

Supporting Information

Box-Copper Catalyzed Cascade Asymmetric Amidation for Chiral *exo*-Methylene Aminoindoline Derivatives

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1. General methods and materials

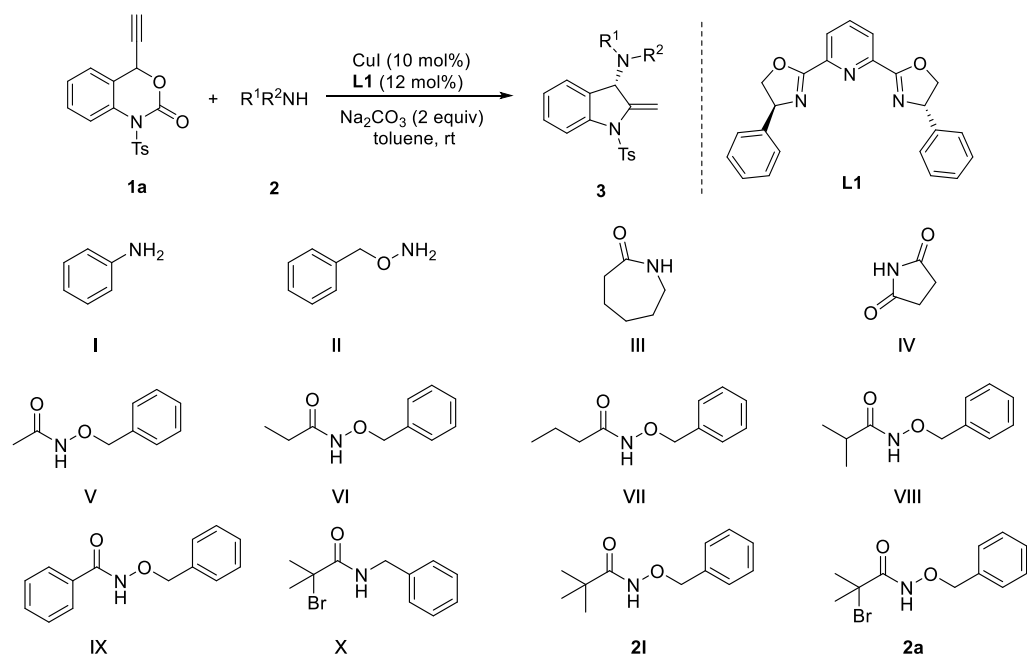
Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen in oven-dried glasswares with magnetic stirring. All reagents obtained from commercial suppliers were used without further purification. Some commonly used solvents for asymmetric catalysis were dried with different drying agents through standard methods reported, including of toluene, methylene chloride (DCM), tetrahydrofuran (THF) as well as fluorobenzene. All other reaction media were used as obtained unless otherwise noted. Flash Chromatography was performed with silica gel (300–400 mesh) from Yantai Chemical Industry Research Institute, P. R. China. Analytical thin-layer chromatography (TLC) was performed with 0.2 ± 0.03 mm coated commercial silica gel plates (GF-254, particle size 0.04–0.05 mm). The ¹H and ¹³C NMR spectra were recorded in CDCl₃ on Varian Inova (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard (CDCl₃, δ 7.26 ppm for proton NMR, δ 77.10 ppm for carbon NMR). The ¹H NMR data were reported as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, td = triplet of doublets, dt = doublet of triplets, dd = doublet of doublets), coupling constants (*J*) and assignment. The data for ¹³C 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 Micromass GCT-TOF mass spectrometer with ESI resource. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using CHIRALCEL IA-H column. The X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractometer. Optical rotations were reported as follows: $[\alpha]_D^{20}$ (c in g per 100 mL, solvent).

2. Preparation of ethynyl benzoxazinones and α -halohydroxamates

The substrates **1** were prepared according to the reported procedures¹. The substrates **2** were synthesized according to the literatures².

3. Optimization of reaction conditions

Table S1 Screening of amine and amide substrates^a

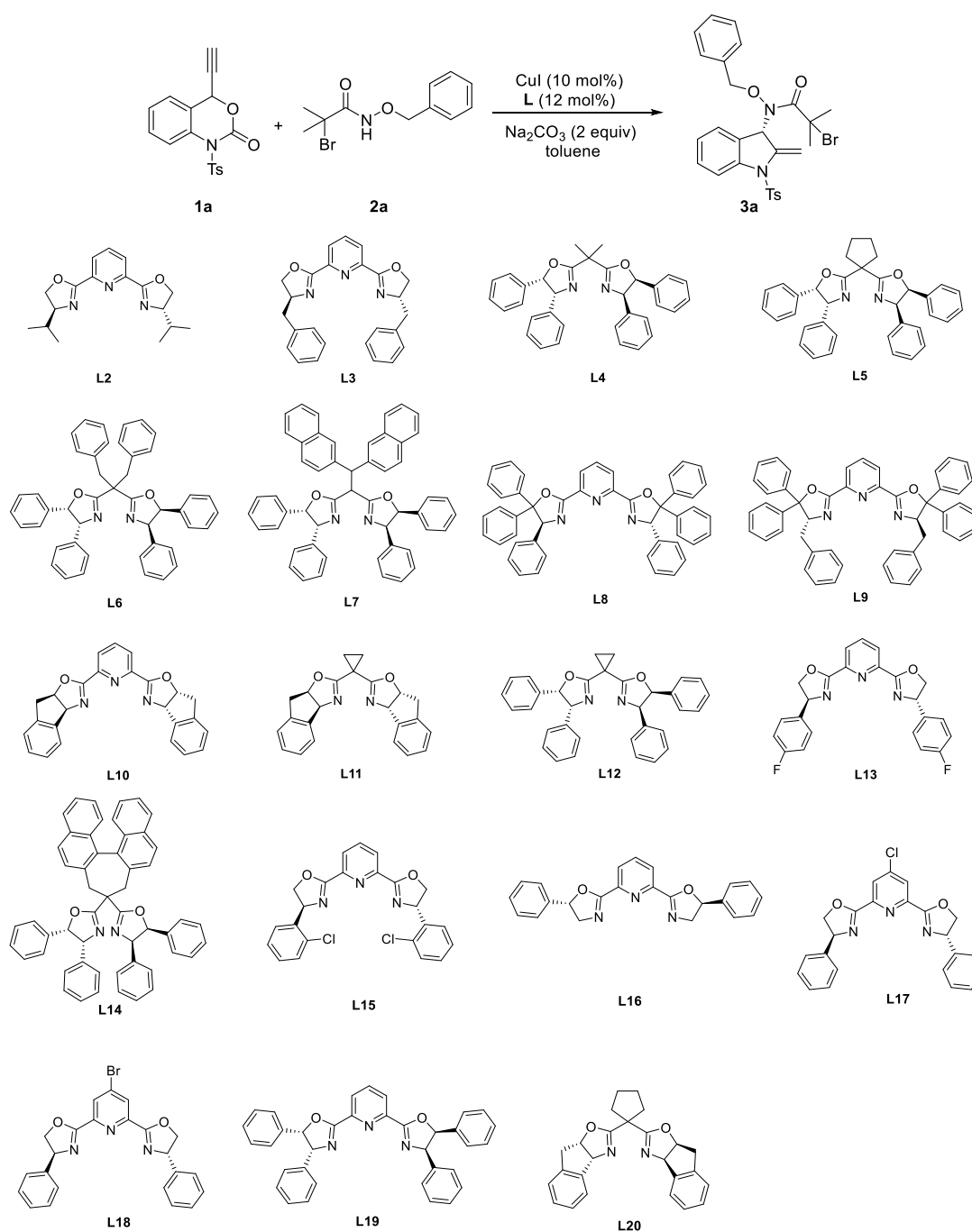


entry	R ¹ R ² NH	t (h)	yield (%) ^b	ee (%) ^c
1	I	14	69	0
2	II	14	73	0
3	III	14	72	0
4	IV	14	60	0
5	V	14	70	4
6	VI	14	58	23
7	VII	14	--	--
8	VIII	14	56	0
9	IX	14	60	0
10	X	14	--	--

11	2l	14	38	45
12	2a	14	52	50

^a Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mol, 2.0 equiv), CuI (0.01 mmol, 10 mol %), **L1** (0.012 mmol, 12 mol %), Na₂CO₃ (0.2 mmol, 2.0 equiv), toluene (2 mL), 25 °C, 14 h. ^b Isolated yield. ^c Determined by HPLC.

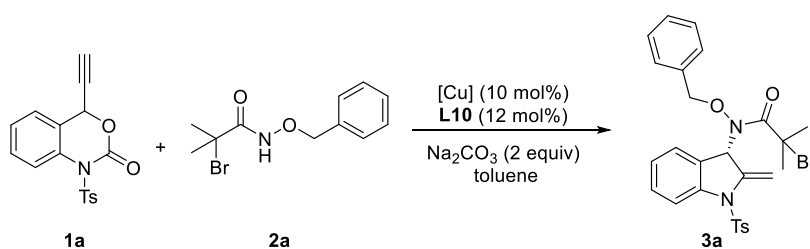
Table S2 Screening of chiral ligands ^a



entry	ligand	yield (%) ^b	ee (%) ^c
1	L2	43	29
2	L3	47	46
3	L4	38	30
4	L5	29	20
5	L6	trace	N.D.
6	L7	31	14
7	L8	44	42
8	L9	52	<i>ent</i> -60
9	L10	62	77
10	L11	54	50
11	L12	31	14
12	L13	43	20
13	L14	trace	N.D.
14	L15	30	37
15	L16	trace	N.D.
16	L17	trace	N.D.
17	L18	32	37
18	L19	trace	N.D.
19	L20	51	<i>ent</i> -42

^a Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mol, 2.0 equiv), CuI (0.01 mmol, 10 mol %), **L** (0.012 mmol, 12 mol %), Na₂CO₃ (0.2 mmol, 2.0 equiv), toluene (2 mL), 25 °C, 14 h. ^b Isolated yield. ^c Determined by HPLC.

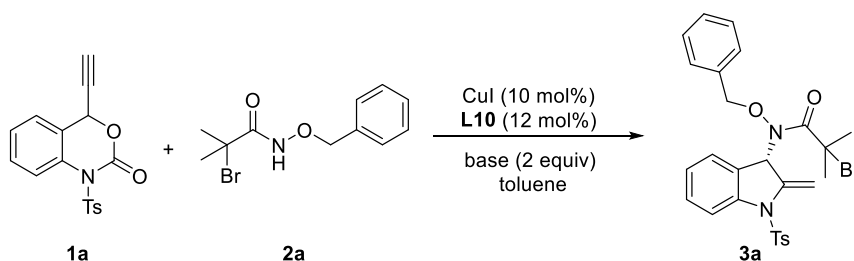
Table S3 Screening of metal salts ^a



entry	metal	yield (%) ^b	ee (%) ^c
1	CuCl	50	72
2	CuBr	52	76
3	CuCN	41	66
4	CuSCN	45	70
5	Cu(CH ₃ CN) ₄ PF ₆	51	72
6	Cu(CH ₃ CN) ₄ BF ₄	52	76
7	Cu(CH ₃ COO) ₂	30	71
8	Cu(OTf) ₂	40	36
9	Cu(acac) ₂	45	74
10	Zn(OTf) ₂	-	-

^a Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mol, 2.0 equiv), metal (0.01 mmol, 10 mol %), **L10** (0.012 mmol, 12 mol %), Na₂CO₃ (0.2 mmol, 2.0 equiv) in toluene (2 mL) at 25 °C for 14 h. ^b Isolated yield. ^c Determined by HPLC.

Table S4 Screening of bases^a

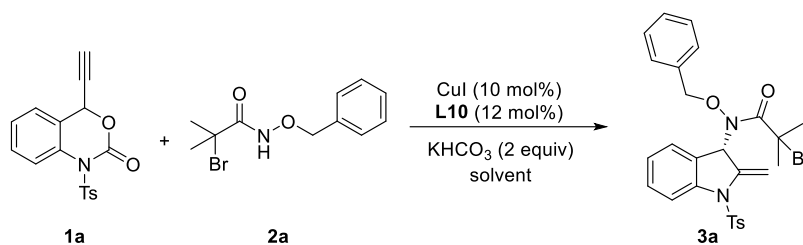


entry	base	yield (%) ^b	ee (%) ^c
1	K ₂ CO ₃	43	62
2	Cs ₂ CO ₃	32	78
3	NaHCO ₃	45	80
4	KHCO ₃	63	90
5	Na ₂ HPO ₄	45	76
6	DIPEA	48	76
7	Et ₃ N	28	50

8	DBU	-	-
9	DMAP	-	-
10 ^d	KHCO ₃	54	90
11 ^e	KHCO ₃	38	90

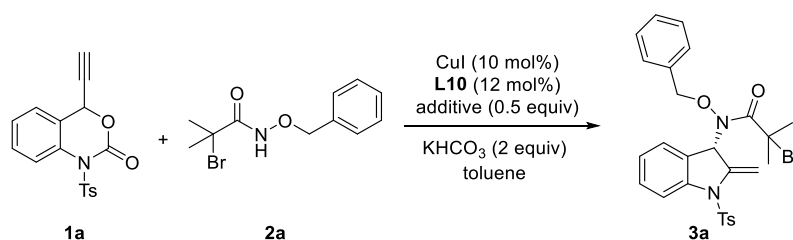
^a Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mol, 2.0 equiv), CuI (0.01 mmol, 10 mol %), **L10** (0.012 mmol, 12 mol %), base (2 equiv) in toluene (2 mL) at 25°C for 14 h. ^b Isolated yield. ^c Determined by HPLC analysis. ^d 3.0 equiv of KHCO₃ was used. ^e 1.0 equiv of KHCO₃ was used.

Table S5 Screening of solvents and reaction temperature ^a



entry	solvent	T (°C)	yield (%) ^b	ee (%) ^c
1	DCM	25	-	-
2	THF	25	-	-
3	CH ₃ CN	25	47	54
4	Acetone	25	57	36
5	m-Xylene	25	55	77
6	p-Xylene	25	59	82
7	Fluorobenzene	25	49	72
8	Toluene	40	63	82
9	Toluene	10	33	90

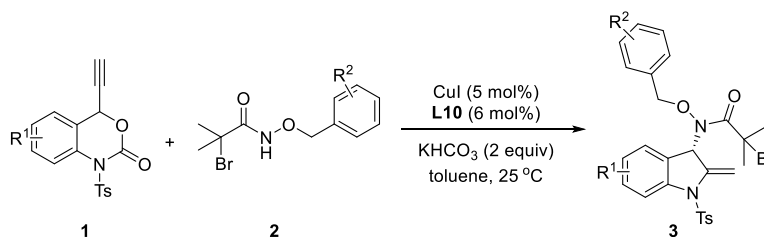
^a Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mol, 2.0 equiv), CuI (0.01 mmol, 10 mol %), **L10** (0.012 mmol, 12 mol %), KHCO₃ (2 equiv) in solvent (2 mL) at 25°C for 14 h. ^b Isolated yield. ^c Determined by HPLC analysis.

Table S6 Screening of additives ^a

entry	additive	yield (%) ^b	ee (%) ^c
1	TBAB	trace	--
2	AgSbF ₆	trace	--
3	KBF ₄	trace	--
4	KOAc	45	80
5	NaHPO ₄	39	75
6	3 Å MS	trace	--
7	4 Å MS	43	78
8	5 Å MS	trace	--
9 ^d	--	62	80
10 ^e	--	70	90
11 ^f	--	47	88

^a Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mol, 2.0 equiv), CuI (0.01 mmol, 10 mol %), **L10** (0.012 mmol, 12 mol %), K₂CO₃ (2 equiv), additive (0.5 equiv) in toluene (2 mL) at 25°C for 14 h. ^b Isolated yield. ^c Determined by HPLC analysis. ^d 24h. ^e CuI (5 mol%), **L10** (6 mol%) was added. ^f CuI (2.5 mol%), **L10** (3 mol%) was added.

4. General procedure for preparation of **3**

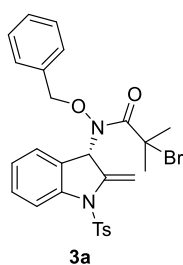


To an oven-dried schlenk tube, CuI (1.0 mg, 0.005 mmol, 5 mol%) and **L10** (2.4 mg, 0.006 mmol, 6 mol%) in dry toluene (2.0 mL) were added under a nitrogen atmosphere. The resulting

mixture was stirred at room temperature for 0.5 hours. Then the substrates **1** (0.1 mmol, 1.0 equiv) and **2** (0.2 mmol, 2.0 equiv) was introduced into the vessel. The mixture was stirred for 12 – 20 hours at 25 °C (monitored by TLC analysis) and then it was subjected to silica gel column to afford the desired products **3**.

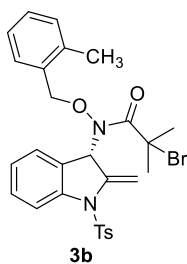
5. Characterization data of products **3**

(*S*)-*N*-(Benzyloxy)-2-bromo-2-methyl-*N*-(2-methylene-1-tosylindolin-3-yl)propanamide (**3a**)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 70% yield (38.8 mg), 90% *ee*, [Daicel Chiralcel IA-H, hexanes/*i*-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254.4 nm, *t* (major) = 8.105, *t* (minor) = 10.382]; $[\alpha]_D^{20}$ = +42.4 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 8.4 Hz, 1H), 7.21 (td, *J* = 8.6, 8.0, 6.4 Hz, 4H), 7.16 – 7.10 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.83 – 6.75 (m, 2H), 6.37 (s, 1H), 5.83 (t, *J* = 2.4 Hz, 1H), 5.05 (t, *J* = 2.4 Hz, 1H), 4.60 (d, *J* = 9.2 Hz, 1H), 4.29 (s, 1H), 2.18 (s, 3H), 1.94 (d, *J* = 8.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 144.9, 144.6, 142.3, 133.9, 133.6, 130.0, 129.6, 129.1, 128.6, 128.3, 127.2, 125.9, 125.5, 124.6, 115.8, 98.4, 62.0, 55.7, 32.0, 31.0, 21.5; IR (KBr) ν_{\max} : 3054, 2854, 1653, 1475, 1359, 1170, 1030, 752, 658, 571. HRMS (ESI): *m/z* = 577.0769 (calcd for C₂₇H₂₇BrN₂O₄S+Na⁺ = 577.0767).

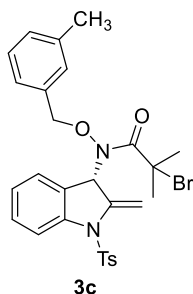
(*S*)-2-Bromo-2-methyl-*N*-((2-methylbenzyl)oxy)-*N*-(2-methylene-1-tosylindolin-3-yl)propanamide (**3b**)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; white oil; 59% yield (33.5 mg), 95% *ee* [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, λ = 254 nm, *t* (major) = 9.74 min, *t* (minor) = 12.93 min]; $[\alpha]_D^{20}$ = +38.5 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.13 (q, *J* = 7.2 Hz, 2H), 7.04 (dd, *J* = 16.0, 7.6 Hz, 5H), 6.44 (s, 1H), 5.85 (d, *J* = 2.8 Hz, 1H), 5.05 (q, *J* = 2.0 Hz, 1H), 4.54 (d, *J* = 52.8 Hz, 2H), 2.16 (s, 3H), 1.94 (s, 6H), 1.75 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 144.9, 144.7, 142.3, 137.9, 134.0, 133.5, 130., 129.9, 129.5, 129.4, 128.1, 127.2, 126.1, 124.6, 115.8, 98.3, 55.7, 53.5, 32.0, 31.0, 21.4, 21.2; IR (KBr) ν_{\max} : 2965, 2858, 1652, 1492, 1360, 1261, 1171, 1033, 946, 870, 748, 658,

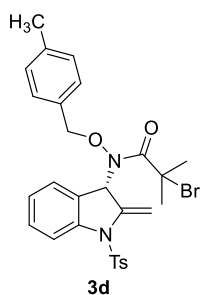
570. HRMS (ESI): $m/z = 591.0924$ (calcd for $C_{28}H_{29}BrN_2O_4S+Na^+ = 591.0924$).

(S)-2-Bromo-2-methyl-N-((3-methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3c)



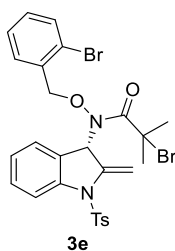
Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 66% yield (37.4 mg). 96% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.42 min, t (minor) = 12.37 min]; $[\alpha]_D^{20} = +67.3$ (c 0.1, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.22 (d, $J = 7.6$ Hz, 1H), 7.18 – 7.02 (m, 5H), 6.63 (d, $J = 7.2$ Hz, 1H), 6.51 (s, 1H), 6.36 (s, 1H), 5.83 (d, $J = 2.4$ Hz, 1H), 5.06 (d, $J = 2.4$ Hz, 1H), 4.59 (d, $J = 9.2$ Hz, 1H), 4.28 (s, 1H), 2.24 (s, 3H), 2.19 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 144.9, 144.7, 142.4, 137.9, 134.0, 133.5, 130.0, 129.9, 129.5, 129.4, 128.1, 127.2, 126.1, 126.0, 125.6, 124.6, 115.8, 98.3, 77.0, 62.1, 55.7, 32.0, 31.1, 21.5, 21.3; IR (KBr) ν_{max} : 2951, 2837, 1653, 1599, 1476, 1361, 1260, 1172, 1032, 803, 749, 659, 571. HRMS (ESI): $m/z = 591.0964$ (calcd for $C_{28}H_{29}BrN_2O_4S+Na^+ = 591.0924$).

(S)-2-Bromo-2-methyl-N-((4-methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3d)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 70% yield (39.8 mg), 93% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 10.26 min, t (minor) = 13.11 min]; $[\alpha]_D^{20} = +56.3$ (c 0.1, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J = 8.4$ Hz, 1H), 7.73 – 7.62 (m, 2H), 7.43 (ddt, $J = 8.4, 7.2, 1.2$ Hz, 1H), 7.23 (dt, $J = 7.6, 1.6$ Hz, 1H), 7.15 (td, $J = 7.6, 1.0$ Hz, 1H), 7.06 (dd, $J = 23.2, 8.0$ Hz, 4H), 6.71 (d, $J = 7.6$ Hz, 2H), 6.37 (s, 1H), 5.85 (t, $J = 2.4$ Hz, 1H), 5.07 (t, $J = 2.0$ Hz, 1H), 4.60 (d, $J = 8.8$ Hz, 1H), 4.28 (s, 1H), 2.32 (s, 3H), 2.22 (s, 3H), 1.96 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 144.9, 144.7, 142.3, 138.5, 134.0, 130.6, 130.0, 129.5, 129.2, 129.0, 127.2, 125.9, 125.6, 124.6, 115.8, 77.3, 76.8, 55.7, 53.5, 32.0, 31.0, 21.5, 21.2; IR (KBr) ν_{max} : 2926, 2855, 1653, 1599, 1463, 1362, 1242, 1172, 985, 809, 705, 659, 571. HRMS (ESI): $m/z = 591.0956$ (calcd for $C_{28}H_{29}BrN_2O_4S+Na^+ = 591.0924$).

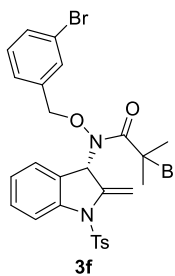
(S)-2-Bromo-N-((2-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3e)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; white oil; 59% yield (37.3 mg), 74% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL • min⁻¹, λ = 254 nm, *t* (major) = 12.15 min, *t* (minor) = 15.04 min]; $[\alpha]_D^{20}$ = +98.5 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.27 – 7.06 (m, 6H), 6.33 (s, 1H), 5.84 (t, *J* = 2.4 Hz, 1H), 5.06 (t, *J* = 2.4 Hz, 1H), 4.83 (s, 1H), 4.68 (s, 1H), 2.24 (s, 3H), 1.93 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 144.8, 144.1, 142.2, 134.2, 133.8, 132.7, 130.6, 129.9, 129.9, 129.5, 127.4, 127.3, 126.2, 125.1, 124.7, 123.3, 115.8, 97.8, 76.2, 55.5, 31.8, 31.1, 21.5; IR (KBr) ν_{\max} : 3054, 2854, 1653, 1475, 1359, 1170, 1030, 752, 658, 571. HRMS (ESI): *m/z* = 654.9868 (calcd for C₂₇H₂₆Br₂N₂O₄S+Na⁺ = 654.9872).

(S)-2-Bromo-N-((3-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3f)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; white oil; 62% yield (39.4 mg), 83% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL • min⁻¹, λ =

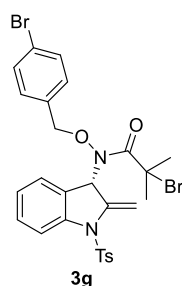


254 nm, *t* (major) = 11.50 min, *t* (minor) = 14.87 min]; $[\alpha]_D^{20}$ = +70.0 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.62 (m, 2H), 7.54 – 7.34 (m, 2H), 7.26 – 7.02 (m, 5H), 6.76 (d, *J* = 7.6 Hz, 2H), 6.43 (s, 1H), 5.87 (t, *J* = 2.4 Hz, 1H), 5.08 (t, *J* = 2.4 Hz, 1H), 4.57 (d, *J* = 9.2 Hz, 1H), 4.22 (d, *J* = 9.2 Hz, 1H), 2.21 (s, 3H), 1.97 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 145.0, 144.6, 142.3, 135.8, 133.0, 131.9, 131.7, 130.3, 129.9, 129.6, 127.4, 127.2, 126.0, 125.1, 124.7, 122.2, 115.8, 98.5, 76.0, 55.0, 32.1, 31.0, 21.5; IR (KBr) ν_{\max} : 2937, 2833, 2041, 1916, 1652, 1572, 1463, 1361, 1237, 1032, 754, 658, 571. HRMS (ESI): *m/z* = 654.9878 (calcd for C₂₇H₂₆Br₂N₂O₄S+Na⁺ = 654.9872).

(S)-2-Bromo-N-((4-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3g)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; white oil; 64% yield

(40.7 mg), 83% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, λ = 254 nm, t (major) = 11.87 min, t (minor) = 15.72 min]; $[\alpha]_D^{20}$ = +63.5 (c 0.1, CHCl₃); ¹H NMR (400

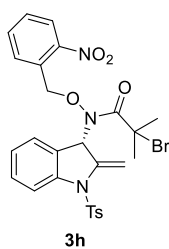


MHz, CDCl₃) δ 8.00 (d, J = 8.4 Hz, 1H), 7.75 – 7.61 (m, 2H), 7.51 – 7.34 (m, 2H), 7.25 – 7.14 (m, 2H), 7.09 (t, J = 7.6 Hz, 3H), 6.76 (d, J = 7.5 Hz, 2H), 6.43 (s, 1H), 5.87 (t, J = 2.4 Hz, 1H), 5.08 (t, J = 2.2 Hz, 1H), 4.57 (d, J = 9.4 Hz, 1H), 4.22 (d, J = 8.9 Hz, 1H), 2.21 (s, 3H), 1.97 (s, 6H). ¹³C NMR (101

MHz, CDCl₃) δ 172.2, 145.0, 144.5, 142.3, 134.0, 132.6, 131.5, 130.7, 130.1, 129.6, 127.2, 125.9, 125.4, 124.6, 122.8, 115.8, 98.6, 76.2, 55.6, 32.1, 31.0, 21.5; IR (KBr) ν_{\max} : 2927, 1653, 1598, 1463, 1362, 1261, 1172, 1090, 946, 874, 754, 659, 571. HRMS (ESI): m/z = 654.9875 (calcd for C₂₇H₂₆Br₂N₂O₄S+Na⁺ = 654.9872).

(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-((2-nitrobenzyl)oxy)propanamide (3h)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 48% yield (28.1 mg), 70% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, λ = 254



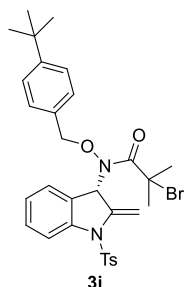
nm, t (major) = 20.01 min, t (minor) = 27.49 min]; $[\alpha]_D^{20}$ = +49.3 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.61 (dd, J = 17.6, 8.0 Hz, 3H), 7.45 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 11.6 Hz, 2H), 7.12 (d, J = 8.0 Hz, 3H), 6.35 (s, 1H), 5.86 (s, 1H), 5.26 – 5.07 (m, 2H), 5.04 (s, 1H), 2.28 (s, 3H), 1.96 (d, J = 4.8 Hz, 6H). ¹³C NMR (101 MHz,

CDCl₃) δ 172.5, 146.5, 144.7, 143.3, 142.1, 134.3, 133.8, 131.3, 130.1, 129.5, 128.7, 128.5, 127.2, 126.0, 124.9, 124.8, 124.7, 115.7, 98.3, 74.5, 62.8, 55.1, 31.5, 21.5; IR (KBr) ν_{\max} : 2928, 2856, 1675, 1528, 1361, 1172, 1090, 912, 811, 739, 660, 572. HRMS (ESI): m/z = 622.0664 (calcd for C₂₇H₂₆BrN₃O₆S+Na⁺ = 622.0618).

(S)-2-Bromo-N-((4-(tert-butyl)benzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3i)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 66% yield (39.9 mg), 78% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, λ = 254 nm, t (major) = 8.24 min, t (minor) = 11.09 min]; $[\alpha]_D^{20}$ = +21.5 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.8 Hz, 1H), 7.24 (dd, J =

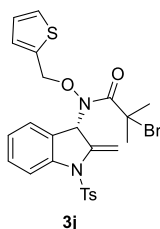
8.1, 2.7 Hz, 3H), 7.16 (t, $J = 7.4$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.75 (d, $J = 8.0$ Hz, 2H), 6.38 (s, 1H), 5.84 (t, $J = 2.4$ Hz, 1H), 5.07 (d, $J = 2.3$ Hz, 1H), 4.60 (d, $J = 8.9$ Hz, 1H), 4.27 (s, 1H),



2.19 (s, 3H), 1.97 (s, 6H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.1, 151.7, 144.9, 144.7, 142.3, 133.9, 130.6, 130.0, 129.5, 129.0, 127.2, 125.9, 125.6, 125.2, 124.6, 115.8, 98.3, 77.2, 55.7, 34.6, 32.0, 31.3, 31.1, 21.4; IR (KBr) ν_{max} : 2963, 2855, 1673, 1598, 1492, 1367, 1261, 1188, 1089, 989, 862, 746, 661, 571. HRMS (ESI): $m/z = 633.1449$ (calcd for $\text{C}_{31}\text{H}_{35}\text{BrN}_2\text{O}_4\text{S}+\text{Na}^+ =$

633.1393).

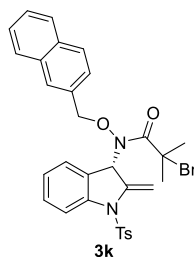
(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-(thiophen-2-ylmethoxy)propanamide (3j)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; white oil; 64% yield (36.3 mg), 86% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 12.83 min, t (minor) = 18.17 min]; $[\alpha]_{\text{D}}^{20} = +42.3$ (c 0.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.4$ Hz, 1H), 7.76 – 7.56 (m, 2H), 7.44 – 7.34 (m, 1H),

7.23 (dd, $J = 5.2, 1.2$ Hz, 1H), 7.21 – 7.17 (m, 1H), 7.15 – 7.07 (m, 3H), 6.86 (dd, $J = 5.2, 3.6$ Hz, 1H), 6.64 – 6.48 (m, 1H), 6.32 (s, 1H), 5.81 (t, $J = 2.4$ Hz, 1H), 5.03 (t, $J = 2.4$ Hz, 1H), 4.78 (d, $J = 10.0$ Hz, 1H), 4.49 (d, $J = 10.0$ Hz, 1H), 2.24 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.4, 144.9, 144.6, 142.3, 135.1, 134.0, 130.1, 129.5, 129.0, 127.4, 127.3, 126.6, 125.8, 125.4, 124.7, 115.8, 98.5, 70.8, 55.6, 32.0, 31.0, 21.5; IR (KBr) ν_{max} : 2977, 2933, 1668, 1468, 1369, 1226, 1175, 1036, 954, 855, 706, 572. HRMS (ESI): $m/z = 583.0347$ (calcd for $\text{C}_{25}\text{H}_{25}\text{BrN}_2\text{O}_4\text{S}_2+\text{Na}^+ = 583.0331$).

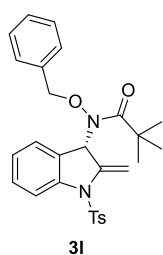
(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-(naphthalen-2-ylmethoxy)propanamide (3k)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 62% yield (37.0 mg), 82% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 14.19 min, t (minor) = 17.01 min]; $[\alpha]_{\text{D}}^{20} = +44.7$ (c 0.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.83 – 7.76 (m, 1H), 7.73 – 7.69 (m, 1H), 7.66 (d, $J = 8.0$ Hz,

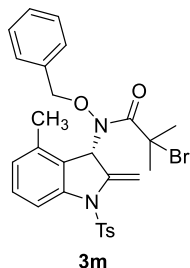
3H), 7.52 – 7.39 (m, 3H), 7.24 (s, 2H), 7.16 (t, $J = 7.2$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 1H), 6.44 (s, 1H), 5.87 (t, $J = 2.4$ Hz, 1H), 5.10 (t, $J = 2.0$ Hz, 1H), 4.76 (d, $J = 9.2$ Hz, 1H), 4.44 (s, 1H), 2.05 (s, 3H), 1.96 (d, $J = 14.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.3, 144.9, 144.7, 142.4, 133.9, 133.2, 132.9, 131.1, 130.1, 129.5, 128.6, 128.0, 128.0, 127.6, 127.2, 126.5, 126.4, 126.2, 126.1, 125.5, 124.6, 115.8, 98.4, 62.1, 55.7, 32.1, 31.0, 21.3; IR (KBr) ν_{max} : 2925, 1653, 1599, 1476, 1361, 1261, 1171, 1090, 987, 858, 752, 659, 571. HRMS (ESI): $m/z = 627.0848$ (calcd for $\text{C}_{31}\text{H}_{29}\text{BrN}_2\text{O}_4\text{S}+\text{Na}^+ = 627.0924$).

(S)-N-(Benzyloxy)-N-(2-methylene-1-tosylindolin-3-yl)pivalamide (3l)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 55% yield (27.4 mg), 62% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 10.12 min, t (minor) = 12.17 min]; $[\alpha]_{\text{D}}^{20} = +42.4$ (c 0.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.4$ Hz, 1H), 7.74 – 7.60 (m, 2H), 7.50 – 7.36 (m, 3H), 7.22 – 7.12 (m, 2H), 7.13 – 7.04 (m, 3H), 6.67 (d, $J = 8.4$ Hz, 2H), 6.48 (s, 1H), 5.83 (t, $J = 2.4$ Hz, 1H), 5.02 (t, $J = 2.0$ Hz, 1H), 4.32 – 4.06 (m, 2H), 2.22 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.8, 145.4, 144.9, 142.3, 136.0, 134.0, 131.6, 131.5, 130.0, 129.9, 129.5, 127.2, 126.9, 124.6, 122.3, 115.8, 98.1, 76.5, 61.4, 39.7, 27.1, 21.5. IR (KBr) ν_{max} : 2966, 2930, 2872, 1735, 1663, 1454, 1364, 1174, 1089, 988, 812, 747, 661, 577. HRMS (ESI): $m/z = 513.1819$ (calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4\text{S}+\text{Na}^+ = 513.1818$).

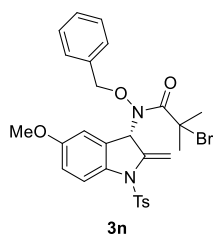
(S)-N-(Benzyloxy)-2-bromo-2-methyl-N-(4-methyl-2-methylene-1-tosylindolin-3-yl)propanamide (3m)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 63% yield (35.8 mg), 85% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.61 min, t (minor) = 13.96 min]; $[\alpha]_{\text{D}}^{20} = +45.2$ (c 0.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.79 (s, 1H), 7.69 – 7.62 (m, 2H), 7.27 – 7.17 (m, 3H), 7.08 (t, $J = 7.2$ Hz, 3H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 7.2$ Hz, 2H), 6.30 (s, 1H), 5.80 (t, $J = 2.4$ Hz, 1H), 5.03 (t, $J = 2.4$ Hz, 1H), 4.61 (d, $J = 9.2$ Hz, 1H), 4.35 (d, $J = 9.2$ Hz, 1H), 2.45 (s, 3H), 2.21 (s, 3H), 1.93 (d, $J = 5.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.2, 144.9,

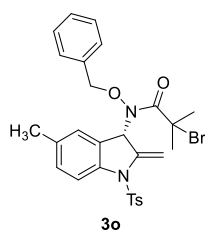
144.8, 142.5, 140.4, 134.1, 133.8, 129.5, 129.1, 128.6, 128.3, 127.2, 125.5, 125.4, 122.7, 116.3, 98.4, 61.9, 55.7, 31.9, 31.1, 22.1, 21.5. IR (KBr) ν_{\max} : 2963, 2872, 1649, 1481, 1367, 1260, 1174, 1090, 802, 747, 661, 568. HRMS (ESI): $m/z = 591.0922$ (calcd for $C_{28}H_{29}BrN_2O_4S+Na^+ = 591.0924$).

(S)-N-(Benzyloxy)-2-bromo-N-(5-methoxy-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3n)



Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 52% yield (30.2 mg), 90% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 14.12 min, t (minor) = 21.26 min]; $[\alpha]_D^{20} = +62.2$ (c 0.1, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J = 9.2$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.47 – 7.38 (m, 2H), 7.29 – 7.21 (m, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.97 – 6.89 (m, 2H), 6.76 (d, $J = 2.8$ Hz, 1H), 6.28 (s, 1H), 5.85 (s, 1H), 5.06 (d, $J = 2.4$ Hz, 1H), 4.65 (s, 1H), 4.45 (s, 1H), 3.78 (s, 3H), 2.24 (s, 3H), 1.96 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 145.6, 137.6, 135.4, 133.8, 133.6, 130.2, 129.2, 128.8, 128.5, 127.2, 126.5, 125.1, 118.7, 118.0, 115.8, 74.9, 56.0, 31.6, 22.7, 21.6, 14.2, 12.9. IR (KBr) ν_{\max} : 2963, 2929, 1652, 1597, 1486, 1388, 1286, 1171, 1089, 960, 856, 749, 677, 581. HRMS (ESI): $m/z = 607.0873$ (calcd for $C_{28}H_{29}BrN_2O_5S+Na^+ = 607.0850$).

(S)-N-(Benzyloxy)-2-bromo-2-methyl-N-(5-methyl-2-methylene-1-tosylindolin-3-yl)propanamide (3o)

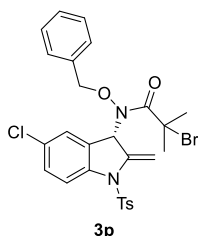


Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 56% yield (31.7 mg), 98% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.98 min, t (minor) = 14.42 min]; $[\alpha]_D^{20} = +76.3$ (c 0.1, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.27 – 7.16 (m, 4H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.99 (s, 1H), 6.85 (d, $J = 7.2$ Hz, 2H), 6.29 (s, 1H), 5.81 (t, $J = 2.4$ Hz, 1H), 5.02 (t, $J = 2.4$ Hz, 1H), 4.61 (d, $J = 8.8$ Hz, 1H), 4.35 (s, 1H), 2.31 (s, 3H), 2.20 (s, 3H), 1.94 (d, $J = 4.0$ Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 145.0, 144.3, 142.2, 137.4, 133.9, 132.2, 130.2, 130.0, 129.5, 128.8, 127.2, 126.7, 125.7, 124.8, 115.9, 98.1, 61.9, 55.7, 32.0, 31.2, 21.4, 18.4. IR (KBr) ν_{\max} : 2970, 2927, 2863, 1683, 1506, 1457, 1372, 1245, 1175, 1089, 913,

808, 744, 662, 599. HRMS (ESI): $m/z = 591.0918$ (calcd for $C_{28}H_{29}BrN_2O_4S+Na^+ = 591.0924$).

(S)-N-(Benzyloxy)-2-bromo-N-(5-chloro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3p)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 60% yield

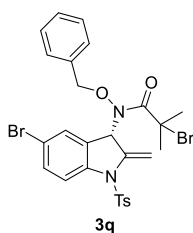


(35.3 mg), 82% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.82 min, t (minor) = 12.42 min]; $[\alpha]_D^{20} = +65.0$ (c 0.1, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.38 (dd, $J = 9.2, 2.4$ Hz, 3H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.19 (d, $J = 2.0$ Hz, 1H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 7.2$ Hz,

2H), 6.23 (s, 1H), 5.85 (t, $J = 2.4$ Hz, 1H), 5.07 (t, $J = 2.4$ Hz, 1H), 4.75 (d, $J = 9.2$ Hz, 1H), 4.48 (s, 1H), 2.26 (s, 3H), 1.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 145.2, 144.1, 140.8, 133.8, 133.6, 130.1, 130.0, 129.63, 129.0, 128.8, 128.5, 127.8, 127.3, 125.5, 116.8, 98.5, 77.1, 55.4, 31.8, 30.9, 21.5; IR (KBr) ν_{max} : 2929, 1655, 1597, 1493, 1362, 1247, 1117, 1020, 950, 858, 739, 665, 585, 499. HRMS (ESI): $m/z = 611.0375$ (calcd for $C_{27}H_{26}BrClN_2O_4S+Na^+ = 611.0377$).

(S)-N-(Benzyloxy)-2-bromo-N-(5-bromo-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3q)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 52% yield (33.2 mg), 77% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, $\lambda = 254$

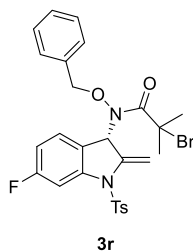


nm, t (major) = 10.23 min, t (minor) = 13.31 min]; $[\alpha]_D^{20} = +57.4$ (c 0.1, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 1H), 7.31 (d, $J = 8.8$ Hz, 4H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.97 (s, 2H), 6.22 (s, 1H), 5.84 (s, 1H), 5.06 (s, 1H), 4.74 (s, 1H), 4.47 (s, 1H), 2.26 (s, 3H), 1.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

172.2, 145.2, 144.0, 141.3, 133.8, 133.6, 132.90, 129.6, 128.9, 128.8, 128.5, 128.4, 128.2, 127.3, 117.5, 117.1, 98.4, 55.4, 31.8, 30.9, 29.7, 21.5; IR (KBr) ν_{max} : 2962, 2926, 2854, 1655, 1596, 1452, 1363, 1248, 1174, 1090, 1019, 912, 809, 736, 664, 581. HRMS (ESI): $m/z = 654.9816$ (calcd for $C_{27}H_{26}Br_2N_2O_4S+Na^+ = 654.9872$).

(S)-N-(Benzyloxy)-2-bromo-N-(6-fluoro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3r)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 56% yield (31.9 mg), 90% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, λ = 254



3r

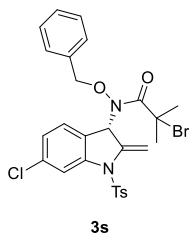
nm, t (major) = 9.38 min, t (minor) = 11.93 min]; $[\alpha]_D^{20} = +36.0$ (c 0.1, CHCl_3);

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 – 7.58 (m, 3H), 7.25 – 7.17 (m, 1H), 7.19 – 7.12 (m, 2H), 7.08 (ddd, J = 8.4, 5.6, 1.2 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.83 – 6.71 (m, 3H), 6.21 (s, 1H), 5.74 (t, J = 2.4 Hz, 1H), 4.97 (t, J = 2.4 Hz, 1H), 4.56 (d, J = 9.2 Hz, 1H), 4.31 – 4.18 (m, 1H), 2.13 (s, 3H), 1.85 (d, J =

6.0 Hz, 6H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -116.00 (s). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.2, 162.81 (d, $J_{\text{C-F}}$ = 246.6 Hz), 144.2, 143.8, 142.6, 142.5, 132.8, 132.6, 128.6, 127.9, 127.7, 127.4, 126.2, 120.0, 110.45 (d, $J_{\text{C-F}}$ = 23.1 Hz), 102.82 (d, $J_{\text{C-F}}$ = 29.5 Hz) 97.3, 60.5, 54.5, 30.8, 30.0, 20.5; IR (KBr) ν_{max} : 2964, 2923, 2847, 1667, 1485, 1366, 1262, 1172, 1089, 802, 706, 586. HRMS (ESI): m/z = 595.0677 (calcd for $\text{C}_{27}\text{H}_{26}\text{BrFN}_2\text{O}_4\text{S} + \text{Na}^+$ = 595.0673).

(S)-N-((Benzyloxy)-2-bromo-N-(6-chloro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3s)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 47% yield (27.3 mg), 75% ee [Daicel Chiralpak IA-H, hexanes/*i*-propanol = 95/5, flow: 1.0 mL/min, λ = 254



3s

nm, t (major) = 9.68 min, t (minor) = 12.58 min]; $[\alpha]_D^{20} = +55.7$ (c 0.1, CHCl_3);

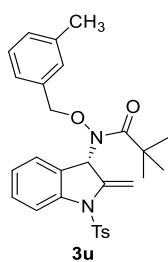
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.31 (s, 1H), 7.29 (s, 2H), 7.14 (d, J = 6.8 Hz, 4H), 6.93 (s, 2H), 6.26 (s, 1H), 5.84 (s, 1H), 5.06 (s, 1H), 4.71 (s, 1H), 4.42 (s, 1H), 2.25 (s, 3H), 1.94 (d, J = 4.4 Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 182.9, 172.3, 145.2, 144.4, 143.2, 135.9,

133.82, 133.6, 130.2, 129.7, 128.9, 128.7, 128.4, 127.3, 124.7, 115.9, 98.3, 61.8, 55.5, 31.8, 31.0, 21.5; IR (KBr) ν_{max} : 2960, 2851, 1721, 1687, 1511, 1468, 1360, 1261, 1172, 1090, 966, 866, 764, 660, 545. HRMS (ESI): m/z = 611.0375 (calcd for $\text{C}_{27}\text{H}_{26}\text{BrClN}_2\text{O}_4\text{S} + \text{Na}^+$ = 611.0377).

(S)-N-((3-Methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)pivalamide (3u)

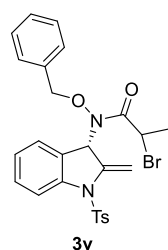
Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 52% yield (26.3 mg), 76% ee, [Daicel Chiralcel IA-H, hexanes/*i*-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 8.833, t (minor) = 10.551]; $[\alpha]_D^{20} = +43.2$ (c 0.1, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.42 (tt, J = 7.2, 2.4 Hz, 1H),

7.20 – 7.00 (m, 7H), 6.56 (d, $J = 7.2$ Hz, 1H), 6.43 (s, 1H), 5.82 (t, $J = 2.4$ Hz, 1H), 5.04 (t, $J = 2.4$ Hz, 1H), 4.36 – 4.09 (m, 2H), 2.26 (s, 3H), 2.20 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.8, 145.5, 144.8, 142.3, 137.9, 134.0, 133.7, 129.7, 129.5, 129.3, 128.2, 127.2, 126.12, 126.0, 125.6, 124.5, 124.5, 115.7, 97.9, 61.4, 39.7, 31.6, 27.1, 21.4, 21.2; IR (KBr) ν_{max} : 2959, 2927, 1652, 1660, 1463, 1362, 1172, 1090, 931, 751, 658, 571. HRMS (EI): $m/z = 504.2093$ (calcd for $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_4\text{S} = 504.2083$).



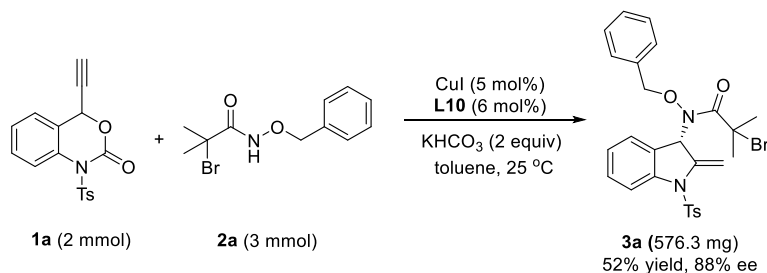
N-(Benzyloxy)-2-bromo-*N*-((*S*)-2-methylene-1-tosylindolin-3-yl)propenamide (**3v**)

Flash column chromatography eluent petroleum ether/ethyl acetate = 20/1; yellow oil; 81% yield (43.2 mg), 1:1 dr, 50% ee, [Daicel Chiralcel IC-H, hexanes/*i*-propanol = 95/5, flow rate = 1.0 mL/min, $\lambda = 254.4$ nm, t (major) = 58.160, t (minor) = 68.143]; $[\alpha]_{\text{D}}^{20} = +31.3$ (c 0.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.4$ Hz, 1H), 7.62 – 7.56 (m, 2H), 7.33 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.26 – 7.21 (m, 4H), 7.05 (tt, $J = 7.6, 1.2$ Hz, 3H), 6.88 (d, $J = 1.6$ Hz, 1H), 6.77 (d, $J = 1.6$ Hz, 1H), 6.35 (s, 1H), 5.80 (t, $J = 2.4$ Hz, 1H), 5.03 (t, $J = 2.4$ Hz, 1H), 4.51 (d, $J = 10.4$ Hz, 1H), 4.23 (d, $J = 5.6$ Hz, 1H), 4.03 (dd, $J = 8.4, 5.2$ Hz, 1H), 2.17 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.9, 144.9, 144.0, 142.9, 134.3, 133.7, 130.4, 129.6, 129.1, 128.7, 127.40, 126.0, 125.5, 124.7, 115.8, 99.6, 79.3, 60.7, 37.2, 31.9, 21.6, 21.0; IR (KBr) ν_{max} : 3033, 2975, 2253, 1674, 1477, 1362, 1172, 1090, 945, 754, 659, 573. HRMS (EI): $m/z = 540.0715$ (calcd for $\text{C}_{26}\text{H}_{25}\text{BrN}_2\text{O}_4\text{S} = 540.0718$).



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

6.1 Scale-up synthesis of **3a**



To an oven-dried three-necked flask, CuI (19.0 mg, 0.1 mmol, 5 mol%) and **L10** (47.2 mg, 0.12 mmol, 6 mol%) in dry toluene (40.0 mL) were added under a nitrogen atmosphere. The resulting

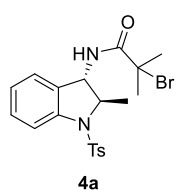
mixture was stirred at room temperature for 0.5 hours. Then the substrates **1a** (654.1 mg, 2.0 mmol, 1.0 equiv) and **2a** (813.1 mg, 3.0 mmol, 1.5 equiv) was introduced into the vessel. The mixture was stirred for 14 hours at 25 °C and then it was subjected to silica gel column (petroleum ether/EtOAc 10:1 v/v) to afford the desired products **3a** as yellow oil in 52% yield (576.3 mg) with 88% ee.

6.2 Procedure for the preparation of **4a**



To an oven-dried schlenk tube, LiAlH₄ (4.6 mg, 0.12 mmol, 1.2 equiv) in dry tetrahydrofuran (1.0 mL) was added under a nitrogen atmosphere. The mixture was cool to -30 °C and stirred for 20 minutes. Then, **3a** (55.4 mg, 0.1 mmol, 1 equiv) in dry tetrahydrofuran (1.0 mL) was added. After stirring for 15 minutes at -30 °C. The crude reaction mixture was directly purified by flash column chromatography on silica gel column (petroleum ether/EtOAc 10:1 v/v) to afford the corresponding **4a** in 67% yield, 6:1 dr and 86% ee.

2-Bromo-2-methyl-*N*-(2-methyl-1-tosylindolin-3-yl)propenamide (**4a**)



Flash column chromatography eluent petroleum ether/ethyl acetate = 10/1; yellow oil; 67% yield (30.2 mg), 6:1 dr, 86% ee, [Daicel Chiralcel IA-H, hexanes/*i*-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254.4 nm, t (major) = 11.888, t (minor) = 13.036]; [α]_D²⁰ = +24.9 (c 0.1, CHCl₃); ¹H NMR (400 MHz,

CDCl₃) δ 8.15 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.27 – 7.13 (m, 6H), 6.82 (s, 1H), 2.61 (p, J = 6.8 Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H), 1.30 – 1.26 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 176.2, 144.9, 135.9, 135.0, 132.2, 130.0, 127.0, 126.4, 124.4, 123.6, 117.6, 117.5, 114.5, 35.8, 21.5, 19.8, 12.6.; IR (KBr) ν_{max} : 3676, 2920, 1655, 1463, 1358, 1186, 1090, 945, 754, 659, 551. HRMS (EI): m/z = 450.0613 (calcd for C₂₀H₂₃BrN₂O₃S = 450.0619).

7. X-Ray data of 3g

Table S7 Crystal data and structure refinement for **3g**

Empirical formula	C ₂₇ H ₂₆ O ₄ Br ₂ SN ₂
Formula weight	634.38
Temperature/K	223(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	8.9489(3)
b/Å	10.2140(2)
c/Å	29.3155(6)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2679.54(11)
Z	4
ρ _{calc} /g/cm ³	1.573
μ/mm ⁻¹	4.863
F(000)	1280.0
Crystal size/mm ³	0.500 × 0.300 × 0.200
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.168 to 155.228
Index ranges	-10 ≤ h ≤ 11, -12 ≤ k ≤ 12, -28 ≤ l ≤ 37
Reflections collected	11354
Independent reflections	5357 [R _{int} = 0.0442, R _{sigma} = 0.0483]
Data/restraints/parameters	5357/0/328
Goodness-of-fit on F ²	1.125
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0614, wR ₂ = 0.1504
Final R indexes [all data]	R ₁ = 0.0638, wR ₂ = 0.1540
Largest diff. peak/hole / e Å ⁻³	0.98/-0.78
Flack parameter	-0.02(2)

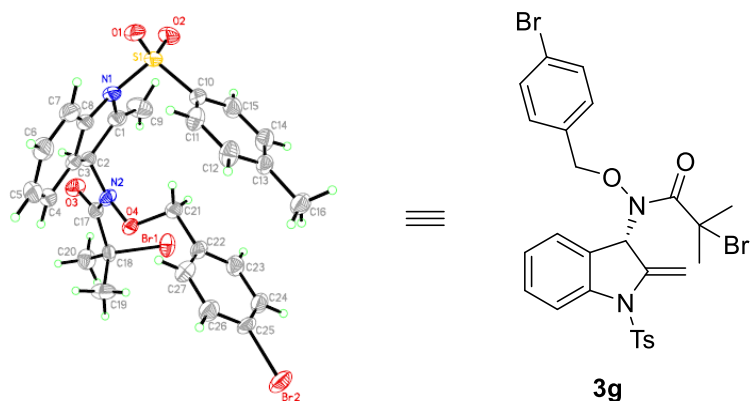
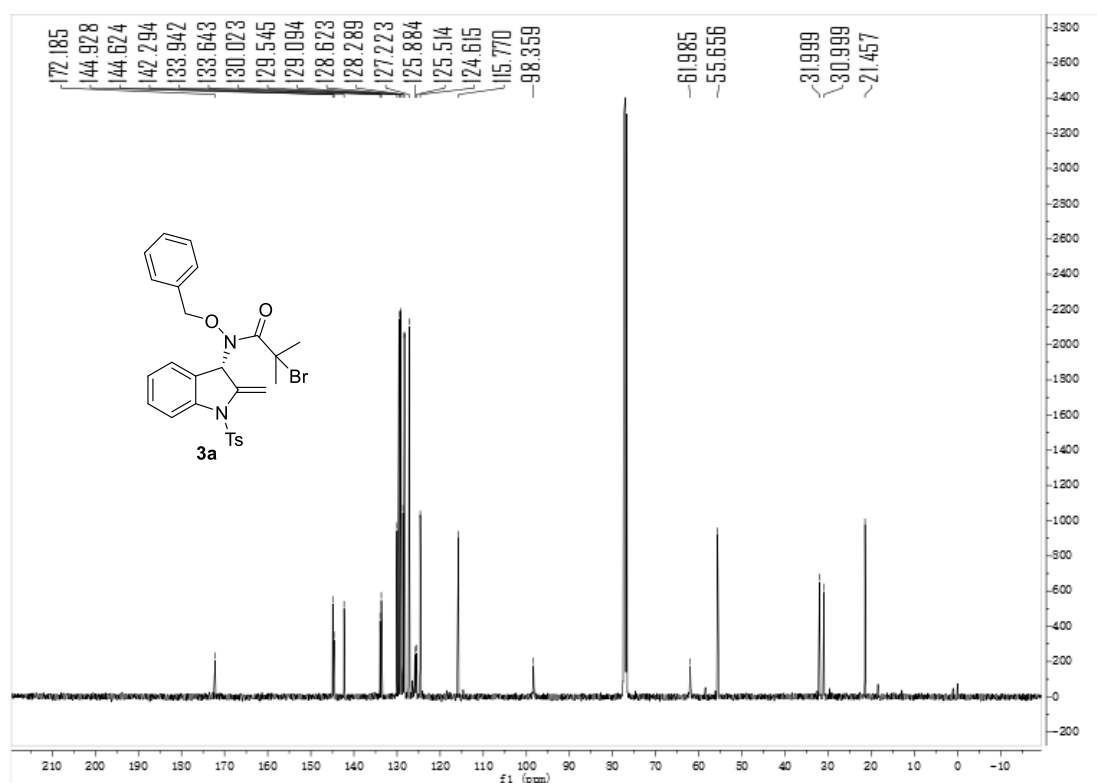
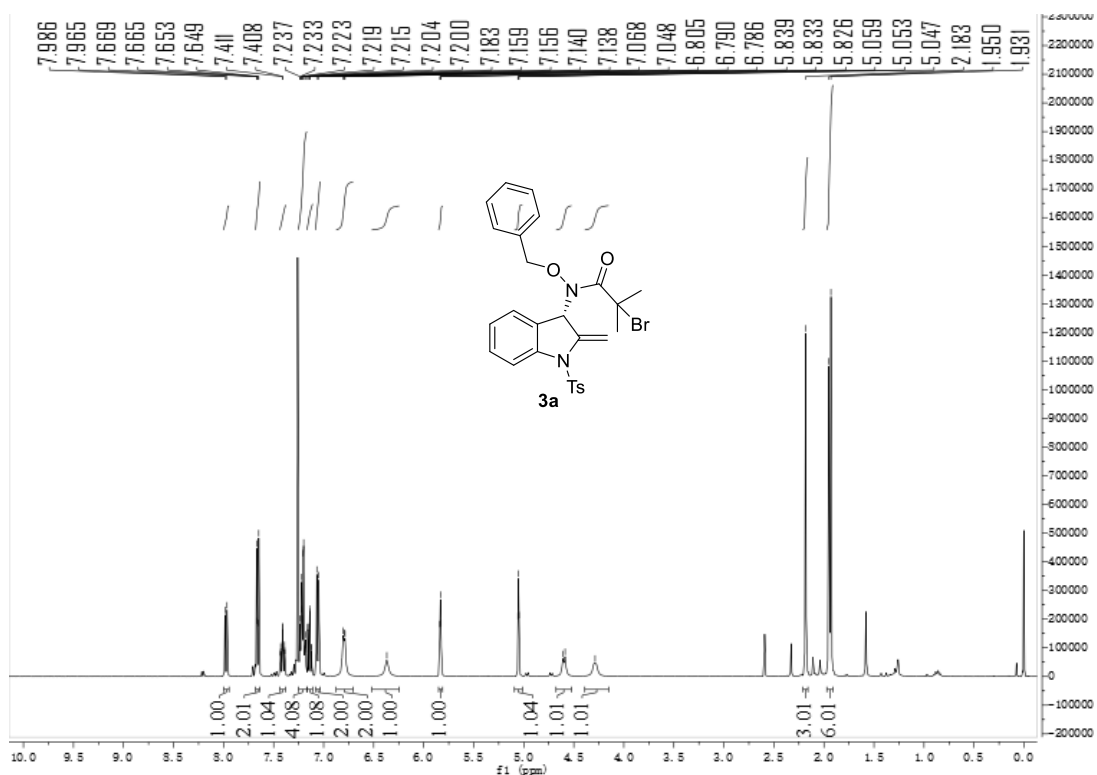


Figure S1. ORTEP drawing of **3g** (50% thermal ellipsoids)

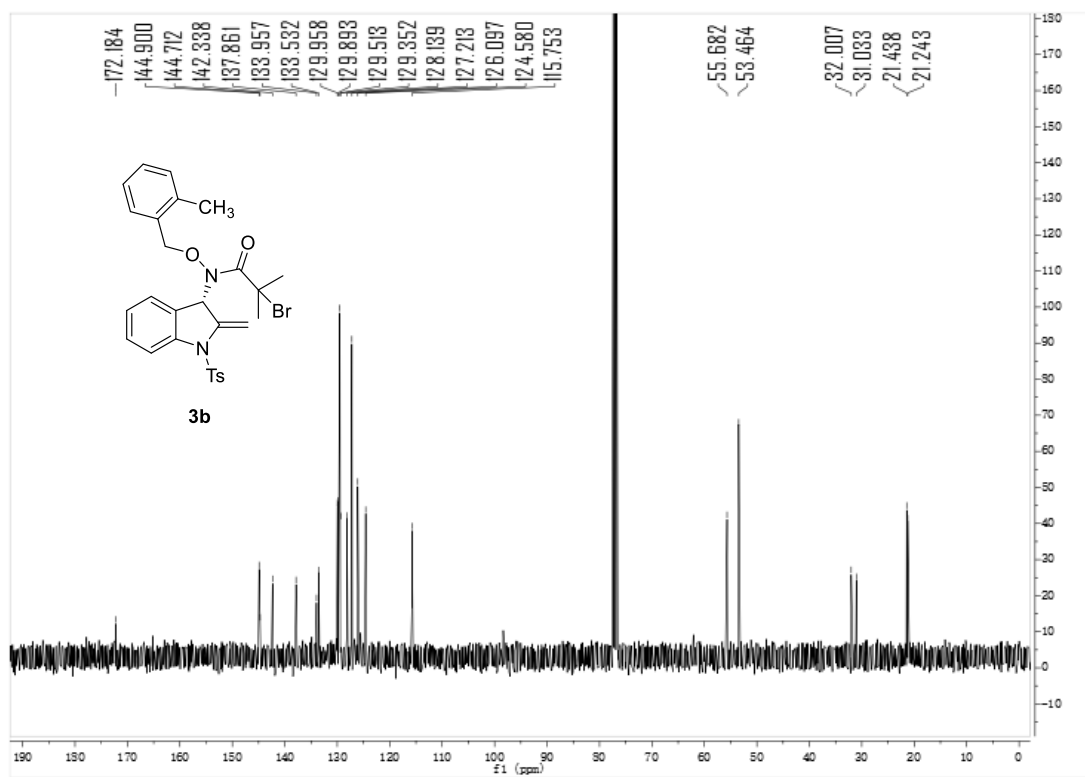
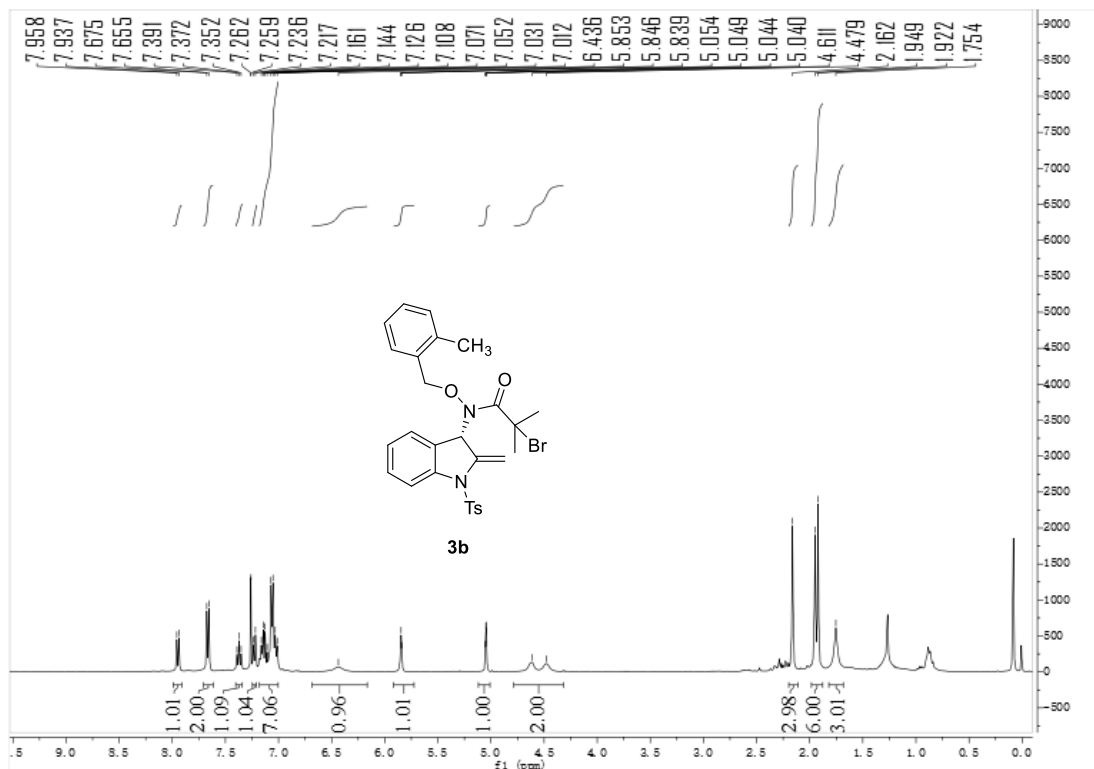
In order to determine the structure and absolute configuration of the product, we dissolved the product **3g** in 0.4 mL ethyl acetate and placed the solution in the NMR tube. Then n-hexane was absorbed with a syringe and slowly added into the NMR tube until it was filled. After that, the NMR tube was sealed and put in the refrigerator, and the product **3g** single crystal was obtained by slow penetration of n-hexane. **CCDC 2040799** (**3g**) 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.

8. NMR spectra

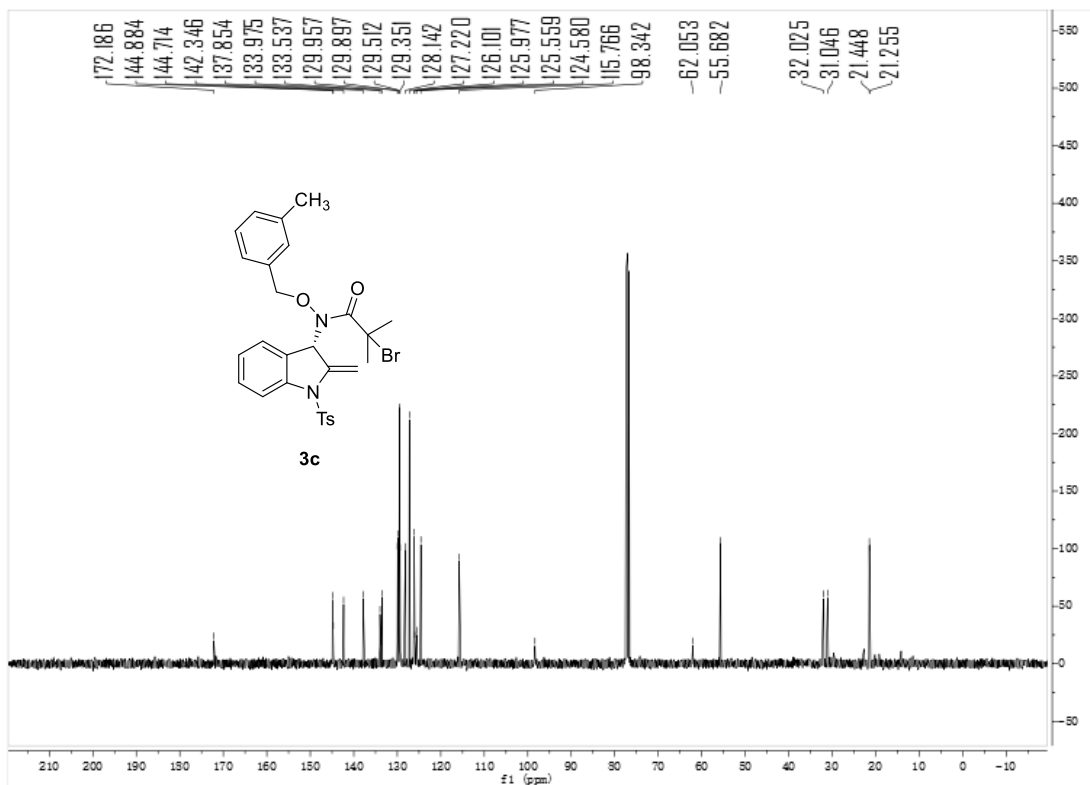
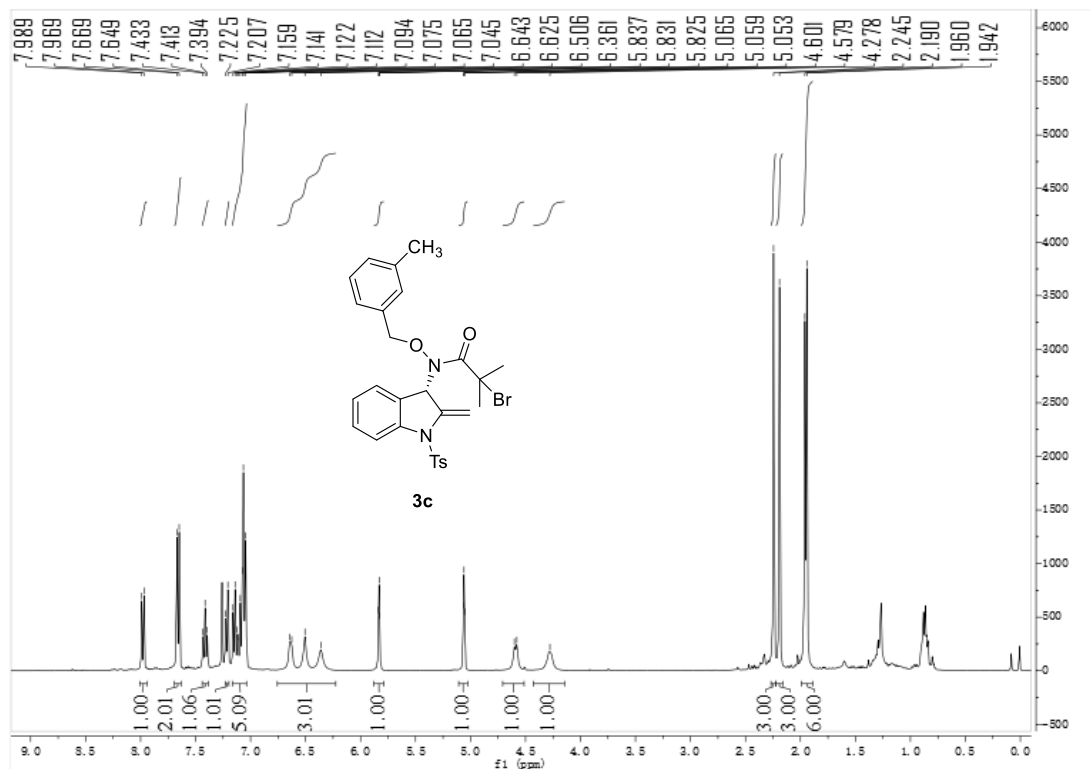
(S)-N-(Benzyloxy)-2-bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3a)



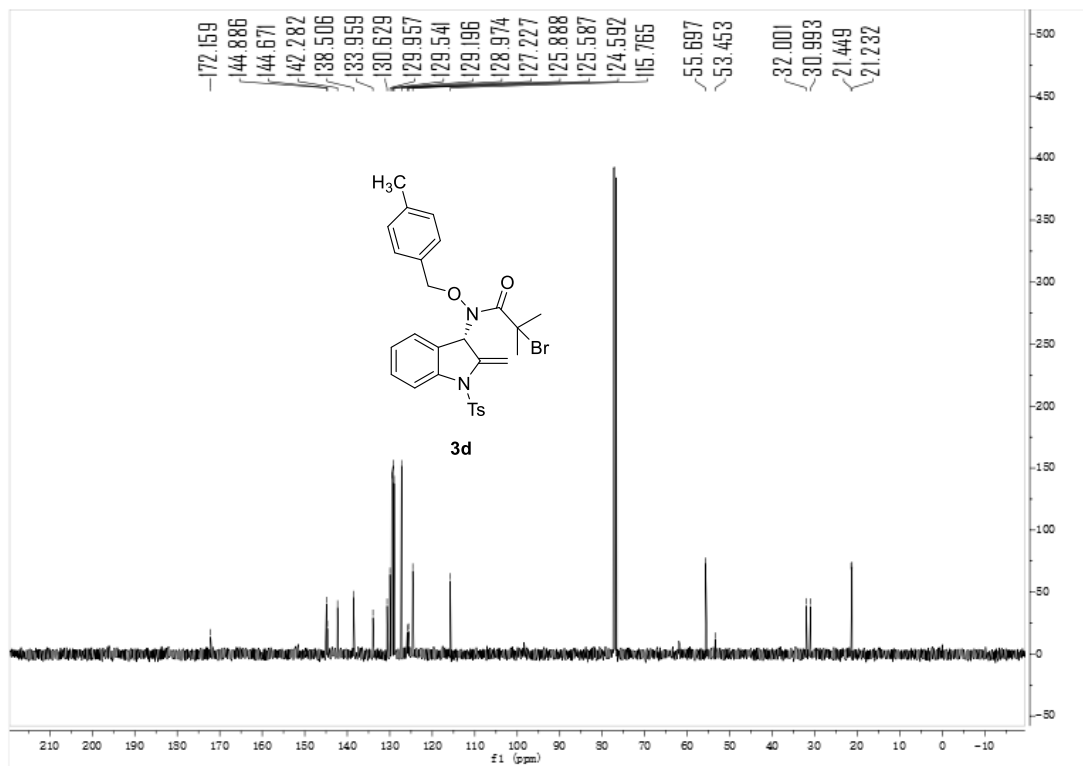
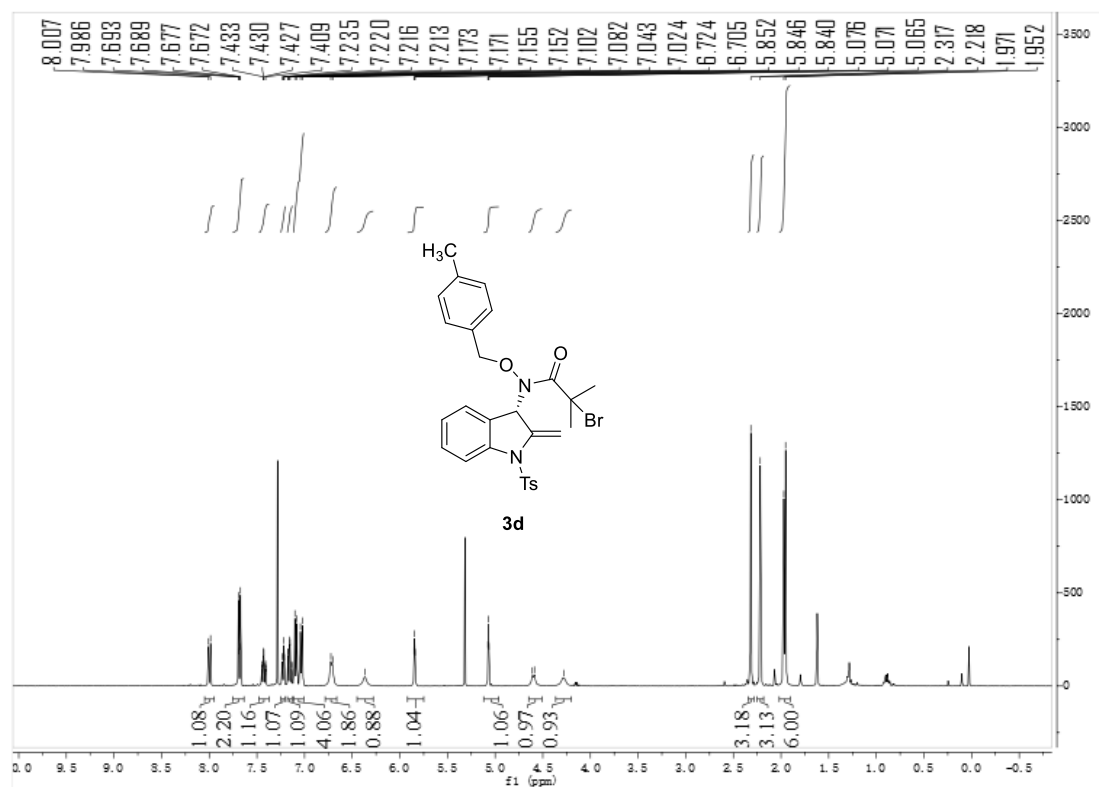
(S)-2-Bromo-2-methyl-N-((2-methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3b)



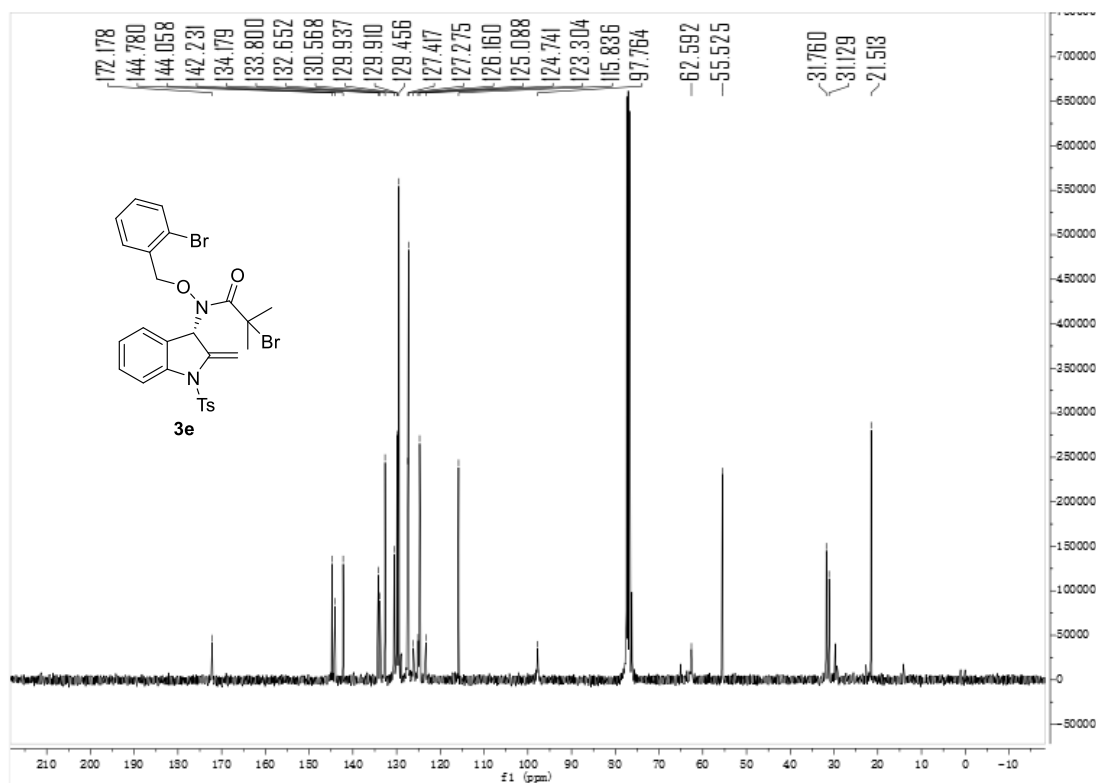
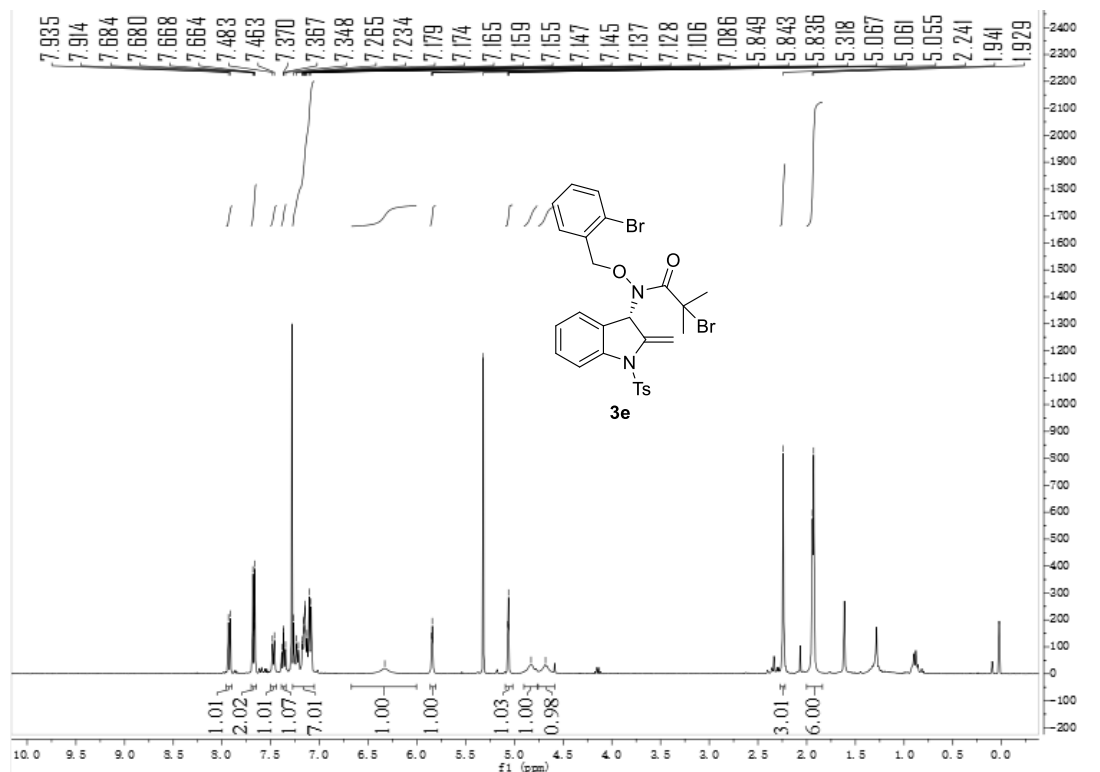
(S)-2-Bromo-2-methyl-N-((3-methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3c)



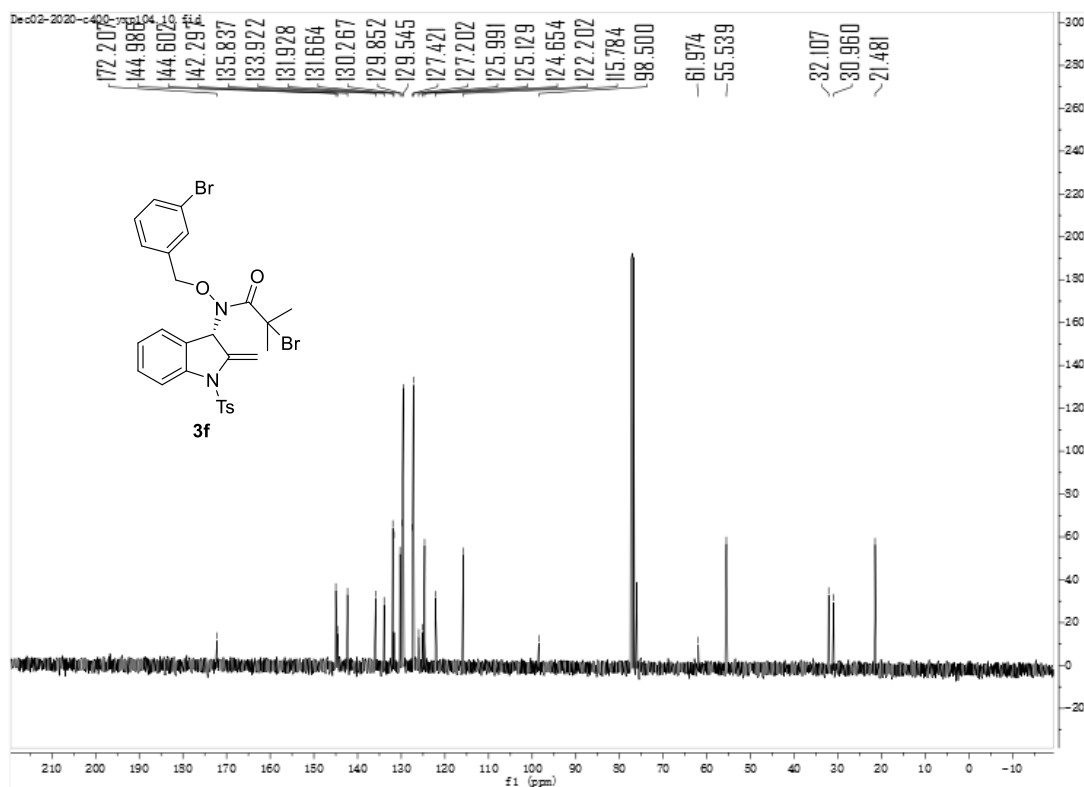
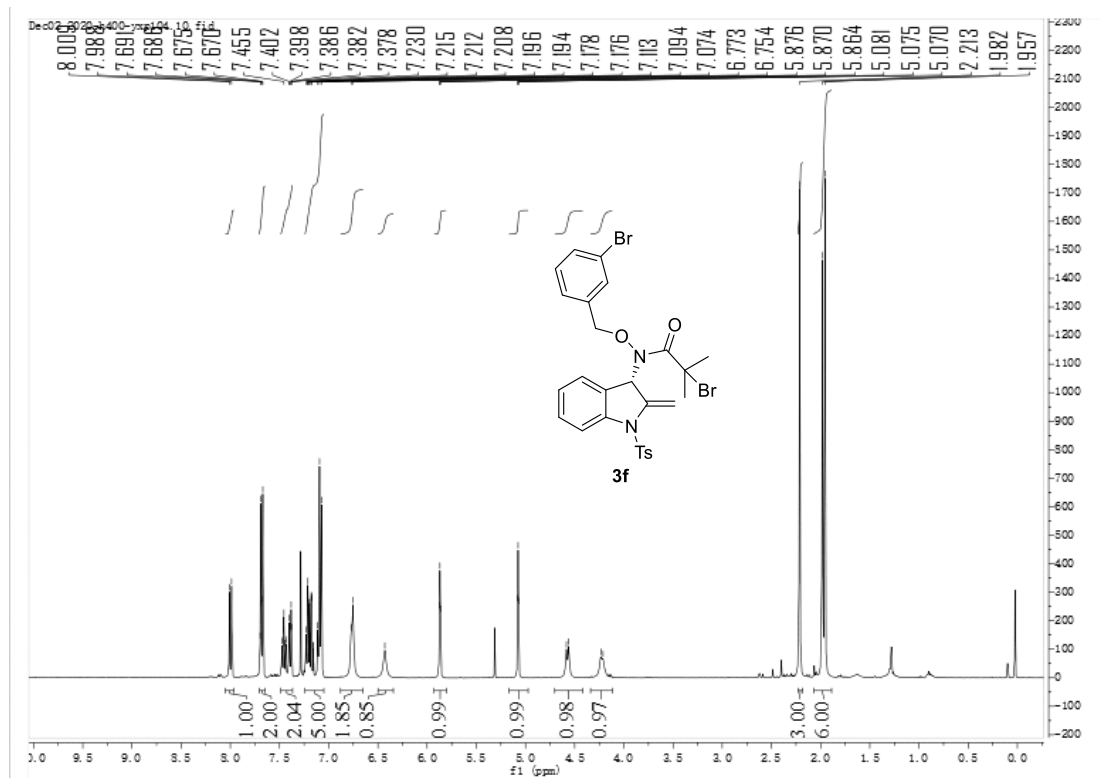
(S)-2-Bromo-2-methyl-N-((4-methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3d)



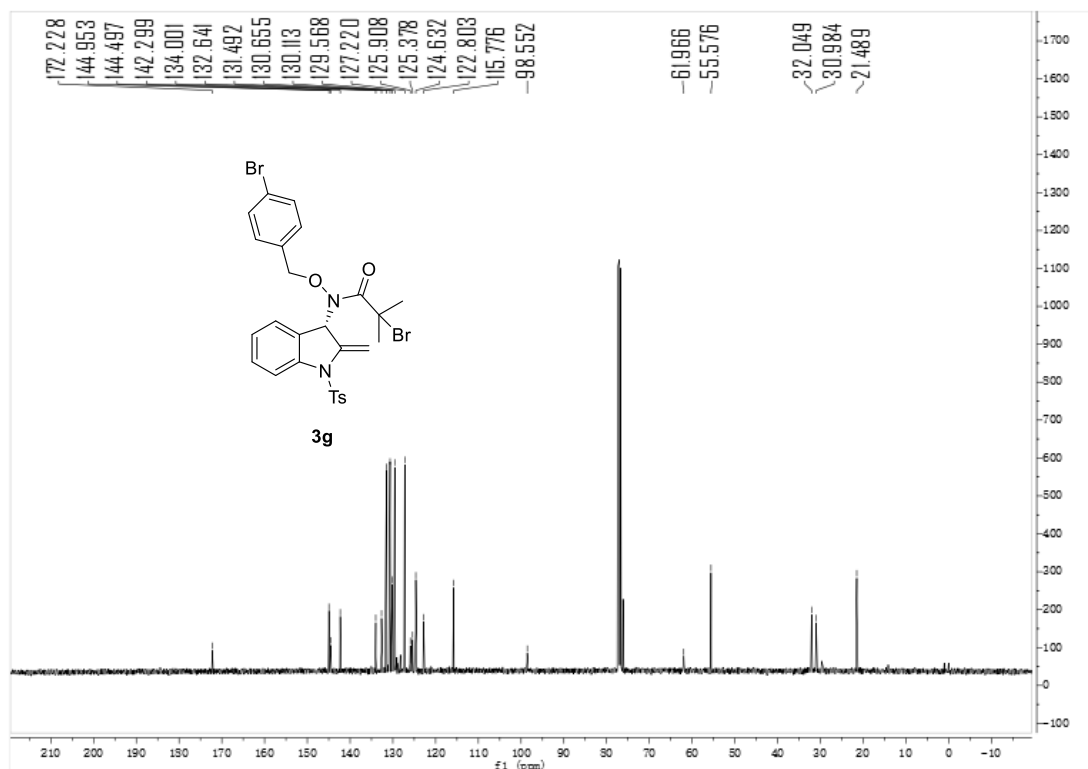
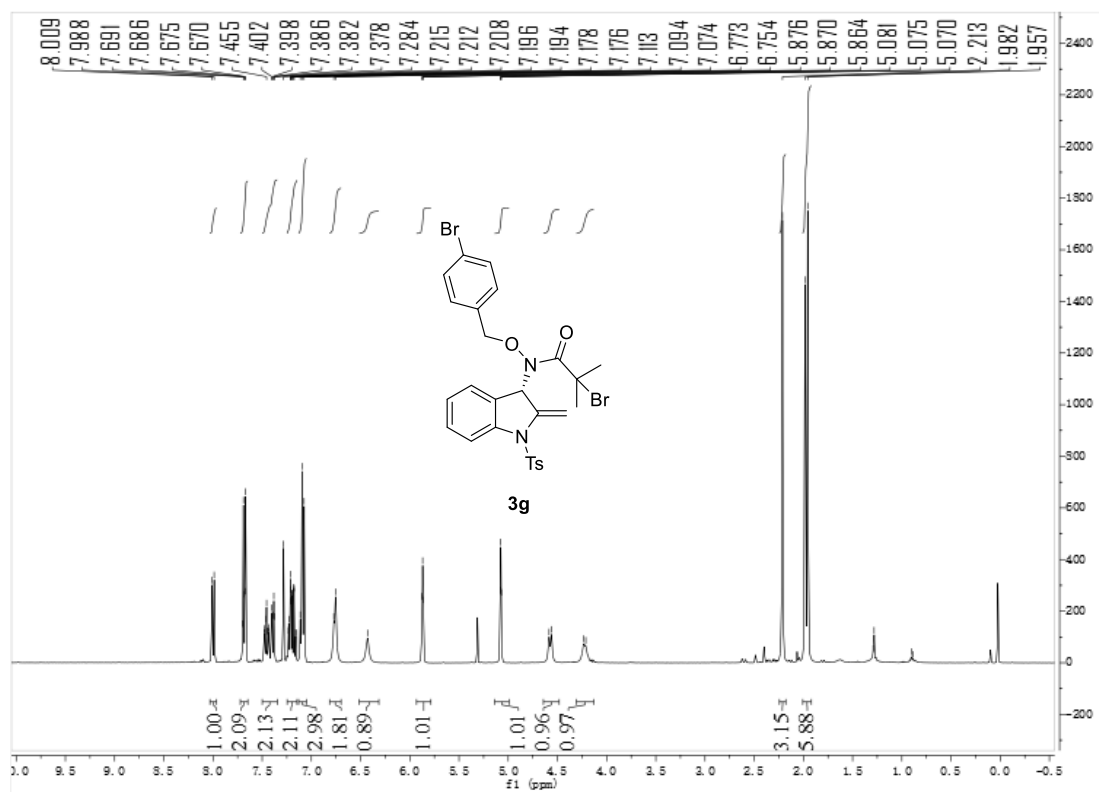
(S)-2-Bromo-N-((2-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3e)



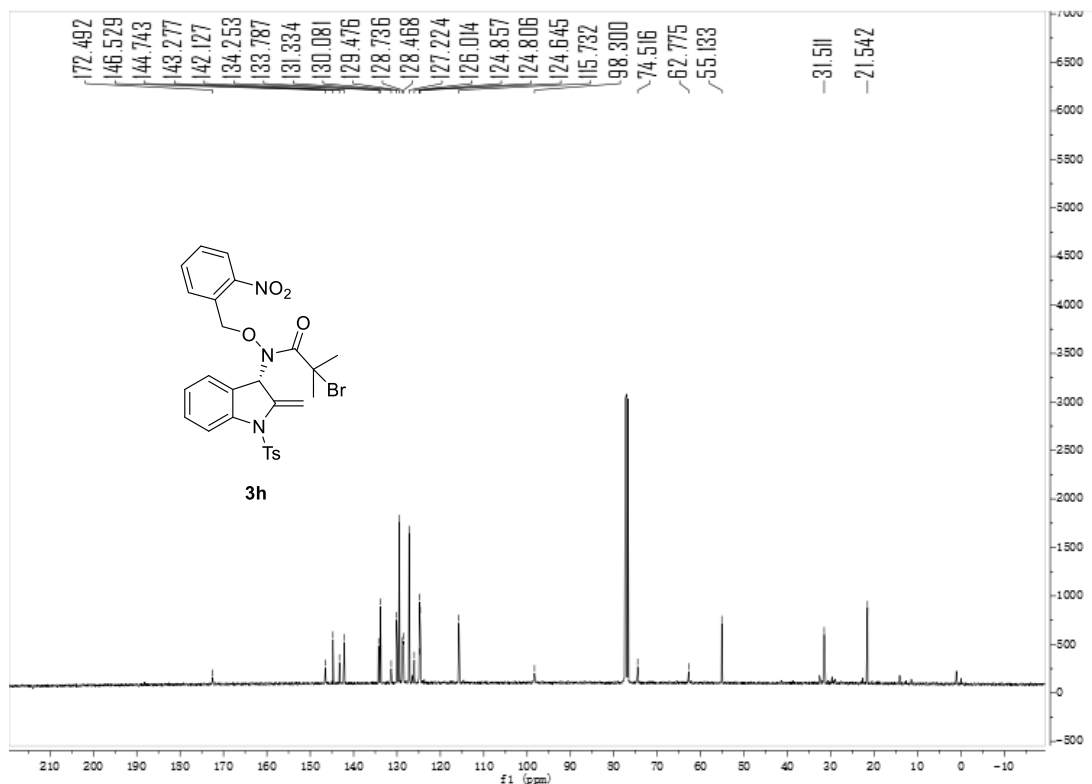
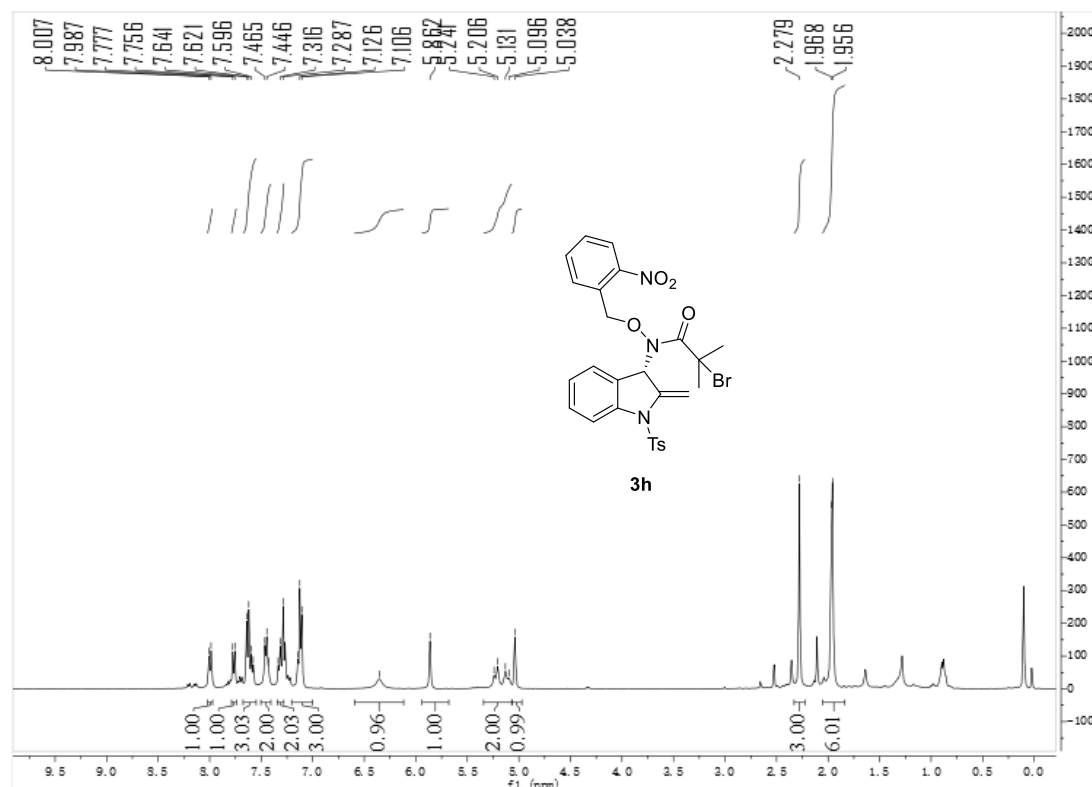
(S)-2-Bromo-N-((3-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3f)



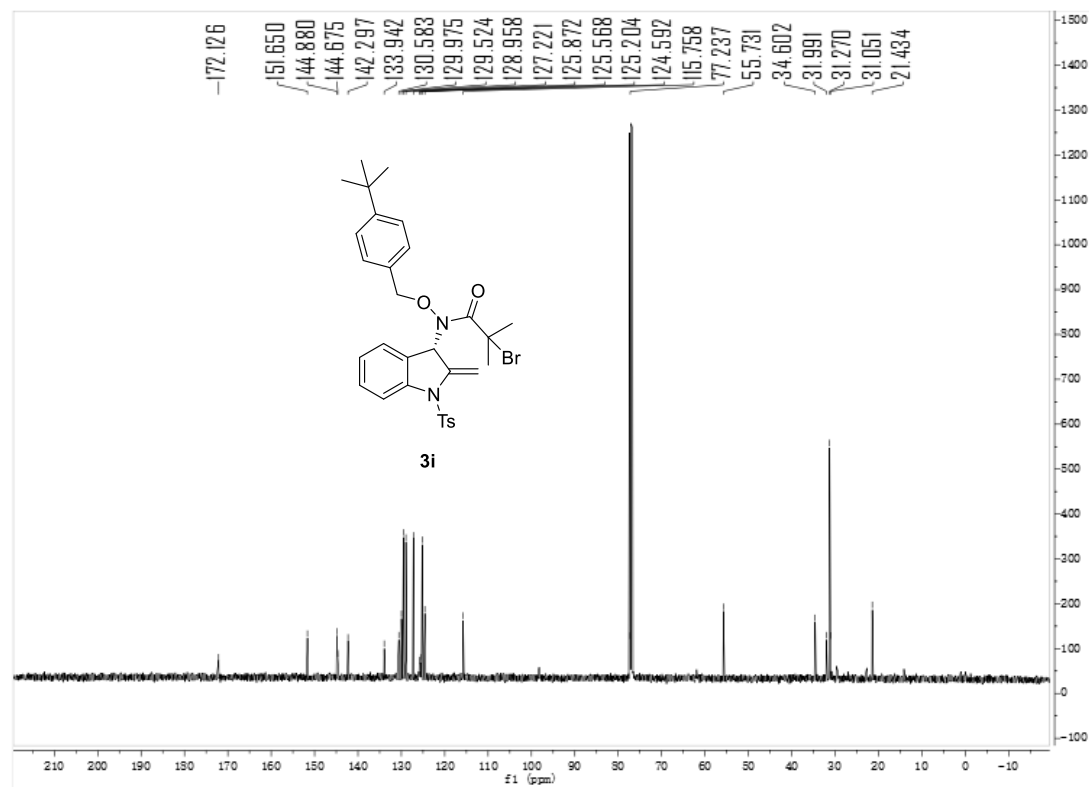
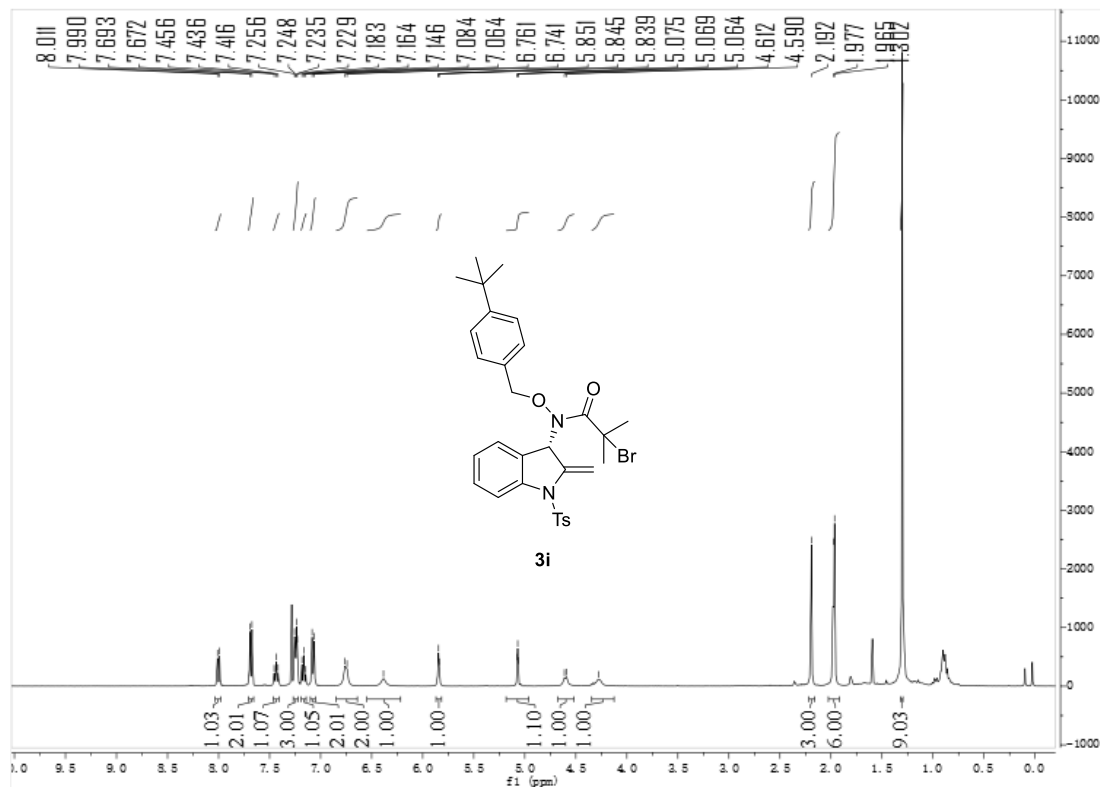
(S)-2-Bromo-N-((4-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3g)



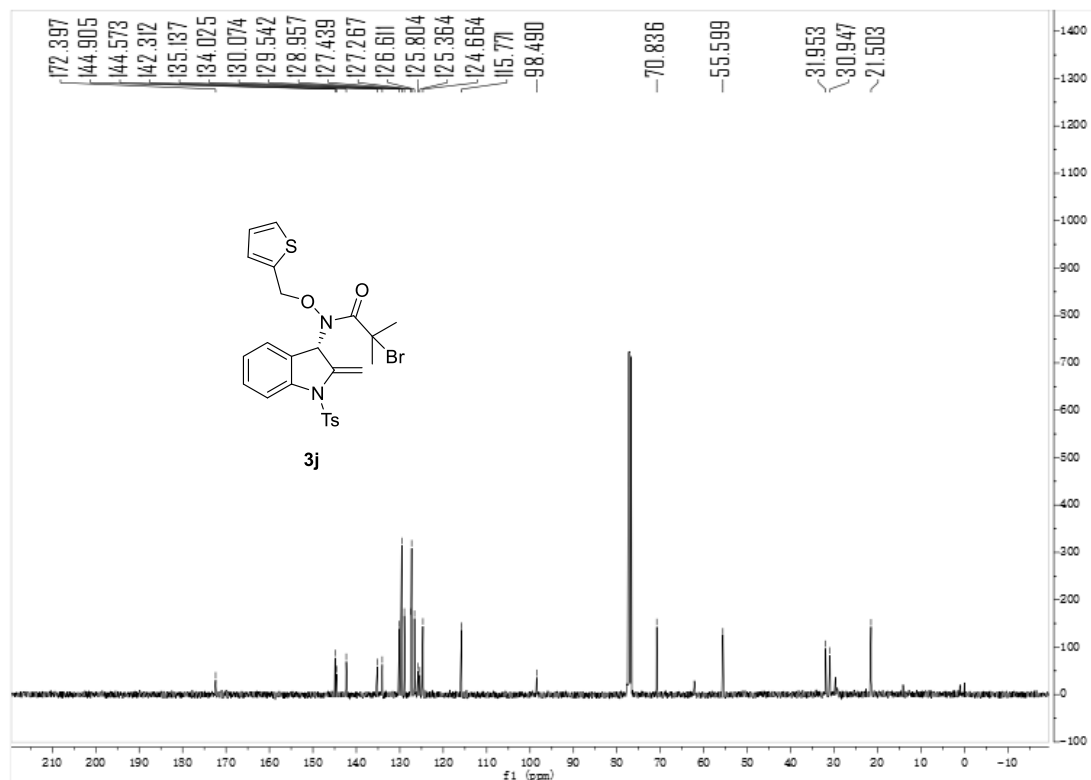
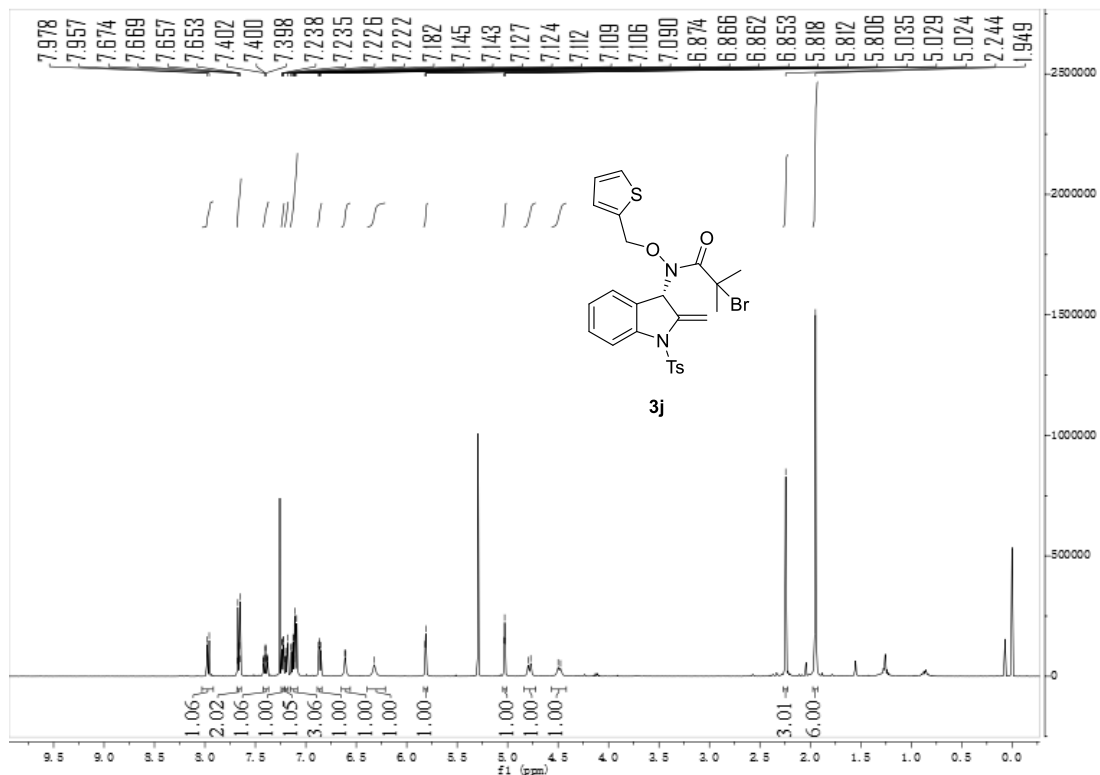
(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-((2-nitrobenzyl)oxy)propanamide (3h)



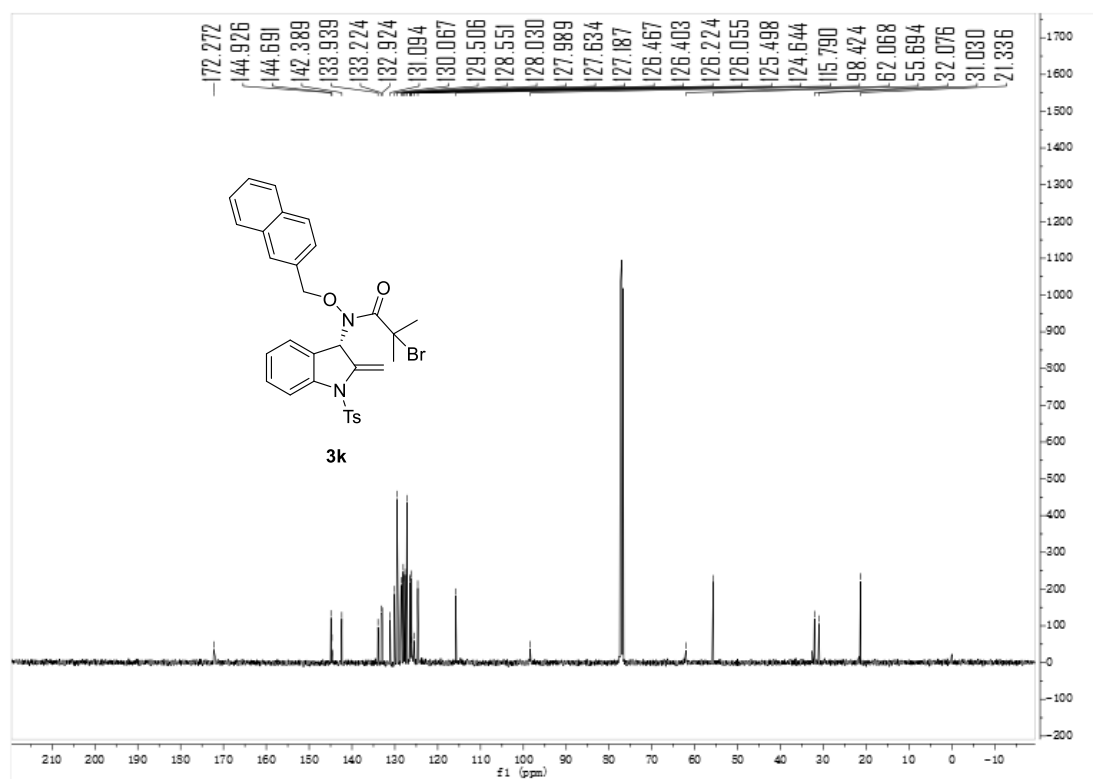
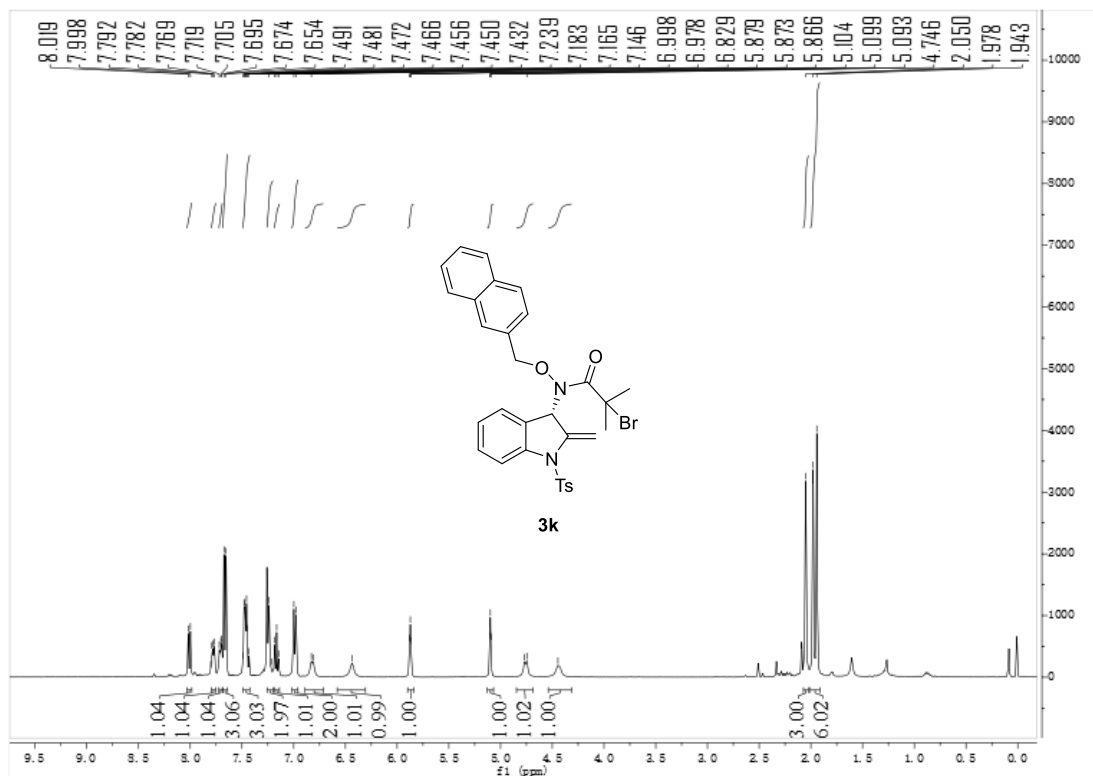
**(S)-2-Bromo-N-((4-*tert*-butyl)benzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)prop
 anamide (3i)**



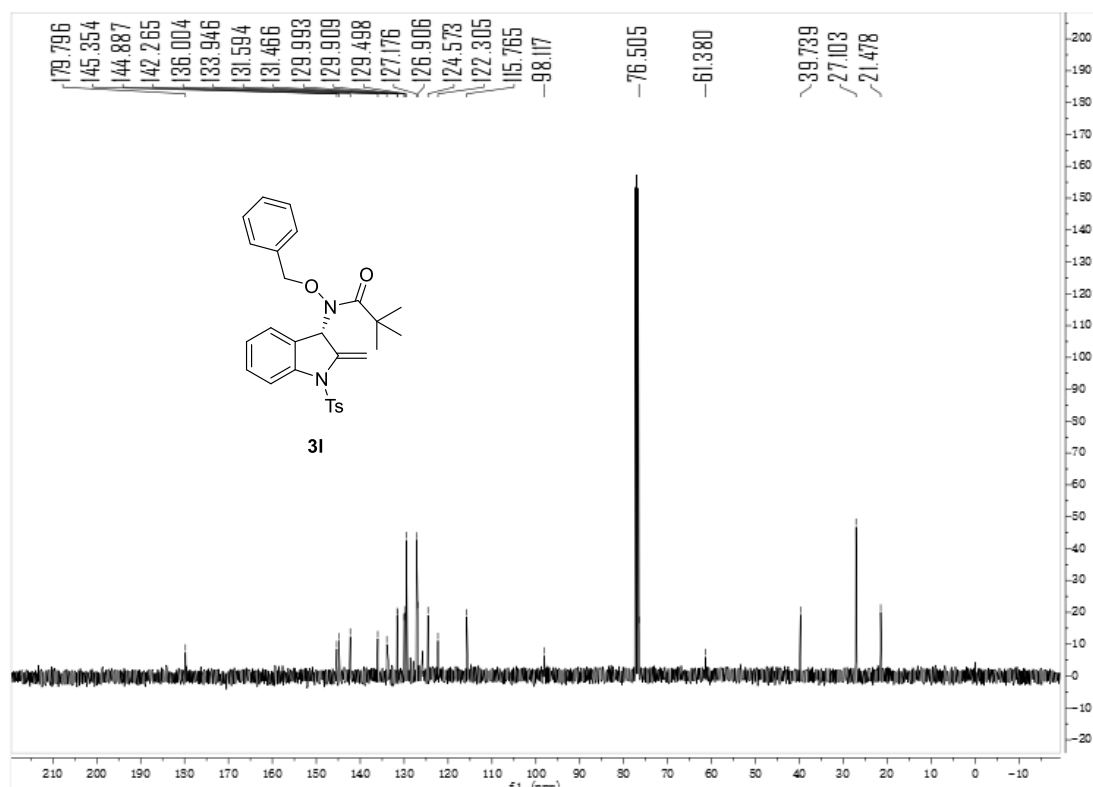
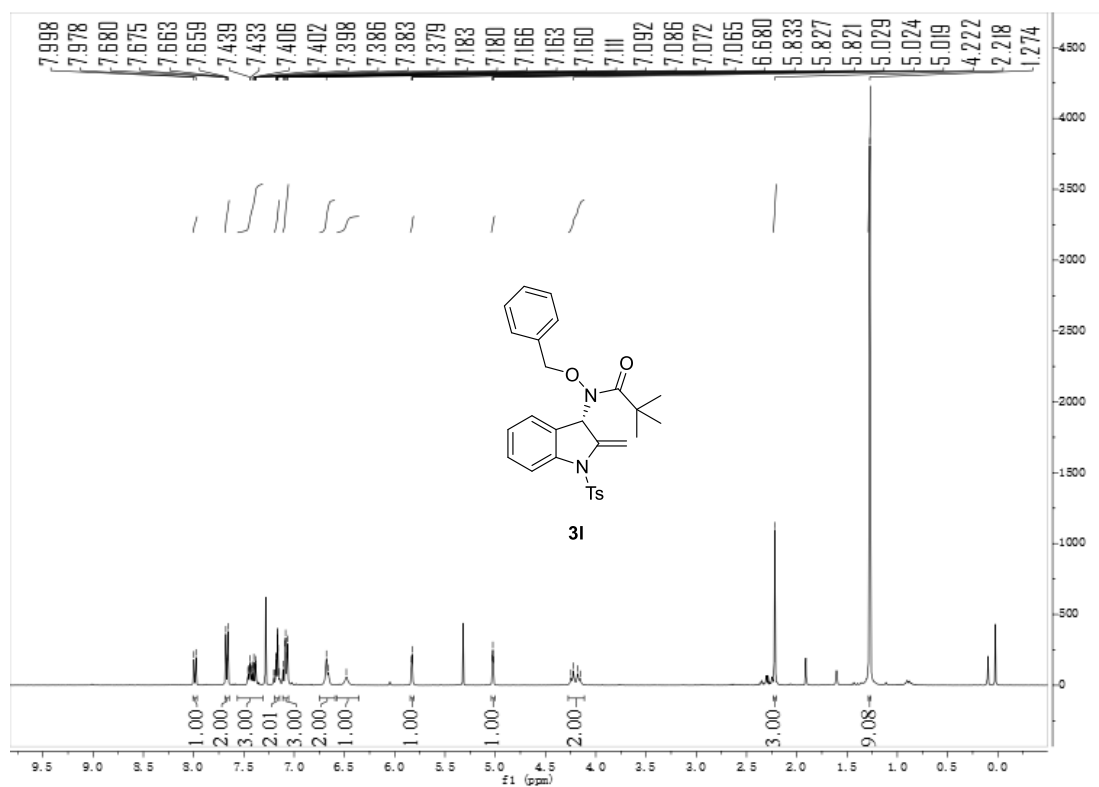
(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-(thiophen-2-ylmethoxy)propanamide (3j)



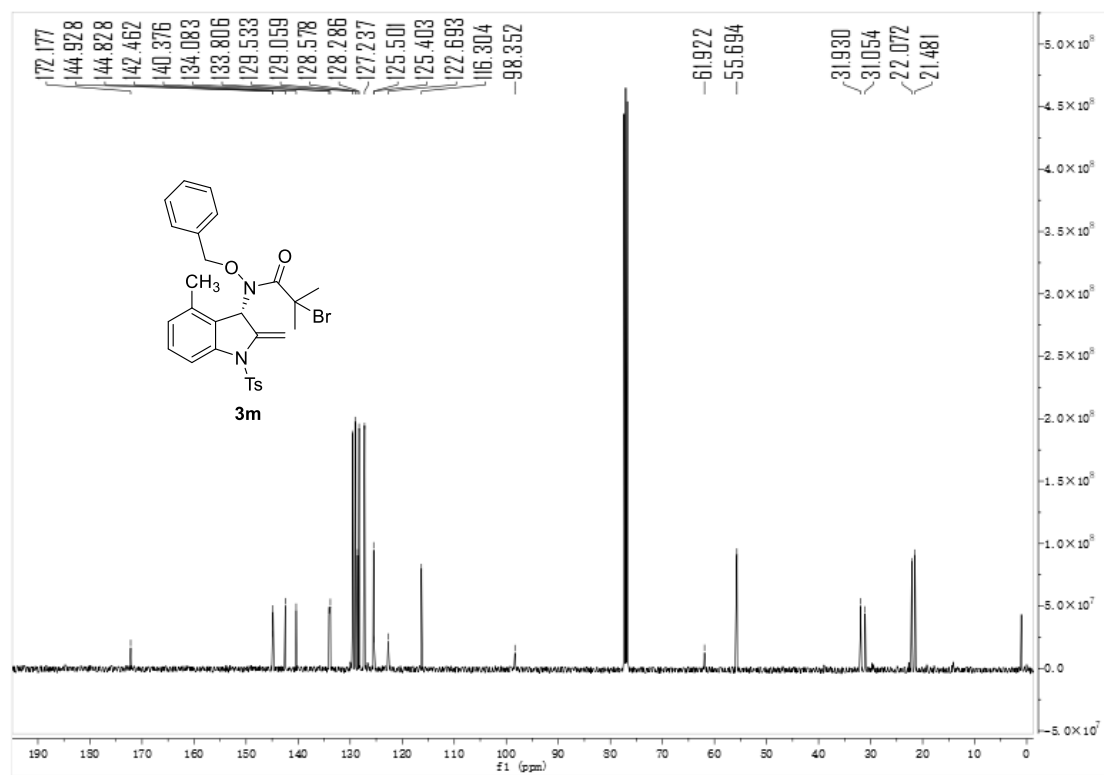
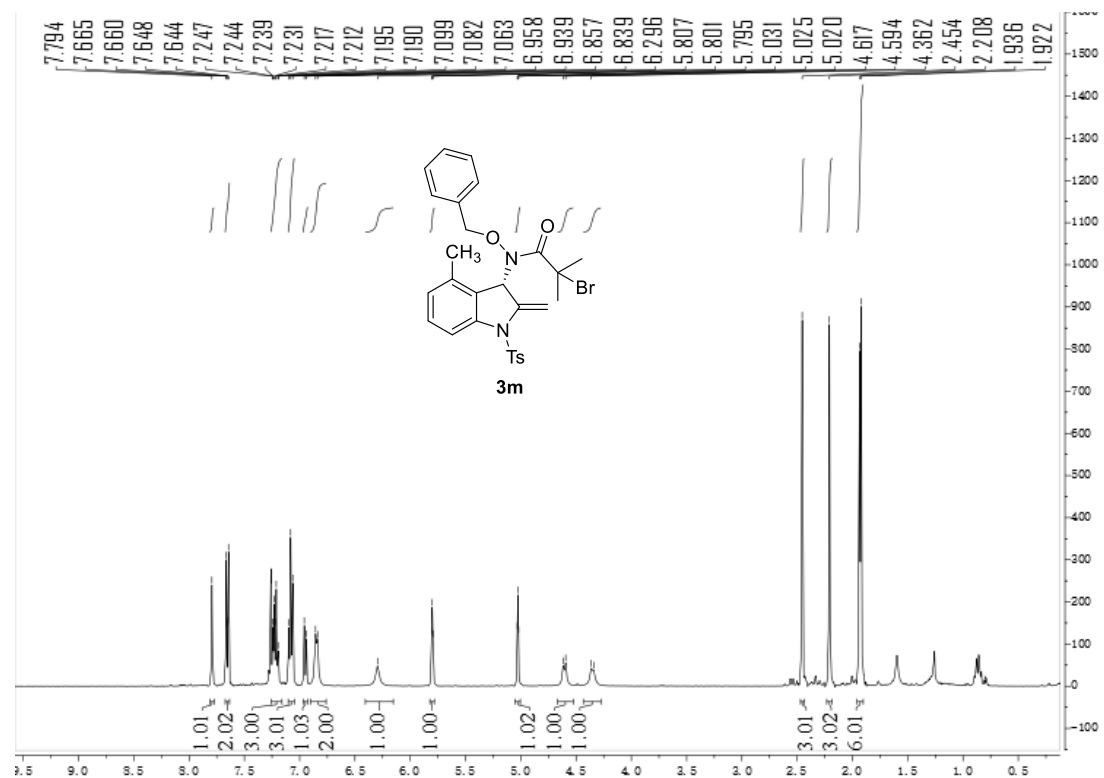
**(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-(naphthalen-2-ylmethoxy)prop
anamide (3k)**



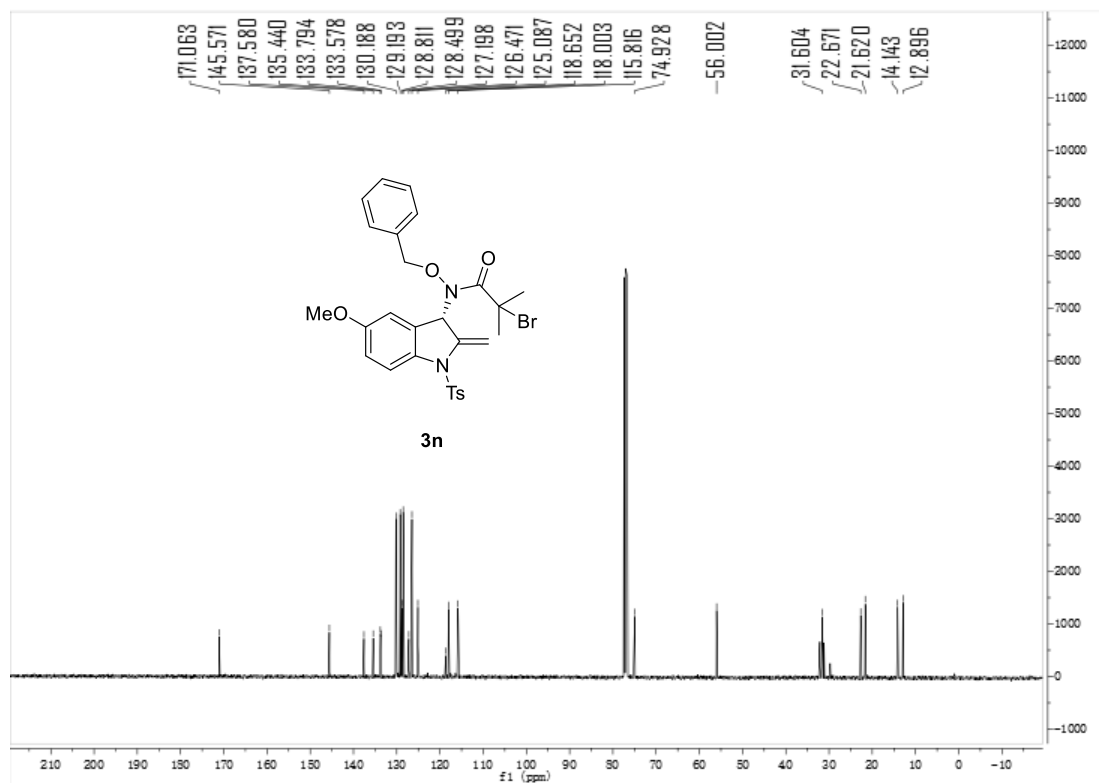
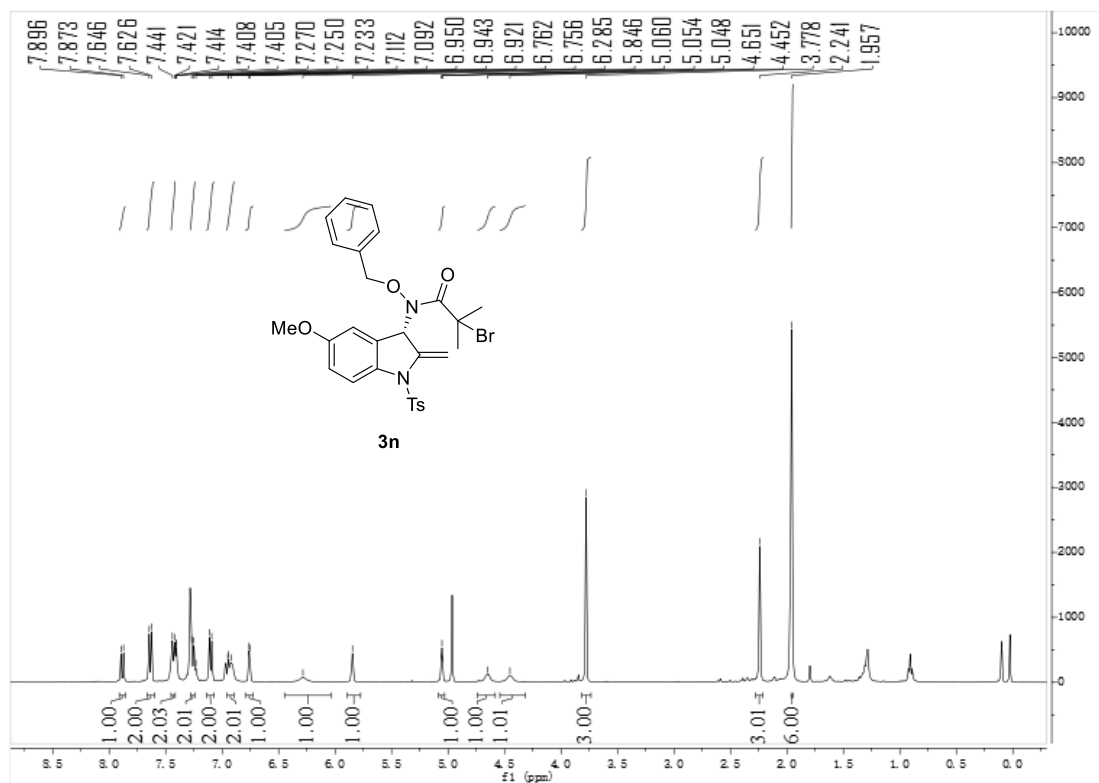
(S)-N-(Benzyloxy)-N-(2-methylene-1-tosylindolin-3-yl)pivalamide (3I)



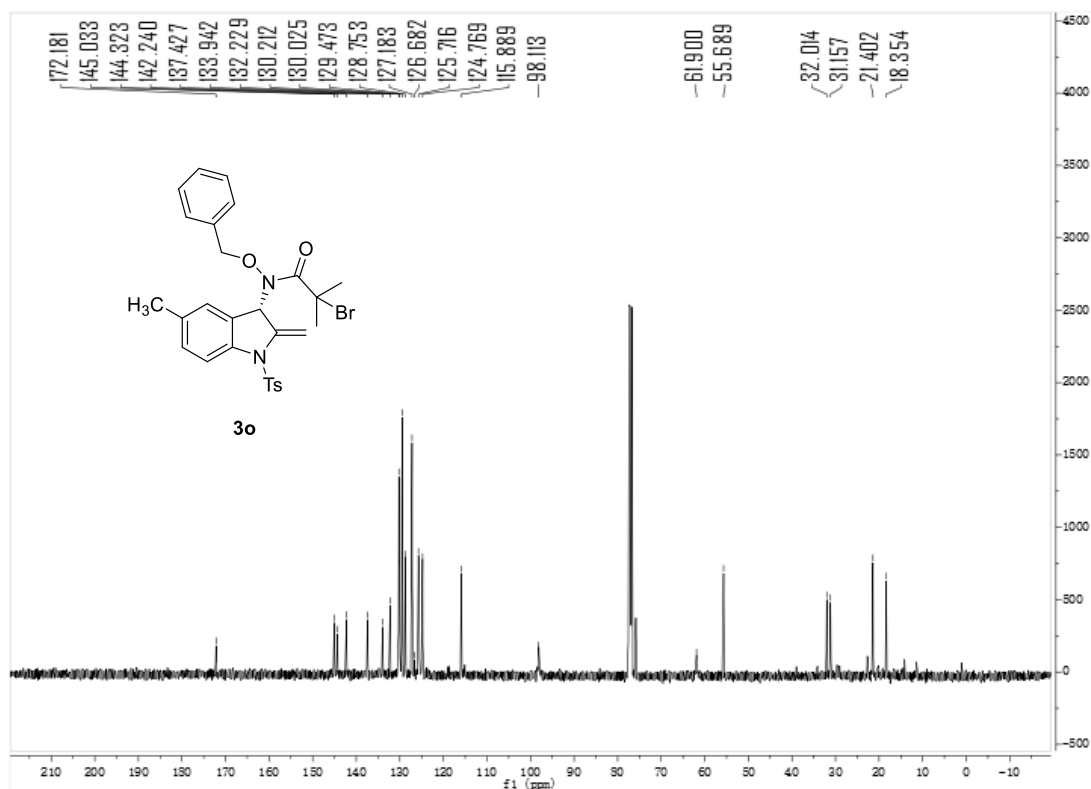
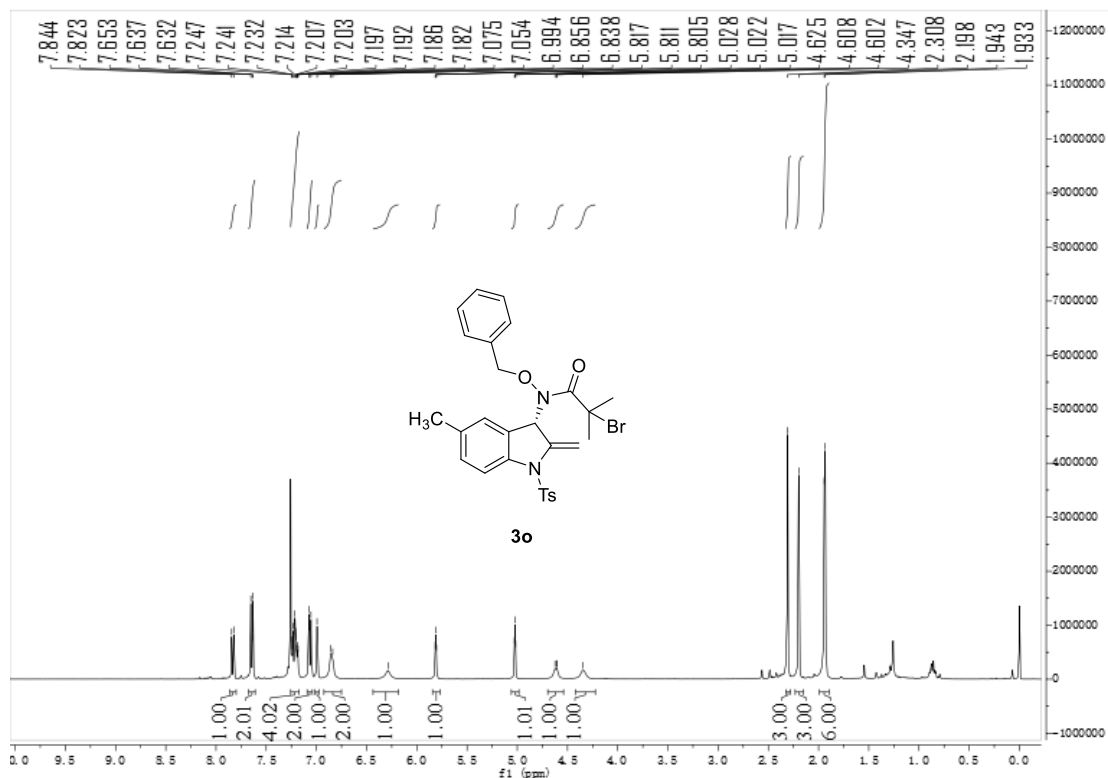
(S)-N-(Benzyloxy)-2-bromo-2-methyl-N-(4-methyl-2-methylene-1-tosylindolin-3-yl)propanamide (3m)



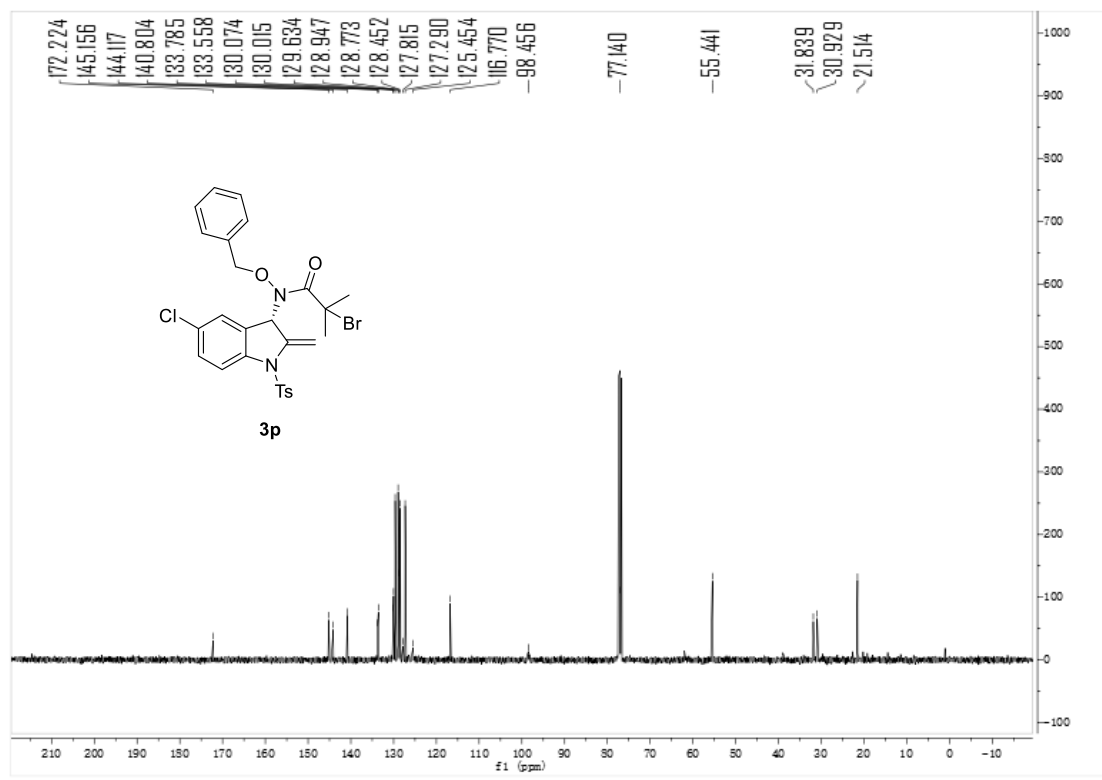
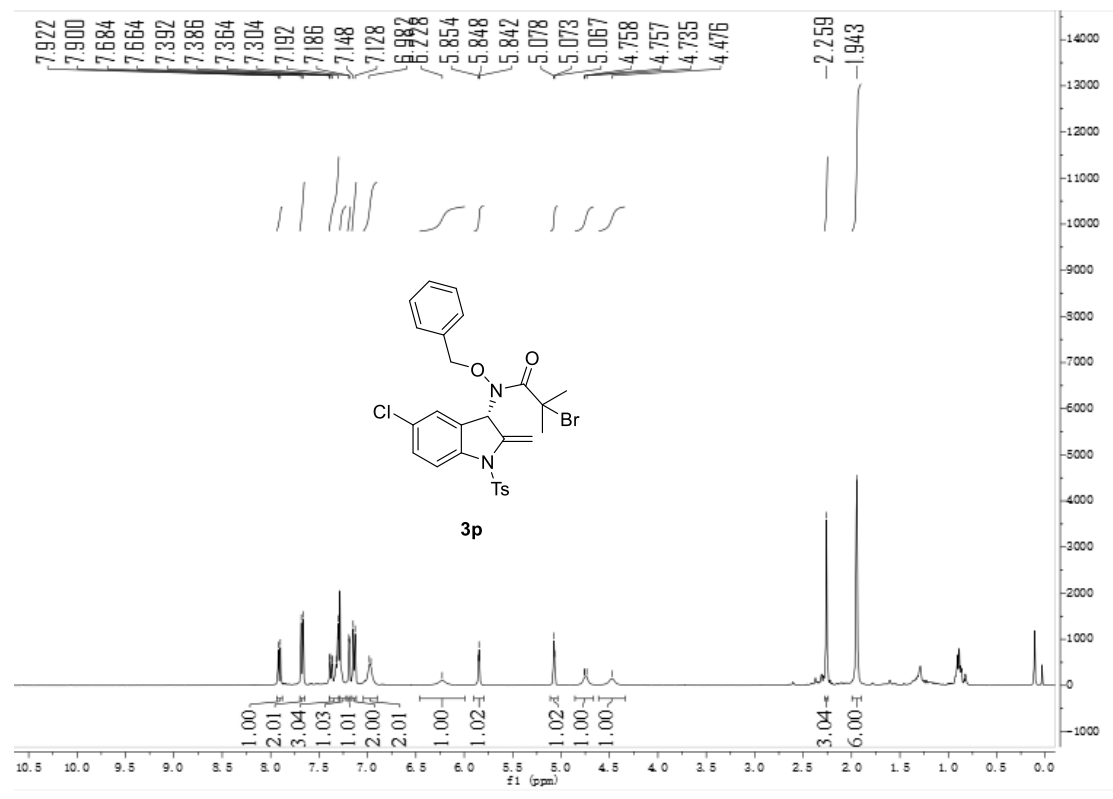
(S)-N-(Benzyloxy)-2-bromo-N-(5-methoxy-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3n)



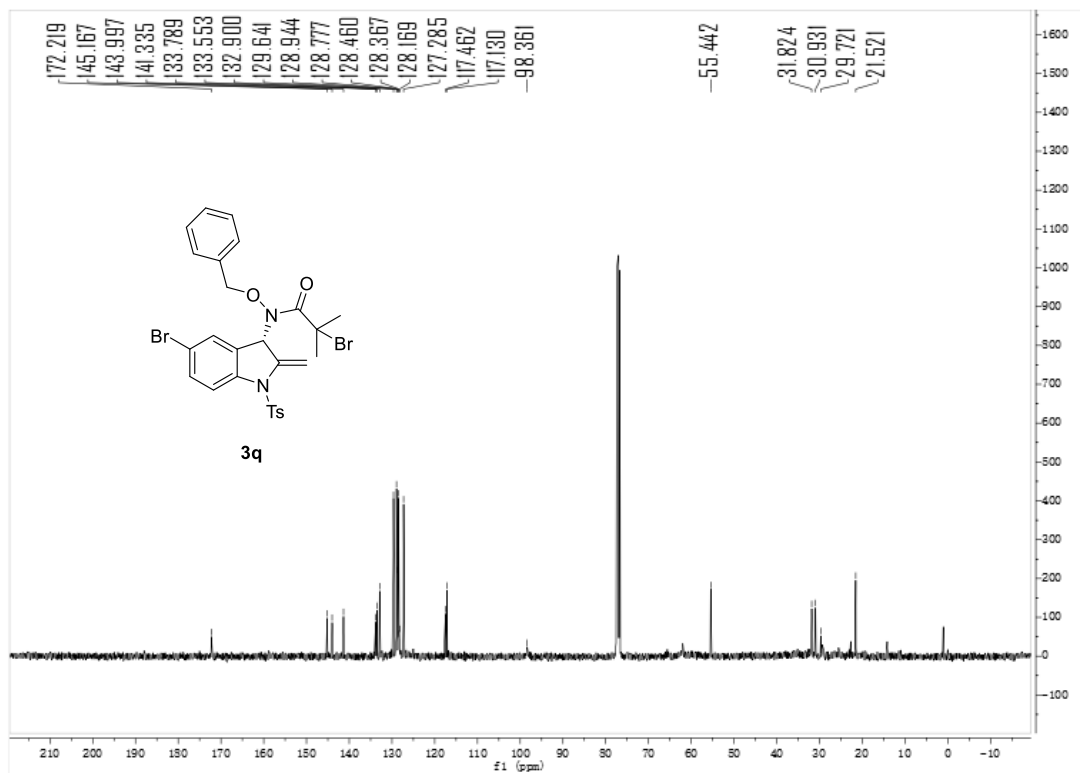
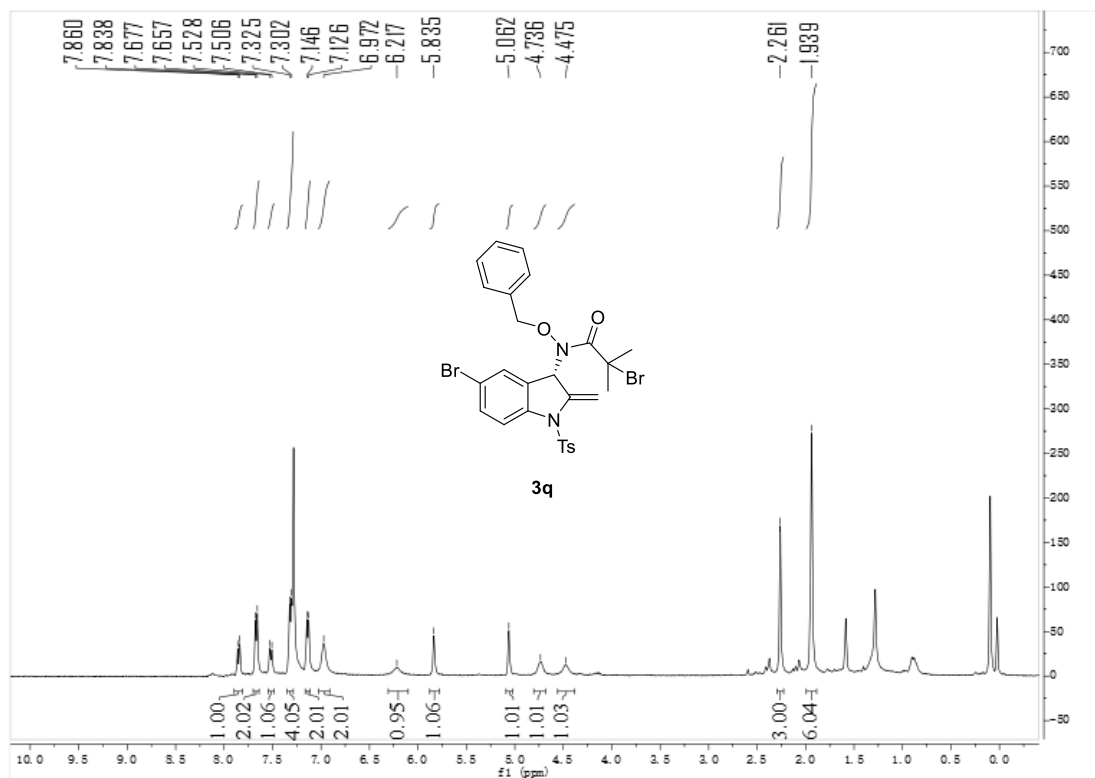
(S)-N-(Benzyloxy)-2-bromo-2-methyl-N-(5-methyl-2-methylene-1-tosylindolin-3-yl)propanamide (3o)



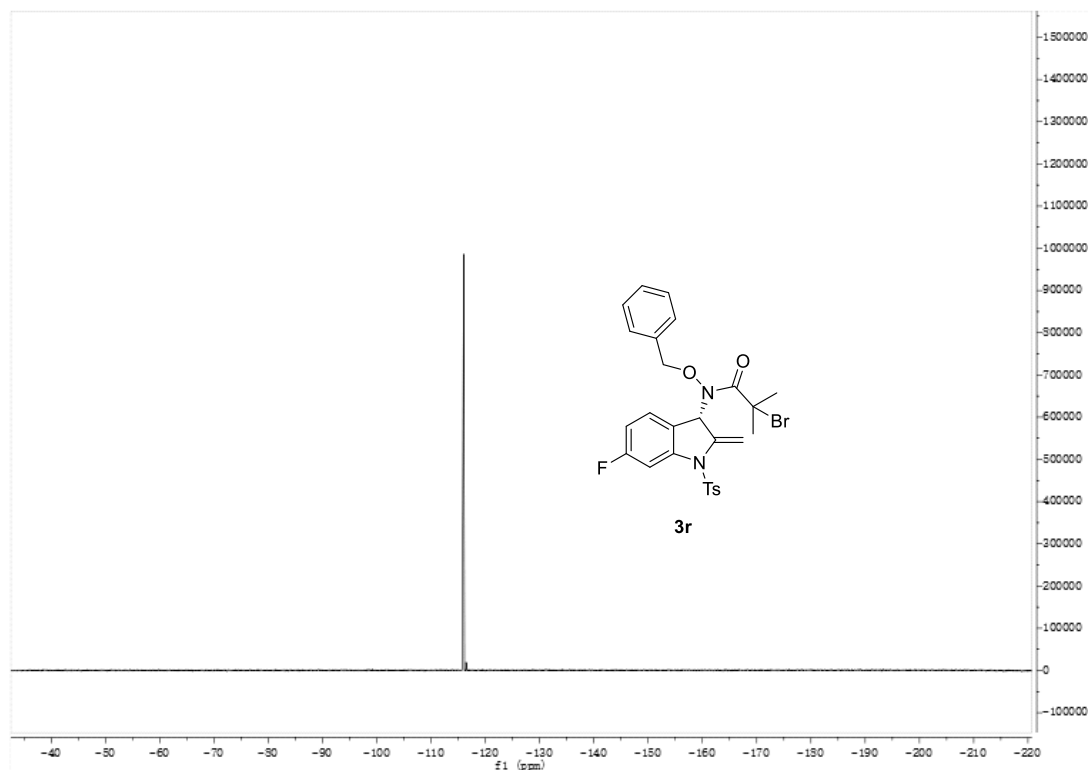
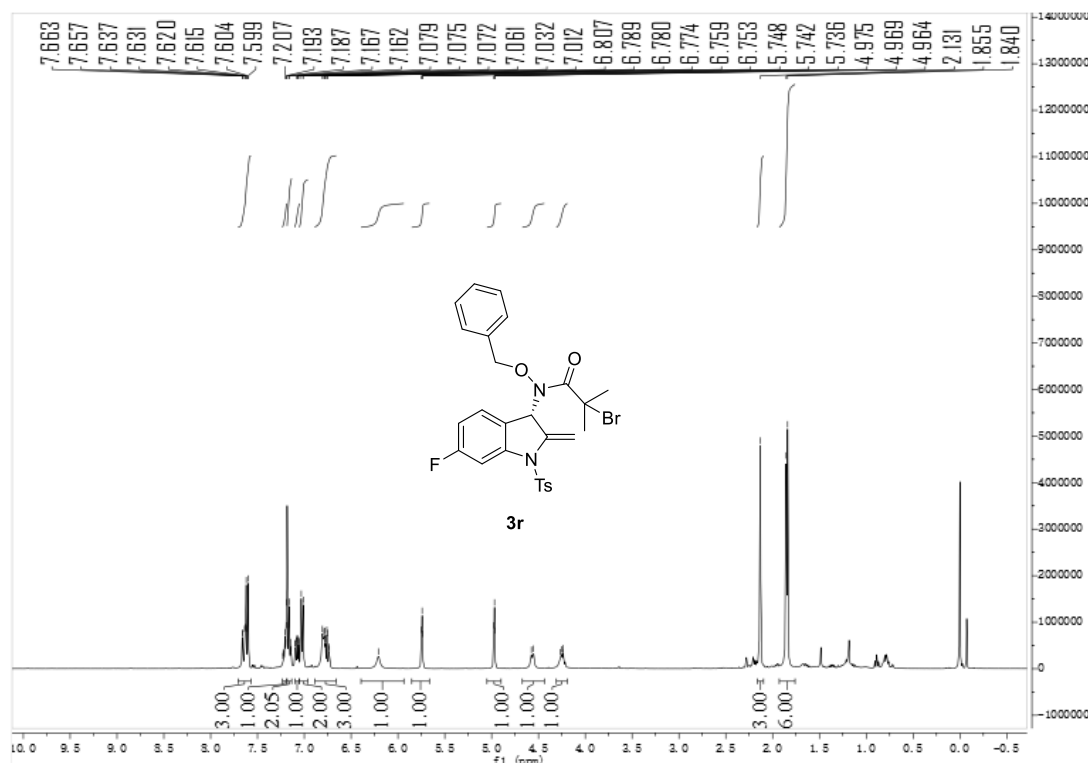
(S)-N-(Benzyloxy)-2-bromo-N-(5-chloro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3p)

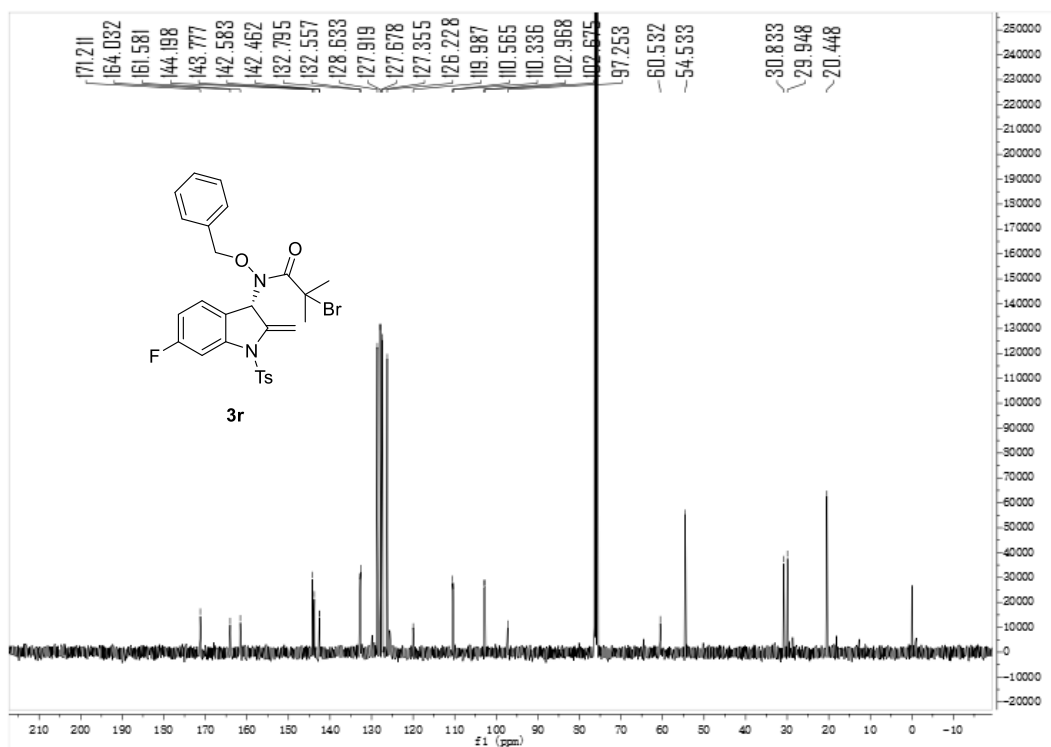


(S)-N-(Benzyloxy)-2-bromo-N-(5-bromo-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3q)

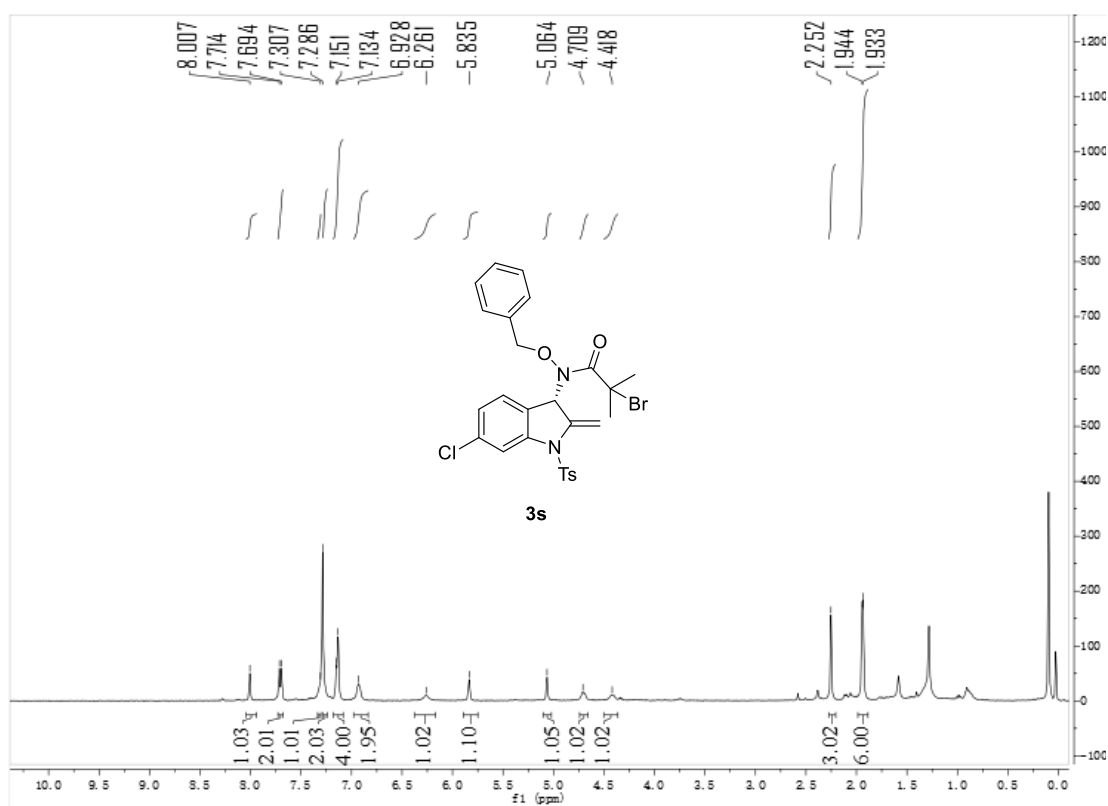


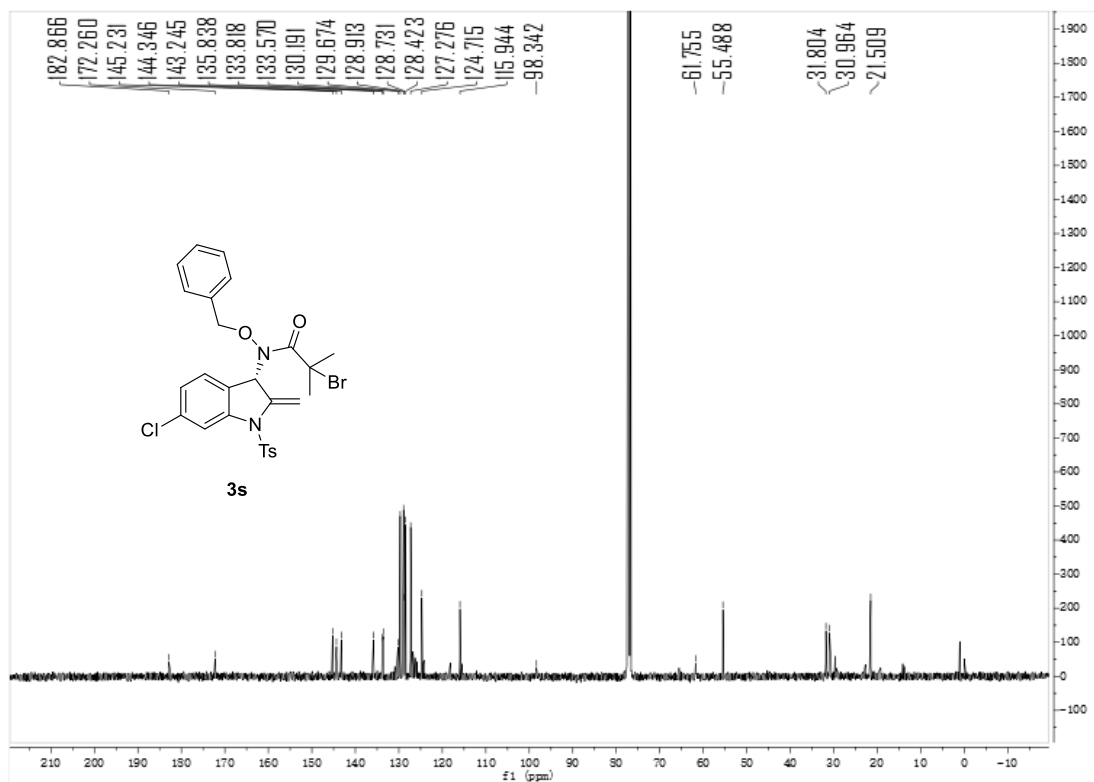
(S)-N-(Benzyloxy)-2-bromo-N-(6-fluoro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3r)



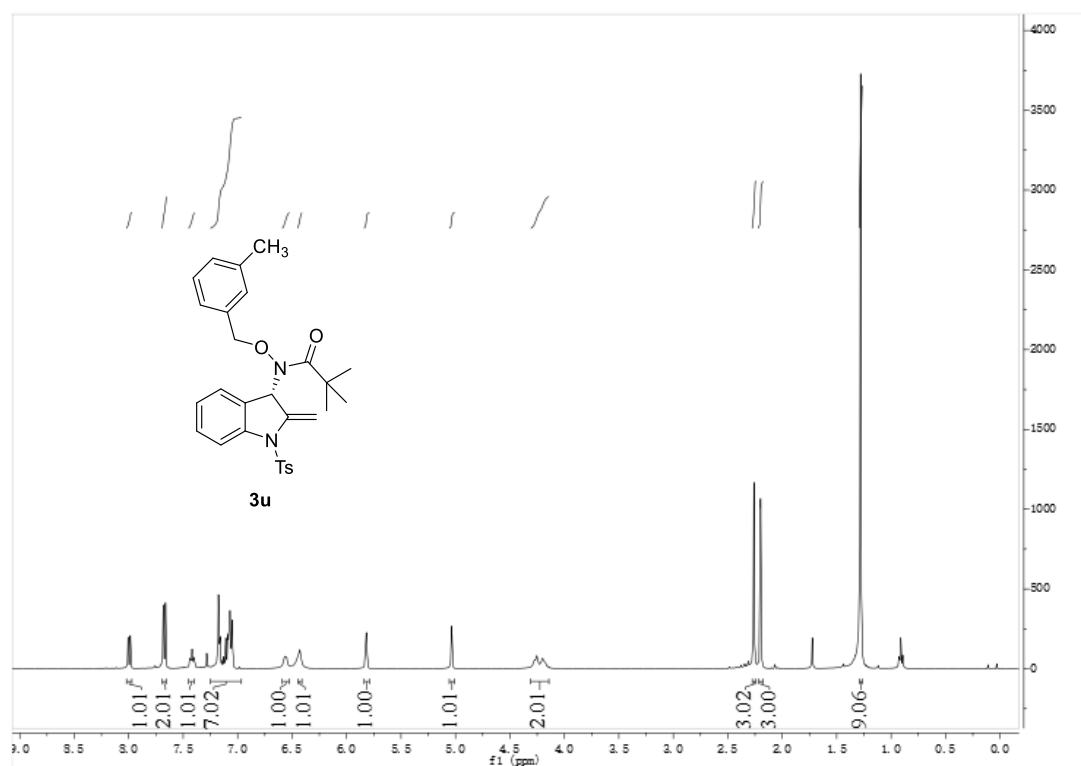


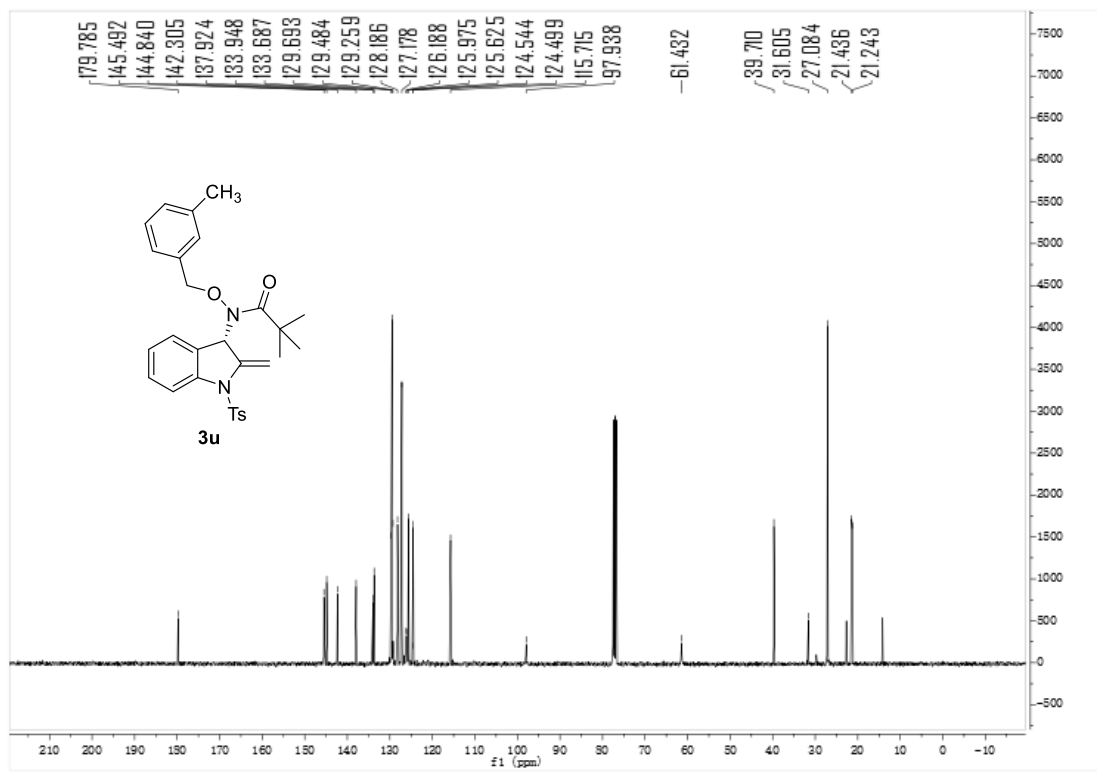
(S)-N-(Benzyloxy)-2-bromo-N-(6-chloro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3s)



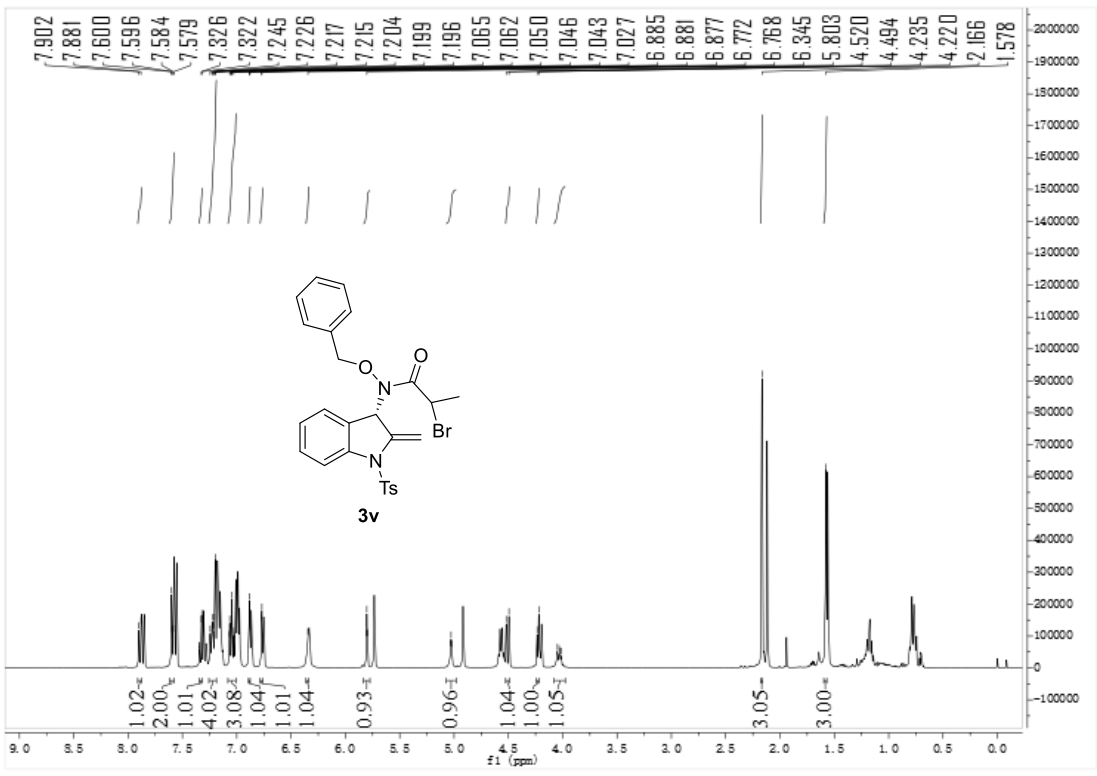


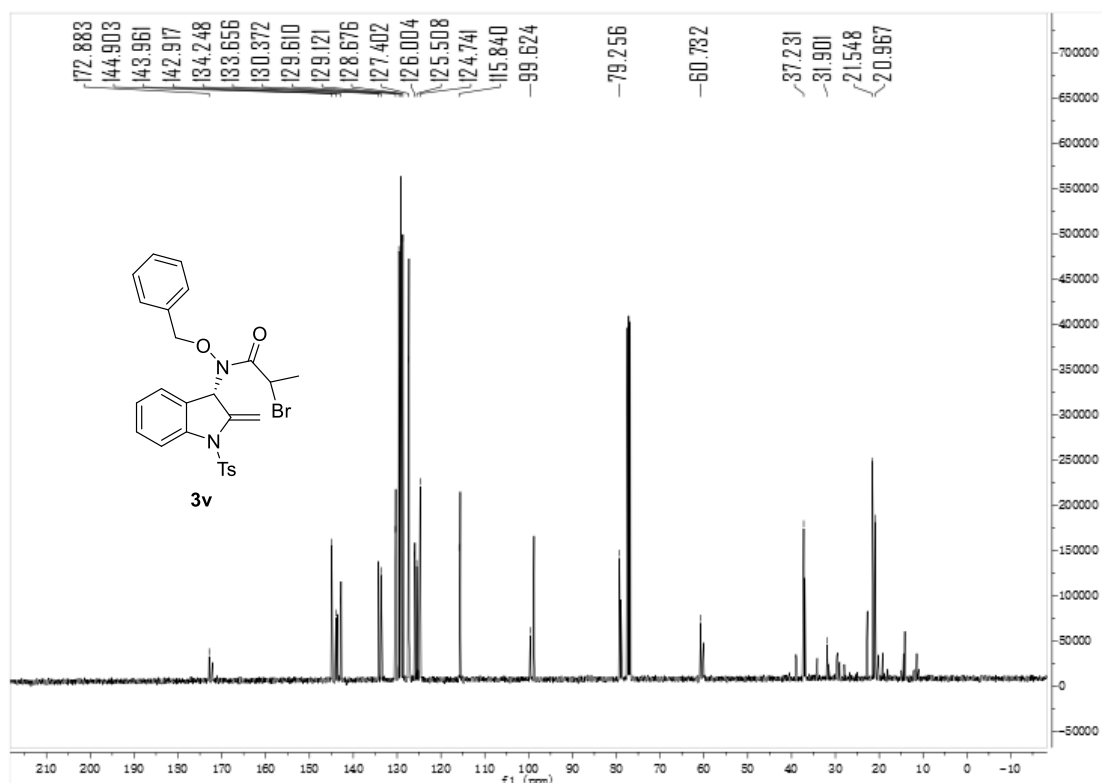
(S)-N-((3-Methylbenzyloxy)-N-(2-methylene-1-tosylindolin-3-yl)pivalamide (3u)



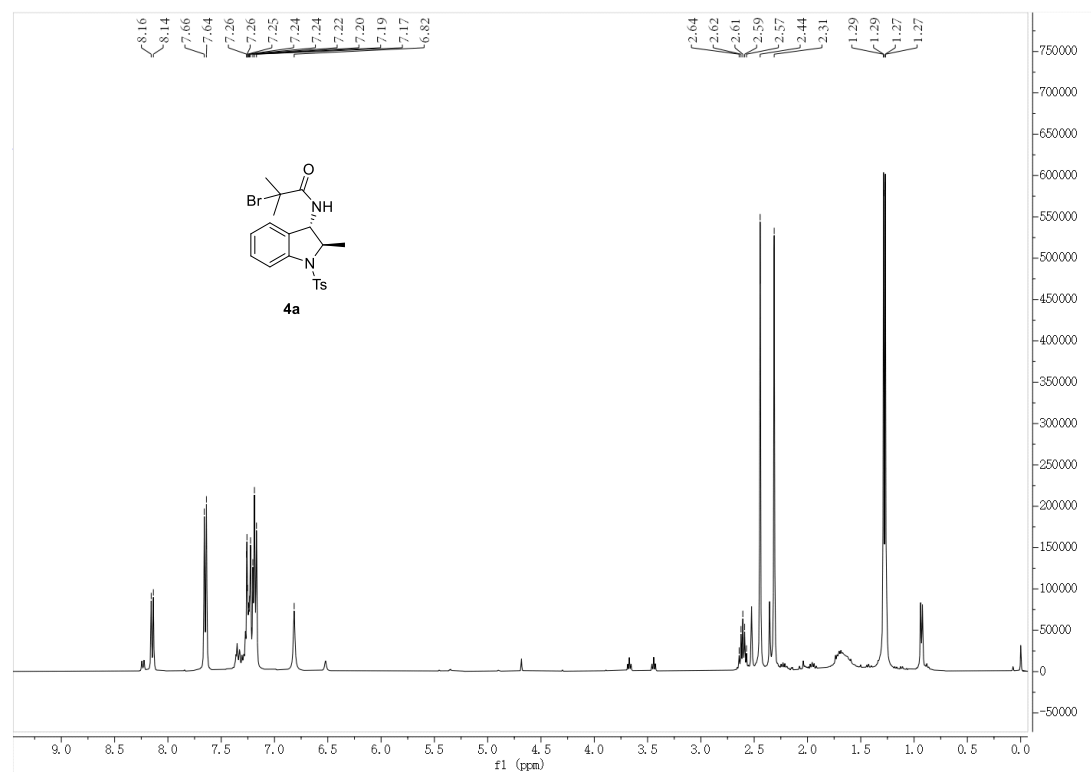


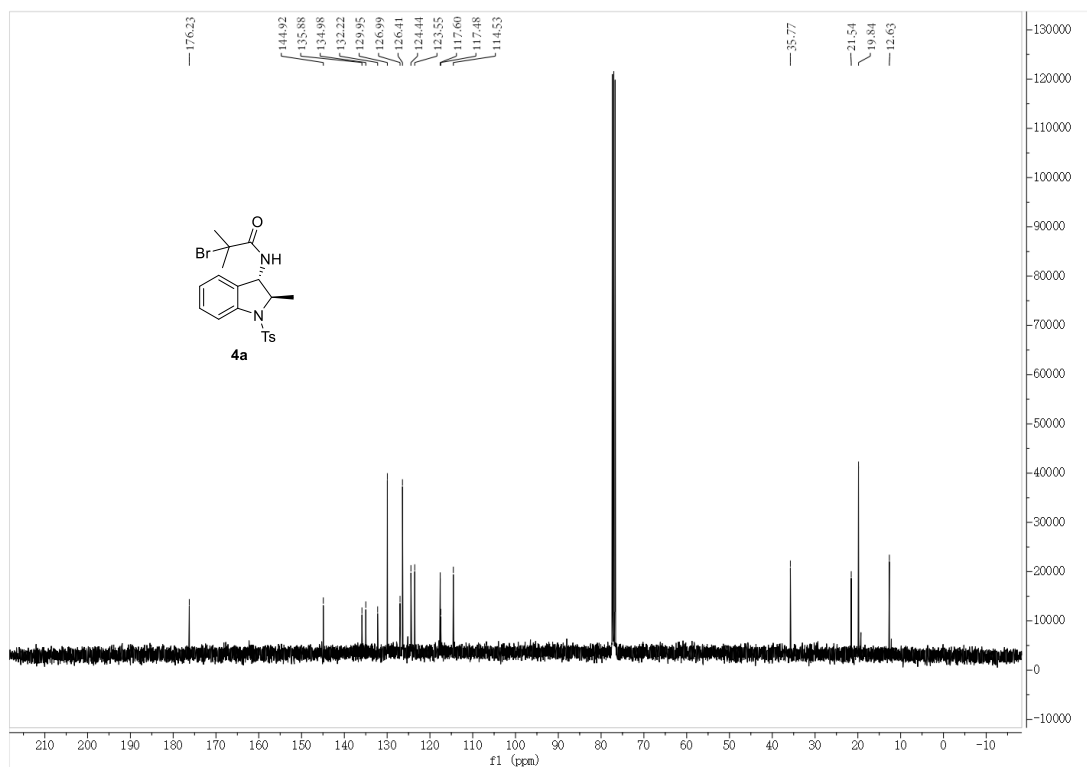
N-(Benzyloxy)-2-bromo-N-((S)-2-methylene-1-tosylindolin-3-yl)propanamide (3v)





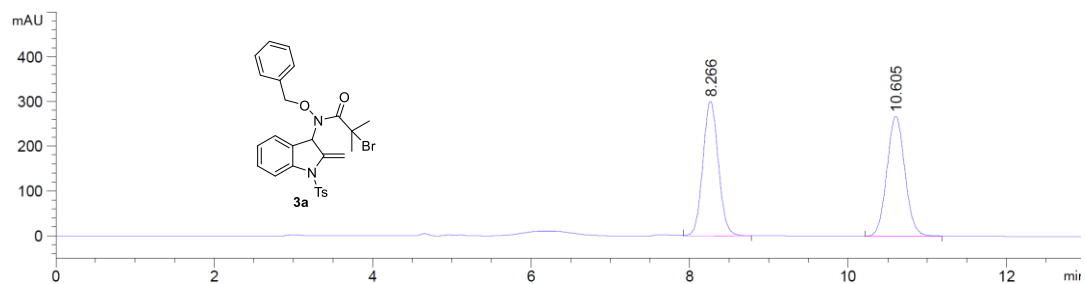
2-Bromo-2-methyl-N-(2-methyl-1-tosylindolin-3-yl)propanamide (4a)



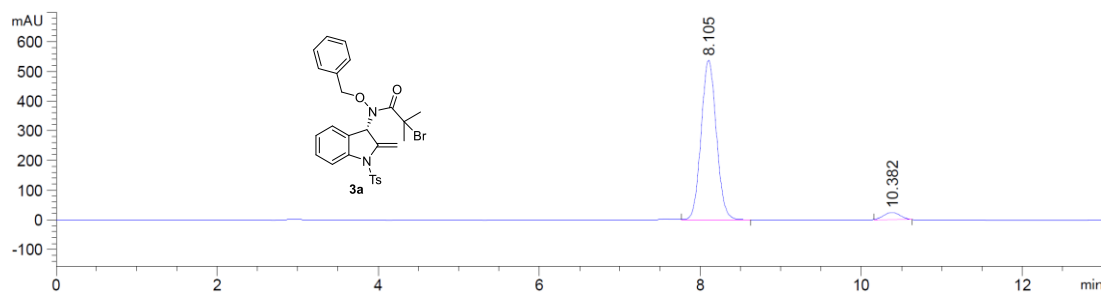


9. HPLC analysis

(S)-N-(Benzyloxy)-2-bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3a)

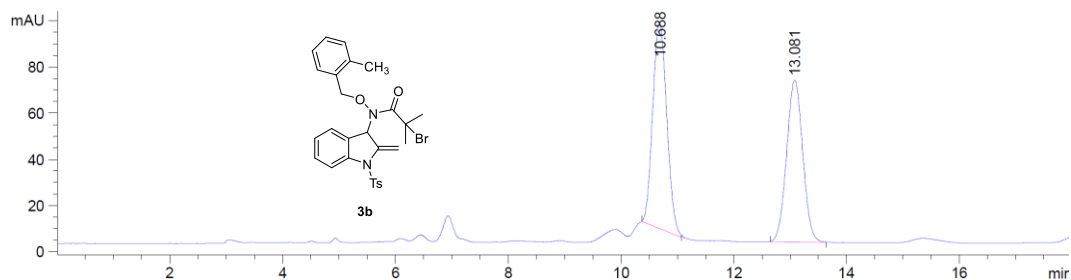


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.266	VB	0.2108	4095.63599	300.81244	49.1807
2	10.605	BB	0.2465	4232.08740	267.59000	50.8193

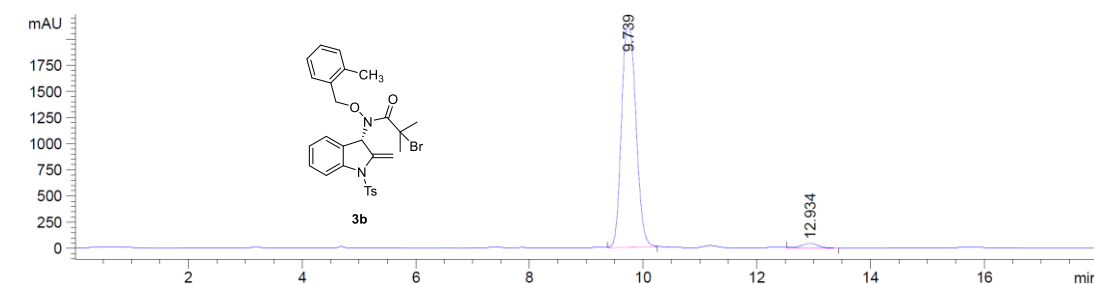


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.105	VB	0.2061	7099.11035	537.44067	95.3038
2	10.382	MM R	0.2362	349.81824	24.68545	4.6962

(S)-2-Bromo-2-methyl-N-((2-methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3b)

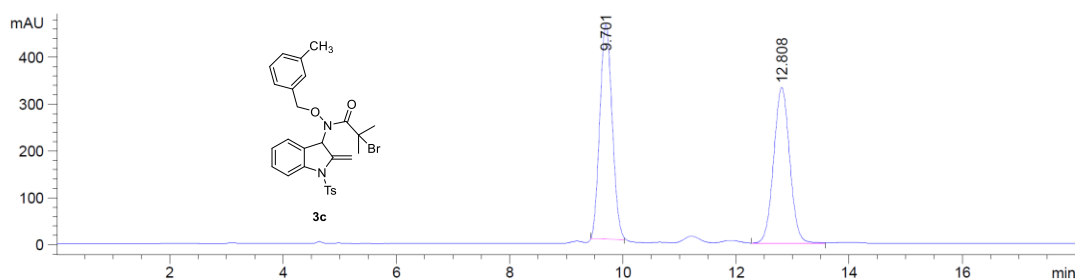


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.688	MM R	0.2879	1540.93823	89.20995	52.4158
2	13.081	BB	0.3106	1398.89844	70.17805	47.5842

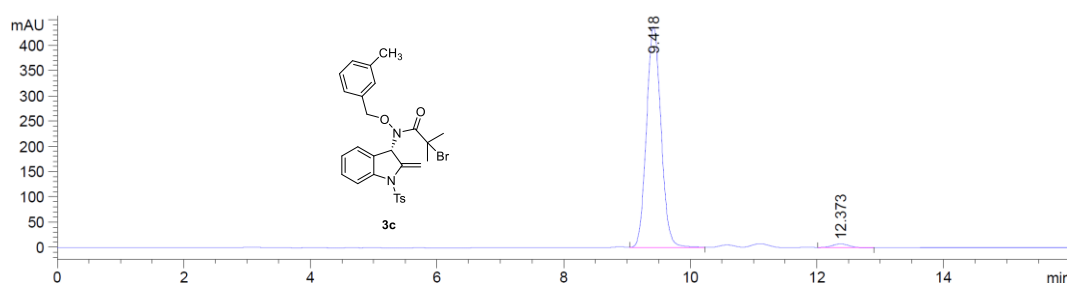


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.739	MM R	0.2940	3.74368e4	2122.28491	97.6240
2	12.934	VB	0.3169	911.15863	44.12291	2.3760

(S)-2-Bromo-2-methyl-N-((3-methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3c)

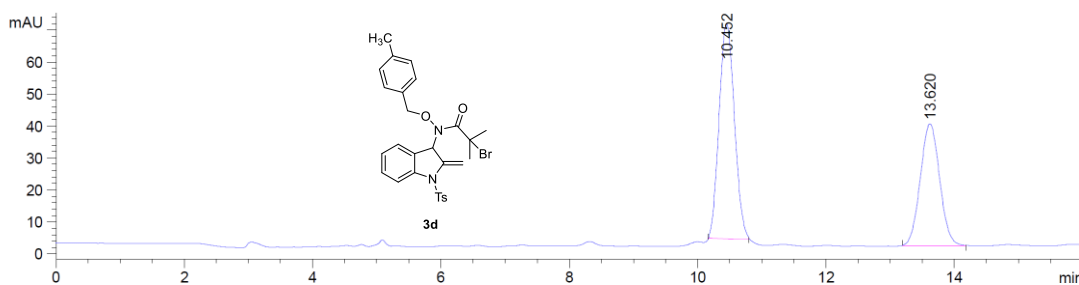


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.701	MM R	0.2525	6934.50977	457.72009	51.4383
2	12.808	VB	0.3060	6546.71387	332.09341	48.5617

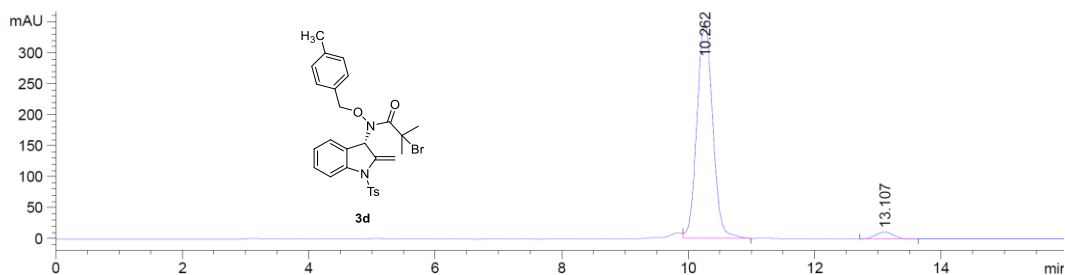


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.418	VB	0.2490	7006.99121	437.21567	98.1587
2	12.373	BB	0.2913	131.43637	7.18949	1.8413

(S)-2-Bromo-2-methyl-N-((4-methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3d)

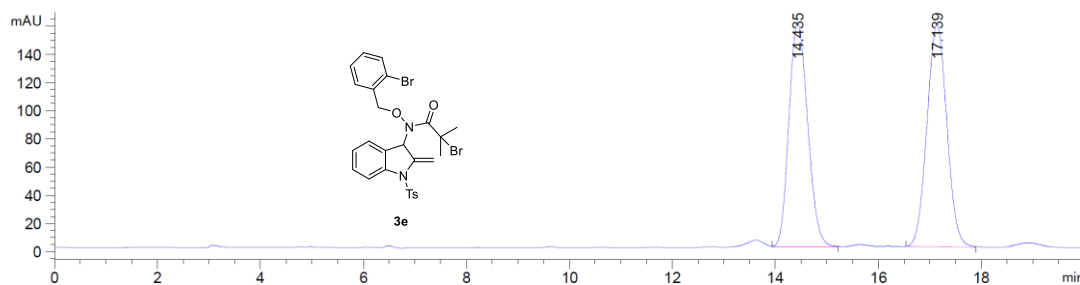


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.452	MM R	0.2766	1113.26782	67.09181	58.1427
2	13.620	BB	0.3248	801.44763	38.19431	41.8573

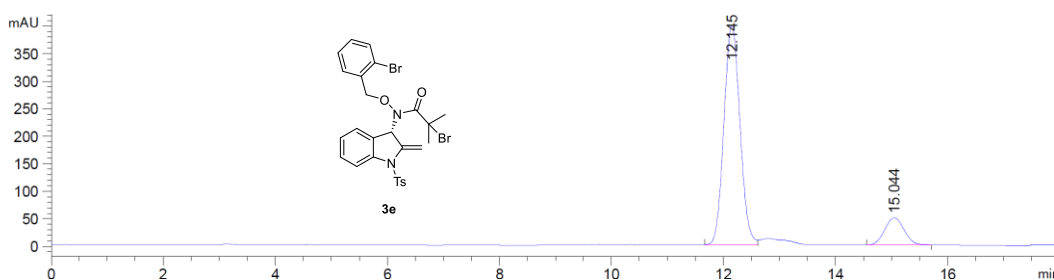


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.262	VB	0.2716	6030.95605	348.94528	96.4527
2	13.107	BB	0.3114	221.80266	11.08792	3.5473

(S)-2-Bromo-N-((2-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide (3e)



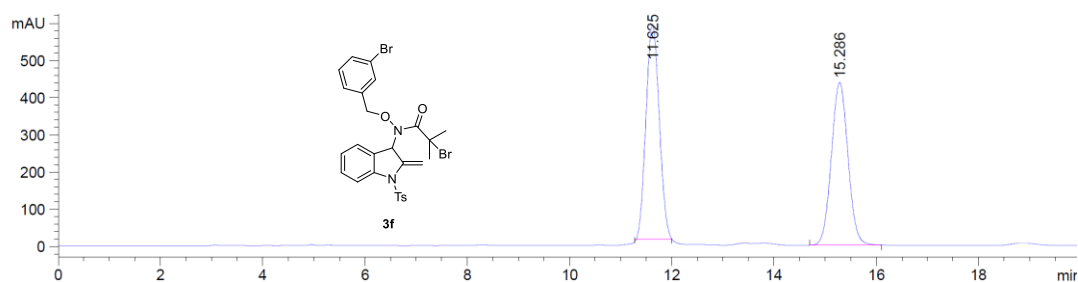
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.435	VB	0.4020	4019.47827	158.42595	48.7142
2	17.139	BB	0.4189	4231.65918	157.77069	51.2858



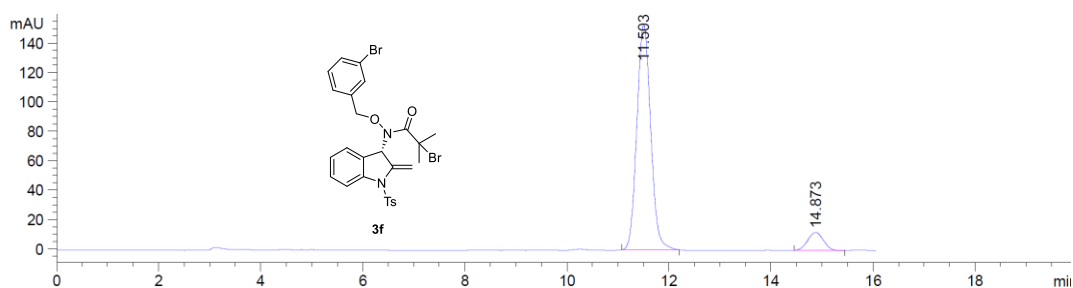
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.145	BV	0.3143	7947.54297	399.22491	86.9564
2	15.044	BB	0.3787	1192.14197	49.55152	13.0436

(S)-2-Bromo-N-((3-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propanamide

mide (3f)



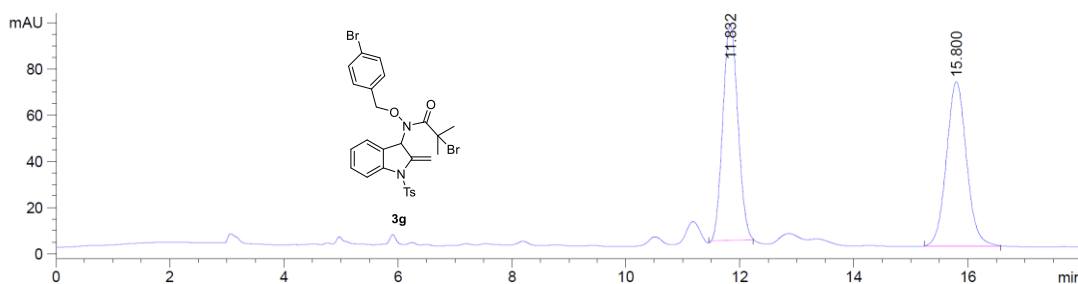
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.625	MM R	0.3020	1.04316e4	575.74109	51.3088
2	15.286	BB	0.3521	9899.39648	437.27695	48.6912



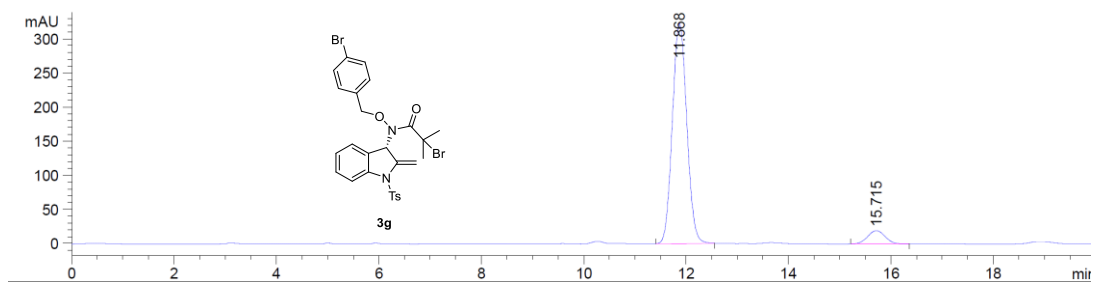
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.503	BB	0.2973	2898.70630	152.84995	91.5935
2	14.873	BB	0.3322	266.04453	12.40339	8.4065

(S)-2-Bromo-N-((4-bromobenzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)propana

mide (3g)

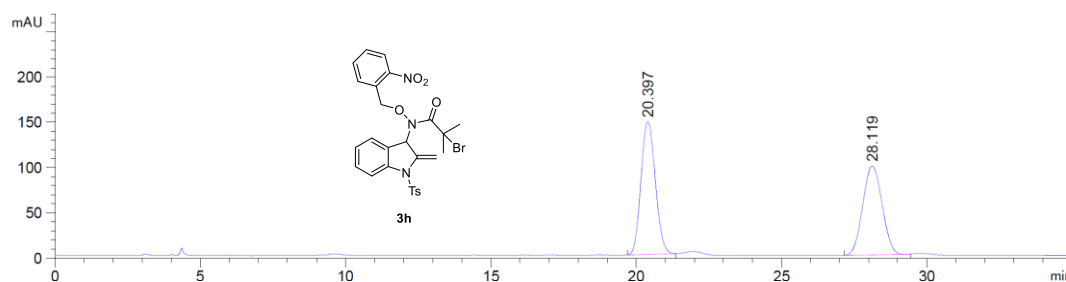


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.832	MM R	0.3060	1717.83191	93.54917	49.4803
2	15.800	BB	0.3788	1753.91956	71.33910	50.5197

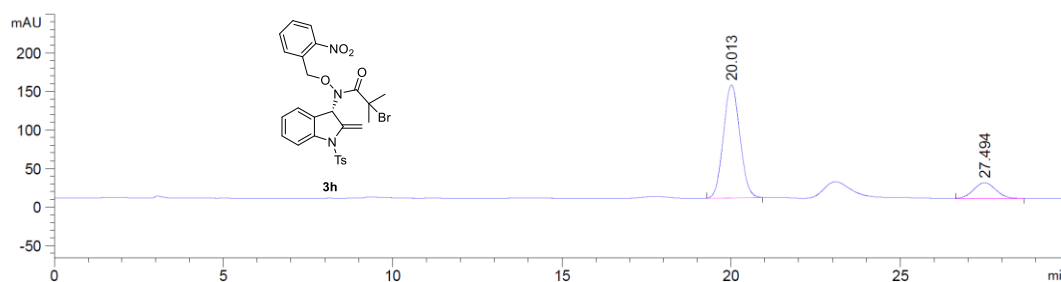


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.868	BB	0.3087	6329.94287	322.91061	93.1754
2	15.715	BB	0.3732	463.63763	19.51573	6.8246

(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-((2-nitrobenzyl)oxy)propanamide (3h)

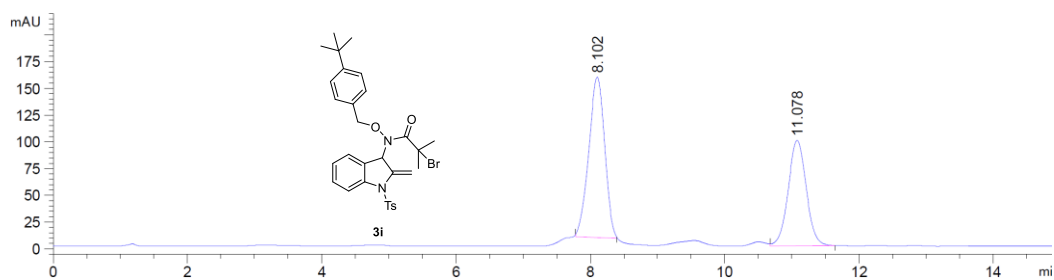


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.397	BB	0.5438	5059.26563	146.90410	52.7727
2	28.119	BB	0.7337	4527.64111	98.23447	47.2273

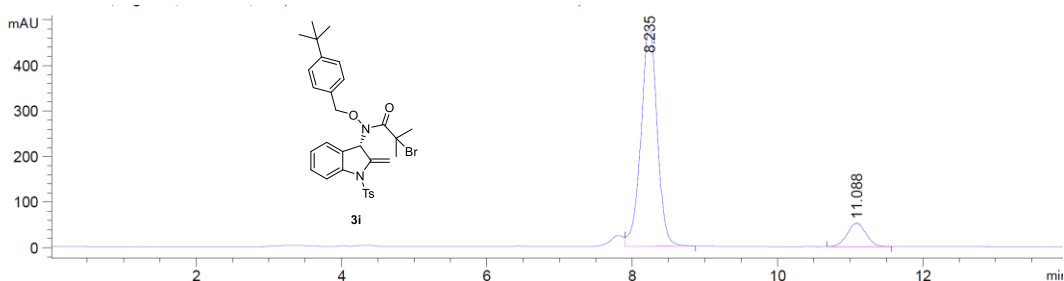


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.013	BB	0.5273	4955.48242	146.26797	84.5142
2	27.494	BB	0.6621	908.01160	20.13618	15.4858

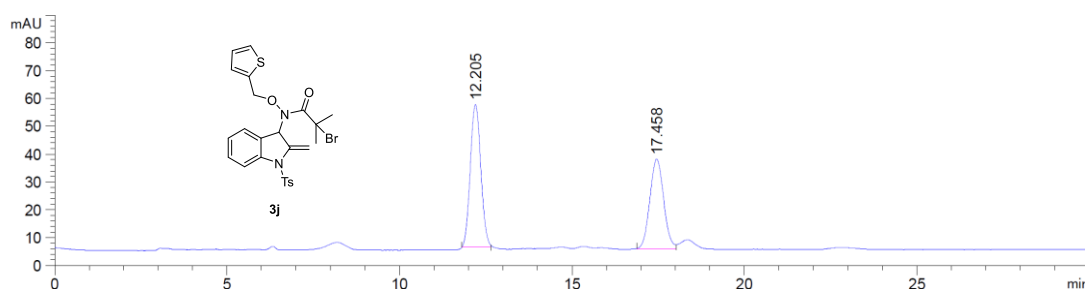
(S)-2-Bromo-N-((4-(tert-butyl)benzyl)oxy)-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)prop

anamide (3i)

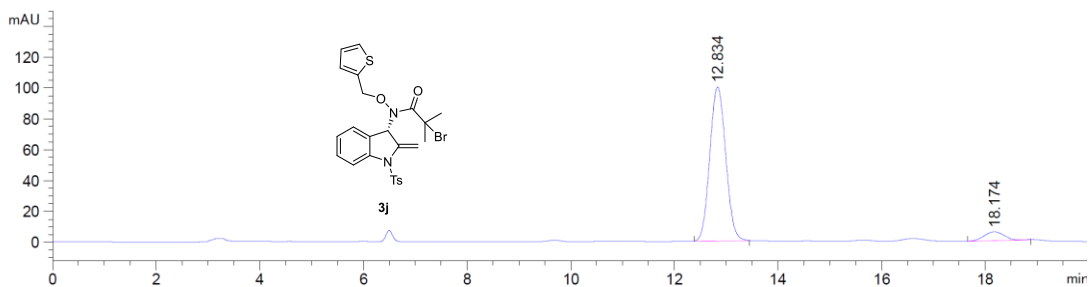
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.102	MM R	0.2743	2467.32739	149.93425	57.2067
2	11.078	VB	0.2882	1845.67664	98.67152	42.7933



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.235	VB	0.2362	7457.28271	482.71515	88.9686
2	11.088	BB	0.2783	924.64154	51.30435	11.0314

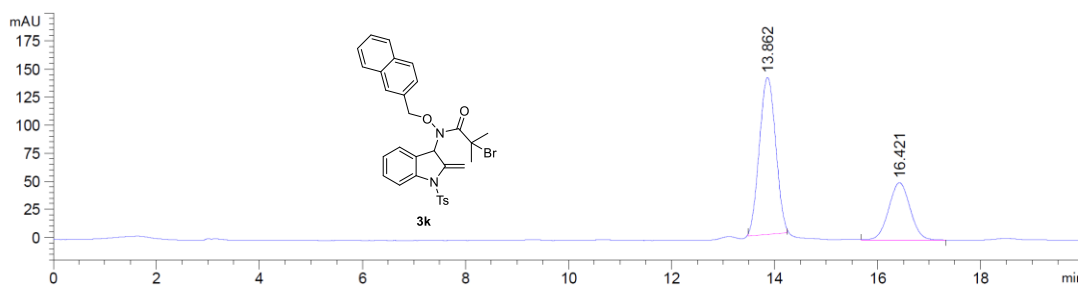
(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-(thiophen-2-ylmethoxy)propanamide (3j)**amide (3j)**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.205	MM R	0.3542	1087.42798	51.16527	54.5912
2	17.458	BV	0.4402	904.51929	32.34726	45.4088

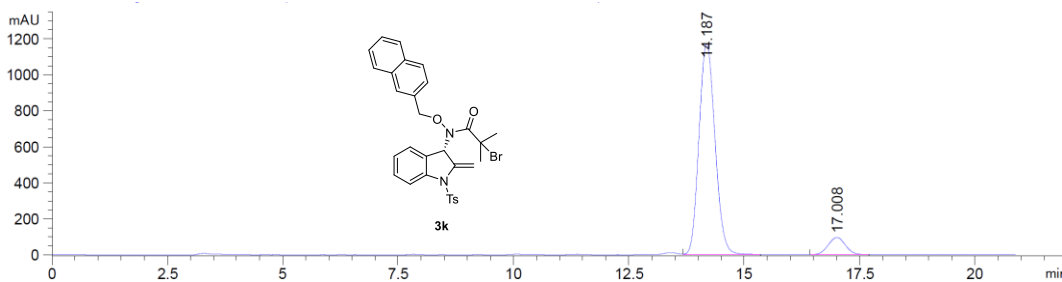


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.834	BB	0.3353	2135.30176	99.92389	93.2438
2	18.174	BB	0.4222	154.71880	5.70914	6.7562

**(S)-2-Bromo-2-methyl-N-(2-methylene-1-tosylindolin-3-yl)-N-(naphthalen-2-ylmethoxy)prop
anamide (3k)**

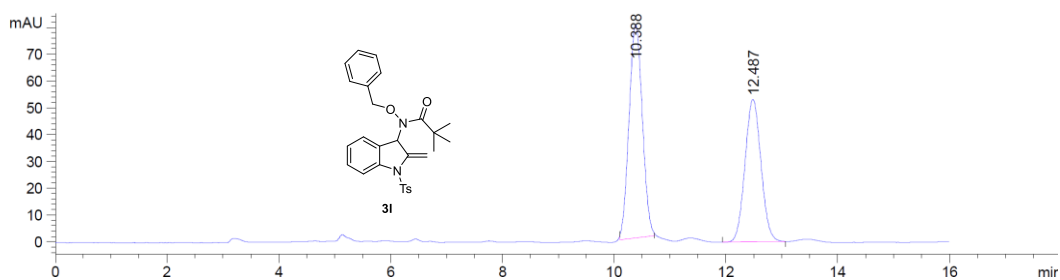


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.862	MM R	0.3664	3077.65698	140.01097	67.0352
2	16.421	MM R	0.4901	1513.44849	51.46753	32.9648

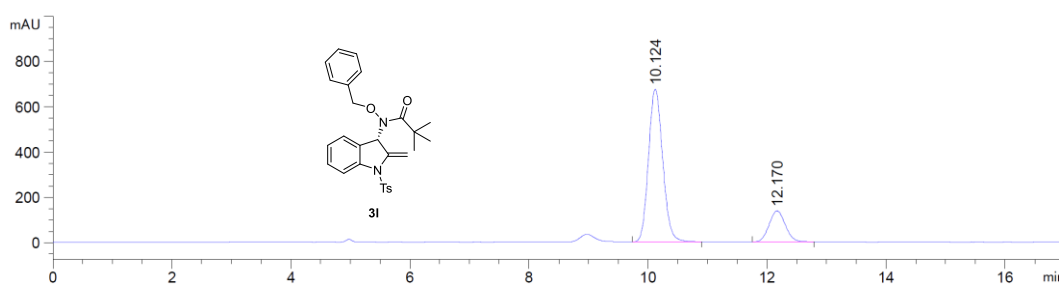


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.187	VB	0.3820	2.83257e4	1171.80188	91.8481
2	17.008	BB	0.4112	2514.03613	95.47507	8.1519

(S)-N-(Benzyloxy)-N-(2-methylene-1-tosylindolin-3-yl)pivalamide (3l)

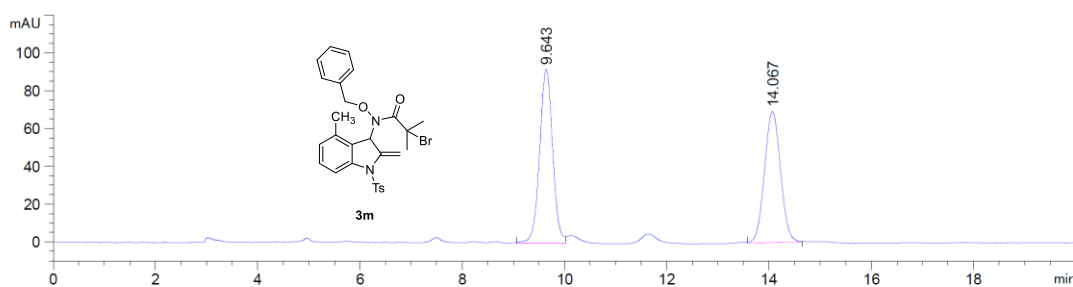


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.388	MM R	0.2754	1316.23193	79.66525	55.4894
2	12.487	VB	0.3096	1055.80811	53.19579	44.5106

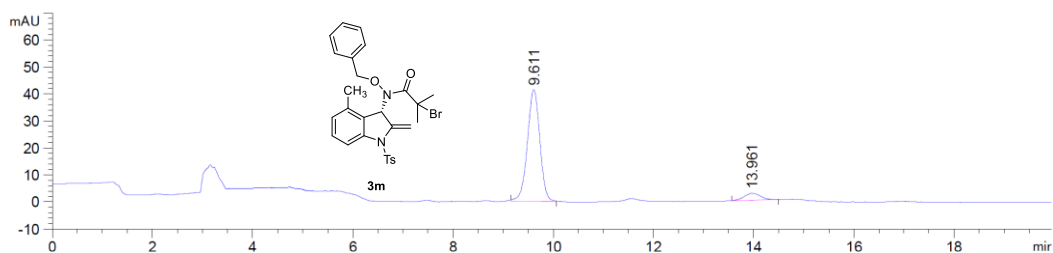


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.124	BB	0.2593	1.11789e4	674.64667	81.1440
2	12.170	BB	0.2955	2597.72534	136.79448	18.8560

(S)-N-(Benzyloxy)-2-bromo-2-methyl-N-(4-methyl-2-methylene-1-tosylindolin-3-yl)propanamide (3m)

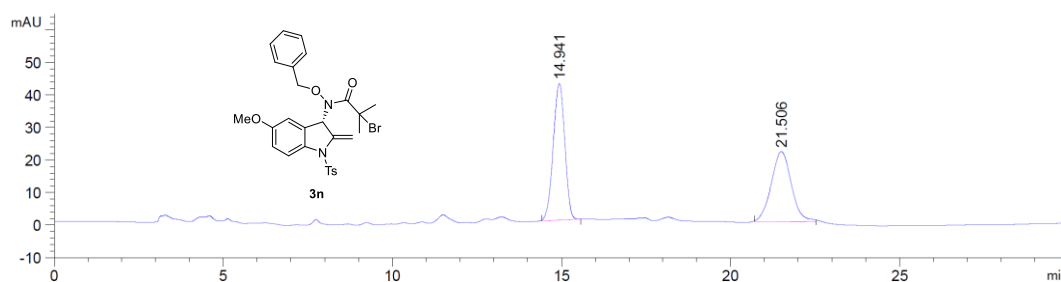


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.643	BV	0.2723	1625.68542	91.94367	51.9643
2	14.067	BB	0.3412	1502.78235	69.24751	48.0357

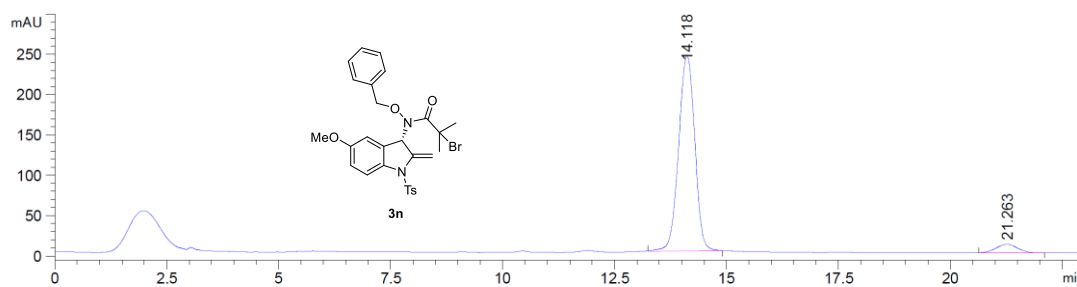


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.611	BB	0.2691	713.18854	41.38291	92.4485
2	13.961	BB	0.2805	58.25528	2.60925	7.5515

(S)-N-(Benzyloxy)-2-bromo-N-(5-methoxy-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3n)

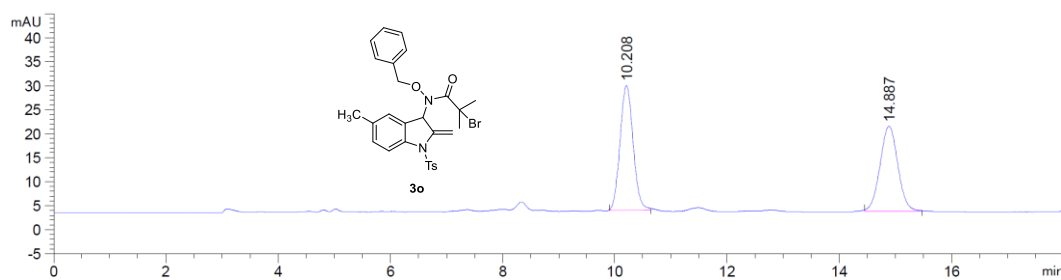


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.941	BB	0.3740	1002.66180	42.07535	52.9784
2	21.506	BB	0.6293	889.92542	21.57003	47.0216

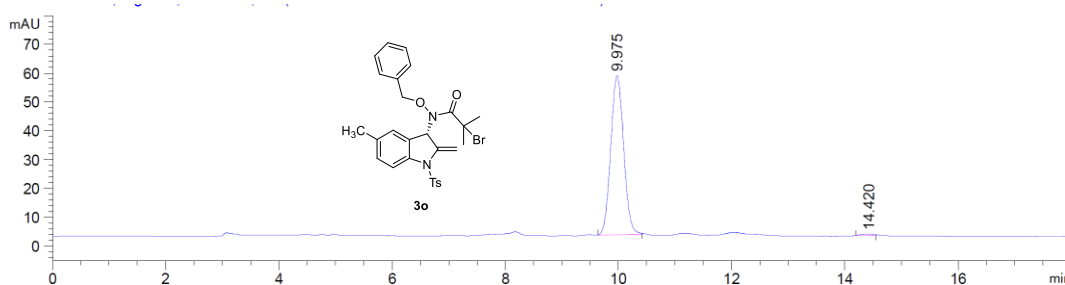


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.118	BB	0.3952	6087.05176	242.23648	94.7272
2	21.263	BB	0.4949	338.82550	10.37760	5.2728

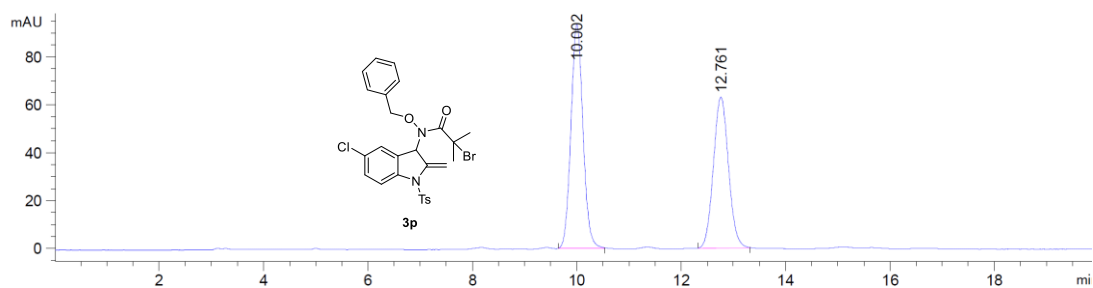
(S)-N-(Benzyloxy)-2-bromo-2-methyl-N-(5-methyl-2-methylene-1-tosylindolin-3-yl)propanamide

uide (3o)

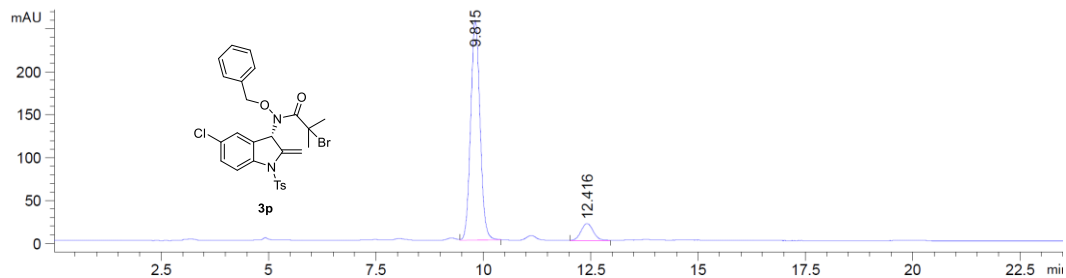
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.208	BB	0.2510	421.95193	26.04315	52.0336
2	14.887	BB	0.3443	388.97043	17.70627	47.9664



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.975	BB	0.2467	874.04199	55.22277	99.1847
2	14.420	MM R	0.2524	7.18452	4.74370e-1	0.8153

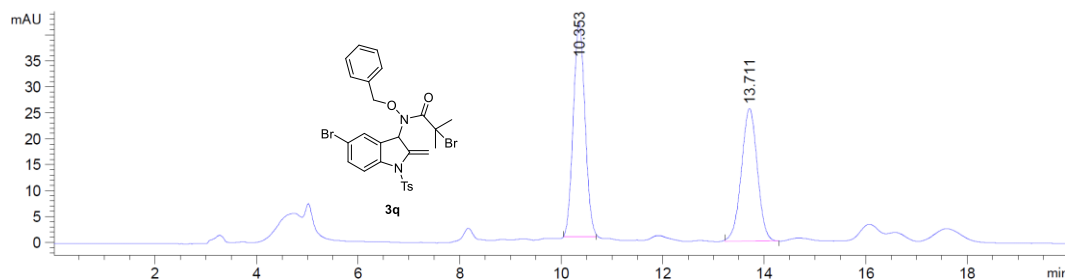
(S)-N-(Benzyloxy)-2-bromo-N-(5-chloro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanam**ide (3p)**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.002	BB	0.2495	1500.86243	93.39989	54.1924
2	12.761	BB	0.3123	1268.64270	63.16268	45.8076

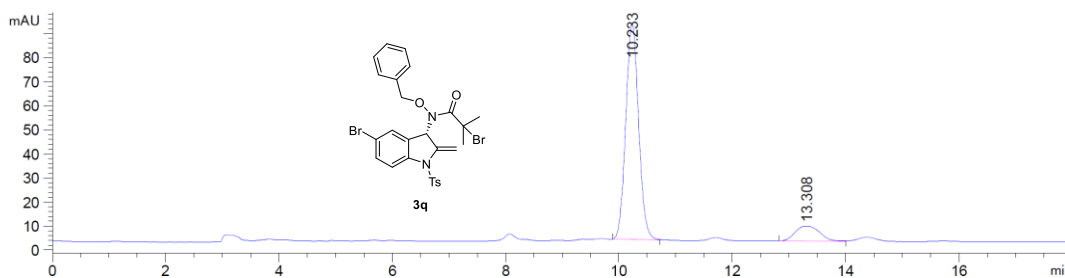


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.815	VB	0.2359	3909.23706	256.38995	91.0926
2	12.416	BB	0.3079	382.26205	19.56794	8.9074

(S)-N-(Benzyloxy)-2-bromo-N-(5-bromo-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3q)

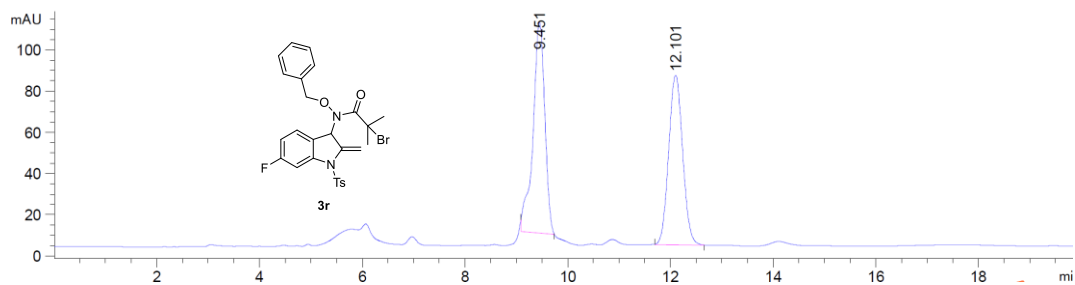


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.353	MM R	0.2670	662.40021	41.34211	54.2298
2	13.711	BB	0.3389	559.06885	25.59157	45.7702

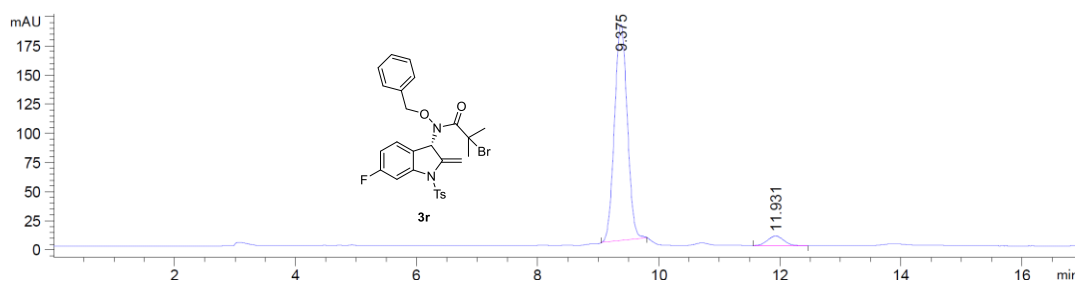


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.233	BB	0.2459	1415.69299	89.81912	88.4761
2	13.308	BV	0.4736	184.39308	6.26146	11.5239

(S)-N-(Benzyloxy)-2-bromo-N-(6-fluoro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3r)

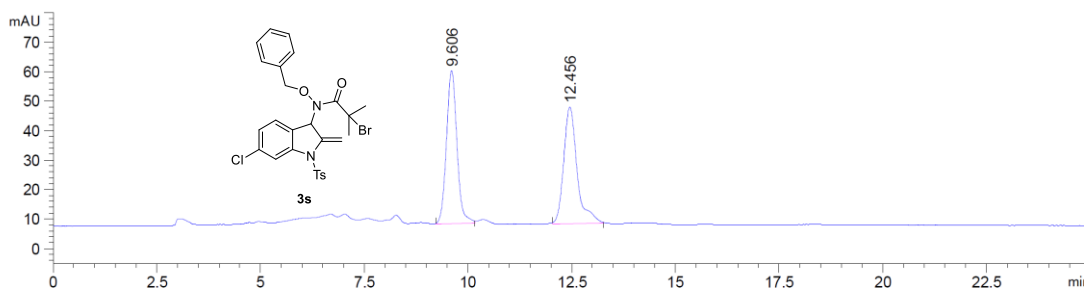


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.451	MM R	0.2670	1638.99817	102.29605	51.2674
2	12.101	BB	0.2967	1557.96057	82.36938	48.7326

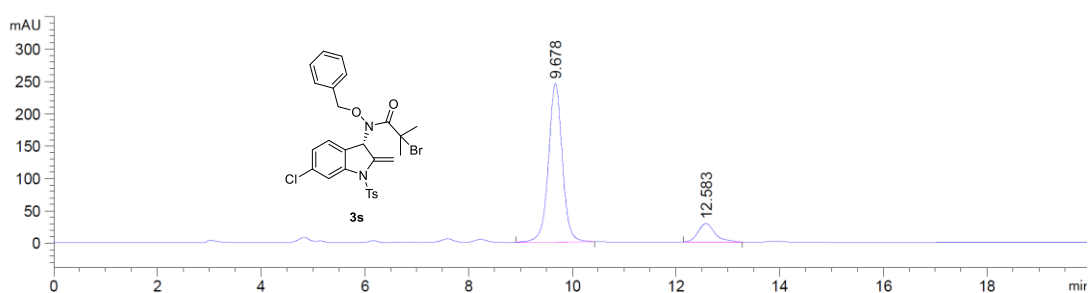


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.375	MM R	0.2450	2720.31006	185.08128	94.7709
2	11.931	BB	0.2944	150.09769	8.16783	5.2291

(S)-N-(Benzyloxy)-2-bromo-N-(6-chloro-2-methylene-1-tosylindolin-3-yl)-2-methylpropanamide (3s)

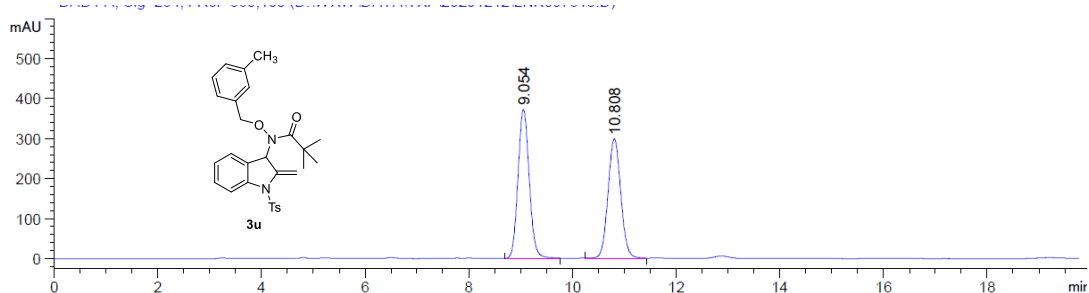


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.606	BB	0.2714	912.21417	51.81789	50.6501
2	12.456	BB	0.3446	888.79614	39.48841	49.3499

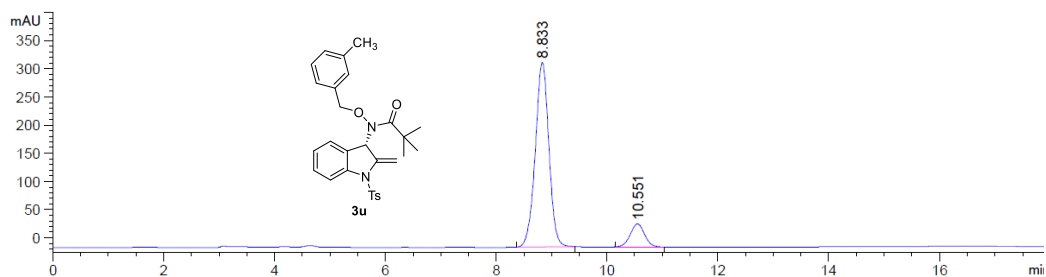


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.678	BB	0.2863	4580.90283	244.81471	87.3332
2	12.583	BB	0.3508	664.41327	28.84024	12.6668

(S)-N-((3-Methylbenzyl)oxy)-N-(2-methylene-1-tosylindolin-3-yl)pivalamide (3u)

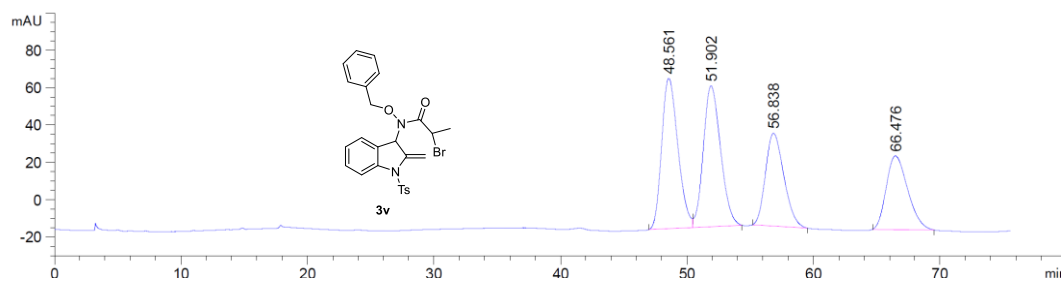


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.054	BB	0.2333	5599.49414	372.61108	52.3129
2	10.808	BB	0.2654	5104.35303	298.66144	47.6871

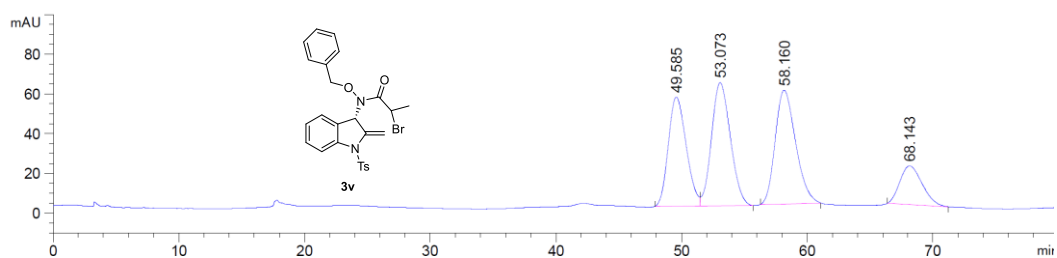


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.833	BB	0.2608	5590.16211	327.99994	88.2302
2	10.551	BB	0.2786	745.72083	41.31083	11.7698

***N*-(Benzyloxy)-2-bromo-*N*-((*S*)-2-methylene-1-tosylindolin-3-yl)propenamide (3v)**

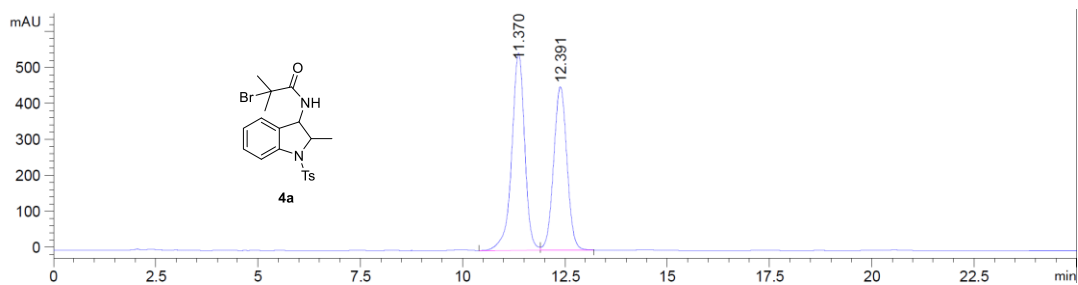


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.561	BV	1.3520	7184.48828	80.59789	29.8297
2	51.902	VB	1.4194	7180.43115	75.50776	29.8129
3	56.838	BB	1.4960	5043.99756	49.78362	20.9425
4	66.476	BB	1.6305	4676.09229	39.57655	19.4149

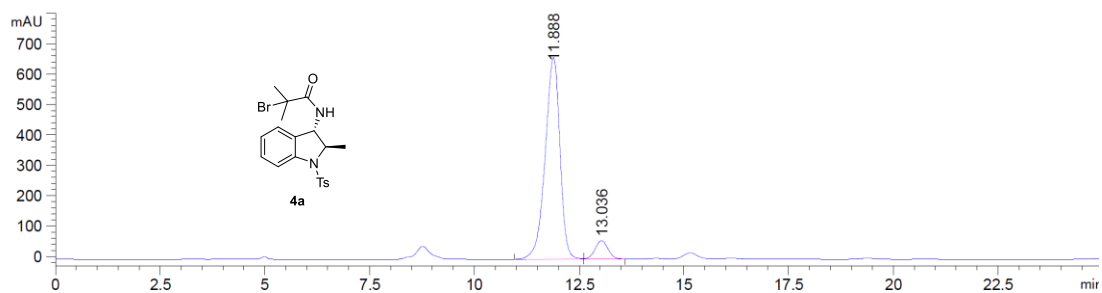


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.585	BV	1.4793	5441.13623	54.94875	26.1031
2	53.073	VB	1.5901	6501.86377	62.07016	31.1918
3	58.160	BB	1.6703	6488.75488	57.25082	31.1289
4	68.143	BB	1.4678	2413.05347	19.49924	11.5763

2-Bromo-2-methyl-N-(2-methyl-1-tosylindolin-3-yl)propenamide (4a)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.370	VV	0.3351	1.21004e4	548.98981	53.9593
2	12.391	VB	0.3549	1.03246e4	454.67355	46.0407



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.888	BB	0.3783	1.62919e4	663.86310	92.6449
2	13.036	BB	0.3329	1293.42920	60.63161	7.3551

10. References

1. (a) Wang, Q.; Li, T.-R.; Lu, L.-Q.; Li, M.-M.; Zhang, K.; Xiao, W.-J. *J. Am. Chem. Soc.*, **2016**, *138*,

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2. (a) Shen, J.; Woodward, R.; Kedenburg, J. P.; Liu, X.; Chen, M.; Fang, L.; Sun, D.; Wang, P. G.; *J. Med. Chem.*, **2008**, *51*, 7417–7427; (b) Jeffrey, C. S.; Barnes, K. L.; Eickhoff, J. A.; Carson, C. R., *J. Am. Chem. Soc.*, **2011**, *133*, 7688–7691; (c) Kang, D.; Zhang, H.; Zhou, Z.; Huang, B.; Naesens, L.; Zhan, P.; Liu, X., *Bioorg. Med. Chem. Lett.* **2016**, *26*, 5182–5186.