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Chiral Phosphoric Acid-Catalyzed Chemo and Enantioselective 1,2-Addition of Isatin-Derived β,γ-Unsaturated α-Ketoesters with 4-Aminoindoles At the C7 Position

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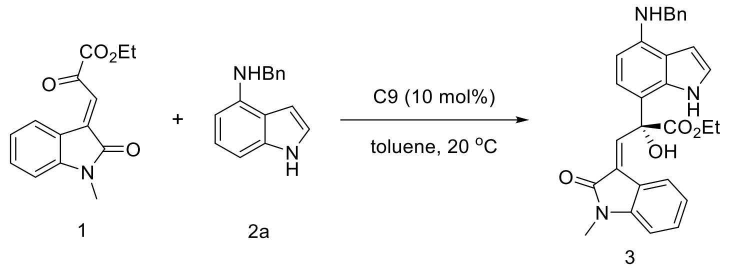
General Remarks

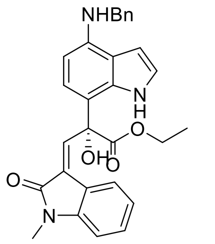
All reactions were carried out in the dried glassware with magnetic stirring. Reagents were obtained from commercial supplier (**http://tansoole.com/ Taitan, china**) and used without further purification, unless otherwise noted. NMR spectra were recorded on Bruker Avance 400 MHz or 500MHz (^{1}H NMR) and 101 MHz or 125 MHz spectrometer (^{13}C NMR). $CDCl_3$ was used as solvent. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (d 7.26 ppm). Chemical shifts (d) reported as part per million (ppm). ^{13}C NMR spectra were referenced to $CDCl_3$ (d 77.16 ppm, the middle peak). High performance liquid chromatography was performed on Shimadzu LC-20AT Series HPLC using Daicel AD-H, OD-H, IC or IG chiral column eluted with a mixture of hexane and isopropyl alcohol. Optical rotations were measured on an Anton Paar MCP200. High resolution mass spectra were performed on a Shimadzu LCMS-IT-TOF mass spectrometer (LCMS-2020). X-ray structure analysis was carried out at an Bruker smart Apex 2， Bruker D8 Venture. Chiral phosphoric acid was obtained from commercial supplier and used without further purification unless otherwise noted. Column chromatography was performed with silica gel (200-300 mesh).

General procedure for the synthesis of products 3



Ethyl (*E*)-3-(1-methyl-2-oxoindolin-3-ylidene)-2-oxopropanoate **1** (0.12 mmol, 1.2 equiv) was added to a mixture solution of catalyst **C9** (0.010 mmol) and N-benzyl-1H-indol-4-amine **2** (0.1 mmol) in toluene (2 mL) at 20 ºC (24–144 h). After completion (monitored by TLC), the mixture was directly purified by silica gel column chromatography (PE : EA = 1 : 1 (v/v)) to afford the title compounds **3**.

ethyl (*R*,*E*)-2-(4-(benzylamino)-1H-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3aa)

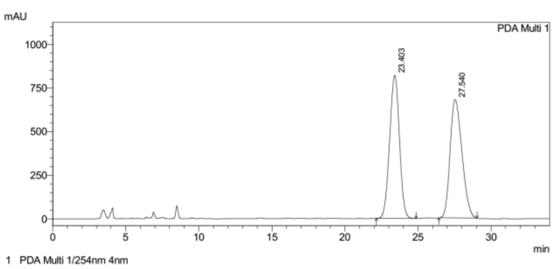


3aa 84% yield, 96% ee

3aa was obtained as a yellow solid in 84% yield (24 h) and 96% ee.

The enantiomeric ex cess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 23.84 min, t_{minor} = 28.58 min; $[\alpha]_D^{20}$ = + 1.7 (*c* 0.17, MeOH);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.61 (s, 1H), 7.42 – 7.39 (m, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.30 – 7.28 (m, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 2.9 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 6.44 – 6.43 (m, 1H), 6.17 (d, *J* = 8.1 Hz, 1H), 4.43 (s, 2H), 4.40 (s, 1H), 4.30 – 4.21 (m, 2H), 3.09 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.82, 168.37, 144.62, 141.96, 139.49, 138.64, 133.86, 131.18, 130.00, 128.74, 128.50, 127.84, 127.40, 122.53, 122.48, 122.22, 120.18, 117.64, 112.42, 107.83, 99.22, 98.24, 78.94, 63.37, 48.37, 26.18, 14.12. ESI-HRMS m/z: 482.2074. [M + H]$^+$, calcd for $C_{29}H_{27}N_3O_4$+H^+, 482.2074.



PeakTable

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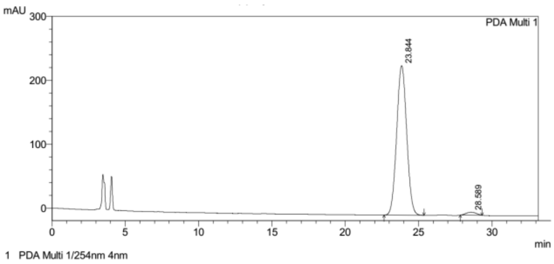

PeakTable

PDA Ch1 254nm 4nm

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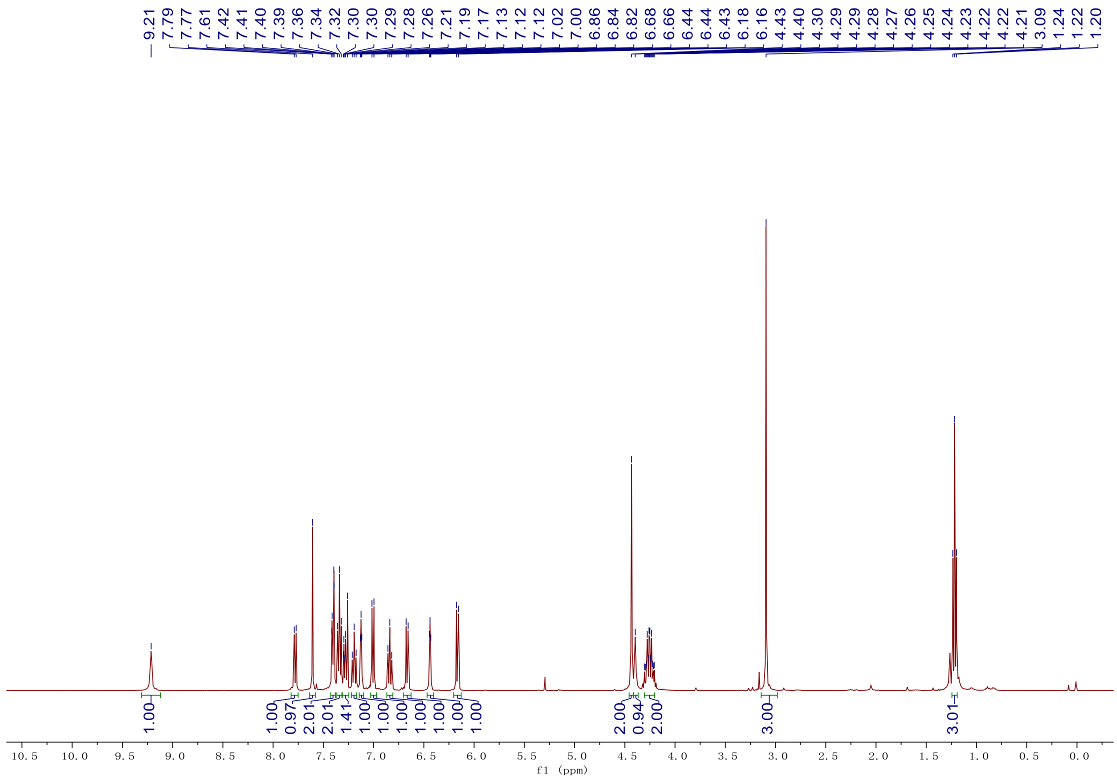
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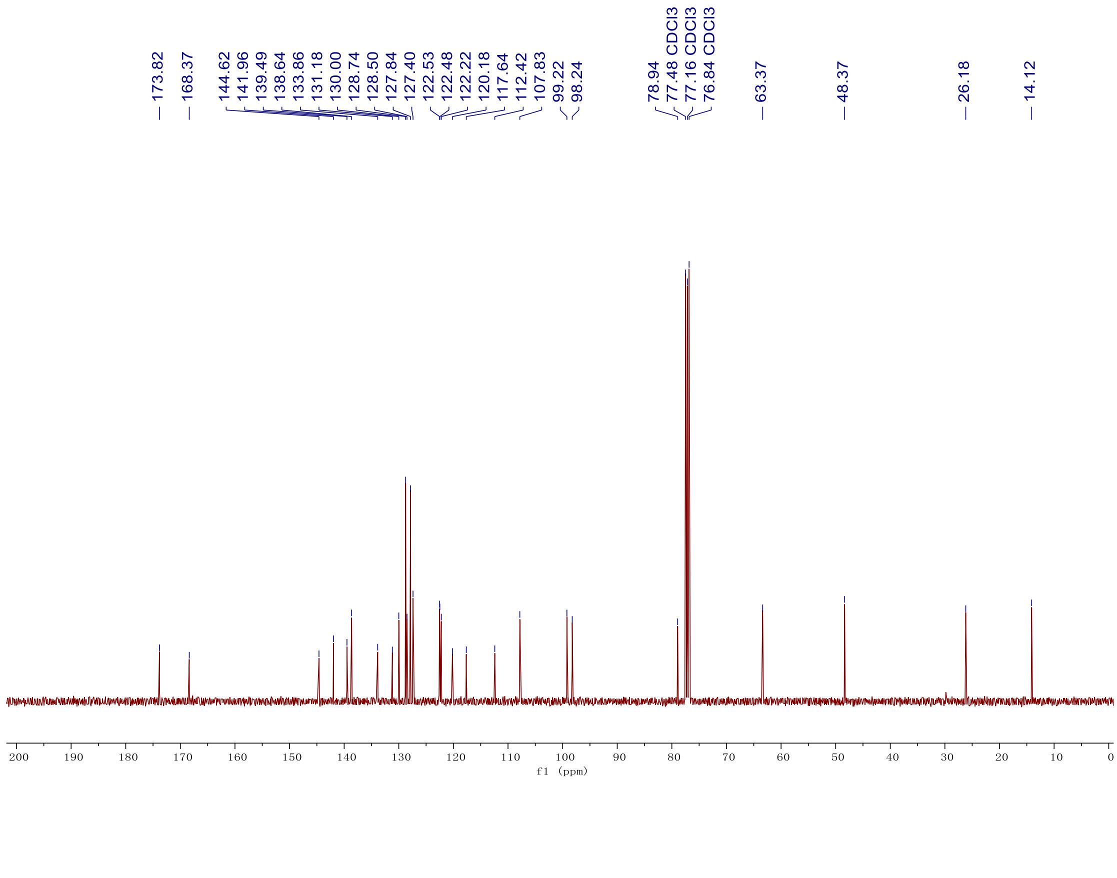
f1 (ppm)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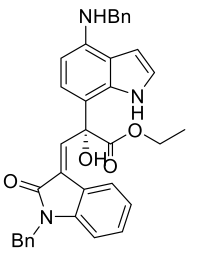
107.83
99.22
98.24
78.94
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.37
48.37
26.18
14.12
f1 (ppm)

ethyl (*R*, *E*)-3-(1-benzyl-2-oxoindolin-3-ylidene)-2-(4-(benzylamino)-1*H*-indol-7-yl)-2-hydroxypropanoate (3ba)

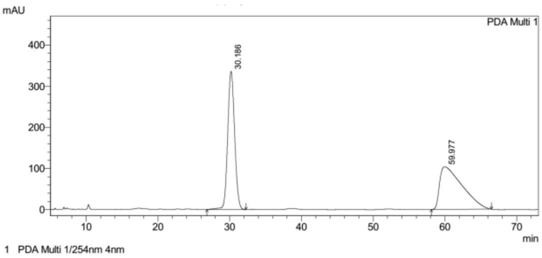


3ba 78% yield, 94% ee

3ba was obtained as a yellow solid in 78% yield (24 h) and 94% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70:30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 30.02 min, t_{minor} = 63.17 min; $[\alpha]_D^{20}$ + 10.2 (*c* 0.39, MeOH);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 7.85 (d, *J* = 7.1 Hz, 1H), 7.68 (s, 1H), 7.44 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.28 (m, 8H), 7.15 – 7.09 (m, 3H), 6.85 (td, *J* = 7.7, 1.0 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.47 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.23 (d, *J* = 8.1 Hz, 1H), 4.99 – 4.89 (m, 2H), 4.48 (s, 2H), 4.33 – 4.24 (m, 2H), 4.14 (s, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.94, 168.41, 143.97, 142.07, 139.50, 138.38, 135.97, 133.82, 131.10, 130.07, 128.88, 128.77, 128.56, 127.84, 127.72, 127.45, 127.42, 122.56, 122.52, 122.33, 120.35, 117.69, 112.25, 108.89, 99.26, 98.36, 79.04, 63.59, 48.37, 43.94, 14.12. ESI-HRMS m/z: 558.2386. $[M + H]^+$, calcd for $C_{35}H_{31}N_3O_4+H^+$, 558.2387.



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

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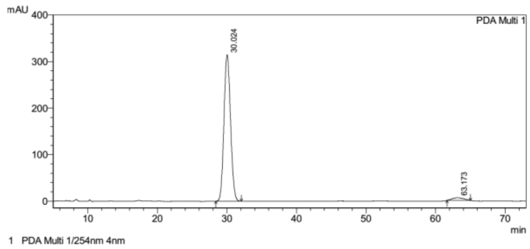

1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

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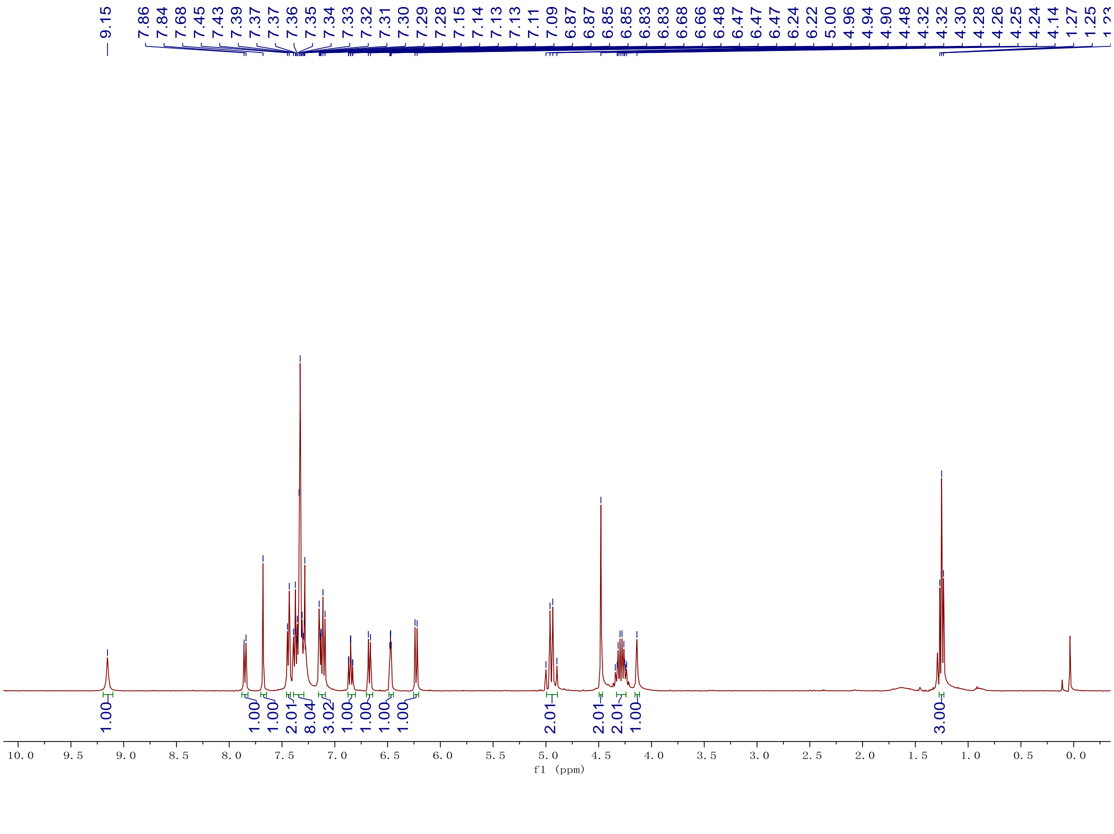
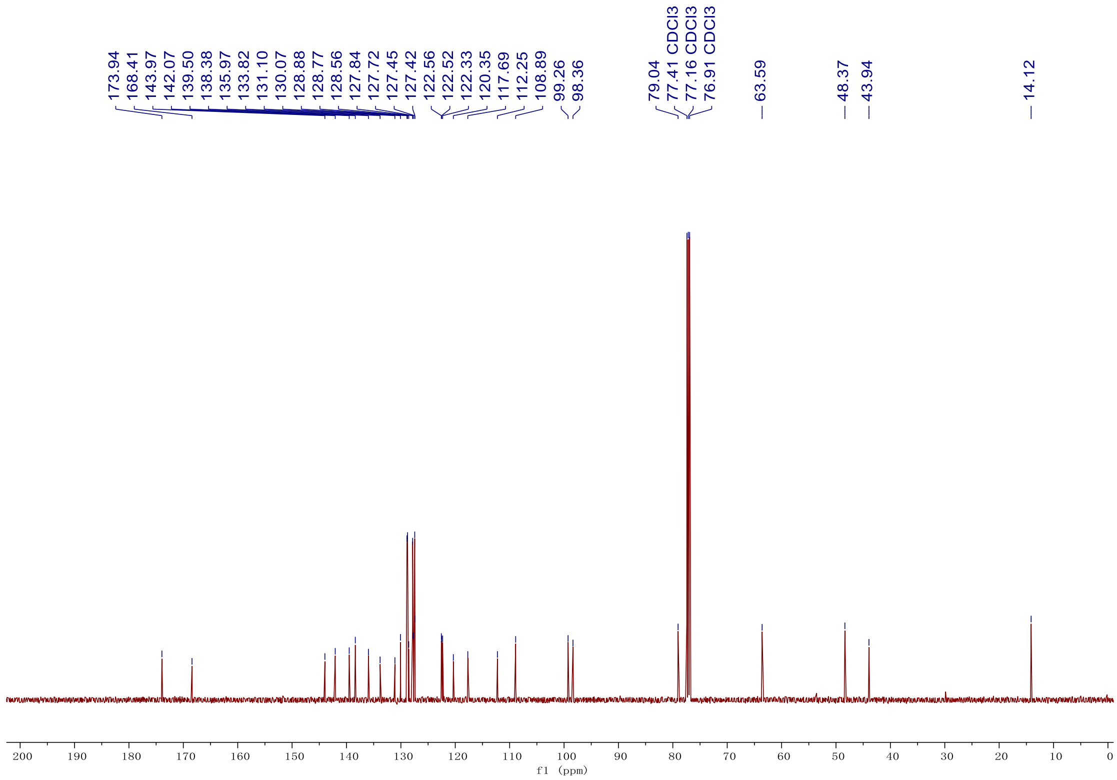
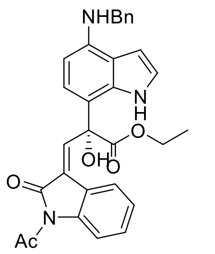
Total		21288196	320540	100.000	100.000



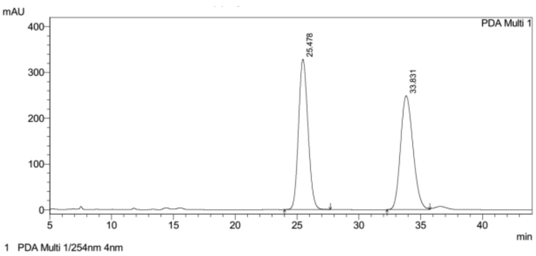


ethyl (*R*, *E*)-3-(1-acetyl-2-oxoindolin-3-ylidene)-2-(4-(benzylamino)-1*H*-indol-7-yl)-2-hydroxypropanoate (3ca)



3ca 76% yield, 95% ee

3ca was obtained as a yellow solid in 76% yield (24 h) and 95% ee. The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 25.43 min, t_{minor} = 34.01 min; $[\alpha]_D^{20}$ = + 5.0 (*c* 0.20, MeOH); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.11 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.92 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.61 (s, 1H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (dd, *J* = 13.0, 5.6 Hz, 2H), 7.12 (t, *J* = 2.9 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.45 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.18 (d, *J* = 8.1 Hz, 1H), 4.45 (s, 2H), 4.34 – 4.20 (m, 2H), 4.13 (s, 1H), 2.72 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.64, 170.87, 168.62, 142.20, 140.97, 139.39, 133.73, 130.60, 130.18, 128.77, 128.06, 127.80, 127.44, 125.06, 122.65, 122.07, 120.81, 117.77, 116.25, 111.75, 99.26, 98.48, 78.90, 63.70, 48.33, 27.08, 14.12. ESI-HRMS m/z: 510.2019. [M + H]$^+$, calcd for $C_{30}H_{27}N_3O_5+H^+$, 510.2023.



PeakTable

PDA Ch1 254nm 4nm

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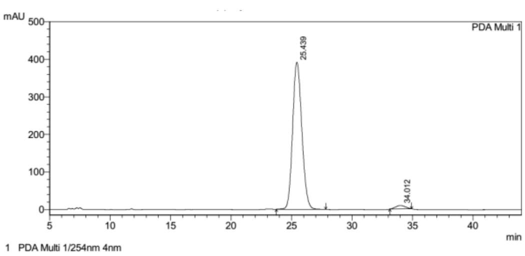

PeakTable

PDA Ch1 254nm 4nm

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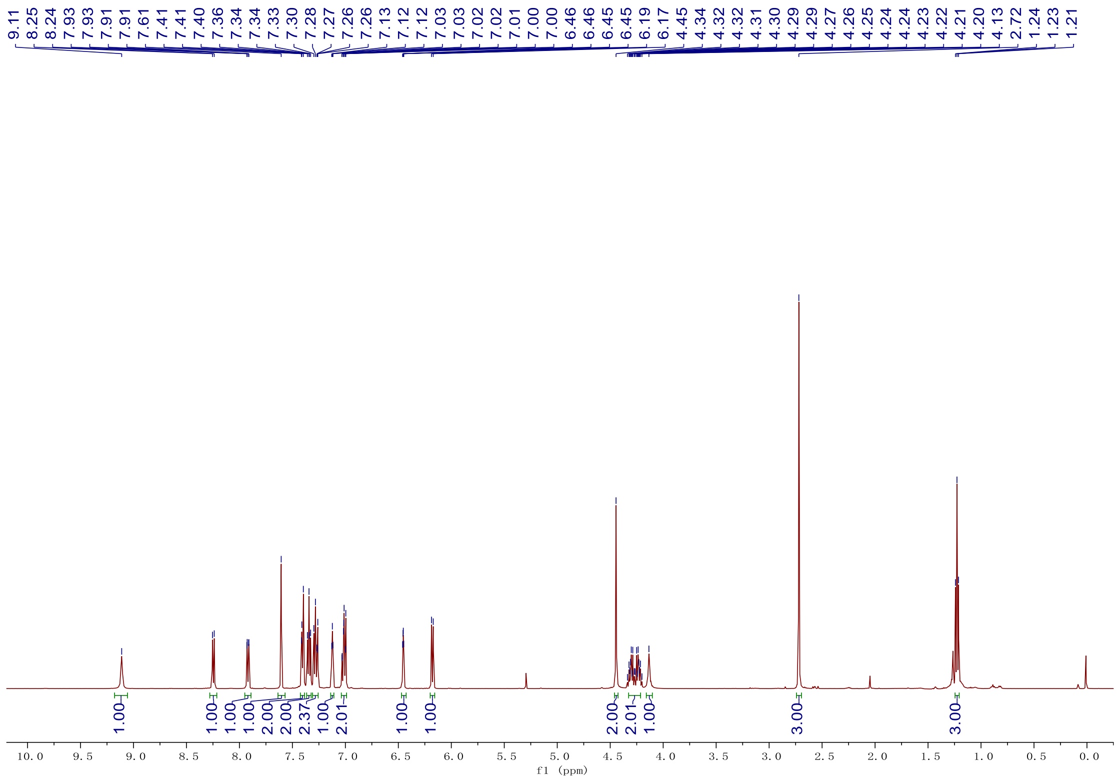
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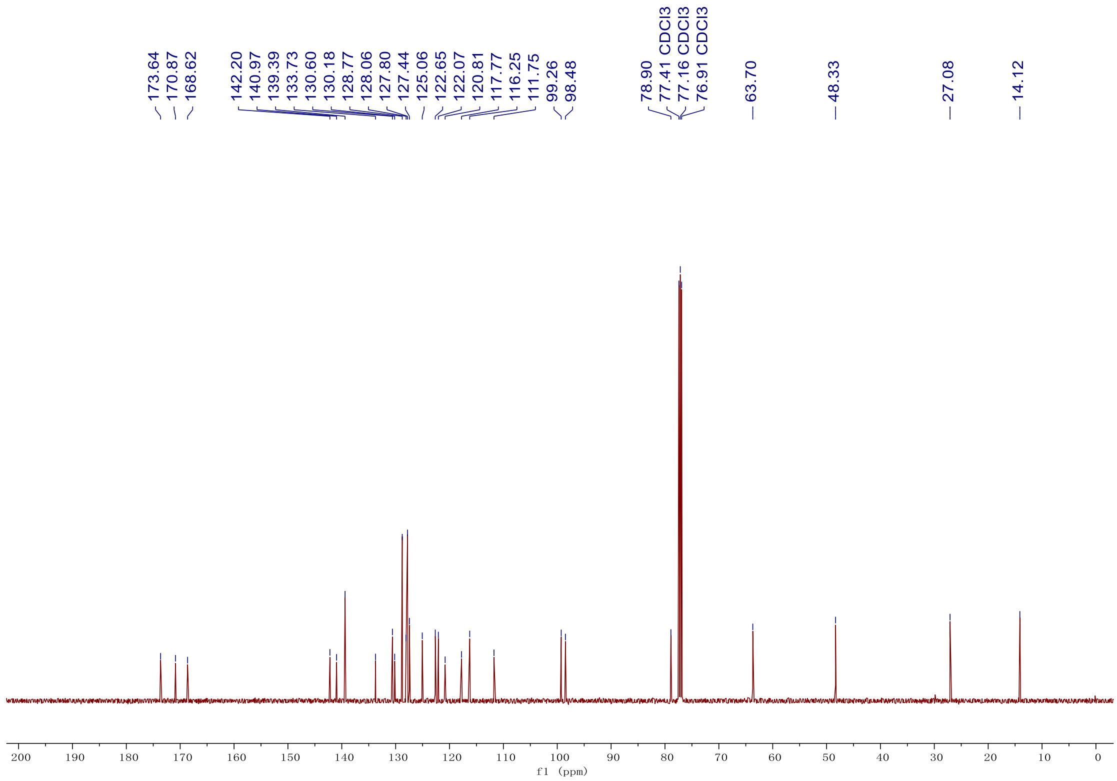
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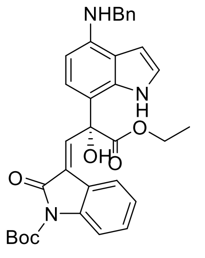
120.81
117.77
116.25
111.75
99.26
98.48
78.90
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
63.70
48.33
27.08
14.12
f1 (ppm)

tert-butyl (*R*, *E*)-3-(2-(4-(benzylamino)-1*H*-indol-7-yl)-3-ethoxy-2-hydroxy-3-oxopropylidene)-2-oxoindoline-1-carboxylate (3da)

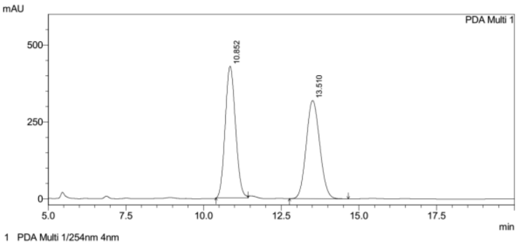


3da 75%yield, 94%ee

3da was obtained as a yellow solid in 75% yield (24 h) and 94% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 :3 0 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 10.87 min, t_{major} = 13.49 min; $[\alpha]_D^{20}$ = + 7.7 (*c* 0.35, MeOH);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.09 (s, 1H), 7.89 – 7.82 (m, 2H), 7.61 (s, 1H), 7.42 – 7.39 (m, 2H), 7.36 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.12 (dd, *J* = 3.3, 2.4 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.96 (td, *J* = 7.7, 1.1 Hz, 1H), 6.44 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.17 (d, *J* = 8.1 Hz, 1H), 4.44 (s, 2H), 4.32 – 4.16 (m, 2H), 4.11 (s, 1H), 1.65 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.78, 166.65, 149.28, 142.12, 140.67, 139.43, 139.04, 133.75, 130.39, 130.34, 128.77, 128.25, 127.84, 127.43, 124.30, 122.59, 122.19, 120.44, 117.70, 114.68, 111.85, 99.25, 98.40, 84.46, 78.79, 63.62, 48.35, 28.25, 14.10. ESI-HRMS m/z: 568.2444. $[M + H]^+$, calcd for $C_{33}H_{33}N_3O_6+H^+$, 568.2442.



PeakTable

PDA Ch1 254nm 4nm

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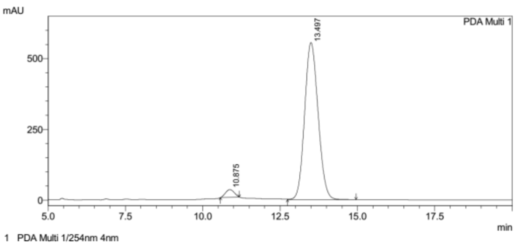
2	13.510	9662697	319479	49.367	42.738
Total		19573226	747526	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
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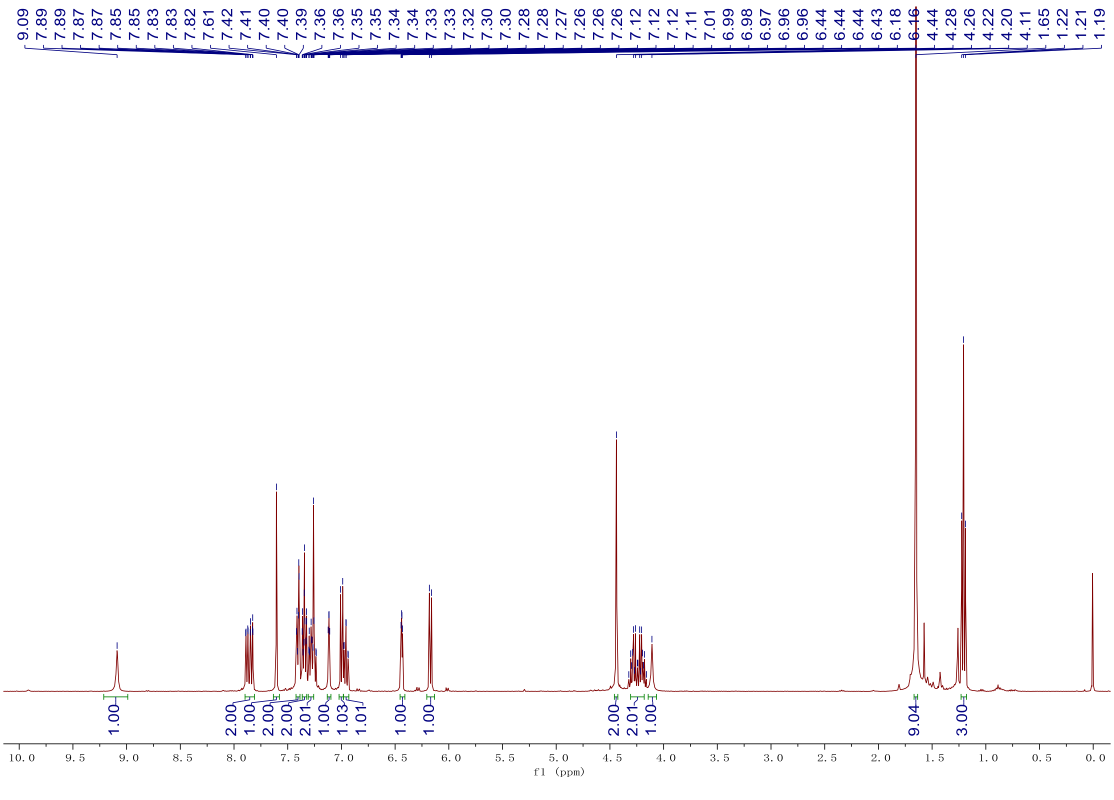
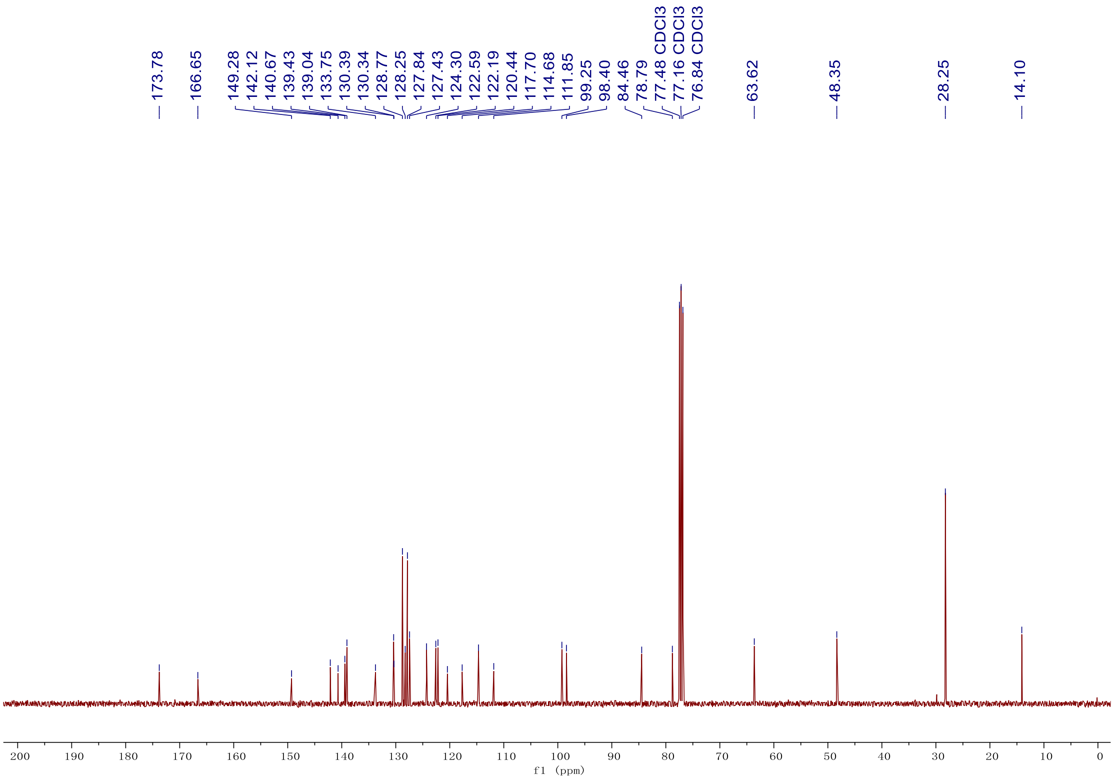
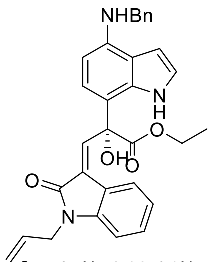




ethyl (*R*, *E*)-3-(1-allyl-2-oxoindolin-3-ylidene)-2-(4-(benzylamino)-1*H*-indol-7-yl)-2-hydroxypropanoate (3ea)

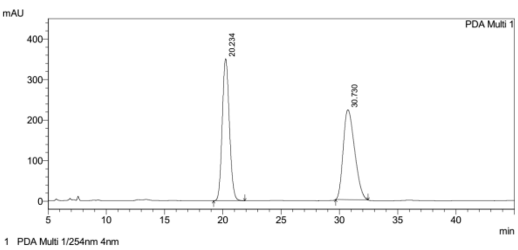


3ea 85% yield, 94% ee

3ea was obtained as a yellow solid in 85% yield (24 h) and 94% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 20.11 min, t_{minor} = 30.82 min; $[\alpha]_D^{20}$ = + 30.7 (*c* 0.43, MeOH);

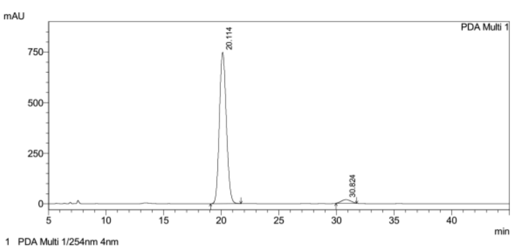
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.60 (s, 1H), 7.42 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.28 (s, 1H), 7.18 (td, *J* = 7.7, 1.2 Hz, 1H), 7.12 (t, *J* = 2.9 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.85 (td, *J* = 7.7, 1.0 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.44 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.87 – 5.78 (m, 1H), 5.25 – 5.19 (m, 2H), 4.45 (s, 2H), 4.34 (dd, *J* = 5.3, 1.7 Hz, 2H), 4.31 – 4.20 (m, 2H), 4.13 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.91, 167.99, 144.02, 142.04, 139.49, 138.22, 133.81, 131.59, 131.09, 130.04, 128.76, 128.52, 127.84, 127.41, 122.55, 122.44, 122.27, 120.28, 117.69, 117.67, 112.30, 108.76, 99.23, 98.34, 78.98, 63.55, 48.36, 42.51, 14.11. ESI-HRMS m/z: 508.2227. $[M + H]^+$, calcd for $C_{31}H_{29}N_3O_4+H^+$, 508.2231.



PeakTable

PDA Ch1 254nm 4nm

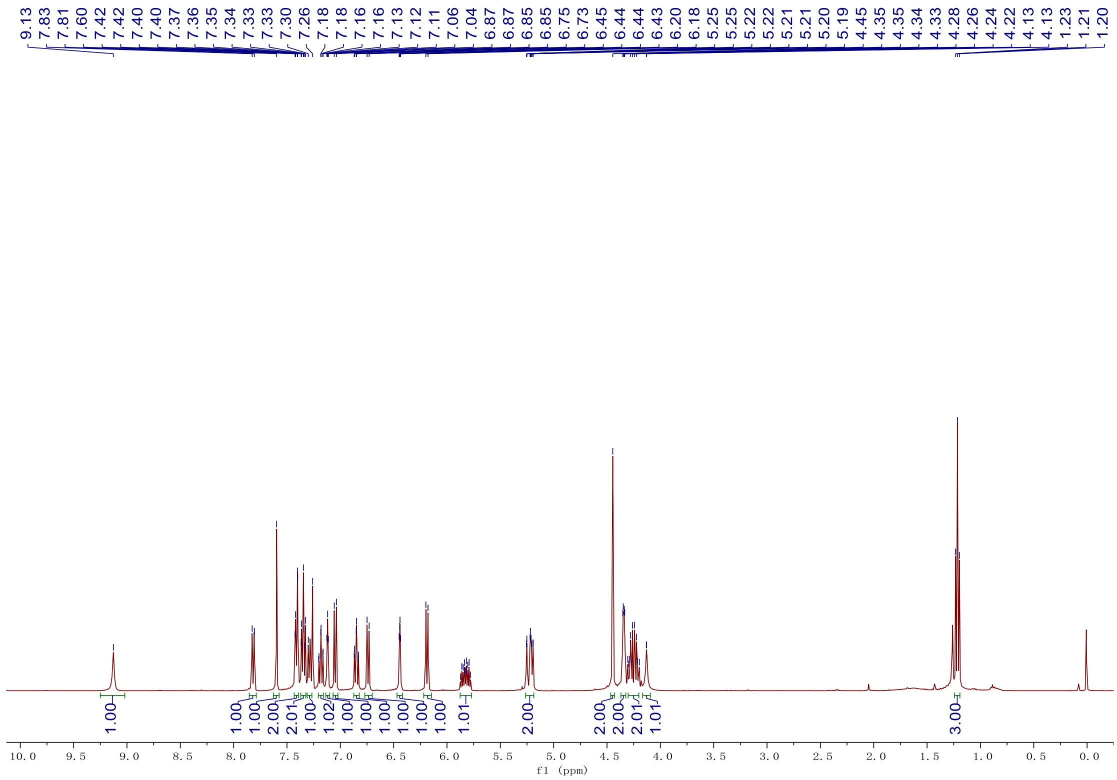
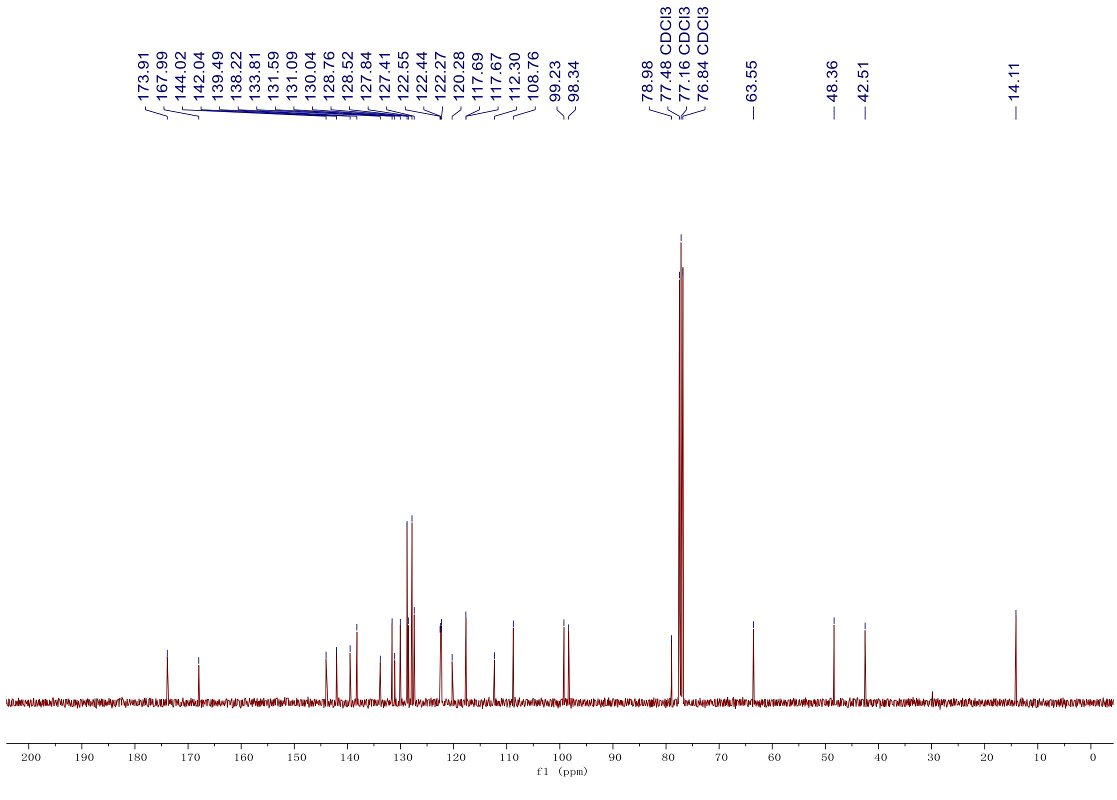
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.234	14893849	350312	49.627	61.244
2	30.730	15117726	221680	50.373	38.756
Total		30011576	571992	100.000	100.000



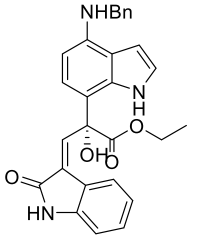
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.114	31371241	747654	96.889	97.692
2	30.824	1007320	17663	3.111	2.308
Total		32378560	765317	100.000	100.000


9.13 7.83 7.81 7.60 7.42 7.42 7.40 7.40 7.37 7.36 7.35 7.34 7.33 7.33 7.30 7.26 7.18 7.18 7.16 7.16 7.13 7.12 7.11 7.06 7.04 6.87 6.87 6.85 6.85 6.75 6.73 6.45 6.44 6.44 6.43 6.20 6.18 5.25 5.25 5.22 5.22 5.21 5.21 5.20 5.19 4.45 4.35 4.35 4.34 4.33 4.28 4.26 4.24 4.22 4.13 1.23 1.21 1.20
1.00 1.00 1.00 2.00 2.01 1.00 1.02 1.00 1.00 1.00 1.00 1.00 1.01 2.00 2.00 2.00 2.01 1.01 3.00
f1 (ppm)

173.91 167.99 144.02 142.04 139.49 138.22 133.81 131.59 131.09 130.04 128.76 128.52 127.84 127.41 122.55 122.44 122.27 120.28 117.69 117.67 112.30 108.76 99.23 98.34 78.98 77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 63.55 48.36 42.51 14.11
f1 (ppm)

ethyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-2-hydroxy-3-(2-oxoindolin-3-ylidene) propanoate (3fa)

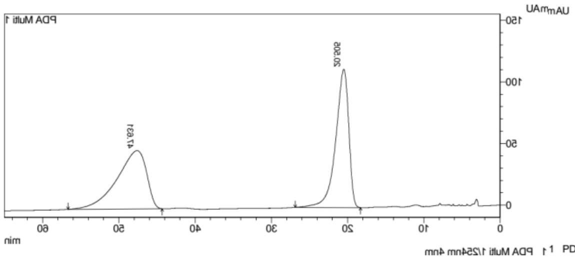


3fa 61% yield, 16% ee

3fa was obtained as a yellow solid in 61% yield (144 h) and 16% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak OD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 19.77 min, t_{minor} = 46.53 min; $[\alpha]_D^{20}$ = + 205.25 (*c* 0.10, MeOH);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (s, 1H), 8.09 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.42 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.83 (td, *J* = 7.7, 1.1 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.44 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.19 (d, *J* = 8.1 Hz, 1H), 4.45 (s, 2H), 4.30 – 4.19 (m, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.84, 169.71, 142.05, 142.00, 139.47, 138.34, 133.81, 131.36, 130.25, 128.78, 127.84, 127.43, 122.61, 122.53, 122.18, 120.79, 117.70, 112.32, 109.77, 99.25, 98.35, 79.02, 63.57, 48.36, 14.13. ESI-HRMS m/z: 468.1921. [M + H]$^+$, calcd for $C_{28}H_{25}N_3O_4$+H^+, 468.1918.

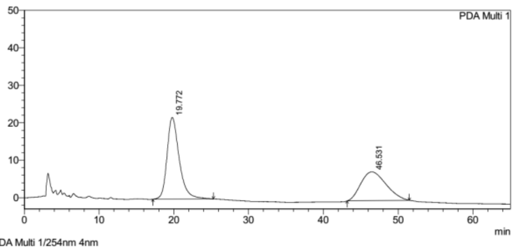


PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.505	13400394	112290	51.122	70.340
2	47.631	12812179	47349	48.878	29.660
Total		26212573	159639	100.000	100.000

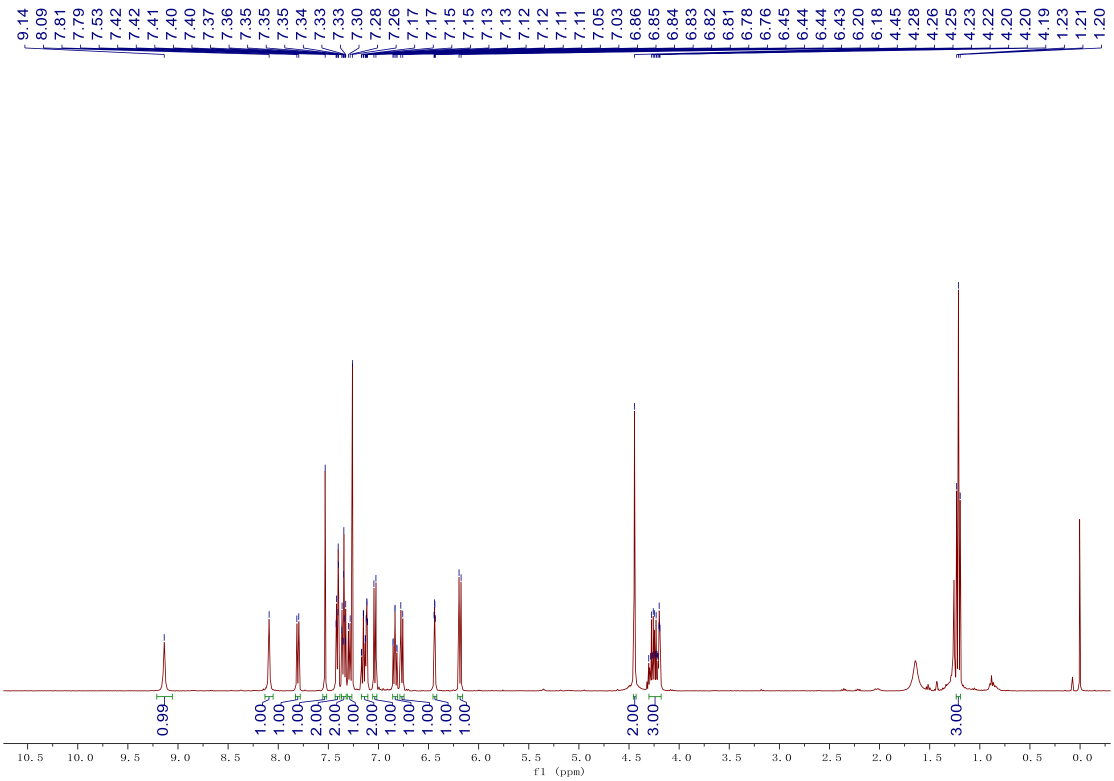


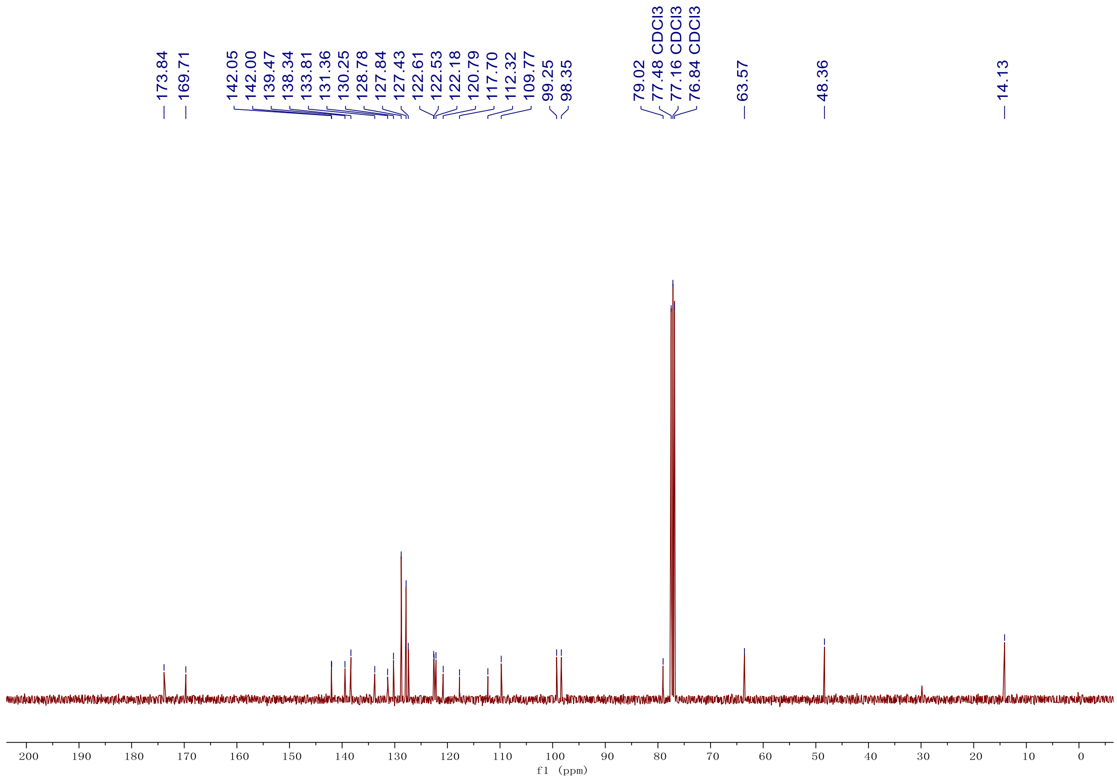
PDA Multi 1/254nm 4nm

PeakTable

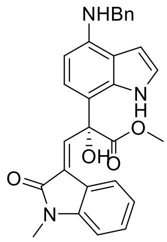
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.772	2469973	21793	57.755	73.925
2	46.531	1806653	7687	42.245	26.075
Total		4276626	29480	100.000	100.000





methyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3ga)

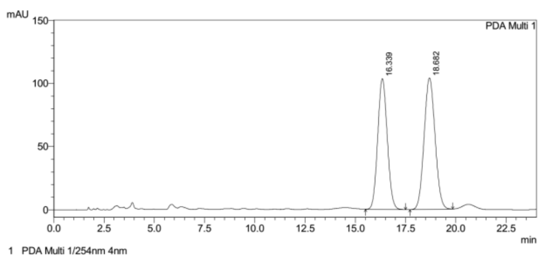


3ga 81% yield, 90% ee

3ga was obtained as a yellow solid in 81% yield (120 h) and 90% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 16.34 min, t_{minor} = 18.69 min; $[\alpha]_D^{20}$ = + 75.0 (*c* 0.39, MeOH);

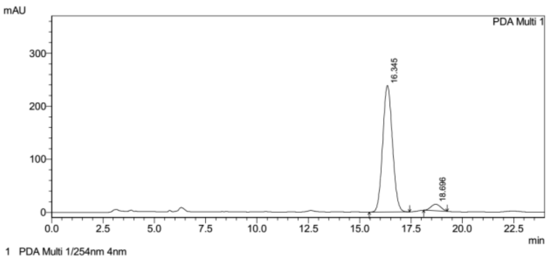
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 7.75 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.61 (s, 1H), 7.41 – 7.39 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.18 (td, *J* = 7.7, 1.3 Hz, 1H), 7.15 – 7.12 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.85 – 6.81 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.44 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.15 (d, *J* = 8.1 Hz, 1H), 4.46 (s, 1H), 4.43 (s, 2H), 3.80 (s, 3H), 3.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.37, 168.36, 144.57, 142.05, 139.47, 138.65, 133.90, 131.37, 130.02, 128.76, 128.57, 127.84, 127.41, 122.62, 122.54, 122.31, 120.11, 117.62, 112.12, 107.84, 99.16, 98.27, 79.04, 54.01, 48.36, 26.14. ESI-HRMS m/z: 468.1917. $[M + H]^+$, calcd for $C_{28}H_{25}N_3O_4+H^+$, 468.1918.



PeakTable

PDA Ch1 254nm 4nm

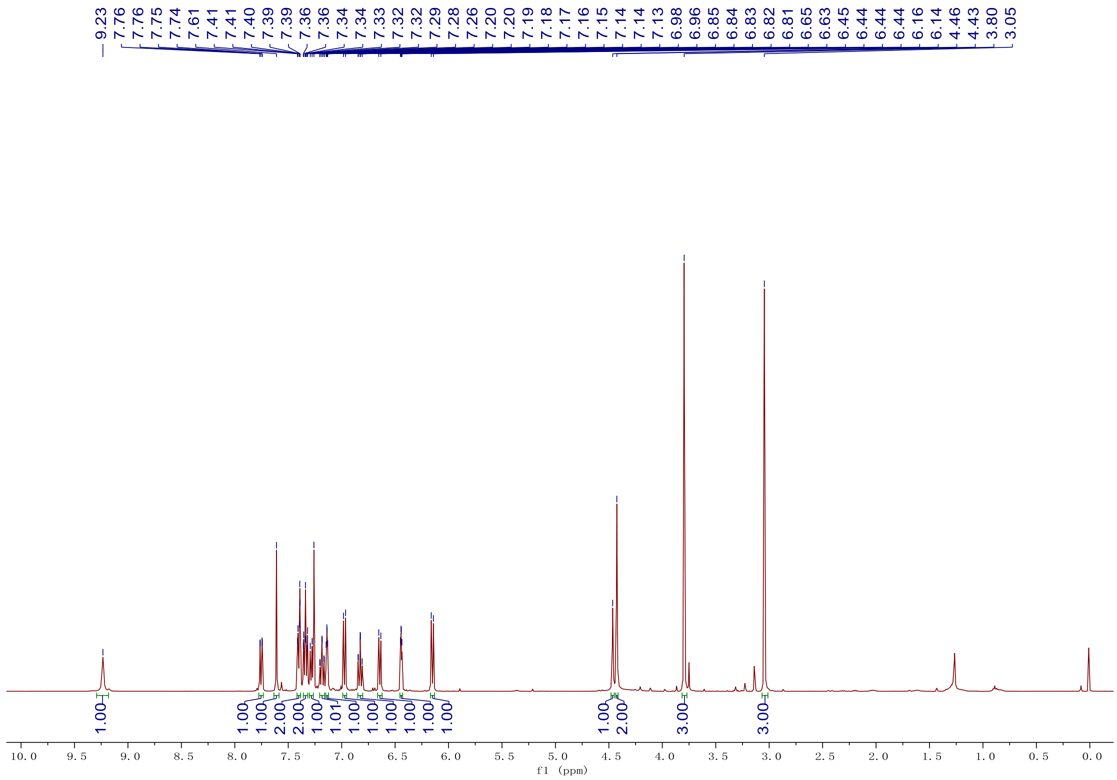
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.339	3411901	103427	46.390	49.863
2	18.682	3942959	103995	53.610	50.137
Total		7354860	207422	100.000	100.000

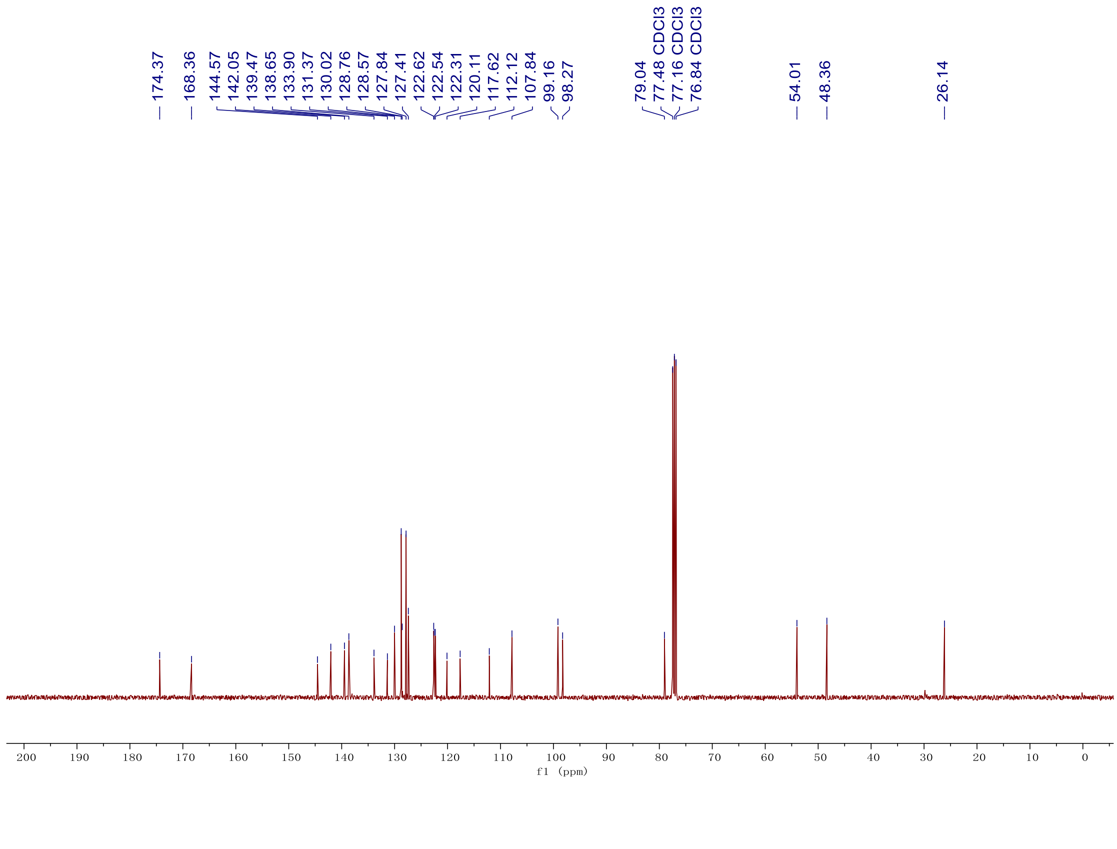


PeakTable

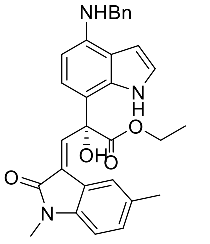
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.345	7871692	238585	95.062	95.100
2	18.696	408921	12294	4.938	4.900
Total		8280613	250879	100.000	100.000


9.23 7.76 7.76 7.75 7.74 7.61 7.41 7.41 7.40 7.39 7.39 7.36 7.36 7.34 7.34 7.33 7.32 7.32 7.29 7.28 7.26 7.20 7.20 7.19 7.18 7.17 7.16 7.15 7.14 7.14 7.13 6.98 6.96 6.85 6.84 6.83 6.82 6.81 6.65 6.63 6.45 6.44 6.44 6.44 6.16 6.14 4.46 4.43 3.80 3.05
1.00 1.00 1.00 2.00 2.00 1.00 1.01 1.00 1.00 1.00 1.00 1.00 1.00 1.00 2.00 3.00 3.00
f1 (ppm)


174.37 168.36 144.57 142.05 139.47 138.65 133.90 131.37 130.02 128.76 128.57 127.84 127.41 122.62 122.54 122.31 120.11 117.62 112.12 107.84 99.16 98.27 79.04 77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 54.01 48.36 26.14
f1 (ppm)

ethyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-3-(1,5-dimethyl-2-oxoindolin-3-ylidene)- 2-hydroxy propanoate (3ha)

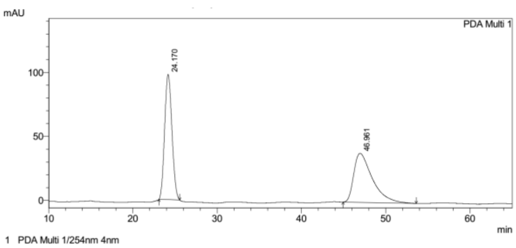


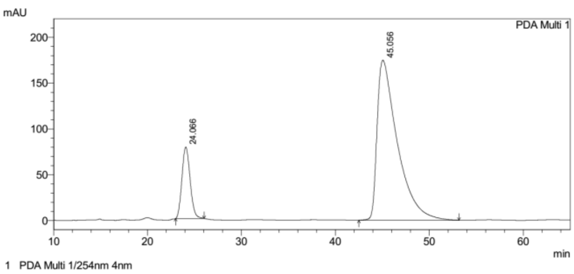
3ha 78% yield, 70% ee

3ha was obtained as a yellow solid in 78% yield (24 h) and 70% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak IG, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 15.28 min, t_{major} = 84.71 min; $[\alpha]_D^{20}$ = + 8.0 (*c* 0.25, MeOH);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.26 (s, 1H), 7.62 (s, 1H), 7.41 – 7.39 (m, 2H), 7.36 – 7.32 (m, 3H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.10 (t, *J* = 2.8 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 1H), 6.42 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.18 (d, *J* = 8.1 Hz, 1H), 4.44 (s, 2H), 4.32 (d, *J* = 2.6 Hz, 1H), 4.29 – 4.20 (m, 2H), 3.40 (s, 3H), 3.11 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.75, 168.21, 155.44, 141.89, 139.49, 138.77, 138.49, 133.91, 131.89, 128.75, 127.81, 127.41, 122.45, 122.39, 120.79, 117.60, 116.17, 114.04, 112.39, 108.20, 99.32, 98.23, 78.68, 63.39, 55.54, 48.34, 26.28, 14.12. ESI-HRMS m/z: 496.2242. [M + H]$^+$, calcd for $C_{30}H_{29}N_3O_4$+H^+, 496.2231.





PeakTable

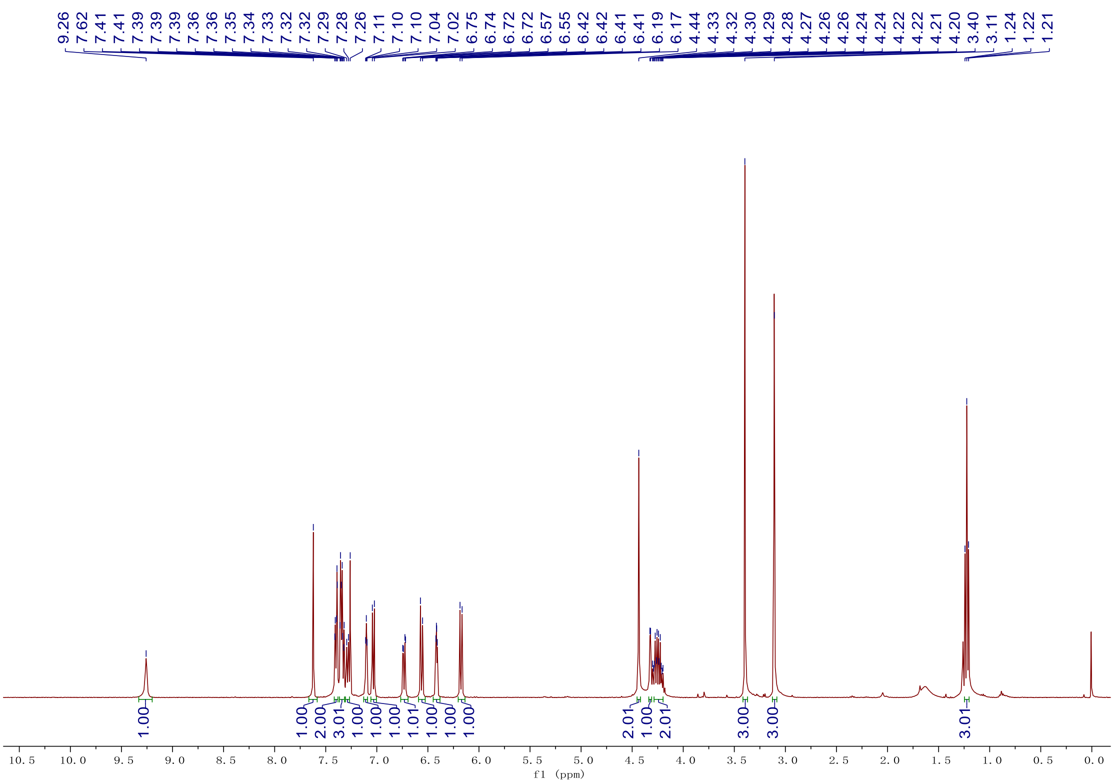
PDA Ch1 254nm 4nm

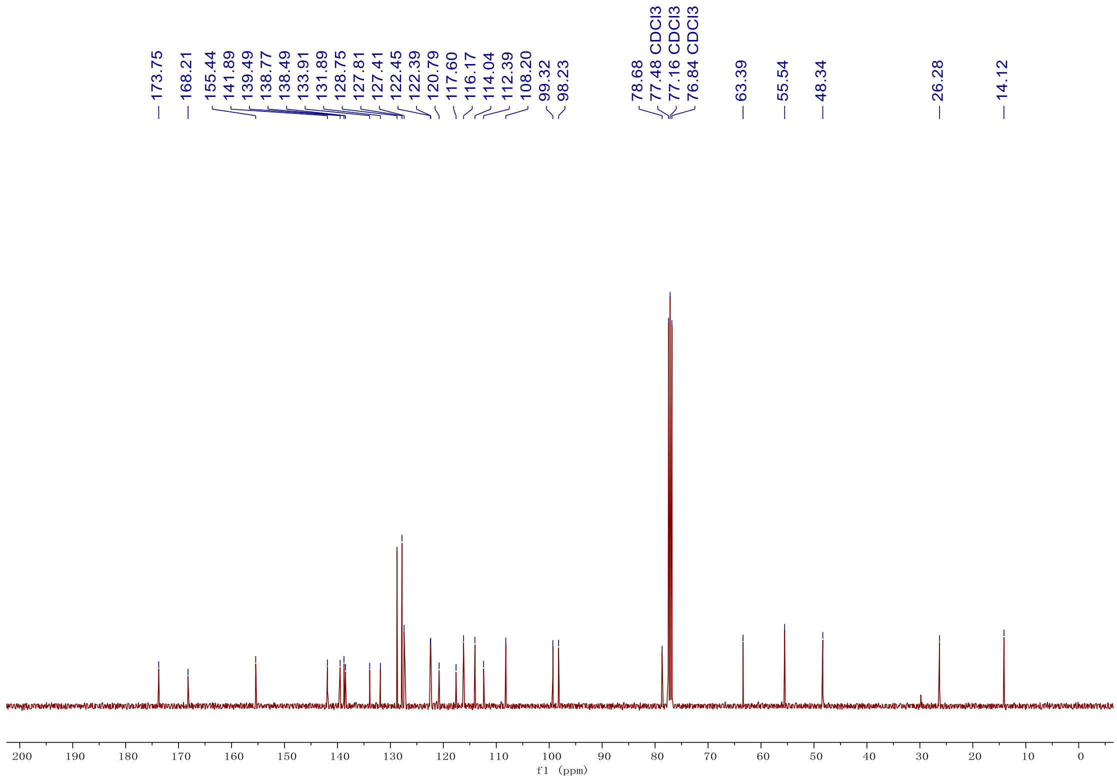
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.170	5893866	97907	50.039	71.859
2	46.961	5884732	38342	49.961	28.141
Total		11778598	136249	100.000	100.000

PeakTable

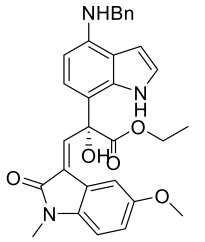
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.066	4727978	77873	15.289	30.844
2	45.056	26195356	174601	84.711	69.156
Total		30923333	252474	100.000	100.000





ethyl (*R*,*E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-2-hydroxy-3-(5-methoxy-1-methyl-2-oxoindolin-3-ylidene) propanoate (3ia)

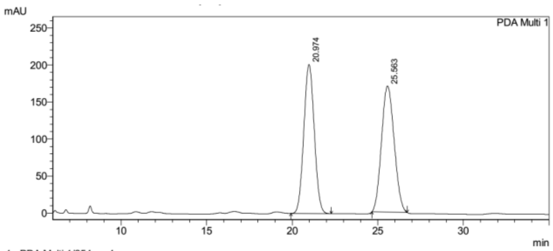


3ia 70% yield, 87% ee

3ia was obtained as a yellow solid in 70% yield (48 h) and 87% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 20.61 min, t_{minor} = 24.84 min; $[\alpha]_D^{20}$ = + 15.0 (*c* 0.32, MeOH);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 7.62 (s, 1H), 7.54 (d, *J* = 2.2 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.11 (t, *J* = 2.9 Hz, 1H), 7.06 – 7.01 (m, 2H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.44 – 6.43 (m, 1H), 6.20 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.45 (s, 2H), 4.27 – 4.24 (m, 2H), 4.19 (s, 1H), 3.15 (s, 3H), 2.16 (s, 3H), 1.22 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.85, 168.36, 142.59, 141.96, 139.53, 137.93, 133.88, 131.71, 131.20, 130.43, 129.04, 128.76, 127.82, 127.40, 122.49, 122.15, 120.18, 117.63, 112.77, 107.58, 99.20, 98.31, 78.93, 63.47, 48.36, 26.28, 21.30, 14.13. ESI-HRMS m/z: 512.2183. $[M + H]^+$, calcd for $C_{30}H_{29}N_3O_5+H^+$, 512.2180.

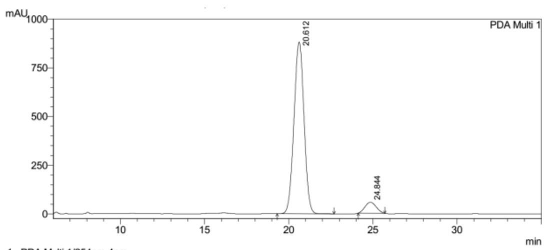


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.974	8565345	201307	49.469	54.186
2	25.563	8749295	170202	50.531	45.814
Total		17314639	371509	100.000	100.000

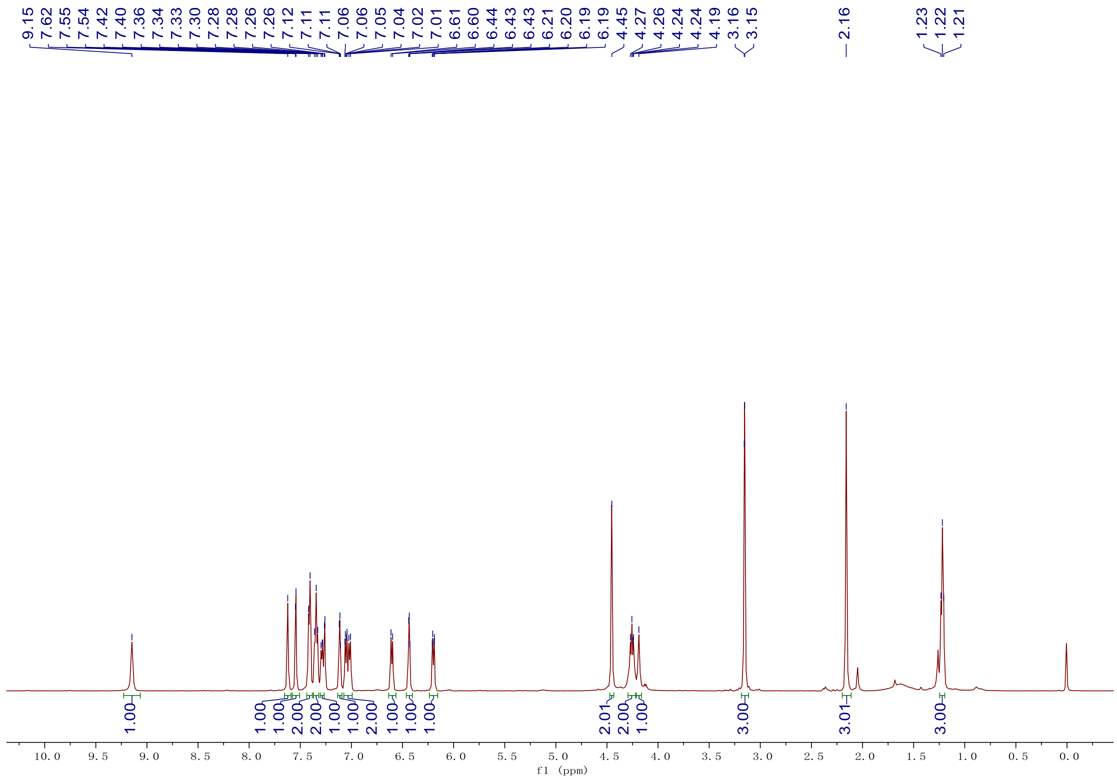


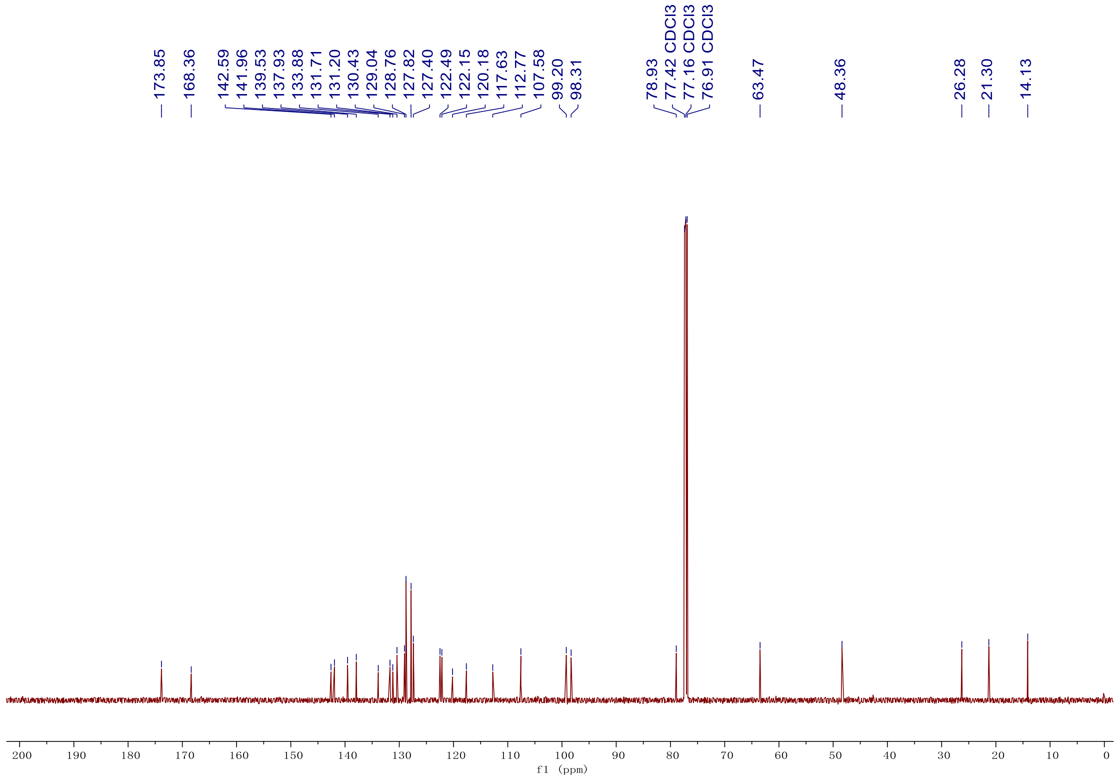
1 PDA Multi 1/254nm 4nm

PeakTable

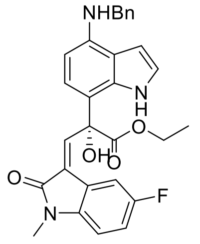
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.612	36791044	882634	93.385	93.997
2	24.844	2605940	56371	6.615	6.003
Total		39396984	939005	100.000	100.000


9.15 7.62 7.55 7.54 7.42 7.40 7.36 7.34 7.33 7.30 7.28 7.26 7.26 7.12 7.11 7.11 7.06 7.06 7.05 7.04 7.02 7.01 6.61 6.60 6.44 6.43 6.21 6.20 6.19 6.19 4.45 4.27 4.26 4.24 4.24 4.19 3.16 3.15 2.16 1.23 1.22 1.21
1.00 1.00 1.00 2.00 2.00 1.00 1.00 2.00 1.00 1.00 1.00 2.01 2.00 1.00 3.00 3.01 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.85 168.36 142.59 141.96 139.53 137.93 133.88 131.71 131.20 130.43 129.04 128.76 127.82 127.40 122.49 122.15 120.18 117.63 112.77 107.58 99.20 98.31 78.93 77.42 CDCl3 77.16 CDCl3 76.91 CDCl3 63.47 48.36 26.28 21.30 14.13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

ethyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-3-(5-fluoro-1-methyl-2-oxoindolin-3-ylidene)-2-hydroxy propanoate (3ja)

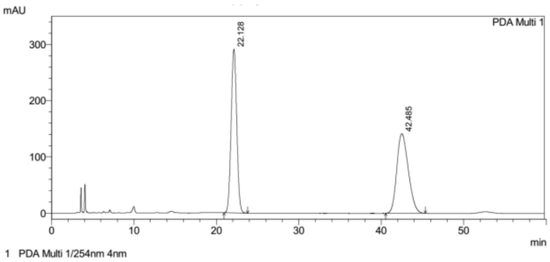


3ja 81% yield, 96% ee

3ja was obtained as a yellow solid in 81% yield (24 h) and 96% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 22.18 min, t_{minor} = 42.52 min; $[\alpha]_D^{20}$ = + 3.7 (*c* 0.39, MeOH);

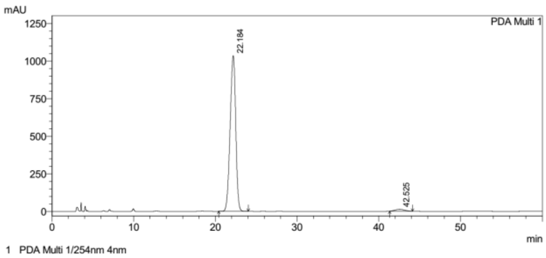
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.10 (s, 1H), 7.69 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.63 (s, 1H), 7.41 (dt, *J* = 6.0, 1.4 Hz, 2H), 7.36 – 7.33 (m, 2H), 7.30 – 7.28 (m, 1H), 7.12 (t, *J* = 2.8 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.92 (td, *J* = 8.7, 2.7 Hz, 1H), 6.62 (dd, *J* = 8.5, 4.3 Hz, 1H), 6.44 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.19 (d, *J* = 8.1 Hz, 1H), 4.45 (s, 2H), 4.31 – 4.22 (m, 3H), 3.18 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.56, 168.13, 158.85 (d, *J* = 237.9 Hz), 142.12, 140.82, 139.86, 139.45, 133.72, 130.52 (d, *J* = 3.1 Hz), 128.76, 127.81, 127.41, 122.62, 122.10, 121.27 (d, *J* = 9.7 Hz), 117.71, 116.34, 116.08, 112.10, 108.07 (d, *J* = 8.4 Hz), 99.17, 98.40, 79.13, 63.63, 48.33, 26.39, 14.11. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.83 (td, *J* = 9.3, 4.5 Hz). ESI-HRMS m/z: 500.1978. [M + H]$^+$, calcd for $C_{29}H_{26}FN_3O_4+H^+$, 500.1980.



PeakTable

PDA Ch1 254nm 4nm

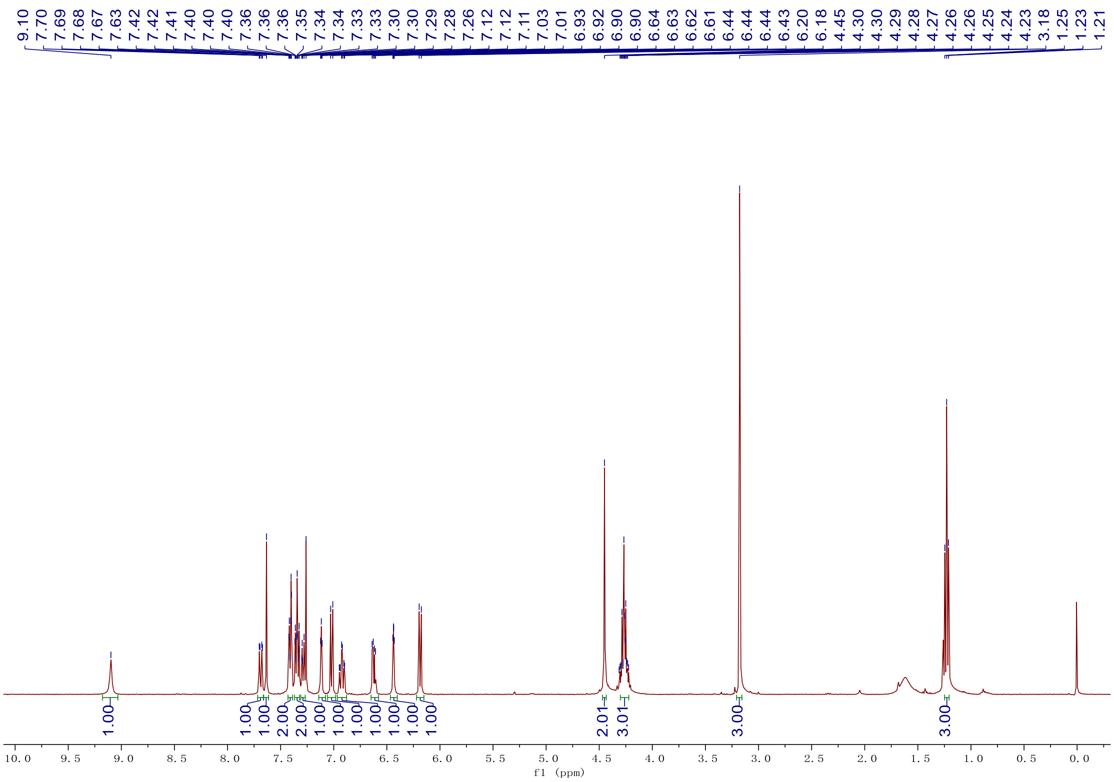
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.128	13785500	291685	50.073	67.276
2	42.485	13745465	141879	49.927	32.724
Total		27530965	433563	100.000	100.000

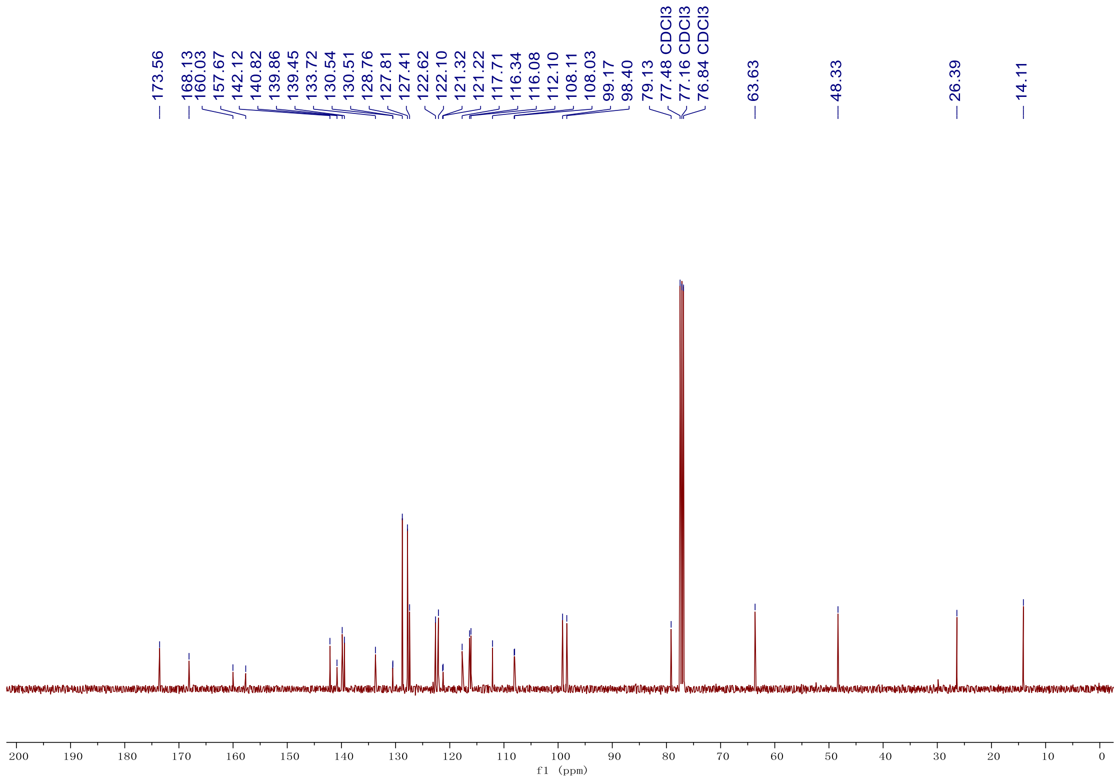


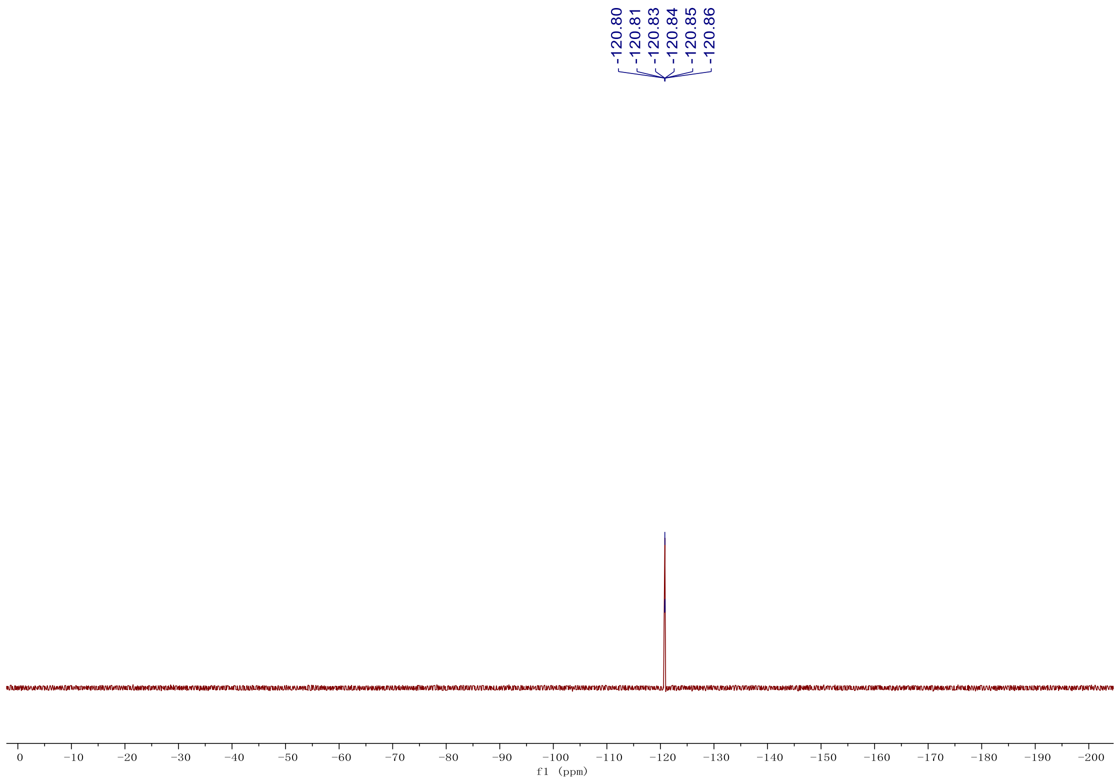
PeakTable

PDA Ch1 254nm 4nm

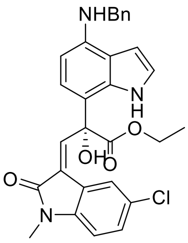
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.184	49298230	1034483	98.016	98.870
2	42.525	997649	11820	1.984	1.130
Total		50295879	1046304	100.000	100.000




173.56
168.13
160.03
157.67
142.12
140.82
139.86
139.45
133.72
130.54
130.51
128.76
127.81
127.41
122.62
122.10
121.32
121.22
117.71
116.34
116.08
112.10
108.11
108.03
99.17
98.40
79.13
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.63
48.33
26.39
14.11
f1 (ppm)


-120.80
-120.81
-120.83
-120.84
-120.85
-120.86
f1 (ppm)

ethyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-3-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-hydroxy propanoate (3ka)

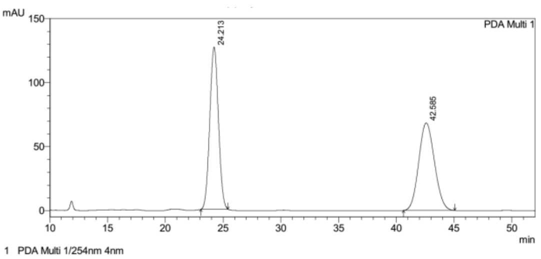


3ka 78% yield, 95% ee

3ka was obtained as a yellow solid in 78% yield (24 h) and 95% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): tmajor = 24.34 min, tminor = 42.46 min; $[\alpha]_D^{20}$ = + 10.2 (c 0.18, MeOH);

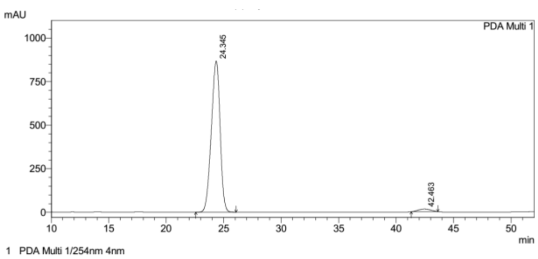
1H NMR (400 MHz, Chloroform-d) δ 9.02 (s, 1H), 7.84 (d, J = 2.1 Hz, 1H), 7.54 (s, 1H), 7.33 (d, J = 7.0 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.21 – 7.17 m, 2H), 7.10 (dd, J = 8.3, 2.2 Hz, 1H), 7.03 (t, J = 2.9 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 8.3 Hz, 1H), 6.35 (dd, J = 3.3, 2.2 Hz, 1H), 6.11 (d, J = 8.1 Hz, 1H), 4.37 (s, 2H), 4.22 – 4.16 (m, 3H), 3.09 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H). 13C NMR (126 MHz, Chloroform-d) δ 173.47, 167.97, 143.25, 142.14, 140.01, 139.47, 133.71, 129.76, 129.72, 128.78, 128.53, 127.81, 127.76, 127.41, 122.64, 122.01, 121.53, 117.73, 112.27, 108.70, 99.20, 98.43, 79.21, 63.71, 48.33, 26.40, 14.13. ESI-HRMS m/z: 516.1684. [M + H]+, calcd for C29H26ClN3O4+H+, 516.1685.



PeakTable

PDA Ch1 254nm 4nm

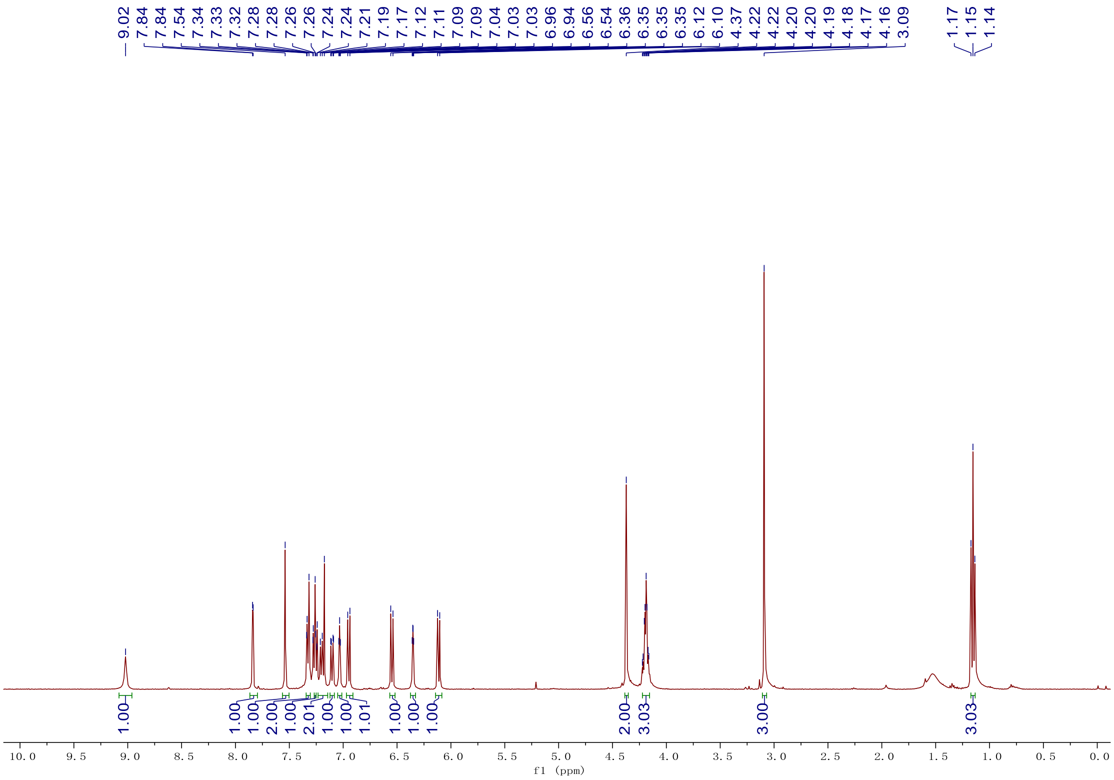
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.213	6599108	126651	50.456	64.940
2	42.585	6479744	68377	49.544	35.060
Total		13078852	195028	100.000	100.000

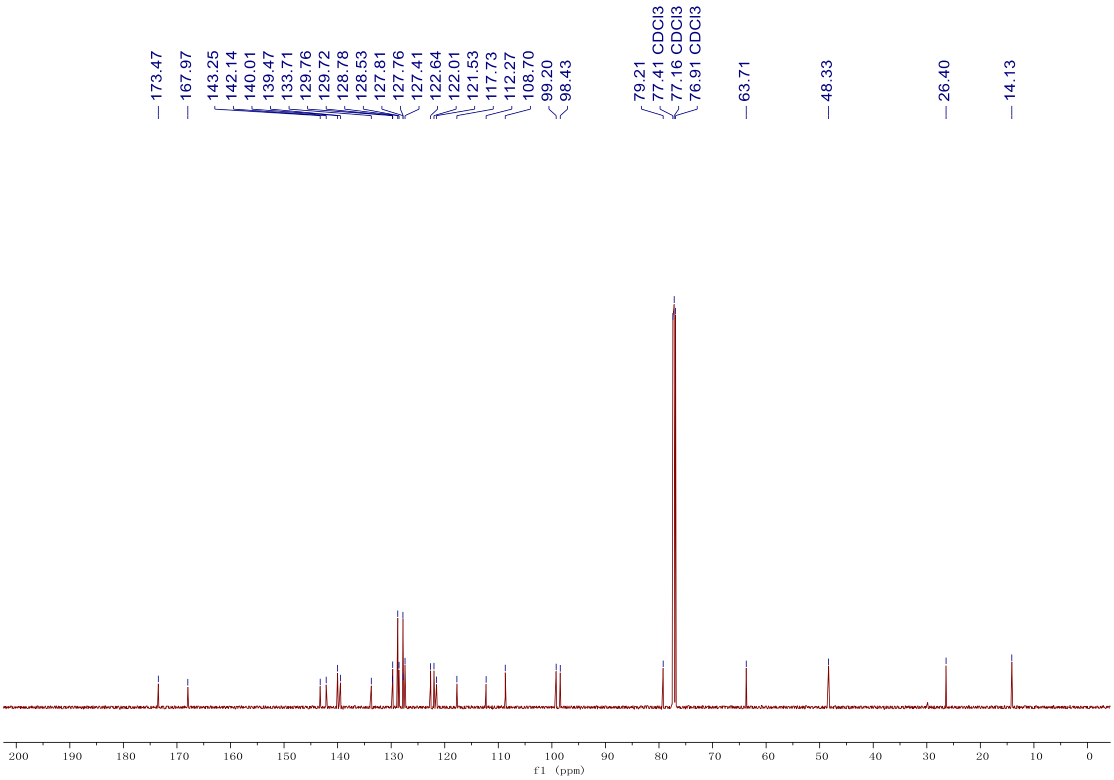


PeakTable

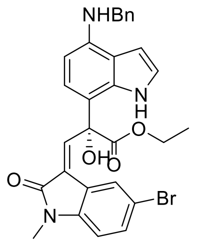
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.345	46198923	868388	97.527	98.272
2	42.463	1171429	15267	2.473	1.728
Total		47370352	883655	100.000	100.000





ethyl (*R*, *E*)-2-(4-(benzylamino)-1H-indol-7-yl)-3-(5-bromo-1-methyl-2-oxoindolin-3-ylidene)-2-hydroxy propanoate (3la)

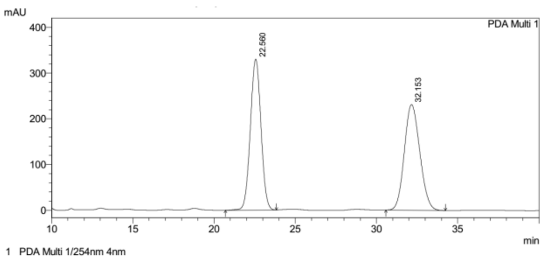


3la 70% yield, 93% ee

3la was obtained as a yellow solid in 70% yield (24 h) and 93% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 22.53 min, t_{minor} = 32.13 min; $[\alpha]_D^{20}$ = + 5.0 (*c* 0.36, MeOH);

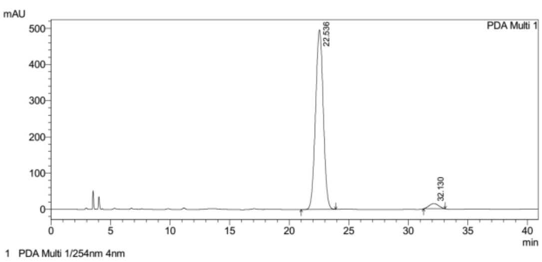
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.62 (s, 1H), 7.43 – 7.40 (m, 2H), 7.37 – 7.32 (m, 3H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.12 (dd, *J* = 3.3, 2.4 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 8.3 Hz, 1H), 6.44 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.20 (d, *J* = 8.1 Hz, 1H), 4.46 (s, 2H), 4.32 – 4.25 (m, 3H), 3.16 (s, 3H), 1.25 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.42, 167.86, 143.65, 142.11, 140.17, 139.47, 133.70, 132.57, 131.23, 129.56, 128.77, 127.80, 127.41, 122.65, 121.99, 121.92, 117.72, 115.15, 112.30, 109.22, 99.19, 98.41, 79.19, 63.69, 48.32, 26.37, 14.14. ESI-HRMS m/z: 560.1181. [M + H]$^+$, calcd for $C_{29}H_{26}BrN_3O_4$+H^+, 560.1179.



PeakTable

PDA Ch1 254nm 4nm

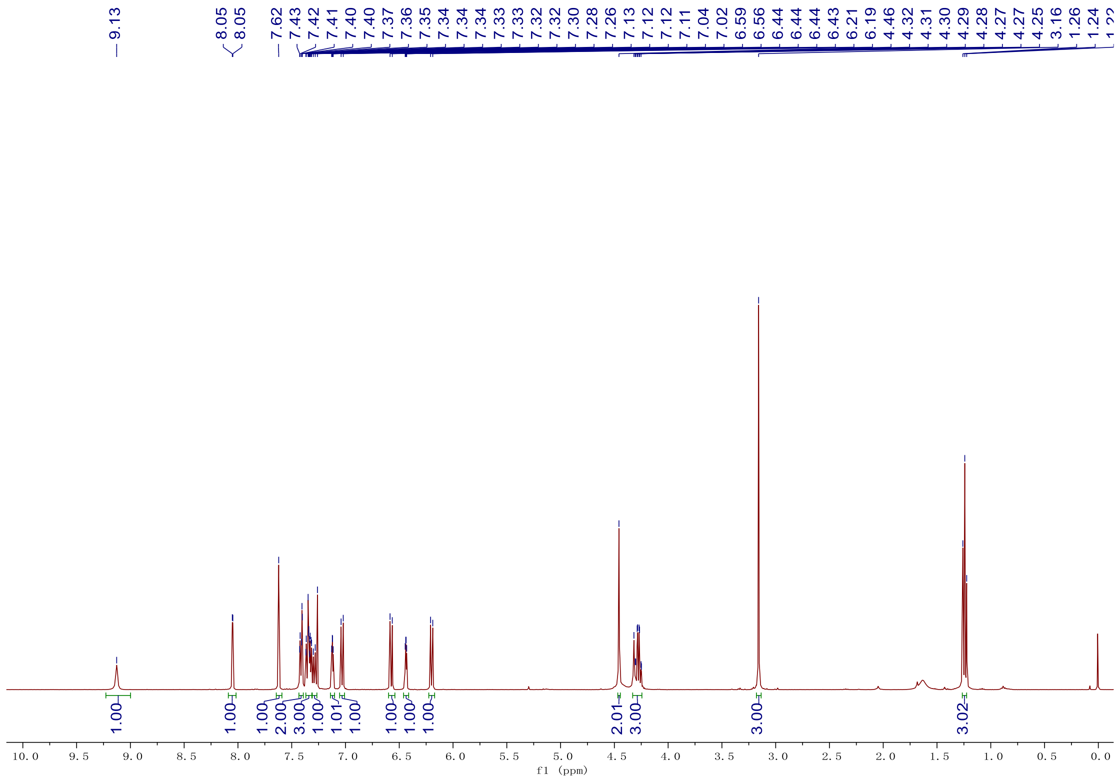
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.560	15048646	330260	49.544	58.828
2	32.153	15325444	231135	50.456	41.172
Total		30374090	561395	100.000	100.000

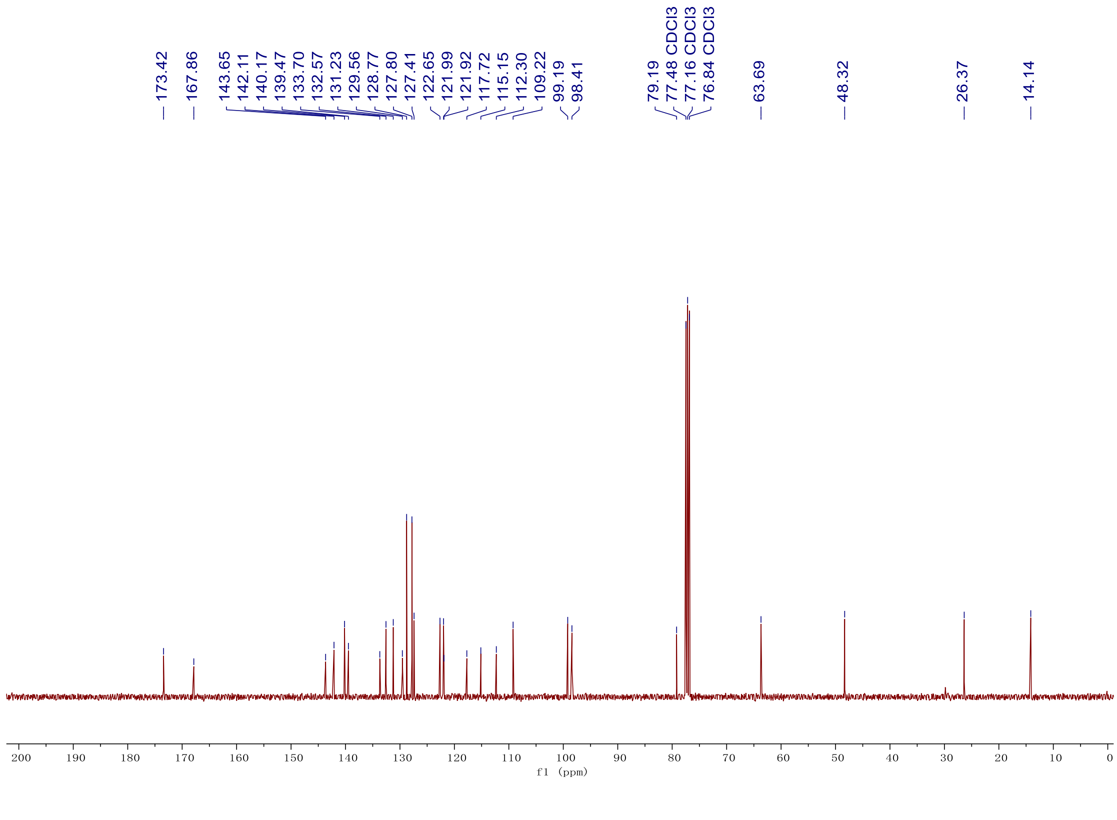


PeakTable

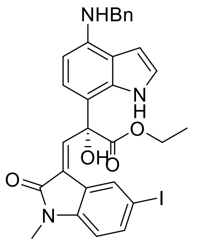
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.536	22323721	495739	96.513	97.204
2	32.130	806632	14262	3.487	2.796
Total		23130354	510001	100.000	100.000





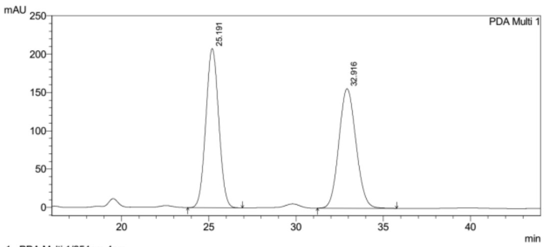
ethyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-2-hydroxy-3-(5-iodo-1-methyl-2-oxoindolin-3-ylidene) propanoate (3ma)



3ma 86% yield, 88% ee

3ma was obtained as a yellow solid in 86% yield (24 h) and 88% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 25.02 min, t_{minor} = 32.59 min; $[\alpha]_D^{20}$ = + 4.2 (*c* 0.34, MeOH); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (s, 1H), 8.18 (d, *J* = 1.7 Hz, 1H), 7.61 (s, 1H), 7.51 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.43 – 7.41 (m, 2H), 7.37 – 7.34 (m, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.13 – 7.12 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 1H), 6.44 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.21 (d, *J* = 8.1 Hz, 1H), 4.46 (s, 2H), 4.31 – 4.25 (m, 3H), 3.15 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.38, 167.68, 144.23, 142.08, 140.15, 139.48, 138.47, 136.83, 133.69, 129.35, 128.77, 127.80, 127.39, 122.67, 122.28, 121.99, 117.71, 112.35, 109.84, 99.20, 98.39, 85.13, 79.11, 63.67, 48.32, 26.32, 14.15. ESI-HRMS m/z: 608.1045. $[M + H]^+$, calcd for $C_{29}H_{26}IN_3O_4+H^+$, 608.1041.

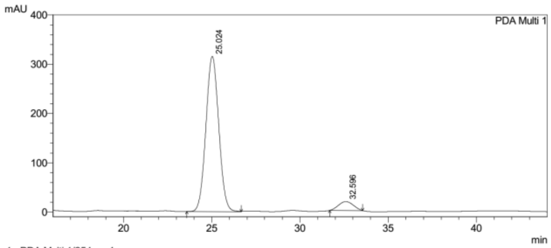


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.191	10685080	207791	50.059	57.116
2	32.916	10659863	156013	49.941	42.884
Total		21344943	363804	100.000	100.000

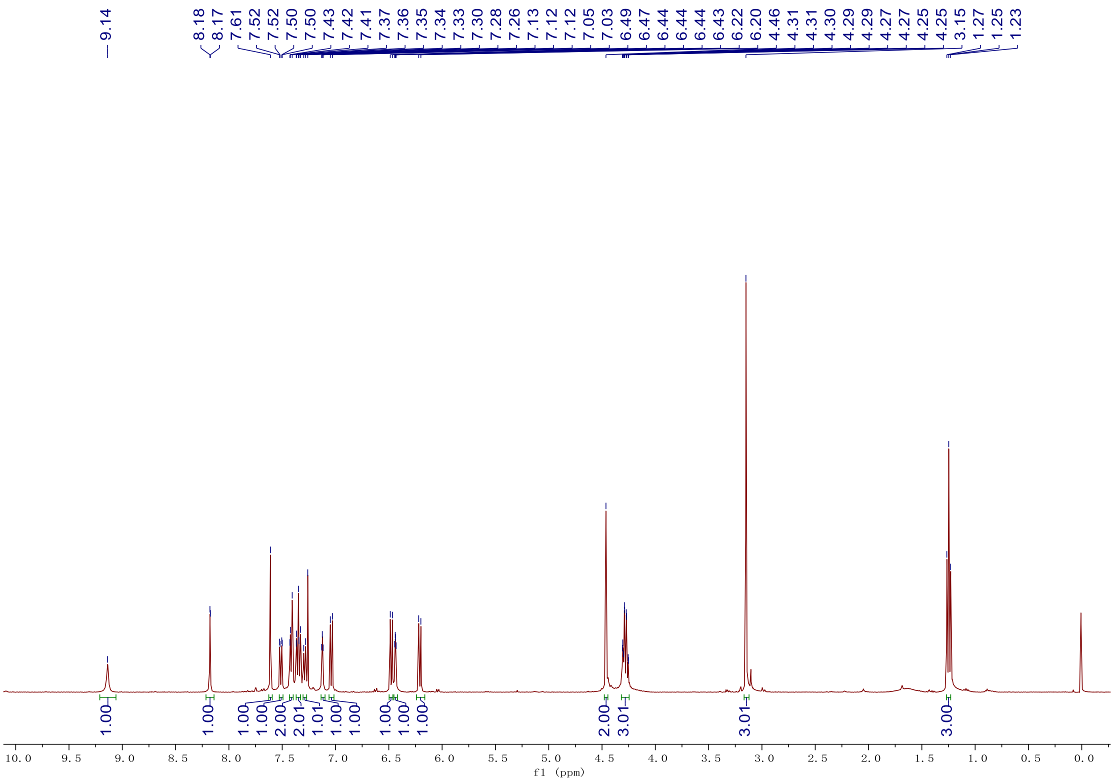


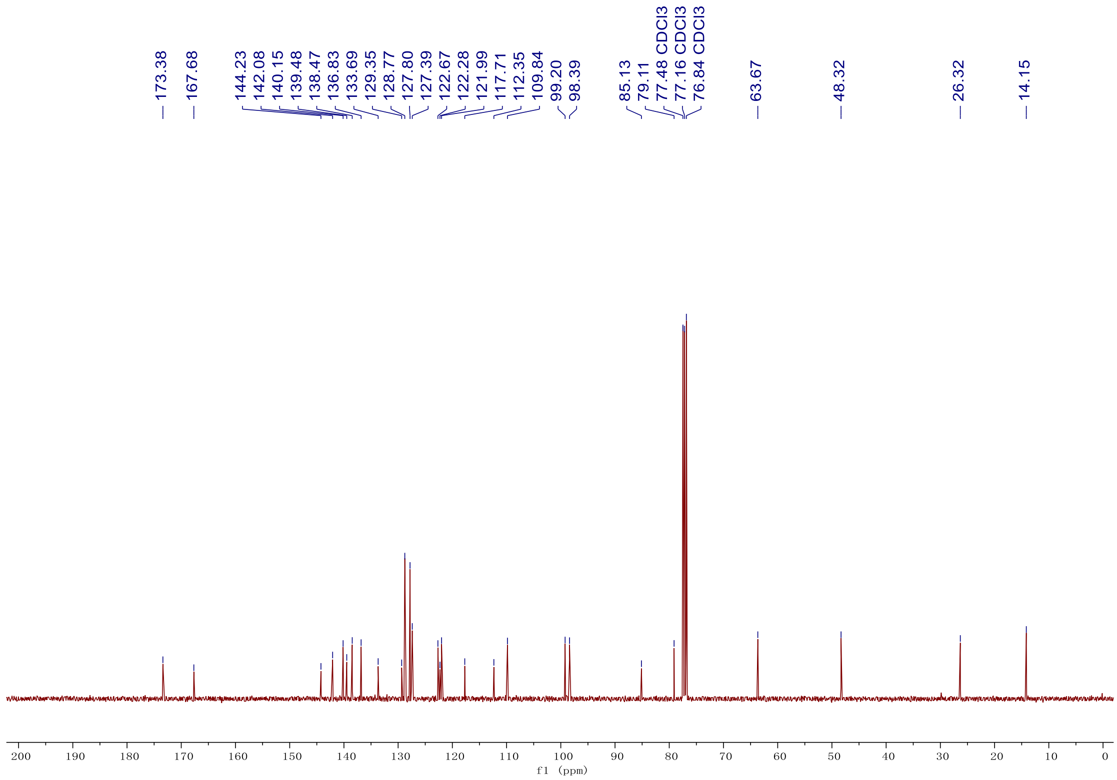
1 PDA Multi 1/254nm 4nm

PeakTable

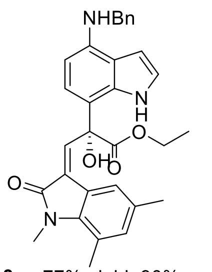
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.024	15987287	315234	93.834	94.592
2	32.596	1050578	18021	6.166	5.408
Total		17037865	333255	100.000	100.000





ethyl (*R*,*E*)-2-(4-(benzylamino)-1H-indol-7-yl)-2-hydroxy-3-(1,5,7-trimethyl-2-oxoindolin-3-ylidene) propanoate (3na)

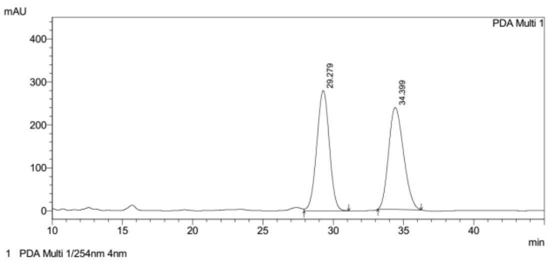


3na 77% yield, 90% ee

3na was obtained as a yellow solid in 77% yield (24 h) and 90% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 29.55 min, t_{minor} = 34.74 min; $[\alpha]_D^{20}$ = + 35.0 (*c* 0.32, MeOH);

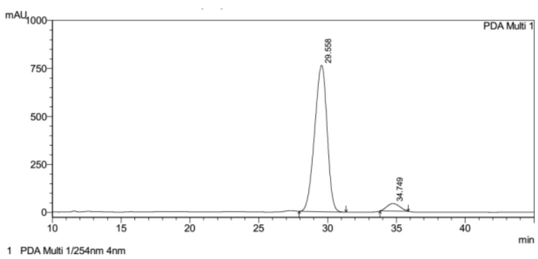
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 7.53 (s, 1H), 7.47 – 7.46 (m, 1H), 7.42 – 7.40 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.12 (dd, *J* = 3.3, 2.4 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.75 – 6.74 (m, 1H), 6.43 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.19 (d, *J* = 8.1 Hz, 1H), 4.44 (s, 2H), 4.29 (s, 1H), 4.27 – 4.23 (m, 2H), 3.38 (s, 3H), 2.42 (s, 3H), 2.07 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.87, 169.20, 141.89, 140.21, 139.56, 137.96, 134.52, 133.91, 131.49, 131.25, 128.75, 127.84, 127.39, 127.04, 122.48, 122.15, 120.86, 118.98, 117.61, 112.76, 99.22, 98.22, 78.63, 63.32, 48.38, 29.78, 20.93, 19.14, 14.11. ESI-HRMS m/z: 510.2390. $[M + H]^+$, calcd for $C_{31}H_{31}N_3O_4$+H^+, 510.2387.



PeakTable

PDA Ch1 254nm 4nm

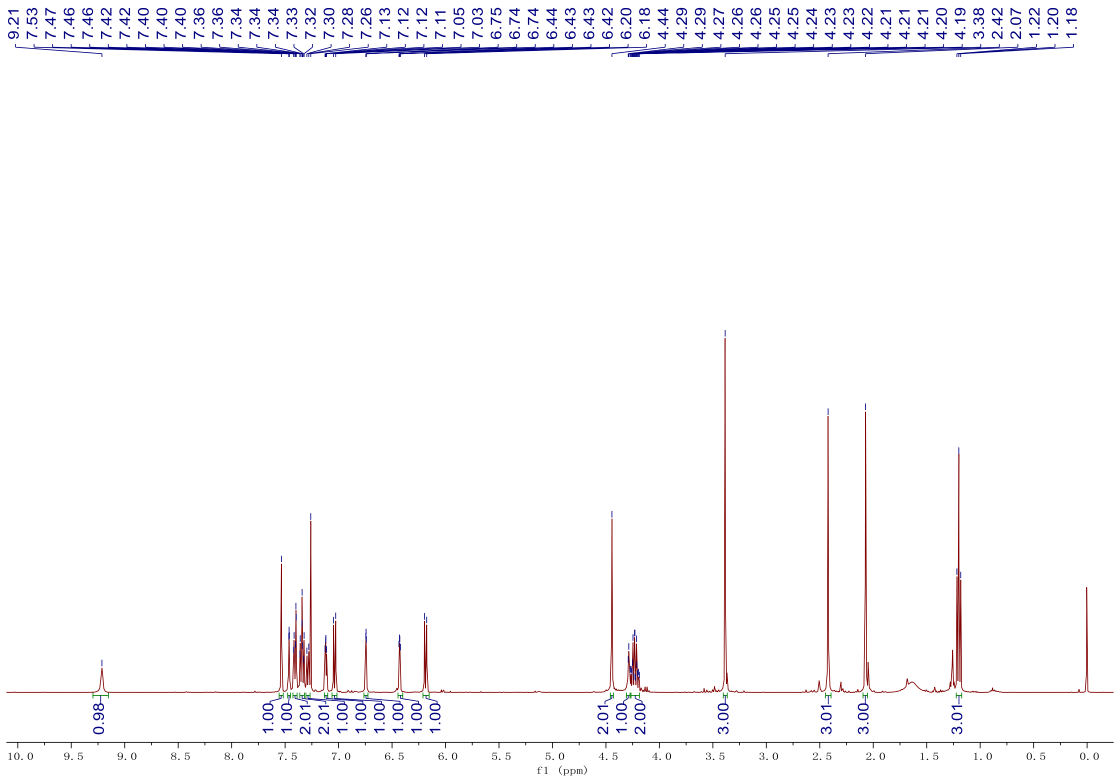
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.279	17372126	279898	49.766	54.121
2	34.399	17535624	237274	50.234	45.879
Total		34907750	517172	100.000	100.000

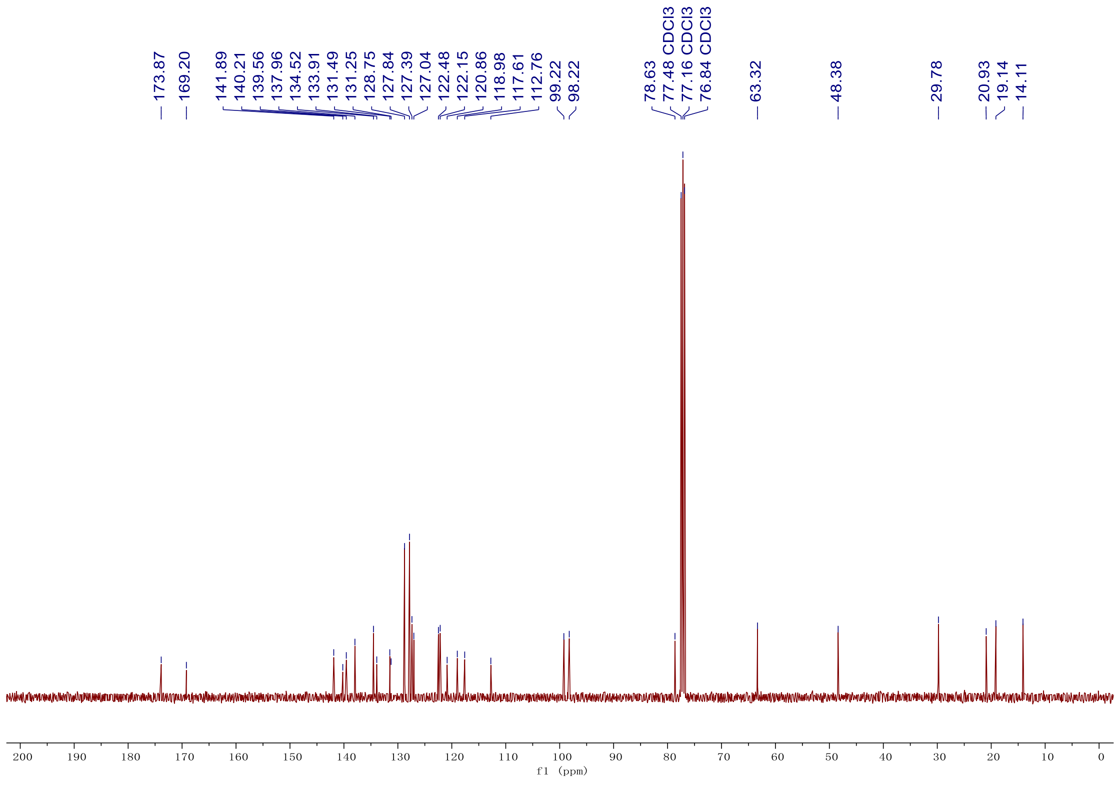


PeakTable

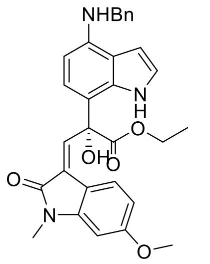
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.558	48216433	764129	95.009	95.149
2	34.749	2532839	38958	4.991	4.851
Total		50749272	803087	100.000	100.000





ethyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-2-hydroxy-3-(6-methoxy-1-methyl-2-oxoindolin-3-ylidene) propanoate (3oa)

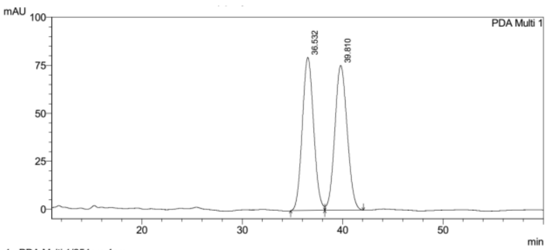


3oa 60% yield, 86% ee

3oa was obtained as a yellow solid in 60% yield (144 h) and 86% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 37.05 min, t_{minor} = 40.47 min; $[\alpha]_D^{20}$ = + 17.5 (*c* 0.19, MeOH);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.11 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.36 – 7.33 (m, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 2.8 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.43 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.34 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.29 (d, *J* = 2.4 Hz, 1H), 6.18 (d, *J* = 8.1 Hz, 1H), 4.44 (s, 2H), 4.29 – 4.19 (m, 2H), 4.03 (s, 1H), 3.78 (s, 3H), 3.18 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.10, 169.08, 161.78, 146.51, 141.98, 139.52, 134.66, 133.88, 130.91, 129.63, 128.77, 127.86, 127.42, 122.50, 122.30, 117.64, 113.22, 112.50, 106.30, 99.23, 98.30, 95.76, 78.89, 63.42, 55.63, 48.40, 26.33, 14.12. ESI-HRMS m/z: 512.2184. [M + H]$^+$, calcd for $C_{30}H_{29}N_3O_5+H^+$, 512.2180.

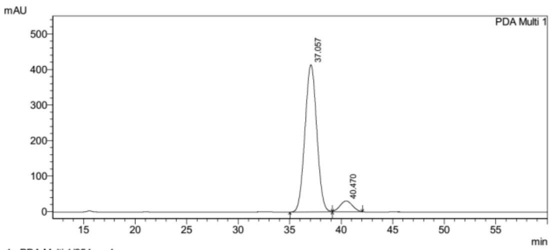


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.532	6275881	79781	49.208	51.397
2	39.810	6477862	75445	50.792	48.603
Total		12753742	155225	100.000	100.000

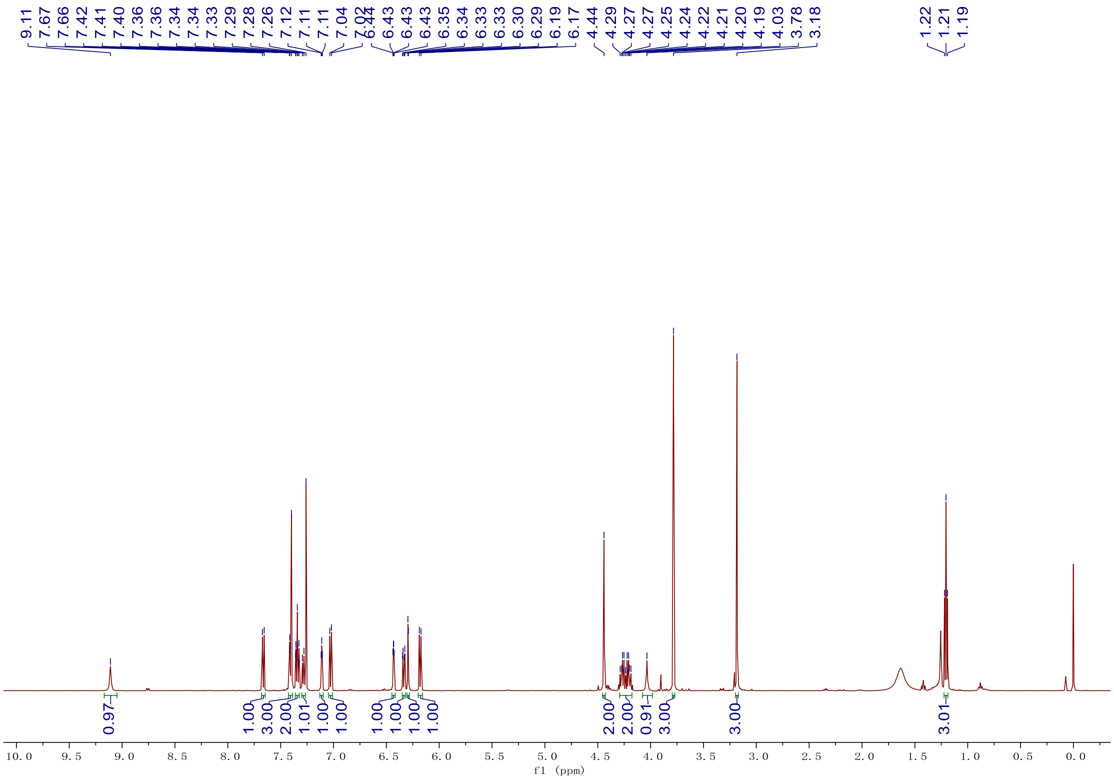


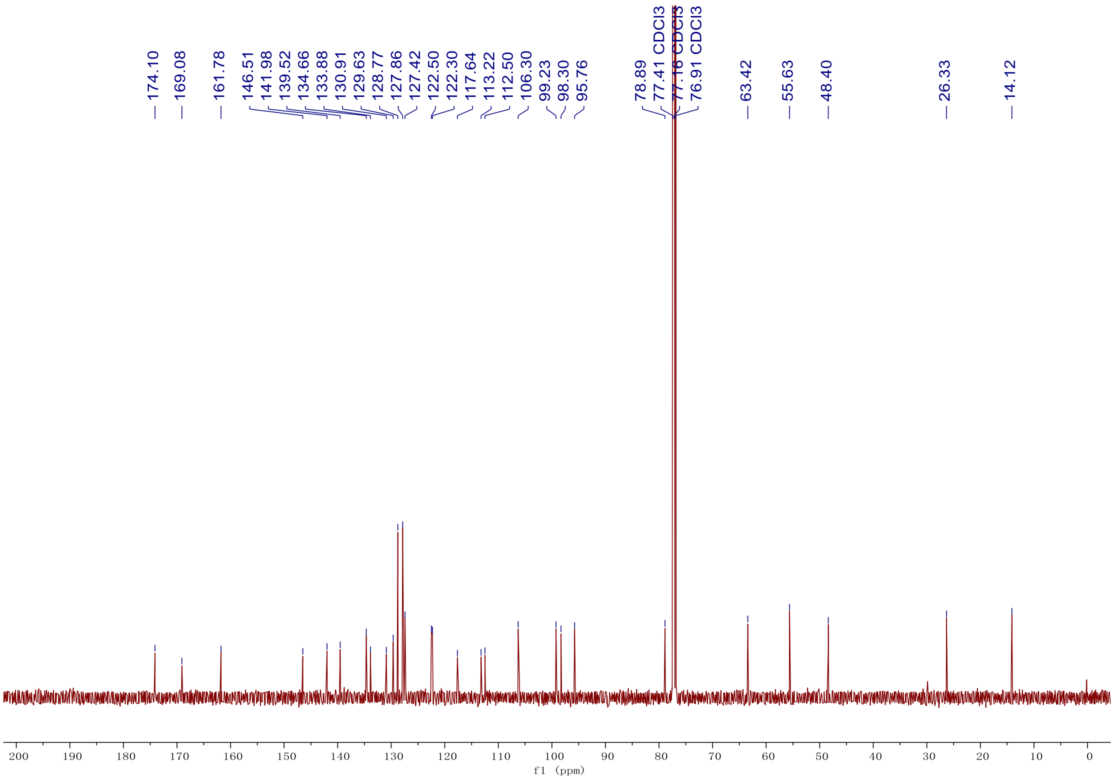
1 PDA Multi 1/254nm 4nm

PeakTable

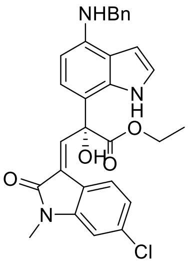
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.057	33077163	414321	92.822	93.162
2	40.470	2557930	30413	7.178	6.838
Total		35635093	444734	100.000	100.000





ethyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-3-(6-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-hydroxy propanoate (3pa)

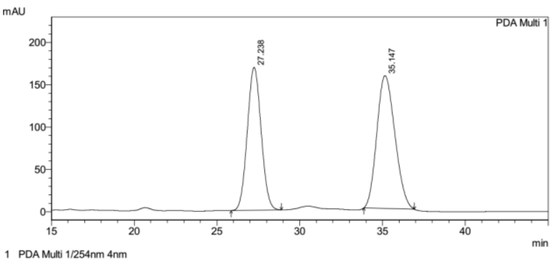


3pa 88% yield, 95% ee

3pa was obtained as a yellow solid in 88% yield (24 h) and 95% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 27.24 min, t_{minor} = 35.33 min; $[\alpha]_D^{20}$ = + 84.3 (*c* 0.25, MeOH);

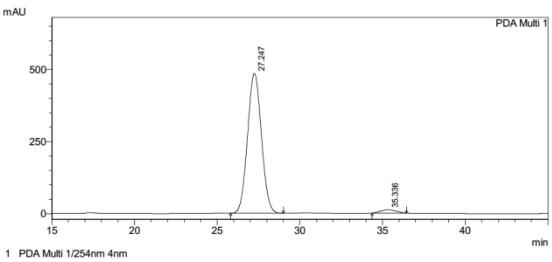
^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 7.63 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.09 (t, *J* = 2.9 Hz, 1H), 6.95 – 6.91 (m, 2H), 6.78 (d, *J* = 1.7 Hz, 1H), 6.41 (t, *J* = 2.6 Hz, 1H), 6.13 (d, *J* = 8.1 Hz, 1H), 4.45 (s, 1H), 4.41 (s, 2H), 4.27 – 4.19 (m, 2H), 3.06 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.56, 168.28, 145.58, 142.04, 139.59, 139.43, 133.77, 130.24, 129.64, 128.73, 127.79, 127.39, 125.30, 124.07, 122.56, 122.18, 119.01, 117.65, 111.97, 111.27, 99.17, 98.30, 78.93, 63.41, 48.30, 26.30, 14.09. ESI-HRMS m/z: 516.1685. [M + H]$^+$, calcd for $C_{29}H_{26}ClN_3O_4$+H$^+$, 516.1685.



PeakTable

PDA Ch1 254nm 4nm

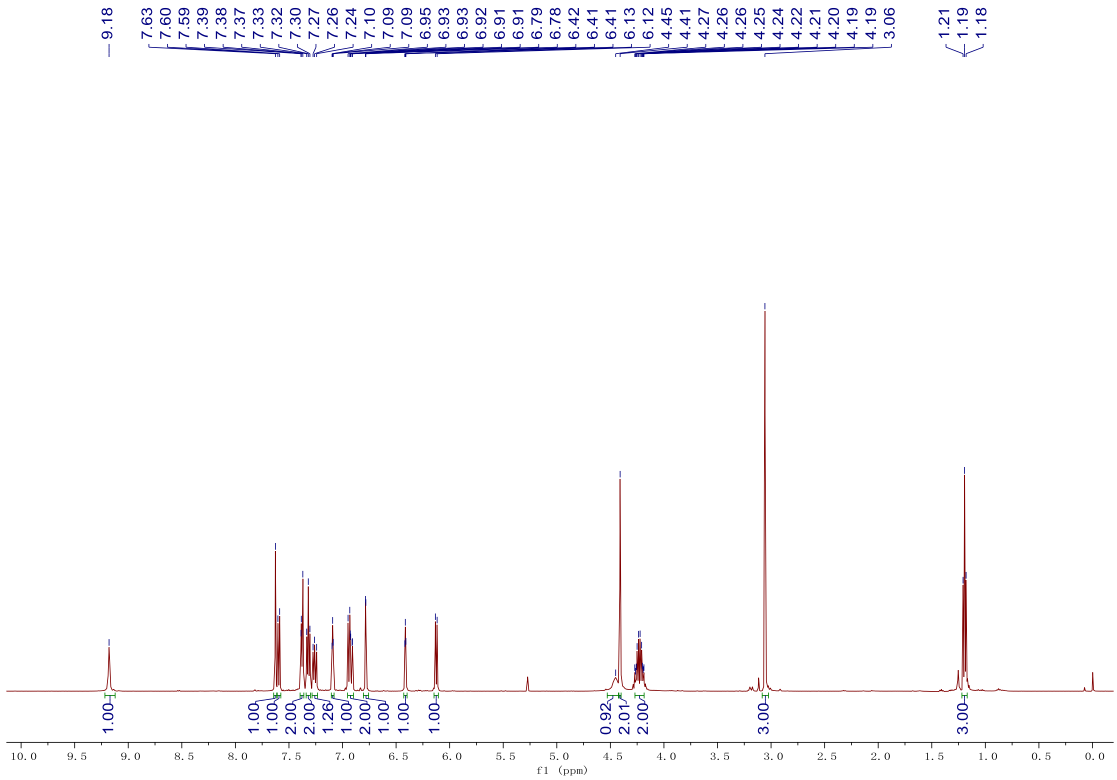
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.238	9831261	168851	45.154	51.799
2	35.147	11941293	157125	54.846	48.201
Total		21772553	325977	100.000	100.000

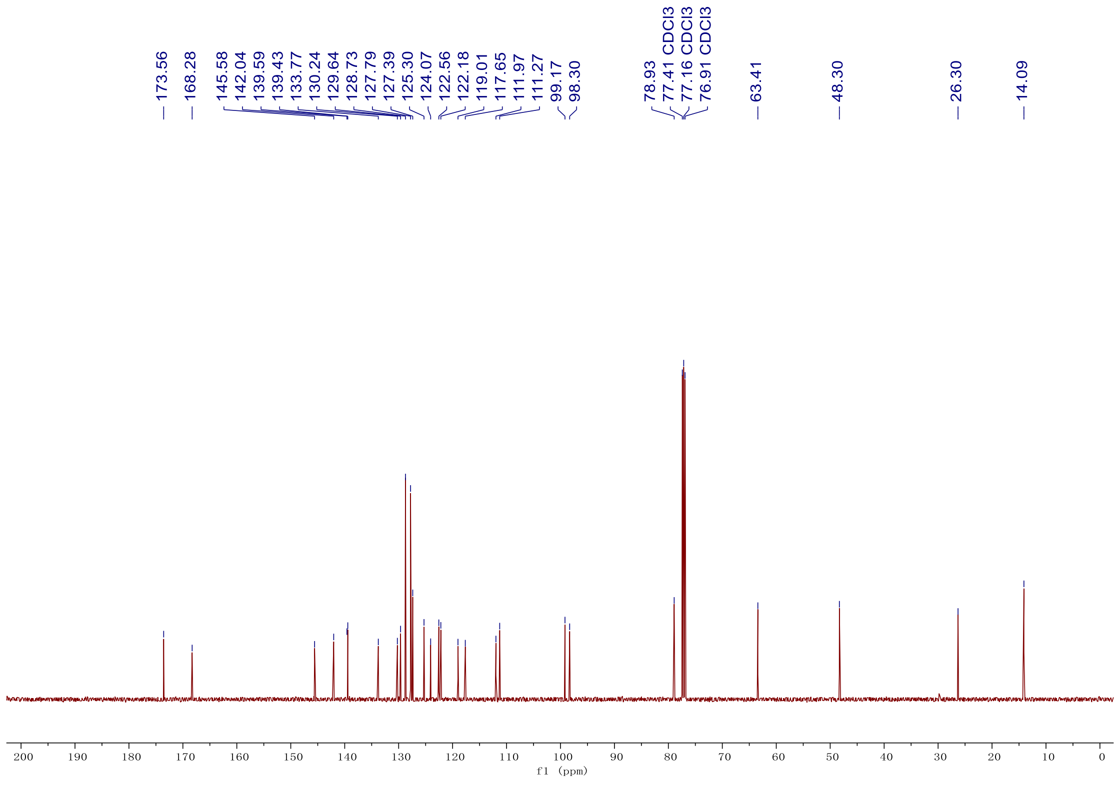


PeakTable

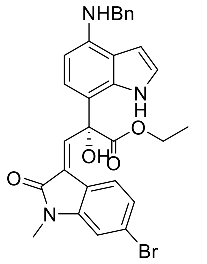
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.247	28360578	484983	97.481	97.766
2	35.336	732816	11080	2.519	2.234
Total		29093394	496063	100.000	100.000


9.18
7.63
7.60
7.59
7.39
7.38
7.37
7.33
7.32
7.30
7.27
7.26
7.24
7.10
7.09
7.09
6.95
6.93
6.93
6.92
6.91
6.91
6.79
6.78
6.42
6.41
6.13
6.12
4.45
4.41
4.27
4.26
4.26
4.25
4.24
4.22
4.21
4.20
4.19
3.06
1.21
1.19
1.18
1.00
1.00
1.00
2.00
2.00
1.26
1.00
2.00
1.00
1.00
1.00
0.92
2.01
2.00
3.00
3.00
f1 (ppm)


173.56
168.28
145.58
142.04
139.59
139.43
133.77
130.24
129.64
128.73
127.79
127.39
125.30
124.07
122.56
122.18
119.01
117.65
111.97
111.27
99.17
98.30
78.93
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
63.41
48.30
26.30
14.09
f1 (ppm)

ethyl (*R*,*E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-3-(6-bromo-1-methyl-2-oxoindolin-3-ylidene)-2-hydroxy propanoate (3qa)

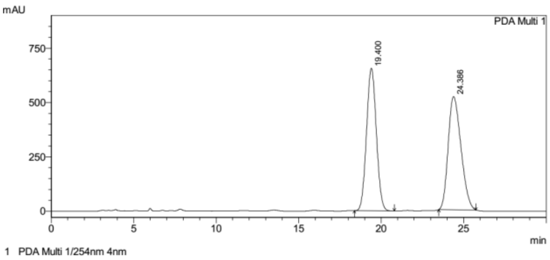


3qa 82% yield, 95% ee

3qa was obtained as a yellow solid in 82% yield (24 h) and 95% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 18.56 min, t_{minor} = 23.45 min; $[\alpha]_D^{20}$ = + 99.5 (*c* 0.41, MeOH);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.61 (s, 1H), 7.39 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.09 (t, *J* = 2.9 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.62 (d, *J* = 1.9 Hz, 1H), 6.41 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.12 (d, *J* = 8.1 Hz, 1H), 4.52 (s, 1H), 4.41 (s, 2H), 4.28 – 4.18 (m, 2H), 3.04 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.56, 168.43, 145.50, 142.01, 139.46, 139.42, 135.86, 133.77, 130.15, 129.40, 128.71, 127.78, 127.37, 122.55, 122.30, 122.16, 118.54, 117.62, 112.02, 108.43, 99.14, 98.26, 78.88, 63.36, 48.28, 26.27, 14.08. ESI-HRMS m/z: 560.1181. [M + H]$^+$, calcd for $C_{29}H_{26}BrN_3O_4$+H^+, 560.1179.

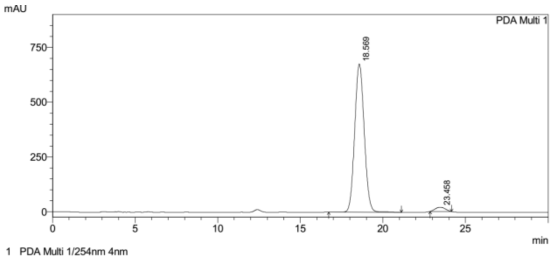


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.400	27171464	656090	49.196	55.781
2	24.386	28059968	520092	50.804	44.219
Total		55231433	1176183	100.000	100.000

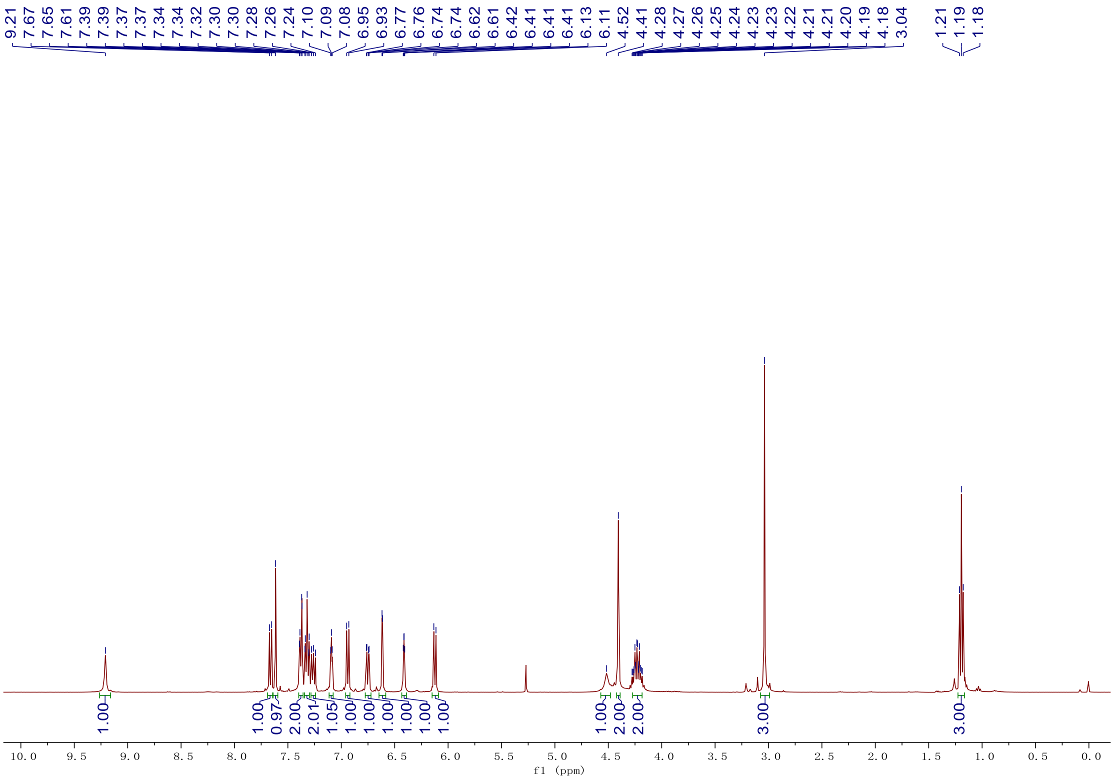


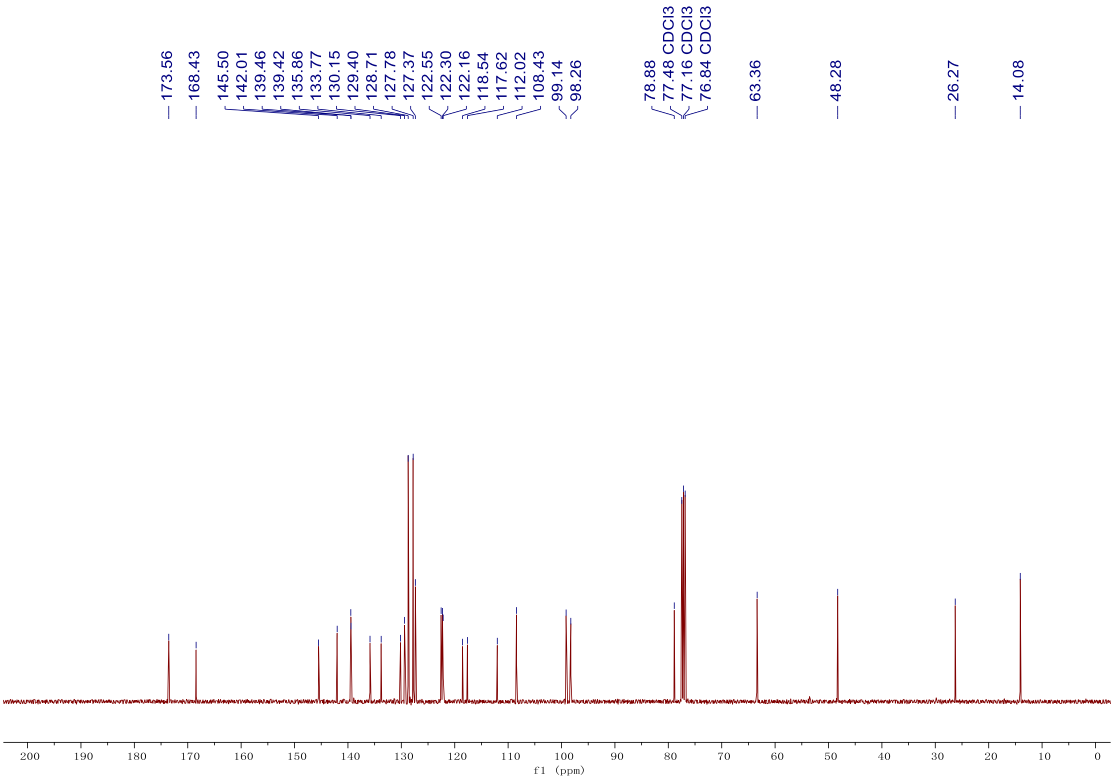
1 PDA Multi 1/254nm 4nm

PeakTable

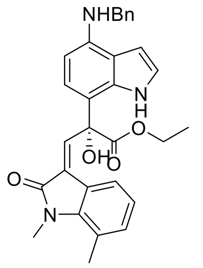
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.569	27217137	676859	97.036	97.171
2	23.458	831388	19705	2.964	2.829
Total		28048525	696564	100.000	100.000





ethyl (*R*, *E*)-2-(4-(benzylamino)-1H-indol-7-yl)-3-(1,7-dimethyl-2-oxoindolin-3-ylidene)-2-hydroxy propanoate (3ra)

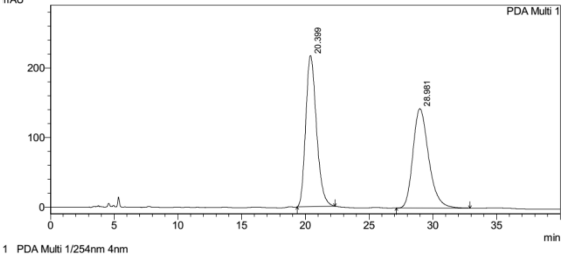


3ra 85% yield, 95% ee

3ra was obtained as a yellow solid in 85% yield (24 h) and 95% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 20.42 min, t_{major} = 28.84 min; $[\alpha]_D^{20}$ = + 104.3 (*c* 0.30, MeOH);

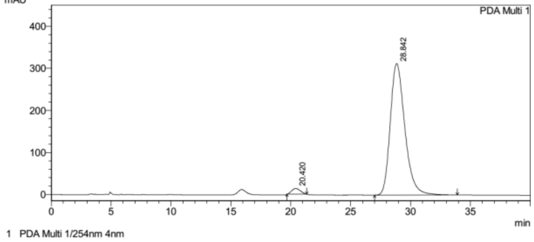
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 7.63 – 7.60 (m, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.13 (t, *J* = 2.9 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.42 (t, *J* = 2.7 Hz, 1H), 6.13 (d, *J* = 8.1 Hz, 1H), 4.80 (s, 1H), 4.40 (s, 2H), 4.28 – 4.19 (m, 2H), 3.20 (s, 3H), 2.35 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.75, 169.22, 142.11, 141.87, 139.53, 139.36, 133.93, 133.71, 131.04, 128.71, 127.85, 127.35, 126.80, 122.47, 122.39, 122.18, 120.75, 119.18, 117.59, 112.36, 99.19, 98.05, 78.70, 63.04, 48.38, 29.61, 19.16, 14.12. ESI-HRMS m/z: 496.2232. [M + H]$^+$, calcd for $C_{30}H_{29}N_3O_4$+H$^+$, 496.2231.



PeakTable

PDA Ch1 254nm 4nm

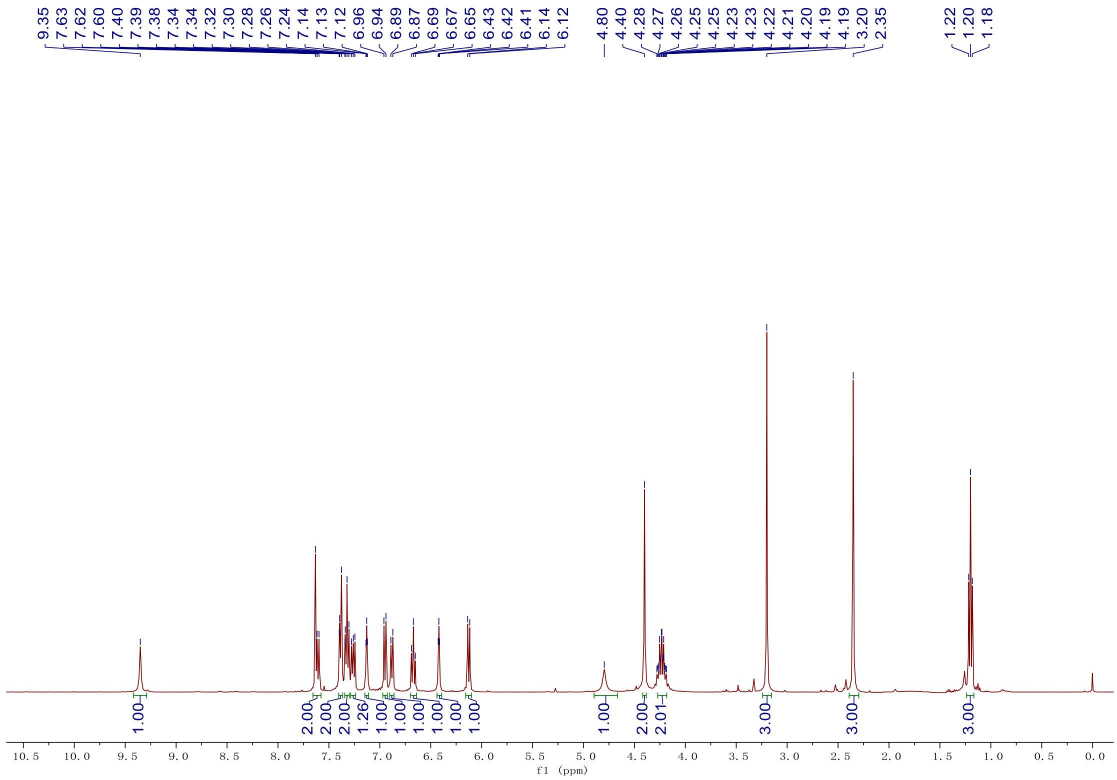
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.399	12747836	217151	50.884	60.276
2	28.981	12304787	143109	49.116	39.724
Total		25052624	360260	100.000	100.000

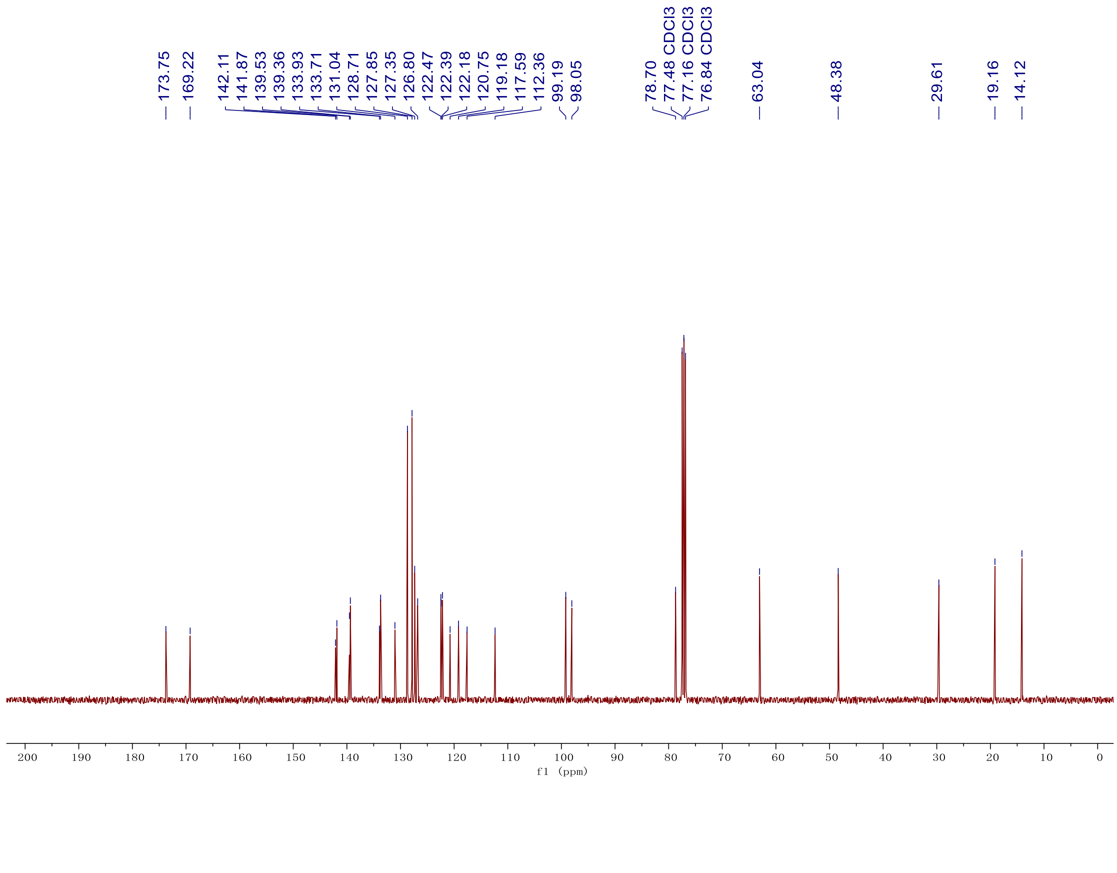


PeakTable

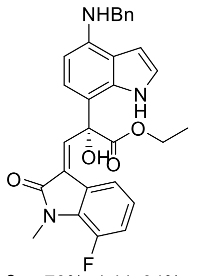
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.420	691367	13564	2.539	4.155
2	28.842	26542919	312921	97.461	95.845
Total		27234286	326485	100.000	100.000


9.35
7.63
7.62
7.60
7.40
7.39
7.38
7.34
7.34
7.32
7.30
7.28
7.26
7.24
7.14
7.13
7.12
6.96
6.94
6.89
6.87
6.69
6.67
6.65
6.43
6.42
6.41
6.14
6.12
4.80
4.40
4.28
4.27
4.26
4.25
4.25
4.23
4.23
4.22
4.21
4.20
4.19
4.19
3.20
2.35
1.22
1.20
1.18
1.00
2.00
2.00
2.00
1.26
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.01
3.00
3.00
3.00
f1 (ppm)

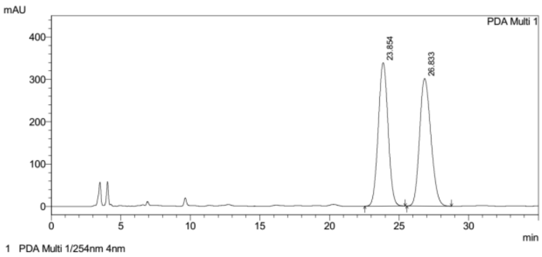

173.75
169.22
142.11
141.87
139.53
139.36
133.93
133.71
131.04
128.71
127.85
127.35
126.80
122.47
122.39
122.18
120.75
119.18
117.59
112.36
99.19
98.05
78.70
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.04
48.38
29.61
19.16
14.12
f1 (ppm)

ethyl (*R*, *E*)-2-(4-(benzylamino)-1H-indol-7-yl)-3-(7-fluoro-1-methyl-2-oxoindolin-3-ylidene)-2-hydroxy propanoate (3sa)



3sa 78% yield, 94% ee

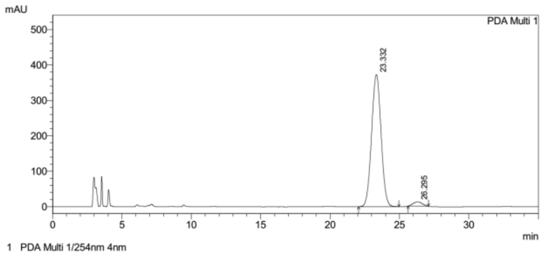
3sa was obtained as a yellow solid in 78% yield (24 h) and 94% ee.
The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 23.33 min, t_{minor} = 26.29 min; $[\alpha]_D^{20}$ = + 110.5 (*c* 0.46, MeOH);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 7.63 (s, 1H), 7.61 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.28 (m, 1H), 7.12 (dd, *J* = 3.3, 2.4 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.96 – 6.91 (m, 1H), 6.78 – 6.72 (m, 1H), 6.44 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.17 (d, *J* = 8.1 Hz, 1H), 4.44 (s, 2H), 4.30 – 4.18 (m, 3H), 3.40 (d, *J* = 2.9 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.72, 168.04, 148.90, 146.49, 142.08, 139.87, 139.44, 133.78, 131.19 (d, *J* = 8.2 Hz), 130.73 (d, *J* = 3.3 Hz), 128.76, 127.83, 127.43, 124.43 (d, *J* = 3.1 Hz), 122.95 (d, *J* = 3.7 Hz), 122.73 (d, *J* = 6.5 Hz), 122.58, 122.22, 118.01, 117.82, 117.67, 112.06, 99.21, 98.35, 78.83, 63.57, 48.35, 28.93 (d, *J* = 6.0 Hz), 14.10. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -137.42 (dq, *J* = 10.9, 3.3 Hz). ESI-HRMS m/z: 500.1981. $[M + H]^+$, calcd for $C_{29}H_{26}FN_3O_4+H^+$, 500.1980.



PeakTable

PDA Ch1 254nm 4nm

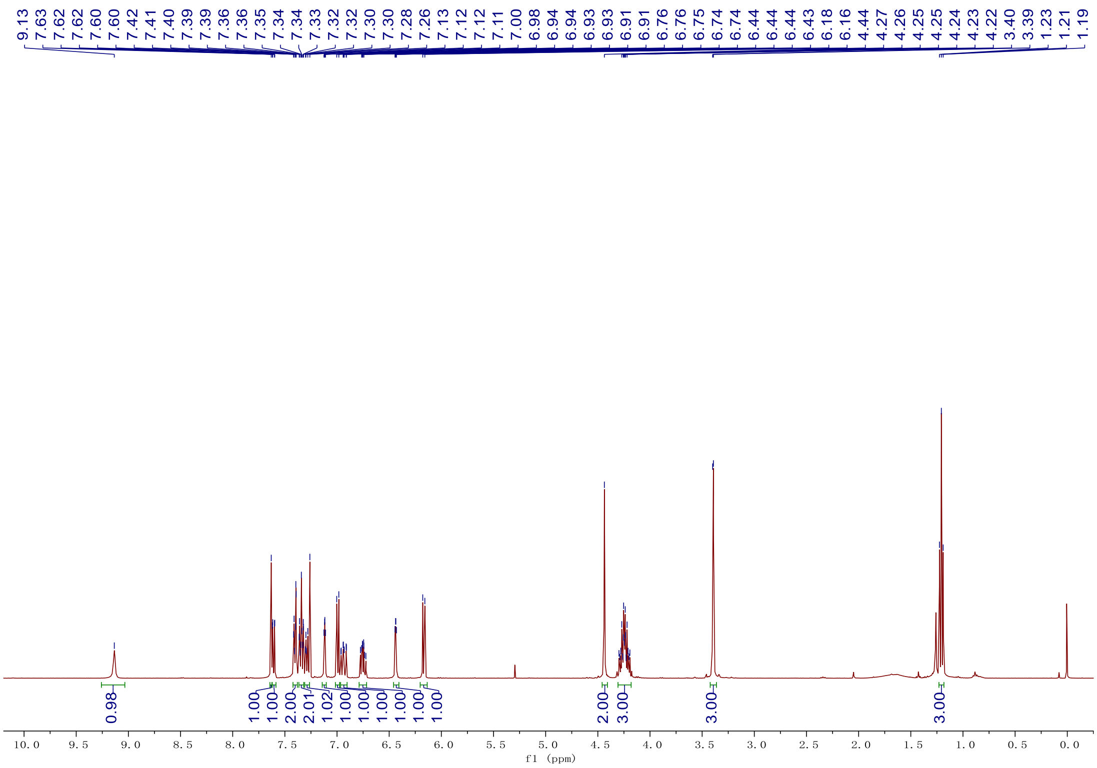
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.854	16546349	338424	49.235	52.929
2	26.833	17060273	300968	50.765	47.071
Total		33606622	639392	100.000	100.000

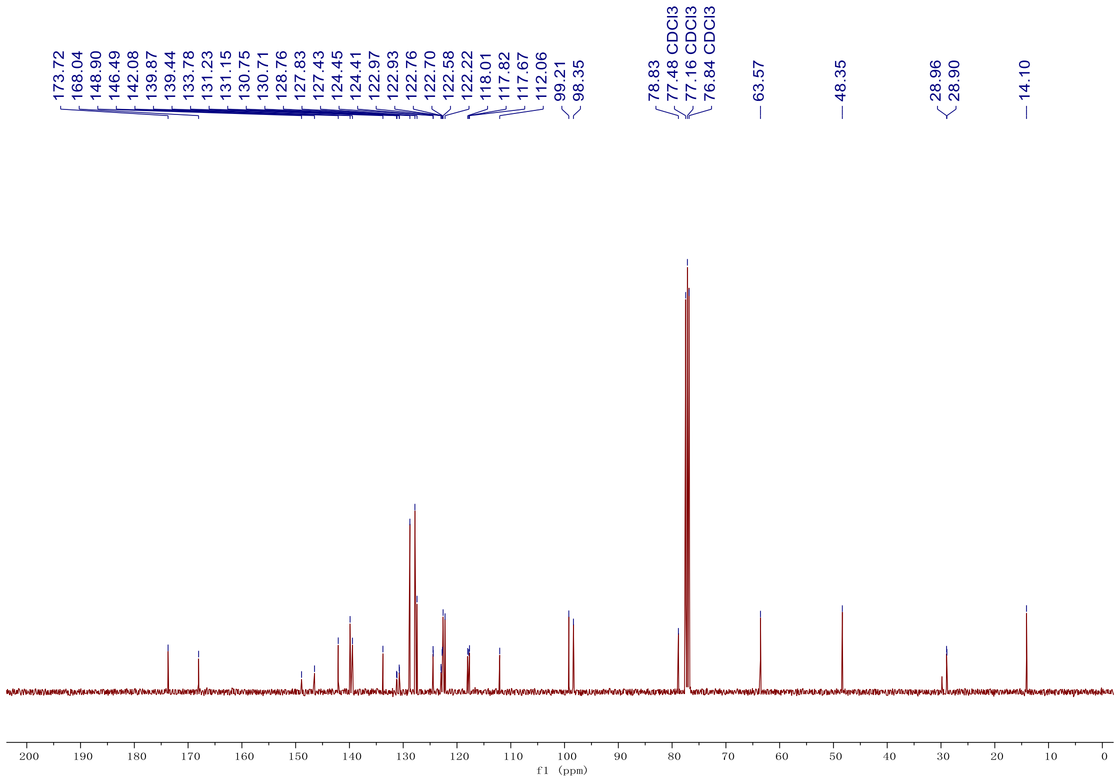


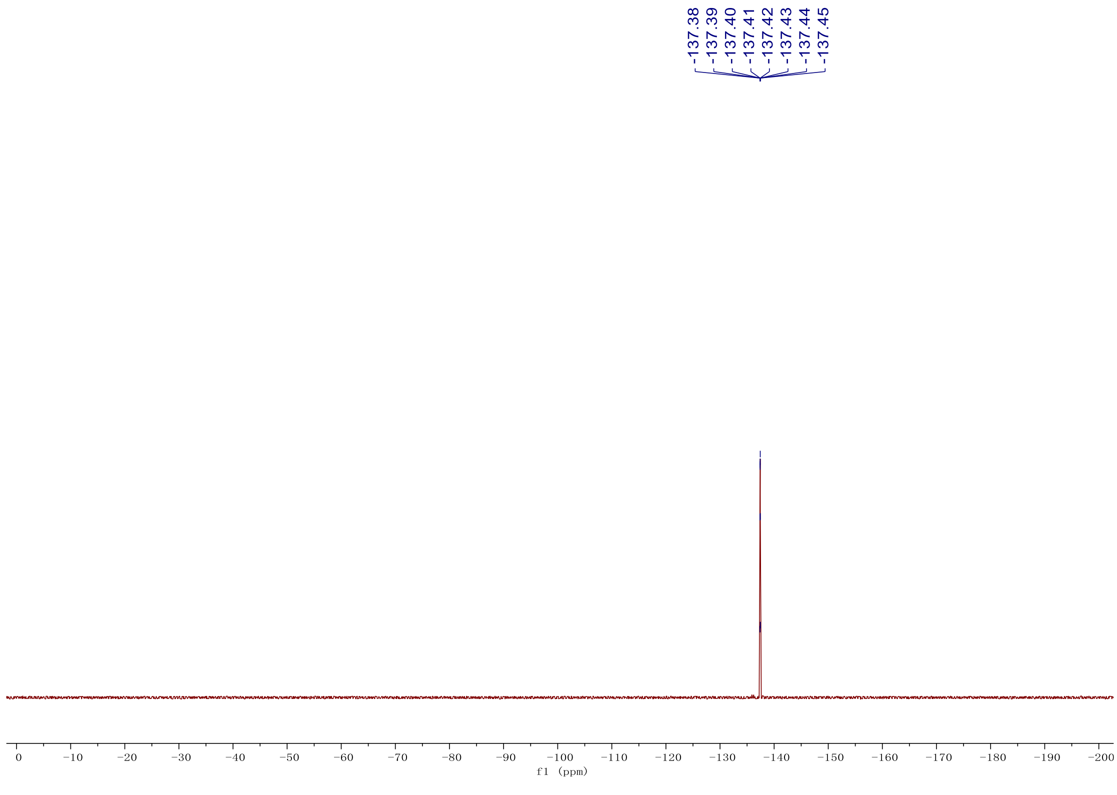
PeakTable

PDA Ch1 254nm 4nm

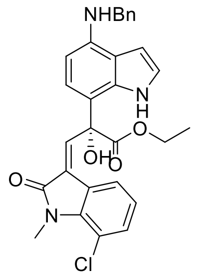
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.332	17738304	372650	97.001	96.936
2	26.295	548343	11781	2.999	3.064
Total		18286647	384431	100.000	100.000




173.72
168.04
148.90
146.49
142.08
139.87
139.44
133.78
131.23
131.15
130.75
130.71
128.76
127.83
127.43
124.45
124.41
122.97
122.93
122.76
122.70
122.58
122.22
118.01
117.82
117.67
112.06
99.21
98.35
78.83
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.57
48.35
28.96
28.90
14.10
f1 (ppm)


-137.38
-137.39
-137.40
-137.41
-137.42
-137.43
-137.44
-137.45
f1 (ppm)

ethyl (*R*, *E*)-2-(4-(benzylamino)-1*H*-indol-7-yl)-3-(7-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-hydroxy propanoate (3ta)

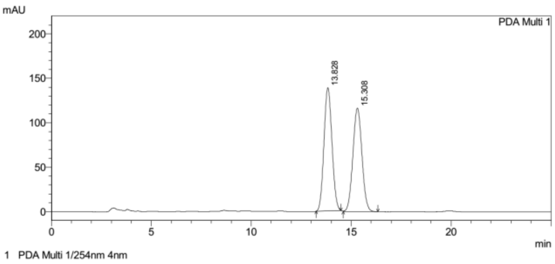


3ta 75% yield, 95% ee

3ta was obtained as a yellow solid in 75% yield (24 h) and 95% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 13.74 min, t_{major} = 15.30 min; $[\alpha]_D^{20}$ = + 118.4 (*c* 0.15, MeOH);

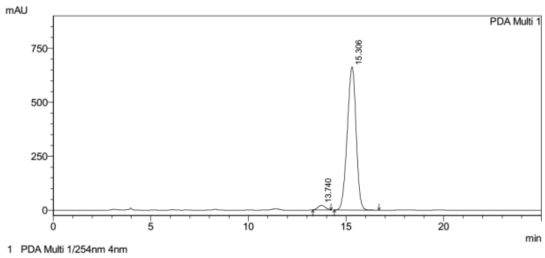
^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.22 (s, 1H), 7.70 – 7.67 (m, 2H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.11 – 7.07 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.68 (t, *J* = 7.9 Hz, 1H), 6.42 (dd, *J* = 3.2, 2.1 Hz, 1H), 6.13 (d, *J* = 8.1 Hz, 1H), 4.53 (s, 1H), 4.41 (s, 2H), 4.27 – 4.19 (m, 2H), 3.43 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.63, 168.76, 142.04, 140.48, 140.11, 139.44, 133.81, 132.19, 130.30, 128.74, 127.83, 127.40, 127.21, 123.16, 122.81, 122.56, 122.22, 117.66, 115.36, 111.91, 99.20, 98.25, 78.74, 63.37, 48.34, 29.81, 14.09. ESI-HRMS m/z: 516.1685. [M + H]$^+$, calcd for $C_{29}H_{26}ClN_3O_4+H^+$, 516.1685.



PeakTable

PDA Ch1 254nm 4nm

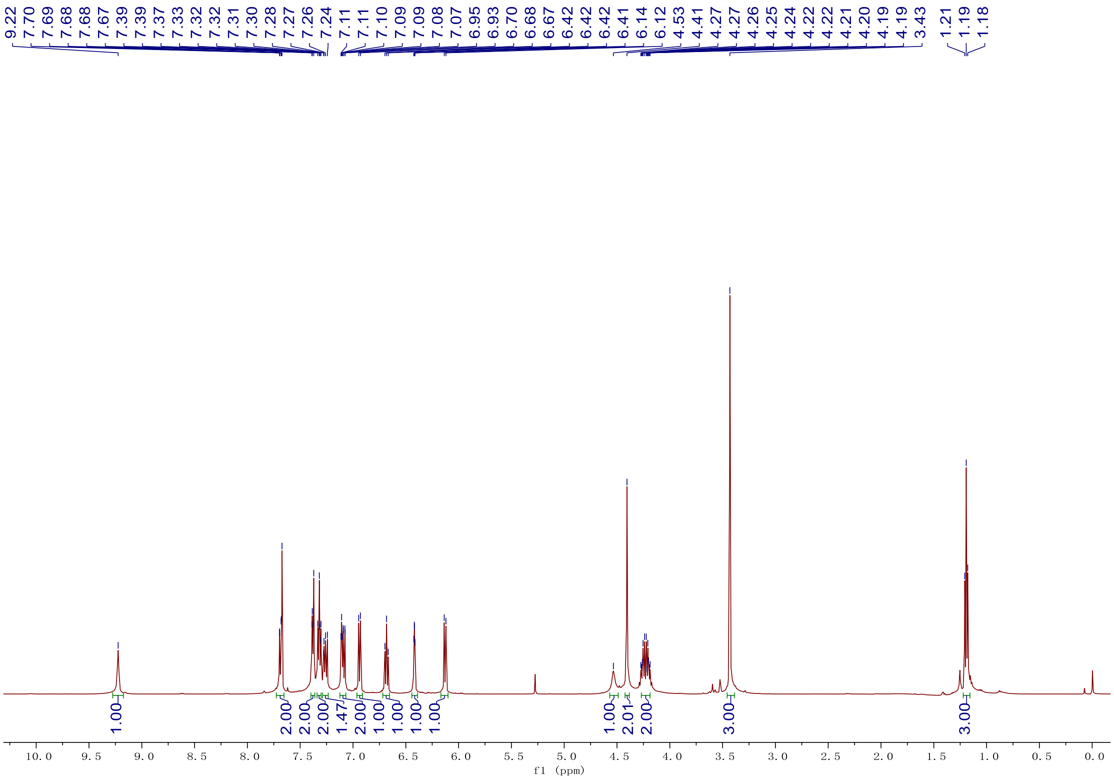
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.828	3870744	138612	51.315	54.320
2	15.308	3672322	116563	48.685	45.680
Total		7543066	255175	100.000	100.000

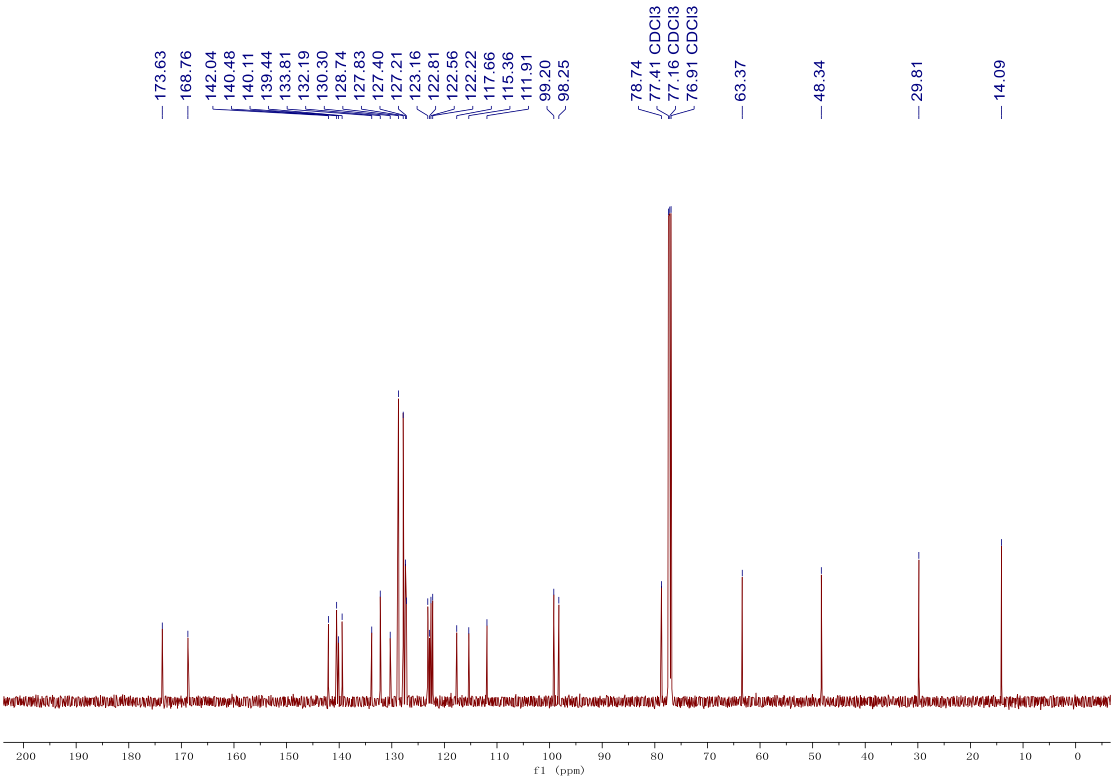


PeakTable

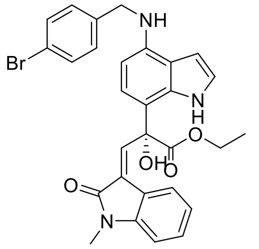
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.740	550706	21075	2.558	3.079
2	15.306	20980370	663375	97.442	96.921
Total		21531076	684450	100.000	100.000



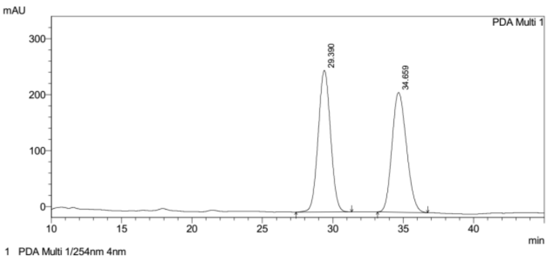


ethyl (*R*, *E*)-2-(4-((4-bromobenzyl)amino)-1*H*-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3ab)



3ab 86% yield, 95% ee

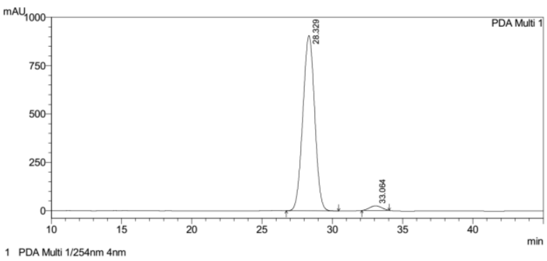
3ab was obtained as a yellow solid in 86% yield (24 h) and 95% ee. The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 28.32 min, t_{minor} = 33.06 min; $[\alpha]_D^{20}$ = + 4.1 (*c* 0.07, MeOH); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 7.78 – 7.76 (m, 1H), 7.56 (s, 1H), 7.45 – 7.42 (m, 2H), 7.27 – 7.24 (m, 2H), 7.20 (td, *J* = 7.7, 1.2 Hz, 1H), 7.12 (dd, *J* = 3.3, 2.4 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.84 (td, *J* = 7.7, 1.1 Hz, 1H), 6.69 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.43 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.08 (d, *J* = 8.1 Hz, 1H), 4.39 (s, 2H), 4.28 – 4.19 (m, 3H), 3.14 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.79, 168.31, 144.71, 141.62, 138.61, 138.26, 133.84, 131.80, 131.21, 130.10, 129.31, 128.42, 122.67, 122.47, 122.13, 121.08, 120.17, 117.67, 112.69, 107.88, 99.34, 98.19, 78.89, 63.46, 47.67, 26.24, 14.11. ESI-HRMS m/z: 560.1182. [M + H]$^+$, calcd for $C_{29}H_{26}BrN_3O_4+H^+$, 560.1179.



PeakTable

PDA Ch1 254nm 4nm

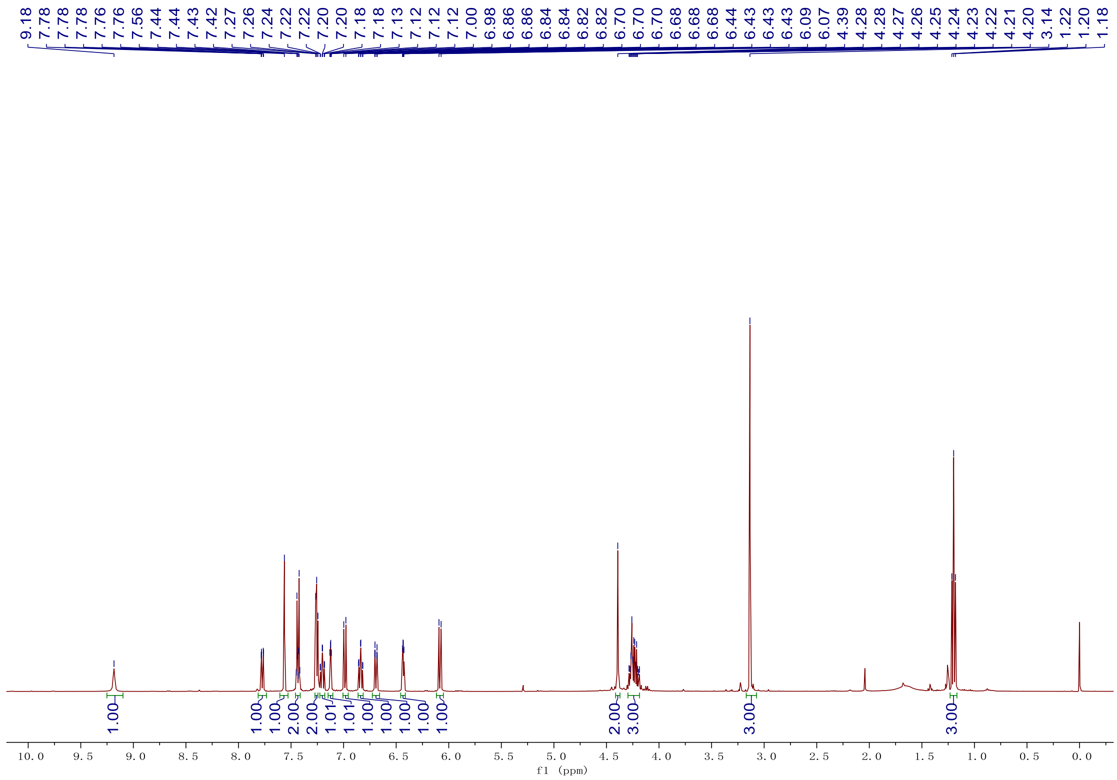
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.390	15493746	253543	50.254	54.216
2	34.659	15337104	214109	49.746	45.784
Total		30830850	467652	100.000	100.000

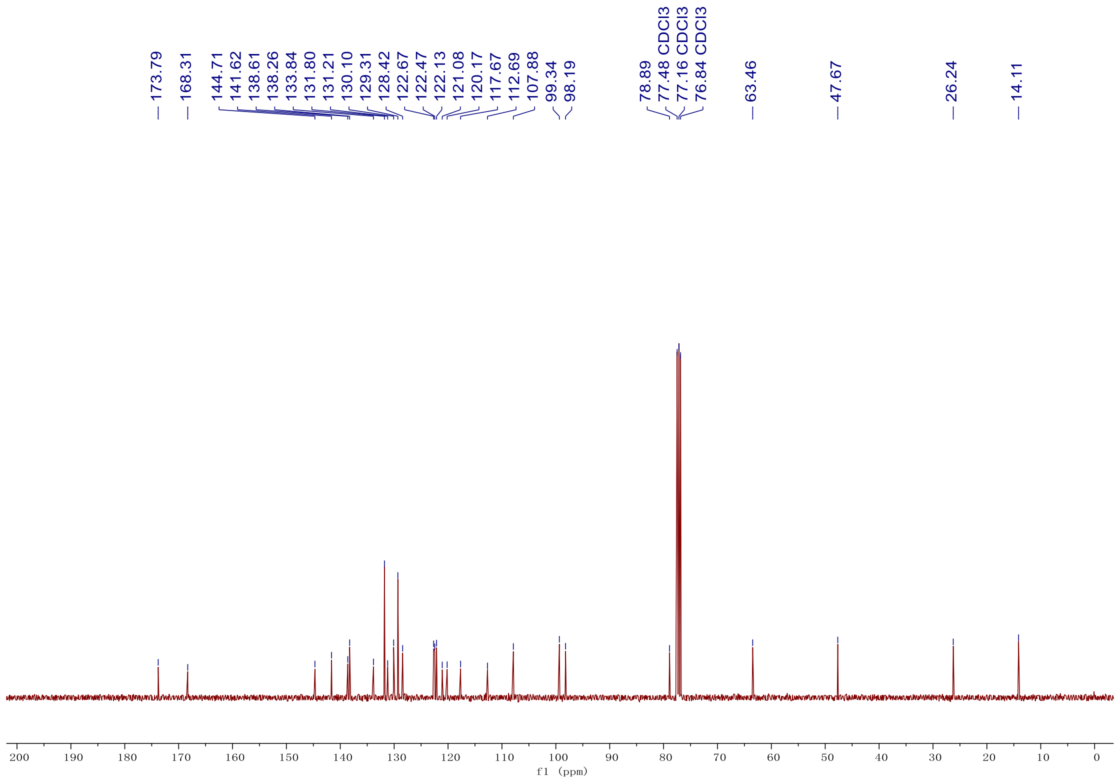


PeakTable

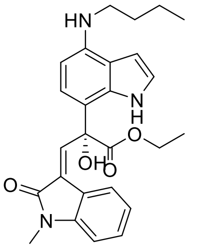
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.329	53081955	906764	97.400	97.462
2	33.064	1417040	23613	2.600	2.538
Total		54498995	930377	100.000	100.000


9.18 7.78 7.78 7.78 7.76 7.56 7.44 7.44 7.43 7.42 7.27 7.26 7.24 7.22 7.22 7.20 7.20 7.18 7.18 7.13 7.12 7.12 7.12 7.00 6.98 6.86 6.84 6.84 6.82 6.82 6.70 6.70 6.70 6.68 6.68 6.68 6.44 6.43 6.43 6.43 6.09 6.07 4.39 4.28 4.28 4.27 4.26 4.25 4.24 4.23 4.22 4.21 4.20 3.14 1.22 1.20 1.18
1.00 1.00 1.00 2.00 2.00 1.01 1.01 1.00 1.00 1.00 1.00 2.00 3.00 3.00 3.00
f1 (ppm)


173.79 168.31 144.71 141.62 138.61 138.26 133.84 131.80 131.21 130.10 129.31 128.42 122.67 122.47 122.13 121.08 120.17 117.67 112.69 107.88 99.34 98.19 78.89 77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 63.46 47.67 26.24 14.11
f1 (ppm)

ethyl (*R*, *E*)-2-(4-(butylamino)-1*H*-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3ac)

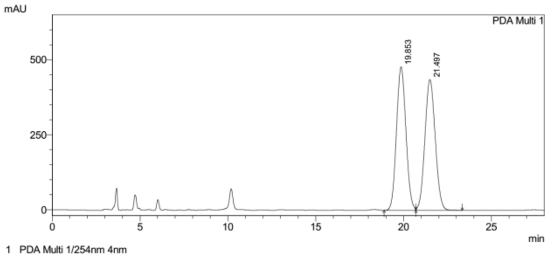


3ac 80% yield, 90% ee

3ac was obtained as a yellow solid in 80% yield (24 h) and 90% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 80 : 20 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 19.89 min, t_{major} = 21.51 min; $[\alpha]_D^{20}$ = + 3.2 (*c* 0.10, MeOH);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.25 (s, 1H), 7.76 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.64 (s, 1H), 7.16 (td, *J* = 7.7, 1.2 Hz, 1H), 7.12 – 7.10 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.81 (td, *J* = 7.7, 1.1 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.42 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.12 (d, *J* = 8.1 Hz, 1H), 4.57 (s, 1H), 4.29 – 4.20 (m, 2H), 3.21 (t, *J* = 7.2 Hz, 2H), 3.03 (s, 3H), 1.70 – 1.63 (m, 2H), 1.50 – 1.41 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.79, 168.42, 144.45, 142.24, 139.11, 133.85, 131.12, 129.86, 128.54, 122.47, 122.32, 122.24, 120.17, 117.54, 111.84, 107.77, 98.76, 98.05, 78.89, 63.19, 43.63, 31.84, 26.09, 20.50, 14.09, 14.06. ESI-HRMS m/z: 448.2230. $[M + H]^+$, calcd for $C_{26}H_{29}N_3O_4+H^+$, 448.2231.

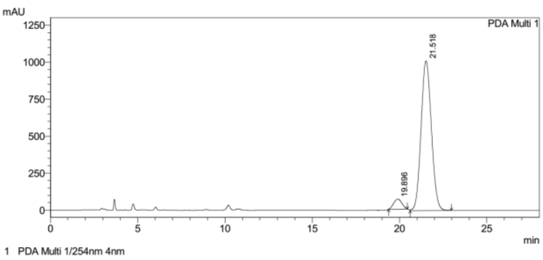


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.853	17872566	478655	49.987	52.308
2	21.497	17881646	436409	50.013	47.692
Total		35754213	915064	100.000	100.000

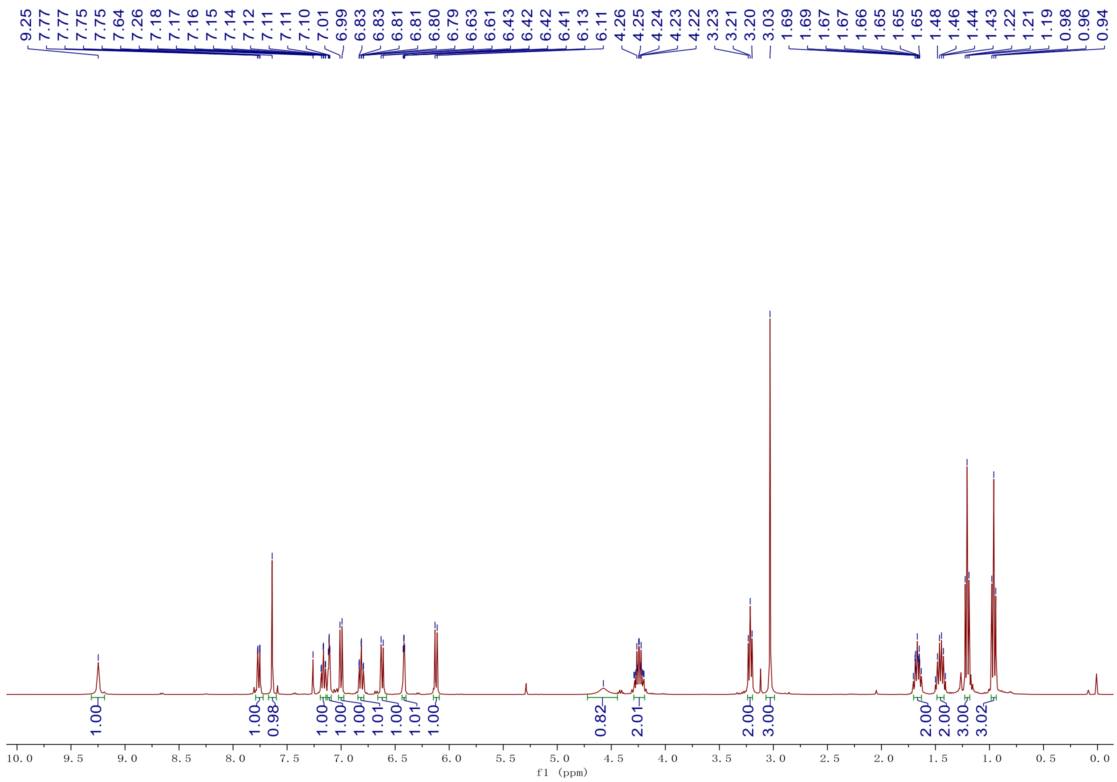


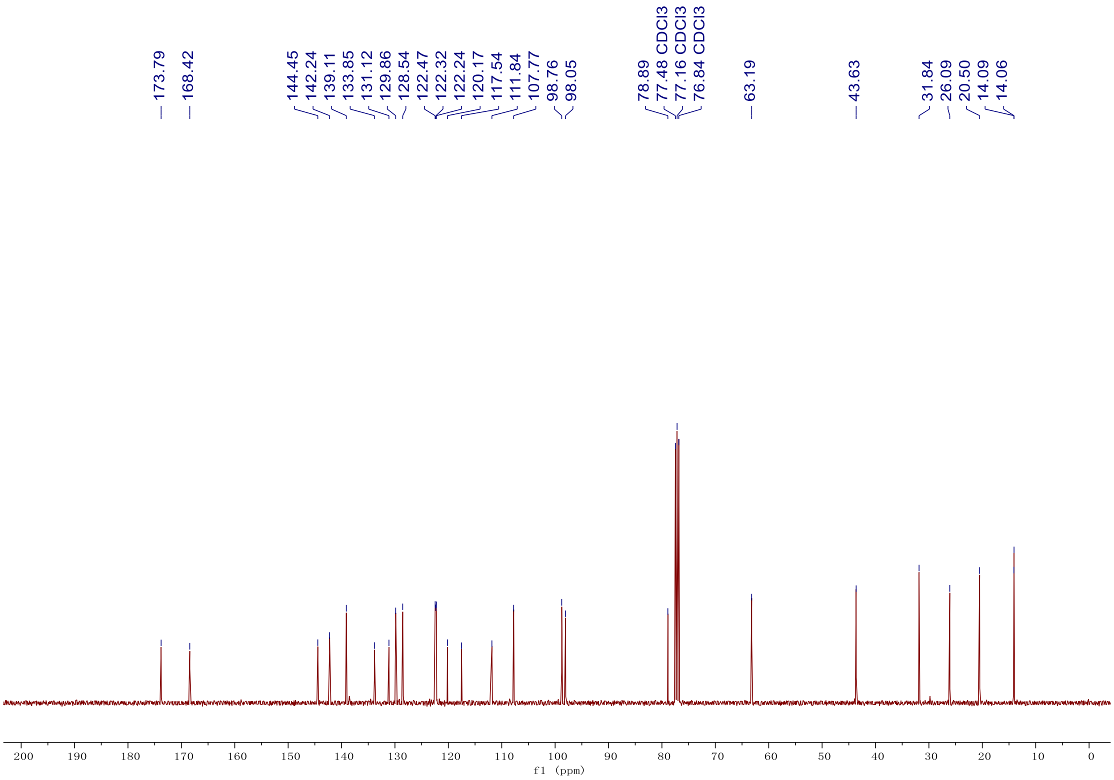
1 PDA Multi 1/254nm 4nm

PeakTable

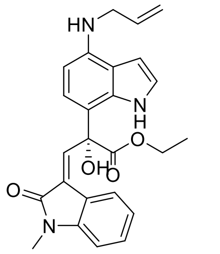
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.896	2234223	68359	5.107	6.329
2	21.518	41516329	1011743	94.893	93.671
Total		43750551	1080102	100.000	100.000





ethyl (*R*, *E*)-2-(4-(allylamino)-1*H*-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene)propanoate (3ad)

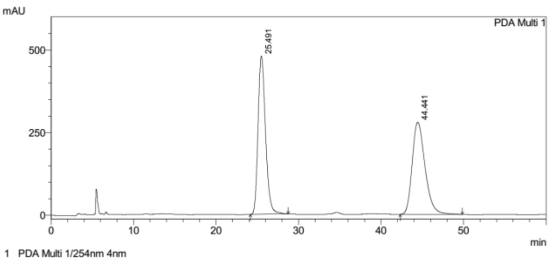


3ad 77% yield, 94% ee

3ad was obtained as a yellow solid in 77% yield (24 h) and 94% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak IC, hexane/i-PrOH = 80 : 20 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 25.46 min, t_{major} = 44.16 min; $[\alpha]_D^{20}$ = + 11.5 (*c* 0.32, MeOH);

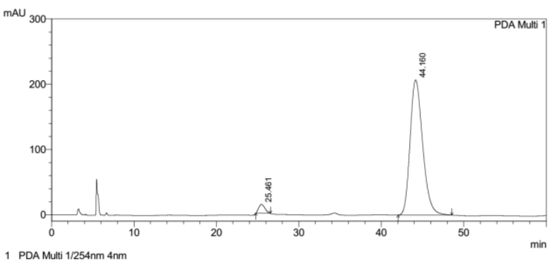
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 7.77 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.62 (s, 1H), 7.17 (td, *J* = 7.7, 1.2 Hz, 1H), 7.12 (t, *J* = 2.8 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.43 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.14 (d, *J* = 8.1 Hz, 1H), 6.06 – 5.97 (m, 1H), 5.33 – 5.28 (m, 1H), 5.17 (dd, *J* = 10.3, 1.5 Hz, 1H), 4.51 (s, 1H), 4.29 – 4.21 (m, 2H), 3.89 – 3.87 (m, 2H), 3.05 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.76, 168.41, 144.50, 141.77, 138.95, 135.56, 133.87, 131.14, 129.91, 128.52, 122.48, 122.47, 122.14, 120.17, 117.75, 116.48, 112.34, 107.79, 99.22, 98.11, 78.90, 63.25, 46.58, 26.11, 14.09. ESI-HRMS m/z: 432.1913. $[M + H]^+$, calcd for $C_{25}H_{26}N_3O_4$+H^+, 432.1918.



PeakTable

PDA Ch1 254nm 4nm

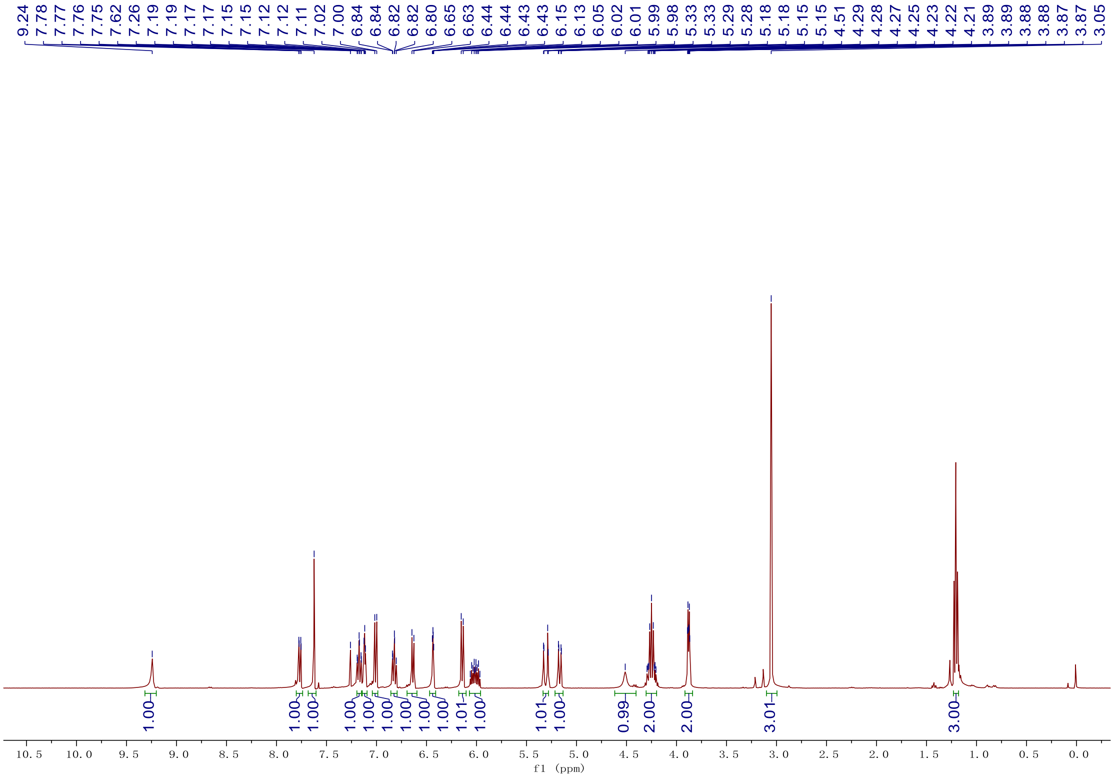
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.491	30142427	478768	49.994	63.202
2	44.441	30149884	278758	50.006	36.798
Total		60292311	757525	100.000	100.000

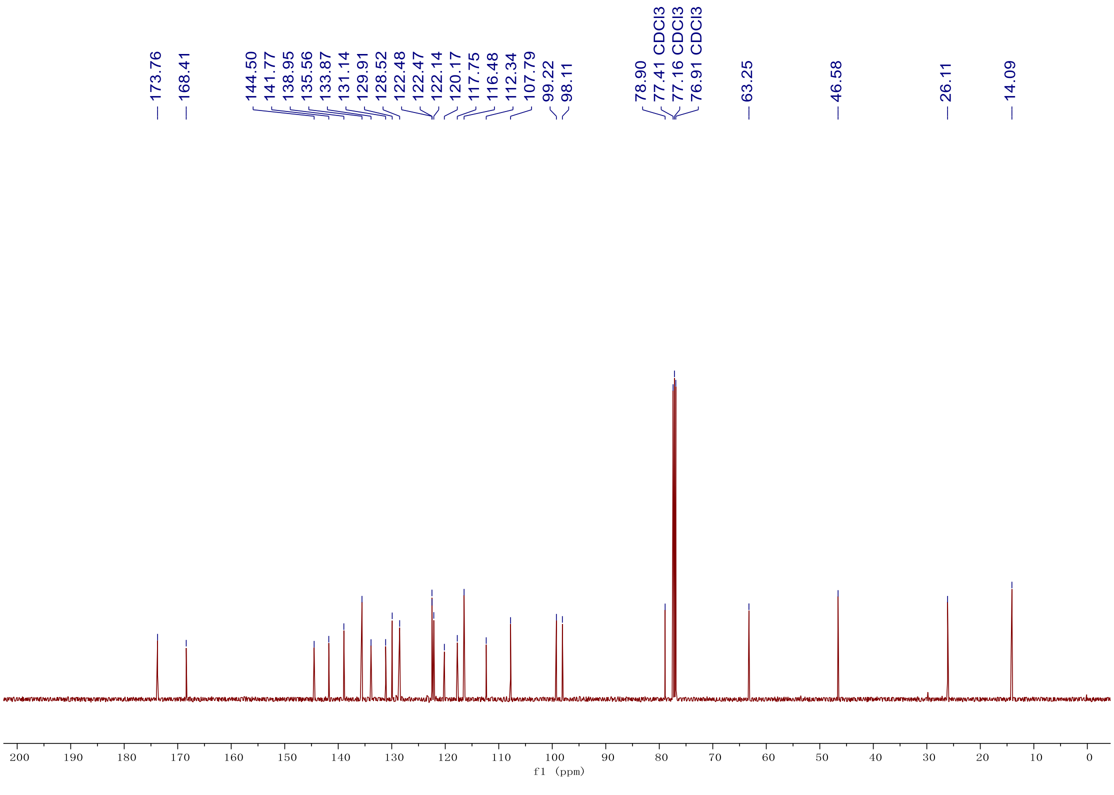


PeakTable

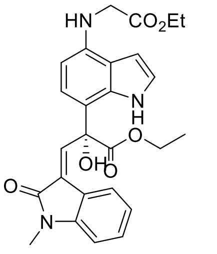
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.461	708018	13461	3.125	6.107
2	44.160	21945436	206967	96.875	93.893
Total		22653453	220429	100.000	100.000


9.24 7.78 7.77 7.76 7.75 7.62 7.26 7.19 7.17 7.17 7.15 7.12 7.12 7.11 7.02 7.00 6.84 6.84 6.82 6.82 6.80 6.65 6.63 6.44 6.44 6.43 6.43 6.15 6.13 6.05 6.02 6.01 5.99 5.98 5.33 5.33 5.29 5.28 5.18 5.18 5.15 5.15 4.51 4.29 4.28 4.27 4.25 4.23 4.22 4.21 3.89 3.89 3.88 3.87 3.87 3.05
1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.01 1.00 1.01 1.00 0.99 2.00 2.00 3.01 3.00
f1 (ppm)

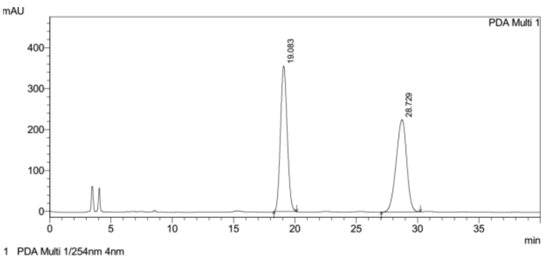

173.76 168.41 144.50 141.77 138.95 135.56 133.87 131.14 129.91 128.52 122.48 122.47 122.14 120.17 117.75 116.48 112.34 107.79 99.22 98.11 78.90 77.41 CDCl3 77.16 CDCl3 76.91 CDCl3 63.25 46.58 26.11 14.09
f1 (ppm)

ethyl (*R*, *E*)-2-(4-((2-ethoxy-2-oxoethyl)amino)-1*H*-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3ae)



3ae 88% yield, 96% ee

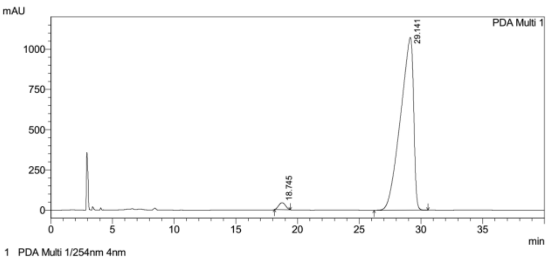
3ae was obtained as a yellow solid in 88% yield (24 h) and 96% ee. The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 18.74 min, t_{major} = 29.14 min; $[\alpha]_D^{20}$ = + 110.3 (*c* 0.50, MeOH); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 1H), 7.19 (td, *J* = 7.7, 1.2 Hz, 1H), 7.13 (t, *J* = 2.9 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.83 (td, *J* = 7.7, 1.1 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.52 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.02 (d, *J* = 8.0 Hz, 1H), 4.68 (s, 1H), 4.29 – 4.22 (m, 4H), 4.00 (s, 2H), 3.13 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.81, 171.25, 168.32, 144.69, 140.88, 138.26, 133.87, 131.36, 130.08, 128.45, 122.72, 122.49, 122.09, 120.15, 117.93, 112.95, 107.86, 99.19, 98.47, 78.85, 63.44, 61.49, 45.82, 26.23, 14.32, 14.09. ESI-HRMS m/z: 478.1972. $[M + H]^+$, calcd for $C_{26}H_{27}N_3O_6+H^+$, 478.1973.



PeakTable

PDA Ch1 254nm 4nm

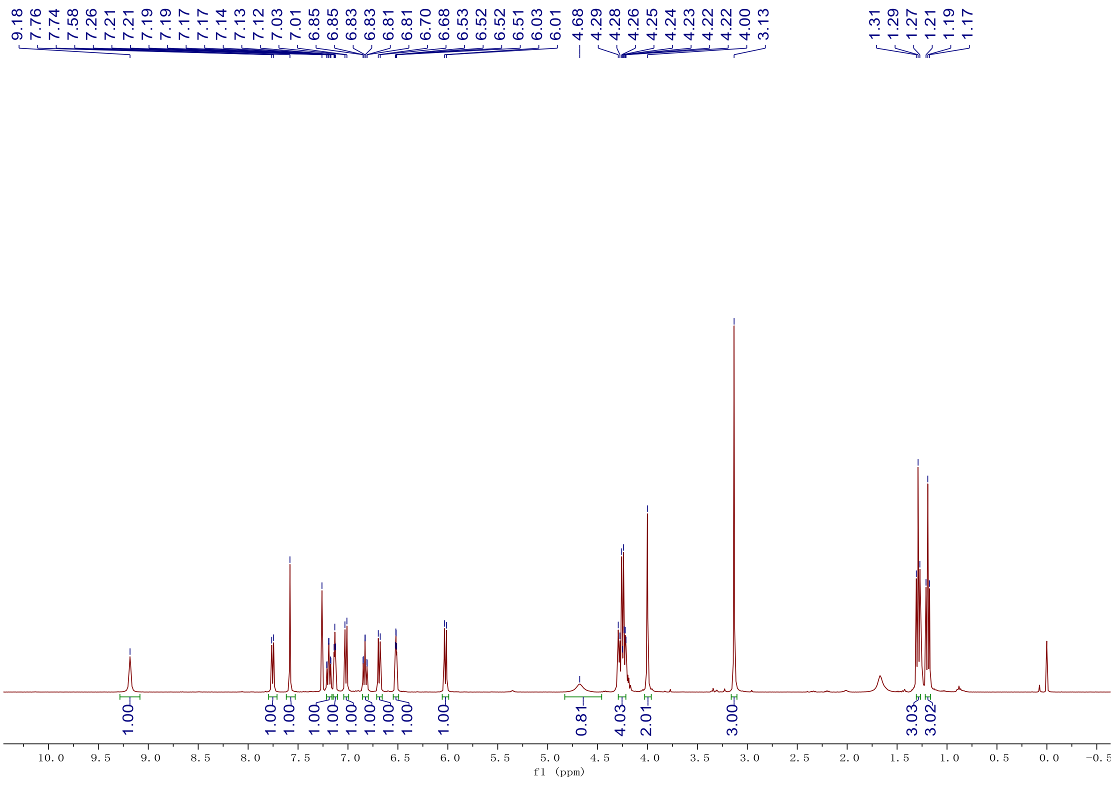
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.083	13599335	355653	50.372	61.207
2	28.729	13398639	225415	49.628	38.793
Total		26997974	581068	100.000	100.000

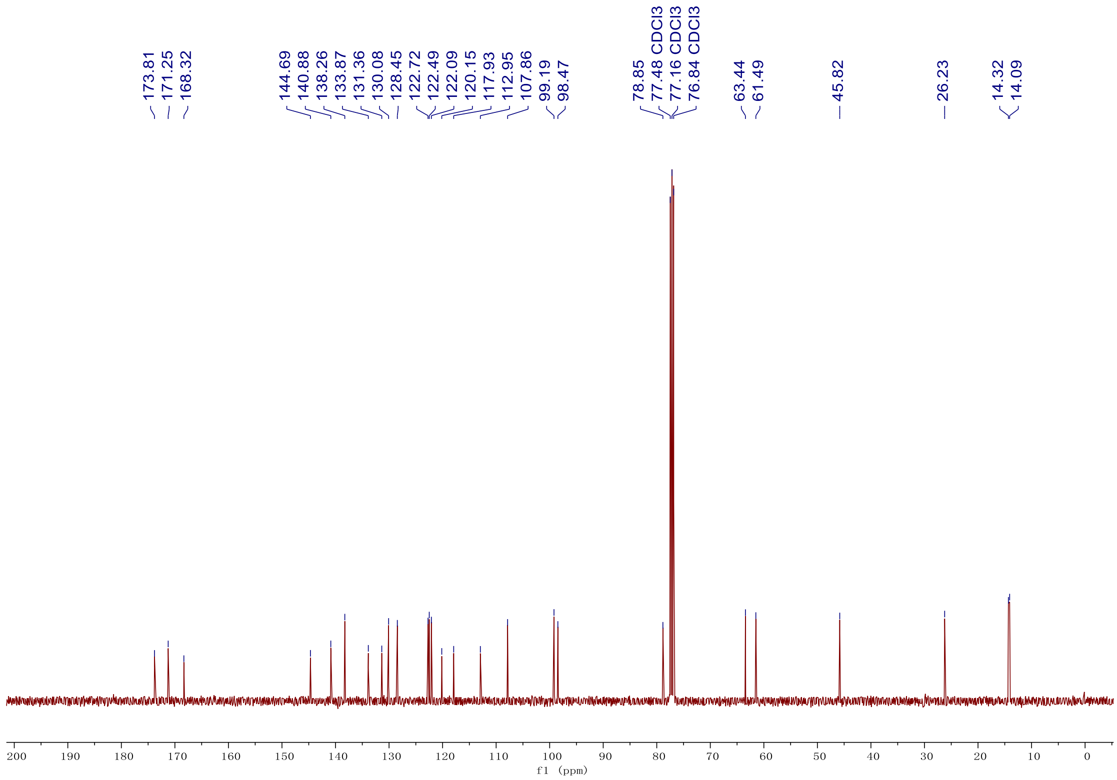


PeakTable

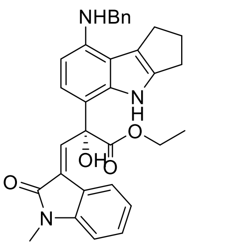
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.745	1624371	42723	2.010	3.830
2	29.141	79192101	1072690	97.990	96.170
Total		80816472	1115413	100.000	100.000



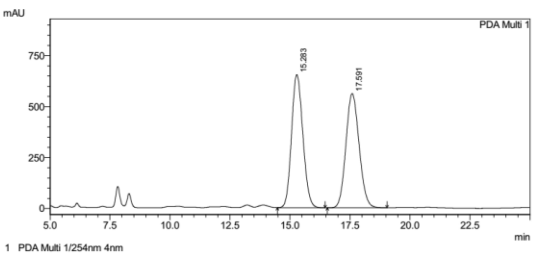


ethyl (*R*, *E*)-2-(8-(benzylamino)-1,2,3,4-tetrahydrocyclopenta[b]indol-5-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3af)



3af 45% yield, 80% ee

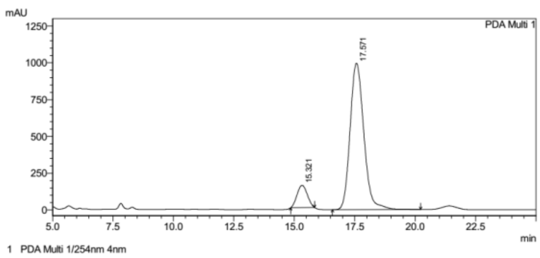
3af was obtained as a reddish brown solid in 45% yield (72 h) and 80% ee. The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 15.32 min, t_{major} = 17.57 min; $[\alpha]_D^{20}$ = + 12.9 (*c* 0.23, MeOH); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.55 (s, 1H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.22 – 7.20 (m, 1H), 6.88 (t, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.10 (d, *J* = 8.1 Hz, 1H), 4.40 (s, 2H), 4.31 – 4.18 (m, 2H), 4.04 (s, 1H), 3.21 (s, 3H), 2.96 (t, *J* = 7.0 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.55 – 2.51 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.04, 168.30, 144.79, 141.92, 141.78, 139.79, 138.44, 138.21, 131.38, 130.08, 128.74, 128.50, 127.46, 127.25, 122.47, 121.20, 120.28, 117.13, 114.64, 112.71, 107.84, 99.39, 78.91, 63.50, 48.28, 29.46, 26.29, 25.86, 25.74, 14.14. ESI-HRMS m/z: 522.2384. [M + H]$^+$, calcd for $C_{32}H_{31}N_3O_4$+H$^+$, 522.2387.



PeakTable

PDA Ch1 254nm 4nm

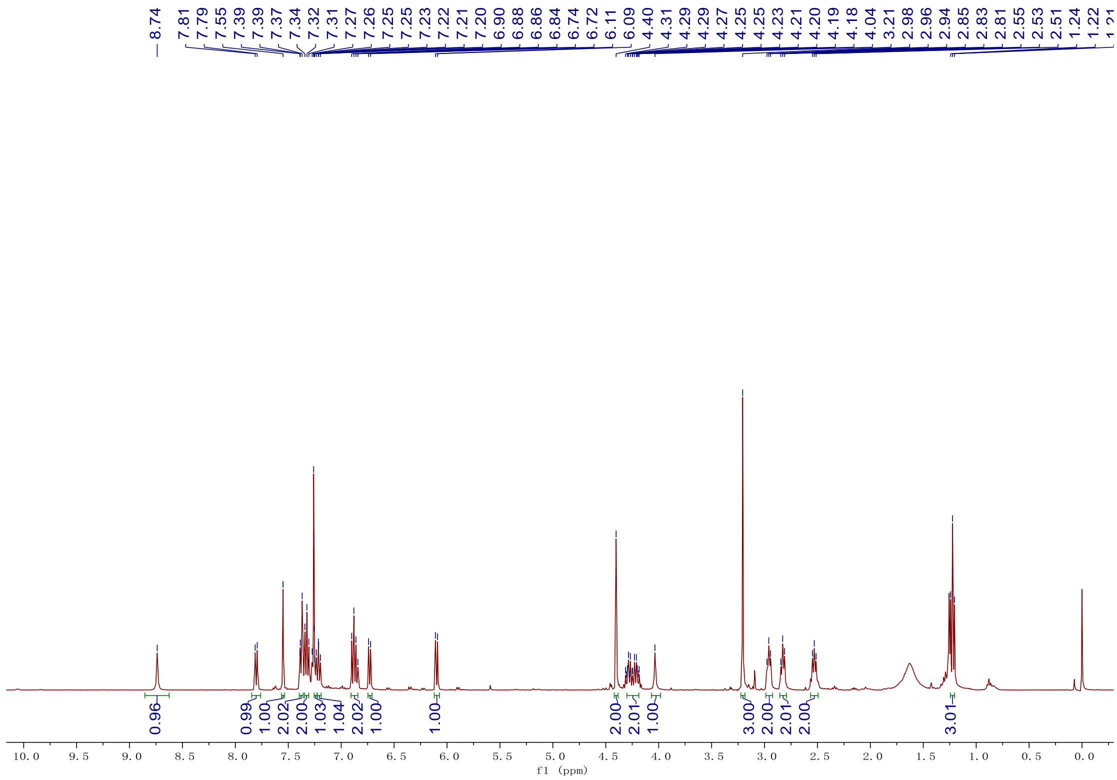
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.283	21483504	653176	49.978	53.812
2	17.591	21502071	560638	50.022	46.188
Total		42985575	1213814	100.000	100.000

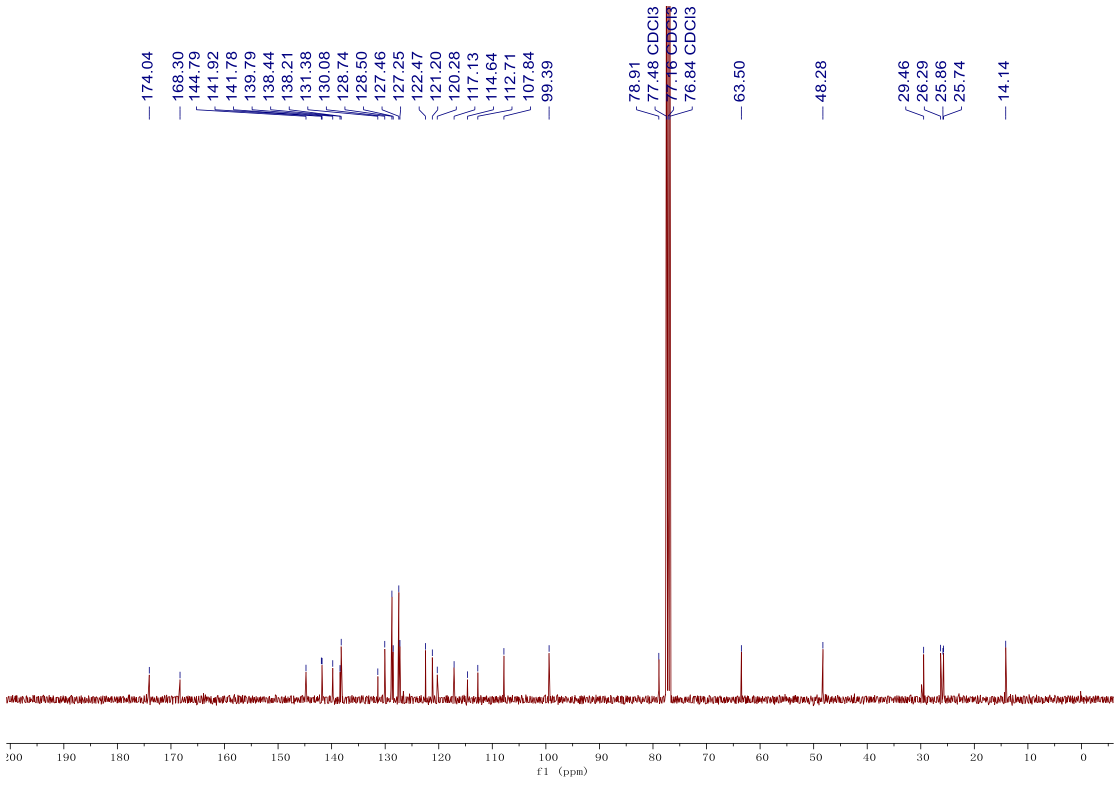


PeakTable

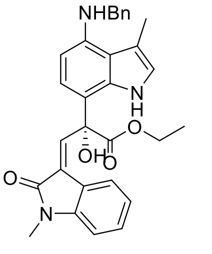
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.321	4473032	152062	10.204	13.248
2	17.571	39362362	995722	89.796	86.752
Total		43835394	1147784	100.000	100.000


8.74
7.81
7.79
7.55
7.39
7.39
7.37
7.34
7.32
7.31
7.27
7.26
7.25
7.25
7.23
7.22
7.21
7.20
6.90
6.88
6.86
6.84
6.74
6.72
6.11
6.09
4.40
4.31
4.29
4.29
4.27
4.25
4.25
4.23
4.21
4.20
4.19
4.18
4.04
3.21
2.98
2.96
2.94
2.85
2.83
2.81
2.55
2.53
2.51
1.24
1.22
0.96
0.99
1.00
2.02
2.00
1.03
1.04
2.02
1.00
1.00
2.00
2.01
1.00
3.00
2.00
2.01
2.00
3.01
f1 (ppm)

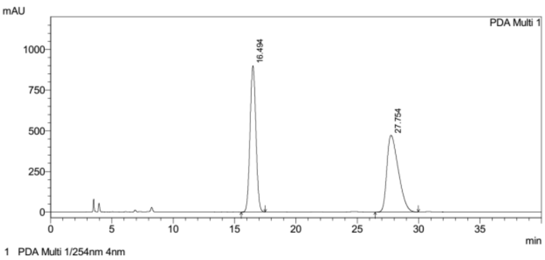

174.04
168.30
144.79
141.92
141.78
139.79
138.44
138.21
131.38
130.08
128.74
128.50
127.46
127.25
122.47
121.20
120.28
117.13
114.64
112.71
107.84
99.39
78.91
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.50
48.28
29.46
26.29
25.86
25.74
14.14
f1 (ppm)

ethyl (*R*, *E*)-2-(4-(benzylamino)-3-methyl-1H-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3ag)



3ag 75% yield, 97% ee

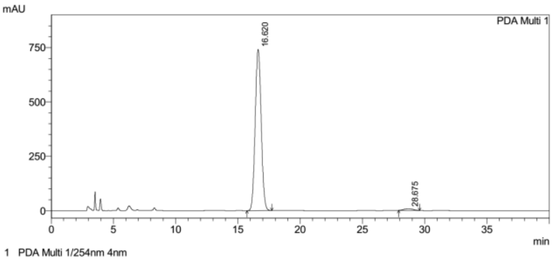
3ag was obtained as a yellow solid in 75% yield (72 h) and 97% ee.
The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 16.62 min, t_{minor} = 28.67 min; $[\alpha]_D^{20}$ = + 70.5 (*c* 0.41, MeOH);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (s, 1H), 7.79 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.59 (s, 1H), 7.42 – 7.39 (m, 2H), 7.36 – 7.32 (m, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.07 (d, *J* = 8.1 Hz, 1H), 4.46 (s, 1H), 4.38 (s, 2H), 4.30 – 4.20 (m, 2H), 3.05 (s, 3H), 2.52 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.81, 168.36, 144.50, 144.01, 139.55, 138.92, 135.12, 131.15, 129.88, 128.75, 128.57, 127.53, 127.29, 122.47, 122.34, 120.70, 120.18, 116.72, 112.18, 110.18, 107.77, 99.11, 78.91, 63.25, 48.33, 26.10, 14.12, 13.14. ESI-HRMS m/z: 496.2230. $[M + H]^+$, calcd for $C_{30}H_{29}N_3O_4+H^+$, 496.2231.



PeakTable

PDA Ch1 254nm 4nm

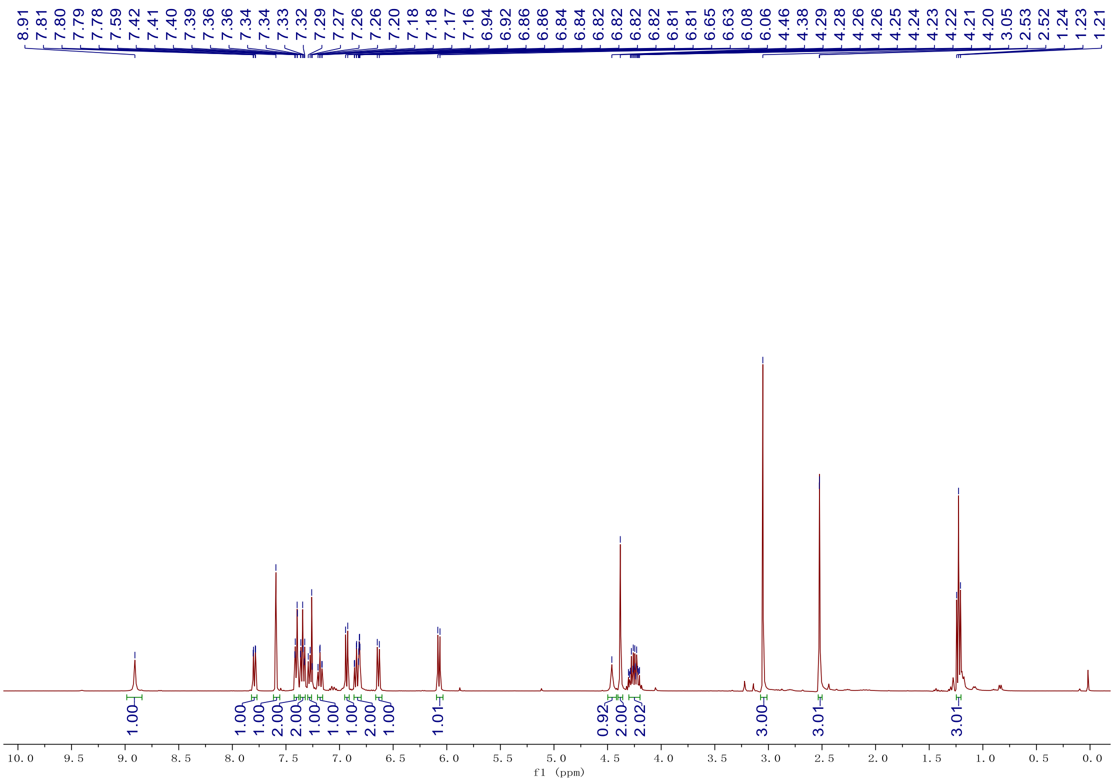
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.494	29852419	898402	49.315	65.552
2	27.754	30682115	472122	50.685	34.448
Total		60534534	1370524	100.000	100.000

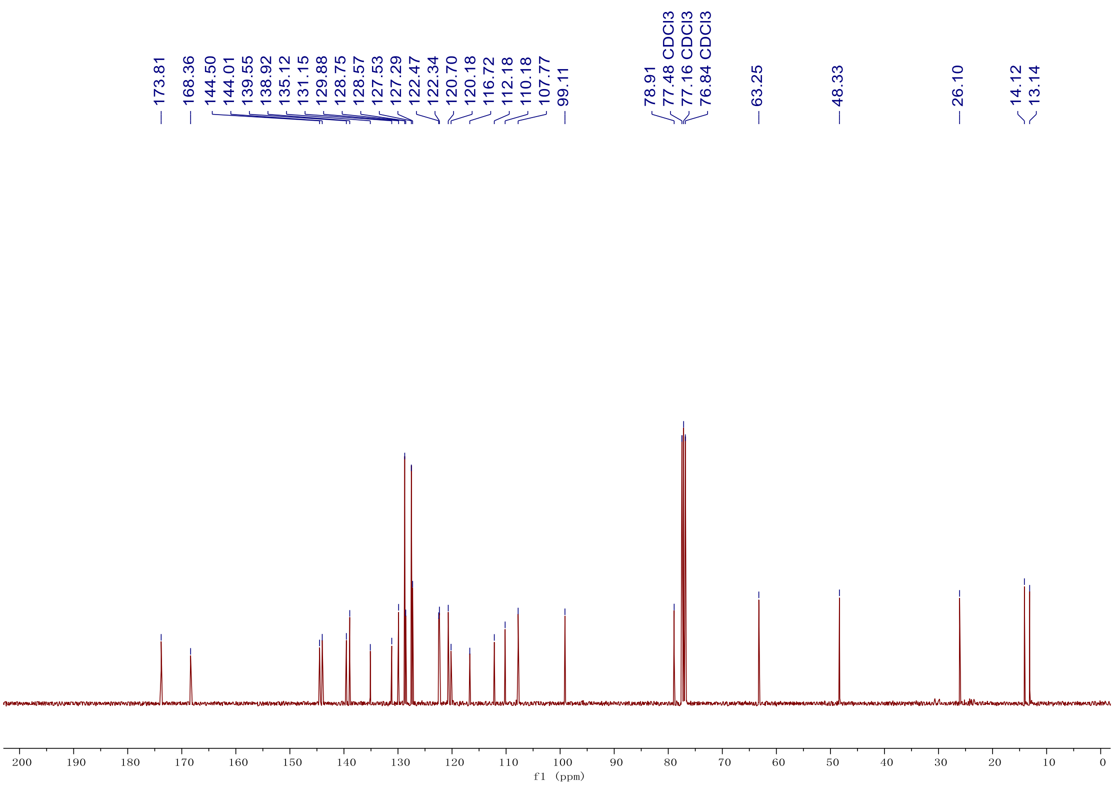


PeakTable

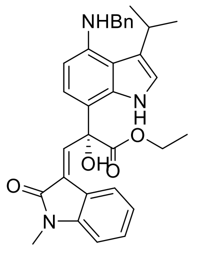
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.620	24863579	742175	98.414	98.985
2	28.675	400712	7612	1.586	1.015
Total		25264291	749787	100.000	100.000



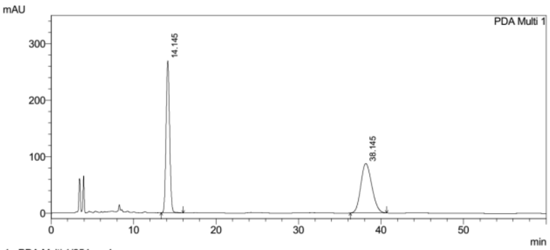


ethyl (*R*, *E*)-2-(4-(benzylamino)-3-isopropyl-1H-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3ah)



3ah 68% yield, 96% ee

3ah was obtained as a yellow solid in 68% yield (96 h) and 96% ee. The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 14.14 min, t_{minor} = 38.46 min; $[\alpha]_D^{20}$ = + 30.5 (*c* 0.20, MeOH); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 7.86 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53 (s, 1H), 7.42 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.28 (m, 1H), 7.22 (td, *J* = 7.7, 1.2 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.12 (d, *J* = 8.2 Hz, 1H), 4.42 (s, 2H), 4.31 – 4.20 (m, 2H), 4.10 (s, 1H), 3.27 – 3.23 (m, 1H), 3.18 (s, 3H), 1.35 (dd, *J* = 6.7, 4.0 Hz, 6H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.88, 168.32, 144.78, 143.70, 139.55, 138.30, 135.15, 130.98, 130.06, 128.79, 128.49, 127.58, 127.33, 123.55, 122.48, 121.96, 120.27, 117.92, 115.72, 112.04, 107.86, 99.35, 79.09, 63.45, 48.48, 27.07, 26.27, 24.65, 24.58, 14.14. ESI-HRMS m/z: 524.2543. $[M + H]^+$, calcd for $C_{32}H_{33}N_3O_4$+H^+, 524.2544.

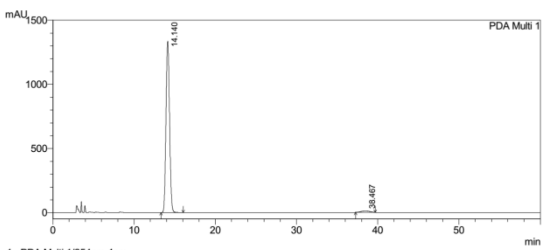


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.145	8103943	269597	49.834	75.444
2	38.145	8157833	87752	50.166	24.556
Total		16261776	357349	100.000	100.000

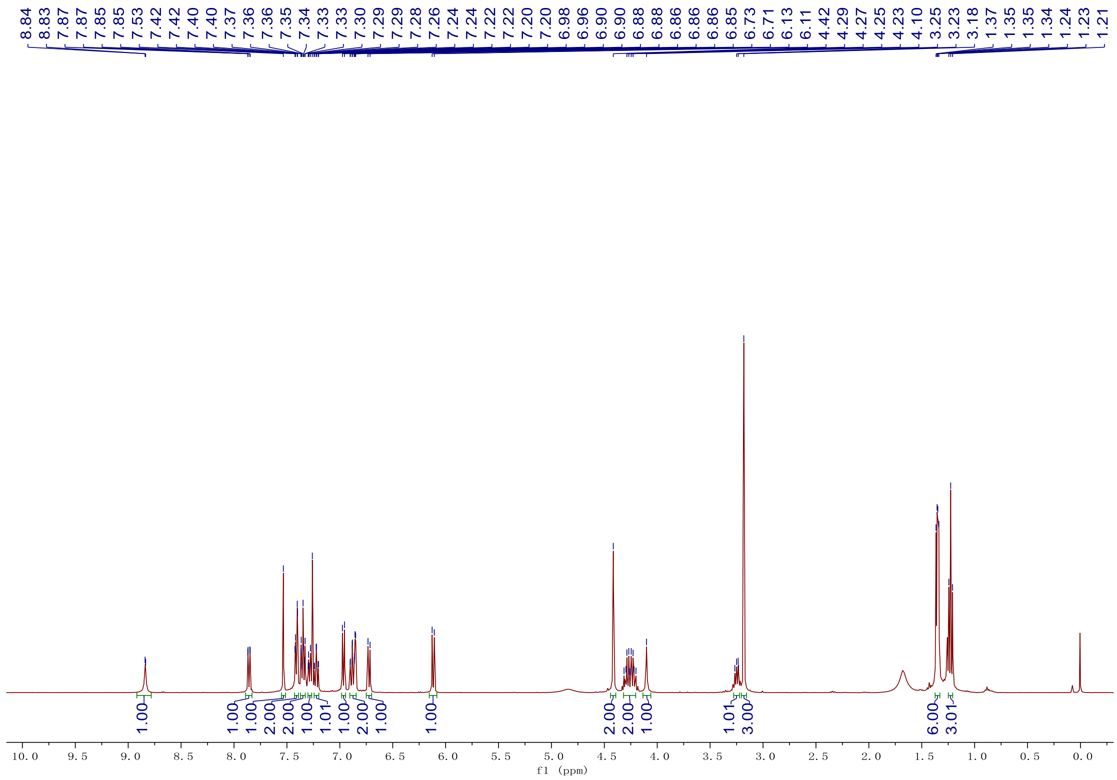


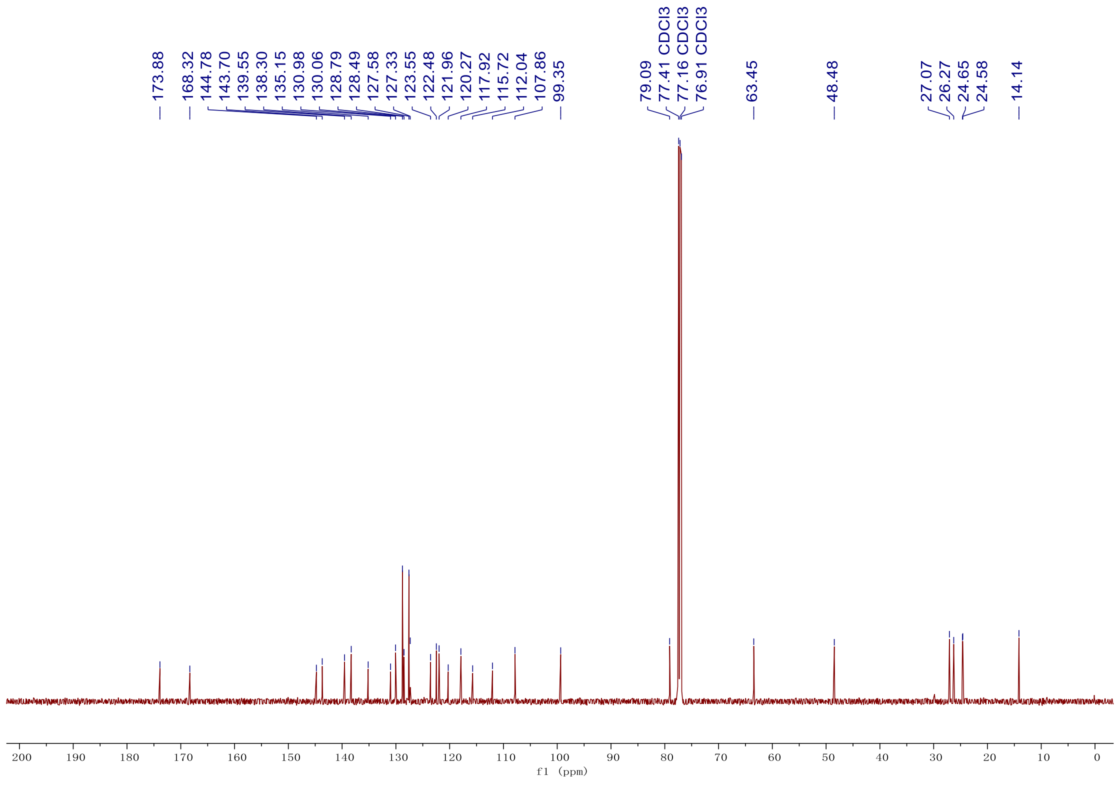
1 PDA Multi 1/254nm 4nm

PeakTable

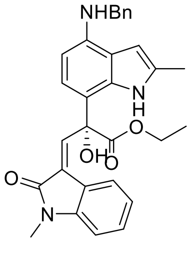
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.140	40800382	1337911	97.813	99.140
2	38.467	912130	11606	2.187	0.860
Total		41712512	1349517	100.000	100.000





ethyl (*R*, *E*)-2-(4-(benzylamino)-2-methyl-1*H*-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3ai)

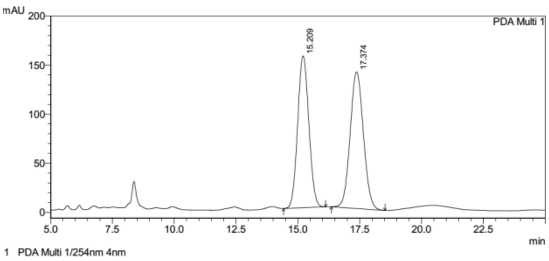


3ai 40% yield, 28% ee

3ai was obtained as a yellow solid in 40% yield (120 h) and 28% ee.

The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{minor} = 15.11 min, t_{major} = 17.29 min; $[\alpha]_D^{20}$ = + 40.3 (*c* 0.09, MeOH);

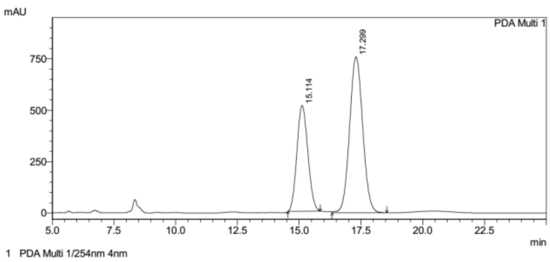
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.56 (s, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.27 (m, 1H), 7.22 (dd, *J* = 8.4, 7.1 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.73 (dd, *J* = 7.8, 2.2 Hz, 1H), 6.15 (d, *J* = 8.1 Hz, 1H), 6.10 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.42 (s, 2H), 4.31 – 4.20 (m, 2H), 4.12 (d, *J* = 9.8 Hz, 1H), 3.19 (d, *J* = 3.5 Hz, 3H), 2.42 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.91, 168.33, 144.76, 141.21, 139.65, 138.35, 138.30, 133.78, 133.34, 131.17, 130.08, 128.73, 128.71, 128.38, 127.81, 127.35, 122.47, 121.12, 120.27, 118.45, 111.98, 107.88, 99.43, 96.19, 78.96, 63.46, 48.39, 26.28, 14.13, 13.92. ESI-HRMS m/z: 496.2230. [M + H]$^+$, calcd for $C_{30}H_{29}N_3O_4+H^+$, 496.2231.



PeakTable

PDA Ch1 254nm 4nm

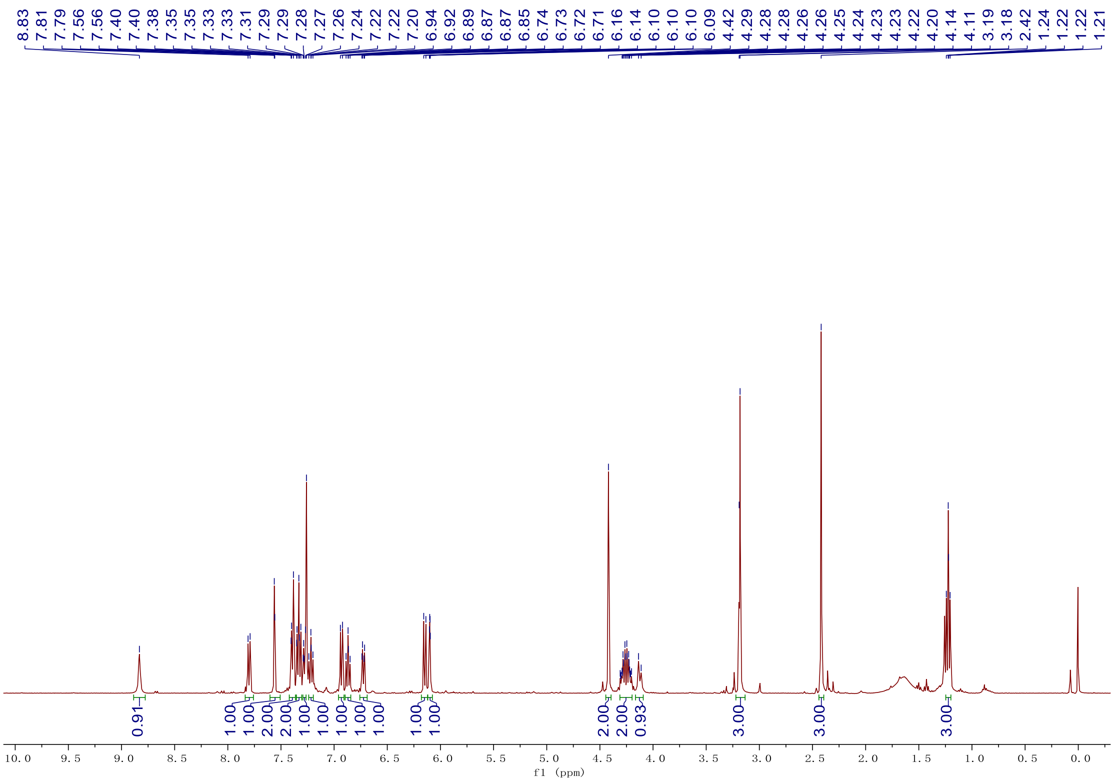
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.209	4862070	154697	48.331	52.626
2	17.374	5197924	139260	51.669	47.374
Total		10059994	293957	100.000	100.000

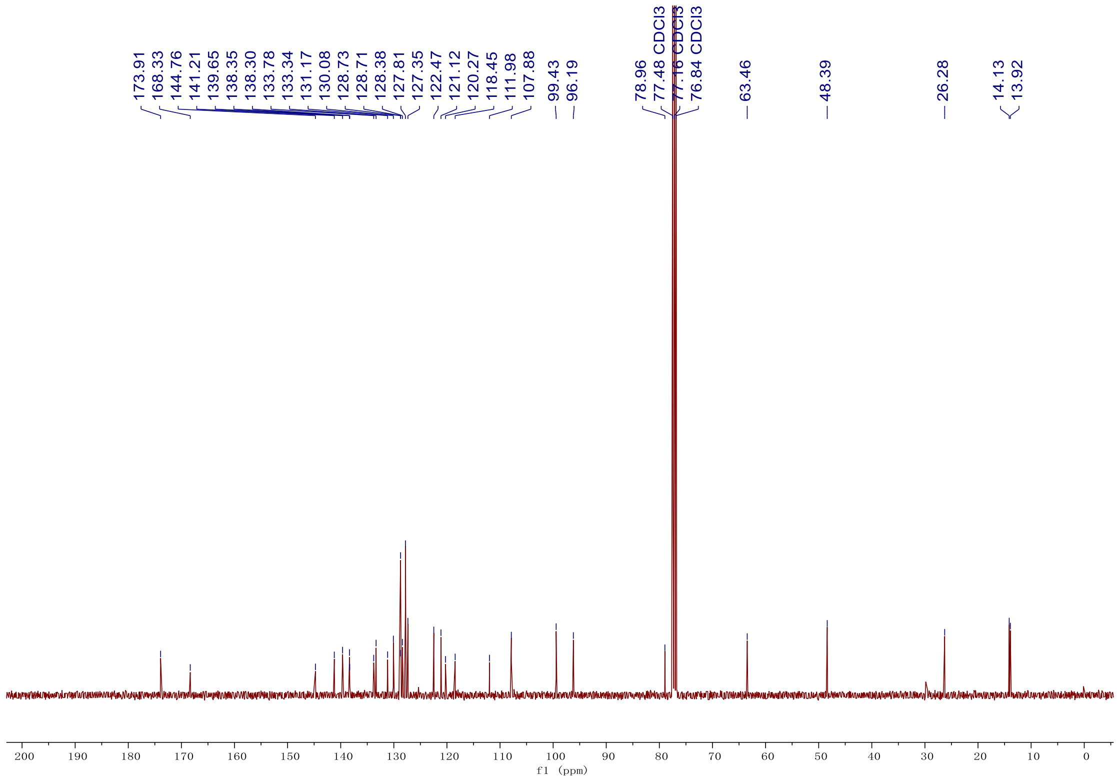


PeakTable

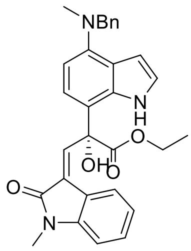
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.114	15841345	513670	36.124	40.424
2	17.299	28011436	757021	63.876	59.576
Total		43852781	1270692	100.000	100.000



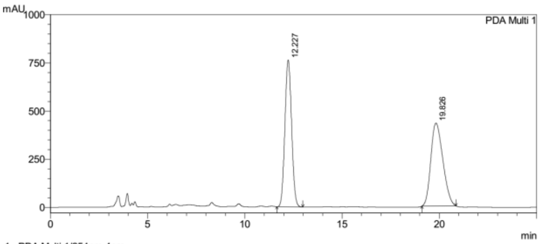


ethyl (*R*, *E*)-2-(4-(benzyl(methyl)amino)-1*H*-indol-7-yl)-2-hydroxy-3-(1-methyl-2-oxoindolin-3-ylidene) propanoate (3aj)



3aj 53% yield, 10% ee

3aj was obtained as a yellow solid in 53% yield (72 h) and 10% ee.
The enantiomeric excess was determined by HPLC (Daicel Chiralpak AD-H, hexane/i-PrOH = 70 : 30 (v/v), λ =254 nm, flow rate = 1.0 mL/min, rt): t_{major} = 12.22 min, t_{minor} = 19.86 min; $[\alpha]_D^{20}$ = + 2.0 (*c* 0.17, MeOH);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.40 – 7.38 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.26 (m, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 2.9 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.70 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.56 (dd, *J* = 3.3, 2.2 Hz, 1H), 6.39 (d, *J* = 8.1 Hz, 1H), 4.57 (s, 2H), 4.37 – 4.35 (d, *J* = 8.4 Hz, 1H), 4.31 – 4.22 (m, 2H), 3.13 (d, *J* = 3.2 Hz, 3H), 2.85 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.70, 168.33, 146.71, 144.70, 139.34, 138.36, 134.73, 131.32, 130.11, 128.54, 128.46, 127.65, 127.06, 122.59, 122.50, 121.55, 120.77, 120.16, 114.55, 107.90, 105.22, 101.49, 78.93, 63.46, 59.46, 39.05, 26.23, 14.13. ESI-HRMS m/z: 496.2232. [M + H]$^+$, calcd for $C_{30}H_{29}N_3O_4$+H$^+$, 496.2231.

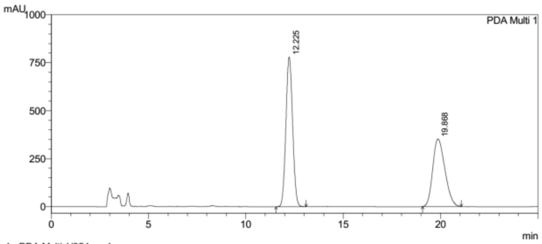


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.227	18234482	762946	49.613	63.919
2	19.826	18519145	430661	50.387	36.081
Total		36753627	1193607	100.000	100.000

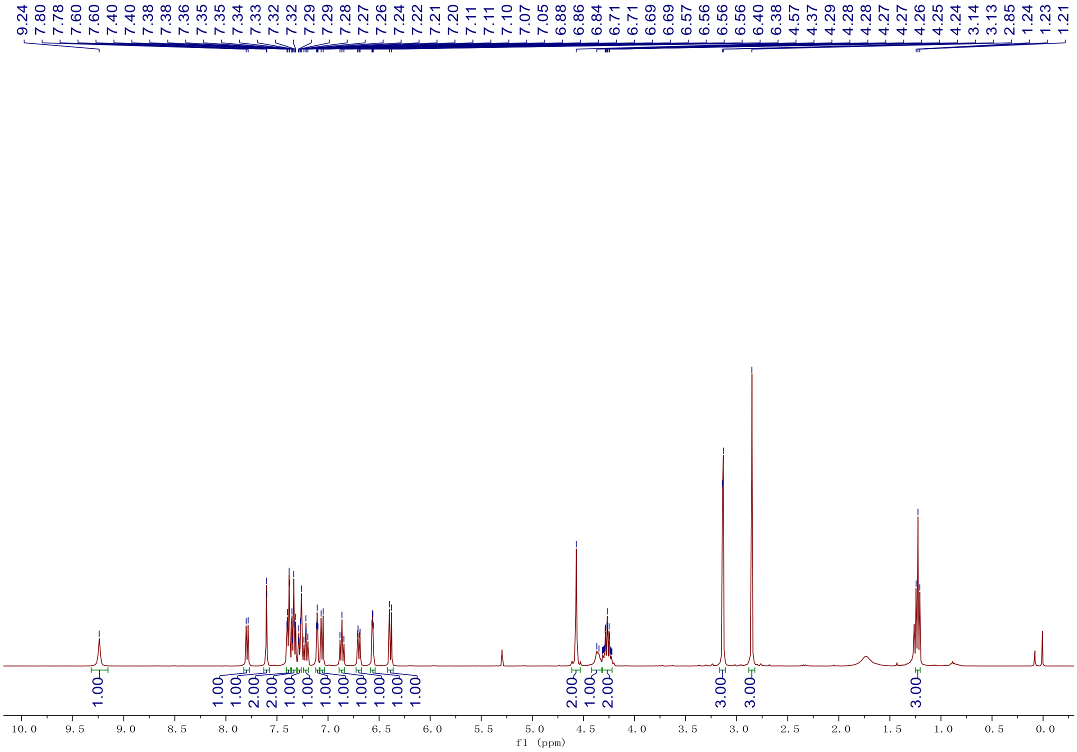


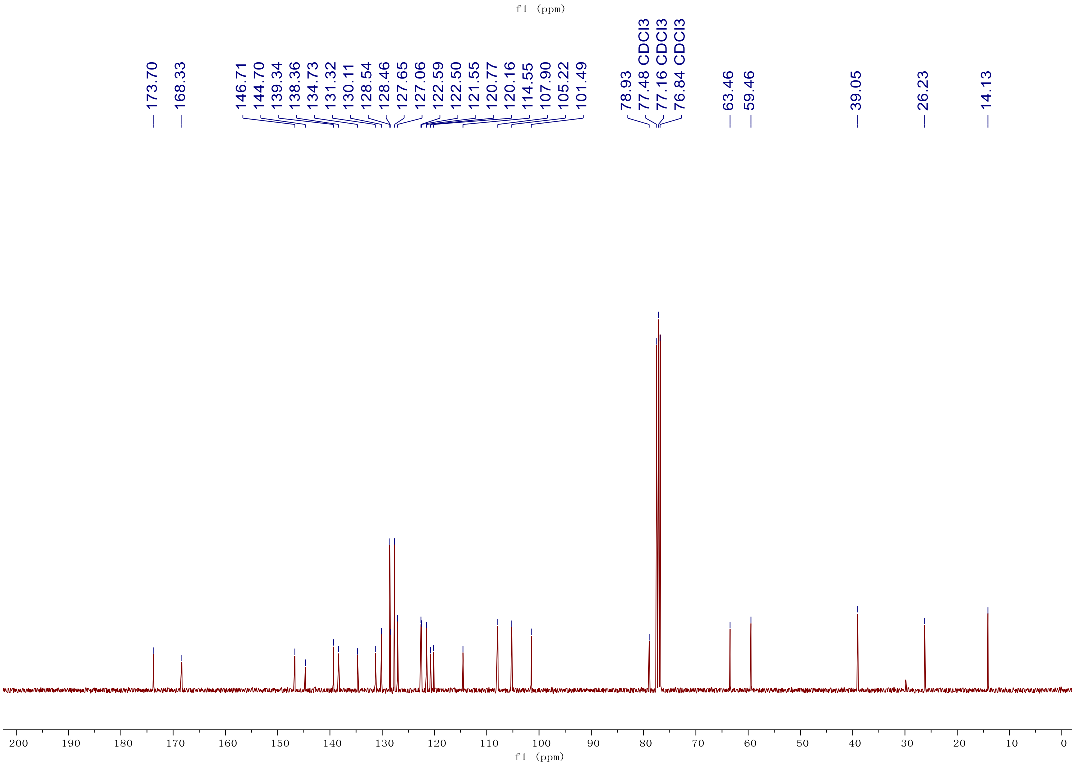
1 PDA Multi 1/254nm 4nm

PeakTable

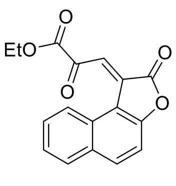
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.225	18733916	781058	55.013	68.896
2	19.868	15319894	352617	44.987	31.104
Total		34053811	1133676	100.000	100.000

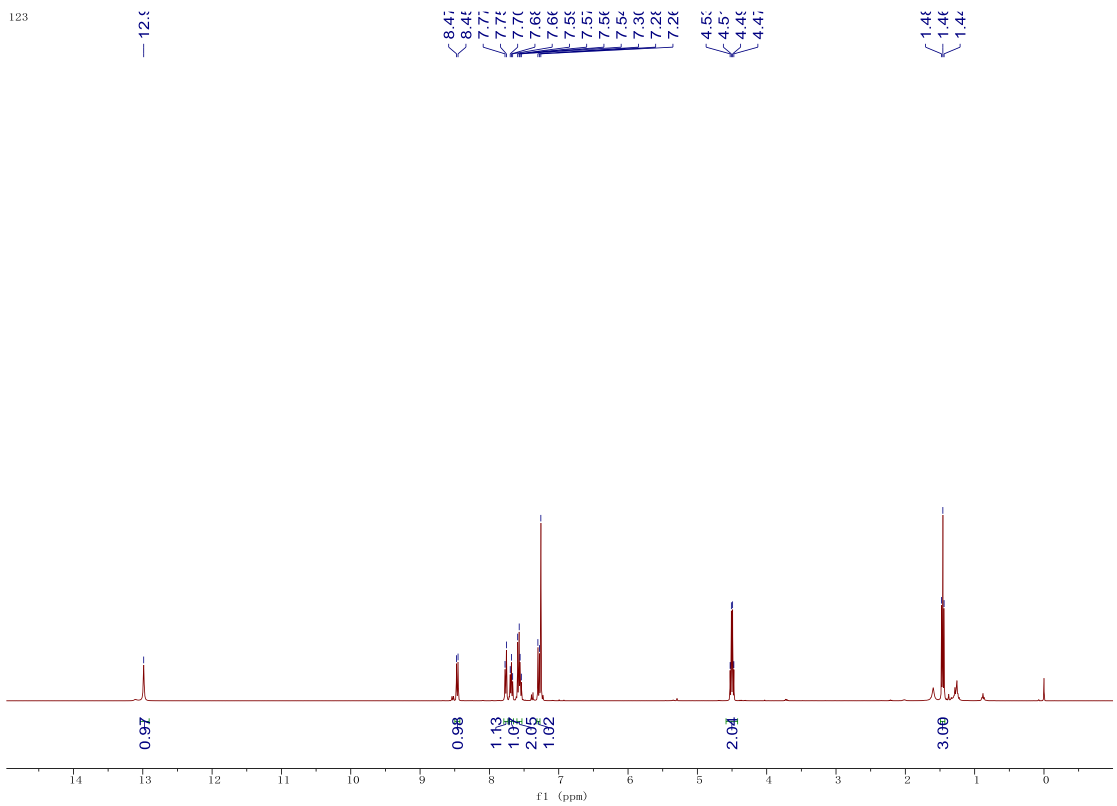


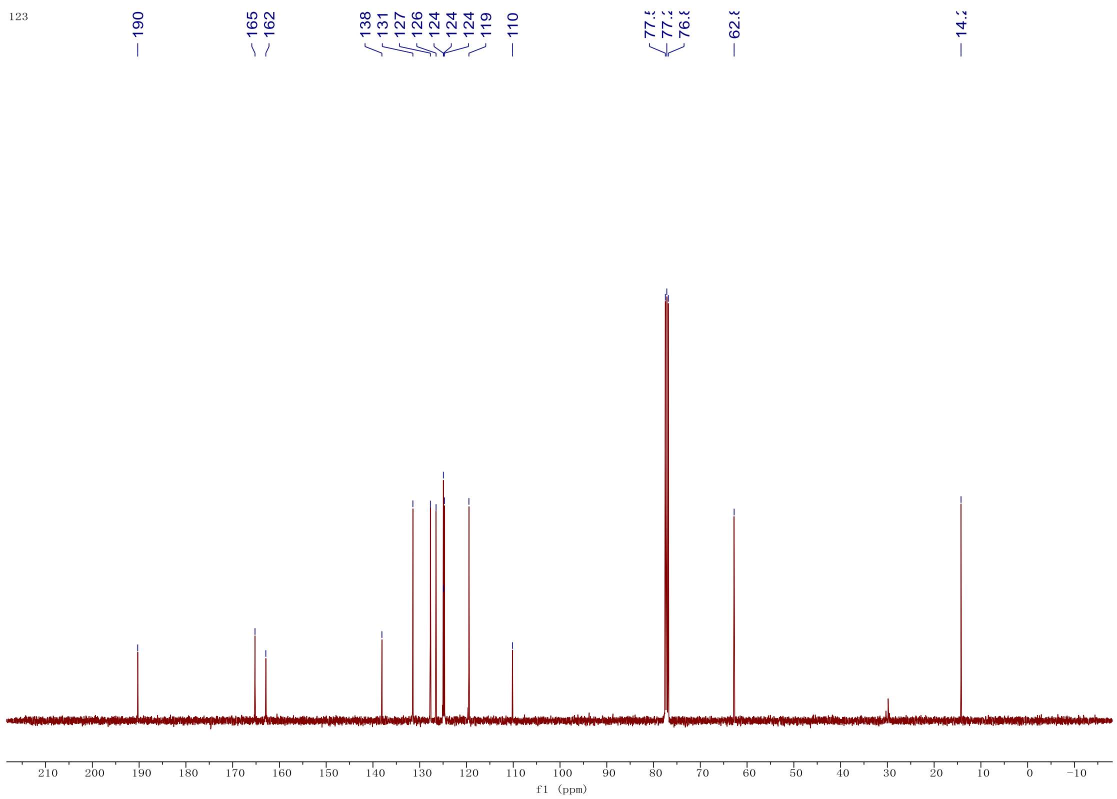


ethyl (E)-2-oxo-3-(2-oxonaphtho[2,1-b]furan-1(2H)-ylidene) propanoate (1u)[1]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.99 (s, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.70 - 7.66 (m, 1H), 7.59 - 7.54 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 165.2, 162.9, 138.1, 131.5, 127.7, 126.5, 124.9, 124.9, 124.7, 119.5, 110.2, 62.8, 14.3. ESI-HRMS m/z: 335.0318. $[M + K]^+$, calcd for $C_{17}H_{12}O_5$+K^+, 335.0316.





1. **1u** was prepared according to reported procedure. (a) V. C. Fäseke and C. Sparr, *Angew. Chem. Int. Ed.* 2016, **55**, 7261; (b) H.-B. Yang, Y.-Z. Zhao, R. Sang, Y. Wei, M. Shi, *Adv. Synth. Catal.* 2014, **356**, 3799.

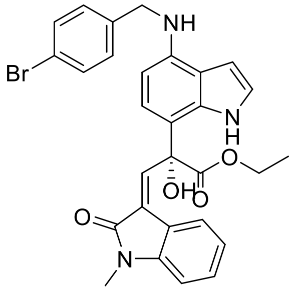
Method for biological activity study

Human colon cancer cells were inoculated in medium containing 10% serum, 1% penicillin and incubated at 37 °C in a 5% CO_2 incubator. Cells in logarithmic growth phase were taken for test. Cell survival rate was determined by Cell Counting Kit-8 (CCK-8), and IC_{50} (the concentration of drug required to reduce cell growth to 50% of that of the control sample) was calculated using Graphpad prism.

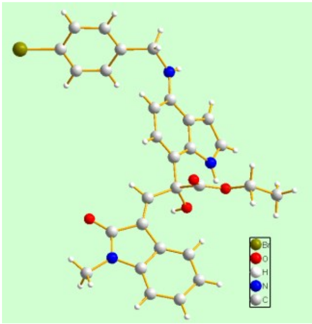
Logarithmic growth phase cells were collected and the cell density was adjusted to 3×10^4 cells/mL with freshly medium into 96-well culture plates. After incubation for 24 h at 37 °C in a volume of 100 µL per well, the chiral compounds were respectively added at concentrations of 25, 12.5, 6.25, 3.125, 1.56, 0.78, 0.39 and 0.195 µM and then incubated for 72 h. The culture medium was discarded. 100 µL culture medium containing 10 µL CCK8 was added to each well and incubated for another 2 h. And then, the absorbance was measured at 490 nm.

The chiral compounds were dissolved in DMSO and further diluted with medium, with the final concentration of DMSO not exceeding 0.25% (v/v). The control group contained cancer cells and DMSO (0.25%) but no compounds, and the blank group contained medium and DMSO (not exceeding 0.25% v/v) without cells. The results for each experimental condition were averaged over 3 replicate wells.

X-ray data of 3ab



3ab



X-ray of 3ab

Table 1 Crystal data and structure refinement for 3ab.

Identification code	**3ab**
Empirical formula	$C_{29}H_{26}BrN_3O_4$
Formula weight	560.44
Temperature/K	192.98
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.1958(14)
b/Å	7.8993(9)
c/Å	13.8896(15)
α/°	90
β/°	104.960(5)
γ/°	90
Volume/Å^3	1292.7(3)
Z	2
ρ_{calc}g/cm^3	1.440
μ/mm^{-1}	1.700
F(000)	576.0
Crystal size/mm^3	0.12 × 0.1 × 0.1
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	5.73 to 121.616
Index ranges	$-15 \leq h \leq 15, 0 \leq k \leq 10, 0 \leq l \leq 18$
Reflections collected	3055
Independent reflections	3055 [R_{int} = ?, R_{sigma} = 0.0547]
Data/restraints/parameters	3055/8/349
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	$R_1 = 0.0485$, $wR_2 = 0.1056$
Final R indexes [all data]	$R_1 = 0.0786$, $wR_2 = 0.1263$
Largest diff. peak/hole / e Å^{-3}	0.39/-0.61
Flack parameter	0.09(3)

Table 2 Fractional Atomic Coordinates (×10[4]) and Equivalent Isotropic Displacement Parameters (Å[2]×10[3]) for 3ab. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
$Br_{(1)}$	832.5(7)	10792.0(14)	-666.4(6)	69.8(3)
$O_{(002)}$	5946(4)	9088(6)	5205(4)	45.9(12)
$O_{(003)}$	6174(4)	2888(6)	4837(3)	39.7(11)
$O_{(004)}$	7809(4)	1846(7)	4179(4)	53.5(13)
$O_{(007)}$	8320(4)	4476(7)	3863(4)	58.2(14)
$N_{(005)}$	7435(5)	8516(8)	6556(4)	43.2(13)
$N_{(006)}$	5071(4)	733(9)	3295(3)	41.9(11)
$N_{(009)}$	3600(5)	3003(9)	144(4)	56.4(17)
$C_{(1)}$	1643(6)	8767(11)	-670(5)	55(2)
$C_{(2)}$	2157(7)	8459(12)	-1414(6)	63(2)
$C_{(3)}$	2763(6)	6952(12)	-1383(5)	57(2)
$C_{(4)}$	2830(5)	5771(15)	-652(4)	47.6(14)
$C_{(5)}$	2266(6)	6101(12)	75(5)	52(2)
$C_{(6)}$	1684(6)	7591(11)	83(5)	54(2)
$C_{(7)}$	3509(7)	4169(11)	-672(5)	58(2)
$C_{(8)}$	4304(5)	3301(10)	1100(4)	41.3(15)
$C_{(9)}$	4882(6)	4784(10)	1378(5)	44.8(16)
$C_{(10)}$	5564(6)	4994(9)	2368(5)	43.2(15)
$C_{(11)}$	5680(5)	3750(8)	3085(4)	37.1(14)
$C_{(12)}$	5095(5)	2235(9)	2786(4)	37.7(14)
$C_{(13)}$	4398(6)	1973(10)	1811(5)	43.7(16)
$C_{(14)}$	3956(6)	317(9)	1775(5)	45.2(18)
$C_{(15)}$	4381(6)	-400(10)	2686(5)	50.4(18)
$C_{(16)}$	6468(5)	3996(8)	4141(4)	35.6(13)
$C_{(17)}$	7649(6)	3486(10)	4053(5)	44.9(16)
$C_{(18)}$	8884(6)	1133(12)	4082(7)	63(2)
$C_{(19B)}$	8620(60)	-740(30)	3950(60)	105(10)
$C_{(20)}$	6412(4)	5770(12)	4492(4)	38.3(12)
$C_{(21)}$	6975(5)	6400(8)	5388(4)	37.2(14)
$C_{(22)}$	6708(6)	8140(9)	5659(5)	41.1(15)
$C_{(23)}$	7406(7)	10071(10)	7079(6)	59(2)
$C_{(24)}$	8130(5)	7096(10)	6922(5)	41.9(16)
$C_{(25)}$	7857(4)	5760(12)	6227(4)	39.5(12)
$C_{(26)}$	8408(6)	4257(10)	6450(5)	46.7(17)
$C_{(27)}$	9257(6)	4072(11)	7338(5)	53.6(19)
$C_{(28)}$	9516(6)	5421(11)	8000(5)	56(2)
$C_{(29)}$	8958(6)	6957(11)	7800(5)	51.6(18)

C(19A)	8890(50)	-710(30)	4400(50)	105(10)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 20201107Lin_ABCZ2728_CF_0m_5. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br(1)	70.3(5)	69.4(6)	62.6(5)	-2.3(6)	4.3(4)	6.7(6)
O(002)	55(3)	39(3)	44(3)	2(2)	13(2)	2(2)
O(003)	45(3)	38(3)	34(2)	-1(2)	7.6(19)	0(2)
O(004)	47(3)	50(3)	64(3)	-3(3)	14(2)	12(2)
O(007)	56(3)	60(4)	62(3)	-4(3)	22(3)	-9(3)
N(005)	56(3)	37(3)	33(3)	-8(2)	5(2)	-7(3)
N(006)	55(3)	34(3)	33(2)	-1(3)	6(2)	-10(4)
N(009)	73(4)	58(4)	27(3)	3(3)	-6(3)	-11(3)
C(1)	52(4)	71(6)	38(3)	-3(4)	8(3)	-14(4)
C(2)	68(5)	70(6)	52(4)	20(4)	18(4)	2(5)
C(3)	54(4)	81(6)	39(4)	10(4)	16(3)	0(4)
C(4)	47(3)	67(4)	28(3)	5(4)	9(2)	1(5)
C(5)	57(4)	68(7)	31(3)	-1(4)	10(3)	-9(4)
C(6)	54(4)	71(6)	36(3)	2(4)	8(3)	-5(4)
C(7)	74(5)	73(6)	23(3)	-1(3)	5(3)	-1(4)
C(8)	49(4)	46(4)	25(3)	2(3)	1(2)	-5(3)
C(9)	57(4)	45(4)	31(3)	5(3)	8(3)	-7(3)
C(10)	52(4)	39(4)	36(3)	3(3)	6(3)	-3(3)
C(11)	46(3)	36(4)	27(3)	-1(3)	6(2)	-2(3)
C(12)	46(4)	35(4)	31(3)	5(3)	8(3)	2(3)
C(13)	44(4)	55(5)	29(3)	2(3)	5(3)	-1(3)
C(14)	49(4)	48(5)	35(3)	-7(3)	5(3)	-9(3)
C(15)	60(4)	37(4)	52(4)	-3(3)	10(3)	-10(3)
C(16)	44(3)	33(3)	28(3)	4(2)	7(2)	-1(3)
C(17)	47(4)	50(5)	35(3)	-4(3)	6(3)	1(3)
C(18)	52(4)	67(7)	76(5)	7(5)	27(4)	20(4)
C(19B)	110(20)	85(9)	150(30)	54(12)	80(20)	47(9)
C(20)	41(3)	39(3)	33(3)	2(4)	6(2)	-4(4)
C(21)	48(3)	35(3)	28(3)	1(2)	10(2)	2(3)
C(22)	48(4)	41(4)	34(3)	3(3)	9(3)	-11(3)
C(23)	75(5)	51(5)	51(4)	-19(4)	16(4)	-11(4)
C(24)	46(4)	48(4)	31(3)	-13(3)	10(3)	-8(3)
C(25)	42(3)	44(3)	29(2)	-3(4)	3(2)	-1(4)
C(26)	49(4)	54(5)	34(3)	3(3)	5(3)	-7(4)
C(27)	53(4)	57(5)	43(4)	4(4)	-1(3)	5(4)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for 20201107Lin_ABCZ2728_CF_0m_5. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$C_{(28)}$	53(4)	65(7)	42(3)	7(4)	-2(3)	-9(4)
$C_{(29)}$	54(4)	57(5)	36(3)	0(3)	-1(3)	-9(4)
$C_{(19A)}$	110(20)	85(9)	150(30)	54(12)	80(20)	47(9)

Table 4 Bond Lengths for 20201107Lin_ABCZ2728_CF_0m_5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
$Br_{(1)}$	$C_{(1)}$	1.881(9)	$C_{(8)}$	$C_{(13)}$	1.425(9)
$O_{(002)}$	$C_{(22)}$	1.232(8)	$C_{(9)}$	$C_{(10)}$	1.421(9)
$O_{(003)}$	$C_{(16)}$	1.418(7)	$C_{(10)}$	$C_{(11)}$	1.380(9)
$O_{(004)}$	$C_{(17)}$	1.314(9)	$C_{(11)}$	$C_{(12)}$	1.400(9)
$O_{(004)}$	$C_{(18)}$	1.465(8)	$C_{(11)}$	$C_{(16)}$	1.544(8)
$O_{(007)}$	$C_{(17)}$	1.210(9)	$C_{(12)}$	$C_{(13)}$	1.416(8)
$N_{(005)}$	$C_{(22)}$	1.363(8)	$C_{(13)}$	$C_{(14)}$	1.411(10)
$N_{(005)}$	$C_{(23)}$	1.432(9)	$C_{(14)}$	$C_{(15)}$	1.361(10)
$N_{(005)}$	$C_{(24)}$	1.419(9)	$C_{(16)}$	$C_{(17)}$	1.530(9)
$N_{(006)}$	$C_{(12)}$	1.385(9)	$C_{(16)}$	$C_{(20)}$	1.491(11)
$N_{(006)}$	$C_{(15)}$	1.363(9)	$C_{(18)}$	$C_{(19B)}$	1.52(2)
$N_{(009)}$	$C_{(7)}$	1.443(9)	$C_{(18)}$	$C_{(19A)}$	1.52(2)
$N_{(009)}$	$C_{(8)}$	1.402(7)	$C_{(20)}$	$C_{(21)}$	1.352(8)
$C_{(1)}$	$C_{(2)}$	1.362(10)	$C_{(21)}$	$C_{(22)}$	1.484(9)
$C_{(1)}$	$C_{(6)}$	1.390(10)	$C_{(21)}$	$C_{(25)}$	1.457(8)
$C_{(2)}$	$C_{(3)}$	1.396(12)	$C_{(24)}$	$C_{(25)}$	1.411(10)
$C_{(3)}$	$C_{(4)}$	1.366(12)	$C_{(24)}$	$C_{(29)}$	1.372(9)
$C_{(4)}$	$C_{(5)}$	1.386(9)	$C_{(25)}$	$C_{(26)}$	1.360(11)
$C_{(4)}$	$C_{(7)}$	1.517(13)	$C_{(26)}$	$C_{(27)}$	1.398(9)
$C_{(5)}$	$C_{(6)}$	1.375(12)	$C_{(27)}$	$C_{(28)}$	1.390(11)
$C_{(8)}$	$C_{(9)}$	1.370(10)	$C_{(28)}$	$C_{(29)}$	1.384(11)

Table 5 Bond Angles for 20201107Lin_ABCZ2728_CF_0m_5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$C_{(17)}$	$O_{(004)}$	$C_{(18)}$	118.2(6)	$C_{(15)}$	$C_{(14)}$	$C_{(13)}$	107.6(6)
$C_{(22)}$	$N_{(005)}$	$C_{(23)}$	123.7(7)	$C_{(14)}$	$C_{(15)}$	$N_{(006)}$	109.2(6)
$C_{(22)}$	$N_{(005)}$	$C_{(24)}$	110.1(6)	$O_{(003)}$	$C_{(16)}$	$C_{(11)}$	111.4(5)
$C_{(24)}$	$N_{(005)}$	$C_{(23)}$	125.9(6)	$O_{(003)}$	$C_{(16)}$	$C_{(17)}$	107.5(5)
$C_{(15)}$	$N_{(006)}$	$C_{(12)}$	109.7(5)	$O_{(003)}$	$C_{(16)}$	$C_{(20)}$	108.4(5)
$C_{(8)}$	$N_{(009)}$	$C_{(7)}$	122.8(6)	$C_{(17)}$	$C_{(16)}$	$C_{(11)}$	105.0(5)
$C_{(2)}$	$C_{(1)}$	$Br_{(1)}$	120.0(6)	$C_{(20)}$	$C_{(16)}$	$C_{(11)}$	111.0(5)
$C_{(2)}$	$C_{(1)}$	$C_{(6)}$	121.1(8)	$C_{(20)}$	$C_{(16)}$	$C_{(17)}$	113.4(5)

Table 5 Bond Angles for 20201107Lin_ABCZ2728_CF_0m_5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$C_{(6)}$	$C_{(1)}$	$Br_{(1)}$	118.9(6)	$O_{(004)}$	$C_{(17)}$	$C_{(16)}$	111.1(6)
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	118.2(7)	$O_{(007)}$	$C_{(17)}$	$O_{(004)}$	125.5(7)
$C_{(4)}$	$C_{(3)}$	$C_{(2)}$	122.3(7)	$O_{(007)}$	$C_{(17)}$	$C_{(16)}$	123.4(7)
$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	117.9(9)	$O_{(004)}$	$C_{(18)}$	$C_{(19B)}$	103(3)
$C_{(3)}$	$C_{(4)}$	$C_{(7)}$	119.0(6)	$O_{(004)}$	$C_{(18)}$	$C_{(19A)}$	106(2)
$C_{(5)}$	$C_{(4)}$	$C_{(7)}$	123.1(8)	$C_{(21)}$	$C_{(20)}$	$C_{(16)}$	126.3(6)
$C_{(6)}$	$C_{(5)}$	$C_{(4)}$	121.4(8)	$C_{(20)}$	$C_{(21)}$	$C_{(22)}$	118.8(6)
$C_{(5)}$	$C_{(6)}$	$C_{(1)}$	119.0(7)	$C_{(20)}$	$C_{(21)}$	$C_{(25)}$	134.7(7)
$N_{(009)}$	$C_{(7)}$	$C_{(4)}$	116.7(6)	$C_{(25)}$	$C_{(21)}$	$C_{(22)}$	106.5(6)
$N_{(009)}$	$C_{(8)}$	$C_{(13)}$	116.9(6)	$O_{(002)}$	$C_{(22)}$	$N_{(005)}$	124.2(7)
$C_{(9)}$	$C_{(8)}$	$N_{(009)}$	123.7(6)	$O_{(002)}$	$C_{(22)}$	$C_{(21)}$	128.3(6)
$C_{(9)}$	$C_{(8)}$	$C_{(13)}$	119.4(5)	$N_{(005)}$	$C_{(22)}$	$C_{(21)}$	107.4(6)
$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	120.2(6)	$C_{(25)}$	$C_{(24)}$	$N_{(005)}$	109.4(5)
$C_{(11)}$	$C_{(10)}$	$C_{(9)}$	122.7(7)	$C_{(29)}$	$C_{(24)}$	$N_{(005)}$	128.0(7)
$C_{(10)}$	$C_{(11)}$	$C_{(12)}$	116.4(5)	$C_{(29)}$	$C_{(24)}$	$C_{(25)}$	122.6(7)
$C_{(10)}$	$C_{(11)}$	$C_{(16)}$	121.2(6)	$C_{(24)}$	$C_{(25)}$	$C_{(21)}$	106.4(7)
$C_{(12)}$	$C_{(11)}$	$C_{(16)}$	122.2(5)	$C_{(26)}$	$C_{(25)}$	$C_{(21)}$	134.8(7)
$N_{(006)}$	$C_{(12)}$	$C_{(11)}$	131.1(5)	$C_{(26)}$	$C_{(25)}$	$C_{(24)}$	118.8(5)
$N_{(006)}$	$C_{(12)}$	$C_{(13)}$	106.1(6)	$C_{(25)}$	$C_{(26)}$	$C_{(27)}$	120.1(7)
$C_{(11)}$	$C_{(12)}$	$C_{(13)}$	122.8(6)	$C_{(28)}$	$C_{(27)}$	$C_{(26)}$	119.6(7)
$C_{(12)}$	$C_{(13)}$	$C_{(8)}$	118.5(6)	$C_{(29)}$	$C_{(28)}$	$C_{(27)}$	121.6(6)
$C_{(14)}$	$C_{(13)}$	$C_{(8)}$	134.1(6)	$C_{(24)}$	$C_{(29)}$	$C_{(28)}$	117.3(7)
$C_{(14)}$	$C_{(13)}$	$C_{(12)}$	107.4(6)				

Table 6 Torsion Angles for 20201107Lin_ABCZ2728_CF_0m_5.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
$Br_{(1)}$	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	179.2(6)	$C_{(12)}$	$C_{(11)}$	$C_{(16)}$	$O_{(003)}$	-24.0(8)
$Br_{(1)}$	$C_{(1)}$	$C_{(6)}$	$C_{(5)}$	179.3(5)	$C_{(12)}$	$C_{(11)}$	$C_{(16)}$	$C_{(17)}$	92.1(7)
$O_{(003)}$	$C_{(16)}$	$C_{(17)}$	$O_{(004)}$	32.4(7)	$C_{(12)}$	$C_{(11)}$	$C_{(16)}$	$C_{(20)}$	-144.9(6)
$O_{(003)}$	$C_{(16)}$	$C_{(17)}$	$O_{(007)}$	-149.7(6)	$C_{(12)}$	$C_{(13)}$	$C_{(14)}$	$C_{(15)}$	-0.9(8)
$O_{(003)}$	$C_{(16)}$	$C_{(20)}$	$C_{(21)}$	55.8(8)	$C_{(13)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	-0.4(10)
$N_{(005)}$	$C_{(24)}$	$C_{(25)}$	$C_{(21)}$	1.4(7)	$C_{(13)}$	$C_{(14)}$	$C_{(15)}$	$N_{(006)}$	0.1(8)
$N_{(005)}$	$C_{(24)}$	$C_{(25)}$	$C_{(26)}$	-178.2(6)	$C_{(15)}$	$N_{(006)}$	$C_{(12)}$	$C_{(11)}$	-179.4(7)
$N_{(005)}$	$C_{(24)}$	$C_{(29)}$	$C_{(28)}$	179.2(7)	$C_{(15)}$	$N_{(006)}$	$C_{(12)}$	$C_{(13)}$	-1.3(8)
$N_{(006)}$	$C_{(12)}$	$C_{(13)}$	$C_{(8)}$	-177.3(6)	$C_{(16)}$	$C_{(11)}$	$C_{(12)}$	$N_{(006)}$	0.0(11)
$N_{(006)}$	$C_{(12)}$	$C_{(13)}$	$C_{(14)}$	1.3(7)	$C_{(16)}$	$C_{(11)}$	$C_{(12)}$	$C_{(13)}$	-177.9(6)
$N_{(009)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	178.9(7)	$C_{(16)}$	$C_{(20)}$	$C_{(21)}$	$C_{(22)}$	-172.5(6)
$N_{(009)}$	$C_{(8)}$	$C_{(13)}$	$C_{(12)}$	-179.5(6)	$C_{(16)}$	$C_{(20)}$	$C_{(21)}$	$C_{(25)}$	7.9(12)

Table 6 Torsion Angles for 20201107Lin_ABCZ2728_CF_0m_5.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
$N_{(009)}$	$C_{(8)}$	$C_{(13)}$	$C_{(14)}$	2.4(13)	$C_{(17)}$	$O_{(004)}$	$C_{(18)}$	$C_{(19B)}$	-163(3)
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	1.7(12)	$C_{(17)}$	$O_{(004)}$	$C_{(18)}$	$C_{(19A)}$	173(3)
$C_{(2)}$	$C_{(1)}$	$C_{(6)}$	$C_{(5)}$	0.6(11)	$C_{(17)}$	$C_{(16)}$	$C_{(20)}$	$C_{(21)}$	-63.5(8)
$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	0.3(12)	$C_{(18)}$	$O_{(004)}$	$C_{(17)}$	$O_{(007)}$	-0.1(11)
$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(7)}$	-179.8(7)	$C_{(18)}$	$O_{(004)}$	$C_{(17)}$	$C_{(16)}$	177.8(6)
$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	-1.9(11)	$C_{(20)}$	$C_{(16)}$	$C_{(17)}$	$O_{(004)}$	152.2(5)
$C_{(3)}$	$C_{(4)}$	$C_{(7)}$	$N_{(009)}$	176.9(7)	$C_{(20)}$	$C_{(16)}$	$C_{(17)}$	$O_{(007)}$	-29.9(9)
$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(1)}$	1.5(11)	$C_{(20)}$	$C_{(21)}$	$C_{(22)}$	$O_{(002)}$	7.2(10)
$C_{(5)}$	$C_{(4)}$	$C_{(7)}$	$N_{(009)}$	-3.2(10)	$C_{(20)}$	$C_{(21)}$	$C_{(22)}$	$N_{(005)}$	-175.9(6)
$C_{(6)}$	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	-2.1(11)	$C_{(20)}$	$C_{(21)}$	$C_{(25)}$	$C_{(24)}$	176.5(7)
$C_{(7)}$	$N_{(009)}$	$C_{(8)}$	$C_{(9)}$	6.6(11)	$C_{(20)}$	$C_{(21)}$	$C_{(25)}$	$C_{(26)}$	-4.0(13)
$C_{(7)}$	$N_{(009)}$	$C_{(8)}$	$C_{(13)}$	-174.1(7)	$C_{(21)}$	$C_{(25)}$	$C_{(26)}$	$C_{(27)}$	178.4(7)
$C_{(7)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	178.2(7)	$C_{(22)}$	$N_{(005)}$	$C_{(24)}$	$C_{(25)}$	1.1(7)
$C_{(8)}$	$N_{(009)}$	$C_{(7)}$	$C_{(4)}$	-74.8(9)	$C_{(22)}$	$N_{(005)}$	$C_{(24)}$	$C_{(29)}$	-179.3(7)
$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	0.1(11)	$C_{(22)}$	$C_{(21)}$	$C_{(25)}$	$C_{(24)}$	-3.1(7)
$C_{(8)}$	$C_{(13)}$	$C_{(14)}$	$C_{(15)}$	177.4(8)	$C_{(22)}$	$C_{(21)}$	$C_{(25)}$	$C_{(26)}$	176.3(7)
$C_{(9)}$	$C_{(8)}$	$C_{(13)}$	$C_{(12)}$	-0.2(10)	$C_{(23)}$	$N_{(005)}$	$C_{(22)}$	$O_{(002)}$	-0.4(11)
$C_{(9)}$	$C_{(8)}$	$C_{(13)}$	$C_{(14)}$	-178.3(8)	$C_{(23)}$	$N_{(005)}$	$C_{(22)}$	$C_{(21)}$	-177.5(6)
$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	$C_{(12)}$	0.7(10)	$C_{(23)}$	$N_{(005)}$	$C_{(24)}$	$C_{(25)}$	175.4(6)
$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	$C_{(16)}$	177.4(6)	$C_{(23)}$	$N_{(005)}$	$C_{(24)}$	$C_{(29)}$	-5.0(12)
$C_{(10)}$	$C_{(11)}$	$C_{(12)}$	$N_{(006)}$	176.6(6)	$C_{(24)}$	$N_{(005)}$	$C_{(22)}$	$O_{(002)}$	174.0(6)
$C_{(10)}$	$C_{(11)}$	$C_{(12)}$	$C_{(13)}$	-1.3(10)	$C_{(24)}$	$N_{(005)}$	$C_{(22)}$	$C_{(21)}$	-3.0(7)
$C_{(10)}$	$C_{(11)}$	$C_{(16)}$	$O_{(003)}$	159.5(6)	$C_{(24)}$	$C_{(25)}$	$C_{(26)}$	$C_{(27)}$	-2.2(10)
$C_{(10)}$	$C_{(11)}$	$C_{(16)}$	$C_{(17)}$	-84.4(8)	$C_{(25)}$	$C_{(21)}$	$C_{(22)}$	$O_{(002)}$	-173.1(6)
$C_{(10)}$	$C_{(11)}$	$C_{(16)}$	$C_{(20)}$	38.6(8)	$C_{(25)}$	$C_{(21)}$	$C_{(22)}$	$N_{(005)}$	3.8(7)
$C_{(11)}$	$C_{(12)}$	$C_{(13)}$	$C_{(8)}$	1.1(10)	$C_{(25)}$	$C_{(24)}$	$C_{(29)}$	$C_{(28)}$	-1.3(11)
$C_{(11)}$	$C_{(12)}$	$C_{(13)}$	$C_{(14)}$	179.6(6)	$C_{(25)}$	$C_{(26)}$	$C_{(27)}$	$C_{(28)}$	1.4(11)
$C_{(11)}$	$C_{(16)}$	$C_{(17)}$	$O_{(004)}$	-86.4(6)	$C_{(26)}$	$C_{(27)}$	$C_{(28)}$	$C_{(29)}$	-0.5(12)
$C_{(11)}$	$C_{(16)}$	$C_{(17)}$	$O_{(007)}$	91.5(7)	$C_{(27)}$	$C_{(28)}$	$C_{(29)}$	$C_{(24)}$	0.4(12)
$C_{(11)}$	$C_{(16)}$	$C_{(20)}$	$C_{(21)}$	178.5(6)	$C_{(29)}$	$C_{(24)}$	$C_{(25)}$	$C_{(21)}$	-178.2(6)
$C_{(12)}$	$N_{(006)}$	$C_{(15)}$	$C_{(14)}$	0.8(9)	$C_{(29)}$	$C_{(24)}$	$C_{(25)}$	$C_{(26)}$	2.2(11)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 20201107Lin_ABCZ2728_CF_0m_5.

Atom	*x*	*y*	*z*	U(eq)
$H_{(003)}$	5563.16	3212.09	4951.02	60
$H_{(006)}$	5445.33	540.4	3917.17	50
$H_{(009)}$	3197.21	2065.61	38.23	68

Table 7 Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å[2]×10[3]) for 20201107Lin_ABCZ2728_CF_0m_5.

Atom	***x***	***y***	***z***	**U(eq)**
$H_{(2)}$	2105.95	9249.51	-1939.22	76
$H_{(3)}$	3142.38	6740.87	-1888.7	69
$H_{(5)}$	2281.26	5281.72	579.25	63
$H_{(6)}$	1316.07	7812.4	594.53	65
$H_{(7A)}$	3162.96	3559.81	-1299.63	70
$H_{(7B)}$	4285.73	4500.62	-691.8	70
$H_{(9)}$	4827.61	5673.39	907.47	54
$H_{(10)}$	5955.51	6034.14	2543.59	52
$H_{(14)}$	3451.92	-203.1	1216.2	54
$H_{(15)}$	4221.9	-1514.28	2869.22	61
$H_{(18C)}$	9504.65	1347.53	4687.48	76
$H_{(18D)}$	9098.09	1607.61	3496.07	76
$H_{(18A)}$	9534.08	1748.35	4515.05	76
$H_{(18B)}$	8936.1	1213.37	3383.68	76
$H_{(19A)}$	8444.5	-1187.97	4549.85	158
$H_{(19B)}$	9281.09	-1339.71	3835.9	158
$H_{(19C)}$	7967.88	-909.89	3374.55	158
$H_{(20)}$	5933.84	6530.41	4042.88	46
$H_{(23A)}$	7126.13	10980.69	6599.1	89
$H_{(23B)}$	8172.96	10349.37	7476.71	89
$H_{(23C)}$	6900.6	9947.22	7520.33	89
$H_{(26)}$	8215.64	3330.44	6001.78	56
$H_{(27)}$	9654.64	3031.03	7487.24	64
$H_{(28)}$	10089.95	5286.06	8603.88	67
$H_{(29)}$	9140.65	7878.9	8252.29	62
$H_{(19D)}$	8956.86	-764.08	5118.53	158
$H_{(19E)}$	9533.2	-1293.99	4250.33	158
$H_{(19F)}$	8179.92	-1250.85	4038.82	158

Table 8 Atomic Occupancy for 20201107Lin_ABCZ2728_CF_0m_5.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
$H_{(18C)}$	0.45(8)	$H_{(18D)}$	0.45(8)	$H_{(18A)}$	0.55(8)
$H_{(18B)}$	0.55(8)	$C_{(19B)}$	0.45(8)	$H_{(19A)}$	0.45(8)
$H_{(19B)}$	0.45(8)	$H_{(19C)}$	0.45(8)	$C_{(19A)}$	0.55(8)
$H_{(19D)}$	0.55(8)	$H_{(19E)}$	0.55(8)	$H_{(19F)}$	0.55(8)