Supporting Information

COAP/Pd-Catalyzed Asymmetric Linear Allylic Alkylation for Chiral 3,3′-Disubstituted Oxindoles Bearing All-Carbon Quaternary Stereocenters and Primary Allylic Alcohol Structures

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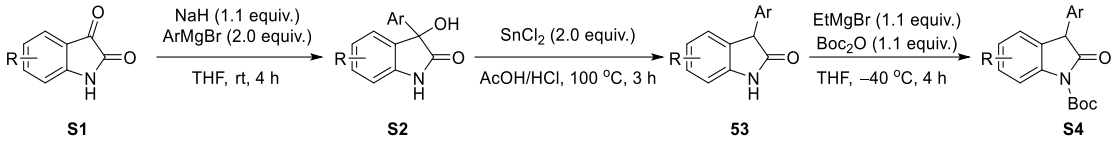
Contents

1. General methods and materials

Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen in oven-dried Schlenk tube with magnetic stirring and all reagents were commercialliy achieved without further purification unless otherwise noted. Some commonly used solvents for asymmetric catalysis were dried with different drying agents through stardand methods reported, including of toluene, dichloro methane (DCM), tetrahdrofuran (THF). Flash Chromatography was performed with si1ica gel (300–400 mesh) from Yantai Chemical Industry Research Institute, P. R. China. Analytical thin-layer chromatography (TLC) was performed with 0.25 ± 0.03 mm coated commercial silica gel plates (GF-254, particle size 0.04–0.05 mm). The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Varian Inova (400 MHz and 101 MHz, respectively) spectrometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.26 ppm for proton NMR, δ 77.10 ppm for carbon NMR). The ^{1}H NMR data were reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets, tt = triplet of triplets, qd = quartet of doublets, ddd = doublet of doublet of doublets, dtt = doublet of triplet of triplets, tdd = triplet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, dddt = doublet of doublet of doublet of triplets), coupling constants (J) and assignment. The data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The IR spectra were recorded on a Varian 1000 FT-IR spectrometer. High-resolution mass spectra (HRMS) for all the compounds were determined on MicroQ-TOF mass spectrometer with ESI resource. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using Chiralpak IC columns. The X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractometer. Optical rotations were performed on Rudolph Aupol IV and reported as follows: $[\alpha]_D^{25}$ (c in g per 100 mL, solvent).

2. General procedure A for the synthesis of 3-substituted oxindoles



To a solution of **S1** (10 mmol) in dry THF (20 mL), NaH (11.0 mmol, 1.1 equiv.) was added at 0 °C and stirred for 30 min. ArMgBr (10.0 mmol) in ether was then added dropwise to the reaction mixture and allowed to warm to room temperature. Then the reaction mixture was quenched with saturated NH_4Cl (30 mL) and extracted with ethyl acetate (3×10 mL). The organic phase was washed with brine. The combined organic layers were dried over Na_2SO_4. Then the solvents were removed under reduced pressure to afford crude product **S2** as light orange solid.[1]

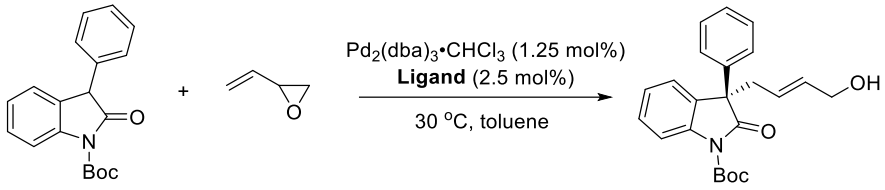
To a solution of **S2** (10 mmol) in AcOH/HCl (45 mL/3 mL), $SnCl_2$ (20.0 mmol, 2.0 equiv.) was added at room temperature. Then the mixture was heated to 100 °C for 3 h. Then, the solution was cooled to room temperature, and then diluted with H_2O (100 mL) and extracted with ethyl acetate (3×20 mL). The organic phase was washed with aqueous sodium hydroxide solution and brine. The combined organic layers were dried over Na_2SO_4. Then the solvents were removed under reduced pressure to afford crude product **S3** as yellow solid.[1]

To a solution of **S3** (7.0 mmol) in THF (20.0 mL), EtMgBr (7.7 mmol,1.1 equiv.) in ether was added dropwise at −40 °C followed by adding $(Boc)_2O$ (7.7 mmol,1.1 equiv.) in one portion. The mixture was stirred at the same temperature for 30 min and warmed to room temperature. Then the mixture was diluted with ether and quenched with saturated NH_4Cl (30.0 mL) and extracted with ethyl acetate (3×10.0 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Purification by flash silica-gel column chromatography using PE/EA (40:1) was carried out to give **S4** as white or yellow solid.[2]

The NMR data of **S4** was reported in the literature.[1,2]

3. Optimization of reaction conditions

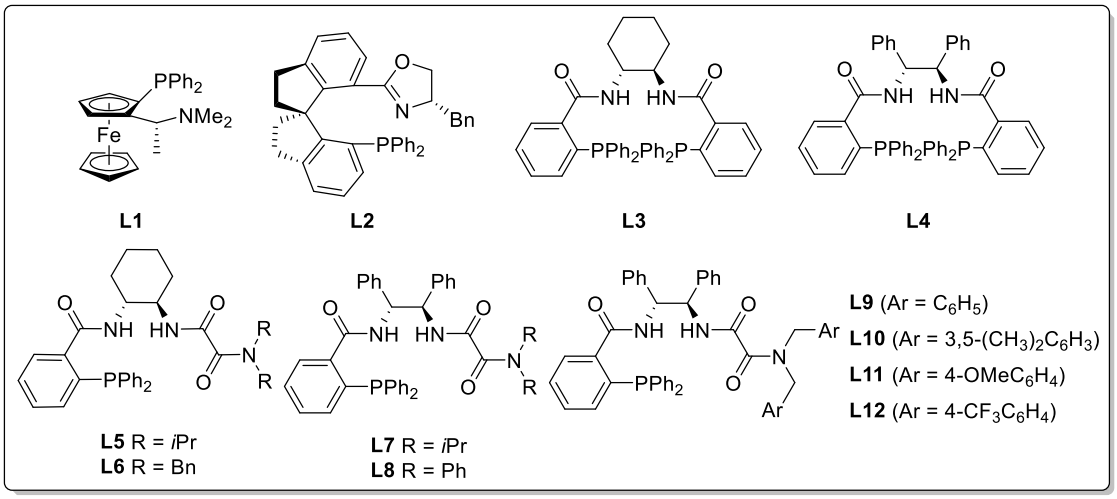
Table S1. Screening of the ligands[a]



A1 **B** **1**

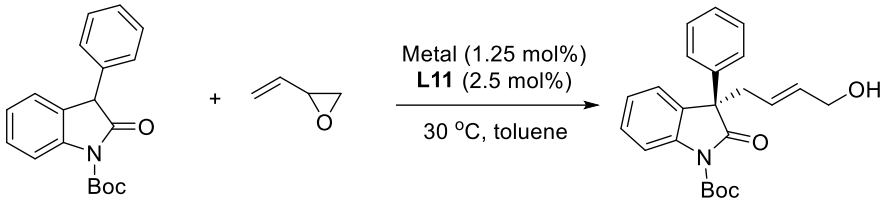
entry	ligand	yield (%)[b]	*ee* (%)[c]
1	**L1**	81	19
2	**L2**	71	35
3	**L3**	58	49
4	**L4**	69	39
5	**L5**	61	6
6	**L6**	64	12
7	**L7**	56	31
8	**L8**	52	36
9	**L9**	77	47
10	**L10**	79	52
11	**L11**	81	63
12	**L12**	80	60

[a] Unless otherwise noted, reactions were carried out with **A1** (0.10 mmol), **B** (0.10 mmol), $Pd_2(dba)_3 \cdot CHCl_3$(1.25 mol%) and **Ligand** (2.5 mol%) in the solvent of toluene (1.0 mL) at 30 °C for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.



Scheme S1. Screening of the ligands

Table S2. Screening of the metal sources[a]

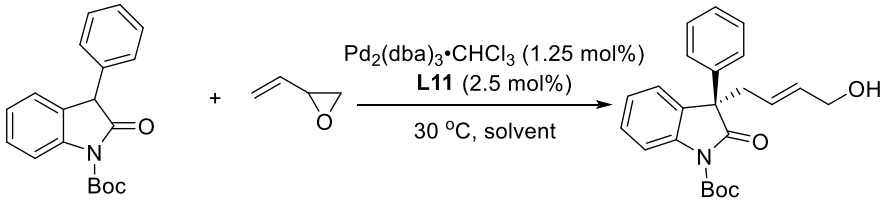


A1 **B** **1**

entry	metal	yield (%)[b]	*ee* (%)[c]
1	$Pd_2(dba)_3$	75	60
2	$Pd_2(dba)_3{\cdot}CHCl_3$	81	63
3[d]	$Pd(dba)_2$	72	61
4[d]	$Pd[(P(tBu)_3]_2$	60	55
5[d]	$Pd(PPh_3)_4$	42	0
6[d]	$PdCl_2$	N.R.	--

[a] Unless otherwise noted, reactions were carried out with **A1** (0.10 mmol), **B** (0.10 mmol), metal source (1.25 mol%) and **L11** (2.5 mol%) in the solvent of toluene (1.0 mL) at 30 °C for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC. [d] 2.5 mol% metal source was used.

Table S3. Screening of the solvents[a]

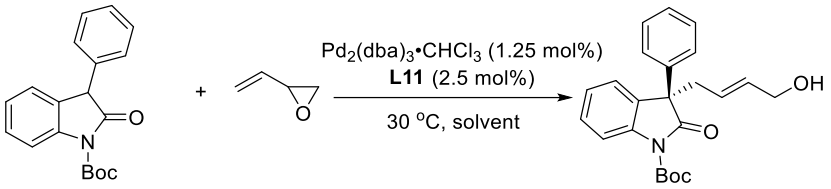


A1 **B** **1**

entry	solvent	yield (%)[b]	*ee* (%)[c]
1	THF	25	63
2	DCM	34	27
3	Acetone	22	33
4	MeCN	18	12
5[e]	MeOH	29	15
6	Toluene	81	63
7	Mesitylene	80	59
8	*m*-Xylene	77	62
9	*p*-Xylene	78	61
10	Fluorobenzene	65	60
11	Pentafluorobenzene	69	34
12	Benzotrifluoride	71	58

[a] Unless otherwise noted, reactions were carried out with **A1** (0.10 mmol), **B** (0.10 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (1.25 mol%) and **L11** (2.5 mol%) in the solvent (1.0 mL) at 30 °C for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.

Table S3. Screening of the mixed solvents[a]

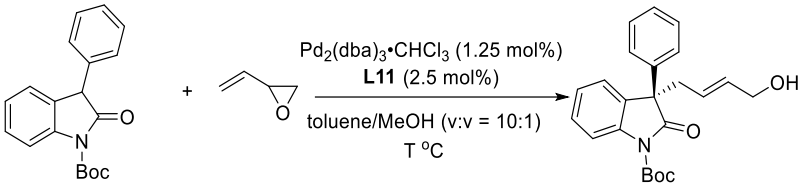


A1 B 1

entry	solvent	yield (%)[b]	*ee* (%)[c]
1	toluene/MeOH (v:v = 10:1)	90	84
2	toluene/EtOH (v:v = 10:1)	84	80
3	toluene/*i*PrOH (v:v = 10:1)	77	79
4	toluene/*t*BuOH (v:v = 10:1)	71	68
5[e]	toluene/MeOH (v:v = 100:1)	85	84
6	toluene/MeOH (v:v = 20:1)	88	84
7	toluene/MeOH (v:v = 4:1)	80	83
8	toluene/MeOH (v:v = 2:1)	74	81
9	toluene/MeOH (v:v = 1.5:1)	61	77
10	toluene/MeOH (v:v = 1:1)	56	76

[a] Unless otherwise noted, reactions were carried out with **A1** (0.10 mmol), **B** (0.10 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (1.25 mol%) and **L11** (2.5 mol%) in the solvent (1.0 mL) at 30 °C for 12 hours. [b] Isolated yield. [c] Determined by ^1H NMR analysis. [d] Determined by chiral HPLC.

Table S4. Screening of the reaction temperature[a]

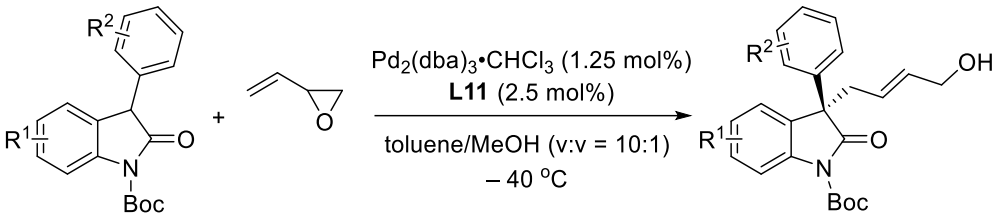


A1 B 1

entry	T (°C)	yield (%)[b]	*ee* (%)[c]
1	30	90	84
2	0	91	93
3	–10	90	94
4	–20	88	94
5	–30	87	94
6	–40	85	95
7	–50	56	90

[a] Unless otherwise noted, reactions were carried out with **A1** (0.10 mmol), **B** (0.10 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (1.25 mol%) and **L11** (2.5 mol%) in the mixed solvents of toluene/MeOH (v:v = 10:1, 1.0 mL) at T °C for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.

General procedure B for preparation of 1–25



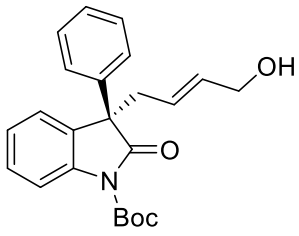
A1-A25 **B** **1-25**

To an oven-dried schlenk tube, $Pd_2(dba)_3 \cdot CHCl_3$ (2.6 mg, 0.0025 mmol) and **L11** (4.2 mg, 0.005 mmol) in dry toluene/MeOH (v:v = 10:1, 2.0 mL) were added under a nitrogen atmosphere. The mixture was stirred for 0.5 hours at room temperature to produce an orange solution. Then 3-substituted oxindoles **A1-A25** (0.20 mmol) and 2-vinyloxirane **B** (0.20 mmol) was added at –40 °C. The mixture was stirred for 4–12 hours at –40 °C. After the reaction was complete (monitored by TLC), it was subjected to silica gel column to afford the desired products **1-25**.

Following the above method, the racemic samples **1-25** were obtained by the use of the $Pd(PPh_3)_4$ (11.56 mg, 0.005 mmol).

***tert*-Butyl (*R, E*)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (1)**

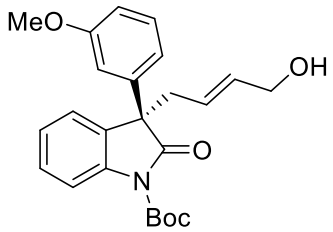
Following *General Procedure B*, the product **1** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 85% yield (64.6 mg); 95% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 20.642, t (minor) = 14.510]; $[\alpha]_D^{25}$= +48.0 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.23 (m, 8H), 5.77 – 5.60 (m, 1H), 5.41 – 5.24 (m, 1H), 3.97 – 3.85 (m, 2H), 3.14 (dd, *J* = 13.8, 8.2 Hz, 1H), 3.08 – 2.95 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 149.3, 139.8, 139.1, 134.6, 130.4, 128.7, 128.6, 127.7, 127.2, 125.4, 125.2, 124.5, 115.2, 84.6, 63.0, 56.8, 41.1, 28.1; IR (KBr) ν_{max}: 2920, 2851, 1727, 1463, 1345, 1286, 1249, 1144, 752, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{25}NNaO_4^+$ [M+Na$^+$] 402.1676, found 402.1676.



1

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-3-(3-methoxyphenyl)-2-oxoindoline-1-carboxylate (2)**

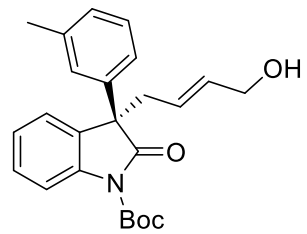
Following *General Procedure B*, the product **2** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 61% yield (50.0 mg), 97% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 32.202, t (minor) =30.026]; $[\alpha]_D^{25}$= +70.1 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.27 (ddd, *J* = 8.4, 6.1, 2.8 Hz, 1H), 7.18 – 7.10 (m, 3H), 6.86 – 6.78 (m, 2H), 6.72 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.58 (dt, *J* = 15.4, 5.8 Hz, 1H), 5.22 (ddd, *J* = 15.0, 8.2, 6.5 Hz, 1H), 3.82 (d, *J* = 5.7 Hz, 2H), 3.68 (s, 3H), 3.02 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.95 – 2.86 (m, 1H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 159.7, 149.3, 140.7, 139.8, 134.6, 130.3, 129.6, 128.6, 125.4, 125.2, 124.5, 119.6, 115.1, 113.8, 112.6, 84.5, 63.0, 56.8, 55.2, 41.0, 28.1; IR (KBr) ν_{max}: 2921, 2851, 1760, 1728, 1601, 1463, 1343, 1286, 1247, 1144, 1049, 753 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NNaO_5^+$ [M+Na$^+$] 432.1782, found 432.1780.



2

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-(m-tolyl)indoline-1-carboxylate (3)**

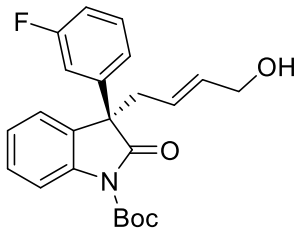
Following *General Procedure B*, the product **3** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 69% yield (54.0 mg), 96% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 32.202, t (minor) = 30.026]; $[\alpha]_D^{25}$= +56.4 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.38 (ddd, *J* = 8.2, 5.6, 3.3 Hz, 1H), 7.26 – 7.06 (m, 6H), 5.73 – 5.63 (m, 1H), 5.32 (dddd, *J* = 15.9, 7.9, 4.7, 1.5 Hz, 1H), 3.93 (d, *J* = 5.5 Hz, 2H), 3.19 – 3.09 (m, 1H), 3.05 – 2.96 (m, 1H), 2.33 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 149.3, 139.8, 139.0, 138.3, 134.5, 130.6, 128.50, 128.48, 127.9, 125.6, 125.2, 124.4, 124.3, 115.1, 84.5, 63.1, 56.8, 41.0, 28.1, 21.6; IR (KBr) ν_{max}: 3421, 2979, 2920, 1760, 1727, 1463, 1286, 1248, 1144, 969, 752 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NNaO_4^+$ [M+Na$^+$] 416.1833, found 416.1836.



3

***tert*-Butyl (*R*, *E*)-3-(3-fluorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (4)**

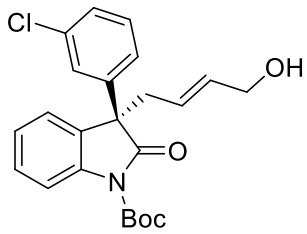
Following *General Procedure B*, the product **4** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 73% yield (58.1 mg); 97% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 15.824, t (minor) = 11.668]; $[\alpha]_D^{25}$= +47.2 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.38 (ddd, *J* = 8.2, 6.6, 2.4 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.26 – 7.19 (m, 2H), 7.12 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.05 (dt, *J* = 10.6, 2.2 Hz, 1H), 6.97 (tdd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 5.67 (dtt, *J* = 15.4, 5.7, 1.2 Hz, 1H), 5.35 – 5.24 (m, 1H), 3.92 (t, *J* = 5.2 Hz, 2H), 3.09 (ddd, *J* = 13.6, 8.1, 1.0 Hz, 1H), 3.02 – 2.93 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 162.9 (d, $J_{C\text{-}F}$ = 247.5 Hz), 149.1, 141.5 (d, $J_{C\text{-}F}$ = 7.1 Hz), 139.8, 134.8, 130.1 (d, $J_{C\text{-}F}$ = 8.4 Hz), 129.7, 128.8, 125.2, 125.0, 124.6, 123.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 115.3, 114.8 (d, $J_{C\text{-}F}$ = 5.3 Hz), 114.6 (d, $J_{C\text{-}F}$ = 7.3 Hz), 84.7, 63.1, 56.6, 41.2, 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.05; IR (KBr) ν_{max}: 3401, 2930, 1760, 1729, 1463, 1286, 1248, 1144, 970, 752 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}FNNaO_4^+$ [M+Na$^+$] 420.1582, found 420.1599.



4

***tert*-Butyl (*R*, *E*)-3-(3-chlorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (5)**

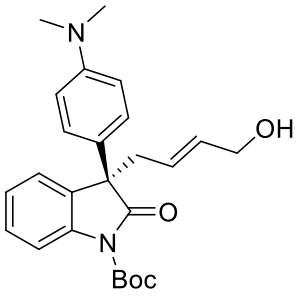
Following *General Procedure B*, the product **5** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 70% yield (58.0 mg); 96% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 15.411, t (minor) = 11.740]; $[\alpha]_D^{25}$= +45.6 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.38 (ddd, *J* = 8.2, 7.0, 1.9 Hz, 1H), 7.30 (dt, *J* = 2.6, 1.3 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.23 (ddd, *J* = 10.1, 2.0, 0.8 Hz, 4H), 5.75 – 5.53 (m, 1H), 5.28 (dddt, *J* = 15.8, 8.0, 6.4, 1.5 Hz, 1H), 3.91 (d, *J* = 5.6 Hz, 2H), 3.13 – 3.04 (m, 1H), 3.01 – 2.92 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 149.1, 141.0, 139.8, 134.9, 134.6, 129.9, 129.6, 128.9, 128.0, 127.6, 125.6, 125.1, 124.8, 124.7, 115.3, 84.8, 63.0, 56.6, 41.2, 28.1; IR (KBr) ν_{max}: 3419, 2920, 1764, 1728, 1469, 1332, 1290, 1257, 1146, 1011, 818, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}ClNNaO_4^+$ [M+Na$^+$] 436.1287, found 436.1308.



5

***tert*-Butyl (*R*, *E*)-3-(4-(dimethylamino)phenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (6)**

Following *General Procedure B*, the product **6** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 74% yield (62.9 mg); 92% *ee* [Daicel Chiralpak

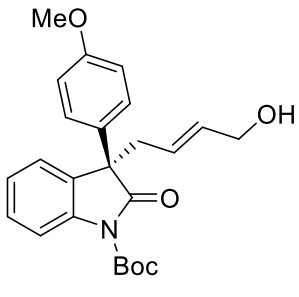


6

IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 69.095, t (minor) = 38.812]; $[\alpha]_D^{25}$= +61.2 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.36 (ddd, *J* = 8.4, 6.7, 2.2 Hz, 1H), 7.26 – 7.15 (m, 4H), 6.71 – 6.63 (m, 2H), 5.74 – 5.58 (m, 1H), 5.40 – 5.24 (m, 1H), 3.95 – 3.83 (m, 2H), 3.14 – 3.06 (m, 1H), 3.01 – 2.95 (m, 1H), 2.93 (s, 6H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 149.9, 149.5, 139.8, 134.2, 130.9, 128.3, 127.9, 126.6, 125.9, 125.2, 124.3, 115.0, 112.5, 84.3, 63.1, 56.0, 41.0, 40.4, 28.1; IR (KBr) ν_{max}: 3432, 2920, 1760, 1725, 1519, 1345, 1286, 1248, 1143, 749 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{25}H_{30}N_2NaO_4^+$ [M+Na$^+$] 445.2098, found 445.2120.

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-3-(4-methoxyphenyl)-2-oxoindoline-1-carboxylate (7)**

Following *General Procedure B*, the product **7** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 71% yield (58.5 mg); 94% *ee* [Daicel Chiralpak

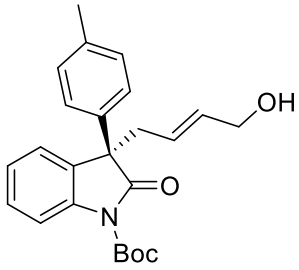


7

IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 40.474, t (minor) = 23.913]; $[\alpha]_D^{25}$= +57.2 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 13.3, 8.2 Hz, 1H), 7.28 (dq, *J* = 8.5, 4.5, 3.9 Hz, 1H), 7.18 – 7.13 (m, 4H), 6.78 – 6.73 (m, 2H), 5.57 (dt, *J* = 15.4, 5.8 Hz, 1H), 5.31 – 5.12 (m, 1H), 3.82 (d, *J* = 5.8 Hz, 2H), 3.69 (s, 3H), 3.00 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.88 (ddd, *J* = 13.7, 6.4, 1.4 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 159.1, 149.3, 139.8, 134.5, 131.1, 130.5, 128.5, 128.4, 125.6, 125.2, 124.4, 115.1, 114.0, 84.5, 63.1, 56.2, 55.3, 41.2, 28.1; IR (KBr) ν_{max}: 3420, 2921, 1728, 1463, 1343, 1286, 1247, 1144, 1049, 753 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NNaO_5^+$ [M+Na$^+$] 432.1782, found 432.1786.

***tert*-Butyl (*R, E*)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-(p-tolyl)indoline-1-carboxylate (8)**

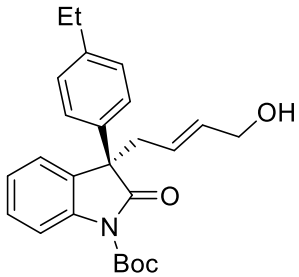
Following *General Procedure B*, the product **8** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 80% yield (63.3 mg); 91% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 27.106, t (minor) = 16.435]; $[\alpha]_D^{25}$= +41.1 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.27 (dt, *J* = 8.6, 4.5 Hz, 1H), 7.16 – 7.08 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 2H), 5.57 (dt, *J* = 15.3, 5.7 Hz, 1H), 5.27 – 5.16 (m, 1H), 3.81 (d, *J* = 5.7 Hz, 2H), 3.02 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.89 (ddd, *J* = 13.7, 6.4, 1.4 Hz, 1H), 2.22 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 149.3, 139.8, 137.5, 136.2, 134.5, 130.6, 129.4, 128.5, 127.1, 125.5, 125.2, 124.4, 115.1, 84.5, 63.1, 56.6, 41.0, 28.1, 21.0; IR (KBr) ν_{max}: 3420, 2920, 1762, 1727, 1463, 1344, 1286, 1249, 1144, 1097, 751 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NNaO_4^+$ [M+Na^+] 416.1833, found 416.1833.



8

***tert*-Butyl (*R, E*)-3-(4-ethylphenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (9)**

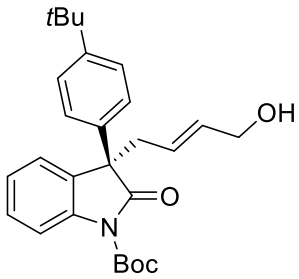
Following *General Procedure B*, the product **9** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 83% yield (67.8 mg), 95% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 25.667, t (minor) = 15.659]; $[\alpha]_D^{25}$= +54.2 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.38 (ddd, *J* = 8.5, 5.6, 3.4 Hz, 1H), 7.29 – 7.23 (m, 4H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.67 (dt, *J* = 15.4, 5.8 Hz, 1H), 5.40 – 5.24 (m, 1H), 3.91 (d, *J* = 5.7 Hz, 2H), 3.14 (dd, *J* = 13.6, 8.1 Hz, 1H), 3.06 – 2.94 (m, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.63 (s, 9H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 149.3, 143.7, 139.8, 136.4, 134.5, 130.6, 128.5, 128.2, 127.2, 125.5, 125.2, 124.4, 115.1, 84.5, 63.0, 56.6, 41.1, 28.4, 28.1, 15.4; IR (KBr) ν_{max}: 3462, 2966, 1728, 1463, 1344, 1286, 1248, 1144, 1098, 750 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{25}H_{29}NNaO_4^+$ [M+Na^+] 430.1989, found 430.2017.



9

***tert*-Butyl (*R*, *E*)-3-(4-(*tert*-butyl)phenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (10)**

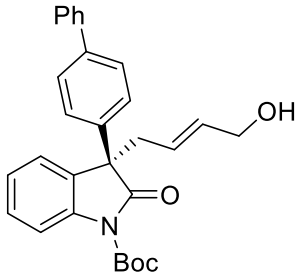
Following *General Procedure B*, the product **10** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 60% yield (51.9 mg); 93% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 19.400, t (minor) = 12.594]; $[\alpha]_D^{25}$= +48.6 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.26 (dd, *J* = 15.7, 7.3 Hz, 3H), 7.20 – 7.11 (m, 4H), 5.57 (dt, *J* = 15.4, 5.8 Hz, 1H), 5.22 (dt, *J* = 15.0, 7.3 Hz, 1H), 3.80 (d, *J* = 5.7 Hz, 2H), 3.05 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.90 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.53 (s, 9H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 150.5, 149.3, 139.8, 136.1, 134.5, 130.5, 128.5, 126.9, 125.6, 125.5, 125.2, 124.4, 115.1, 84.5, 63.1, 56.6, 41.1, 34.4, 31.3, 28.1; IR (KBr) ν_{max}: 3367, 2961, 1732, 1457, 1344, 1287, 1250, 1147, 1098, 753 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{33}NNaO_4^+$ [M+Na^+] 458.2302, found 458.2303.



10

***tert*-Butyl (*R*, *E*)-3-([1,1'-biphenyl]-4-yl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (11)**

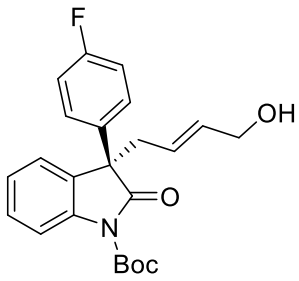
Following *General Procedure B*, the product **3cf** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 69% yield (109.1 mg); 91% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 35.151, t (minor) = 22.278]; $[\alpha]_D^{25}$= +62.4 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.57 (dt, *J* = 8.5, 2.9 Hz, 4H), 7.49 – 7.33 (m, 6H), 7.29 (d, *J* = 2.3 Hz, 2H), 5.71 (dt, *J* = 15.4, 5.7 Hz, 1H), 5.48 – 5.22 (m, 1H), 3.95 (d, *J* = 5.7 Hz, 2H), 3.19 (dd, *J* = 13.6, 8.0 Hz, 1H), 3.07 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.65 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 149.3, 140.6, 140.5, 139.9, 138.1, 134.6, 130.3, 128.8, 128.6, 127.7, 127.5, 127.4, 127.1, 125.4, 125.2, 124.5, 115.2, 84.6, 63.1, 56.7, 41.1, 28.1; IR (KBr) ν_{max}: 3434, 2919, 1727, 1463, 1345, 1286, 1249, 1144, 1002, 752 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{29}NNaO_4^+$ [M+Na^+] 478.1989, found 478.2002.



11

***tert*-Butyl (*R, E*)-3-(4-fluorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (12)**

Following *General Procedure B*, the product **12** was obtained after column chromatography

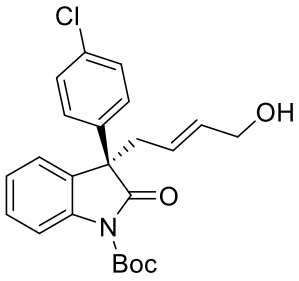


12

(petroleum ether/EtOAc v:v = 5:1); colorless oil; 61% yield (48.8 mg); 93% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 19.183, t (minor) = 12.412]; $[\alpha]_D^{25}$= +71.4 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.39 (ddd, *J* = 8.5, 6.6, 2.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 2H), 7.06 – 6.95 (m, 2H), 5.78 – 5.57 (m, 1H), 5.30 (dddt, *J* = 15.8, 8.0, 6.5, 1.5 Hz, 1H), 3.92 (dd, *J* = 5.8, 1.5 Hz, 2H), 3.10 (dd, *J* = 13.8, 8.2 Hz, 1H), 3.03 – 2.93 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 162.2 (d, J_{C-F} = 248.2p Hz), 149.2, 139.8, 134.8, 130.0, 129.0 (d, J_{C-F} = 8.2 Hz), 128.7, 125.1 (d, J_{C-F} = 12.8 Hz), 124.6, 115.6, 115.3 (d, J_{C-F} = 13.0 Hz), 84.7, 63.0, 56.2, 41.4, 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.72; IR (KBr) ν_{max}: 3420, 2923, 1727, 1478, 1294, 1248, 1141, 818, 719, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}FNNaO_4^+$ [M+Na$^+$] 420.1582, found 420.1587.

***tert*-Butyl (*R, E*)-3-(4-chlorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (13)**

Following *General Procedure B*, the product **13** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 75% yield (62.0 mg); 87% *ee* [Daicel Chiralpak

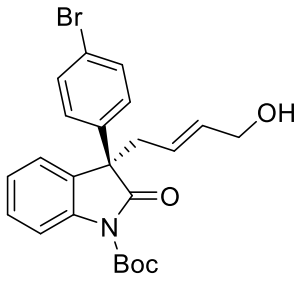


13

IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 18.380, t (minor) = 11.410]; $[\alpha]_D^{25}$= +64.0 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.40 (ddd, *J* = 8.2, 7.1, 1.9 Hz, 1H), 7.31 – 7.20 (m, 6H), 5.73 – 5.62 (m, 1H), 5.36 – 5.25 (m, 1H), 3.93 (s, 2H), 3.14 – 3.05 (m, 1H), 3.02 – 2.94 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 149.2, 139.8, 137.5, 134.8, 133.8, 129.8, 128.8, 128.8, 128.7, 125.1, 125.0, 124.6, 115.3, 84.7, 63.0, 56.4, 41.2, 28.1; IR (KBr) ν_{max}: 3435, 2921, 1728, 1468, 1332, 1290, 1257, 1146, 1011, 818, 694 cm^{-1} ; HRMS (ESI) m/z: calcd for $C_{23}H_{24}ClNNaO_4^+$ [M+Na$^+$] 436.1287, found 436.1287.

***tert*-Butyl (*R*, *E*)-3-(4-bromophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (14)**

Following *General Procedure B*, the product **14** was obtained after column chromatography

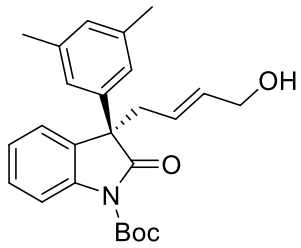


14

(petroleum ether/EtOAc v:v = 5:1); colorless oil; 60% yield (54.7 mg); 87% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 19.536, t (minor) = 11.871]; $[\alpha]_D^{25}$= +65.6 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.33 (m, 3H), 7.29 – 7.19 (m, 4H), 5.74 – 5.60 (m, 1H), 5.37 – 5.22 (m, 1H), 3.93 (d, *J* = 5.6 Hz, 2H), 3.08 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.98 (ddd, *J* = 13.6, 6.5, 1.4 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 149.2, 139.8, 138.1, 134.9, 131.8, 129.7, 129.1, 128.8, 125.1, 124.9, 124.6, 122.0, 115.3, 84.8, 63.0, 56.4, 41.1, 28.1; IR (KBr) ν_{max}: 3400, 2919, 1728, 1466, 1331, 1291, 1259, 1148, 1015, 816, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}BrNNaO_4^+$ [M+Na^+] 480.0781, found 480.0771.

***tert*-Butyl (*R*, *E*)-3-(3,5-dimethylphenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (15)**

Following *General Procedure B*, the product **15** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 92% yield (75.1 mg), 97% *ee* [Daicel Chiralpak

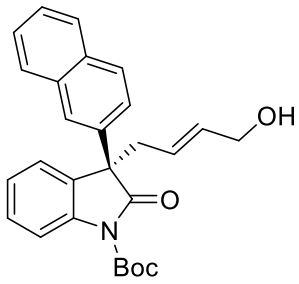


15

IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 22.816, t (minor) = 12.712]; $[\alpha]_D^{25}$= +58.4 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.38 (ddd, *J* = 8.5, 6.0, 3.0 Hz, 1H), 7.27 – 7.19 (m, 2H), 6.93 (s, 3H), 5.73 – 5.61 (m, 1H), 5.31 (dddd, *J* = 15.2, 8.1, 6.4, 1.4 Hz, 1H), 3.92 (d, *J* = 5.7 Hz, 2H), 3.13 (dd, *J* = 13.6, 8.1 Hz, 1H), 3.00 (ddd, *J* = 13.6, 6.4, 1.4 Hz, 1H), 2.29 (s, 6H), 1.64 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 149.4, 139.8, 139.0, 138.1, 134.4, 130.7, 129.4, 128.4, 125.6, 125.2, 125.0, 124.5, 115.1, 84.5, 63.1, 56.8, 41.0, 28.1, 21.5; IR (KBr) ν_{max}: 3481, 2918, 1727, 1463, 1342, 1286, 1247, 1144, 1001, 750 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{25}H_{29}NNaO_4^+$ [M+Na^+] 430.1989, found 430.2008.

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-3-(naphthalen-2-yl)-2-oxoindoline-1-carboxylate (16)**

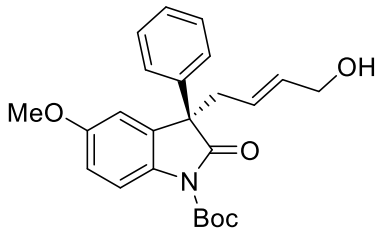
Following *General Procedure B*, the product **16** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 81% yield (81.3 mg), 95% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 210.8 nm, t (major) = 31.560, t (minor) = 19.543]; $[\alpha]_D^{25}$= +41.6 (c 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.61 (m, 4H), 7.43 – 7.30 (m, 4H), 7.17 (dd, *J* = 6.1, 4.4 Hz, 2H), 5.68 – 5.52 (m, 1H), 5.35 – 5.17 (m, 1H), 3.81 (d, *J* = 5.7 Hz, 2H), 3.13 (dd, *J* = 13.6, 8.1 Hz, 1H), 3.02 (ddd, *J* = 13.7, 6.3, 1.4 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 149.3, 139.9, 136.5, 134.7, 133.1, 132.7, 130.5, 128.7, 128.6, 128.2, 127.5, 126.4, 126.3, 125.3, 125.3, 125.1, 124.6, 115.2, 84.6, 63.1, 57.0, 41.0, 28.1; IR (KBr) ν_{max}: 3412, 2922, 1727, 1463, 1344, 1286, 1248, 1144, 1002, 752, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{27}NNaO_4^+$ [M+Na^+] 452.1833, found 452.1870.



16

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-5-methoxy-2-oxo-3-phenylindoline-1-carboxylate (17)**

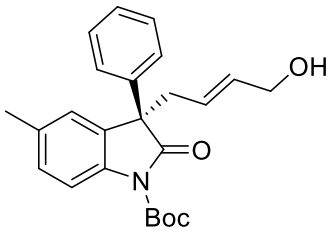
Following *General Procedure B*, the product **17** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 81% yield (66.7 mg); 98% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 210.8 nm, t (major) = 30.377, t (minor) = 20.489]; $[\alpha]_D^{25}$= +77.2 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.36 – 7.27 (m, 5H), 6.90 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.79 (d, *J* = 2.7 Hz, 1H), 5.79 – 5.61 (m, 1H), 5.41 – 5.22 (m, 1H), 3.92 (d, *J* = 5.7 Hz, 2H), 3.81 (s, 3H), 3.12 (dd, *J* = 13.7, 8.2 Hz, 1H), 3.01 (ddd, *J* = 13.6, 6.1, 1.5 Hz, 1H), 1.62 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 156.8, 149.3, 139.0, 134.7, 133.2, 131.8, 128.7, 127.7, 127.3, 125.3, 116.1, 113.3, 111.4, 84.4, 63.0, 57.2, 55.7, 40.9, 28.1; IR (KBr) ν_{max}: 3446, 2931, 1726, 1614, 1496, 1342, 1294, 1253, 1142, 1018, 841, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NNaO_5^+$ [M+Na^+] 432.1782, found 432.1782.



17

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (18)**

Following *General Procedure B*, the product **18** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 69% yield (54.0 mg); 98% *ee* [Daicel Chiralpak

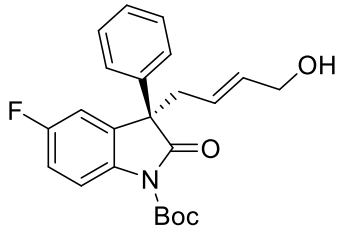


18

IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 24.520, t (minor) = 16.569]; $[\alpha]_D^{25}$= +64.6 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.27 – 7.17 (m, 5H), 7.08 (ddd, *J* = 8.3, 1.9, 0.8 Hz, 1H), 6.94 (d, *J* = 1.9 Hz, 1H), 5.60 (dtt, *J* = 15.4, 5.8, 1.3 Hz, 1H), 5.22 (dddt, *J* = 15.8, 7.9, 6.3, 1.5 Hz, 1H), 3.83 (dd, *J* = 5.7, 1.4 Hz, 2H), 3.11 – 2.99 (m, 1H), 2.95 – 2.81 (m, 1H), 2.28 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 149.3, 139.3, 137.4, 134.5, 134.1, 130.4, 129.1, 128.7, 127.6, 127.3, 125.6, 114.9, 84.4, 63.1, 57.0, 40.9, 28.1, 21.2; IR (KBr) ν_{max}: 3461, 2918, 1727, 1342, 1286, 1247, 1144, 1001, 838, 750 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NNaO_4^+$ [M+Na$^+$] 416.1833, found 416.1832.

***tert*-Butyl (*R*, *E*)-5-fluoro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (19)**

Following *General Procedure B*, the product **19** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 76% yield (60.7 mg); 96% *ee* [Daicel Chiralpak

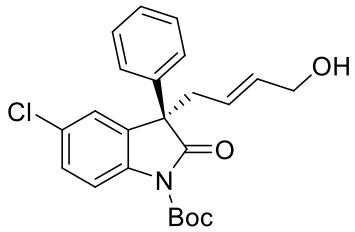


19

IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 16.382, t (minor) = 12.591]; $[\alpha]_D^{25}$= +51.2 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 9.0, 4.6 Hz, 1H), 7.33 (qd, *J* = 6.1, 5.2, 2.6 Hz, 5H), 7.08 (td, *J* = 8.9, 2.8 Hz, 1H), 6.96 (dd, *J* = 7.8, 2.8 Hz, 1H), 5.70 (dt, *J* = 15.4, 5.6 Hz, 1H), 5.41 – 5.25 (m, 1H), 3.94 (d, *J* = 5.5 Hz, 2H), 3.13 (dd, *J* = 13.7, 8.1 Hz, 1H), 3.05 – 2.96 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 159.9 (d, $J_{C\text{-}F}$ = 239.9 Hz), 149.2, 138.5, 135.7 (d, $J_{C\text{-}F}$ = 2.2 Hz), 135.0, 132.3 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.8, 127.9, 127.1, 124.7, 116.5 (d, $J_{C\text{-}F}$ = 7.9 Hz), 115.2 (d, $J_{C\text{-}F}$ = 22.9 Hz), 112.5 (d, $J_{C\text{-}F}$ = 24.4 Hz), 84.8, 62.9, 57.07, 57.05, 40.9, 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −117.28; IR (KBr) ν_{max}: 3444, 2922, 1727, 1478, 1294, 1248, 1141, 1001, 818, 718, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}FNNaO_4^+$ [M+Na$^+$] 420.1582, found 420.1592.

***tert*-Butyl (*R*, *E*)-5-chloro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (20)**

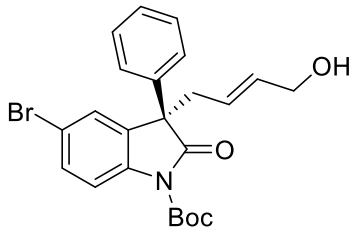
Following *General Procedure B*, the product **20** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 59% yield (48.5 mg); 96% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 15.673, t (minor) = 11.667]; $[\alpha]_D^{25}$= +58.1 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.7 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.19 (d, *J* = 2.3 Hz, 1H), 5.75 – 5.62 (m, 1H), 5.37 – 5.24 (m, 1H), 3.93 (d, *J* = 5.5 Hz, 2H), 3.10 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.99 (ddd, *J* = 13.6, 6.3, 1.4 Hz, 1H), 1.60 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 149.1, 138.4, 138.4, 135.1, 132.3, 130.0, 128.9, 128.7, 128.0, 127.1, 125.2, 124.7, 116.5, 84.9, 63.0, 57.0, 40.9, 28.1; IR (KBr) ν_{max}: 3419, 2920, 1728, 1468, 1332, 1290, 1258, 1145, 1011, 818, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}ClNNaO_4^+$ [M+Na$^+$] 436.1287, found 436.1282.



20

***tert*-Butyl (*R*, *E*)-5-bromo-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (21)**

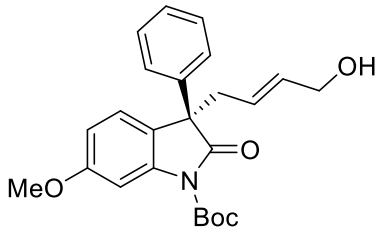
Following *General Procedure B*, the product **21** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 67% yield (61.4 mg); 97% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 17.553, t (minor) = 12.516]; $[\alpha]_D^{25}$= +63.0 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 1H), 7.28 – 7.18 (m, 7H), 5.65 – 5.57 (m, 1H), 5.27 – 5.18 (m, 1H), 3.85 (d, *J* = 5.7 Hz, 2H), 3.02 (dd, *J* = 13.3, 8.4 Hz, 1H), 2.92 (ddt, *J* = 13.6, 6.3, 1.3 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 149.1, 138.9, 138.4, 135.1, 132.7, 131.6, 128.9, 128.1, 128.0, 127.1, 124.6, 117.5, 116.9, 85.0, 62.9, 56.9, 40.9, 28.1; IR (KBr) ν_{max}: 3412, 2929, 1728, 1466, 1332, 1291, 1258, 1148, 1014, 815, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}BrNNaO_4^+$ [M+Na$^+$] 480.0781, found 480.0778.



21

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-6-methoxy-2-oxo-3-phenylindoline-1-carboxylate (22)**

Following *General Procedure B*, the product **22** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 69% yield (56.5 mg); 98% *ee* [Daicel Chiralpak

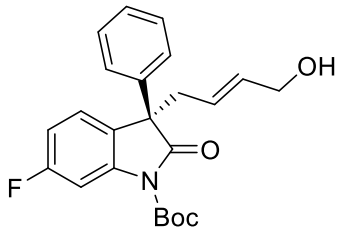


22

IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 25.138, t (minor) = 17.488]; $[\alpha]_D^{25}$= +70.0 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.4 Hz, 1H), 7.39 – 7.27 (m, 5H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.75 – 5.62 (m, 1H), 5.39 – 5.27 (m, 1H), 3.94 (d, *J* = 5.7 Hz, 2H), 3.88 (s, 3H), 3.10 (dd, *J* = 13.6, 8.1 Hz, 1H), 3.04 – 2.94 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 159.9, 149.2, 140.8, 139.5, 134.4, 128.6, 127.6, 127.2, 125.8, 125.6, 122.0, 110.2, 101.7, 84.5, 63.1, 56.3, 55.6, 41.2, 28.1; IR (KBr) ν_{max}: 3460, 2931, 1726, 1614, 1496, 1446, 1342, 1294, 1253, 1142, 1018, 841, 803, 720, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NNaO_5^+$ [M+Na^+] 432.1782, found 432.1797.

***tert*-Butyl (*R*, *E*)-6-fluoro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (23)**

Following *General Procedure B*, the product **23** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 72% yield (57.5 mg); 97% *ee* [Daicel Chiralpak

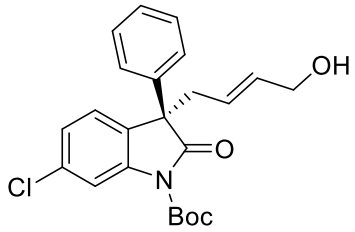


23

IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 15.922, t (minor) = 11.917]; $[\alpha]_D^{25}$= +77.1 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 10.2, 2.4 Hz, 1H), 7.28 – 7.19 (m, 5H), 7.09 (dd, *J* = 8.4, 5.6 Hz, 1H), 6.85 (td, *J* = 8.6, 2.5 Hz, 1H), 5.58 (dt, *J* = 15.4, 5.7 Hz, 1H), 5.28 – 5.16 (m, 1H), 3.84 (d, *J* = 5.7 Hz, 2H), 3.01 (dd, *J* = 13.7, 8.1 Hz, 1H), 2.96 – 2.86 (m, 1H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 162.6 (d, $J_{C\text{-}F}$ = 245.8 Hz), 149.0, 140.8 (d, $J_{C\text{-}F}$ = 12.4 Hz), 138.8, 134.8, 128.8, 127.9, 127.2, 126.2 (d, $J_{C\text{-}F}$ = 9.6 Hz), 125.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 125.0, 111.2 (d, $J_{C\text{-}F}$ = 22.7 Hz), 103.9 (d, $J_{C\text{-}F}$ = 29.6 Hz), 85.0, 63.0, 56.5, 41.1, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –110.80; IR (KBr) ν_{max}: 3482, 2924, 1728, 1478, 1344, 1294, 1248, 1141, 818, 719, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}FNNaO_4^+$ [M+Na^+] 420.1582, found 420.1582.

***tert*-Butyl (*R*, *E*)-6-chloro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (24)**

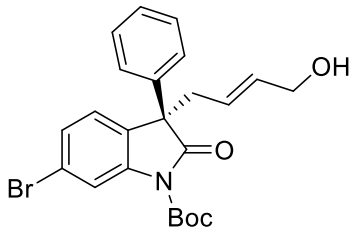
Following *General Procedure B*, the product **24** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 83% yield (68.9 mg); 97% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 13.964, t (minor) = 11.498]; $[\alpha]_D^{25}$= +62.5 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.29 (m, 5H), 7.24 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 5.75 – 5.63 (m, 1H), 5.33 (dddt, *J* = 15.8, 7.9, 6.4, 1.5 Hz, 1H), 3.96 (dd, *J* = 5.6, 1.4 Hz, 2H), 3.16 – 3.07 (m, 1H), 3.06 – 2.97 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 149.0, 140.7, 138.6, 134.9, 134.3, 128.8, 128.7, 127.9, 127.1, 126.1, 124.9, 124.6, 116.0, 85.1, 63.0, 56.6, 41.0, 28.0; IR (KBr) ν_{max}: 3421, 2920, 1728, 1468, 1332, 1290, 1257, 1145, 1011, 818, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}ClNNaO_4^+$ [M+Na$^+$] 436.1287, found 436.1304.



24

***tert*-Butyl (*R*, *E*)-6-bromo-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (25)**

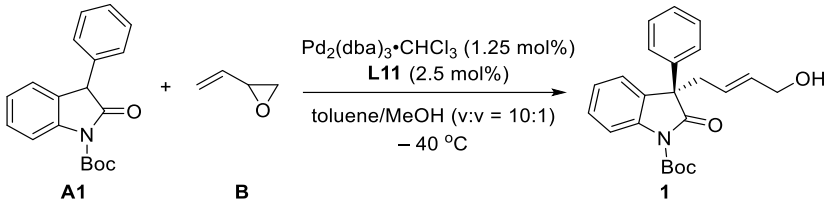
Following *General Procedure B*, the product **25** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 55% yield (50.7 mg); 97% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 13.888, t (minor) = 11.700]; $[\alpha]_D^{25}$= +52.2 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 1.8 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.36 – 7.29 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 1H), 5.75 – 5.63 (m, 1H), 5.39 – 5.26 (m, 1H), 3.96 (d, *J* = 5.6 Hz, 2H), 3.11 (dd, *J* = 13.7, 8.1 Hz, 1H), 3.02 (ddd, *J* = 13.7, 6.4, 1.4 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 149.0, 140.8, 138.5, 134.9, 129.3, 128.8, 127.9, 127.5, 127.1, 126.4, 124.8, 122.2, 118.7, 85.1, 63.0, 56.6, 40.9, 28.0; IR (KBr) ν_{max}: 3388, 2918, 1728, 1466, 1332, 1290, 1258, 1148, 1016, 816, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{24}BrNNaO_4^+$ [M+Na$^+$] 480.0781, found 480.0780.



25

4. Scale-up synthesis and further transformations of the adducts

4.1 Gram scale synthesis of 3af



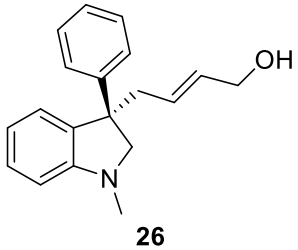
To an oven-dried 50 mL schlenk flask, $Pd_2(dba)_3 \cdot CHCl_3$ (64 mg, 0.0625 mmol, 1.25 mol%) and **L11** (101.5 mg, 0.125 mmol, 2.5 mol%) in dry toluene/MeOH (v:v = 10:1, 20 mL) were added under a nitrogen atmosphere. The mixture was stirred for 1.0 hour at room temperature to produce an orange solution. Then 3-substituted oxindoles **A1** (1.90 g, 5 mmol) and 2-vinyloxirane **B** (0.35 g, 5 mmol) was added at –40 °C. Afterwards, the solution was stirred at –40 °C for 12.0 hours. At last, it was subjected to silica gel column (PE/EA v:v = 5:1) to afford **1** as colorless oil in 82% yield (1.55 g) with 95% *ee*.

4.2 Further transformation of the adduct 1

To an oven-dried schlenk tube, **1** (0.2 mmol, 1.0 equiv.) and the solvent of THF (1.0 mL) were added. Then $LiAlH_4$ (1.0 mmol, 5.0 equiv.) was added under 0 ℃. The reaction mixture was stirred at 60 ℃ under N_2 atmosphere for 12 hours. After the reaction completed, NaOH (1M, 2.0 mL) was added to quench the reaction and the water layer was extracted with EtOAc (2.0 mL×3). The combined organic layer was washed with brine (2.0 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using PE/EA (2/1) as the eluent to give the product **26** in 84 % yield.

***(R, E)*-4-(1-Methyl-3-phenylindolin-3-yl)but-2-en-1-ol (26)**

The product **26** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1);



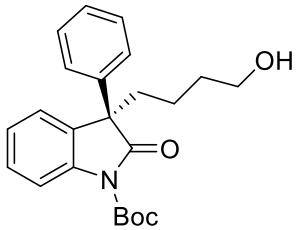
colorless oil; 84% yield (46.8 mg), 93% *ee* [Daicel Chiralpak AD, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 9.644, t (minor) = 10.649]; [α] = +93.4 (c 0.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 4H), 7.22 – 7.12 (m, 2H), 7.03 (dd, J = 7.4, 1.3 Hz, 1H), 6.72 (td, J = 7.4, 1.0 Hz, 1H), 6.54 (d, J = 7.9 Hz, 1H), 5.68 – 5.47 (m, 2H), 4.01 – 3.90 (m, 2H), 3.49 (d, J = 9.0 Hz, 1H), 3.40 (d, J = 9.0

Hz, 1H), 2.92 – 2.79 (m, 2H), 2.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 145.7, 134.9, 132.3, 129.0, 128.3, 128.1, 126.9, 126.4, 124.8, 117.8, 107.8, 69.2, 63.5, 52.0, 41.7, 36.0; IR (KBr) ν_{max}: 3360, 2921, 1735, 1603, 1488, 1466, 1242, 967, 741, 697 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{19}H_{22}NO^+$ [M+H$^+$] 280.1696, found 280.1701.

To an oven-dried schlenk tube, **1** (0.2 mmol) and Pd/C (0.20 mmol, wt 10%) were added. Then the solvent of MeOH (1.0 mL) was added. The reaction mixture was stirred at room temperature under H_2 atmosphere for 12 hours. It was filtered. The filtrate was concentrated and purified by column chromatography on silica gel using PE/EA (2/1) as the eluent to give the product **27** in 82 % yield.

***tert*-Butyl (*R*)-3-(4-hydroxybutyl)-2-oxo-3-phenylindoline-1-carboxylate (27)**

The product **27** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1);



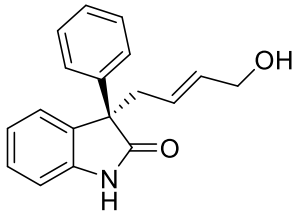
27

colorless oil; 82% yield (62.4 mg), 92% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 9.070, t (minor) = 8.101]; [α] = +96.7 (c 0.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.27 (m, 5H), 7.26 – 7.16 (m, 3H), 2.47 (td, *J* = 12.7, 4.3 Hz, 1H), 2.16 (td, *J* = 12.8, 4.1 Hz, 1H), 1.62 (s, 9H), 1.33 – 1.24 (m, 2H), 1.19 – 1.06 (m, 1H), 0.90 (tdd, *J* = 12.4, 6.1, 3.3 Hz, 1H), 0.82 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 149.4, 140.2, 140.1, 131.1, 128.6, 128.3, 127.5, 127.1, 124.8, 124.5, 115.2, 84.3, 57.0, 38.4, 28.1, 26.7, 22.9, 13.8; IR (KBr) ν_{max}: 2957, 1763, 1727, 1463, 1346, 1286, 1246, 1146, 752, 719, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{27}NNaO_4^+$ [M+Na$^+$] 404.1833, found 404.1833.

To an oven-dried schlenk tube, **1** (0.2 mmol, 1.0 equiv.) and the solvent of MeOH (1.0 mL) were added. Then NaOMe (0.06 mmol, 0.3 equiv.) were added. The reaction mixture was stirred at room temperature under N_2 atmosphere for 1 hour. After the reaction completed, NH_4Cl (1M, 2.0 mL) was added to quench the reaction and the water layer was extracted with EtOAc (2.0 mL×3). The combined organic layer was washed with brine (2.0 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using PE/EA (2/1) as the eluent to give the product **28** in 82 % yield.

***(R, E)*-3-(4-Hydroxybut-2-en-1-yl)-3-phenylindolin-2-one (28)**

The product **28** was obtained after column chromatography (petroleum ether/EtOAc v:v = 2:1); colorless oil; 82% yield (45.8 mg), 94% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 12.247, t (minor) = 17.416]; [α] = +27.0 (c 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.42 – 7.21 (m, 7H), 7.14 – 7.04 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 5.71 (dt, *J* = 15.4, 5.7 Hz, 1H), 5.40 – 5.21 (m, 1H), 3.89 (d, *J* = 5.6 Hz, 2H), 3.14 (dd, *J* = 13.5, 8.2 Hz, 1H), 3.05 – 2.92 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.7, 141.0, 139.4, 134.2, 132.5, 128.7, 128.3, 127.5, 126.9, 125.6, 125.2, 122.6, 110.2, 63.0, 57.2, 40.0; IR (KBr) ν_{max}: 3217, 2921, 1698, 1617, 1470, 1326, 1215, 968, 747, 694, 659 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{18}H_{17}NNaO_2^+$ [M+Na^+] 302.1152, found 302.1153.

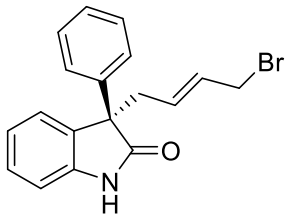


28

To an oven-dried schlenk tube, **1** (0.2 mmol, 1.0 equiv.) and HBr (48% w.t.) were added. The reaction mixture was stirred at room temperature for 3 hours. After the reaction completed, saturated $NaHCO_3$ solution (2.0 mL) was added to quench the reaction and the water layer was extracted with EtOAc (2.0 mL×3). The combined organic layer was washed with brine (2.0 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using PE/EA (5/1) as the eluent to give the product **29** in 71 % yield.

***(R, E)*-3-(4-Bromobut-2-en-1-yl)-3-phenylindolin-2-one (29)**

The product **29** was obtained after column chromatography (petroleum ether/EtOAc v:v = 5:1); colorless oil; 71% yield (48.5mg), 94% *ee* [Daicel Chiralpak IC, hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 19.061, t (minor) = 8.952]; [α] = +51.2 (c 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.46 – 7.27 (m, 6H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 5.76 (dt, *J* = 15.2, 7.7 Hz, 1H), 5.48 (dt, *J* = 14.8, 7.3 Hz, 1H), 3.92 – 3.65 (m, 2H), 3.07 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 141.0, 139.0, 132.0, 131.0, 129.6, 128.7, 128.4, 127.6, 127.0, 125.4, 122.6,



29

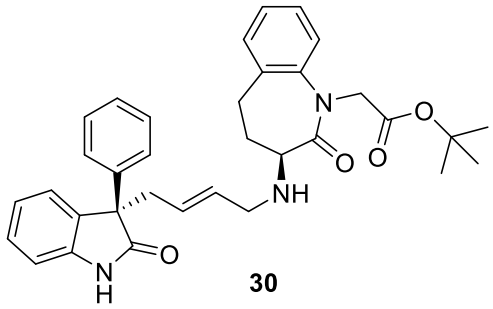
110.4, 56.9, 39.7, 32.4; IR (KBr) ν_{max}: 3205, 1702, 1616, 1469, 1202, 963, 747, 694, 659, 591 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{18}H_{16}BrNNaO^+$ [M+Na^+] 364.0308, found 364.0303.

General procedure C for preparation of 30–34

To a schlenk tube, **29** (0.2 mmol, 1.0 equiv.), amino compound (0.8 mmol, 4.0 equiv) and the solvent of MeCN (1.0 mL) were added. Then K_2CO_3 (0.24 mmol, 1.2 equiv.) were added. The reaction mixture was stirred at 60 °C. After the reaction was complete (monitored by TLC), water was added to quench the reaction and the water layer was extracted with EtOAc (2.0 mL×3). The combined organic layer was washed with brine (2.0 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. it was subjected to silica gel column to afford the desired products **30**-**34**.

***tert*-Butyl 2-((*S*)-2-oxo-3-(((*E*)-4-((*R*)-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)amino)-2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)acetate (30)**

Following *General Procedure C*, the product **30** was obtained after column chromatography

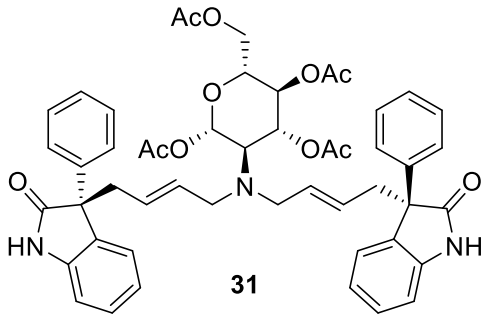


30

(DCM/MeOH v:v = 20:1); colorless oil; 71% yield (78.5 mg); [α] = –50.7 (c 0.08, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.37 – 7.19 (m, 11H), 7.10 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 5.44 (dt, *J* = 14.0, 6.6 Hz, 1H), 5.25 (dt, *J* = 14.9, 7.1 Hz, 1H), 4.44 (s, 2H), 3.16 (ddd, *J* = 29.3, 12.4, 7.7 Hz, 2H), 3.05 (dd, *J* = 13.3, 6.2 Hz, 1H), 2.97 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.82 (ddd, *J* = 29.0, 13.5, 7.4 Hz, 2H), 2.60 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.27 (tt, *J* = 13.5, 7.4 Hz, 1H), 1.89 (td, *J* = 12.0, 7.4 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, CD_3OD) δ 180.8, 172.6, 168.2, 141.5, 140.8, 139.7, 135.5, 132.7, 130.2, 129.2, 128.4, 128.2, 128.0, 127.9, 127.0, 126.9, 126.6, 124.9, 122.3, 122.1, 109.8, 81.8, 57.0, 56.7, 50.9, 39.3, 35.9, 27.7, 26.9; IR (KBr) ν_{max}: 2976, 1715, 1667, 1455, 1365, 1219, 1150, 753, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{34}H_{38}N_3O_4^+$ [M+H^+] 552.2857, found 552.2858.

(2*S*, 3*R*, 4*R*, 5*S*, 6*R*)-6-(Acetoxymethyl)-3-(bis((*E*)-4-((*R*)-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)amino)tetrahydro-2H-pyran-2,4,5-triyl triacetate (31)

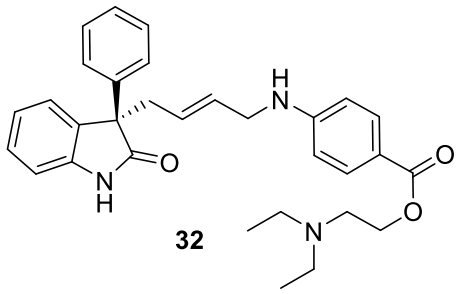
Following *General Procedure C*, the product **30** was obtained after column chromatography (petroleum ether/EtOAc v:v = 2:1); colorless oil; 49% yield (85.4 mg); [α] = +44.0 (c 0.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 2H), 7.37 – 7.20 (m, 10H), 7.15 (td, *J* = 7.7, 1.3 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 2H), 6.98 (td, *J* = 7.5, 1.1 Hz, 2H), 6.91 (d, *J* = 7.7 Hz, 2H), 5.38 (d, *J* = 8.8 Hz, 1H), 5.10 – 4.99 (m, 2H), 4.99 – 4.92 (m, 1H), 4.91 – 4.77 (m, 3H), 4.17 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.92 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.53 (dd, *J* = 10.0, 2.4 Hz, 1H), 3.14 (dd, *J* = 13.0, 7.7 Hz, 2H), 2.83 (dd, *J* = 13.0, 6.7 Hz, 2H), 2.72 (dd, *J* = 10.5, 8.8 Hz, 1H), 2.52 (ddd, *J* = 46.7, 15.3, 5.6 Hz, 4H), 1.99 – 1.89 (m, 9H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8, 169.6, 168.7, 168.6, 167.8, 140.2, 138.8, 132.0, 131.3, 127.7, 127.2, 126.5, 125.6, 124.9, 123.7, 121.8, 109.4, 91.5, 71.3, 69.0, 67.8, 62.3, 60.8, 56.8, 49.0, 39.5, 20.2, 19.7, 19.6; IR (KBr) ν_{max}: 2920, 1710, 1471, 1364, 1213, 1031, 799, 660, 485 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{50}H_{52}N_3O_{11}^+$ [M+H$^+$] 870.3597, found 870.3600.



31

2-(Diethylamino)ethyl (*R*, *E*)-4-((4-(2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)amino)benzoate (32)

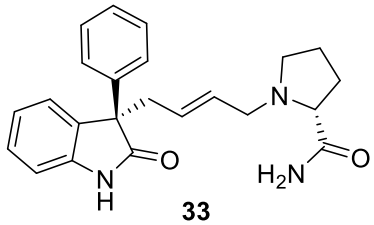
Following *General Procedure C*, the product **32** was obtained after column chromatography (DCM/MeOH v:v = 20:1); colorless oil; 50% yield (50.0 mg); [α] = +16.0 (c 0.10, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.75 – 7.71 (m, 2H), 7.35 – 7.26 (m, 6H), 7.13 – 7.05 (m, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.65 (ddt, *J* = 12.9, 6.5, 2.3 Hz, 3H), 5.86 – 5.74 (m, 1H), 5.64 (ddt, *J* = 15.0, 11.8, 7.3 Hz, 1H), 4.52 (t, *J* = 5.1 Hz, 1H), 3.80 (dq, *J* = 7.1, 3.6, 2.5 Hz, 2H), 3.75 (d, *J* = 7.4 Hz, 1H), 3.35 (s, 1H), 3.24 (dd, *J* = 13.3, 6.5 Hz, 1H), 3.16 – 2.91 (m, 7H), 1.17 (dt, *J* = 14.1, 5.6 Hz, 6H); ^{13}C NMR (101 MHz, CD_3OD) δ 180.6, 166.1, 154.1, 141.8, 132.8, 131.4, 131.1, 130.7, 128.4, 127.3, 126.4, 125.0, 122.5, 113.4, 113.0, 57.0, 56.9, 56.5, 55.0, 53.5, 53.3, 39.5, 10.3, 6.5; IR (KBr) ν_{max}: 3204, 1695, 1599, 1469, 1367, 1267, 1170, 1085, 754, 697 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{31}H_{36}N_3O_3^+$ [M+H$^+$] 498.2752, found 498.2752.



32

(*R*)-1-((*E*)-4-((*R*)-2-oxo-3-Phenylindolin-3-yl)but-2-en-1-yl)pyrrolidine-2-carboxamide (33)

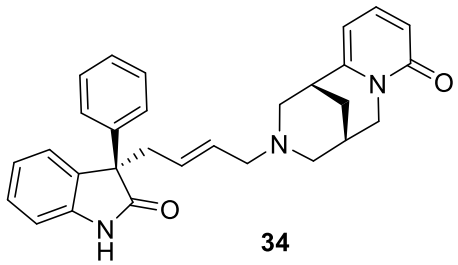
Following *General Procedure C*, the product **33** was obtained after column chromatography (DCM/MeOH v:v = 20:1); colorless oil; 95% yield (71.3 mg); [α] = +46.7 (c 0.09, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.33 – 7.16 (m, 6H), 7.14 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.02 (td, *J* = 7.5, 1.1 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.65 – 5.47 (m, 1H), 5.21 (dt, *J* = 14.9, 7.0 Hz, 1H), 3.14 (q, *J* = 7.3 Hz, 1H), 2.98 (qd, *J* = 12.3, 11.2, 6.7 Hz, 4H), 2.84 (dd, *J* = 13.4, 7.3 Hz, 1H), 2.21 – 1.99 (m, 2H), 1.71 (dddd, *J* = 23.1, 11.7, 7.8, 4.2 Hz, 3H); ^{13}C NMR (101 MHz, CD_3OD) δ 182.3, 179.5, 143.0, 141.3, 134.3, 131.6, 129.6, 129.4, 128.4, 127.9, 126.0, 123.6, 111.1, 67.2, 58.6, 57.2, 54.0, 40.7, 31.4, 24.6; IR (KBr) ν_{max}: 3157, 2803, 1702, 1617, 1470, 1195, 969, 752, 95, 659, 602 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{26}N_3O_2^+$ [M+H$^+$] 376.2020, found 376.2024.



33

(1*R*,5*S*)-3-((*E*)-4-((*R*)-2-oxo-3-Phenylindolin-3-yl)but-2-en-1-yl)-1,2,3,4,5,6-hexahydro-8H-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one (34)

Following *General Procedure C*, the product **34** was obtained after column chromatography (petroleum ether/EtOAc v:v = 2:1); colorless oil; 98% yield (88.5 mg); [α] = –60.4 (c 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.40 – 7.32 (m, 2H), 7.29 (t, *J* = 1.6 Hz, 1H), 7.27 – 7.16 (m, 4H), 7.13 (d, *J* = 6.7 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.48 (dd, *J* = 9.0, 1.4 Hz, 1H), 5.97 (dd, *J* = 6.9, 1.4 Hz, 1H), 5.36 (dt, *J* = 14.0, 6.7 Hz, 1H), 5.13 (dt, *J* = 14.8, 7.1 Hz, 1H), 3.95 (d, *J* = 15.4 Hz, 1H), 3.82 (dd, *J* = 15.4, 6.7 Hz, 1H), 3.12 – 3.03 (m, 1H), 2.94 – 2.81 (m, 2H), 2.69 (dt, *J* = 13.8, 7.5 Hz, 2H), 2.57 – 2.39 (m, 2H), 2.19 (ddd, *J* = 39.8, 8.8, 2.8 Hz, 2H), 1.91 – 1.71 (m, 2H), 1.63 (dt, *J* = 12.8, 3.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 163.9, 151.8, 141.9, 139.9, 139.1, 132.7, 131.3, 128.5, 128.2, 128.0, 127.3, 126.9, 125.0, 122.3, 116.4, 110.2, 105.3, 60.8, 59.2, 58.1, 57.2, 50.0, 40.5, 35.5, 27.7, 25.8; IR (KBr) ν_{max}: 2934, 1712, 1642, 1542, 1470, 1135, 973, 798, 752, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{30}N_3O_2^+$ [M+H$^+$] 452.2333, found 452.2361.

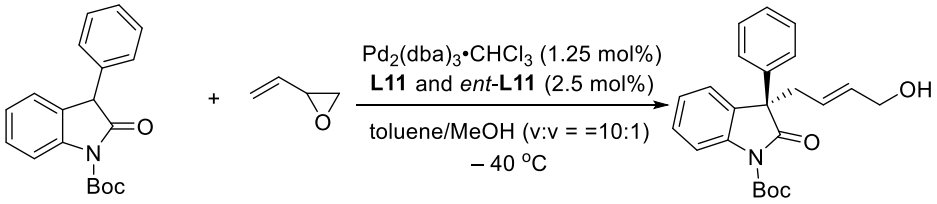


34

5. Study of the non-linear effect

To an oven-dried schlenk tube, $Pd_2(dba)_3{\cdot}CHCl_3$ (2.6 mg, 0.0025 mmol), **L11** (x mg) and *ent*-**L11** (y mg) in the mixed solvents of toluene/MeOH (v:v = 10:1, 1.0 mL) were added under a nitrogen atmosphere. The mixture was stirred for 1.0 hour at 25 °C to produce an orange solution. After that, the solution was cooled to −40 °C and stirred for additional 15 minutes, followed by the addition of 3-substituted oxindole **A1** (61.8 mg, 0.20 mmol). Then, the mixture was stirred for additional 10 minutes, and a solution of 2-vinyloxirane **B** (44.7 mg, 0.20 mmol) in the mixed solvents of toluene/MeOH (v:v = 10:1, 1.0 mL) was added dropwise. Subsequently, the mixture was stirred at −40 °C for 12 hours and then it was subjected to silica gel column (petroleum ether/EtOAc v:v = 5:1) to afford the desired product **1**.

Table S9. Study of the non-linear effect



A1 **B** **1**

entry	x/y (mg)	ee (%) (**L11**+*ent*-**L11**)	yield (%)[b]	*ee* (%)[c]
1	2.1/2.1	0	84	0
2	2.5/1.7	20	82	25
3	2.9/1.3	40	84	55
4	3.4/0.8	60	81	83
5	3.8/0.4	80	80	94
6	4.2/0	100	85	95

[a] Unless otherwise noted, reactions were carried out with **A1** (0.20 mmol), **B** (0.20 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (1.25 mol%) and **L11** and *ent*-**L11** (2.5 mol%) in the mixed solvents of toluene/MeOH (v:v = 10:1, 2.0 mL) at −40 °C for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.

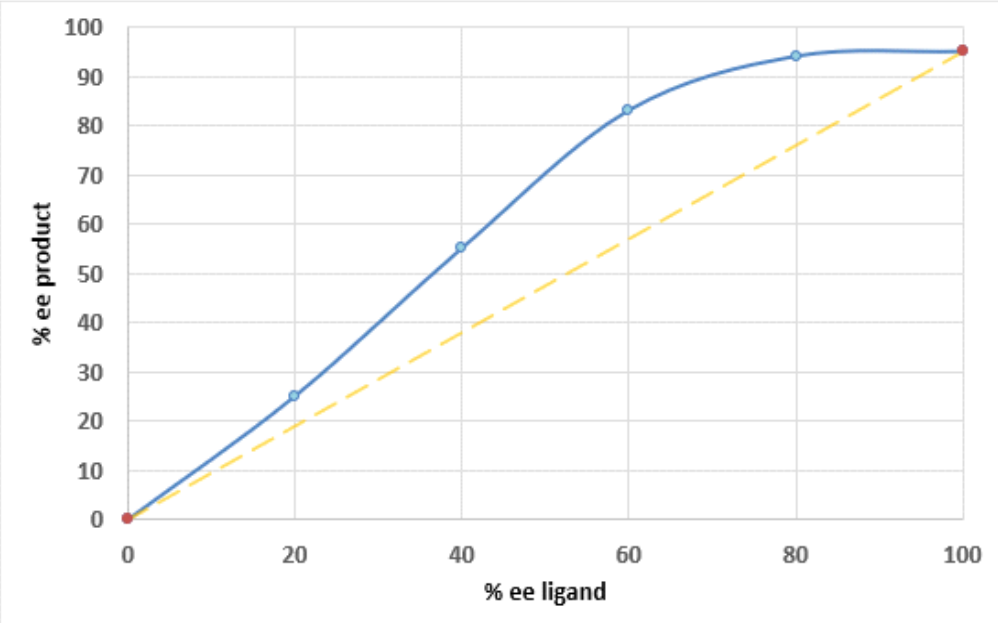


Fig. S1 Study of the non-linear effect

6. X-Ray data of 7

Table S10. Crystal data and structure refinement for **7**

Identification code	ga20230228bb_0m_a
Empirical formula	$C_{24}H_{27}NO_5$
Formula weight	409.46
Temperature/K	120.00
Crystal system	monoclinic
Space group	C_2
a/Å	22.512(5)
b/Å	19.096(4)
c/Å	10.544(2)
α/°	90
β/°	95.883(7)
γ/°	90
Volume/Å^3	4508.9(17)
Z	8
ρcalcg/cm^3	1.206
μ/mm^{-1}	0.437
F(000)	1744.0
Crystal size/mm^3	0.2 × 0.15 × 0.13
Radiation	GaKα (λ = 1.34138)
2θ range for data collection/°	5.592 to 106.64
Index ranges	$-26 \le h \le 26$, $-21 \le k \le 21$, $-12 \le l \le 12$

Reflections collected	39458
Independent reflections	7684 [R_{int} = 0.0604, R_{sigma} = 0.0469]
Data/restraints/parameters	7684/359/606
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.2027
Final R indexes [all data]	R_1 = 0.0771, wR_2 = 0.2077
Largest diff. peak/hole / e Å^{-3}	0.52/-0.28
Flack parameter	0.04(15)

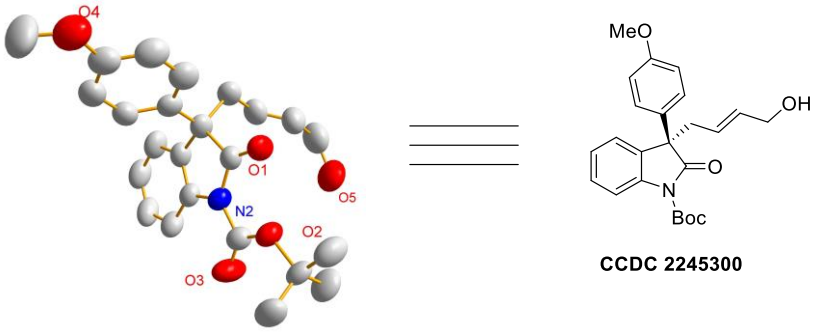


Fig. S2 ORTEP drawing of **7** (50% thermal ellipsoids)

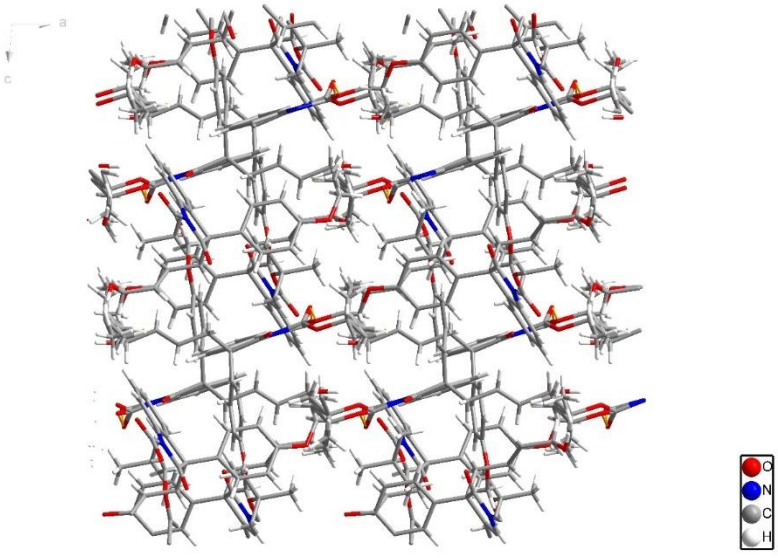
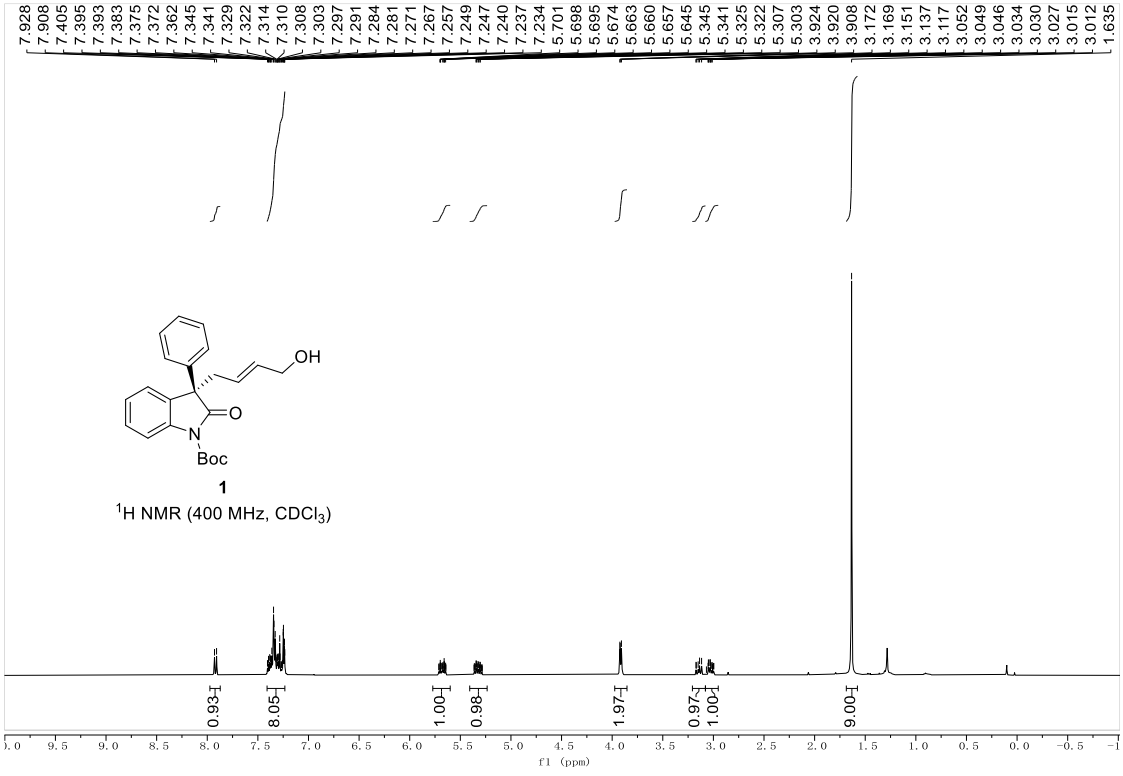


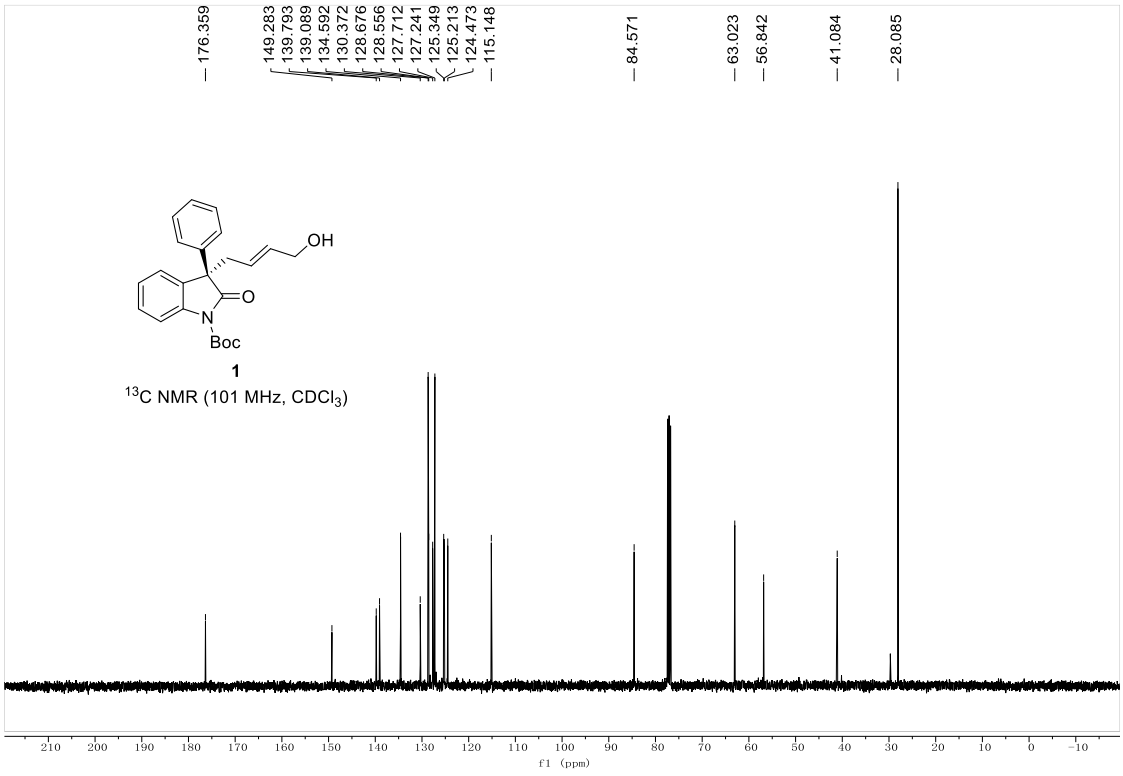
Figure S3. Packing of moleculars in a unit cell of **7**

The product **7** (30 mg) was dissolved in methanol until the solution was supersaturated. Then diethyl ether was added until the solution was turbid. Methanol was further added until the solution became clear. The solution was sealed up and several holes were made on the cap. As the solvents evaporating, the crystals **7** were obtained. CCDC **2245300** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

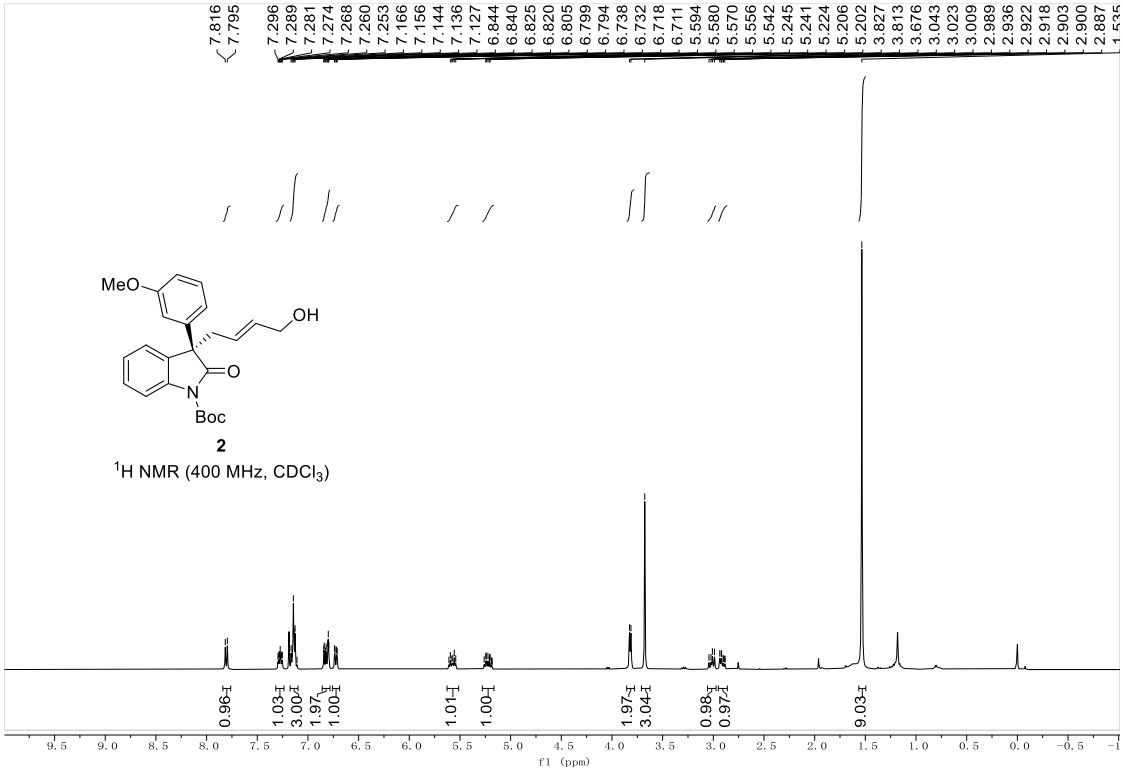
7. NMR spectra

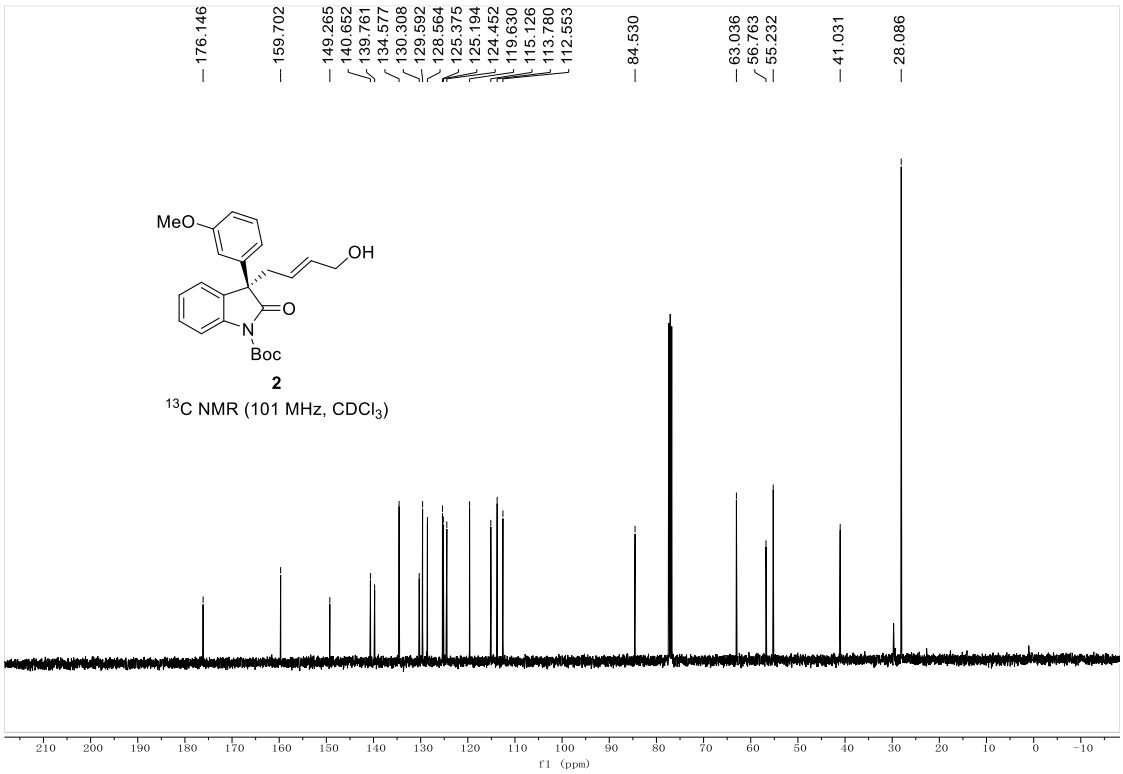
tert-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (1)



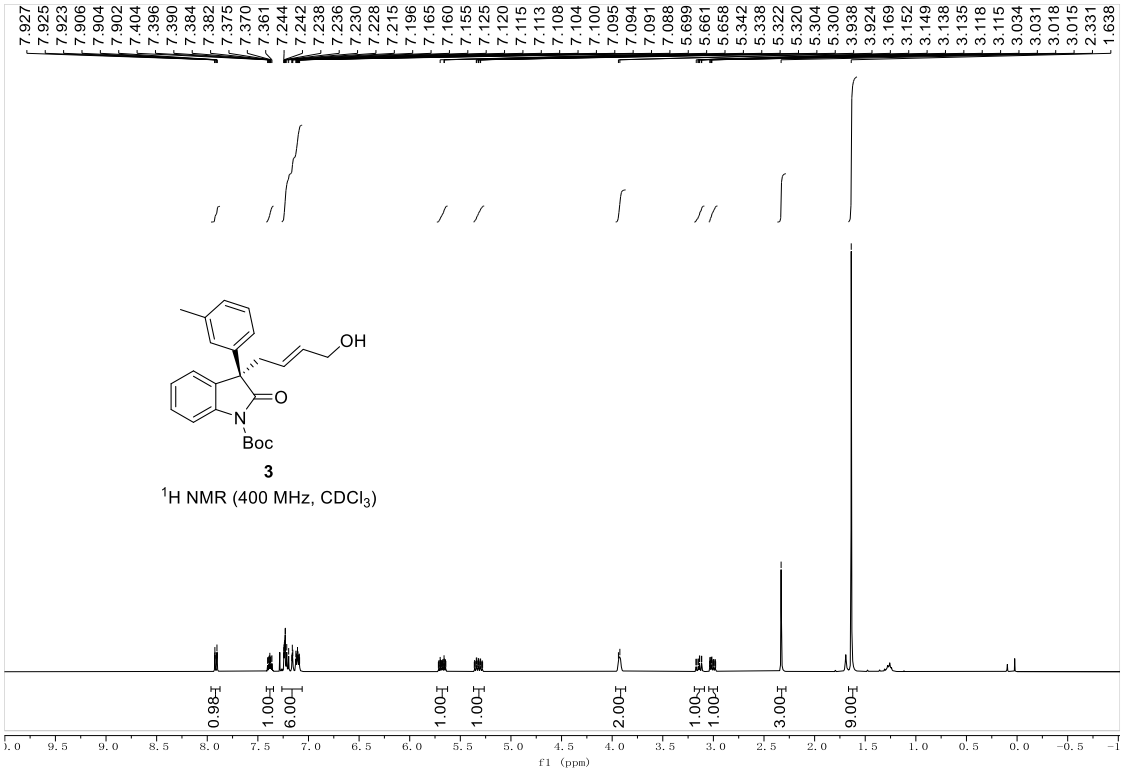


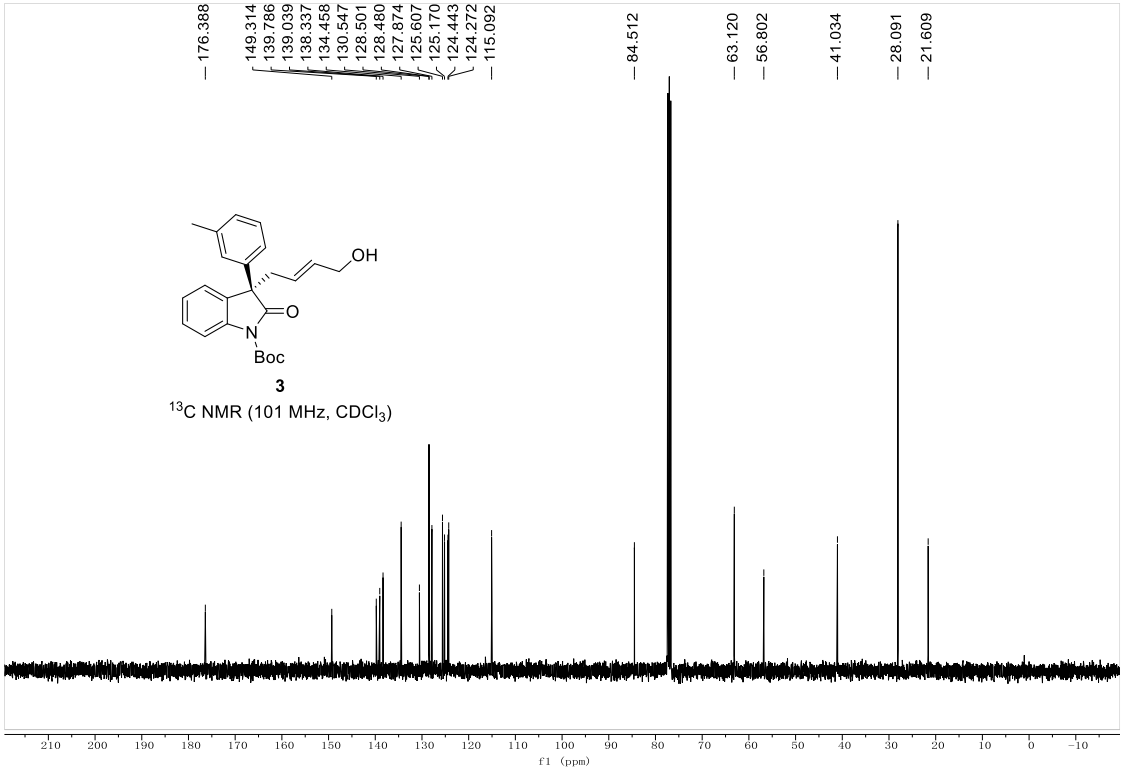
***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-3-(3-methoxyphenyl)-2-oxoindoline-1-carboxyl ate (2)**



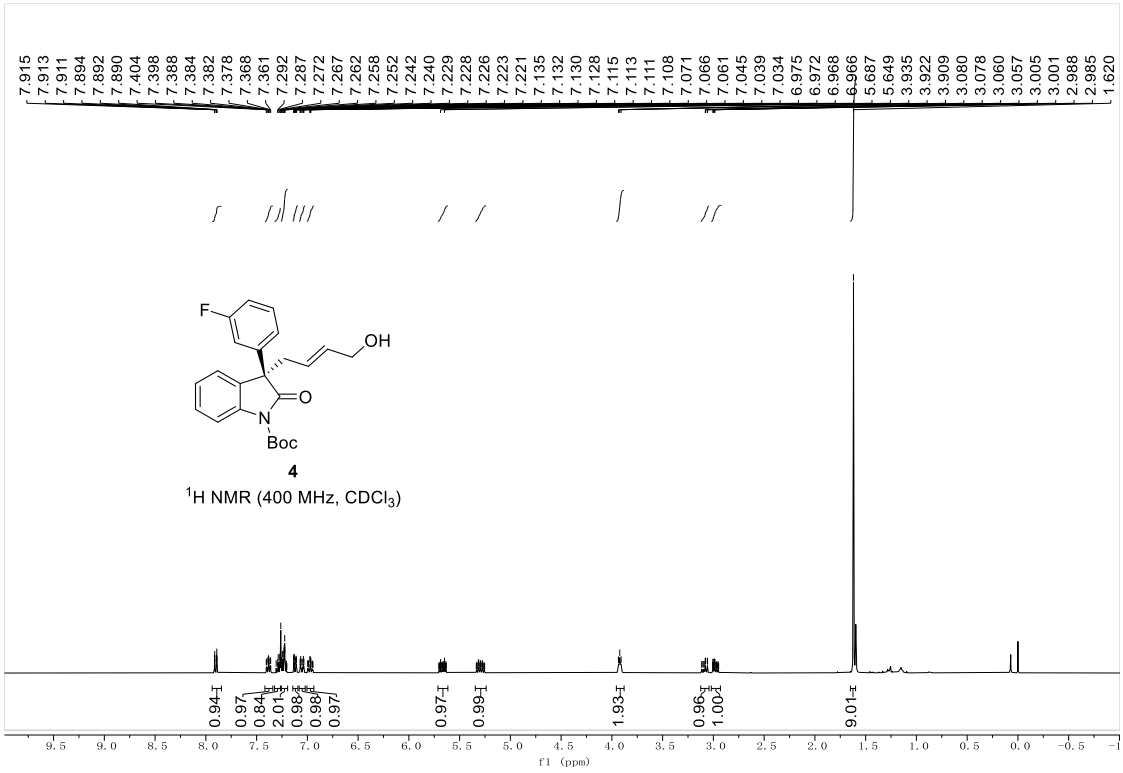


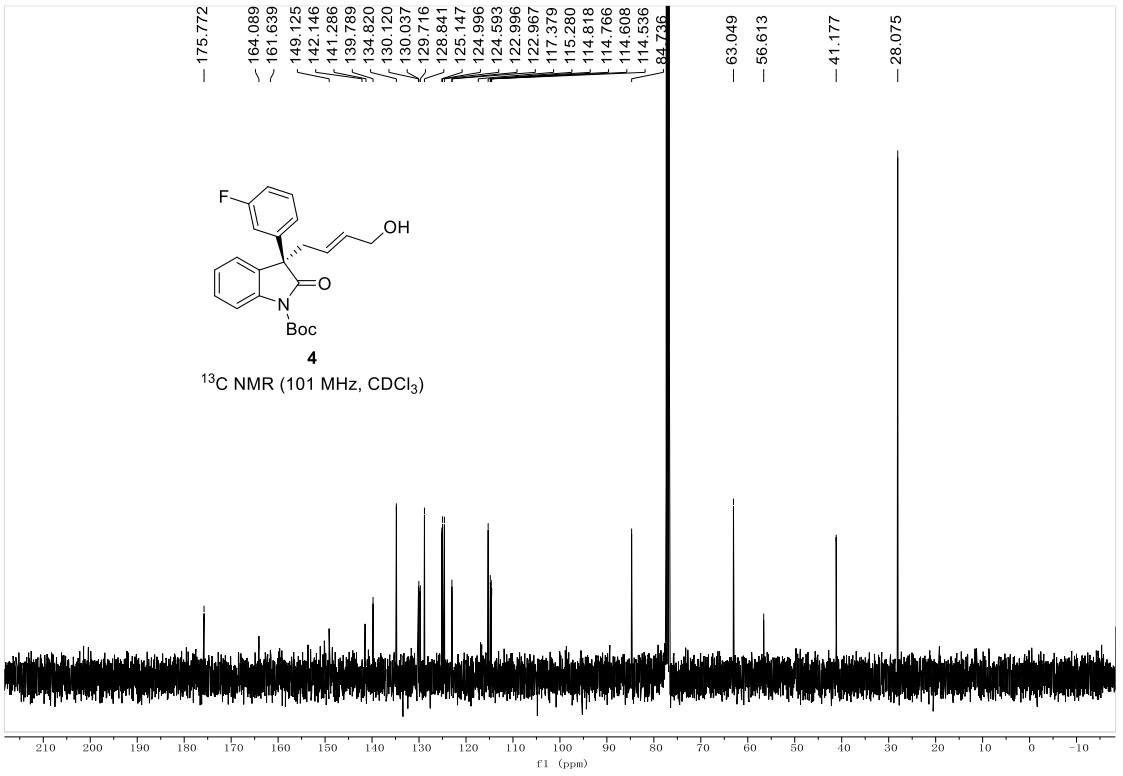
***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-(m-tolyl)indoline-1-carboxylate (3)**

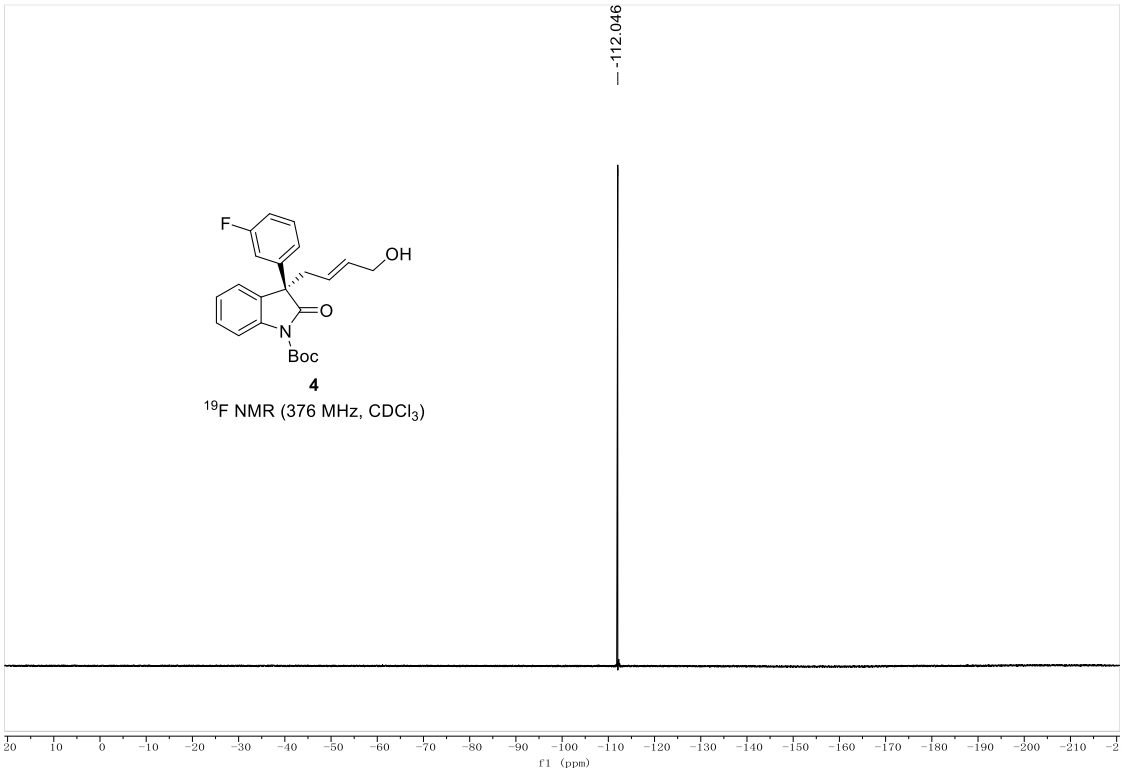




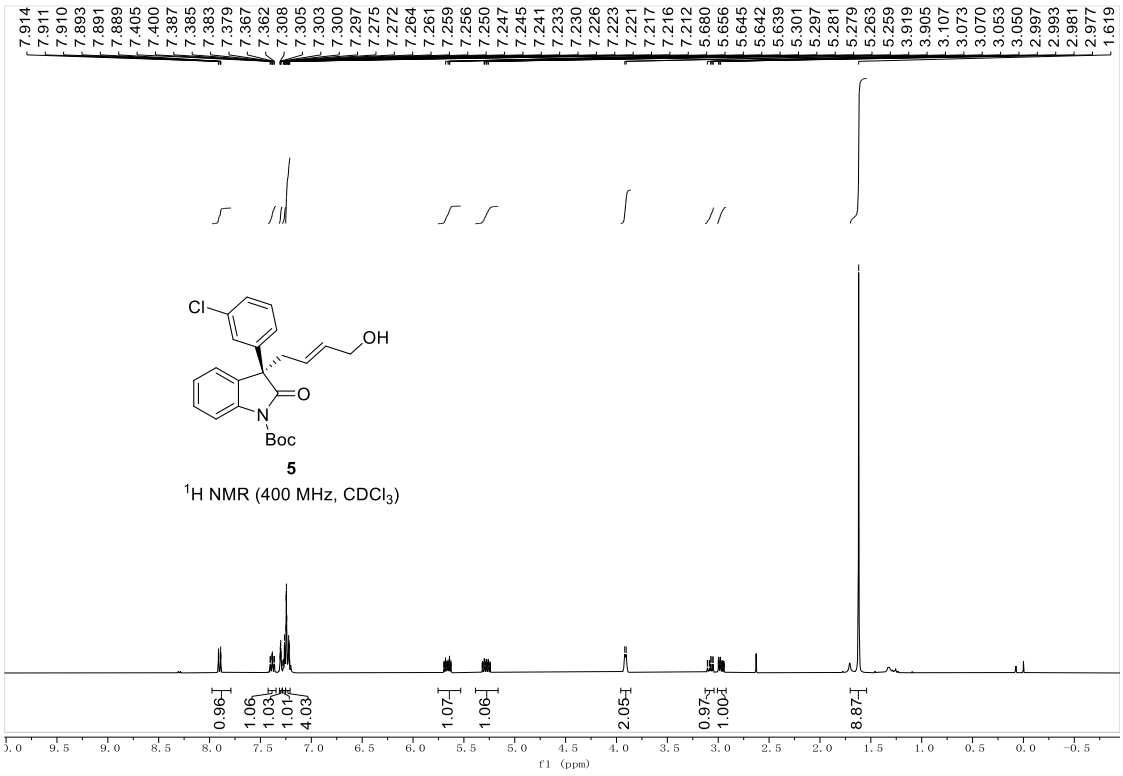
***tert*-Butyl (*R*, *E*)-3-(3-fluorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (4)**

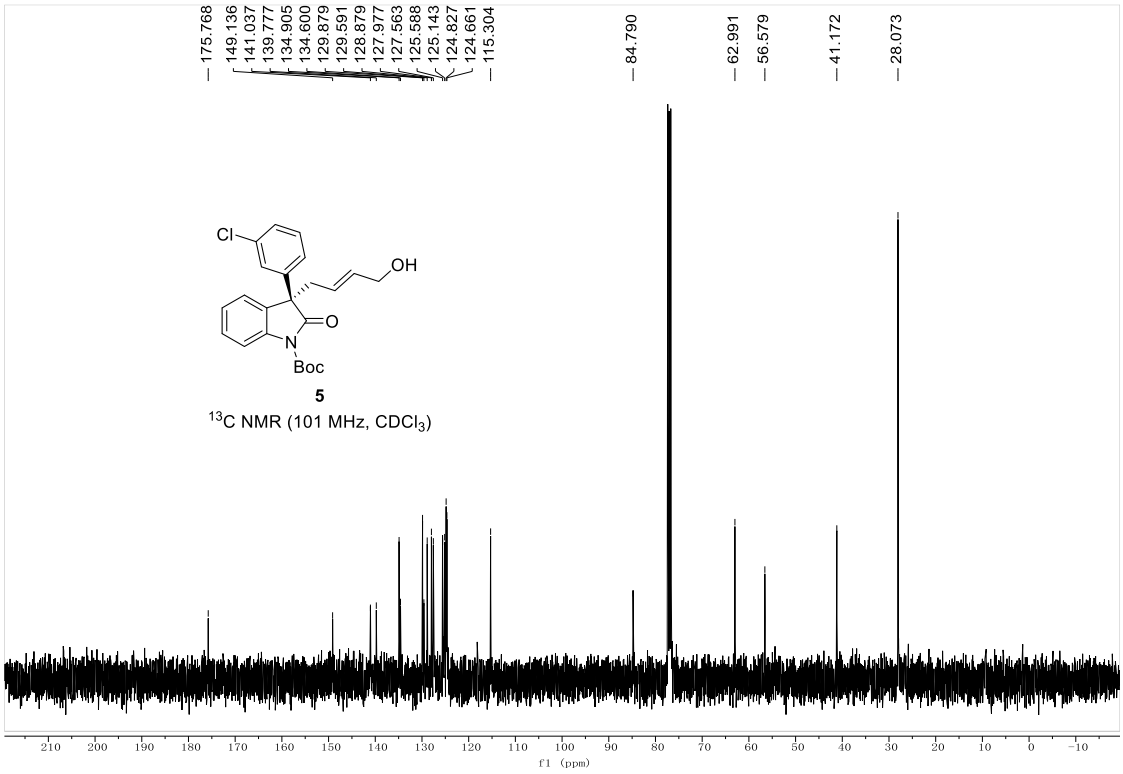




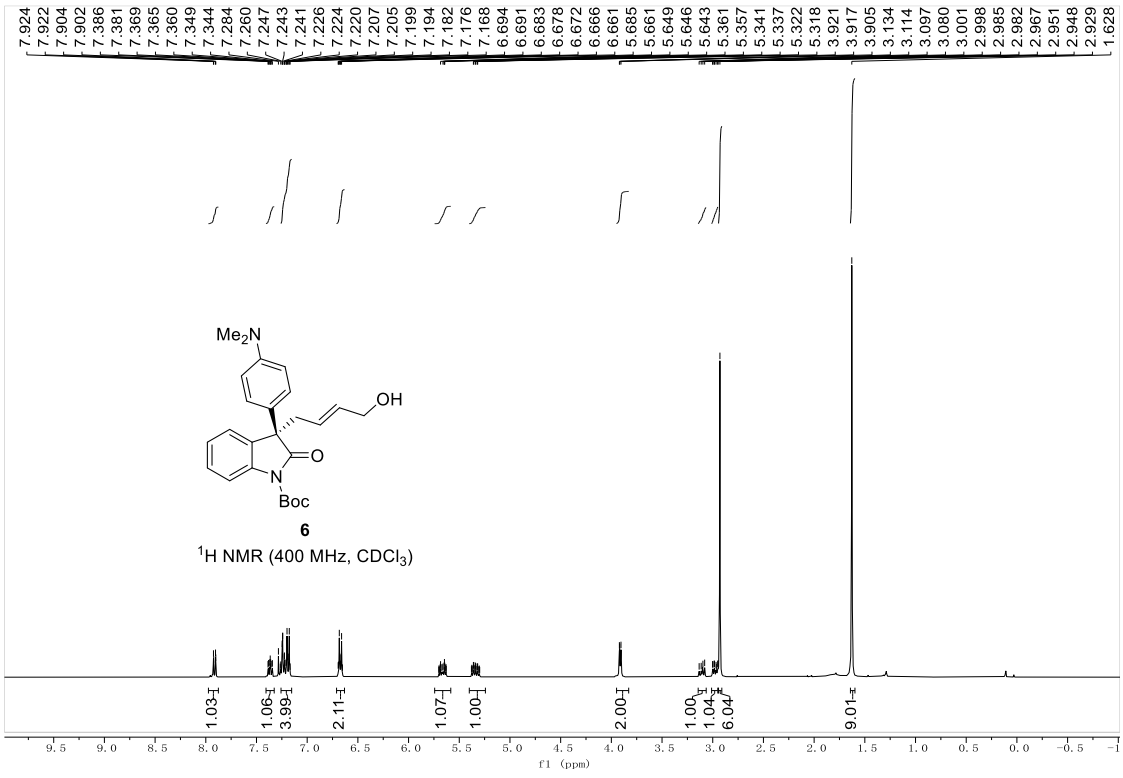


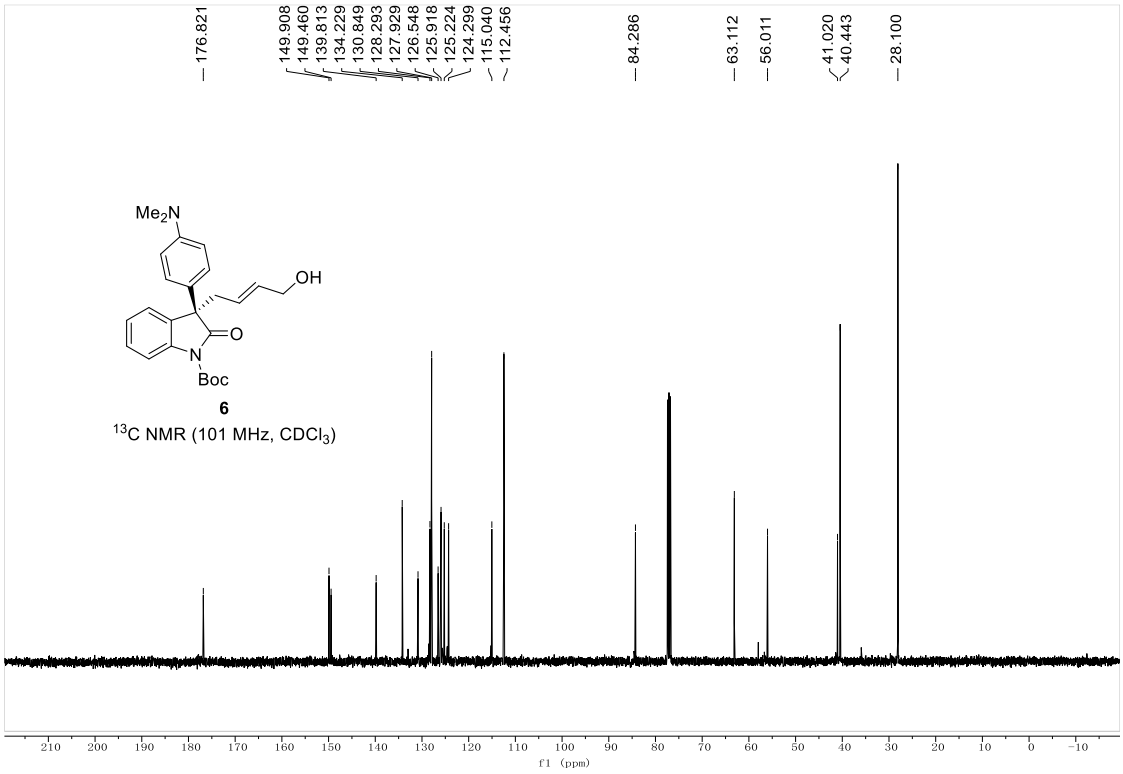
***tert*-Butyl (*R, E*)-3-(3-chlorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (5)**



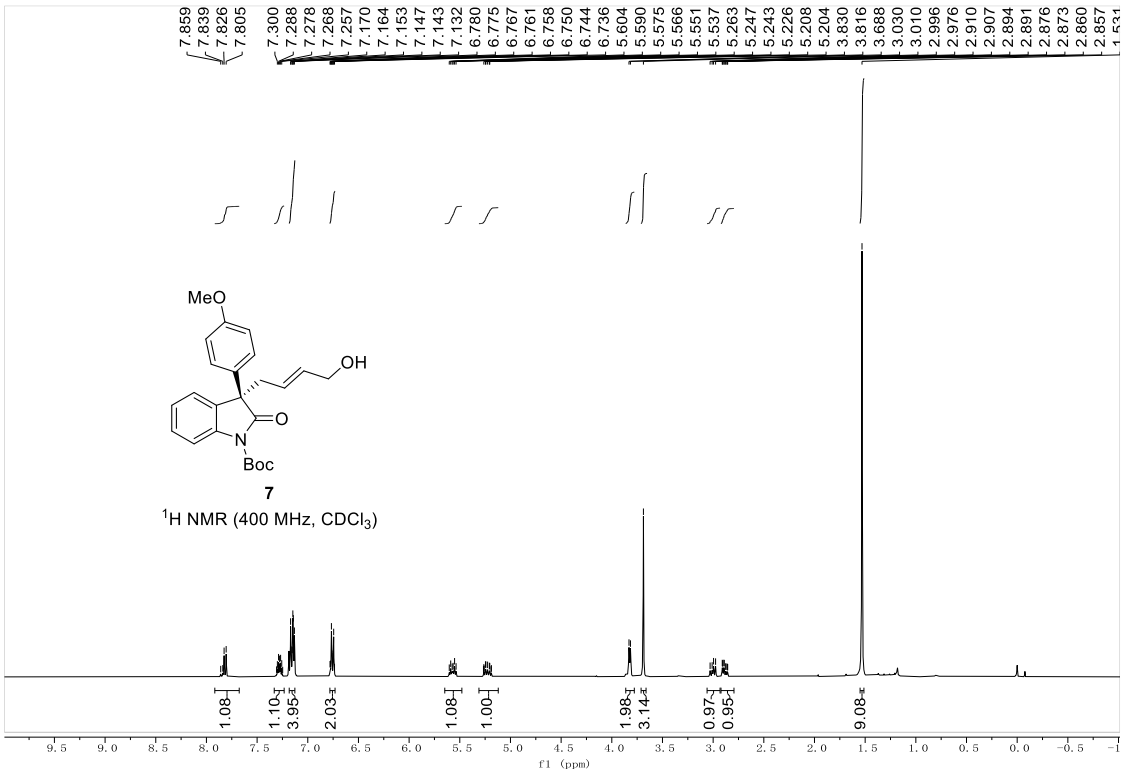


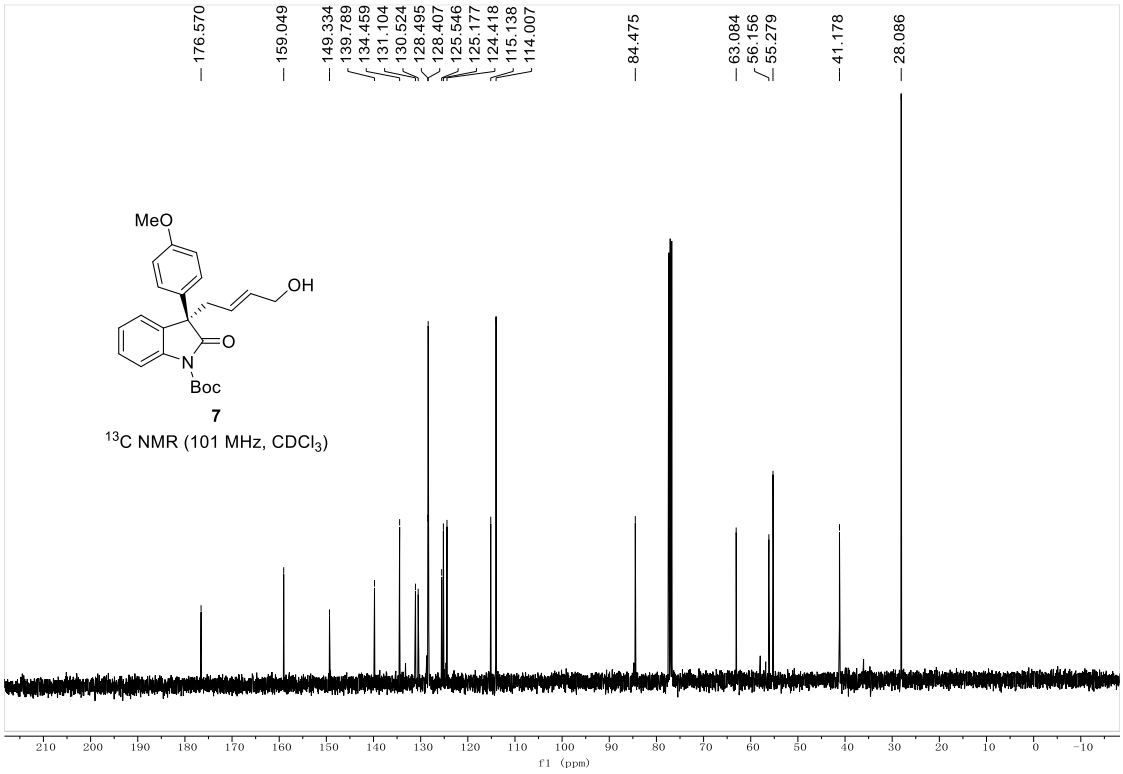
***tert*-Butyl (*R*, *E*)-3-(4-(dimethylamino)phenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (6)**



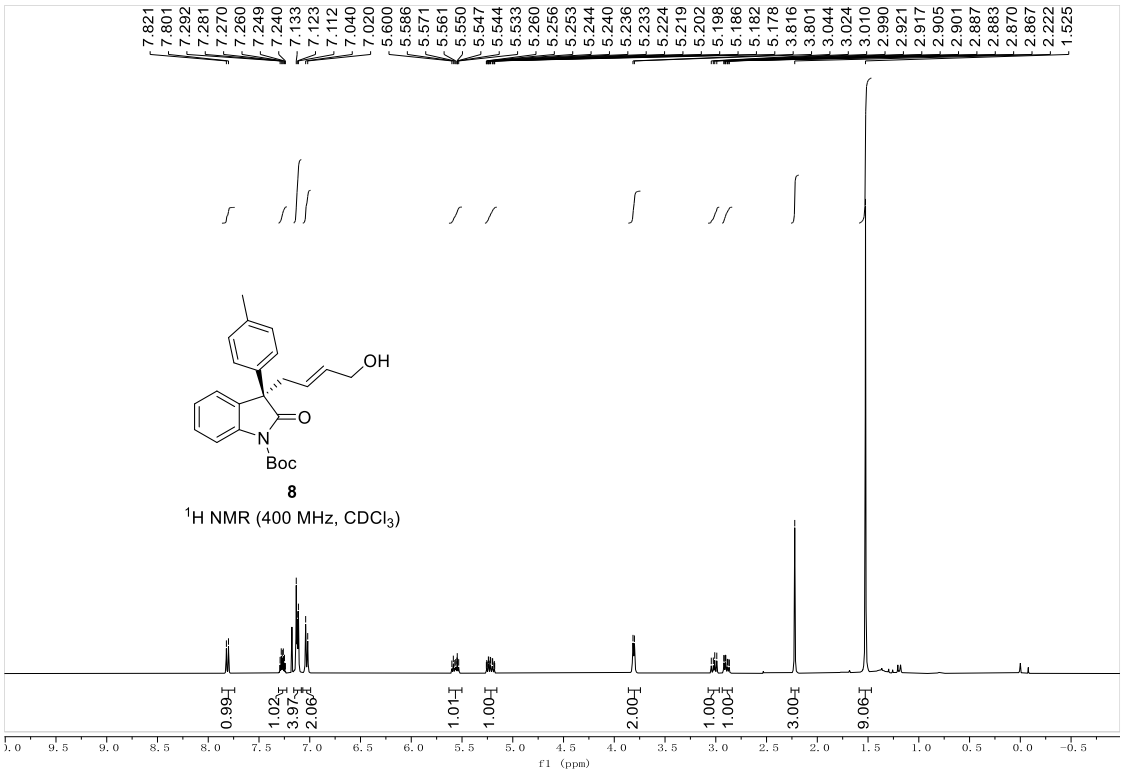


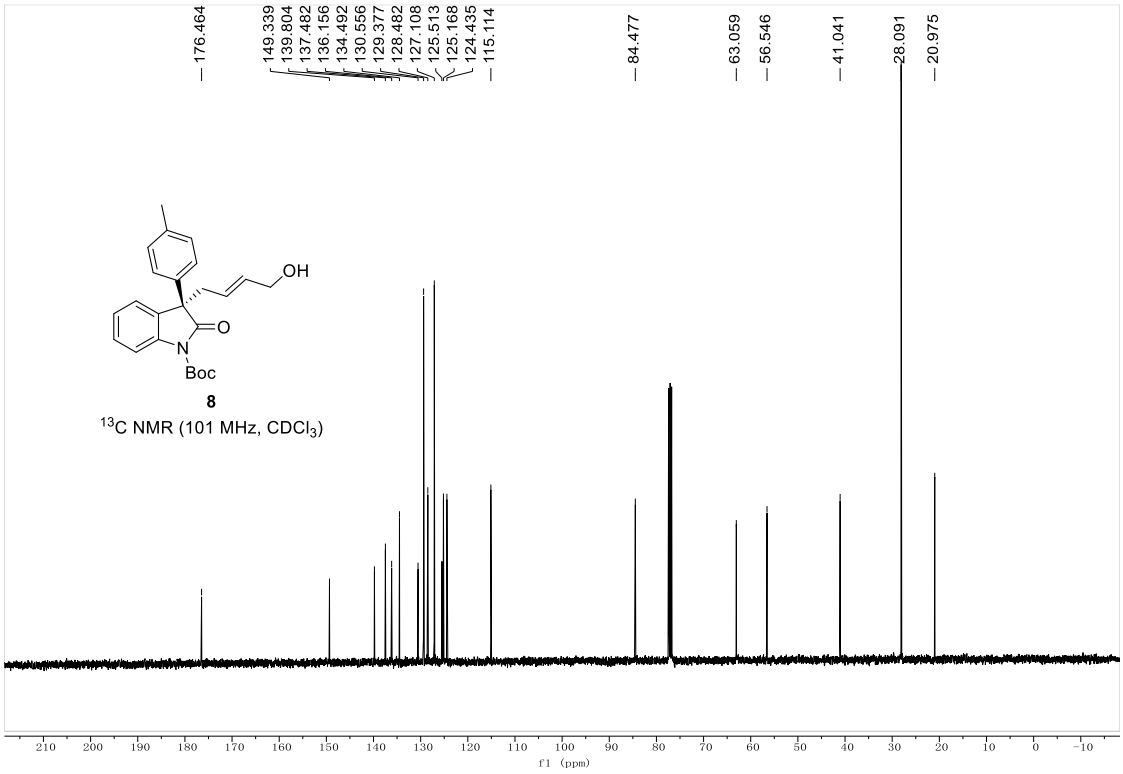
***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-3-(4-methoxyphenyl)-2-oxoindoline-1-carboxyl ate (7)**



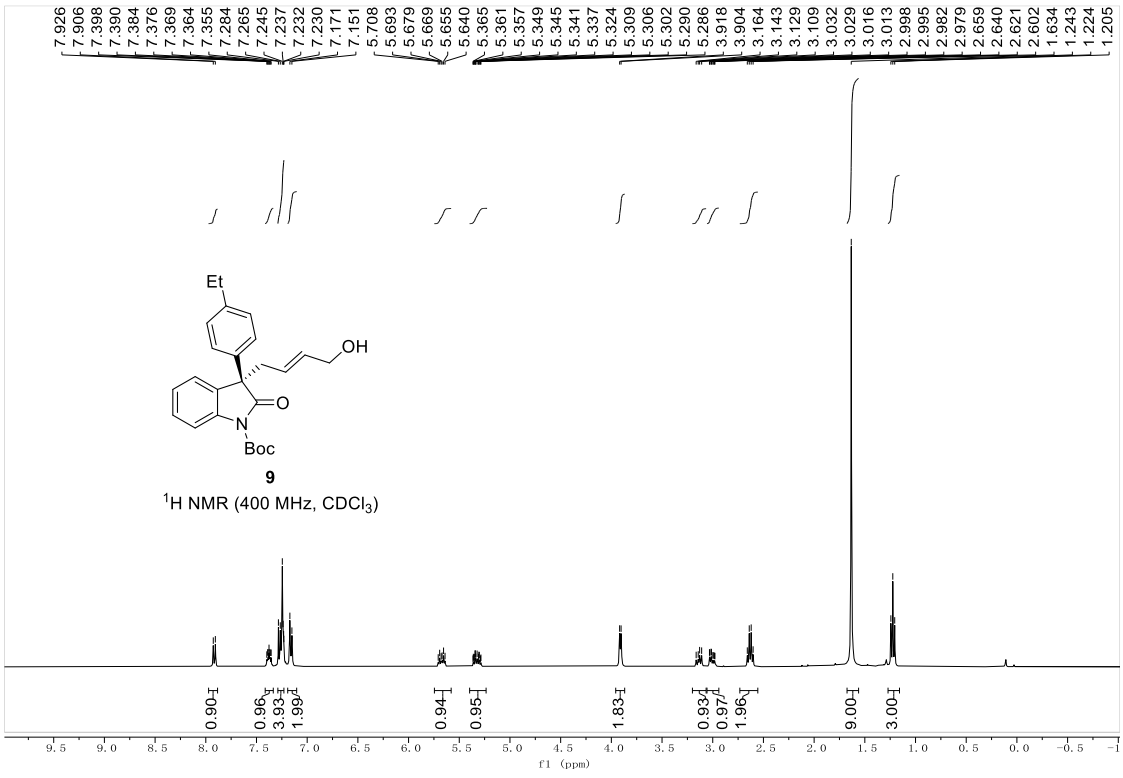


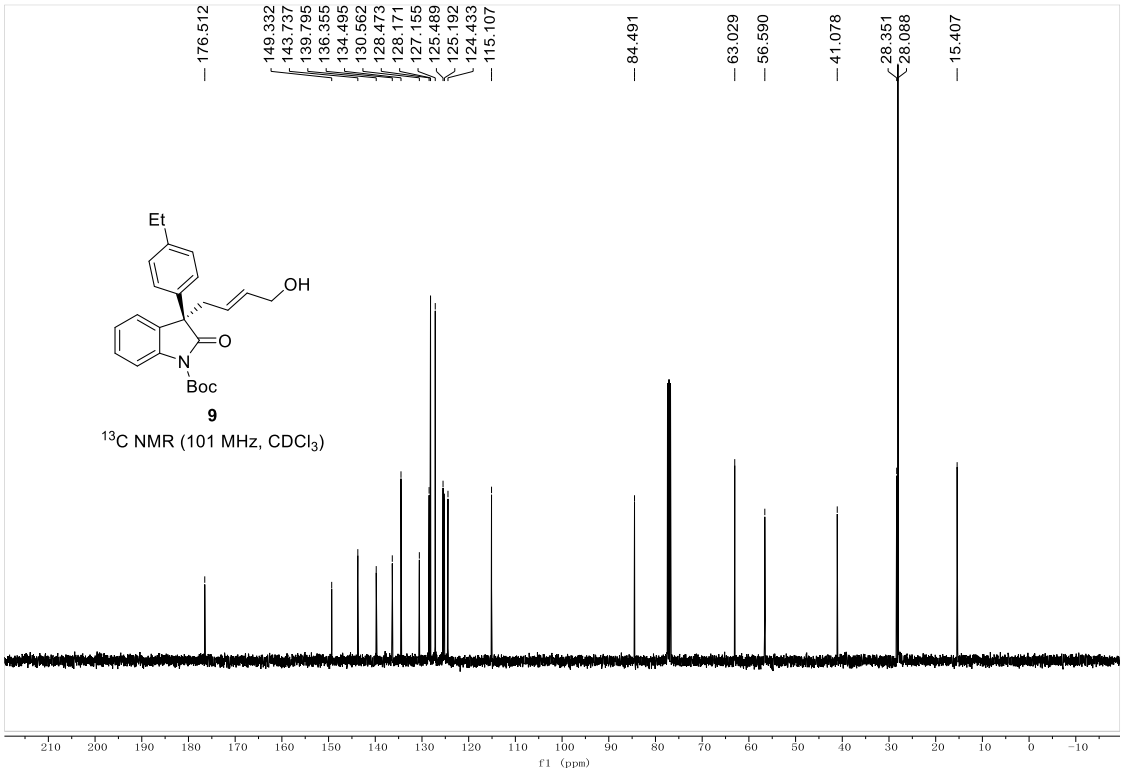
***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-(p-tolyl)indoline-1-carboxylate (8)**



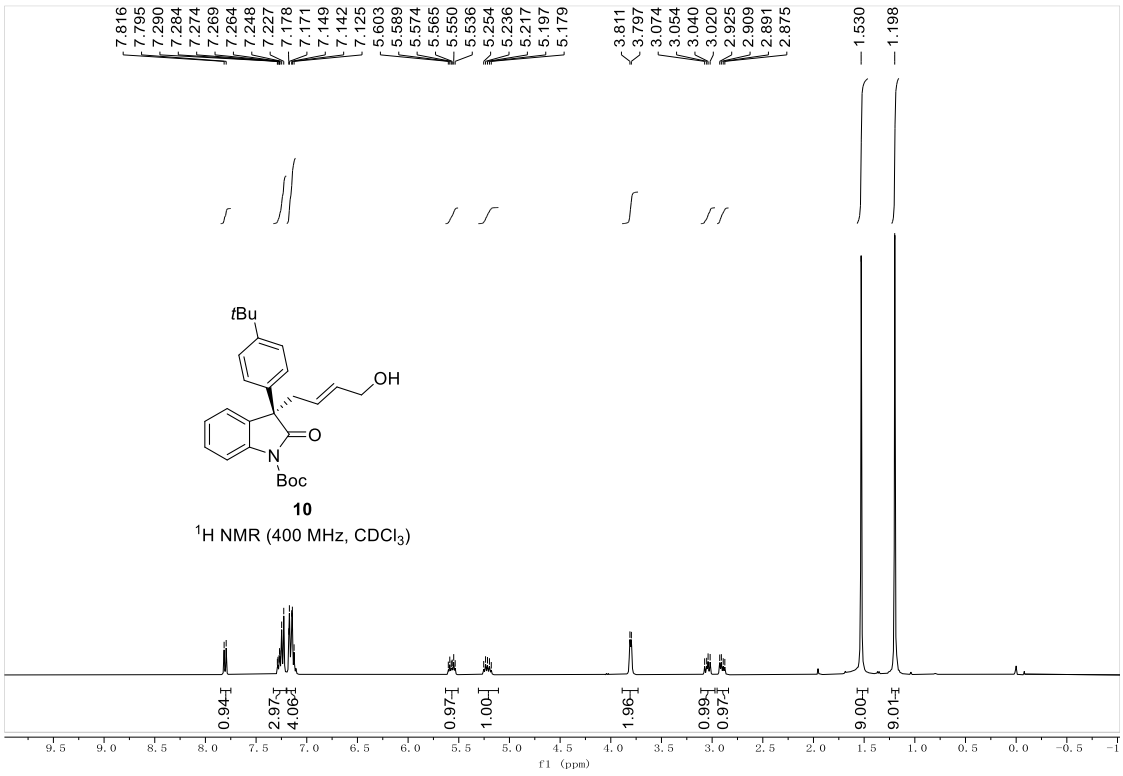


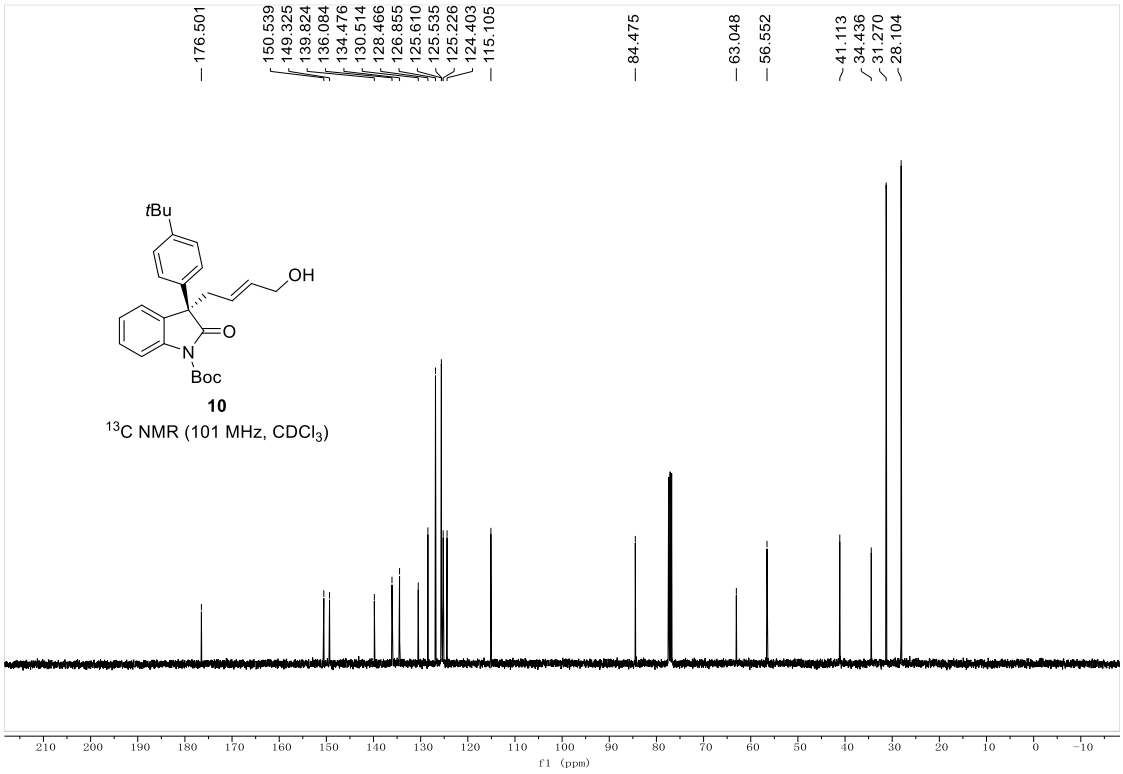
tert-Butyl (_R_, _E_)-3-(4-ethylphenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (9)



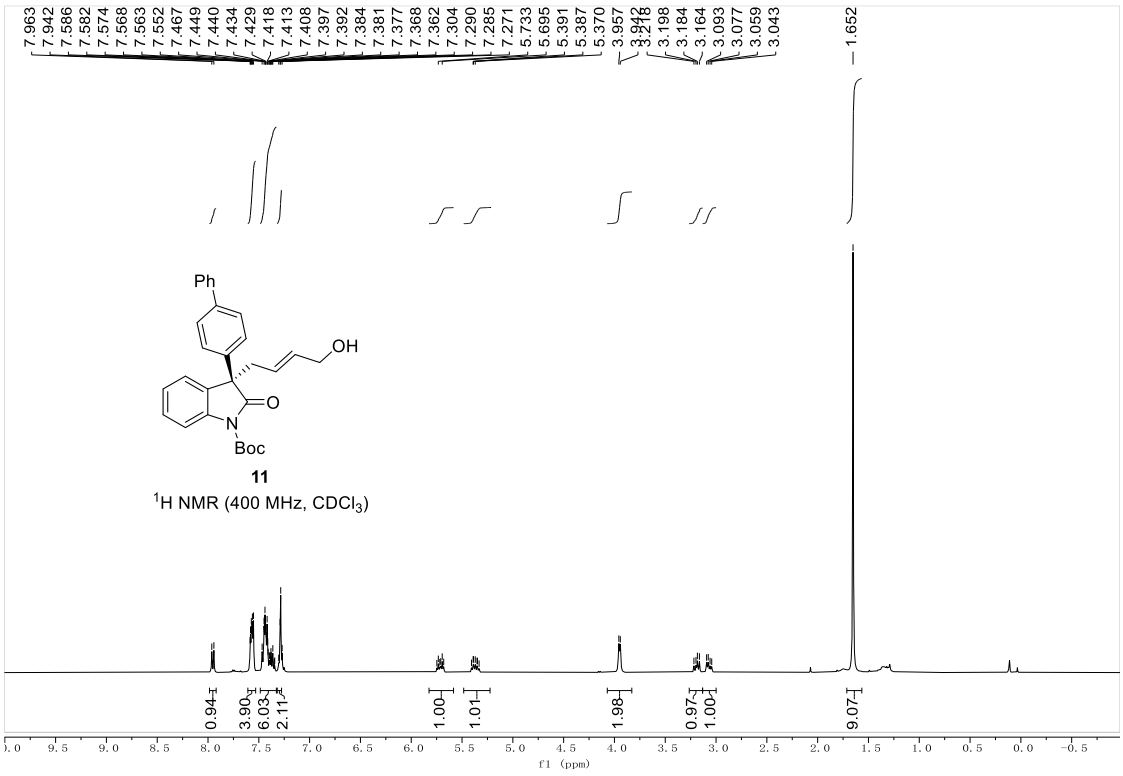


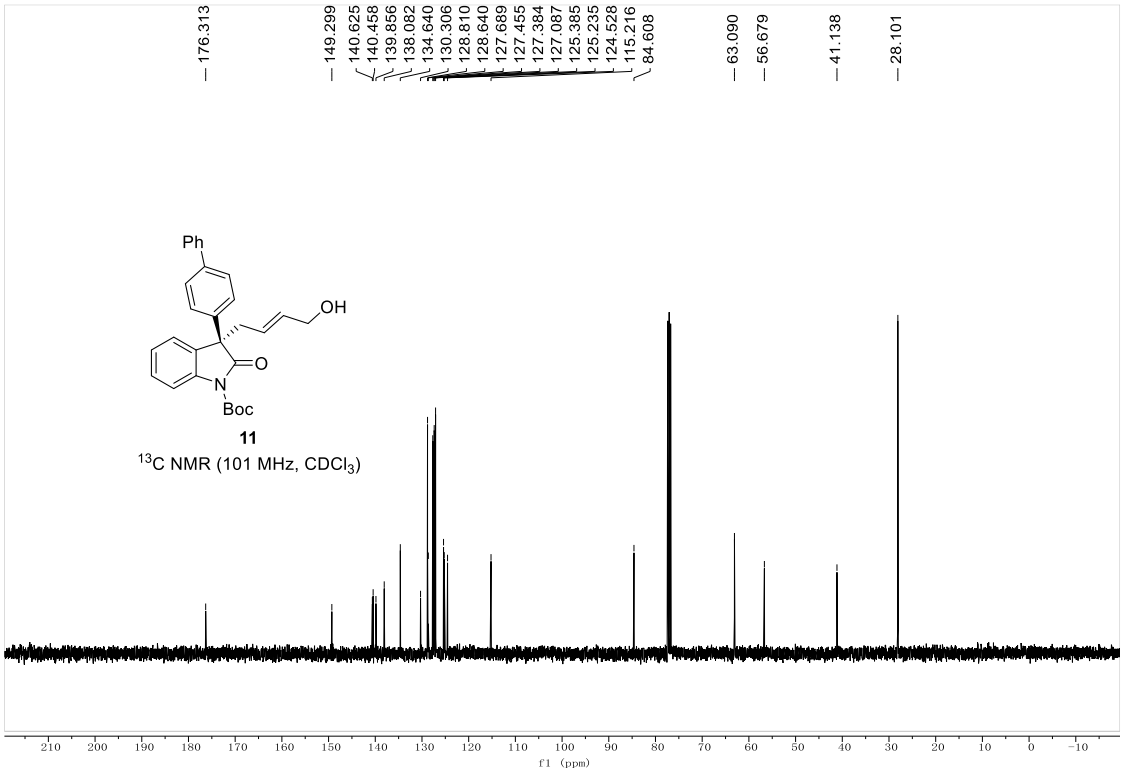
***tert*-Butyl (*R*, *E*)-3-(4-(*tert*-butyl)phenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (10)**



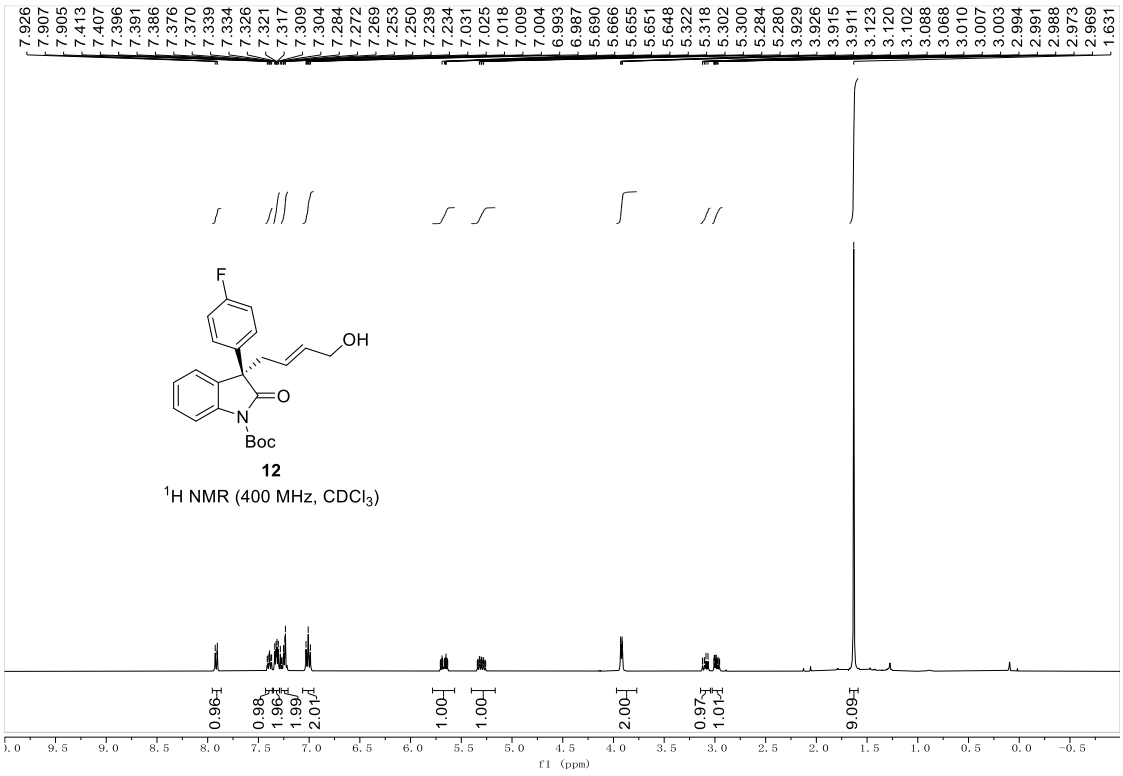


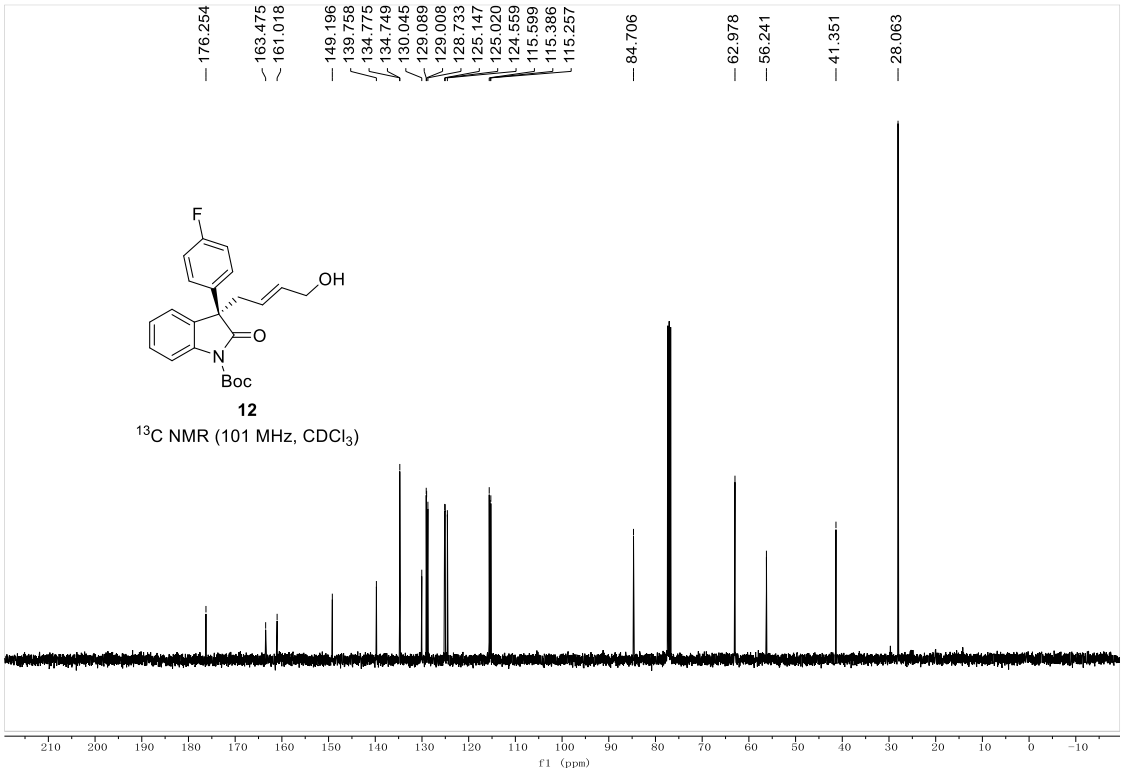
tert-Butyl (_R_, _E_)-3-([1,1'-biphenyl]-4-yl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (11)

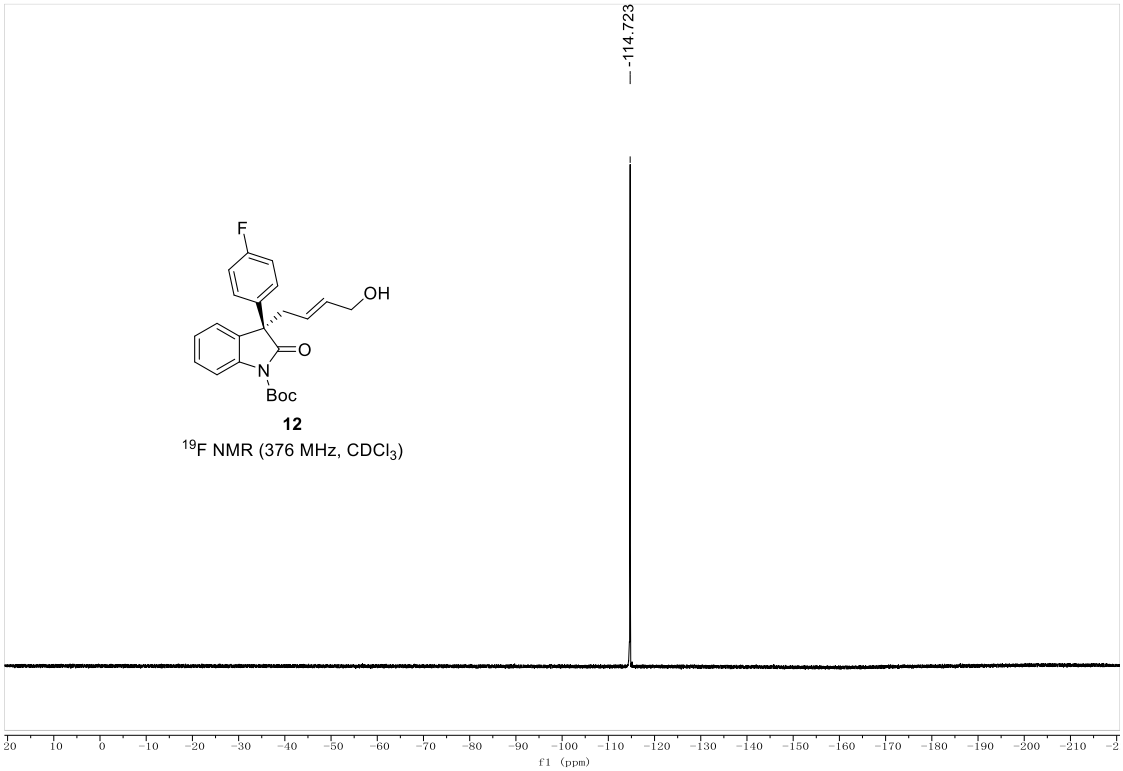




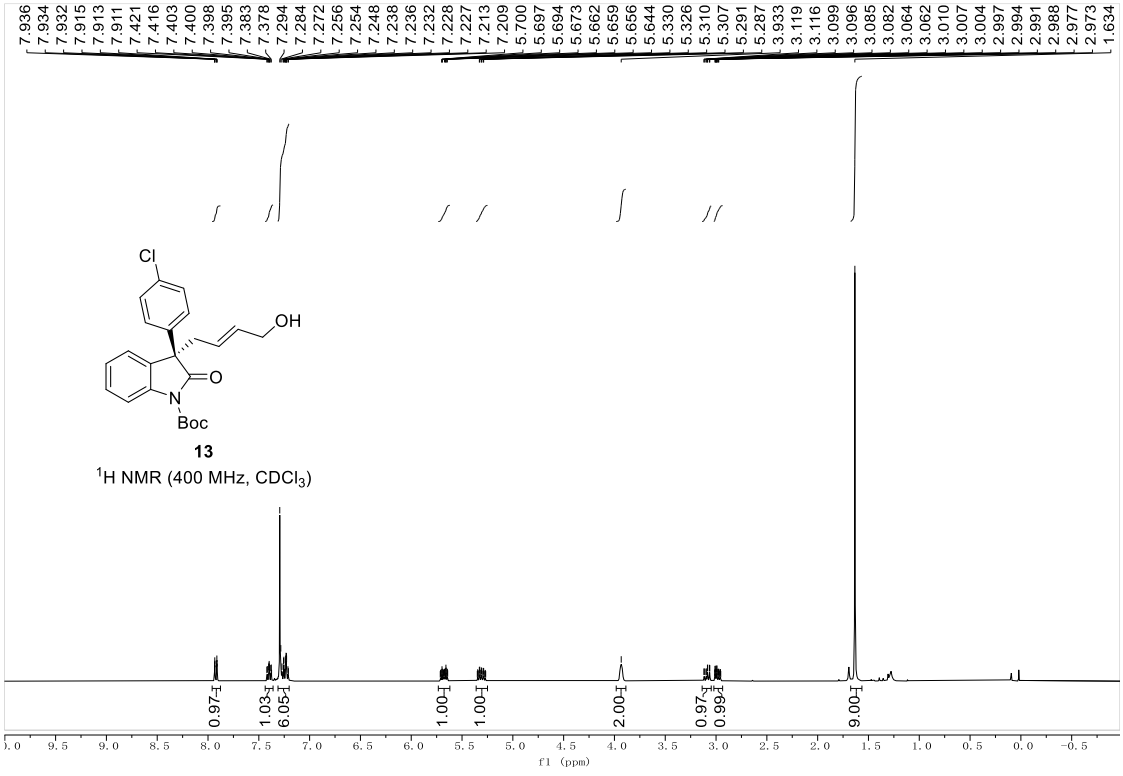
***tert*-Butyl (*R, E*)-3-(4-fluorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (12)**

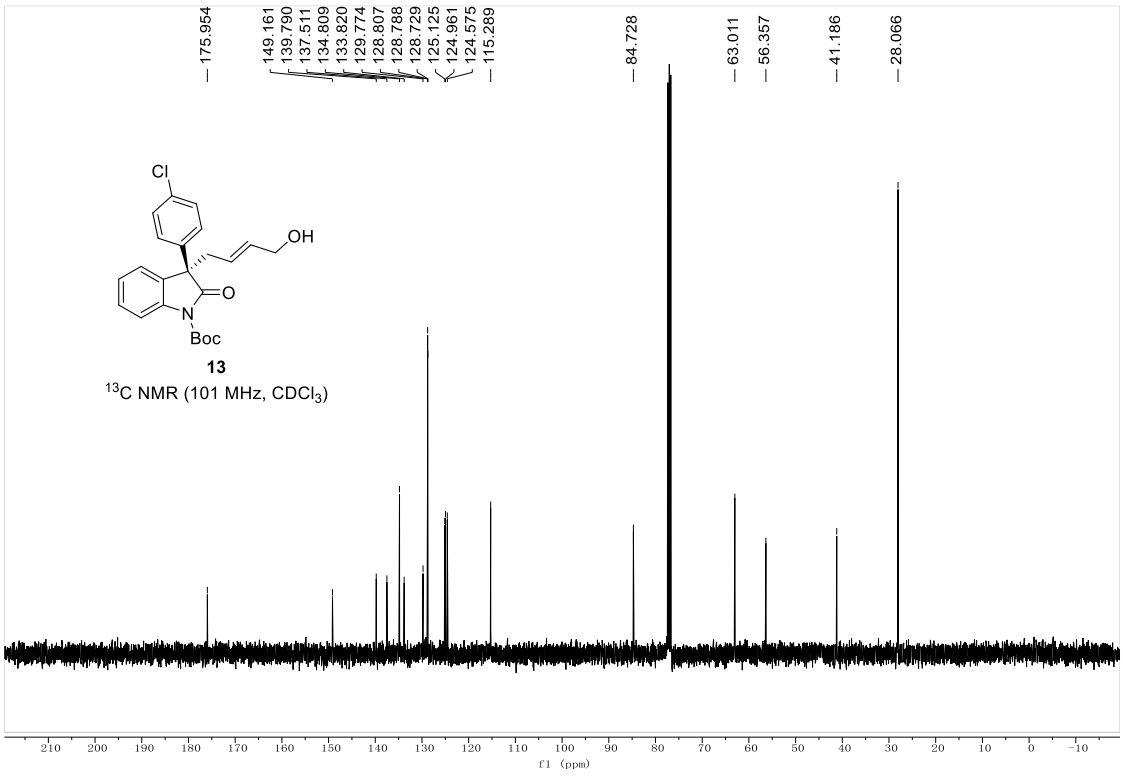



176.254
163.475
161.018
149.196
139.758
134.775
134.749
130.045
129.089
129.008
128.733
125.147
125.020
124.559
115.599
115.386
115.257
84.706
62.978
56.241
41.351
28.063
F
OH
O
N
Boc
12
13C NMR (101 MHz, CDCl3)
f1 (ppm)

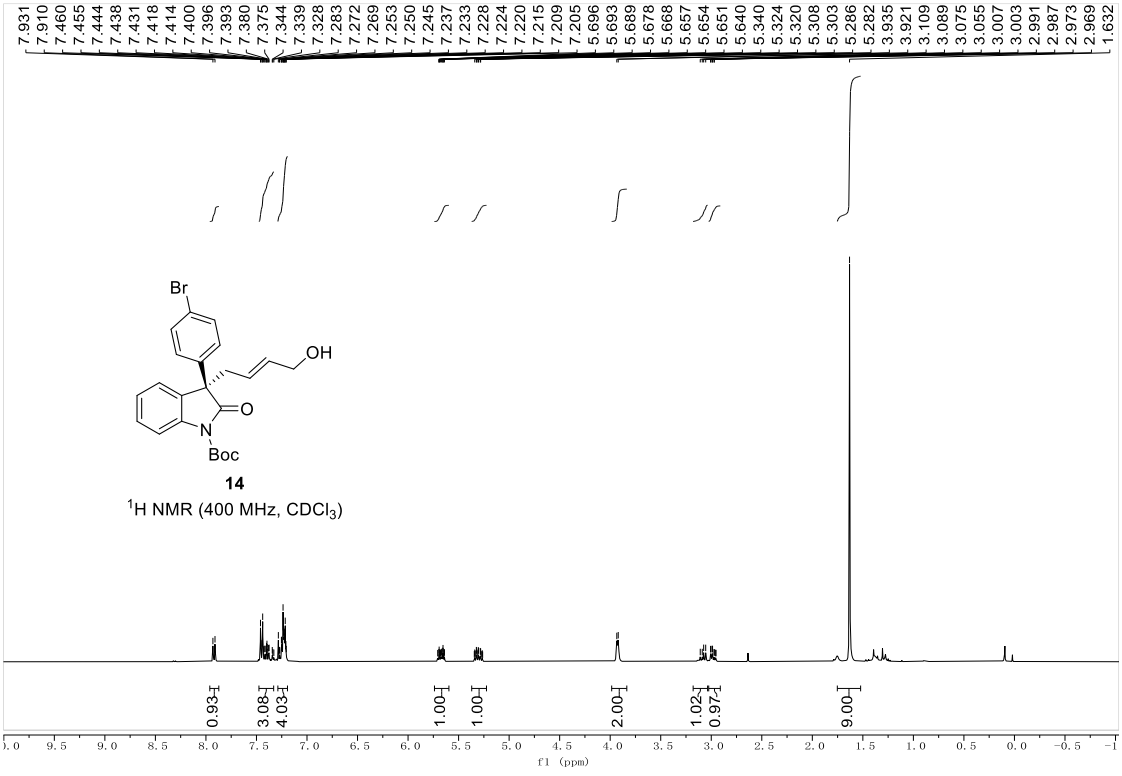

-114.723
F
OH
O
N
Boc
12
19F NMR (376 MHz, CDCl3)
f1 (ppm)

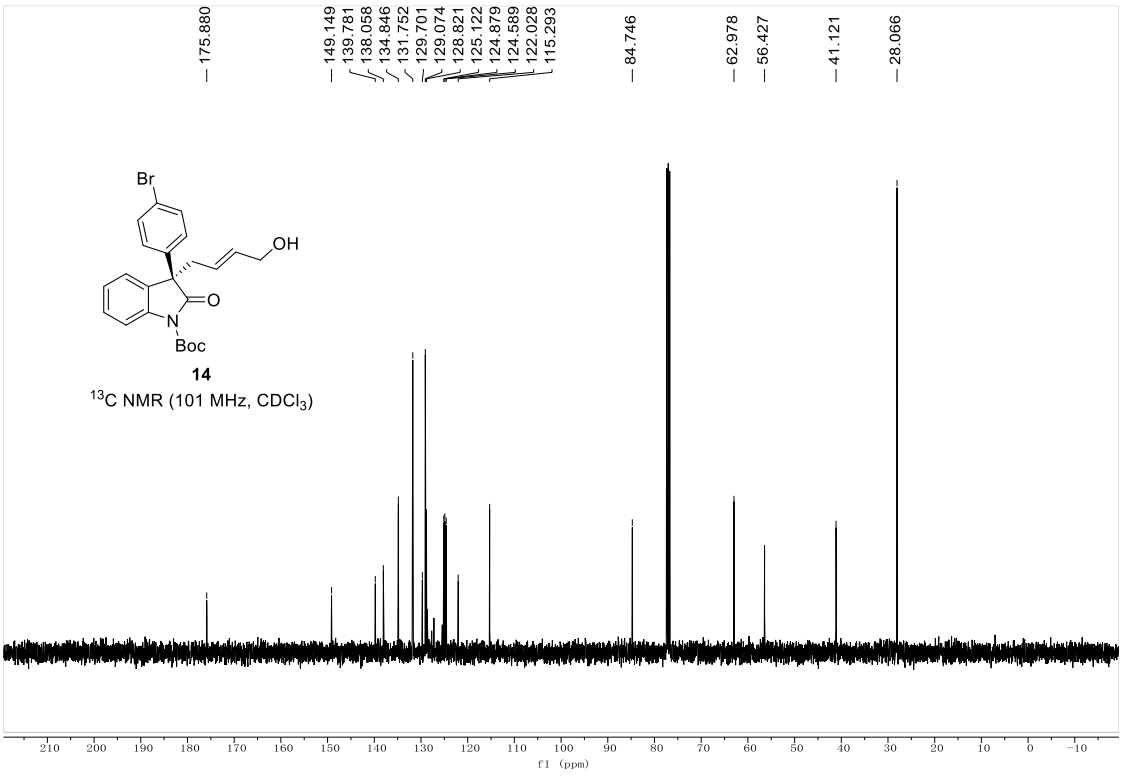
***tert*-Butyl (*R*, *E*)-3-(4-chlorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (13)**



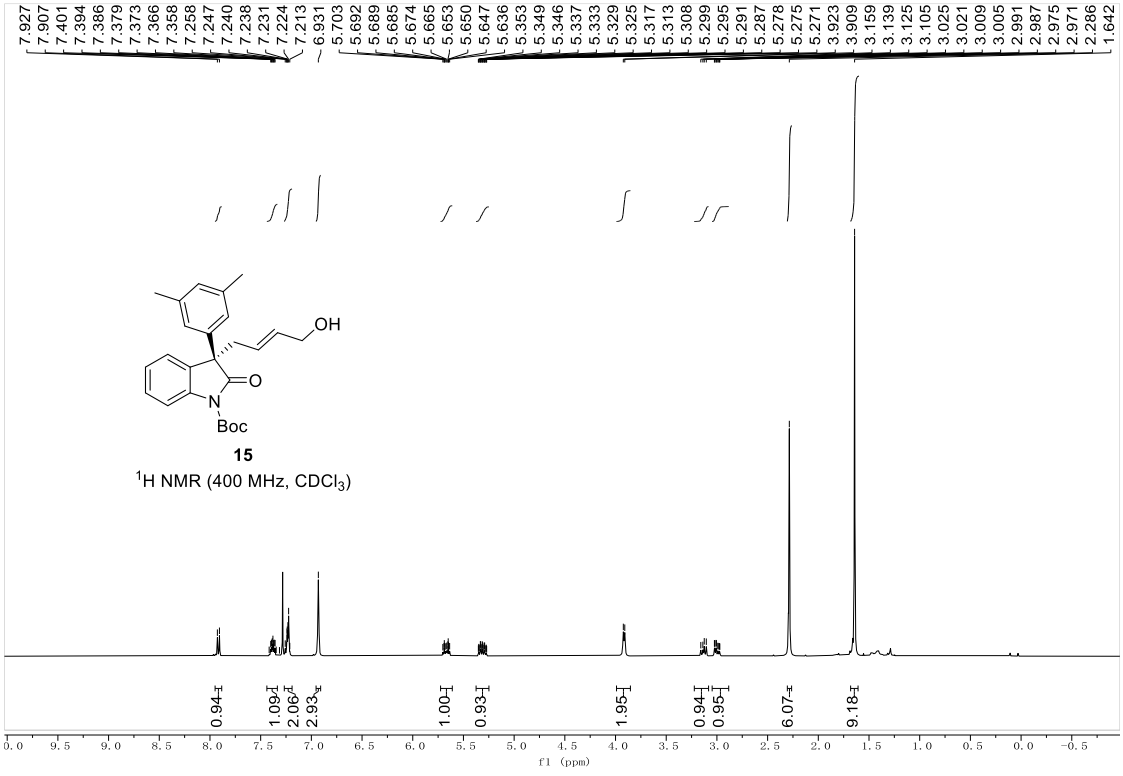


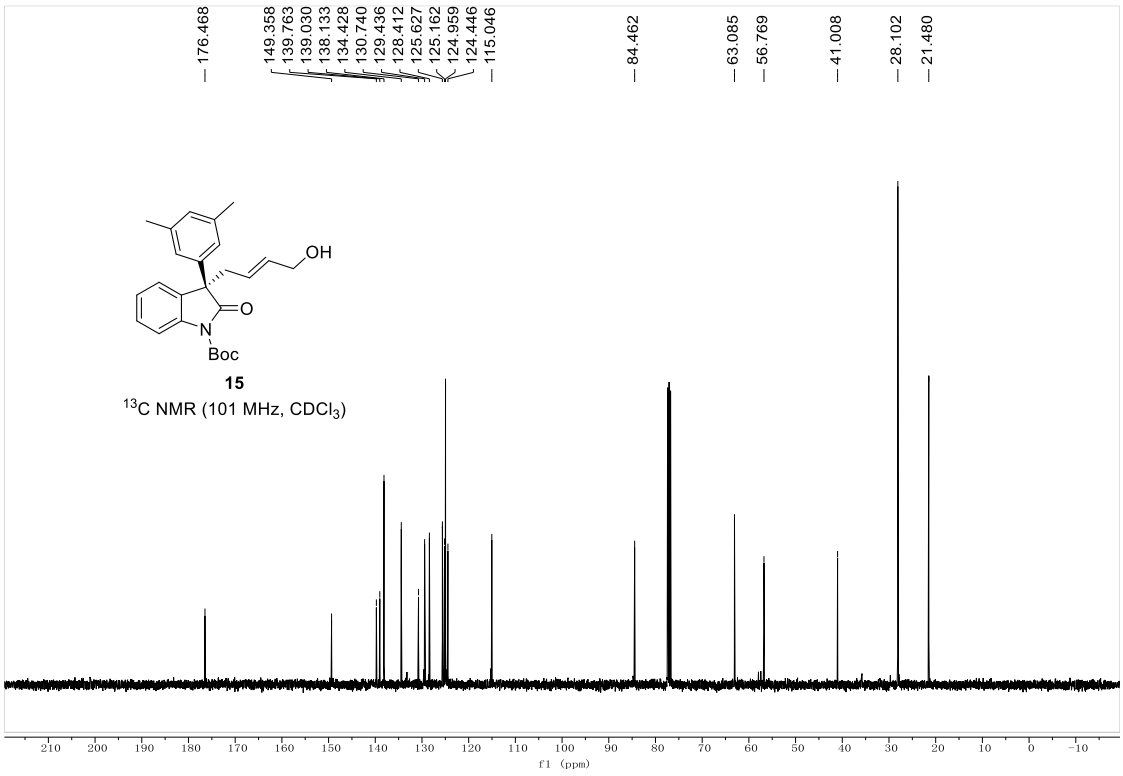
***tert*-Butyl (*R*, *E*)-3-(4-bromophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (14)**



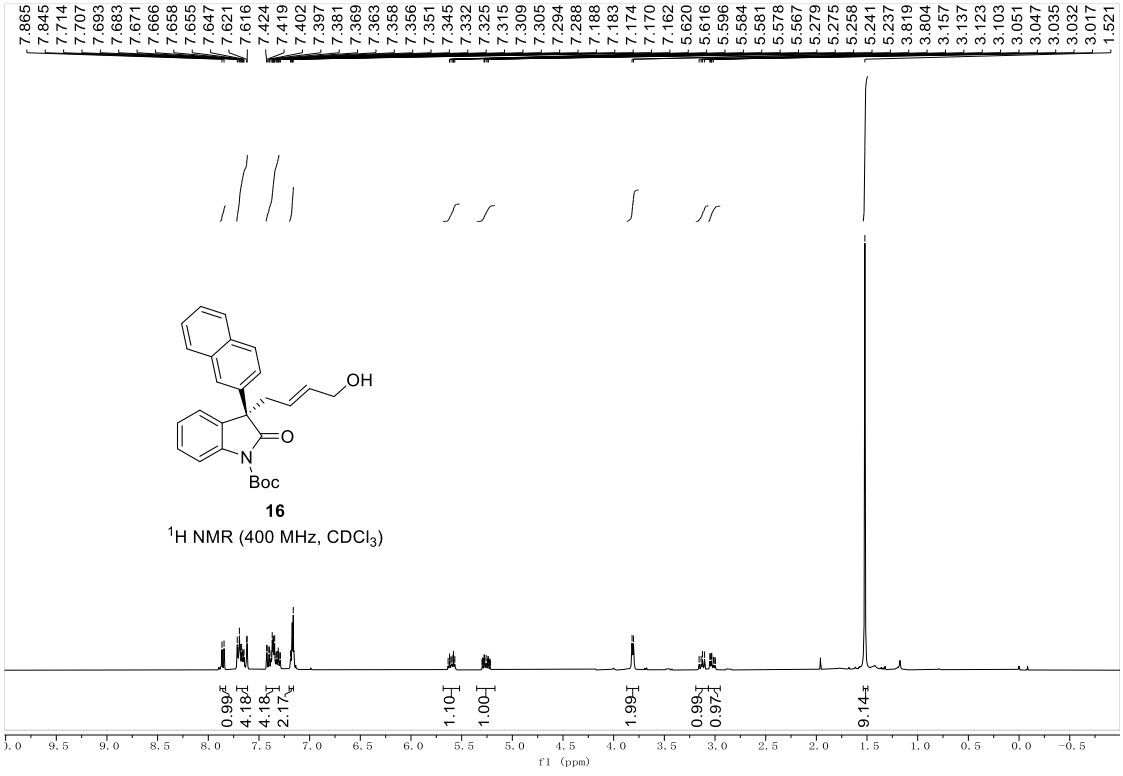


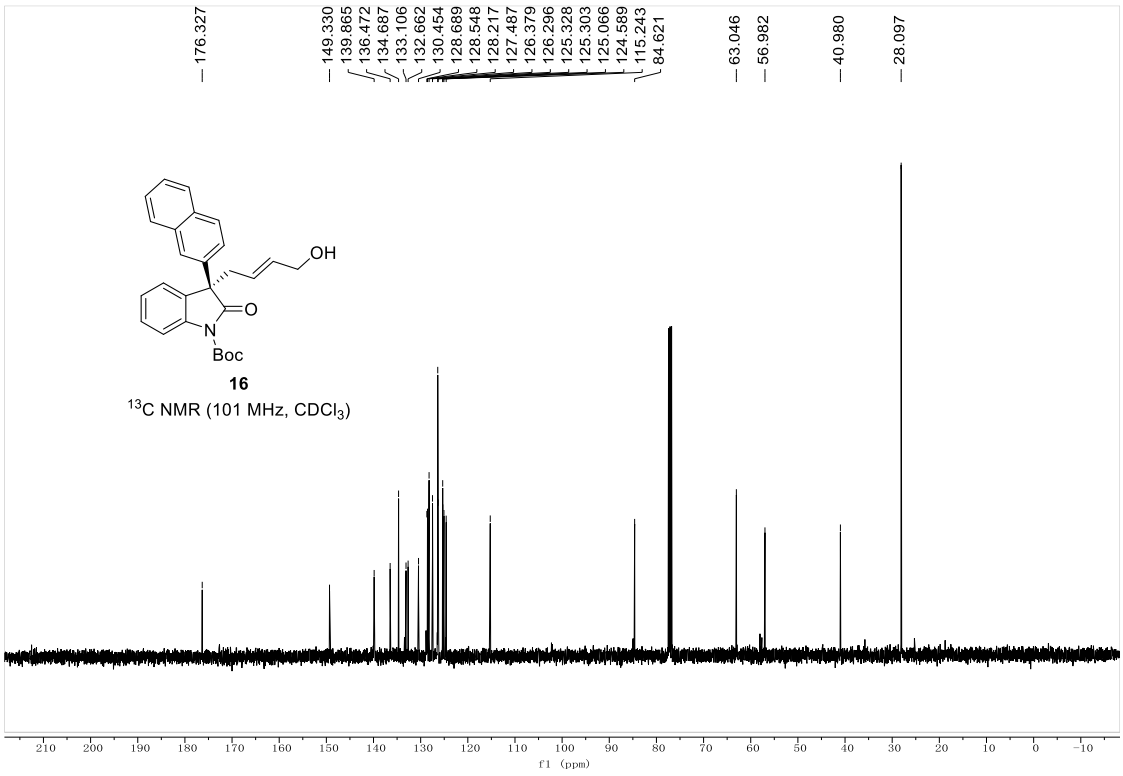
***tert*-Butyl (*R*, *E*)-3-(3,5-dimethylphenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (15)**



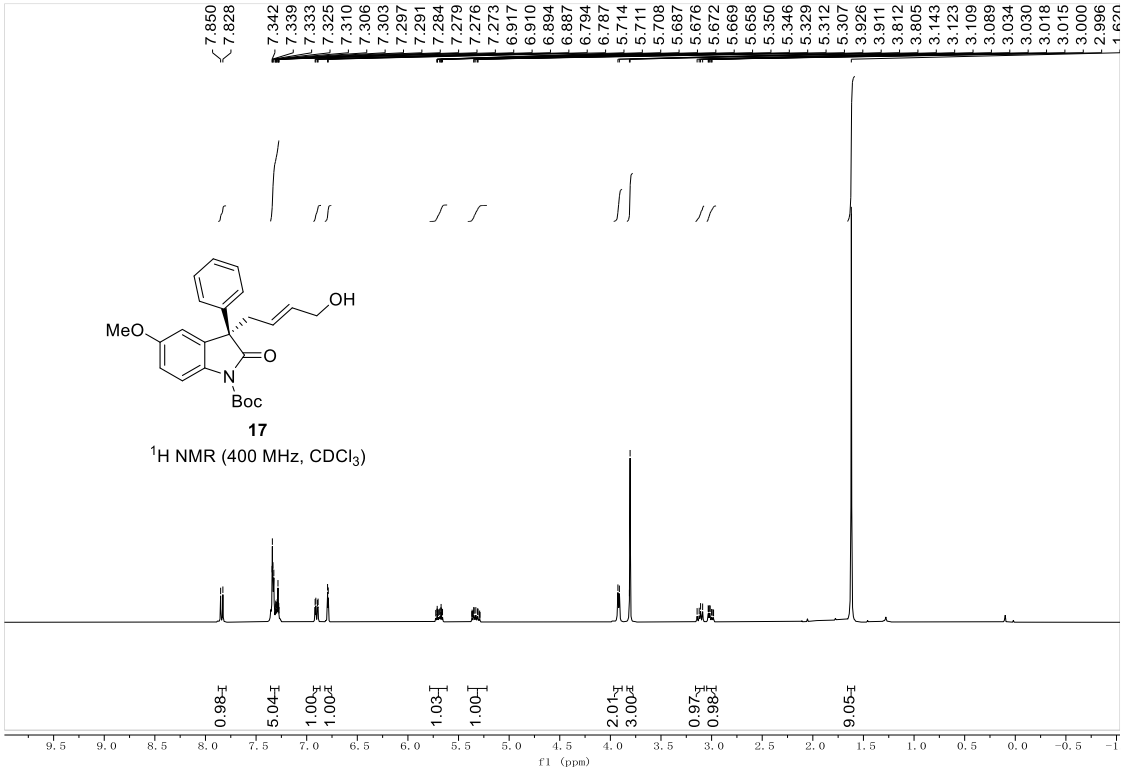


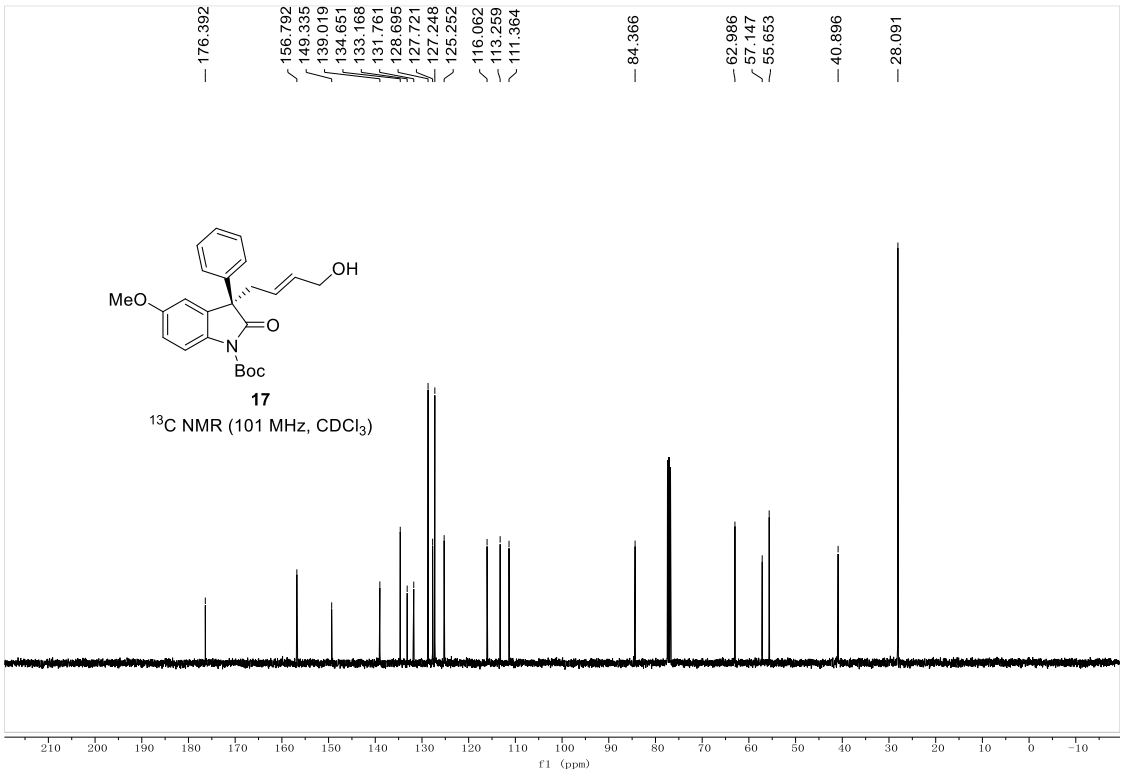
***tert*-Butyl (*R, E*)-3-(4-hydroxybut-2-en-1-yl)-3-(naphthalen-2-yl)-2-oxoindoline-1-carboxylate (16)**



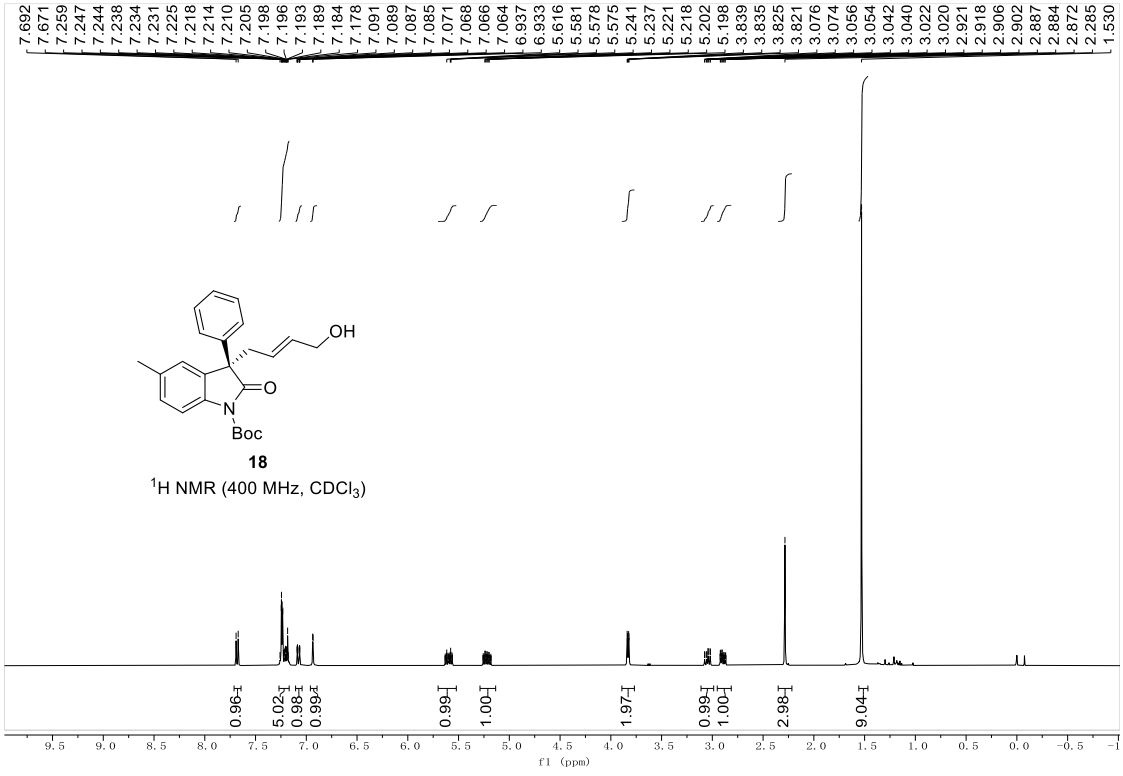


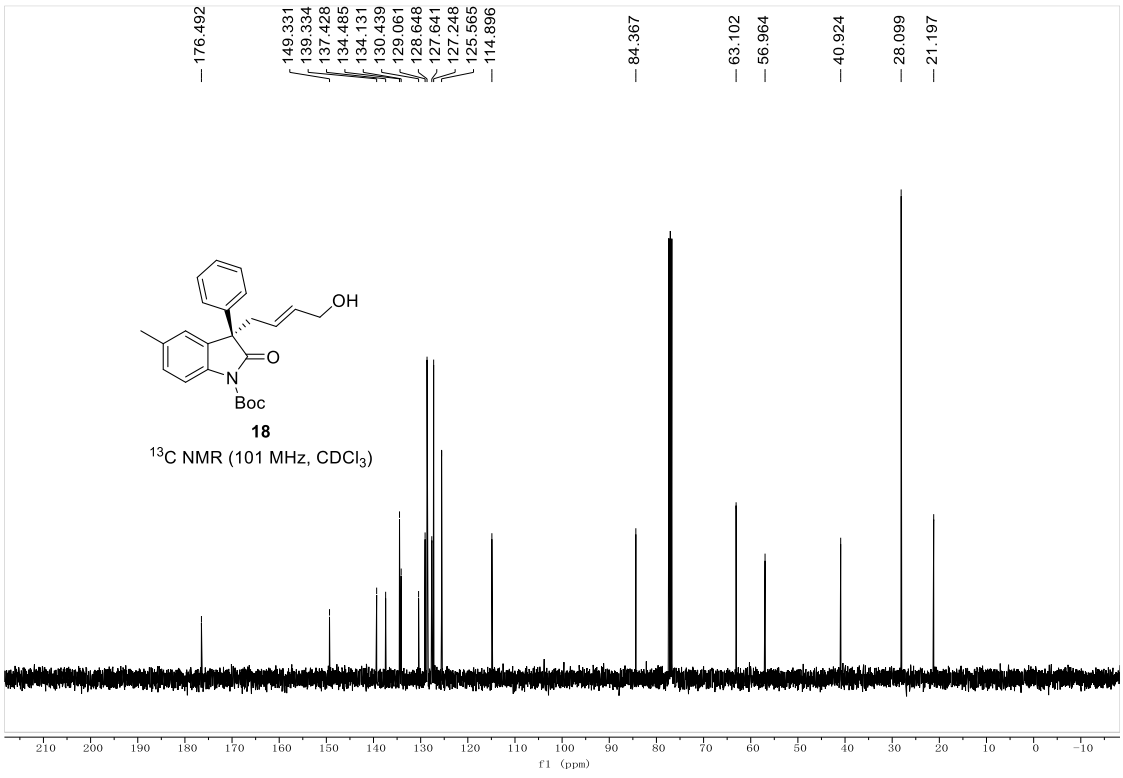
tert-Butyl (_R_, _E_)-3-(4-hydroxybut-2-en-1-yl)-5-methoxy-2-oxo-3-phenylindoline-1-carboxyla te (17)



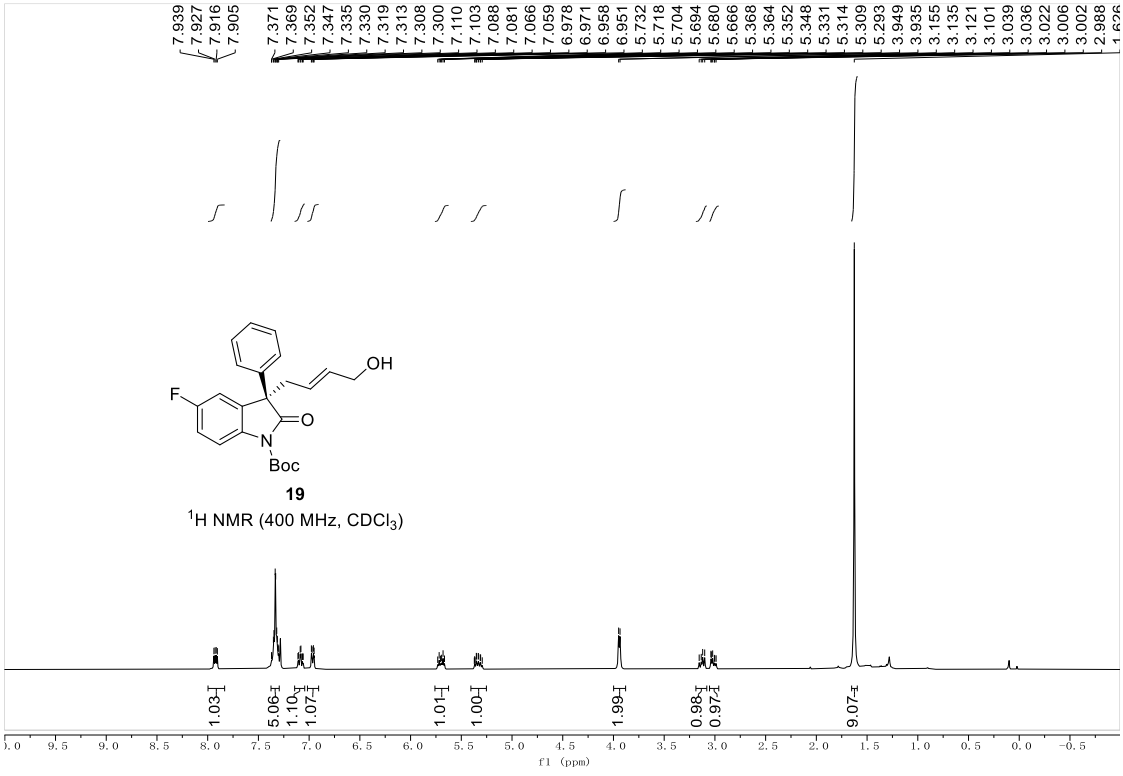


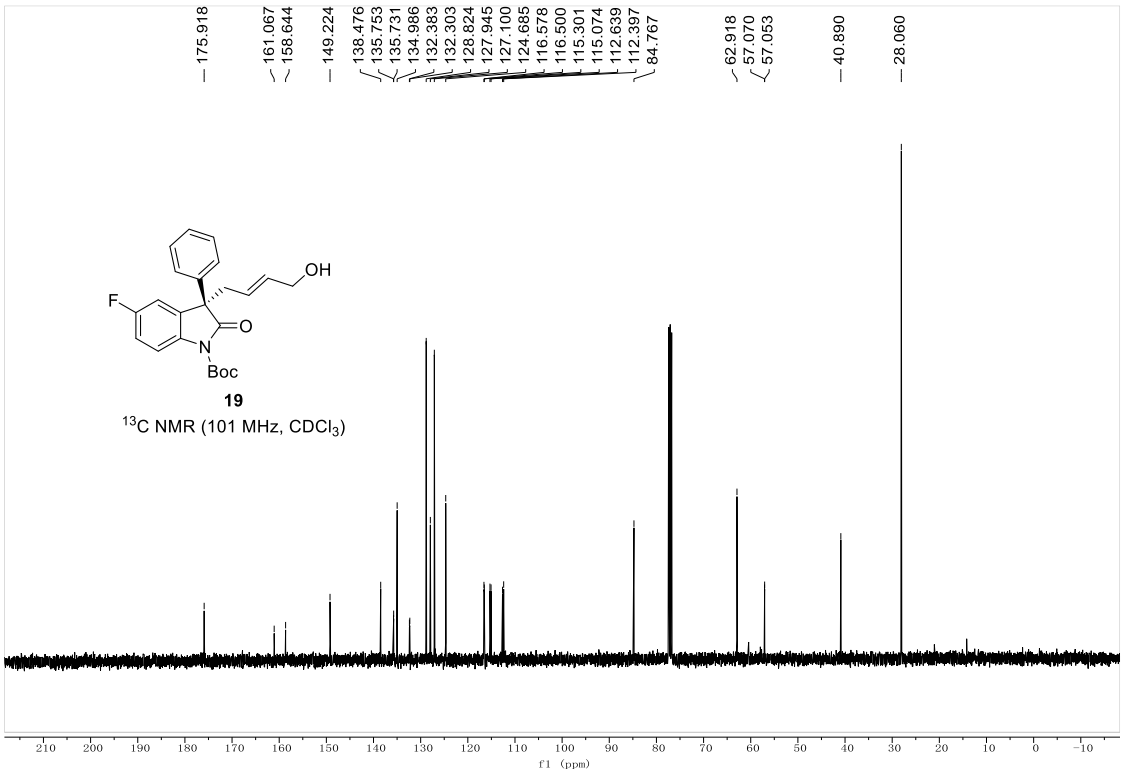
***tert*-Butyl (*R, E*)-3-(4-hydroxybut-2-en-1-yl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (18)**

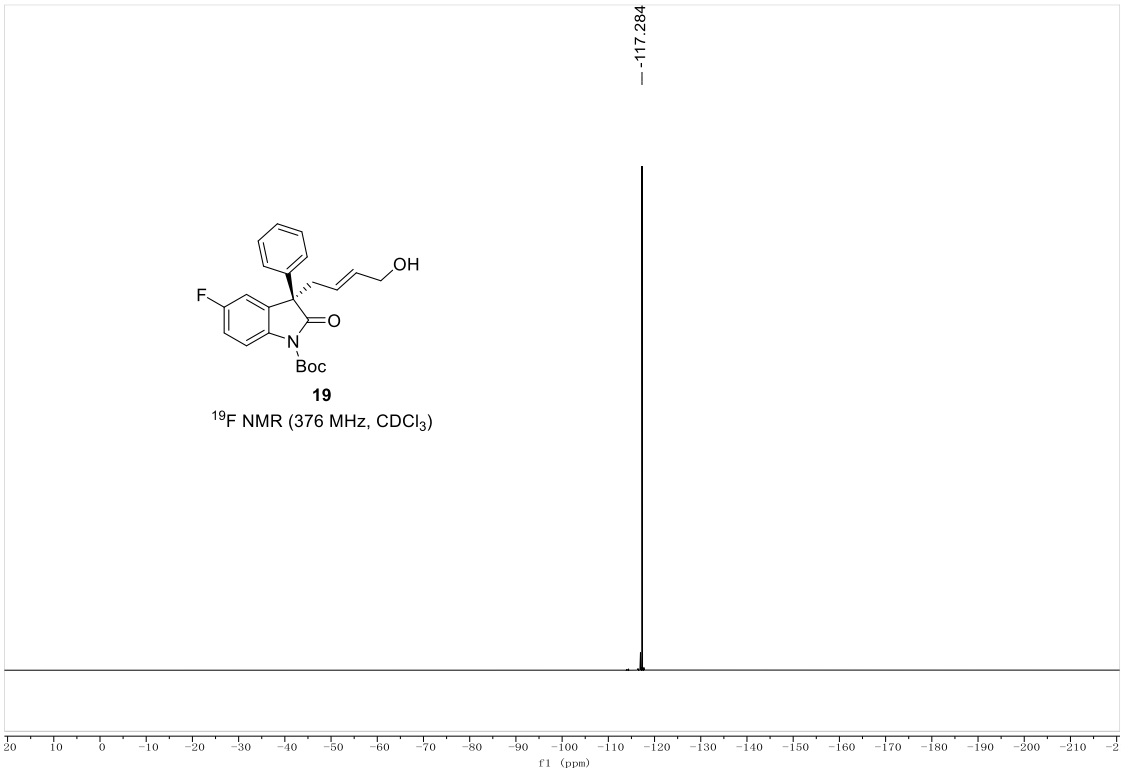




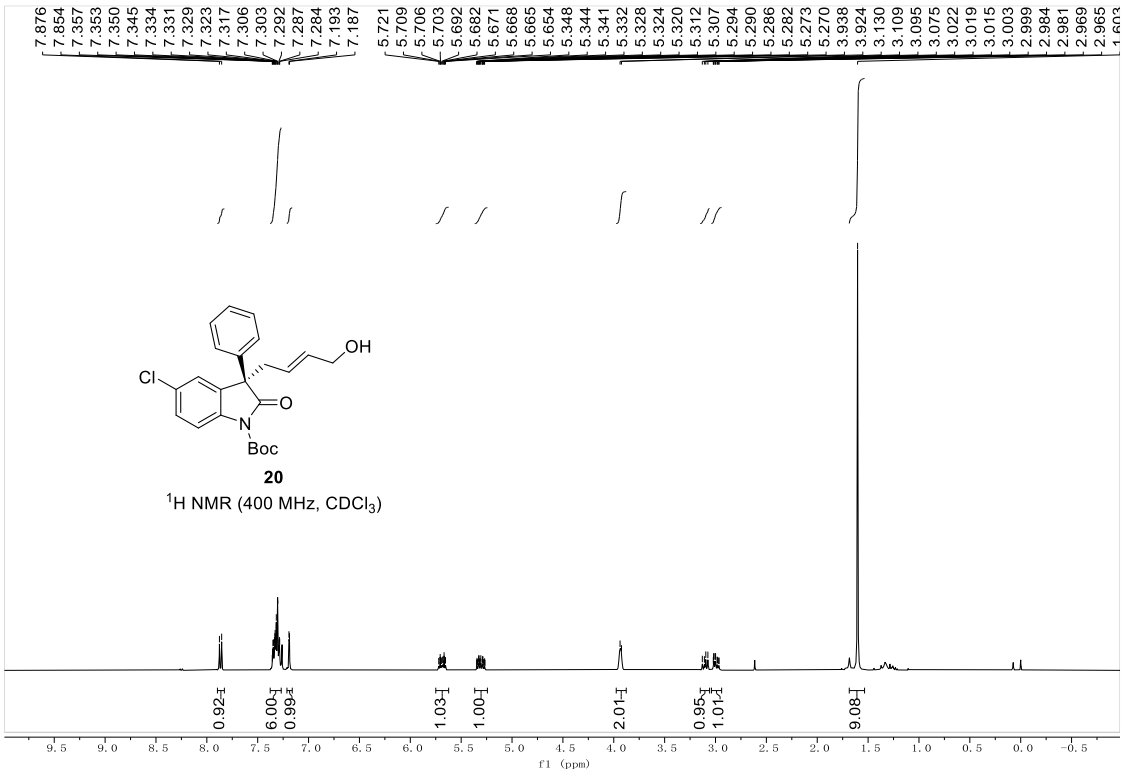
***tert*-Butyl (*R*, *E*)-5-fluoro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (19)**

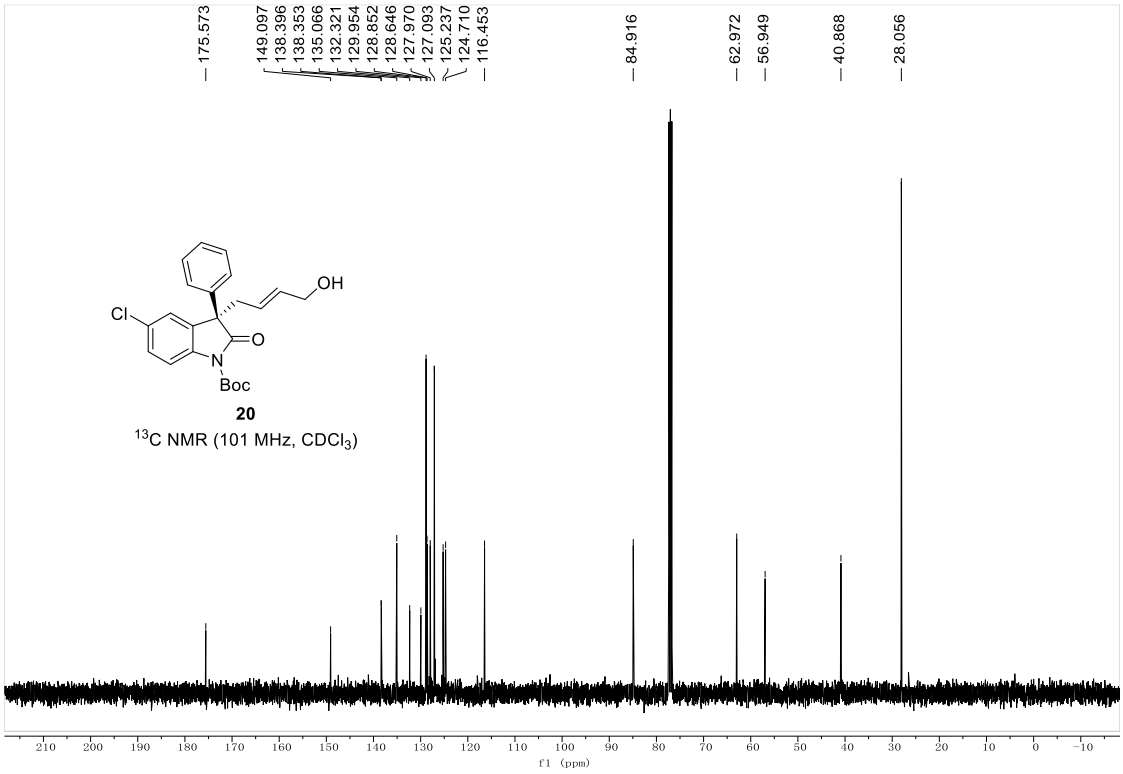




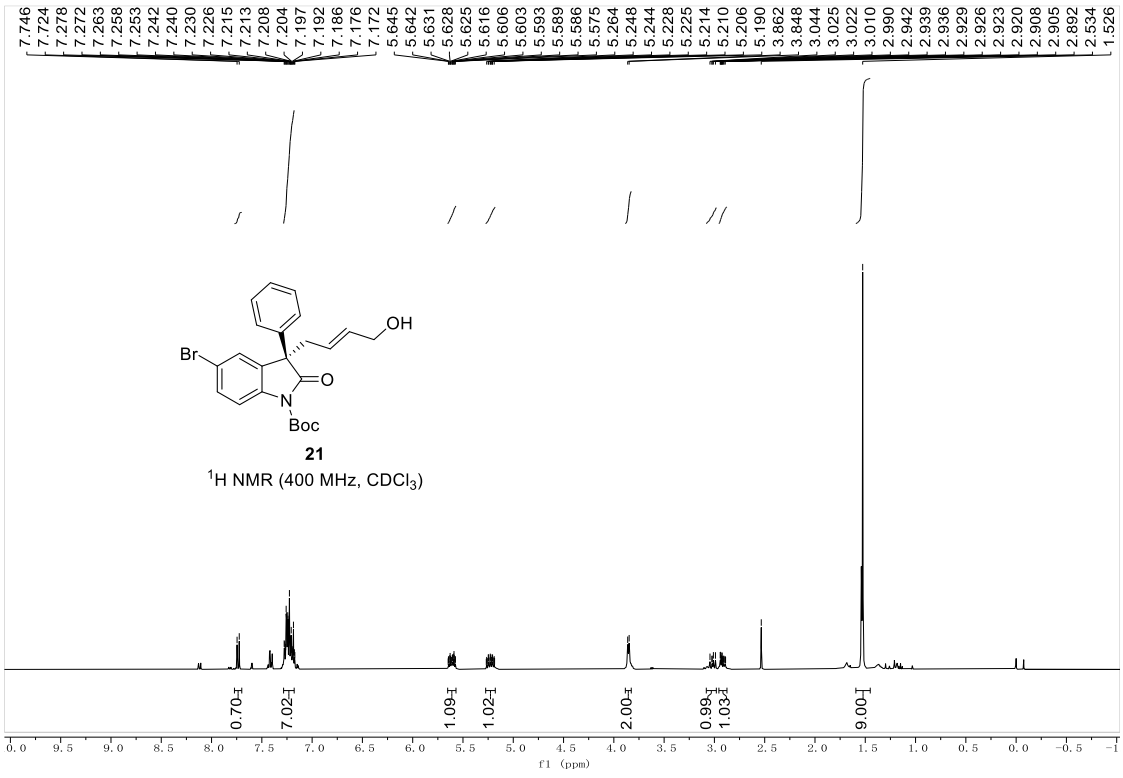


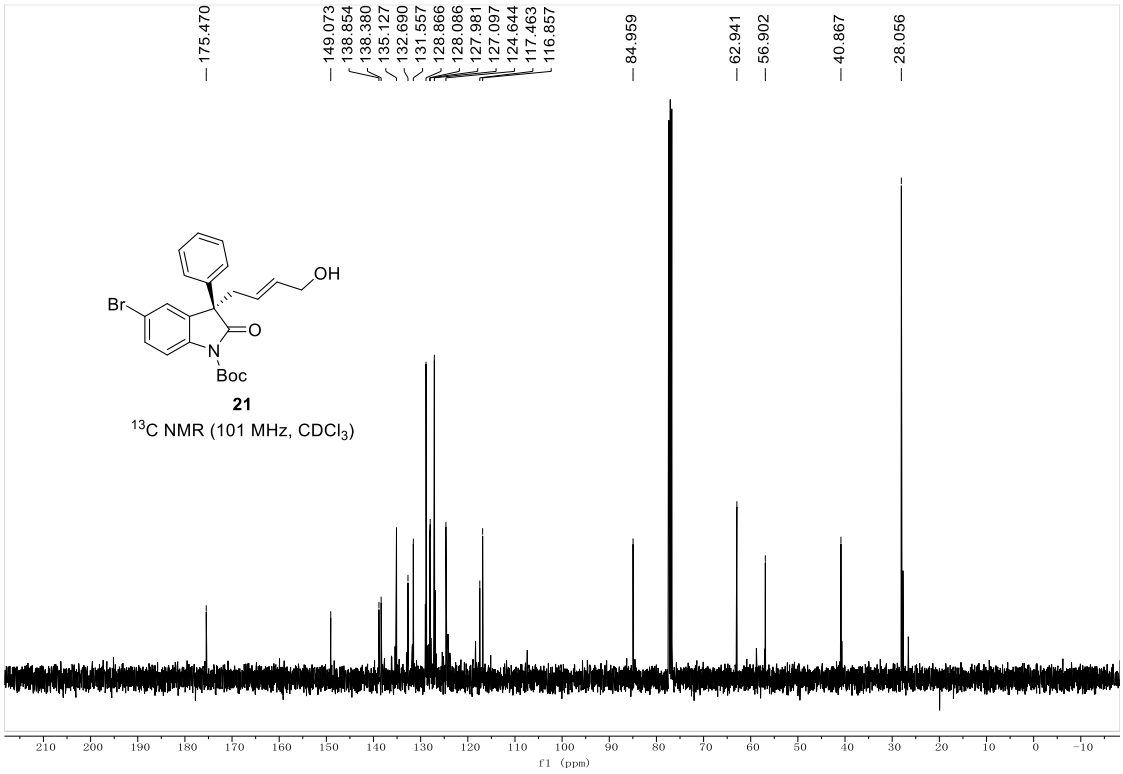
***tert*-Butyl (*R, E*)-5-chloro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (20)**



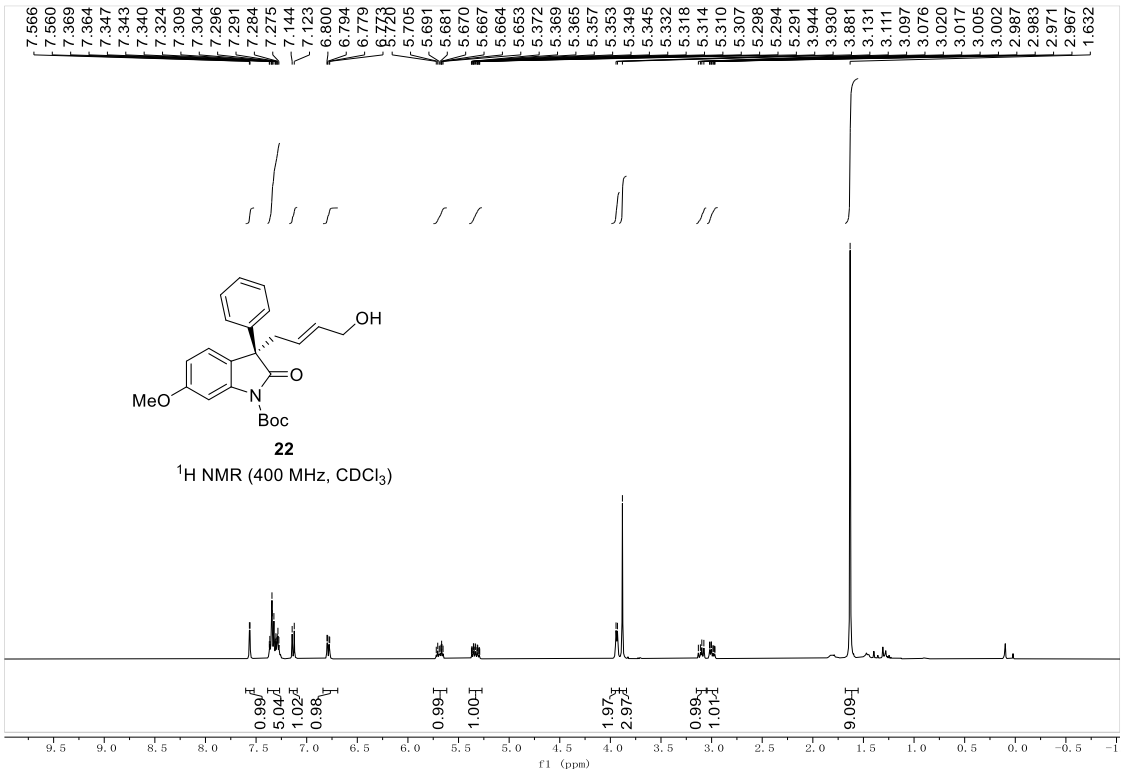


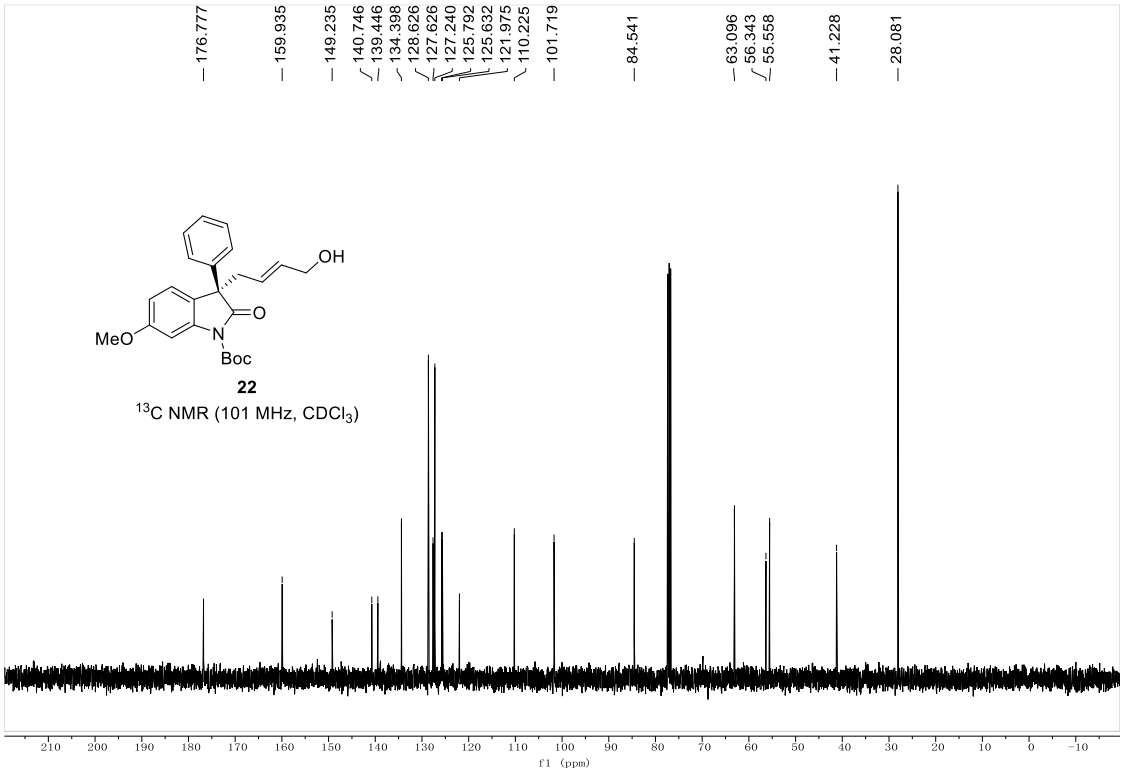
***tert*-Butyl (*R, E*)-5-bromo-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (21)**



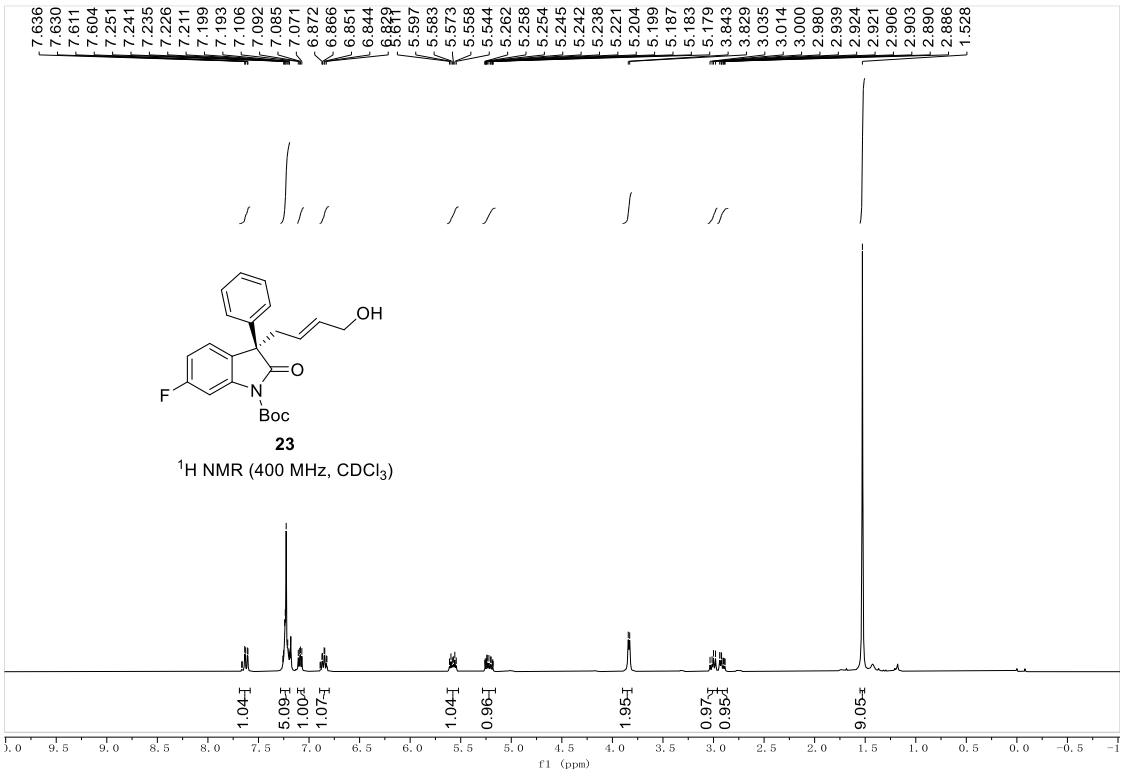


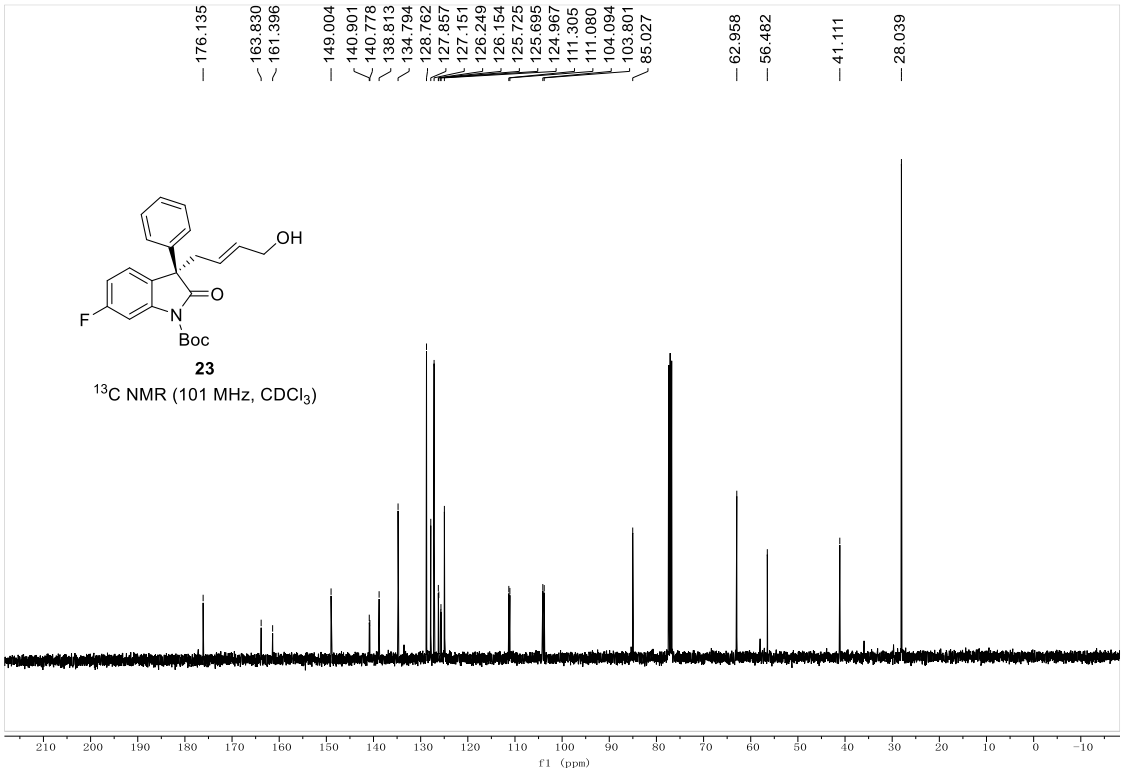
***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-6-methoxy-2-oxo-3-phenylindoline-1-carboxylate (22)**





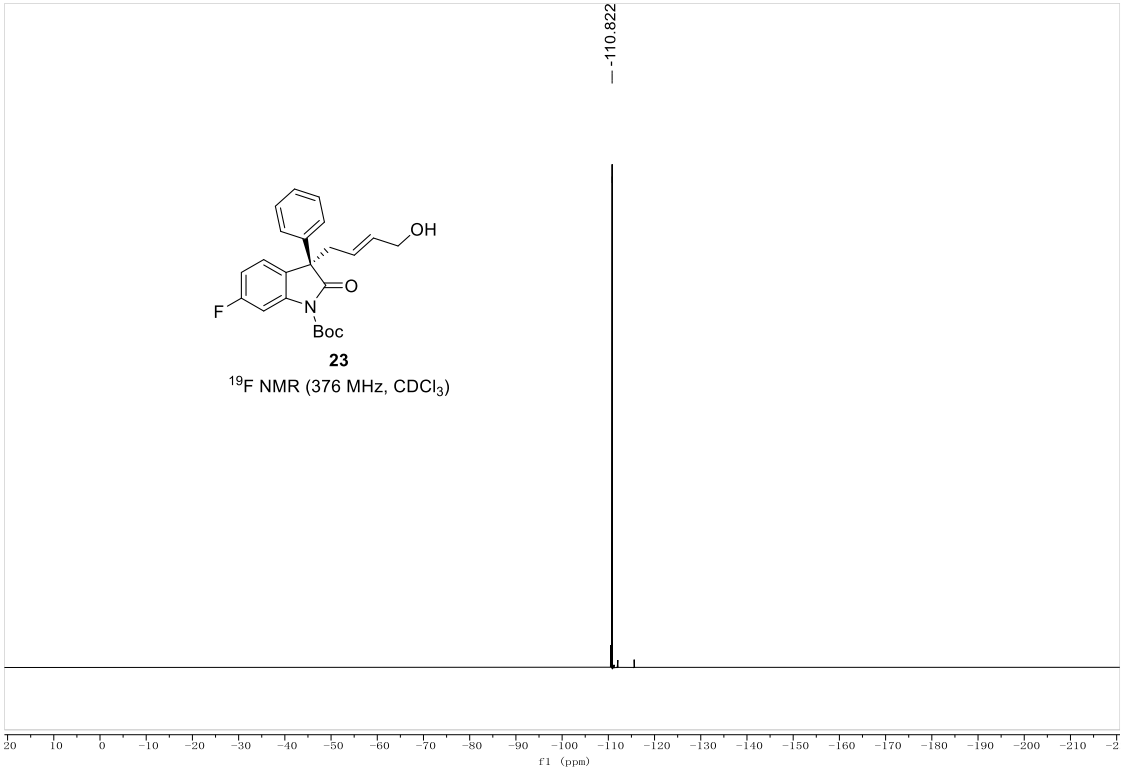
***tert*-Butyl (*R, E*)-6-fluoro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (23)**





23

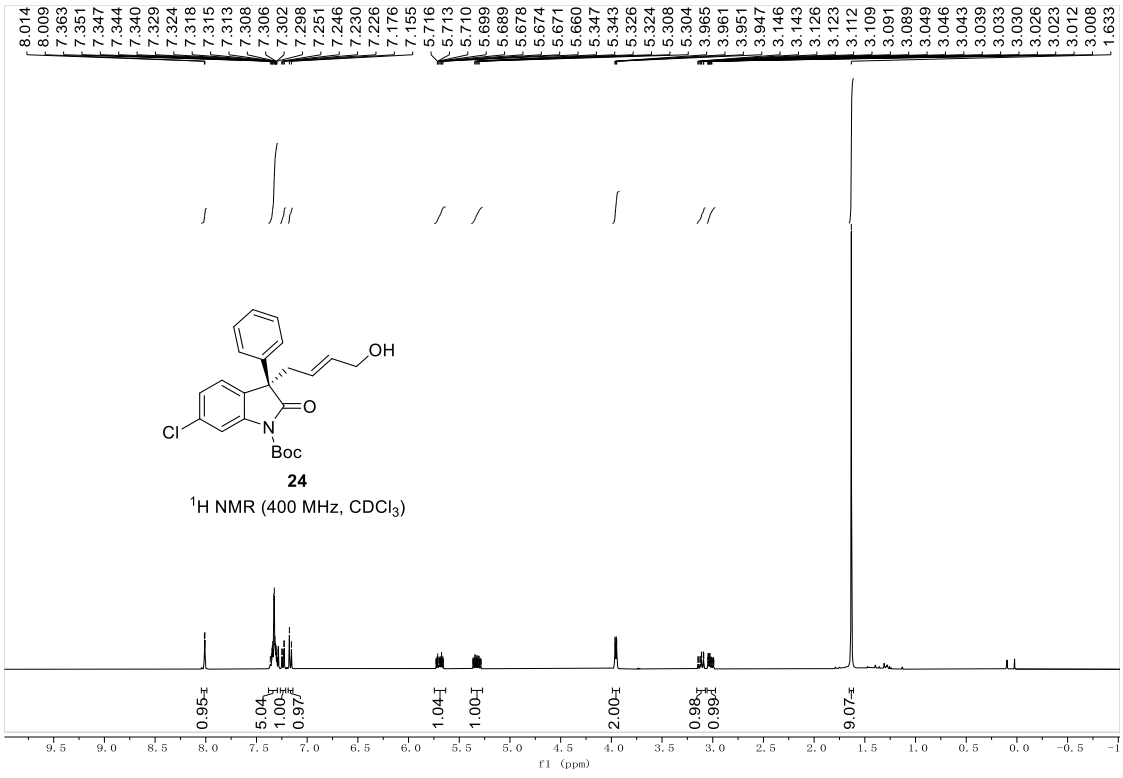
^{13}C NMR (101 MHz, $CDCl_3$)

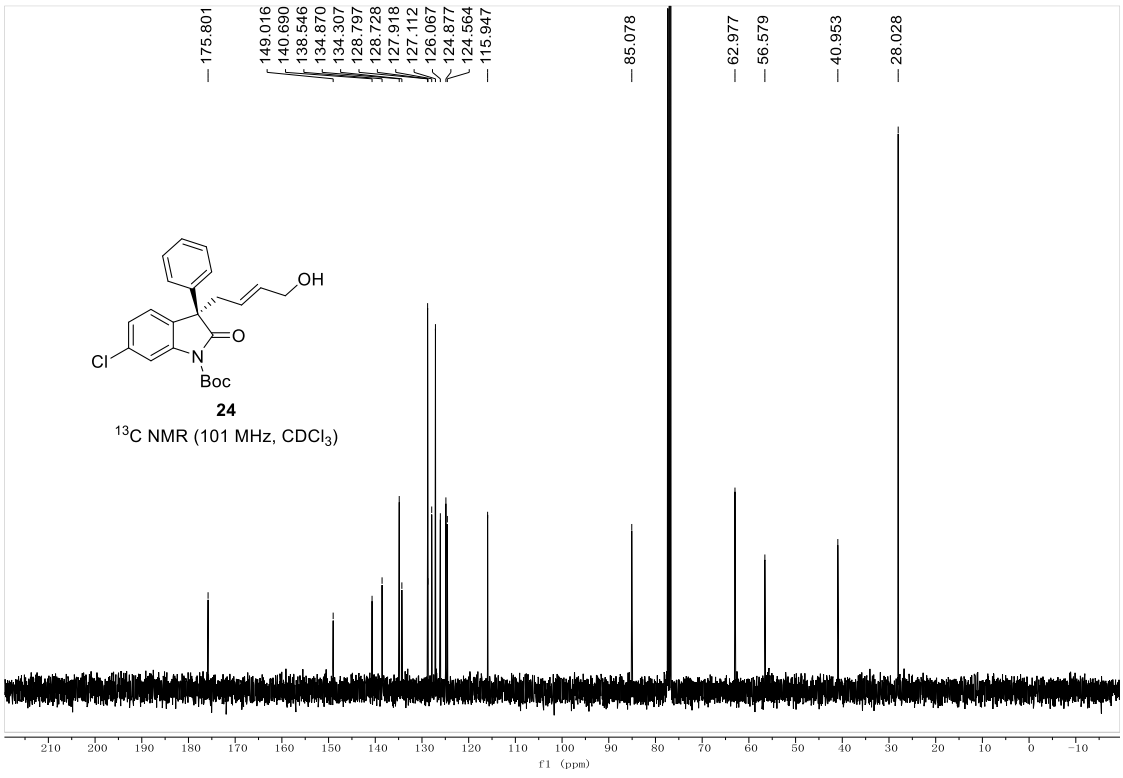


23

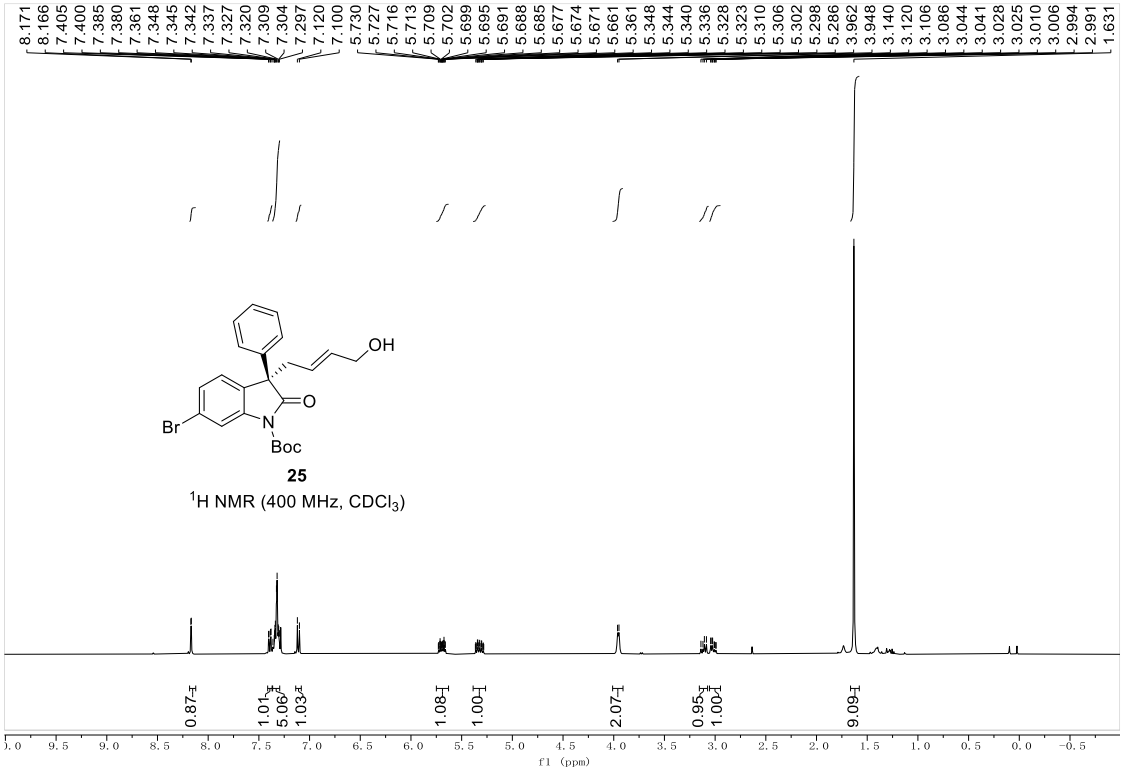
^{19}F NMR (376 MHz, $CDCl_3$)

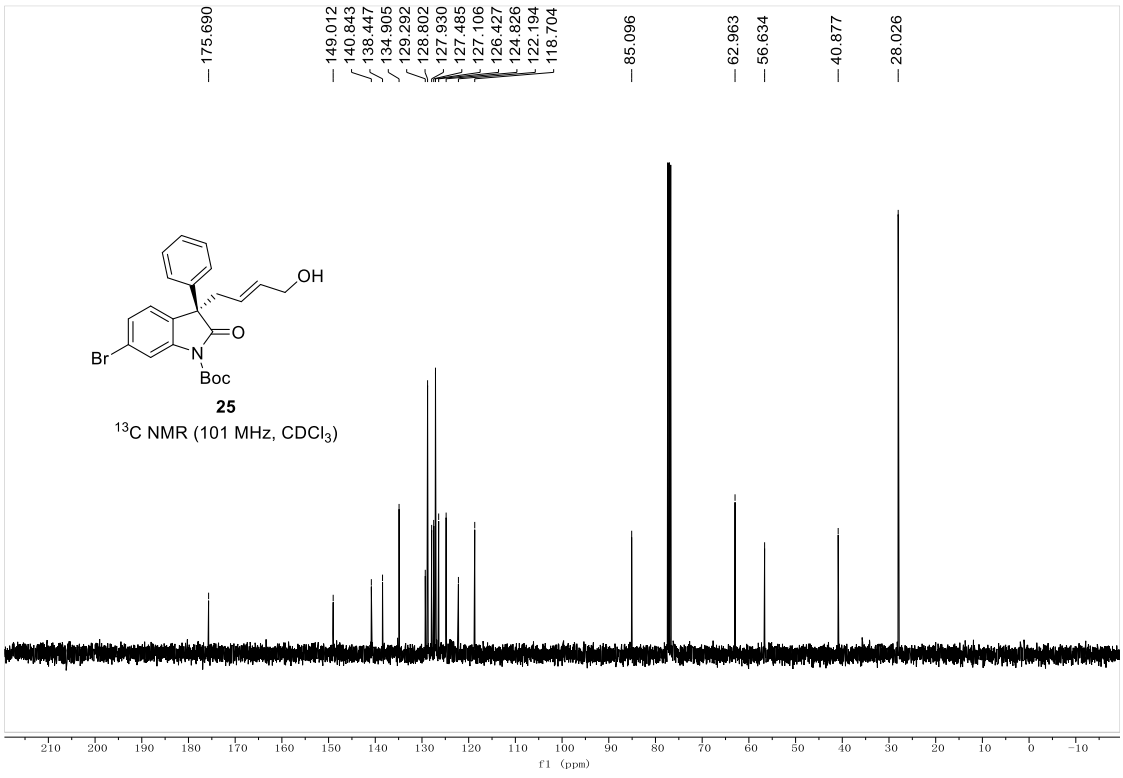
***tert*-Butyl (*R*, *E*)-6-chloro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (24)**



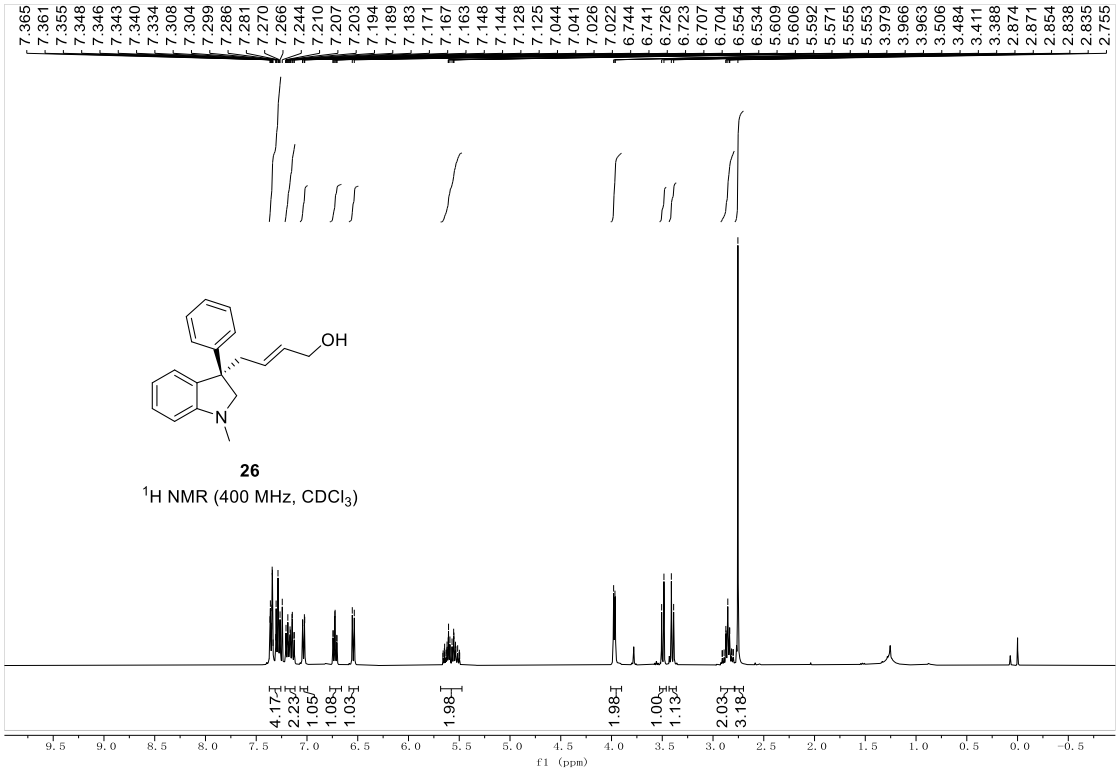


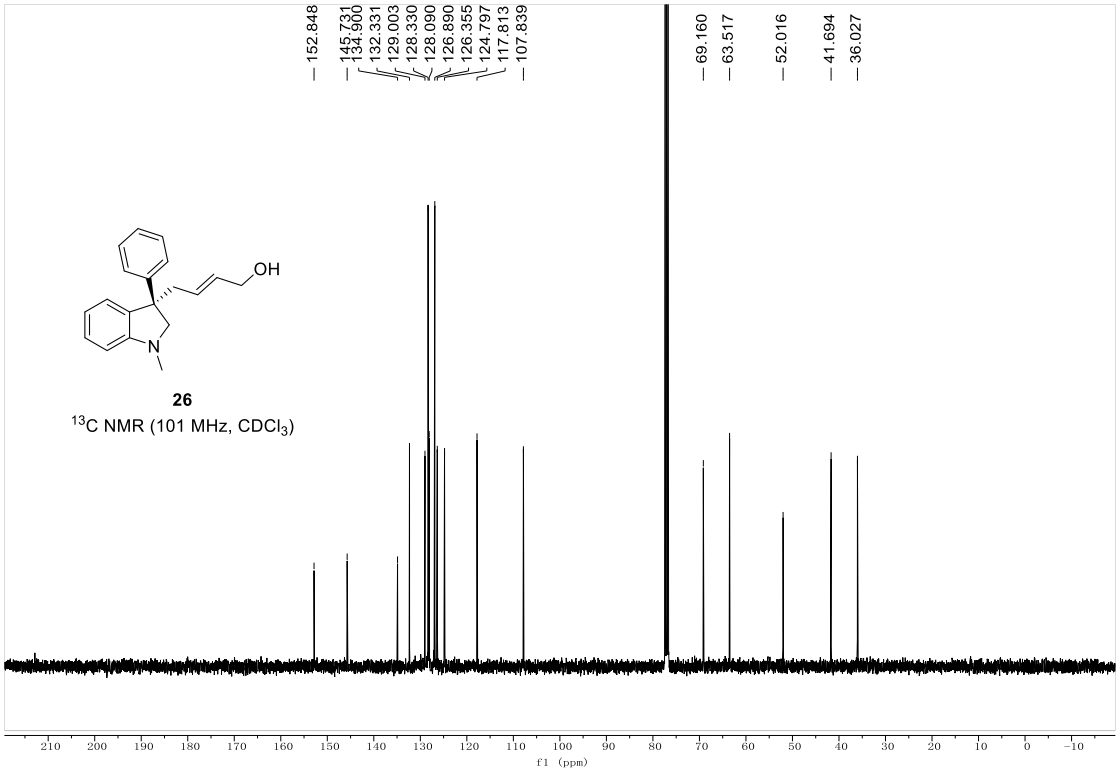
***tert*-Butyl (*R, E*)-6-bromo-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (25)**



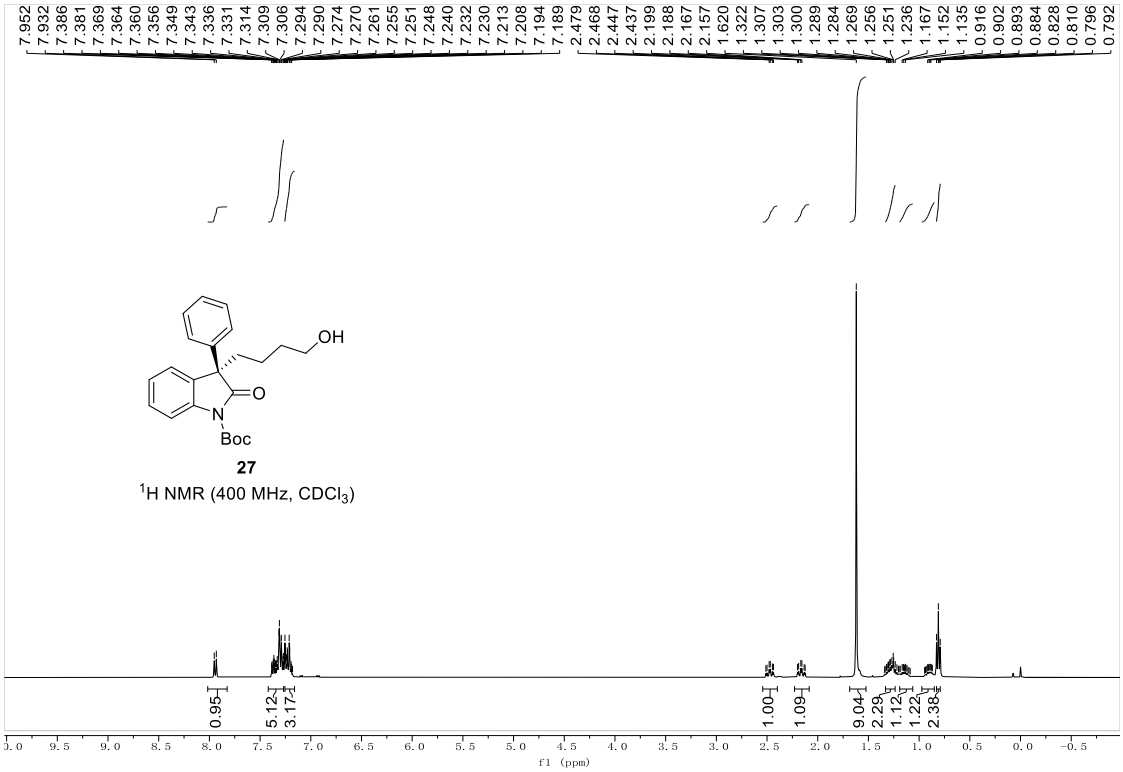


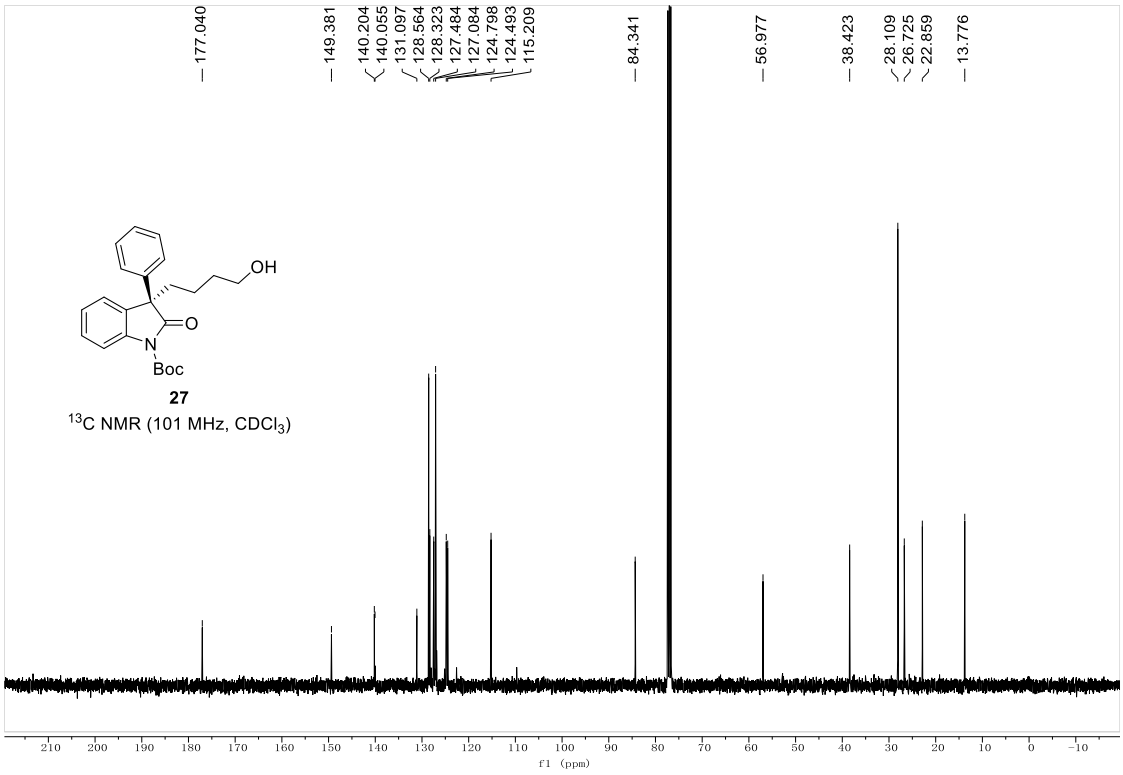
***(R, E)*-4-(1-Methyl-3-phenylindolin-3-yl)but-2-en-1-ol (26)**



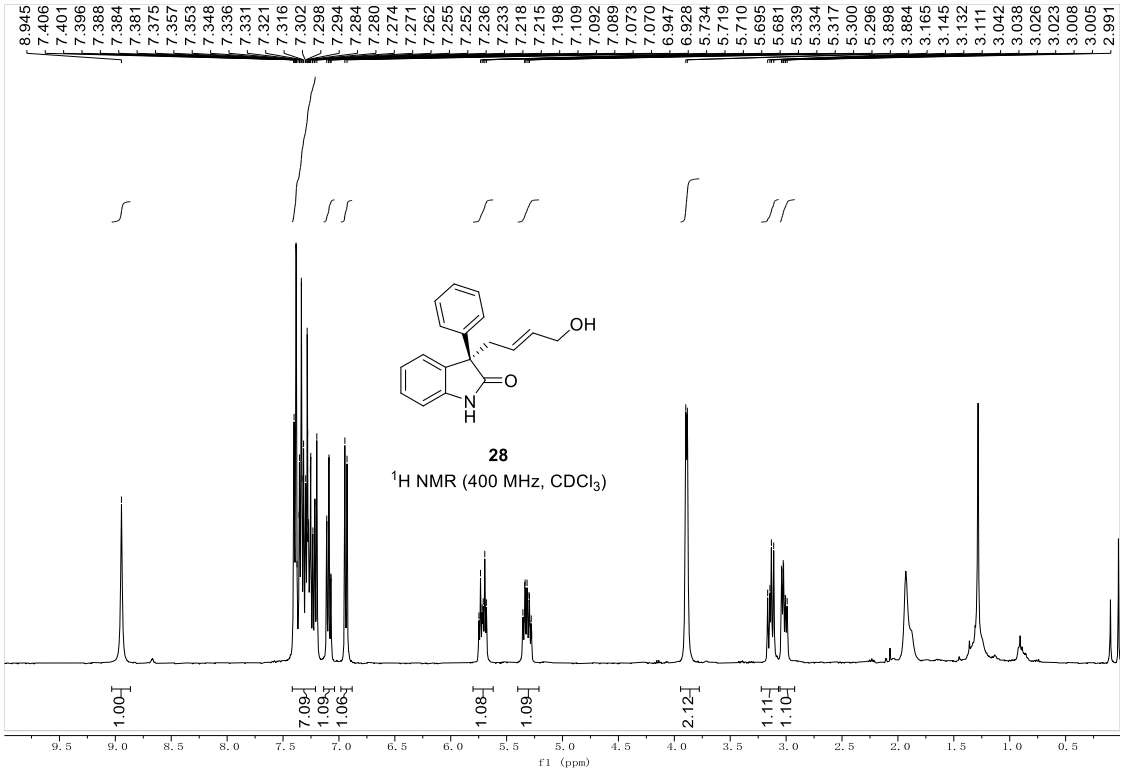


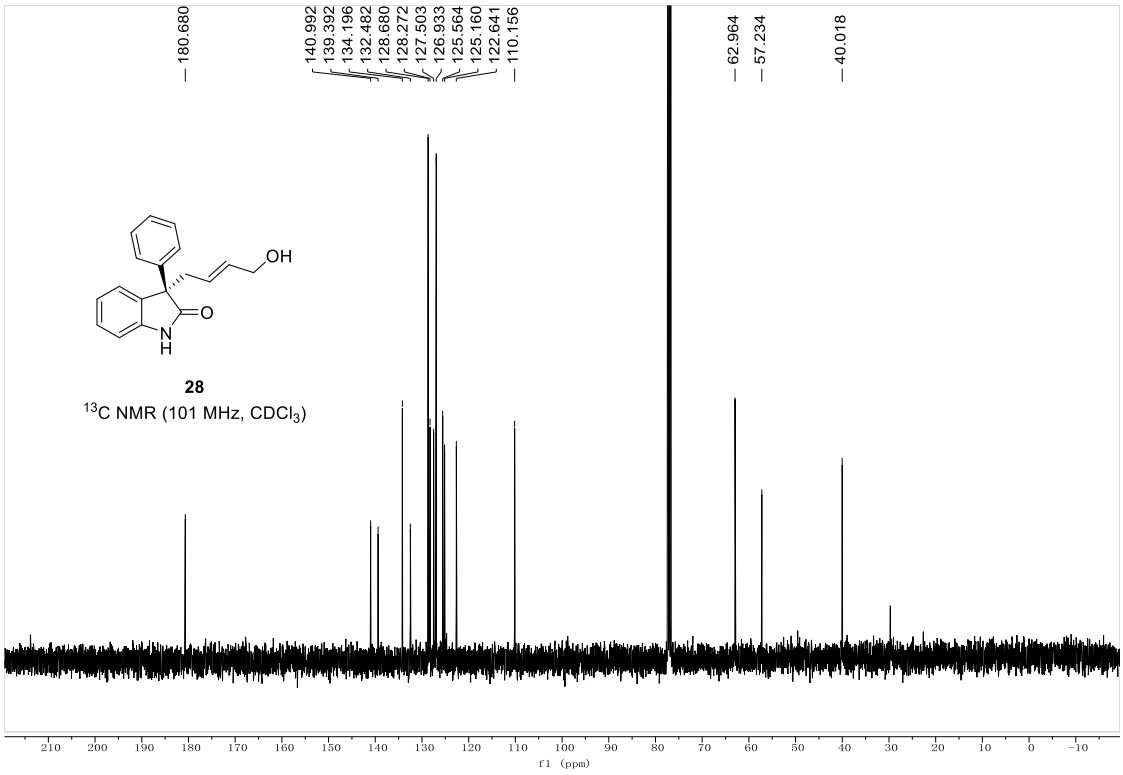
tert-Butyl (*R*)-3-(4-hydroxybutyl)-2-oxo-3-phenylindoline-1-carboxylate (27)



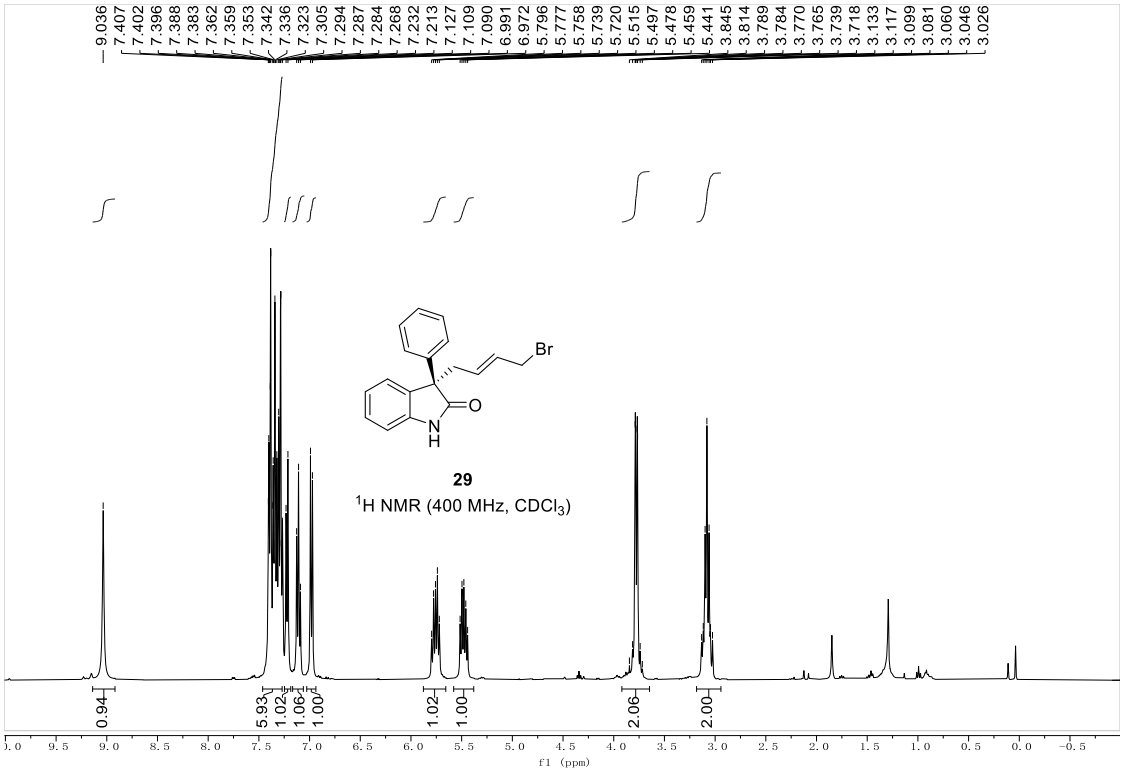


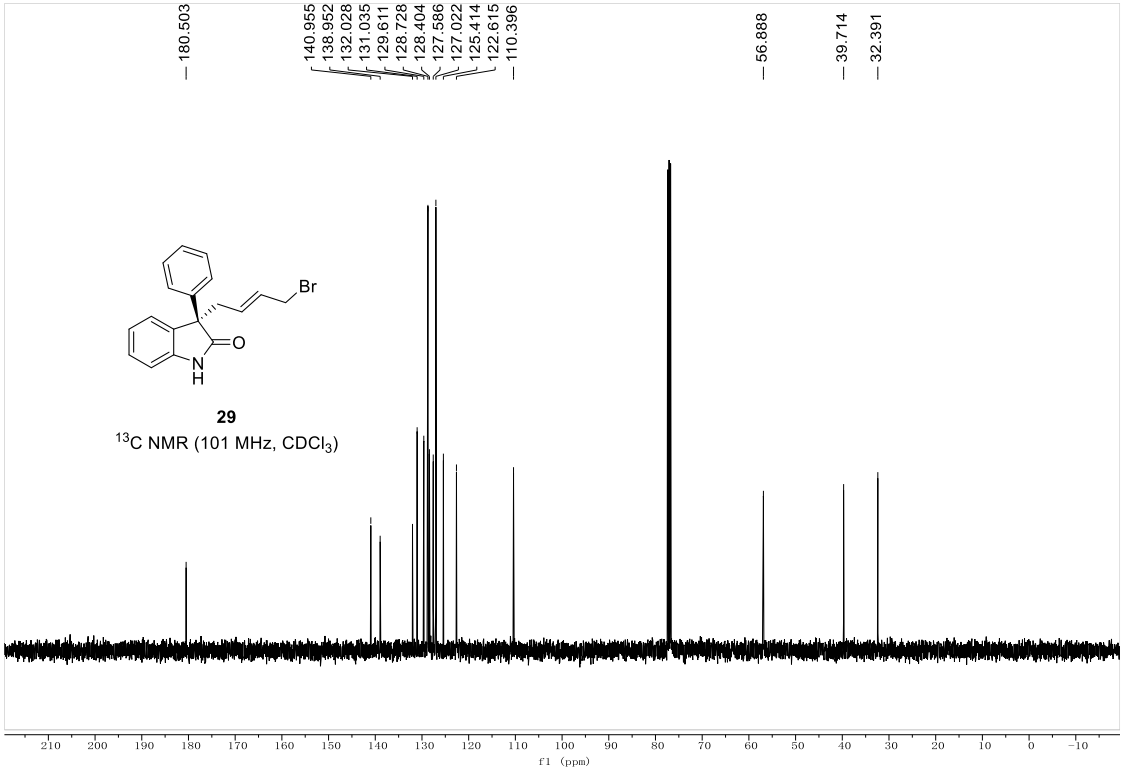
***(R, E)*-3-(4-Hydroxybut-2-en-1-yl)-3-phenylindolin-2-one (28)**



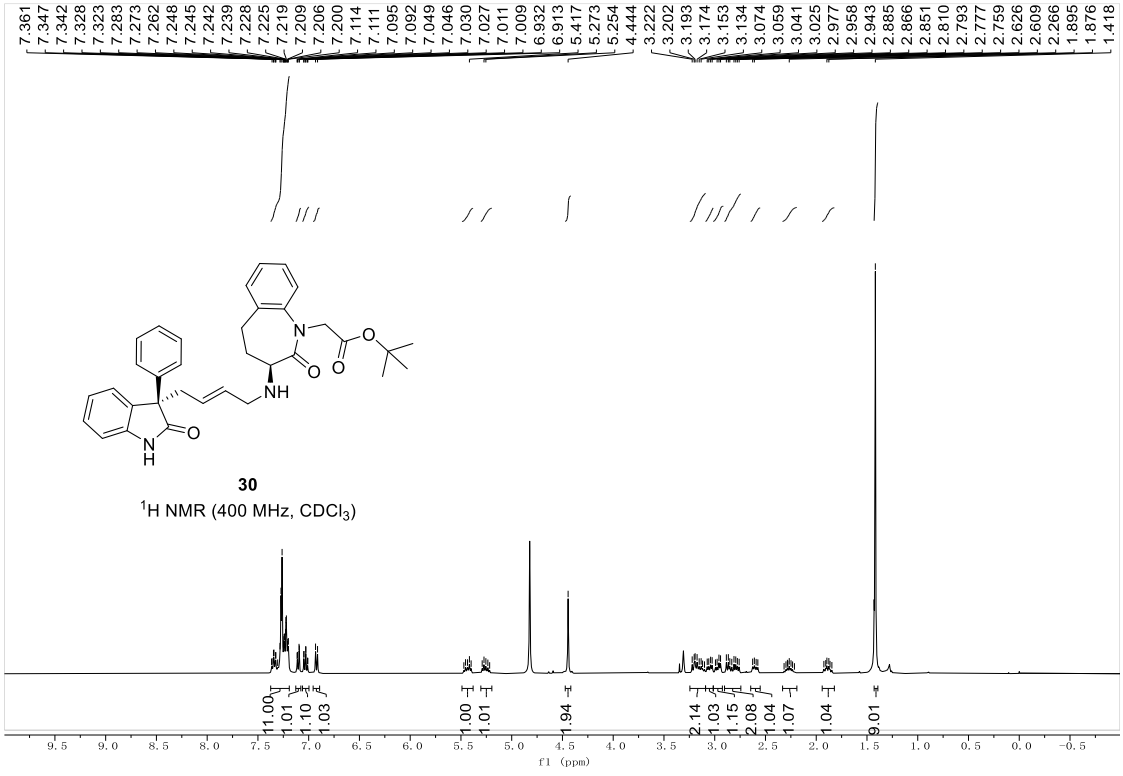


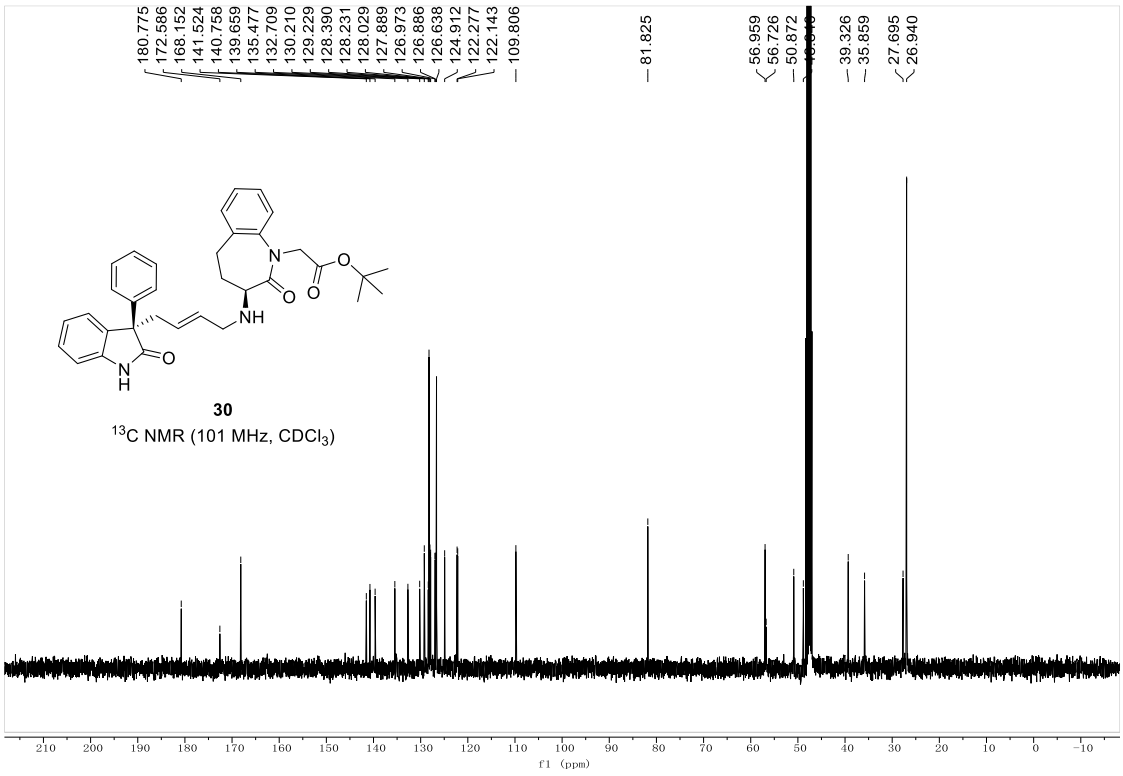
***(R, E)*-3-(4-Bromobut-2-en-1-yl)-3-phenylindolin-2-one (29)**



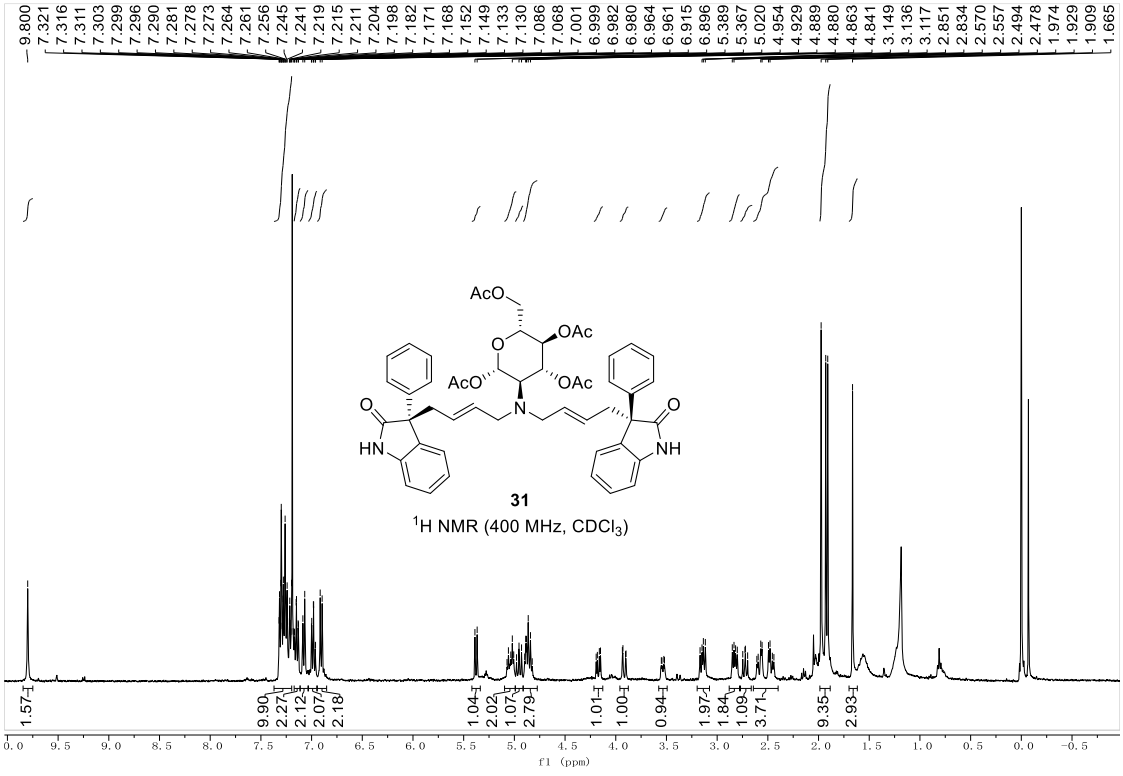


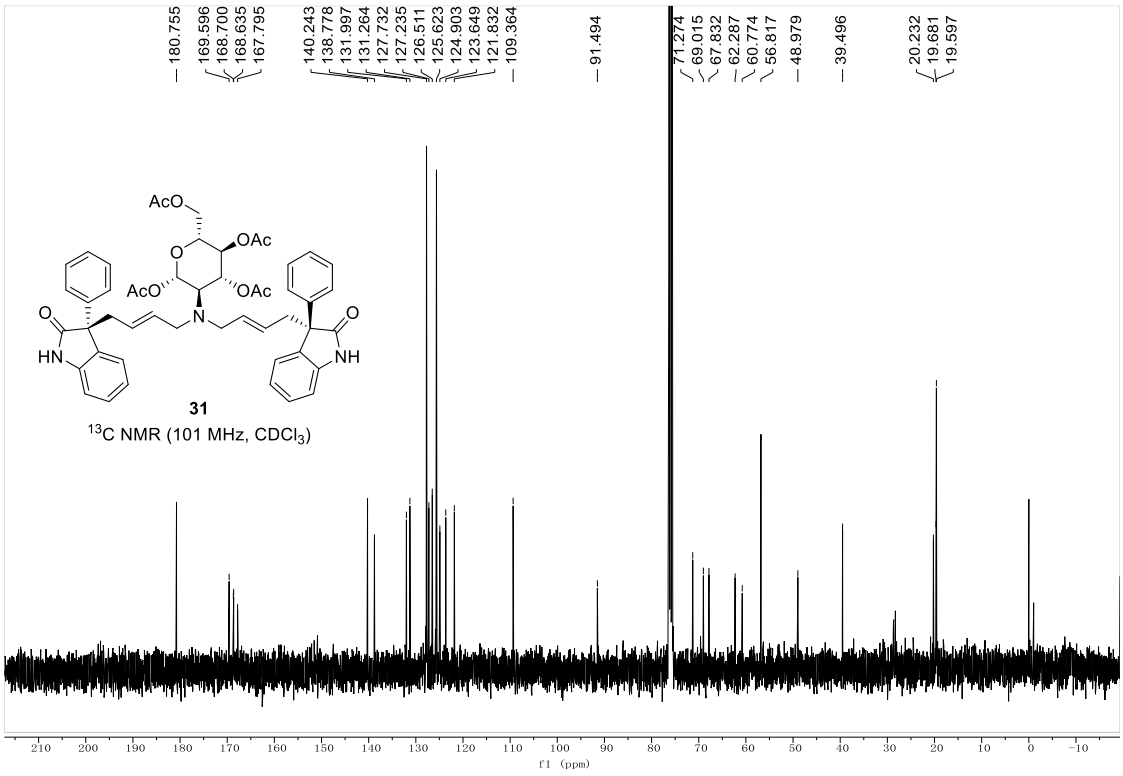
***tert*-Butyl 2-((*S*)-2-oxo-3-(((*E*)-4-((*R*)-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)amino)-2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)acetate (30)**



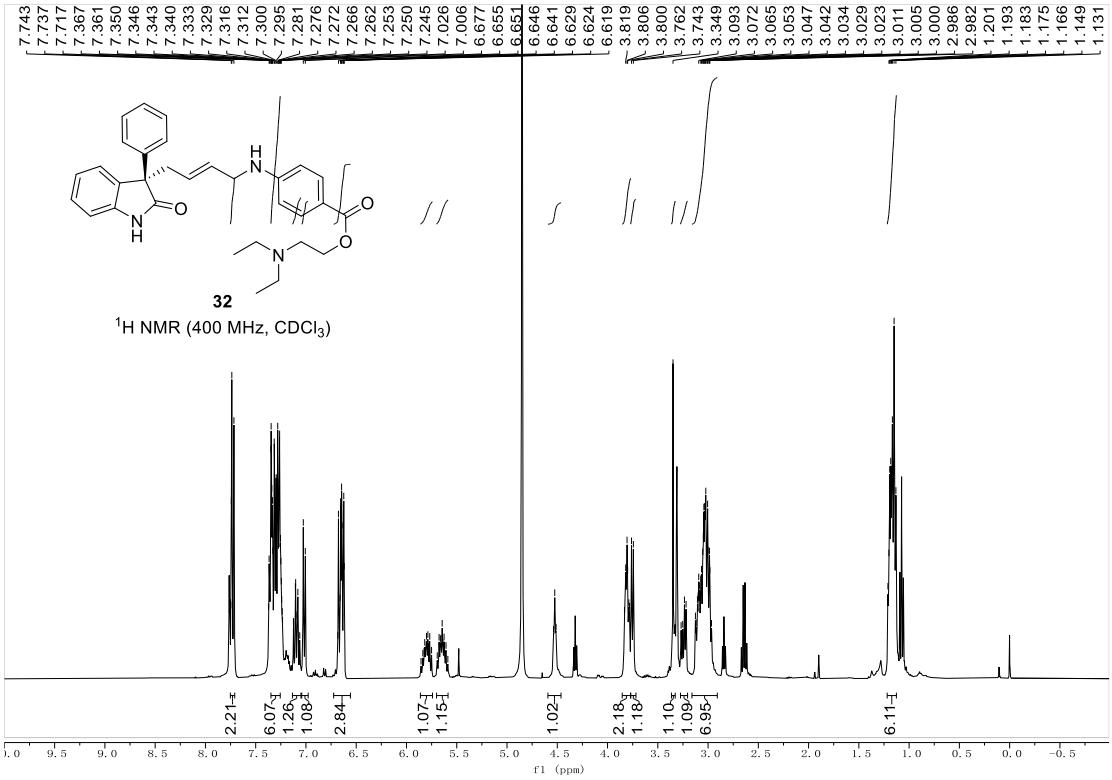


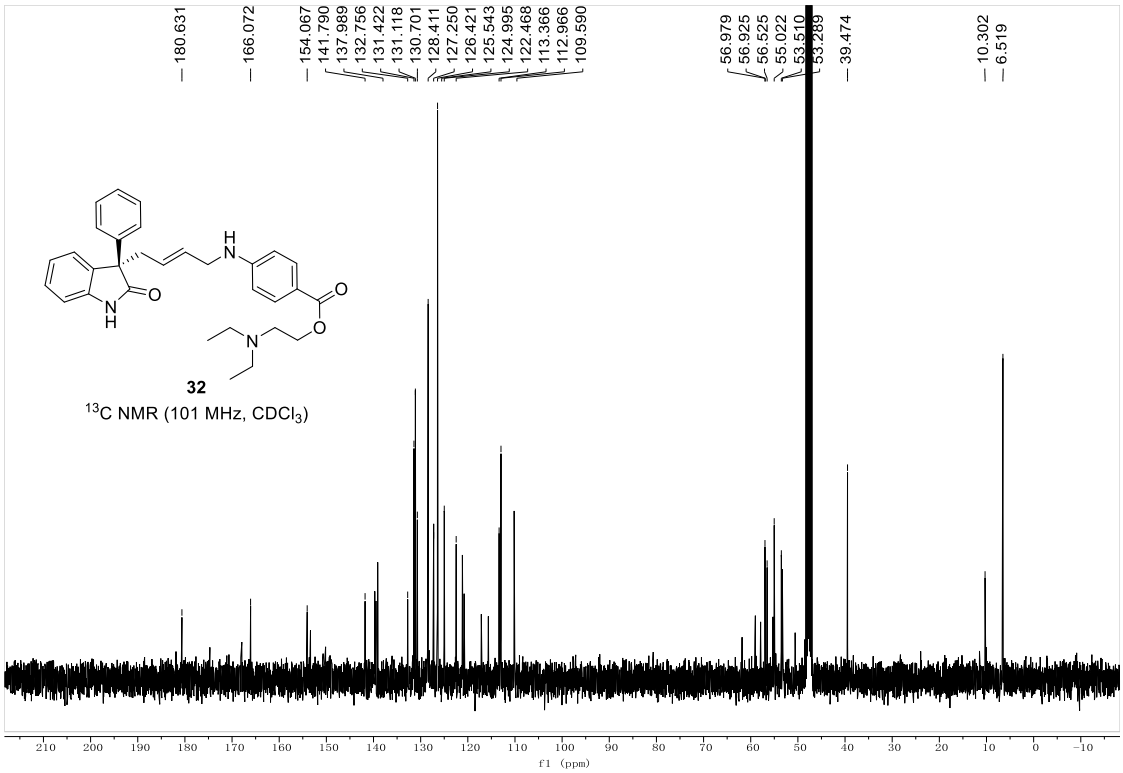
(2*S*, 3*R*, 4*R*, 5*S*, 6*R*)-6-(Acetoxymethyl)-3-(bis((*E*)-4-((*R*)-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)amino)tetrahydro-2H-pyran-2,4,5-triyl triacetate (31)



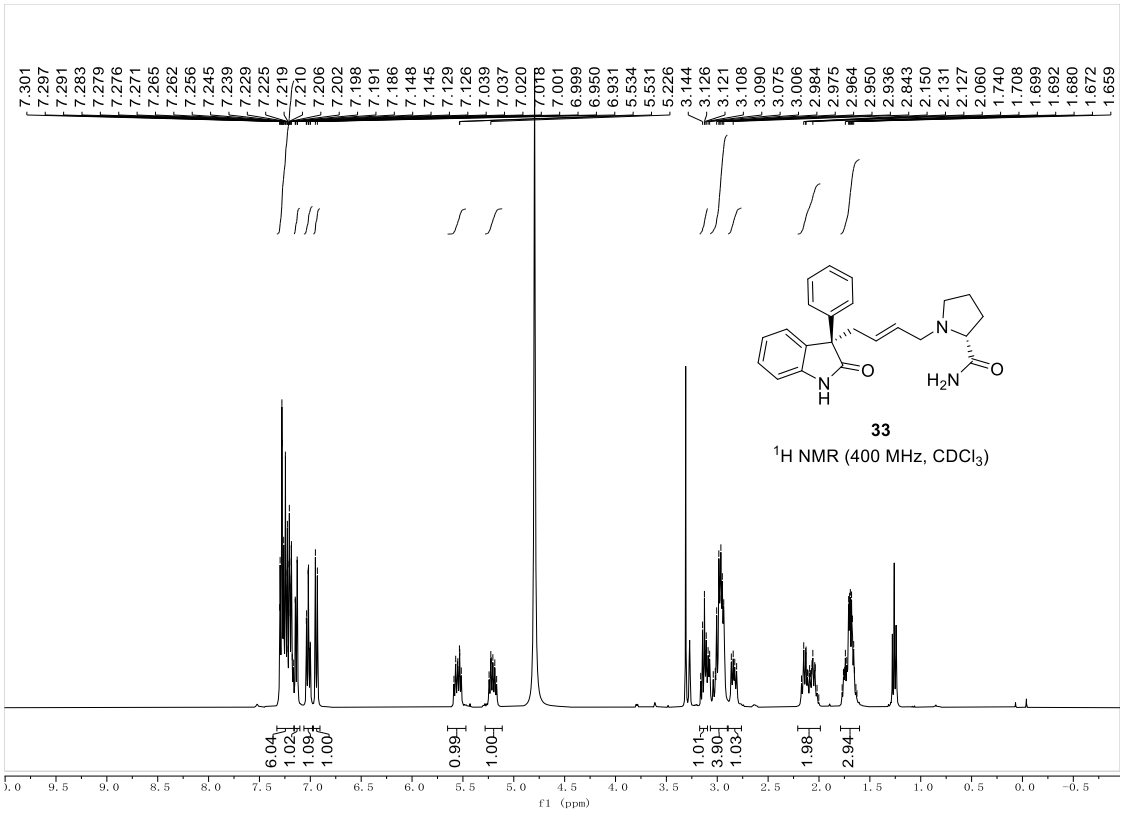


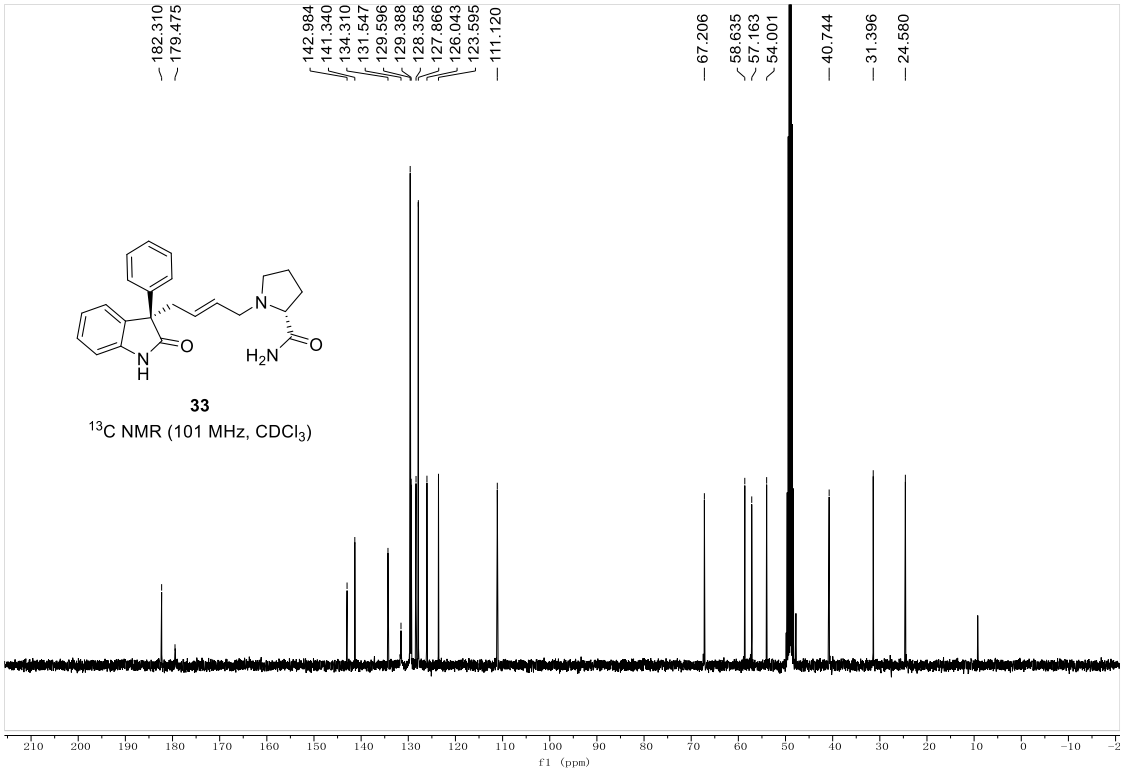
2-(Diethylamino)ethyl (*R, E*)-4-((4-(2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)amino)benzoate (32)



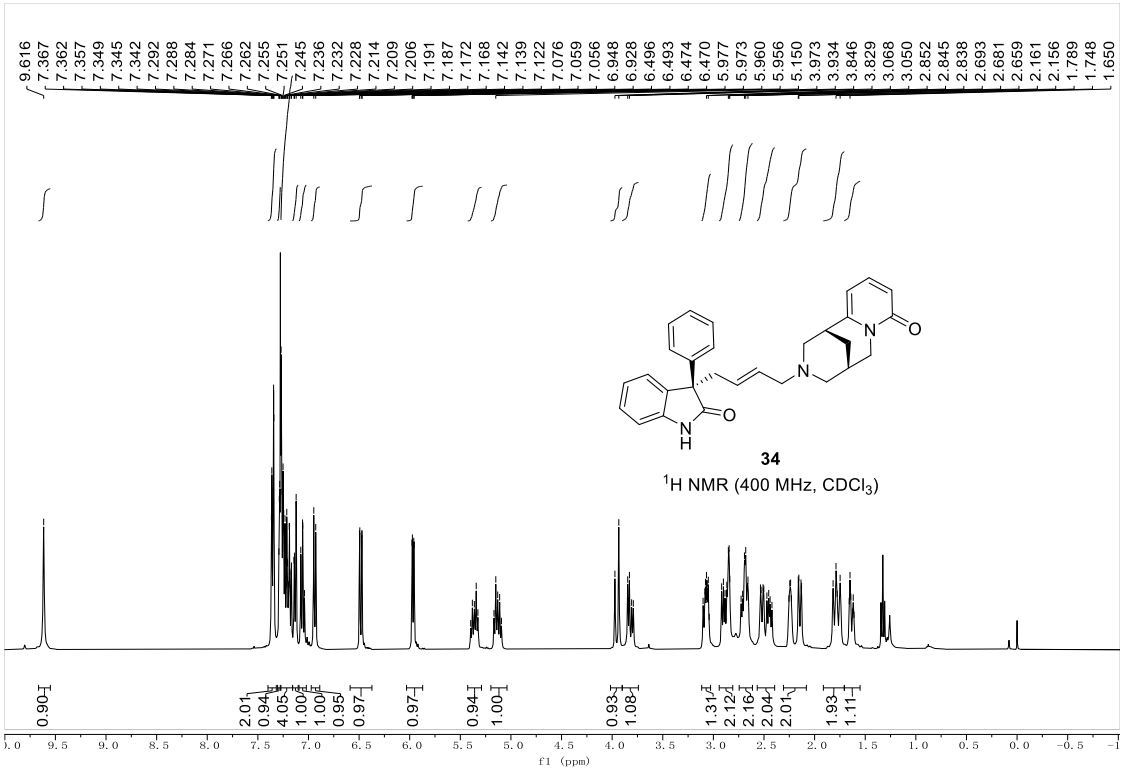


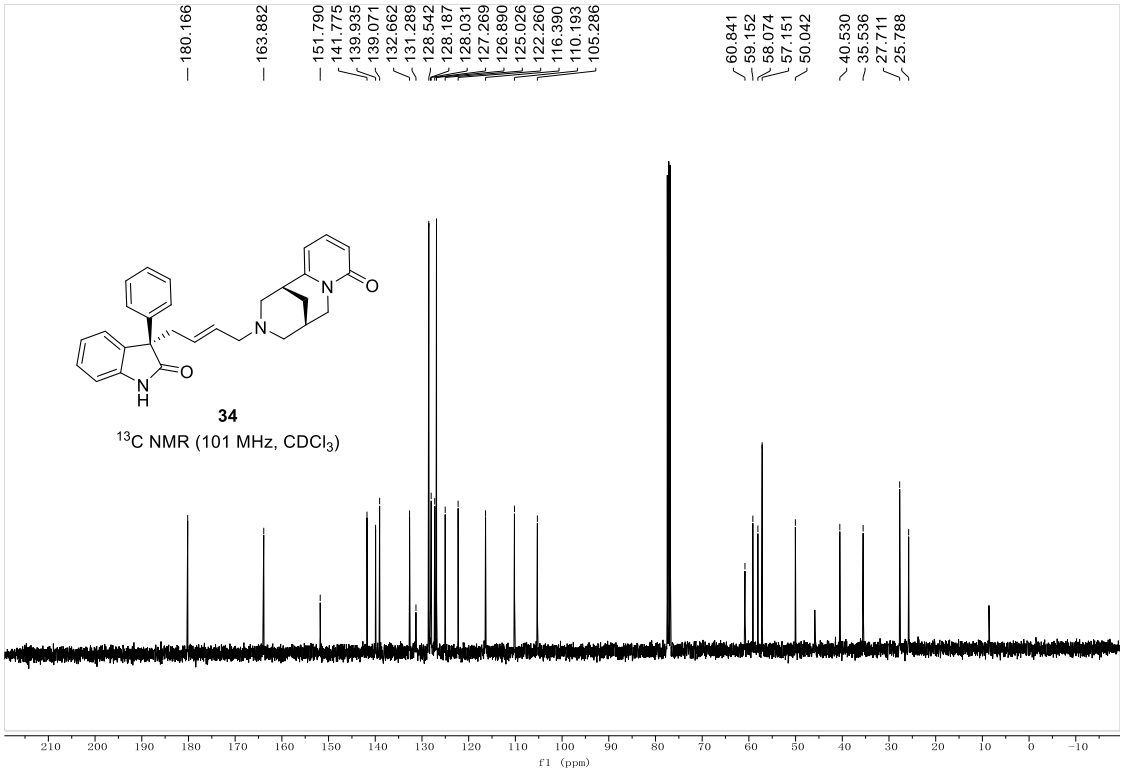
(*R*)-1-((*E*)-4-((*R*)-2-oxo-3-Phenylindolin-3-yl)but-2-en-1-yl)pyrrolidine-2-carboxamide (33)





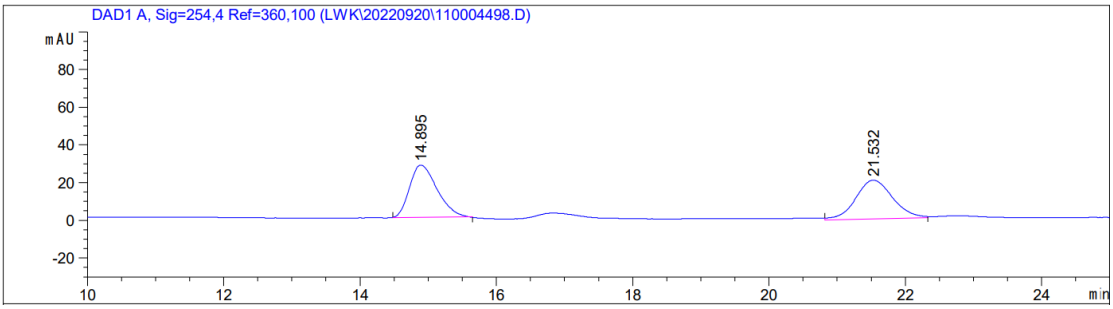
(1*R*,5*S*)-3-((*E*)-4-((*R*)-2-oxo-3-Phenylindolin-3-yl)but-2-en-1-yl)-1,2,3,4,5,6-hexahydro-8H-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one (34)



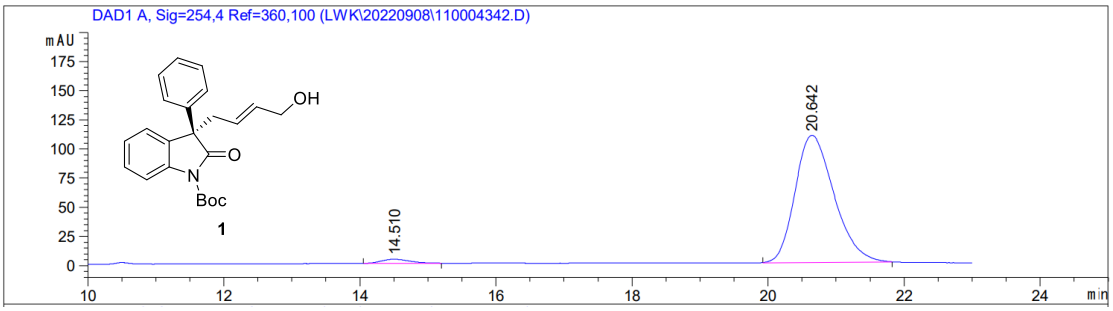


8. HPLC analysis

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (1)**

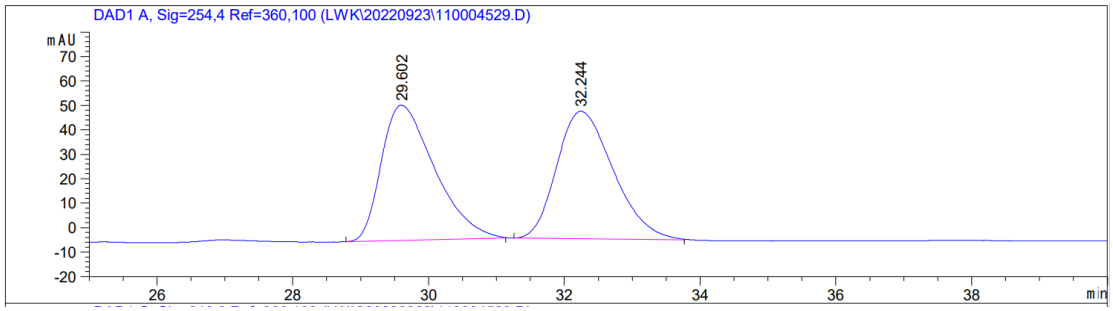


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.895	MM R	0.4683	780.19434	27.76660	50.0184
2	21.532	MM R	0.6304	779.62061	20.61099	49.9816

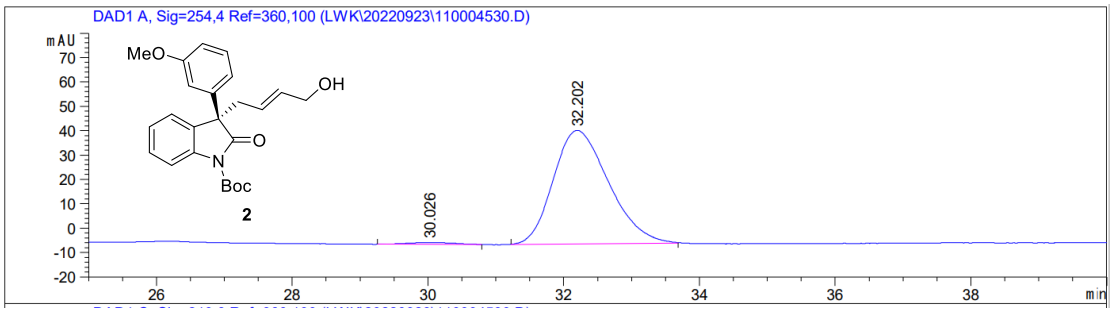


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.510	BB	0.3667	103.79066	3.55447	2.3287
2	20.642	BB	0.6132	4353.22461	109.16947	97.6713

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-3-(3-methoxyphenyl)-2-oxoindoline-1-carboxylate (2)**

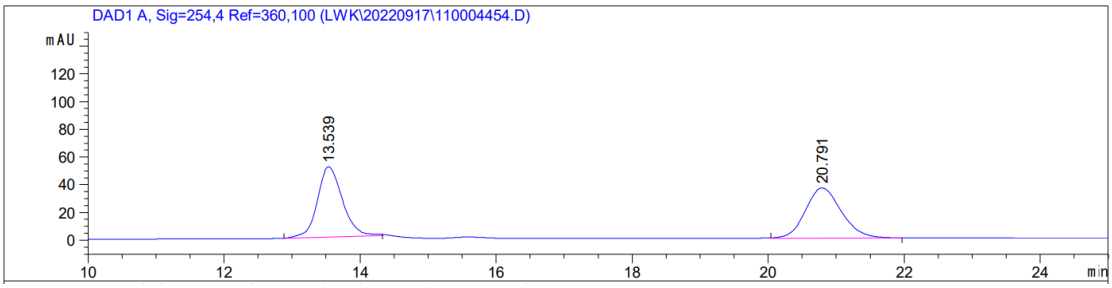


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.602	BB	0.7814	3013.53955	55.33070	50.0347
2	32.244	BB	0.8873	3009.35913	52.14118	49.9653

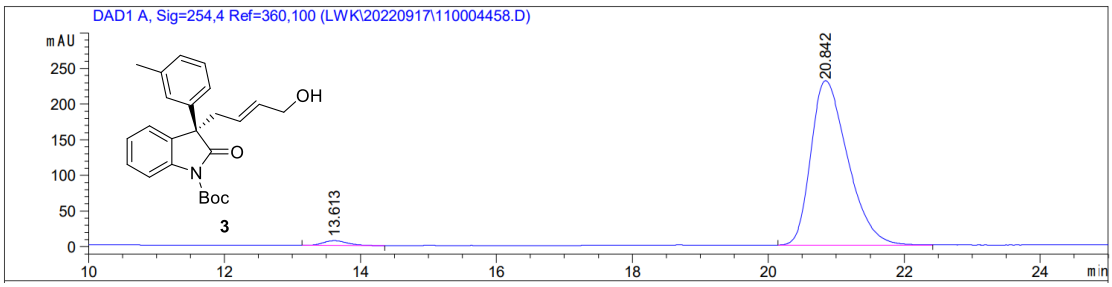


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.026	MM R	0.7985	37.65936	7.86027e-1	1.4018
2	32.202	BB	0.8147	2648.83350	46.63419	98.5982

tert-Butyl (_R_, _E_)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-(m-tolyl)indoline-1-carboxylate (3)

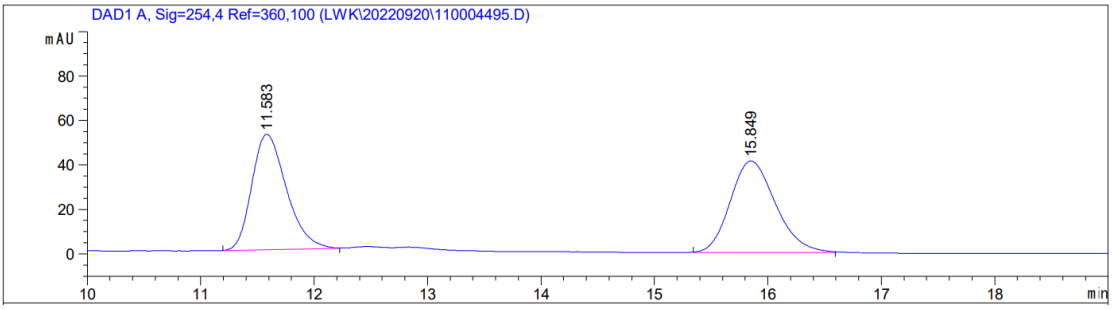


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.539	MM R	0.4312	1313.61157	50.77024	49.6791
2	20.791	BB	0.5652	1330.58252	36.17081	50.3209

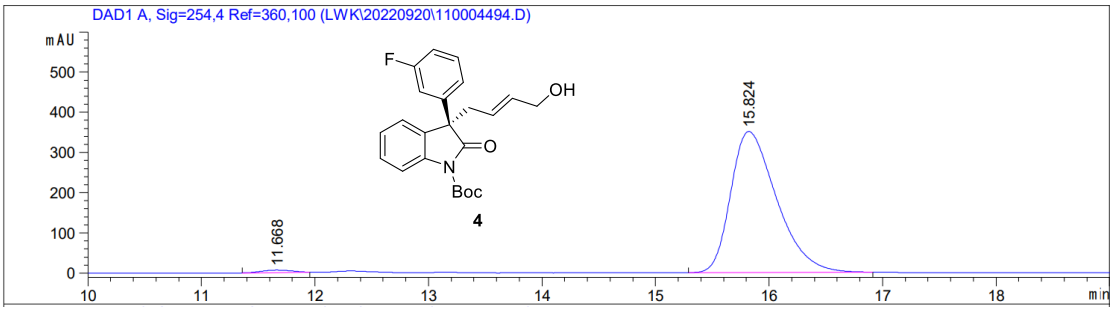


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.613	BB	0.3798	167.36639	6.69130	1.8940
2	20.842	BB	0.5787	8669.28613	230.53284	98.1060

***tert*-Butyl (*R*, *E*)-3-(3-fluorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (4)**

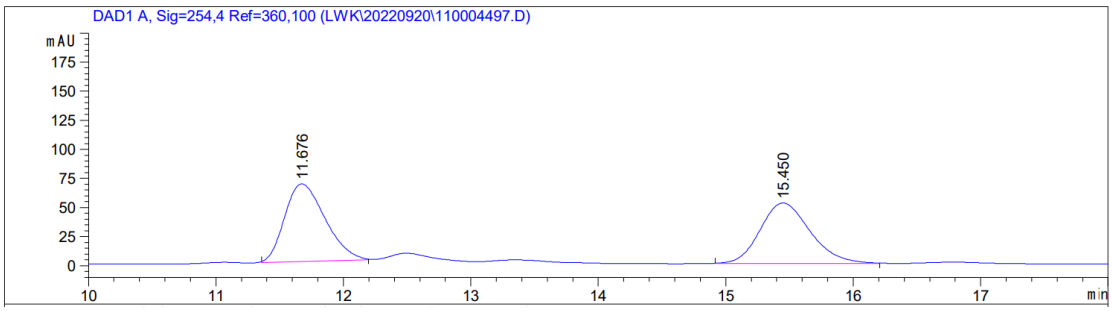


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.583	BB	0.3277	1102.70447	51.93147	49.2107
2	15.849	BB	0.4267	1138.07703	41.14437	50.7893

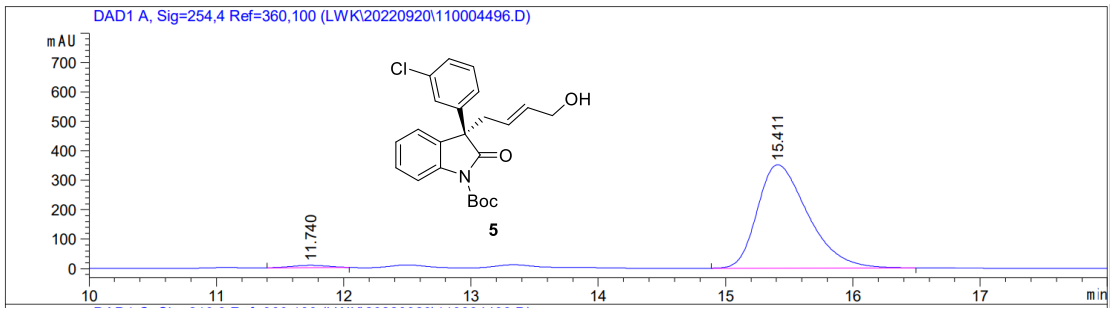


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.668	MM R	0.3201	123.88526	6.44950	1.2365
2	15.824	BB	0.4307	9895.20020	351.17252	98.7635

***tert*-Butyl (*R*, *E*)-3-(3-chlorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (5)**

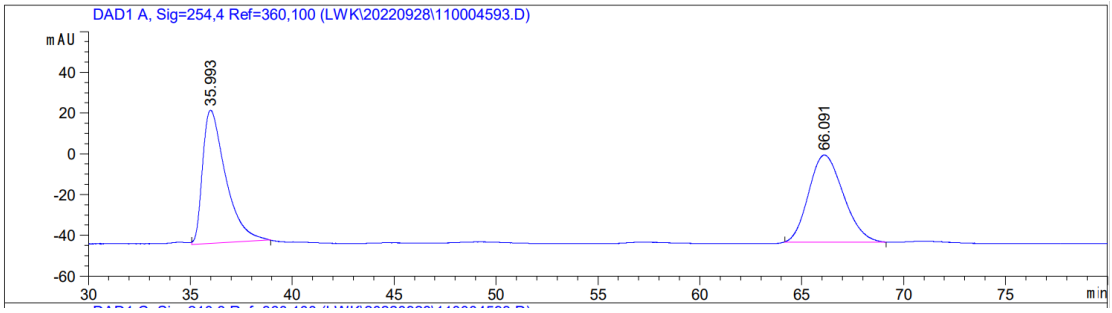


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.676	MM R	0.3673	1472.84558	66.82629	50.8806
2	15.450	BB	0.4209	1421.86670	52.02248	49.1194

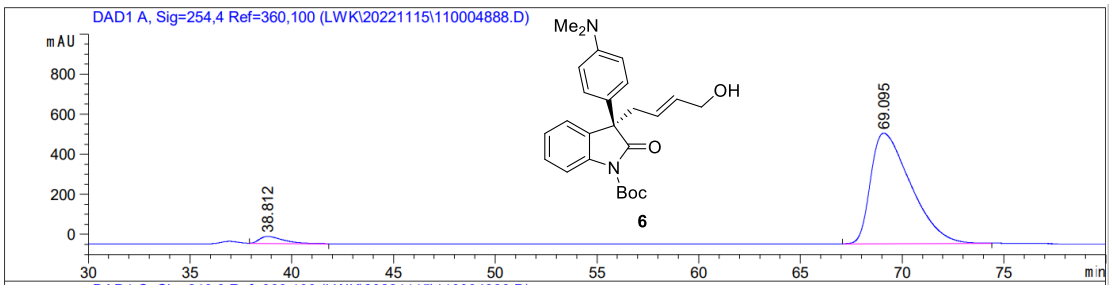


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.740	MM R	0.3455	172.91733	8.34221	1.7552
2	15.411	BB	0.4235	9678.58008	351.23306	98.2448

***tert*-Butyl (*R*, *E*)-3-(4-(dimethylamino)phenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (6)**

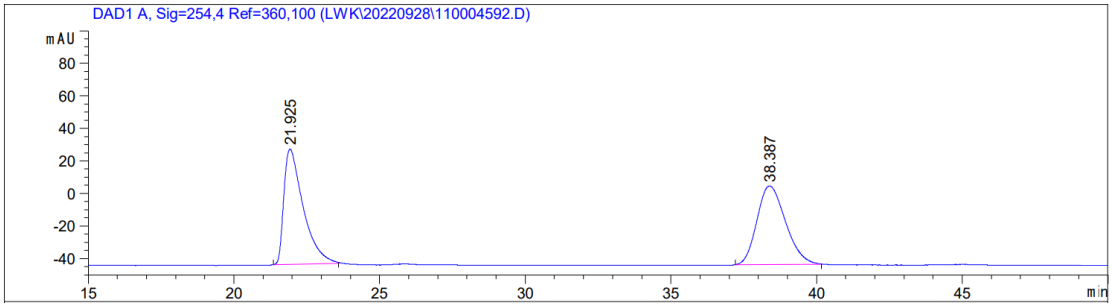


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.993	MM R	1.3071	5122.06641	65.30984	50.3548
2	66.091	BB	1.3978	5049.89209	42.75983	49.6452

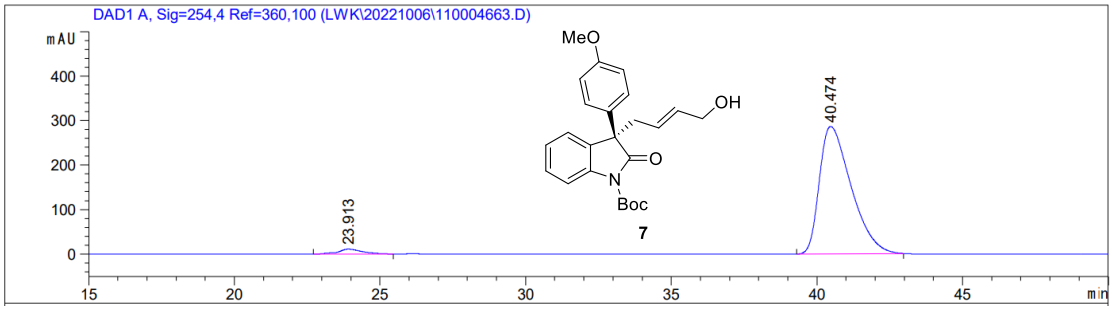


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.812	MM R	1.3840	2963.70679	35.68980	3.7736
2	69.095	BB	2.0381	7.55735e4	551.70789	96.2264

tert-Butyl (_R_, _E_)-3-(4-hydroxybut-2-en-1-yl)-3-(4-methoxyphenyl)-2-oxoindoline-1-carboxyl ate (7)

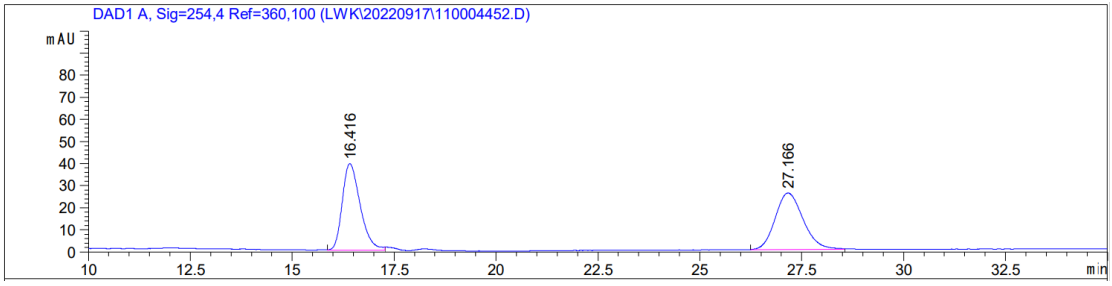


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.925	BB	0.6740	3268.88550	70.88786	49.6715
2	38.387	BB	0.9189	3312.12524	48.36847	50.3285

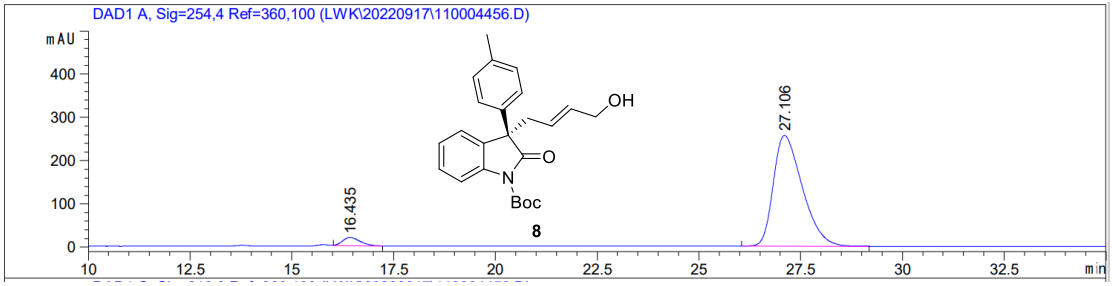


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.913	MM R	0.9764	655.69263	11.19182	2.9290
2	40.474	BB	1.1346	2.17308e4	286.58707	97.0710

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-(p-tolyl)indoline-1-carboxylate (8)**

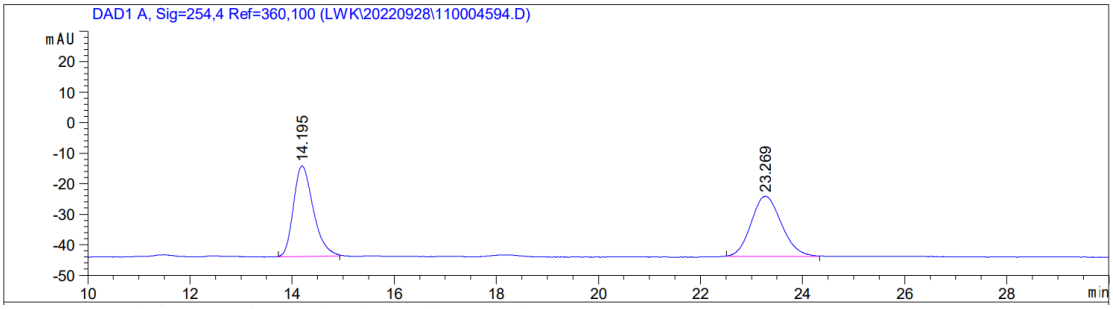


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.416	BB	0.4705	1197.18958	39.17538	49.5560
2	27.166	BB	0.7230	1218.64172	25.61898	50.4440

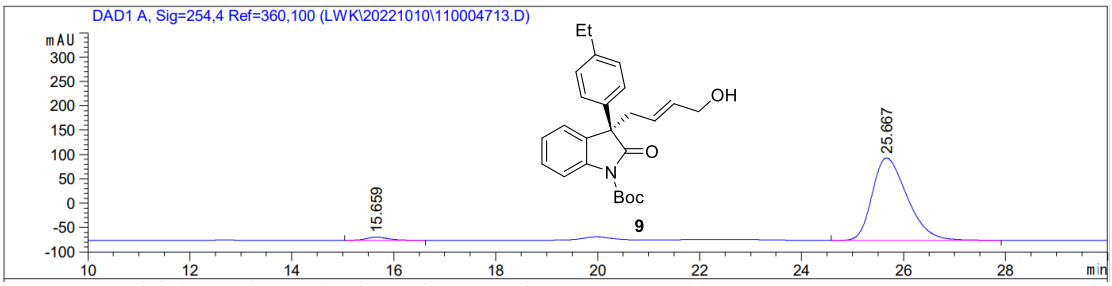


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.435	MM R	0.5015	563.34393	18.72179	4.2432
2	27.106	BB	0.7713	1.27131e4	256.04669	95.7568

***tert*-Butyl (*R*, *E*)-3-(4-ethylphenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (9)**

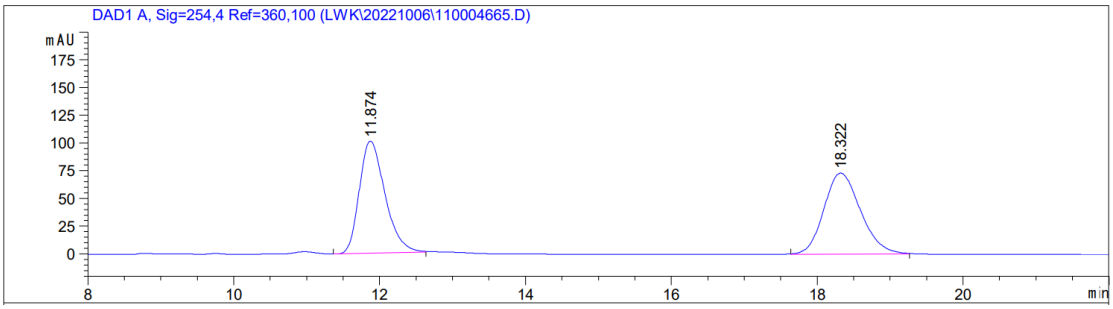


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.195	BB	0.4134	801.40765	29.64263	49.8467
2	23.269	BB	0.6231	806.33807	19.63576	50.1533

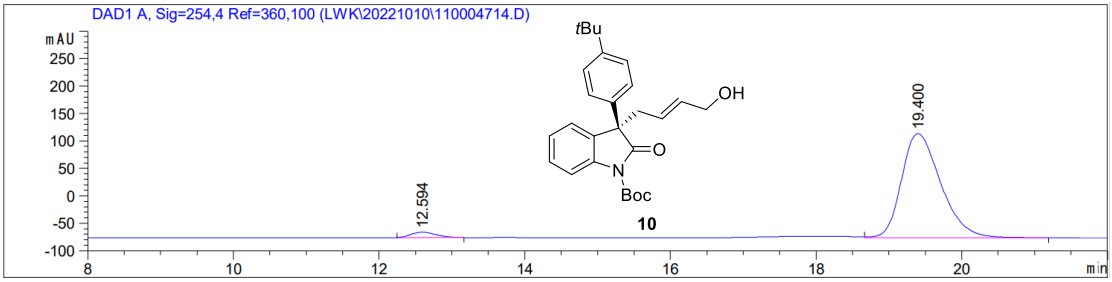


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.659	BB	0.4692	204.82936	6.68925	2.4759
2	25.667	VB	0.7397	8068.17969	169.37366	97.5241

tert-Butyl (_R_, _E_)-3-(4-(_tert_-butyl)phenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (10)

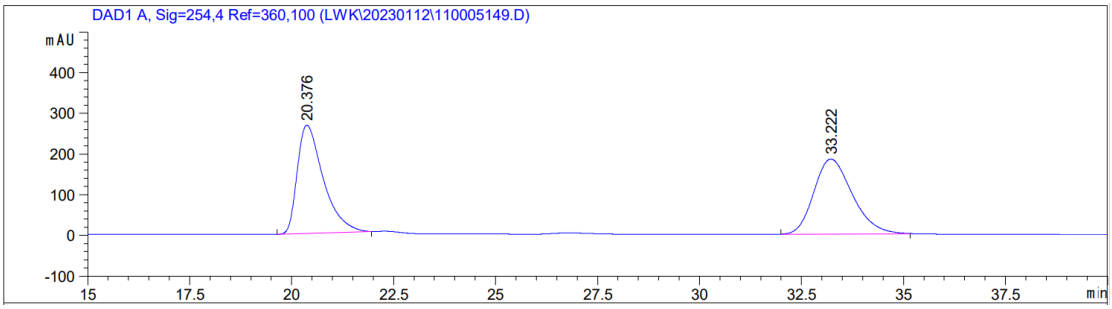


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.874	VB	0.3776	2474.49072	101.06794	49.2457
2	18.322	BB	0.5411	2550.29883	73.08298	50.7543

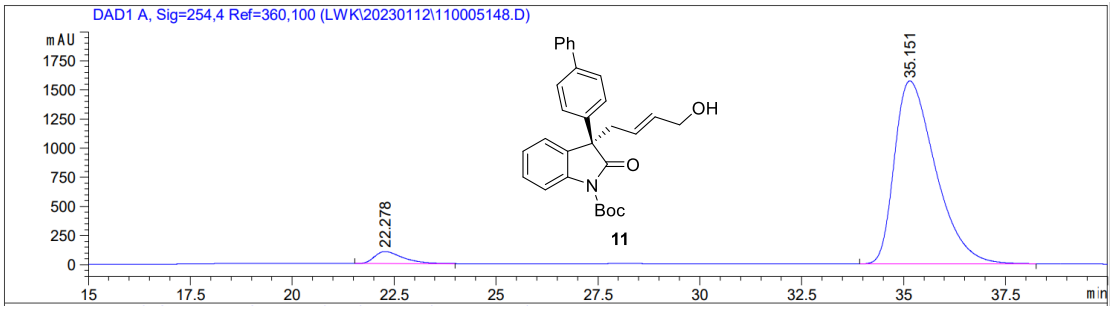


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.594	MM R	0.3977	234.43657	9.82387	3.1935
2	19.400	VB	0.5763	7106.68164	190.03984	96.8065

***tert*-Butyl (*R*, *E*)-3-([1,1'-biphenyl]-4-yl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (11)**

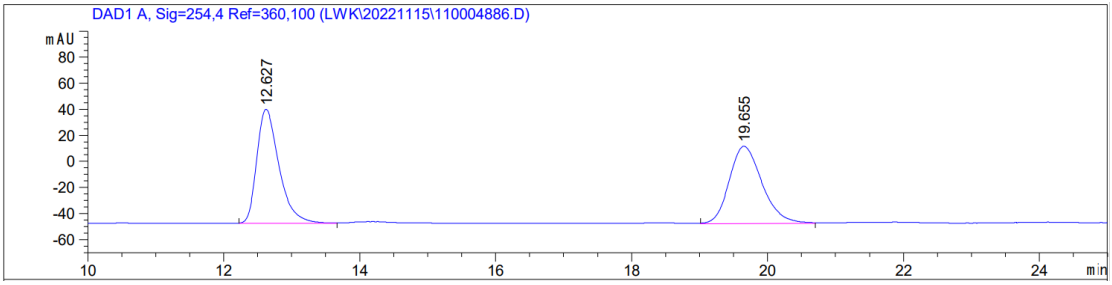


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.376	BB	0.6713	1.18087e4	266.32895	49.3622
2	33.222	BB	1.0042	1.21138e4	184.45320	50.6378

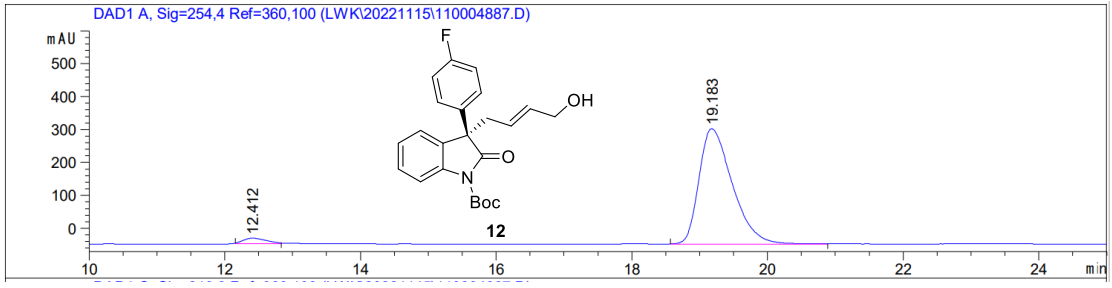


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.278	BB	0.7283	5040.01416	103.84022	4.3771
2	35.151	BB	1.0671	1.10106e5	1572.04419	95.6229

***tert*-Butyl (*R*, *E*)-3-(4-fluorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (12)**

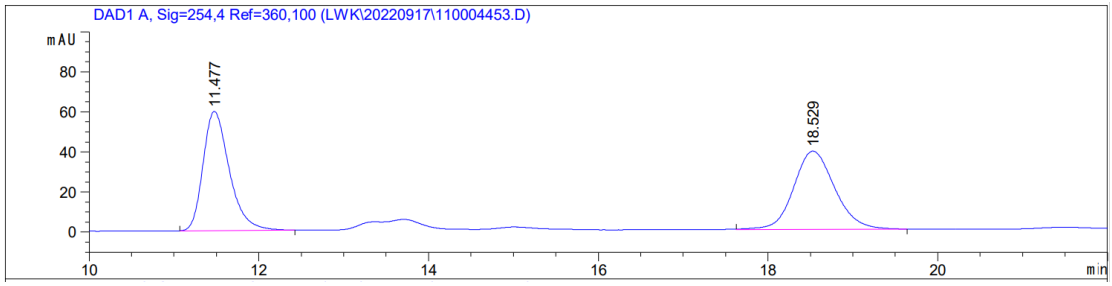


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.627	BV	0.3539	1994.52429	87.52332	50.0122
2	19.655	MM R	0.5586	1993.55408	59.48217	49.9878

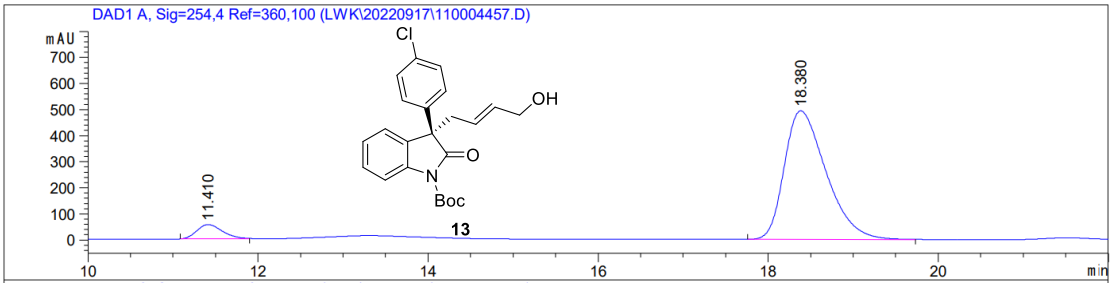


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.412	MM R	0.3989	414.87775	17.33274	3.3671
2	19.183	BB	0.5257	1.19067e4	349.32394	96.6329

***tert*-Butyl (*R*, *E*)-3-(4-chlorophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (13)**

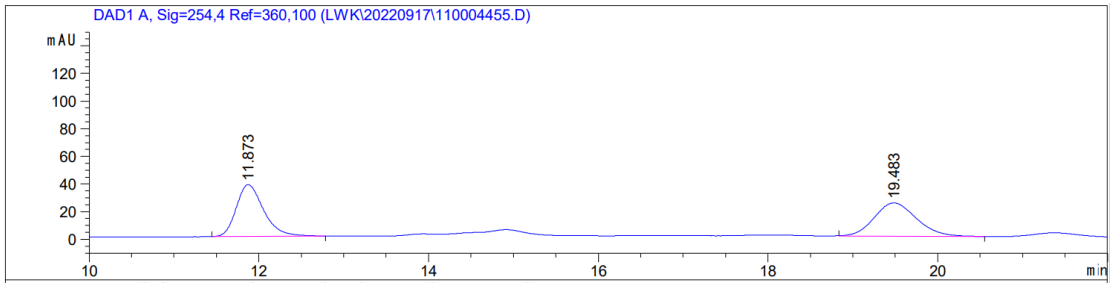


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.477	BB	0.3309	1280.63159	59.54227	49.2898
2	18.529	BB	0.5176	1317.53552	39.05719	50.7102

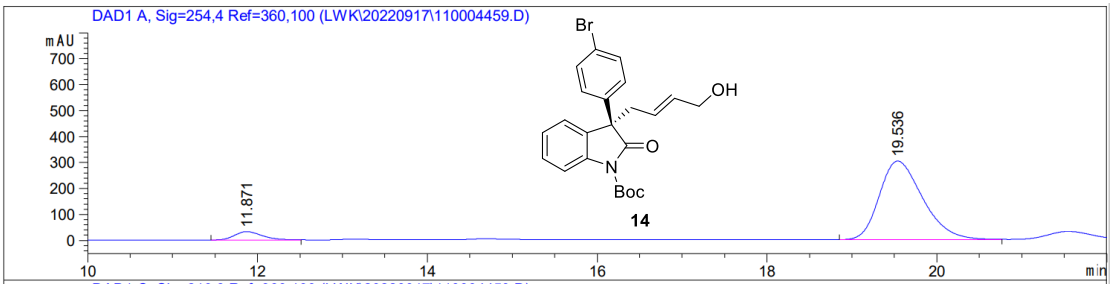


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.410	MM R	0.3535	1169.61768	55.14174	6.4993
2	18.380	BB	0.5242	1.68263e4	493.03995	93.5007

***tert*-Butyl (*R*, *E*)-3-(4-bromophenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (14)**

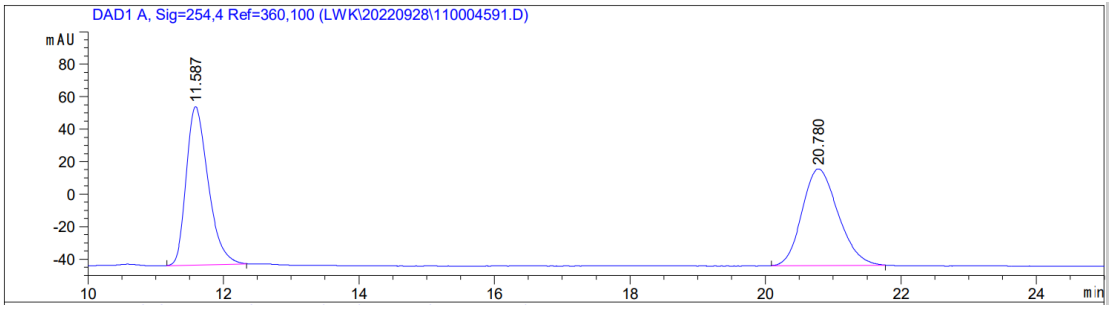


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.873	BB	0.3442	842.69434	37.49939	50.3521
2	19.483	BB	0.5272	830.90820	24.04439	49.6479

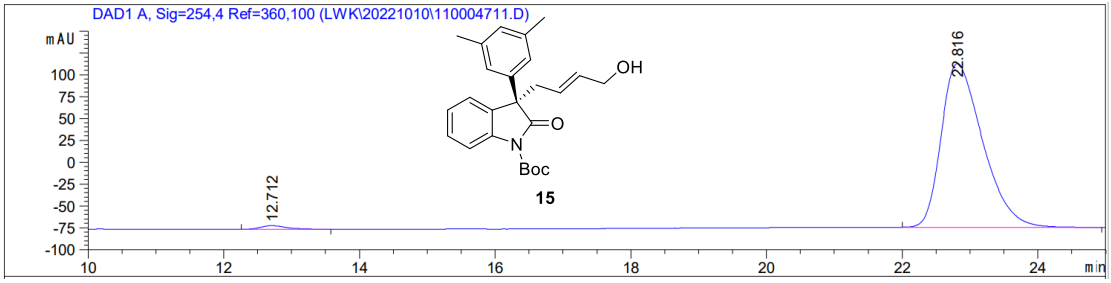


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.871	BB	0.3485	721.35590	32.05935	6.2863
2	19.536	BB	0.5441	1.07537e4	302.94357	93.7137

***tert*-Butyl (*R*, *E*)-3-(3,5-dimethylphenyl)-3-(4-hydroxybut-2-en-1-yl)-2-oxoindoline-1-carboxylate (15)**

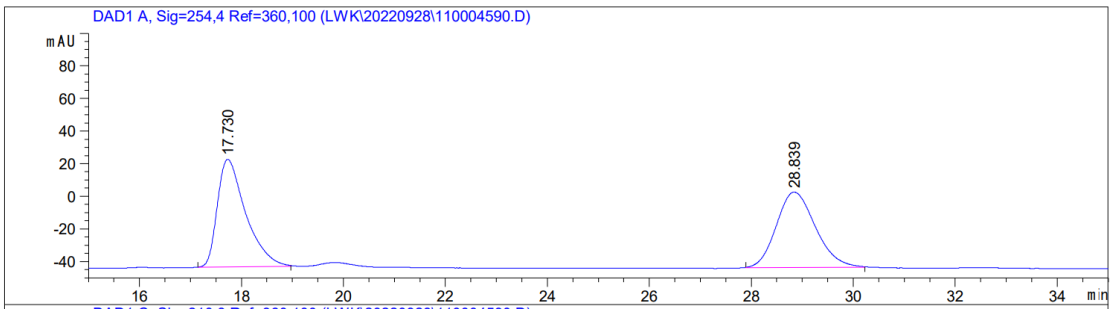


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.587	BB	0.3473	2202.50342	97.58189	49.9030
2	20.780	BB	0.5685	2211.06226	59.64873	50.0970

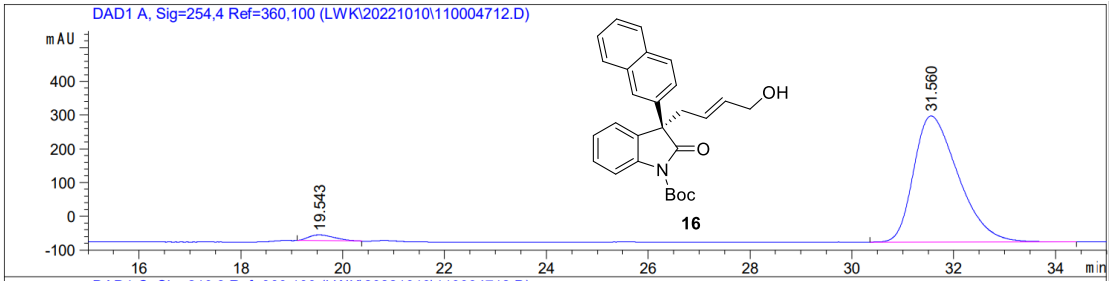


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.712	BB	0.4017	116.12218	4.26381	1.4352
2	22.816	BB	0.6523	7975.15186	187.49161	98.5648

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-3-(naphthalen-2-yl)-2-oxoindoline-1-carboxylate (16)**

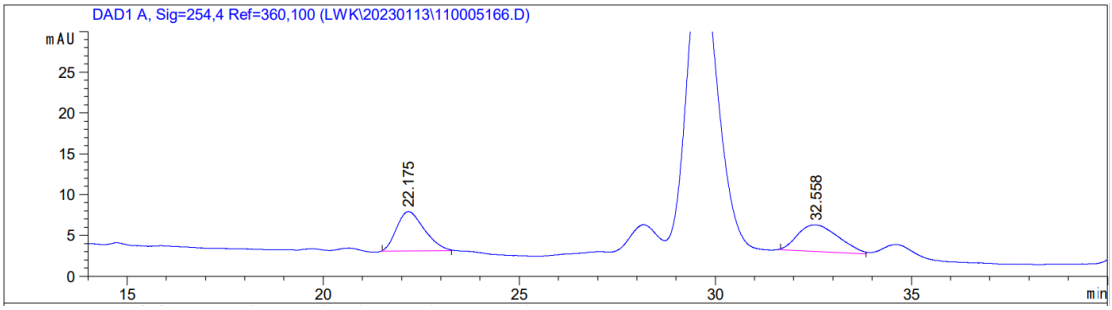


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.730	BB	0.5795	2547.16626	66.10419	50.7754
2	28.839	BB	0.7936	2469.36816	46.34451	49.2246

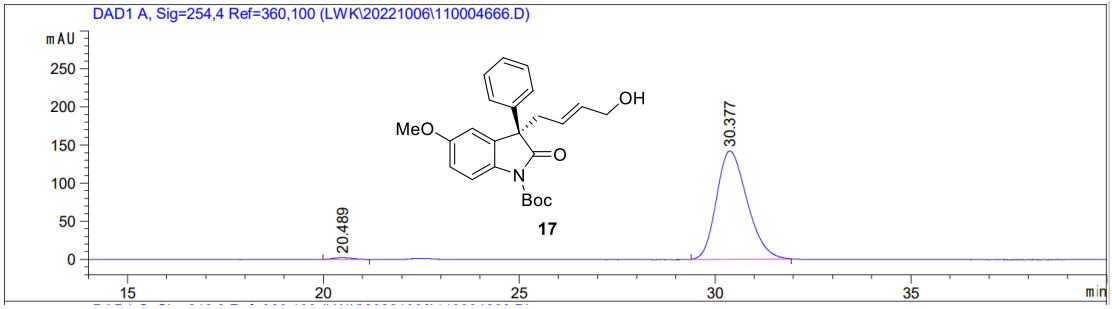


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.543	MM R	0.5780	580.93353	16.75029	2.4965
2	31.560	BB	0.9397	2.26887e4	374.03711	97.5035

tert-Butyl (_R_, _E_)-3-(4-hydroxybut-2-en-1-yl)-5-methoxy-2-oxo-3-phenylindoline-1-carboxylate (17)

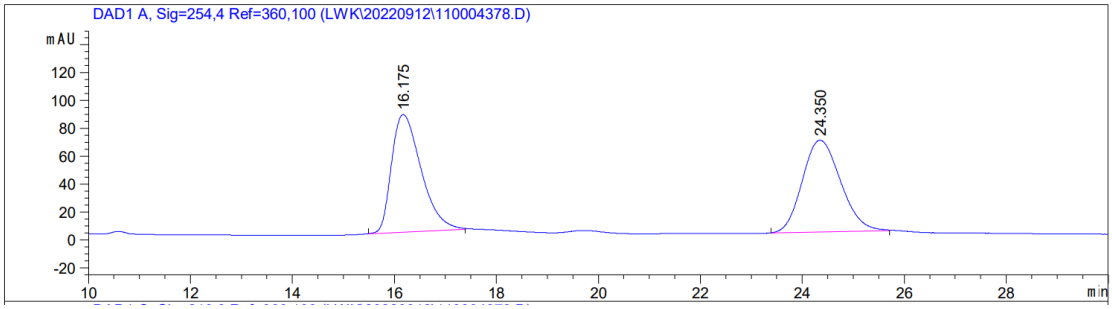


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.175	BB	0.6130	236.39684	4.81283	50.2273
2	32.558	MM R	1.2072	234.25708	3.23425	49.7727

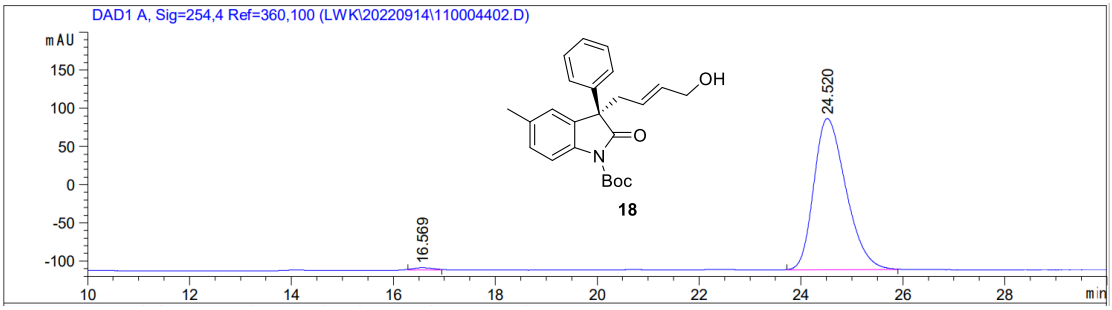


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.489	MM R	0.5530	70.14021	2.11398	0.8956
2	30.377	BB	0.8242	7761.71973	142.33061	99.1044

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (18)**

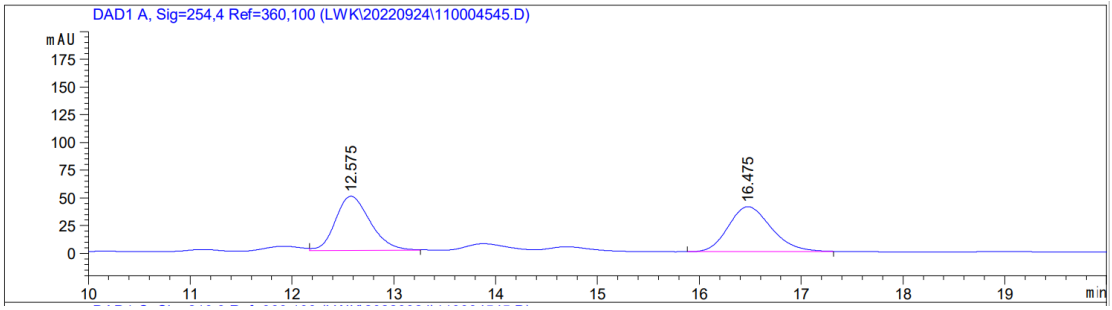


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.175	BB	0.6239	3402.19824	84.46485	49.7312
2	24.350	BB	0.7920	3438.97754	65.98479	50.2688

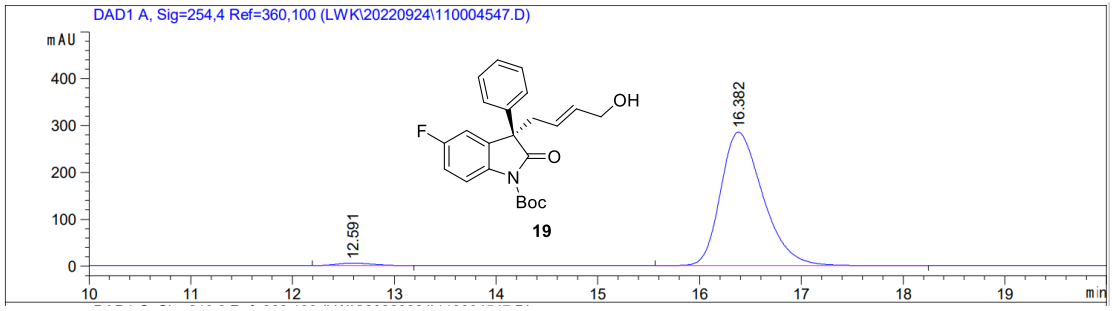


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.569	MM R	0.4539	81.96997	3.01003	0.9360
2	24.520	BB	0.6712	8675.39453	198.00359	99.0640

***tert*-Butyl (*R*, *E*)-5-fluoro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (19)**

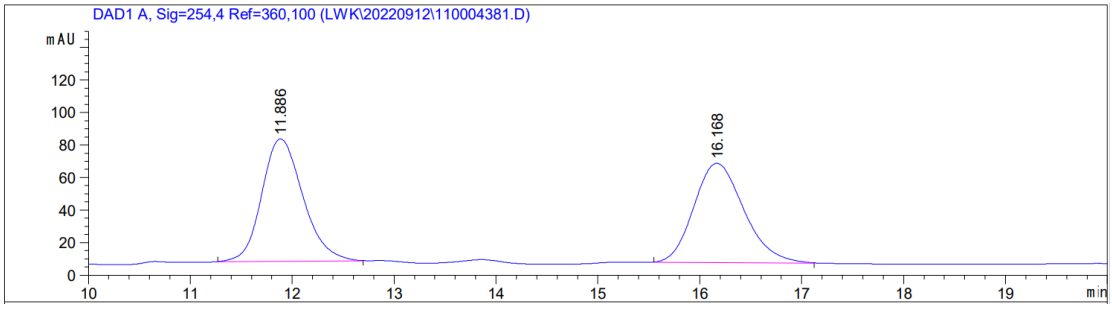


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.575	MM R	0.3931	1150.50757	48.77592	49.2228
2	16.475	MM R	0.4882	1186.83862	40.51813	50.7772

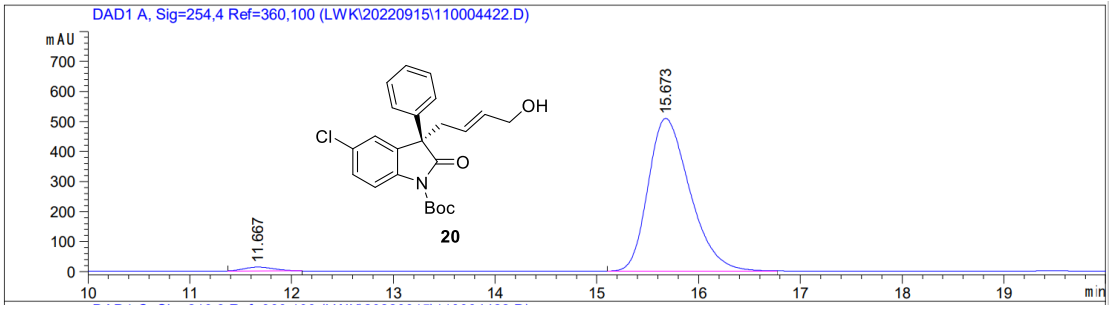


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.591	MM R	0.4503	153.42296	5.67835	1.8274
2	16.382	VB	0.4459	8242.42871	284.58130	98.1726

***tert*-Butyl (*R*, *E*)-5-chloro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (20)**

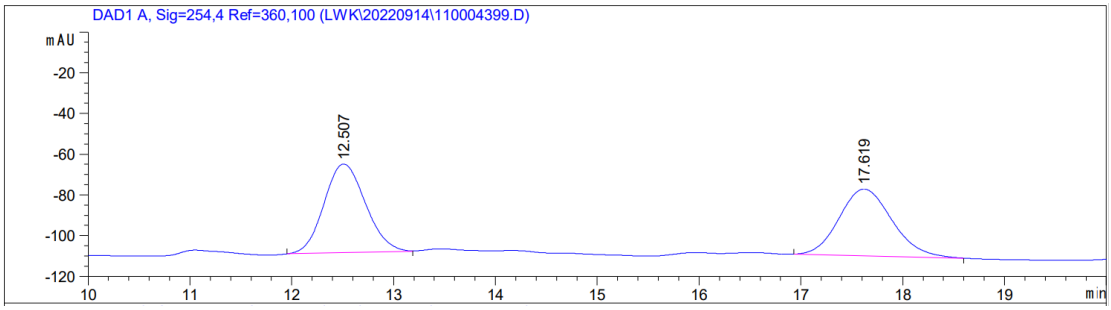


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.886	BB	0.4357	2120.04663	75.47655	50.2953
2	16.168	BB	0.5196	2095.15356	61.16976	49.7047

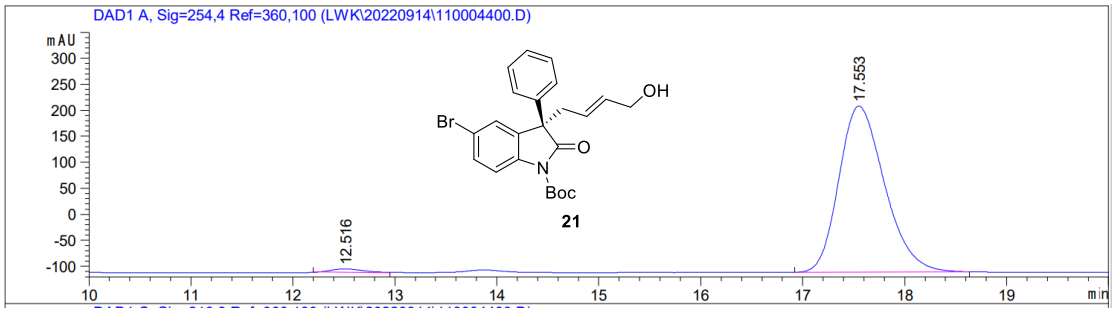


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.667	MM R	0.3377	259.18661	12.79217	1.7593
2	15.673	BB	0.4383	1.44732e4	508.11060	98.2407

***tert*-Butyl (*R, E*)-5-bromo-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (21)**

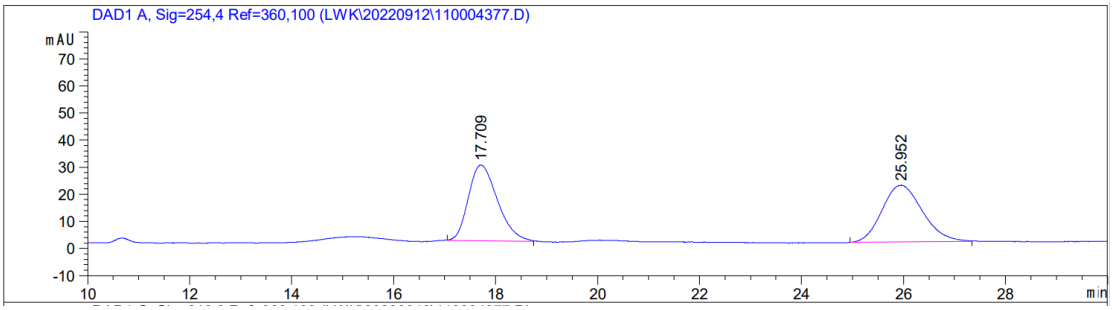


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.507	MM R	0.4713	1232.44763	43.57935	50.7614
2	17.619	BB	0.5697	1195.47559	32.92076	49.2386

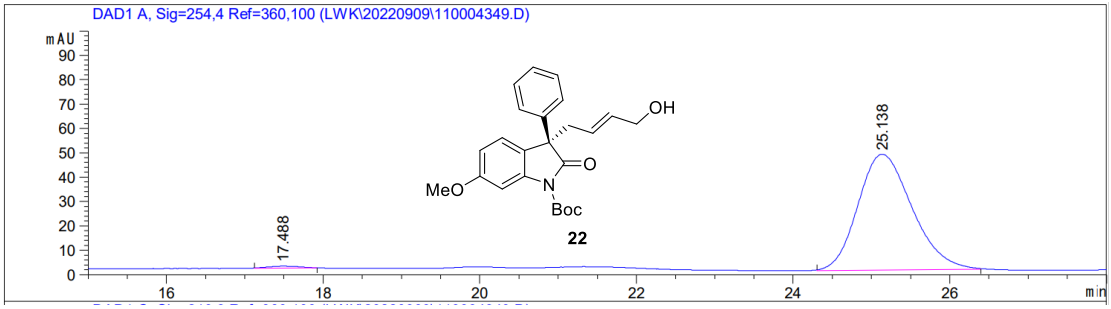


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.516	MM R	0.3741	145.03342	6.46160	1.4346
2	17.553	BB	0.4841	9964.30176	319.30762	98.5654

***tert*-Butyl (*R*, *E*)-3-(4-hydroxybut-2-en-1-yl)-6-methoxy-2-oxo-3-phenylindoline-1-carboxylate (22)**

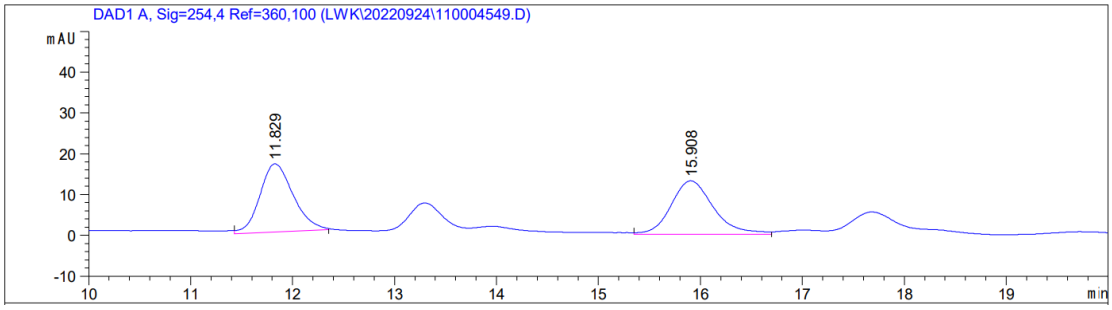


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.709	BB	0.6094	1109.43958	27.93438	49.1171
2	25.952	BB	0.7612	1149.32312	20.91083	50.8829

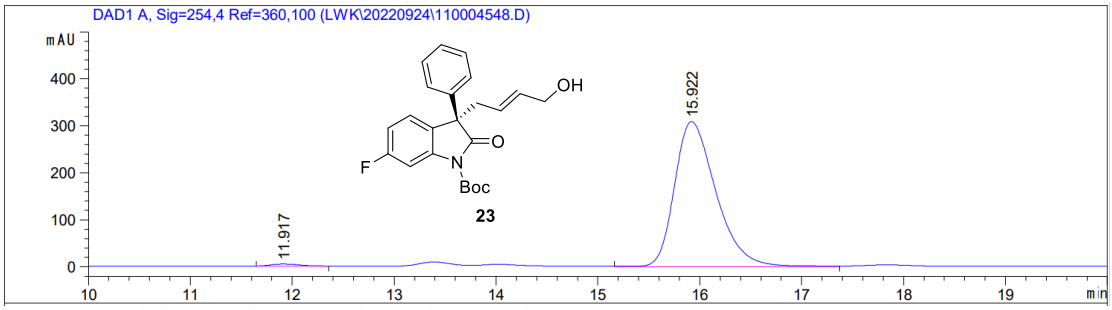


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.488	MM R	0.4628	22.18959	7.99058e-1	0.9645
2	25.138	BB	0.7200	2278.35889	47.46977	99.0355

***tert*-Butyl (*R*, *E*)-6-fluoro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (23)**

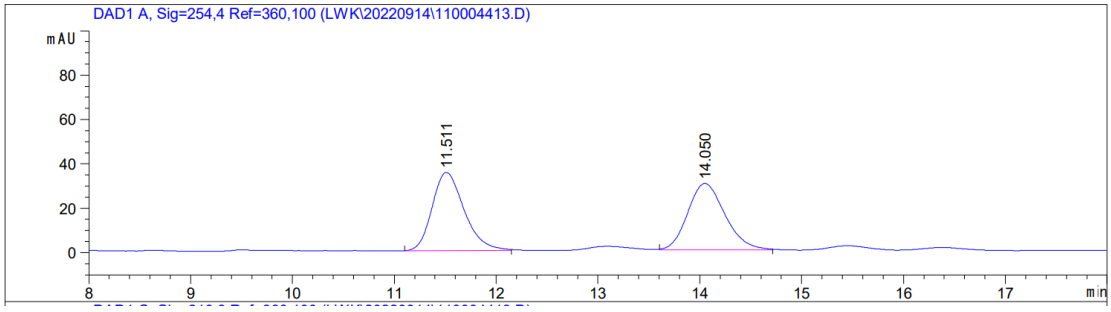


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.829	MM R	0.3776	377.84961	16.67560	49.8883
2	15.908	BV	0.4459	379.54111	13.10474	50.1117

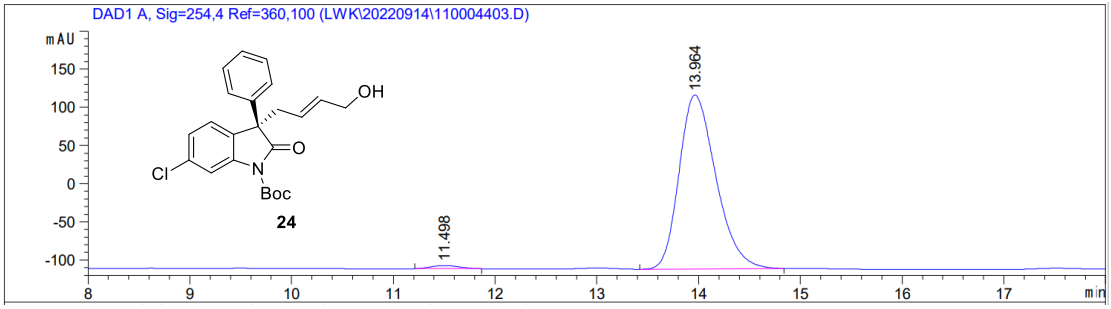


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.917	MM R	0.3587	98.57403	4.57992	1.1144
2	15.922	VV	0.4348	8746.79395	308.52325	98.8856

***tert*-Butyl (*R*, *E*)-6-chloro-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (24)**

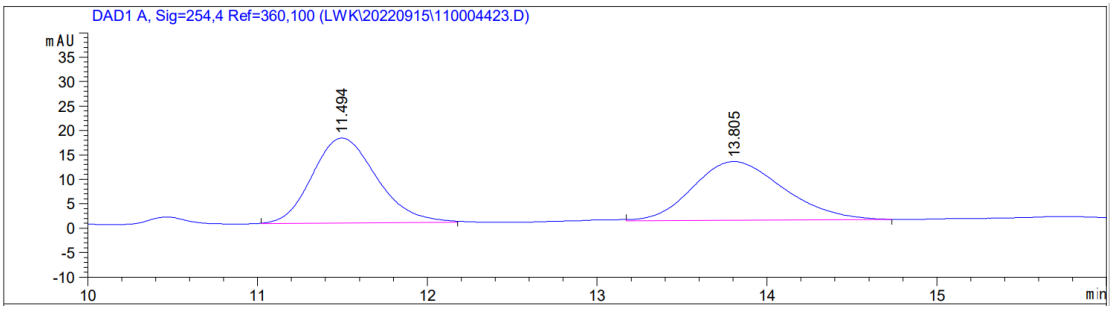


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.511	BB	0.3395	765.00372	35.20119	50.0446
2	14.050	BB	0.3890	763.64130	29.99889	49.9554

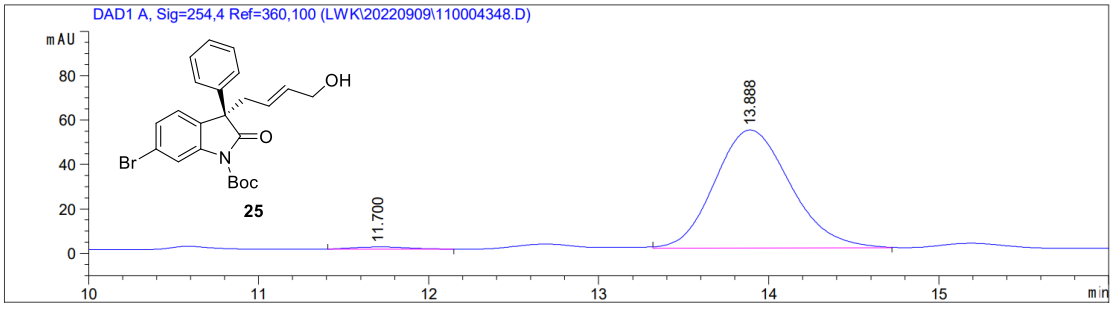


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.498	MM R	0.2932	69.51347	3.95159	1.1996
2	13.964	VB	0.3871	5725.16357	227.90720	98.8004

tert-Butyl (_R_, _E_)-6-bromo-3-(4-hydroxybut-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (25)

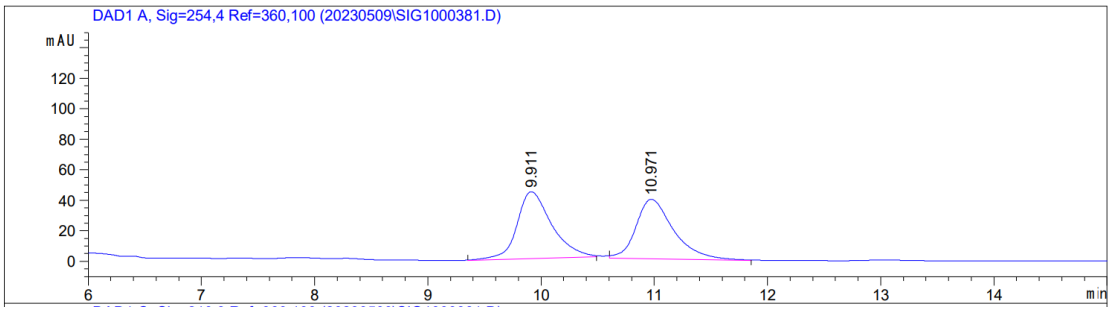


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.494	BB	0.4016	458.84186	17.40090	50.5119
2	13.805	MM R	0.6223	449.54120	12.03940	49.4881

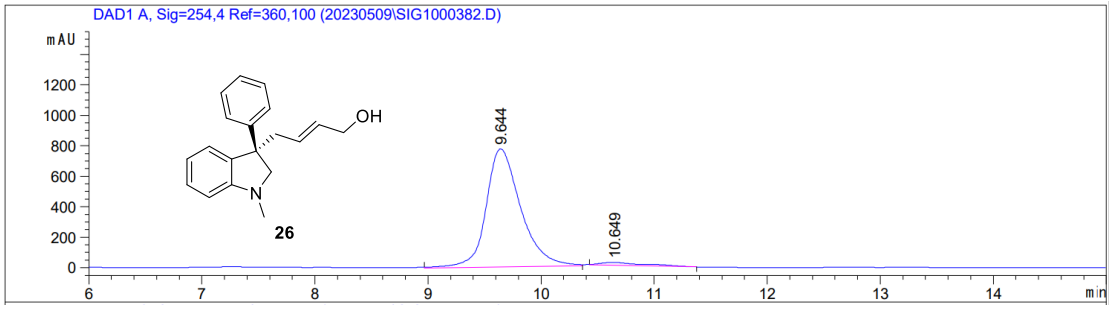


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.700	MM R	0.3826	23.07956	1.00526	1.3820
2	13.888	BB	0.4791	1646.87781	53.20132	98.6180

***(R, E)*-4-(1-Methyl-3-phenylindolin-3-yl)but-2-en-1-ol (26)**

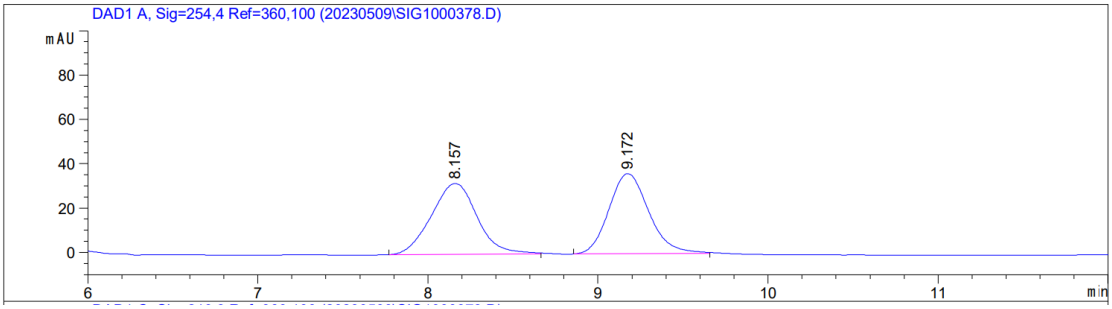


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.911	MM R	0.3551	932.39752	43.76265	50.7345
2	10.971	MM R	0.3868	905.40149	39.01663	49.2655

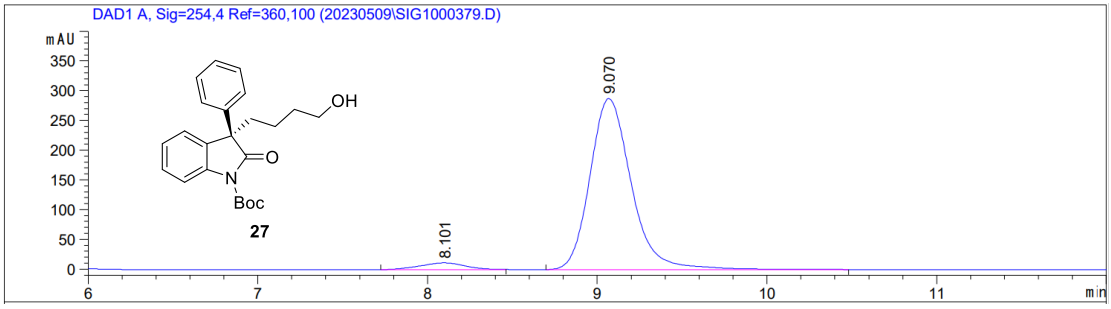


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.644	MM R	0.3559	1.65594e4	775.51672	96.8637
2	10.649	MM R	0.4607	536.17450	19.39591	3.1363

***tert*-Butyl (*R*)-3-(4-hydroxybutyl)-2-oxo-3-phenylindoline-1-carboxylate (27)**

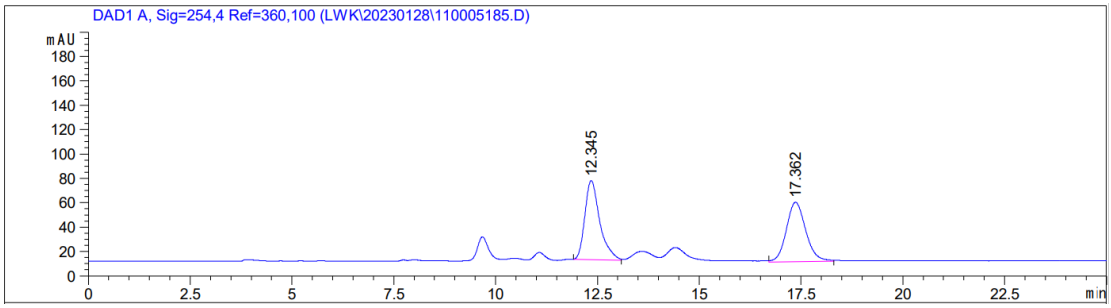


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.157	BB	0.2854	602.98523	32.06502	50.4985
2	9.172	BB	0.2527	591.07928	36.17029	49.5015

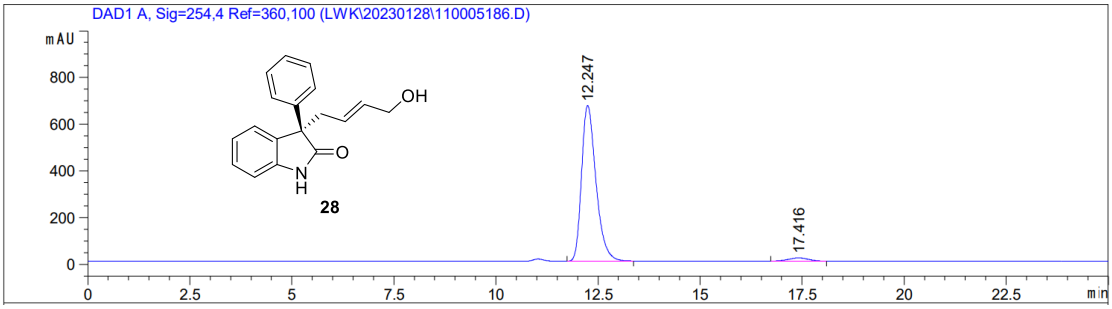


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.101	MM R	0.3039	202.93930	11.13076	3.9806
2	9.070	MM R	0.2836	4895.25830	287.72177	96.0194

***(R, E)*-3-(4-Hydroxybut-2-en-1-yl)-3-phenylindolin-2-one (28)**

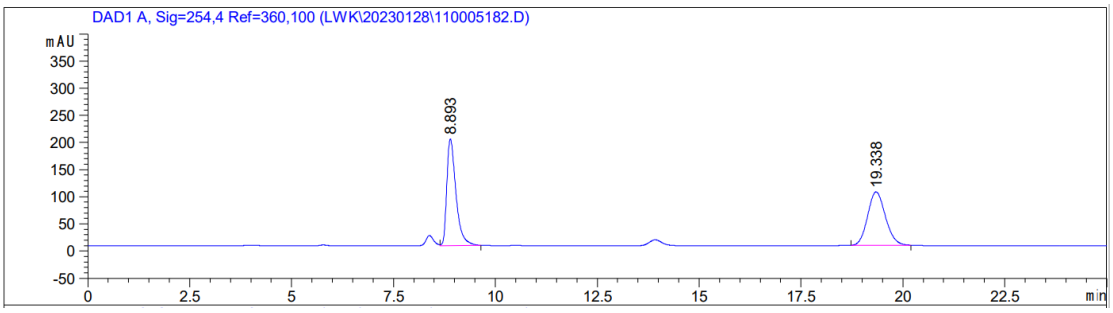


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.345	MM R	0.4245	1653.14612	64.90147	50.4570
2	17.362	MM R	0.5539	1623.19788	48.83967	49.5430

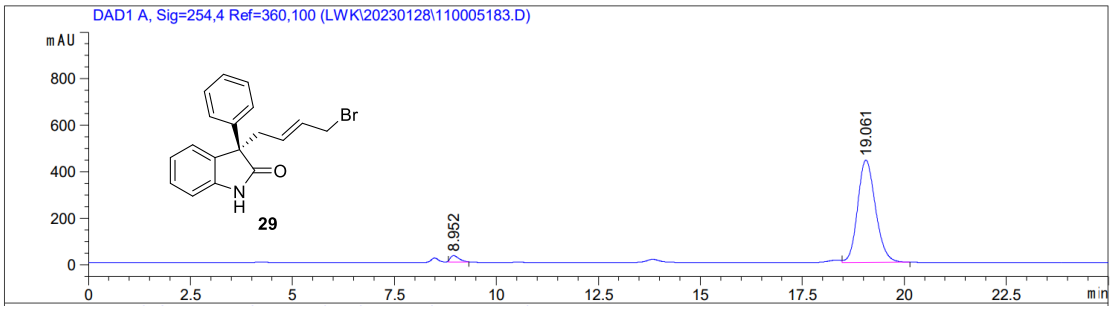


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.247	BB	0.3764	1.63843e4	667.46289	97.2138
2	17.416	MM R	0.5666	469.58798	13.81413	2.7862

***(R, E)*-3-(4-Bromobut-2-en-1-yl)-3-phenylindolin-2-one (29)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.893	VB	0.2376	3055.99121	196.29881	50.4884
2	19.338	BB	0.4685	2996.86157	98.61857	49.5116



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.952	MM R	0.2466	408.32028	27.59982	2.9560
2	19.061	VB	0.4711	1.34048e4	440.37579	97.0440

9. References

[1] J.-T. Xia and X.-P. Hu, Copper-Catalyzed Asymmetric Propargylic Alkylation with Oxindoles: Diastereo- and Enantioselective Construction of Vicinal Tertiary and All-Carbon Quaternary Stereocenters, *Org. Lett*. 2020, **22**, 1102.

[2] S.-W. Duan, J. An, J.-R. Chen and W.-J. Xiao, Facile Synthesis of Enantioenriched C^{γ}-Tetrasubstituted α-Amino Acid Derivatives via an Asymmetric Nucleophilic Addition/Protonation Cascade, *Org. Lett*. 2011, **13**, 2290.