

Supporting Information

**Enantioselective Access to Spirooxindole δ -lactones and Acyclic 3, 3'-
Disubstituted Oxindole-Derivatives by N-heterocyclic Carbene
Catalysts**

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I. General Information

Commercially available materials were used as received, unless otherwise noted, all reactions and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. Reactions were checked by TLC analysis and plates were visualized with short-wave UV light (254 nm). The ^1H , ^{13}C NMR and ^{19}F spectra were obtained in CDCl_3 using a Bruker-BioSpin AVANCE III HD NMR spectrometer at 400 MHz, 100 MHz and 376 MHz respectively. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. HPLC analysis of the compounds was done using chiralcel IC column using hexane and isopropanol as eluent, and the column temperature is 40 °C. The Rudolph Autopol V polarimeter was employed to gauge the optical rotation. The melting point was measured by Shanghai Instrument electrooptical SGW X-4A micro melting point instrument. High resolution mass spectra(HRMS) were recorded on Thermo Scientific Q Exactive mass spectrometry equipped with an APCI source. Crystal structure data was collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The following abbreviations are used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

II. X-ray crystallographic analysis

CCDC 2407944 (**3bc**) suitable for X-ray crystallography was obtained by crystallization via evaporation from its hexane/DCM solution.

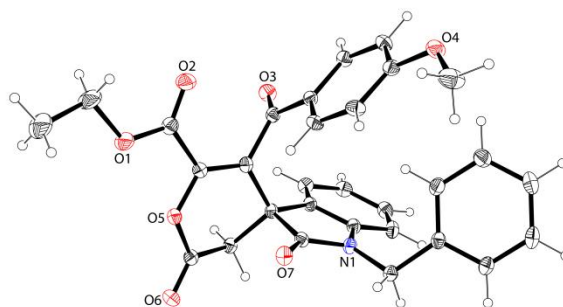


Figure 1. X-Ray crystallographic data of **3bc**

CCDC 2407944 (**3bc**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Table 1. Crystal data and structure refinement for **3bc**

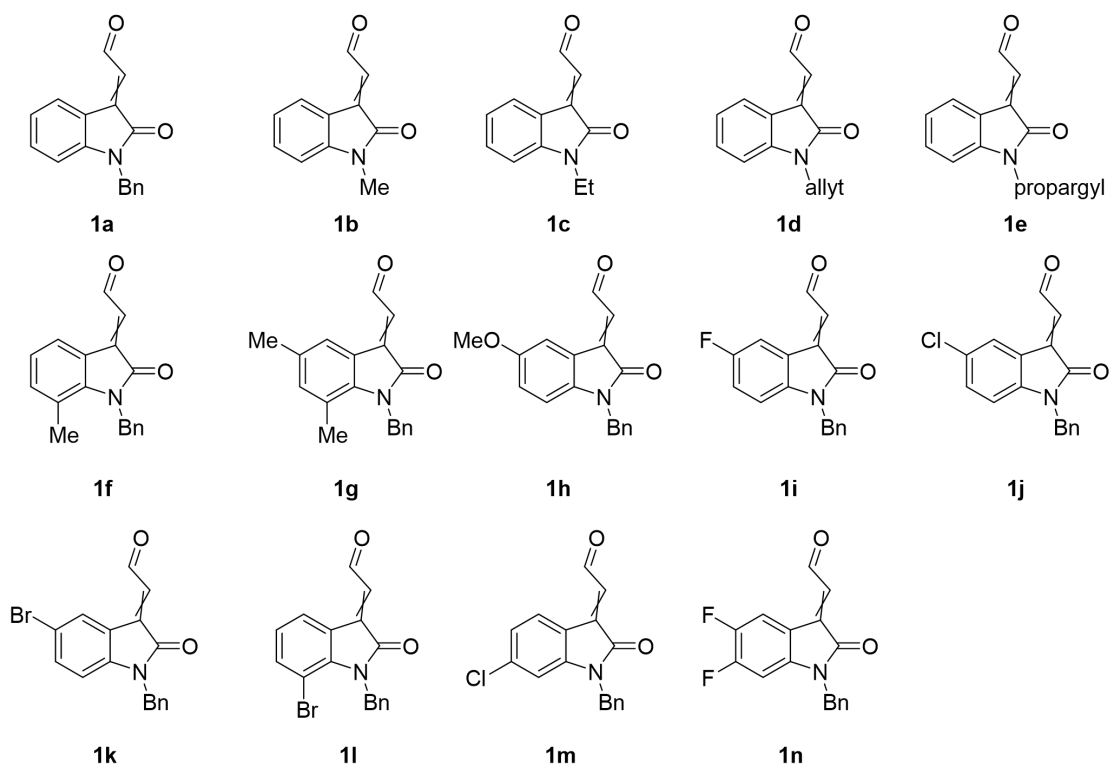
Identification code	3bc
Empirical formula	$\text{C}_{30}\text{H}_{25}\text{NO}_7$
Formula weight	511.51
Temperature	173.0 K
Wavelength	1.54178
Crystal system	Monoclinic

Space group	P2 ₁	
Unit cell dimensions	a = 9.0595(3)	a = 90
	b = 9.2127(3)	b = 102.057(2)
	c = 15.4455(5)	g = 90
Volume	1260.68(7) ³	
Z	2	
Density (calculated)	1.347 Mg/m ³	
Absorption coefficient	0.796 mm ⁻¹	
F(000)	536	
Crystal size	0.14 × 0.12 × 0.11 mm ³	
Theta range for data collection	4.992 to 72.052	
Index ranges	-10 ≤ h ≤ 11, -11 ≤ k ≤ 11, -19 ≤ l ≤ 18	
Reflections collected	16713	
Independent reflections	4871 [R(int) = 0.0426]	
Completeness to theta	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.6778	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4871 / 1 / 345	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2σ(I)]	R1 = 0.0344, wR2 = 0.0785	
R indices (all data)	R1 = 0.0387, wR2 = 0.0811	
Absolute structure parameter	-0.03(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.233 and -0.163 e. ⁻³	

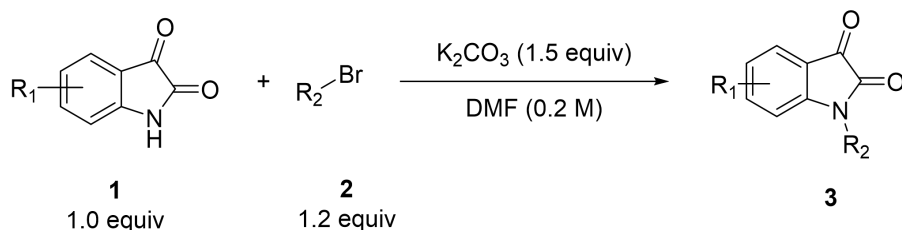
III. Experimental Section

1. General procedure for the synthesis of indole-enal

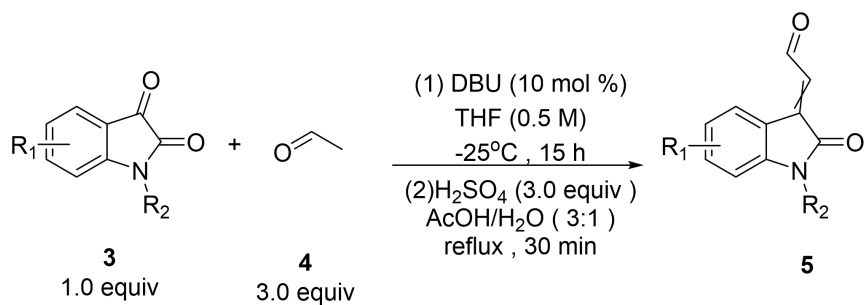
1. Substrates 1a-1m are known compounds and were prepared according to the literature reports.^[1-2]



2. Substrates **1a** and **1n** were synthesized according to the following procedure:



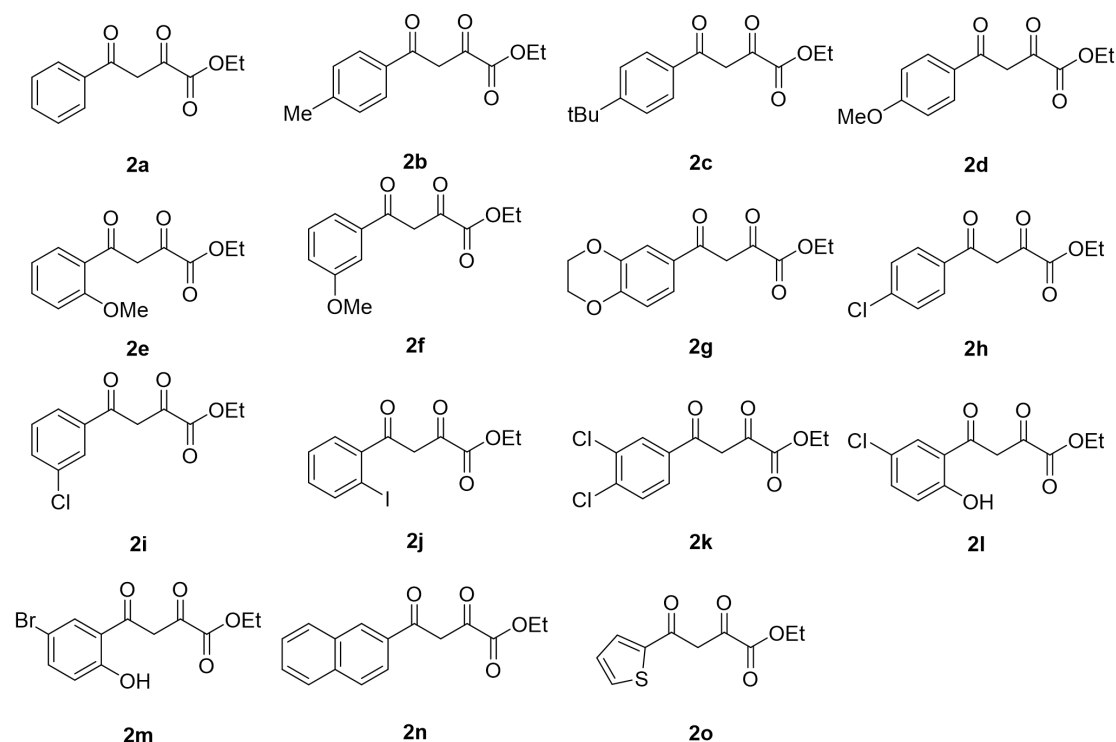
To a solution of isatin **1** (2.0 mmol) in DMF (10 mL) was added potassium carbonate (3.0 mmol) followed by **2** (2.4 mmol). The mixture was stirred for 2 h at room temperature (the progress of the reaction was monitored by TLC). After completion of the reaction the mixture was diluted with cold water (50 mL) followed by EtOAc (50 mL) and stirred for 10 min. The organic layer separated was collected and the aqueous layer was extracted with additional EtOAc (2×50 mL). The organic layers were collected, combined, dried over anhydrous Na_2SO_4 , filtered and concentrated under vacuo. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate to afford the desired product **3**.



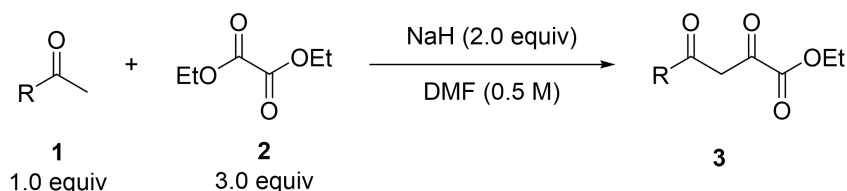
To a solution of N-protected isatin (1.0 equiv, 10 mmol) in THF (0.5 M) were added DBU (10 mol %) and acetaldehyde (3.0 equiv), and the reaction mixture was kept at -25 °C for 15 h. After completion of the reaction, the mixture was kept at room temperature and a 3:1 mixture of AcOH/H₂O (10 mL) and a few drops of conc. H₂SO₄ were added. This mixture was then refluxed for 30 min in an oil bath. The reaction mixture was diluted with water, extracted with dichloromethane, and washed with water followed by brine. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude was purified by silica column chromatography using petroleum ether/ethyl acetate mixture as eluent (90:10, v/v) to obtain compounds 5.

2. General procedure for the synthesis of ethyl 2,4-oxo-4-R-butanoate

1. Substrates **2a-2o** are known compounds and were prepared according to the literature reports.^[3]



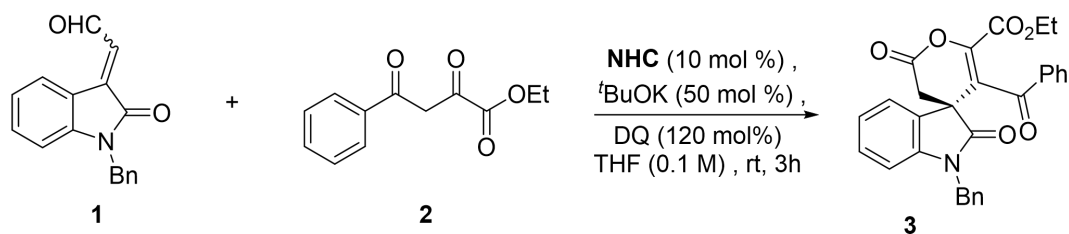
2. Substrates **2a** and **2o** were synthesized according to the following procedure:



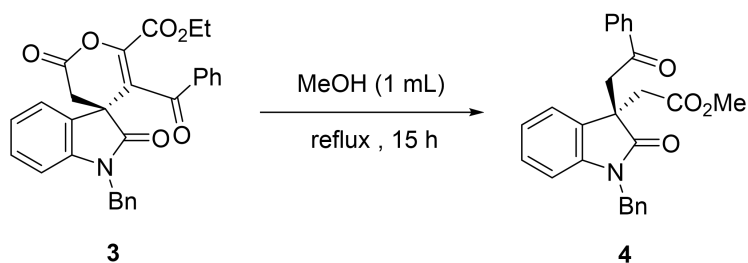
To sodium hydride (2.0 equiv) in DMF (0.5 M) was added drop wise in ice cold condition under nitrogen atmosphere. Then **1** (1.0 equiv, 10 mmol) was added and stirred for 30 min at room temperature. Finally diethyl oxalate **2** (3.0 equiv) was added and the reaction mixture was again stirred for 3h at room temperature. The completion of the reaction was monitored by TLC and quenched with crushed ice. Then the reaction mixture was extracted with ethyl acetate (2×100 mL), washed with

water (150 mL) and brine solution (150 mL). The organic layer was separated, dried over anhydrous sodium sulphate and evaporation of solvent afforded the expected product **3**

IV. General procedure for [3+3] cycloaddition reaction



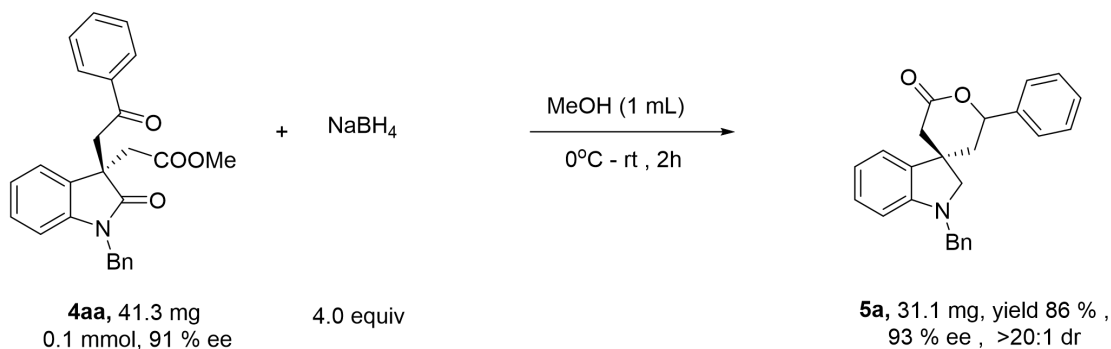
Compound **1** (0.10 mmol) and compound **2** (0.15 mmol), *t*BuOK (50 mol%), NHC precursor (10 mol%), DQ (120 mol%) and were added to 15 mL Schlenk tube, after vacuum replacement of argon, THF (1 mL) was added to this solution at room temperature, and the mixture was stirred for 3 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200-300 mesh, PE/EA v/v = 3:1 as the eluent) to produce the respective products **3**.



Compound **3** (0.1 mmol) was added to 15 ml pressure-resistant tube, MeOH (1 mL) was added to this solution at 80 °C and the mixture was stirred for 15 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200-300 mesh, PE/EA v/v = 4:1 as the eluent) to produce the respective products **4**.

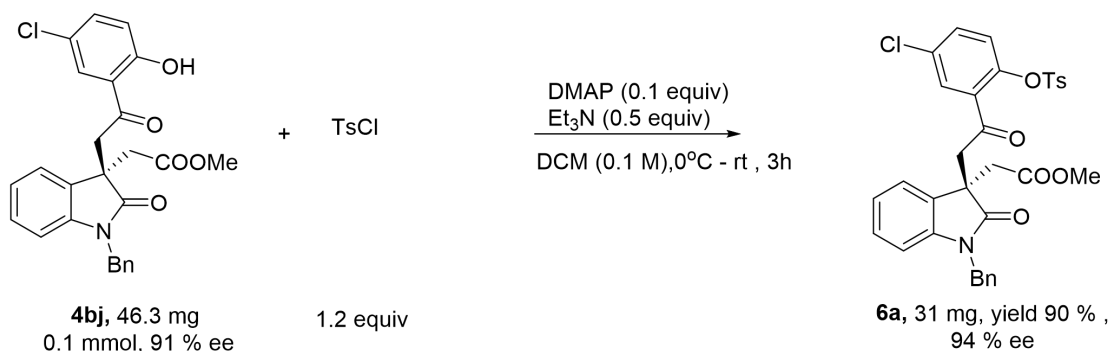
V. Procedures for derivatizations of products

1.



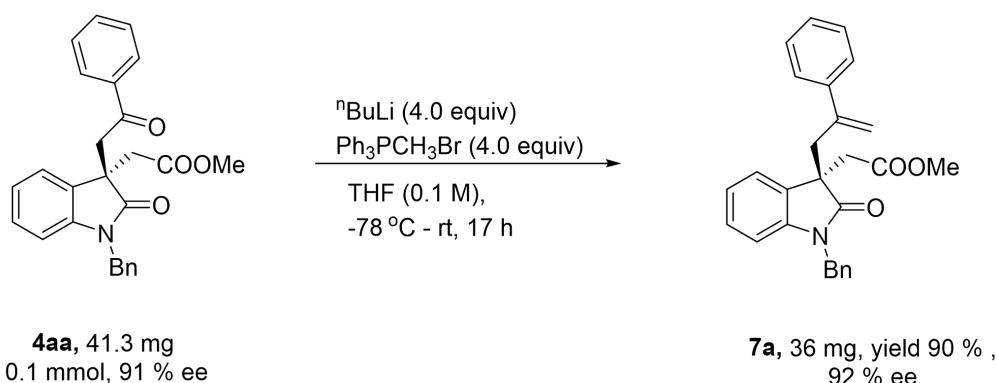
Compound **4aa** (41 mg, 1.0 equiv) was added to 15 mL Schlenk tube, after vacuum replacement of argon, MeOH (1 mL) was added to this solution at 0 °C. NaBH₄ (15.2 mg, 4.0 equiv) is added to the mixed solution of 4aa in MeOH. The mixture was allowed to stir at this temperature for further 2 h, with its progression being observed using TLC. Following the completion of the reaction, saturated solution of H₂O (2 mL) was added and the aqueous phase was extracted with ethyl acetate (5 mL×3). The combined extracts were dried by Na₂SO₄. After the removal of solvent, purification by flash column chromatography (hexane/ethyl acetate = 3:1) was carried out to give pure product **5a** (colorless oil, 31 mg, 86 % yield , 93 % ee, dr > 20:1).

2.



To a solution of the suitable alcohol, **4bj** (0.1 mmol) in dry DCM (1 mL), and cooled to 0 °C, was added, portion-wise and drop-wise, 4-dimethylaminopyridine (0.01 mmol), p-toluenesulfonyl chloride (1.2 mmol) and triethylamine (0.05 mmol). The reaction mixture was stirred at 0 °C until TLC showed complete consumption of starting material. The resulting suspension was diluted with diethyl ether (2 mL), stirred for a further 30 min, and the precipitate removed by filtration. The solution was then washed sequentially with water (3 mL), 10% NaHCO₃ (2 x 3 mL) and a saturated aqueous NaCl solution (2 mL). The combined organic layers were dried over Na₂SO₄, filtered, The solution was directly purified by silica gel column chromatography (hexane/ethyl acetate = 3:1) to afford **6a** (white solid, 31 mg, 90% yield, 94% ee).

3.

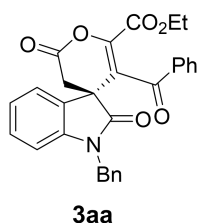


Methyltriphenylphosphonium bromide (143 mg, 0.4 mmol, 4.0 equiv) was suspended in freshly distilled THF (1 mL) and cooled to -78 °C. n-BuLi (0.4 mmol, 4.0 equiv) was added in batches and the resulting solution was stirred for 1 h. The resulting solution was then stirred while warming to room temperature for 1 h. and then reaction was cooled to -78 °C. **4aa** (0.1 mmol, 1.0 equiv) was added. The resulting solution was then stirred while warming to room temperature for 15 h. The solution was directly purified by silica gel column chromatography (hexane/ethyl acetate = 3:1) to afford **7a** (colorless oil, 36 mg, 90% yield, 92% ee).

VI.Reference:

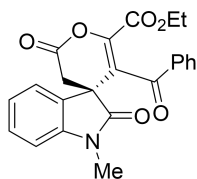
- [1] R.K. Kumar; Y. Sreenivas; S. Sandhya; K. Ajit; M. Parimal; B. Rao; P. Manojit. Ultrasound-based approach to spiro-2,3-dihydroquinazolin-4(1H)-ones: their in vitro evaluation against chorismate mutase. *Tetrahedron Letters.*, **2013**, 54, 495–501.
- [2] T. Vivekanand, B.S. Vachan, M. Karuppasamy, I. Muthukrishnan, U. Maheswari, S. Nagarajan, N. Bhuvanesh, V. Sridharan, Diastereoselective ABB' Three-Component Synthesis of Highly Functionalized Spirooxindoles Bearing Five Consecutive Asymmetric Carbons, *J. Org. Chem.*, **2019**, 84, 4009-4016.
- [3]. S. Rajendran; B. Govindharasu; K. Maruthan; A. Jayachitra; Padmini, V. Multiple biological activities and molecular docking studies of newly synthesized 3-(pyridin-4-yl)-1H-pyrazole-5-carboxamide chalcone hybrids, *Bioorg. Med. Chem. Lett.*, **2016**, 26, 5624-5630.

VII. Characterizations of new compounds



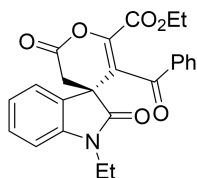
Ethyl-(R)-5'-benzoyl-1-benzyl-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3aa): Orange solid (38 mg, 79 % yield). Mp: 66.1–71.6 °C. HPLC:

91% ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 30.003 min, tr (minor) = 26.149 min. $[\alpha]_D^{20} = +14.3$ (c = 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ : 7.72 (d, *J* = 9.7 Hz, 2H), 7.55–7.49 (m, 1H), 7.41–7.32 (m, 3H), 7.25 (d, *J* = 2.0 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 7.15–7.10 (m, 3H), 7.01–6.96 (m, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 4.76 (q, *J* = 15.7 Hz, 2H), 4.02 (dd, *J* = 7.1, 5.3 Hz, 2H), 3.10 (d, *J* = 3.2 Hz, 2H), 1.03 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 190.9, 174.3, 163.2, 159.6, 143.6, 142.3, 136.2, 134.6, 133.7, 129.9, 128.8, 128.6, 127.8, 127.1, 126.5, 124.7, 124.3, 123.5, 110.1, 62.7, 50.3, 44.3, 36.6, 13.4. HRMS (APCI) *m/z* calcd for C₂₉H₂₄NO₆⁺ (*M*+*H*)⁺ 482.1598, found 482.1578.



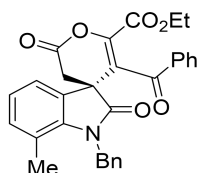
3ab

Ethyl(*R*)-5'-benzoyl-1-methyl-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3ab): Yellow solid (34 mg, 85 % yield). Mp: 64.7–68.9 °C. HPLC: 93% ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 70.609 min, tr (minor) = 38.824 min. $[\alpha]_D^{20} = +23.6$ (c = 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ : 7.75–7.73 (m, 1H), 7.57–7.49 (m, 1H), 7.43–7.33 (m, 2H), 7.28–7.23 (m, 4H), 7.15–7.06 (m, 2H), 6.96 (d, *J* = 10.0 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 1H), 4.89–4.61 (m, 2H), 4.18–3.83 (m, 2H), 3.29–2.89 (m, 2H), 2.21 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 191.2, 175.4, 163.4, 159.8, 143.9, 140.6, 136.8, 136.6, 134.0, 133.7, 129.0, 128.9, 128.7, 127.5, 127.4, 125.6, 124.8, 123.7, 122.2, 120.9, 62.8, 50.1, 45.7, 37.3, 18.7, 13.5. HRMS (APCI) *m/z* calcd for C₂₃H₂₀NO₆⁺ (*M*+*H*)⁺ 406.1285, found 406.1240



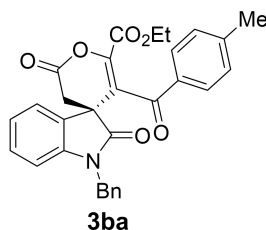
3ac

Ethyl(*R*)-5'-benzoyl-1-ethyl-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3ac): Orange oil (41mg, 98 % yield). HPLC: 93% ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 41.648 min, tr (minor) = 32.954 min. $[\alpha]_D^{20} = +145.6$ (c = 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ : 7.65 (d, *J* = 7.0 Hz, 2H), 7.51–7.46 (m, 1H), 7.38–7.31 (m, 2H), 7.24 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.06–6.99 (m, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 4.03 (tq, *J* = 7.2, 3.7 Hz, 2H), 3.67–3.49 (m, 2H), 3.04 (s, 2H), 1.05 (dt, *J* = 11.9, 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ : 191.0, 173.8, 163.5, 143.5, 142.4, 136.3, 133.7, 130.1, 128.8, 128.6, 126.7, 124.7, 123.4, 109.1, 62.8, 50.2, 36.2, 35.3, 13.6, 12.3. HRMS (APCI) *m/z* calcd for C₂₄H₂₂NO₆⁺ (*M*+*H*)⁺ 420.1442, found 420.1444



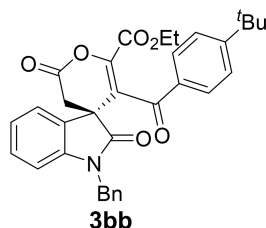
3ad

Ethyl-(*R*)-5'-benzoyl-1-benzyl-7-methyl-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3ad): Brown solid (45 mg, 92 % yield). Mp 67.8–70.1 °C. HPLC: 84 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 26.941 min, tr (minor) = 30.908 min. $[\alpha]_D^{20} = +43.6$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.75–7.73 (m, 1H), 7.57–7.49 (m, 1H), 7.43–7.33 (m, 2H), 7.28–7.23 (m, 4H), 7.15–7.06 (m, 2H), 6.96 (d, $J = 10.0$ Hz, 2H), 6.47 (d, $J = 8.0$ Hz, 1H), 4.89–4.61 (m, 2H), 4.18–3.83 (m, 2H), 3.29–2.89 (m, 2H), 2.21 (s, 3H), 1.02 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 191.2, 175.4, 163.4, 159.8, 143.9, 140.6, 136.8, 136.6, 134.0, 133.7, 129.0, 128.9, 128.7, 127.5, 127.4, 125.6, 124.8, 123.7, 122.2, 120.9, 62.8, 50.1, 45.7, 37.3, 18.7, 13.5. HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{26}\text{NO}_6^+$ ($\text{M}+\text{H}$) $^+$ 496.1755, found 496.1720.



3ba

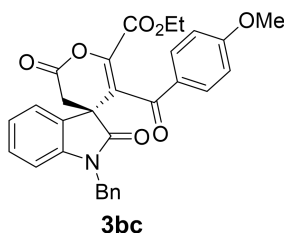
Ethyl(*R*)-5'-benzoyl-1-benzyl-5,6-difluoro-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3ba): Orange solid (49 mg, 96 % yield). Mp 76.4–77.8 °C, HPLC: 82 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 34.268 min, tr (minor) = 31.813 min. $[\alpha]_D^{20} = +20.6$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.64 (s, 1H), 7.34 (s, 1H), 7.25 (dd, $J = 7.0, 3.5$ Hz, 4H), 7.18 (d, $J = 8.1$ Hz, 1H), 7.15 (d, $J = 8.2$ Hz, 2H), 7.11 (d, $J = 3.6$ Hz, 2H), 7.02–6.95 (m, 1H), 6.58 (d, $J = 7.9$ Hz, 1H), 4.85 (d, $J = 15.8$ Hz, 1H), 4.70 (d, $J = 15.7$ Hz, 1H), 4.03 (dq, $J = 7.2, 3.5$ Hz, 2H), 3.08 (d, $J = 1.3$ Hz, 1H), 3.00 (d, $J = 13.5$ Hz, 1H), 2.37 (s, 3H), 1.03 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 190.4, 174.2, 163.3, 159.7, 144.7, 143.2, 142.3, 134.6, 133.8, 129.9, 129.4, 129.0, 128.9, 128.8, 127.7, 127.1, 126.6, 124.9, 124.4, 123.5, 110.0, 62.6, 50.4, 44.3, 36.7, 21.7, 13.5. HRMS (APCI) m/z calcd for $\text{C}_{29}\text{H}_{22}\text{F}_2\text{NO}_6^+$ ($\text{M}+\text{H}$) $^+$ 518.1410, found 518.1417.



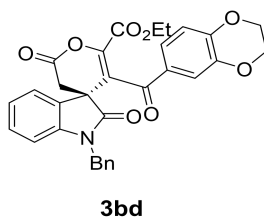
3bb

Ethyl(*R*)-1-benzyl-5'-(4-(tert-butyl)benzoyl)-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3bb): Red oil (28 mg, 53 % yield). HPLC: 88 % ee

(Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 28.197 min, tr (minor) = 22.209 min. $[\alpha]_{\text{D}}^{20} = -27.1$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.68 (d, $J = 8.5$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 9.4$ Hz, 3H), 7.19–7.12 (m, 4H), 6.96 (d, $J = 6.7$ Hz, 1H), 6.57 (d, $J = 7.8$ Hz, 1H), 4.77 (s, 2H), 3.98 (dd, $J = 7.1, 3.0$ Hz, 2H), 3.77 (s, 1H), 3.10 (d, $J = 2.5$ Hz, 2H), 1.30 (s, 9H), 0.96 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 190.6, 174.4, 163.4, 159.7, 157.6, 143.7, 142.3, 134.7, 133.9, 129.9, 128.8, 128.7, 127.7, 127.1, 126.8, 125.6, 124.7, 124.2, 123.5, 110.1, 62.6, 50.5, 44.3, 36.6, 35.2, 31.0, 13.3. HRMS (APCI) m/z calcd for $\text{C}_{33}\text{H}_{32}\text{NO}_6^+(\text{M}+\text{H})^+$ 538.2224, found 538.2216.

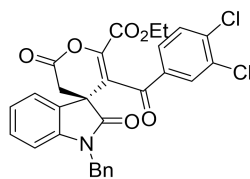


Ethyl(*R*)-1-benzyl-5'-(4-methoxybenzoyl)-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3bc): Orange solid (48 mg, 94 % yield). Mp 85.7–87.4 °C, HPLC: 93 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 71.310 min, tr (minor) = 62.655 min. $[\alpha]_{\text{D}}^{20} = +5.8$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.71 (d, $J = 8.9$ Hz, 2H), 7.26–7.21 (m, 3H), 7.20 (d, $J = 6.3$ Hz, 1H), 7.17–7.12 (m, 1H), 7.07 (dd, $J = 6.8, 2.8$ Hz, 2H), 7.02–6.96 (m, 1H), 6.83 (d, $J = 8.9$ Hz, 2H), 6.58 (d, $J = 7.9$ Hz, 1H), 4.88 (d, $J = 15.8$ Hz, 1H), 4.70 (d, $J = 15.8$ Hz, 1H), 4.10–4.01 (m, 2H), 3.82 (s, 3H), 3.08 (s, 2H), 1.05 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 189.2, 174.3, 164.1, 163.4, 159.7, 142.9, 142.3, 134.6, 131.2, 129.9, 129.3, 128.8, 127.7, 127.0, 126.5, 125.1, 124.5, 123.5, 113.9, 110.0, 62.6, 55.5, 50.4, 44.3, 36.7, 13.5. HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{26}\text{NO}_7^+(\text{M}+\text{H})^+$ 512.1704, found 512.1697.



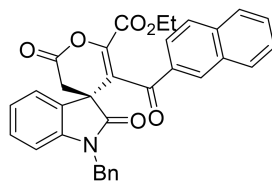
Ethyl(*R*)-1-benzyl-5'-(2,3-dihydrobenzo[b][1,4]dioxine-6-carbonyl)-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3bd): Orange solid (53 mg, 98 % yield). Mp 60.3–63.4 °C, HPLC: 87 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 59.493 min, tr (minor) = 53.766 min. $[\alpha]_{\text{D}}^{20} = -91.0$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.33–7.26 (m, 3H), 7.25 (s, 2H), 7.20–7.09 (m, 4H), 7.02–6.96 (m, 1H), 6.81 (d, $J = 8.2$ Hz, 1H), 6.59 (d, $J = 7.8$ Hz, 1H), 4.92 (d, $J = 15.8$ Hz, 1H), 4.71 (d, $J = 15.8$ Hz, 1H), 4.30–4.17 (m, 4H), 4.13–4.02 (m, 2H), 3.16–2.98 (m, 2H), 1.08 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 189.2, 174.3, 163.5, 159.8, 148.8, 143.6, 143.1, 142.4, 134.8, 130.2, 130.0, 128.9, 127.8, 127.2, 126.7, 125.0, 124.5, 123.6, 123.3, 118.2, 117.5, 110.2, 64.8, 64.0, 62.7, 50.5, 44.4, 36.8, 13.7. HRMS (APCI) m/z calcd

for $C_{31}H_{26}INO_8^+(M+H)^+$ 540.1653, found 540.1644.



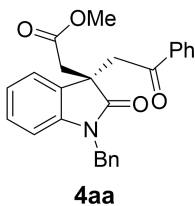
3be

Ethyl(*R*)-1-benzyl-5'-(3,4-dichlorobenzoyl)-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3be): Yellow solid (36 mg, 66 % yield). Mp 57.9–59.0 °C. HPLC: 90 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 90:10, flow rate 0.3 mL/min, tr (major) = 242.538 min, tr (minor) = 234.514 min. $[\alpha]_D^{20} = +4.8$ ($c = 0.2$, CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) δ : 7.79 (d, $J = 2.0$ Hz, 1H), 7.54 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.26 (d, $J = 6.4$ Hz, 3H), 7.19 (d, $J = 6.1$ Hz, 2H), 7.12–7.08 (m, 2H), 7.06–6.99 (m, 1H), 6.66 (d, $J = 8.1$ Hz, 1H), 4.89 (d, $J = 33.6$ Hz, 1H), 4.70 (d, $J = 15.7$ Hz, 1H), 4.12 (t, $J = 7.2$ Hz, 2H), 3.10 (d, $J = 8.2$ Hz, 1H), 3.00 (d, $J = 14.0$ Hz, 1H), 1.15 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 188.6, 173.9, 162.9, 159.5, 143.5, 142.2, 138.2, 135.6, 134.4, 133.4, 130.7, 130.2, 128.8, 127.9, 127.8, 127.1, 126.1, 124.4, 124.2, 123.7, 110.1, 62.9, 50.3, 44.3, 36.4, 13.6. HRMS (APCI) m/z calcd for $C_{29}H_{21}Cl_2NO_6^+$ ($M+H$) $^+$ 550.0819, found 550.0823.

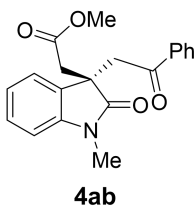


3bf

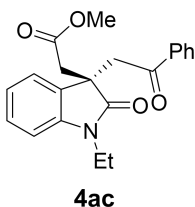
Ethyl(*R*)-5'-(2-naphthoyl)-1-benzyl-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate (3bf): Orange solid (36 mg, 66 % yield). Mp 69.1–75.1 °C. HPLC: 93 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 33.1038 min, tr (minor) = 29.683 min. $[\alpha]_D^{20} = +23.7$ ($c = 0.2$, CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) δ : 8.26 (s, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 5.4$ Hz, 1H), 7.60 (d, $J = 8.1$ Hz, 1H), 7.56–7.50 (m, 2H), 7.24 (d, $J = 7.4$ Hz, 1H), 7.11 (d, $J = 7.9$ Hz, 2H), 7.08–7.04 (m, 2H), 7.01–6.96 (m, 3H), 6.51 (d, $J = 7.8$ Hz, 1H), 4.77–4.61 (m, 2H), 4.05–3.95 (m, 2H), 3.00 (d, $J = 13.3$ Hz, 3H), 0.99 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 190.7, 174.3, 163.3, 159.7, 143.7, 142.3, 135.8, 134.5, 133.6, 132.3, 131.3, 129.9, 129.8, 129.0, 128.8, 128.7, 128.7, 127.8, 127.7, 127.0, 126.9, 126.4, 125.0, 124.5, 123.7, 123.6, 110.1, 62.7, 62.0, 50.4, 44.3, 37.1, 36.7, 34.1, 14.0, 13.5, 13.6. HRMS (APCI) m/z calcd for $C_{33}H_{26}NO_6^+$ ($M+H$) $^+$ 532.1755, found 532.1749.



Methyl(*R*)-2-(1-benzyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4aa): White solid (40 mg, 98 % yield). Mp: 63.2–65.3 °C. HPLC: 92% ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 15.043 min, tr (minor) = 10.932 min. $[\alpha]_D^{20} = +19.5$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.87 (d, $J = 7.1$ Hz, 2H), 7.56–7.50 (m, 1H), 7.45 (d, $J = 6.8$ Hz, 2H), 7.44–7.39 (m, 2H), 7.38–7.30 (m, 3H), 7.28 (d, $J = 7.3$ Hz, 1H), 7.17–7.11 (m, 1H), 6.96–6.90 (m, 1H), 6.74 (d, $J = 8.6$ Hz, 1H), 5.14–4.84 (m, 2H), 4.11 (d, $J = 17.8$ Hz, 1H), 3.61 (d, $J = 17.8$ Hz, 1H), 3.54 (s, 3H), 3.16 (d, $J = 15.8$ Hz, 1H), 2.84 (d, $J = 15.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.8, 179.1, 170.3, 143.5, 136.46, 136.1, 133.3, 130.6, 128.7, 128.5, 128.3, 128.0, 127.4, 127.4, 123.6, 122.3, 109.3, 51.7, 47.1, 44.3, 41.1. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 414.1700, found 414.1692.

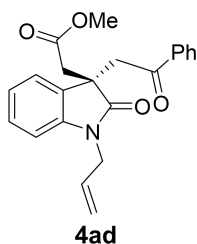


Methyl(*R*)-2-(1-methyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate. Brown oil (37 mg, 98 % yield). HPLC: 93% ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 16.774 min, tr (minor) = 14.502 min. $[\alpha]_D^{20} = +14.2$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.83 (d, $J = 7.0$ Hz, 2H), 7.54–7.49 (m, 1H), 7.42–7.37 (m, 2H), 7.32 (d, $J = 8.7$ Hz, 1H), 7.27 (d, $J = 11.1$ Hz, 1H), 6.99–6.94 (m, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 4.05 (d, $J = 17.9$ Hz, 1H), 3.56–3.51 (m, 4H), 3.31 (s, 3H), 3.12 (d, $J = 16.0$ Hz, 1H), 2.79 (d, $J = 15.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.0, 179.1, 170.5, 144.5, 136.5, 133.38, 130.73, 128.6, 128.5, 128.0, 123.6, 122.3, 108.3, 51.8, 47.1, 44.4, 40.9, 26.69. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 428.1856, found 428.1848.

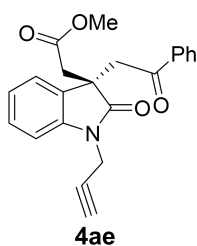


Methyl(*R*)-2-(1-ethyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4ac): Brown oil (33 mg, 95 % yield). HPLC: 93% ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 69.544 min, tr (minor) = 69.544 min).

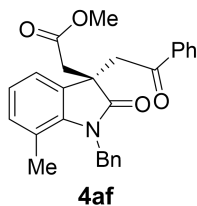
= 67.201 min. $[\alpha]_{\text{D}}^{20} = +27.3$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.84 (d, $J = 7.0$ Hz, 2H), 7.54–7.49 (m, 1H), 7.43–7.35 (m, 2H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.26 (d, $J = 7.8$ Hz, 1H), 6.98–6.93 (m, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 4.03 (d, $J = 17.8$ Hz, 1H), 3.85 (q, $J = 7.2$ Hz, 2H), 3.52 (d, $J = 16.6$ Hz, 4H), 3.12 (d, $J = 15.9$ Hz, 1H), 2.79 (d, $J = 15.8$ Hz, 1H), 1.35 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 195.9, 178.6, 170.5, 143.6, 136.6, 133.3, 130.9, 128.6, 128.4, 128.1, 123.9, 122.1, 108.4, 51.7, 47.1, 44.4, 41.0, 35.0, 12.3. HRMS (APCI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 352.1543, found 352.1539.



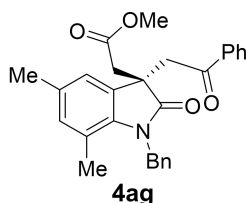
Methyl(*R*)-2-(1-allyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4ad): Brown oil (34 mg, 94 % yield). HPLC: 94 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 12.238 min, t_r (minor) = 10.921 min. $[\alpha]_{\text{D}}^{20} = +12.3$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.84 (d, $J = 8.3$ Hz, 2H), 7.55–7.47 (m, 1H), 7.43–7.37 (m, 2H), 7.32 (d, $J = 7.4$ Hz, 1H), 7.26–7.20 (m, 1H), 6.99–6.92 (m, 1H), 6.89 (d, $J = 7.7$ Hz, 1H), 5.95 (ddd, $J = 22.5$, 10.4, 5.3 Hz, 1H), 5.43 (d, $J = 17.2$ Hz, 1H), 5.28 (d, $J = 10.4$ Hz, 1H), 4.44 (s, 2H), 4.07 (d, $J = 17.9$ Hz, 1H), 3.62–3.52 (m, 4H), 3.13 (d, $J = 15.9$ Hz, 1H), 2.80 (d, $J = 15.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.8, 178.7, 170.3, 143.6, 136.4, 133.2, 131.7, 130.6, 128.5, 128.3, 128.0, 123.5, 122.2, 117.6, 109.1, 51.7, 47.0, 44.4, 42.81, 41.0. HRMS (APCI) m/z calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 364.1543, found 364.1537.



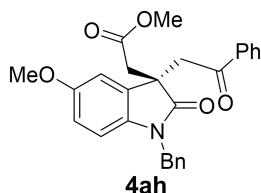
Methyl(*R*)-2-(2-oxo-3-(2-oxo-2-phenylethyl)-1-(prop-2-yn-1-yl)indolin-3-yl)acetate (4ae): Brown oil (33 mg, 92 % yield). HPLC: 93 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 14.419 min, t_r (minor) = 11.351 min. $[\alpha]_{\text{D}}^{20} = +31.3$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.83 (d, $J = 7.1$ Hz, 2H), 7.56–7.45 (m, 1H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 7.5$ Hz, 1H), 7.33–7.27 (m, 1H), 7.12 (d, $J = 7.8$ Hz, 1H), 7.04–6.97 (m, 1H), 4.72 (d, $J = 20.3$ Hz, 1H), 4.51 (d, $J = 20.2$ Hz, 1H), 4.06 (d, $J = 17.9$ Hz, 1H), 3.55 (d, $J = 17.9$ Hz, 4H), 3.14 (d, $J = 15.9$ Hz, 1H), 2.83 (d, $J = 15.9$ Hz, 1H), 2.29 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.9, 178.2, 170.4, 142.7, 136.4, 133.4, 130.5, 128.6, 128.6, 128.1, 123.8, 122.8, 109.3, 72.3, 51.9, 47.1, 44.5, 41.0, 29.8, 41.0. HRMS (APCI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 362.1387, found 362.1380.



Methyl(*R*)-2-(1-benzyl-7-methyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4af): Brown oil (40 mg, 94 % yield). HPLC: 93 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 14.502 min, tr (minor) = 16.774 min. $[\alpha]_{\text{D}}^{20} = +15.3$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.88 (d, $J = 7.1$ Hz, 2H), 7.56–7.51 (m, 1H), 7.43 (q, $J = 7.7$ Hz, 4H), 7.37–7.33 (m, 2H), 7.28 (d, $J = 7.3$ Hz, 1H), 7.13 (s, 1H), 6.93 (d, $J = 7.9$ Hz, 1H), 6.62 (d, $J = 7.9$ Hz, 1H), 5.07–4.94 (m, 2H), 4.09 (d, $J = 17.9$ Hz, 1H), 3.63 (s, 1H), 3.55 (s, 3H), 3.14 (d, $J = 15.8$ Hz, 1H), 2.84 (d, $J = 15.8$ Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.9, 179.1, 170.5, 141.2, 136.6, 136.3, 133.3, 131.8, 130.8, 128.8, 128.7, 128.7, 128.6, 128.2, 127.5, 124.5, 109.1, 51.8, 47.3, 44.4, 41.2, 21.2. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 428.1856, found 428.1848.

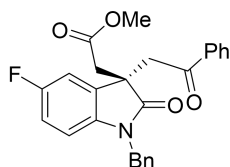


Methyl(*R*)-2-(1-benzyl-5,7-dimethyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4ag): Brown oil (43 mg, 97 % yield). HPLC: 91 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 30.006 min, tr (minor) = 13.907 min. $[\alpha]_{\text{D}}^{20} = +26.3$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.89 (d, $J = 9.8$ Hz, 2H), 7.58–7.49 (m, 1H), 7.46–7.30 (m, 6H), 7.30–7.23 (m, 1H), 6.95 (s, 1H), 6.73 (s, 1H), 5.23 (s, 2H), 4.09 (d, $J = 17.8$ Hz, 1H), 3.64 (d, $J = 32.4$ Hz, 4H), 3.08 (d, $J = 15.6$ Hz, 1H), 2.83 (d, $J = 15.6$ Hz, 1H), 2.21 (d, $J = 19.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.9, 179.9, 170.4, 139.2, 138.4, 136.5, 133.2, 132.9, 131.7, 131.6, 128.7, 128.5, 128.1, 126.9, 126.0, 121.8, 119.4, 51.7, 46.6, 45.6, 44.5, 41.7, 20.8, 18.7. HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{28}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 442.2013, found 442.2006.



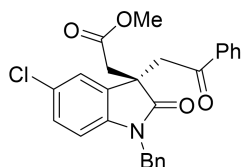
Methyl(*R*)-2-(1-benzyl-5-methoxy-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4ah): Brown oil (43 mg, 98 % yield). HPLC: 94 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 18.126 min, tr (minor) = 13.642 min. $[\alpha]_{\text{D}}^{20} = +27.8$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.88 (d, $J = 8.2$ Hz, 1H), 7.58–7.50 (m, 1H), 7.42 (q, $J = 7.6, 7.1$ Hz, 3H), 7.38–7.31 (m, 2H), 7.28 (d, $J = 7.3$ Hz, 1H), 7.21 (d, $J = 8.2$ Hz, 1H), 7.10–6.99 (m, 1H), 6.97 (d,

$J = 2.4$ Hz, 1H), 6.93 (s, 1H), 6.65–6.62 (m, 1H), 5.08–4.92 (m, 2H), 4.10 (d, $J = 17.9$ Hz, 1H), 3.76 (d, $J = 2.8$ Hz, 1H), 3.65 (d, $J = 24.1$ Hz, 3H), 3.57 (d, $J = 4.6$ Hz, 3H), 3.16 (d, $J = 16.0$ Hz, 1H), 2.83 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.8, 178.7, 170.3, 155.6, 136.4, 136.1, 133.3, 128.7, 128.5, 128.0, 127.4, 127.4, 112.3, 111.4, 109.5, 56.0, 55.6, 51.7, 47.5, 44.4, 44.3, 41.0. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_5^+$ ($\text{M}+\text{H}$) $^+$ 444.1805, found 444.1798.



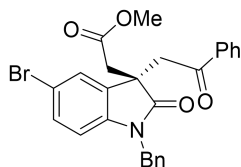
4ai

Methyl-(*R*)-2-(1-benzyl-5-fluoro-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4ai): Brown oil (42 mg, 97 % yield). HPLC: 91 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 10.721 min, t_r (minor) = 8.186 min. $[\alpha]_{\text{D}}^{20} = +13.1$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.89 (d, $J = 8.3$ Hz, 2H), 7.55 (d, $J = 14.8$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 4H), 7.40–7.33 (m, 2H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.15 (dd, $J = 8.2$, 2.6 Hz, 1H), 6.88–6.78 (m, 1H), 6.64 (dd, $J = 8.6$, 4.2 Hz, 1H), 5.01 (q, $J = 15.9$ Hz, 2H), 4.13 (d, $J = 18.0$ Hz, 1H), 3.60 (d, $J = 18.1$ Hz, 4H), 3.19 (d, $J = 16.2$ Hz, 1H), 2.83 (d, $J = 16.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 195.7, 179.0, 170.3, 160.2, 157.8, 139.6, 139.6, 136.3, 135.9, 133.5, 132.5, 132.4, 128.9, 128.7, 128.1, 127.7, 127.4, 114.7, 114.4, 112.4, 112.1, 109.8, 109.8, 51.9, 47.6, 47.6, 44.5, 44.4, 40.9. ^{19}F NMR (376 MHz, CDCl_3) δ : -120.64. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{FNO}_4^+$ ($\text{M}+\text{H}$) $^+$ 432.1606, found 432.1600.



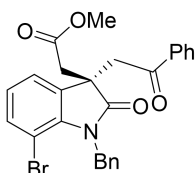
4aj

Methyl(*R*)-2-(1-benzyl-5-chloro-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4aj): Brown oil (43 mg, 97 % yield). HPLC: 93 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 9.806 min, t_r (minor) = 7.722 min. $[\alpha]_{\text{D}}^{20} = -15.9$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.89 (d, $J = 8.2$ Hz, 2H), 7.58–7.52 (m, 1H), 7.46–7.40 (m, 4H), 7.35 (d, $J = 7.0$ Hz, 3H), 7.31 (s, 1H), 7.11 (dd, $J = 8.3$, 2.1 Hz, 1H), 6.65 (d, $J = 8.3$ Hz, 1H), 5.07–4.95 (m, 2H), 4.12 (d, $J = 18.1$ Hz, 1H), 3.61 (d, $J = 21.1$ Hz, 4H), 3.16 (d, $J = 16.2$ Hz, 1H), 2.82 (d, $J = 16.1$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 195.6, 178.8, 170.2, 142.4, 136.2, 135.7, 133.6, 132.6, 128.9, 128.7, 128.3, 128.1, 127.8, 127.7, 127.4, 124.3, 110.3, 51.9, 47.3, 44.5, 44.5, 41.0. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{ClNO}_4^+$ ($\text{M}+\text{H}$) $^+$ 448.1310, found 448.1304.



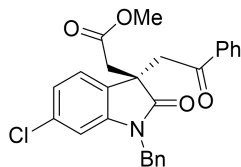
4ak

Methyl(*R*)-2-(1-benzyl-5-bromo-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4ak): Brown oil (48 mg, 98 % yield). HPLC: 87 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 9.931 min, tr (minor) = 7.822 min. $[\alpha]_D^{20} = +17.4$ (c = 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ: 7.88 (d, *J* = 7.2 Hz, 2H), 7.58–7.53 (m, 1H), 7.47–7.42 (m, 4H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 3H), 6.60 (d, *J* = 8.3 Hz, 1H), 5.06–4.95 (m, 2H), 4.11 (d, *J* = 18.1 Hz, 1H), 3.61 (d, *J* = 20.3 Hz, 4H), 3.15 (d, *J* = 16.2 Hz, 1H), 2.81 (d, *J* = 16.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 195.6, 178.7, 170.2, 142.9, 136.2, 135.7, 133.6, 133.0, 131.3, 128.9, 128.7, 128.2, 127.7, 127.4, 127.0, 115.2, 110.8, 52.0, 47.3, 44.5, 41.1. HRMS (APCI) *m/z* calcd for C₂₆H₂₃BrNO₄⁺ (M+H)⁺ 492.0805, found 492.0797.



4al

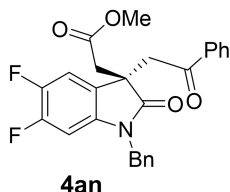
Methyl(*R*)-2-(1-benzyl-7-bromo-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4al): Brown oil (45 mg, 93 % yield). HPLC: 93 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 17.729 min, tr (minor) = 8.951 min. $[\alpha]_D^{20} = -19.4$ (c = 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ: 7.87 (d, *J* = 7.1 Hz, 2H), 7.58–7.52 (m, 1H), 7.47–7.39 (m, 4H), 7.37–7.32 (m, 3H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.86–6.79 (m, 1H), 5.47 (d, *J* = 5.4 Hz, 2H), 4.10 (d, *J* = 15.0 Hz, 1H), 3.65 (d, *J* = 17.9 Hz, 1H), 3.59 (s, 3H), 3.11 (d, *J* = 15.9 Hz, 1H), 2.83 (d, *J* = 15.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 195.6, 180.0, 170.2, 141.3, 138.2, 136.3, 134.5, 134.2, 133.6, 128.7, 128.5, 128.1, 126.9, 126.7, 126.4, 123.6, 122.5, 102.6, 51.9, 46.8, 45.3, 44.6, 41.5. HRMS (APCI) *m/z* calcd for C₂₆H₂₃BrNO₄⁺ (M+H)⁺ 492.0805, found 492.0796.



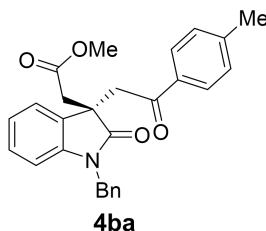
4am

Methyl(*R*)-2-(1-benzyl-6-chloro-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4am): Brown oil (44 mg, 98 % yield). HPLC: 91 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 9.946 min, tr (minor) = 7.787 min. $[\alpha]_D^{20} = +13.5$ (c = 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ:

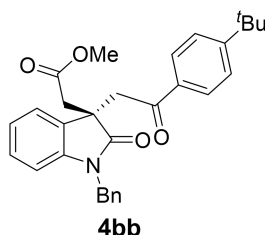
7.89 (d, $J = 8.3$ Hz, 2H), 7.58–7.53 (m, 1H), 7.47–7.41 (m, 4H), 7.38–7.34 (m, 3H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.11 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.65 (d, $J = 8.4$ Hz, 1H), 5.07–4.95 (m, 2H), 4.12 (d, $J = 18.0$ Hz, 1H), 3.61 (d, $J = 21.2$ Hz, 4H), 3.16 (d, $J = 16.2$ Hz, 1H), 2.82 (d, $J = 16.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 195.6, 178.8, 170.2, 142.4, 136.2, 135.7, 133.6, 132.6, 128.9, 128.7, 128.3, 128.1, 127.8, 127.7, 127.4, 124.3, 110.3, 51.9, 47.3, 44.5, 44.5, 41.0. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{ClNO}_4^+$ ($\text{M}+\text{H}$) $^+$ 448.1310, found 448.1304.



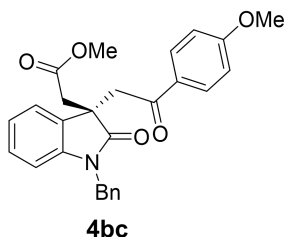
Methyl(*R*)-2-(1-benzyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (4an): Brown oil (40 mg, 97 % yield). HPLC: 80 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 7.851 min, t_r (minor) = 6.671 min. $[\alpha]_D^{20} = +19.4$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.88 (d, $J = 7.5$ Hz, 2H), 7.55 (d, $J = 6.4$ Hz, 1H), 7.46–7.35 (m, 6H), 7.30 (d, $J = 9.1$ Hz, 2H), 6.57–6.51 (m, 1H), 4.97 (q, $J = 15.8$ Hz, 2H), 4.10 (d, $J = 18.0$ Hz, 1H), 3.57 (d, $J = 19.8$ Hz, 4H), 3.18 (d, $J = 16.4$ Hz, 1H), 2.80 (d, $J = 16.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.7, 179.1, 170.2, 136.2, 135.4, 133.7, 129.0, 128.8, 128.1, 127.9, 127.5, 114.1, 113.9, 99.7, 99.5, 52.0, 47.2, 44.7, 44.4, 40.9. ^{19}F NMR (376 MHz, CDCl_3) δ : -136.6, -145.9. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{22}\text{F}_2\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 450.1511, found 450.1505.



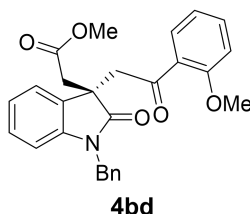
Methyl (*R*)-2-(1-benzyl-2-oxo-3-(2-oxo-2-(p-tolyl)ethyl)indolin-3-yl)acetate (4ba): Brown oil (42 mg, 98 % yield). HPLC: 90 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 17.838 min, t_r (minor) = 12.811 min. $[\alpha]_D^{20} = +12.4$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.77 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 7.6$ Hz, 2H), 7.34 (q, $J = 7.4$ Hz, 3H), 7.28 (d, $J = 7.0$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.16–7.10 (m, 1H), 6.92 (t, $J = 7.5$ Hz, 1H), 6.73 (d, $J = 7.8$ Hz, 1H), 5.17–4.83 (m, 2H), 4.07 (d, $J = 17.7$ Hz, 1H), 3.56 (d, $J = 24.0$ Hz, 4H), 3.16 (d, $J = 15.8$ Hz, 1H), 2.84 (d, $J = 15.8$ Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 195.5, 179.3, 170.5, 144.2, 143.7, 136.3, 134.1, 130.8, 129.3, 128.8, 128.4, 128.3, 127.5, 123.7, 122.4, 109.4, 51.8, 47.3, 44.4, 44.3, 41.2, 21.7. HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{26}\text{NO}_7^+$ ($\text{M}+\text{H}$) $^+$ 496.1755, found 496.1767.



Methyl(*R*)-2-(1-benzyl-3-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bb): Brown oil (46 mg, 93 % yield). HPLC: 88 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 15.511 min, tr (minor) = 10.143 min. $[\alpha]_D^{20} = +17.2$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.73 (d, $J = 8.5$ Hz, 2H), 7.35 (dd, $J = 12.0, 8.0$ Hz, 4H), 7.28–7.22 (m, 3H), 7.19 (d, $J = 7.3$ Hz, 1H), 7.07–7.00 (m, 1H), 6.86–6.79 (m, 1H), 6.65 (d, $J = 7.8$ Hz, 1H), 5.01–4.83 (m, 2H), 3.99 (d, $J = 17.8$ Hz, 1H), 3.47 (d, $J = 31.6$ Hz, 4H), 3.09 (d, $J = 15.8$ Hz, 1H), 2.77 (d, $J = 15.8$ Hz, 1H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.5, 179.2, 170.4, 157.1, 143.6, 136.2, 134.0, 130.8, 128.8, 128.3, 128.1, 127.5, 127.5, 125.5, 123.6, 122.3, 109.3, 51.7, 47.2, 44.4, 41.2, 35.1, 31.1. HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{32}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 470.2326, found 470.2319.

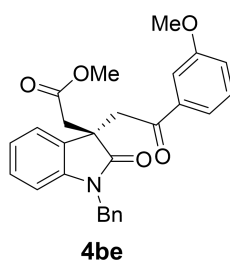


Methyl(*R*)-2-(1-benzyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bc): Brown oil (42 mg, 96 % yield). HPLC: 93 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 26.717 min, tr (minor) = 17.829 min. $[\alpha]_D^{20} = +20.6$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.85 (d, $J = 8.9$ Hz, 2H), 7.44 (d, $J = 7.2$ Hz, 2H), 7.39–7.30 (m, 3H), 7.28 (d, $J = 8.5$ Hz, 1H), 7.17–7.09 (m, 1H), 6.96–6.90 (m, 1H), 6.88 (d, $J = 8.9$ Hz, 2H), 6.73 (d, $J = 7.8$ Hz, 1H), 5.22–4.85 (m, 2H), 4.04 (d, $J = 17.5$ Hz, 1H), 3.84 (s, 3H), 3.53 (s, 3H), 3.19–2.82 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 194.3, 179.3, 170.5, 163.7, 143.7, 136.3, 130.9, 130.5, 129.7, 128.9, 128.8, 128.4, 127.5, 127.5, 123.7, 122.3, 113.8, 109.4, 55.6, 51.8, 47.3, 44.4, 44.1, 41.2. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_5^+$ ($\text{M}+\text{H}$) $^+$ 444.1805, found 444.1802.

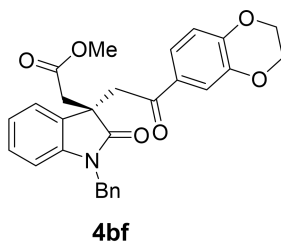


Methyl(*R*)-2-(1-benzyl-3-(2-(2-methoxyphenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bd): Brown oil (41 mg, 92 % yield). HPLC: 94 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 22.445 min, tr (minor) = 19.155 min. $[\alpha]_D^{20} = +12.4$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3)

δ : 7.52–7.46 (m, 2H), 7.45–7.38 (m, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.19–7.06 (m, 2H), 6.97–6.87 (m, 3H), 6.71 (d, J = 7.8 Hz, 1H), 5.09–4.92 (m, 2H), 4.04 (d, J = 18.1 Hz, 1H), 3.89 (s, 3H), 3.61 (d, J = 18.1 Hz, 1H), 3.49 (s, 3H), 3.17–2.86 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.8, 179.4, 170.4, 158.7, 143.8, 136.4, 133.9, 131.0, 130.5, 128.8, 128.2, 127.7, 127.6, 127.5, 123.6, 122.2, 120.7, 111.6, 109.2, 55.6, 51.7, 49.8, 47.6, 44.4, 41.3. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_5^+$ ($\text{M}+\text{H}$) $^+$ 444.1805, found 444.1802.

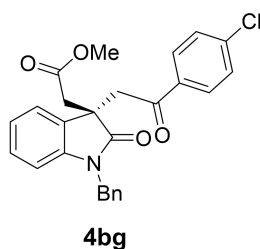


Methyl(*R*)-2-(1-benzyl-3-(2-(3-methoxyphenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4be): Brown oil (42 mg, 94 % yield). HPLC: 88 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 19.184 min, t_r (minor) = 13.412 min. $[\alpha]_{\text{D}}^{20}$ = +19.3 (c = 0.2, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.46 (dd, J = 13.6, 7.8 Hz, 3H), 7.36 (d, J = 9.4 Hz, 3H), 7.32 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.3 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.08 (dd, J = 8.2, 3.6 Hz, 1H), 6.96–6.90 (m, 1H), 6.75 (d, J = 7.8 Hz, 1H), 5.13–4.91 (m, 2H), 4.09 (d, J = 17.8 Hz, 1H), 3.80 (s, 3H), 3.60 (d, J = 17.8 Hz, 1H), 3.53 (s, 3H), 3.15 (d, J = 15.8 Hz, 1H), 2.84 (d, J = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 195.8, 179.2, 170.4, 159.8, 143.7, 137.9, 136.2, 130.7, 129.6, 128.8, 128.4, 127.6, 127.5, 123.7, 122.4, 120.9, 120.1, 112.1, 109.4, 55.5, 51.8, 47.3, 44.6, 44.4, 41.3. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_5^+$ ($\text{M}+\text{H}$) $^+$ 444.1805, found 444.1802.

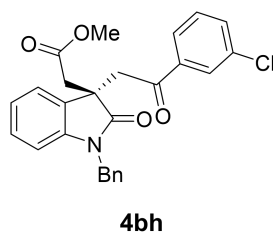


Methyl(*R*)-2-(1-benzyl-3-(2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bf): Brown oil (46 mg, 97 % yield). HPLC: 88 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 34.989 min, t_r (minor) = 24.496 min. $[\alpha]_{\text{D}}^{20}$ = -83.2 (c = 0.2, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.45 (d, J = 5.3 Hz, 2H), 7.43–7.35 (m, 3H), 7.32 (d, J = 4.4 Hz, 1H), 7.31–7.27 (m, 2H), 7.12 (d, J = 7.8 Hz, 1H), 6.95–6.89 (m, 1H), 6.85 (d, J = 9.1 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 5.02 (q, J = 15.8 Hz, 2H), 4.30–4.27 (m, 2H), 4.26–4.23 (m, 2H), 4.01 (d, J = 17.7 Hz, 1H), 3.52 (s, 4H), 3.15 (d, J = 15.9 Hz, 1H), 2.83 (d, J = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.1, 179.2, 170.3, 148.1, 143.5, 143.2, 136.1, 130.7, 130.3, 128.8, 128.7, 128.2, 127.4, 127.4, 123.5, 122.2, 117.6, 117.1, 109.2, 64.6, 64.0, 51.6, 47.2, 44.3, 44.0, 41.1. HRMS (APCI) m/z

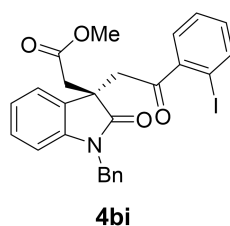
calcd for $C_{28}H_{26}NO_6^+$ (M+H) $^+$ 472.1755, found 472.1748.



Methyl(*R*)-2-(1-benzyl-3-(2-(4-chlorophenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bg): Brown oil (44 mg, 98 % yield). HPLC: 80 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 13.907 min, tr (minor) = 9.754 min. $[\alpha]_D^{20} = +6.7$ (c = 0.2, CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) δ : 7.81 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 6.7 Hz, 2H), 7.40–7.35 (m, 3H), 7.31 (dd, J = 12.3, 3.6 Hz, 3H), 7.14 (d, J = 7.7 Hz, 1H), 6.94 (s, 1H), 6.75 (d, J = 7.9 Hz, 1H), 5.01 (q, J = 15.8 Hz, 2H), 4.10 (d, J = 17.8 Hz, 1H), 3.58 (d, J = 24.9 Hz, 4H), 3.12 (d, J = 15.9 Hz, 1H), 2.82 (d, J = 15.8 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ : 194.7, 179.0, 170.4, 143.6, 139.9, 136.1, 134.8, 130.6, 129.6, 129.6, 128.9, 128.9, 128.8, 128.5, 127.6, 127.5, 123.6, 122.4, 109.4, 51.8, 47.2, 44.4, 44.2, 41.2. HRMS (APCI) m/z calcd for $C_{23}H_{23}ClNO_2^+$ (M+H) $^+$ 448.1310, found 448.1304.

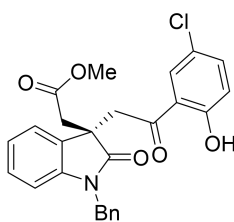


Methyl(*R*)-2-(1-benzyl-3-(2-(3-chlorophenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bh): Brown oil (42 mg, 94 % yield). HPLC: 94 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 22.629 min, tr (minor) = 9.137 min. $[\alpha]_D^{20} = +9.7$ (c = 0.2, CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) δ : 7.81 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 6.7 Hz, 2H), 7.40–7.35 (m, 3H), 7.31 (dd, J = 12.3, 3.6 Hz, 3H), 7.14 (d, J = 7.7 Hz, 1H), 6.94 (s, 1H), 6.75 (d, J = 7.9 Hz, 1H), 5.01 (q, J = 15.8 Hz, 2H), 4.10 (d, J = 17.8 Hz, 1H), 3.58 (d, J = 24.9 Hz, 4H), 3.12 (d, J = 15.9 Hz, 1H), 2.82 (d, J = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 194.7, 179.0, 170.4, 143.6, 139.9, 136.1, 134.8, 130.6, 129.6, 129.6, 128.9, 128.9, 128.8, 128.5, 127.6, 127.5, 123.6, 122.4, 109.4, 51.8, 47.2, 44.4, 44.2, 41.2. HRMS (APCI) m/z calcd for $C_{23}H_{23}ClNO_2^+$ (M+H) $^+$ 448.1310, found 448.1304.



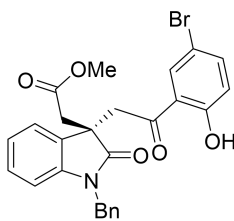
Methyl(*R*)-2-(1-benzyl-3-(2-(2-iodophenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate

(4bi): Brown oil (48 mg, 90 % yield). HPLC: 91 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 15.064 min, tr (minor) = 10.944 min. $[\alpha]_{\text{D}}^{20} = -8.5$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.87 (d, $J = 9.7$ Hz, 2H), 7.52 (d, $J = 6.1$ Hz, 1H), 7.44 (d, $J = 5.0$ Hz, 2H), 7.41 (s, 1H), 7.37–7.31 (m, 3H), 7.28 (d, $J = 5.8$ Hz, 1H), 7.17–7.11 (m, 1H), 6.96–6.90 (m, 1H), 6.74 (d, $J = 7.8$ Hz, 1H), 5.11–4.94 (m, 2H), 4.11 (d, $J = 17.8$ Hz, 1H), 3.61 (d, $J = 17.9$ Hz, 1H), 3.54 (s, 3H), 3.16 (d, $J = 15.9$ Hz, 1H), 2.84 (d, $J = 15.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 195.8, 179.1, 170.3, 143.5, 136.4, 136.1, 133.3, 130.6, 128.7, 128.5, 128.3, 128.0, 127.4, 127.4, 123.6, 122.3, 109.3, 51.7, 47.1, 44.3, 41.1. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{INO}_4^+$ ($\text{M}+\text{H}$) $^+$ 540.0666, found 540.0661.



4bj

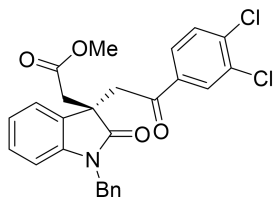
Methyl(*R*)-2-(1-benzyl-3-(2-(5-chloro-2-hydroxyphenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bj): Brown oil (43 mg, 92 % yield). HPLC: 86 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 31.288 min, tr (minor) = 26.050 min. $[\alpha]_{\text{D}}^{20} = +17.2$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 11.58 (s, 1H), 7.86 (d, $J = 2.4$ Hz, 1H), 7.51 (dd, $J = 8.9, 2.4$ Hz, 1H), 7.43 (d, $J = 9.7$ Hz, 2H), 7.38–7.27 (m, 6H), 7.21–7.15 (m, 2H), 6.99–6.93 (m, 1H), 6.81 (d, $J = 8.9$ Hz, 2H), 5.00 (d, $J = 2.9$ Hz, 2H), 4.18 (d, $J = 18.0$ Hz, 1H), 3.63 (d, $J = 38.8$ Hz, 4H), 3.06 (d, $J = 15.9$ Hz, 1H), 2.79 (d, $J = 15.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 201.1, 178.7, 170.3, 161.3, 143.6, 139.4, 135.9, 132.1, 130.2, 128.8, 128.7, 127.7, 127.7, 127.4, 123.5, 122.5, 120.7, 120.3, 110.7, 109.5, 51.9, 47.0, 44.4, 43.7, 41.5.; HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{ClNO}_5^+$ ($\text{M}+\text{H}$) $^+$ 464.1259, found 464.1071.



4bk

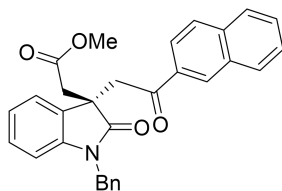
Methyl(*R*)-2-(1-benzyl-3-(2-(5-bromo-2-hydroxyphenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bk): Brown oil (47 mg, 93 % yield). HPLC: 92 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 30.289 min, tr (minor) = 26.471 min. $[\alpha]_{\text{D}}^{20} = +23.7$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 11.58 (s, 1H), 7.86 (d, $J = 2.4$ Hz, 1H), 7.51 (dd, $J = 8.9, 2.4$ Hz, 1H), 7.43 (d, $J = 6.9$ Hz, 2H), 7.34 (s, 2H), 7.29 (dd, $J = 6.7, 3.8$ Hz, 2H), 7.17 (d, $J = 7.8$ Hz, 1H), 6.99–6.93 (m, 1H), 6.83–6.77 (m, 2H), 5.00 (d, $J = 2.9$ Hz, 2H), 4.18 (d, $J = 18.0$ Hz, 1H), 3.65 (d, $J = 18.0$ Hz, 1H), 3.58 (s, 3H), 3.06 (d, $J = 15.9$ Hz, 1H), 2.79

(d, $J = 15.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 201.0, 178.5, 170.1, 161.2, 143.5, 139.3, 135.8, 132.0, 130.1, 128.7, 128.5, 127.6, 127.6, 123.4, 122.4, 120.6; 120.2, 110.5, 109.4, 51.8, 46.8, 44.3, 43.6, 41.3. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{BrNO}_5^+$ ($\text{M}+\text{H}$) $^+$ 508.0754, found 508.0750.



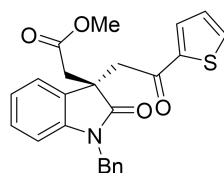
4bl

Methyl(*R*)-2-(1-benzyl-3-(2-(3,4-dichlorophenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bl): Brown oil (47 mg, 98 % yield). HPLC: 85 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 13.817 min, t_r (minor) = 9.785 min. $[\alpha]_{\text{D}}^{20} = +6.3$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.94 (d, $J = 2.0$ Hz, 1H), 7.69 (dd, $J = 8.4$, 2.1 Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 1H), 7.47–7.40 (m, 2H), 7.39–7.32 (m, 2H), 7.32–7.27 (m, 2H), 7.19–7.11 (m, 1H), 6.94 (t, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 5.12–4.92 (m, 2H), 4.09 (d, $J = 17.9$ Hz, 1H), 3.58 (d, $J = 14.4$ Hz, 4H), 3.09 (d, $J = 15.9$ Hz, 1H), 2.81 (d, $J = 15.9$ Hz, 1H), ^{13}C NMR (100 MHz, CDCl_3) δ : 193.8, 178.8, 170.4, 143.6, 138.1, 136.0, 136.0, 133.4, 130.8, 130.4, 130.2, 128.9, 128.6, 127.7, 127.5, 127.2, 123.6, 122.5, 109.5, 51.9, 47.2, 44.4, 44.2, 41.2. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{21}\text{Cl}_2\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 482.0920, found 482.0914.



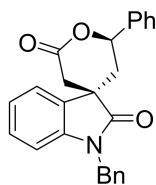
4bm

Methyl(*R*)-2-(1-benzyl-3-(2-(naphthalen-2-yl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (4bm): Orange oil (41 mg, 90 % yield). HPLC: 89 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, t_r (major) = 18.221 min, t_r (minor) = 13.396 min. $[\alpha]_{\text{D}}^{20} = +19.4$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (s, 1H), 7.91 (d, $J = 8.6$ Hz, 2H), 7.87–7.82 (m, 2H), 7.61–7.53 (m, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.41–7.32 (m, 3H), 7.29 (d, $J = 8.6$ Hz, 1H), 7.18–7.11 (m, 1H), 6.98–6.89 (m, 1H), 6.76 (d, $J = 7.8$ Hz, 1H), 5.04 (d, $J = 24.9$ Hz, 2H), 4.26 (d, $J = 17.7$ Hz, 1H), 3.74 (d, $J = 17.7$ Hz, 1H), 3.56 (s, 3H), 3.22 (d, $J = 15.8$ Hz, 1H), 2.89 (d, $J = 15.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 195.8, 179.3, 170.5, 143.7, 136.2, 135.7, 133.9, 132.5, 130.8, 130.0, 129.7, 128.8, 128.7, 128.5, 128.5, 127.8, 127.6, 127.5, 126.9, 123.8, 123.7, 122.4, 109.4, 51.8, 47.4, 44.5, 44.5, 41.3. HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{26}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 464.1856, found 464.1851.



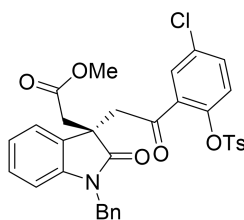
4bn

Methyl(*R*)-2-(1-benzyl-2-oxo-3-(2-oxo-2-(thiophen-2-yl)ethyl)indolin-3-yl)acetate (4bn): Orange oil (40 mg, 96 % yield). HPLC: 92 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 19.681 min, tr (minor) = 16.439 min. $[\alpha]_D^{20} = +36.9$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.61 (d, $J = 3.9$ Hz, 1H), 7.52 (d, $J = 5.0$ Hz, 1H), 7.34 (d, $J = 7.5$ Hz, 2H), 7.28 (d, $J = 7.5$ Hz, 2H), 7.20 (d, $J = 10.0$ Hz, 2H), 7.07 (d, $J = 7.7$ Hz, 1H), 7.03–6.98 (m, 1H), 6.90–6.83 (m, 1H), 6.65 (d, $J = 7.8$ Hz, 1H), 5.04–4.82 (m, 2H), 3.88 (d, $J = 17.1$ Hz, 1H), 3.45 (s, 3H), 3.11 (d, $J = 16.0$ Hz, 1H), 2.93 (d, $J = 13.0$ Hz, 2H), 2.81 (d, $J = 16.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 188.8, 178.9, 170.3, 143.8, 143.6, 136.1, 134.1, 132.4, 130.4, 128.8, 128.5, 128.2, 127.6, 127.5, 123.9, 122.4, 109.4, 62.1, 51.8, 47.4, 44.9, 44.4, 40.9, 37.2, 34.2, 14.1. HRMS (APCI) m/z calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 420.1264, found 420.1258.



5a

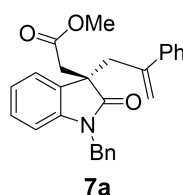
(3*R*,6'*R*)-1-benzyl-6'-phenyl-5',6'-dihydrospiro[indoline-3,4'-pyran]-2,2'(3'*H*)-dione (5a): Yellow oil (31 mg, 86 % yield). dr>20:1. HPLC: 93 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 13.245 min, tr (minor) = 10.958 min. $[\alpha]_D^{20} = +49.3$ ($c = 0.2$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.29 (d, $J = 3.9$ Hz, 6H), 7.25–7.13 (m, 6H), 7.08–7.01 (m, 1H), 6.72 (d, $J = 7.8$ Hz, 1H), 4.86 (d, $J = 15.7$ Hz, 2H), 4.63 (d, $J = 15.6$ Hz, 1H), 3.52 (d, $J = 6.2$ Hz, 1H), 3.42 (d, $J = 6.6$ Hz, 1H), 2.49 (dt, $J = 13.9, 7.0$ Hz, 1H), 2.30 (dd, $J = 14.6, 3.8$ Hz, 1H), 2.26 – 2.10 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 181.3, 144.0, 142.4, 135.7, 132.0, 128.9, 128.4, 128.3, 127.8, 127.7, 127.4, 126.0, 123.3, 123.1, 109.7, 71.3, 58.9, 50.0, 46.6, 44.1, 39.6. HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{22}\text{NO}_3^+$ ($\text{M}+\text{H}$) $^+$ 384.1594, found 384.1590.



6a

Methyl(*R*)-2-(1-benzyl-3-(2-(5-chloro-2-(tosyloxy)phenyl)-2-oxoethyl)-2-oxoindolin-3-yl)acetate (6a): White solid (31 mg, 90 % yield). Mp 72.1–73.9 °C. HPLC: 94 %

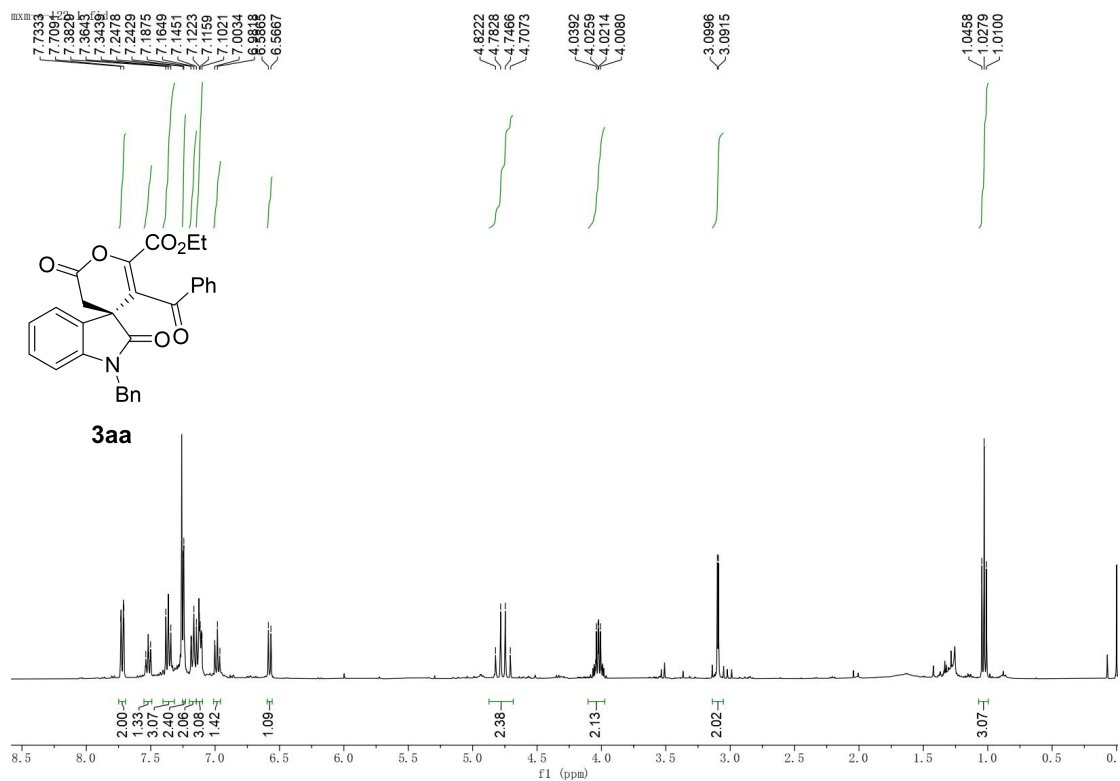
ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 14.902 min, tr (minor) = 10.833 min. $[\alpha]_{\text{D}}^{20} = +45.2$ (c = 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ : 7.58 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.36–7.32 (m, 3H), 7.31–7.26 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.17–7.11 (m, 2H), 6.92 (td, *J* = 7.6, 1.1 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.03–4.93 (m, 2H), 4.09 (d, *J* = 6.7 Hz, 1H), 3.91 (d, *J* = 17.9 Hz, 1H), 3.51 (s, 3H), 2.98 (d, *J* = 15.8 Hz, 1H), 2.81 (d, *J* = 15.8 Hz, 1H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 195.0, 170.0, 145.1, 136.1, 133.1, 132.7, 130.2, 130.1, 129.9, 128.8, 128.7, 128.5, 127.5, 124.7, 123.7, 122.4, 109.3, 51.8, 48.5, 47.3, 44.4, 41.3, 21.9, 19.3. HRMS (APCI) *m/z* calcd for C₃₃H₂₉ClNO₇S⁺ (M+H)⁺ 618.1348, found 618.1350.



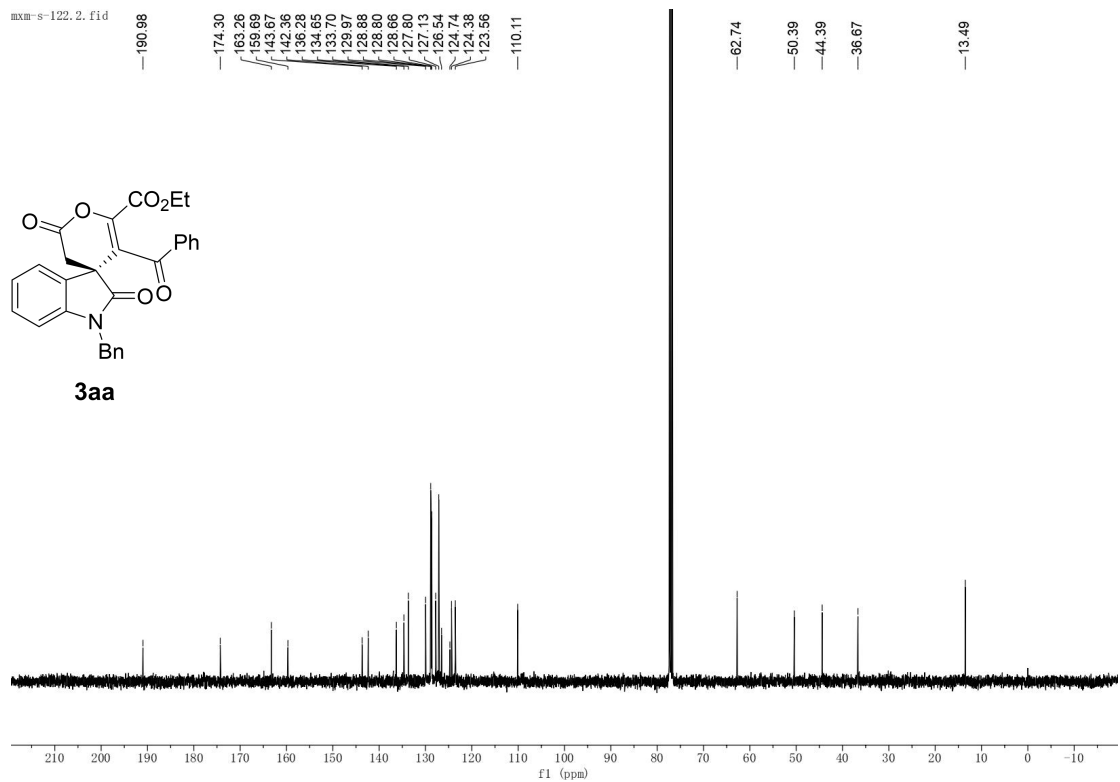
Methyl(*R*)-2-(1-benzyl-2-oxo-3-(2-phenylallyl)indolin-3-yl)acetate (7a): Orange oil (36 mg, 90 % yield). HPLC: 92 % ee (Chiralpak IC column, 254 nm, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, tr (major) = 35.729 min, tr (minor) = 13.132 min. $[\alpha]_{\text{D}}^{20} = +38.5$ (c = 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ : 7.87 (d, *J* = 8.2 Hz, 2H), 7.57–7.50 (m, 1H), 7.49–7.38 (m, 4H), 7.38–7.31 (m, 3H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.177.09 (m, 1H), 6.97–6.89 (m, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.10–4.94 (m, 2H), 4.11 (d, *J* = 17.8 Hz, 1H), 4.00 (dd, *J* = 7.1, 5.5 Hz, 2H), 3.61 (d, *J* = 17.8 Hz, 1H), 3.14 (d, *J* = 15.7 Hz, 1H), 2.83 (d, *J* = 15.7 Hz, 1H), 1.08 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 195.9, 179.2, 169.9, 143.7, 136.6, 136.2, 133.4, 130.8, 128.8, 128.6, 128.4, 128.1, 127.6, 127.5, 123.7, 122.3, 109.4, 60.8, 47.3, 44.5, 44.4, 41.5, 14.1. HRMS (APCI) *m/z* calcd for C₂₇H₂₆NO₃⁺ (M+H)⁺ 412.1907, found 412.1904.

VIII.NMR Spectrum

^1H NMR-**3aa** (400 MHz, CD_3Cl_3)

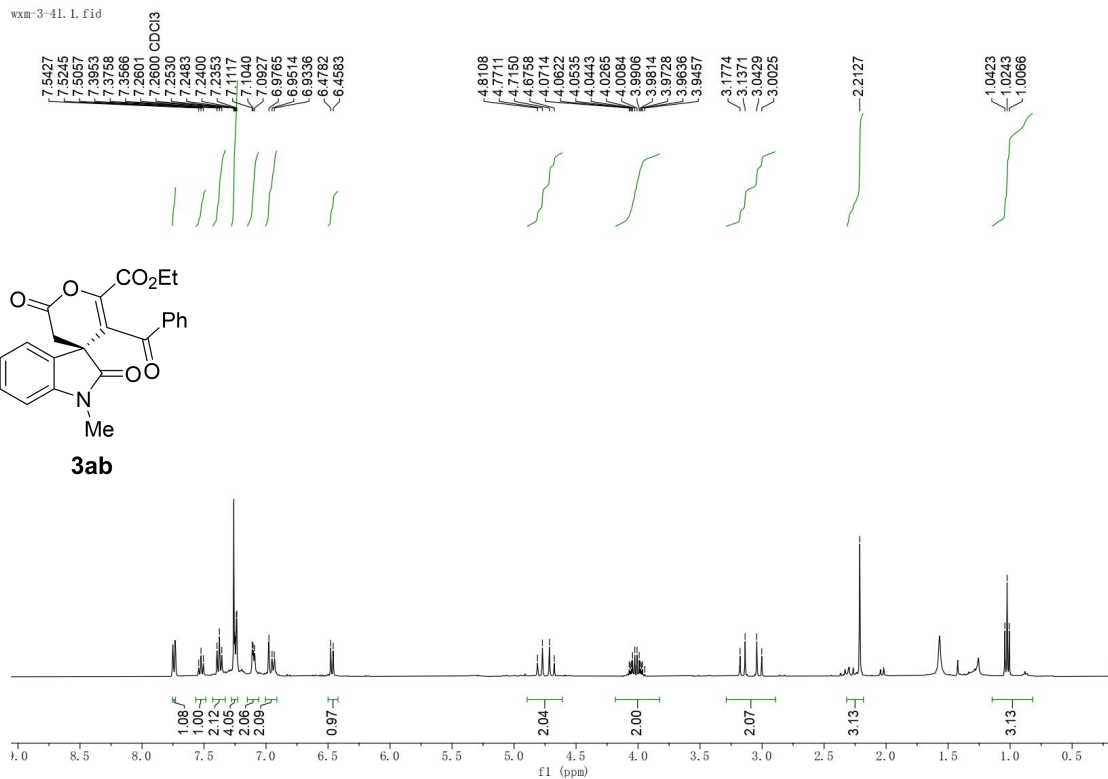


^{13}C NMR-**3aa** (100 MHz, CD_3Cl_3)



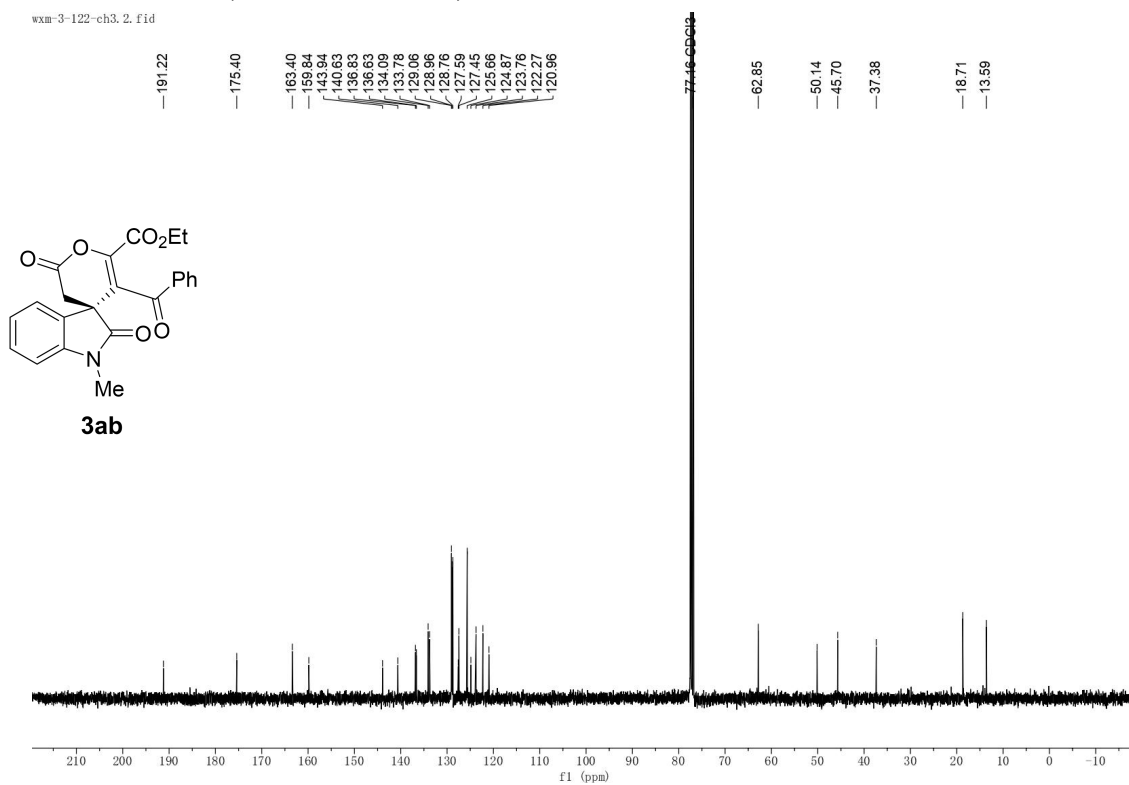
¹H NMR-**3ab** (400 MHz, CDCl₃)

wxm-3-41.1.fid



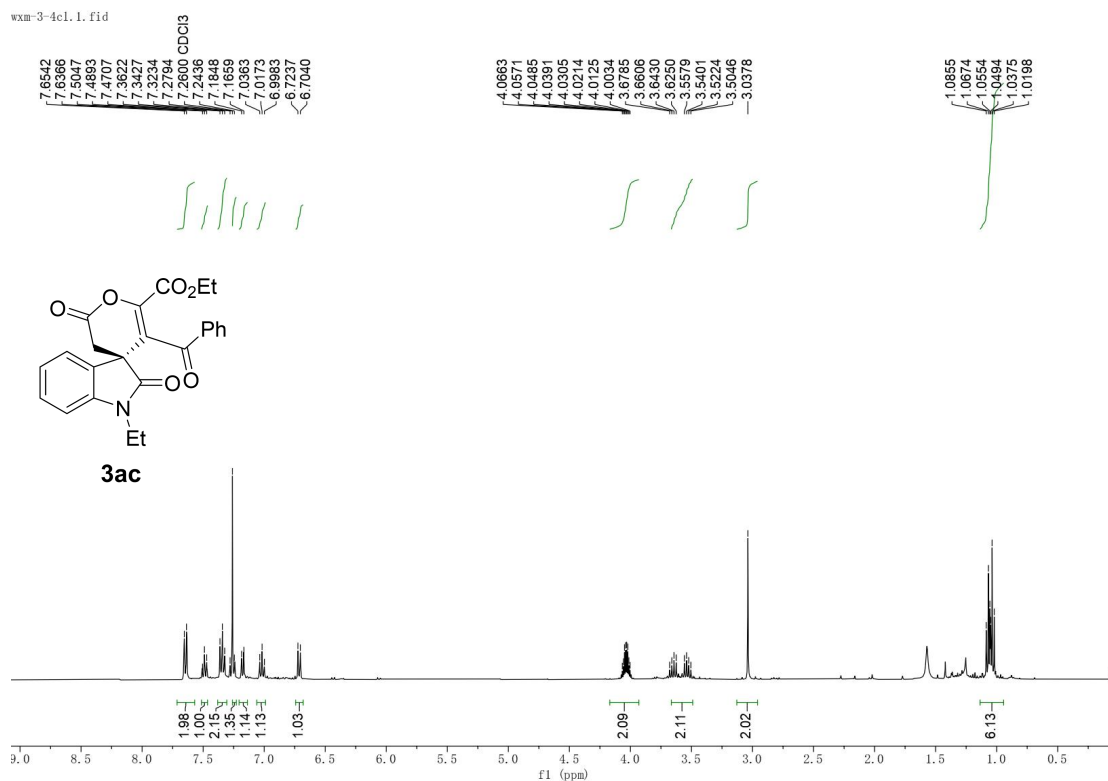
¹³C NMR-**3ab** (100 MHz, CDCl₃)

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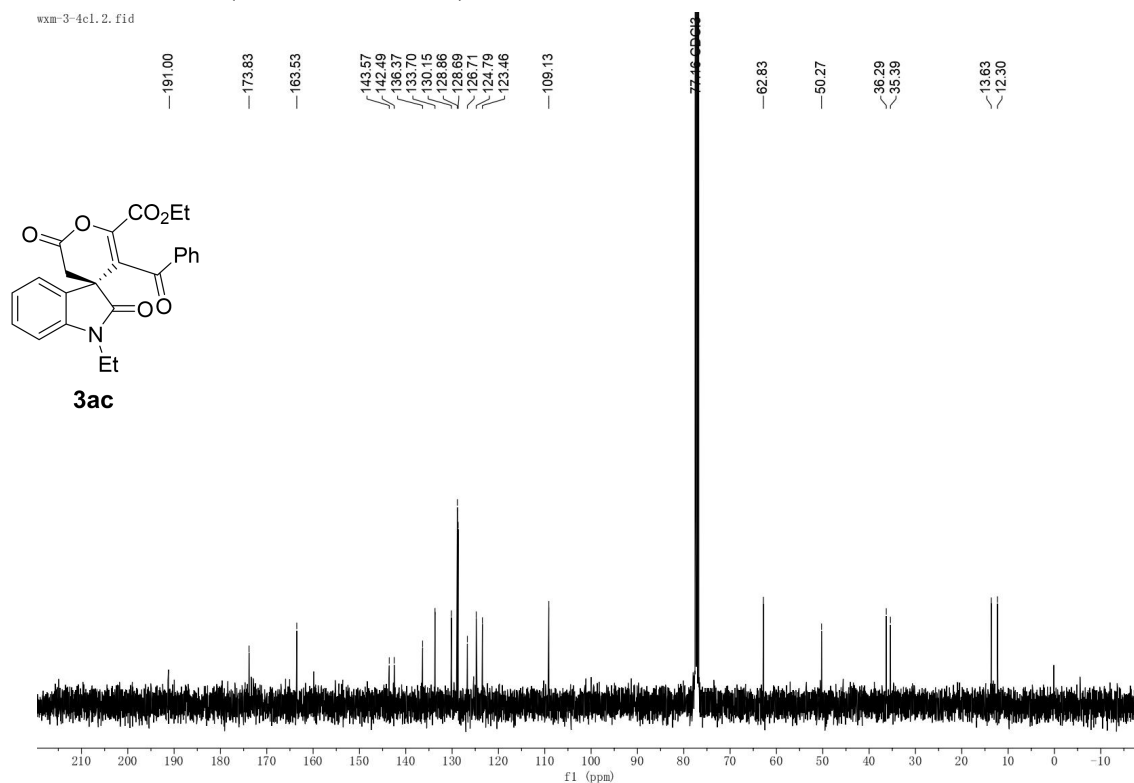
¹H NMR-**3ac** (400 MHz, CDCl₃)

wxm-3-4cl.1.fid

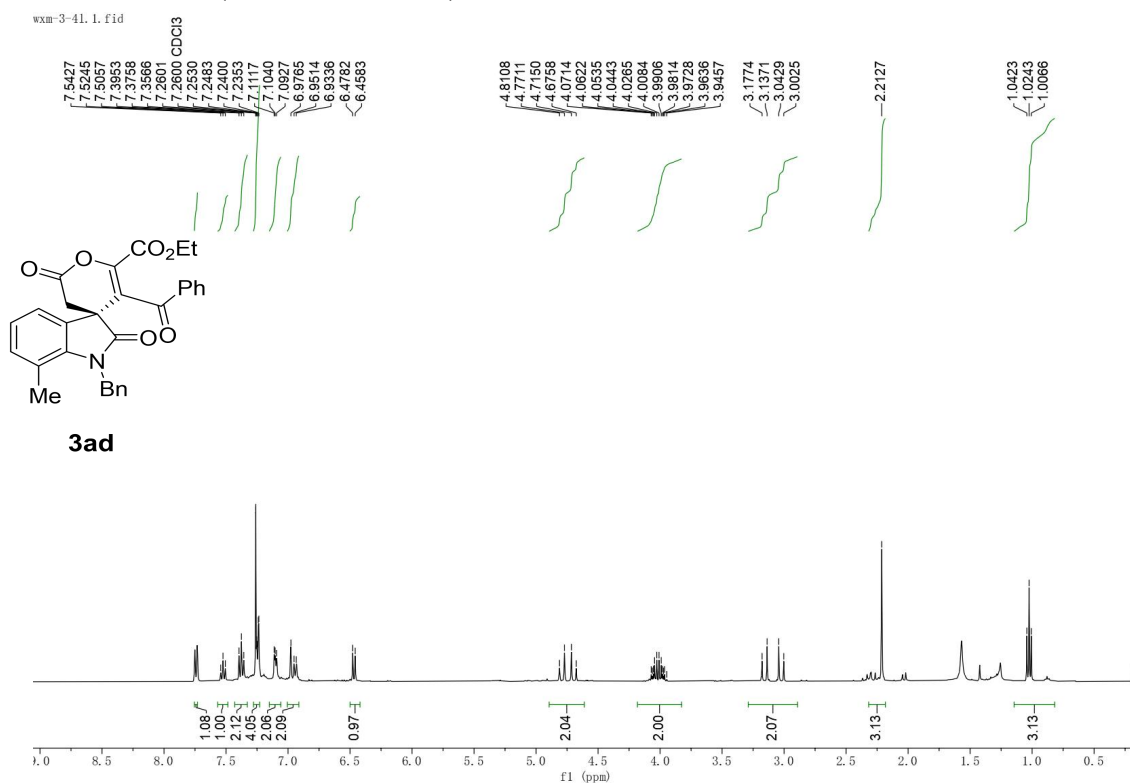


¹³C NMR-**3ac** (100 MHz, CDCl₃)

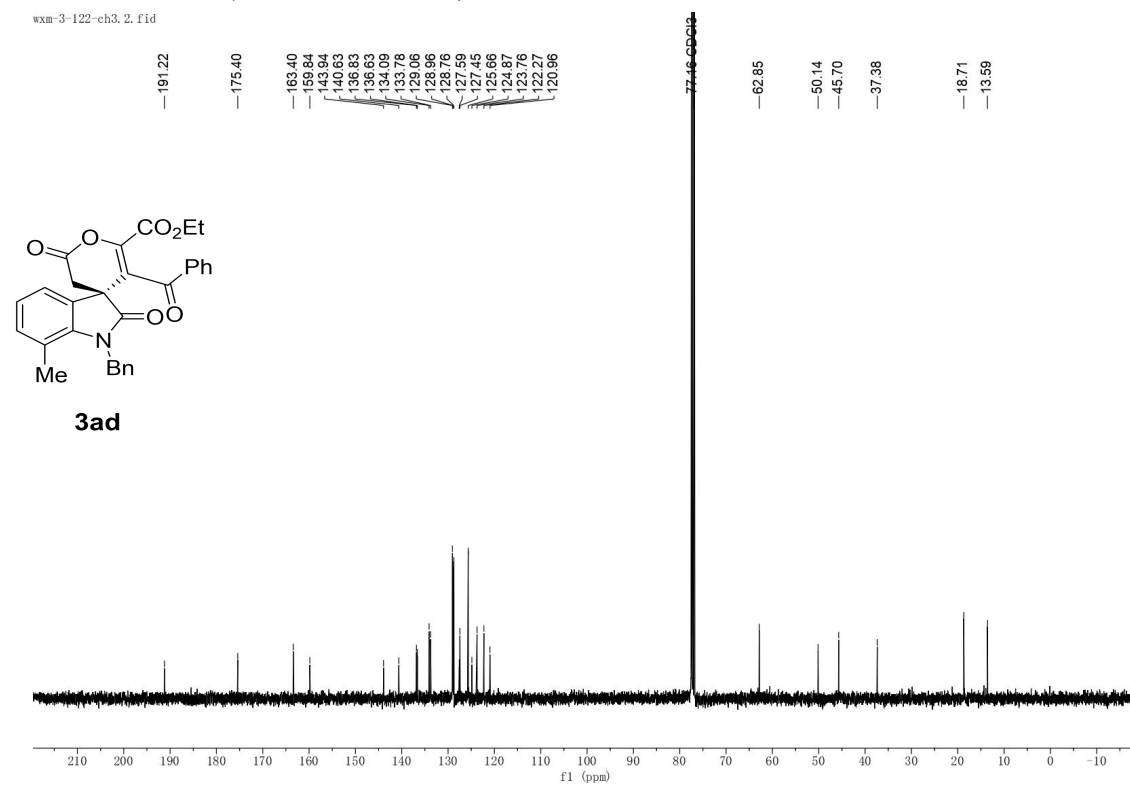
wxm-3-4cl.2.fid



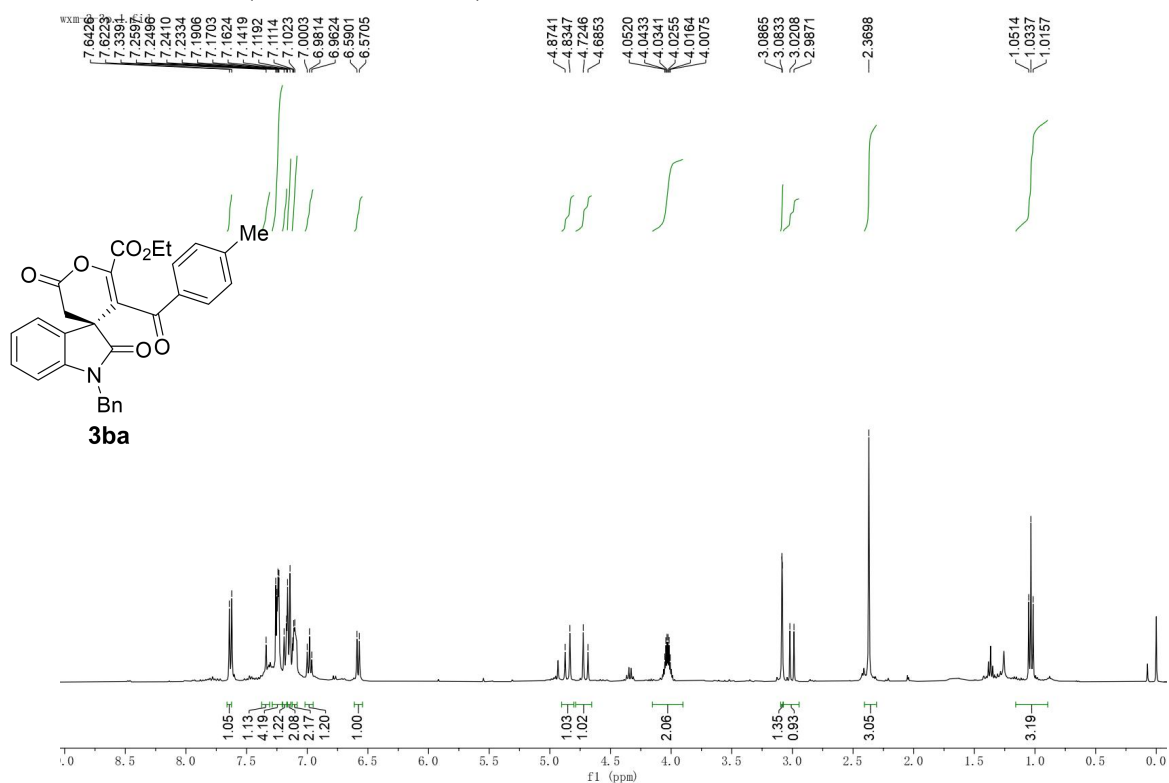
¹H NMR-**3ad** (400 MHz, CDCl₃)



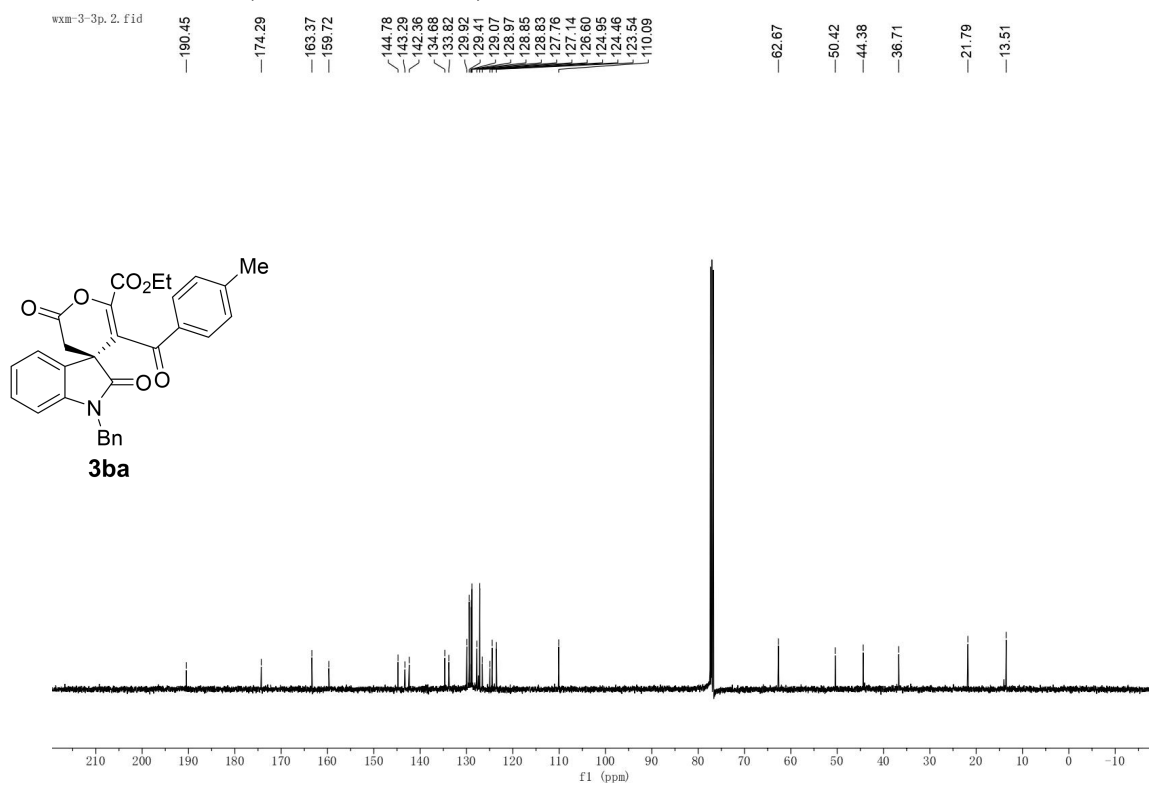
¹³C NMR-**3ad** (100 MHz, CDCl₃)



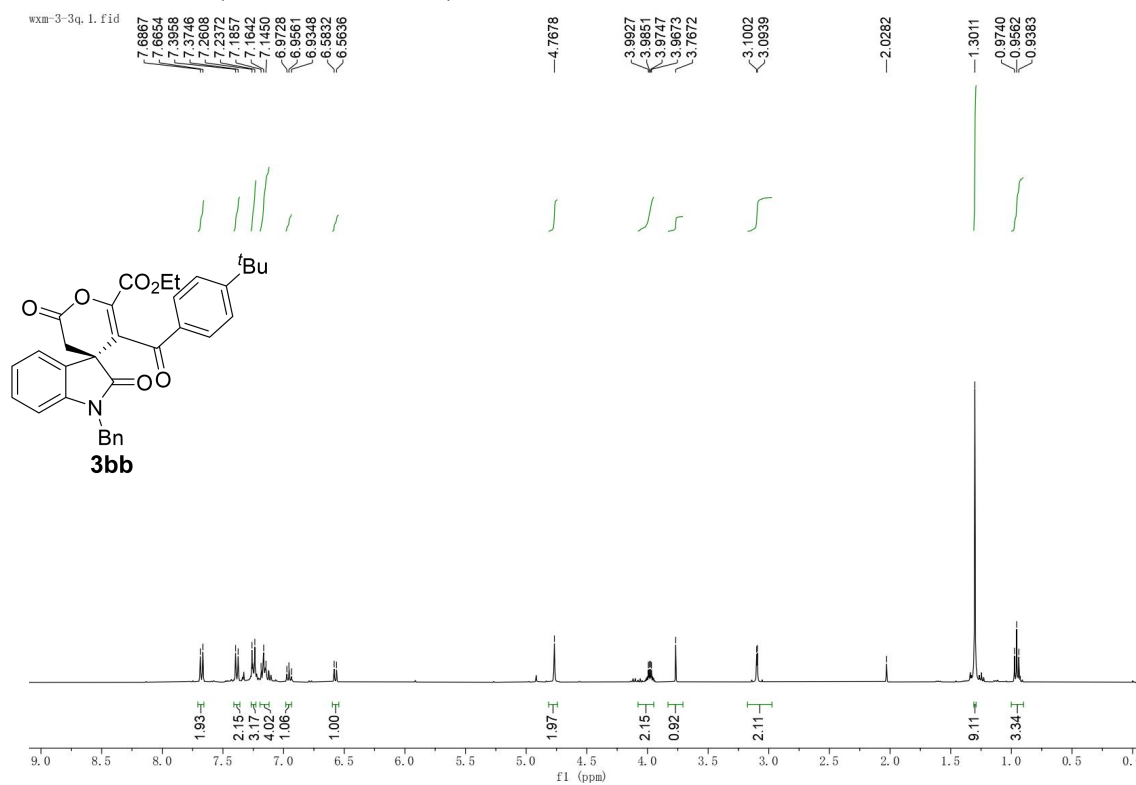
¹H NMR-**3ba** (400 MHz, CDCl₃)



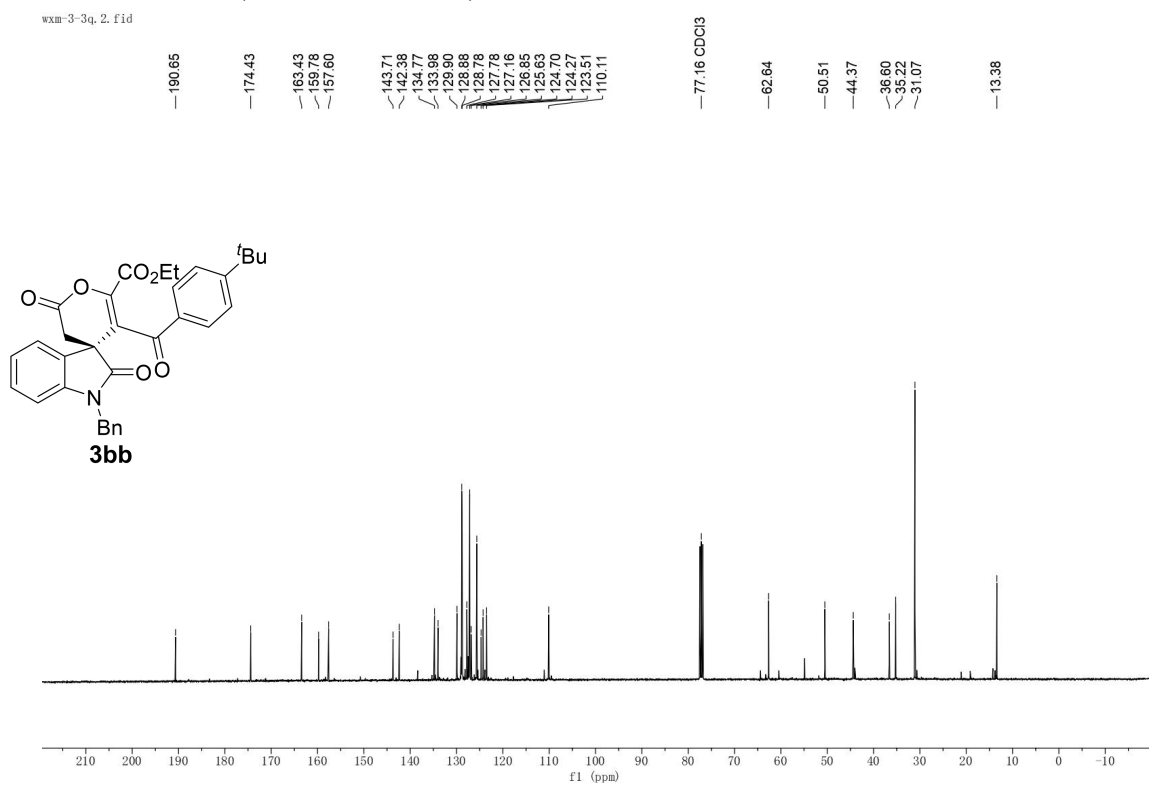
¹³C NMR-**3ba** (100 MHz, CDCl₃)



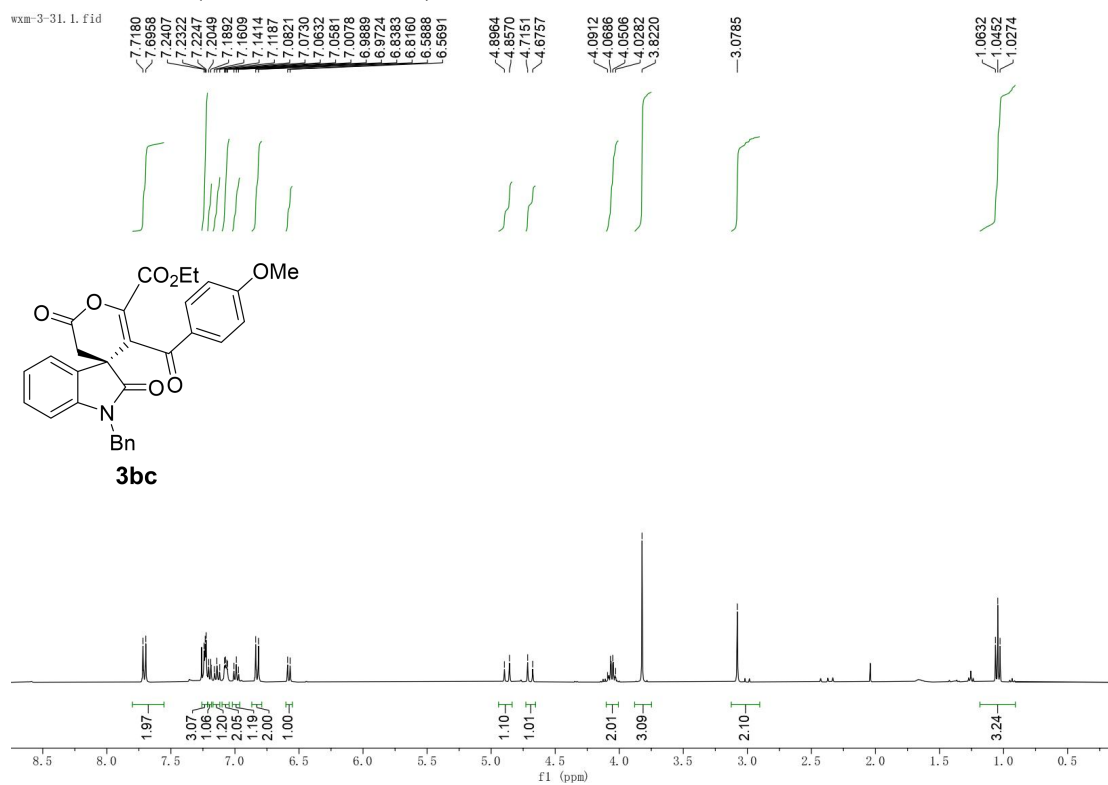
¹H NMR-**3bb** (400 MHz, CDCl₃)



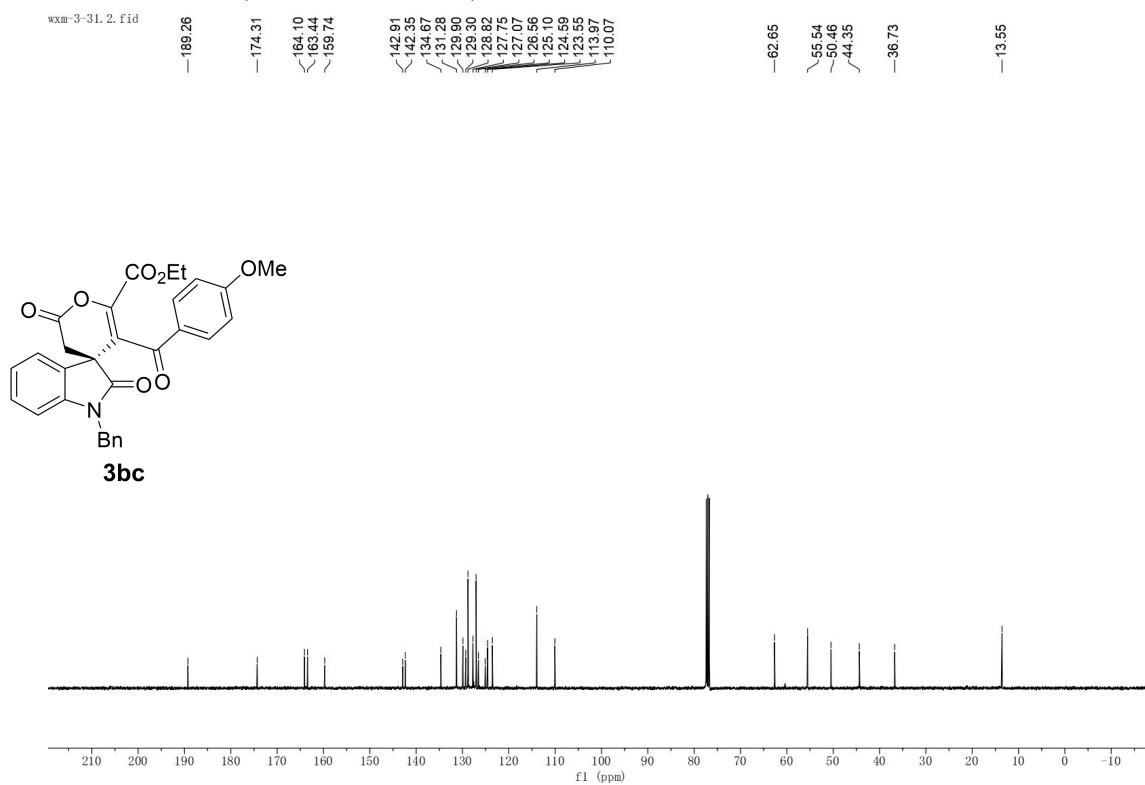
¹³C NMR-**3bb** (100 MHz, CDCl₃)



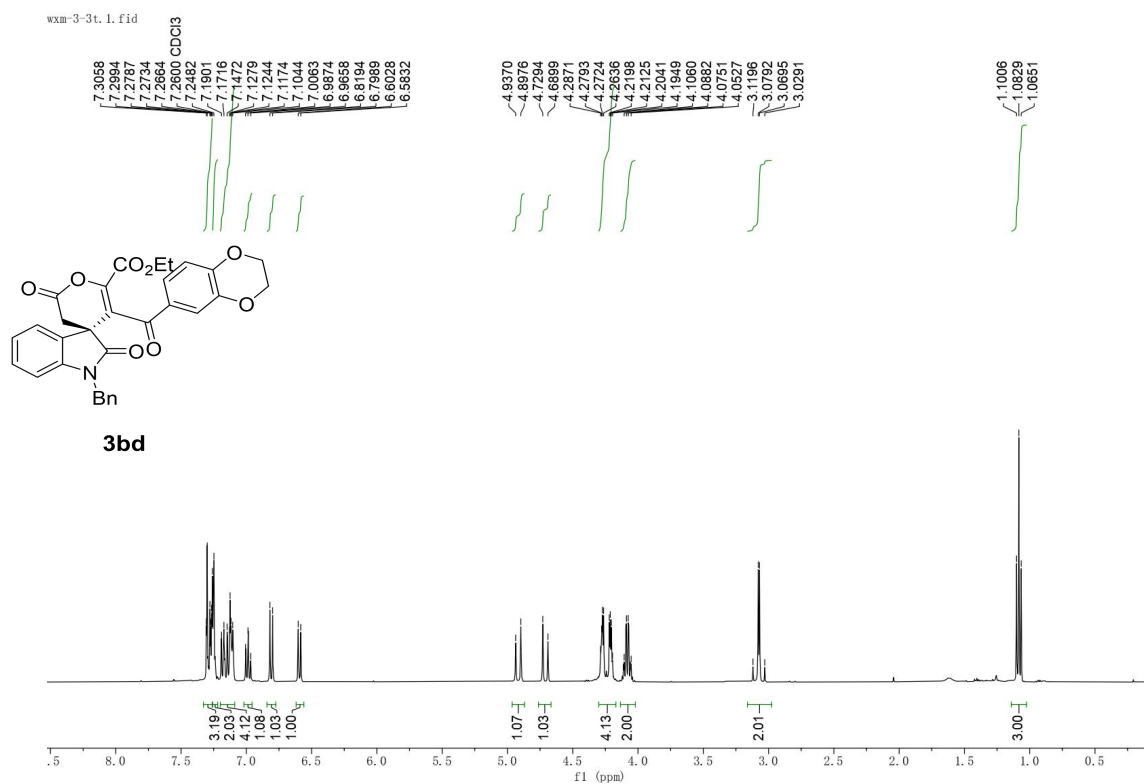
¹H NMR-**3bc** (400 MHz, CDCl₃)



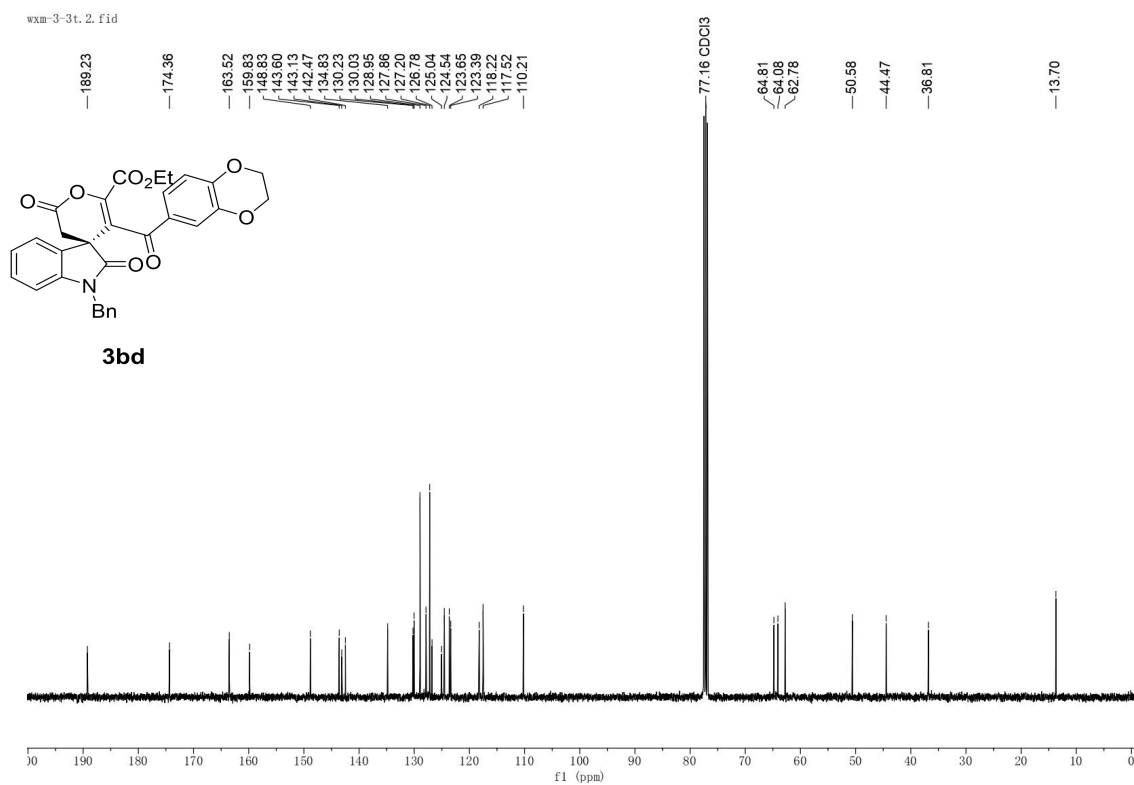
¹³C NMR-**3bc** (100 MHz, CDCl₃)



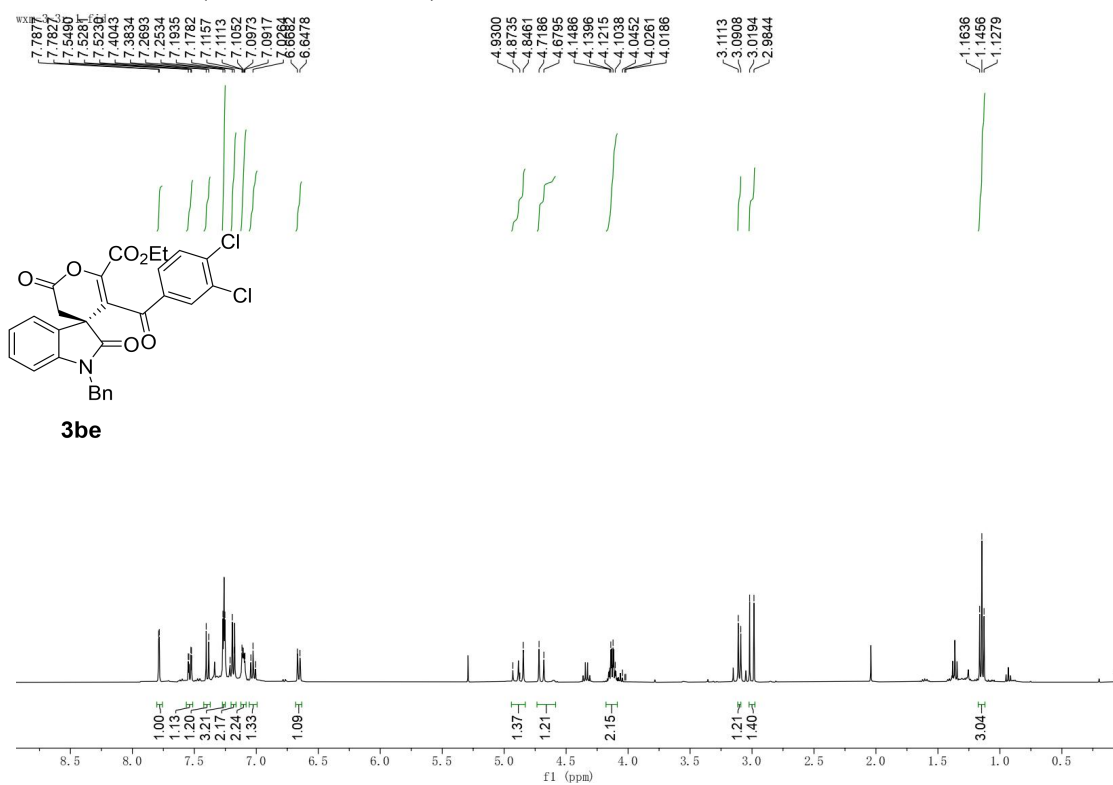
¹H NMR-**3bd** (400 MHz, CDCl₃)



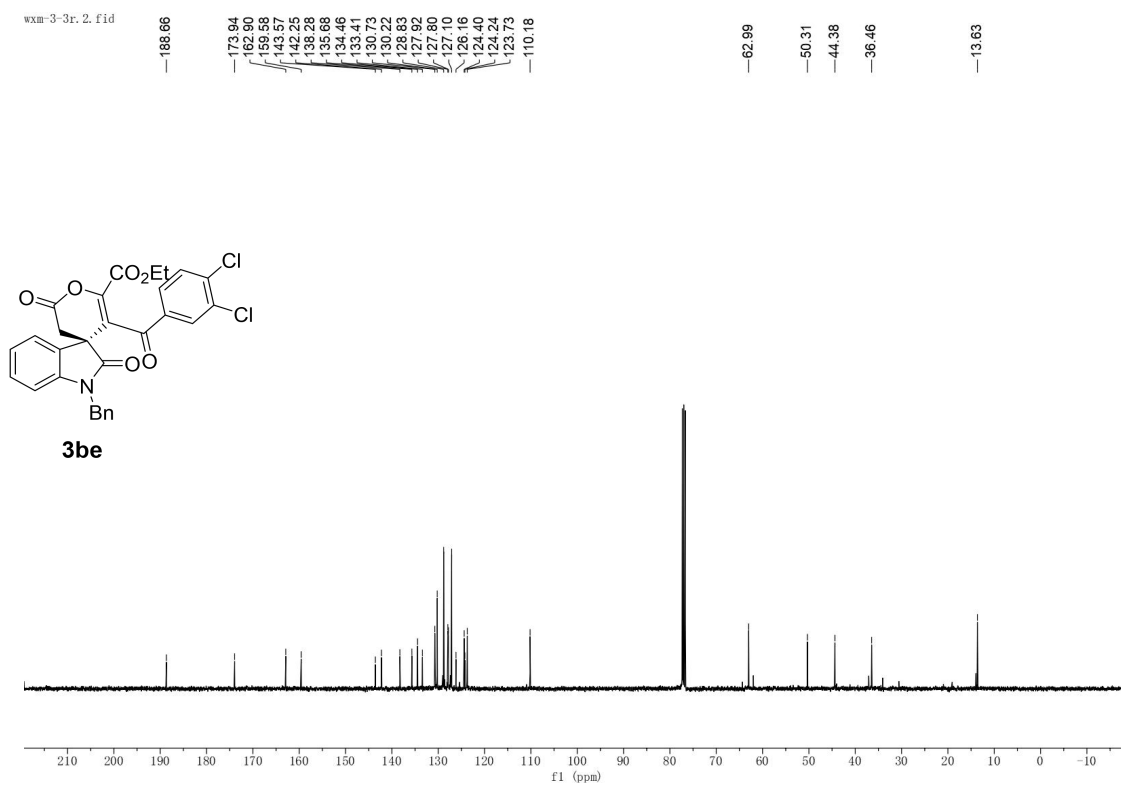
¹³C NMR-**3bd** (100 MHz, CDCl₃)



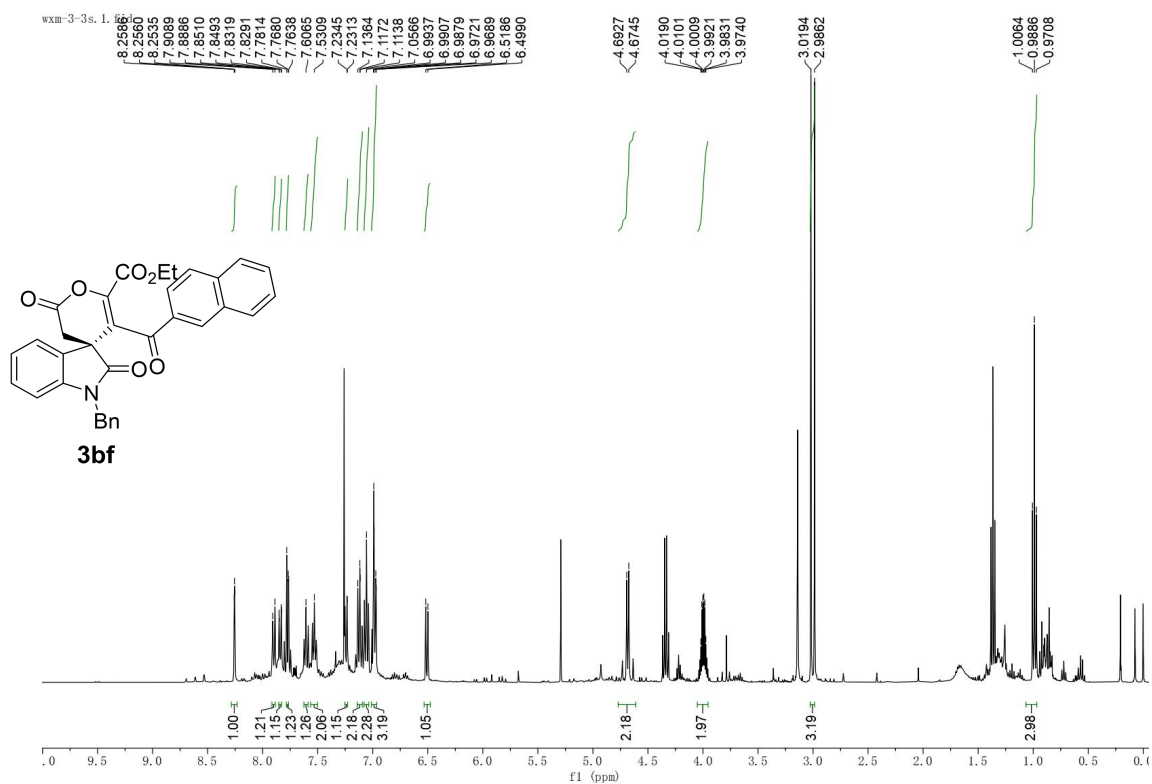
¹H NMR-**3be** (400 MHz, CDCl₃)



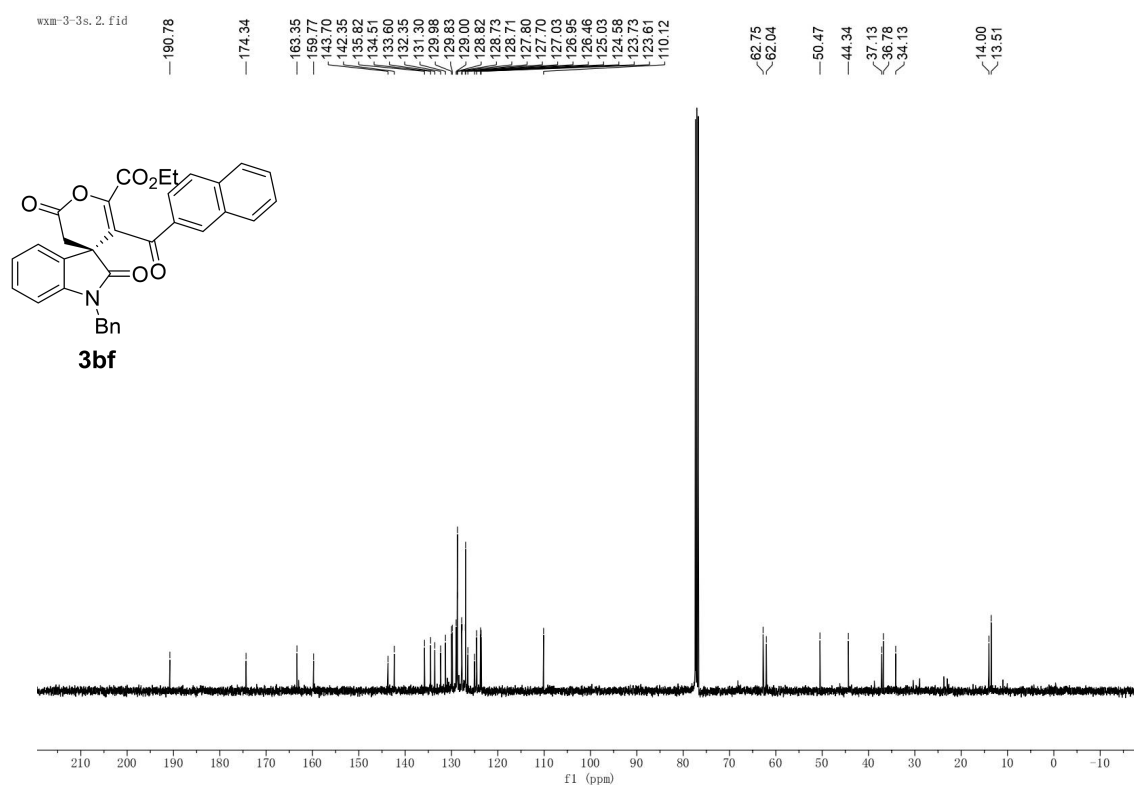
¹³C NMR-**3be** (100 MHz, CDCl₃)



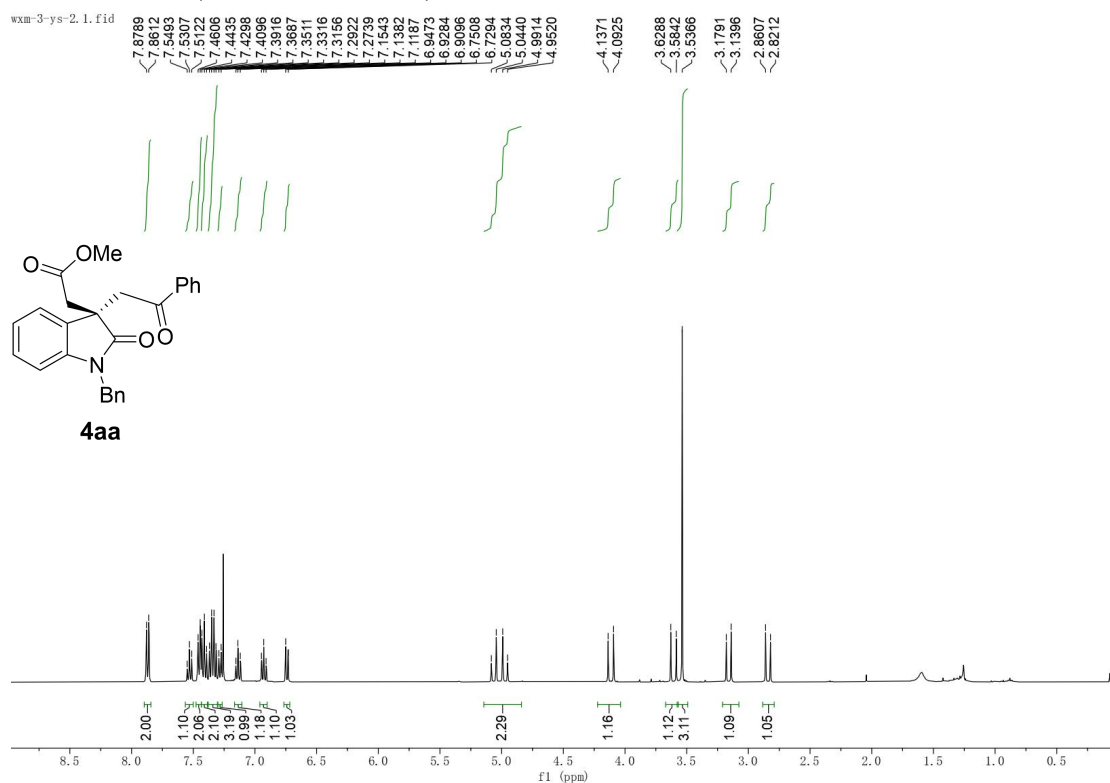
¹H NMR-**3bf** (400 MHz, CDCl₃)



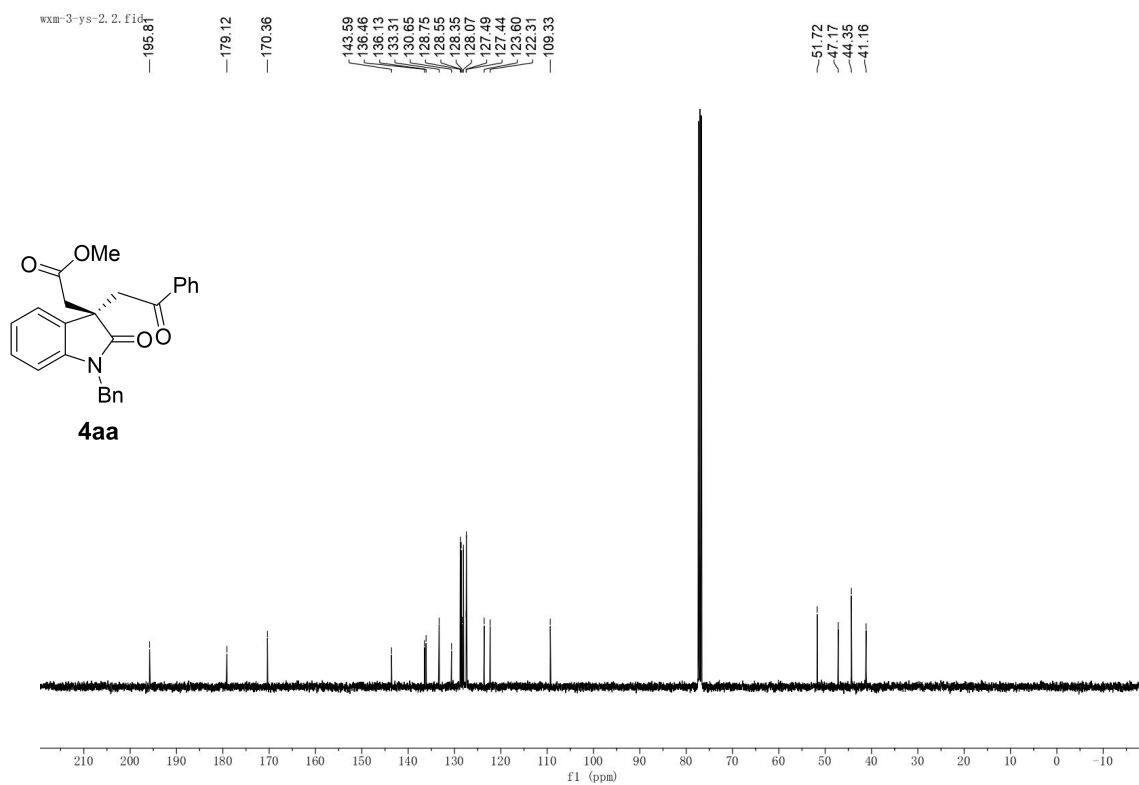
¹³C NMR-**3bf** (100 MHz, CDCl₃)



¹H NMR-4aa (400 MHz, CDCl₃)

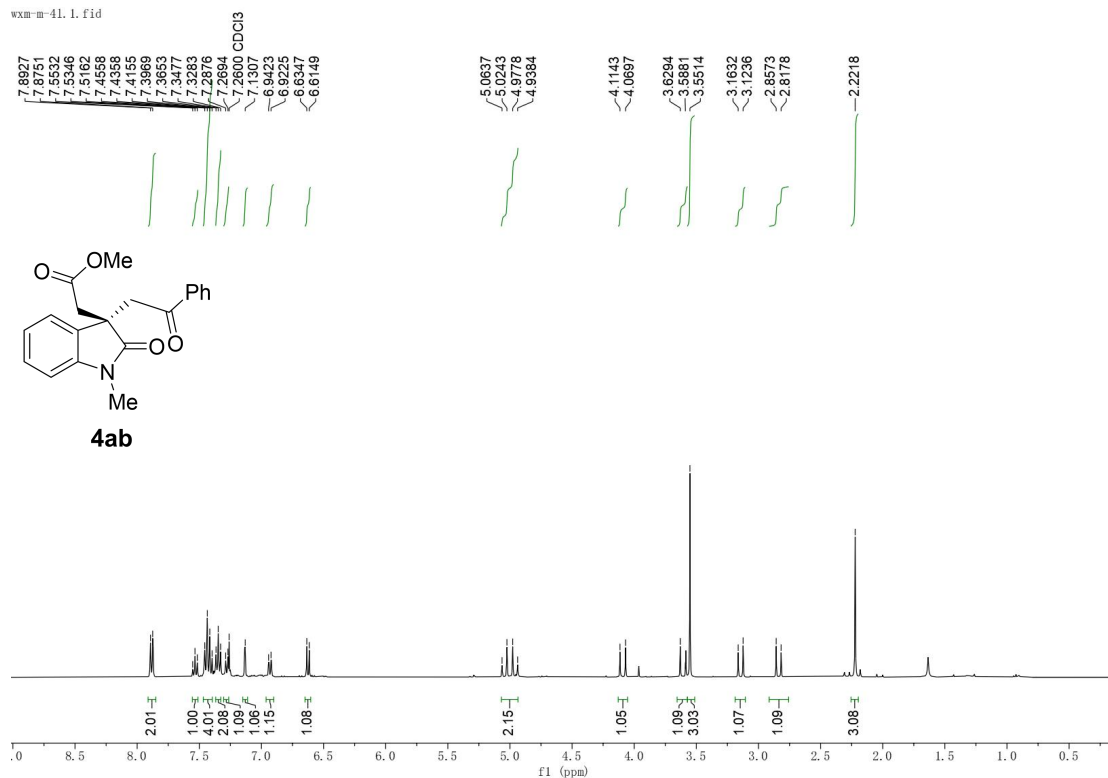


¹³C NMR-4aa (100 MHz, CDCl₃)



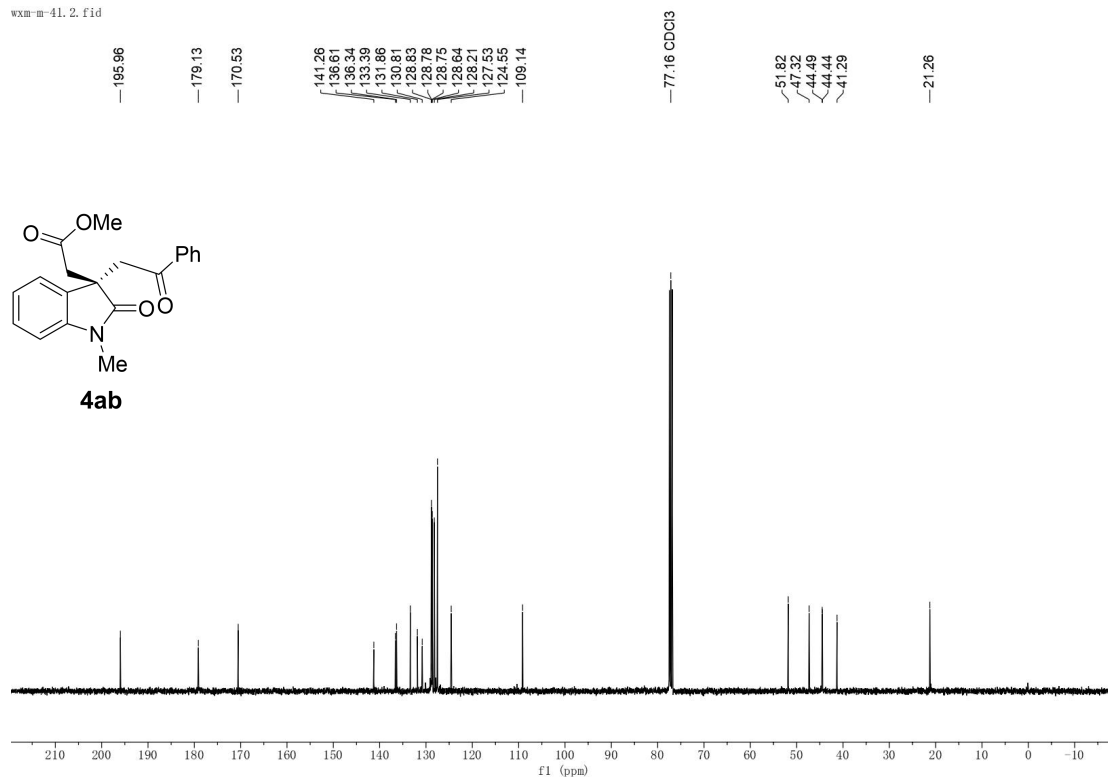
¹H NMR-**4ab** (400 MHz, CDCl₃)

wxm-m-41.1.fid



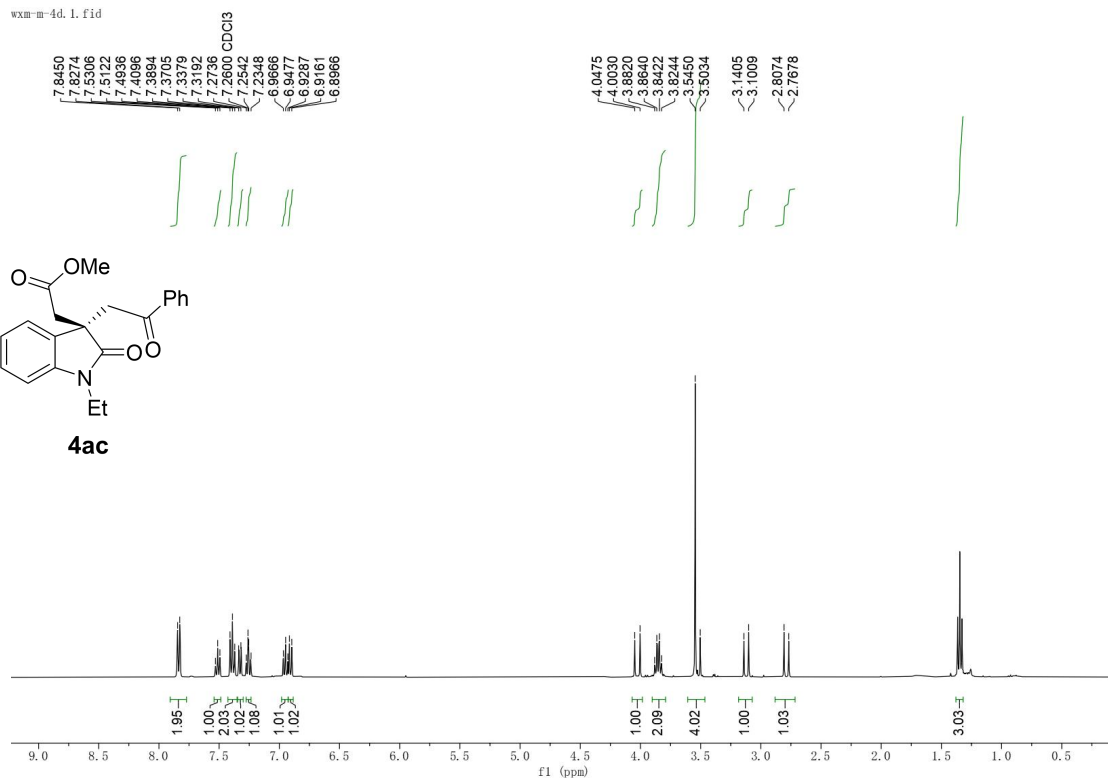
¹³C NMR-**4ab** (100 MHz, CDCl₃)

wxm-m-41.2.fid



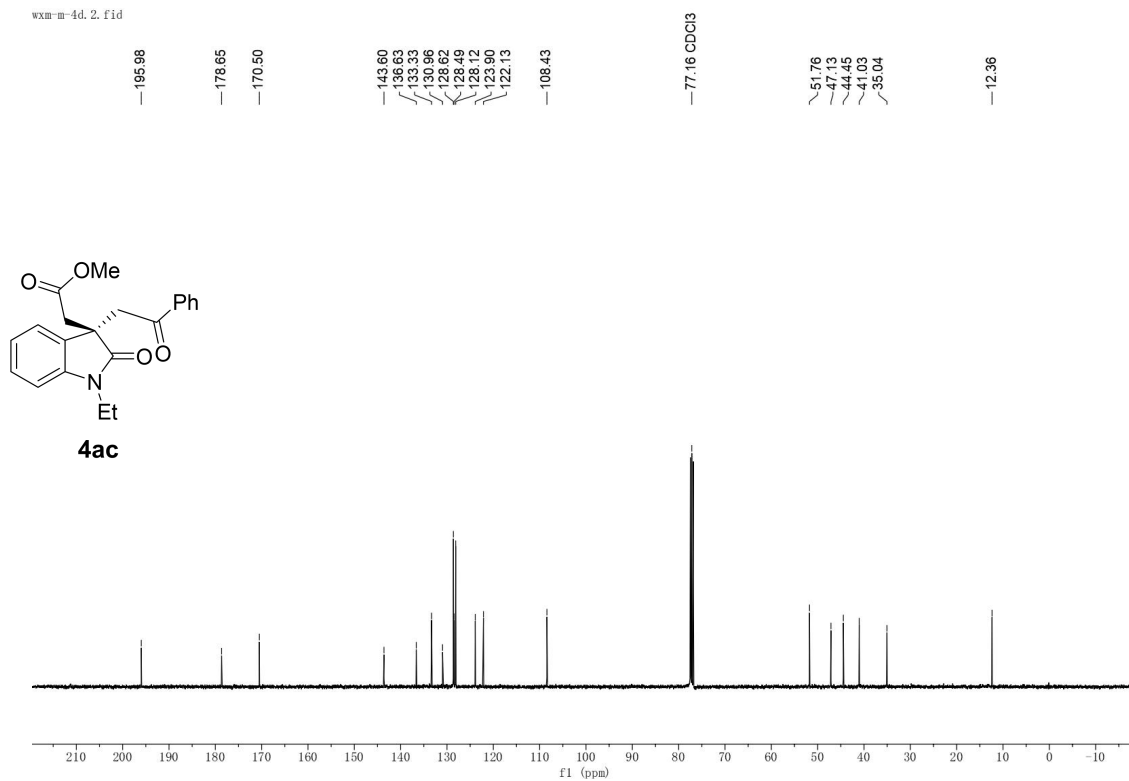
¹H NMR-**4ac** (400 MHz, CDCl₃)

wxm-m-4d.1.fid

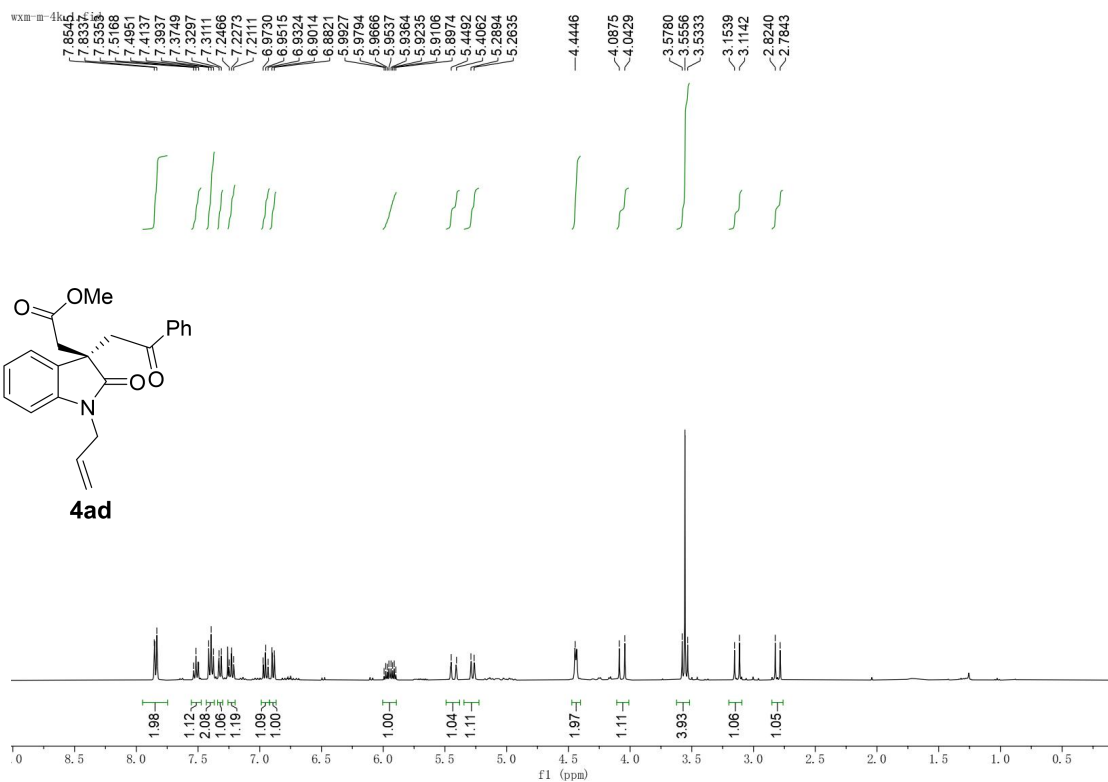


¹³C NMR-**4ac** (100 MHz, CDCl₃)

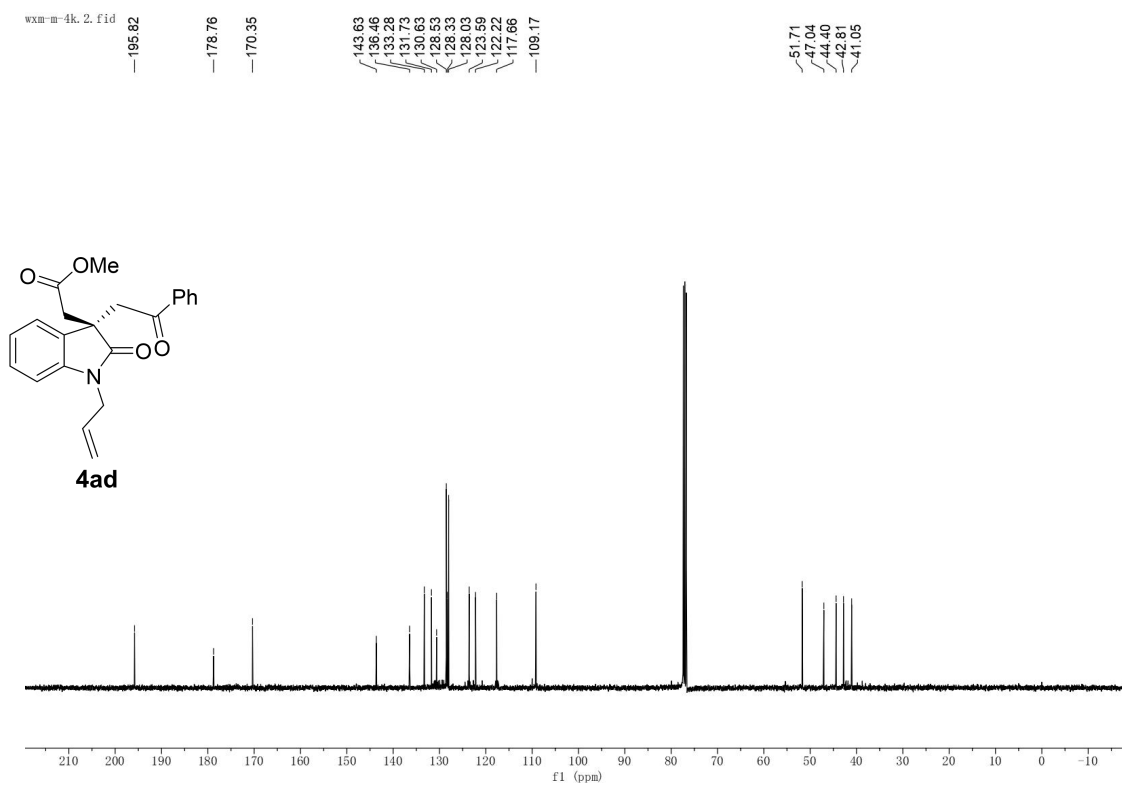
wxm-m-4d.2.fid



¹H NMR-**4ad** (400 MHz, CDCl₃)

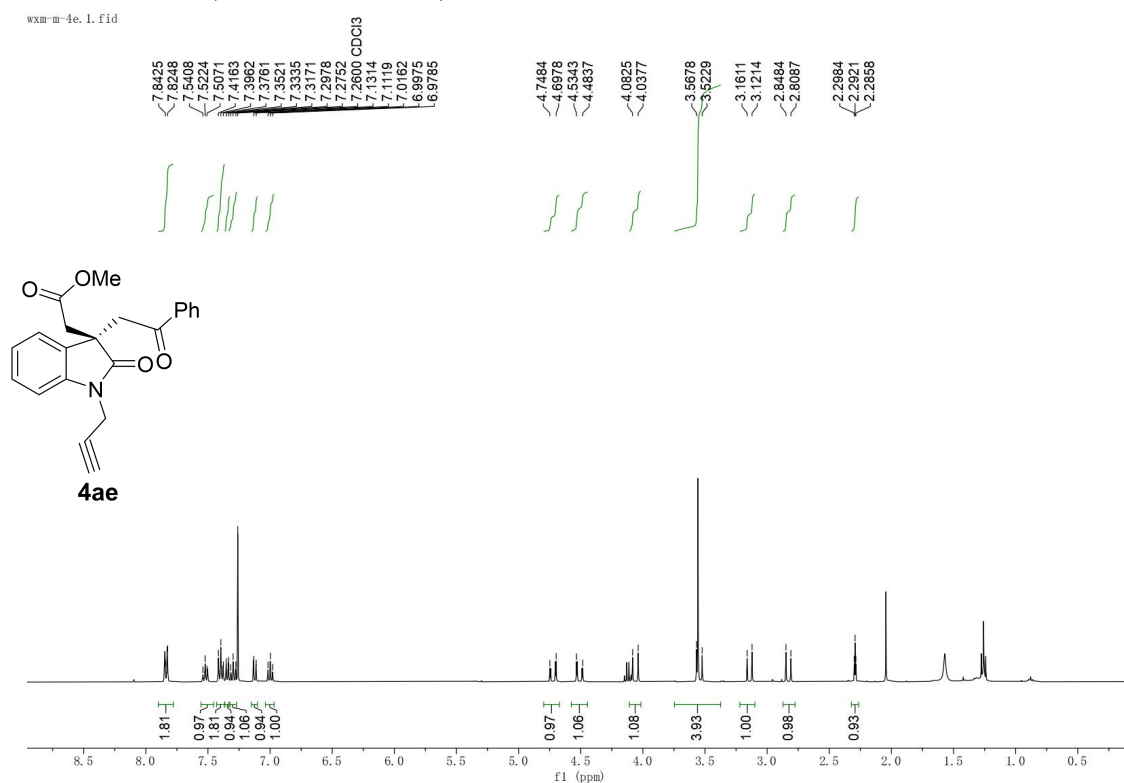


¹³C NMR-**4ad** (100 MHz, CDCl₃)



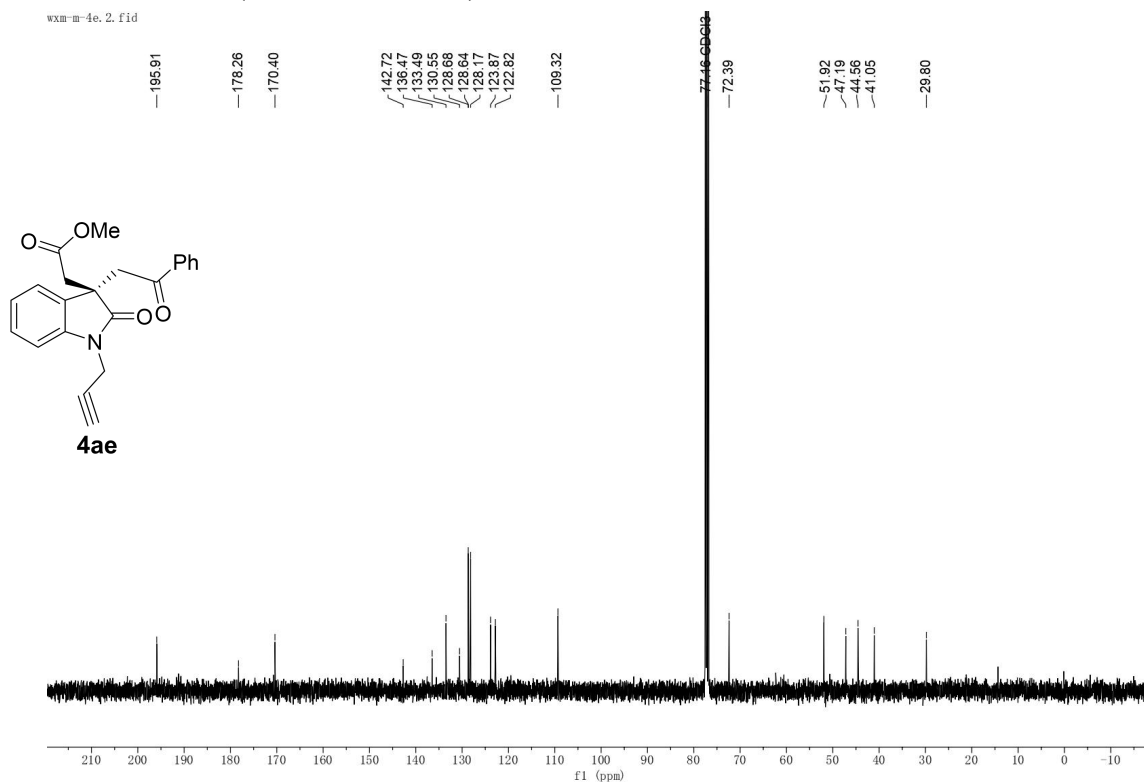
¹H NMR-4ae (400 MHz, CDCl₃)

wxm-m-4e.1.fid



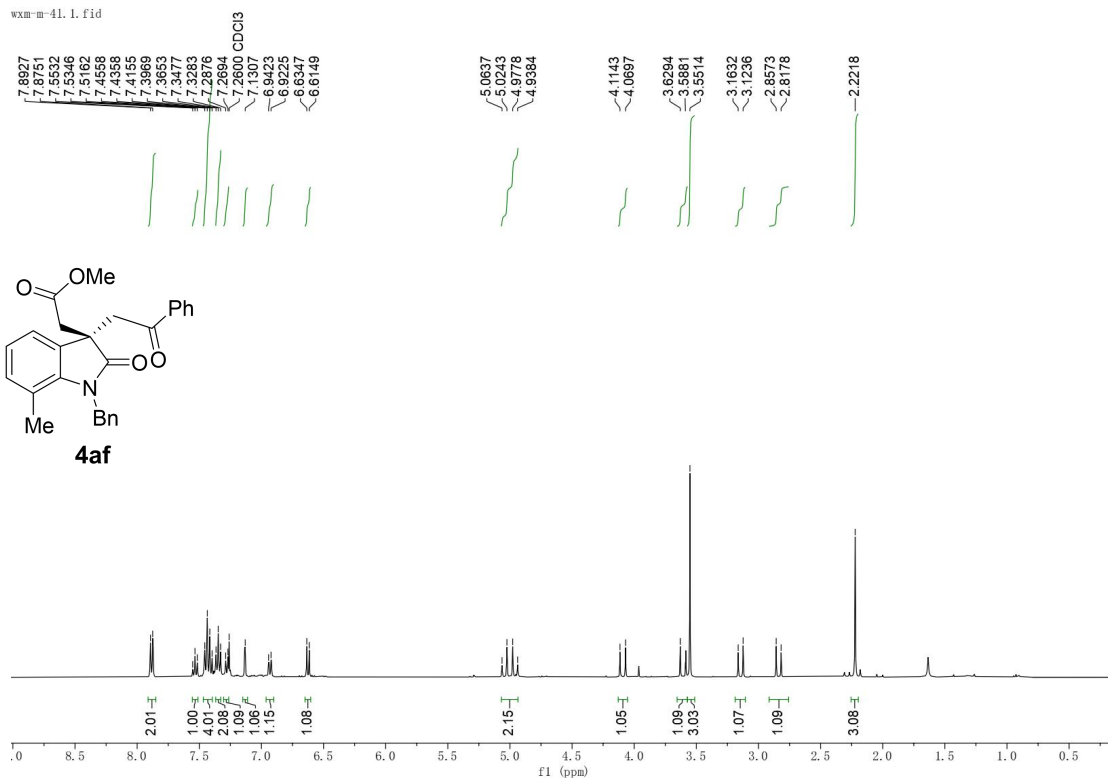
¹³C NMR-4ae (100 MHz, CDCl₃)

wxm-m-4e.2.fid



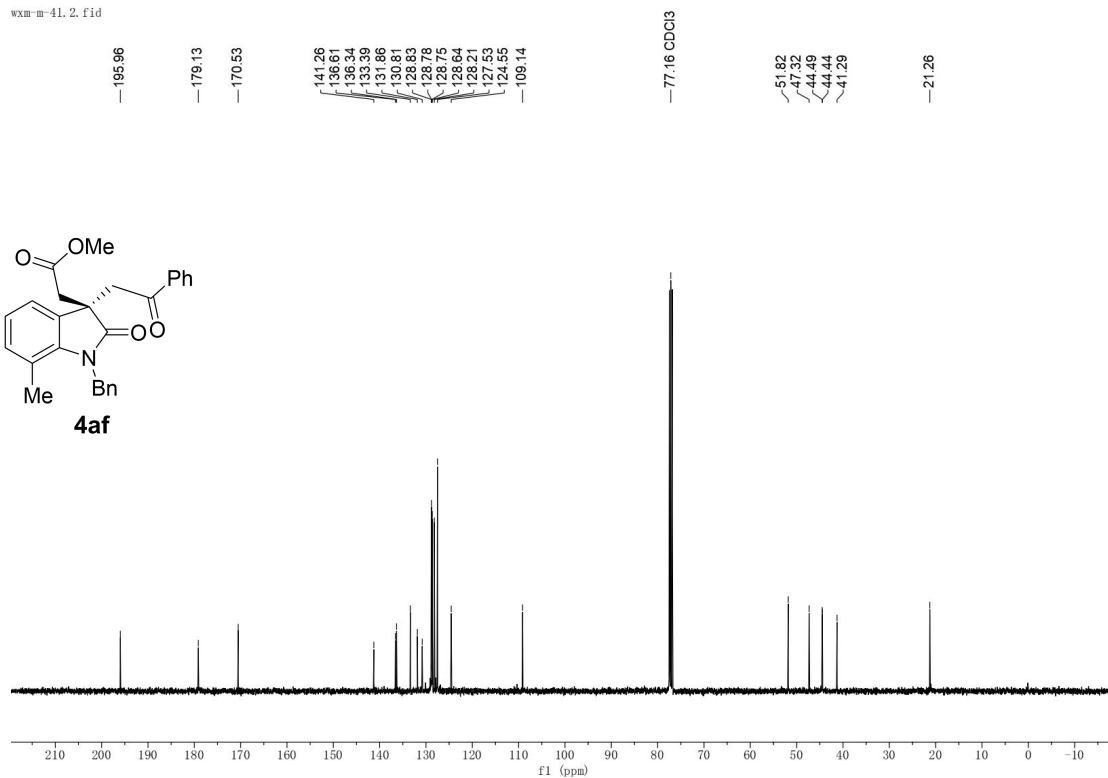
¹H NMR-4af (400 MHz, CDCl₃)

wxm-m-41.1.fid

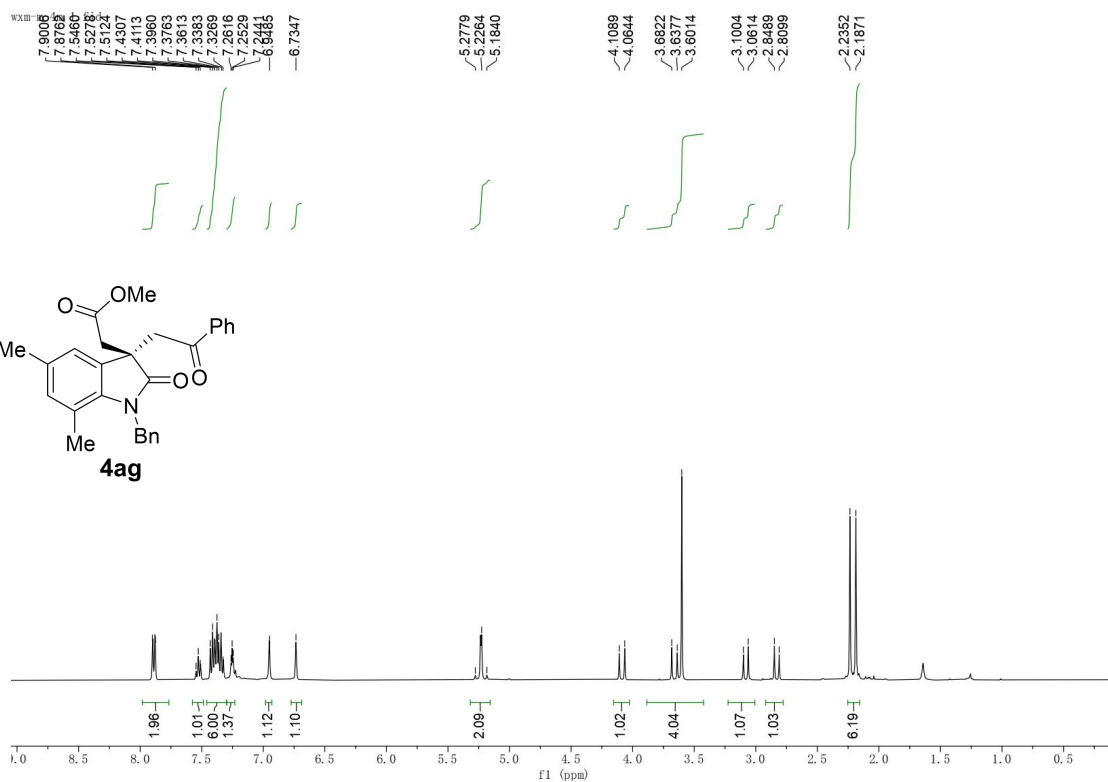


¹³C NMR-4af (100 MHz, CDCl₃)

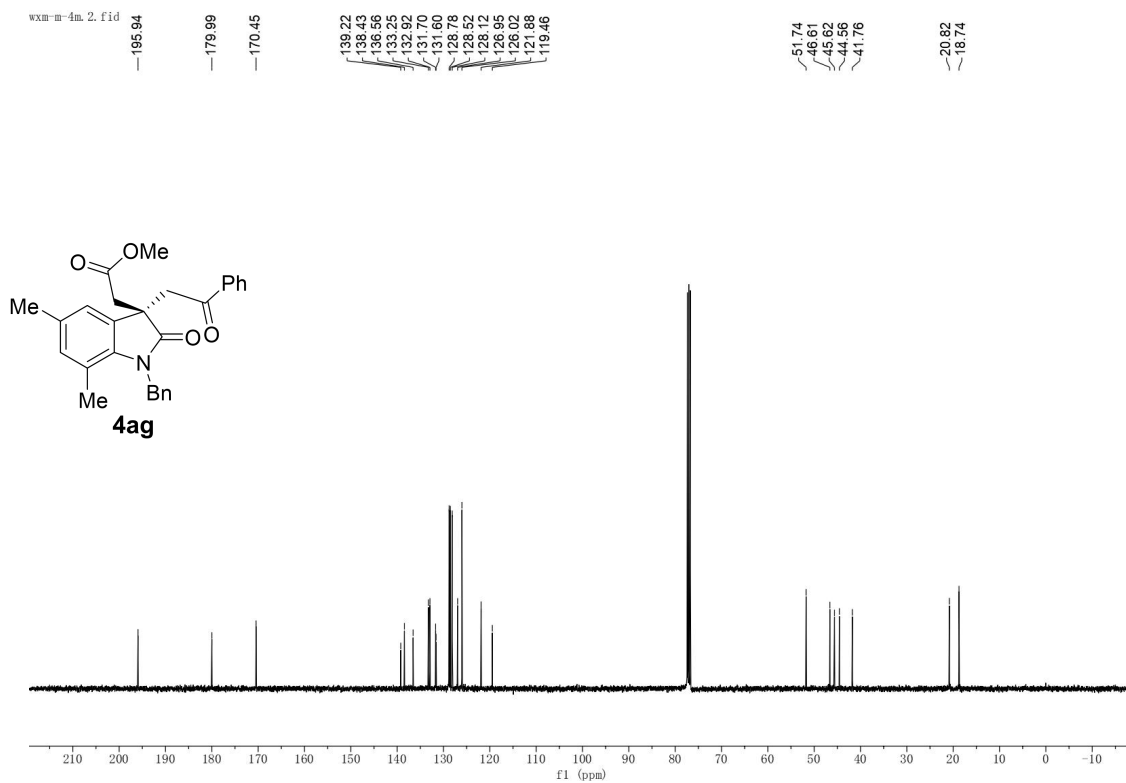
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¹H NMR-**4ag** (400 MHz, CDCl₃)

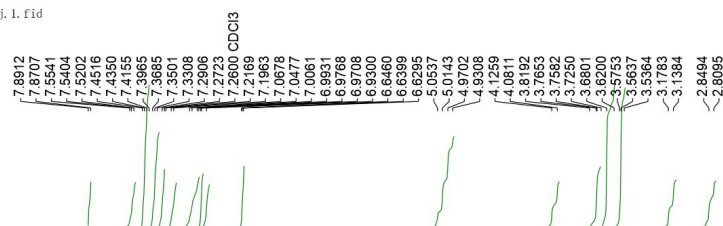


¹³C NMR-**4ag** (100 MHz, CDCl₃)



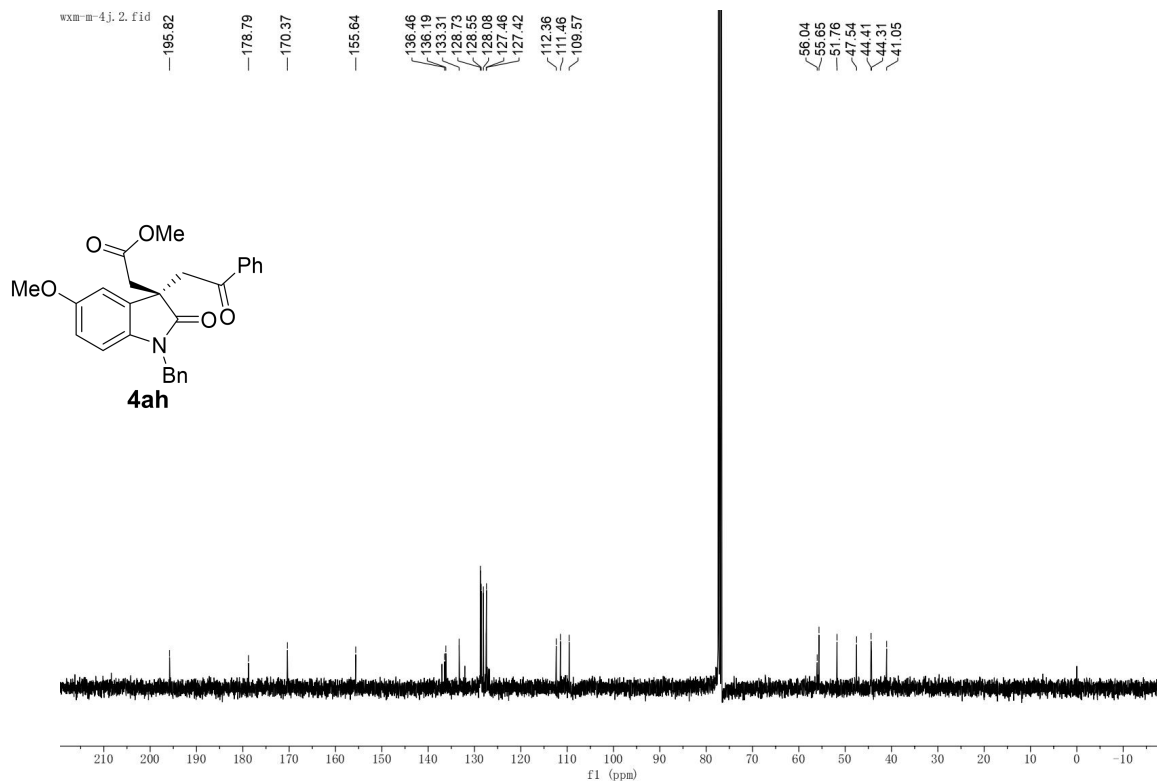
¹H NMR-**4ah** (400 MHz, CDCl₃)

wxlm-4j.1.fid



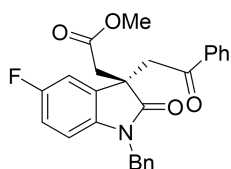
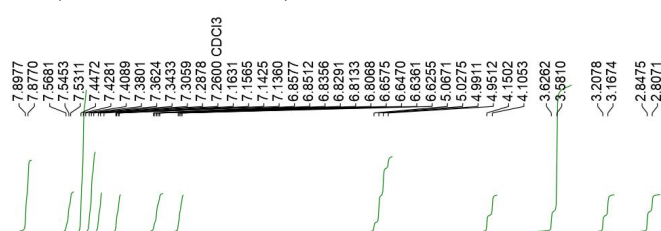
¹³C NMR-**4ah** (100 MHz, CDCl₃)

wxlm-4j.2.fid

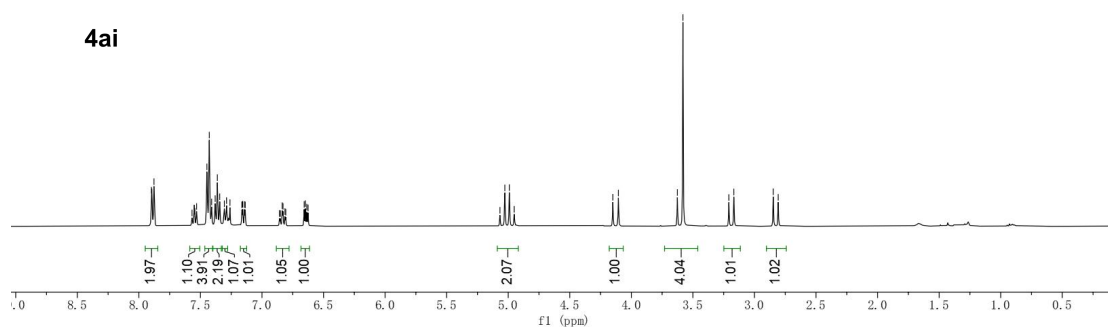


¹H NMR-4ai(400 MHz, CDCl₃)

wxnm-4g.1.fid

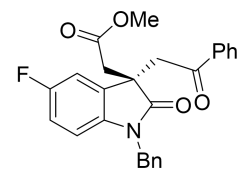


4ai

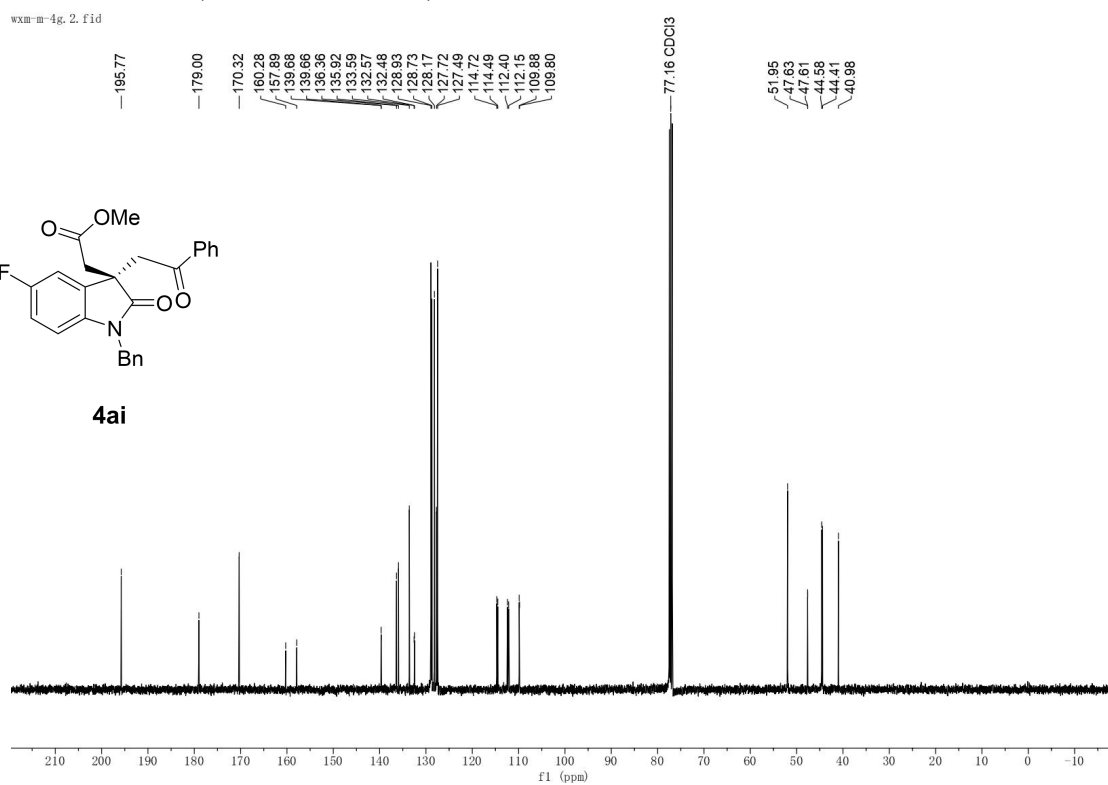


¹³C NMR-4ai (100 MHz, CDCl₃)

wxnm-4g.2.fid

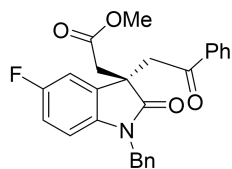


4ai

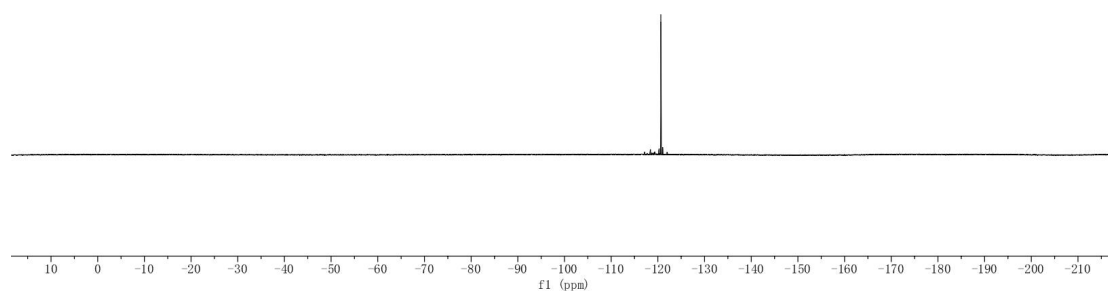


¹⁹F NMR-**4ai** (376 MHz, CDCl₃)

wxm-m-4g. 4. fid

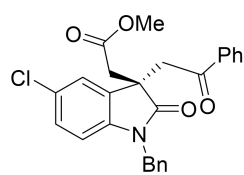


4ai

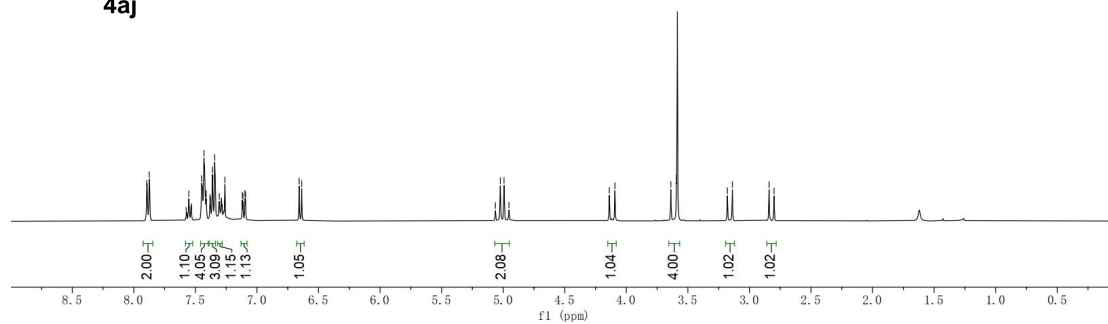


¹H NMR-**4aj** (400 MHz, CDCl₃)

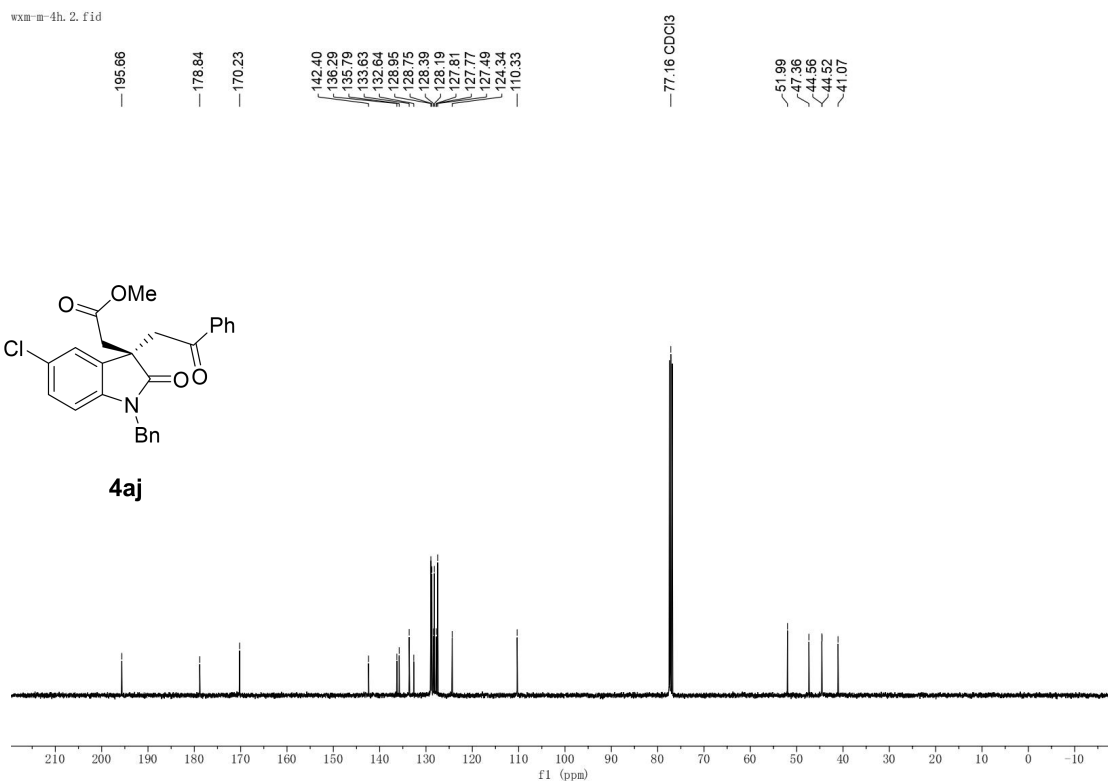
wxm-m-4h. 1. fid



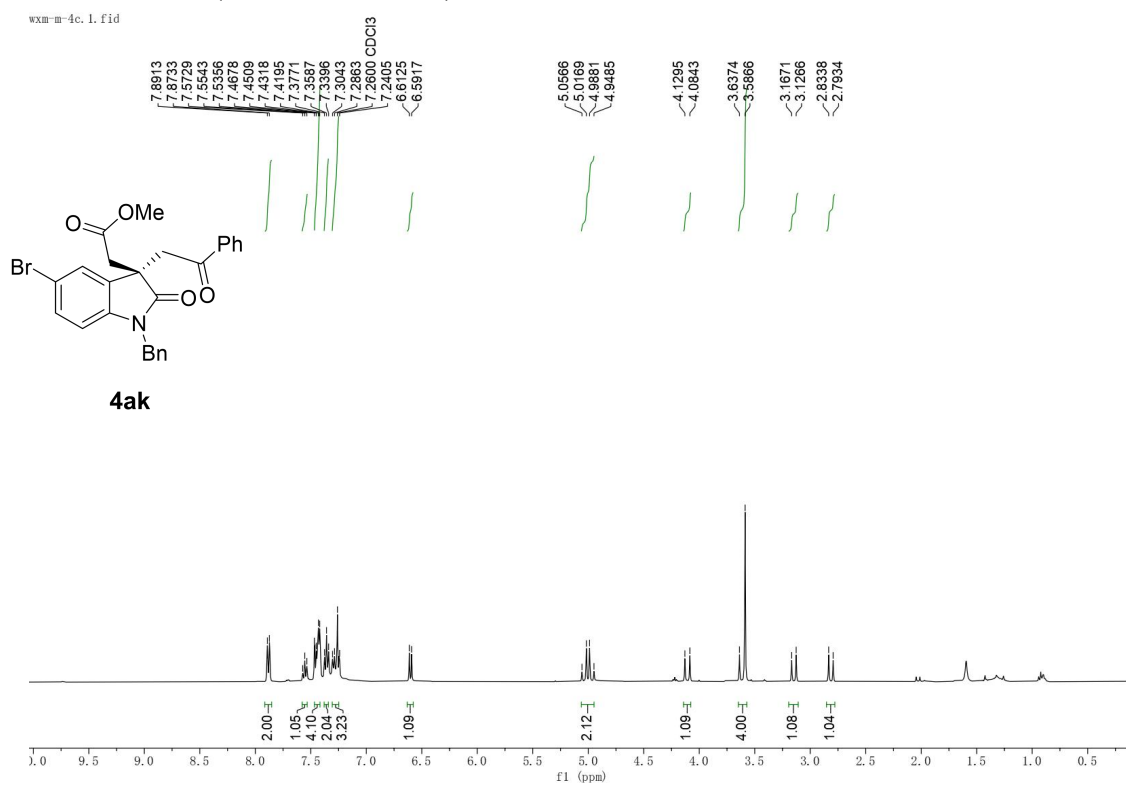
4aj



^{13}C NMR-**4aj** (100 MHz, CDCl_3)

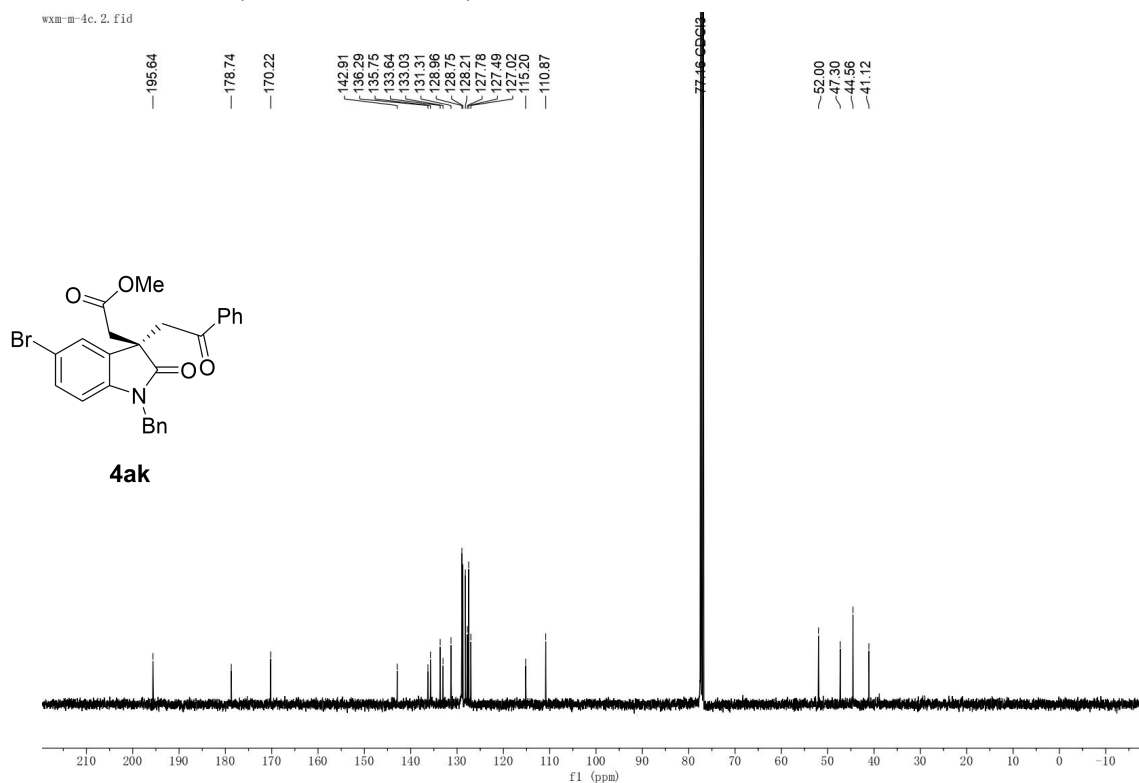


^1H NMR-**4ak** (400 MHz, CDCl_3)



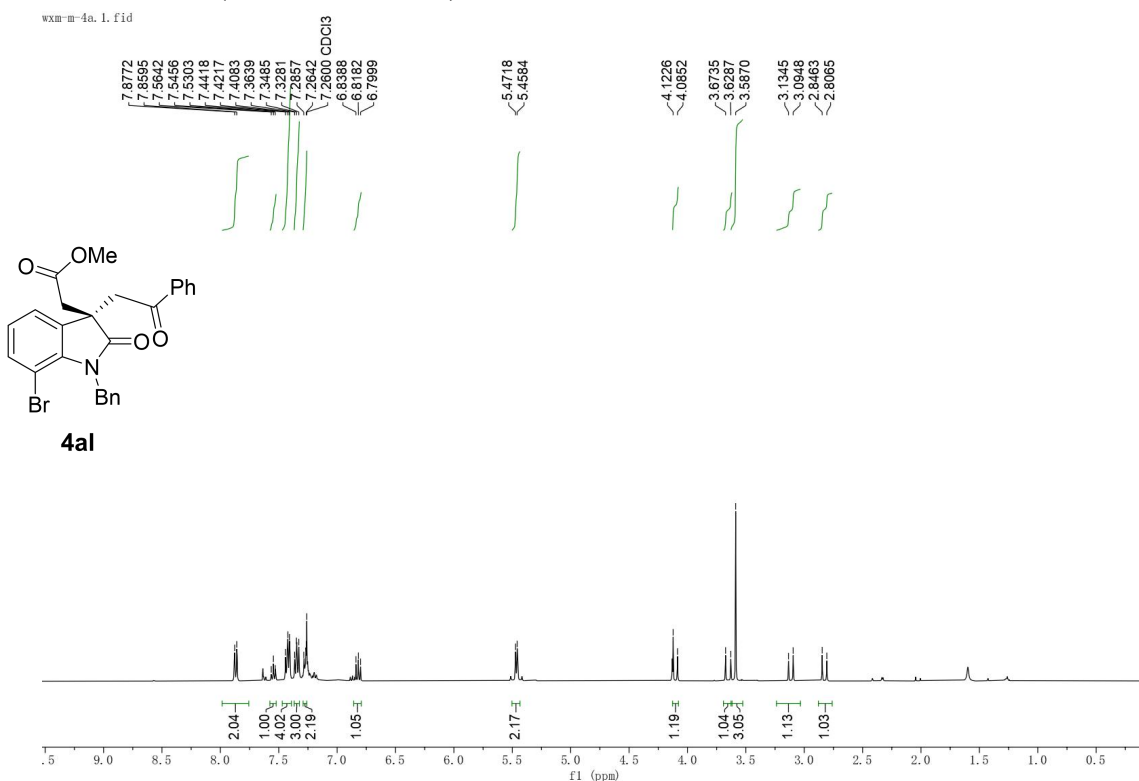
¹³C NMR-**4ak** (100 MHz, CDCl₃)

wxm-m-4c.2.fid



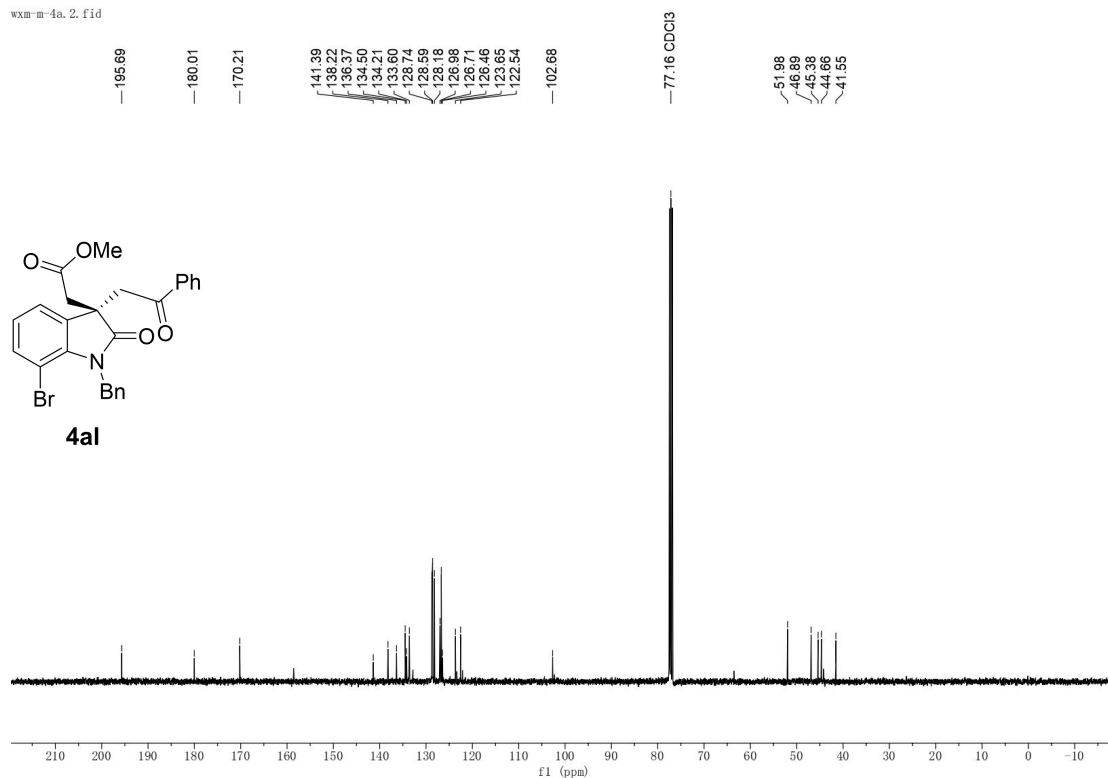
¹H NMR-**4al** (400 MHz, CDCl₃)

wxm-m-4a.1.fid



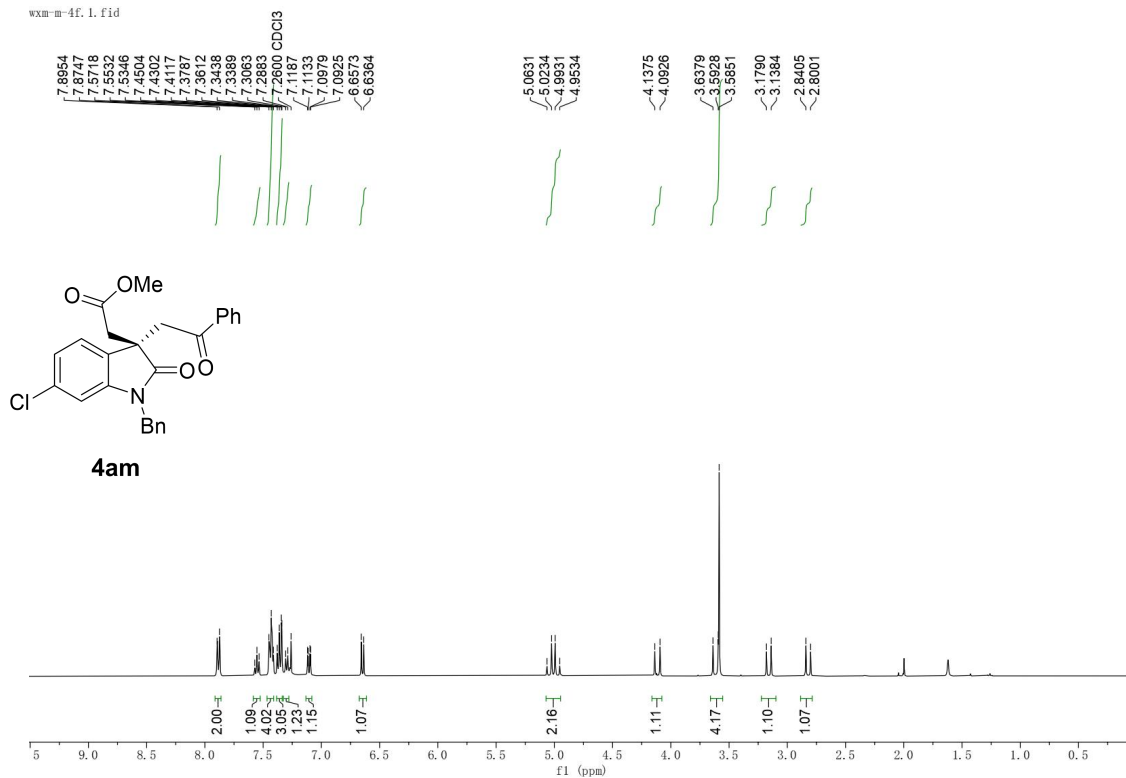
¹³C NMR-**4al** (100 MHz, CDCl₃)

wxm-m-4a.2.fid

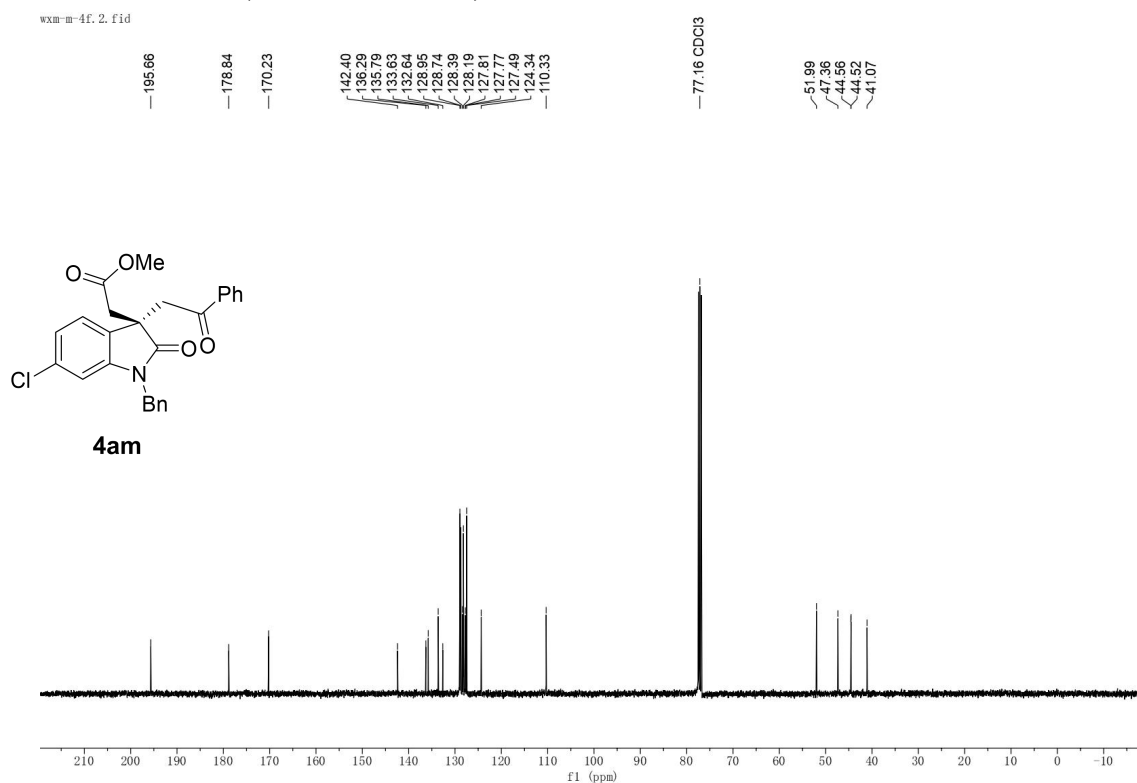


¹H NMR-**4am** (400 MHz, CDCl₃)

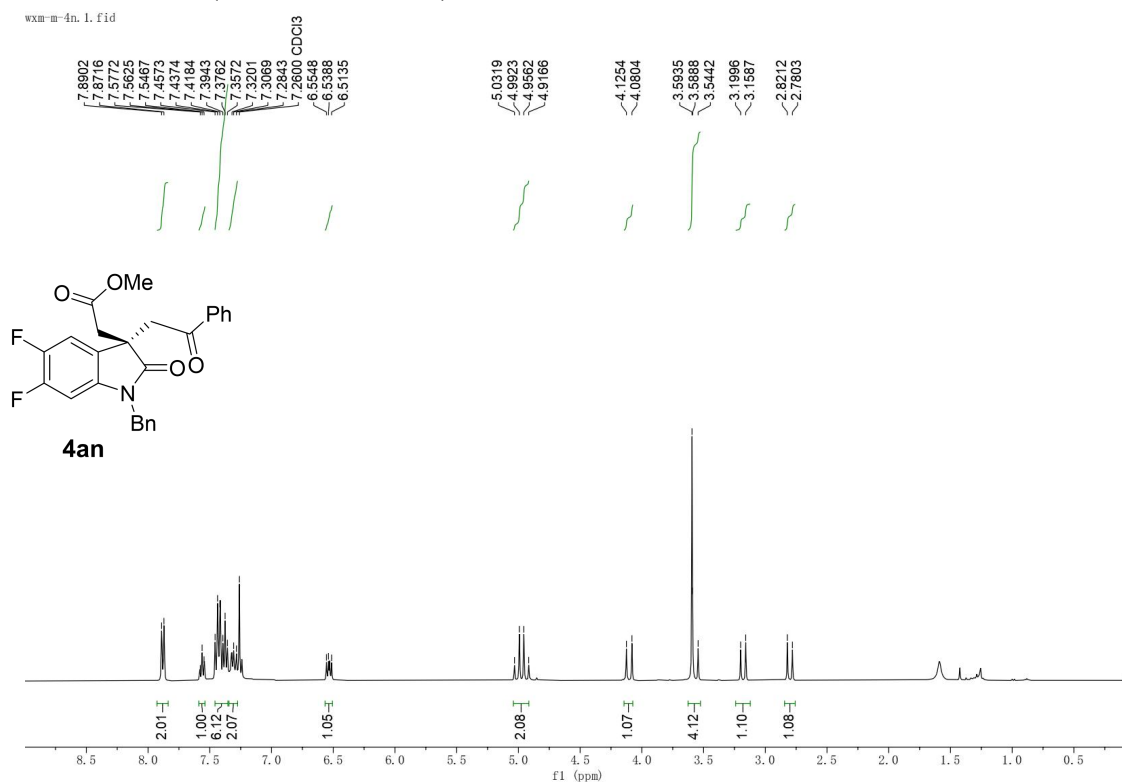
wxm-m-4f.1.fid



¹³C NMR-**4am** (100 MHz, CDCl₃)

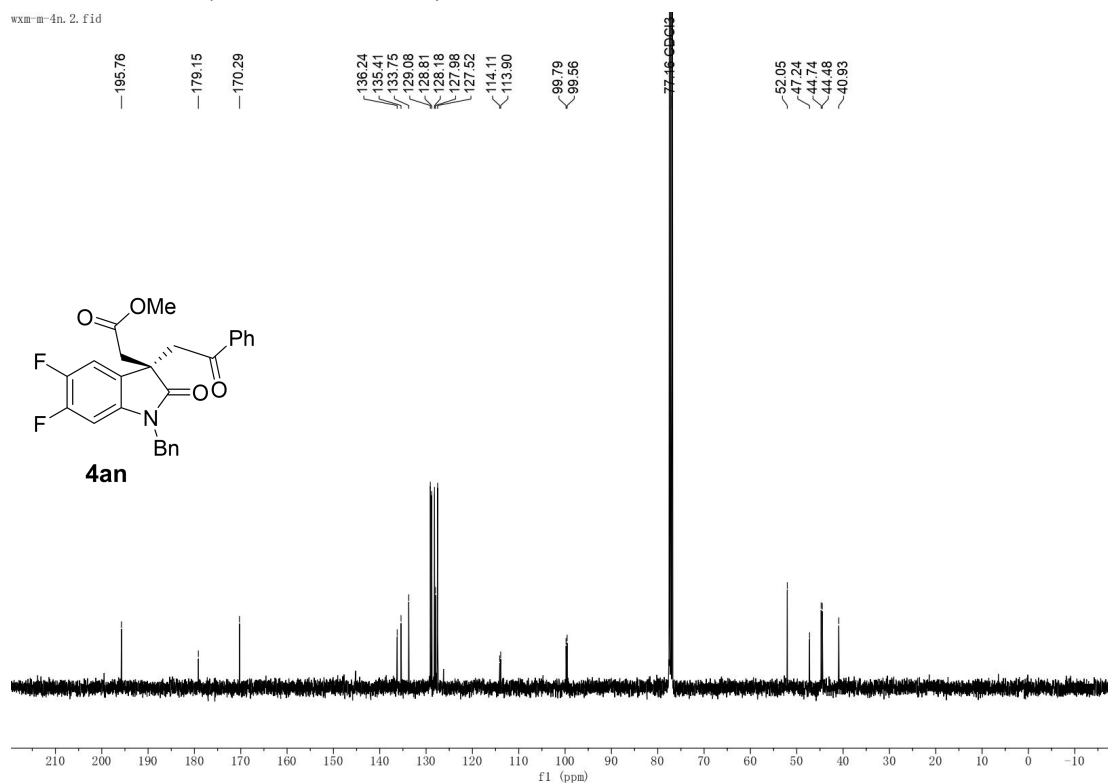


¹H NMR-**4an** (400 MHz, CDCl₃)



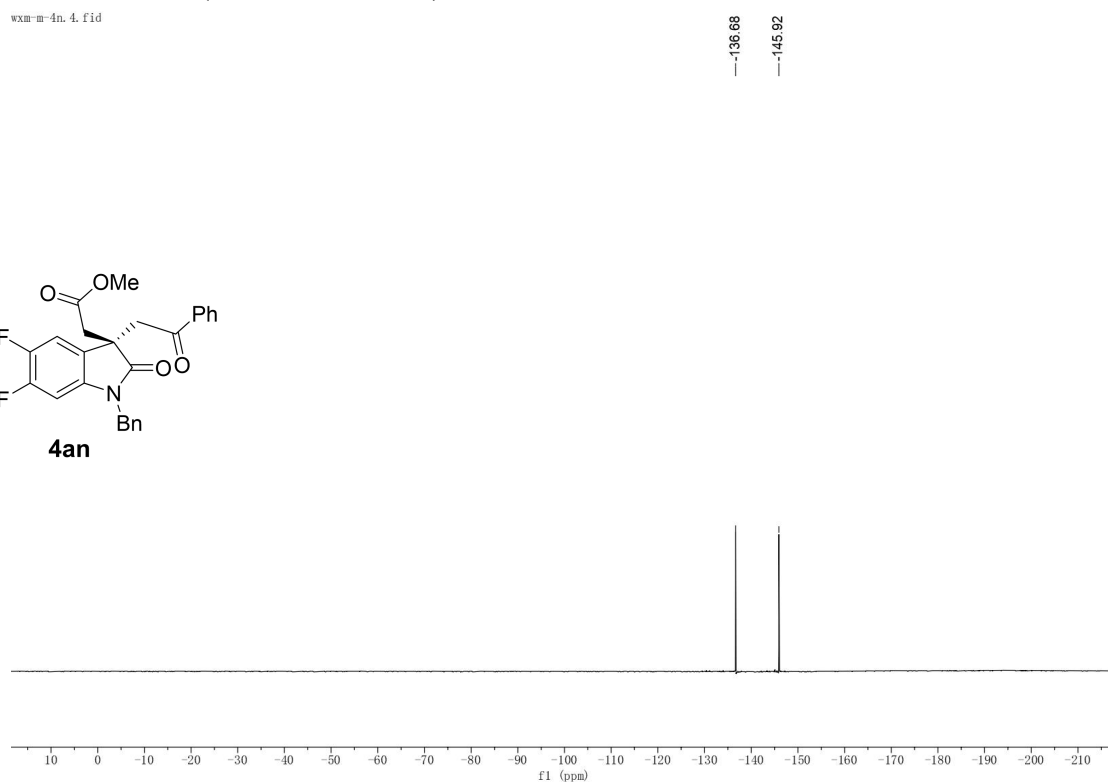
¹³C NMR-4an (100 MHz, CDCl₃)

wxm-m-4n.2.fid



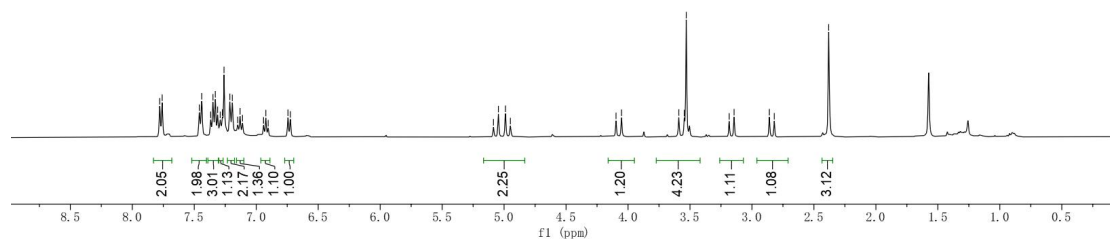
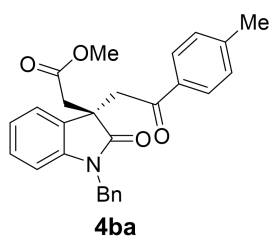
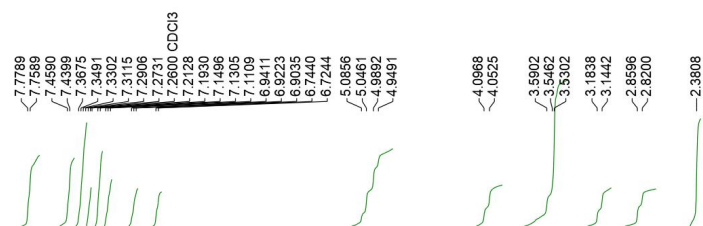
¹⁹F NMR-4an (376 MHz, CDCl₃)

wxm-m-4n.4.fid



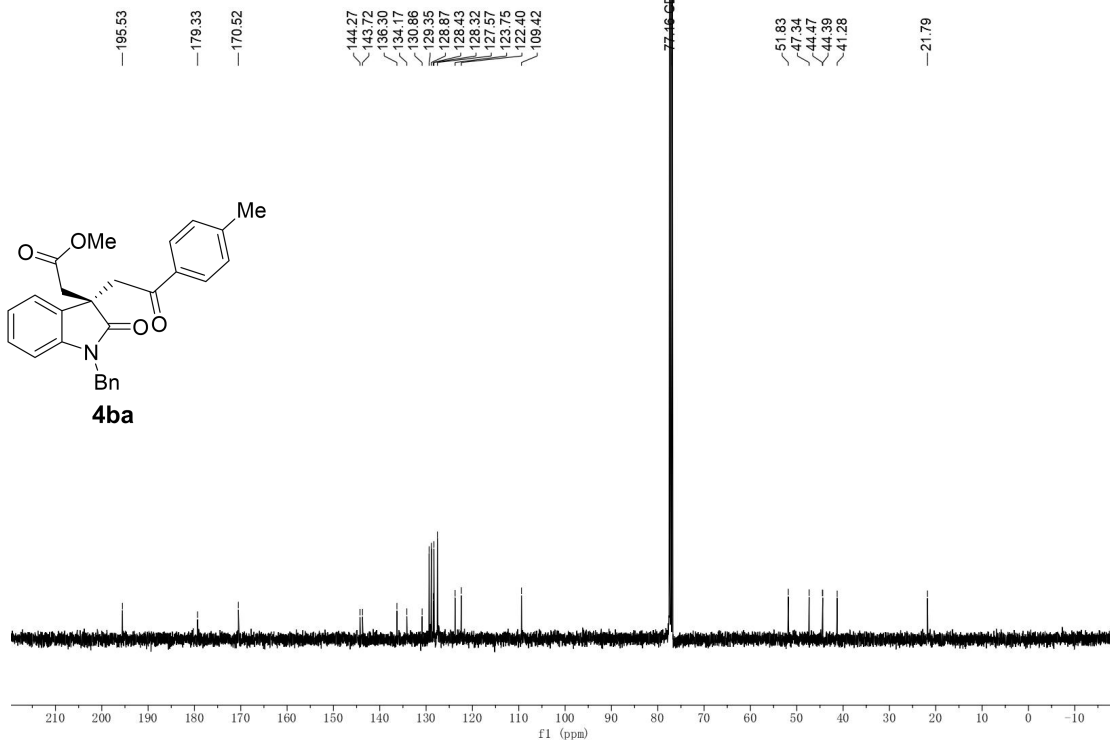
¹H NMR-4ba (400 MHz, CDCl₃)

wxnm-3p.1.fid

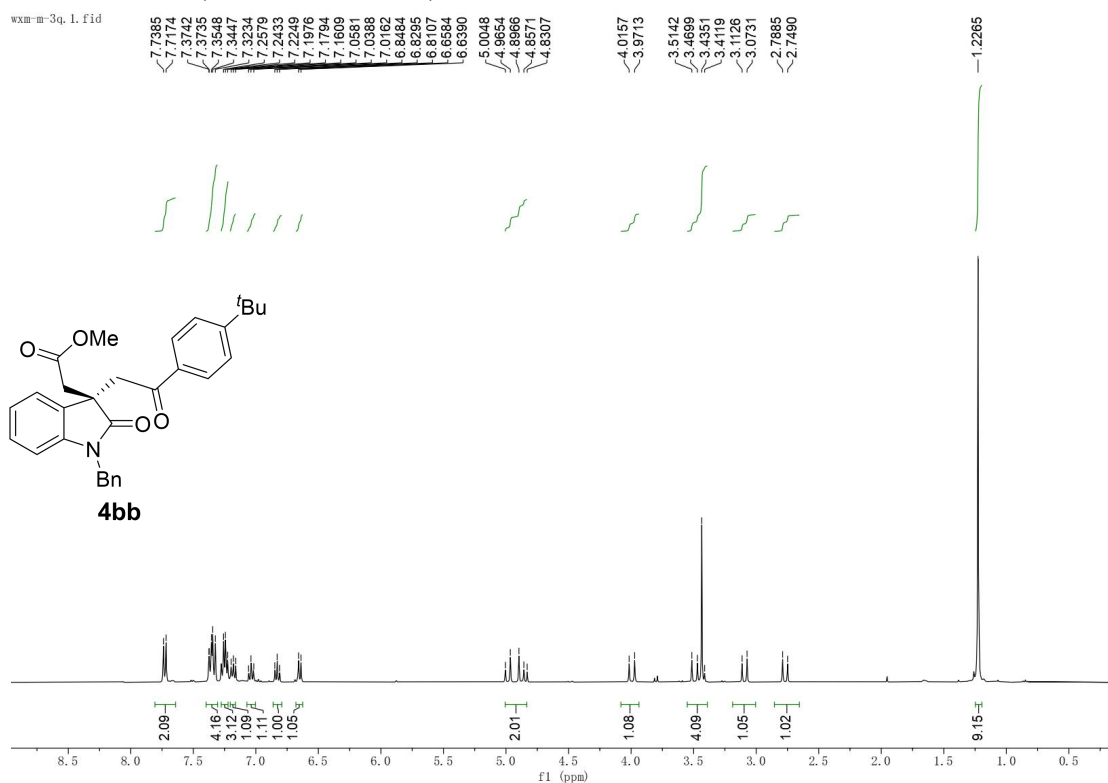


¹³C NMR-4ba (100 MHz, CDCl₃)

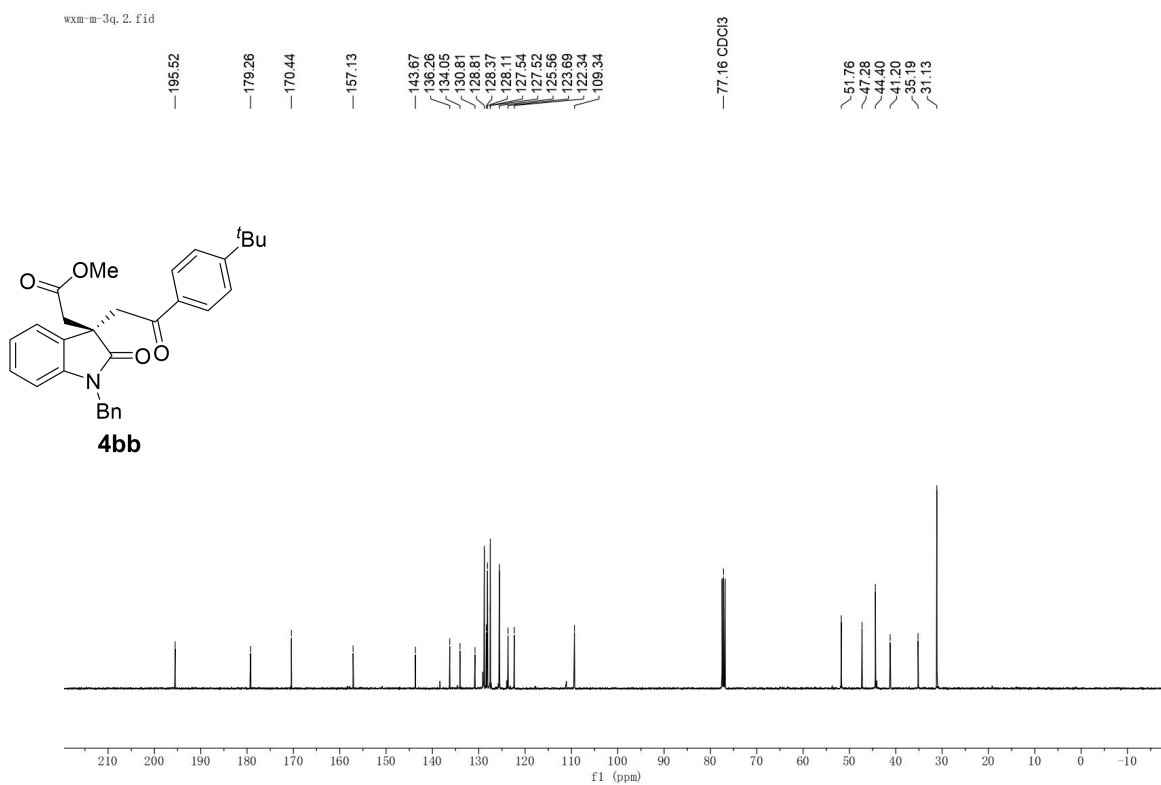
wxnm-3p.2.fid



¹H NMR-**4bb** (400 MHz, CDCl₃)

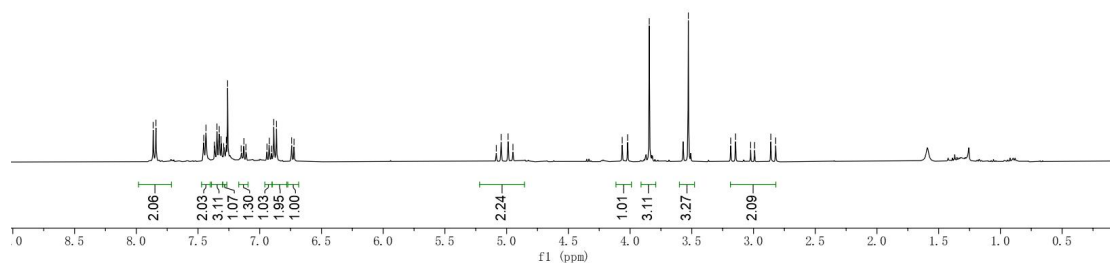
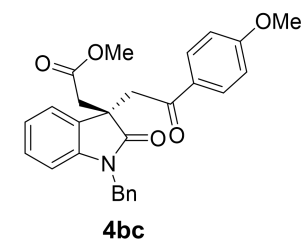
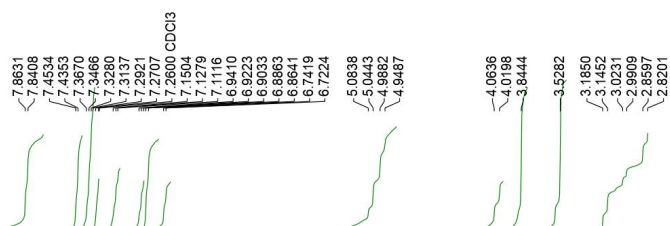


¹³C NMR-**4bb** (100 MHz, CDCl₃)



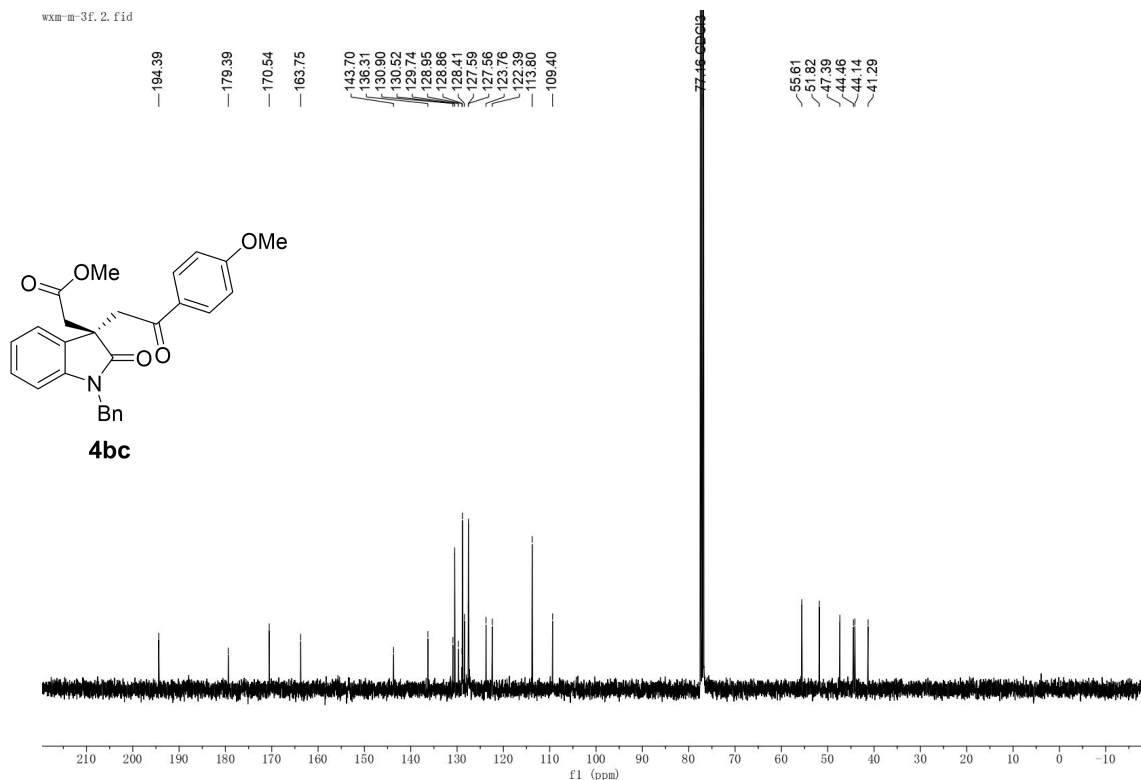
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wxlm-m-3f.1.fid



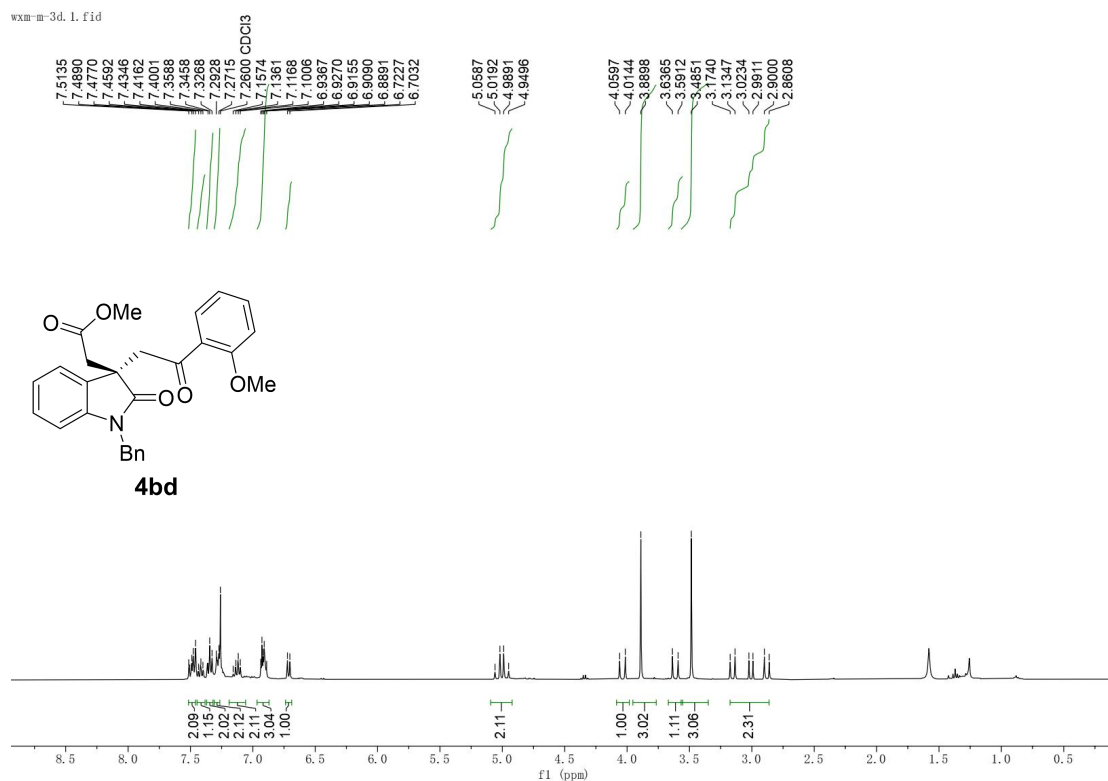
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wxlm-m-3f.2.fid



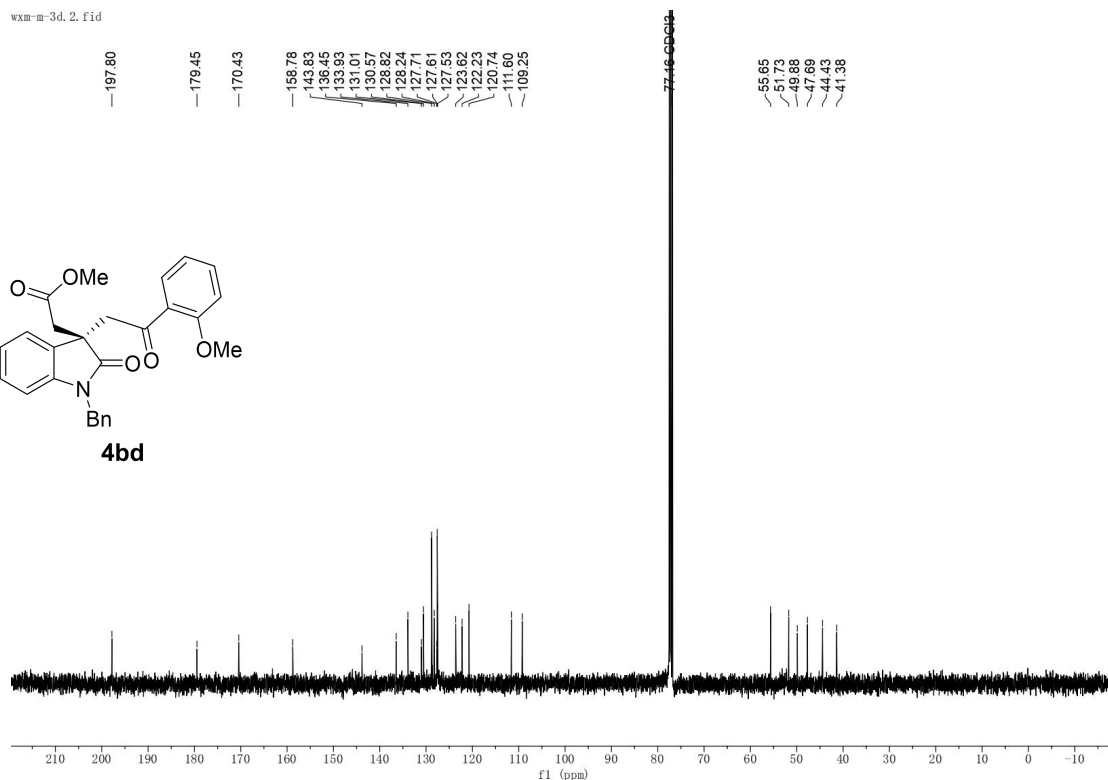
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wxm-m-3d.1.fid



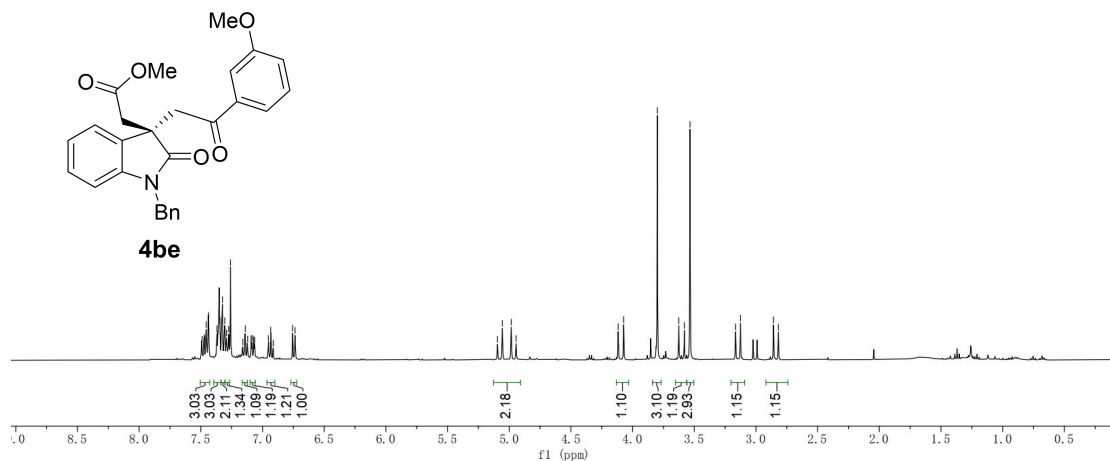
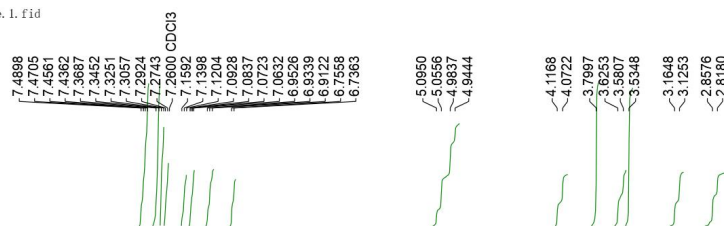
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wxm-m-3d.2.fid



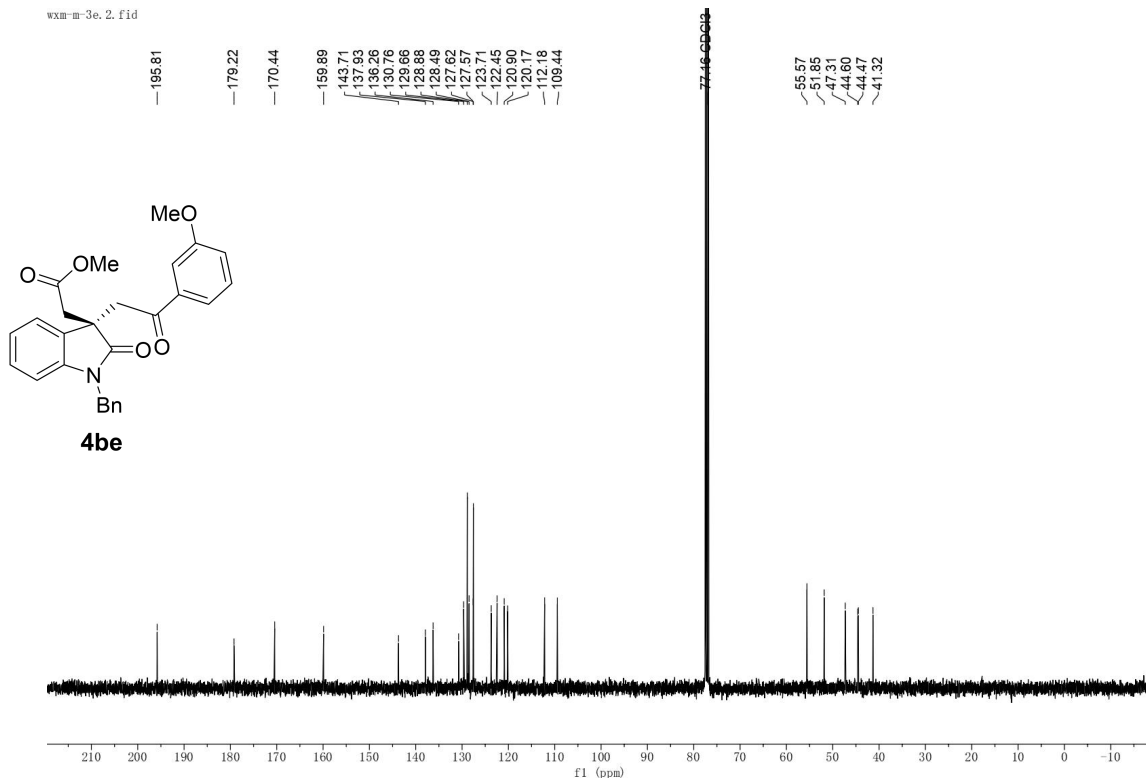
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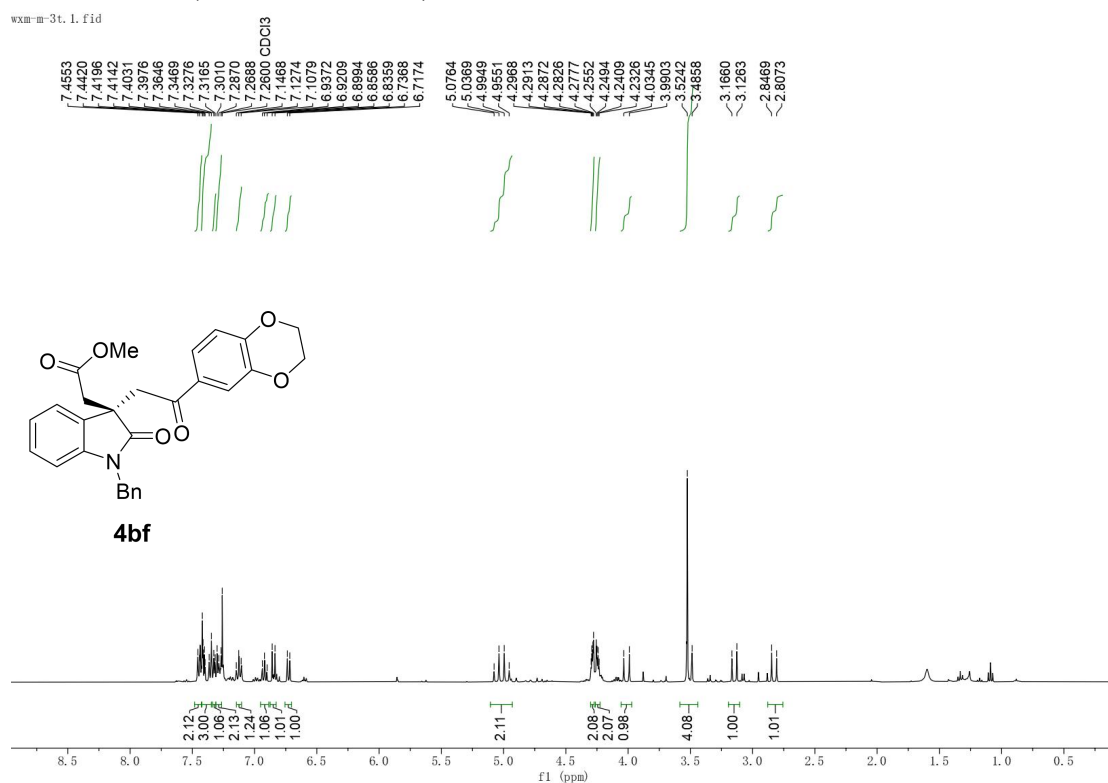


¹³C NMR-4be (100 MHz, CDCl₃)

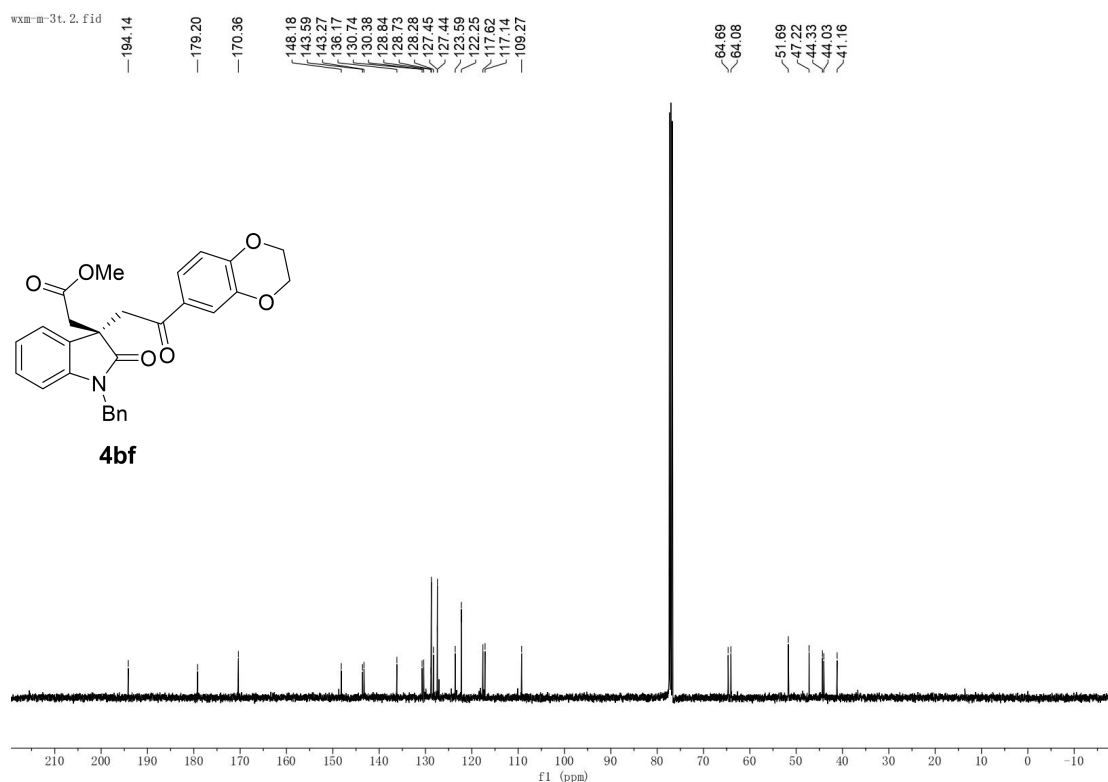
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¹H NMR-**4bf** (400 MHz, CDCl₃)

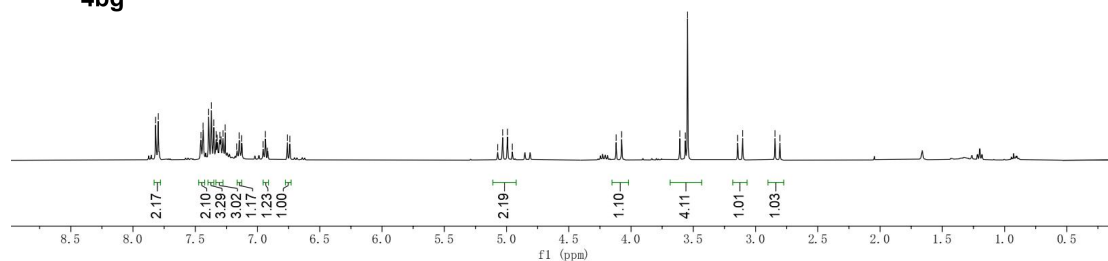
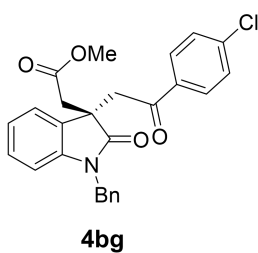
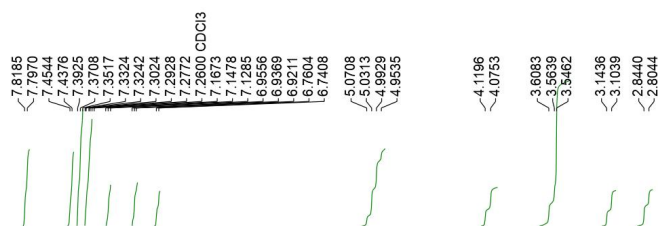


¹³C NMR-**4bf** (100 MHz, CDCl₃)



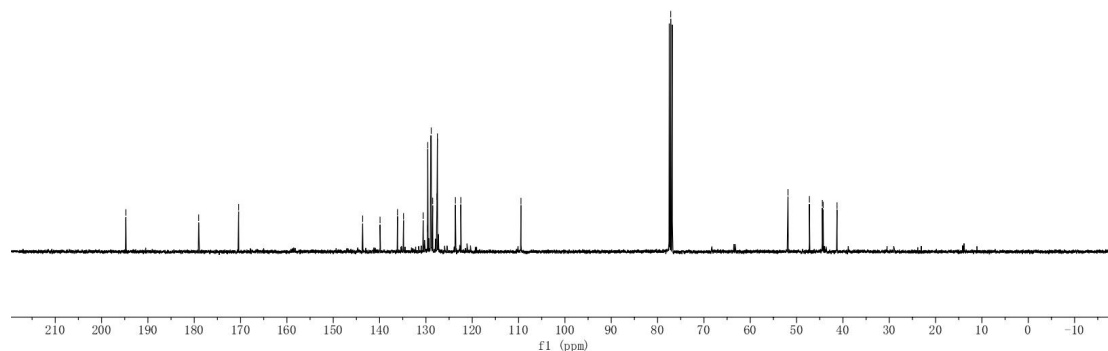
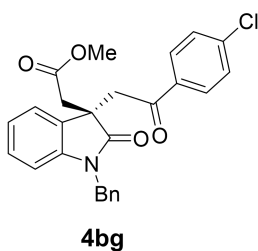
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wxm-m-3n.1.fid



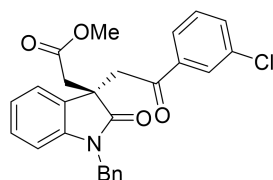
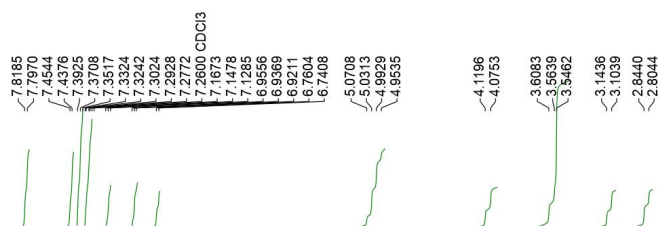
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wxm-m-3n.2.fid

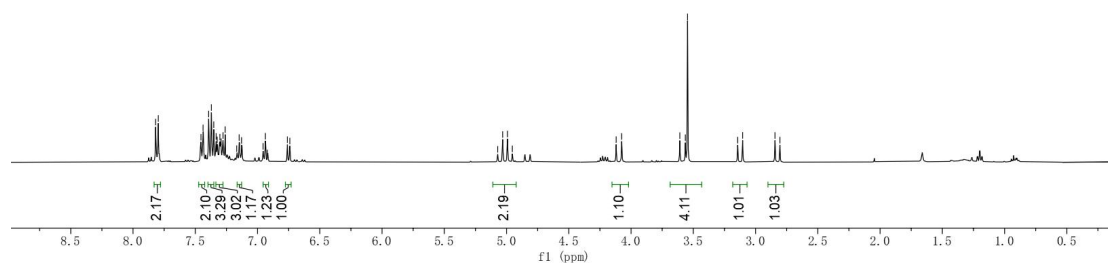


¹H NMR-4bh (400 MHz, CDCl₃)

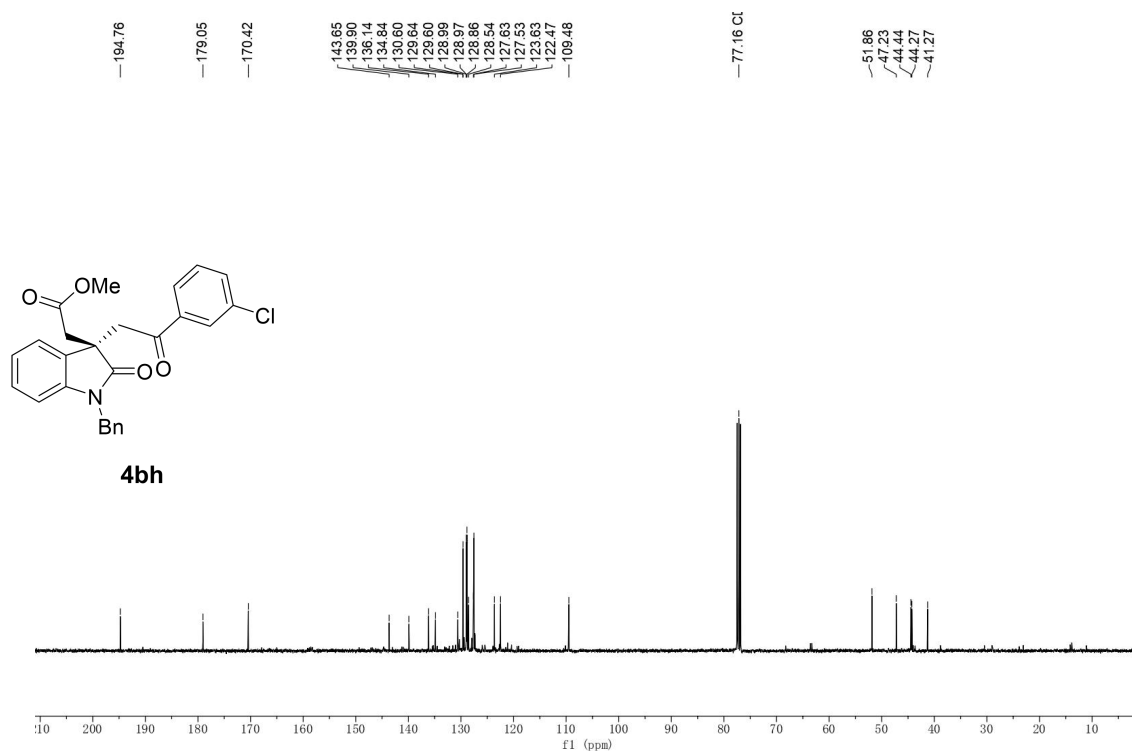
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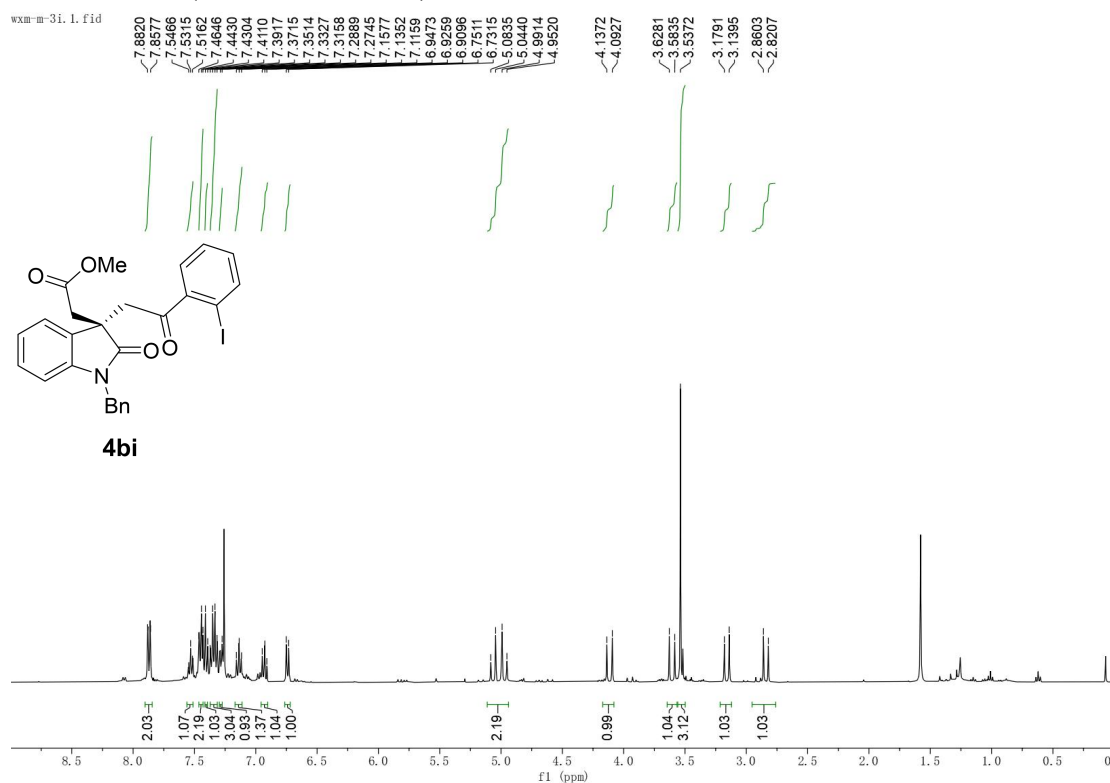
4bh



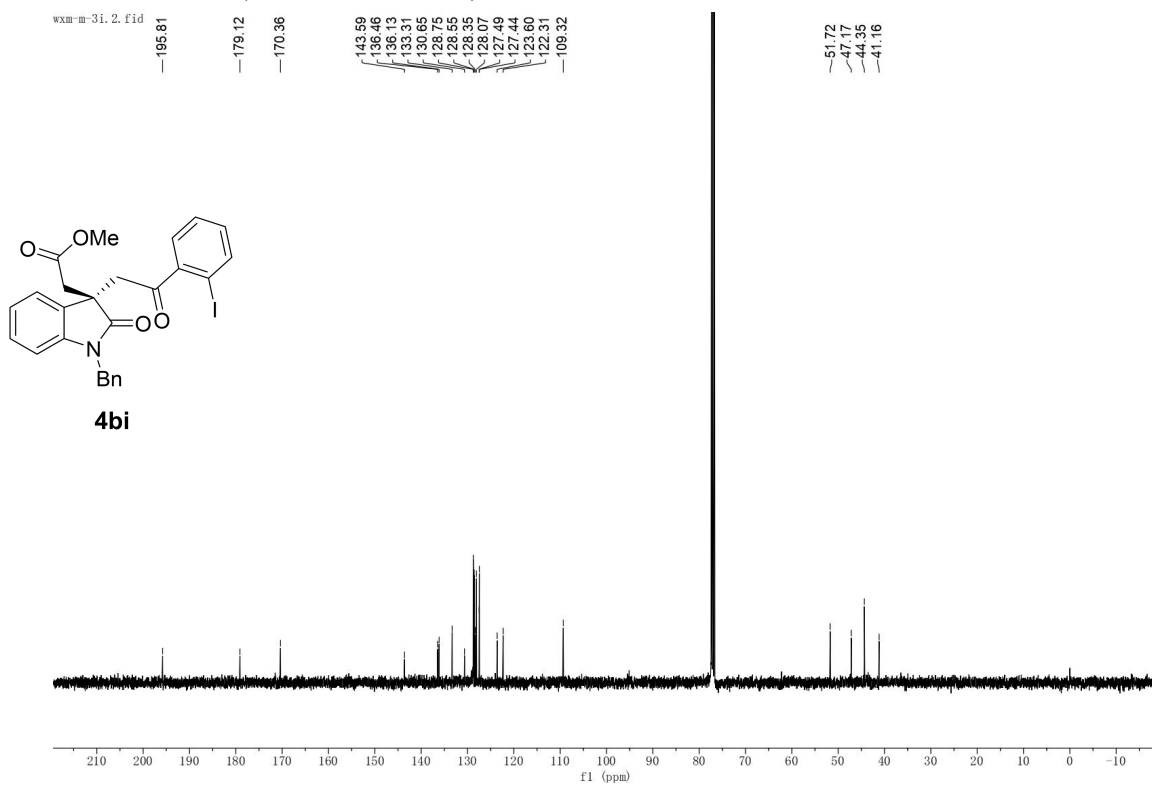
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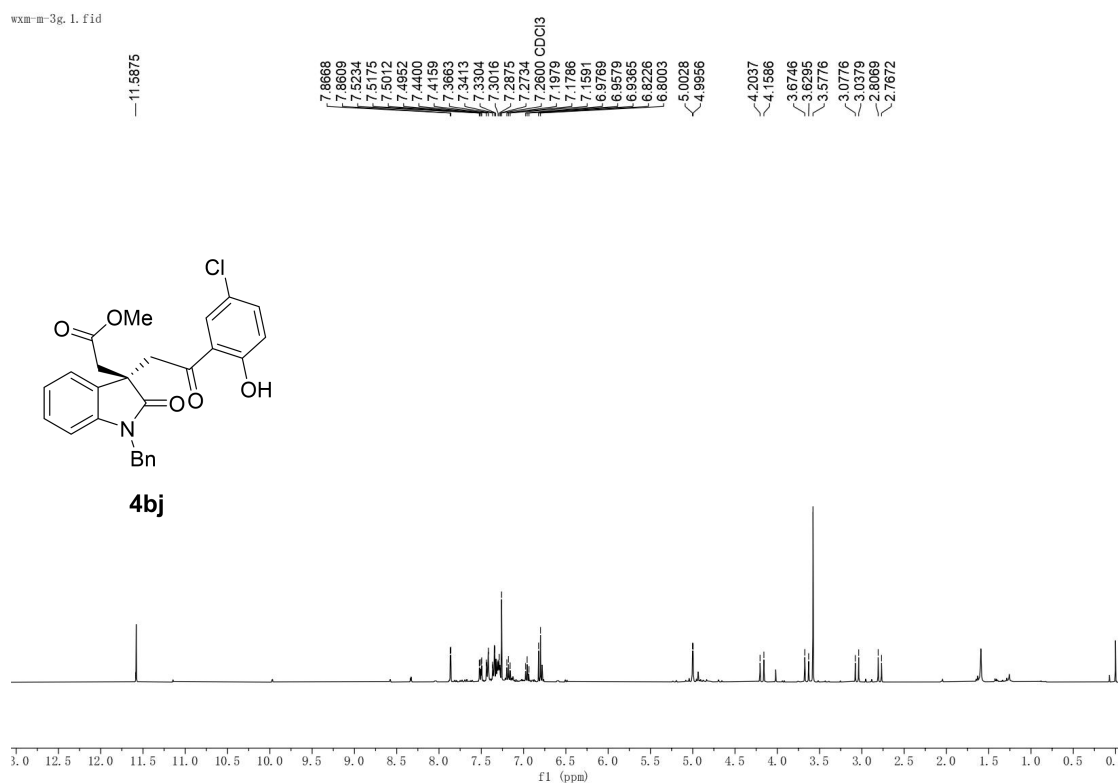
¹H NMR-**4bi** (400 MHz, CDCl₃)



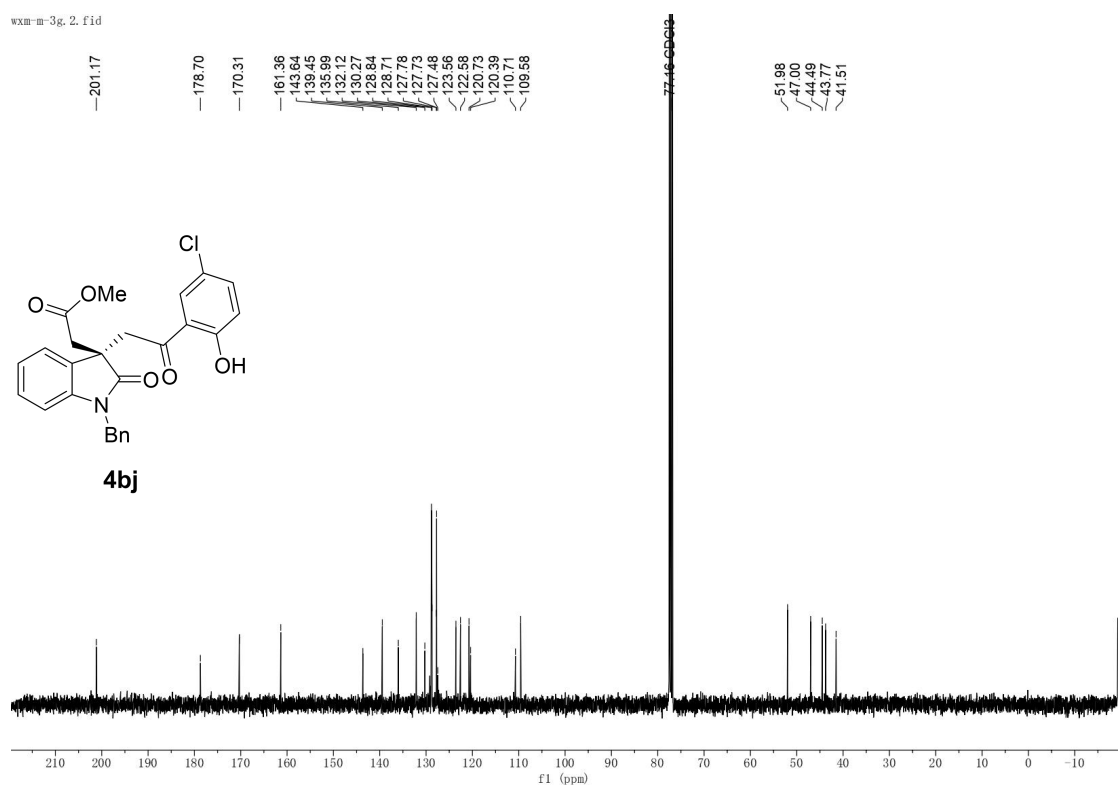
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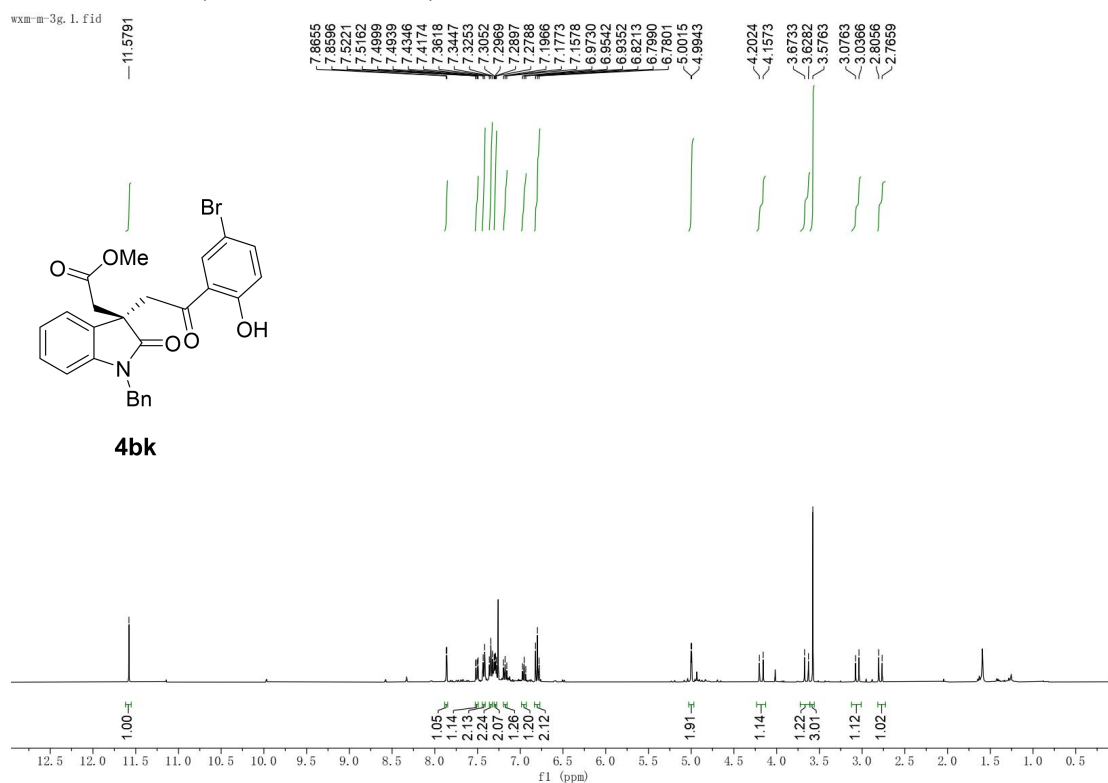
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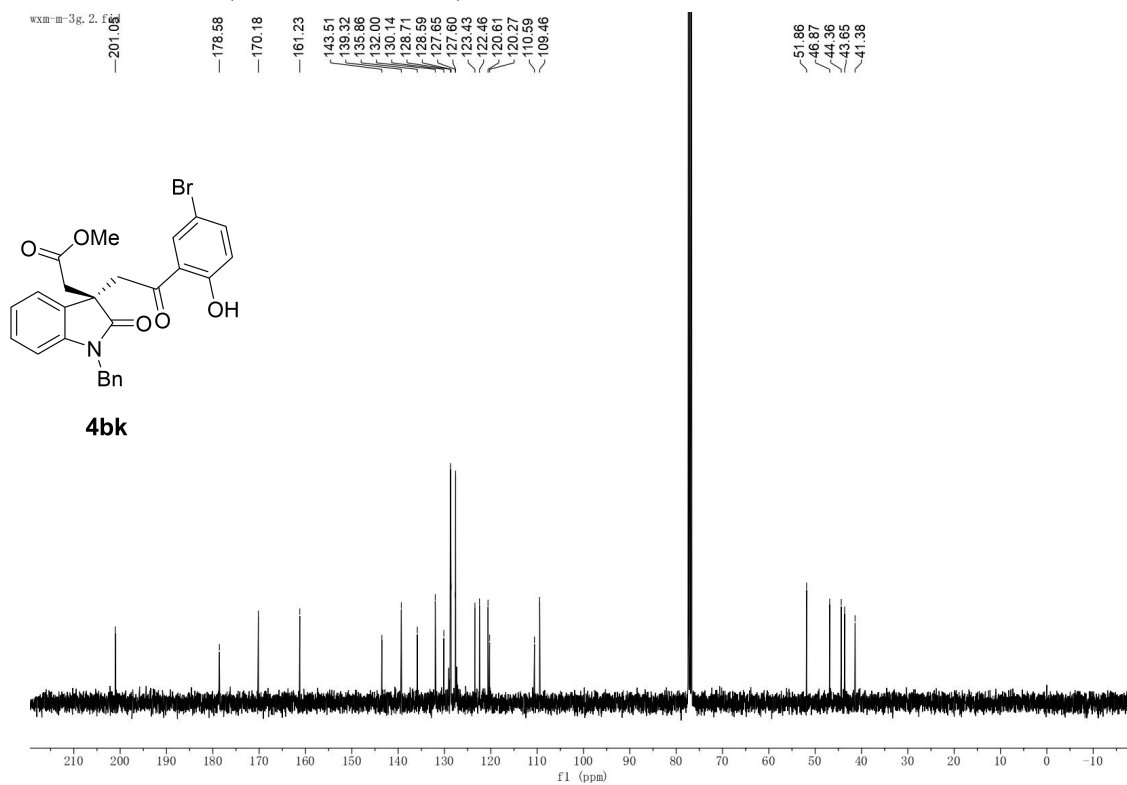
¹³C NMR-**4bj** (100 MHz, CDCl₃)



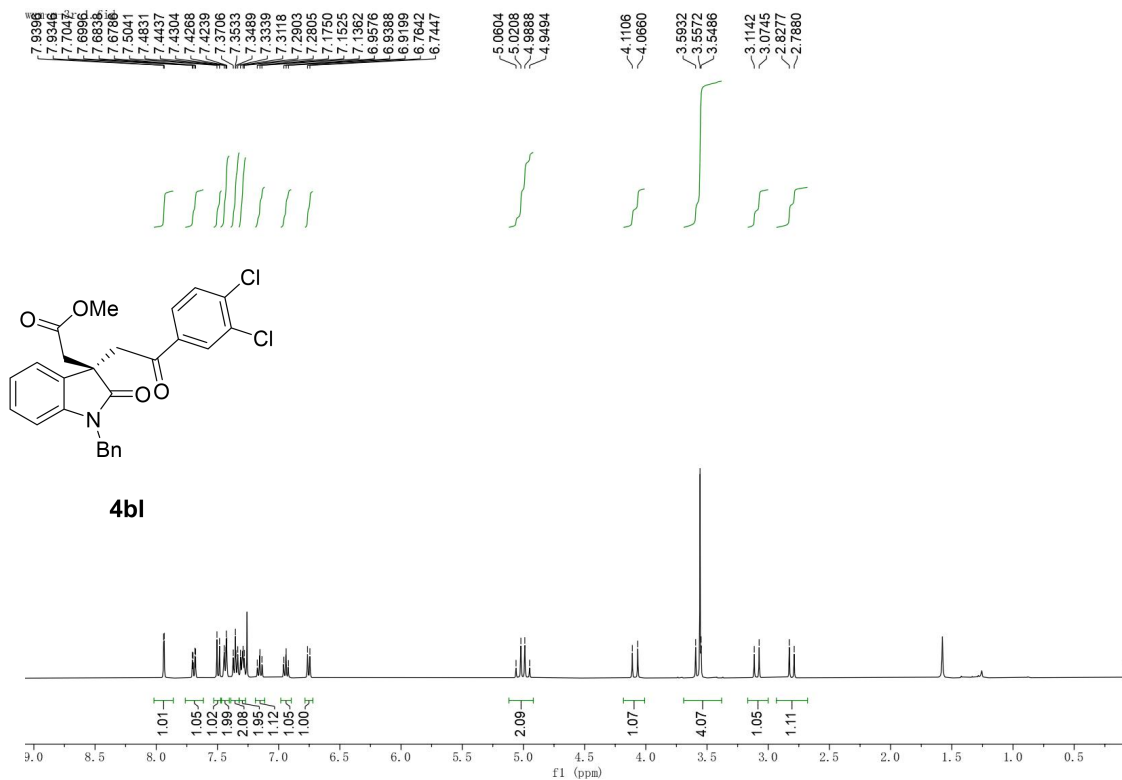
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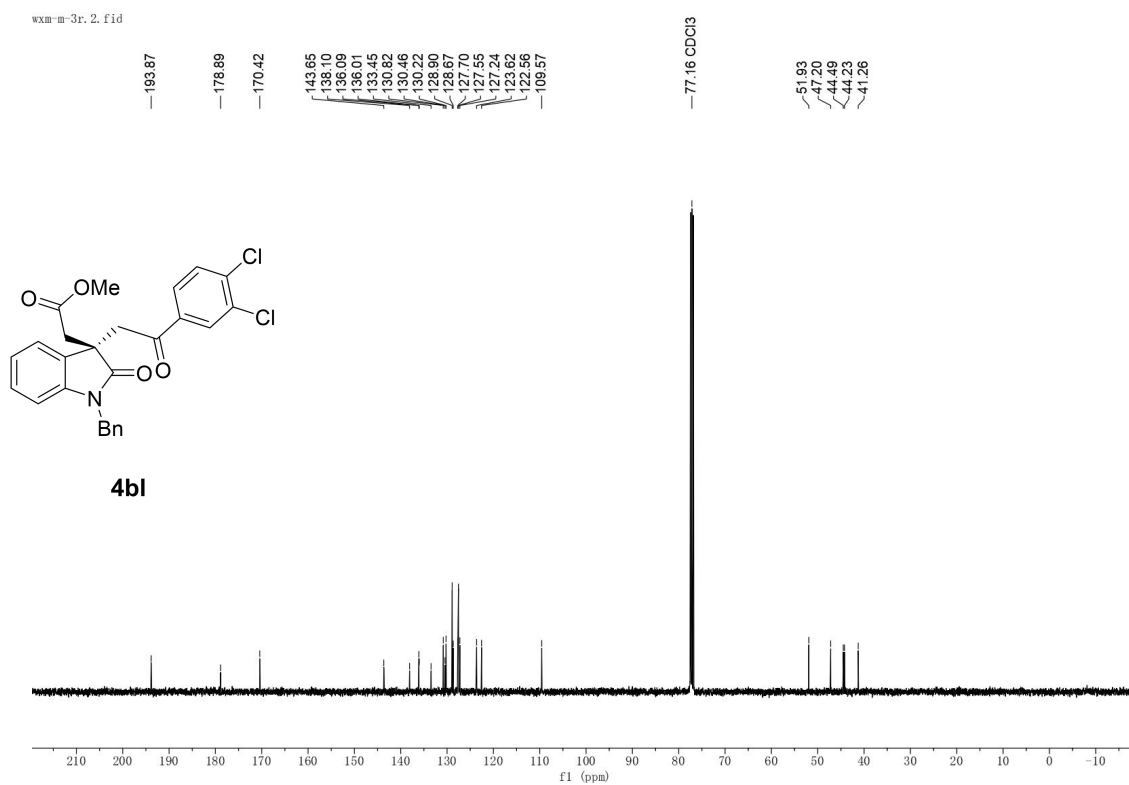
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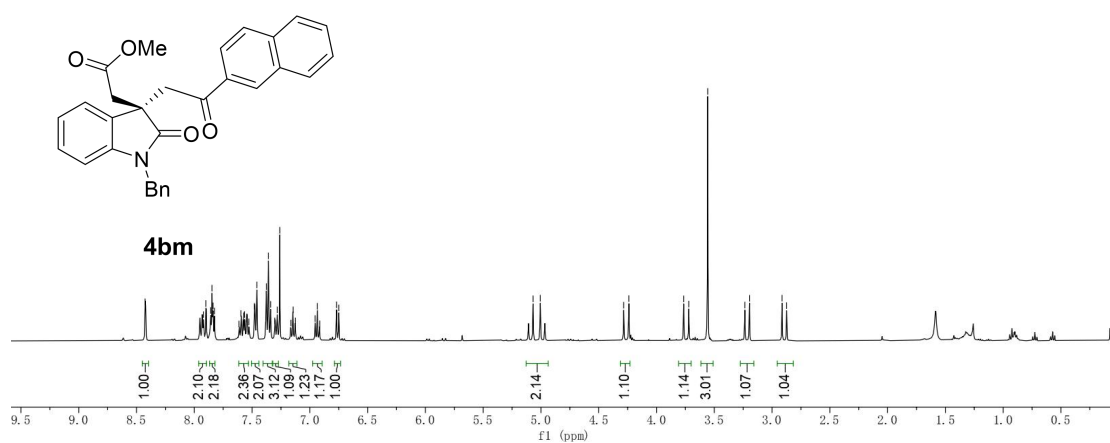
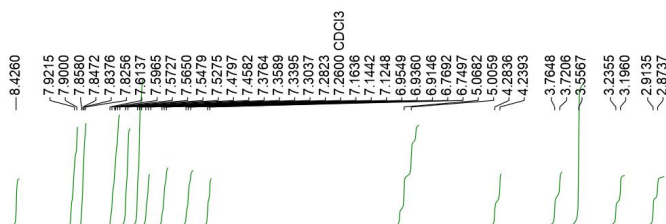


¹³C NMR-**4bl** (100 MHz, CDCl₃)



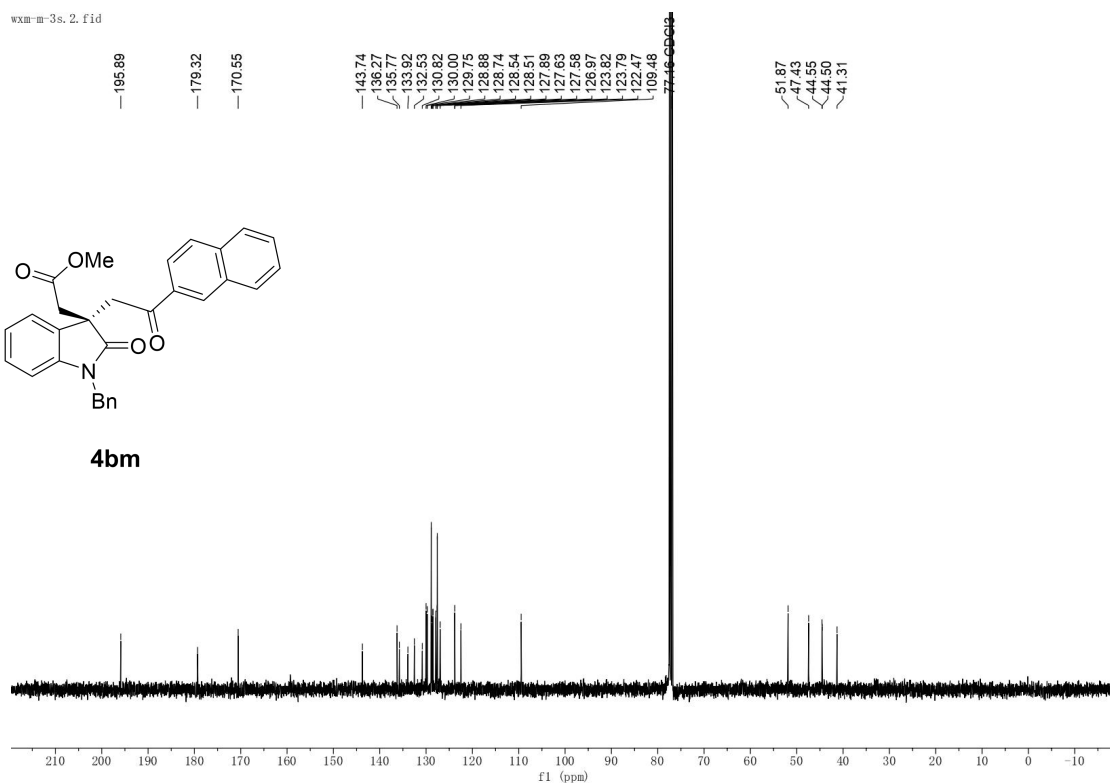
¹H NMR-**4bm**(400 MHz, CDCl₃)

wxlm-3s.1.fid

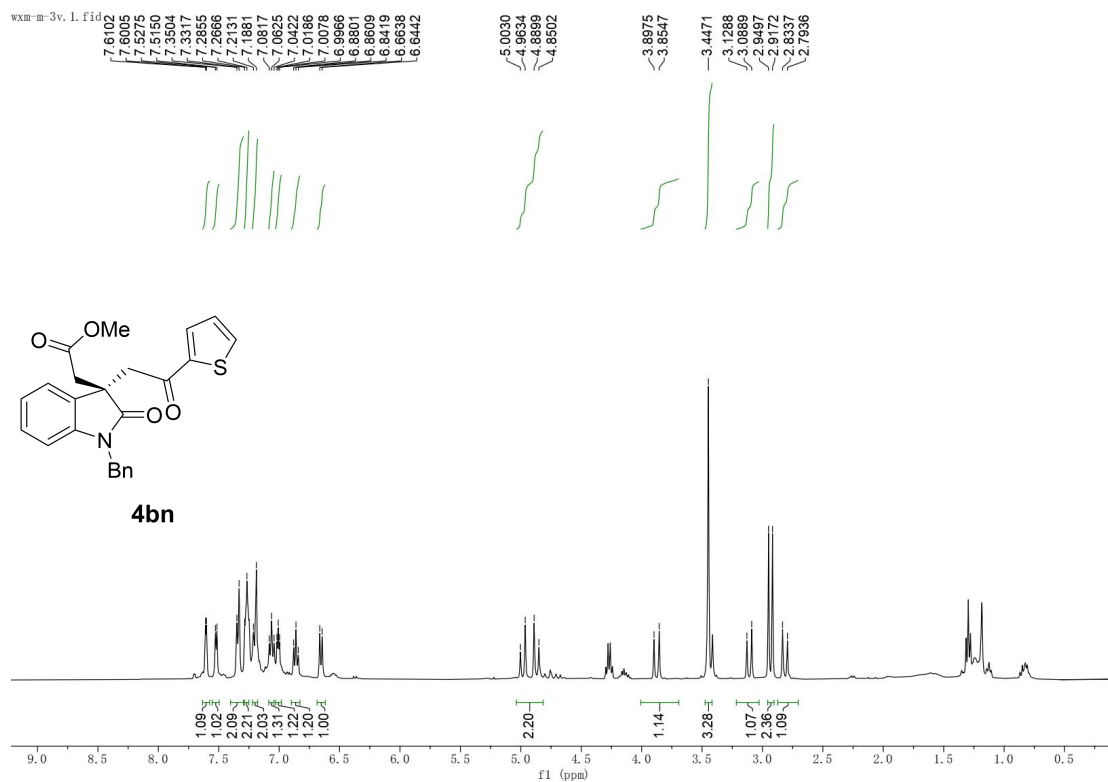


¹³C NMR-**4bm** (100 MHz, CDCl₃)

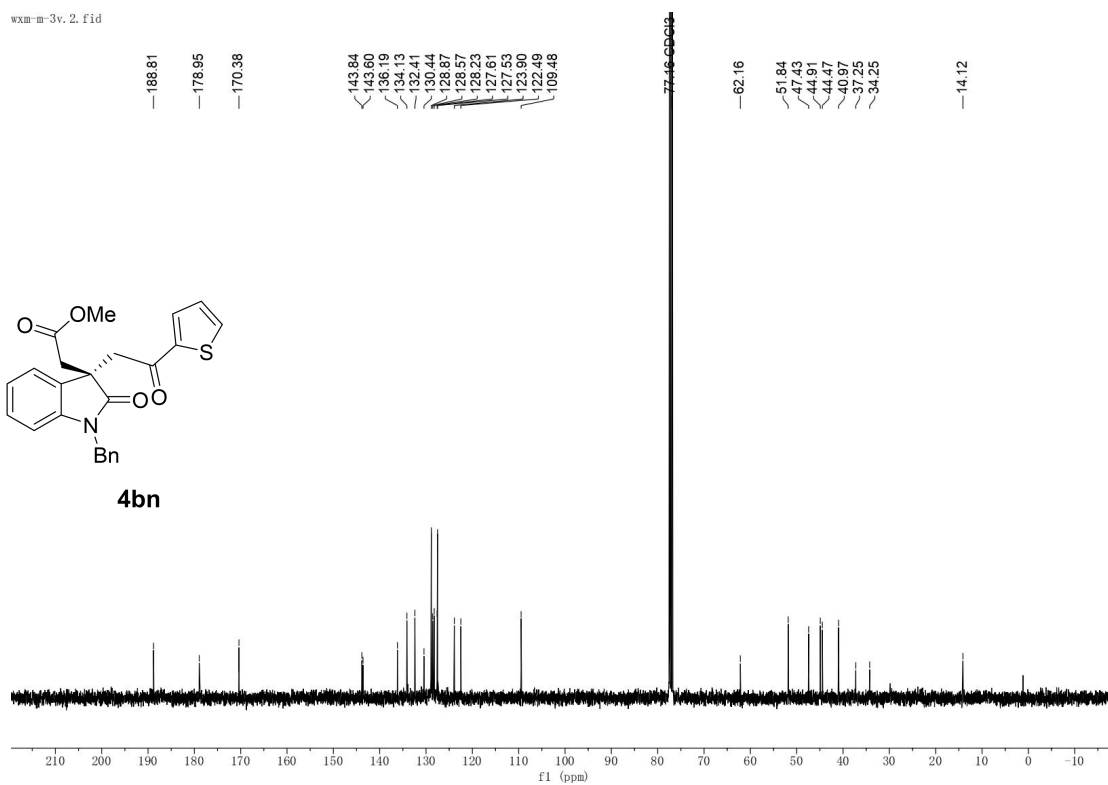
wxlm-3s.2.fid



¹H NMR-**4bn** (400 MHz, CDCl₃)

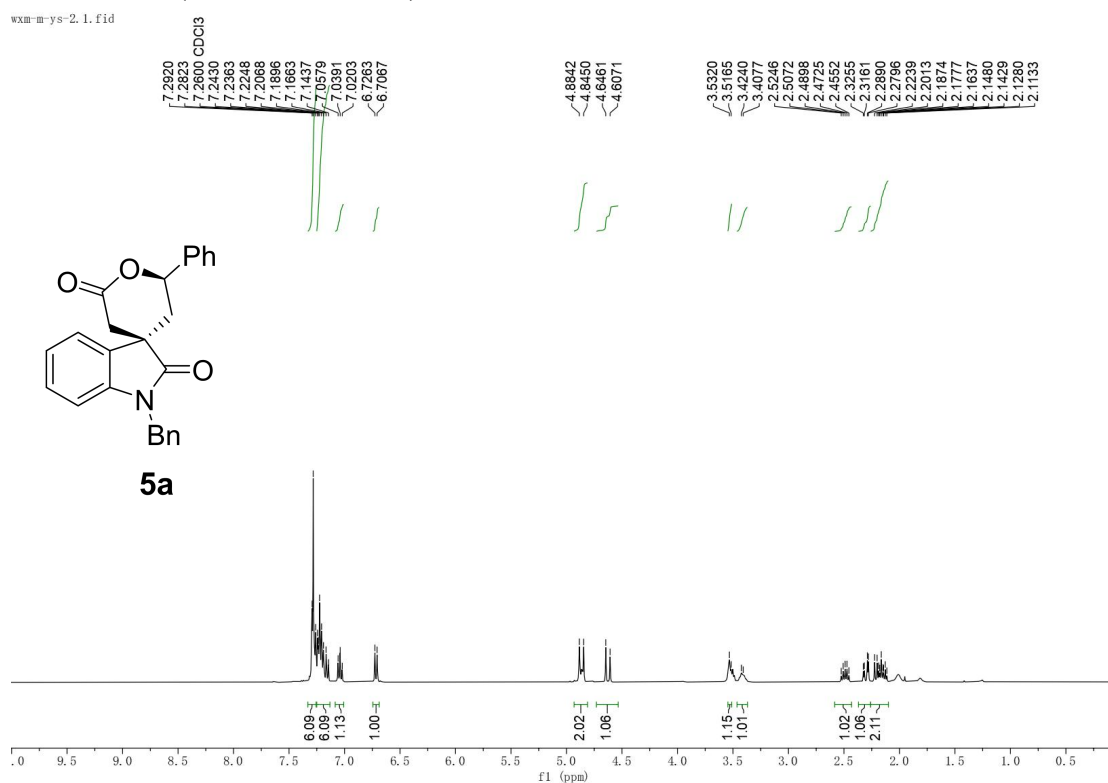


¹³C NMR-**4bn** (100 MHz, CDCl₃)



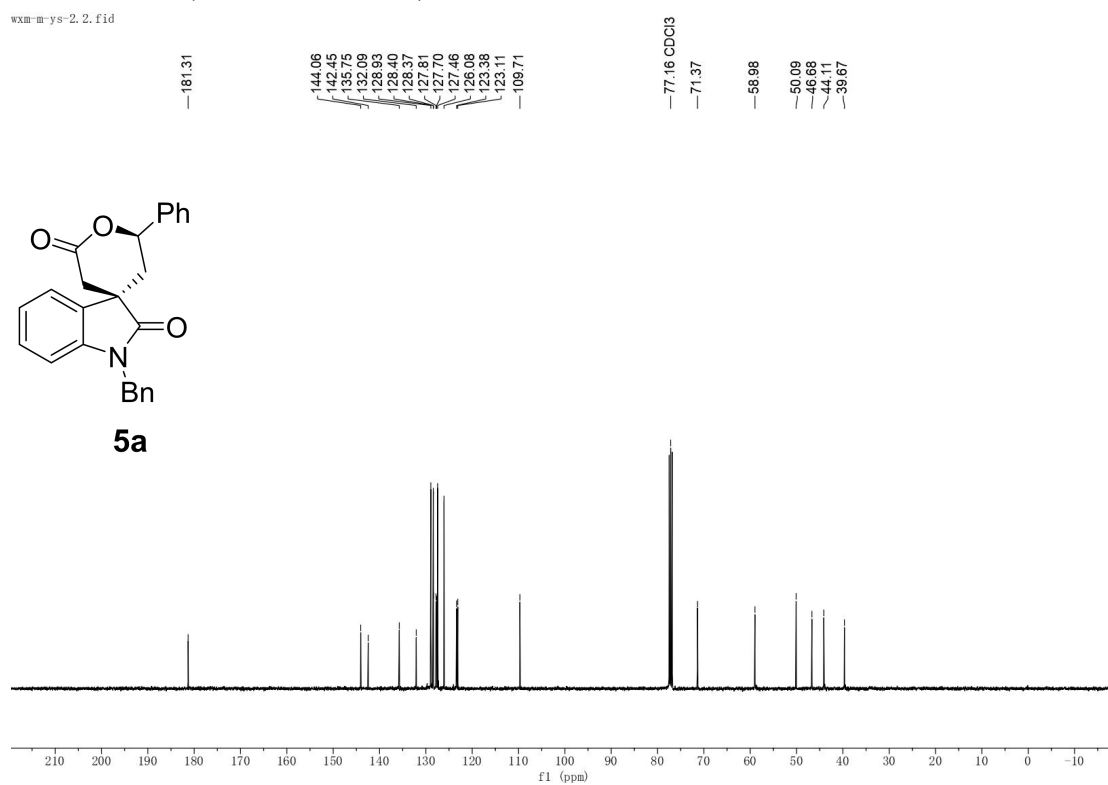
¹H NMR-**5a** (400 MHz, CDCl₃)

wxnm-ys-2.1.fid

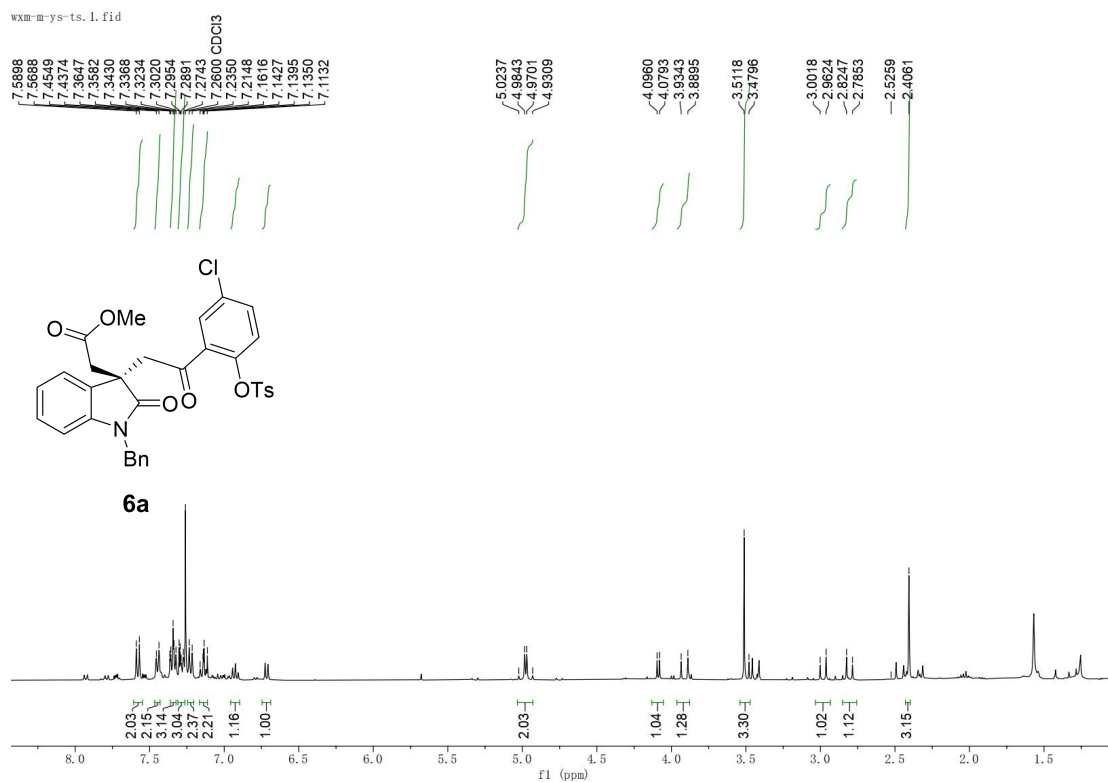


¹³C NMR-**5a** (100 MHz, CDCl₃)

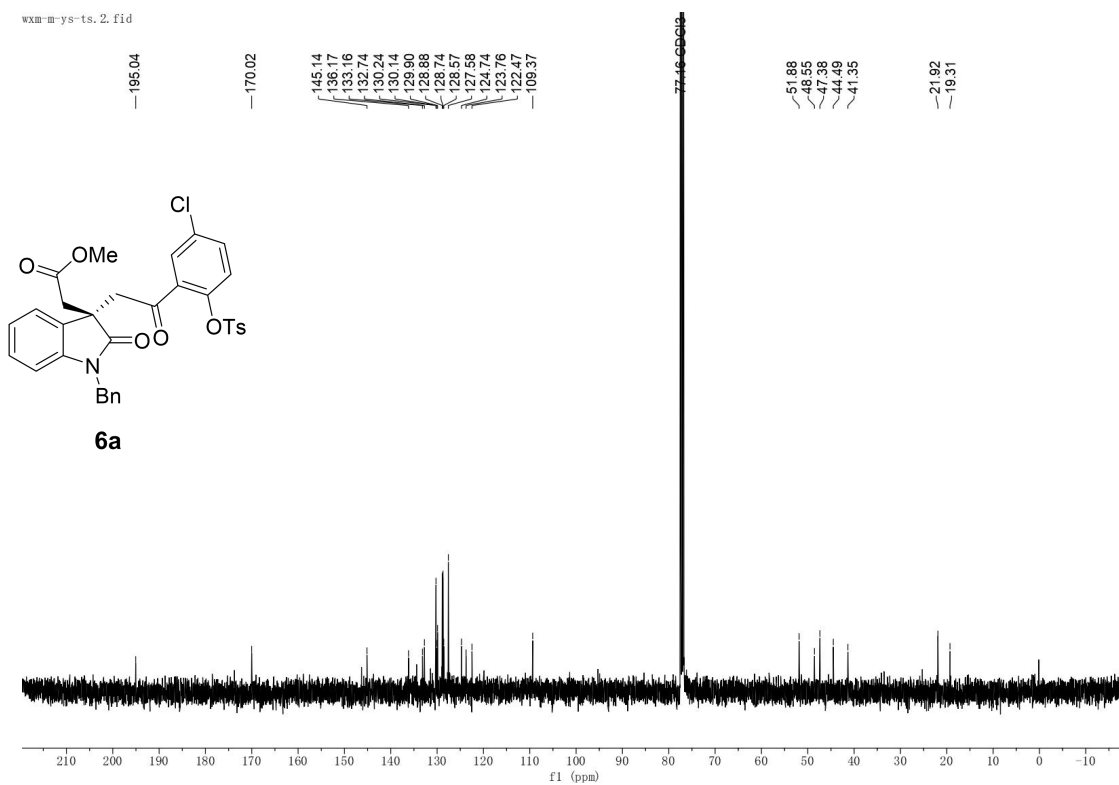
wxnm-ys-2.2.fid



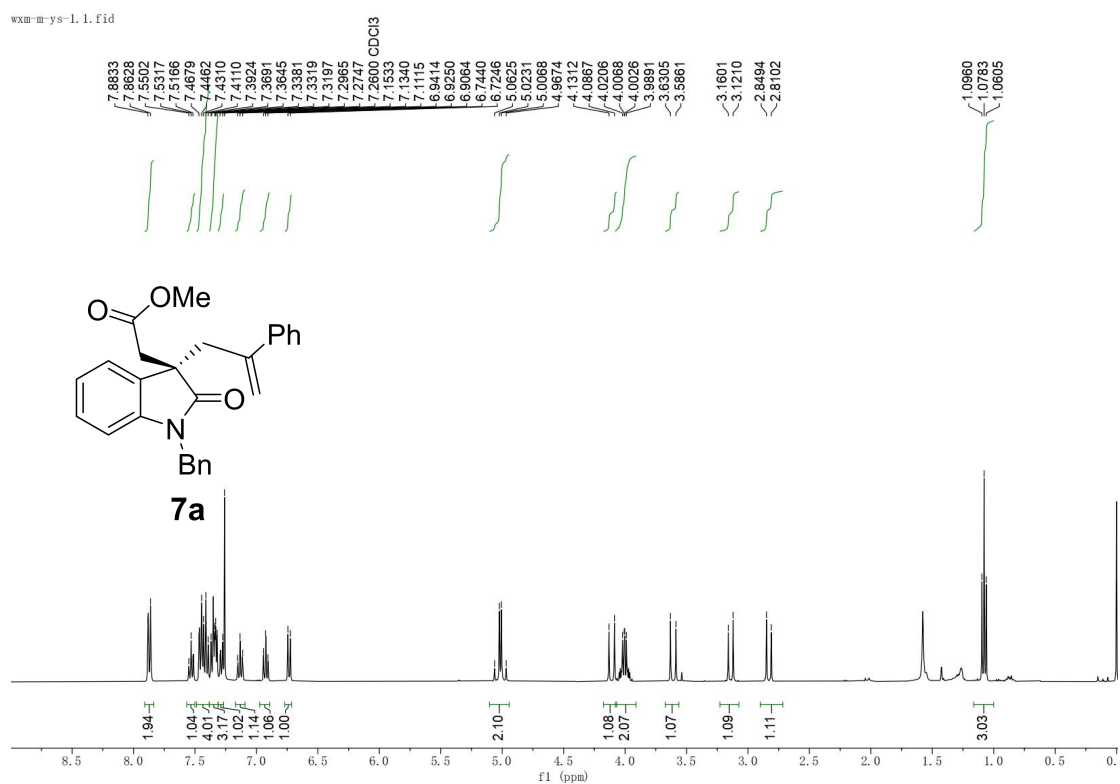
¹H NMR-6a (400 MHz, CDCl₃)



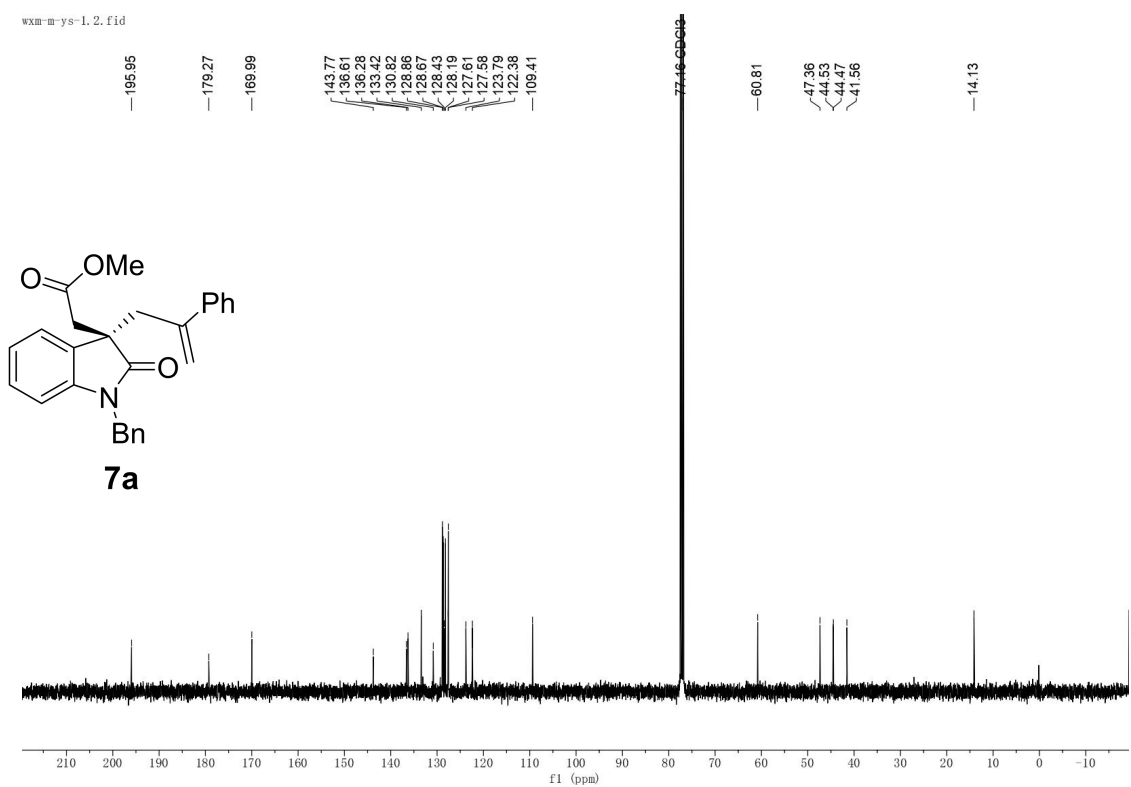
¹³C NMR-6a (100 MHz, CDCl₃)



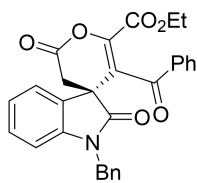
¹H NMR-**7a** (400 MHz, CDCl₃)



¹³C NMR-**7a** (100 MHz, CDCl₃)

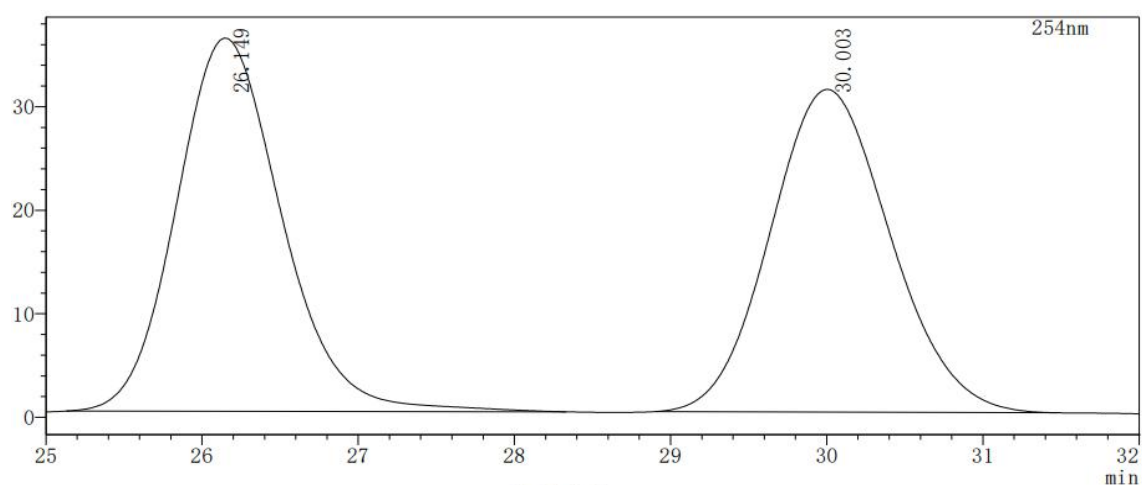


IX.Chiral HPLC analysis trace



3aa

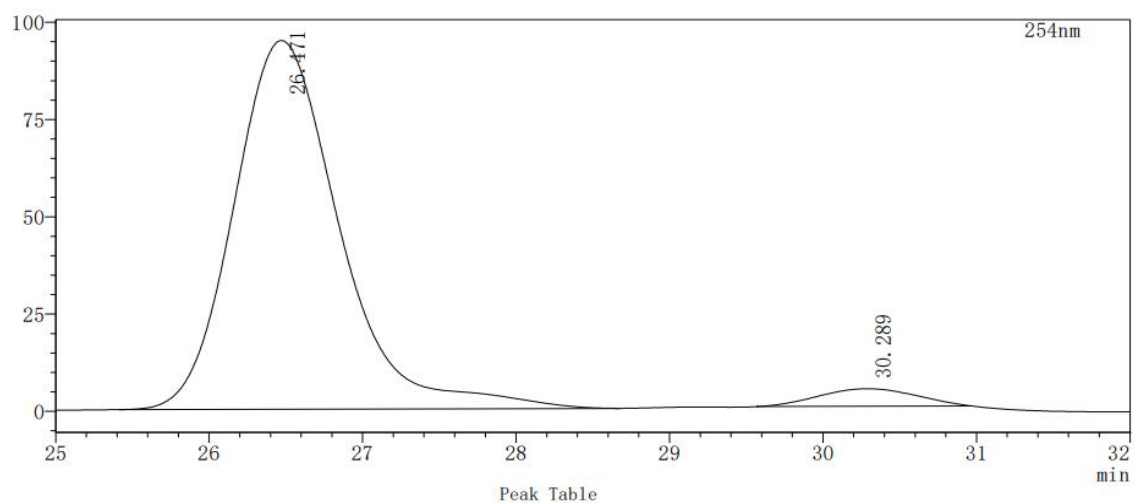
racemic-3aa



Peak Table

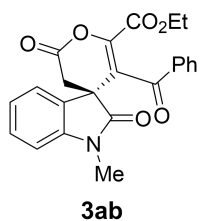
Peak#	Ret. Time	Area	Height	Area%
1	26.149	1692920	36040	50.457
2	30.003	1662281	31156	49.543
Total		3355201	67196	100.000

chiral-3aa

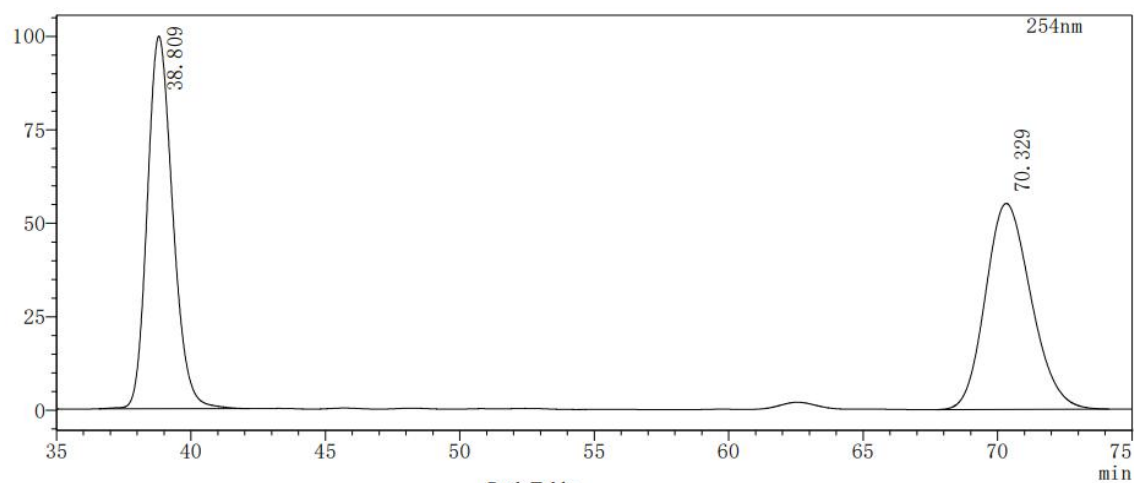


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	26.471	4528201	94772	95.772
2	30.289	199904	4524	4.228
Total		4728105	99296	100.000



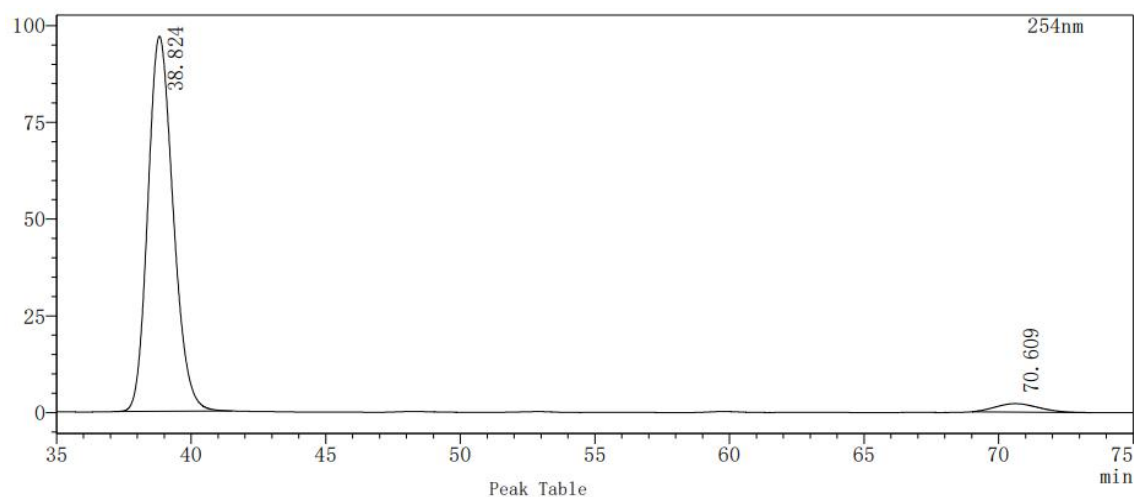
racemic-3ab



Peak Table

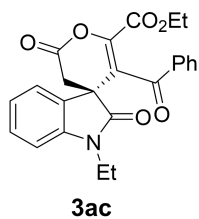
254nm					
Peak#	Ret. Time	Area	Height	Area%	
1	38.809	6572127	99647	50.309	
2	70.329	6491291	55078	49.691	
Total		13063419	154725	100.000	

chiral-3ab

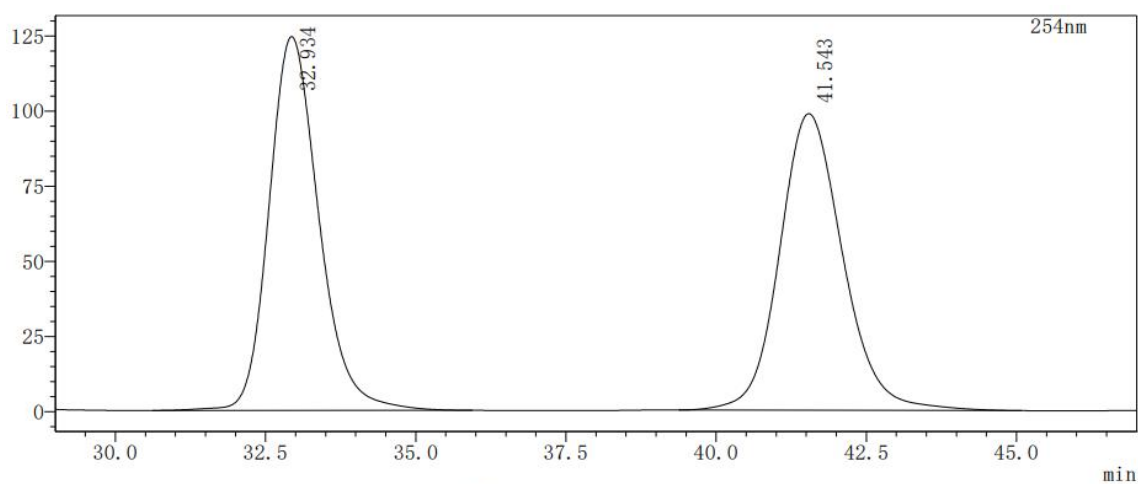


Peak Table

254nm					
Peak#	Ret. Time	Area	Height	Area%	
1	38.824	6339840	96943	96.374	
2	70.609	238546	2165	3.626	
Total		6578386	99108	100.000	



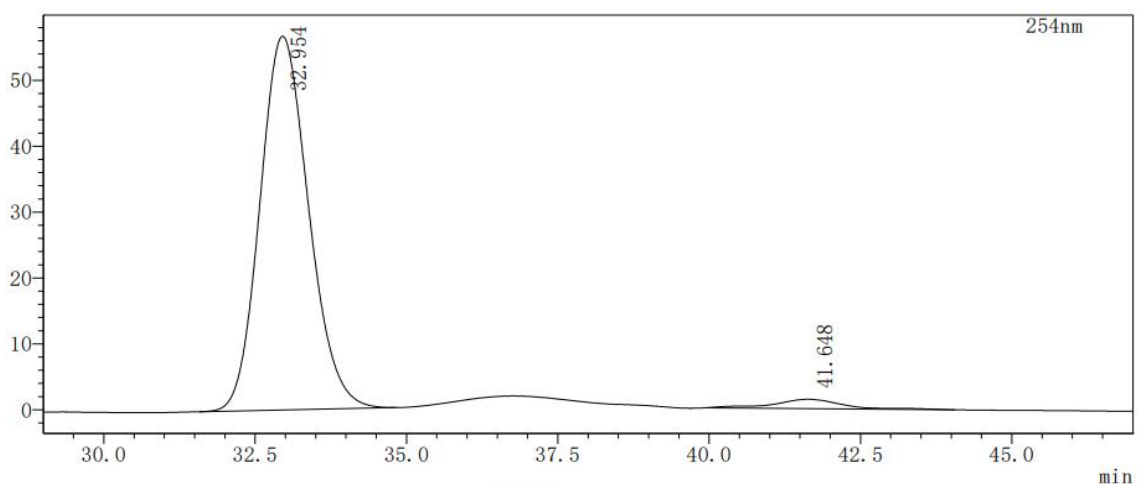
racemic-3ac



Peak Table

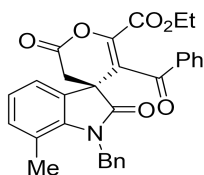
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	32.934	7187319	124389	49.880
2	41.543	7221797	98685	50.120
Total		14409116	223074	100.000

chiral-3ac



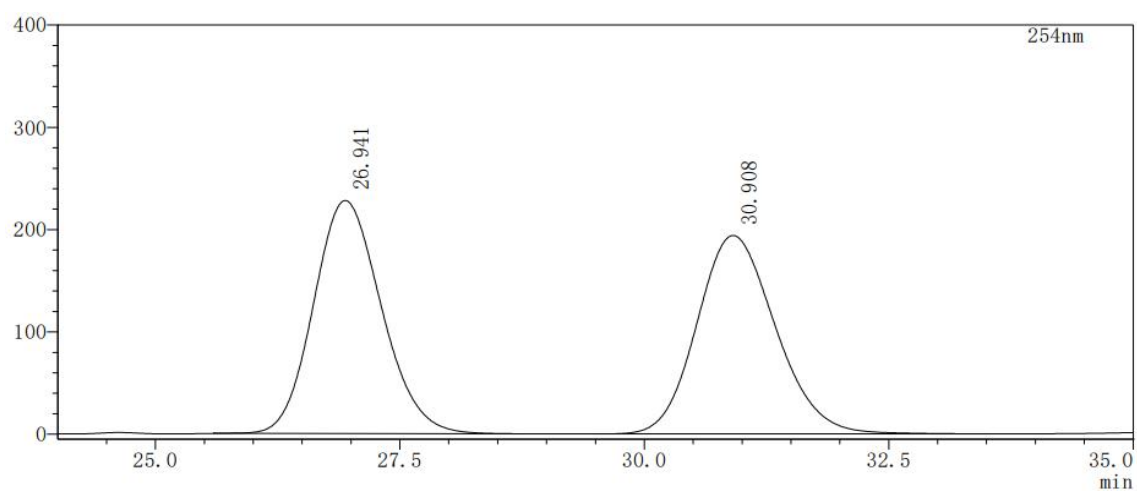
Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	32.954	3175722	56754	96.440
2	41.648	117225	1425	3.560
Total		3292948	58178	100.000



3ad

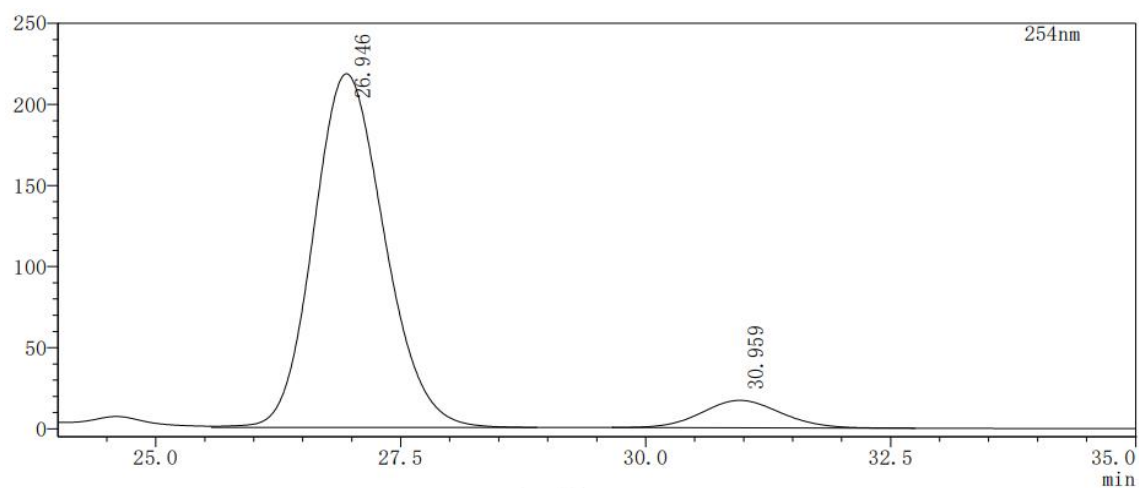
racemic-3ad



Peak Table

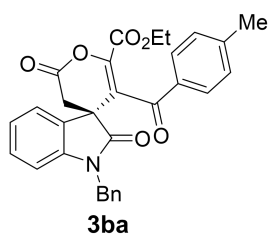
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	26.941	11011412	227875	50.378
2	30.908	10846034	193954	49.622
Total		21857446	421829	100.000

chiral-3ad

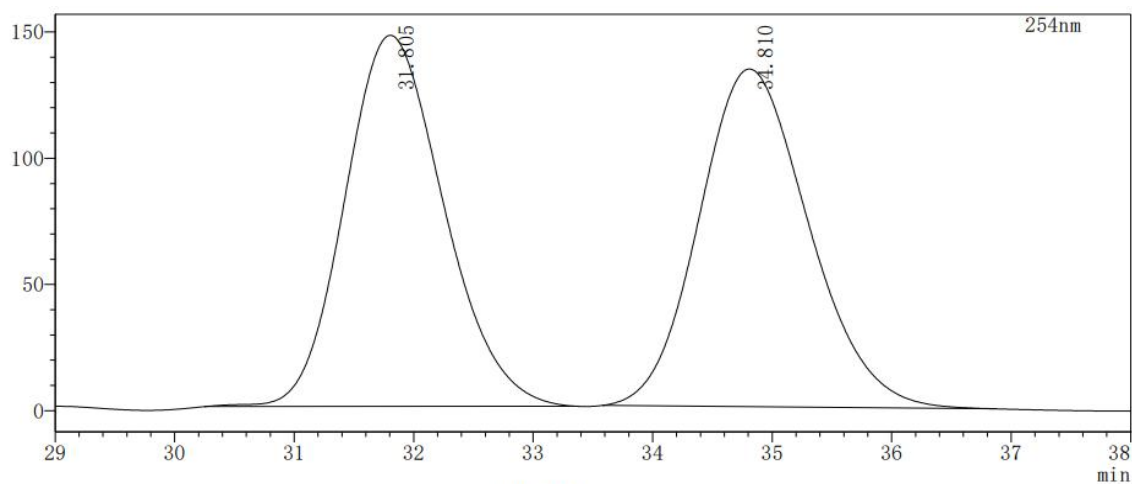


Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	26.946	10989476	218087	92.013
2	30.959	953948	16908	7.987
Total		11943424	234995	100.000



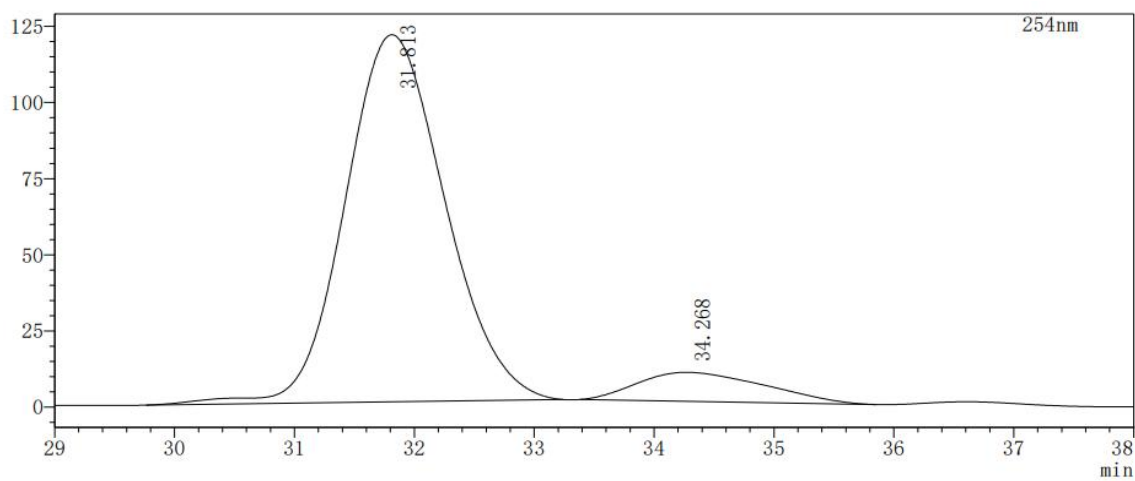
racemic-3ba



Peak Table

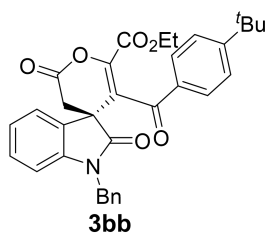
Peak#	Ret. Time	Area	Height	Area%
1	31.805	8461689	147020	49.844
2	34.810	8514526	133749	50.156
Total		16976215	280769	100.000

chiral-3ba

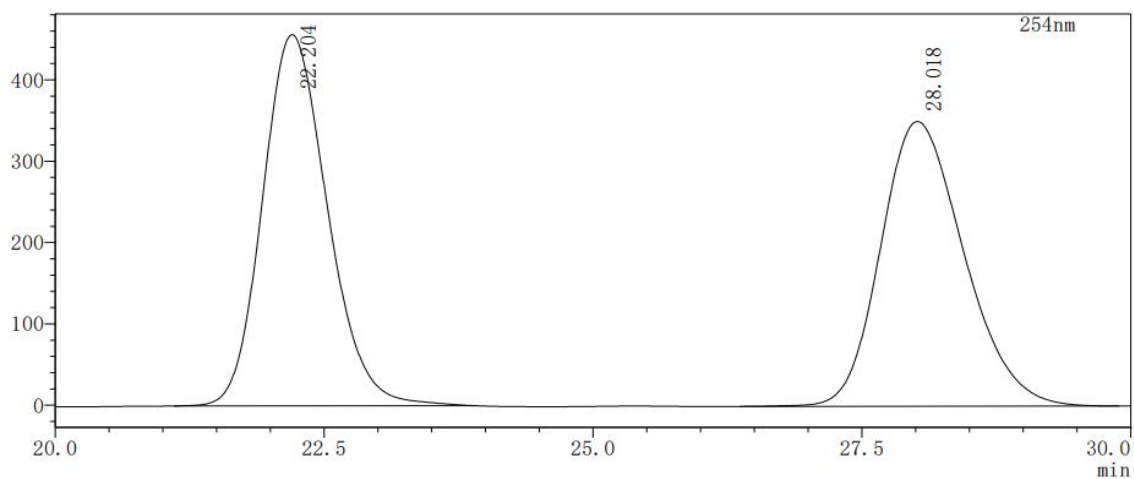


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	31.813	6979661	120520	90.877
2	34.268	700675	9514	9.123
Total		7680336	130034	100.000



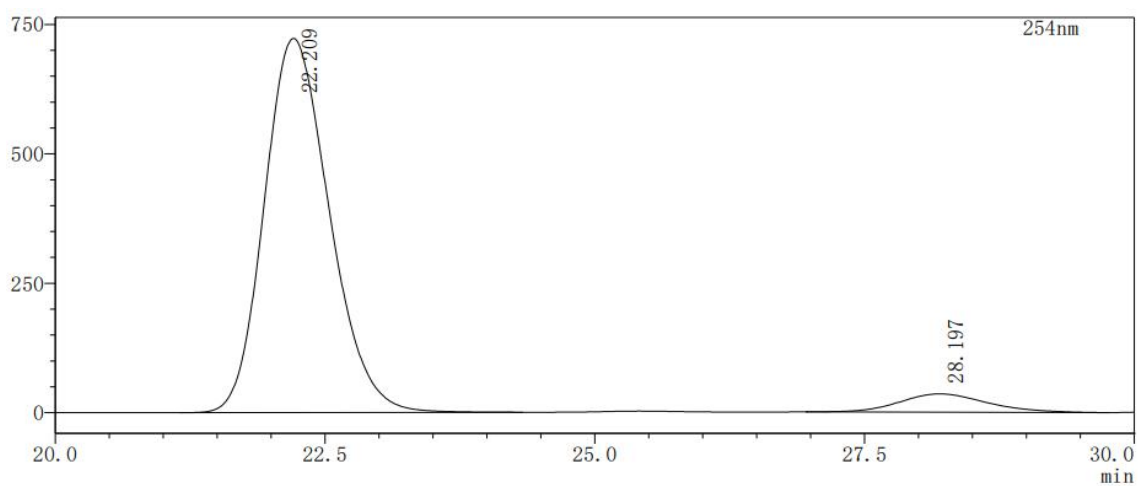
racemic-3bb



Peak Table

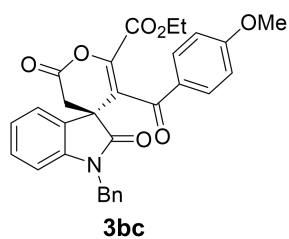
Peak#	Ret. Time	Area	Height	Area%
1	22.204	19181409	456365	50.434
2	28.018	18851052	350117	49.566
Total		38032461	806482	100.000

chiral-3bb

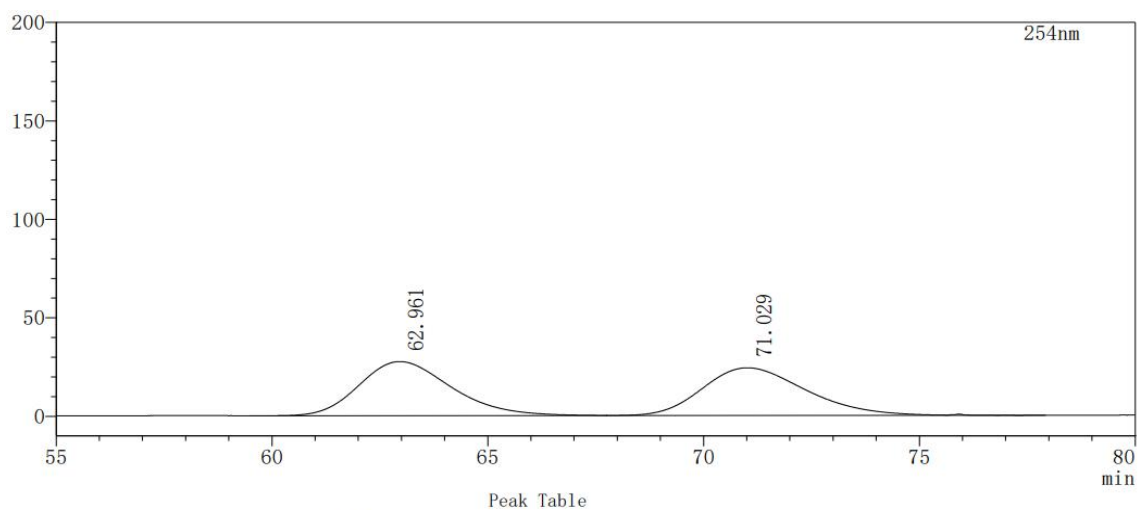


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	22.209	30323802	722762	93.815
2	28.197	1999155	35348	6.185
Total		32322957	758110	100.000

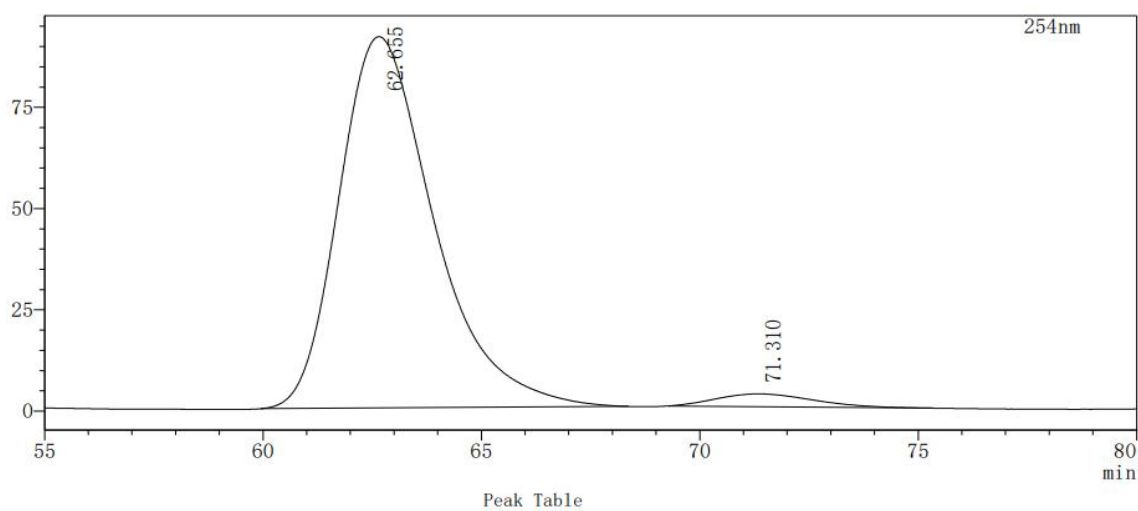


racemic-3bc

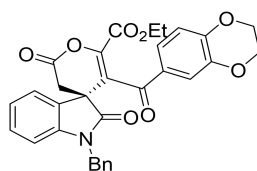


Peak#	Ret. Time	Area	Height	Area%
1	62.961	4078082	27466	50.185
2	71.029	4048089	24205	49.815
Total		8126171	51671	100.000

chiral-3bc

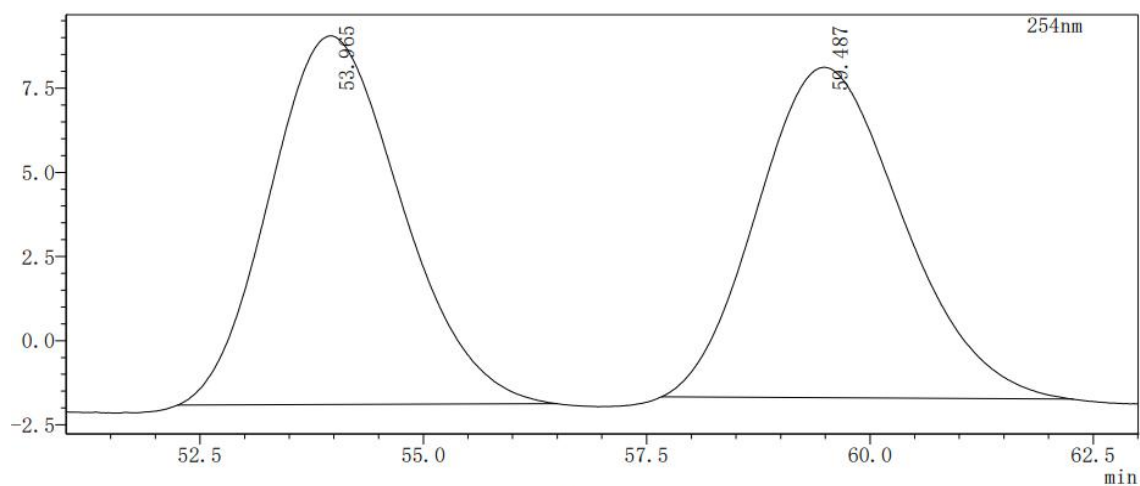


Peak#	Ret. Time	Area	Height	Area%
1	62.655	13865014	91667	96.613
2	71.310	486067	3154	3.387
Total		14351081	94821	100.000



3bd

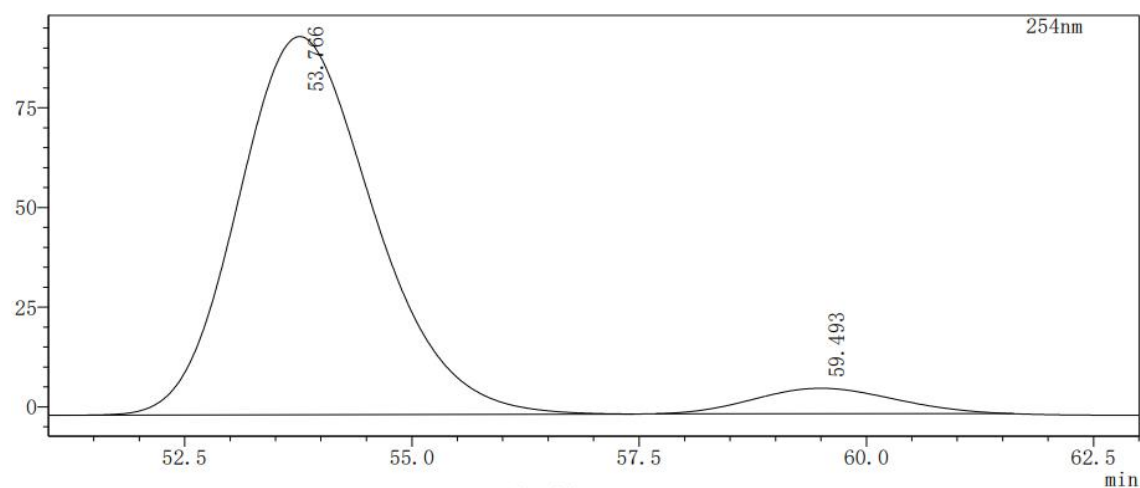
racemic-3bf



Peak Table

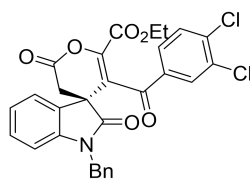
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	53.965	1122036	10952	50.281
2	59.487	1109476	9814	49.719
Total		2231513	20766	100.000

chiral-3bf



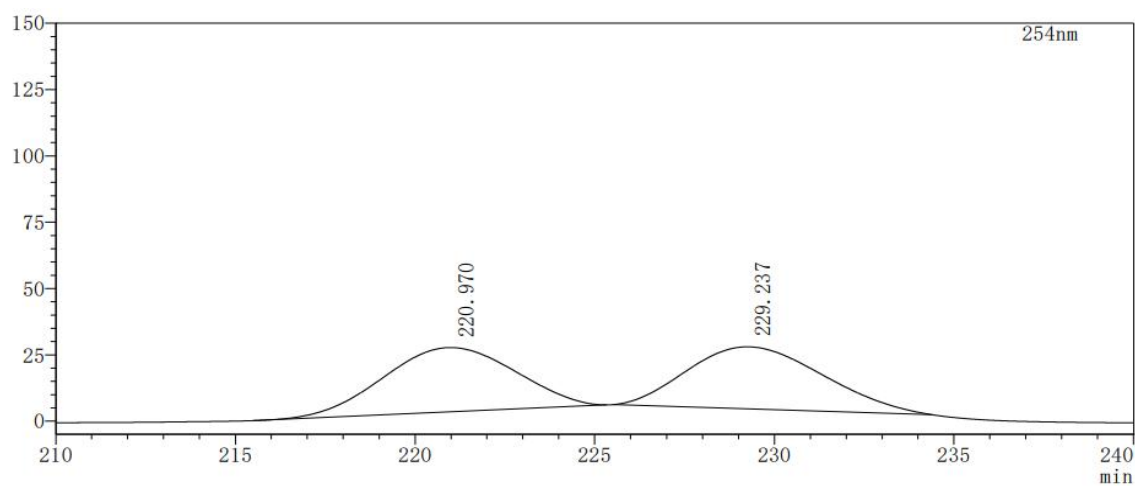
Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	53.766	9888015	94834	93.503
2	59.493	687042	6372	6.497
Total		10575057	101207	100.000



3be

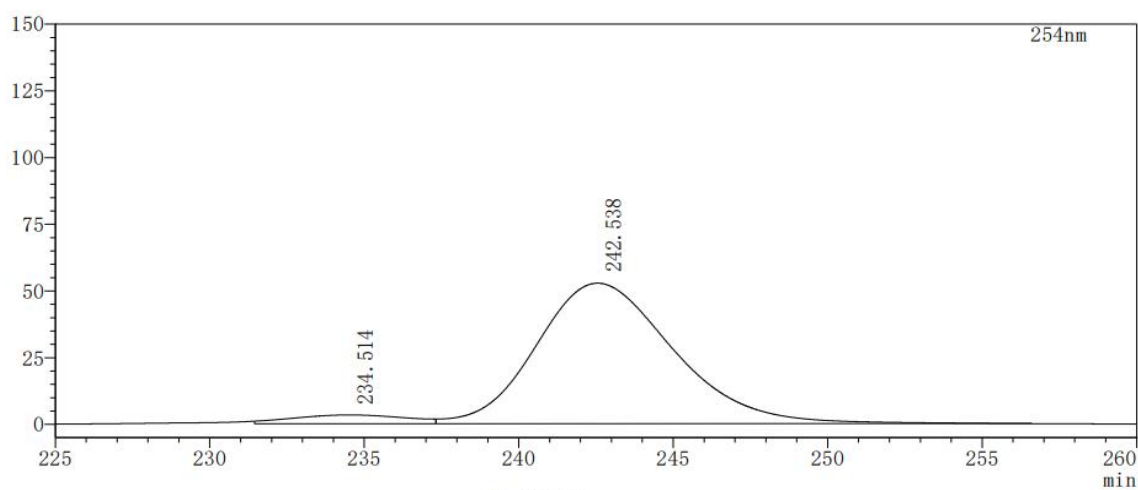
racemic-3be



Peak Table

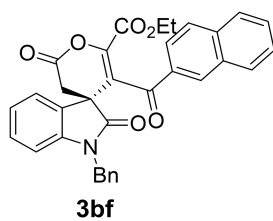
Peak#	Ret. Time	Area	Height	Area%
1	220.970	6181536	24253	50.196
2	229.237	6133316	23374	49.804
Total		12314852	47626	100.000

chiral-3be

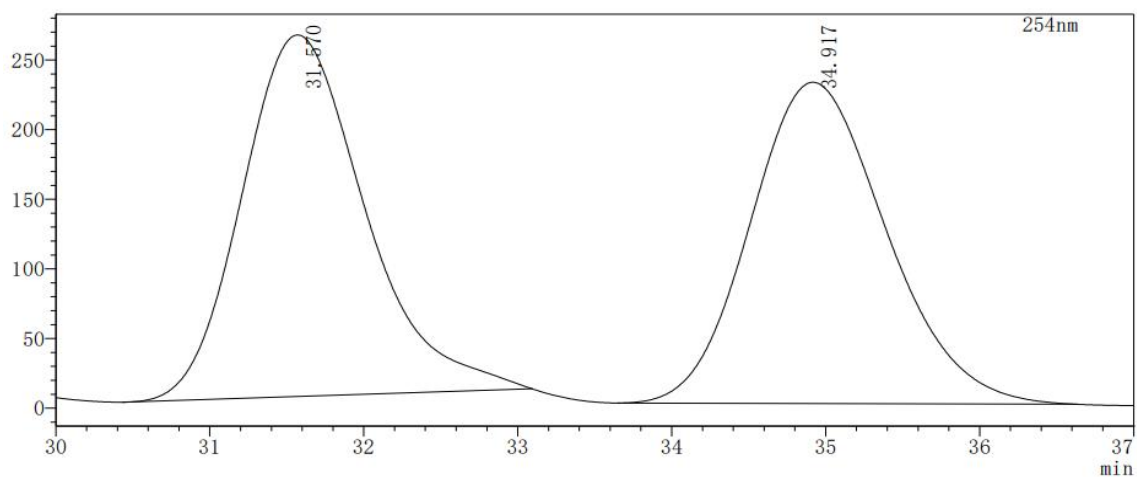


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	234.514	837252	3254	4.889
2	242.538	16288131	52646	95.111
Total		17125383	55899	100.000



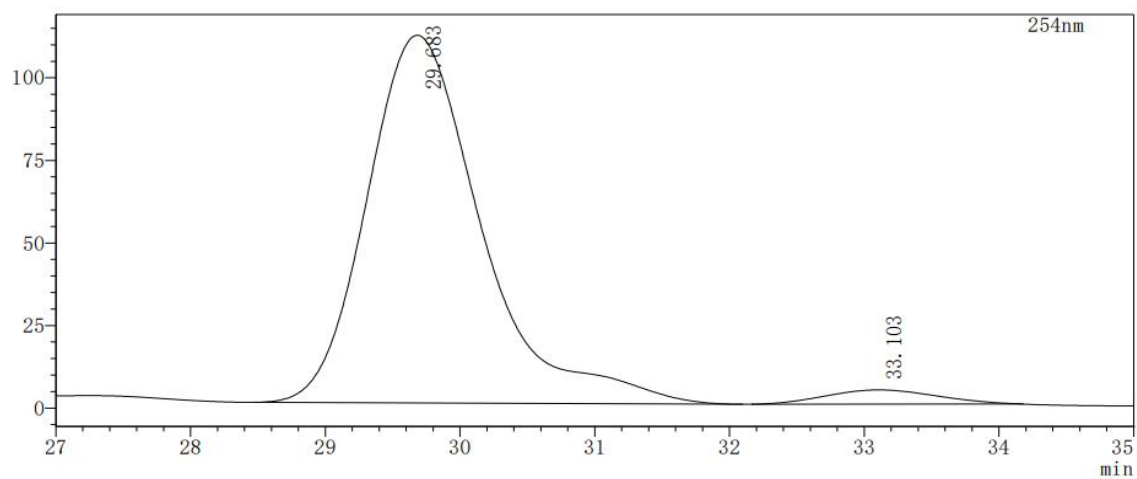
racemic-3bf



Peak Table

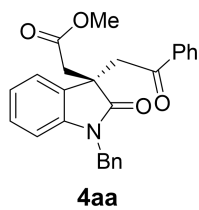
Peak#	Ret. Time	Area	Height	Area%
1	31.570	14370963	259582	50.418
2	34.917	14132628	230715	49.582
Total		28503591	490297	100.000

chiral-3bf

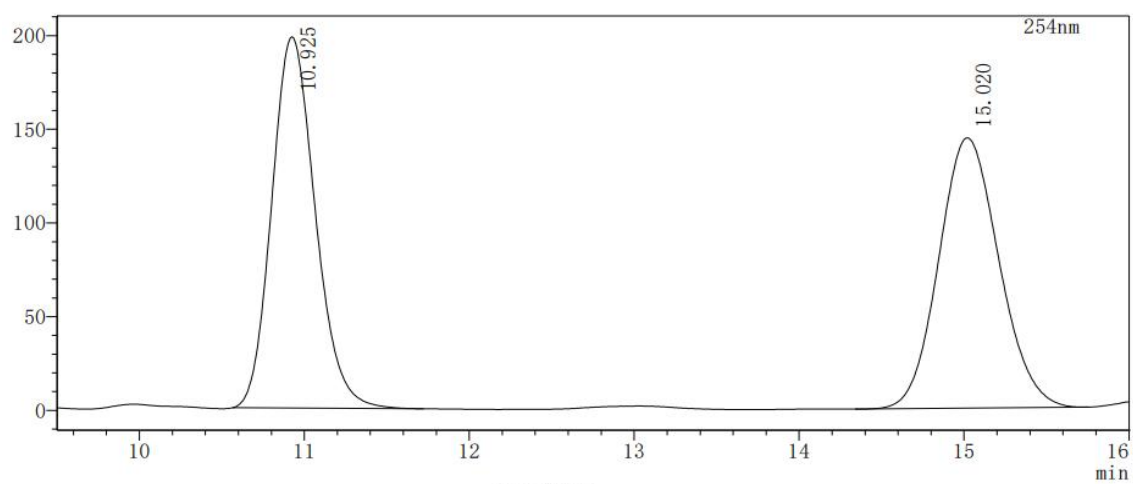


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	29.683	6579571	111350	96.375
2	33.103	247515	4313	3.625
Total		6827085	115663	100.000



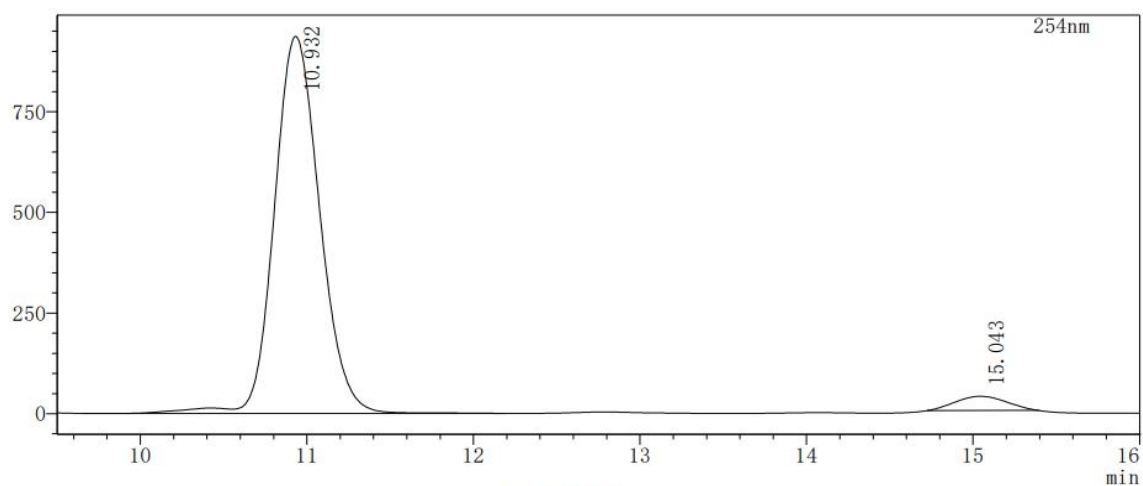
racemic-4aa



Peak Table

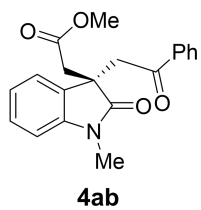
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	10.925	3631878	198105	49.810
2	15.020	3659650	144278	50.190
Total		7291528	342382	100.000

chiral-4aa

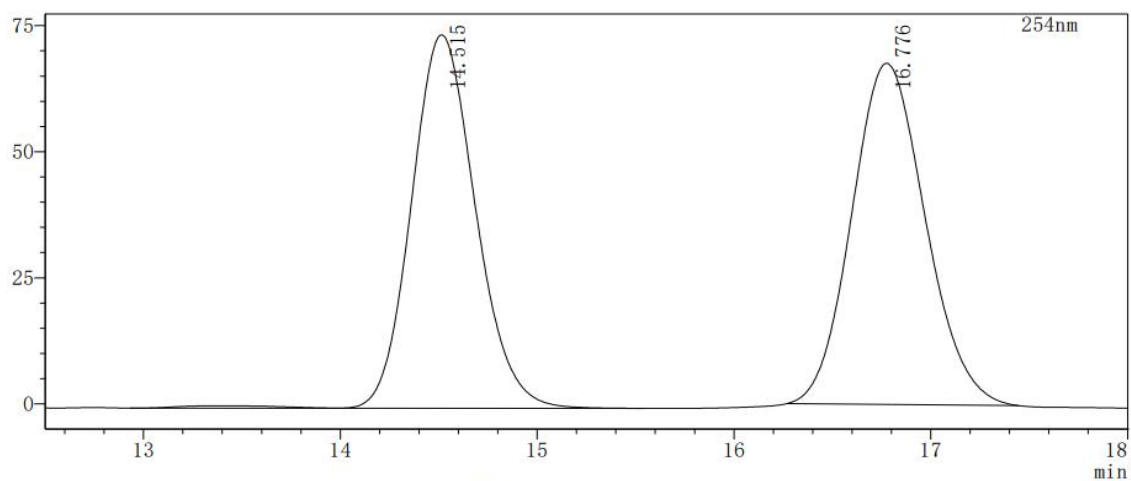


Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	10.932	17788963	936753	95.930
2	15.043	754652	35273	4.070
Total		18543615	972026	100.000



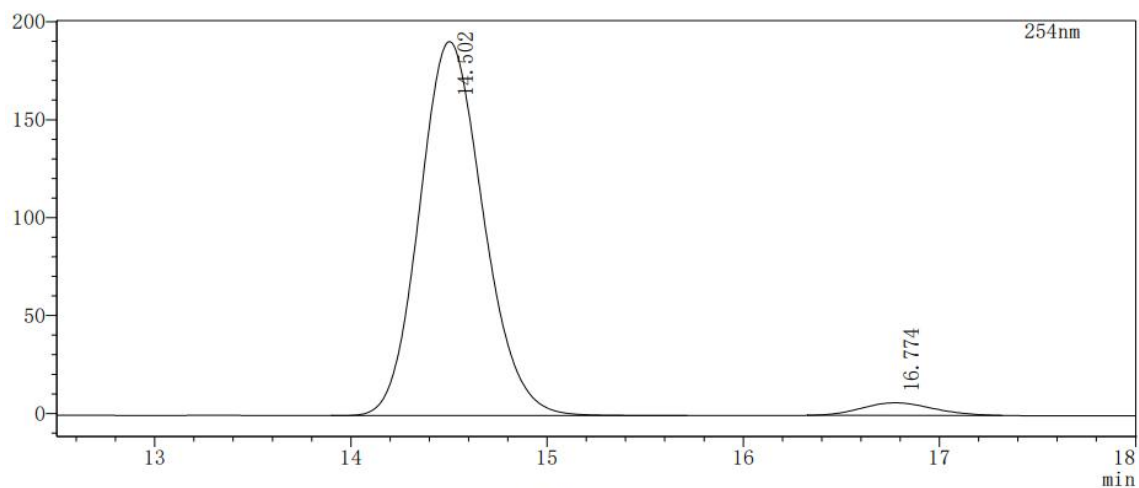
racemic-4ab



Peak Table

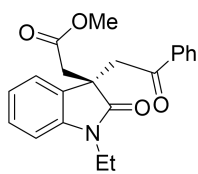
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	14.515	1689959	74032	49.031
2	16.776	1756788	67648	50.969
Total		3446747	141679	100.000

chiral-4ab



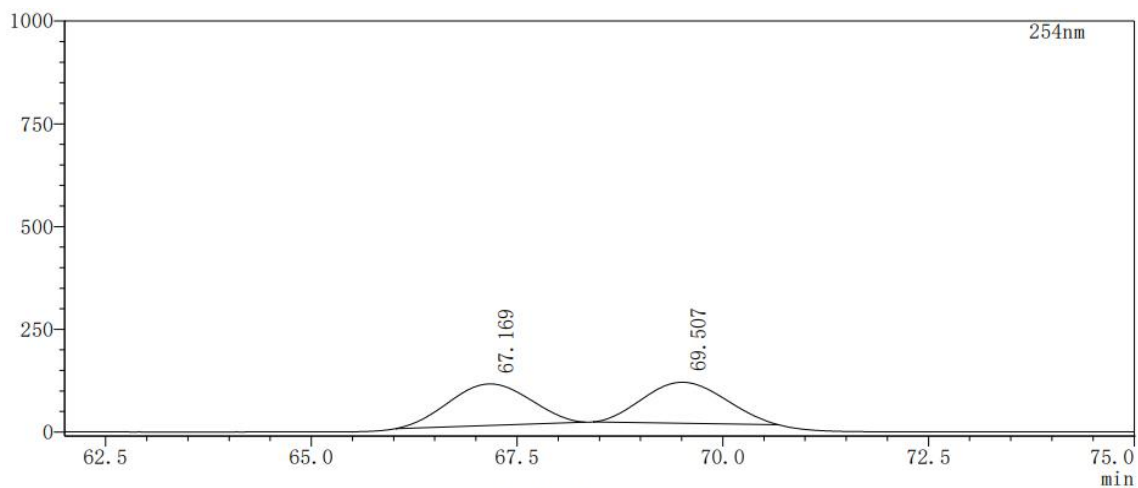
Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	14.502	4321013	191011	96.367
2	16.774	162898	6434	3.633
Total		4483911	197446	100.000



4ac

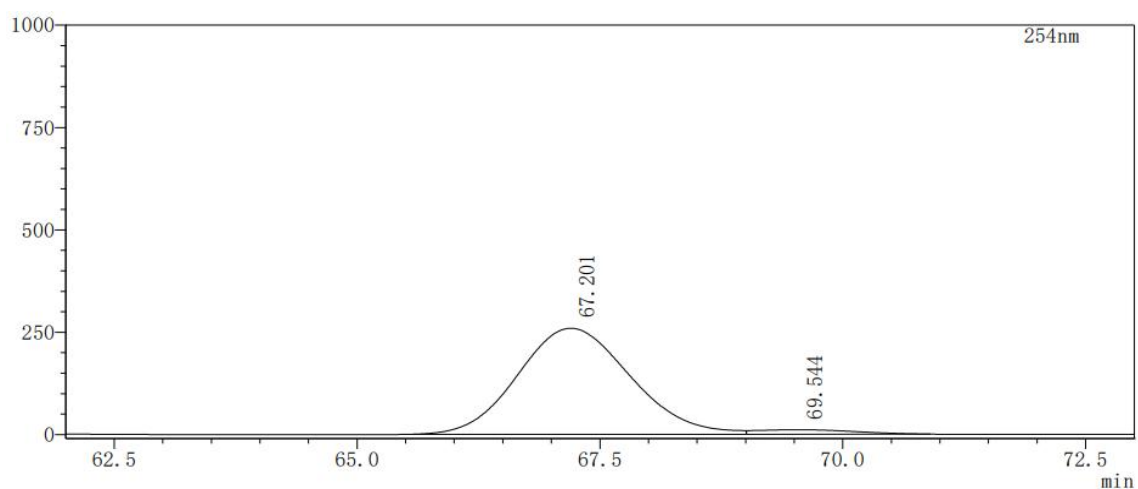
racemic-4ac



Peak Table

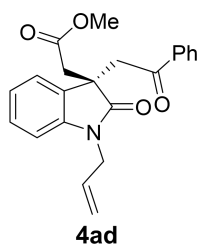
Peak#	Ret. Time	Area	Height	Area%
1	67.169	6919921	100684	49.932
2	69.507	6938777	99769	50.068
Total		13858699	200453	100.000

chiral-4ac

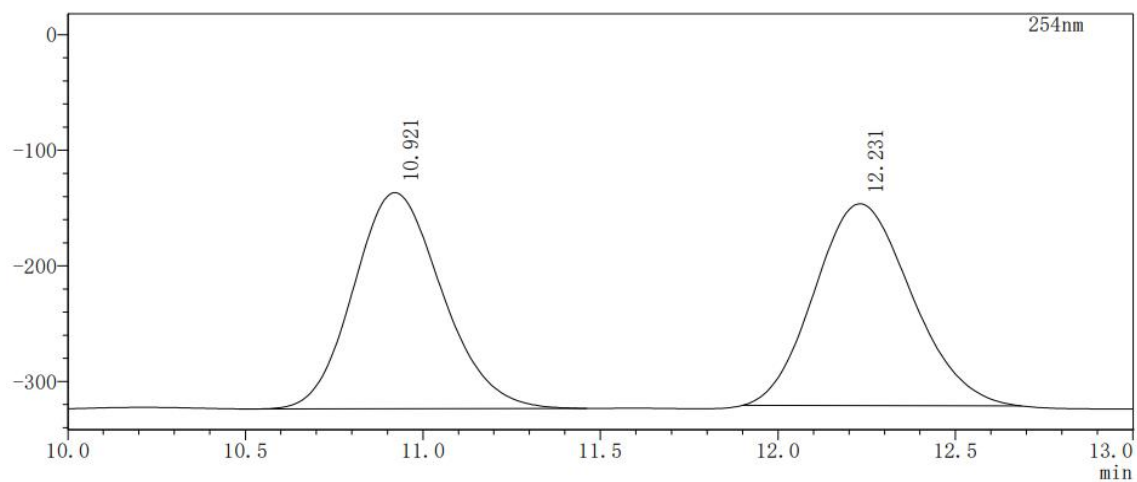


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	67.201	20925884	259047	96.508
2	69.544	757125	10918	3.492
Total		21683009	269965	100.000



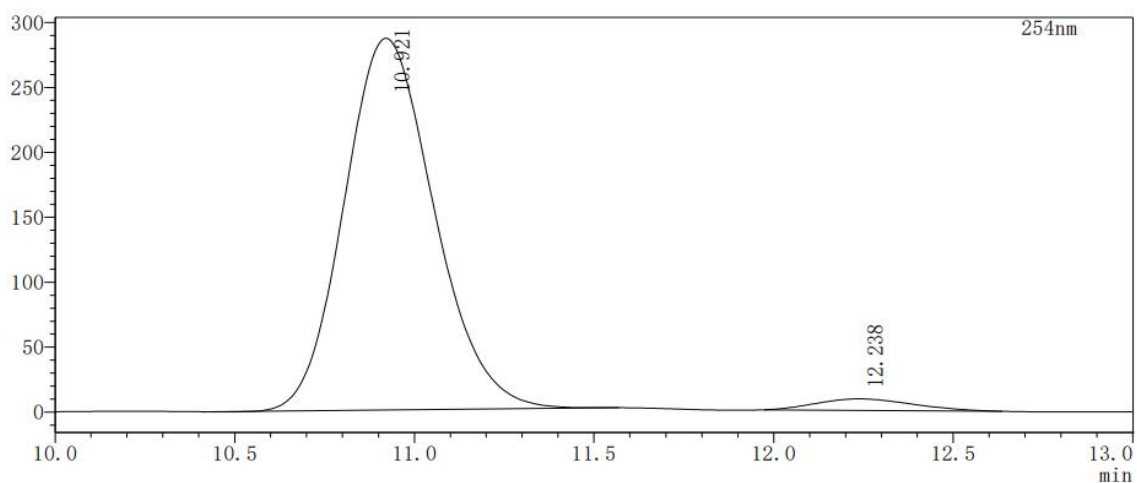
racemic-4ad



Peak Table

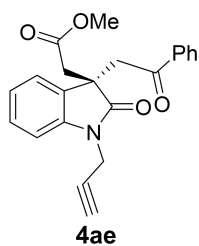
Peak#	Ret. Time	Area	Height	Area%
1	10.921	3243626	186893	49.322
2	12.231	3332840	174703	50.678
Total		6576466	361596	100.000

chiral-4ad

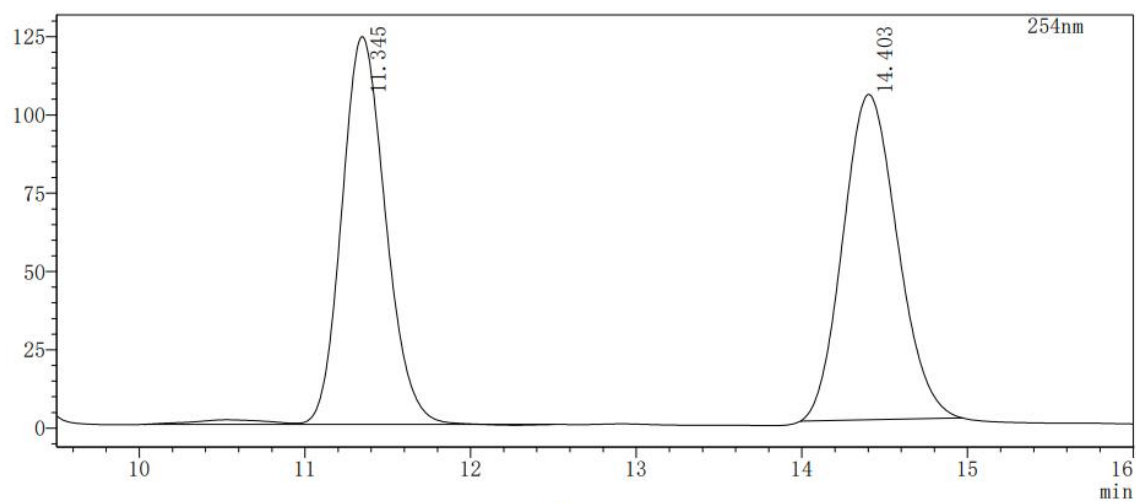


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	10.921	4985830	286206	96.800
2	12.238	164816	8855	3.200
Total		5150646	295061	100.000



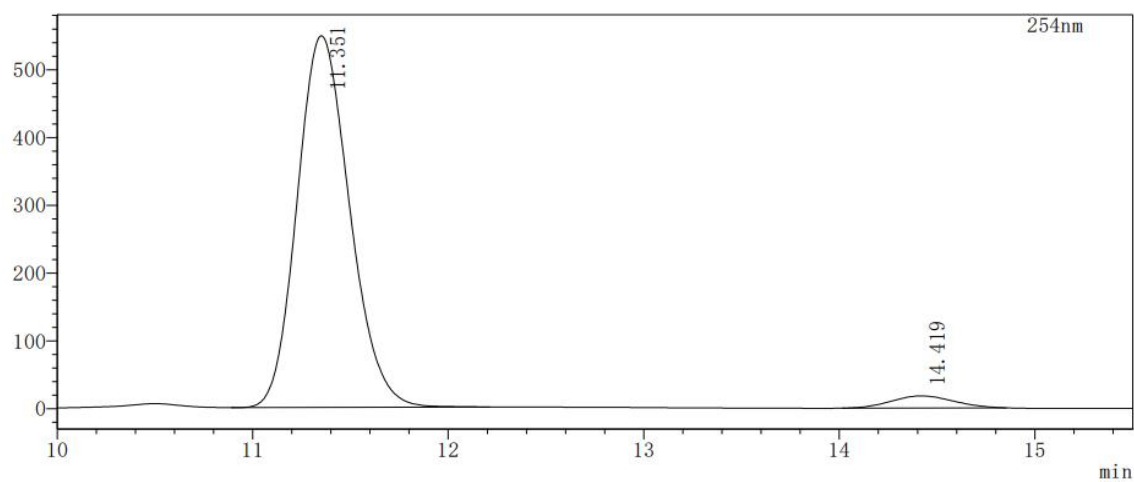
racemic-4ae



Peak Table

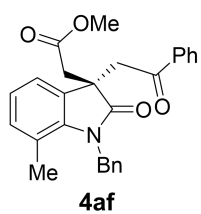
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	11.345	2320023	123829	49.362
2	14.403	2380023	103854	50.638
Total		4700046	227683	100.000

chiral-4ae

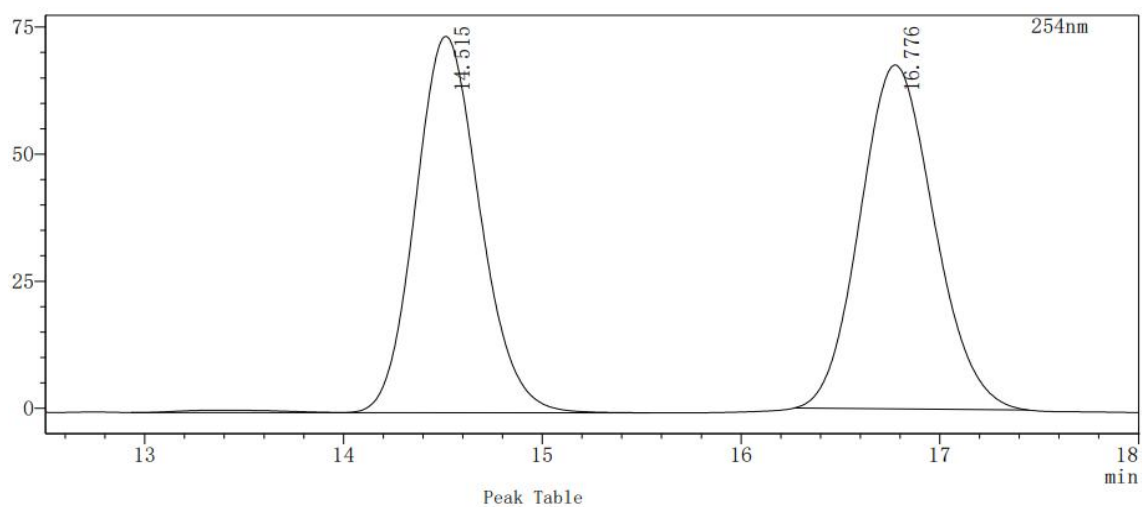


Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	11.351	10227568	548450	96.286
2	14.419	394485	17807	3.714
Total		10622053	566257	100.000



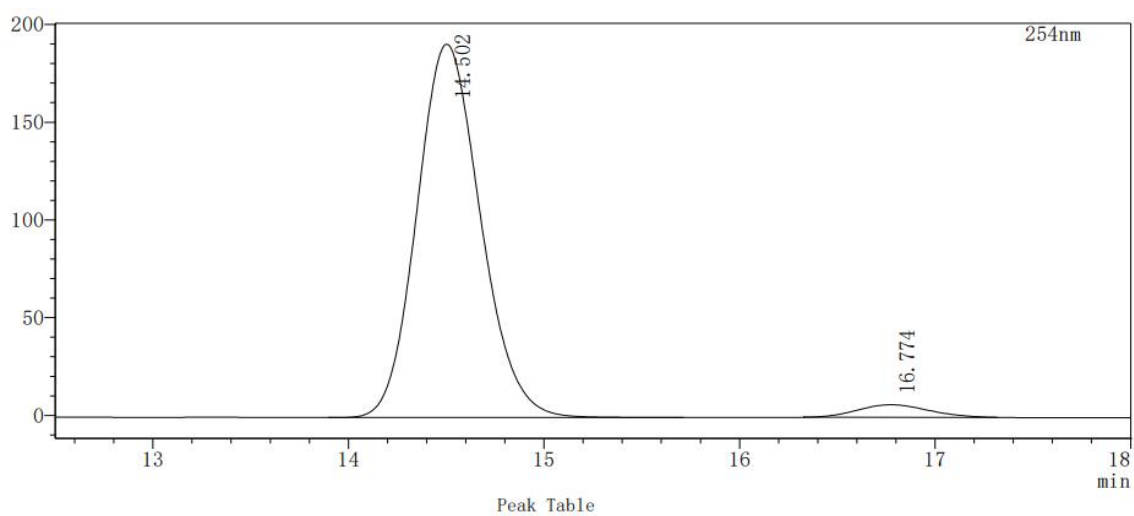
racemic-4af



254nm

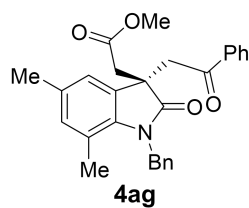
Peak#	Ret. Time	Area	Height	Area%
1	14.515	1689959	74032	49.031
2	16.776	1756788	67648	50.969
Total		3446747	141679	100.000

chiral-4af

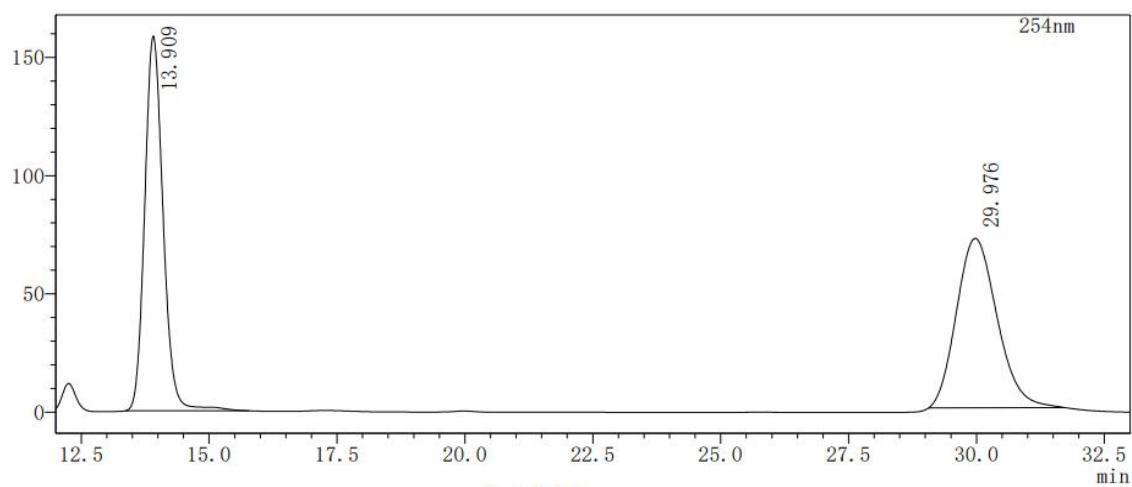


254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.502	4321013	191011	96.367
2	16.774	162898	6434	3.633
Total		4483911	197446	100.000



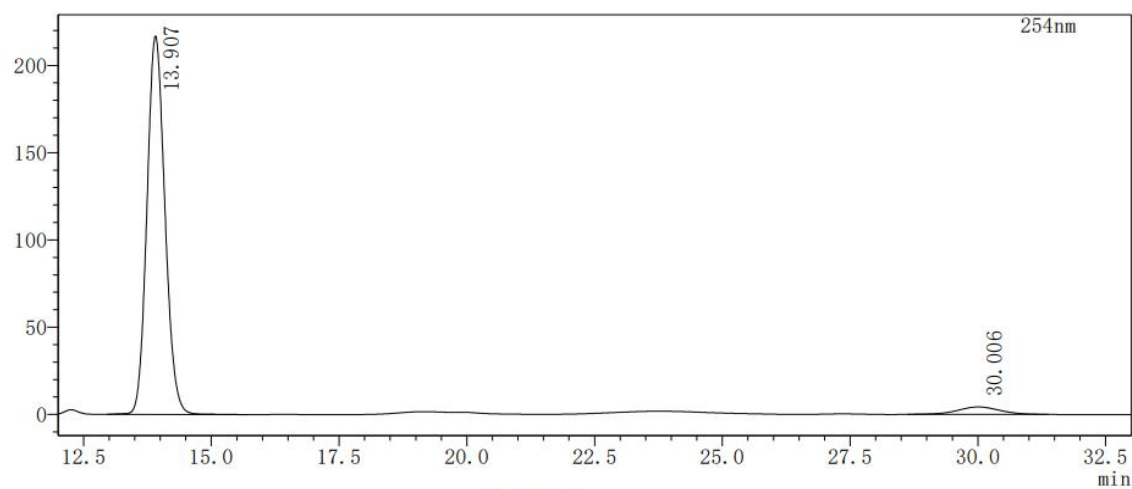
racemic-4ag



Peak Table

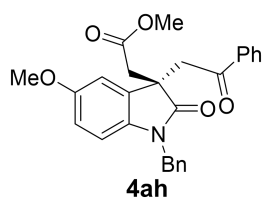
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	13.909	3967705	158463	50.063
2	29.976	3957660	71625	49.937
Total		7925365	230088	100.000

chiral-4ag

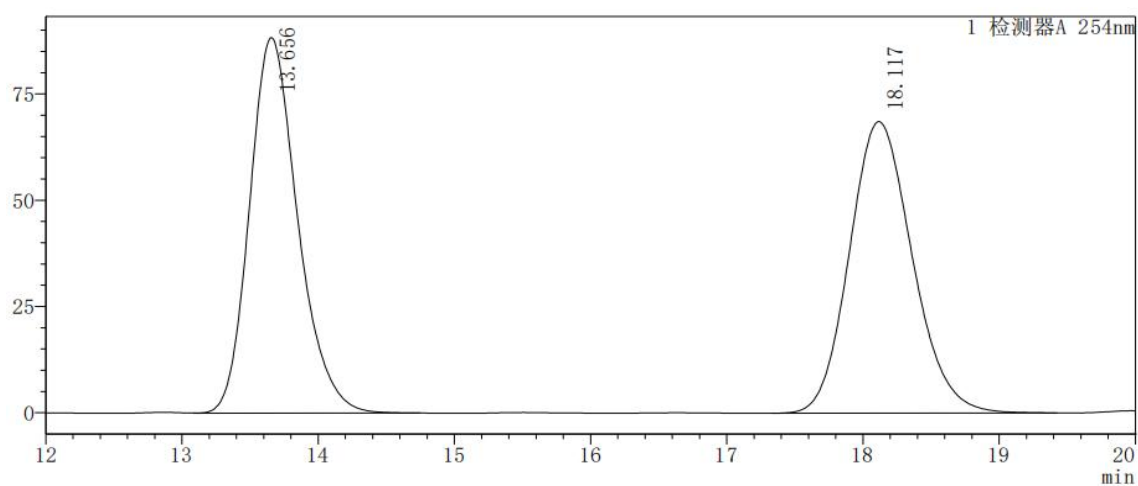


Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	13.907	5309584	216854	95.608
2	30.006	243937	4252	4.392
Total		5553521	221106	100.000

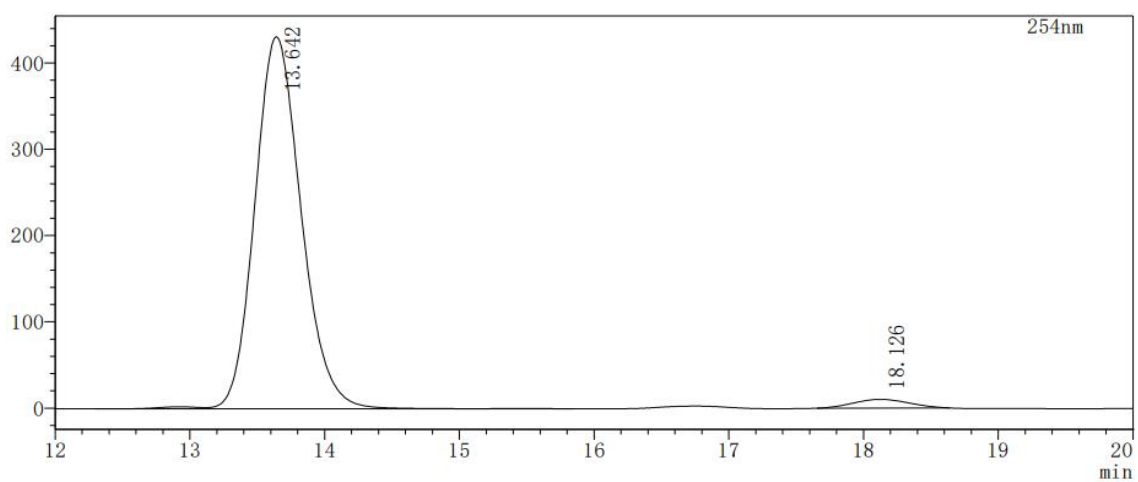


racemic-4ah

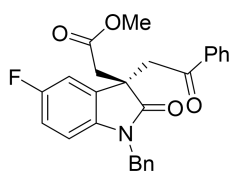


检测器A 254nm				
Peak#	Ret. Time	Area	Height	Area%
1	13.656	2173901	88392	49.698
2	18.117	2200313	68597	50.302
总计		4374214	156989	100.000

chiral-4ah

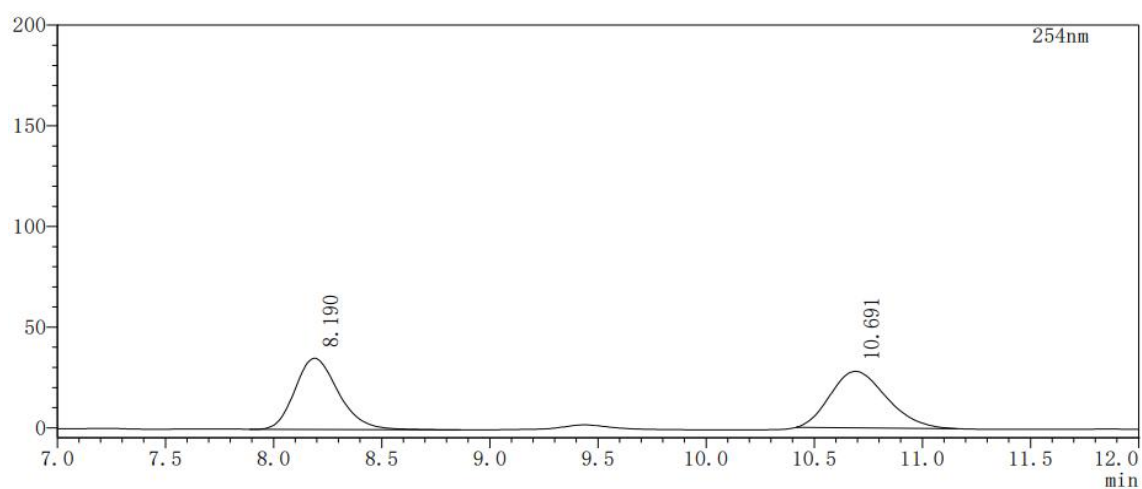


Peak Table				
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	13.642	10341537	431267	97.285
2	18.126	288558	10065	2.715
Total		10630095	441332	100.000



4ai

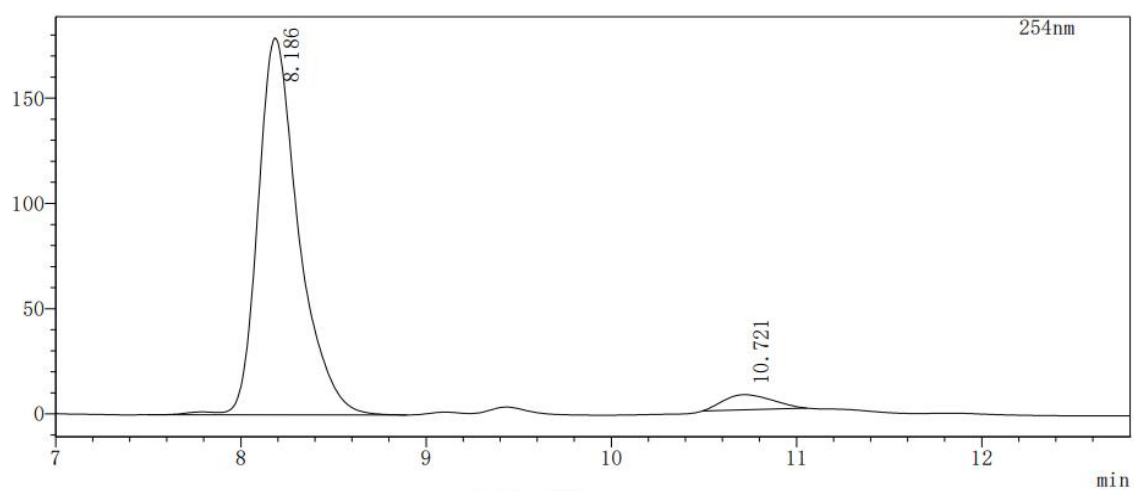
racemic-4ai



Peak Table

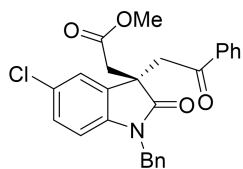
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	8.190	495406	35438	49.364
2	10.691	508171	28088	50.636
Total		1003576	63526	100.000

chiral-4ai



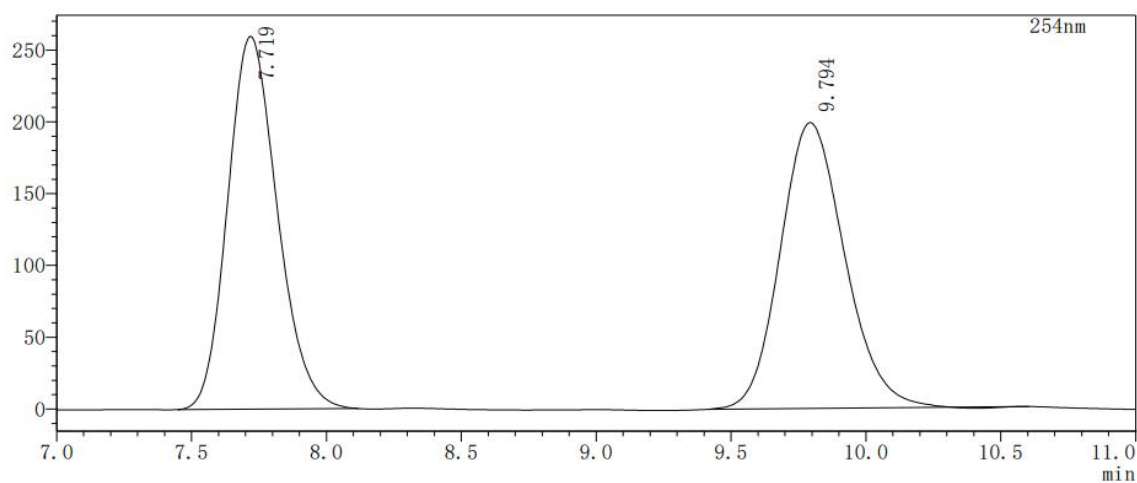
Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	8.186	2738321	179089	95.434
2	10.721	131012	7135	4.566
Total		2869333	186223	100.000



4aj

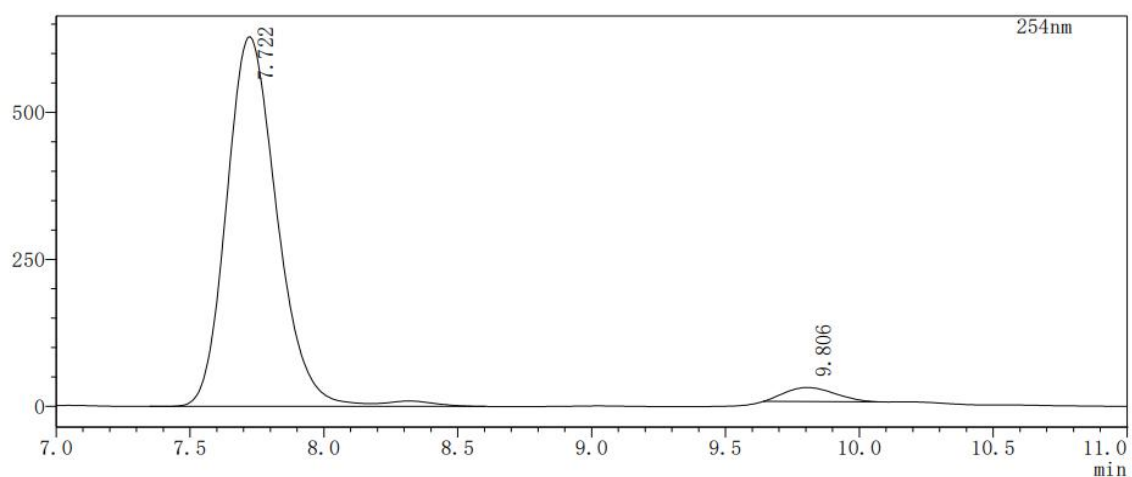
racemic-4aj



Peak Table

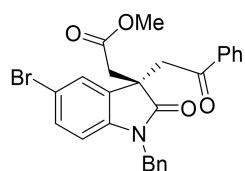
Peak#	Ret. Time	Area	Height	Area%
1	7.719	3326082	259654	50.235
2	9.794	3294960	198975	49.765
Total		6621042	458629	100.000

chiral-4aj



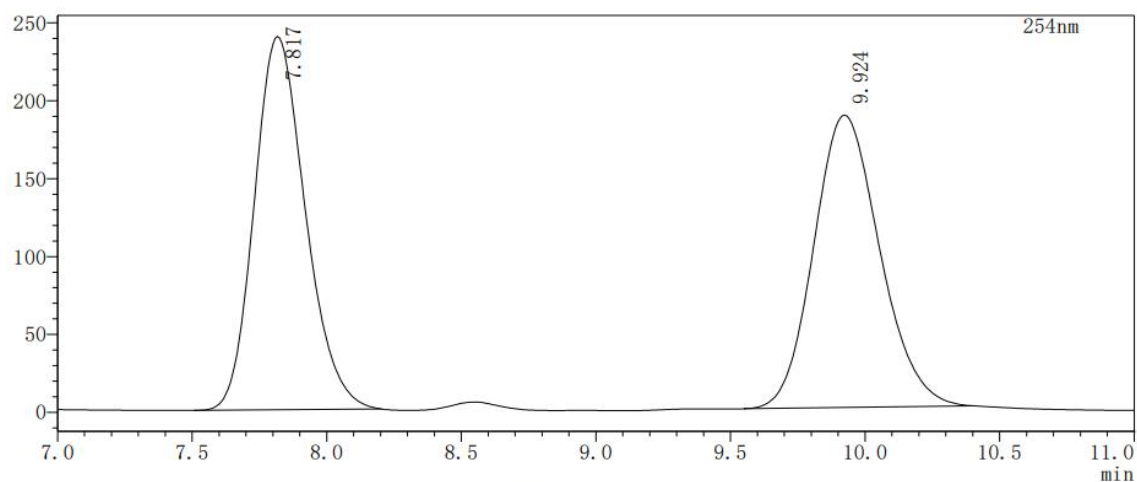
Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	7.722	8289296	628451	96.400
2	9.806	309526	23816	3.600
Total		8598822	652267	100.000



4ak

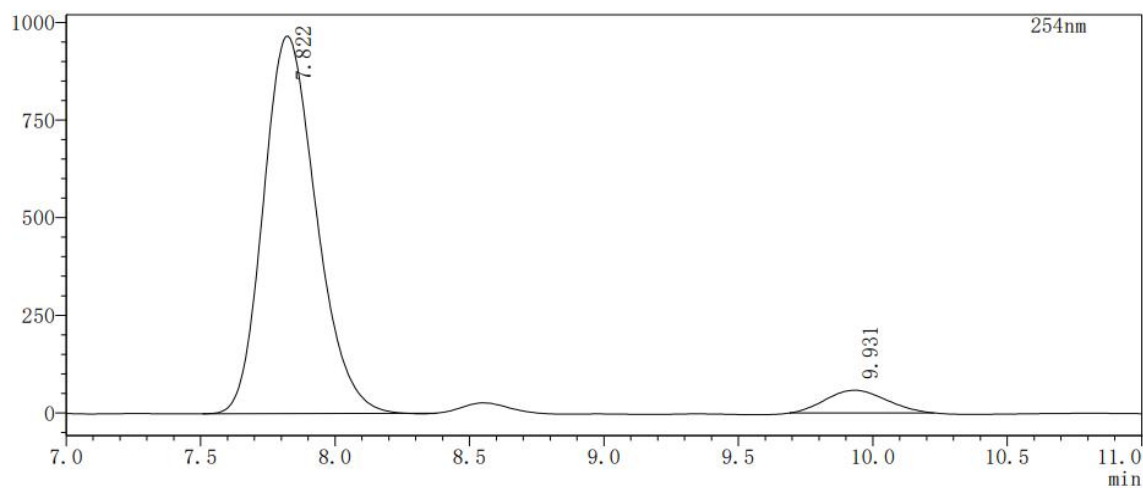
racemic-4ak



Peak Table

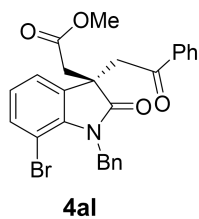
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	7.817	3162427	239551	49.697
2	9.924	3201028	187658	50.303
Total		6363455	427209	100.000

chiral-4ak

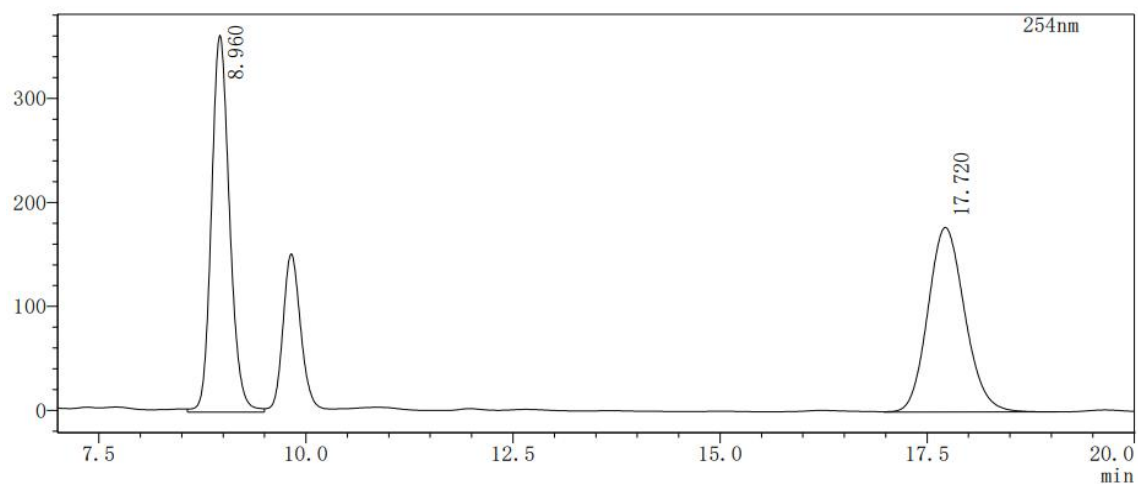


Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	7.822	13238852	967007	93.572
2	9.931	909468	57935	6.428
Total		14148321	1024942	100.000



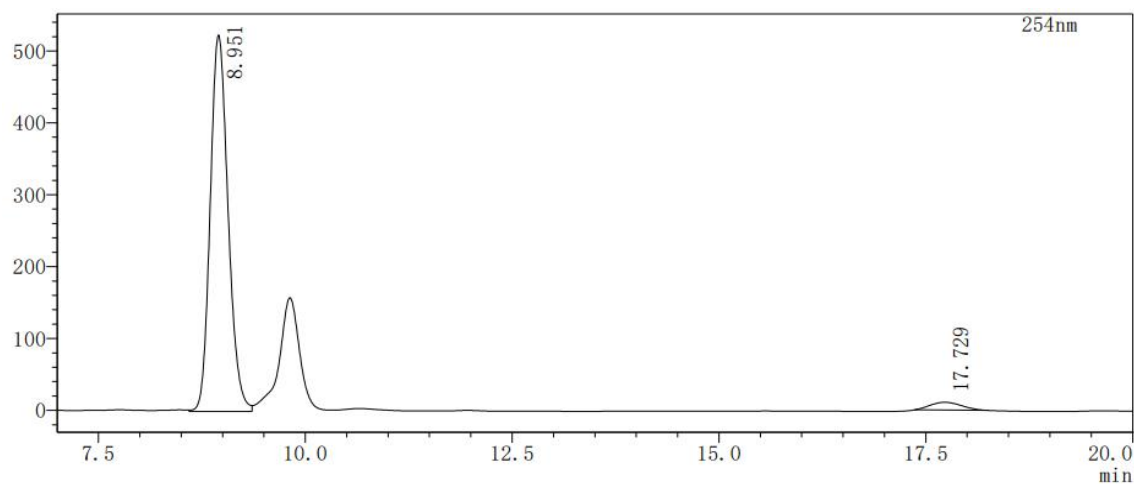
racemic-4al



Peak Table

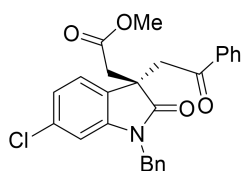
Peak#	Ret. Time	Area	Height	Area%
1	8.960	5531583	362323	50.190
2	17.720	5489684	177395	49.810
Total		11021267	539718	100.000

chiral-4al



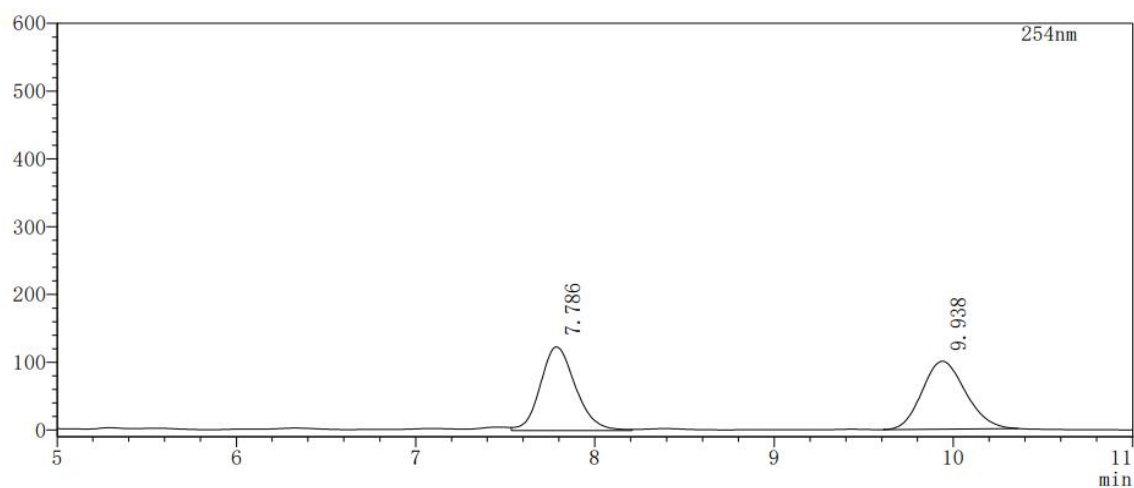
Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	8.951	7868192	523821	96.469
2	17.729	287983	10883	3.531
Total		8156175	534704	100.000



4am

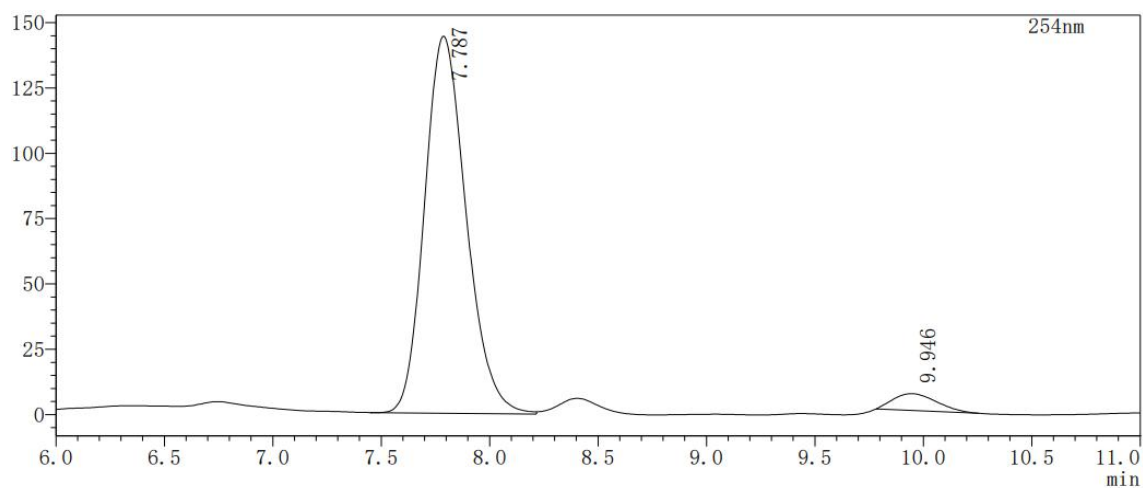
racemic-4am



Peak Table

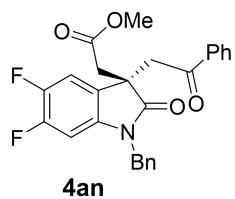
Peak#	Ret. Time	Area	Height	Area%
1	7.786	1686987	123491	49.989
2	9.938	1687719	100183	50.011
Total		3374706	223674	100.000

chiral-4am

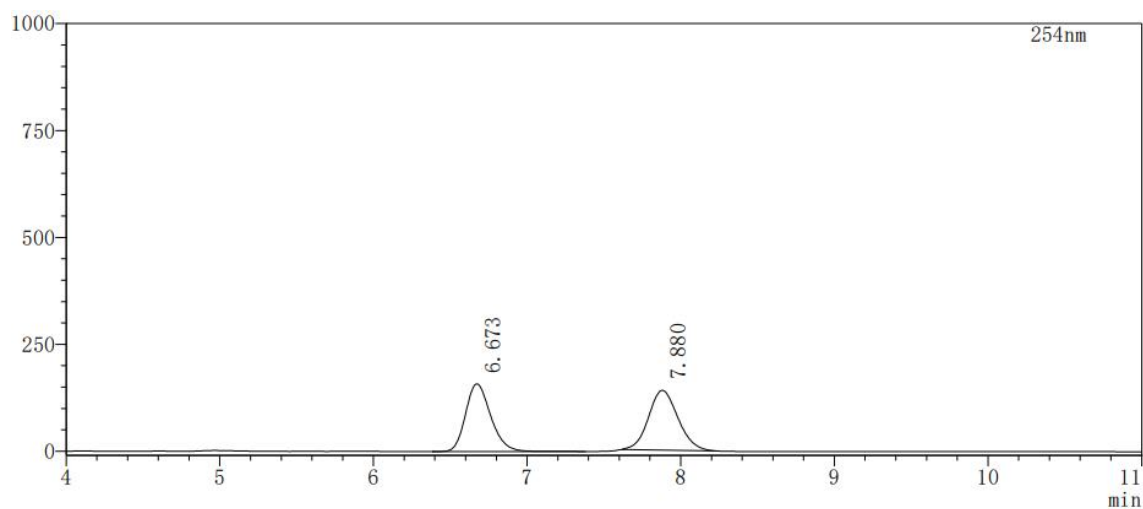


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	7.787	1925536	144207	95.606
2	9.946	88489	6386	4.394
Total		2014024	150593	100.000



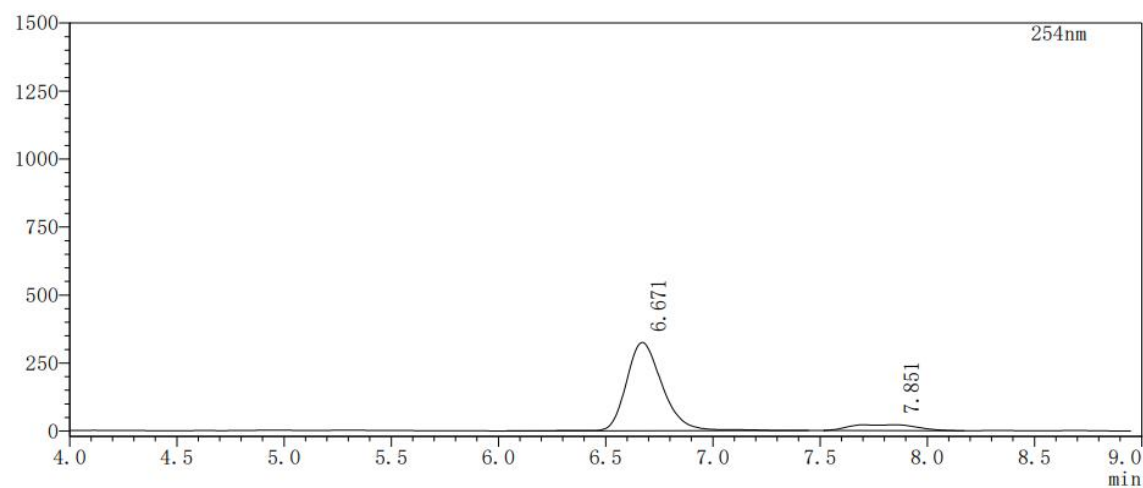
racemic-4an



Peak Table

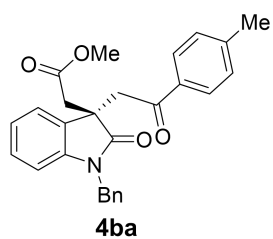
Peak#	Ret. Time	Area	Height	Area%
1	6.673	1803098	158217	49.177
2	7.880	1863436	139588	50.823
Total		3666533	297805	100.000

chiral-4an

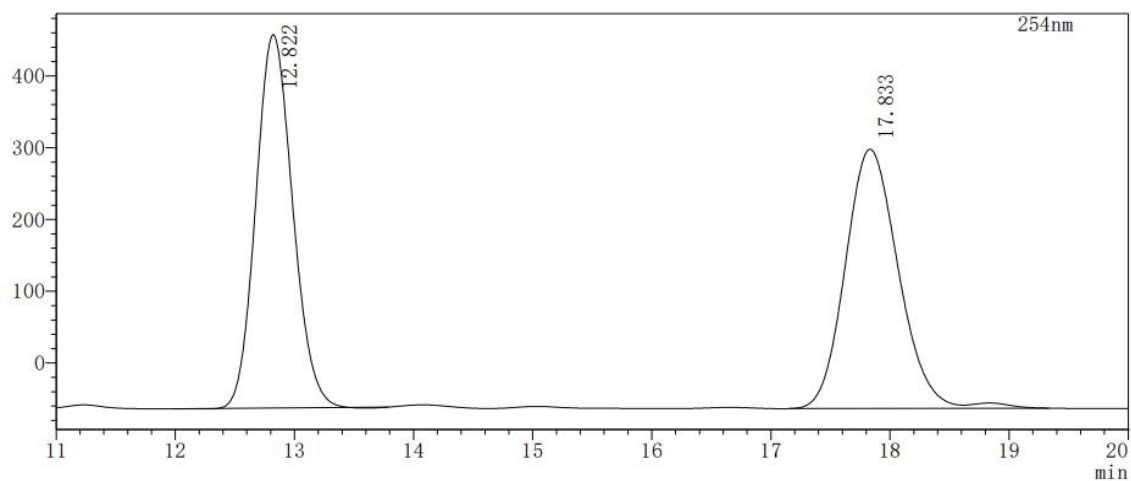


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	6.671	3787572	323886	89.238
2	7.851	456794	21350	10.762
Total		4244365	345236	100.000



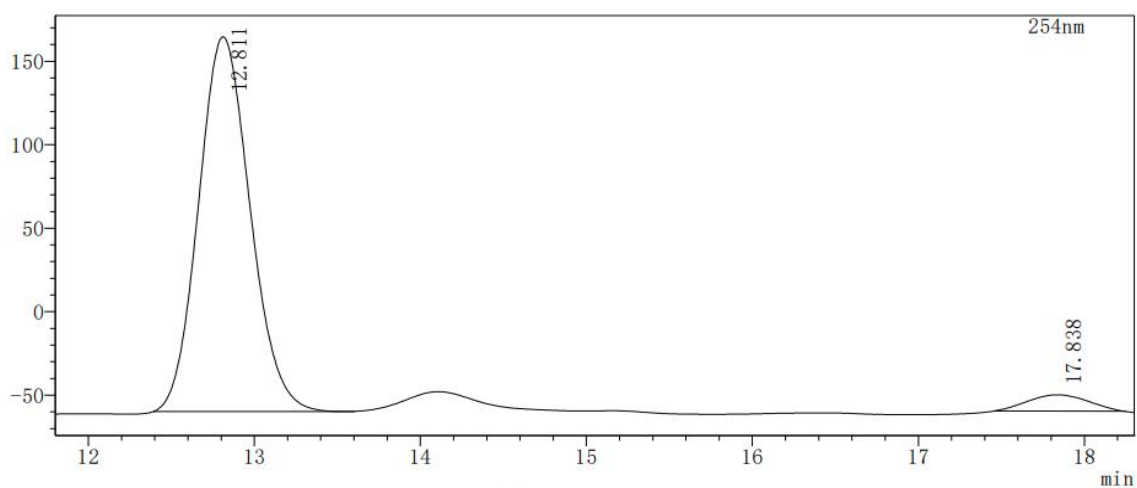
racemic-4ba



Peak Table

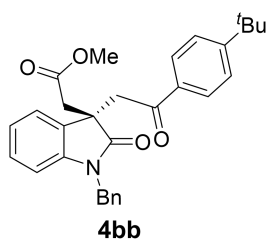
Peak#	Ret. Time	Area	Height	Area%
1	12.822	11164467	520398	49.795
2	17.833	11256313	361324	50.205
Total		22420780	881722	100.000

chiral-4ba

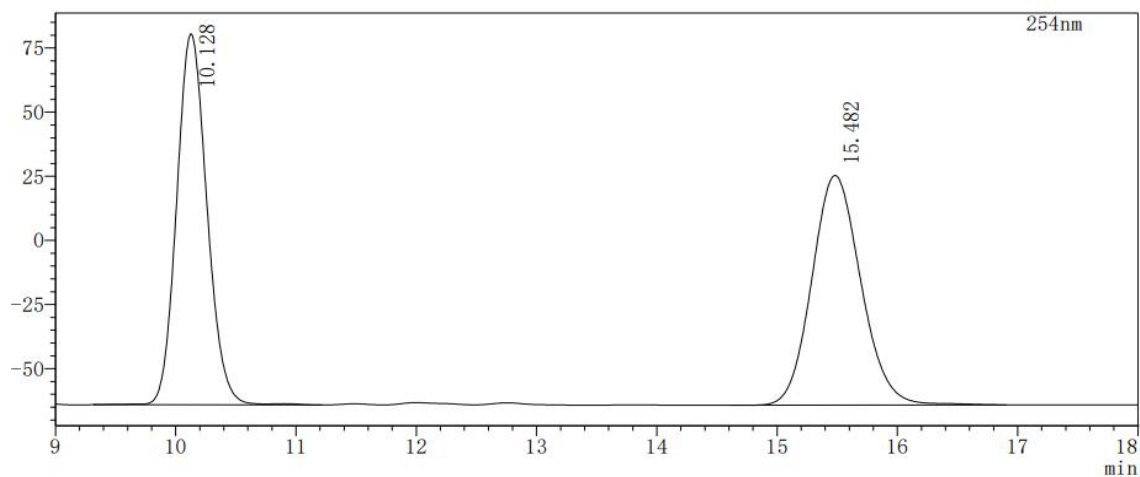


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	12.811	4849496	224526	95.128
2	17.838	248394	9782	4.872
Total		5097890	234308	100.000



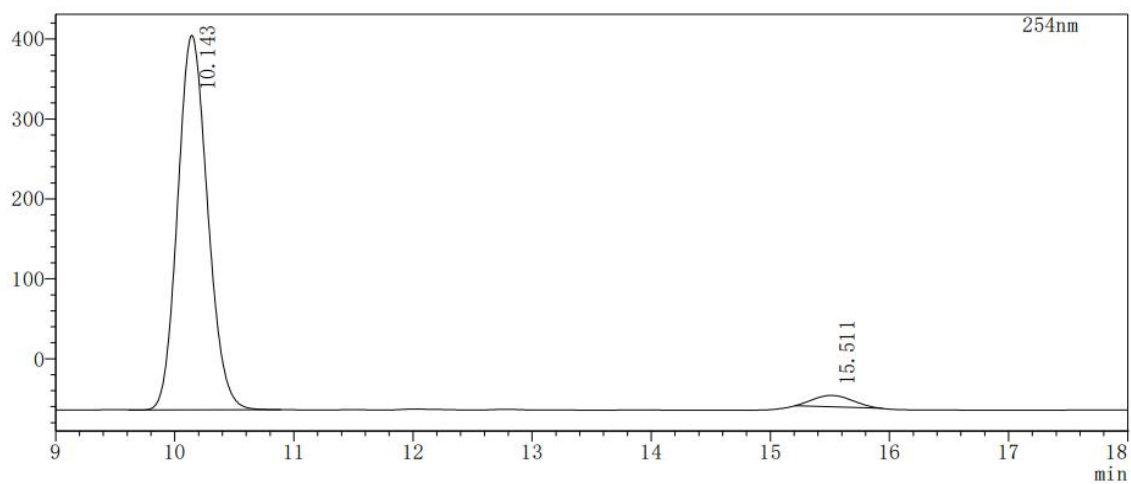
racemic-4bb



Peak Table

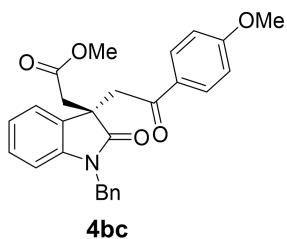
Peak#	Ret. Time	Area	Height	Area%
1	10.128	2534300	144637	49.969
2	15.482	2537487	89533	50.031
Total		5071787	234170	100.000

chiral-4bb

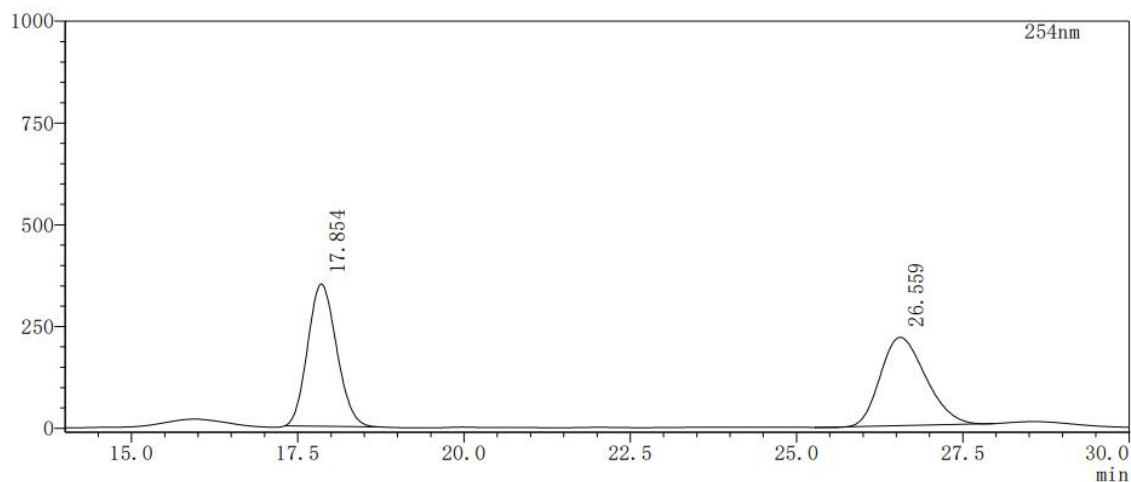


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	10.143	8191148	468665	96.139
2	15.511	328967	14236	3.861
Total		8520115	482901	100.000



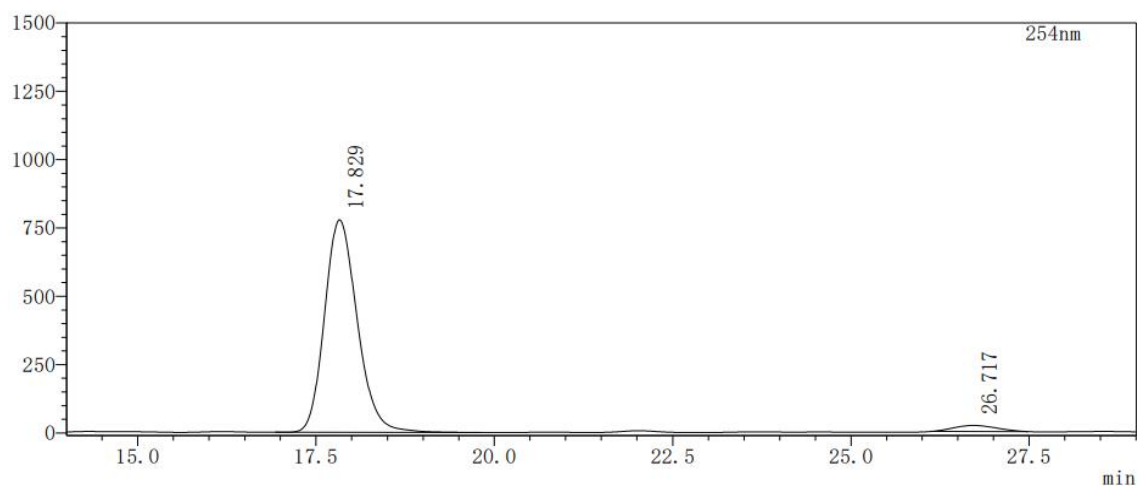
racemic-4bc



Peak Table

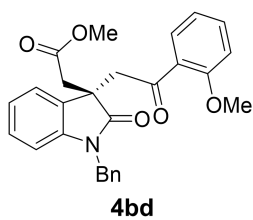
Peak#	Ret. Time	Area	Height	Area%
1	17.854	10626216	349451	50.900
2	26.559	10250609	216748	49.100
Total		20876826	566199	100.000

chiral-4bc

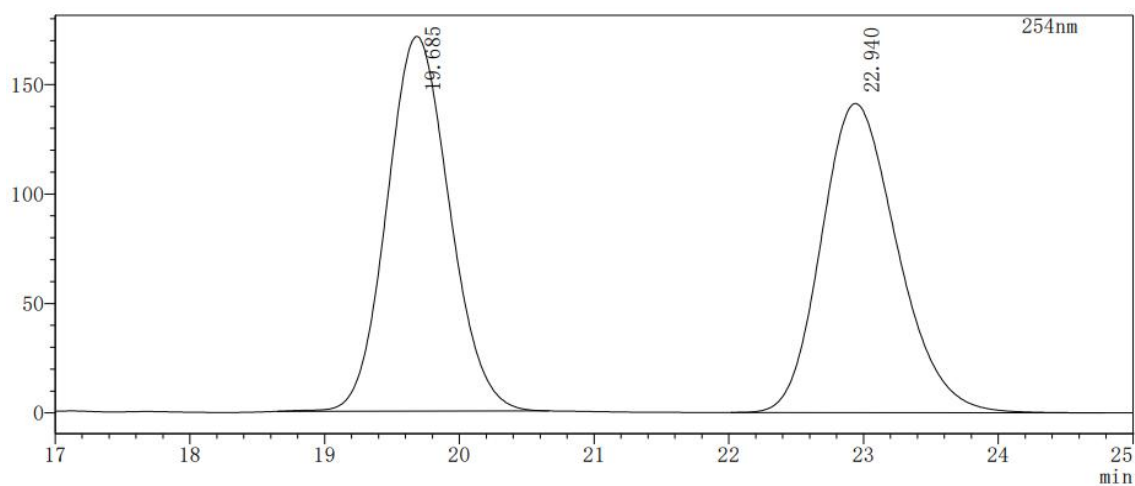


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	17.829	24837922	777453	96.412
2	26.717	924390	22098	3.588
Total		25762312	799550	100.000



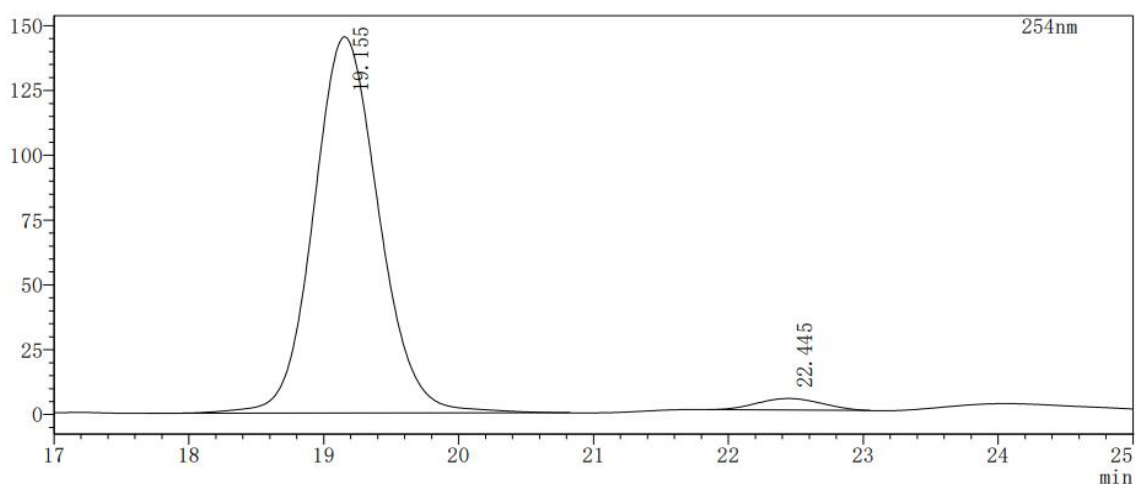
racemic-4bd



Peak Table

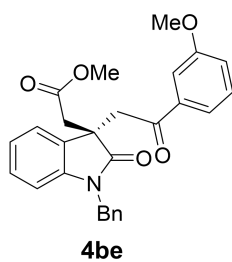
Peak#	Ret. Time	Area	Height	Area%
1	19.685	5526068	171151	49.910
2	22.940	5546061	141180	50.090
Total		11072129	312331	100.000

chiral-4bd

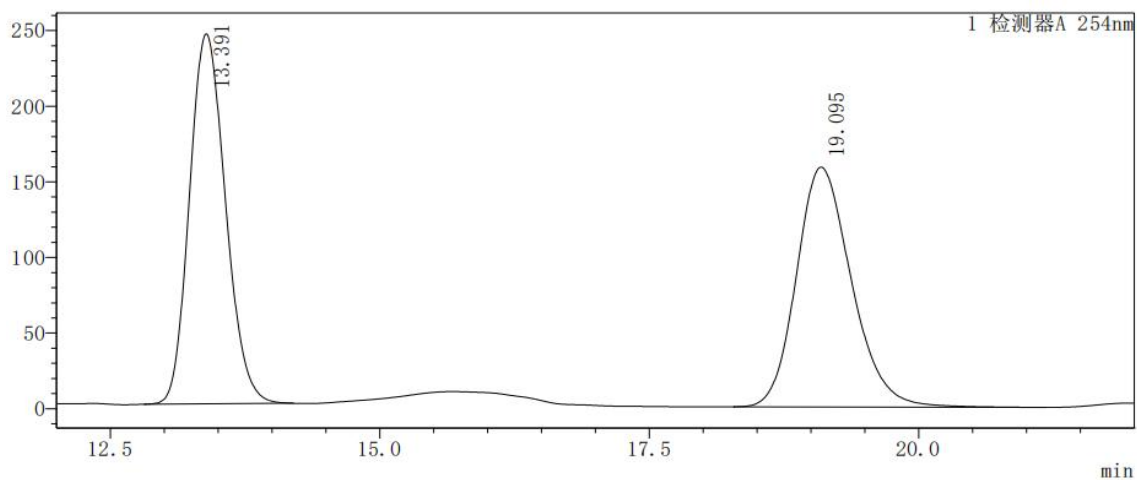


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	19.155	4883337	145146	97.042
2	22.445	148831	4449	2.958
Total		5032168	149596	100.000

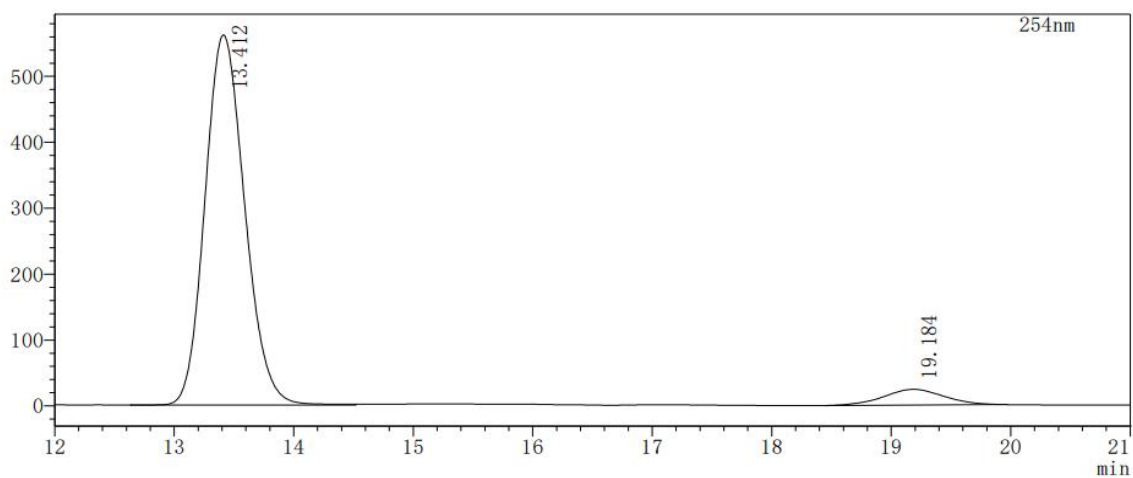


racemic-4be

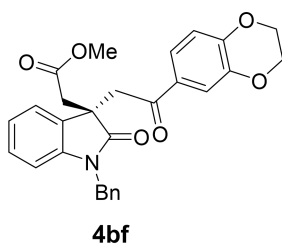


检测器A 254nm				
Peak#	Ret. Time	Area	Height	Area%
1	13.391	5693344	244630	50.257
2	19.095	5635199	158607	49.743
总计		11328543	403237	100.000

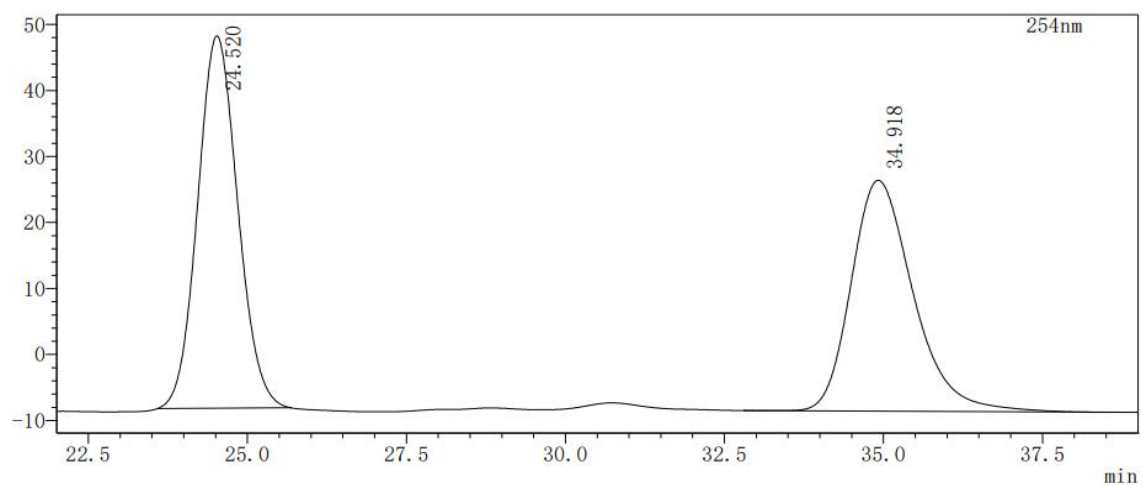
chiral-4be



Peak Table				
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	13.412	12990866	561620	93.906
2	19.184	843014	23843	6.094
Total		13833881	585463	100.000



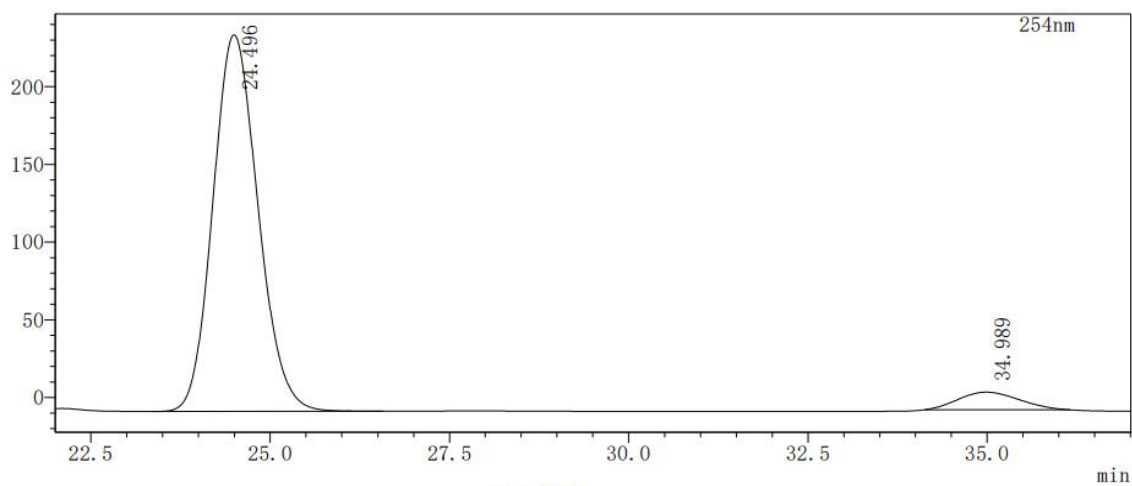
racemic-4bf



Peak Table

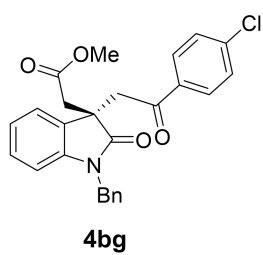
Peak#	Ret. Time	Area	Height	Area%
1	24.520	2473890	56400	50.956
2	34.918	2381029	34988	49.044
Total		4854919	91388	100.000

chiral-4bf

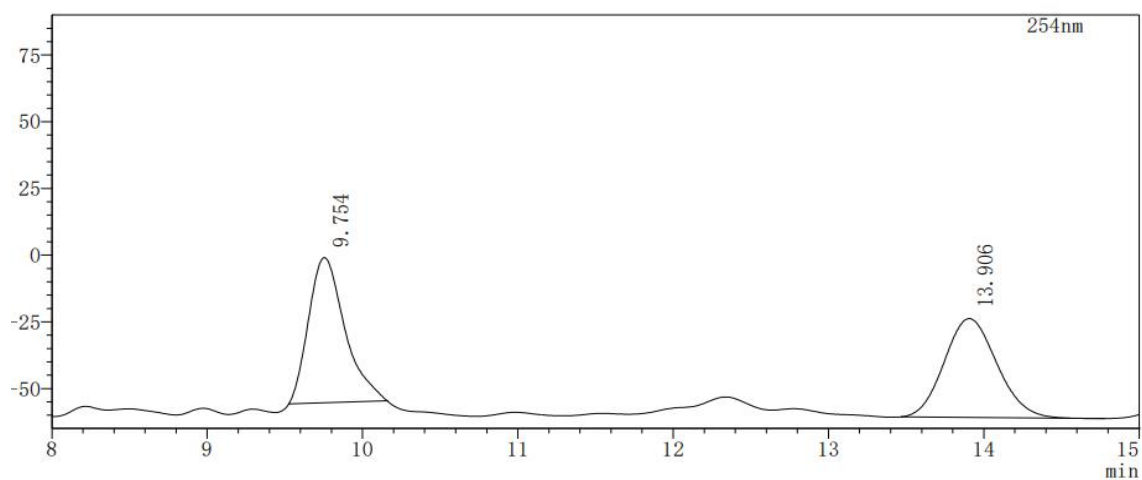


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	24.496	10617224	242182	94.078
2	34.989	668349	11321	5.922
Total		11285574	253503	100.000



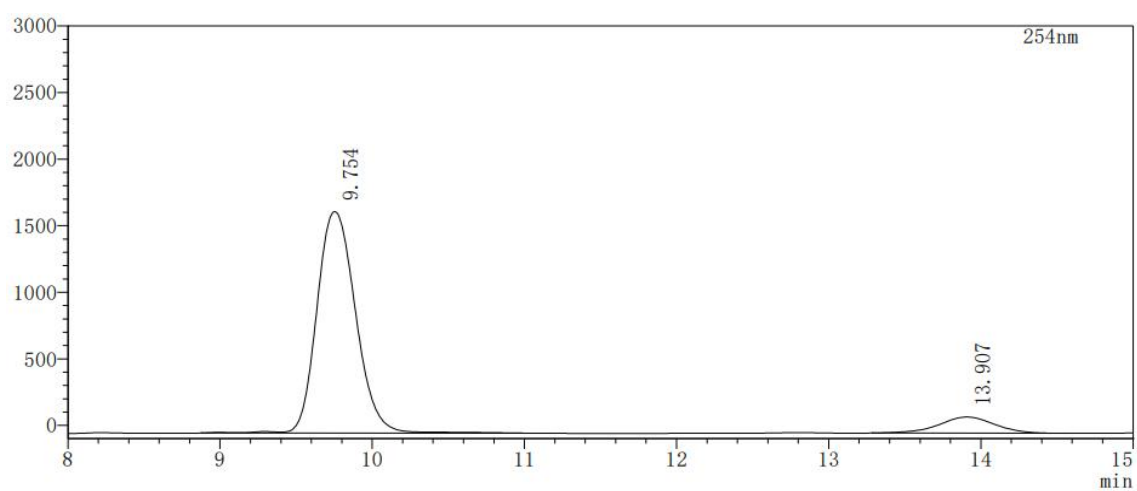
racemic-4bg



Peak Table

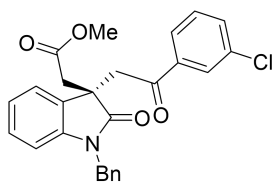
Peak#	Ret. Time	Area	Height	Area%
1	9.754	886654	54422	50.399
2	13.906	872621	37053	49.601
Total		1759275	91475	100.000

chiral-4bg



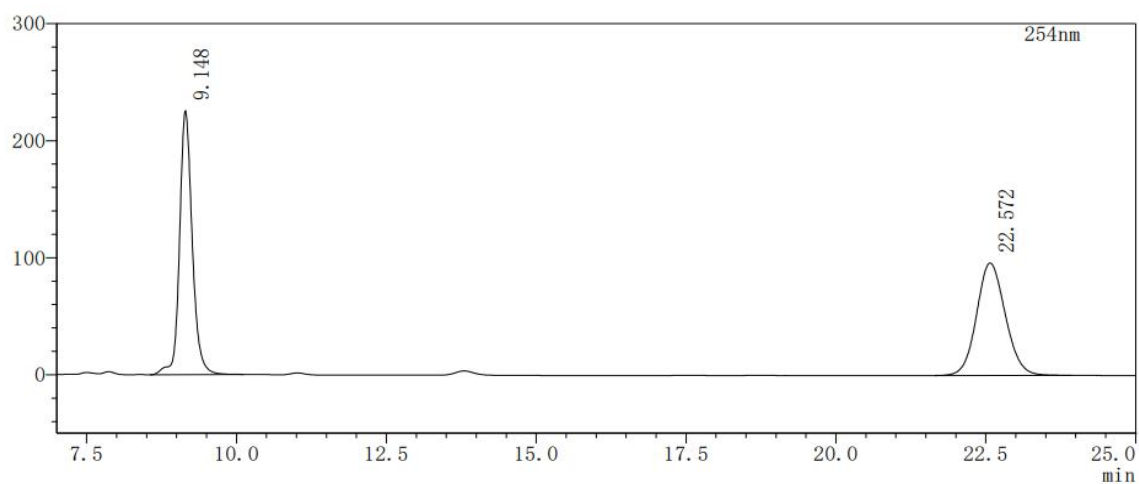
Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	9.754	29591950	1663579	90.481
2	13.907	3113217	121481	9.519
Total		32705166	1785060	100.000



4bh

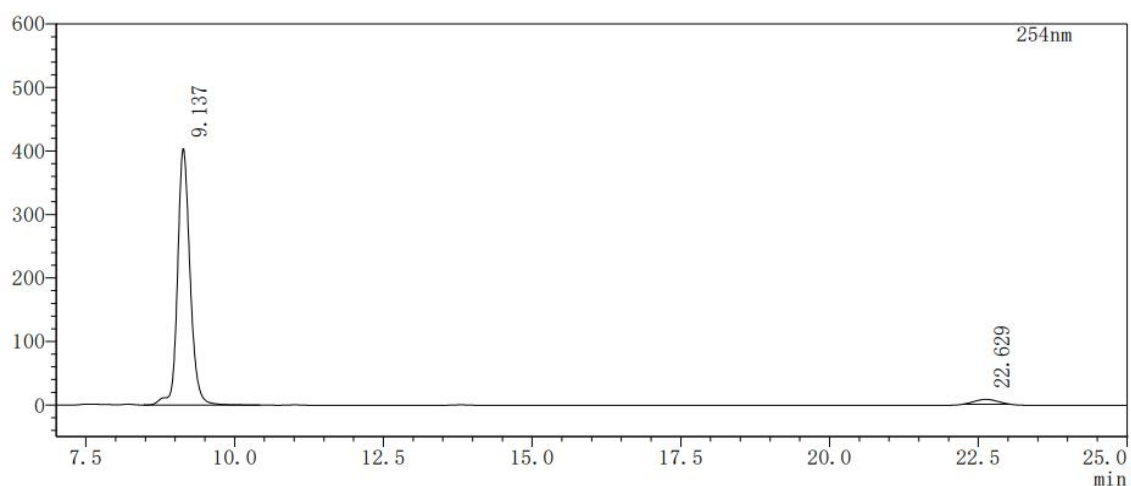
racemic-4bh



Peak Table

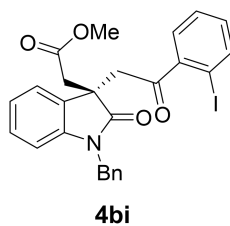
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	9.148	3329015	225365	50.991
2	22.572	3199654	96088	49.009
Total		6528668	321453	100.000

chiral-4bh

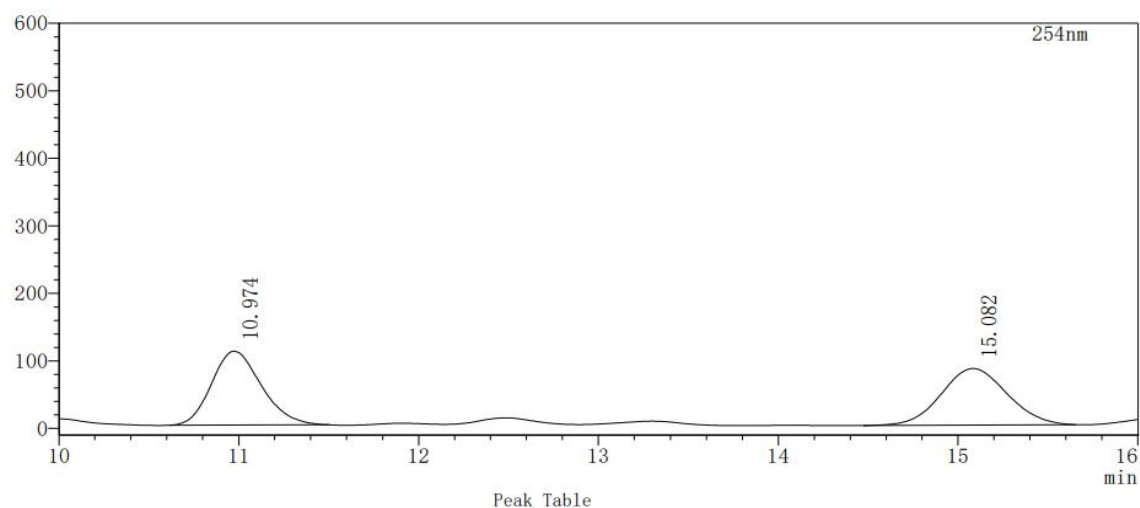


Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	9.137	5935516	403863	96.864
2	22.629	192183	7447	3.136
Total		6127699	411310	100.000



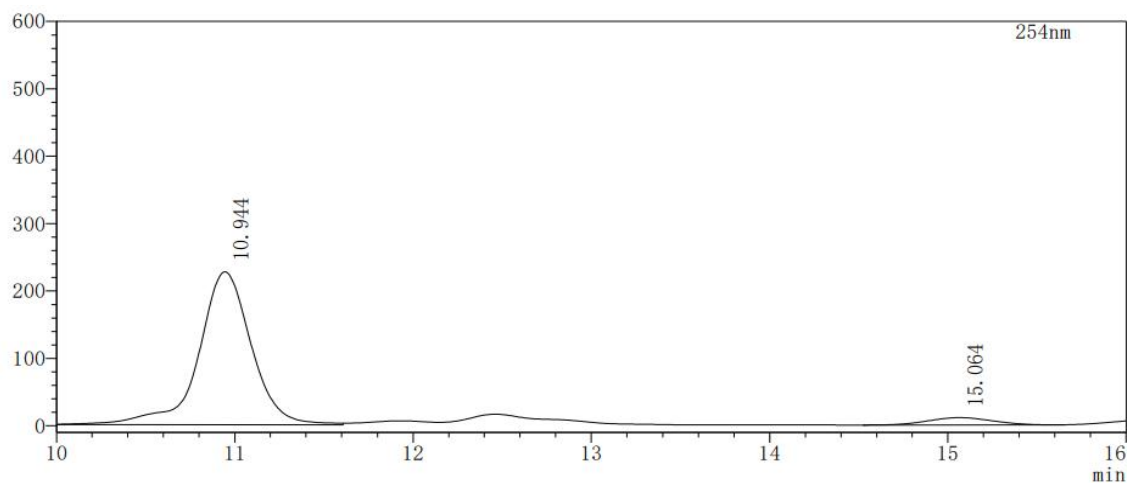
racemic-4bi



Peak Table

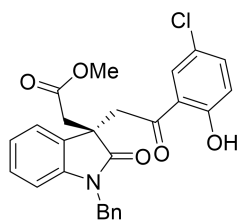
Peak#	Ret. Time	Area	Height	Area%
1	10.974	2105109	109456	49.680
2	15.082	2132205	83734	50.320
Total		4237314	193190	100.000

chiral-4bi



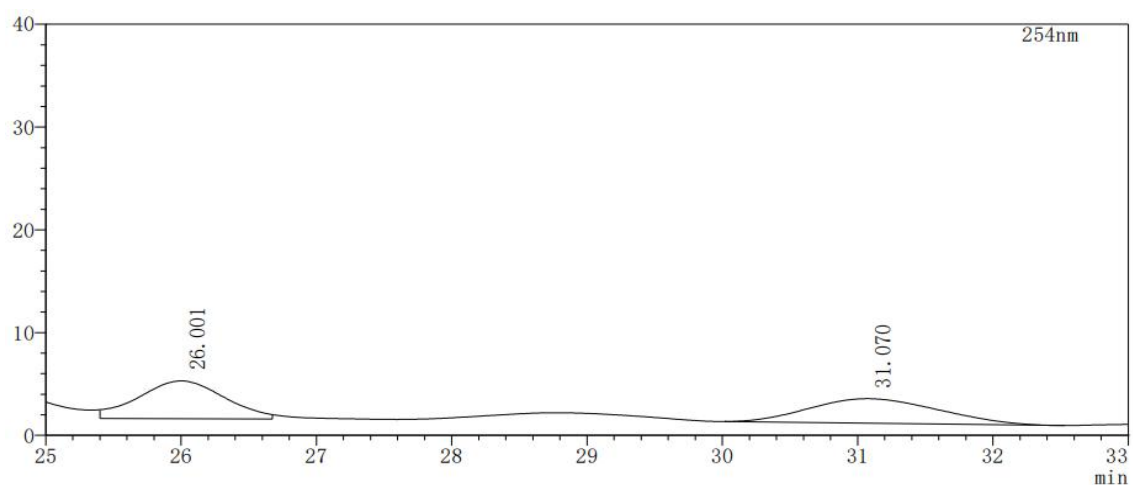
Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	10.944	4683413	226975	94.570
2	15.064	268906	10809	5.430
Total		4952319	237784	100.000



4bj

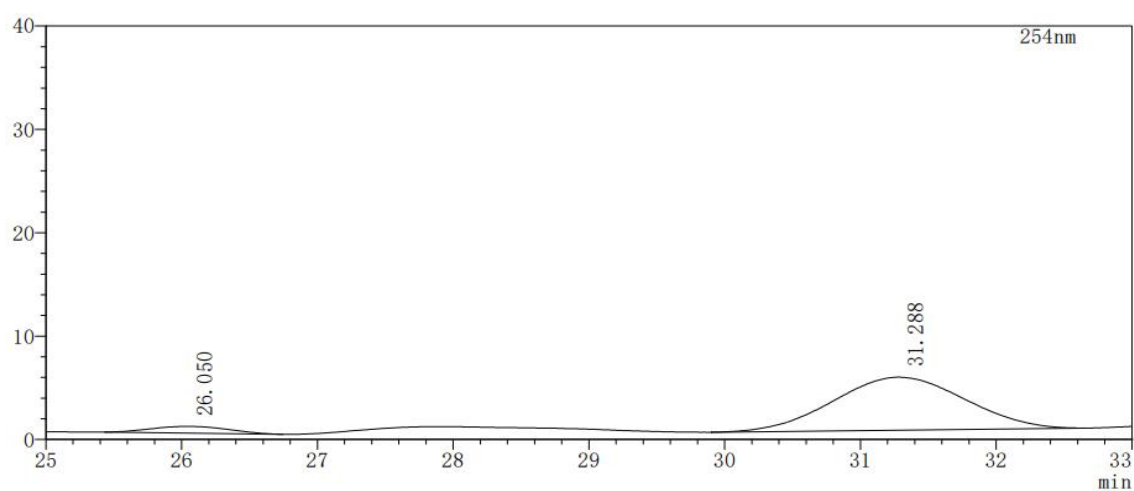
racemic-4bj



Peak Table

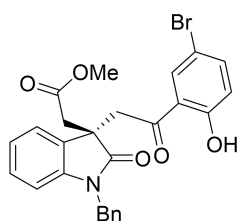
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	26.001	161891	3674	50.582
2	31.070	158163	2390	49.418
Total		320054	6064	100.000

chiral-4bj



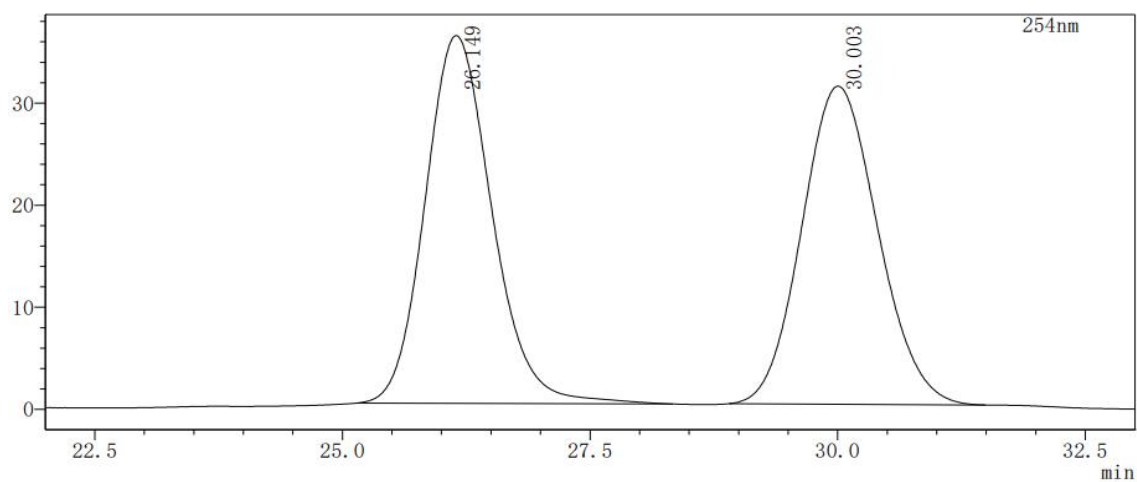
Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	26.050	25971	659	7.017
2	31.288	344156	5119	92.983
Total		370127	5778	100.000



4bk

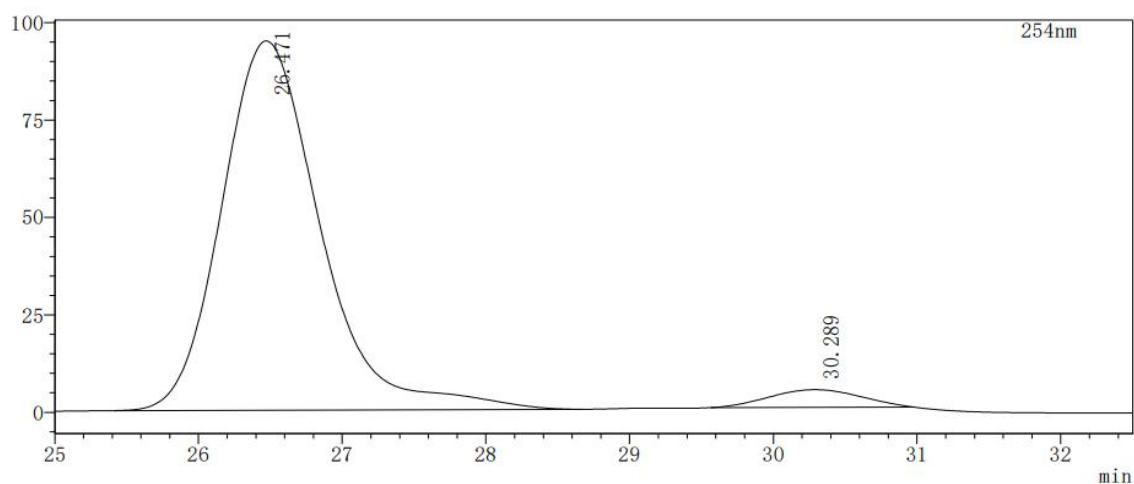
racemic-4bk



Peak Table

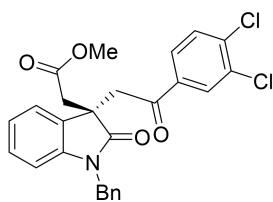
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	26.149	1692920	36040	50.457
2	30.003	1662281	31156	49.543
Total		3355201	67196	100.000

chiral-4bk



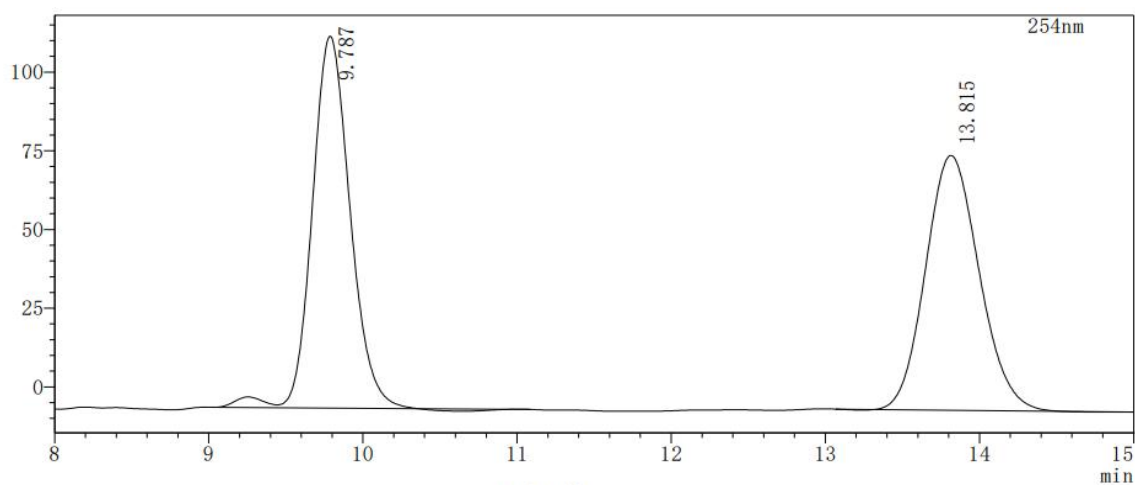
Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	26.471	4528201	94772	95.772
2	30.289	199904	4524	4.228
Total		4728105	99296	100.000



4bl

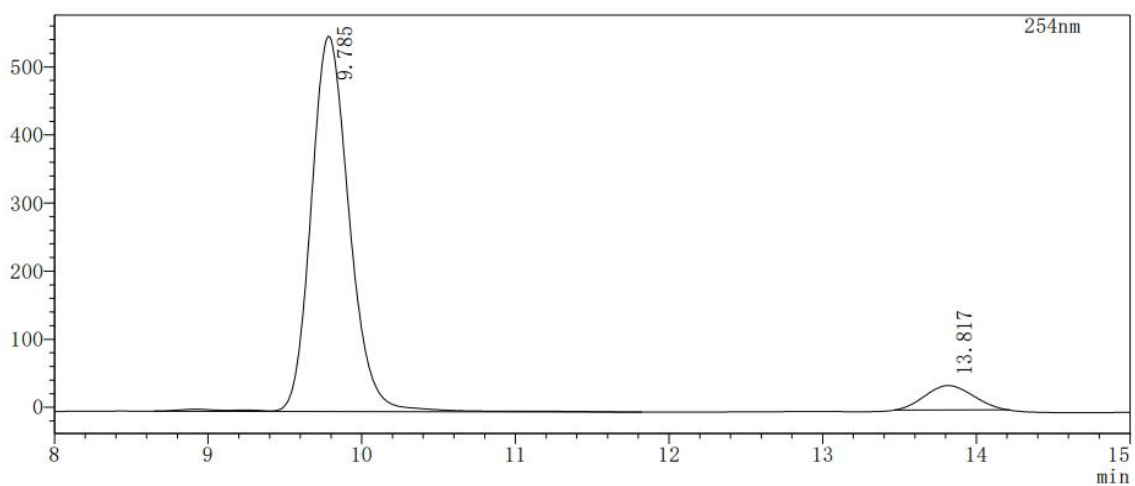
racemic-4bl



Peak Table

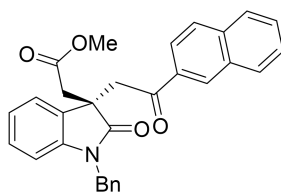
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	9.787	2021134	118114	50.884
2	13.815	1950927	80927	49.116
Total		3972061	199041	100.000

chiral-4bl



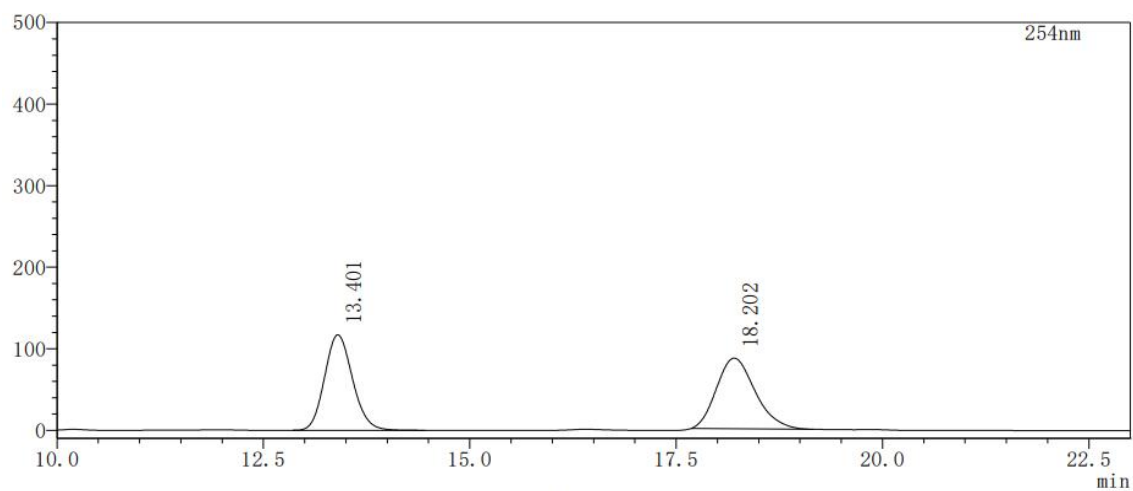
Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	9.785	9564408	551250	92.416
2	13.817	784862	35844	7.584
Total		10349270	587094	100.000



4bm

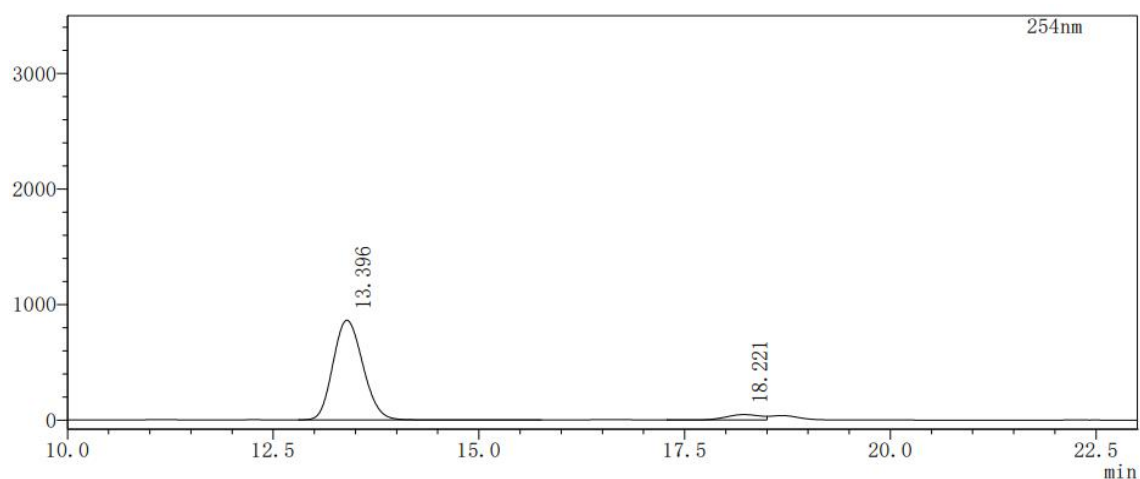
racemic-4bm



Peak Table

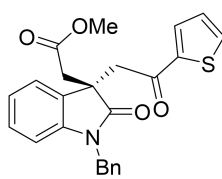
Peak#	Ret. Time	Area	Height	Area%
1	13.401	2757140	117084	49.439
2	18.202	2819721	86537	50.561
Total		5576861	203621	100.000

chiral-4bm



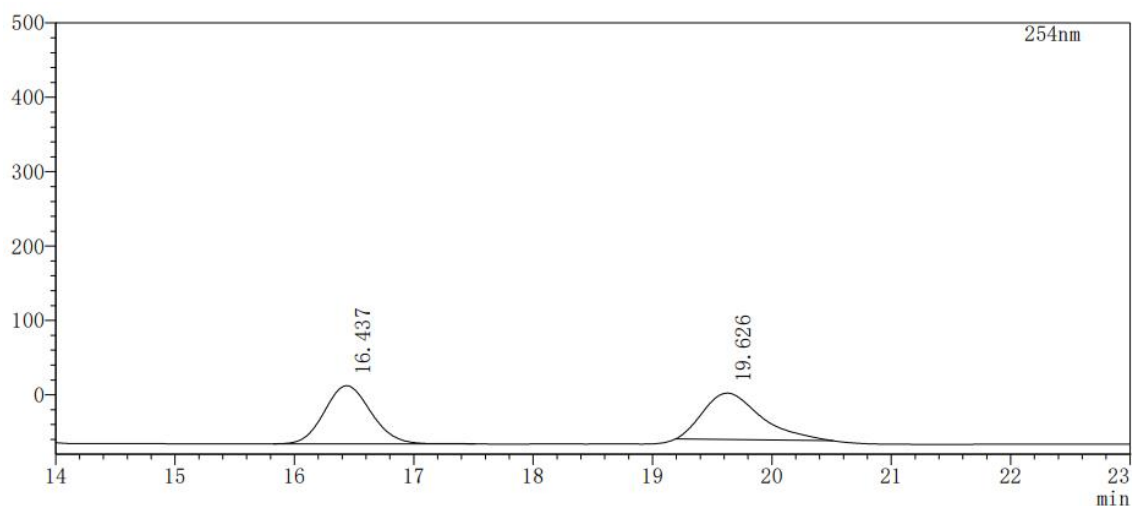
Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	13.396	21810003	862680	94.217
2	18.221	1338679	46182	5.783
Total		23148683	908862	100.000



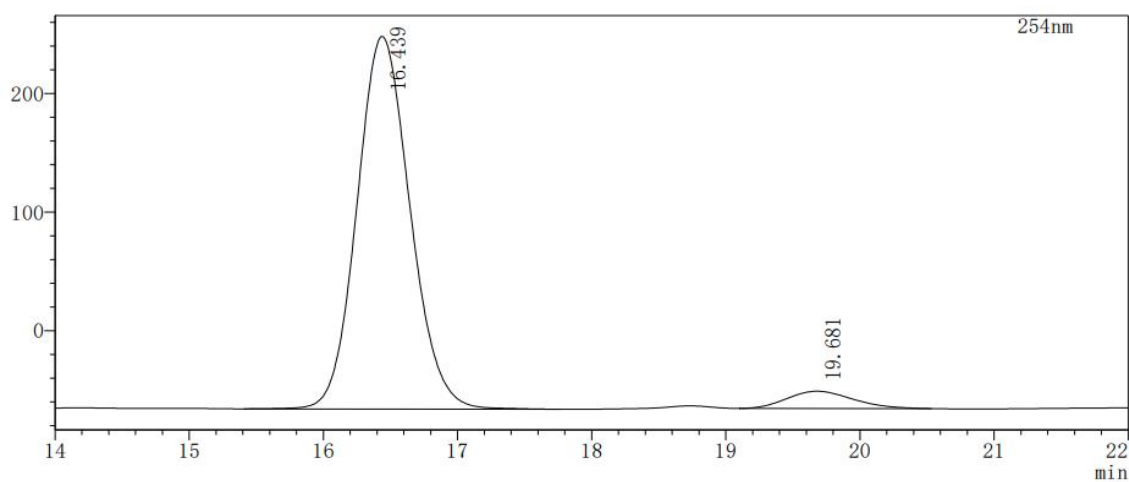
4bn

racemic-4bn

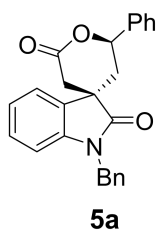


Peak Total				
Peak#	Ret. Time	Area	Height	Area%
1	16.437	2119420	78148	50.068
2	19.626	2113690	62434	49.932
Total		4233110	140582	100.000

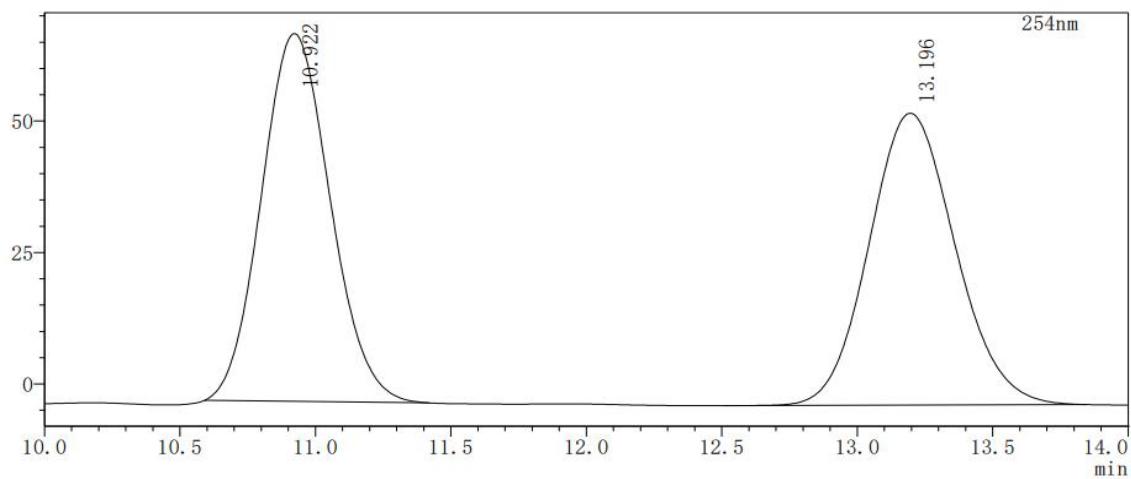
chiral-4bn



Peak Table				
Peak#	Ret. Time	Area	Height	Area%
1	16.439	8642055	314092	94.546
2	19.681	498500	14584	5.454
Total		9140556	328675	100.000



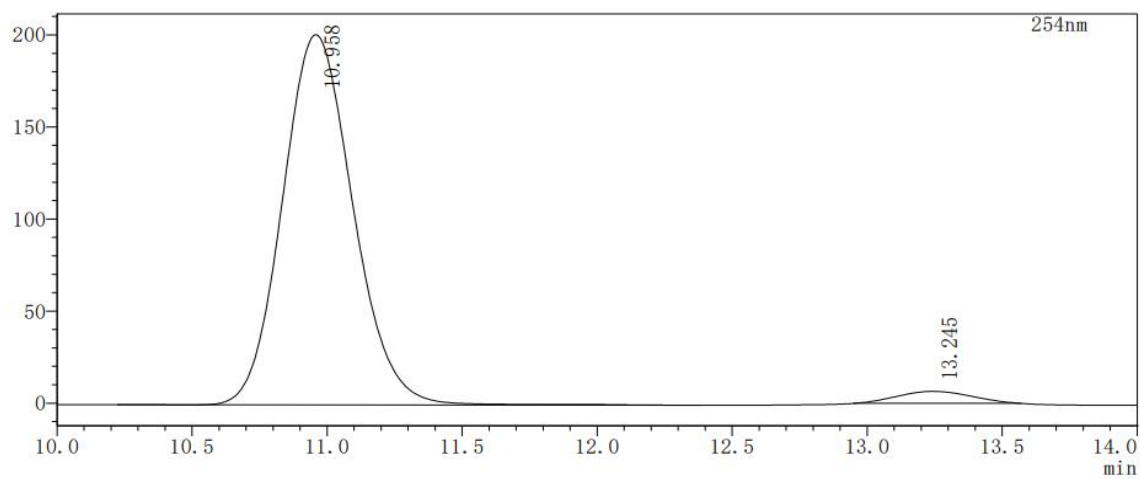
racemic-5a



Peak Table

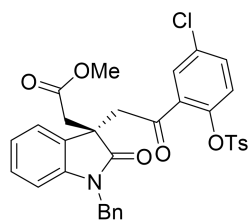
254nm				
Peak#	Ret. Time	Area	Height	Area%
1	10.922	1235737	69937	50.185
2	13.196	1226621	55502	49.815
Total		2462358	125439	100.000

chiral-5a



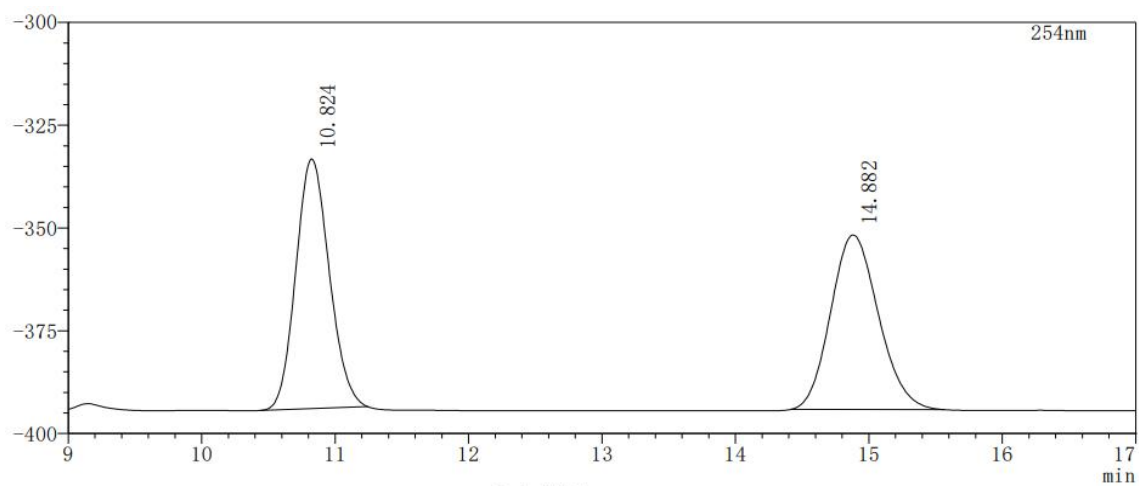
Peak Table

254nm				
Peak#	Ret. Time	Area	Height	Area%
1	10.958	3648636	201033	96.689
2	13.245	124928	6536	3.311
Total		3773563	207569	100.000



6a

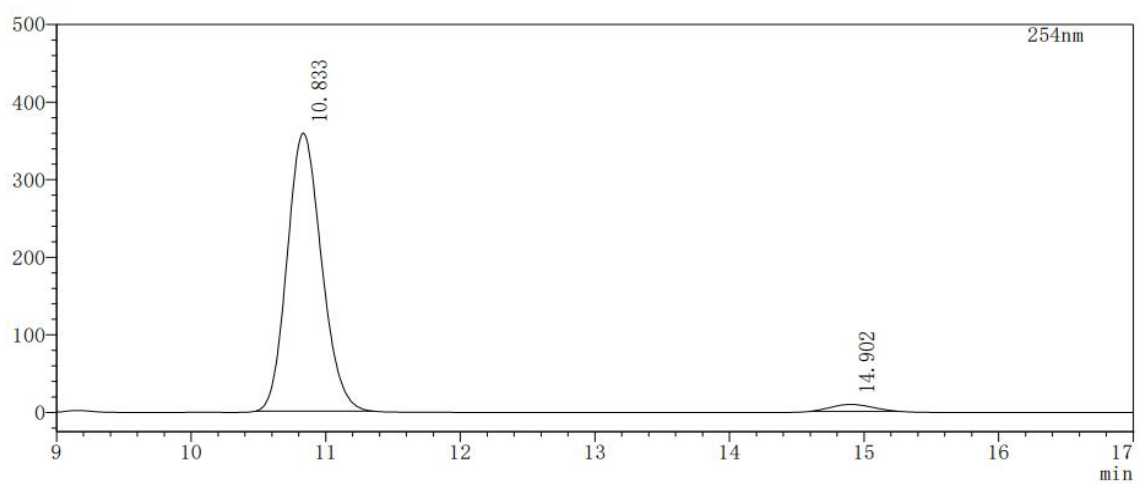
racemic-6a



Peak Table

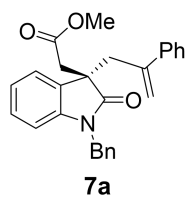
Peak#	Ret. Time	Area	Height	Area%
1	10.824	1058250	60744	50.041
2	14.882	1056497	42459	49.959
Total		2114747	103203	100.000

chiral-6a

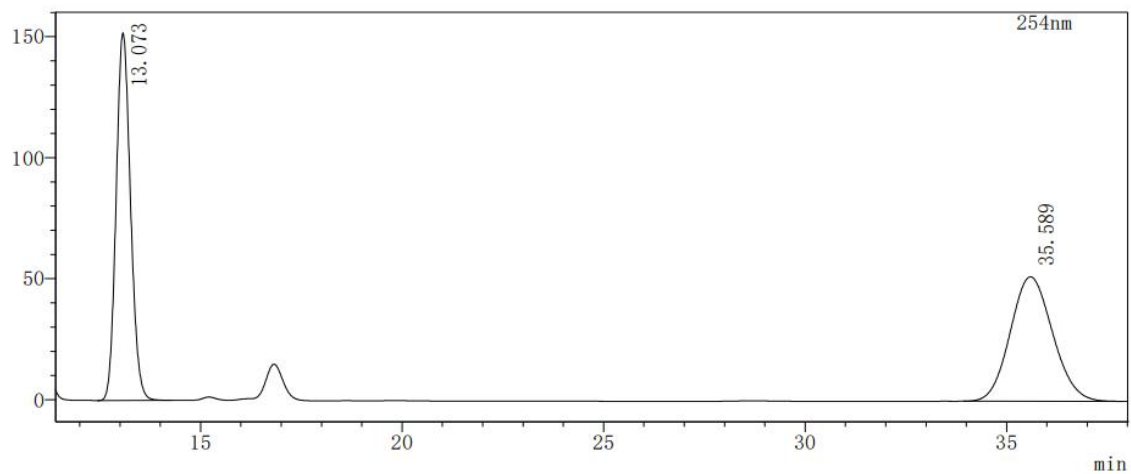


Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	10.833	6355747	358408	97.055
2	14.902	192885	8997	2.945
Total		6548632	367405	100.000



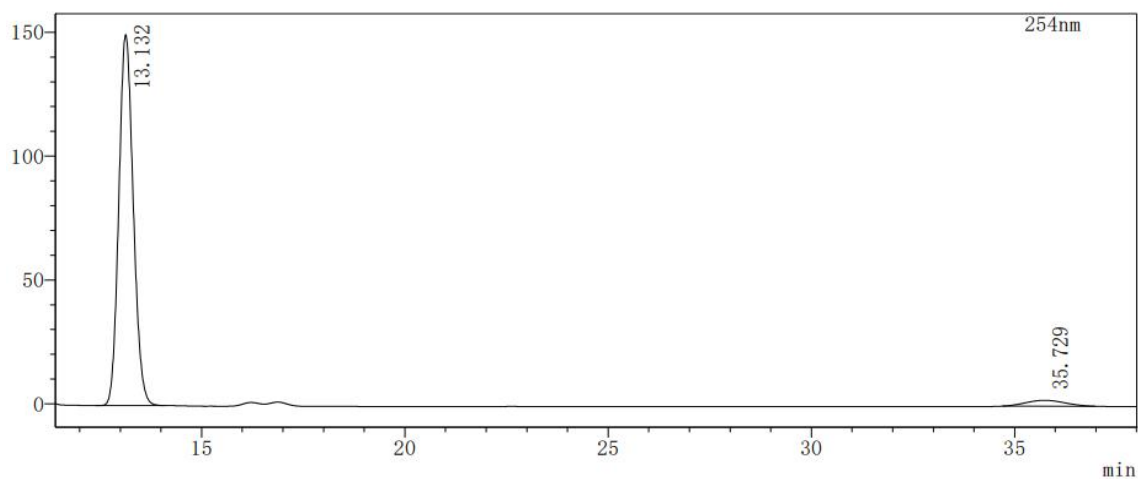
racemic-7a



Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	13.073	3767122	151865	50.071
2	35.589	3756386	51441	49.929
Total		7523508	203306	100.000

chiral-7a



Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	13.132	3707090	149781	95.968
2	35.729	155732	2350	4.032
Total		3862822	152130	100.000