Electronic Supplementary Information

Palladium-Catalyzed Tandem Heck/Carbonylation/Aminocarbonylation En Route to Chiral Heterocyclic α-Ketoamides

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1. General Considerations

All the solvents and reagents were purchased from commercial suppliers. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a 400 MHz or/and 500 MHz Bruker FT-NMR spectrometers. All chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High Resolution Mass (MS) analysis was obtained using on a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI). Melting points were measured on a Mel-Temp apparatus and are uncorrected. Optical rotations were measured on Autopol IV automatic polarimeter. Enantiomeric ratios were determined by chiral HPLC on a Shimadzu instrument using a chiral stationary phase column with hexane and i-PrOH as solvents. The chiral HPLC condition methods were calibrated with the corresponding racemic mixtures. Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates (GF254) under UV light. Flash chromatography was performed on silica gel 60 (200–300 mesh). Substrates **1a**-**m** were synthesized according to the literature procedures.[1] Substrates **5a**-**h** were synthesized according to the literature procedures.[2] **2a**-**l** were purchased from commercial sources and used without further purification.

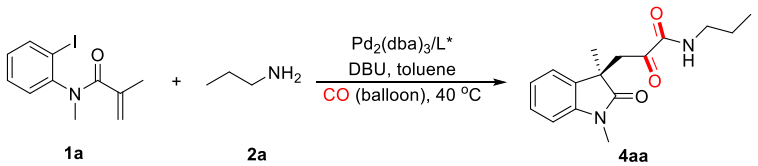
2. Experimental Sections

General procedure:

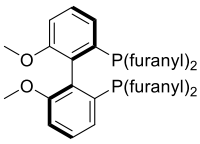
In a dry 10 mL Schlenk tube, L***** (0.012 mmol, 12 mol%), $Pd_2(dba)_3$ (0.005 mmol, 5% mol% or 0.0025 mmol, 2.5 mol%) were added, and the tube was vacuumed and refilled with Ar for 3 times followed by injection 0.5 mL of solvent. The mixture was stirred at room temperature for 45 min under Ar balloon. Then substrates **1** or **5** (0.1 mmol, 1.0 equiv), alkylamines (0.15 mmol, 1.5 equiv), base (0.12 mmol, 1.2 equiv) and 0.5 mL of solvent were added to the mixture. After the tube was vacuumed and refilled with CO for 3 times, the mixture was stirred at 40 ^oC under balloon pressure of CO. After completion of the reaction, it was cooled to room temperature before addition of saturated brine (10 mL) and EtOAc (10 mL) to the reaction mixture. The aqueous phase was further extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the desired products.

Screening of the chiral ligands for the synthesis of 4aa.

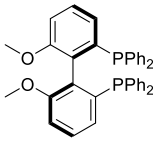
Table S1. Screening of the chiral ligands under optimal racemic reaction conditions.[a]



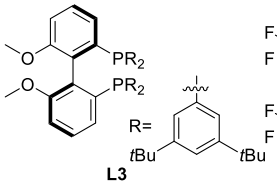
1a **2a** **4aa**



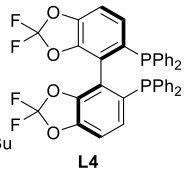
L1
80% yield, 86% ee



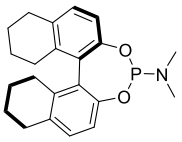
L2
N.D.



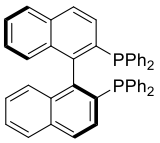
L3
24% yield, 1% ee



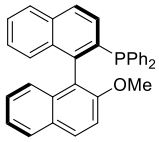
L4
N.D.



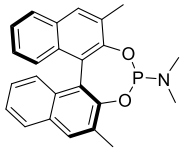
L5
36% yield, -13% ee



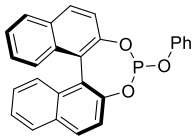
L6
trace



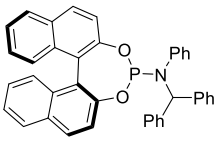
L7
77% yield, 0% ee



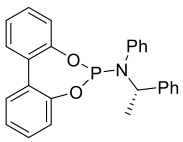
L8
<10% yield, 22% ee



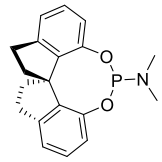
L9
29% yield, 0% ee



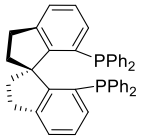
L10
15% yield, -1% ee



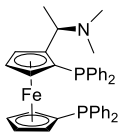
L11
65% yield, 1% ee



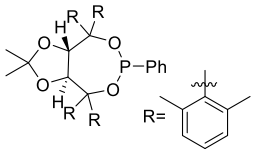
L12
trace



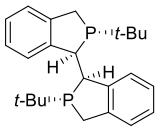
L13
26% yield, 6% ee



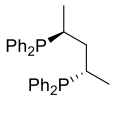
L14
44% yield, -14% ee



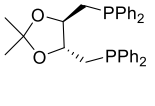
L15
85% yield, 23% ee



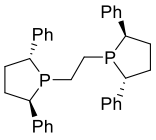
L16
<10% yield, -6% ee



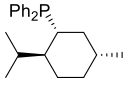
L17
26% yield, 4% ee



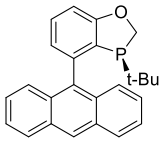
L18
58% yield, 8% ee



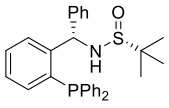
L19
52% yield, 6% ee



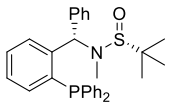
L20
83% yield, -7% ee



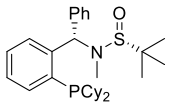
L21
84% yield, -26% ee



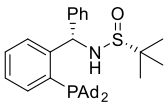
L22
trace



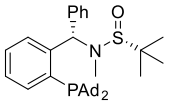
L23
87% yield, -8% ee



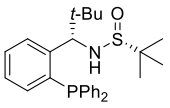
L24
88% yield, -13% ee



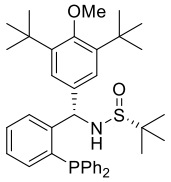
L25
50% yield, -8% ee



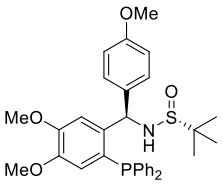
L26
37% yield, -2% ee



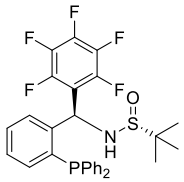
L27
83% yield, 2% ee



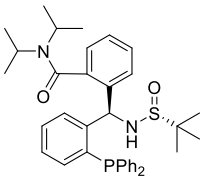
L28
24% yield, 1% ee



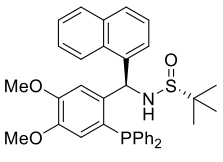
L29
51% yield, 35% ee



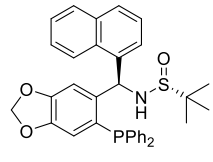
L30
52% yield, -2% ee



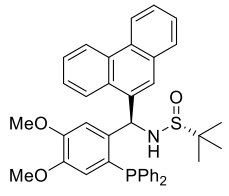
L31
77% yield, 8% ee



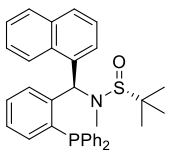
L32
59% yield, -8% ee



L33
60% yield, 5% ee



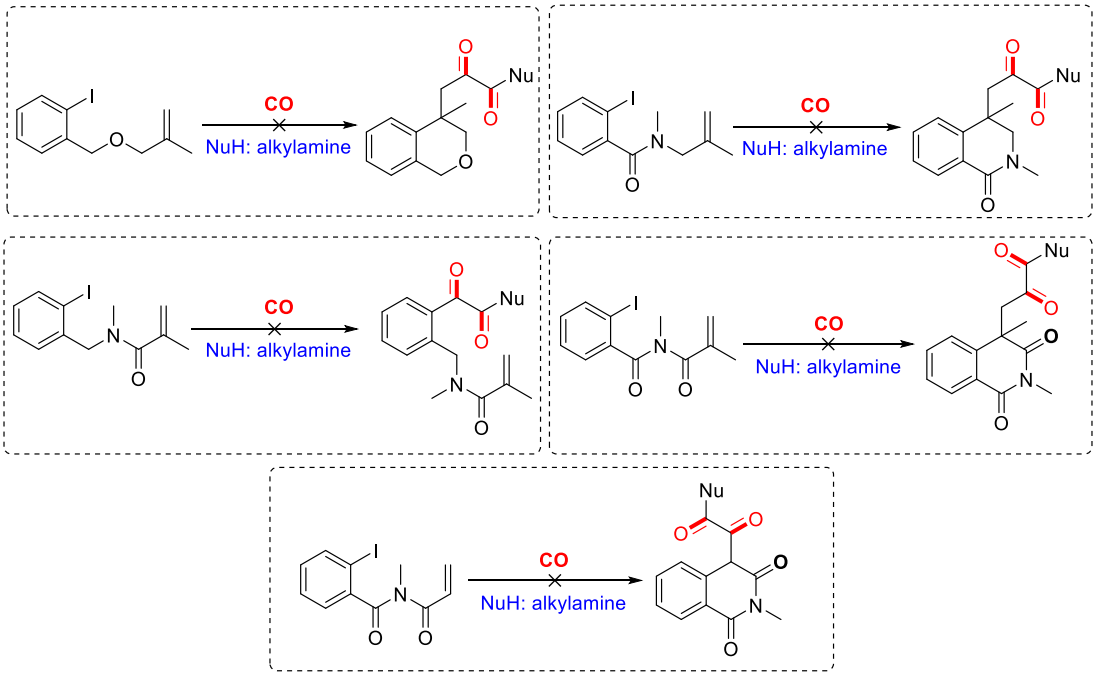
L34
46% yield, -9% ee



L35
83% yield, -18% ee

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv), $Pd_2(dba)_3$ (5 mol%), L* ([P]: 24 mol%), DBU (1.2 equiv) in 1.0 mL of solvent, 40 °C, 15 h, CO balloon (1 atm). Determined by HPLC analysis using a chi-ral stationary phase.

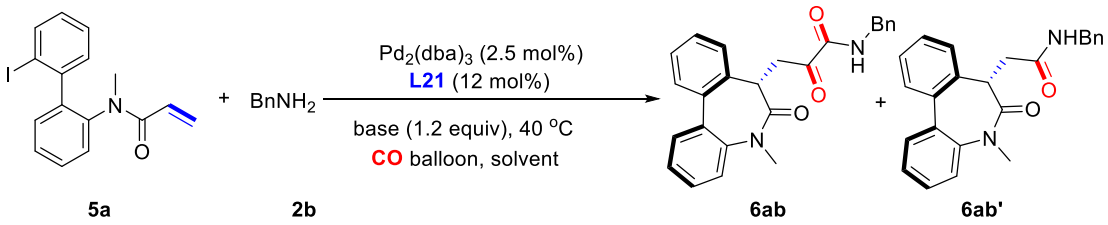
Attempts to construct six-membered heterocycle substituted α-ketoamides



Scheme S1. Failures in enantioselective tandem 6-*exo*-trig Heck/carbonylation/aminocarbonylation.

Detailed Information of Conditions Optimization for 6ab[a,f]

Table S2:

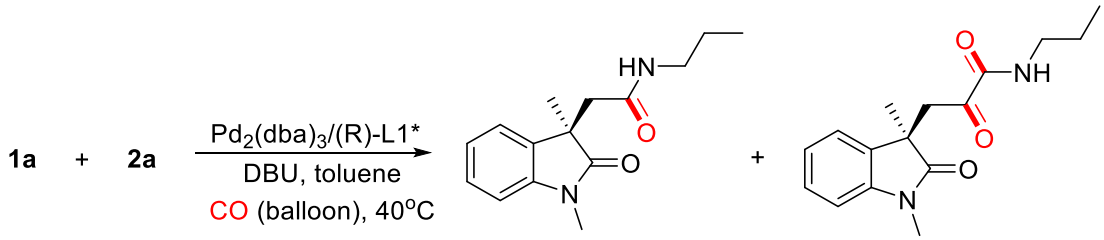


entry	base	solvent	6ab :6ab'[c]	yield of 6ab / %	ee of 6ab / %[d]
1	Cs_2CO_3	toulene	4:1	78[b]	94
2	DABCO	toulene	1.25:1	-	-
3	Et_3N	toulene	0:1	-	-

4[g]	-	toulene	0:1	-	-
5	*t*-BuOK	toulene	2.5:1	-	-
6	Cs_2CO_3	*o*-xylene	5:1	-	94
7	Cs_2CO_3	PhCN	4:1	-	-
8	Cs_2CO_3	PhCl	3:1	-	-
9	Cs_2CO_3	dioxane	5:1	-	93
10	Cs_2CO_3	$PhCF_3$	1.25:1	-	-
11	Cs_2CO_3	THF	1:1	-	-
12	Cs_2CO_3	DMSO	1:1	-	-
13[e]	**Cs_2CO_3**	**mesitylene**	**10:1**	**86**[b]	**94**

[a] Reaction conditions: **5a** (0.05 mmol), **2b** (1.5 equiv), $Pd_2(dba)_3$ (2.5 mol%), **L21** (12 mol%), base (1.2 equiv) in 0.5 mL of solvent, 40 °C, 10 h, CO balloon (1 atm). [b] Isolated yield. [c] Determined by ^1H NMR. [d] Determined by HPLC analysis using a chiral stationary phase. [e] 0.1 mmol of **5a** in 1.0 mL of solvent. [f] Only a single diastereomer was observed, > 20 : 1 d.r. [g] 3.0 equiv of **2b**, no extra base was added.

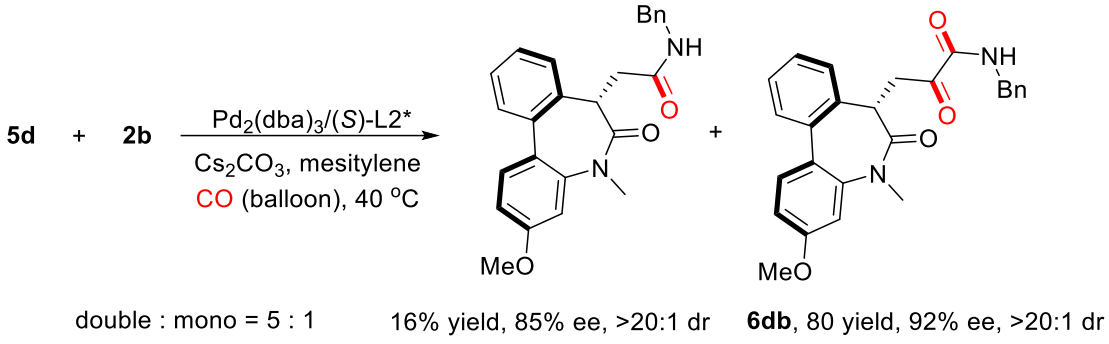
Procedures for 1 mmol-scale reaction



double : mono = 9.5 : 1 **3aa**, 8% yield, 95% ee **4aa**, 76% yield, 91% ee

In a dry 50 mL two-necked bottle, (R)-L1* (0.12 mmol, 12 mol%), $Pd_2(dba)_3$ (0.05 mmol, 5% mol%) were added, and the bottle was vacuumed and refilled with Ar for 3 times followed by injection 5.0 mL of toluene. The mixture was stirred at room temperature for 45 min under Ar balloon. Then substrates **1a** (1.0 mmol, 1.0 equiv), **2a** (1.5 mmol, 1.5 equiv), DBU (0.12 mmol, 1.2 equiv) and 5.0 mL of toluene were added to the mixture. After the bottle was vacuumed and refilled with CO for 3 times,

the mixture was stirred at 40 °C under balloon pressure of CO. After completion of the reaction, it was cooled to room temperature before addition of saturated brine (50 mL) and EtOAc (50 mL) to the reaction mixture. The aqueous phase was further extracted with EtOAc (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give **3aa** (21.3 mg, 8% yield, 95% ee) and **4aa** (218.9 mg, 76% yield, 91% ee).



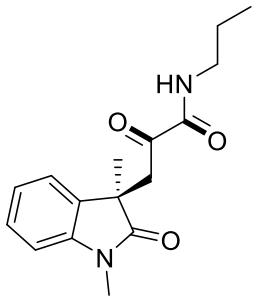
In a dry 50 mL two-necked bottle, (*S*)-L2* (0.12 mmol, 12 mol%), $Pd_2(dba)_3$ (0.025 mmol, 2.5 mol%) were added, and the bottle was vacuumed and refilled with Ar for 3 times followed by injection 5.0 mL of mesitylene. The mixture was stirred at room temperature for 45 min under Ar balloon. Then substrates **5d** (1.0 mmol, 1.0 equiv), **2b** (1.5 mmol, 1.5 equiv), Cs_2CO_3 (1.2 mmol, 1.2 equiv) and 5.0 mL of mesitylene were added to the mixture. After the tube was vacuumed and refilled with CO for 3 times, the mixture was stirred at 40 °C under balloon pressure of CO. After completion of the reaction, it was cooled to room temperature before addition of saturated brine (50 mL) and EtOAc (50 mL) to the reaction mixture. The aqueous phase was further extracted with EtOAc (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the amide product (65.0 mg, 16% yield, 85% ee, >20:1 d.r.) and **6db** (342.3 mg, 80% yield, 92% ee, >20:1 d.r.).

Procedures for the Derivatization of 4aa and 6db

The preparation of compound **7** was described as an example. $NaBH_4$ (15.2 mg, 2.0

equiv) was add to a mixture of **4aa** (57.6 mg, 0.2 mmol, 1.0 equiv) in MeOH (5.0 mL) at -5 ºC under Ar atmosphere and the mixture was stirring at that temperature for 1h. Then the mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (6 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford 2-hydroxy-*N*-propylpropanamide. $LiAlH_4$ (15.2 mg, 2.0 equiv) was added to a mixture of 2-hydroxy-N-propylpropanamide in dry THF (3.0 mL) at room temperature under Ar atmosphere and the mixture was stirring at that temperature for 2h. The mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The 6:1 dr was determinded by ^{1}H NMR and **7** (24.4 mg, 45% yield) was abtained by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1).

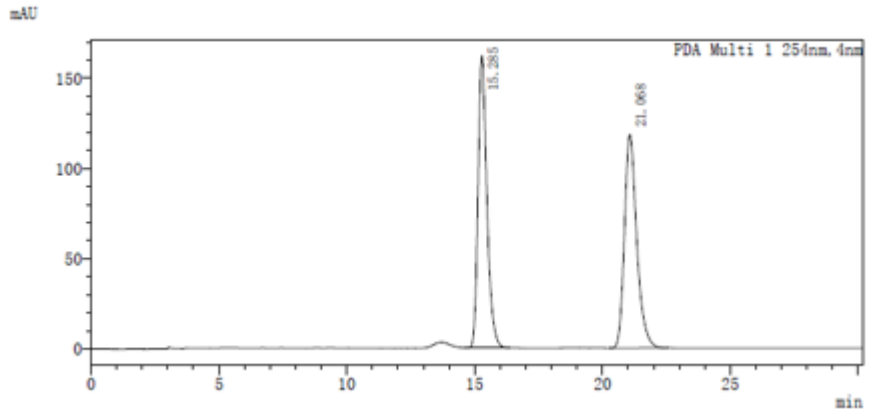
3. Characterization Data for the Products



(*R*)-3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2-oxo-*N*-propylpropanamide (4aa)

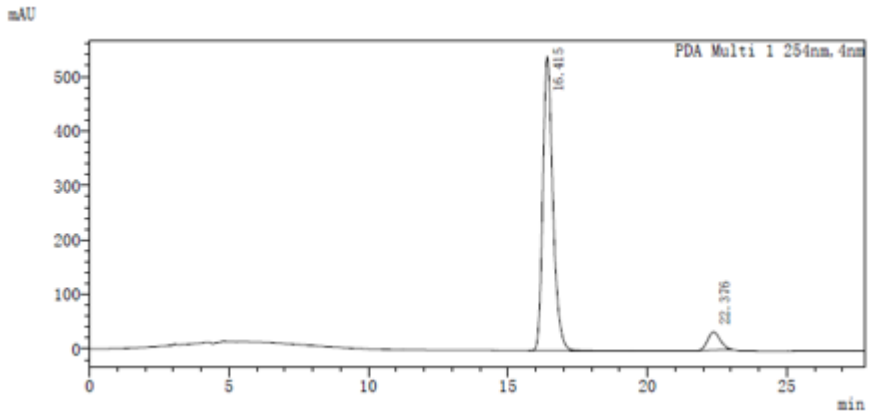
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (23.1 mg, 80% yield, 86% ee); $[\alpha]_D^{25}$ = -12.0 (c = 0.15 in MeOH, 86% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 6.5 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 4.7 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.67 (s, 1H), 3.86 (dd, *J* = 19.1, 2.0 Hz, 1H), 3.42 (dd, *J* = 19.2, 2.0 Hz, 1H), 3.28 (s, 3H), 3.22 – 3.09 (m, 2H), 1.50 – 1.43 (m, 2H), 1.39 (s, 3H), 0.86 (td, *J* = 7.4, 2.1 Hz, 3H); **^{13}C NMR**

(126 MHz, $CDCl_3$) δ 195.81, 180.13, 159.63, 143.90, 133.06, 128.21, 122.49, 122.07, 108.18, 44.96, 44.19, 41.08, 26.48, 24.87, 22.50, 11.33. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{16}H_{19}N_2O_3^-$ 287.1401; Found 287.1403. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 16.415 min, t (minor) = 22.376 min.



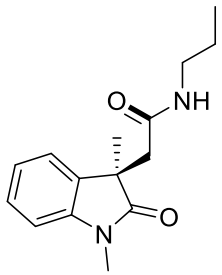
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	15.285	3912153	161787	49.704	0.624
2	21.068	3958800	118352	50.296	0.858



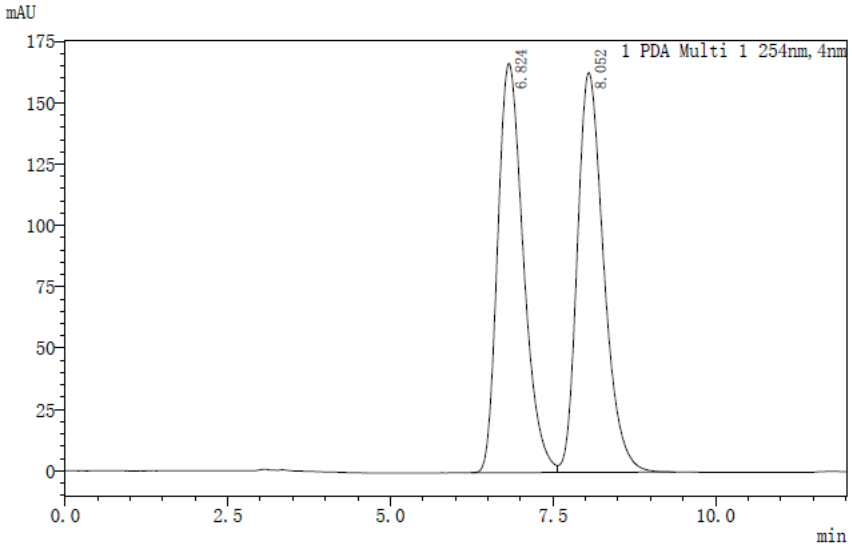
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	16.415	13561759	539427	92.810	0.649
2	22.376	1050709	33374	7.190	0.847



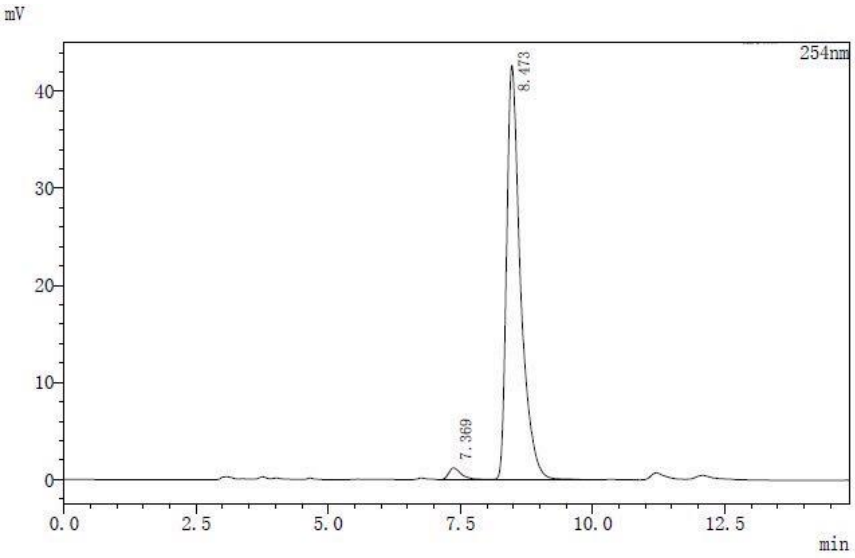
***(R)*-2-(1,3-dimethyl-2-oxoindolin-3-yl)-N-propylacetamide (3aa)**

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:2) gave the product as a colorless oil (21.3 mg, 8% yield, 95% ee); $[\alpha]_D^{25}$ = +26.3 (c = 0.19 in MeOH, 95% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 2H), 7.10 – 7.00 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.34 (s, 1H), 3.23 (s, 3H), 3.06 (dd, *J* = 13.1, 6.9 Hz, 2H), 2.70 (dd, *J* = 55.6, 14.7 Hz, 2H), 1.51 – 1.32 (m, 5H), 0.81 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.78, 168.99, 142.93, 133.48, 128.24, 122.91, 108.37, 46.37, 44.10, 41.24, 26.47, 23.72, 22.82, 11.41. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{15}H_{19}N_2O_2^-$ 259.1452; Found 259.1453. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.473 min, t (minor) = 7.369 min.

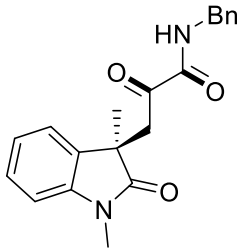


PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.824	166800	4578317	49.842	--
2	8.052	162927	4607348	50.158	1.685

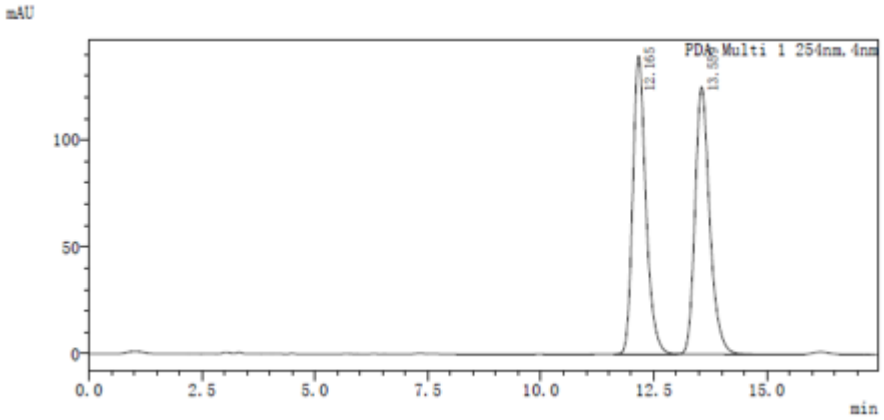


NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	7.369	1229	21039	2.610	--
2	8.473	42718	784918	97.390	2.519



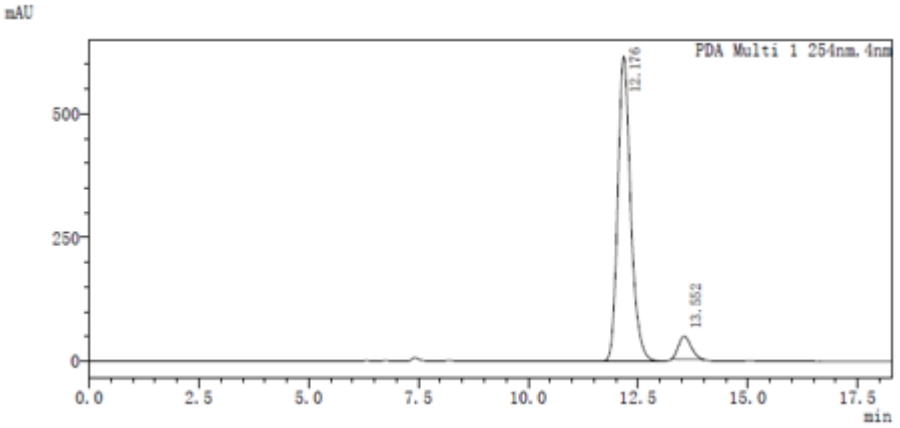
(*R*)-*N*-benzyl-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2-oxopropanamide (4ab)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (27.4 mg, 81% yield, 86% ee); $[\alpha]_D^{25}$ = +75.6 (c = 0.23 in MeOH, 86% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 4H), 7.19 – 7.10 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.42 – 4.29 (m, 2H), 3.88 (d, *J* = 19.1 Hz, 1H), 3.44 (d, *J* = 19.1 Hz, 1H), 3.25 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.51, 180.06, 159.42, 143.90, 136.76, 132.96, 128.91, 128.26, 127.98, 127.96, 122.53, 122.12, 108.22, 45.00, 44.25, 43.52, 26.50, 24.84. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{20}H_{19}N_2O_3^-$ 335.1401; Found 335.1399. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 12.176 min, t (minor) = 13.552 min.



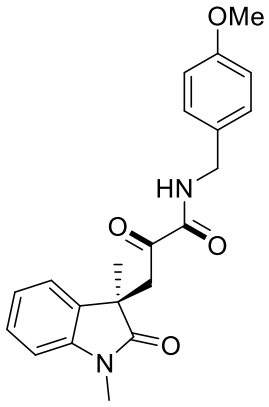
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	12.165	2829071	139385	50.008	0.527
2	13.559	2828184	125010	49.992	0.585



PDA Ch1 254nm

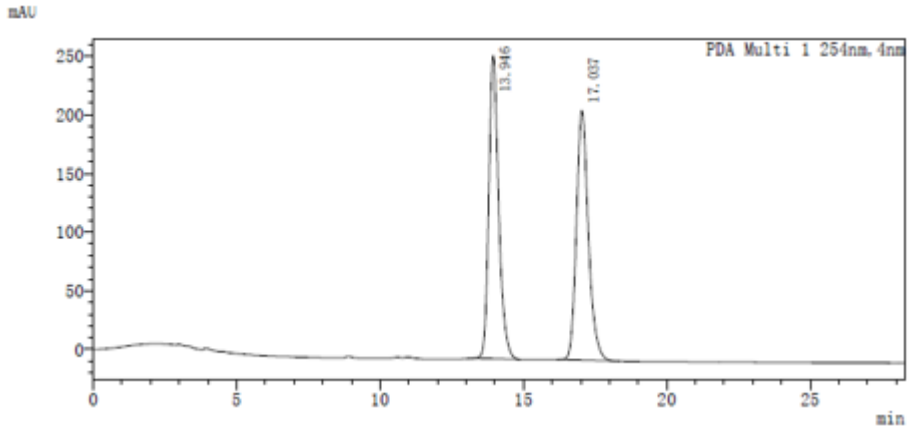
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	12.176	12618209	615392	93.229	0.531
2	13.552	916485	46134	6.771	0.542



(*R*)-3-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*-(4-methoxybenzyl)-2-oxopropanamide (4ac)

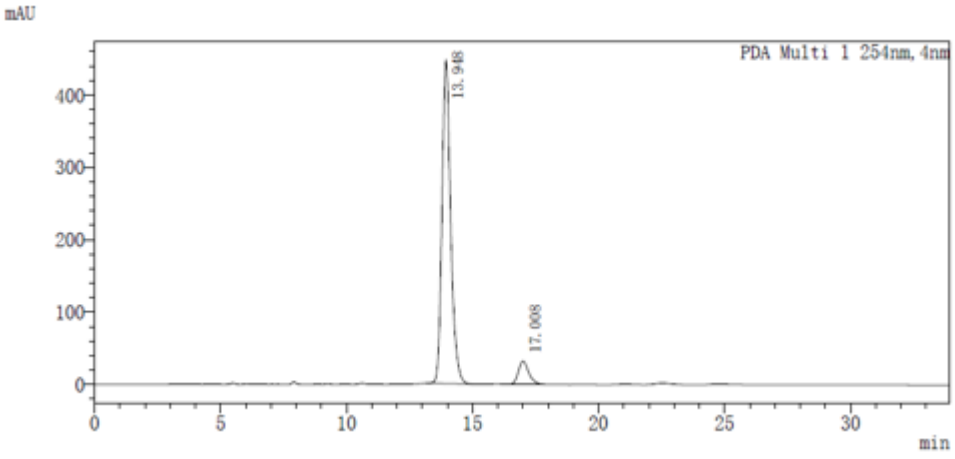
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave

the product as a colorless oil (27.7 mg, 76% yield, 84% ee); $[\alpha]_D^{25}$ = -9.2 (c = 0.13 in MeOH, 84% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.7 Hz, 1H), 7.11 (dd, *J* = 13.9, 7.8 Hz, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 4.36 – 4.22 (m, 2H), 3.87 (d, *J* = 19.1 Hz, 1H), 3.77 (s, 3H), 3.43 (d, *J* = 19.1 Hz, 1H), 3.25 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.59, 180.09, 159.43, 159.33, 143.91, 132.99, 129.38, 128.84, 128.26, 122.53, 122.12, 114.32, 108.22, 55.43, 45.00, 44.28, 43.04, 26.51, 24.85. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{21}H_{21}N_2O_4^-$ 365.1507; Found 365.1504. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 13.948 min, t (minor) = 17.008 min.



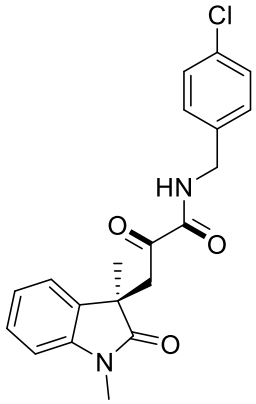
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	13.946	6195588	258226	50.038	0.618
2	17.037	6186278	212905	49.962	0.748



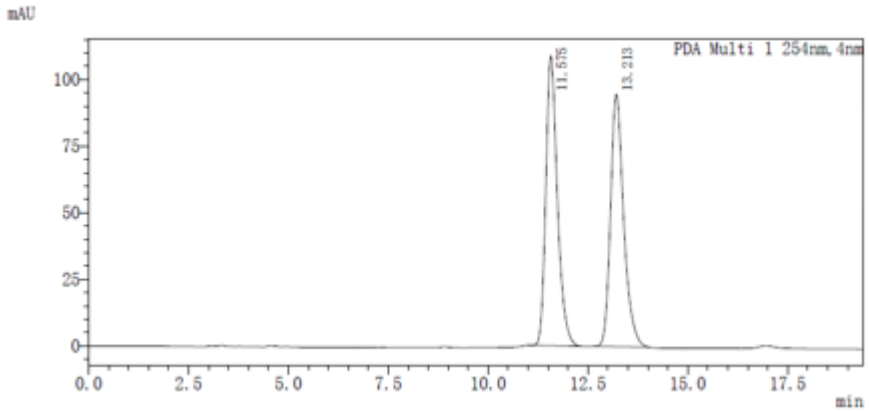
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	13.948	10719721	446767	92.130	0.617
2	17.008	915722	32052	7.870	0.745



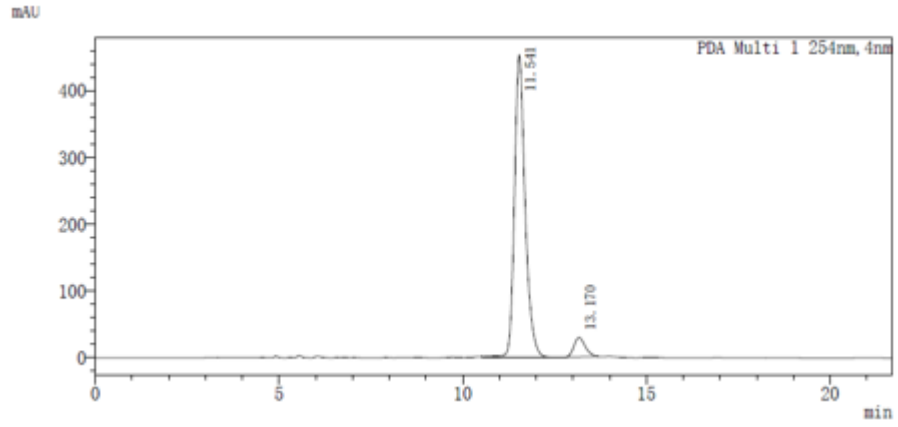
(*R*)-*N*-(4-chlorobenzyl)-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2-oxopropanamide (4ad)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (24.2 mg, 65% yield, 87% ee); $[\alpha]_D^{25}$ = -11.3 (c = 0.16 in MeOH, 87% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 4H), 7.13 – 7.09 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.32 (d, *J* = 6.1 Hz, 2H), 3.86 (d, *J* = 19.0 Hz, 1H), 3.42 (d, *J* = 19.0 Hz, 1H), 3.26 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.46, 180.03, 159.51, 143.91, 135.34, 133.91, 132.94, 129.31, 129.08, 128.33, 122.57, 122.15, 108.28, 45.08, 44.19, 42.83, 26.54, 24.85. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{20}H_{18}ClN_2O_3^-$ 369.1011; Found 369.1018. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 11.541 min, t (minor) = 13.170 min.



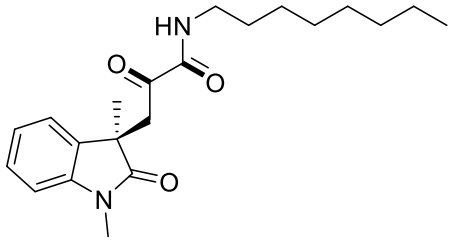
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.575	2180213	108797	50.042	0.520
2	13.213	2176561	94722	49.958	0.593



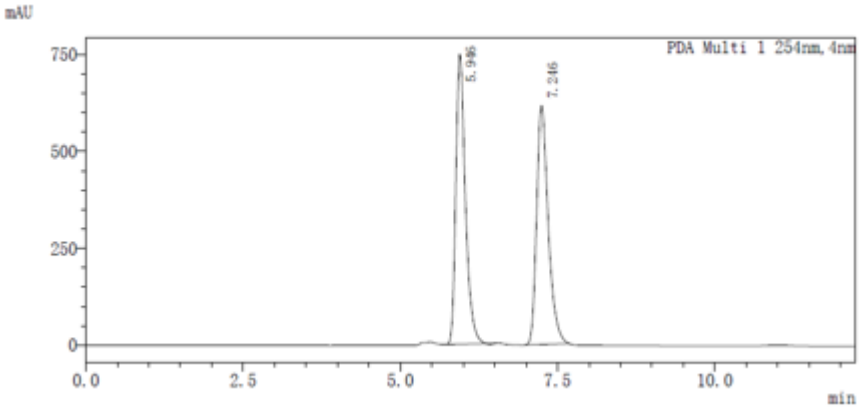
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.541	9261502	453243	93.682	0.520
2	13.170	624611	29148	6.318	0.573



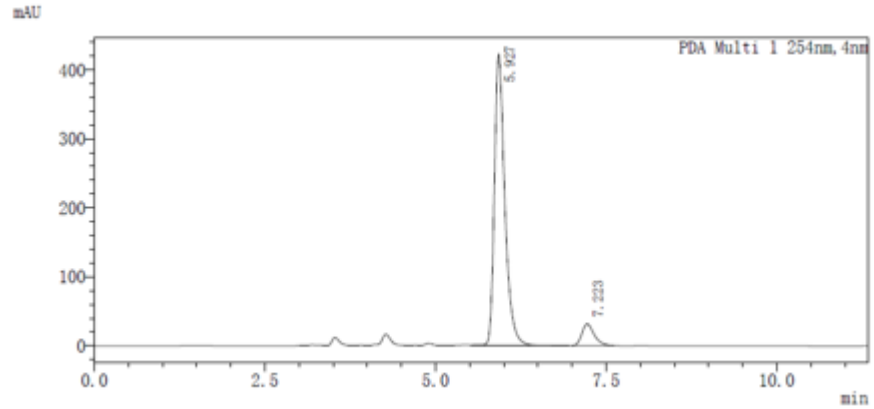
(*R*)-3-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*-octyl-2-oxopropanamide (4ae)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (34.4 mg, 91% yield, 84% ee); $[\alpha]_D^{25}$ = -8.8 (c = 0.25 in MeOH, 84% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.63 (s, 1H), 3.86 (d, *J* = 19.2 Hz, 1H), 3.41 (d, *J* = 19.2 Hz, 1H), 3.27 (s, 3H), 3.21– 3.12 (m, 2H), 1.45 – 1.37 (m, 5H), 1.31 – 1.20 (m, 13H), 0.86 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.84, 180.17, 159.57, 143.93, 133.08, 128.25, 122.52, 122.09, 108.20, 44.97, 44.25, 39.44, 31.86, 29.24, 29.22, 26.89, 26.52, 24.91, 22.73, 14.20, 14.17. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{21}H_{29}N_2O_3^-$ 357.2184; Found 357.2179. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 5.927 min, t (minor) = 7.223 min.



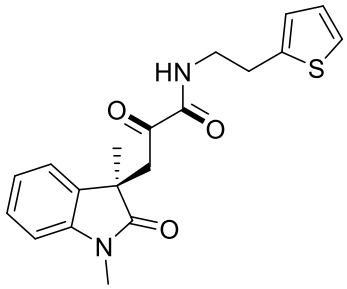
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	5.946	7898757	746703	50.053	0.283
2	7.246	7881984	615227	49.947	0.340



PDA Ch1 254nm

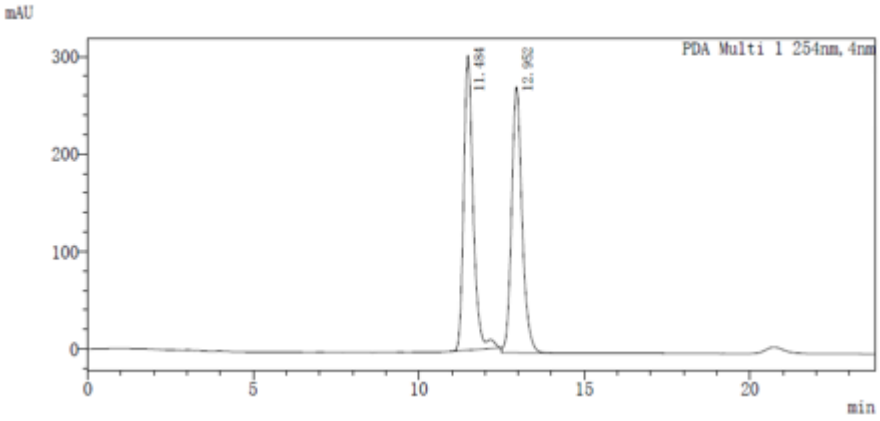
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	5.927	4558645	422509	92.026	0.283
2	7.223	394994	31522	7.974	0.336



(*R*)-3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2-oxo-*N*-(2-(thiophen-2-yl)ethyl)propenamide (4af)

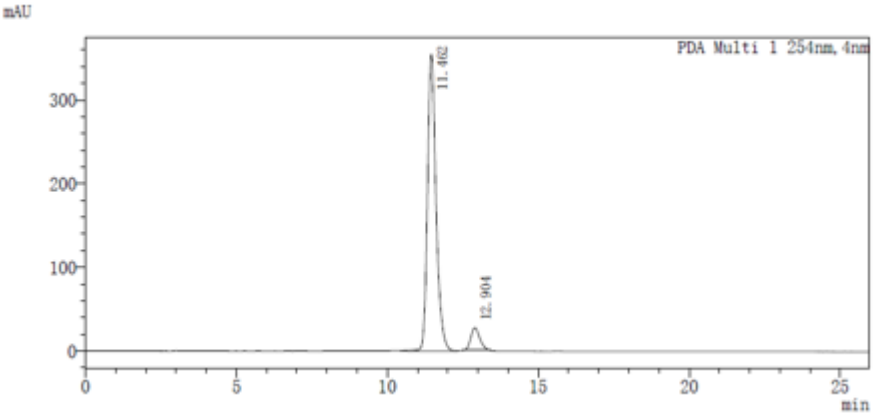
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (27.5 mg, 77% yield, 85% ee); $[\alpha]_D^{25}$ = -16.0 (c = 0.20 in MeOH, 85% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.3 Hz, 1H), 7.13 –

7.10 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.79 (s, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 3.84 (d, *J* = 19.0 Hz, 1H), 3.56 – 3.35 (m, 3H), 3.26 (s, 3H), 2.96 (t, *J* = 6.8 Hz, 2H), 1.38 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.39, 180.05, 159.62, 143.86, 140.40, 132.97, 128.24, 127.21, 125.60, 124.25, 122.51, 122.08, 108.22, 44.97, 44.05, 40.69, 29.59, 26.50, 24.89. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{19}H_{19}N_2O_3S^-$ 355.1122; Found 355.1130. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 11.462 min, t (minor) = 12.904 min.



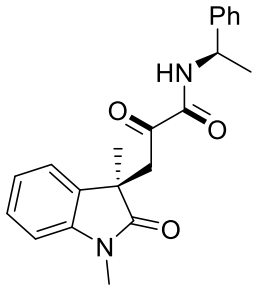
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.484	6021652	302263	49.952	0.506
2	12.952	6033179	272997	50.048	0.568



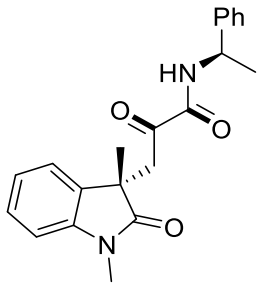
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.462	7028226	354688	92.482	0.508
2	12.904	571325	27186	7.518	0.558



3-((*R*)-1,3-Dimethyl-2-oxoindolin-3-yl)-2-oxo-*N*-((*R*)-1-phenylethyl)propenamide (4ag)

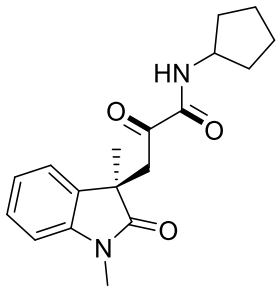
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (22.3 mg, 64% yield, 86% de); $[\alpha]_D^{25}$ = +5.0 (c = 0.12 in MeOH, 86% de); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 4H), 7.18 (d, *J* = 7.1 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.95 (p, *J* = 7.0 Hz, 1H), 3.83 (d, *J* = 19.3 Hz, 1H), 3.46 (d, *J* = 19.3 Hz, 1H), 3.26 (s, 3H), 1.44 (d, *J* = 6.9 Hz, 3H), 1.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.69, 180.10, 158.54, 143.80, 141.91, 132.91, 128.81, 128.18, 127.77, 126.22, 122.49, 122.06, 108.15, 49.15, 44.85, 44.27, 26.45, 24.89, 21.55. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{21}H_{21}N_2O_3^-$ 349.1558; Found 349.1551.



3-((*S*)-1,3-Dimethyl-2-oxoindolin-3-yl)-2-oxo-*N*-((*R*)-1-phenylethyl)propenamide (4ag')

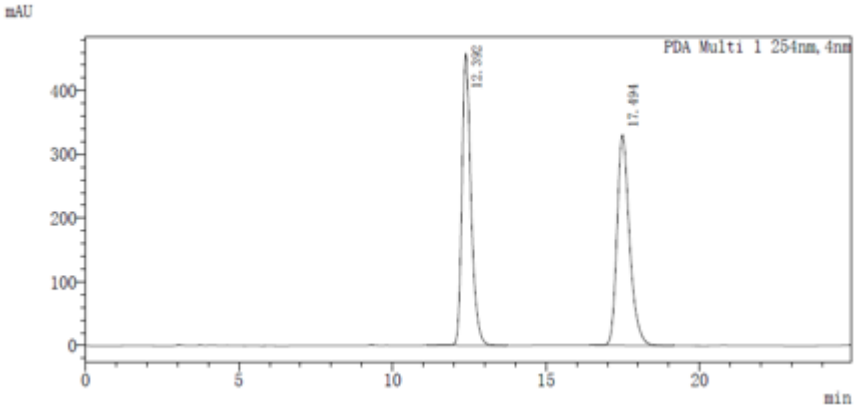
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a white solid (22.6 mg, 65% yield, 89% de): mp 138-140 °C; $[\alpha]_D^{25}$ = +28.0 (c = 0.20 in MeOH, 89% de); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 4H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 2H), 4.95 (p, *J* = 7.1 Hz, 1H), 3.85 (d, *J* = 19.2 Hz, 1H), 3.41 (d, *J* = 19.2 Hz, 1H), 3.26 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.38 (s, 3H); **^{13}C NMR** (126

MHz, $CDCl_3$) δ 195.81, 180.07, 158.59, 143.94, 141.90, 133.01, 128.92, 128.28, 127.88, 126.23, 122.52, 122.13, 108.21, 49.16, 44.95, 44.30, 26.51, 24.88, 21.52.



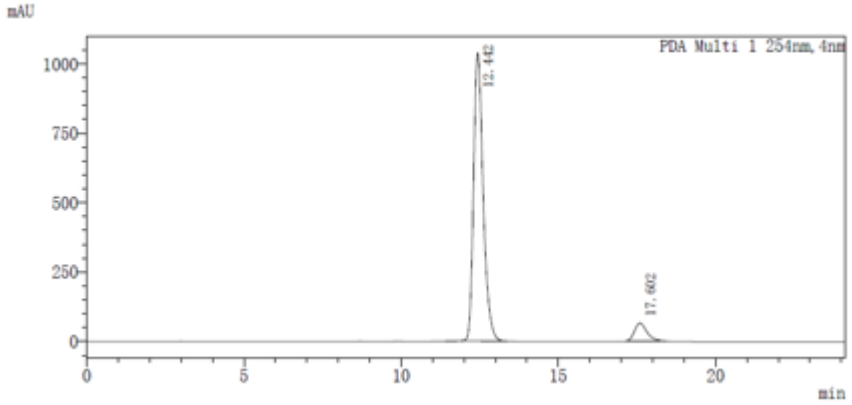
(*R*)-*N*-cyclopentyl-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2-oxopropanamide (4ah)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (26.2 mg, 83% yield, 85% ee); $[\alpha]_D^{25}$ = -6.7 (c = 0.18 in MeOH, 85% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 7.11 (d, *J* = 6.8 Hz, 1H), 7.00 (t, *J* = 4.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.58 (s, 1H), 4.12 – 4.02 (m, 1H), 3.85 (d, *J* = 19.4 Hz, 1H), 3.44 (d, *J* = 19.4 Hz, 1H), 3.28 (s, 3H), 2.01 – 1.81 (m, 2H), 1.63 – 1.50 (m, 4H), 1.39 (s, 3H), 1.38 – 1.23 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.00, 180.21, 159.07, 143.94, 133.10, 128.25, 122.52, 122.09, 108.19, 51.13, 44.91, 44.36, 32.96, 32.86, 26.52, 24.94, 23.75. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{18}H_{21}N_2O_3^-$ 313.1558; Found 313.1566. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 12.442 min, t (minor) = 17.602 min.



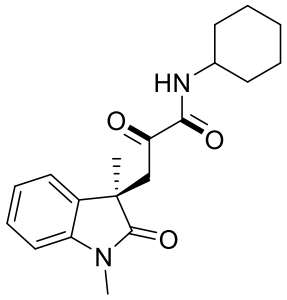
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	12.392	9431895	457771	50.074	0.529
2	17.494	9403924	330378	49.926	0.731



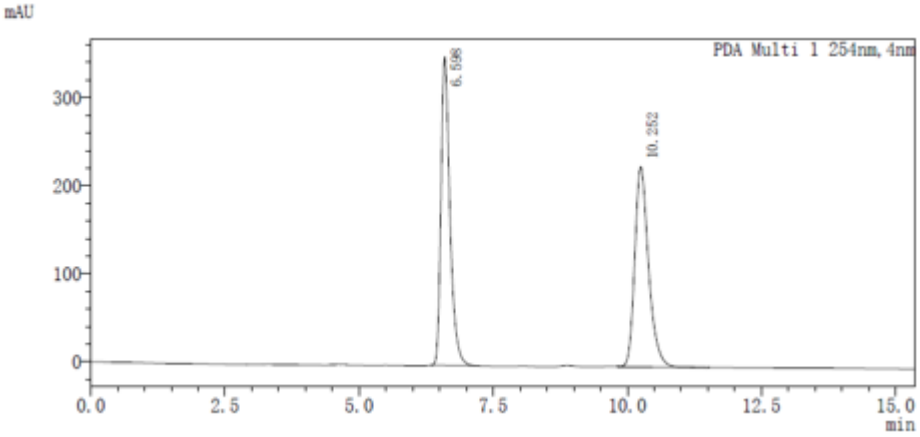
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	12.442	21948947	1036417	92.900	0.547
2	17.602	1677358	63466	7.100	0.701



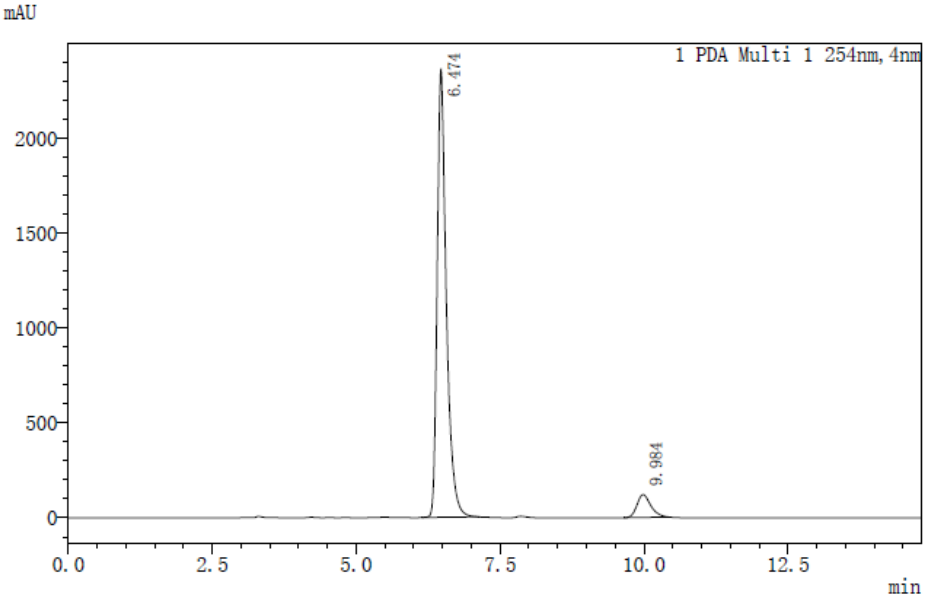
(*R*)-*N*-cyclohexyl-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2-oxopropanamide (4ai)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (28.8 mg, 88% yield, 86% ee); $[\alpha]_D^{25}$ = -5.0 (c = 0.12 in MeOH, 86% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 3.85 (d, *J* = 19.4 Hz, 1H), 3.68 – 3.56 (m, 1H), 3.44 (d, *J* = 19.4 Hz, 1H), 3.28 (s, 3H), 1.85 – 1.75 (m, 2H), 1.66 – 1.60 (m, 2H), 1.39 (s, 3H), 1.37 – 1.27 (m, 3H), 1.17-1.03 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.14, 180.24, 158.59, 143.95, 133.12, 128.25, 122.53, 122.10, 108.20, 48.38, 44.93, 44.38, 32.67, 32.64, 26.53, 25.44, 24.95, 24.69. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{19}H_{23}N_2O_3^-$ 327.1714; Found 327.1707. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 6.474 min, t (minor) = 9.984 min.



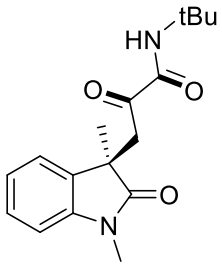
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.598	4075339	350426	49.919	0.307
2	10.252	4088592	227575	50.081	0.466



PDA Ch1 254nm

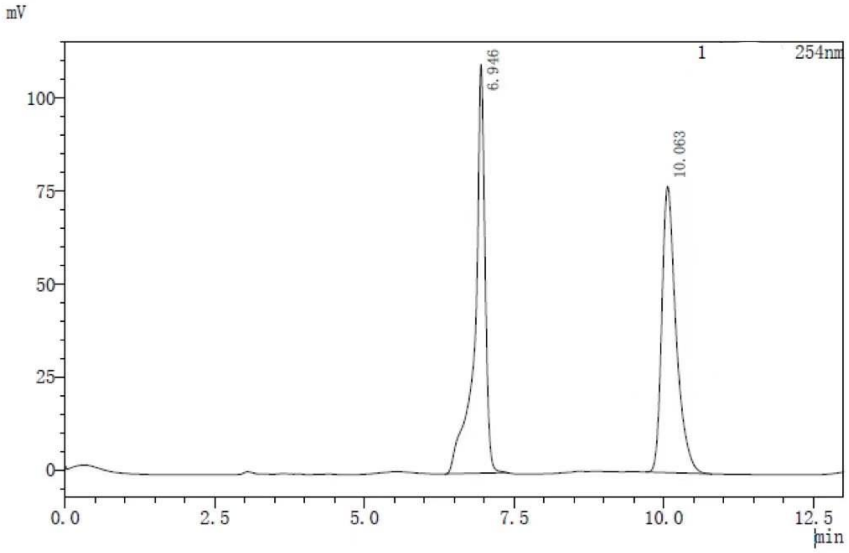
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.474	2362029	26039342	92.902	--
2	9.984	120030	1989367	7.098	9.574



(*R*)-*N*-(tert-butyl)-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2-oxopropanamide (4aj)

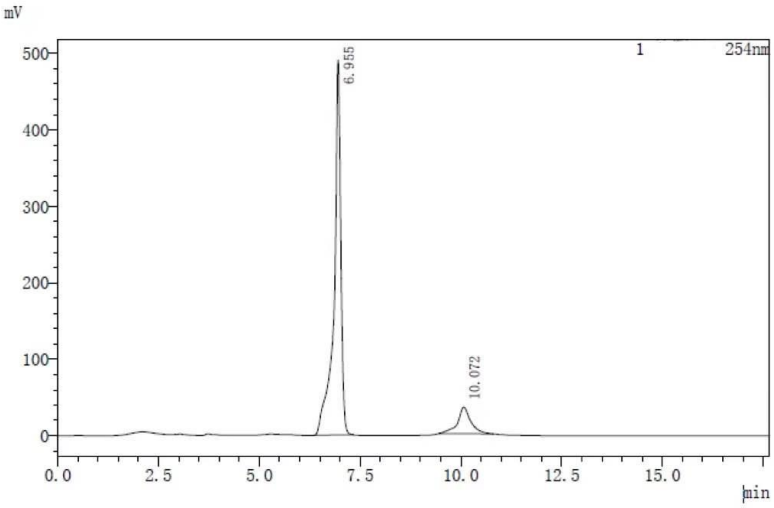
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:6) gave

the product as a colorless oil (10.2 mg, 34% yield, 75% ee); $[\alpha]_D^{25}$ = -6.0 (c = 0.30 in MeOH, 75% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 3.83 (d, *J* = 19.4 Hz, 1H), 3.44 (d, *J* = 19.4 Hz, 1H), 3.29 (s, 3H), 1.38 (s, 3H), 1.28 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.61, 180.13, 158.60, 143.80, 132.99, 128.09, 122.36, 121.96, 108.04, 51.23, 44.75, 43.91, 28.14, 26.39, 24.87. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_3^+$ 303.1703; Found 303.1703. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 6.955 min, t (minor) = 10.072 min.



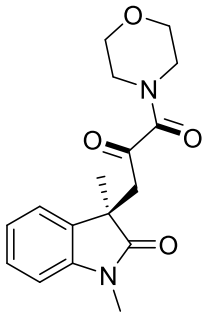
254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.946	109967	1294685	50.336	--
2	10.063	77020	1277417	49.664	9.353



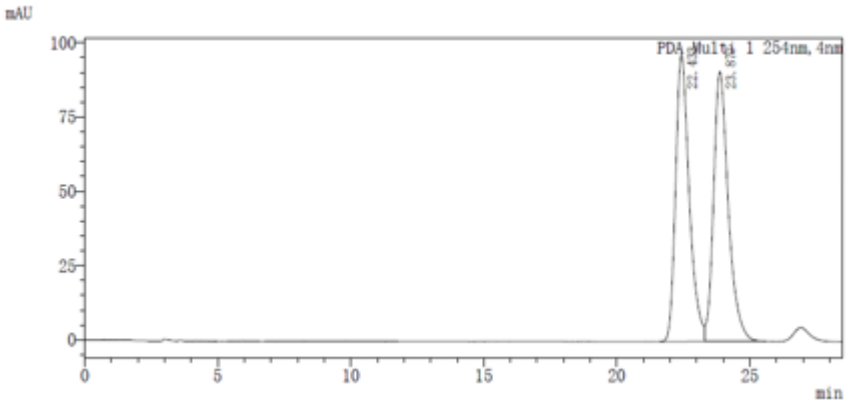
254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.955	489910	5703724	87.736	--
2	10.072	34936	797284	12.264	8.310



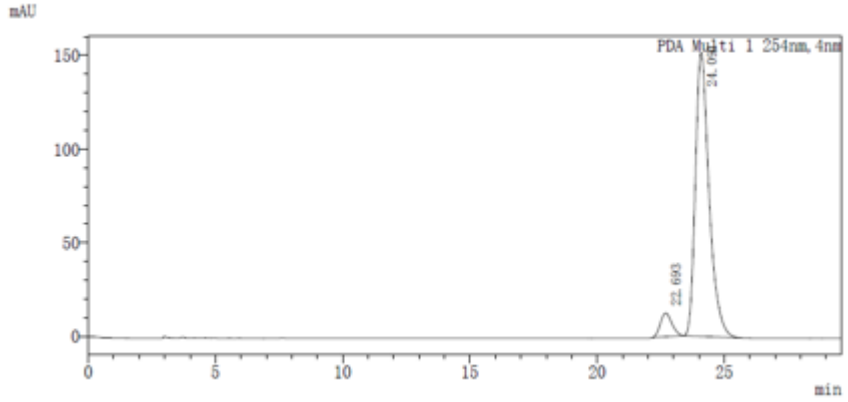
(*R*)-3-(1,3-Dimethyl-2-oxoindolin-3-yl)-1-morpholinopropane-1,2-dione (4ak)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (23.4 mg, 74% yield, 86% ee); $[\alpha]_D^{25}$ = +5.3 (c = 0.19 in MeOH, 86% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 3.68-3.60 (m, 3H), 3.57-3.48 (m, 4H), 3.29 – 3.18 (m, 6H), 1.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.74, 179.90, 164.01, 143.58, 132.80, 128.31, 122.58, 122.11, 108.33, 66.82, 66.50, 46.61, 45.91, 45.33, 42.04, 26.50, 24.72. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{17}H_{19}N_2O_4^-$ 315.1350; Found 315.1342. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 24.091 min, t (minor) = 22.693 min.



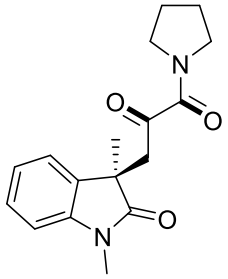
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	22.433	3441568	96485	49.530	0.920
2	23.877	3506859	90784	50.470	0.980



PDA Ch1 254nm

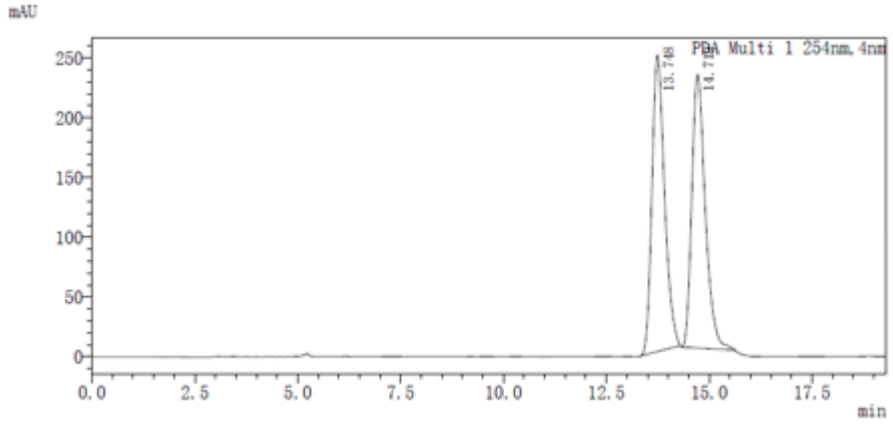
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	22.693	396899	12621	6.530	0.849
2	24.091	5680770	151480	93.470	0.959



(*R*)-3-(1,3-Dimethyl-2-oxoindolin-3-yl)-1-(pyrrolidin-1-yl)propane-1,2-dione (4al)

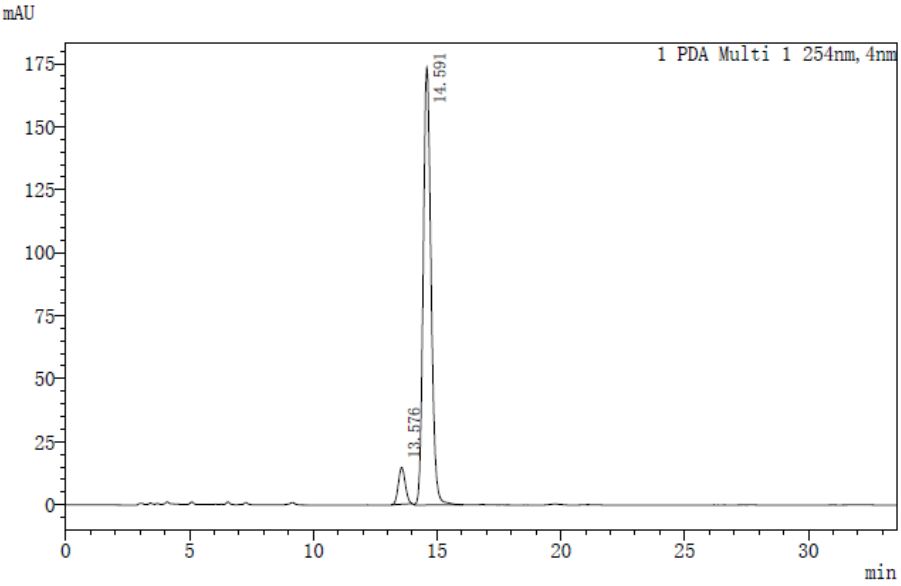
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (18.8 mg, 63% yield, 86% ee); $[\alpha]_D^{25}$ = -1.3 (c = 0.15 in MeOH, 86% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.80 (d, *J* = 17.9 Hz, 1H), 3.43 – 3.34 (m, 3H), 3.28 (d, *J* = 15.0 Hz, 1H), 3.26 (s, 3H), 3.24 – 3.18 (m, 1H),

1.81 – 1.70 (m, 4H), 1.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.86, 180.19, 161.84, 143.76, 133.10, 128.16, 122.48, 122.28, 108.21, 47.26, 46.55, 46.14, 45.37, 26.54, 26.39, 24.86, 23.57. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{17}H_{19}N_2O_3^-$ 299.1401; Found 299.1393. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 85/15, 1.0 mL/min, λ = 254 nm, t (major) = 14.591 min, t (minor) = 13.576 min.



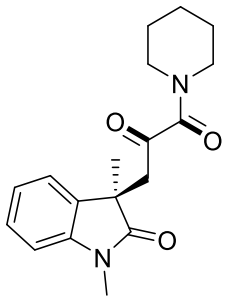
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	13.748	5253611	247806	50.049	0.561
2	14.719	5243288	228654	49.951	0.599



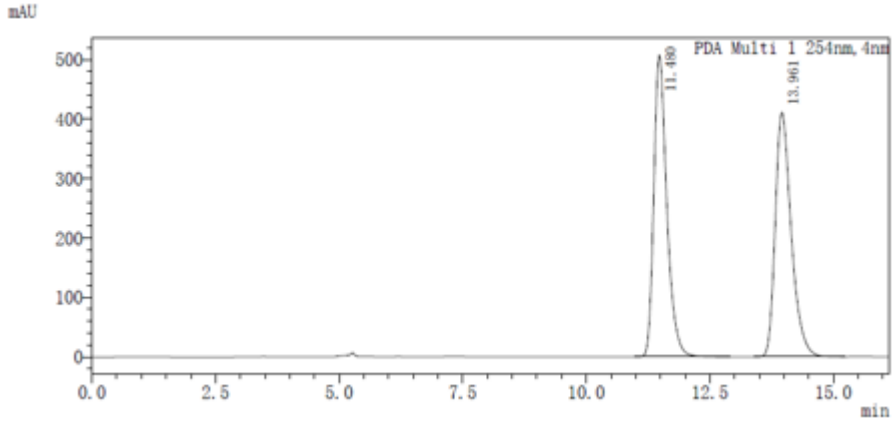
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	13.576	14591	283857	6.909	--
2	14.591	173591	3824603	93.091	1.835



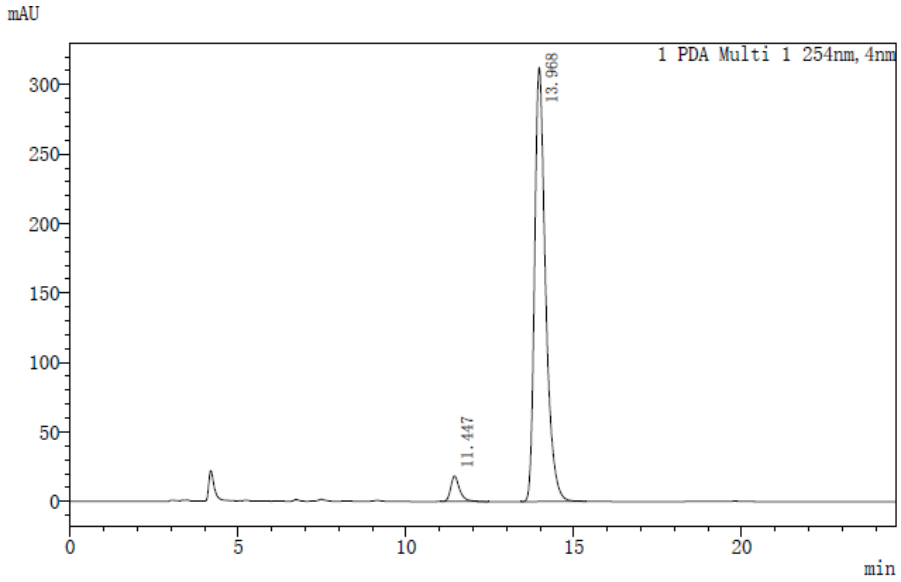
(*R*)-3-(1,3-Dimethyl-2-oxoindolin-3-yl)-1-(piperidin-1-yl)propane-1,2-dione (4am)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (17.7 mg, 56% yield, 91% ee); $[\alpha]_D^{25}$ = -11.7 (c = 0.12 in MeOH, 91% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.63 (d, *J* = 18.1 Hz, 1H), 3.55 – 3.47 (m, 1H), 3.44 – 3.36 (m, 1H), 3.30 – 3.21 (m, 4H), 3.17 – 3.06 (m, 2H), 1.63-1.57 (m, 2H), 1.56-1.50 (m, 2H), 1.49-1.44 (m, 2H), 1.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.37, 180.12, 164.58, 143.74, 133.00, 128.24, 122.59, 122.23, 108.31, 46.91, 46.65, 45.21, 42.73, 26.59, 26.44, 25.45, 24.86, 24.45. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{18}H_{21}N_2O_3^-$ 313.1558; Found 313.1559. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 85/15, 1.0 mL/min, λ = 254 nm, t (major) = 13.968 min, t (minor) = 11.447 min.



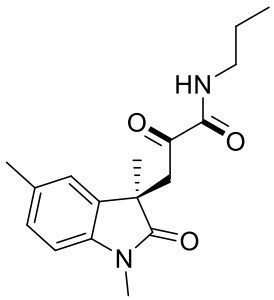
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.480	9295902	507057	50.060	0.476
2	13.961	9273589	411314	49.940	0.585



PDA Ch1 254nm

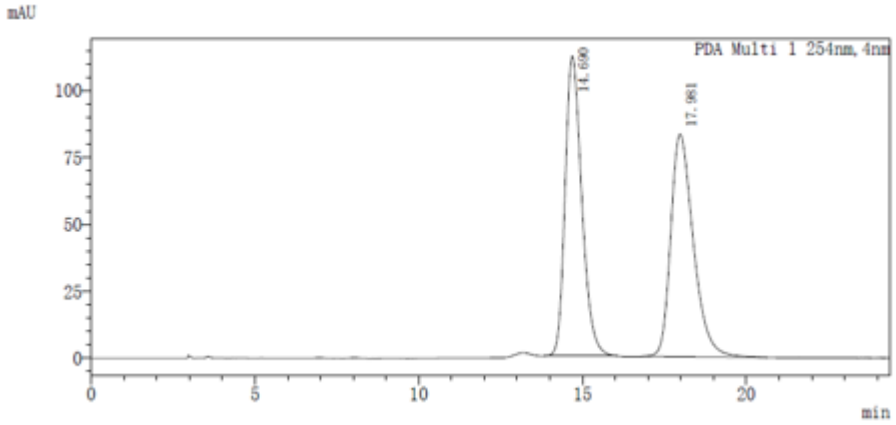
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	11.447	18359	338337	4.552	--
2	13.968	312487	7093838	95.448	4.805



(*R*)-2-oxo-*N*-propyl-3-(1,3,5-trimethyl-2-oxoindolin-3-yl)propenamide (4ba)

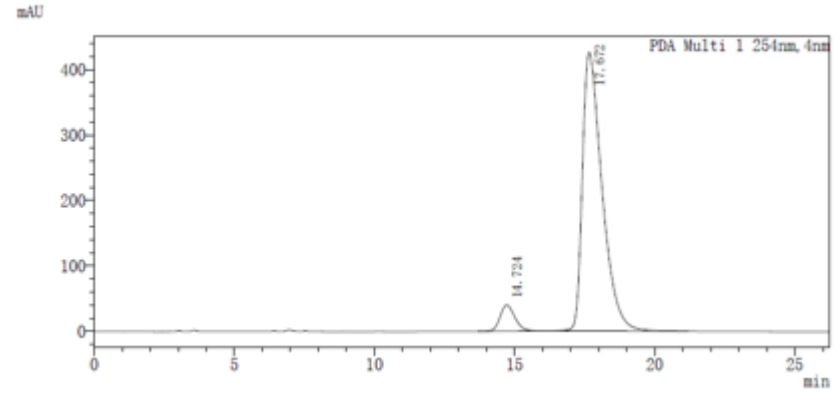
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (21.3 mg, 71% yield, 87% ee); $[\alpha]_D^{25}$ = +31.8 (c = 0.17 in MeOH, 87% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.8 Hz, 1H), 6.92 (s, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.67 (s, 1H), 3.84 (d, *J* = 19.3 Hz, 1H), 3.40 (d, *J* = 19.2 Hz, 1H), 3.25 (s, 3H), 3.23 – 3.07 (m, 2H), 2.29 (s, 3H), 1.47 (dt, *J* = 14.6, 7.4 Hz, 2H), 1.37 (s, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.85, 180.12, 159.66, 141.54, 133.10, 132.02, 128.45, 122.98, 107.91, 44.98, 44.26, 41.10, 26.54, 24.98, 22.53, 21.21, 11.35. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{17}H_{21}N_2O_3^-$ 301.1558; Found 301.1563. The enantiomeric ratio was determined by Daicel Chiralcel OD-H (0.46 cm×25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ =

254 nm, t (major) = 17.672 min, t (minor) = 14.724 min.



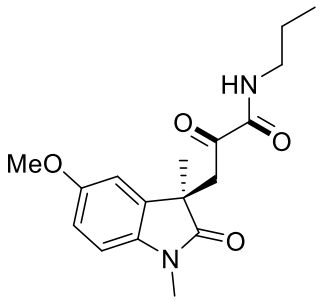
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	14.690	3985240	112090	49.858	0.928
2	17.981	4007937	83233	50.142	1.239



PDA Ch1 254nm

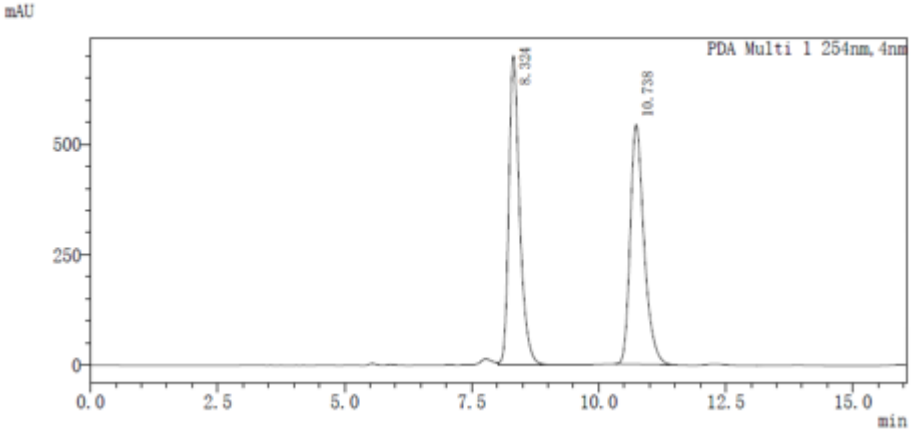
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	14.724	1463361	39922	6.571	0.958
2	17.672	20805109	425500	93.429	1.261



(*R*)-3-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-2-oxo-*N*-propylpropanamide (4ca)

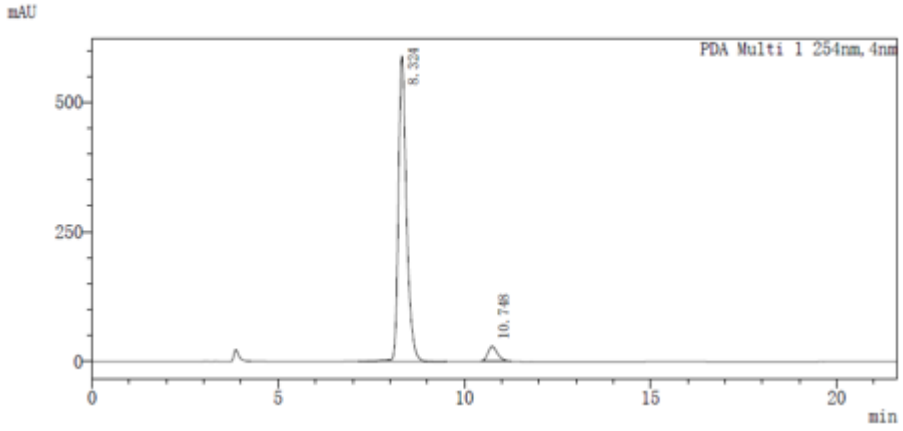
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (24.9 mg, 78% yield, 89% ee); $[\alpha]_D^{25}$ = +32.0 (c = 0.10 in MeOH, 89% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.78 (s, 2H), 6.73 (s, 1H), 6.67 (s,

1H), 3.82 (d, *J* = 19.4 Hz, 1H), 3.76 (s, 3H), 3.42 (d, *J* = 19.3 Hz, 1H), 3.25 (s, 3H), 3.22 – 3.08 (m, 2H), 1.52 – 1.42 (m, 2H), 1.38 (s, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.79, 179.81, 159.60, 156.06, 137.46, 134.46, 112.16, 109.92, 108.45, 55.89, 45.37, 44.26, 41.11, 26.61, 24.97, 22.54, 11.37. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{17}H_{21}N_2O_4^-$ 317.1507; Found 317.1511. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 8.324 min, t (minor) = 10.748 min.



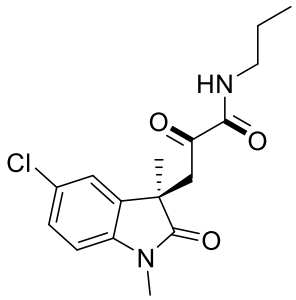
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.324	10406640	699542	50.230	0.386
2	10.738	10311313	542544	49.770	0.493



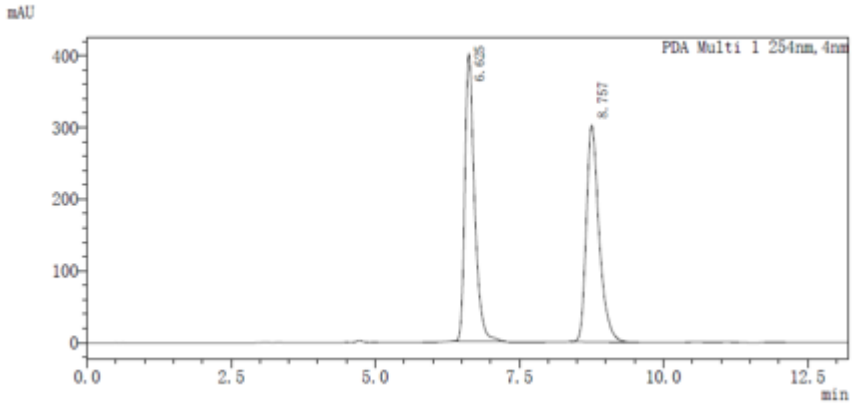
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.324	8877147	588656	94.422	0.389
2	10.748	524458	28691	5.578	0.485



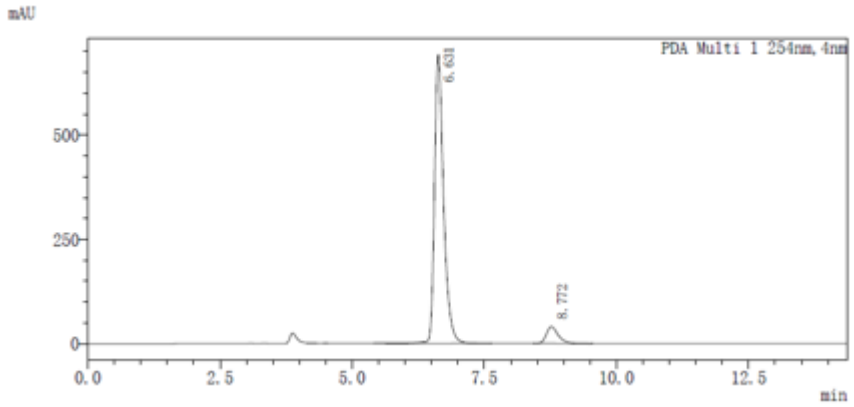
(*R*)-3-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-2-oxo-*N*-propylpropanamide (4da)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (24.1 mg, 75% yield, 86% ee); $[\alpha]_D^{25}$ = +36.7 (c = 0.12 in MeOH, 86% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.3 Hz, 1H), 7.10 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.68 (s, 1H), 3.83 (d, *J* = 19.5 Hz, 1H), 3.47 (d, *J* = 19.5 Hz, 1H), 3.27 (s, 3H), 3.24 – 3.13 (tq, *J* = 12.9, 6.5 Hz, 2H), 1.49 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.40 (s, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.68, 179.69, 159.46, 142.55, 134.82, 128.17, 127.91, 122.75, 109.14, 45.12, 44.37, 41.16, 26.66, 24.78, 22.54, 11.38. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{16}H_{18}ClN_2O_3^-$ 321.1011; Found 321.1003. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 6.631 min, t (minor) = 8.772 min.



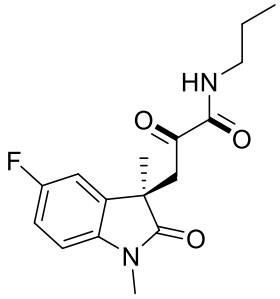
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.625	4685988	400161	50.052	0.308
2	8.757	4676272	301960	49.948	0.403



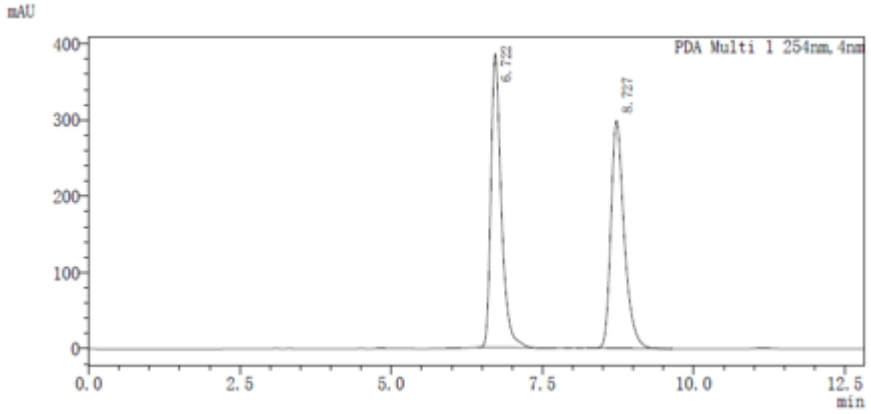
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.631	8321794	691285	93.014	0.314
2	8.772	625068	40512	6.986	0.403



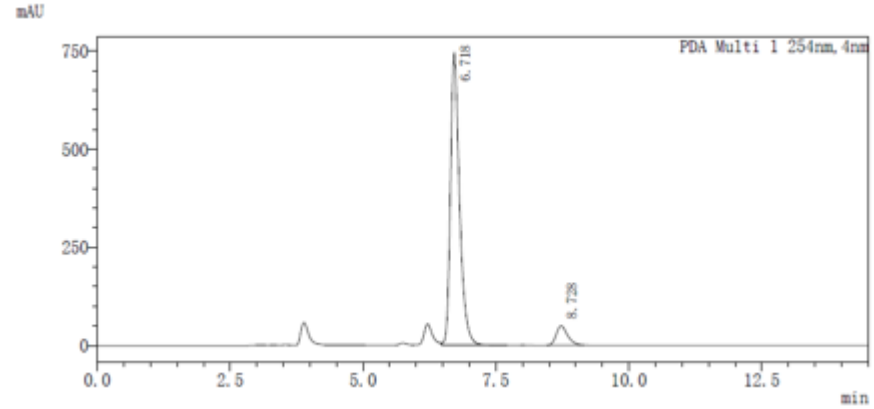
(*R*)-3-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)-2-oxo-*N*-propylpropanamide (4ea)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (26.8 mg, 78% yield, 85% ee); $[\alpha]_D^{25}$ = -1.3 (c = 0.16 in MeOH, 85% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.96 (t, *J* = 8.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.66 (s, 1H), 3.81 (d, *J* = 19.4 Hz, 1H), 3.45 (d, *J* = 19.4 Hz, 1H), 3.26 (s, 3H), 3.23 – 3.09 (m, 2H), 1.48 (dd, *J* = 14.5, 7.3 Hz, 2H), 1.39 (s, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.72, 179.81, 159.51, 159.34 (d, $^1J_{C\text{-}F}$ = 240.7 Hz), 139.87, 134.74 (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 114.34 (d, $^2J_{C\text{-}F}$ = 23.9 Hz), 110.50 (d, $^2J_{C\text{-}F}$ = 25.2 Hz), 108.64 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 45.39, 44.26, 41.16, 26.68, 24.77, 22.54, 11.37; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -120.65. HRMS (ESI) *m/z*: $[M\text{-}H]^-$ Calcd for $C_{16}H_{18}FN_2O_3^-$ 305.1307; Found 305.1304. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 6.718 min, t (minor) = 8.728 min.



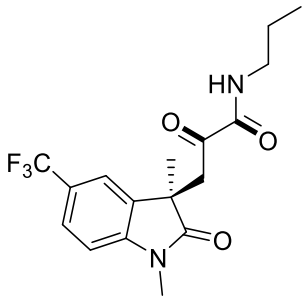
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.722	4603643	384819	50.152	0.313
2	8.727	4575783	298494	49.848	0.400



PDA Ch1 254nm

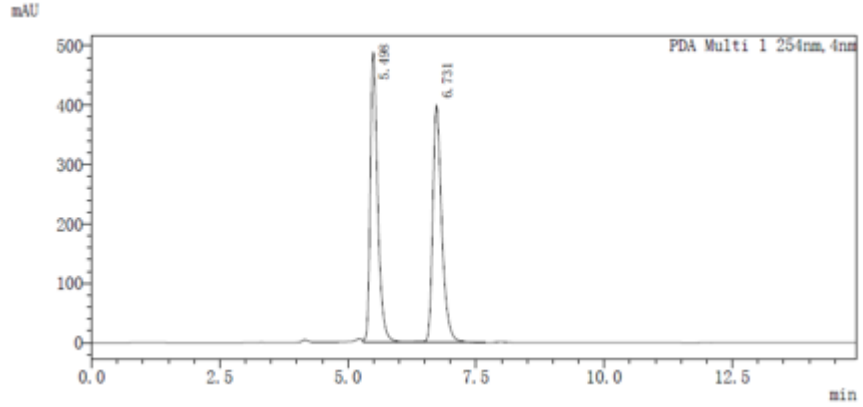
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.718	8956640	743660	92.453	0.316
2	8.728	731149	49590	7.547	0.394



(*R*)-3-(1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-2-oxo-*N*-propylpropanamide (4fa)

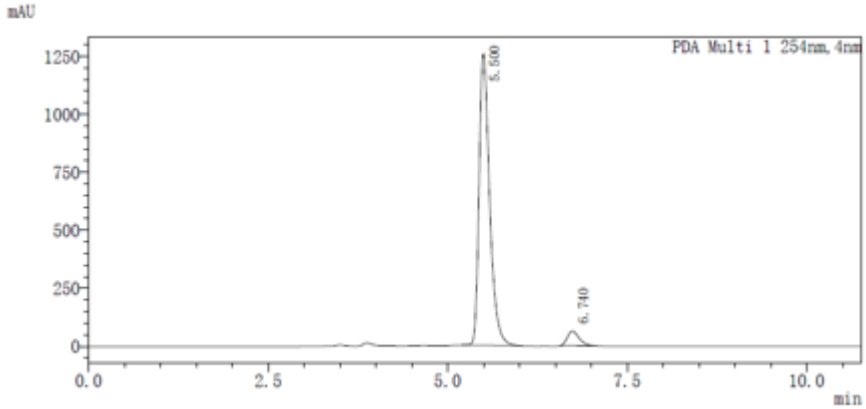
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (23.5 mg, 66% yield, 89% ee); $[\alpha]_D^{25}$ = +1.4 (c = 0.14 in MeOH, 89% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 1H), 7.34 (s,

1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.65 (s, 1H), 3.86 (d, *J* = 19.5 Hz, 1H), 3.50 (d, *J* = 19.5 Hz, 1H), 3.31 (s, 3H), 3.24 – 3.09 (m, 2H), 1.48 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.43 (d, *J* = 14.3 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.66, 180.09, 159.39, 146.93, 133.68, 126.13 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.78 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 124.48 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 119.14 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 107.94, 44.83, 44.45, 41.14, 26.72, 24.72, 22.49, 11.35; ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.38. HRMS (ESI) *m/z*: $[M\text{-}H]^-$ Calcd for $C_{17}H_{18}F_3N_2O_3^-$ 355.1275; Found 355.1284. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 5.500 min, t (minor) = 6.740 min.



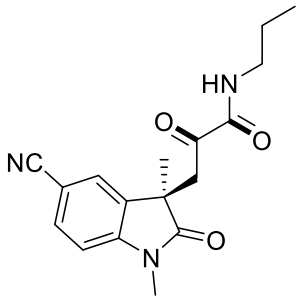
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	5.498	4971693	488798	50.083	0.270
2	6.731	4955182	399281	49.917	0.323



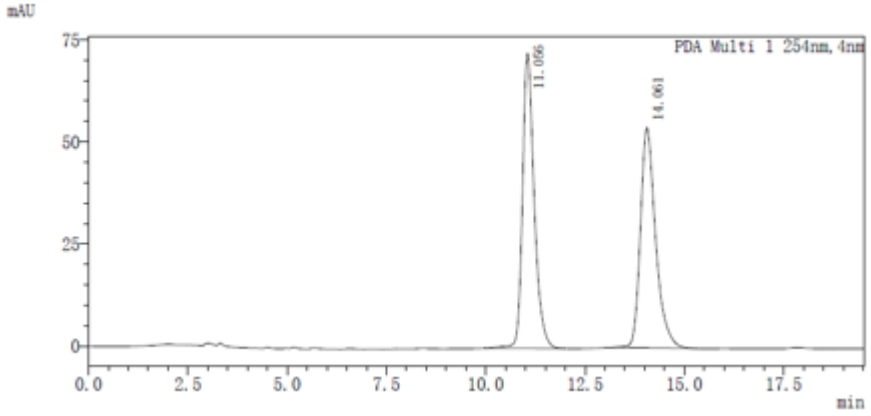
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	5.500	12825608	1255453	94.729	0.273
2	6.740	713588	62701	5.271	0.311



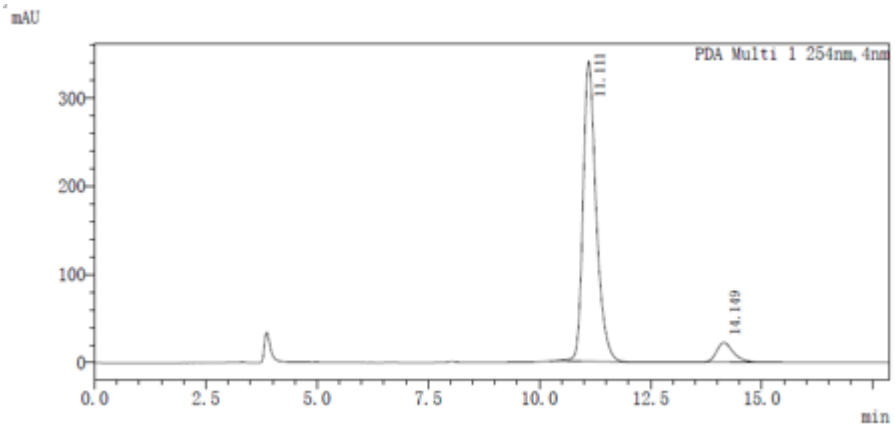
(*R*)-3-(5-Cyano-1,3-dimethyl-2-oxoindolin-3-yl)-2-oxo-*N*-propylpropanamide (4ga)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (18.9 mg, 60% yield, 85% ee); $[\alpha]_D^{25}$ = +45.4 (c = 0.26 in MeOH, 85% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.36 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.65 (s, 1H), 3.84 (d, *J* = 19.6 Hz, 1H), 3.50 (d, *J* = 19.6 Hz, 1H), 3.29 (s, 3H), 3.17 (tq, *J* = 13.8, 6.8 Hz, 2H), 1.55 – 1.44 (m, 2H), 1.40 (s, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.62, 179.81, 159.27, 147.84, 134.22, 133.68, 125.46, 119.20, 108.61, 105.64, 44.63, 44.46, 41.16, 26.74, 24.54, 22.49, 11.35. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{17}H_{18}N_3O_3^-$ 312.1354; Found 312.1358. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 11.111 min, t (minor) = 14.149 min.



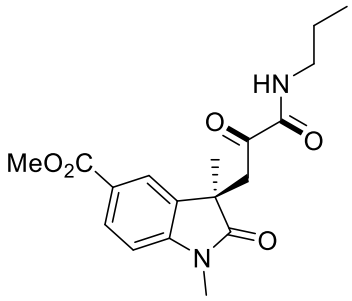
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.056	1477303	72119	50.725	0.523
2	14.061	1435049	53849	49.275	0.677



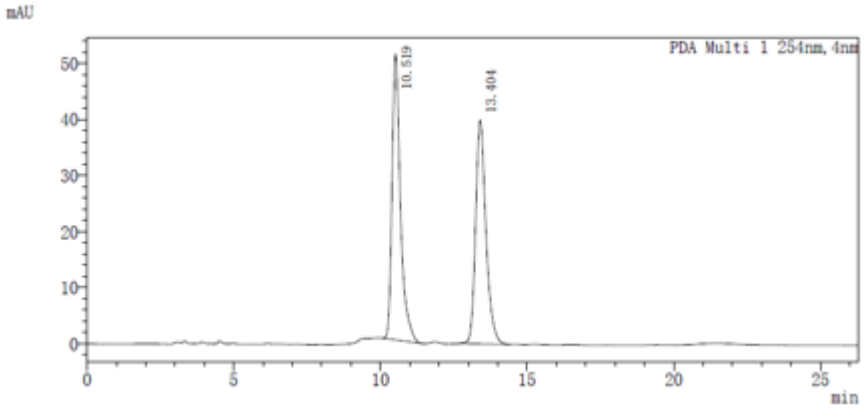
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.111	6980379	339988	92.422	0.528
2	14.149	572317	22049	7.578	0.674



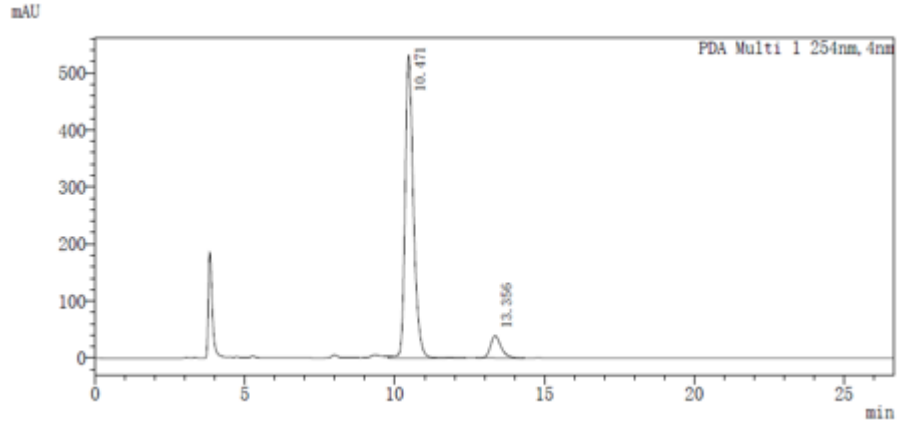
Methyl (*R*)-3-(2,3-dioxo-3-(propylamino)propyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (4ha)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (18.5 mg, 53% yield, 83% ee); $[\alpha]_D^{25}$ = +50.0 (c = 0.10 in MeOH, 83% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.77 (s, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.64 (s, 1H), 3.93 – 3.82 (m, 4H), 3.50 (d, *J* = 19.6 Hz, 1H), 3.30 (s, 3H), 3.26 – 3.06 (m, 2H), 1.54 – 1.42 (m, 2H), 1.40 (s, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.71, 180.49, 166.95, 159.40, 148.14, 133.15, 131.09, 124.51, 123.24, 107.77, 52.14, 44.65, 44.59, 41.13, 26.73, 24.82, 22.52, 11.36. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{18}H_{21}N_2O_5^-$ 345.1456; Found 345.1464. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 10.471 min, t (minor) = 13.356 min.



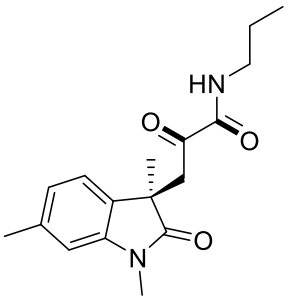
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	10.519	1016133	50954	50.900	0.499
2	13.404	980209	39965	49.100	0.632



PDA Ch1 254nm

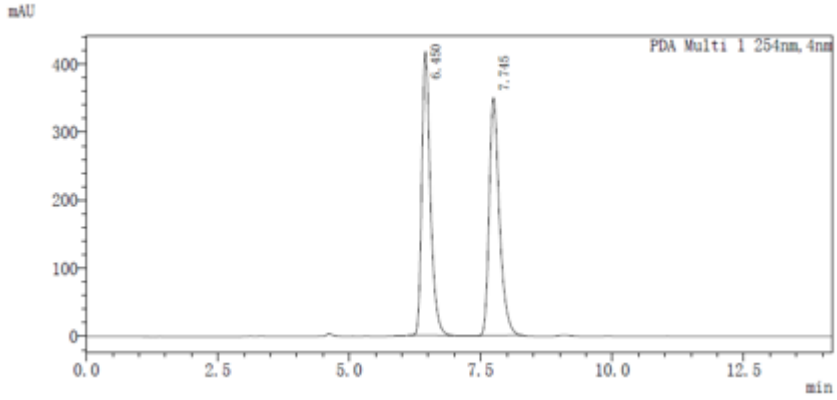
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	10.471	10267778	530569	91.519	0.497
2	13.356	951475	38992	8.481	0.630



(*R*)-2-oxo-*N*-propyl-3-(1,3,6-trimethyl-2-oxoindolin-3-yl)propenamide (4ia)

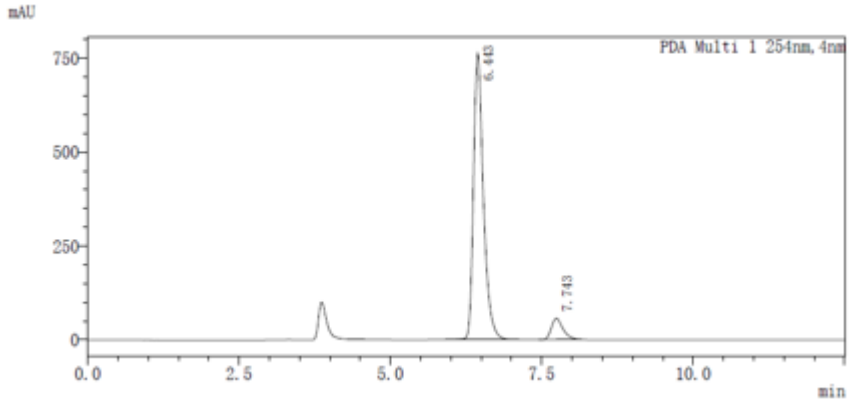
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (21.5 mg, 71% yield, 84% ee); $[\alpha]_D^{25}$ = +1.7 (c = 0.12 in MeOH, 84% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.70 (s, 1H), 6.66 (s, 1H), 3.84 (d, *J* = 19.2 Hz, 1H), 3.39 (d, *J* =

19.2 Hz, 1H), 3.26 (s, 3H), 3.21 – 3.06 (m, 2H), 2.37 (s, 3H), 1.51 – 1.40 (m, 2H), 1.37 (s, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.95, 180.47, 159.63, 143.97, 138.34, 130.11, 123.00, 121.85, 109.20, 44.76, 44.26, 41.10, 26.49, 24.99, 22.53, 21.95, 11.36. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{17}H_{21}N_2O_3^-$ 301.1558; Found 301.1565. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 6.443 min, t (minor) = 7.743 min.



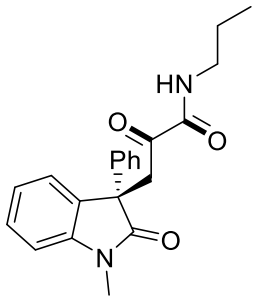
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.450	4734380	416017	49.896	0.302
2	7.745	4754023	349163	50.104	0.358



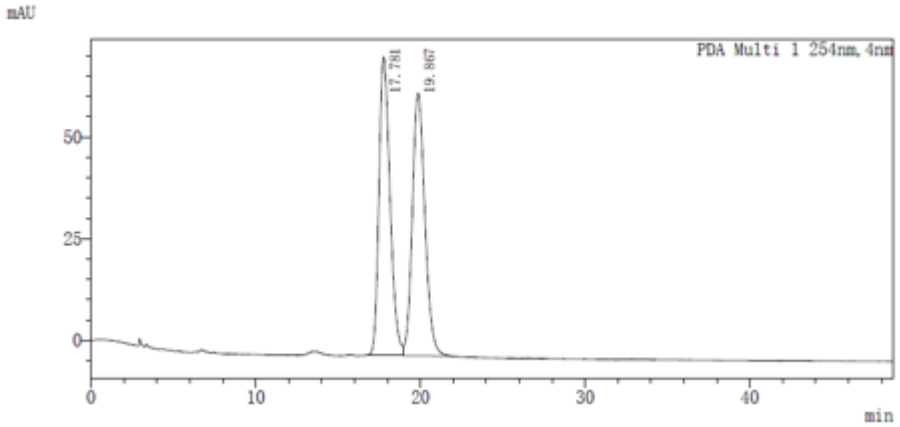
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.443	8684111	761521	92.057	0.302
2	7.743	749311	56538	7.943	0.354



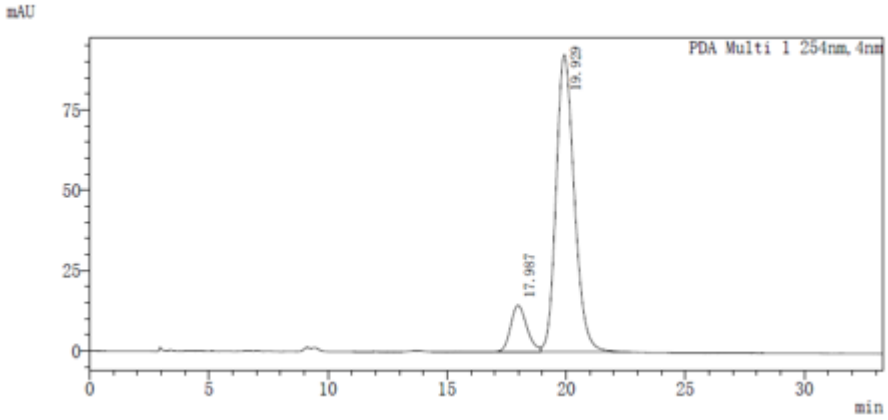
(*S*)-3-(1-Methyl-2-oxo-3-phenylindolin-3-yl)-2-oxo-*N*-propylpropanamide (4ja)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a yellow solid (9.8 mg, 28% yield, 76% ee): mp 80-83 °C; $[\alpha]_D^{25}$ = -38.0 (c = 0.10 in MeOH, 76% ee); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 7H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.68 (s, 1H), 4.30 (d, *J* = 19.2 Hz, 1H), 3.91 (d, *J* = 19.2 Hz, 1H), 3.27 (s, 3H), 3.21 – 3.11 (m, 2H), 1.53 – 1.40 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.66, 178.35, 159.60, 144.85, 139.13, 131.27, 128.86, 128.75, 127.83, 126.68, 124.38, 122.61, 108.47, 52.76, 44.74, 41.14, 26.81, 22.53, 11.37. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{21}H_{21}N_2O_3^-$ 349.1558; Found 349.1558. The enantiomeric ratio was determined by Daicel Chiralcel OD-H (0.46 cm×25 cm), Hexanes/IPA = 85/15, 1.0 mL/min, λ = 254 nm, t (major) = 19.929 min, t (minor) = 17.987 min.



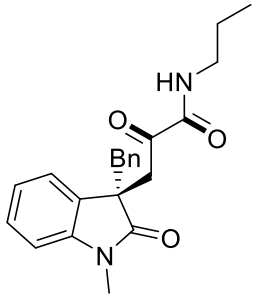
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	17.781	3433039	73530	49.997	1.227
2	19.867	3433427	64647	50.003	1.384



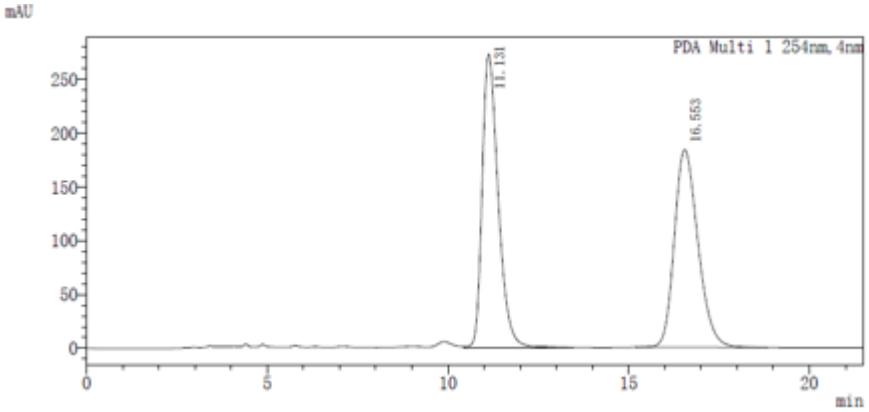
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	17.987	677381	14448	12.089	1.239
2	19.929	4925893	92436	87.911	1.387



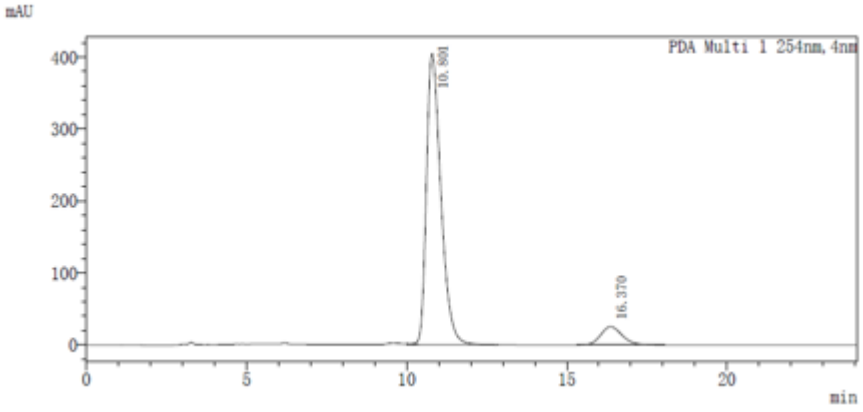
(*R*)-3-(3-Benzyl-1-methyl-2-oxoindolin-3-yl)-2-oxo-*N*-propylpropanamide (4ka)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (19.8 mg, 54% yield, 83% ee); $[\alpha]_D^{25}$ = -29.3 (c = 0.15 in MeOH, 83% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 – 7.00 (m, 4H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 2H), 6.66 (s, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 3.98 (d, *J* = 19.2 Hz, 1H), 3.56 (d, *J* = 19.2 Hz, 1H), 3.15 (ddt, *J* = 20.3, 13.6, 6.7 Hz, 2H), 3.05 (s, 2H), 3.00 (s, 3H), 1.52 – 1.39 (m, 2H), 1.20 (d, *J* = 6.1 Hz, 1H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.66, 178.77, 159.63, 144.43, 134.63, 130.29, 130.15, 128.33, 127.61, 126.89, 123.01, 122.03, 107.86, 50.65, 44.51, 43.15, 41.11, 26.10, 22.52, 11.36. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{22}H_{23}N_2O_3^-$ 363.1714; Found 363.1709. The enantiomeric ratio was determined by Daicel Chiralcel OD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 10.801 min, t (minor) = 16.370 min.



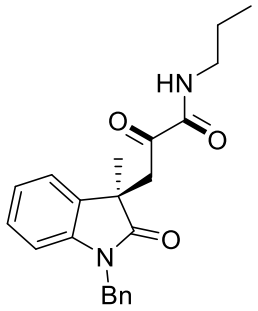
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.131	8393979	272759	50.082	0.797
2	16.553	8366502	183896	49.918	1.190



PDA Ch1 254nm

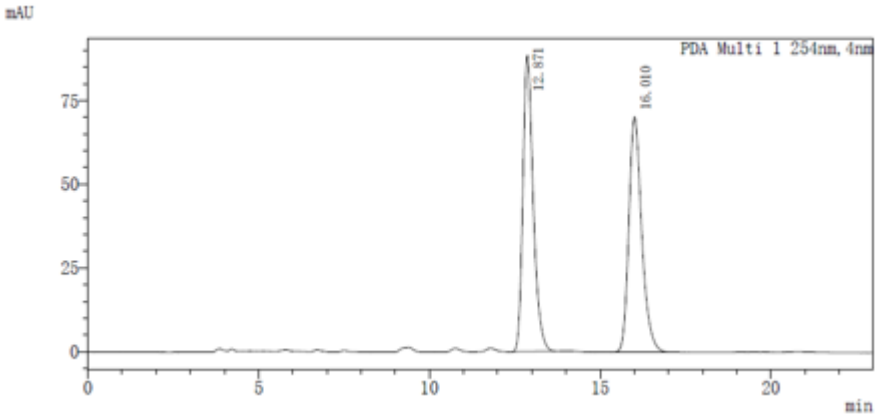
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	10.801	12692360	404452	91.440	0.815
2	16.370	1188223	25405	8.560	1.223



(*R*)-3-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)-2-oxo-*N*-propylpropanamide (4la)

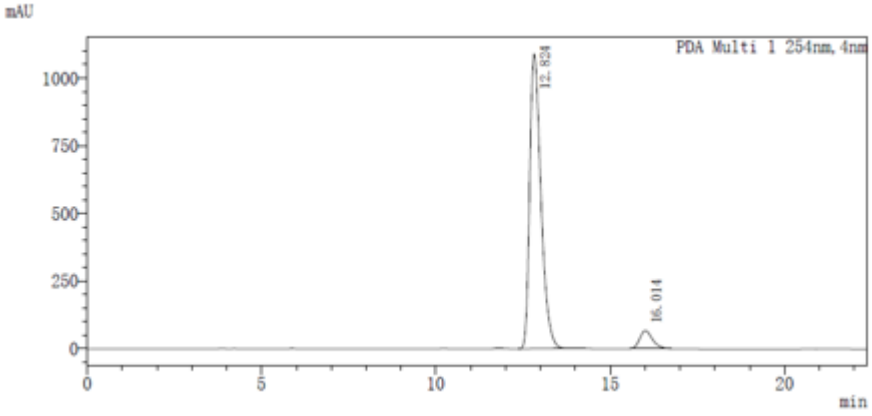
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product as a yellow solid (23.2 mg, 64% yield, 87% ee): mp 83-85 ^{o}C; $[\alpha]_D^{25}$ = -2.5 (c = 0.16 in MeOH, 87% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 2H), 4.97 (s, 2H), 3.93 (d, *J* = 19.3 Hz, 1H), 3.48

(d, *J* = 19.2 Hz, 1H), 3.27 – 3.08 (m, 2H), 1.53 – 1.40 (m, 5H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.81, 180.22, 159.65, 142.95, 136.18, 133.07, 128.87, 128.12, 127.64, 127.43, 122.58, 122.05, 109.39, 45.06, 44.14, 44.04, 41.13, 25.59, 22.56, 11.39. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{22}H_{23}N_2O_3^-$ 363.1714; Found 363.1705. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 12.824 min, t (minor) = 16.014 min.



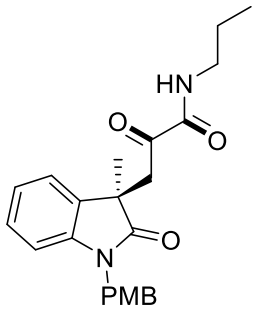
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	12.871	1868282	88291	50.353	0.551
2	16.010	1842116	70135	49.647	0.679



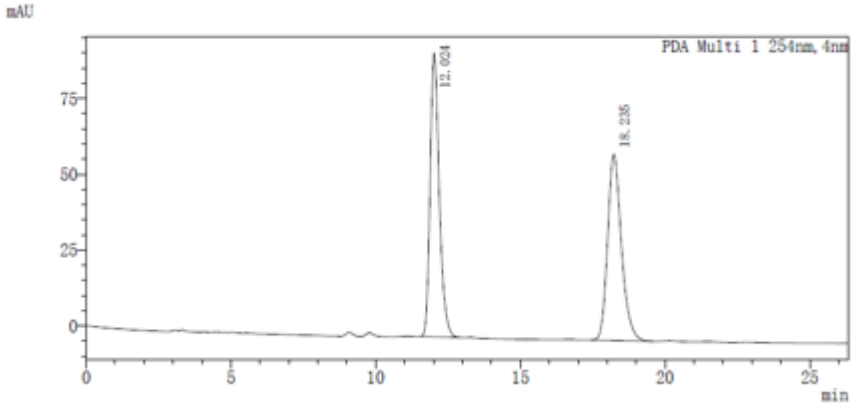
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	12.824	24407658	1088651	93.472	0.582
2	16.014	1704481	66568	6.528	0.672



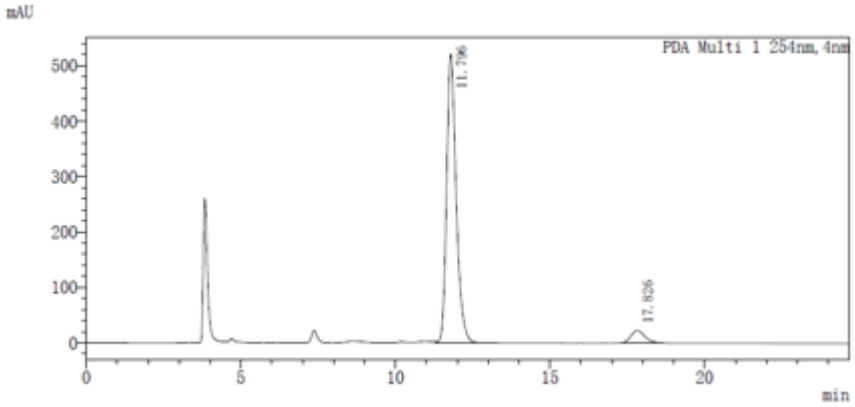
(*R*)-3-(1-(4-Methoxybenzyl)-3-methyl-2-oxoindolin-3-yl)-2-oxo-*N*-propylpropan amide (4ma)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product as a colorless oil (22.9 mg, 58% yield, 88% ee); $[\alpha]_D^{25}$ = +63.2 (c = 0.25 in MeOH, 88% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.16 – 7.09 (dd, *J* = 17.2, 7.8 Hz, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.69 (s, 1H), 4.92 (q, *J* = 15.5 Hz, 2H), 3.92 (d, *J* = 19.2 Hz, 1H), 3.78 (s, 3H), 3.47 (d, *J* = 19.2 Hz, 1H), 3.23 – 3.09 (m, 2H), 1.53 – 1.40 (m, 5H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.83, 180.14, 159.67, 159.18, 142.99, 133.11, 128.83, 128.26, 128.10, 122.52, 122.04, 114.30, 109.40, 55.41, 45.07, 44.01, 43.61, 41.14, 25.54, 22.57, 11.40. HRMS (ESI) *m/z*: $[M-H]^-$ Calcd for $C_{23}H_{25}N_2O_4^-$ 393.1820; Found 393.1829. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm×25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 11.796 min, t (minor) = 17.826 min.



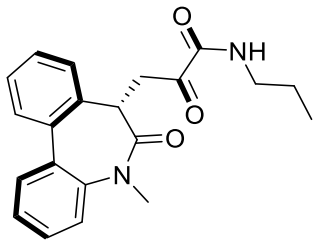
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	12.024	2046805	93479	50.110	0.570
2	18.235	2037860	61366	49.890	0.859



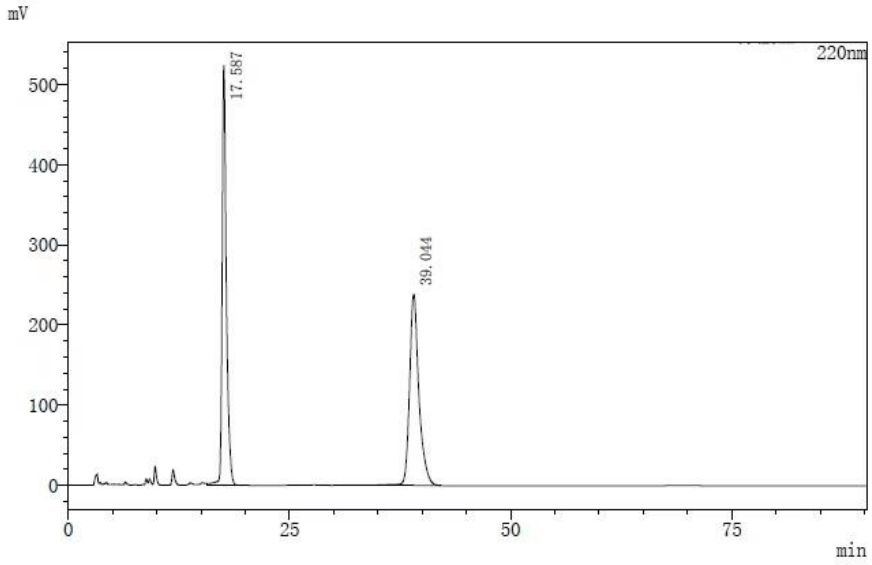
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.796	11200741	521478	94.053	0.556
2	17.826	708227	22466	5.947	0.832



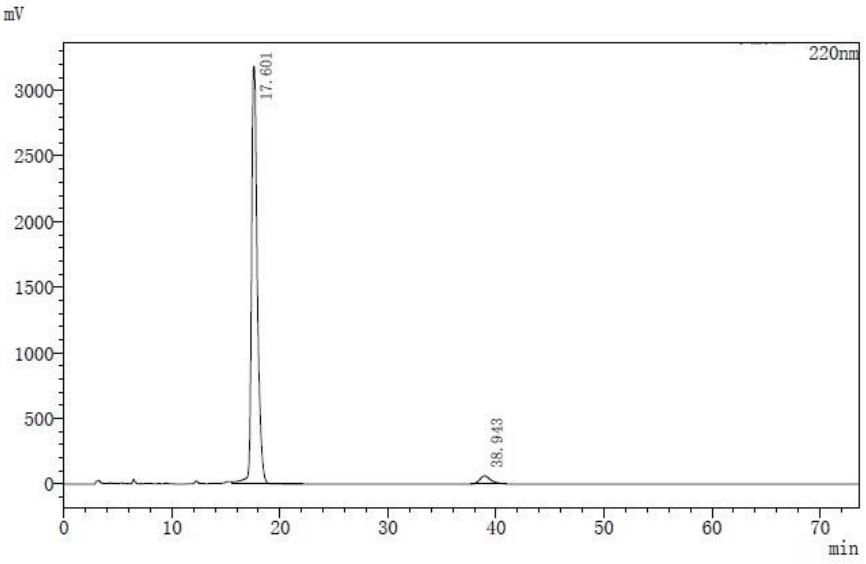
(a*R*, *S*)-3-(5-methyl-6-oxo-6,7-dihydro-5H-dibenzo[b,d]azepin-7-yl)-2-oxo-N-propylpropanamide (6aa)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (20.5 mg, 59% yield); $[\alpha]_D^{25}$ = -42.7 (c = 0.15 in MeOH, 93% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.50 – 7.35 (m, 5H), 7.33 (td, *J* = 7.7, 1.2 Hz, 1H), 6.92 (s, 1H), 4.28 (dd, *J* = 19.0, 11.0 Hz, 1H), 3.84 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.39 – 3.21 (m, 6H), 1.56 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.45, 171.51, 160.15, 141.54, 136.83, 136.80, 133.84, 130.01, 128.91, 128.85, 128.59, 127.55, 125.54, 124.02, 122.67, 41.16, 41.07, 36.25, 35.25, 22.63, 11.42. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{21}H_{23}N_2O_3^+$ 351.1703; Found 351.1693. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 38.9 min, t (major) = 17.6 min.



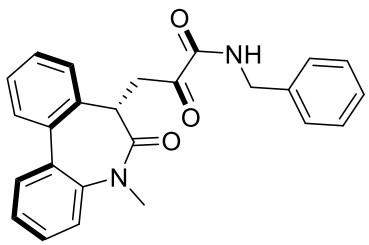
220nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	17.587	523551	17337340	49.814	--
2	39.044	238694	17467045	50.186	16.561



220nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	17.601	3185297	119471153	96.469	--
2	38.943	61788	4373016	3.531	16.132

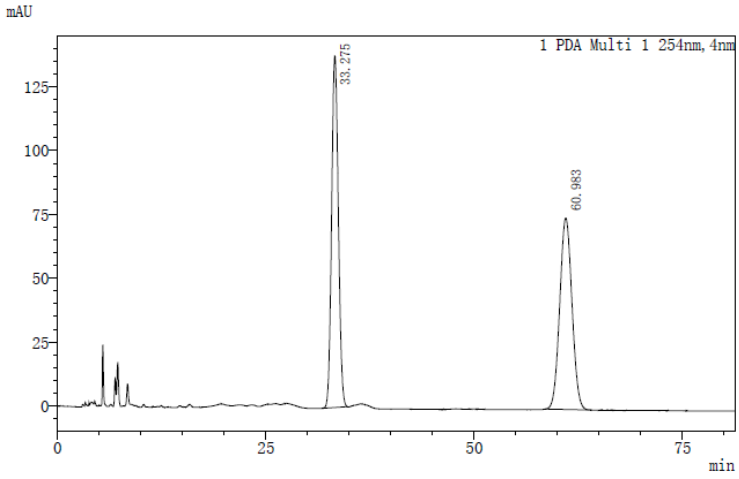


(a*R*,

_S_)-_N_-benzyl-3-(5-methyl-6-oxo-6,7-dihydro-5_H_-dibenzo[_b,d_]azepin-7-yl)-2-oxop

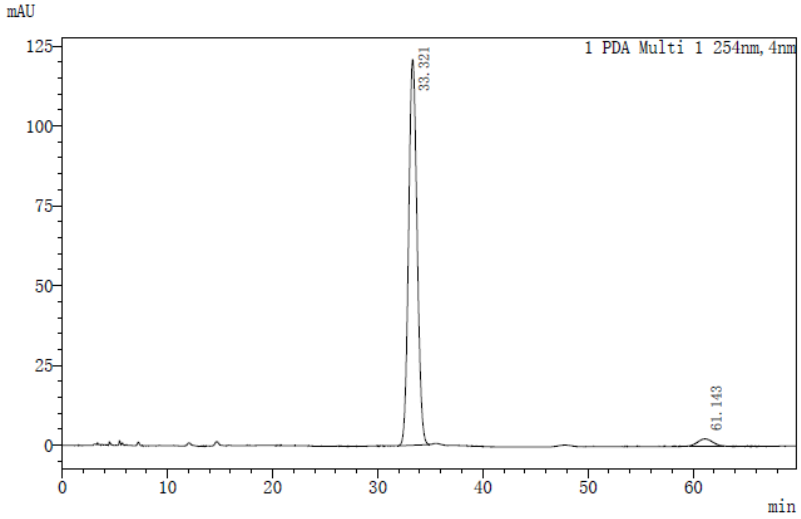
ropanamide (6ab)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (34.2 mg, 86% yield); $[\alpha]_D^{25}$ = -40.0 (c = 0.1 in MeOH, 94% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 6.5 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.43-7.37 (m, 3H), 7.33 (t, *J* = 6.9 Hz, 3H), 7.30-7.25 (m, 3H), 7.18 (s, 1H), 4.49 (d, *J* = 4.6 Hz, 2H), 4.33 (dd, *J* = 18.9, 11.1 Hz, 1H), 3.85 (d, *J* = 10.9 Hz, 1H), 3.36 (d, *J* = 18.9 Hz, 1H), 3.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.16, 171.52, 160.03, 141.54, 137.03, 136.83, 136.81, 133.84, 130.04, 128.96, 128.89, 128.65, 128.04, 127.98, 127.61, 125.59, 124.03, 122.70, 43.63, 41.16, 36.29, 35.34. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{23}N_2O_3^+$ 399.1703; Found 399.1697. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 61.1 min, t (major) = 33.3 min.



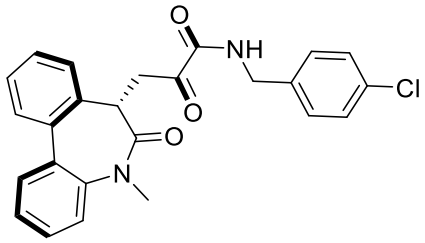
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	33.275	137744	7714464	50.156	--
2	60.983	74998	7666395	49.844	13.188



PDA Ch1 254nm

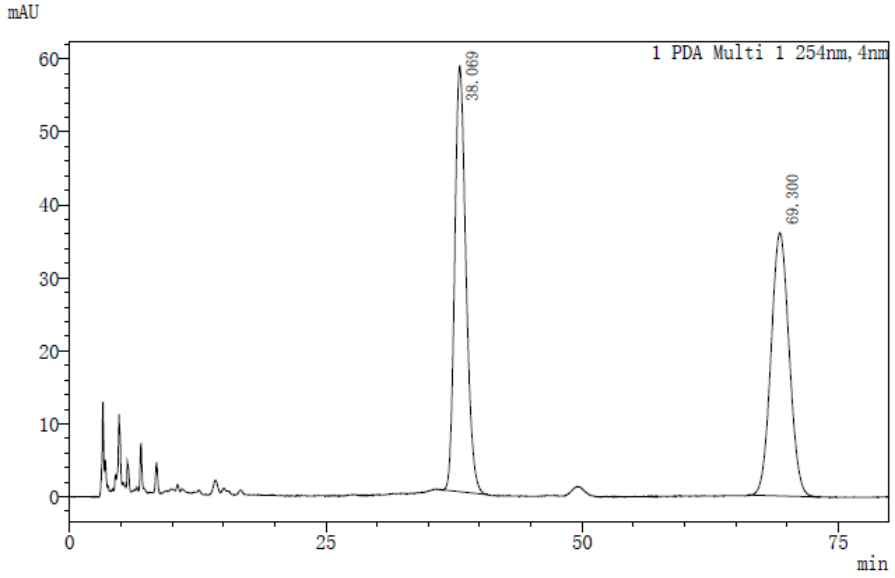
NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	33.321	120846	6776699	97.034	--
2	61.143	2209	207156	2.966	13.472



(a*R*, *S*)-*N*-(4-chlorobenzyl)-3-(5-methyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2-oxopropanamide (6ad)

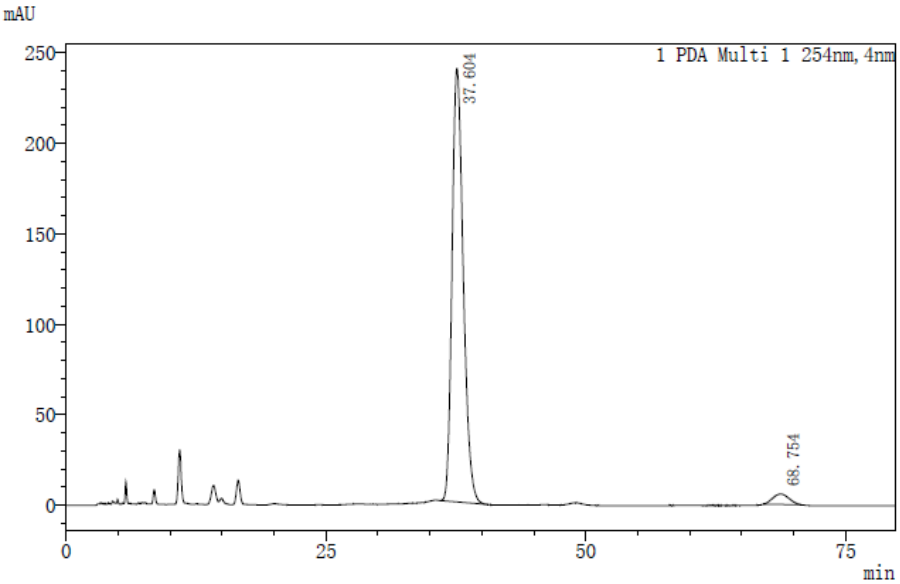
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a white solid (34.8 mg, 81% yield): mp 162-165 °C; $[\alpha]_D^{25}$ = -24.0 (c = 0.1 in MeOH, 93% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.50-7.45 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.35-7.29 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 3H), 4.46 (d, *J* = 5.8 Hz, 2H), 4.34 (dd, *J* = 18.8, 11.1 Hz, 1H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.33 (d, *J* = 19.5 Hz, 1H), 3.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.08, 171.53, 160.11, 141.51, 136.83, 136.74, 135.60, 133.86, 133.82, 130.05, 129.37, 129.10, 128.96, 128.91, 128.68, 127.65, 125.62, 124.00, 122.70, 42.91, 41.20, 36.31, 35.30. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{25}H_{22}ClN_2O_3^+$ 433.1313; Found 433.1321. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0

mL/min, λ = 254 nm, t (minor) = 68.7 min, t (major) = 37.6 min.



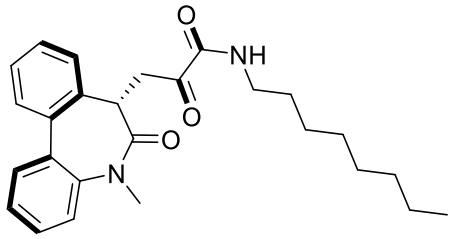
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	38.069	58392	4453979	50.136	--
2	69.300	36033	4429737	49.864	11.888



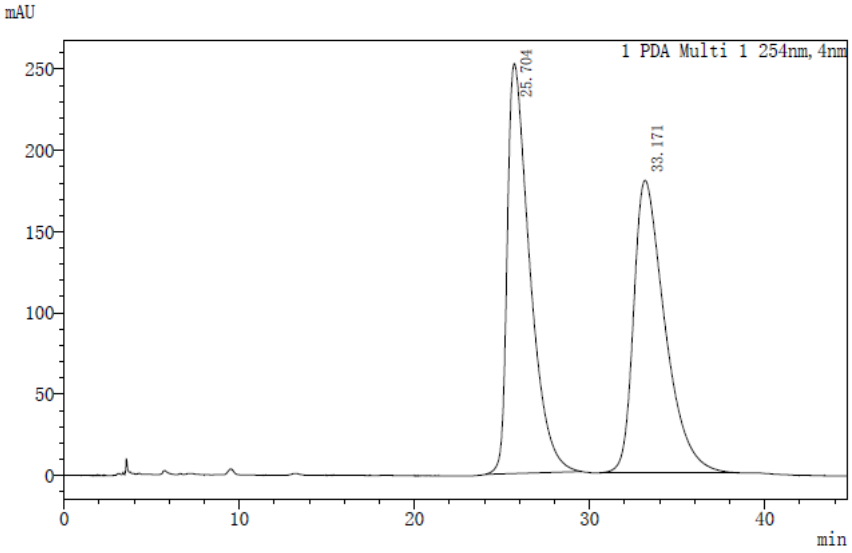
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	37.604	239721	17956914	96.629	--
2	68.754	5790	626430	3.371	12.651



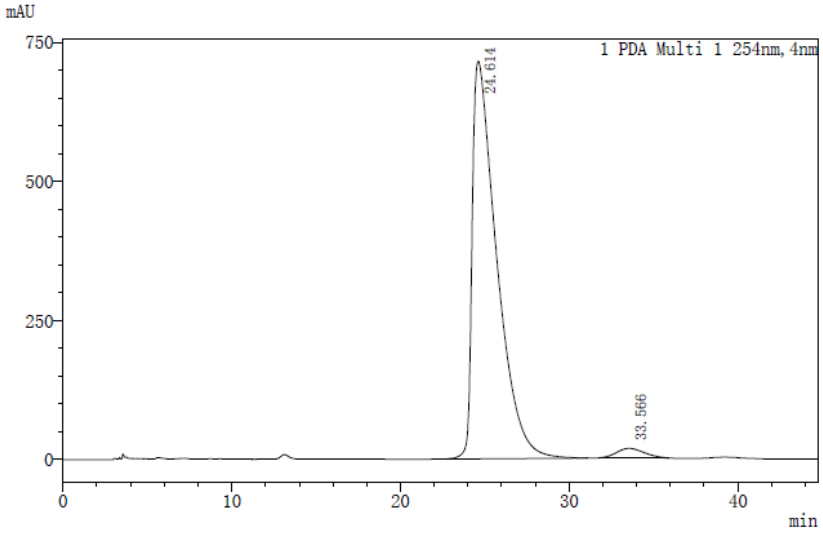
(a*R*,*S*)-3-(5-methyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-*N*-octyl-2-oxopropanamide (6ae)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product as a colorless oil (30.8 mg, 73% yield); $[\alpha]_D^{25}$ = -54.0 (c = 0.1 in MeOH, 95% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 5.6 Hz, 2H), 7.50-7.32 (m, 5H), 7.34 (t, *J* = 7.0 Hz, 1H), 6.88 (s, 1H), 4.29 (dd, *J* = 19.0, 11.0 Hz, 1H), 3.84 (d, *J* = 10.9 Hz, 1H), 3.40 – 3.27 (m, 6H), 1.53 (t, *J* = 6.1 Hz, 2H), 1.36-1.20 (m, 10H), 0.88 (t, *J* = 6.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.51, 171.54, 160.11, 141.57, 136.86, 136.83, 133.87, 130.05, 128.95, 128.88, 128.63, 127.59, 125.58, 124.07, 122.71, 41.09, 39.54, 36.30, 35.29, 31.89, 29.35, 29.31, 29.28, 26.99, 22.76, 14.20. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{26}H_{33}N_2O_3^+$ 421.2486; Found 421.2483. The enantiomeric ratio was determined by FLM Chiralcel MX(2) (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 33.6 min, t (major) = 24.6 min.



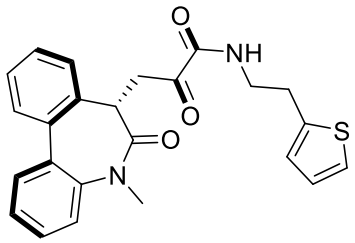
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	25.704	252242	22480306	50.142	--
2	33.171	179877	22352595	49.858	2.729



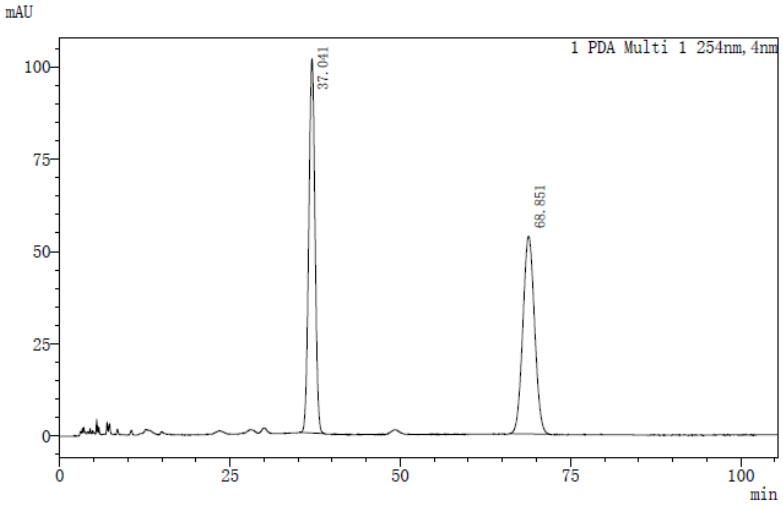
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	24.614	714827	71970445	97.478	--
2	33.566	16766	1861916	2.522	3.200



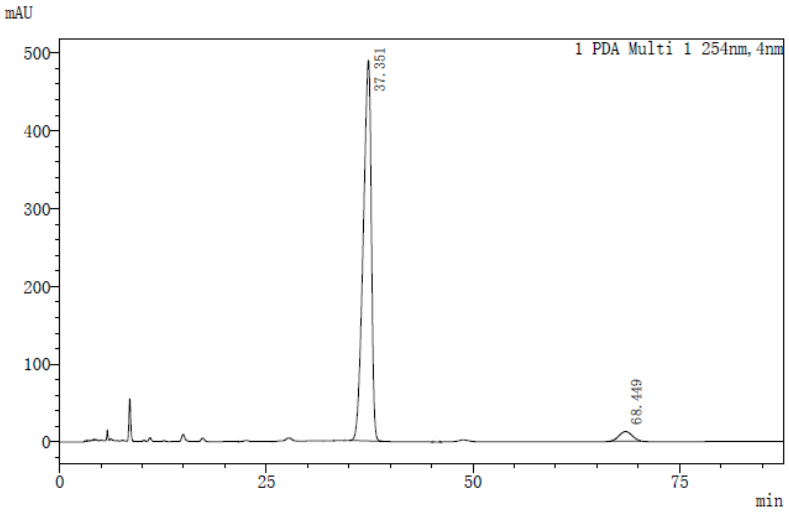
(a*R*, *S*)-3-(5-methyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2-oxo-*N*-(2-(thiophen-2-yl)ethyl)propenamide (6af)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (31.6 mg, 76% yield); $[\alpha]_D^{25}$ = -50.0 (c = 0.1 in MeOH, 92% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.55 (m, 2H), 7.47 (dd, *J* = 15.9, 7.9 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 4.3 Hz, 1H), 7.03 (s, 1H), 6.93 (s, 1H), 6.83 (s, 1H), 4.29 (dd, *J* = 18.7, 11.2 Hz, 1H), 3.84 (d, *J* = 10.7 Hz, 1H), 3.68 – 3.51 (m, 2H), 3.34 (d, *J* = 21.3 Hz, 1H), 3.32 (s, 3H), 3.07 (t, *J* = 6.3 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.11, 171.50, 160.13, 141.53, 140.57, 136.83, 133.84, 130.04, 128.95, 128.89, 128.65, 127.61, 127.28, 125.72, 125.59, 124.32, 124.02, 122.71, 41.08, 40.77, 36.30, 35.25, 29.72. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2O_3S^+$ 419.1424; Found 419.1431. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 68.4 min, t (major) = 37.4 min.



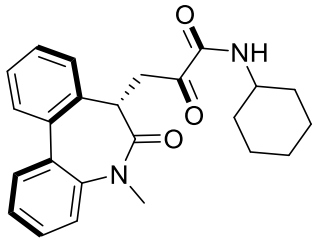
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	37.041	101322	6441948	50.190	--
2	68.851	53559	6393123	49.810	13.081



PDA Ch1 254nm

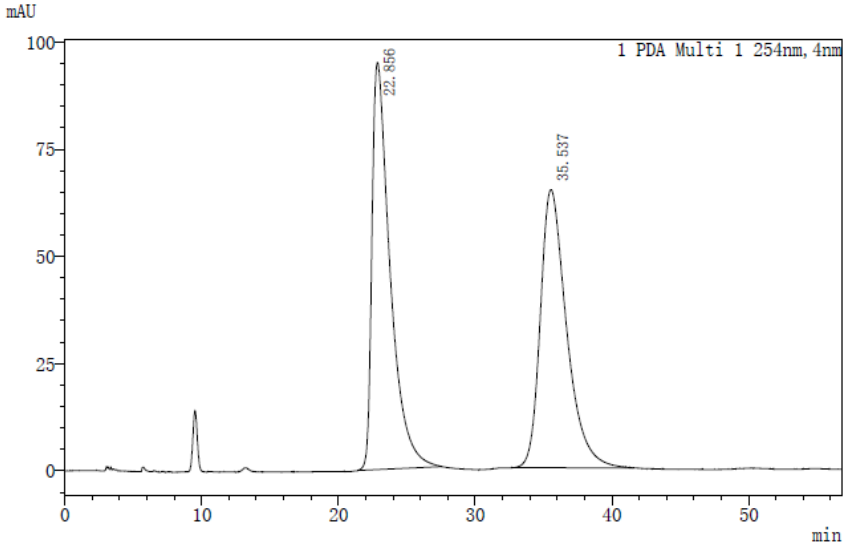
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	37.351	489367	33248763	96.211	--
2	68.449	12107	1309382	3.789	12.992



(a*R*, *S*)-*N*-cyclohexyl-3-(5-methyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b,d*]azepin-7-yl)-2-oxo-propanamide (6ai)

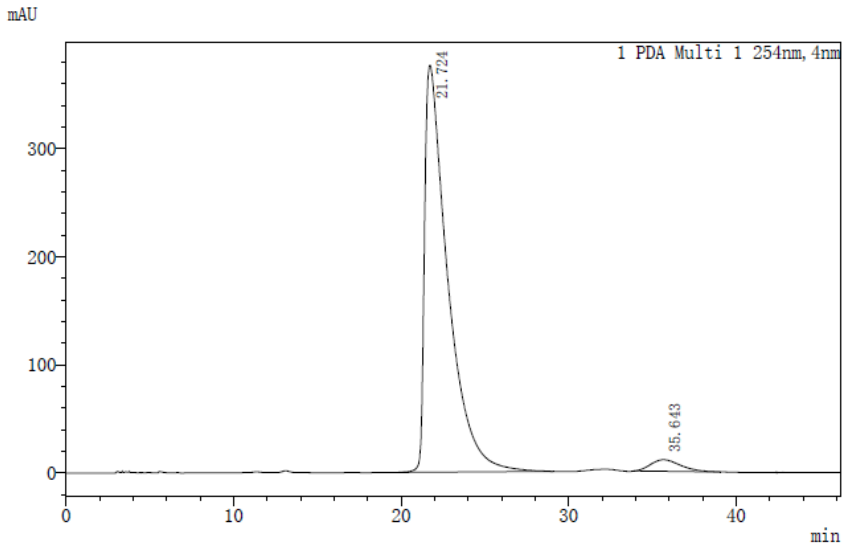
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product as a colorless oil (31.2 mg, 80% yield); $[\alpha]_D^{25}$ = -70.0 (c = 0.1 in MeOH, 93% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.57 (m, 2H), 7.51 – 7.37 (m, 5H), 7.33 (t, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 4.27 (dd, *J* = 19.0, 11.0 Hz, 1H), 3.83 (d, *J* = 11.0 Hz, 1H), 3.76 (d, *J* = 9.5 Hz, 1H), 3.37 (d, *J* = 19.1 Hz, 1H), 3.33 (s, 3H), 1.91 (dd, *J* = 23.1, 12.4 Hz, 2H), 1.72 (t, *J* = 12.7 Hz, 2H), 1.65-1.60 (m, 2H), 1.43-1.32 (m, 2H), 1.21 – 1.16 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.76, 171.54, 159.12, 141.58, 136.89, 136.82, 133.88, 130.04, 128.95, 128.88, 128.61, 127.58, 125.57, 124.08, 122.70, 48.42, 41.04, 36.28, 35.30, 32.80, 32.73, 25.51, 24.76. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{27}N_2O_3^+$ 391.2016; Found 391.2029.

The enantiomeric ratio was determined by FLM Chiralcel MX(2) (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 35.6 min, t (major) = 21.7 min.



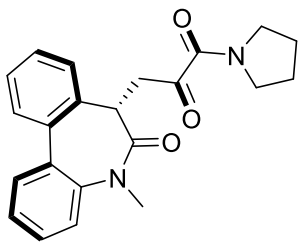
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	22.856	94943	8763597	50.262	--
2	35.537	64857	8672268	49.738	4.453



PDA Ch1 254nm

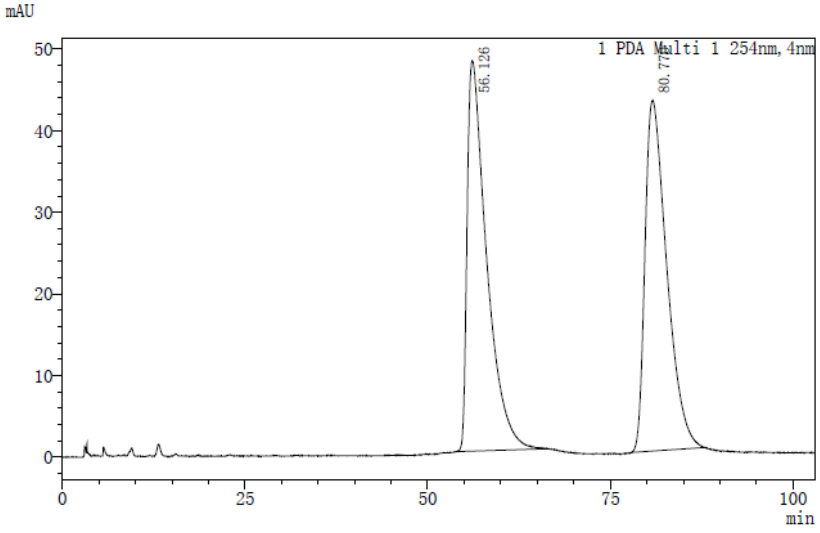
NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	21.724	376384	36069917	96.434	--
2	35.643	10726	1333720	3.566	4.955



(a*R*,

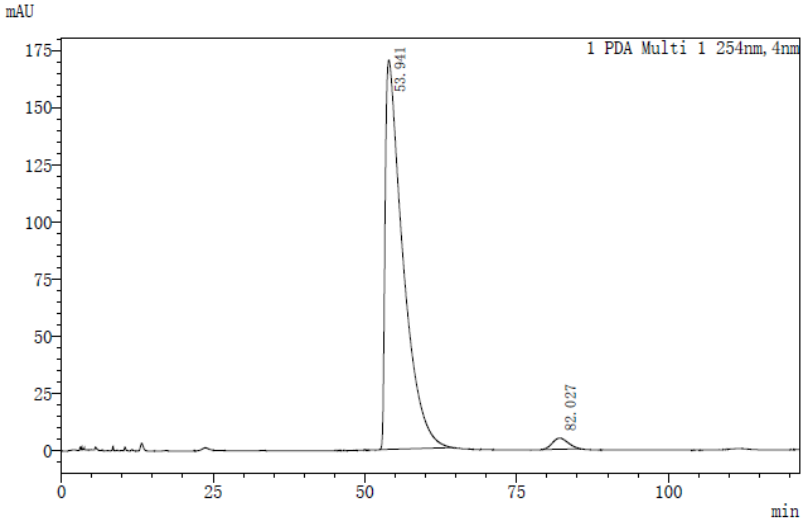
S)-3-(5-methyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-1-(pyrrolidin-1-yl)propane-1,2-dione (6ak)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:2) gave the product as a colorless oil (18.2 mg, 50% yield); $[\alpha]_D^{25}$ = -36.0(c = 0.1 in MeOH, 95% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 6.4 Hz, 2H), 7.51-7.40 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 4.03 (dd, *J* = 18.2, 11.3 Hz, 1H), 3.90 (dd, *J* = 11.3, 2.7 Hz, 1H), 3.67-3.52 (m, 4H), 3.41 (dd, *J* = 18.2, 3.1 Hz, 1H), 3.32 (s, 3H), 1.98 – 1.83 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.91, 171.80, 163.29, 141.57, 136.96, 136.94, 133.89, 130.06, 128.88, 128.64, 127.55, 125.59, 124.04, 122.76, 47.39, 46.35, 40.89, 37.50, 36.37, 26.47, 23.86. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2O_3^+$ 363.1703; Found 363.1691. The enantiomeric ratio was determined by FLM Chiralcel MX(2) (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 82.0 min, t (major) = 53.9 min.



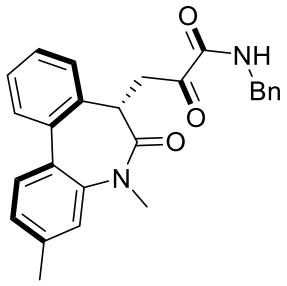
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	56.126	47909	8885930	49.976	--
2	80.770	42972	8894570	50.024	4.772



PDA Ch1 254nm

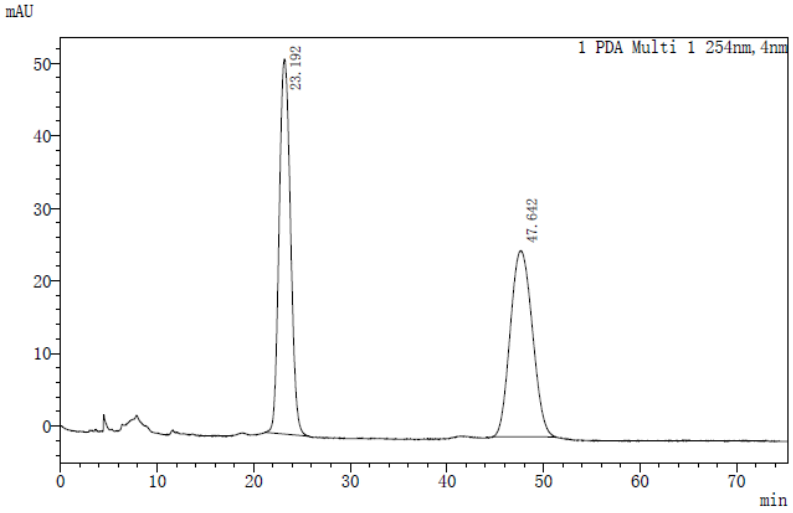
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	53.941	170132	34633473	97.522	--
2	82.027	4856	879935	2.478	5.518



(a*R*, *S*)-*N*-benzyl-3-(3,5-dimethyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2-oxo-propanamide (6bb)

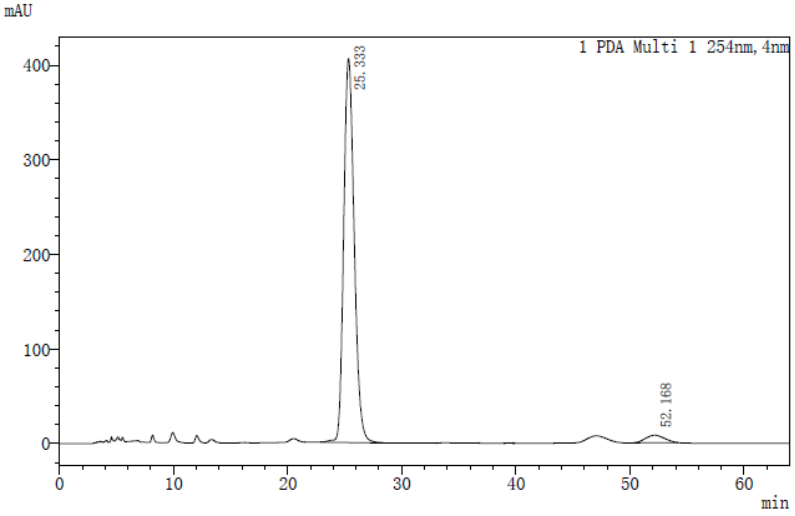
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (37.0 mg, 90% yield); $[\alpha]_D^{25}$ = -46.0 (c = 0.1 in MeOH, 93% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.48-7.36 (m, 4H), 7.34 – 7.30 (m, 2H), 7.26 (d, *J* = 8.7 Hz, 3H), 7.20 (d, *J* = 9.4 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 4.48 (d, *J* = 5.5 Hz, 2H), 4.33 (dd, *J* = 18.7, 11.1 Hz, 1H), 3.84 (d, *J* = 10.8 Hz, 1H), 3.34 (d, *J* = 19.0 Hz, 1H), 3.30 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.23, 171.43, 160.02, 141.35, 139.01, 137.03, 136.83, 136.56, 131.00, 129.80, 128.93, 128.65, 128.43, 128.01, 127.95, 127.53, 126.55, 123.98, 123.07, 43.59, 41.18, 36.27, 35.36, 21.39. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_3^+$ 413.1860; Found 413.1831. The enantiomeric ratio

was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 52.2 min, t (major) = 25.3 min.



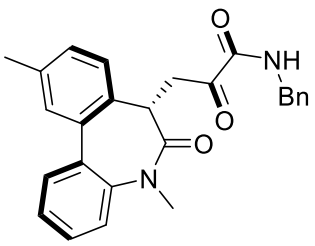
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	23.192	51708	4208920	50.791	--
2	47.642	25647	4077763	49.209	7.699



PDA Ch1 254nm

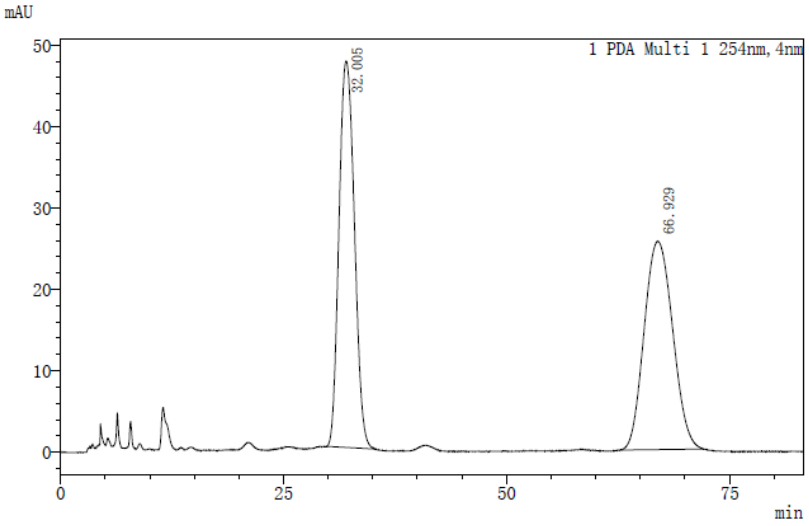
NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	25.333	405869	25956307	96.637	--
2	52.168	7849	903261	3.363	11.208



(a*R*,

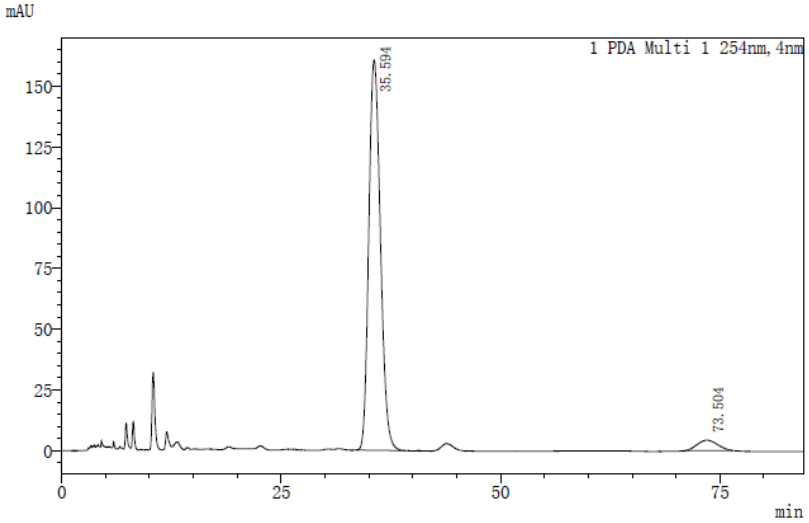
(*S*)-*N*-benzyl-3-(5,10-dimethyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2-oxo propanamide (6cb)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a white solid (36.7 mg, 89% yield): mp 159-162 °C; $[\alpha]_D^{25}$ = -38.0 (c = 0.1 in MeOH, 91% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.42-7.38 (m, 2H), 7.35 – 7.31 (m, 3H), 7.30-7.25 (m, 5H), 7.18 (s, 1H), 4.49 (d, *J* = 5.6 Hz, 2H), 4.31 (dd, *J* = 18.9, 11.0 Hz, 1H), 3.81 (d, *J* = 10.8 Hz, 1H), 3.34 (dd, *J* = 19.2, 2.7 Hz, 1H), 3.30 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.23, 171.69, 160.04, 141.54, 137.28, 137.04, 136.65, 134.02, 133.92, 129.97, 129.68, 129.29, 128.95, 128.76, 128.03, 127.96, 125.51, 123.91, 122.69, 43.60, 40.80, 36.29, 35.36, 21.27. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_3^+$ 413.1860; Found 413.1868. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 73.5 min, t (major) = 35.6 min.



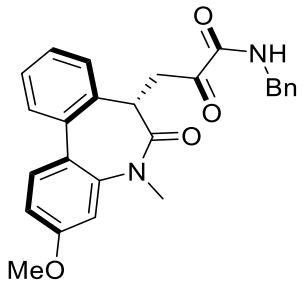
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	32.005	47445	5700452	50.063	--
2	66.929	25547	5686200	49.937	7.715



PDA Ch1 254nm

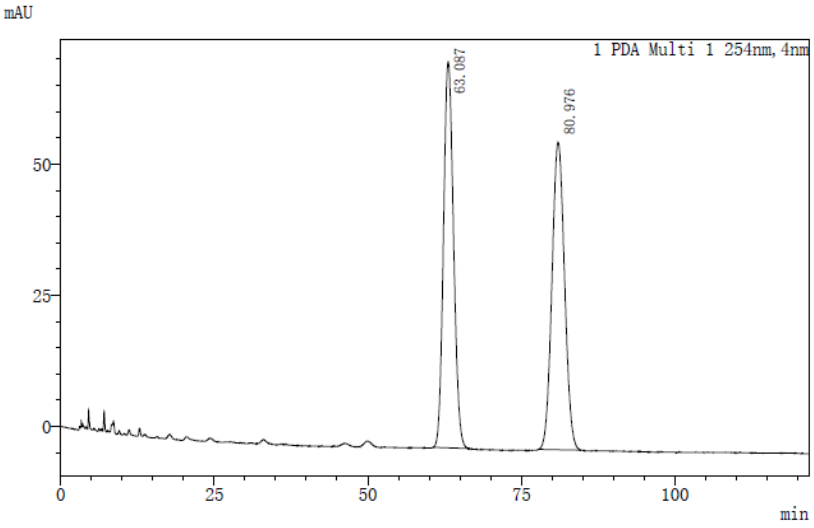
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	35.594	160684	14766171	95.579	--
2	73.504	4247	682987	4.421	11.188



(a*R*, *S*)-*N*-benzyl-3-(3-methoxy-5-methyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2-oxopropanamide (6db)

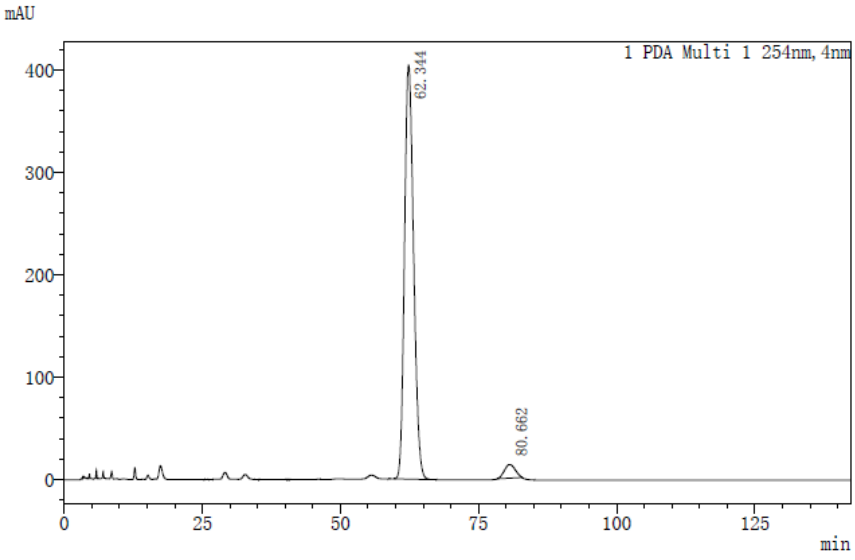
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) gave the product as a colorless oil (37.1 mg, 87% yield); $[\alpha]_D^{25}$ = -48.0 (c = 0.1 in MeOH, 92% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 13.3, 8.0 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.36-7.25 (m, 6H), 7.20 (s, 1H), 6.93-6.85 (m, 2H), 4.48 (d, *J* = 5.3 Hz, 2H), 4.33 (dd, *J* = 18.8, 11.2 Hz, 1H), 3.89 (s, 3H), 3.85 (d, *J* = 10.6 Hz, 1H), 3.34 (d, *J* = 19.4 Hz, 1H), 3.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.19, 171.38, 160.01, 142.46, 137.02, 136.70, 136.20, 130.91, 128.93, 128.38, 128.28, 128.01, 127.94, 127.60, 127.54, 126.66, 124.00, 111.65, 107.97, 55.67, 43.58, 41.22, 36.29, 35.36. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_4^+$ 429.1809; Found 429.1822. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46

cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 80.7 min, t (major) = 62.3 min.



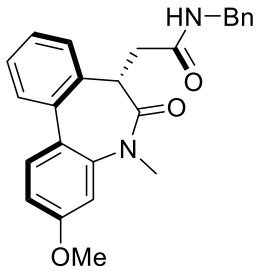
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	63.087	73645	8340573	49.933	--
2	80.976	58617	8362863	50.067	5.262



PDA Ch1 254nm

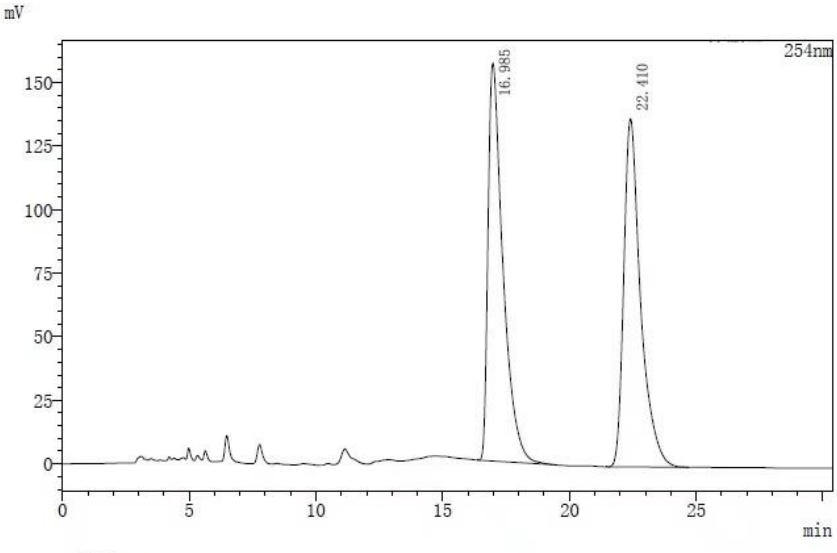
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	62.344	404409	46412587	96.222	--
2	80.662	13344	1822219	3.778	5.379



(aR,

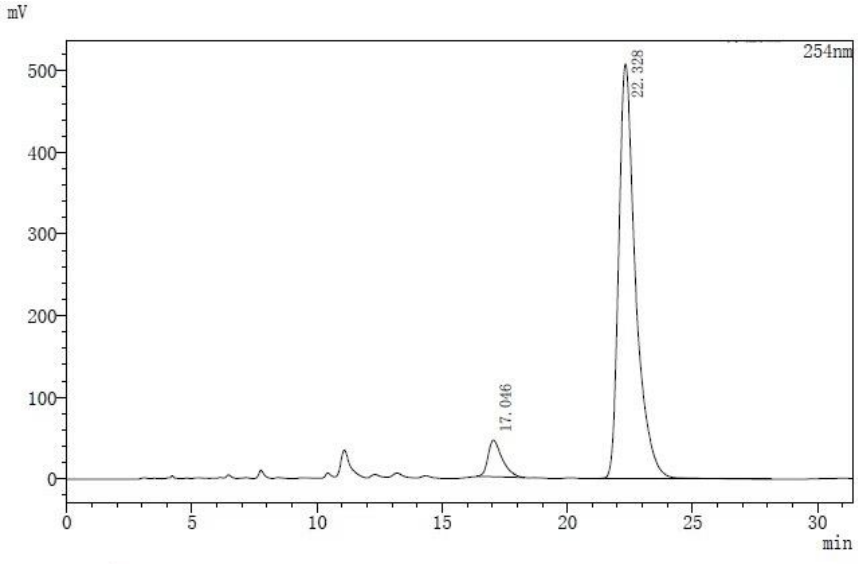
S)-N-benzyl-2-(3-methoxy-5-methyl-6-oxo-6,7-dihydro-5H-dibenzo[b,d]azepin-7-yl)acetamide

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:2) gave the product as a colorless oil (65.0 mg, 16% yield, 1 mmol scale); $[\alpha]_D^{25}$ = -78.0 (c = 0.10 in MeOH, 85% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.37 (dd, *J* = 9.3, 5.7 Hz, 2H), 7.30 (dd, *J* = 13.7, 6.4 Hz, 3H), 7.24 – 7.14 (m, 3H), 7.04 (s, 1H), 6.95 – 6.82 (m, 2H), 4.42 (ddd, *J* = 38.1, 14.8, 5.6 Hz, 2H), 3.97 (dd, *J* = 10.6, 3.3 Hz, 1H), 3.88 (s, 3H), 3.46 (dd, *J* = 13.9, 10.9 Hz, 1H), 3.22 (s, 3H), 2.77 (dd, *J* = 14.1, 3.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.88, 171.43, 159.90, 142.12, 138.65, 137.15, 136.61, 130.85, 128.55, 128.14, 128.11, 127.66, 127.31, 127.23, 126.61, 123.38, 111.79, 108.02, 55.59, 43.49, 42.78, 36.19, 34.49. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{25}H_{23}N_2O_3^-$ 399.1714; Found 399.1712. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 17.046 min, t (major) = 22.328 min.



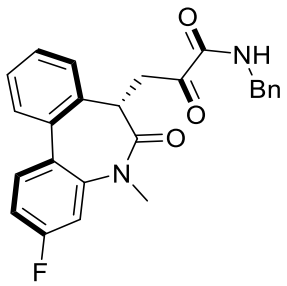
254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	16.985	156541	6381381	50.102	--
2	22.410	137029	6355513	49.898	5.030



254nm

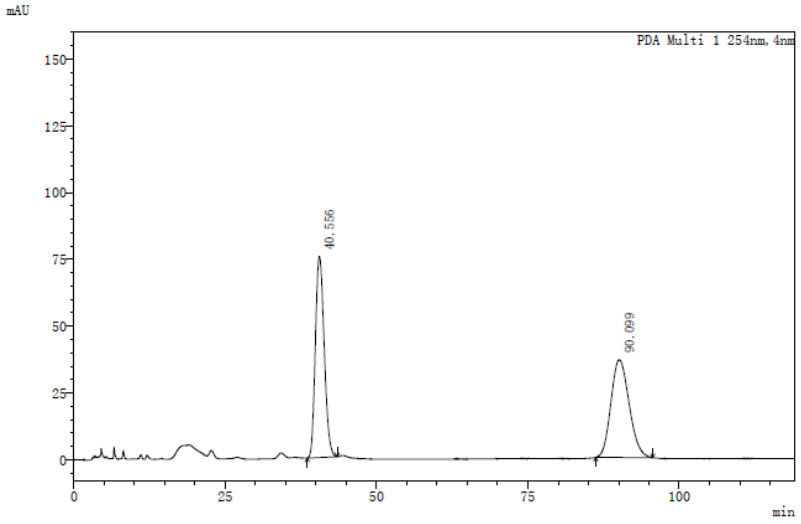
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	17.046	44755	1763149	6.857	--
2	22.328	508567	23948525	93.143	4.907



(a*R*, *S*)-*N*-benzyl-3-(3-fluoro-5-methyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2-oxopropanamide (6eb)

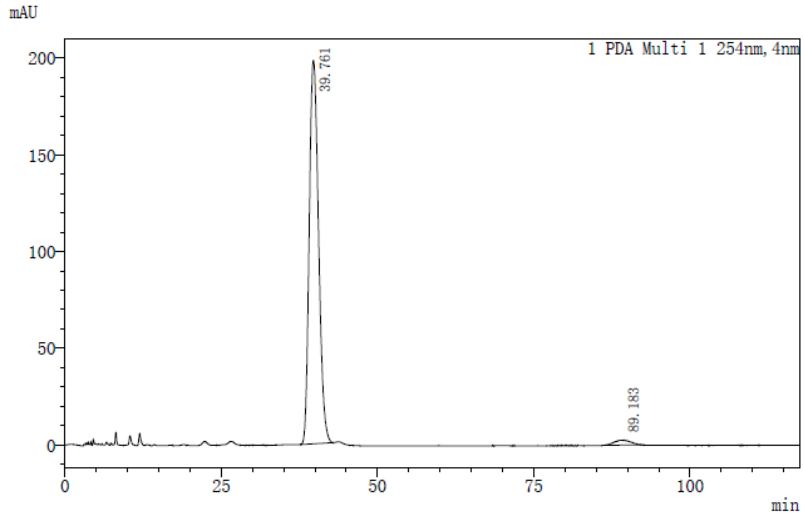
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product as a colorless oil (36.5 mg, 88% yield); $[\alpha]_D^{25}$ = -80.0 (c = 0.23 in MeOH, 95% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57-7.50 (m, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.40 (dd, *J* = 19.9, 7.4 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.24 (m, 3H), 7.19 (s, 1H), 7.12 (d, *J* = 10.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 4.49 (d, *J* = 5.6 Hz, 2H), 4.33 (dd, *J* = 18.8, 11.1 Hz, 1H), 3.83 (d, *J* = 10.9 Hz, 1H), 3.36 (d, *J* = 18.9 Hz, 1H), 3.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.05, 171.29, 162.66 (d, *J* = 249.1 Hz), 159.93, 142.63(d, *J* = 9.7 Hz), 137.00, 136.36, 136.07, 131.46 (d, *J* = 9.2 Hz), 130.02 (d, *J* = 3.2 Hz), 129.02, 128.95, 128.55, 128.02, 127.98, 127.71, 124.13, 112.92 (d, *J* = 21.4 Hz), 109.60 (d, *J* = 23.8Hz), 43.60, 41.18, 36.19, 35.32. ^{19}F

NMR (471 MHz, $CDCl_3$) δ -112.08. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{22}FN_2O_3^+$ 417.1609; Found 417.1626. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 89.2 min, t (major) = 39.8 min.



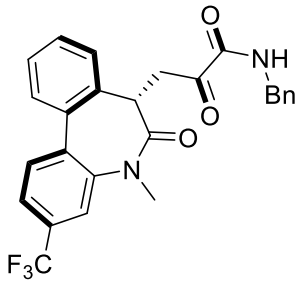
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	40.556	75364	7642022	49.995	--
2	90.099	36642	7643555	50.005	12.078



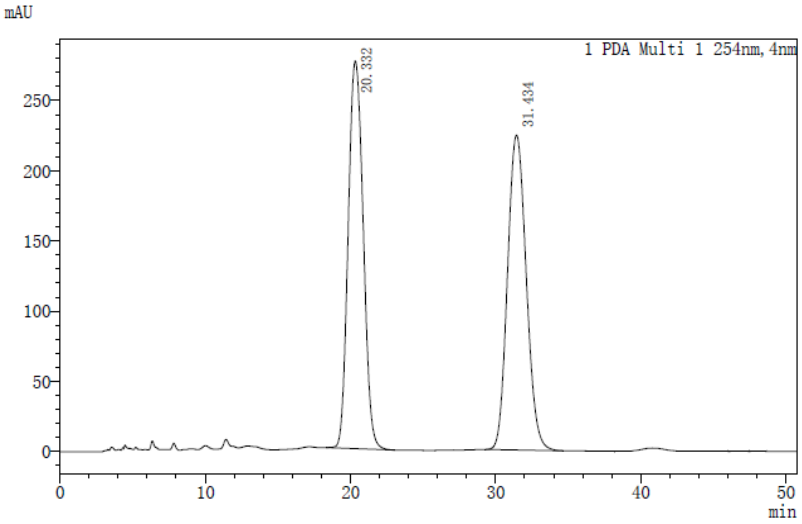
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	39.761	198169	20488975	97.731	--
2	89.183	2538	475633	2.269	12.710



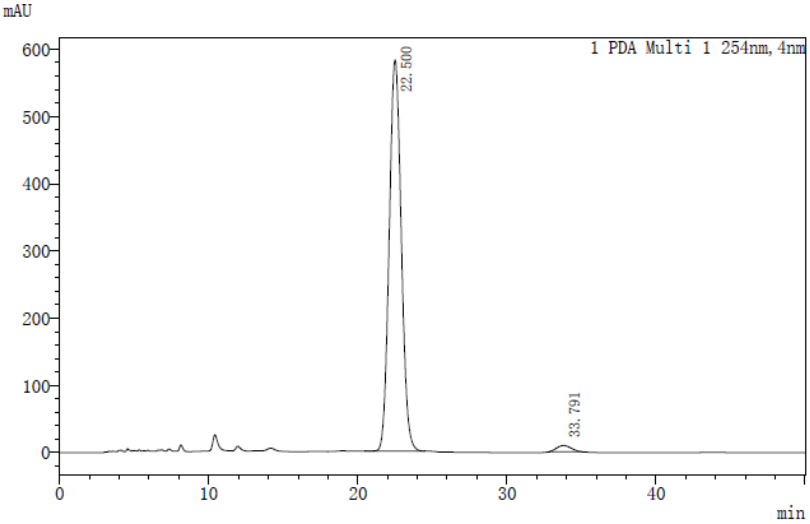
(a*R*, *S*)-*N*-benzyl-3-(5-methyl-6-oxo-3-(trifluoromethyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2-oxopropanamide (6fb)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product as a colorless oil (32.4 mg, 70% yield); $[\alpha]_D^{25}$ = -36.0 (c = 0.1 in MeOH, 96% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.61-7.56 (m, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.38 – 7.24 (m, 5H), 7.18 (s, 1H), 4.49 (d, *J* = 5.5 Hz, 2H), 4.34 (dd, *J* = 18.9, 11.0 Hz, 1H), 3.81 (d, *J* = 10.7 Hz, 1H), 3.39 (d, *J* = 19.0 Hz, 1H), 3.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.98, 171.31, 159.89, 141.75, 137.06, 136.96, 136.88, 135.64, 131.10 (q, *J* = 33.1 Hz), 130.77, 129.85, 128.97, 128.81, 128.01, 127.89, 124.30, 123.81 (q, *J* = 272.9 Hz), 122.08 (q, *J* = 3.5 Hz), 119.71 (q, *J* = 3.8 Hz), 43.63, 41.15, 36.33, 35.26. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.45. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{26}H_{22}F_3N_2O_3^+$ 467.1577; Found 467.1577. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 33.8 min, t (major) = 22.5 min.



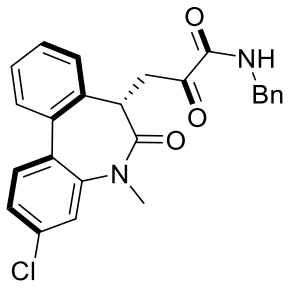
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	20.332	276150	19890999	49.742	--
2	31.434	224309	20097565	50.258	5.206



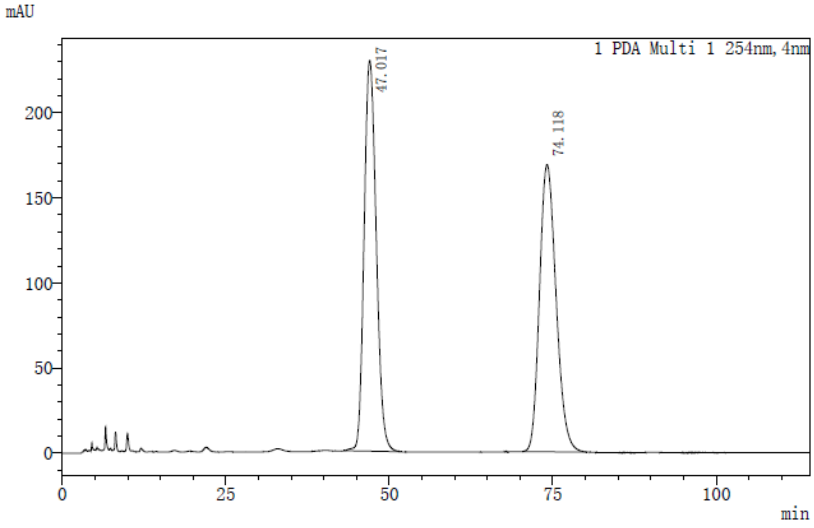
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	22.500	582187	32674584	98.164	--
2	33.791	9231	611273	1.836	6.810



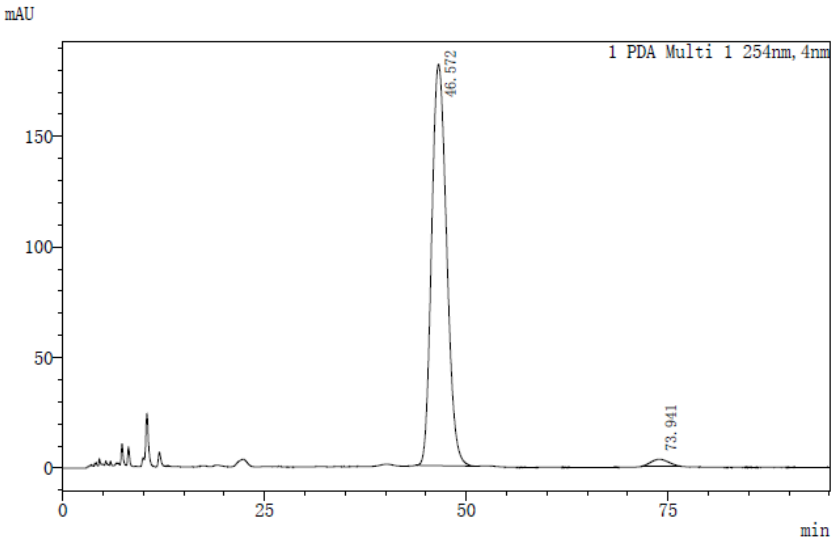
(a*R*, *S*)-*N*-benzyl-3-(3-chloro-5-methyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2- oxopropanamide (6gb)

Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product as a colorless oil (32.6 mg, 75% yield); $[\alpha]_D^{25}$ = -52.0 (c = 0.1 in MeOH, 96% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (t, *J* = 8.1 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.43-7.37 (m, 3H), 7.36 – 7.26 (m, 6H), 7.19 (s, 1H), 4.49 (d, *J* = 5.6 Hz, 2H), 4.33 (dd, *J* = 18.8, 11.1 Hz, 1H), 3.81 (d, *J* = 10.8 Hz, 1H), 3.36 (d, *J* = 18.9 Hz, 1H), 3.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.01, 171.27, 159.92, 142.33, 136.99, 136.51, 135.90, 134.51, 132.29, 131.06, 129.28, 128.96, 128.52, 128.02, 127.98, 127.76, 125.77, 124.19, 122.74, 43.61, 41.17, 36.26, 35.30. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{22}ClN_2O_3^+$ 433.1313; Found 433.1303. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 73.9 min, t (major) = 46.6 min.



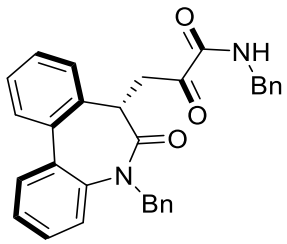
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	47.017	229630	29588213	49.957	--
2	74.118	168690	29639697	50.043	6.775



PDA Ch1 254nm

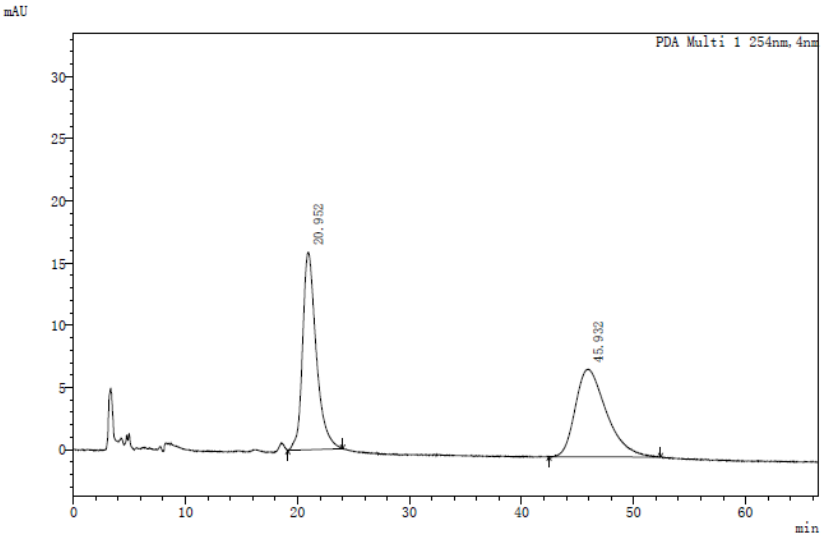
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	46.572	181471	23428831	97.952	--
2	73.941	3212	489884	2.048	7.169



(a*R*, *S*)-*N*-benzyl-3-(5-benzyl-6-oxo-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-7-yl)-2-oxopropanamide (6hb)

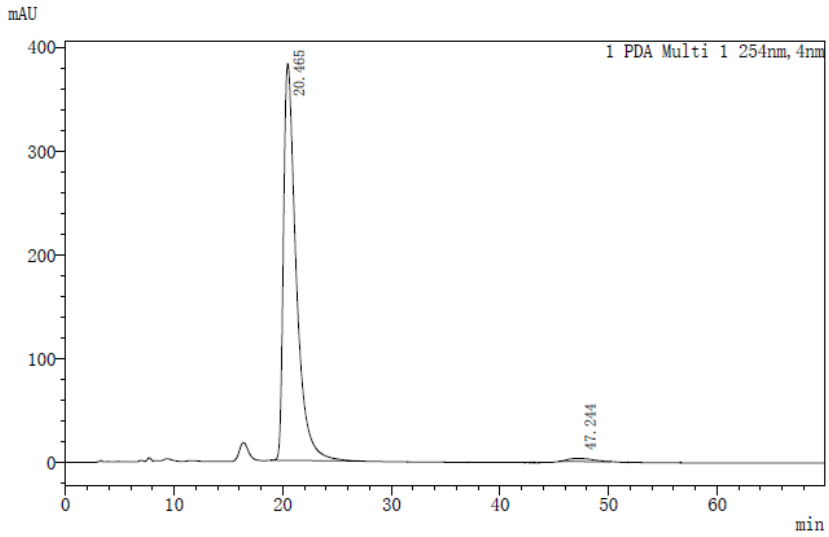
Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product as a colorless oil (41.2 mg, 87% yield); $[\alpha]_D^{25}$ = -78.0 (c = 0.1 in MeOH, 96% ee, >20:1 dr); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 3H), 7.42 (t, *J* = 6.7 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.35-7.31 (m, 3H), 7.29-7.23 (m, 5H), 7.17 – 7.11 (m, 3H), 6.95 (d, *J* = 6.9 Hz, 2H), 5.06 – 4.94 (m, 2H), 4.48 (qd, *J* = 14.9, 6.0 Hz, 2H), 4.37 (dd, *J* = 19.1, 11.3 Hz, 1H), 3.95 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.44 (dd, *J* = 19.1, 2.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.17, 171.06, 160.01, 140.59, 137.46, 137.03, 136.89, 136.42, 134.52, 130.01, 129.05, 128.93, 128.85, 128.55, 128.47, 128.01, 127.94, 127.65, 126.92, 126.64, 125.93, 124.08, 123.03, 52.45, 43.57, 41.15, 35.50. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{27}N_2O_3^+$ 475.2016;

Found 475.2019. The enantiomeric ratio was determined by Daicel Chiralcel OD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 47.2 min, t (major) = 20.5 min.



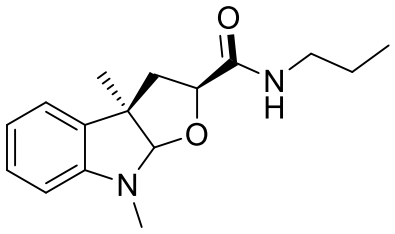
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	20.952	15893	1346345	49.715	--
2	45.932	7044	1361786	50.285	6.980



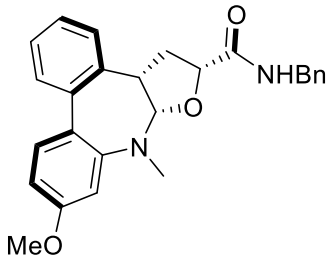
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	20.465	382659	31050544	98.481	--
2	47.244	3112	479045	1.519	8.553



(2*S*,3a*R*)-3a,8-Dimethyl-*N*-propyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole-2-carboxamidev(7)

The 6:1 dr was determinded by ^{1}H NMR. Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:2) gave the product as a colorless oil (24.4 mg, 45% yield); $[\alpha]_D^{25}$ = +60.0 (c = 0.11 in MeOH); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.22 (s, 1H), 5.12 (s, 1H), 4.51 (dd, *J* = 9.1, 2.8 Hz, 1H), 3.03 (s, 3H), 2.83 (td, *J* = 13.3, 7.0 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.49 (dd, *J* = 12.9, 9.2 Hz, 1H), 1.36 (s, 3H), 1.18 – 1.09 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.53, 148.75, 134.60, 128.57, 123.17, 119.10, 107.44, 106.39, 79.18, 51.93, 42.70, 40.60, 32.03, 24.06, 22.61, 11.49. HRMS (ESI) *m*/*z*: $[M-H]^-$ Calcd for $C_{16}H_{21}N_2O_2^-$ 273.1609; Found 273.1609.



(a*R*,

4b*S*,6*R*,7a*S*)-*N*-benzyl-10-methoxy-8-methyl-4b,5,7a,8-tetrahydro-6*H*-dibenzo[*b*,*d*]furo[3,2-*f*]azepine-6-carboxamide (8)

The 3:1 dr was determinded by ^{1}H NMR. Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 2:1) gave the product as a colorless oil (15.8 mg, 38% yield); $[\alpha]_D^{25}$ = +134.0 (c = 0.1 in MeOH); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.31 – 7.26 (m, 3H), 7.25-7.23 (m, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.72 (t, *J* = 4.5 Hz, 1H), 6.68 – 6.60 (m, 2H), 5.57 (d, *J* = 8.8 Hz, 1H), 4.47 (dd, *J* = 15.0,

7.3 Hz, 1H), 4.28 (dd, *J* = 11.1, 5.9 Hz, 1H), 4.10 (dd, *J* = 15.0, 5.0 Hz, 1H), 3.66 (s, 3H), 3.53 (dt, *J* = 13.4, 8.2 Hz, 1H), 2.92 (s, 3H), 2.29 – 2.20 (m, 1H), 1.78 (dd, *J* = 24.4, 12.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.94, 159.88, 146.99, 138.71, 138.20, 136.50, 130.31, 130.08, 129.89, 128.87, 128.75, 128.03, 127.48, 127.41, 127.31, 108.34, 108.16, 104.47, 77.54, 55.22, 49.12, 42.69, 40.69, 35.40. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{26}H_{27}N_2O_3^+$ 415.2016; Found 415.2008.

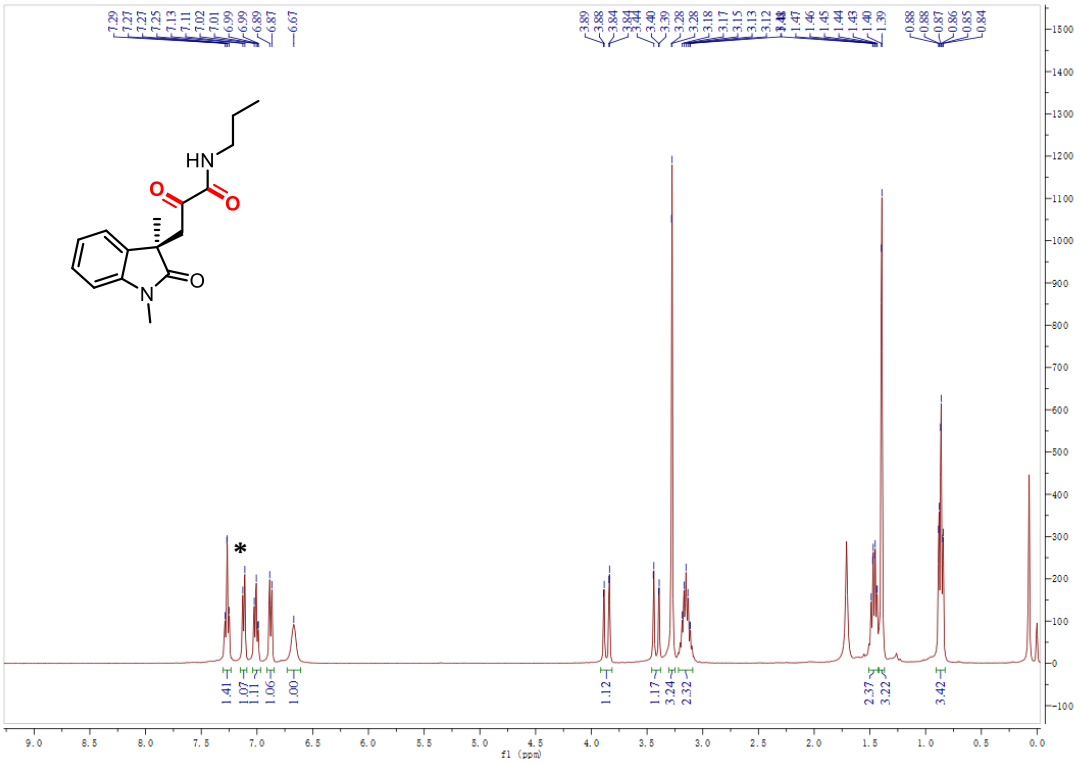
4. References

[1] Y. Feng, S. Yang, S. Zhao, D.-P. Zhang, X. Li, H. Liu, Y. Dong, F.-G. Sun, Nickel-Catalyzed Reductive Aryl Thiocarbonylation of Alkene via Thioester Group Transfer Strategy, *Org. Lett.* 2020, **22**, 6734−6738.

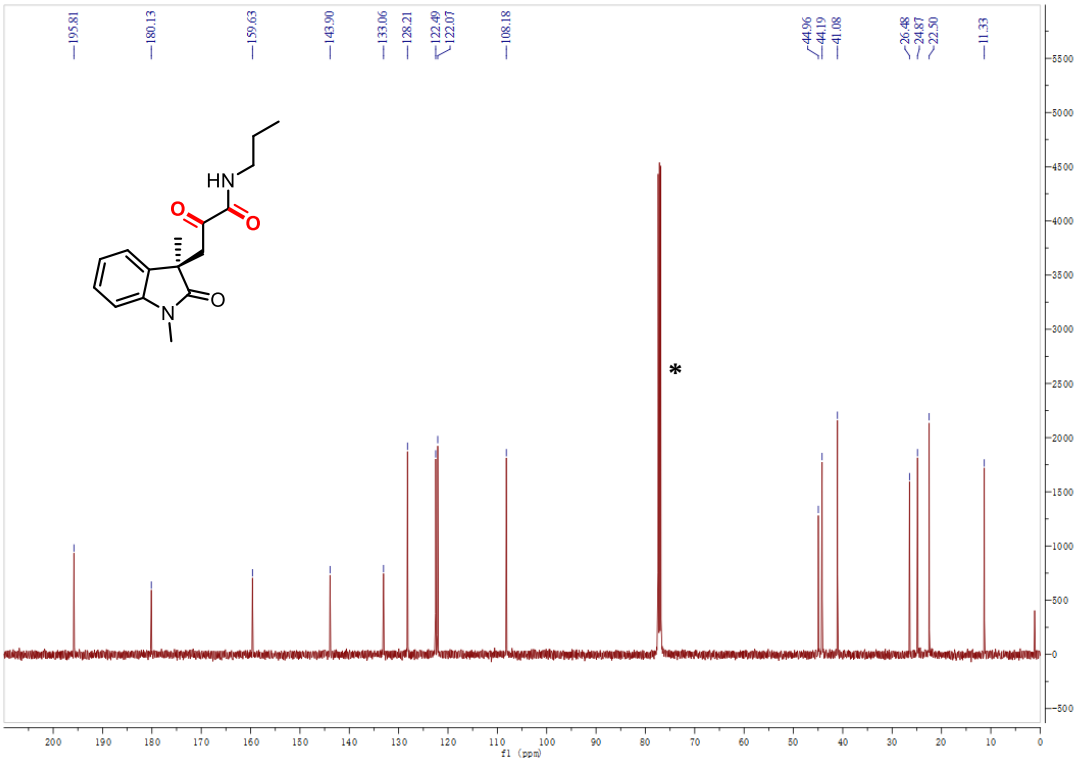
[2] H. Hu, Y. Peng, T. Yu, S. Cheng, S. Luo, Q. Zhu, Palladium-Catalyzed Enantioselective 7-*exo*-Trig Carbopalladation/Carbonylation: Cascade Reactions To Achieve Atropisomeric Dibenzo[*b*,*d*]azepin-6-ones, *Org. Lett.* 2021, **23**, 3636−3640.

5. Copies of NMR and NOE Spectra

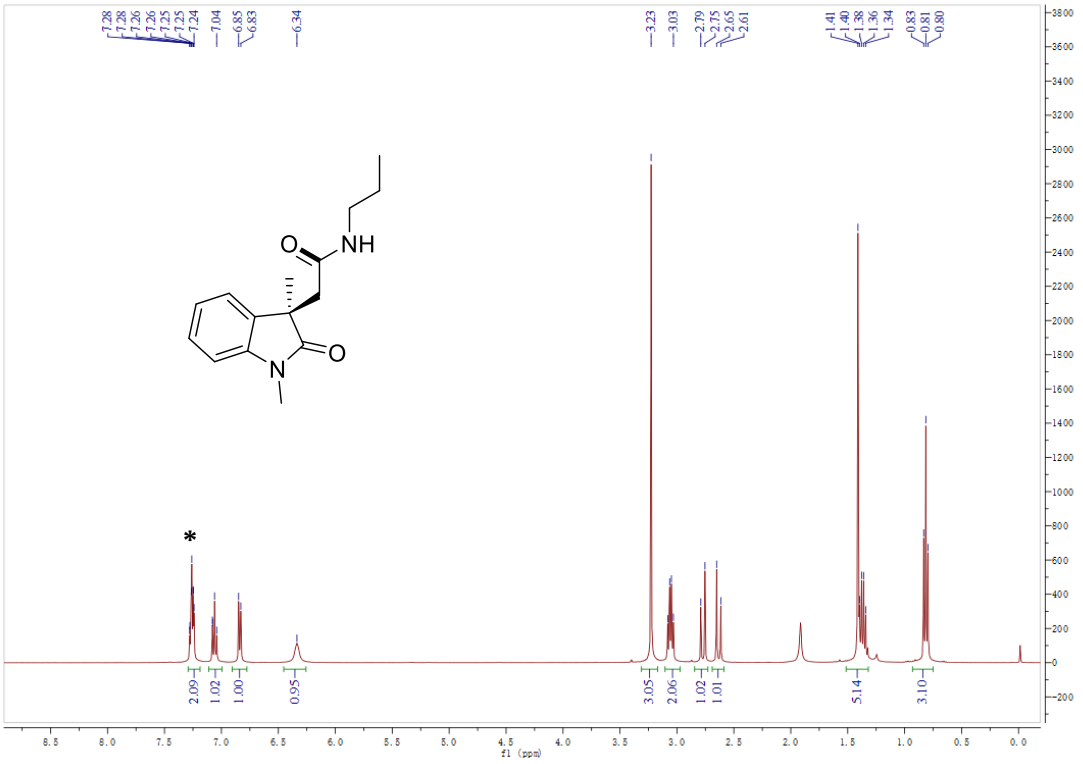
^{1}H NMR of 4aa (500 MHz, $CDCl_3$, *solvent)



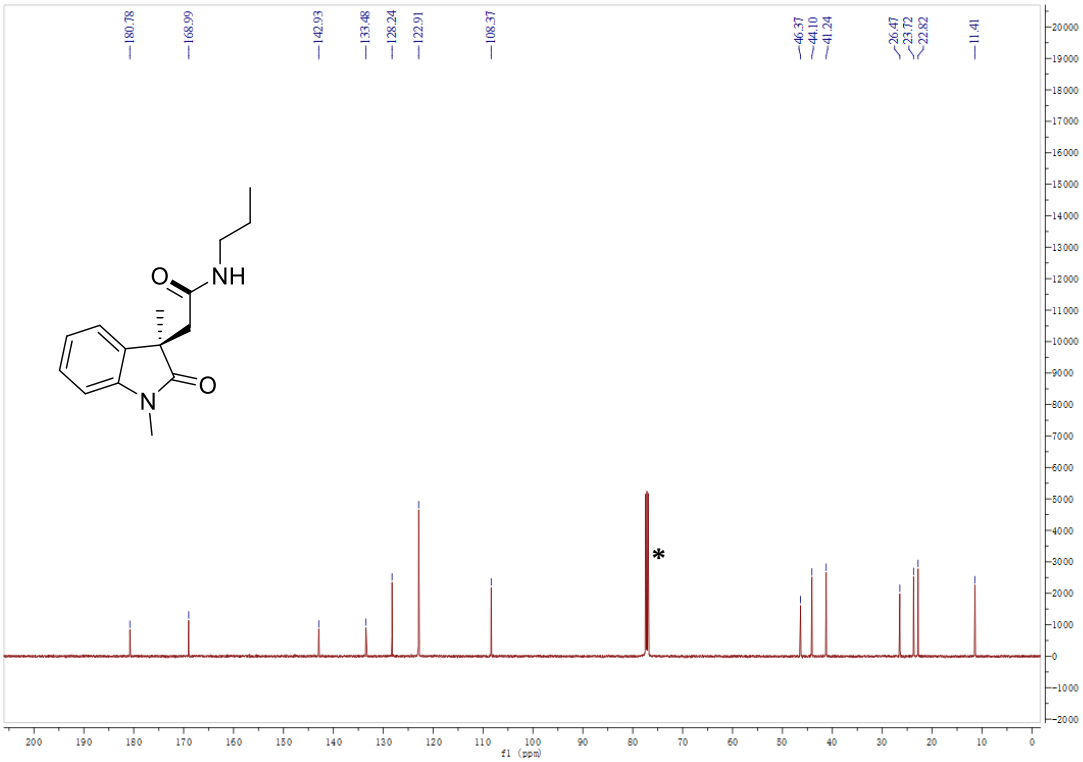
^{13}C NMR of 4aa (126 MHz, $CDCl_3$, *solvent)



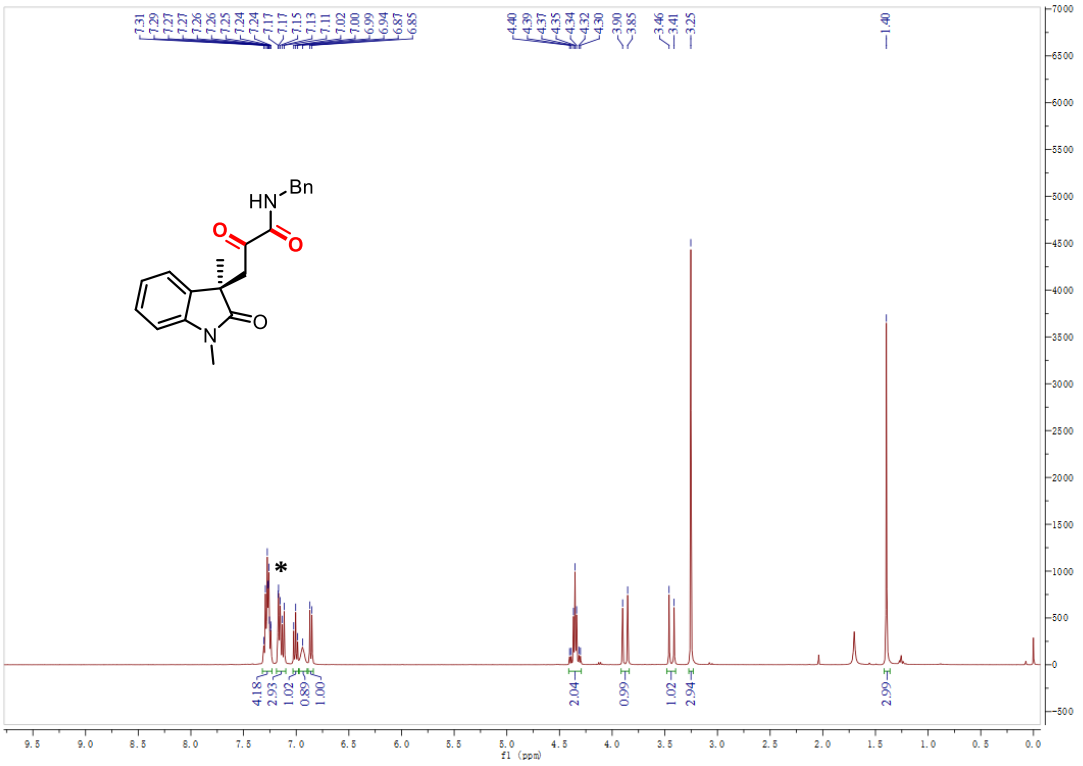
^{1}H NMR of 3aa (400 MHz, $CDCl_3$, *solvent)



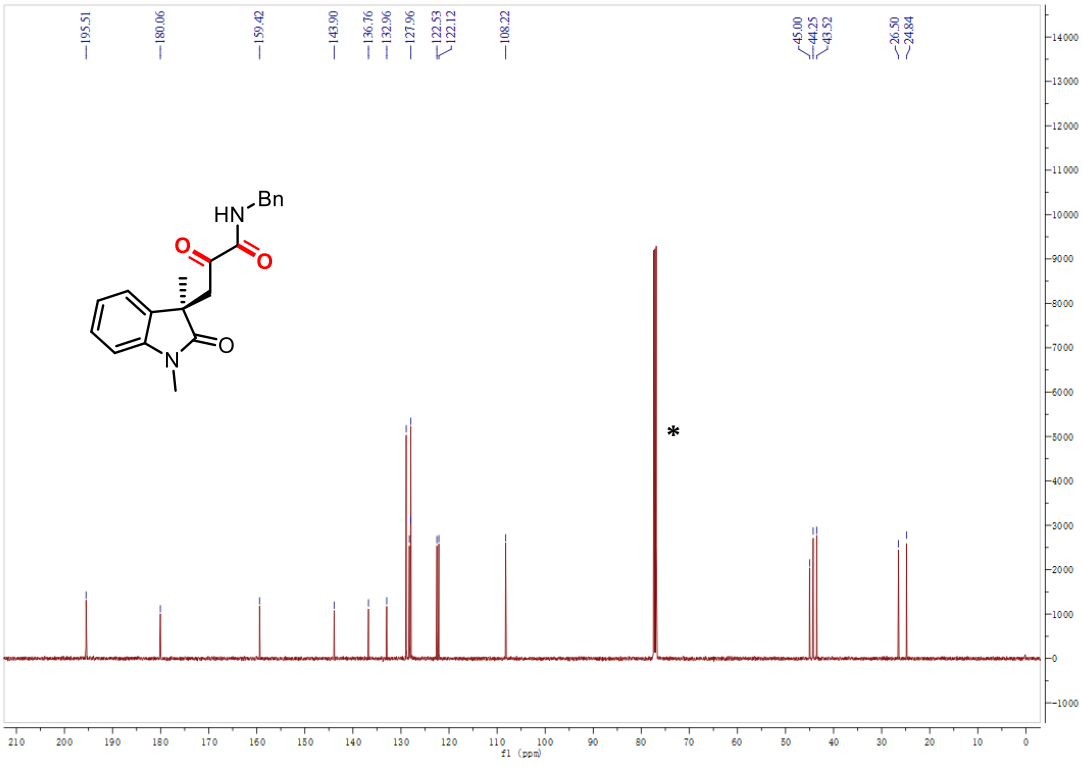
^{13}C NMR of 3aa (126 MHz, $CDCl_3$, *solvent)



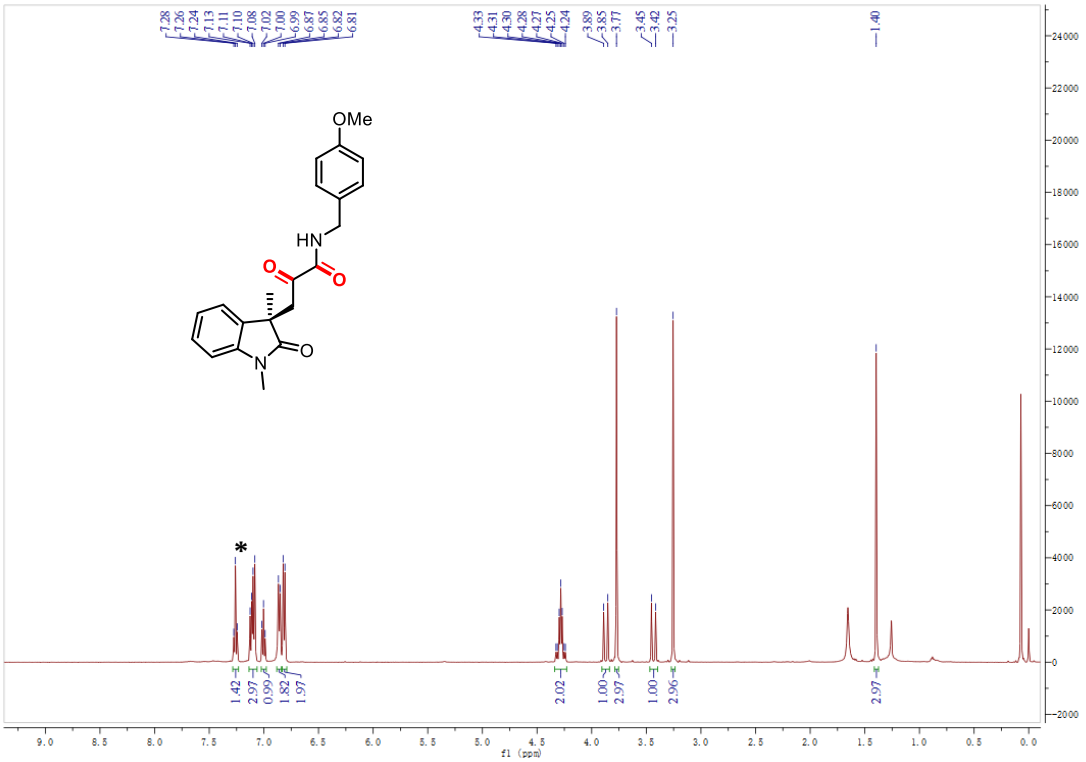
^{1}H NMR of 4ab (500 MHz, $CDCl_3$, *solvent)



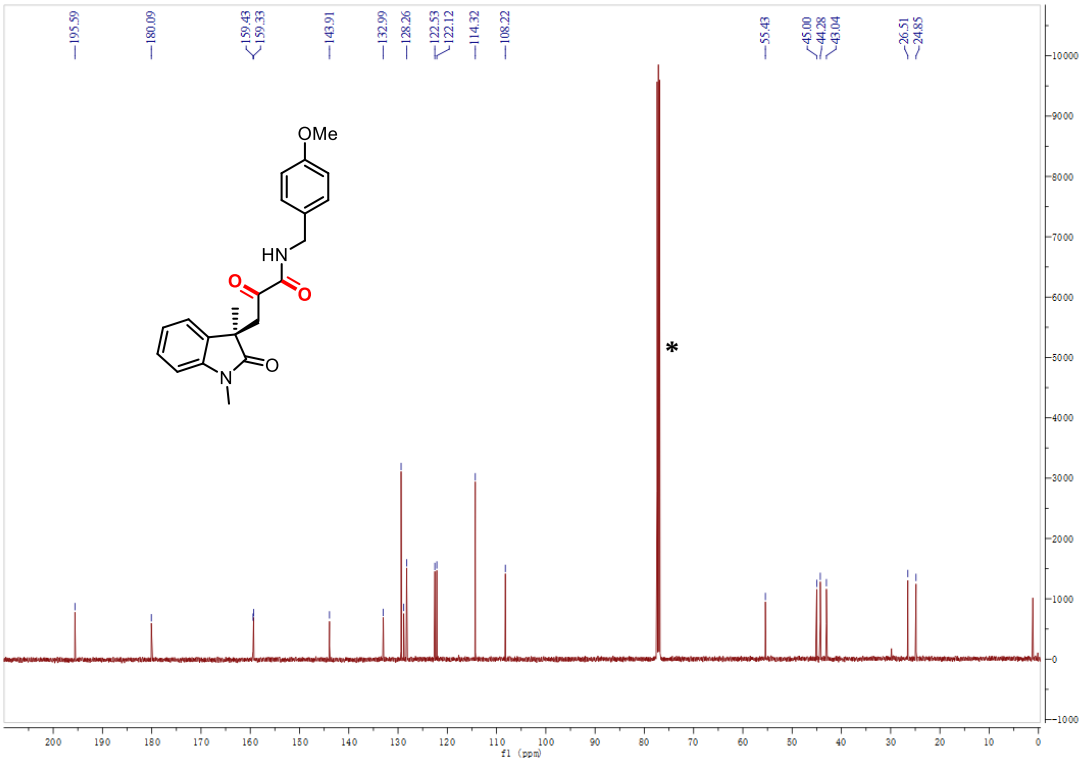
^{13}C NMR of 4ab (126 MHz, $CDCl_3$, *solvent)



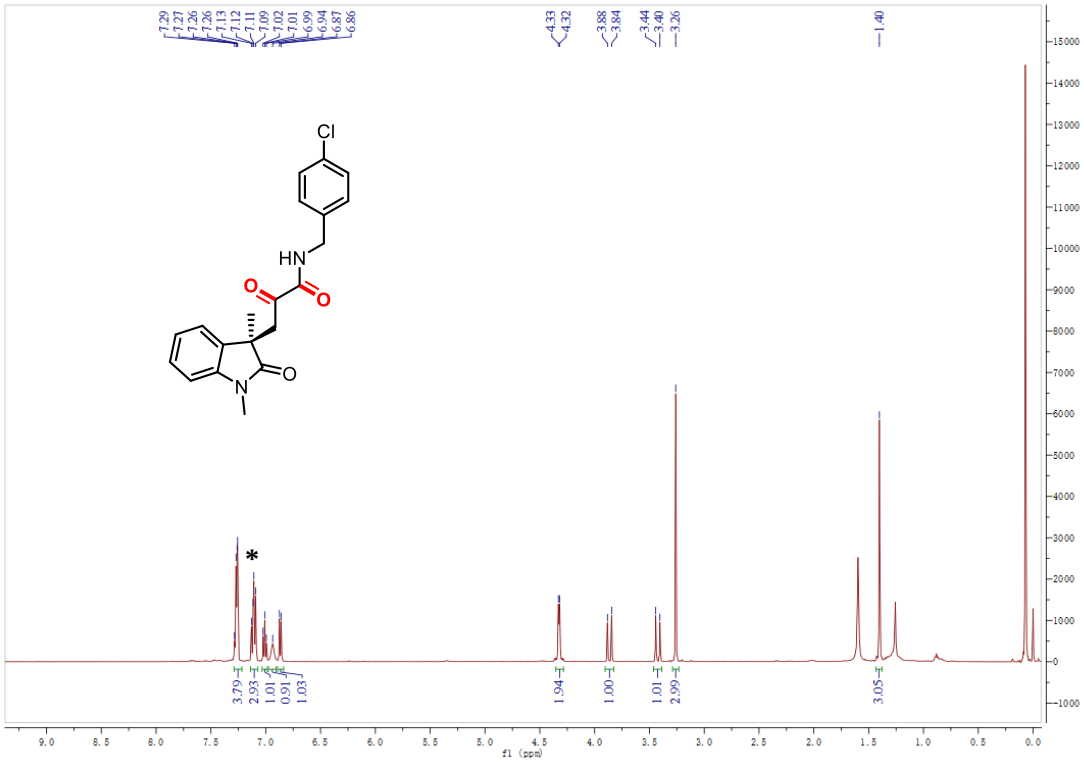
^{1}H NMR of 4ac (500 MHz, $CDCl_3$, *solvent)



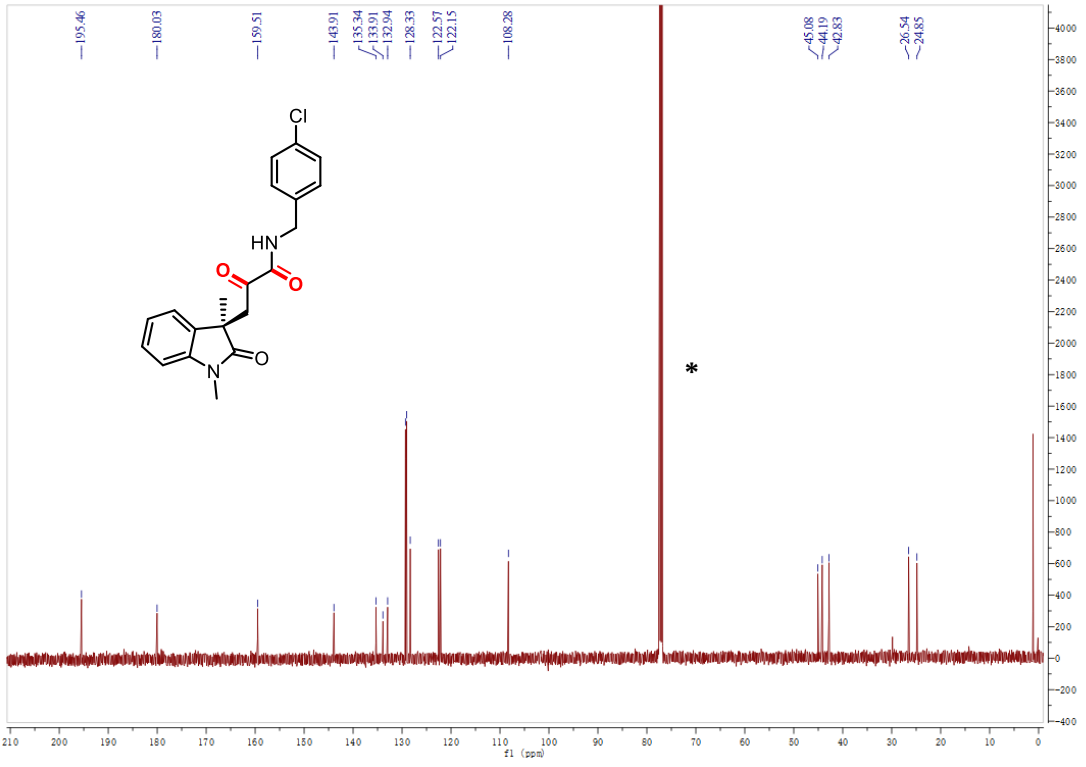
^{13}C NMR of 4ac (126 MHz, $CDCl_3$, *solvent)



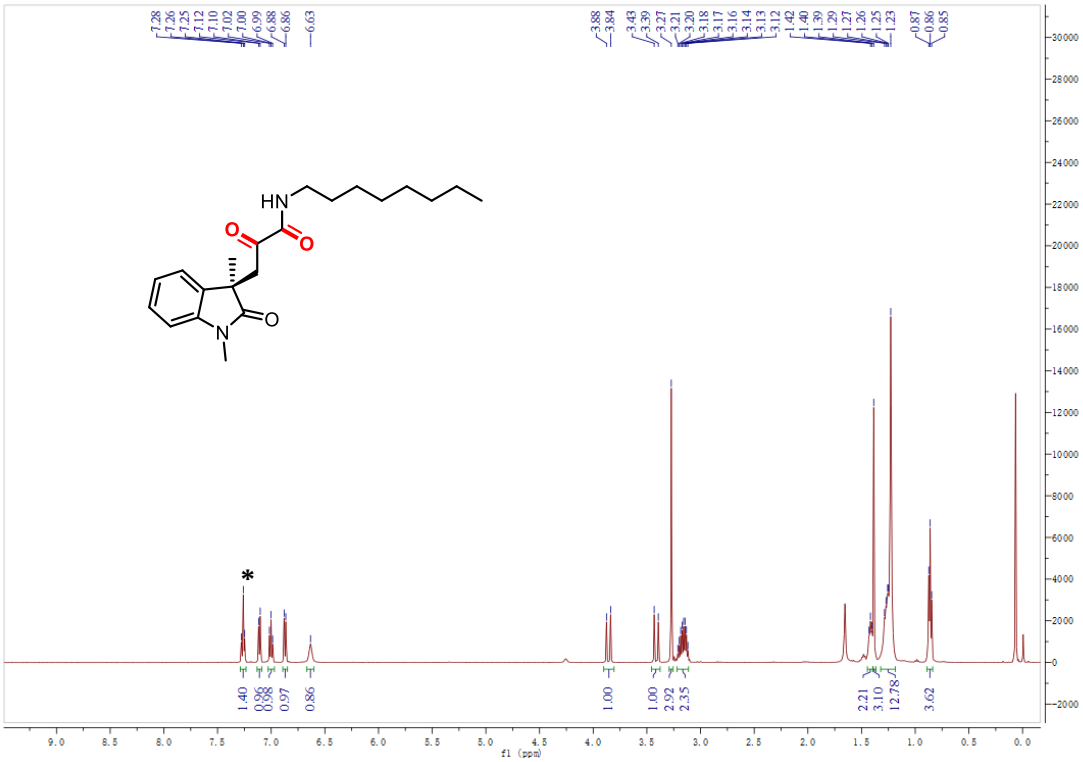
^{1}H NMR of 4ad (500 MHz, $CDCl_3$, *solvent)



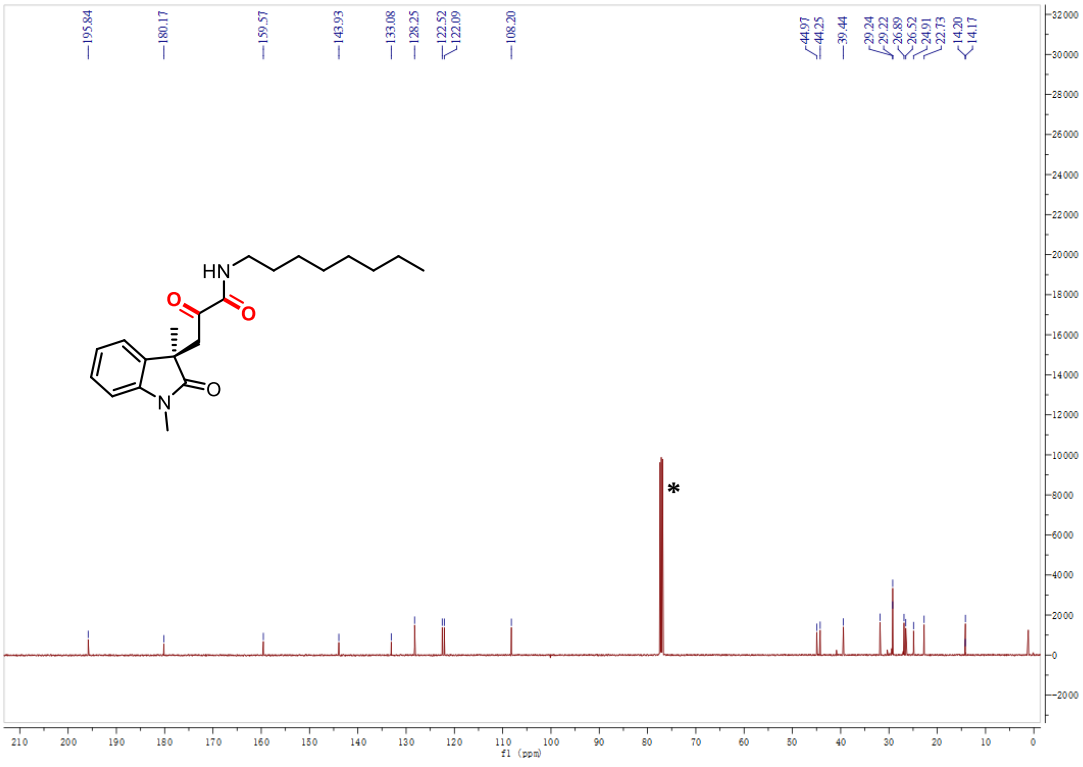
^{13}C NMR of 4ad (126 MHz, $CDCl_3$, *solvent)



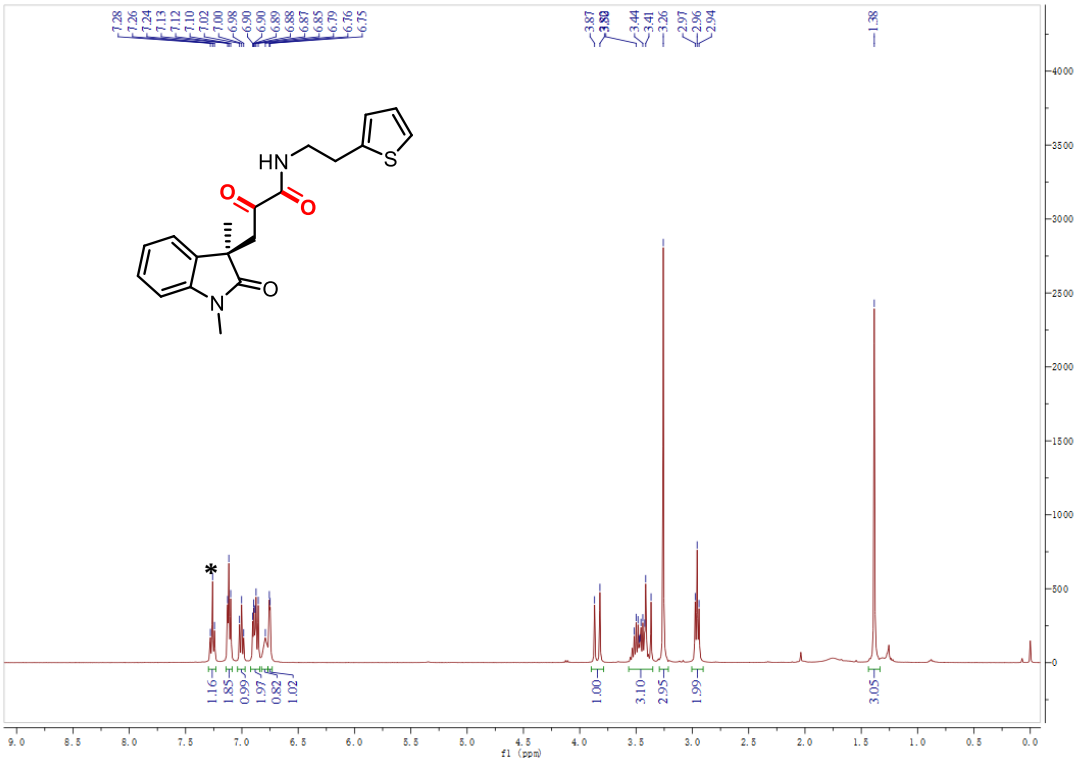
^{1}H NMR of 4ae (500 MHz, $CDCl_3$, *solvent)



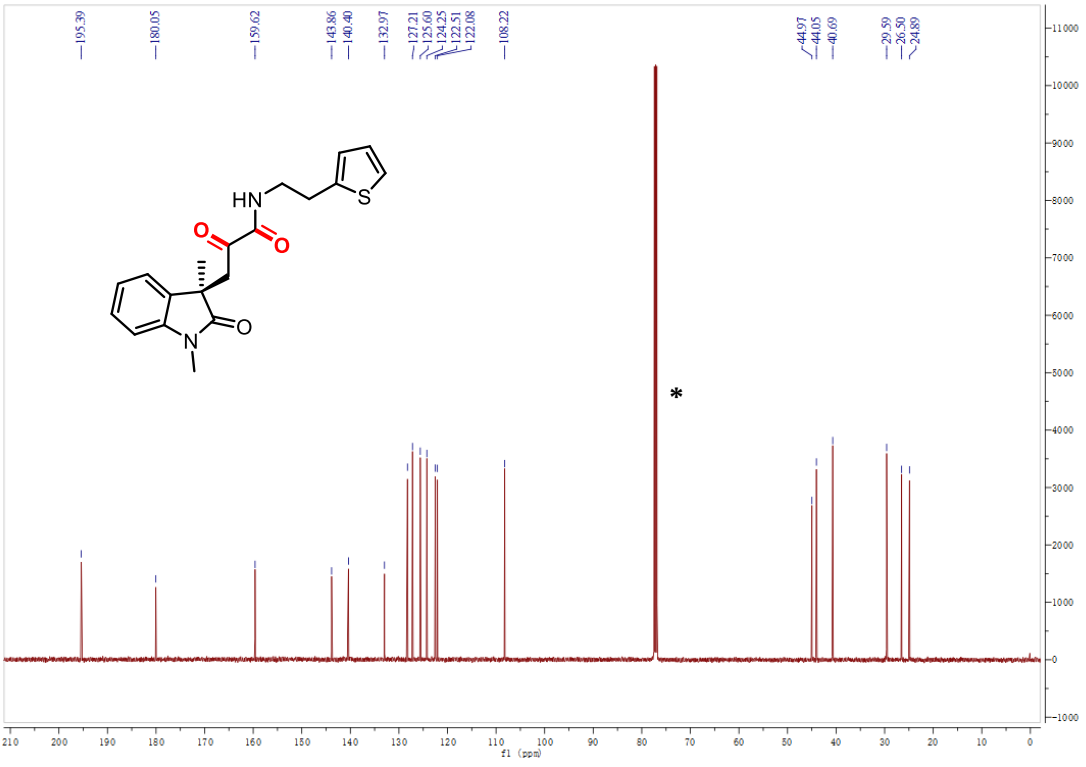
^{13}C NMR of 4ae (126 MHz, $CDCl_3$, *solvent)



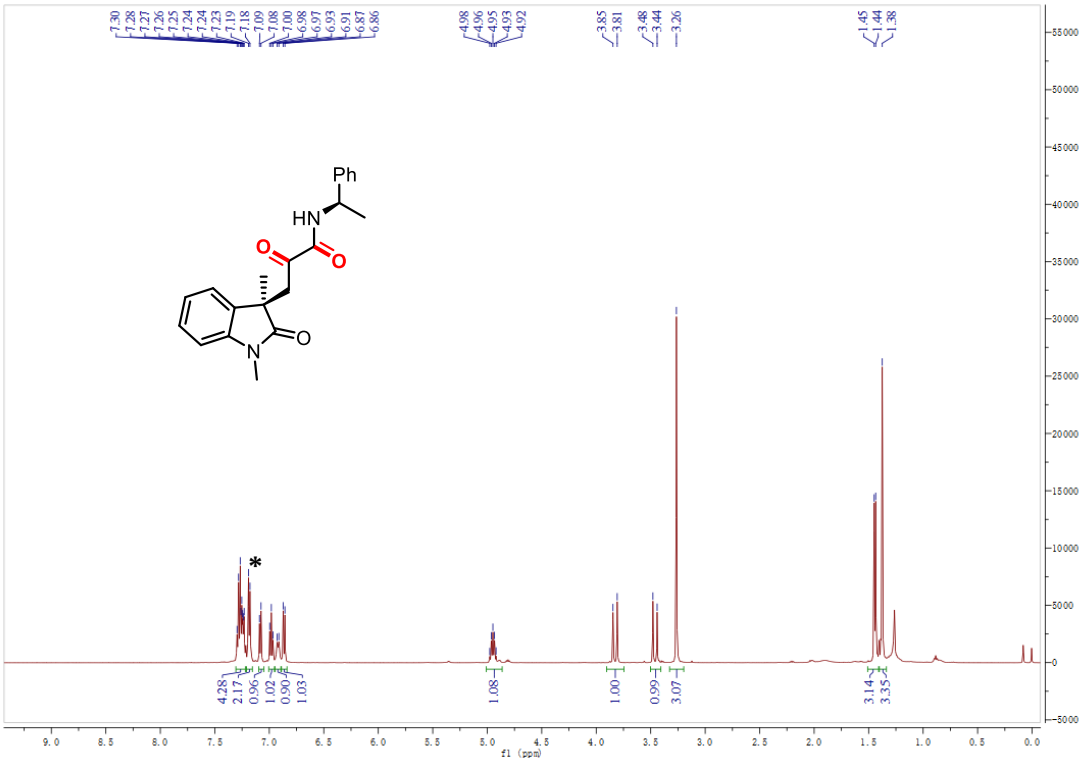
^{1}H NMR of 4af (500 MHz, $CDCl_3$, *solvent)



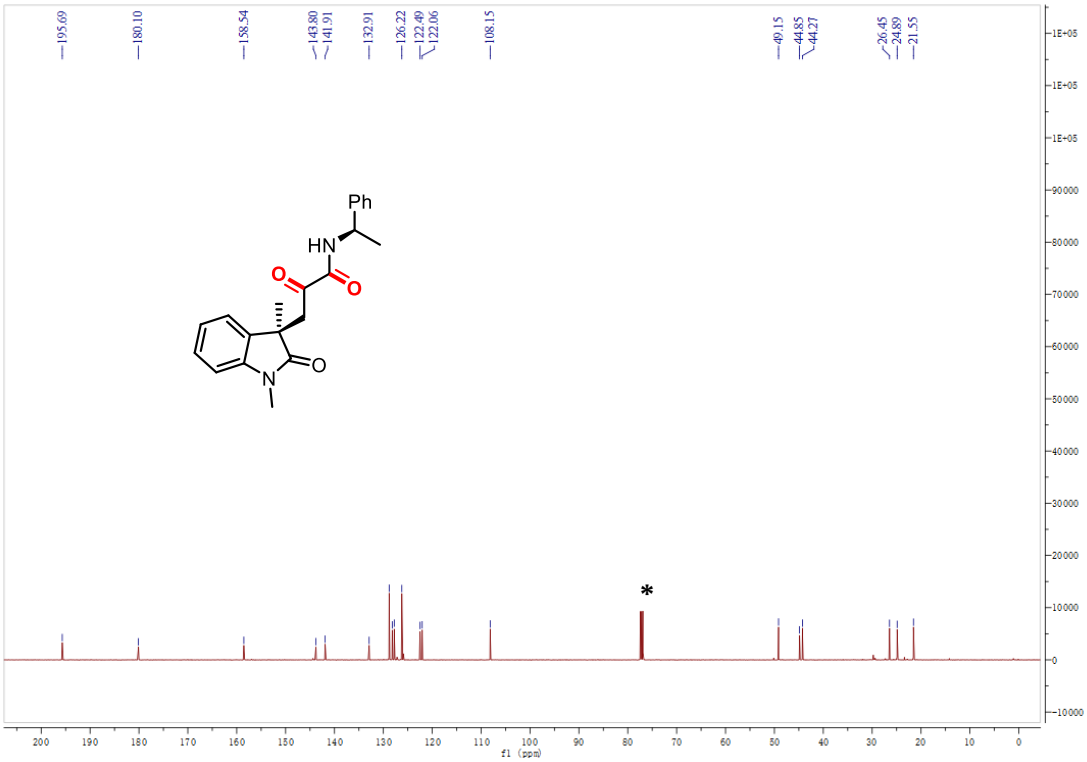
^{13}C NMR of 4af (126 MHz, $CDCl_3$, *solvent)



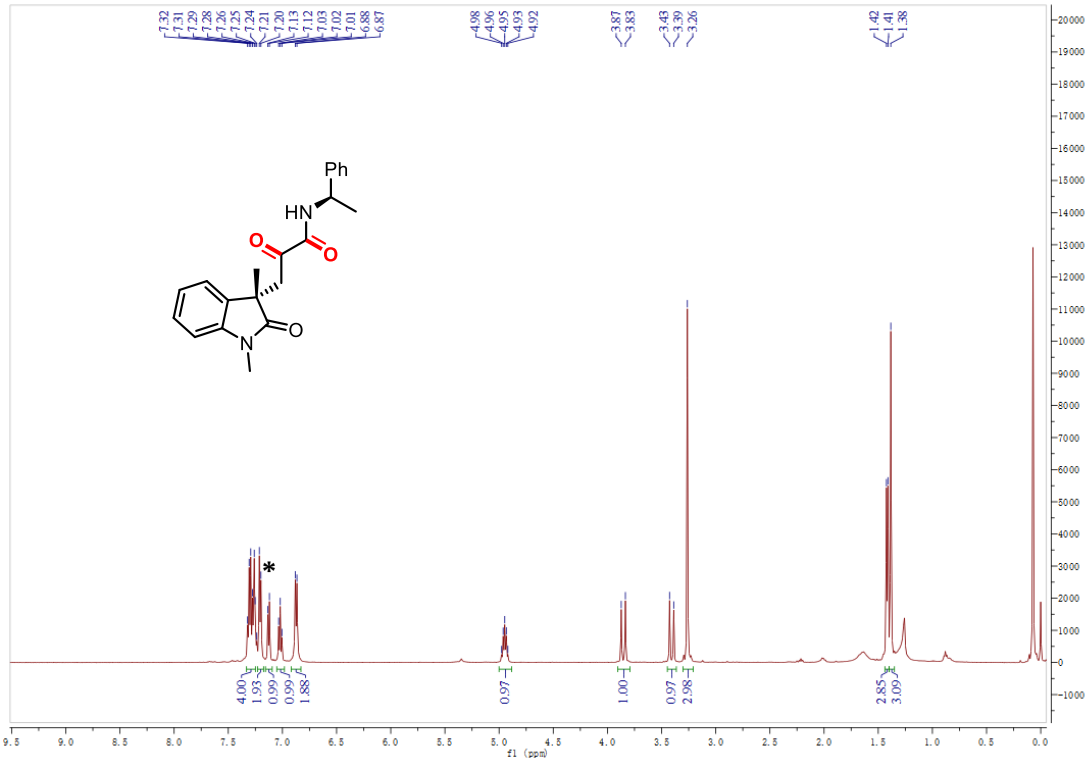
^{1}H NMR of 4ag (500 MHz, $CDCl_3$, *solvent)



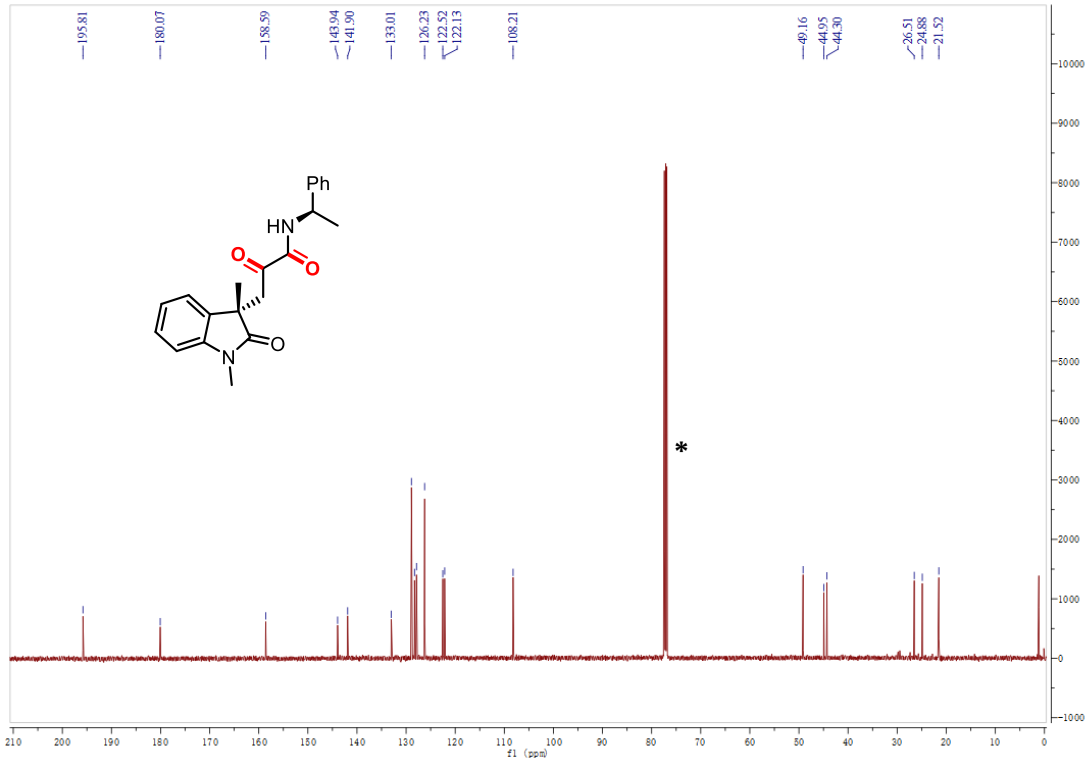
^{13}C NMR of 4ag (126 MHz, $CDCl_3$, *solvent)



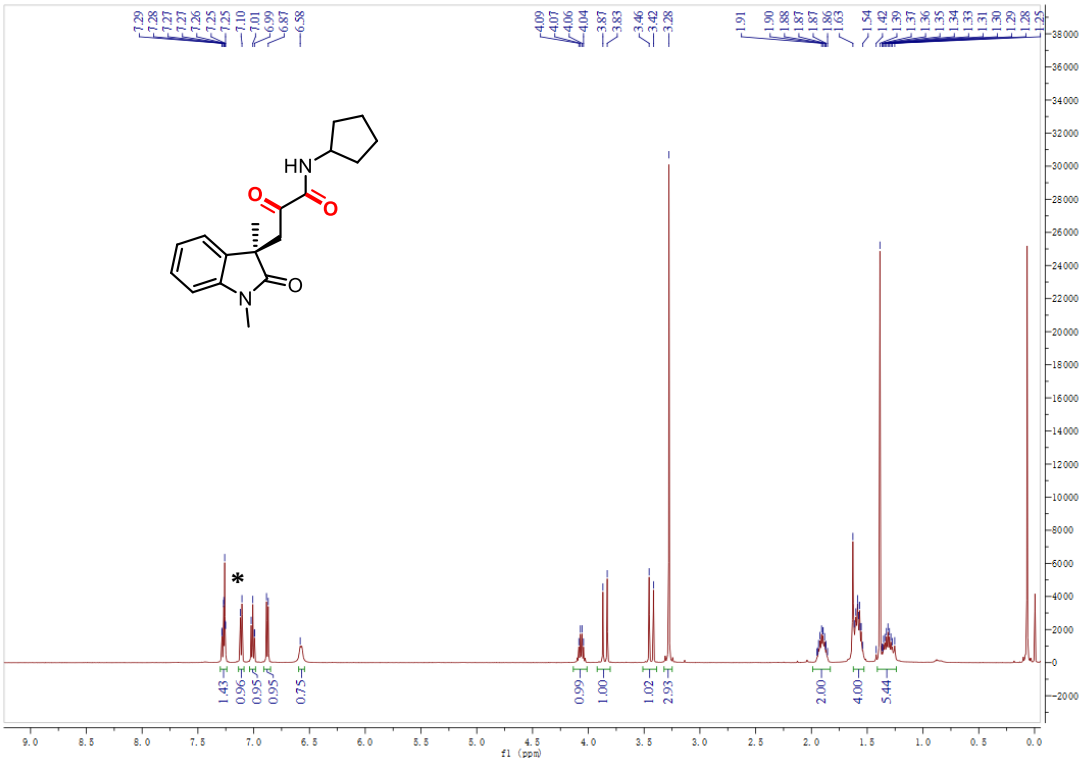
^{1}H NMR of 4ag' (500 MHz, $CDCl_3$, *solvent)



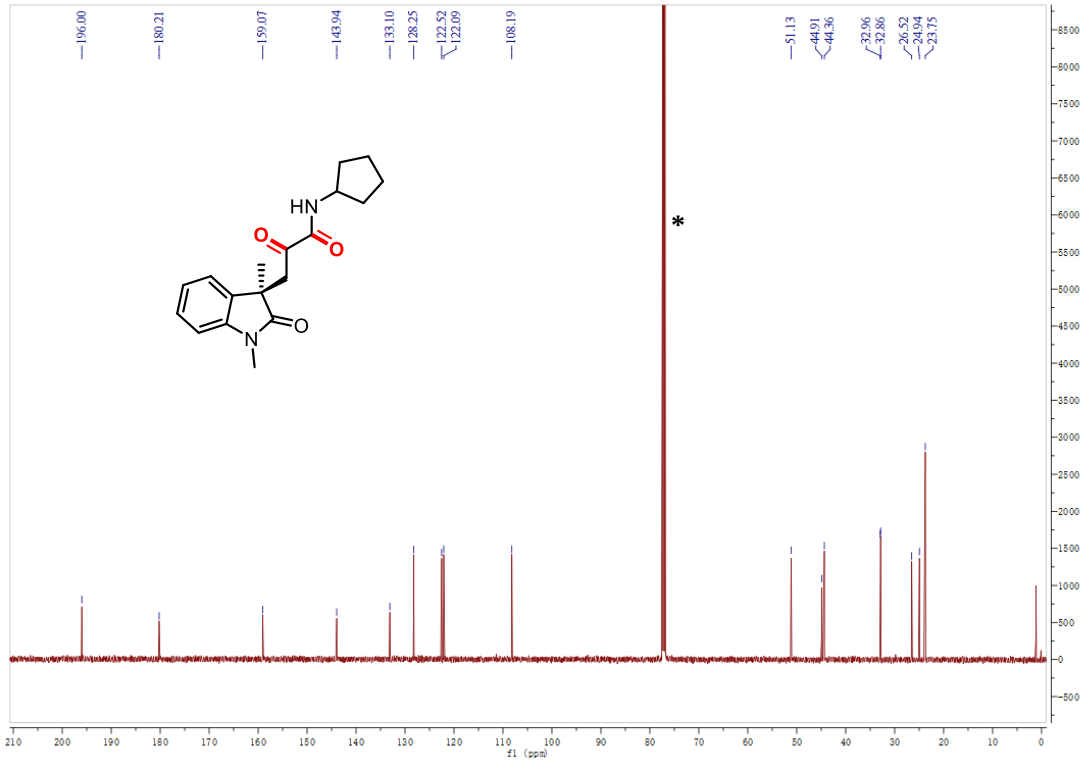
^{13}C NMR of 4ag' (126 MHz, $CDCl_3$, *solvent)



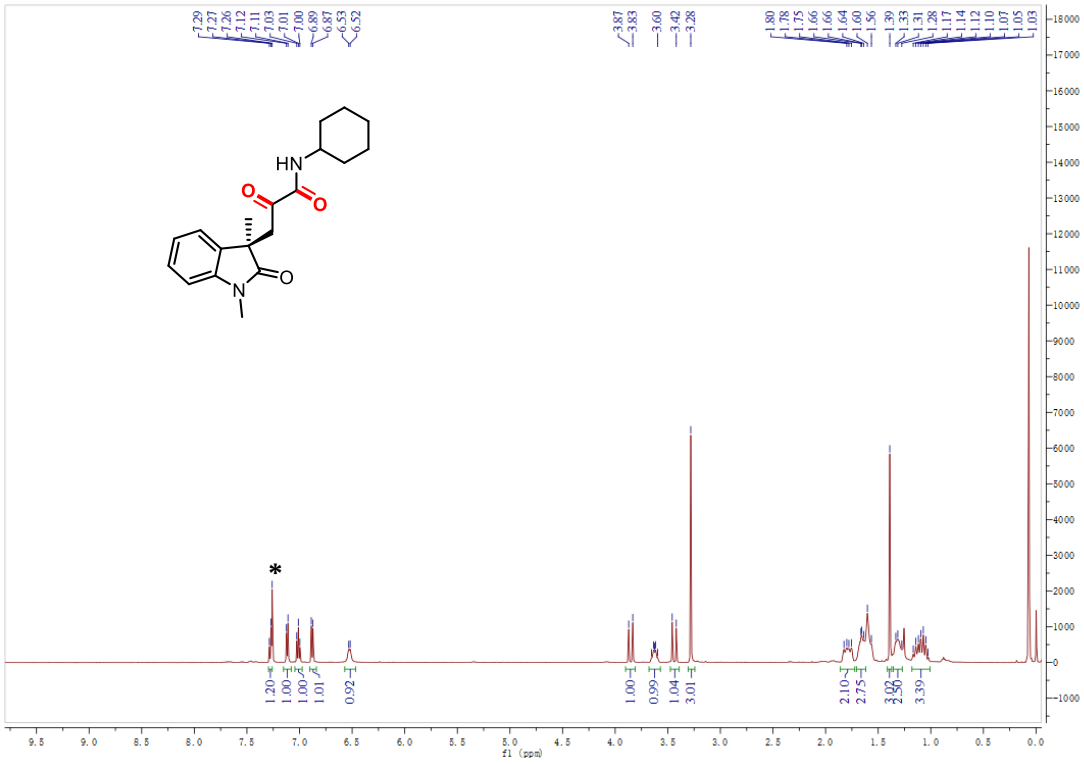
^{1}H NMR of 4ah (500 MHz, $CDCl_3$, *solvent)



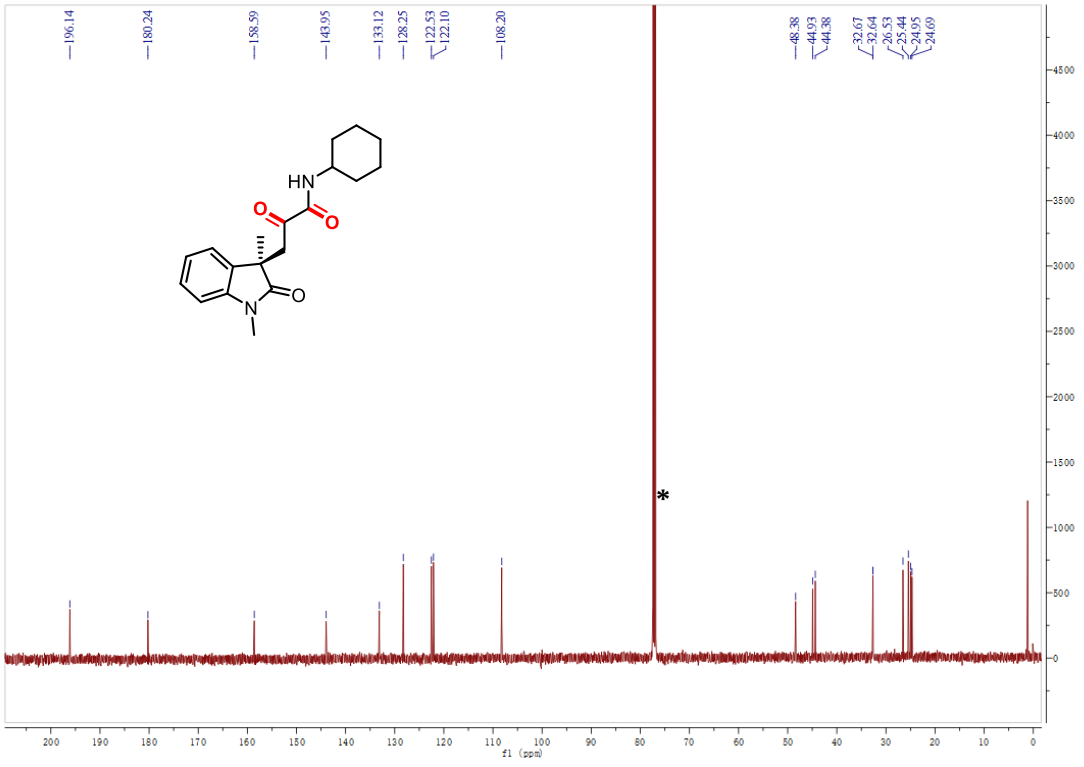
^{13}C NMR of 4ah (126 MHz, $CDCl_3$, *solvent)



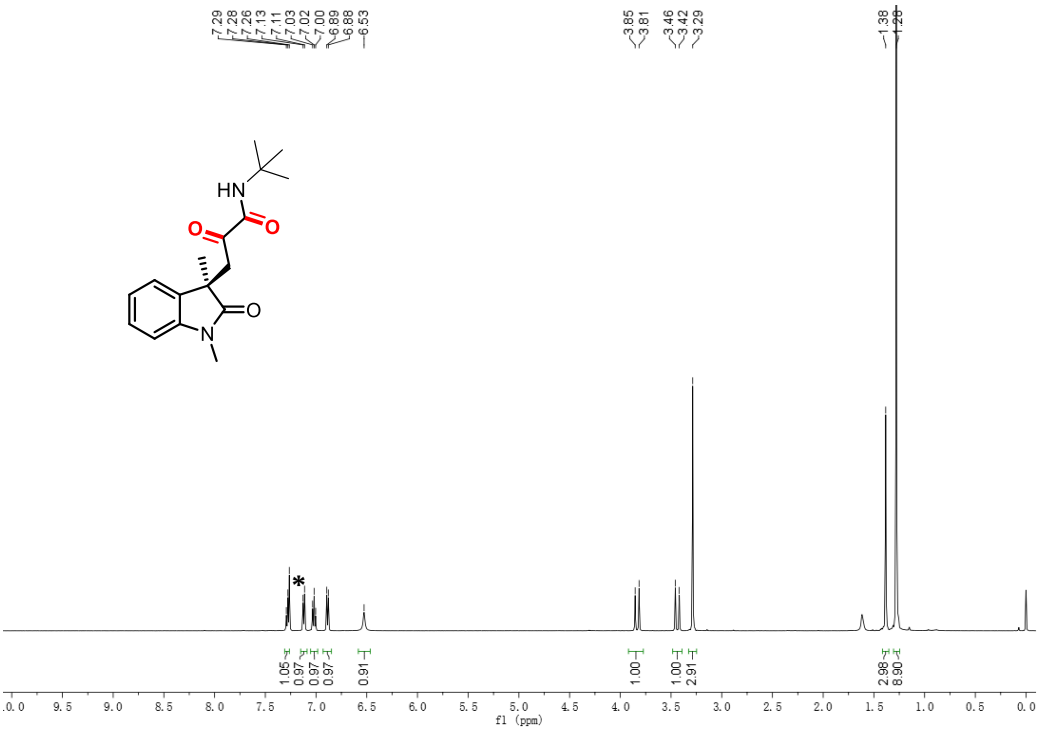
^{1}H NMR of 4ai (500 MHz, $CDCl_3$, *solvent)



^{13}C NMR of 4ai (126 MHz, $CDCl_3$, *solvent)



^{1}H NMR of 4aj (500 MHz, $CDCl_3$, *solvent)



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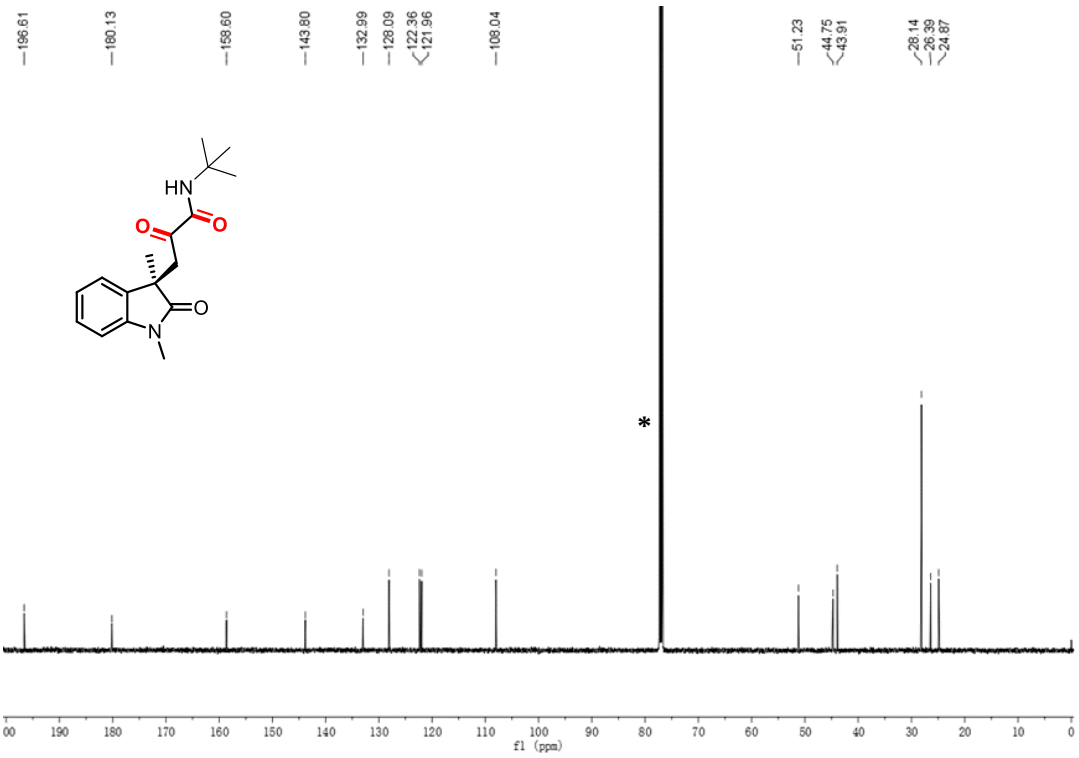
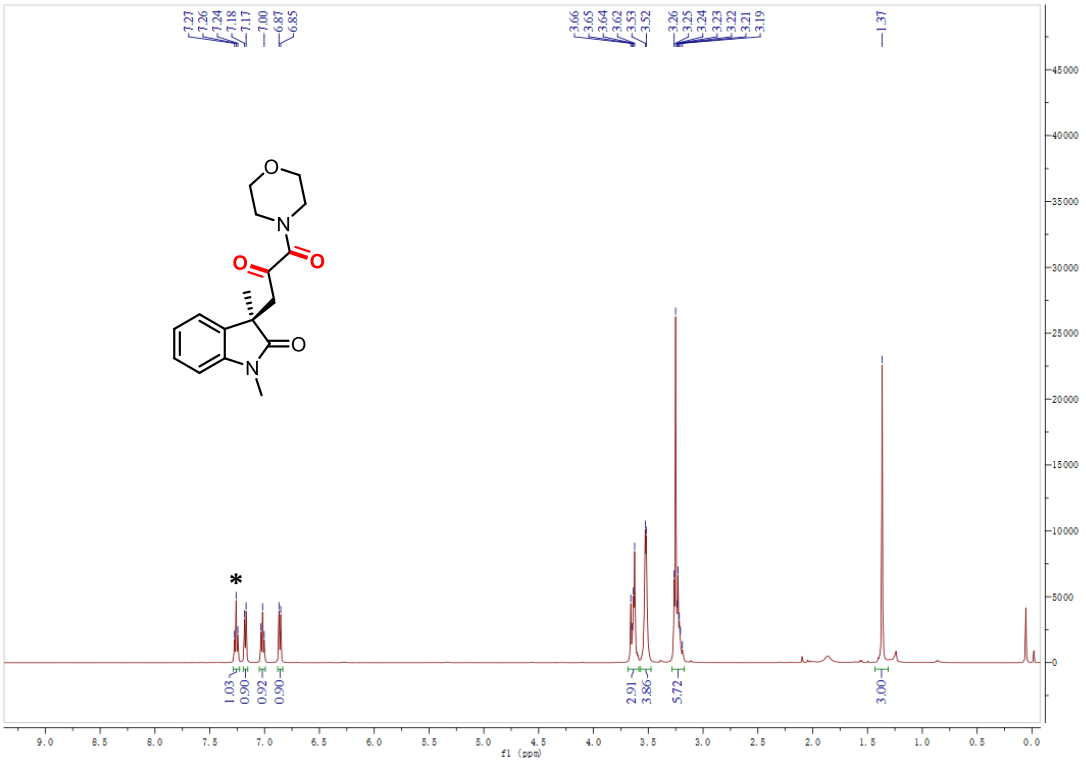
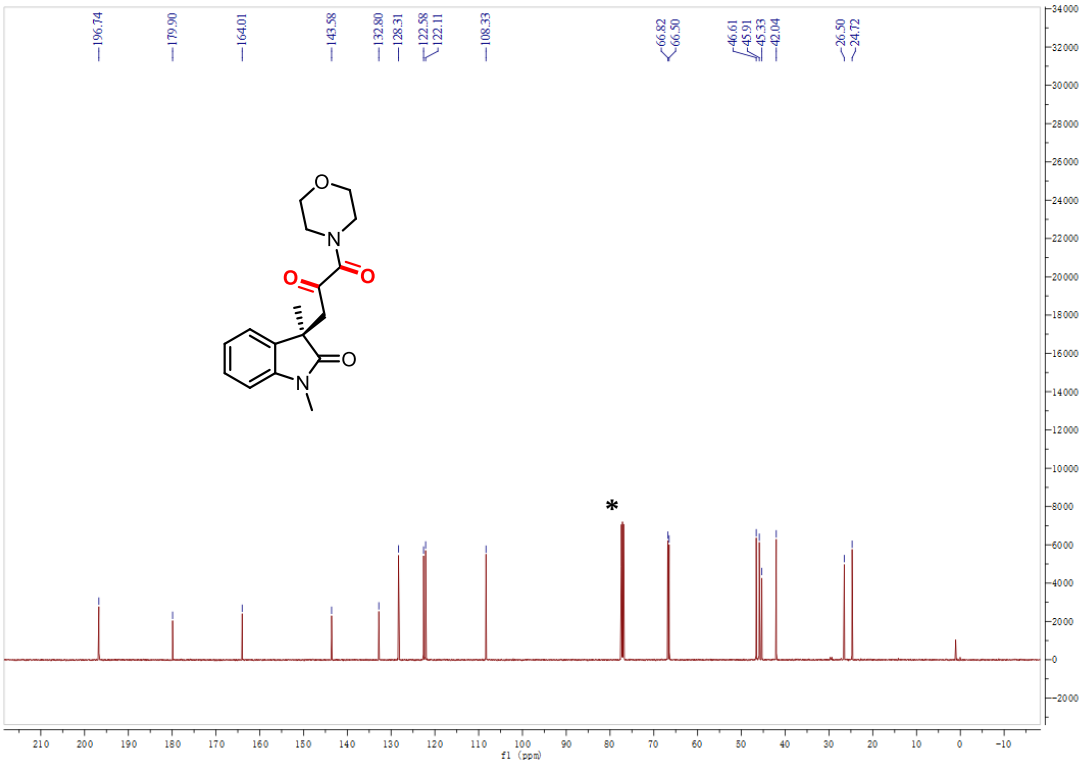


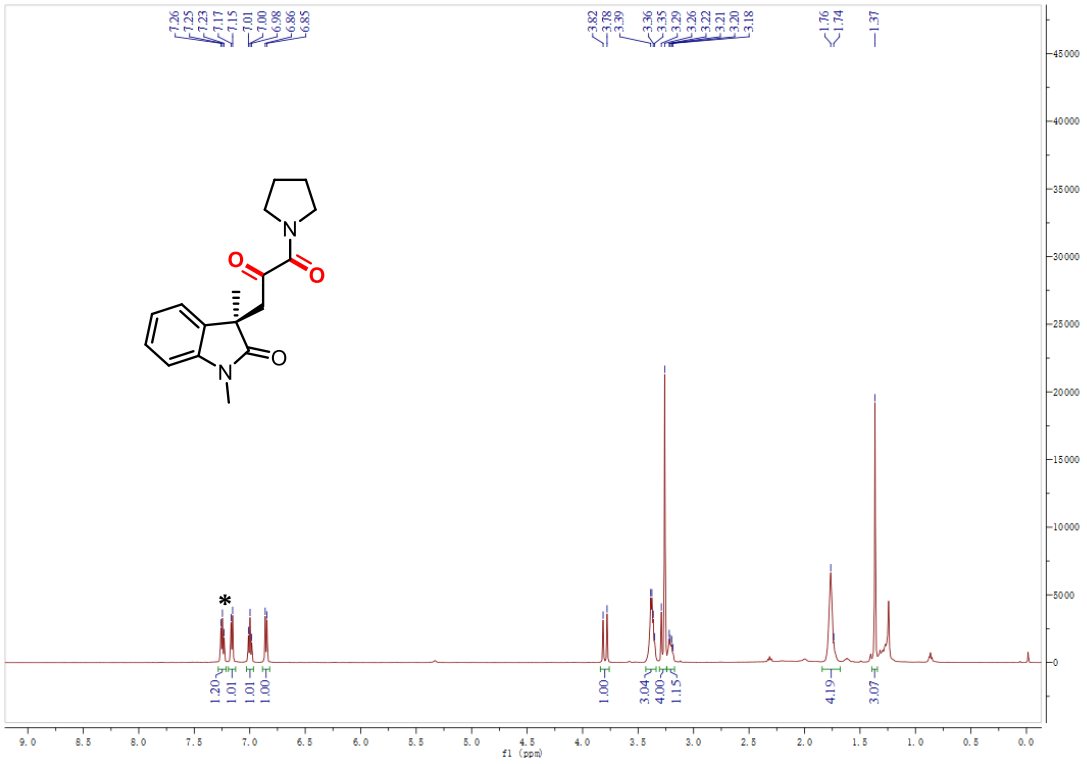
^{1}H NMR of 4ak (500 MHz, $CDCl_3$, *solvent)



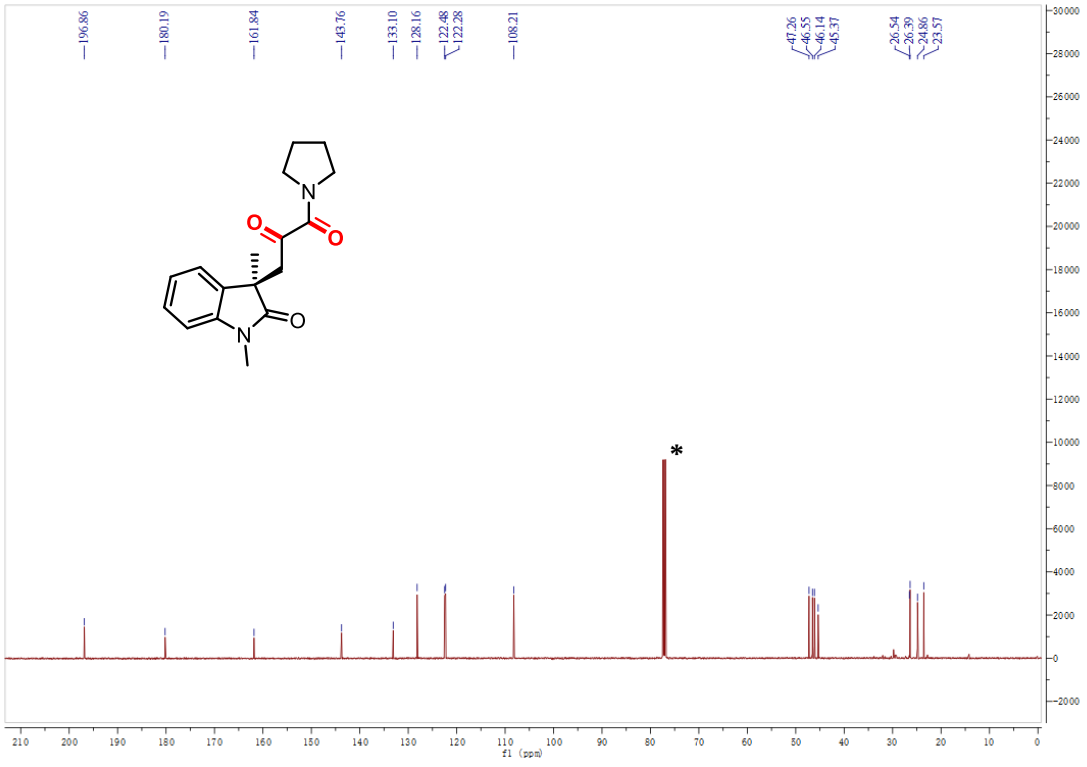
^{13}C NMR of 4ak (126 MHz, $CDCl_3$, *solvent)



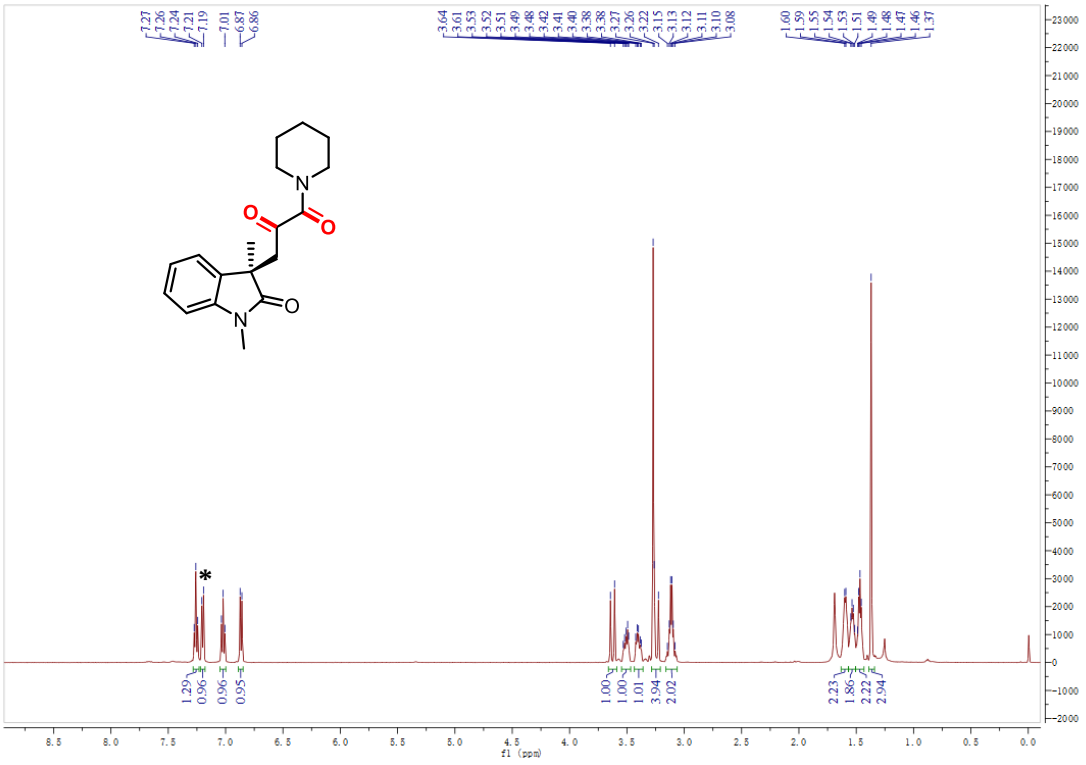
^{1}H NMR of 4al (500 MHz, $CDCl_3$, *solvent)



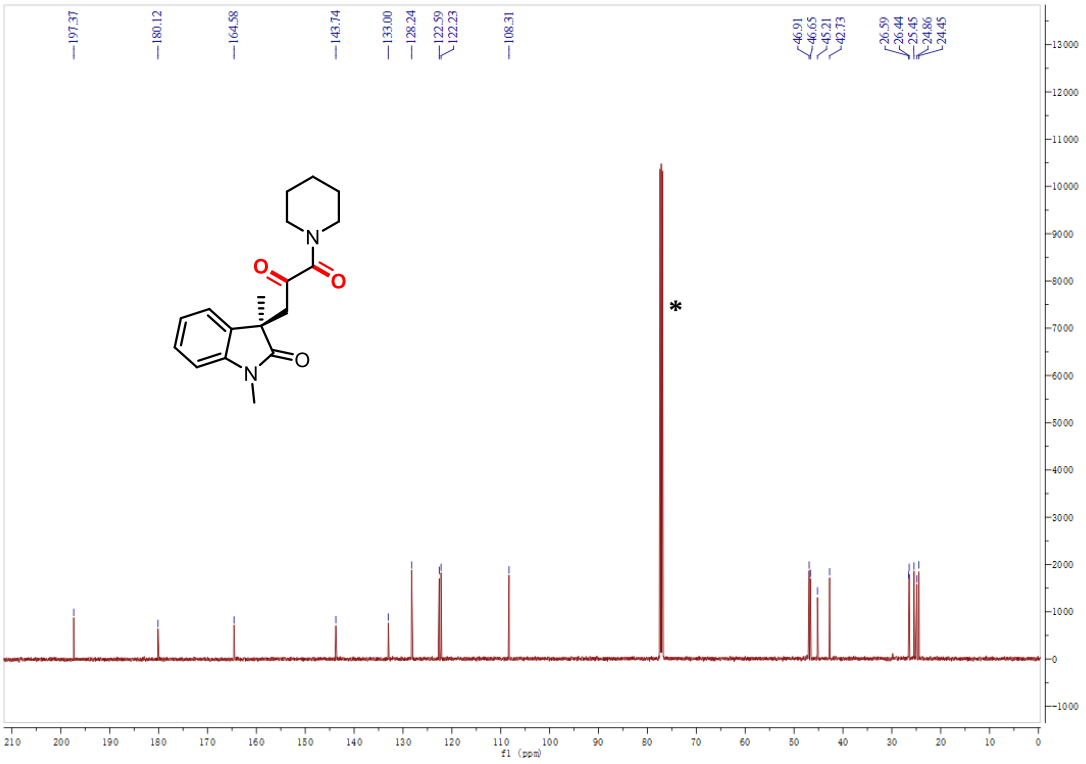
^{13}C NMR of 4al (126 MHz, $CDCl_3$, *solvent)



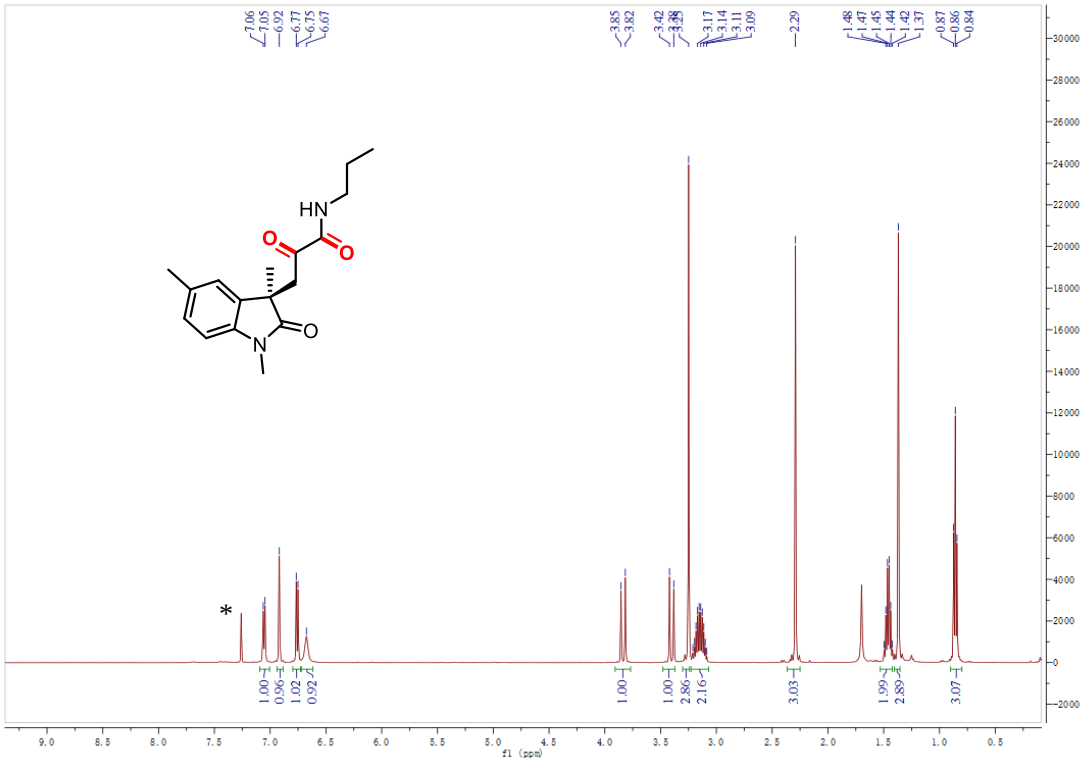
^{1}H NMR of 4am (500 MHz, $CDCl_3$, *solvent)



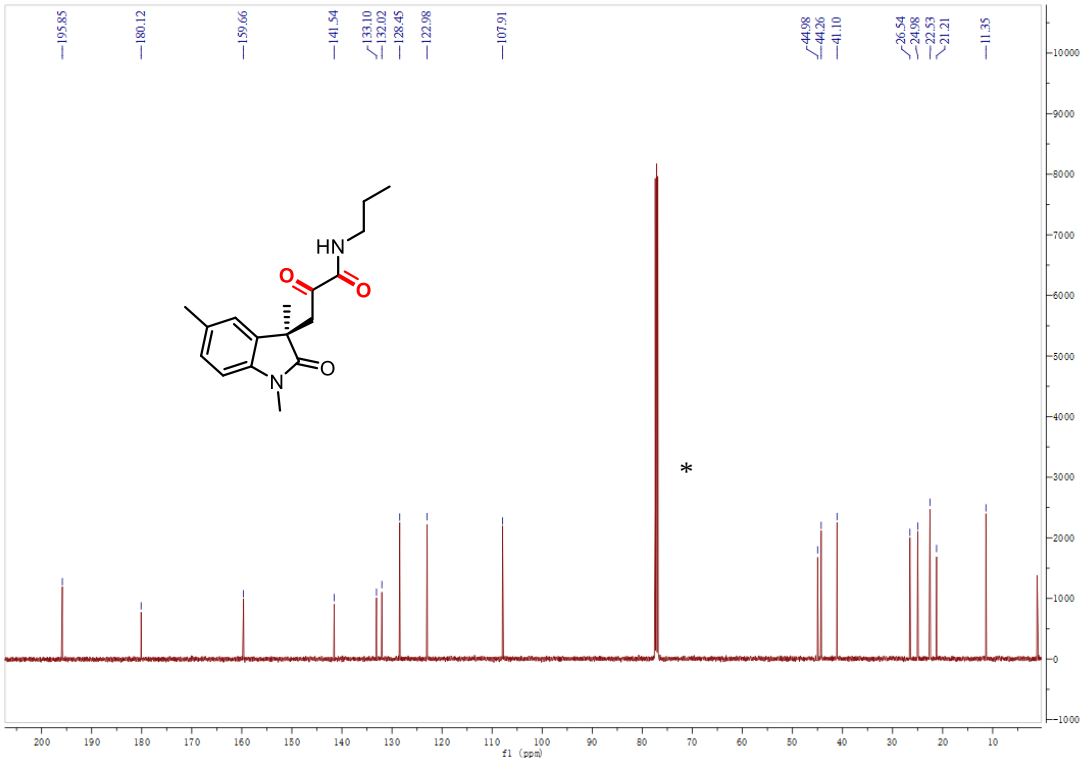
^{13}C NMR of 4am (126 MHz, $CDCl_3$, *solvent)



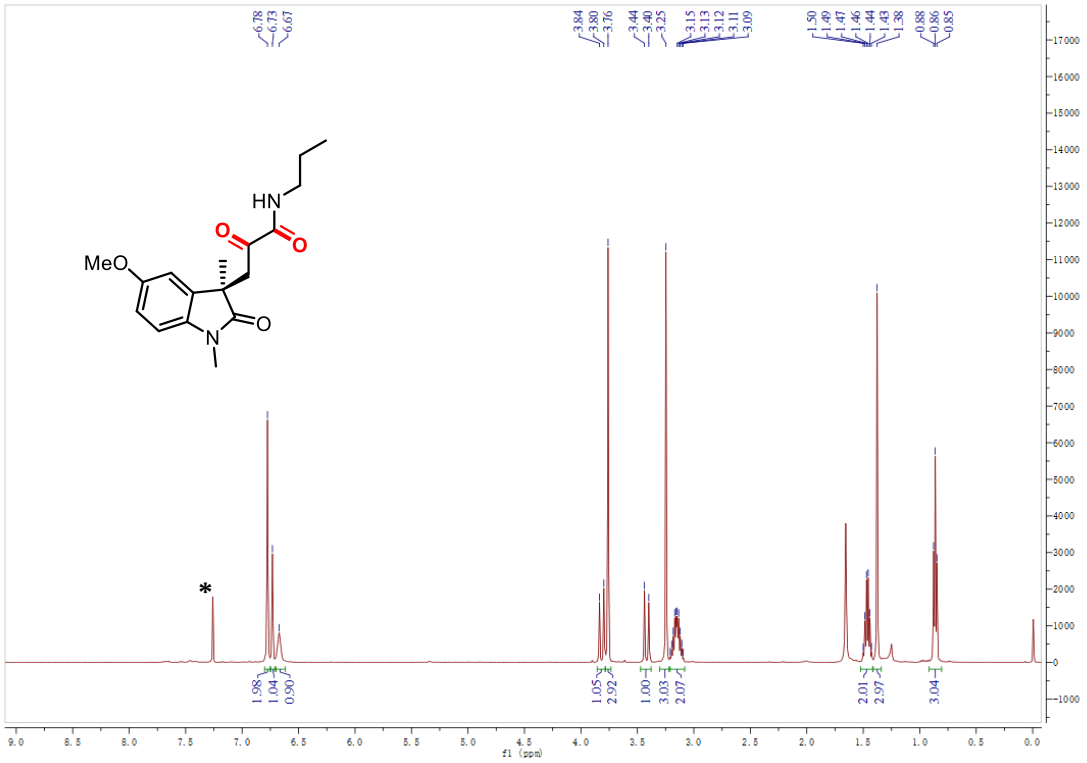
^{1}H NMR of 4ba (500 MHz, $CDCl_3$, *solvent)



^{13}C NMR of 4ba (126 MHz, $CDCl_3$, *solvent)



^{1}H NMR of 4ca (500 MHz, $CDCl_3$, *solvent)



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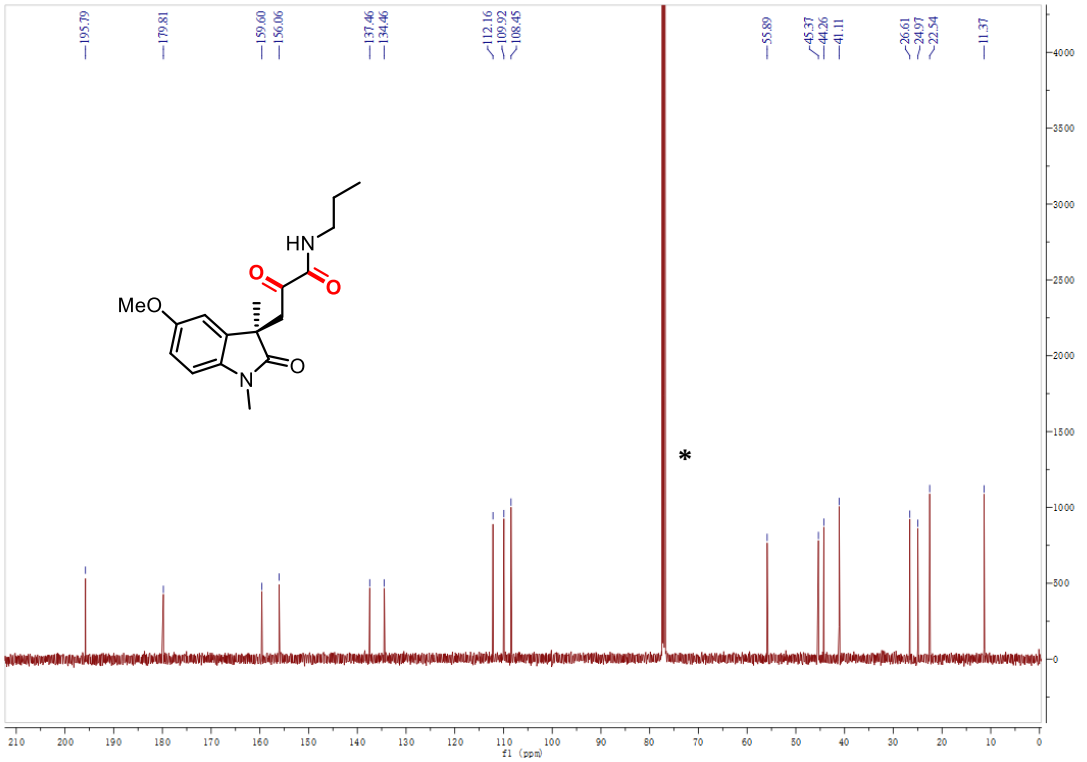
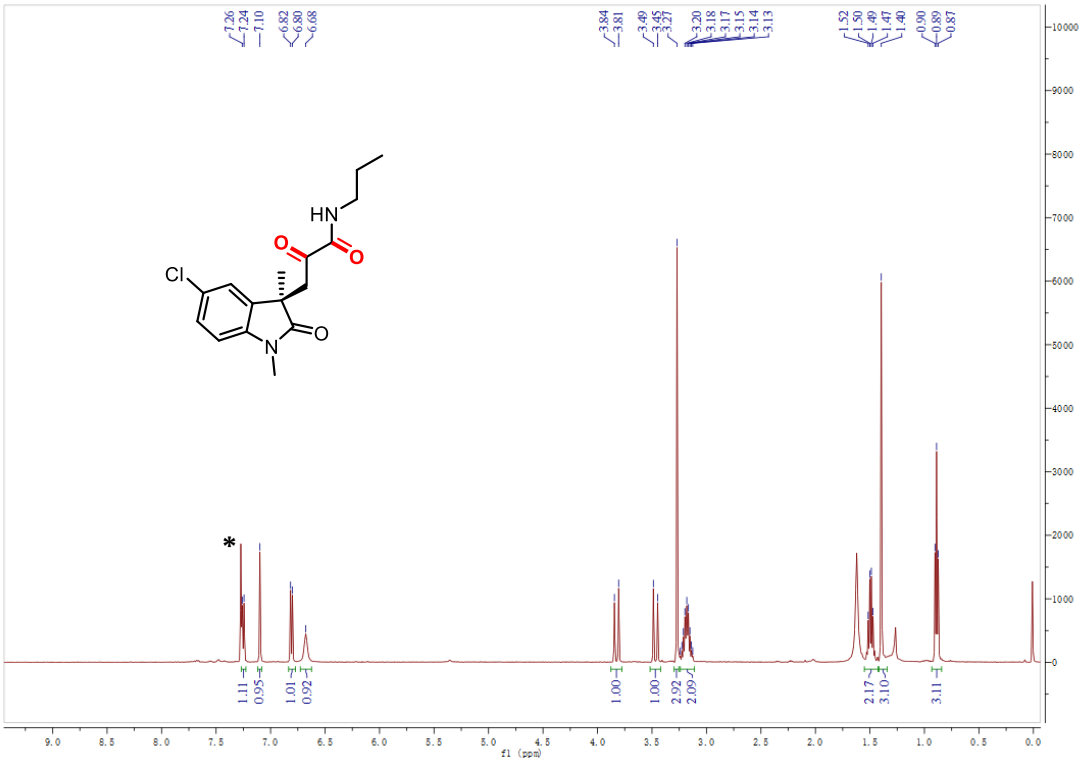
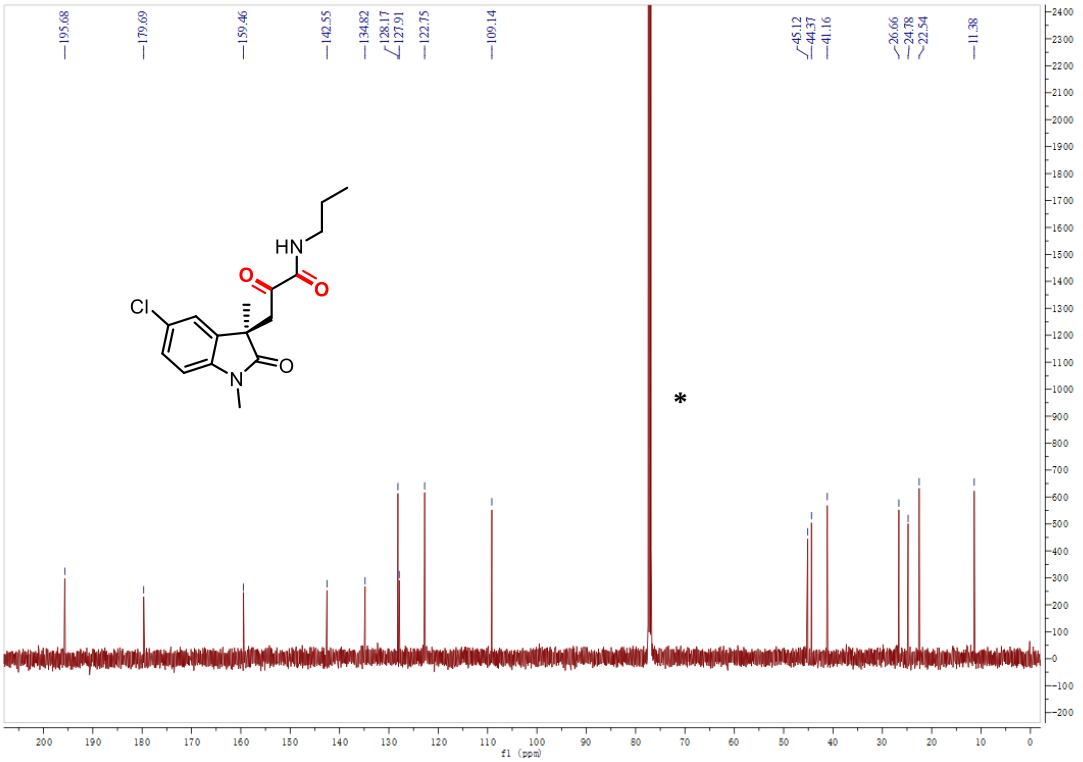


^{1}H NMR of 4da (500 MHz, $CDCl_3$, *solvent)



^{13}C NMR of 4da (126 MHz, $CDCl_3$, *solvent)



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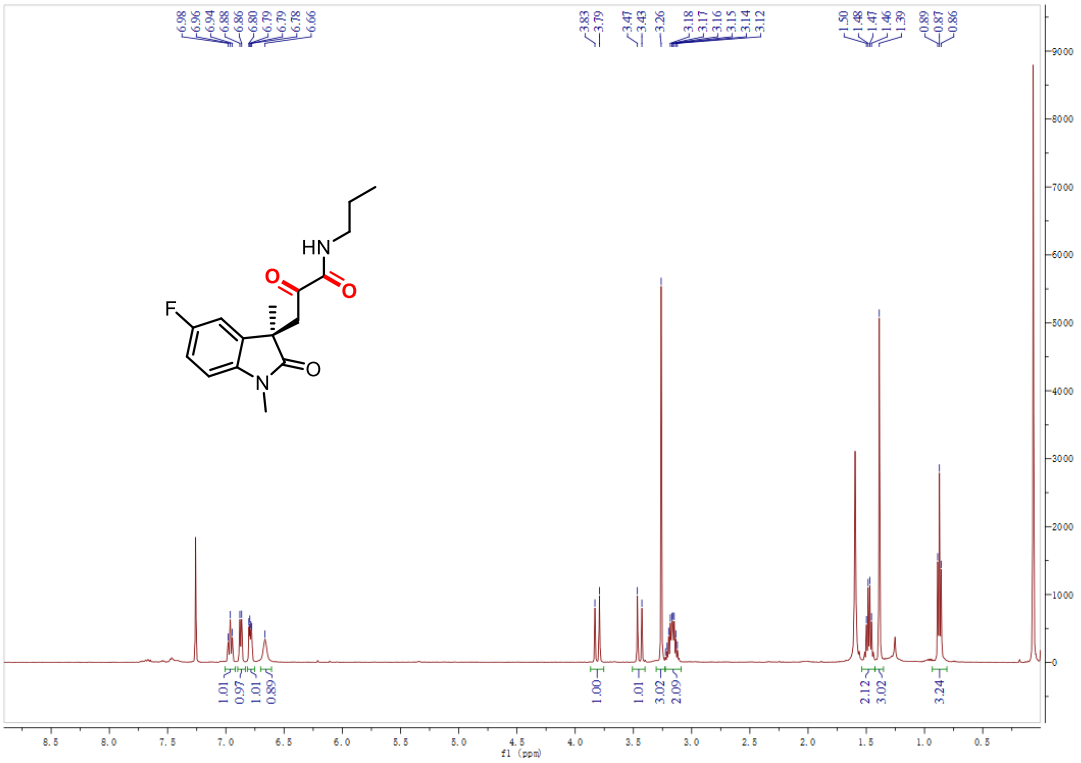

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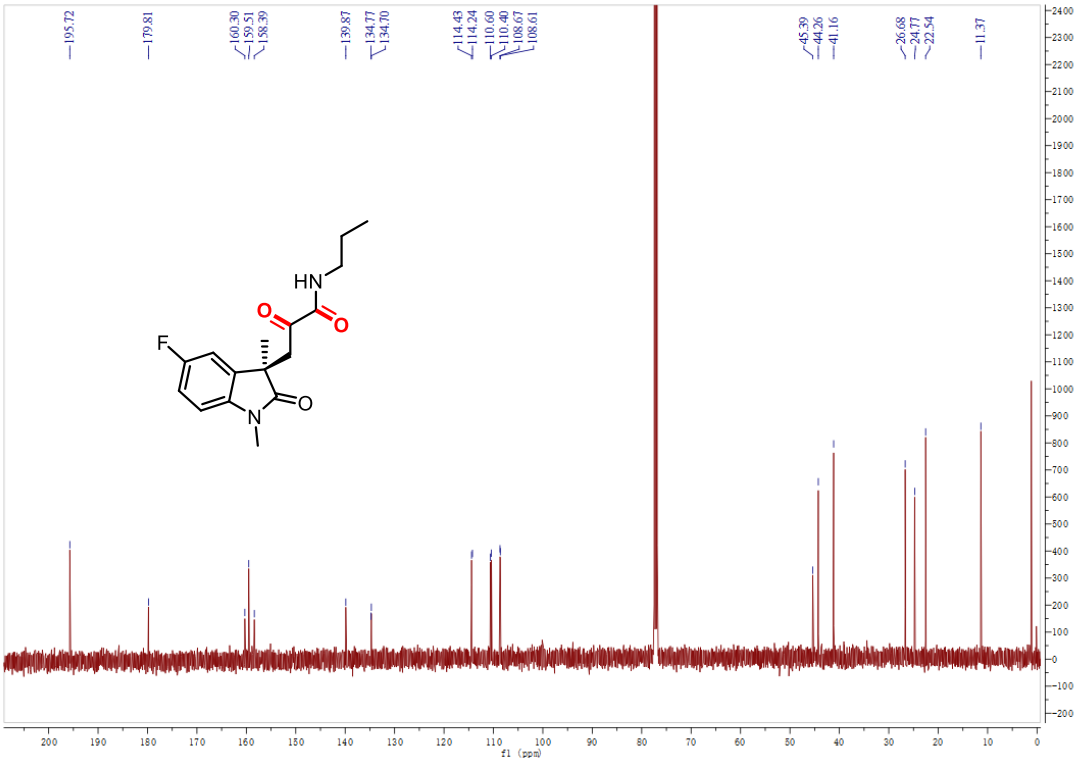
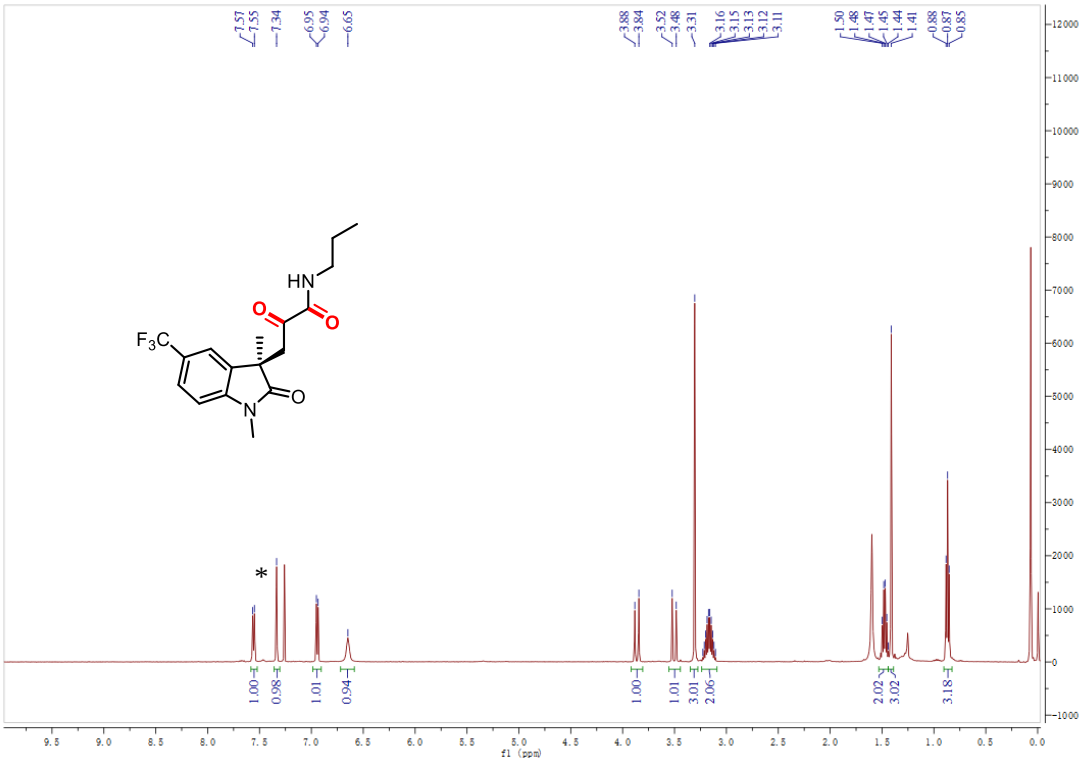
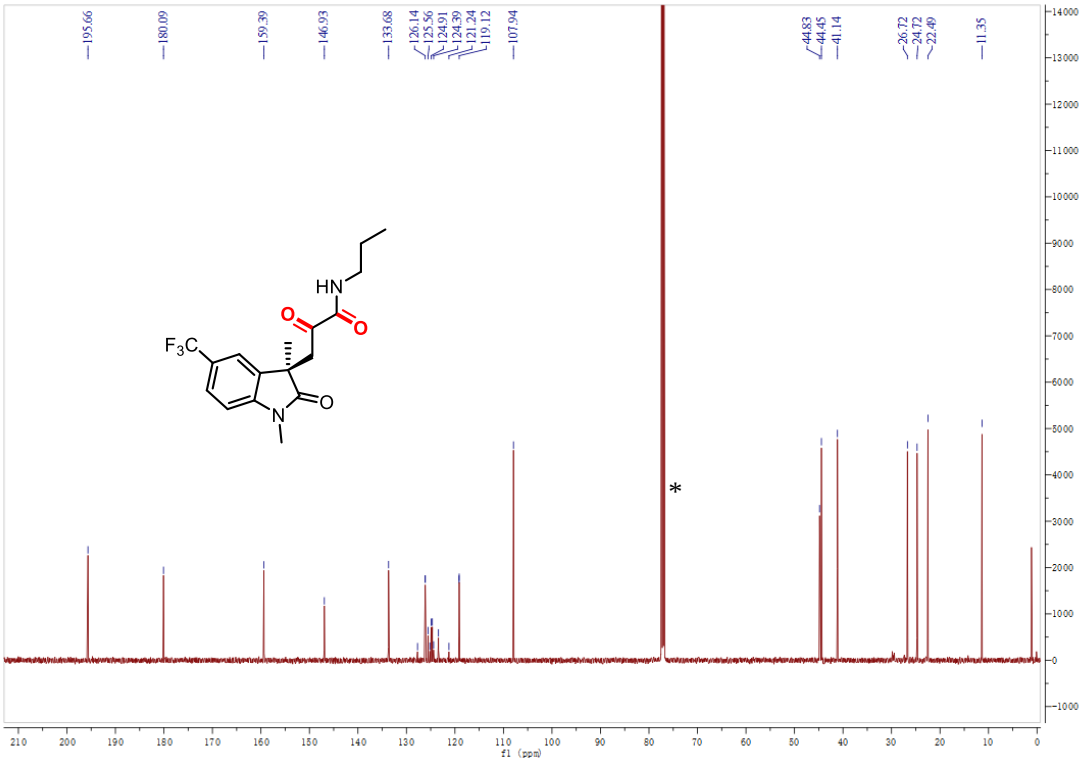


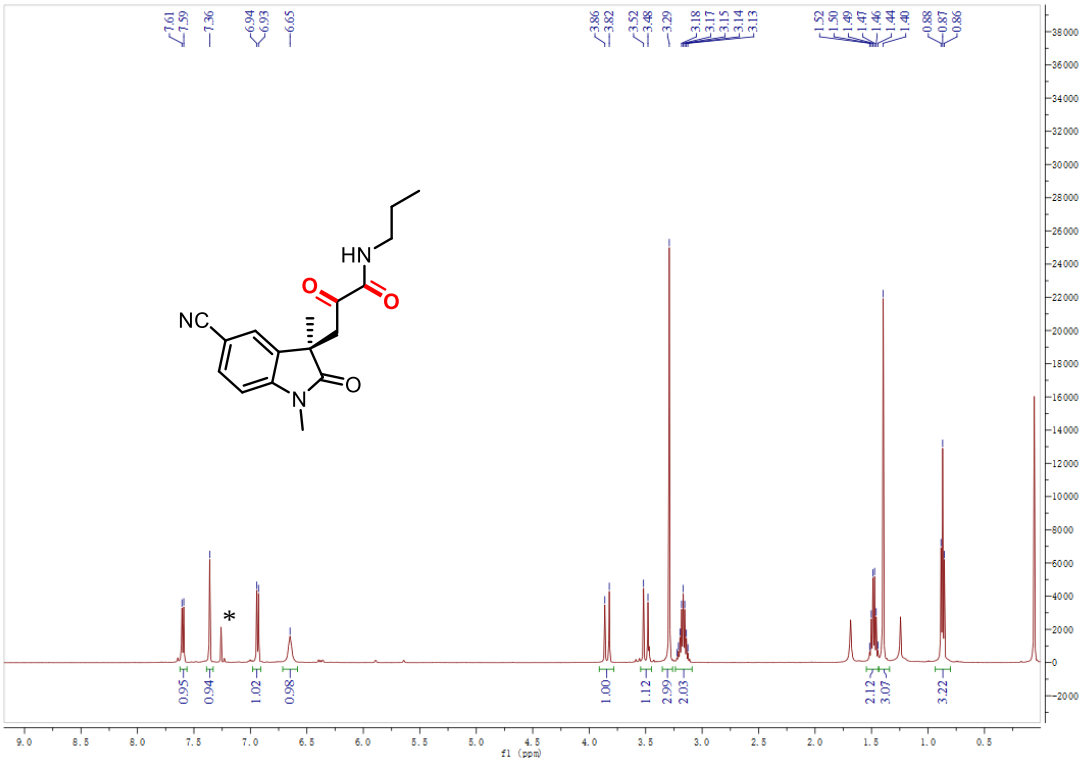
^{1}H NMR of 4fa (500 MHz, $CDCl_3$, *solvent)



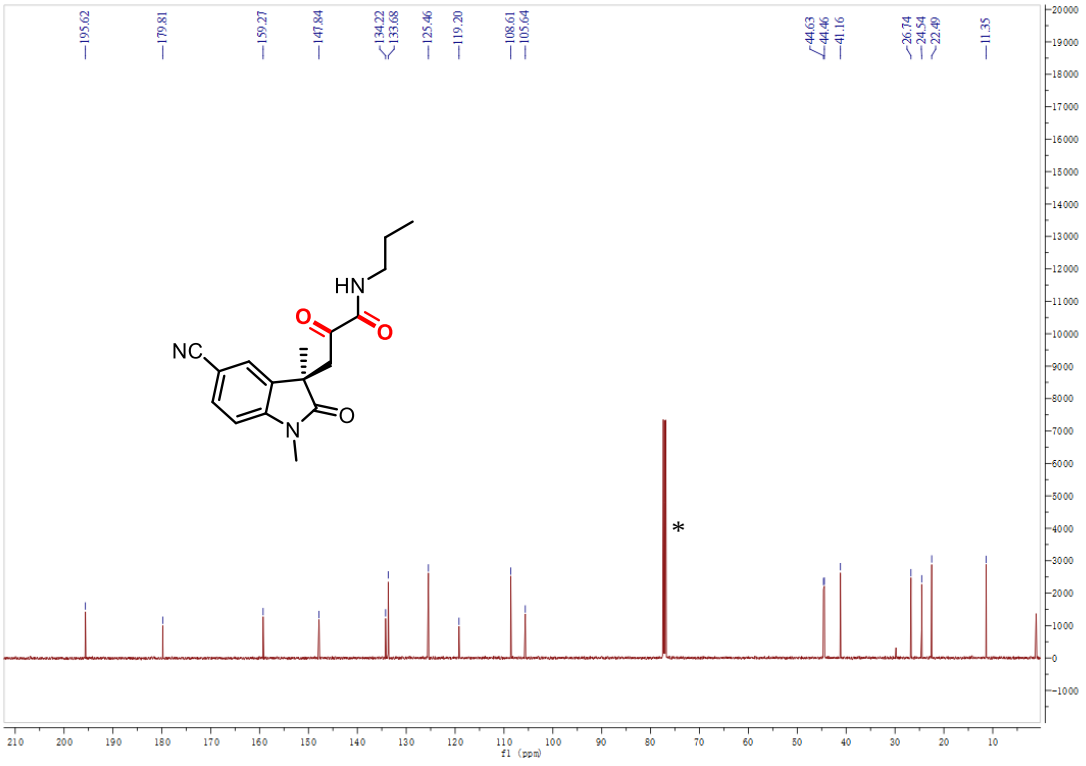
^{13}C NMR of 4fa (126 MHz, $CDCl_3$, *solvent)



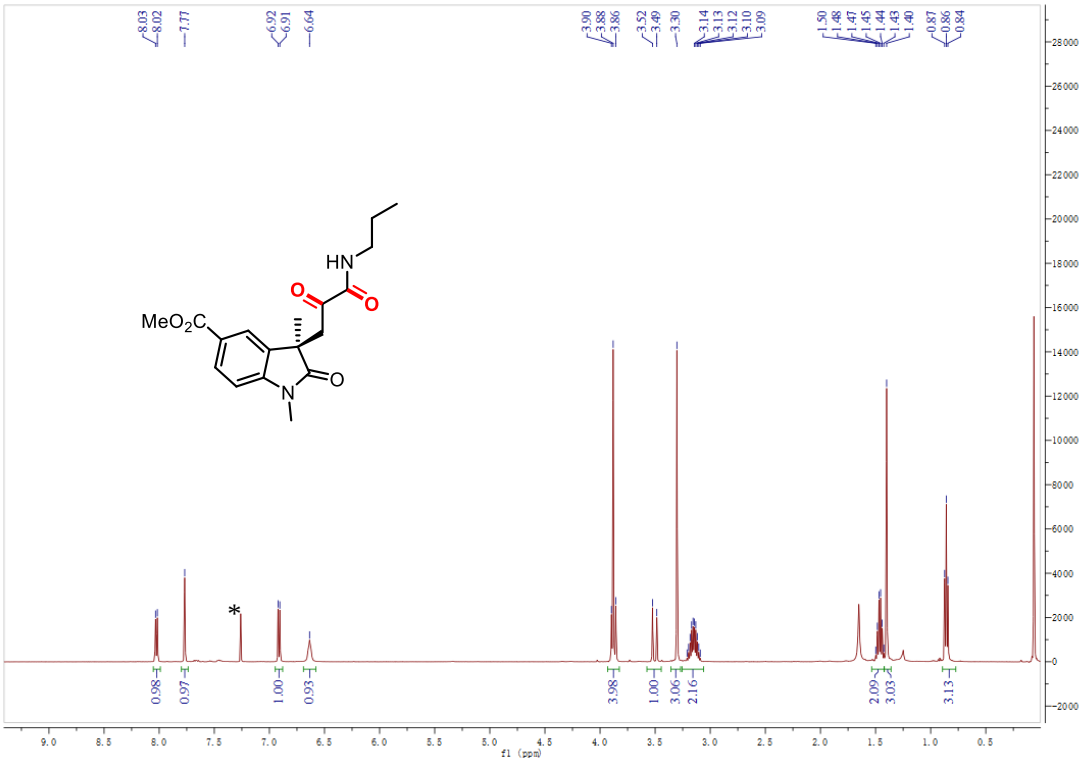
^{1}H NMR of 4ga (500 MHz, $CDCl_3$, *solvent)



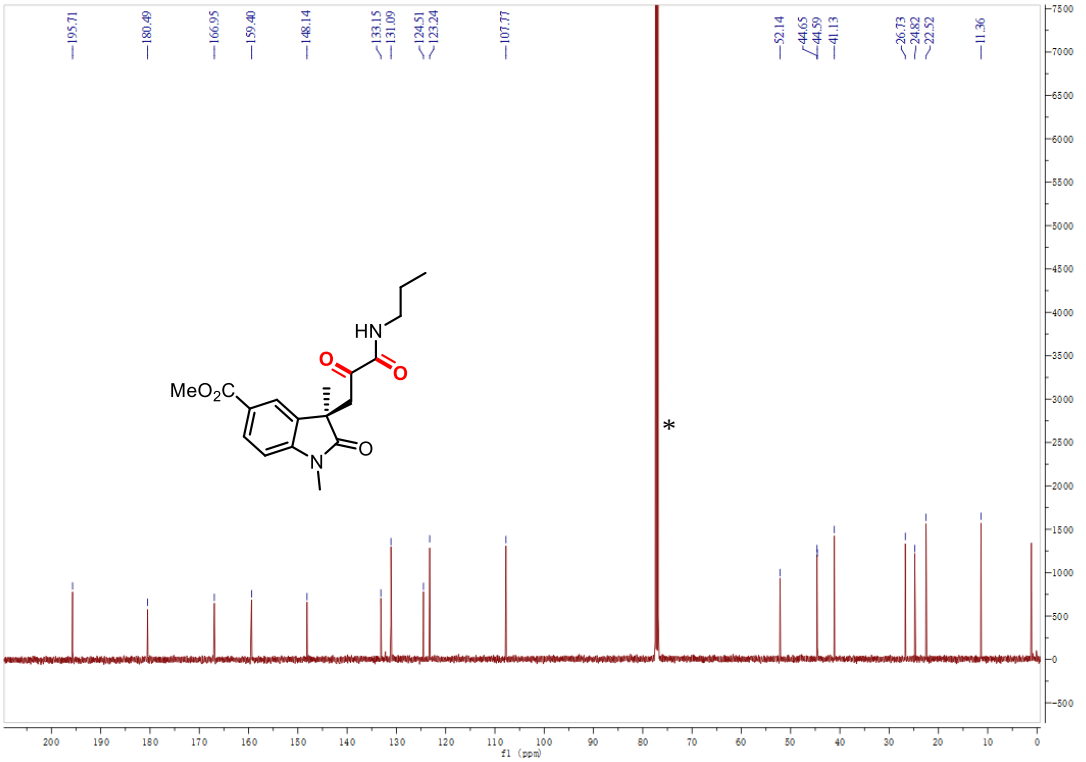
^{13}C NMR of 4ga (126 MHz, $CDCl_3$, *solvent)



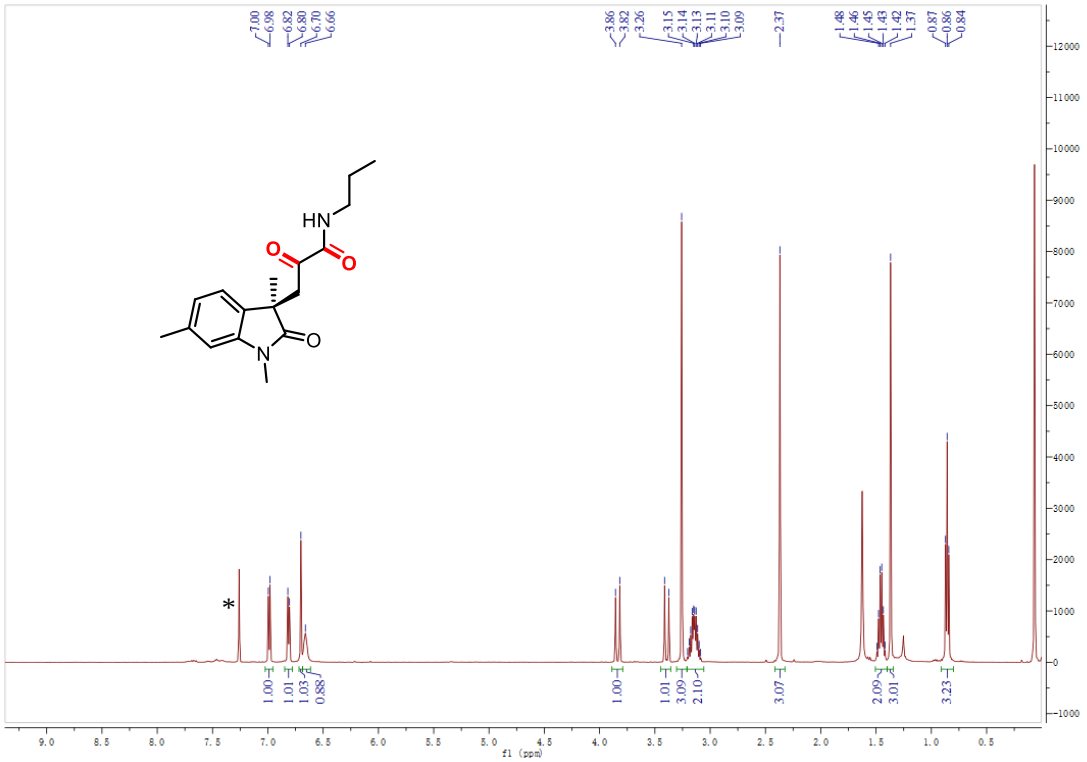
^{1}H NMR of 4ha (500 MHz, $CDCl_3$, *solvent)



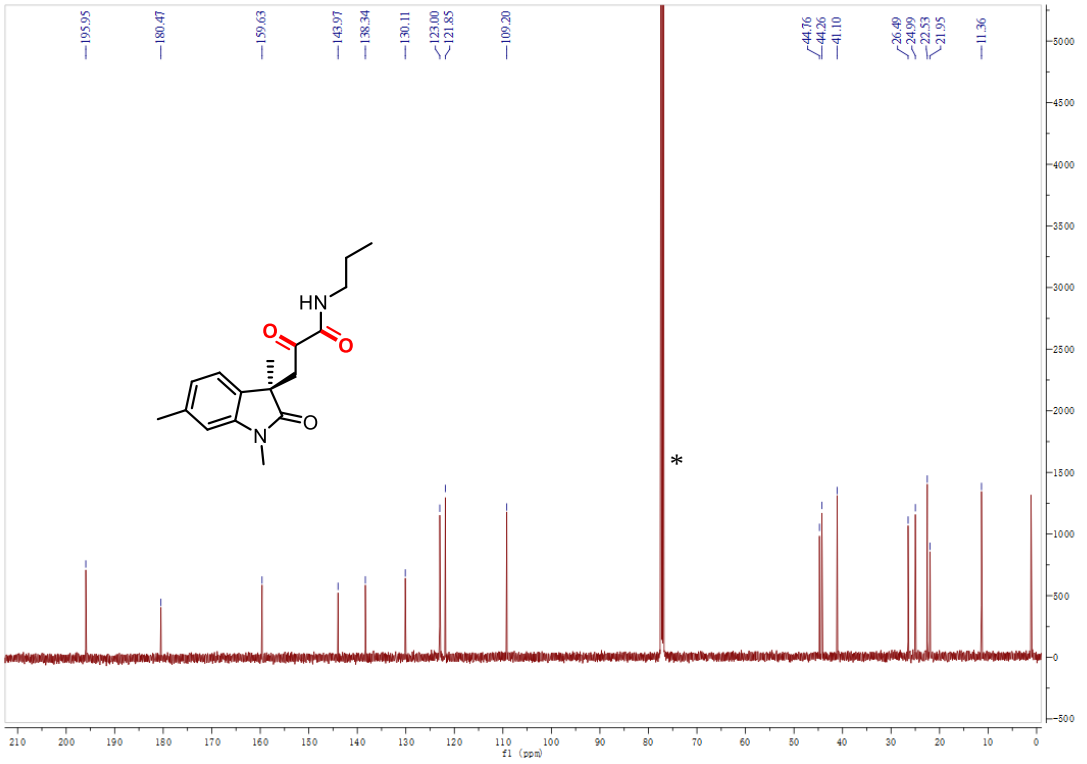
^{13}C NMR of 4ha (126 MHz, $CDCl_3$, *solvent)



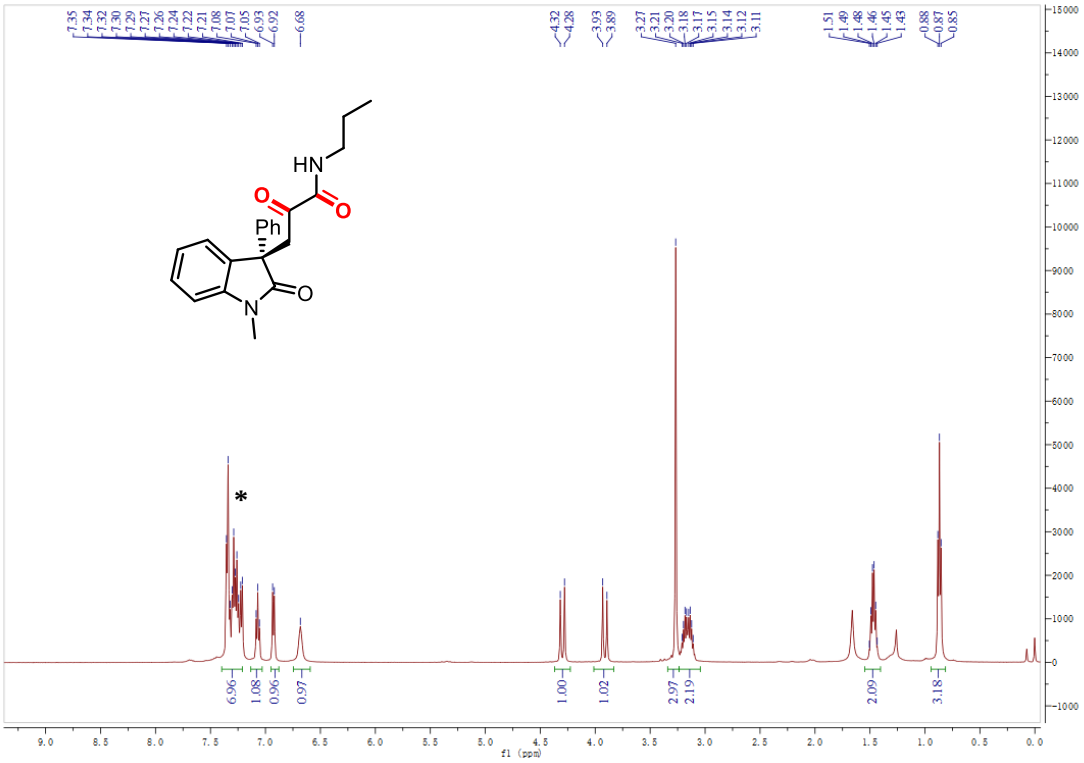
^{1}H NMR of 4ia (500 MHz, $CDCl_3$, *solvent)



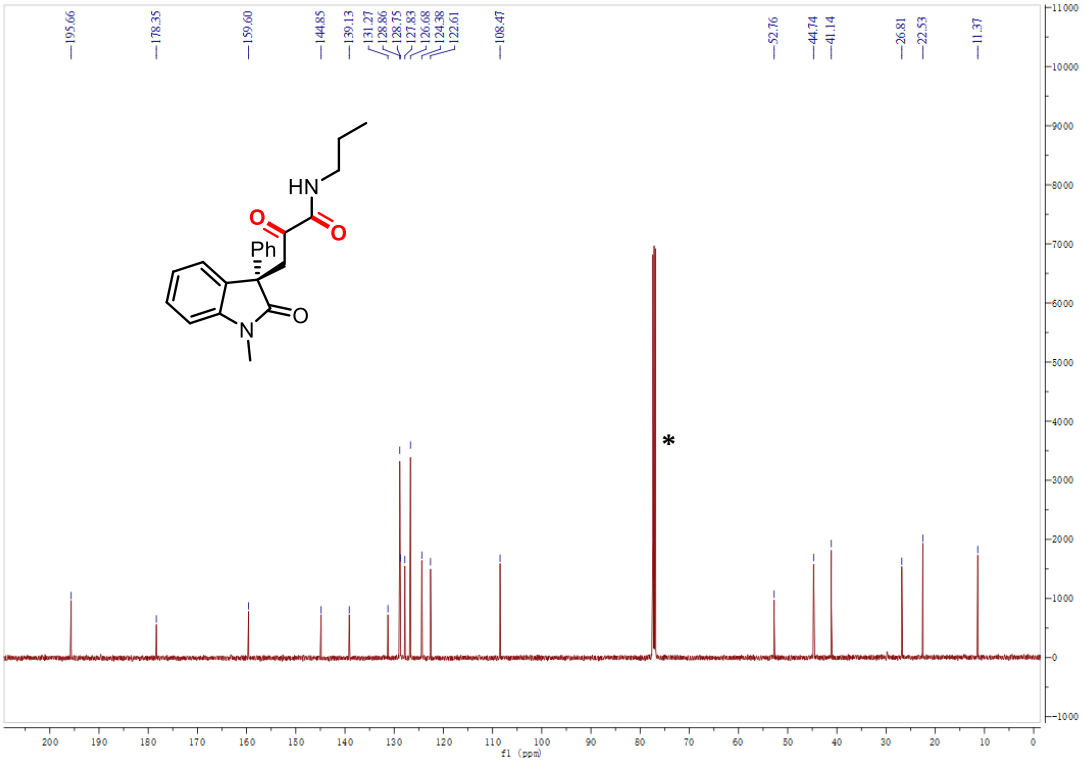
^{13}C NMR of 4ia (126 MHz, $CDCl_3$, *solvent)



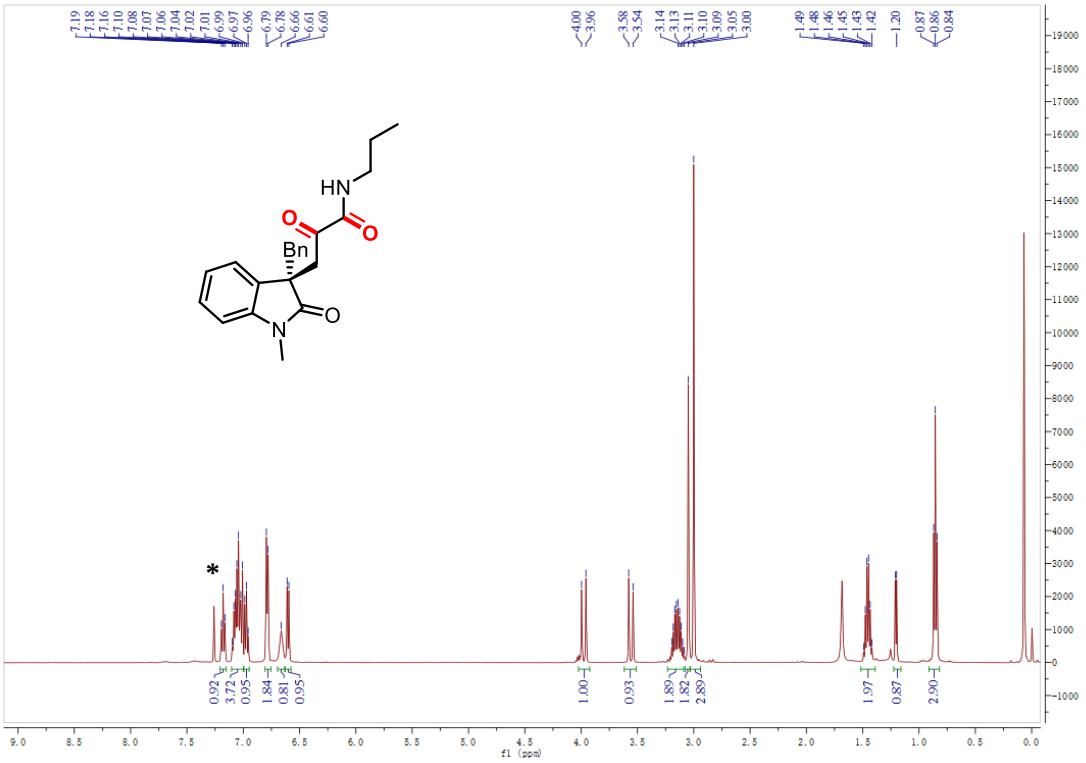
^{1}H NMR of 4ja (500 MHz, $CDCl_3$, *solvent)



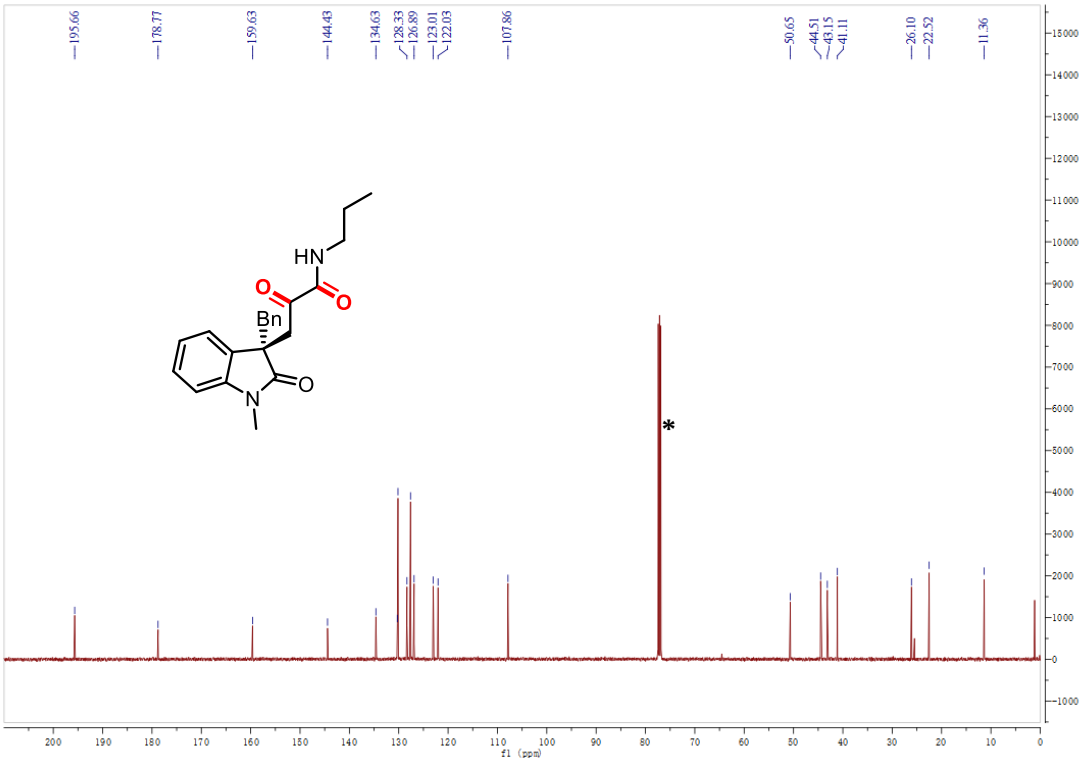
^{13}C NMR of 4ja (126 MHz, $CDCl_3$, *solvent)



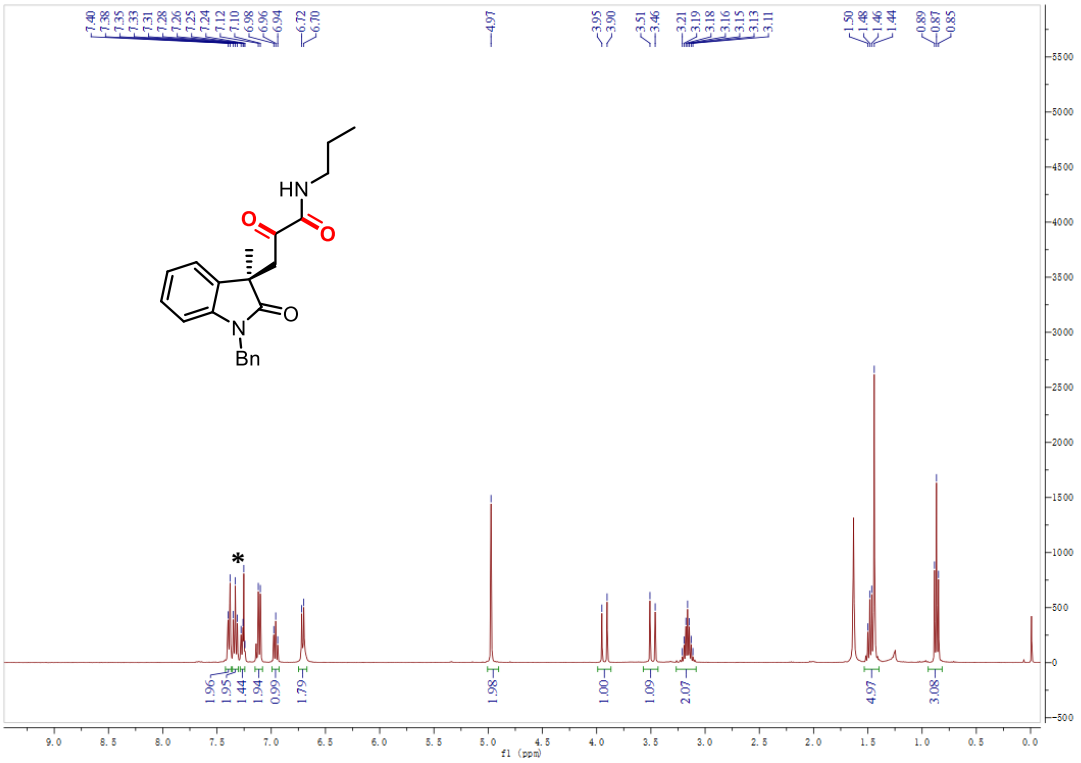
^{1}H NMR of 4ka (500 MHz, $CDCl_3$, *solvent)



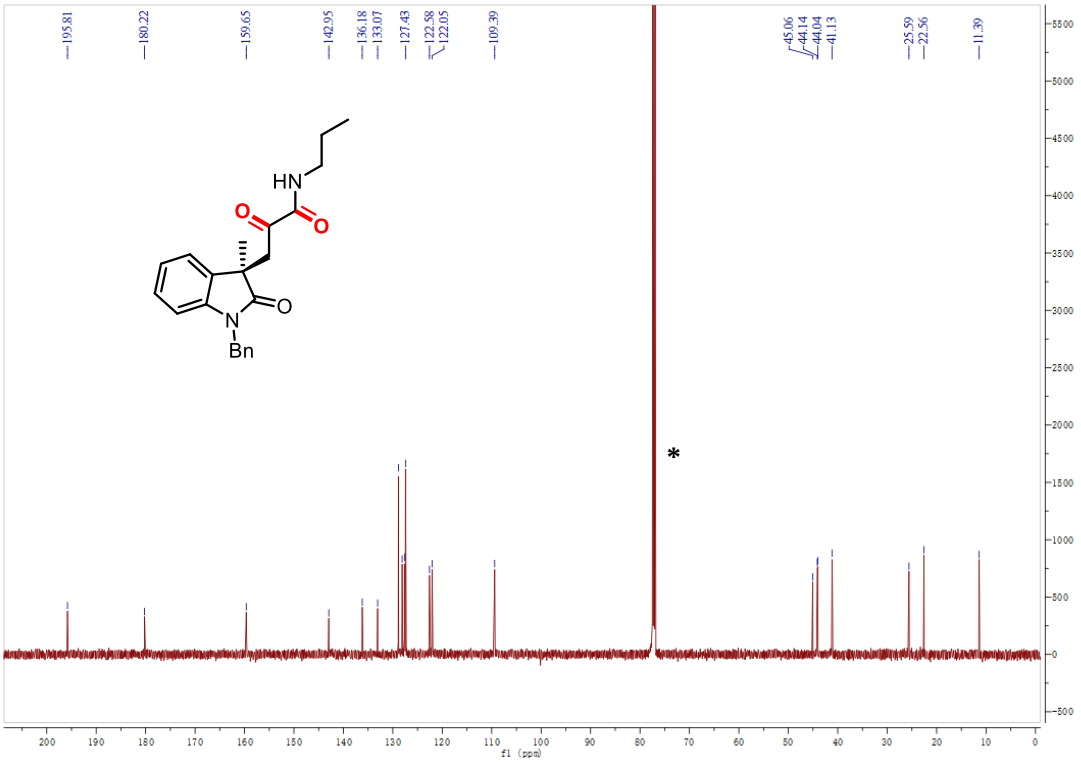
^{13}C NMR of 4ka (126 MHz, $CDCl_3$, *solvent)



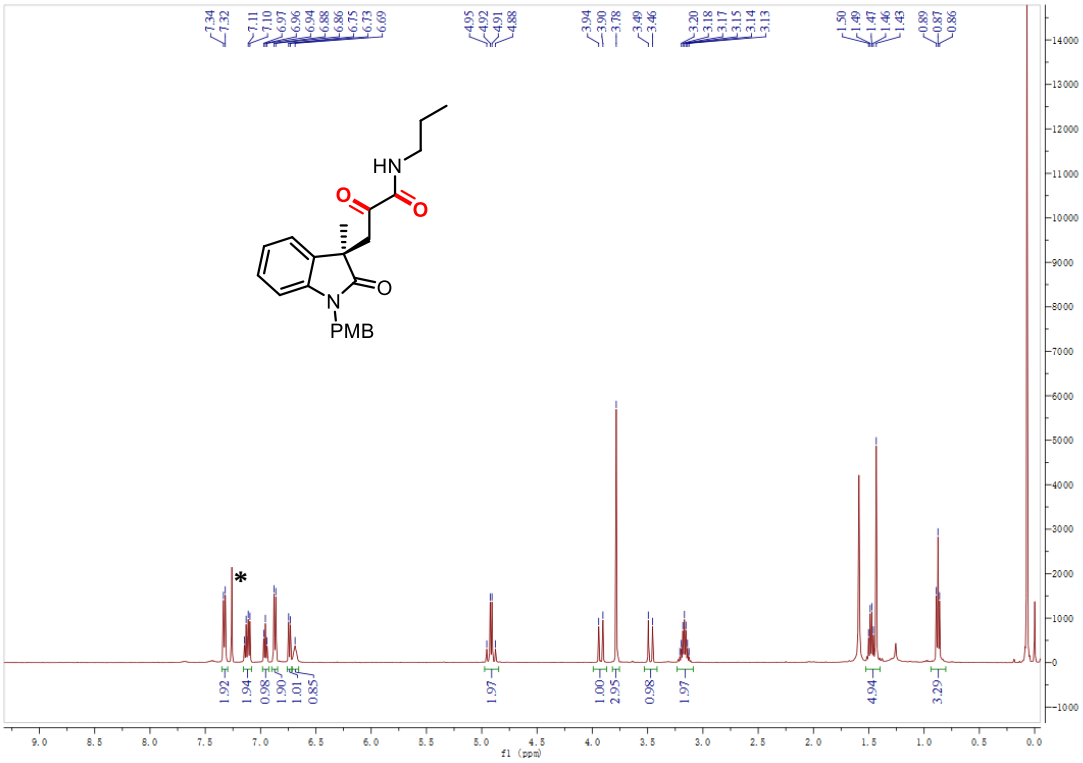
^{1}H NMR of 4la (500 MHz, $CDCl_3$, *solvent)



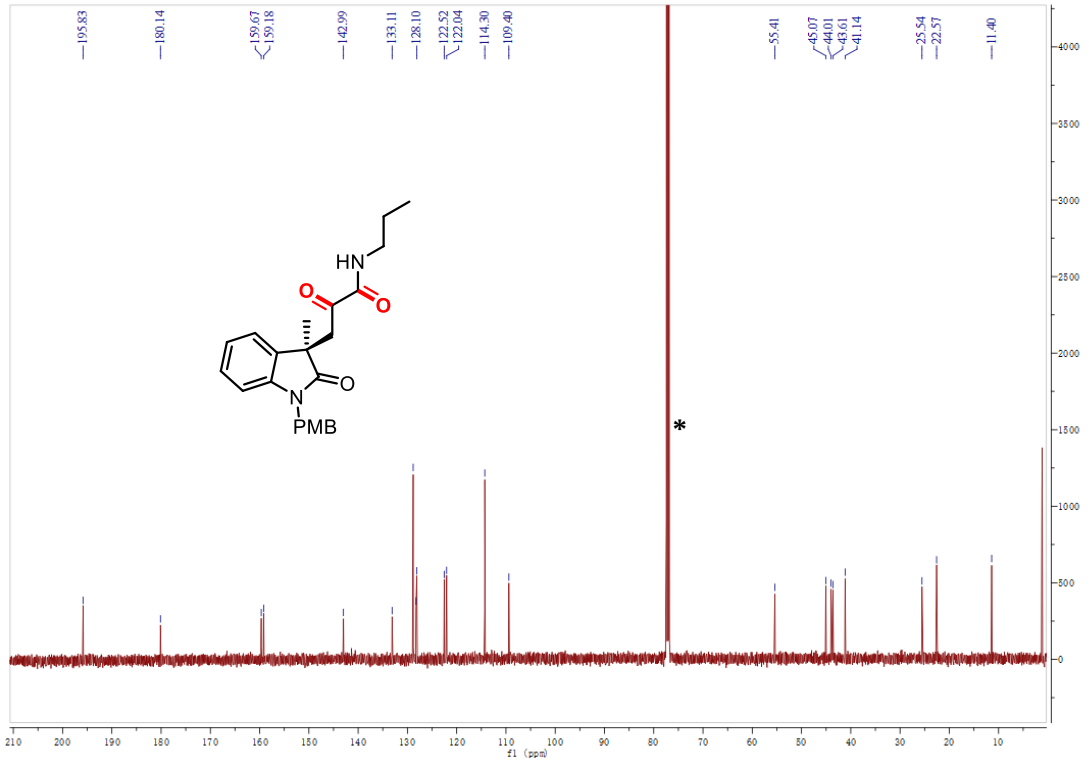
^{13}C NMR of 4la (126 MHz, $CDCl_3$, *solvent)



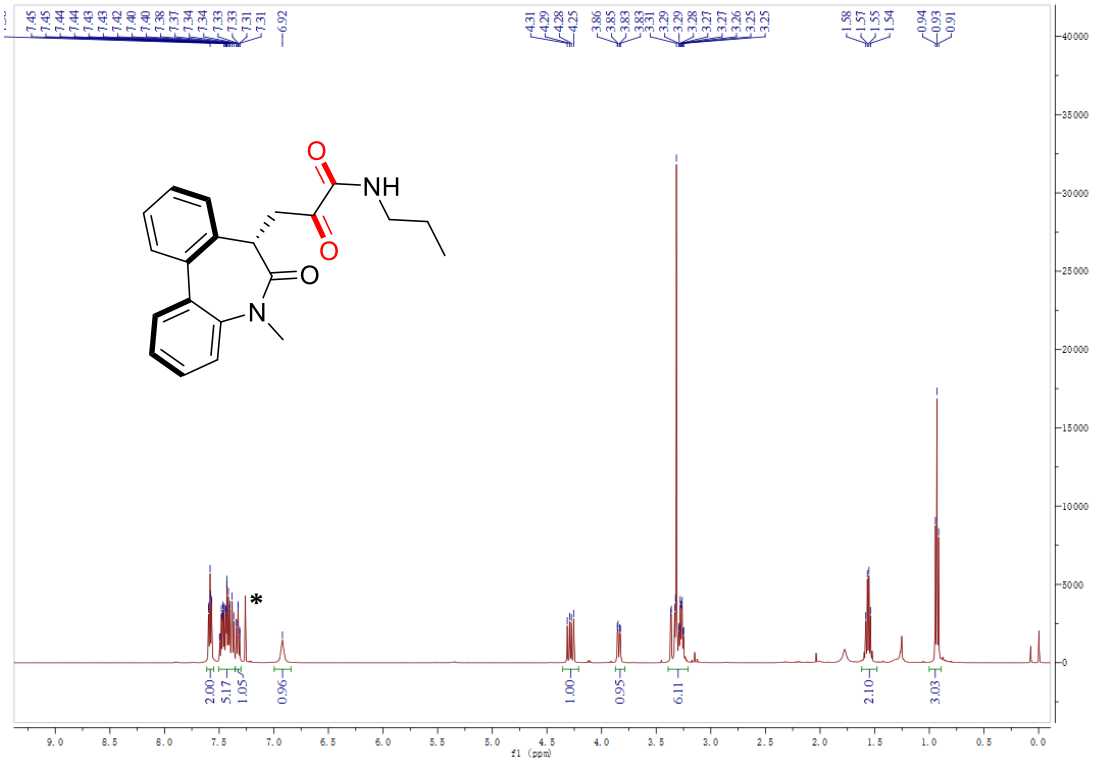
^{1}H NMR of 4ma (500 MHz, $CDCl_3$, *solvent)



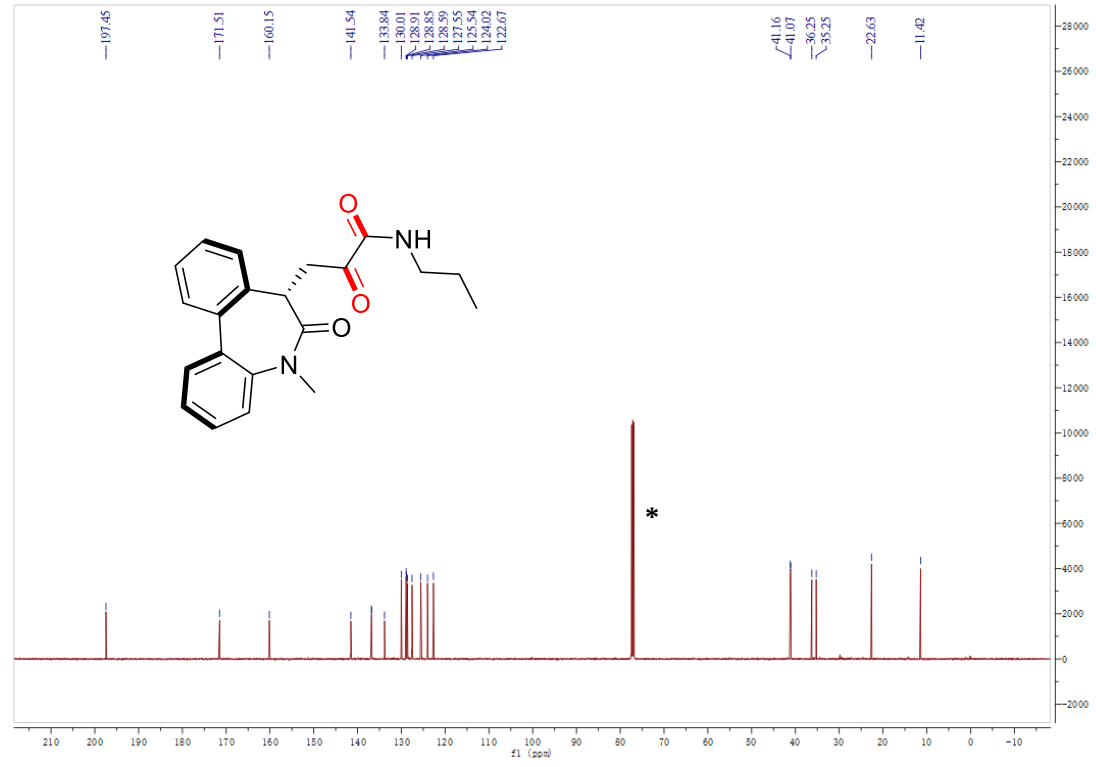
^{13}C NMR of 4ma (126 MHz, $CDCl_3$, *solvent)



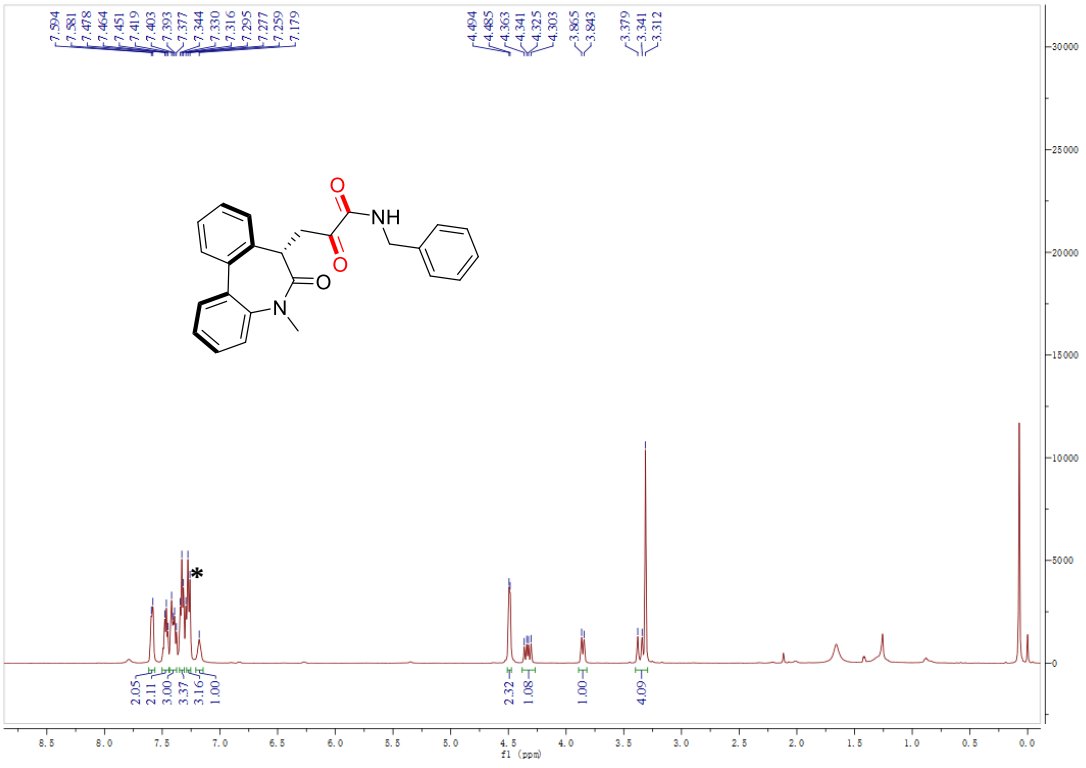
^{1}H NMR of 6aa (500 MHz, $CDCl_3$, *solvent)



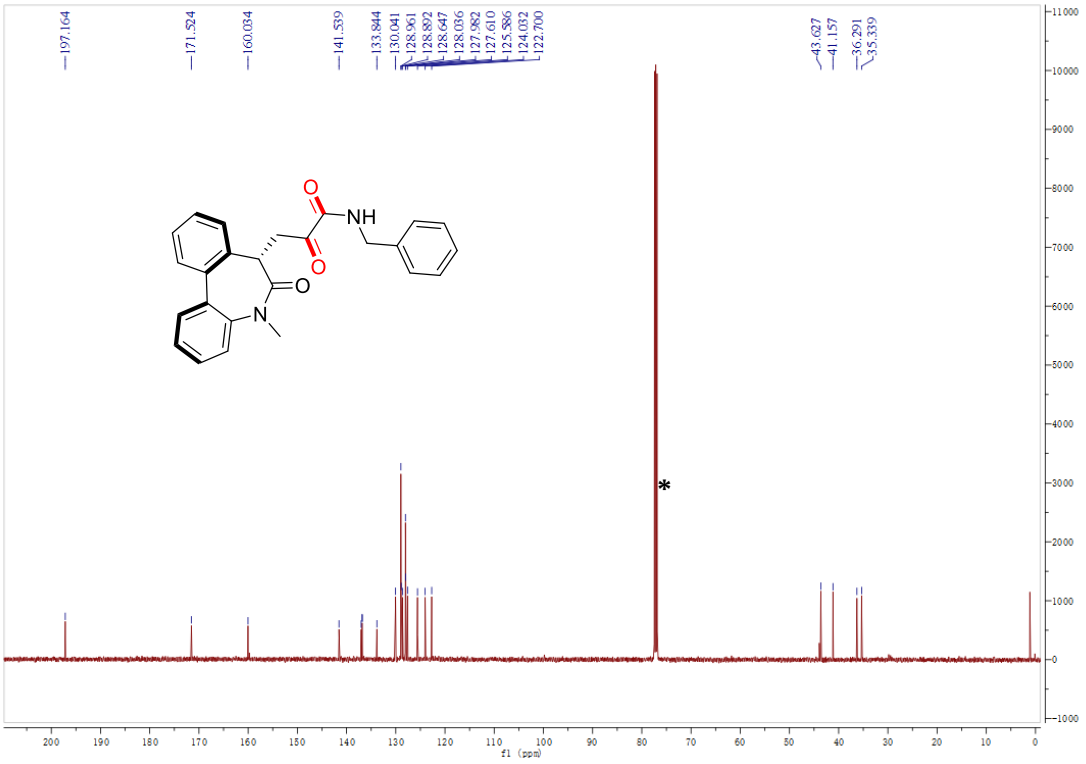
^{13}C NMR of 6aa (126 MHz, $CDCl_3$, *solvent)



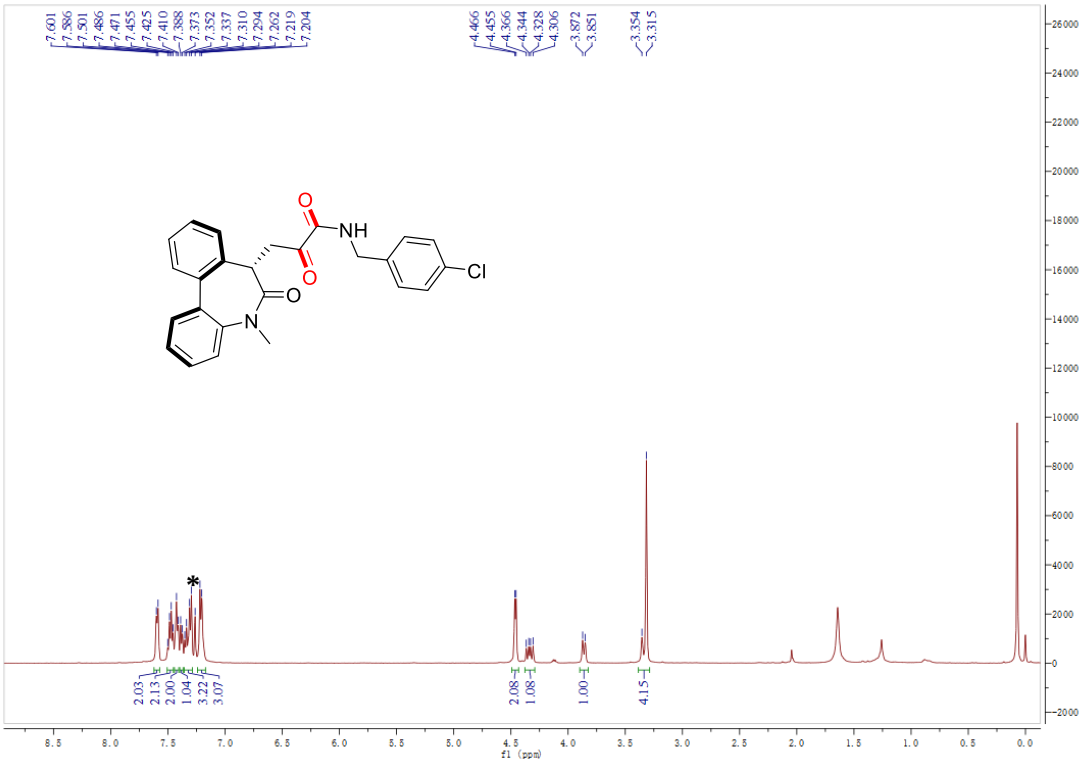
^{1}H NMR of 6ab (500 MHz, $CDCl_3$, *solvent)



^{13}C NMR of 6ab (126 MHz, $CDCl_3$, *solvent)



^{1}H NMR of 6ad (500 MHz, $CDCl_3$, *solvent)



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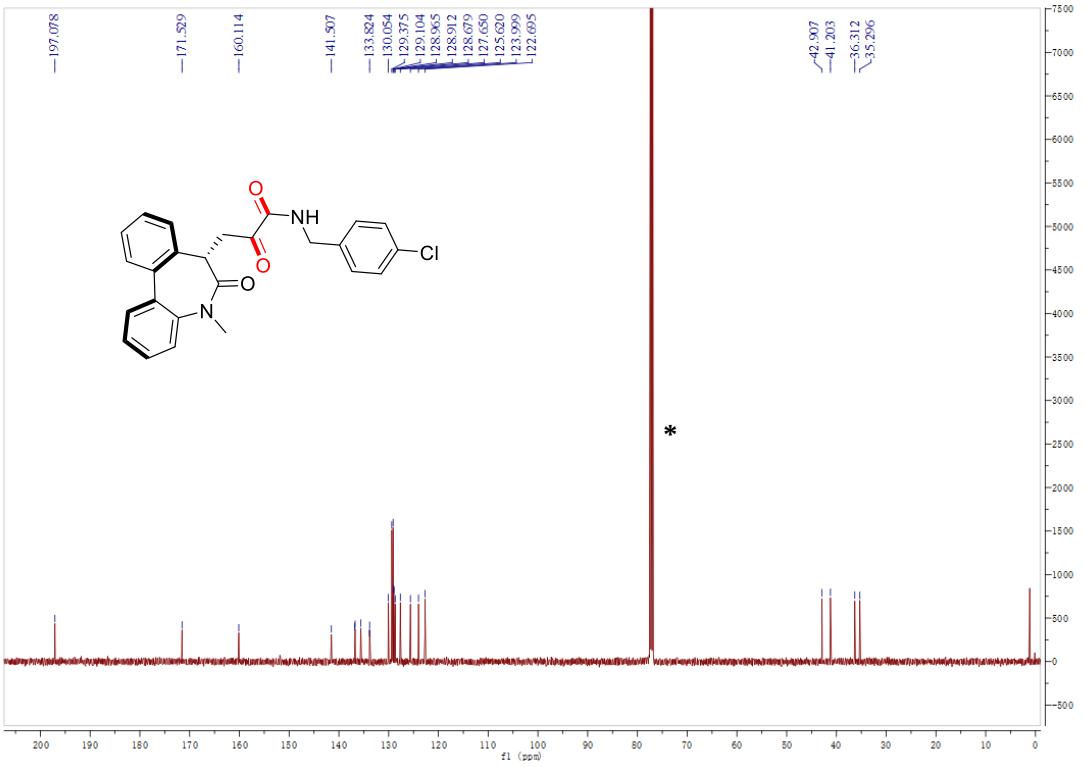
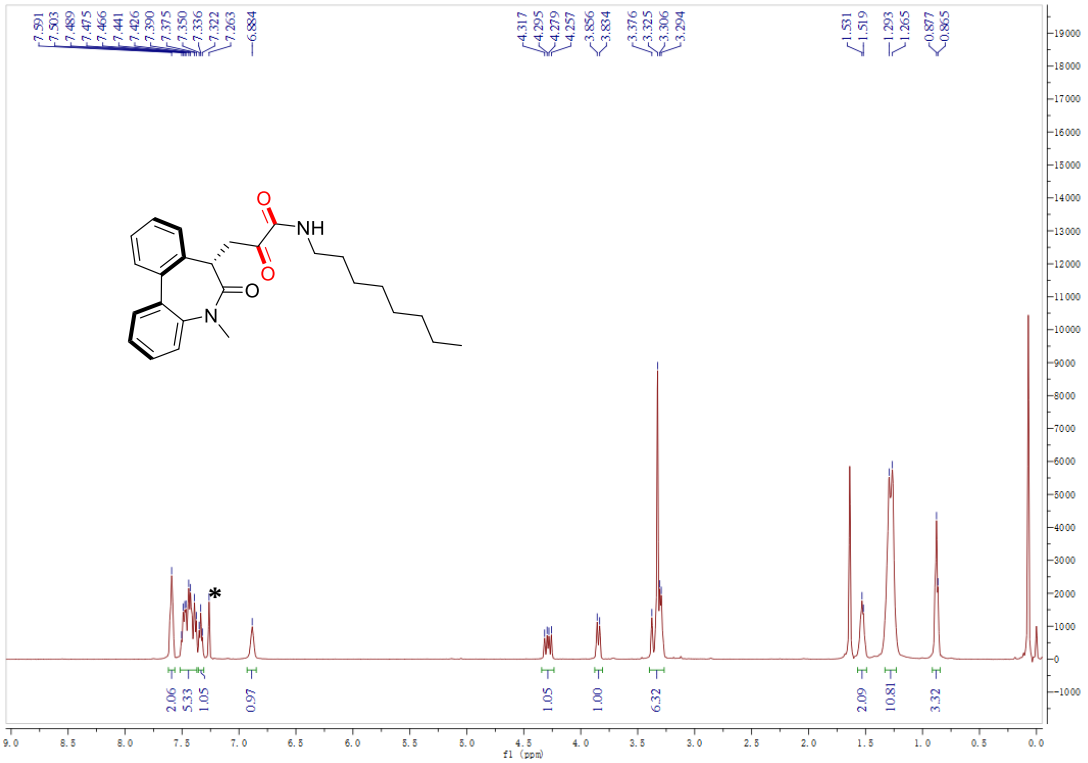
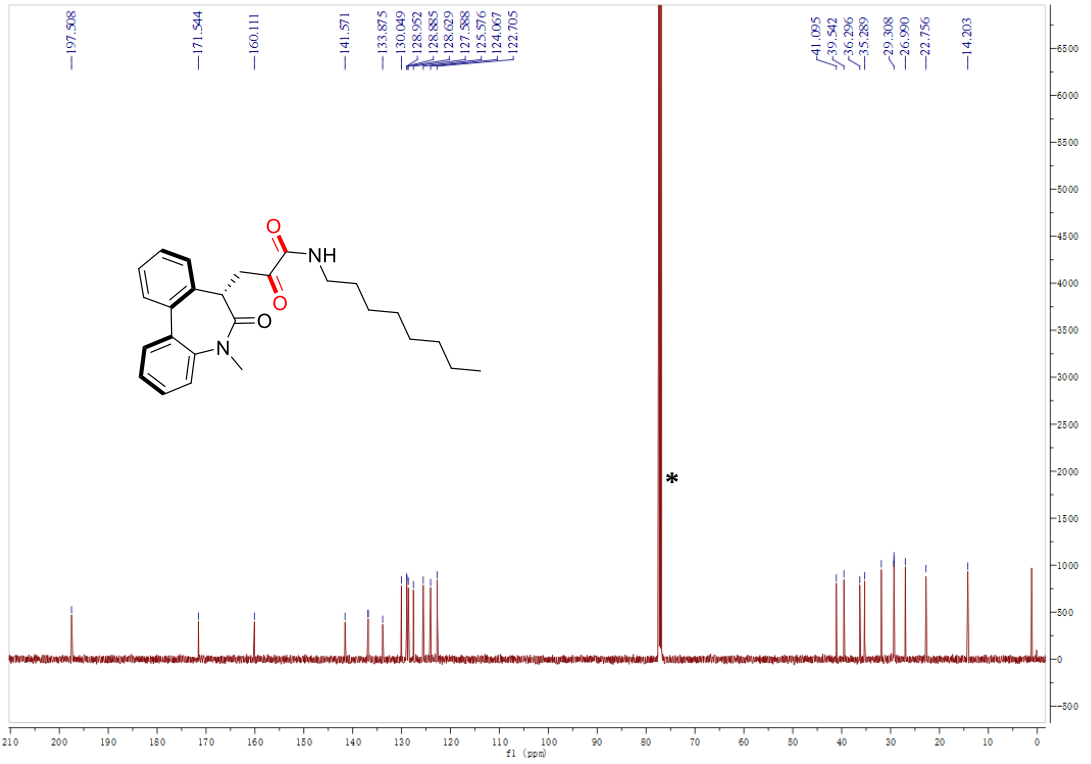


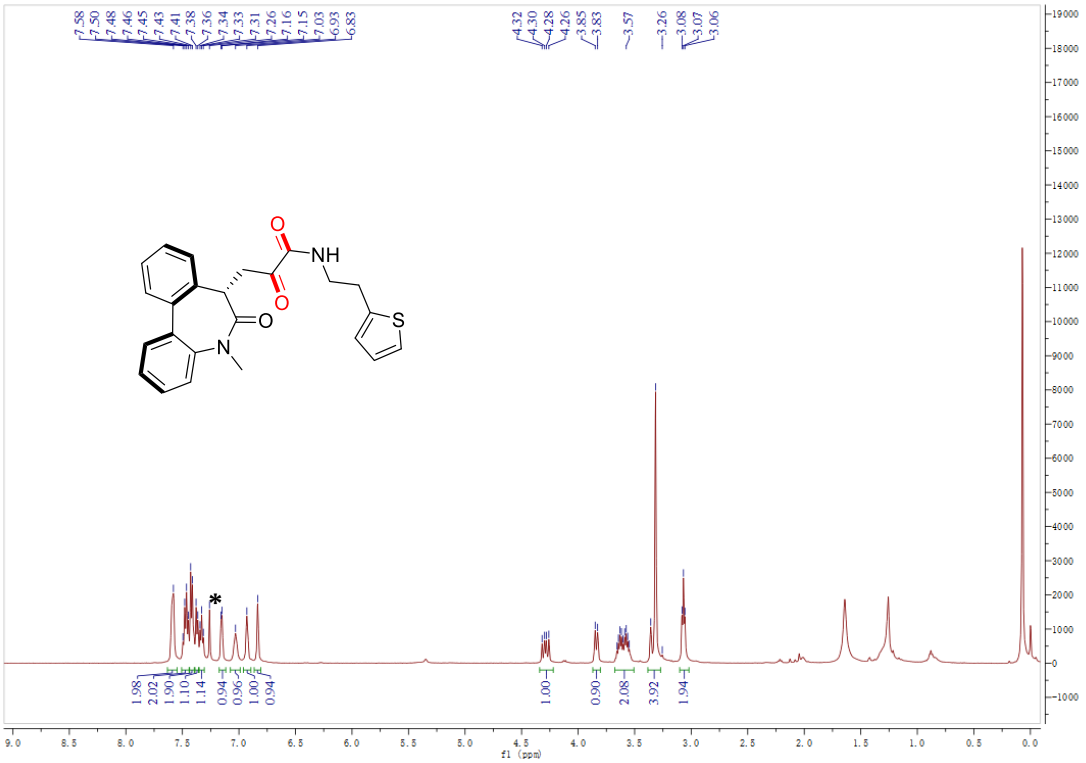
^{1}H NMR of 6ae (500 MHz, $CDCl_3$, *solvent)



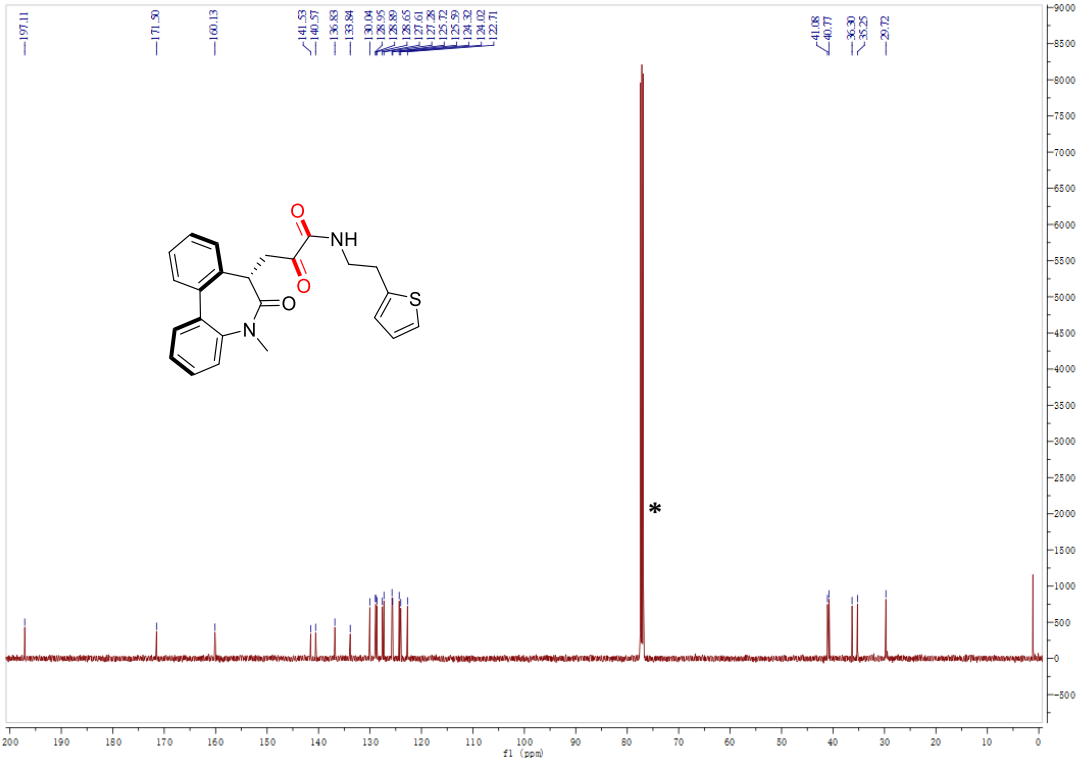
^{13}C NMR of 6ae (126 MHz, $CDCl_3$, *solvent)



^{1}H NMR of 6af (500 MHz, $CDCl_3$, *solvent)



^{1}H NMR of 6af (126 MHz, $CDCl_3$, *solvent)



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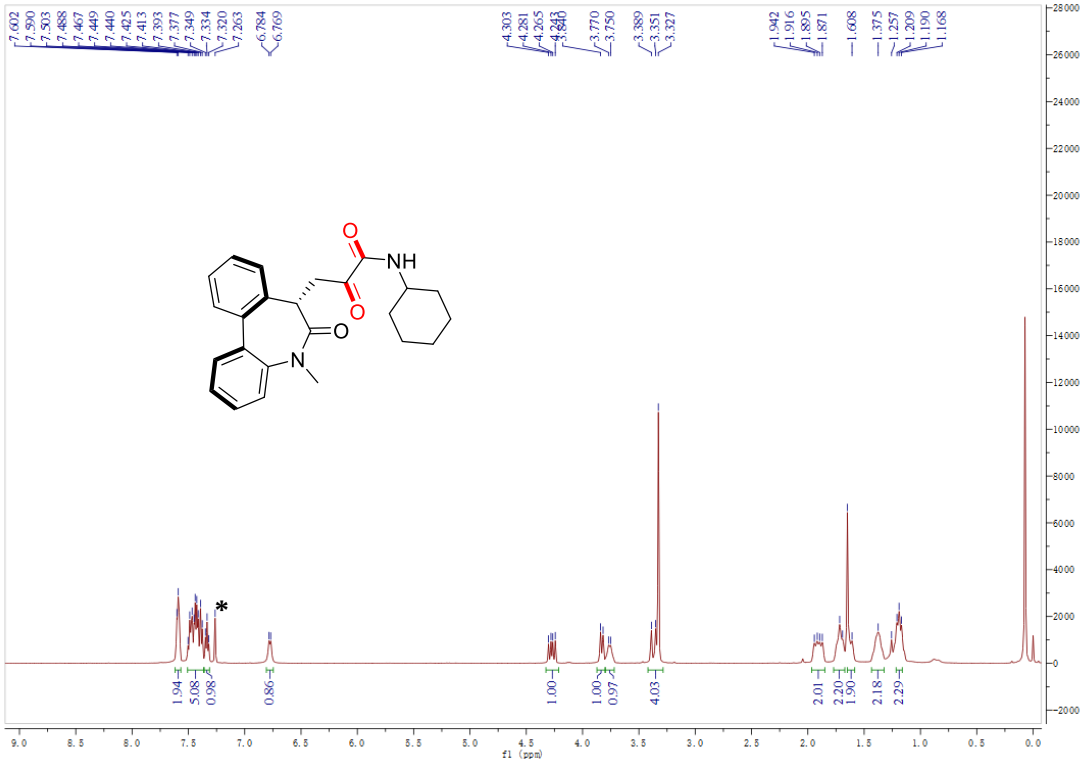

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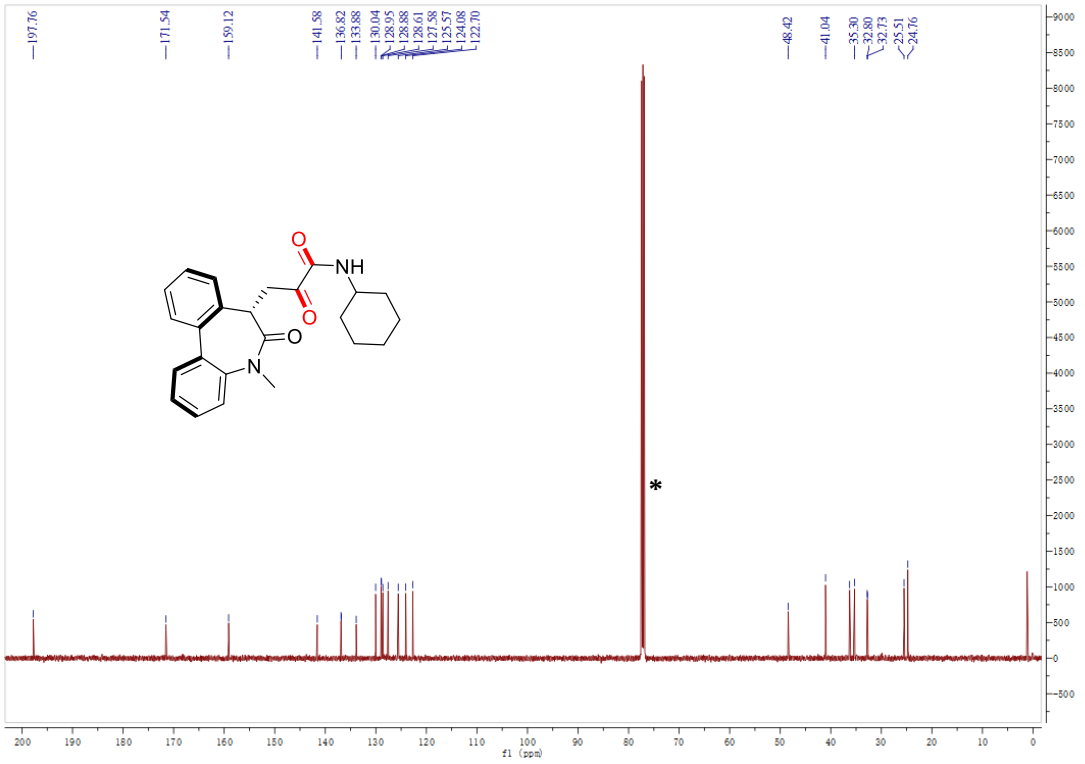
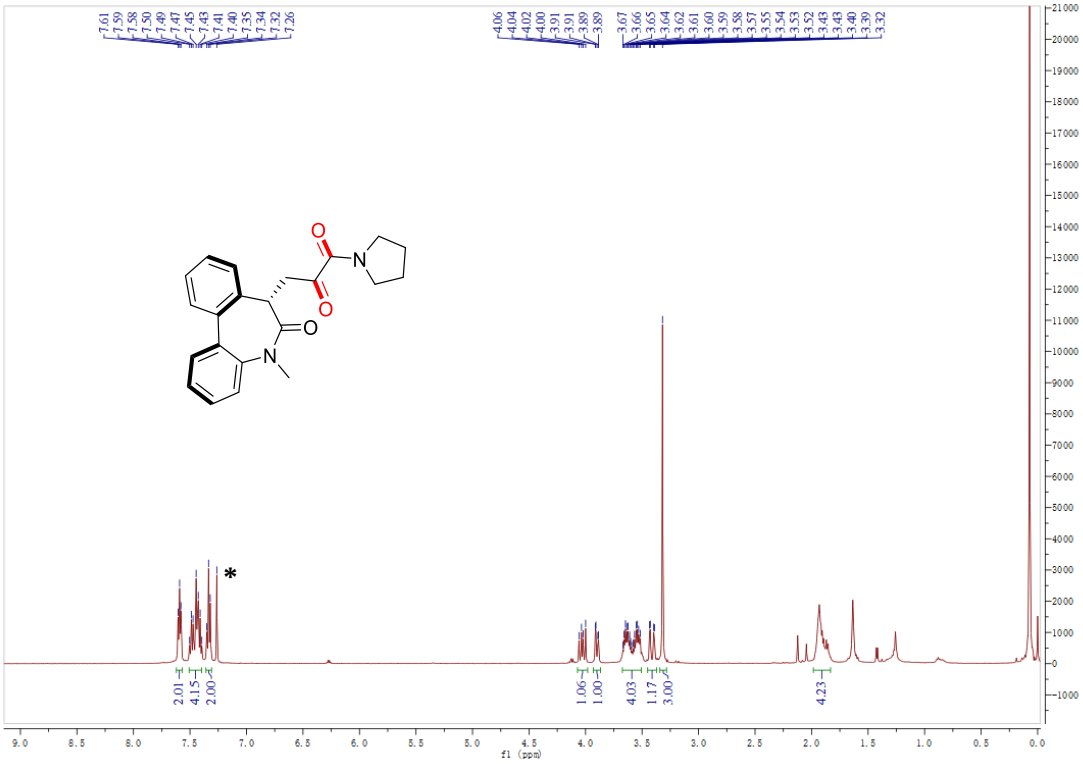
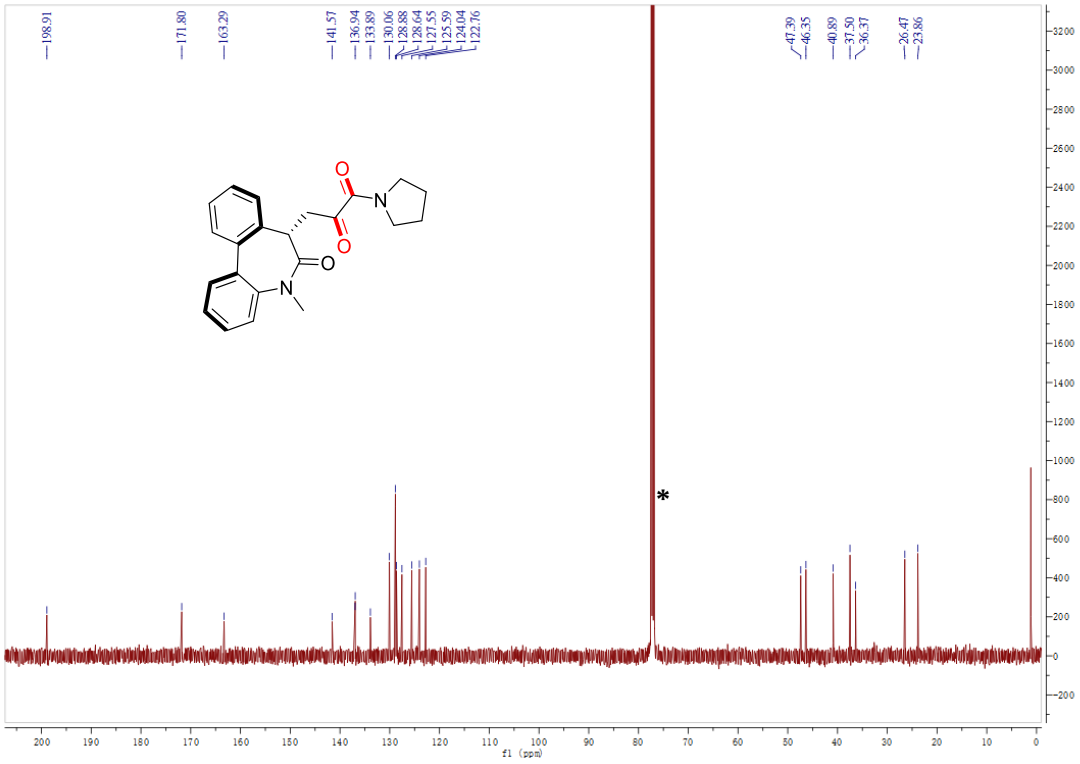


^{1}H NMR of 6ak (500 MHz, $CDCl_3$, *solvent)



^{13}C NMR of 6ak(126 MHz, $CDCl_3$, *solvent)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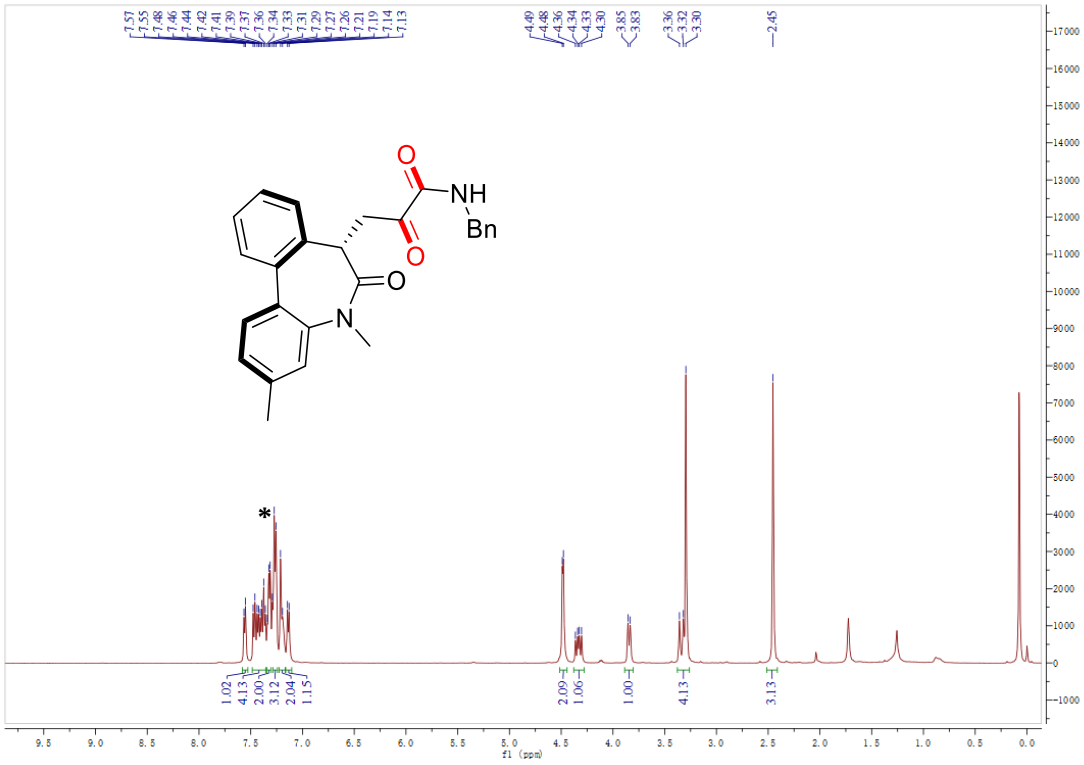
122.76
47.39
46.35
40.89
37.50
36.37
26.47
23.86
O
O
O
N
N
*
f1 (ppm)

^{1}H NMR of 6bb (500 MHz, $CDCl_3$, *solvent)



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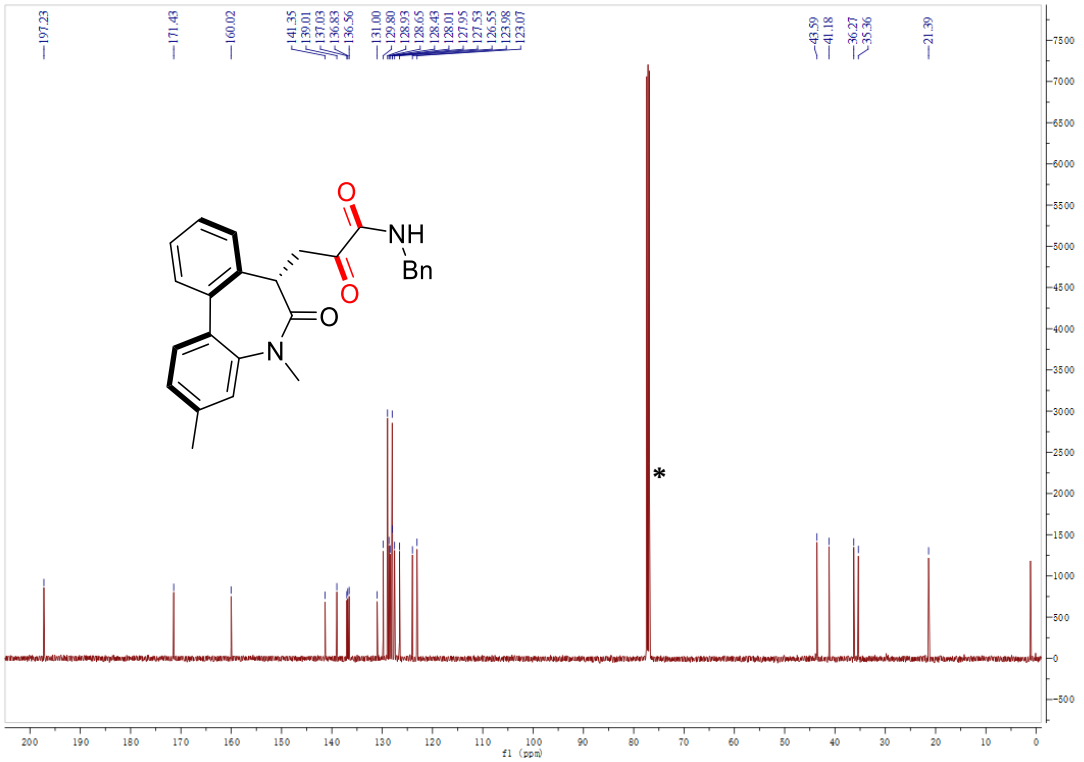

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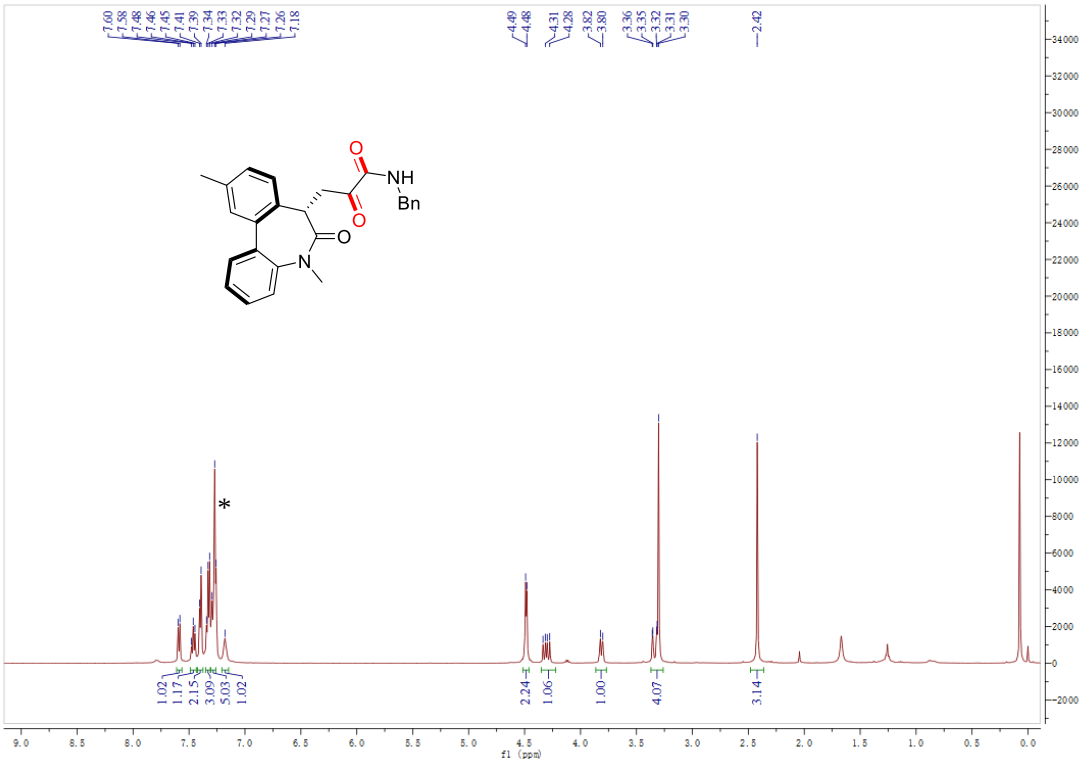

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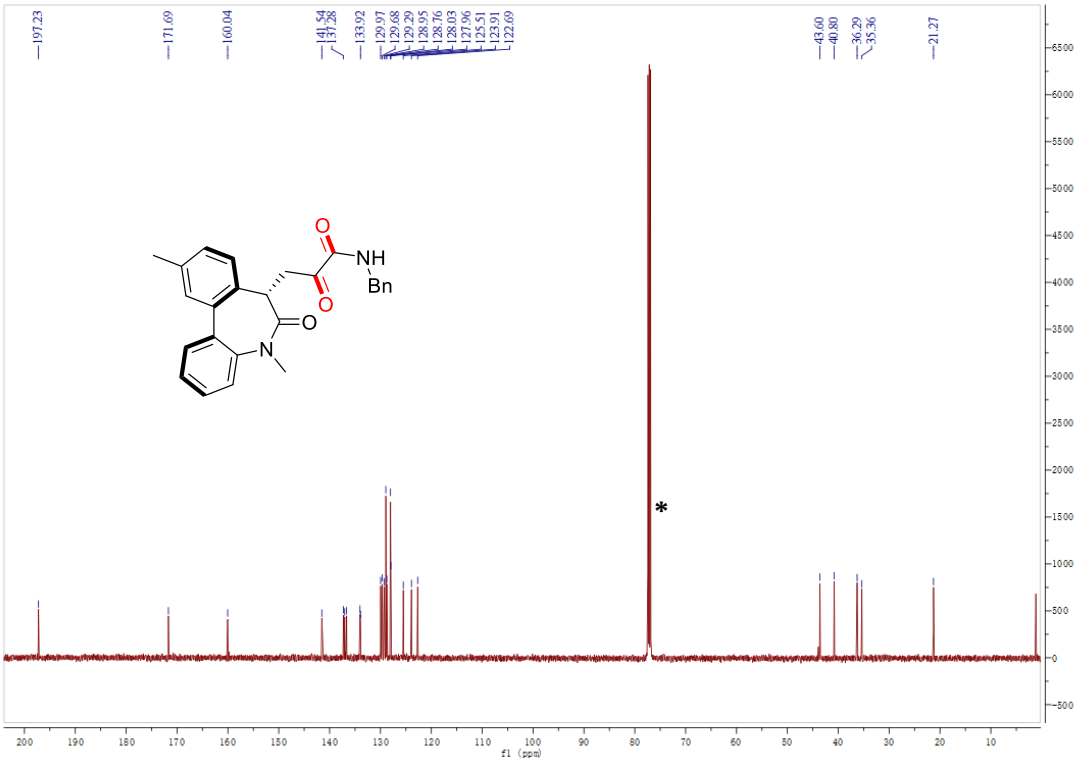
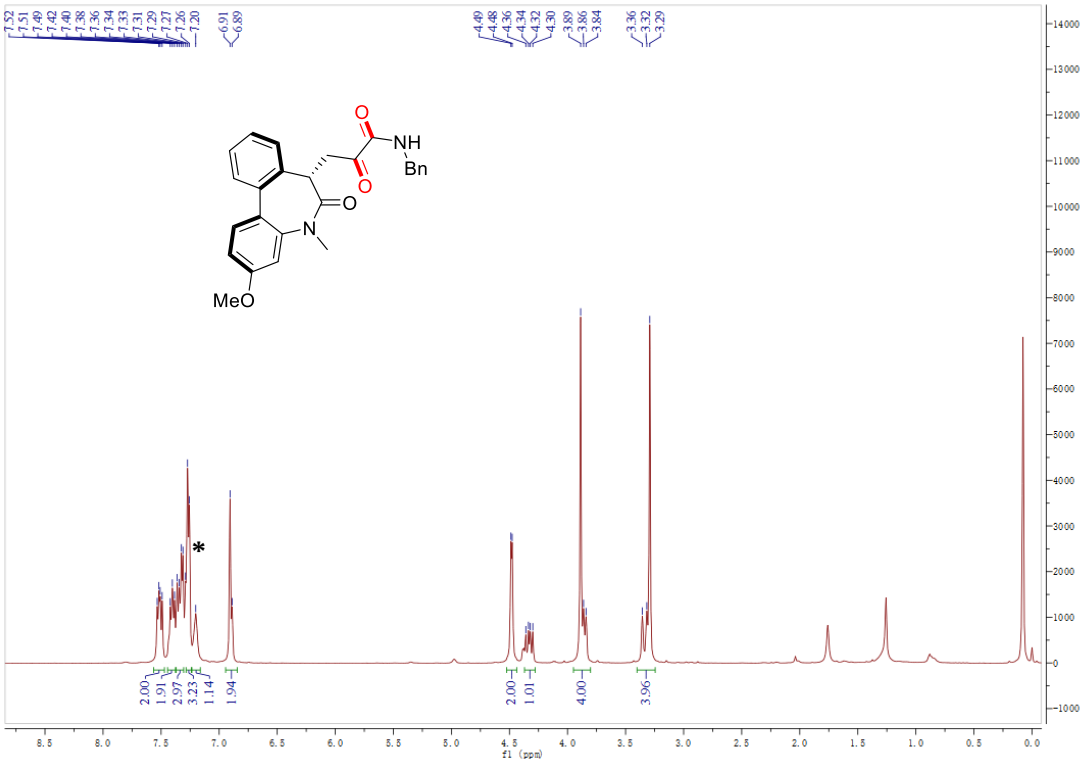
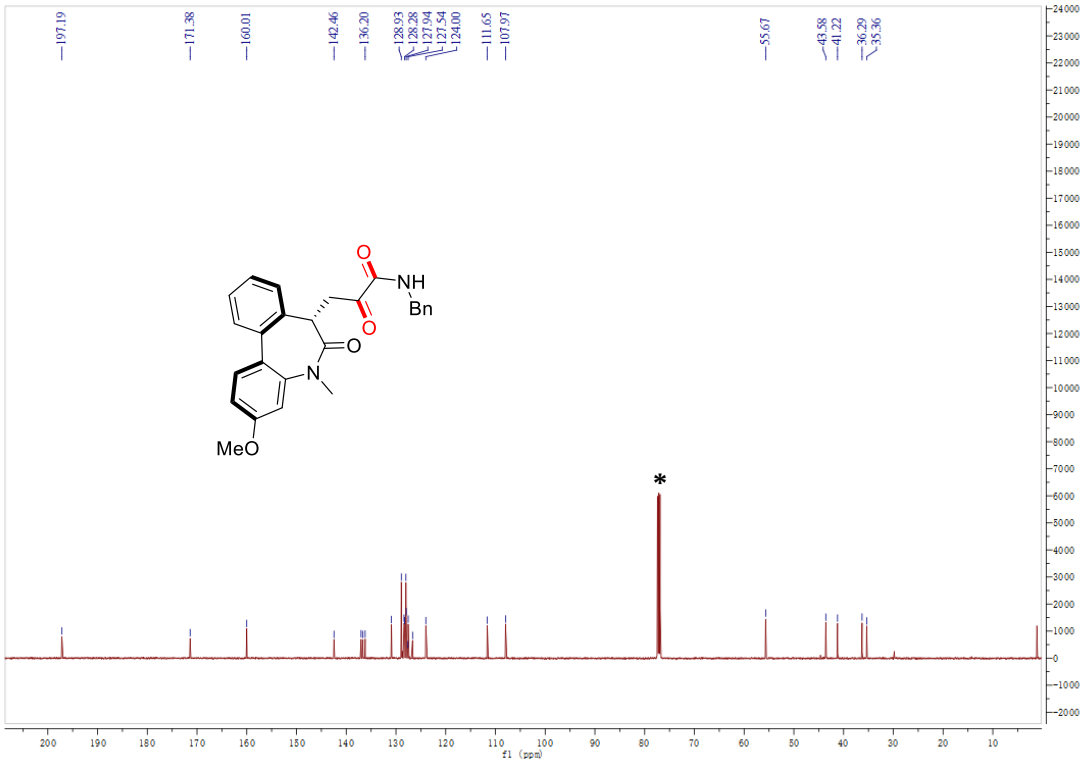


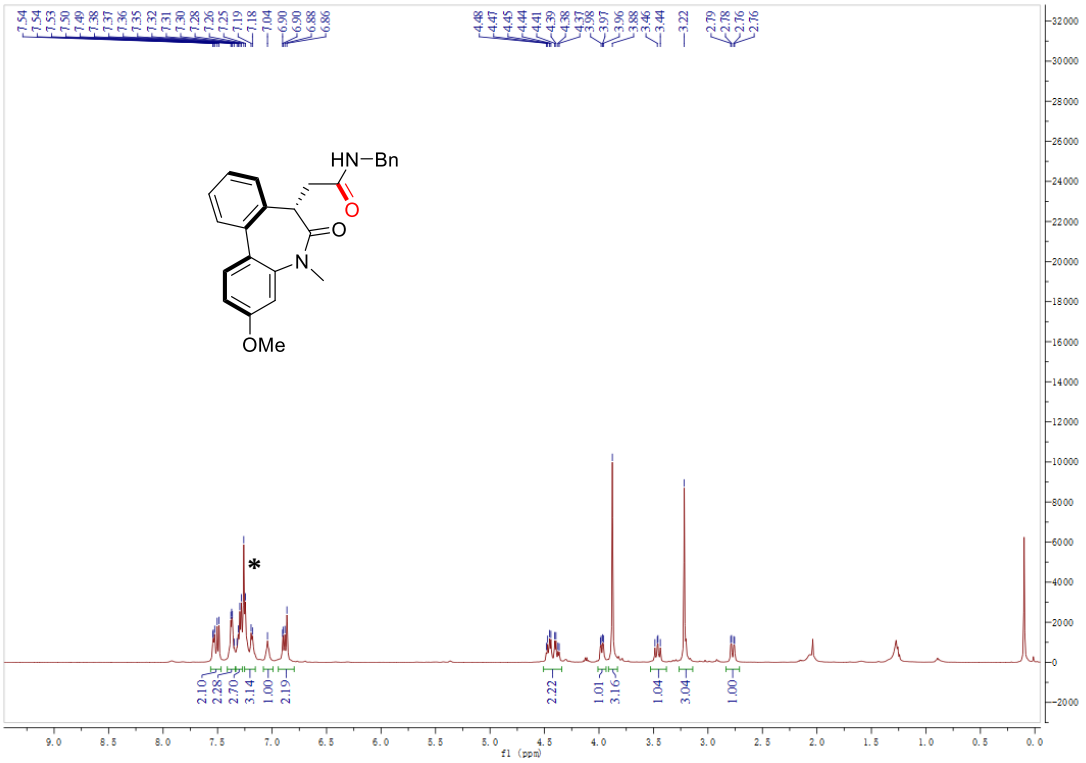
^{1}H NMR of 6db (500 MHz, $CDCl_3$, *solvent)



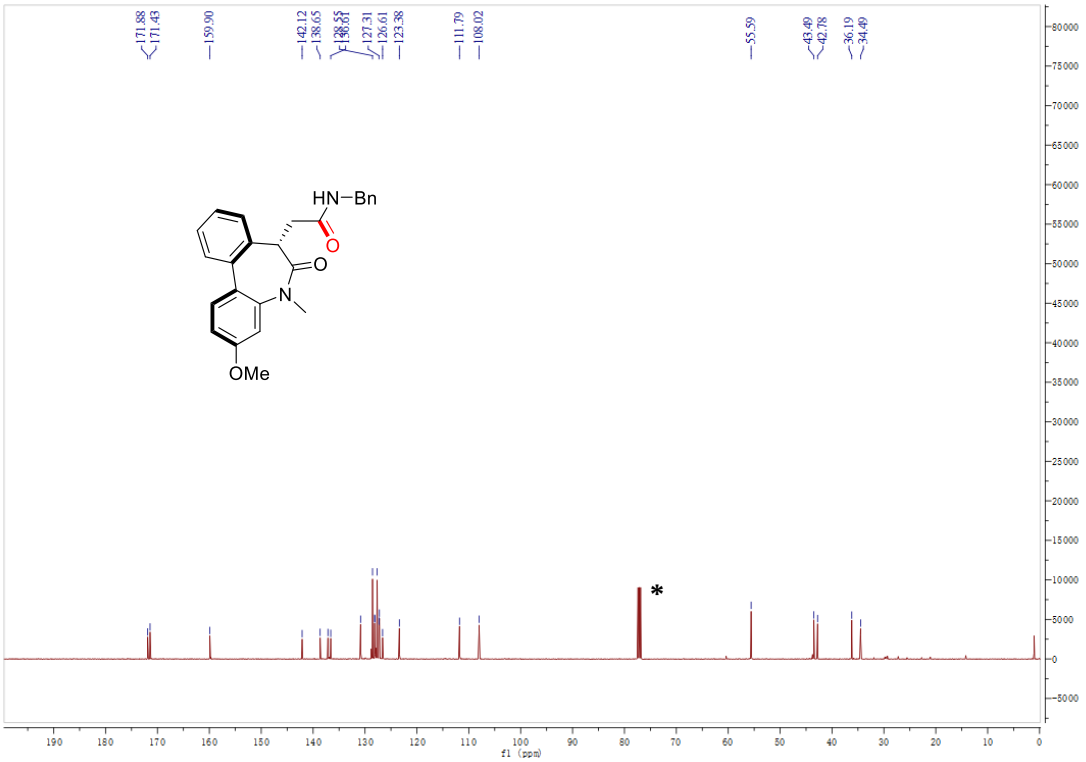
^{13}C NMR of 6db (126 MHz, $CDCl_3$, *solvent)



^{1}H NMR of mono insertion (500 MHz, $CDCl_3$, *solvent)



^{13}C NMR of mono insertion (126 MHz, $CDCl_3$, *solvent)



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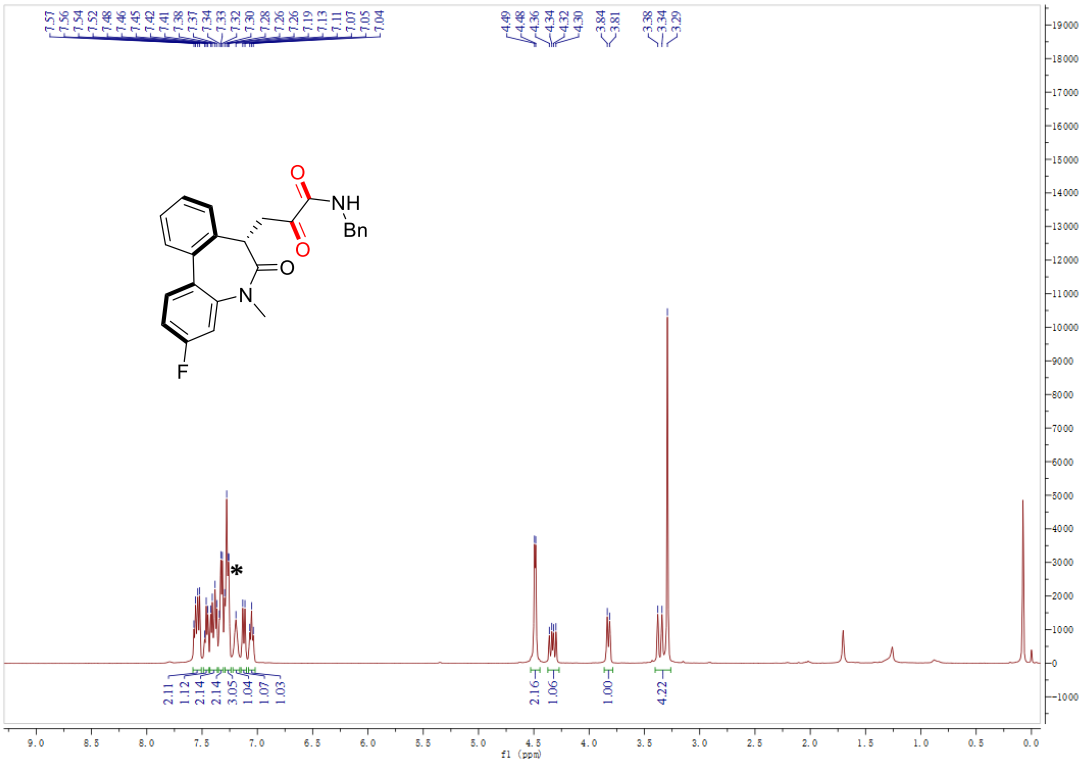
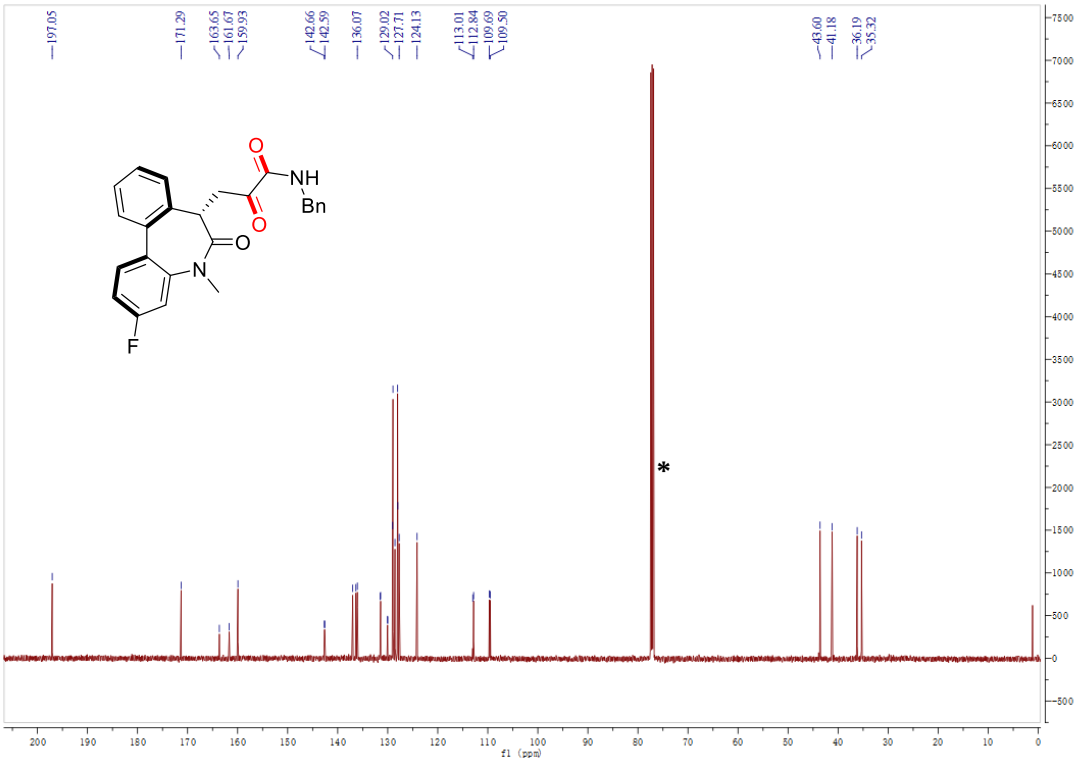
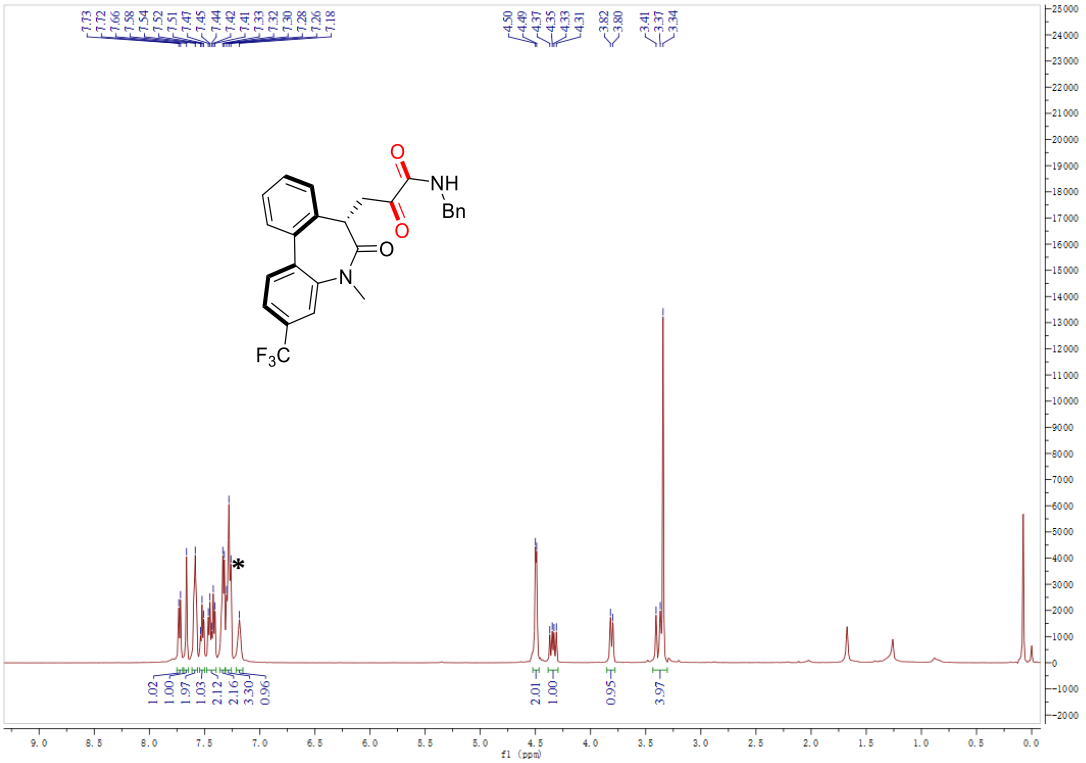


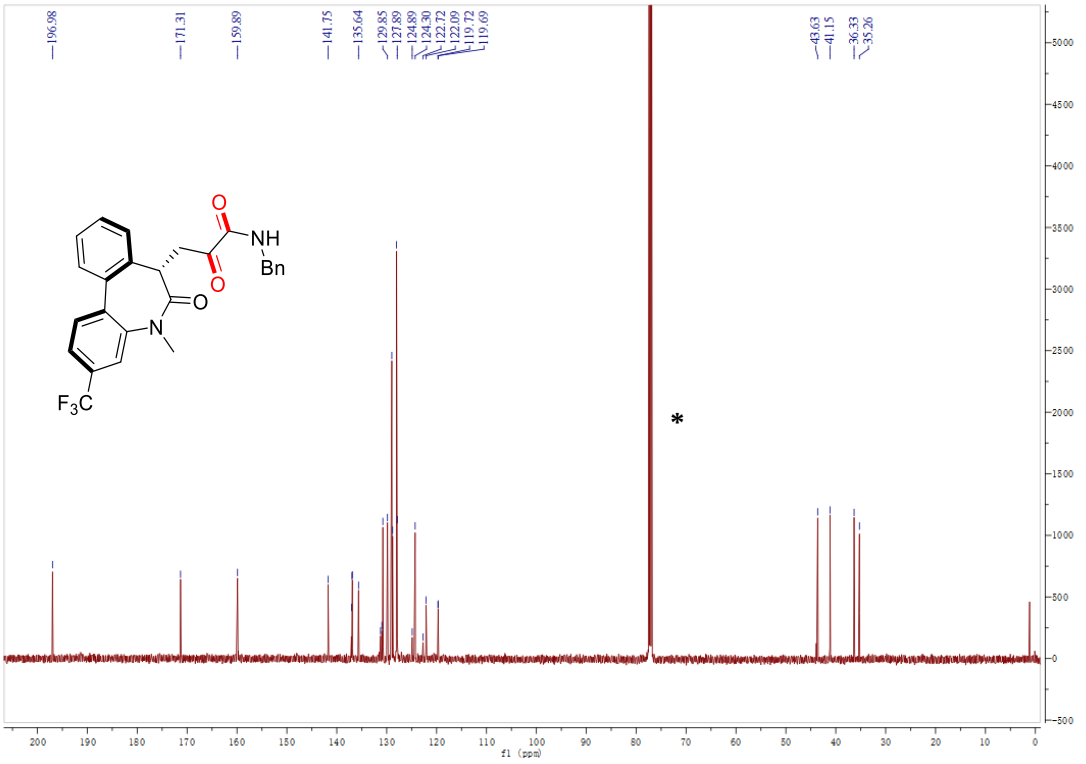
^{13}C NMR of 6eb (126 MHz, $CDCl_3$, *solvent)



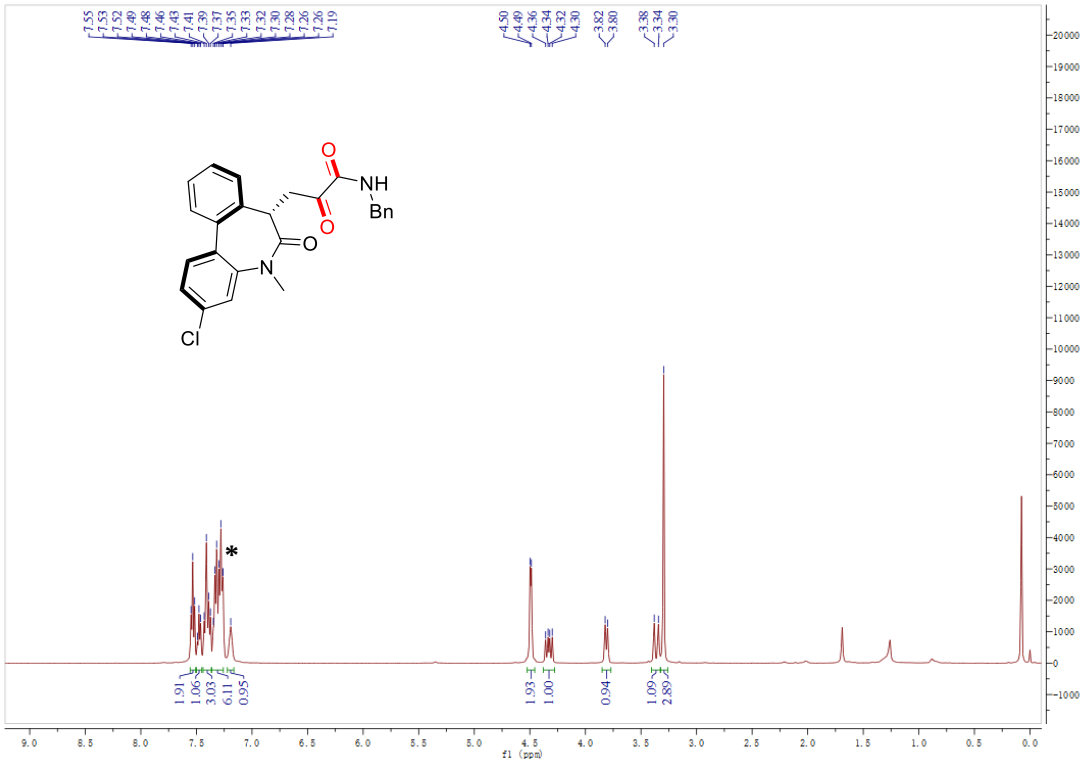
^{1}H NMR of 6fb (500 MHz, $CDCl_3$, *solvent)



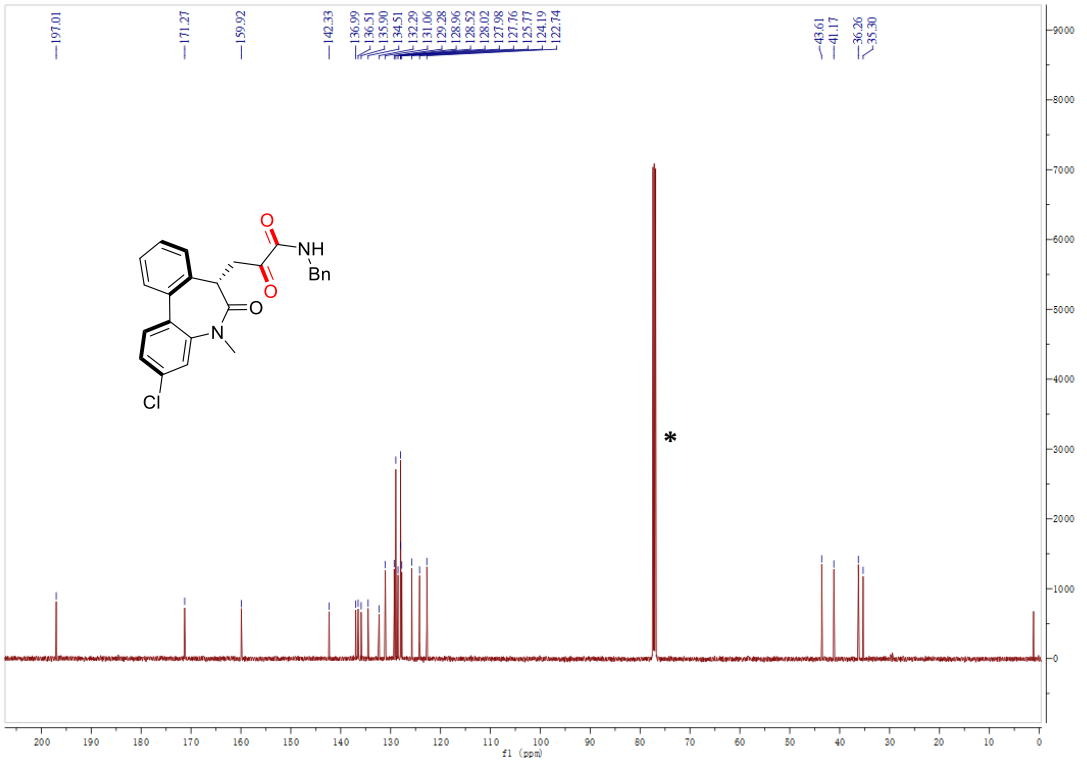
^{13}C NMR of 6fb (126 MHz, $CDCl_3$, *solvent)



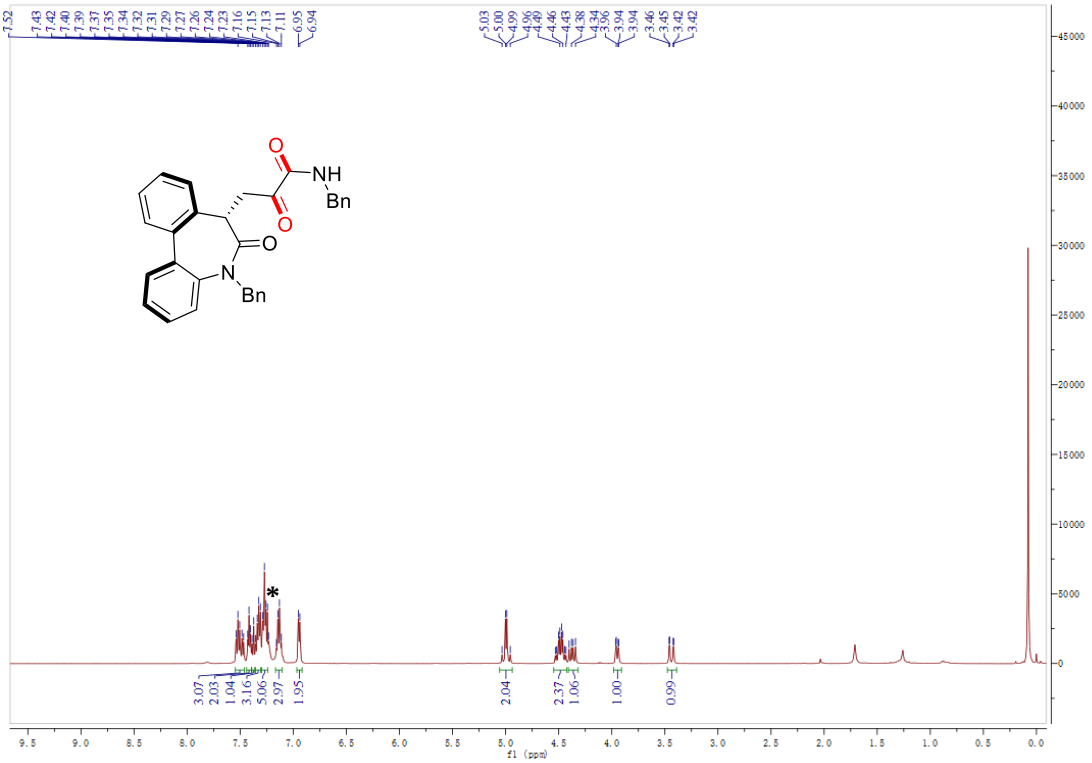
^{1}H NMR of 6gb (500 MHz, $CDCl_3$, *solvent)



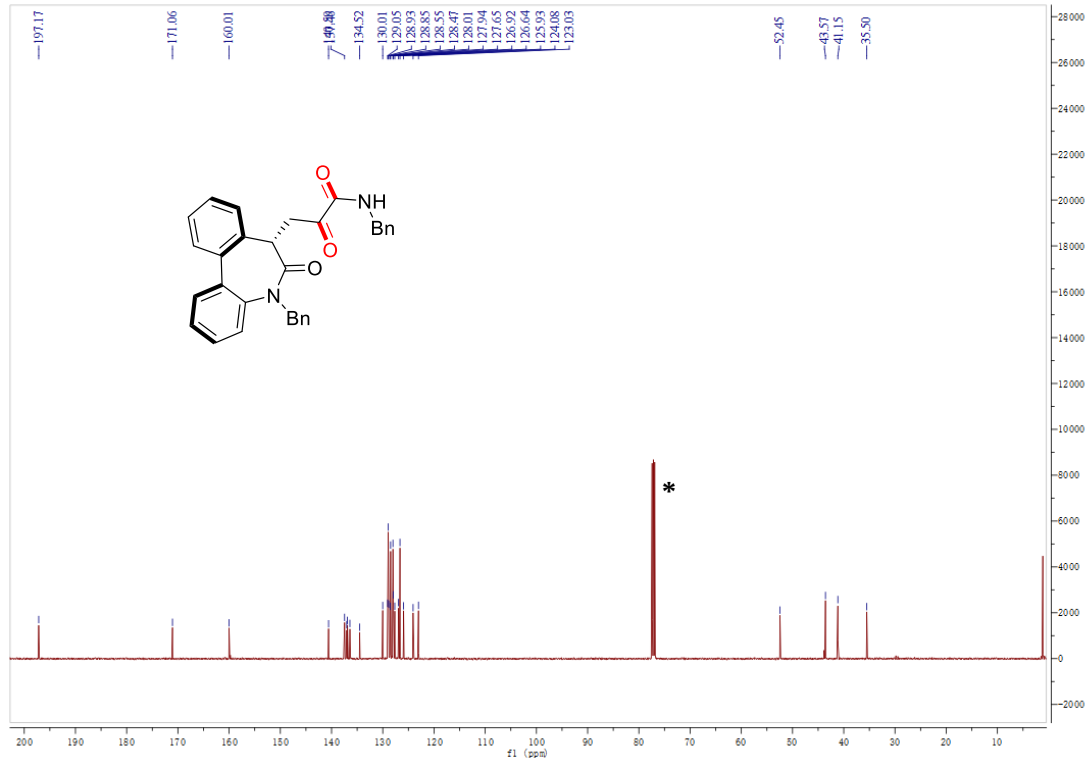
^{13}C NMR of 6gb (126 MHz, $CDCl_3$, *solvent)



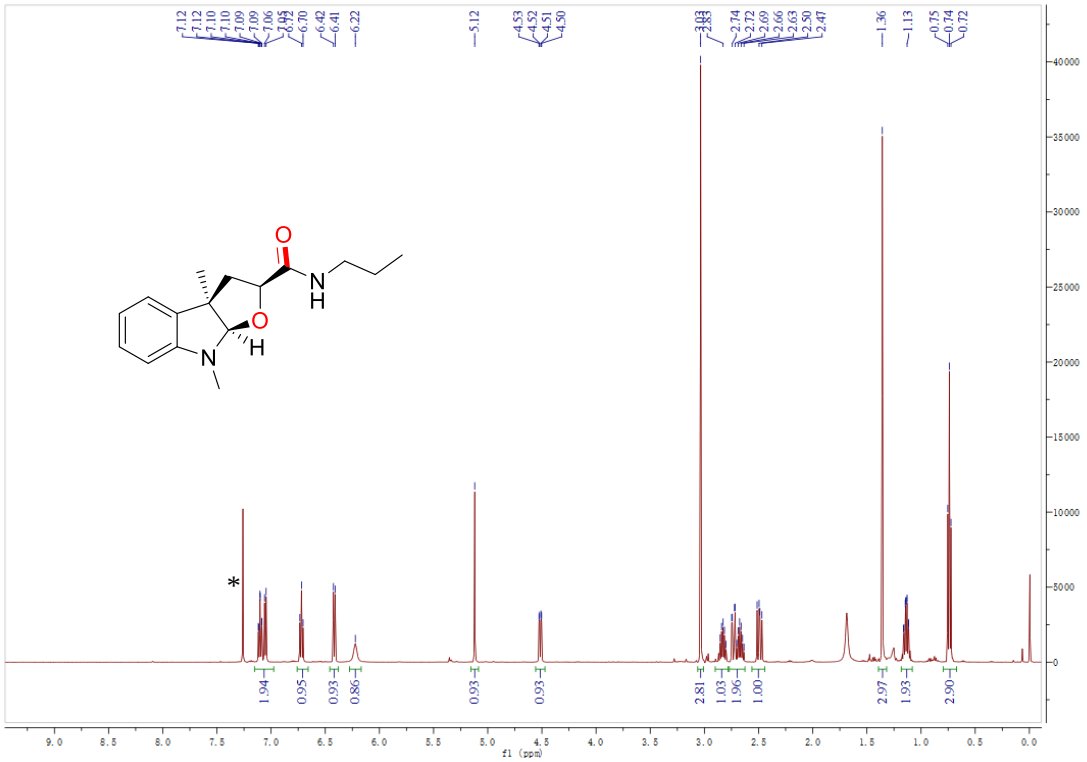
^{1}H NMR of 6hb (500 MHz, $CDCl_3$, *solvent)



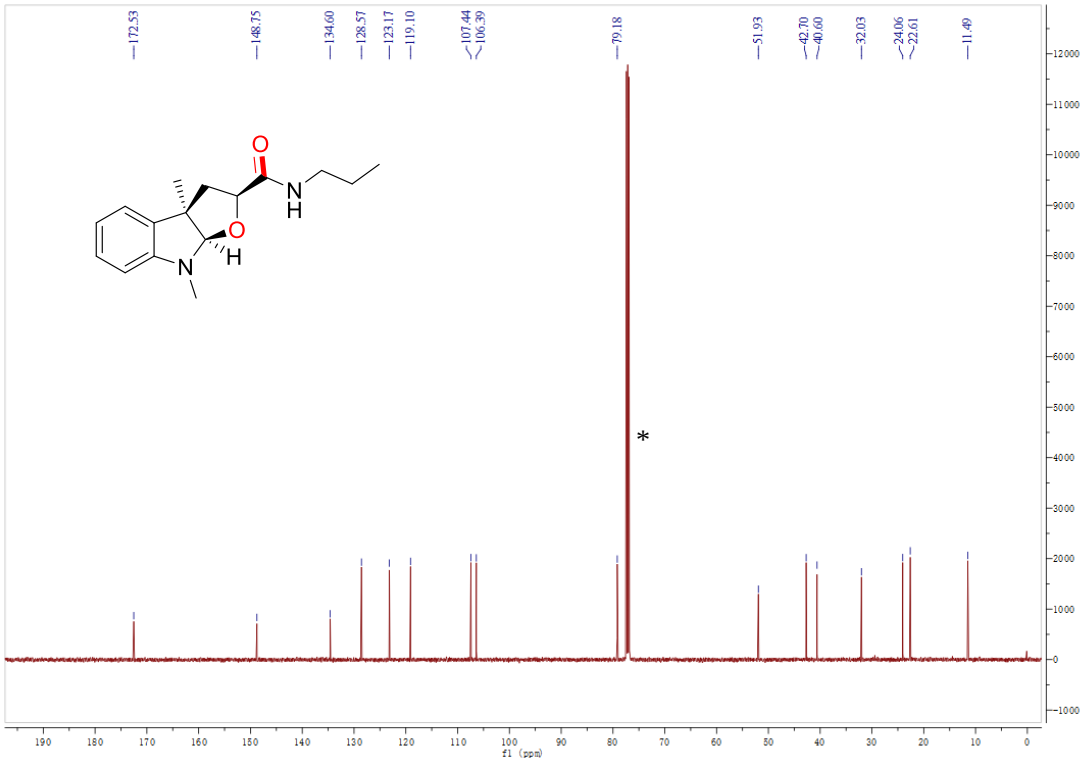
^{13}C NMR of 6hb (126 MHz, $CDCl_3$, *solvent)



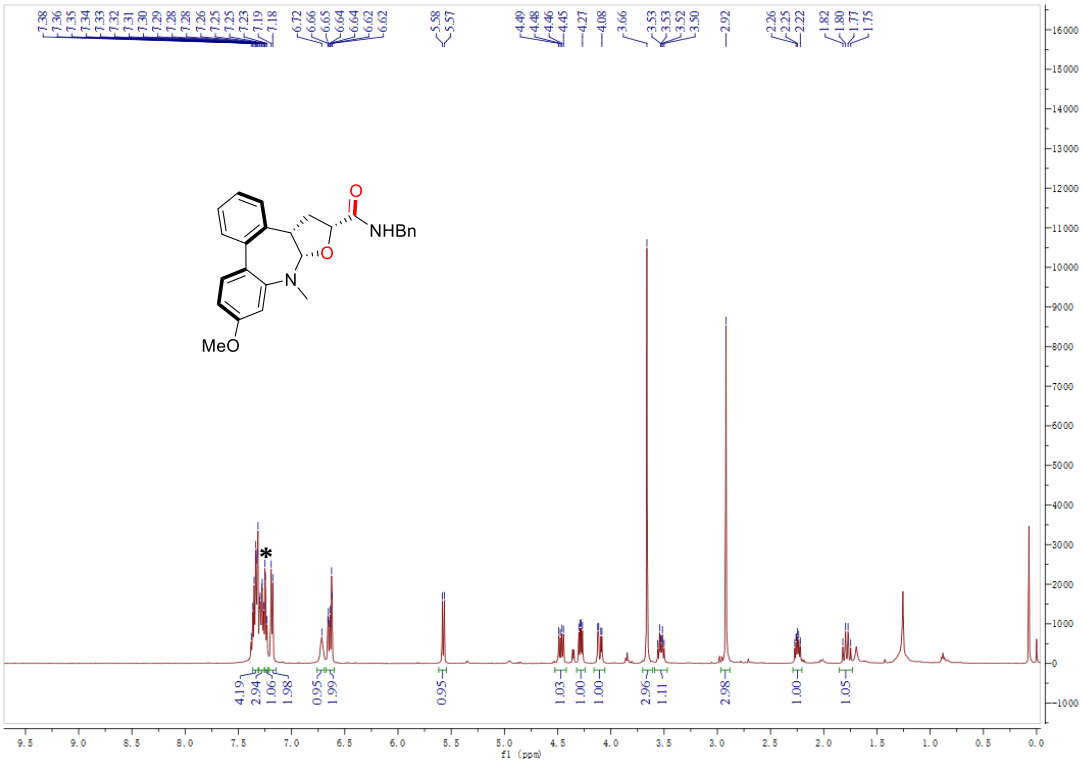
^{1}H NMR of 7 (500 MHz, $CDCl_3$, *solvent)



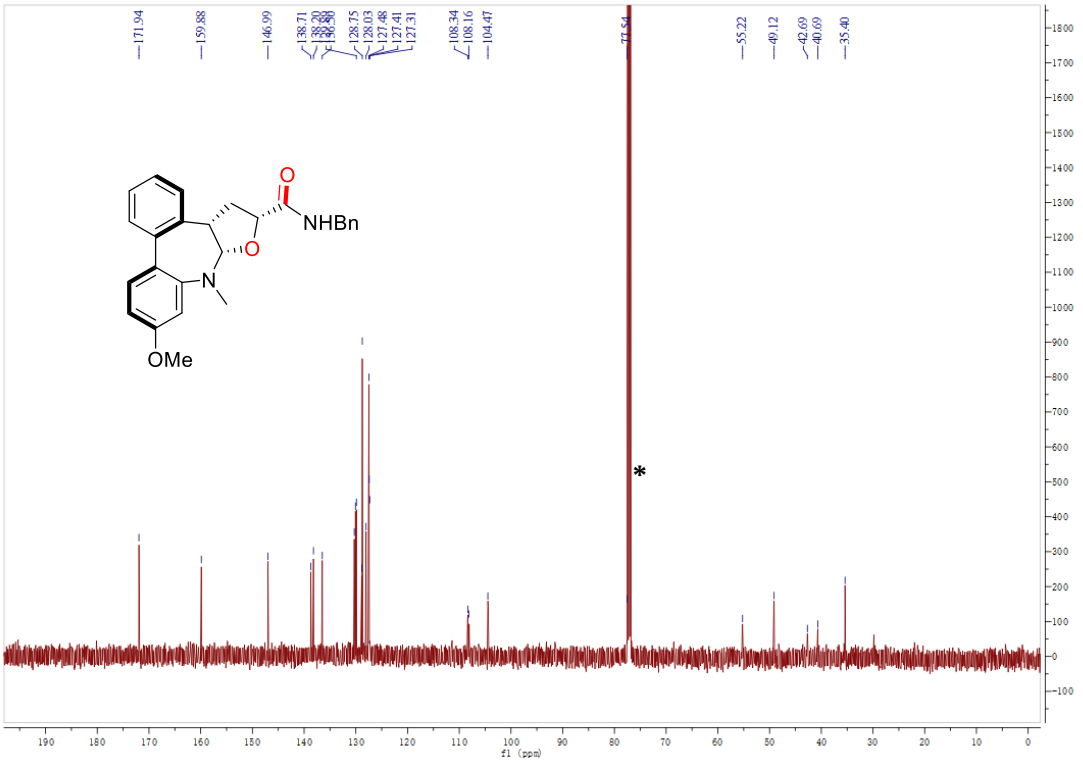
^{13}C NMR of 7 (126 MHz, $CDCl_3$, *solvent)



^{1}H NMR of 8 (500 MHz, $CDCl_3$, *solvent)



^{13}C NMR of 8 (126 MHz, $CDCl_3$, *solvent)



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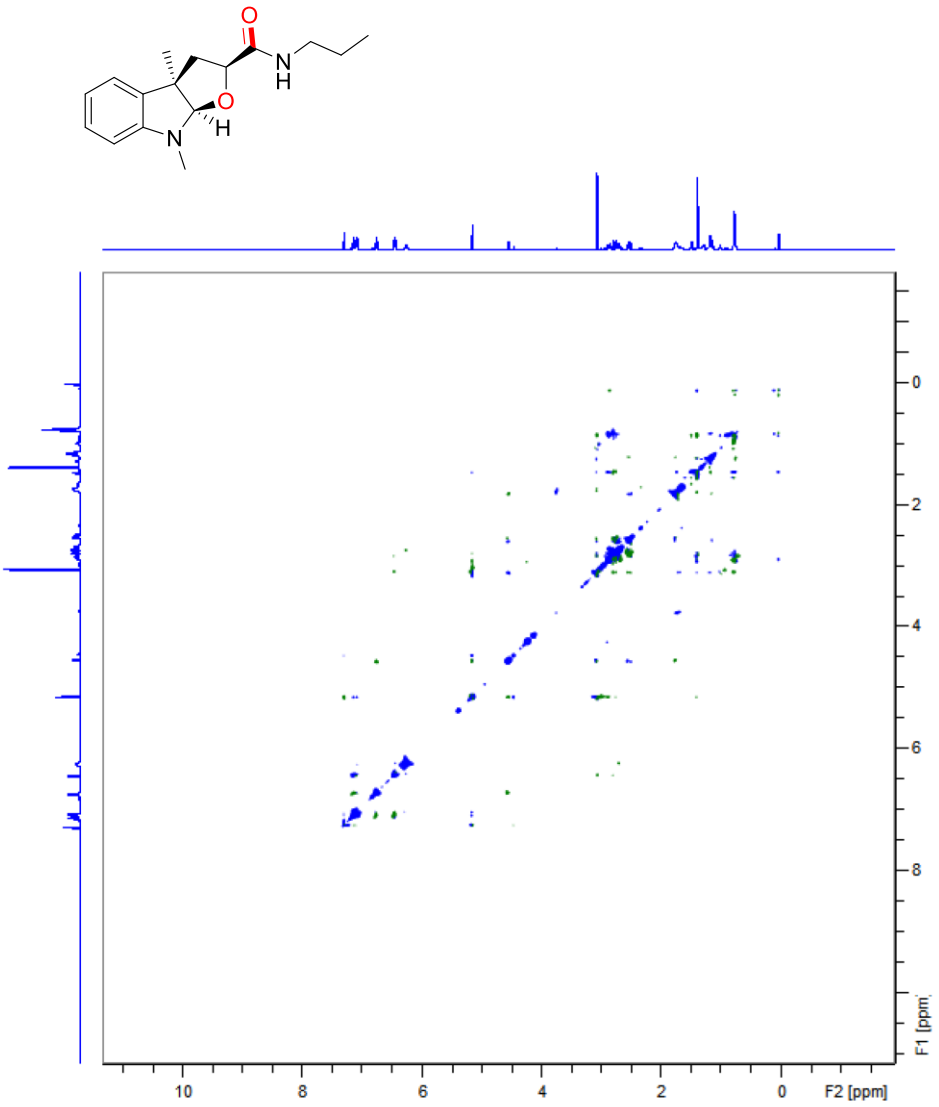

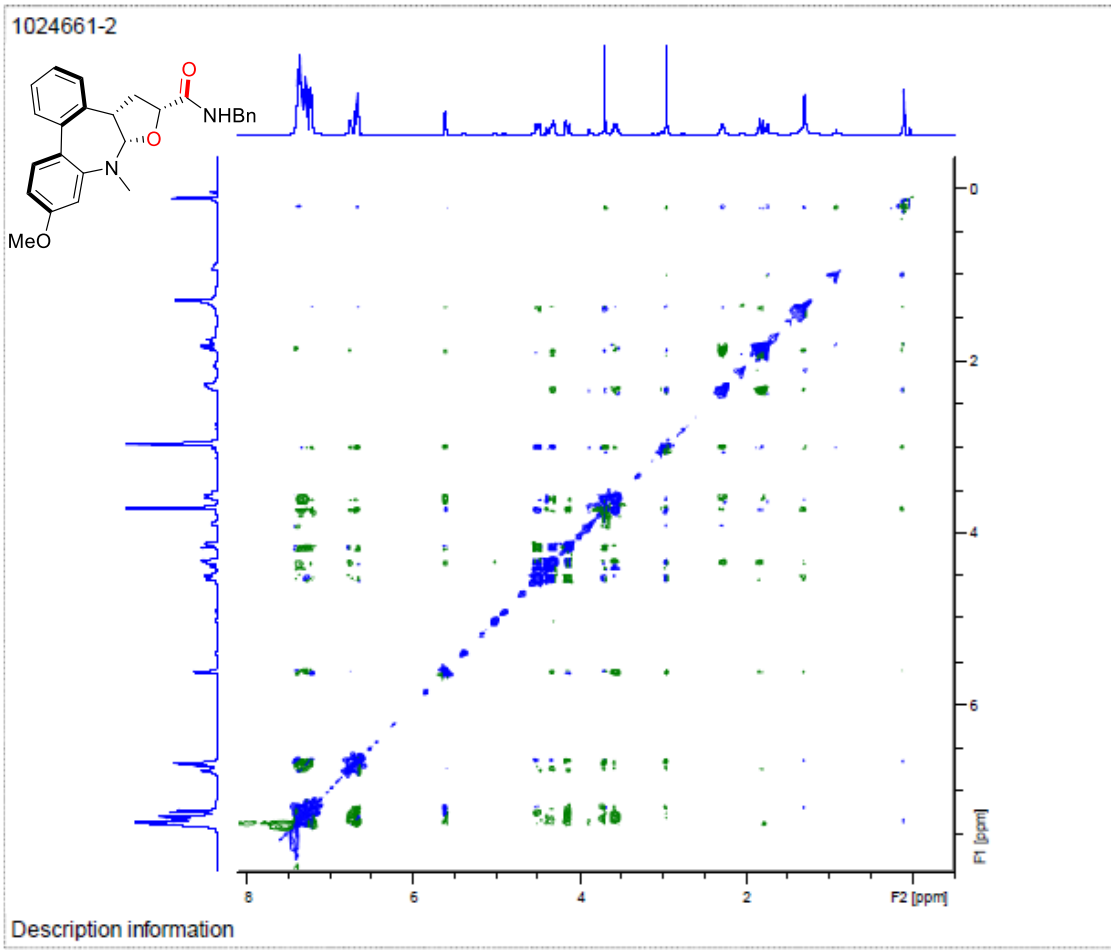
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