

Bifunctional Thiourea Catalyzed Asymmetric Michael Addition of Anthrone to Methyleneindolinones

Huaili Zhao^a, Mingyan Xiao^a, Lubin Xu^a, Liang Wang^{a,b*} and Jian Xiao^{a,b*}

^a College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao, 266109, China.

^b Open Project Program of Hubei Key Laboratory of Drug Synthesis and Optimization, Jingchu University of Technology (Nos. OPP2015YB01 and OPP2015ZD02)

Supporting Information

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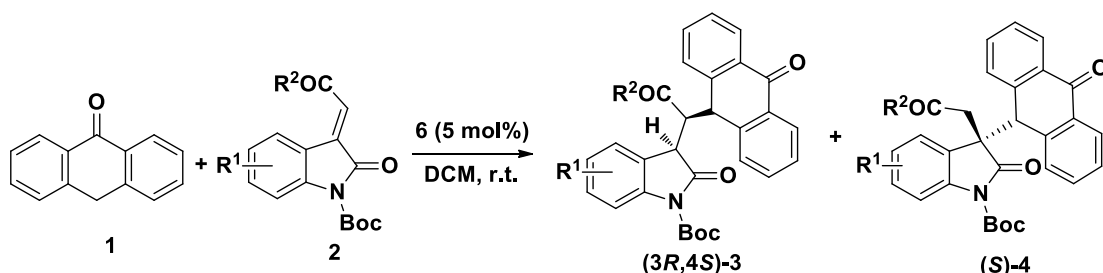
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1. General Methods

All the chemical reagents were purchased from commercial companies. All reactions were performed in flask and monitored by TLC (0.2 mm silica gel-coated HSGF 254 plate). The reaction mixtures were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate.

Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Bruker AMX 500 spectrophotometer (CDCl_3 as solvent). Chemical shifts were reported in ppm using tetramethylsilane (TMS, δ (ppm) = 0.00 ppm) as the internal standard, and relative to the signal of chloroform-d (δ 7.26, singlet). The number of protons for a given resonance was indicated by nH. Coupling constants were reported as a J value in Hz. The following abbreviations were used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), and multiplet (m). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were reported in ppm using solvent CDCl_3 (δ (ppm) = 77.17 ppm) as an internal standard. HRMS analyses were performed on a Waters XEVO QTOF mass spectrometer. X-ray structure for compounds was determined on X-ray single crystal diffractometer (Model Specifications: D8 QUEST). Specific rotations values were measured with a digital polarimeter (Model Specifications: P850A), equipped with a sodium lamp source (589.3 nm), at 25 °C in a 10 cm cell and the indicated solvent. The compounds 3-alkylideneindolin-2-ones **2** were prepared according the reported procedures.^[1]

2. Experimental Procedures



General procedure for reaction of anthrone with methyleneindolinones

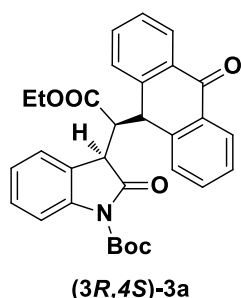
To a 10 mL flask with a magnetic bar, were added dichloromethane (2 mL), anthrone **1** (0.36 mmol), 3-alkylideneindolin-2-ones **2** (0.3 mmol) and chiral catalyst **6** (8.92 mg, 5 mol%). The mixture was then stirred at room temperature and monitored by TLC until **2** was consumed up. Then the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired product **3** or **4**.

References

^[1] G. Wang, X. Liu, T. Huang, Y. Kuang, L. Lin, X. Feng, *Org. Lett.*, **2013**, *15*, 76.

3. Characterization of Products

(*R*)-tert-butyl-3-((*S*)-2-ethoxy-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)ethyl)-2-oxoindoline-1-carboxylate (**3a**)

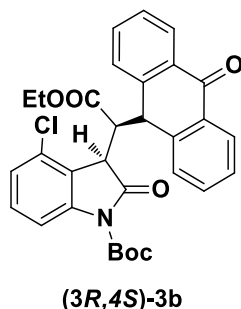


white solid, melting point 182-184 °C, yield 95%;

major isomer: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.22 (ddd, $J = 7.6, 7.1, 4.7$ Hz, 2H), 8.10 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 7.58-7.53 (m, 1H), 7.52-7.41 (m, 3H), 7.38-7.33 (m, 1H), 7.21 (t, $J = 7.9$ Hz, 1H), 6.97 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 7.6$ Hz, 1H), 5.40 (d, $J = 10.4$ Hz, 1H), 3.69-3.63 (m, 1H), 3.61 (d, $J = 4.1$ Hz, 1H), 3.53-3.45 (m, 1H), 2.95 (dd, $J = 10.4, 4.1$ Hz, 1H), 1.70 (s, 9H), 0.69 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 185.5, 174.0, 170.5, 149.1, 142.7, 142.6, 140.3, 133.2, 133.1, 132.4, 129.6, 128.7, 128.6, 128.4, 128.2, 128.0, 124.9, 124.2, 123.7, 115.2, 84.6, 61.3, 60.8, 44.4, 41.6, 28.3, 13.6.

HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{29}\text{NO}_6\text{Na}$, $[\text{M}+\text{Na}]$: 534.1893; found: 534.1898.

(*R*)-tert-butyl 4-chloro-3-((*S*)-2-ethoxy-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)ethyl)-2-oxoindoline-1-carboxylate (**3b**)

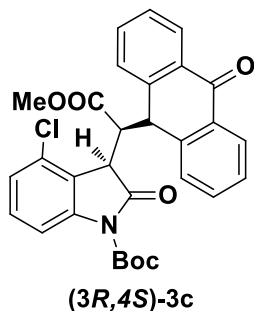


white solid, melting point 84-86 °C, yield 93%;

major isomer: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.26 (d, $J = 7.6$ Hz, 1H), 8.20 (dd, $J = 8.4, 4.7$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.46-7.38 (m, 2H), 7.37-7.31 (m, 1H), 7.15 (t, $J = 8.2$ Hz, 1H), 6.92 (d, $J = 8.1$ Hz, 1H), 5.33 (d, $J = 10.9$ Hz, 1H), 3.67 (d, $J = 3.8$ Hz, 1H), 3.66-3.59 (m, 1H), 3.48 (dd, $J = 10.9, 3.9$ Hz, 1H), 3.45-3.38 (m, 1H), 1.71 (s, 9H), 0.63 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 185.3, 172.7, 170.3, 148.9, 142.6, 142.4, 141.7, 133.1, 132.9, 132.2, 130.3, 129.9, 129.61, 128.4, 128.3, 128.1, 127.9, 127.8, 124.8, 122.6, 113.4, 84.8, 77.2, 60.6, 58.7, 44.5, 41.4, 28.2, 13.4.

HRMS (ESI): calcd. for $\text{C}_{31}\text{H}_{28}\text{NO}_6\text{NaCl}$, $[\text{M}+\text{Na}]$: 568.1503; found: 568.1504.

(R)-tert-butyl 4-chloro-3-((S)-2-methoxy-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)ethyl)-2-oxindoline-1-carboxylate (3c)

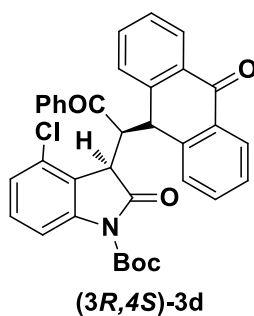


yellow solid, melting point 95-97 °C, yield 96%;

major isomer: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.26 (d, $J = 7.8$ Hz, 1H), 8.23-8.15 (m, 2H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.61-7.56 (m, 1H), 7.55-7.39 (m, 4H), 7.15 (q, $J = 8.1$ Hz, 1H), 6.93 (d, $J = 8.1$ Hz, 1H), 5.34 (d, $J = 10.9$ Hz, 1H), 3.69 (d, $J = 3.8$ Hz, 1H), 3.51 (dd, $J = 10.8, 3.9$ Hz, 1H), 3.04 (s, 3H), 1.71 (s, 9H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 185.0, 172.5, 170.7, 148.7, 142.4, 142.2, 141.5, 132.9, 132.7, 132.0, 130.0, 129.8, 129.4, 128.2, 128.0, 127.9, 127.8, 127.7, 124.7, 122.3, 113.3, 84.6, 58.5, 51.3, 44.2, 41.4, 28.0.

HRMS (ESI): calcd. for $\text{C}_{30}\text{H}_{26}\text{NO}_6\text{NaCl}$, $[\text{M}+\text{Na}]$: 554.1346; found: 554.1350.

(R)-tert-butyl 4-chloro-2-oxo-3-((S)-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)-2-phenylethyl)indoline-1-carboxylate (3d)

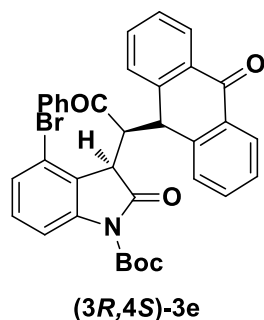


yellow solid, melting point 95-97 °C, yield 60%;

major isomer: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.32 (dd, $J = 13.8, 7.6$ Hz, 2H), 8.02 (d, $J = 7.5$ Hz, 1H), 7.65-7.51 (m, 3H), 7.20 (t, $J = 7.3$ Hz, 1H), 7.13-6.97 (m, 8H), 6.66 (d, $J = 8.1$ Hz, 1H), 5.44 (d, $J = 10.6$ Hz, 1H), 4.60 (dd, $J = 10.7, 3.8$ Hz, 1H), 3.71 (d, $J = 3.7$ Hz, 1H), 1.75 (s, 9H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 200.1, 185.4, 173.2, 149.0, 143.1, 142.0, 141.6, 136.8, 133.1, 132.9, 132.8, 132.3, 132.2, 129.8, 129.6, 129.5, 128.3, 128.0, 127.9, 127.7, 127.5, 127.4, 124.4, 122.6, 113.6, 84.7, 58.5, 45.0, 42.8, 28.2.

HRMS (ESI) calcd. for $\text{C}_{35}\text{H}_{28}\text{NO}_5\text{NaCl}$, $[\text{M}+\text{Na}]$: 600.1554; found: 600.1552.

(R)-tert-butyl 4-bromo-2-oxo-3-((S)-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)-2-phenylethyl)indoline-1-carboxylate (3e)

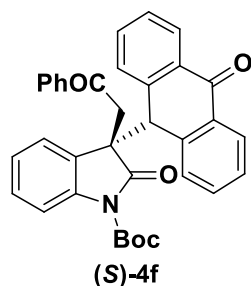


yellow solid, melting point 95-97 °C, yield 54%;

major isomer: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.31 (t, $J = 8.2$ Hz, 2H), 8.04 (d, $J = 7.5$ Hz, 1H), 7.63 (dd, $J = 6.9, 4.7$ Hz, 2H), 7.58-7.50 (m, 1H), 7.24-6.96 (m, 8H), 6.89 (t, $J = 8.1$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 1H), 5.42 (d, $J = 10.6$ Hz, 1H), 4.68 (dd, $J = 10.7, 3.6$ Hz, 1H), 3.65 (d, $J = 3.4$ Hz, 1H), 1.75 (s, 9H). $^{13}\text{C NMR}$ (125MHz, CDCl_3) δ 200.2, 185.7, 173.2, 149.1, 143.2, 142.2, 141.8, 137.1, 133.3, 133.2, 132.9, 132.4, 130.1, 129.7, 128.3, 128.2, 128.0, 127.8, 127.6, 124.7, 118.3, 114.2, 84.8, 58.7, 46.4, 43.0, 28.3.

HRMS (ESI) calcd. for $\text{C}_{35}\text{H}_{28}\text{NO}_5\text{NaBr}$, $[\text{M}+\text{Na}]$: 644.1049; found: 644.1038.

(S)-tert-butyl 2-oxo-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate (4f)

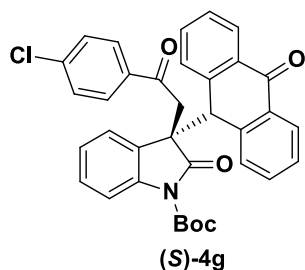


yellow solid, melting point 182-185 °C, yield 60%; $[\alpha]_{\text{D}}^{25} = +2.94$ (λ 589.3nm, c 0.68, CH_3OH).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.16 (d, $J = 7.7$ Hz, 1H), 7.78-7.70 (m, 5H), 7.63-7.48 (m, 3H), 7.44-7.36 (m, 4H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.18-7.10 (m, 1H), 6.78 (t, $J = 7.5$ Hz, 1H), 5.93 (d, $J = 7.2$ Hz, 1H), 4.68 (s, 1H), 4.09 (d, $J = 17.9$ Hz, 1H), 3.70 (d, $J = 17.8$ Hz, 1H), 1.59 (s, 9H). $^{13}\text{C NMR}$ (125MHz, CDCl_3) δ 194.8, 183.8, 178.1, 148.2, 140.5, 138.7, 137.6, 135.9, 135.6, 133.7, 133.6, 131.6, 131.4, 129.6, 129.3, 129.0, 128.8, 128.7, 128.1, 128.0, 127.4, 126.4, 125.6, 123.8, 114.7, 83.9, 55.8, 52.2, 45.8, 28.3.

HRMS (ESI) calcd. for $\text{C}_{35}\text{H}_{29}\text{NO}_5\text{Na}$, $[\text{M}+\text{Na}]$: 566.1943; found 566.1940.

(S)-tert-butyl 3-(2-(4-chlorophenyl)-2-oxoethyl)-2-oxo-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate (4g)

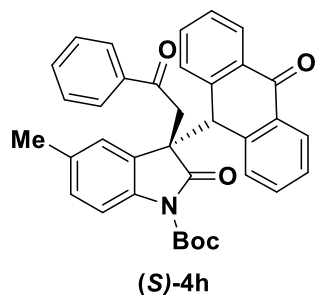


yellow solid, melting point 121-123 °C, yield 50%; $[\alpha]_D^{25} = -2.85$ (λ 589.3nm, c 0.391, CH₃OH).

¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, $J = 7.7$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 1H), 7.70 (t, $J = 7.9$ Hz, 4H), 7.62-7.57 (m, 1H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 9.0$ Hz, 3H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.15 (t, $J = 7.8$ Hz, 1H), 6.79 (t, $J = 7.5$ Hz, 1H), 5.92 (d, $J = 7.4$ Hz, 1H), 4.68 (s, 1H), 4.07 (d, $J = 17.9$ Hz, 1H), 3.64 (d, $J = 17.9$ Hz, 1H), 1.59 (s, 9H). **¹³C NMR** (125 MHz, CDCl₃) δ 193.7, 183.7, 178.0, 148.1, 140.5, 140.1, 138.5, 137.5, 135.5, 134.2, 133.5, 132.3, 131.6, 131.4, 129.5, 129.4, 129.3, 129.0, 128.9, 128.7, 128.6, 128.0, 127.3, 126.7, 126.3, 125.5, 123.8, 123.7, 114.6, 83.9, 55.8, 52.1, 45.6, 28.2.

HRMS (ESI): calcd. for C₃₅H₂₈NO₅NaCl, [M+Na]: 600.1554; found: 600.1552.

tert-butyl (S)-5-methyl-2-oxo-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate (4h)



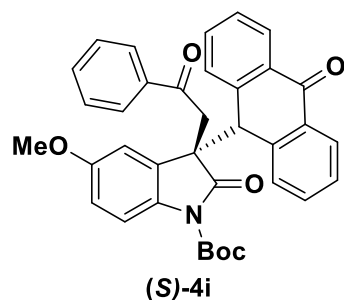
White solid, melting point 173-175 °C, yield 57%; $[\alpha]_D^{25} = -14.01$ (λ 589.3nm, c 0.666, CH₃OH).

¹H NMR (500 MHz, CDCl₃): δ 8.18 (d, $J = 7.6$ Hz, 1H), 7.78 (d, $J = 7.4$ Hz, 2H), 7.73 (d, $J = 4.6$ Hz, 3H), 7.60 (m, 1H), 7.52 (t, $J = 6.9$ Hz, 2H), 7.40 (t, $J = 7.7$ Hz, 3H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 8.3$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 5.64 (s, 1H), 4.67 (s, 1H), 4.09 (d, $J = 23.2$ Hz, 1H), 3.64 (d, $J = 17.9$ Hz, 1H), 2.06 (s, 3H), 1.58 (s, 9H).

¹³C NMR (125 MHz, CDCl₃) δ 194.7, 183.5, 178.2, 148.3, 138.8, 138.0, 137.7, 136.0, 135.9, 133.6, 133.6, 133.4, 131.5, 131.4, 129.7, 129.3, 1289.0, 128.7, 128.1, 128.0, 127.0, 126.3, 125.5, 124.7, 114.4, 83.7, 55.8, 52.3, 45.6, 28.3, 27.0, 20.9.

HRMS (ESI): Calcd. for C₃₆H₃₁NO₅Na, [M+Na]: 580.2100; Found: 580.2097.

tert-butyl (S)-5-methoxy-2-oxo-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate (4i)



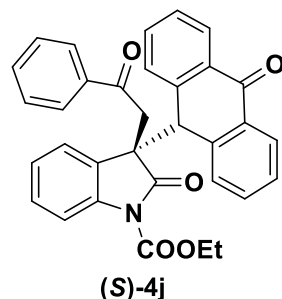
White solid, melting point 187-190 °C, yield 71%; $[\alpha]_D^{25} = -5.22$ (λ 589.3nm, c 0.421, CH₃OH).

¹H NMR (500 MHz, CDCl₃): δ 8.19 (d, $J = 7.7$ Hz, 1H), 7.77 (d, $J = 7.7$ Hz, 3H), 7.73 (d, $J = 4.0$ Hz, 2H), 7.60 (dt, $J = 8.1, 4.2$ Hz, 1H), 7.53 (t, $J = 6.8$ Hz, 2H), 7.40 (t, $J = 7.6$ Hz, 3H), 7.32 – 7.27 (m, 2H), 6.65 (dd, $J = 8.9, 2.4$ Hz, 1H), 5.50 (d, $J = 2.3$ Hz, 1H), 4.68 (s, 1H), 4.09 (d, $J = 17.9$ Hz, 1H), 3.61 (d, $J = 17.9$ Hz, 1H), 3.58 (s, 3H), 1.58 (s, 9H).

¹³C NMR (125 MHz, CDCl₃): δ 194.7, 183.8, 178.1, 156.0, 148.3, 138.7, 137.7, 136.0, 135.8, 133.8, 133.7, 131.6, 131.4, 129.8, 128.9, 128.8, 128.8, 128.1, 128.0, 127.2, 126.8, 126.4, 115.7, 114.6, 110.3, 83.7, 55.8, 55.6, 52.2, 45.8, 28.3.

HRMS (ESI): Calcd. for C₃₆H₃₁NO₆, [M+Na]: 596.2049; Found: 596.2048.

ethyl (S)-2-oxo-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate (4j)



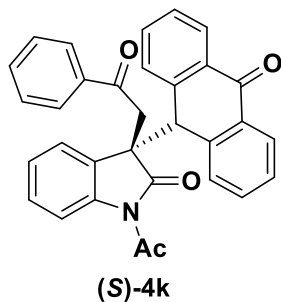
White solid, melting point 205-207 °C, yield 36%; $[\alpha]_D^{25} = 5.93$ (λ 589.3nm, c 0.1, CH₃OH).

¹H NMR (500 MHz, CDCl₃): δ 8.18 (d, $J = 7.7$ Hz, 1H), 7.76 (dd, $J = 10.3, 5.9$ Hz, 4H), 7.63 – 7.59 (m, 1H), 7.54 (dd, $J = 7.3, 4.8$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 1H), 7.40 (dd, $J = 12.9, 7.3$ Hz, 3H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.16 (t, $J = 7.8$ Hz, 1H), 6.80 (t, $J = 7.5$ Hz, 1H), 5.93 (d, $J = 7.4$ Hz, 1H), 4.70 (s, 1H), 4.47 – 4.32 (m, 2H), 4.10 (d, $J = 17.9$ Hz, 1H), 3.72 (d, $J = 17.8$ Hz, 1H), 1.43 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 194.8, 183.6, 177.8, 150.1, 140.3, 138.6, 137.6, 136.0, 135.7, 133.8, 133.7, 131.6, 131.3, 129.7, 129.4, 128.9, 128.8, 128.8, 128.2, 128.1, 127.5, 126.5, 125.8, 124.1, 123.8, 114.8, 63.1, 55.9, 52.1, 46.1, 14.5.

HRMS (ESI): Calcd. for C₃₃H₂₅NO₅Na, [M+Na]: 538.1630; Found: 538.1633.

(S)-1-acetyl-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indolin-2-one (4k)



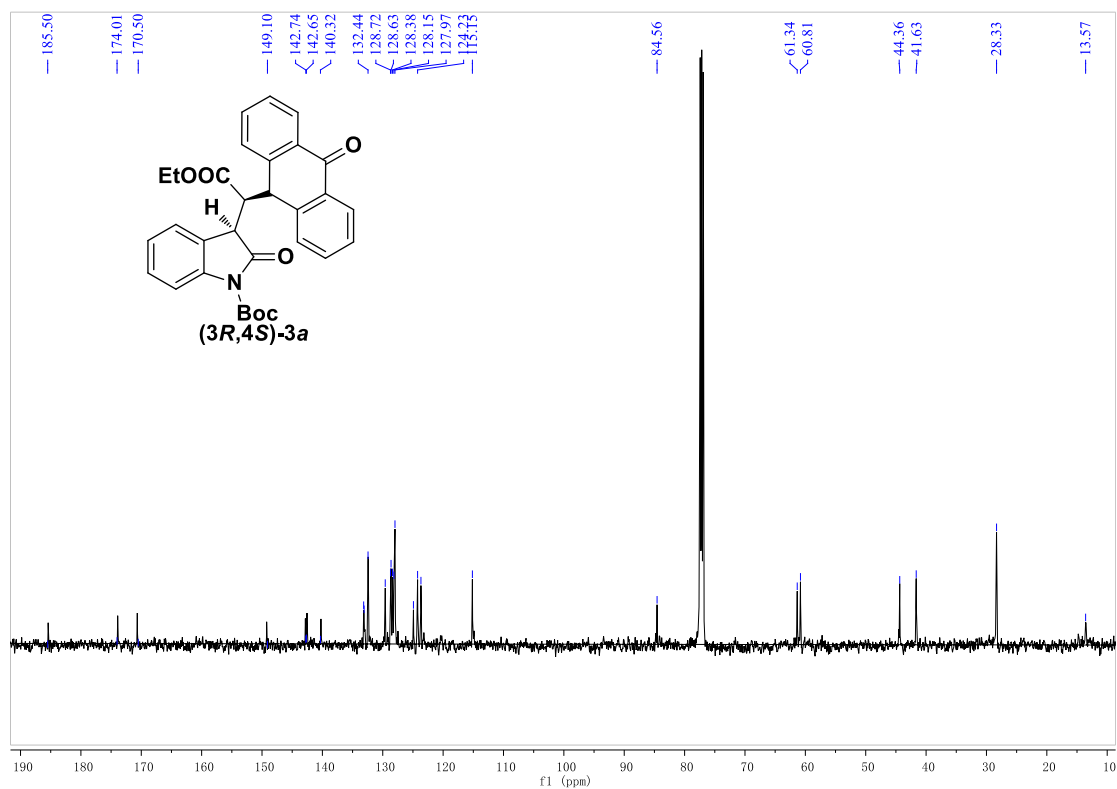
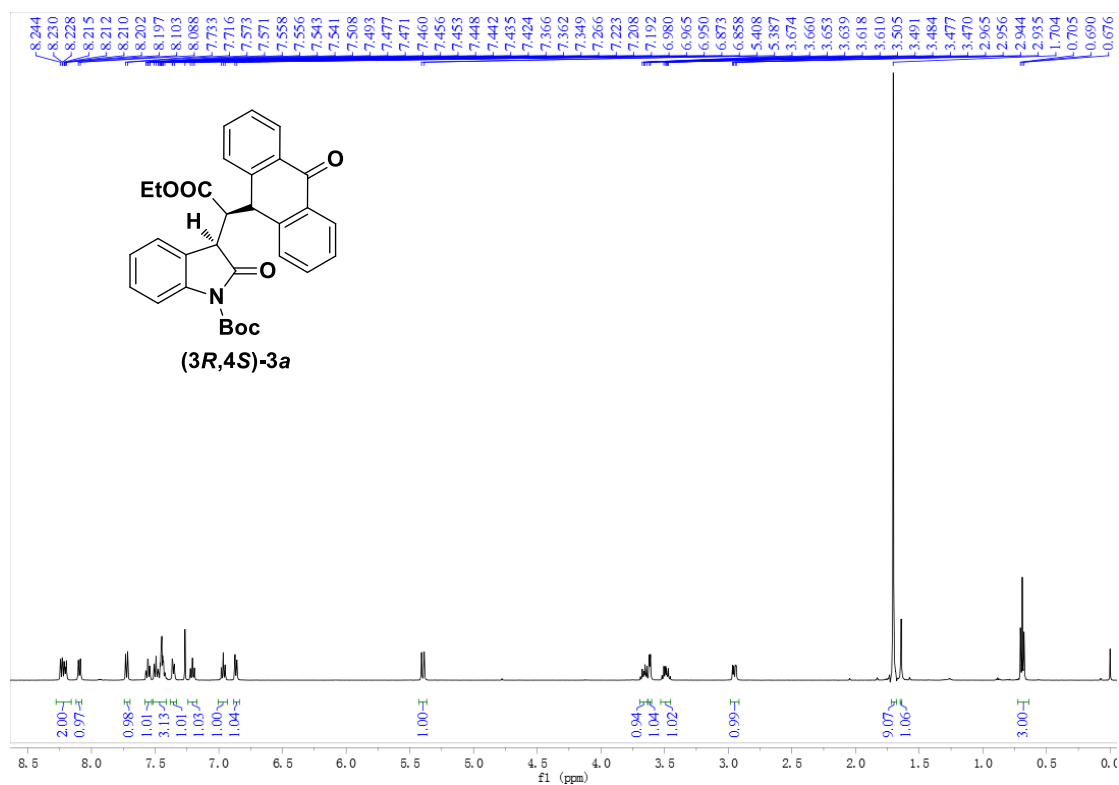
White solid, melting point 228-230 °C, yield 38%; $[\alpha]_D^{25} = 7.60$ (λ 589.3nm, c 0.163, CH₃OH).

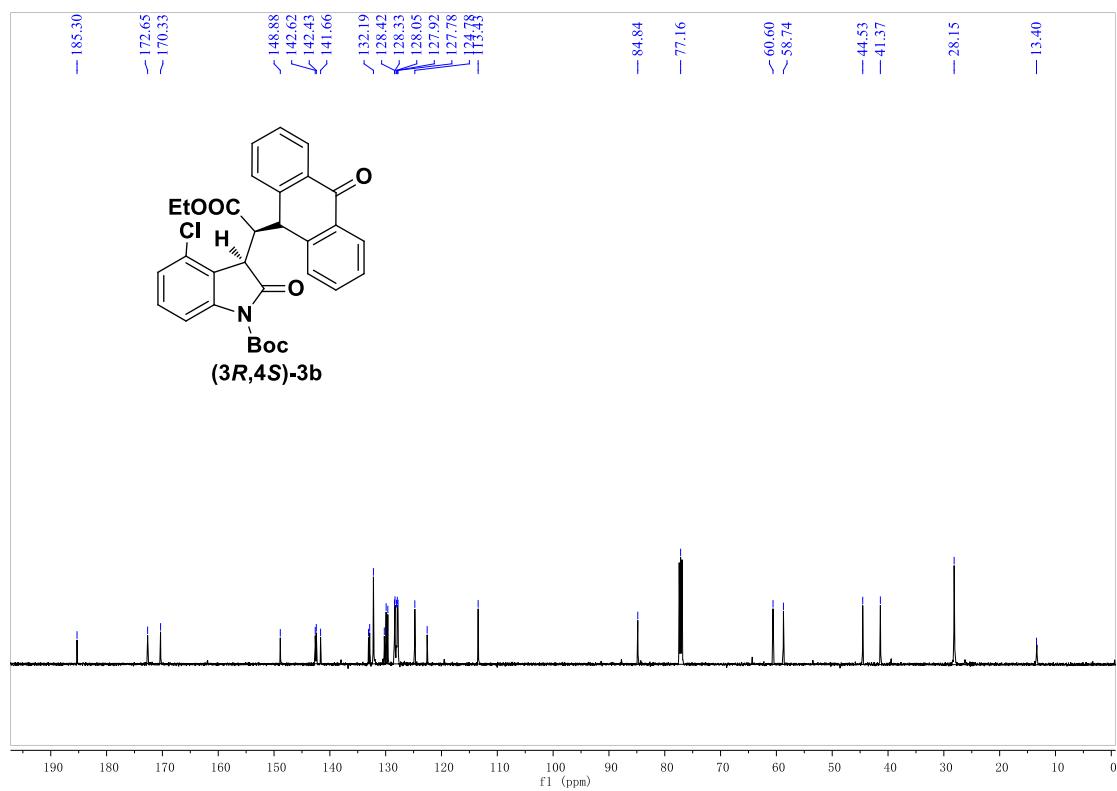
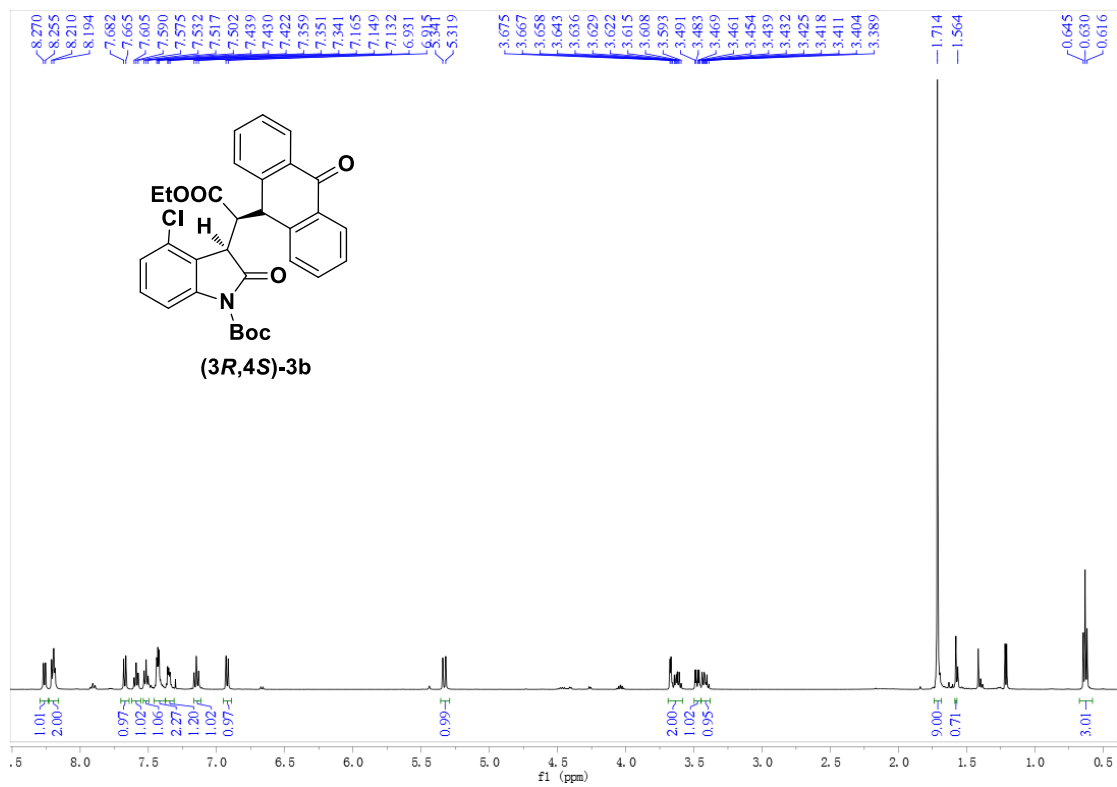
¹H NMR (500 MHz, CDCl₃): δ 8.17 (d, J = 7.6 Hz, 1H), 7.82 (dd, J = 16.2, 7.9 Hz, 2H), 7.76 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.56 (dd, J = 13.9, 6.5 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.43 (m, 3H), 7.34 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.03 (d, J = 7.4 Hz, 1H), 4.67 (s, 1H), 4.02 (d, J = 17.8 Hz, 1H), 3.80 (d, J = 17.8 Hz, 1H), 2.58 (s, 3H).

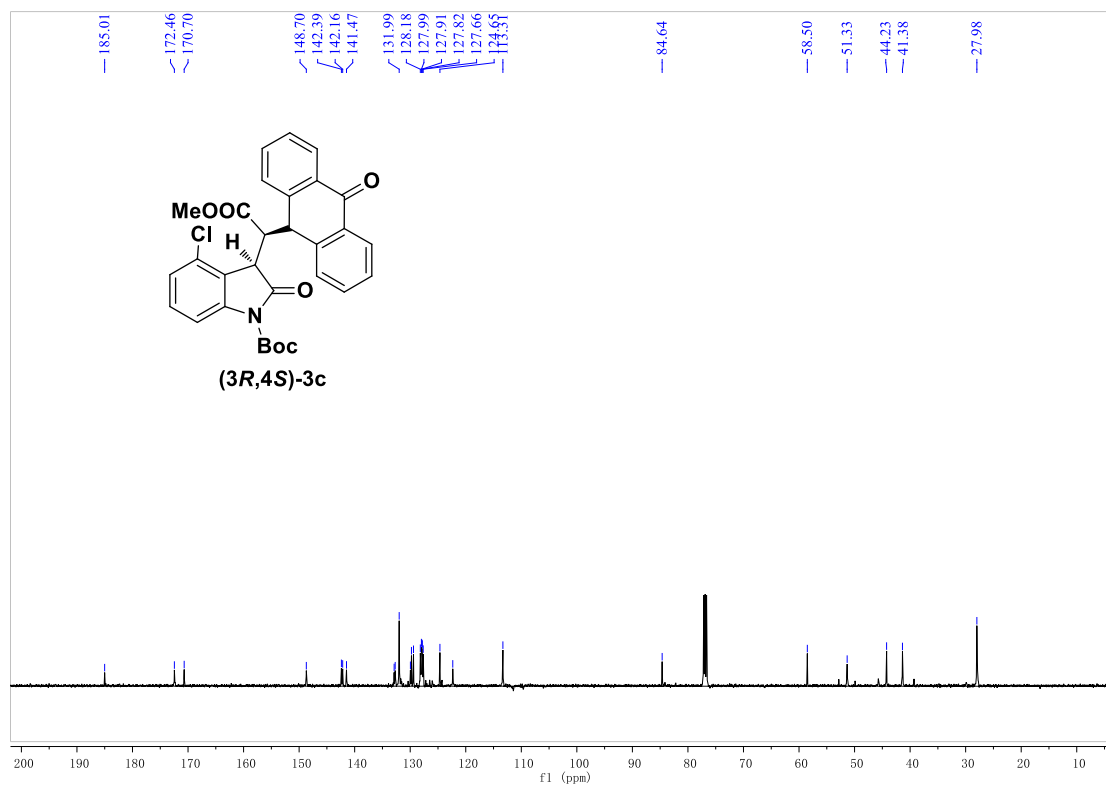
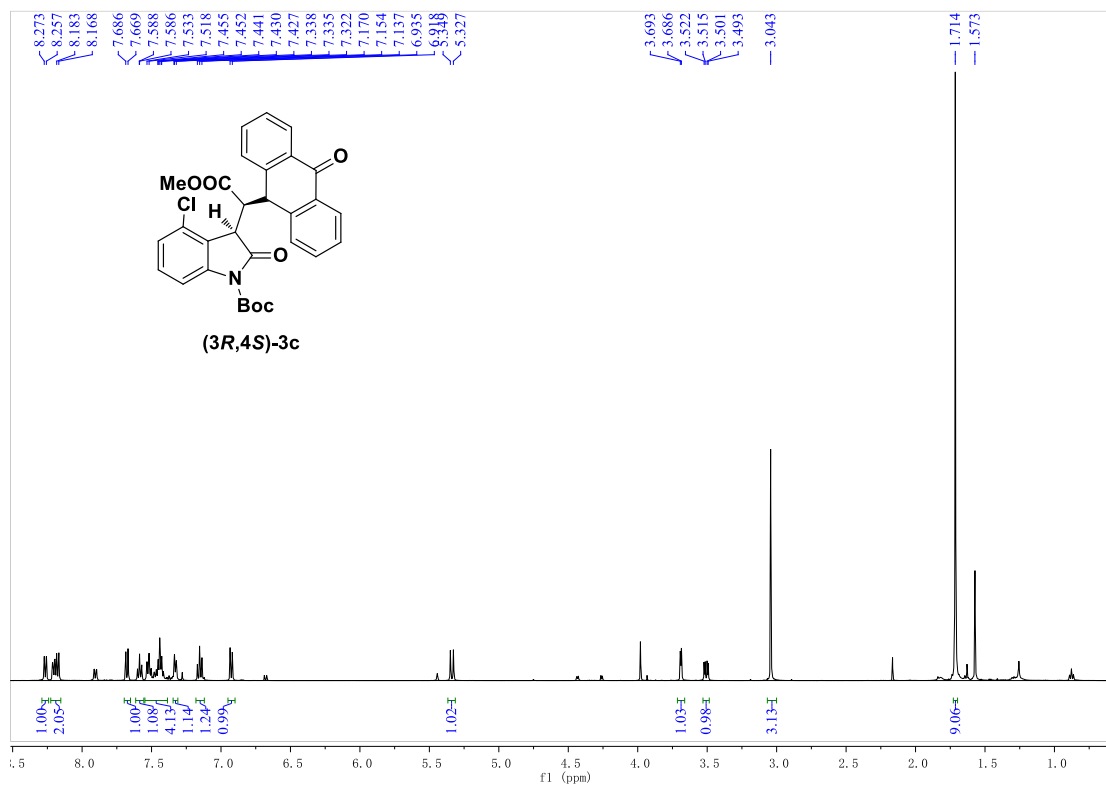
¹³C NMR (125 MHz, CDCl₃) δ 195.0, 183.6, 180.1, 167.0, 141.0, 138.4, 137.6, 135.9, 135.6, 133.9, 131.6, 131.2, 129.5, 129.4, 128.9, 128.6, 128.1, 127.4, 126.8, 126.1, 124.5, 123.6, 116.2, 55.9, 52.3, 46.1, 26.7.

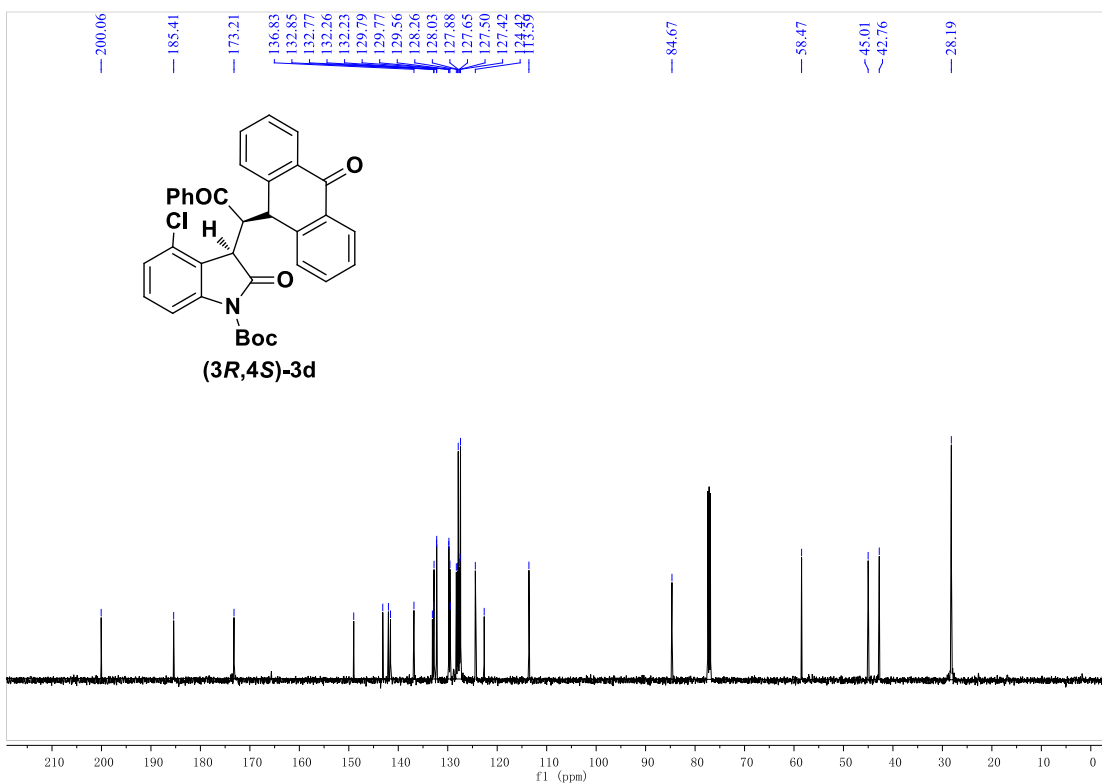
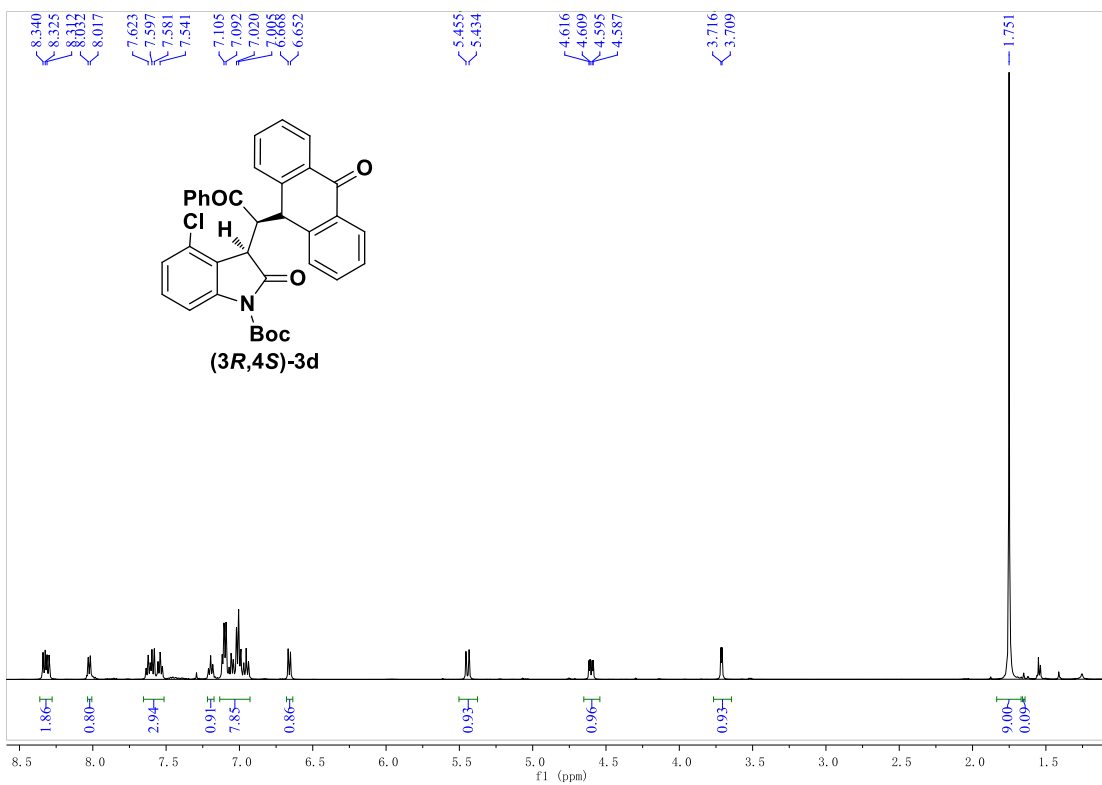
HRMS (ESI): Calcd. for C₃₂H₂₂NO₄Na, [M+Na]: 508.1525; Found: 508.1526.

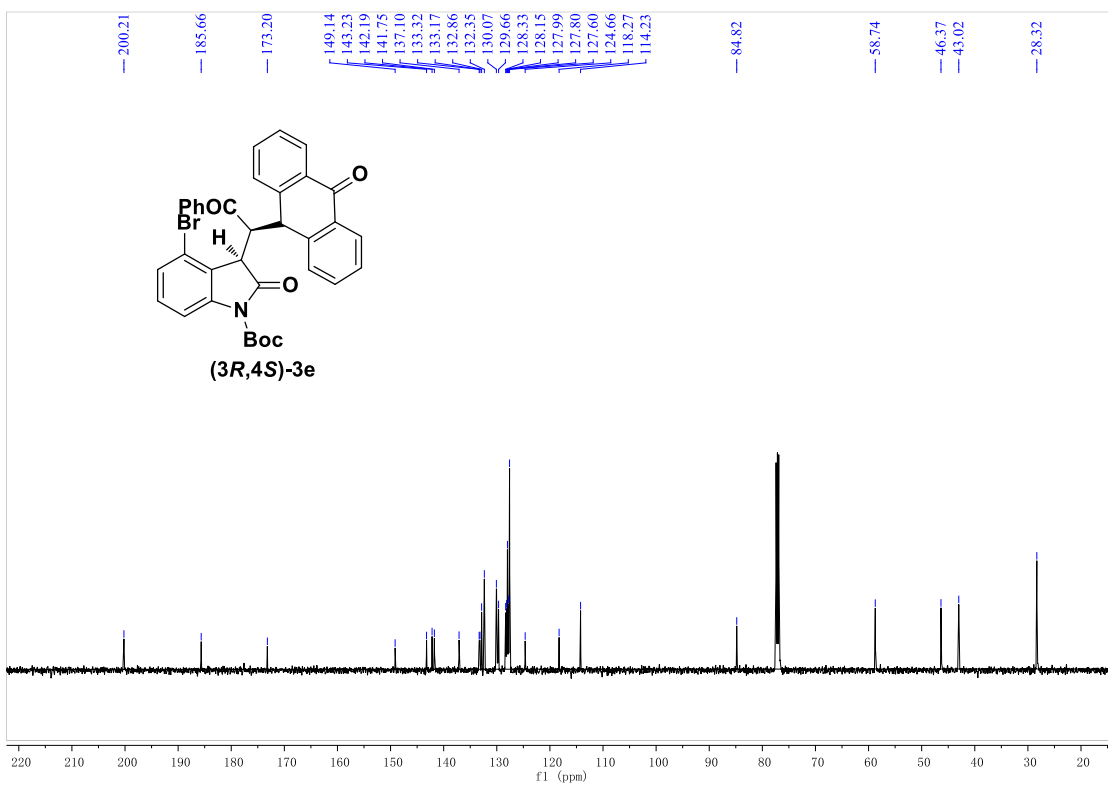
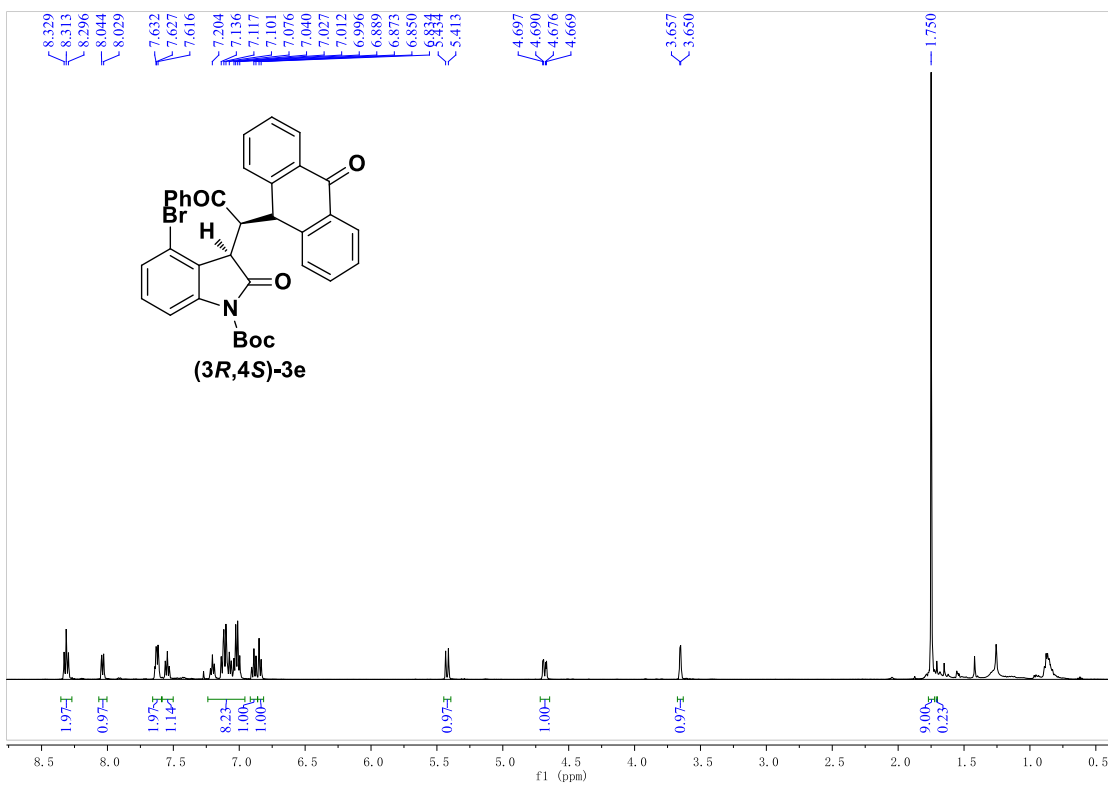
4. ^1H and ^{13}C NMR Spectra

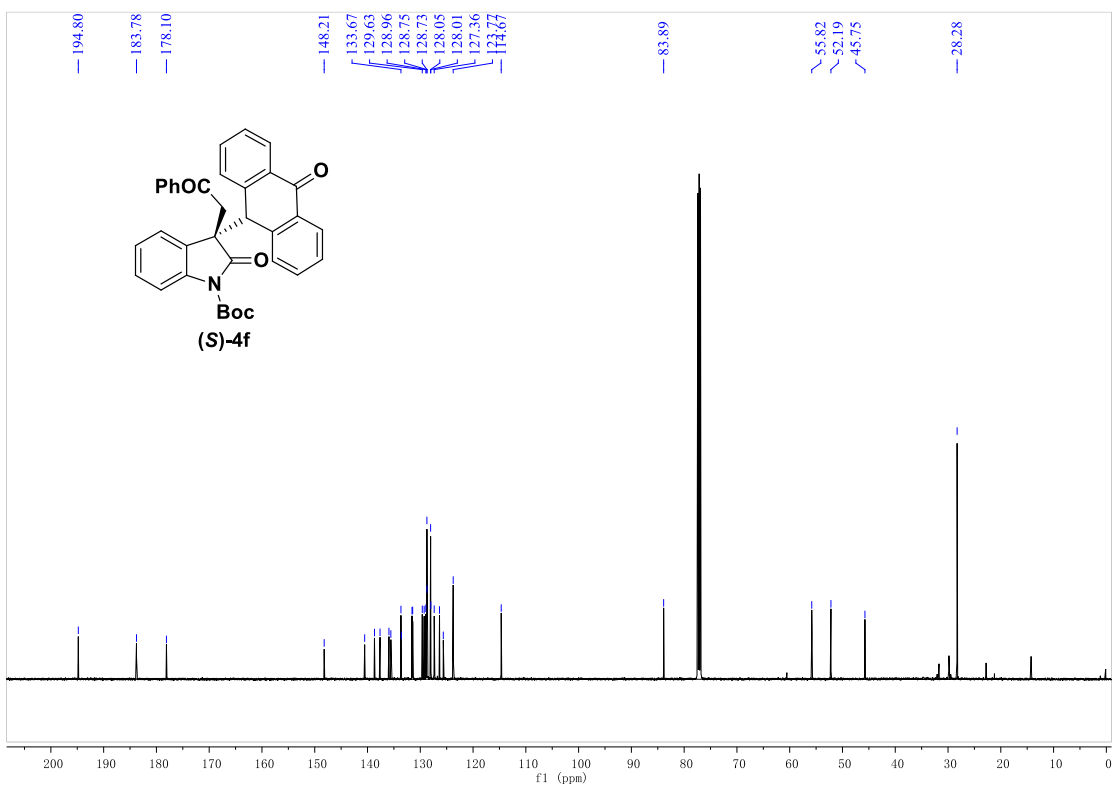
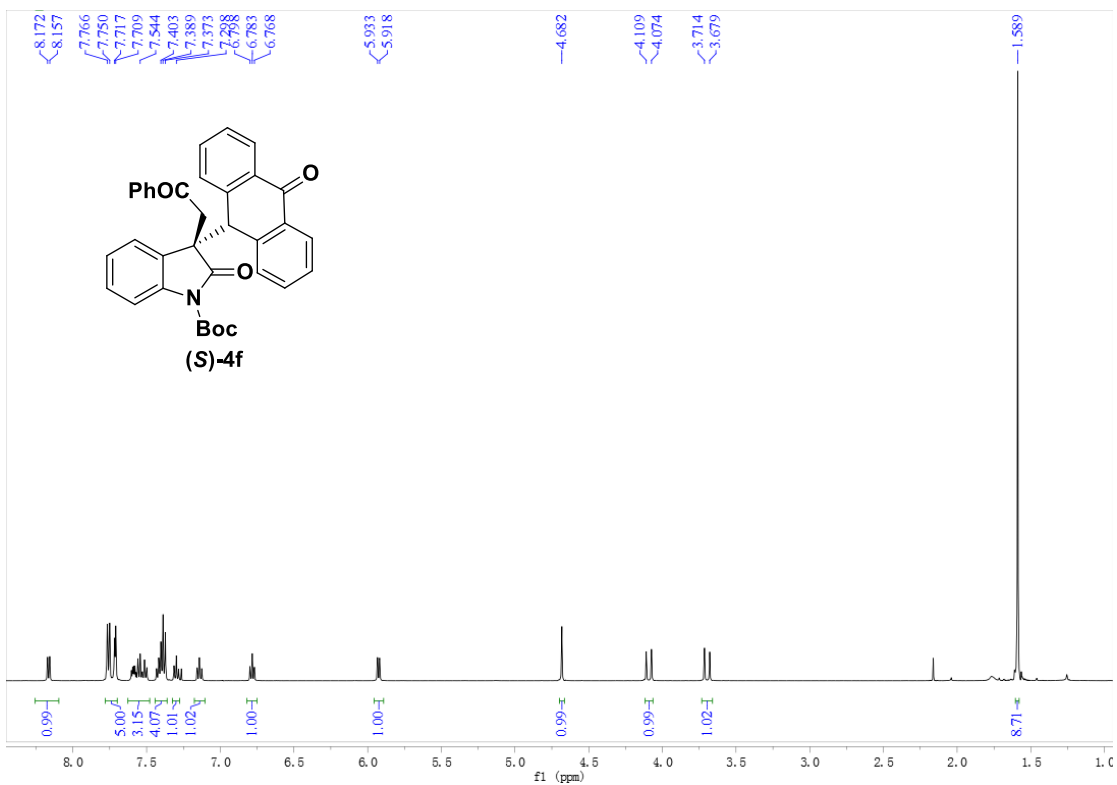


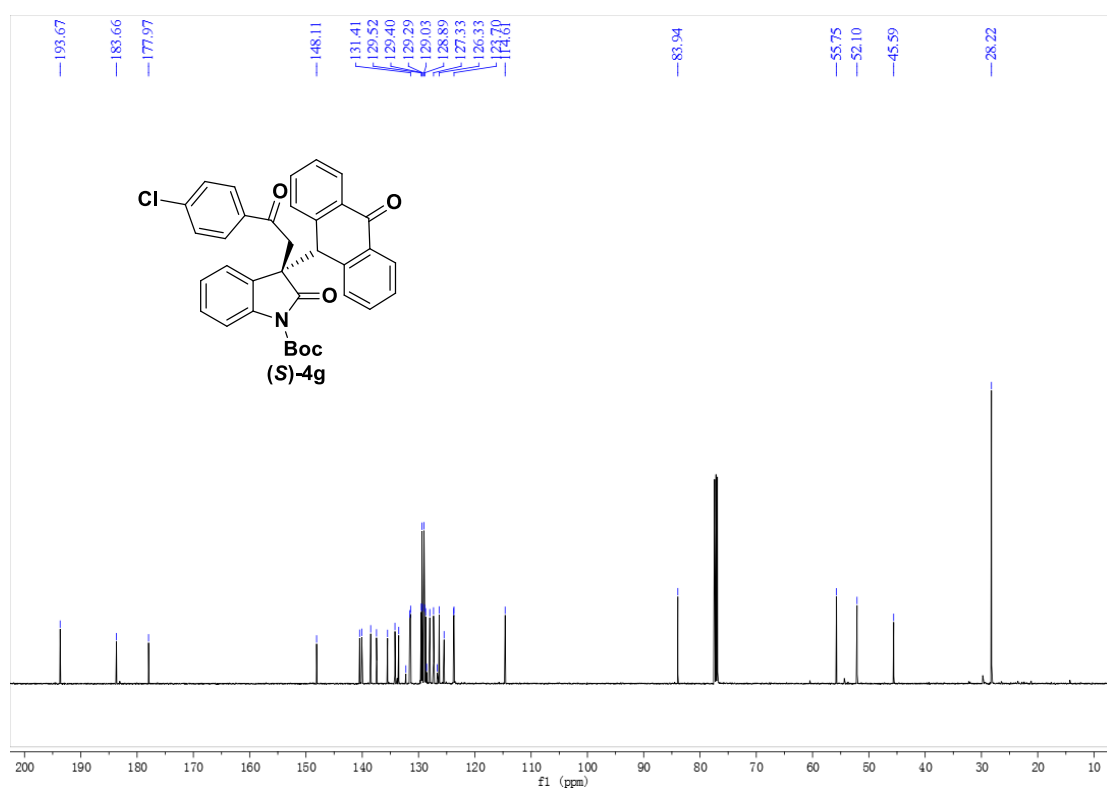
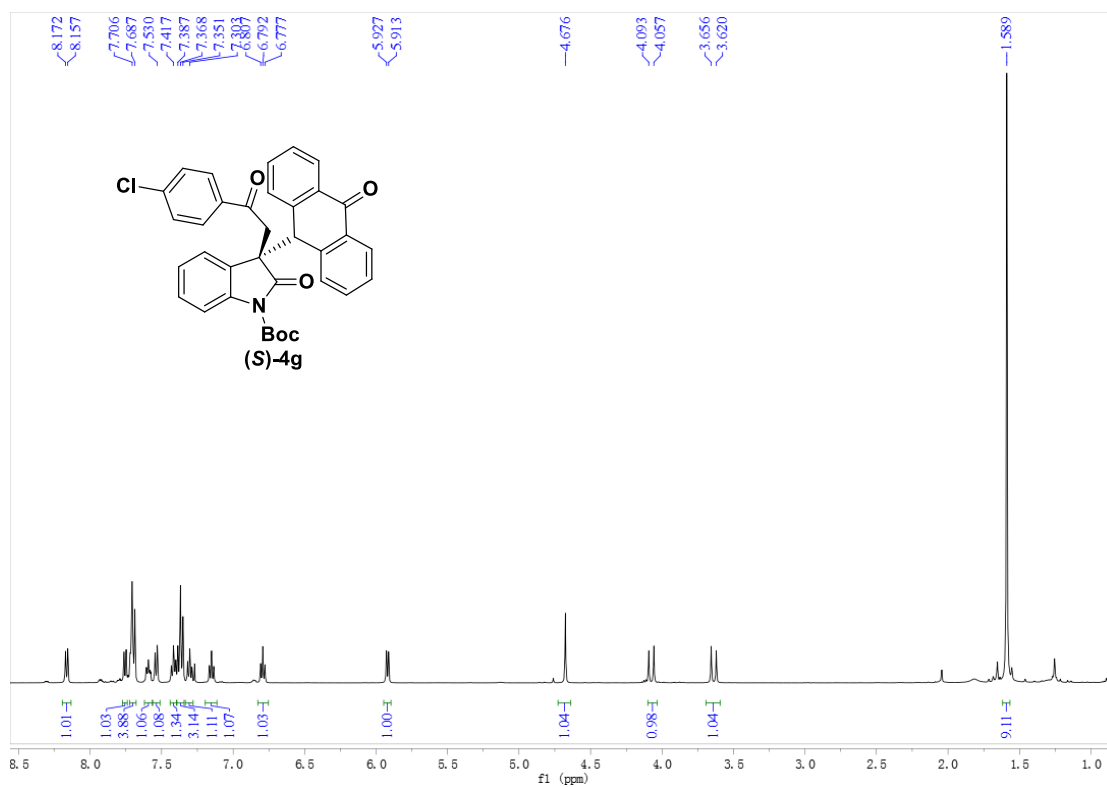


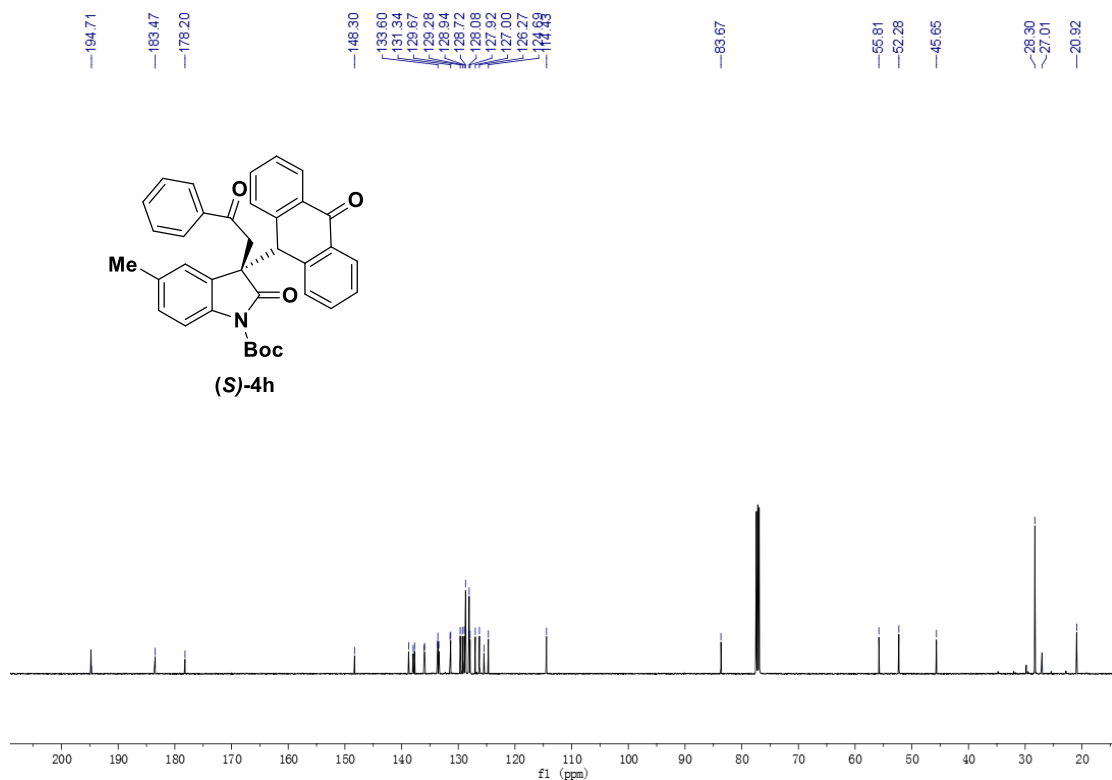
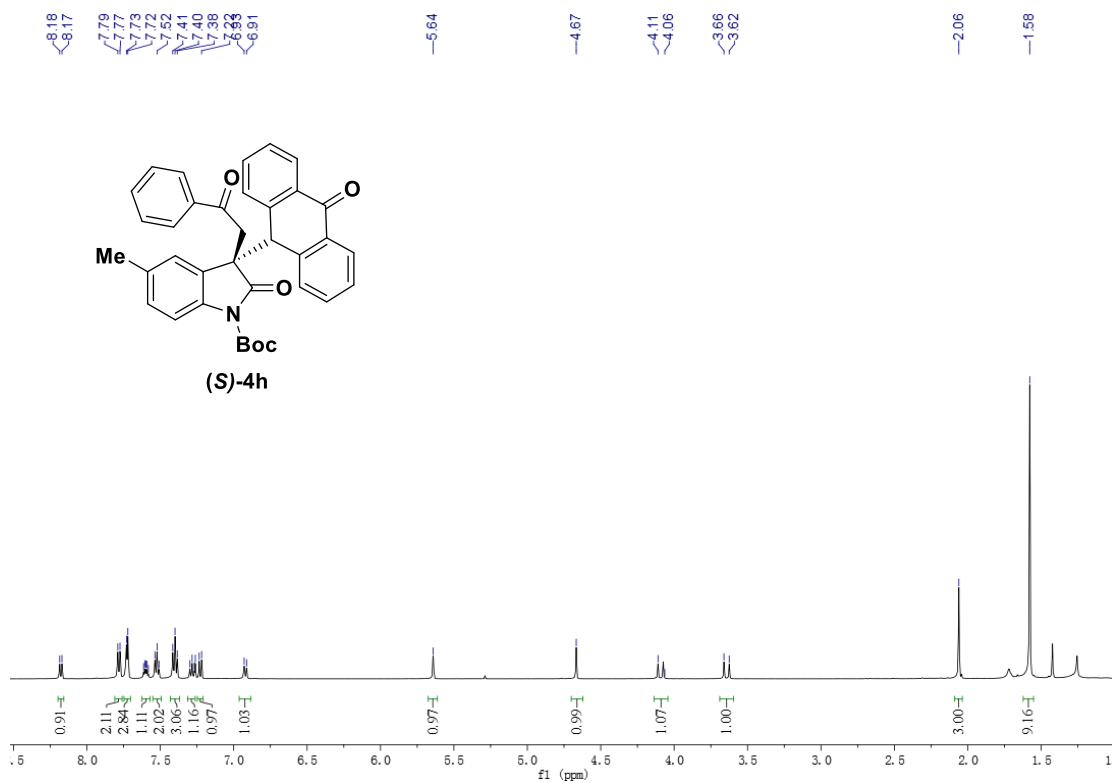


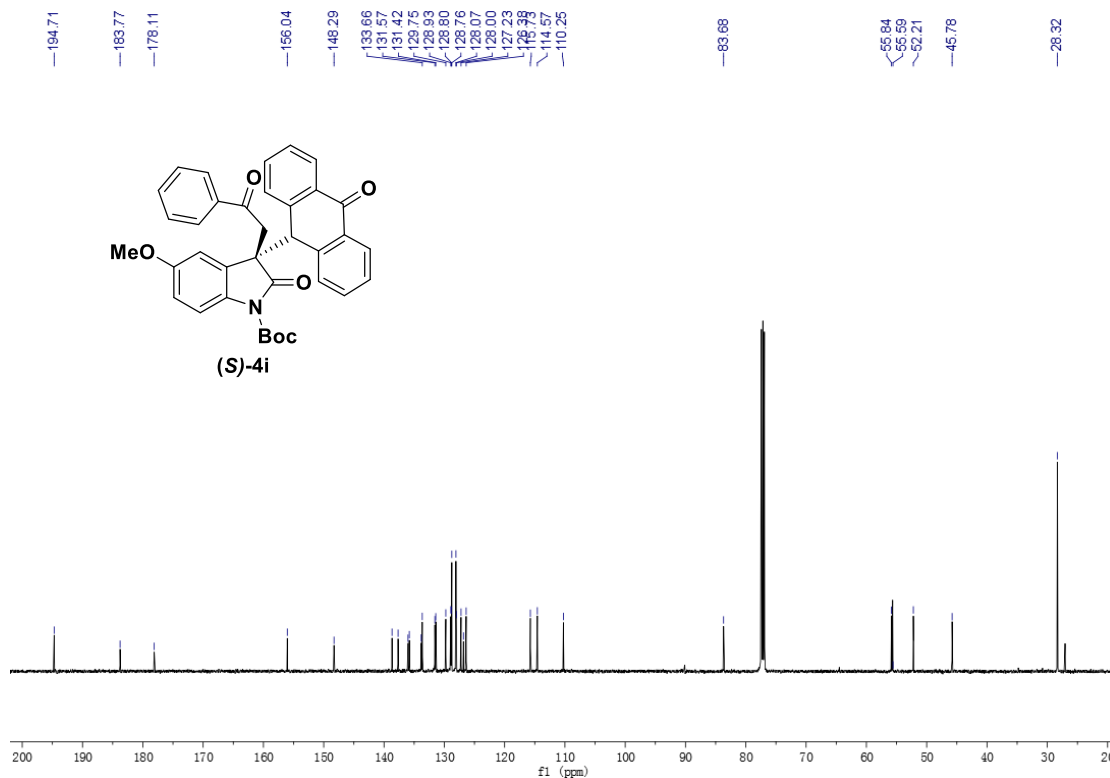
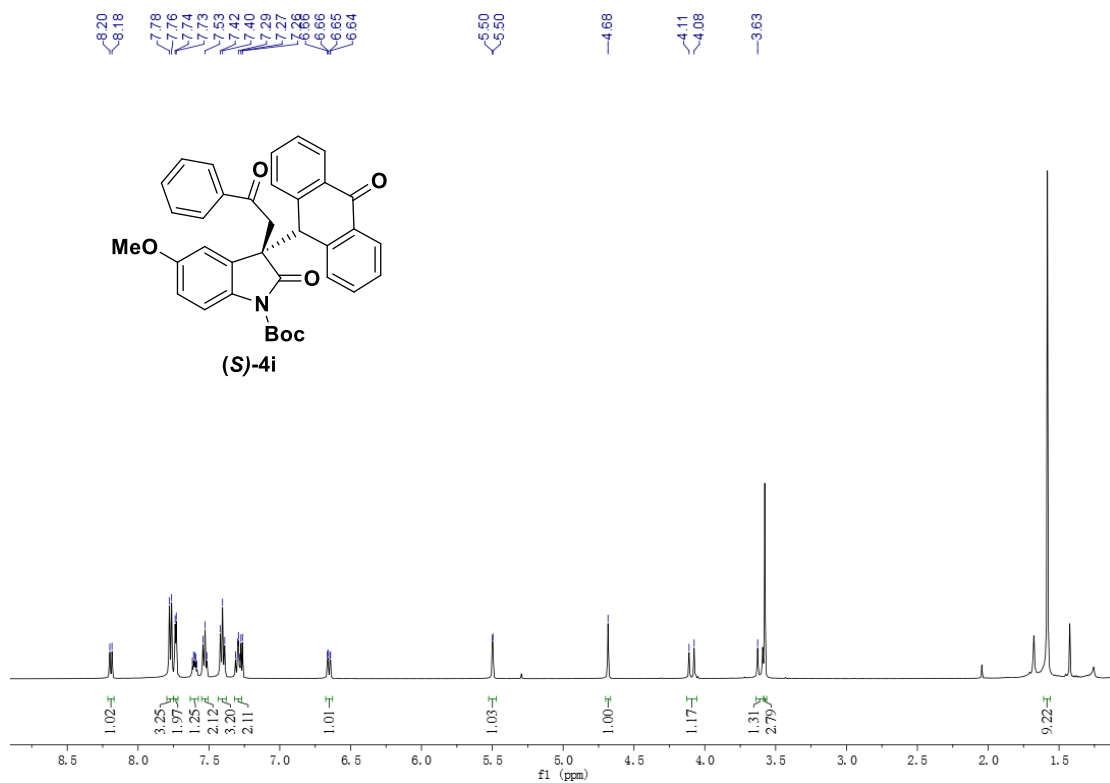


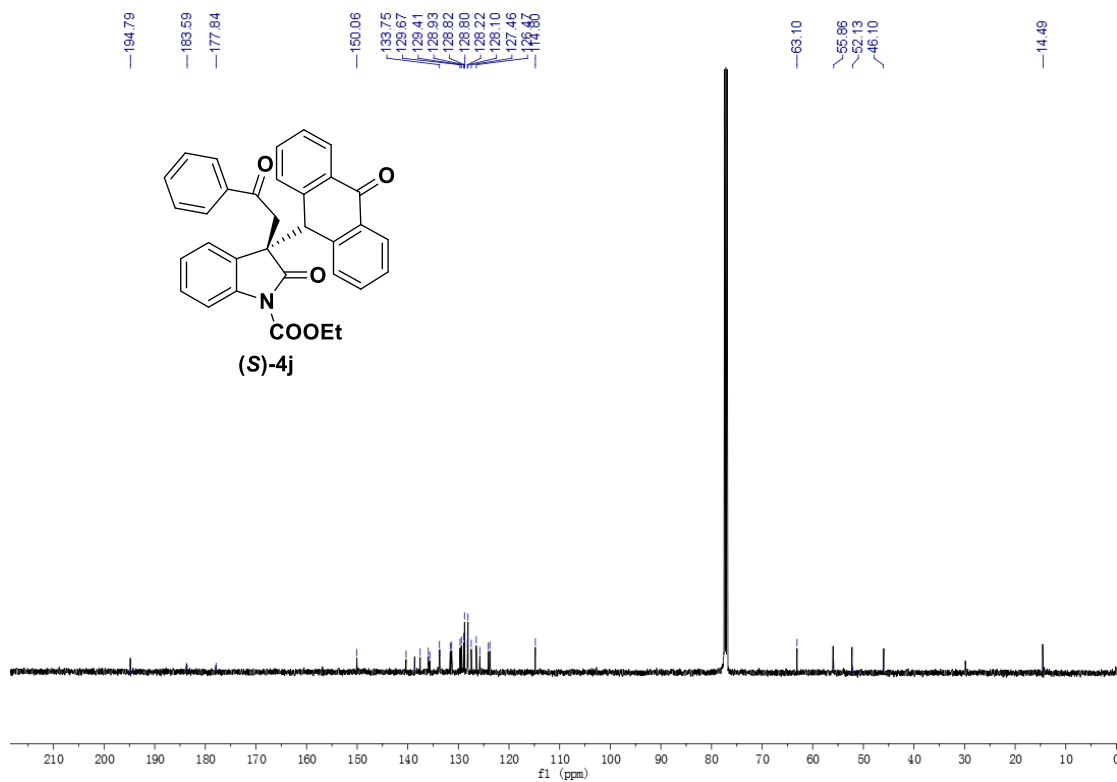
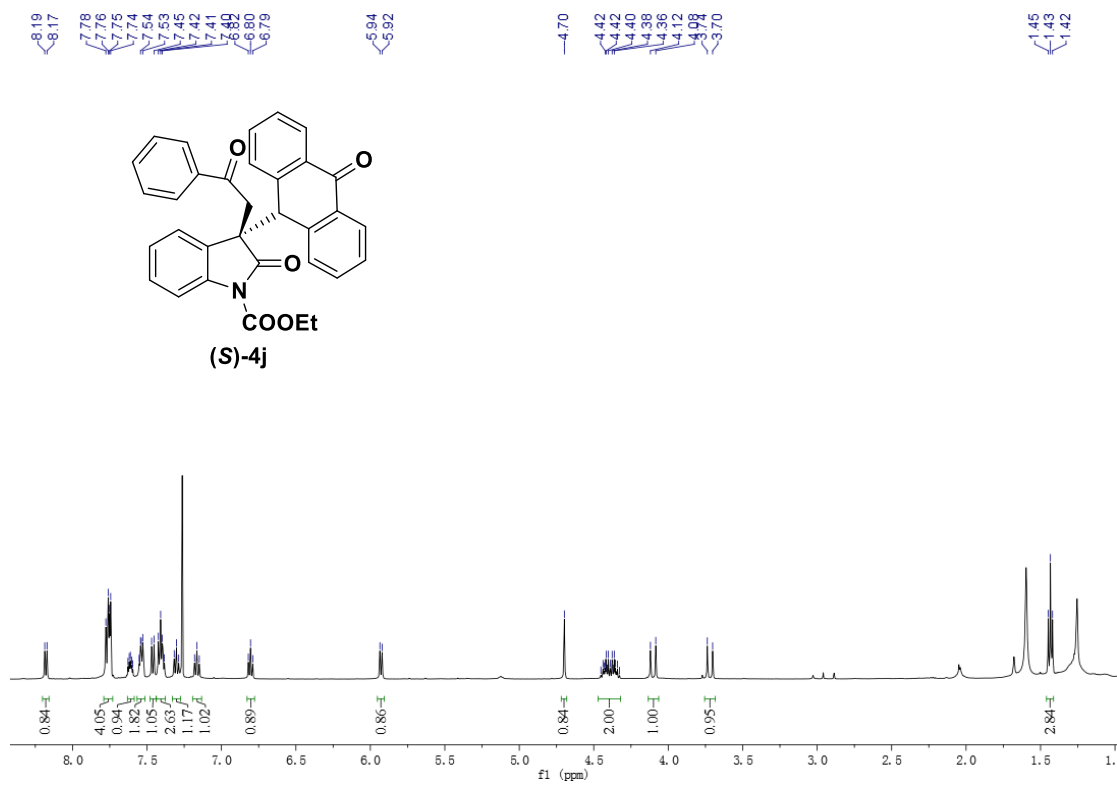


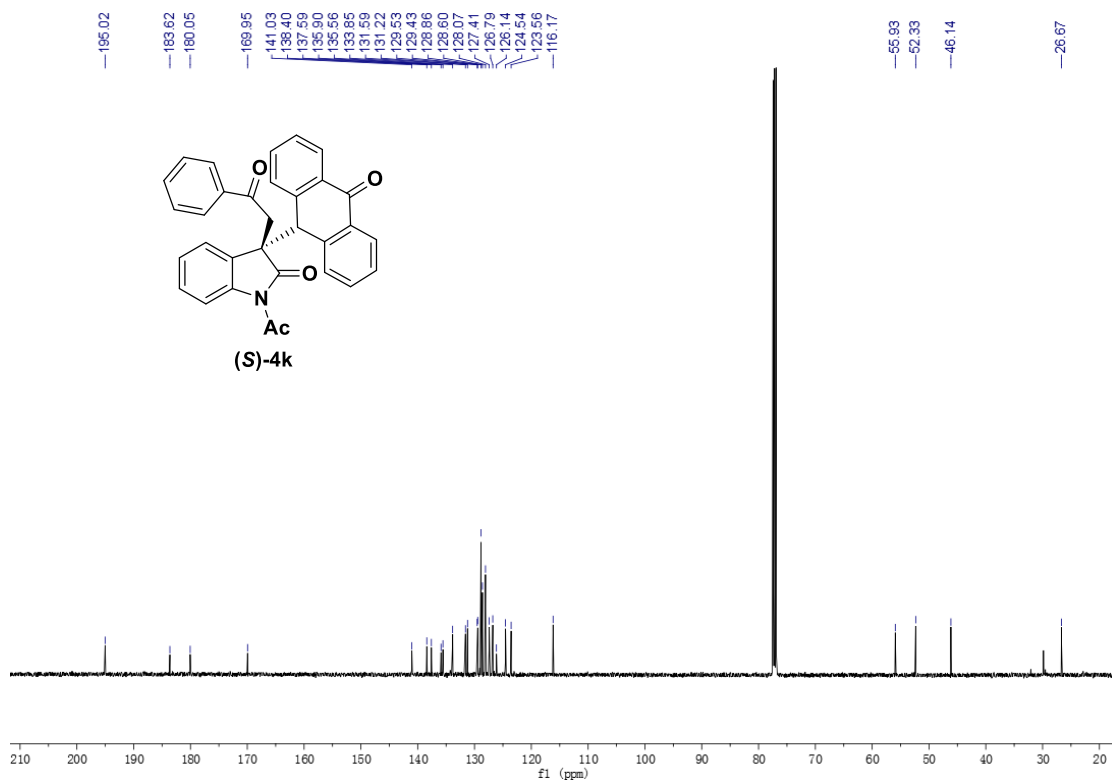
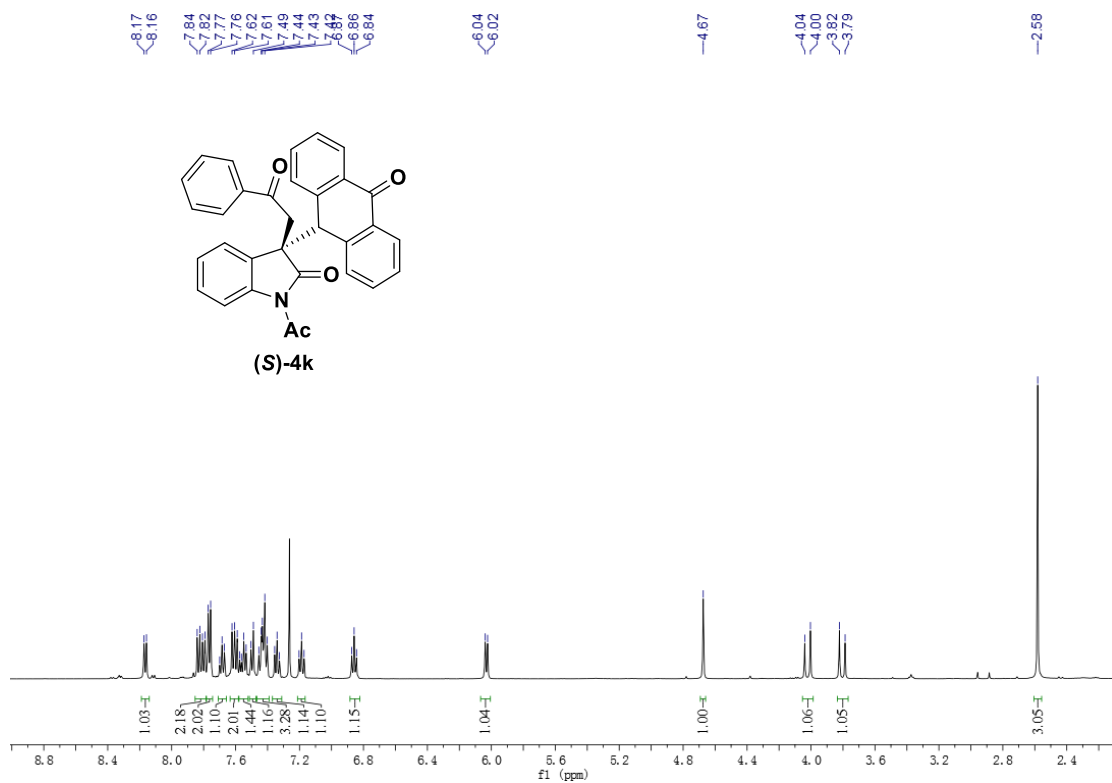






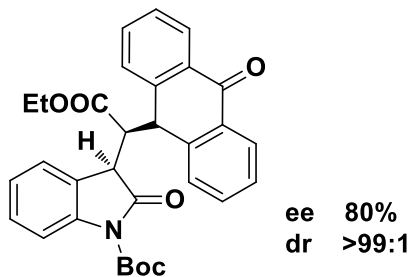




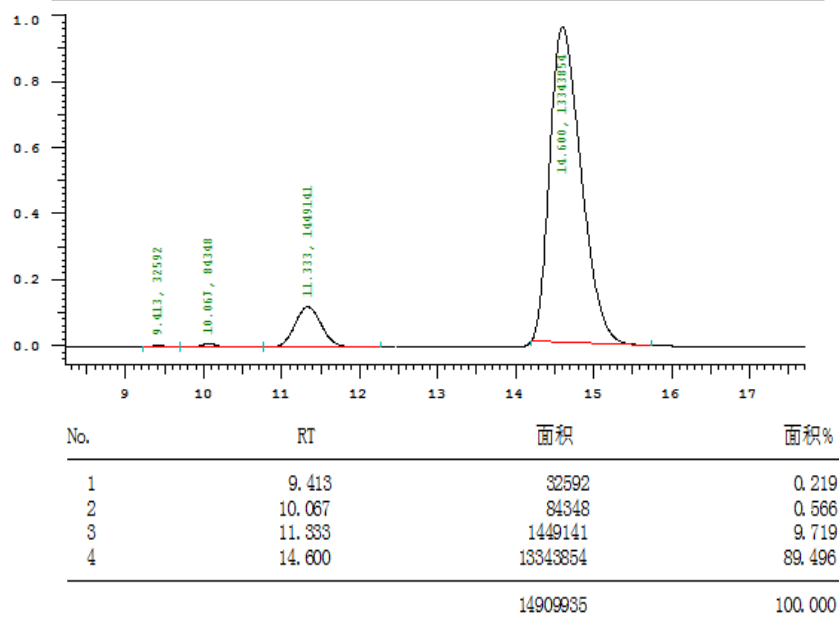
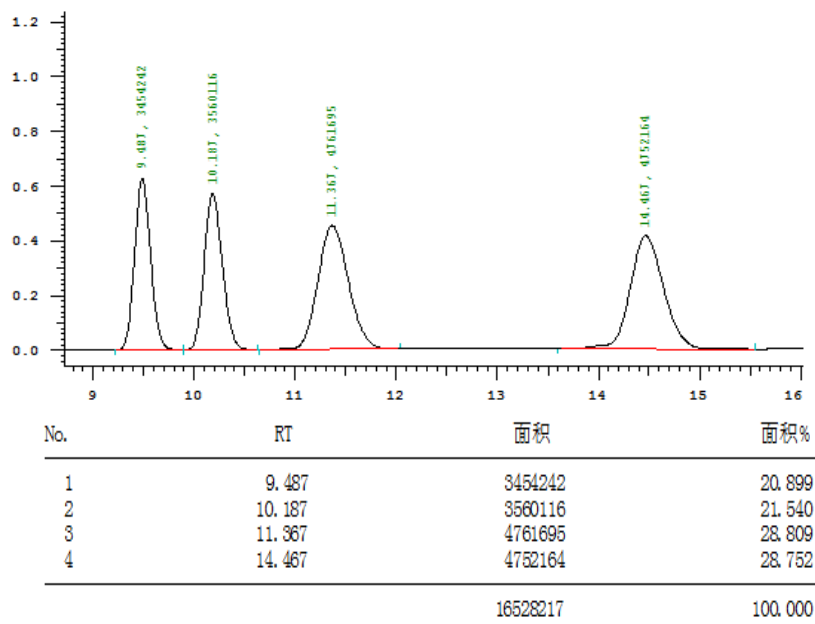


5. HPLC Spectra

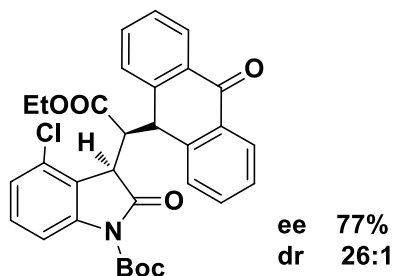
(*R*)-tert-butyl 3-((*S*)-2-ethoxy-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)ethyl)-2-oxoindoline-1-carboxylate ((**3R,4S**)-**3a**)



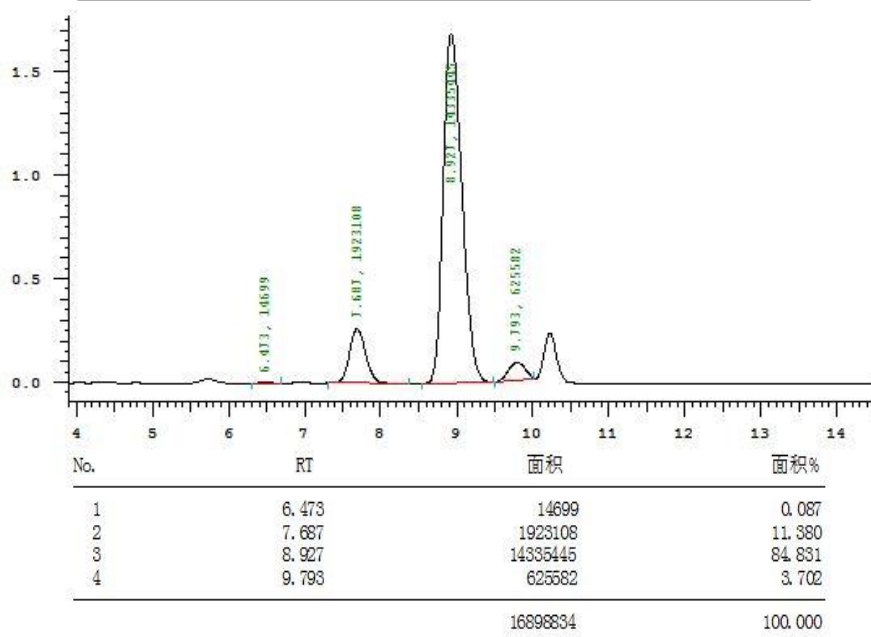
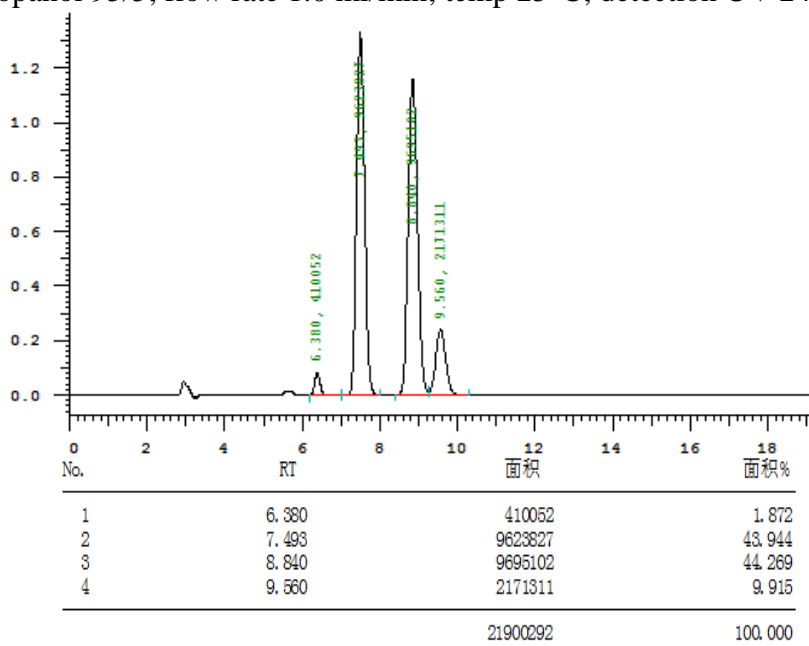
The ee determined by chiral HPLC; CHIRALPAK AD-H (4.6 mm ϕ \times 250 mmL); hexane/2-propanol 95/5; flow rate 1.0 ml/min; temp 25 $^{\circ}$ C; detection UV 210 nm.



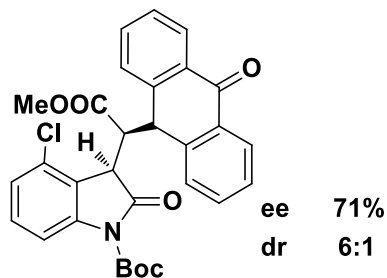
(*R*)-tert-butyl 4-chloro-3-((*S*)-2-ethoxy-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)ethyl)-2-oxindoline-1-carboxylate (**(3*R*,4*S*)-3b**)



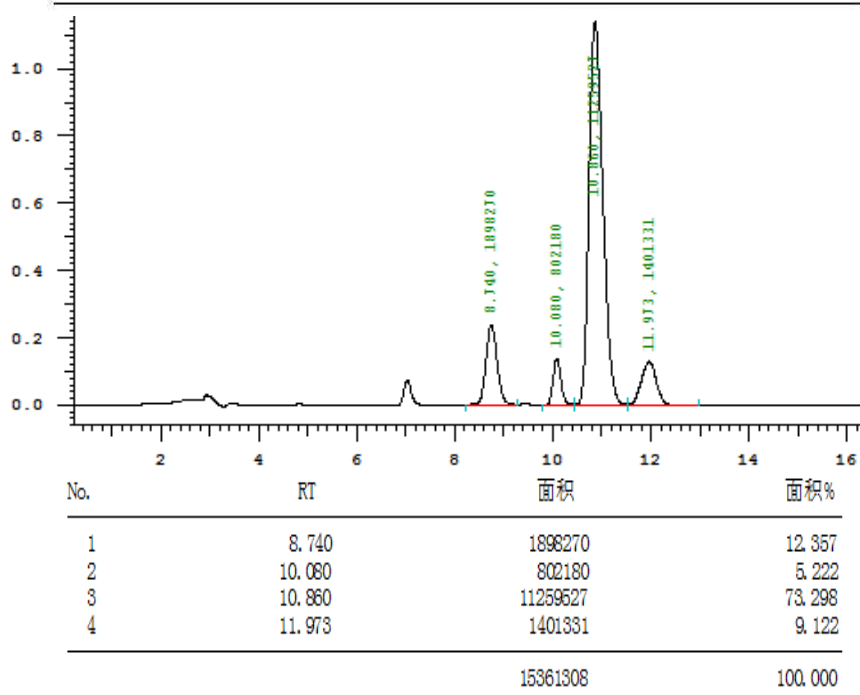
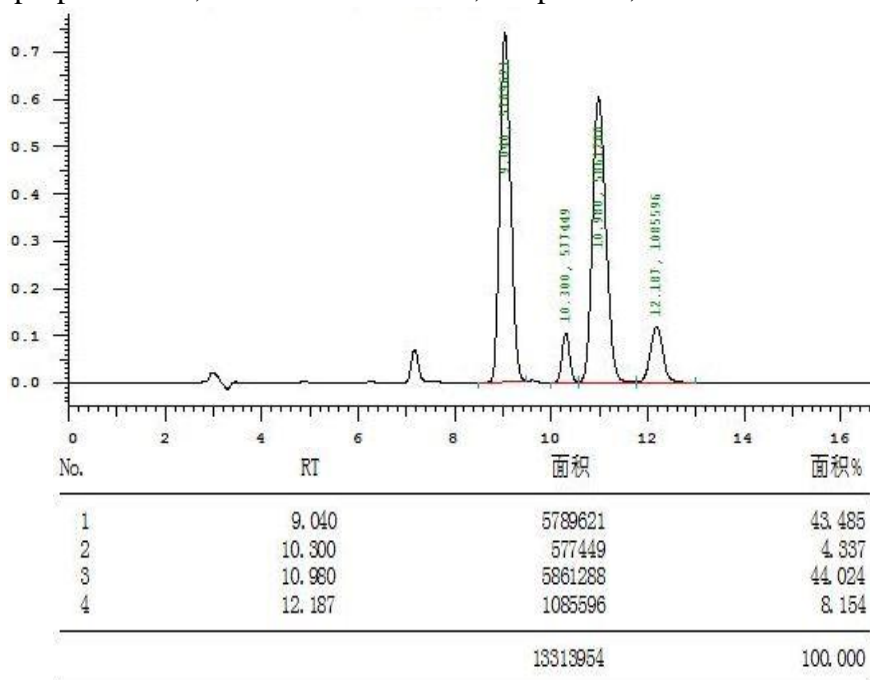
The ee determined by chiral HPLC; CHIRALPAK AD-H (4.6 mm ϕ \times 250 mmL); hexane/2-propanol 95/5; flow rate 1.0 ml/min; temp 25 $^{\circ}$ C; detection UV 245 nm.



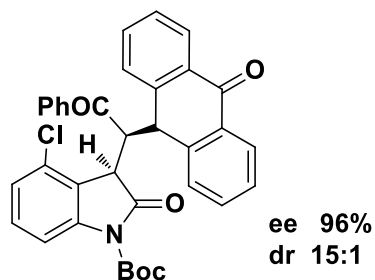
(*R*)-tert-butyl 4-chloro-3-((*S*)-2-methoxy-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)ethyl)-2-oxindoline-1-carboxylate (**(3*R*,4*S*)-3c**)



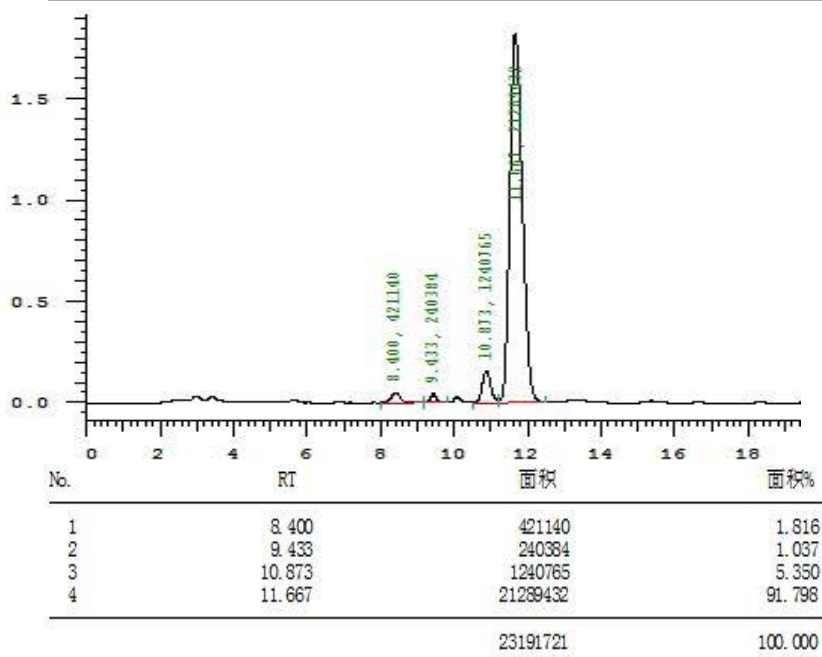
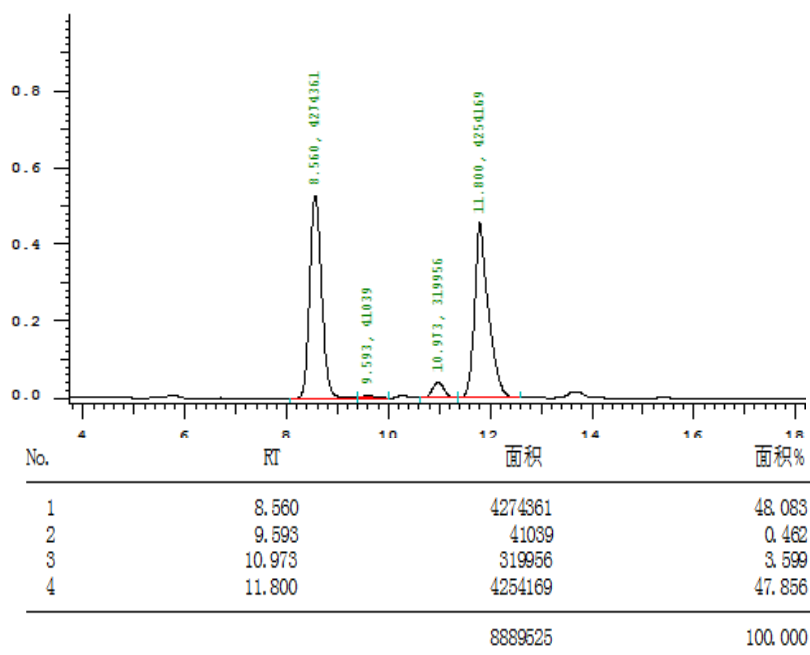
The ee determined by chiral HPLC; CHIRALPAK AD-H (4.6 mm ϕ ×250 mmL); hexane/2-propanol 95/5; flow rate 1.0 ml/min; temp 25 °C; detection UV 241 nm.



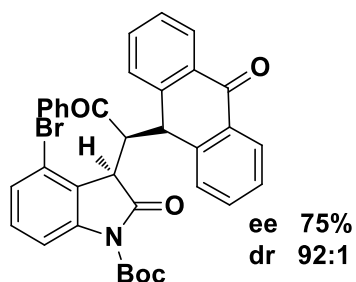
(*R*)-tert-butyl 4-chloro-2-oxo-3-((*S*)-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)-2-phenylethyl)indoline-1-carboxylate ((*3R,4S*)-**3d**)



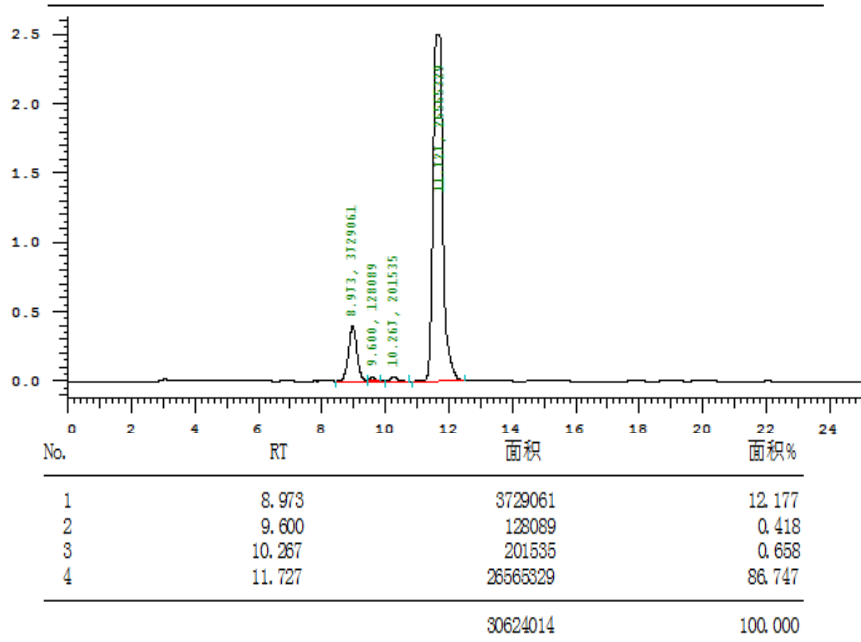
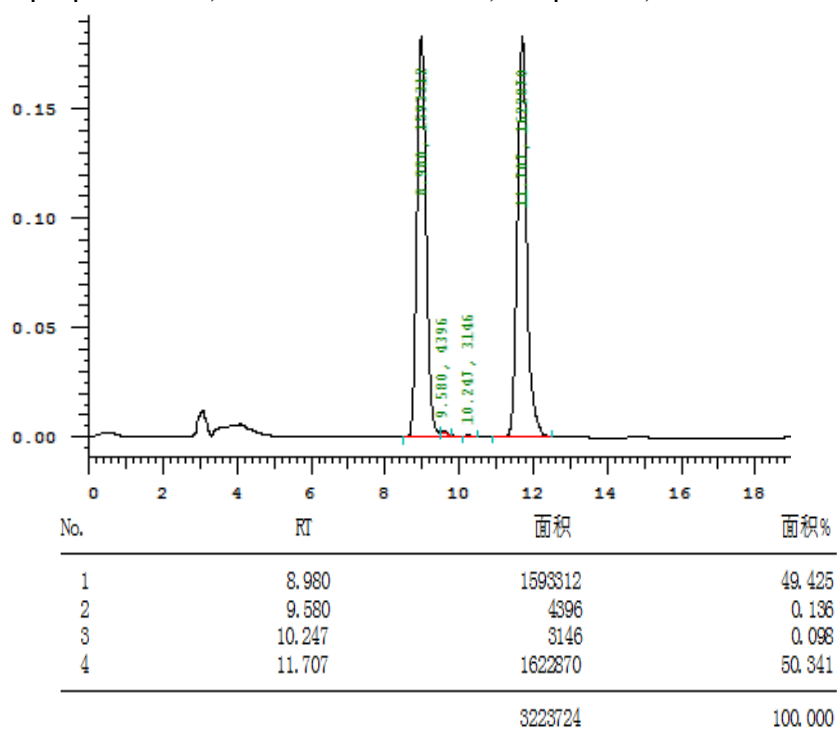
The ee determined by chiral HPLC; CHIRALPAK AD-H (4.6 mm ϕ \times 250 mmL); hexane/2-propanol 95/5; flow rate 1.0 ml/min; temp 25 $^{\circ}$ C; detection UV 224 nm.



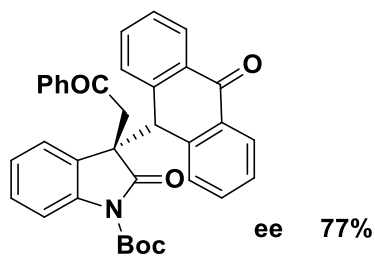
(*R*)-tert-butyl 4-bromo-2-oxo-3-((*S*)-2-oxo-1-(10-oxo-9,10-dihydroanthracen-9-yl)-2-phenylethyl)indoline-1-carboxylate ((*3R,4S*)-**3e**)



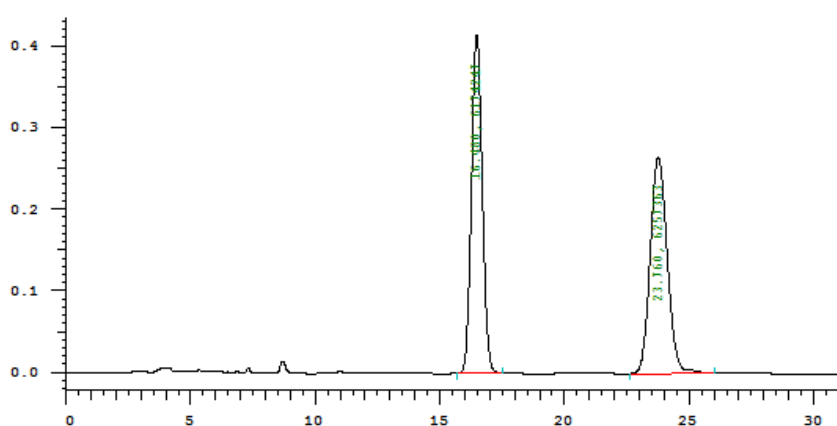
The ee determined by chiral HPLC; CHIRALPAK AD-H (4.6 mm ϕ \times 250 mmL); hexane/2-propanol 95/5; flow rate 1.0 ml/min; temp 25 $^{\circ}$ C; detection UV 260 nm.



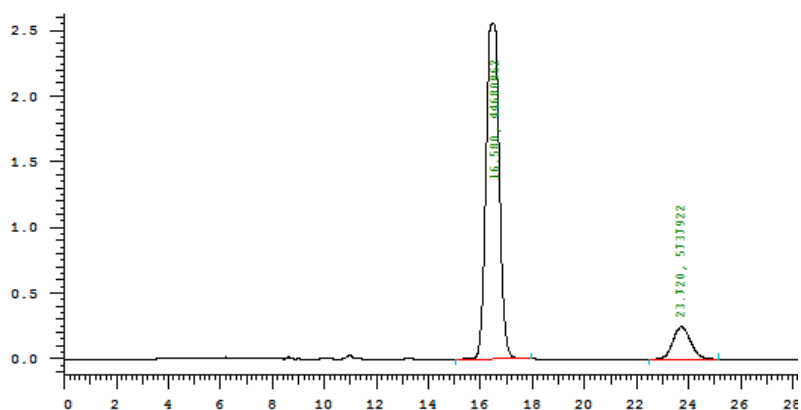
(*S*)-tert-butyl 2-oxo-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate ((*S*)-**4f**)



The ee determined by chiral HPLC; CHIRALPAK AD-H (4.6 mm ϕ ×250 mmL); hexane/2-propanol 76/24; flow rate 0.8 ml/min; temp 25 °C; detection UV 260 nm.

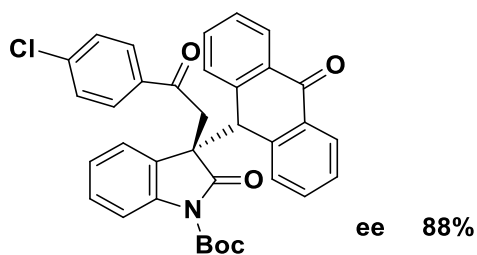


No.	RT	面积	面积%
1	16.480	6174247	49.666
2	23.760	6257363	50.334
		12431610	100.000

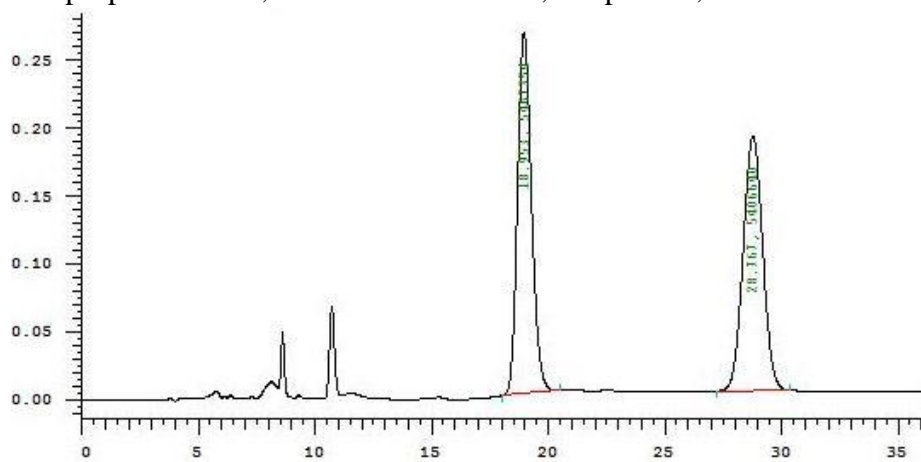


No.	RT	面积	面积%
1	16.580	44680862	88.619
2	23.720	5737922	11.381
		50418784	100.000

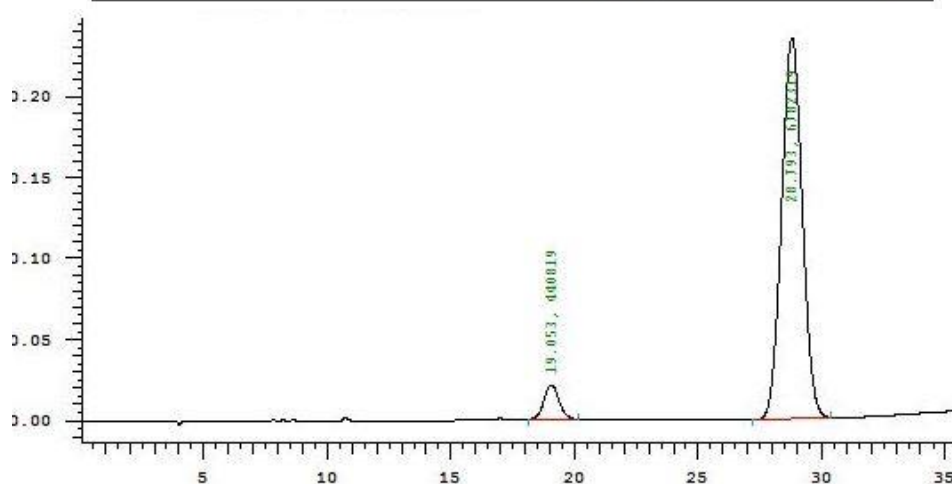
(*S*)-tert-butyl 3-(2-(4-chlorophenyl)-2-oxoethyl)-2-oxo-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate ((*S*)-**4g**)



The ee determined by chiral HPLC; CHIRALPAK AD-H (4.6 mm ϕ \times 250 mmL); hexane/2-propanol 76/24; flow rate 0.8 ml/min; temp 25 $^{\circ}$ C; detection UV 260 nm.

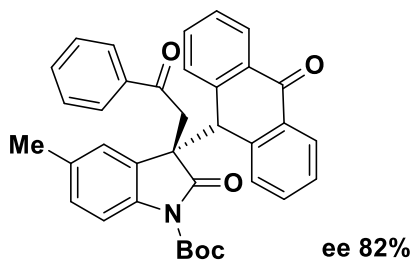


No.	RT	面积	面积%
1	18.953	5467354	50.279
2	28.767	5406640	49.721
		10873994	100.000

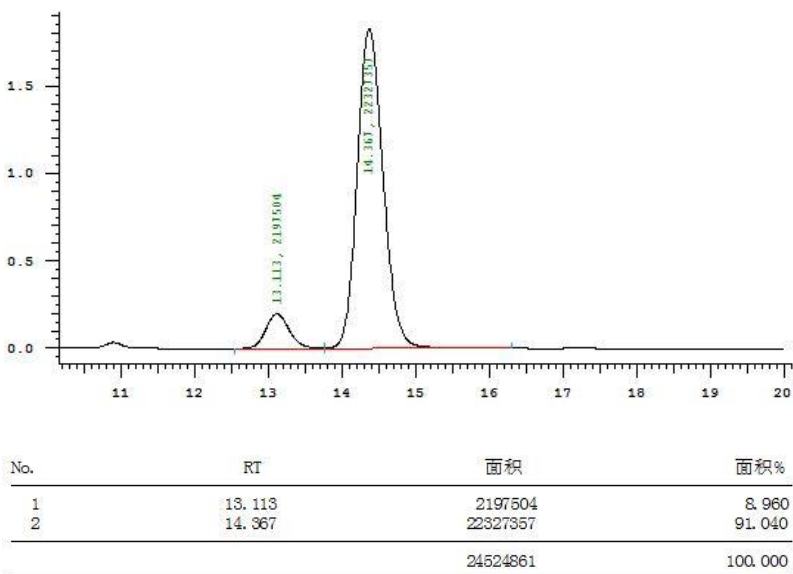
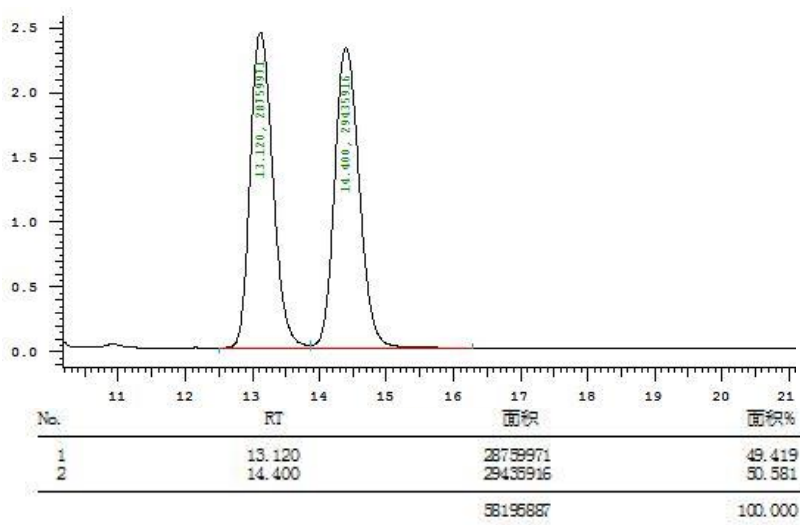


No.	RT	面积	面积%
1	19.053	440819	6.103
2	28.793	6782319	93.897
		7223138	100.000

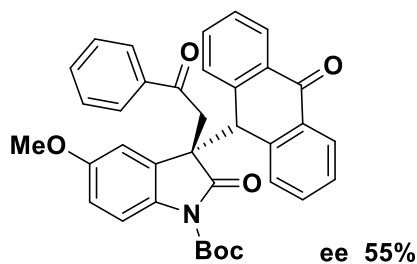
tert-butyl (S)-5-methyl-2-oxo-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate ((S)-4h)



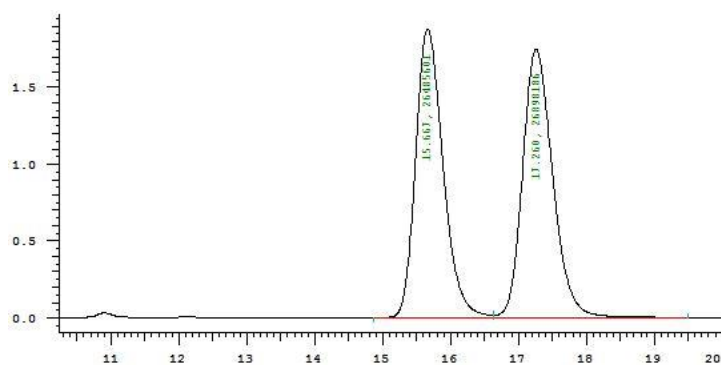
The ee determined by chiral HPLC; CHIRALPAK IA (4.6 mm ϕ ×250 mmL); hexane/2-propanol 76/24; flow rate 0.8 ml/min; temp 25 °C; detection UV 210 nm.



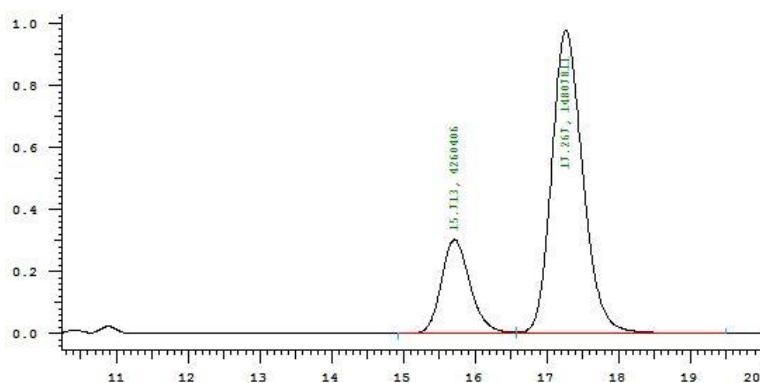
tert-butyl (S)-5-methoxy-2-oxo-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate ((S)-4i)



The ee determined by chiral HPLC; CHIRALPAK IA (4.6 mm ϕ ×250 mmL); hexane/2-propanol 76/24; flow rate 0.8 ml/min; temp 25 °C; detection UV 210 nm.

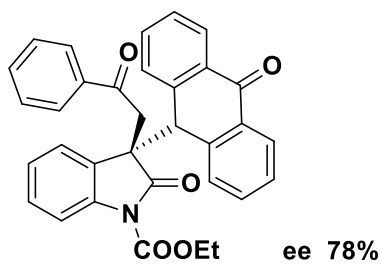


No.	RT	面积	面积%
1	15.667	26485601	49.614
2	17.260	26898186	50.386
			100.000

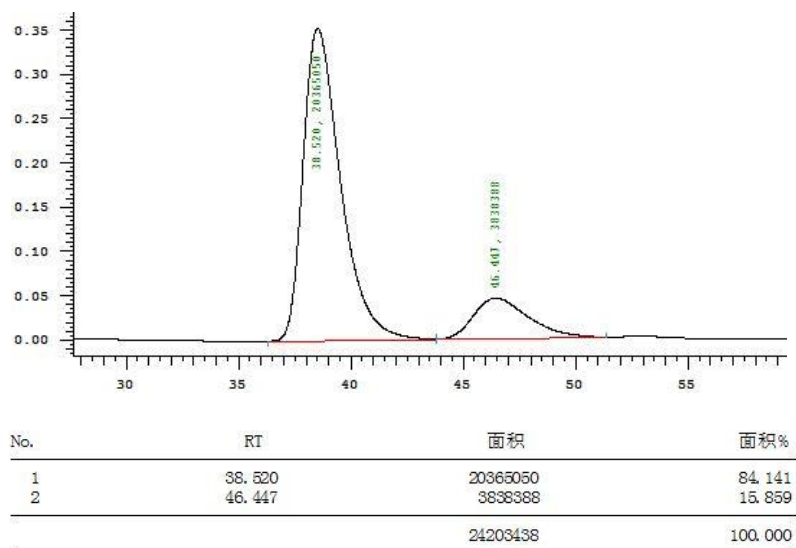
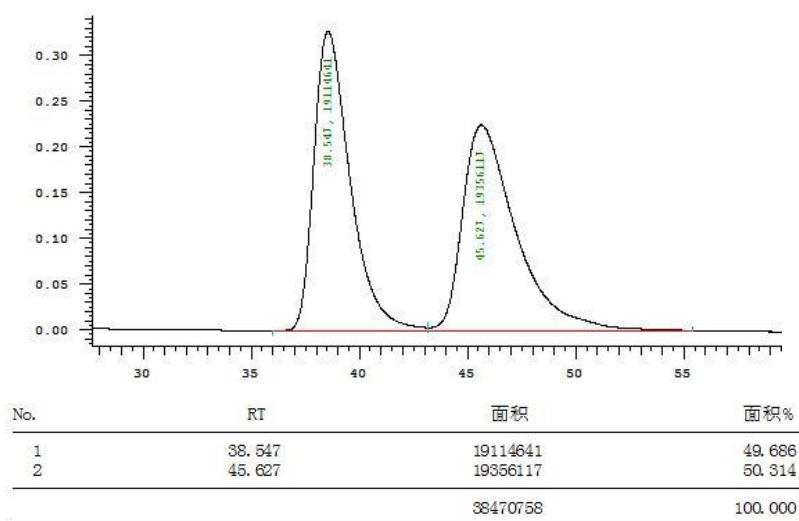


No.	RT	面积	面积%
1	15.713	4260406	22.343
2	17.267	14807811	77.657
			100.000

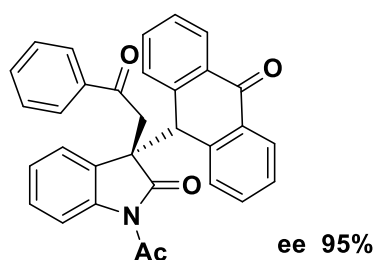
ethyl (S)-2-oxo-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indoline-1-carboxylate ((S)-4j)



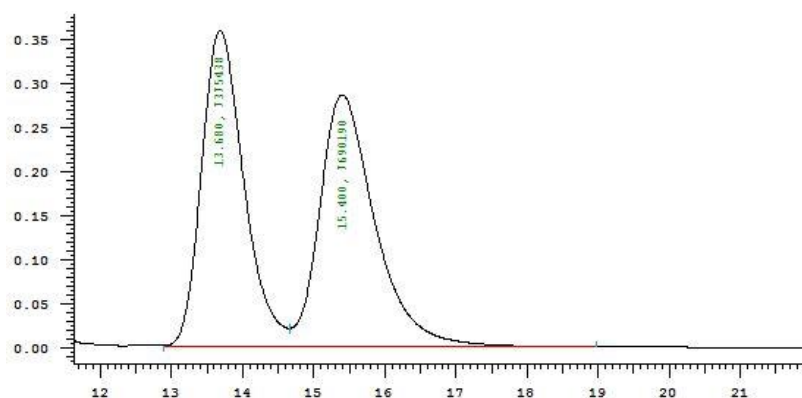
The ee determined by chiral HPLC; CHIRALPAK IC (4.6 mm ϕ ×250 mmL); hexane/2-propanol 70/30; flow rate 0.8 ml/min; temp 25 °C; detection UV 210 nm.



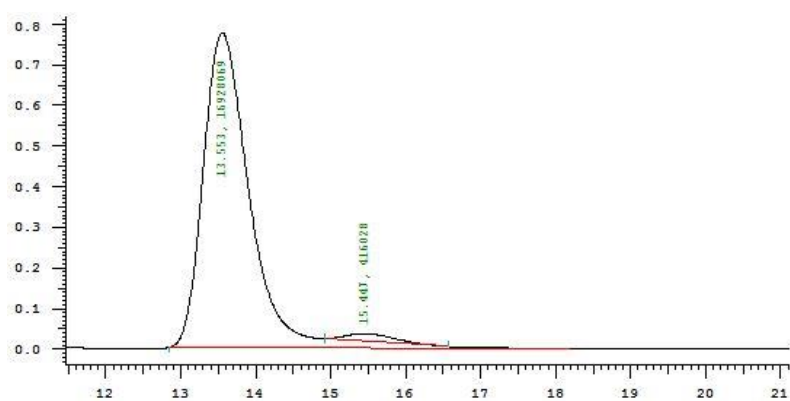
(S)-1-acetyl-3-(2-oxo-2-phenylethyl)-3-(10-oxo-9,10-dihydroanthracen-9-yl)indolin-2-one
((S)-4k)



The ee determined by chiral HPLC; CHIRALPAK OD-H (4.6 mm ϕ \times 250 mmL); hexane/2-propanol 76/24; flow rate 0.8 ml/min; temp 25 $^{\circ}$ C; detection UV 206 nm.

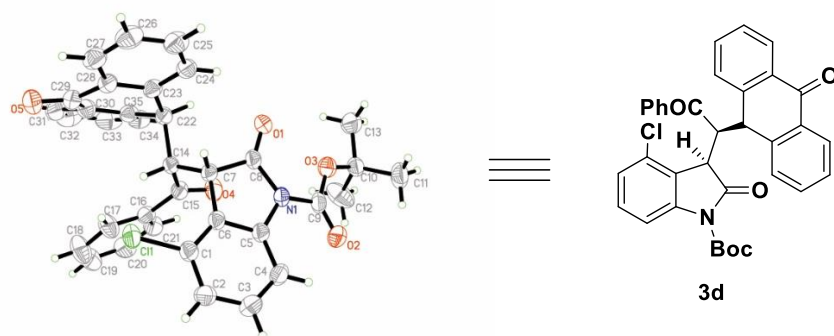


No.	RT	面积	面积%
1	13.680	7375438	48.955
2	15.400	7690190	51.045
		15065628	100.000



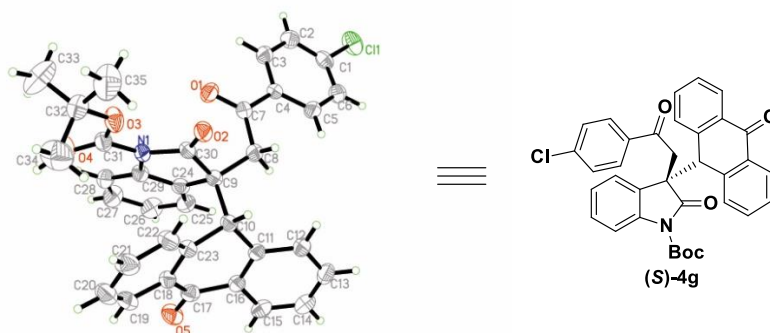
No.	RT	面积	面积%
1	13.553	16928069	97.601
2	15.447	416028	2.399
		17344097	100.000

6. X-Ray Crystal Structures for 3d and 4g



(Displacement ellipsoids are drawn at the 50% probability level)

CCDC number	1432612
Identification code	3d
Empirical formula	C ₃₅ H ₂₈ ClNO ₅
Formula weight	578.03
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Crystal description	Block
Crystal colour	Colorless
Space group	P 21/c
Unit cell dimensions	a = 15.0110(17) Å α = 90.00 ° b = 9.7516(8) Å β = 120.444(8) ° c = 23.371(3) Å γ = 90.00 °
Volume	2949.4(6) Å ³
Z	4
Density (calculated)	1.302 Mg/m ³
Absorption coefficient	1.505 mm ⁻¹
F(000)	1208
Crystal size	0.11 x 0.12 x 0.12 mm ³
Theta range for data collection	3.42 to 67.24 °
Index ranges	-14 ≤ h ≤ 17, -10 ≤ k ≤ 11, -27 ≤ l ≤ 27
Reflections collected	17500
Independent reflections	5291 [R(int) = 0.0803]
Data / restraints / parameters	5291 / 0 / 383
Goodness-of-fit on F ²	1.152
Final R indices [I > 2σ(I)]	R1 = 0.0788, wR2 = 0.2118
R indices (all data)	R1 = 0.1144, wR2 = 0.2821
Largest diff. peak and hole	0.348 and -0.483 e.Å ⁻³



(Displacement ellipsoids are drawn at the 50% probability level)

CCDC number	1432547
Identification code	(S)-4g
Empirical formula	C ₃₅ H ₂₈ ClNO ₅
Formula weight	578.03
Temperature	293(2) K
Wavelength	1.54184
Crystal system	Monoclinic
Crystal description	Block
Crystal colour	Colorless
Space group	P 21
Unit cell dimensions	a = 9.6470(9) Å α = 90.00 ° b = 15.6825(15) Å β = 100.860(10) ° c = 9.8683(11) Å γ = 90.00 °
Volume	1466.2(3) Å ³
Z	2
Density (calculated)	1.309 Mg/m ³
Absorption coefficient	1.514
F(000)	604
Crystal size	0.11 x 0.12 x 0.11 mm ³
Theta range for data collection	5.8740 to 54.6660 °
Index ranges	-11 ≤ h ≤ 7, -18 ≤ k ≤ 18, -11 ≤ l ≤ 11
Reflections collected	9196
Independent reflections	5094 [R(int) = 0.0598]
Data / restraints / parameters	5094 / 1363 / 383
Goodness-of-fit on F ²	1.055
Final R indices [I > 2σ(I)]	R1 = 0.0596, wR2 = 0.1063
R indices (all data)	R1 = 0.1032, wR2 = 0.1362
Largest diff. peak and hole	0.919 and -0.412 e.Å ⁻³