

Supporting Information

Imidazolylpyridine-In(OTf)₃ catalyzed enantioselective allylation of ketimines derived from isatins

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1. Experimental Section

1.1 General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX500 (500 MHz) spectrometer and tetramethylsilane (TMS) was used as a reference. Most of the products were known compounds and were identified by comparison of their physical and spectra data with those of authentic samples. Mass spectra are taken on a Thermo Scientific ISQ LT GC-MS instrument in the electron ionization (EI) mode. Enantiomeric excesses (ee) were determined by chiral HPLC using a Venusil CA column and Venusil CO column.

1.2 Procedure for the synthesis of ketimines derived from isatins

Isatin ketimines were synthesized by using the standard literature procedures.¹ To the solution of the isatin (5 mmol) in ethanol (10 mL) was added the corresponding aniline (5 mmol) in one portion. Then, the reaction mixture was reacted in reflux and stirred for 2h. Once the reaction completed, the contents were cooled to room temperature. The precipitated isatin ketimine was collected by filtration and then washed with a 10% ethanol/hexane mixture. The solid product was then air dried and used without further purification.

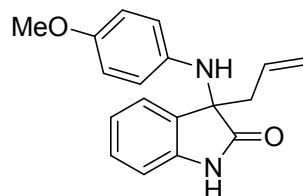
1.3 General procedure for the synthesis of 3-allyl 3-aminoxindoles

A mixture of In(OTf)₃ (0.005 mmol) and L1 (0.005 mmol) in methanol (1 mL) was stirred at room temperature for 1h. To the mixture were then added isatinimine (0.2 mmol), allyltributyltin (0.3 mmol) (caution! allyltributyltin is toxic and reactions should be conducted in a well-ventilated fume cupboard). After the starting material was consumed as indicated by TLC, the reaction mixture was poured into water and then extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with water (3 × 10 mL), dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography.

[1] N. A. Aslam, S. A. Babu, S. Rani, S. Mahajan, J. Solanki, M. Yasuda and A. Baba, *Eur. J. Org. Chem.*, **2015**, 4168.

2. Characterization of compounds

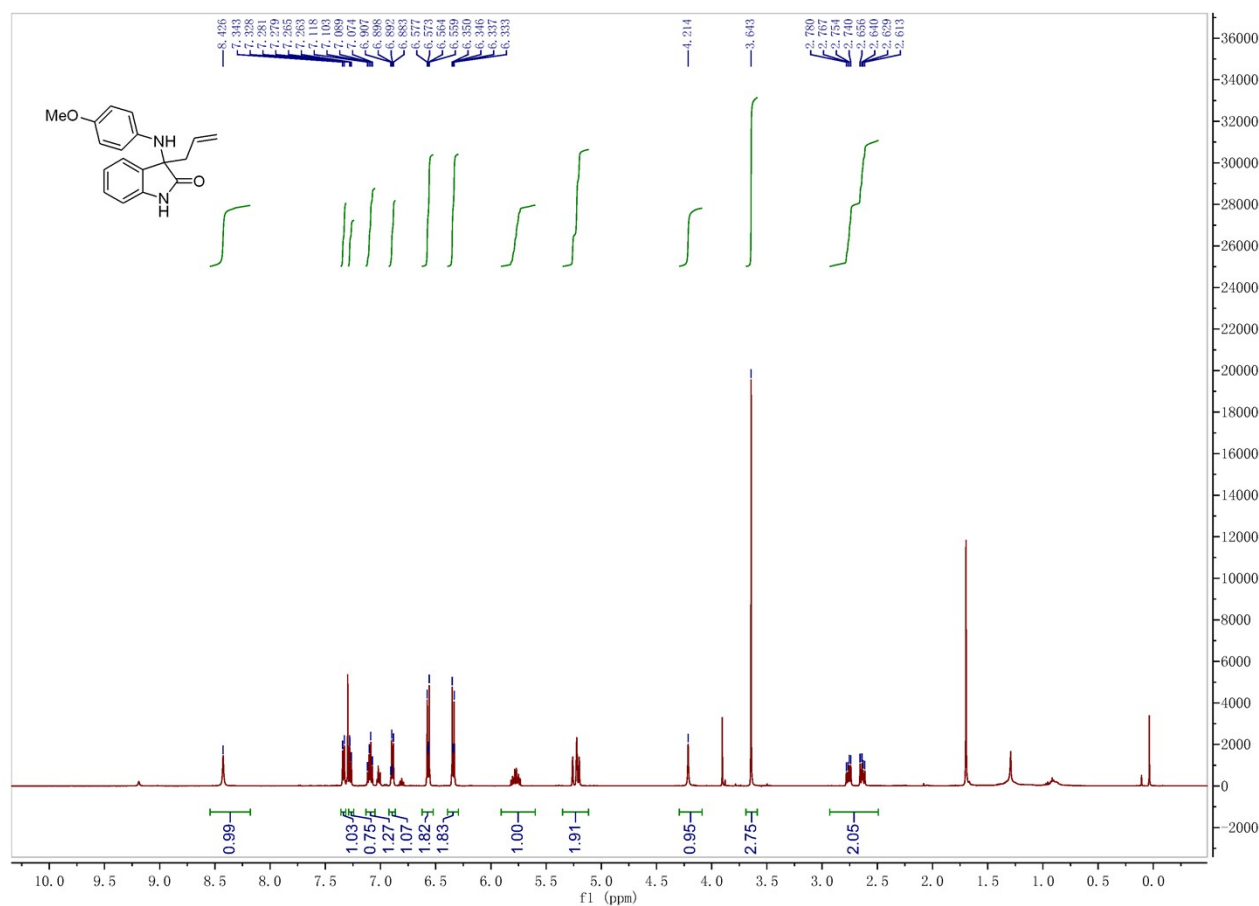
2.1 3-allyl-3-((4-methoxyphenyl)amino)indolin-2-one (2a)

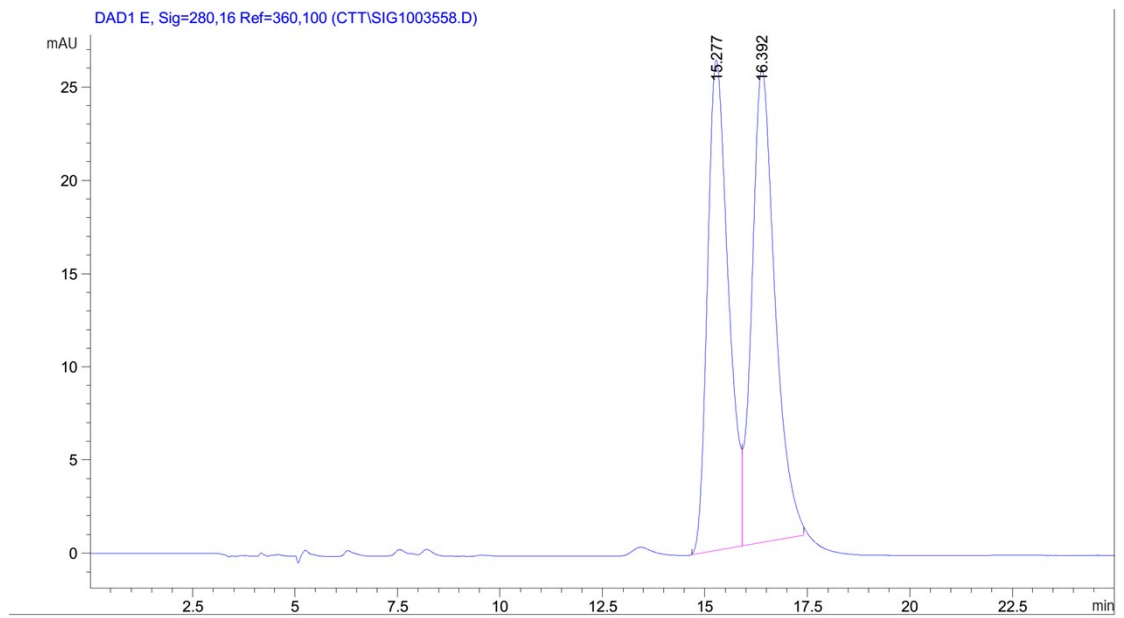
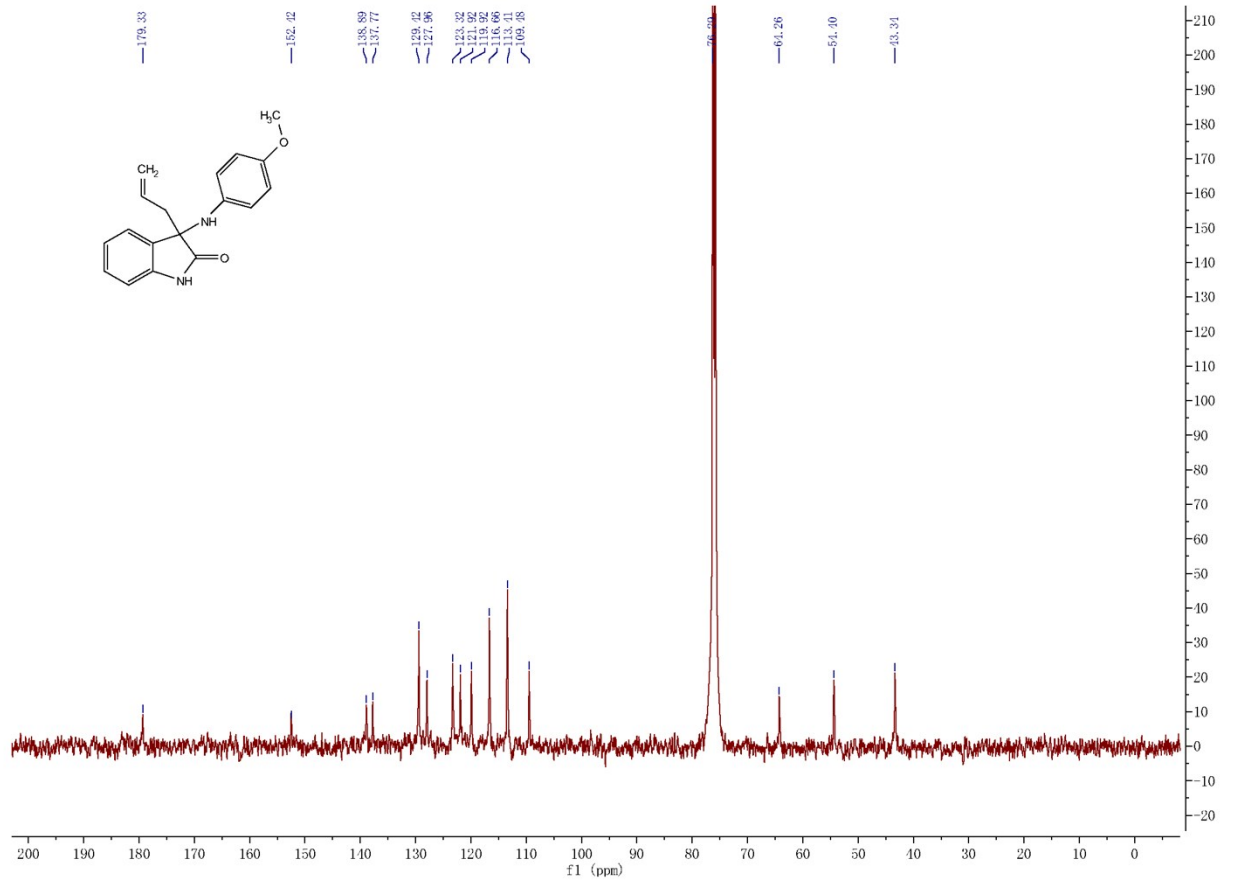


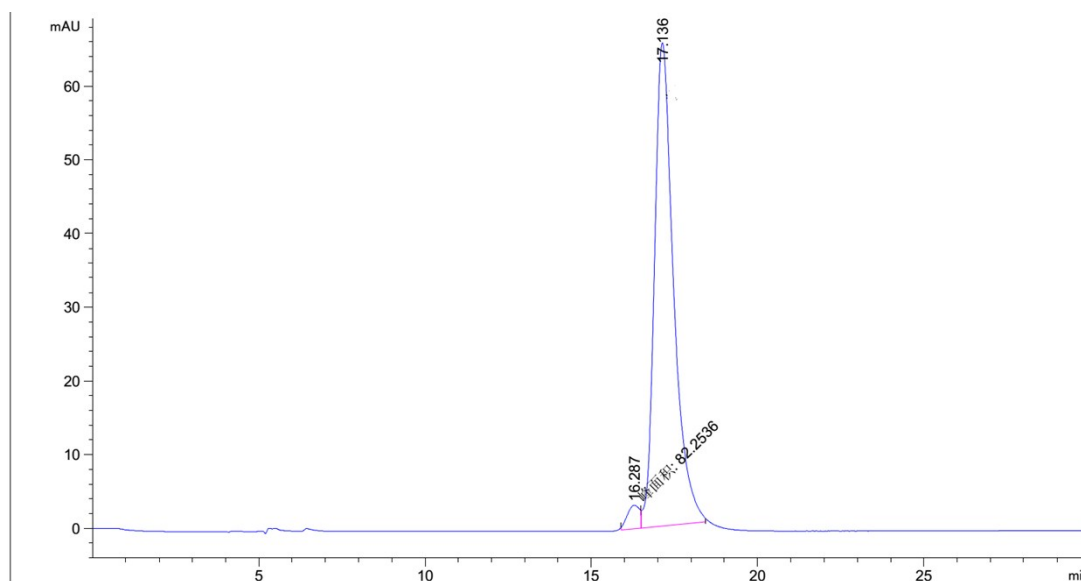
Chemical Formula: C₁₈H₁₈N₂O₂

Exact Mass: 294.14

Isolated as a colorless solid. $[\alpha]_D^{25} = +68.8$ (c = 0.50 in CH₂Cl₂). The *ee* (94%) was determined by HPLC analysis, Venusil CA column, Hexane/i-PrOH 80:20, flow rate=0.7 mL/min, UV= 280 nm, minor enantiomer $t_1 = 16.3$ min, major enantiomer $t_2 = 17.1$ min. ¹H NMR (500 MHz, CDCl₃) δ 8.43 (s, 1H), 7.34 (d, $J = 7.4$ Hz, 1H), 7.27 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.10 (dd, $J = 15.2, 7.2$ Hz, 1H), 6.89 (d, $J = 7.7$ Hz, 1H), 6.61 – 6.53 (m, 2H), 6.38 – 6.31 (m, 2H), 5.92 – 5.66 (m, 1H), 5.23 (t, $J = 14.7$ Hz, 2H), 4.21 (s, 1H), 3.64 (s, 3H), 2.70 (ddd, $J = 21.2, 13.3, 7.4$ Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 179.33, 152.42, 138.89, 137.77, 129.42, 127.96, 123.32, 121.92, 119.92, 116.66, 113.41, 109.48, 76.29, 64.26, 54.40, 43.34. MS (EI) m/z : 294 [M⁺].



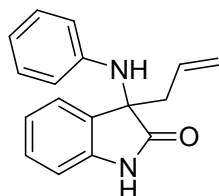




信号 1: DAD1 E, Sig=280,16 Ref=360,100

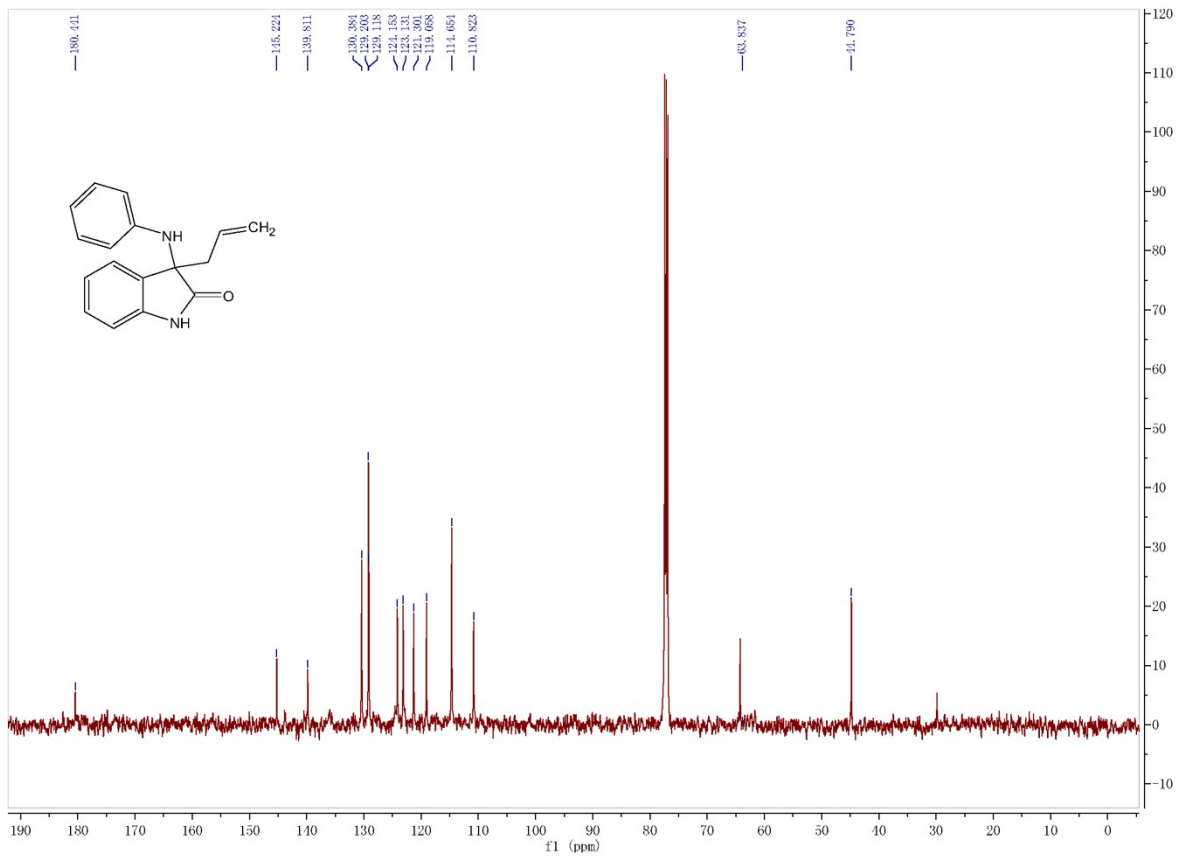
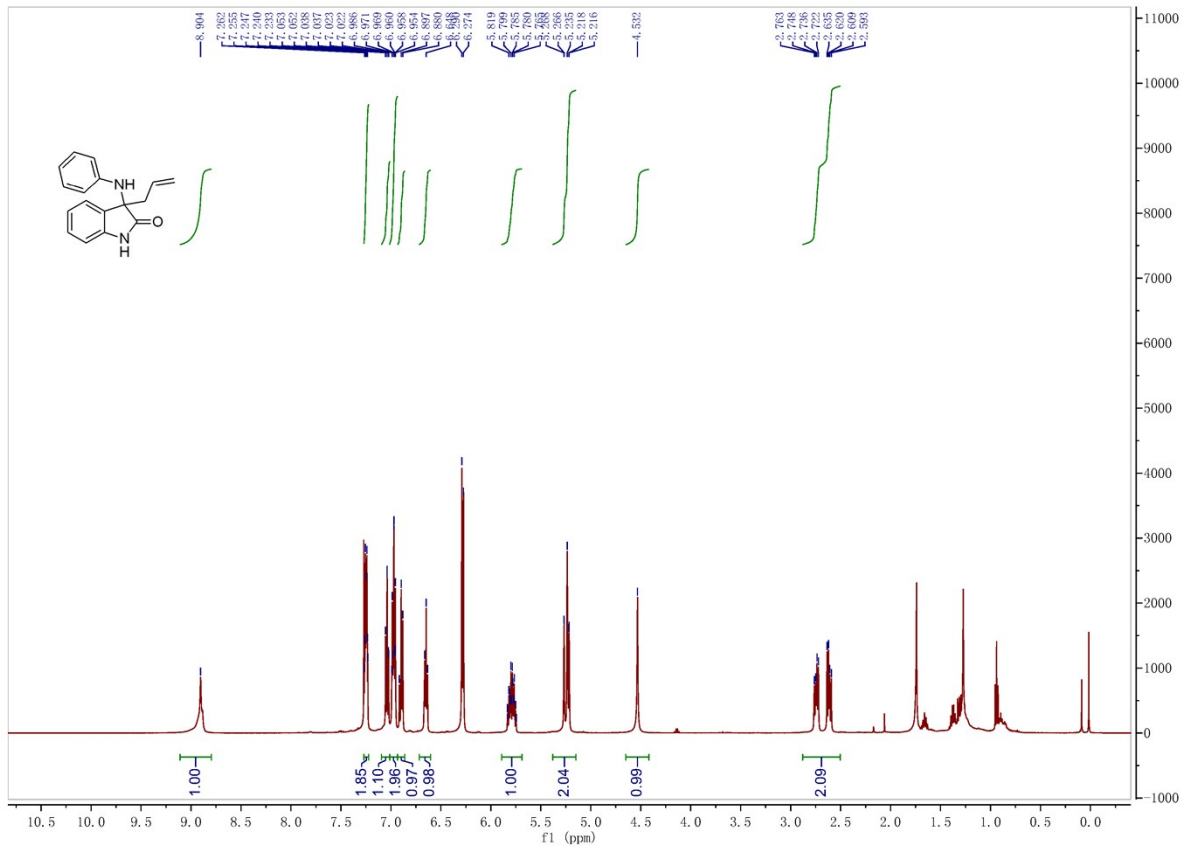
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.287	MF	0.4307	82.25359	3.18324	3.0464
2	17.136	FM	0.6656	2617.78369	65.55392	96.9536

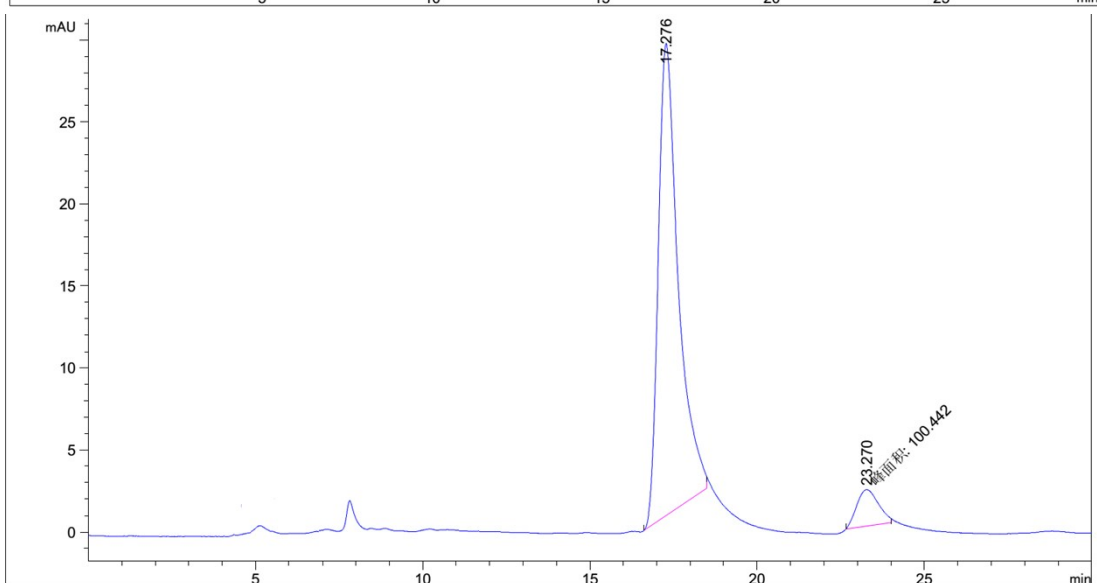
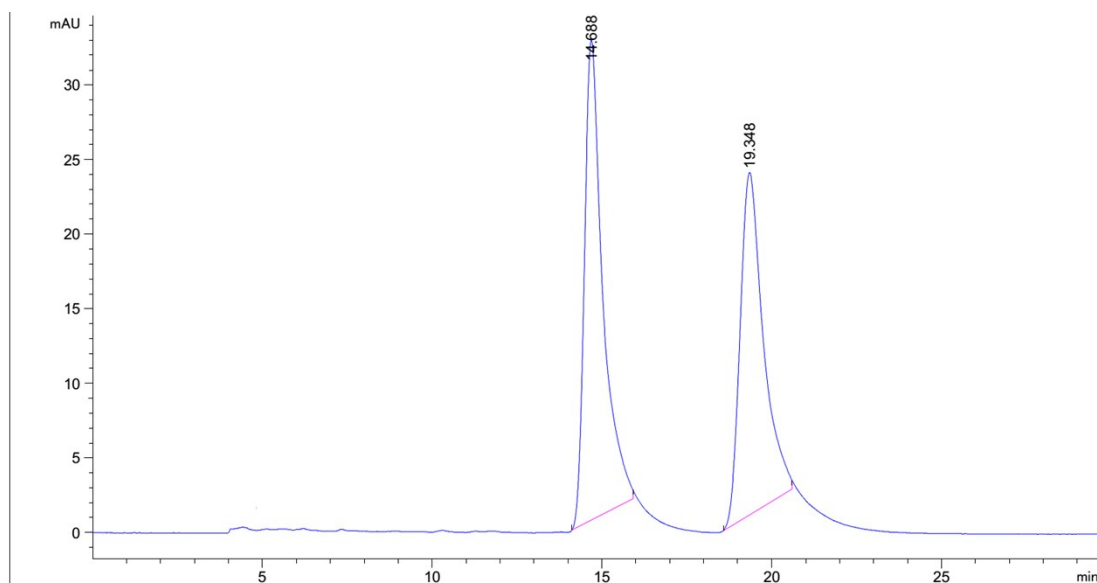
2.2 3-allyl-3-(phenylamino)indolin-2-one (2b)



Chemical Formula: C₁₇H₁₆N₂O
Exact Mass: 264.13

Isolated as a colorless solid. $[\alpha]_D^{25} = +60.0$ (c = 0.72 in CH₂Cl₂). The *ee* (84%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate = 0.7 mL/min, UV = 280 nm, minor enantiomer $t_1 = 21.3$ min, major enantiomer $t_2 = 17.3$ min. ¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 1H), 7.27 – 7.22 (m, 2H), 7.04 (td, $J = 7.7, 0.8$ Hz, 1H), 7.01 – 6.93 (m, 2H), 6.90 (t, $J = 8.9$ Hz, 1H), 6.65 (t, $J = 7.3$ Hz, 1H), 5.89 – 5.69 (m, 1H), 5.38 – 5.15 (m, 2H), 4.53 (s, 1H), 2.68 (ddd, $J = 64.3, 13.3, 7.4$ Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 180.44, 145.22, 139.81, 130.38, 129.16, 124.15, 123.13, 121.30, 119.06, 114.65, 110.82, 64.24, 44.79. MS (EI) m/z : 264 [M⁺].

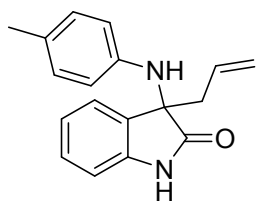




信号 1: DAD1 E, Sig=280,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.276	BB	0.6193	1202.56042	28.79307	92.2915
2	23.270	MM	0.7513	100.44203	2.22831	7.7085

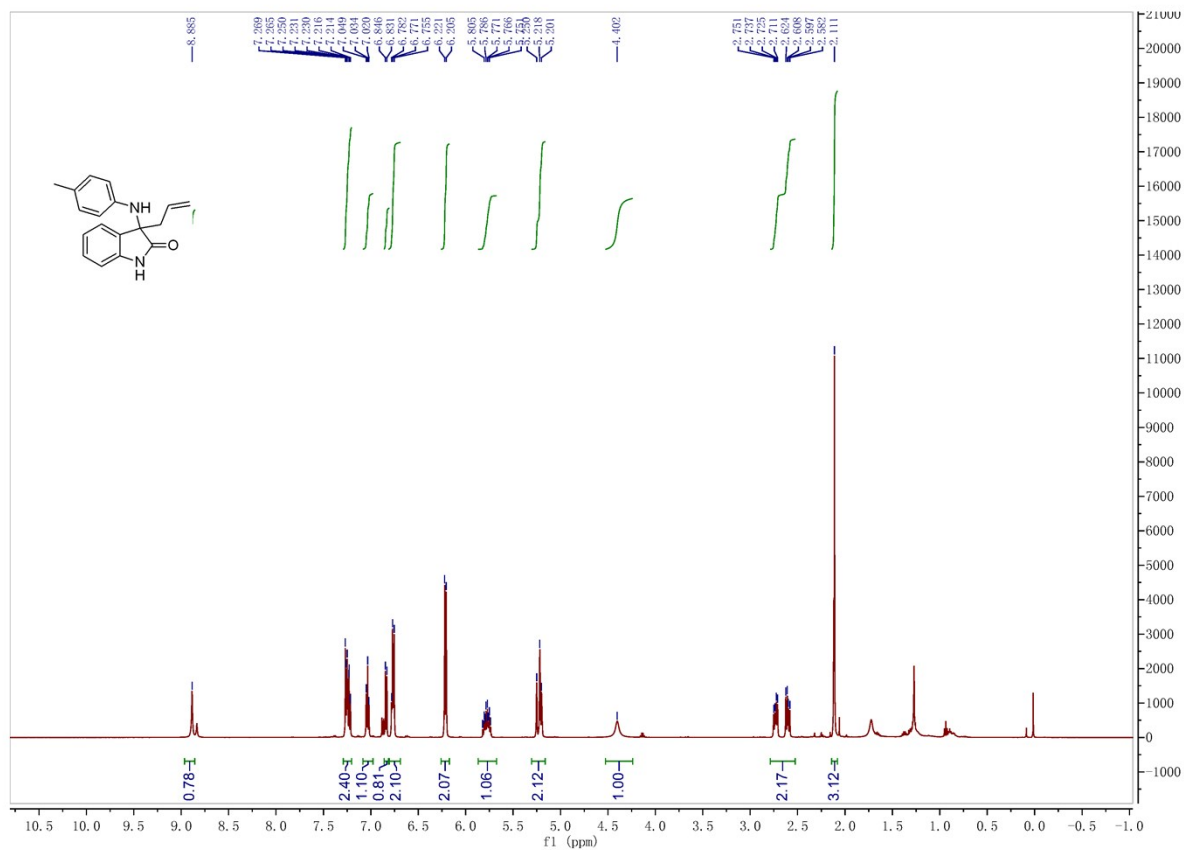
2.3 3-allyl-3-(p-tolylamino)indolin-2-one (2c)

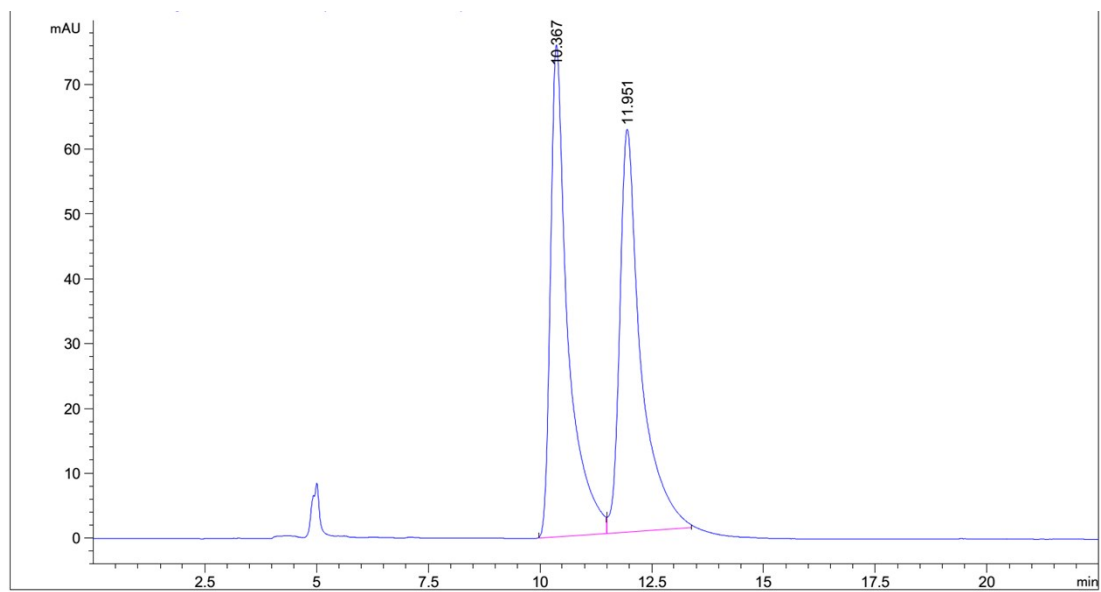
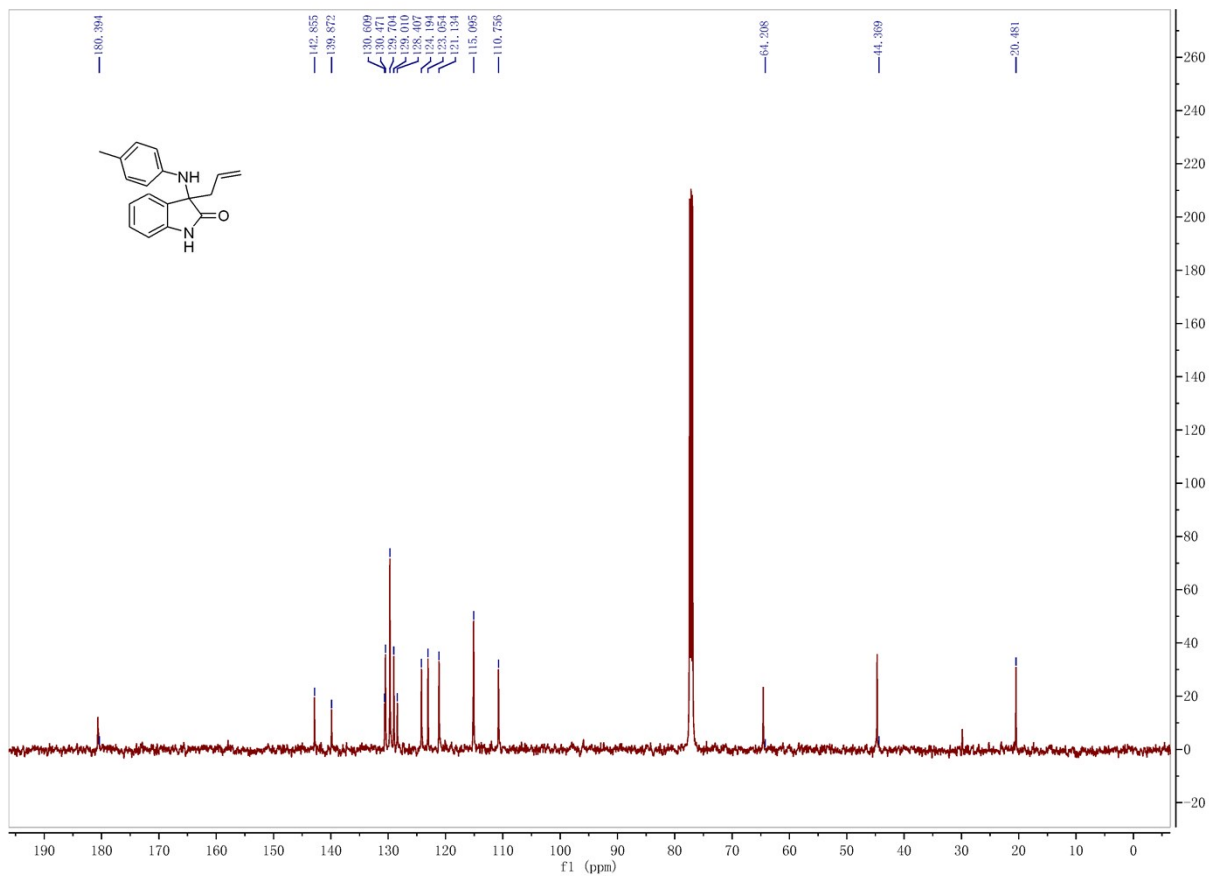


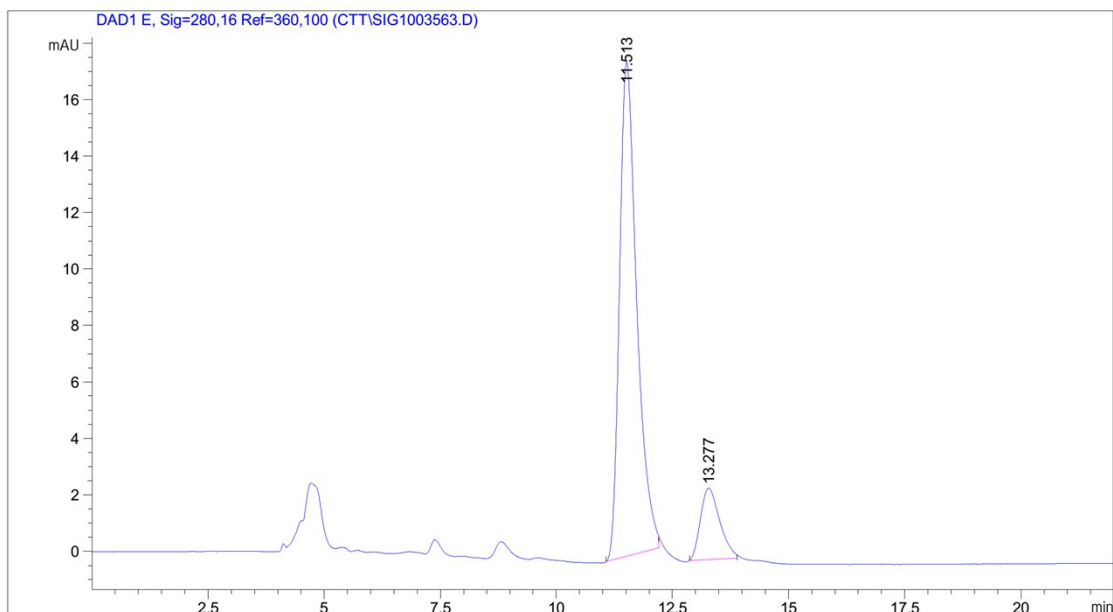
Chemical Formula: C₁₈H₁₈N₂O
Exact Mass: 278.14

Isolated as a colorless solid. $[\alpha]_D^{25} = +68.7$ (c = 0.61 in CH₂Cl₂). The ee (72%) was determined by

HPLC analysis, Venusil CA column, Hexane/i-PrOH 80:20, flow rate=0.7 mL/min, UV= 254 nm, minor enantiomer $t_1 = 13.3$ min, major enantiomer $t_2 = 11.5$ min. ^1H NMR (500 MHz, CDCl_3) δ 8.89 (s, 1H), 7.29 – 7.20 (m, 2H), 7.03 (t, $J = 7.2$ Hz, 1H), 6.84 (d, $J = 7.7$ Hz, 1H), 6.77 (t, $J = 6.9$ Hz, 2H), 6.21 (d, $J = 8.4$ Hz, 2H), 5.78 (ddt, $J = 14.8, 10.1, 7.4$ Hz, 1H), 5.22 (t, $J = 12.4$ Hz, 2H), 4.40 (s, 1H), 2.67 (ddd, $J = 64.4, 13.3, 7.4$ Hz, 2H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 180.39, 142.86, 139.87, 130.54, 129.70, 129.01, 128.41, 124.19, 123.05, 121.13, 115.09, 110.76, 44.37, 20.48. MS (EI) m/z : 278 $[\text{M}^+]$.



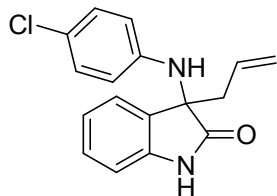




信号 1: DAD1 E, Sig=280,16 Ref=360,100

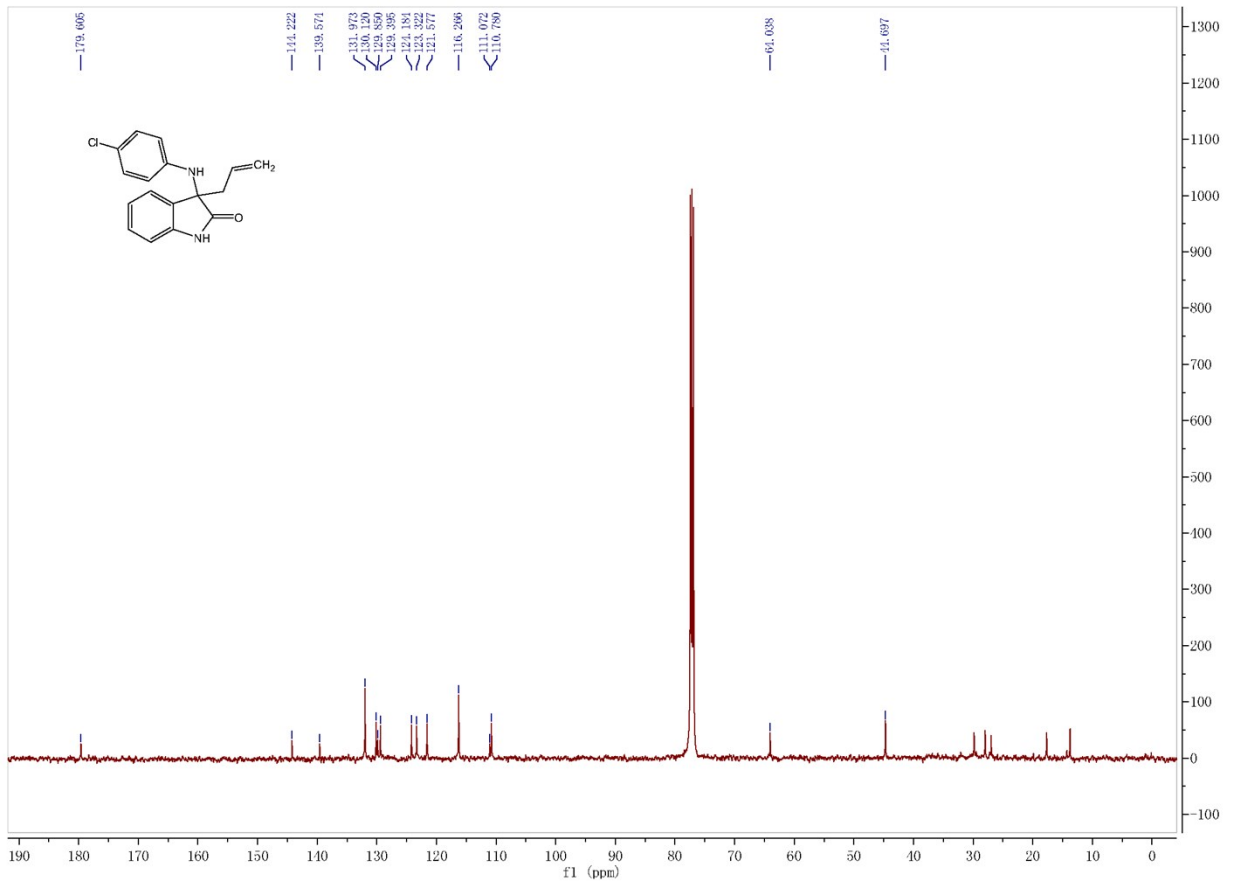
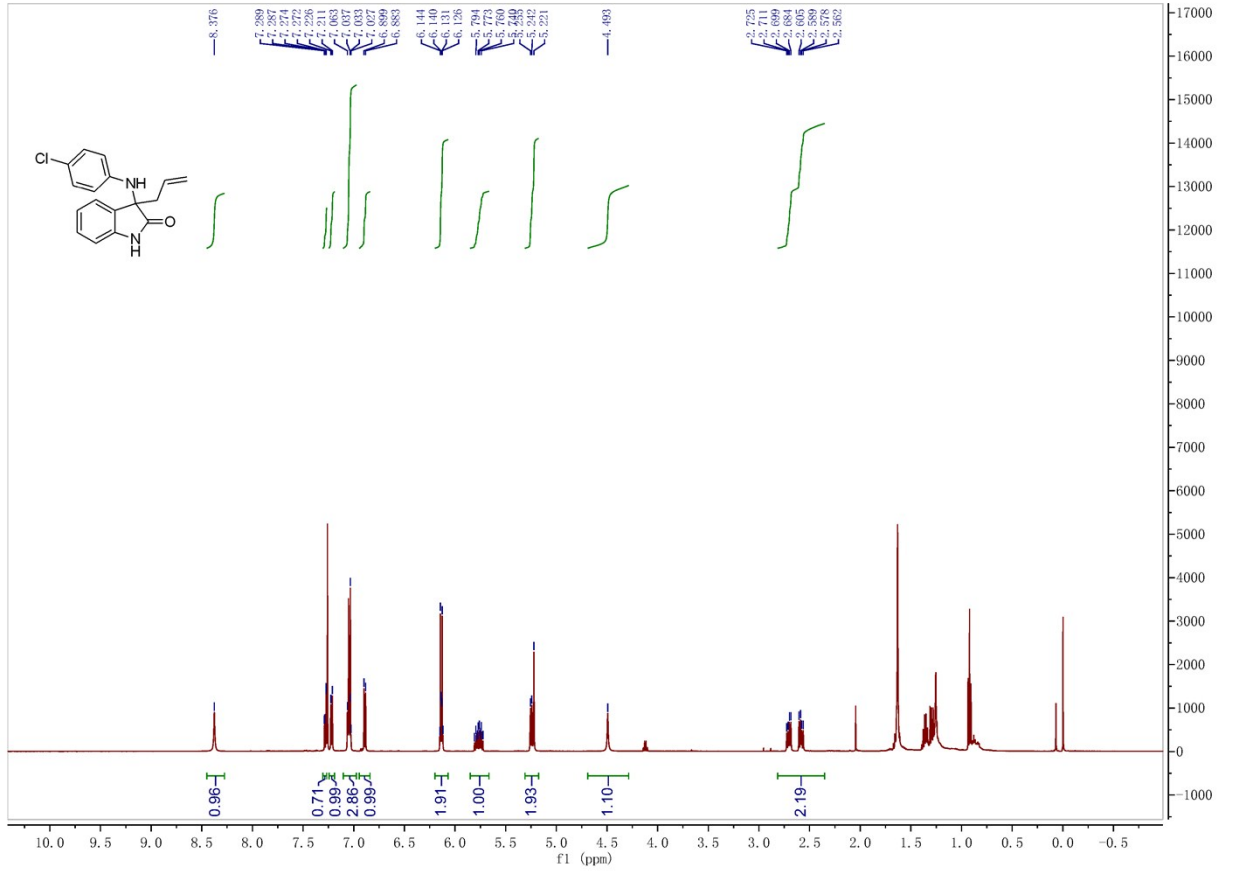
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1	11.513	BB	0.3872	452.04260	17.50709	86.1199
2	13.277	BB	0.4280	72.85679	2.52954	13.8801

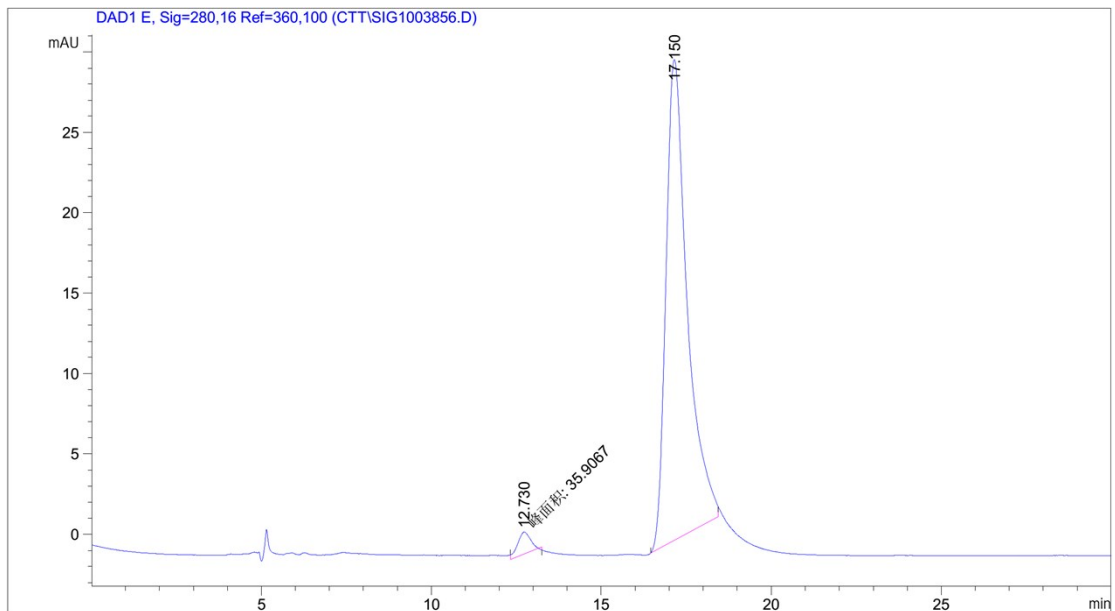
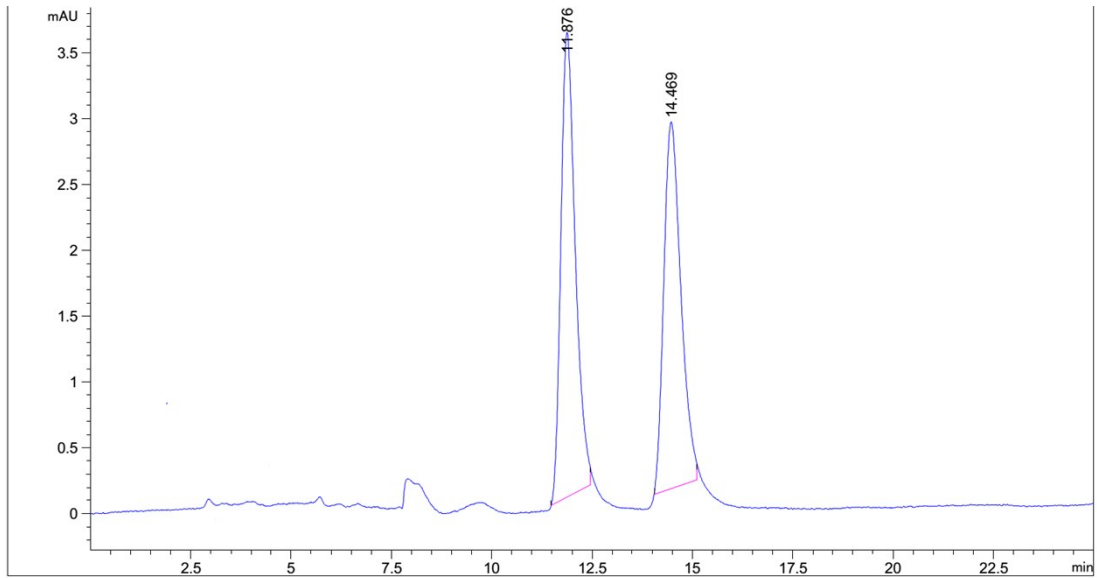
2,4 3-allyl-3-((4-chlorophenyl)amino)indolin-2-one (**2d**)



Chemical Formula: C₁₇H₁₅ClN₂O
Exact Mass: 298.09

Isolated as a brown solid. $[\alpha]_D^{25} = +87.3$ (c = 0.81 in CH₂Cl₂). The *ee* (94%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=0.7 mL/min, UV= 280 nm, minor enantiomer $t_1 = 12.7$ min, major enantiomer $t_2 = 17.1$ min. ¹H NMR (500 MHz, CDCl₃) δ 8.38 (s, 1H), 7.28 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.22 (d, $J = 7.3$ Hz, 1H), 7.10 – 6.97 (m, 3H), 6.89 (d, $J = 7.8$ Hz, 1H), 6.20 – 6.07 (m, 2H), 5.77 (ddt, $J = 17.4, 10.3, 7.4$ Hz, 1H), 5.31 – 5.18 (m, 2H), 4.49 (s, 1H), 2.64 (ddd, $J = 61.0, 13.4, 7.4$ Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 179.61, 144.22, 139.57, 131.97, 130.12, 129.85, 129.40, 124.18, 123.32, 121.58, 116.27, 111.07, 110.78, 64.04, 44.70. MS (EI) m/z : 298 [M⁺].

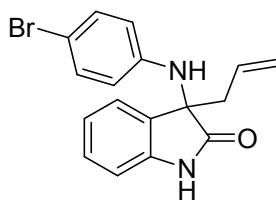




信号 1: DAD1 E, Sig=280,16 Ref=360,100

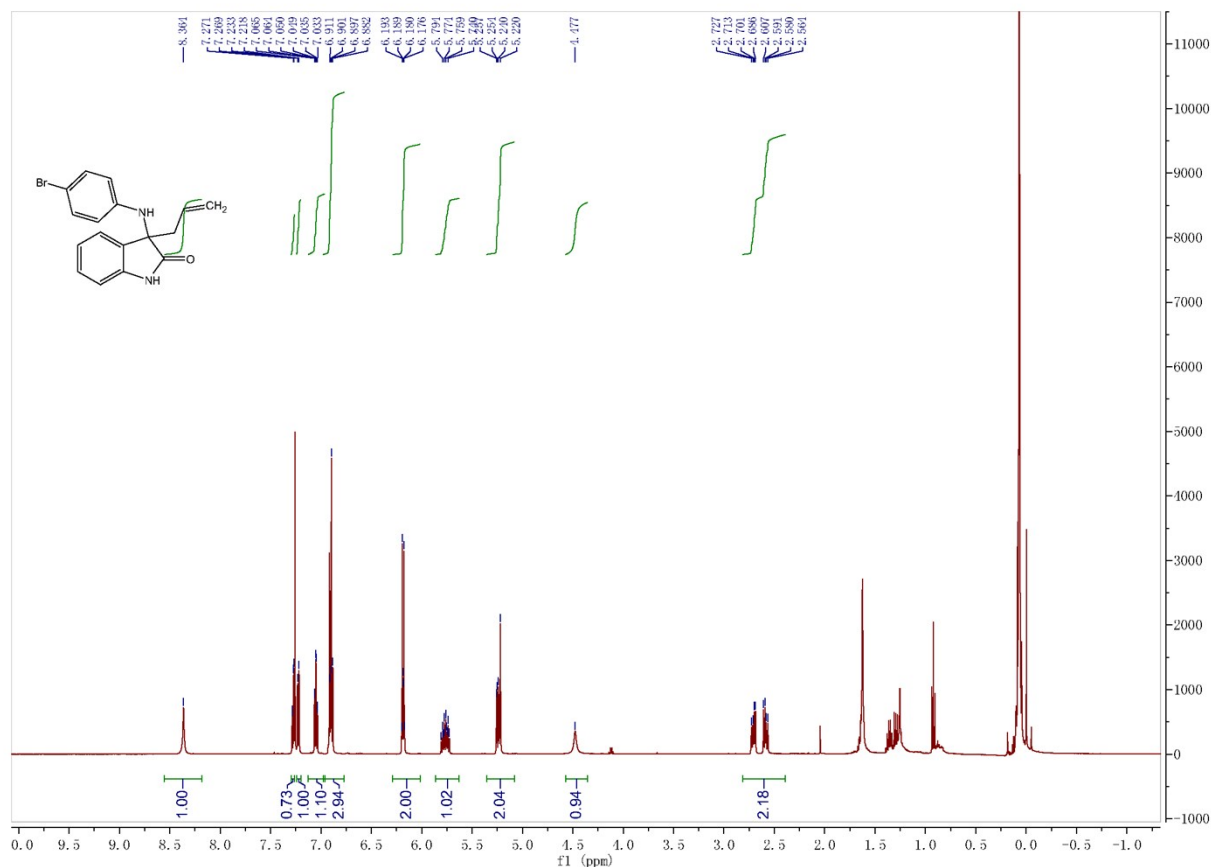
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.730	MM	0.4378	35.90672	1.36705	2.6770
2	17.150	BB	0.6455	1305.40759	29.89285	97.3230

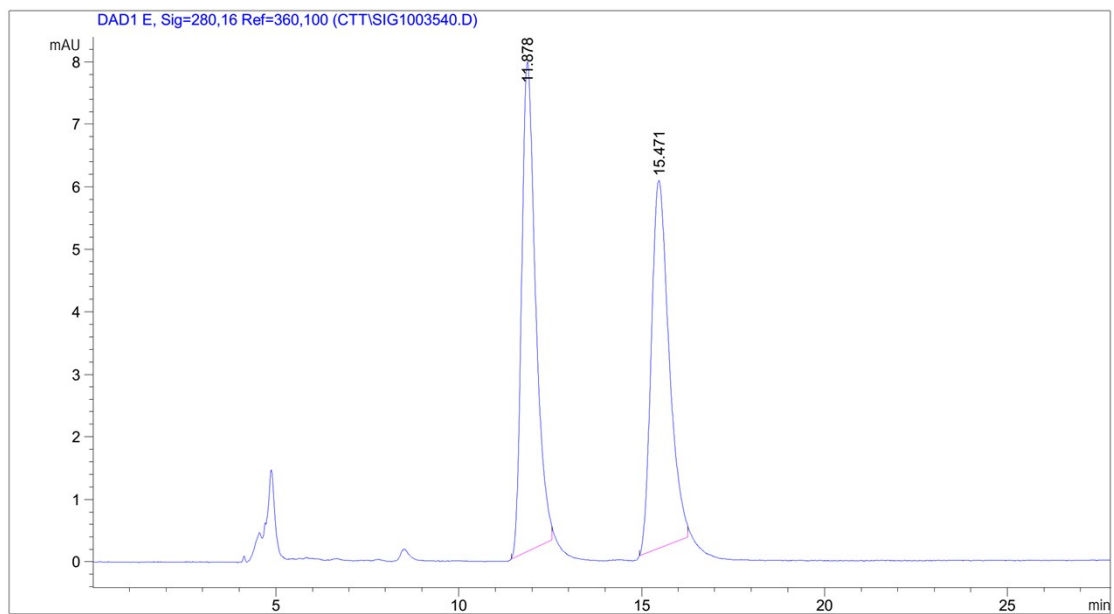
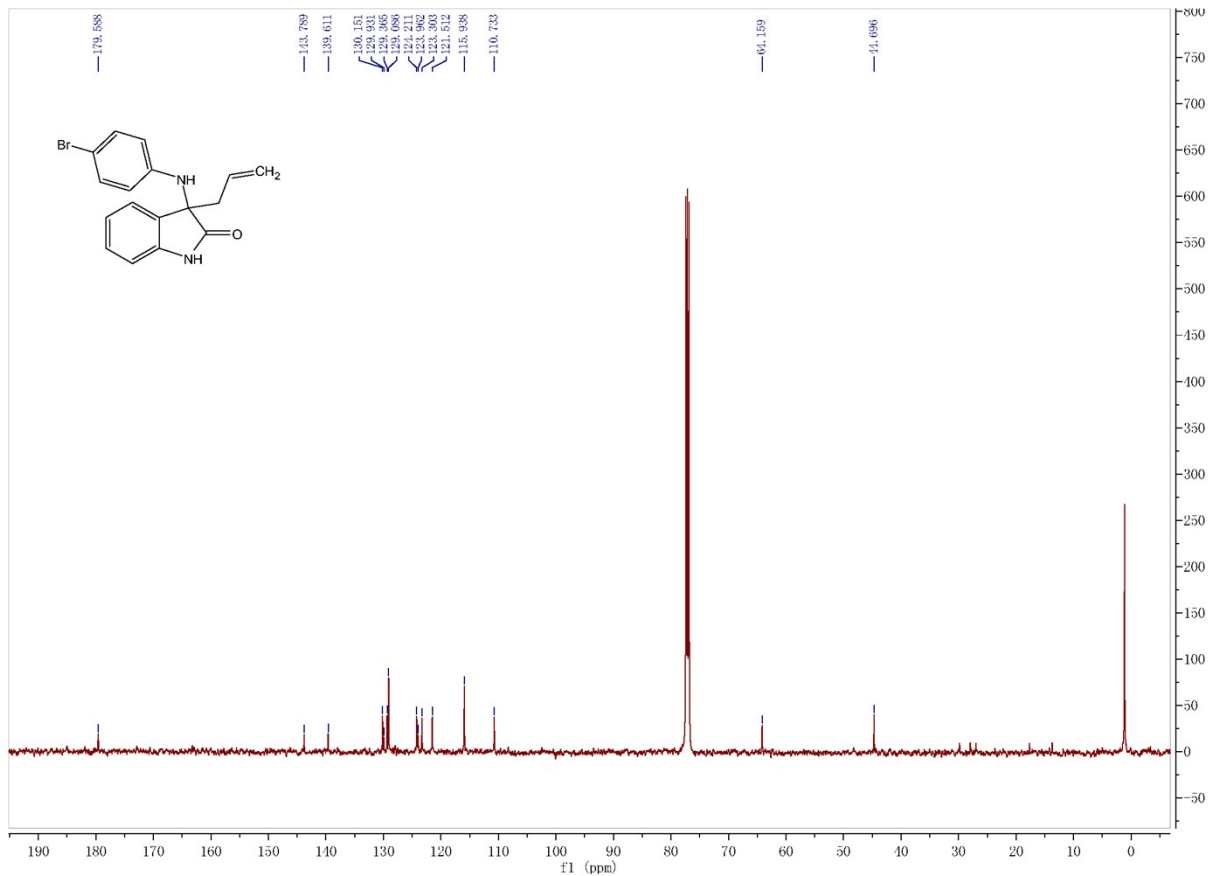
2.5 3-allyl-3-((4-bromophenyl)amino)indolin-2-one (2e)

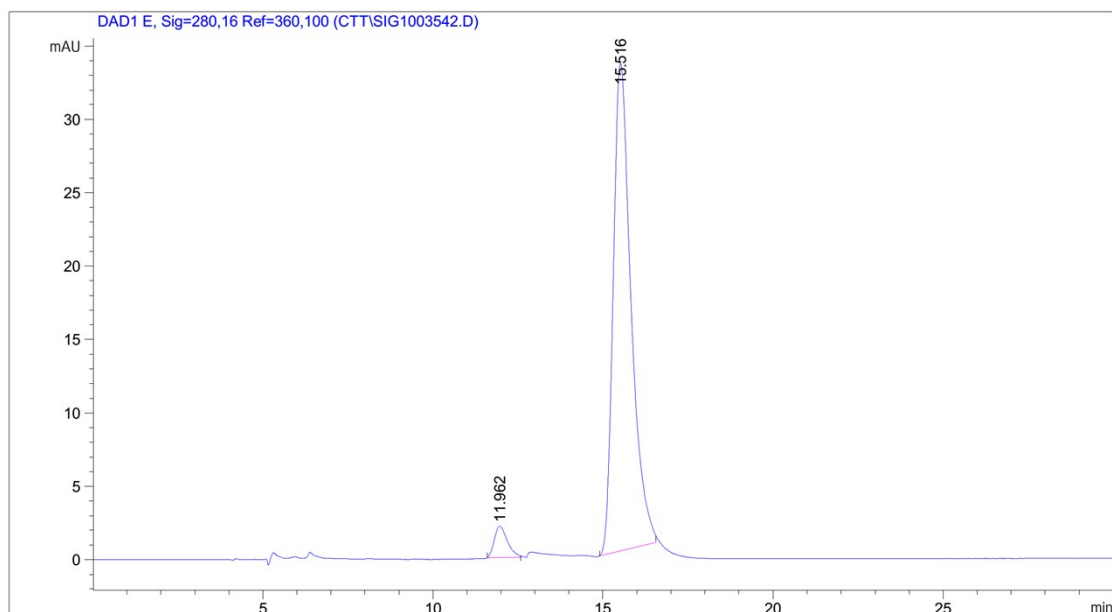


Chemical Formula: C₁₇H₁₅BrN₂O
Exact Mass: 342.04

Isolated as a brown solid. $[\alpha]_D^{25} = +81.5$ ($c = 0.79$ in CH_2Cl_2). The *ee* (91%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=0.7 mL/min, UV= 280 nm, minor enantiomer $t_1 = 12.0$ min, major enantiomer $t_2 = 15.5$ min. ^1H NMR (500 MHz, CDCl_3) δ 8.36 (s, 1H), 7.28 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.23 (d, $J = 7.3$ Hz, 1H), 7.05 (td, $J = 7.6, 0.8$ Hz, 1H), 6.90 (dd, $J = 8.2, 6.1$ Hz, 3H), 6.29–6.01 (m, 2H), 5.77 (ddt, $J = 17.3, 10.2, 7.5$ Hz, 1H), 5.24 (dd, $J = 12.9, 5.7$ Hz, 2H), 4.48 (s, 1H), 2.65 (ddd, $J = 61.1, 13.3, 7.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 179.59, 143.79, 139.61, 130.15, 129.93, 129.36, 129.09, 124.21, 123.96, 123.30, 121.51, 115.94, 110.73, 64.16, 44.70. MS (EI) m/z : 342 $[\text{M}^+]$.



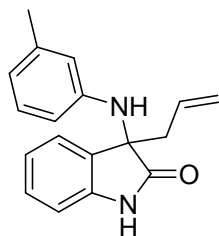




信号 1: DAD1 E, Sig=280,16 Ref=360,100

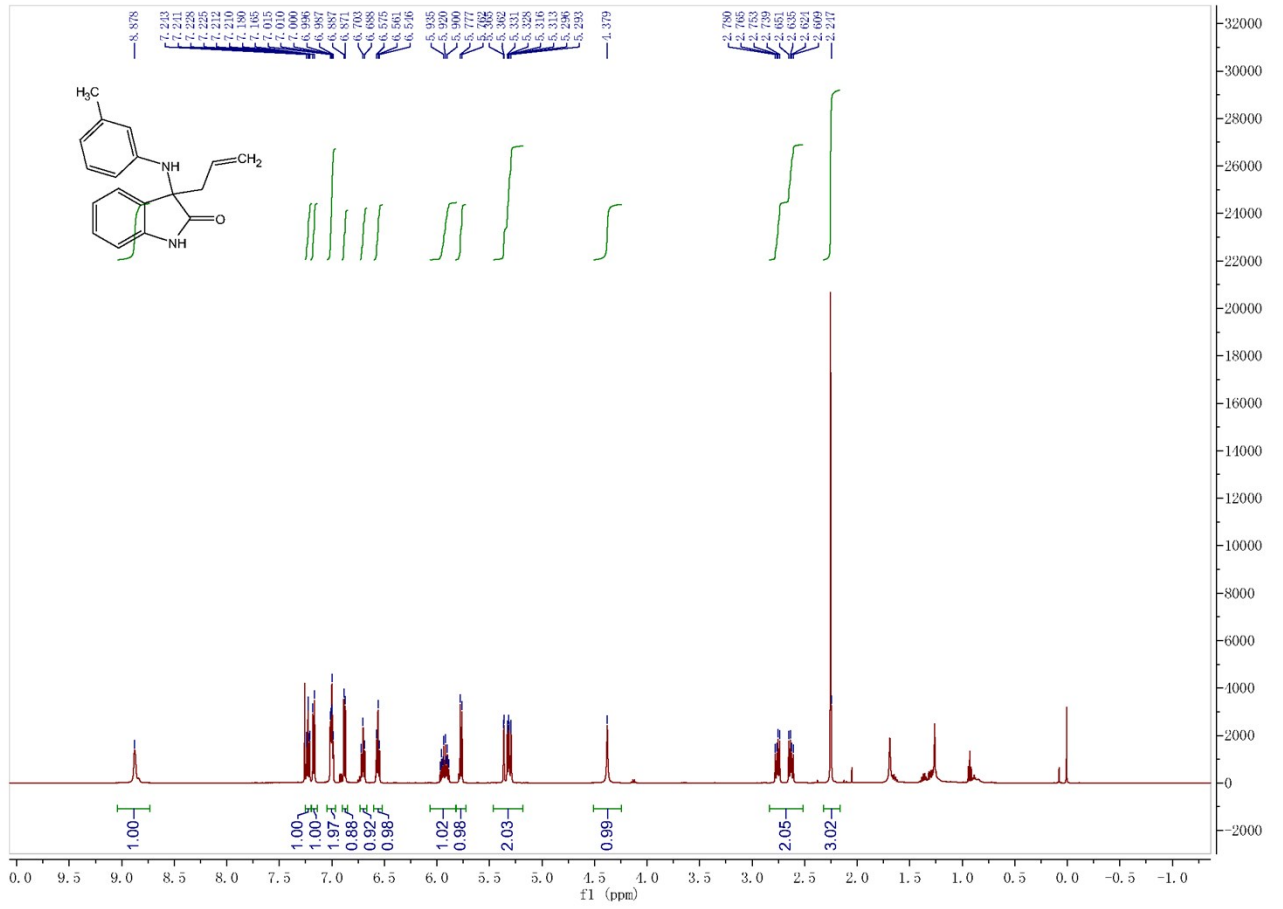
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.962	BB	0.4017	56.85746	2.14203	4.4940
2	15.516	BB	0.5484	1208.34241	33.21575	95.5060

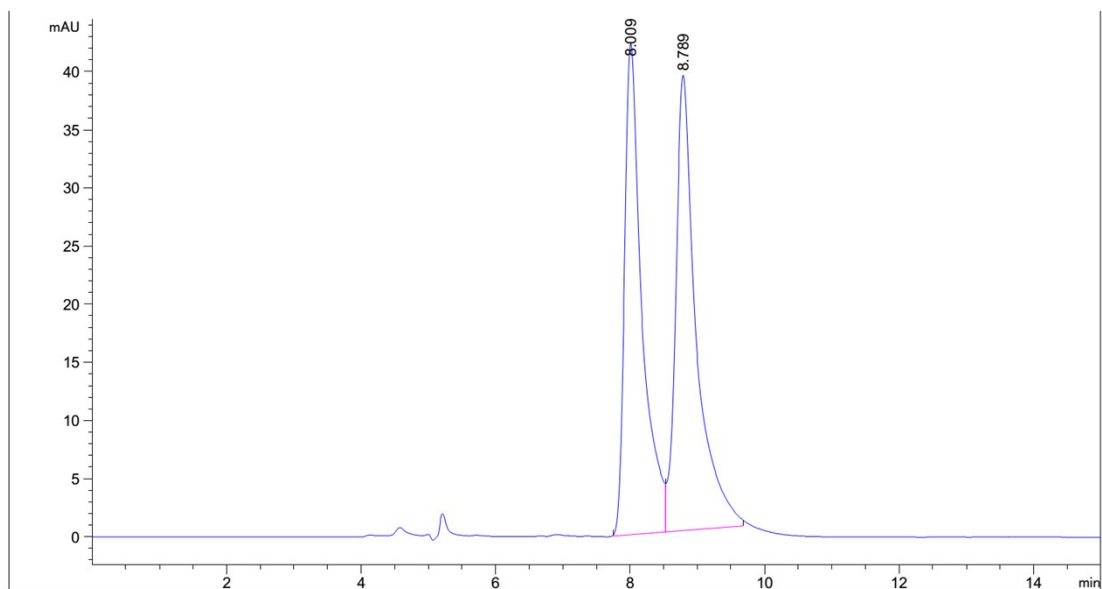
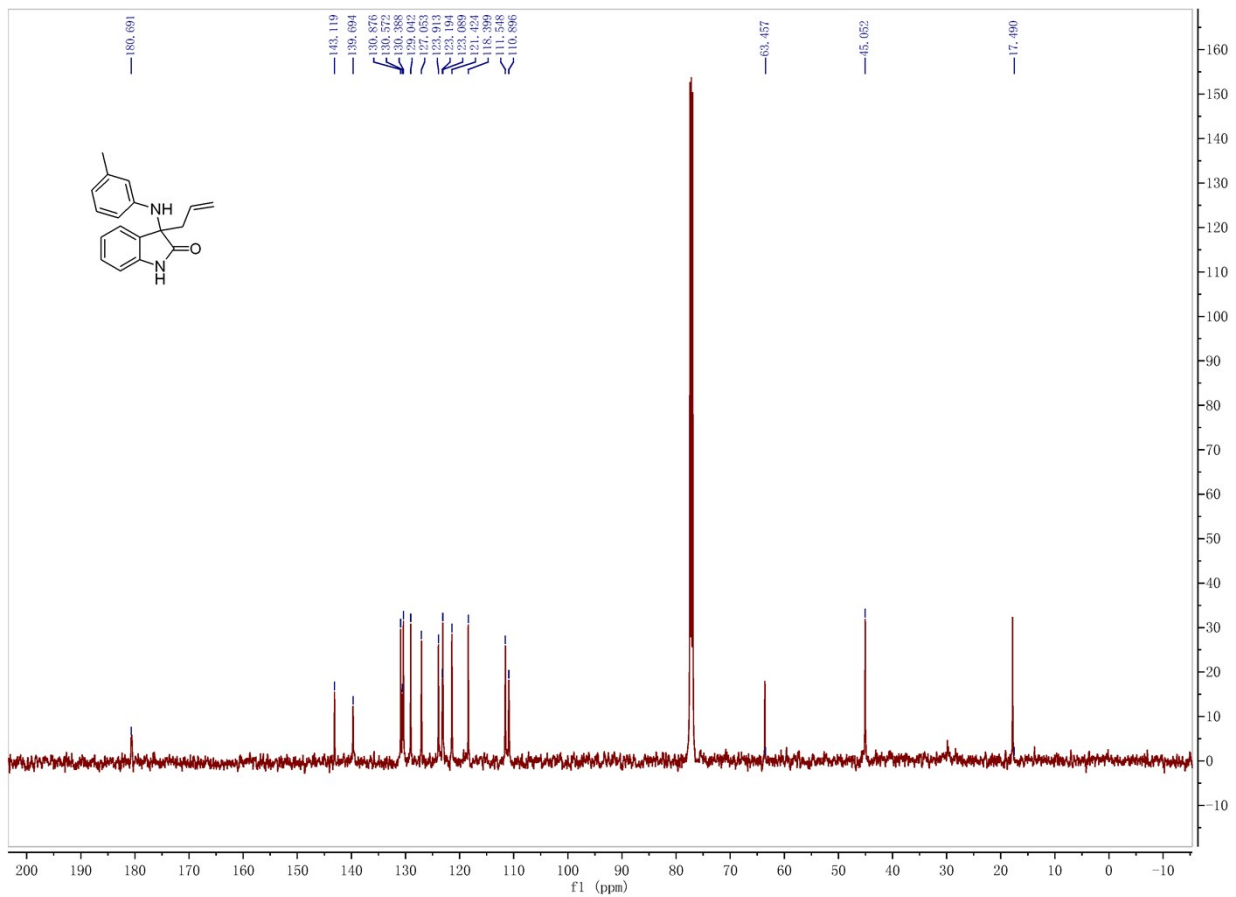
2.6 3-allyl-3-(*m*-tolylamino)indolin-2-one (2g)

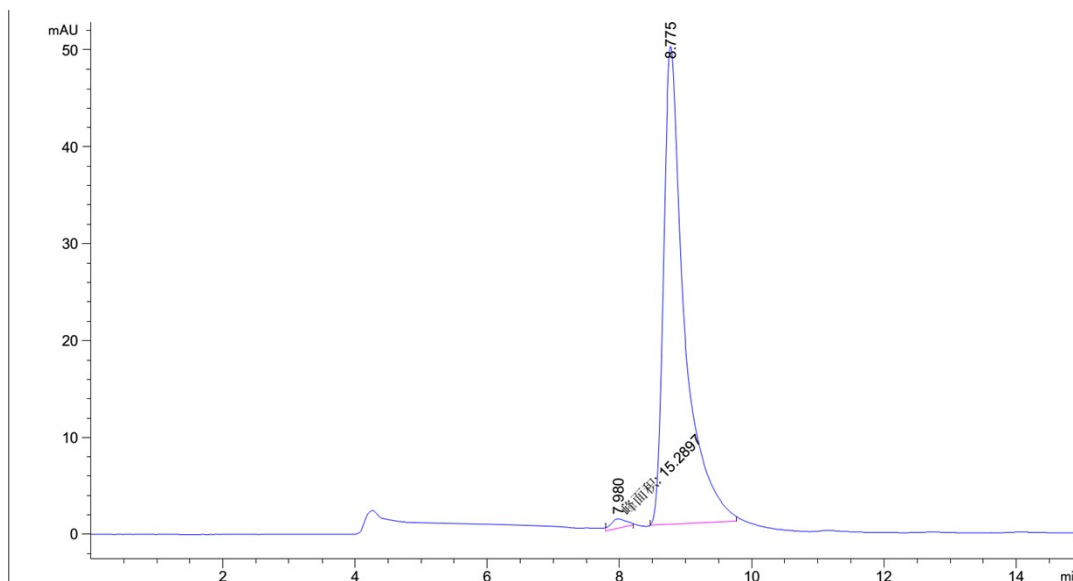


Chemical Formula: C₁₈H₁₈N₂O
Exact Mass: 278.14

Isolated as a colorless solid. $[\alpha]_D^{25} = +62.5$ ($c = 0.79$ in CH₂Cl₂). The *ee* (97%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=0.7 mL/min, UV= 280 nm, minor enantiomer $t_1 = 8.0$ min, major enantiomer $t_2 = 8.8$ min. ¹H NMR (500 MHz, CDCl₃) δ 8.88 (s, 1H), 7.23 (td, $J = 7.7, 1.1$ Hz, 1H), 7.17 (d, $J = 7.3$ Hz, 1H), 7.04 – 6.97 (m, 2H), 6.88 (d, $J = 7.8$ Hz, 1H), 6.70 (t, $J = 7.7$ Hz, 1H), 6.56 (t, $J = 7.1$ Hz, 1H), 5.93 (ddt, $J = 17.4, 10.0, 7.5$ Hz, 1H), 5.77 (d, $J = 7.8$ Hz, 1H), 5.33 (ddd, $J = 13.6, 11.6, 1.4$ Hz, 2H), 4.38 (s, 1H), 2.69 (ddd, $J = 64.9, 13.4, 7.5$ Hz, 2H), 2.25 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 180.69, 143.12, 139.69, 130.88, 130.57, 130.39, 129.04, 127.05, 123.91, 123.19, 123.09, 121.42, 118.40, 111.55, 110.90, 63.46, 45.05, 17.49. MS (EI) m/z : 278 [M⁺].



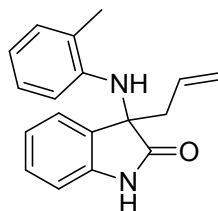




信号 1: DAD1 E, Sig=280,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.980	MM	0.2650	15.28968	9.61651e-1	1.4013
2	8.775	BB	0.3145	1075.77979	49.30687	98.5987

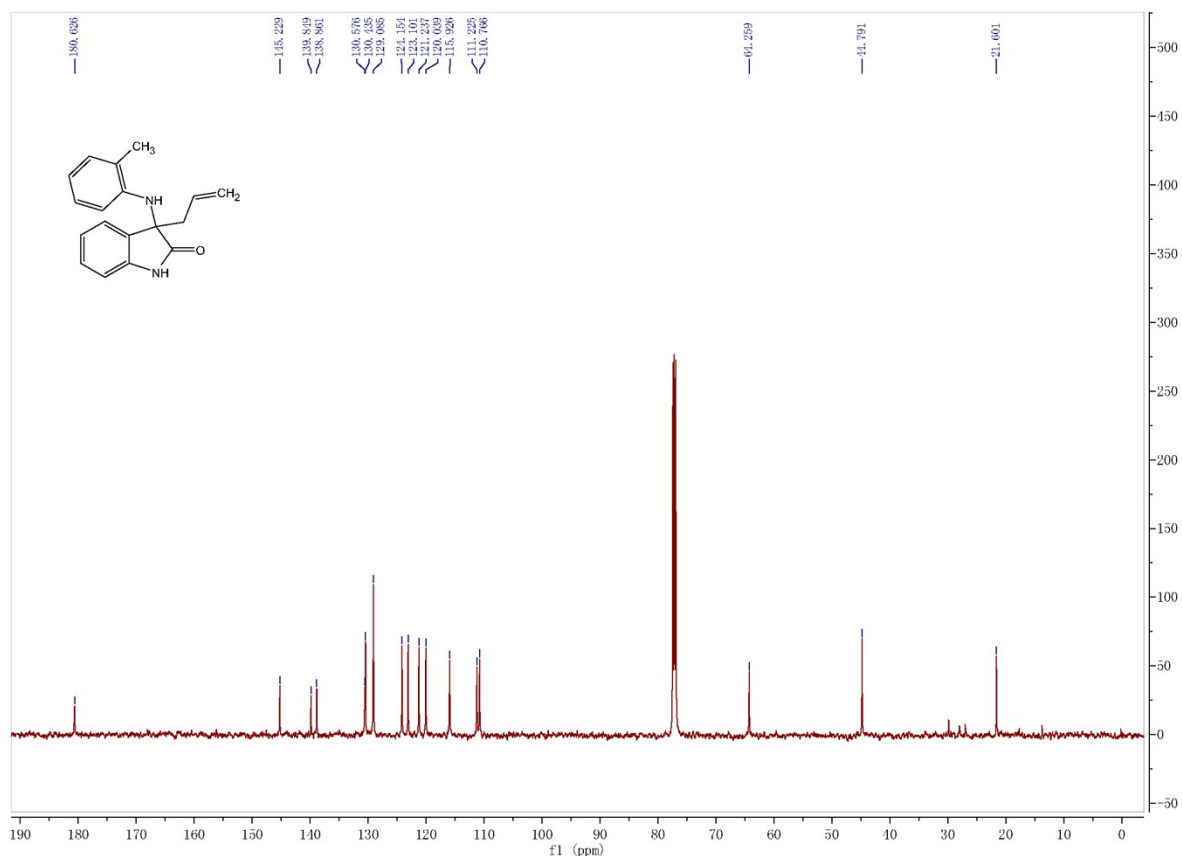
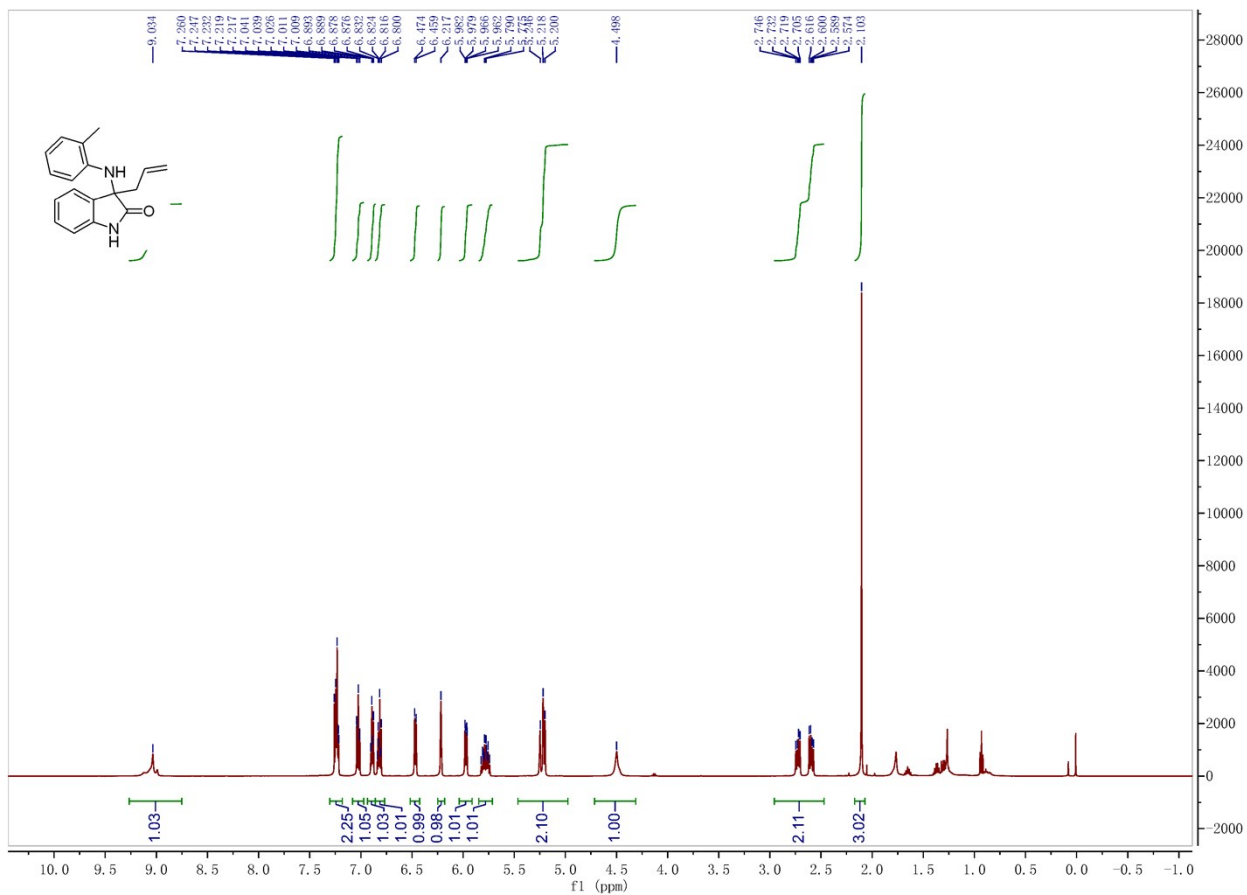
2.7.3-allyl-3-(*o*-tolylamino)indolin-2-one (**2h**)

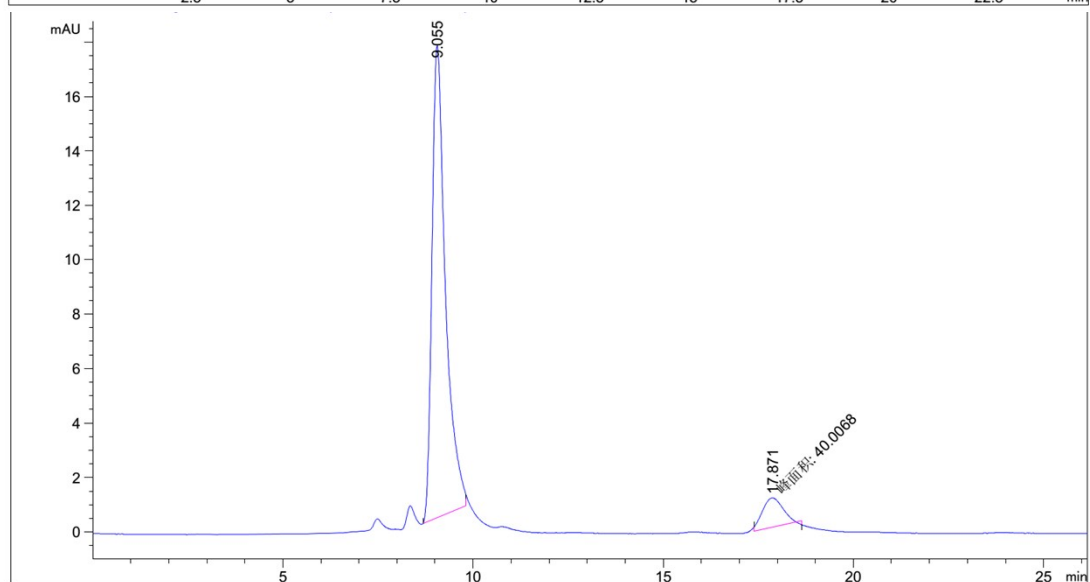
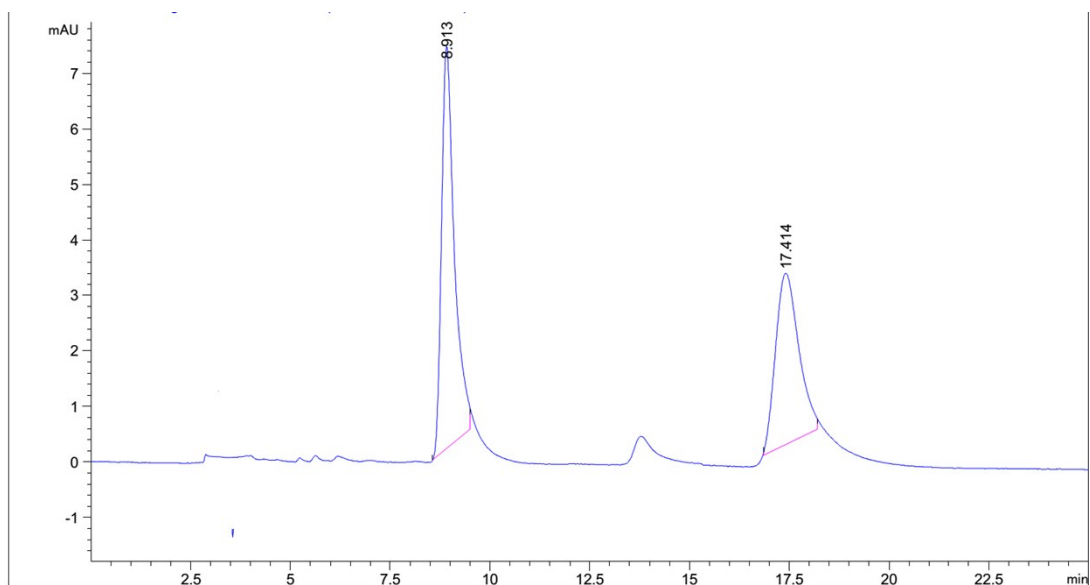


Chemical Formula: C₁₈H₁₈N₂O
Exact Mass: 278.14

f

Isolated as a colorless solid. $[\alpha]_D^{25} = +106.4$ (c =0.55 in CH₂Cl₂). The *ee* (83%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=1.0 mL/min, UV= 280 nm, minor enantiomer $t_1 = 17.8$ min, major enantiomer $t_2 = 9.0$ min. ¹H NMR (500 MHz, CDCl₃) δ 9.03 (s, 1H), 7.32 – 7.17 (m, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.82 (td, *J* = 7.8, 3.8 Hz, 1H), 6.47 (d, *J* = 7.4 Hz, 1H), 6.22 (s, 1H), 5.97 (d, *J* = 9.6 Hz, 1H), 5.77 (dddd, *J* = 17.3, 9.9, 7.5, 2.6 Hz, 1H), 5.37 – 5.03 (m, 2H), 4.50 (s, 1H), 2.66 (ddd, *J* = 65.8, 13.3, 7.4 Hz, 2H), 2.10 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 180.61, 145.21, 139.84, 138.85, 130.56, 130.42, 129.07, 124.14, 123.09, 121.22, 120.03, 115.91, 111.21, 110.75, 64.25, 44.79, 21.60. MS (EI) *m/z*: 278 [M⁺].

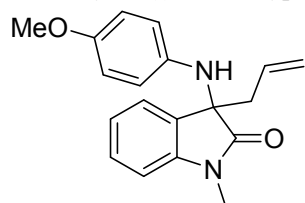




信号 1: DAD1 E, Sig=280,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.055	BB	0.3644	428.94345	17.35337	91.4689
2	17.871	MM	0.6210	40.00675	1.07376	8.5311

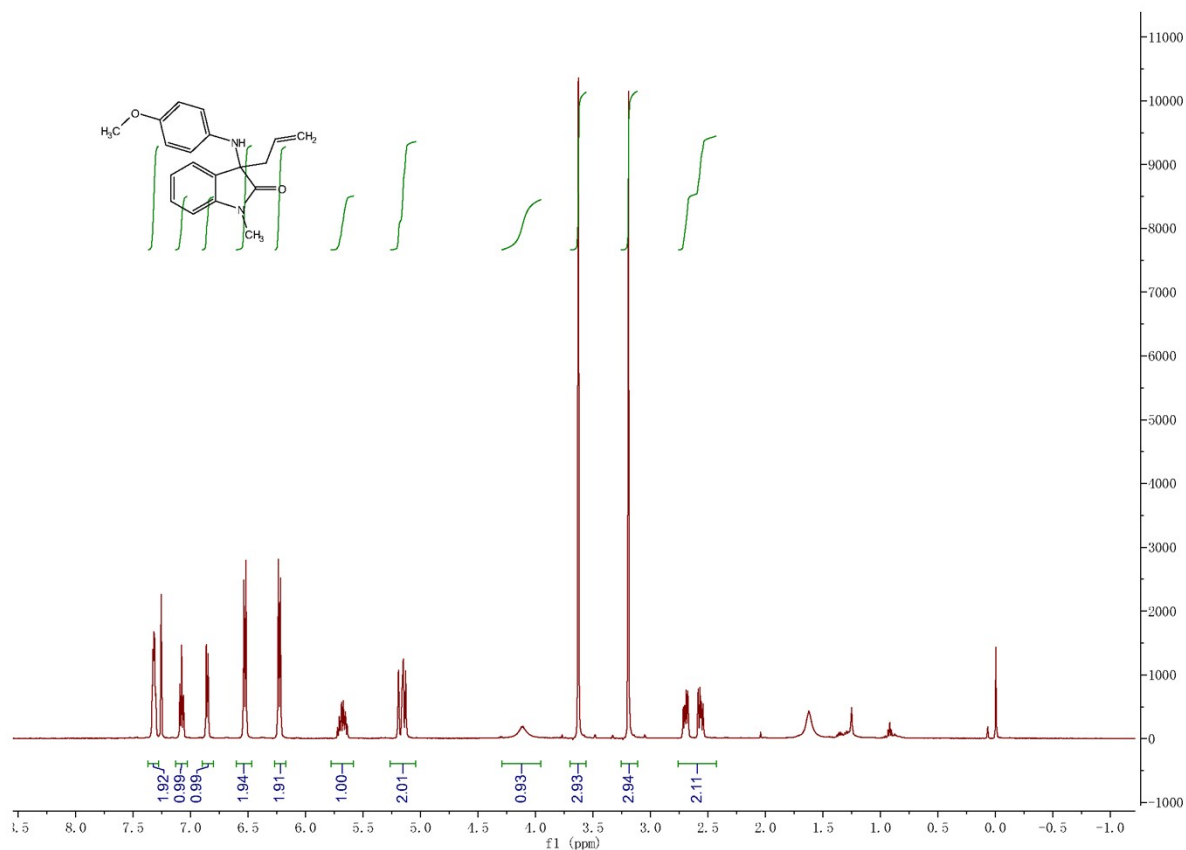
2.8 3-allyl-3-((4-methoxyphenyl)amino)-1-methylindolin-2-one (**2i**)

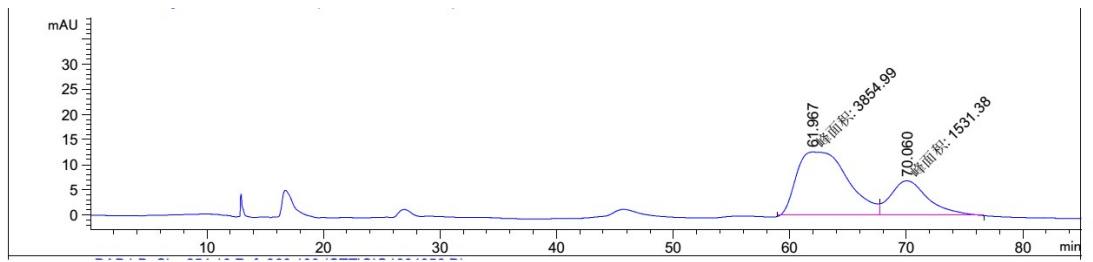
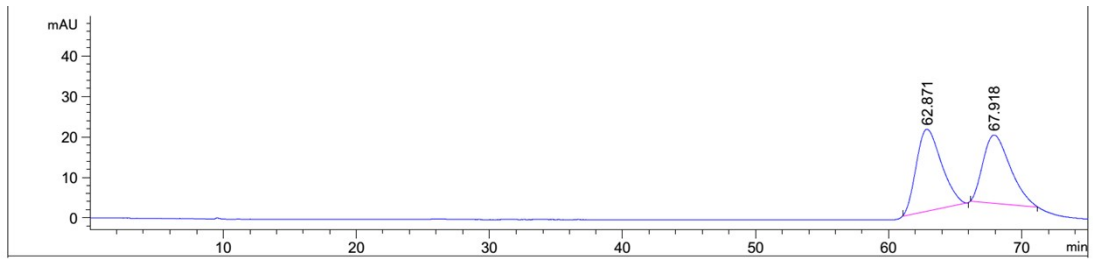
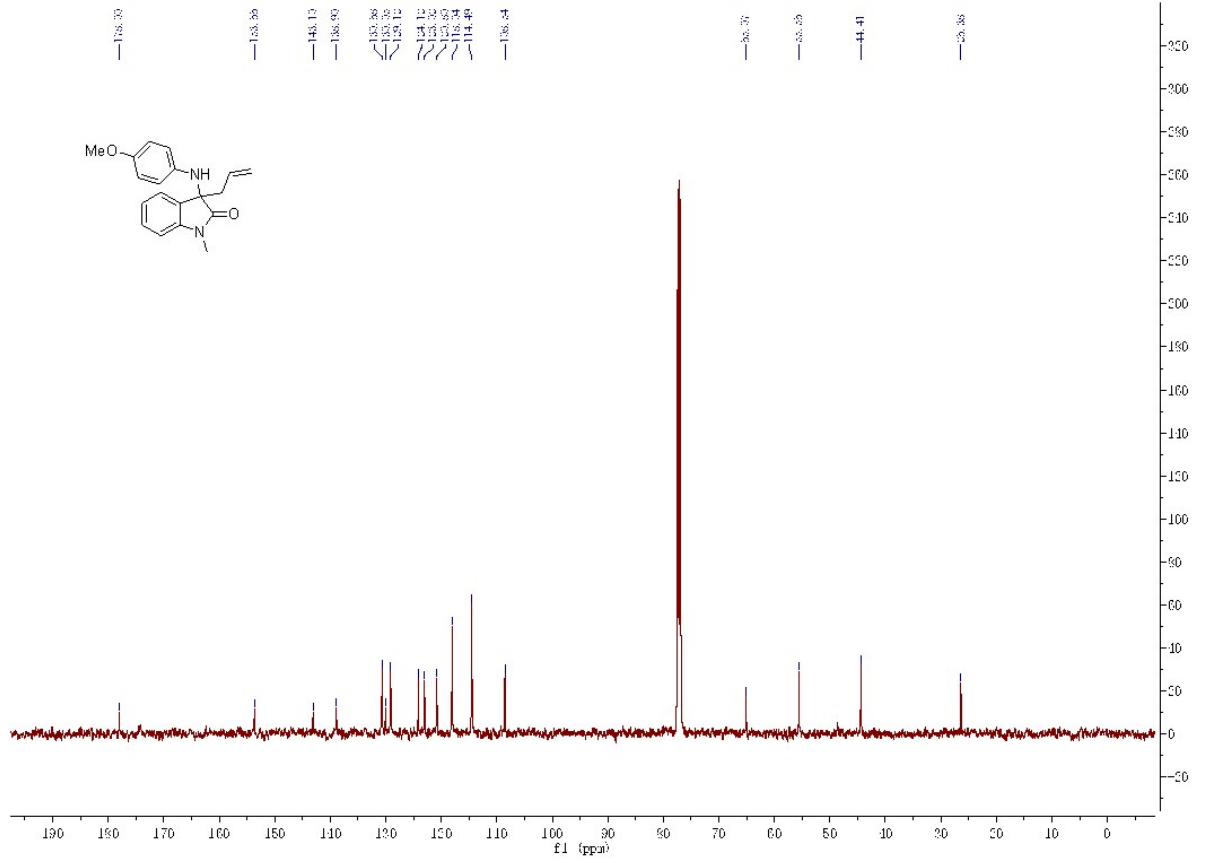


Chemical Formula: C₁₉H₂₀N₂O₂
Exact Mass: 308.15

Isolated as a colorless solid. $[\alpha]_D^{25} = +103.7$ (c = 0.60 in CH₂Cl₂). The *ee* (43%) was determined by

HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 95:5, flow rate=0.5 mL/min, UV= 254 nm, minor enantiomer $t_1 = 70.0$ min, major enantiomer $t_2 = 61.9$ min. ^1H NMR (500 MHz, CDCl_3) δ 7.32 (dt, $J = 7.1, 3.8$ Hz, 2H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.53 (d, $J = 8.8$ Hz, 2H), 6.23 (d, $J = 8.8$ Hz, 2H), 5.78 – 5.58 (m, 1H), 5.16 (dd, $J = 17.5, 13.9$ Hz, 2H), 4.12 (s, 1H), 3.63 (s, 3H), 3.19 (s, 3H), 2.63 (ddd, $J = 66.2, 13.2, 7.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 178.00, 153.66, 143.10, 138.90, 130.68, 130.05, 129.12, 124.12, 123.02, 120.80, 118.04, 114.49, 108.54, 65.07, 55.56, 44.41, 26.38. MS (EI) m/z : 308 $[\text{M}^+]$.

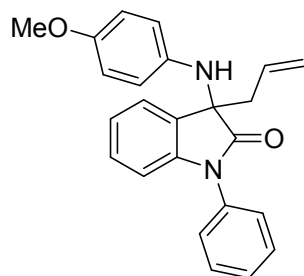




信号 1: DAD1 A, Sig=254,4 Ref=360,100

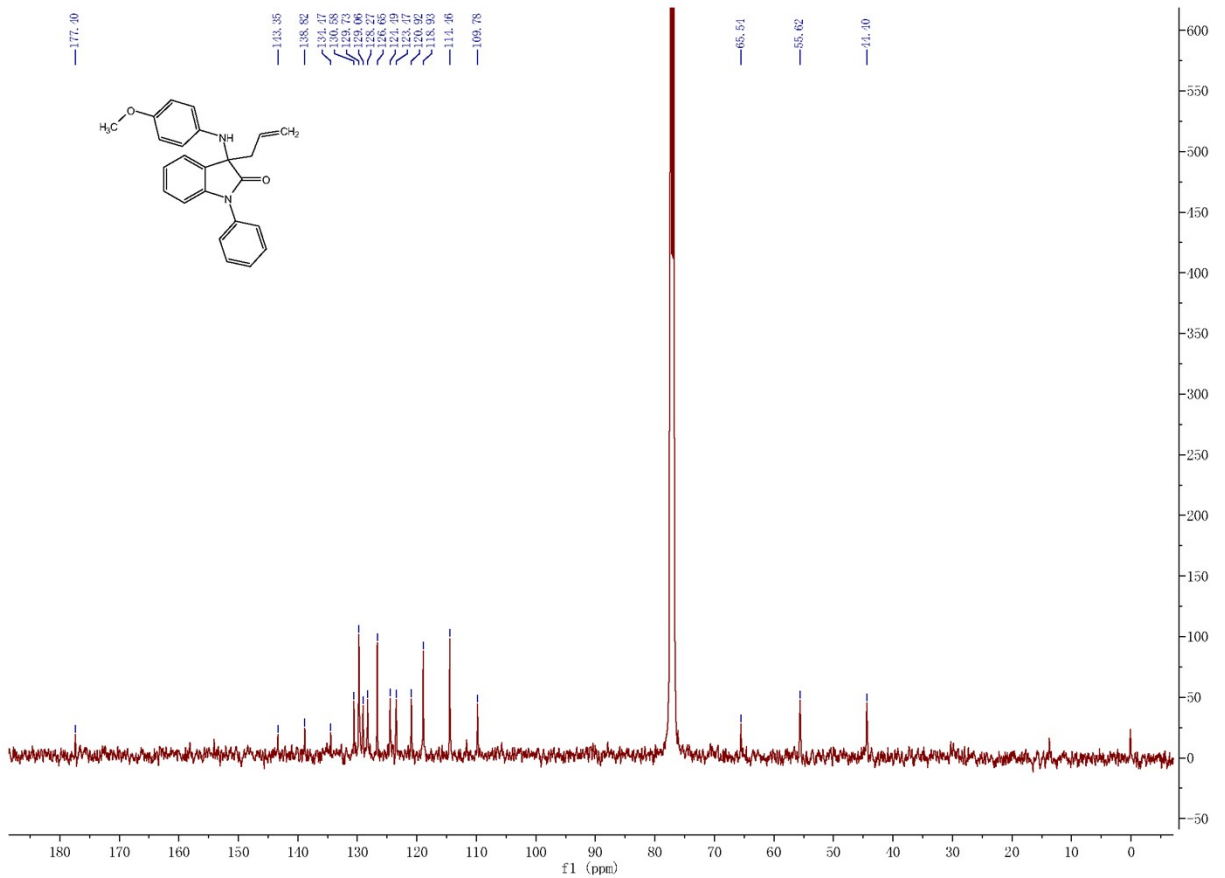
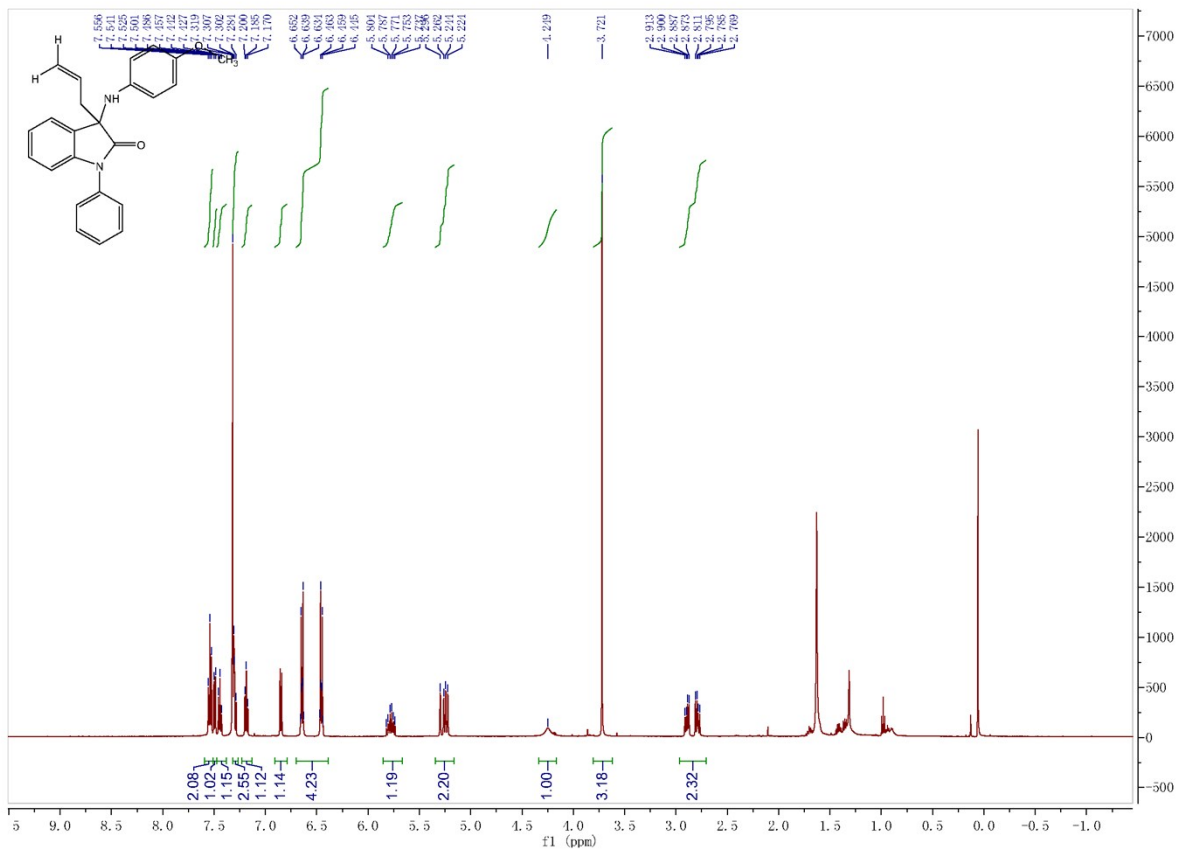
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	61.967	MF	5.0990	3854.99023	12.60041	71.5693
2	70.060	FM	3.7098	1531.38123	6.87986	28.4307

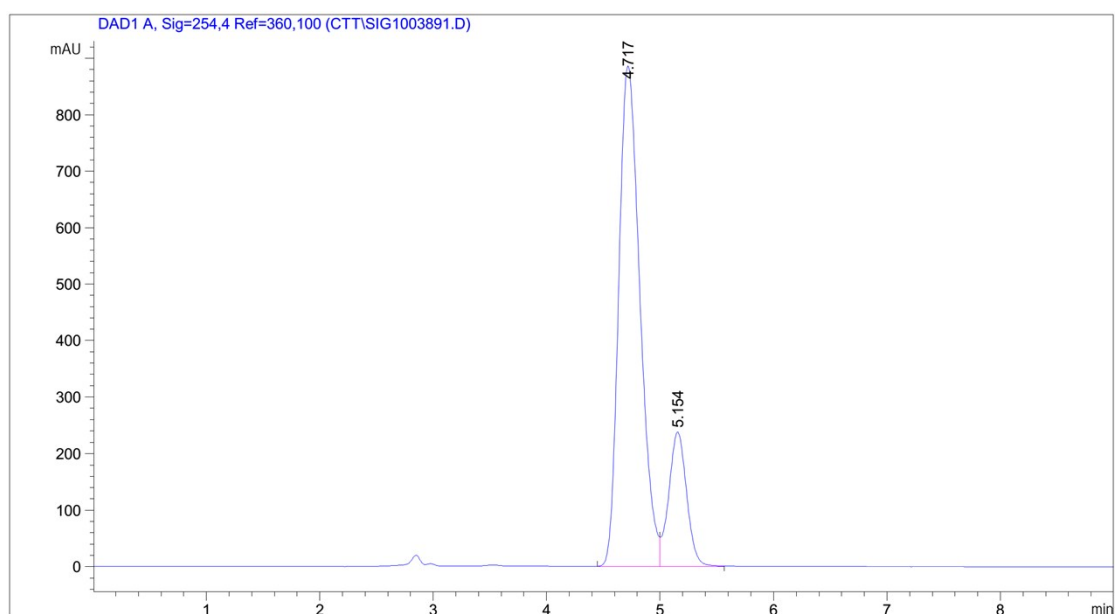
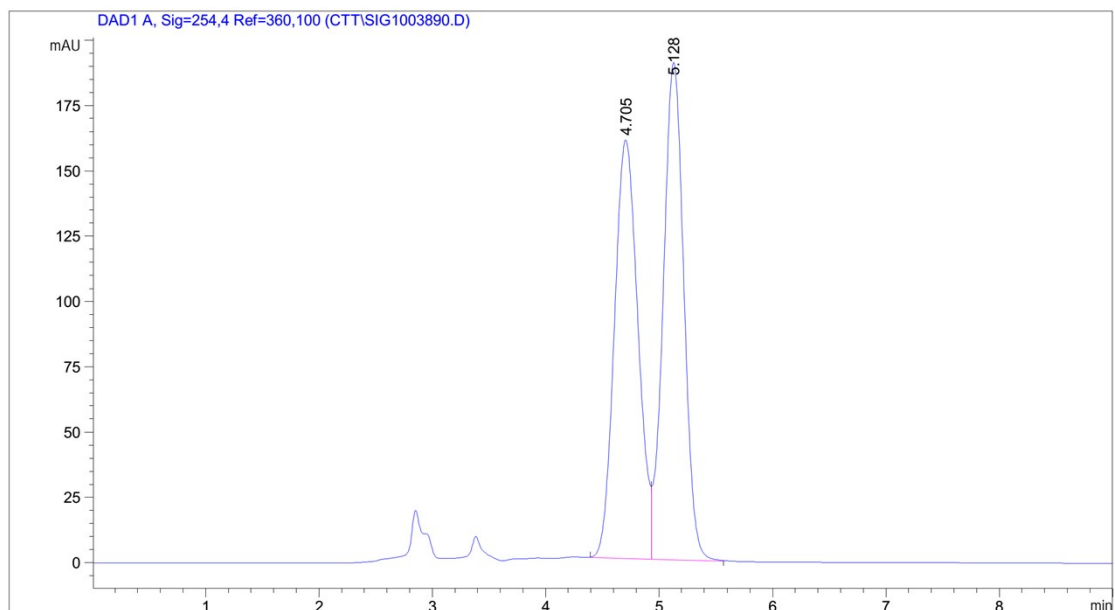
2.9 3-allyl-3-((4-methoxyphenyl)amino)-1-phenylindolin-2-one (2j)



Chemical Formula: C₂₄H₂₂N₂O₂
Exact Mass: 370.17

Isolated as a colorless solid. $[\alpha]_D^{25} = +113.2$ (c = 0.75 in CH₂Cl₂). The *ee* (63%) was determined by HPLC analysis, Venusil CO column, Hexane/*i*-PrOH 65:35, flow rate = 0.7 mL/min, UV = 254 nm, minor enantiomer $t_1 = 5.2$ min, major enantiomer $t_2 = 4.7$ min. ¹H NMR (500 MHz, CDCl₃) δ 7.54 (t, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.70 – 6.39 (m, 4H), 5.78 (td, *J* = 16.9, 8.0 Hz, 1H), 5.26 (dd, *J* = 22.4, 13.6 Hz, 2H), 4.25 (s, 1H), 3.72 (s, 3H), 2.84 (ddd, *J* = 21.3, 13.1, 7.4 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 177.40, 143.35, 138.82, 134.47, 130.58, 129.73, 129.06, 128.27, 126.65, 124.49, 123.47, 120.92, 118.93, 114.46, 109.78, 65.54, 55.62, 44.40. MS (EI) *m/z*: 370 [M⁺].

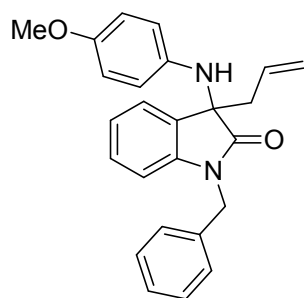




信号 1: DAD1 A, Sig=254,4 Ref=360,100

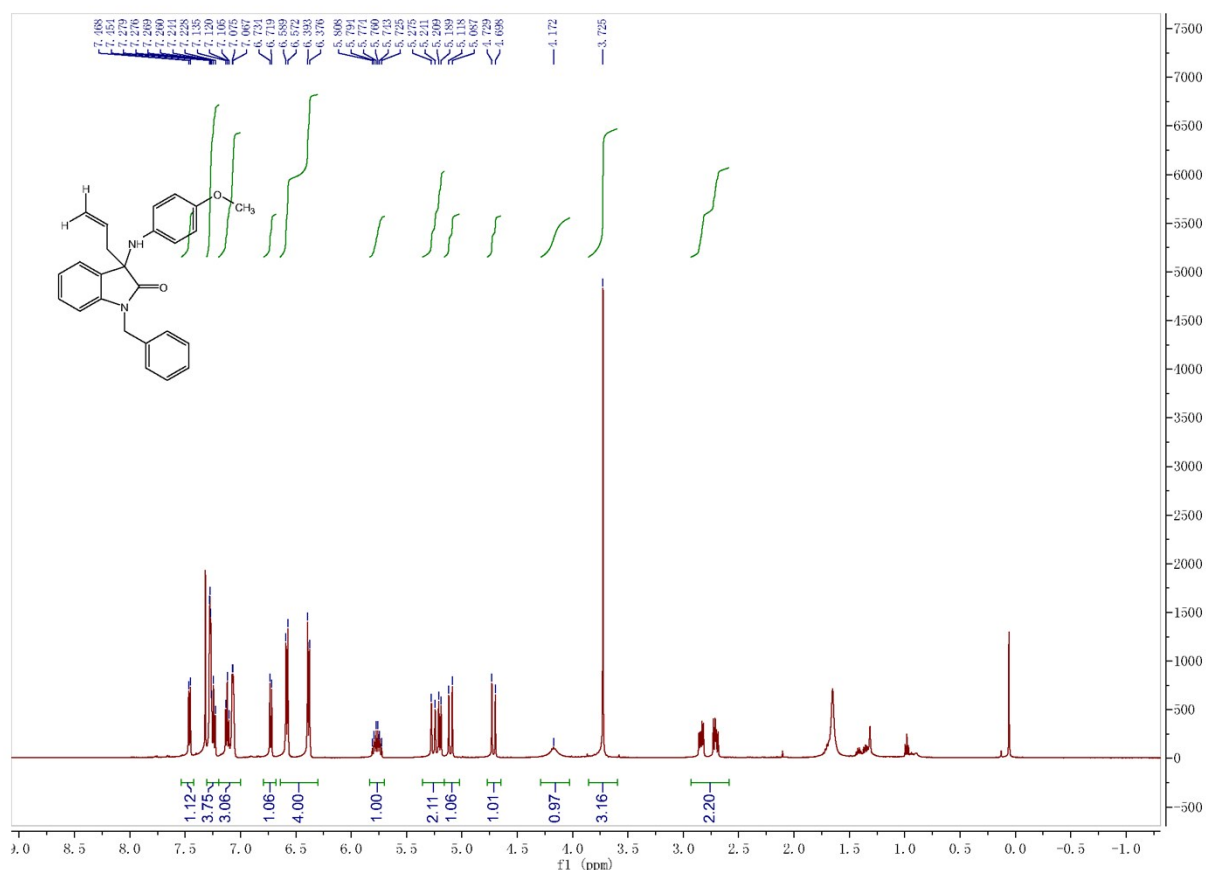
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	4.717	BV	0.2013	1.14909e4	886.35156	81.4924
2	5.154	VB	0.1680	2609.67896	237.86870	18.5076

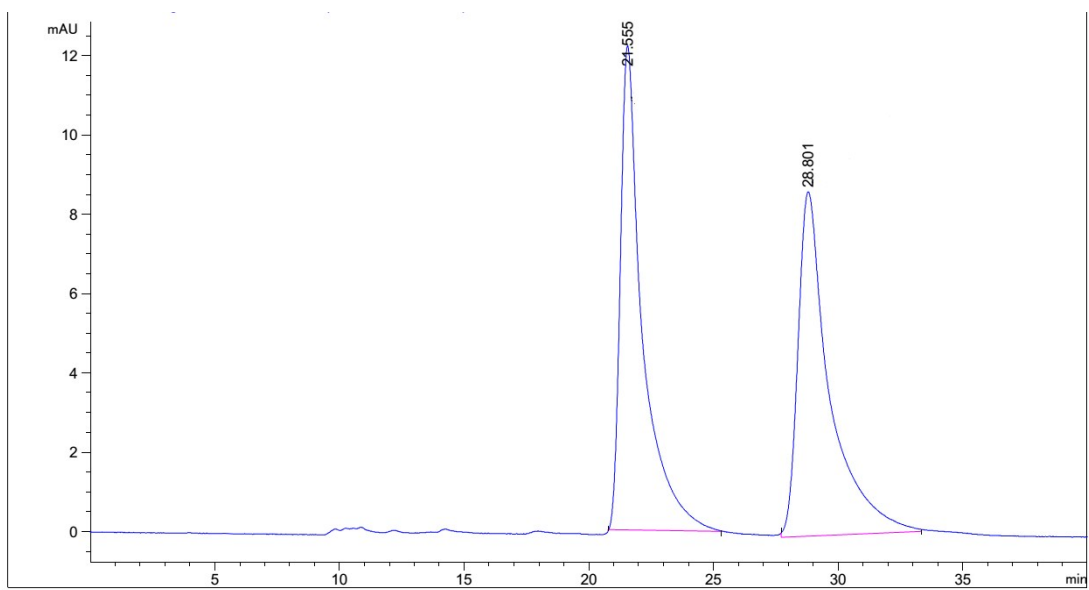
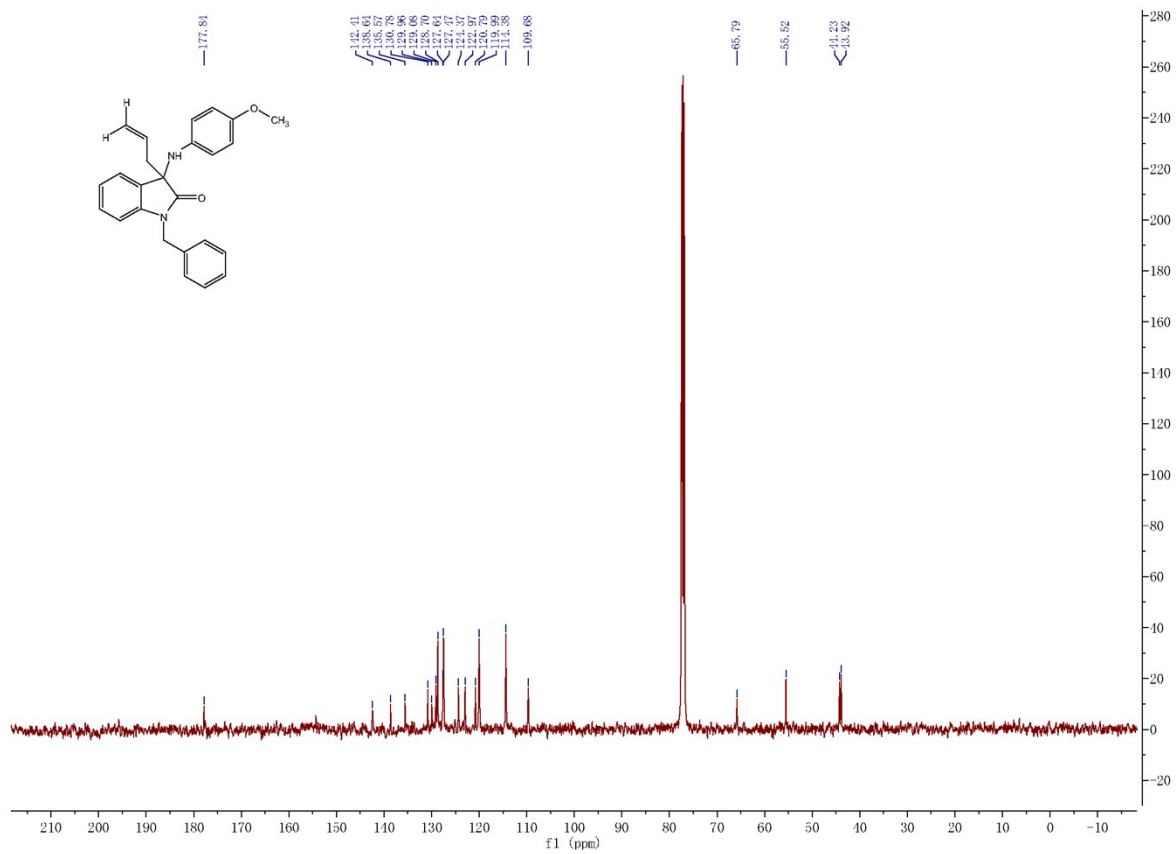
2.10 3-allyl-1-benzyl-3-((4-methoxyphenyl)amino)indolin-2-one (2k)

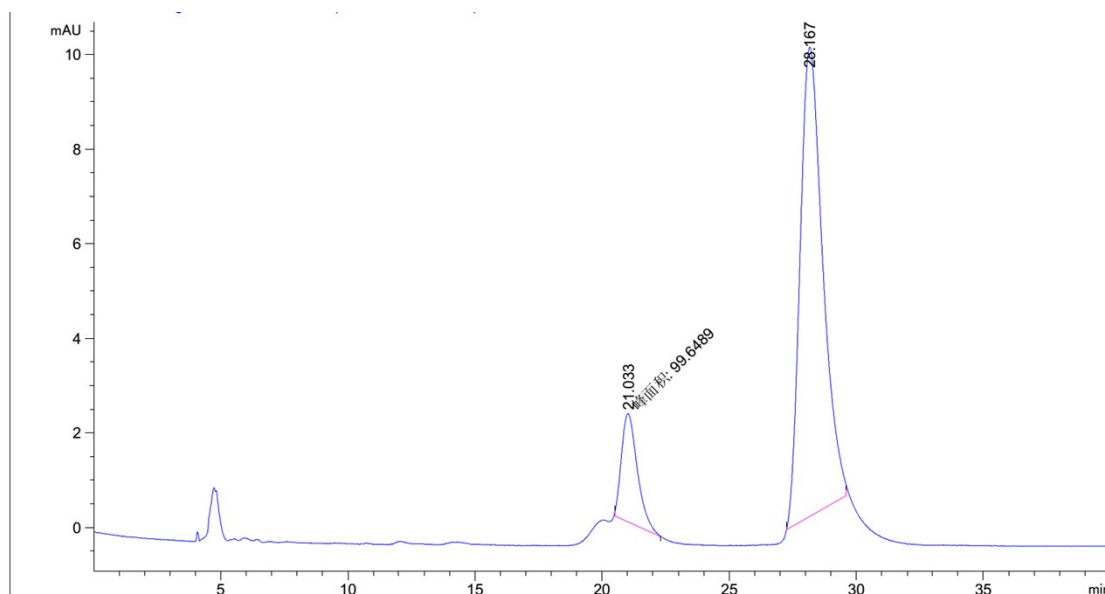


Chemical Formula: $C_{25}H_{24}N_2O_2$
Exact Mass: 384.18

Isolated as a colorless solid. $[\alpha]_D^{25} = +97.6$ ($c = 0.68$ in CH_2Cl_2). The ee (74%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=1.0 mL/min, UV= 280 nm, minor enantiomer $t_1 = 21.0$ min, major enantiomer $t_2 = 28.2$ min. 1H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, $J = 7.3$ Hz, 1H), 7.30 – 7.20 (m, 4H), 7.20 – 7.00 (m, 3H), 6.73 (d, $J = 7.8$ Hz, 1H), 6.48 (dd, $J = 98.0, 8.7$ Hz, 4H), 5.77 (td, $J = 17.3, 8.1$ Hz, 1H), 5.23 (dd, $J = 29.8, 13.6$ Hz, 2H), 5.10 (d, $J = 15.6$ Hz, 1H), 4.71 (d, $J = 15.7$ Hz, 1H), 4.17 (s, 1H), 3.73 (s, 3H), 2.77 (ddd, $J = 21.4, 13.2, 7.4$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.84, 142.41, 138.64, 135.57, 130.78, 129.96, 129.08, 128.70, 127.64, 127.47, 124.37, 122.97, 120.79, 119.99, 114.38, 109.68, 77.00, 65.79, 55.52, 44.23, 43.92. MS (EI) m/z : 384 $[M]^+$.



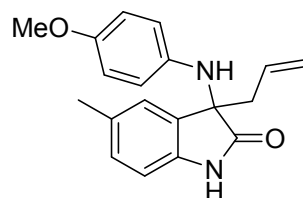




信号 1: DAD1 E, Sig=280,16 Ref=360,100

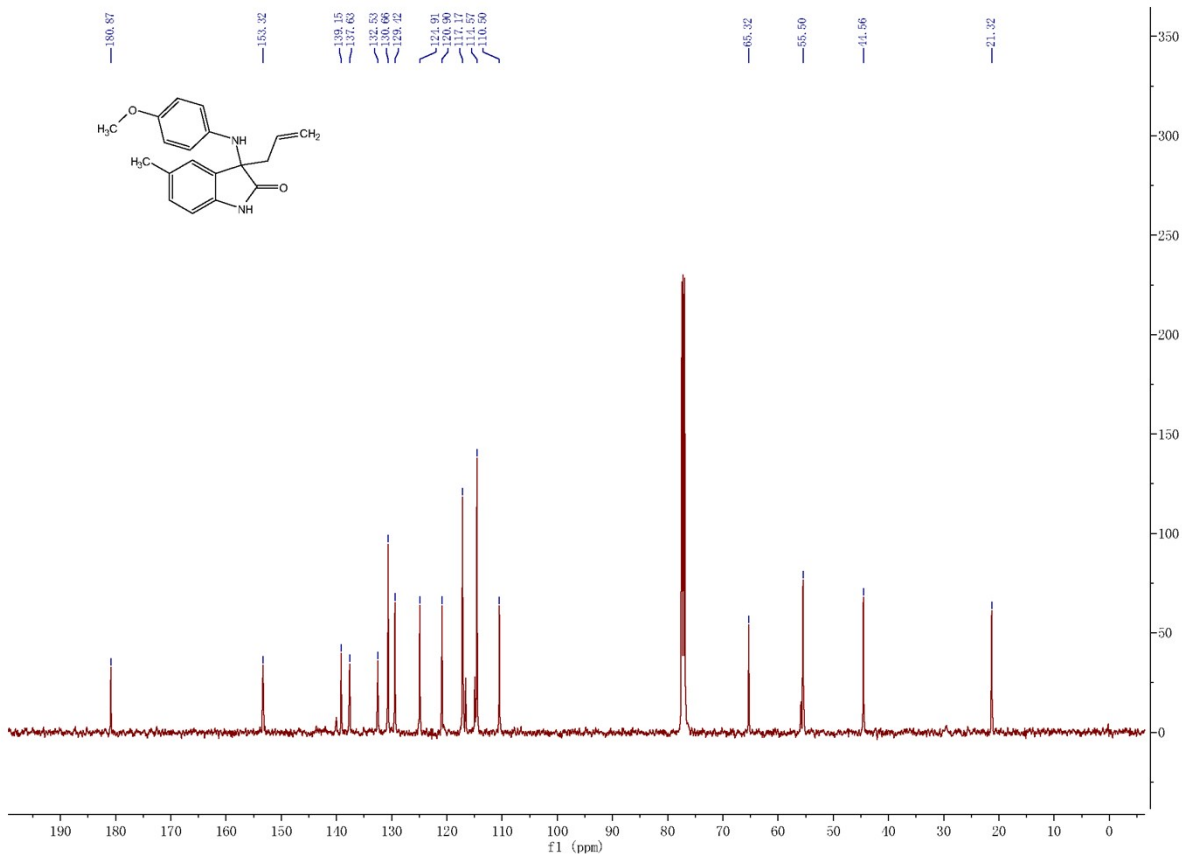
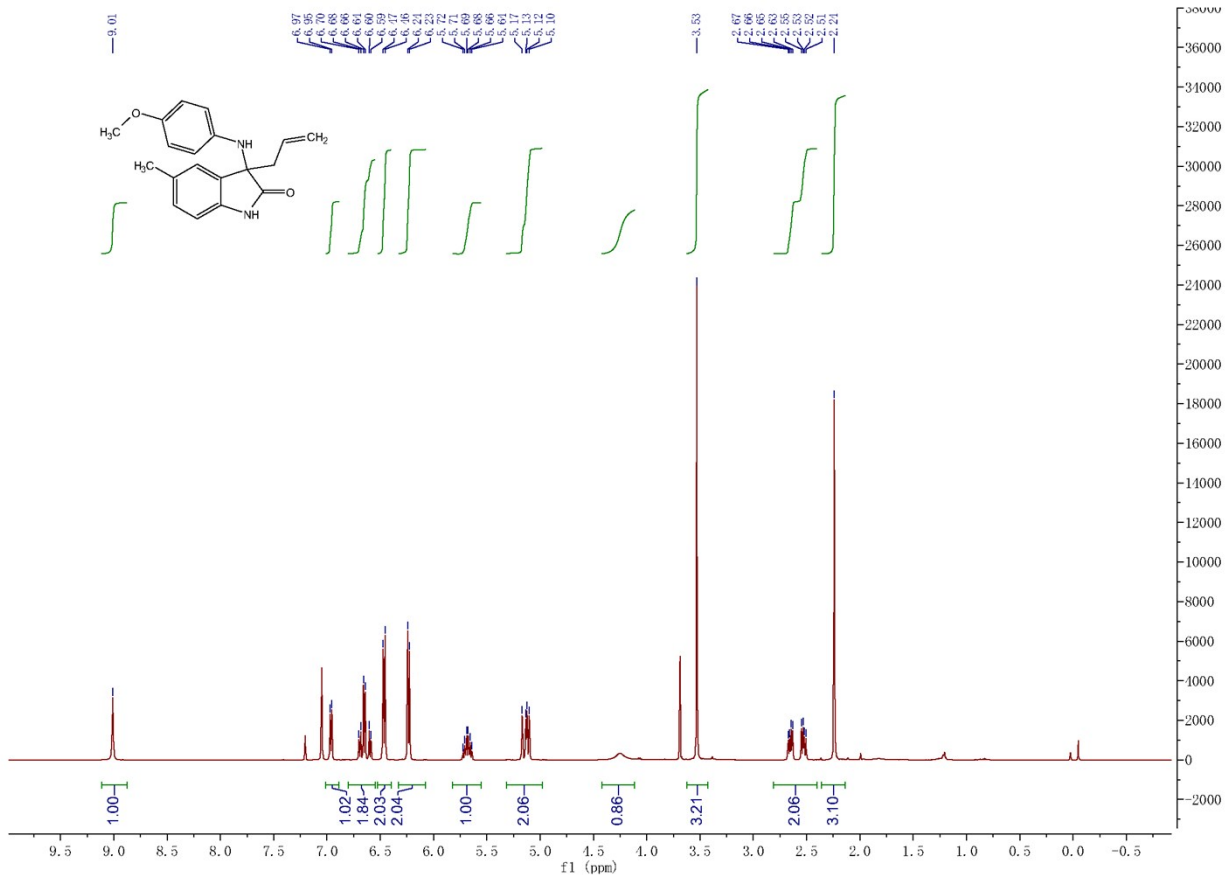
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.027	MM	0.7710	112.82544	2.43887	13.1001
2	28.167	MM	1.1903	748.42957	10.47948	86.8999

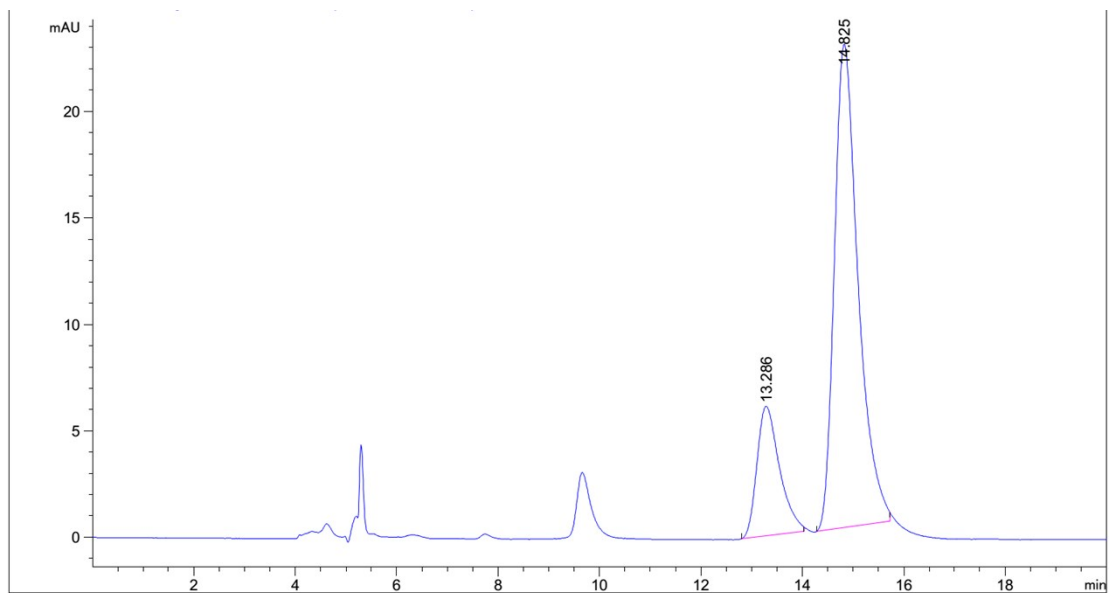
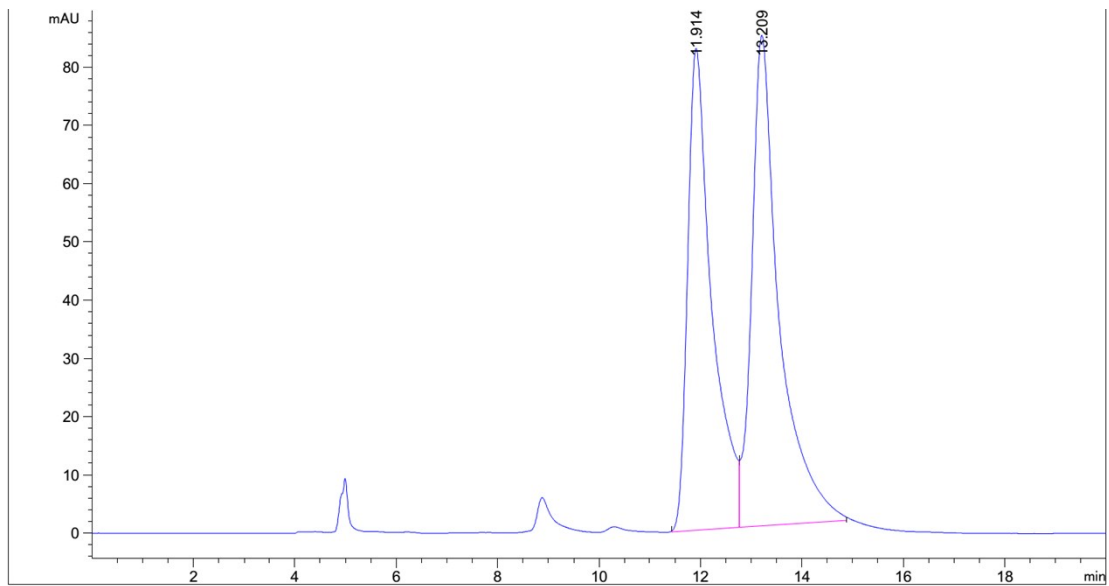
2.11 3-allyl-3-((4-methoxyphenyl)amino)-5-methylindolin-2-one (2I)



Chemical Formula: C₁₉H₂₀N₂O₂
Exact Mass: 308.15

Isolated as a white solid. $[\alpha]_D^{25} = +59.3$ (c=0.84 in CH₂Cl₂). The ee (60%) was determined by HPLC analysis, Venusil CA column, Hexane/i-PrOH 80:10, flow rate=0.7 mL/min, UV= 280 nm, minor enantiomer t₁ = 13.3 min, major enantiomer t₂= 14.8 min. ¹H NMR (500 MHz, CDCl₃) δ 9.01 (s, 1H), 6.96 (d, J = 7.9 Hz, 1H), 6.80 – 6.55 (m, 2H), 6.46 (d, J = 8.9 Hz, 2H), 6.23 (d, J = 8.9 Hz, 2H), 5.67 (dt, J = 17.5, 8.8 Hz, 1H), 5.13 (dd, J = 19.2, 13.6 Hz, 2H), 4.25 (s, 1H), 3.53 (s, 3H), 2.59 (ddd, J = 63.1, 13.3, 7.4 Hz, 2H), 2.24 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 180.87, 153.32, 139.15, 137.63, 132.53, 130.66, 129.42, 124.91, 120.90, 117.17, 114.57, 110.50, 65.32, 55.50, 44.56, 21.32. MS (EI) m/z: 308 [M⁺].

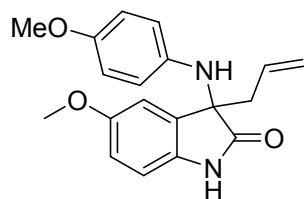




信号 1: DAD1 E, Sig=280,16 Ref=360,100

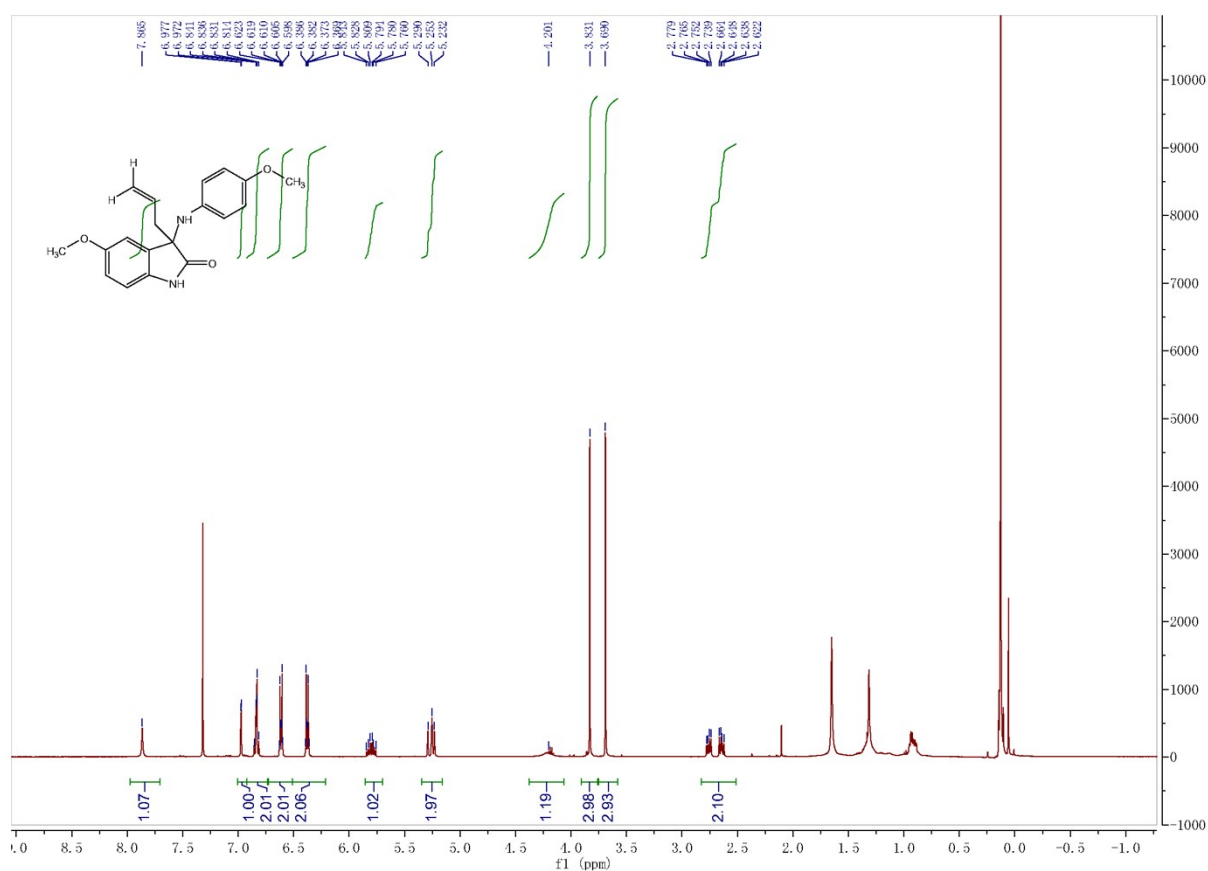
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.286	BB	0.4587	188.15355	6.08632	19.6725
2	14.825	MM	0.5579	768.27759	22.94965	80.3275

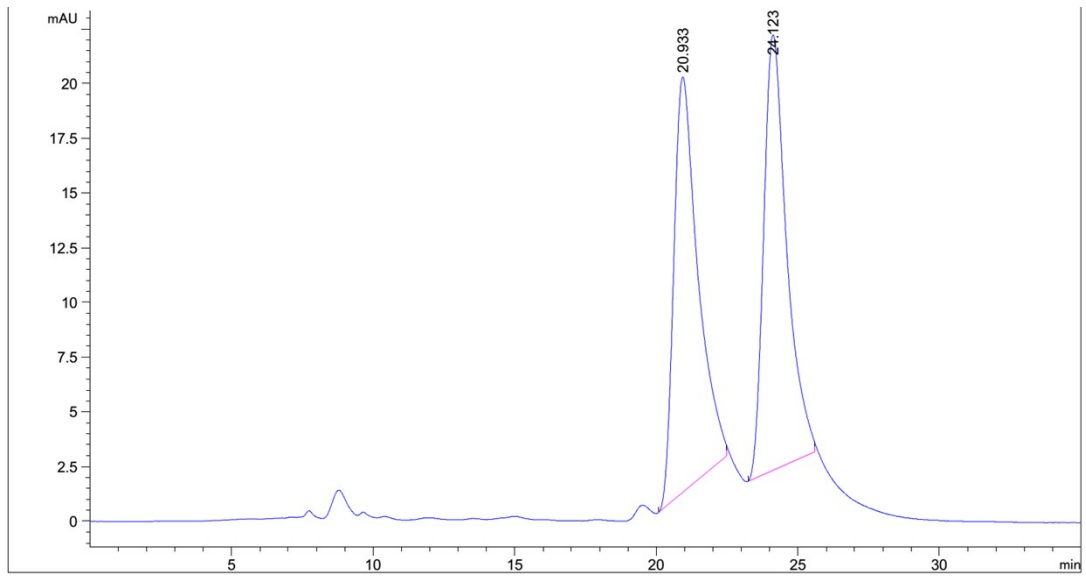
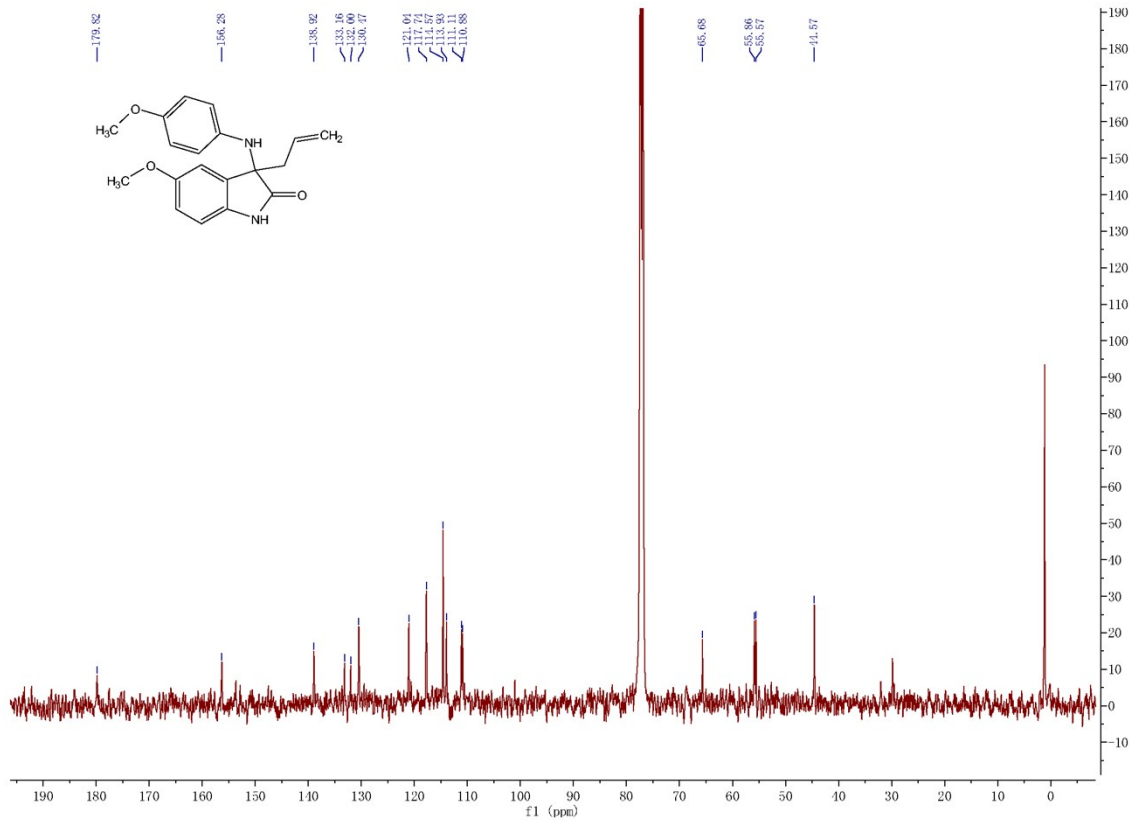
2.12 3-allyl-5-methoxy-3-((4-methoxyphenyl)amino)indolin-2-one (2m)

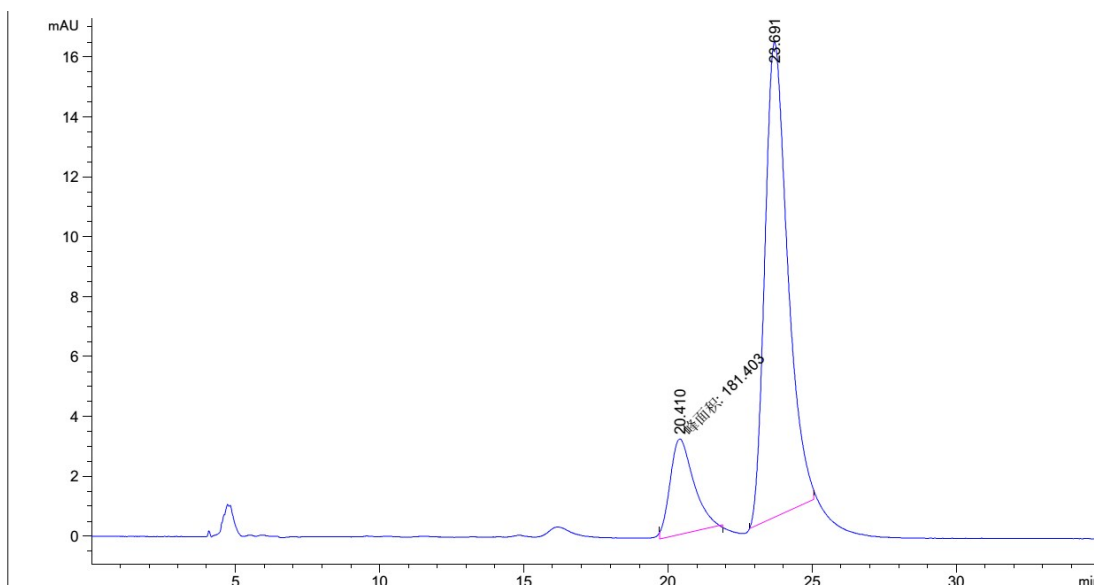


Chemical Formula: C₁₉H₂₀N₂O₃
 Exact Mass: 324.15

Isolated as a white solid. $[\alpha]_D^{25} = +73.2$ ($c = 0.88$ in CH₂Cl₂). The ee (71%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=0.7 mL/min, UV= 280 nm, minor enantiomer $t_r = 20.4$ min, major enantiomer $t_r = 23.7$ min. ¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 1H), 6.97 (d, $J = 2.1$ Hz, 1H), 6.92 – 6.72 (m, 2H), 6.74 – 6.51 (m, 2H), 6.51 – 6.21 (m, 2H), 5.80 (td, $J = 17.0, 8.9$ Hz, 1H), 5.26 (t, $J = 14.5$ Hz, 2H), 4.20 (s, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 2.70 (ddd, $J = 21.4, 13.3, 7.4$ Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 179.82, 156.28, 138.92, 133.16, 132.00, 130.47, 121.04, 117.74, 114.57, 113.93, 111.11, 110.88, 65.68, 55.86, 55.57, 44.57. MS (EI) m/z : 324 [M⁺].



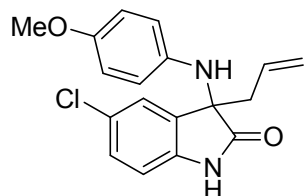




信号 1: DAD1 E, Sig=280,16 Ref=360,100

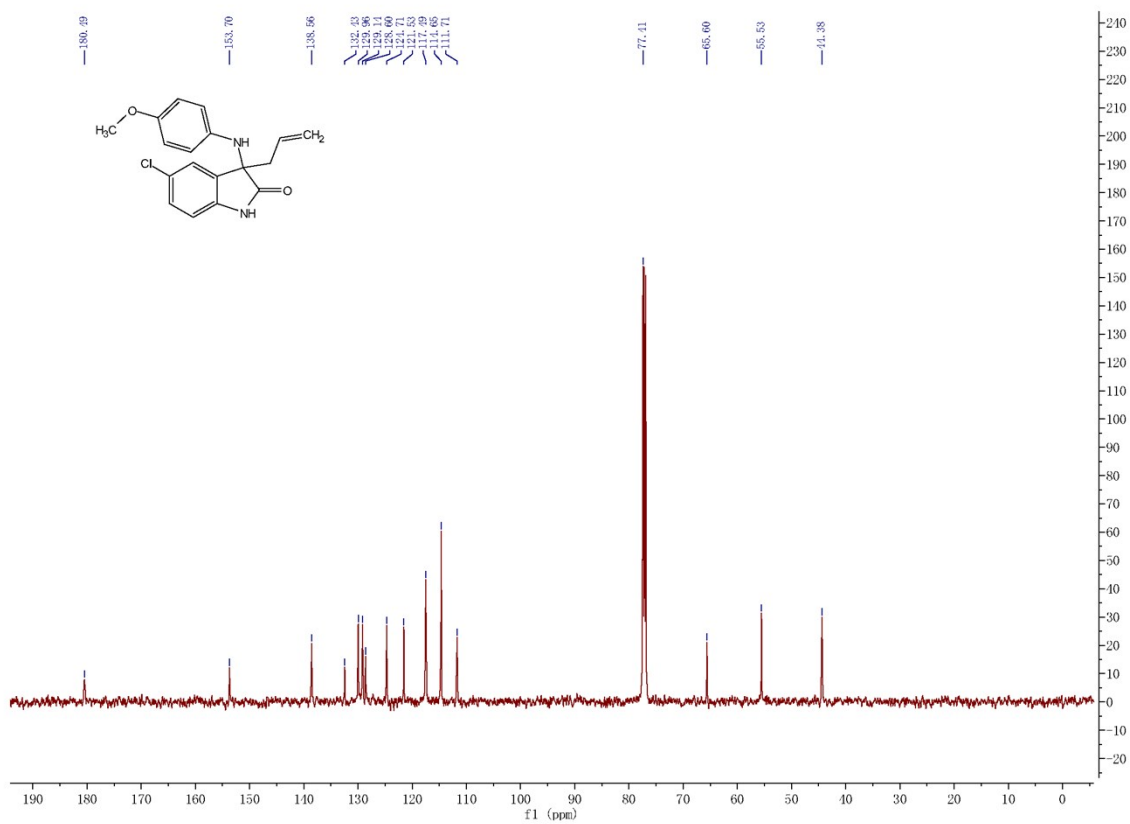
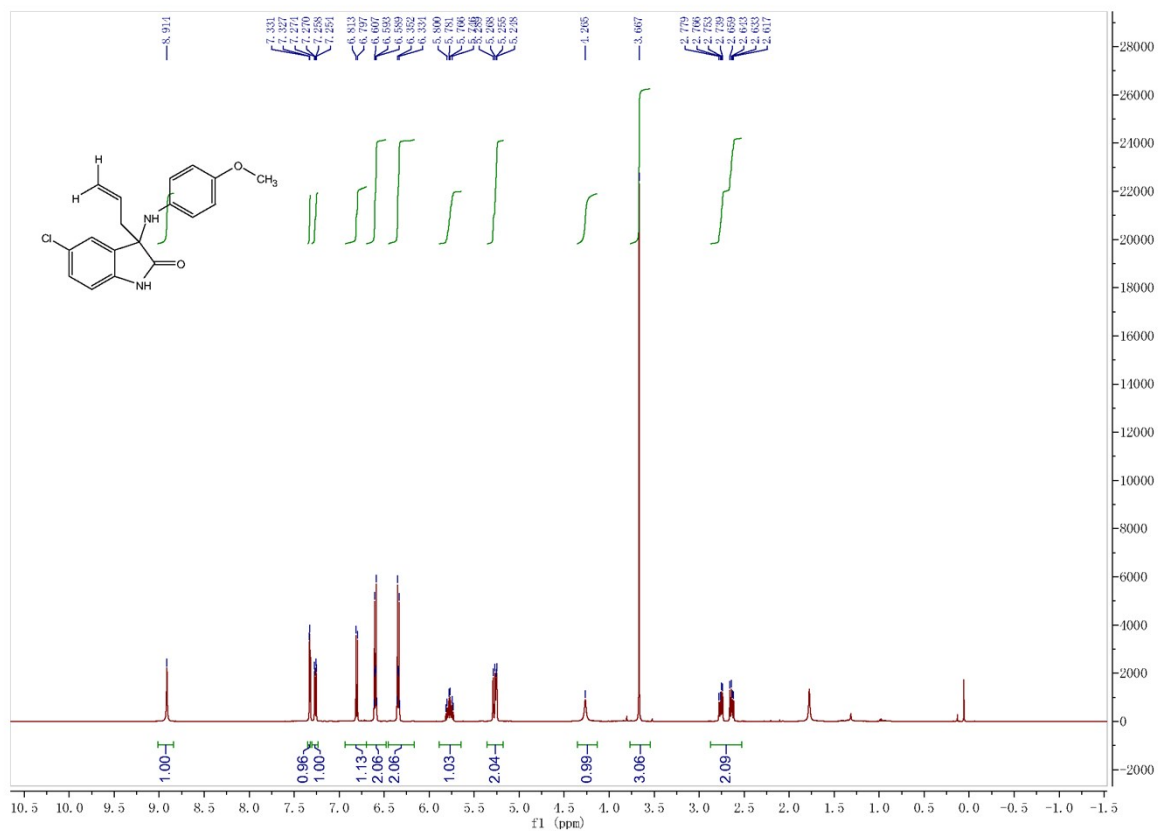
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.410	MM	0.9110	166.20190	3.04074	14.3584
2	23.691	MM	1.0094	991.32404	16.36743	85.6416

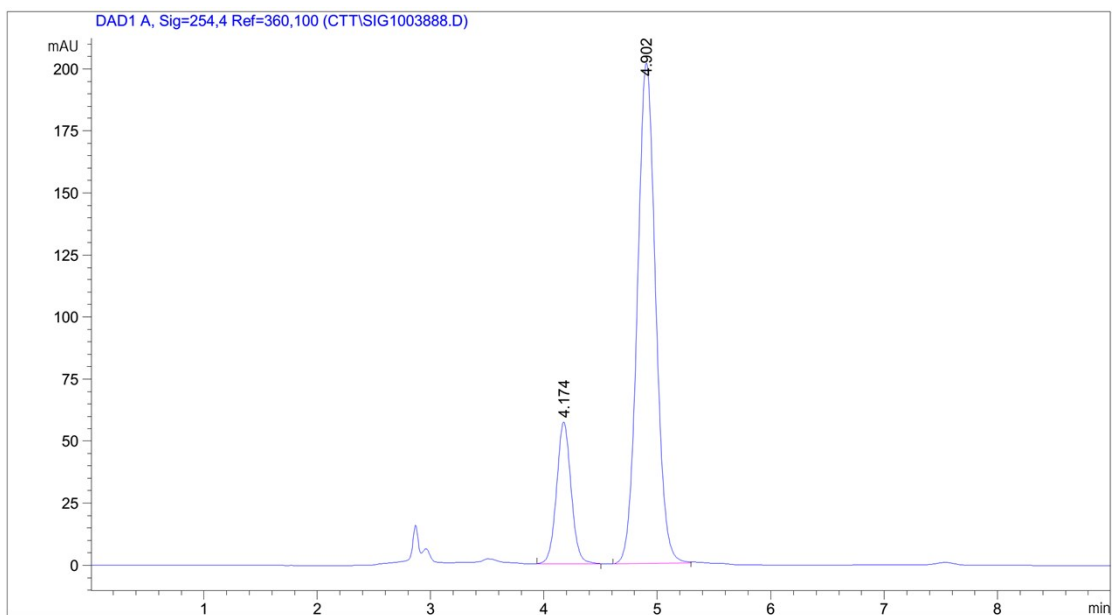
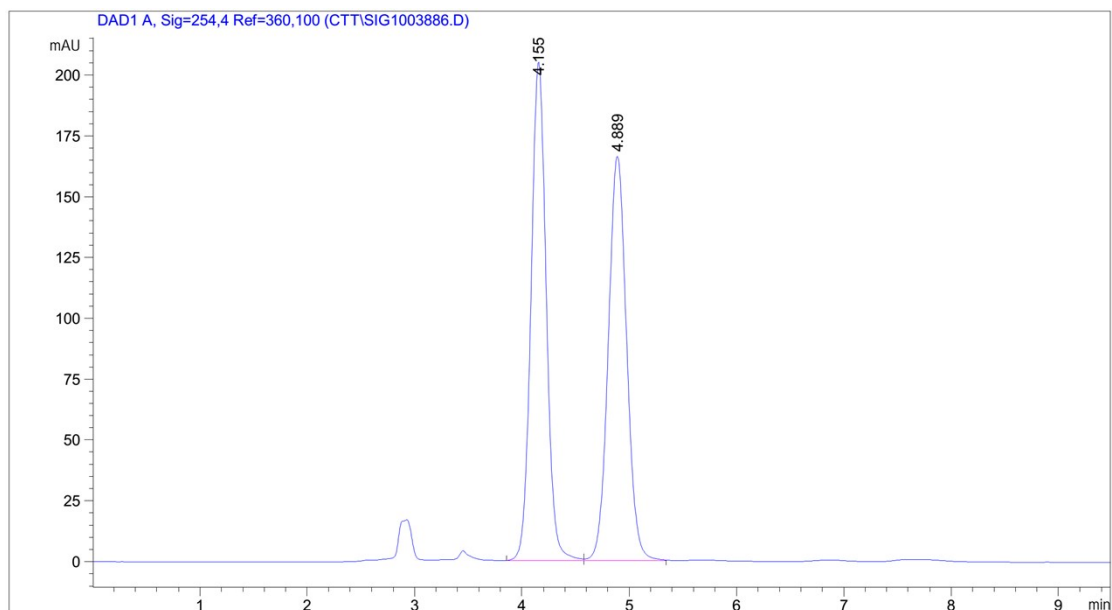
2.13 3-allyl-5-chloro-3-((4-methoxyphenyl)amino)indolin-2-one (**2n**)



Chemical Formula: C₁₈H₁₇ClN₂O₂
Exact Mass: 328.10

Isolated as a white solid. $[\alpha]_D^{25} = +67.2$ (c = 0.90 in CH₂Cl₂). The *ee* (63%) was determined by HPLC analysis, Venusil CO column, Hexane/*i*-PrOH 65:35, flow rate = 0.7 mL/min, UV = 254 nm, minor enantiomer $t_1 = 4.2$ min, major enantiomer $t_2 = 4.9$ min. ¹H NMR (500 MHz, CDCl₃) δ 8.91 (s, 1H), 7.33 (d, *J* = 1.9 Hz, 1H), 7.26 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.70 – 6.48 (m, 2H), 6.45 – 6.16 (m, 2H), 5.77 (td, *J* = 17.1, 7.6 Hz, 1H), 5.27 (dd, *J* = 13.6, 6.8 Hz, 2H), 4.27 (s, 1H), 3.67 (s, 3H), 2.70 (ddd, *J* = 21.3, 13.3, 7.4 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 180.49, 153.70, 138.56, 132.43, 129.96, 129.14, 128.60, 124.71, 121.53, 117.49, 114.65, 111.71, 77.41, 65.60, 55.53, 44.38. MS (EI) *m/z*: 328 [M⁺].

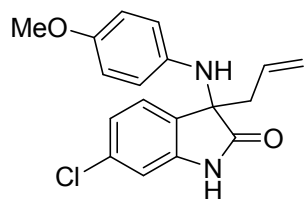




信号 1: DAD1 A, Sig=254,4 Ref=360,100

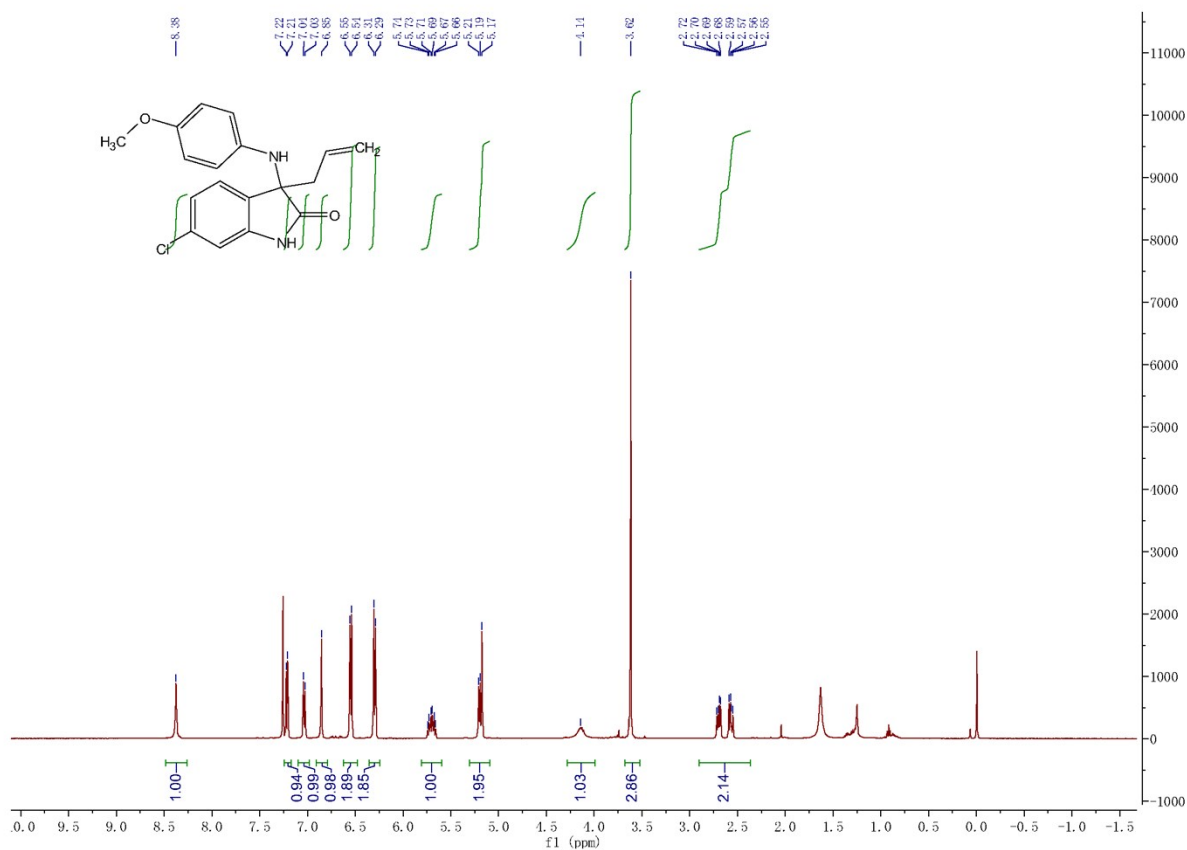
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	4.174	BB	0.1355	506.31784	57.08508	18.3382
2	4.902	BB	0.1724	2254.68140	201.72751	81.6618

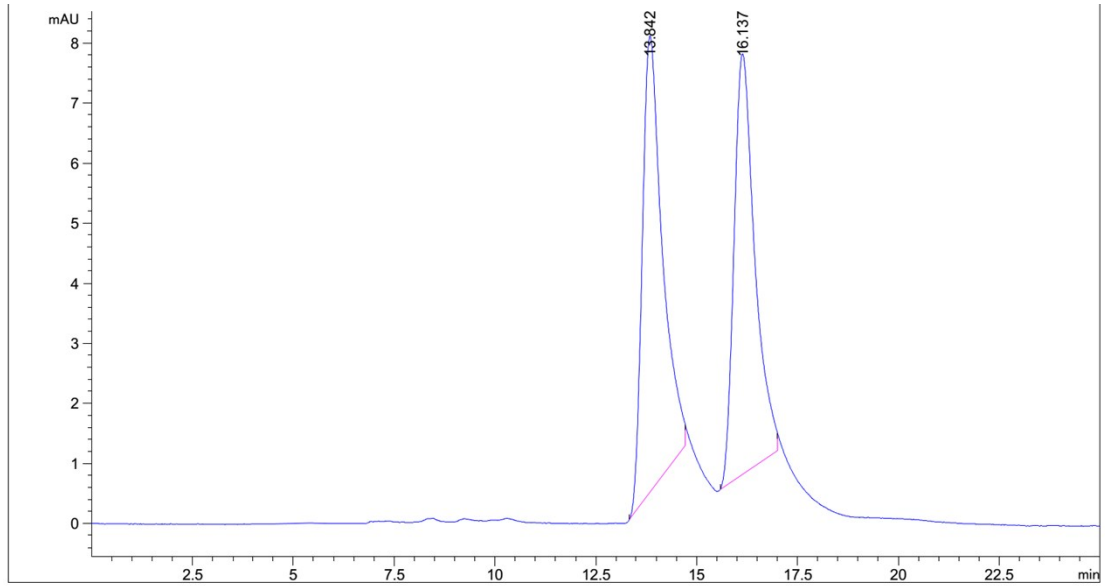
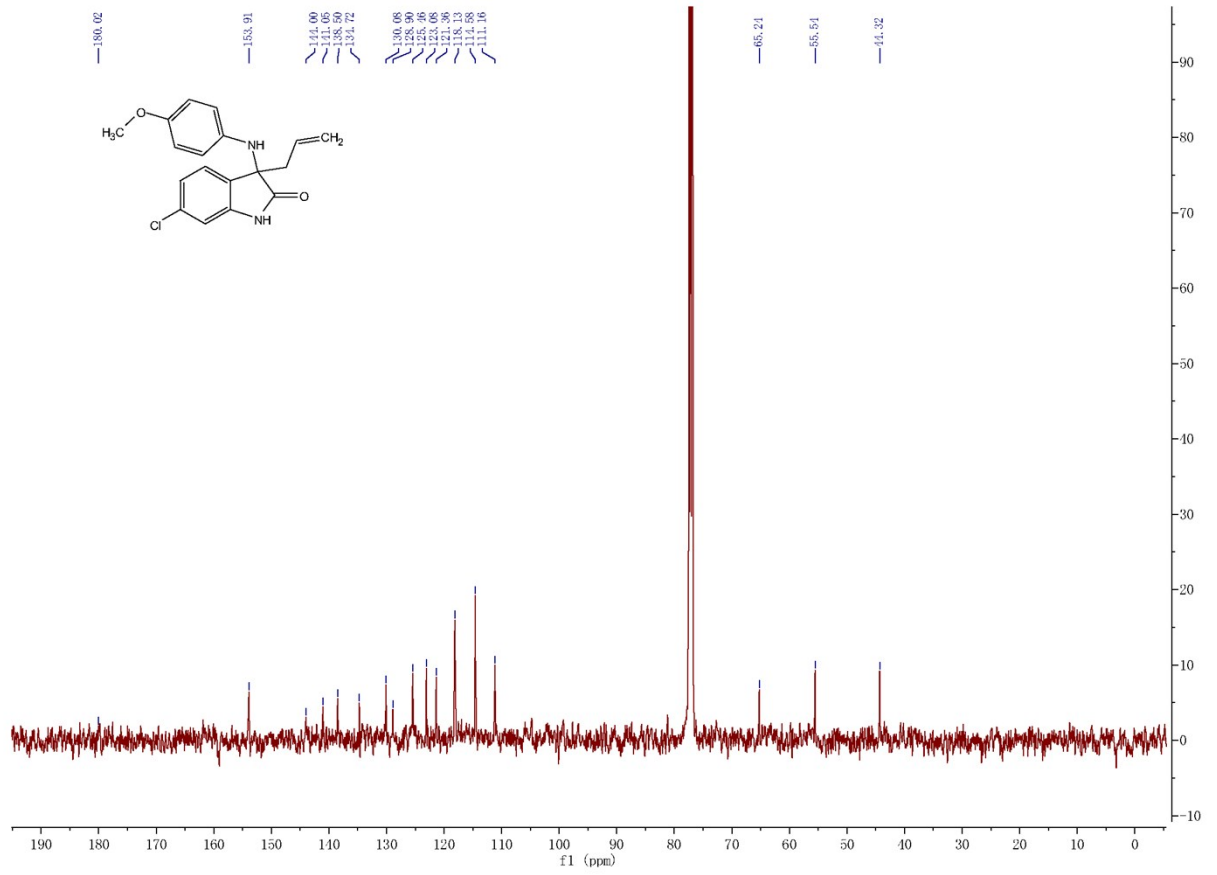
2.14 3-allyl-6-chloro-3-((4-methoxyphenyl)amino)indolin-2-one (2o)

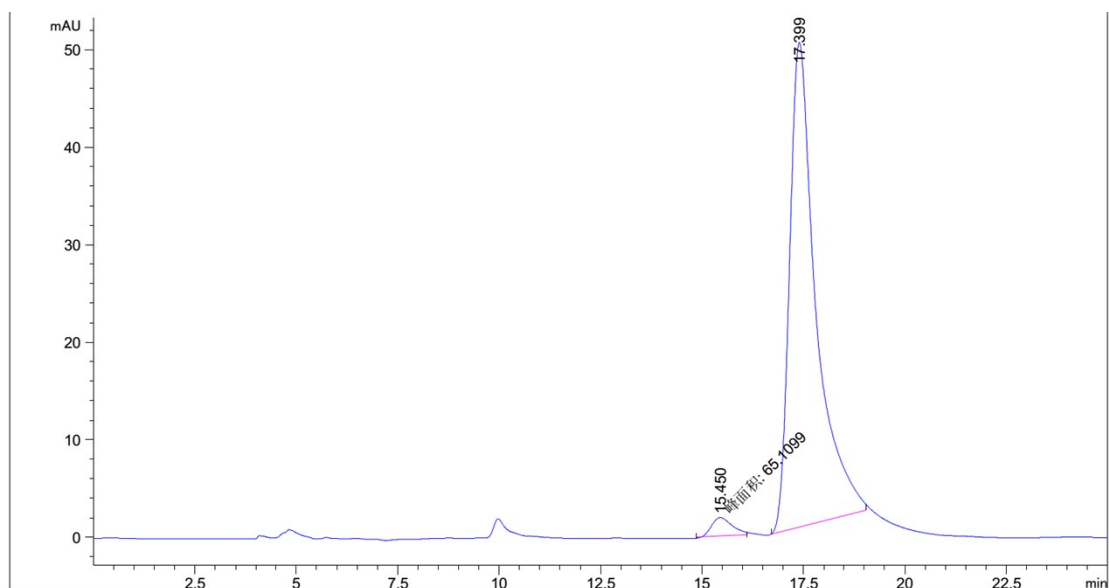


Chemical Formula: C₁₈H₁₇ClN₂O₂
Exact Mass: 328.10

Isolated as a white solid. $[\alpha]_D^{25} = +116.4$ ($c = 0.56$ in CH₂Cl₂). The ee (94%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=1.0 mL/min, UV= 280 nm, minor enantiomer $t_1 = 15.4$ min, major enantiomer $t_2 = 17.4$ min. ¹H NMR (500 MHz, CDCl₃) δ 8.38 (s, 1H), 7.22 (d, $J = 7.9$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.85 (s, 1H), 6.55 (d, $J = 8.8$ Hz, 2H), 6.30 (d, $J = 8.8$ Hz, 2H), 5.72 (dd, $J = 17.1, 7.6$ Hz, 1H), 5.31 – 5.09 (m, 2H), 4.14 (s, 1H), 3.62 (s, 3H), 2.63 (ddd, $J = 64.3, 13.3, 7.4$ Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 180.02, 153.91, 144.00, 141.05, 138.50, 134.72, 130.08, 128.90, 125.46, 123.08, 121.36, 118.13, 114.58, 111.16, 65.24, 55.54, 44.32. MS (EI) m/z : 328 [M⁺].



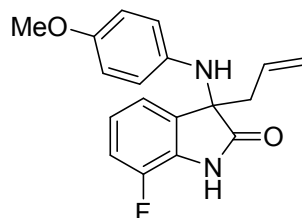




信号 1: DAD1 E, Sig=280,16 Ref=360,100

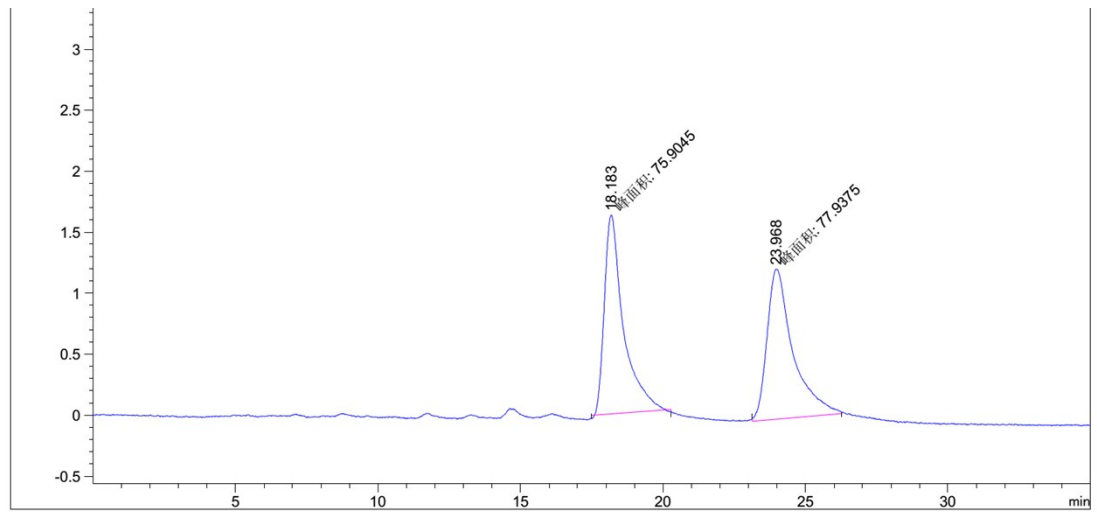
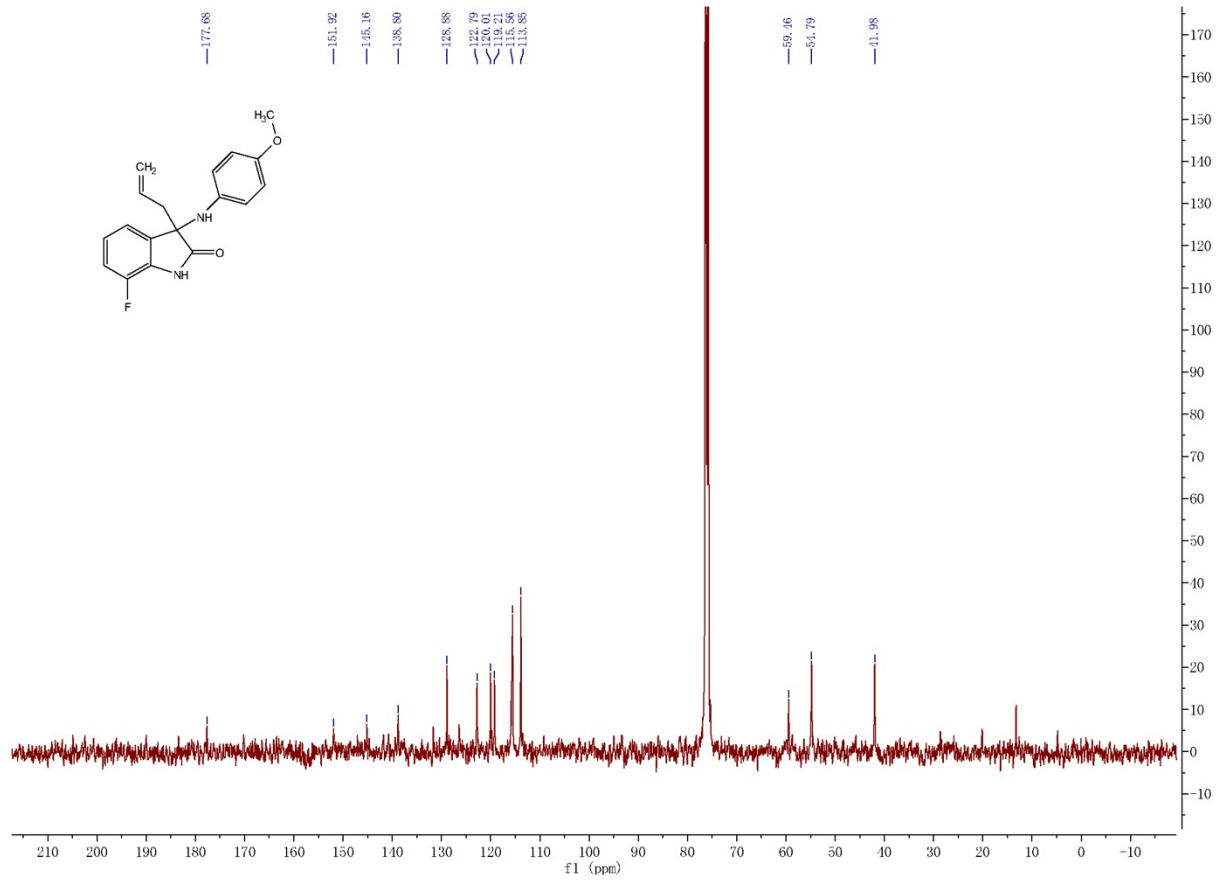
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.450	MM	0.5803	65.10992	1.87015	2.8205
2	17.399	BB	0.6587	2243.36157	49.69175	97.1795

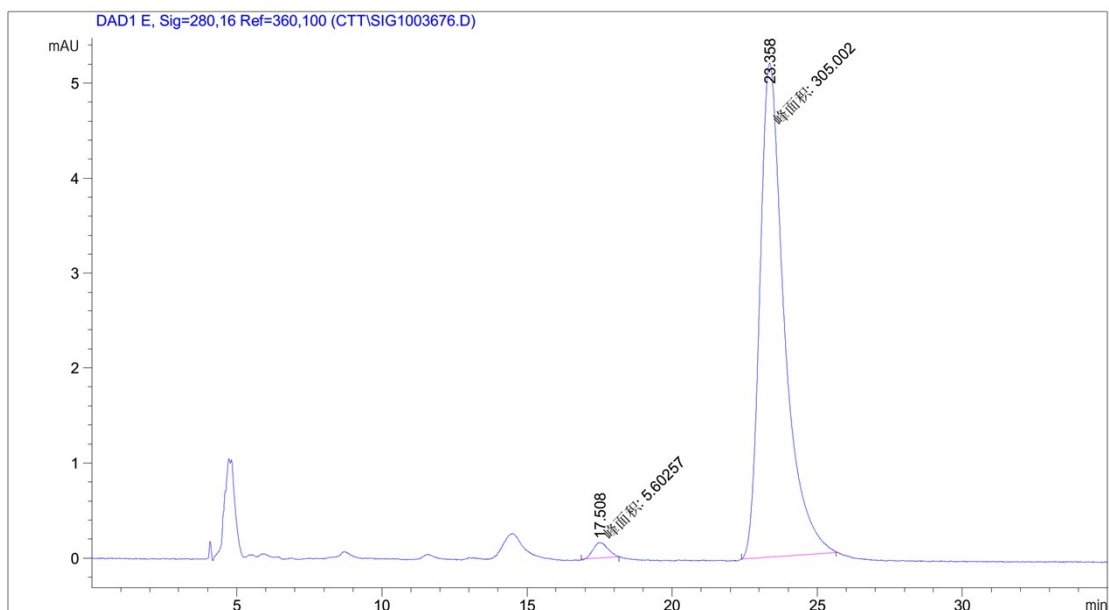
2.15 3-allyl-7-fluoro-3-((4-methoxyphenyl)amino)indolin-2-one (**2p**)



Chemical Formula: C₁₈H₁₇FN₂O₂
Exact Mass: 312.13

Isolated as a brown solid. $[\alpha]_D^{25} = +80.6$ (c=0.71 in CH₂Cl₂). The ee (96%) was determined by HPLC analysis, Venusil CA column, Hexane/i-PrOH 80:20, flow rate=0.7 mL/min, UV= 280 nm, minor enantiomer t₁ = 17.5 min, major enantiomer t₂= 23.4 min. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.11 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.03 – 6.93 (m, 2H), 6.74 – 6.65 (m, 2H), 6.63 – 6.56 (m, 2H), 5.59 (dtd, *J* = 17.8, 8.4, 6.5 Hz, 1H), 5.15 – 4.98 (m, 2H), 3.69 (s, 3H), 2.63 (ddd, *J* = 61.8, 13.4, 7.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 177.68, 151.92, 145.16, 138.80, 128.88, 122.79, 120.01, 119.21, 115.56, 113.85, 59.46, 54.79, 41.98. MS (EI) *m/z*: 312 [M⁺].





信号 1: DAD1 E, Sig=280,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.508	MM	0.5851	5.60257	1.59589e-1	1.8038
2	23.358	MM	0.9767	305.00156	5.20454	98.1962

3. X-ray crystallographic analysis of 2a

