Supporting Information

NHC-Catalyzed Stereoselective Synthesis of Spirooxindole Lactones by *in situ* Generated Oxindole-embedded *o*-Quinone Methides and Aldehydes

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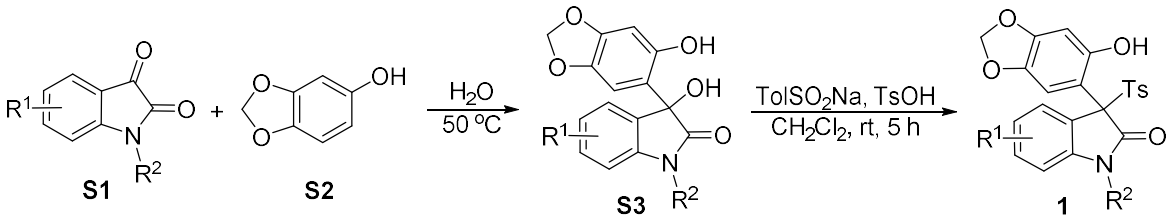
1. General Information

All ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 spectrometer and Bruker AVANCE NEO 600 spectrometer using tetramethylsilane as internal reference, and chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. ^{19}F NMR spectra were collected on Bruker AVANCE III HD 400 spectrometer and and Bruker AVANCE NEO 600 spectrometer at room temperature. Optical rotation was measured by the Perkin Elmer 341 polarimeter. The X-ray data was detected by SMART APEX II (Cu−$K\alpha$ radiation, λ = 1.54184) which was purchased from Bruker. The HRMS analyses were obtained on a Bruker Apex II FT-ICR mass spectrometer with ESI ionization method. The ee value determination was carried out using HPLC with chiral Chirapak column on Agilent 1260 with a UV-detector. Melting points were taken on an X–4 melting point apparatus and were uncorrected. Dichloromethane was freshly distilled from phosphorous pentoxide. THF and toluene were freshly distilled from a deep-blue solution of sodium-benzophenone under nitrogen. PhCl was dried by calcium hydride and freshly distilled under nitrogen atmosphere. DABCO, Et_3N and Cs_2CO_3 were purchased from commercial suppliers and used directly. All syntheses and manipulations were carried out under a dry nitrogen atmosphere. Flash column chromatography was carried out utilizing 200–300 mesh silica gel.

N-Heterocyclic carbene catalysts **A**–**F** were synthesized according to the literatures.[1]

2. Preparation of substrates

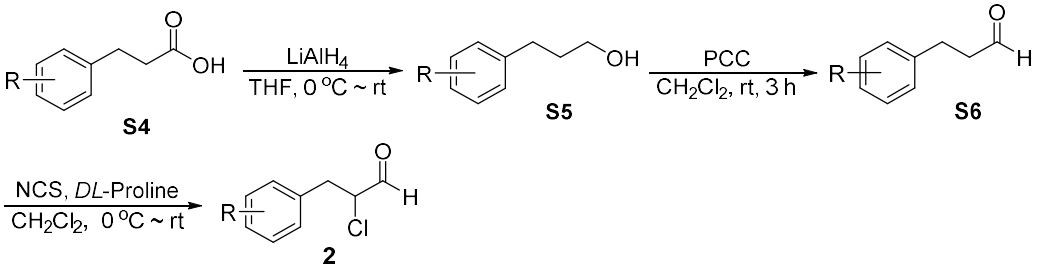
2.1 General procedure for the preparation of **1**[2]



A round-bottom flask was charged with isatin **S1** (12 mmol), phenol **S2** (18 mmol, 1.5 equiv.) and H_2O (50 mL). The reaction mixture was stirred vigorously at 50 °C and monitored by TLC. After the consumption of **S1**, the reaction mixture was extracted with ethyl acetate, and the combined organic layers were dried over anhydrous sodium sulfate. The solvent was concentrated in vacuo, and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1) to afford product **S3**.

$TolSO_2Na$ (1.66 g, 12 mmol, 1.2 equiv.) and TsOH (3.10 g, 18 mmol, 1.8 equiv.) were placed in a dried round-bottom flask, dry CH_2Cl_2 (30 mL) was added and the mixture was stirred at room temperature for 10 min. Then, a solution of **S3** (10 mmol) in CH_2Cl_2 (30 mL) was added and stirred for 5 h. The reaction mixture was quenched and adjusted to pH = 8 by saturated $NaHCO_3$. After extracted with CH_2Cl_2, the combined organic phases were washed with 1M HCl and brine, dried over Na_2SO_4, filtered and concentrated. The crude mixture was filtered by a short silica gel column (hexane/ethyl acetate) to afforded **1**.

2.2 General procedure for the preparation of α-chloroaldehyde **2**[3]

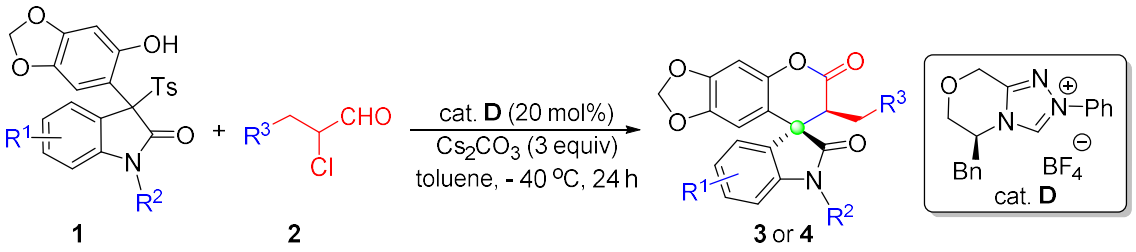


To the stirred solution of saturated acid **S4** (10 mmol) in anhydrous THF (50 mL) at 0 °C was added $LiAlH_4$ (30 mmol, 3.0 equiv.) in portions. Then, the solution was warmed to room temperature until completion of the reaction (monitored by TLC). After cooling down in ice-bath, a solution of aqueous saturated ammonium chloride was added carefully until H_2 evolvement ceased. The mixture was extracted with ethyl acetate and washed with brine. The combined organic phases were dried over by anhydrous Na_2SO_4, filtered through celite followed by evaporation under reduced pressure which was used in the next step without further purification.

PCC (Pyridinium chlorochromate, 15 mmol, 1.5 equiv.) was added slowly to the solution of alcohol **S5** (10 mmol) in CH_2Cl_2 (50 mL). The reaction was stirred for 3 h at room temperature until full conversion of **S5** (monitored by TLC). Then, the reaction mixture was filtered through celite, washed with CH_2Cl_2 and concentrated under reduced pressure to afford the crude product **S6**, which was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 10/1) to afford aldehyde.

To a stirred solution of aldehyde **S6** (1.34 g, 10 mmol) in CH_2Cl_2 (40 mL) was added *DL*-proline (230.0 mg, 2 mmol, 0.2 equiv.) and NCS (1.33 g, 10 mmol, 1.0 equiv.) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, and then warmed to rt and stirred for additional 1.5 h. The reaction was quenched by pentane (50 mL) and filtered through a short plug of celite. The organic phase was concentrated under reduced pressure and the residue was subjected to flash column chromatography (petroleum ether/ethyl acetate:15:1) to furnish α-chloroaldehyde **2** as a colorless oil (1.09 g, 65% yield).

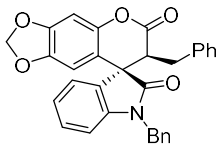
3. General procedure



Under argon atmosphere, a flame-dried 25 mL Schlenk tube was charged with **1** (0.1 mmol), **2** (0.25 mmol, 2.5 equiv.), Cs_2CO_3 (97.7 mg, 0.3 mmol, 3.0 equiv.) and Cat. **D** (7.6 mg, 0.02 mmol, 20 mol %). The tube was evacuated, filled with argon for 3 times and dry toluene (1.5 mL) was added at –40 °C. Subsequently, the resulting solution was continuously stirred at –40 °C for 24 h (monitored by TLC). The reaction mixture

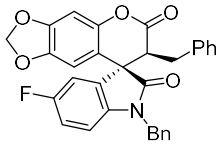
was filtered through silica gels column and the solvent was removed in *vacuo*. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:1 – 3:1) to obtain the products **3** or **4**.

(3*S*,7'*S*)-1,7'-dibenzylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3a)



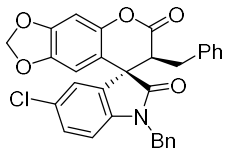
White solid, 38.7 mg, 79% yield, >20:1 dr, 96% ee, m.p. 130.1 – 131.7 °C, $[\alpha]_D^{18}$ +127 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 6H), 7.14 – 7.06 (m, 5H), 6.96 (d, J = 6.7 Hz, 2H), 6.86 (d, J = 7.9 Hz, 1H), 6.65 (s, 1H), 5.92 (s, 1H), 5.88 (s, 1H), 5.86 (s, 1H), 4.89 (d, J = 15.6 Hz, 1H), 4.83 (d, J = 15.6 Hz, 1H), 3.39 (dd, J = 8.2, 2.6 Hz, 1H), 3.21 (dd, J = 13.8, 8.2 Hz, 1H), 2.17 (dd, J = 13.9, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 167.9, 148.5, 147.2, 144.3, 144.2, 139.5, 135.4, 129.8, 129.0, 128.9, 128.7, 128.3, 128.2, 128.0, 127.7, 127.5, 126.3, 124.5, 123.8, 115.5, 110.1, 105.7, 101.9, 99.7, 54.6, 48.1, 44.1, 31.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{23}NO_5Na$: 512.1468; Found: 512.1468. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 83/17, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 31.053 min (minor), 35.370 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-5-fluorospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3b)



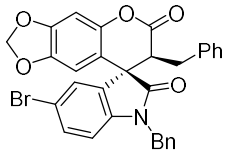
Yellow solid, 46.7 mg, 92% yield, >20:1 dr, 99% ee, m.p. 228.3 – 229.2 °C, $[\alpha]_D^{18}$ +192 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 5H), 7.17 – 7.05 (m, 3H), 6.98 (td, J = 8.8, 2.5 Hz, 1H), 6.95 – 6.86 (m, 2H), 6.83 – 6.72 (m, 2H), 6.69 (s, 1H), 5.93 (s, 1H), 5.91 (s, 1H), 5.90 (s, 1H), 4.86 (q, J = 15.6 Hz, 2H), 3.38 (dd, J = 7.6, 3.4 Hz, 1H), 3.30 (dd, J = 13.8, 7.6 Hz, 1H), 2.22 (dd, J = 13.8, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 167.5, 160.9, 158.4, 148.7, 147.1, 144.4, 140.0, 140.0, 139.0, 135.1, 129.7, 129.6, 129.0, 128.7, 128.3, 128.1, 127.5, 126.5, 116.4, 116.2, 114.8, 112.7, 112.4, 110.8, 110.7, 105.3, 102.0, 99.9, 54.9, 54.9, 47.8, 44.3, 31.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –118.34 (s). HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}FNO_5Na$: 530.1374; Found: 530.1382. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 15.726 min (minor), 29.175 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-5-chlorospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3c)



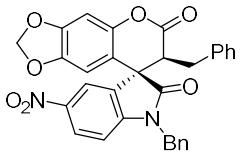
White solid, 37.2 mg, 71% yield, >20:1 dr, 91% ee, m.p. 146.3 – 147.7 °C, $[\alpha]_D^{19}$ +202 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 3H), 7.23 – 7.21 (m, 3H), 7.17 – 7.07 (m, 3H), 7.06 – 7.01 (m, 2H), 6.99 – 6.97 (m, 2H), 6.66 (s, 1H), 5.91 – 5.89 (m, 3H), 5.32 (d, *J* = 16.0 Hz, 1H), 5.23 (d, *J* = 16.0 Hz, 1H), 3.38 (dd, *J* = 8.1, 3.0 Hz, 1H), 3.19 (dd, *J* = 14.0, 8.1 Hz, 1H), 2.27 (dd, *J* = 14.0, 3.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 167.5, 148.7, 147.1, 144.4, 140.4, 139.0, 137.1, 132.4, 131.2, 128.9, 128.7, 128.3, 127.5, 126.8, 126.5, 124.6, 123.2, 116.3, 115.1, 105.5, 102.0, 99.8, 54.2, 48.0, 45.2, 31.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}ClNO_5Na$: 546.1078; Found: 546.1078. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 9.085 min (minor), 36.592 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-5-bromospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3d)



White solid, 35.8 mg, 63% yield, >20:1 dr, 87% ee, m.p. 223.4 – 234.6 °C, $[\alpha]_D^{19}$ +178 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 6H), 7.12 – 7.10 (m, 4H), 6.88 – 6.86 (m, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 5.94 (s, 1H), 5.92 (s, 1H), 5.90 (s, 1H), 4.88 (d, *J* = 15.5 Hz, 1H), 4.81 (d, *J* = 15.5 Hz, 1H), 3.39 (dd, *J* = 7.0, 3.8 Hz, 1H), 3.34 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.22 (dd, *J* = 13.7, 3.6 Hz, 1H). ^{1}H NMR (400 MHz, $CDCl_3$) δ 174.8, 167.5, 148.7, 147.1, 144.4, 143.0, 138.8, 134.9, 132.6, 130.0, 129.0, 128.6, 128.3, 128.2, 127.9, 127.5, 126.5, 116.4, 114.8, 111.3, 105.3, 102.0, 99.9, 54.6, 47.7, 44.2, 31.6. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}BrNO_5Na$: 590.0573; Found: 590.0589. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 75/25, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 37.534 min (minor), 41.221 min (major).

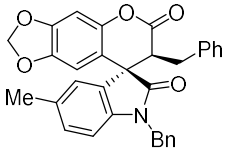
(3*S*,7'*S*)-1,7'-dibenzyl-5-nitrospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3e)



White solid, 32.0 mg, >20:1 dr, 60% yield, >99% ee, m.p. 156.3 – 157.6 °C, $[\alpha]_D^{20}$ +242 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.37 – 7.31 (m, 5H), 6.99 – 6.97 (m, 3H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.70 (d, *J* = 5.9 Hz, 3H), 5.88 (d, *J* = 6.7 Hz, 2H), 5.77 (s, 1H), 4.95 (d, *J* = 15.5 Hz, 1H), 4.88 (d, *J* = 15.5 Hz, 1H), 3.60 – 3.57 (m, 1H), 3.46 (dd, *J* = 14.6, 5.7 Hz, 1H), 2.23 (dd, *J* = 14.6, 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 167.2, 149.2, 149.0, 147.1, 144.5, 143.9, 138.4, 134.4, 129.3, 128.7, 128.6, 128.4, 128.2, 127.7, 126.4, 126.3, 120.9, 114.0, 109.4, 104.8, 102.1, 100.1, 54.2, 47.3, 44.6, 31.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{31}H_{23}N_2O_7$: 535.1500; Found: 535.1491. HPLC (Chiralpak AD–

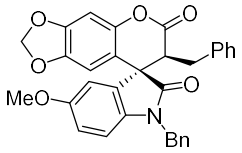
H column, *n*-hexane/*i*-PrOH = 55/45, flow rate = 1.0 mL/min, λ = 220 nm): t_R = 15.603 min (minor), 19.308 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-5-methylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3f)



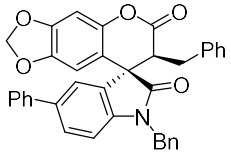
White solid, 45.8 mg, 91% yield, >20:1 dr, 90% ee, m.p. 234.1 – 235.3 °C, $[\alpha]_D^{19}$ +215 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 5H), 7.13 – 7.05 (m, 4H), 6.93 – 6.89 (m, 2H), 6.84 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 5.94 (s, 1H), 5.92 (d, *J* = 1.3 Hz, 1H), 5.90 (d, *J* = 1.2 Hz, 1H), 4.89 (d, *J* = 15.5 Hz, 1H), 4.82 (d, *J* = 15.5 Hz, 1H), 3.38 (dd, *J* = 7.6, 3.5 Hz, 1H), 3.28 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.25 (s, 3H), 2.22 (dd, *J* = 14.0, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 168.0, 148.4, 147.2, 144.2, 141.7, 139.5, 135.5, 133.5, 130.0, 129.0, 128.9, 128.7, 128.5, 128.2, 128.0, 127.9, 127.5, 126.2, 125.3, 115.7, 109.7, 105.7, 101.8, 99.7, 54.6, 48.0, 44.1, 31.5, 21.1. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{32}H_{25}NO_5Na$: 526.1624; Found: 526.1637. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 12.628 min (minor), 18.135 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-5-methoxyspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3g)



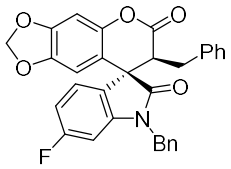
White solid, 48.7 mg, 92% yield, >20:1 dr, 90% ee, m.p. 225.1 – 226.2 °C, $[\alpha]_D^{18}$ +183 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 5H), 7.12 – 7.08 (m, 3H), 6.94 (d, *J* = 6.7 Hz, 2H), 6.81 – 6.79 (m, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.68 (s, 1H), 6.64 (s, 1H), 5.94 (s, 1H), 5.92 (s, 1H), 5.90 (s, 1H), 4.89 (d, *J* = 15.5 Hz, 1H), 4.81 (d, *J* = 15.5 Hz, 1H), 3.69 (s, 3H), 3.38 (dd, *J* = 7.4, 3.0 Hz, 1H), 3.30 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.23 (dd, *J* = 13.7, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 167.9, 156.7, 148.5, 147.1, 144.3, 139.5, 137.4, 135.5, 129.2, 128.9, 128.8, 128.2, 127.9, 127.5, 126.2, 115.5, 114.5, 111.3, 110.6, 105.7, 101.9, 99.7, 55.8, 55.0, 48.0, 44.2, 31.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{32}H_{25}NO_6Na$: 542.1574; Found: 542.1576. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 20.042 min (minor), 34.554 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-5-phenylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3h)



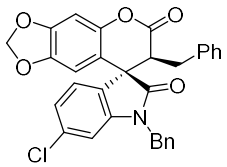
White solid, 43.9 mg, >20:1 dr, 78% yield, 88% ee, m.p. 121.4 – 122.9 °C, $[\alpha]_D^{20}$ +245 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.2, 1.6 Hz, 1H), 7.40 – 7.26 (m, 10H), 7.20 (d, J = 1.3 Hz, 1H), 7.10 – 7.01 (m, 3H), 6.93 – 6.89 (m, 3H), 6.69 (s, 1H), 5.96 (s, 1H), 5.85 – 5.82 (m, 2H), 4.91 (s, 2H), 3.42 – 3.34 (m, 2H), 2.25 (dd, J = 13.3, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 168.0, 148.5, 147.2, 144.3, 143.4, 140.1, 139.5, 137.2, 135.4, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3, 128.1, 127.6, 127.4, 126.8, 126.4, 123.5, 115.4, 110.2, 105.6, 101.9, 99.8, 54.7, 48.1, 44.3, 31.6. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{37}H_{28}NO_5$: 566.1962; Found: 566.1955. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 30/70, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 31.188 min (minor), 42.298 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-6-fluorospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3i)



White solid, 43.6 mg, >20:1 dr, 86% yield, 95% ee, m.p. 110.1 – 112.6 °C, $[\alpha]_D^{20}$ +228 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.30 – 7.28 (m, 3H), 7.14 – 7.08 (m, 3H), 7.02 – 6.99 (m, 1H), 6.92 (d, J = 7.0 Hz, 2H), 6.77 – 6.74 (m, 1H), 6.69 (s, 1H), 6.60 – 6.58 (m, 1H), 5.93 – 5.90 (m, 3H), 4.87 (d, J = 15.6 Hz, 1H), 4.80 (d, J = 15.6 Hz, 1H), 3.39 – 3.37 (m, 1H), 3.27 (dd, J = 14.0, 7.7 Hz, 1H), 2.21 (dd, J = 14.0, 3.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 167.7, 148.6, 147.1, 145.6, 145.6, 144.3, 139.2, 134.8, 129.1, 128.8, 128.3, 128.2, 127.5, 126.4, 125.8, 125.7, 123.3, 123.3, 115.2, 110.2, 110.0, 105.4, 101.9, 99.8, 98.9, 98.7, 54.2, 48.1, 44.3, 31.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ –108.93 (s). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{31}H_{23}FNO_5$: 508.1555; Found: 508.1550. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 13.582 min (minor), 16.532 min (major).

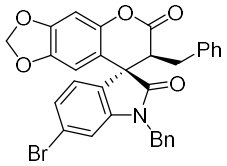
(3*S*,7'*S*)-1,7'-dibenzyl-6-chlorospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3j)



White solid, 48.9 mg, 78% yield, >20:1, 94% ee, m.p. 236.9 – 237.7 °C, $[\alpha]_D^{18}$ +186 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.13 – 7.09 (m, 3H), 7.06 – 7.03 (m, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.93 – 6.92 (m, 2H), 6.84 (s, 1H), 6.69 (s, 1H), 5.93 (s, 1H), 5.91 (s, 1H), 5.90 (s, 1H), 4.87 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 3.38 (dd, J = 7.6, 3.3 Hz, 1H), 3.27 (dd, J = 13.9, 7.7 Hz, 1H), 2.21 (dd, J = 13.9, 3.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 167.6, 148.7, 147.1, 145.2, 144.4, 139.1, 135.6, 134.8, 129.1, 128.8, 128.3, 128.2, 127.4, 126.4, 125.5, 123.7, 114.9, 110.6, 105.4, 102.0, 99.9, 54.2, 47.9, 44.3, 31.5.

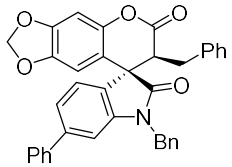
HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}ClNO_5Na$: 546.1078; Found: 546.1076. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 11.605 min (major), 14.283 min (minor).

(3*S*,7'*S*)-1,7'-dibenzyl-6-bromospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3k)



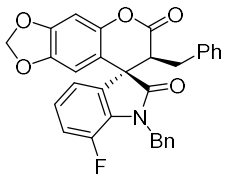
White solid, 39.8 mg, 70% yield, >20:1 dr, 93% ee, m.p. 245.7 – 247.2 °C, $[\alpha]_D^{18}$ +238 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 – 7.27 (m, 5H), 7.20 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.15 – 7.08 (m, 3H), 6.99 (d, *J* = 1.4 Hz, 1H), 6.92 – 6.91 (m, 3H), 6.69 (s, 1H), 5.93 (s, 1H), 5.92 (s, 1H), 5.90 (s, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 3.37 (dd, *J* = 7.6, 3.4 Hz, 1H), 3.27 (dd, *J* = 13.9, 7.7 Hz, 1H), 2.21 (dd, *J* = 13.9, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 175.1, 167.5, 148.7, 147.1, 145.4, 144.4, 139.1, 134.8, 129.1, 128.7, 128.3, 128.2, 127.4, 127.0, 126.6, 126.4, 125.8, 123.4, 114.8, 113.3, 105.4, 102.0, 99.9, 54.3, 47.9, 44.2, 31.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}BrNO_5Na$: 590.0573; Found: 339.0559. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 11.288 min (minor), 14.784 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-6-phenylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3l)



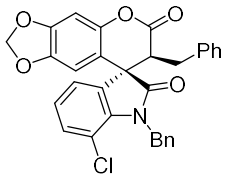
White solid, 48.0 mg, >20:1 dr, 85% yield, 96% ee, m.p. 133.3 – 1347 °C, $[\alpha]_D^{20}$ +219 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.50 – 7.44 (m, 4H), 7.40 – 7.38 (m, 1H), 7.33 (d, *J* = 4.4 Hz, 4H), 7.29 – 7.26 (m, 2H), 7.13 – 7.09 (m, 4H), 7.04 (d, *J* = 1.1 Hz, 1H), 6.96 (d, *J* = 6.6 Hz, 2H), 6.70 (s, 1H), 6.01 (s, 1H), 5.93 – 5.91 (m, 2H), 4.95 (d, *J* = 15.6 Hz, 1H), 4.90 (d, *J* = 15.6 Hz, 1H) 3.44 – 3.42 (m, 1H), 3.29 (dd, *J* = 14.0, 7.8 Hz, 1H), 2.29 (dd, *J* = 14.0, 3.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 175.5, 167.9, 148.5, 147.2, 144.7, 144.3, 143.2, 140.4, 139.4, 135.4, 129.0, 129.0, 128.8, 128.3, 128.0, 128.0, 127.5, 127.2, 126.9, 126.3, 124.8, 122.7, 115.5, 108.7, 105.7, 101.9, 99.8, 54.5, 48.2, 44.2, 31.6. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{37}H_{28}NO_5$: 566.1962; Found: 566.1954. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 35/65, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 36.503 min (minor), 39.938 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-7-fluorospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3m)



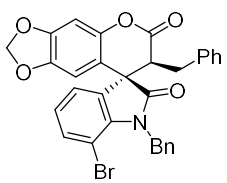
White solid, 44.7 mg, 88% yield, >20:1 dr, 92% ee, m.p. 237.1 – 238.4 °C, $[\alpha]_D^{18}$ +54 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 5H), 7.14 – 7.01 (m, 5H), 6.92 – 6.86 (m, 3H), 6.67 (s, 1H), 5.89 (dd, J = 6.5, 1.2 Hz, 2H), 5.86 (s, 1H), 5.03 – 4.95 (m, 2H), 3.37 (dd, J = 7.9, 3.2 Hz, 1H), 3.20 (dd, J = 14.1, 8.0 Hz, 1H), 2.18 (dd, J = 14.0, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 167.5, 148.9, 148.7, 147.1, 146.4, 144.3, 139.1, 136.6, 131.1, 131.1, 131.0, 130.9, 128.8, 128.7, 128.3, 127.9, 127.8, 127.8, 126.4, 124.6, 124.5, 120.5, 120.5, 118.0, 117.8, 115.0, 105.5, 102.0, 99.8, 54.8, 54.8, 48.0, 45.7, 45.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –131.94 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{31}H_{22}FNO_5Na$: 530.1374; Found: 530.1347. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 10.182 min (minor), 29.873 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-7-chlorospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3n)



White solid, 49.3 mg, 94% yield, >20:1 dr, 86% ee, m.p. 156.8 – 157.5 °C, $[\alpha]_D^{19}$ +194 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 6H), 7.18 – 7.08 (m, 3H), 7.06 – 7.01 (m, 2H), 6.99 – 6.97 (m, 2H), 6.68 (s, 1H), 5.93 – 5.91 (m, 3H), 5.33 (d, J = 16.0 Hz, 1H), 5.24 (d, J = 16.0 Hz, 1H), 3.37 (dd, J = 8.1, 3.0 Hz, 1H), 3.19 (dd, J = 14.0, 8.1 Hz, 1H), 2.27 (dd, J = 14.0, 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 167.5, 148.7, 147.1, 144.4, 140.4, 139.0, 137.1, 132.4, 131.2, 128.9, 128.7, 128.3, 127.5, 126.8, 126.5, 124.6, 123.2, 116.3, 115.2, 105.5, 102.0, 99.8, 54.3, 48.0, 45.2, 31.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}ClNO_5Na$: 546.1078; Found: 546.1078. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 40/60, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 8.280 min (minor), 30.610 min (major).

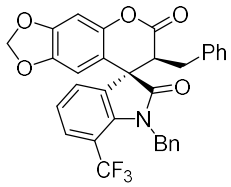
(3*S*,7'*S*)-1,7'-dibenzyl-7-bromospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3o)



White solid, 47.7 mg, 84% yield, >20:1 dr, 88% ee, m.p. 196.3 – 198.1 °C, $[\alpha]_D^{18}$ +179 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$)

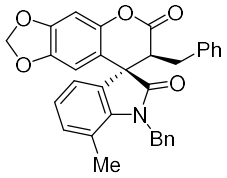
δ 7.49 (d, J = 8.0 Hz, 1H), 7.29 – 7.07 (m, 9H), 7.00 (t, J = 7.8 Hz, 3H), 6.66 (s, 1H), 5.92 (s, 2H), 5.90 (s, 1H), 5.37 (d, J = 16.3 Hz, 1H), 5.28 (d, J = 16.2 Hz, 1H), 3.37 (dd, J = 8.1, 2.8 Hz, 1H), 3.18 (dd, J = 13.9, 8.2 Hz, 1H), 2.29 (dd, J = 13.9, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 167.4, 148.7, 147.1, 144.4, 141.8, 139.0, 137.0, 135.8, 131.6, 128.9, 128.7, 128.3, 127.4, 126.6, 126.5, 125.0, 123.8, 115.2, 105.4, 103.4, 102.0, 99.8, 54.2, 48.1, 44.8, 31.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}BrNO_5Na$: 590.0573; Found: 590.0575. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 40/60, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 8.294 min (minor), 30.418 min (major).

(3*S*,7'*S*)-1,7'-dibenzyl-7-(trifluoromethyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3p)



White solid, 36.5 mg, >20:1 dr, 66% yield, 98% ee, m.p. 107.5 – 108.9 °C, $[\alpha]_D^{20}$ +102 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 1H), 7.30 – 7.06 (m, 11H), 6.95 (d, J = 6.9 Hz, 2H), 6.69 (s, 1H), 5.94 – 5.89 (m, 3H), 5.21 (d, J = 16.9 Hz, 1H), 5.03 (d, J = 16.9 Hz, 1H), 3.44 – 3.42 (m, 1H), 3.21 (dd, J = 14.2, 7.7 Hz, 1H), 2.31 (dd, J = 14.2, 3.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 167.2, 148.8, 147.2, 144.4, 142.5, 138.7, 135.8, 131.1, 128.8, 128.4, 128.4, 127.2, 126.5, 126.0, 123.2, 114.8, 105.2, 102.0, 100.0, 52.9, 47.9, 45.9, 31.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ –54.91 (s). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{32}H_{23}F_3NO_5$: 558.1523; Found: 558.1518. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 6.272 min (minor), 17.414 min (major).

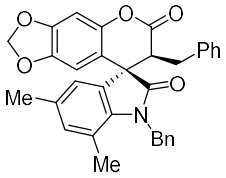
(3*S*,7'*S*)-1,7'-dibenzyl-7-methylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3q)



Yellow solid, 45.3 mg, 90% yield, >20:1 dr, > 99% ee, m.p. 106.3 – 107.9 °C, $[\alpha]_D^{18}$ +268 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 3H), 7.21 – 7.03 (m, 10H), 6.67 (s, 1H), 6.00 (s, 1H), 5.93 (s, 1H), 5.91 (s, 1H), 5.19 (d, J = 16.8 Hz, 1H), 5.06 (d, J = 16.8 Hz, 1H), 3.37 (dd, J = 8.6, 2.0 Hz, 1H), 3.19 (dd, J = 13.7, 8.7 Hz, 1H), 2.36 – 2.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 167.9, 148.4, 147.2, 144.2, 142.5, 139.4, 137.3, 133.8, 129.1, 129.0, 128.3, 127.4, 126.4, 125.7, 123.9, 122.4, 120.8, 116.1, 105.8, 101.9, 99.7, 54.1, 48.3, 45.3, 31.5, 18.9. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{32}H_{25}NO_5Na$: 526.1624; Found: 526.1637. HPLC

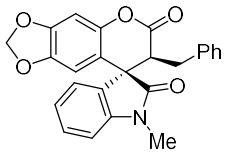
(Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 11.684 min (minor), 50.528 min .(major)

(3*S*,7'*S*)-1,7'-dibenzyl-5,7-dimethylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3r)



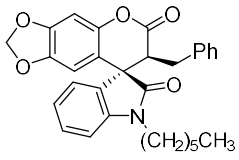
White solid, 43.5 mg, 84% yield, >20:1 dr, 92% ee, m.p. 124.3 – 125.6 °C, $[\alpha]_D^{18}$ +208 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.30 – 7.10 (m, 8H), 7.04 – 7.02 (m, 2H), 6.88 (s, 1H), 6.79 (s, 1H), 6.67 (s, 1H), 6.02 (s, 1H), 5.92 (dd, *J* = 10.0, 1.2 Hz, 2H), 5.17 (d, *J* = 16.8 Hz, 1H), 5.03 (d, *J* = 16.7 Hz, 1H), 3.36 (dd, *J* = 8.2, 2.7 Hz, 1H), 3.23 (dd, *J* = 13.8, 8.2 Hz, 1H), 3.35 (dd, *J* = 13.8, 2.6 Hz, 1H), 2.30 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.3, 168.0, 148.4, 147.2, 144.2, 140.0, 139.6, 137.4, 134.2, 133.5, 129.0, 128.9, 128.8, 128.2, 127.4, 126.3, 125.8, 123.1, 120.5, 116.3, 105.8, 101.9, 99.7, 54.1, 48.2, 45.2, 31.5, 20.8, 18.7. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{33}H_{27}NO_5Na$: 540.1781; Found: 540.1775. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 40/60, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 36.632 min (minor), 50.335 min (major).

(3*S*,7'*S*)-7'-benzyl-1-methylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3s)



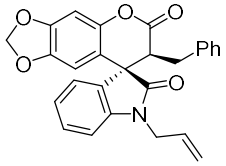
Yellow solid, 26.9 mg, 65% yield, >20:1 dr, 97% ee, m.p. 223.9 – 224.3 °C, $[\alpha]_D^{19}$ +222 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.46 – 7.42 (m, 1H), 7.20 – 7.08 (m, 5H), 6.99 – 6.96 (m, 3H), 6.66 (s, 1H), 5.91 (s, 2H), 5.87 (s, 1H), 3.35 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.15 – 3.12 (m, 4H), 2.23 (dd, *J* = 13.9, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 175.2, 168.0, 148.4, 147.1, 145.1, 144.1, 139.2, 130.0, 129.0, 128.2, 128.1, 126.3, 124.5, 123.8, 115.5, 108.9, 105.8, 101.8, 99.7, 54.6, 47.8, 31.3, 26.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{25}H_{19}NO_5Na$: 436.1155; Found: 436.1155. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 14.382 min (minor), 17.281 min (major).

(3*S*,7'*S*)-7'-benzyl-1-hexylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3t)



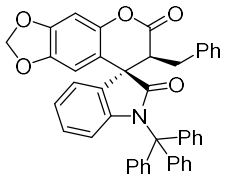
Reddish brown liquid, 40.1 mg, 83% yield, >20:1 dr, 91% ee, $[\alpha]_D^{19}$ +236 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 1H), 7.17 – 7.06 (m, 5H), 7.01 – 6.98 (m, 3H), 6.61 (s, 1H), 5.90 (s, 1H), 5.84 (dd, *J* = 16.9, 1.1 Hz, 2H), 3.73 – 7.61 (m, 2H), 3.35 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.17 (dd, *J* = 13.9, 8.2 Hz, 1H), 2.18 (dd, *J* = 13.8, 2.5 Hz, 1H), 1.71– 1.63 (m, 2H), 1.32 – 1.26 (m, 6H), 0.85 – 0.82 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 168.0, 148.4, 147.1, 144.6, 144.2, 139.5, 129.9, 128.9, 128.3, 128.3, 126.3, 124.6, 123.6, 115.6, 109.3, 105.7, 101.9, 99.6, 54.6, 47.9, 40.3, 31.4, 31.3, 27.4, 26.5, 22.5, 14.0. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{30}H_{29}NO_5Na$: 546.1078; Found: 546.1076. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 33.486 min (minor), 43.341 min (major).

(3*S*,7'*S*)-1-allyl-7'-benzylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3u)



Yellow solid, 28.1 mg, 64% yield, >20:1 dr, 84% ee, m.p. 182.7 – 184.6 °C, $[\alpha]_D^{19}$ +303 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 1H), 7.19 – 7.08 (m, 5H), 7.01 – 6.95 (m, 3H), 6.66 (s, 1H), 5.92 (s, 1H), 5.90 (s, 1H), 5.87 (s, 1H), 5.85 – 5.76 (m, 1H), 5.26 – 5.22 (m, 2H), 4.30 (d, *J* = 5.2 Hz, 2H), 3.37 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.18 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.22 (dd, *J* = 13.8, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 167.9, 148.5, 147.2, 144.3, 144.2, 139.4, 130.9, 129.8, 128.9, 128.3, 128.1, 126.3, 124.5, 123.8, 118.2, 115.4, 109.9, 105.7, 101.9, 99.7, 54.6, 48.0, 42.5, 31.4. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{27}H_{21}NO_5Na$: 462.1311; Found: 462.1310. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 48/52, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 9.128 min (minor), 11.622 min (major).

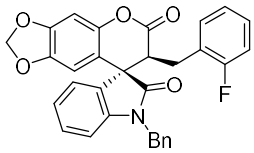
(3*S*,7'*S*)-7'-benzyl-1-tritylspiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (3v)



White solid, 33.4 mg, 52% yield, >20:1 dr, 91% ee, m.p. 278.9 – 280.3 °C, $[\alpha]_D^{19}$ +115 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 6H), 7.25 – 7.15 (m, 9H), 7.08 – 6.99 (m, 4H), 6.98 – 6.91 (m, 2H), 6.73 – 6.71 (m, 2H), 6.64 (s, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 6.08 (s, 1H), 5.97 (dd, *J* = 12.4, 1.3 Hz, 2H), 3.21 (dd, *J* = 7.8, 3.2 Hz, 1H), 2.87 (dd, *J* = 14.2, 7.8 Hz, 1H), 1.63 (dd, *J* = 14.2, 3.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 167.8, 148.3, 147.1, 144.7, 144.2, 141.8, 139.9, 128.9, 128.8, 128.6, 128.1, 127.8, 127.0, 126.0, 123.9, 123.3, 116.4, 115.7, 105.4, 101.9, 99.8, 74.9, 54.9, 48.1, 31.3. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{43}H_{31}NO_5Na$:

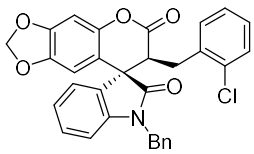
664.2094; Found: 664.2094. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 10.506 min (minor), 15.852 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(2-fluorobenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4a)



White solid, 35.0 mg, 69% yield, 5:1 dr, 91% ee, m.p. 105.2 – 106.7 ºC, $[\alpha]_D^{19}$ +254 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 6H, major + minor), 7.22 – 7.05 (m, 4H, major + minor), 6.99 – 6.80 (m, 3H, major + minor), 6.68 (s, 1H), 5.93 – 5.89 (m, 3H, major + minor), 4.95 – 4.82 (m, 2H, major + minor), 3.56 (dd, *J* = 8.7, 3.3 Hz, 1H, major), 3.39 (dd, *J* = 8.3, 2.5 Hz, 1H, minor), 3.22 (dd, *J* = 13.8, 8.2 Hz, 1H, minor), 3.10 (dd, *J* = 13.9, 8.8 Hz, 1H, major), 2.40 (dd, *J* = 13.9, 2.9 Hz, 1H, major), 2.21 (d, *J* = 13.9, 2.0 Hz, 1H, minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ (major + minor) 175.4, 168.0, 167.8, 162.2, 159.7, 148.5, 147.2, 147.1, 144.3, 144.2, 143.9, 139.4, 135.4, 132.3, 132.3, 129.8, 129.7, 129.0, 128.9, 128.3, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 126.3, 125.9, 125.8, 124.9, 124.5, 123.9, 123.9, 123.8, 123.7, 115.5, 115.5, 114.9, 114.7, 110.1, 109.8, 105.7, 101.9, 99.7, 54.6, 48.1, 45.7, 44.1, 31.4, 29.7, 26.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –117.20 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{31}H_{22}FNO_5Na$: 530.1374; Found: 530.1374. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 40/60, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 41.119 min (minor), 56.525 min (major).

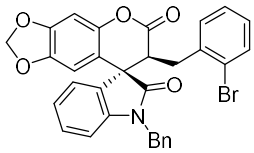
(3*S*,7'*S*)-1-benzyl-7'-(2-chlorobenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4b)



White solid, 37.7 mg, 72% yield, 10:1 dr, >99% ee, m.p. 216.4 – 217.6 ºC, $[\alpha]_D^{19}$ +285 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 6H, major + minor), 7.16 – 7.09 (m, 3H, major + minor), 7.05 – 6.96 (m, 3H, major + minor), 6.87 – 6.82 (m, 1H, major + minor), 6.69 (s, 1H), 5.92 – 5.90 (m, 3H, major + minor), 4.98 – 4.82 (m, 2H, major + minor), 3.73 (dd, *J* = 8.5, 4.4 Hz, 1H, major), 3.39 (dd, *J* = 8.3, 2.8 Hz, 1H, minor), 3.28 – 3.20 (m, 1H, major + minor), 2.49 (dd, *J* = 14.1, 4.3 Hz, 1H, major), 2.21 (dd, *J* = 13.8, 2.6 Hz, 1H, minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ (major + minor) 175.4, 167.6, 148.5, 147.2, 144.2, 143.9, 136.0, 135.4, 133.5, 132.7, 129.7, 129.1, 129.0, 128.9, 128.3, 128.0, 127.9, 127.5, 127.4, 127.4, 126.5, 125.4, 123.4, 115.4, 109.8, 105.7, 101.9, 99.7, 54.6, 44.6, 44.2, 30.3. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}ClNO_5Na$: 546.1078;

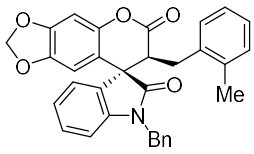
Found: 546.1075. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 38.842 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(2-bromobenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4c)



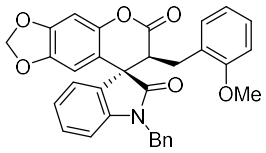
White solid, 35.8 mg, 63% yield, >20:1 dr, 92% ee, m.p. 222.2 – 224.0 °C, $[\alpha]_D^{19}$ +176 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 7H), 7.07 – 6.91 (m, 5H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 5.92 – 5.90 (m, 3H), 4.97 (d, *J* = 15.5 Hz, 1H), 4.87 (d, *J* = 15.4 Hz, 1H), 3.79 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.32 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.50 (dd, *J* = 14.4, 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 167.6, 148.5, 147.1, 144.3, 143.8, 137.6, 135.4, 132.6, 132.4, 129.7, 129.0, 128.1, 128.0, 127.6, 127.3, 127.1, 125.4, 123.9, 123.4, 115.4, 109.8, 105.7, 101.9, 99.7, 54.5, 44.6, 44.2, 32.6. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}BrNO_5Na$: 590.0573; Found: 590.0582. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 26.192 min (minor), 39.859 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(2-methylbenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4d)



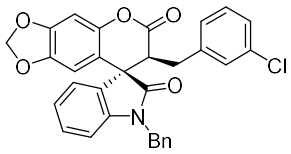
White solid, 48.3 mg, 96% yield, >20:1 dr, 95% ee, m.p. 224.7 – 225.8 °C, $[\alpha]_D^{19}$ +185 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 6H), 7.08 – 7.02 (m, 2H), 6.98 – 6.86 (m, 5H), 6.68 (s, 1H), 5.93 (s, 1H), 5.90 (s, 1H), 5.88 (s, 1H), 5.00 (d, *J* = 15.5 Hz, 1H), 4.82 (d, *J* = 15.5 Hz, 1H), 3.47 (dd, *J* = 8.3, 3.1 Hz, 1H), 3.25 (dd, *J* = 14.5, 8.4 Hz, 1H), 2.20 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 167.7, 148.5, 147.3, 144.3, 144.0, 137.2, 136.1, 135.4, 130.2, 129.8, 129.2, 129.0, 128.0, 128.0, 127.6, 126.3, 125.8, 124.8, 123.7, 115.3, 110.0, 105.8, 101.9, 99.7, 54.7, 46.5, 44.2, 28.4, 19.6. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{32}H_{25}NO_5Na$: 526.1624; Found: 526.1605. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 30/70, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 22.512 min (minor), 28.566 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(2-methoxybenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4e)



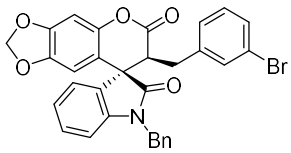
Yellow solid, 41.0 mg, 79% yield, >20:1 dr, 95% ee, m.p. 227.4 – 229.1 °C, $[\alpha]_D^{19}$ +290 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 6H), 7.16 – 7.03 (m, 4H), 6.80 (d, J = 7.9 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 6.67 – 6.64 (m, 2H), 5.91 (s, 2H), 5.89 (s, 1H), 4.95 (d, J = 15.5 Hz, 1H), 4.86 (d, J = 15.5 Hz, 1H), 3.67 – 3.64 (m, 4H), 3.05 (dd, J = 13.5, 8.6 Hz, 1H), 2.40 (dd, J = 13.5, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 168.1, 157.0, 148.4, 147.3, 144.1, 144.0, 135.5, 132.1, 129.5, 128.9, 128.1, 127.9, 127.7, 127.5, 126.9, 125.2, 123.0, 120.3, 115.8, 109.7, 109.6, 105.7, 101.8, 99.6, 54.7, 54.7, 44.7, 44.1, 27.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{32}H_{25}NO_6Na$: 542.1574; Found: 542.1573. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 40/60, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 30.027 min (minor), 44.550 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(3-chlorobenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4f)



White solid, 39.8 mg, 76% yield, 4:1 dr, 91% ee, m.p. 171.6 – 172.9 °C, $[\alpha]_D^{19}$ +222 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (major + minor) 7.37 – 7.23 (m, 6H), 7.18 – 7.01 (m, 4H), 7.01 – 6.83 (m, 2H), 6.79 (s, 1H), 6.69 (d, J = 2.4 Hz, 1H), 6.03 – 5.75 (m, 3H), 4.95 – 4.78 (m, 2H), 3.38 (dd, J = 7.5, 3.4 Hz, 1H), 3.22 (dd, J = 14.0, 7.8 Hz, 1H), 2.20 (dd, J = 14.0, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (major + minor) 175.3, 175.2, 167.9, 167.8, 148.6, 148.5, 147.2, 147.1, 144.4, 144.3, 144.2, 144.1, 141.3, 139.4, 135.4, 133.9, 130.0, 129.8, 129.5, 129.0, 129.0, 128.9, 128.3, 128.1, 128.0, 128.0, 127.8, 127.6, 127.5, 127.1, 126.5, 126.3, 124.5, 123.8, 115.5, 115.4, 110.1, 110.0, 105.7, 105.6, 101.9, 101.9, 99.8, 54.6, 54.4, 48.1, 47.8, 44.1, 31.4, 31.3. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}ClNO_5Na$: 546.1078; Found: 546.1077. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 27.774 min (minor), 30.624 min (major).

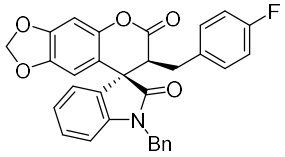
(3*S*,7'*S*)-1-benzyl-7'-(3-bromobenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4g)



White solid, 41.5 mg, 73% yield, >20:1 dr, 97% ee, m.p. 219.1 – 220.7 °C, $[\alpha]_D^{19}$ +268 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$)

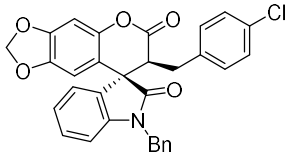
δ 7.33 – 7.24 (m, 6H), 7.15 – 7.07 (m, 5H), 6.98 – 6.96 (m, 2H), 6.86 (d, J = 7.9 Hz, 1H), 6.67 (s, 1H), 5.92 (s, 1H), 5.91 – 5.88 (m, 2H), 4.90 (d, J = 15.5 Hz, 1H), 4.83 (d, J = 15.6 Hz, 1H), 3.39 (dd, J = 8.2, 2.8 Hz, 1H), 3.22 (dd, J = 13.8, 8.3 Hz, 1H), 2.21 (dd, J = 13.9, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 167.9, 148.5, 147.2, 144.3, 144.2, 139.4, 135.4, 129.8, 128.9, 128.9, 128.3, 128.1, 128.0, 127.5, 126.3, 124.5, 123.8, 115.5, 110.0, 105.7, 101.9, 99.7, 54.6, 48.1, 44.1, 31.4. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}BrNO_5Na$: 590.0573; Found: 590.0573. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 40/60, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 27.388 min (minor), 34.310 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(4-fluorobenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4h)



White solid, 38.1 mg, 75% yield, >20:1 dr, 99% ee, m.p. 132.2– 134.1 °C, $[\alpha]_D^{20}$ +36 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 6H), 7.15 – 7.10 (m, 2H), 6.93 – 6.79 (m, 5H), 6.69 (s, 1H), 5.92 – 5.90 (m, 3H), 4.88 (d, J = 15.6 Hz, 1H), 4.84 (d, J = 15.6 Hz, 1H), 3.34 (dd, J = 8.1, 2.8 Hz, 1H), 3.19 (dd, J = 14.0, 8.2 Hz, 1H), 2.20 (dd, J = 14.0, 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 167.9, 162.7, 160.2, 148.5, 147.1, 144.3, 144.2, 135.3, 135.0, 135.0, 130.5, 130.4, 129.9, 129.0, 128.1, 128.0, 127.5, 124.4, 123.8, 115.4, 115.1, 114.9, 110.1, 105.6, 101.9, 99.8, 54.5, 48.2, 44.1, 30.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –116.69 (s). HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}FNO_5$: 530.1374; Found: 530.1386. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 25.812 min (minor), 30.158 min (major).

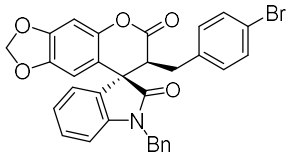
(3*S*,7'*S*)-1-benzyl-7'-(4-chlorobenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4i)



White solid, 44.0 mg, 84% yield, >20:1 dr, 90% ee, m.p. 219.6 – 220.6 °C, $[\alpha]_D^{19}$ +231 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 6H), 7.14 – 7.06 (m, 4H), 6.87 (d, J = 8.0 Hz, 3H), 6.67 (s, 1H), 5.91 (s, 2H), 5.88 (s, 1H), 4.89 – 4.81 (m, 2H), 3.34 (dd, J = 7.9, 2.6 Hz, 1H), 3.17 (dd, J = 13.9, 8.1 Hz, 1H), 2.20 (dd, J = 13.8, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 167.9, 148.6, 147.1, 144.4, 144.1, 137.8, 135.3, 132.1, 130.3, 129.9, 129.0, 128.3, 128.0, 128.0, 127.5, 124.4, 123.9, 115.4, 110.1, 105.6, 101.9, 99.7, 54.5, 47.9, 44.1, 30.9. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}ClNO_5Na$: 546.1078; Found: 546.1078. HPLC (Chiralpak IC

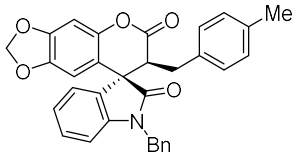
column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 26.579 min (minor), 32.572 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(4-bromobenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4j)



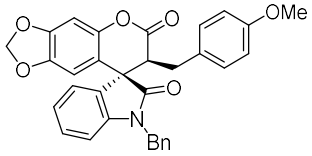
White solid, 48.9 mg, 86% yield, >20:1 dr, 93% ee, m.p. 205.3 – 206.4 °C, $[\alpha]_D^{19}$ +243 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.34 – 7.21 (m, 8H), 7.14 – 7.08 (m, 2H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.67 (s, 1H), 5.91 – 5.88 (m, 3H), 4.89 – 4.80 (m, 2H), 3.34 (dd, *J* = 8.1, 3.0 Hz, 1H), 3.16 (dd, *J* = 14.0, 8.1 Hz, 1H), 2.19 (dd, *J* = 14.0, 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 175.2, 167.8, 148.6, 147.1, 144.4, 144.1, 138.3, 135.3, 131.3, 130.7, 129.9, 129.0, 128.0, 127.9, 127.5, 124.5, 123.9, 120.2, 115.4, 110.1, 105.6, 101.9, 99.7, 54.5, 47.9, 44.1, 31.0. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{22}BrNO_5Na$: 590.0573; Found: 590.0577. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 28.066 min (minor), 34.420 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(4-methylbenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4k)



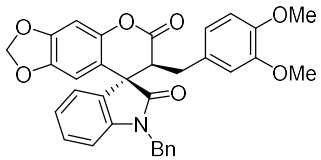
Yellow solid, 48.3 mg, 96% yield, >20:1 dr, 91% ee, m.p. 211.3 – 212.6 °C, $[\alpha]_D^{19}$ +278 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.33 – 7.22 (m, 6H), 7.13 – 7.09 (m, 2H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.88 – 6.84 (m, 3H), 6.66 (s, 1H), 5.92 (s, 1H), 5.89 – 5.86 (m, 2H), 4.88 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 3.35 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.16 (dd, *J* = 13.9, 8.4 Hz, 1H), 2.23 (s, 3H), 2.18 (dd, *J* = 13.9, 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 175.4, 168.0, 148.5, 147.2, 144.3, 144.2, 136.4, 135.8, 135.4, 129.8, 129.0, 129.0, 128.8, 128.2, 128.0, 127.5, 124.5, 123.8, 115.5, 110.0, 105.7, 101.9, 99.7, 54.6, 48.2, 44.1, 31.0, 21.0. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{32}H_{25}NO_5Na$: 526.1624; Found: 526.1624. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 30/70, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 26.385 min (minor), 44.382 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(4-methoxybenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4l)



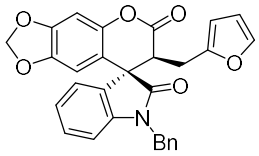
White solid, 47.8 mg, 92% yield, >20:1 dr, 96% ee, m.p. 131.1 – 132.6 °C, $[\alpha]_D^{19}$ +222 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 7H), 7.13 (d, J = 4.2 Hz, 2H), 6.90 – 6.84 (m, 3H), 6.69 – 6.66 (m, 3H), 5.91 (s, 1H), 5.90 (dd, J = 8.8, 1.2 Hz, 2H), 4.88 (d, J = 15.6 Hz, 1H), 4.83 (d, J = 15.6 Hz, 1H), 3.72 (s, 3H), 3.33 (dd, J = 8.2, 2.6 Hz, 1H), 3.14 (dd, J = 13.9, 8.3 Hz, 1H), 2.14 (dd, J = 13.9, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 168.0, 158.1, 148.5, 147.2, 144.2, 144.2, 135.4, 131.5, 130.0, 129.8, 128.9, 128.3, 127.9, 127.4, 124.4, 123.8, 115.6, 113.7, 110.0, 105.7, 101.9, 99.7, 55.2, 54.6, 48.3, 44.1, 30.6. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{32}H_{25}NO_6Na$: 542.1574; Found: 542.1571. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 40.512 min (minor), 62.047 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(3,4-dimethoxybenzyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4m)



White solid, 41.7 mg, 76% yield, >20:1 dr, 91% ee, m.p. 175.6 – 176.7 °C, $[\alpha]_D^{19}$ +167 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 6H), 7.10 – 7.05 (m, 2H), 6.85 (d, J = 7.9 Hz, 1H), 6.69 (s, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.46 – 6.43 (m, 2H), 5.92 – 5.90 (m, 3H), 4.91 (d, J = 15.5 Hz, 1H), 4.80 (d, J = 15.5 Hz, 1H), 3.79 (s, 3H), 3.68 (s, 3H), 3.37 (dd, J = 7.4, 3.2 Hz, 1H), 3.24 (dd, J = 14.0, 7.4 Hz, 1H), 2.19 (dd, J = 14.0, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 168.2, 148.5, 148.5, 147.4, 147.1, 144.3, 144.1, 135.4, 132.1, 129.7, 129.0, 128.1, 128.0, 127.5, 124.6, 123.6, 120.5, 115.6, 112.4, 111.0, 110.0, 105.6, 101.9, 99.7, 55.9, 55.6, 54.5, 48.3, 44.1, 31.1. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{33}H_{27}NO_7Na$: 572.1679; Found: 572.1693. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 30.667 min (minor), 35.297 min (major).

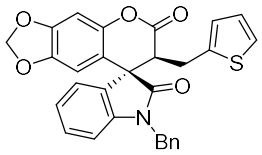
(3*S*,7'*S*)-1-benzyl-7'-(furan-2-ylmethyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4n)



White solid, 32.6 mg, >20:1 dr, 68% yield, 89% ee, m.p. 103.6 – 104.4 °C, $[\alpha]_D^{20}$ –132 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^1H NMR (600 MHz, $CDCl_3$)

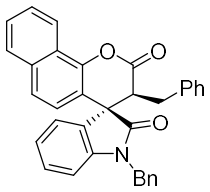
δ 7.34 – 7.23 (m, 6H), 7.11 (s, 1H), 7.08 – 7.04 (m, 2H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 1.0 Hz, 1H), 6.06 – 6.05 (m, 1H), 5.93 – 5.88 (m, 3H), 5.70 (d, *J* = 3.1 Hz, 1H), 4.90 (d, *J* = 15.5 Hz, 1H), 4.82 (d, *J* = 15.5 Hz, 1H), 3.62 – 3.60 (m, 1H), 3.30 (dd, *J* = 15.3, 7.4 Hz, 1H), 2.34 (dd, *J* = 15.3, 4.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 175.2, 167.5, 151.7, 148.5, 147.1, 144.3, 143.8, 140.8, 135.4, 129.5, 128.9, 128.0, 127.8, 127.5, 124.4, 123.9, 115.5, 110.5, 109.7, 106.9, 105.6, 101.9, 99.8, 54.1, 44.4, 44.1, 24.6. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{29}H_{22}NO_6$: 480.1442; Found: 480.1439. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 15.442 min (minor), 41.772 min (major).

(3*S*,7'*S*)-1-benzyl-7'-(thiophen-2-ylmethyl)spiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromene]-2,6'(7'*H*)-dione (4o)



Deep red solid, 37.6 mg, >20:1 dr, 76% yield, 91% ee, m.p. 114.3 – 115.8 °C, $[\alpha]_D^{20}$ +89 (c = 0.5, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.33 – 7.30 (m, 3H), 7.28 – 7.26 (m, 3H), 7.16 – 7.13 (m, 2H), 7.04 – 7.03 (m, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.77 – 6.75 (m, 1H), 6.71 (s, 1H), 6.56 (d, *J* = 3.1 Hz, 1H), 5.93 – 5.91 (m, 3H), 4.94 – 4.78 (m, 2H), 3.45 – 3.40 (m, 2H), 2.48 – 2.42 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 175.1, 167.7, 148.5, 147.1, 144.3, 144.1, 141.5, 135.3, 129.9, 129.0, 128.0, 127.7, 127.4, 126.7, 126.1, 124.5, 124.1, 123.9, 115.5, 110.0, 105.6, 101.9, 99.8, 54.3, 48.3, 44.1, 31.6, 26.0, 22.7, 14.1. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{29}H_{22}NO_5S$: 496.1213; Found: 496.1214. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 35/65, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 14.424 min (minor), 36.406 min (major).

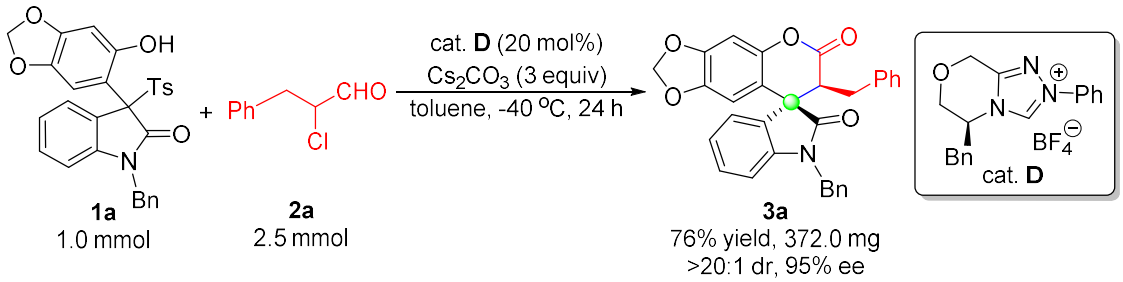
(3*S*,4*S*)-1',3-dibenzylspiro[benzo[*h*]chromene-4,3'-indoline]-2,2'(3*H*)-dione (4q)



White solid, 48.7 mg, 98% yield, >20:1 dr, 98% ee, m.p. 107.1 – 108.2 °C, $[\alpha]_D^{19}$ +246 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.32 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.72 (m, 1H), 7.56 – 7.48 (m, 2H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.35 – 7.22 (m, 6H), 7.16 – 7.07 (m, 5H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.52 (d, *J* = 8.6 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 3.55 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.31 (dd, *J* = 13.9, 8.4 Hz, 1H), 2.31 (dd, *J* = 13.9, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 175.3, 167.9, 147.9, 144.4, 139.5, 135.4, 134.3, 129.8, 129.0, 128.9, 128.4, 128.3, 128.0, 127.5, 127.4, 127.4, 126.8, 126.4, 124.5, 124.1, 124.0, 123.9, 123.0, 121.9, 117.7, 110.1, 55.2, 48.2, 44.2, 31.5. HRMS (ESI): $[M+H]^+$ Calcd. for $C_{34}H_{26}NO_3$: 496.1907;

Found: 496.1903. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 17.716 min (minor), 26.064 min (major).

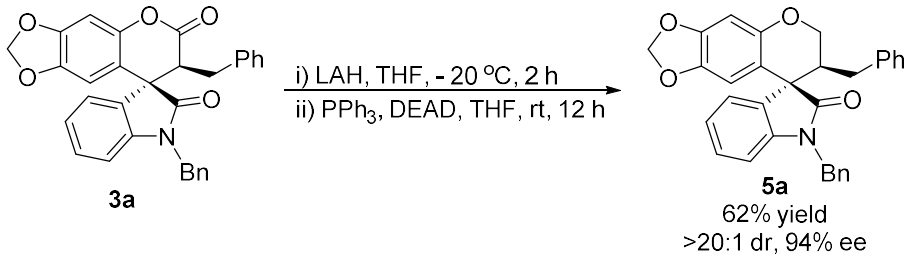
4. Scale-up synthesis of product 3a



Under argon atmosphere, a flame-dried 50 mL Schlenk tube was charged with **1a** (513.6 mg, 1.0 mmol), **2a** (421.6 mg, 2.5 mmol, 2.5 equiv.), Cs_2CO_3 (977.5 mg, 3.0 mmol, 3.0 equiv.) and Cat. **D** (76 mg, 0.02 mmol, 20 mol %). The tube was evacuated and backfilled with nitrogen for 3 times. Then, dry toluene (15 mL) was added to the mixture at –40 °C. The resulting solution was continuously stirred at –40 °C for 24 h (monitored by TLC). The reaction mixtures were filtrated through flash silica gels to remove the inorganic salt and the solvent was removed in *vacuo*. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to obtain the product **3a** (372.0 mg, 76% yield, >20:1 dr, 95% ee).

5. General procedure for the synthetic transformations of 3a

5.1 General procedure for the synthesis of **5a**

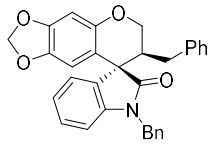


To a 25 mL Schlenk reaction flask equipped with a magnetic stir bar, which was added $LiAlH_4$ (15.2 mg, 0.4 mmol, 2.0 equiv.). The flask was sealed, evacuated, and backfilled with argon three times using standard Schlenk techniques, dry THF (2.0 mL) was added *via* syringe at –20 °C. Then, a solution of **3a** (97.9 mg, 0.2 mmol) in THF (1.0 mL) was slowly added *via* syringe. The reaction mixture was stirred for 2 h. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with wet Na_2SO_4 solid. The mixture was stirred for 1 h, filtered by celite and washed with ethyl acetate. The combined organics were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product which was used directly for next step.

To a 25 mL Schlenk reaction flask equipped with a magnetic stir bar, was added the above crude product (~0.20 mmol), PPh_3 (94.3 mg, 0.36 mmol, 1.8 equiv.). The flask was sealed, evacuated, and backfilled with argon three times using standard Schlenk techniques. Then, dry THF (2.0 mL) and diethyl azodicarboxylate

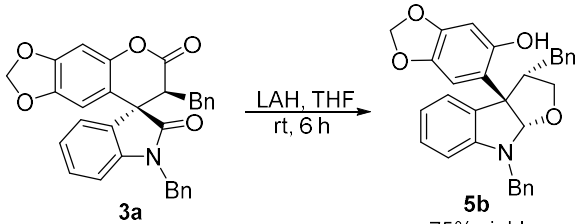
(52.3 mg, 0.3 mmol, 3.0 equiv.) were added slowly at 0 °C. The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure and the product was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to afford the product **5a** as a white solid (29.5 mg, 62% yield, >20:1 dr, 94% ee).

(3*S*,7'*S*)-1,7'-dibenzyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-*g*]chromen]-2-one (5a)



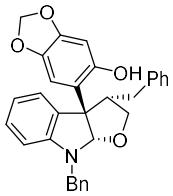
White solid, 29.5 mg, 62% yield, >20:1 dr, 94% ee, m.p. 82.9 – 84.1 °C, $[\alpha]_D^{19}$ +182 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.27 – 7.19 (m, 4H), 7.17 – 7.07 (m, 3H), 6.95 (d, *J* = 7.1 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.42 (s, 1H), 5.79 – 5.77 (m, 3H), 5.00 – 4.91 (m, 2H), 4.79 (d, *J* = 11.2 Hz, 1H), 4.06 (dd, *J* = 10.9, 3.6 Hz, 1H), 2.68 – 2.60 (m, 3H), 2.34 – 2.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 150.8, 147.9, 143.8, 141.9, 138.7, 136.0, 133.0, 128.9, 128.7, 128.5, 127.8, 127.5, 126.5, 123.7, 123.5, 112.7, 109.2, 106.5, 101.1, 99.0, 64.5, 52.6, 44.1, 42.9, 32.7. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{25}NO_4Na$: 498.1675; Found: 498.1675. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 12.825 min (minor), 17.415 min (major).

5.2 General procedure for the synthesis of **5b**



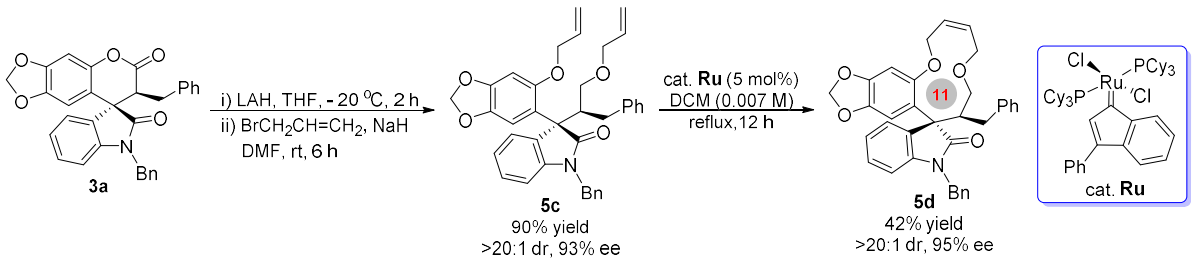
Under an argon atmosphere, a solution of $LiAlH_4$ (22.8 mg, 0.4 mmol, 6.0 equiv.) in anhydrous THF (1.0 mL) was added dropwise to a solution of **3a** (49.0 mg, 0.1 mmol) in anhydrous THF (1.0 mL) at 0 °C. The resulting mixture was stirred at room temperature under an argon atmosphere for 6 h. The reaction mixture was quenched with wet Na_2SO_4 solid, filtered and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 7/1) on silica to give the product **5b** as a white solid (35.8 mg, 75% yield, >20:1 dr, 94% ee).

6-((3*S*,*3aS*,*8aS*)-3,8-dibenzyl-2,3,8,8*a*-tetrahydro-3*aH*-furo[2,3-*b*]indol-3a-yl)benzo[*d*][1,3]dioxol-5-ol (5b)



White solid, 35.8 mg, 75% yield, >20:1 dr, 94% ee, m.p. 56.1 – 57.9 °C, $[\alpha]_D^{19}$ –30 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.31 (dd, J = 16.1, 7.7 Hz, 4H), 7.29 – 7.24 (m, 5H), 7.18 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.2 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 6.70 (s, 1H), 6.50 (s, 1H), 6.41 (s, 1H), 6.38 (d, J = 7.8 Hz, 1H), 5.88 (d, J = 1.0 Hz, 1H), 5.82 (d, J = 0.9 Hz, 1H), 4.67 (d, J = 16.2 Hz, 1H), 4.59 (d, J = 16.2 Hz, 1H), 3.60 (d, J = 11.1 Hz, 1H), 3.50 (d, J = 10.6 Hz, 1H), 2.65 – 2.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 149.0, 147.7, 142.2, 140.5, 137.7, 132.3, 129.1, 128.6, 128.5, 128.4, 127.3, 127.3, 126.2, 122.1, 121.7, 118.5, 106.3, 104.2, 103.3, 101.3, 93.8, 62.1, 60.7, 49.2, 47.9, 32.7. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{31}H_{27}NO_4Na$: 500.1832; Found: 500.1832. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 87/13, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 17.823 min (minor), 22.594 min (major).

5.3 General procedure for the syntheses of **5c** and **5d**



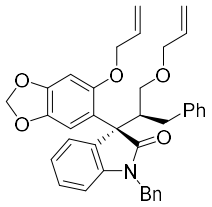
To a 25 mL Schlenk reaction flask equipped with a magnetic stir bar was added $LiAlH_4$ (15.2 mg, 0.4 mmol, 2.0 equiv.). The flask was sealed, evacuated, and backfilled with argon three times using standard Schlenk techniques. Then, dry THF (2.0 mL) was added at –20 °C and a solution of **3a** (97.9 mg, 0.2 mmol) in THF (1.0 mL) was added. The reaction mixture was stirred for 2 h. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with wet Na_2SO_4 solid and was stirred for 1 h. The mixture was filtered by celite and washed with ethyl acetate. The combined organics were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product which was used directly for the next step.

To a solution of NaH (60%, 2.4 equiv.) in DMF (0.4 mL) was slowly added a solution of the compound **3a** (49.0 mg, 0.1 mmol) in DMF (0.6 mL) under the atmosphere of argon at 0 °C. The mixture was stirred for 1 h at 0 °C and then a solution of allyl bromide (36.3 mg, 0.3 mmol, 3.0 equiv.) in DMF (0.5 mL) was added dropwise. The mixture was stirred at room temperature for 6 h. After the reaction was completed, the reaction was quenched with saturated brine and extracted with ethyl acetate three times. The organic layer was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel

(petroleum ether/ethyl acetate= 6/1) to furnish the product **5c** (51.6 mg, 90% yield, >20:1 dr, 93% ee) as a colorless oil.

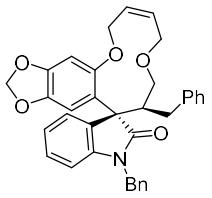
A stirred solution of **5c** (39 mg, 0.1 mmol) in toluene (15 mL) was degassed by three freeze-thaw cycles under argon atmosphere and Grubbs reagent Cat. Ru (4.6 mg, 0.005 mmol, 0.05 equiv.) was added at room temperature. The reaction mixture was degassed again by three freeze-thaw cycles and then was refluxed for 12 h. The reaction mixture was extracted with ethyl acetate three times. The organic layer was washed with water and saturated brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the product **5d** (24.0 mg, 44% yield, >20:1 dr, 94% ee) as a yellow oil.

(*S*)-3-((*S*)-1-(allyloxy)-3-phenylpropan-2-yl)-3-(6-(allyloxy)benzo[*d*][1,3]dioxol-5-yl)-1-benzylindolin-2-one (5c)



Colorless oil, 51.6 mg, 90% yield, >20:1 dr, 93% ee, $[\alpha]_D^{19}$ –81 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3Hz, 2H), 7.33 – 7.19 (m, 4H), 7.15 – 7.05 (m, 4H), 6.95 – 6.93 (m, 3H), 6.86 – 6.82 (m, 1H), 6.74 (d, J = 7.8 Hz, 1H), 6.42 (s, 1H), 5.88 (s, 2H), 5.63 – 5.53 (m, 2H), 5.14 – 5.05 (m, 3H), 5.00 – 4.96 (m, 2H), 4.71 (d, J = 15.4 Hz, 1H), 4.13 – 4.02 (m, 2H), 3.91 (d, J = 8.7 Hz, 1H), 3.68 – 3.58 (m, 2H), 3.53 – 3.49 (m, 1H), 3.20 (s, 1H), 2.51 – 2.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 152.1, 147.1, 143.7, 141.8, 140.9, 136.6, 134.9, 133.4, 133.0, 128.9, 128.7, 128.0, 128.0, 127.6, 127.5, 125.6, 123.7, 122.4, 121.5, 117.8, 116.3, 108.4, 108.3, 101.4, 97.4, 71.6, 71.4, 70.8, 56.9, 46.1, 44.5, 35.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{37}H_{35}NO_5Na$: 596.2407; Found: 596.2407. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 32.091 min (minor), 38.225 min (major).

(3*R*,12'*S*,*Z*)-1,12'-dibenzyl-6',9',11',12'-tetrahydrospiro[indoline-3,13'-[1,3]dioxolo[4',5':4,5]benzo-[1,2-*g*][1,6]dioxacycloundecin]-2-one (5d)

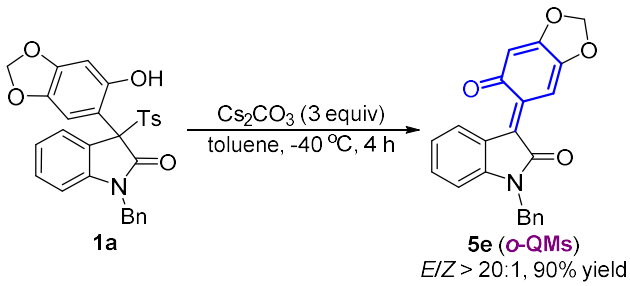


Yellow oil, 24.0 mg, 44% yield, >20:1 dr, 95% ee, $[\alpha]_D^{19}$ –16 (c = 1.00, CH_2Cl_2), purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.4 Hz, 1H), 7.41 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.25 (s, 1H), 7.14 – 7.03 (m, 4H), 6.97– 6.90 (m, 3H), 6.71 (dd, J = 7.7 Hz, 3H), 6.54 (s, 2H), 6.17 – 611 (m, 1H), 5.86 (s, 1H), 5.81 (s, 1H), 5.74 – 5.67

(m, 1H), 5.09 (d, J = 15.5 Hz, 1H), 4.99 (d, J = 15.5 Hz, 1H), 4.90 (dd, J = 12.4, 6.4 Hz, 1H), 4.67 (dd, J = 12.4, 6.9 Hz, 1H), 4.24 – 4.20 (m, 1H), 4.09 (dd, J = 12.8, 3.2 Hz, 1H), 4.00 – 3.94 (m, 1H), 3.84 (dd, J = 12.7, 7.8 Hz, 1H), 3.54 (dd, J = 12.4, 5.4 Hz, 1H), 2.45 (dd, J = 13.3, 9.1 Hz, 1H), 2.20 (dd, J = 13.3, 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 151.8, 147.1, 141.9, 141.6, 141.6, 135.9, 135.5, 134.7, 129.0, 128.8, 127.8, 127.8, 127.8, 127.6, 125.5, 124.2, 123.3, 120.7, 109.0, 108.8, 101.4, 96.9, 69.6, 62.0, 61.6, 60.1, 43.9, 41.1, 36.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{35}H_{31}NO_5Na$: 568.2091; Found: 568.2091. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 254 nm): t_R = 12.912 min (minor), 28.246 min (major).

6. Control experiments

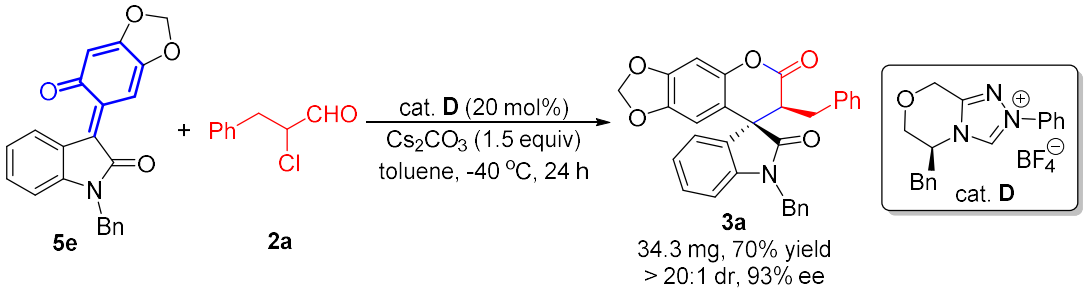
6.1 Isolation and preparation of the *ortho*-quinone methides (*o*-QMs) **5e**



Under an argon atmosphere, a flame-dried 25 mL Schlenk tube was charged with **1a** (154.1 mg, 0.3 mmol) and Cs_2CO_3 (879.3 mg, 0.9 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon for 3 times. Then, dry toluene (5 mL) was added at –40 °C. The resulting solution was stirred at –40 °C for 4 h (monitored by TLC). The reaction mixture was filtrated through flash silica gels to remove inorganic salt and the solvent was removed *in vacuo*. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to furnish the product **5e** (321.6 mg, 90% yield,) as a purple solid.

(*E*)-1-benzyl-3-(6-oxobenzo[*d*][1,3]dioxol-5(6*H*)-ylidene)indolin-2-one (5e). Purple solid, 321.6 mg, *E*/*Z* >20:1, 90% yield, m.p. 152.7 – 153.9 °C, purified by column chromatography on silica gel (petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.0 Hz, 1H), 8.59 (s, 1H), 7.29 – 7.18 (m, 6H), 6.91 (t, J = 7.8 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 5.93 (s, 2H), 5.92 (s, 1H), 4.92 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 169.2, 159.5, 150.3, 144.2, 136.5, 135.8, 132.7, 130.6, 128.8, 127.8, 127.6, 127.4, 127.2, 122.4, 122.0, 108.7, 102.8, 101.5, 101.1, 43.5. HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{22}H_{15}NO_4Na$: 380.0892; Found: 380.0893.

6.2 Control experiment with isolated *o*-QMs **5e**



Under an argon atmosphere, a flame-dried 25 mL Schlenk tube was charged with **5e** (35.7 mg, 0.1 mmol, **2** (42.2 mg, 0.25 mmol, 2.5 equiv.), Cs_2CO_3 (48.9 mg, 0.15 mmol, 1.5 equiv.) and Cat. **D** (7.6 mg, 0.02 mmol, 20 mol %). The tube was evacuated and backfilled with argon for 3 times. Then, dry toluene (1.5 mL) was added quickly at –40 °C. The resulting solution was stirred at –40 °C for 24 h (monitored by TLC). The reaction mixture was filtrated through flash silica gels to remove inorganic salt and the solvent was removed *in vacuo*. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to yield the product **3a** (34.3 mg, 70% yield, >20:1 dr, 93% ee).

7. Preparation for the Single Crystal of Compound 3b

In a 5 mL glass vial, the compound **3b** (20 mg) was dissolved in $CHCl_3$ (1 mL) and then *n*-hexane (4 mL) was added slowly. The solution was kept aside for overnight, and the crystal was formed. The crystal was subjected for single-crystal XRD to determine the absolute configuration.

8. Single Crystal XRD Data of Compound 3b

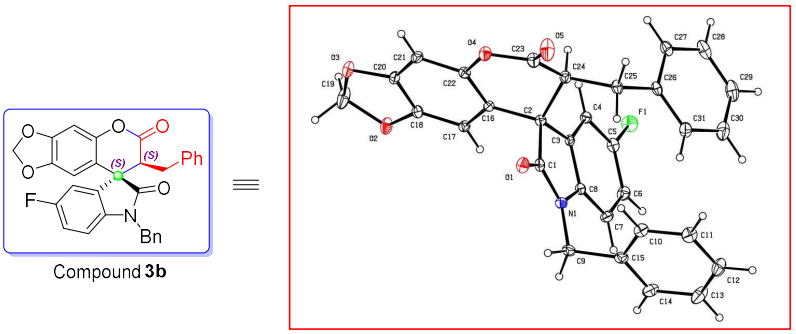


Figure S1. ORTEP representation (20% thermal probability ellipsoids) of the crystal structure of compound **3b** (CCDC 2324543).

Table S1. Crystallographic data and refinement details for compound **3b**

Identification code	Compound **3b**
Empirical formula	$C_{31}H_{22}FNO_5$
Formula weight	507.49
Temperature/*K*	150.00(10)
Crystal system	*orthorhombic*
Space group	$P2_12_12_1$
a/Å	9.67378(10)
b/Å	9.99752(9)
c/Å	25.0687(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2424.49(4)
Z	4
ρ_{calc} g/cm^3	1.390
μ/mm^{-1}	0.824
F(000)	1056.0
Crystal size/mm^3	0.18 × 0.14 × 0.12
Radiation	Cu *Kα* (λ = 1.54184)
2θ range for data collection/°	7.052 to 152.62
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 11$, $-31 \le l \le 22$
Reflections collected	13770
Independent reflections	4746 [R_{int} = 0.0257, R_{sigma} = 0.0262]
Data/restraints/parameters	4746/0/344
Goodness-of-fit on F^2	1.072
Final *R* indexes [$I>=2\sigma(I)$]	R_1 = 0.0291, wR_2 = 0.0741
Final *R* indexes [all data]	R_1 = 0.0317, wR_2 = 0.0752
Largest diff. peak/hole / *e* Å^{-3}	0.19/-0.13
Flack parameter	0.03(6)

9. References

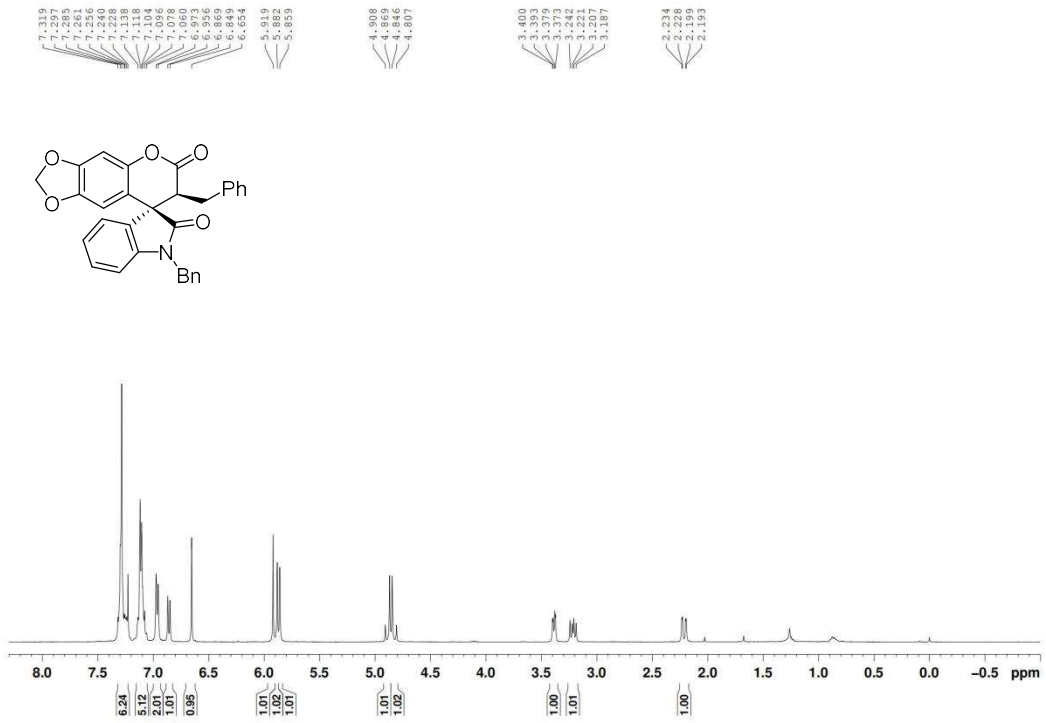
[1] a) M. S. Kerr, J. Read de Alaniz and T. Rovis, *J. Org. Chem.* 2005, **70**, 5725; b) P. C. Chiang, M. Rommel and J. W. Bode, *J. Am. Chem. Soc.* 2009, **131**, 8714; c) S. Kobayashi, T. Kinoshita, H. Uehara, T. Sudo and I. Ryu, *Org. Lett.* 2009, **11**, 3934; d) C. D. Campbell, C. J. Collett, J. E. Thomson, A. M. Slawin and A. D. Smith, *Org. Biomol. Chem.* 2011, **9**, 4205; e) I. Piel, M. Steinmetz, K. Hirano, R. Frohlich, S. Grimme and F. Glorius, *Angew. Chem. Int. Ed.* 2011, **50**, 4983; f) C. Zhao, F. Li and J. Wang, *Angew. Chem. Int. Ed.* 2016, **55**, 1820; g) L. Dai, Z. H. Xia, Y. Y. Gao, Z. H. Gao and S. Ye, *Angew. Chem. Int. Ed.* 2019, **58**, 18124; h) Y. Wu, M. Li, J. Sun, G. Zheng and Q. Zhang, *Angew. Chem. Int. Ed.* 2022, **61**, e202117340.

[2] a) W. Guo, B. Wu, X. Zhou, P. Chen, X. Wang, Y. G. Zhou, Y. Liu and C. Li, *Angew. Chem. Int. Ed.*, 2015, **54**, 4522; b) N. Kumar, J. Kaur, A. Kumar, N. Islam and S. S. Chimni, *Asian J. Org. Chem.*, 2016, **5**, 1334; c) P. Chen, K. Wang, W. Guo, X. Liu, Y. Liu and C. Li, *Angew. Chem. Int. Ed.*, 2017, **56**, 3689; d) L. Wang, Z. Huang, X. Guo, J. Liu, J. Dong and X. Xu, *Chem. Commun.*, 2022, **58**, 6433.

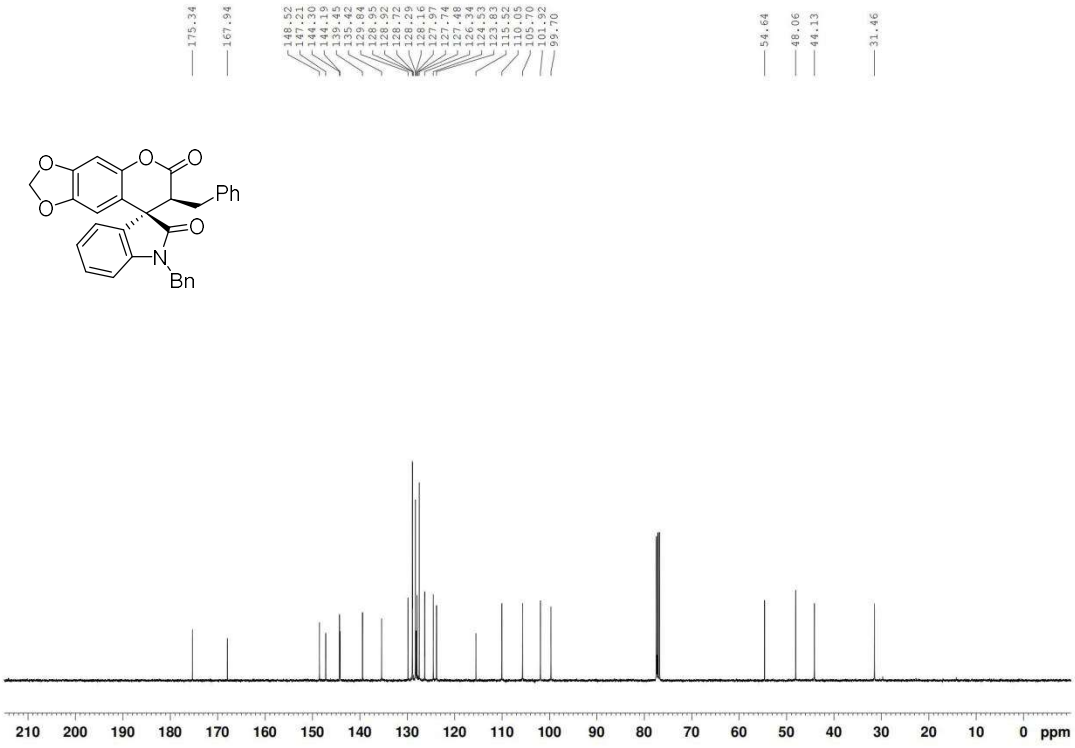
[3] a) T. Borg, J. Danielsson, M. Mohiti, P. Restorp and P. Somfai, *Adv. Synth. Catal.*, 2011, **353**, 2022; b) Y. Jing, C. G. Daniliuc, A. Studer, *Org. Lett.*, 2014, **16**, 4932; c) S. Wang, J. Izquierdo, C. Rodríguez-Escrich and M. A. Pericàs, *ACS Catal.*, 2017, **7**, 2780.

10. NMR Spectra of compounds 3a–3v, 4a–4o, 4q and 5a–5e

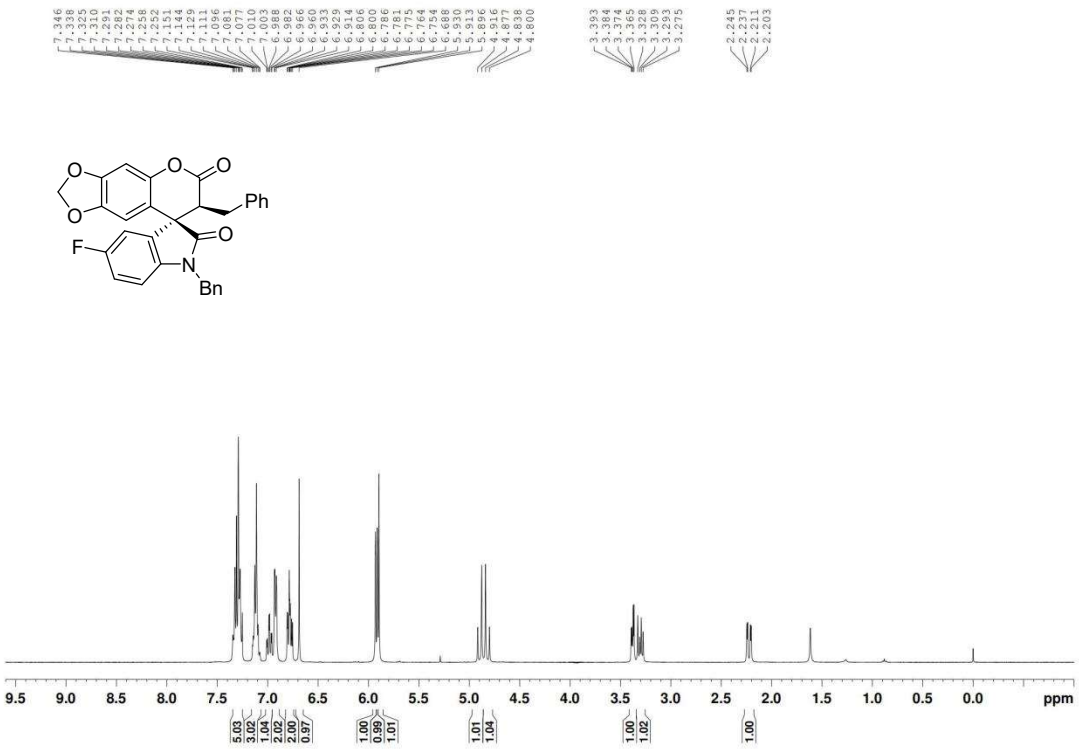
^{1}H NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz)



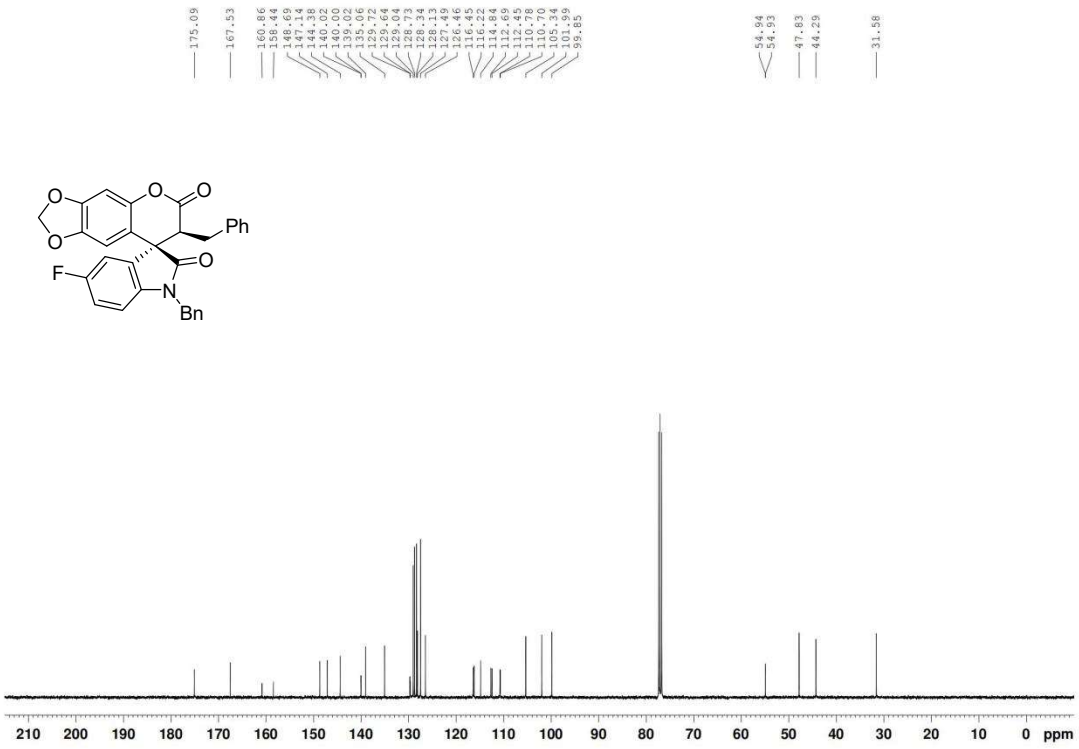
^{13}C NMR spectrum of compound **3a** ($CDCl_3$, 100 MHz)



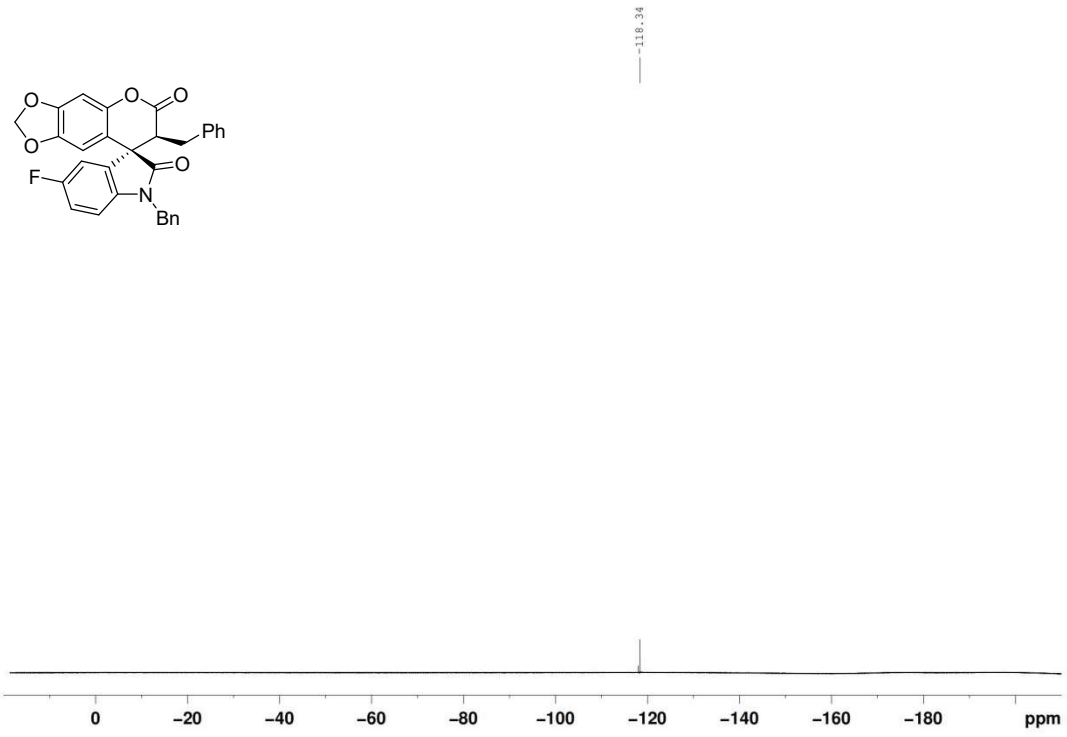
^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz)



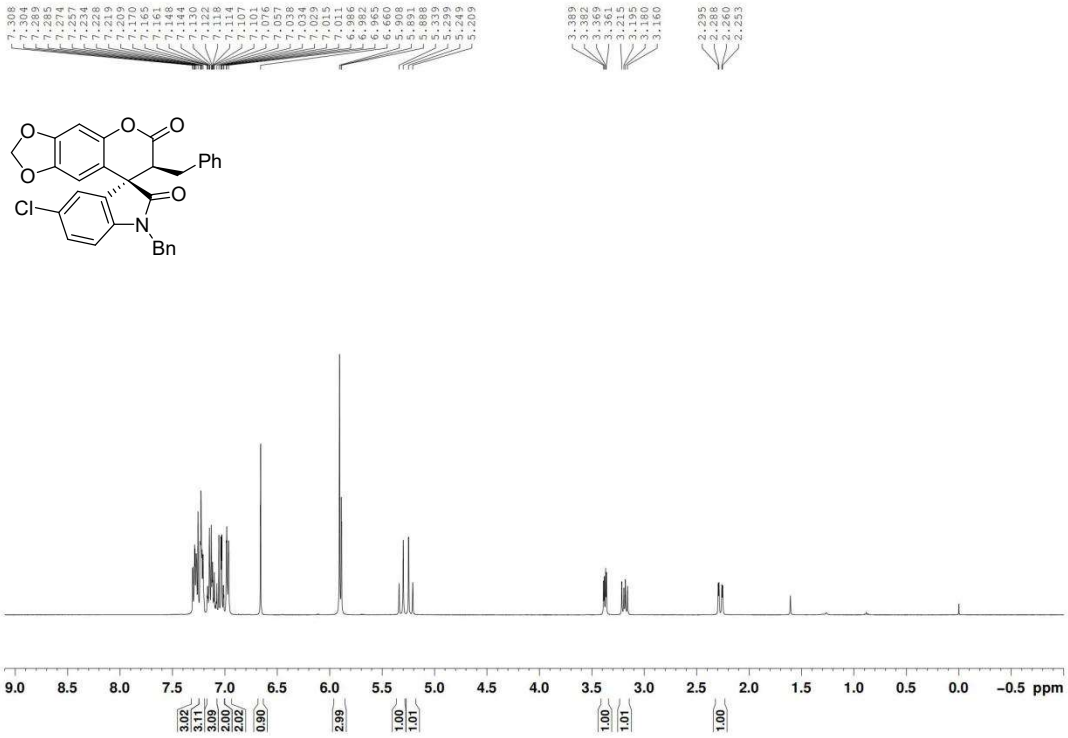
^{13}C NMR spectrum of compound **3b** ($CDCl_3$, 100 MHz)



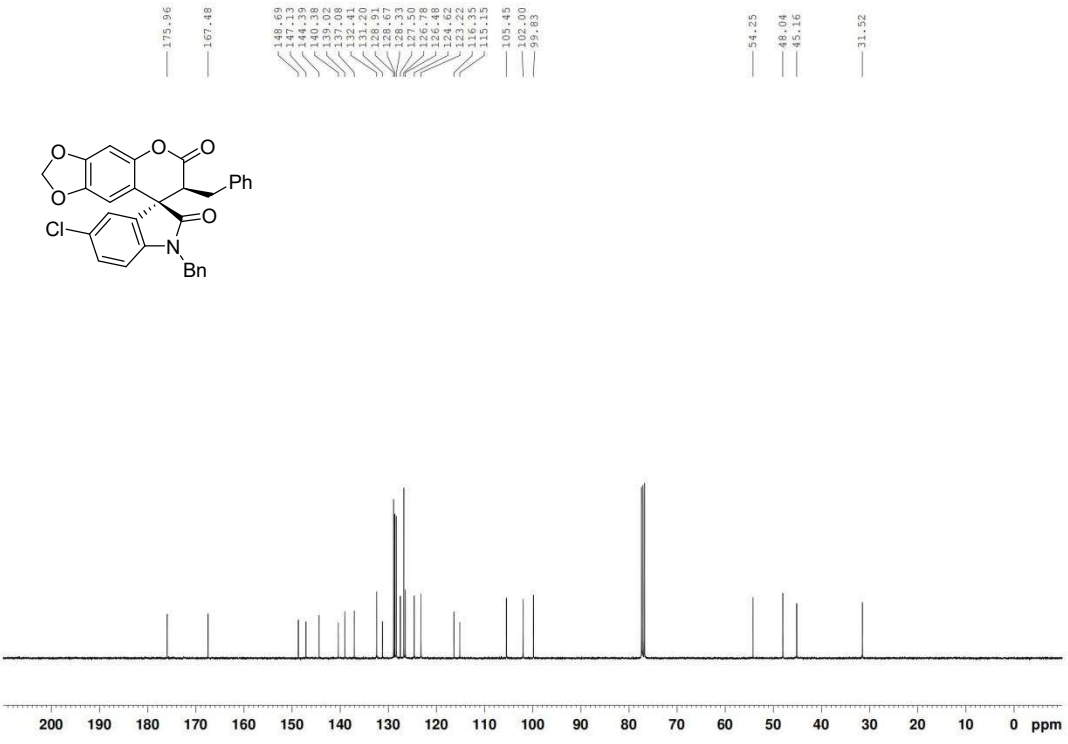
^{19}F NMR spectrum of compound **3b** ($CDCl_3$, 376 MHz)



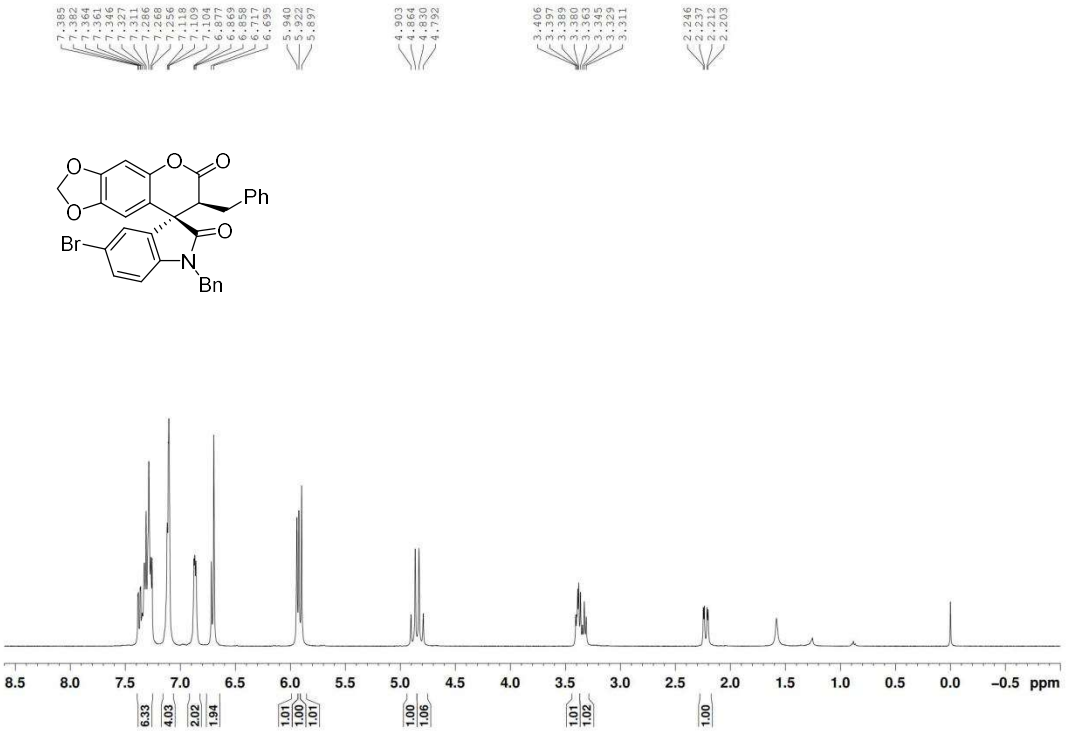
^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 400 MHz)



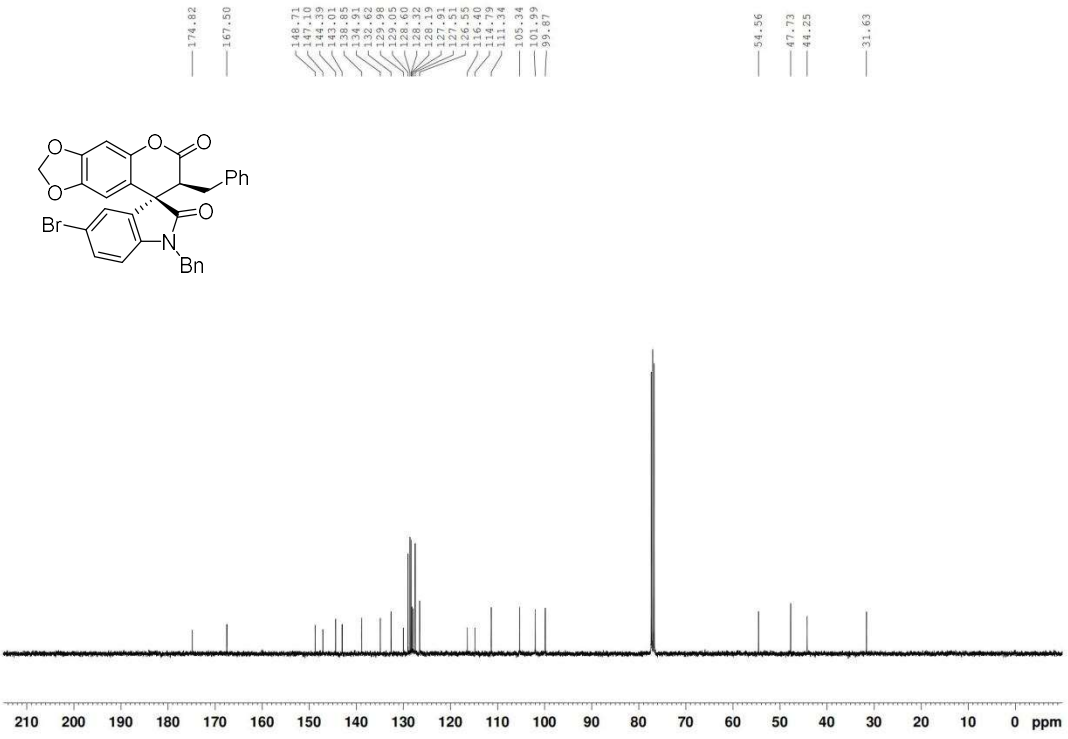
^{13}C NMR spectrum of compound **3c** ($CDCl_3$, 100 MHz)



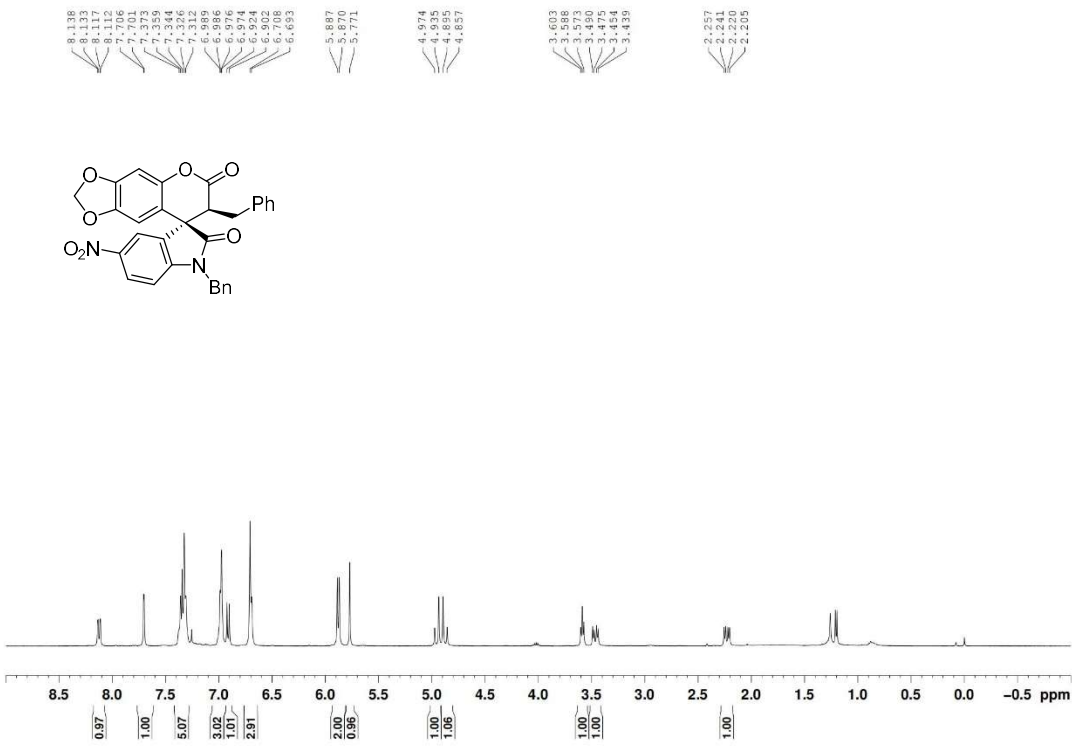
^{1}H NMR spectrum of compound **3d** ($CDCl_3$, 400 MHz)



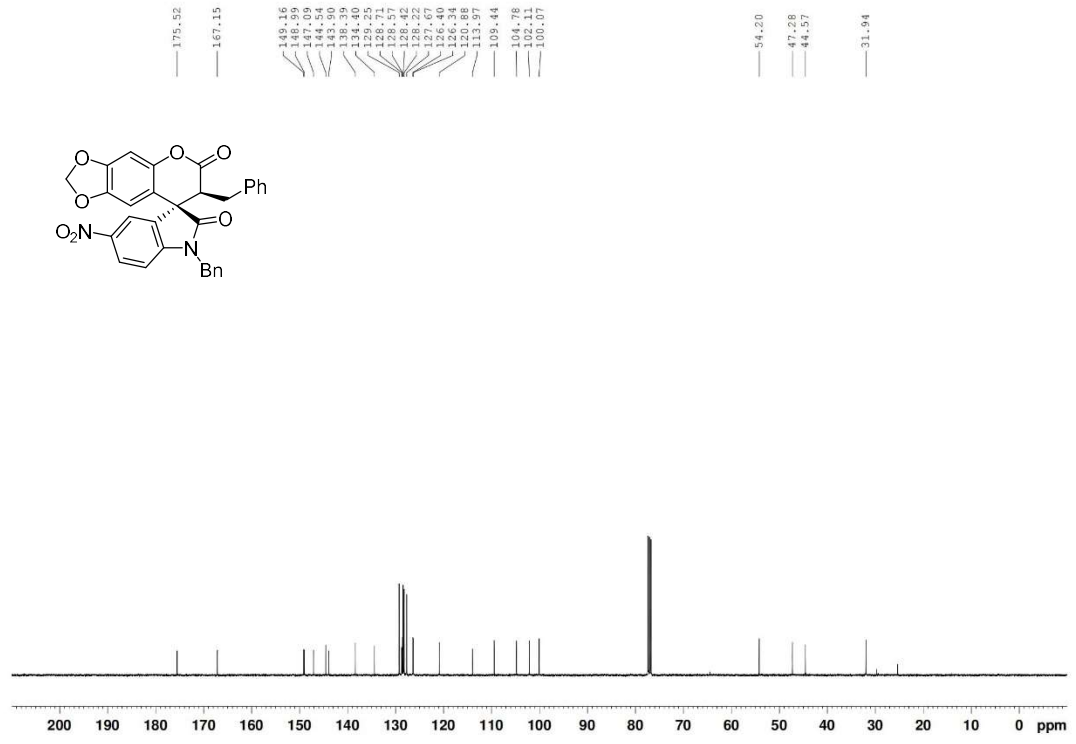
^{13}C NMR spectrum of compound **3d** ($CDCl_3$, 100 MHz)



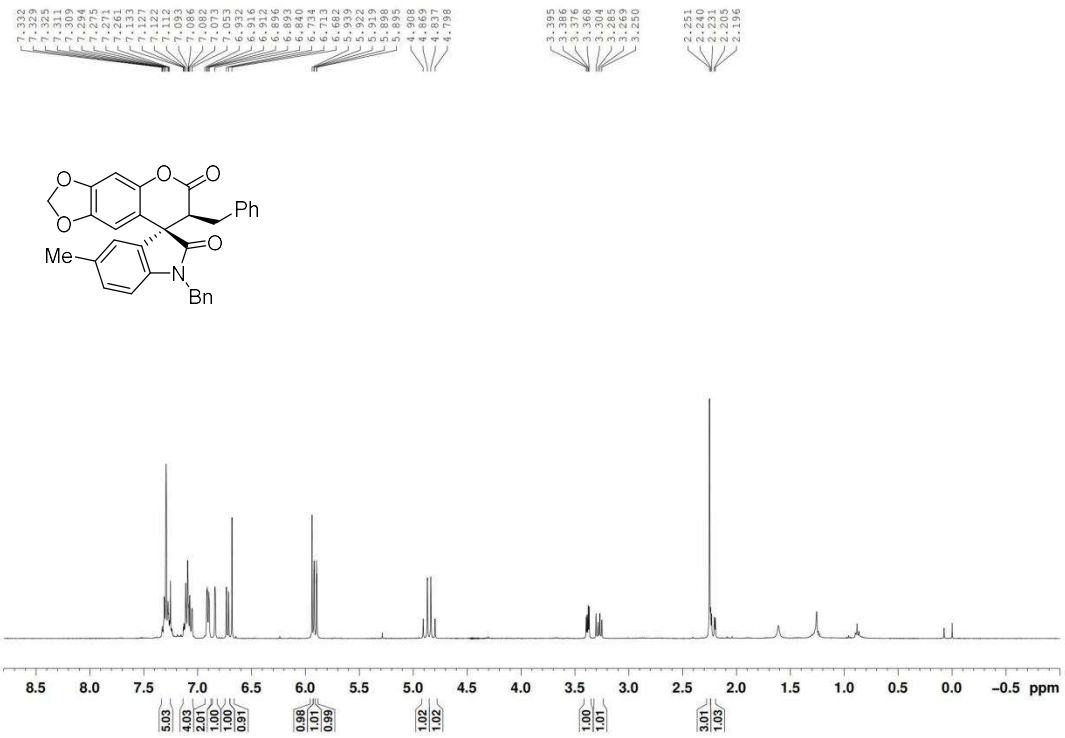
^{1}H NMR spectrum of compound **3e** ($CDCl_3$, 400 MHz)



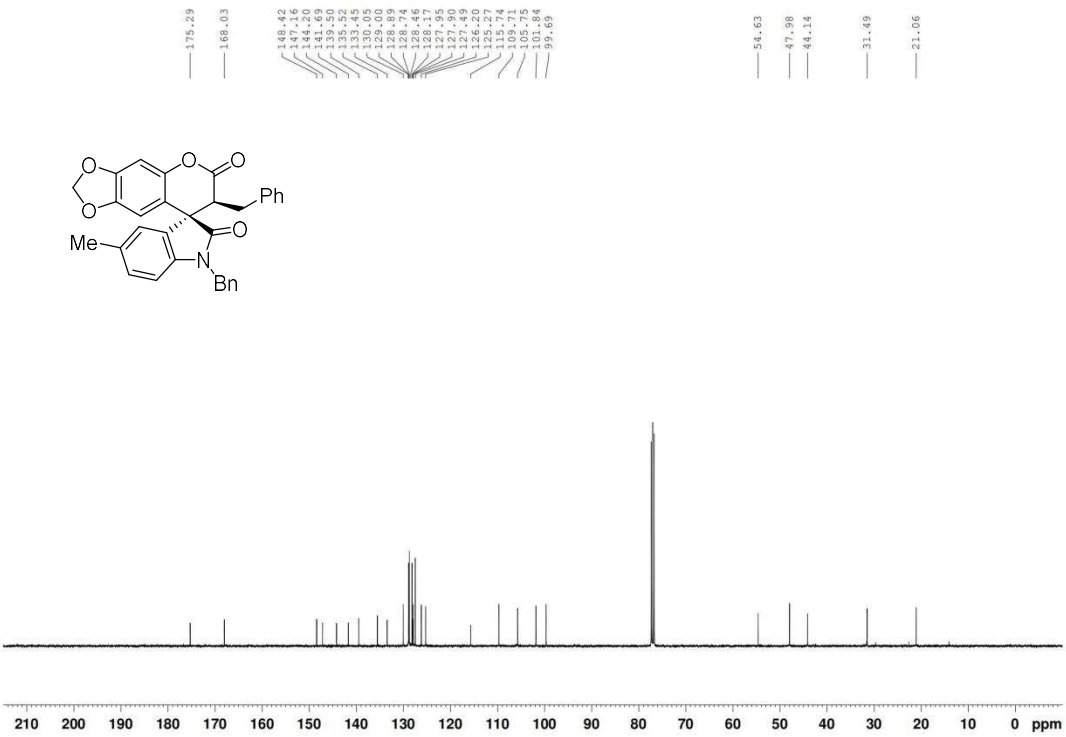
^{13}C NMR spectrum of compound **3e** ($CDCl_3$, 100 MHz)



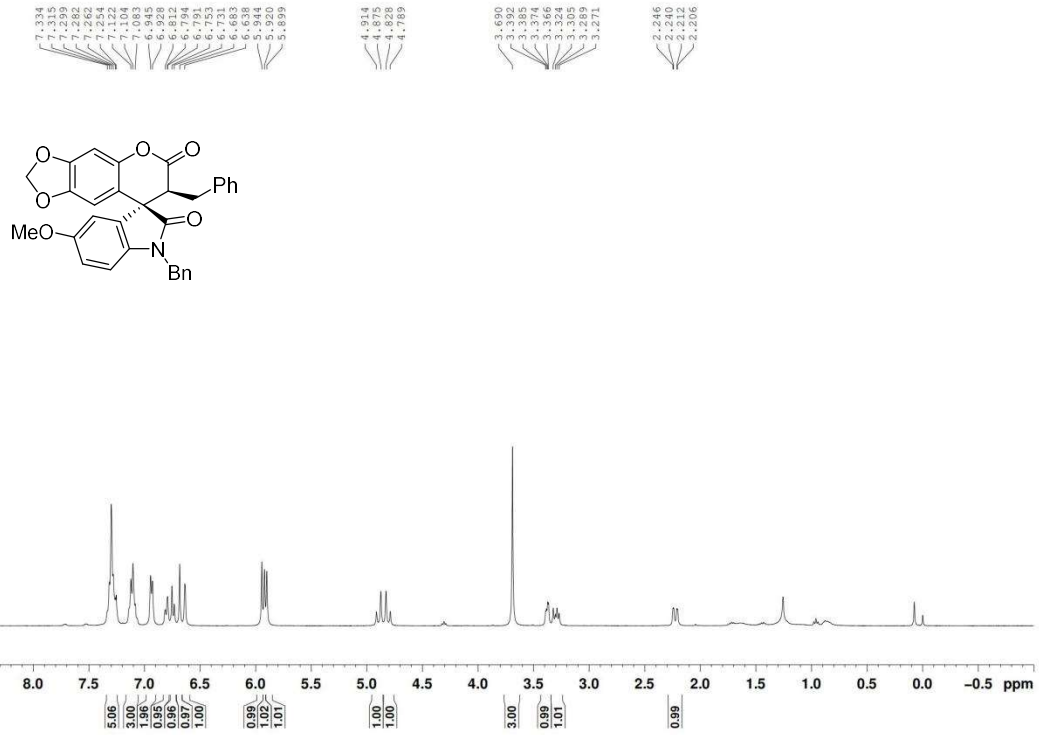
^{1}H NMR spectrum of compound **3f** ($CDCl_3$, 400 MHz)



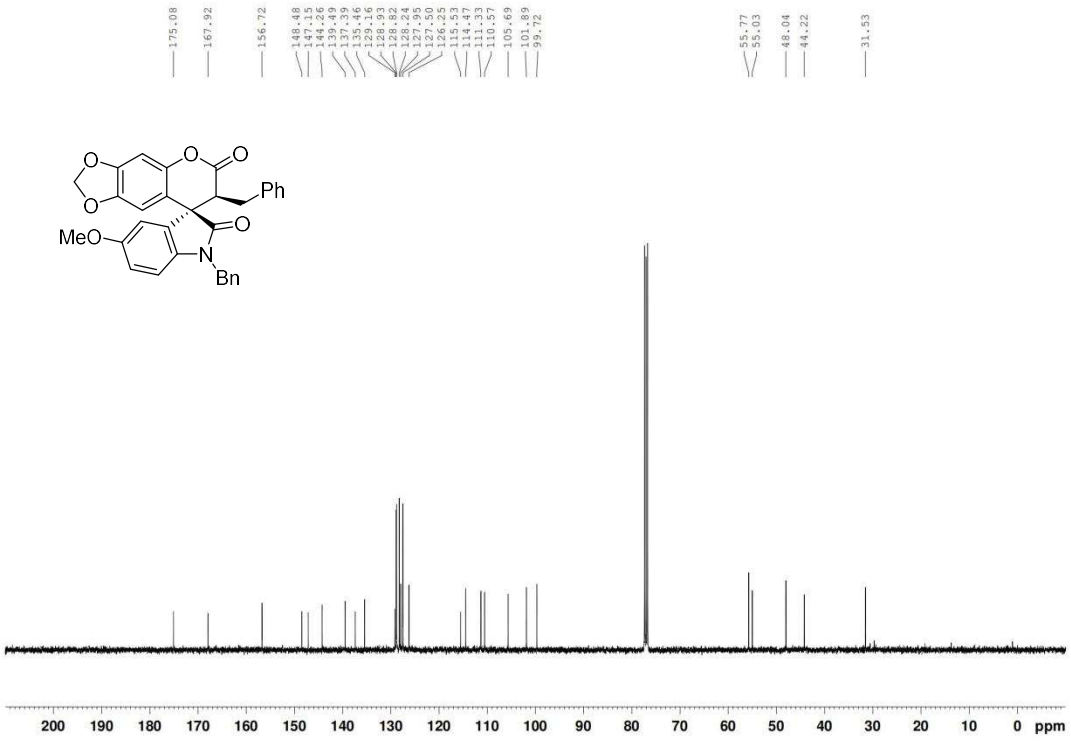
^{13}C NMR spectrum of compound **3f** ($CDCl_3$, 100 MHz)



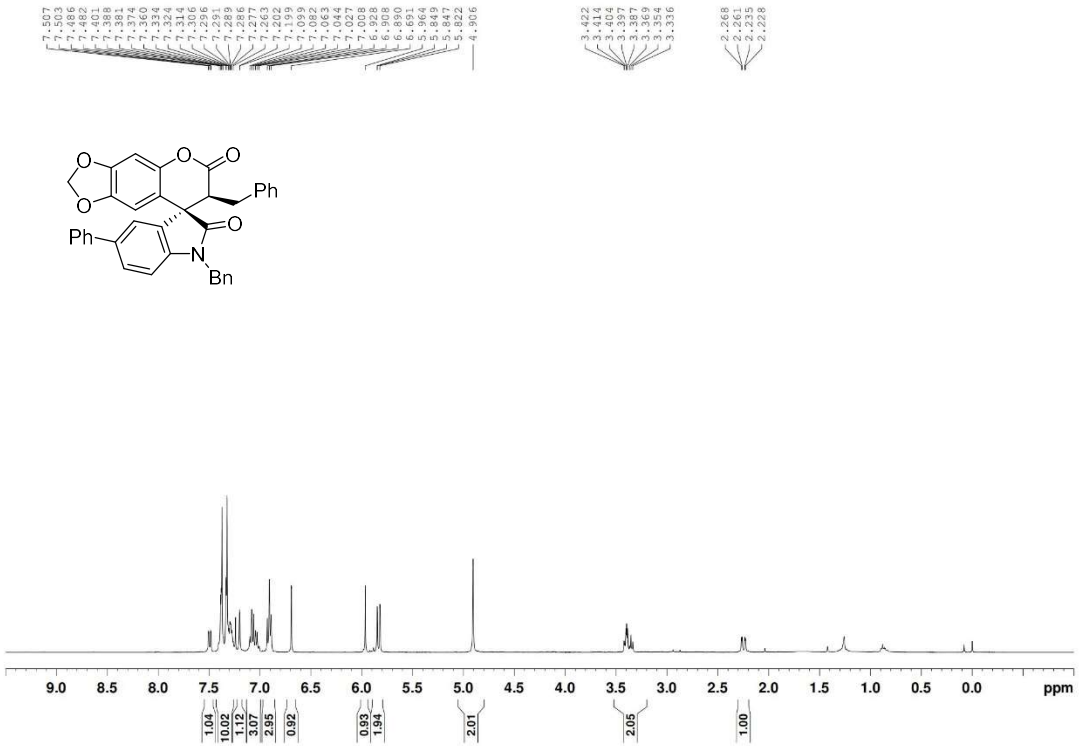
^{1}H NMR spectrum of compound **3g** ($CDCl_3$, 400 MHz)



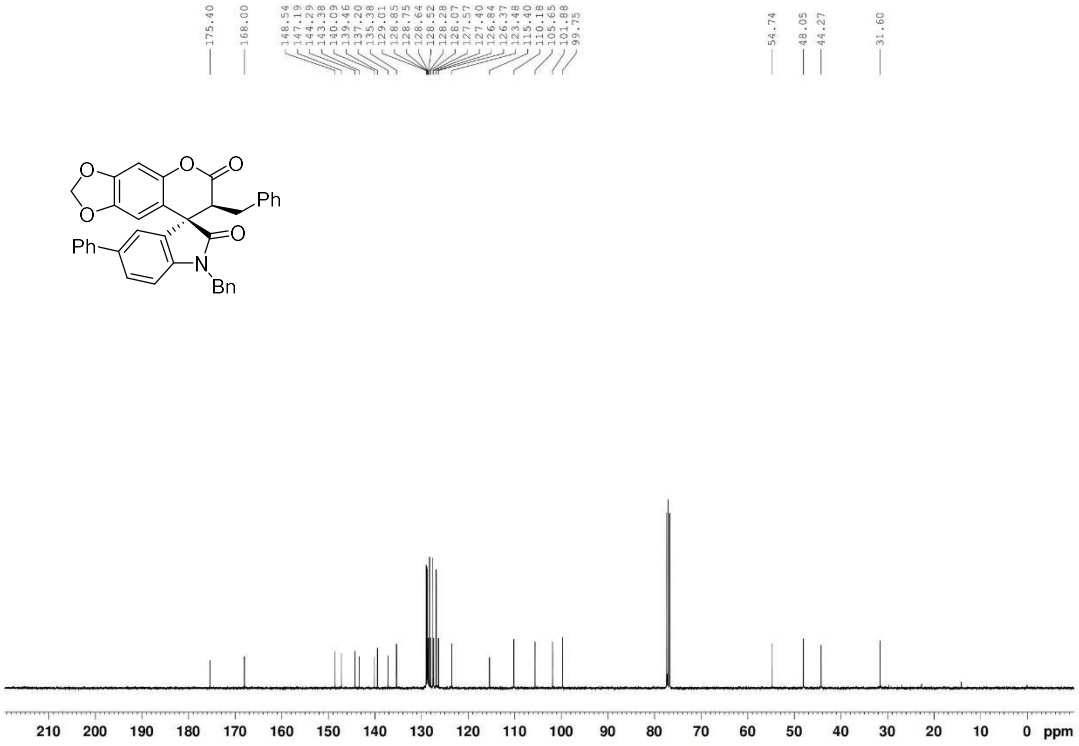
^{13}C NMR spectrum of compound **3g** ($CDCl_3$, 100 MHz)



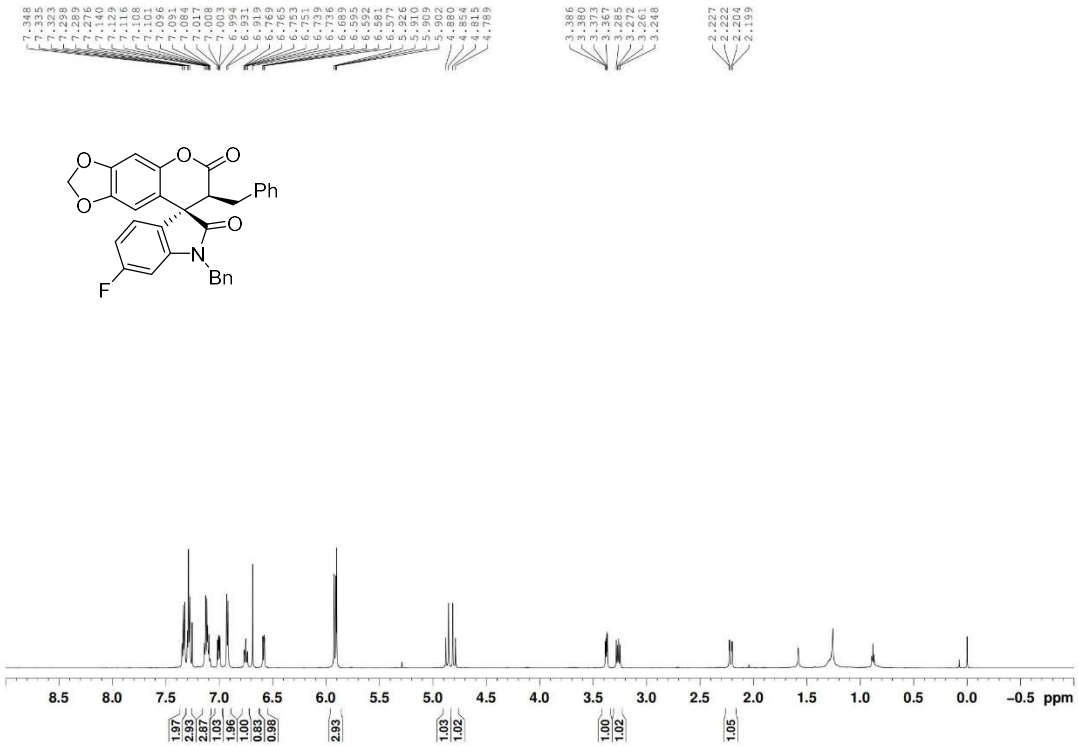
^{1}H NMR spectrum of compound **3h** ($CDCl_3$, 600 MHz)



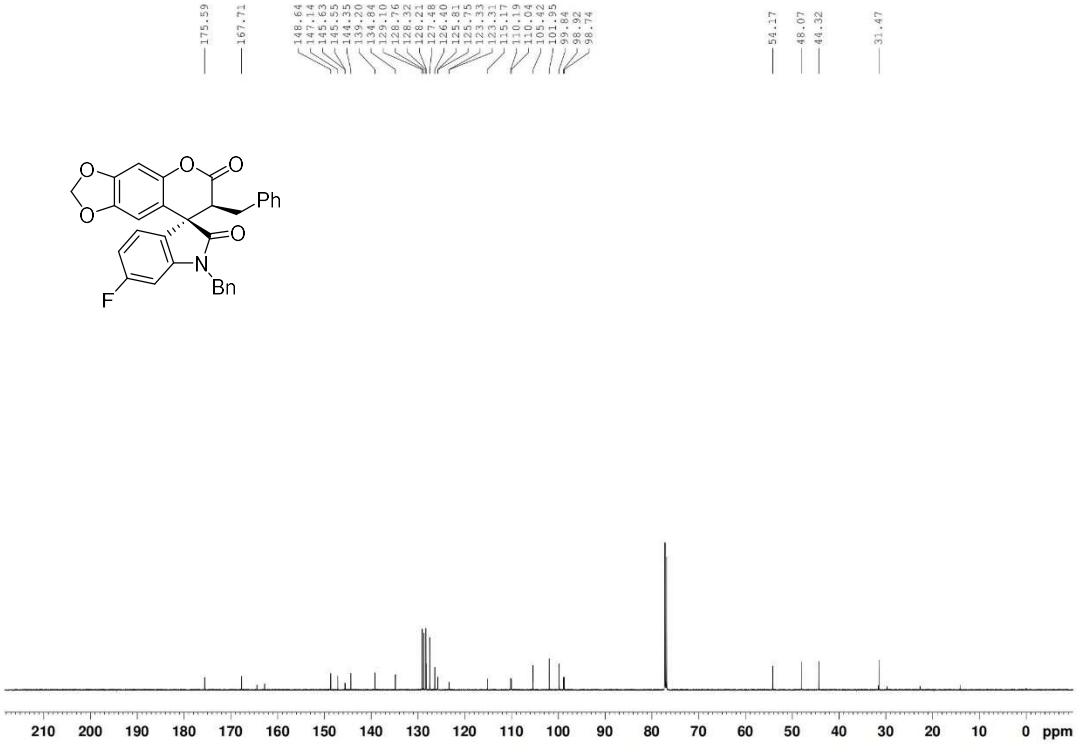
^{13}C NMR spectrum of compound **3h** ($CDCl_3$, 151 MHz)



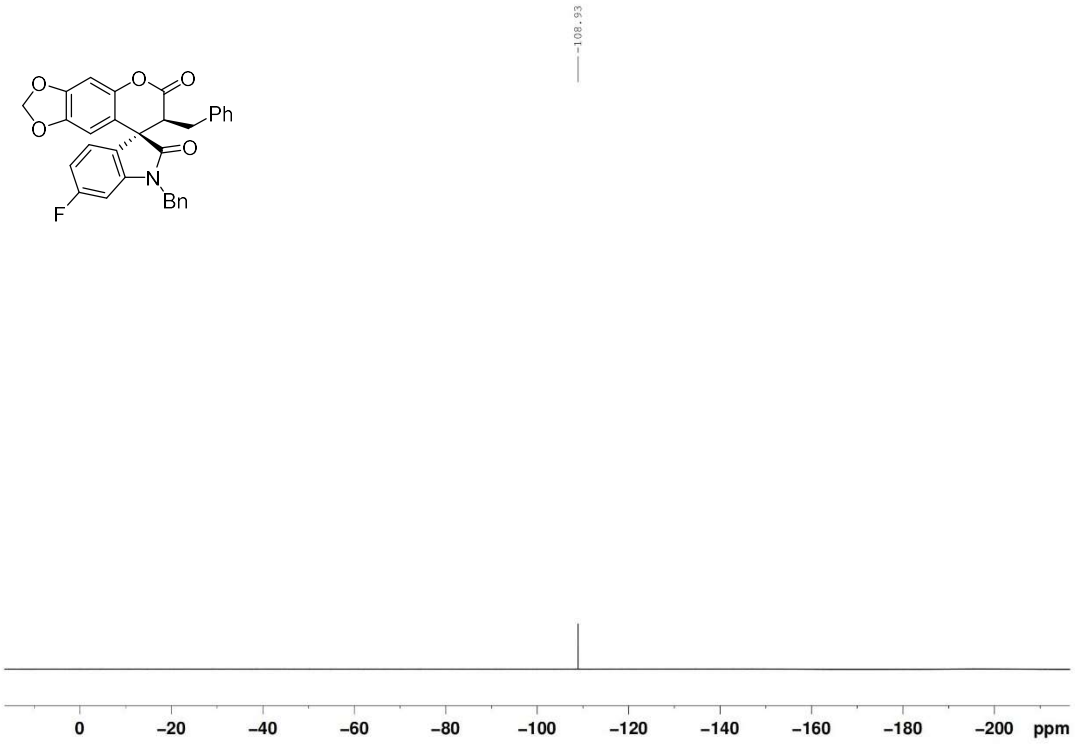
^{1}H NMR spectrum of compound **3i** ($CDCl_3$, 600 MHz)



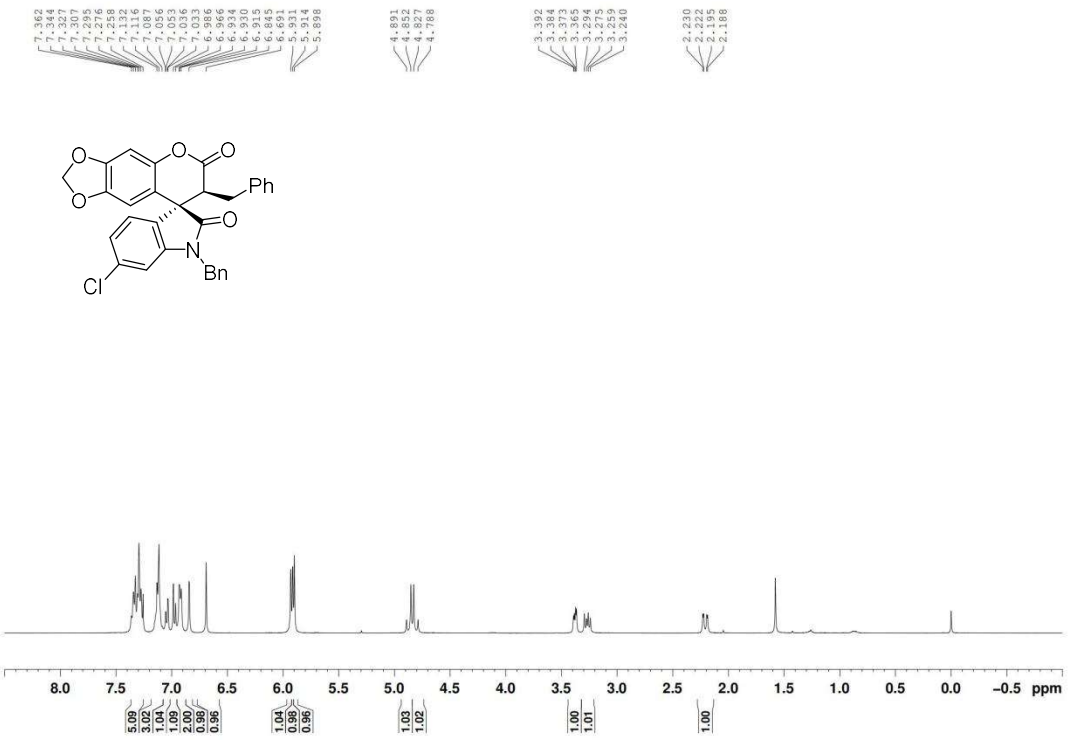
^{13}C NMR spectrum of compound **3i** ($CDCl_3$, 151 MHz)



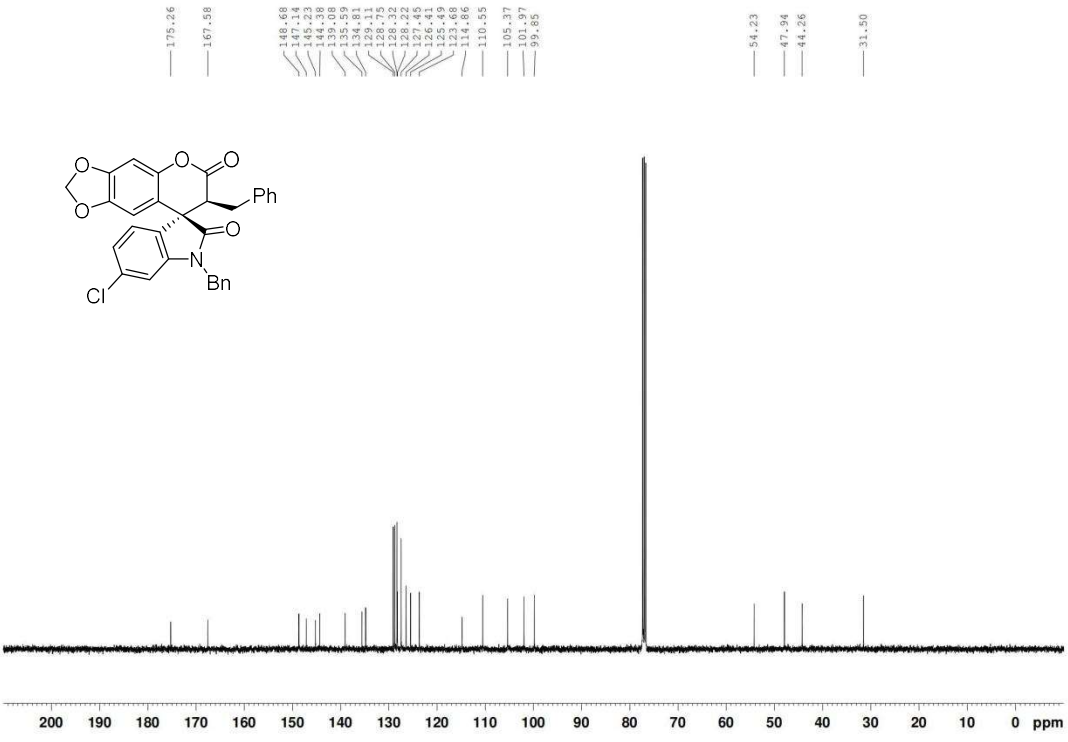
^{19}F NMR spectrum of compound **3i** ($CDCl_3$, 565 MHz)



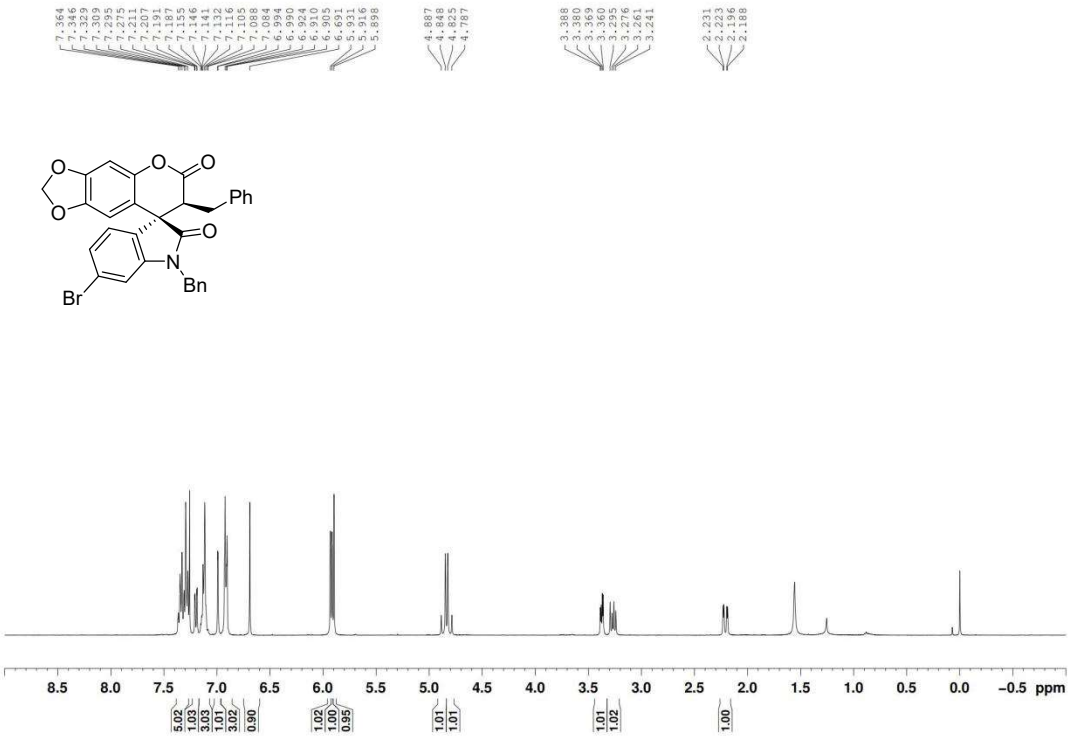
^{1}H NMR spectrum of compound **3j** ($CDCl_3$, 400 MHz)



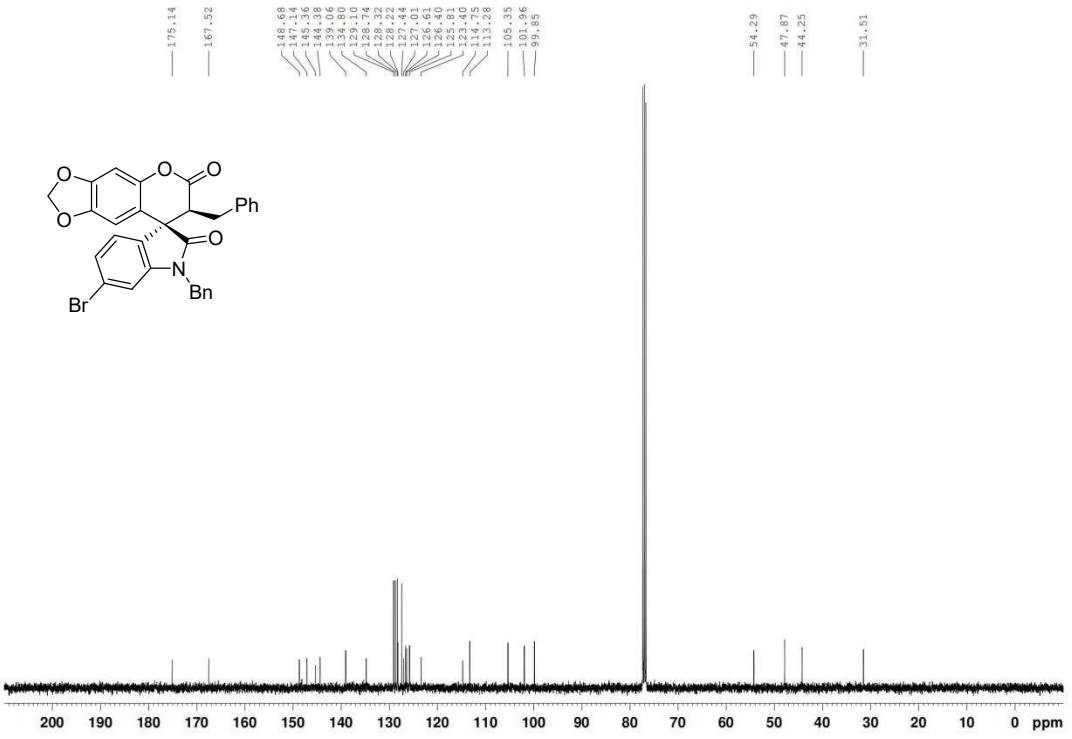
^{13}C NMR spectrum of compound **3j** ($CDCl_3$, 100 MHz)



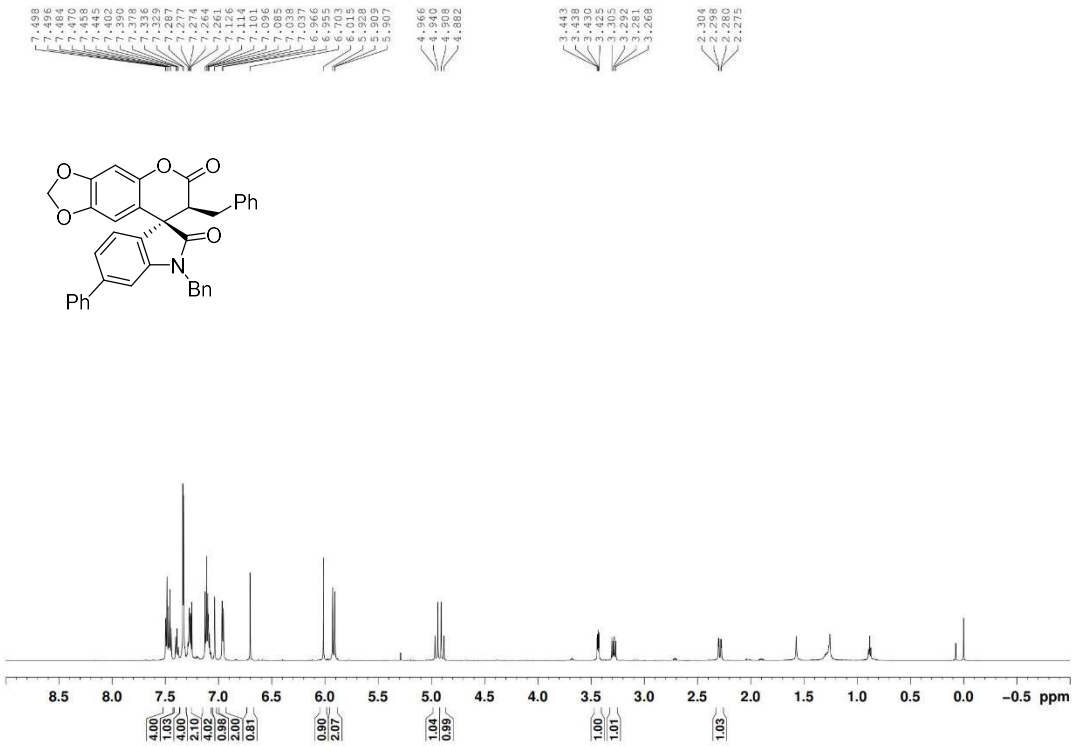
^{1}H NMR spectrum of compound **3k** ($CDCl_3$, 400 MHz)



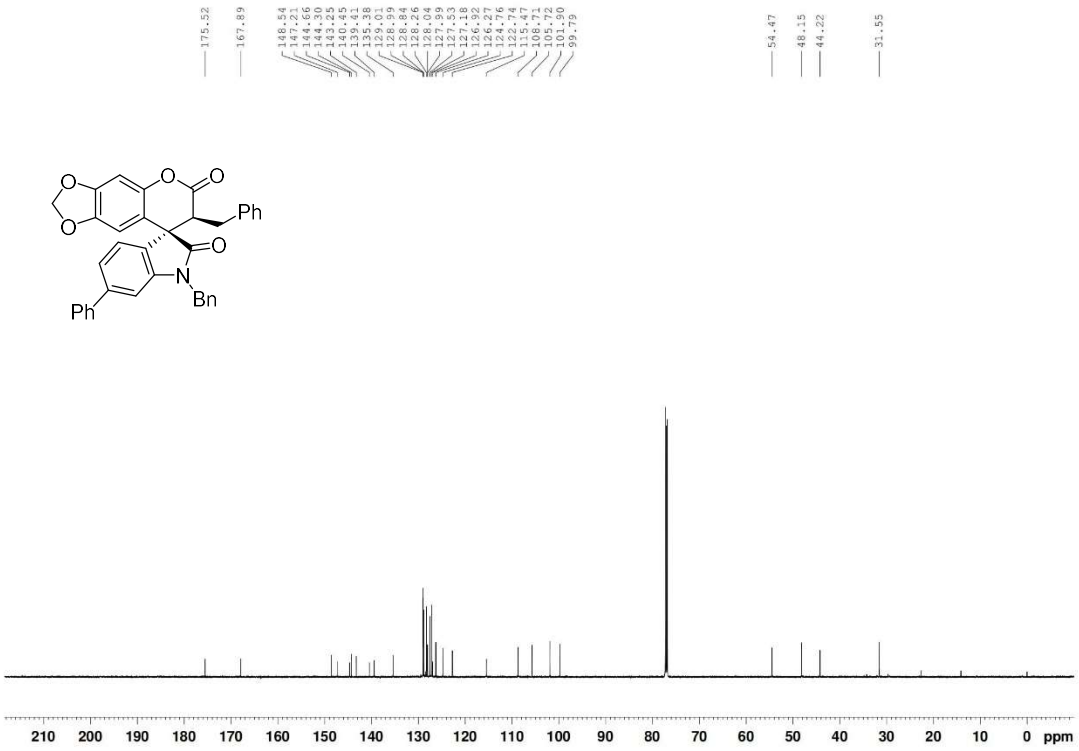
^{13}C NMR spectrum of compound **3k** ($CDCl_3$, 100 MHz)



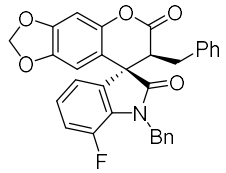
^{1}H NMR spectrum of compound **3l** ($CDCl_3$, 600 MHz)

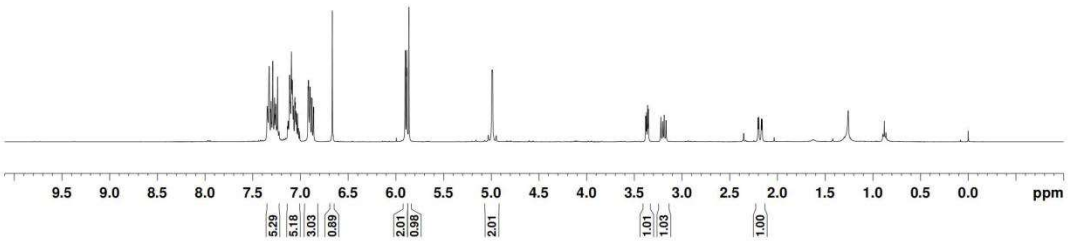


^{13}C NMR spectrum of compound **3l** ($CDCl_3$, 151 MHz)

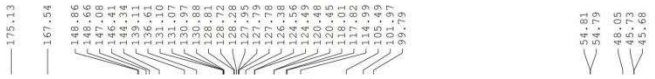


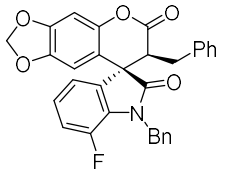
^{1}H NMR spectrum of compound **3m** ($CDCl_3$, 400 MHz)

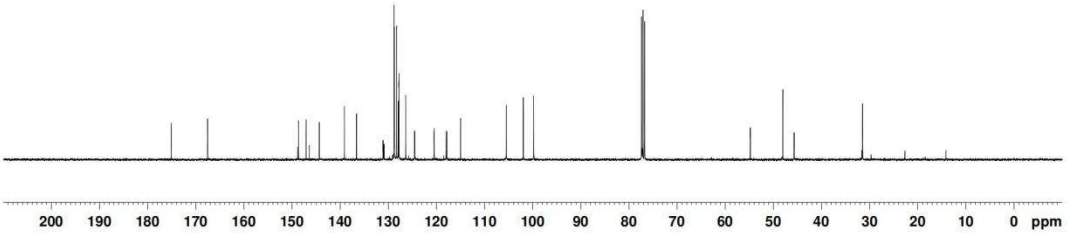




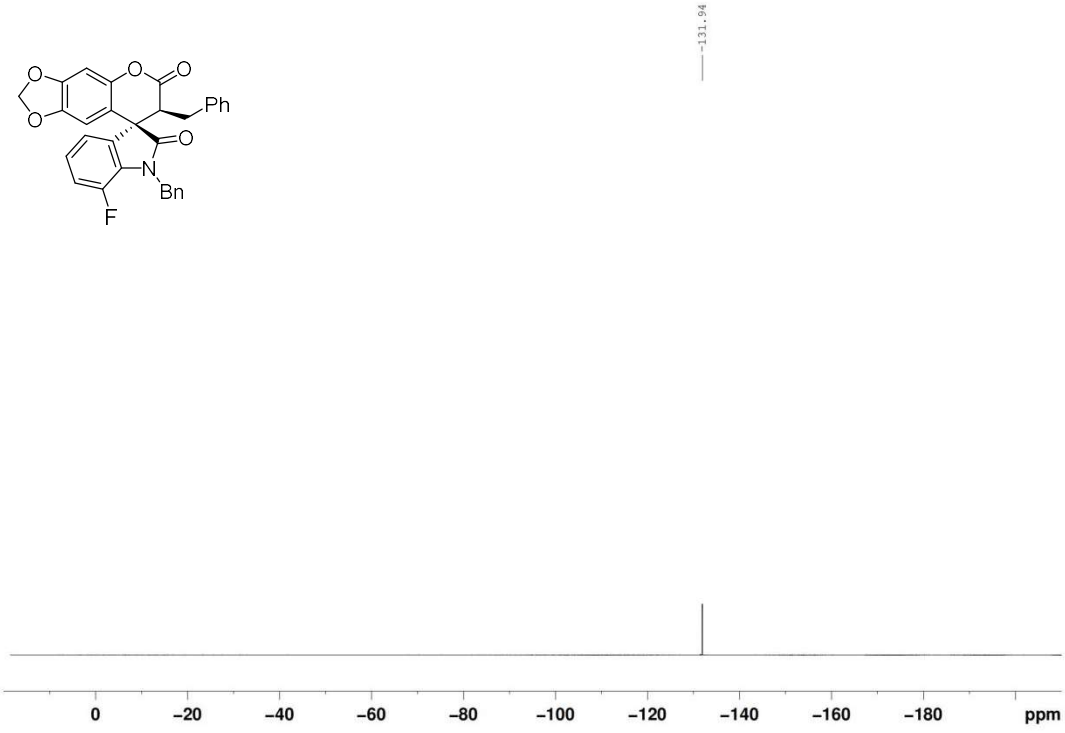
^{13}C NMR spectrum of compound **3m** ($CDCl_3$, 100 MHz)



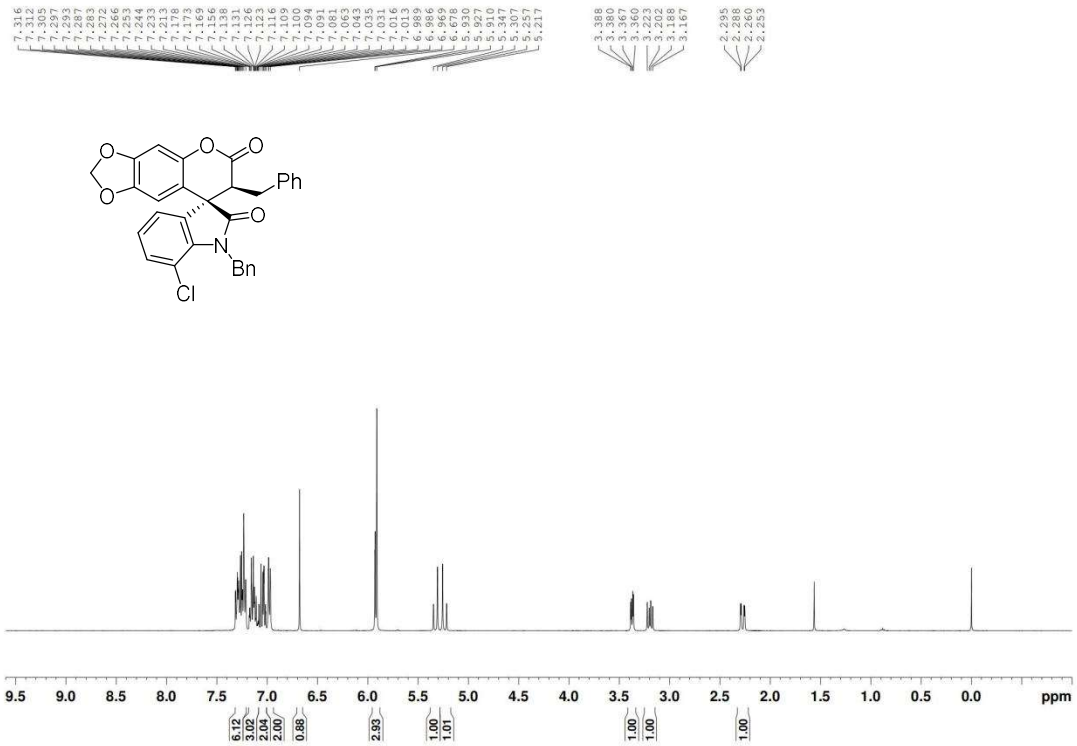




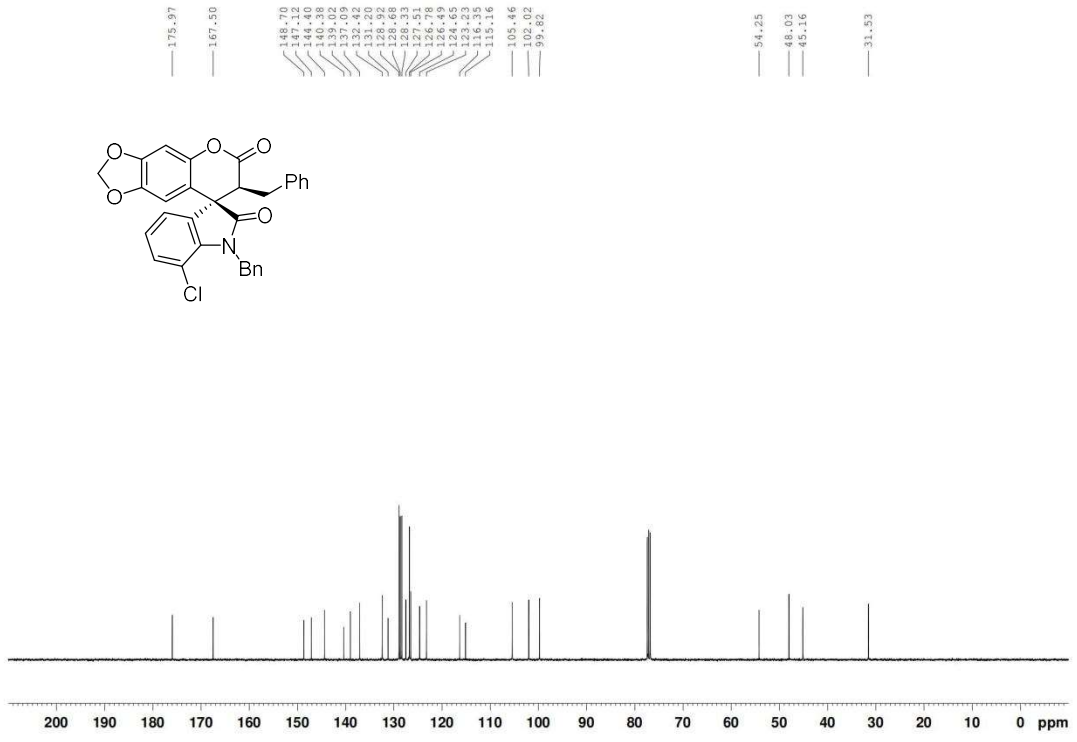
^{19}F NMR spectrum of compound **3m** ($CDCl_3$, 376 MHz)



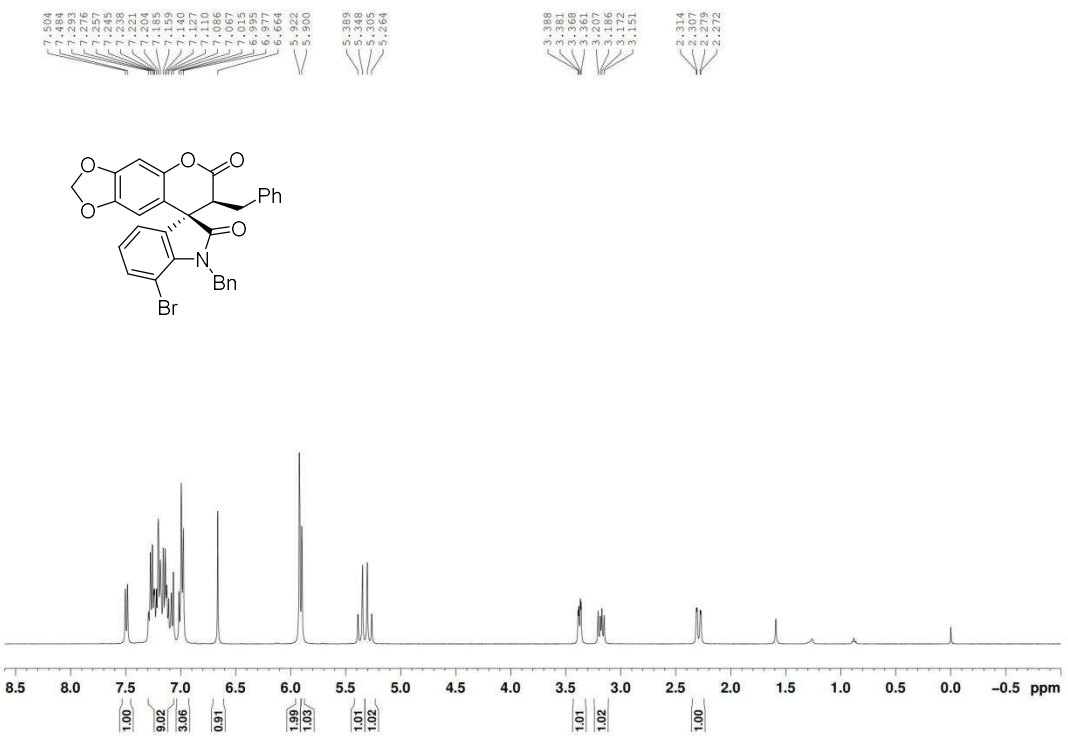
^{1}H NMR spectrum of compound **3n** ($CDCl_3$, 400 MHz)



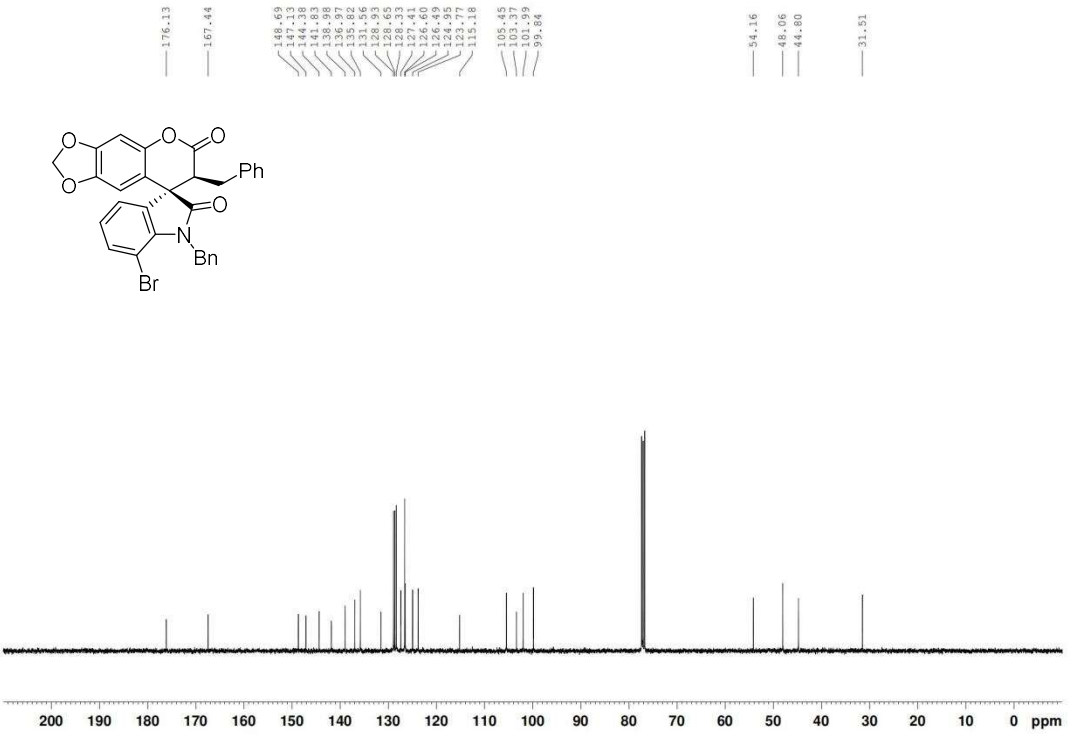
^{13}C NMR spectrum of compound **3n** ($CDCl_3$, 100 MHz)



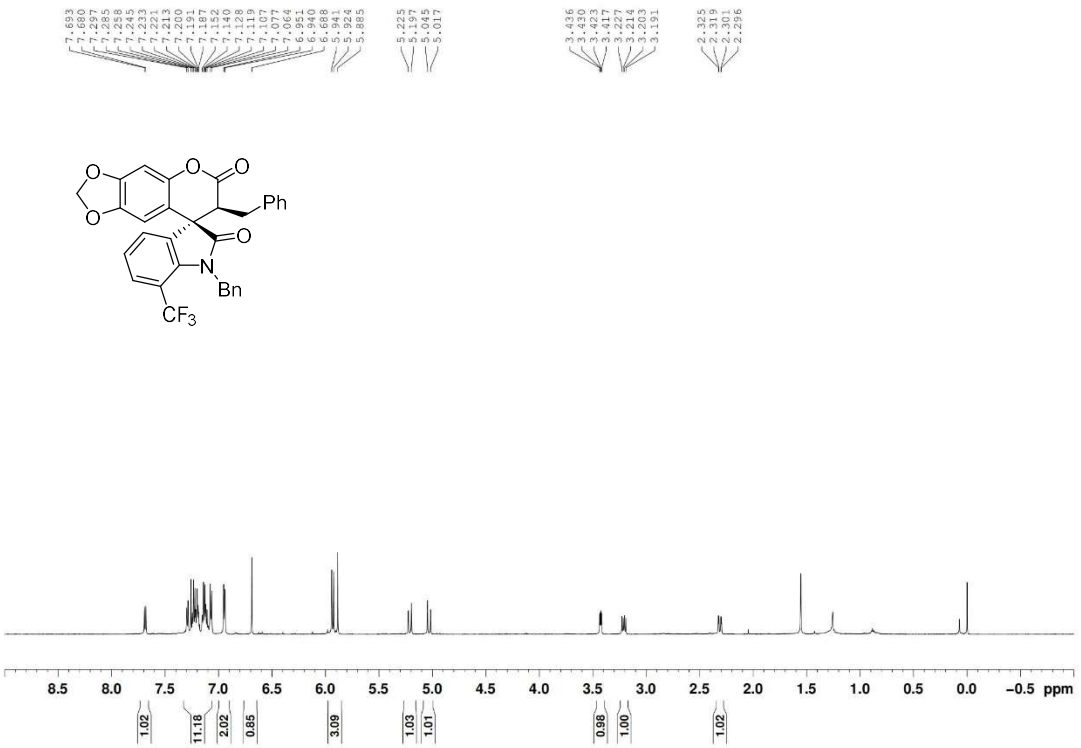
^{1}H NMR spectrum of compound **3o** ($CDCl_3$, 400 MHz)



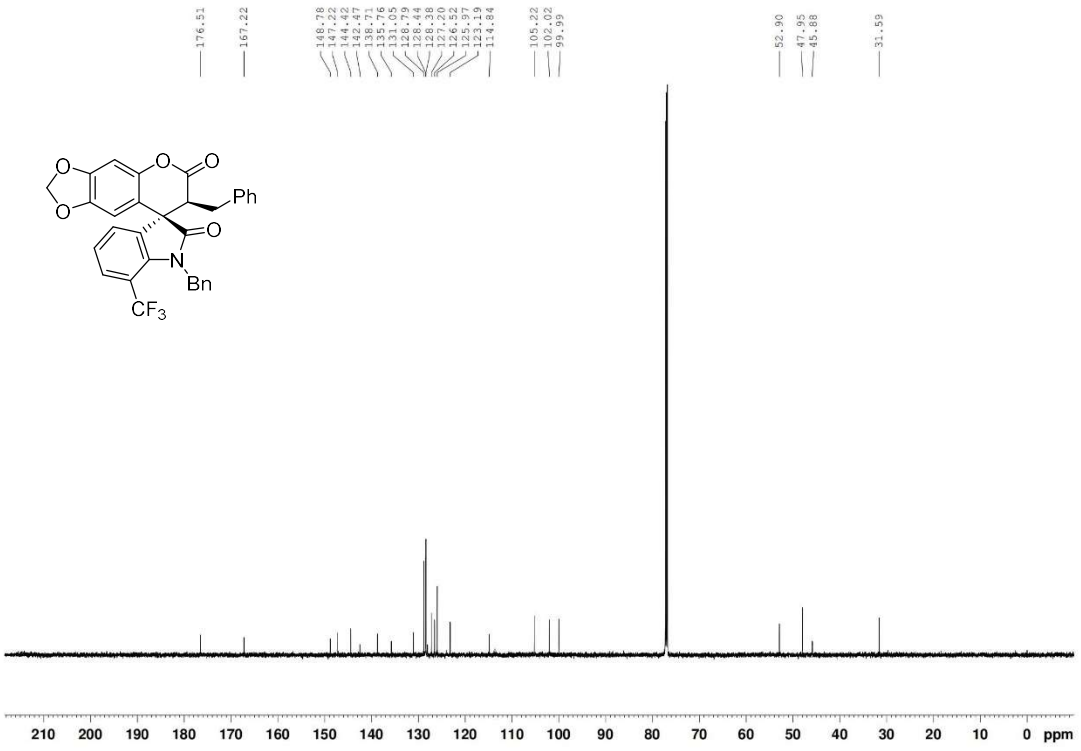
^{13}C NMR spectrum of compound **3o** ($CDCl_3$, 100 MHz)



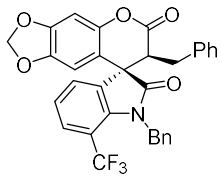
^{1}H NMR spectrum of compound **3p** ($CDCl_3$, 600 MHz)

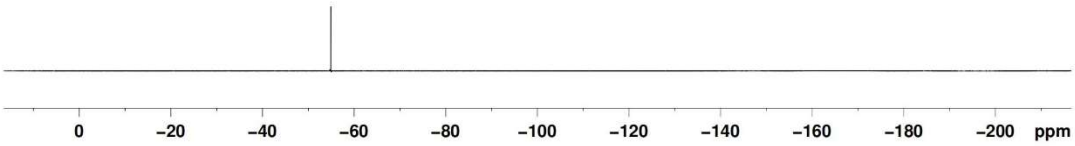


^{13}C NMR spectrum of compound **3p** ($CDCl_3$, 151 MHz)

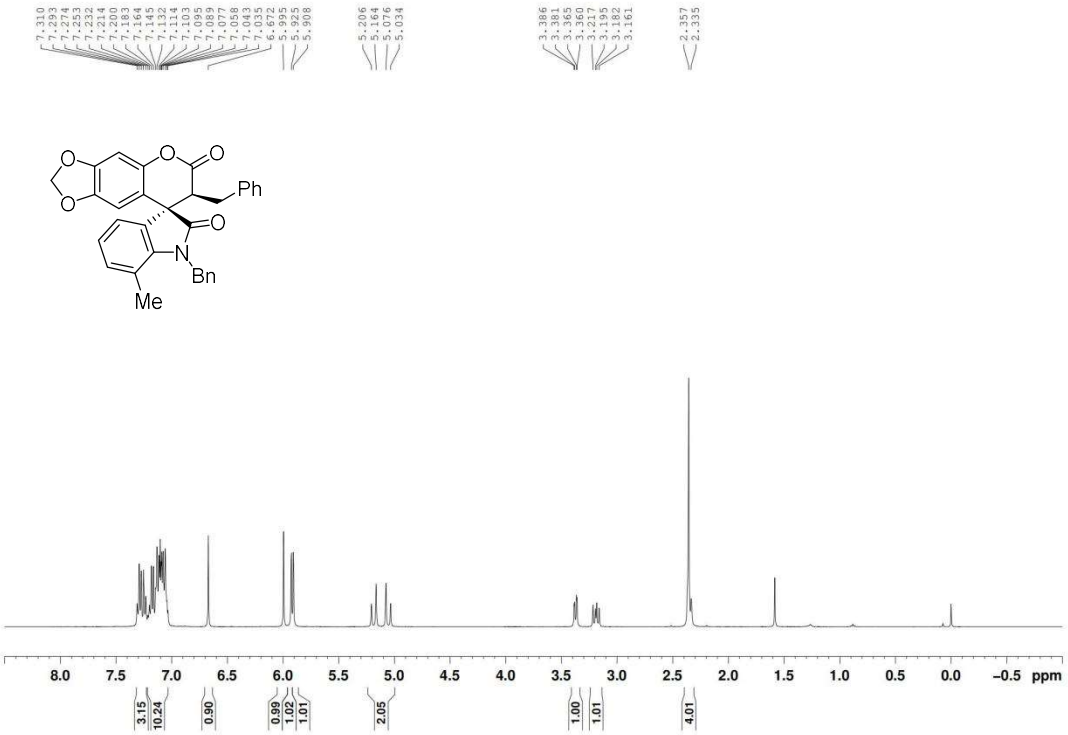


^{19}F NMR spectrum of compound **3p** ($CDCl_3$, 376 MHz)

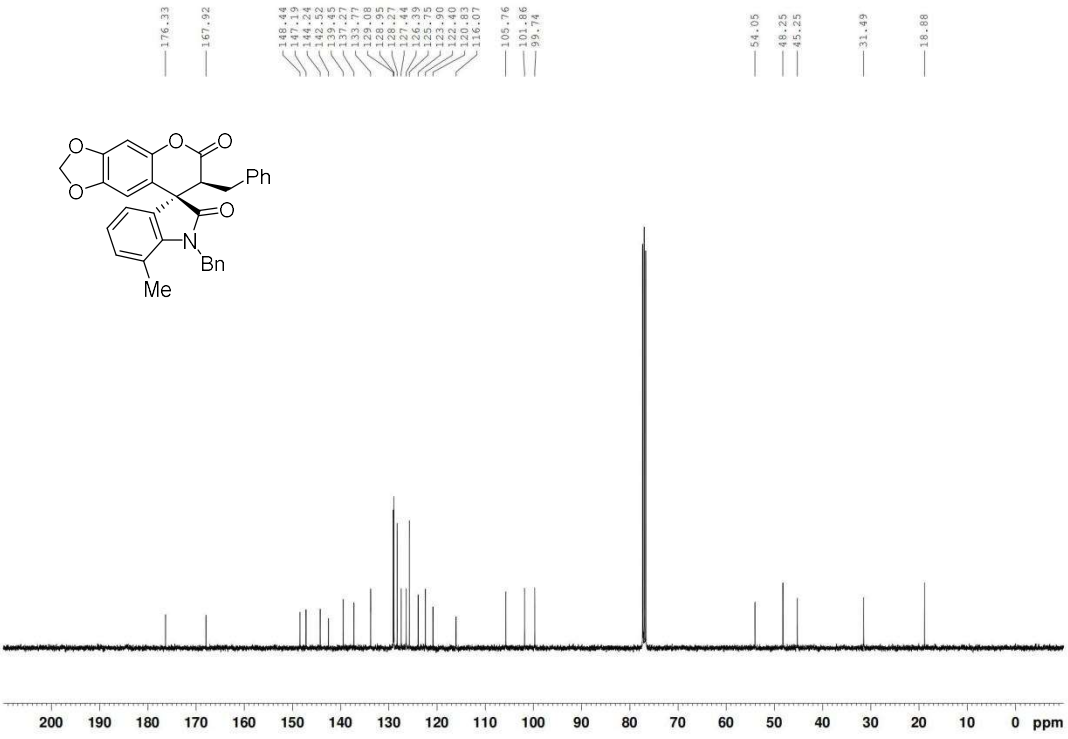




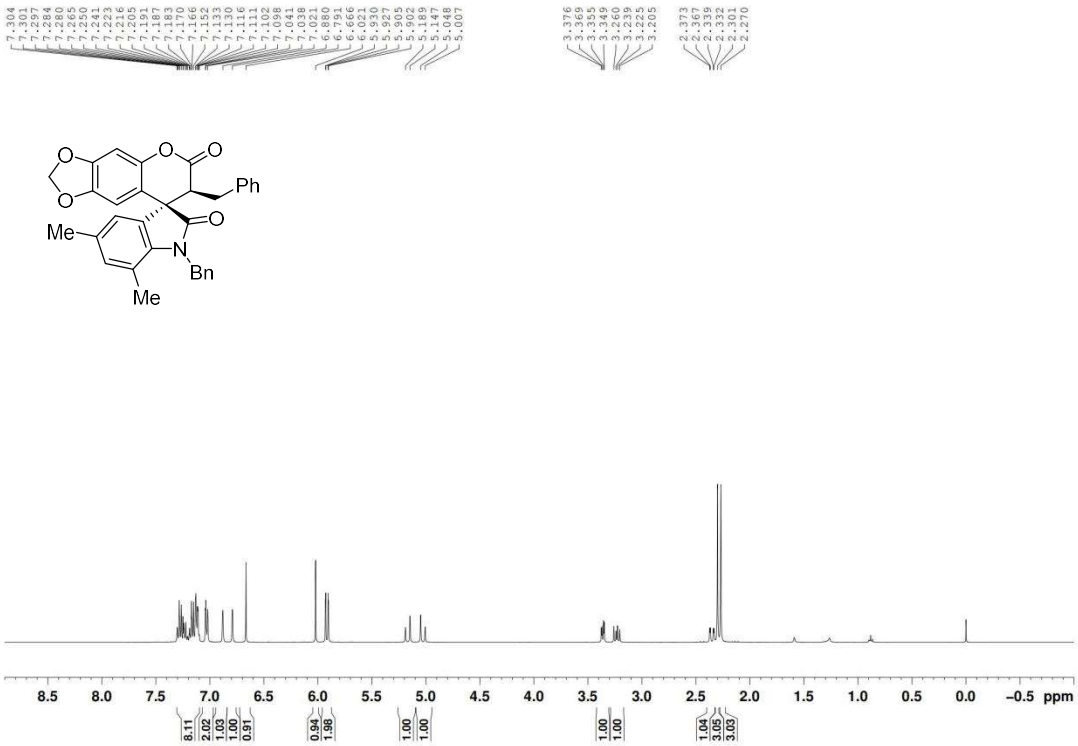
^{1}H NMR spectrum of compound **3q** ($CDCl_3$, 400 MHz)



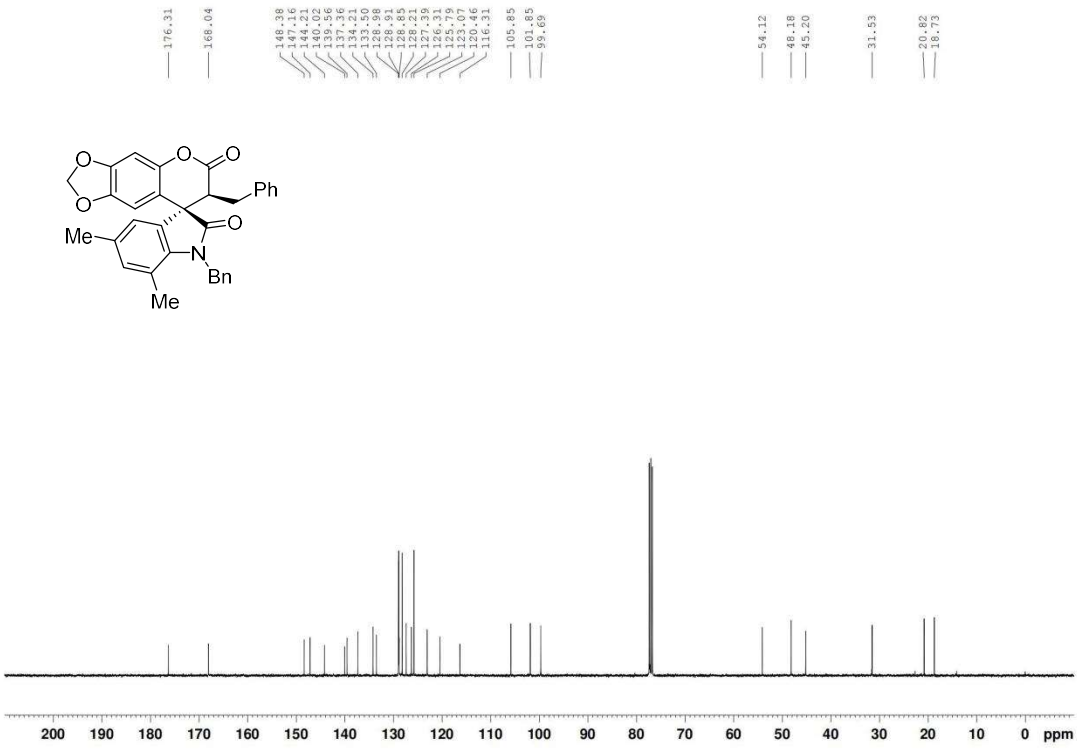
^{13}C NMR spectrum of compound **3q** ($CDCl_3$, 100 MHz)



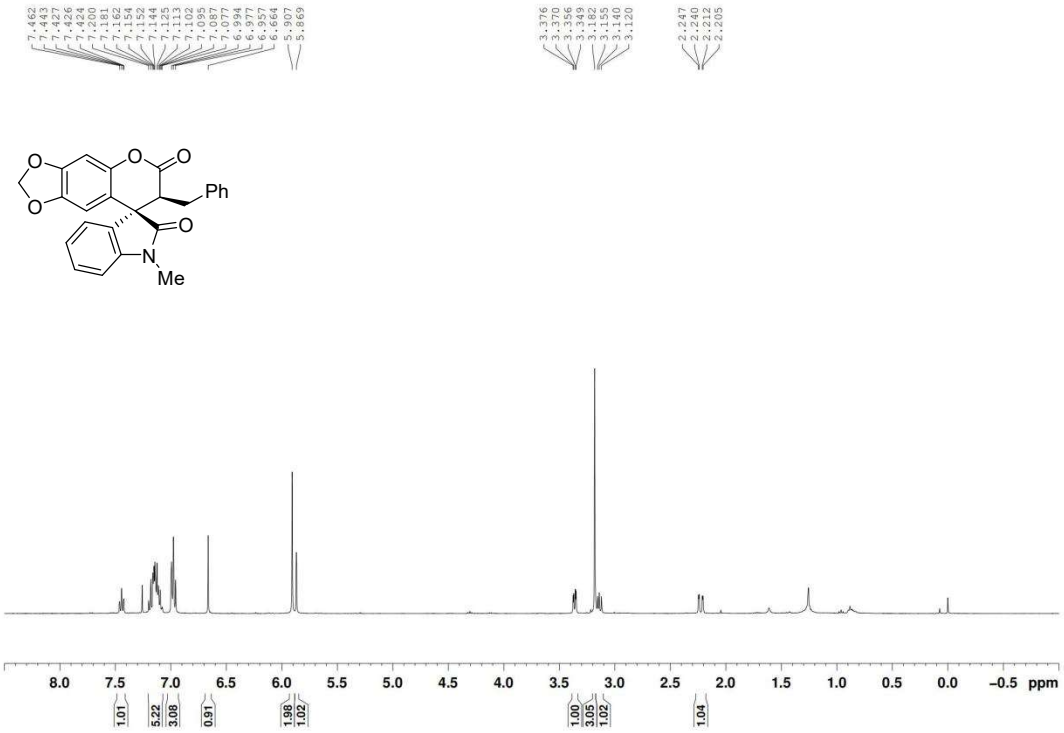
^{1}H NMR spectrum of compound **3r** ($CDCl_3$, 400 MHz)



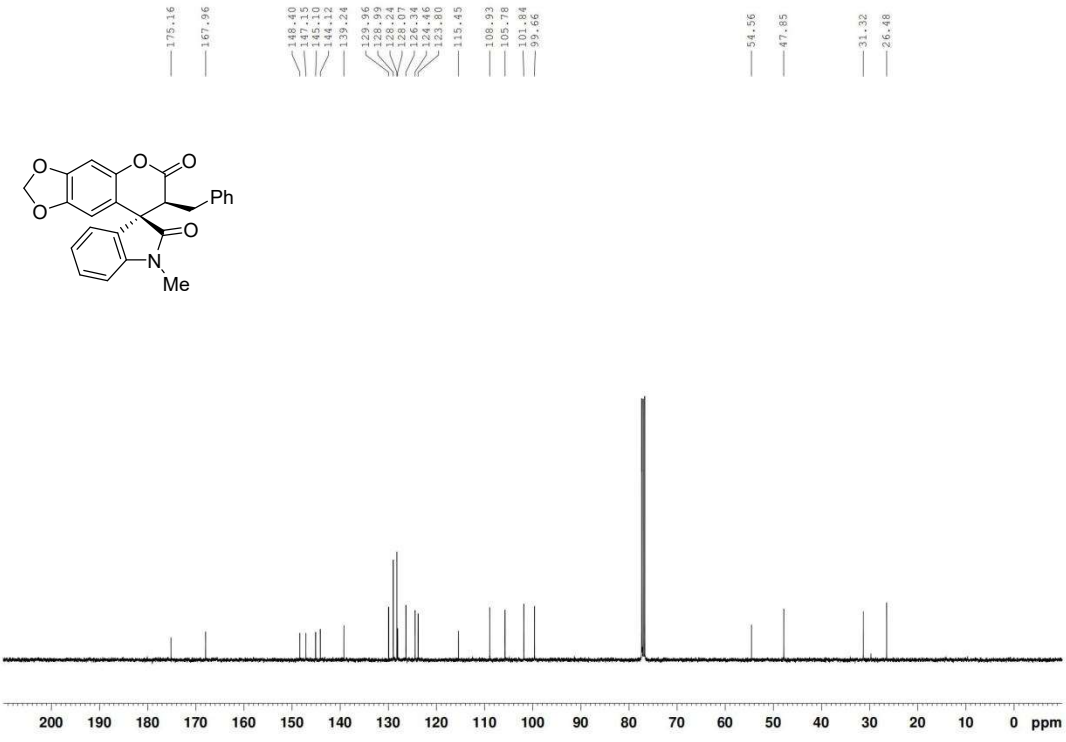
^{13}C NMR spectrum of compound **3r** ($CDCl_3$, 100 MHz)



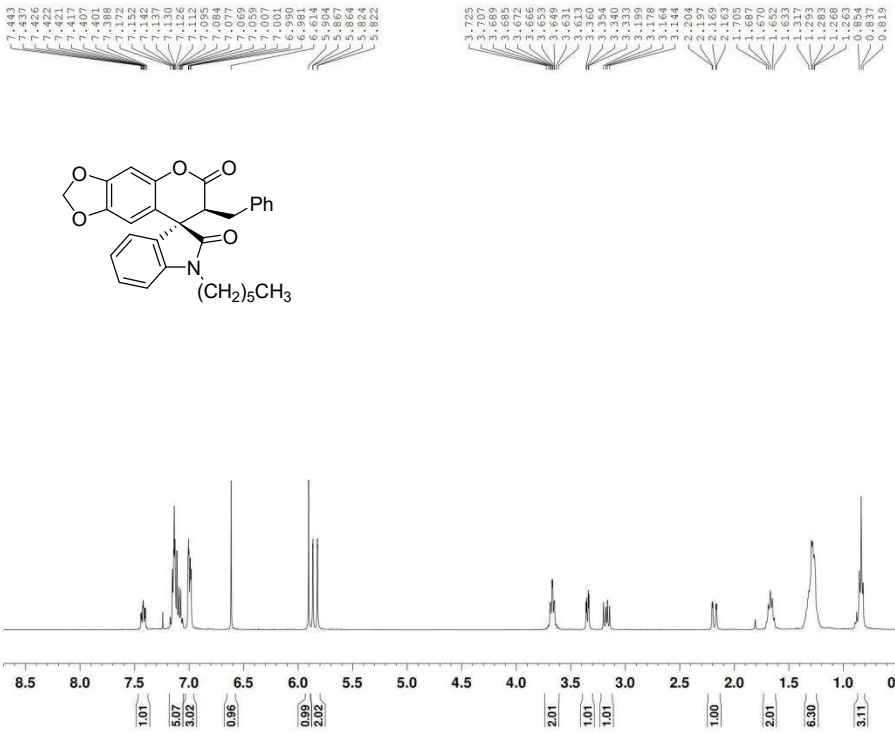
^{1}H NMR spectrum of compound **3s** ($CDCl_3$, 400 MHz)



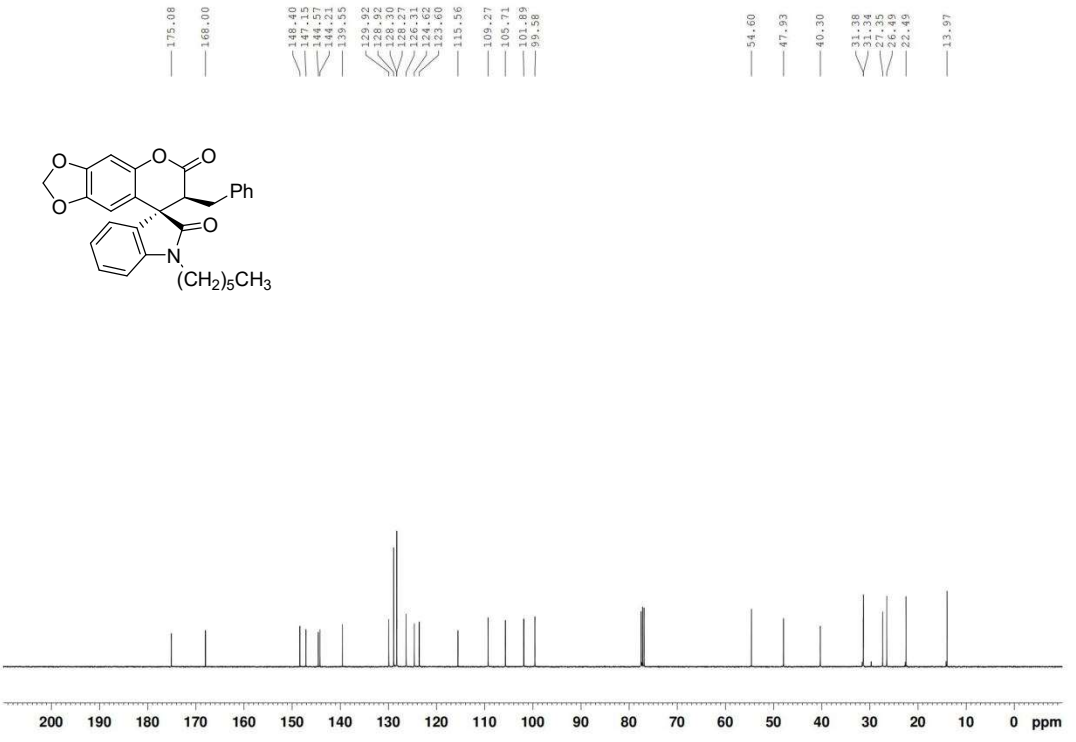
^{13}C NMR spectrum of compound **3s** ($CDCl_3$, 100 MHz)



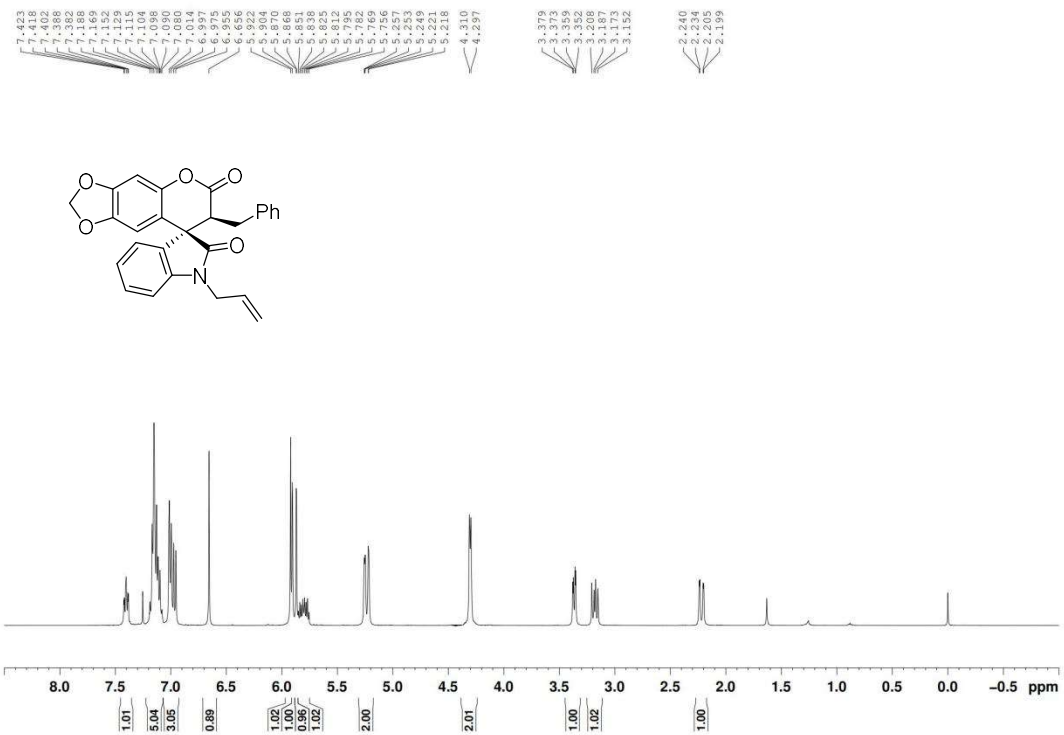
^{1}H NMR spectrum of compound **3t** ($CDCl_3$, 400 MHz)



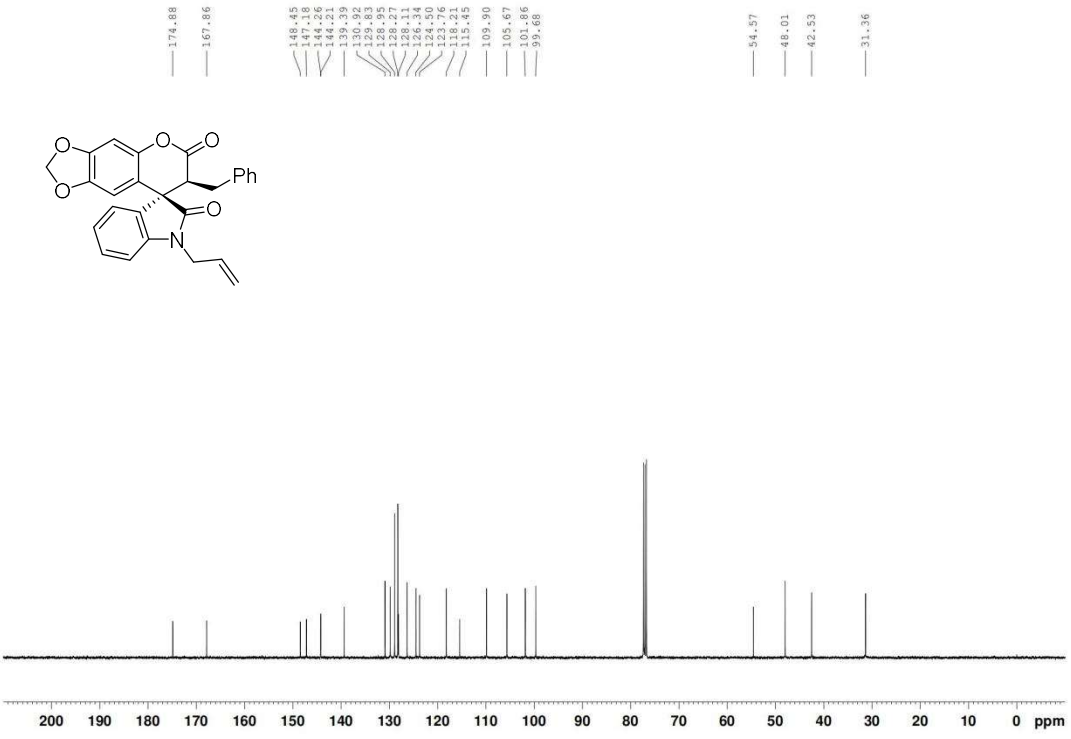
^{13}C NMR spectrum of compound **3t** ($CDCl_3$, 100 MHz)



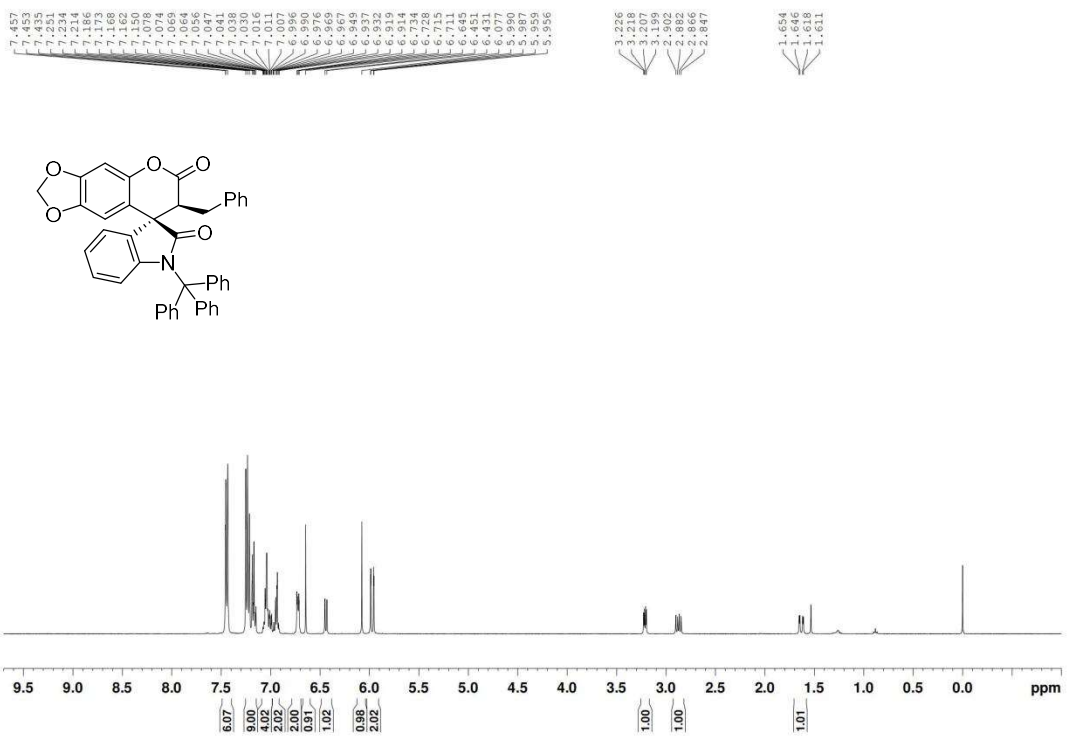
^{1}H NMR spectrum of compound **3u** ($CDCl_3$, 400 MHz)



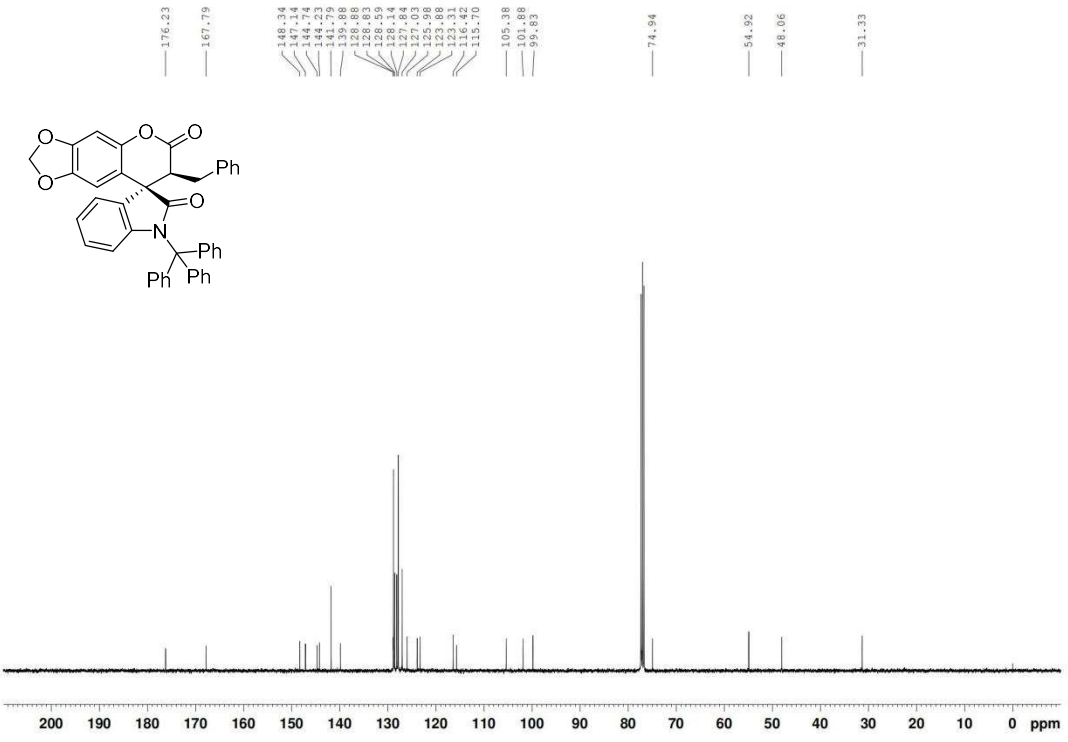
^{13}C NMR spectrum of compound **3u** ($CDCl_3$, 100 MHz)



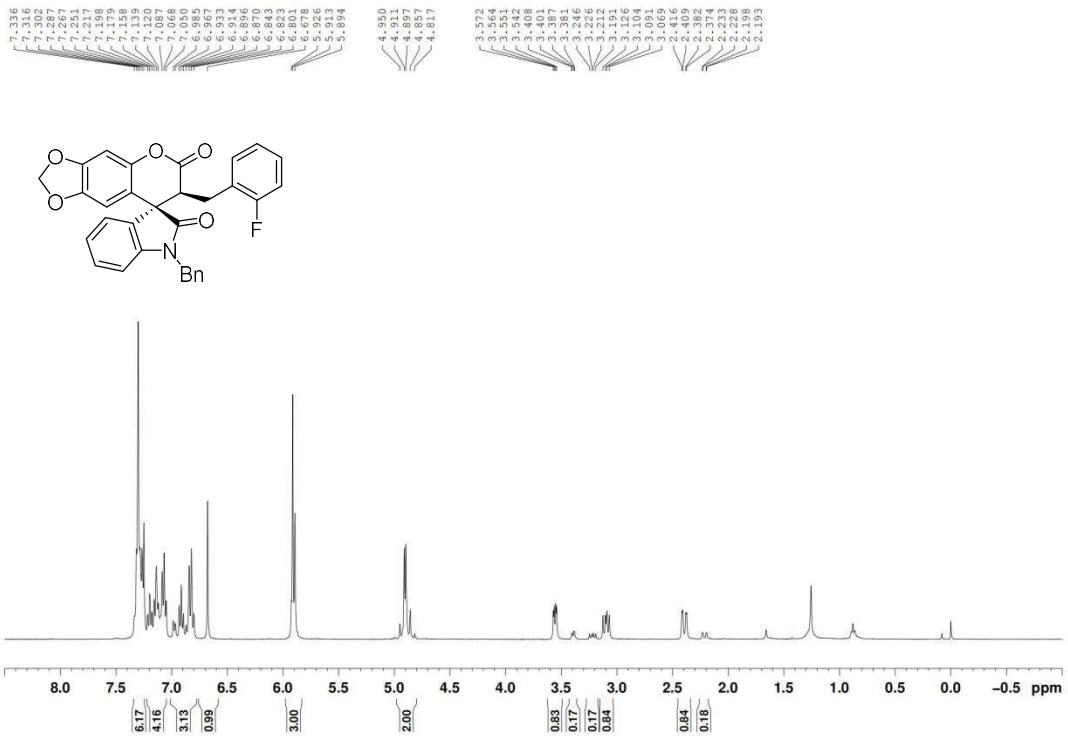
^{1}H NMR spectrum of compound **3v** ($CDCl_3$, 400 MHz)



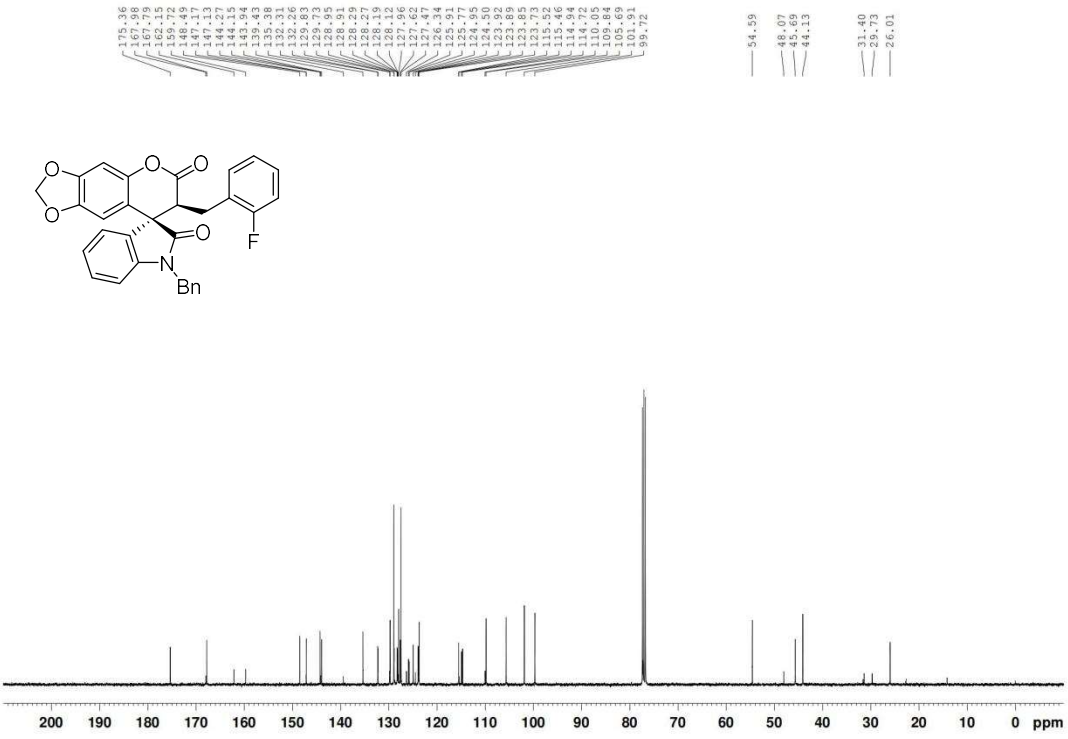
^{13}C NMR spectrum of compound **3v** ($CDCl_3$, 100 MHz)



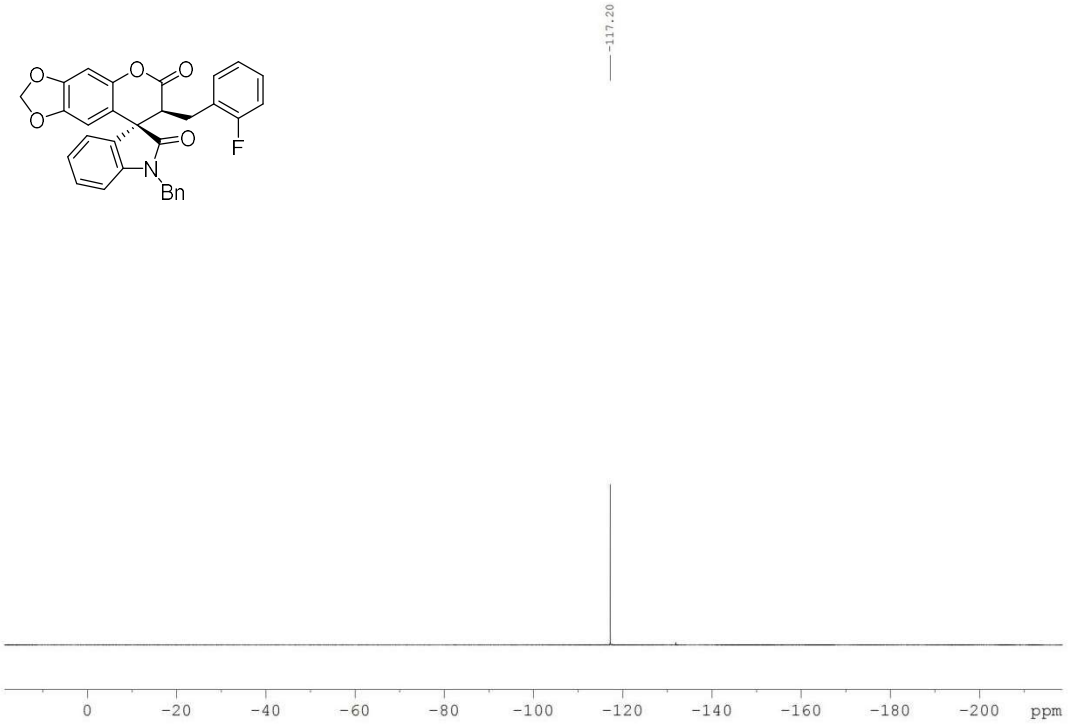
^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)



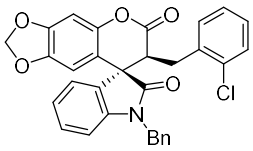
^{13}C NMR spectrum of compound **4a** ($CDCl_3$, 100 MHz)

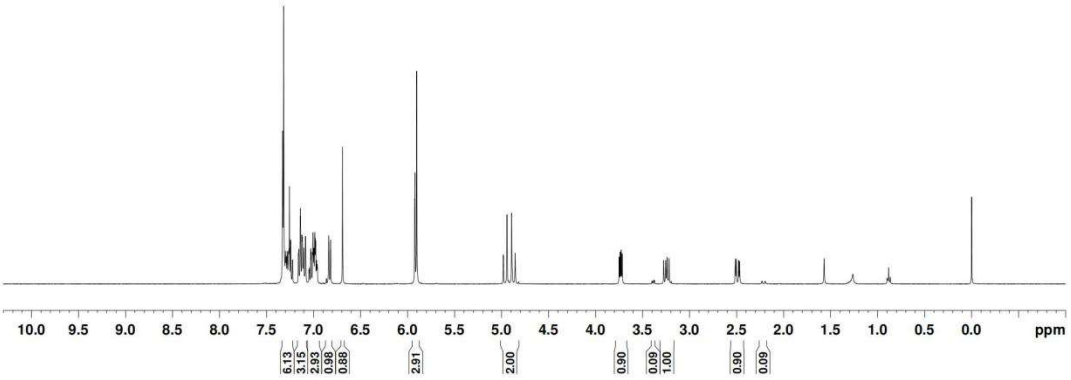


^{19}F NMR spectrum of compound **4a** ($CDCl_3$, 376 MHz)

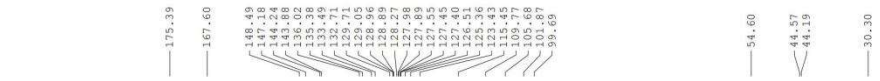


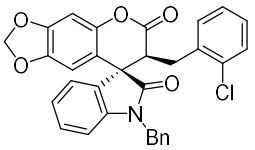
^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 400 MHz)

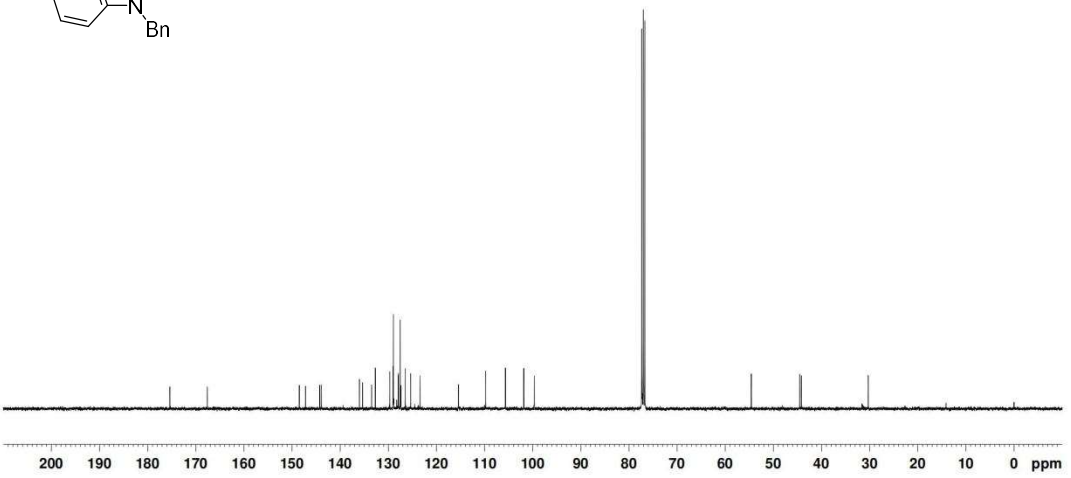




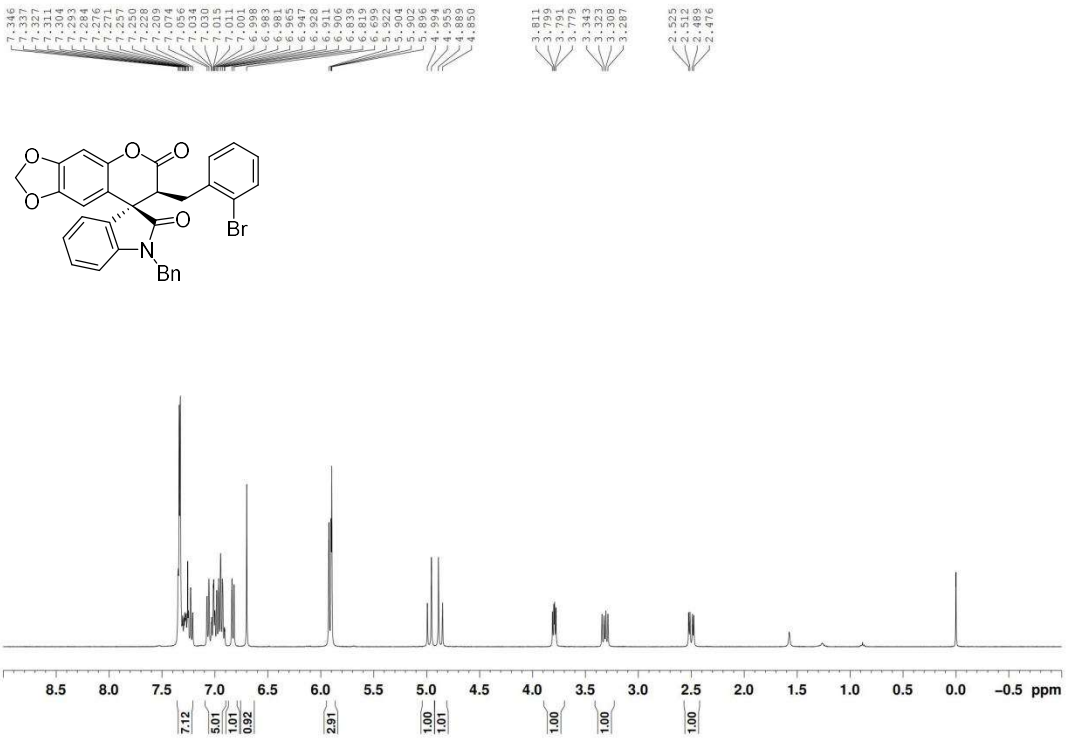
^{13}C NMR spectrum of compound **4b** ($CDCl_3$, 100 MHz)



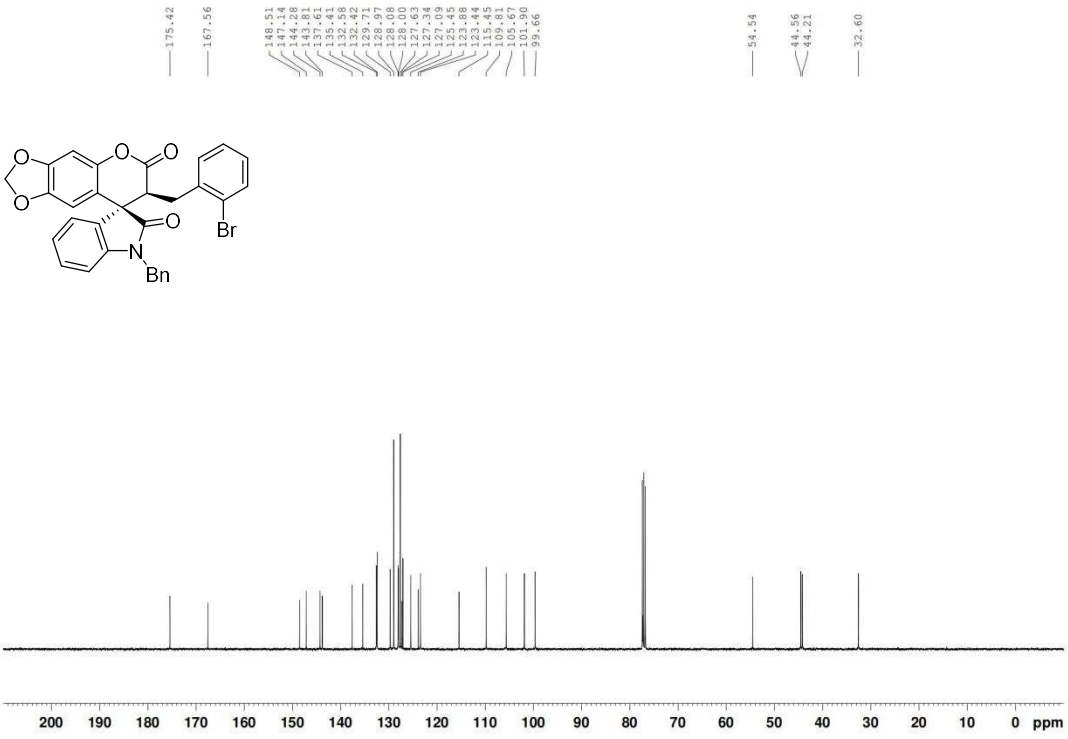




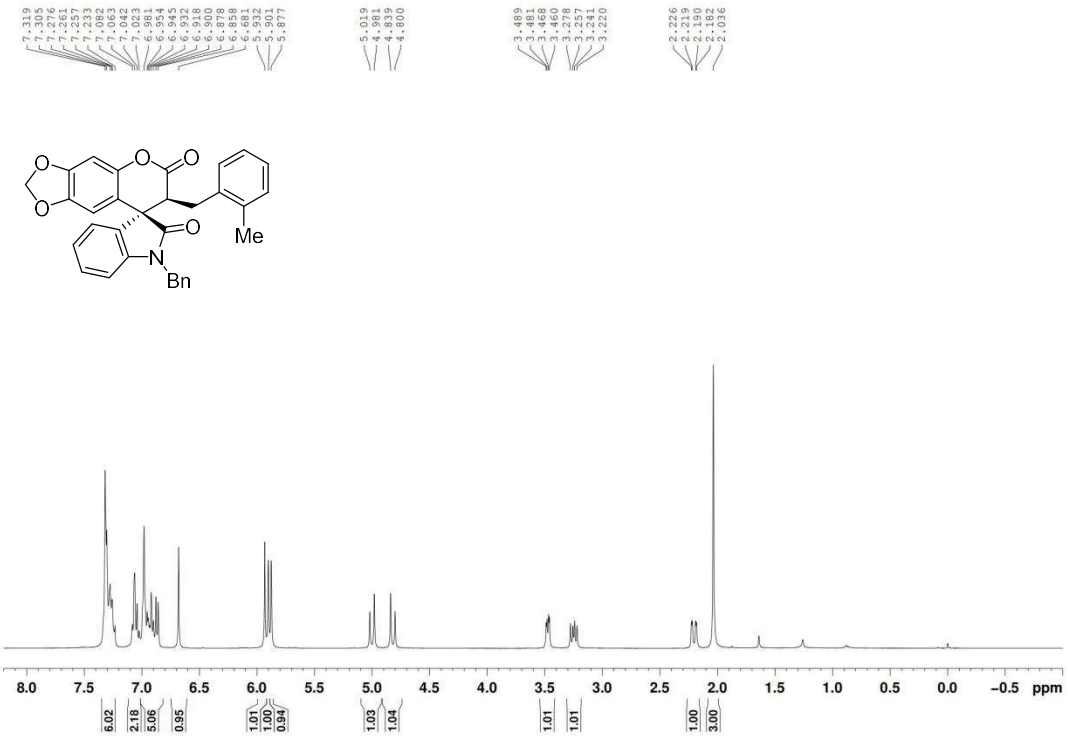
^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)



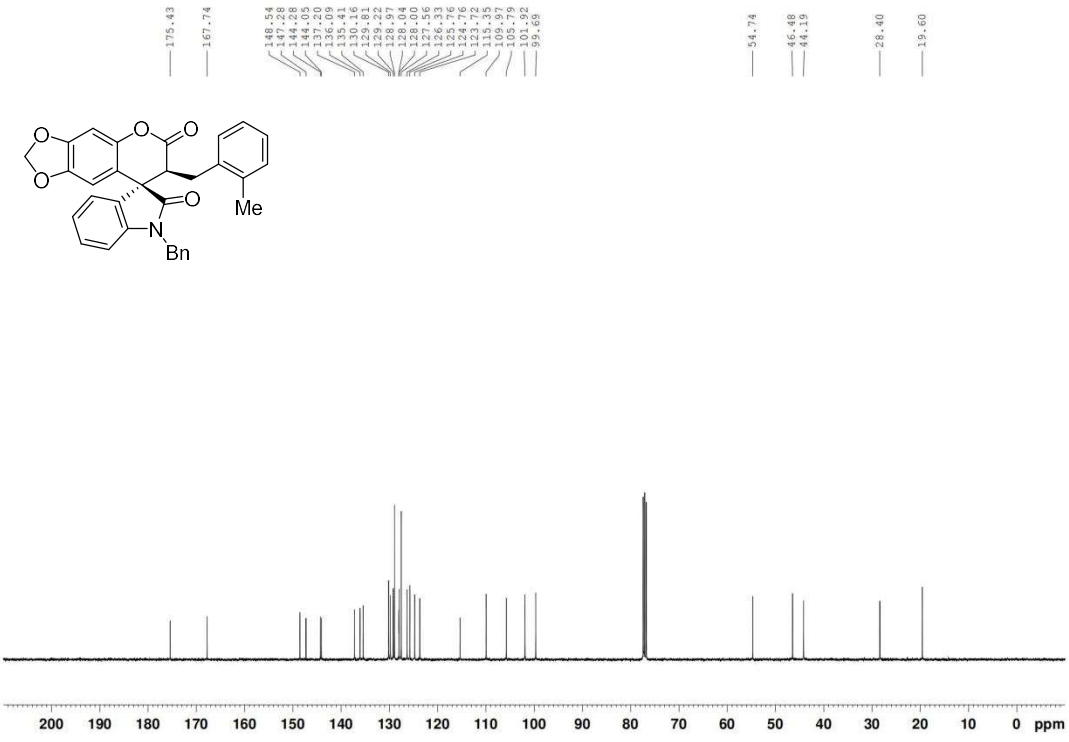
^{13}C NMR spectrum of compound **4c** ($CDCl_3$, 100 MHz)



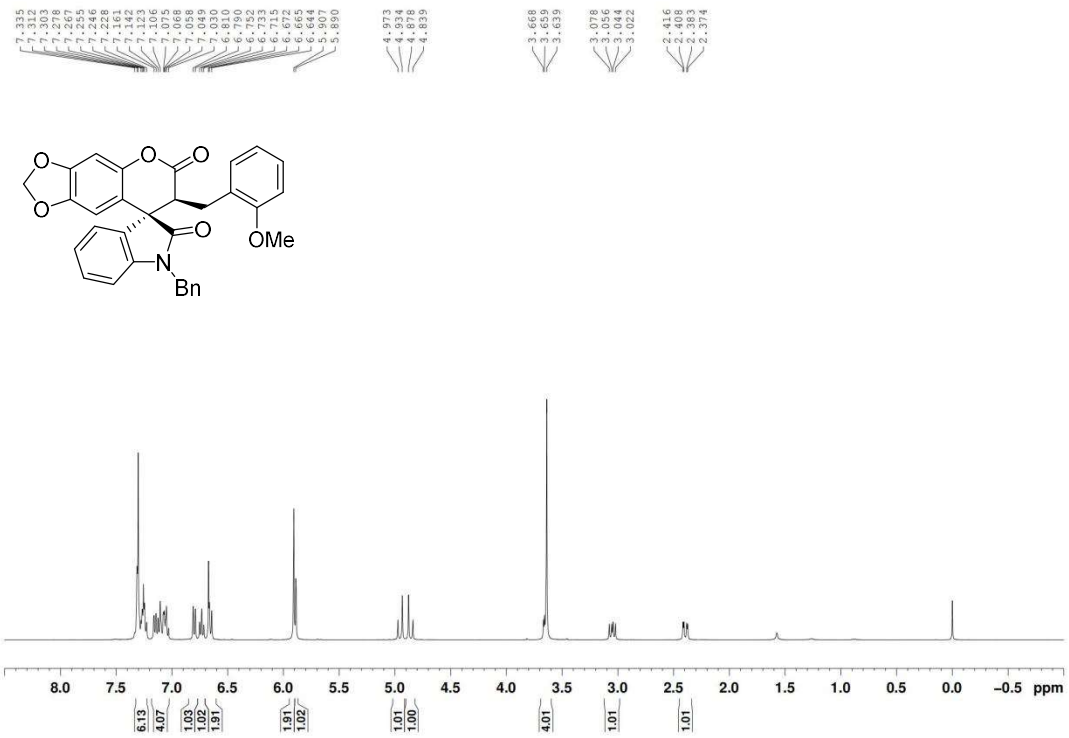
^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)



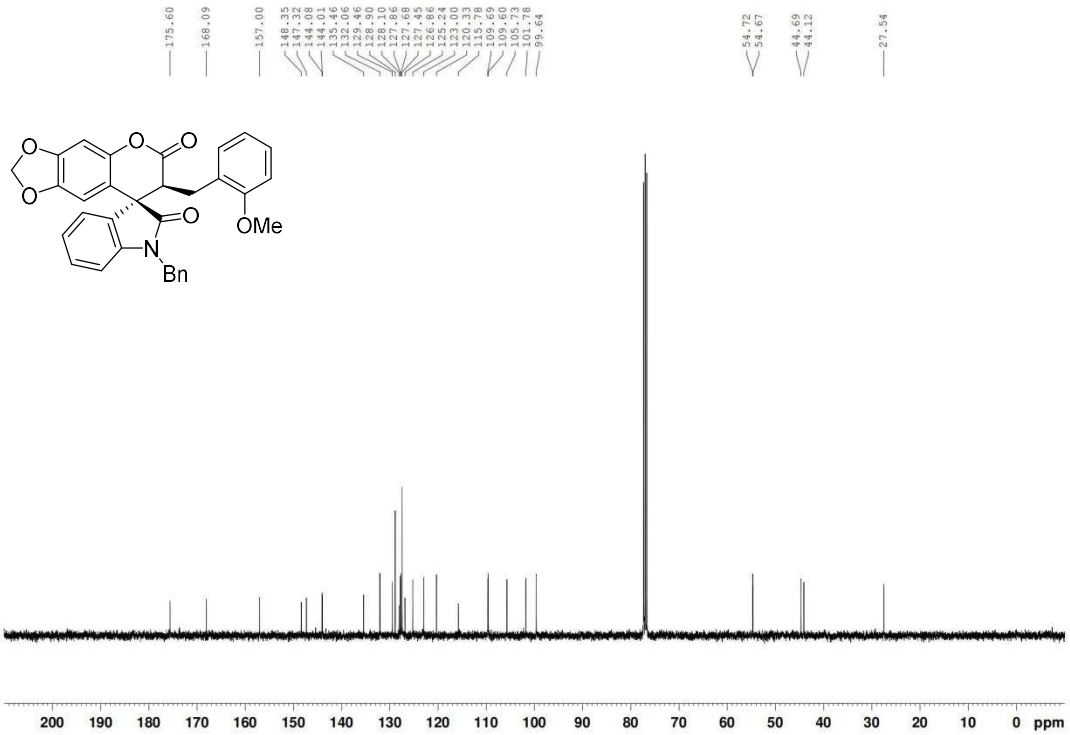
^{13}C NMR spectrum of compound **4d** ($CDCl_3$, 100 MHz)



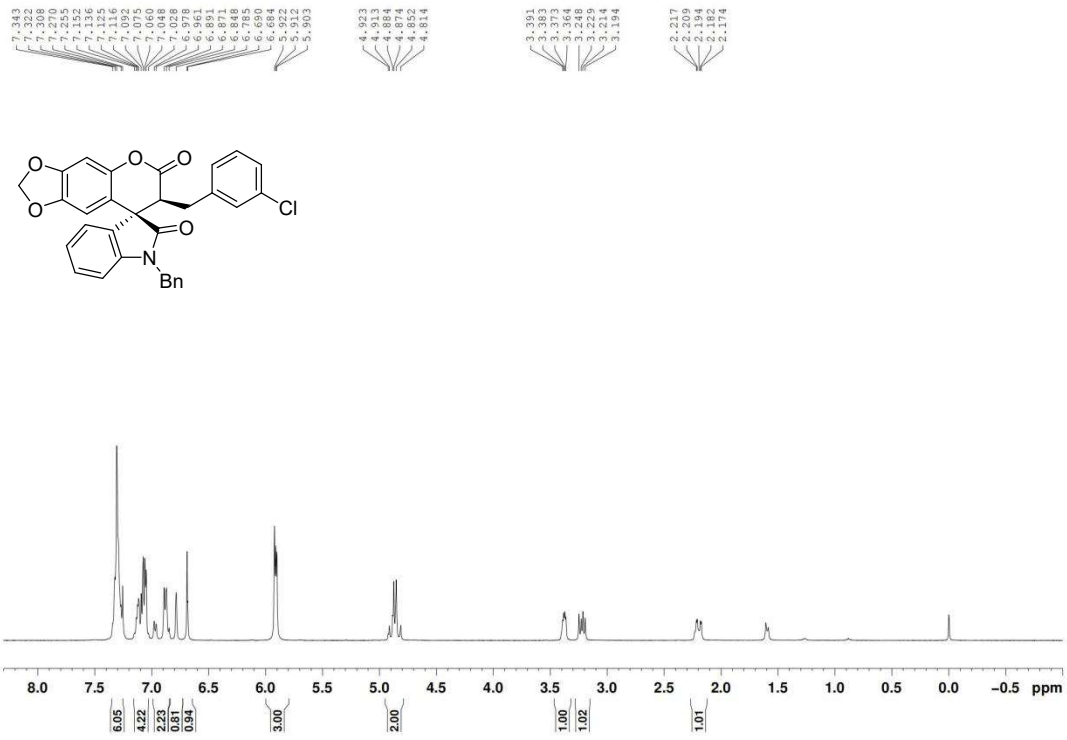
^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 400 MHz)



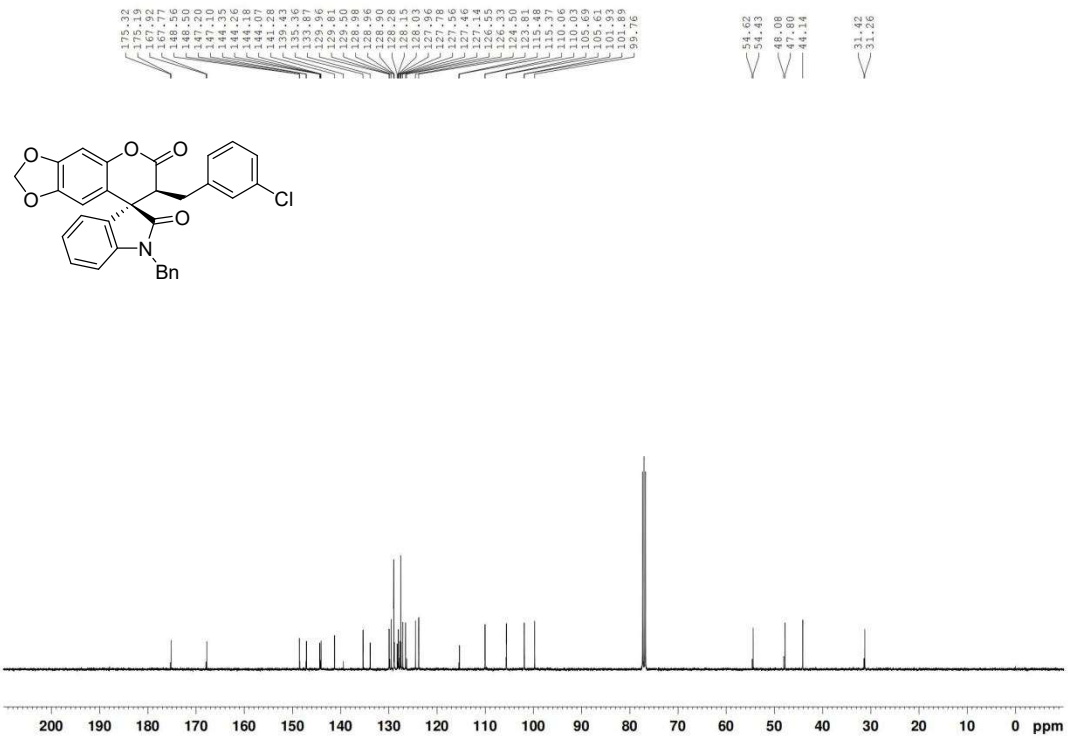
^{13}C NMR spectrum of compound **4e** ($CDCl_3$, 100 MHz)



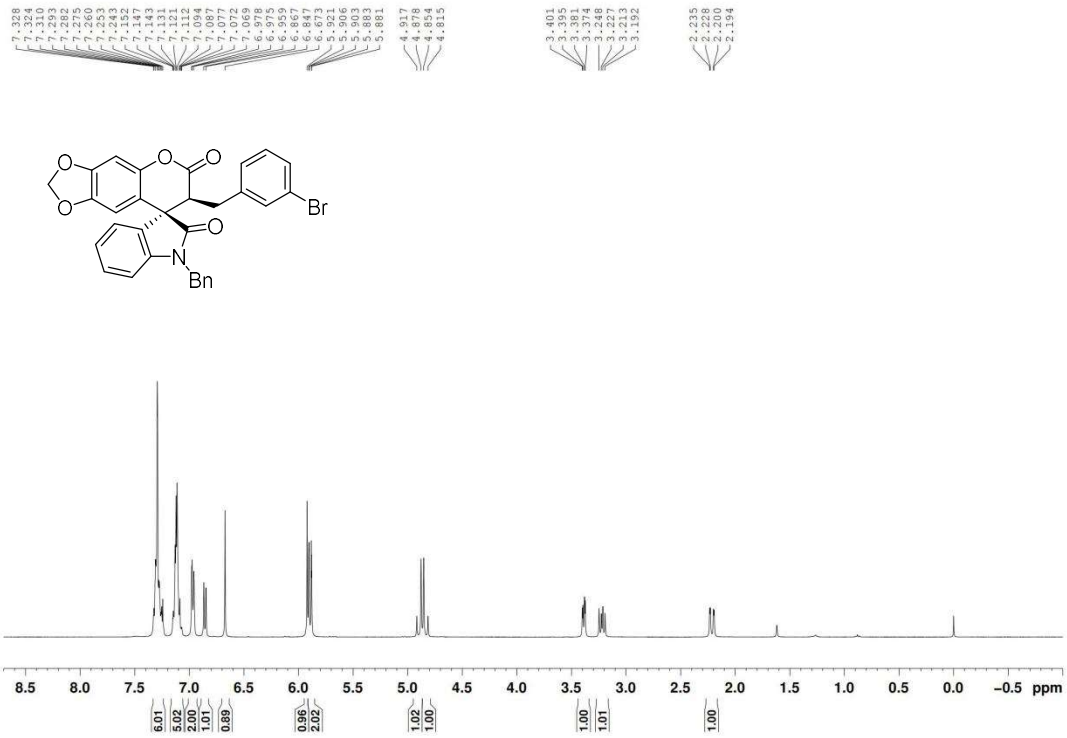
^{1}H NMR spectrum of compound **4f** ($CDCl_3$, 400 MHz)



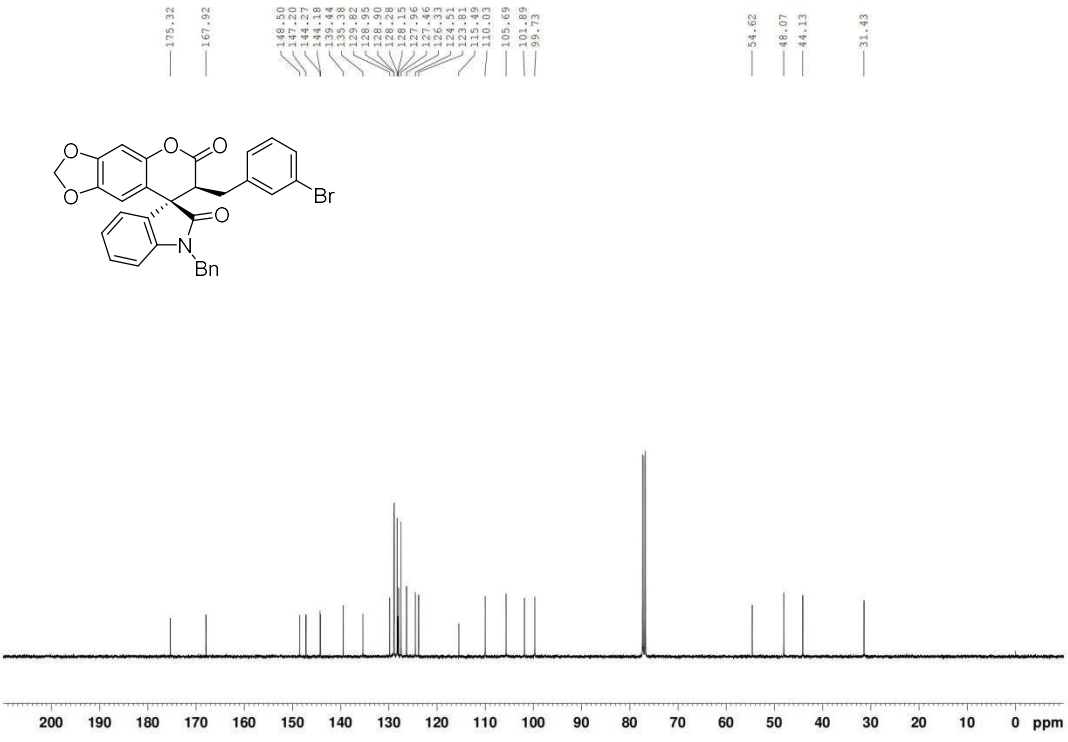
^{13}C NMR spectrum of compound **4f** ($CDCl_3$, 100 MHz)



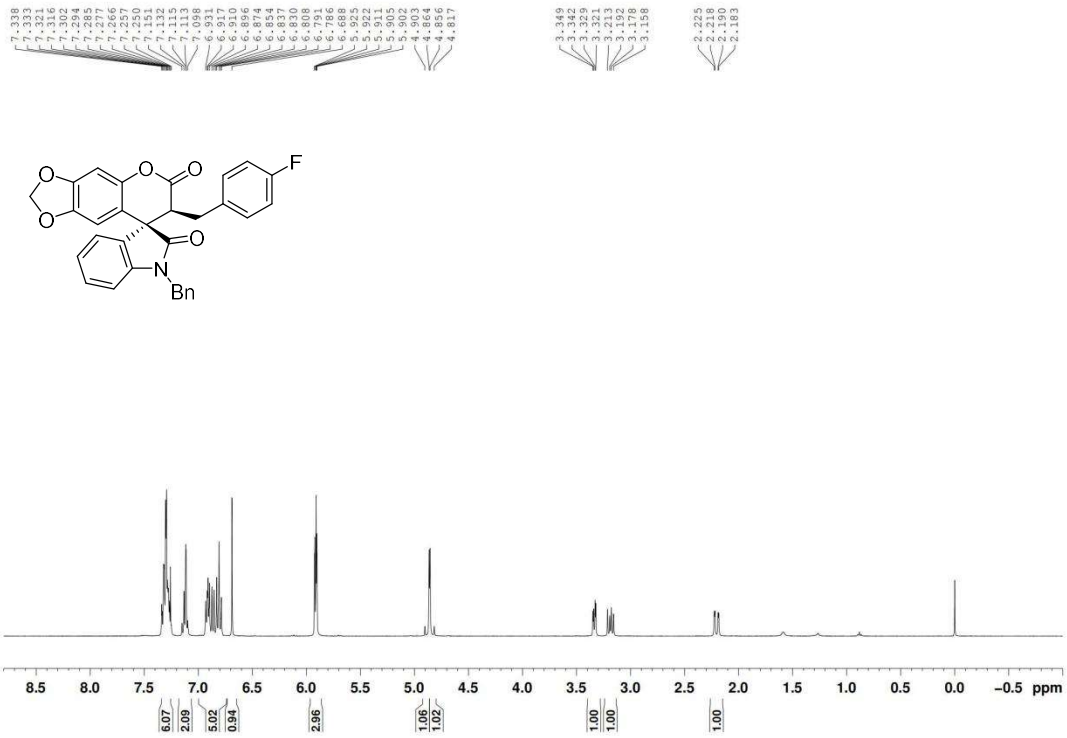
^{1}H NMR spectrum of compound **4g** ($CDCl_3$, 400 MHz)



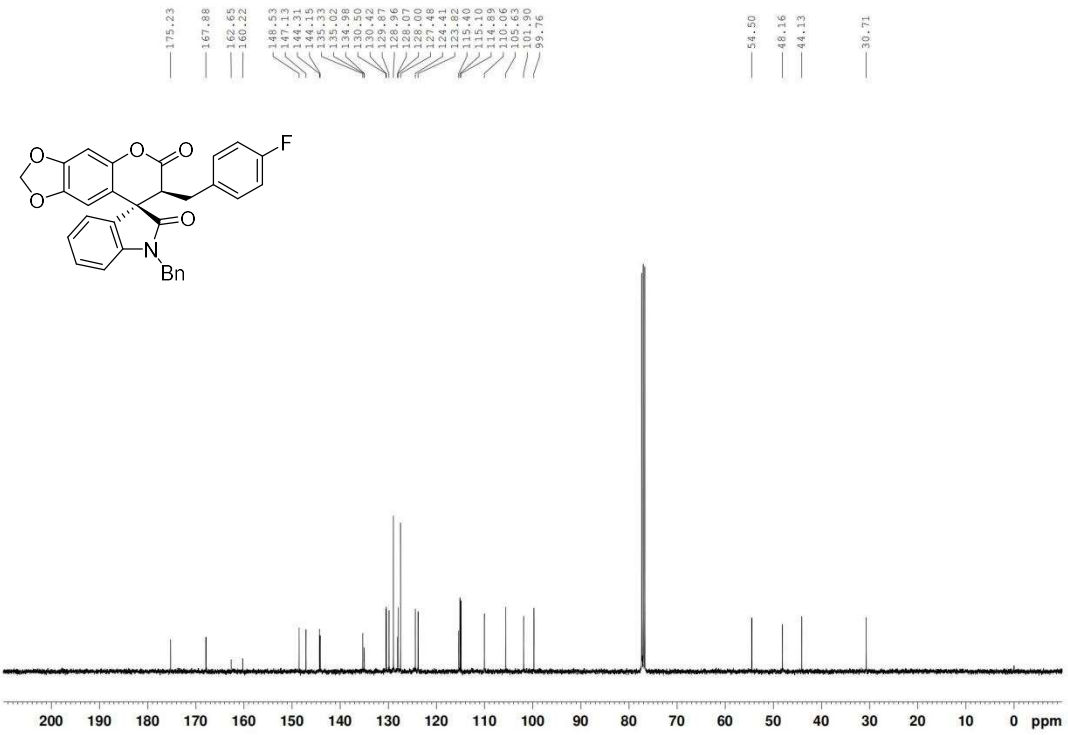
^{13}C NMR spectrum of compound **4g** ($CDCl_3$, 100 MHz)



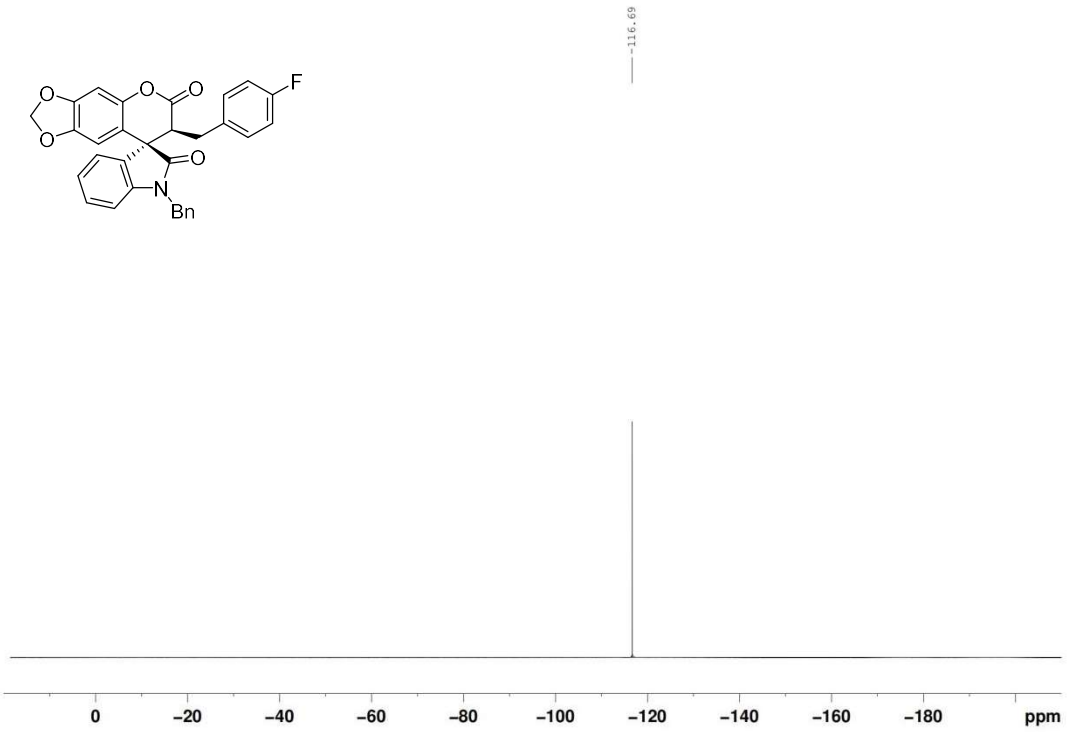
^{1}H NMR spectrum of compound **4h** ($CDCl_3$, 400 MHz)



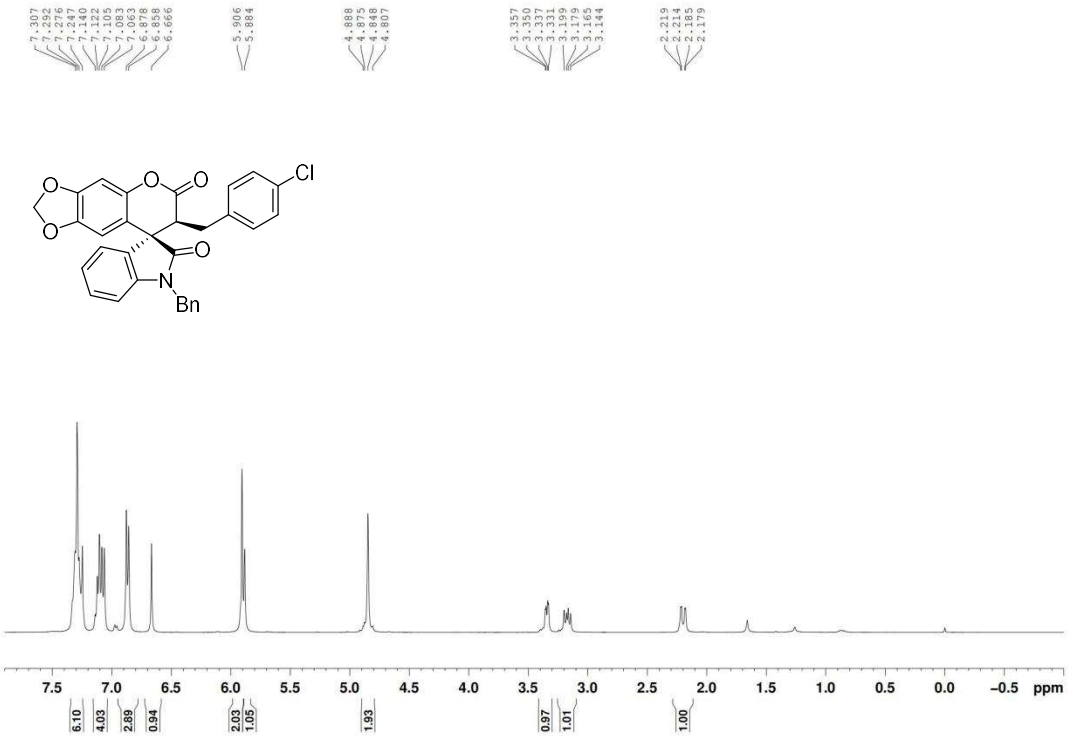
^{13}C NMR spectrum of compound **4h** ($CDCl_3$, 100 MHz)



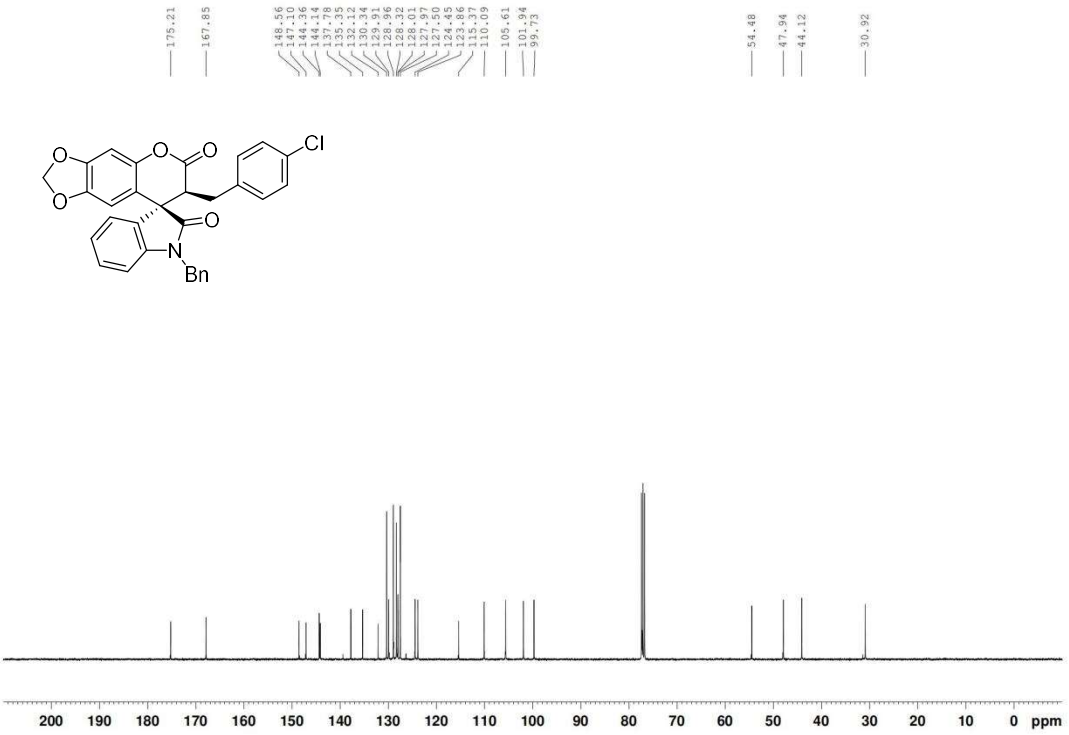
^{19}F NMR spectrum of compound **4h** ($CDCl_3$, 376 MHz)



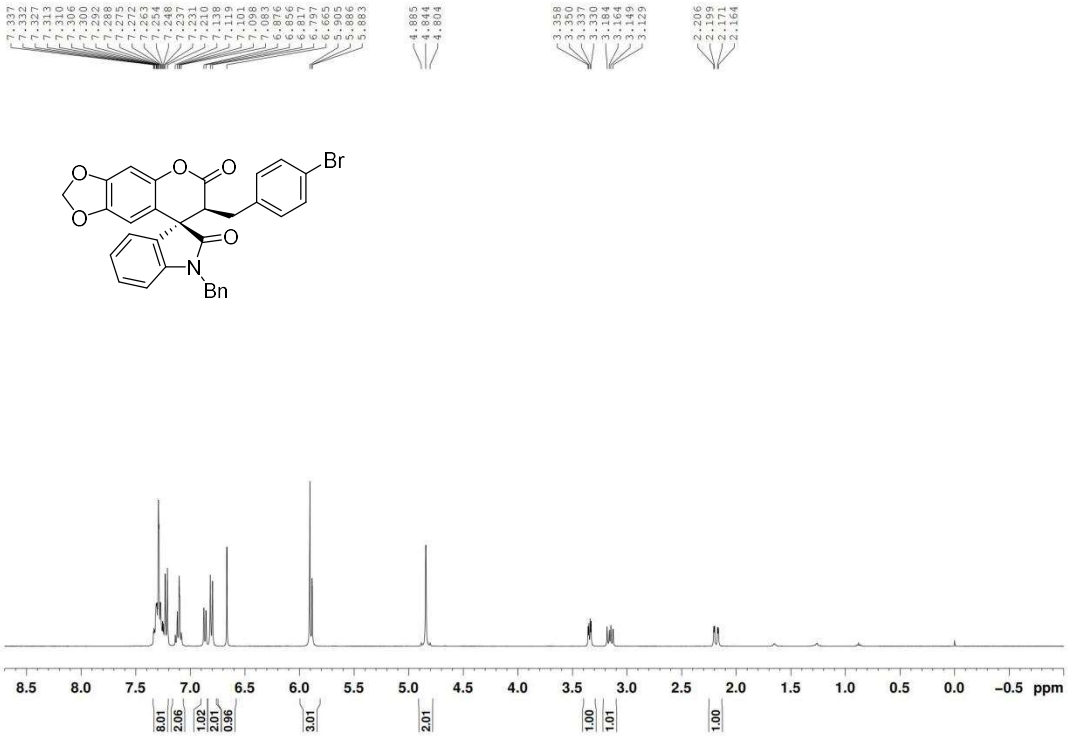
^{1}H NMR spectrum of compound **4i** ($CDCl_3$, 400 MHz)



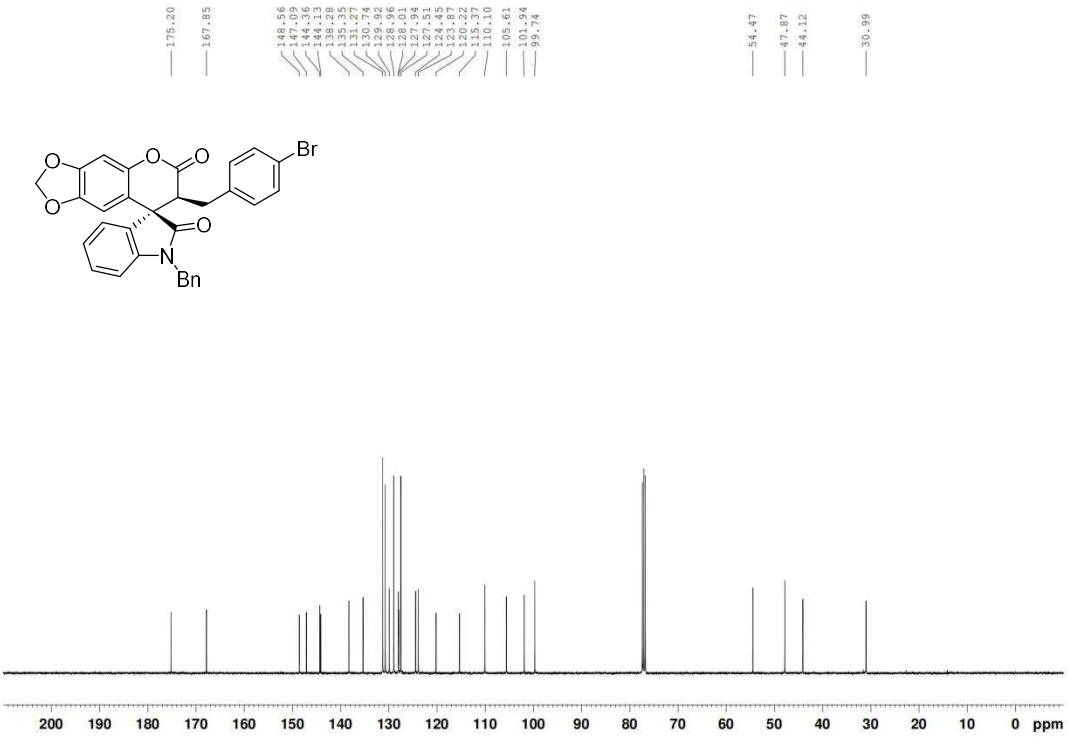
^{13}C NMR spectrum of compound **4i** ($CDCl_3$, 100 MHz)



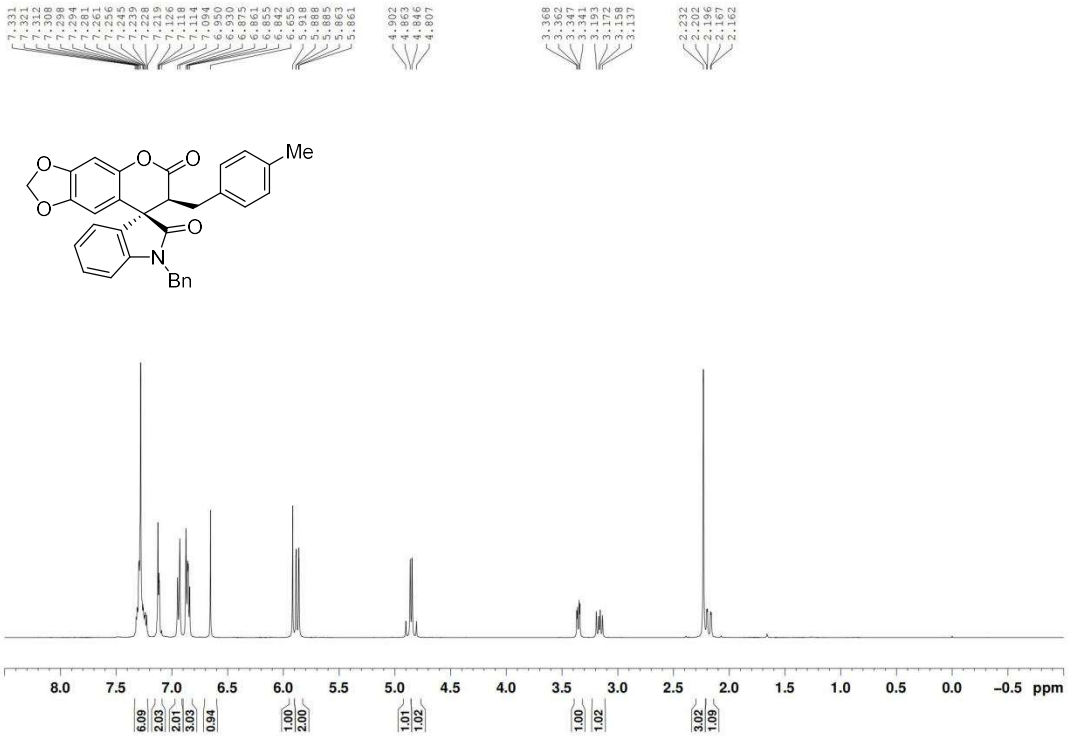
^{1}H NMR spectrum of compound **4j** ($CDCl_3$, 400 MHz)



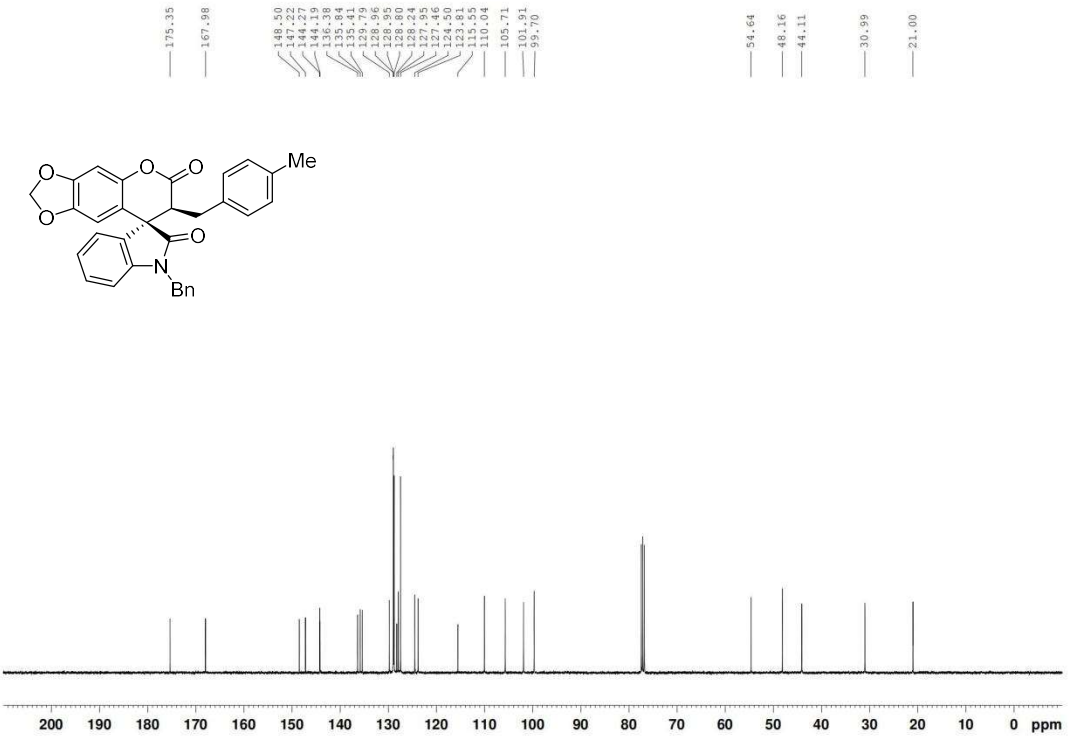
^{13}C NMR spectrum of compound **4j** ($CDCl_3$, 100 MHz)



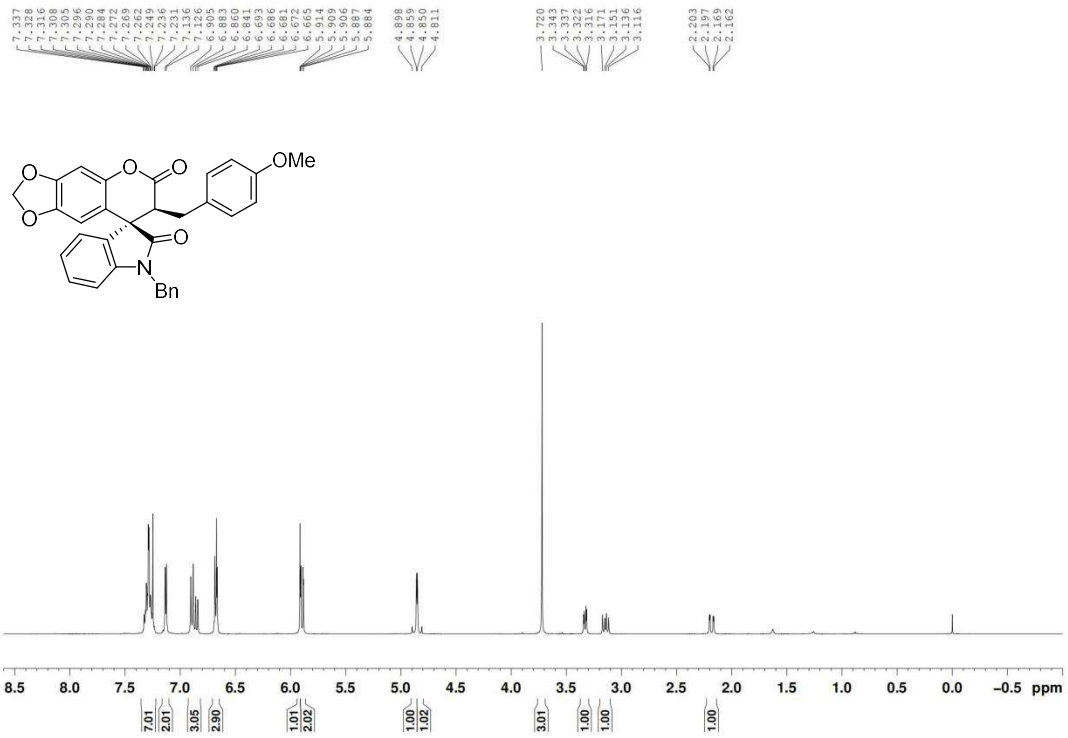
^{1}H NMR spectrum of compound **4k** ($CDCl_3$, 400 MHz)



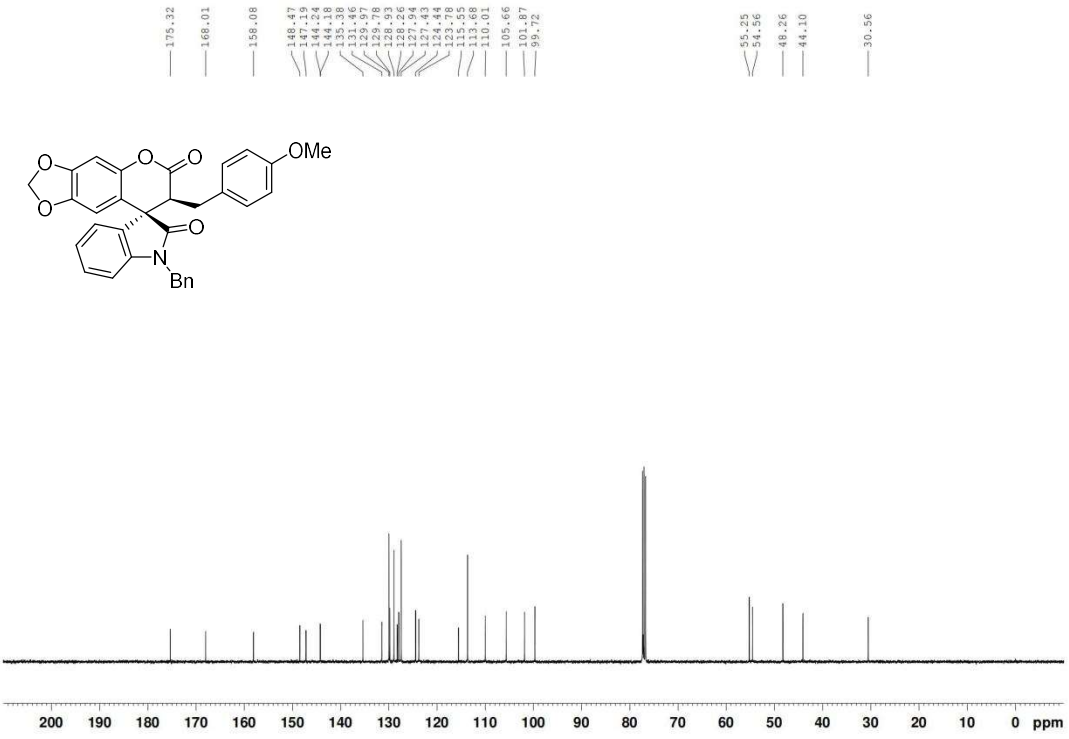
^{13}C NMR spectrum of compound **4k** ($CDCl_3$, 100 MHz)



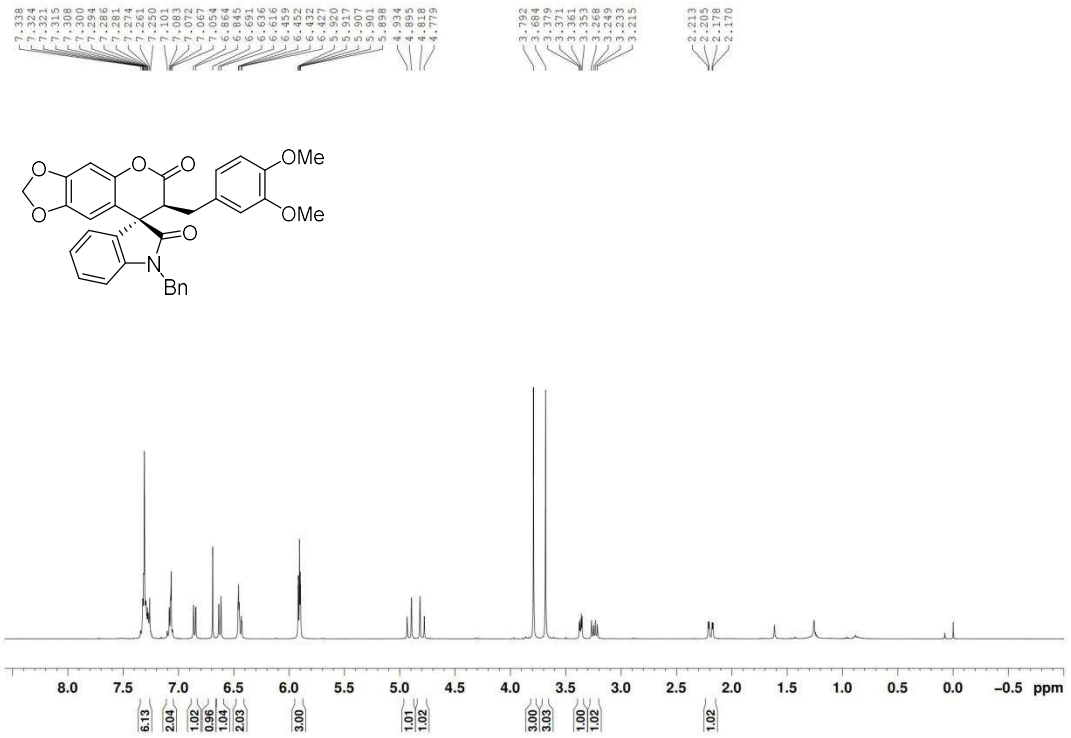
^{1}H NMR spectrum of compound **4l** ($CDCl_3$, 400 MHz)



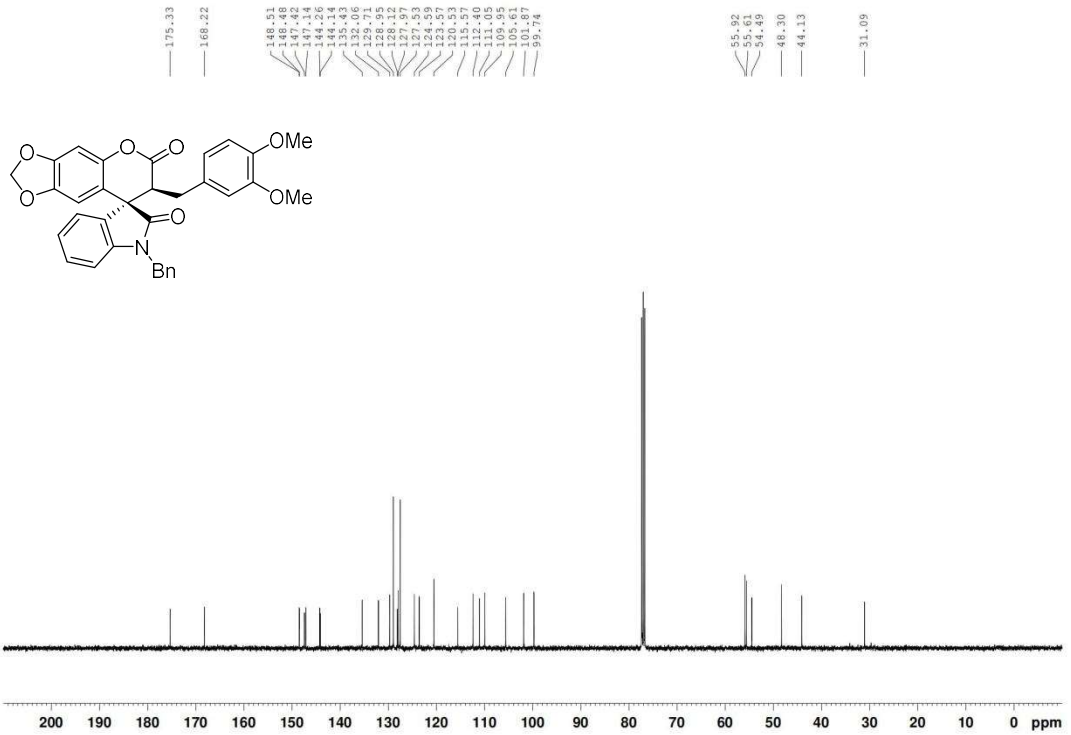
^{13}C NMR spectrum of compound **4l** ($CDCl_3$, 100 MHz)



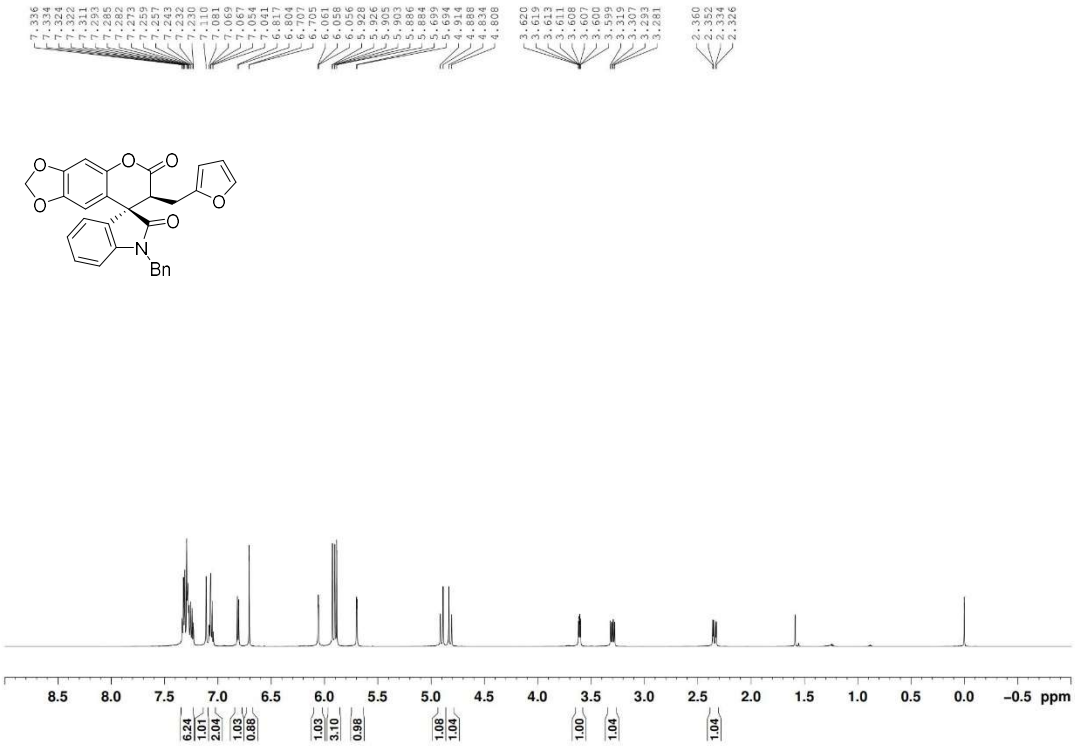
^{1}H NMR spectrum of compound **4m** ($CDCl_3$, 400 MHz)



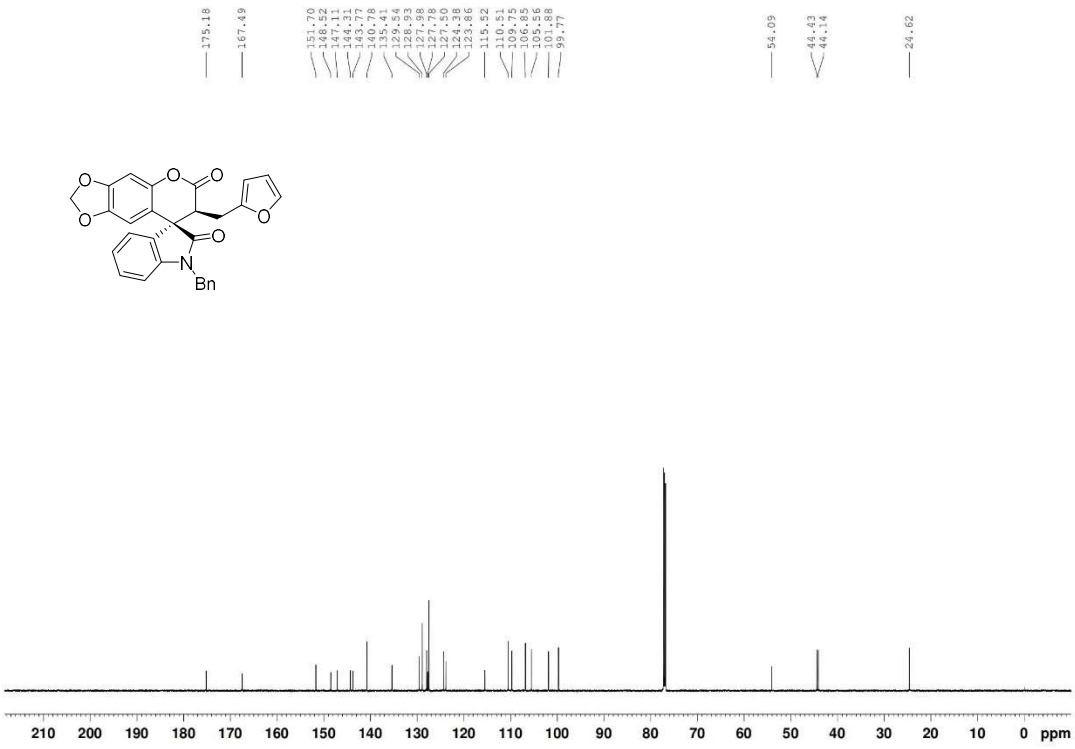
^{13}C NMR spectrum of compound **4m** ($CDCl_3$, 100 MHz)



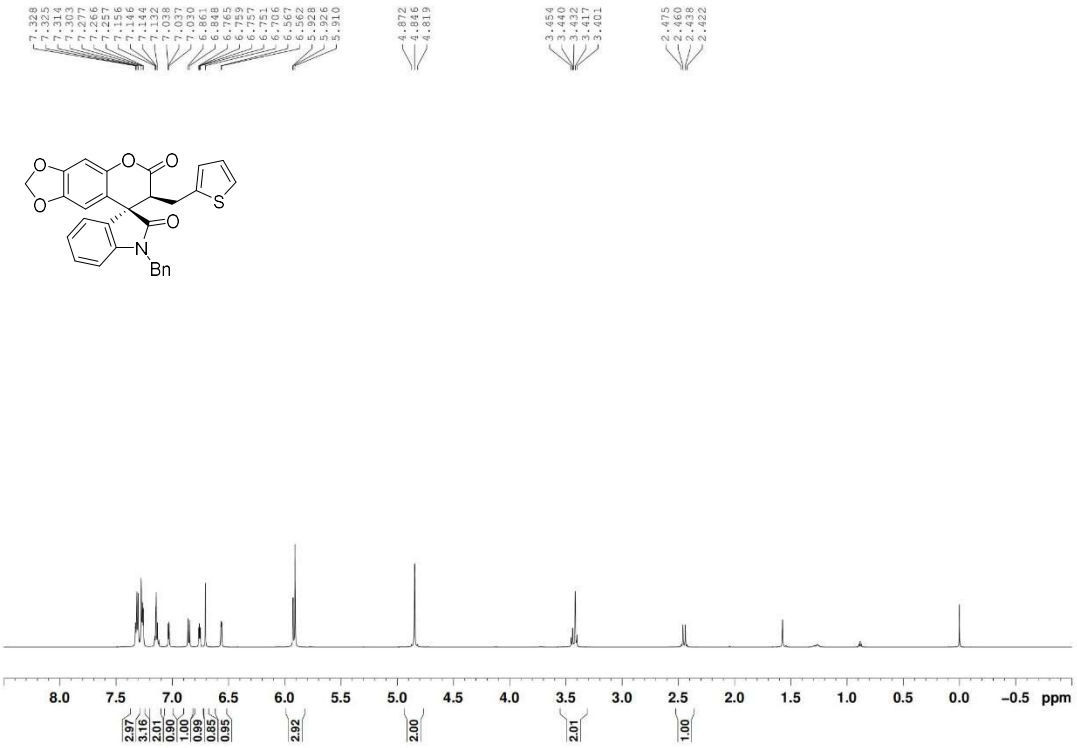
^{1}H NMR spectrum of compound **4n** ($CDCl_3$, 600 MHz)



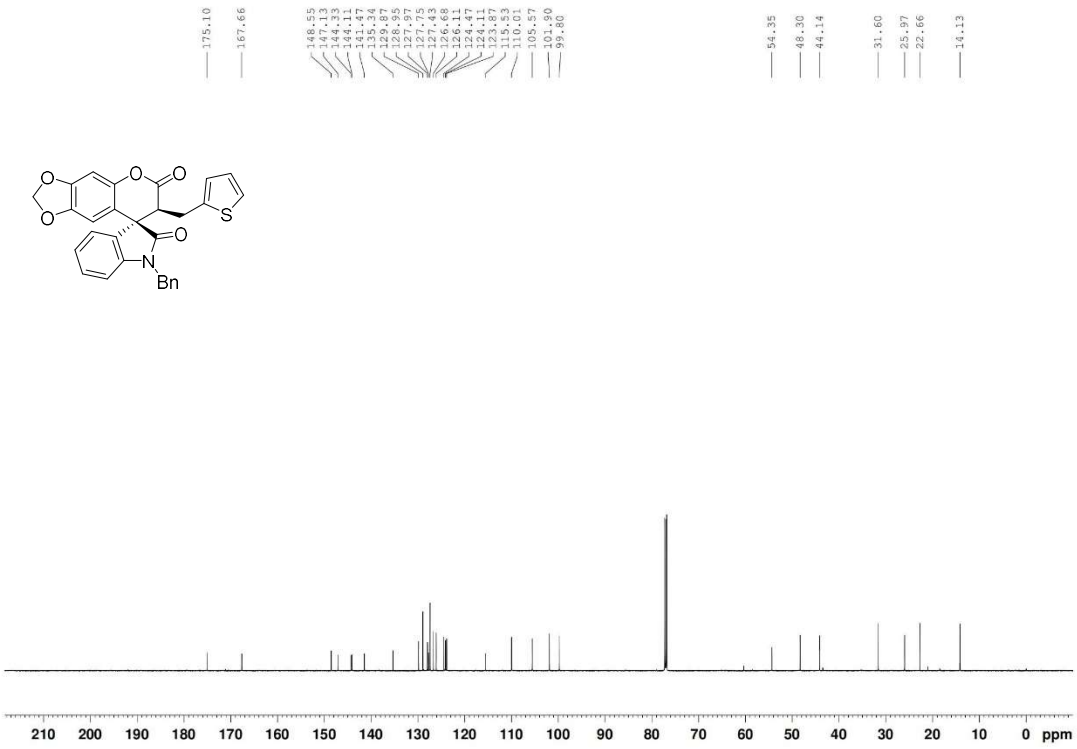
^{13}C NMR spectrum of compound **4n** ($CDCl_3$, 151 MHz)



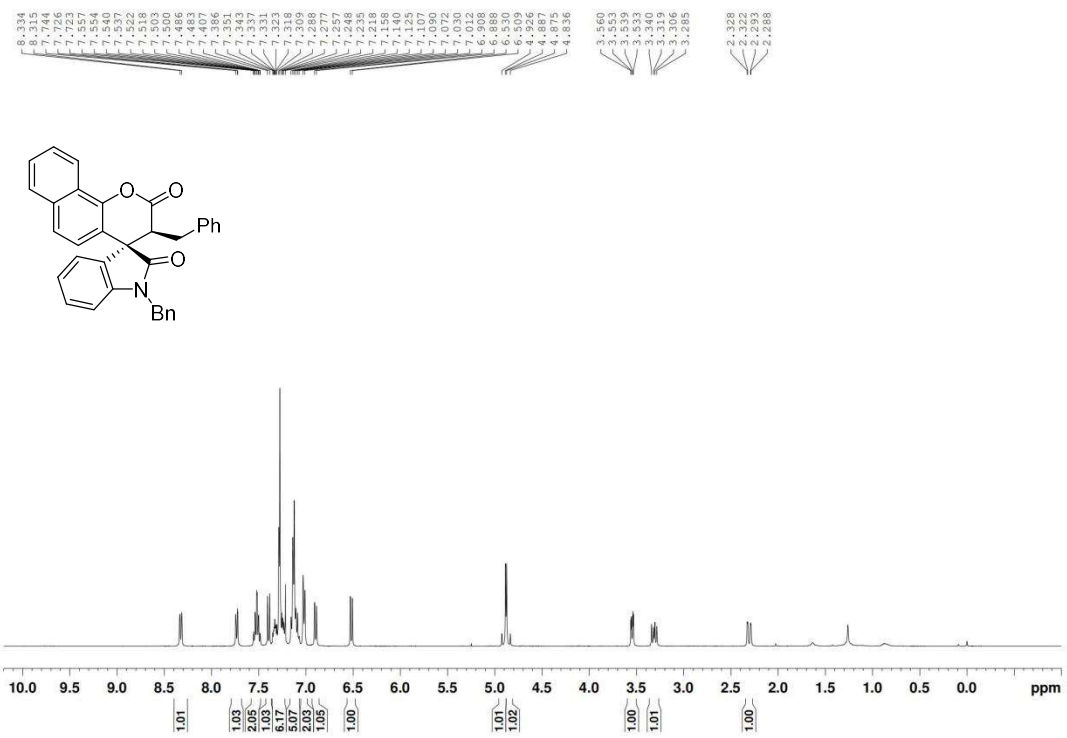
^{1}H NMR spectrum of compound **4o** ($CDCl_3$, 600 MHz)



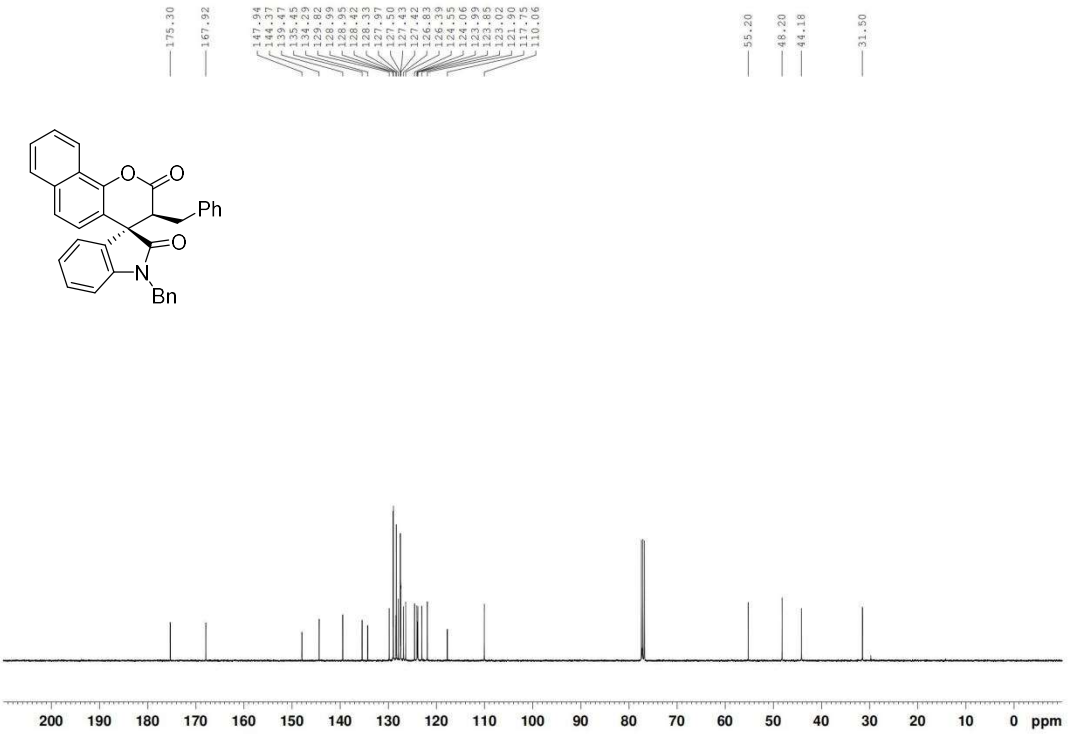
^{13}C NMR spectrum of compound **4o** ($CDCl_3$, 151 MHz)



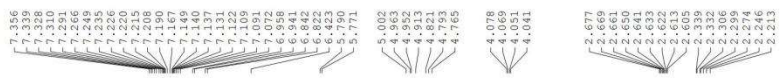
^{1}H NMR spectrum of compound **4q** ($CDCl_3$, 400 MHz)

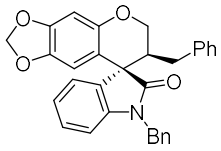


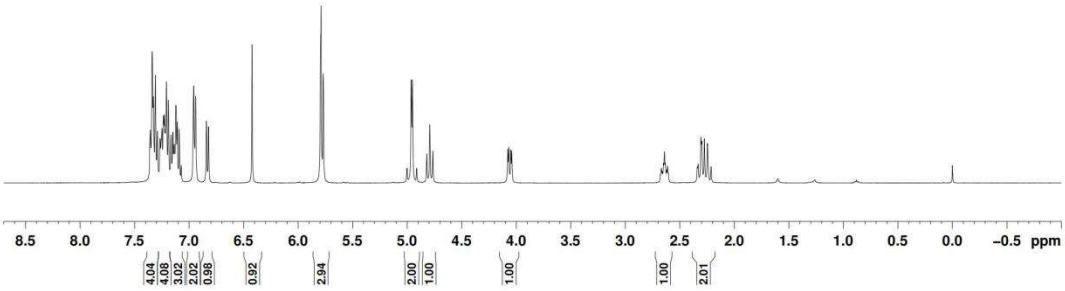
^{13}C NMR spectrum of compound **4q** ($CDCl_3$, 100 MHz)



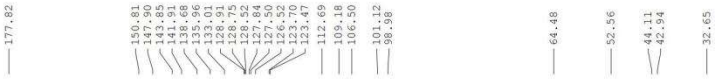
^{1}H NMR spectrum of compound **5a** ($CDCl_3$, 400 MHz)

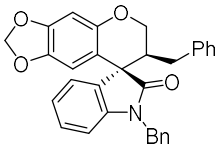


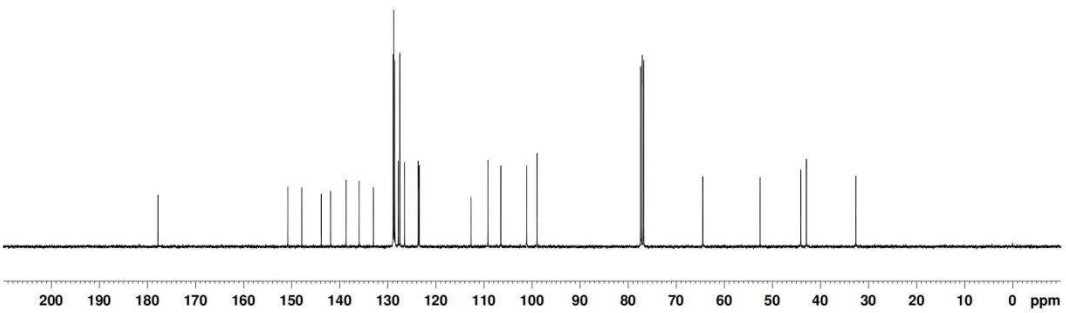




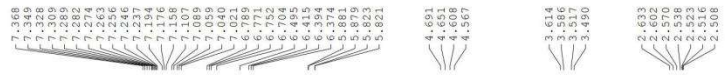
^{13}C NMR spectrum of compound **5a** ($CDCl_3$, 100 MHz)

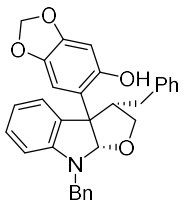


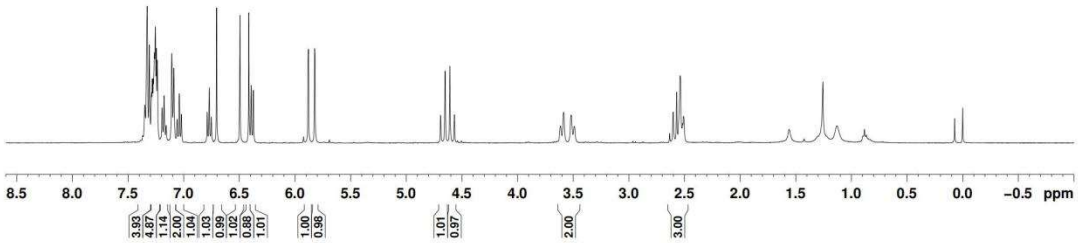




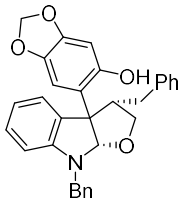
^{1}H NMR spectrum of compound **5b** ($CDCl_3$, 400 MHz)

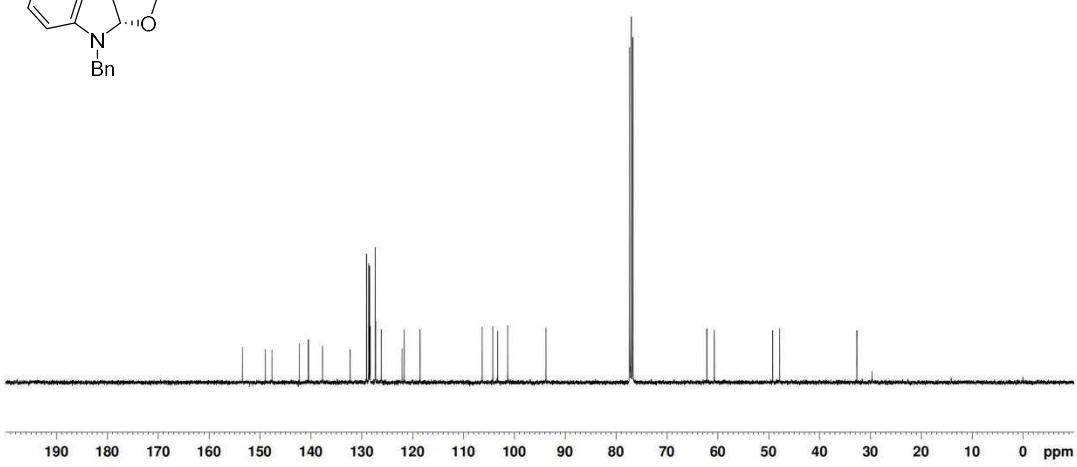




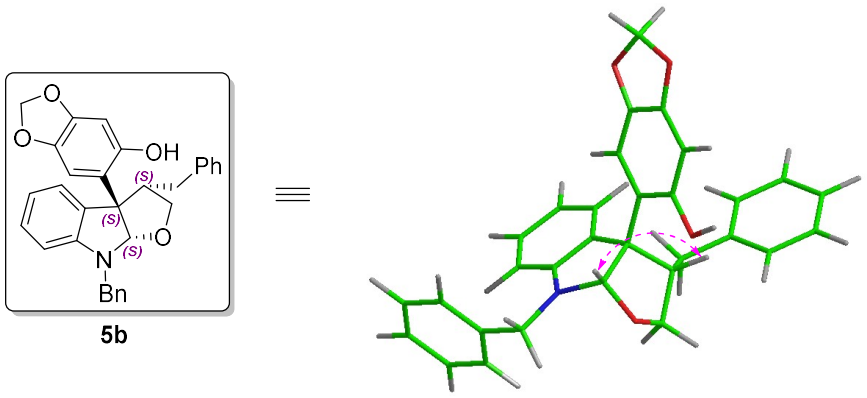


^{13}C NMR spectrum of compound **5b** ($CDCl_3$, 100 MHz)

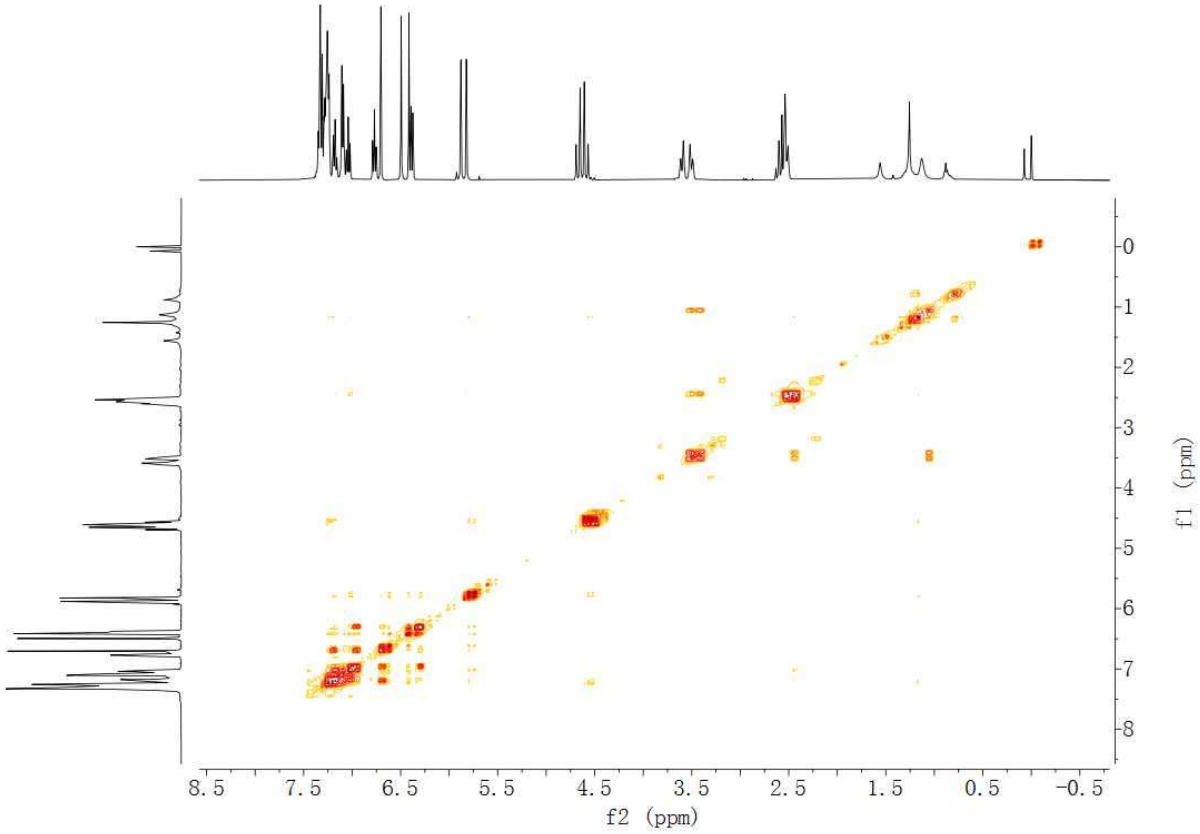




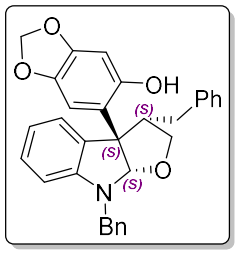
$^{1}H-^{1}H$ COSY correlation of compound **5b** (400 MHz, $CDCl_3$)



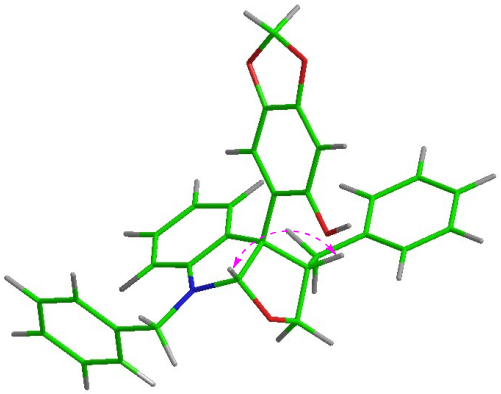
5b



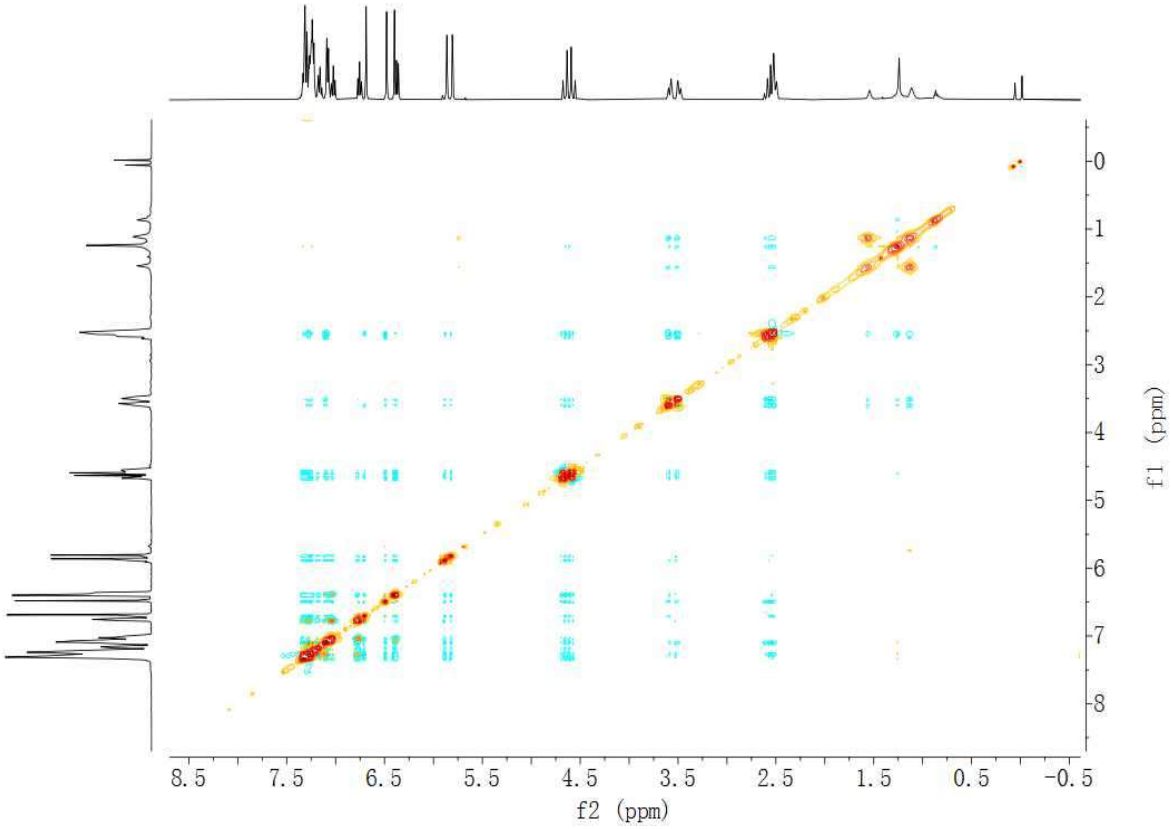
NOESY correlation of compound **5b** (400 MHz, $CDCl_3$)



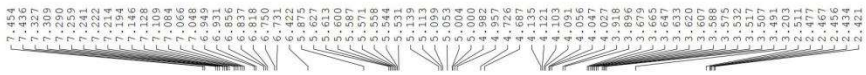
5b

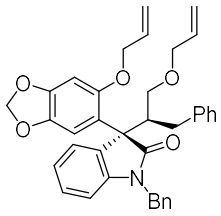


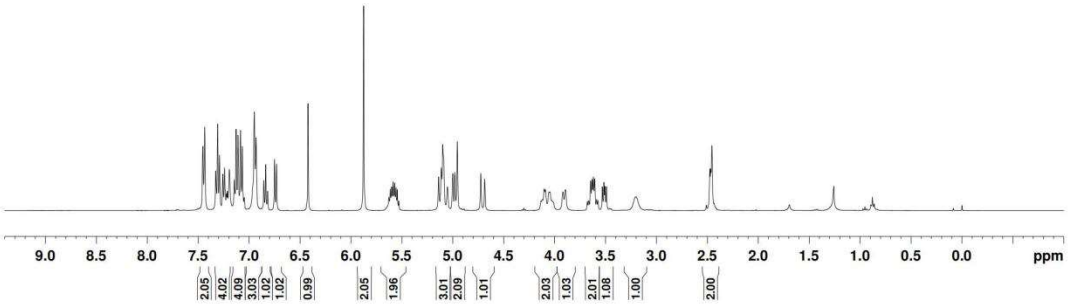
5b



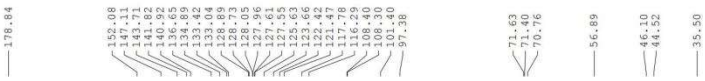
^{1}H NMR spectrum of compound **5c** ($CDCl_3$, 400 MHz)

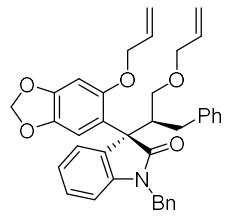


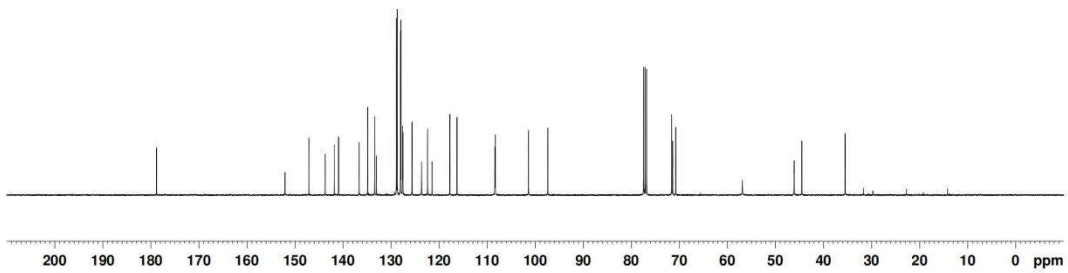




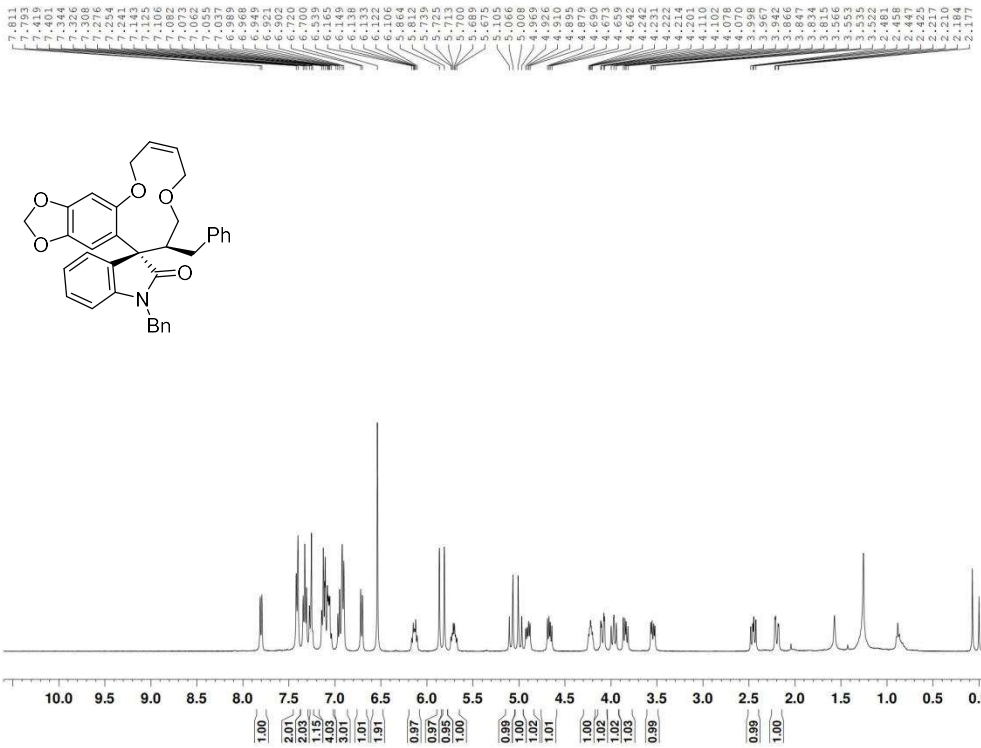
^{13}C NMR spectrum of compound **5c** ($CDCl_3$, 100 MHz)



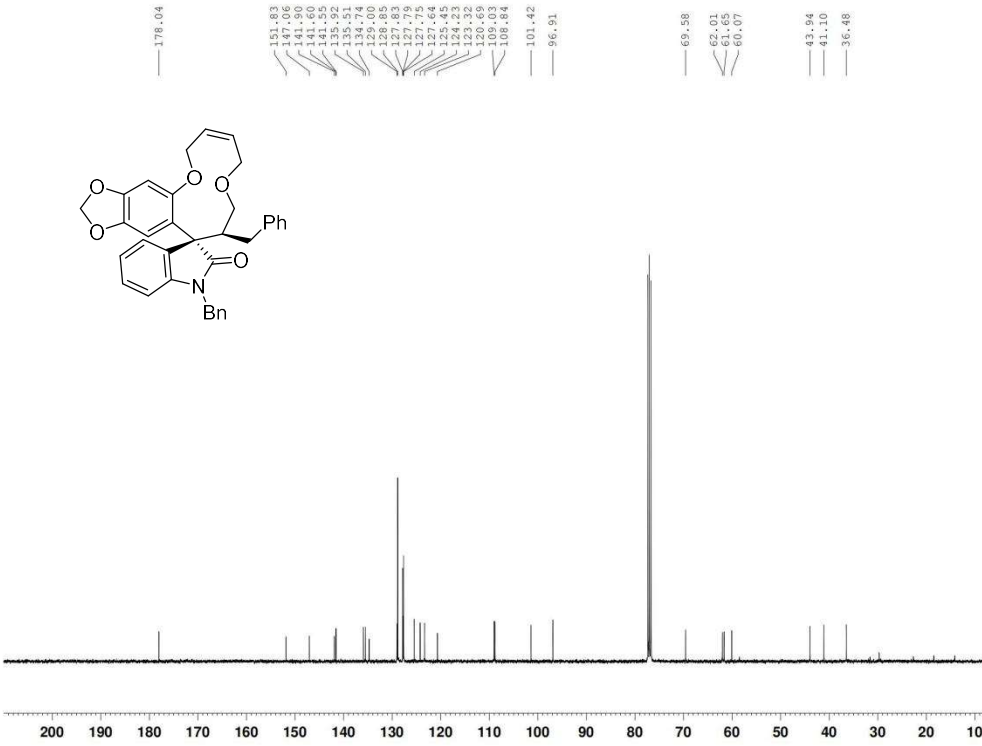




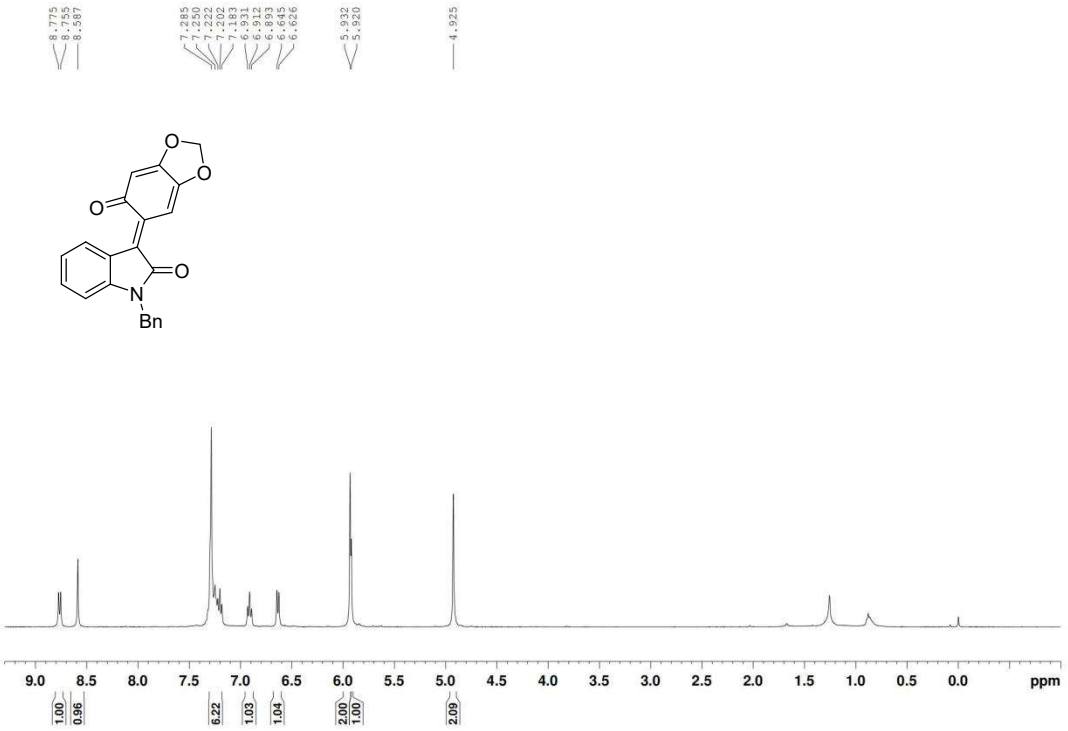
^{1}H NMR spectrum of compound **5d** ($CDCl_3$, 400 MHz)



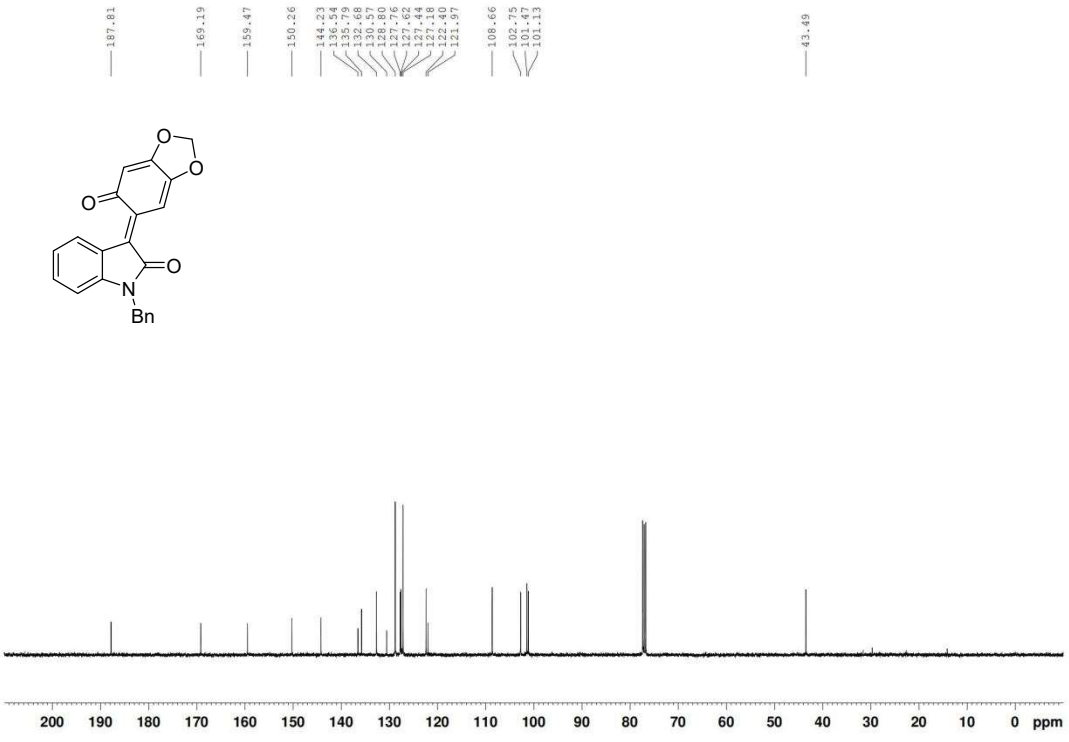
^{13}C NMR spectrum of compound **5d** ($CDCl_3$, 100 MHz)



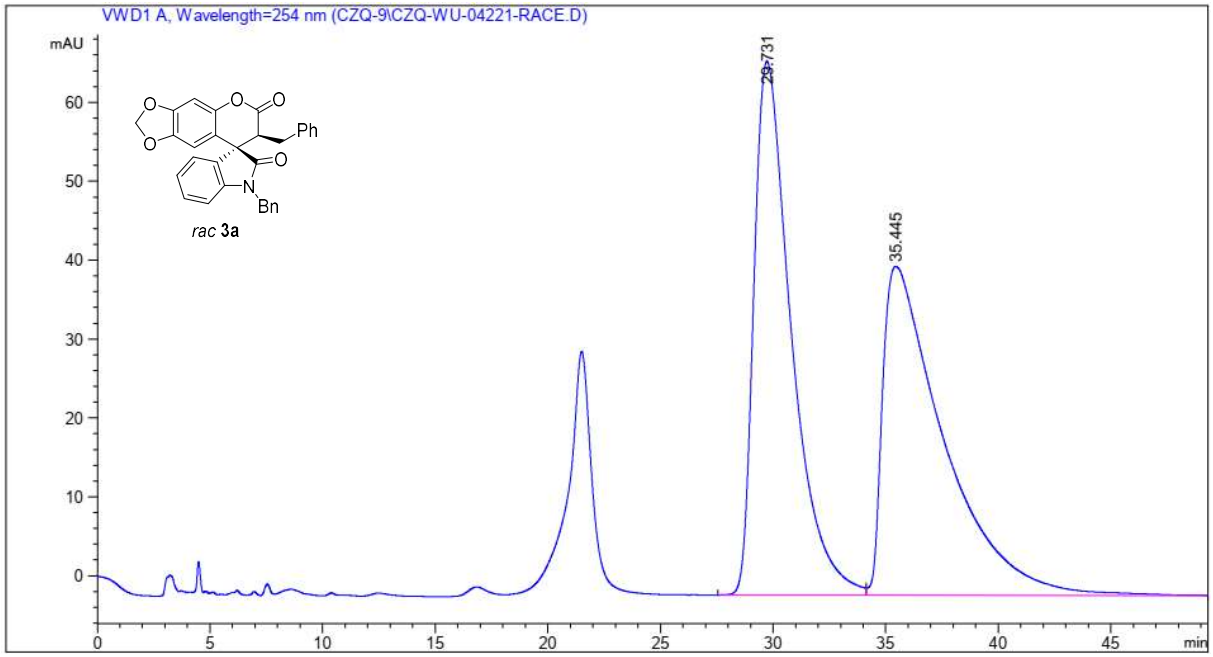
^{1}H NMR spectrum of compound **5e** ($CDCl_3$, 400 MHz)



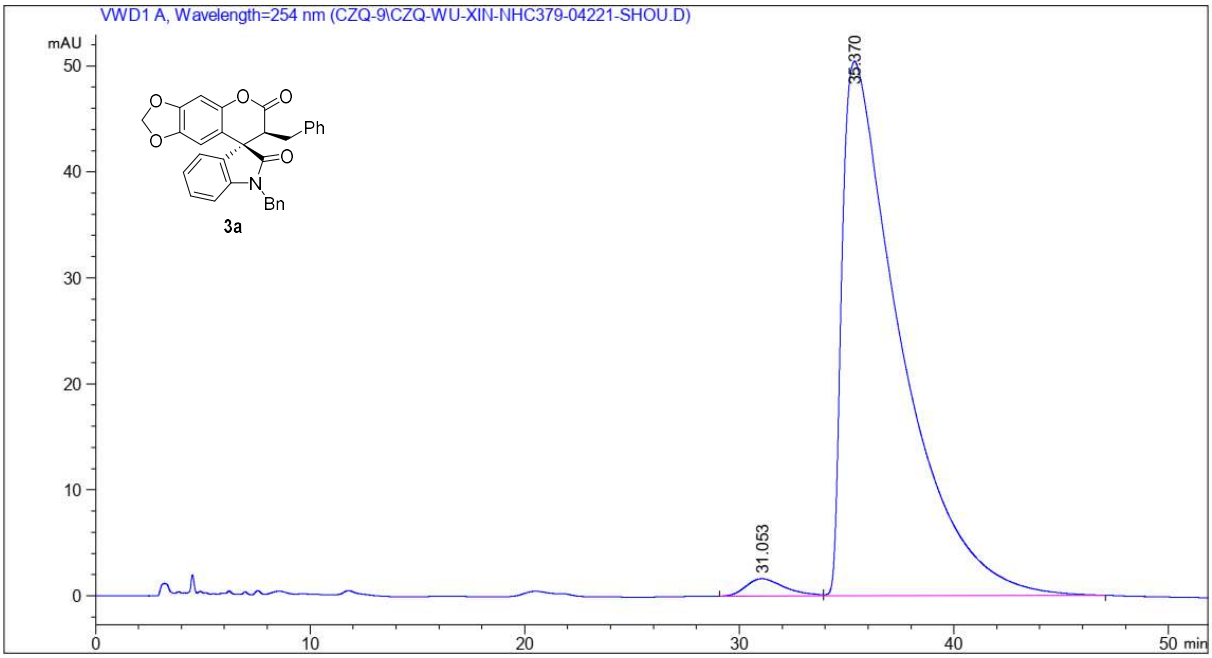
^{13}C NMR spectrum of compound **5e** ($CDCl_3$, 100 MHz)



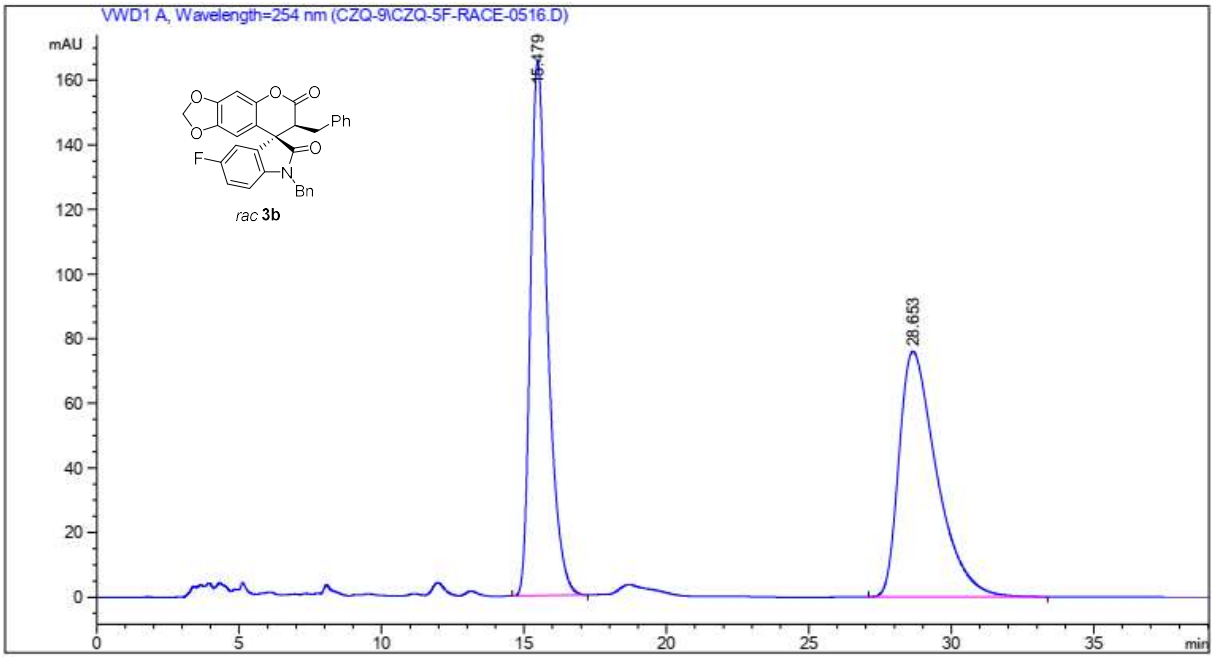
11. HPLC Spectra of compounds 3a–3v, 4a–4o, 4q and 5a–5d



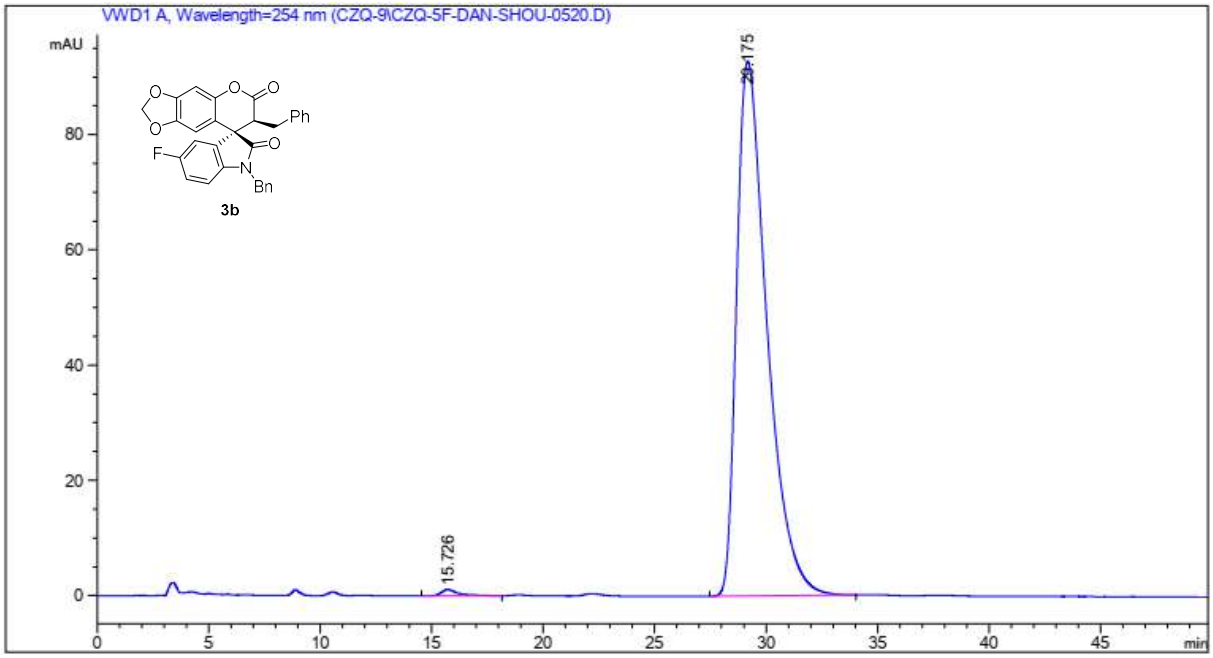
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	30.636	7792.57031	67.68628	49.8320
2	PDA 254.0 nm	36.529	7845.10889	41.66190	50.1680



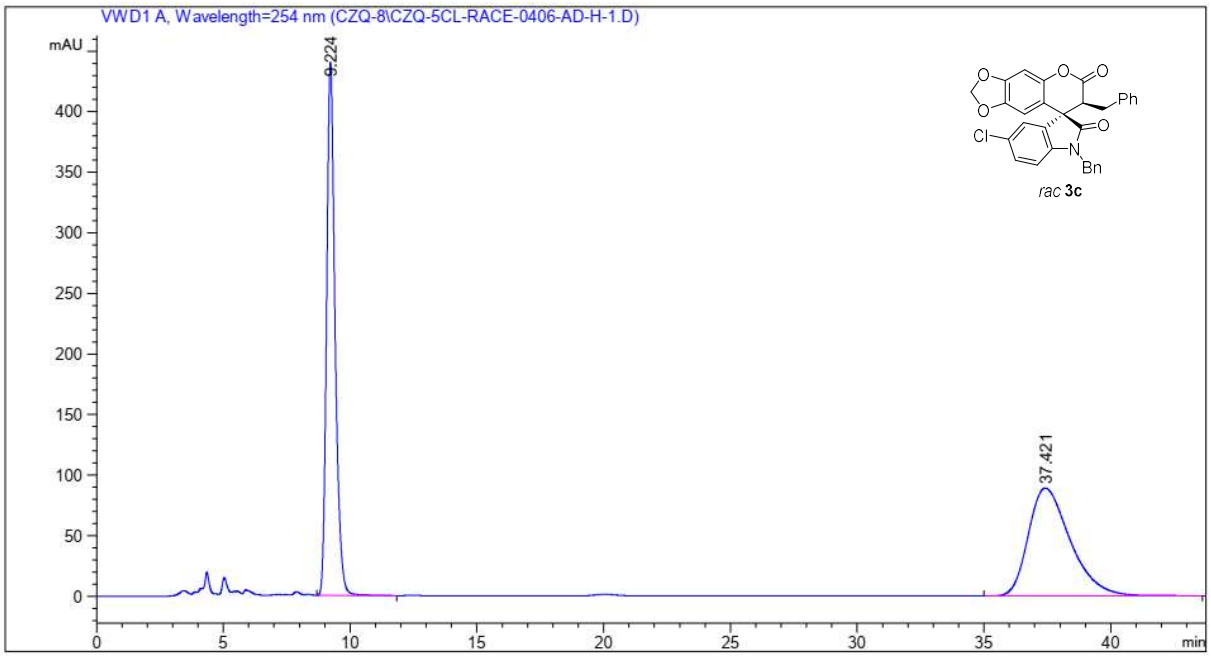
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	31.053	205.12457	1.64141	2.0993
2	PDA 254.0 nm	35.370	9565.96387	50.45354	97.9007



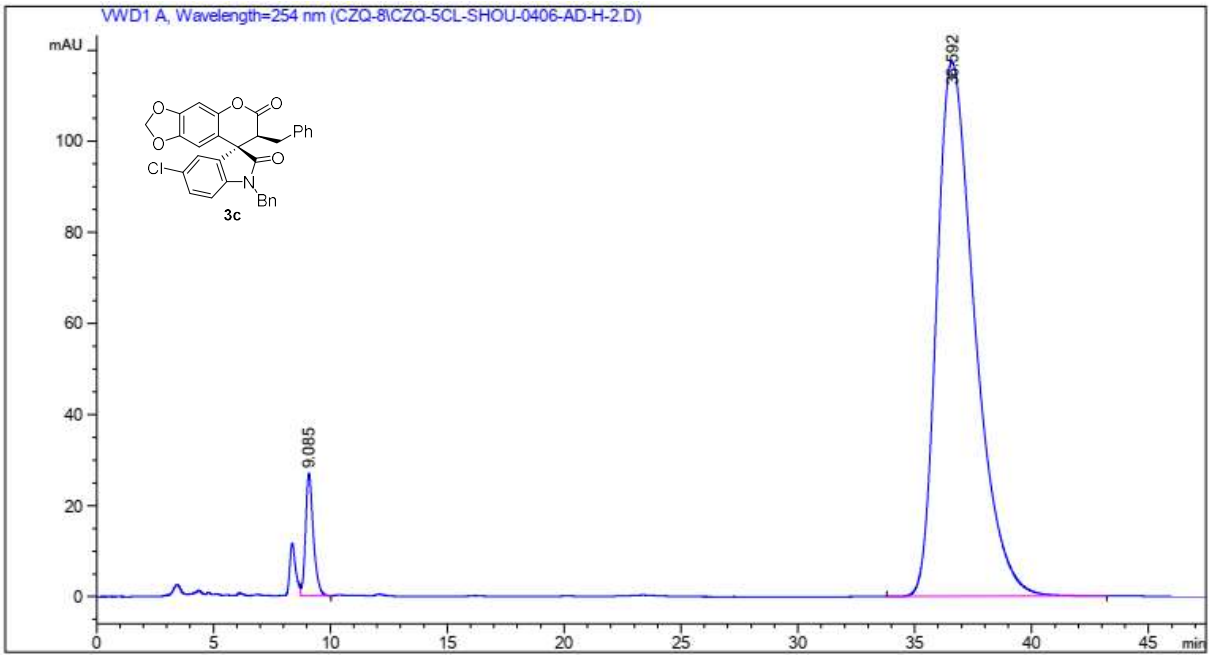
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	15.479	6988.32568	165.35936	50.0642
2	PDA 254.0 nm	28.653	6970.39893	75.94314	49.9358



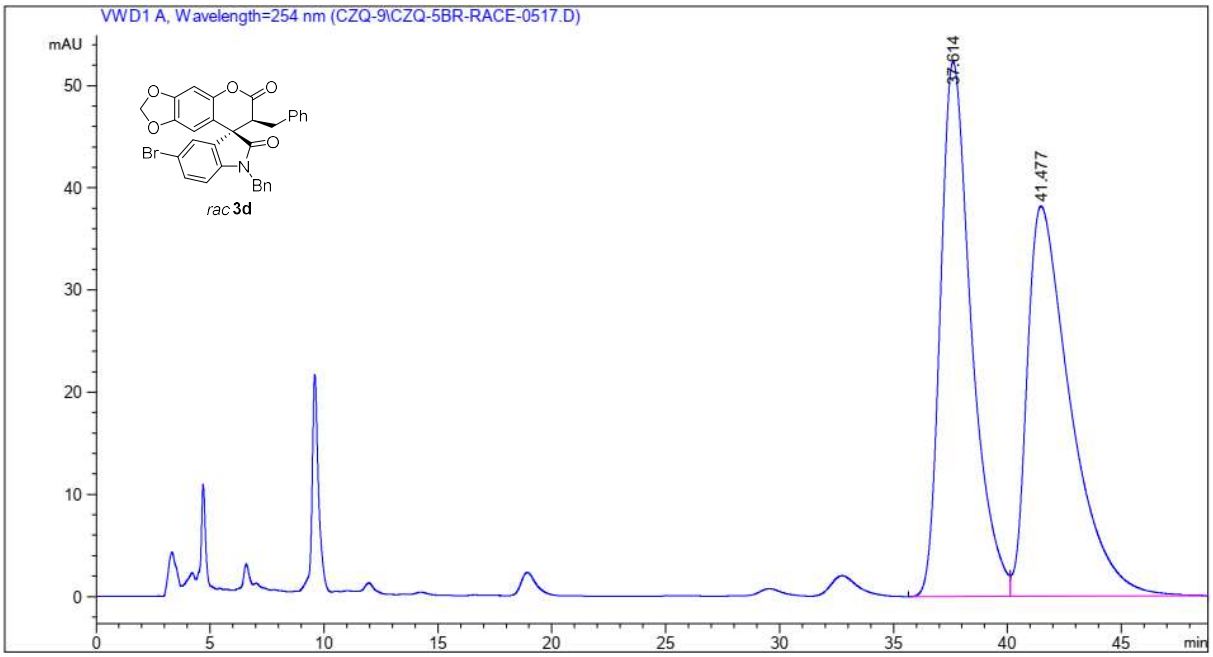
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	15.726	60.29297	1.11178	0.6829
2	PDA 254.0 nm	29.175	8769.07227	92.83614	99.3171



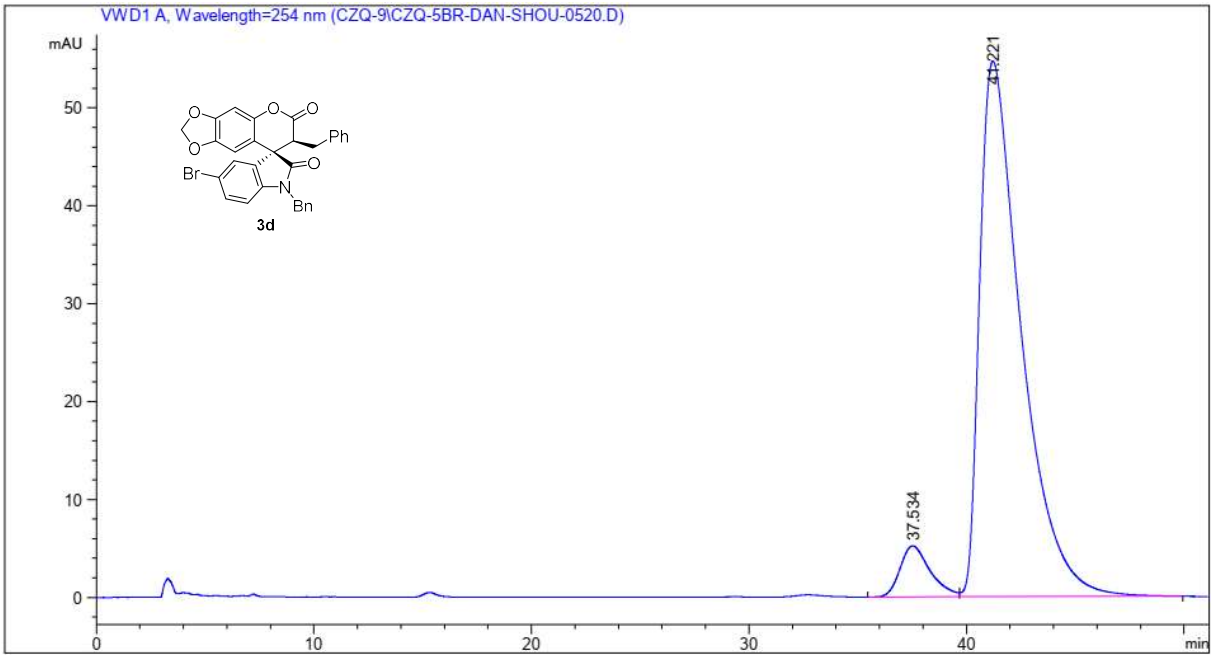
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	9.224	1.02387e4	440.33499	49.9778
2	PDA 254.0 nm	37.421	1.02478e4	89.05914	50.0222



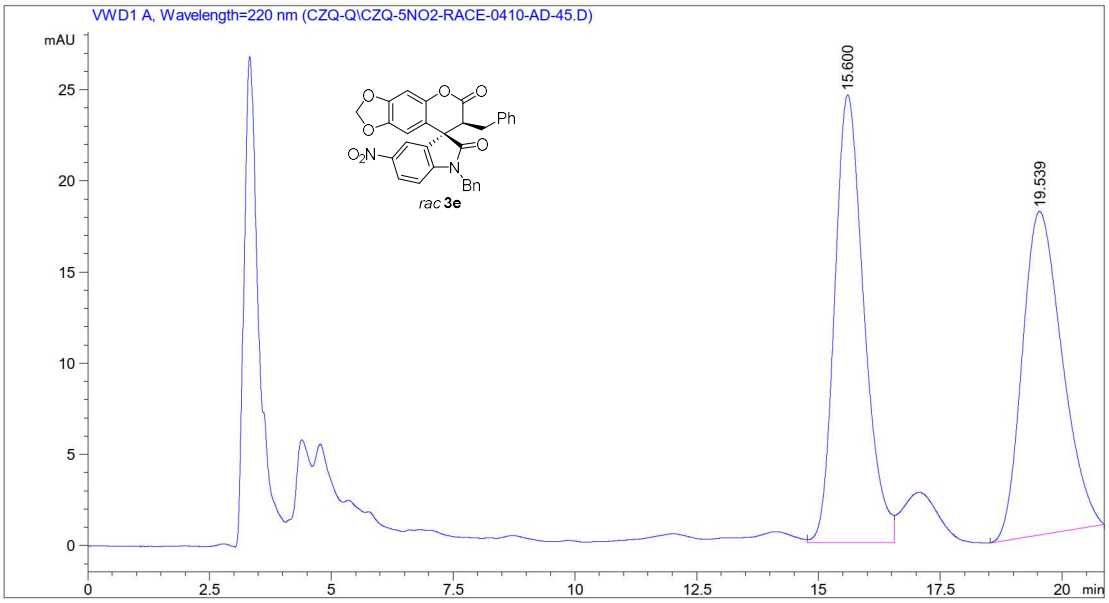
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	9.085	620.10455	26.86867	4.4715
2	PDA 254.0 nm	36.592	1.32478e4	117.42579	95.5285



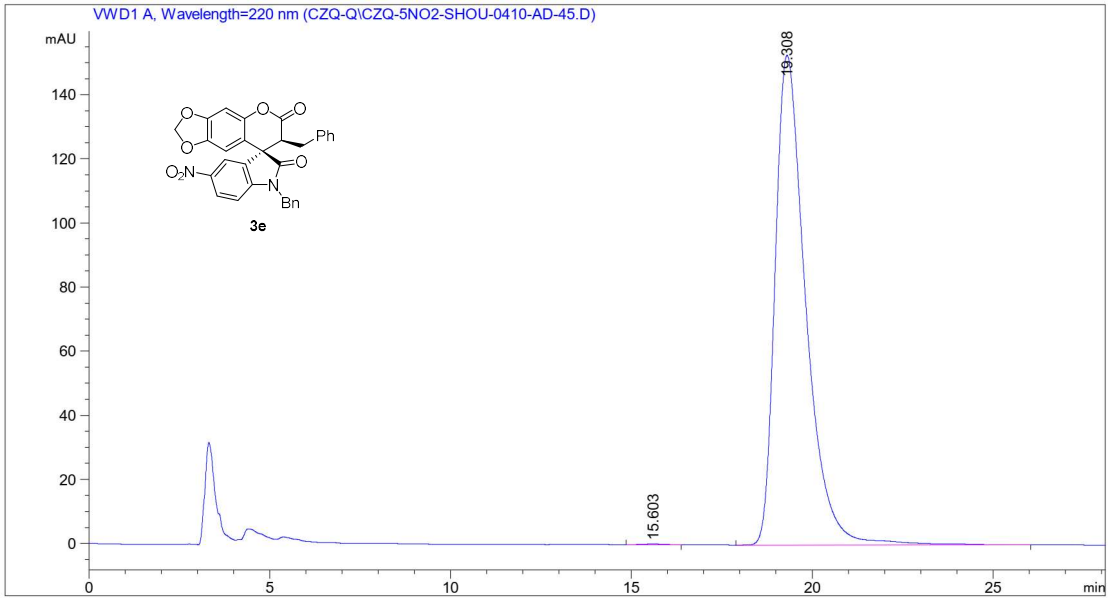
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	37.614	4952.22510	52.33844	49.5999
2	PDA 254.0 nm	41.477	5032.10986	38.20591	50.4001



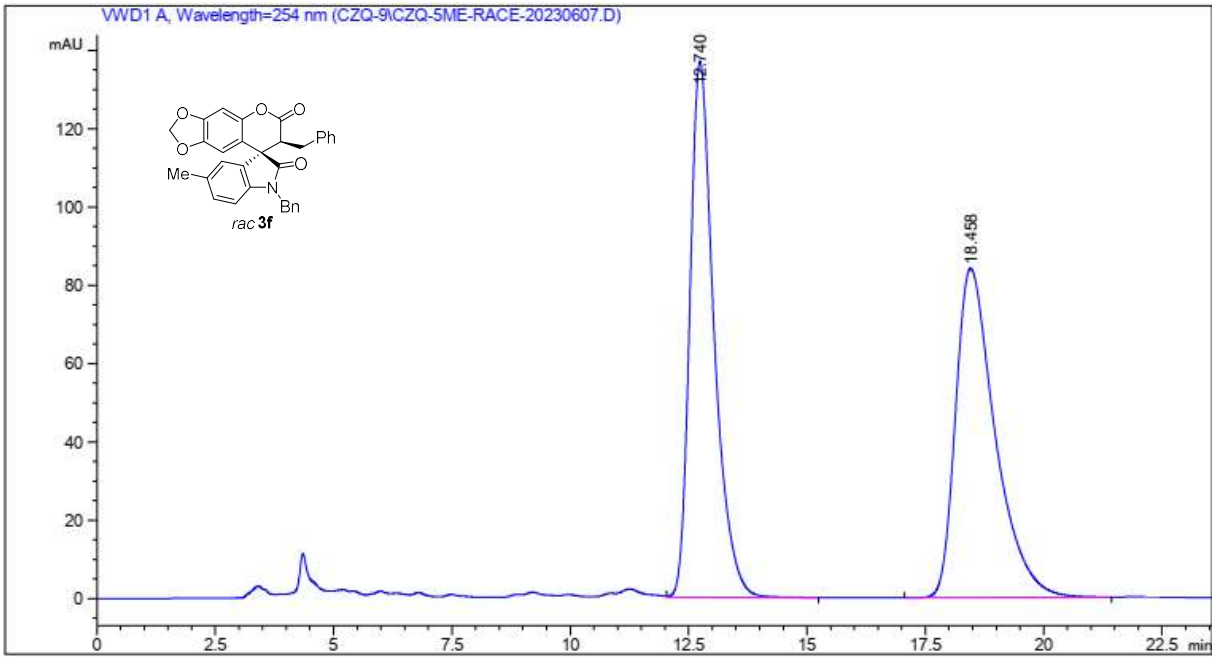
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	37.534	502.83112	5.22041	6.4854
2	PDA 254.0 nm	41.221	7250.39551	54.71442	93.5146



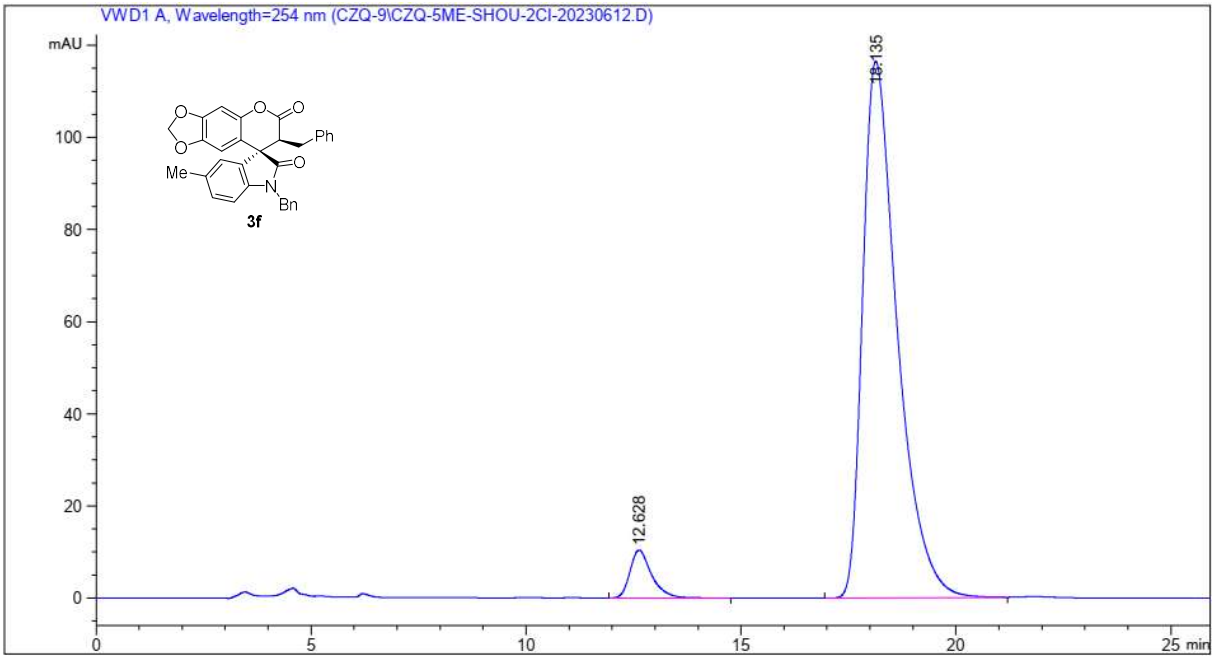
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 220.0 nm	15.600	1024.99280	24.55524	50.4935
2	PDA 220.0 nm	19.539	1004.95544	17.73695	49.5065



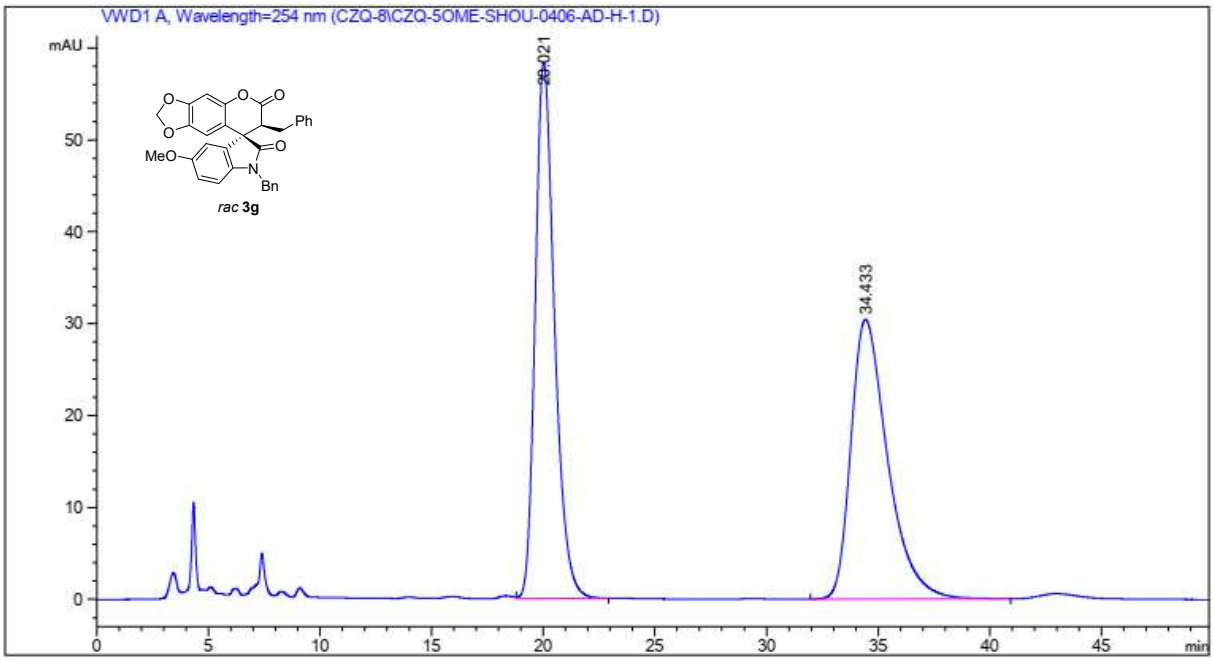
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 220.0 nm	15.603	8.94669	2.26344e-1	0.0994
2	PDA 220.0 nm	19.308	8993.23828	152.75951	99.9006



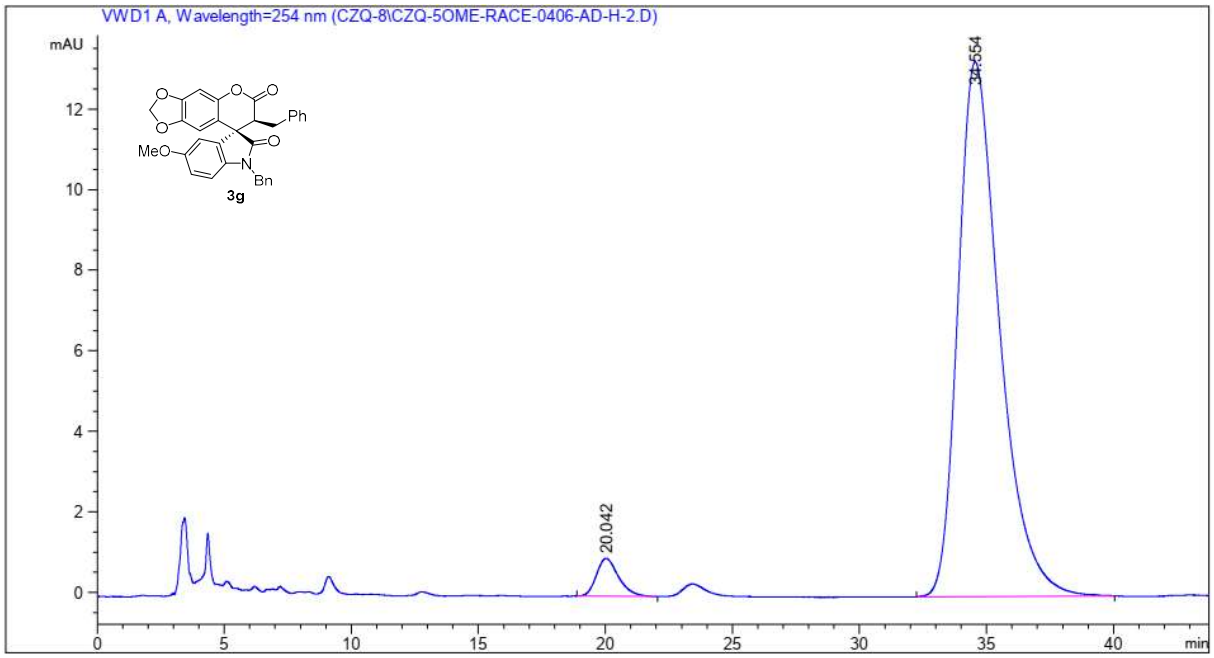
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	12.740	4838.11084	136.78374	49.8634
2	PDA 254.0 nm	18.458	4864.61377	84.05011	50.1366



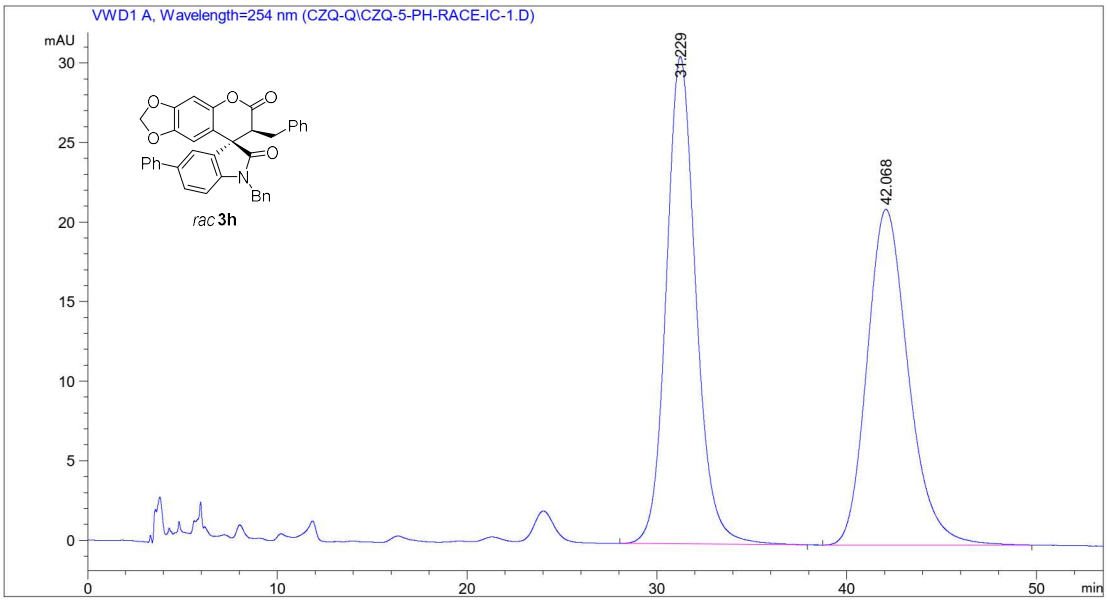
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	12.628	362.06055	390.09644	5.2657
2	PDA 254.0 nm	18.135	6513.83008	116.52373	94.7343



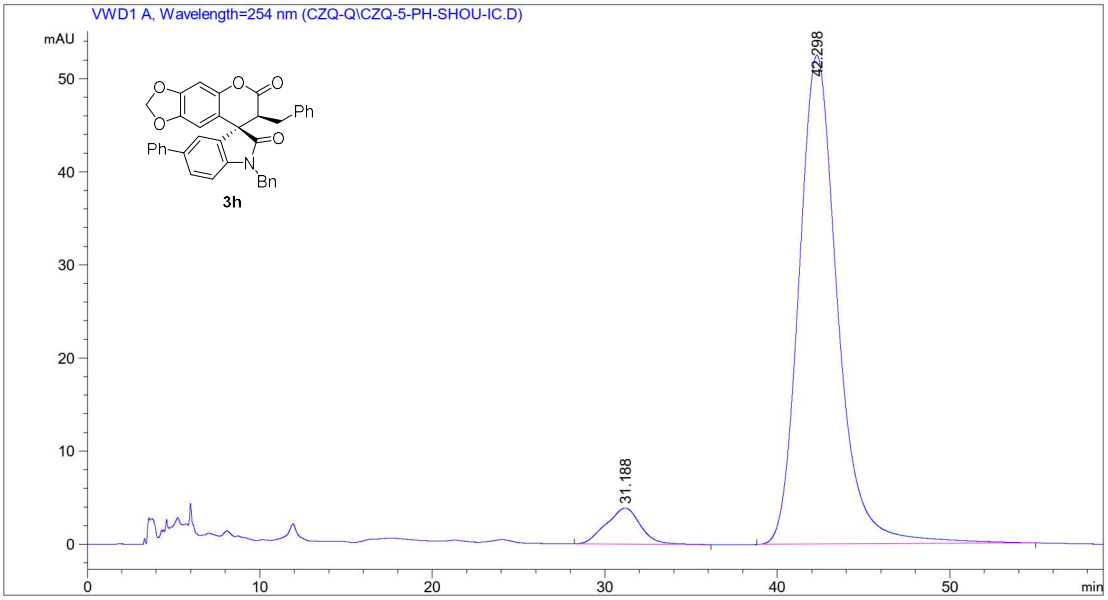
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	20.021	3500.96655	58.34473	50.1880
2	PDA 254.0 nm	34.433	3474.74463	30.40070	49.8120



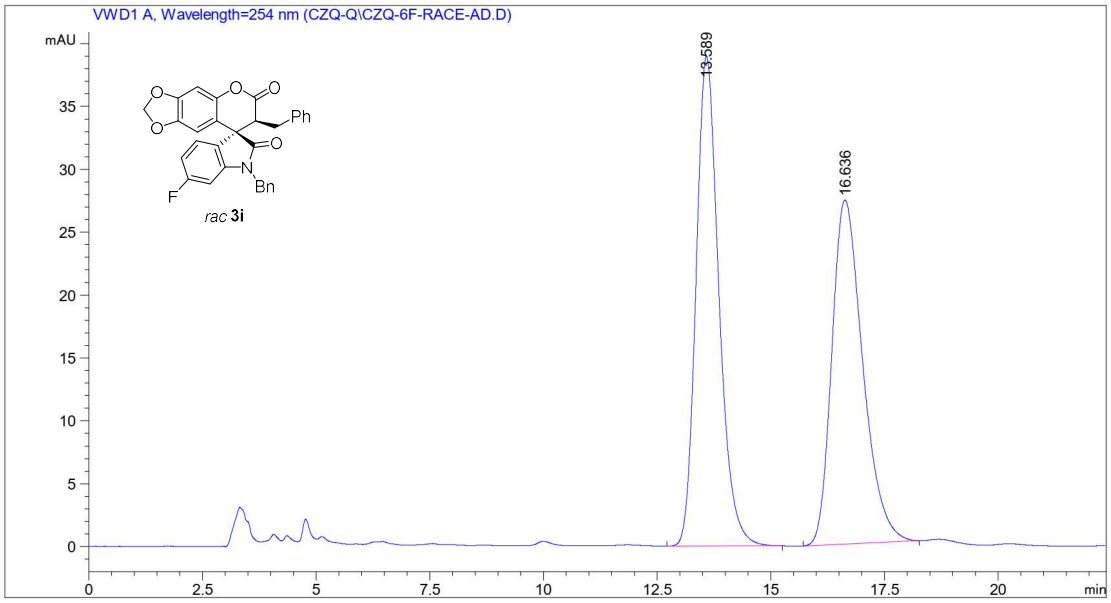
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	20.042	57.30474	9.40746e-1	3.6587
2	PDA 254.0 nm	34.554	1508.95447	13.27624	96.3413



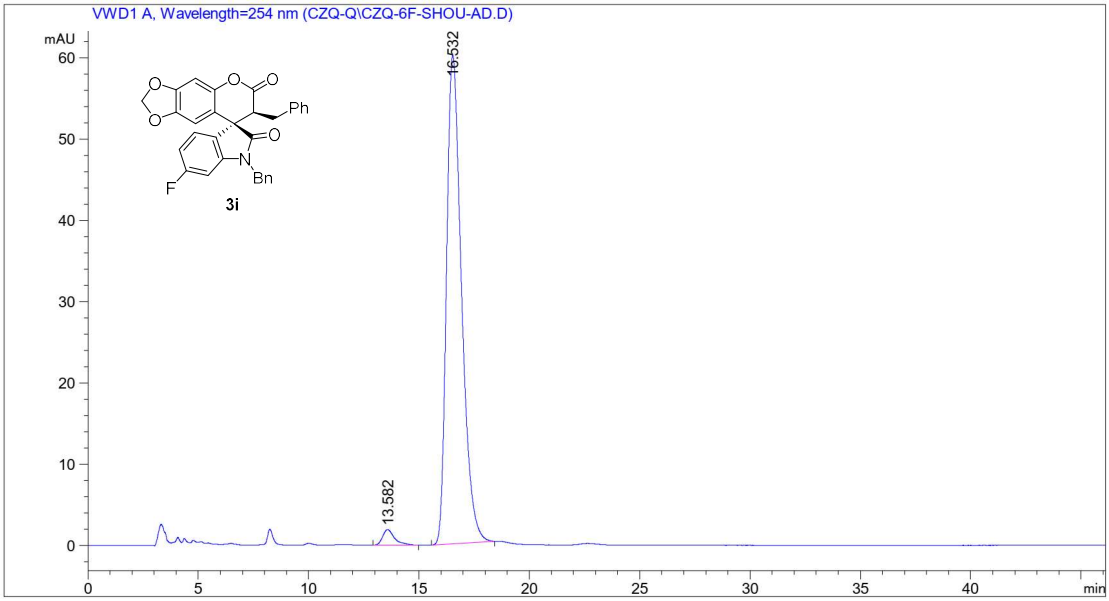
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	31.229	3322.78296	30.62305	51.0184
2	PDA 254.0 nm	42.068	3190.12671	21.09669	48.9816



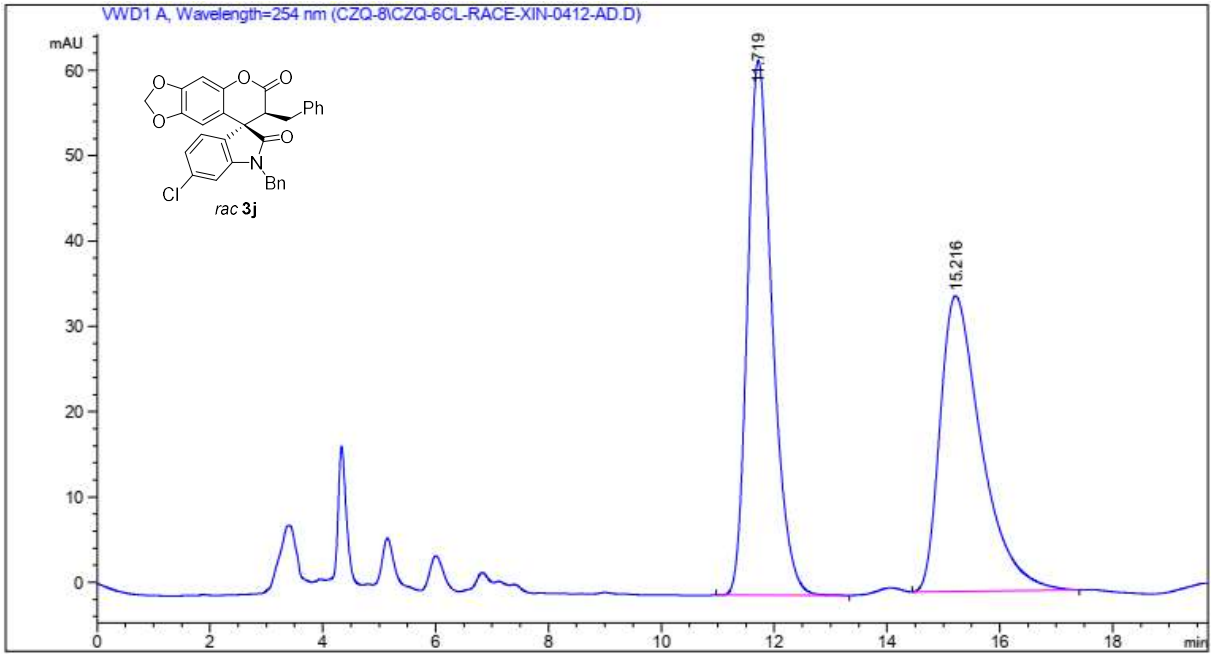
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	31.188	530.09558	3.86420	6.1103
2	PDA 254.0 nm	42.298	8145.36963	52.49854	93.8897



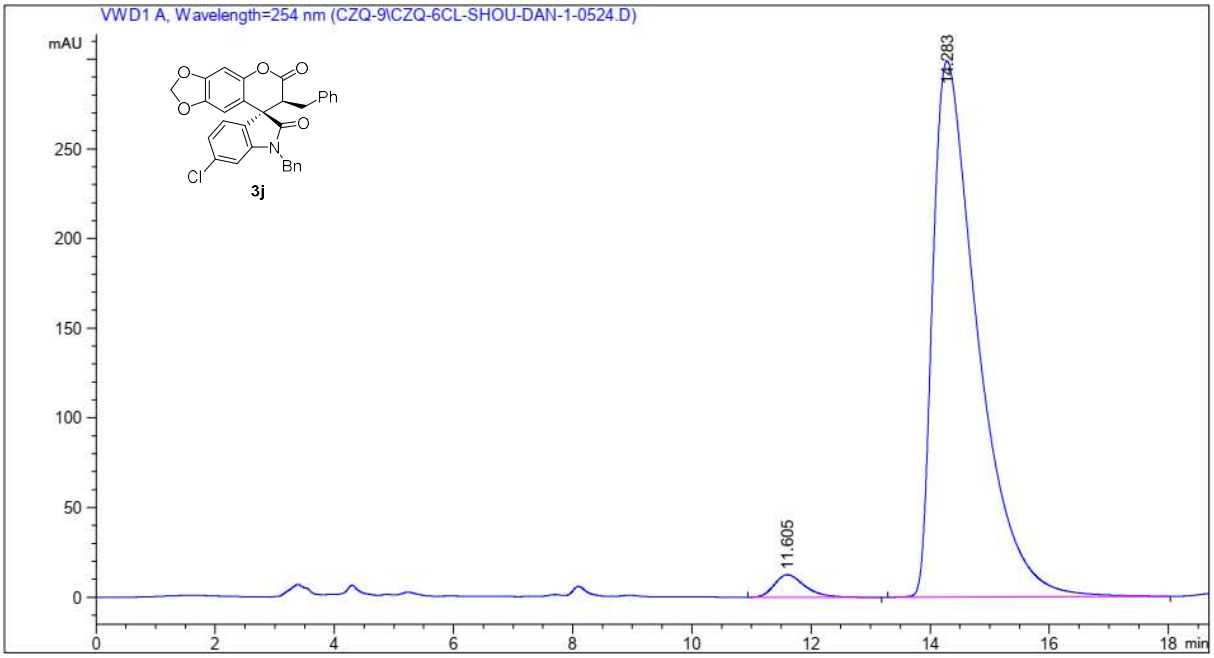
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	13.589	1358.33569	38.94492	51.2685
2	PDA 254.0 nm	16.636	1291.11816	27.36017	48.7315



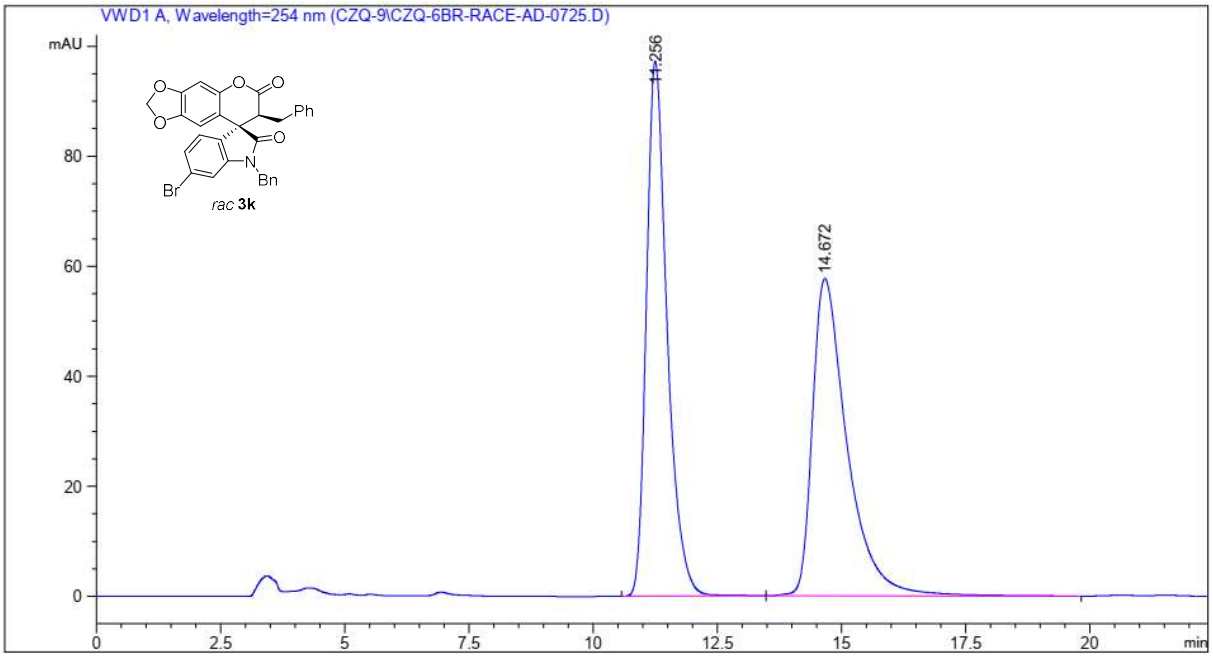
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	13.582	71.86649	1.91658	2.4778
2	PDA 254.0 nm	16.532	2828.49951	60.10563	97.5222



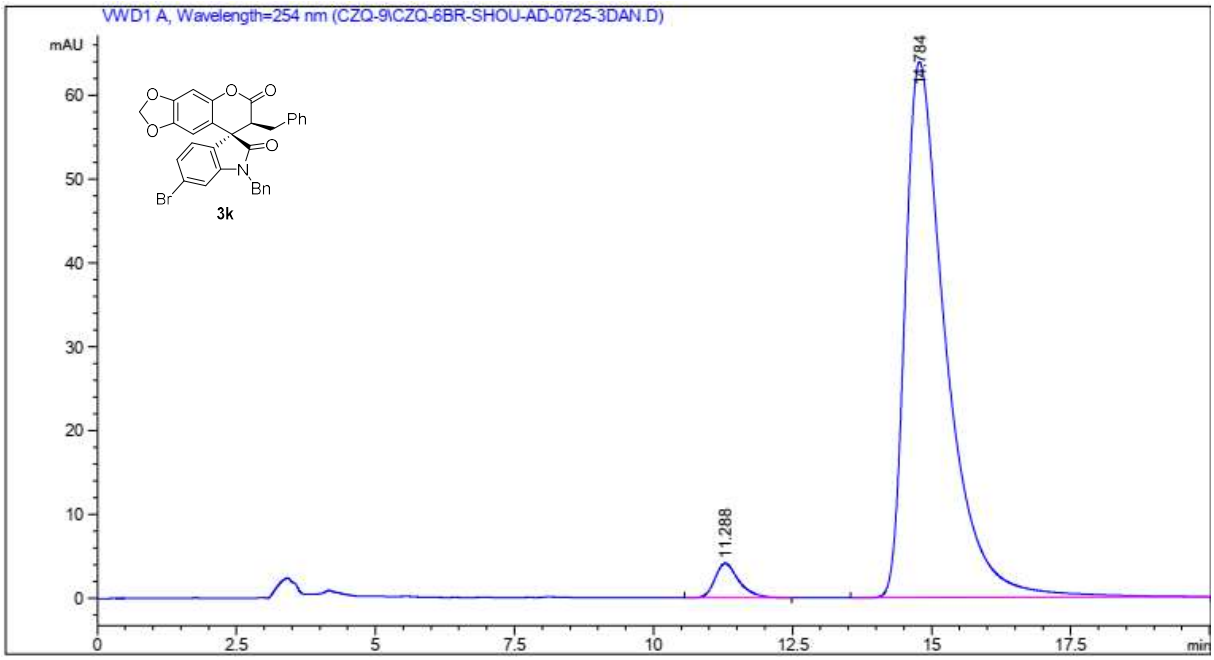
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	11.719	1917.44775	62.67554	52.1192
2	PDA 254.0 nm	15.216	1761.52087	34.64141	47.8808



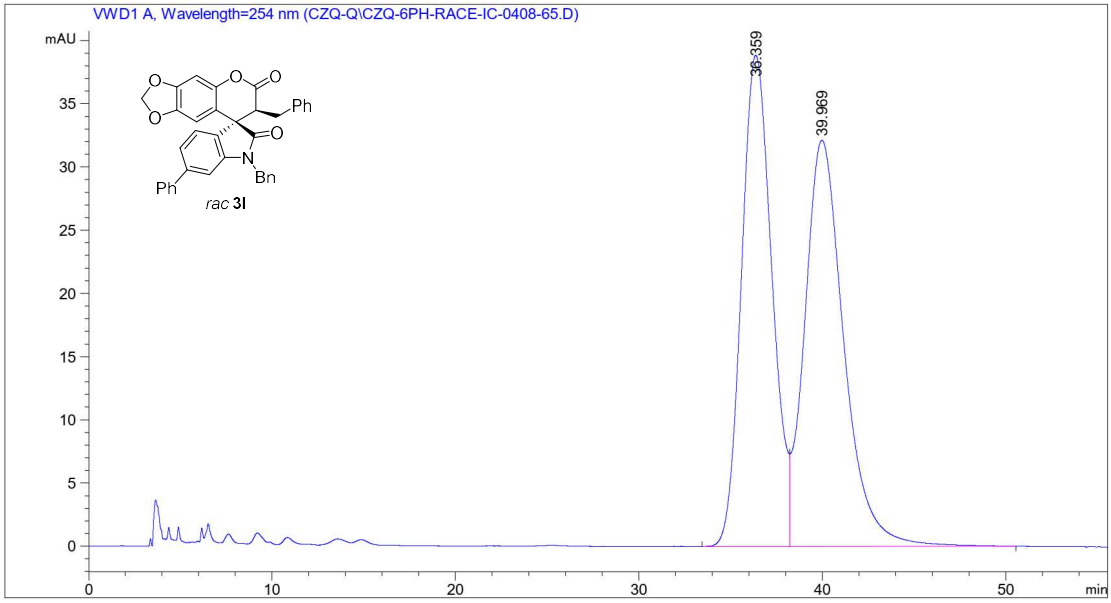
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	11.605	442.81454	12.53001	2.7671
2	PDA 254.0 nm	14.283	1.55601e4	298.98843	97.2329



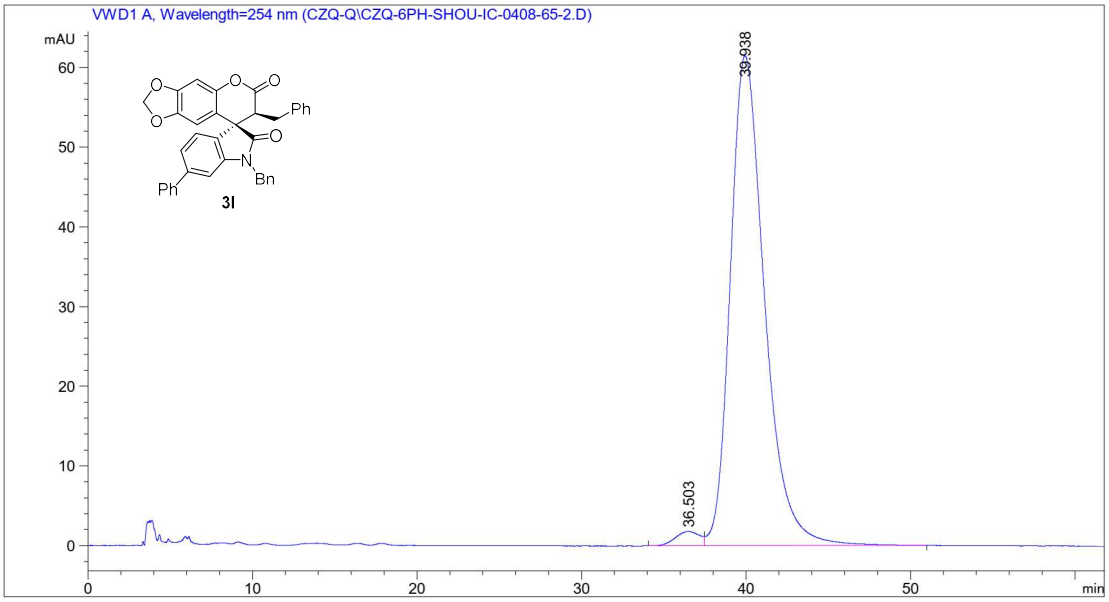
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	11.256	2829.21899	97.23276	50.2011
2	PDA 254.0 nm	14.672	2806.55591	57.69843	49.7989



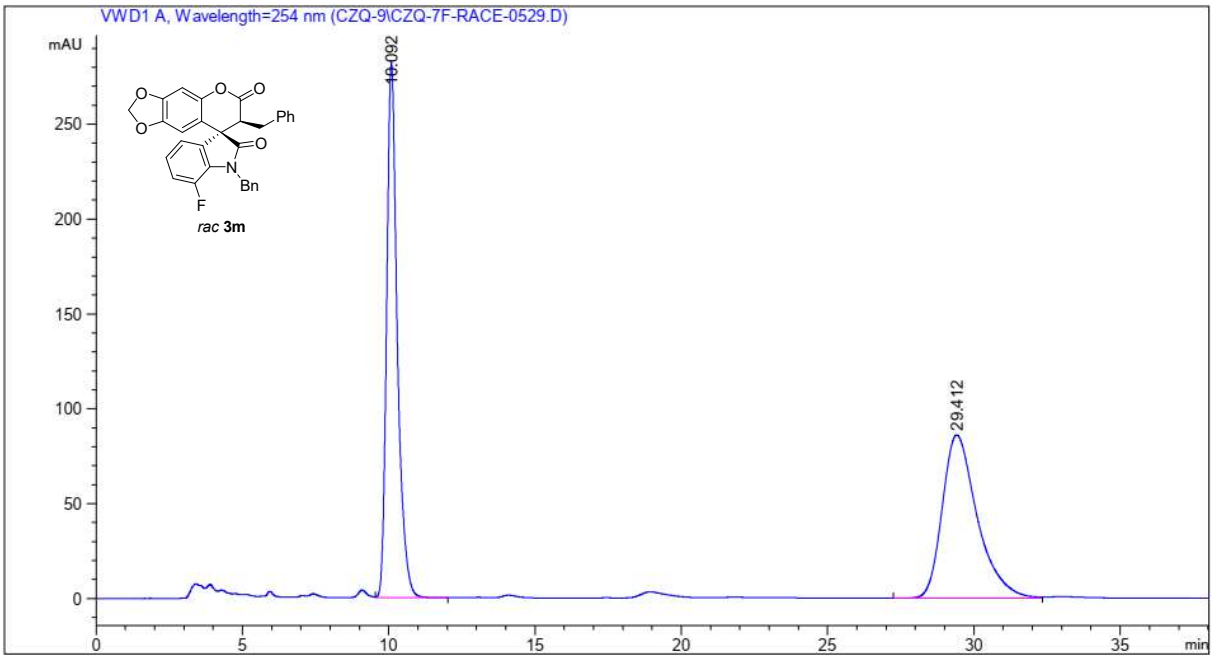
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	11.288	122.39032	4.11314	3.6318
2	PDA 254.0 nm	14.784	3247.59912	63.87044	96.3682



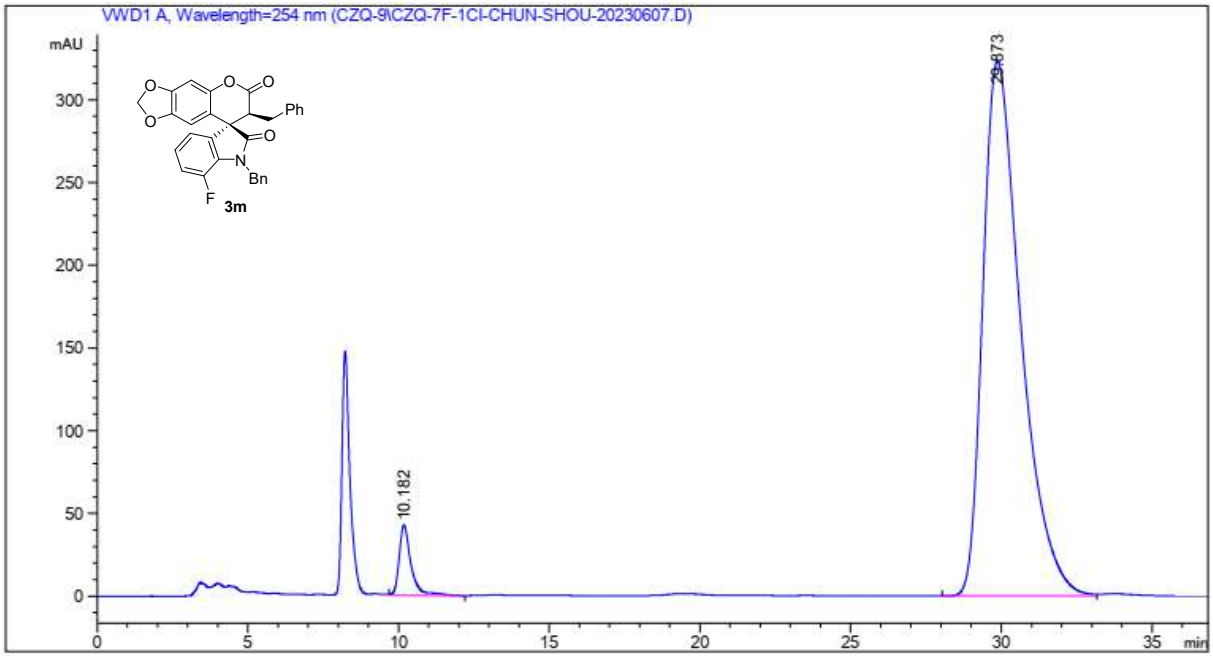
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	36.359	4481.51855	38.85182	48.4311
2	PDA 254.0 nm	39.969	4771.86816	32.13577	51.5689



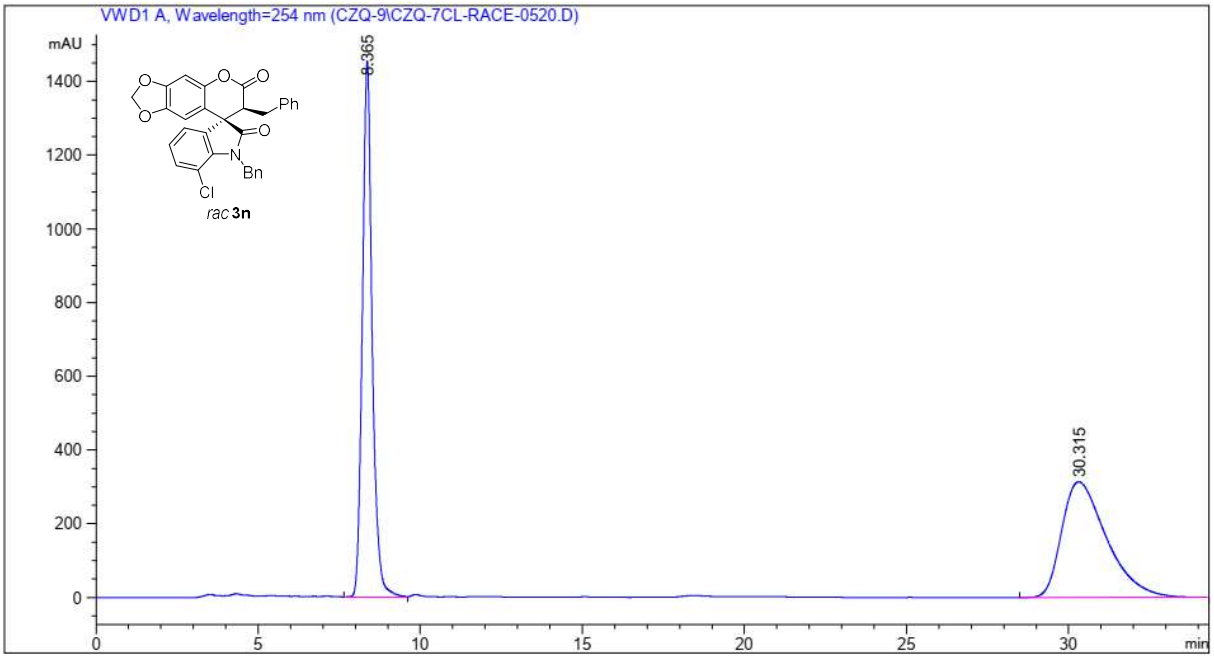
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	36.503	186.40221	1.80940	2.0438
2	PDA 254.0 nm	39.938	8934.08887	61.50807	97.9562



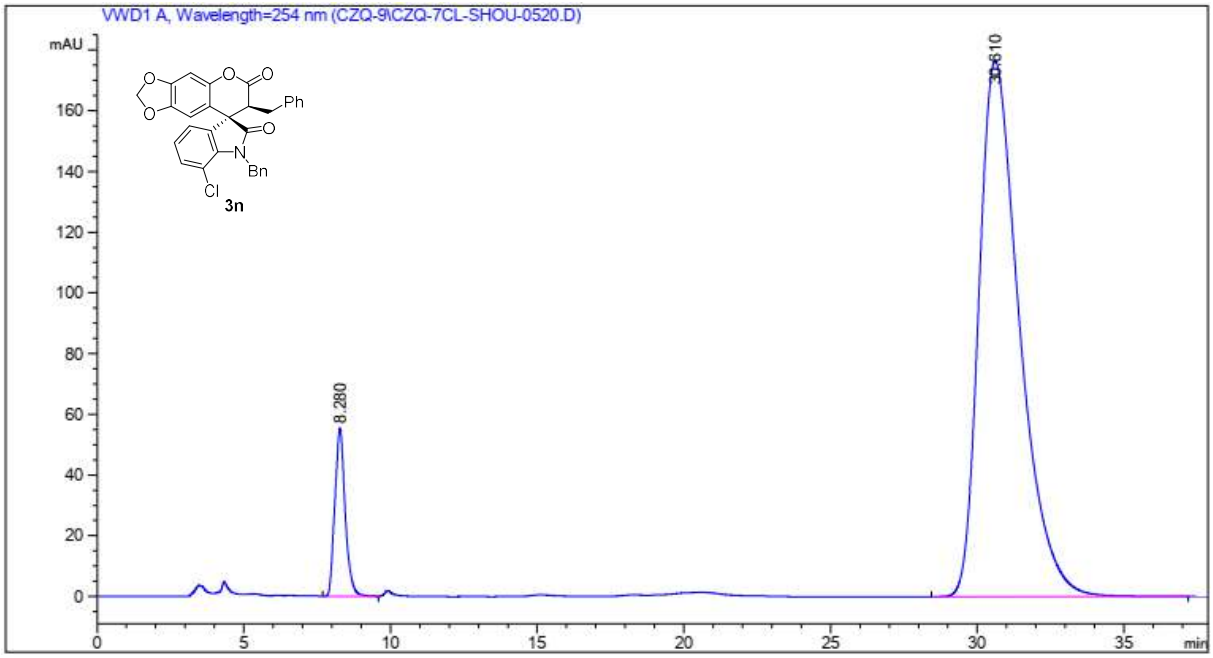
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	10.092	7129.82129	282.43674	49.9712
2	PDA 254.0 nm	29.412	7138.04785	86.01691	50.0288



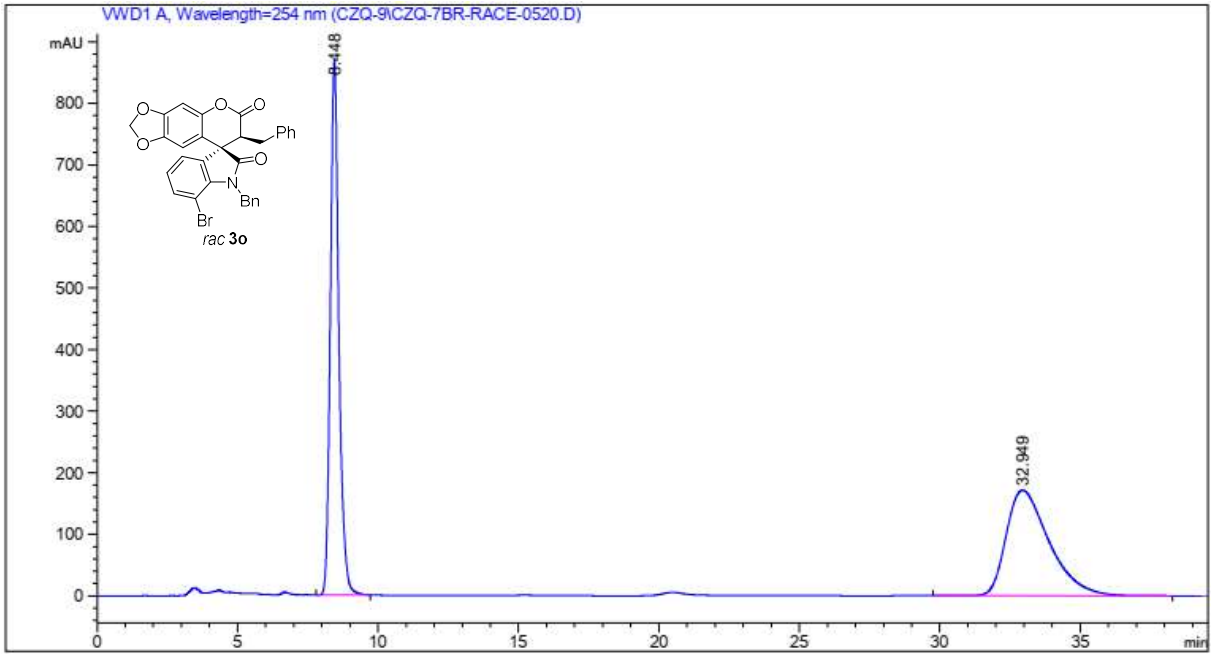
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	10.182	1158.47681	42.37434	3.9425
2	PDA 254.0 nm	29.873	2.82258e4	323.31876	96.0575



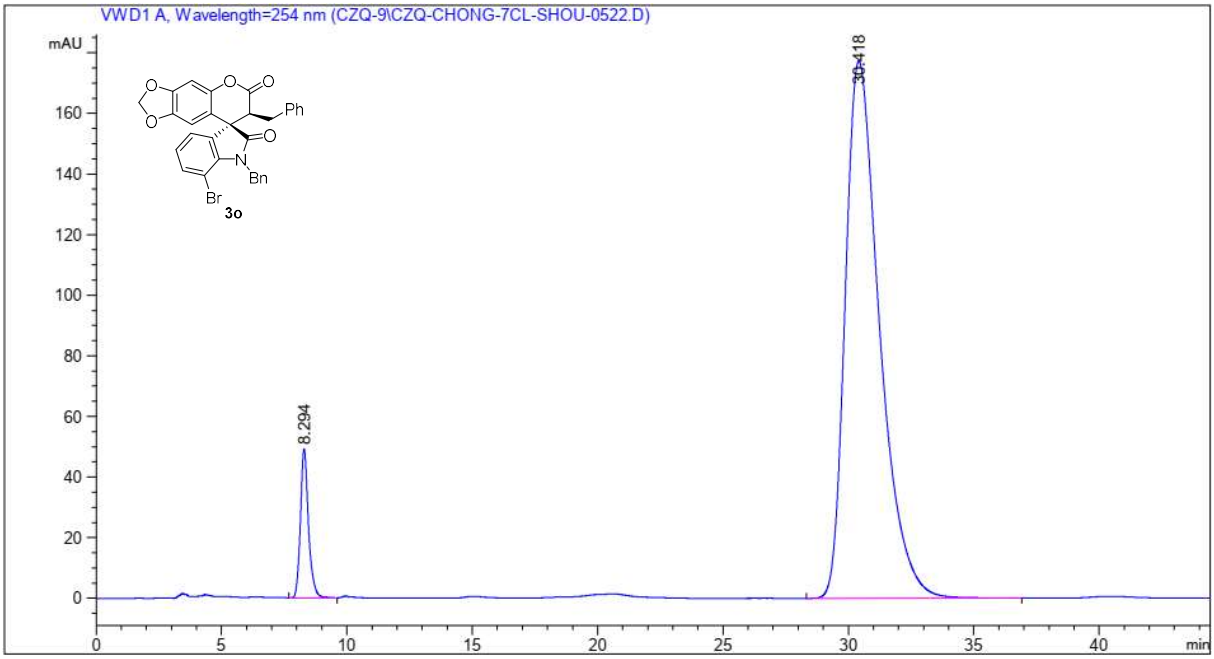
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	8.365	3.06129e4	1452.96033	50.3803
2	PDA 254.0 nm	30.315	3.01507e4	313.56512	49.6197



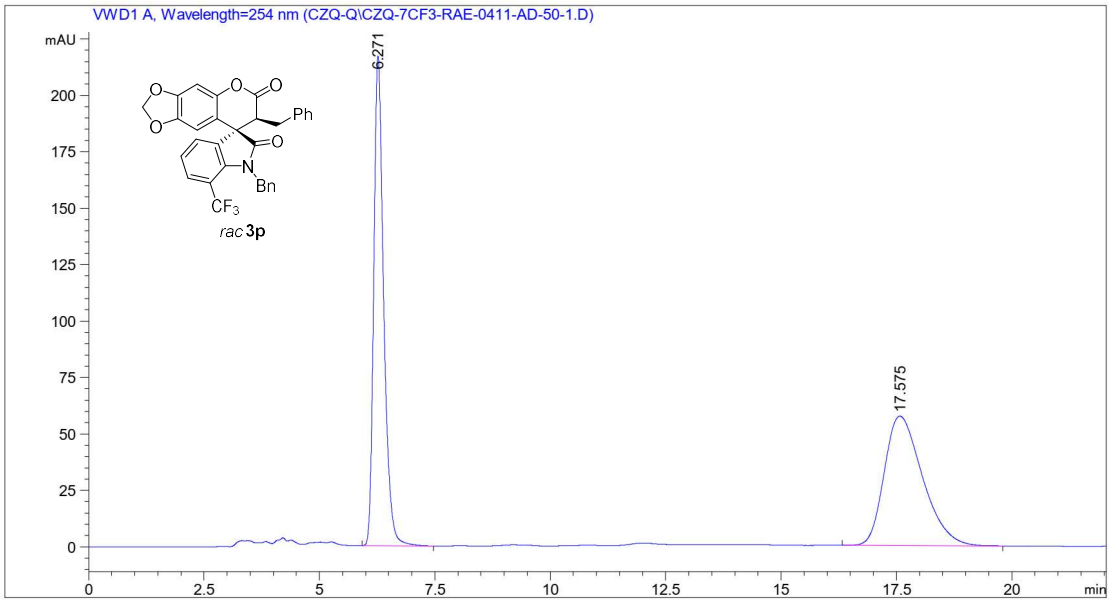
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	8.280	1358.41638	55.35059	7.4448
2	PDA 254.0 nm	30.610	1.68880e4	176.36806	92.5552



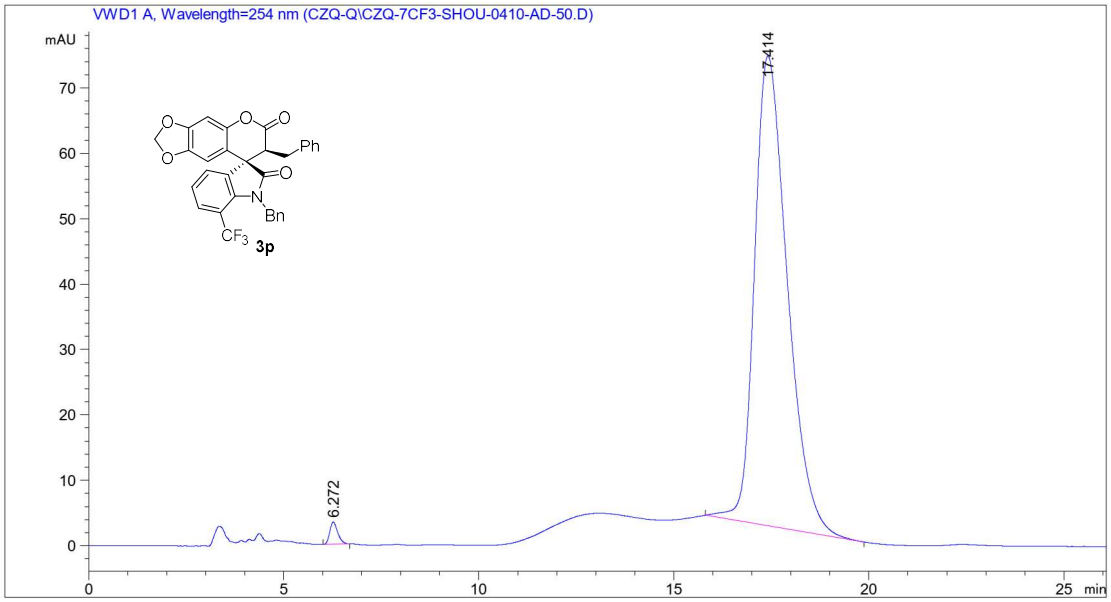
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	8.448	1.83382e4	868.62122	50.1431
2	PDA 254.0 nm	32.949	1.82336e4	171.35616	49.8569



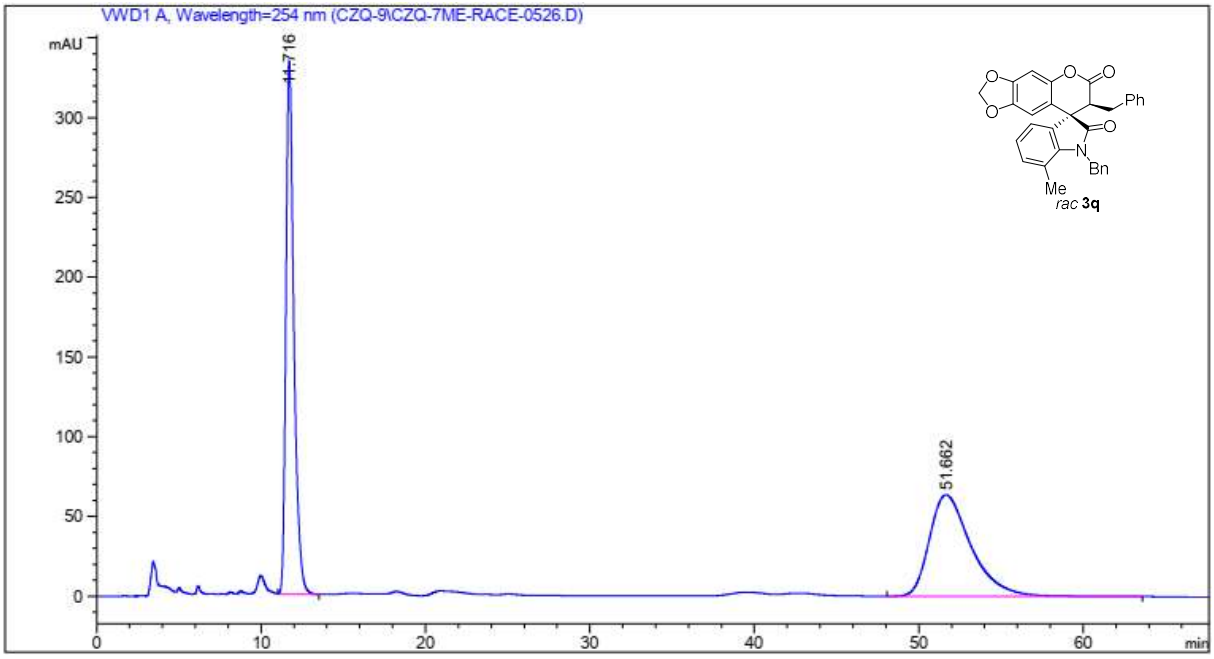
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	8.294	1095.21509	49.18624	6.1346
2	PDA 254.0 nm	30.418	1.67578e4	177.28758	93.8654



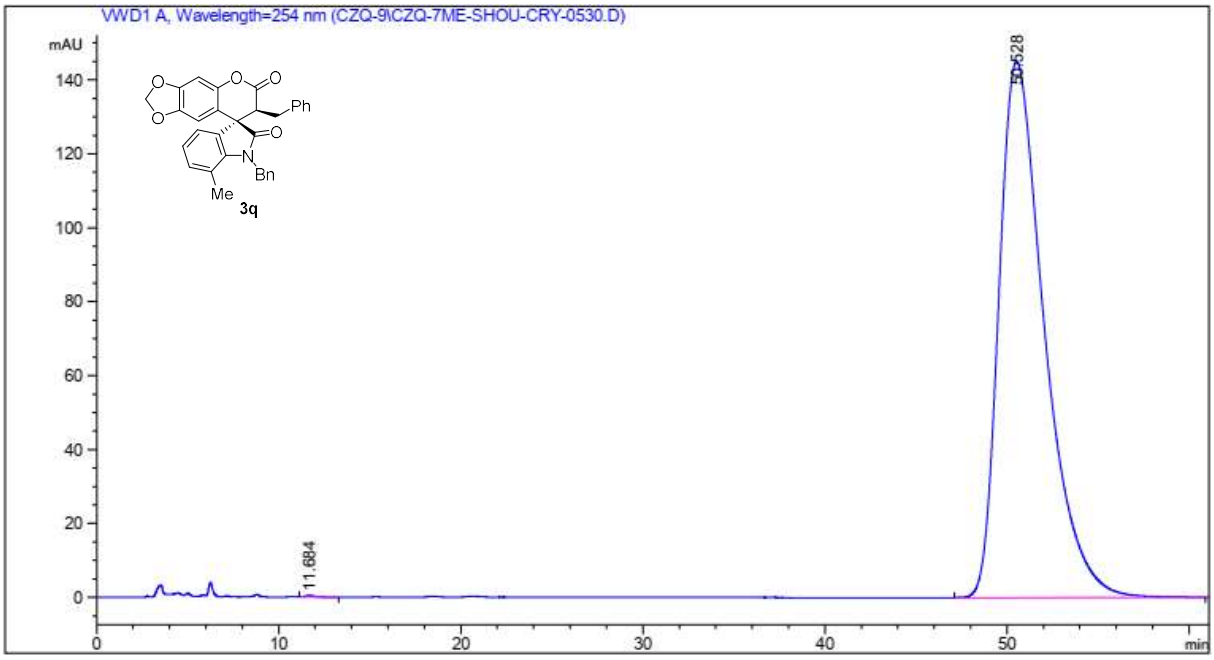
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	6.271	3226.35620	216.76897	49.4366
2	PDA 254.0 nm	17.575	3299.89990	57.33051	50.5634



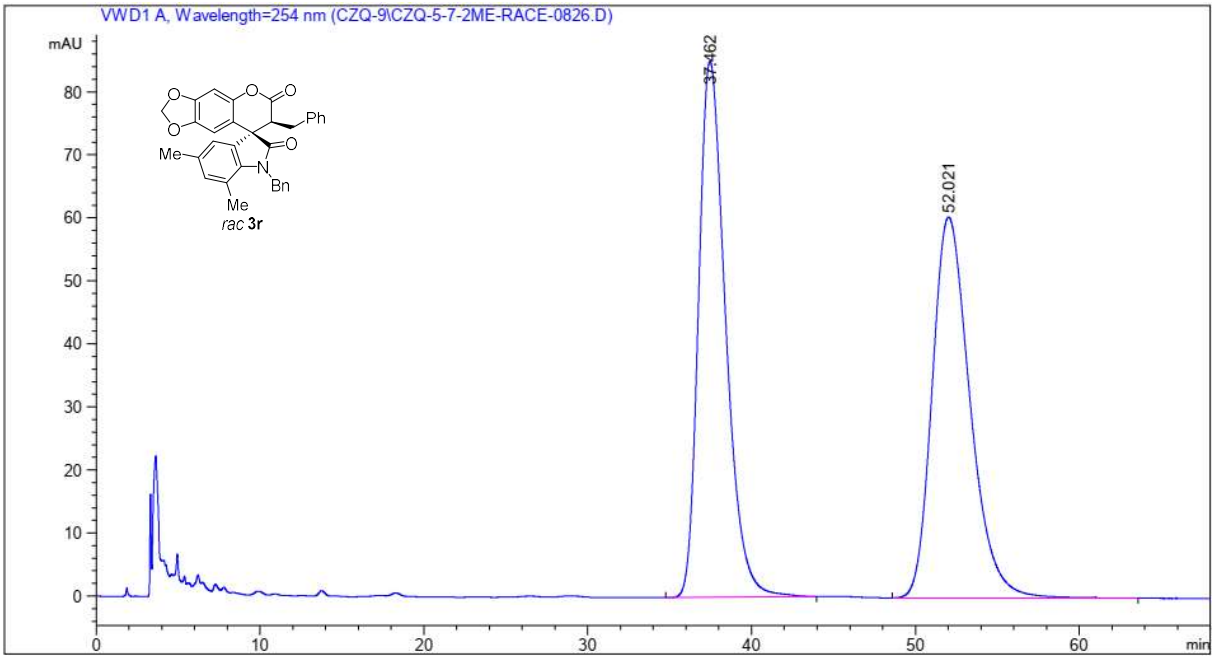
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	6.272	48.58934	3.41051	1.1407
2	PDA 254.0 nm	17.414	4211.00342	71.82191	98.8593



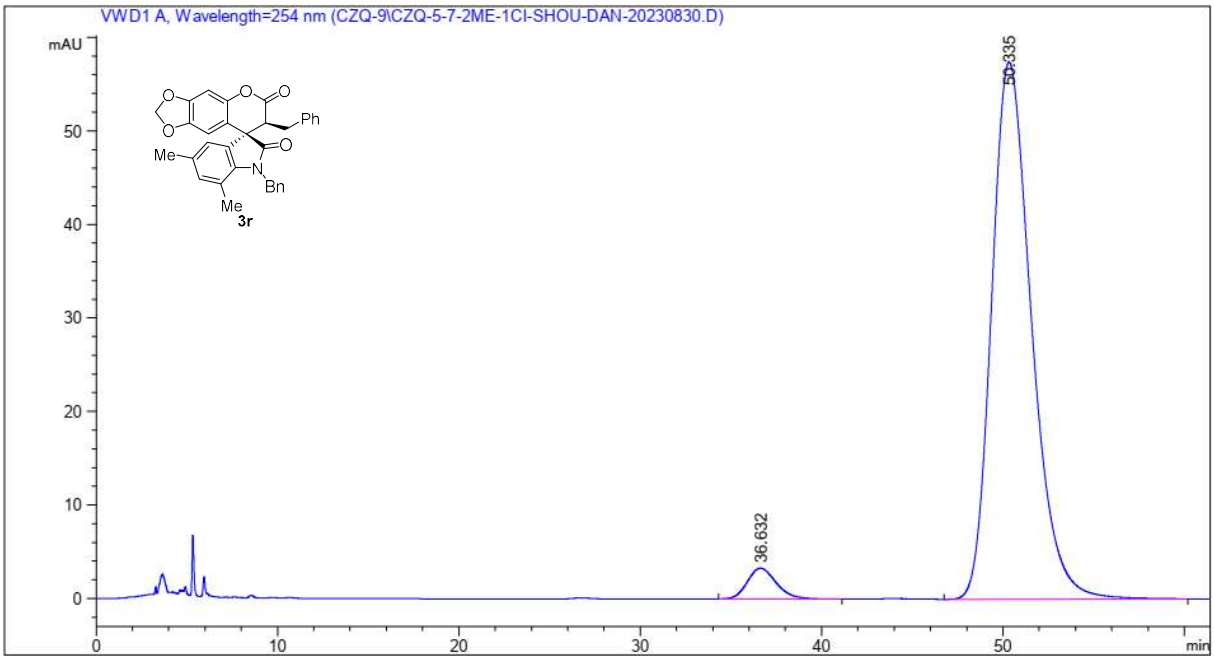
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	11.716	1.12275e4	334.22433	50.0589
2	PDA 254.0 nm	51.662	1.12011e4	63.60102	49.9411



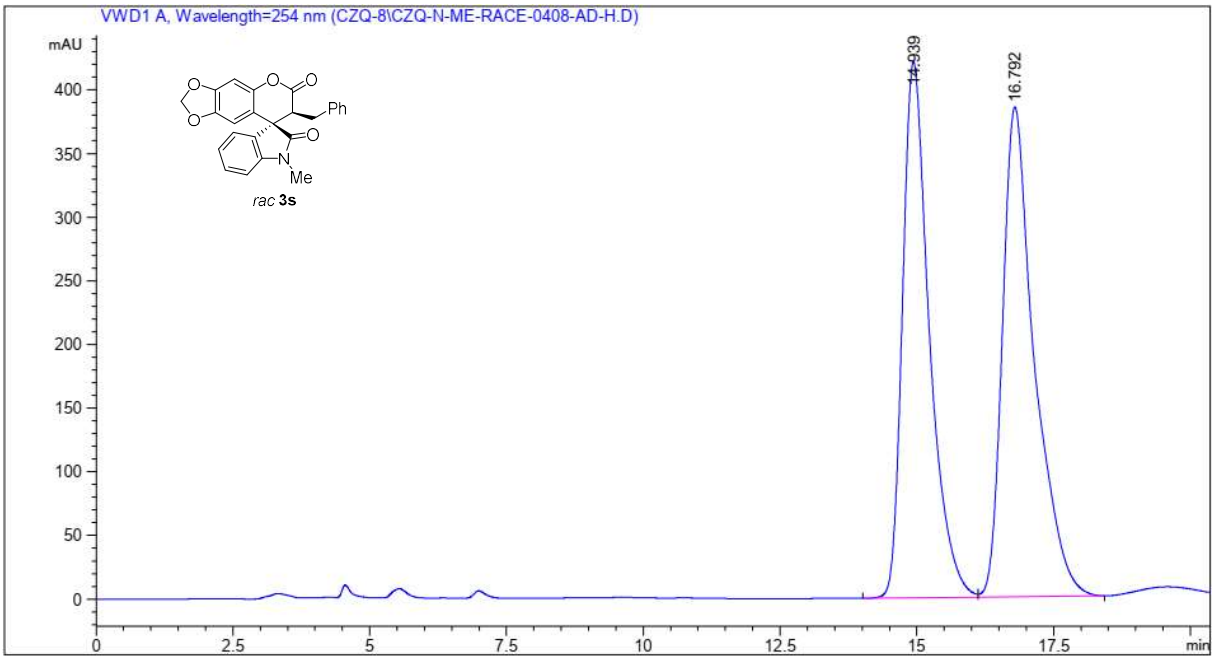
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	11.684	15.39236	4.63013e-1	0.0615
2	PDA 254.0 nm	50.528	2.50232e4	144.96622	99.9385



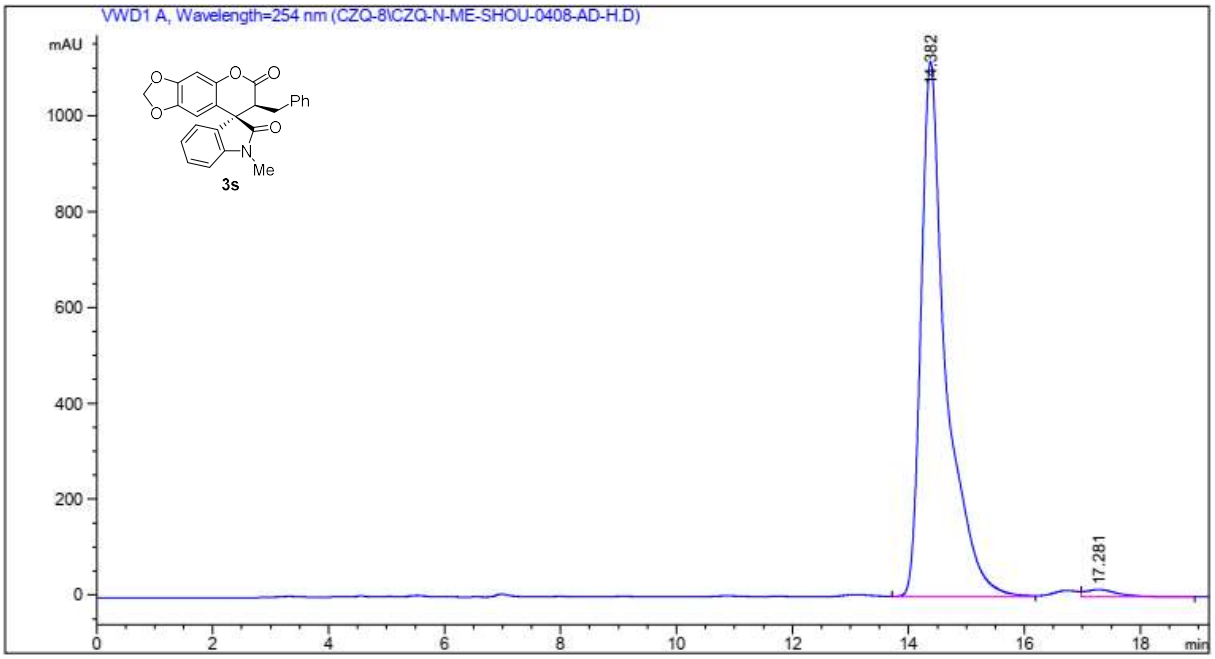
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	37.462	9724.91895	85.07308	50.0888
2	PDA 254.0 nm	52.021	9690.44727	60.43052	49.9112



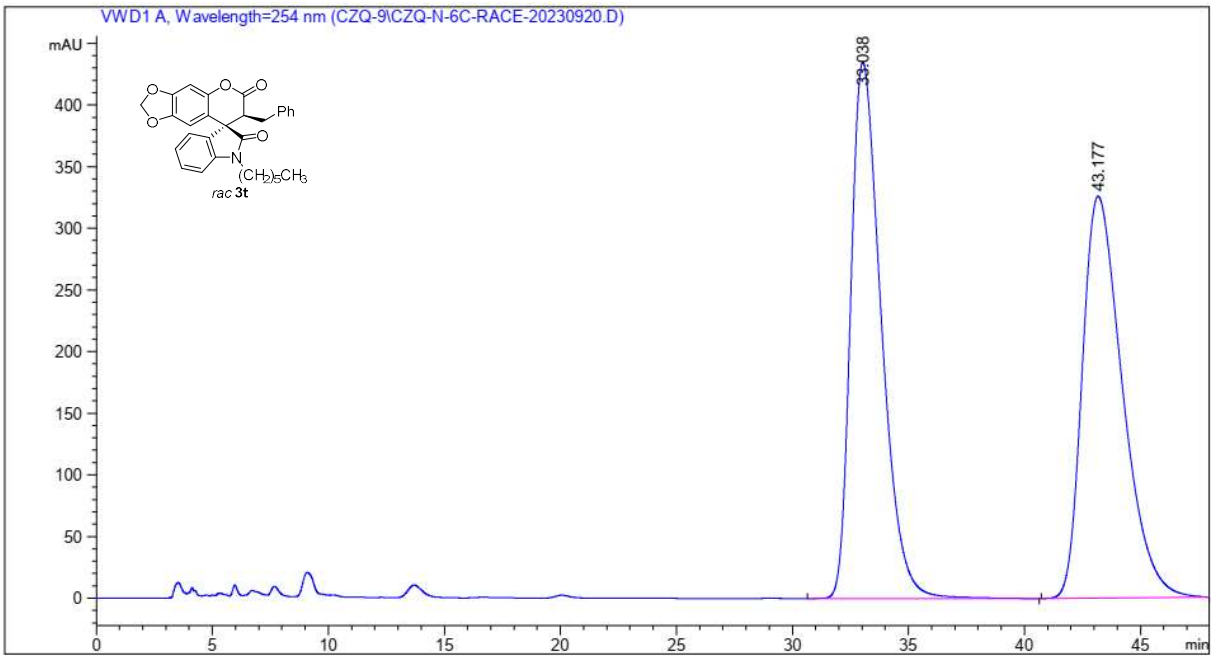
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	36.632	370.03708	3.29934	4.0523
2	PDA 254.0 nm	50.335	8761.46484	57.45690	95.9477



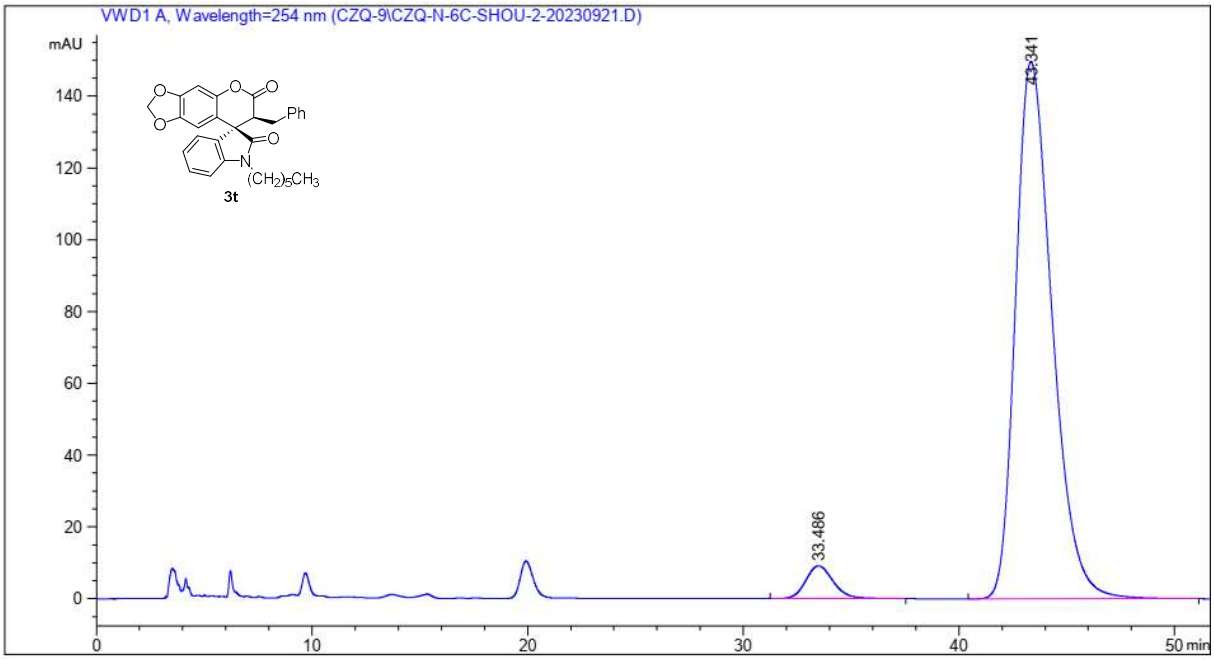
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	14.939	1.43572e4	421.01617	47.9185
2	PDA 254.0 nm	16.792	1.56045e4	384.70831	52.0815



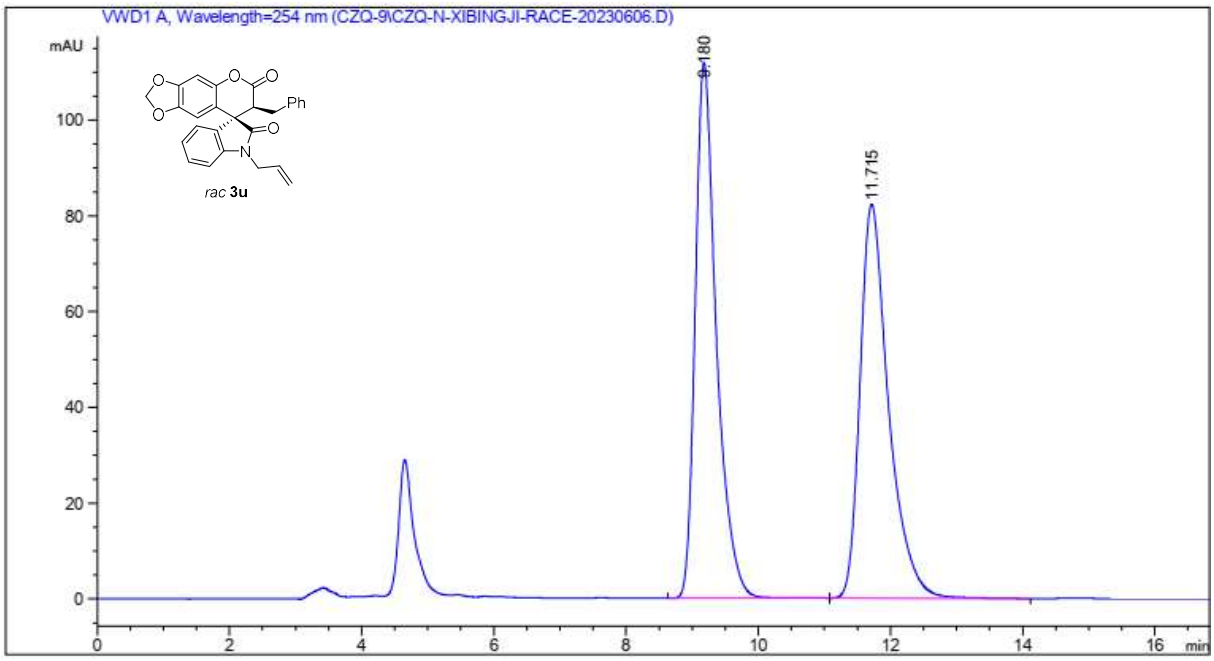
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	14.382	3.33993e4	1116.60913	98.2518
2	PDA 254.0 nm	17.281	594.26111	15.22666	1.7482



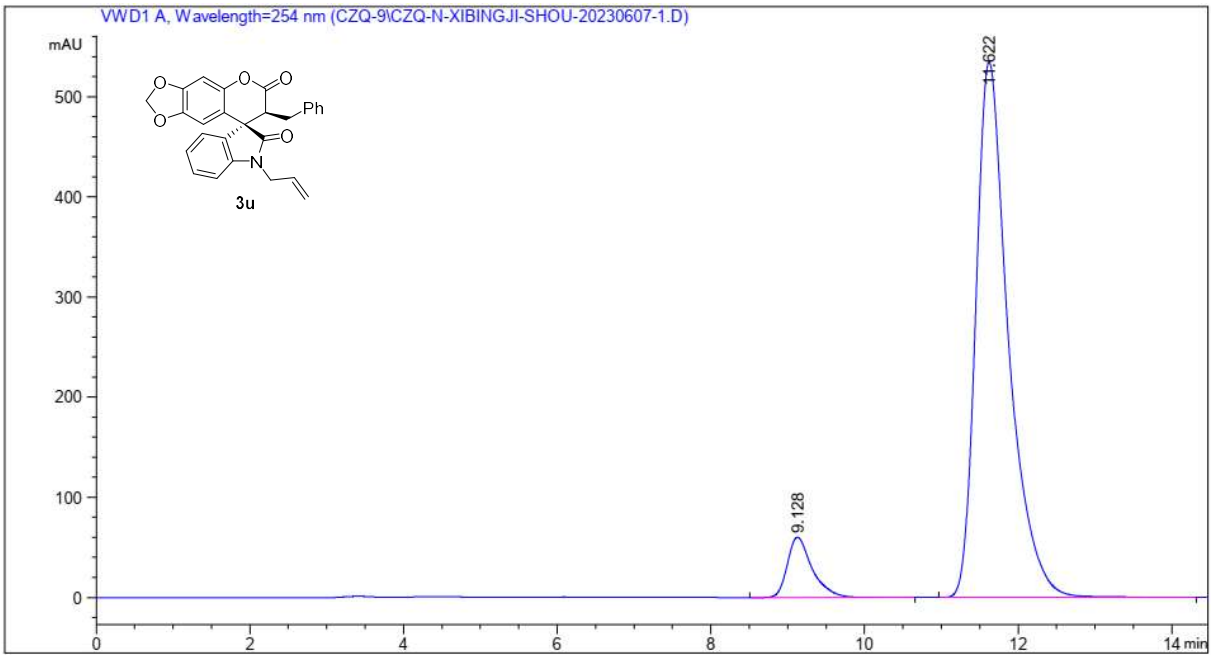
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	33.038	3.96307e4	434.77213	50.3390
2	PDA 254.0 nm	43.177	3.90969e4	325.79700	49.6610



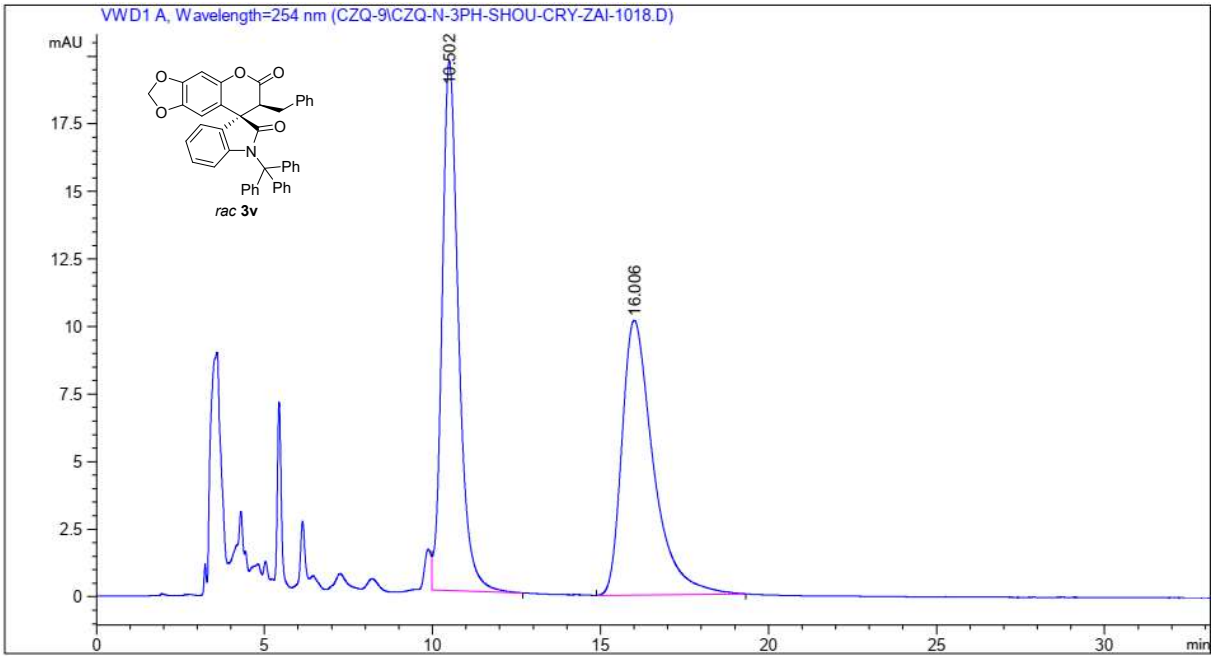
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	33.486	815.66412	9.14215	4.4241
2	PDA 254.0 nm	43.341	1.76213e4	149.67892	95.5759



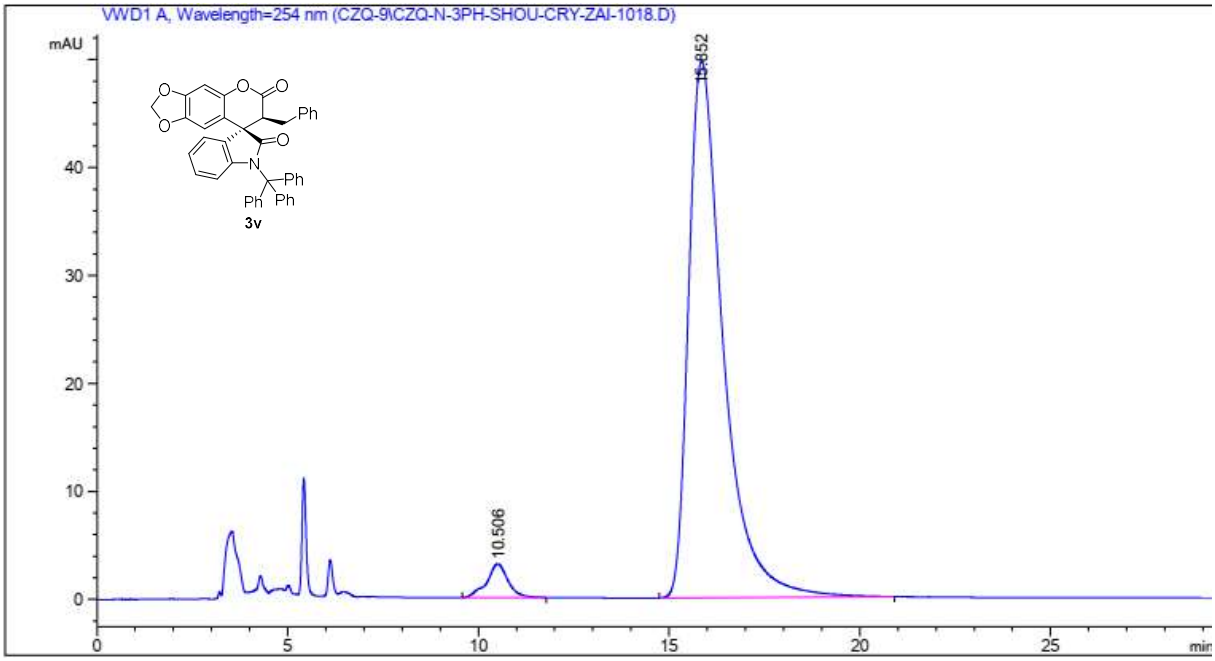
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	9.180	2486.61792	111.79607	50.2074
2	PDA 254.0 nm	11.715	2466.07227	82.20253	49.7926



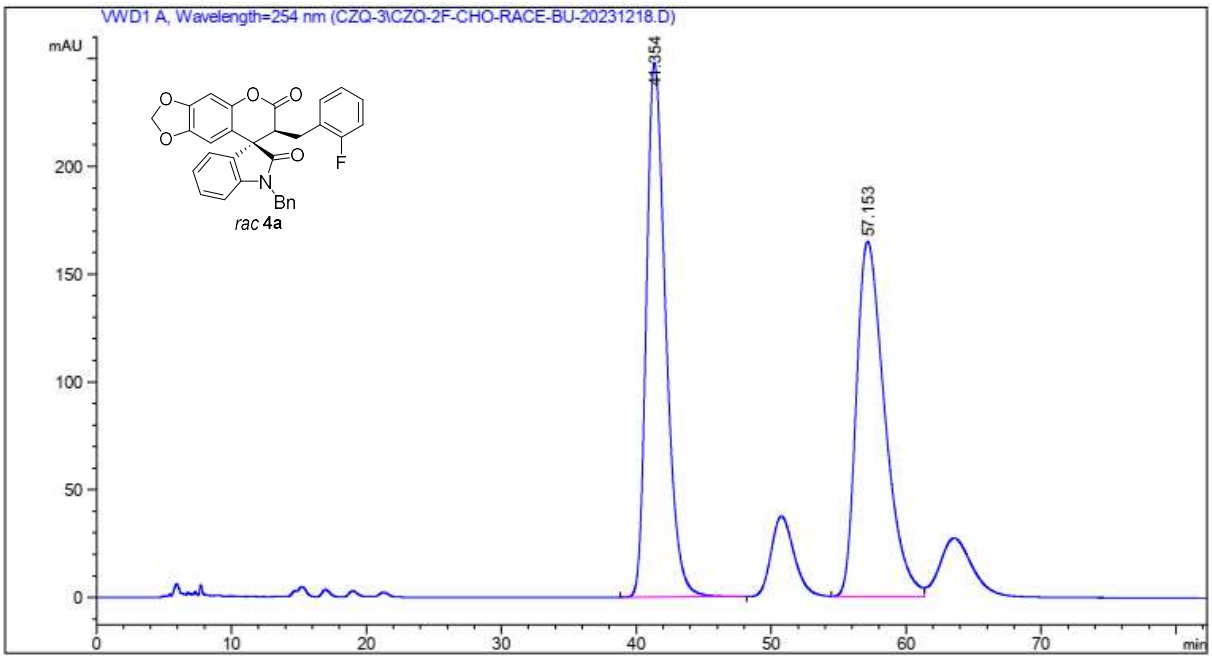
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	9.128	1343.22522	60.08673	7.8884
2	PDA 254.0 nm	11.622	1.56847e4	534.42255	92.1116



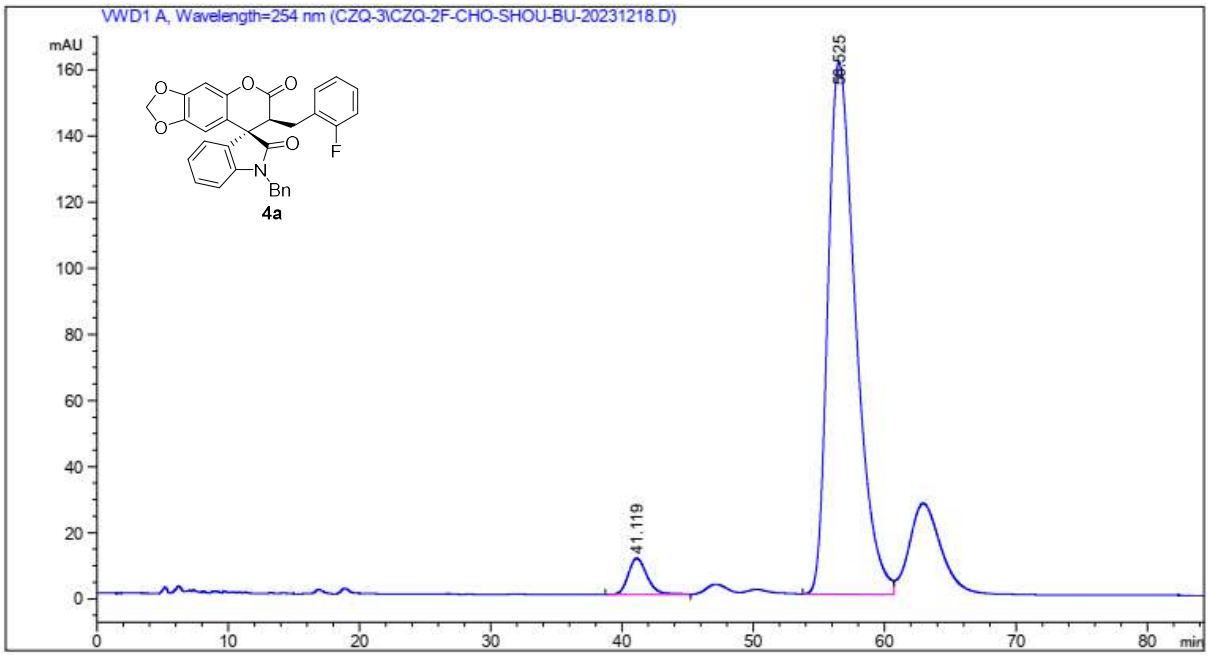
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	10.502	669.06635	19.60707	50.3768
2	PDA 254.0 nm	16.006	659.05719	10.16693	49.6232



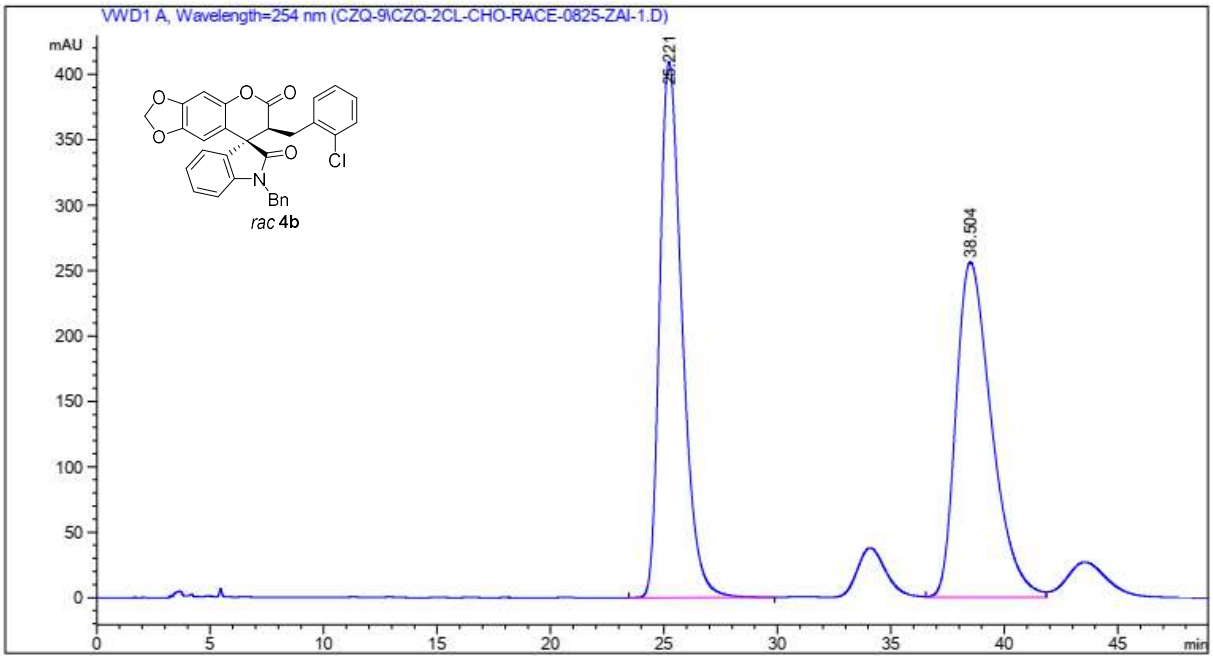
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	10.506	120.86175	3.11864	3.7128
2	PDA 254.0 nm	15.852	3134.41333	49.69964	96.2872



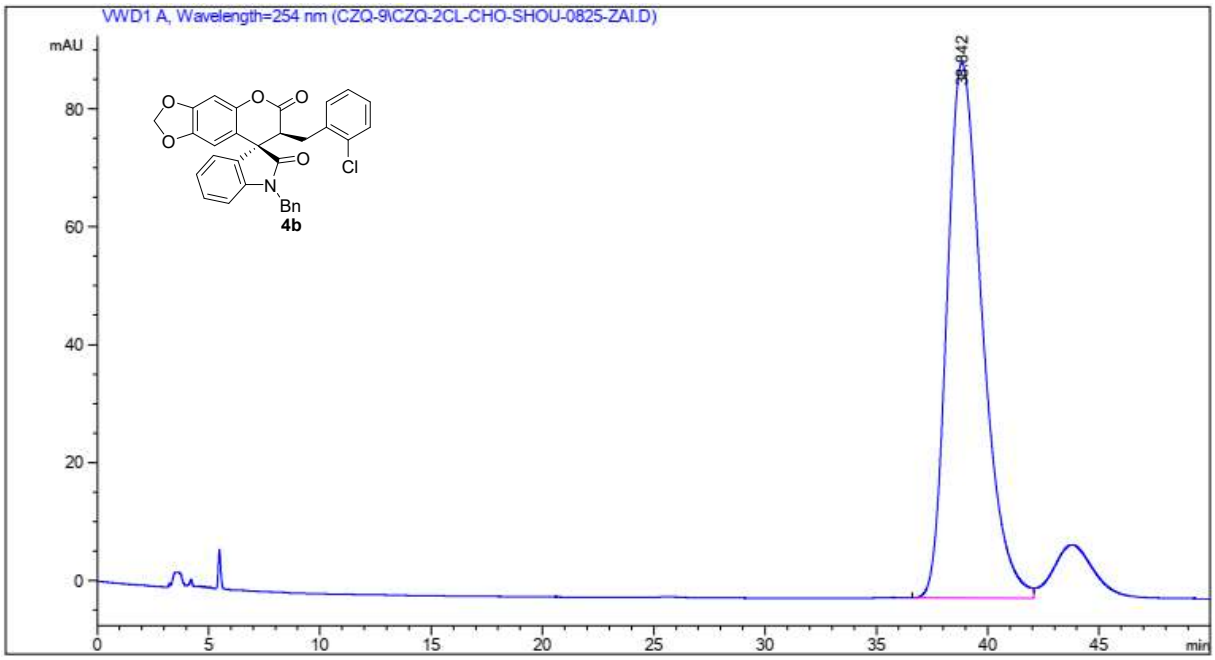
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	41.354	2.45646e4	247.87384	50.4086
2	PDA 254.0 nm	57.153	2.41663e4	164.88376	49.5914



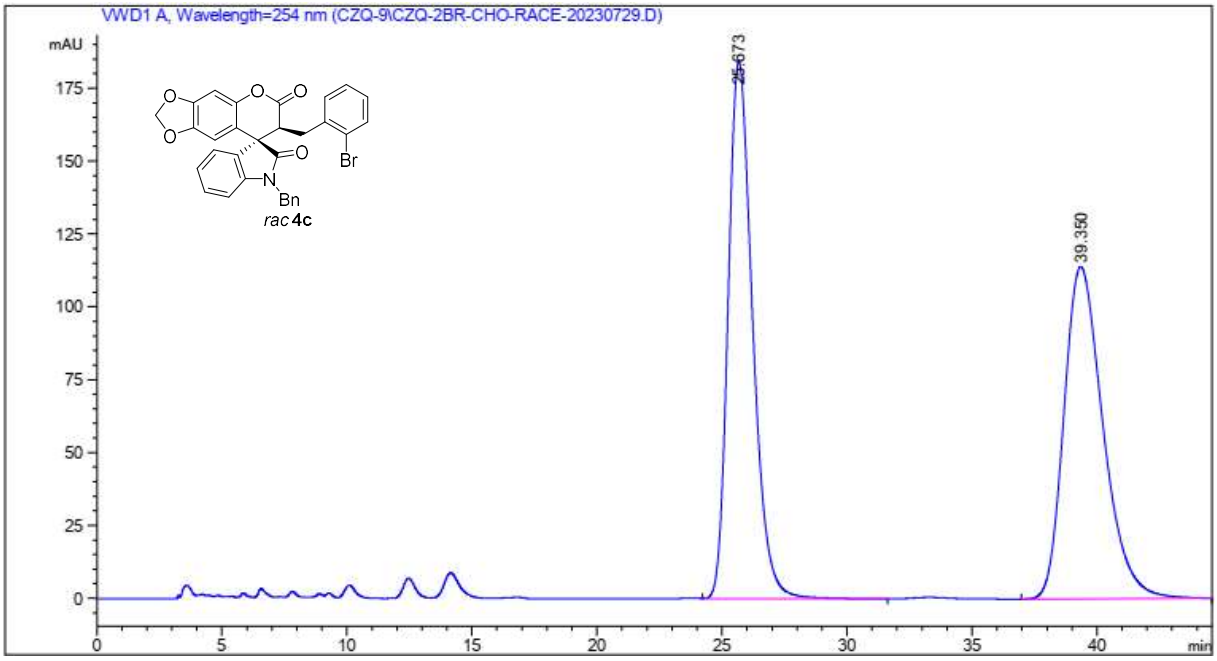
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	41.119	1095.81348	10.97163	4.4351
2	PDA 254.0 nm	56.525	2.36119e4	161.06013	95.5649



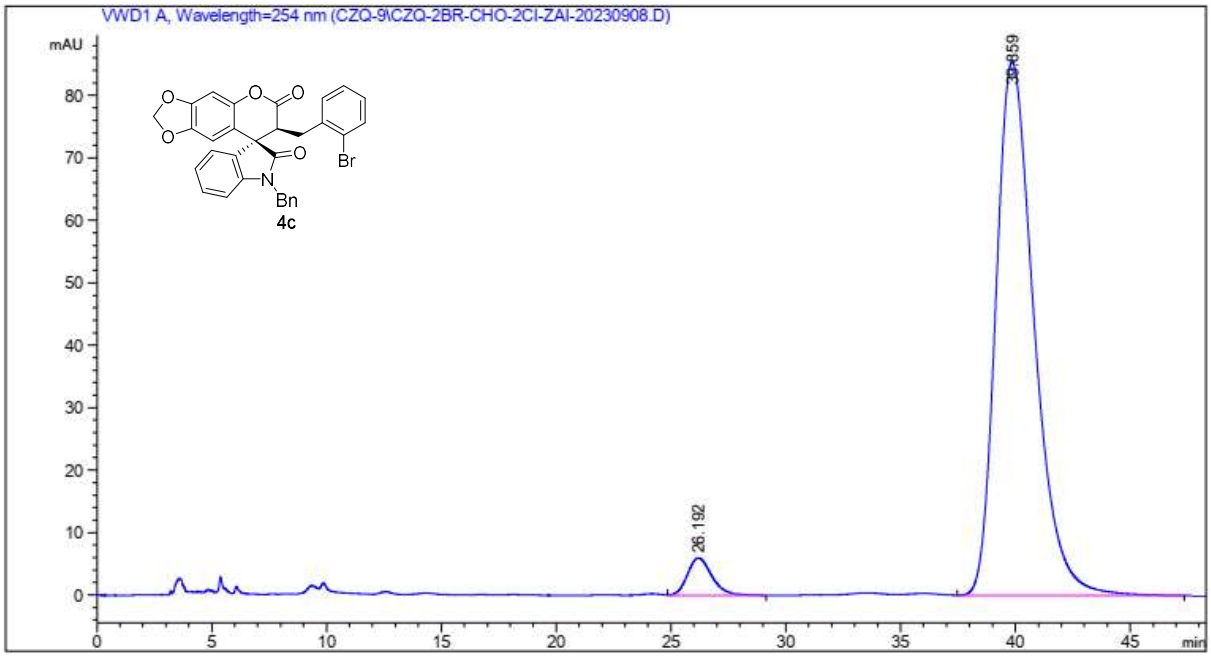
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	25.221	2.81150e4	409.46027	50.1642
2	PDA 254.0 nm	38.504	2.79309e4	256.25357	49.8358



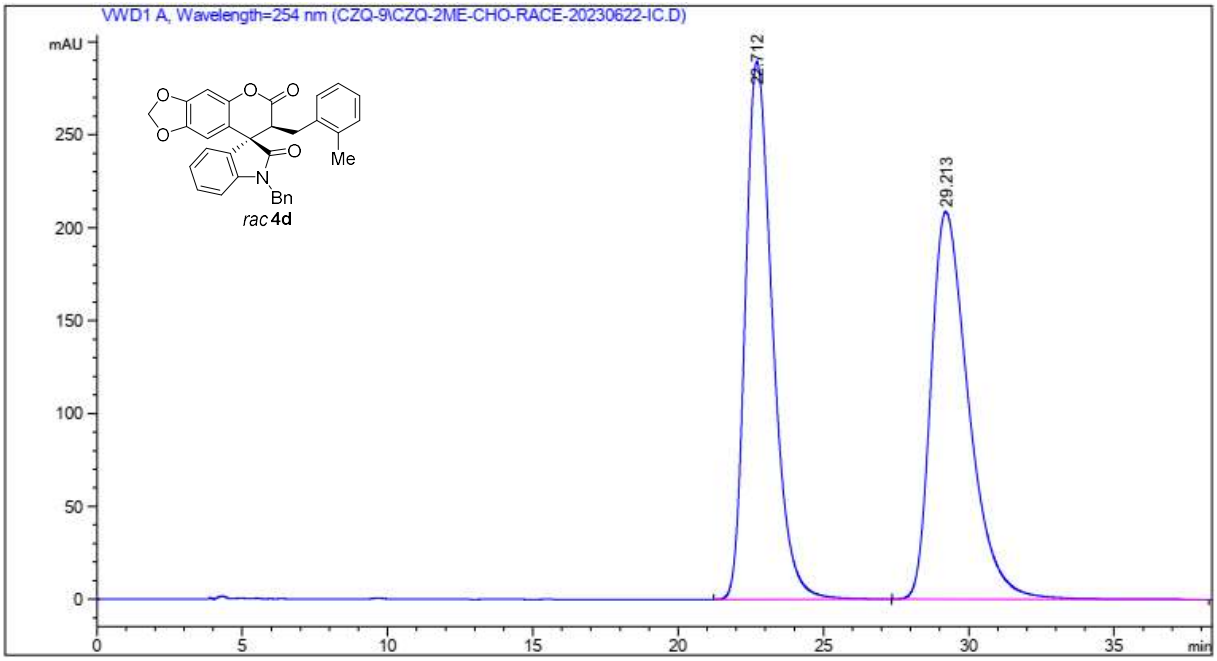
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	38.842	9957.25098	90.86143	100.0000



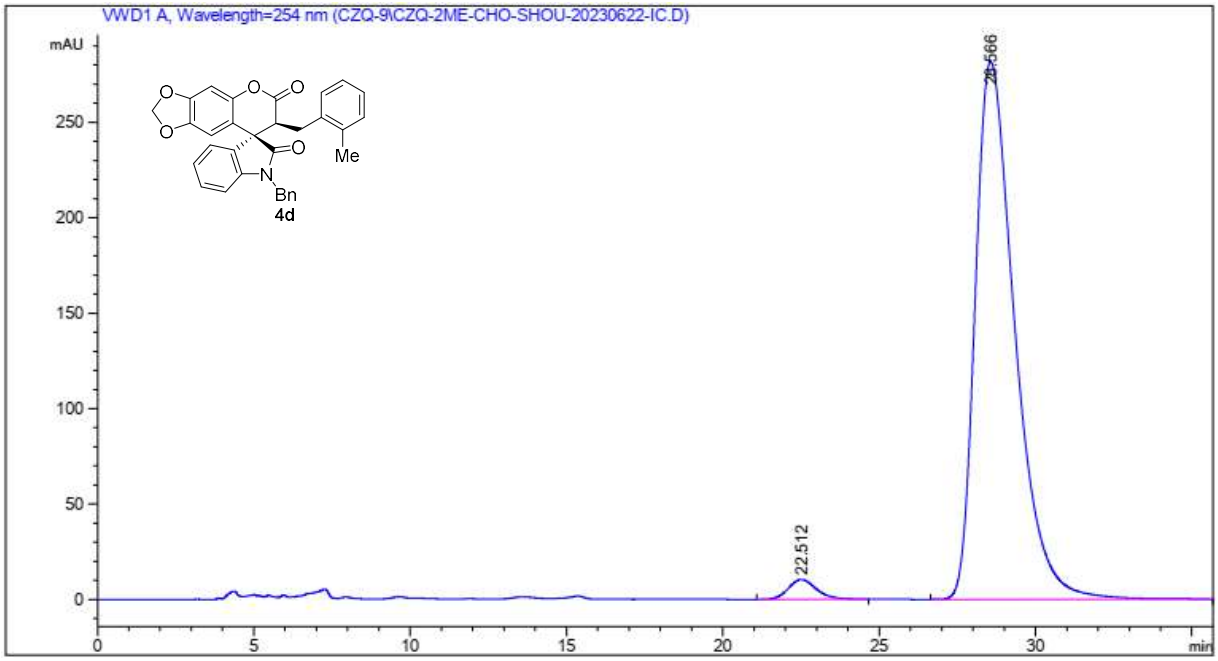
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	25.673	1.24970e4	184.39963	50.2575
2	PDA 254.0 nm	39.350	1.23689e4	113.93971	49.7425



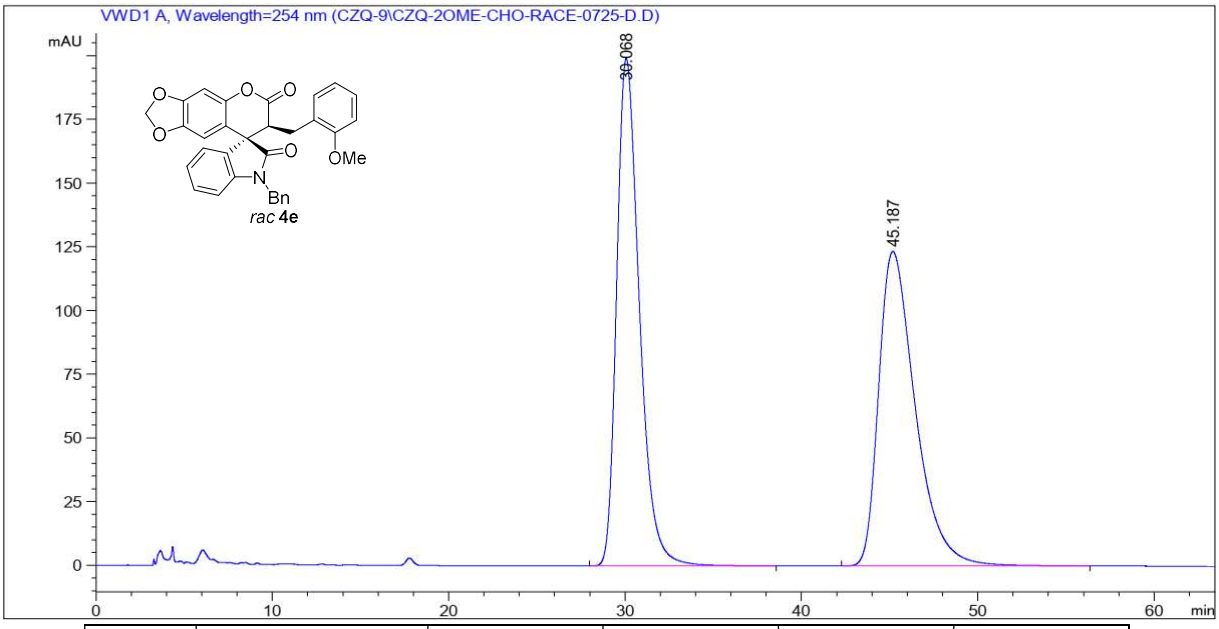
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	26.192	441.03802	5.97378	4.2782
2	PDA 254.0 nm	39.859	9868.03516	85.50339	95.7218



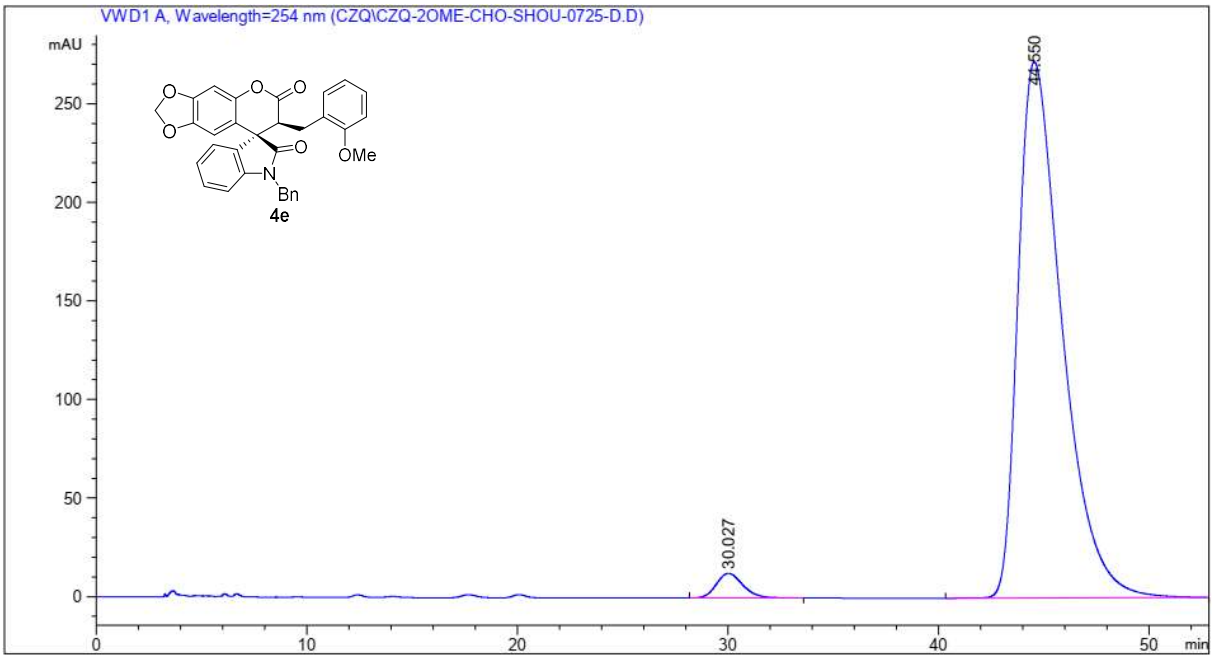
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	22.712	1.87539e4	289.43787	50.0120
2	PDA 254.0 nm	29.213	1.87449e4	208.50301	49.9880



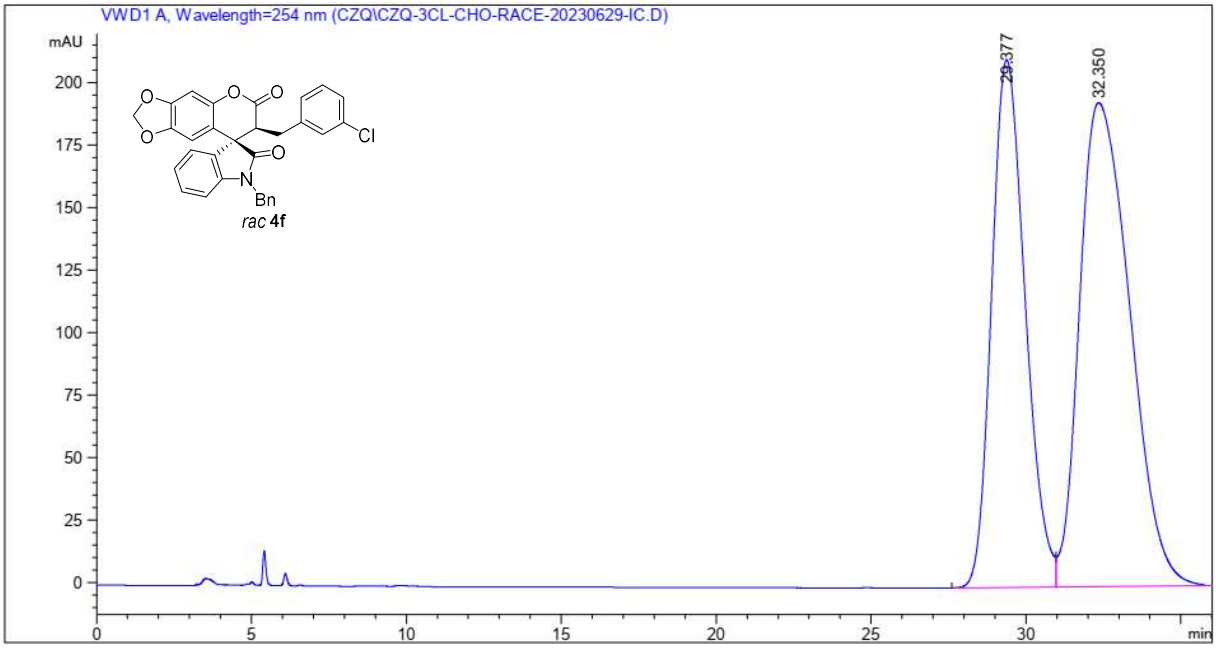
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	22.512	647.56964	10.37674	2.5563
2	PDA 254.0 nm	28.566	2.46852e4	281.76318	97.4437



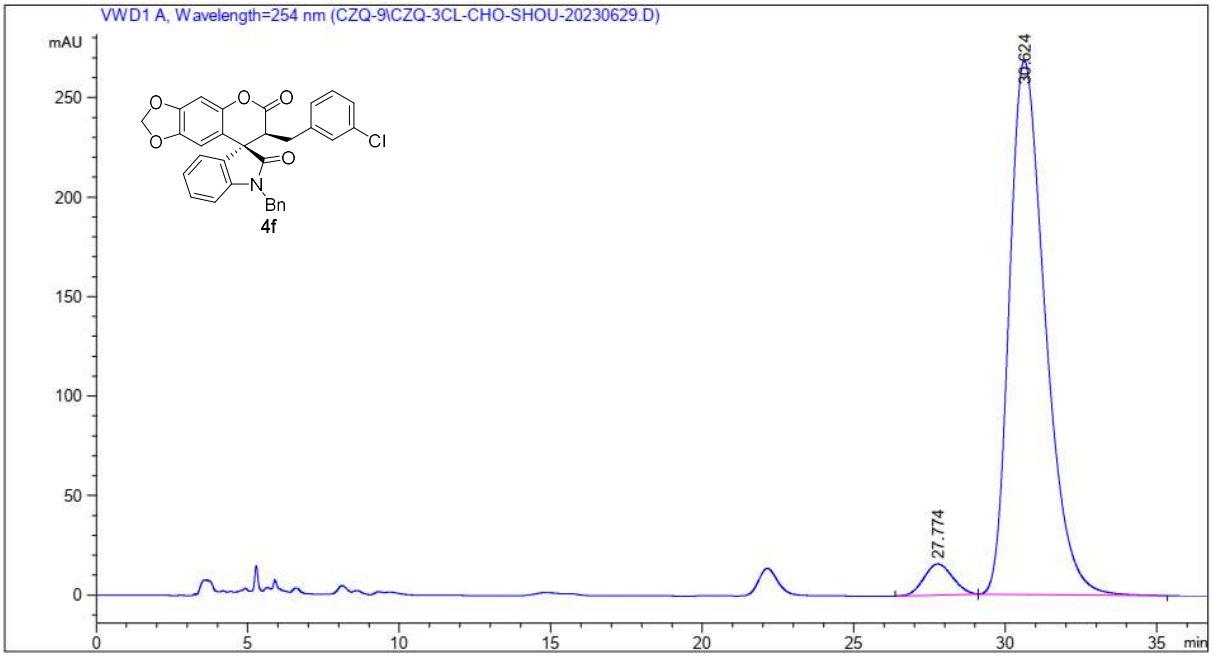
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	30.068	1.77979e4	199.15611	49.9972
2	PDA 254.0 nm	45.187	1.77999e4	123.38029	50.0028



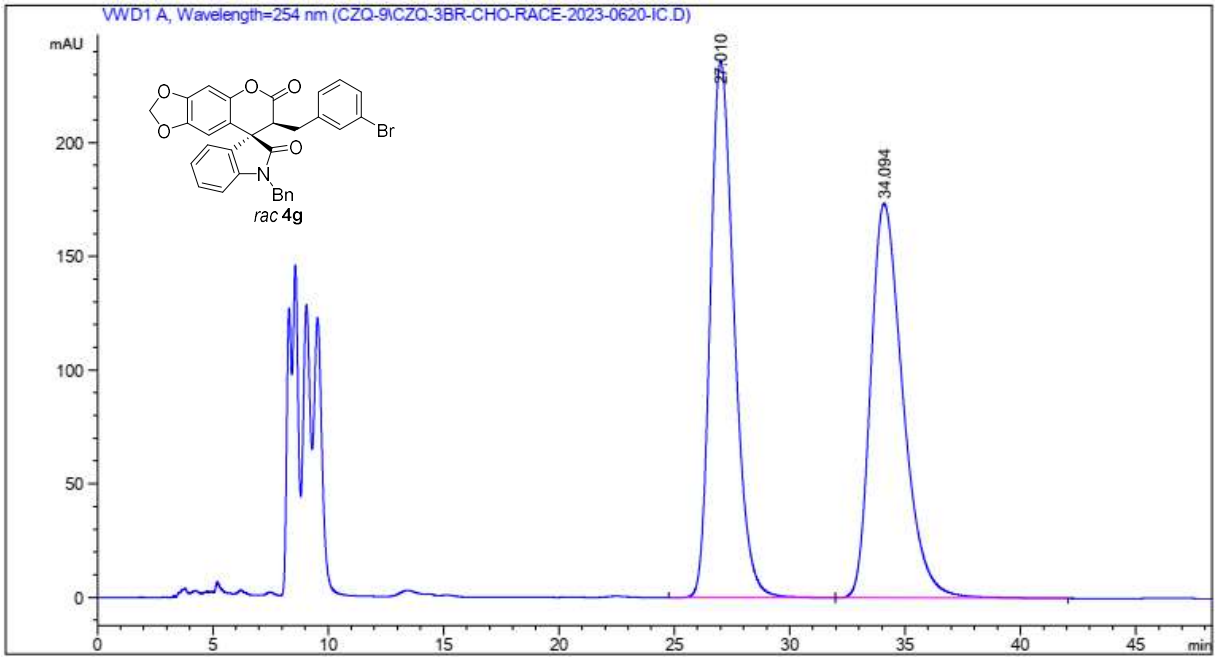
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	30.027	1095.84290	12.49169	2.7034
2	PDA 254.0 nm	44.550	3.94400e4	271.91876	97.2966



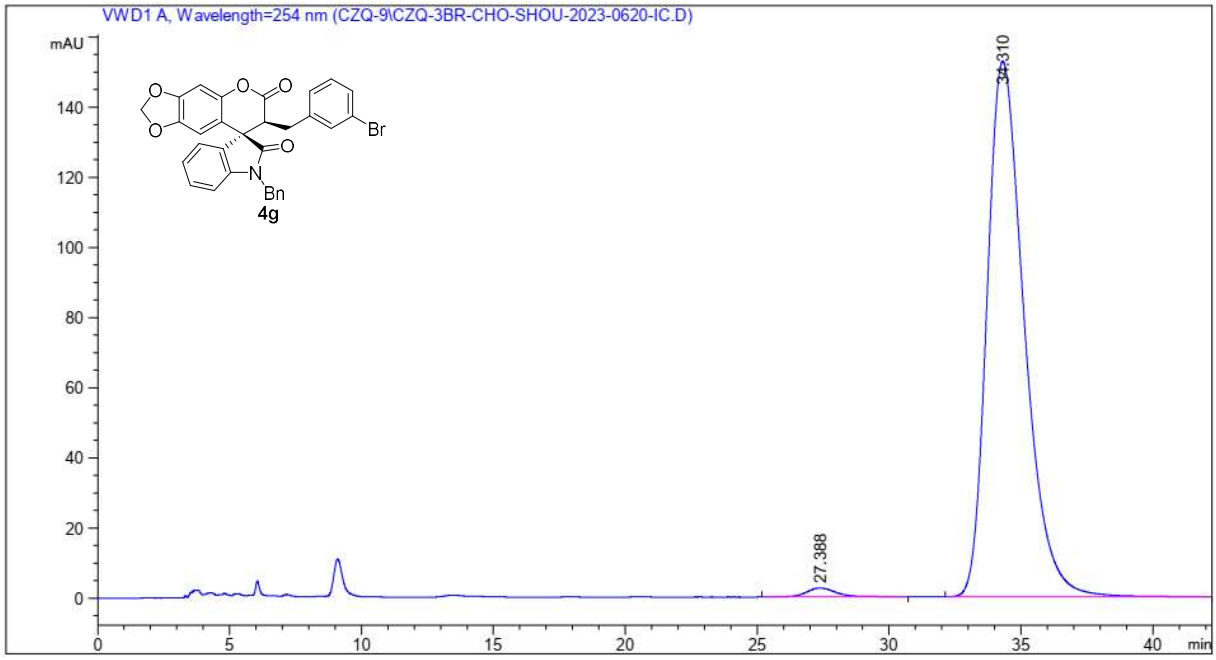
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	29.377	1.58795e4	210.96196	42.0888
2	PDA 254.0 nm	32.350	2.18490e4	193.48170	57.9112



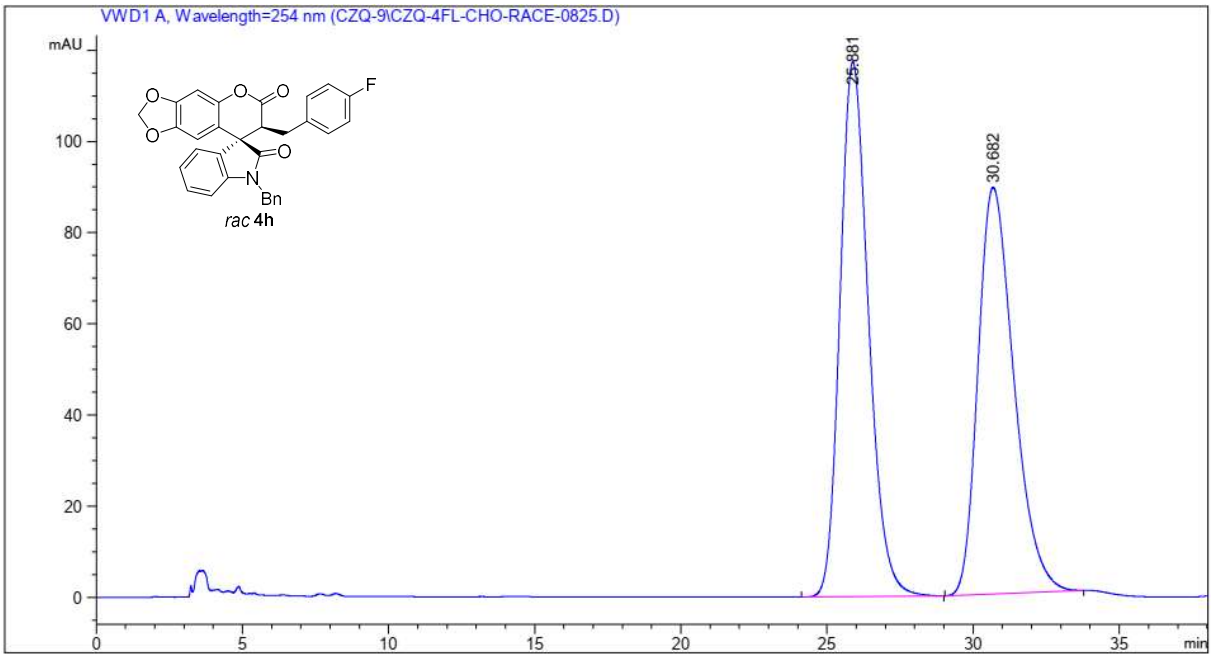
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	27.774	1018.62811	15.58698	4.4362
2	PDA 254.0 nm	30.624	2.19431e4	268.25656	95.5638



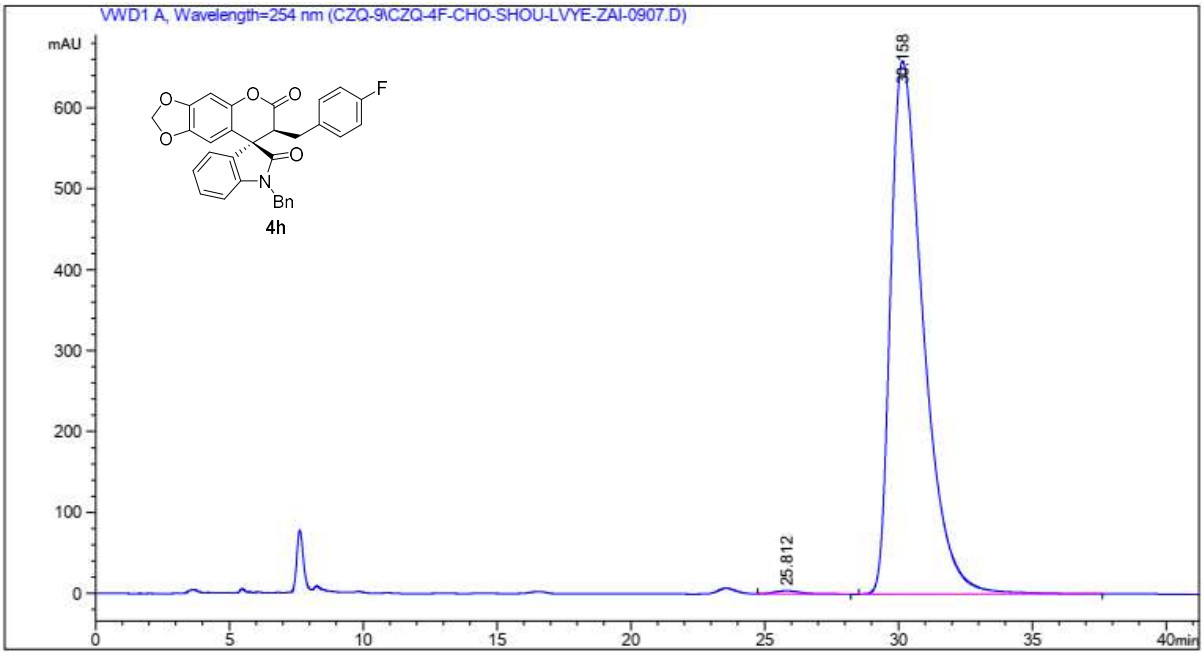
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	27.010	1.68724e4	235.97592	50.1227
2	PDA 254.0 nm	34.094	1.67898e4	173.43828	49.8773



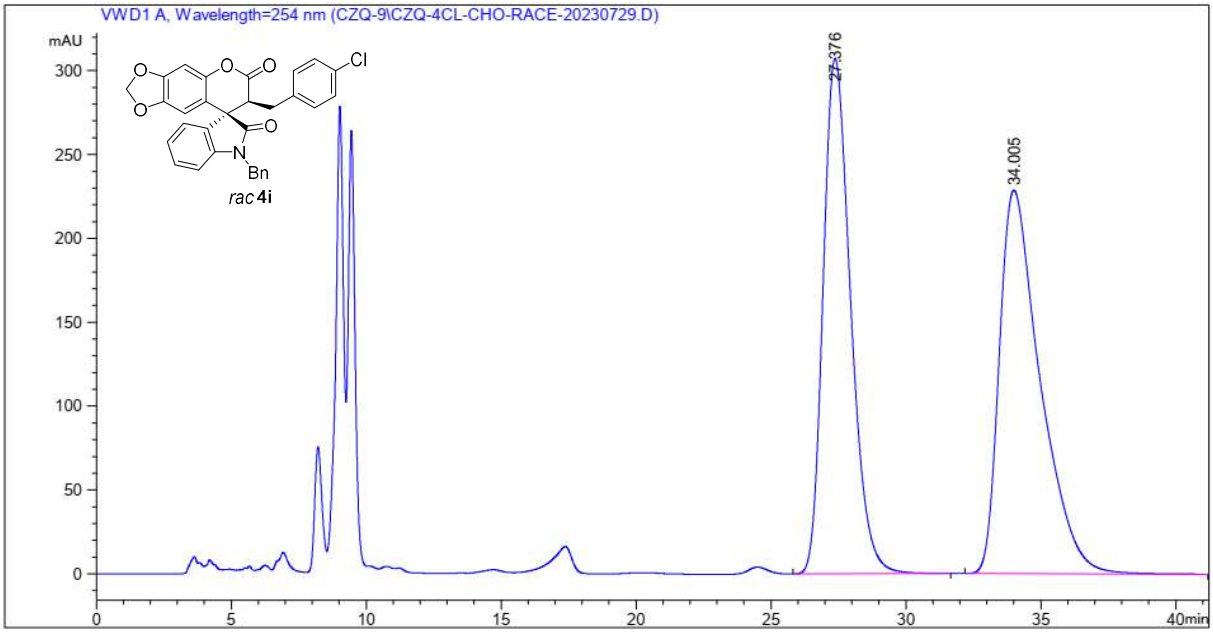
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	27.388	202.94321	2.54997	1.3406
2	PDA 254.0 nm	34.310	1.49353e4	152.71385	98.6594



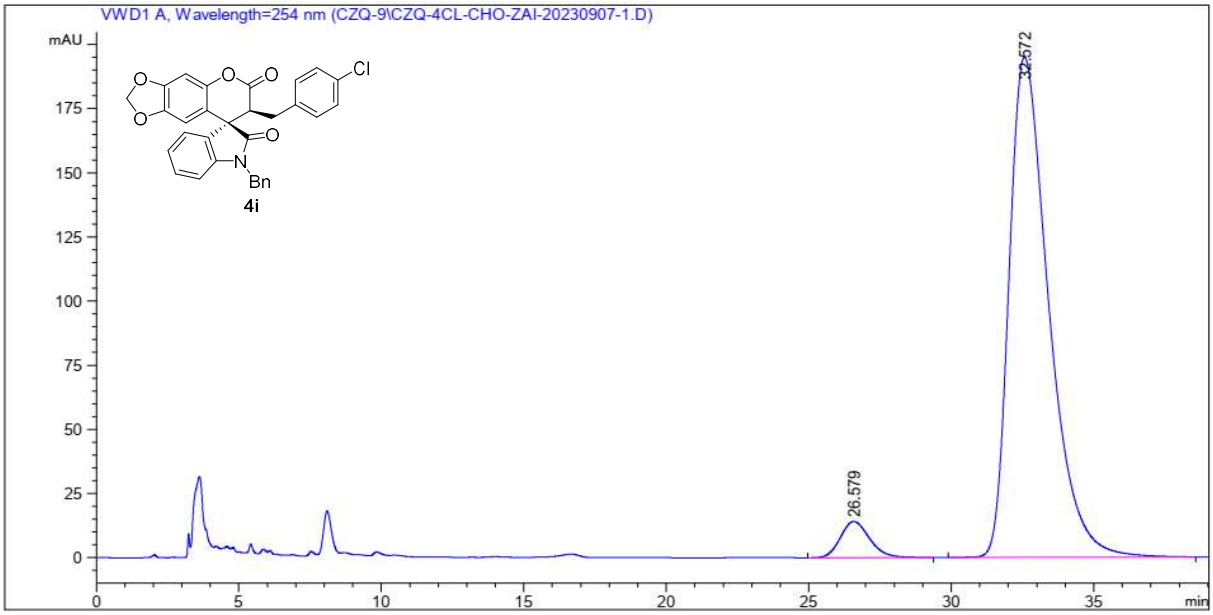
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	25.881	7935.60107	117.35586	51.0909
2	PDA 254.0 nm	30.682	7596.71338	89.20211	48.9091



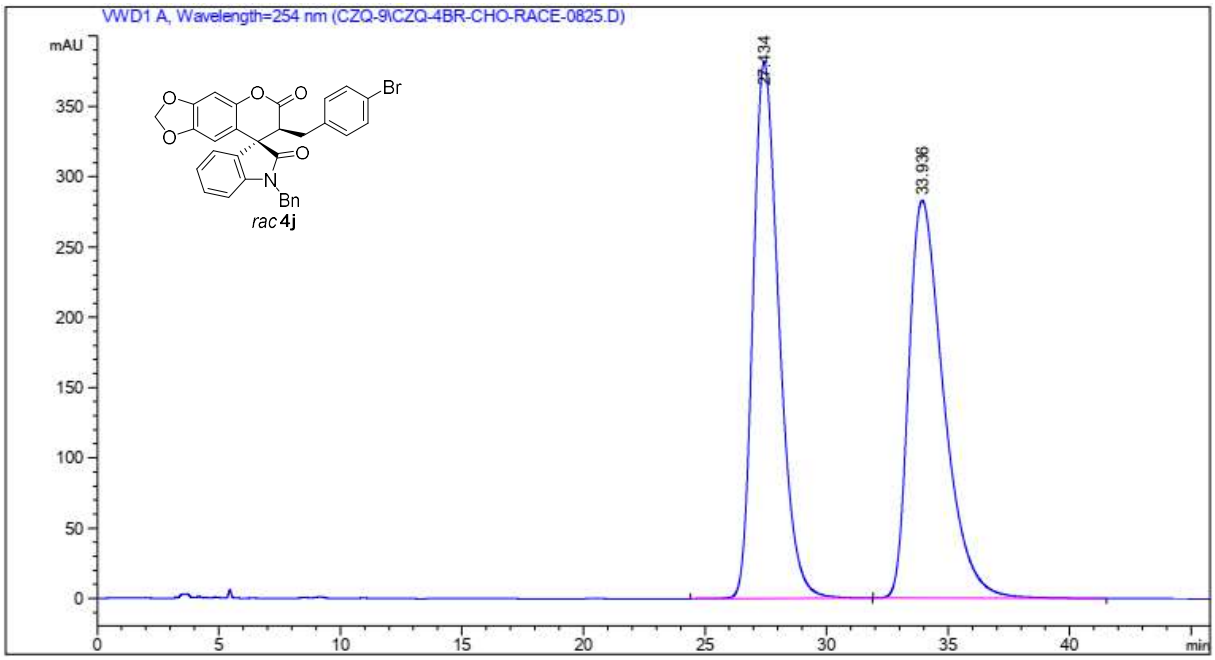
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	25.812	242.62831	3.86184	0.4322
2	PDA 254.0 nm	30.158	5.58954e4	658.78931	99.5678



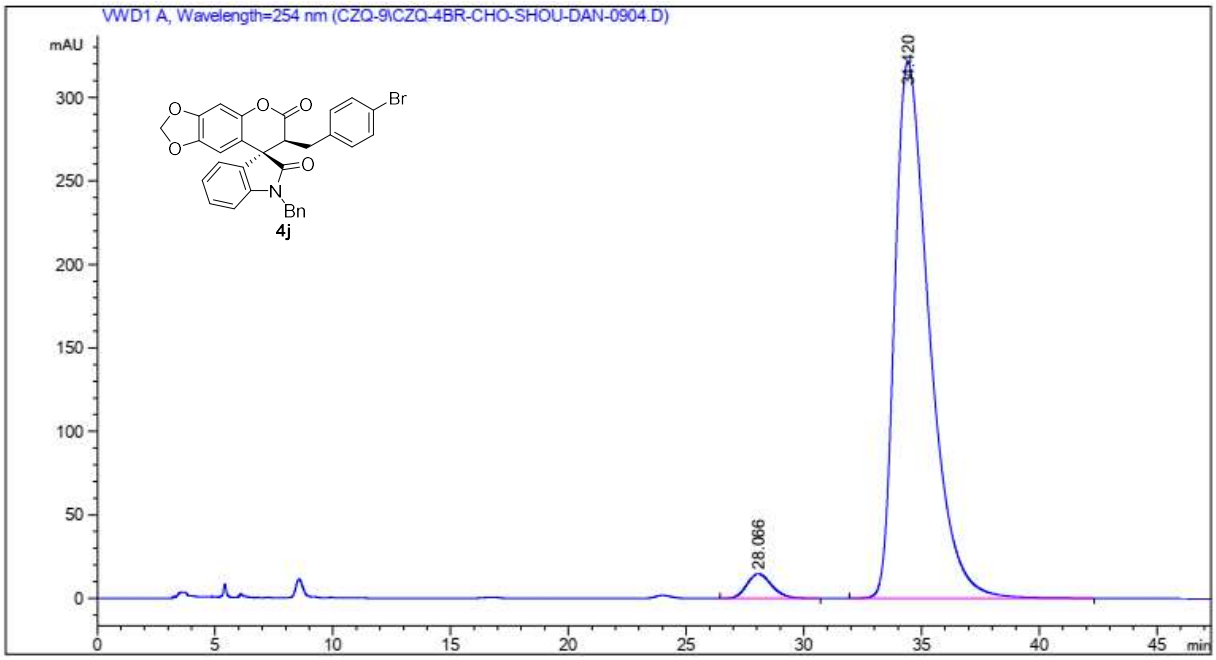
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	27.376	2.17413e4	307.34335	47.5057
2	PDA 254.0 nm	34.005	2.40244e4	4228.61296	52.4943



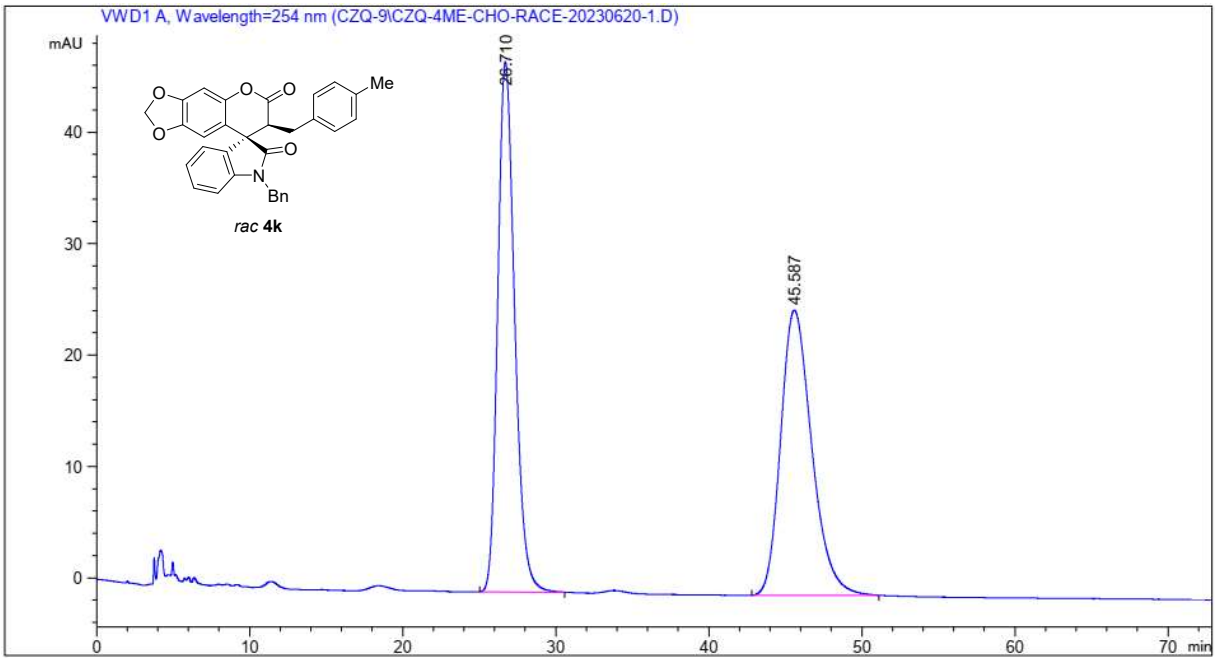
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	26.579	1012.61975	14.10623	5.1156
2	PDA 254.0 nm	32.572	1.87822e4	195.06737	94.8844



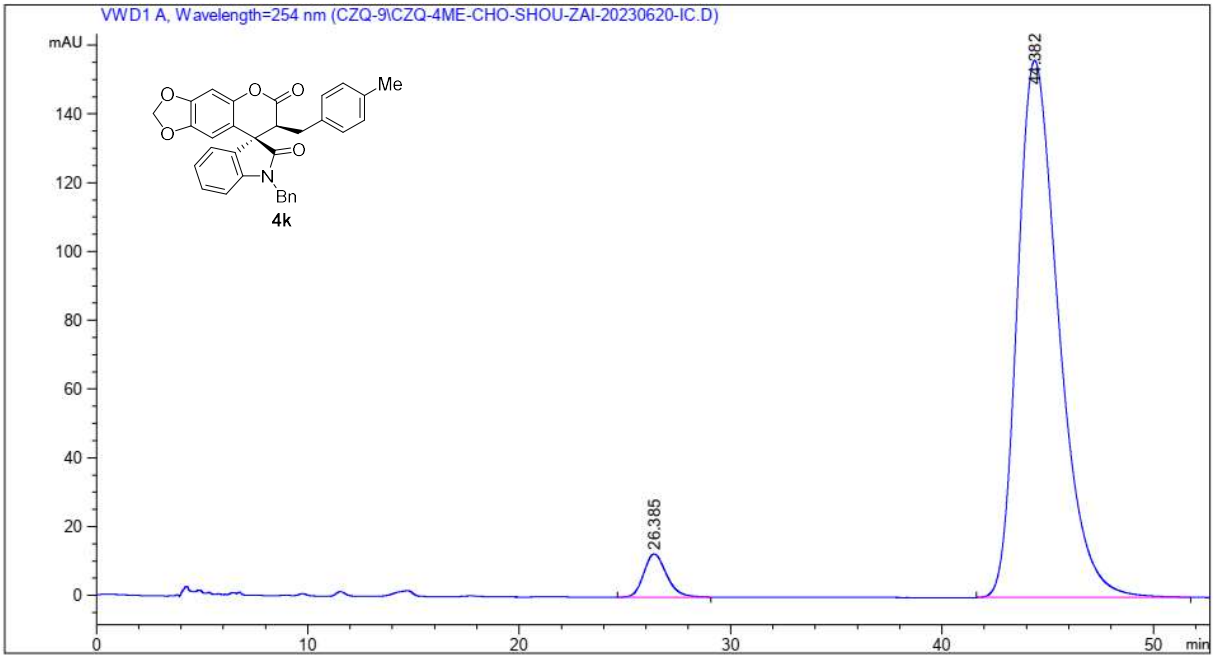
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	27.434	2.82793e4	381.24344	49.9951
2	PDA 254.0 nm	33.936	2.82849e4	282.93646	50.0049



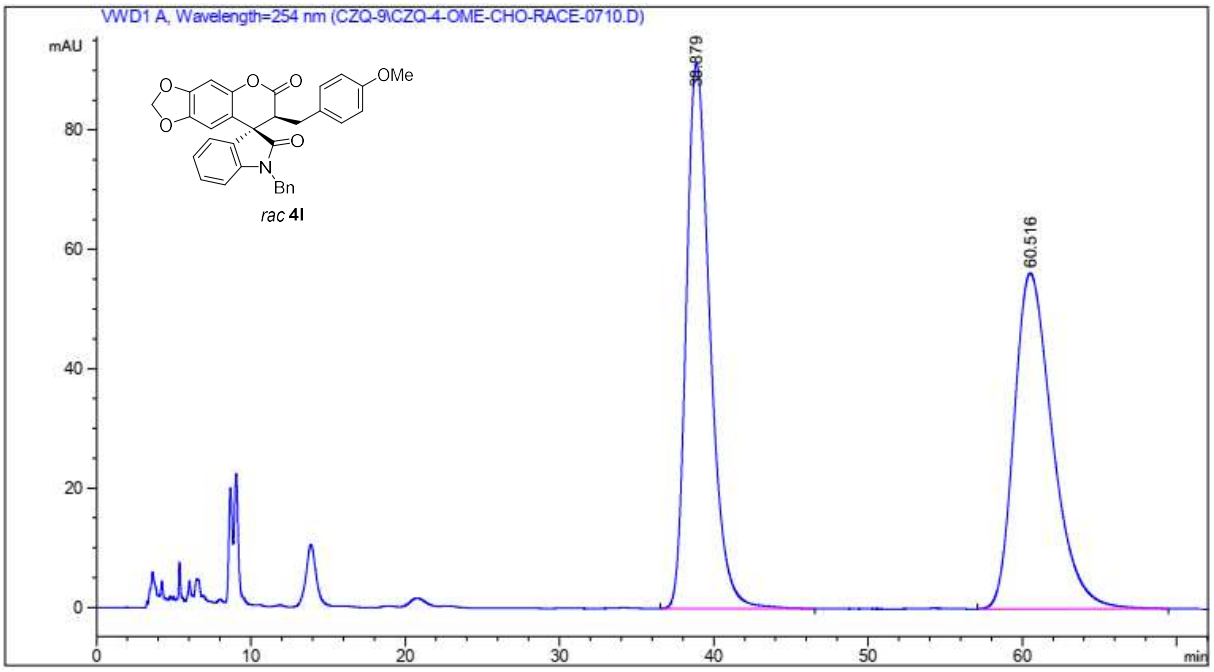
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	28.066	1100.61108	14.80378	3.2587
2	PDA 254.0 nm	34.420	3.26741e4	321.30475	96.7413



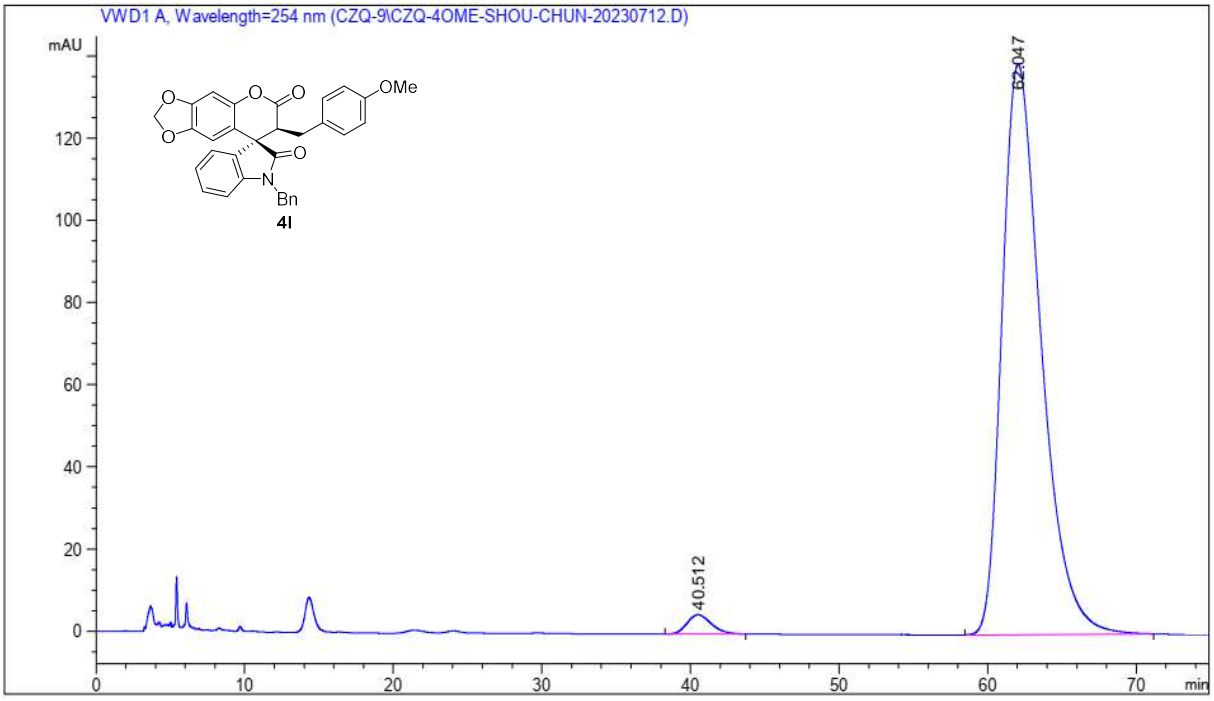
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	26.710	3656.90894	47.58177	50.3261
2	PDA 254.0 nm	45.587	3609.52441	25.59332	49.6739



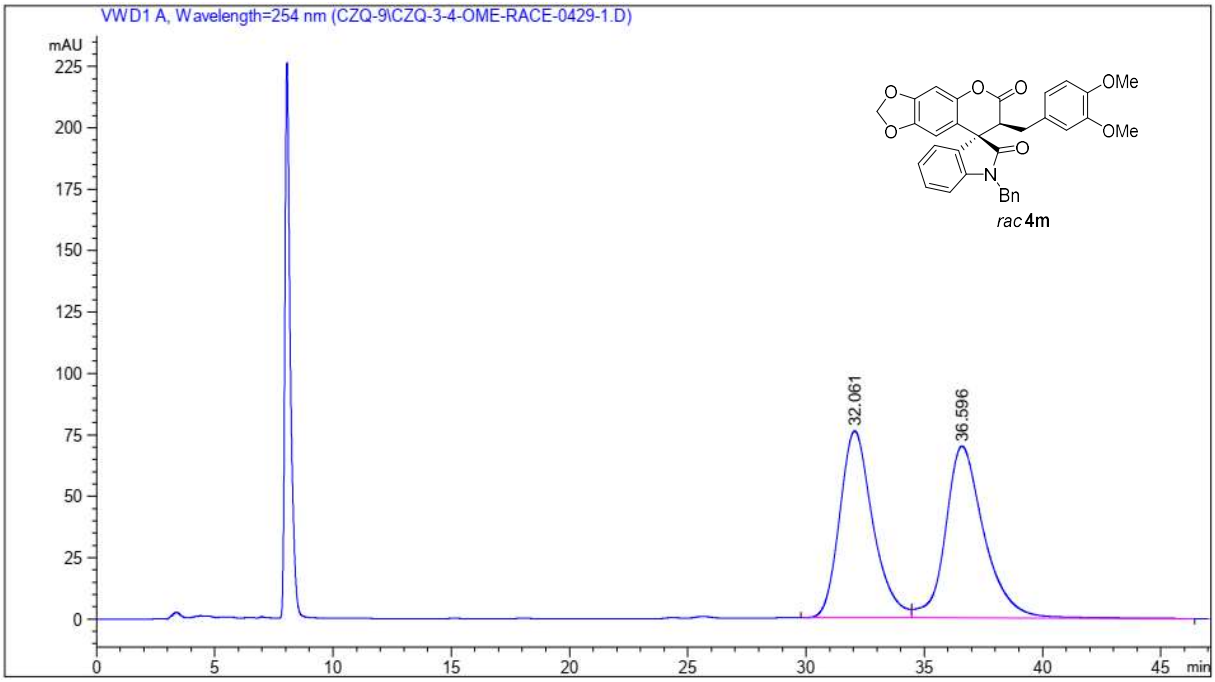
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	26.385	942.30835	12.58103	4.2714
2	PDA 254.0 nm	44.382	2.11186e4	156.14299	95.7286



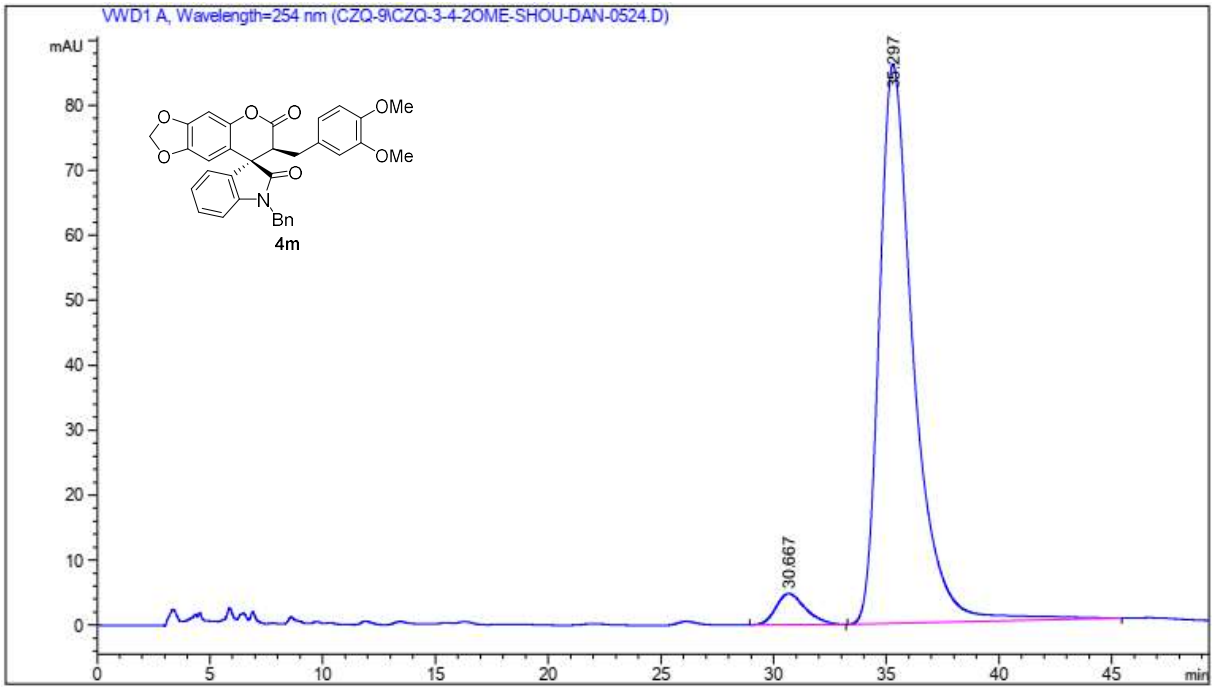
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	38.879	9742.93945	91.34114	50.1668
2	PDA 254.0 nm	60.516	9678.14453	56.24915	49.8332



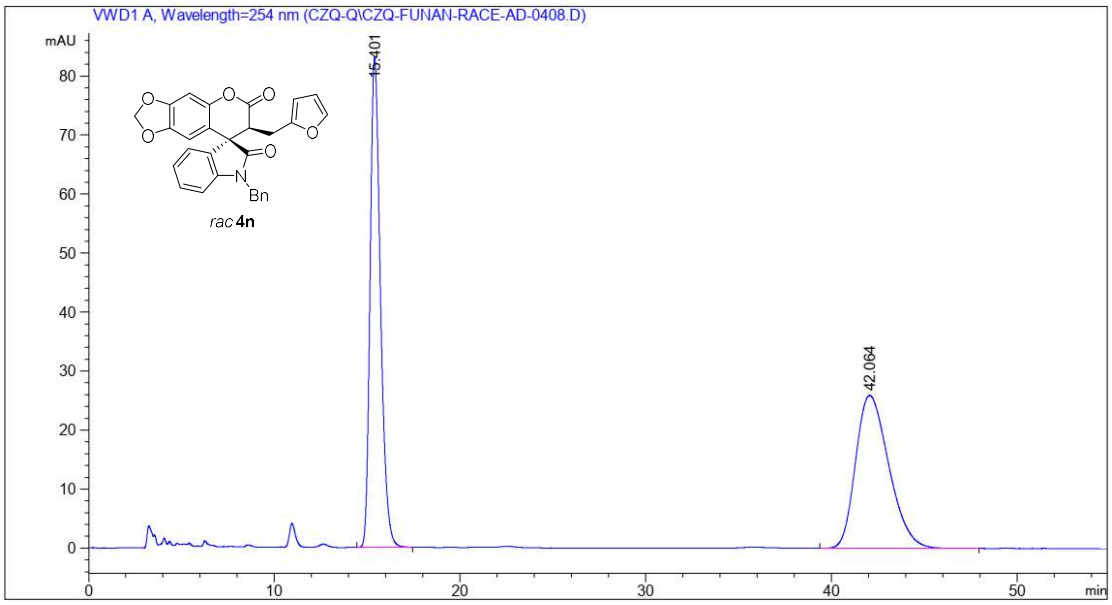
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	40.512	537.72357	4.71128	2.0757
2	PDA 254.0 nm	62.047	2.53681e4	138.86932	97.9243



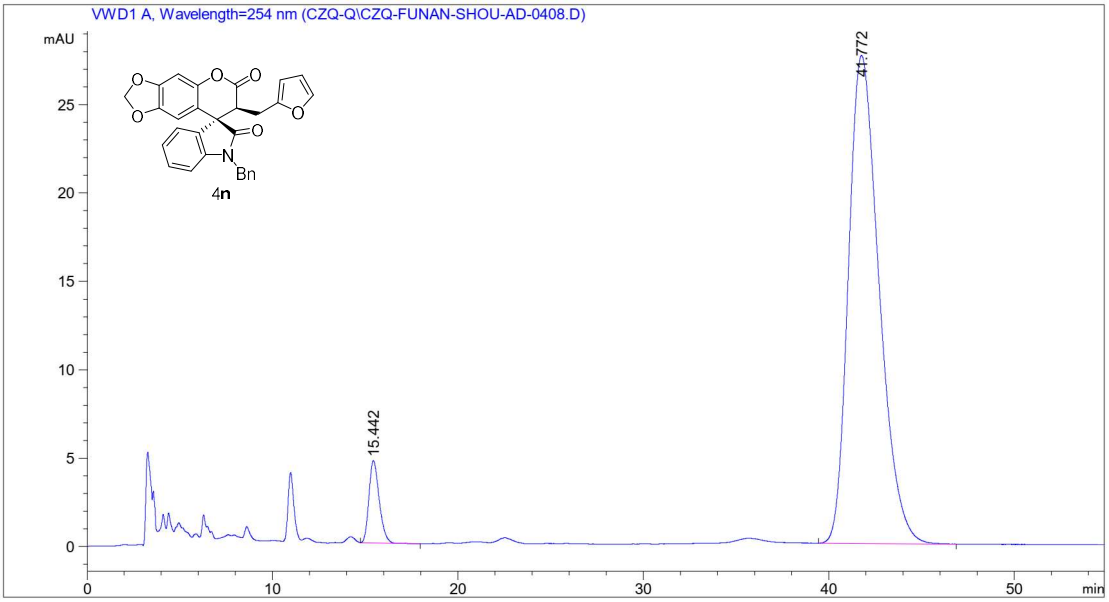
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	32.061	7400.74072	76.05070	48.2116
2	PDA 254.0 nm	36.596	7949.80322	69.95824	51.7884



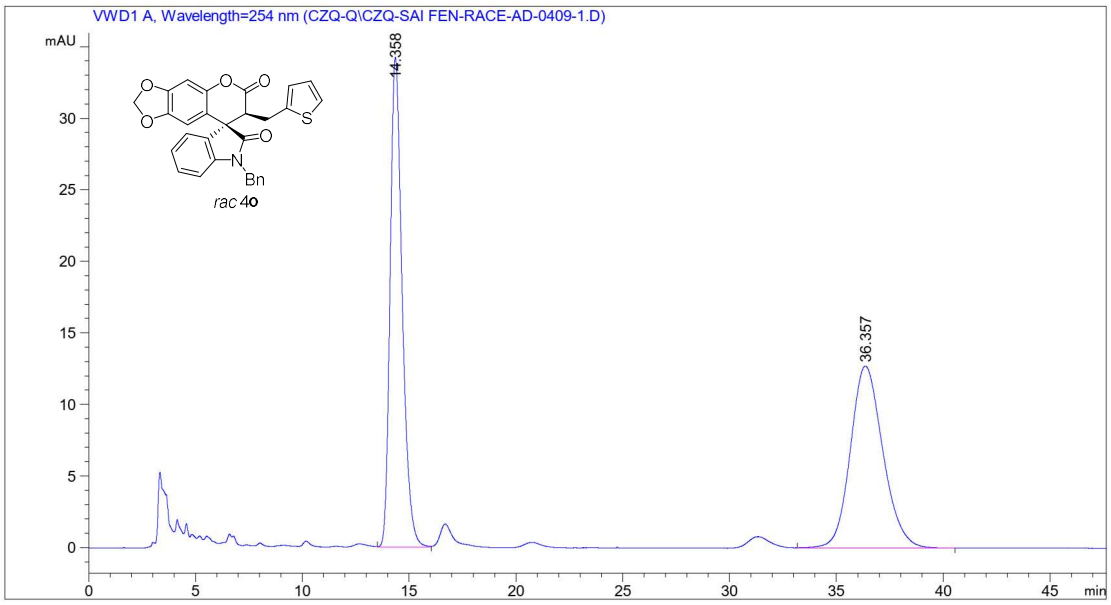
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	30.667	437.60999	4.80110	4.5805
2	PDA 254.0 nm	35.297	9116.13965	86.10291	95.4195



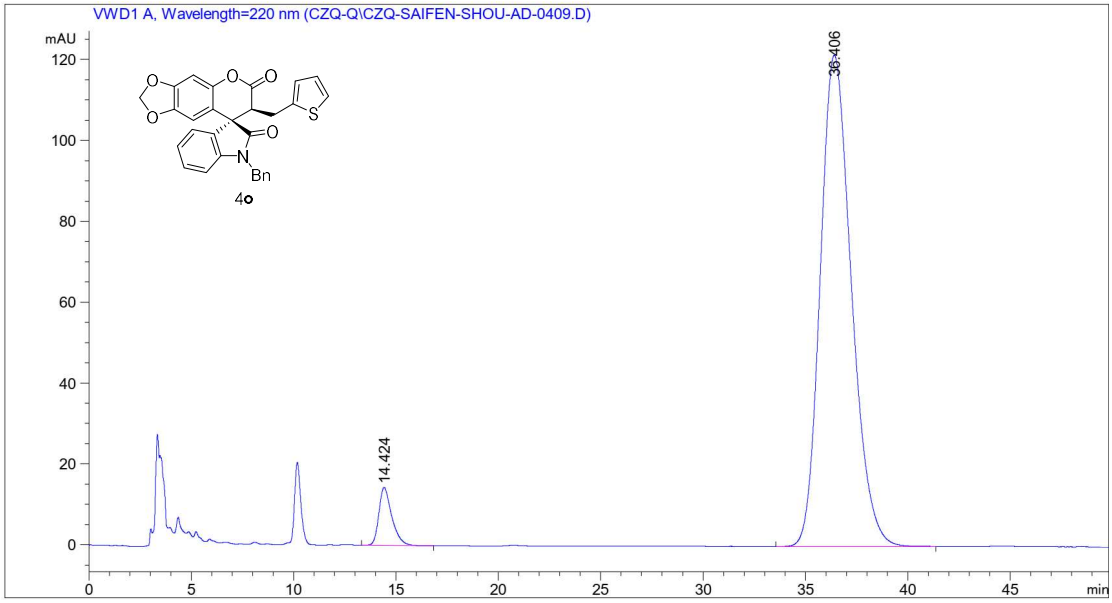
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	15.401	3211.52612	83.02571	49.9190
2	PDA 254.0 nm	42.064	3221.94287	25.90264	50.0810



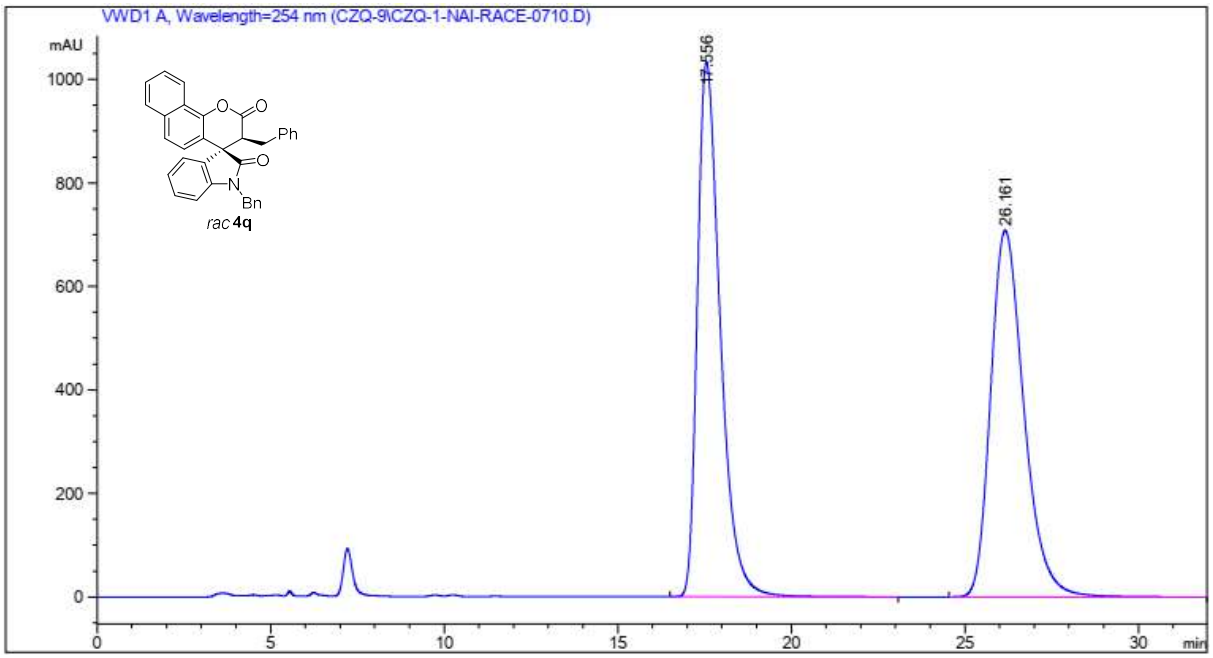
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	15.442	181.37396	4.66625	5.4193
2	PDA 254.0 nm	41.772	3165.43530	27.59027	94.5807



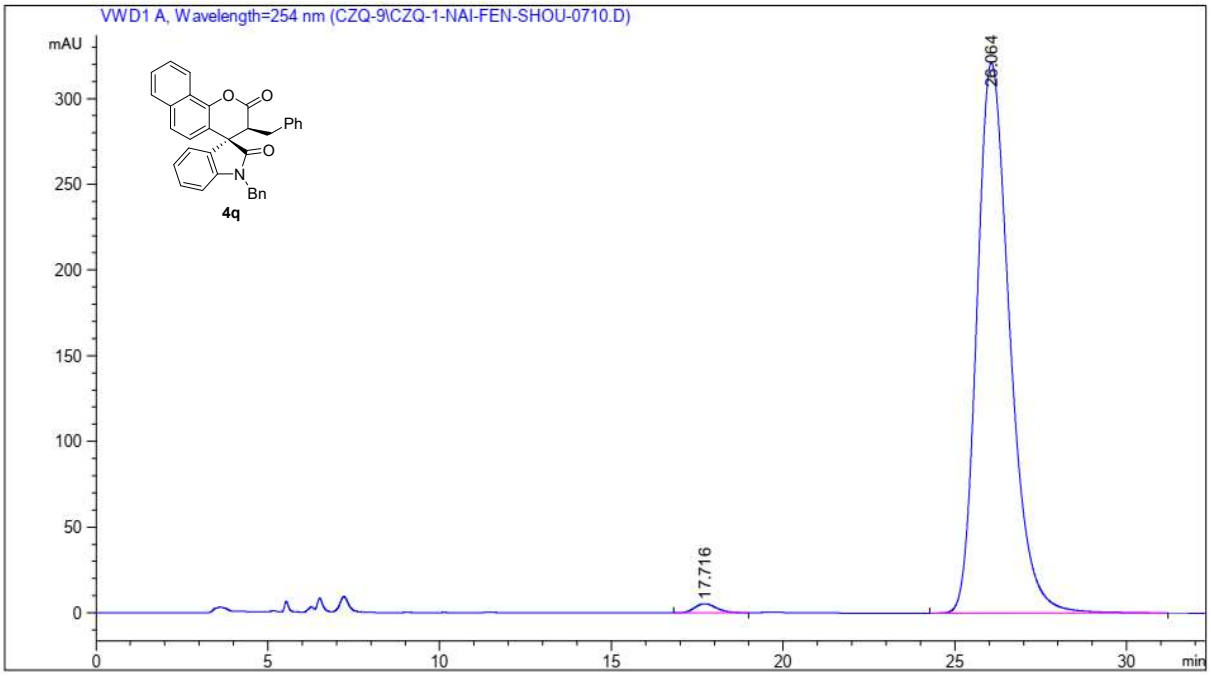
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	14.358	1344.13879	34.23613	49.9944
2	PDA 254.0 nm	36.357	1344.44214	12.71589	50.0056



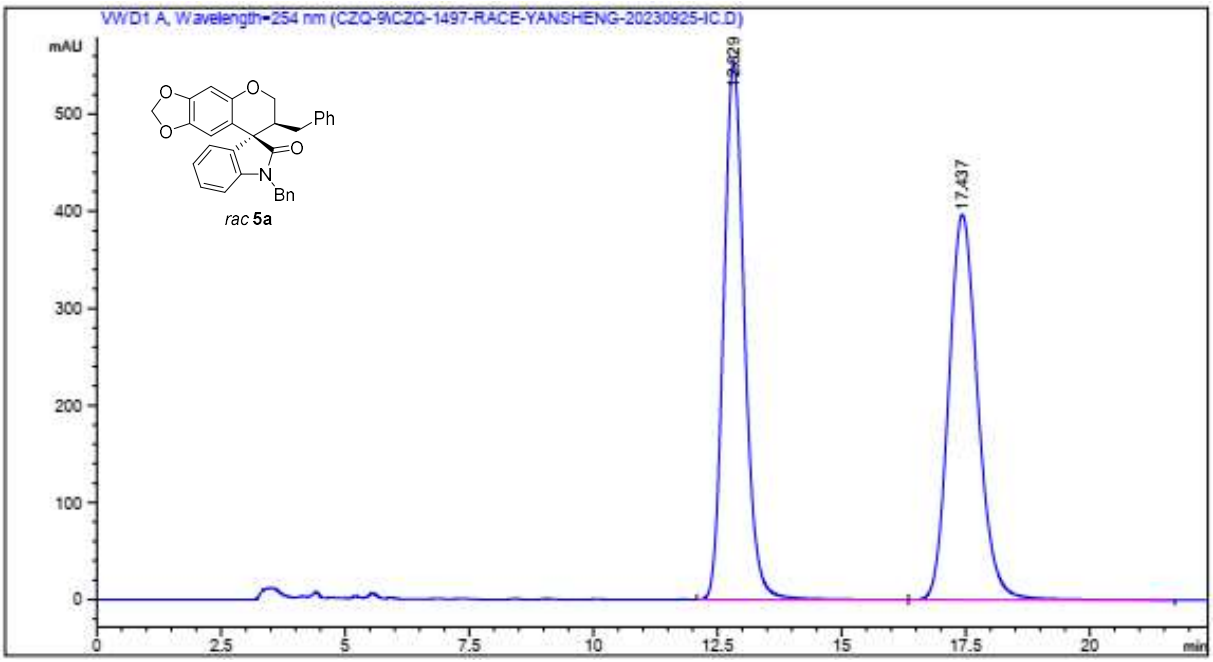
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	14.424	629.46582	14.34530	4.6839
2	PDA 254.0 nm	36.406	1.28095e4	121.45863	95.3161



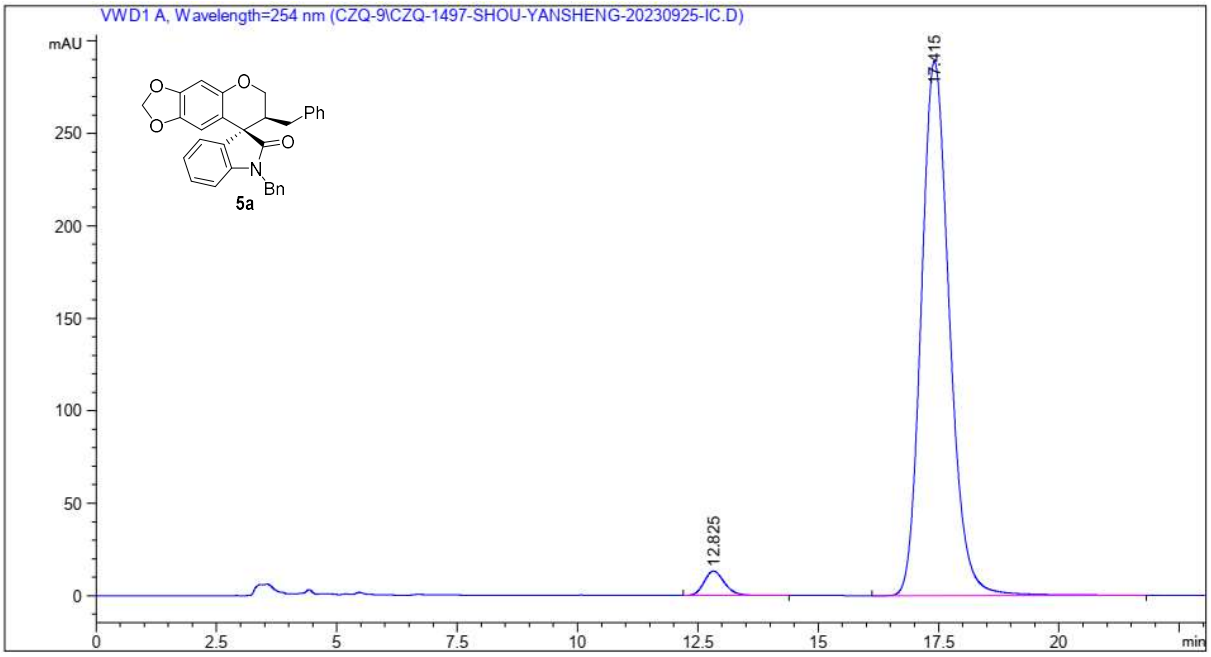
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	19.585	3.48033e4	790.32184	53.0628
2	PDA 254.0 nm	26.238	3.07856e4	507.30722	46.9372



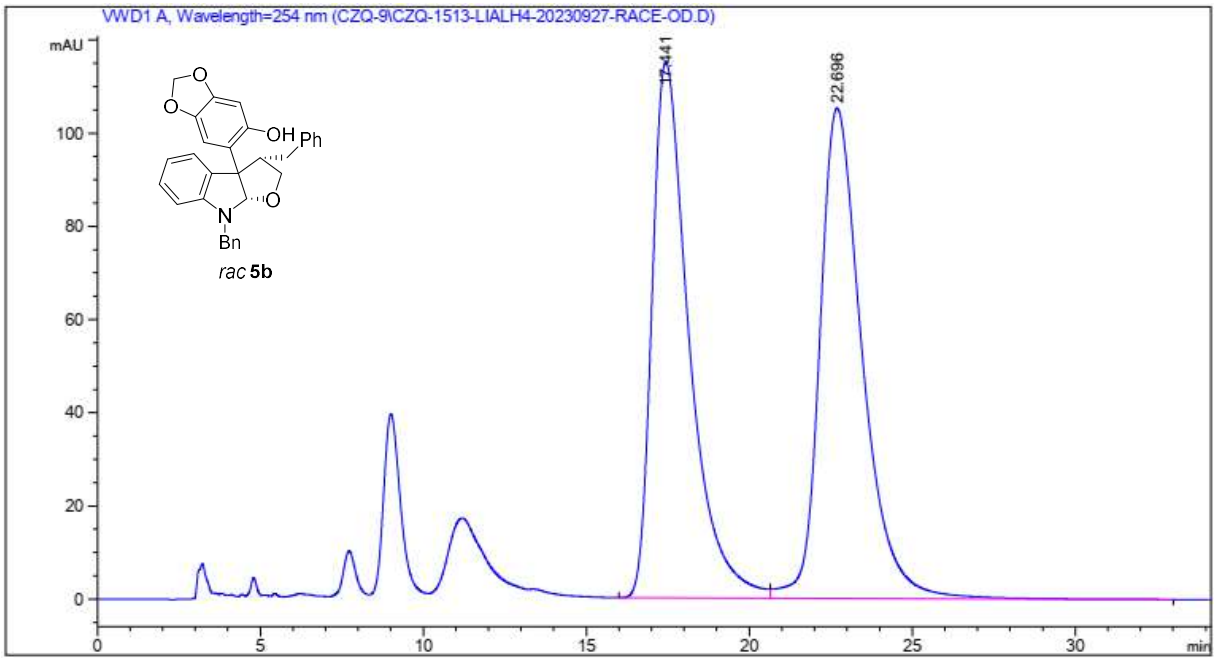
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	17.716	239.68336	5.38165	1.1145
2	PDA 254.0 nm	26.064	2.12658e4	321.20316	98.8855



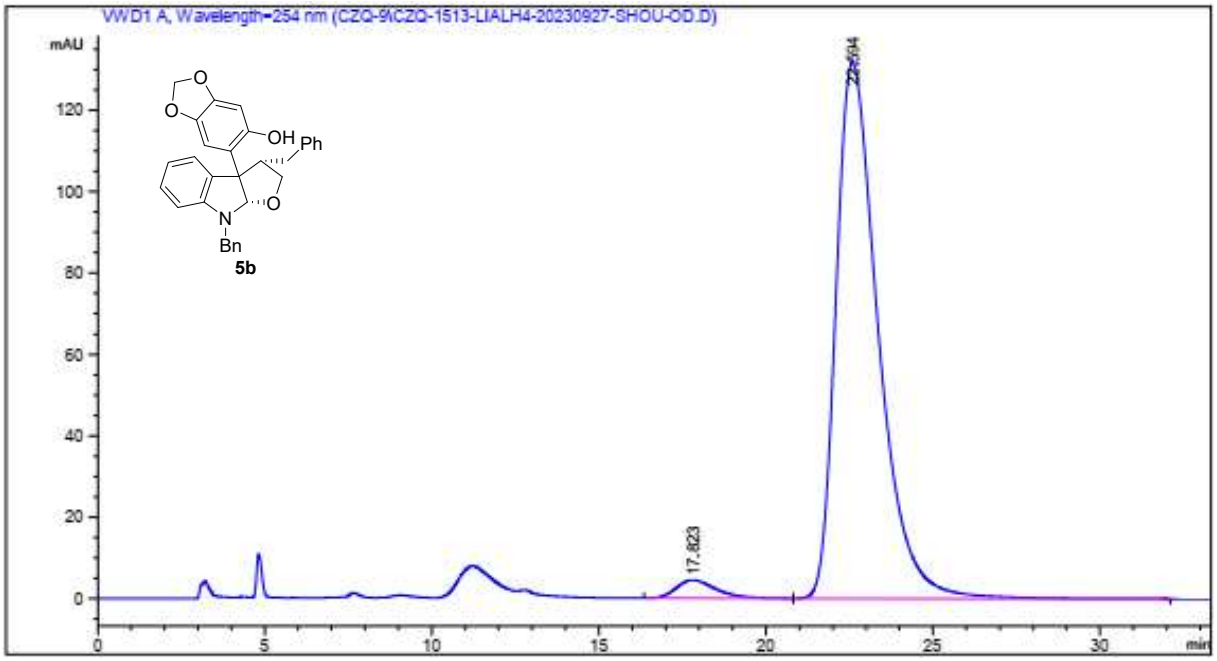
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	12.829	1.61482e4	552.68109	49.9856
2	PDA 254.0 nm	17.437	1.61575e4	396.92844	50.0144



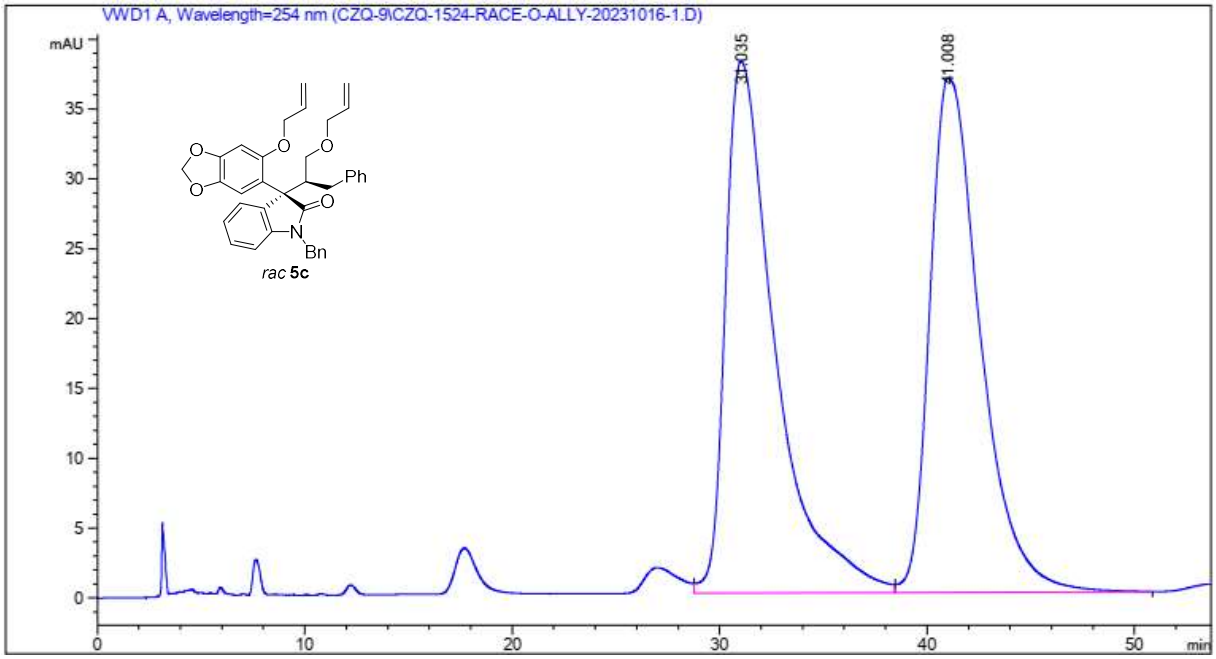
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	12.825	388.83307	13.15648	3.2032
2	PDA 254.0 nm	17.415	1.17502e4	288.99985	96.7968



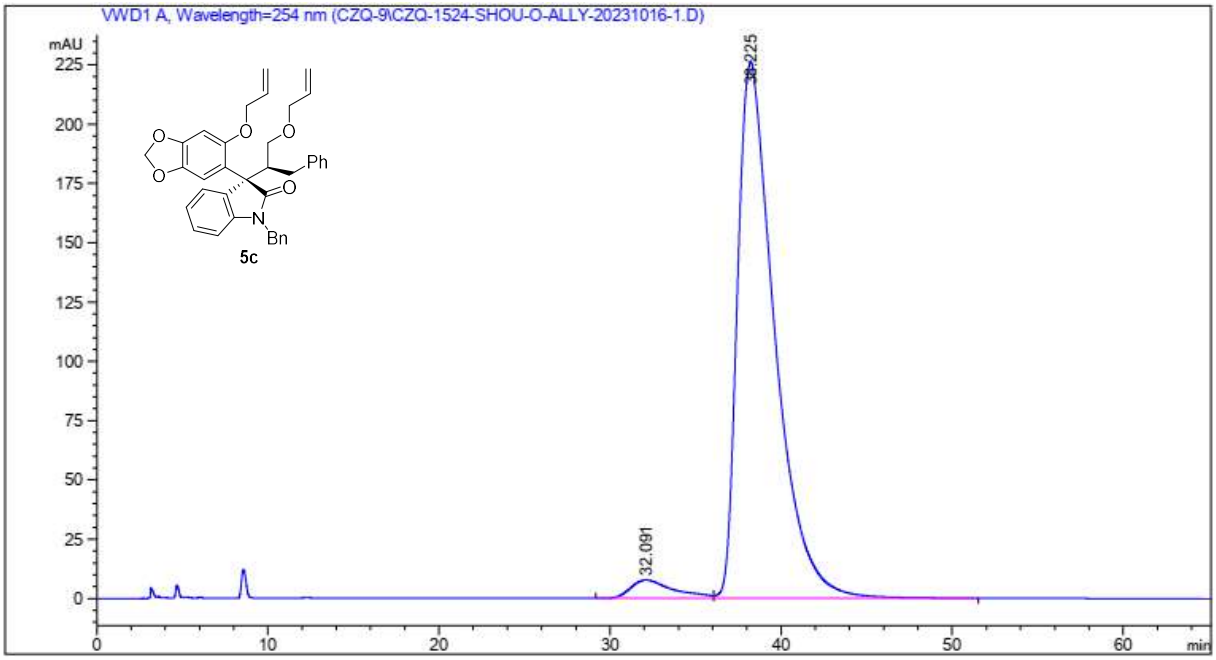
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	17.441	9095.26465	114.96246	48.8206
2	PDA 254.0 nm	22.696	9534.71875	105.25622	51.1794



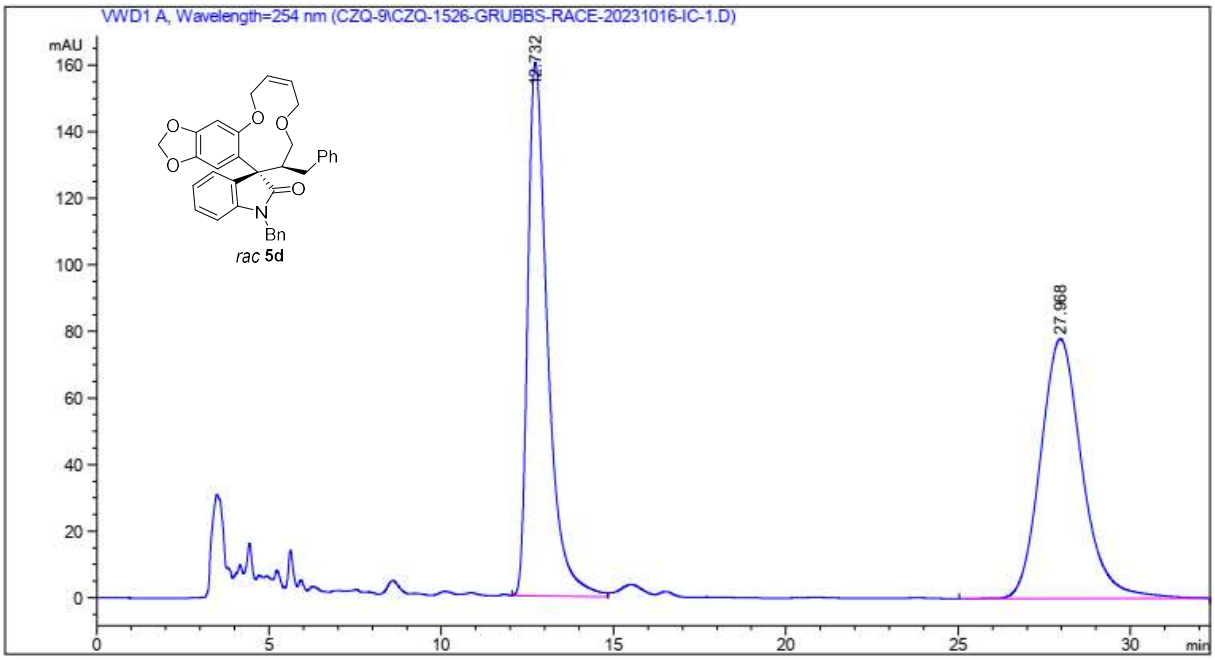
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	17.823	371.74213	4.45950	3.1177
2	PDA 254.0 nm	22.594	1.15517e4	131.73196	96.8823



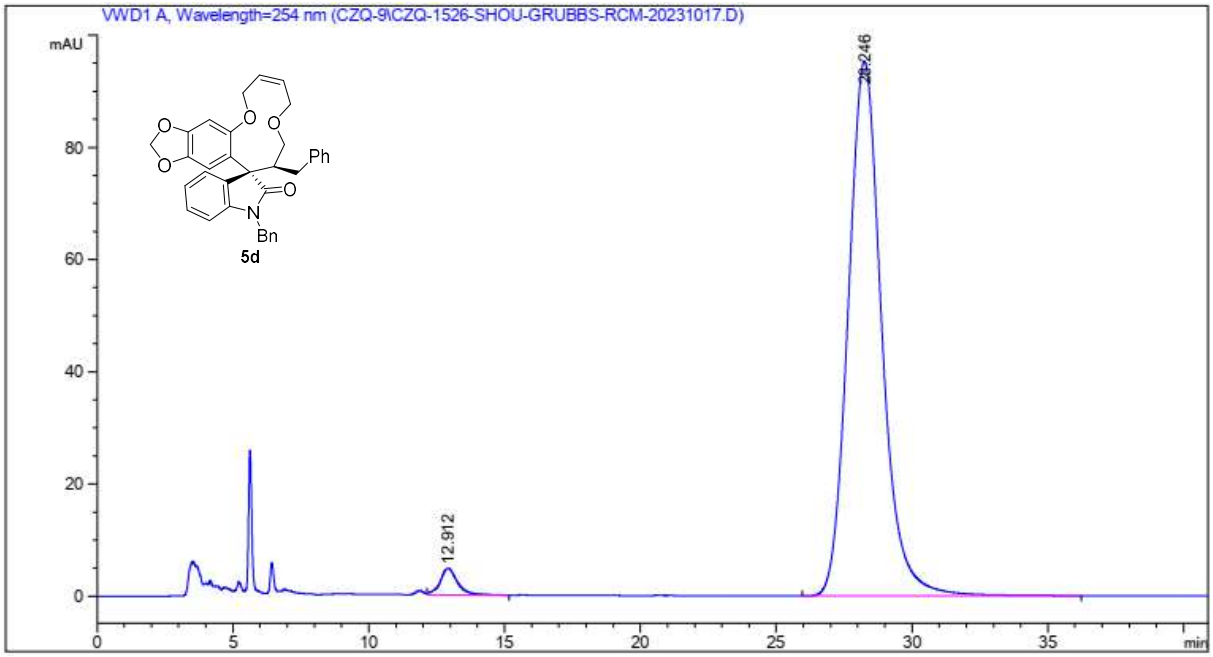
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	31.035	6360.46777	38.10089	50.4903
2	PDA 254.0 nm	41.008	6236.92627	36.80893	49.5097



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	32.091	1348.17419	7.71993	3.7966
2	PDA 254.0 nm	38.225	3.41620e4	226.38808	96.2034



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	12.732	6404.42969	160.30928	49.5372
2	PDA 254.0 nm	27.968	6524.09717	78.02768	50.4628



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.0 nm	12.912	212.58983	4.75658	2.5417
2	PDA 254.0 nm	28.246	8151.43896	95.30463	97.4583