Supplementary Information:

Highly efficient synthesis of chiral quaternary 3-aminooxindoles promoted by Zinc (II) Chloride *via* Et_2Zn catalyzed addition of Grignard reagents to Isaltin-derived *N*-*tert*-butanesulfinyl ketimines

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General Methods.

All experiments were carried out in dried glassware with magnetic stirring under an atmosphere of dry nitrogen. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ solutions using a 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm, δ) relative to $CDCl_3$ (δ 7.26 for ^{1}H NMR), or $CDCl_3$ (δ 77.0 for ^{13}C NMR). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Commercial reagents were used as received unless

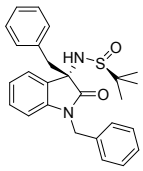
otherwise indicated. All solvents were purified and dried prior to use according to standard methods. Optical rotations were measured on a polarimeter and reported as follows: (c g/100 mL, solvent).

General reaction procedure for 4.

A suspension of ketimine **3** (0.2937 mmol) and $ZnCl_2$ (0.1762 mmol) in 2 ml of dried THF under nitrogen at mosphere was stirred for 30 mins at -20 °C. The corresponding Grignard reagent (0.8811 mmol) was then slowly added. After Et_2Zn (0.08811 mmol) was added completely, dropwise, the reaction mixture was stirred for 18-24 h at -20 °C. The reaction was quenched with 10 drops of a saturated NaCl solution, and the mixture was diluted with EA, dried by anhydrous Na_2SO_4 and concentrated *in vacco*. The crude addition product **4** was purified by flash chromatography (petroleum ether/ethyl acetate 5:1 to 1:1) to obtain the title product.

Characterization NMR and HRMS or HPLC of the Obtained Compounds.

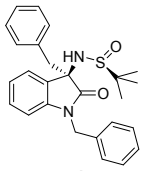
(*S*)-*N*-((*S*)-1,3-dibenzyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4a**



4a

a white solid with the yield (92%). mp: 86-91 °C. $[\alpha]_D^{29}$ 55.8 (c1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 3.50 (dd, *J* = 22.0, 12.7 Hz, 2H), 4.52 (s, 1H), 4.72 (dd, *J* = 134.4, 16.1 Hz, 2H), 6.43 (d, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 7.1 Hz, 2H), 6.90 (d, *J* = 7.3 Hz, 2H), 7.04-7.35 (m, 8H), 7.66 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.45, 43.70, 45.22, 56.64, 65.91, 109.62, 122.71, 126.03, 126.59, 127.09, 127.32, 127.88, 128.13, 128.64, 129.68, 130.44, 133.67, 134.83, 142.66, 175.59. HRMS (ESI) calcd For $[C_{26}H_{29}N_2O_2S, M+H]^+$: 433.1944, found: 433.1942.

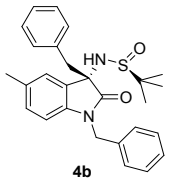
(*S*)-*N*-((*R*)-1,3-dibenzyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4a'**



4a'

a pale yellow solid. $[\alpha]_D^{29}$ -45 (c1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 9H), 3.33 (dd, *J* = 41.9, 12.9 Hz, 2H), 4.62 (s, 1H), 4.78 (dd, *J* = 184.6, 16.1 Hz, 2H), 6.44 (d, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 2H), 6.91 (d, J = 7.3 Hz, 2H), 7.05-7.25 (m, 7H), 7.29 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.76, 44.02, 44.77, 56.00, 65.08, 110.05, 122.40, 125.91, 126.64, 127.13, 127.16, 127.98, 128.60, 129.97, 130.66, 133.41, 135.10, 143.58, 177.15.

(*S*)-*N*-((*S*)-1,3-dibenzyl-5-methyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4b**

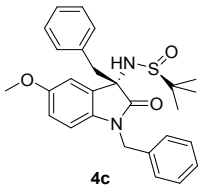


4b

a pale yellow solid with the yield (92%). mp: 48-49 °C. $[\alpha]_D^{29}$ 51.2 (c1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 2.39 (s, 3H), 3.47 (dd, *J* = 33.7, 12.7 Hz, 2H), 4.11 (s, 1H), 4.71 (dd, *J* = 136.0, 16.0 Hz, 2H),

6.32 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 7.0 Hz, 2H), 6.94 (m, 3H), 7.25-7.04 (m, 6H), 7.46 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.25, 22.47, 43.69, 45.25, 56.62, 65.94, 109.34, 126.58, 126.66, 127.07, 127.25, 127.80, 128.11, 128.59, 130.01, 130.48, 132.25, 133.75, 134.96, 140.27, 175.53. HRMS (ESI) calcd For $[C_{27}H_{31}N_2O_2S, M+H]^+$: 447.2101, found: 447.2098.

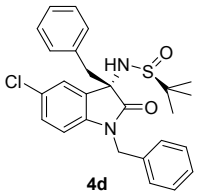
(*S*)-*N*-((*S*)-1,3-dibenzyl-5-methoxy-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4c**



4c

a white solid with the yield (94%). mp: 69-70 °C. $[\alpha]_D^{29}$ 49.9 (c1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 9H), 3.55 (s, 2H), 3.84 (s, 3H), 4.70 (dd, *J* = 146.3, 16.0 Hz, 2H), 4.76 (s, 1H), 6.32 (d, *J* = 8.6 Hz, 1H), 6.72-6.62 (m, 3H), 6.93 (d, *J* = 7.3 Hz, 2H), 7.23-7.06 (m, 6H), 7.39 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.63, 43.86, 44.74, 56.06, 66.75, 110.25, 112.77, 114.84, 126.61, 127.10, 127.31, 128.12, 128.61, 128.85, 130.45, 133.46, 134.82, 135.96, 156.03, 175.24. HRMS (ESI) calcd For $[C_{27}H_{30}N_2O_2S, M+H]^+$: 485.1869, found: 485.1871.

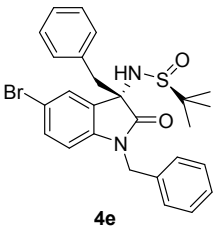
(*S*)-*N*-((*S*)-1,3-dibenzyl-5-chloro-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4d**



4d

a white solid with the yield (75%). mp: 45-48 °C. $[\alpha]_D^{29}$ 25.4 (c1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 9H), 3.48 (dd, *J* = 21.3, 13.0 Hz, 2H), 4.11 (s, 1H), 4.71 (dd, *J* = 129.0, 16.1 Hz, 2H), 6.35 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 6.9 Hz, 2H), 6.93 (d, *J* = 7.2 Hz, 2H), 7.25-7.09 (m, 7H), 7.61 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.41, 43.83, 45.08, 56.89, 66.01, 110.62, 126.19, 126.56, 127.30, 127.51, 128.22, 128.30, 128.72, 129.65, 129.85, 130.40, 133.20, 134.34, 141.13, 175.12. HRMS (ESI) calcd For $[C_{26}H_{27}ClN_2O_2SNa, M+Na]^+$: 489.1374, found: 489.1382.

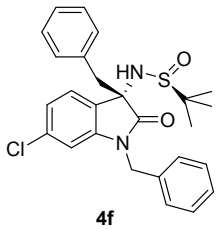
(*S*)-*N*-((*S*)-1,3-dibenzyl-5-bromo-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4e**



4e

a white solid with the yield (80%). mp: 79-80 °C. $[\alpha]_D^{29}$ 30.9 (c1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 9H), 3.48 (dd, *J* = 22.9, 12.8 Hz, 2H), 4.06 (s, 1H), 4.72 (dd, *J* = 134.7, 16.1 Hz, 2H), 6.30 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 7.1 Hz, 2H), 6.93 (d, *J* = 7.3 Hz, 2H), 7.12-7.22 (m, 7H), 7.75 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.43, 43.81, 45.13, 56.87, 65.91, 111.13, 115.44, 126.55, 127.32, 127.51, 128.32, 128.74, 128.93, 130.20, 130.41, 132.57, 133.20, 134.30, 141.62, 175.00. HRMS (ESI) calcd For $[C_{26}H_{27}BrN_2O_2SNa, M+Na]^+$: 533.0869, found: 533.0864.

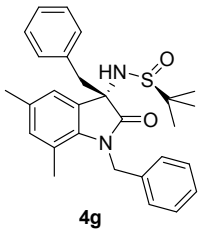
(*S*)-*N*-((*S*)-1,3-dibenzyl-6-chloro-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4f**



4f

a white solid with the yield (85%). mp: 58-60 °C. $[\alpha]_D^{29}$ 13.9 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 9H), 3.47 (dd, *J* = 36.1, 12.7 Hz, 2H), 4.19 (s, 1H), 4.71 (dd, *J* = 124.8, 16.1 Hz, 2H), 6.45 (d, *J* = 1.8 Hz, 1H), 6.72 (d, *J* = 6.9 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 2H), 7.27-7.09 (m, 7H), 7.55 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.42, 43.80, 45.03, 56.77, 65.61, 110.22, 122.75, 126.31, 126.53, 127.02, 127.33, 127.58, 128.33, 128.80, 130.39, 133.24, 134.24, 135.47, 143.86, 175.61. HRMS (ESI) calcd For $[C_{26}H_{27}ClN_2O_2SNa, M+Na]^+$: 489.1374, found: 489.1370.

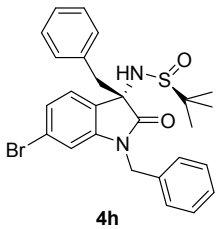
(*S*)-*N*-((*S*)-1,3-dibenzyl-5,7-dimethyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfonamide **4g**



4g

a pale yellow solid with the yield (95%). mp: 67-69 °C. $[\alpha]_D^{29}$ 57.8 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 2.00 (s, 3H), 2.37 (s, 3H), 3.46 (dd, *J* = 31.7, 12.7 Hz, 2H), 4.08 (s, 1H), 4.96 (dd, *J* = 76.0, 17.0 Hz, 2H), 6.59 (d, *J* = 6.2 Hz, 2H), 6.78 (s, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 7.12-7.24 (m, 6H), 7.34 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 18.37, 20.92, 22.48, 44.91, 45.33, 56.60, 65.20, 119.74, 124.62, 125.24, 126.83, 127.09, 128.13, 128.70, 130.59, 132.24, 133.85, 134.23, 137.06, 138.46, 176.46. HRMS (ESI) calcd For $[C_{28}H_{32}N_2O_2SNa, M+Na]$ +: 483.2077, found: 483.2079.

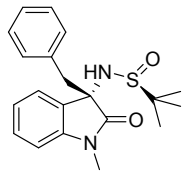
(*S*)-*N*-((*S*)-1,3-dibenzyl-6-bromo-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4h**



4h

a white solid with the yield (92%). mp: 62-64 °C. $[\alpha]_D^{29}$ 35.1 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 9H), 3.46 (dd, *J* = 39.8, 12.8 Hz, 2H), 4.06 (s, 1H), 4.71 (dd, *J* = 119.9, 16.1 Hz, 2H), 6.61 (s, 1H), 6.73 (d, *J* = 7.0 Hz, 2H), 6.92 (d, *J* = 6.9 Hz, 2H), 7.12-7.27 (m, 7H), 7.48 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.41, 43.80, 45.00, 56.78, 65.63, 112.93, 123.42, 125.68, 126.53, 126.87, 127.35, 127.59, 128.35, 128.81, 130.39, 133.22, 134.23, 143.97, 175.50. HRMS (ESI) calcd For $[C_{26}H_{27}BrN_2O_2SNa, M+Na]^+$: 533.0869, found: 533.0867.

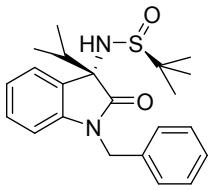
(*S*)-*N*-((*S*)-3-benzyl-1-methyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4h'**



4h'

a white solid with the yield (75%). mp: 108-109 °C. $[\alpha]_D^{29}$ 39.9 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 2.96 (s, 3H), 3.38 (dd, *J* = 26.4, 12.6 Hz, 2H), 4.04 (s, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 6.8 Hz, 2H), 7.04-7.16 (m, 4H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.42, 26.01, 45.70, 56.66, 65.88, 108.19, 122.66, 125.75, 125.95, 127.05, 127.80, 128.09, 129.57, 130.09, 133.54, 143.16, 175.53. HRMS (ESI) calcd For $[C_{20}H_{24}N_2O_2SNa, M+Na]^+$: 379.1451, found: 379.1457.

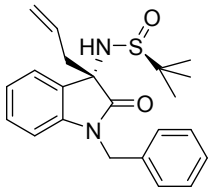
(*S*)-*N*-((*S*)-1-benzyl-3-isopropyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4i**



4i

a white solid with the yield (84%). mp: 95-97 °C. $[\alpha]_D^{29}$ 4.4 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.17 (s, 9H), 1.61 (s, 3H), 2.40 (m, 1H), 4.03 (s, 1H), 4.93 (dd, *J* = 23.9, 15.7 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 7.11 (m, 1H), 7.24-7.41 (m, 6H), 7.52 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 16.42, 16.72, 22.43, 36.19, 43.77, 56.48, 57.87, 109.25, 122.72, 126.40, 127.19, 127.33, 127.41, 127.69, 128.74, 129.48, 135.59, 143.08, 175.48. HRMS (ESI) calcd For $[C_{22}H_{28}N_2O_2SNa, M+Na]^+$: 407.1764, found: 407.1767.

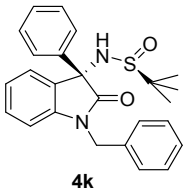
(*S*)-*N*-((*S*)-3-allyl-1-benzyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4j**



4j

a pale yellow solid with the yield (92%). mp: 55-57 °C. $[\alpha]_D^{29}$ 16.3 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 9H), 2.62-2.84 (m, 2H), 4.33 (s, 1H), 4.95 (dd, *J* = 89.2, 15.8 Hz, 2H), 5.10 (t, *J* = 16.7 Hz, 2H), 5.52-5.66 (m, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.19-7.40 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.72, 43.19, 44.20, 56.14, 63.36, 109.95, 120.76, 122.65, 125.48, 126.59, 127.35, 127.57, 128.75, 129.81, 130.26, 135.55, 143.24, 177.42. HRMS (ESI) calcd For $[C_{22}H_{26}N_2O_2SNa, M+Na]$ +: 405.1607, found: 405.1607.

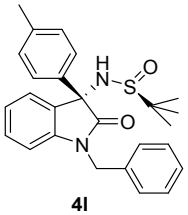
(*S*)-*N*-((*S*)-1-benzyl-2-oxo-3-phenylindolin-3-yl)-2-methylpropane-2-sulfinamide **4k**



4k

a pale yellow solid with the yield (85%). mp: 115-118 °C. $[\alpha]_D^{25}$ 30.5 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H), 4.37 (s, 1H), 4.96 (dd, *J* = 40.5, 15.8 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.25-7.40 (m, 9H), 7.50-7.55 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.52, 44.02, 56.97, 67.85, 109.78, 123.23, 126.70, 127.15, 127.72, 128.71, 128.77, 128.86, 129.43, 129.83, 135.38, 139.22, 142.52, 175.7. HRMS (ESI) calcd For $[C_{25}H_{26}N_2O_2SNa, M+Na]^+$: 441.1607, found: 441.1611.

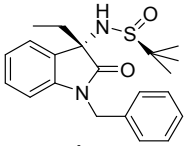
(*S*)-*N*-((*S*)-1-benzyl-2-oxo-3-(p-tolyl)indolin-3-yl)-2-methylpropane-2-sulfinamide **4l**



4l

a pale yellow solid with the yield (88%). mp: 67-68 °C. $[\alpha]_D^{29}$ 9.6 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H), 2.35 (s, 3H), 4.35 (s, 1H), 4.94 (dd, *J* = 40.9, 15.8 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 1H), 7.12-7.21 (m, 3H), 7.24-7.33 (m, 6H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.12, 22.52, 43.99, 56.97, 67.62, 109.78, 123.22, 126.90, 127.10, 127.13, 127.70, 128.79, 129.56, 129.79, 135.39, 136.17, 138.70, 142.46, 175.80. HRMS (ESI) calcd For $[C_{26}H_{28}N_2O_2SNa, M+Na]^+$: 455.1764, found: 455.1768.

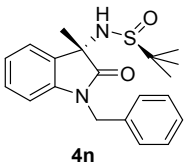
(*S*)-*N*-((*S*)-1-benzyl-3-ethyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4m**



4m

a white solid with the yield (95%). mp: 74-76 °C. $[\alpha]_D^{29}$ 12.3 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (t, *J* = 7.4 Hz, 3H), 1.17 (s, 9H), 2.20 (q, *J* = 7.5 Hz, 2H), 3.89 (s, 1H), 4.94 (s, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.22-7.35 (m, 6H), 7.52 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 8.15, 22.39, 32.22, 43.82, 56.41, 65.46, 109.44, 123.04, 125.55, 127.22, 127.73, 128.12, 128.79, 129.57, 135.50, 142.85, 176.42. HRMS (ESI) calcd For $[C_{21}H_{27}N_2O_2S, M+H]^+$: 371.1788, found: 371.1793.

(*S*)-*N*-((*S*)-1-benzyl-3-methyl-2-oxoindolin-3-yl)-2-methylpropane-2-sulfinamide **4n**

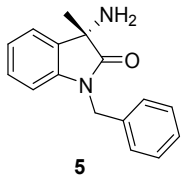


4n

a pale yellow solid with the yield (94%). mp: 76-77 °C. $[\alpha]_D^{29}$ 4.8 (c1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H), 1.66 (s, 3H), 4.27 (s, 1H), 4.96 (dd, *J* = 43.1, 16.3 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* =

7.2 Hz, 1H), 7.20-7.40 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.62, 25.55, 44.13, 56.01, 60.60, 110.02, 122.90, 124.75, 127.17, 127.39, 128.84, 129.67, 135.59, 142.55, 178.22.

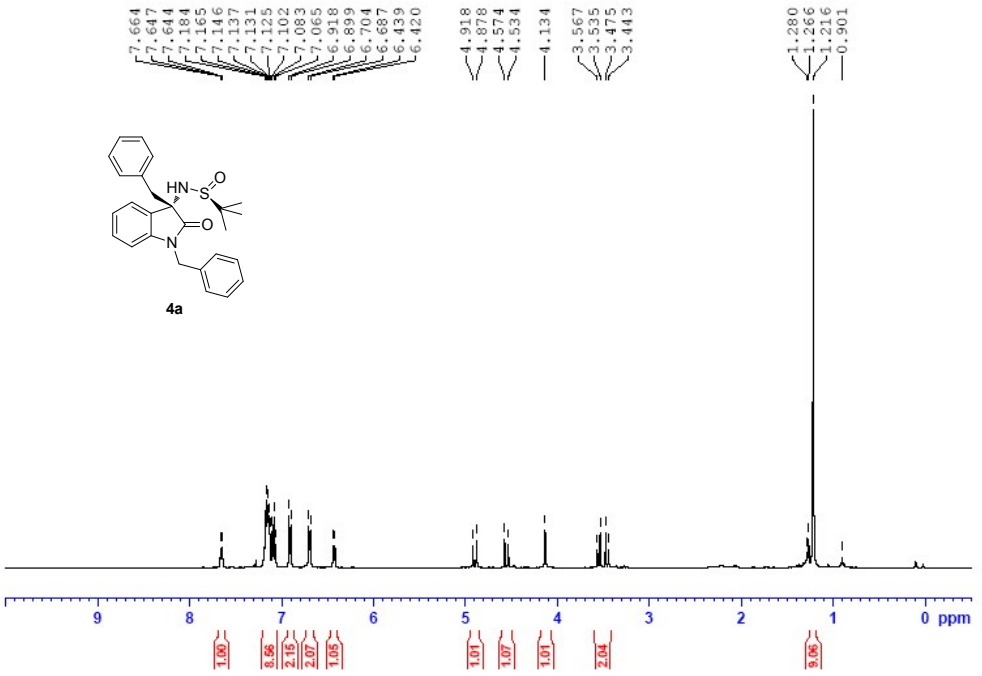
(*S*)-3-amino-1-benzyl-3-methylindolin-2-one **5**



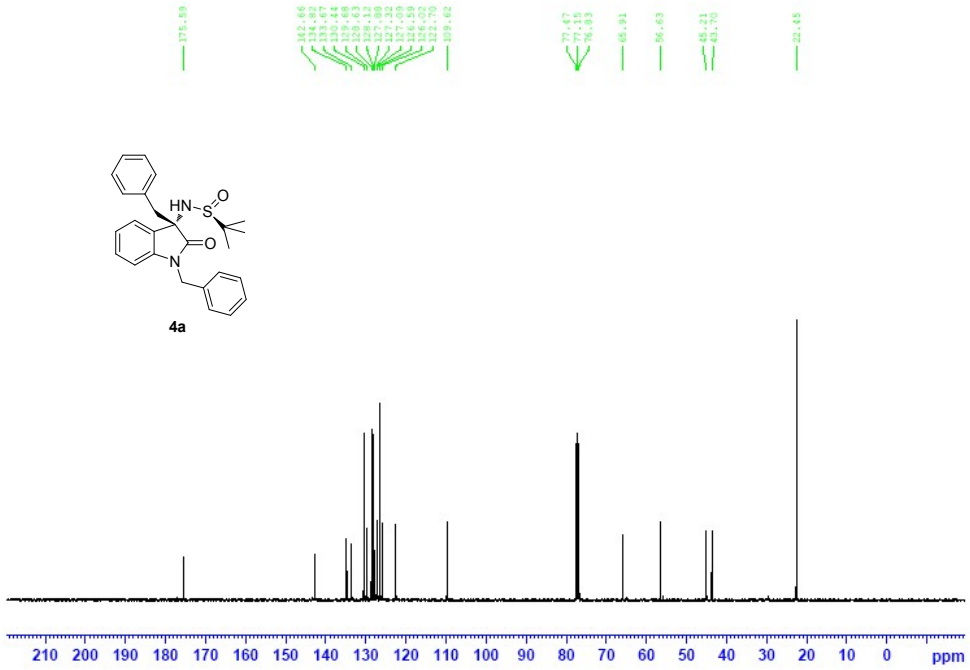
5

a pale yellow solid. $[\alpha]_D^{29}$ -30.6 (c1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 3H), 2.09 (s, 2H), 4.92 (dd, *J* = 64.0, 15.2 Hz, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.25-7.37 (m, 5H), 7.44 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 25.72, 43.71, 57.87, 109.34, 123.02, 123.44, 127.23, 127.70, 128.85, 133.20, 135.82, 141.76, 181.18.

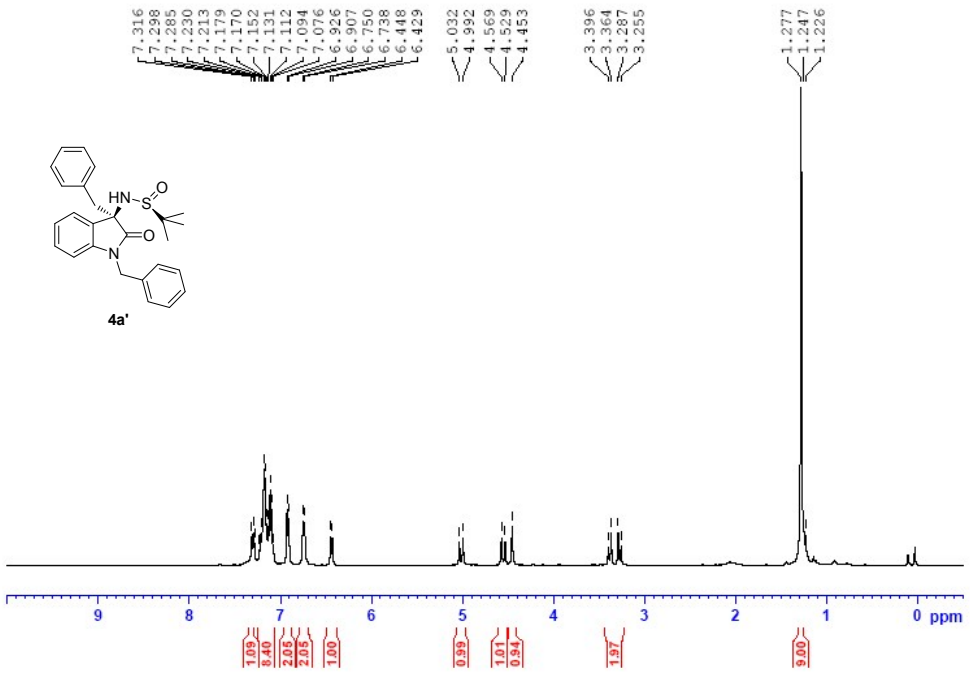
1. ^{1}H NMR Spectrum of 4a.



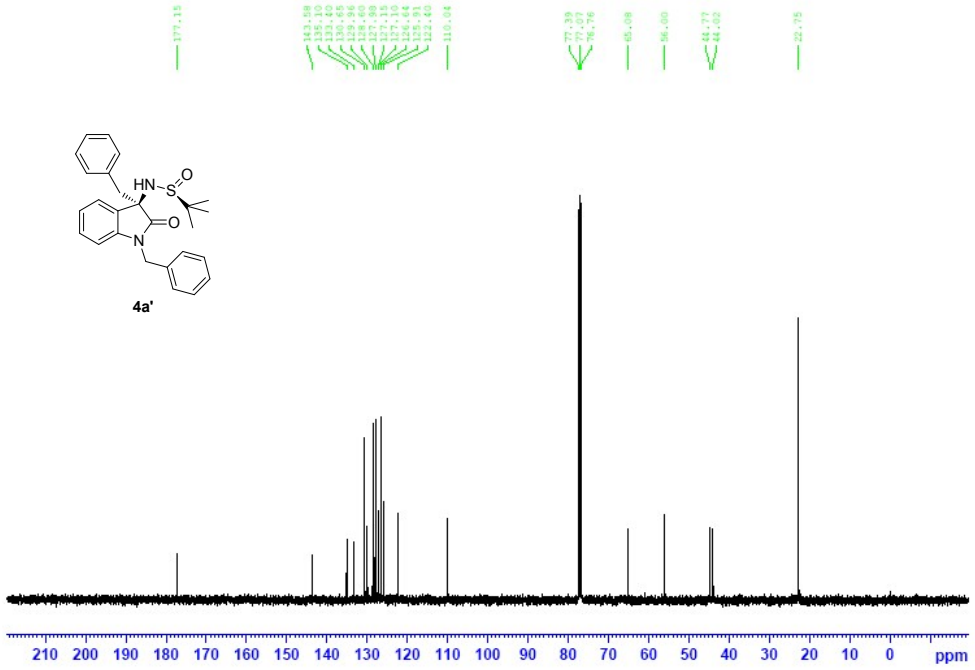
2. ^{13}C NMR Spectrum of 4a.



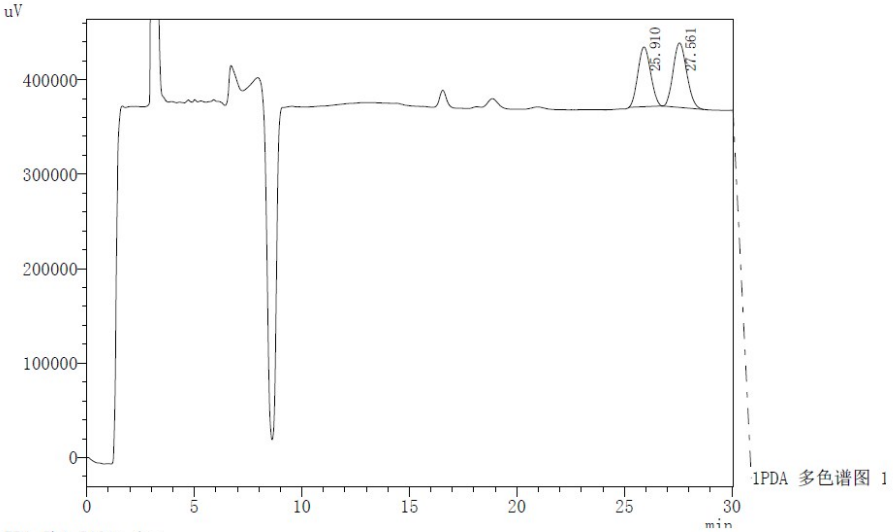
3. ^{1}H NMR Spectrum of 4a'.



4. ^{13}C NMR Spectrum of 4a'.



5. HPLC (4a mixed with 4a')

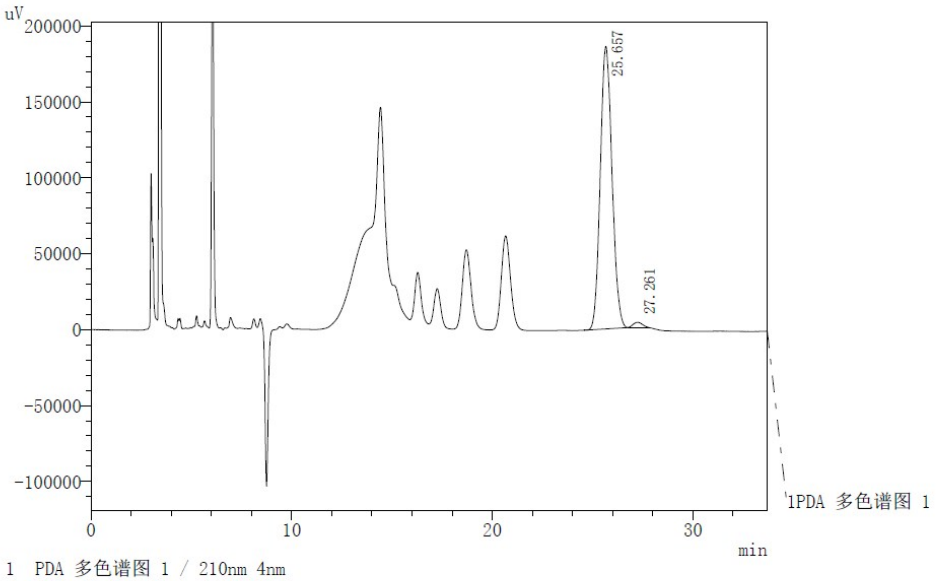


PDA Ch1 210nm 4nm

峰#	保留时间	面积	高度	面积 %	浓度
1	25.910	2596415	63322	46.473	46.473
2	27.561	2990463	68227	53.527	53.527
总计		5586878	131549	100.000	

Chiracel AD-H Column (4.6*250 mm); detected at 210nm; n-hexane / i-propanol = 90 / 10; flow = 1.0 mL / min; Retention time: 25.9 min (4a), 27.5 min (4a').

6. HPLC (4a without purification)



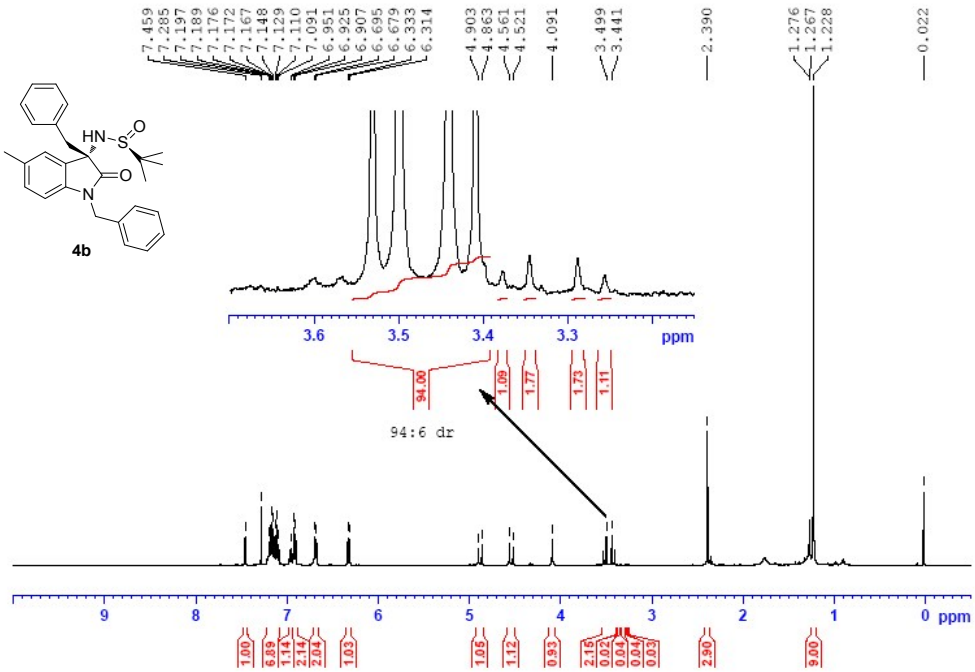
1 PDA 多色谱图 1 / 210nm 4nm

PDA Ch1 210nm 4nm

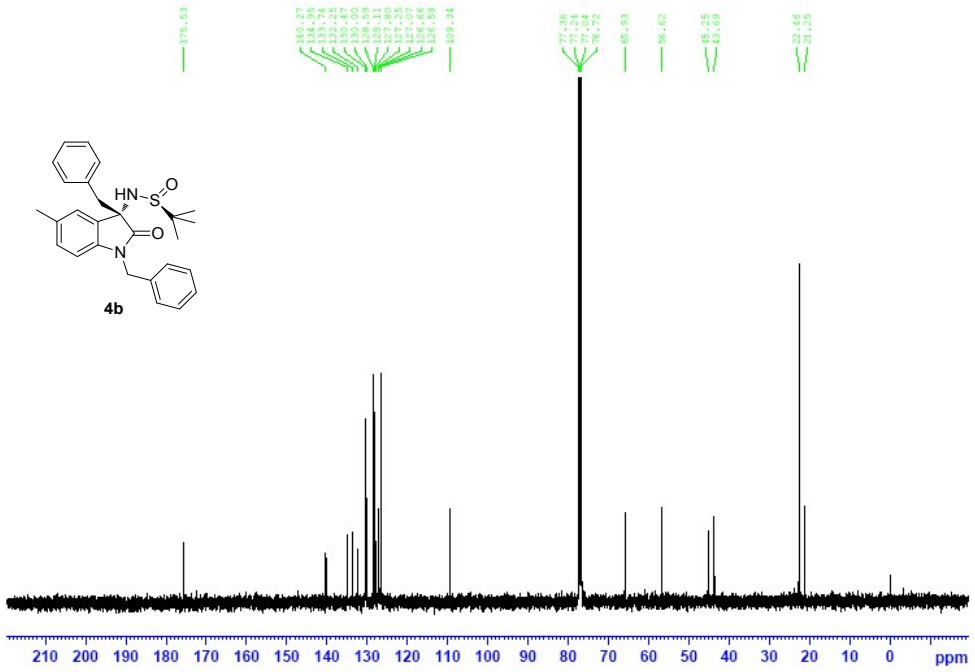
峰#	保留时间	面积	高度	面积 %	浓度
1	25.657	7583850	186139	98.529	98.529
2	27.261	113225	3479	1.471	1.471
总计		7697075	189618	100.000	

Chiracel AD-H Column (4.6*250 mm); detected at 210 nm; n-hexane / i-propanol = 90 / 10; flow = 1.0 mL/min; Retention time: 25.7 min (4a), 27.3 min (4a’). 98.5:1.5 dr.

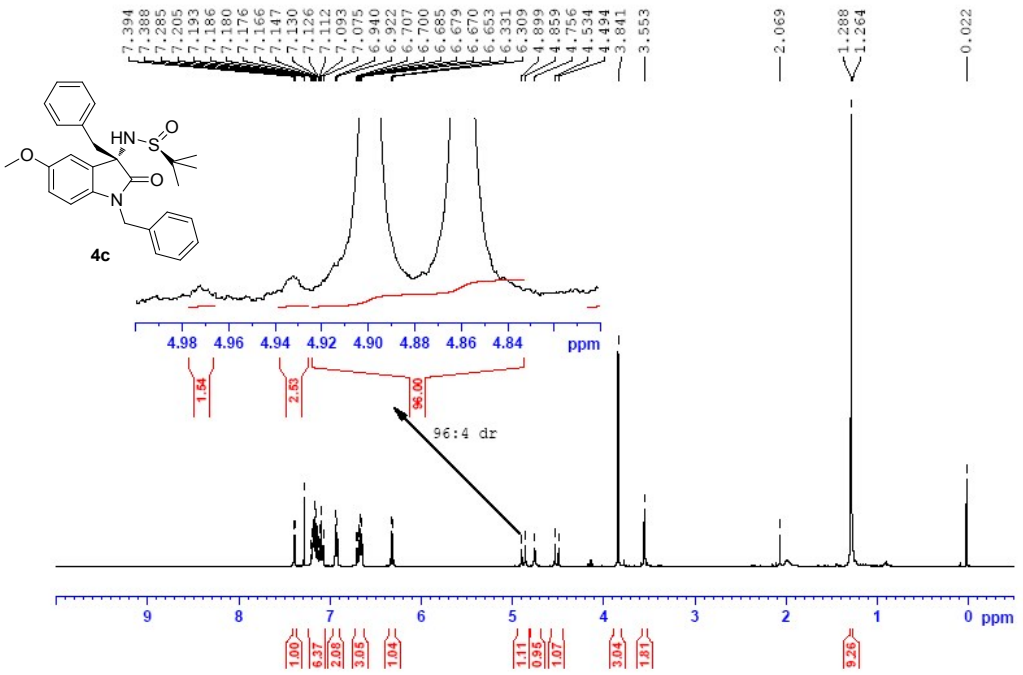
7. ^{1}H NMR Spectrum of 4b.



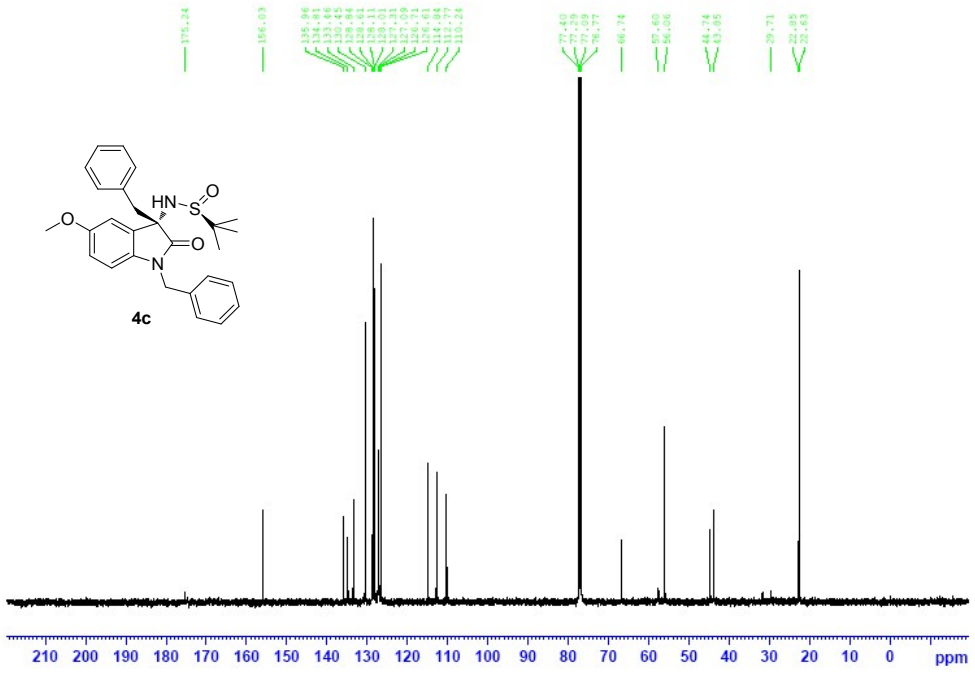
8. ^{13}C NMR Spectrum of 4b.



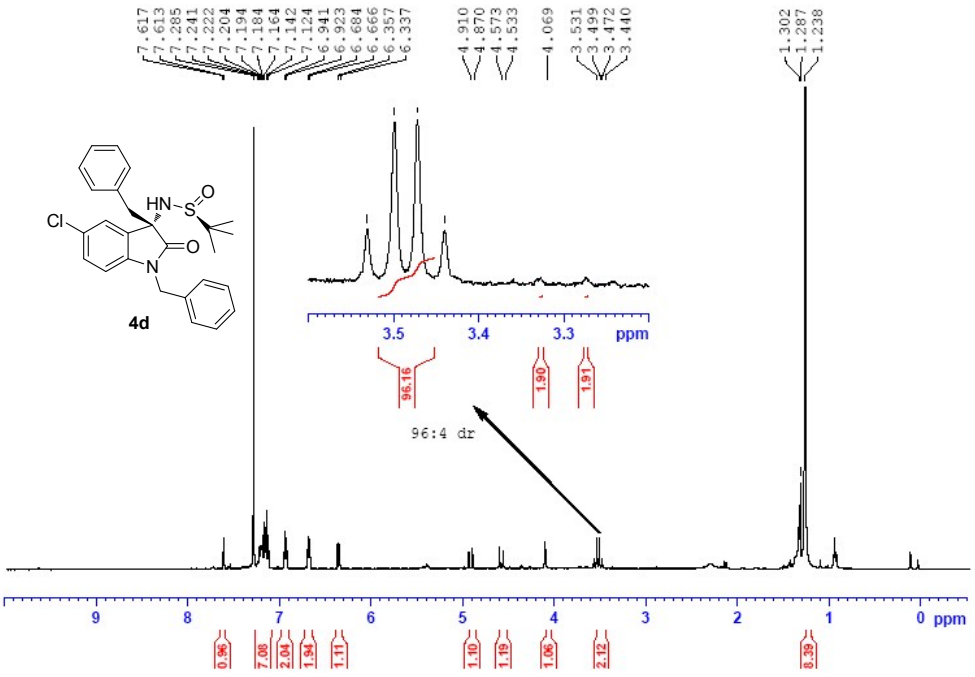
9. ^{1}H NMR Spectrum of 4c.



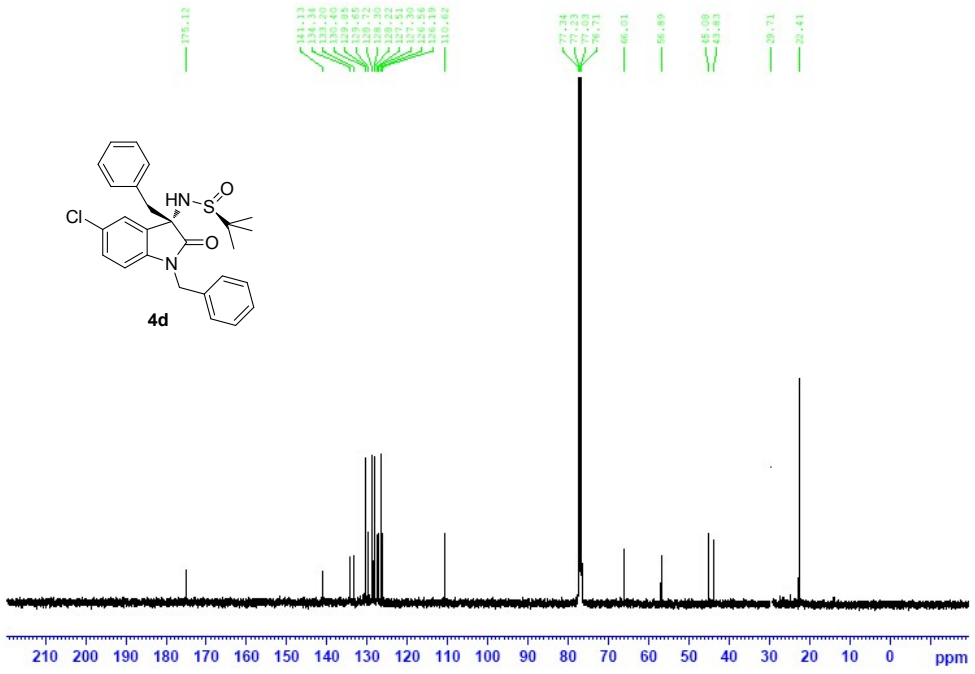
10. ^{13}C NMR Spectrum of 4c.



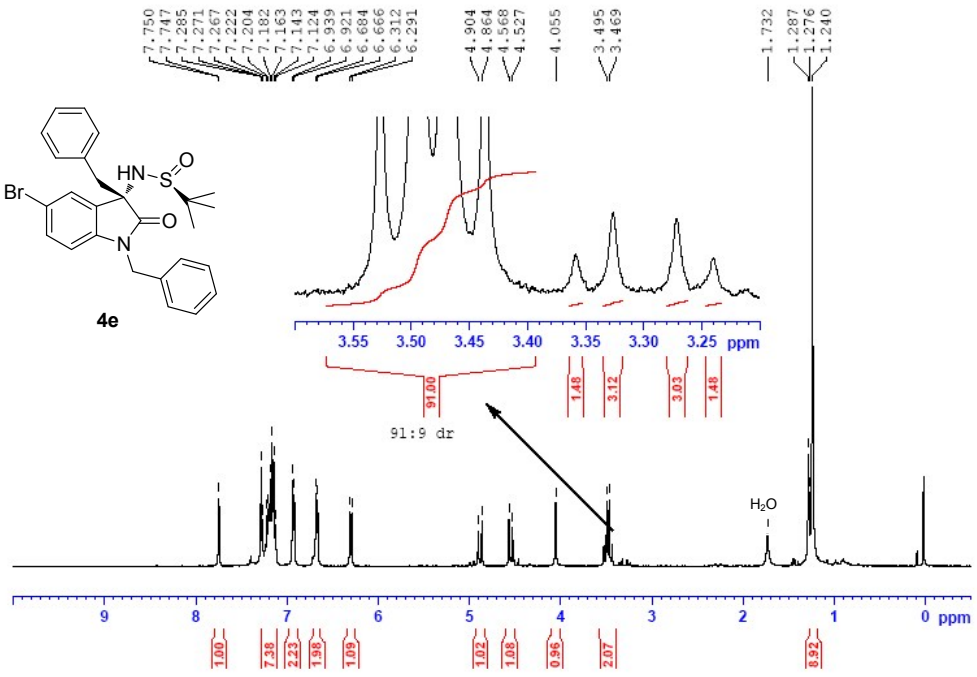
11. ^{1}H NMR Spectrum of 4d.



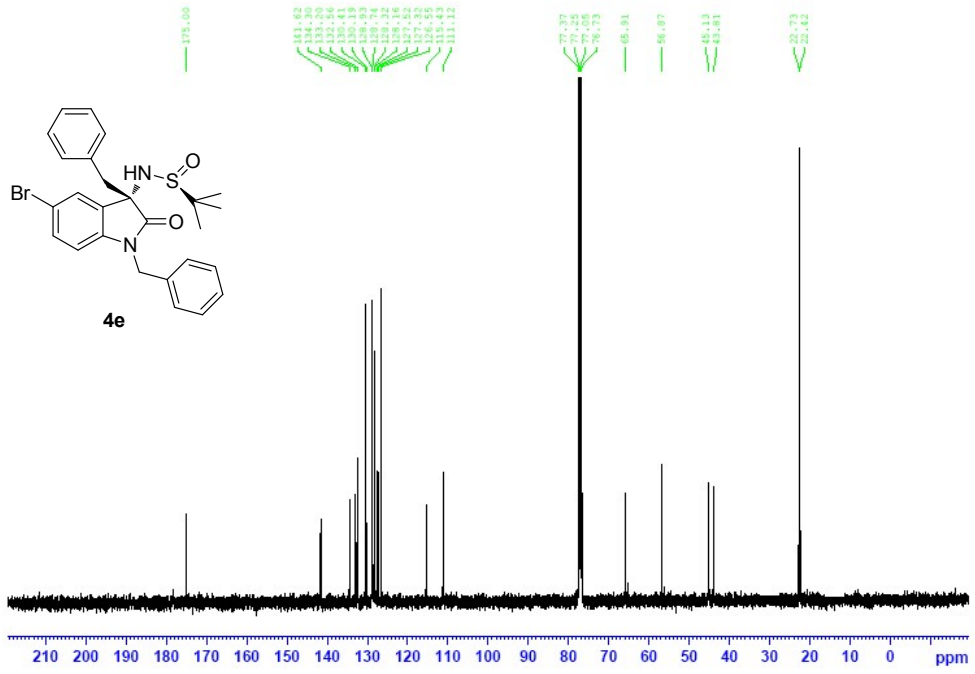
12. ^{13}C NMR Spectrum of 4d.



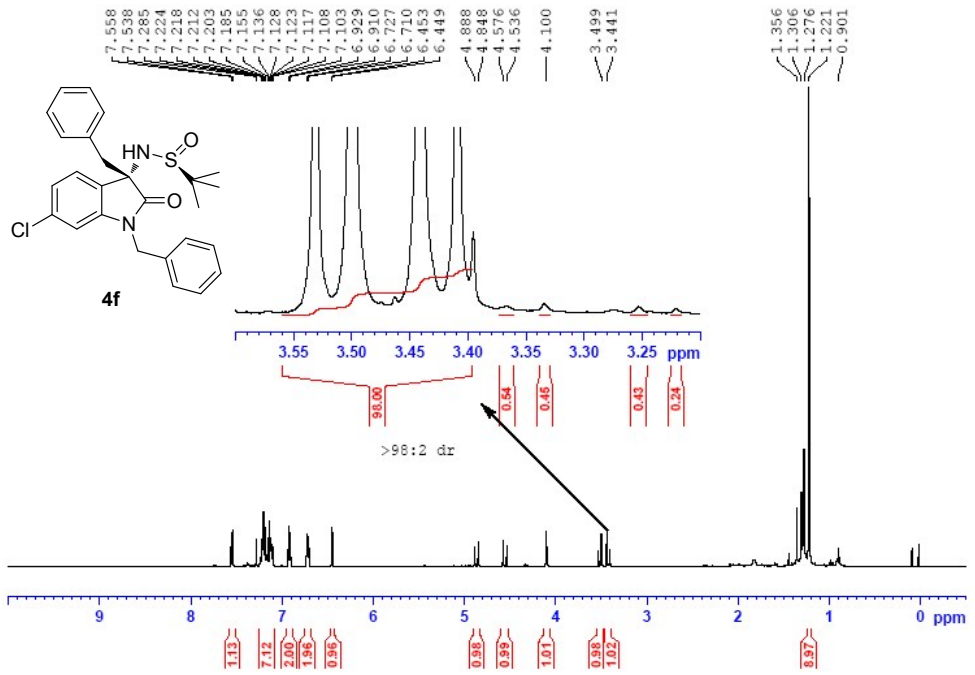
13. ^{1}H NMR Spectrum of 4e.



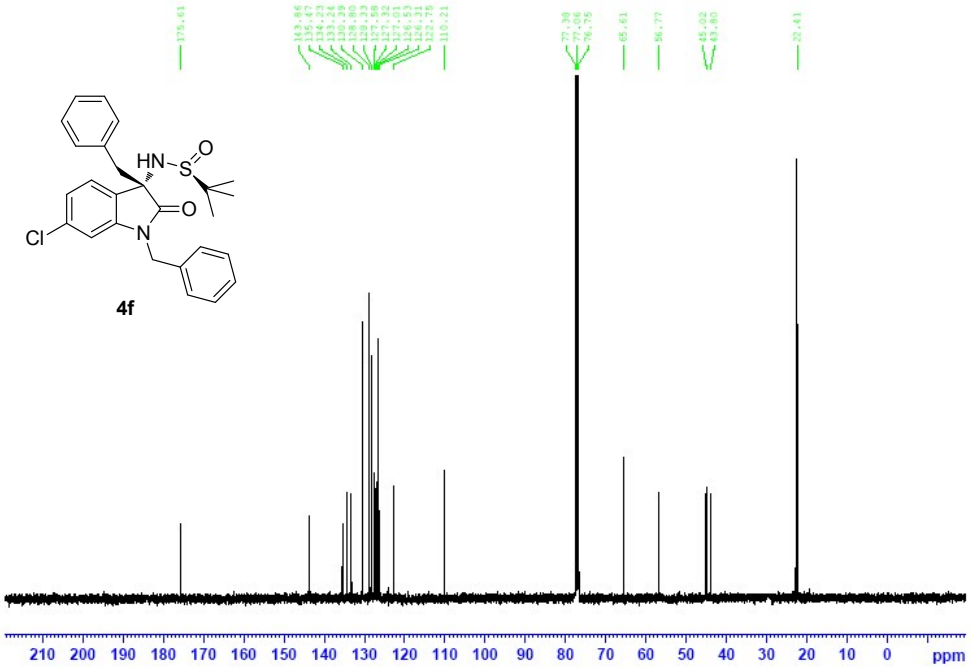
14. ^{13}C NMR Spectrum of 4e.



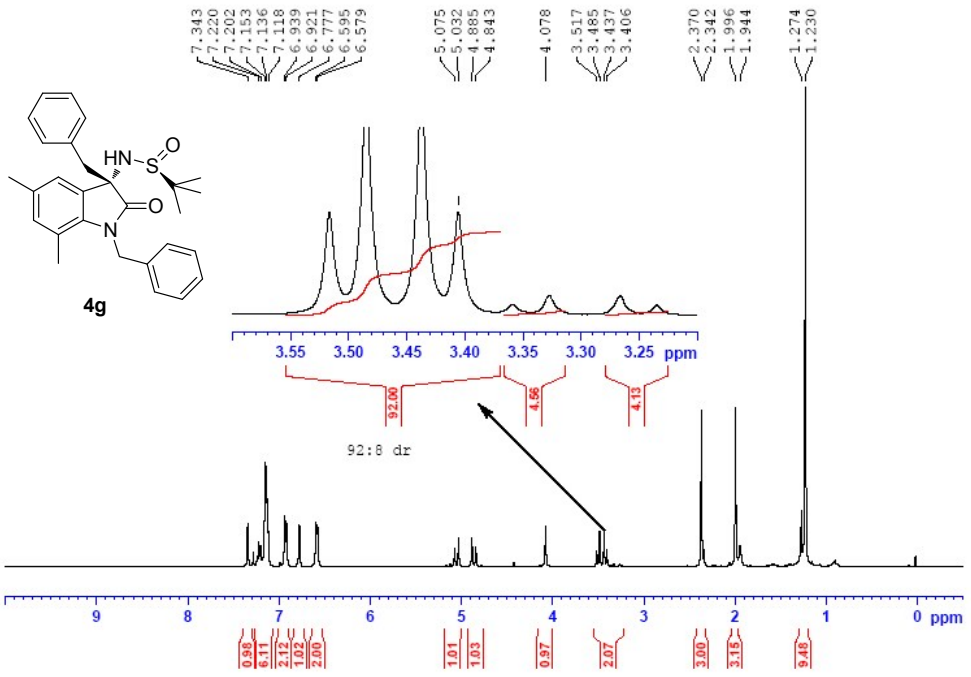
15. ^{1}H NMR Spectrum of 4f.



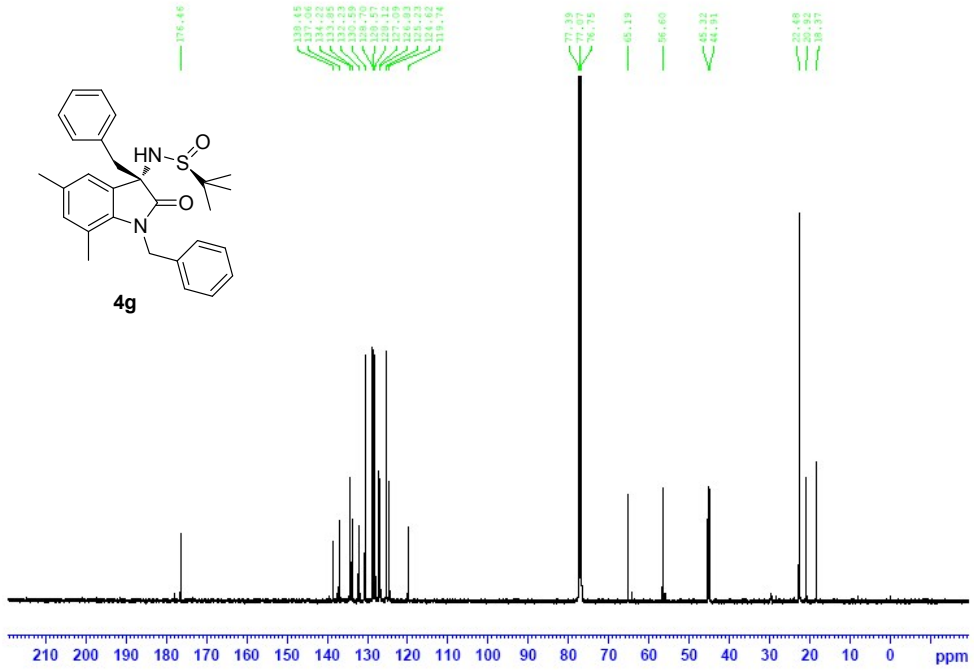
16. ^{13}C NMR Spectrum of 4f.



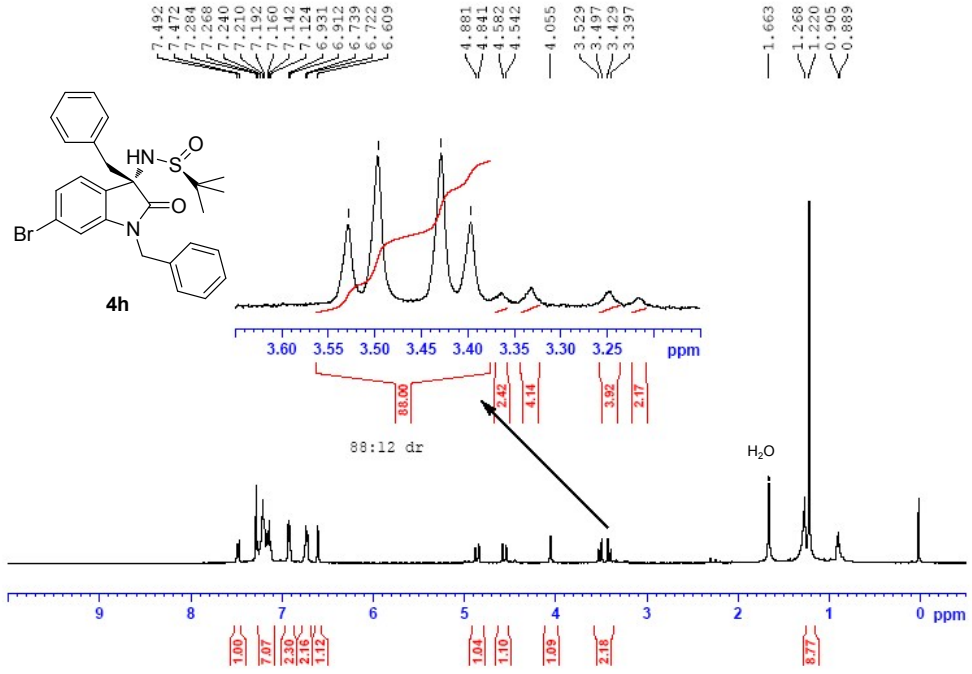
17. ^{1}H NMR Spectrum of 4g.



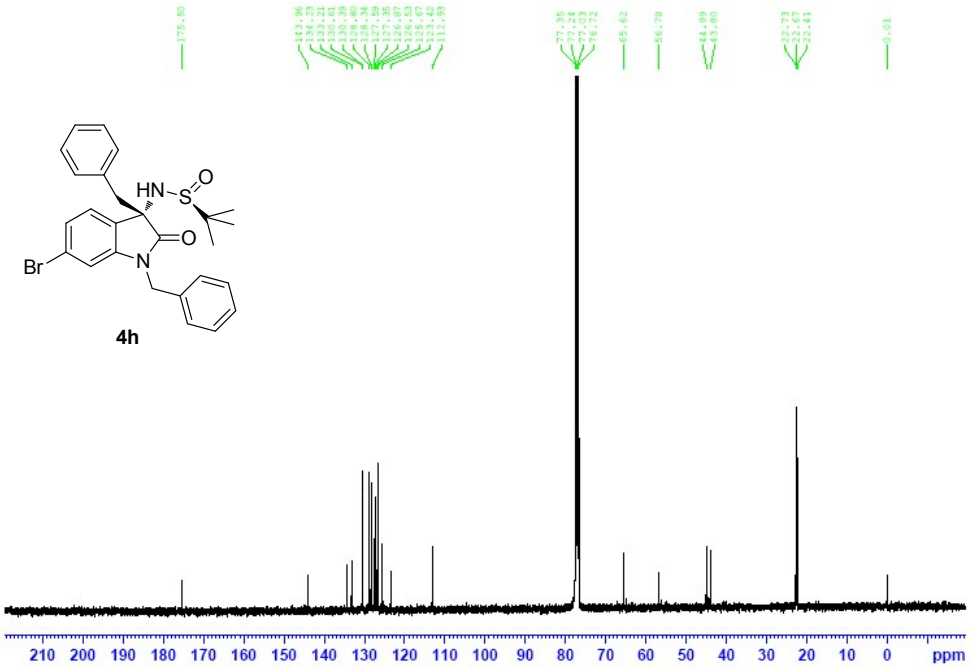
18. ^{13}C NMR Spectrum of 4g.



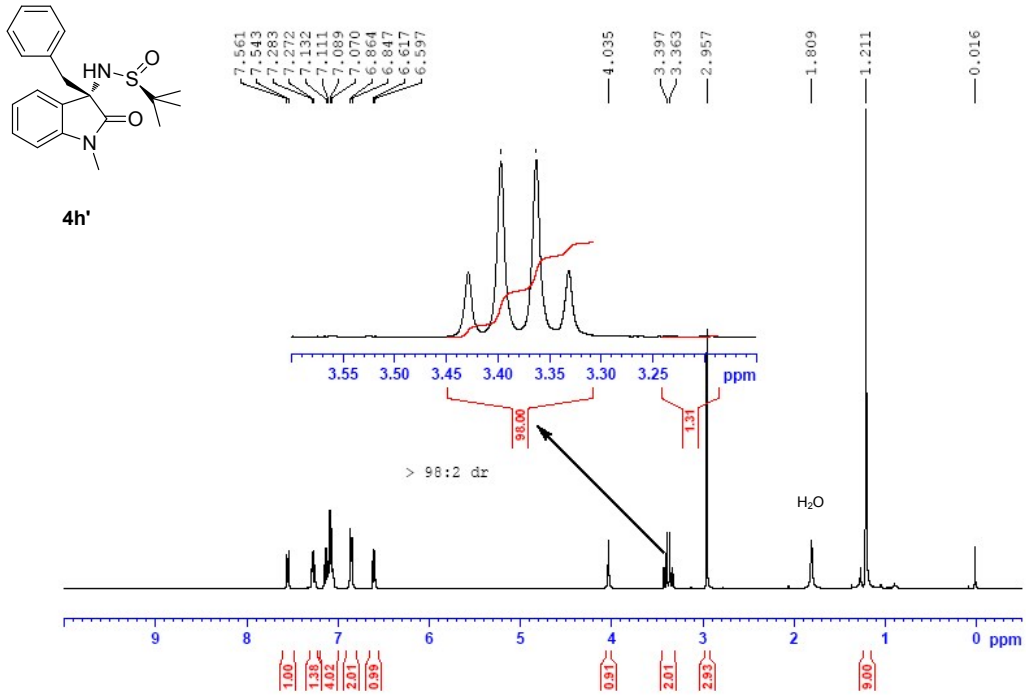
19. ^{1}H NMR Spectrum of 4h.



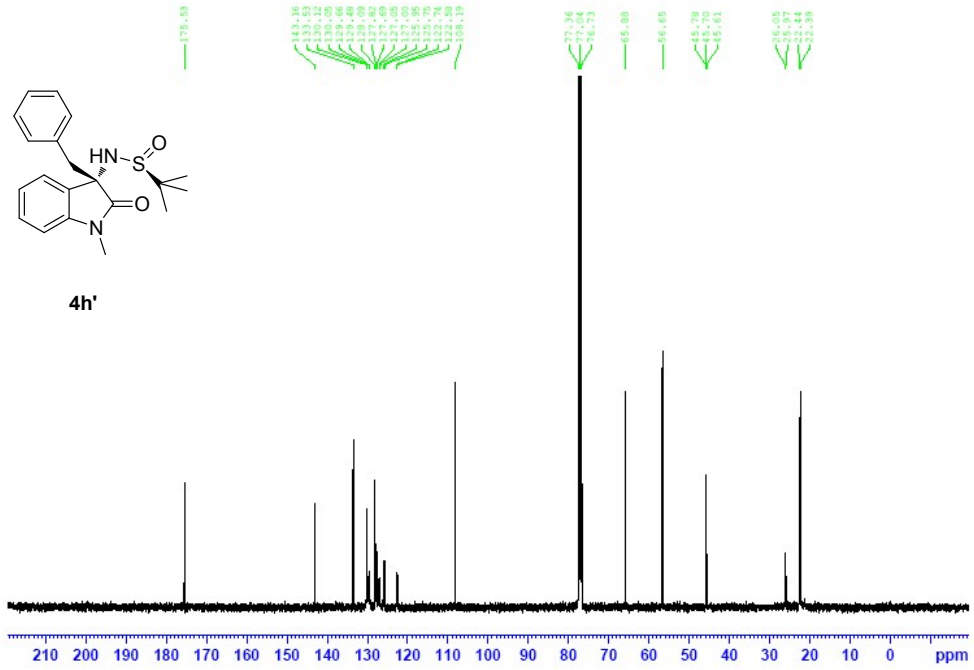
20. ^{13}C NMR Spectrum of 4h.



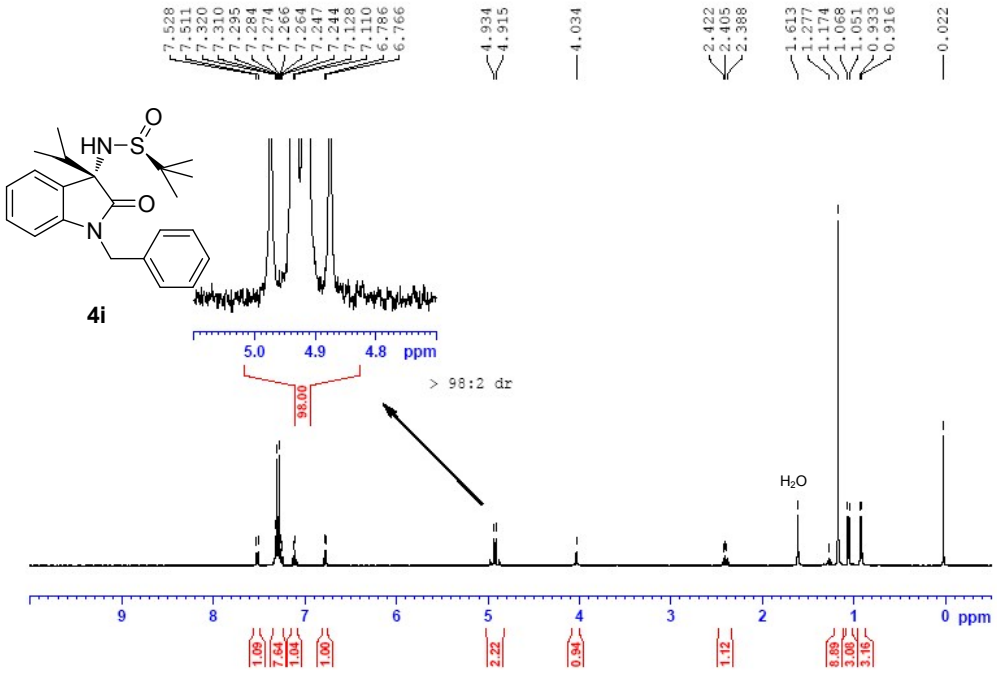
21. ^{1}H NMR Spectrum of 4h'.



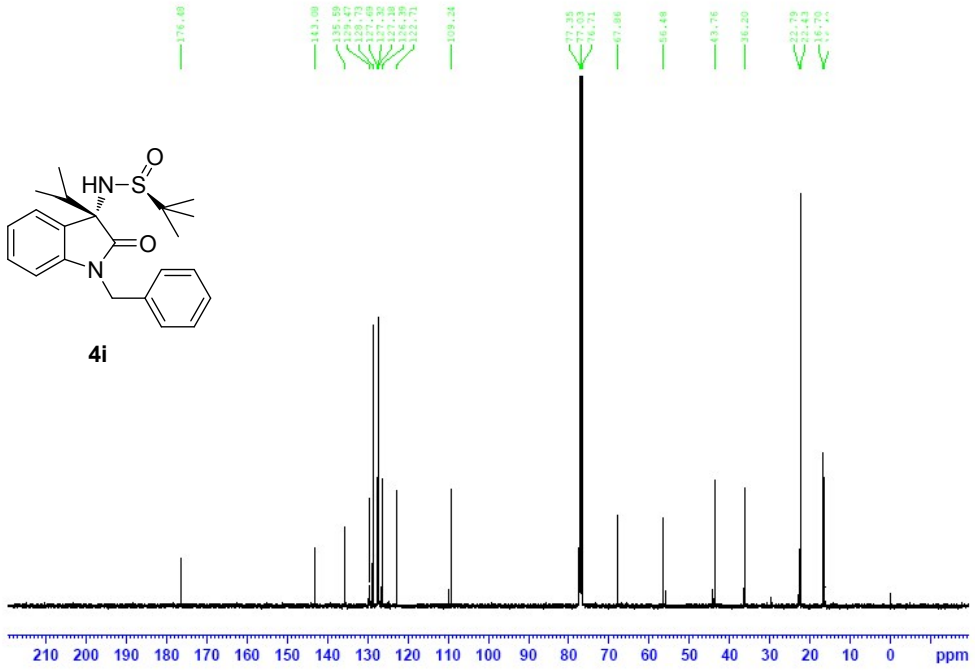
22. ^{13}C NMR Spectrum of 4h'.



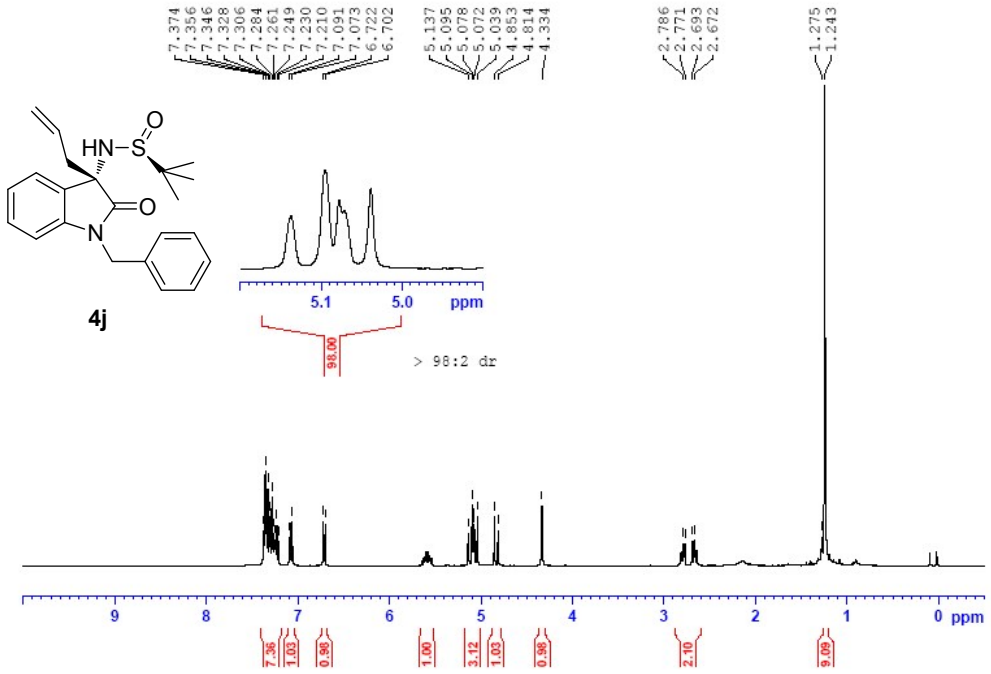
23. ^{1}H NMR Spectrum of 4i.



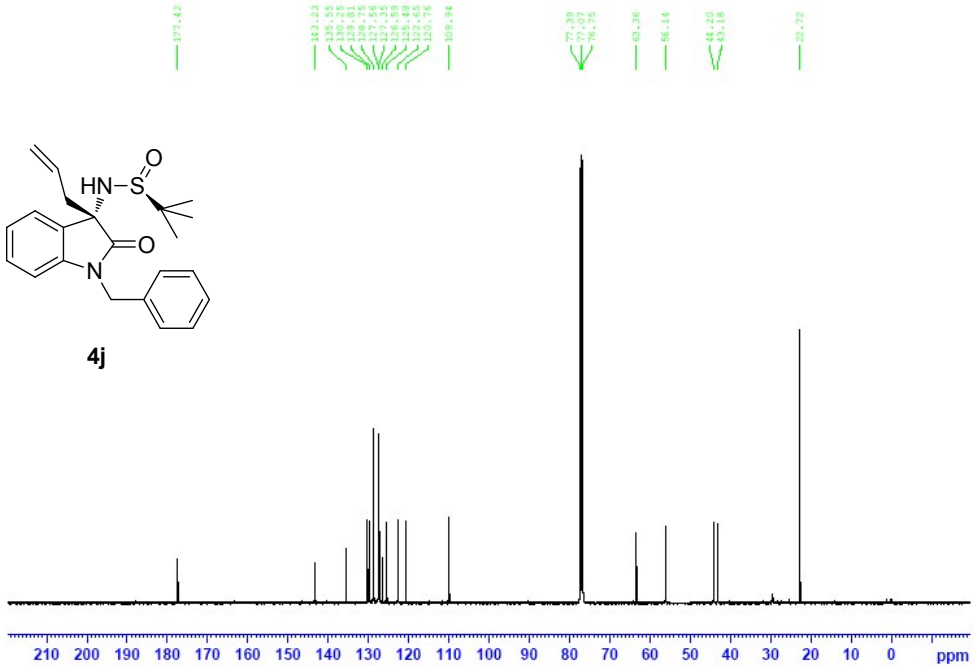
24. ^{13}C NMR Spectrum of 4i.



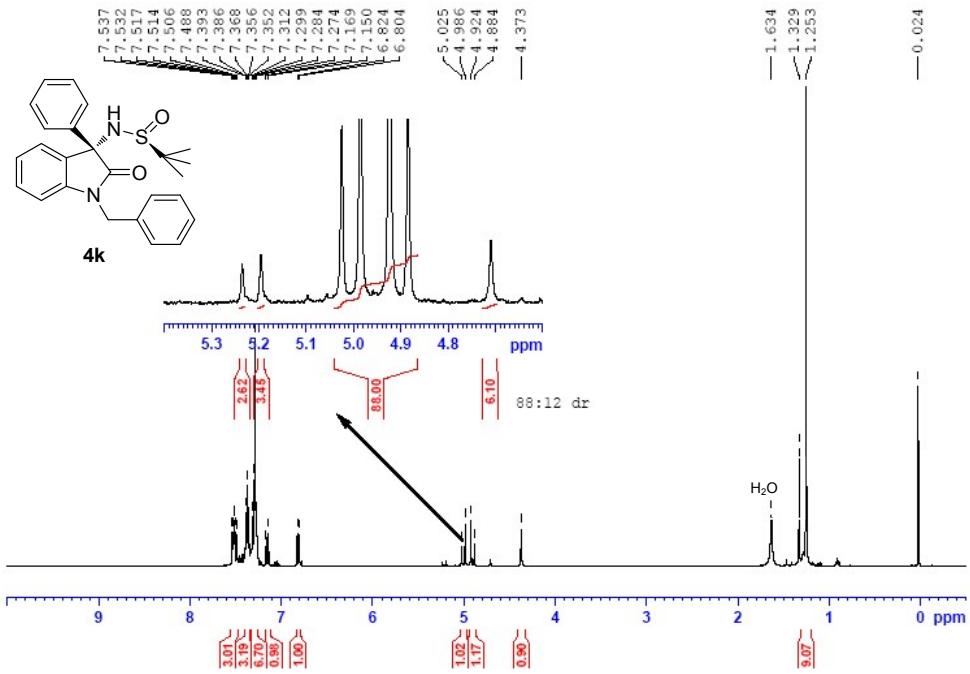
25. ^{1}H NMR Spectrum of 4j.



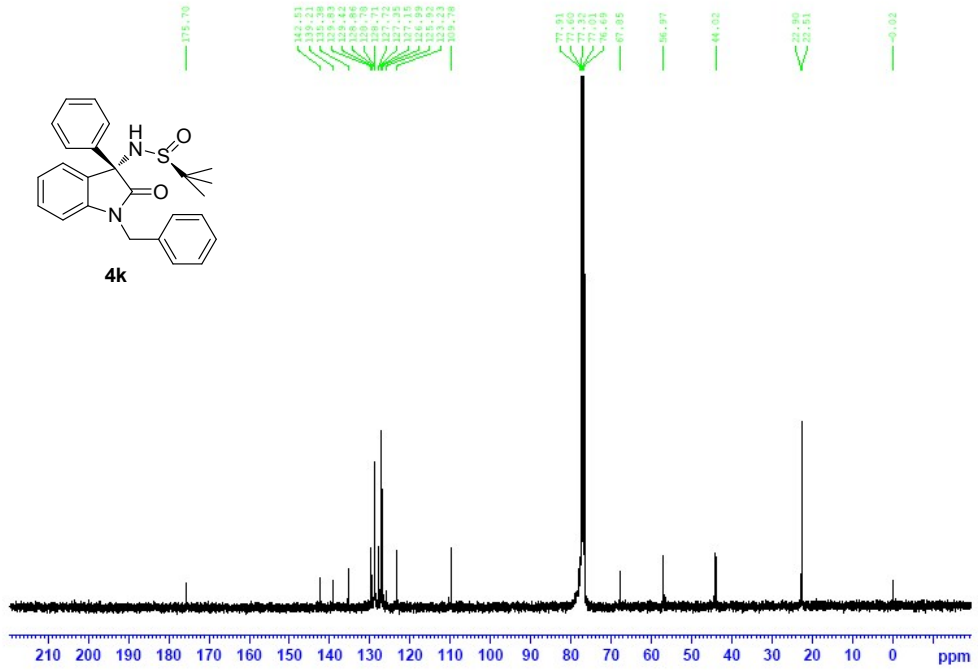
26. ^{13}C NMR Spectrum of 4j.



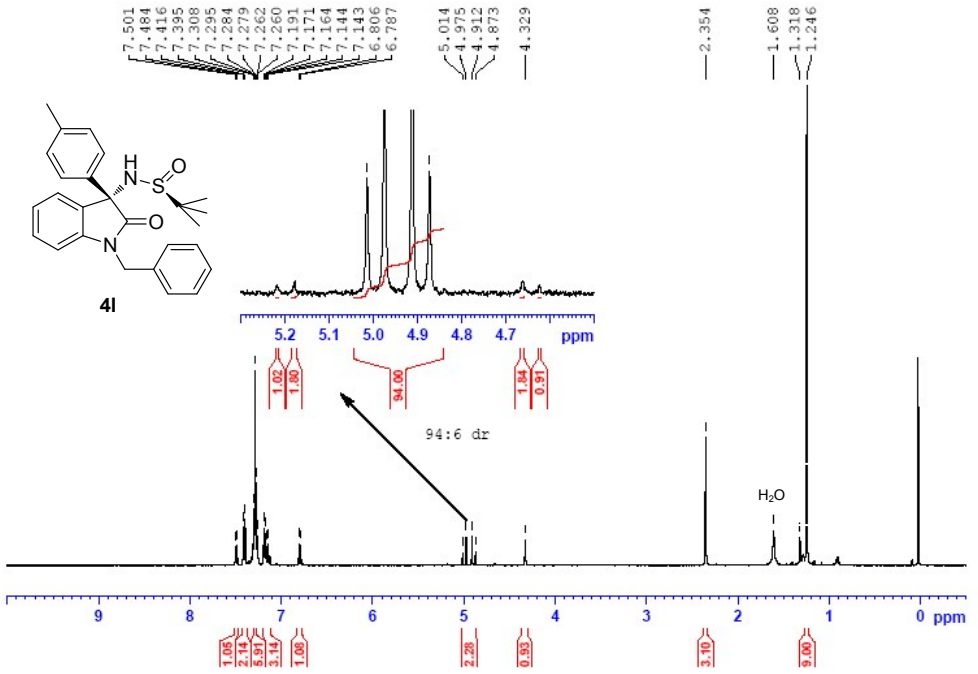
27. ^{1}H NMR Spectrum of 4k.



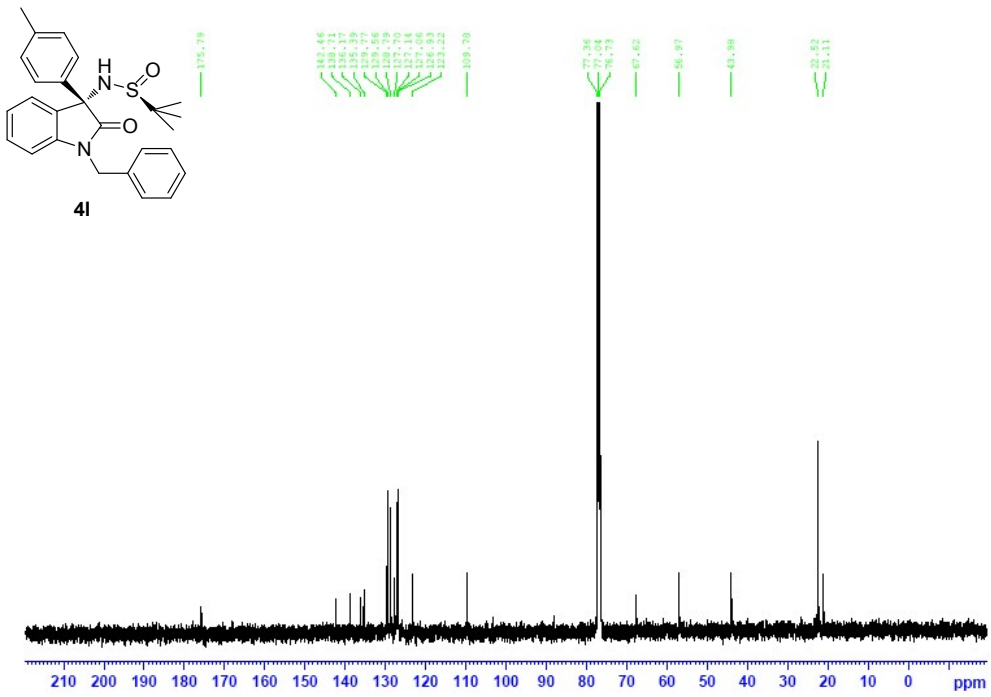
28. ^{13}C NMR Spectrum of 4k.



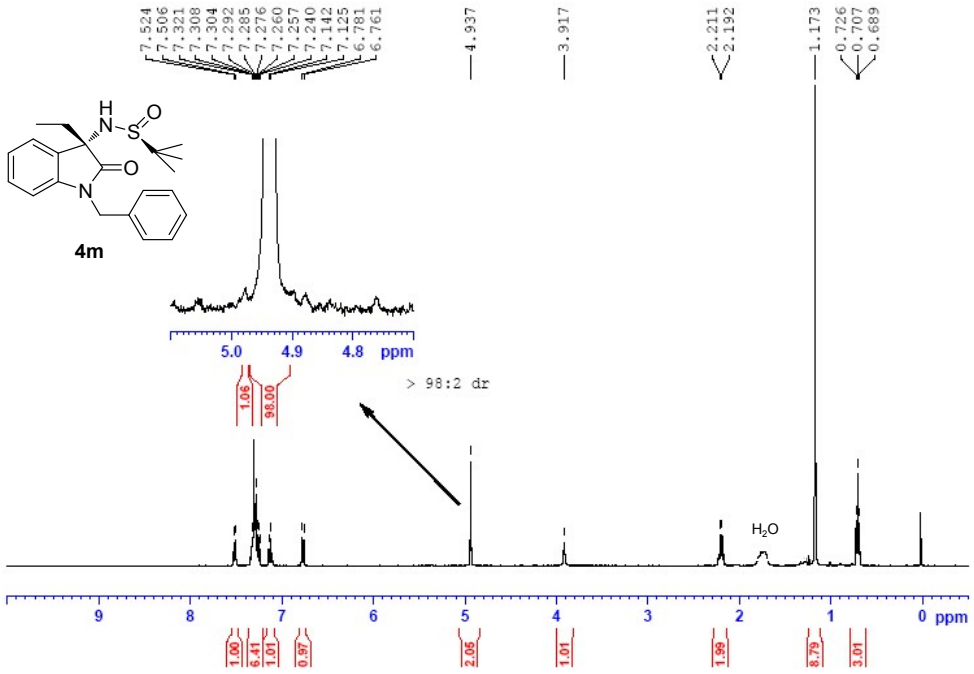
29. ^{1}H NMR Spectrum of 4l.



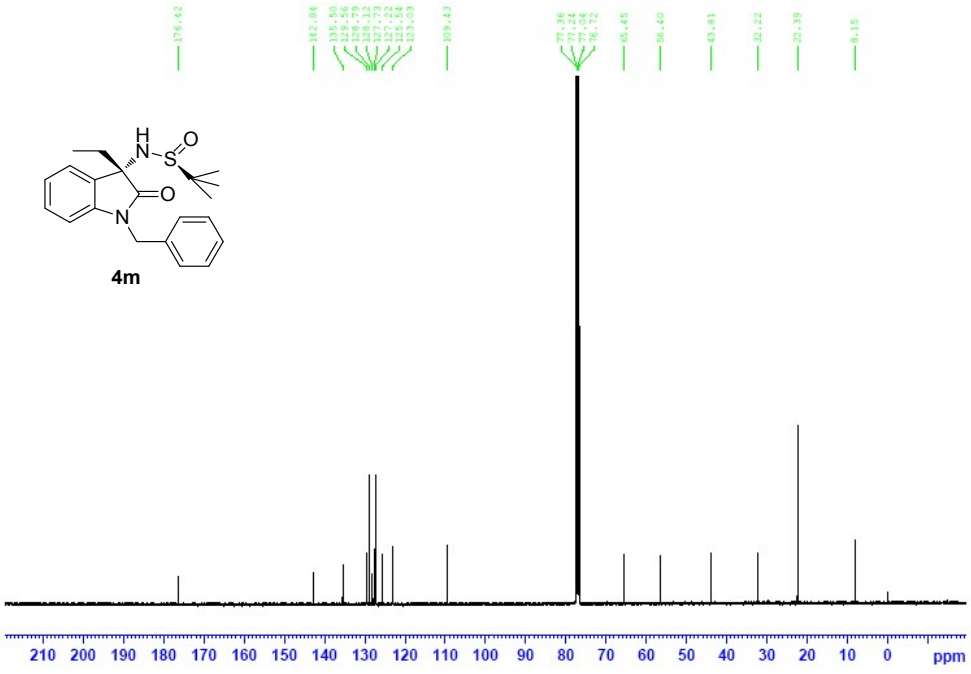
30. ^{13}C NMR Spectrum of 4l.



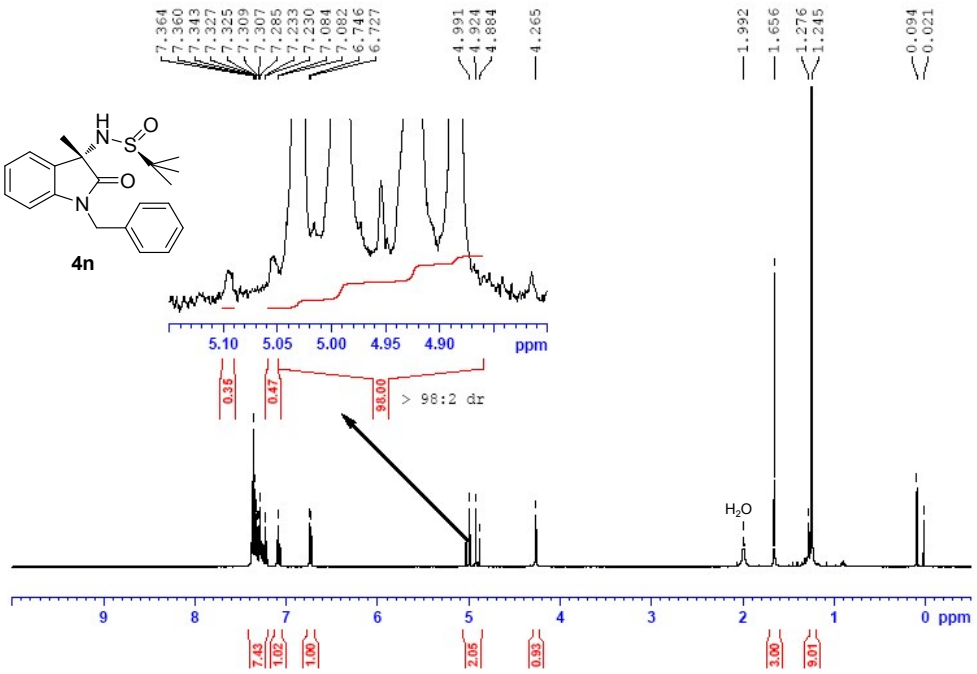
31. ^{1}H NMR Spectrum of 4m.



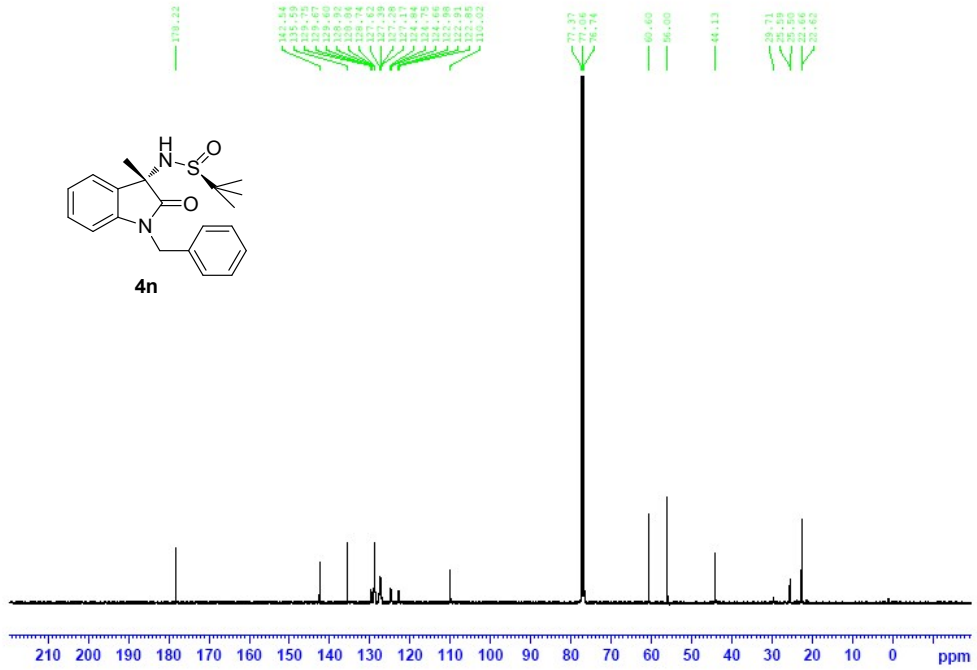
32. ^{13}C NMR Spectrum of 4m.



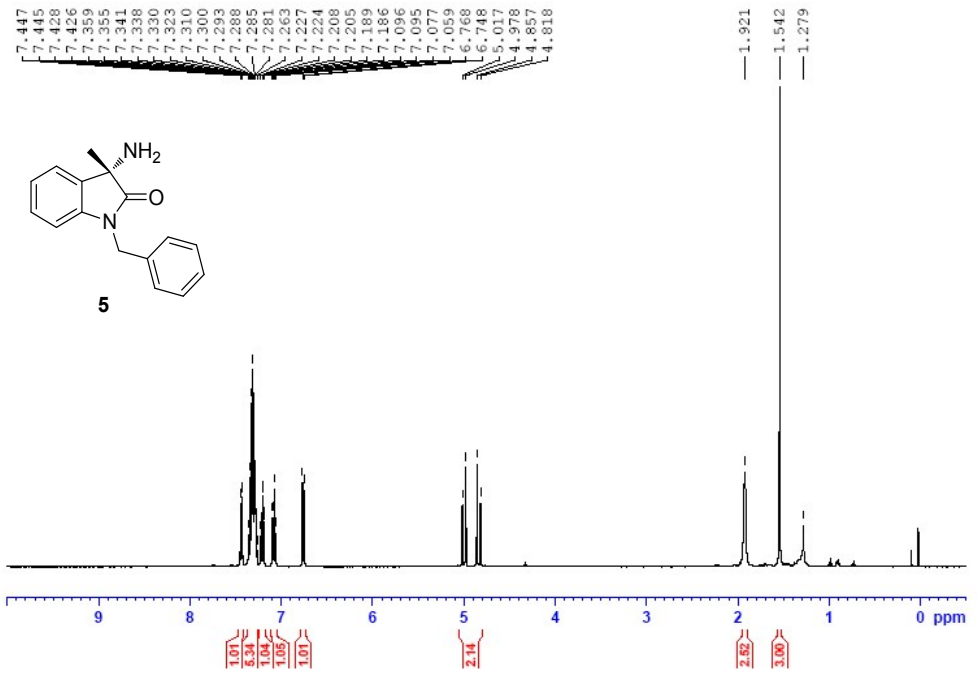
33. ^{1}H NMR Spectrum of 4n.



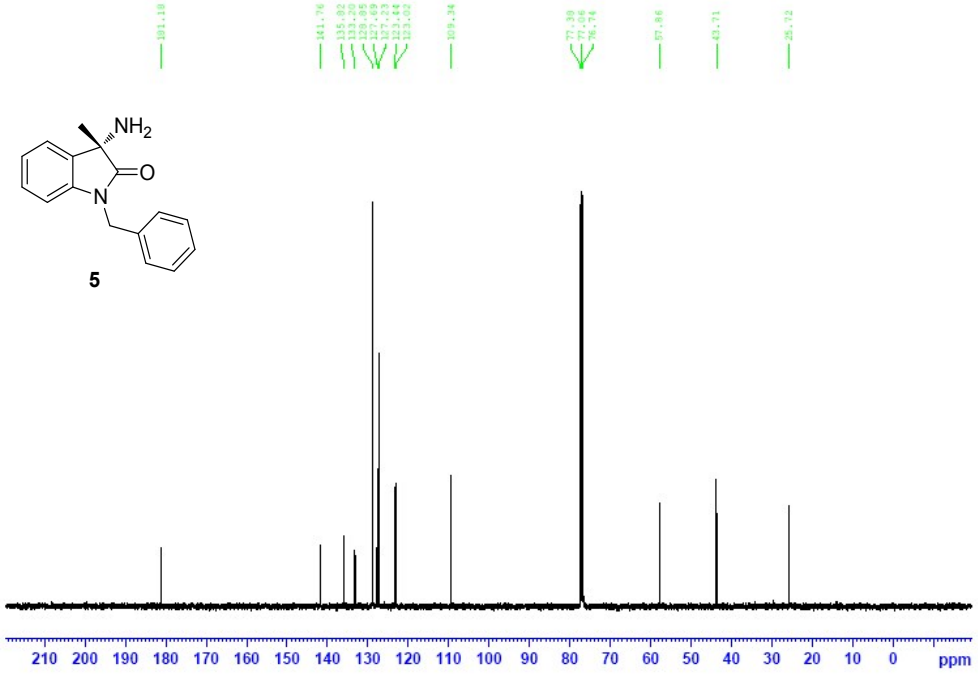
34. ^{13}C NMR Spectrum of 4n.



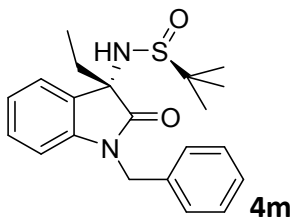
35. ^{1}H NMR Spectrum of 5.



36. ^{13}C NMR Spectrum of 5.



37. Determination of the Absolute Configuration of 4m by single-crystal X-ray analysis.



4m

The absolute configuration of **4m** was confirmed by diffraction measurements on the crystal. The Supplementary crystallographic data were deposited as **CCDC 152303**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K, e-mail:deposit@ccdc.cam.ac.uk.

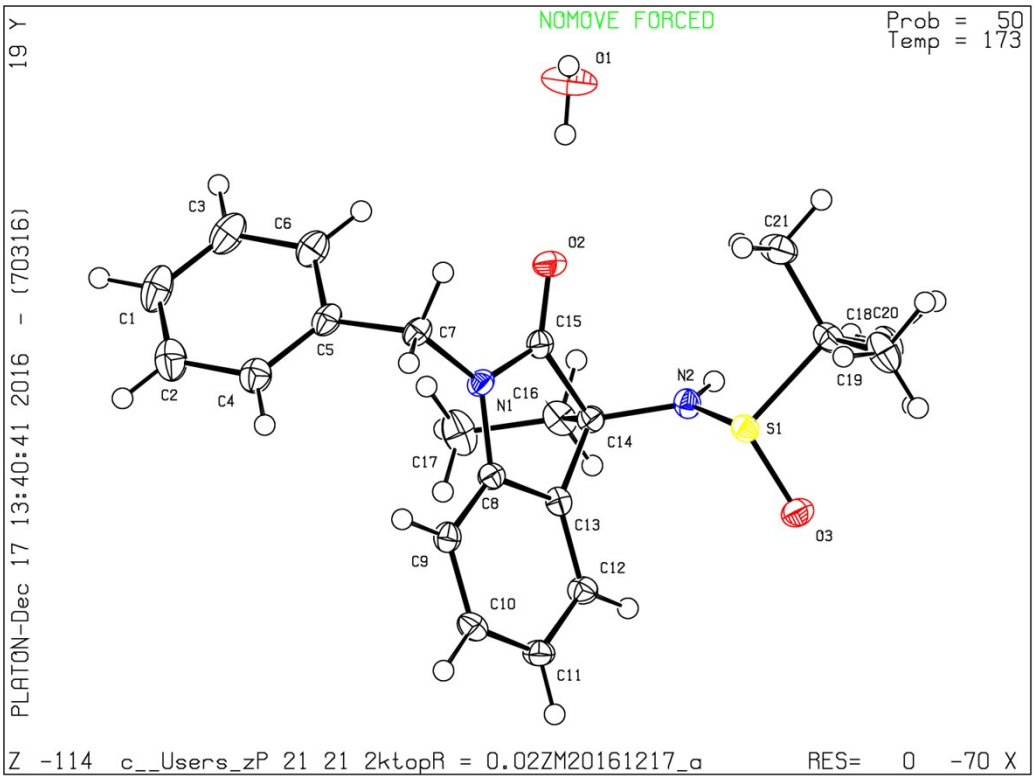


Figure X-ray structure of **4m**

Table 1. Crystal data and structure refinement for 4m.

Identification code	**4m**	
Empirical formula	C21 H26 N2 O2 S	
Formula weight	370.51	
Temperature	173(2) K	
Wavelength	1.54184 A	
Unit cell dimensions	a = 8.62560(10) A	alpha = 90 deg.
	b = 22.3286(3) A	beta = 90 deg.
	c = 10.6389(2) A	gamma = 90 deg.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for a 4m. U(eq) is defined as one third of the trace of the orthogonal Uij tensor.

	x	y	z	U(eq)
S(1)	2101(1)	6332(1)	7152(1)	17(1)
O(3)	407(1)	6421(1)	7415(1)	23(1)
O(2)	5588(1)	5816(1)	5091(1)	23(1)
N(1)	4660(1)	6649(1)	4068(1)	18(1)

O(1)	8437(1)	5529(1)	6268(1)	38(1)
N(2)	2355(1)	5803(1)	6102(1)	18(1)
C(15)	4519(1)	6124(1)	4708(1)	17(1)
C(8)	3201(1)	6911(1)	3846(1)	17(1)
C(18)	2882(2)	5959(1)	8565(1)	21(1)
C(10)	1331(2)	7627(1)	3220(1)	21(1)
C(7)	6157(1)	6908(1)	3722(1)	20(1)
C(11)	158(2)	7266(1)	3677(1)	21(1)
C(5)	6701(1)	6731(1)	2421(1)	21(1)
C(9)	2890(2)	7461(1)	3295(1)	19(1)
C(12)	500(1)	6715(1)	4233(1)	19(1)
C(14)	2769(1)	5972(1)	4816(1)	17(1)
C(13)	2035(2)	6542(1)	4317(1)	17(1)
C(16)	2437(2)	5425(1)	3971(1)	23(1)
C(20)	1908(2)	5409(1)	8884(1)	28(1)
C(4)	6464(2)	7107(1)	1396(1)	25(1)
C(2)	7071(2)	6960(1)	222(1)	32(1)
C(6)	7525(2)	6197(1)	2249(1)	26(1)
C(21)	4576(2)	5804(1)	8301(1)	29(1)
C(3)	8125(2)	6054(1)	1074(2)	31(1)
C(1)	7902(2)	6436(1)	62(1)	34(1)
C(17)	2835(2)	5525(1)	2587(1)	33(1)
C(19)	2773(2)	6435(1)	9598(1)	30(1)

Table 3. Bond lengths [A] and angles [deg] for a 4m.

S(1)-O(3)	1.5010(9)
S(1)-N(2)	1.6408(10)
S(1)-C(18)	1.8457(12)
O(2)-C(15)	1.2189(15)
N(1)-C(15)	1.3619(15)
N(1)-C(8)	1.4082(15)
N(1)-C(7)	1.4621(15)
O(1)-H(31)	0.80(2)
O(1)-H(32)	0.89(2)
N(2)-C(14)	1.4624(15)
N(2)-H(2)	0.8800
C(15)-C(14)	1.5514(16)
C(8)-C(9)	1.3870(16)
C(8)-C(13)	1.3933(17)
C(18)-C(20)	1.5253(17)
C(18)-C(21)	1.5273(19)
C(18)-C(19)	1.5316(18)

C(10)-C(11)	1.3822(18)
C(10)-C(9)	1.3970(18)
C(10)-H(10)	0.9500
C(7)-C(5)	1.5141(17)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(11)-C(12)	1.3976(17)
C(11)-H(11)	0.9500
C(5)-C(4)	1.3918(19)
C(5)-C(6)	1.4007(18)
C(9)-H(9)	0.9500
C(12)-C(13)	1.3823(17)
C(12)-H(12)	0.9500
C(14)-C(13)	1.5187(16)
C(14)-C(16)	1.5431(16)
C(16)-C(17)	1.5288(18)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(4)-C(2)	1.394(2)
C(4)-H(4)	0.9500
C(2)-C(1)	1.384(2)
C(2)-H(2A)	0.9500
C(6)-C(3)	1.389(2)
C(6)-H(6)	0.9500
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(3)-C(1)	1.387(2)
C(3)-H(3)	0.9500
C(1)-H(1)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
O(3)-S(1)-N(2)	110.56(5)
O(3)-S(1)-C(18)	105.27(6)
N(2)-S(1)-C(18)	100.40(6)
C(15)-N(1)-C(8)	111.24(10)
C(15)-N(1)-C(7)	123.11(10)

C(8)-N(1)-C(7)	125.60(10)
H(31)-O(1)-H(32)	108(2)
C(14)-N(2)-S(1)	118.98(8)
C(14)-N(2)-H(2)	120.5
S(1)-N(2)-H(2)	120.5
O(2)-C(15)-N(1)	125.72(11)
O(2)-C(15)-C(14)	126.03(11)
N(1)-C(15)-C(14)	108.21(9)
C(9)-C(8)-C(13)	122.41(11)
C(9)-C(8)-N(1)	127.73(11)
C(13)-C(8)-N(1)	109.81(10)
C(20)-C(18)-C(21)	112.69(11)
C(20)-C(18)-C(19)	111.37(11)
C(21)-C(18)-C(19)	110.36(12)
C(20)-C(18)-S(1)	110.12(9)
C(21)-C(18)-S(1)	107.56(9)
C(19)-C(18)-S(1)	104.35(8)
C(11)-C(10)-C(9)	122.05(11)
C(11)-C(10)-H(10)	119.0
C(9)-C(10)-H(10)	119.0
N(1)-C(7)-C(5)	113.58(10)
N(1)-C(7)-H(7A)	108.8
C(5)-C(7)-H(7A)	108.8
N(1)-C(7)-H(7B)	108.8
C(5)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7
C(10)-C(11)-C(12)	120.52(12)
C(10)-C(11)-H(11)	119.7
C(12)-C(11)-H(11)	119.7
C(4)-C(5)-C(6)	119.09(12)
C(4)-C(5)-C(7)	120.82(11)
C(6)-C(5)-C(7)	120.00(12)
C(8)-C(9)-C(10)	116.40(11)
C(8)-C(9)-H(9)	121.8
C(10)-C(9)-H(9)	121.8
C(13)-C(12)-C(11)	118.36(11)
C(13)-C(12)-H(12)	120.8
C(11)-C(12)-H(12)	120.8
N(2)-C(14)-C(13)	116.17(10)
N(2)-C(14)-C(16)	107.24(9)
C(13)-C(14)-C(16)	112.49(10)
N(2)-C(14)-C(15)	111.30(10)
C(13)-C(14)-C(15)	101.32(9)
C(16)-C(14)-C(15)	108.05(10)

C(12)-C(13)-C(8)	120.26(11)
C(12)-C(13)-C(14)	130.96(11)
C(8)-C(13)-C(14)	108.72(11)
C(17)-C(16)-C(14)	113.85(10)
C(17)-C(16)-H(16A)	108.8
C(14)-C(16)-H(16A)	108.8
C(17)-C(16)-H(16B)	108.8
C(14)-C(16)-H(16B)	108.8
H(16A)-C(16)-H(16B)	107.7
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(5)-C(4)-C(2)	120.30(13)
C(5)-C(4)-H(4)	119.8
C(2)-C(4)-H(4)	119.8
C(1)-C(2)-C(4)	120.31(14)
C(1)-C(2)-H(2A)	119.8
C(4)-C(2)-H(2A)	119.8
C(3)-C(6)-C(5)	120.13(14)
C(3)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(1)-C(3)-C(6)	120.42(13)
C(1)-C(3)-H(3)	119.8
C(6)-C(3)-H(3)	119.8
C(2)-C(1)-C(3)	119.73(13)
C(2)-C(1)-H(1)	120.1
C(3)-C(1)-H(1)	120.1
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5

H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5