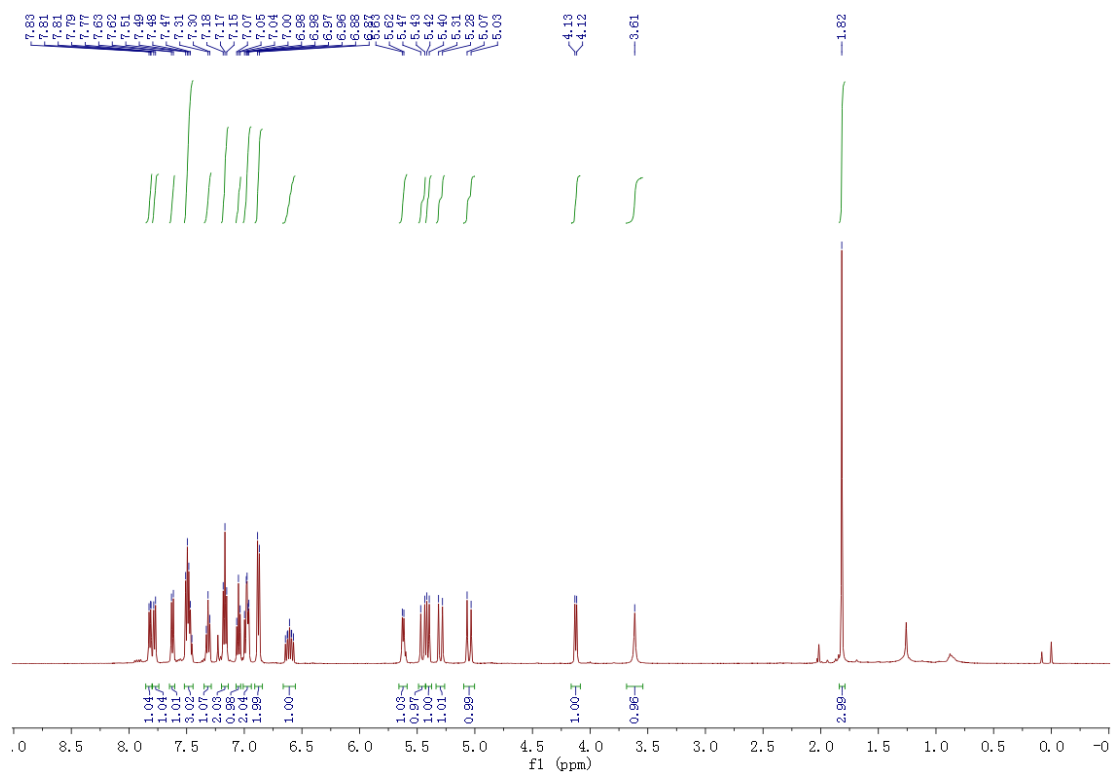
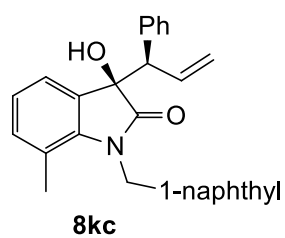
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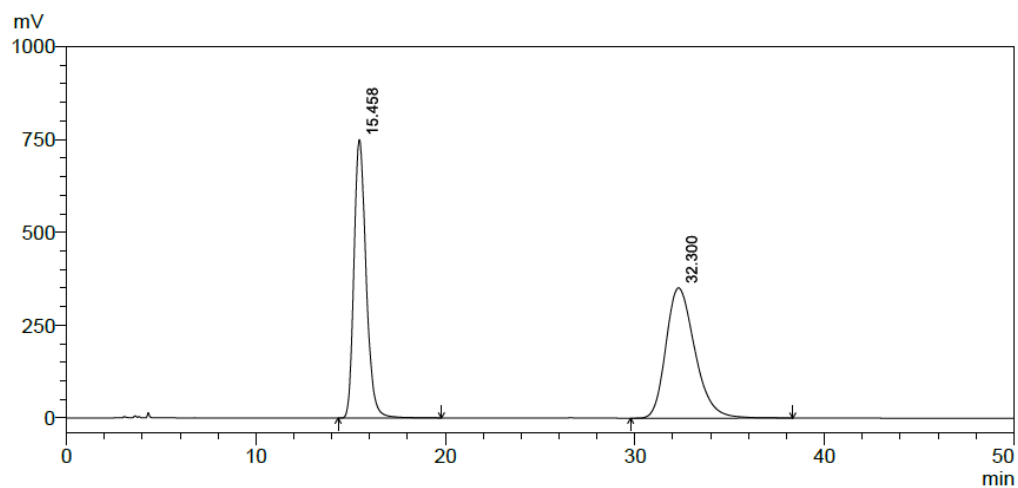
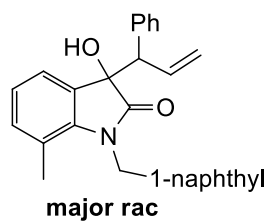
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.798	49238788	1394582	47.445	65.189
2	23.245	54542454	744697	52.555	34.811
Total		103781242	2139280	100.000	100.000



PeakTable

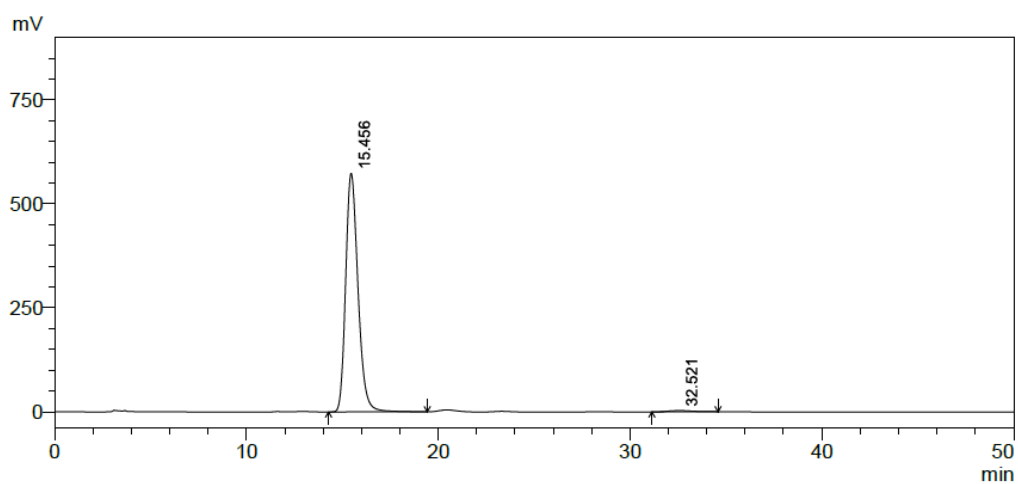
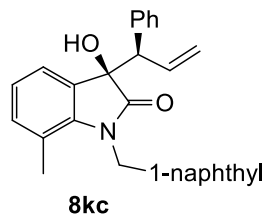
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.850	17390827	487216	98.956	99.462
2	23.343	183551	2636	1.044	0.538
Total		17574378	489852	100.000	100.000





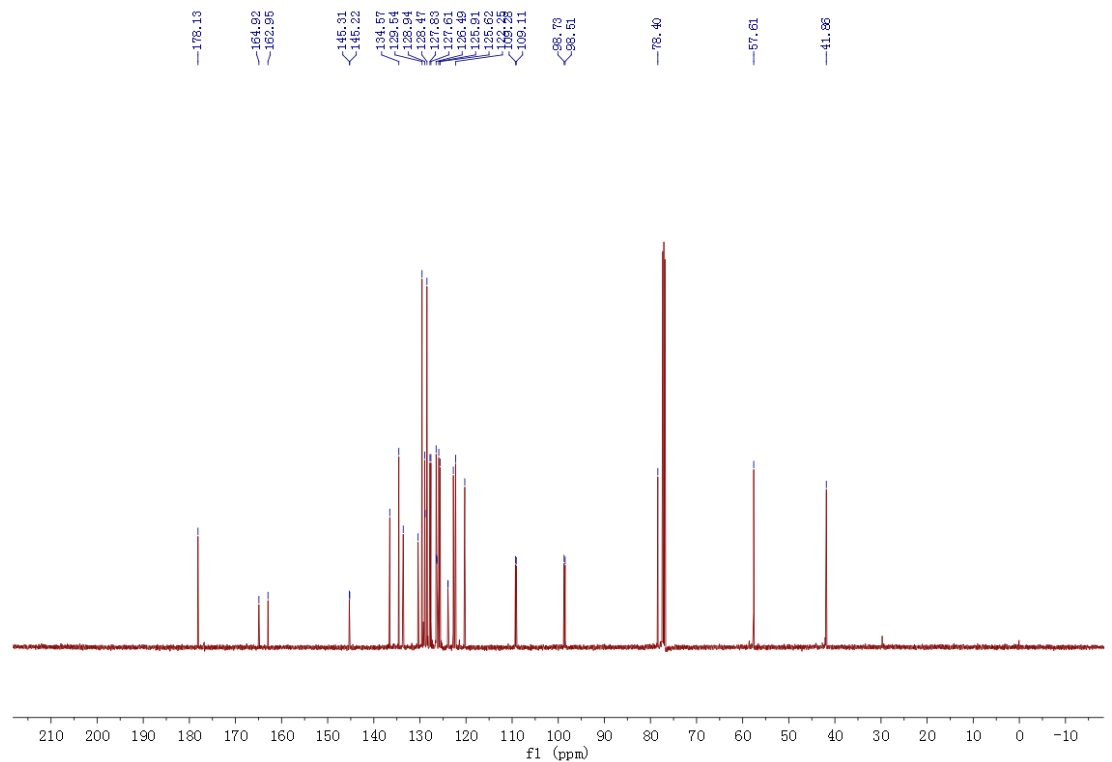
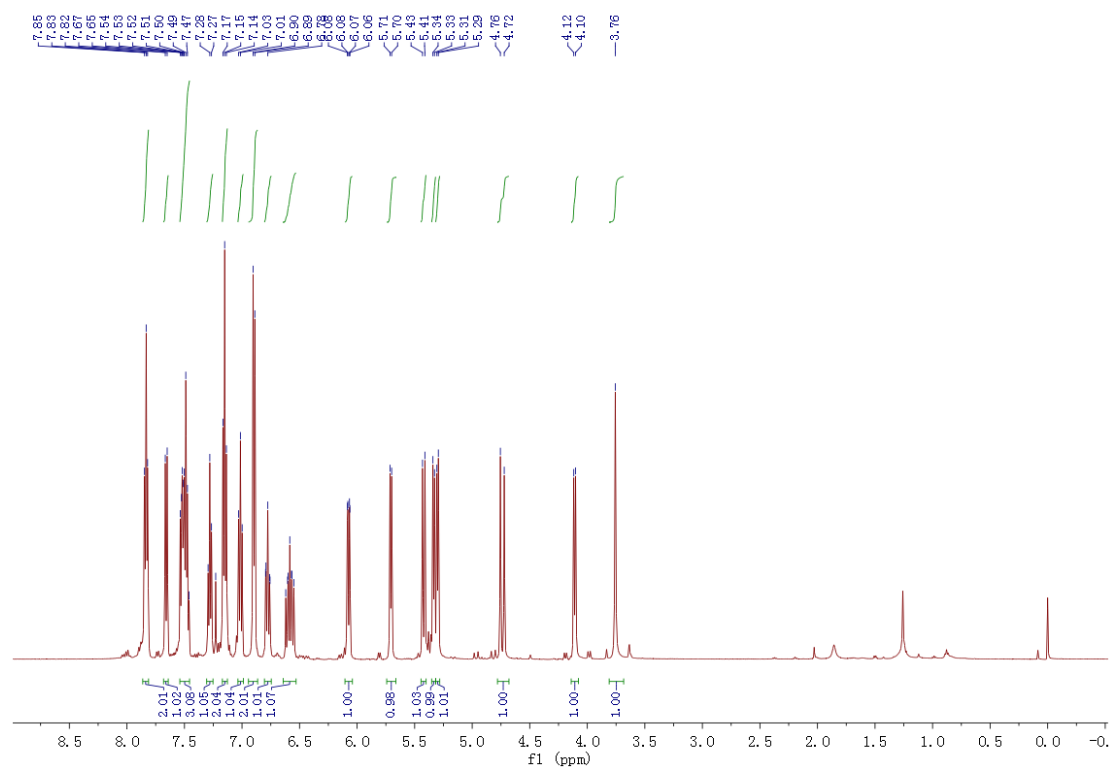
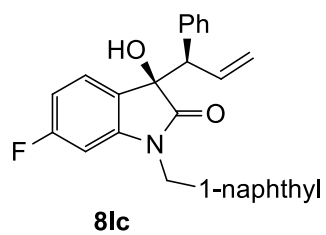
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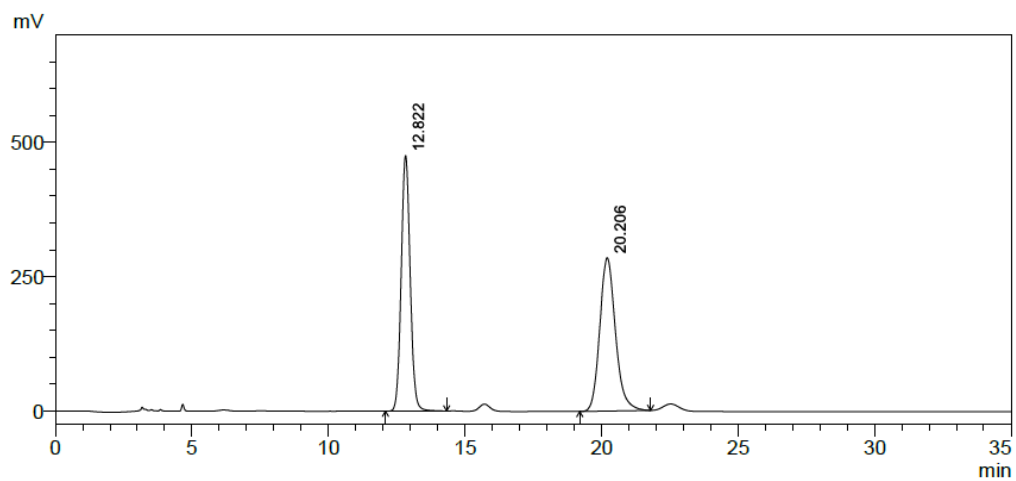
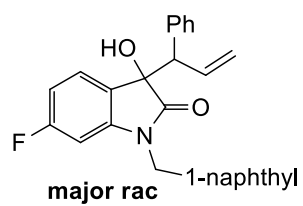
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.458	33454203	749591	47.289	68.113
2	32.300	37289210	350924	52.711	31.887
Total		70743413	1100515	100.000	100.000



PeakTable

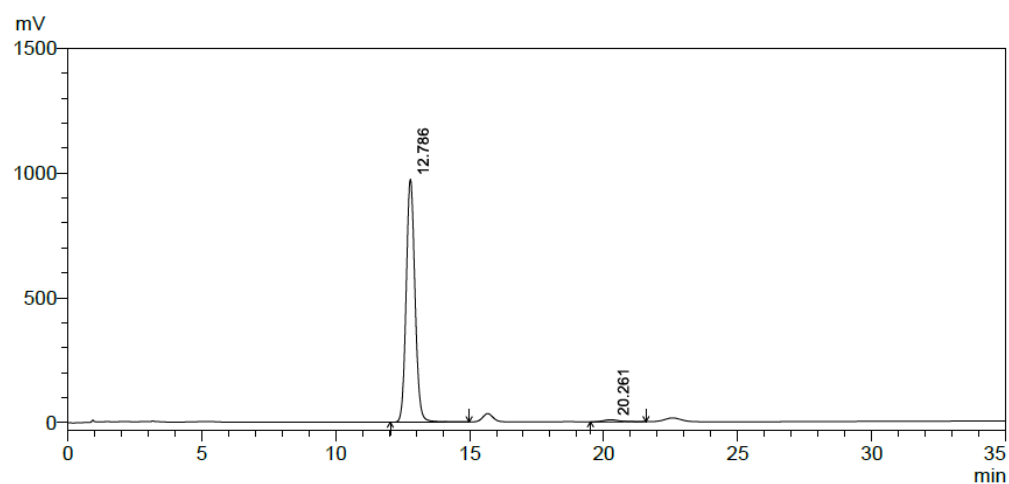
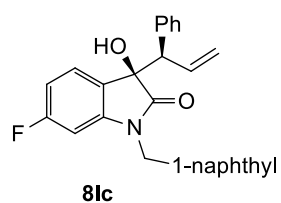
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.456	25639126	573822	98.925	99.497
2	32.521	278635	2902	1.075	0.503
Total		25917761	576725	100.000	100.000





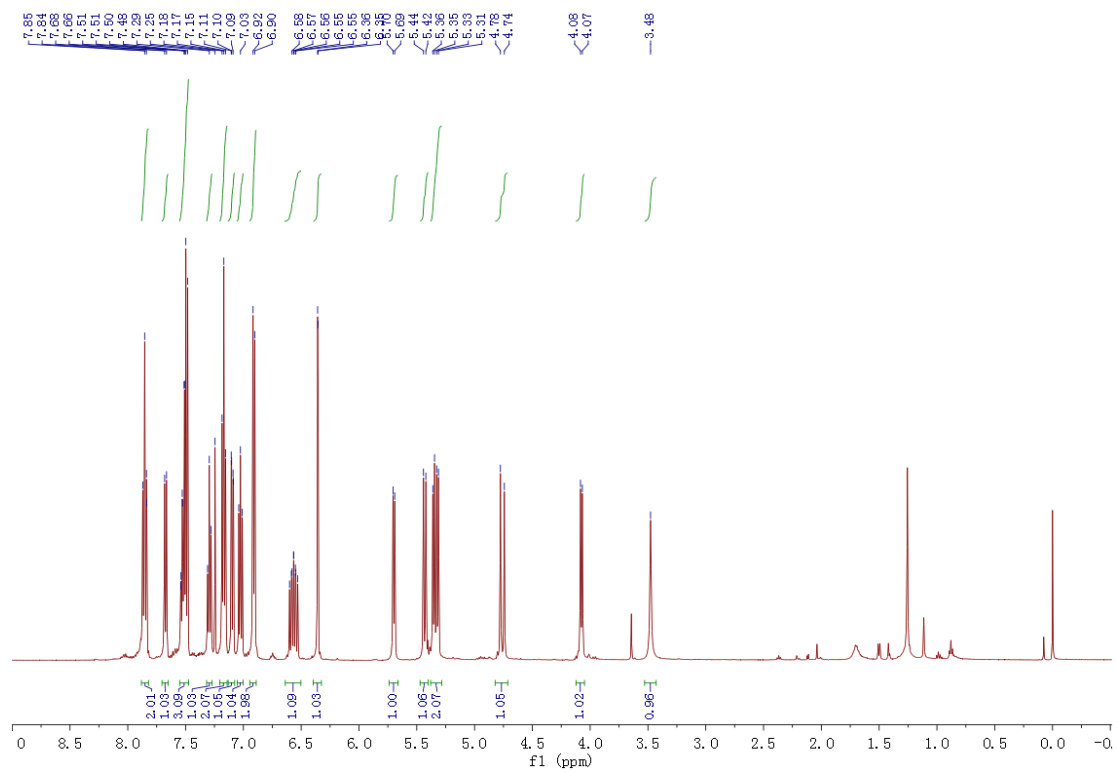
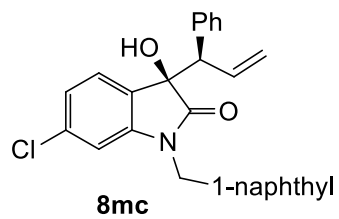
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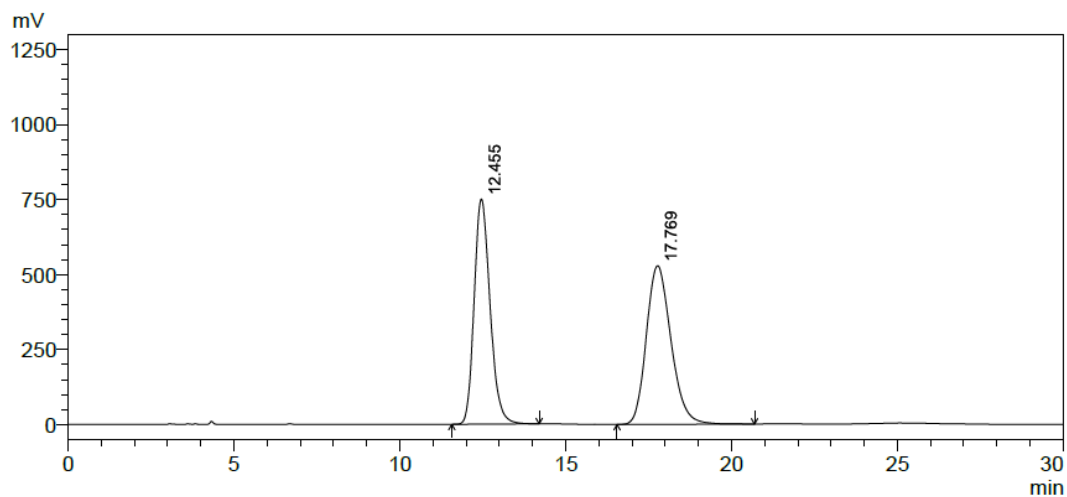
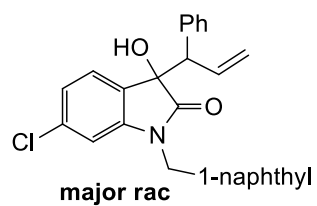
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.822	10841532	475521	48.710	62.501
2	20.206	11415987	285303	51.290	37.499
Total		22257519	760824	100.000	100.000



PeakTable

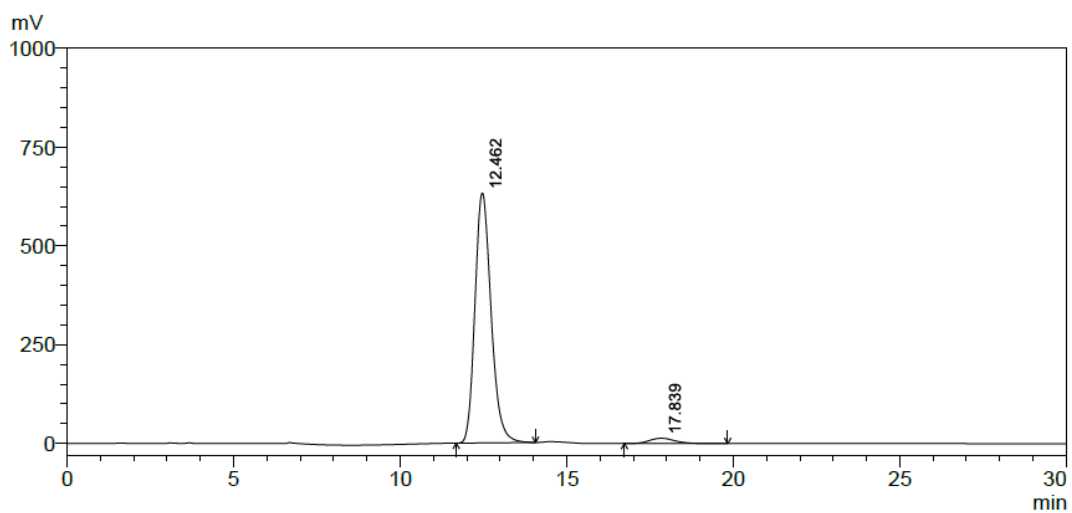
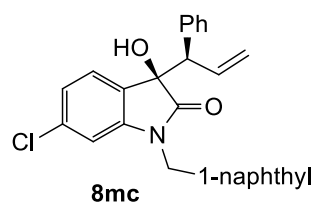
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.786	22207648	972923	98.563	99.176
2	20.261	323824	8082	1.437	0.824
Total		22531472	981005	100.000	100.000





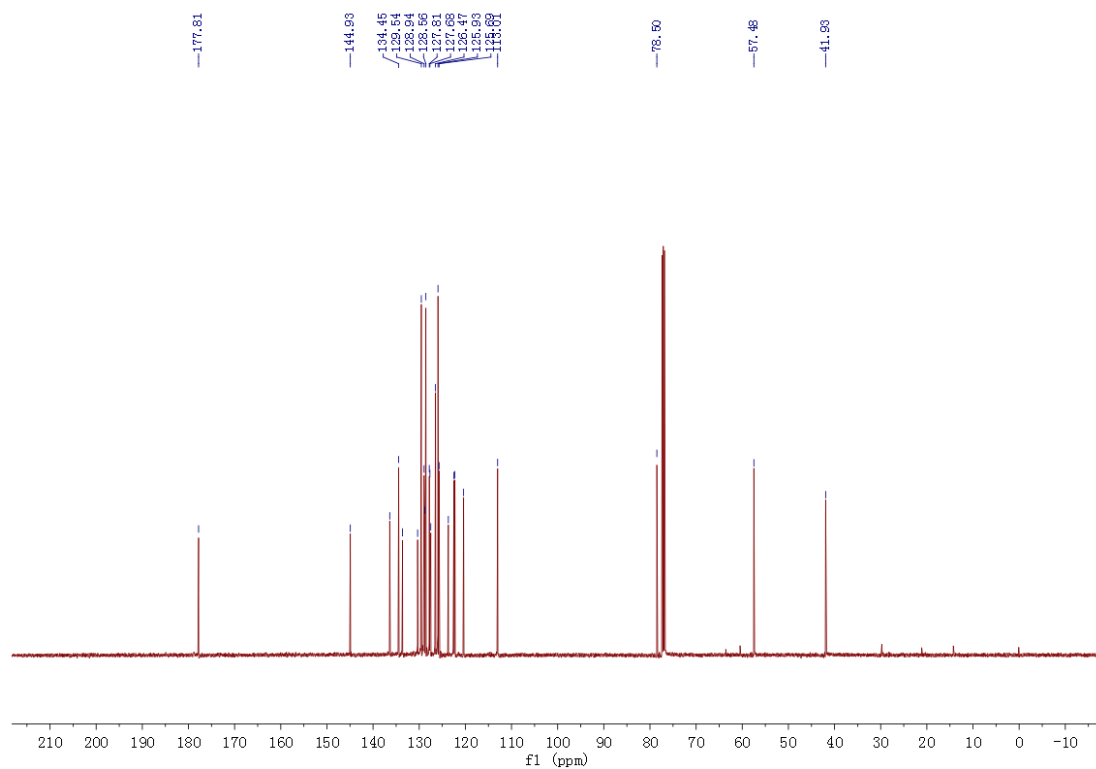
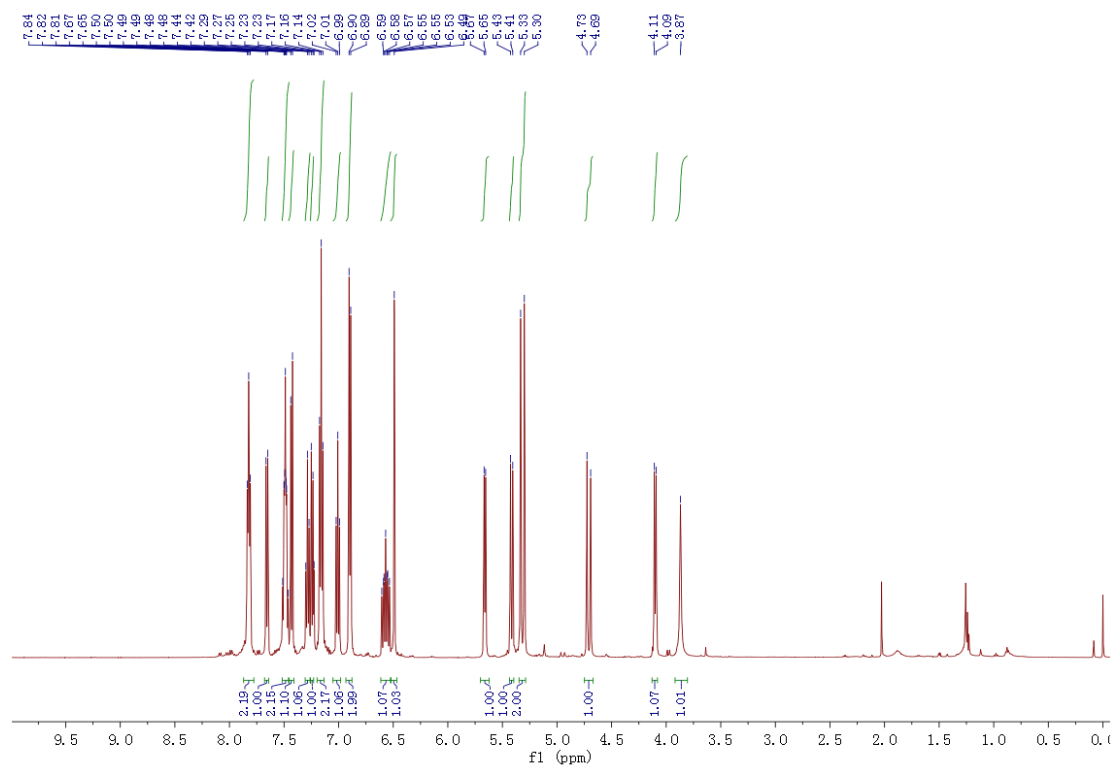
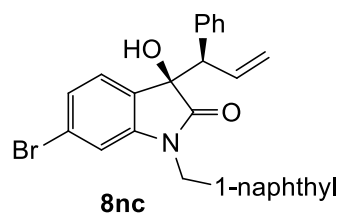
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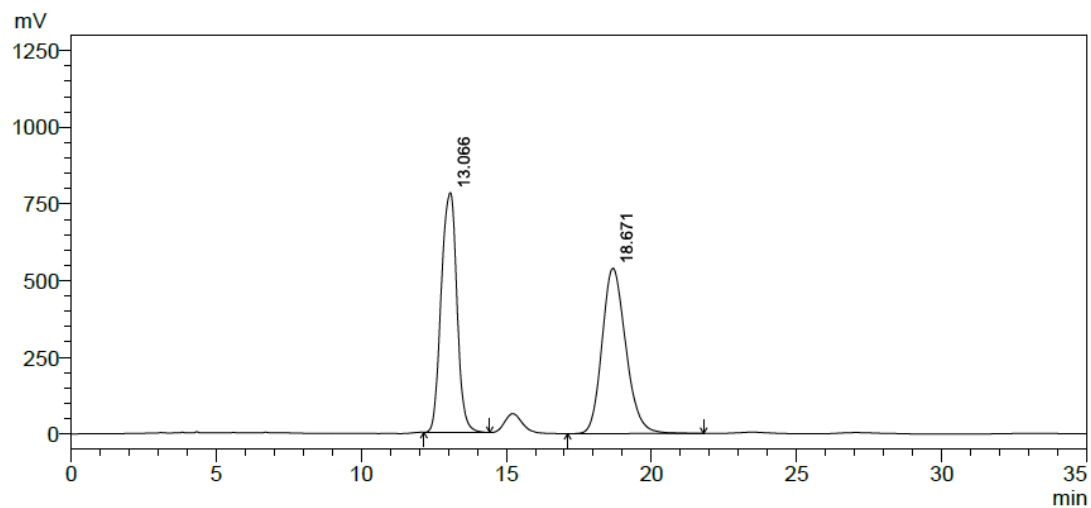
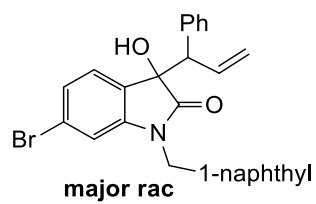
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.455	25004206	749945	47.765	58.651
2	17.769	27343966	528711	52.235	41.349
Total		52348172	1278655	100.000	100.000



PeakTable

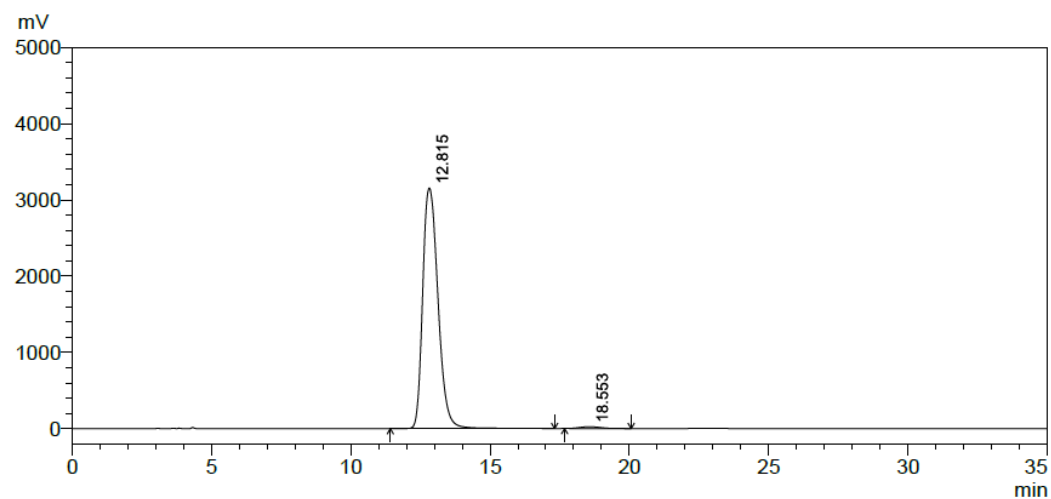
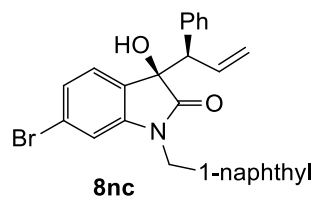
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.462	21342180	633163	96.773	97.937
2	17.839	711622	13336	3.227	2.063
Total		22053802	646499	100.000	100.000





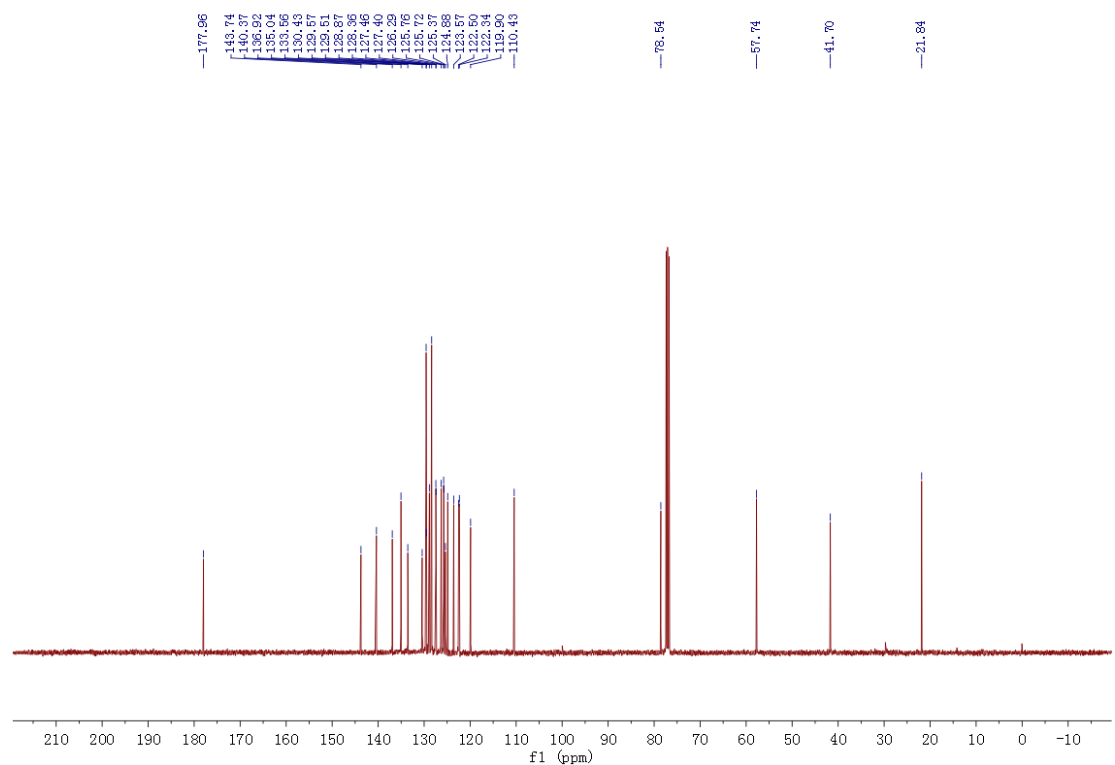
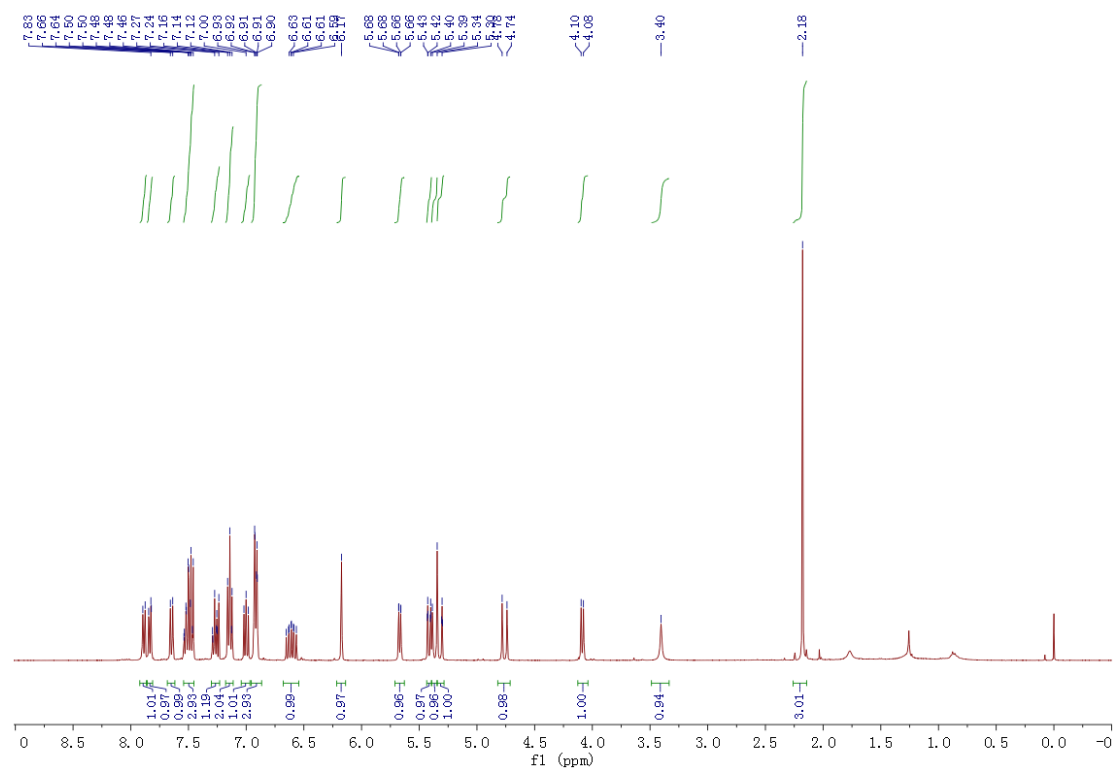
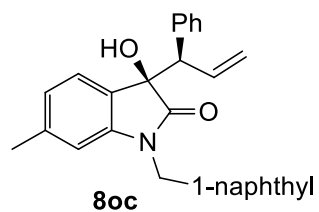
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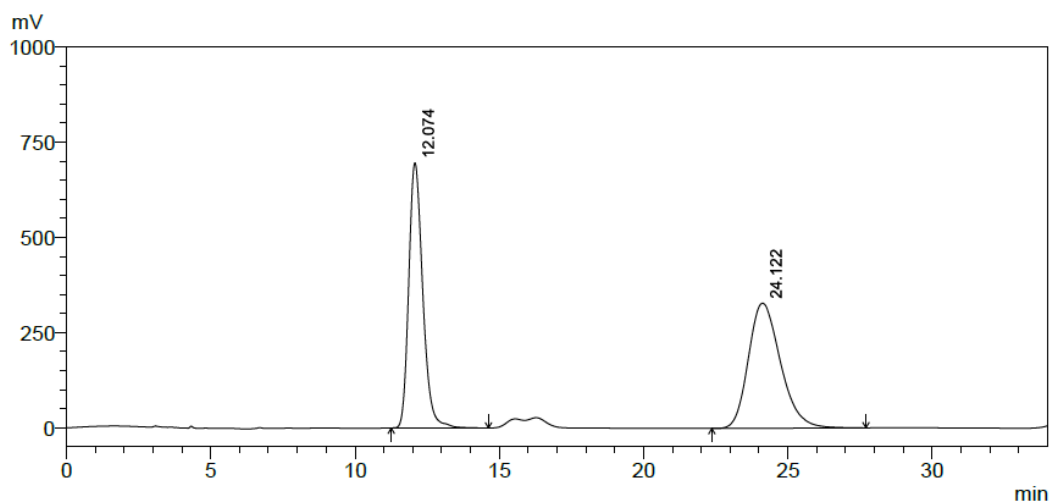
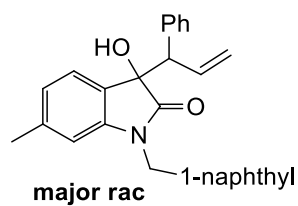
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.066	29414857	781881	48.896	59.169
2	18.671	30743425	539565	51.104	40.831
Total		60158282	1321446	100.000	100.000



PeakTable

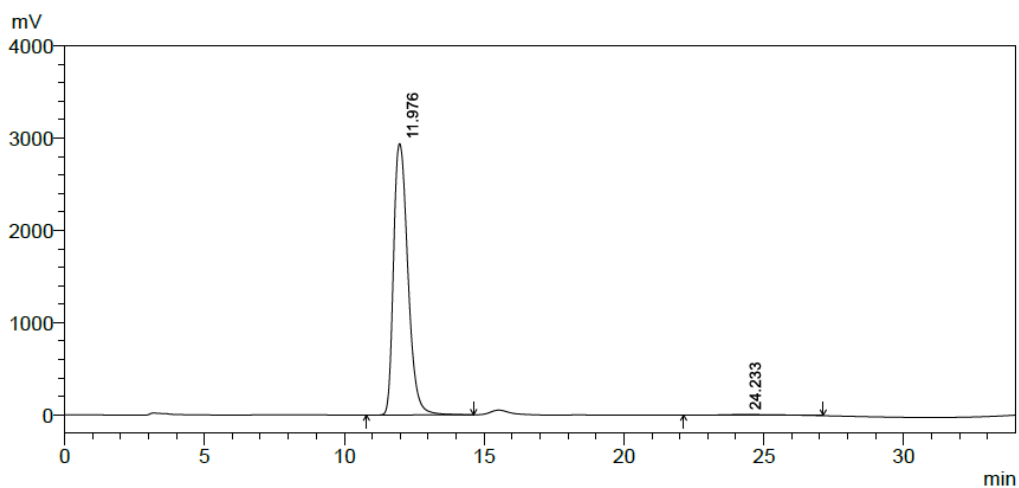
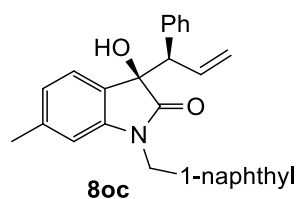
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.815	120647568	3154366	98.964	99.261
2	18.553	1263181	23493	1.036	0.739
Total		121910748	3177859	100.000	100.000





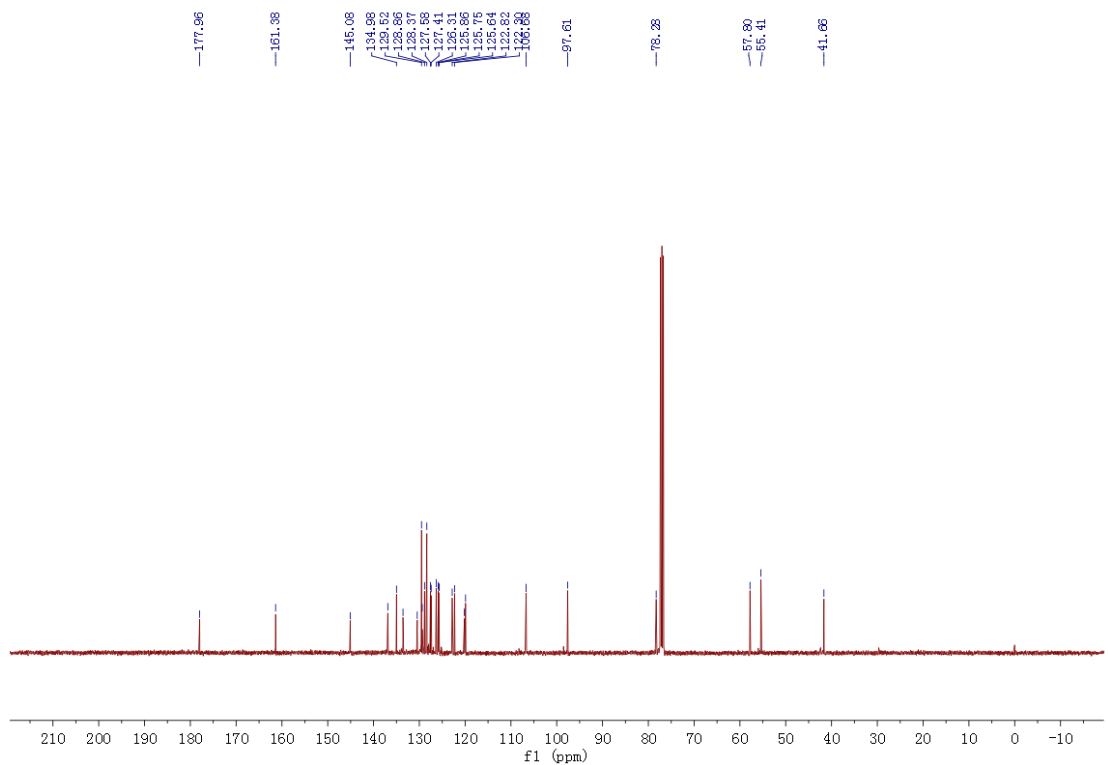
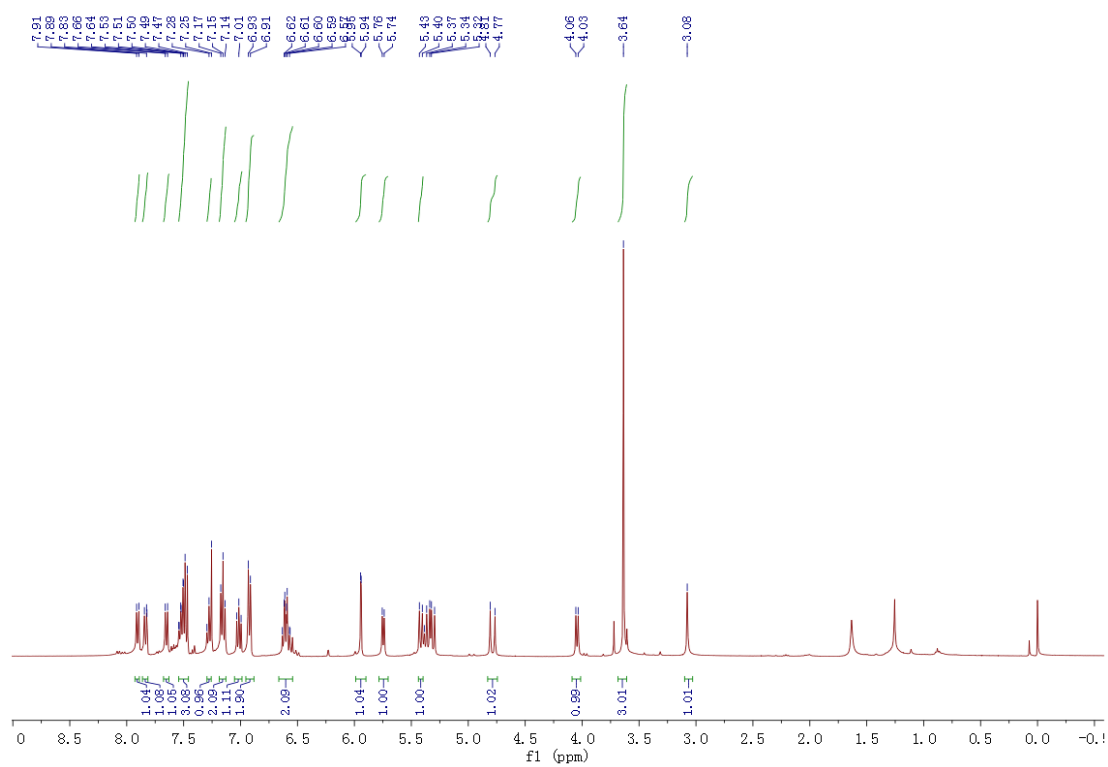
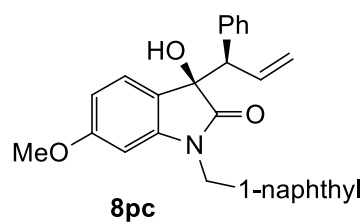
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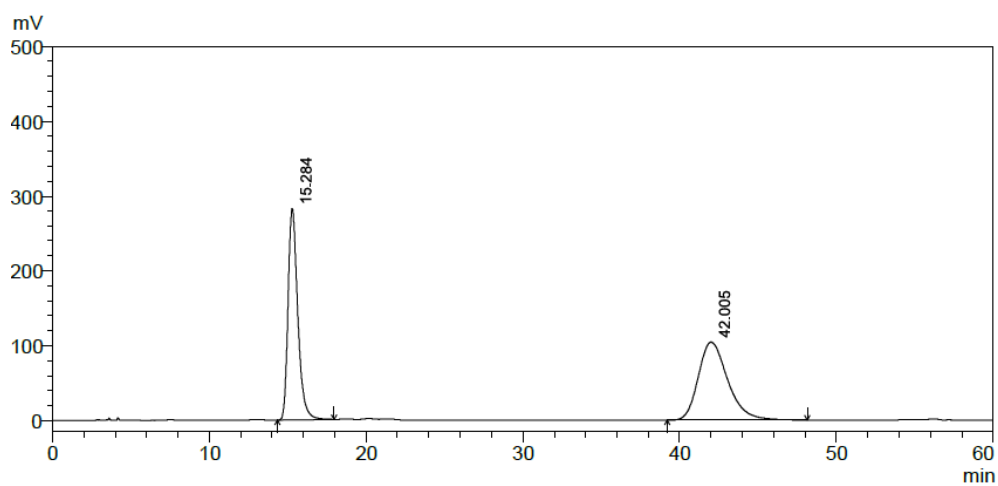
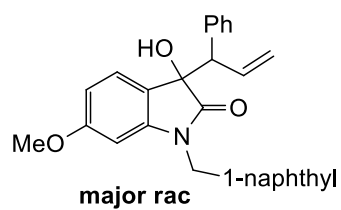
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.074	23489996	696858	48.034	67.968
2	24.122	25412890	328410	51.966	32.032
Total		48902886	1025268	100.000	100.000



PeakTable

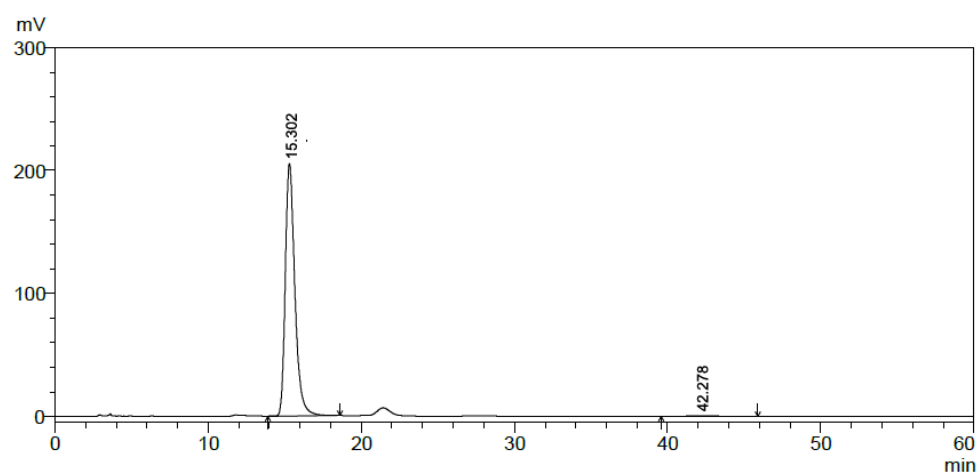
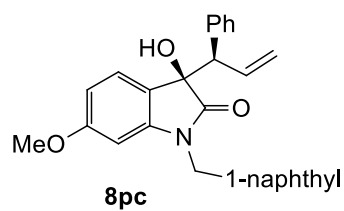
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.976	105148218	2943014	99.364	99.757
2	24.233	673179	7168	0.636	0.243
Total		105821398	2950181	100.000	100.000





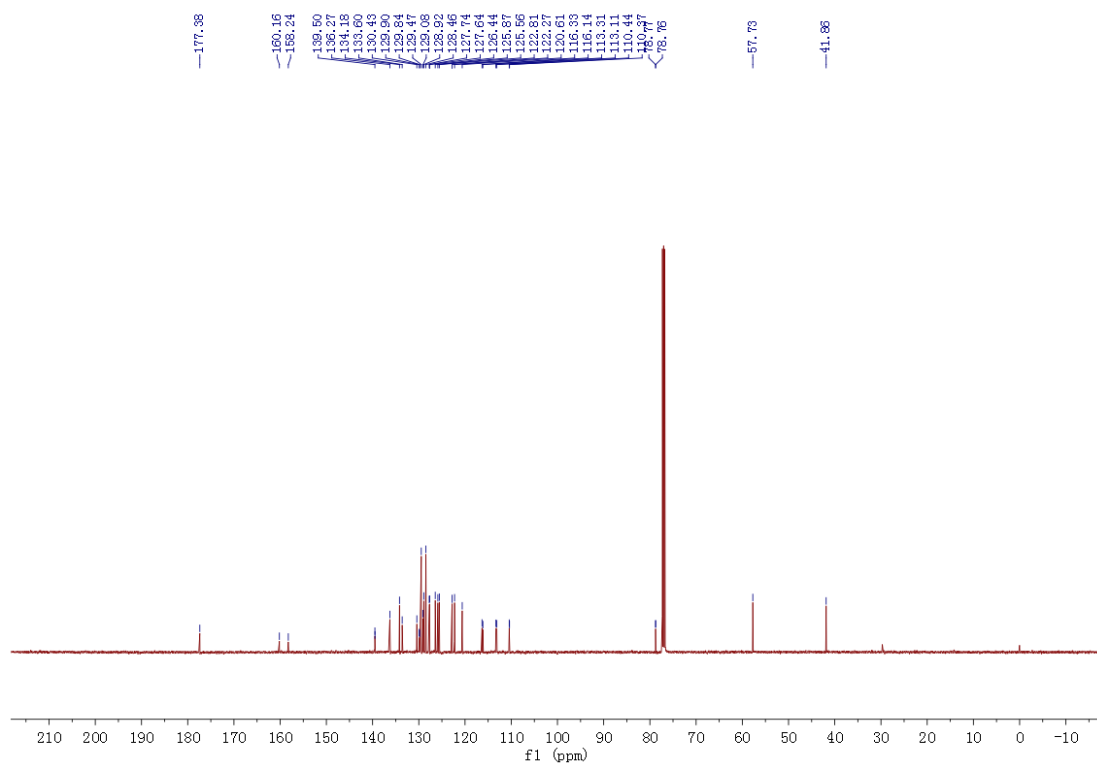
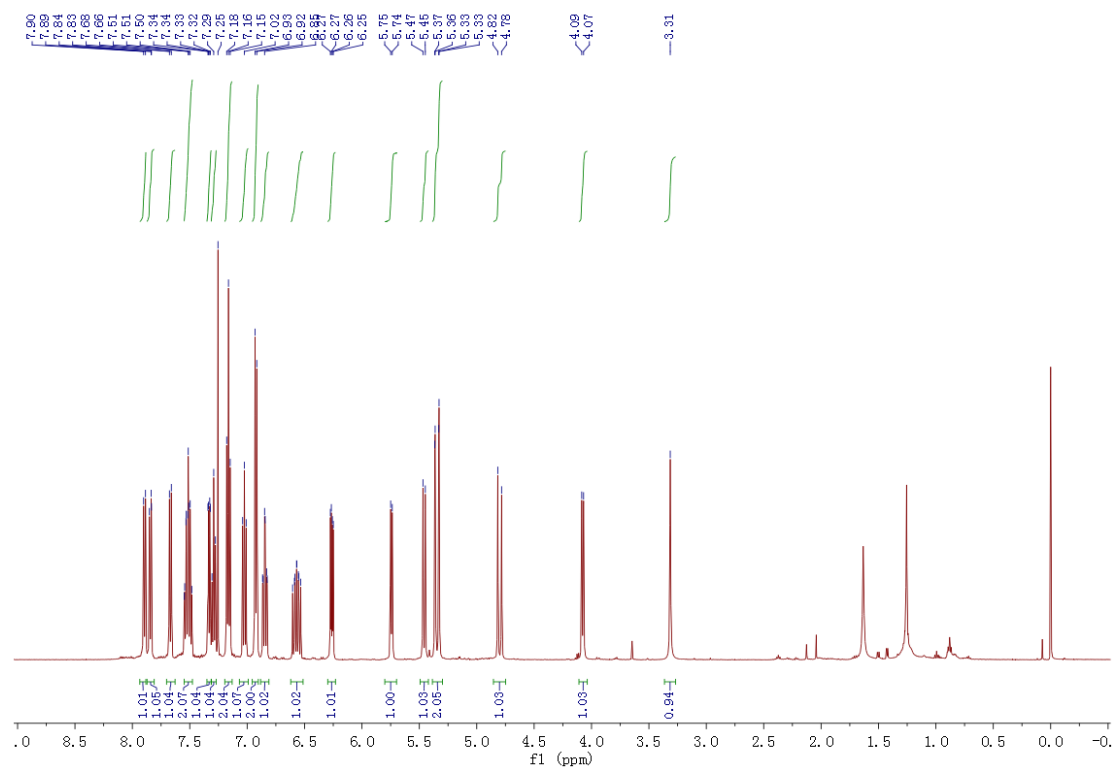
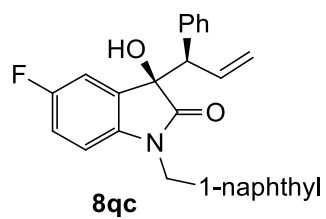
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PeakTable

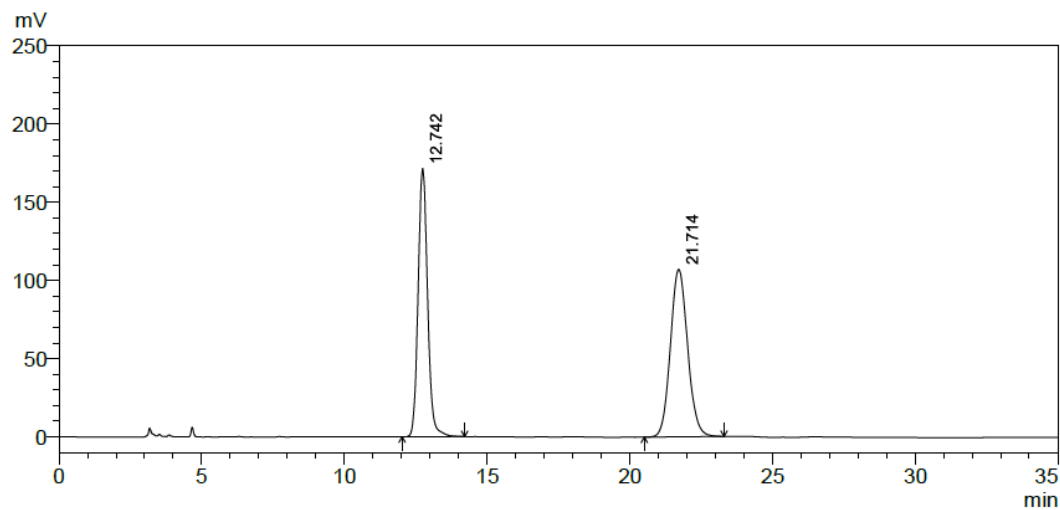
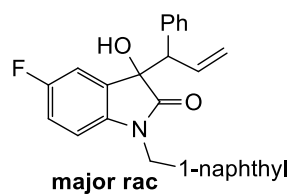
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.284	12171331	282692	47.088	73.025
2	42.005	13676698	104427	52.912	26.975
Total		25848030	387118	100.000	100.000



PeakTable

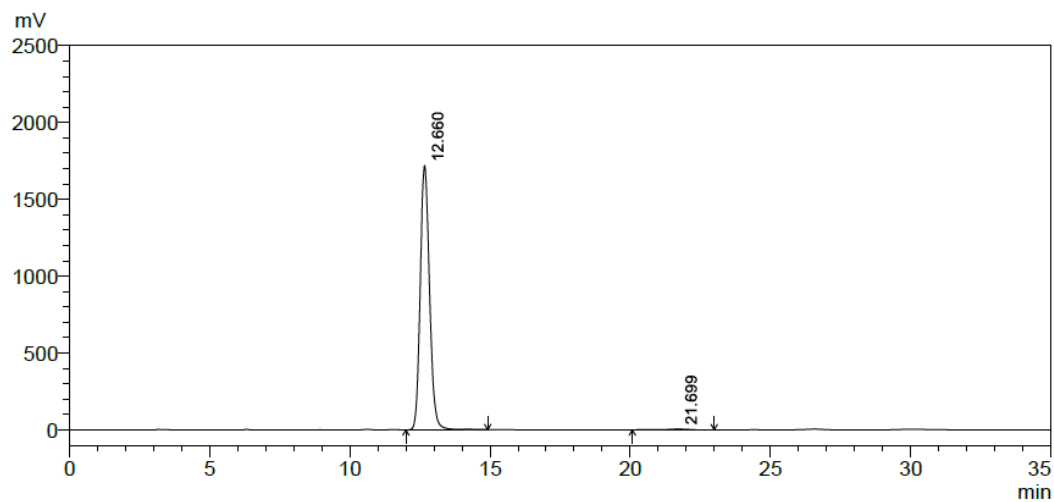
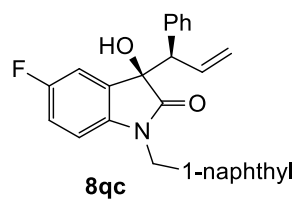
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.302	8928810	205305	99.383	99.787
2	42.278	55449	438	0.617	0.213
Total		8984259	205743	100.000	100.000





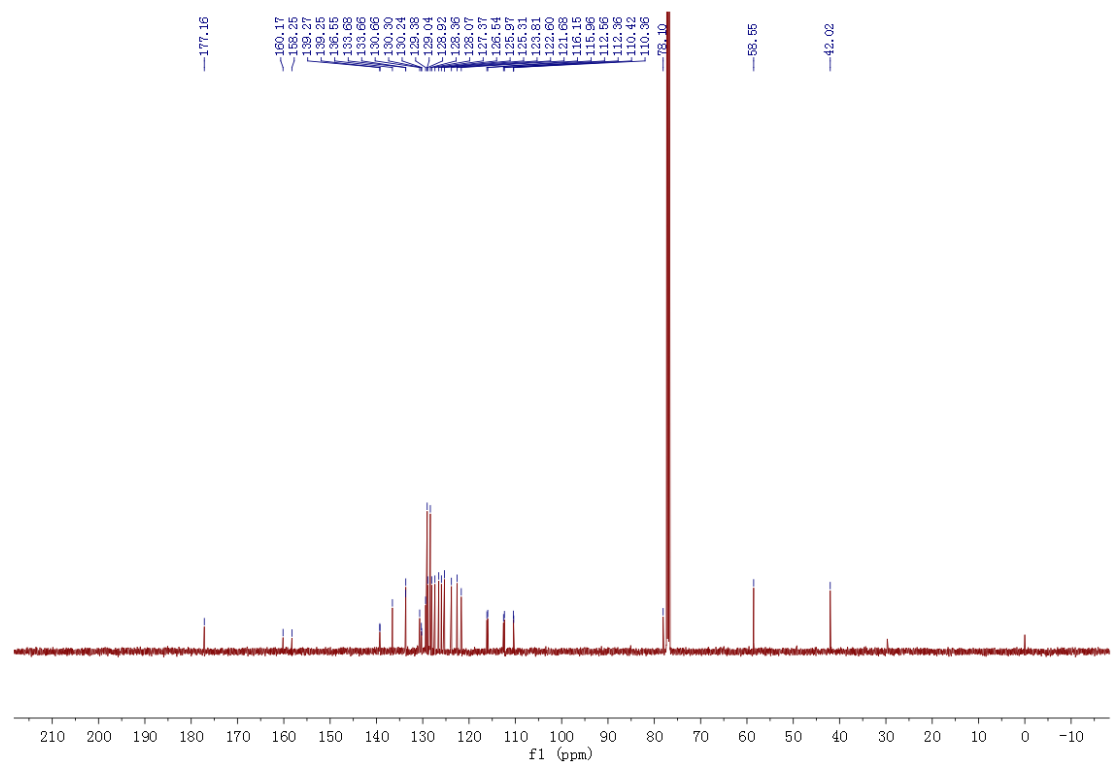
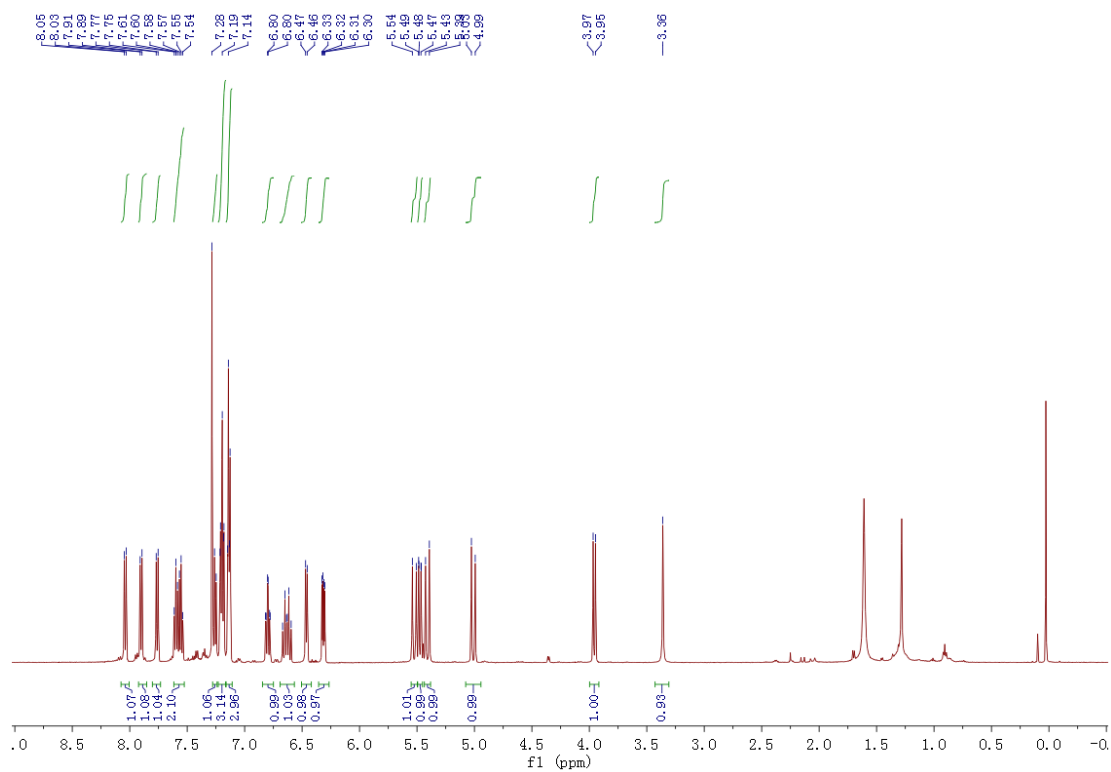
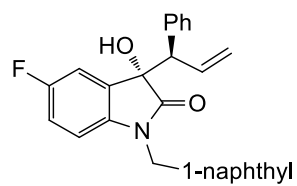
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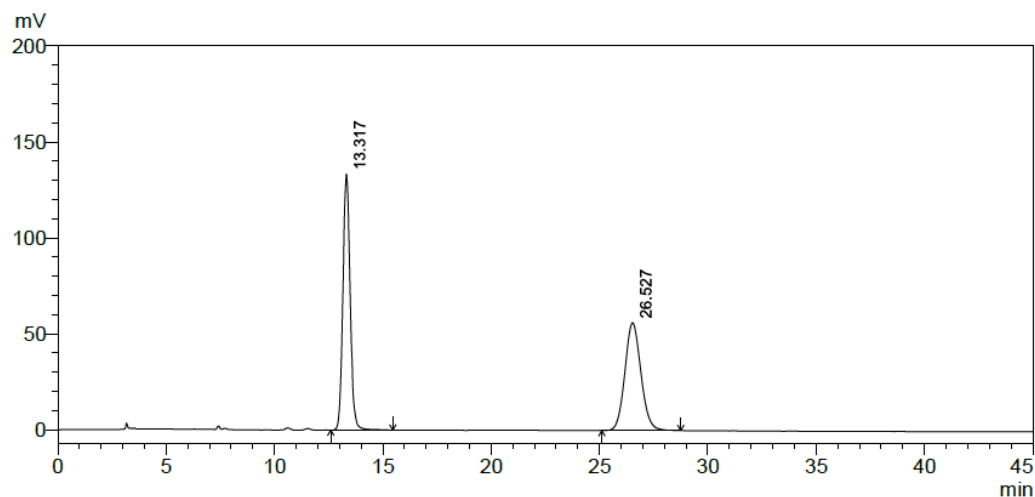
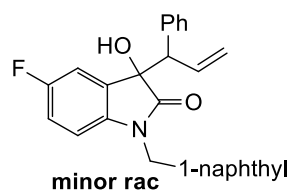
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.742	3963908	171594	46.873	61.563
2	21.714	4492783	107135	53.127	38.437
Total		8456691	278730	100.000	100.000



PeakTable

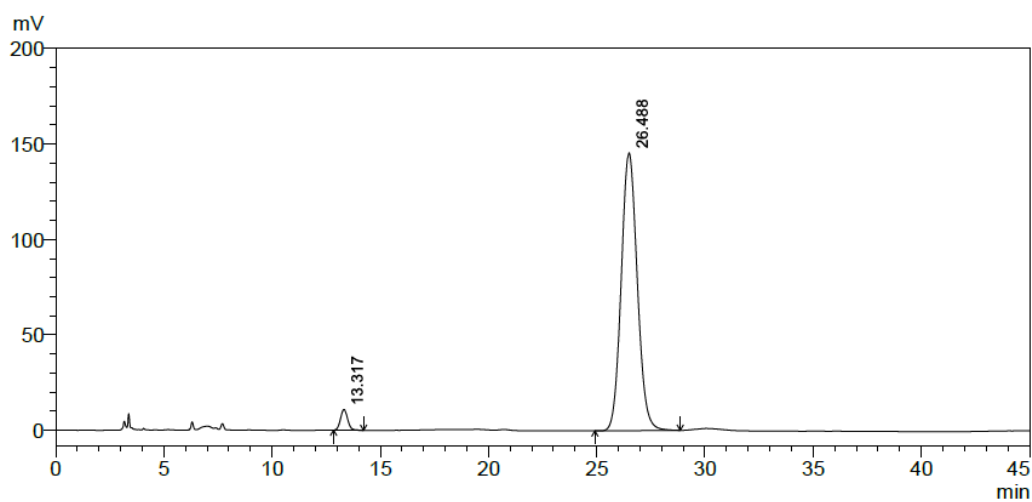
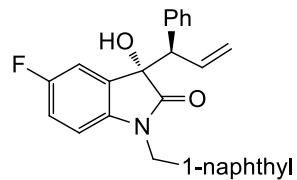
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.660	39630952	1720285	99.282	99.683
2	21.699	286590	5465	0.718	0.317
Total		39917542	1725751	100.000	100.000





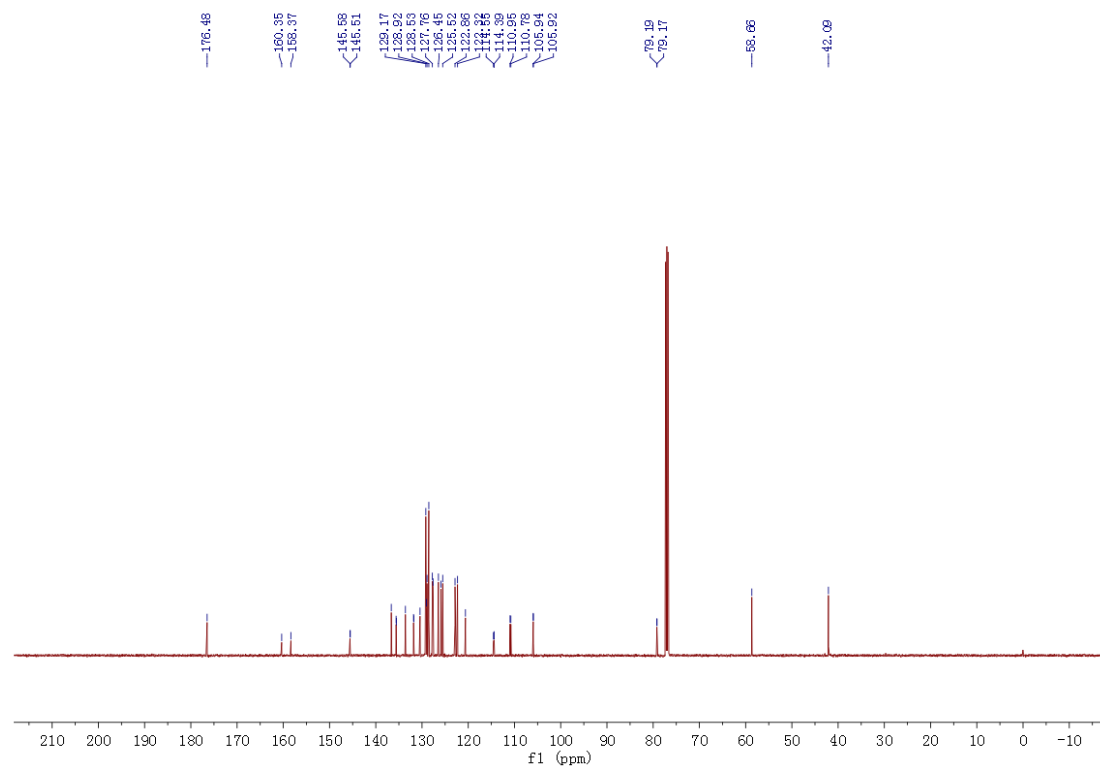
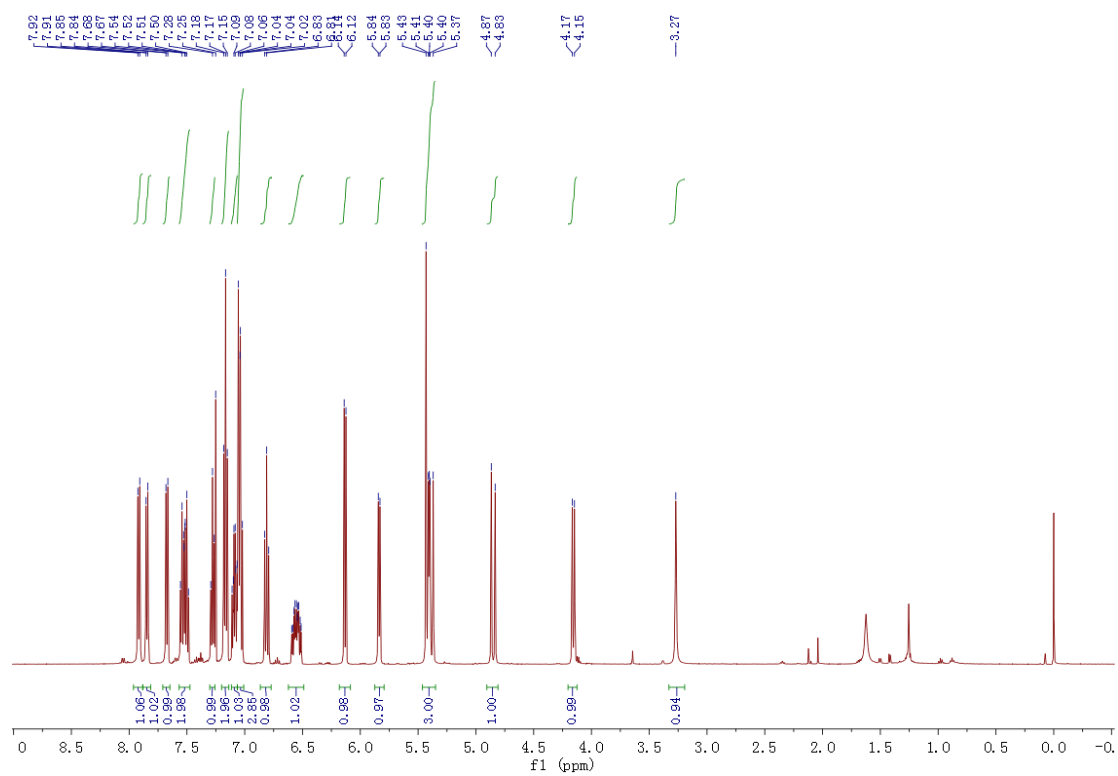
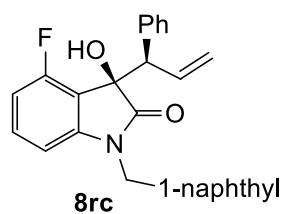
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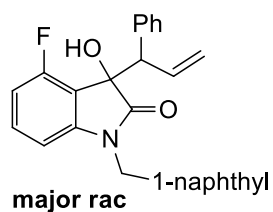
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.317	3113325	133455	51.809	70.374
2	26.527	2895950	56181	48.191	29.626
Total		6009275	189636	100.000	100.000



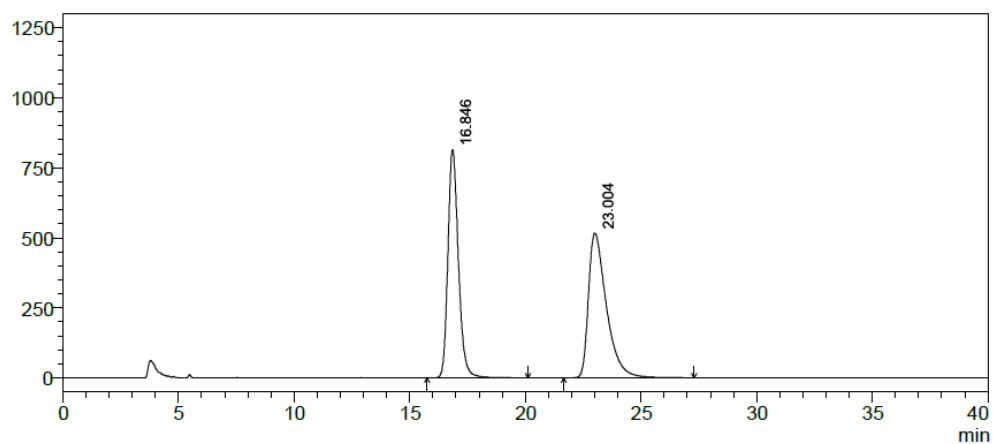
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.317	247445	10839	3.182	6.926
2	26.488	7528048	145675	96.818	93.074
Total		7775493	156515	100.000	100.000



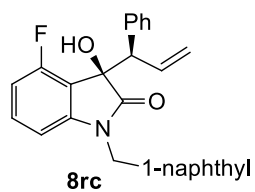


mV

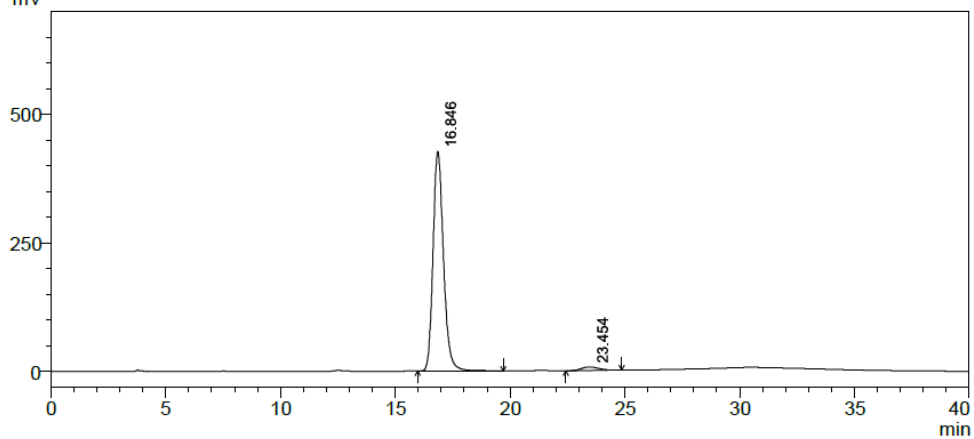


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.846	25745710	814654	48.045	61.198
2	23.004	27841452	516522	51.955	38.802
Total		53587162	1331175	100.000	100.000

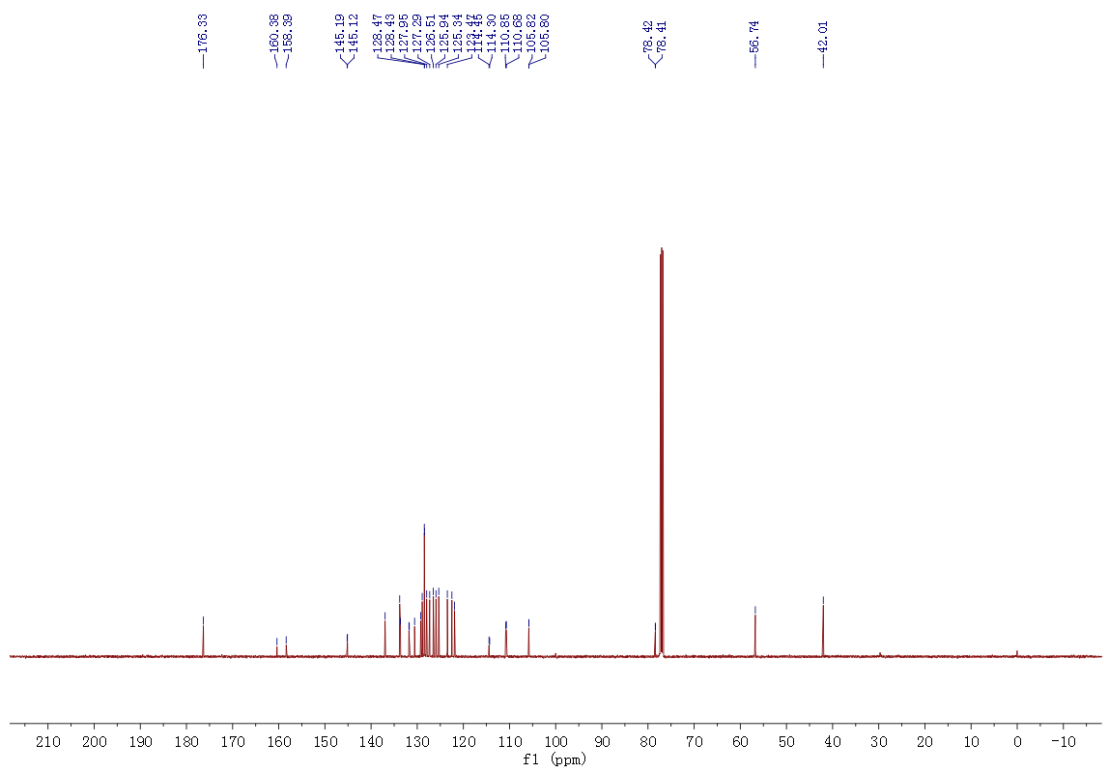
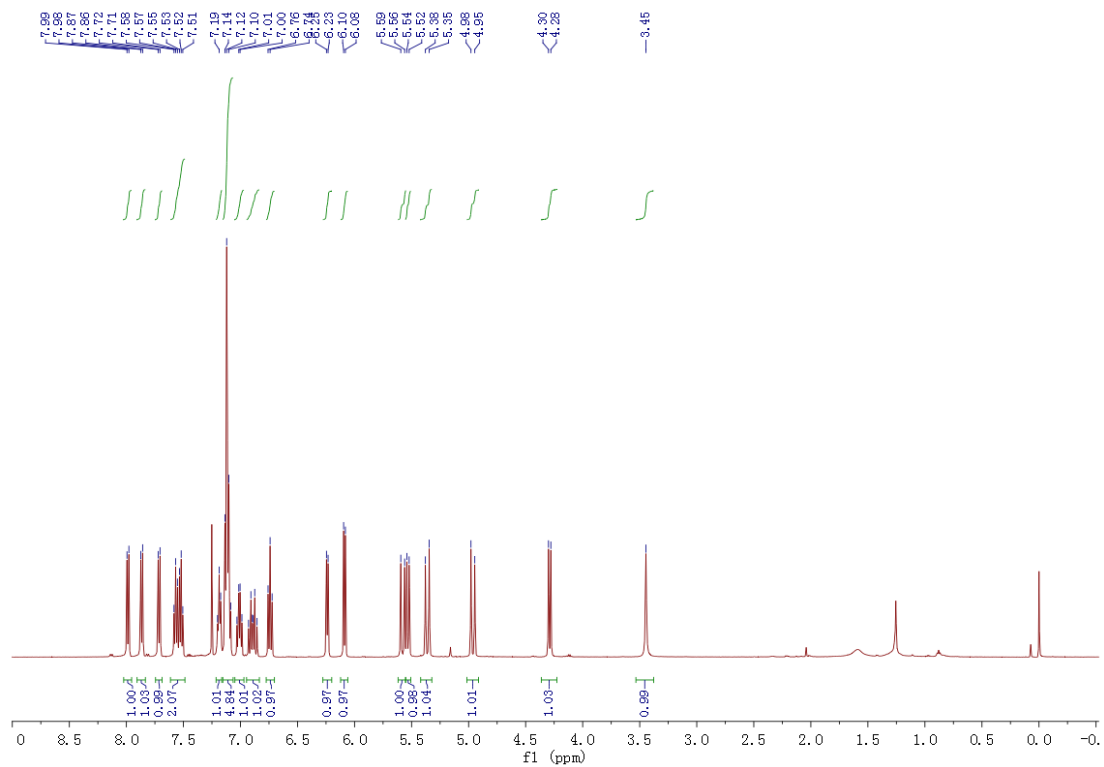
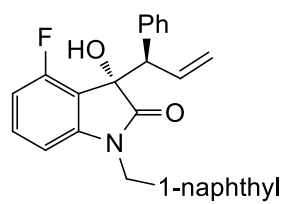


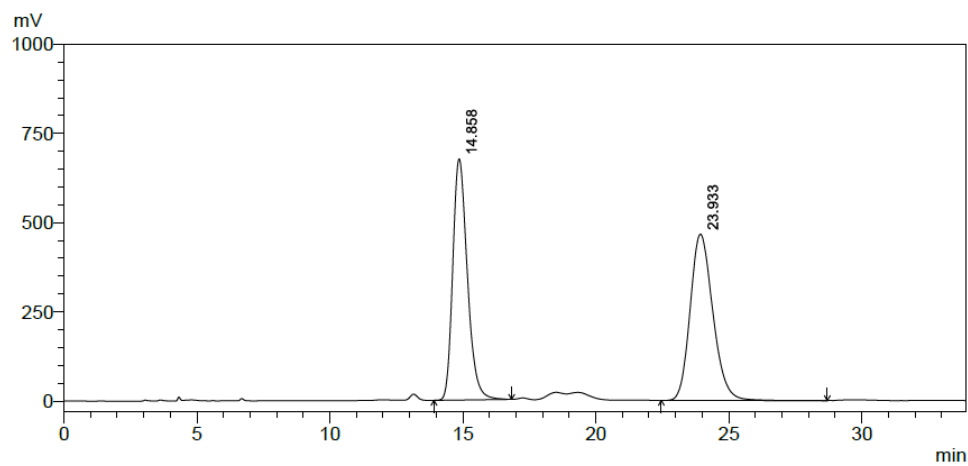
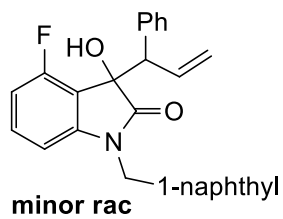
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PeakTable

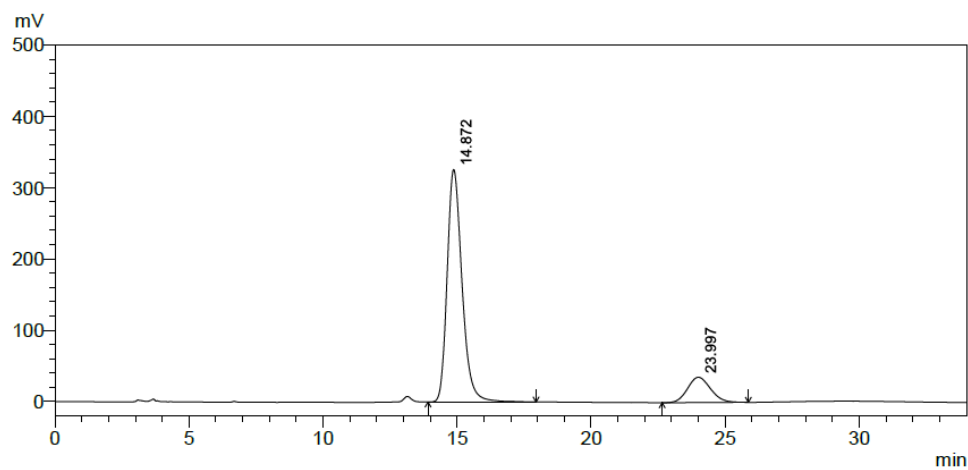
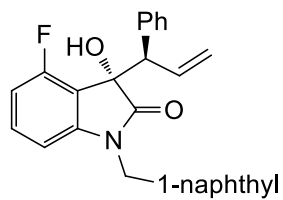
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.846	13595894	427814	97.331	98.428
2	23.454	372853	6832	2.669	1.572
Total		13968747	434646	100.000	100.000





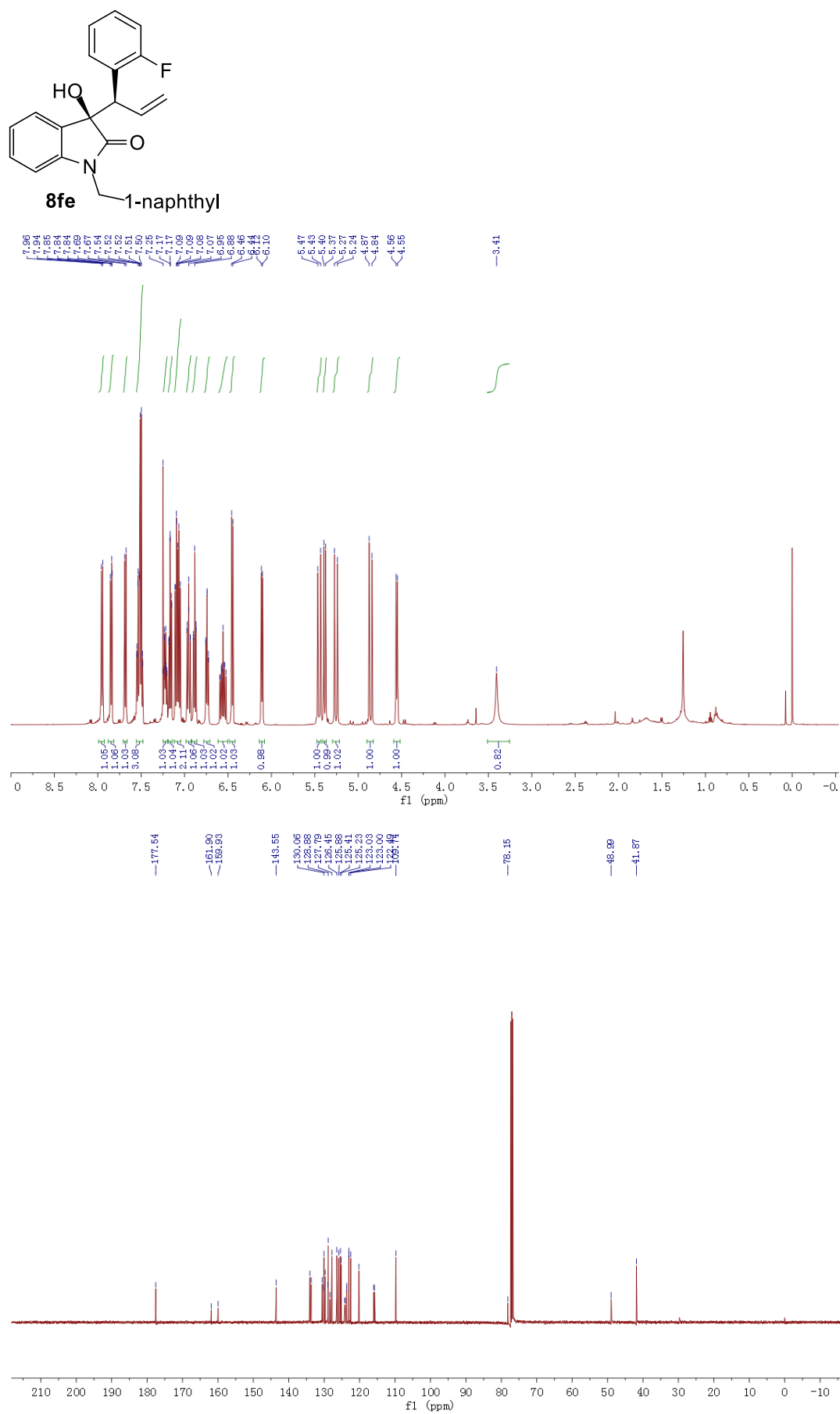
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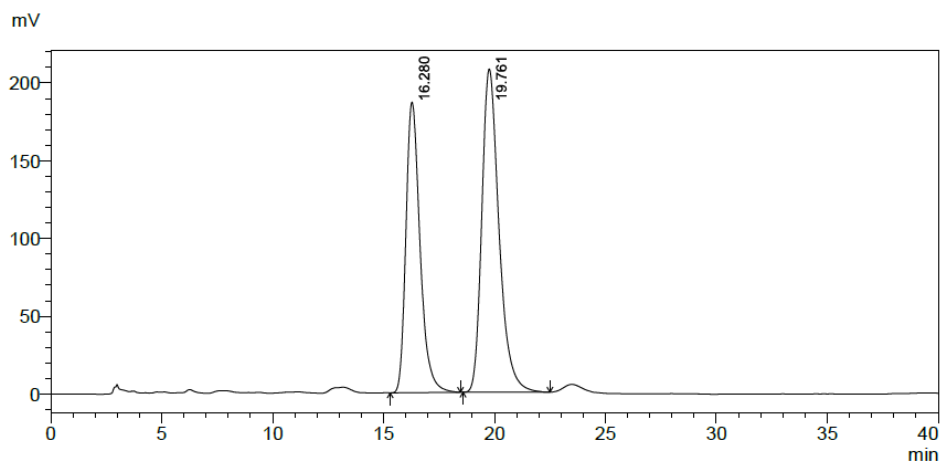
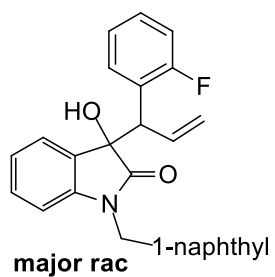
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.858	25756023	676135	48.170	59.191
2	23.933	27713271	466166	51.830	40.809
Total		53469294	1142301	100.000	100.000



PeakTable

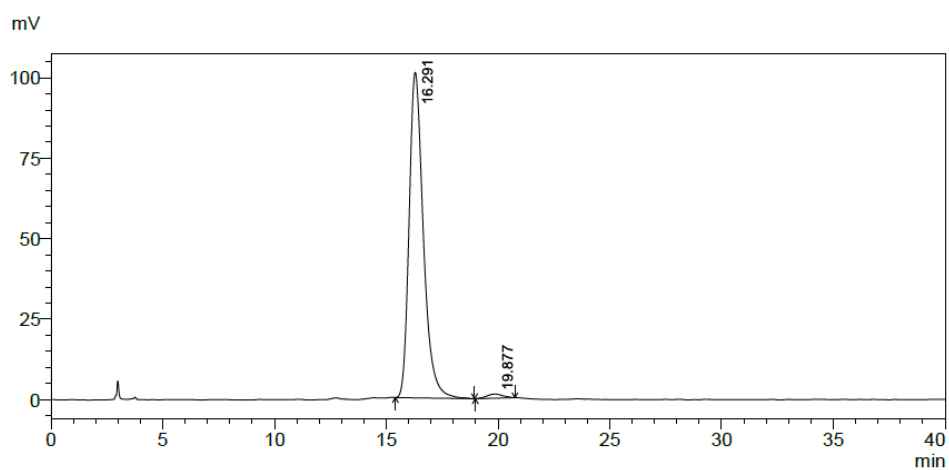
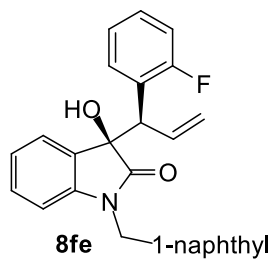
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.872	12546563	325915	85.597	90.205
2	23.997	2111227	35391	14.403	9.795
Total		14657791	361306	100.000	100.000





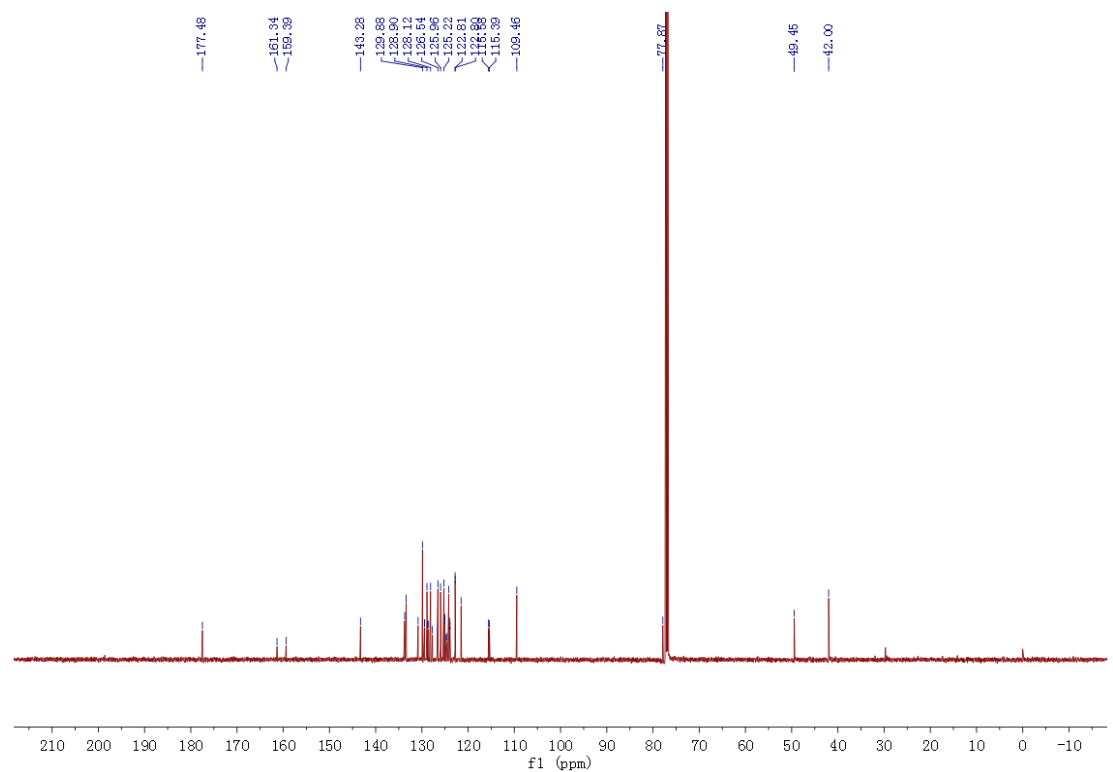
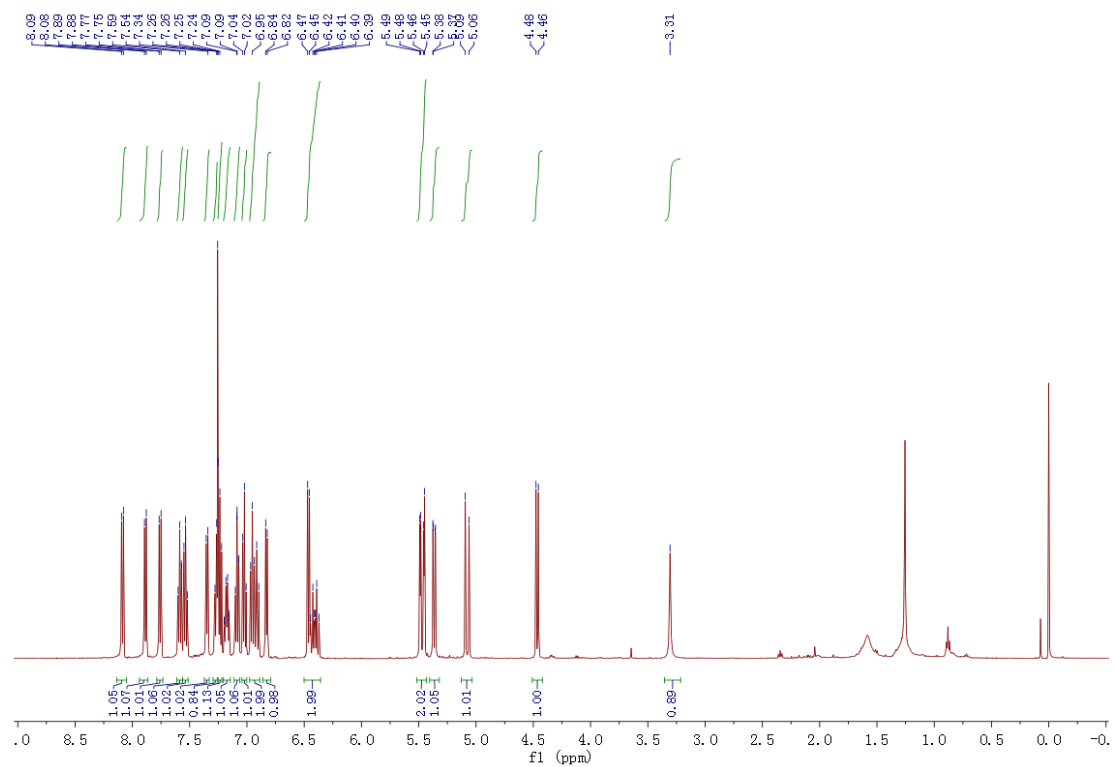
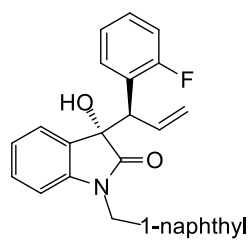
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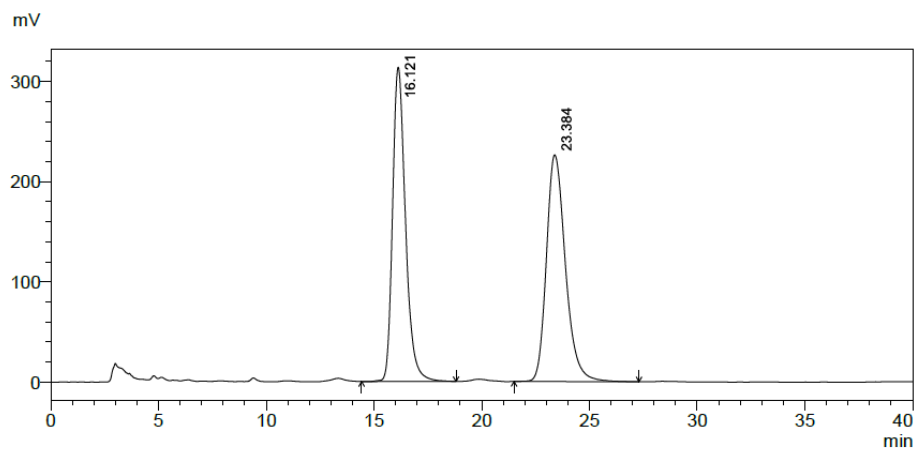
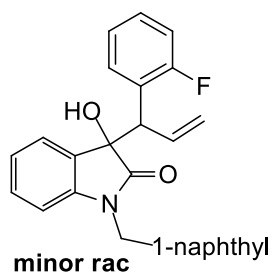
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.280	8265006	186825	42.487	47.337
2	19.761	11188166	207846	57.513	52.663
Total		19453172	394671	100.000	100.000



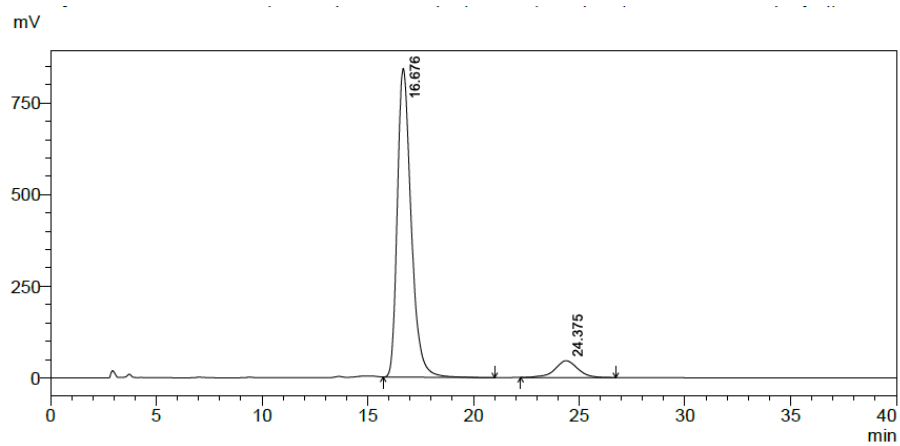
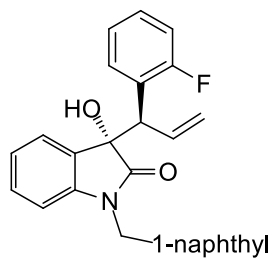
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.291	4471230	101106	98.592	98.776
2	19.877	63867	1253	1.408	1.224
Total		4535097	102359	100.000	100.000

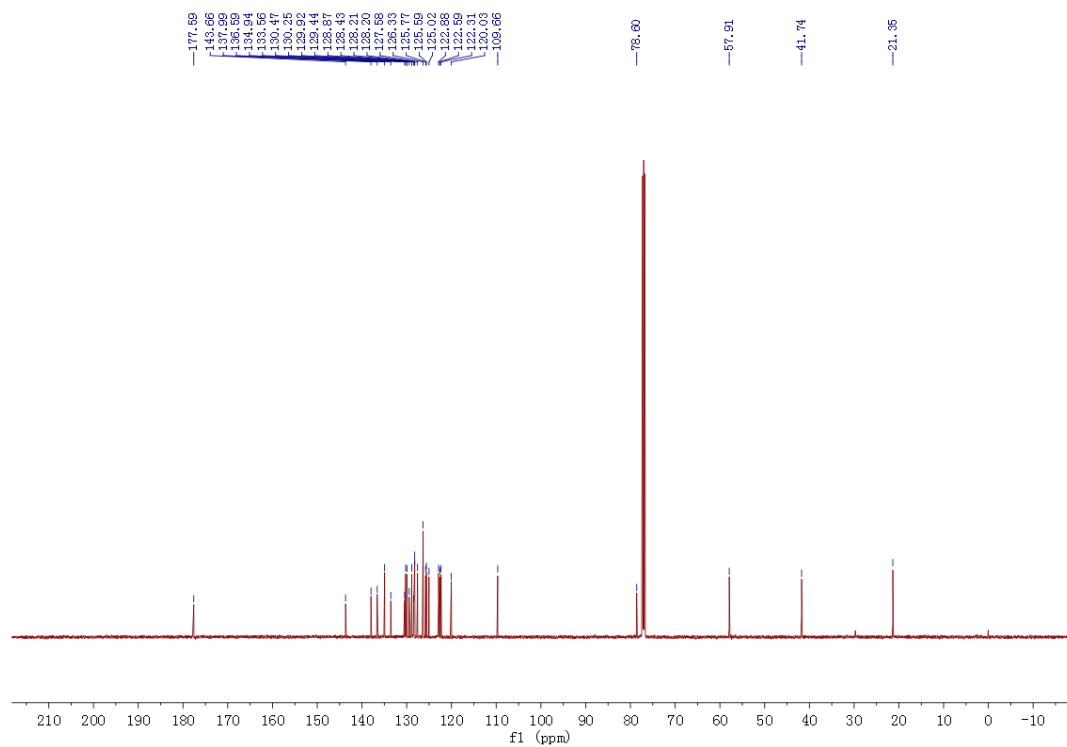
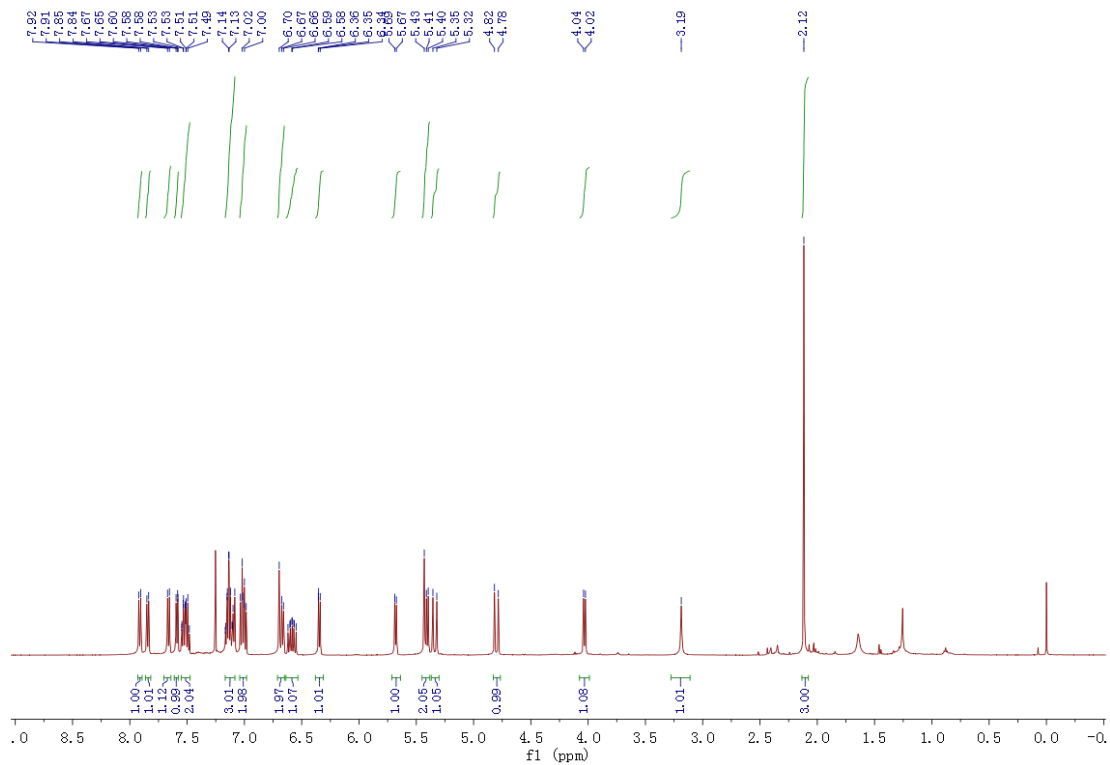
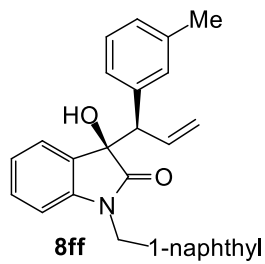


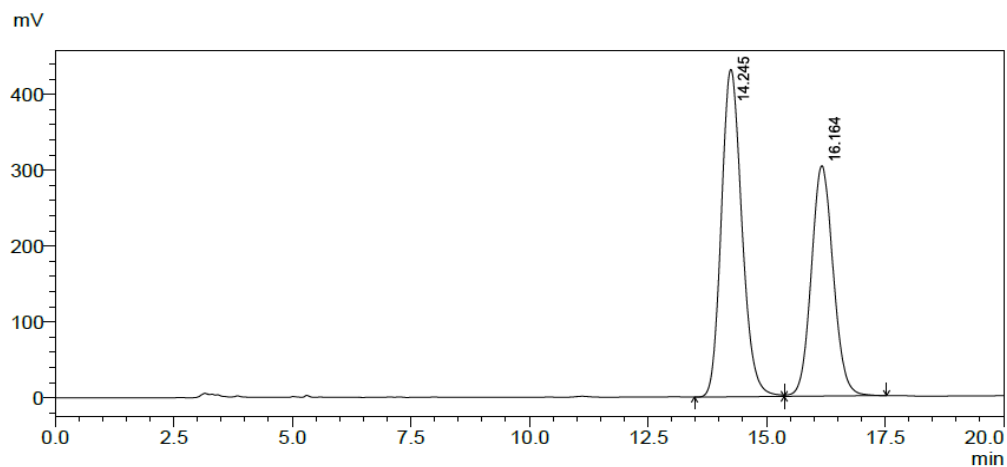
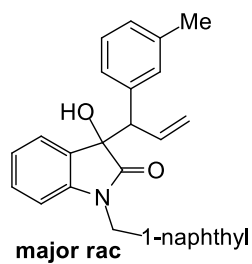


Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.121	13085574	313588	48.499	58.090
2	23.384	13895638	226247	51.501	41.910
Total		26981212	539835	100.000	100.000



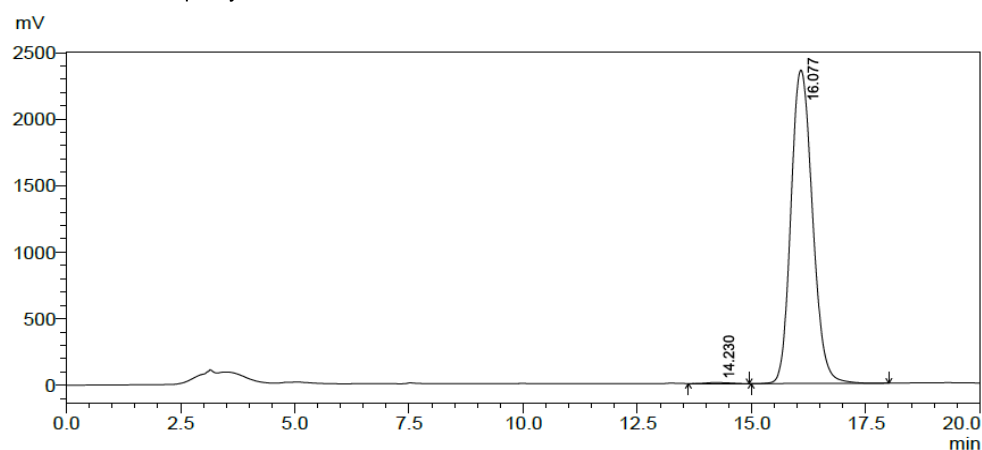
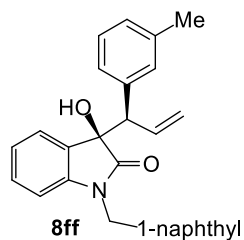
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.676	38191267	841886	91.679	94.834
2	24.375	3466486	45865	8.321	5.166
Total		41657753	887752	100.000	100.000





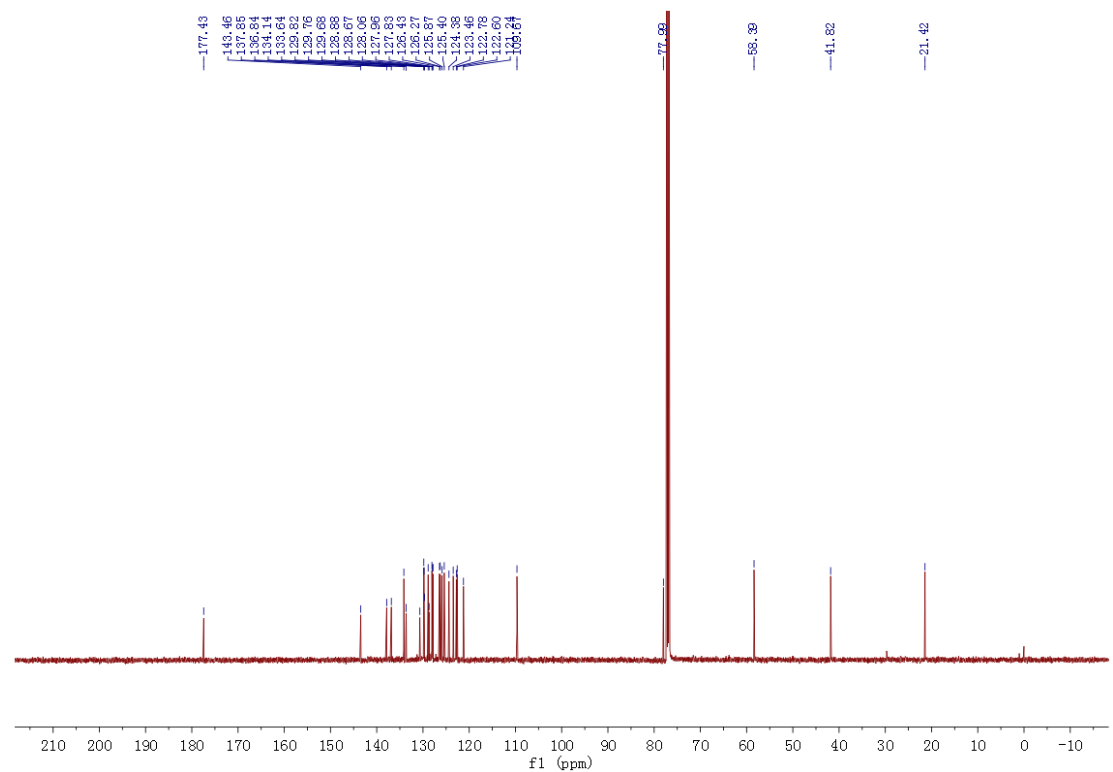
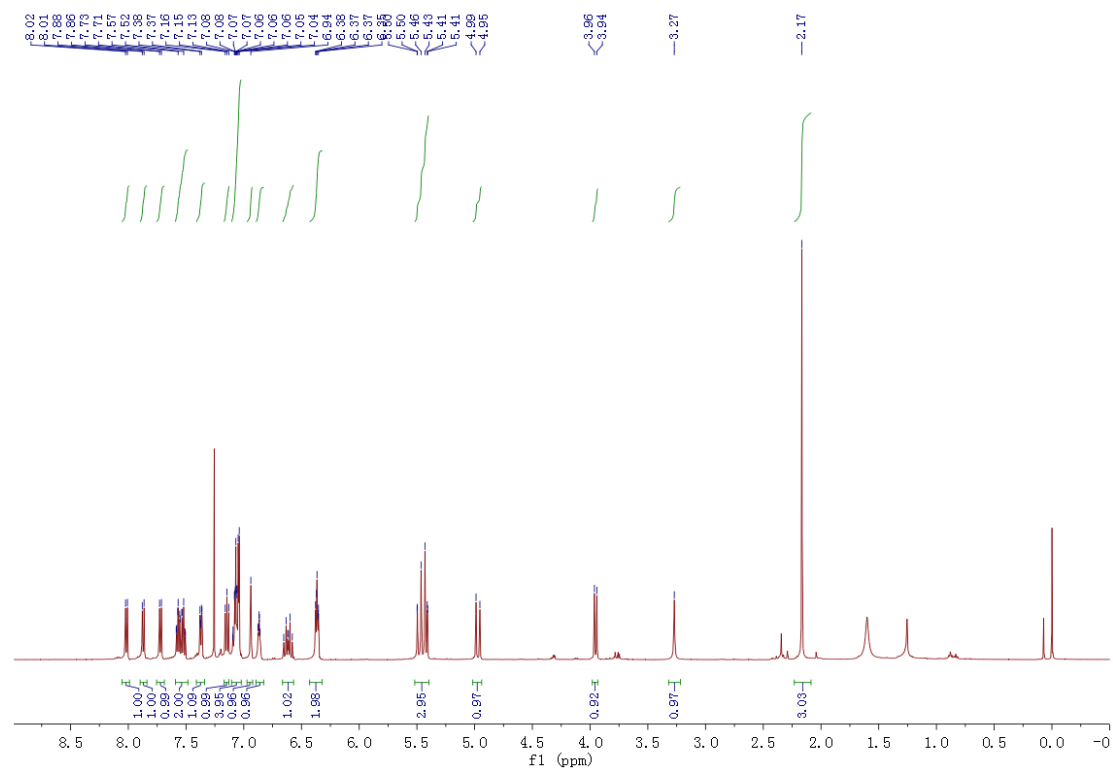
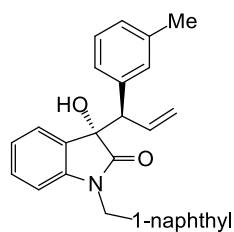
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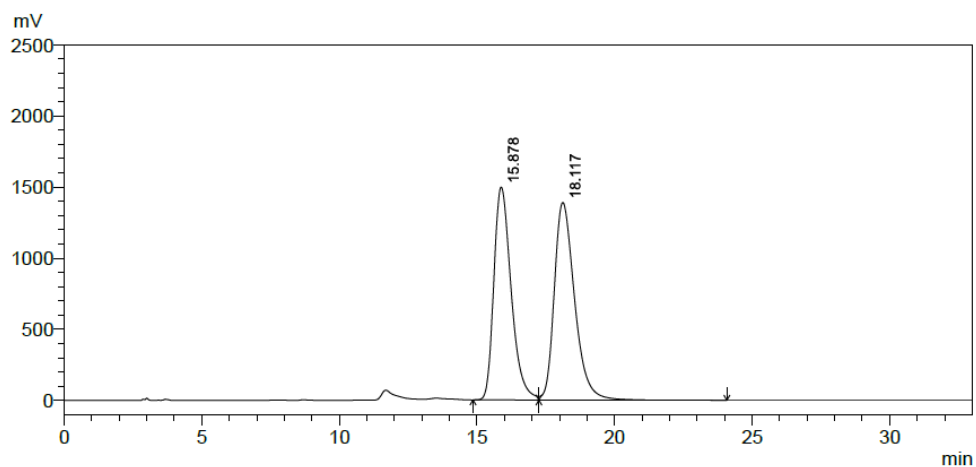
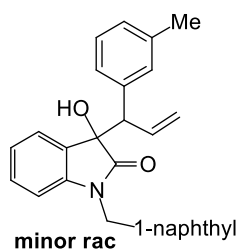
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.245	13014731	431693	57.108	58.707
2	16.164	9774925	303636	42.892	41.293
Total		22789656	735328	100.000	100.000



PeakTable

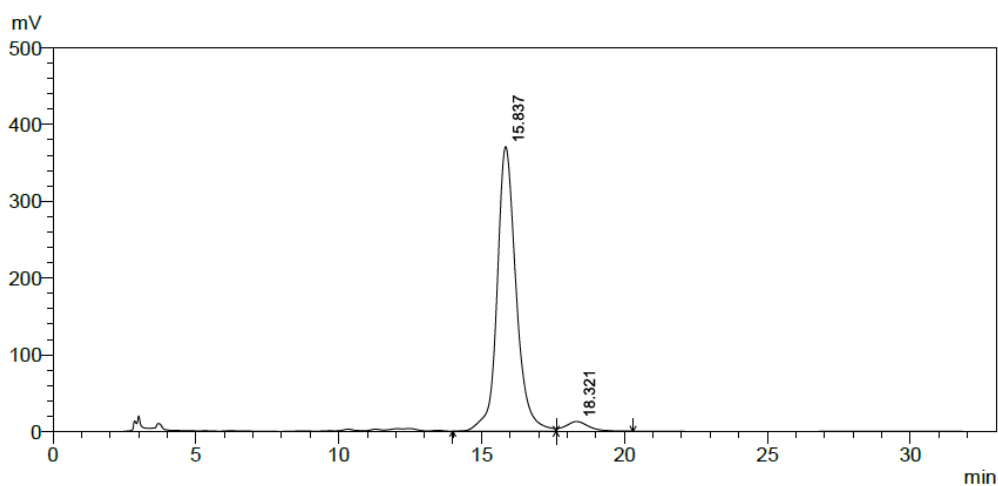
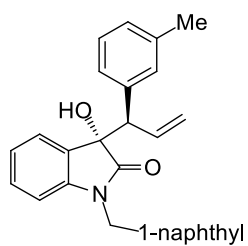
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.230	281650	8632	0.363	0.365
2	16.077	77392829	2355491	99.637	99.635
Total		77674478	2364123	100.000	100.000





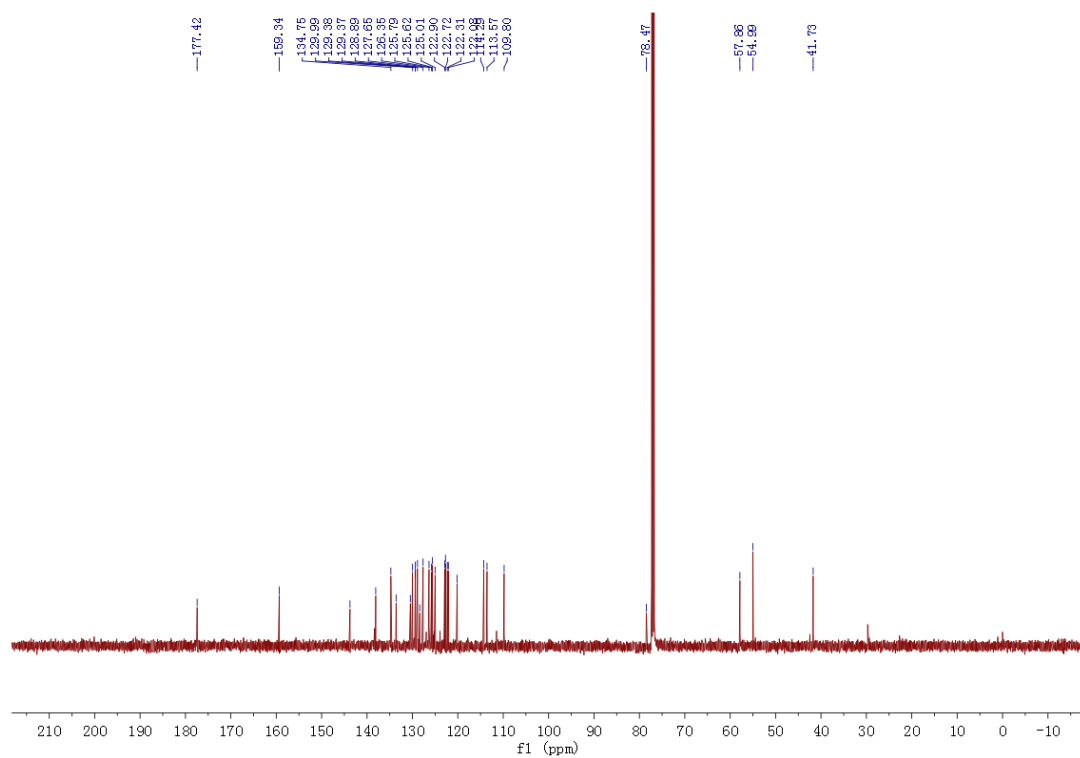
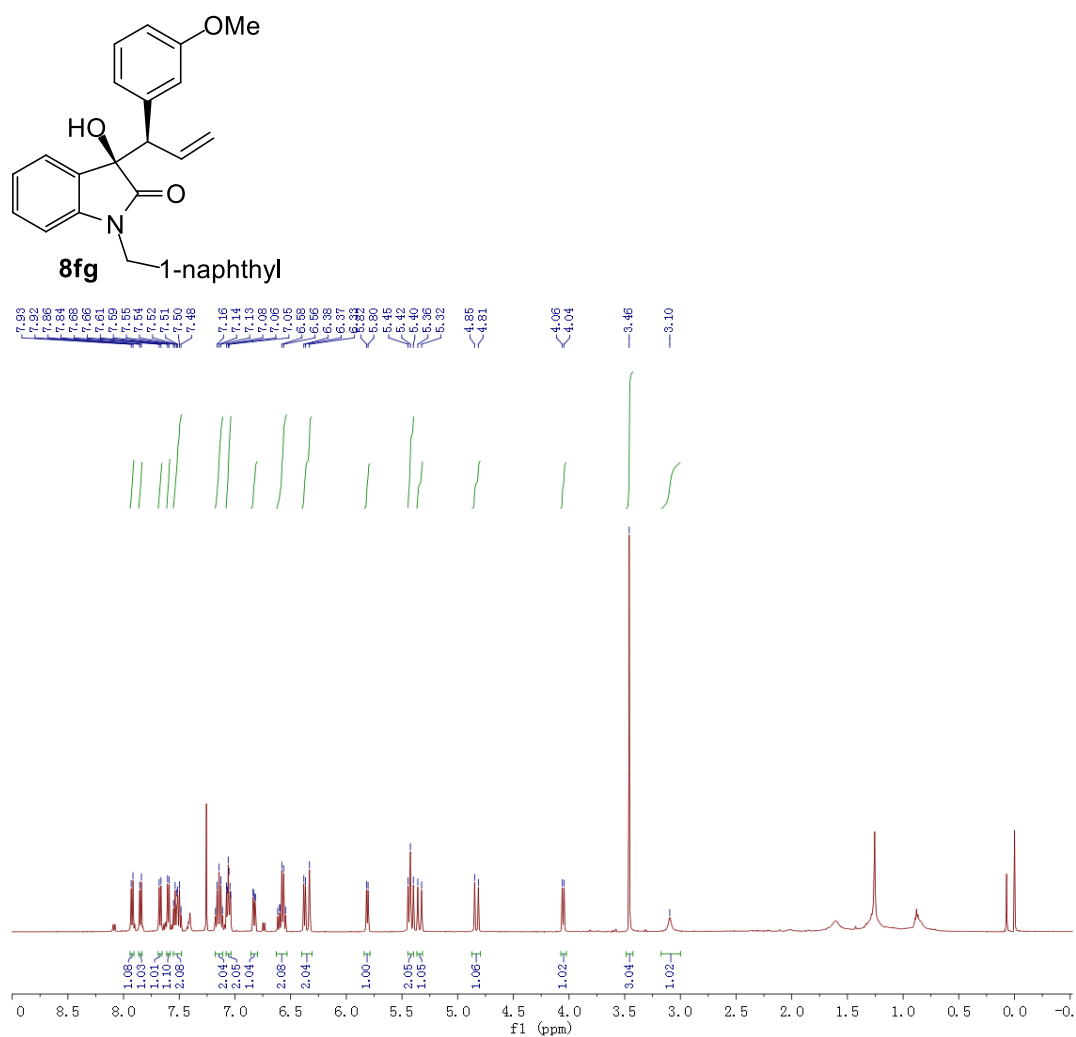
PeakTable

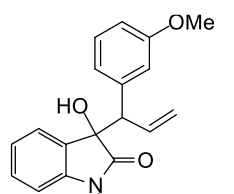
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.878	65452253	1495737	47.888	51.862
2	18.117	71226470	1388357	52.112	48.138
Total		136678723	2884094	100.000	100.000



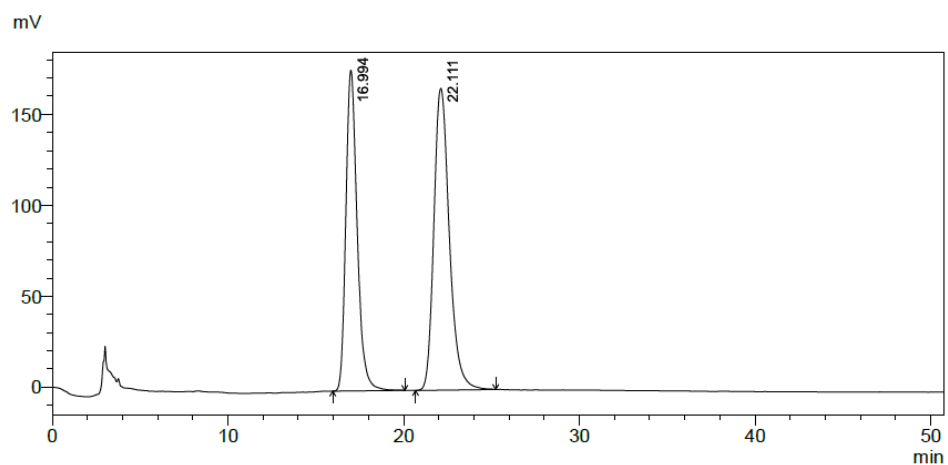
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.837	17084596	370569	95.935	96.667
2	18.321	723924	12777	4.065	3.333
Total		17808519	383346	100.000	100.000



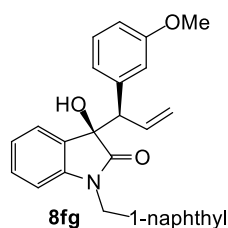


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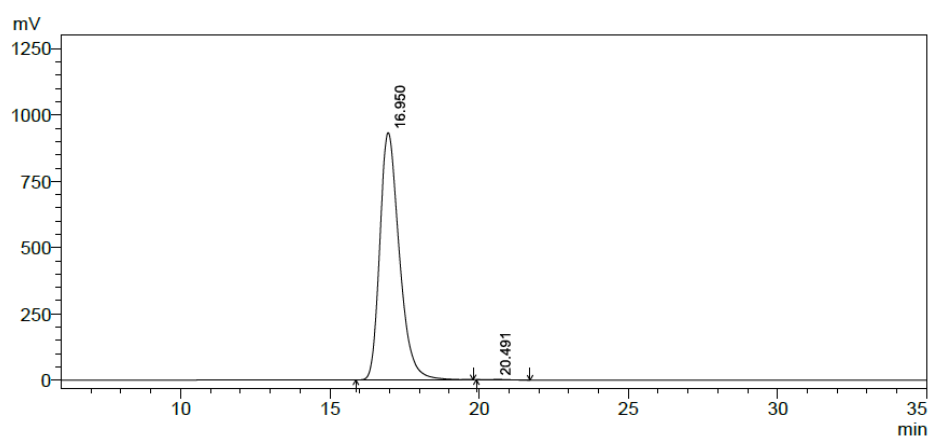


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.994	7885330	176421	43.650	51.512
2	22.111	10179394	166061	56.350	48.488
Total		18064725	342483	100.000	100.000

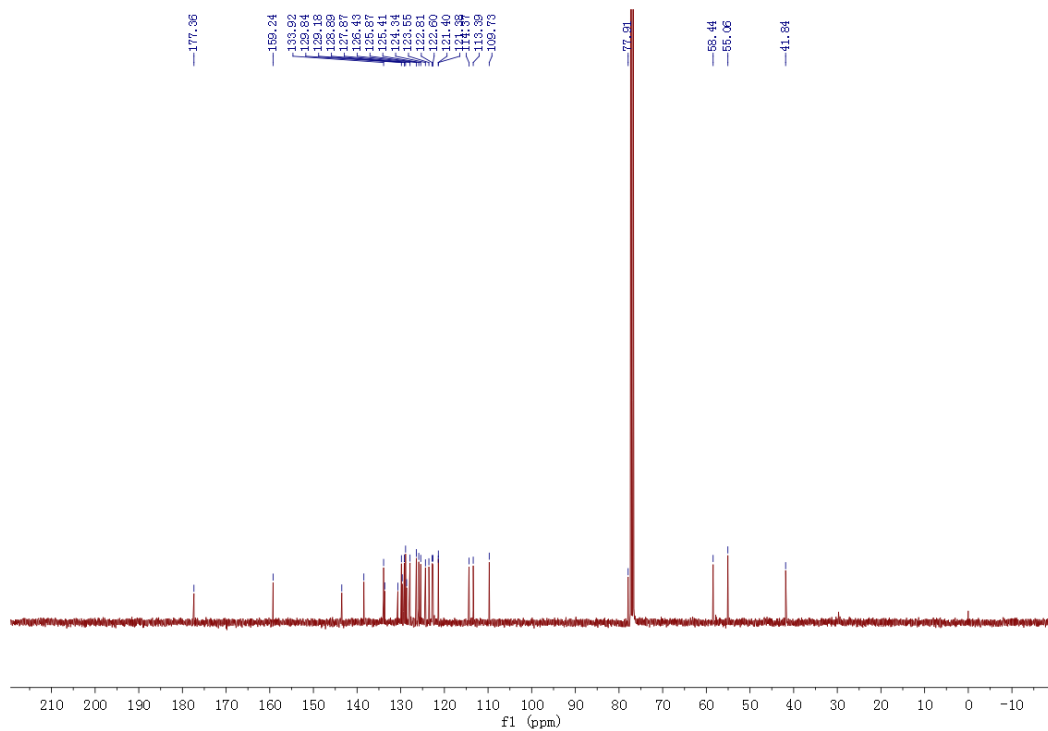
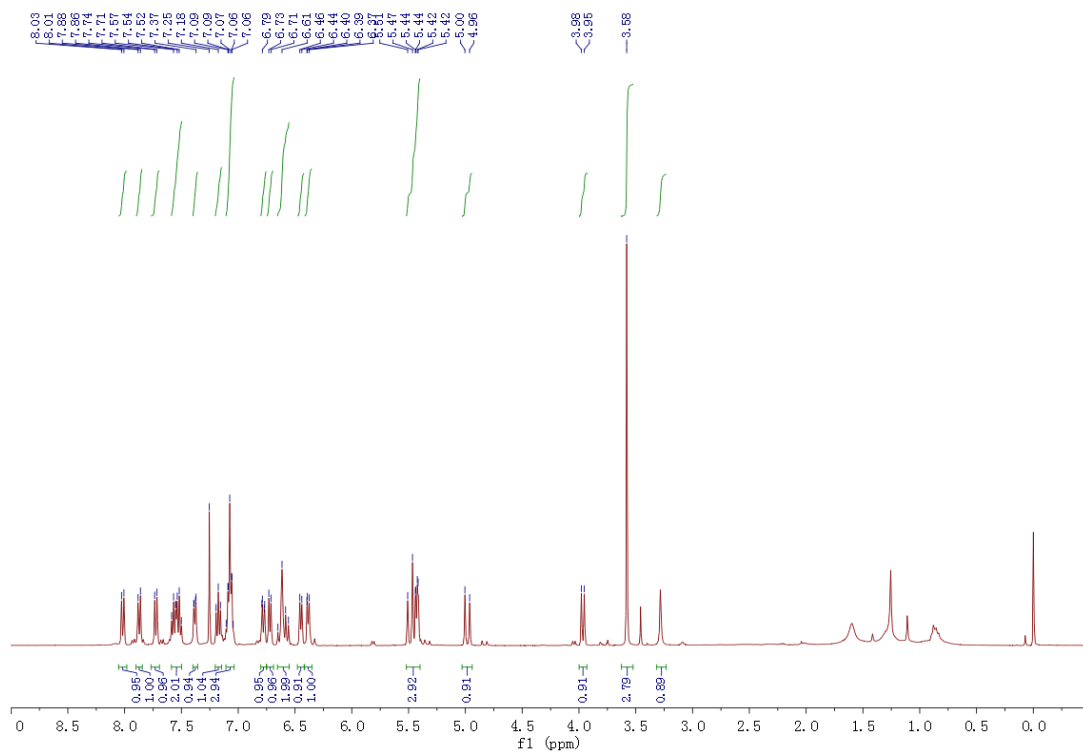
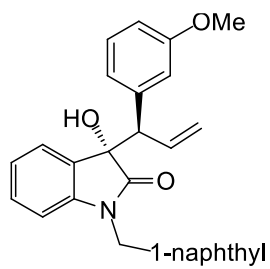


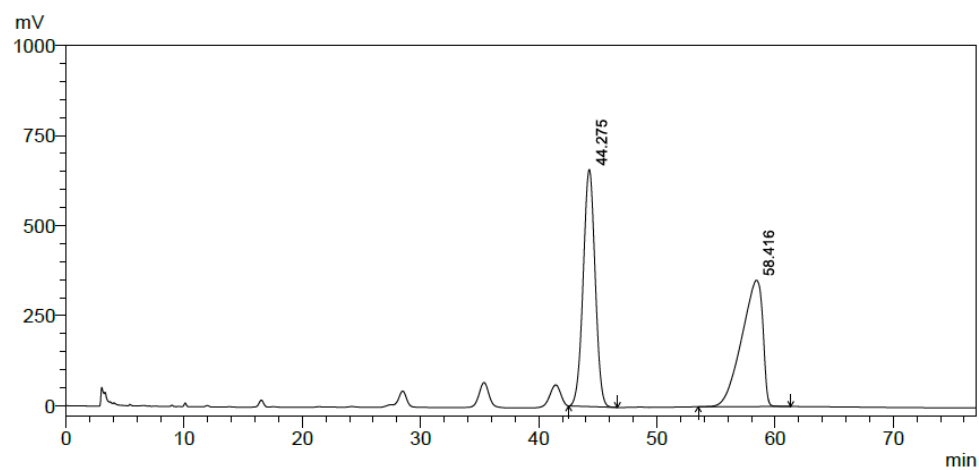
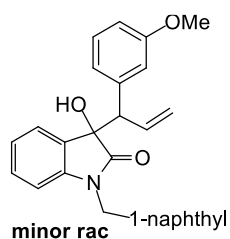
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PeakTable

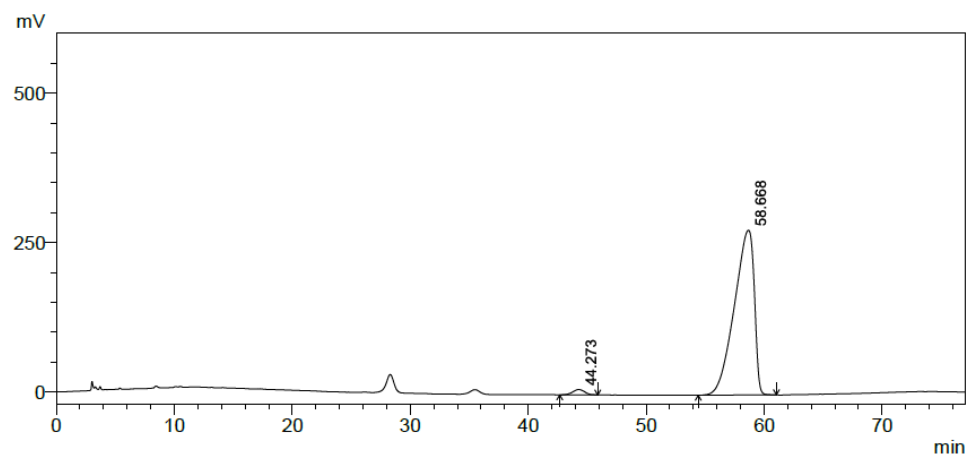
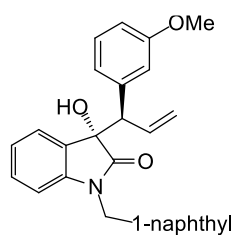
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.950	42385330	932167	99.837	99.842
2	20.491	69131	1475	0.163	0.158
Total		42454461	933642	100.000	100.000





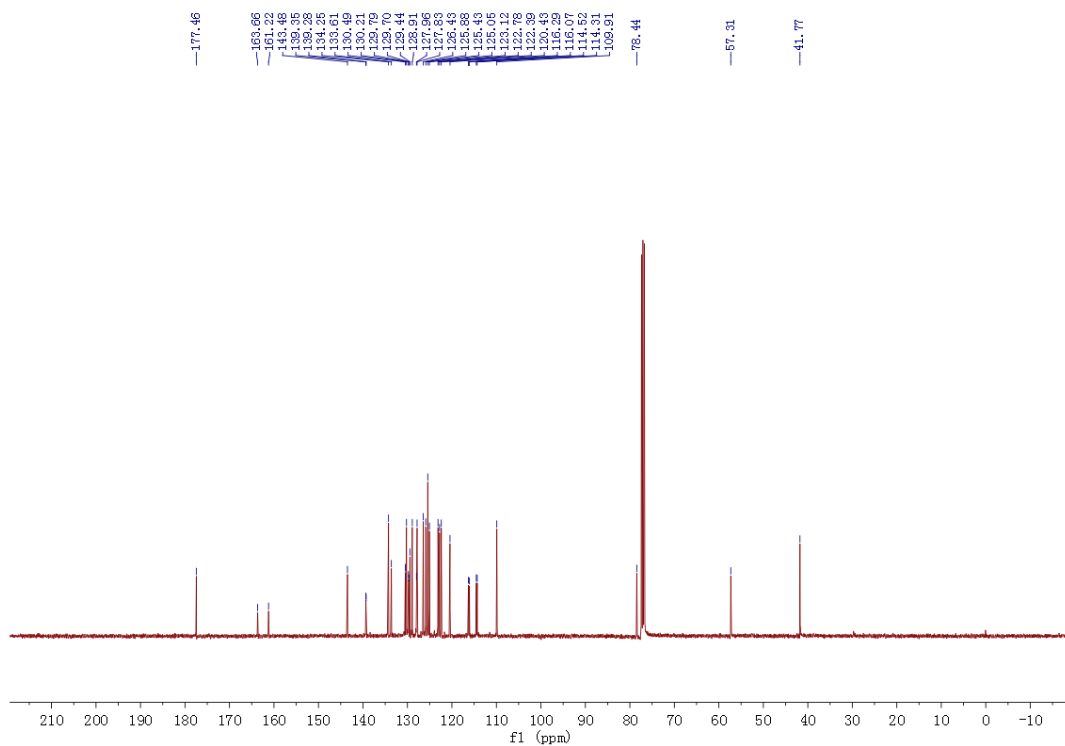
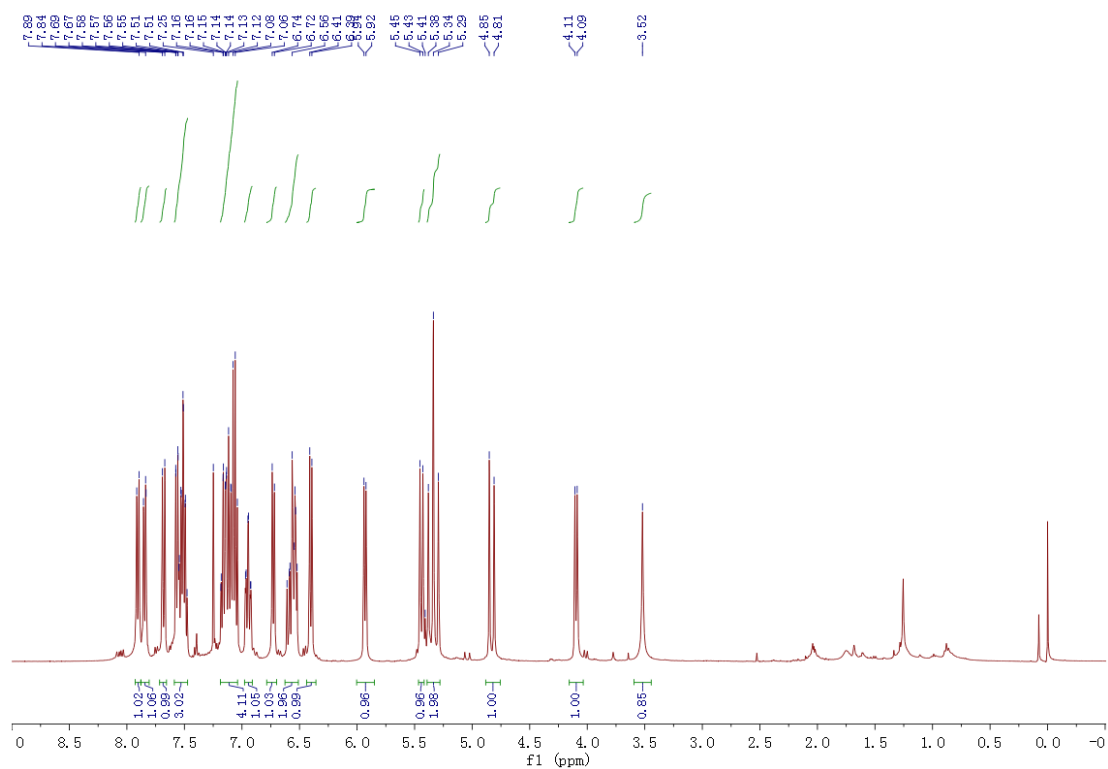
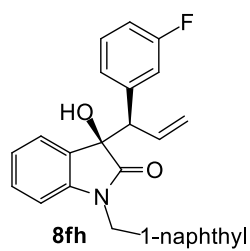
PeakTable

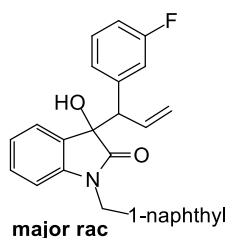
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.275	46398275	658316	51.577	65.241
2	58.416	43560102	350731	48.423	34.759
Total		89958377	1009047	100.000	100.000



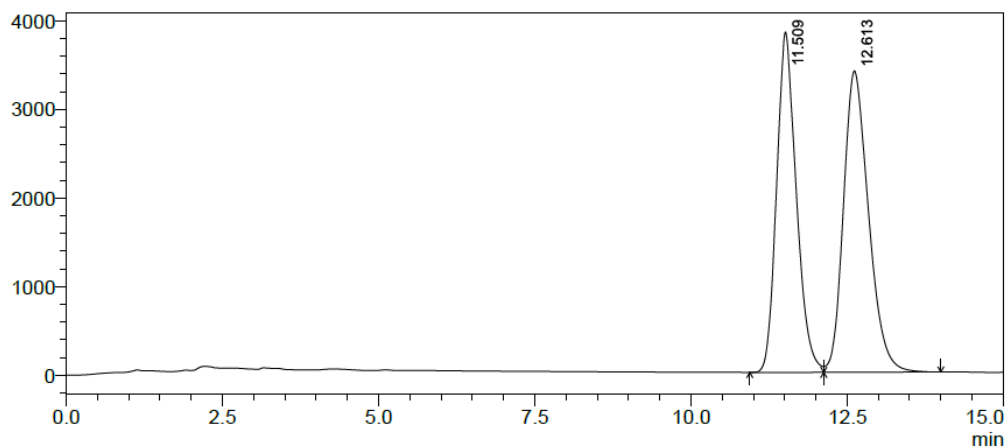
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.273	642586	9005	1.947	3.164
2	58.668	32367313	275633	98.053	96.836
Total		33009899	284638	100.000	100.000



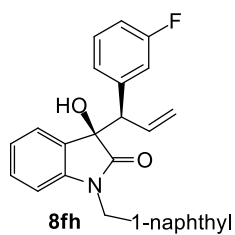


mV

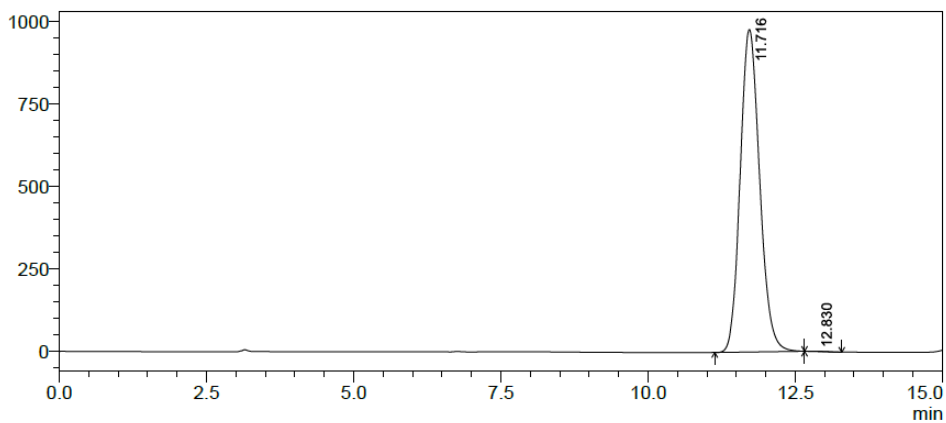


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.509	84290280	3843592	47.014	53.041
2	12.613	94997302	3402845	52.986	46.959
Total		179287582	7246438	100.000	100.000

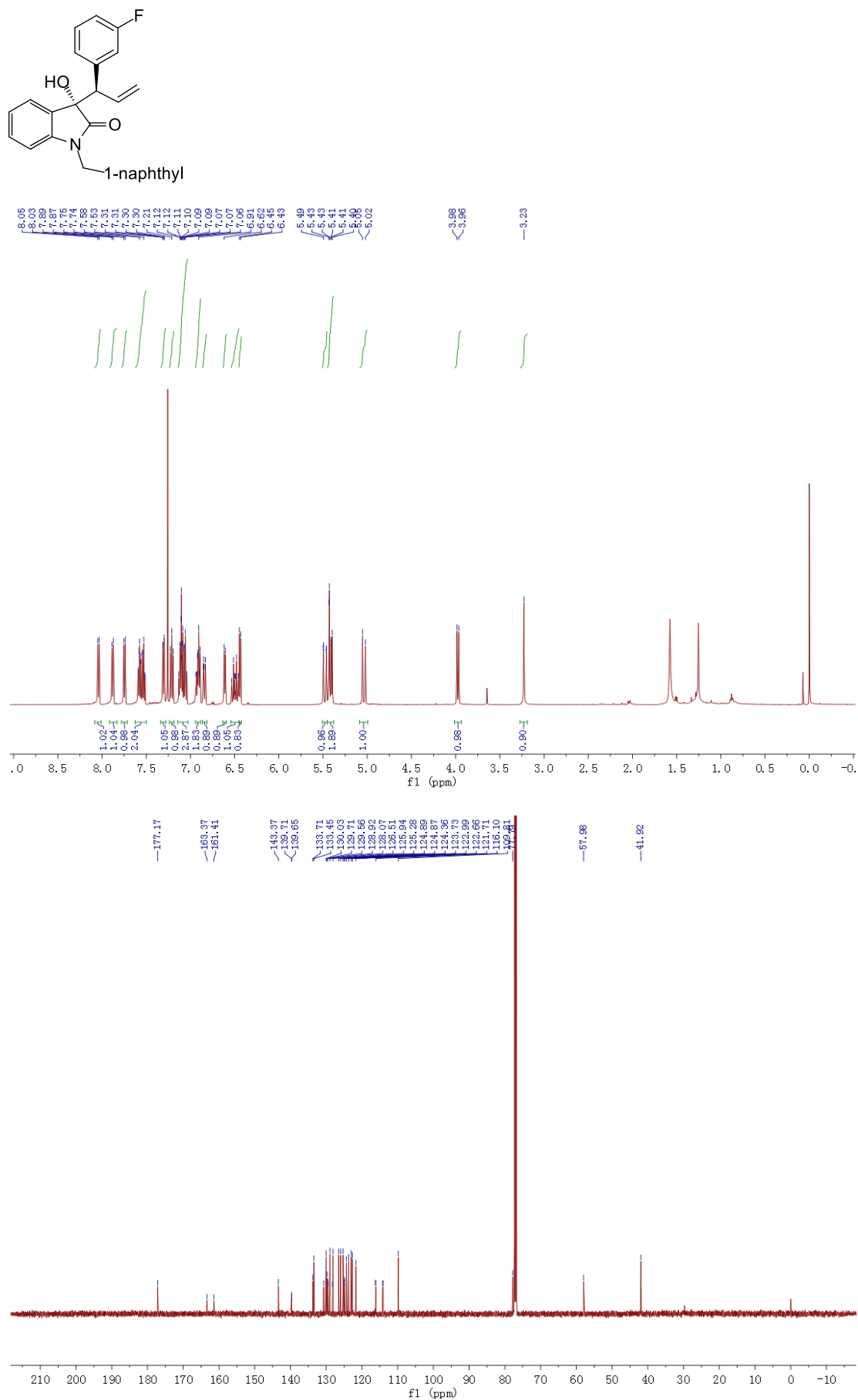


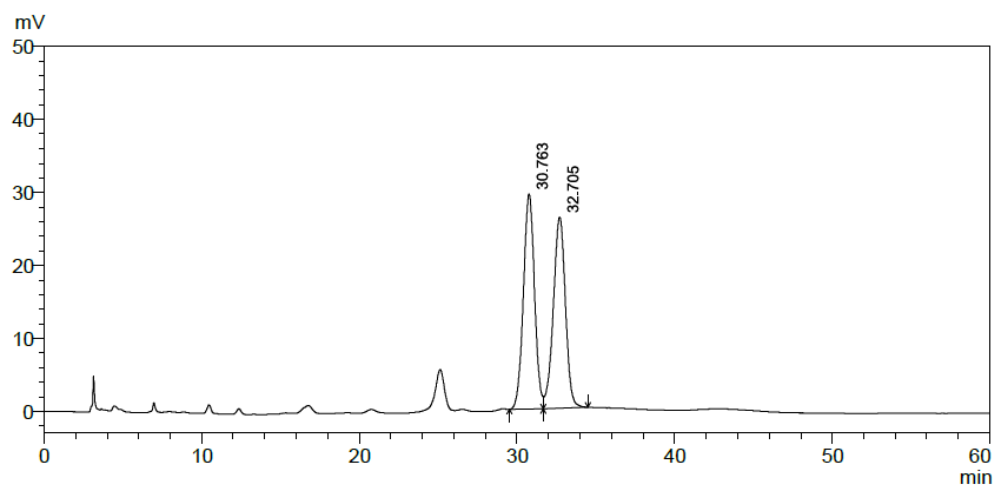
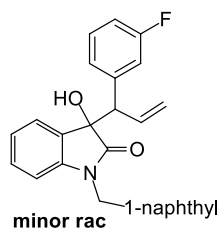
mV



PeakTable

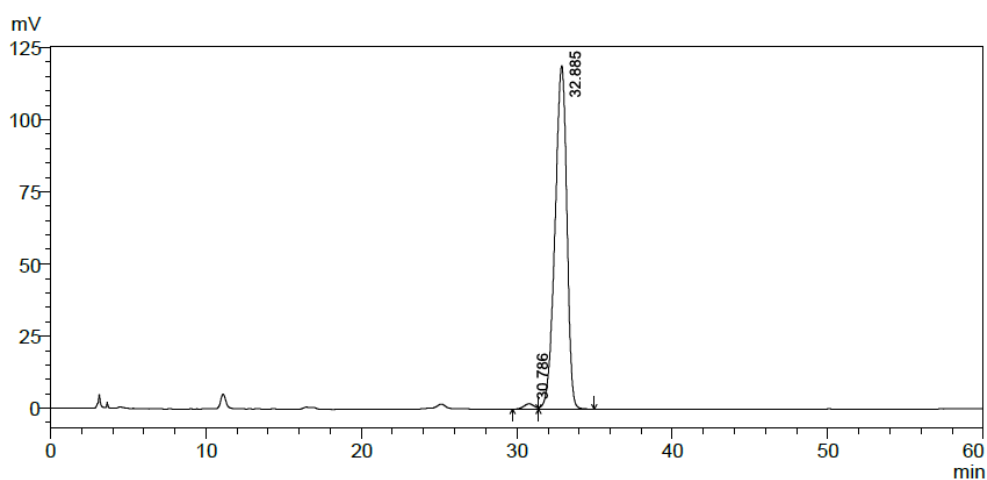
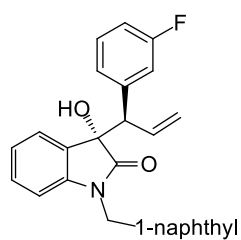
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.716	22479959	978808	99.893	99.871
2	12.830	24030	1260	0.107	0.129
Total		22503989	980067	100.000	100.000





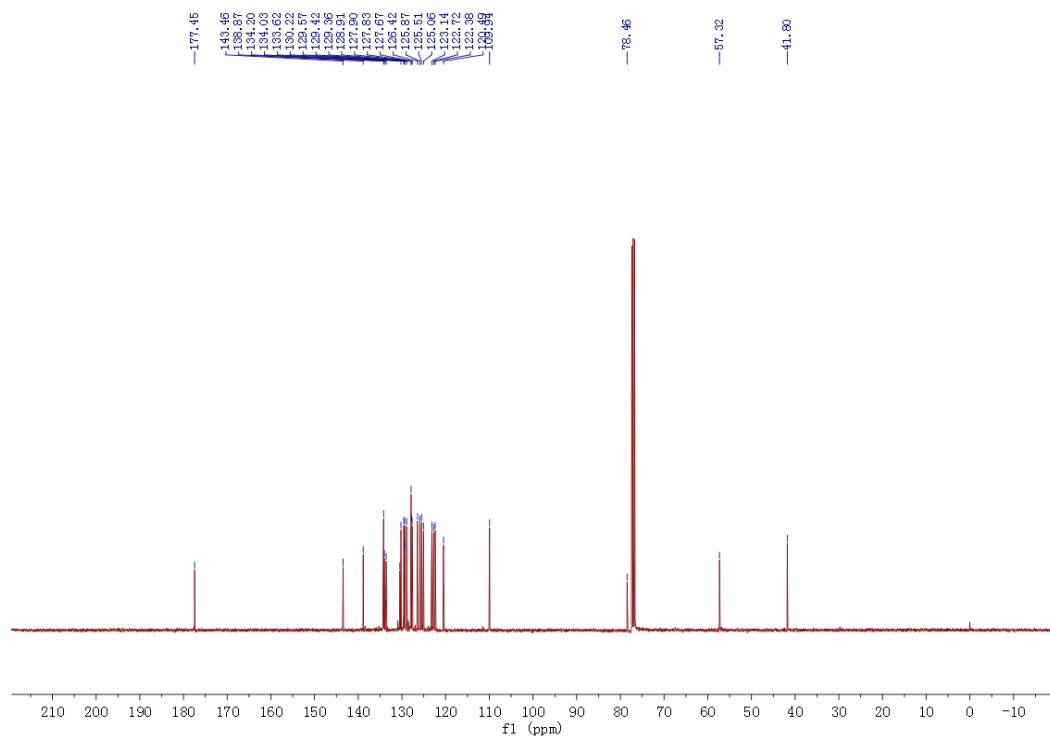
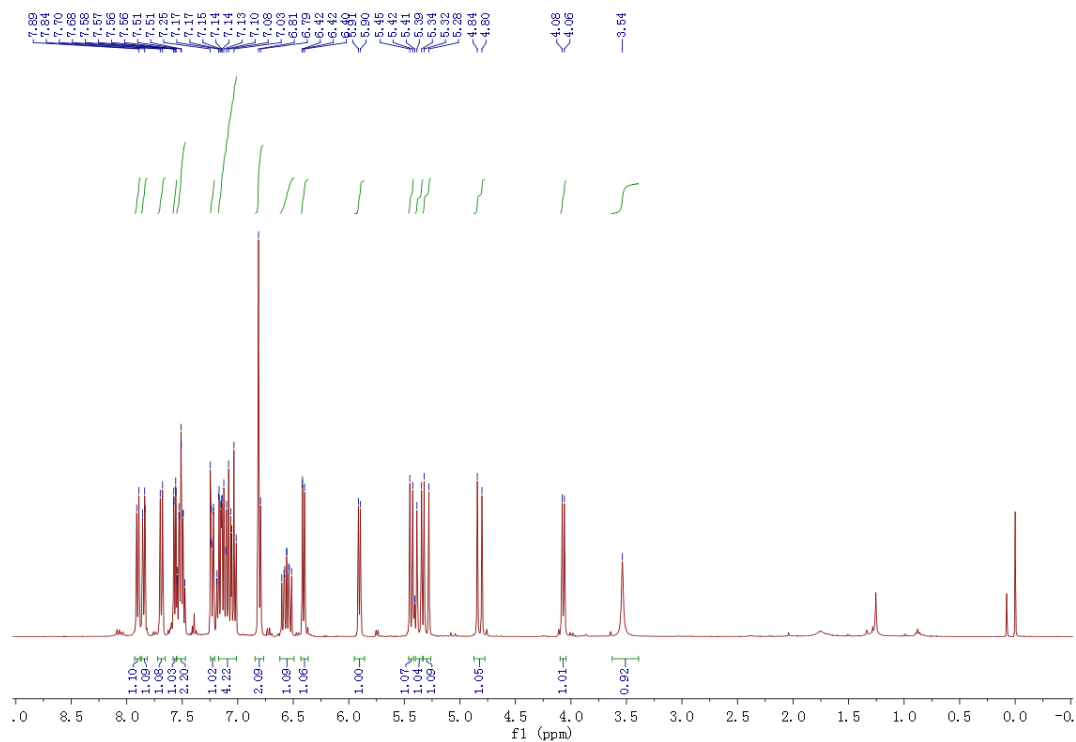
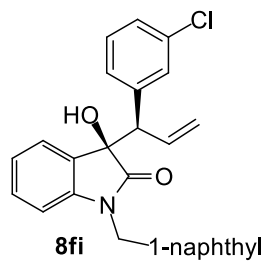
PeakTable

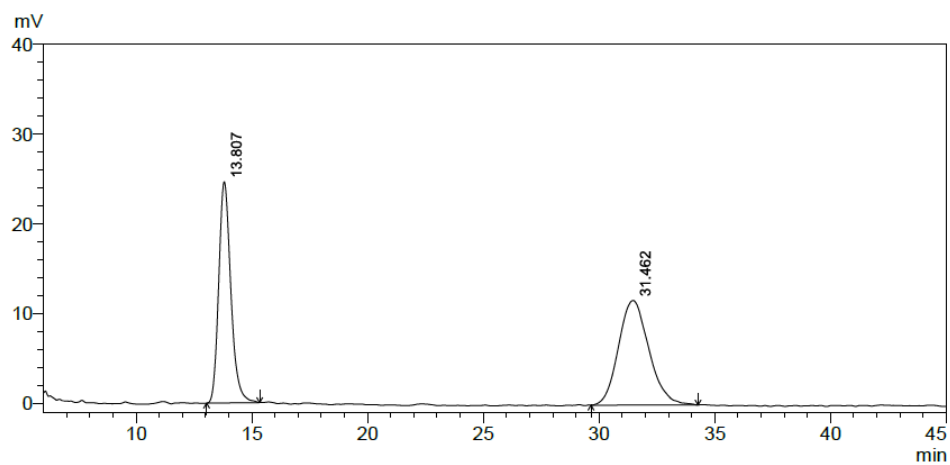
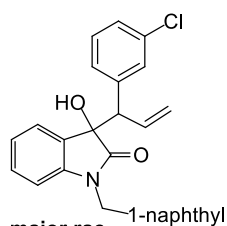
Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.763	1444486	29451	50.915	52.960
2	32.705	1392578	26158	49.085	47.040
Total		2837064	55609	100.000	100.000



PeakTable

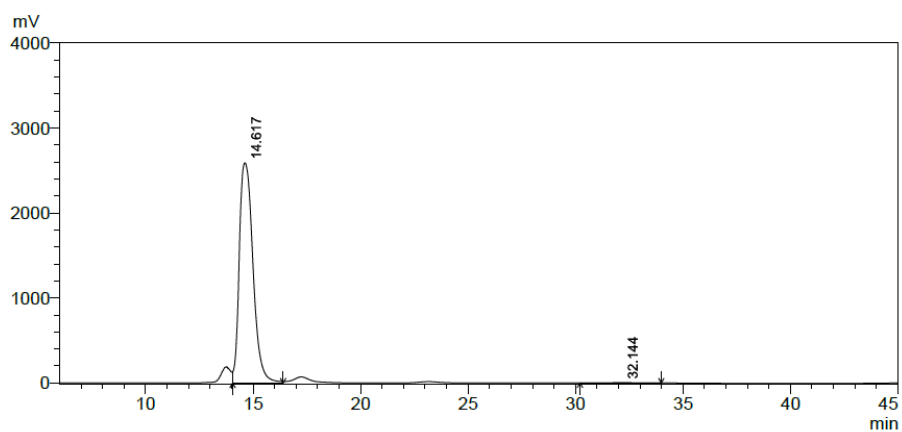
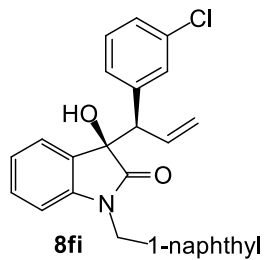
Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.786	87100	1855	1.362	1.535
2	32.885	6308688	118982	98.638	98.465
Total		6395788	120837	100.000	100.000





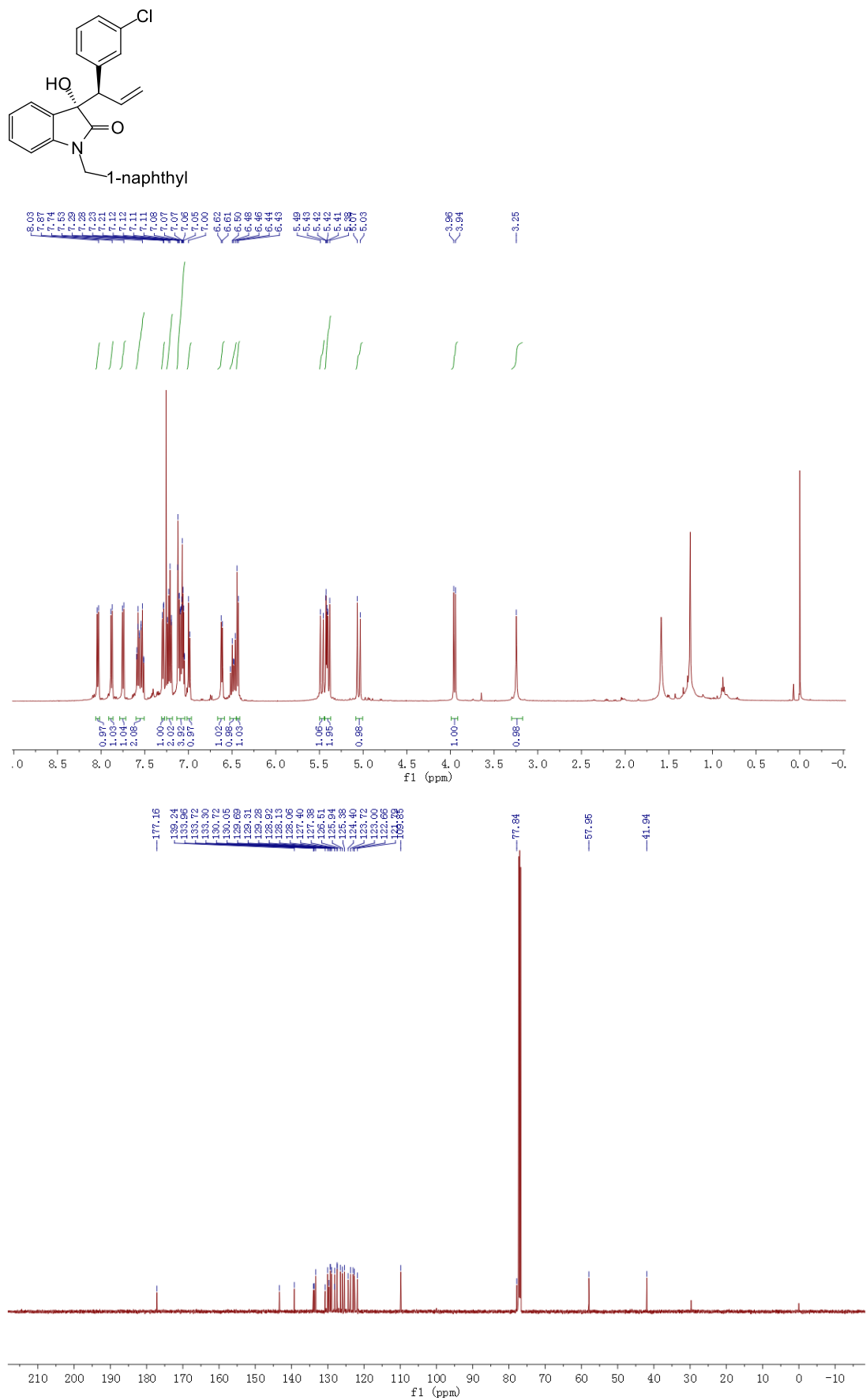
PeakTable

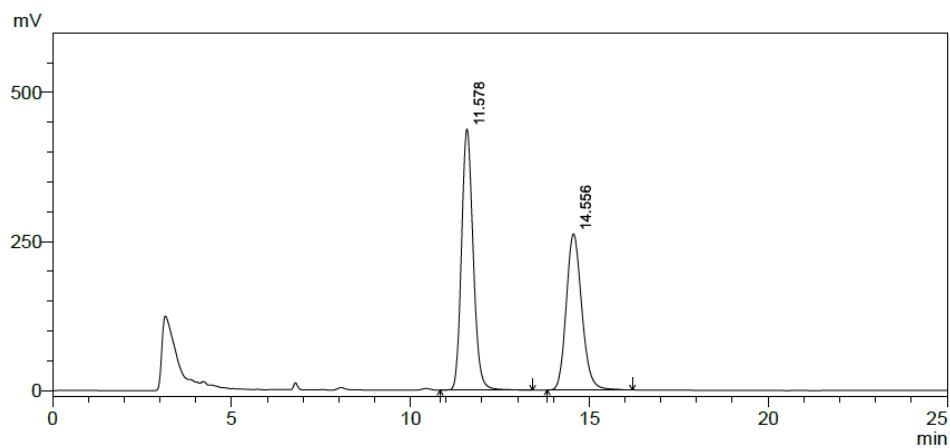
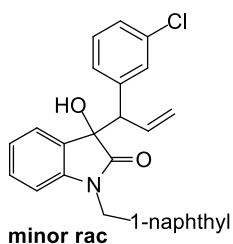
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.807	896540	24671	45.649	67.872
2	31.462	1067443	11678	54.351	32.128
Total		1963983	36349	100.000	100.000



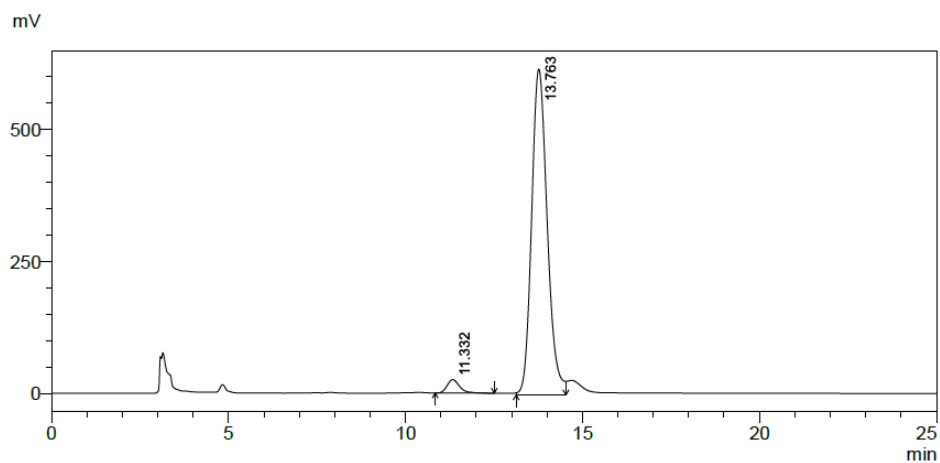
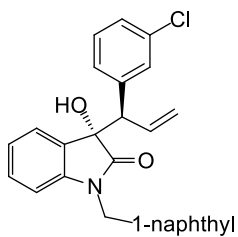
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.617	114753539	2589952	99.822	99.928
2	32.144	204734	1861	0.178	0.072
Total		114958273	2591814	100.000	100.000

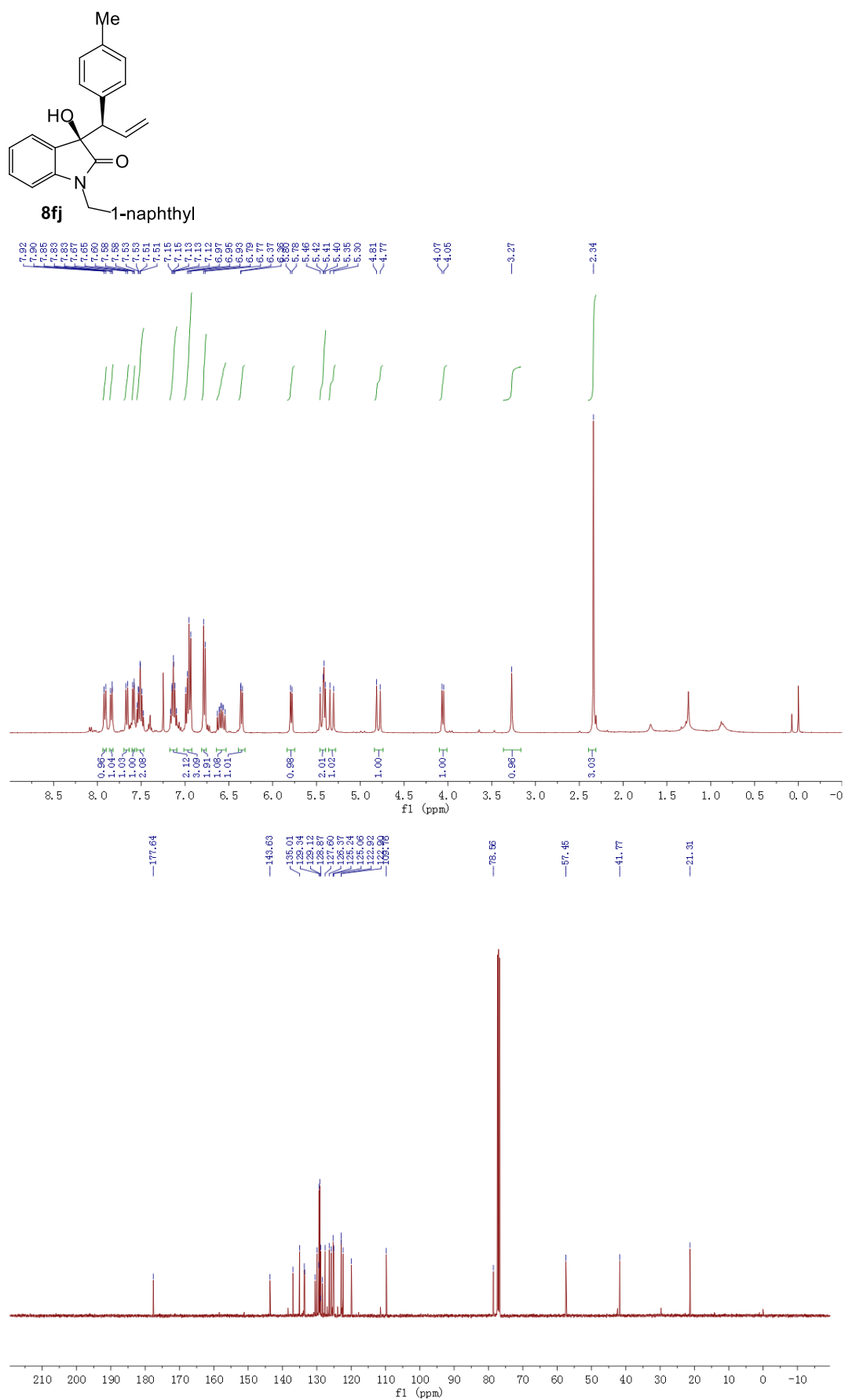


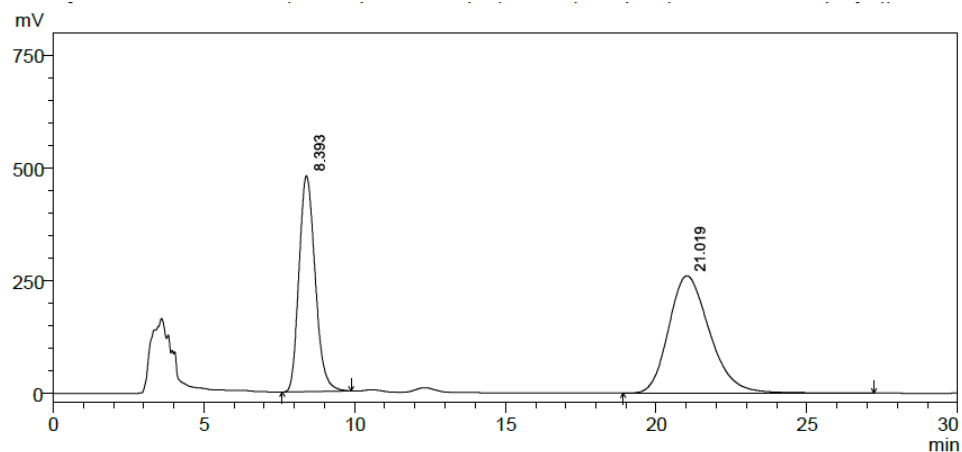
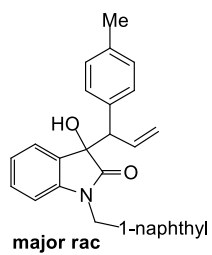


PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.578	9914598	438130	55.584	62.593
2	14.556	7922472	261841	44.416	37.407
Total		17837070	699971	100.000	100.000



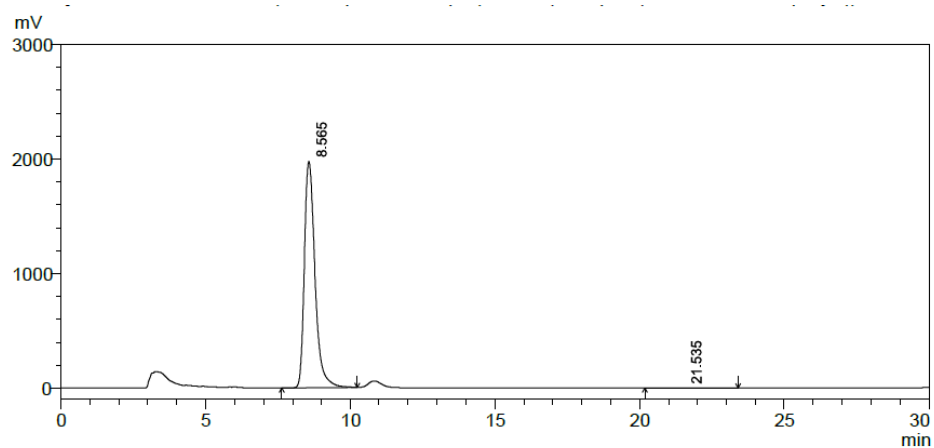
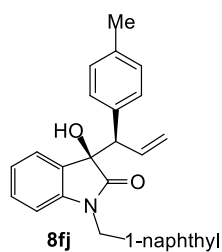
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.332	627273	25523	3.209	3.969
2	13.763	18917833	617553	96.791	96.031
Total		19545106	643076	100.000	100.000





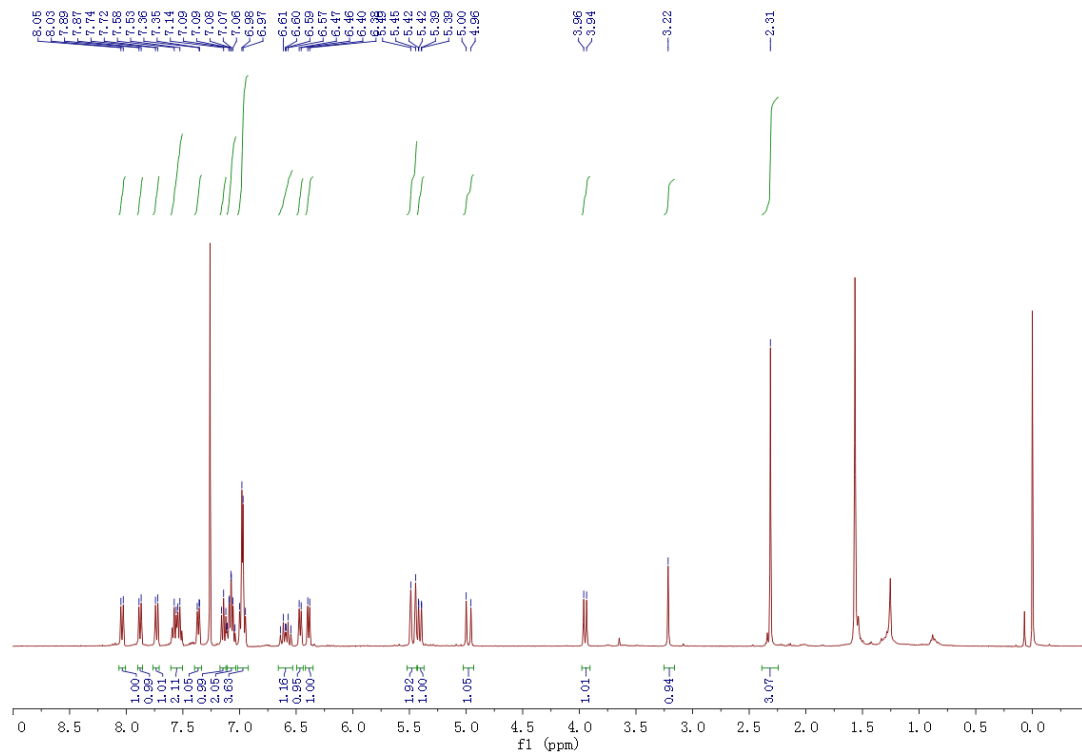
PeakTable

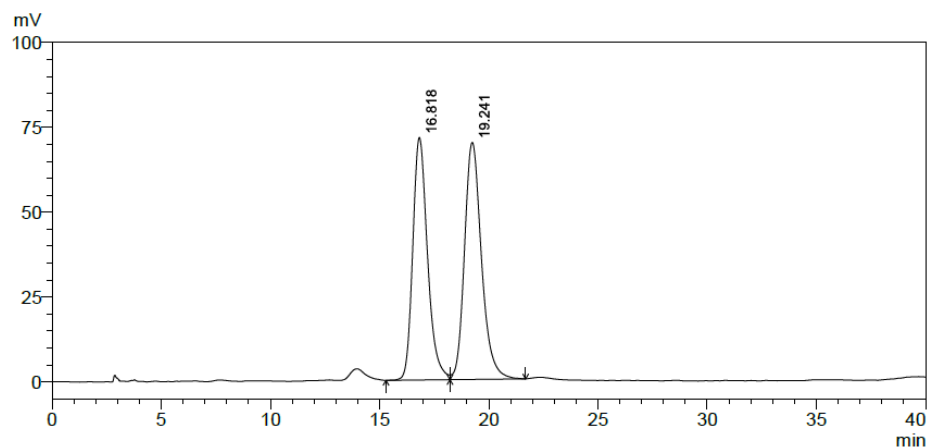
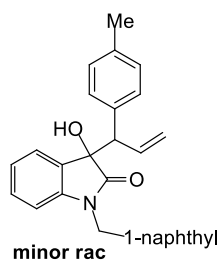
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.393	17788808	479187	41.898	64.791
2	21.019	24668811	260404	58.102	35.209
Total		42457618	739591	100.000	100.000



PeakTable

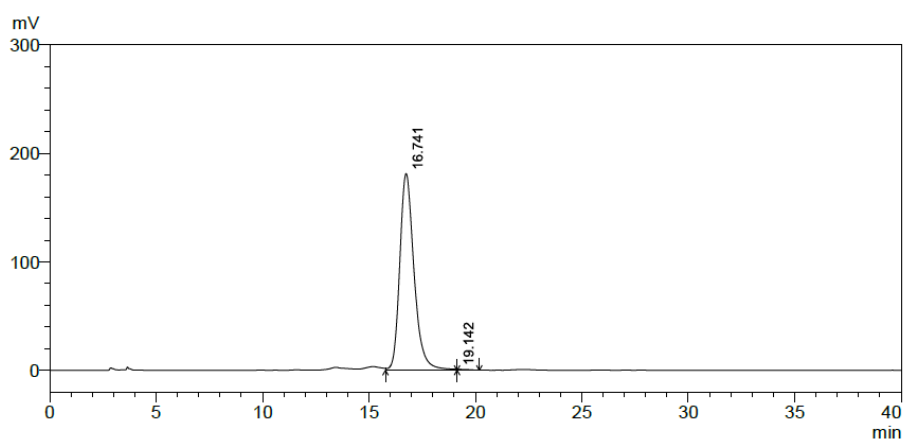
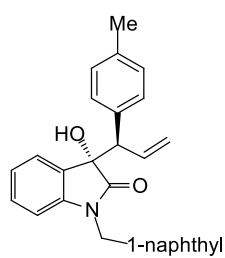
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.565	50546424	1978241	99.770	99.925
2	21.535	116402	1484	0.230	0.075
Total		50662826	1979725	100.000	100.000





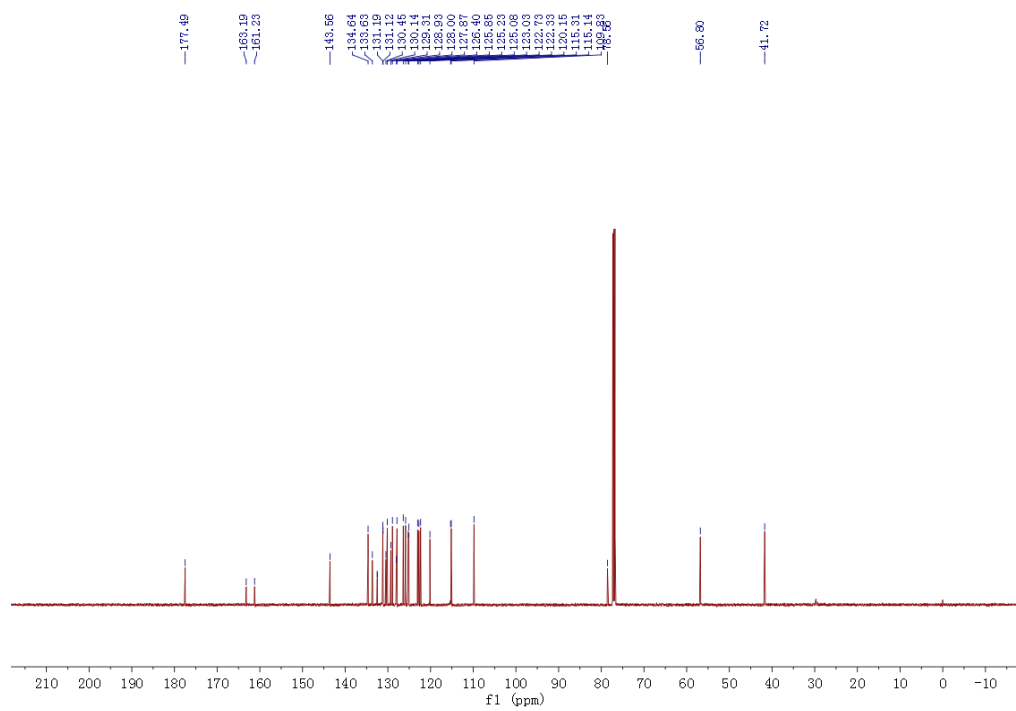
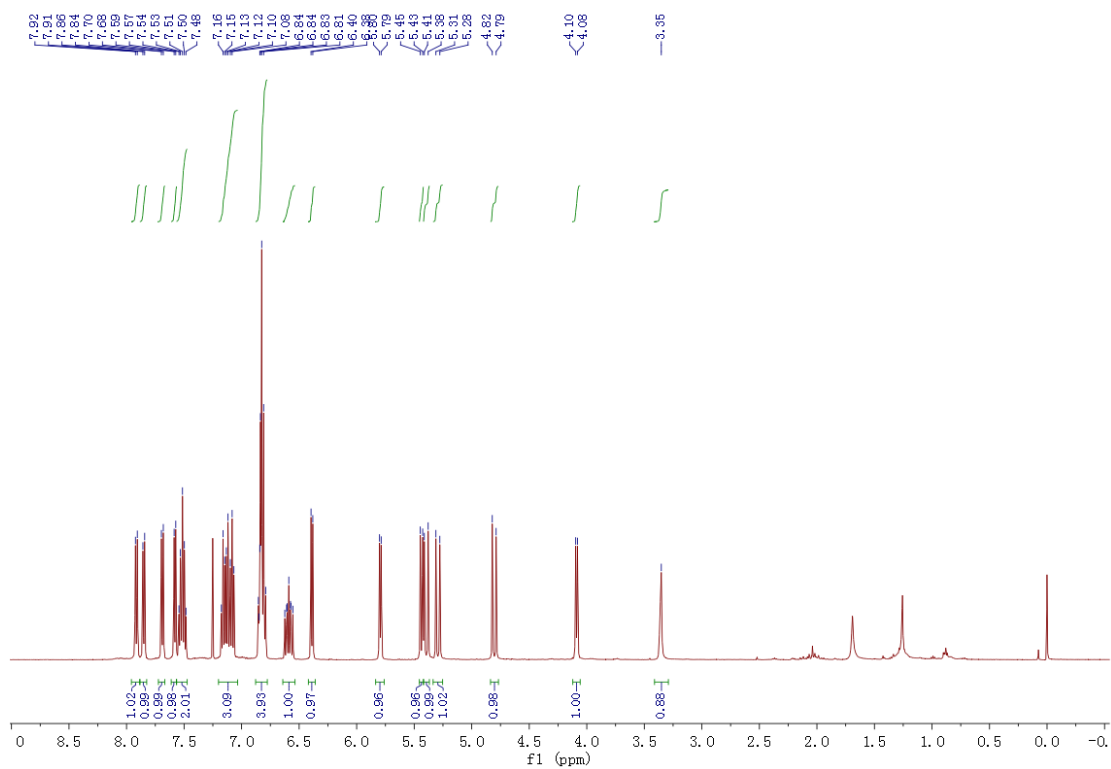
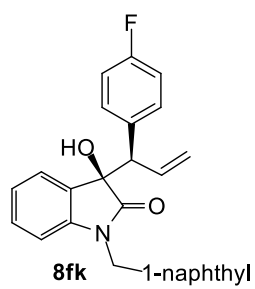
PeakTable

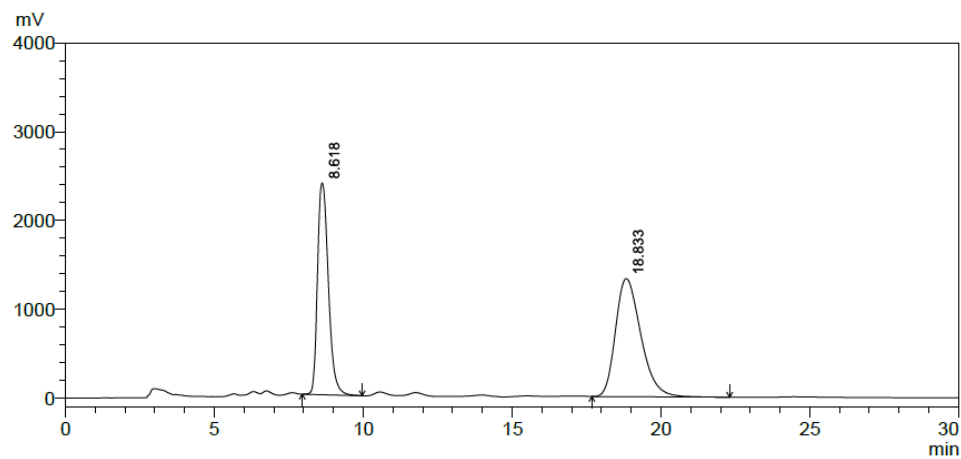
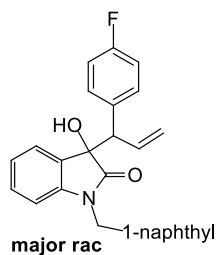
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.818	3364137	71527	47.052	50.586
2	19.241	3785748	69871	52.948	49.414
Total		7149885	141398	100.000	100.000



PeakTable

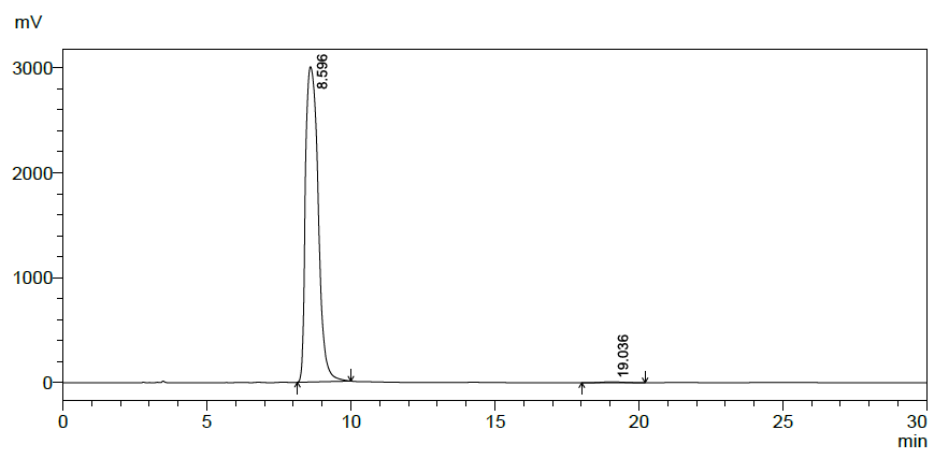
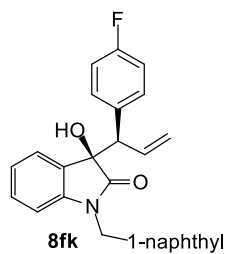
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.741	8486791	181363	99.652	99.487
2	19.142	29662	935	0.348	0.513
Total		8516453	182298	100.000	100.000





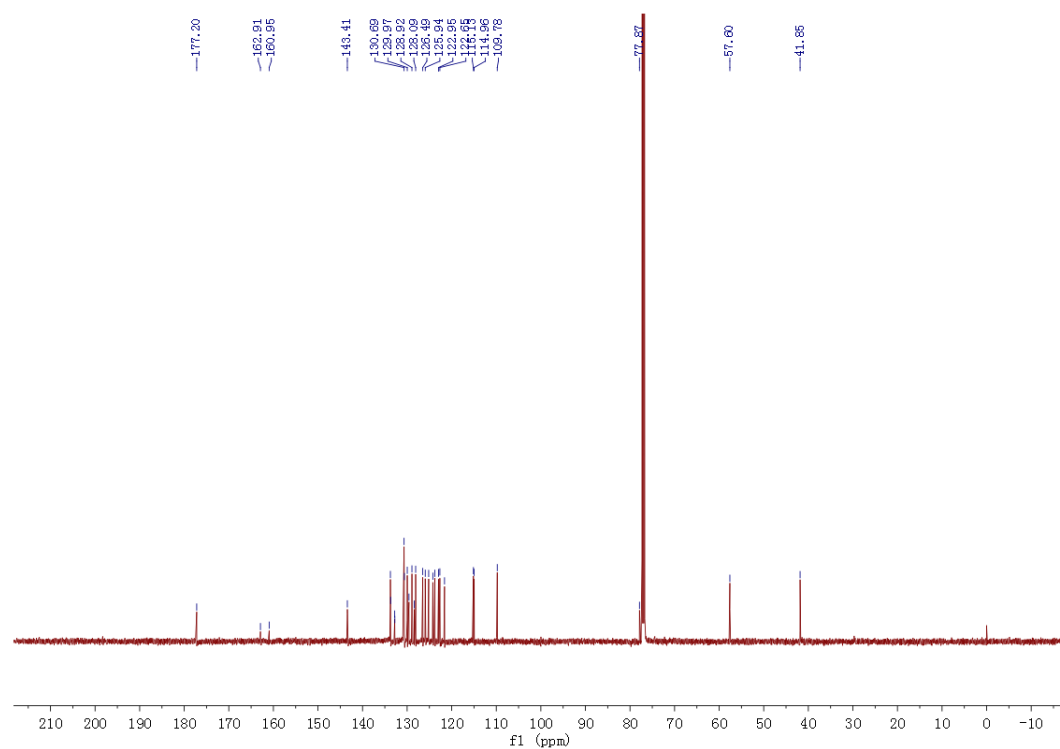
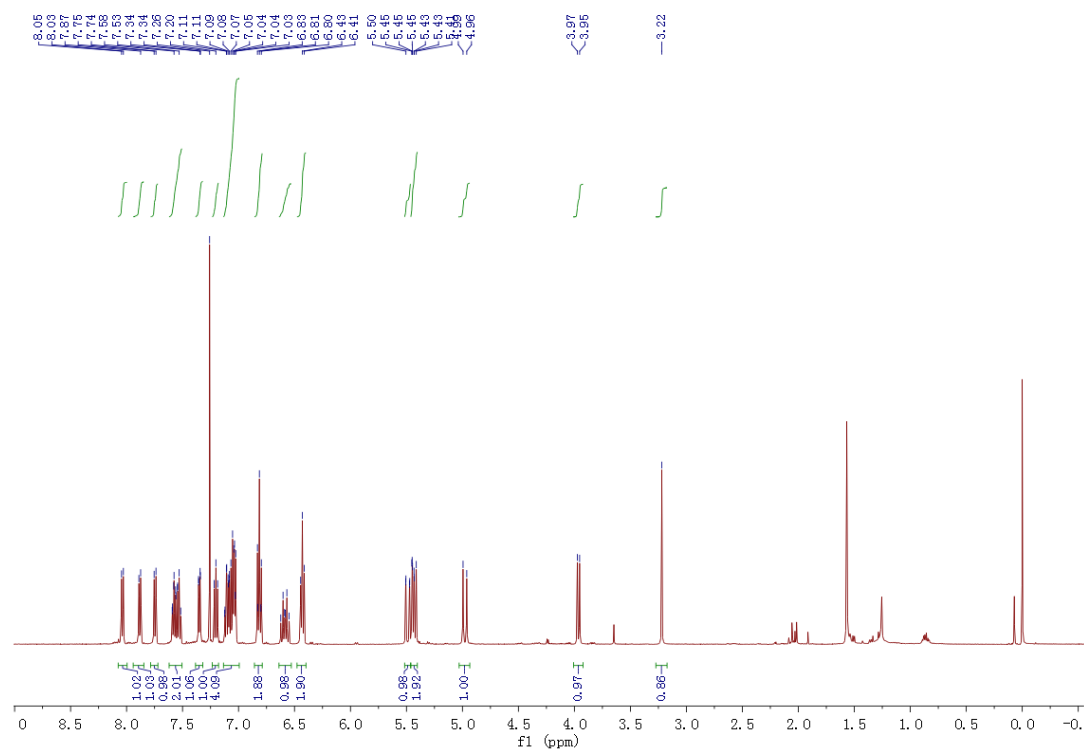
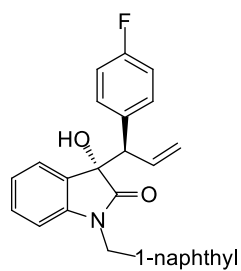
PeakTable

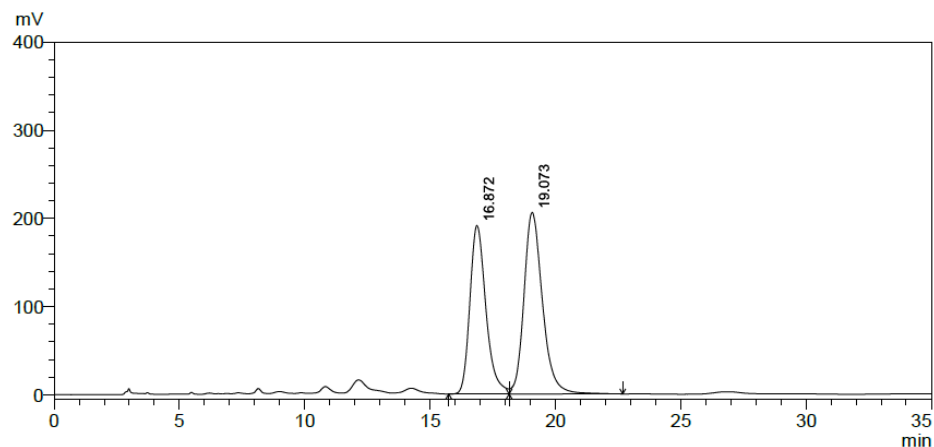
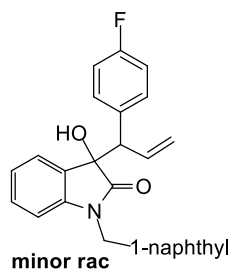
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.618	60497329	2385507	43.486	64.197
2	18.833	78623302	1330427	56.514	35.803
Total		139120631	3715934	100.000	100.000



PeakTable

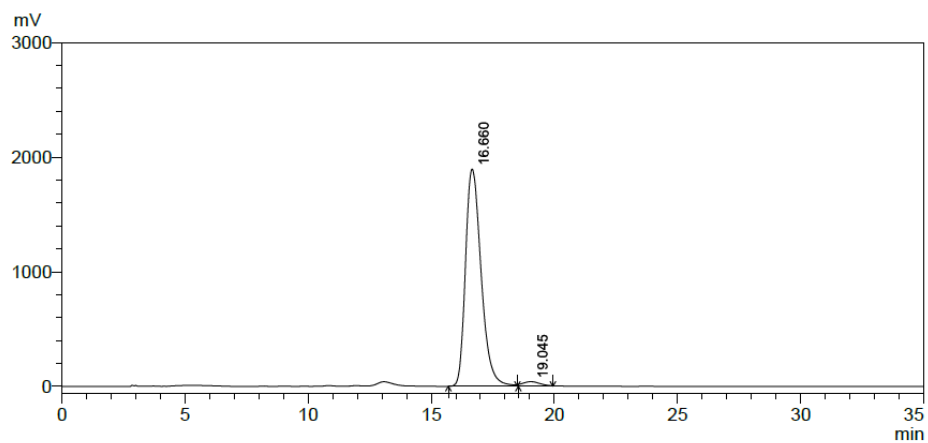
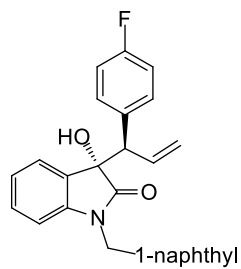
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.596	91739177	3004986	99.537	99.735
2	19.036	426532	7977	0.463	0.265
Total		92165708	3012963	100.000	100.000





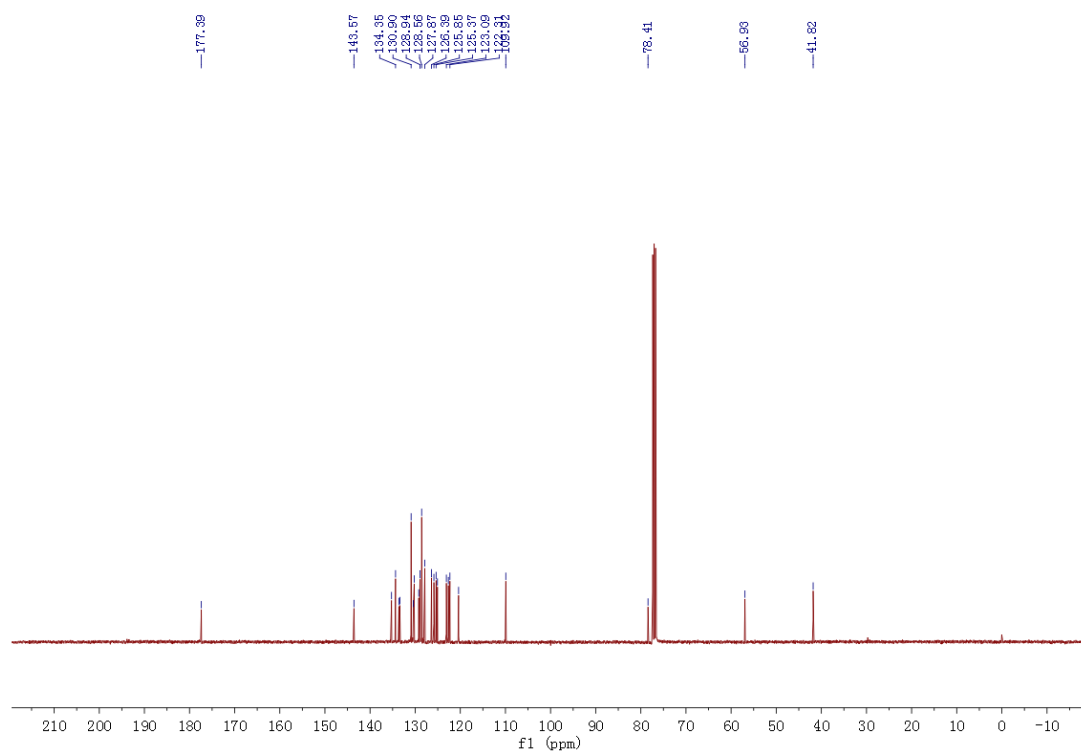
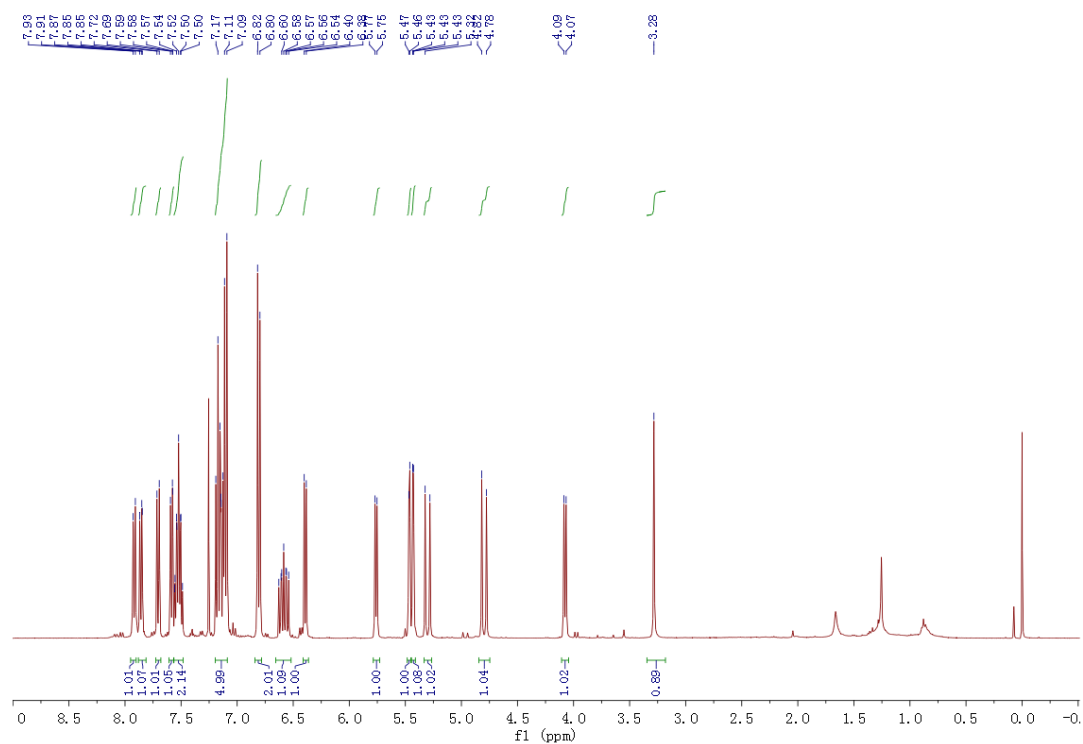
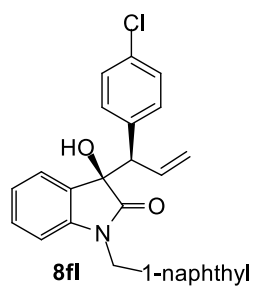
PeakTable

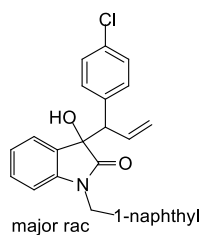
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.872	8506507	191264	44.586	48.150
2	19.073	10572341	205964	55.414	51.850
Total		19078847	397228	100.000	100.000



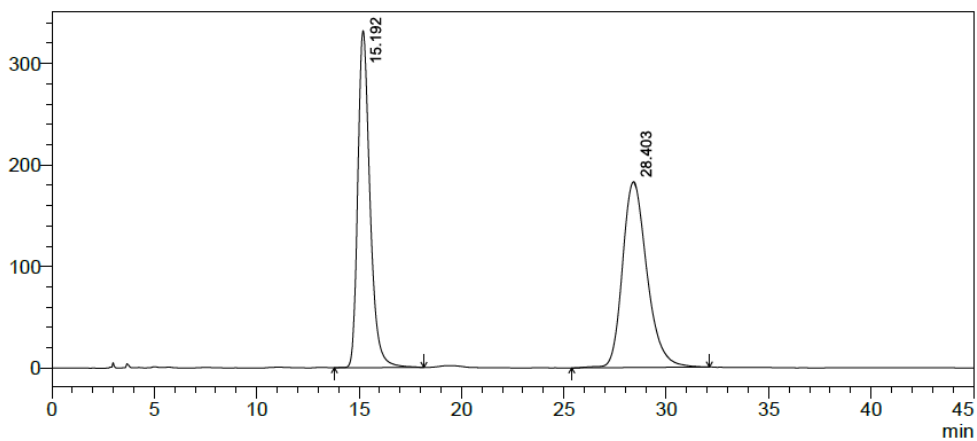
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.660	83873476	1894966	97.626	97.899
2	19.045	2039517	40667	2.374	2.101
Total		85912993	1935633	100.000	100.000



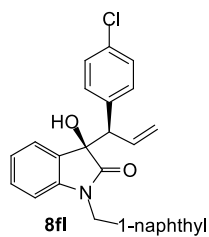


mV

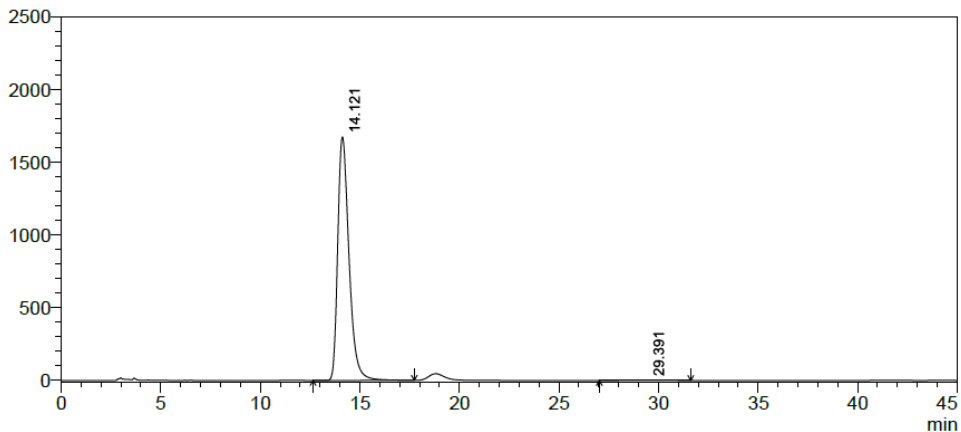


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.192	13701072	331929	47.383	64.459
2	28.403	15214488	183014	52.617	35.541
Total		28915559	514944	100.000	100.000

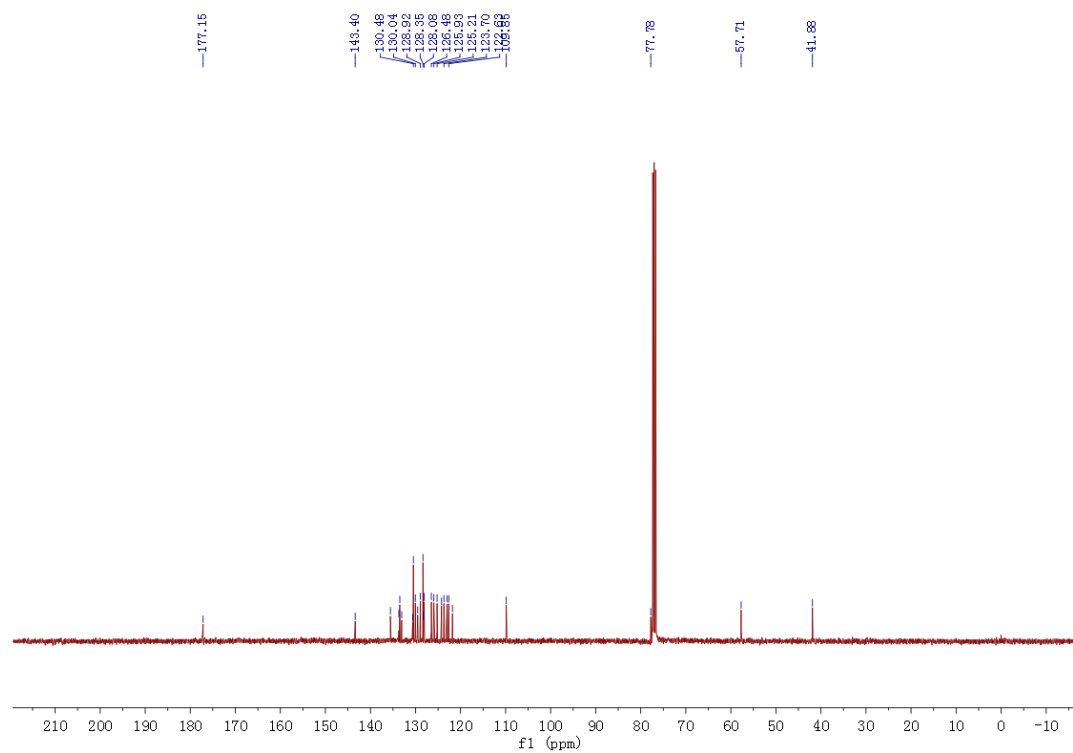
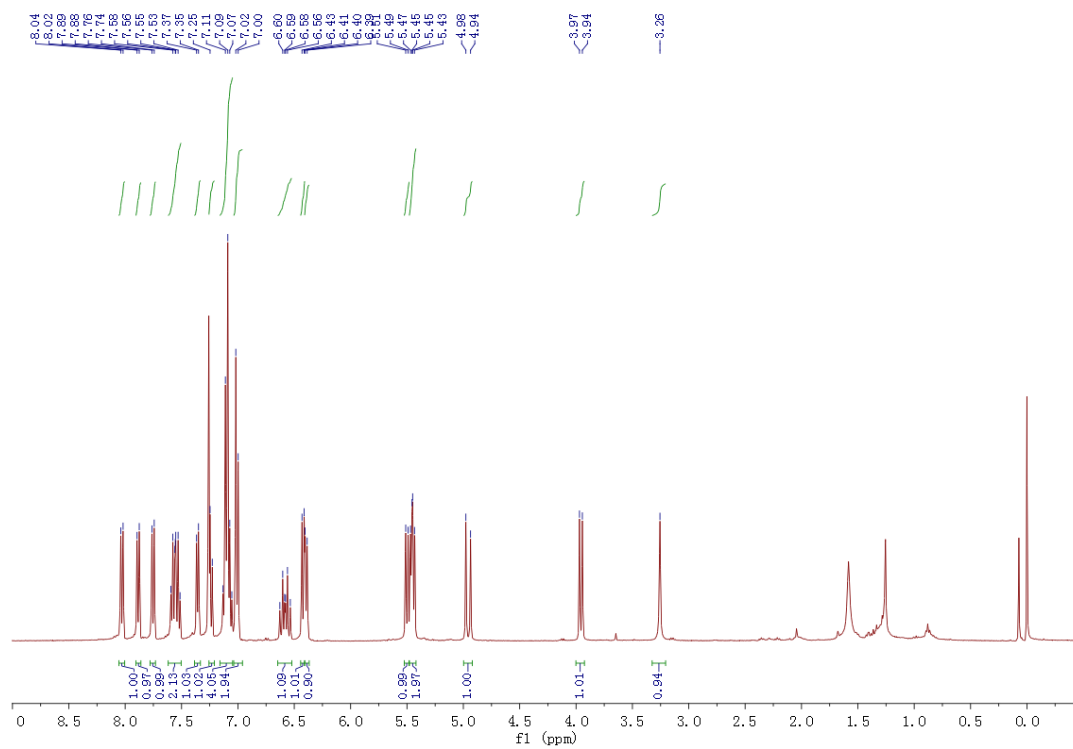
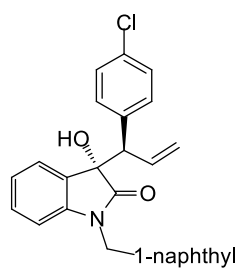


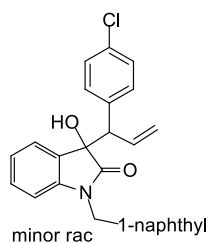
mV



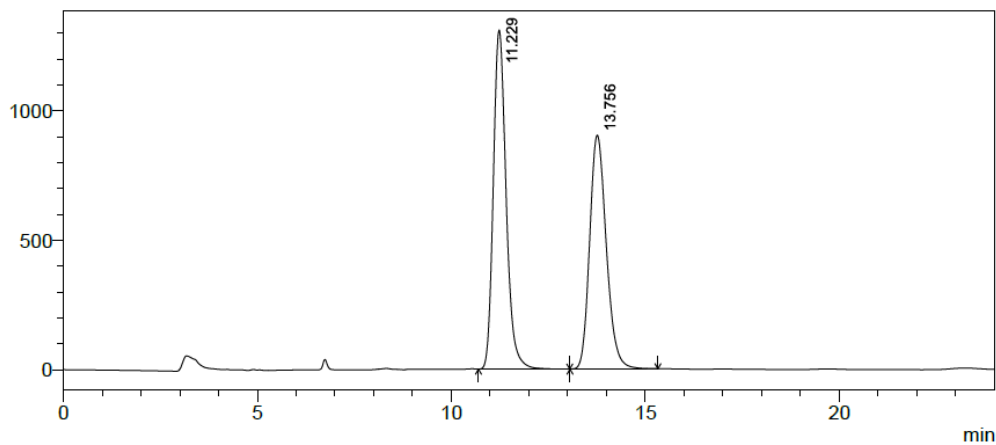
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.121	65692751	1672585	99.560	99.872
2	29.391	290350	2145	0.440	0.128
Total		65983102	1674731	100.000	100.000



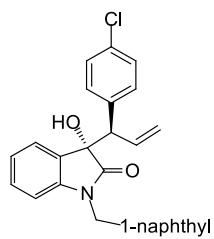


mV

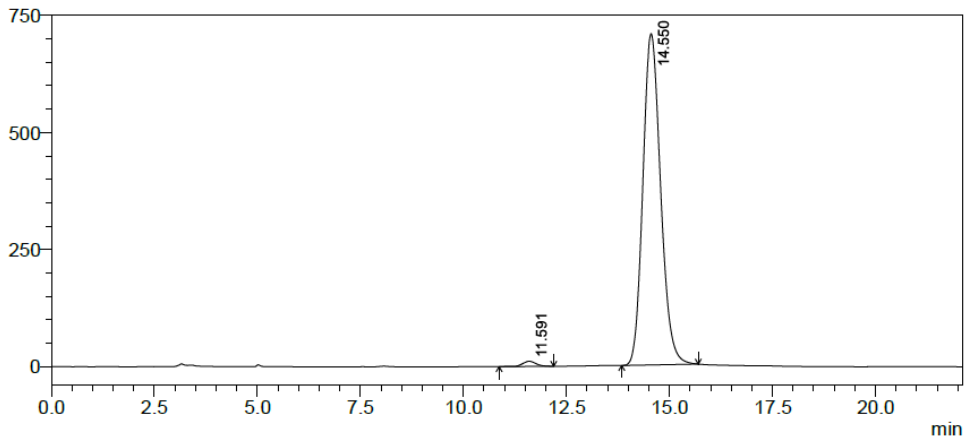


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.229	30062783	1311253	52.725	59.188
2	13.756	26955697	904162	47.275	40.812
Total		57018480	2215415	100.000	100.000

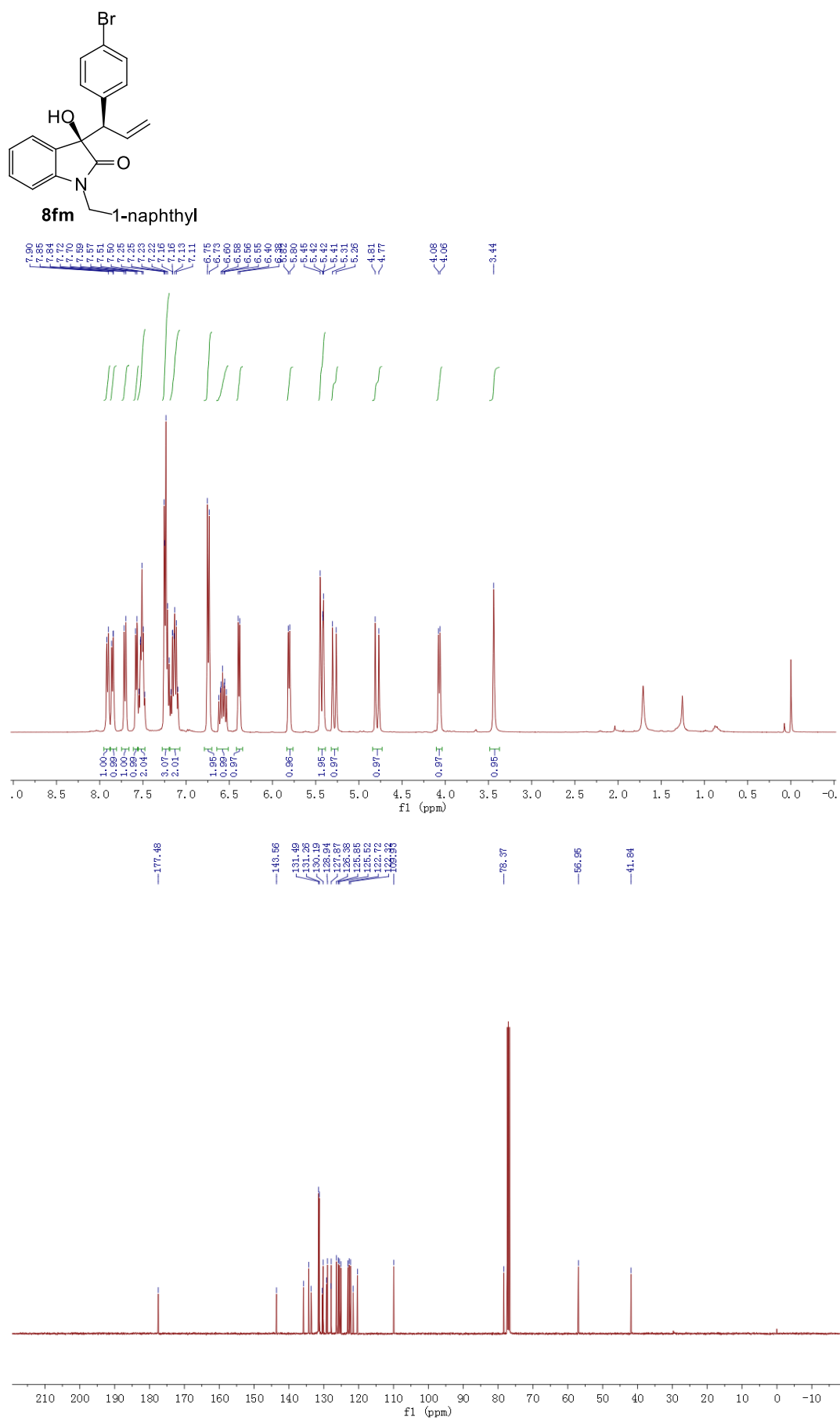


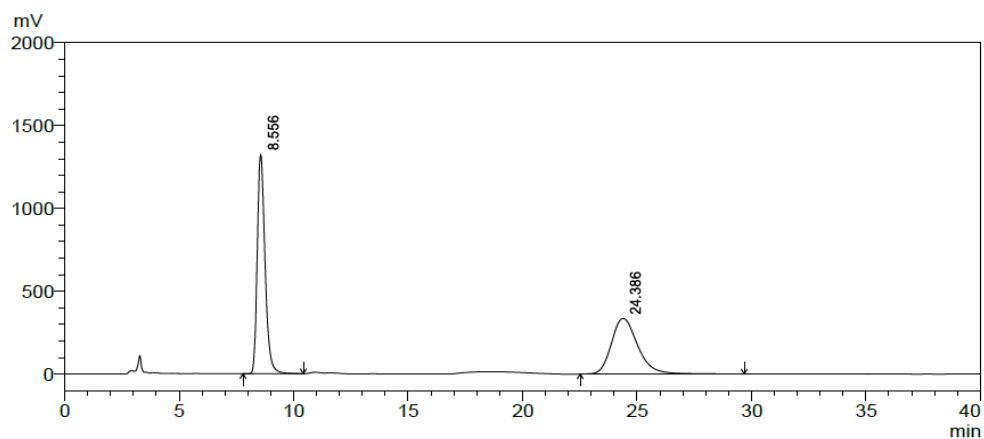
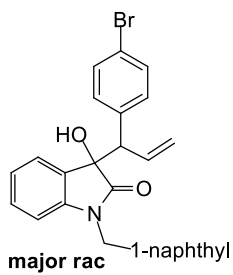
mV



PeakTable

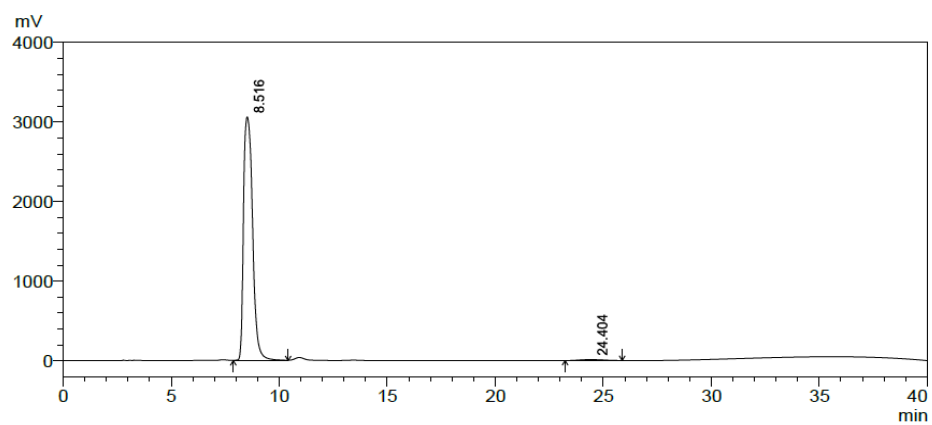
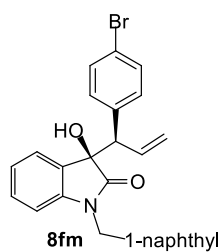
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.591	244201	10928	1.140	1.522
2	14.550	21177455	706925	98.860	98.478
Total		21421656	717853	100.000	100.000





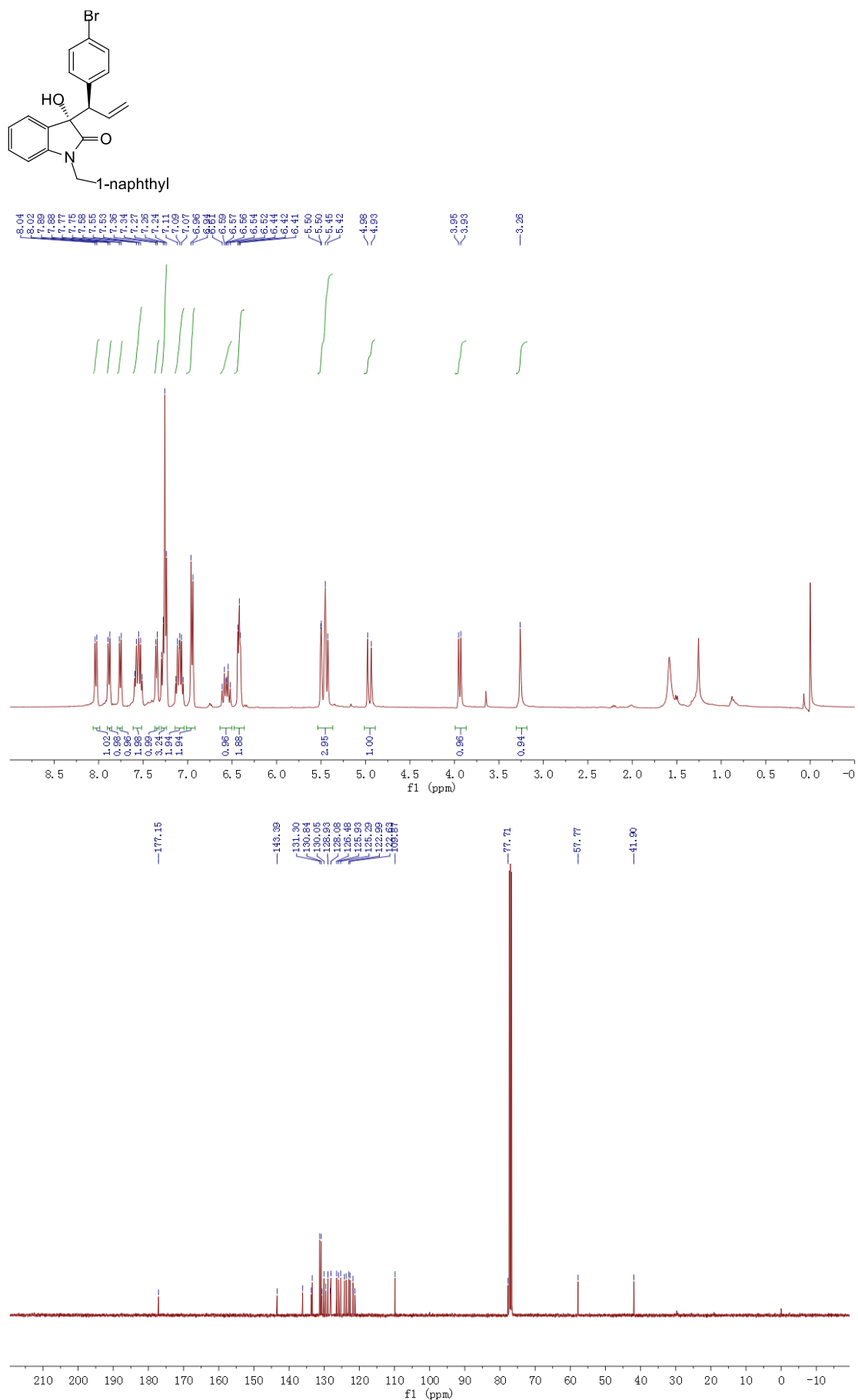
PeakTable

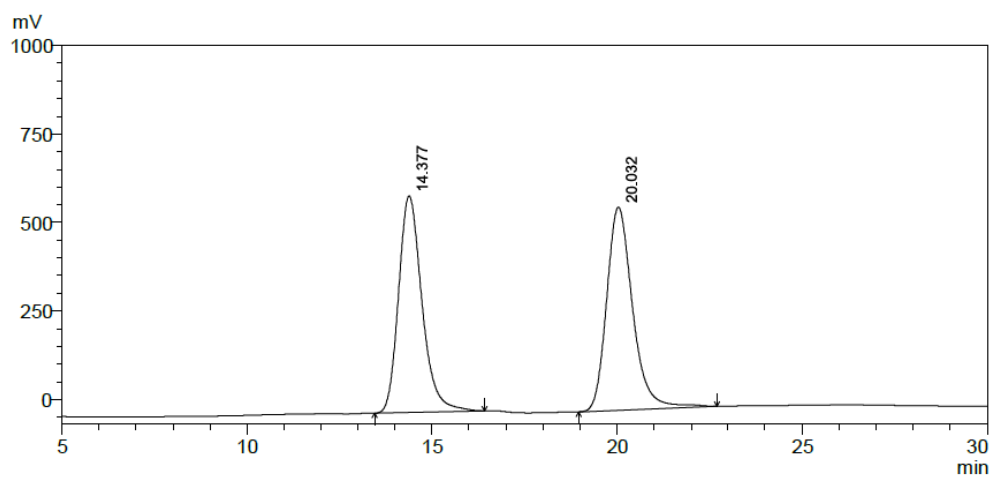
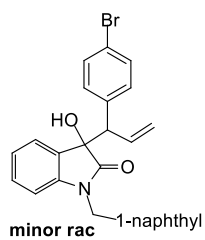
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.556	31255499	1324543	53.875	79.800
2	24.386	26759741	335276	46.125	20.200
Total		58015240	1659819	100.000	100.000



PeakTable

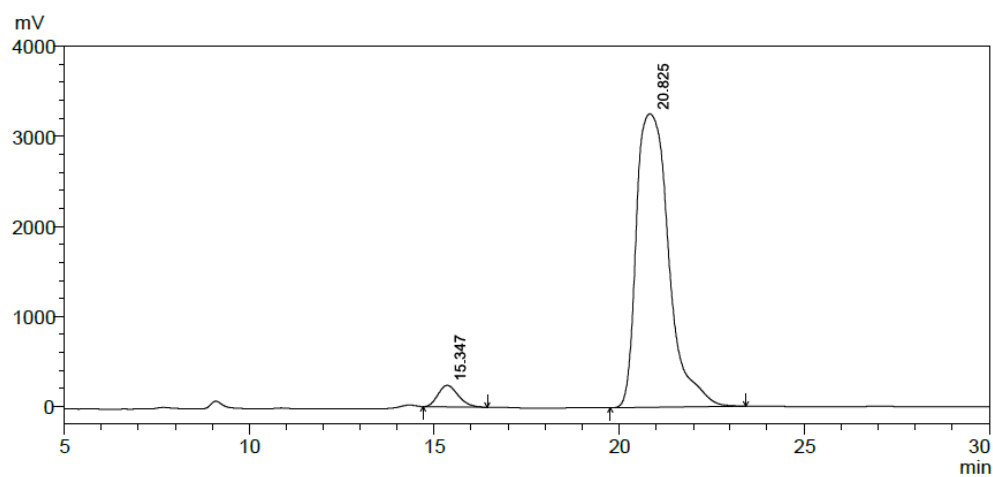
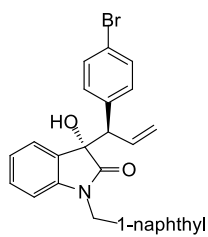
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.516	89636543	3065051	98.975	99.576
2	24.404	928478	13064	1.025	0.424
Total		90565021	3078114	100.000	100.000





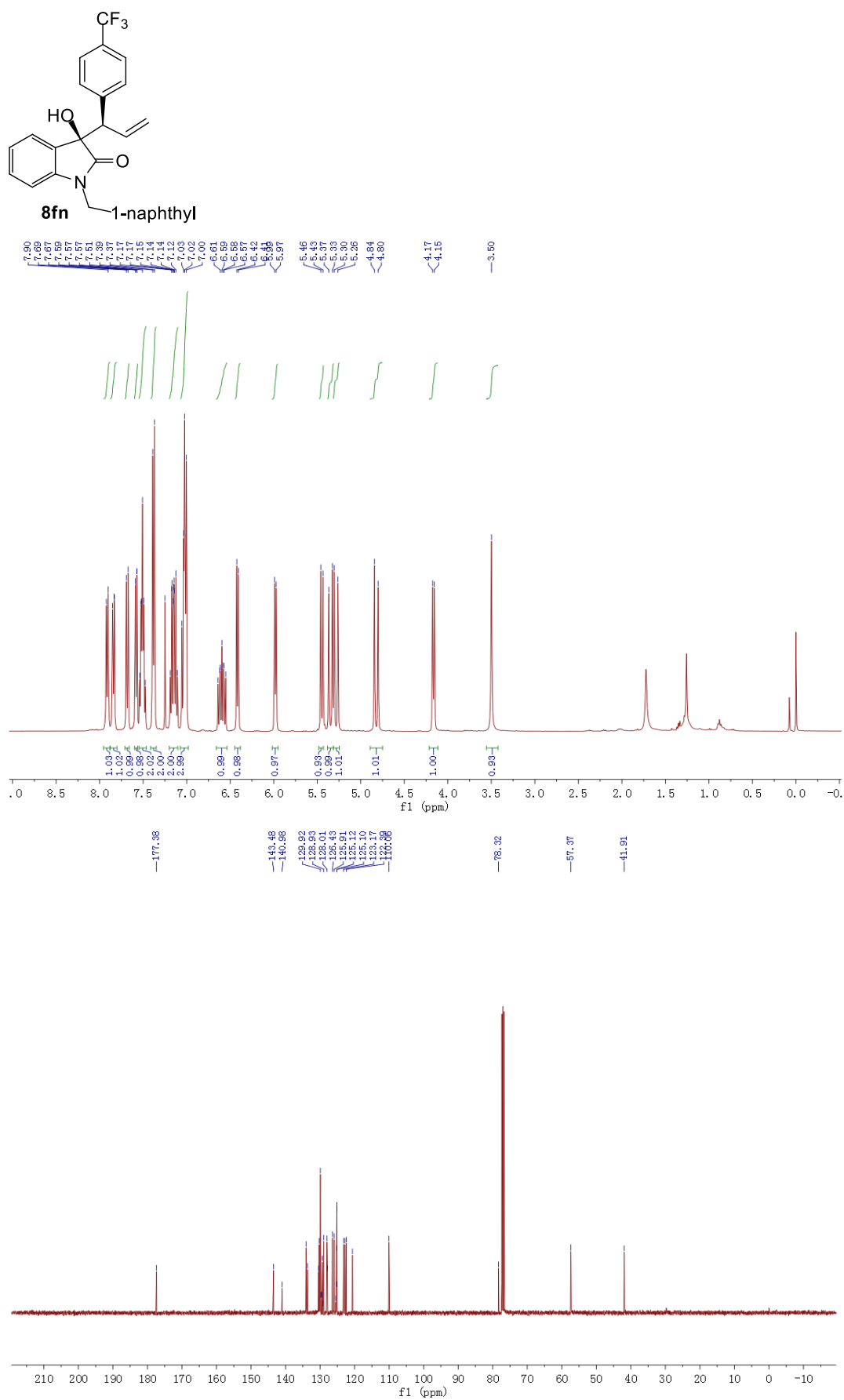
PeakTable

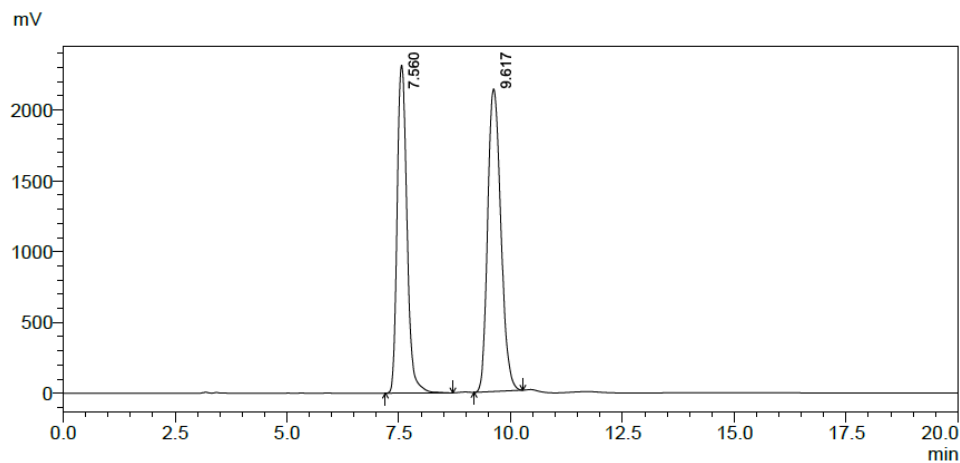
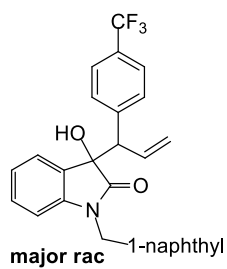
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.377	26907836	611783	48.986	51.618
2	20.032	28021389	573439	51.014	48.382
Total		54929225	1185222	100.000	100.000



PeakTable

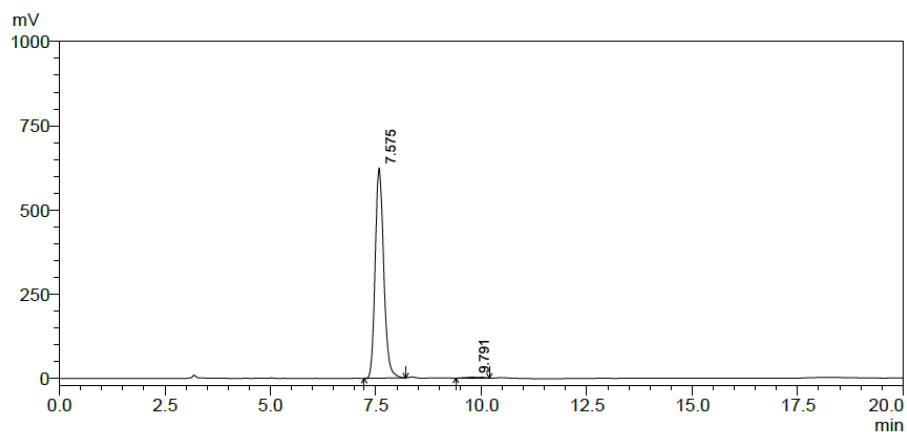
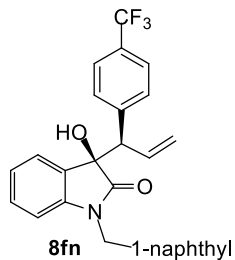
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.347	9109478	239556	4.379	6.843
2	20.825	198921044	3260994	95.621	93.157
Total		208030522	3500550	100.000	100.000





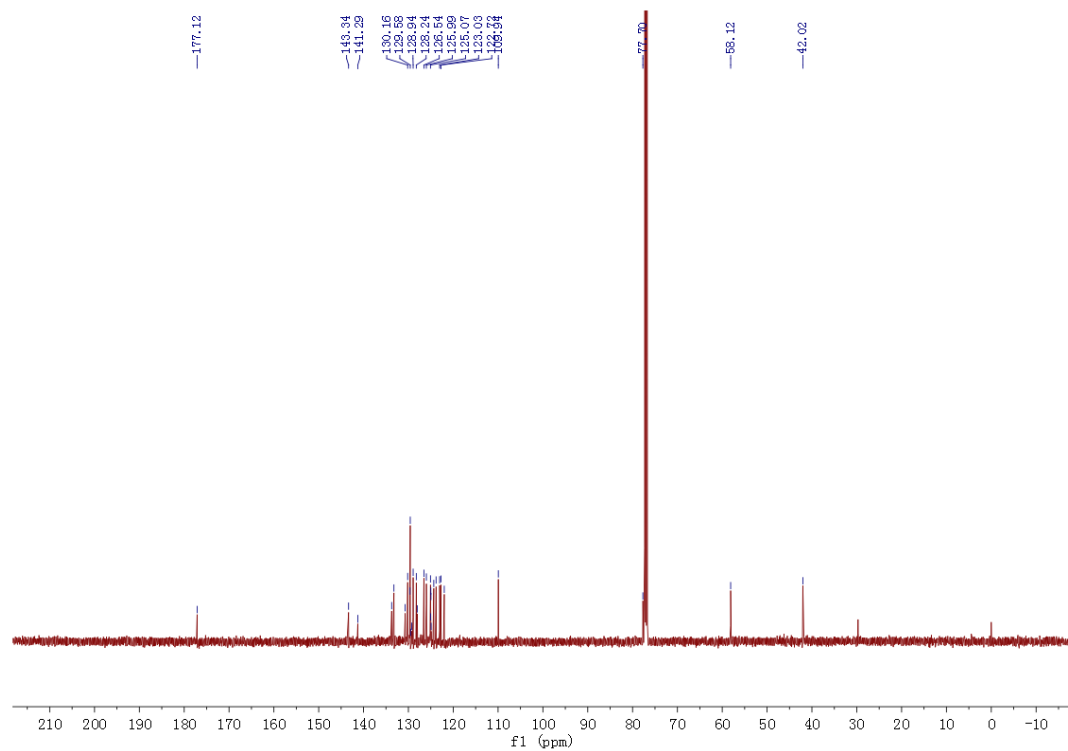
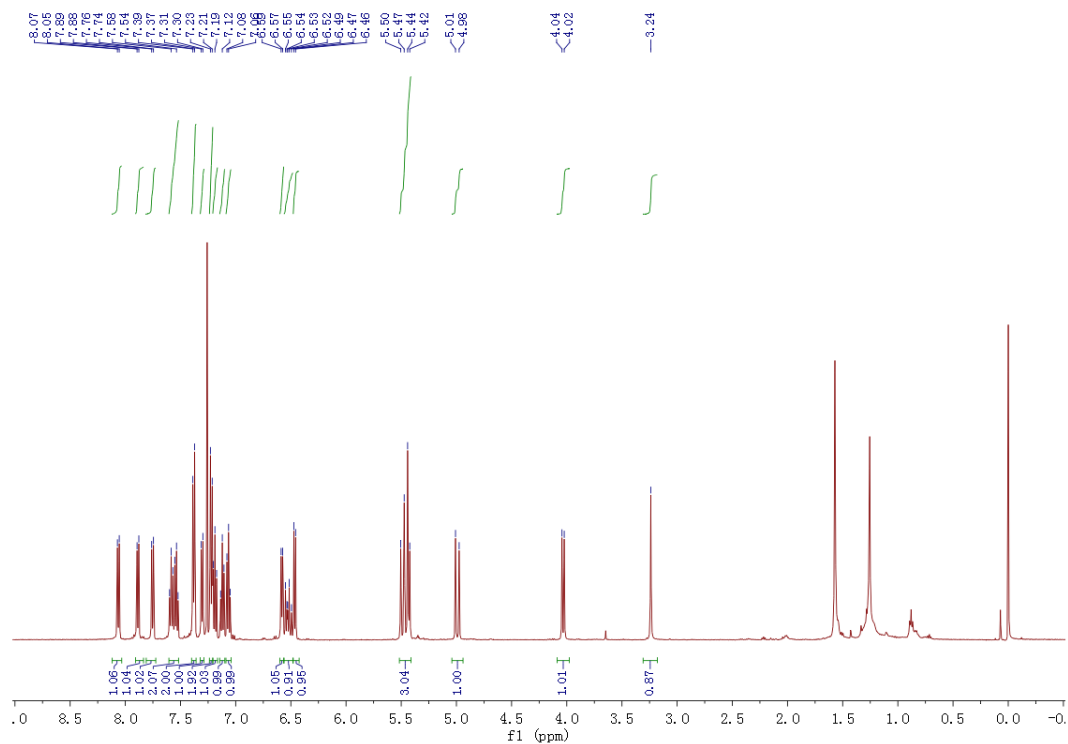
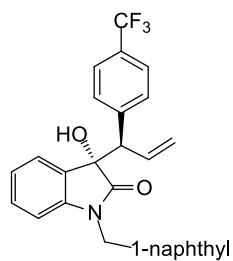
PeakTable

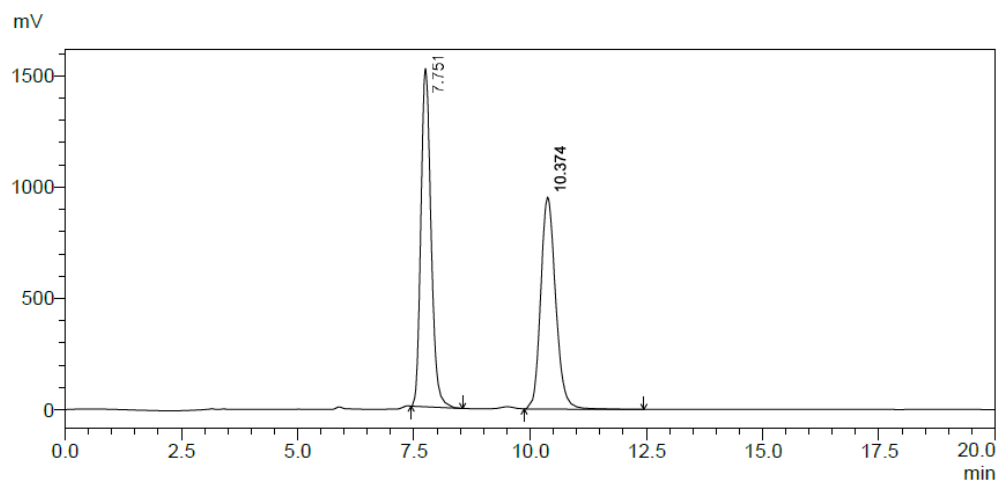
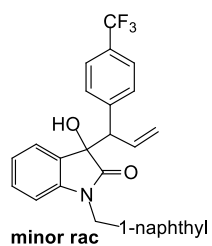
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.560	35484707	2316190	44.742	52.010
2	9.617	43824290	2137123	55.258	47.990
Total		79308997	4453313	100.000	100.000



PeakTable

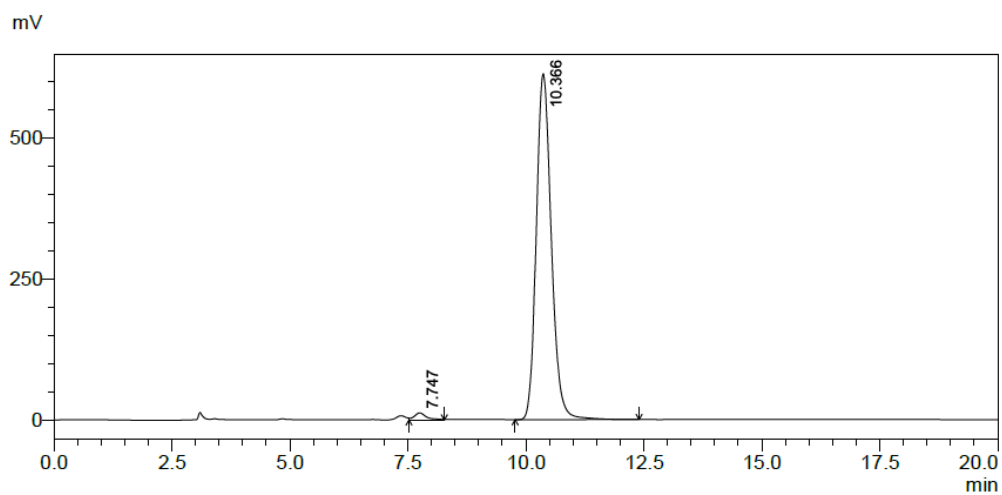
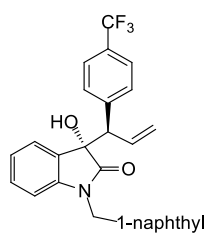
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.575	8789572	623840	99.164	99.552
2	9.791	74122	2805	0.836	0.448
Total		8863693	626645	100.000	100.000





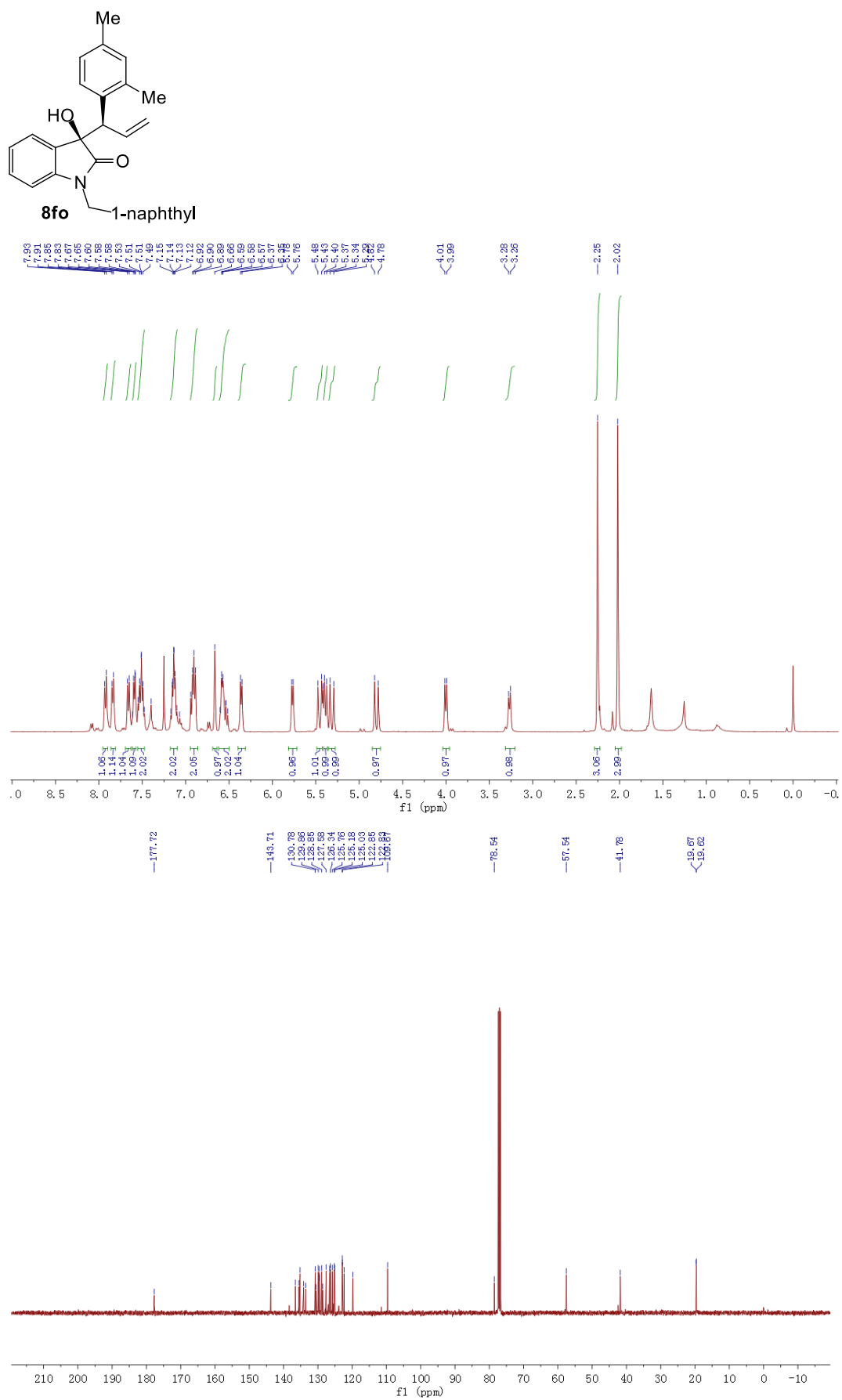
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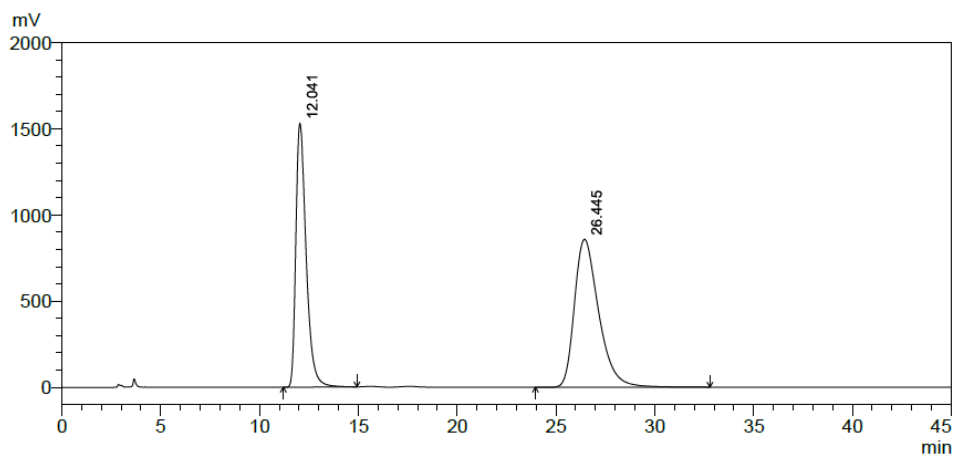
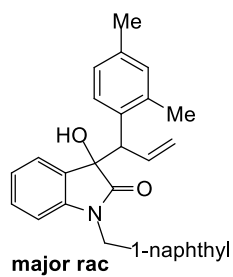
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.751	23041164	1519352	52.130	61.454
2	10.374	21158389	952978	47.870	38.546
Total		44199553	2472330	100.000	100.000



PeakTable

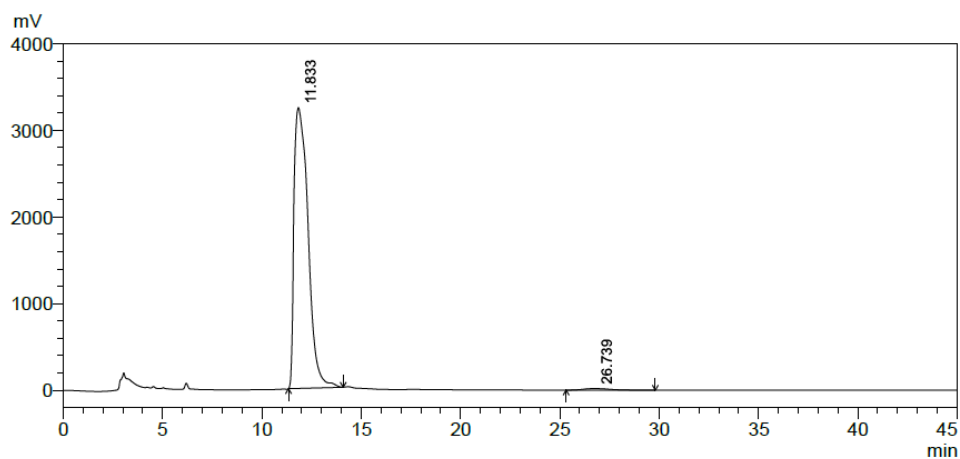
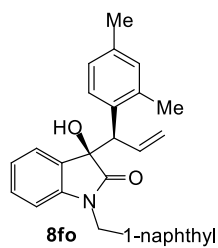
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.747	224820	12337	1.629	1.974
2	10.366	13572065	612523	98.371	98.026
Total		13796885	624860	100.000	100.000





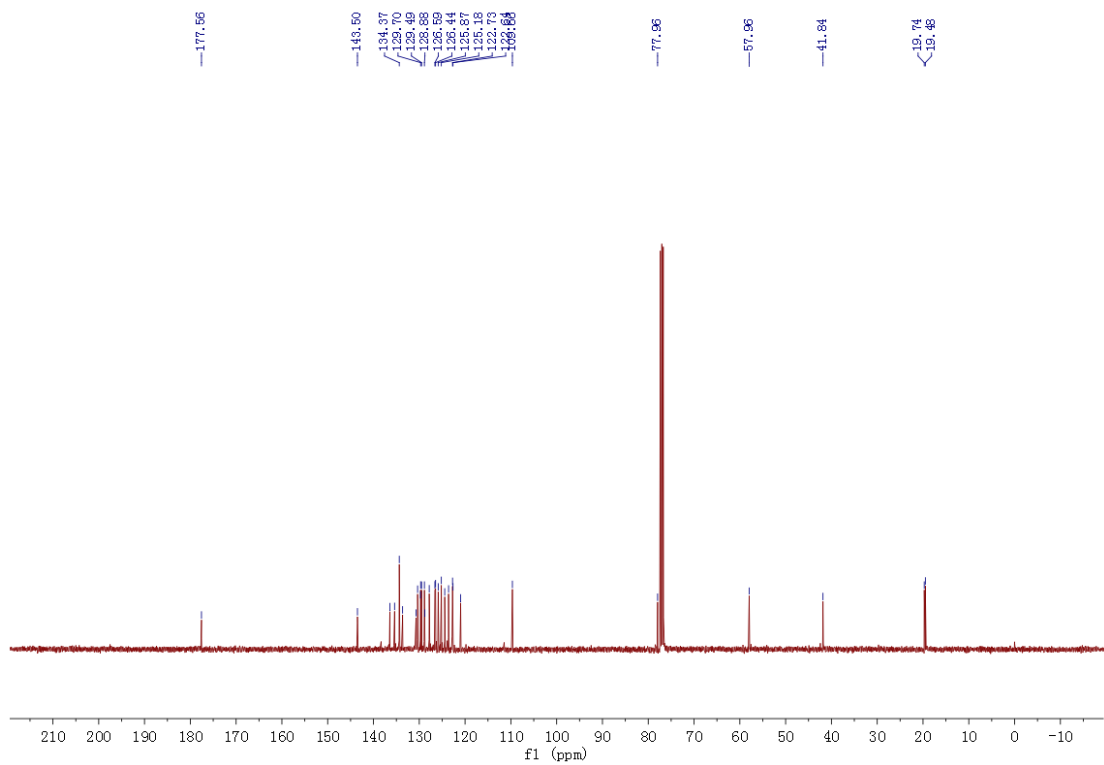
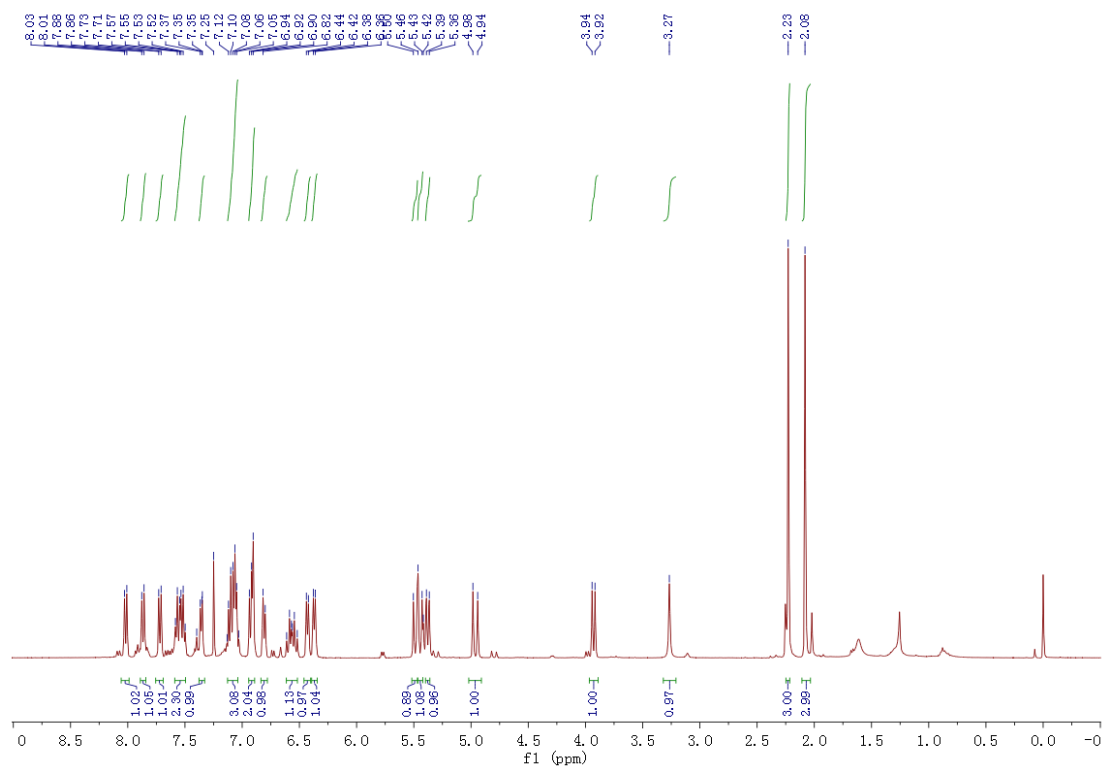
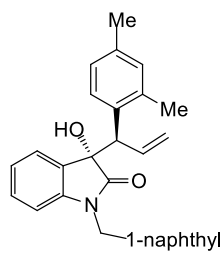
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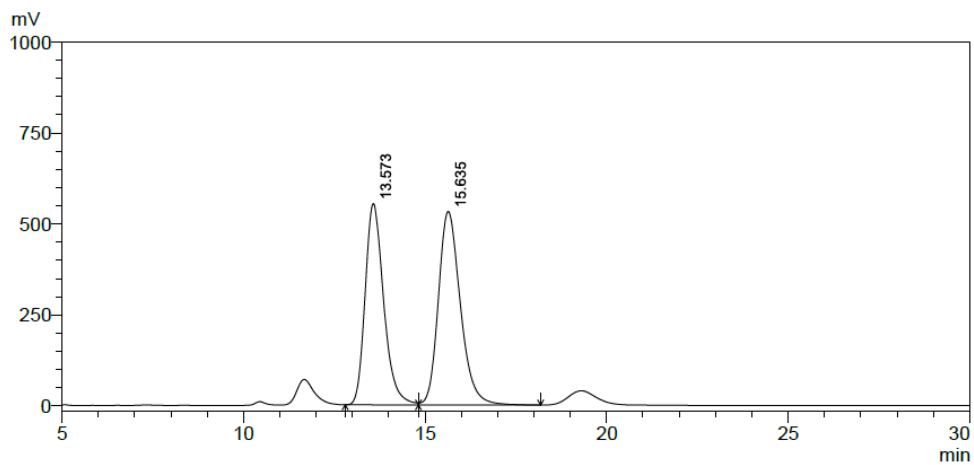
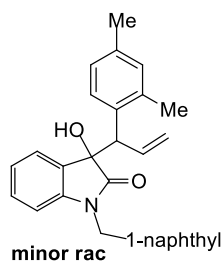
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.041	55446864	1531124	43.086	64.091
2	26.445	73243310	857878	56.914	35.909
Total		128690174	2389002	100.000	100.000



PeakTable

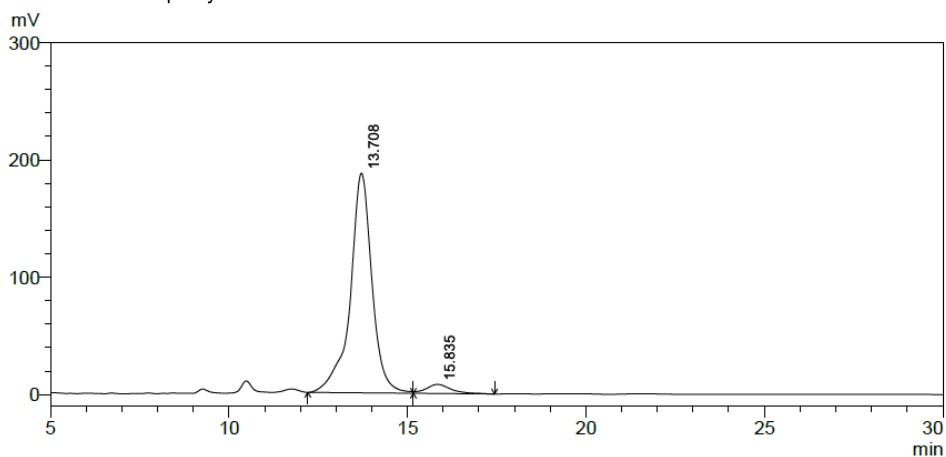
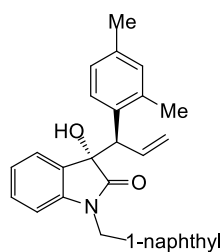
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.833	159180393	3240942	98.962	99.419
2	26.739	1670425	18933	1.038	0.581
Total		160850818	3259875	100.000	100.000





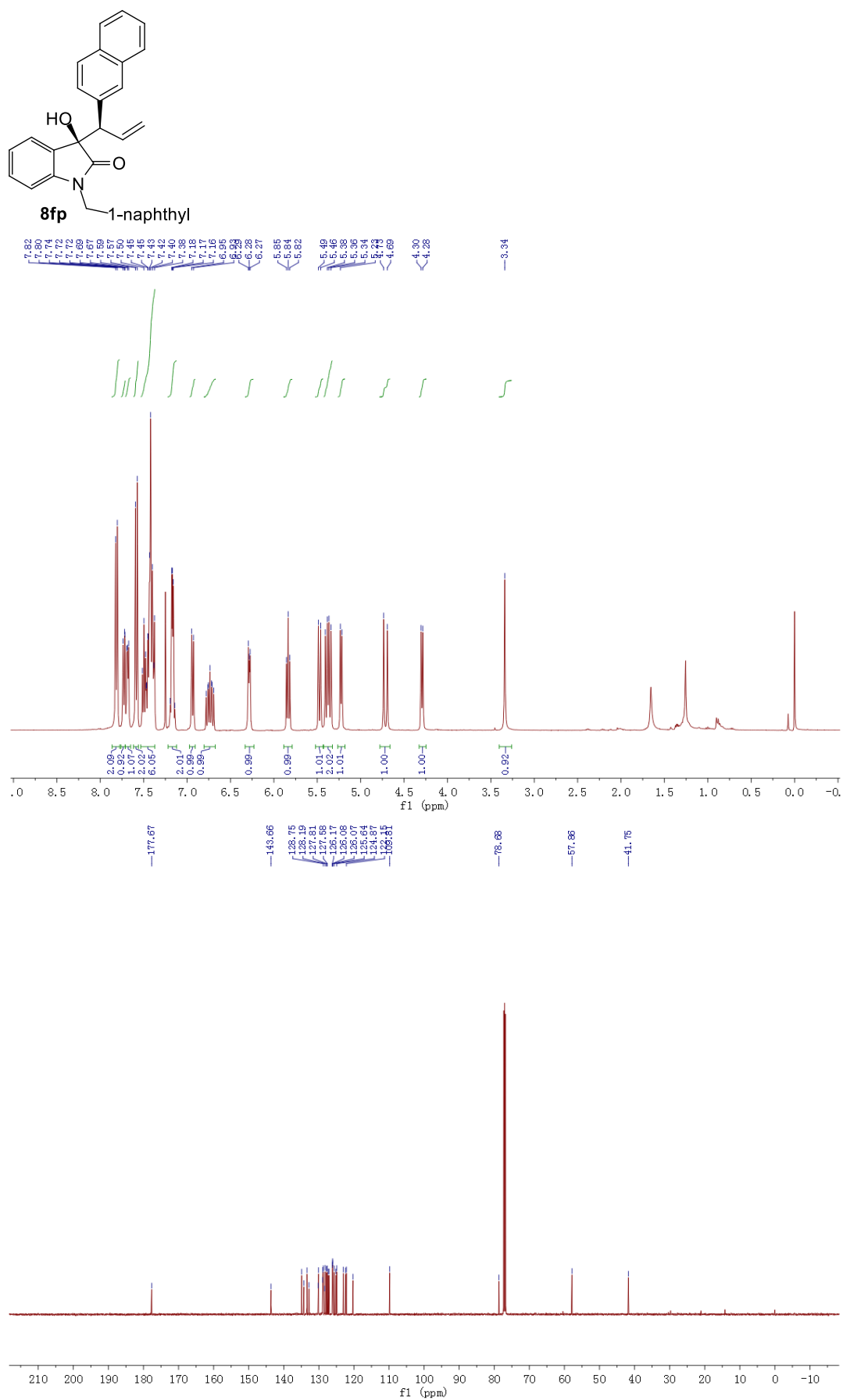
PeakTable

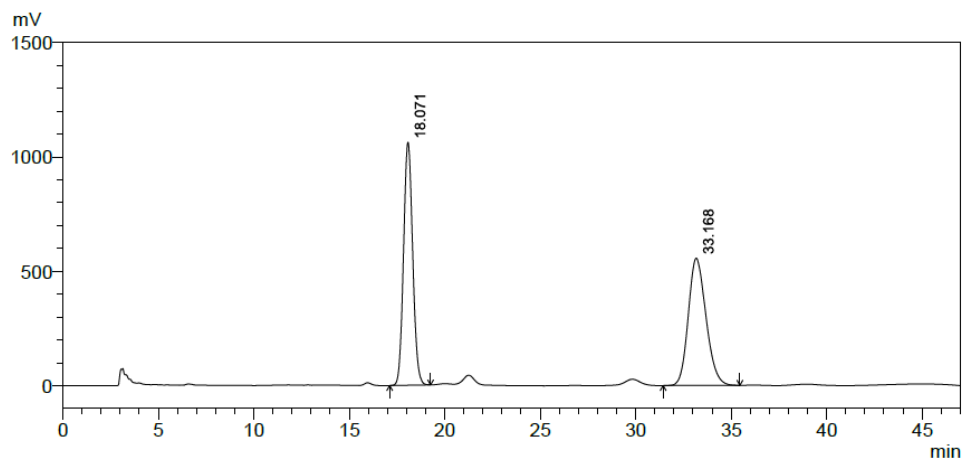
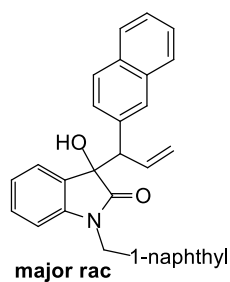
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.573	19677347	553172	46.719	50.976
2	15.635	22440828	531987	53.281	49.024
Total		42118175	1085159	100.000	100.000



PeakTable

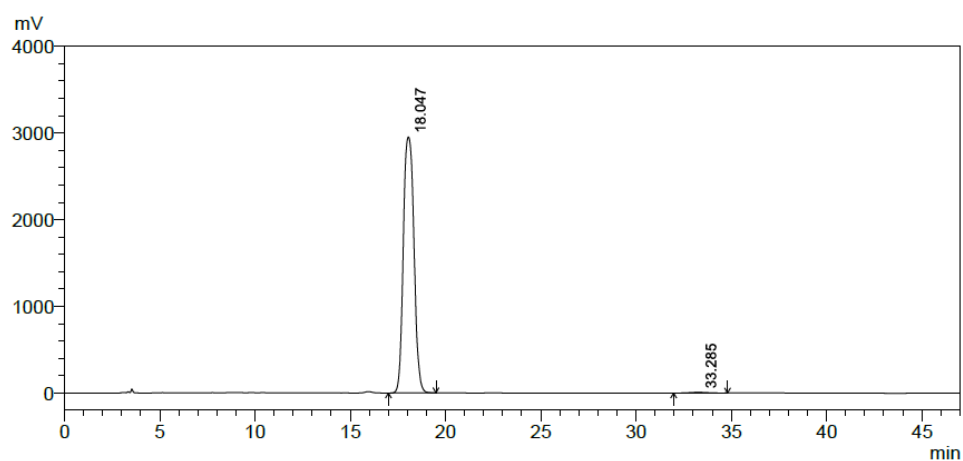
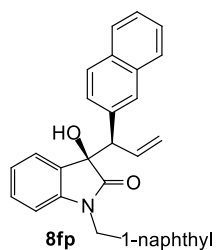
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.708	7934716	187207	95.451	96.031
2	15.835	378146	7738	4.549	3.969
Total		8312862	194945	100.000	100.000





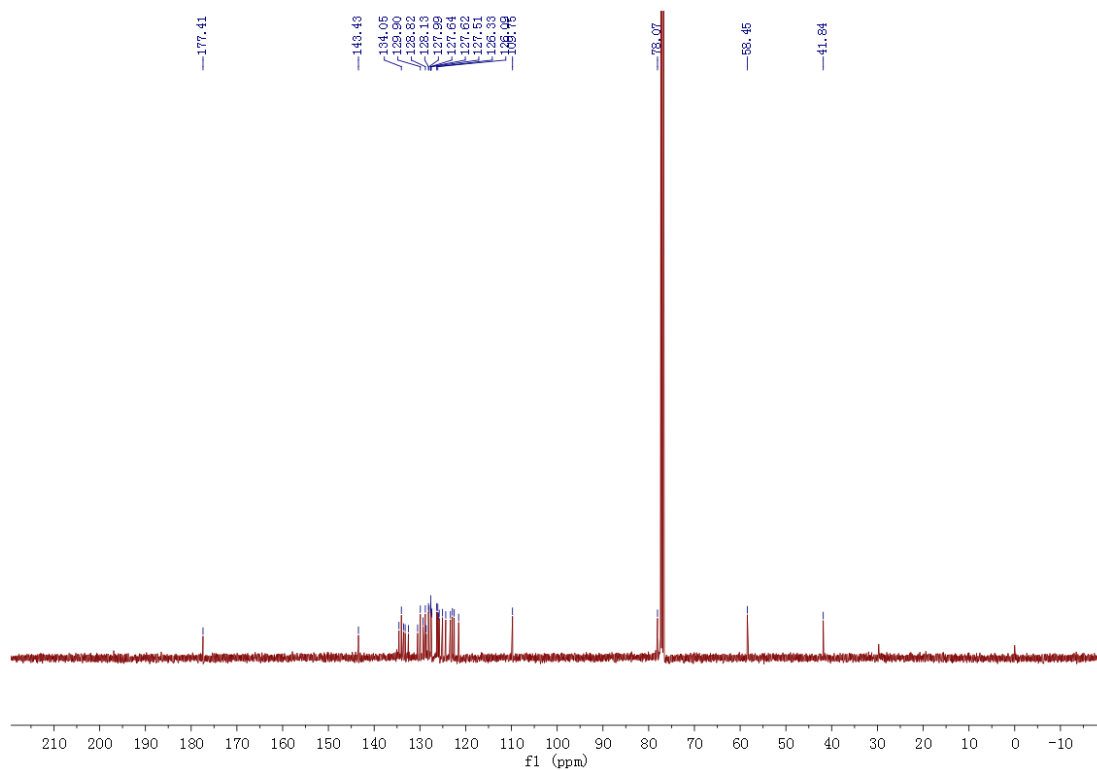
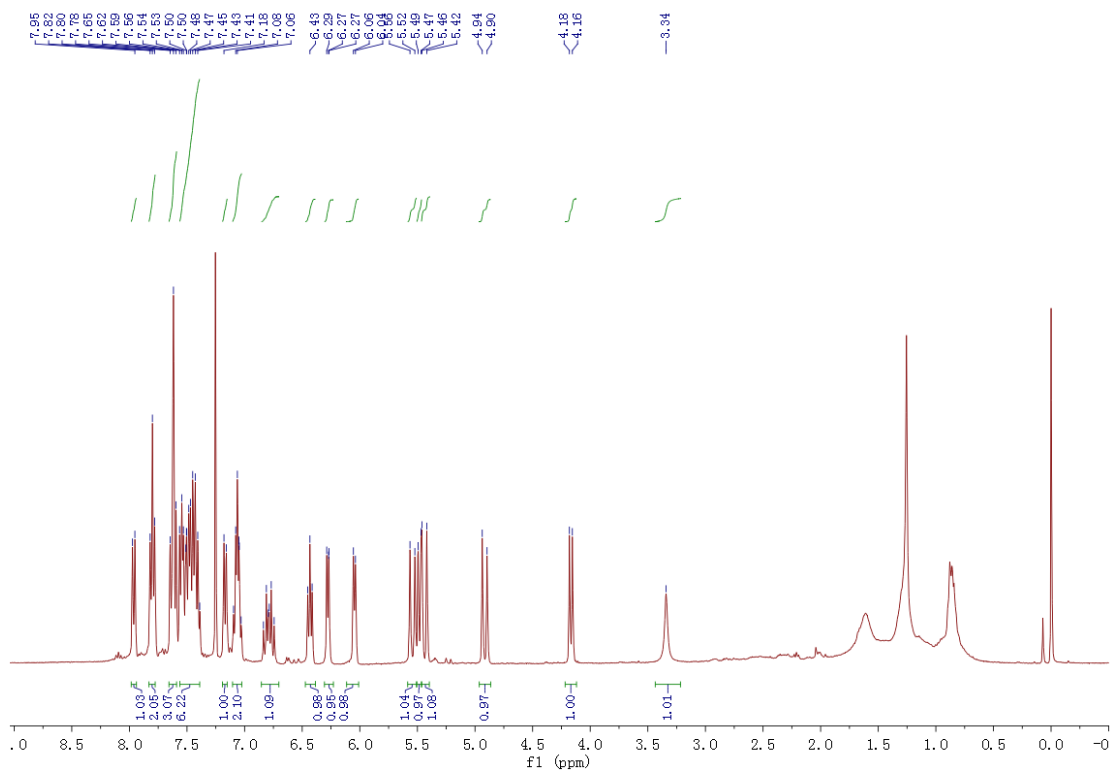
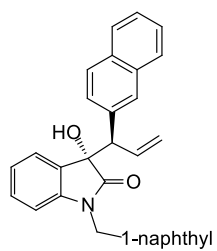
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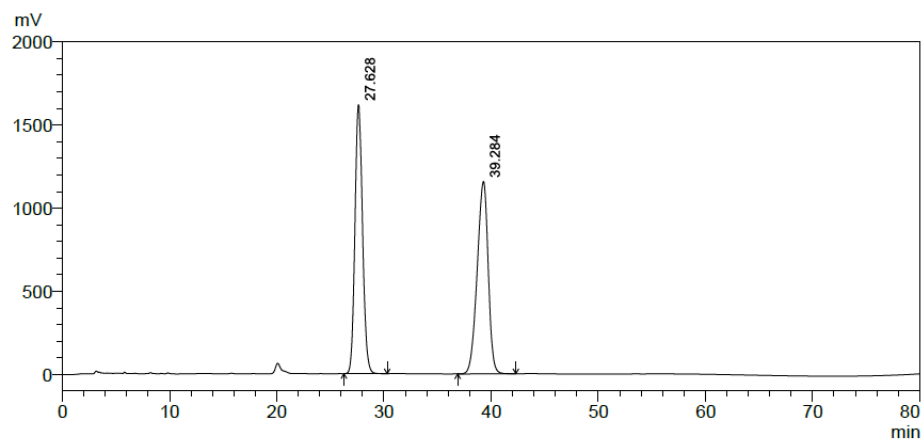
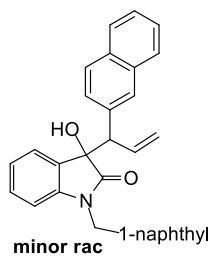
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.071	35265575	1062359	49.573	65.630
2	33.168	35872709	556344	50.427	34.370
Total		71138285	1618703	100.000	100.000



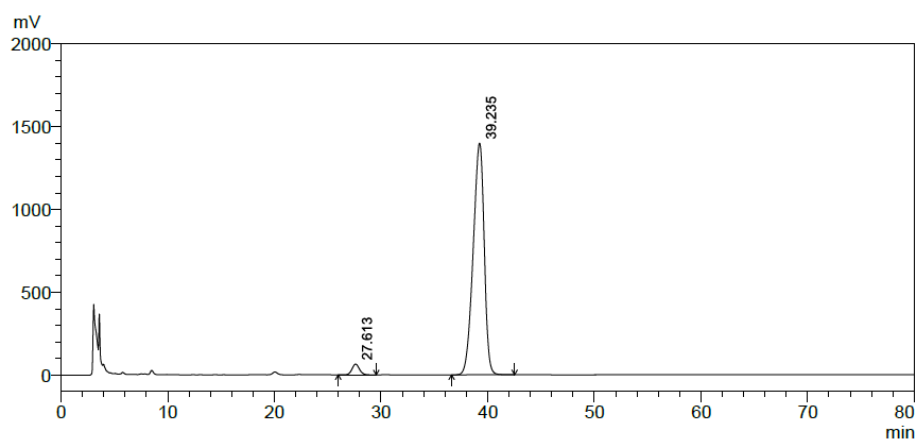
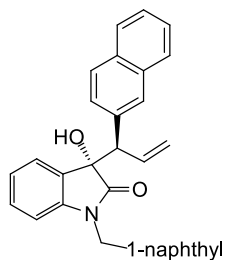
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.047	114318211	2953935	99.585	99.744
2	33.285	475965	7577	0.415	0.256
Total		114794176	2961512	100.000	100.000

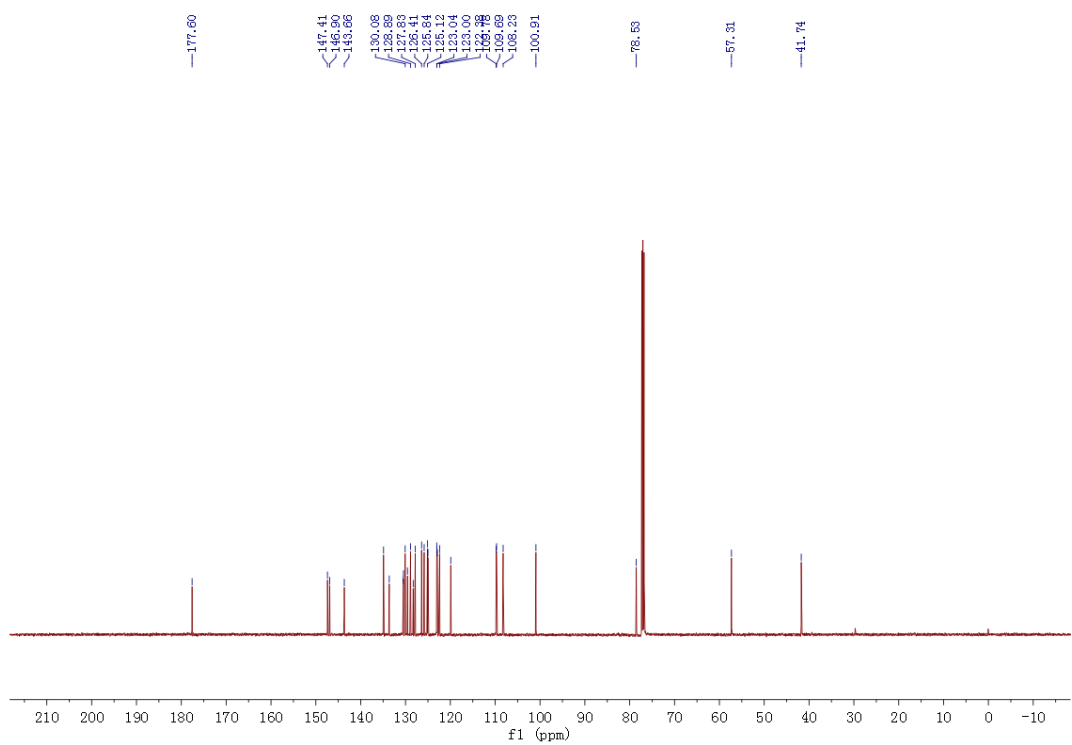
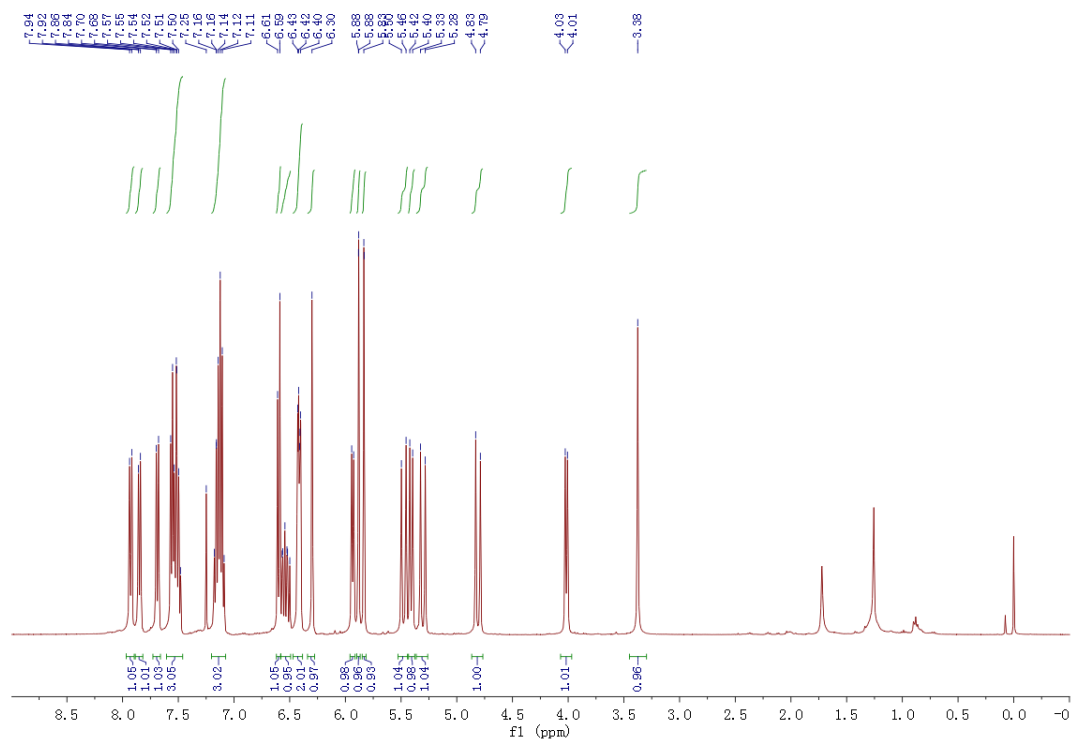
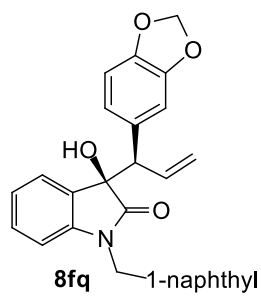


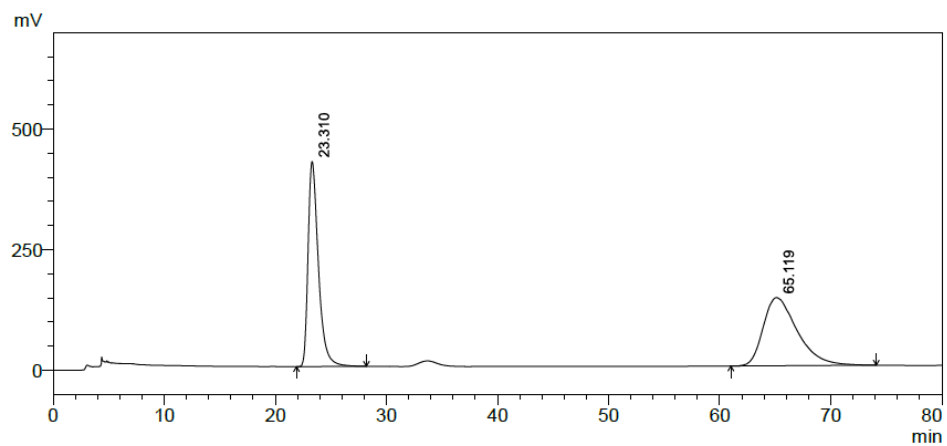
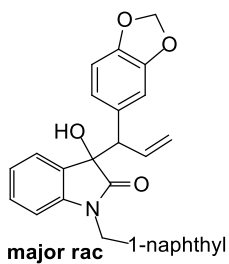


Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.628	80091822	1618556	49.239	58.323
2	39.284	82568167	1156592	50.761	41.677
Total		162659990	2775148	100.000	100.000



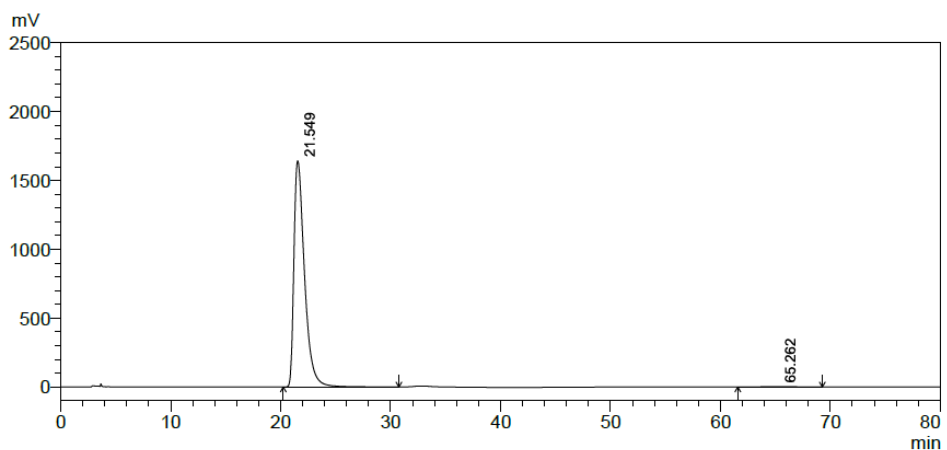
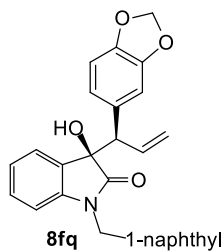
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.613	3144810	64887	3.034	4.432
2	39.235	100523760	1399304	96.966	95.568
Total		103668570	1464190	100.000	100.000





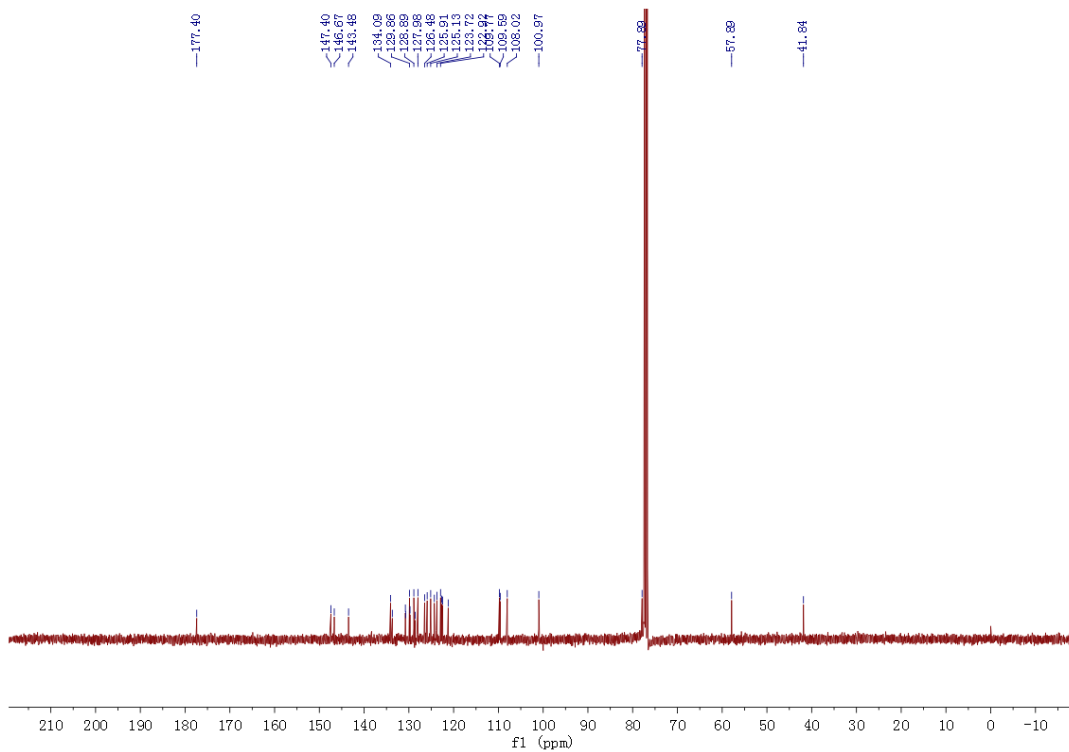
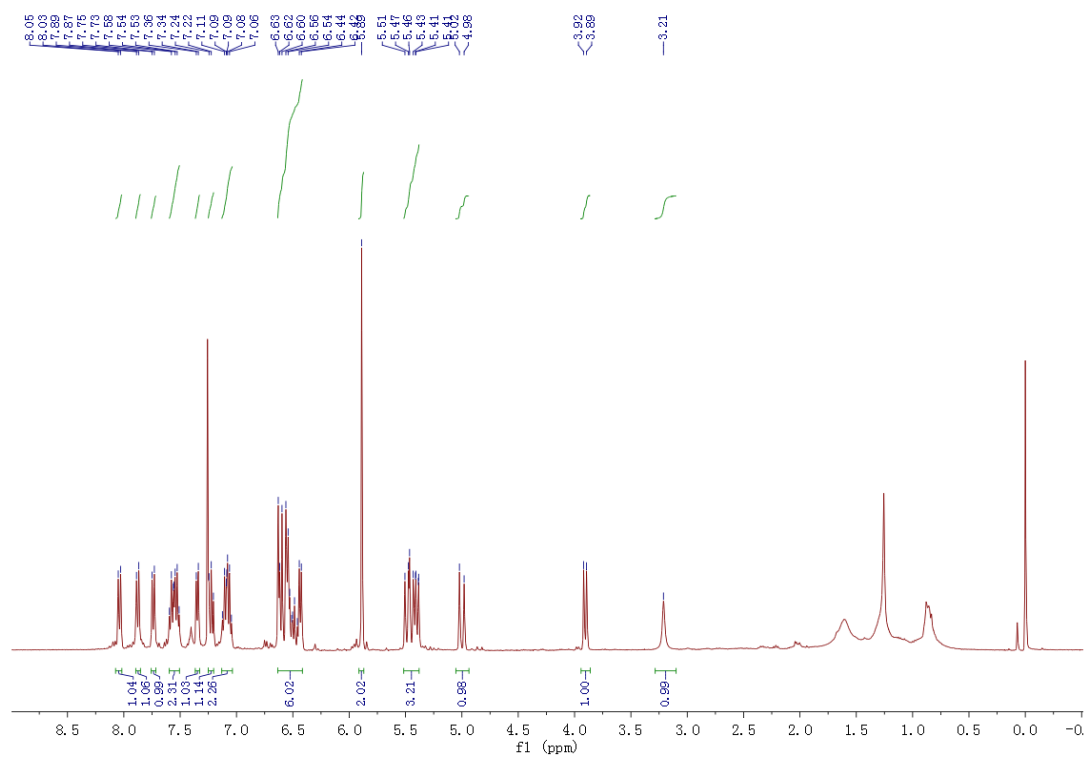
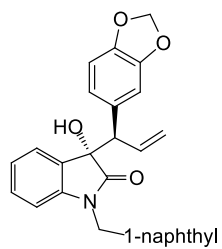
PeakTable

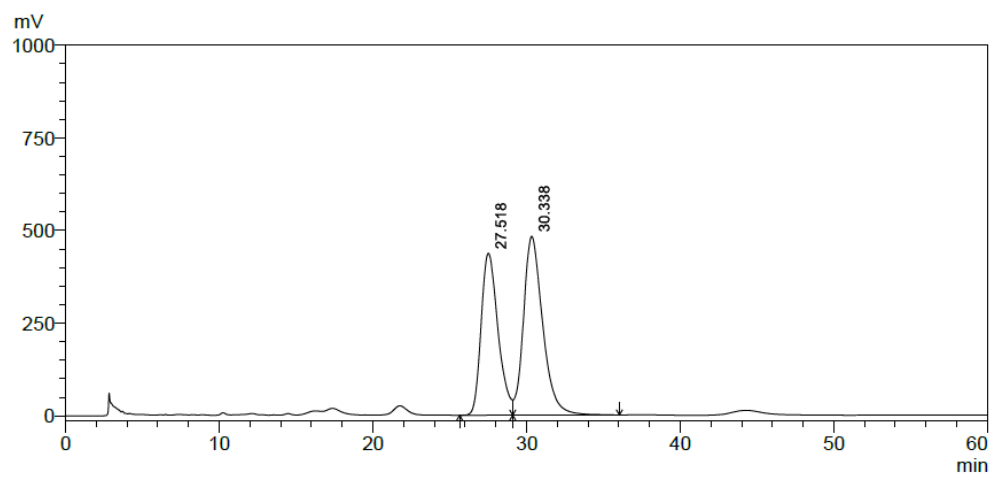
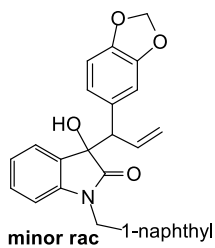
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.310	27458029	424814	47.653	75.039
2	65.119	30162908	141308	52.347	24.961
Total		57620937	566122	100.000	100.000



PeakTable

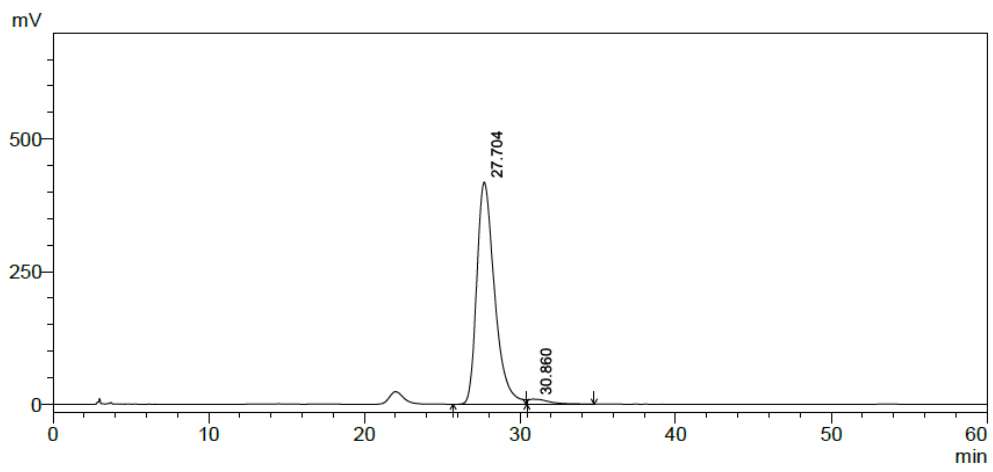
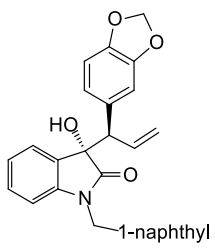
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.549	110146171	1642685	99.740	99.914
2	65.262	287330	1407	0.260	0.086
Total		110433502	1644092	100.000	100.000





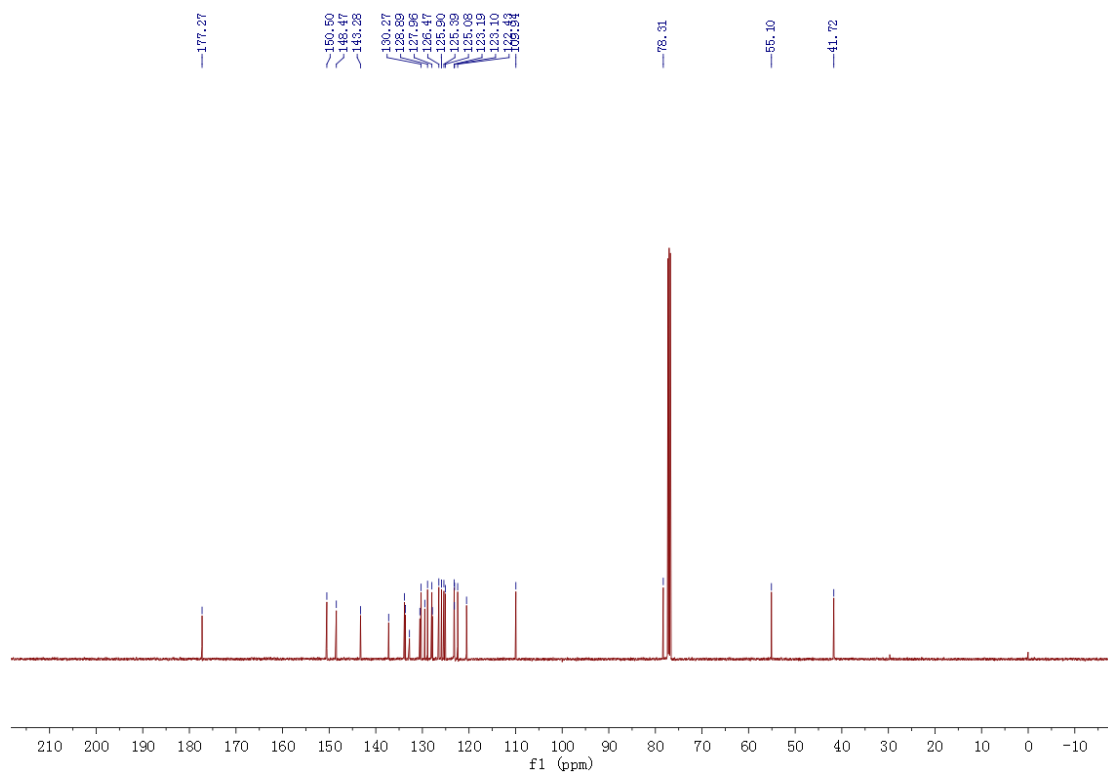
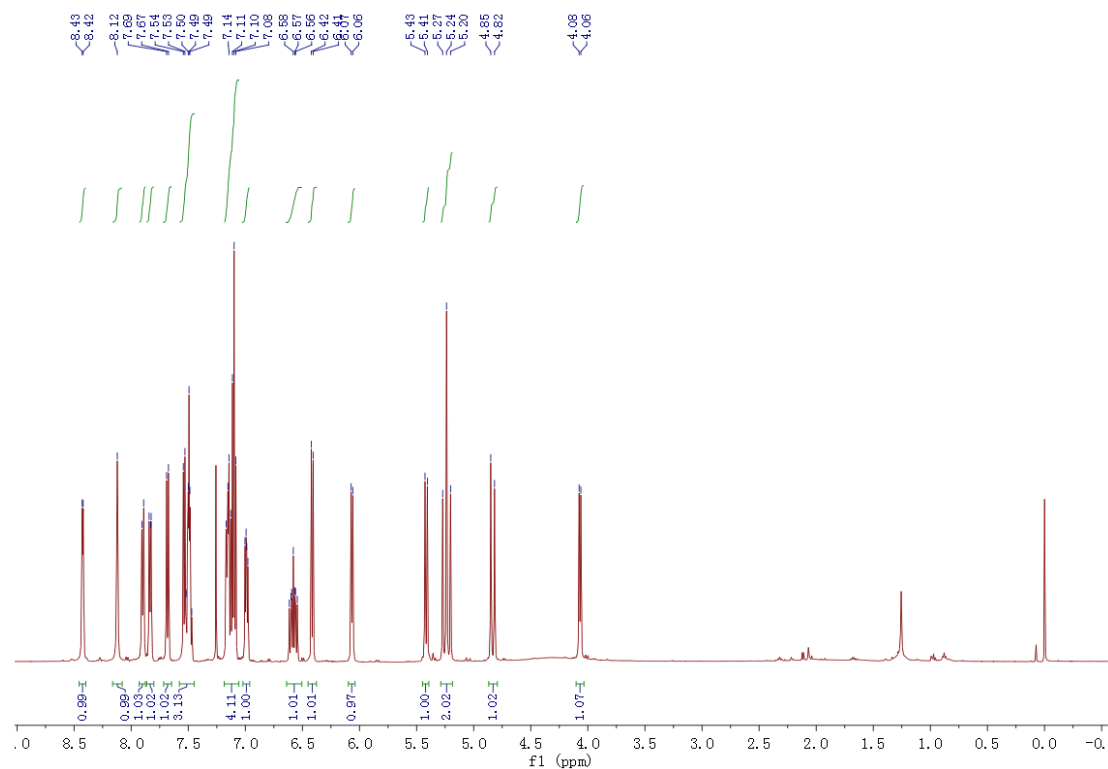
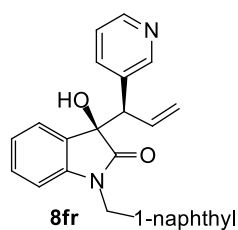
PeakTable

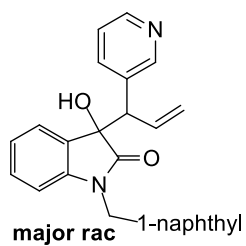
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.518	33385264	436975	44.259	47.513
2	30.338	42045592	482724	55.741	52.487
Total		75430856	919699	100.000	100.000



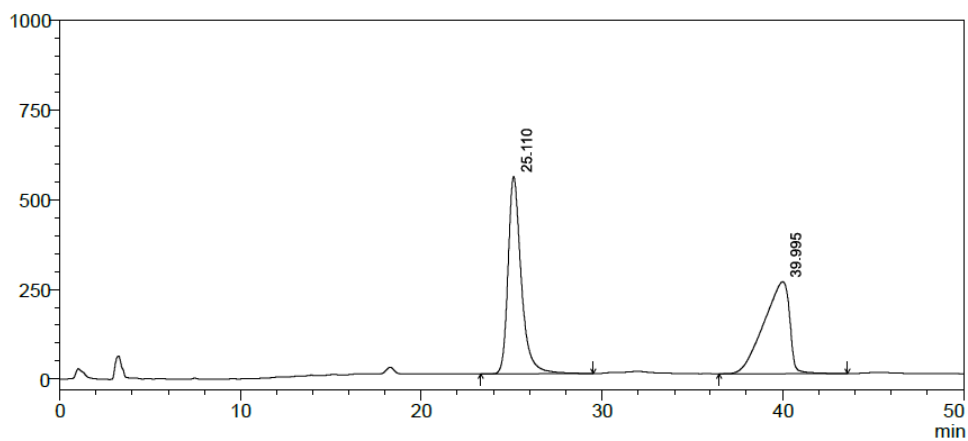
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.704	33292966	418847	97.251	97.801
2	30.860	941123	9418	2.749	2.199
Total		34234089	428265	100.000	100.000



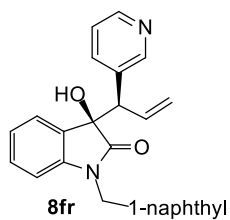


mV

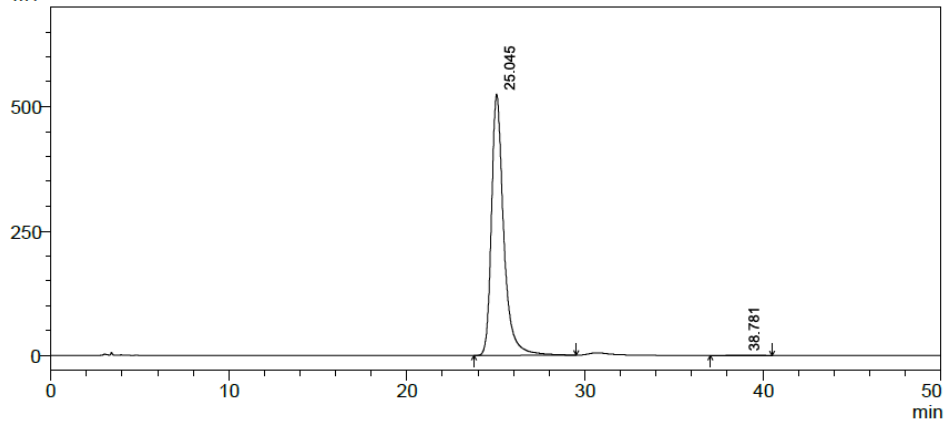


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.110	28038378	551200	52.314	68.245
2	39.995	25557493	256480	47.686	31.755
Total		53595872	807680	100.000	100.000

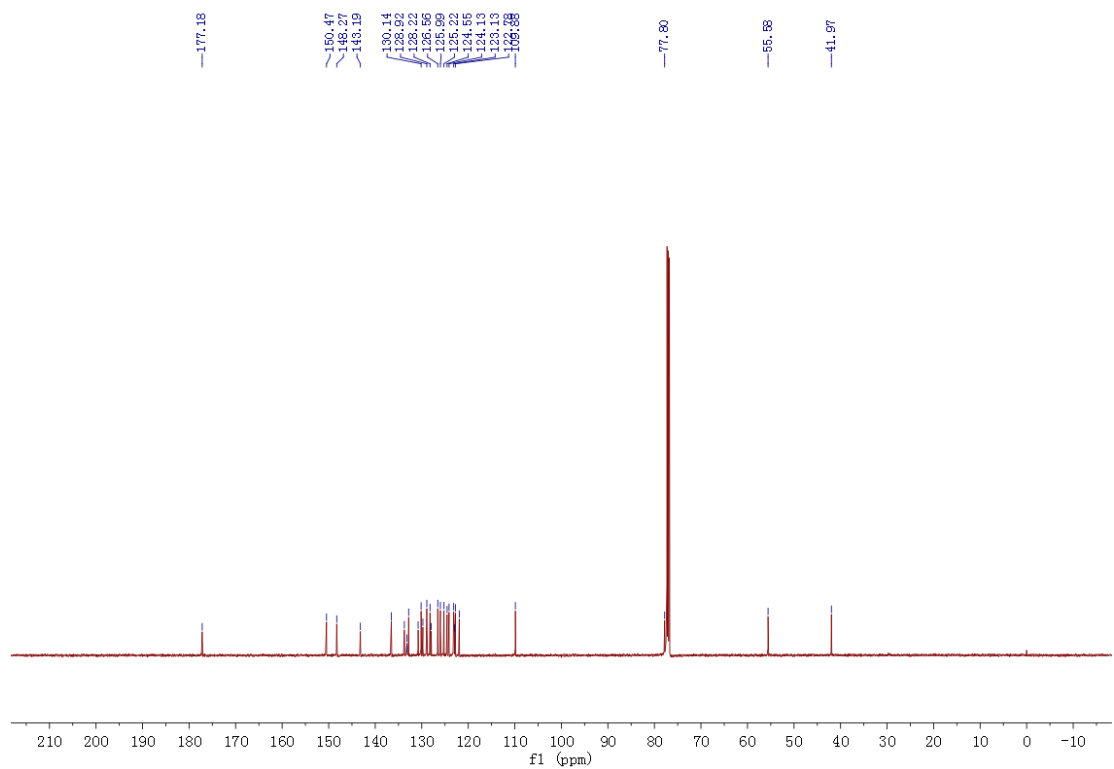
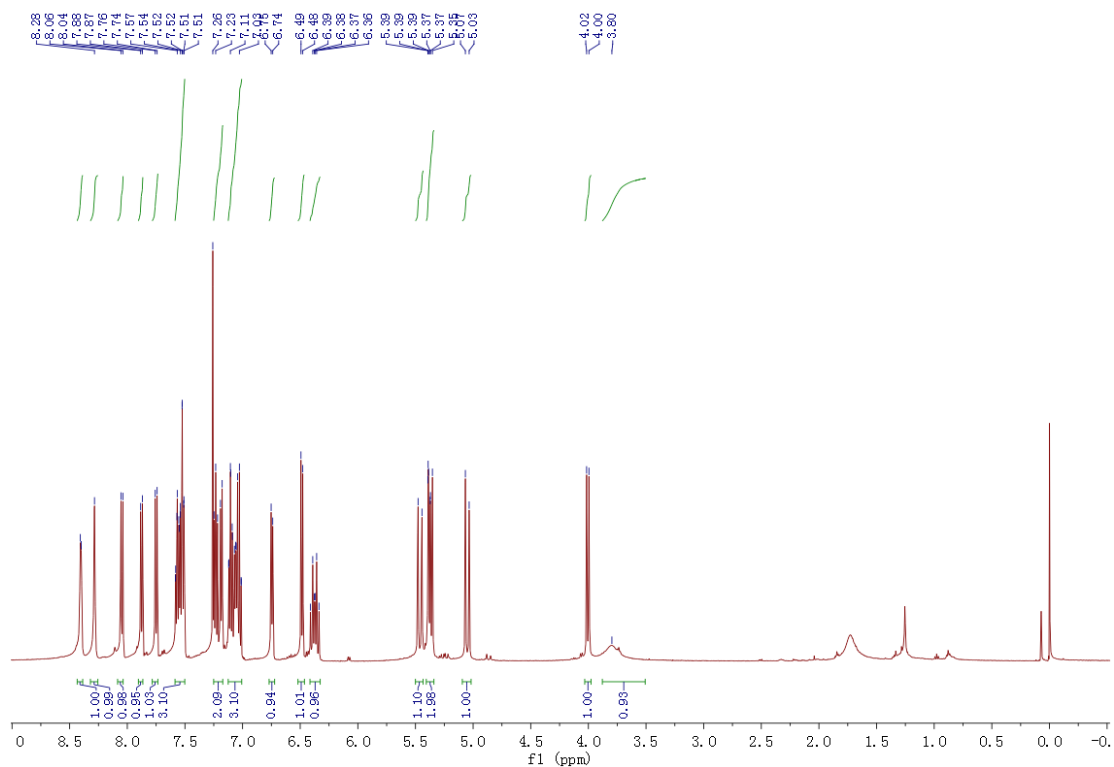
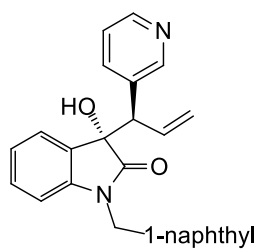


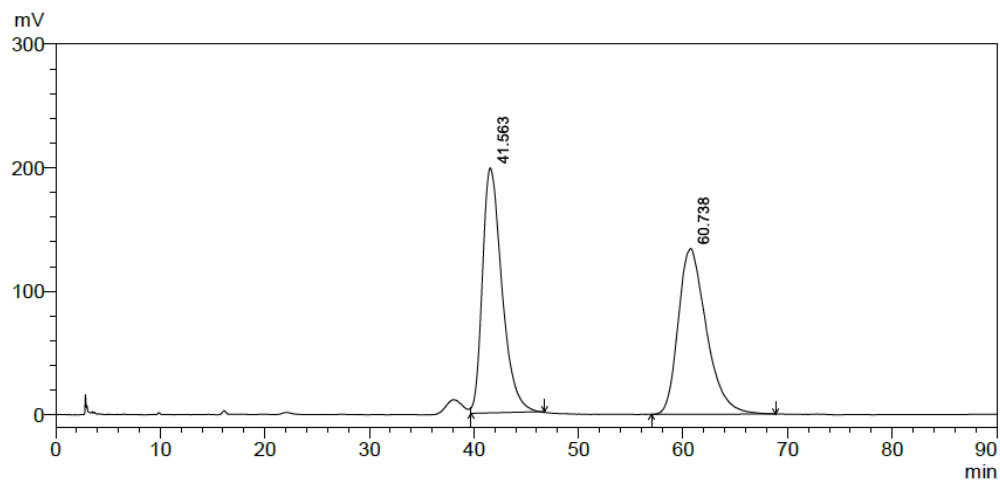
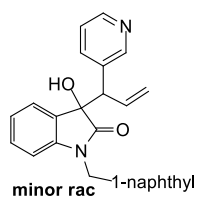
mV



PeakTable

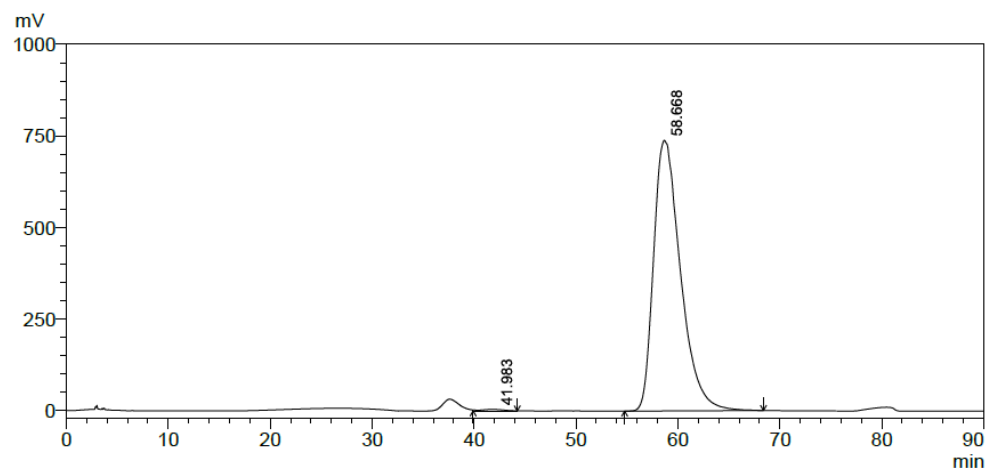
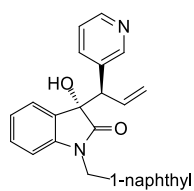
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.045	25053122	524209	99.556	99.761
2	38.781	111704	1257	0.444	0.239
Total		25164826	525466	100.000	100.000





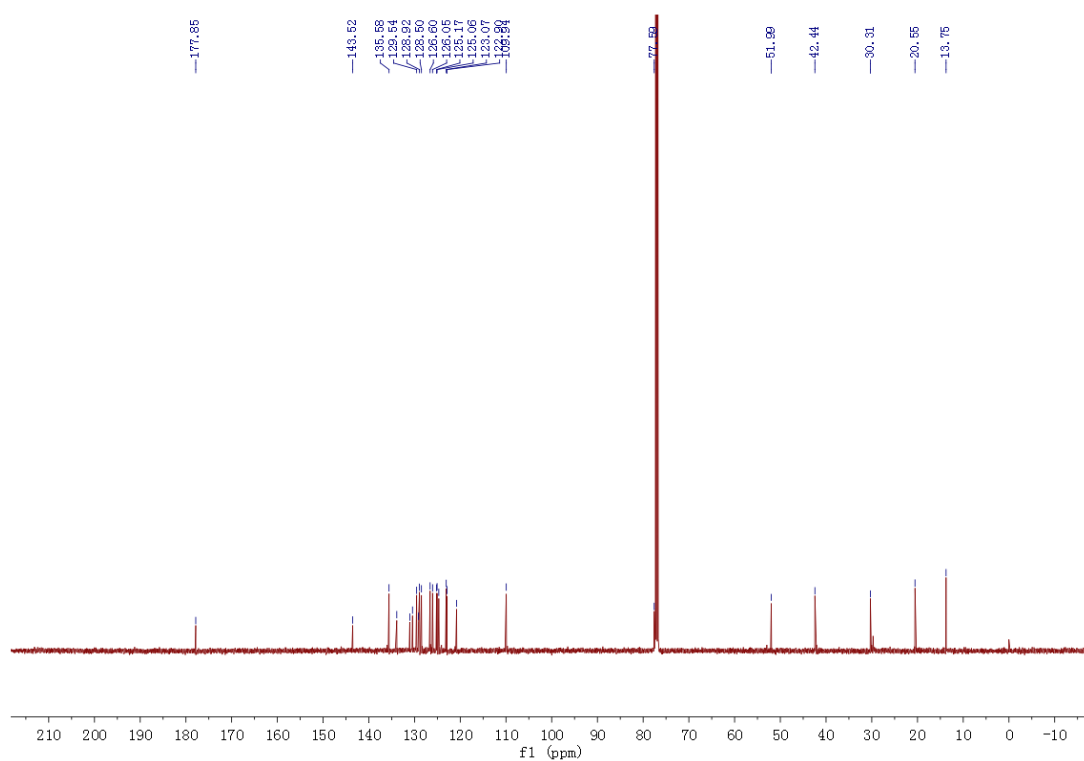
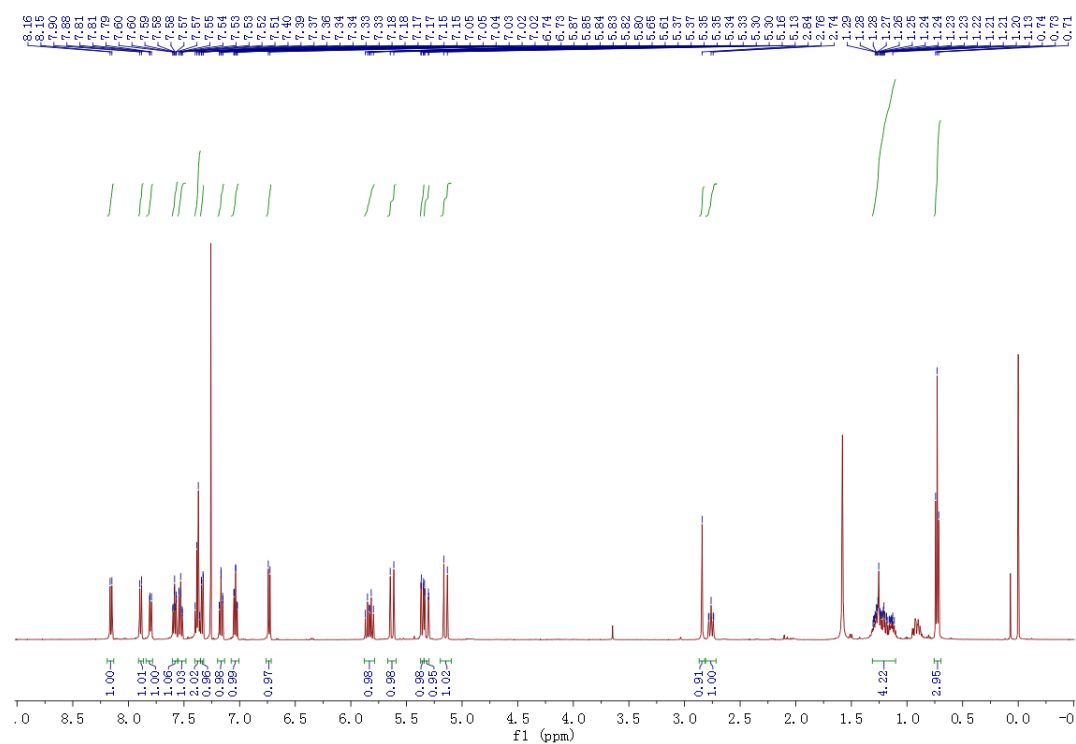
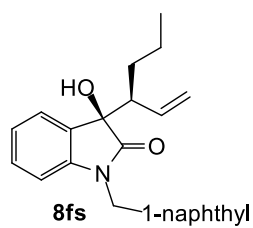
PeakTable

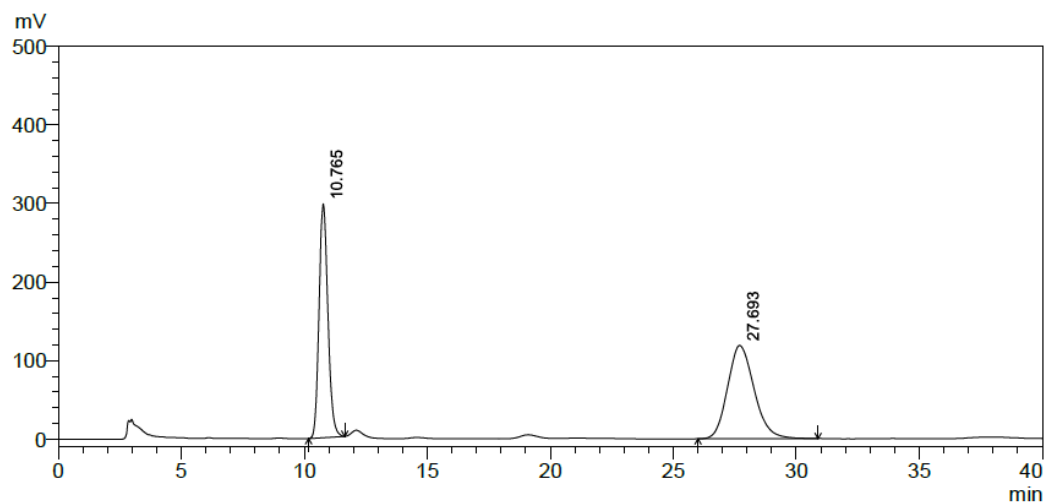
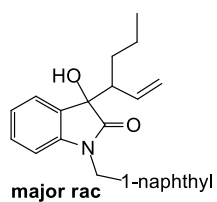
Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.563	25652557	198378	50.469	59.646
2	60.738	25176043	134215	49.531	40.354
Total		50828601	332592	100.000	100.000



PeakTable

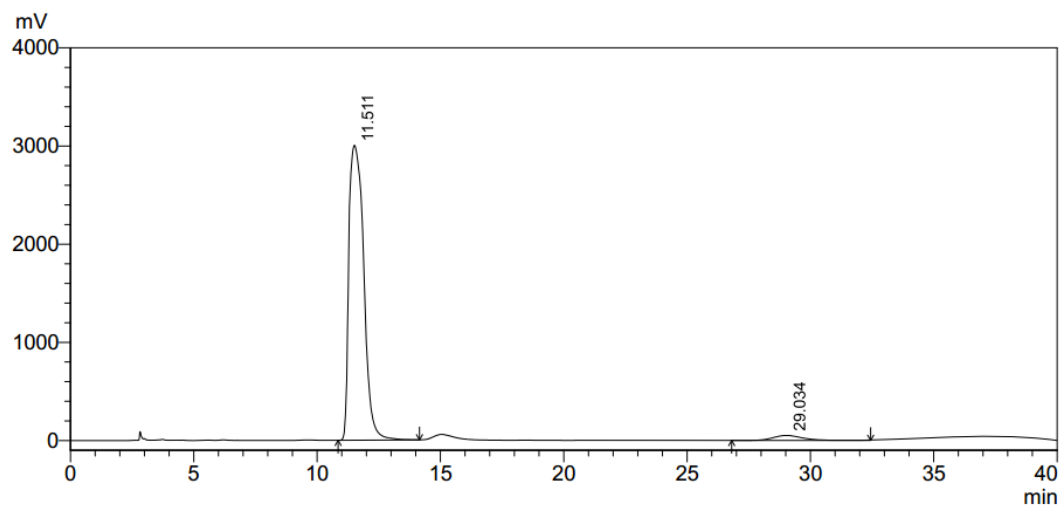
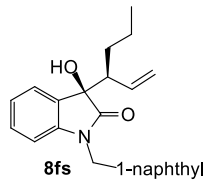
Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.983	600208	4148	0.440	0.558
2	58.668	135791815	738827	99.560	99.442
Total		136392023	742975	100.000	100.000





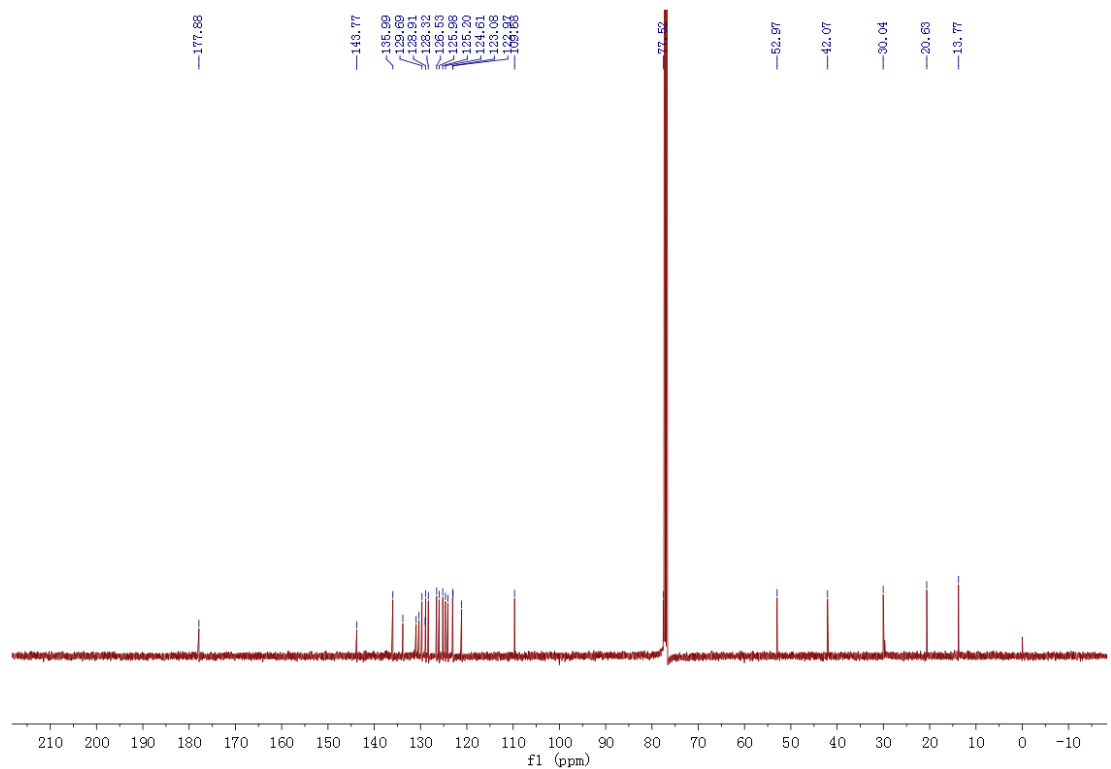
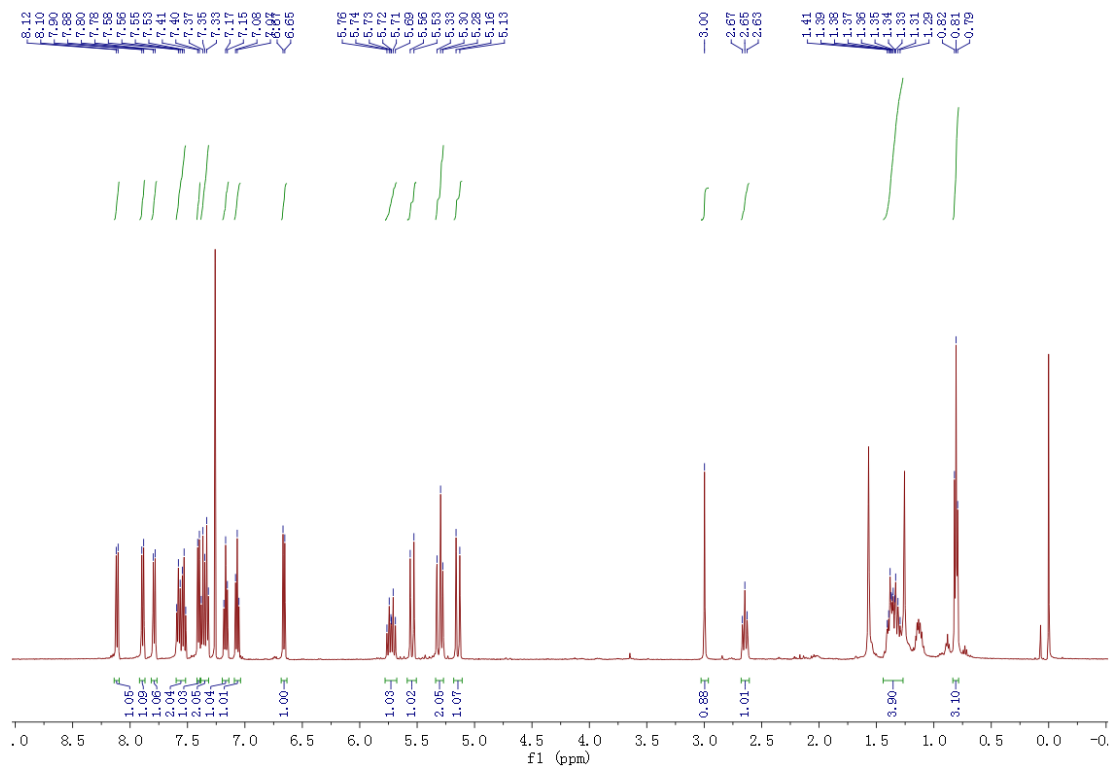
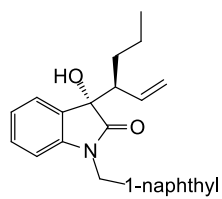
PeakTable

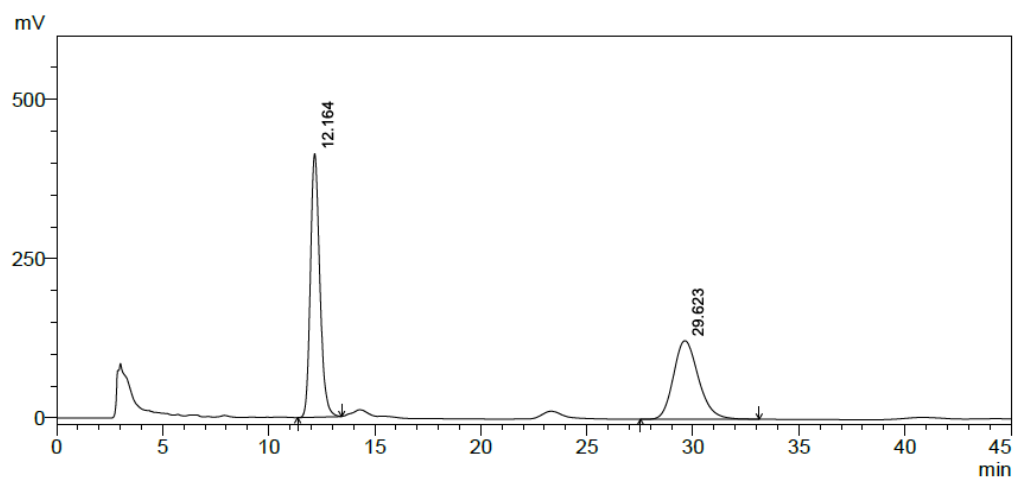
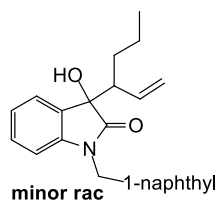
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.765	7455089	297532	45.573	71.479
2	27.693	8903395	118721	54.427	28.521
Total		16358485	416253	100.000	100.000



PeakTable

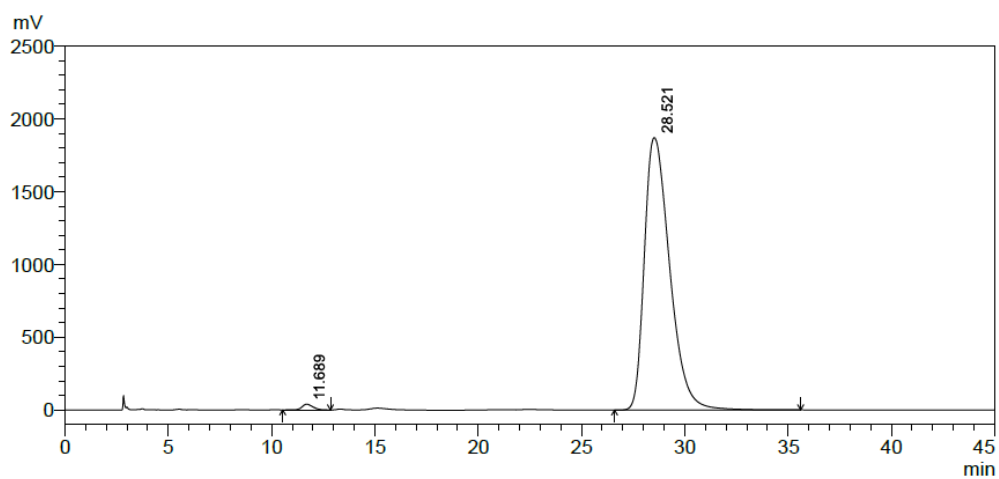
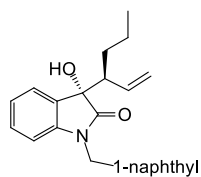
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.511	125495967	3004088	96.669	98.332
2	29.034	4324532	50948	3.331	1.668
Total		129820499	3055037	100.000	100.000





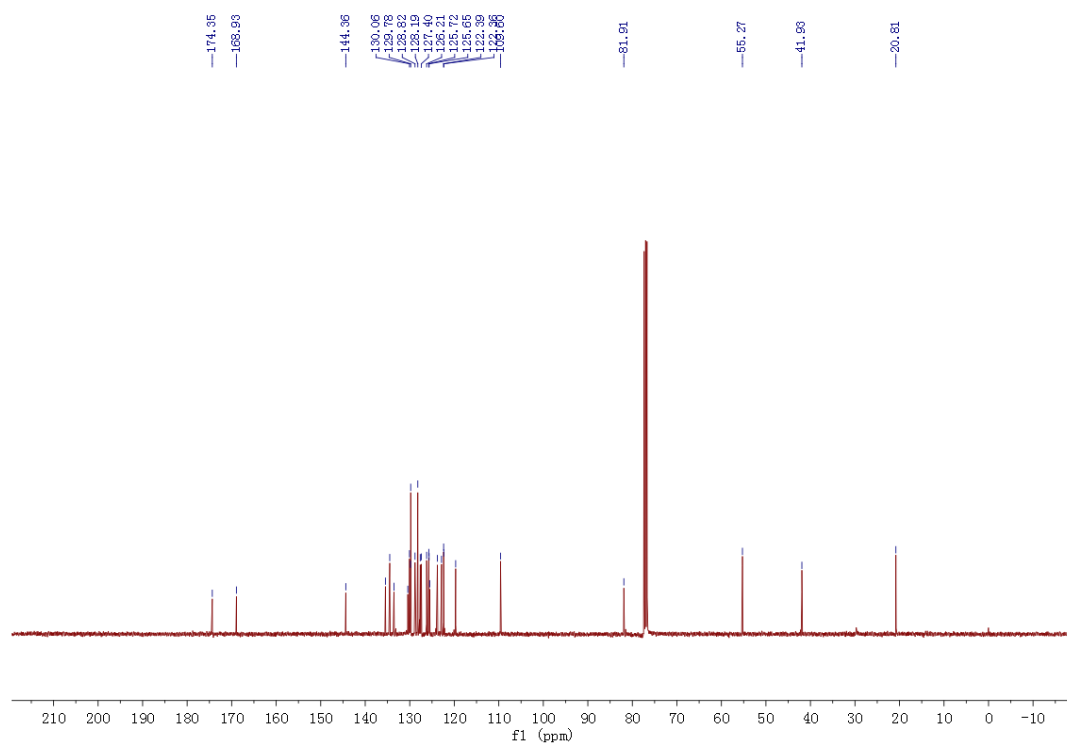
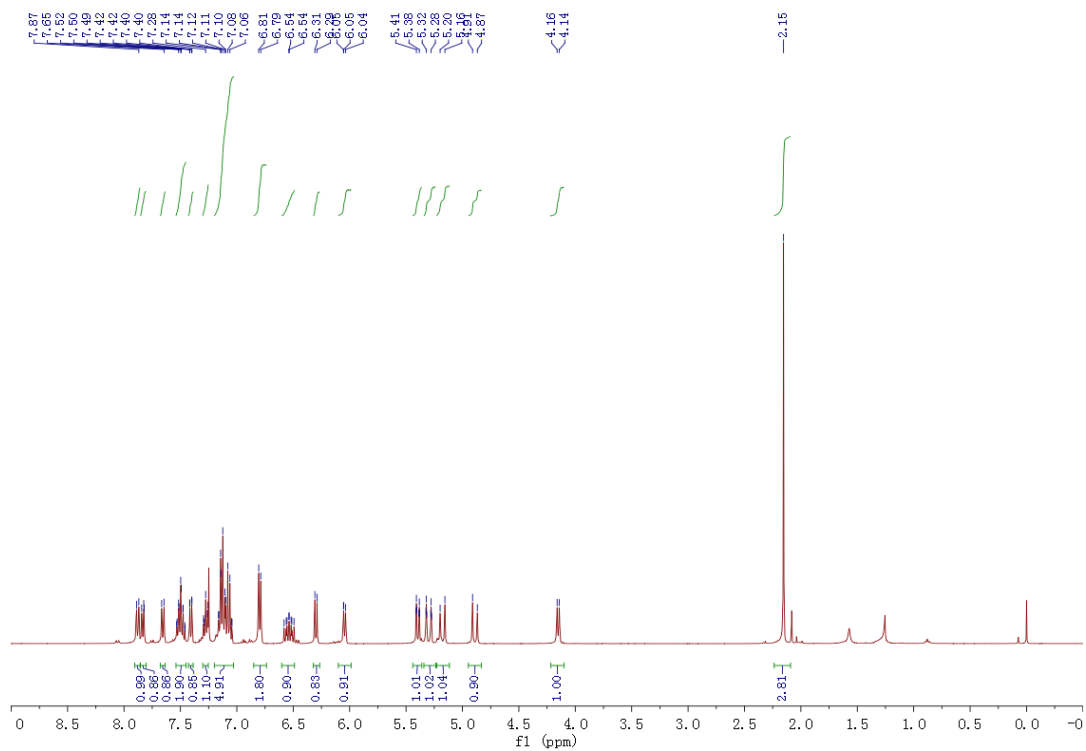
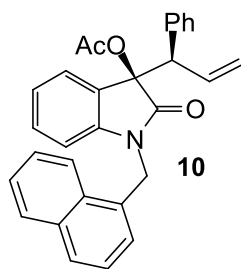
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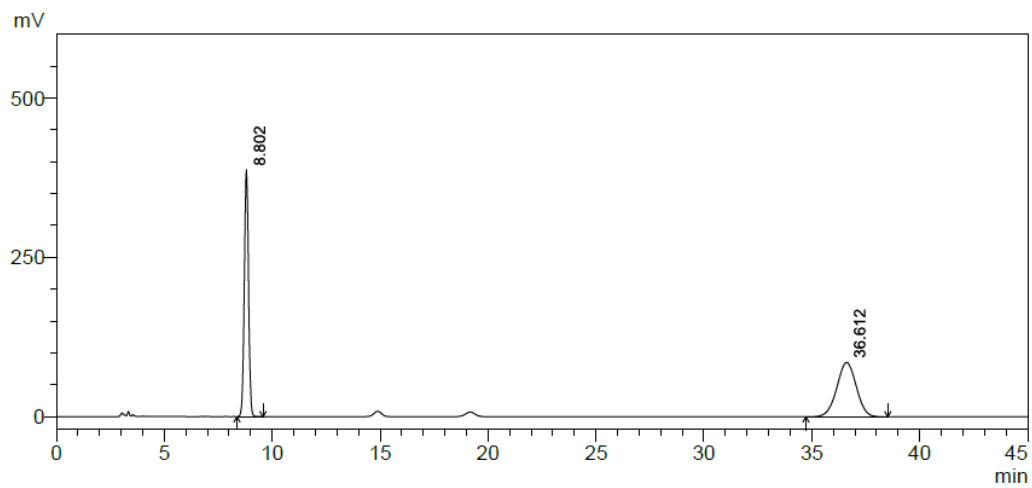
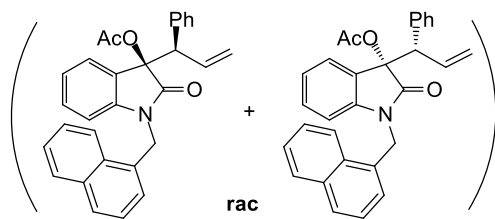
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.164	12739336	413622	55.688	77.038
2	29.623	10137113	123284	44.312	22.962
Total		22876449	536906	100.000	100.000



PeakTable

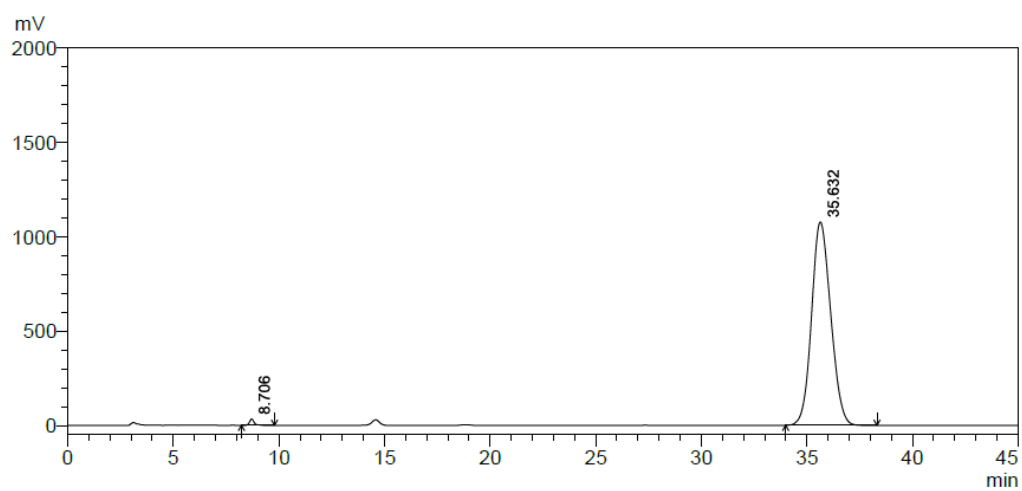
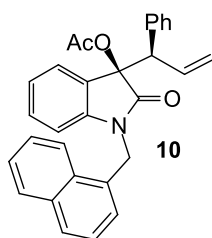
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.689	1407182	39062	0.873	2.045
2	28.521	159757790	1871182	99.127	97.955
Total		161164972	1910244	100.000	100.000





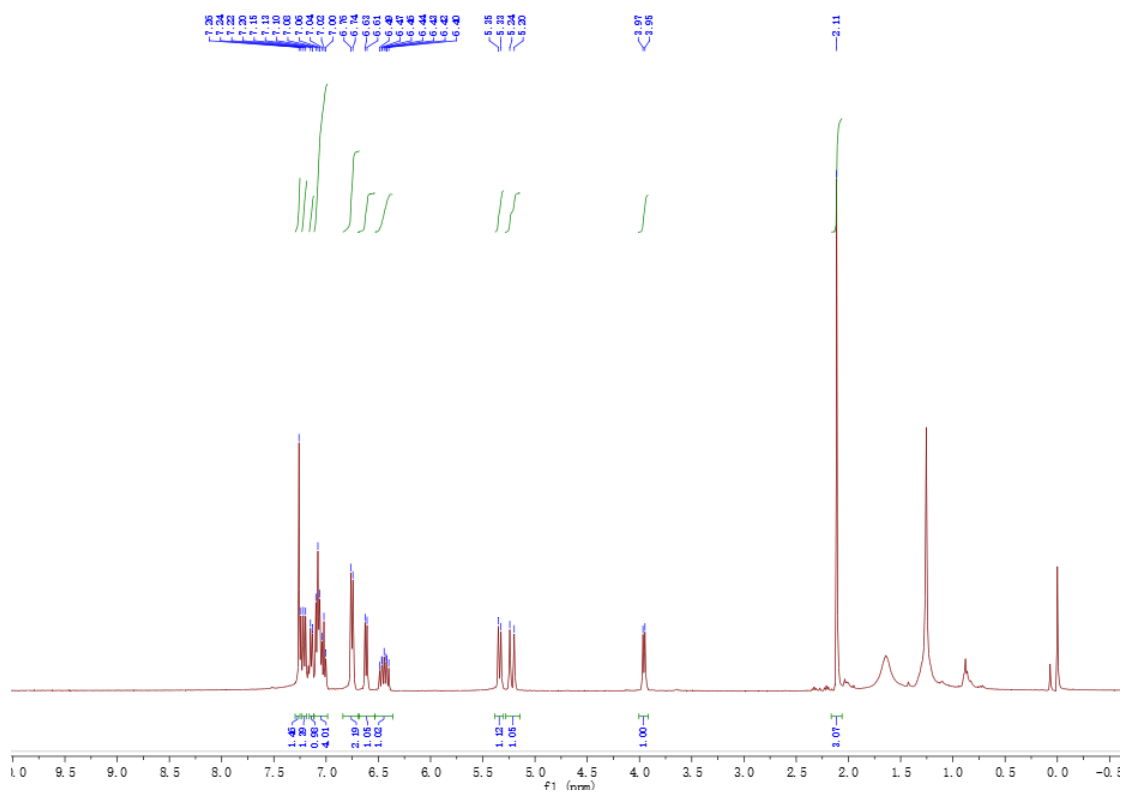
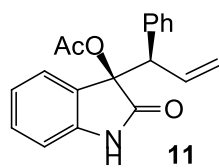
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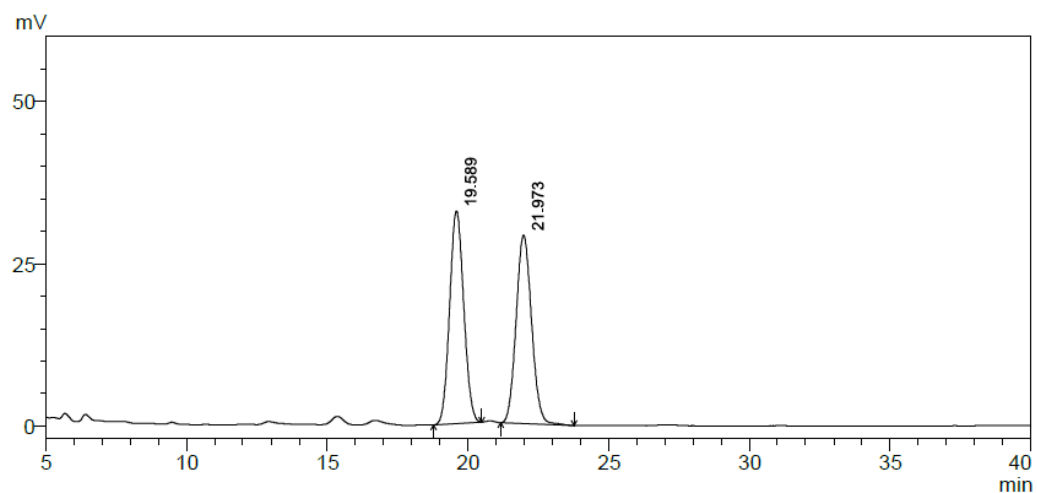
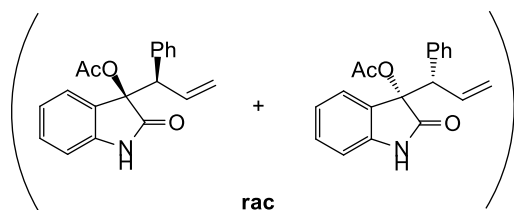
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.802	5264142	387072	49.607	81.969
2	36.612	5347492	85147	50.393	18.031
Total		10611635	472219	100.000	100.000



PeakTable

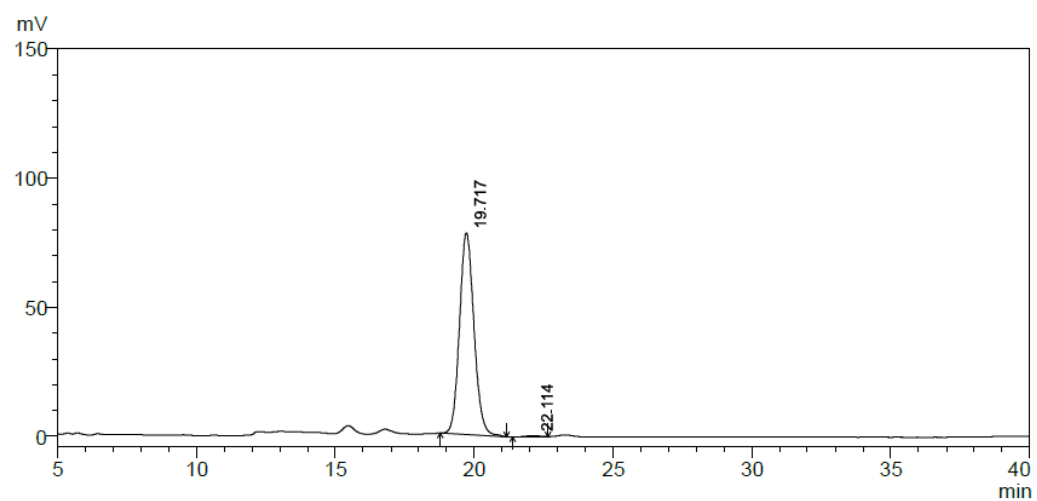
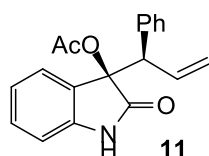
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.706	508790	33670	0.744	3.030
2	35.632	67920755	1077648	99.256	96.970
Total		68429546	1111318	100.000	100.000





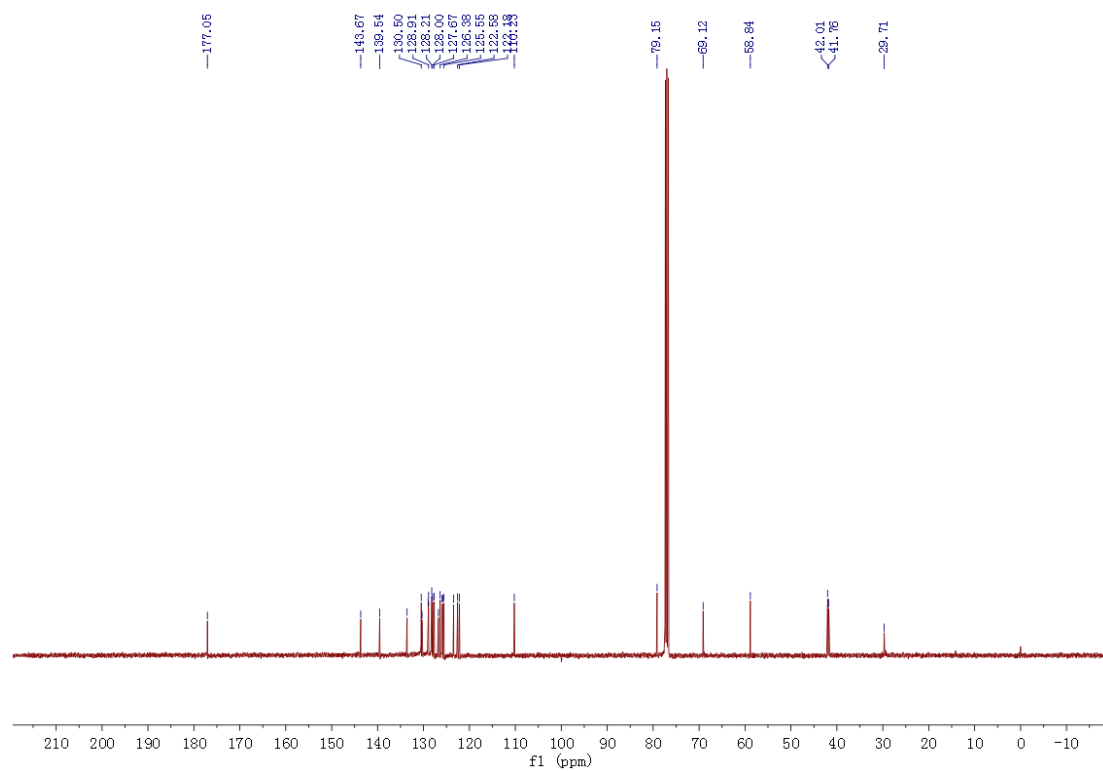
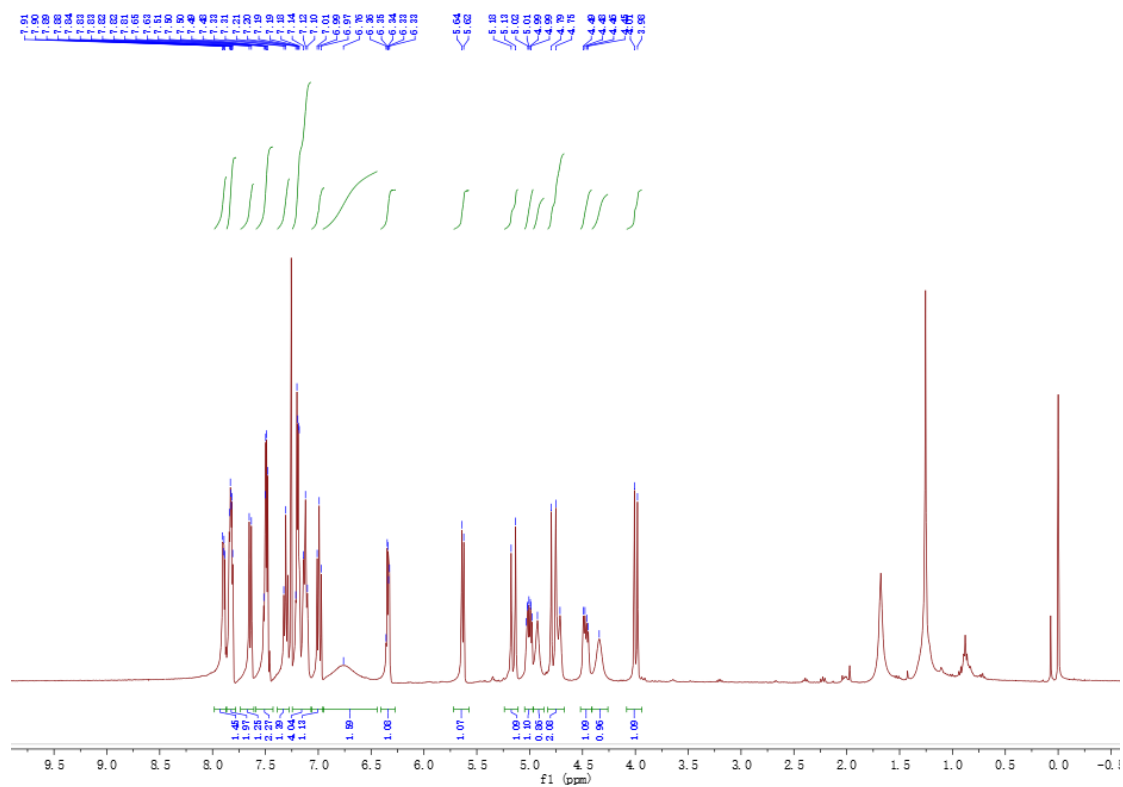
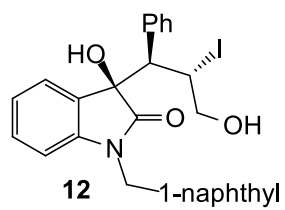
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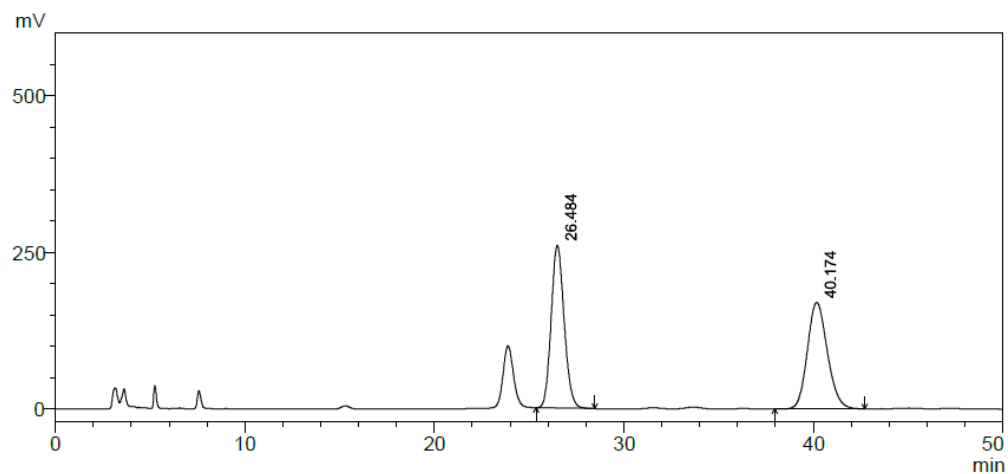
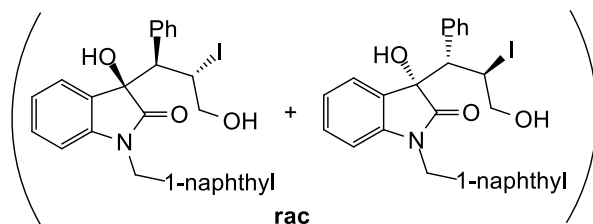
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.589	1142481	32759	50.742	53.014
2	21.973	1109071	29034	49.258	46.986
Total		2251552	61792	100.000	100.000



PeakTable

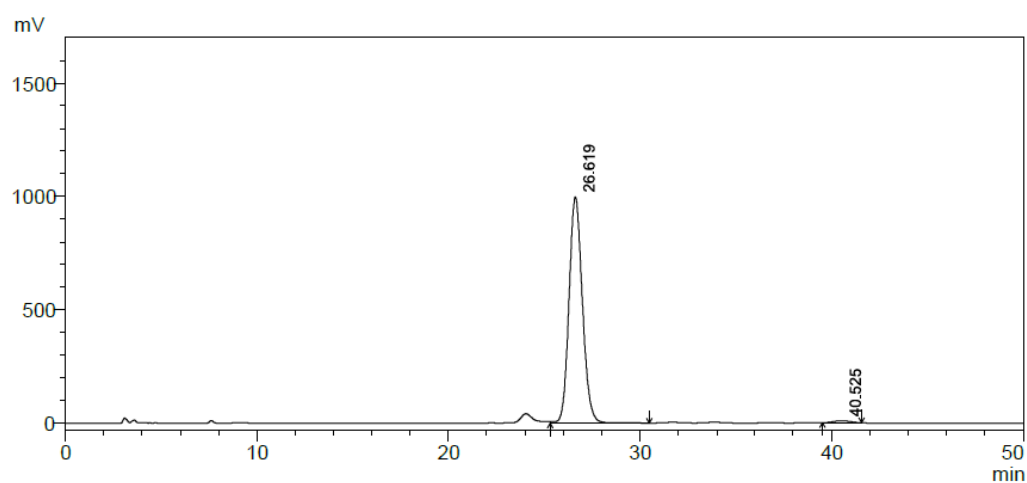
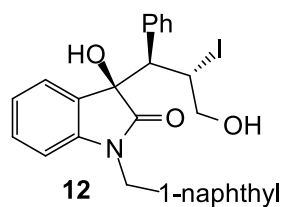
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.717	2843107	78279	99.500	99.459
2	22.114	14296	426	0.500	0.541
Total		2857402	78705	100.000	100.000





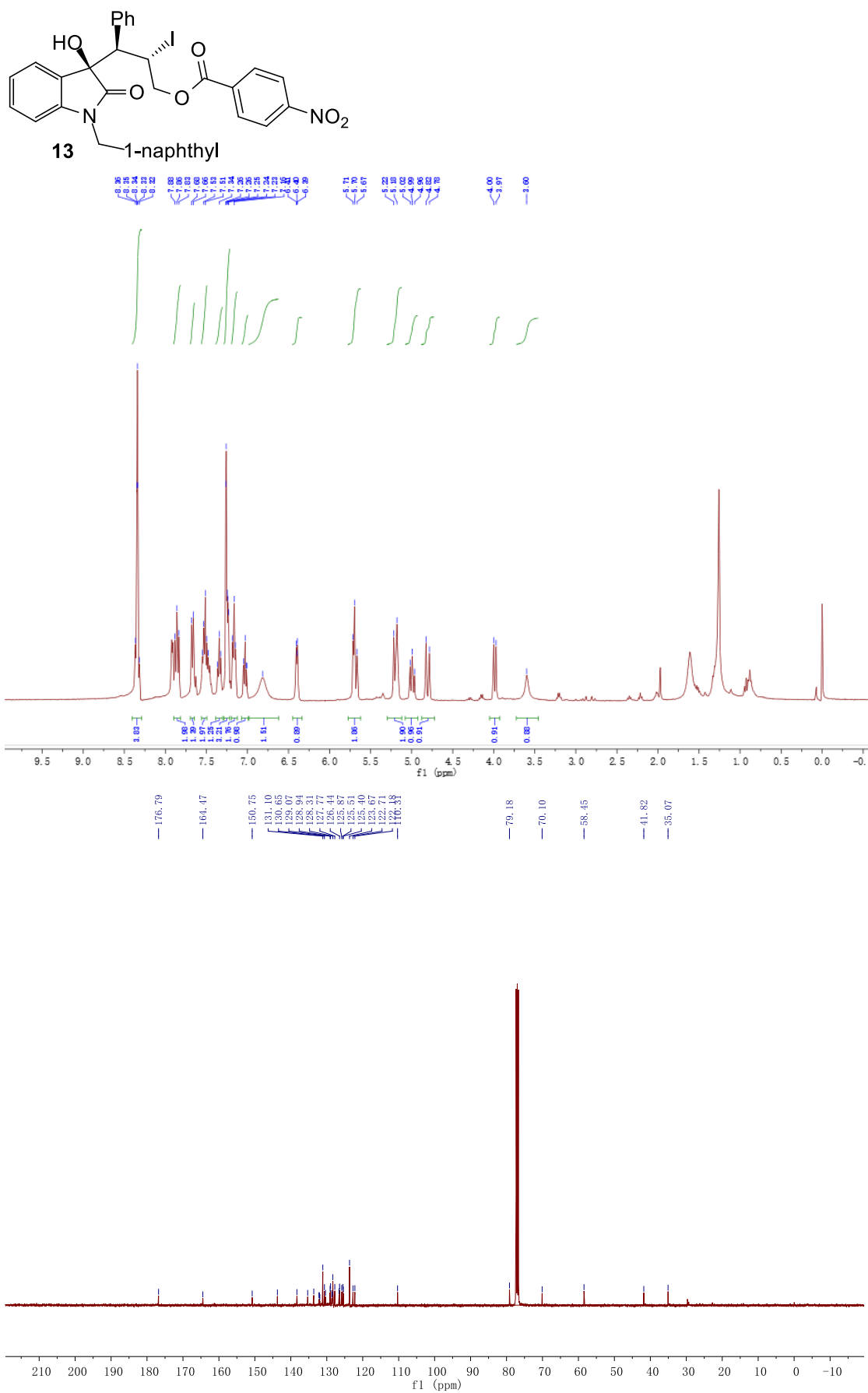
PeakTable

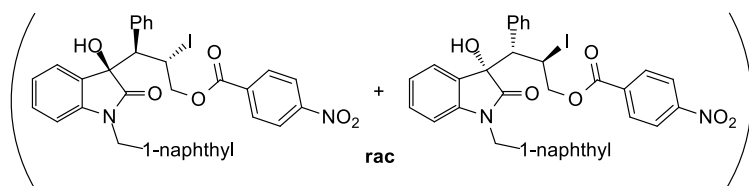
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.484	12407898	259977	49.904	60.461
2	40.174	12455521	170011	50.096	39.539
Total		24863419	429988	100.000	100.000



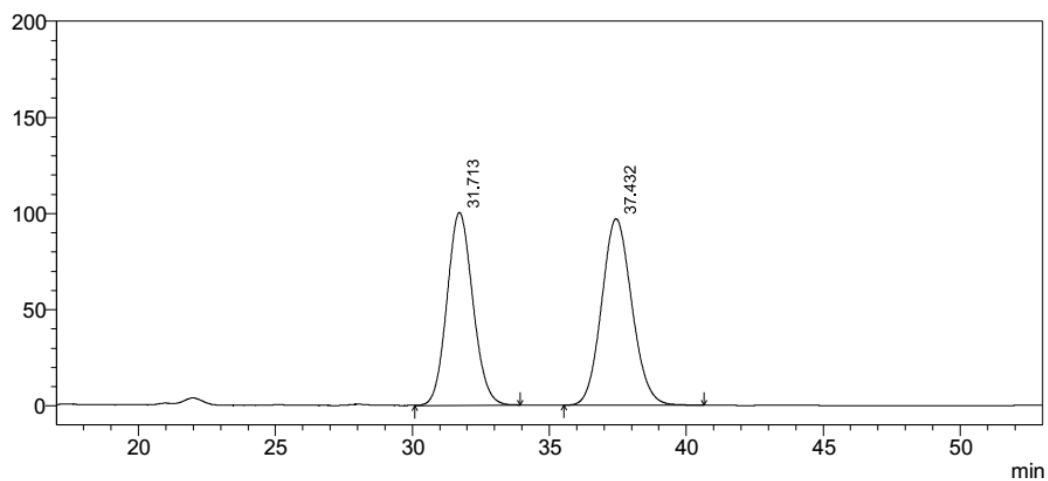
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.619	48738209	997798	98.939	99.167
2	40.525	522616	8379	1.061	0.833
Total		49260824	1006177	100.000	100.000



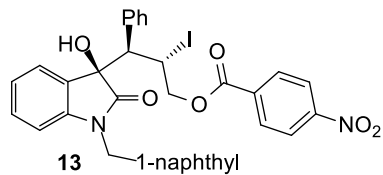


mV

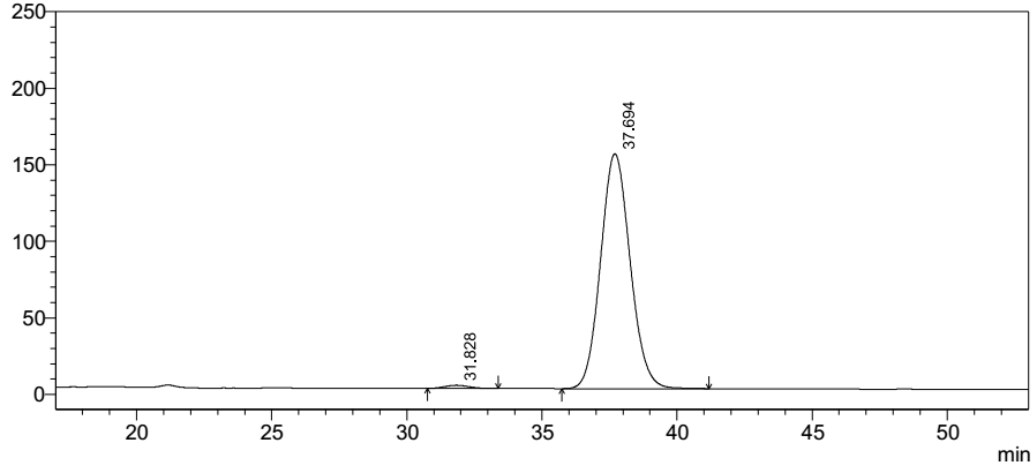


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.713	6575301	100316	46.892	50.857
2	37.432	7447035	96937	53.108	49.143
Total		14022336	197253	100.000	100.000



mV



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.828	134117	2121	1.134	1.363
2	37.694	11693606	153501	98.866	98.637
Total		11827723	155622	100.000	100.000