Supporting Information

Manganese-Catalyzed Asymmetric Oxidation of Methylene C-H of Spirocyclic Oxindoles and Dihydroquinolinones with Hydrogen Peroxide

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Materials and methods.

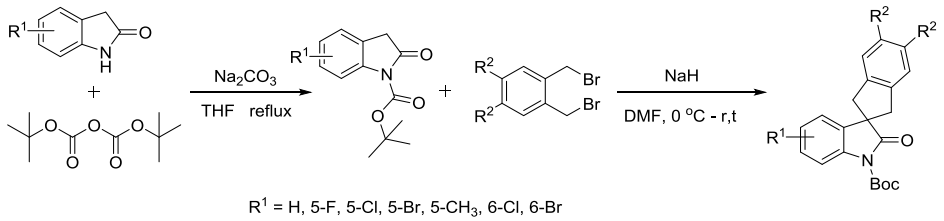
All reagents and solvents were obtained from commercial suppliers without further purification unless noted otherwise. The chiral N4 ligands and the corresponding manganese complexes **C1-C6** were prepared according to the published methods[1]. Flash column chromatography was performed over silica gel (200-300 mesh) to provide the products.

Instrumentation.

^{1}H and ^{13}C NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts for protons are reported in ppm, and the spectra are referenced to residual ^{1}H and ^{13}C signals of the solvents ($CDCl_3$, δ_H = 7.26 ppm; δ_C = 77.2 ppm). The high resolution mass spectra (HRMS) were recorded on an Agilent 6530 Q-TOF LC-MS. GC-MS analysis were performed with an Agilent 7890A/5975C GC-MS system with an HP-5MS column. Optical rotation was recorded with a Perkin-Elmer 341 polarimeter (sodium lamp, 1-dm cuvette, c in g/100 mL, 20 ^{o}C). HPLC analysis for measuring enantiomeric excess (*ee*) values was performed with a SHIMADZU system (SHIMADZU LC-20AT pump, SHIMADZU LC-20A Absorbance Detector) with Chiralpak AD and OD columns (Daicel Chemical Industries, LTD).

General procedure for synthesis of spirocyclic substrates 1

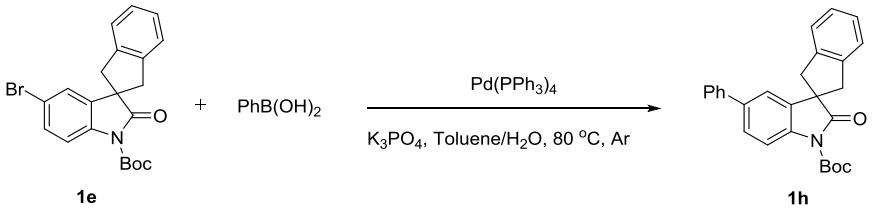
The spirocyclic oxindole and dihydroquinolinone substrates were synthesized according to the published strategies[2,3].



To a solution of 2-oxindole (15.0 mmol) in THF (60 mL) at RT was added anhydrous Na_2CO_3 (14.3 g, 135.0 mmol) and Boc_2O (8.62 mL, 37.6 mmol) sequentially. The reaction mixture was heated to reflux and maintained at this temperature for 2 h after which it was cooled to RT. The resulting precipitated material was filtered off under suction using THF (3 × 10 mL) and concentrated in vacuo. Purification by column chromatography (SiO_2, Petroleum ether/EtOAc, 50:1→20:1) gave the title compounds as solid. Then, to a solution of above

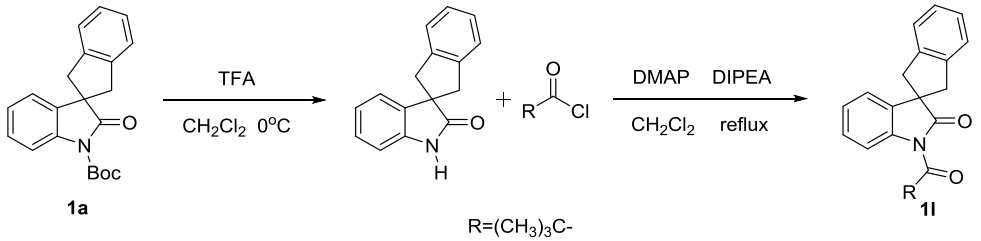
compounds (4.29 mmol) in DMF (68 mL) at 0 ℃ was added NaH (60% in mineral oil, 377 mg, 9.43 mmol) in one portion. The mixture was stirred for 1 h 30 min at 0 ℃ after which a solution of o-xylylene dibromide (5.15 mmol) in DMF (6.3 mL) was added dropwise via syringe over 30 min. Following the addition, the mixture was allowed to warm to RT slowly over 16 h. The reaction was quenched with H_2O (40 mL) and diluted with EtOAc (40 mL). The layers were separated and the aqueous layer further extracted with EtOAc (40 mL). The combined organic layers were washed with brine (80 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (SiO_2, Petroleum ether/EtOAc, 20:1) gave the desired spirocyclic compounds **1a-g**, **1i-k (**33%-39% isolated yield based on *tert*-butyl 2-oxoindoline-1-carboxylate**)**.

The compound **1h** was prepared in analogy to a literature procedure, which obtained by Heck cross-coupling reaction with the substrate **1e** and phenylboronic acid[4].



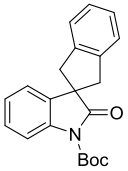
1e **1h**

To a solution of **1e** (0.414g, 1.0 mmol) in Toluene/H_2O (10 mL/3 mL) at RT was added $PhB(OH)_2$ (0.304 g, 1.5mmol), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol) and K_3PO_4 (0.53g, 2.5 mmol) sequentially under argon atmosphere. The reaction mixture was heated to 80 ^oC and maintained at this temperature for 6 h after which it was cooled to RT. The reaction was extracted with toluene (10 mL) and the organic layer was washed with H_2O (3 × 5 mL), brine (10 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (SiO_2, dry load, Petroleum ether/EtOAc, 50:1) afforded the title compound **1h** as light yellow solid (353 mg, 86% isolated yield).



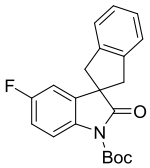
To a solution of **1a** (0.335 g, 1.0 mmol) in CH_2Cl_2 (10 mL) at 0 ℃ was added TFA (1.0 mL, 13.0 mmol) dropwise. The reaction mixture was stirred at 0 ℃ for 30 min, after which it was added aq. $NaHCO_3$ (10 mL) and diluted with CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer further extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with H_2O (3 × 10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated *in vacuo* to obtain crude product. Then, to a solution of the crude product in CH_2Cl_2 (20 mL) at RT was added DMAP (*N*,*N*-dimethylpyridin-4-amine, 12 mg, 0.1 mmol), DIPEA (*N*,*N*-diisopropylpropan- ethylamine, 0.33 mL, 2.0 mmol) and acyl chloride (1.5 mmol) under argon atmosphere. The reaction mixture was heated to reflux and maintained at this temperature for 4 h after which it was cooled to RT. The reaction was quenched with H_2O (10 mL) and diluted with CH_2Cl_2. The layers were separated and the aqueous layer further extracted with CH_2Cl_2 (20 mL). The combined organic layers were washed with H_2O (3× 10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography (SiO_2, dry load, Petroleum ether:EtOAc, 20:1) gave the title compound **1l** as White solid (271 mg, 85% isolated yield).

***tert*-butyl 2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1a)**



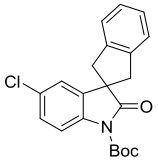
White solid, 503 mg, 35% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.25-7.29 (m, 5H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 3.69 (d, *J* = 15.6 Hz, 2H), 3.13 (d, *J* = 15.6 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.8, 149.2, 140.5, 138.0, 134.8, 128.1, 127.0, 124.7, 124.4, 121.3, 114.8, 84.3, 54.3, 45.3, 28.0.

***tert*-butyl 5'-fluoro-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1b)**



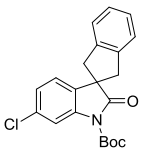
Orange red solid, 560 mg, 37% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.85 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.26 (s, 4H), 7.96 (td, *J* = 8.8, 2.8 Hz, 1H), 6.54 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.69 (d, *J* = 15.6 Hz, 2H), 3.12 (d, *J* = 15.6 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.4, 160.1 (d, *J* = 242 Hz), 149.3, 140.2, 136.6 (d, *J* = 9 Hz), 134.1, 127.4, 124.6, 116.3 (d, *J* = 8 Hz), 114.7 (d, *J* = 23 Hz), 109.0 (d, *J* = 24 Hz), 84.7, 54.7, 45.3, 28.1.

***tert*-butyl 5'-chloro-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1c)**



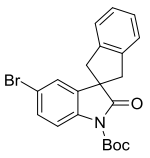
White solid, 602 mg, 38% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.23-7.26 (m, 5H), 6.80 (s, 1H), 3.68 (d, *J* = 15.6 Hz, 2H), 3.12 (d, *J* = 15.6 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.2, 149.2, 140.2, 136.8, 136.6, 130.1 128.3, 127.4, 124.6, 121.7, 116.3, 84.8, 54.5, 45.3, 28.1.

***tert*-butyl 6'-chloro-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1d)**



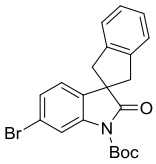
Light yellow solid, 617 mg, 39% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.93 (d, *J* = 2.0 Hz 1H), 7.25 (s, 4H), 6.98 (dd, *J* = 8.0 , 2.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.68 (d, *J* = 16.0 Hz, 2H), 3.10 (d, *J* = 15.6 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.4, 149.1, 140.4, 139.2, 133.9, 133.3, 127.4, 124.8, 124.6, 122.3, 115.7, 85.0, 54.3, 45.4, 28.1.

***tert*-butyl 5'-bromo-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1e)**



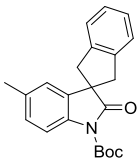
White solid, 638 mg, 36% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.26 (s, 4H), 6.94 (d, *J* = 2.8 Hz, 1H), 3.68 (d, *J* = 15.6 Hz, 2H), 3.13 (d, *J* = 15.6 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.1, 149.2, 140.1, 137.3, 137.0, 131.2, 127.4, 124.6, 124.5, 117.7, 116.7, 84.9, 54.4, 45.4, 28.1.

***tert*-butyl 6'-bromo-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1f)**



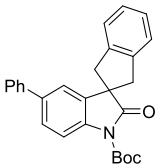
White solid, 638 mg, 36% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.10 (t, *J* = 2.0 Hz, 1H), 7.25 (s, 4H), 7.13 (dt, *J* = 8.0, 1.6 Hz, 1H), 6.70 (dd, *J* = 8.0 1.6 Hz, 1H), 3.68 (d, *J* = 15.6 Hz, 2H), 3.10 (d, *J* = 16.8 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.2, 149.1, 140.3, 139.3, 133.8, 127.7, 127.4, 124.6, 122.7, 121.7, 118.5, 85.0, 54.3, 45.3, 28.1.

***tert*-butyl 5'-methyl-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1g)**



White solid, 494 mg, 33% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.25 (s, 4H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 3.67 (d, *J* = 15.6 Hz, 2H), 3.13 (d, *J* = 15.6 Hz, 2H), 2.20 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ179.2, 149.4, 140.8, 135.8, 135.0, 134.5, 128.7, 127.1, 124.5, 122.0, 114.7, 84.3, 54.3, 45.5, 28.2, 21.0.

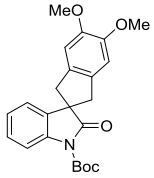
***tert*-butyl 2'-oxo-5'-phenyl-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1h)**



Light yellow solid, 353 mg, 86% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.93 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.51 (dt, *J* = 8.4, 2.0 Hz, 1H), 7.34-7.42 (m, 4H), 7.30 (dd, *J* = 6.4, 1.6 Hz, 1H), 7.26 (s, 4H), 7.08 (t, *J* = 2.0 Hz, 1H), 3.72 (d, *J* = 17.2 Hz, 2H), 3.22 (d, *J* = 16.8

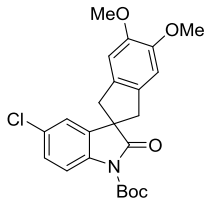
Hz, 2H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ179.1, 149.4, 140.6, 140.4, 138.1, 137.6, 135.6, 128.8, 127.3, 127.1, 126.9, 124.6, 120.1, 115.3, 84.6, 54.4, 45.6, 28.2; HRMS $[M+Na]^+$ Calcd for $C_{27}H_{25}NO_3Na$: 434.1727, found: 434.1725.

***tert*-butyl 5,6-dimethoxy-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1i)**



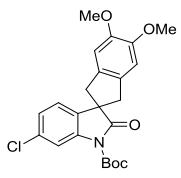
White solid, 559 mg, 33% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.78 (s, 2H), 3.89 (s, 6H), 3.63 (d, *J* = 15.2 Hz, 2H), 3.07 (d, *J* = 15.2 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.9, 149.4, 148.7, 138.3, 135.2, 132.2, 128.2, 124.8, 121.5, 114.9, 107.6, 84.4, 56.1, 54.8, 45.5, 28.2.

***tert*-butyl 5'-chloro-5,6-dimethoxy-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1j)**



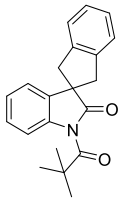
White solid, 610 mg, 36% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.80 (d, *J* = 8.8 Hz, 1H), 7.23 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.77 (s, 2H), 3.88 (s, 6H), 3.61 (d, *J* = 15.2 Hz, 2H), 3.03 (d, *J* = 15.2 Hz, 2H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.0, 149.2, 148.8, 136.9, 136.8, 131.6, 130.1, 128.2, 121.7, 116.2, 107.6, 84.7, 56.1, 54.8, 45.3, 28.1.

***tert*-butyl 6'-chloro-5,6-dimethoxy-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (1k)**



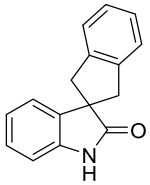
White solid, 593 mg, 35% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.78 (s, *2*H), 3.88 (s, 6H), 3.62 (d, *J* = 15.2 Hz, 2H), 3.03 (d, *J* = 15.2 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 178.3, 149.1, 148.9, 139.2, 133.9, 133.5, 131.8, 124.8, 122.3, 115.7, 107.7, 84.9, 56.1, 54.6, 45.4, 28.1.

1'-pivaloyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one (1l)



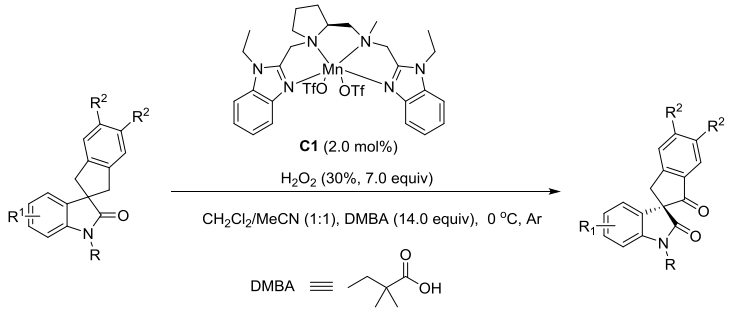
White solid, 271 mg, 85% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.22-7.28 (m, 5H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 3.65 (d, *J* = 16.0 Hz, 2H), 3.19 (d, *J* = 16.0 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 182.8, 179.8, 140.6, 139.5, 135.6, 128.2, 127.3, 124.7, 124.6, 121.7, 114.1, 54.4, 45.0, 43.5, 26.9.

1,3-dihydrospiro[indene-2,3'-indolin]-2'-one (1m)



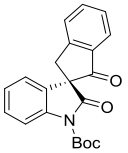
White solid, 119 mg, 92% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.86 (s, 1H, NH), 7.18-7.26 (m, 5H), 6.83-6.94 (m, 3H), 3.65 (d, *J* = 15.6 Hz, 2H), 3.13 (d, *J* = 15.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 183.3, 141.2, 139.9, 136.8, 128.0, 127.1, 124.6, 122.7, 121.9, 110.0, 54.8, 44.1.

General procedure for the asymmetric oxidation of spirocyclic substrate 1



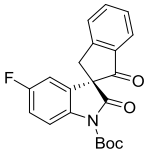
A 10 mL Schlenk tube was charged with substrate 1 (0.2 mmol, 1.0 equiv), manganese catalyst **C1** (2.0 mol%),1 mL of CH_2Cl_2, 2,2-dimethylbutanoic acid (DMBA, 0.35 mL, 14 equiv) and a stir bar under argon. Then a solution of H_2O_2 (7.0 equiv, 30% aqueous solution diluted in 1 mL of MeCN) was added dropwise over 2 h using a syringe pump and the mixture was stirred at 0 ℃ for additional 2 h. The reaction mixture was then quenched with sodium sulfite and $NaHCO_3$ then purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1) to give the desired spirocyclic compound.

***tert*-butyl (*R*)-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2a)**



White solid, 44 mg, 63% isolated yield; $[\alpha]_D^{20}$ = +32.8 (*c* = 0.68 in $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.87 (d, *J* = 17.2 Hz, 1H), 3.46 (d, *J* = 17.2 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.8, 173.2, 153.6, 148.9, 140.9, 135.9, 134.4, 129.1, 128.8, 128.4, 126.5, 125.7, 124.9, 121.9, 115.6, 84.7, 63.6, 38.7, 28.1; HRMS $[M+Na]^+$ Calcd for $C_{21}H_{19}NO_4Na$: 372.1206, found: 372.1212; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 6.85 min, 11.18 min; Chiralcel AD-H, 20 ^{o}C, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2a**] = 6.86 min, t_R = [*ent*-**2a**] = 11.45 min; 91% ee.

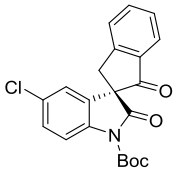
***tert*-butyl (*R*)-5'-fluoro-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2b)**



Light yellow solid, 41 mg, 56% isolated yield; $[\alpha]_D^{20}$ = +47.5 (*c* = 0.116 in $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.94 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.05 (td, *J* = 9.0, 2.8 Hz, 1H), 6.66 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.89 (d, *J* = 17.6 Hz, 1H), 3.45 (d, *J* = 17.2 Hz, 1H), 1.63

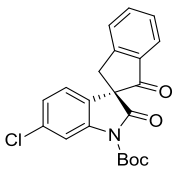
(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.2, 172.8, 160.0 (d, *J* = 243.0 Hz), 153.4, 148.9, 136.9, 136.2, 134.2, 130.2 (d, *J* = 9.0 Hz), 128.6, 126.6, 125.9, 117.0 (d, *J* = 8.0 Hz), 115.6 (d, *J* = 22.0 Hz), 109.7 (d, *J* = 25.0 Hz), 84.9, 63.7, 38.5, 28.1; HRMS $[M+Na]^+$ Calcd for $C_{21}H_{18}FNO_4Na$: 390.1112, found: 390.1125; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 6.53 min, 9.13 min; Chiralcel AD-H, 20 ^{o}C, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2b**] = 6.67 min, t_R = [*ent*-**2b**] = 9.29 min; 88% ee.

***tert*-butyl (*R*)-5'-chloro-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2c)**



White solid, 51 mg, 67% isolated yield; $[\alpha]_D^{20}$ = +78.1 (*c* = 0.22 in $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.91 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.89 (s, 1H), 3.87 (d, *J* = 17.2 Hz, 1H), 3.45 (d, *J* = 17.6 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.0, 172.5, 153.3, 148.7, 139.5, 136.2, 134.2, 130.4, 130.3 129.1, 128.6, 126.5, 125.9, 122.3, 116.9, 85.1, 63.4, 38.5, 28.1; HRMS $[M+Na]^+$ Calcd for $C_{21}H_{18}ClNO_4Na$: 406.0817, found: 406.0817; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 7.32 min, 11.02 min; Chiralcel AD-H, 20 ^{o}C, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2c**] = 7.32 min, t_R = [*ent*-**2c**] = 11.05 min; 89% ee.

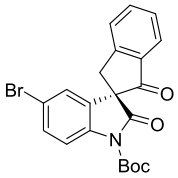
***tert*-butyl (*R*)-6'-chloro-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2d)**



Light yellow solid, 50 mg, 65% isolated yield; $[\alpha]_D^{20}$ = +56.5 (*c* = 0.32 in $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.03 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.85 (d, *J* =

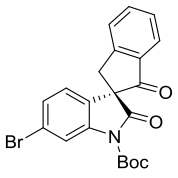
8.0 Hz, 1H), 3.87 (d, *J* = 17.2 Hz, 1H), 3.44 (d, *J* = 17.6 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.3, 172.7, 153.4, 148.7, 141.8, 136.1, 134.9, 134.2, 128.6, 127.0, 126.5, 125.9, 125.0, 122.9, 116.4, 85.3, 63.2, 38.5, 28.0; HRMS $[M+Na]^+$ Calcd for $C_{21}H_{18}ClNO_4Na$: 406.0817, found: 406.0827; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 6.72 min, 10.91 min; Chiralcel AD-H, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2d**] = 6.73 min, t_R = [*ent*-**2d**] = 10.92 min; 88% ee.

***tert*-butyl (*R*)-5'-bromo-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2e)**



White solid, 50 mg, 58% isolated yield; $[\alpha]_D^{20}$ = +35.6 (*c* = 0.50 in $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.46-7.51 (m, 2H), 7.04 (d, *J* = 2.0 Hz, 1H), 3.87 (d, *J* = 17.2 Hz, 1H), 3.46 (d, *J* = 17.6 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.1, 172.5, 153.4, 148.7, 139.9, 136.2, 134.1, 132.0, 130.7, 128.6, 126.6, 125.9, 125.1, 117.7, 117.3, 85.1, 63.3, 38.5, 28.1; HRMS $[M+Na]^+$ Calcd for $C_{21}H_{18}BrNO_4Na$: 450.0311, found: 450.0322; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 7.58 min, 11.88 min; Chiralcel AD-H, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2e**] = 7.79 min, t_R = [*ent*-**2e**] = 12.49 min; 88% ee.

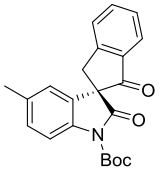
***tert*-butyl (*R*)-6'-bromo-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2f)**



White solid, 44 mg, 52% isolated yield; $[\alpha]_D^{20}$ = +37.1 (*c* = 0.66 in $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.18 (d, *J* = 1.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.72 (td, *J* = 7.4, 1.2 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.26 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.86 (d, *J* = 17.6 Hz, 1H), 3.44 (d, *J* = 17.2 Hz, 1H), 1.64 (s, 9H);

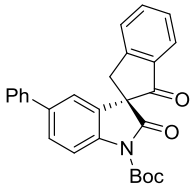
^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.2, 172.6, 153.4, 148.7, 141.9, 136.2, 134.2, 128.6, 127.9, 127.6, 126.6, 125.8, 123.2, 122.7, 119.2, 85.3, 63.3, 38.4, 28.0.; HRMS $[M+Na]^+$ Calcd for $C_{21}H_{18}BrNO_4Na$: 450.0311, found: 450.0305; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 6.96 min, 11.39 min; Chiralcel AD-H, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2f**] = 6.97 min, t_R = [*ent*-**2f**] = 11.41 min; 87% ee.

***tert*-butyl (*R*)-5'-methyl-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2g)**



White solid, 35 mg, 48% isolated yield; $[\alpha]_D^{20}$ = +44.7 (*c* = 0.30 in $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.71 (s, 1H), 3.86 (d, *J* = 17.2 Hz, 1H), 3.44 (d, *J* = 17.6 Hz, 1H), 2.26 (s, 3H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 199.0, 173.4, 153.7, 149.0, 138.5, 135.9, 134.6, 134.5, 129.6, 128.8, 128.4, 126.5, 125.7, 122.5, 115.4, 84.5, 63.6, 38.7, 28.1, 21.0; HRMS $[M+Na]^+$ Calcd for $C_{22}H_{21}NO_4Na$: 386.1363, found: 386.1367; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 8.45 min, 12.18 min; Chiralcel AD-H, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2g**] = 8.27 min, t_R = [*ent*-**2g**] = 11.83 min; 88% ee.

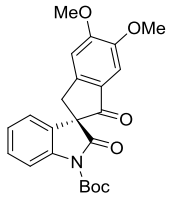
***tert*-butyl (*R*)-1,2'-dioxo-5'-phenyl-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2h)**



White solid, 38 mg, 45% isolated yield; $[\alpha]_D^{20}$ = +32.5 (*c* = 0.24 in $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.45-7.50 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 3.92 (d, *J* = 17.6 Hz, 1H), 3.53 (d, *J* = 17.6 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.8, 173.3, 153.6,

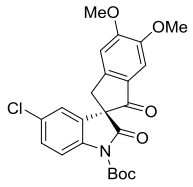
148.9, 140.2, 138.3, 136.0, 134.4, 129.4, 128.8, 128.5, 128.0, 127.4, 127.0, 126.5, 125.8, 120.6, 116.0, 84.8, 63.7, 38.7, 28.1; HRMS $[M+Na]^+$ Calcd for $C_{27}H_{23}NO_4Na$: 448.1519, found: 448.1527; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 14.14 min, 21.73 min; Chiralcel AD-H, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2h**] = 14.23 min, t_R = [*ent*-**2h**] = 21.84 min; 77% ee.

***tert*-butyl (*R*)-5,6-dimethoxy-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (2i)**



White solid, 46 mg, 56% isolated yield; $[\alpha]_D^{20}$ = +53.8 (*c* = 0.65 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 4.02 (s, 3H), 3.92 (s, 3H), 3.76 (d, *J* = 16.8 Hz, 1H), 3.36 (d, *J* = 16.8 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 197.2, 173.5, 156.5, 150.2, 149.4, 148.9, 140.9, 129.0, 127.1, 124.8, 121.9, 115.6, 107.3, 105.6, 84.6, 63.9, 56.5, 56.2, 38.5, 28.1; HRMS $[M+Na]^+$ Calcd for $C_{23}H_{23}NO_6Na$: 432.1418, found: 432.1419; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 18.92 min, 26.31 min; Chiralcel OD-H, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2i**] = 18.69 min, t_R = [*ent*-**2i**] = 26.42 min; 69%; ee.

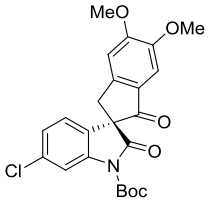
***tert*-butyl (*R*)-5'-chloro-5,6-dimethoxy-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline] -1'- carboxylate (2j)**



White solid, 47 mg, 53% isolated yield; $[\alpha]_D^{20}$ = +40.0 (*c* = 0.21 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.89 (d, *J* = 8.8 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.18 (s, 1H), 7.01 (s, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 4.03 (s, 3H), 3.93 (s, 3H), 3.76 (d, *J* = 17.2 Hz, 1H), 3.34 (d, *J* = 16.8 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 196.3, 172.8, 156.8, 150.4, 149.1, 148.8, 139.5, 130.7, 130.2, 129.0, 126.8, 122.2, 116.8, 107.3, 105.7, 84.9,

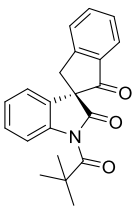
63.7, 56.5, 56.3, 38.3, 28.1; HRMS $[M+Na]^+$ Calcd for $C_{23}H_{22}NO_6ClNa$: 466.1028, found: 466.1031; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 37.94 min, 44.91 min; Chiralcel IA, 20 ^oC, 210 nm, 95/5 *n*-hexane/*i*-PrOH, 0.8 mL/min, t_R [**2j**] = 38.24 min, t_R = [*ent*-**2j**] = 45.29 min; 60% ee.

tert-butyl (*R*)-6'-chloro-5,6-dimethoxy-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-indoline] -1'-carboxylate (2k)



White solid, 51 mg, 57% isolated yield; $[\alpha]_D^{20}$ = +21.0 (*c* = 0.10 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.18 (s, 1H), 7.11 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.00 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H), 3.92 (s, 3H), 3.75 (d, *J* = 17.2 Hz, 1H), 3.33 (d, *J* = 17.2 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 196.5, 173.0, 156.7, 150.4, 149.1, 148.7, 141.8, 134.7, 127.4, 126.9, 124.8, 122.8, 116.4, 107.3, 105.6, 85.1, 63.5, 56.5, 56.3, 38.3, 28.0; HRMS $[M+Na]^+$ calcud for $C_{23}H_{22}NO_6ClNa$: 466.1028, found: 466.1032; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 17.05 min, 23.51 min; Chiralcel IA, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2k**] = 16.98 min, t_R = [*ent*-**2k**] = 23.47 min, 55% ee.

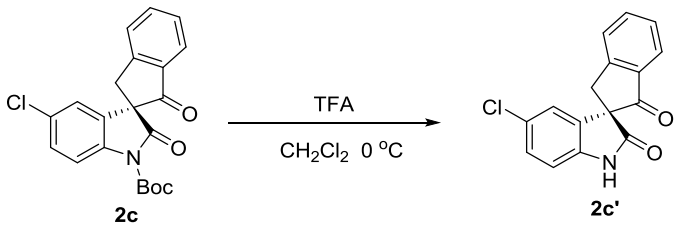
(*R*)-1'-pivaloylspiro[indene-2,3'-indoline]-1,2'(3*H*)-dione (2l)



White solid, 28 mg, 42% isolated yield; $[\alpha]_D^{20}$ = +37.6 (*c* = 0.21 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.32 (td, *J* = 7.8, 1.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.88 (d, *J* = 17.2 Hz, 1H), 3.50 (d, *J* = 17.2 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.6, 182.4, 174.5, 153.7, 142.1, 136.0, 134.2, 129.8, 129.0, 128.4, 126.5, 125.8, 124.7, 122.0, 114.6, 63.8, 43.6, 37.8, 26.9;

HRMS $[M+Na]^+$ Calcd for $C_{21}H_{19}NO_3Na$: 356.1257, found: 356.1269; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 6.48 min, 8.10 min; Chiralcel AD-H, 20 °C, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**2l**] = 6.49 min, t_R = [*ent*-**2l**] = 8.11 min; 87% ee.

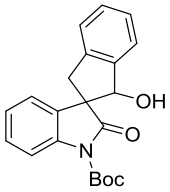
(*R*)-5'-chlorospiro[indene-2,3'-indoline]-1,2'(3*H*)-dione (2c')



To a solution of **2c** (66 mg, 0.171 mmol) in CH_2Cl_2 (5 mL) at 0 ℃ was added TFA (0.5 mL, 6.5 mmol) dropwise. The reaction mixture was stirred at 0 ℃ for 30 min, after which it was added aq. $NaHCO_3$ (10 mL) and diluted with CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer further extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with H_2O (3 × 10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography (SiO_2, dry load, Petroleum ether:EtOAc, 3:1) gave the title compound **2c'**.

Light orange solid, 41 mg, 82% isolated yield; $[\alpha]_D^{20}$ = +78.3 (*c* = 0.22 in $CHCl_3$) [$[\alpha]_D^{20}$ = +33.1 (*c* = 0.175, $CDCl_3$), 61% ee][2]; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.62 (s, 1H, N-H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.85-6.87 (m, 2H), 3.85 (d, *J* = 17.2 Hz, 2H), 3.45 (d, *J* = 17.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.9, 153.5, 140.5, 136.0, 134.7, 132.2, 128.9, 128.5, 128.3, 126.6, 125.8, 122.9, 111.4, 63.5, 37.4.

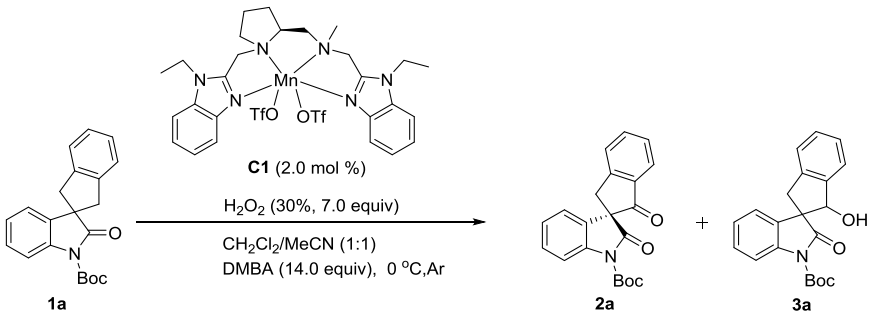
***tert*-butyl 1-hydroxy-2'-oxo-1,3-dihydrospiro[indene-2,3'-indoline]-1'-carboxylate (3a)**



White solid, 16 mg, 23% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.40-7.41 (m, 1H), 7.26-7.35 (m, 5H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.2

Hz, 1H), 5.72 (s, 1H), 3.61 (d, *J* = 15.6 Hz, 1H), 3.12 (d, *J* = 15.6 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 177.4, 149.2, 142.5, 140.1, 139.2, 129.0, 128.9, 127.7, 124.9, 124.8 ,124.5, 124.2, 122.5, 115.4, 84.6, 83.0, 62.1, 41.6, 28.2; HRMS $[M+Na]^+$ Calcd for $C_{21}H_{21}NO_4Na$: 374.1363, found: 374.1364. HPLC-separation conditions: Sample dissolved in EtOH, Chiralcel AD-H, 20 ^{o}C, 210 nm, 95/5 *n*-hexane/*i*-PrOH, 0.5 mL/min.

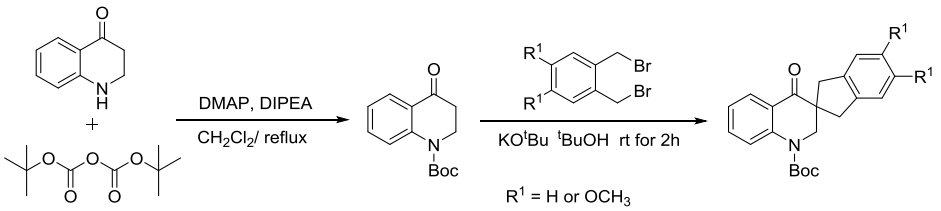
Gram-scale reaction for the asymmetric oxidation of 1a



Substrate **1a** (1.005 g, 2.86 mmol, 1.0 equiv), manganese catalyst **C1** (2.0 mol %) were added into a 50 mL of *Schlenk* tube, followed by 6 mL of CH_2Cl_2 and 2,2-dimethylbutanoic acid (DMBA, 5.0 mL, 14 equiv) with a magnetic stir bar under argon. Then 7 equiv of H_2O_2 (30% aqueous solution diluted in 6 mL of MeCN) was added dropwise over 3 h using a syringe pump and the mixture was stirred at 0 ℃ for additional 3 h. The reaction mixture was then quenched with sodium sulfite and then purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1-10:1) to give the desired spirocyclic compound **2a** (white solid, 0.408 g, 39% yield, 90% ee) and **3a** (white solid, 0.211 g, 20% yield, 0% ee).

General procedure for synthesis of spirocyclic substrates 4

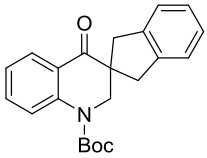
The 2,3-dihydroquinolin-4(1*H*)-one derivatives were synthesized according to the reported method[5,6].



To a solution of 2,3-dihydroquinolin-4-one (0.74 g, 5 mmol) in CH_2Cl_2 (30 mL) at rt was added DMAP (60 mg, 0.5 mmol), DIPEA (1.65 mL, 10.0 mmol) and Boc_2O (1.73 mL, 7.5

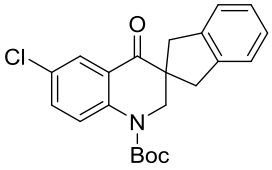
mmol) under argon atmosphere. The reaction mixture was heated to reflux and maintained at this temperature for 4 h after which it was cooled to RT. Purification by column chromatography (SiO_2, dry load, Petroleum ether/EtOAc, 20:1) gave the compound. Then, to a mixture of *t*-BuOK (0.50 g, 4.44 mmol, 2.22 equiv.) in dry *t*-BuOH (10 mL) was added ketone (2.0 mmol, 1.0 equiv.) under an inert atmosphere. The mixture was stirred at rt for 10-15 min. To this mixture, α,α'-dibromo xylene (2.0 mmol, 1.0 equiv.) was added and resulting mixture was stirred at rt for 2 h. The reaction mixture was concentrated on a rotary evaporator to give residue. The residue was diluted with water (5 mL) and 15% HCl (5 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated to give crude product. It was purified by column chromatography (petroleum ether/ethyl acetate, 50:1-25:1) to give the product **4** (53%-85% isolated yield based on *tert*-butyl 4-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate).

tert-butyl 4'-oxo-1,3-dihydro-2'_H_-spiro[indene-2,3'-quinoline]-1'(4'_H_)-carboxylate (4a)



White solid, 524 mg, 75% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.14-7.24 (m, 5H), 3.98 (s, 2H), 3.42 (d, *J* = 16.0 Hz, 2H), 2.87 (d, *J* = 16.0 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 197.3, 153.3, 143.9, 140.3, 134.1, 128.2, 127.0, 124.9, 123.9, 123.4, 82.1, 55.2, 52.2, 39.1, 28.2. HRMS $[M+H]^+$ Calcd for $C_{22}H_{24}NO_3$: 350.1751, found: 350.1751.

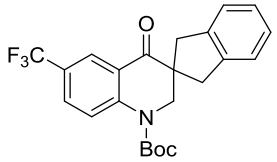
tert-butyl 6'-chloro-4'-oxo-1,3-dihydro-2'_H_-spiro[indene-2,3'-quinoline]-1'(4'_H_)-carboxylate (4b)



White solid, 605 mg, 79% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.01 (s, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.46 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.21 (s, 4H), 3.98 (s, 2H), 3.42 (d, *J* =

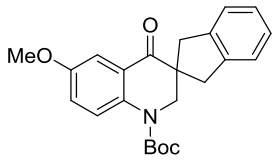
16.0 Hz, 2H), 2.87 (d, *J* = 16.8 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 196.2, 153.1, 142.3, 140.0, 133.9, 129.6, 127.6, 127.1, 124.9, 82.5, 54.9, 52.1, 39.0, 28.1. HRMS $[M+H]^+$ Calcd for $C_{22}H_{23}ClNO_3$: 384.1361, found: 384.1358.

4'-oxo-6'-(trifluoromethyl)-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (4c)



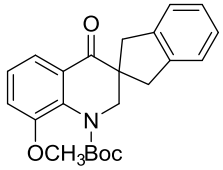
White solid, 567 mg, 68% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.34 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.21 (s, 4H), 4.02 (s, 2H), 3.44 (d, *J* = 16.0 Hz, 2H), 2.89 (d, *J* = 16.0 Hz, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 196.1, 153.0, 146.4, 139.8, 130.3, 127.1, 125.7, 124.9, 123.8, 123.4, 83.0, 54.8, 52.1, 39.0, 28.1. HRMS $[M+H]^+$ Calcd for $C_{23}H_{23}F_3NO_3$: 418.1625, found: 418.1623.

6'-methoxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (4d)



White solid, 622 mg, 82% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.81 (d, *J* = 9.2 Hz, 1H), 7.50 (s, 1H), 7.21 (s, 4H), 7.12 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.96 (s, 2H), 3.84 (s, 3H), 3.43 (d, *J* = 16.0 Hz, 2H), 2.88 (d, *J* = 16.4 Hz, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 197.5, 155.9, 153.5, 140.2, 137.7, 127.0, 125.0, 124.9, 124.6, 122.6, 109.1, 81.9, 55.7, 55.3, 52.3, 39.2, 28.2. HRMS $[M+H]^+$ Calcd for $C_{23}H_{26}NO_4$: 380.1856, found: 380.1857.

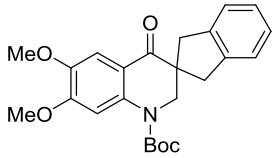
8'-methoxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (4e)



White solid, 402 mg, 53% isolated yield;^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.19-7.24 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 1H), 3.86-4.10 (m, 5H), 3.43 (d, *J* = 16.8

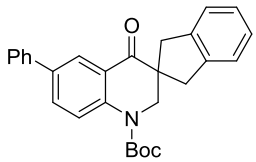
Hz, 2H), 2.91 (d, *J* = 16.8 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 198.4, 153.8, 152.8, 134.1, 127.0, 126.5, 125.6, 124.8, 119.3, 116.7, 81.1, 56.9, 56.0, 53.8, 40.1, 28.0. HRMS $[M+H]^+$ Calcd for $C_{23}H_{26}NO_4$: 380.1856, found: 380.1862.

***tert*-butyl 6',7'-dimethoxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (4f)**



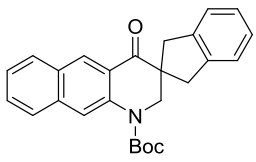
White solid, 695 mg, 85% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.50 (s, 1H), 7.49 (s, 1H), 7.20 (s, 4H), 3.98 (s, 3H), 3.96 (s, 2H), 3.92 (s, 3H), 3.43 (d, *J* = 16.0 Hz, 2H), 2.85 (d, *J* = 16.0 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 196.3, 153.9, 153.3, 145.8, 140.4, 139.5, 126.9, 124.9, 117.1, 108.3, 105.7, 82.0, 56.3, 56.1, 54.8, 52.7, 39.1, 28.2. HRMS $[M+H]^+$ Calcd for $C_{24}H_{28}NO_5$: 410.1962, found: 410.1963.

***tert*-butyl 4'-oxo-6'-phenyl-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (4g)**



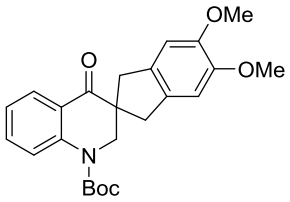
White solid, 655 mg, 77% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.31 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.21 (s, 4H), 4.02 (s, 2H), 3.47 (d, *J* = 16.0 Hz, 2H), 2.91 (d, *J* = 16.0 Hz, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 197.3, 153.4, 143.0, 140.2, 139.6, 136.7, 132.6, 128.9, 127.6, 127.0, 126.9, 126.3, 124.9, 124.0, 123.7, 82.3, 55.1, 52.3, 39.2, 28.2. HRMS $[M+H]^+$ Calcd for $C_{28}H_{28}NO_3$: 426.2064, found: 426.2064.

***tert*-butyl 4-oxo-1',3'-dihydro-2*H*-spiro[benzo[g]quinoline-3,2'-indene]-1(4*H*)-carboxylate (4h)**



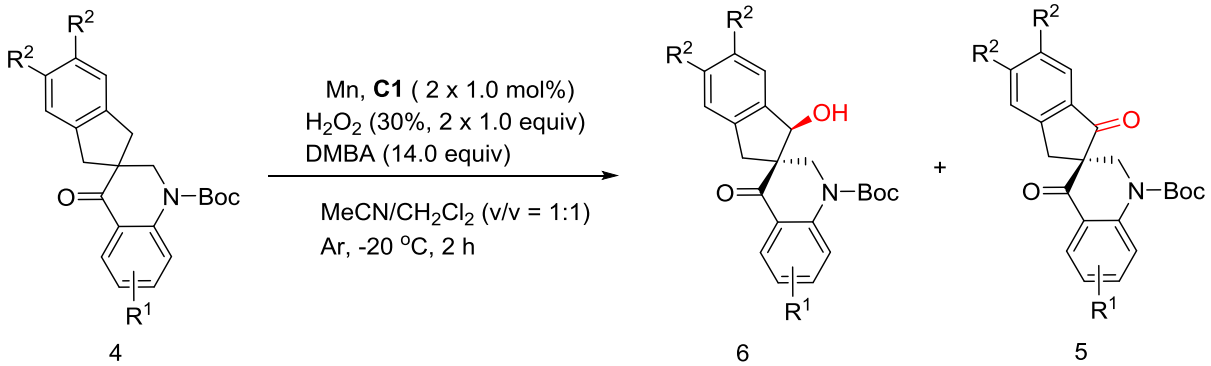
Light yellow solid, 551 mg, 69% isolated yield;^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 9.36 (d, *J* = 8.8 Hz, 1H), 7.91-7.96 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.20-7.25 (m, 4H), 4.03 (s, 2H), 3.53 (d, *J* = 15.6 Hz, 2H), 2.95 (d, *J* = 16.0 Hz, 2H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 199.7, 153.5, 146.0, 140.5, 134.7, 131.5, 130.9, 129.3, 128.3, 127.0, 126.8, 125.7, 124.8, 122.6, 118.3, 82.4, 57.9, 52.8, 40.6, 28.2. HRMS $[M+H]^+$ Calcd for $C_{26}H_{26}NO_3$: 400.1907, found: 400.1907.

5,6-dimethoxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (4i)



Light yellow solid, 515 mg, 63% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.74 (s, 2H), 4.03 (s, 2H), 3.86 (s, 6H), 3.37 (d. *J* = 15.6 Hz, 2H), 2.84 (d, *J* = 15.6 Hz, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 197.4, 153.4, 148.5, 143.8, 134.1, 131.7, 128.2, 123.9, 123.7, 123.3, 107.9, 82.1, 56.1, 55.5, 52.5, 39.2, 28.2. HRMS $[M+H]^+$ Calcd for $C_{24}H_{28}NO_5$: 410.1962, found: 410.1960.

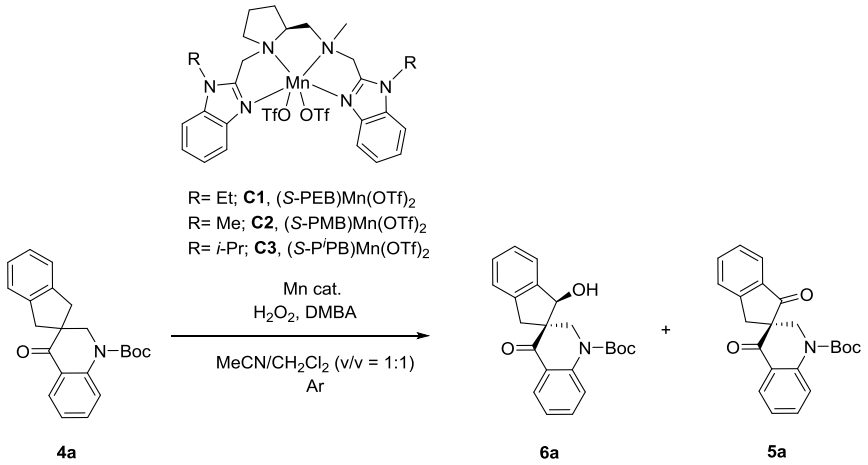
General procedure for the asymmetric hydroxylation of spirocyclic substrate 4



A 10 mL Schlenk tube was charged with substrate 4 (0.2 mmol, 1.0 equiv), manganese catalyst **C1** (1.0 mol%),1 mL of CH_2Cl_2, 2,2-dimethylbutanoic acid (DMBA, 0.35 mL, 14 equiv) and a stir bar under argon. Then a solution of H_2O_2 (1.0 equiv, 30% aqueous solution

diluted in 0.5 mL of MeCN) was added dropwise over 30 min using a syringe pump and the mixture was stirred at -20 ℃ for additional 30 min. After, manganese catalyst **C1** (1.0 mol%) and H_2O_2 (1.0 equiv, 30% aqueous solution diluted in 0.5 mL of MeCN, over 30 min) were added again, total reaction time was 2 h. The reaction mixture was then quenched with sodium sulfite and $NaHCO_3$ then purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1) to give the desired spirocyclic alcohol compound.

Table S1 Optimization of asymmetric hydroxylation catalysed by manganese catalyst



entry	Mn cat.	H_2O_2 (equiv)	*t* (^oC)	conv. (%)	yield (%) **6a/5a**	ee (%)
1[b]	**C1**	2.0	0	54	27/14	98/90
2[c]	**C1**	7.0	0	63	26/34	97/94
3	**C1**	2.0	0	60	37/14	98/90
4[d]	**C1**	2.0	0	66	37/17	98/90
5	**C2**	2.0	0	53	34/19	94/82
6	**C3**	2.0	0	51	34/14	94/89
7	**C1**	2.0	-20	63	38/15	98/96
8	**C1**	7.0	-20	61	22/23	98/96
9[e]	**C1**	2.0	-20	12	8/Trace	92
10[f]	**C1**	2.0	-20	47	20/8	91/77

[a]Reaction conditions: substrate **4a** (0.2 mmol), manganese Mn catalyst (1.0 mol%) and 2,2-dimethylbutanoic acid (DMBA, 14.0 equiv) were dissolved in 1.0 mL of CH_2Cl_2 under Ar atmosphere, H_2O_2 (1.0 equiv, 30% aqueous solution diluted in 0.5 mL of MeCN) was added dropwise over 30 min and stirred for additional 30 min; after, Mn catalyst (1.0 mol%) was added to the reaction, and second addition of H_2O_2 (1.0 equiv) was performed in the same manner, total reaction time of 2 h, isolated yield.

[b] **C1** (2.0 mol%) was added in one times and H_2O_2 (2.0 equiv, 30% aqueous solution diluted in 1.0 mL of MeCN) was added dropwise over 1 h.

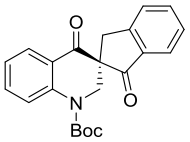
[c] **C1** (2.0 mol%) was added in one times and H_2O_2 (7.0 equiv, 30% aqueous solution diluted in 1.0 mL of MeCN) was added dropwise over 1 h.

[d] 3.0 mol% of **C1**.

[e] 14 equic of EHA.

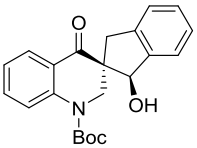
[f] 14 equic of AcOH.

tert-butyl (*S*)-1,4'-dioxo-1,3-dihydro-2'H-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (5a)



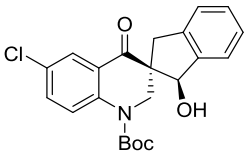
White solid, 25mg, 34% isolated yield; $[\alpha]_D^{20}$ = -40.3 (*c* = 0.33 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.01 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.78 (t, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.56 (td, *J* = 7.8, 1.6 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 4.51 (d, *J* = 13.6 Hz, 1H), 4.16 (d, *J* = 14.0 Hz, 1H), 3.73 (d, *J* = 17.2 Hz, 1H), 3.03 (d, *J* = 17.2 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 201.2, 193.5, 152.3, 144.3, 135.5, 135.1, 134.4, 128.1, 126.6, 124.8, 124.4, 124.2, 124.1, 82.5, 61.5, 51.1, 35.3, 28.2; HRMS $[M+Na]^+$ Calcd for $C_{22}H_{21}NO_4Na$: 386.1363, found: 386.1368; HPLC-separation conditions: Sample dissolved in EtOH, t_S [racemate] = 19.48 min, 21.41 min; Chiralcel AD-H, 20 °C, 210 nm, 95/5 *n*-hexane/*i*-PrOH, 0.8 mL/min, t_R [**5a**] = 21.02 min, t_R= [*ent*-**5a**] = 22.76 min; 94% ee.

***tert*-butyl (1*R*,2*R*)-1-hydroxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (6a)**



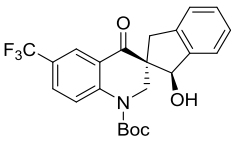
White solid, 28 mg, 38% isolated yield; $[\alpha]_D^{20}$ = +51.7 (*c* = 0.232 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.53 (t , *J* = 7.8 Hz, 1H), 7.43-7.44 (m, 1H), 7.28-7.30 (m, 2H), 7.20-7.22 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 5.16 (s, 1H), 4.18 (d, *J* = 13.2 Hz, 1H), 4.12 (d, *J* = 14.0 Hz, 1H), 3.57 (d, *J* = 16.4 Hz, 1H), 2.85 (d, *J* = 16.8 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 196.8, 153.1, 143.8, 143.0, 139.3, 134.4, 128.9, 128.0, 127.6, 125.1, 124.7, 123.9, 123.8, 123.3, 82.5, 79.7, 58.6, 52.0, 37.5, 28.2; HRMS $[M+Na]^+$ Calcd for $C_{22}H_{23}NO_4Na$: 388.1519, found: 388.1536; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 12.17 min, 16.27 min; Chiralcel IA, 20 °C, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**6a**] = 11.70 min, t_R = [*ent*-**6a**] = 15.62 min; 98% ee, dr > 20:1

***tert*-butyl (1*R*,2*R*)-6'-chloro-1-hydroxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (6b)**



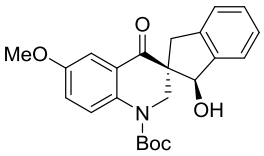
White solid, 26mg, 33% isolated yield; $[\alpha]_D^{20}$ = +34.9 (*c* = 0.172 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.97 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.42-7.48 (m, 2H), 7.29-7.31 (m, 2H), 7.21-7.23 (m, 1H), 5.17 (s, 1H), 4.20 (d, *J* = 13.6 Hz, 1H), 4.06 (d, *J* = 13.6 Hz, 1H), 3.60 (d, *J* = 16.4 Hz, 1H), 2.81 (d, *J* = 16.8 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 195.4, 152.9, 152.3, 142.6, 142.2, 139.3, 134.2, 129.6, 129.1, 127.8, 127.5, 125.2, 124.8, 82.9, 79.6, 58.6, 51.9, 37.4, 28.2; HRMS $[M+Na]^+$ Calcd for $C_{22}H_{22}ClNO_4Na$: 422.1130, found: 422.1128; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 11.97 min, 19.07 min; Chiralcel IA, 20 ^oC, 210 nm, 95/5 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**6b**] = 12.00 min, t_R = [*ent*-**6b**] = 19.11 min; 94% ee, dr > 20:1

***tert*-butyl (1*R*,2*R*)-1-hydroxy-4'-oxo-6'-(trifluoromethyl)-1,3-dihydro-2'*H*-spiro [indene-2,3' -quinoline]-1'(4'*H*)-carboxylate (6c)**



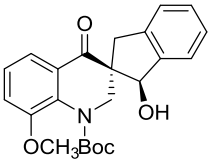
White solid, 21mg, 24% isolated yield; $[\alpha]_D^{20}$ = +37.9 (*c* = 0.290 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.31 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.43-7.45 (m, 1H), 7.30-7.33 (m, 2H), 7.23-7.24 (m, 1H), 5.19 (s, 1H), 4.26 (d, *J* = 13.6 Hz, 1H), 4.10 (d, *J* = 13.6 Hz, 1H), 3.64 (d, *J* = 16.4 Hz, 1H), 2.82 (d, *J* = 16.8 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 195.2, 152.7, 146.3, 142.5, 139.2, 130.6, 129.2, 127.8, 126.1, 125.6, 125.2, 124.8, 123.7, 123.4, 83.4, 79.6, 58.5, 51.9, 37.3, 28.2; HRMS $[M+Na]^+$ Calcd for $C_{23}H_{22}F_3NO_4Na$: 456.1393, found: 456.1412; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 18.63 min, 25.61 min; Chiralcel AD-H, 20 ^oC, 210 nm, 95/5 *n*-hexane/*i*-PrOH, 0.8 mL/min, t_R [**6c**] = 18.60 min, t_R = [*ent*-**6c**] = 25.79 min; 94% ee, dr > 20:1

***tert*-butyl (1*R*,2*R*)-1-hydroxy-6'-methoxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (6d)**



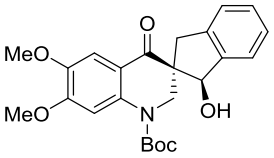
White solid, 32 mg, 41% isolated yield; $[\alpha]_D^{20}$ = +34.4 (*c* = 0.960 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.75-7.81 (m, 1H), 7.43-7.46 (m, 1H), 7.28-7.30 (m ,2H), 7.20-7.23 (m, 1H), 7.10-7.14 (m, 2H), 5.16 (s, 1H), 4.16 (d, *J* = 13.2 Hz, 1H), 4.09 (d, *J* = 14.0 Hz, 1H), 3.82 (s, 3H), 3.58 (d, *J* = 16.4 Hz, 1H), 2.85 (d, *J* = 16.4 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 196.8, 155.9, 153.3, 143.0, 139.4, 137.7, 129.0, 127.7, 125.1, 125.0, 124.8, 124.5, 123.0, 109.0, 82.2, 79.7, 58.7, 55.7, 52.1, 37.6, 28.3; HRMS $[M+Na]^+$ Calcd for $C_{23}H_{25}NO_5Na$: 418.1625, found: 418.1642; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 14.61 min, 25.85 min; Chiralcel IA, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**6d**] = 14.61 min, t_R = [*ent*-**6d**] = 26.05 min; 98% ee, dr = 1.6:1

***tert*-butyl (1*S*,2*R*)-1-hydroxy-8'-methoxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (6e)**



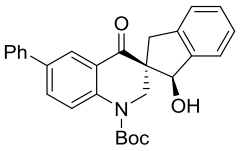
White solid, 18 mg, 23% isolated yield; $[\alpha]_D^{20}$ = +46.7 (*c* = 0.214 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 6.4 Hz, 1H), 7.18-7.29 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 1H), 5.18 (s, 1H), 3.90-4.35 (m, 5H), 3.41-3.55 (m, 1H), 2.83-3.06 (m, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 197.7, 152.8, 134.1, 128.8, 127.6, 125.7, 124.9, 119.2, 116.9, 81.4, 80.6, 60.6, 55.9, 53.7, 38.2, 28.0; HRMS $[M+Na]^+$ Calcd for $C_{23}H_{25}NO_5Na$: 418.1625, found: 418.1633; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 41.42 min, 56.14 min; Chiralcel IA, 20 ^oC, 210 nm, 95/5 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**6e**] = 41.36 min, t_R = [*ent*-**6e**] = 56.61. min; 99% ee, dr > 20 :1

***tert*-butyl (1*R*,2*R*)-1-hydroxy-6',7'-dimethoxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (6f)**



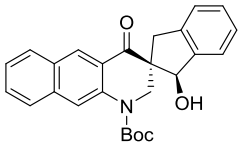
White solid, 31 mg, 37% isolated yield; $[\alpha]_D^{20}$ = +103.3 (*c* = 0.300 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.48-7.50 (m, 1H), 7.44 (s, 2H), 7.27-7.30 (m ,2H), 7.22-7.23 (m, 1H), 5.12 (s, 1H), 4.12 (s, 2H), 3.97 (s, 3H), 3.89 (s, 3H), 3.56 (d, *J* = 16.4 Hz, 1H), 2.85 (d, *J* = 16.0 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 195.8, 154.3, 153.1, 145.9, 143.1, 139.6, 128.9, 127.6, 125.1, 124.8, 116.9, 108.1, 105.7, 82.3, 79.6, 57.8, 56.3, 56.0, 52.5, 37.6, 28.3; HRMS $[M+Na]^+$ Calcd for $C_{24}H_{27}NO_6Na$: 448.1731, found: 448.1737; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 43.60 min, 81.41 min; Chiralcel IA, 20 ^oC, 210 nm, 96/4 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**6f**] = 43.37 min, t_R = [*ent*-**6f**] = 82.37 min; 98% ee, dr = 3.3:1

***tert*-butyl (1*R*,2*R*)-1-hydroxy-4'-oxo-6'-phenyl-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (6g)**



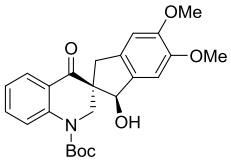
White solid, 32 mg, 36% isolated yield; $[\alpha]_D^{20}$ = +35.1 (*c* = 0.228 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.26 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 6.8 Hz, 2H), 7.42-7.46 (m, 3H), 7.22-7.37 (m, 4H), 5.19 (s, 1H), 4.22 (d, *J* = 13.6 Hz, 1H), 4.15 (d, *J* = 13.6 Hz, 1H), 3.62 (d, *J* = 16.4 Hz, 1H), 2.87 (d, *J* = 16.4 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 196.8, 153.1, 143.0, 142.9, 139.5, 139.3, 136.7, 133.0, 129.0, 128.9, 127.7, 127.6, 126.8, 126.1, 125.2, 124.8, 124.0, 123.7, 82.6, 79.8, 58.6, 52.0, 37.6, 28.3; HRMS $[M+Na]^+$ Calcd for $C_{28}H_{27}NO_4Na$: 464.1832, found: 464.1827; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 33.96 min, 42.78 min; Chiralcel AD-H, 20 ^oC, 210 nm, 90/10 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**6g**] = 34.11 min, t_R = [*ent*-**6g**] = 43.84 min; 96% ee, dr = 15.7:1

***tert*-butyl (1'*R*,3*R*)-1'-hydroxy-4-oxo-1',3'-dihydro-2*H*-spiro[benzo[g]quinoline-3,2'-indene]-1(4*H*)-carboxylate (6h)**



Light yellow solid, 18 mg, 22% isolated yield; $[\alpha]_D^{20}$ = +29.3 (*c* = 0.256 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 9.30 (d, *J* = 8.8 Hz, 1H), 7.89-7.97 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.46-7.49 (m 2H), 7.30-7.32 (m, 2H), 7.22-7.25 (m, 1H), 5.20 (s, 1H), 4.21 (d, *J* = 13.2 Hz, 1H), 4.16 (d, *J* = 12.8 Hz, 1H), 3.61 (d, *J* = 16.0 Hz, 1H), 2.96 (d, *J* = 16.4 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 199.6, 153.2, 146.4, 143.3, 139.8, 135.2, 131.3, 130.9, 129.5, 128.9, 128.4, 127.6, 126.7, 125.9, 125.1, 124.8, 122.6, 118.2, 82.8, 80.4, 60.4, 52.6, 39.0, 28.2; HRMS $[M+Na]^+$ Calcd for $C_{26}H_{25}NO_4Na$: 438.1676, found: 438.1686; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 12.83 min, 17.96 min; Chiralcel IA, 20 ^oC, 210 nm, 95/5 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**6h**] = 12.72 min, t_R = [*ent*-**6h**] = 17.87 min; 99% ee, dr = 18.6:1

***tert*-butyl (1*R*,2*R*)-1-hydroxy-5,6-dimethoxy-4'-oxo-1,3-dihydro-2'*H*-spiro[indene-2,3'-quinoline]-1'(4'*H*)-carboxylate (6i)**



Light yellow solid, 26 mg, 31% isolated yield; $[\alpha]_D^{20}$ = +8.3 (*c* = 0.156 in $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.53 (t , *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.94 (s, 1H), 6,71 (s, 1H), 5.69 (s, 1H), 4.23 (d, *J* = 13.6 Hz, 1H), 4.16 (d, *J* = 14.0 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.97 (s, 2H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ 197.1, 153.7, 149.9, 148.9, 143.9, 134.3, 134.2, 130.7, 128.0, 123.9, 123.9, 123.3, 107.4, 107.1, 82.3, 78.3, 59.7, 56.1, 48.4, 37.2, 28.2; HRMS $[M+Na]^+$ Calcd for $C_{24}H_{27}NO_6Na$: 448.1731, found: 448.1729; HPLC-separation conditions: Sample dissolved in EtOH, t_R [racemate] = 16.69 min, 18.97 min; Chiralcel AD-H, 20 ^oC, 210 nm, 99/1 *n*-hexane/*i*-PrOH, 1.0 mL/min, t_R [**6i**] = 16.47 min, t_R = [*ent*-**6i**] = 18.52 min; 70% ee, dr = 14.3:1

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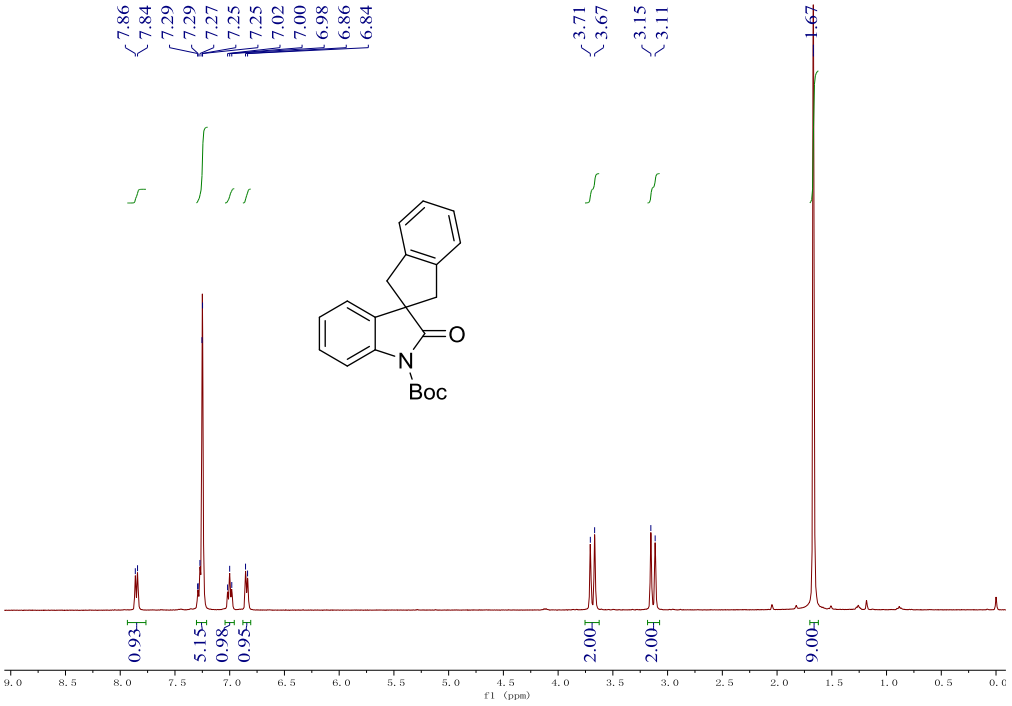
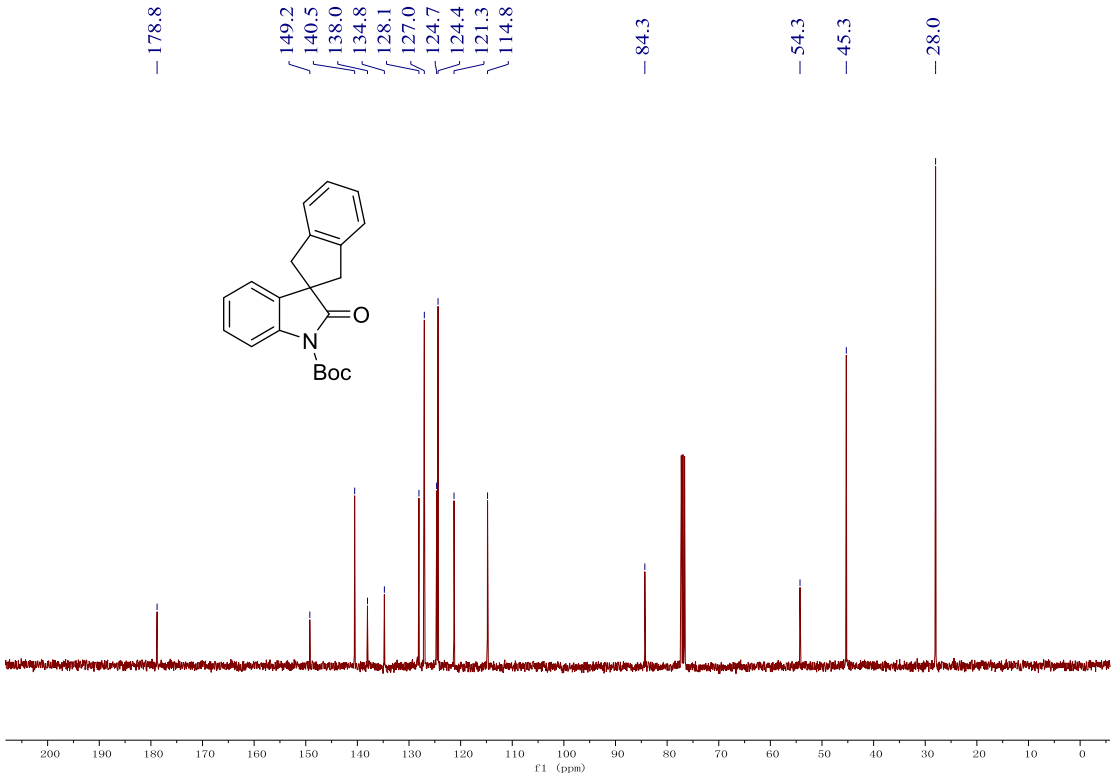
Copyies of ^{1}H NMR and ^{13}C NMR Spectra for substrates and spirocyclic products

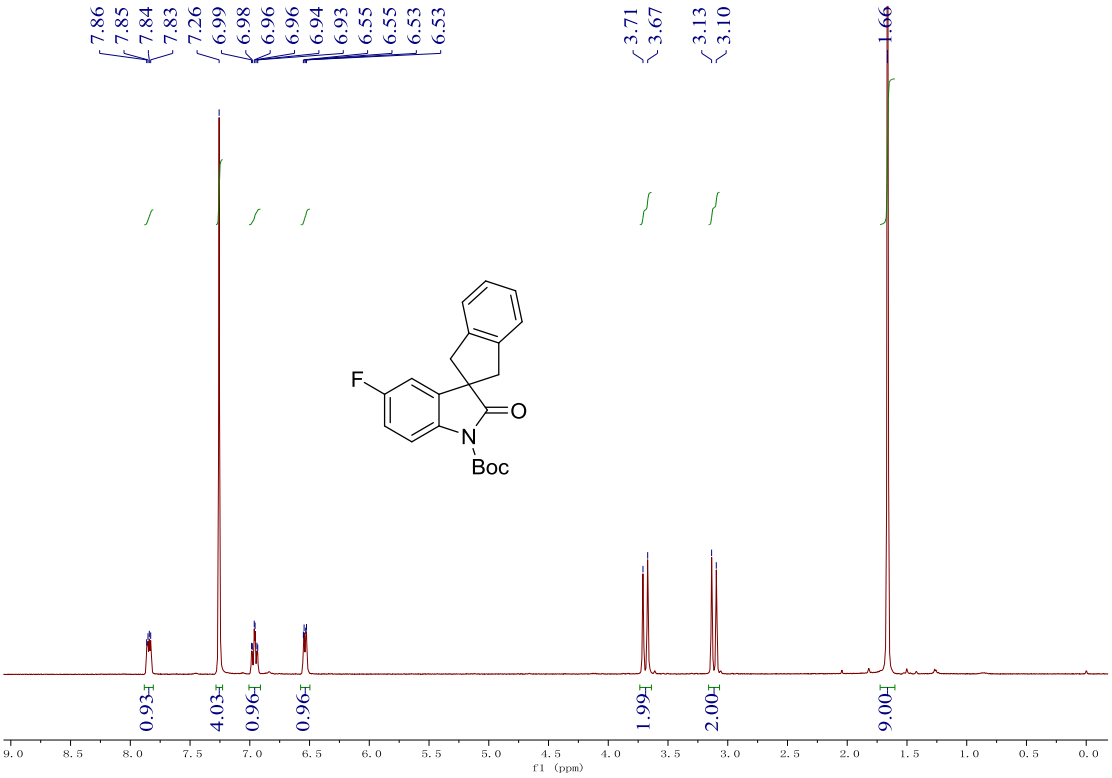
^{1}H NMR Spectrum of **1a**



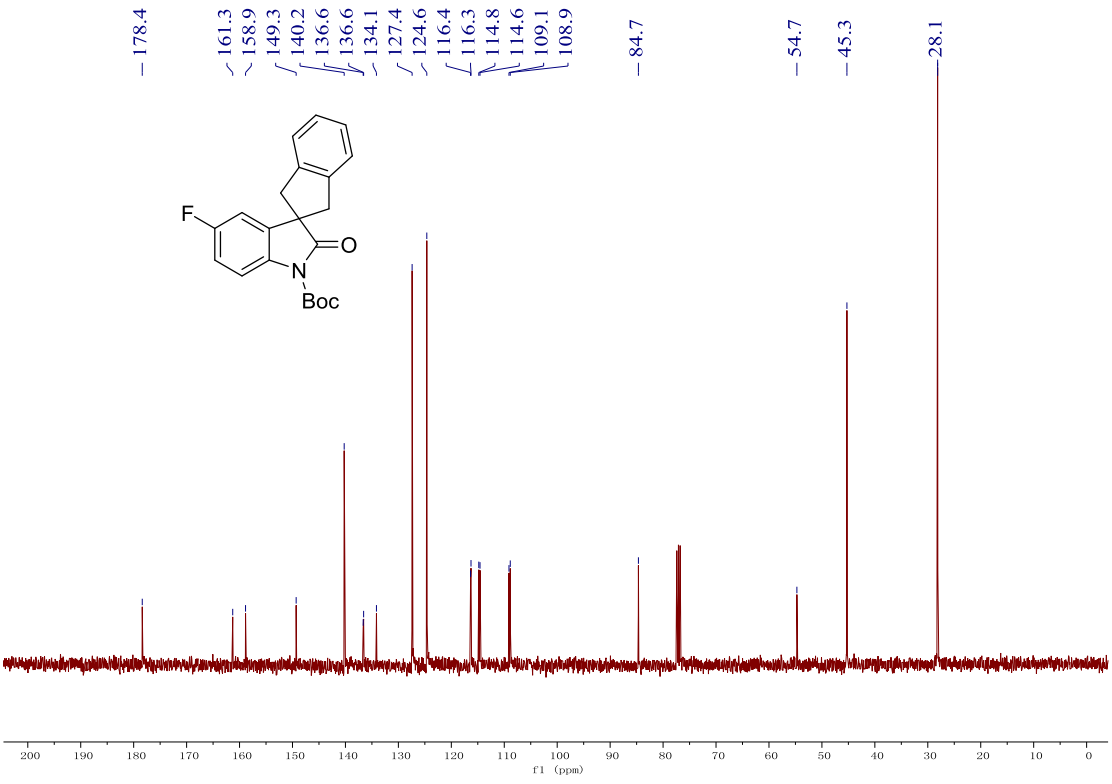
^{13}C NMR Spectrum of **1a**



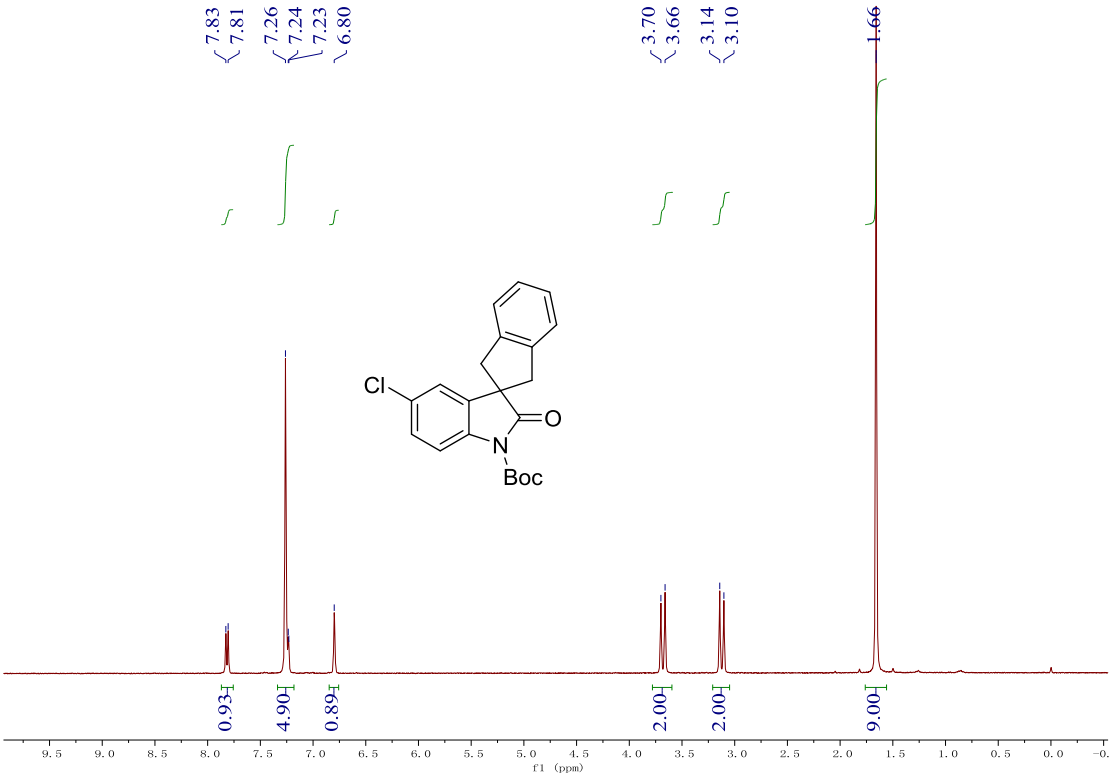
^{1}H NMR Spectrum of **1b**



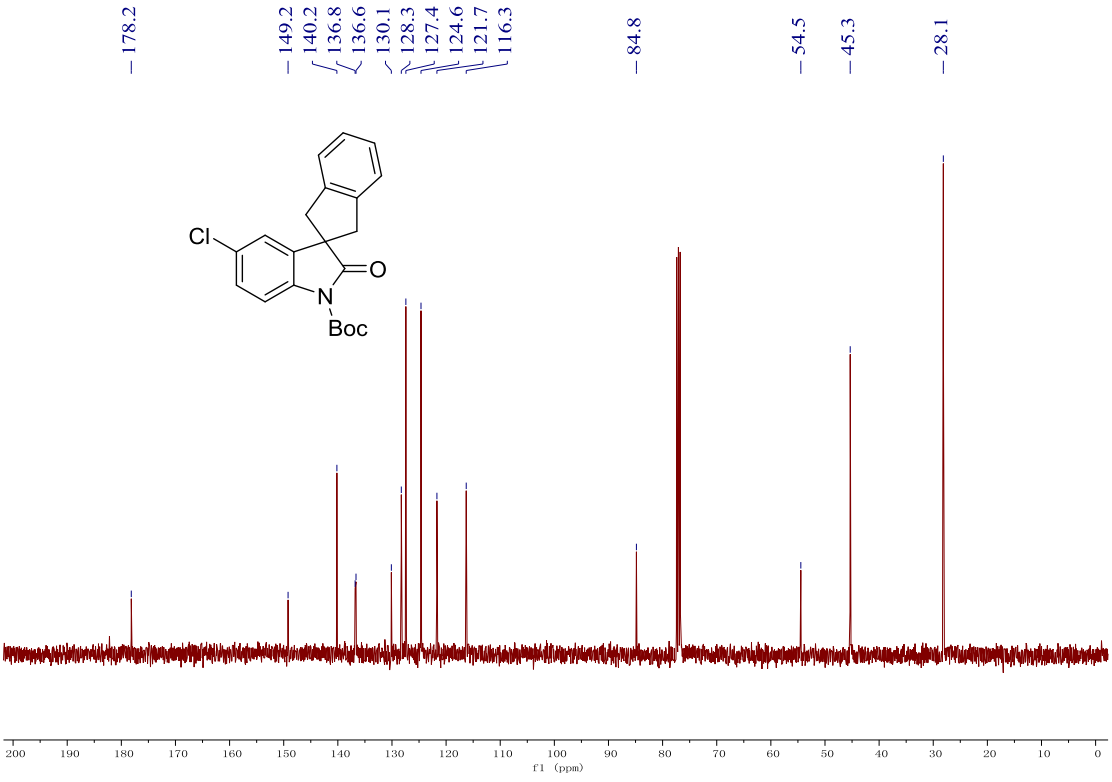
^{13}C NMR Spectrum of **1b**



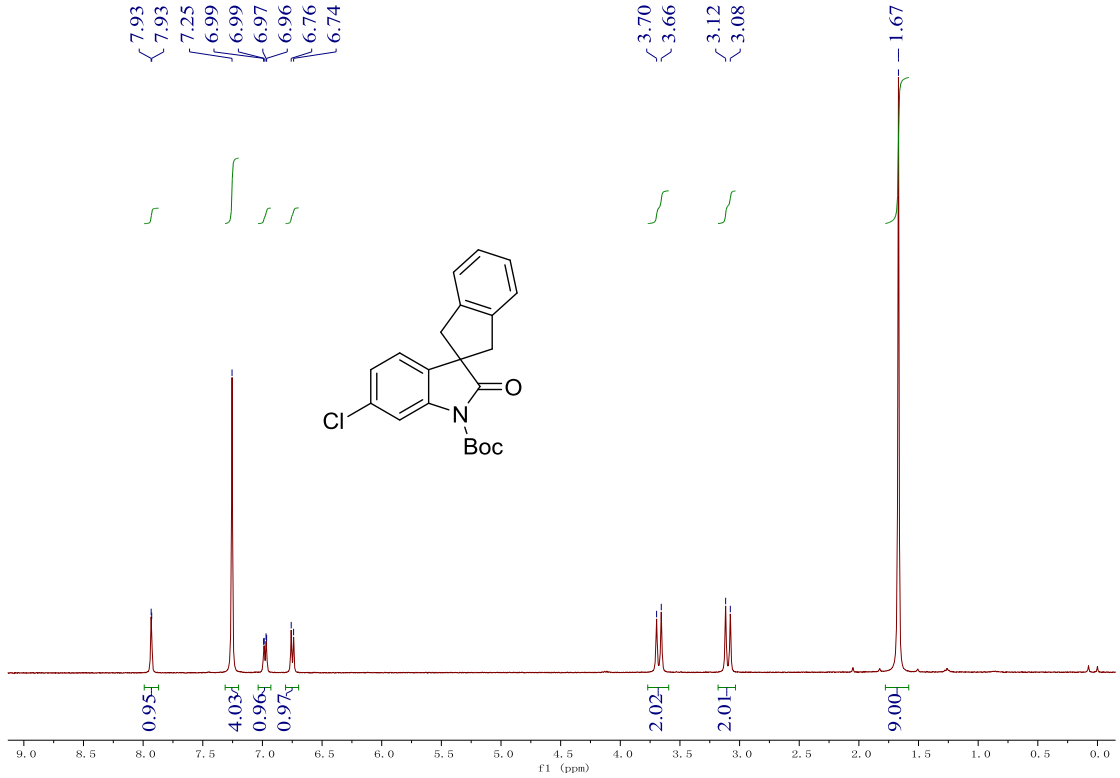
^{1}H NMR Spectrum of **1c**



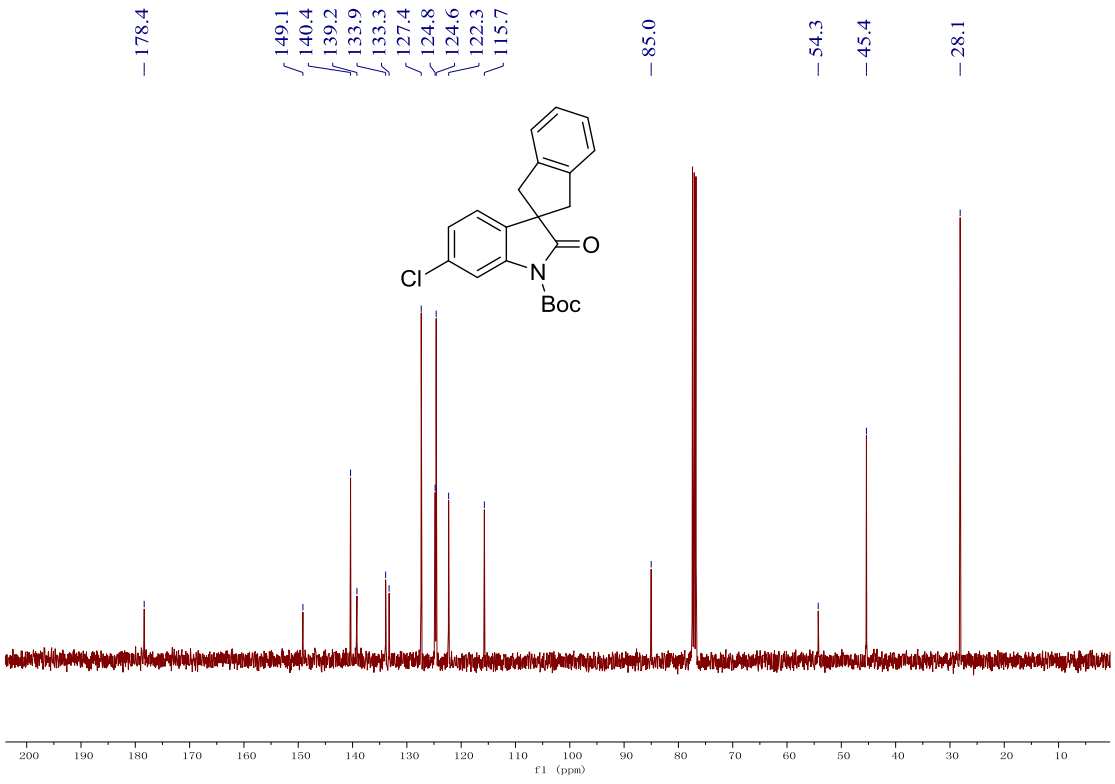
^{13}C NMR Spectrum of **1c**



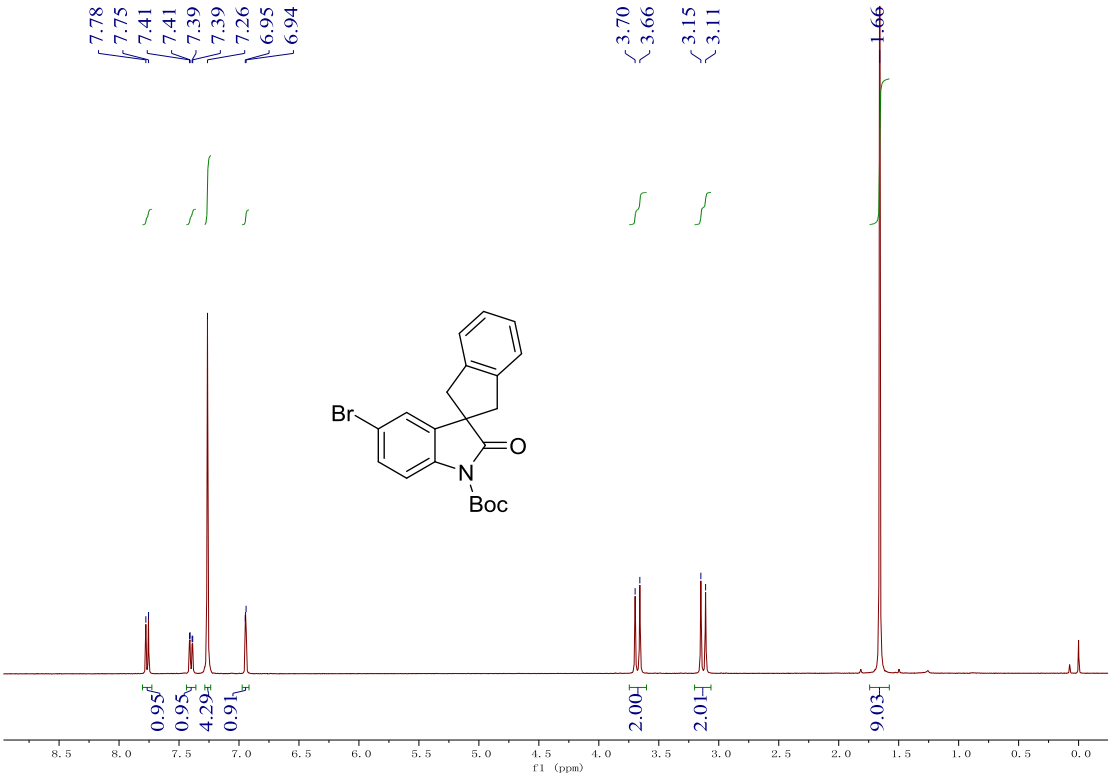
^{1}H NMR Spectrum of **1d**



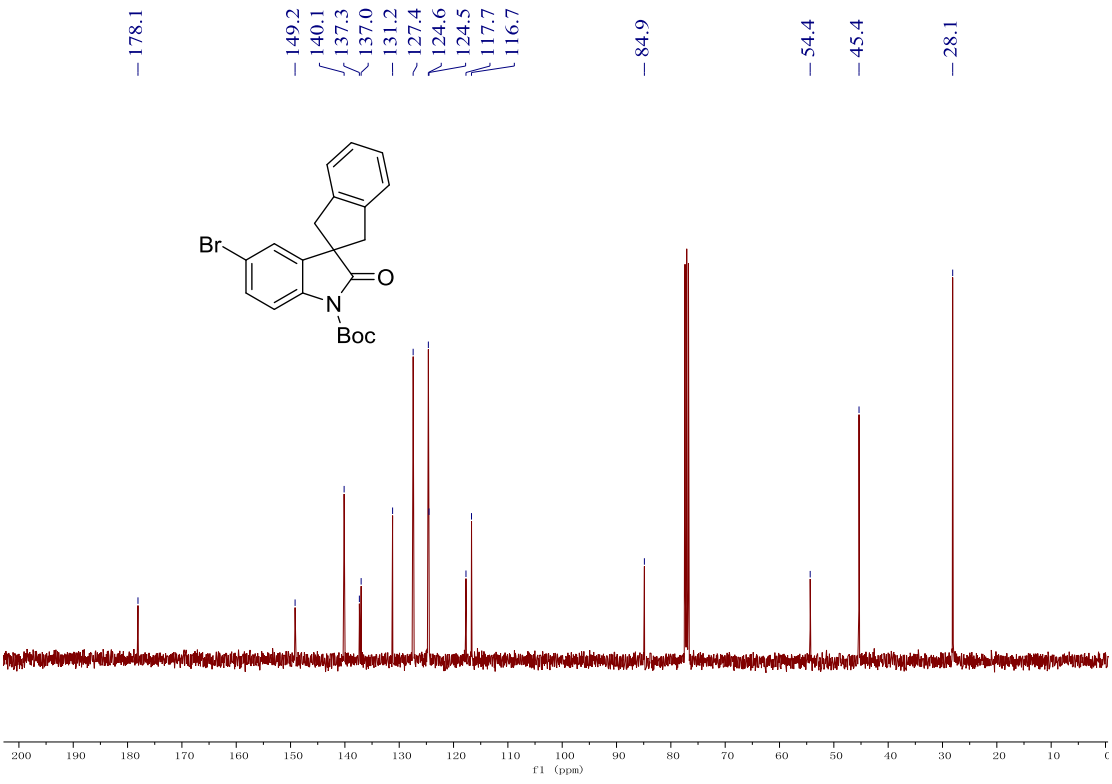
^{13}C NMR Spectrum of **1d**



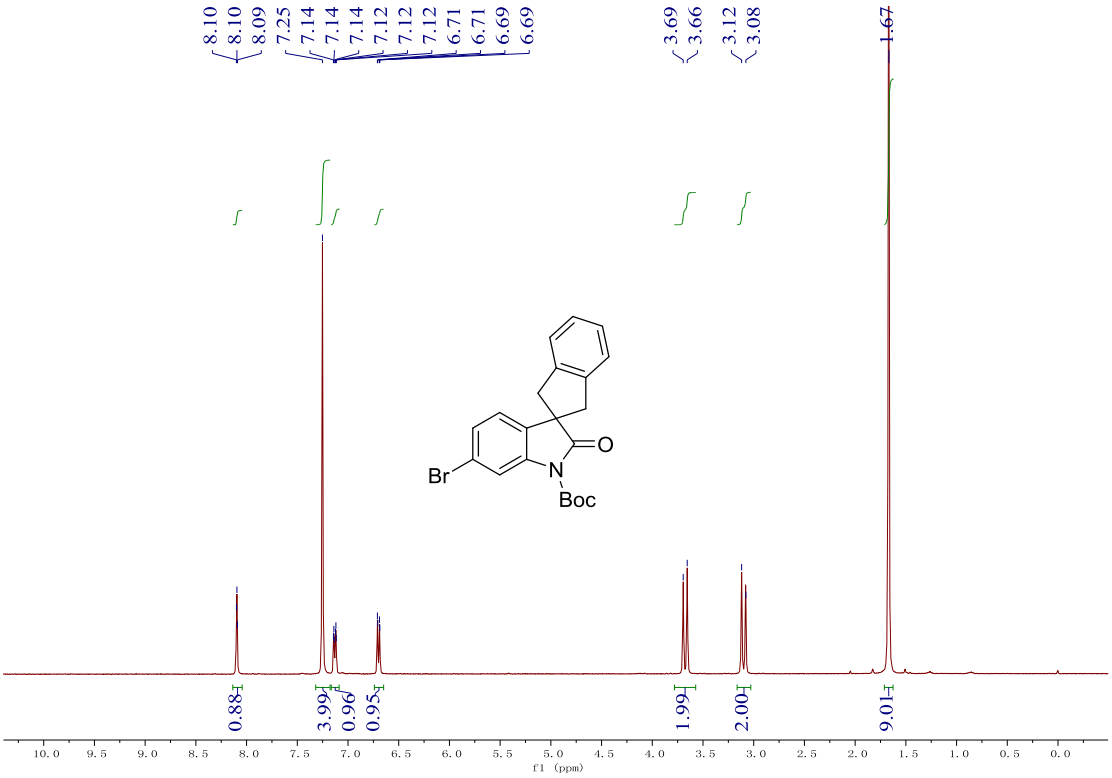
^{1}H NMR Spectrum of **1e**



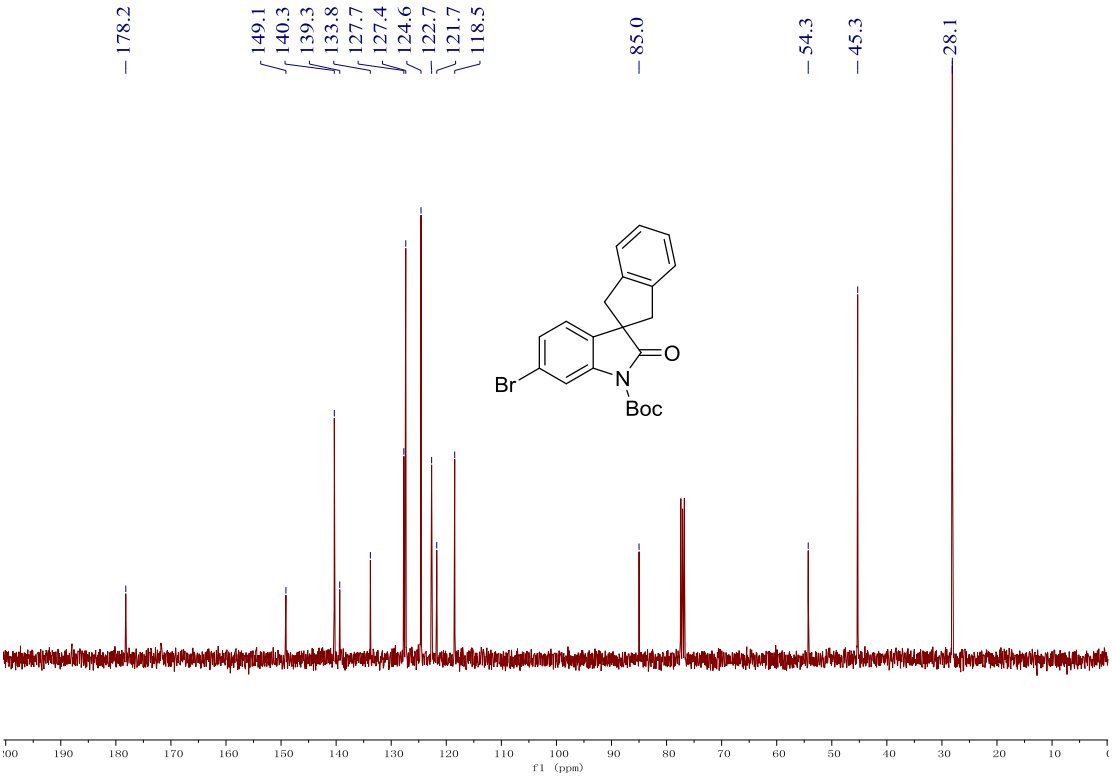
^{13}C NMR Spectrum of **1e**



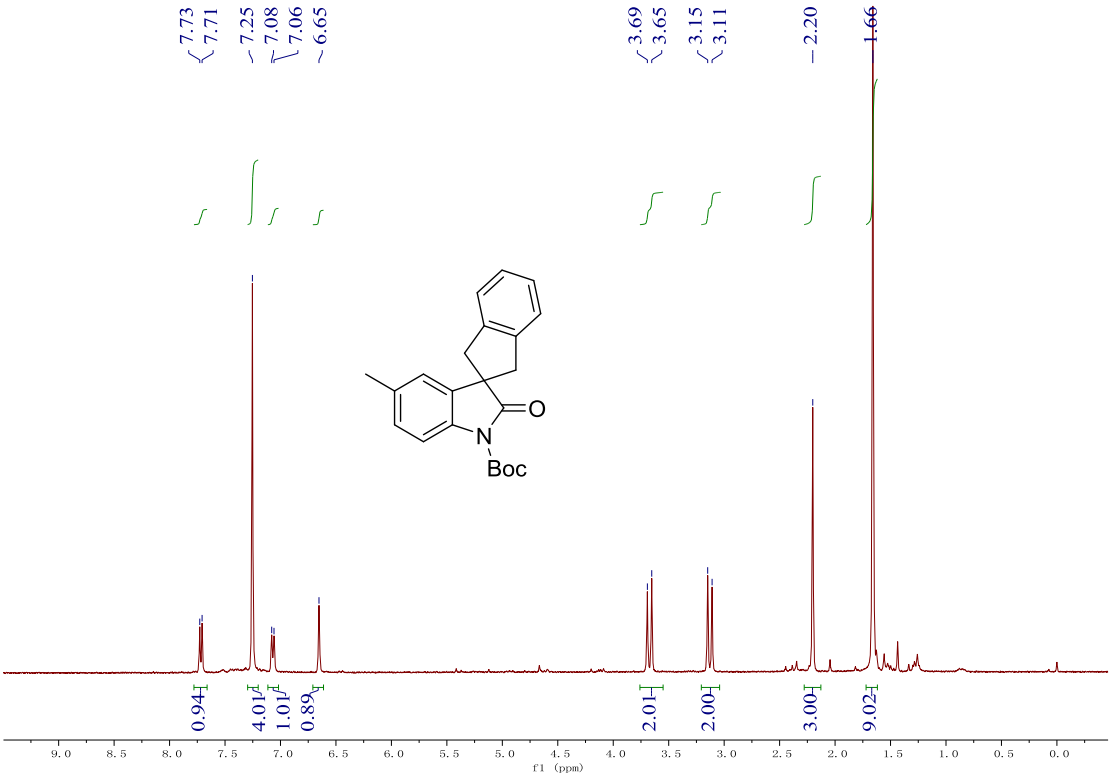
^{1}H NMR Spectrum of **1f**



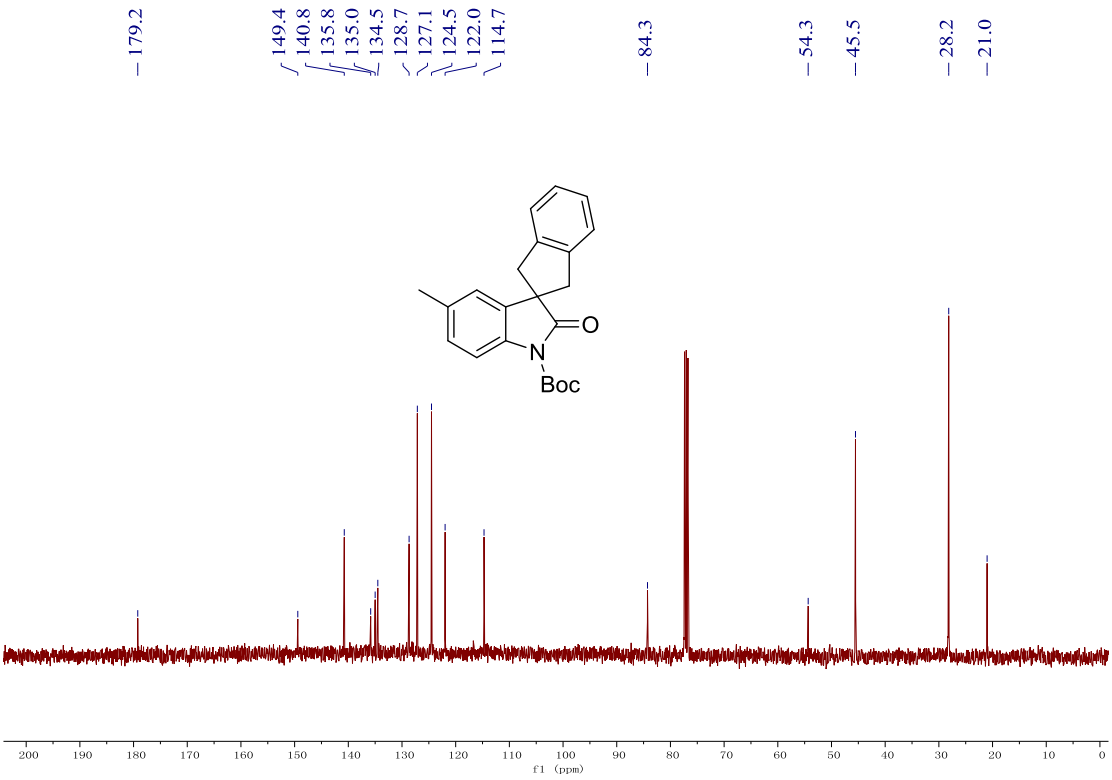
^{13}C NMR Spectrum of **1f**



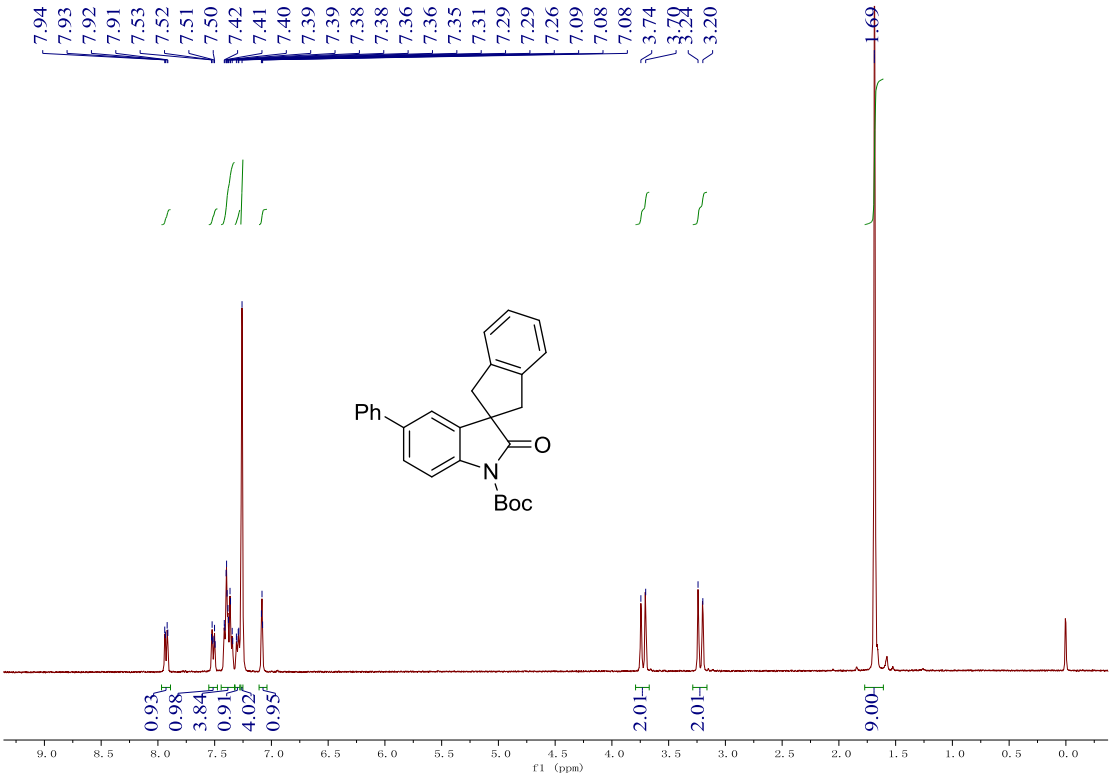
^{1}H NMR Spectrum of **1g**



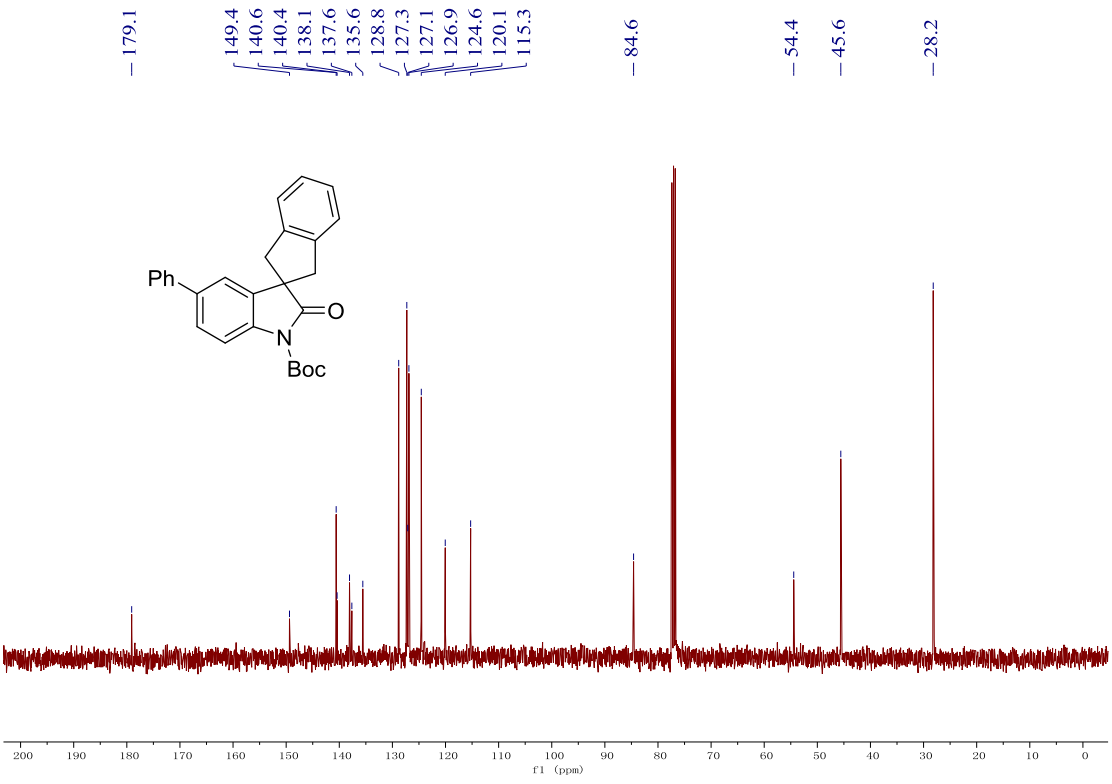
^{13}C NMR Spectrum of **1g**



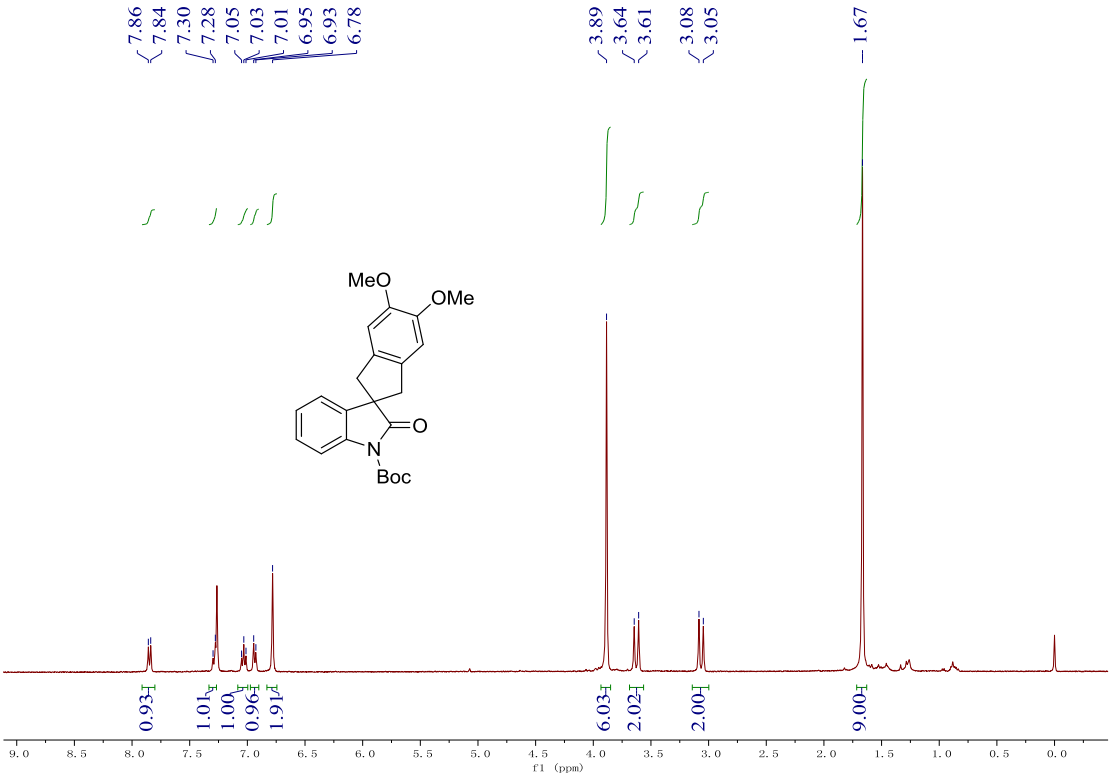
^{1}H NMR Spectrum of **1h**



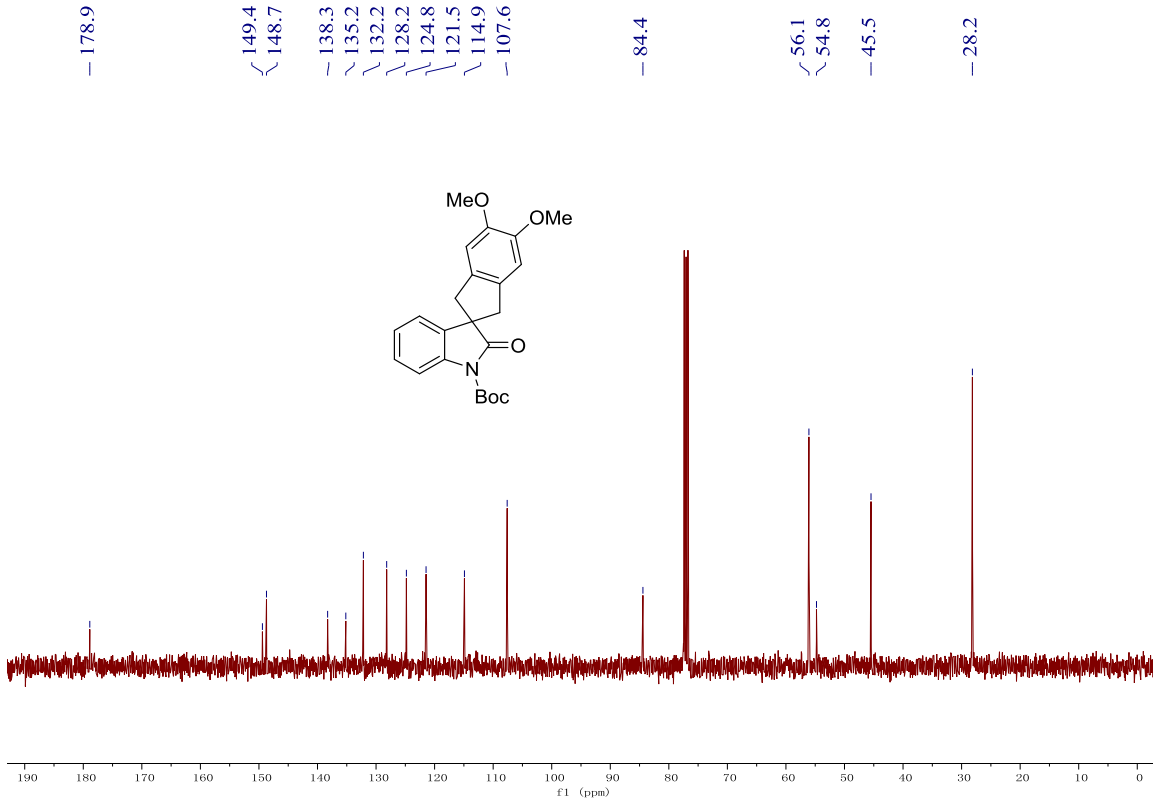
^{13}C NMR Spectrum of **1h**



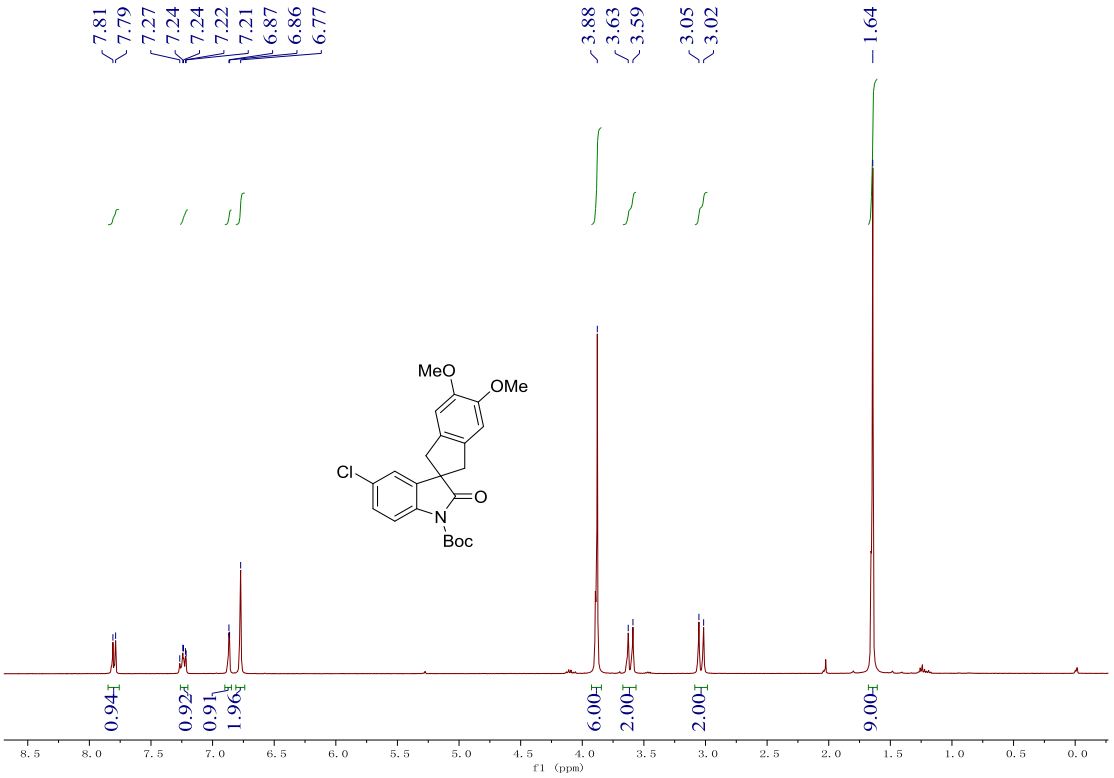
^{1}H NMR Spectrum of **1i**



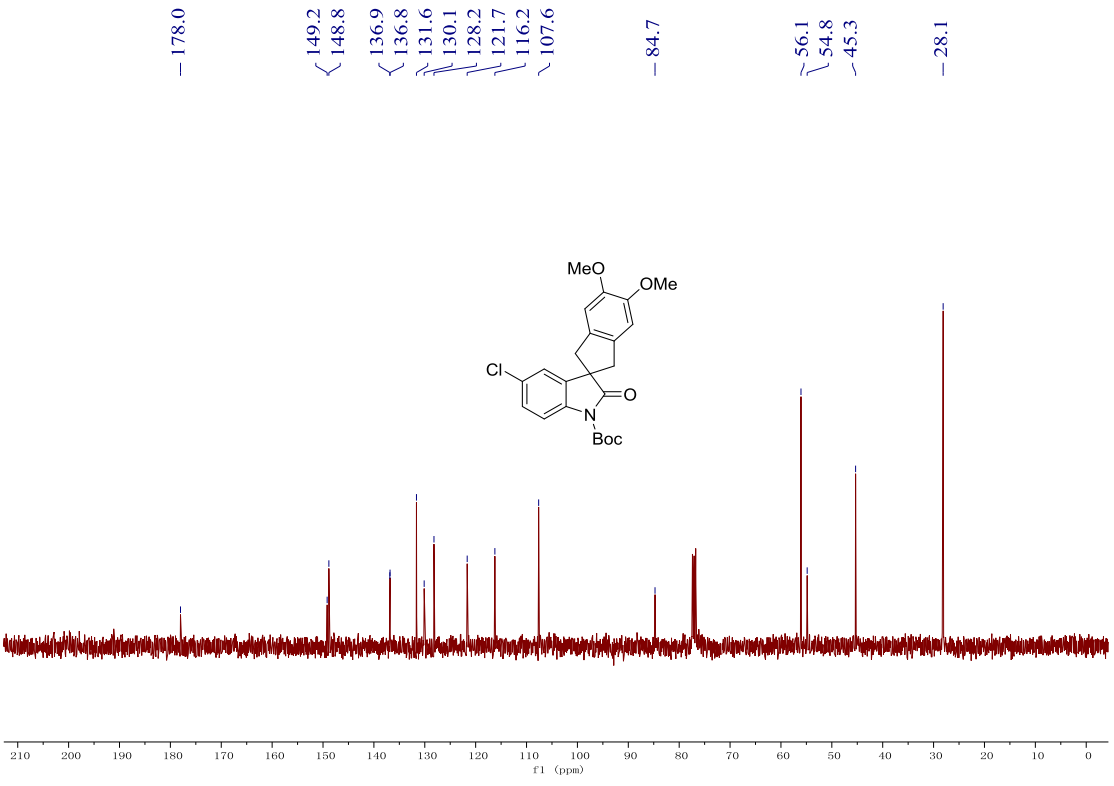
^{13}C NMR Spectrum of **1i**



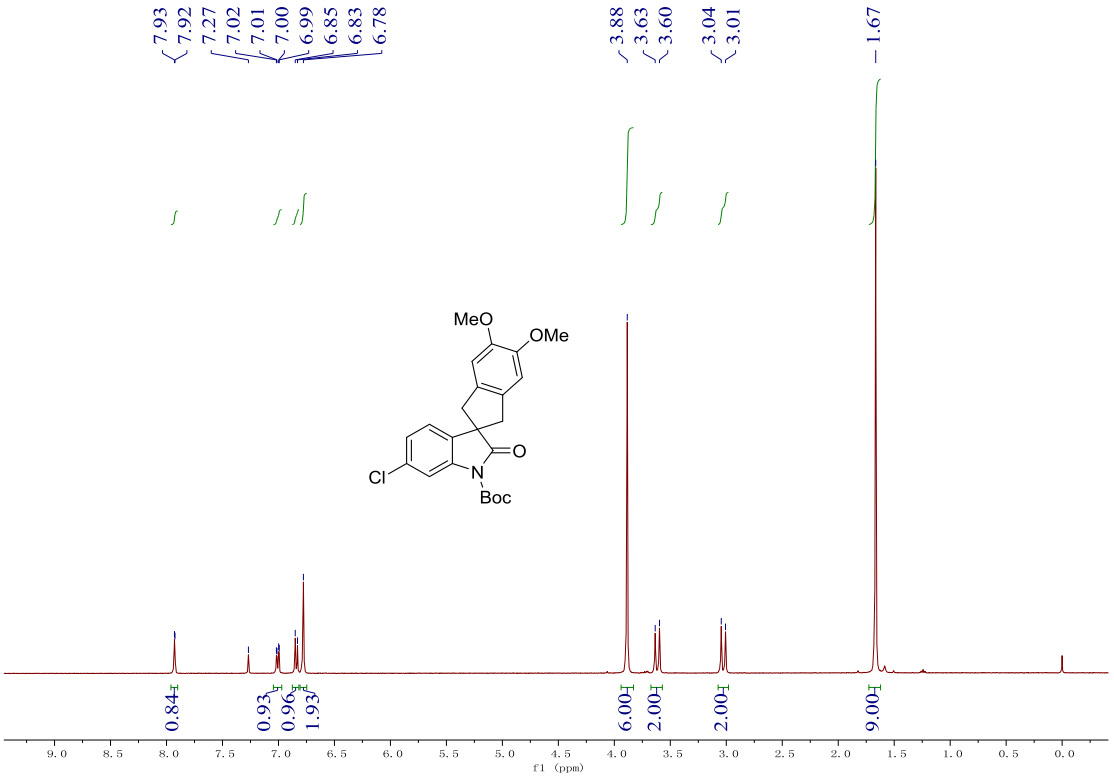
^{1}H NMR Spectrum of **1j**



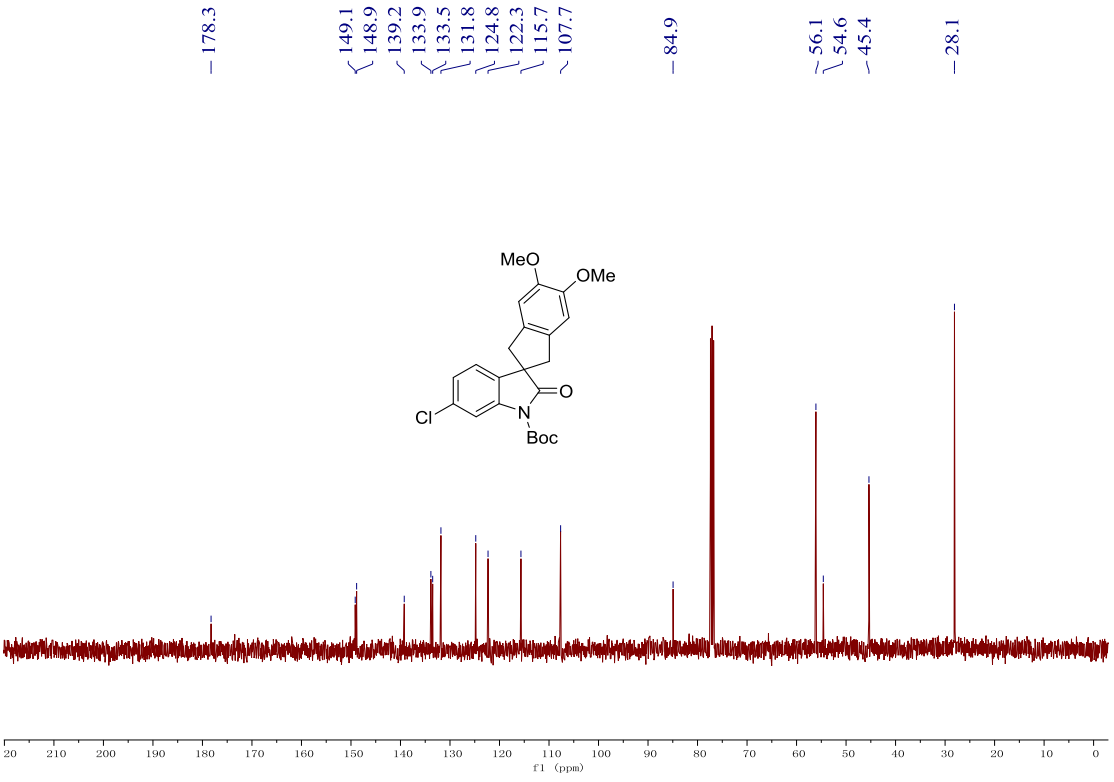
^{13}C NMR Spectrum of **1j**



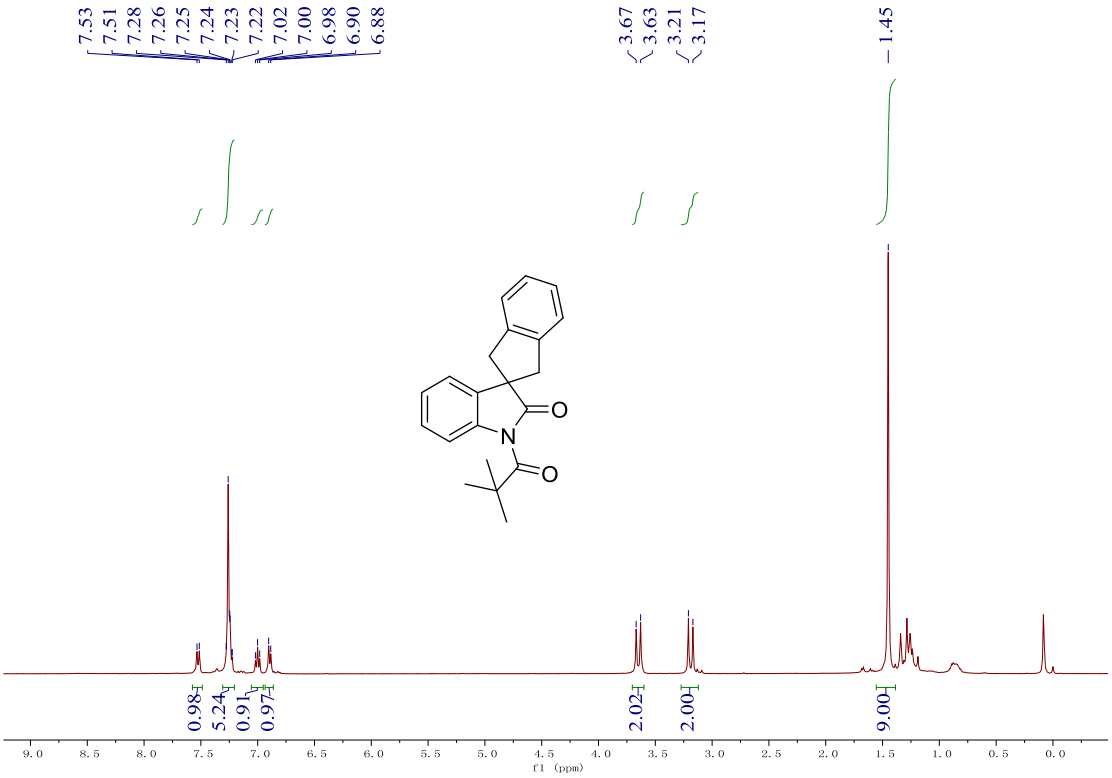
^{1}H NMR Spectrum of **1k**



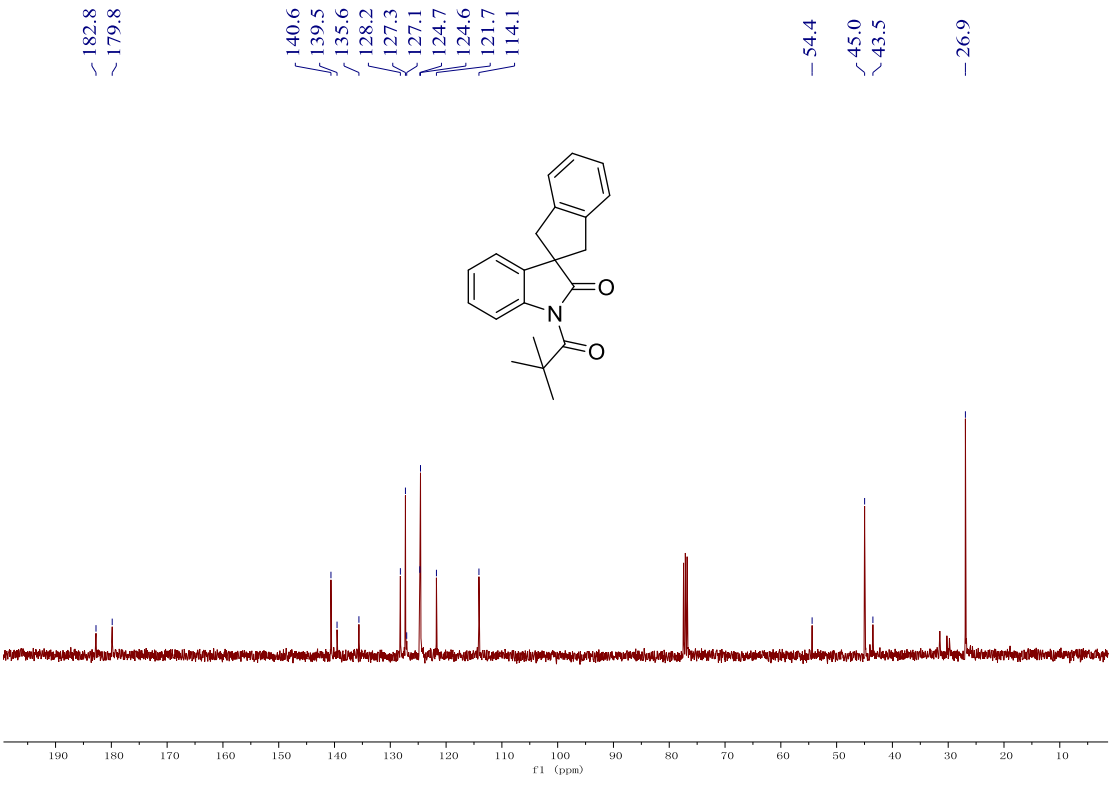
^{13}C NMR Spectrum of **1k**



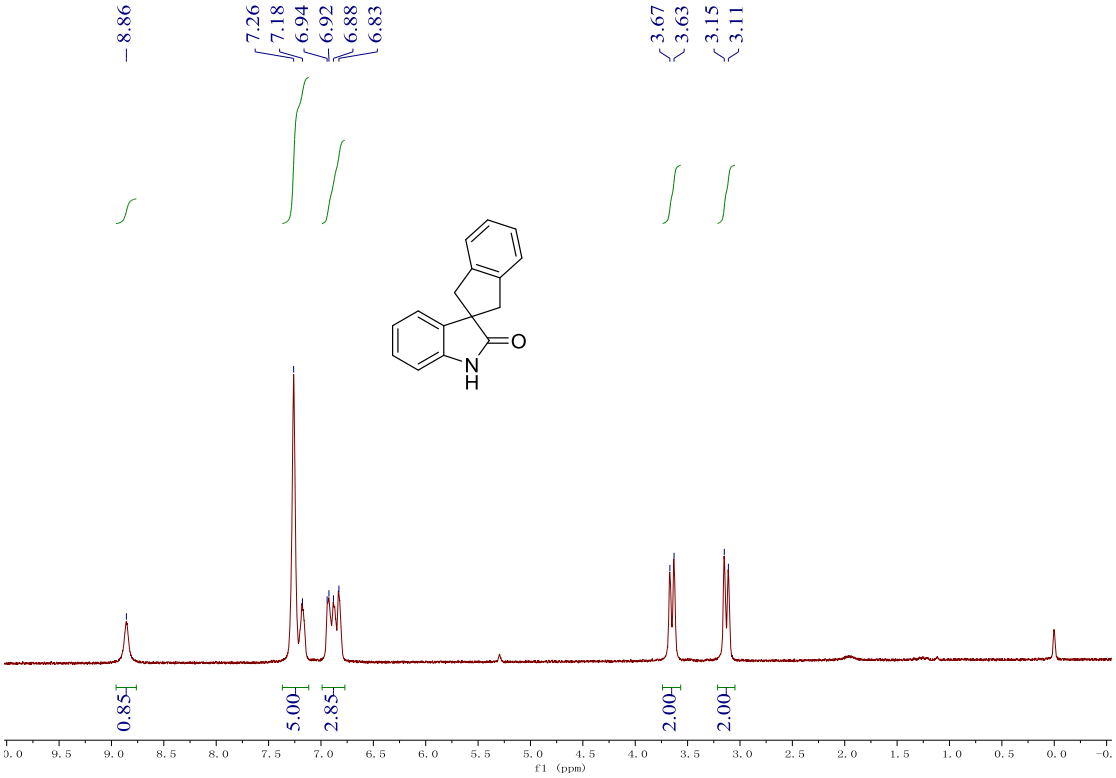
^{1}H NMR Spectrum of **1l**



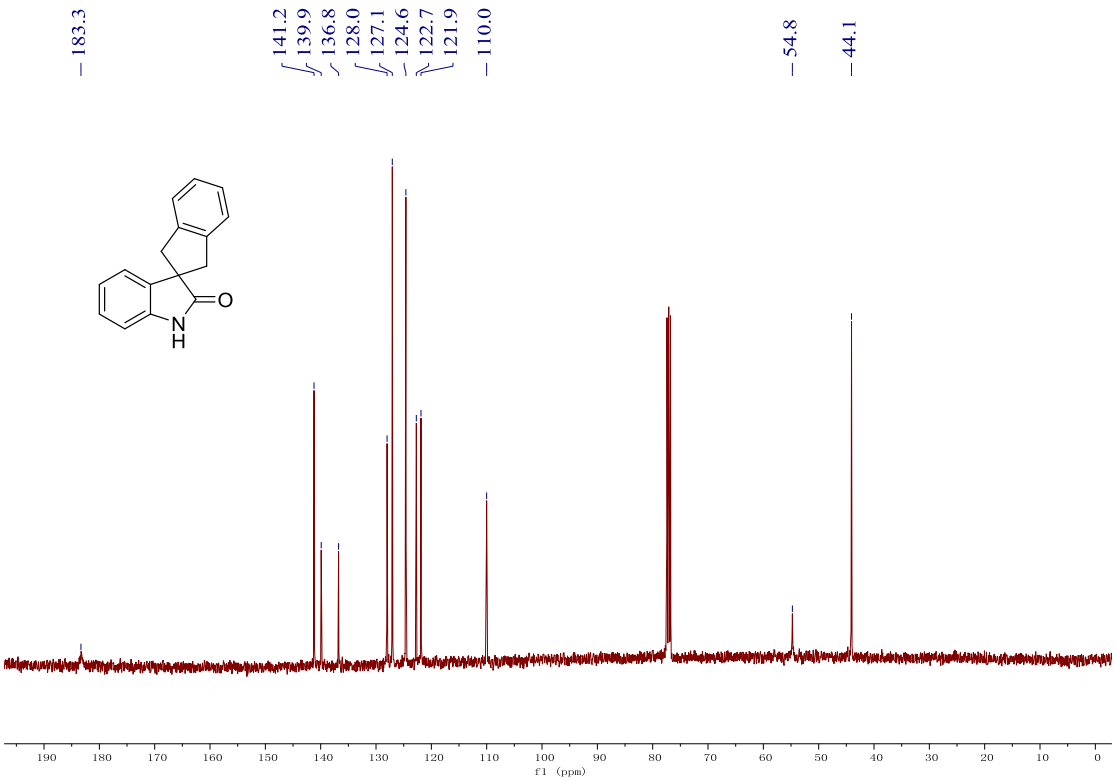
^{13}C NMR Spectrum of **1l**



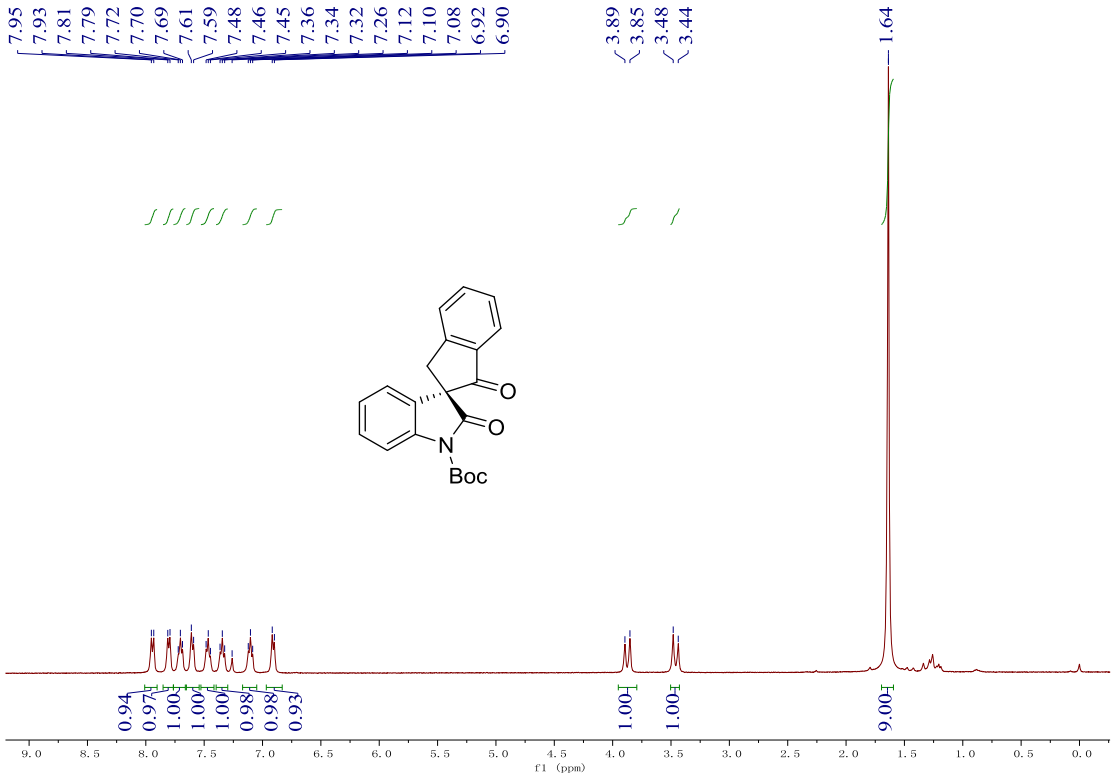
^{1}H NMR Spectrum of **1m**



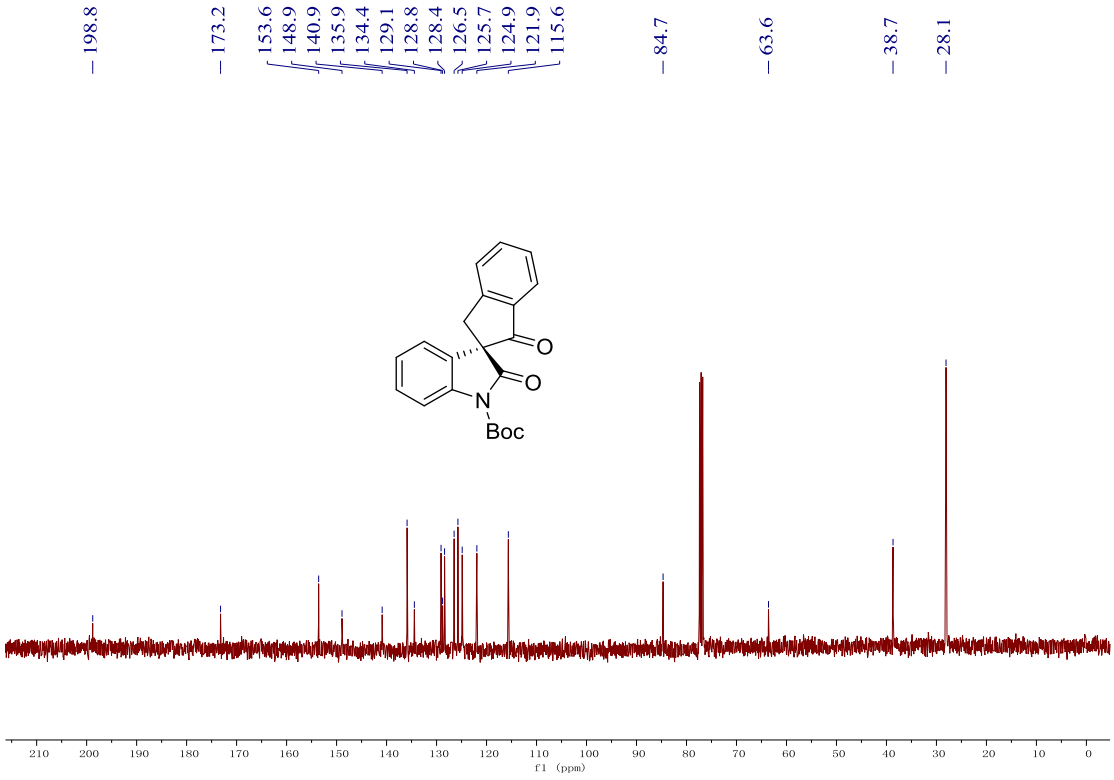
^{13}C NMR Spectrum of **1l**



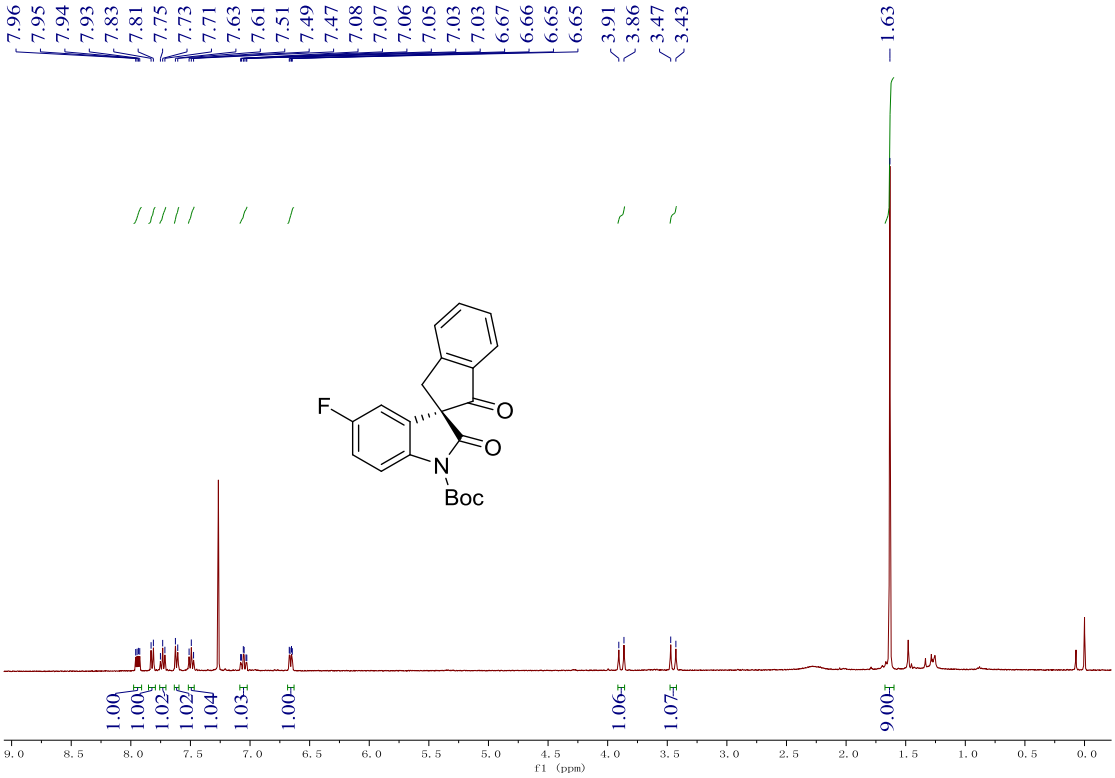
^{1}H NMR Spectrum of **2a**



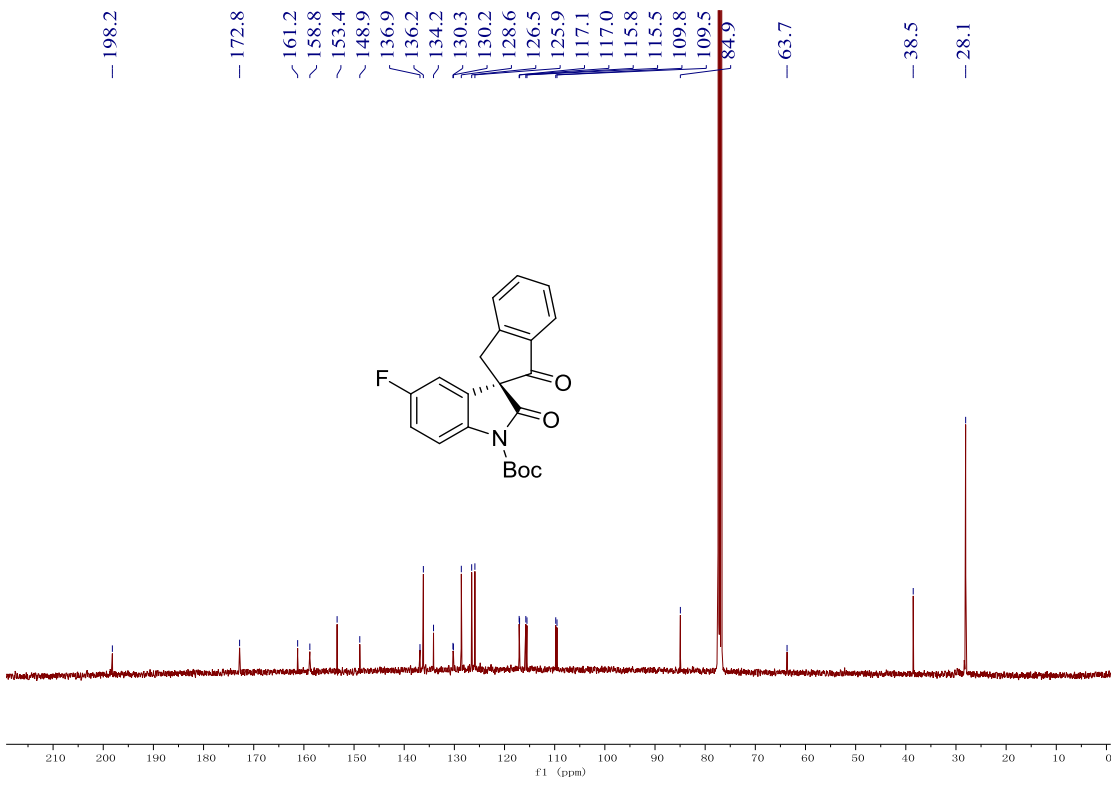
^{13}C NMR Spectrum of **2a**



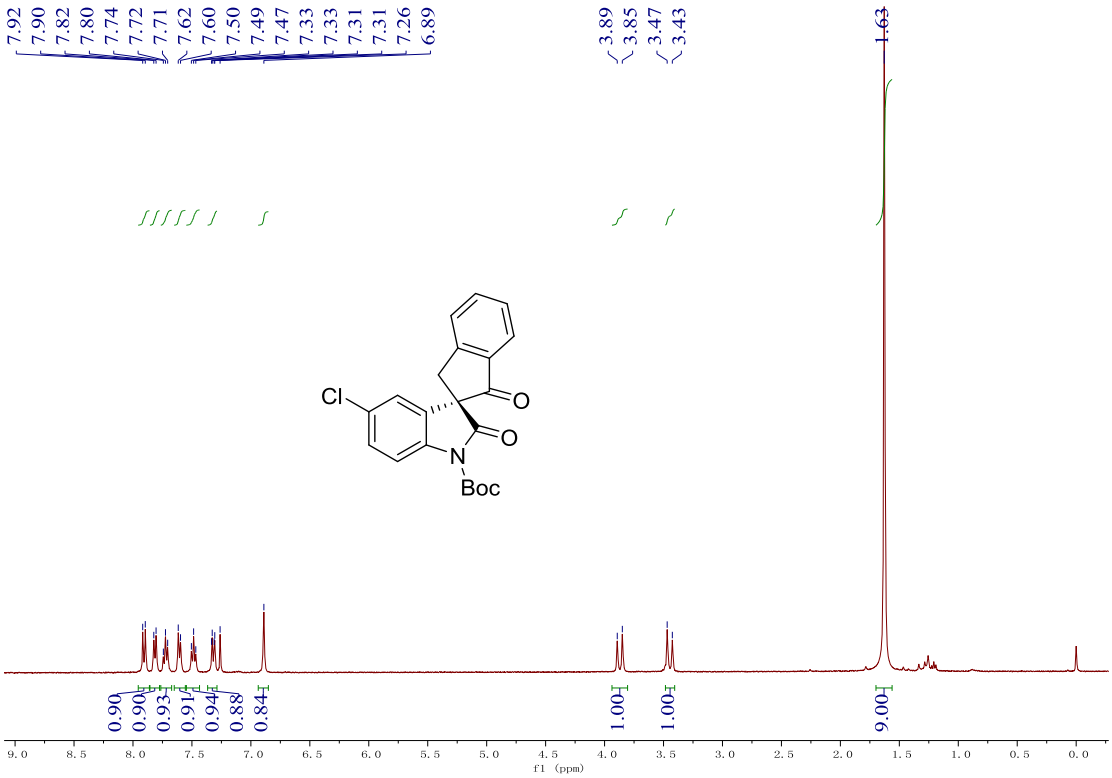
^{1}H NMR Spectrum of **2b**



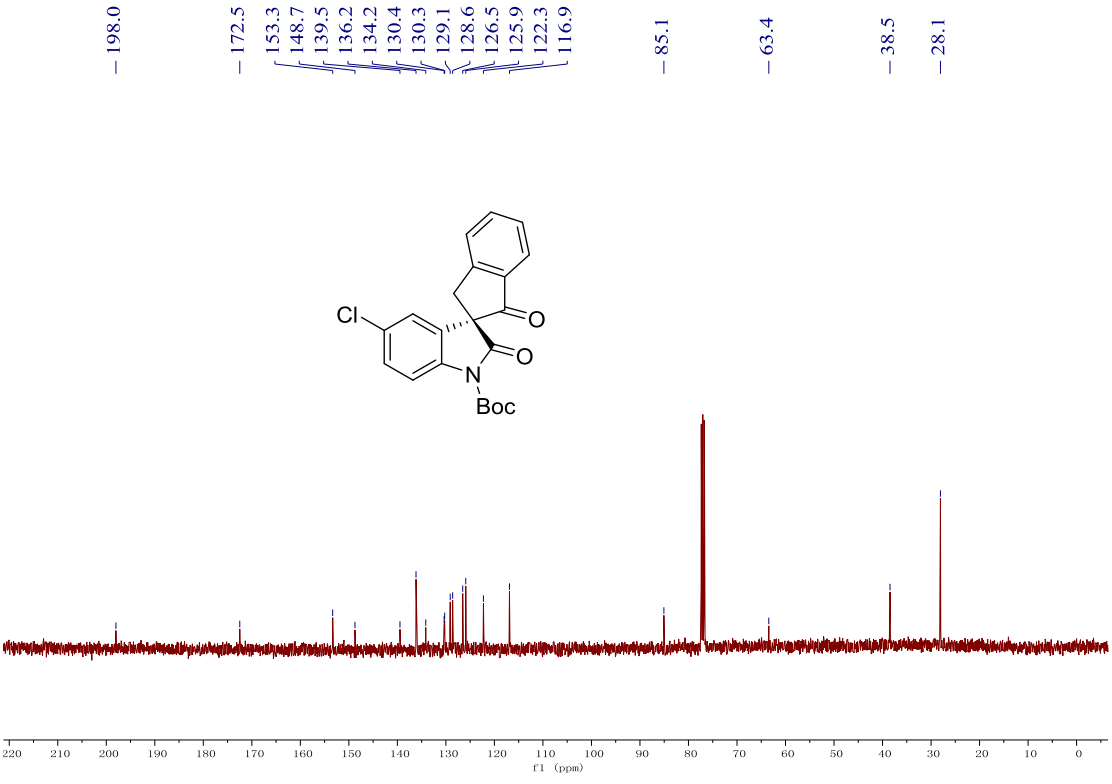
^{13}C NMR Spectrum of **2b**



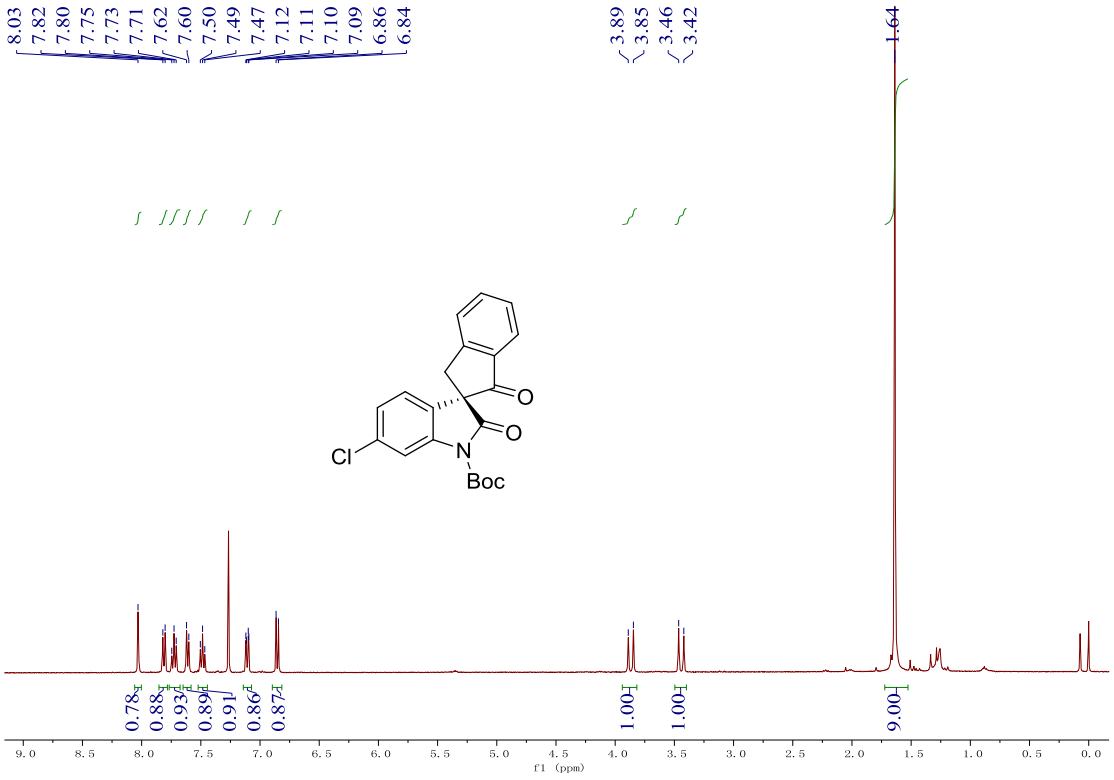
^{1}H NMR Spectrum of **2c**



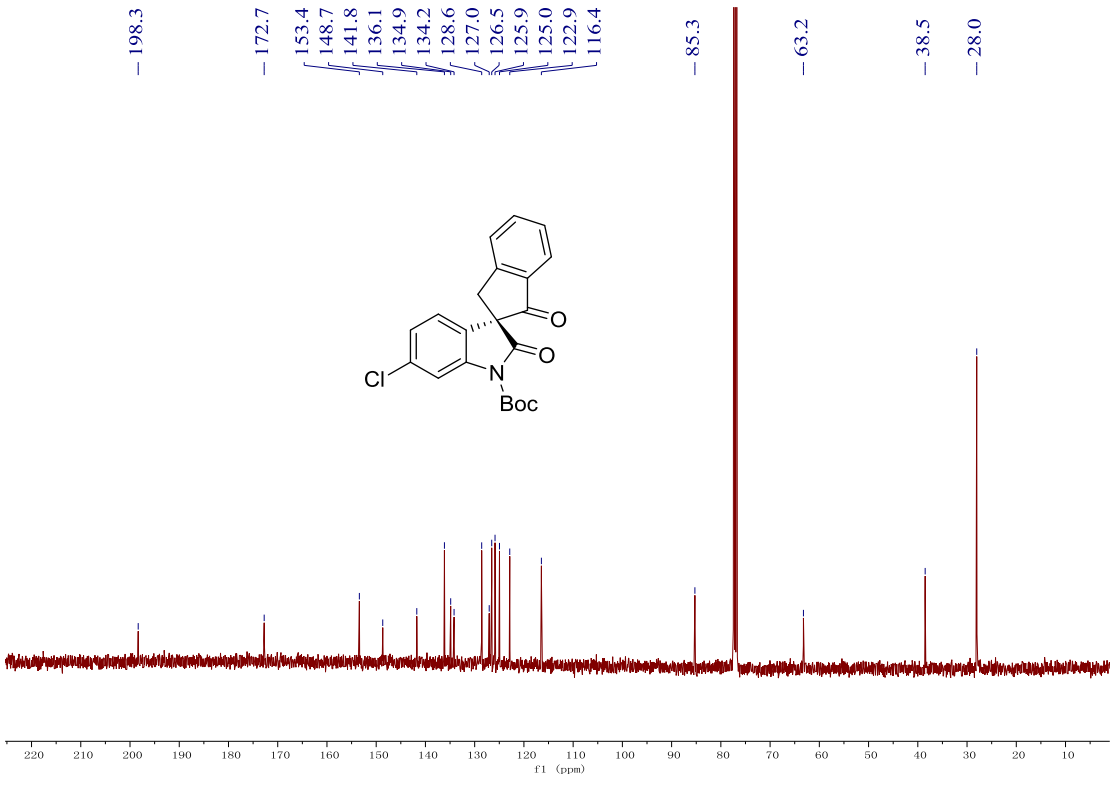
^{13}C NMR Spectrum of **2c**



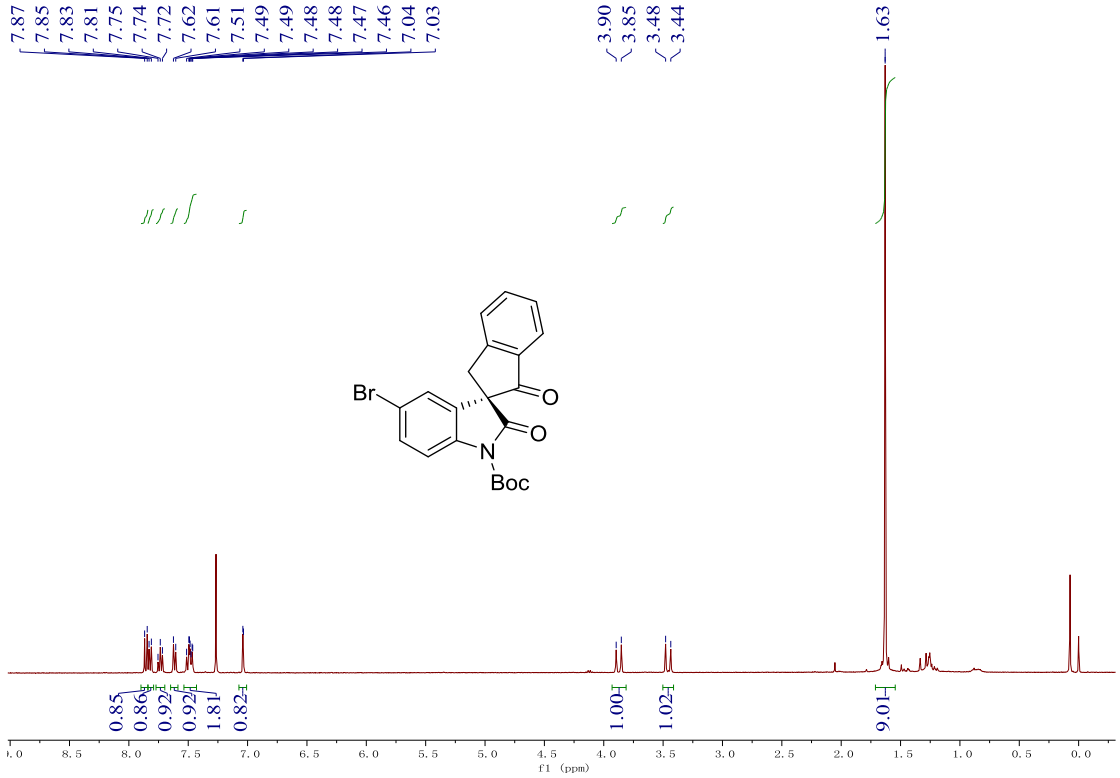
^{1}H NMR Spectrum of **2d**



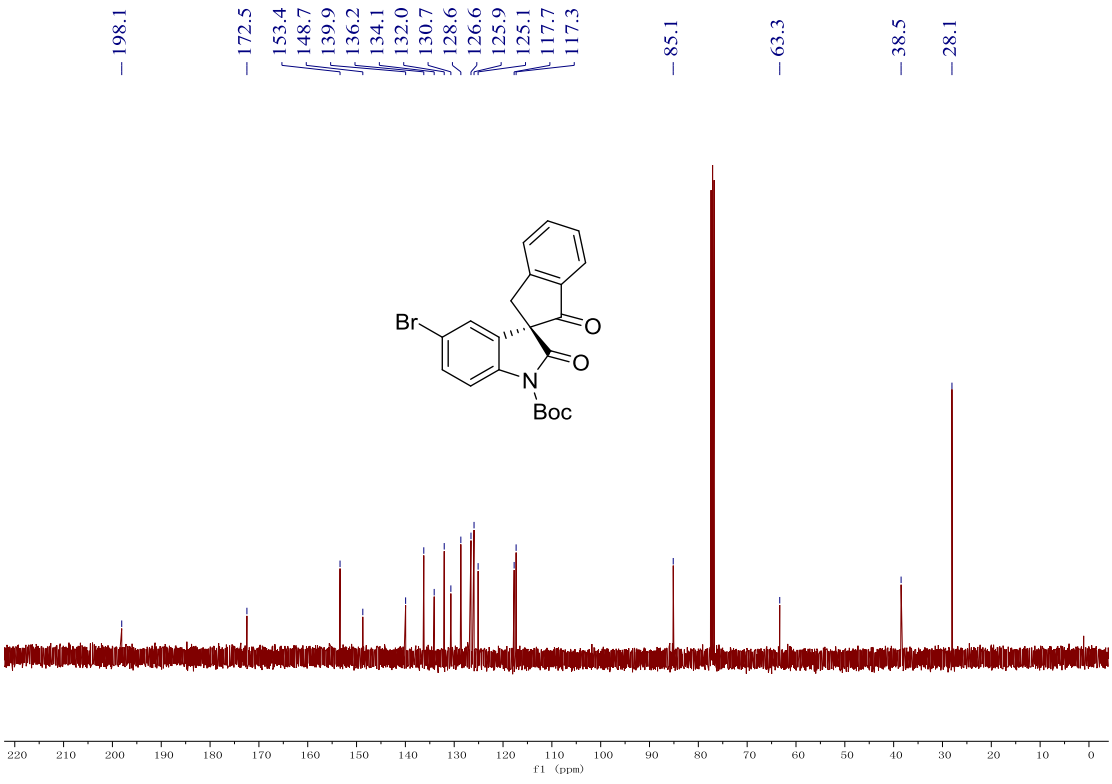
^{13}C NMR Spectrum of **2d**



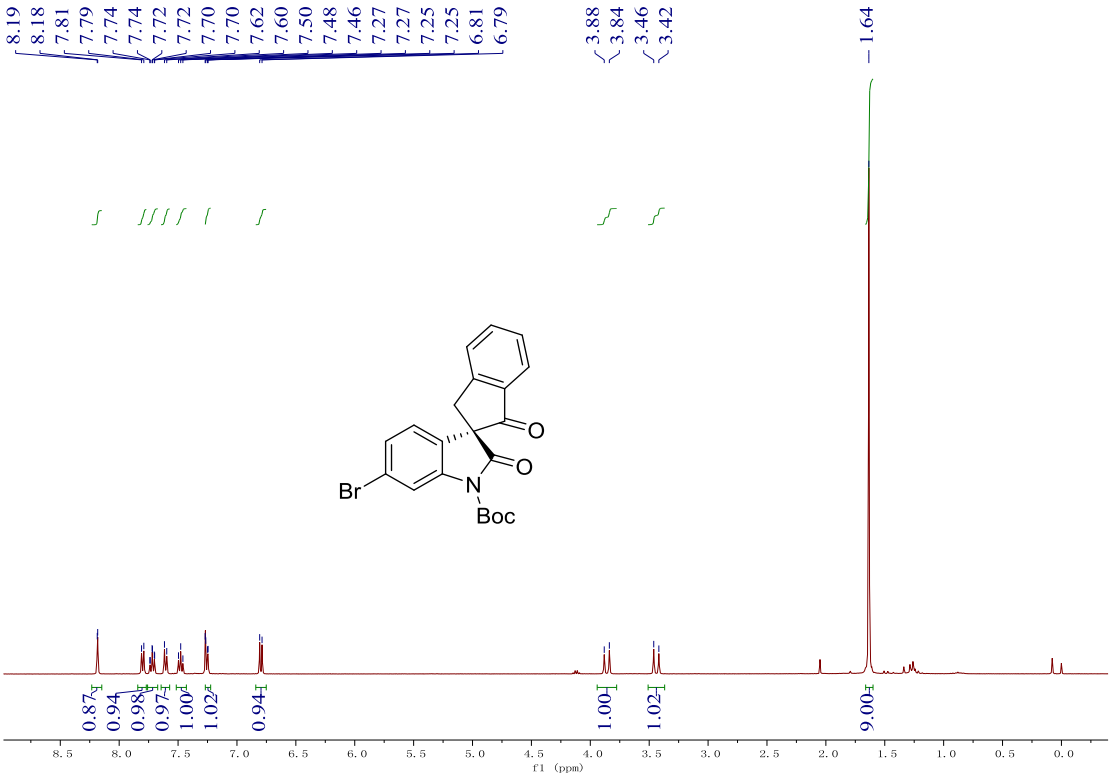
^{1}H NMR Spectrum of **2e**



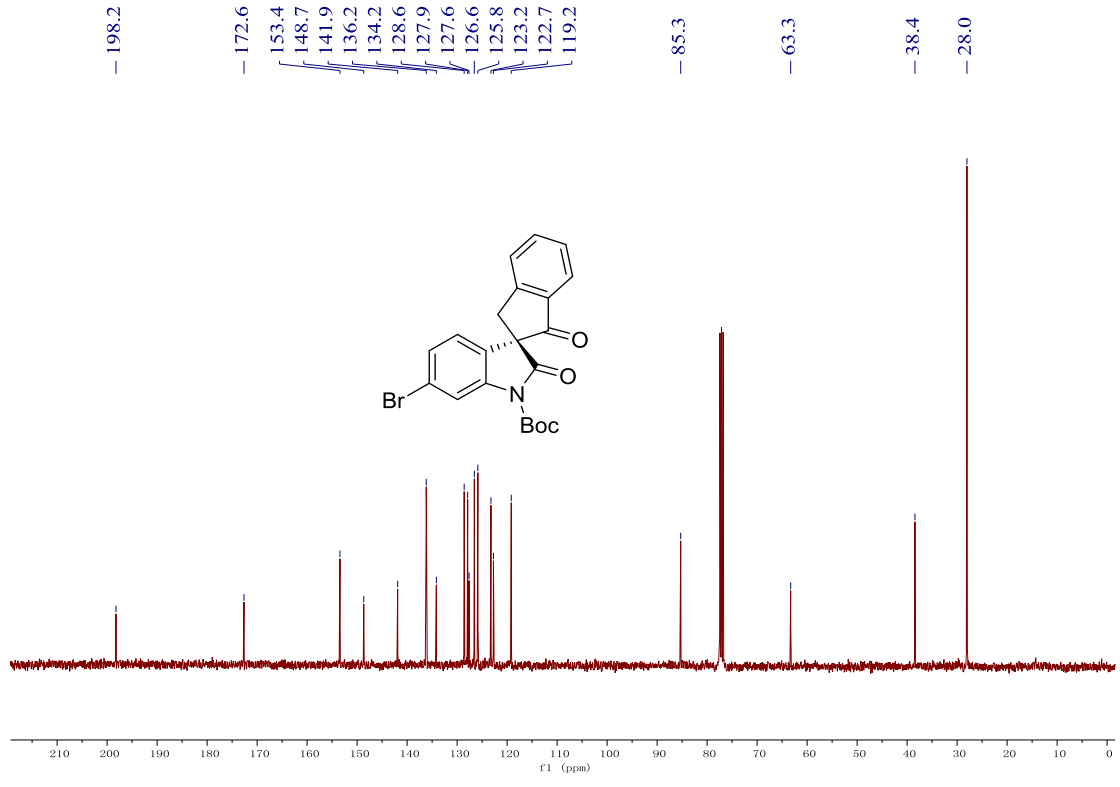
^{13}C NMR Spectrum of **2e**



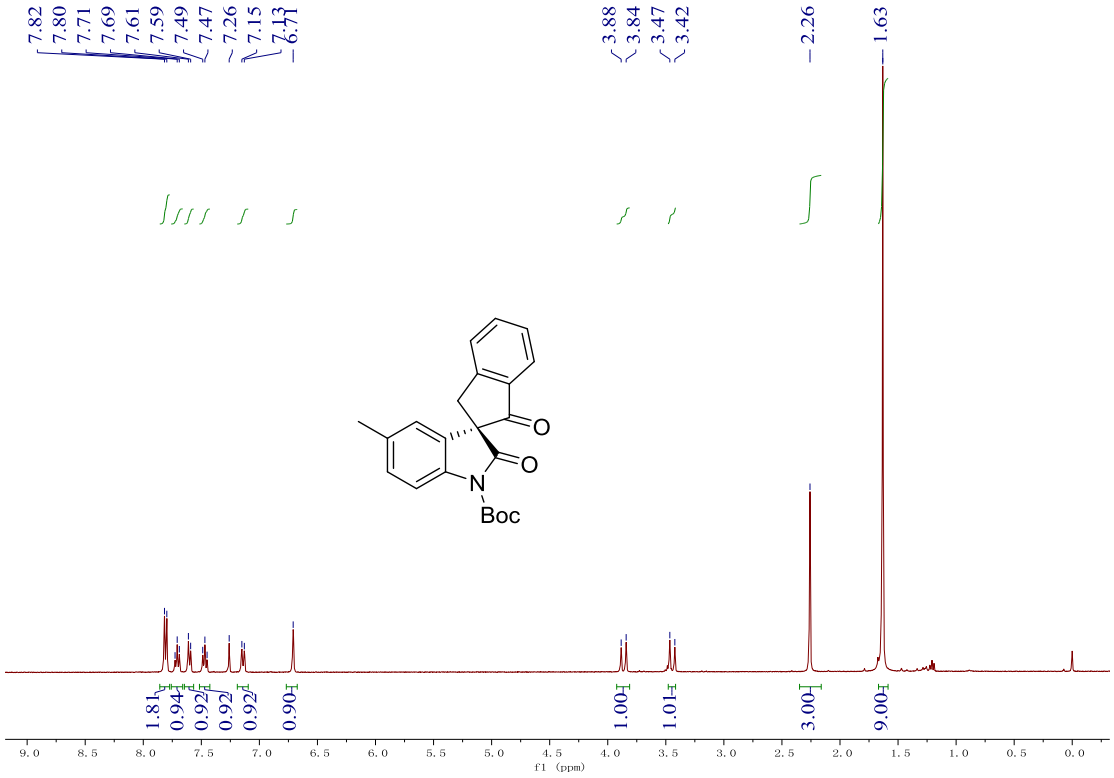
^{1}H NMR Spectrum of **2f**



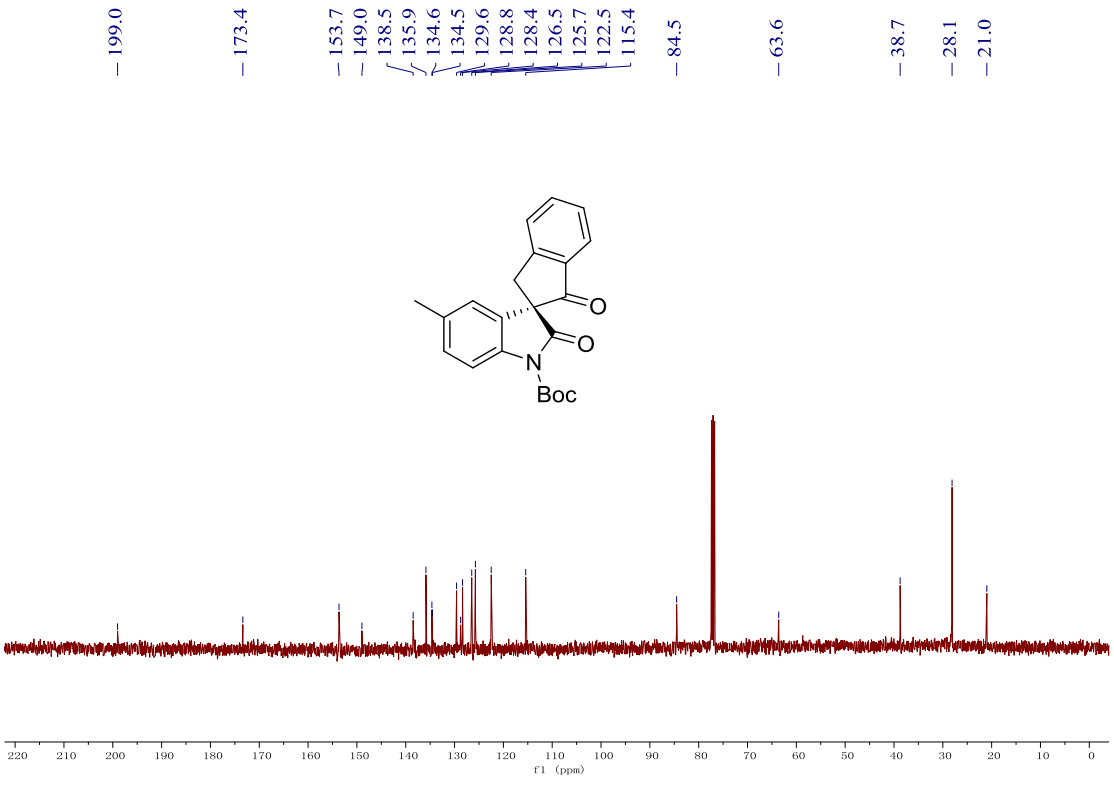
^{13}C NMR Spectrum of **2f**



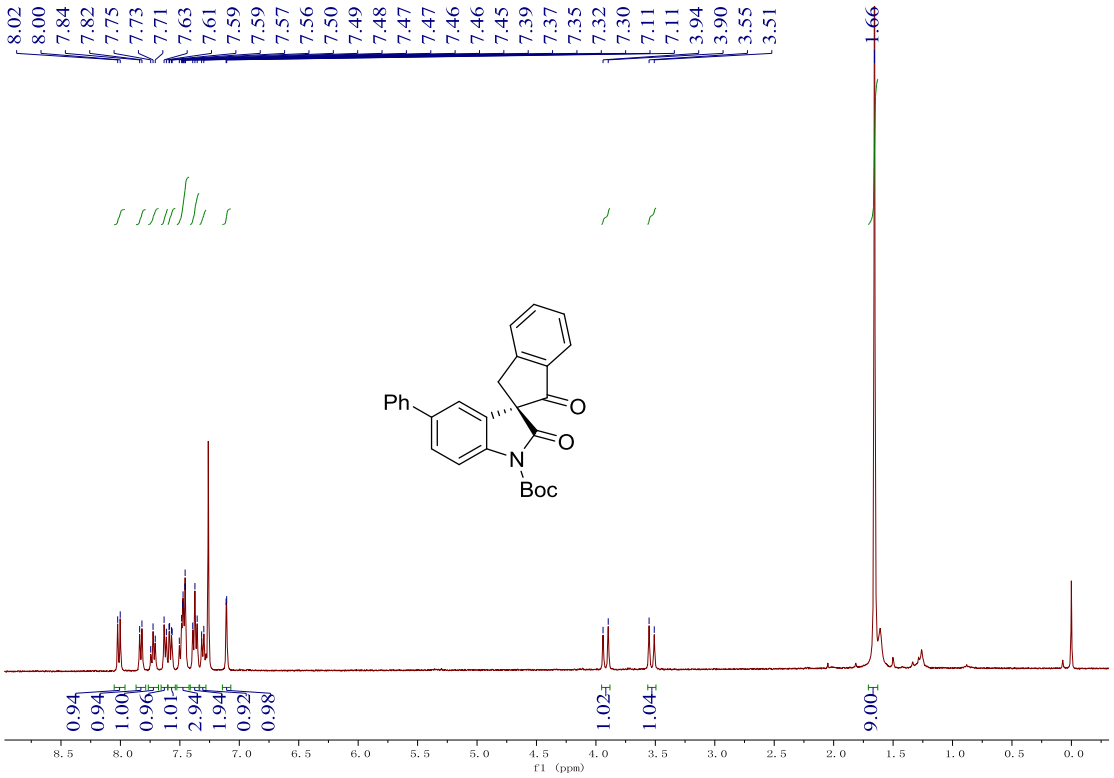
^{1}H NMR Spectrum of **2g**



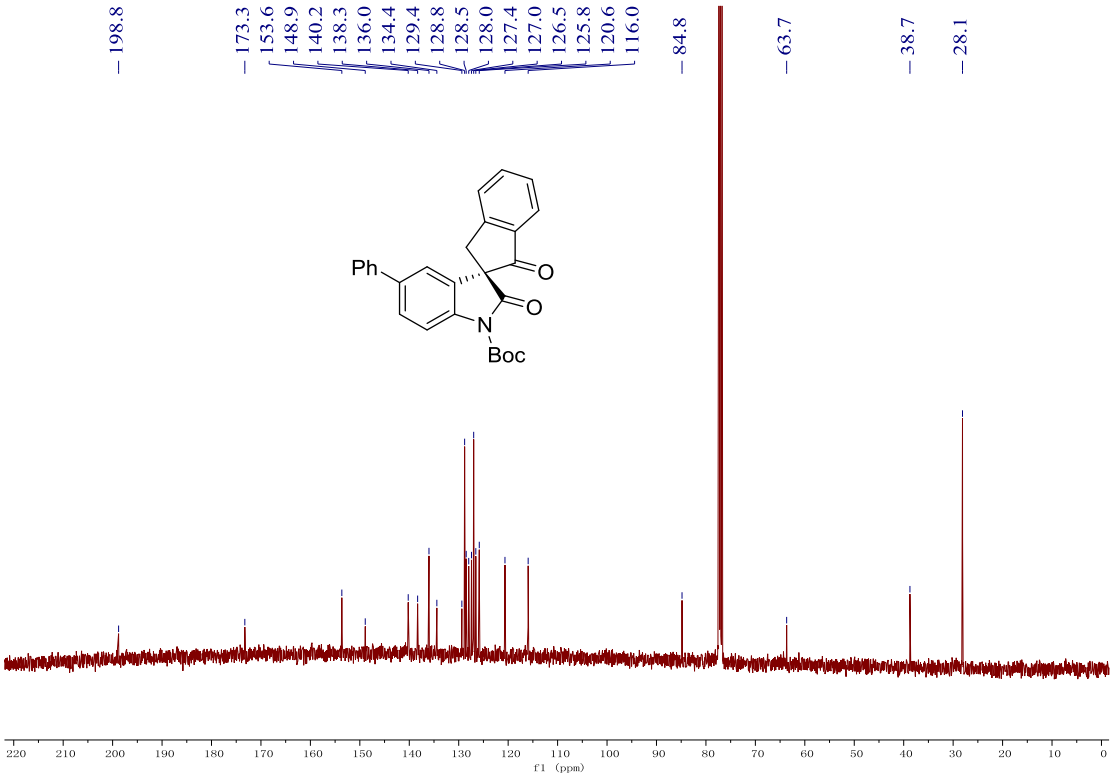
^{13}C NMR Spectrum of **2g**



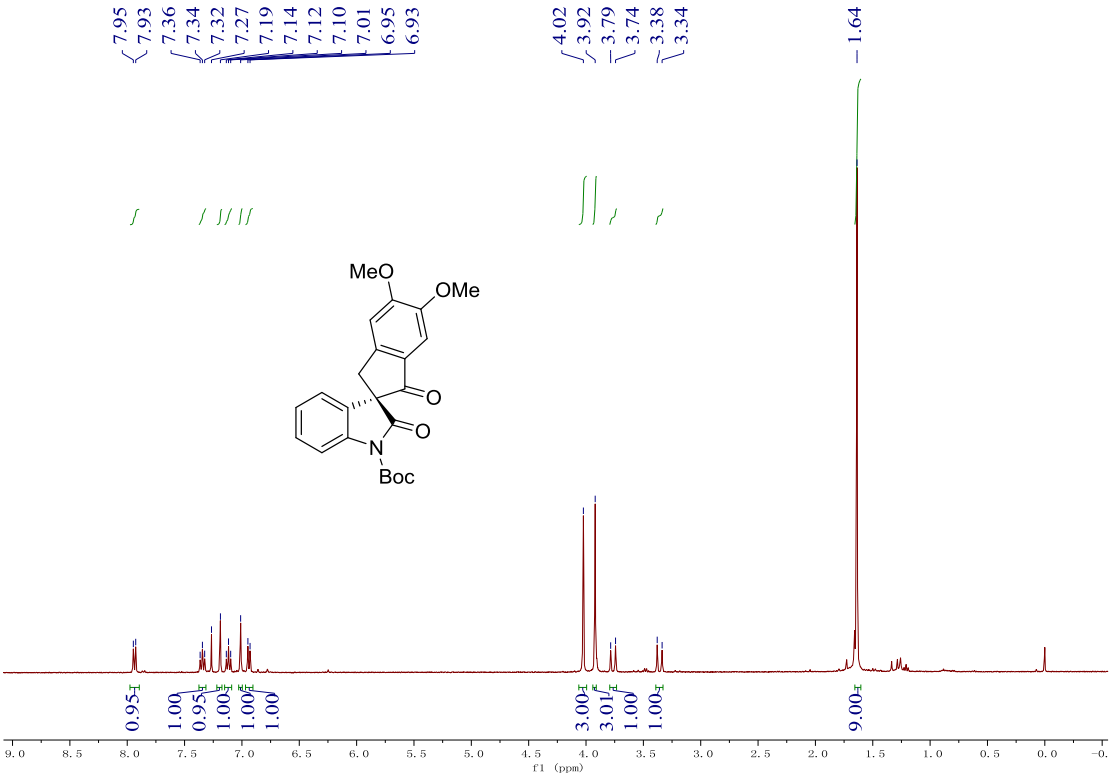
^{1}H NMR Spectrum of **2h**



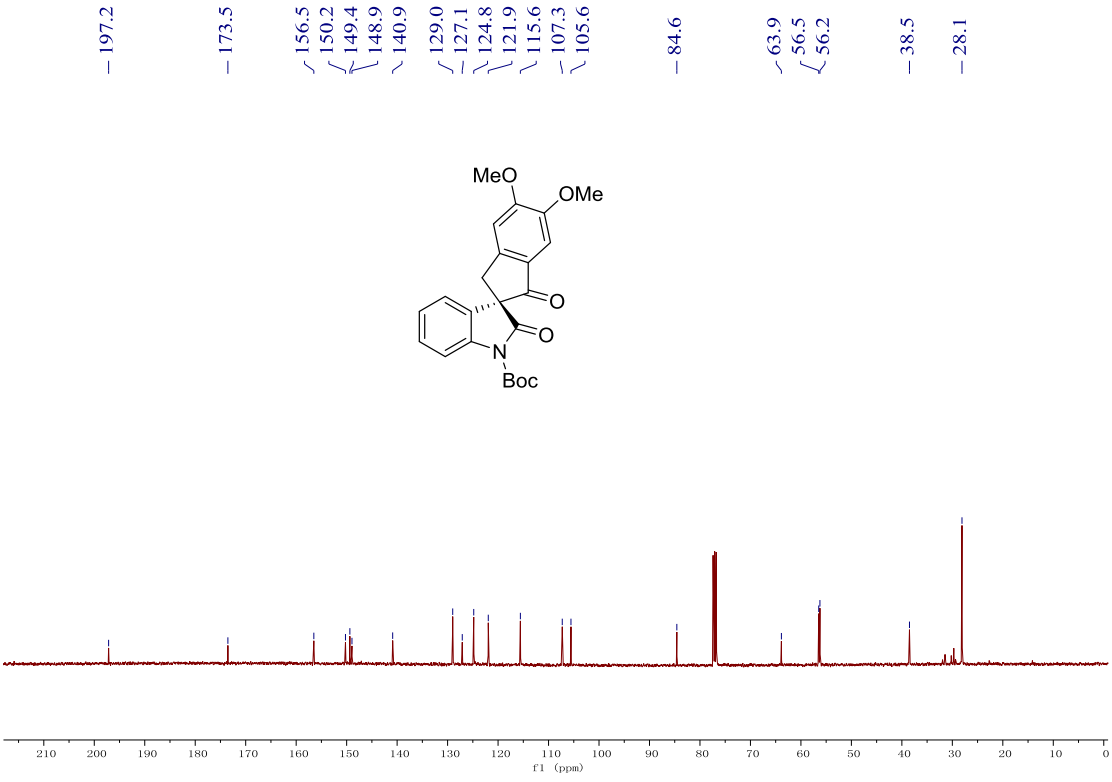
^{13}C NMR Spectrum of **2h**



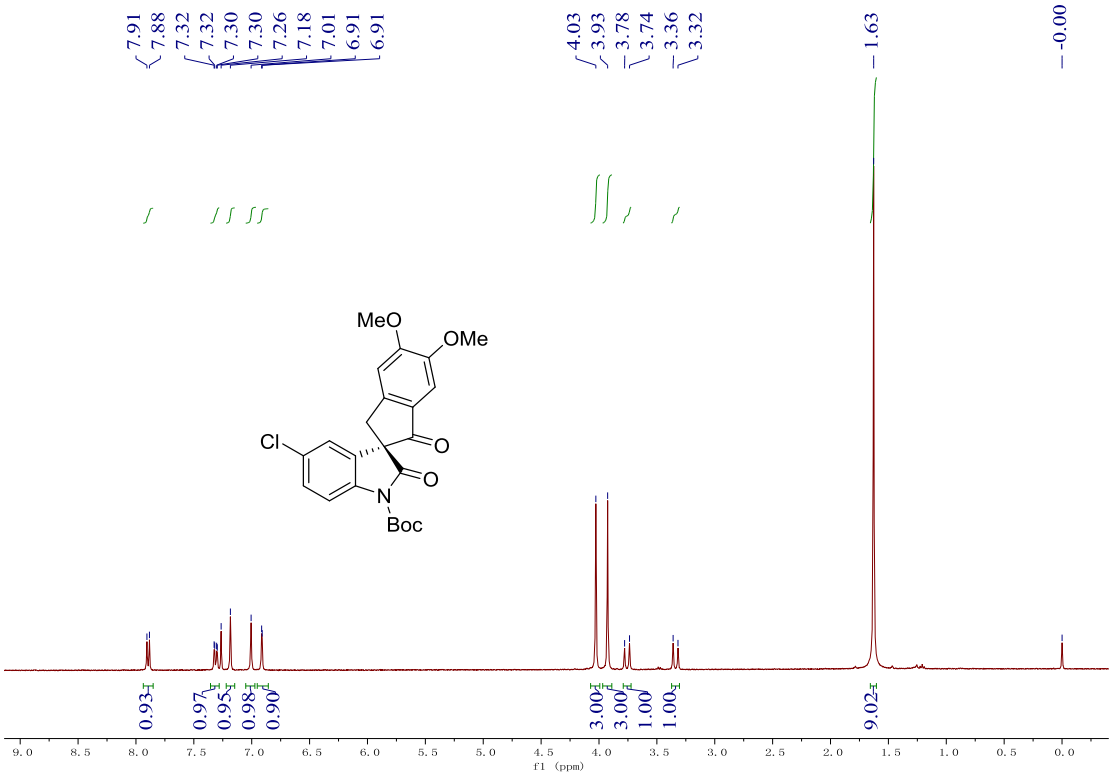
^{1}H NMR Spectrum of **2i**



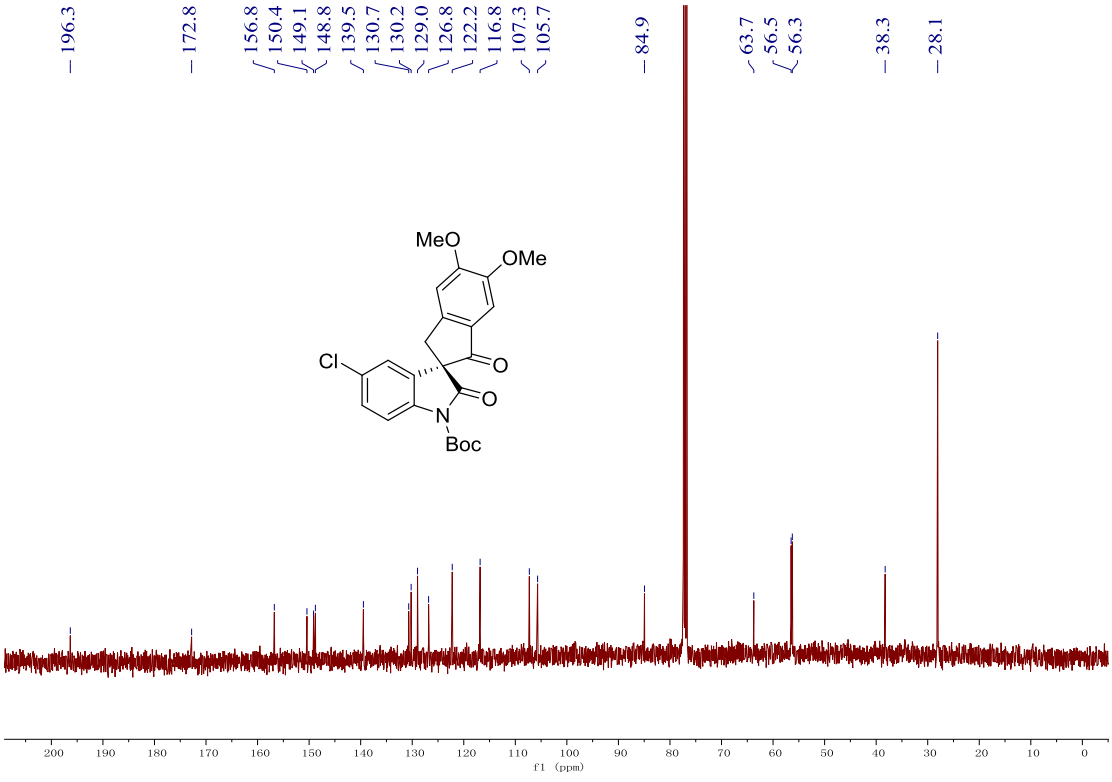
^{13}C NMR Spectrum of **2i**



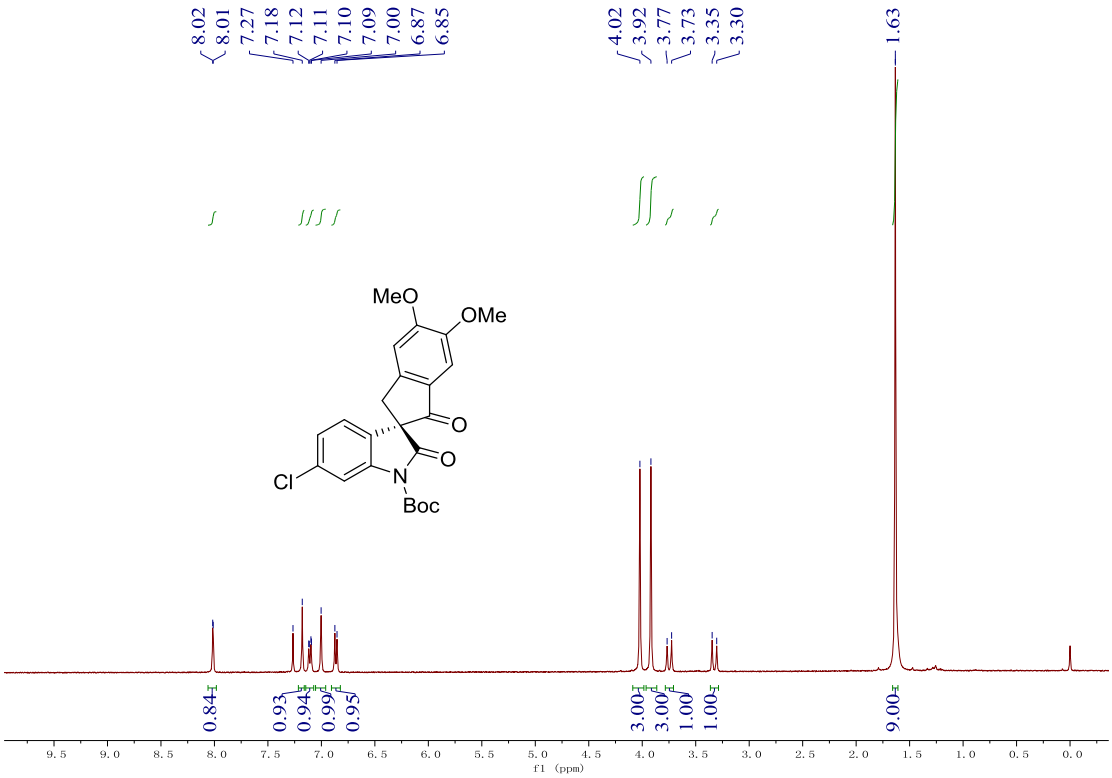
^{1}H NMR Spectrum of **2j**



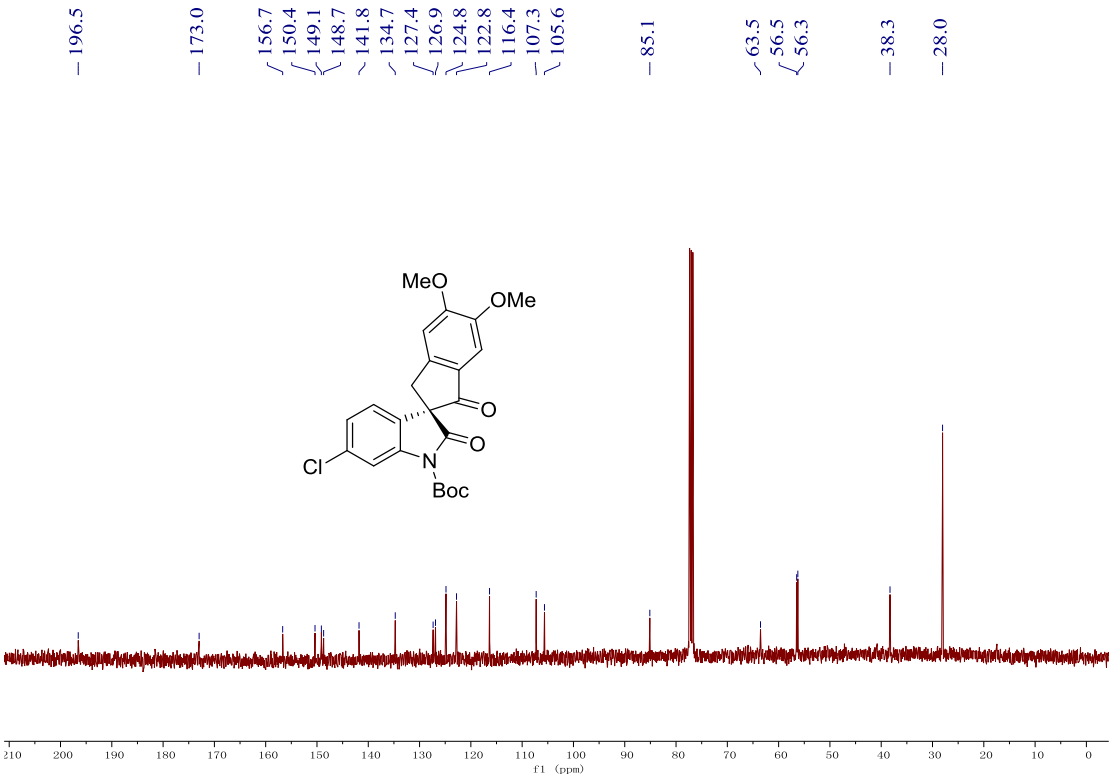
^{13}C NMR Spectrum of **2j**



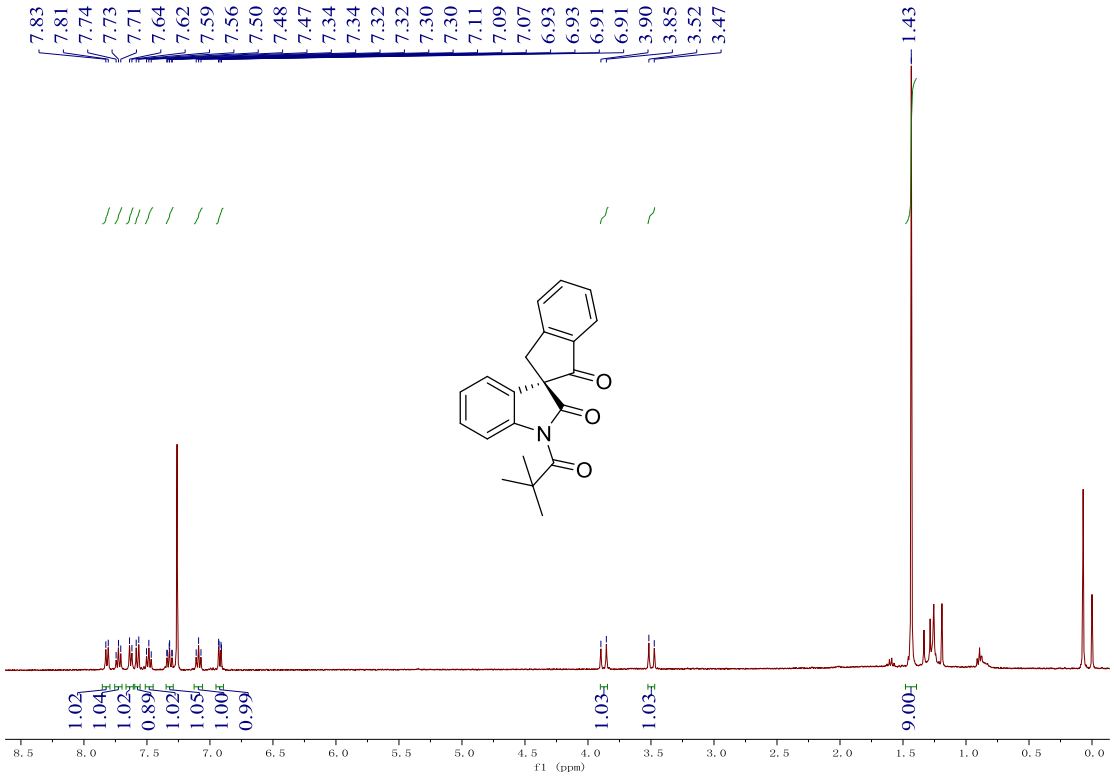
^{1}H NMR Spectrum of **2k**



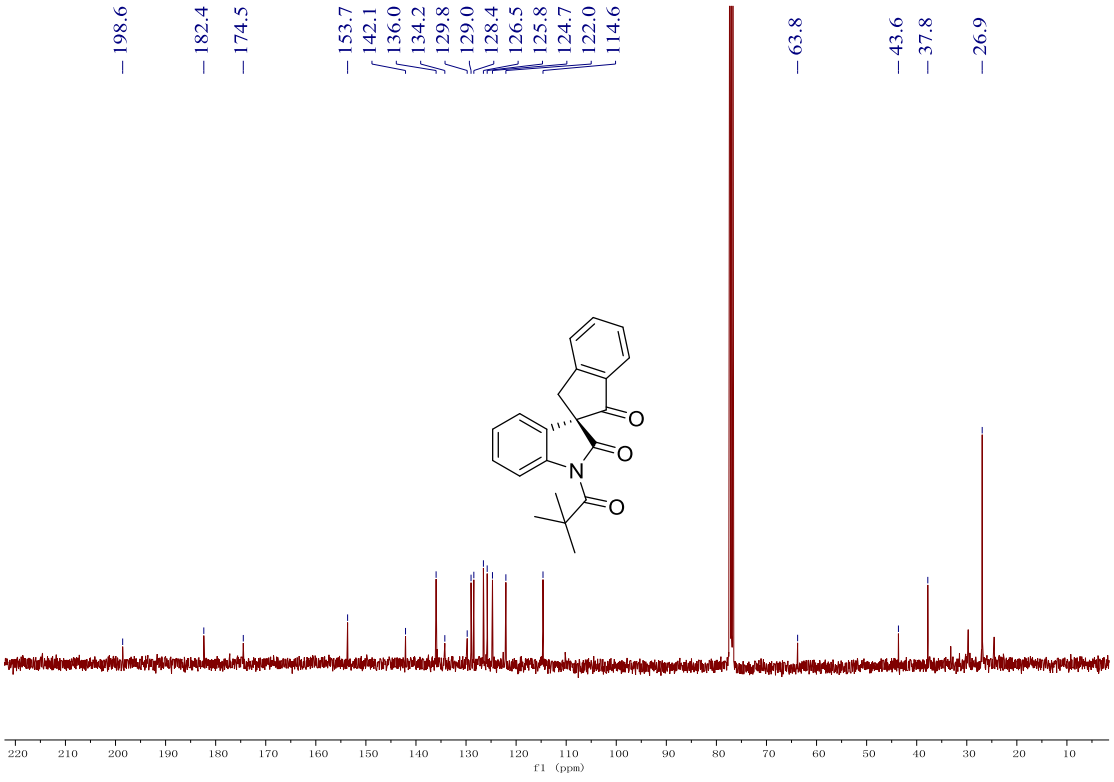
^{13}C NMR Spectrum of **2k**



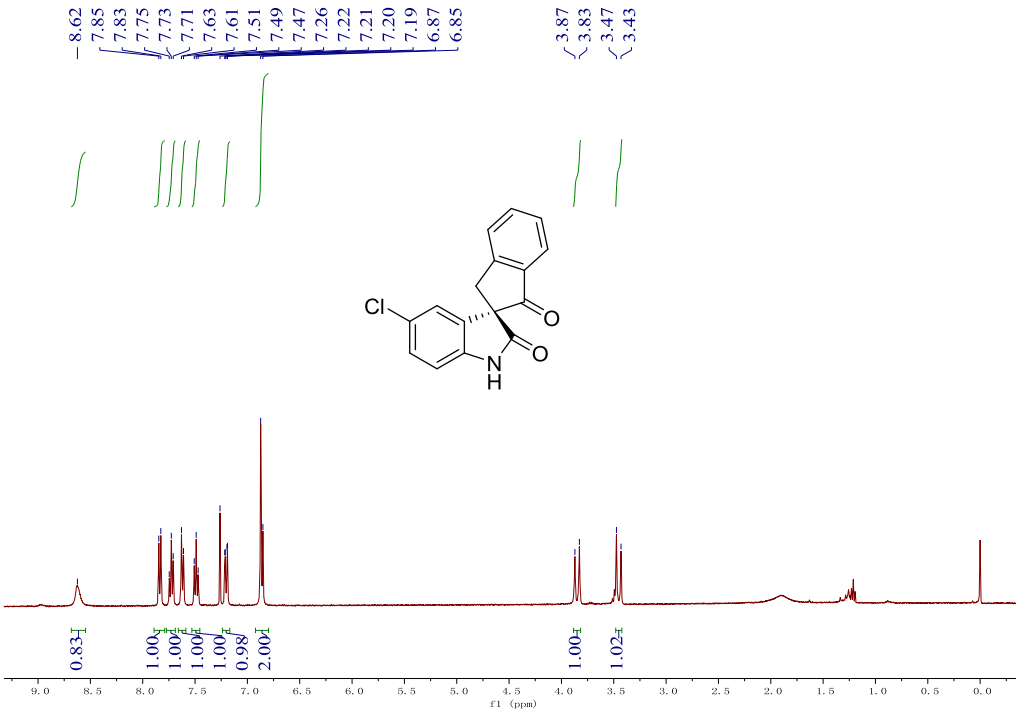
^{1}H NMR Spectrum of **2l**



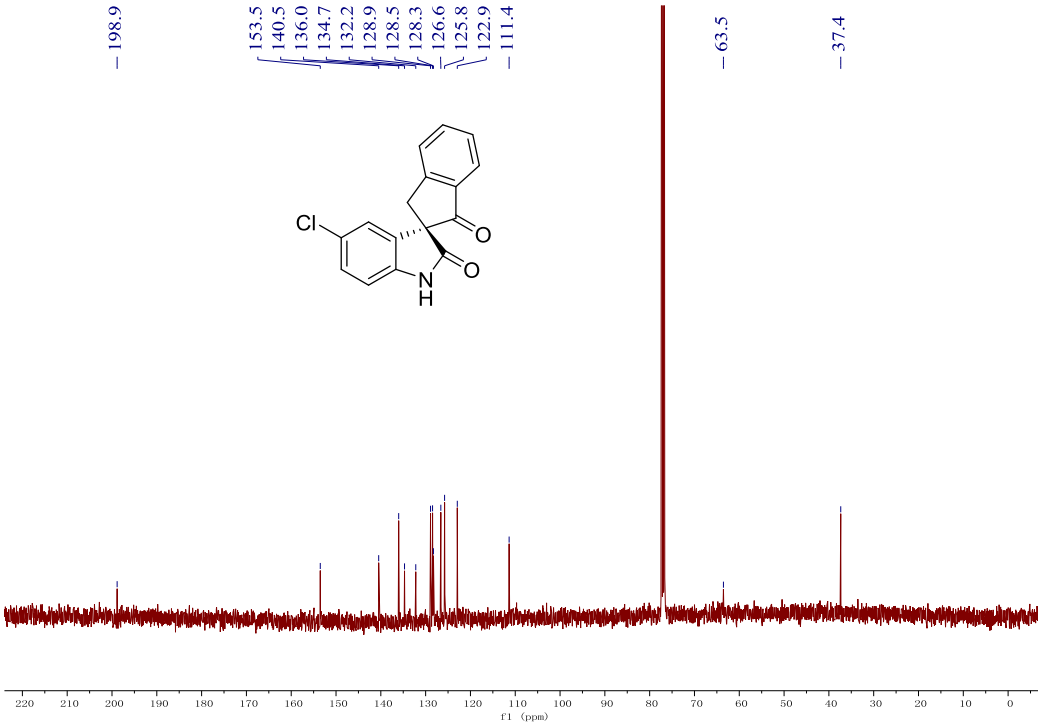
^{13}C NMR Spectrum of **2l**



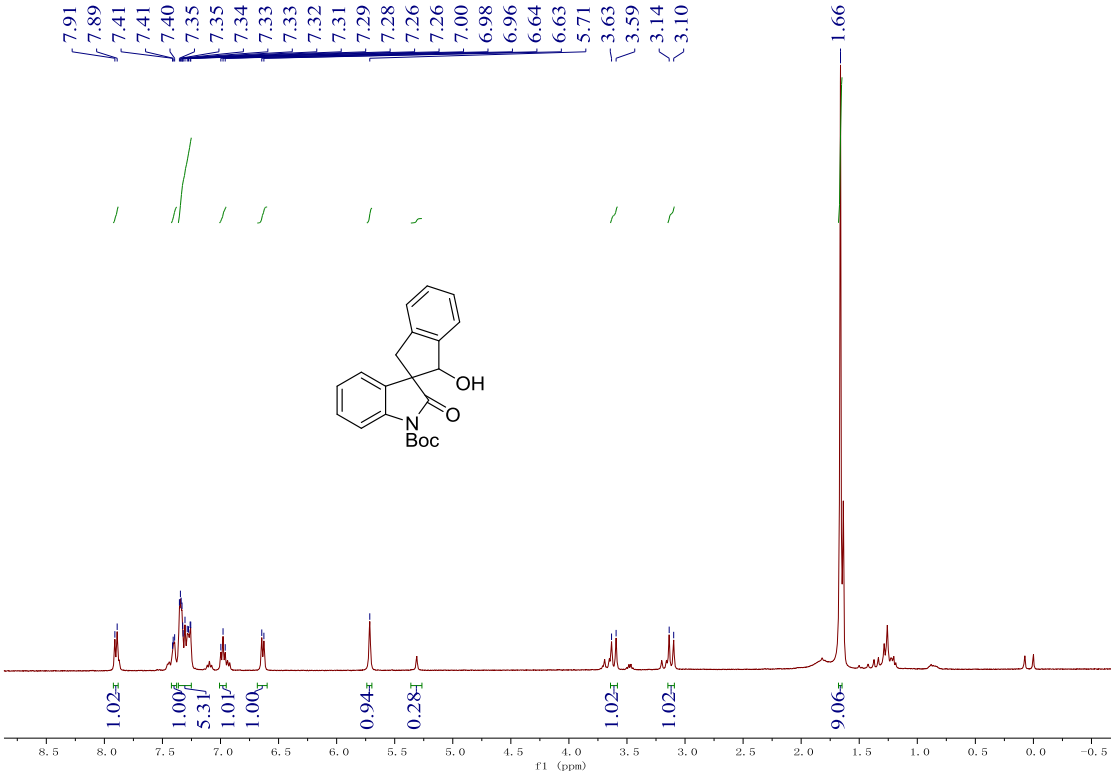
^{1}H NMR Spectrum of **2c'**



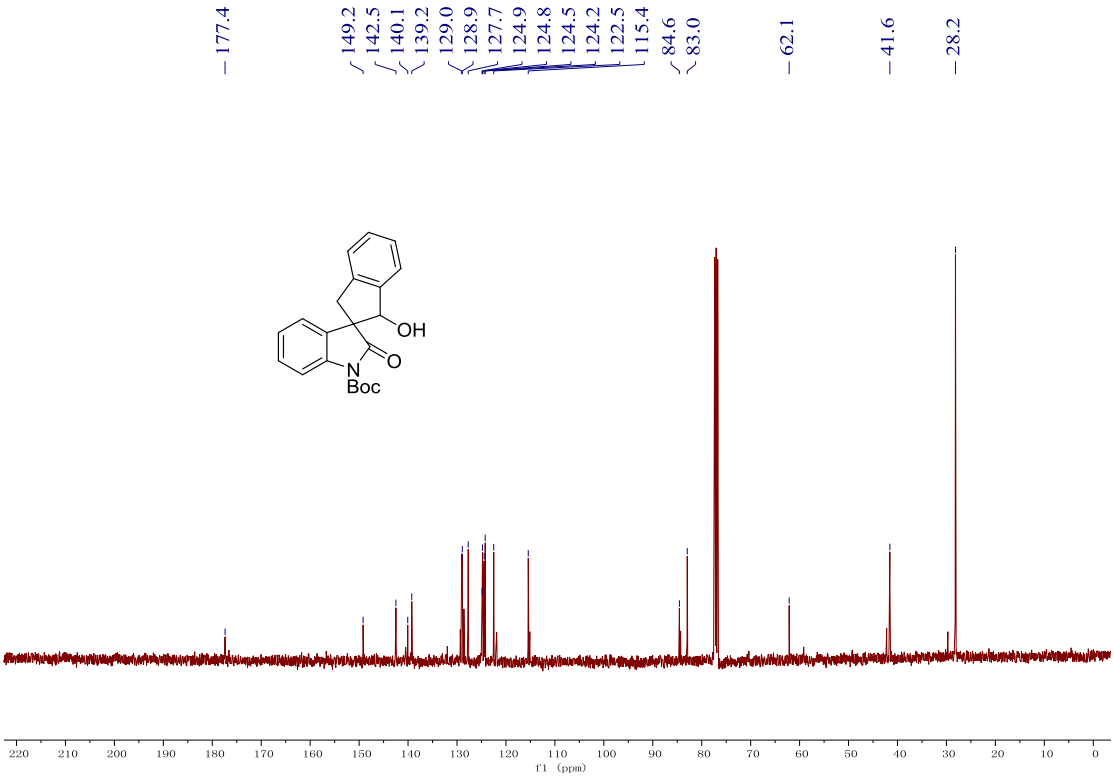
^{13}C NMR Spectrum of **2c'**



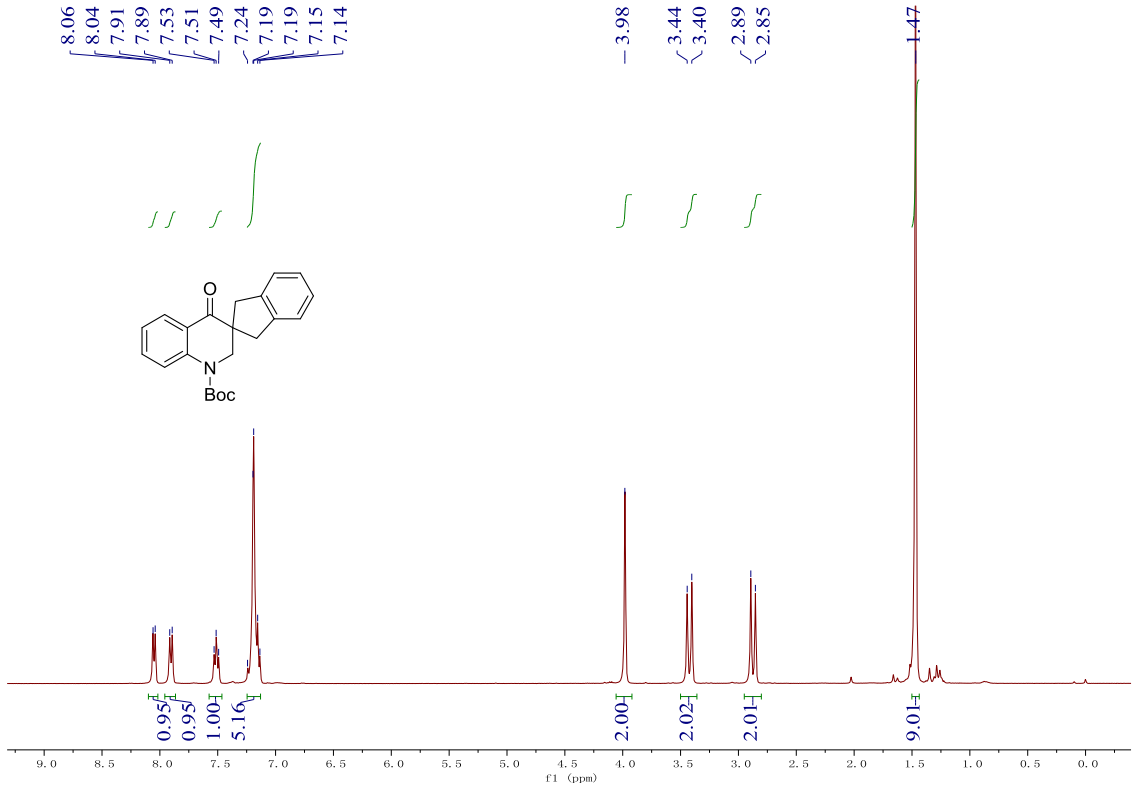
^{1}H NMR Spectrum of **3a**



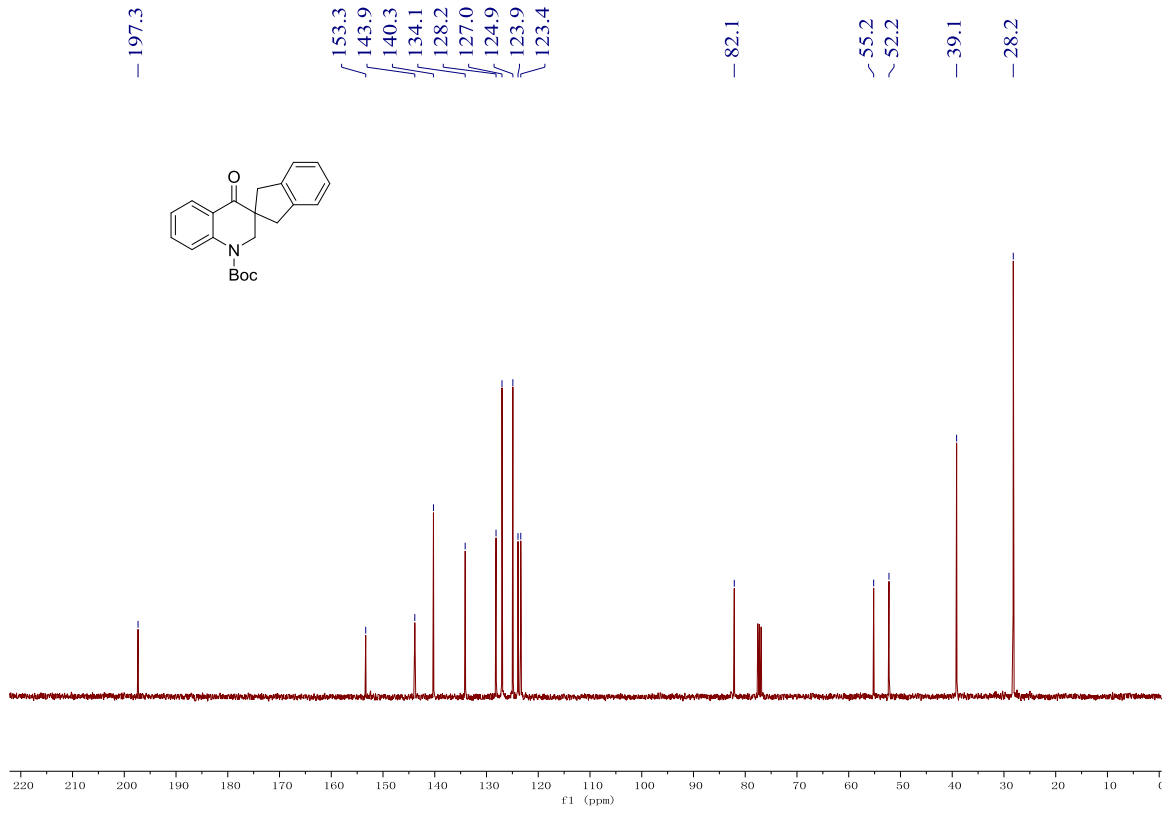
^{13}C NMR Spectrum of **3a**



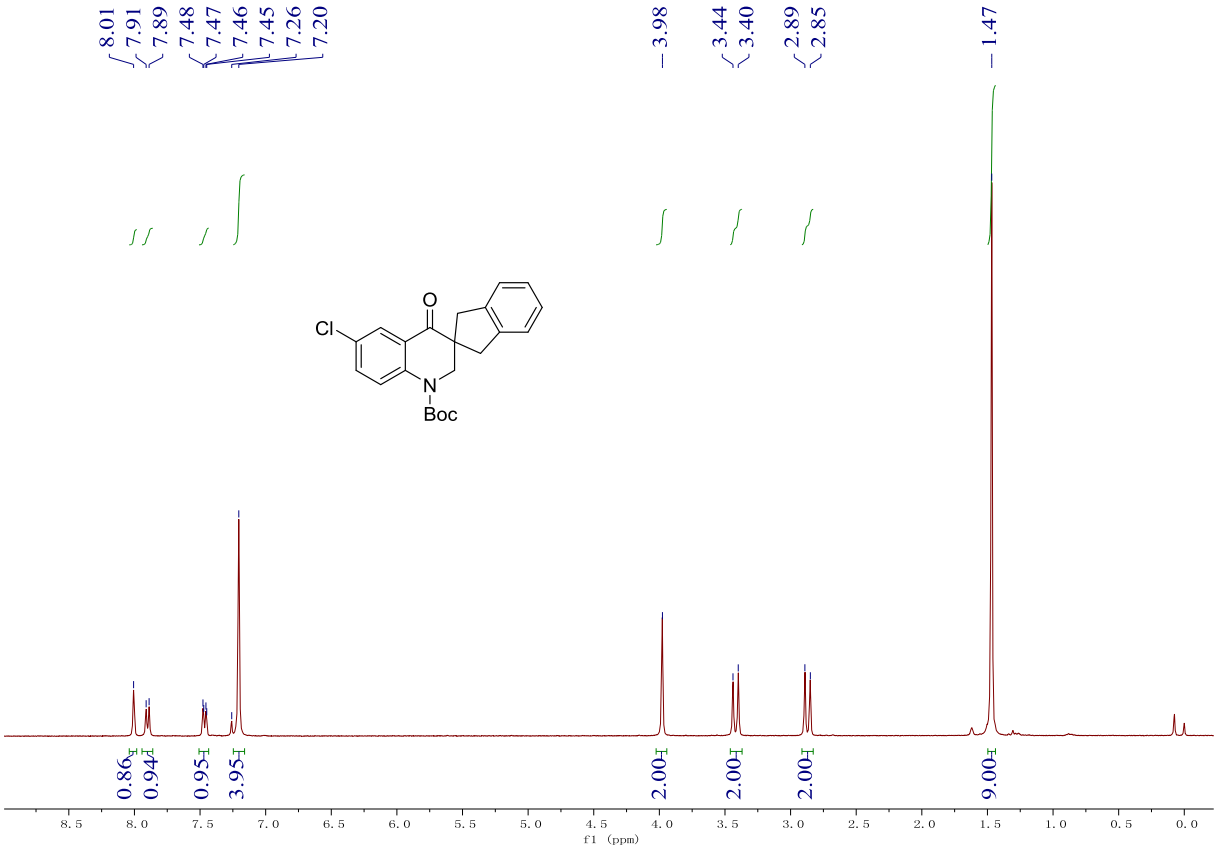
^{1}H NMR Spectrum of **4a**



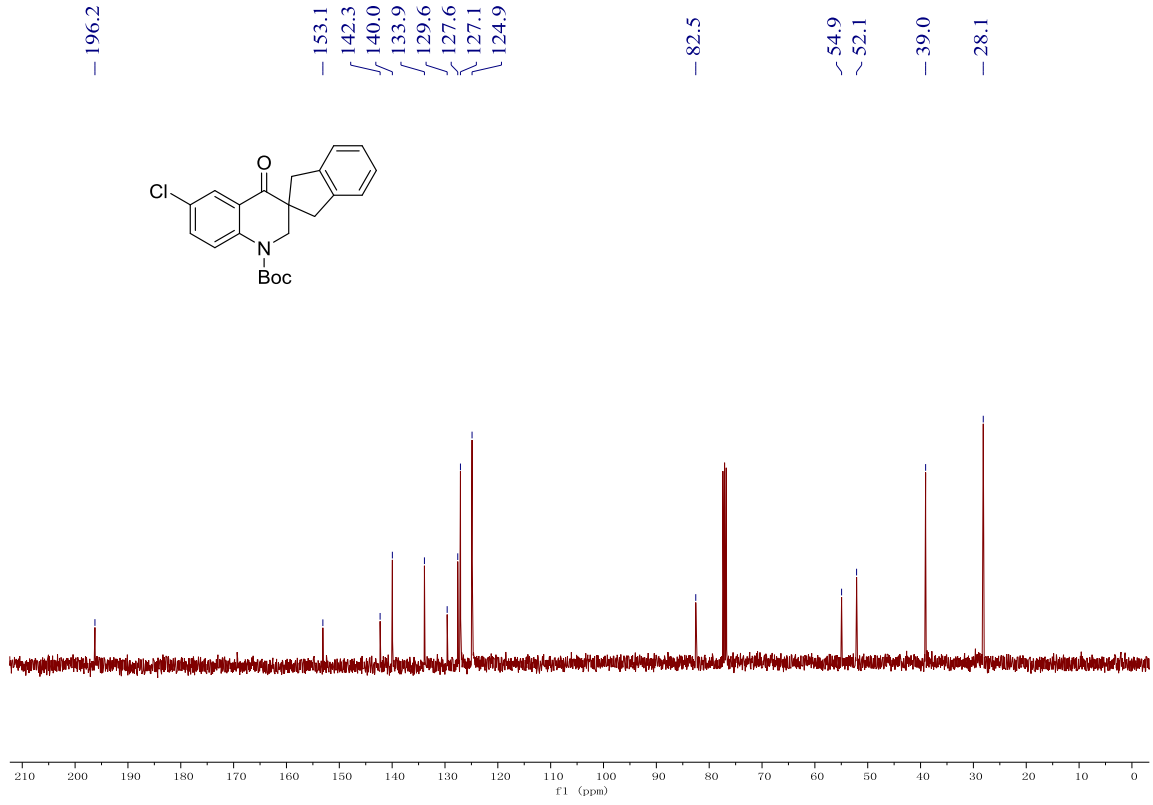
^{13}C NMR Spectrum of **4a**



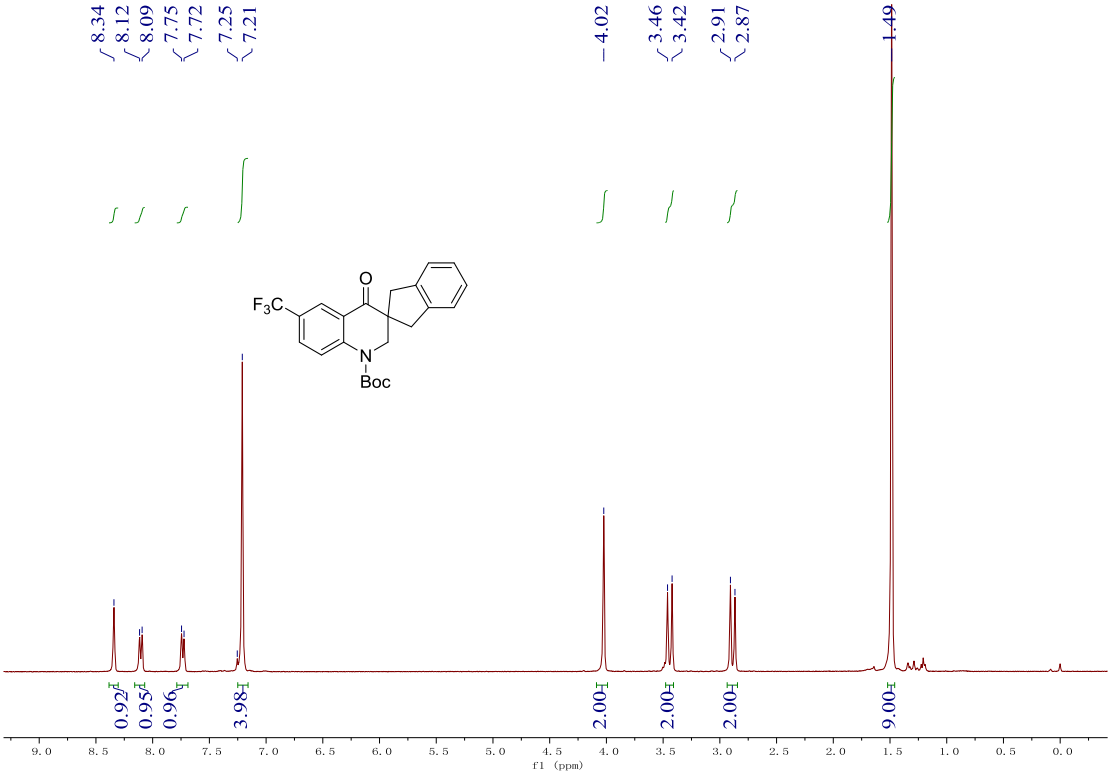
^{1}H NMR Spectrum of **4b**



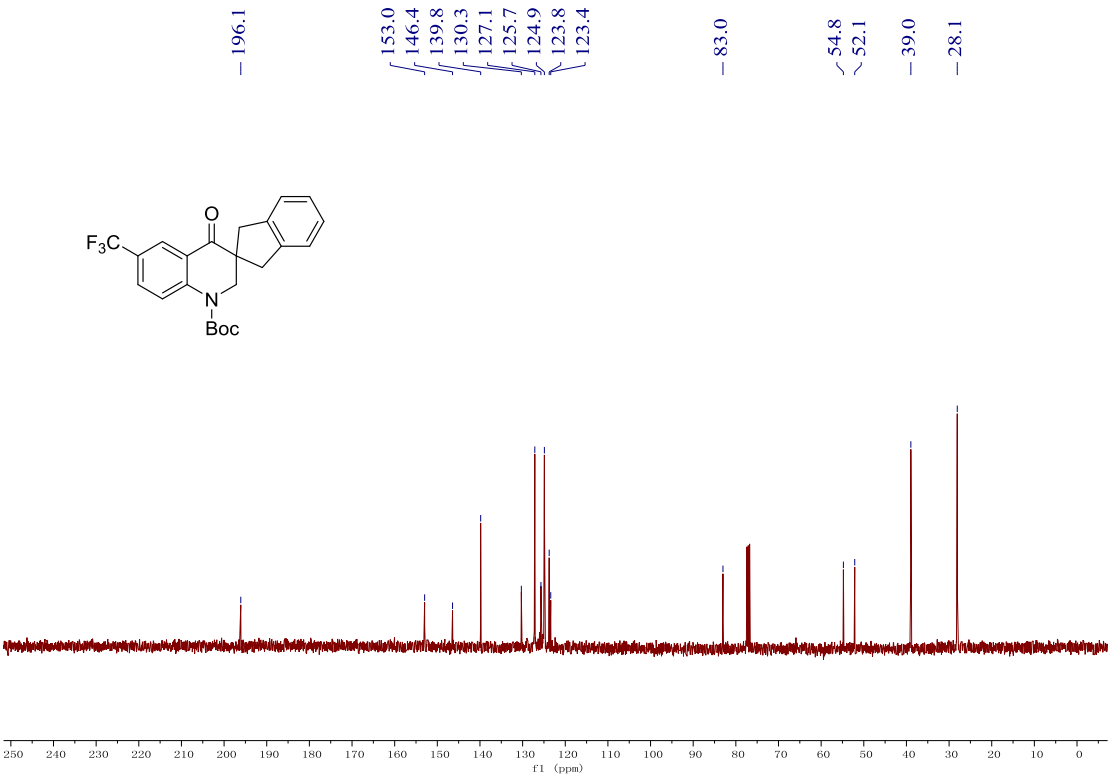
^{13}C NMR Spectrums of **4b**



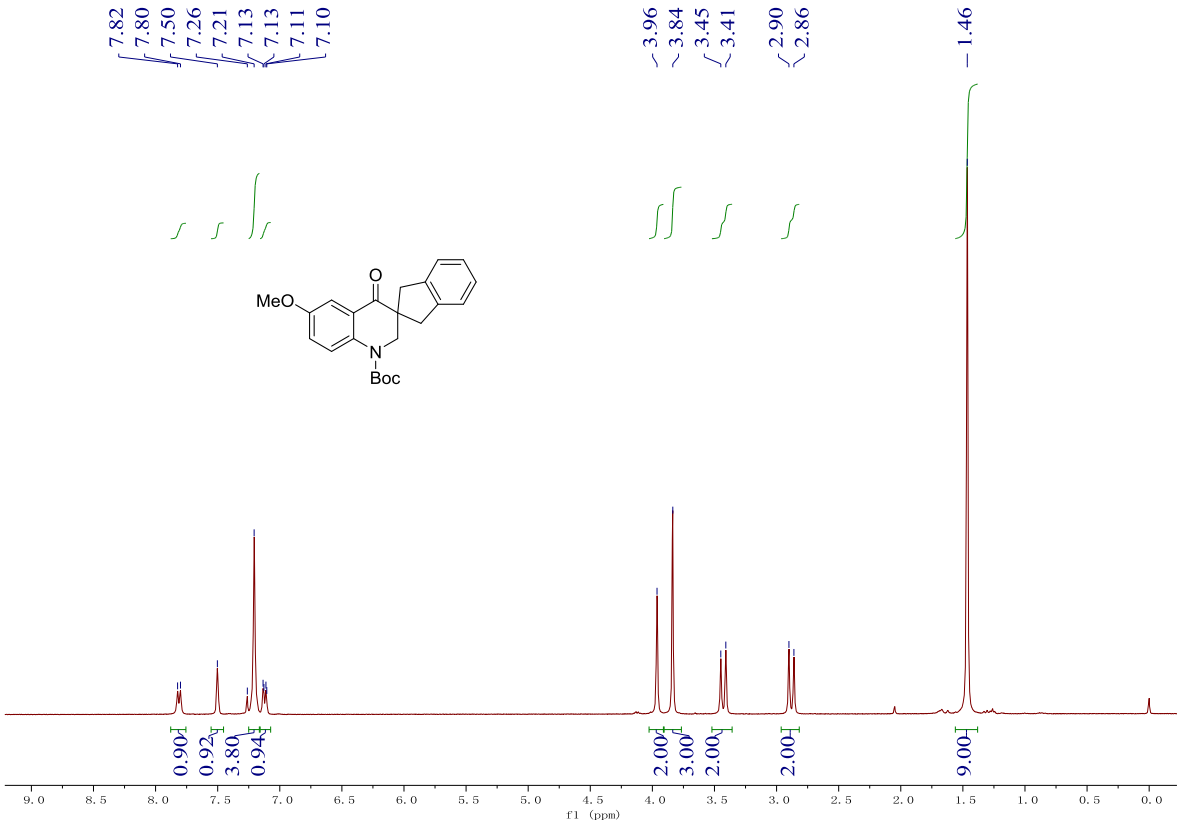
^{1}H NMR Spectrum of **4c**



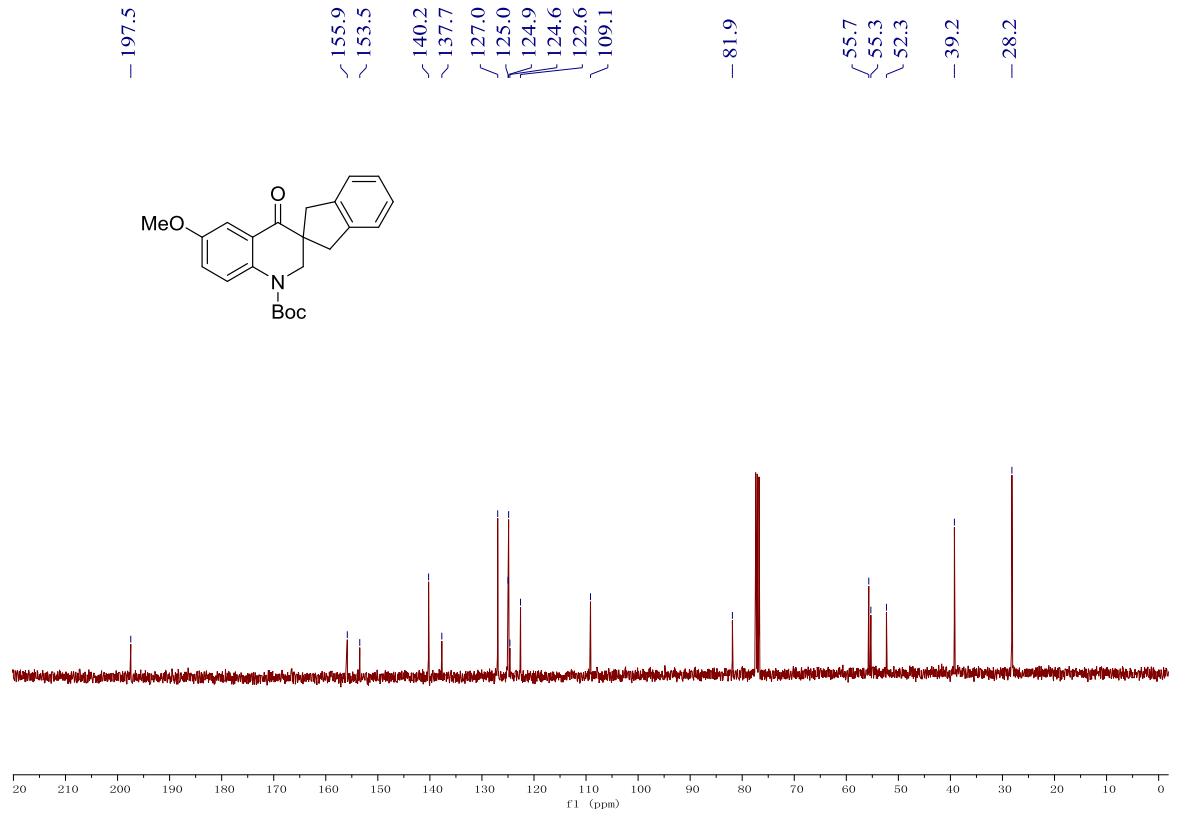
^{13}C NMR Spectrum of **4c**



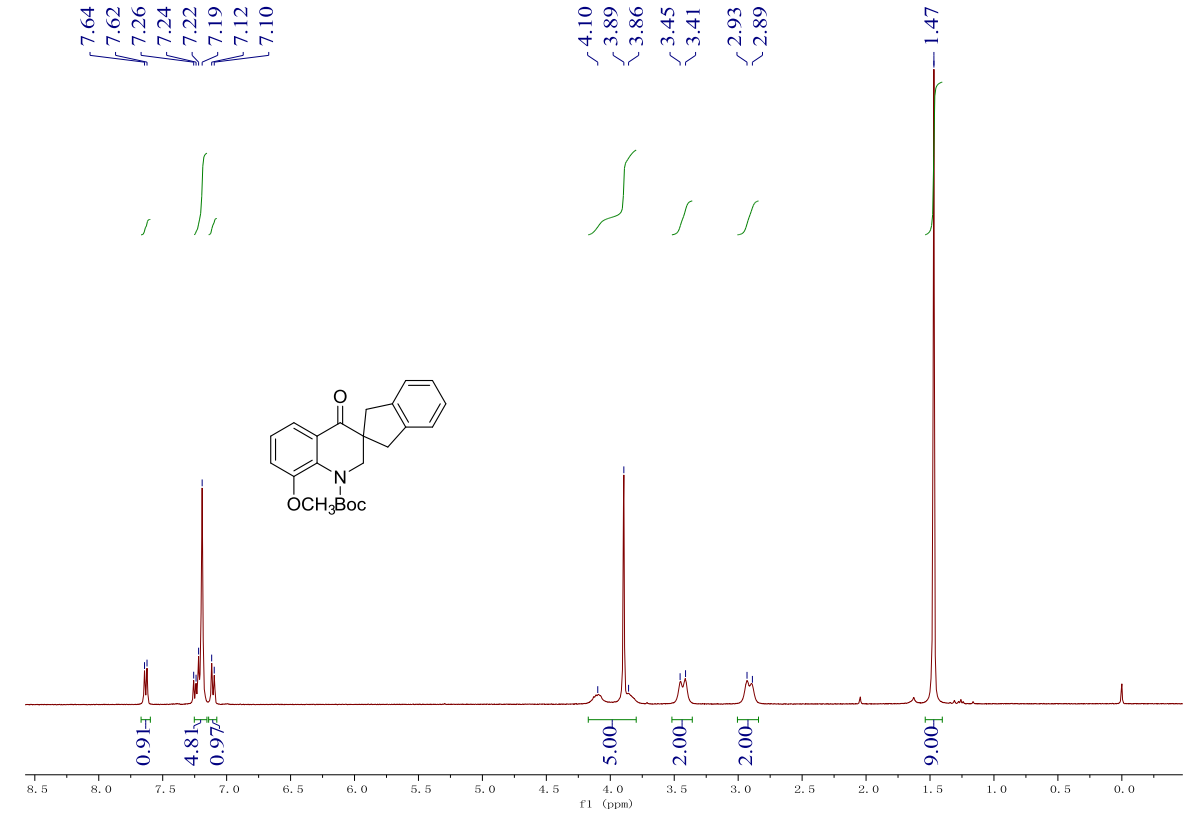
^{1}H NMR Spectrum of **4d**



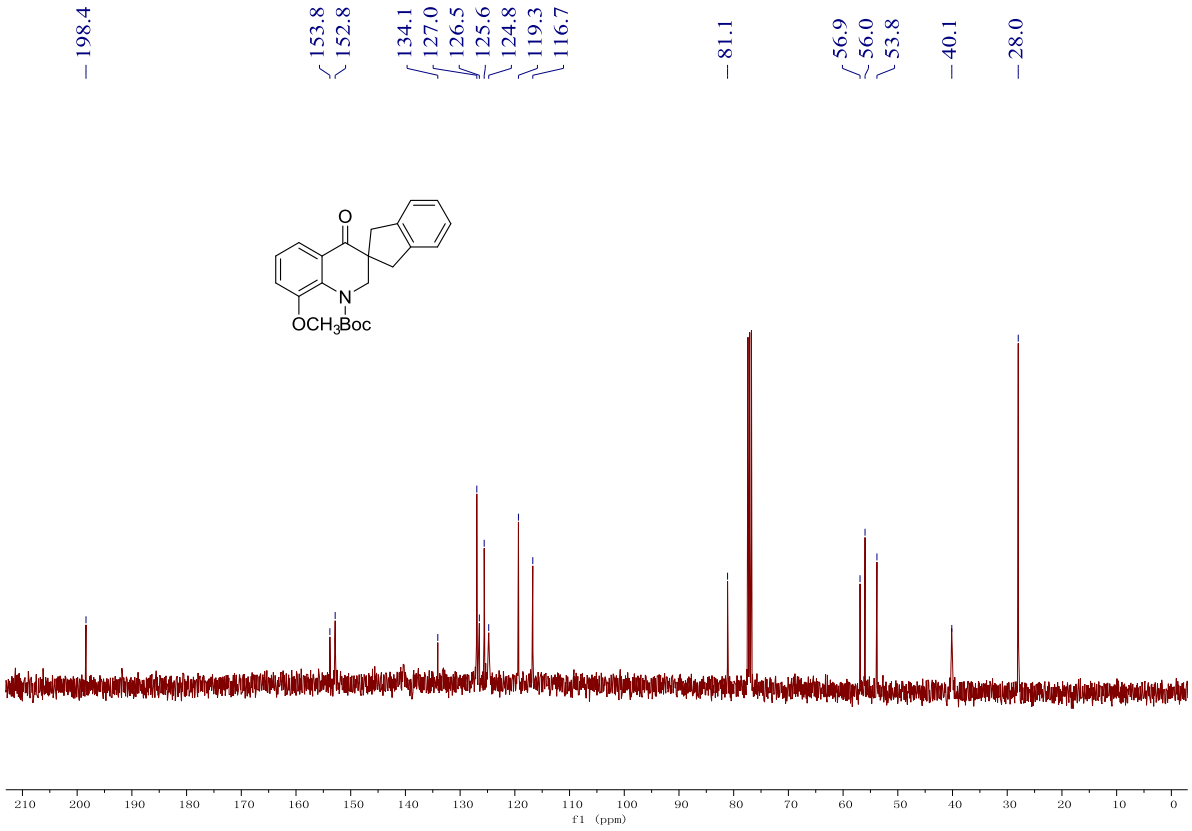
^{13}C NMR Spectrum of **4d**



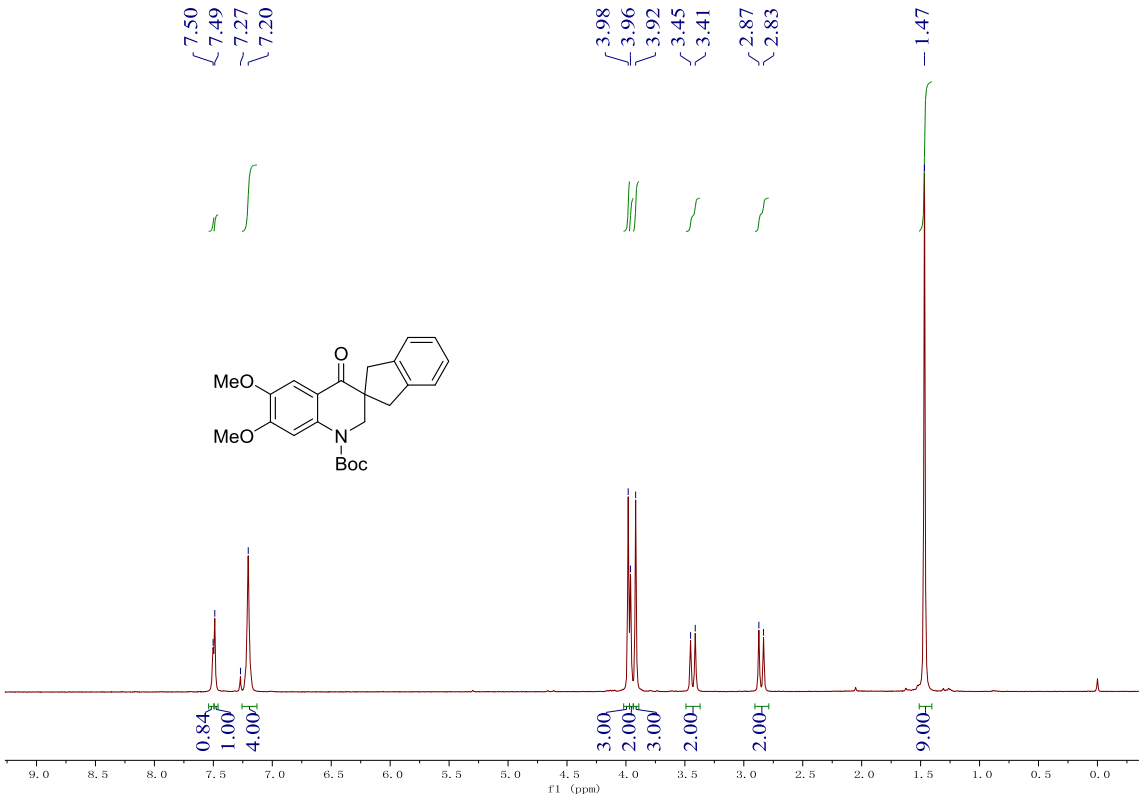
^{1}H NMR Spectrum of **4e**



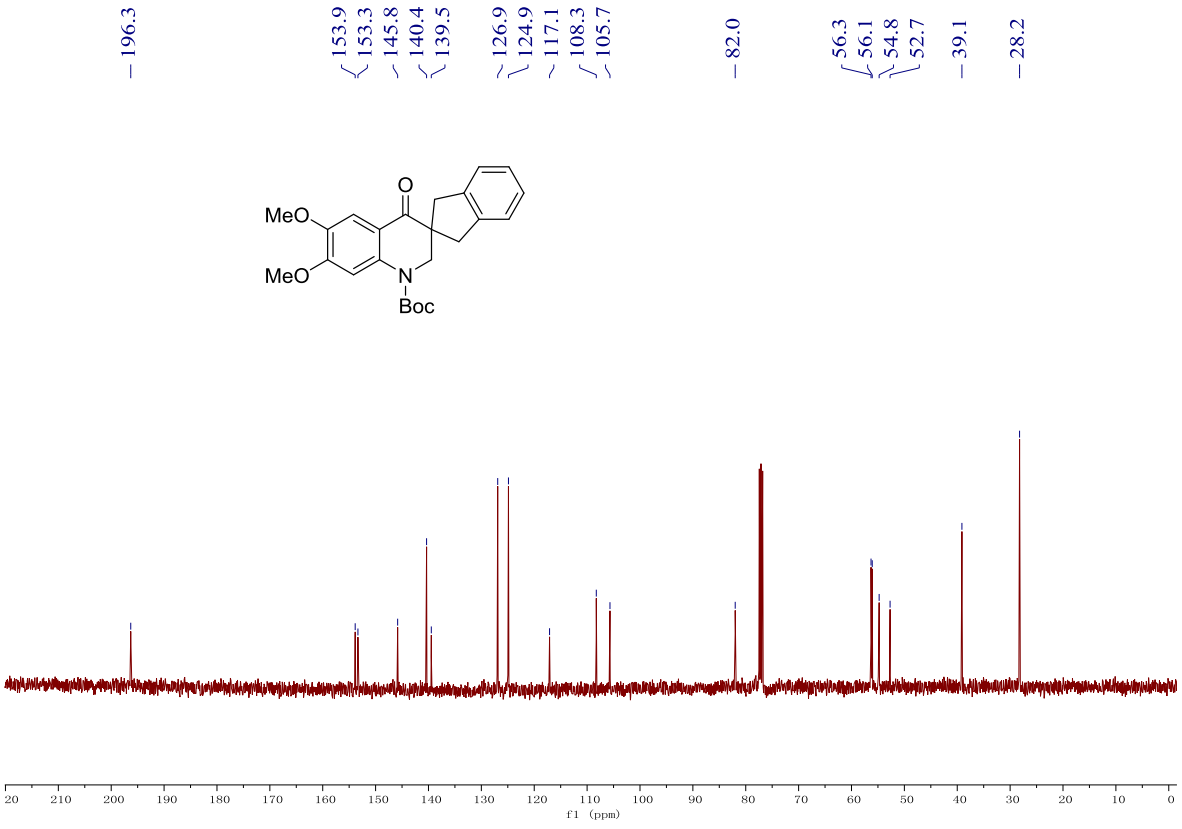
and ^{13}C NMR Spectrums of **4e**



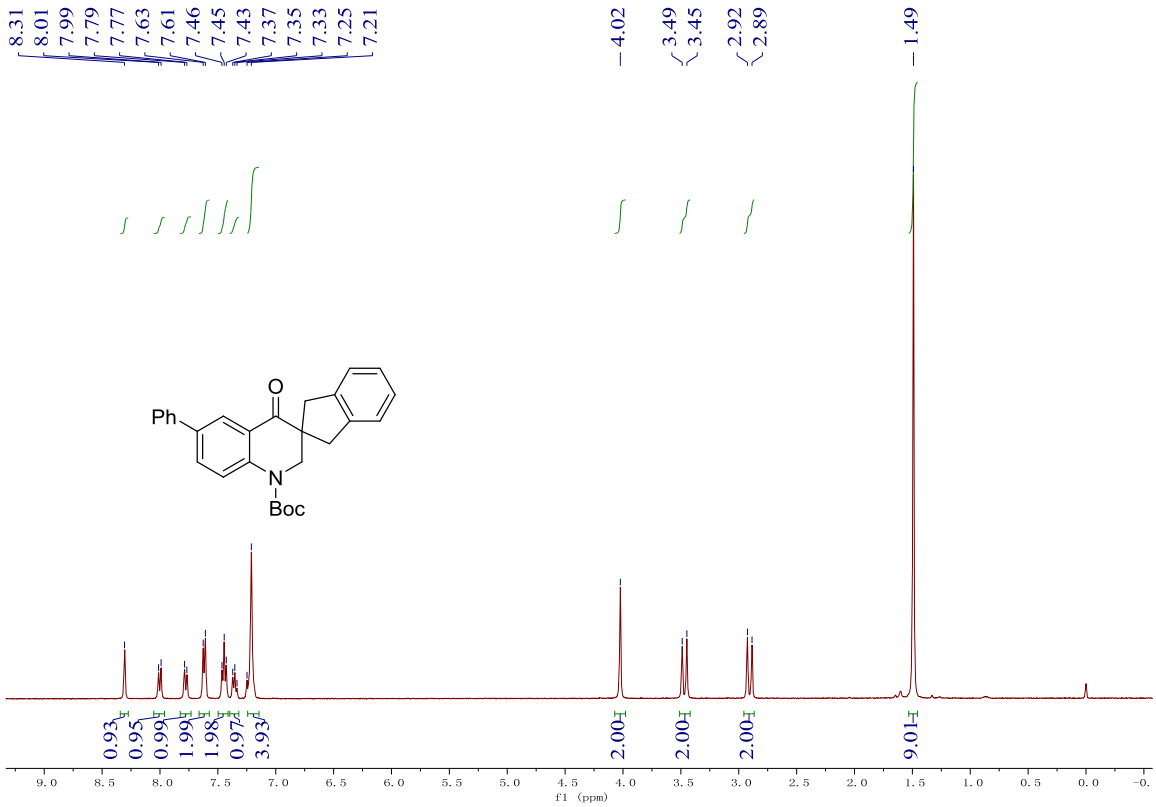
^{1}H NMR Spectrum of **4f**



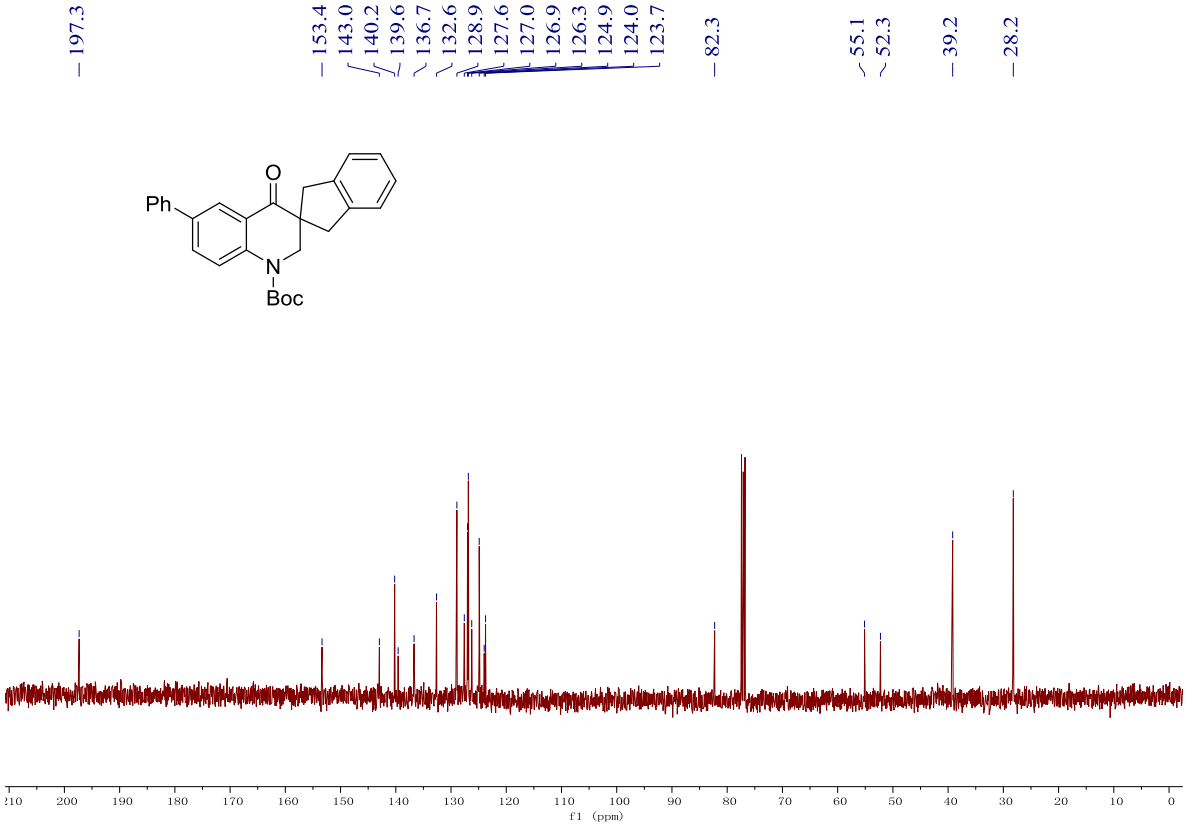
^{13}C NMR Spectrum of **4f**



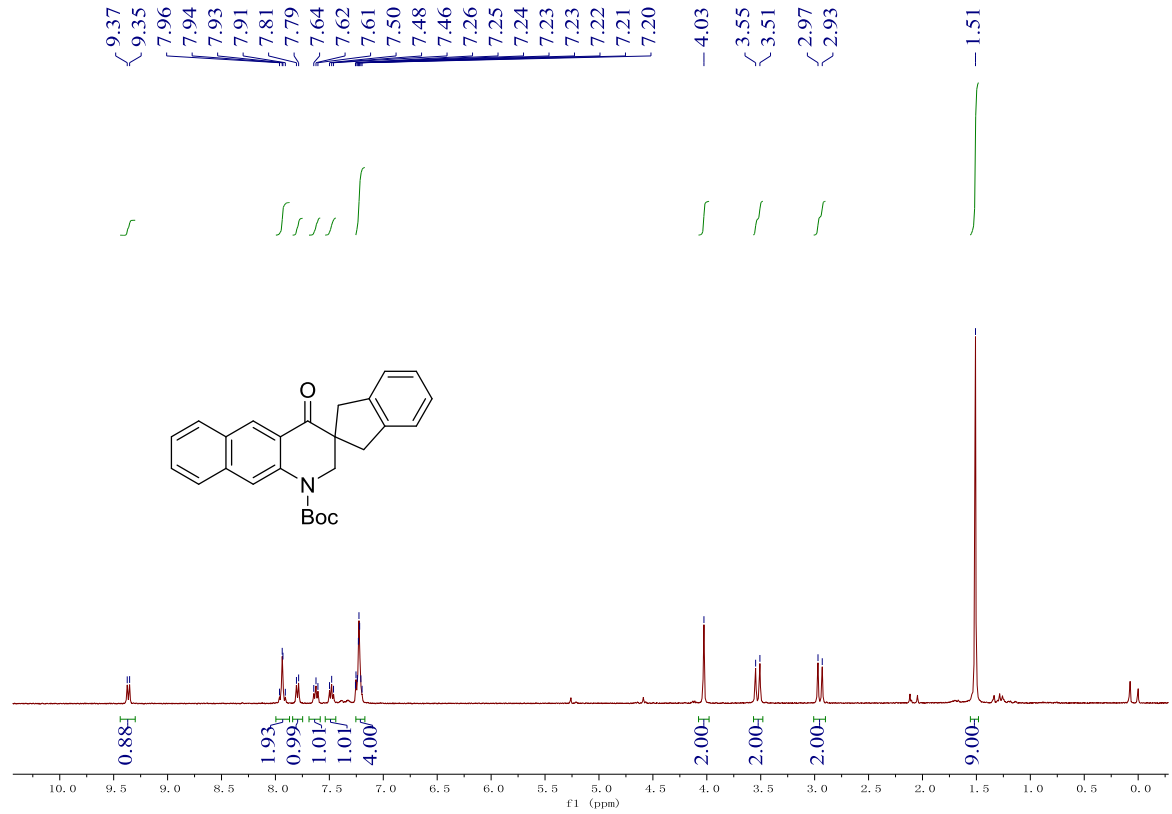
^{1}H NMR Spectrum of **4g**



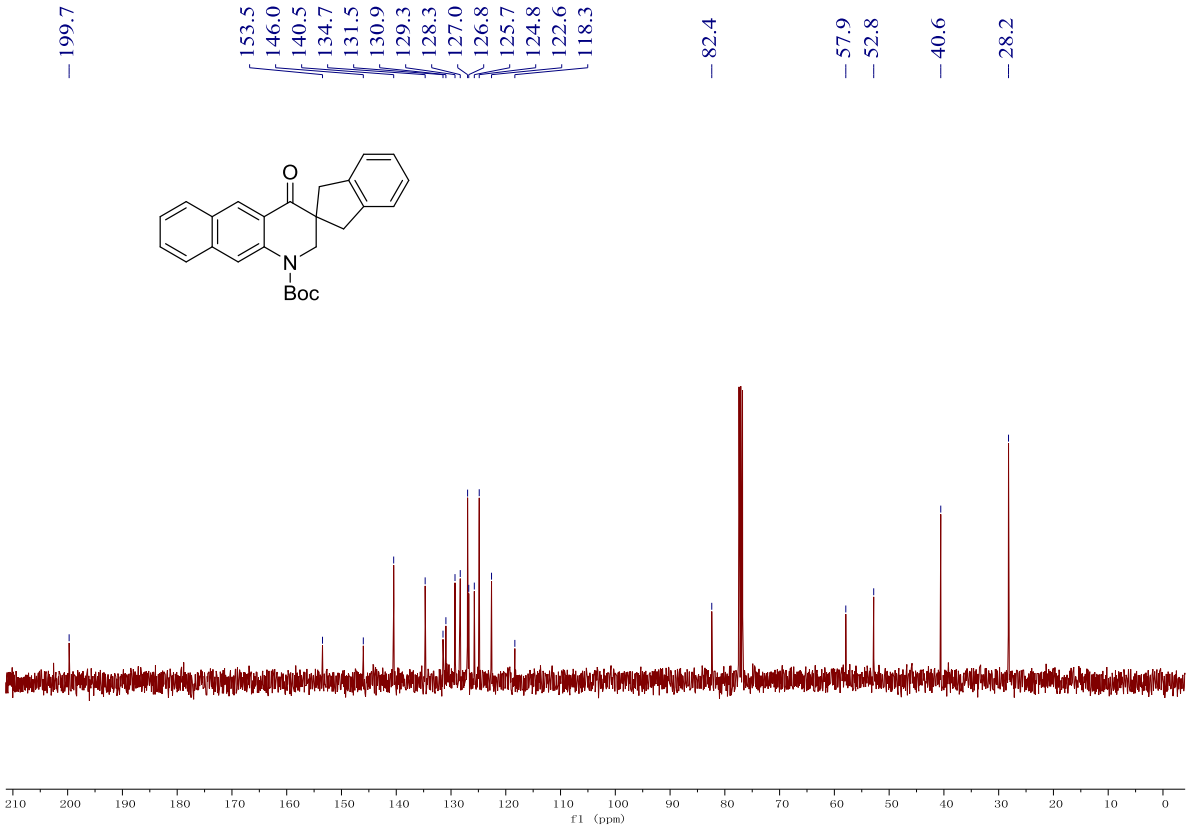
^{13}C NMR Spectrum of **4g**



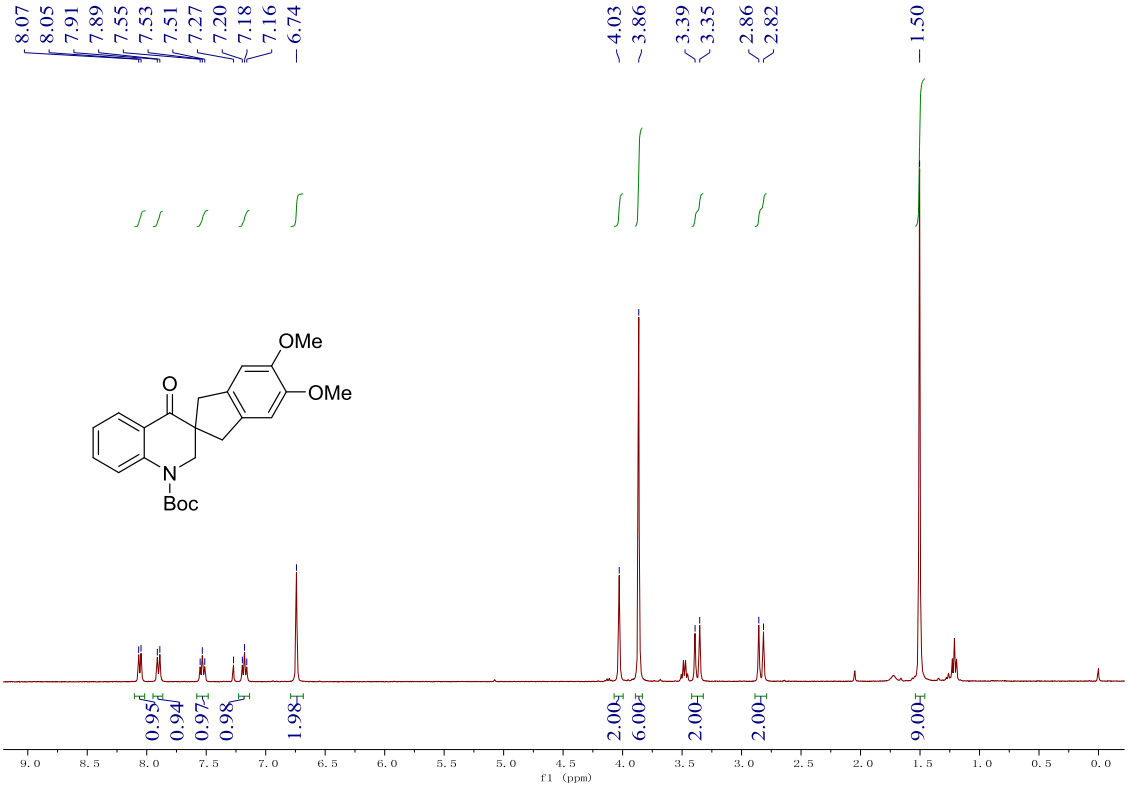
^{1}H NMR Spectrum of **4h**



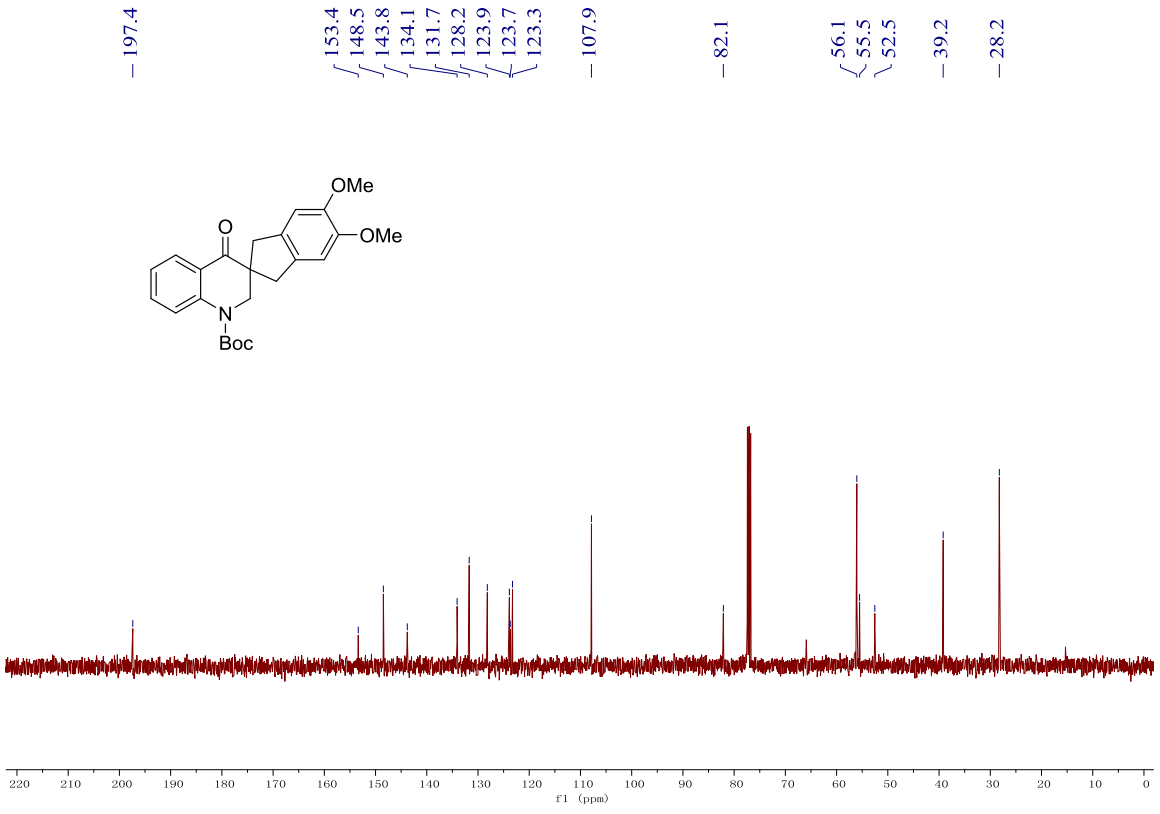
^{13}C NMR Spectrum of **4h**



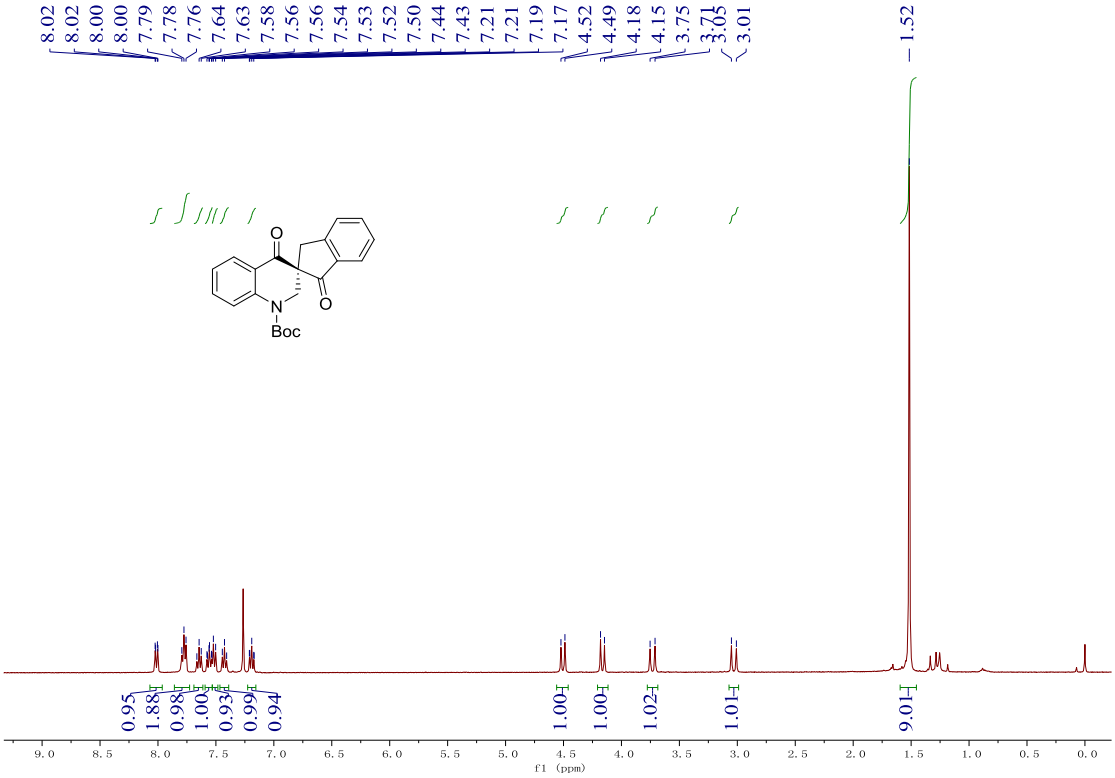
^{1}H NMR Spectrum of **4i**



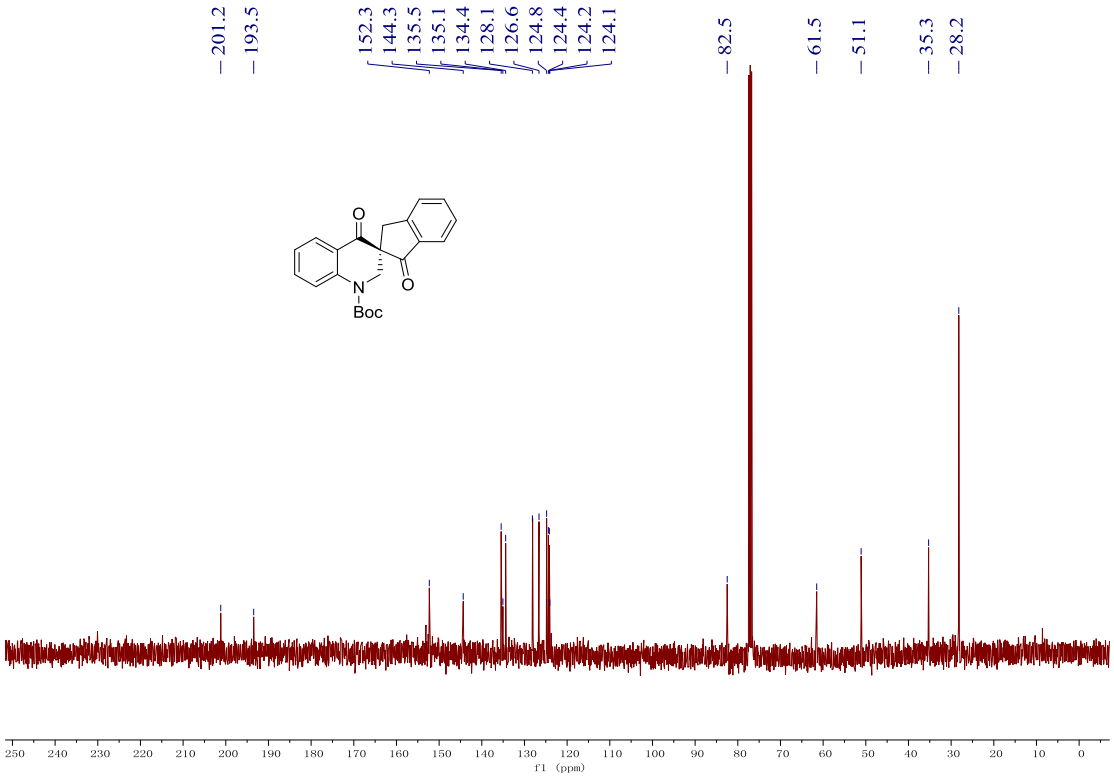
^{13}C NMR Spectrum of **4i**



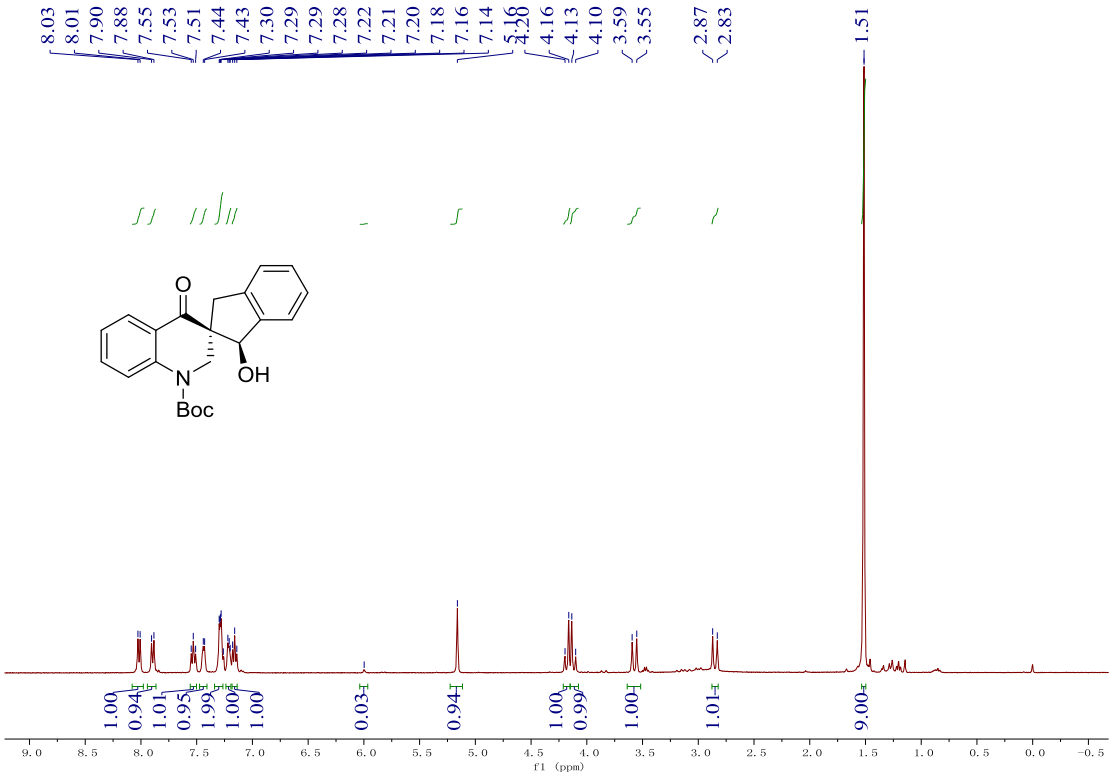
^{1}H NMR Spectrum of **5a**



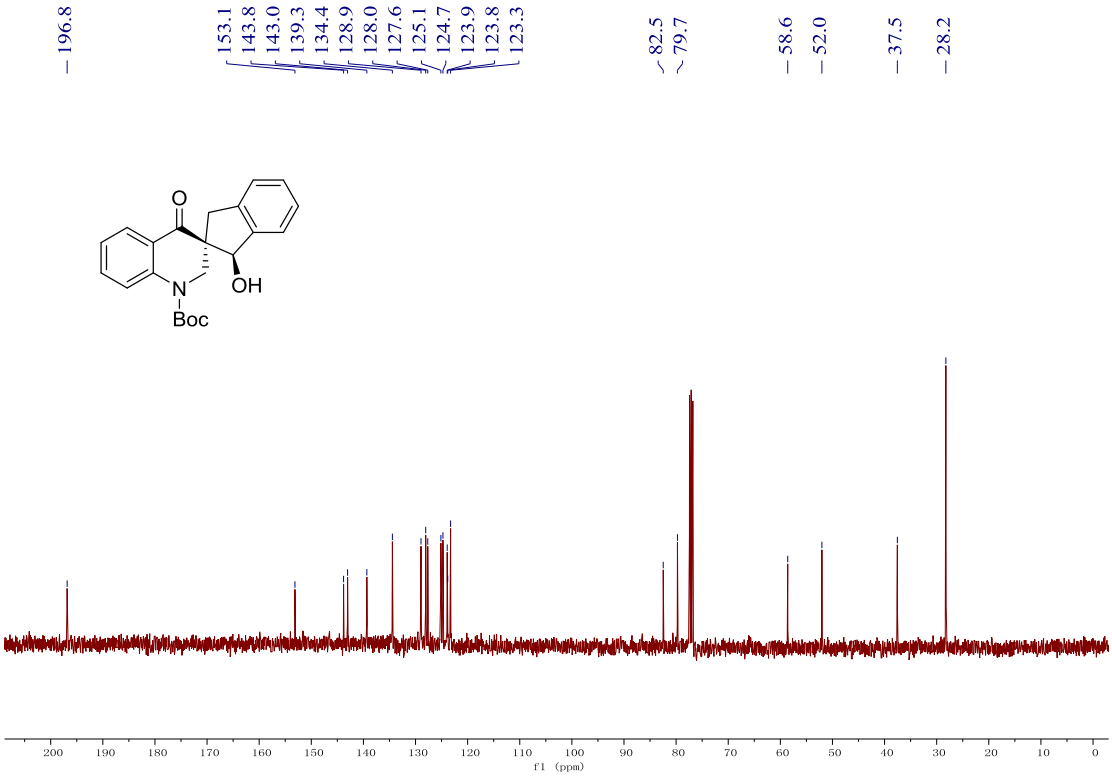
^{13}C NMR Spectrum of **5a**



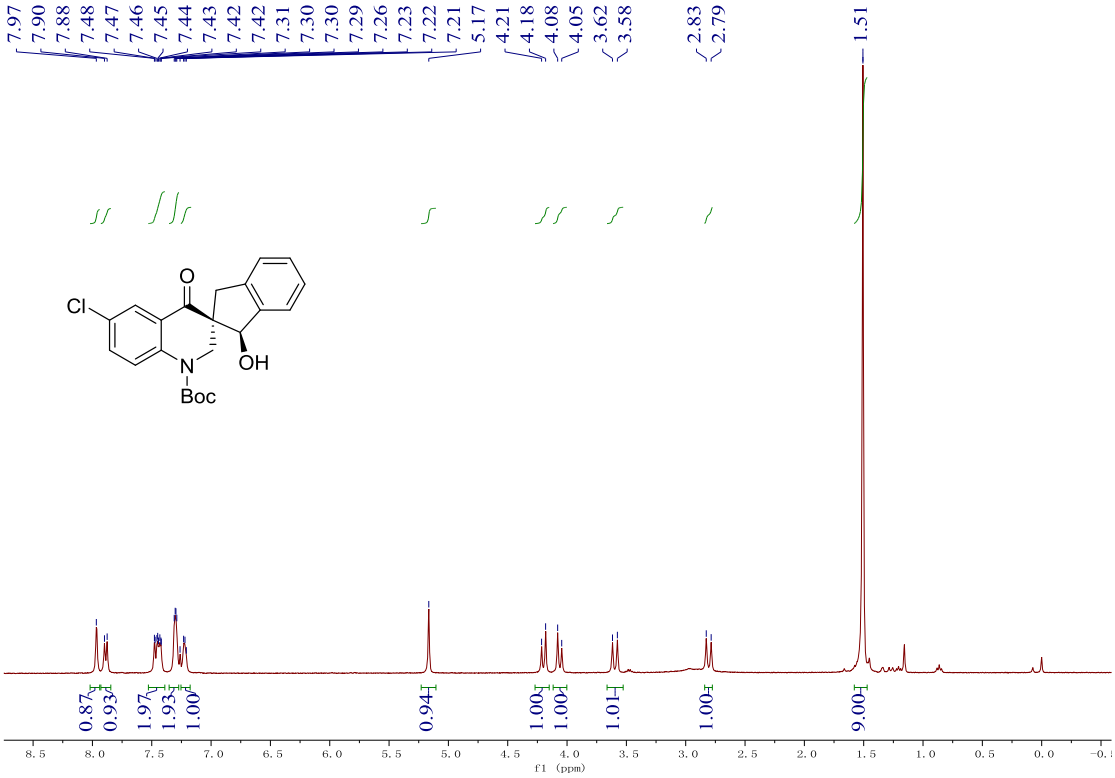
^{1}H NMR Spectrum of **6a**



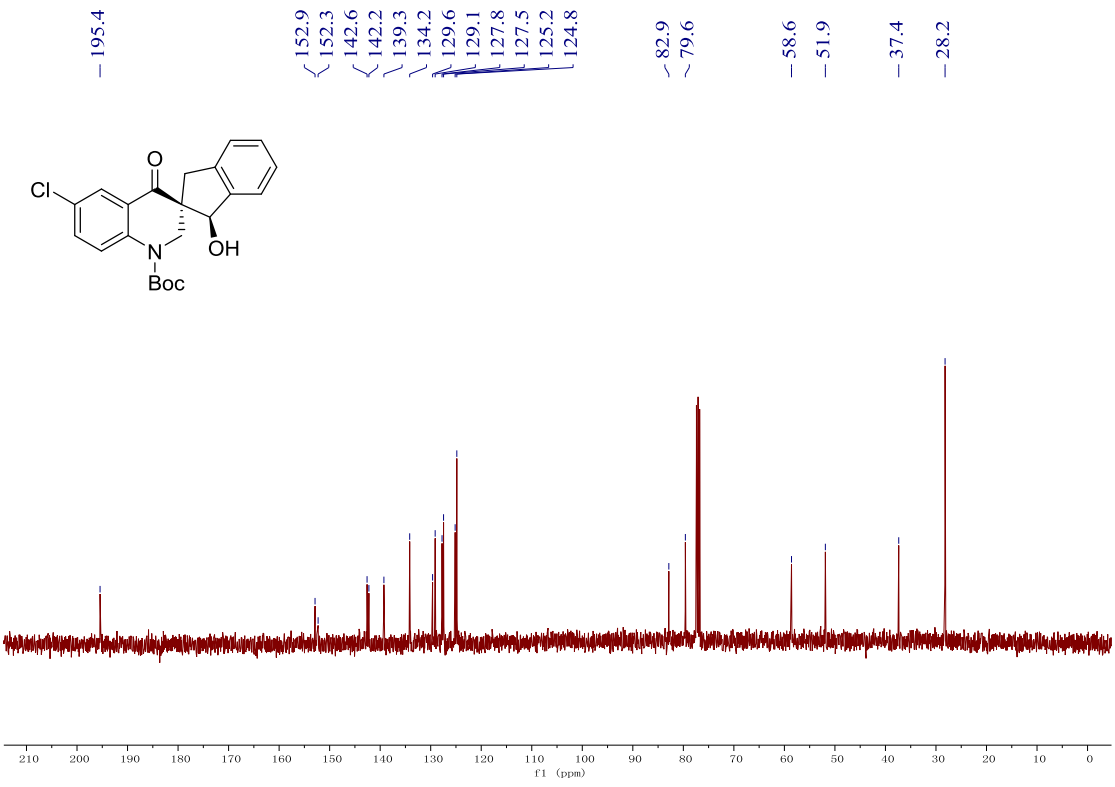
^{13}C NMR Spectrum of **6a**



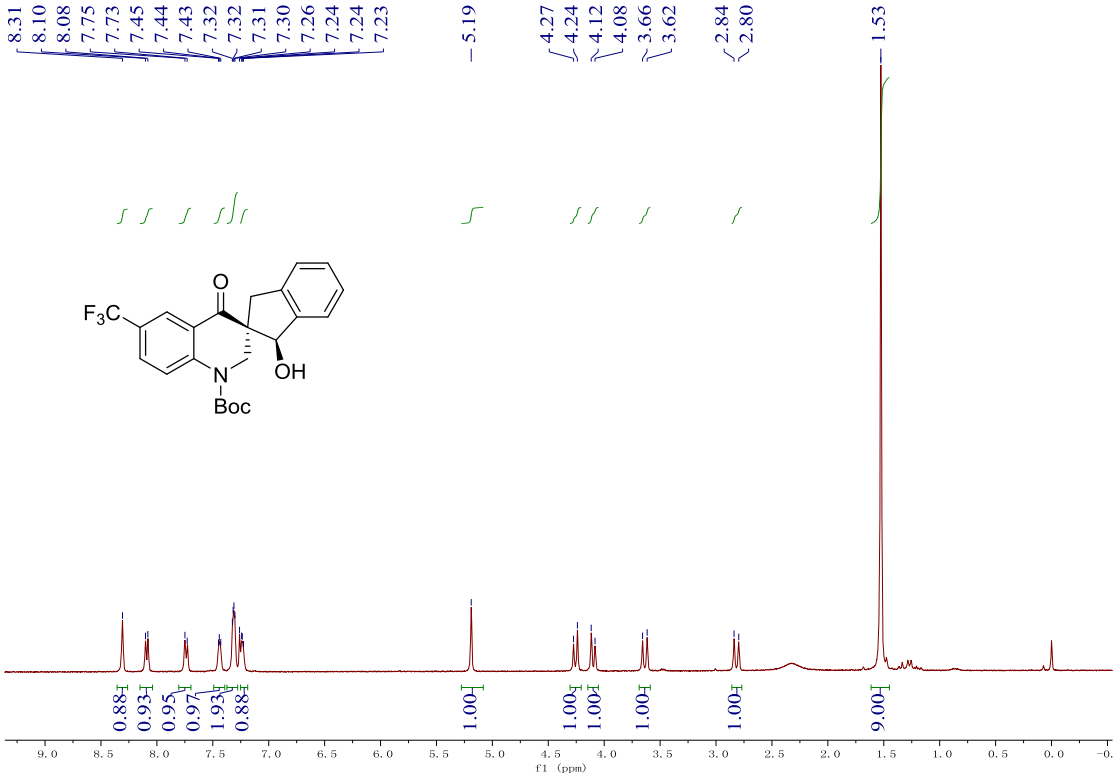
^{1}H NMR Spectrum of **6b**



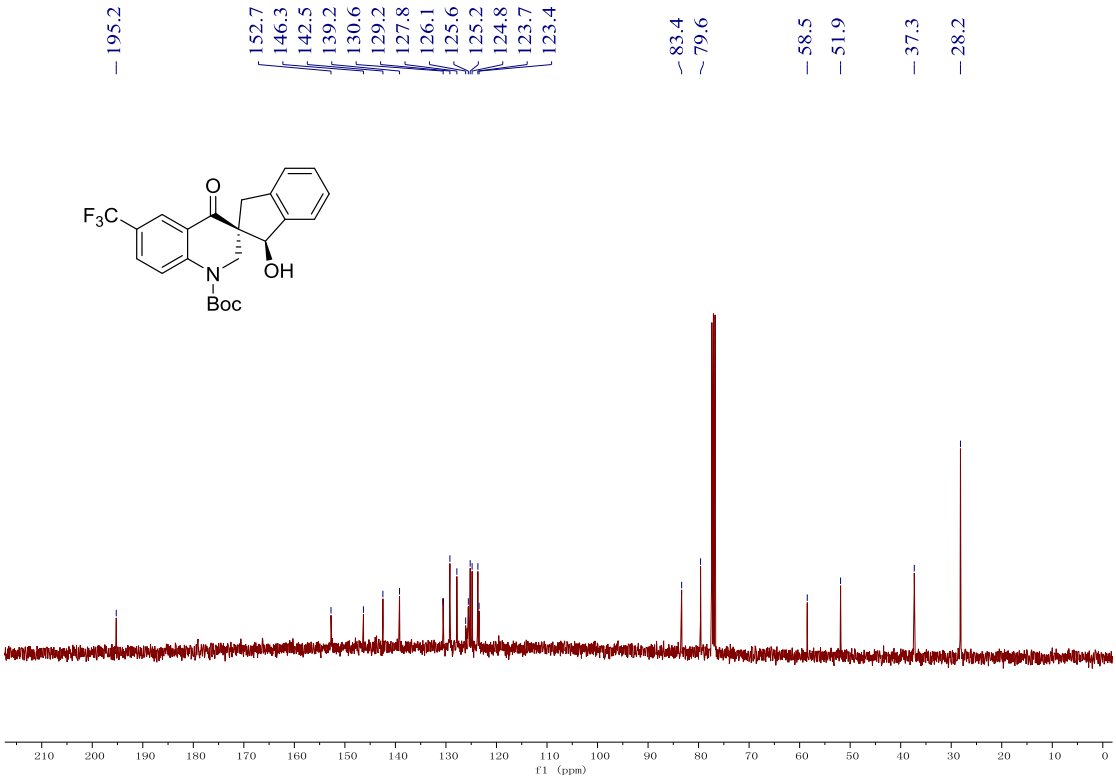
^{13}C NMR Spectrum of **6b**



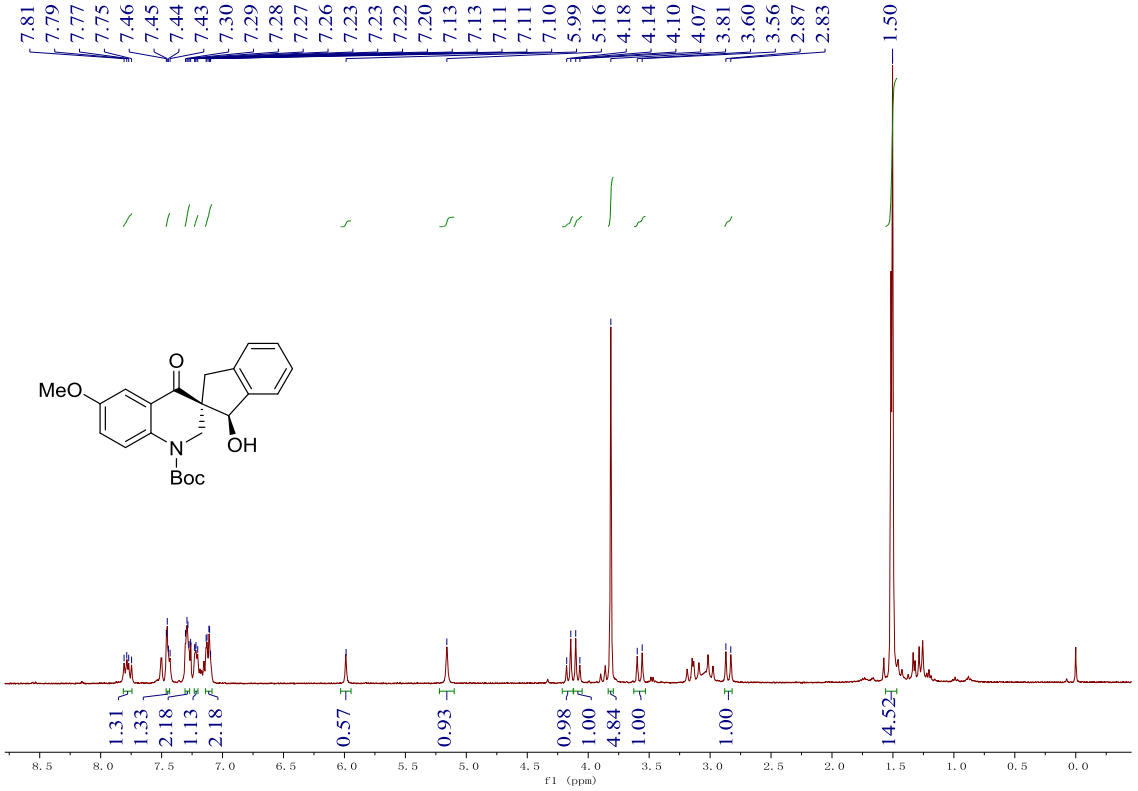
^{1}H NMR Spectrum of **6c**



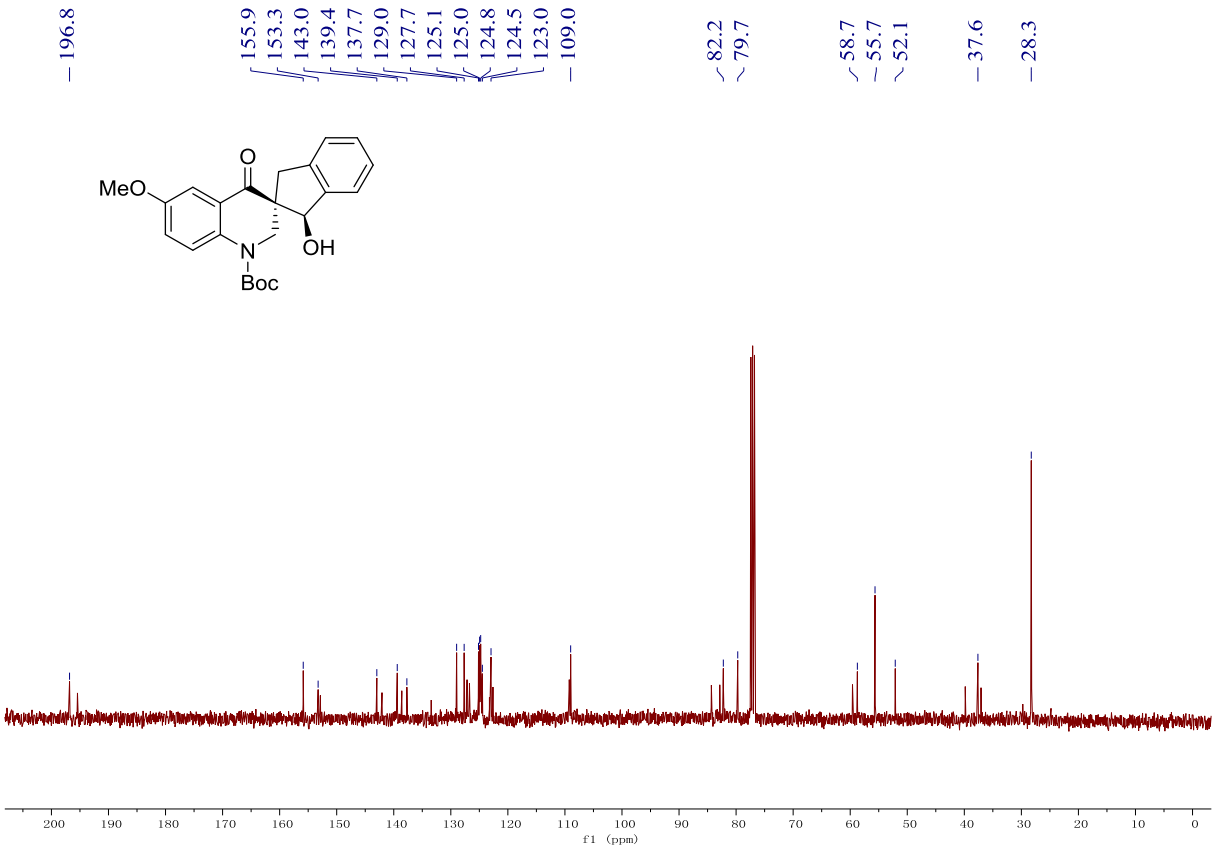
^{13}C NMR Spectrum of **6c**



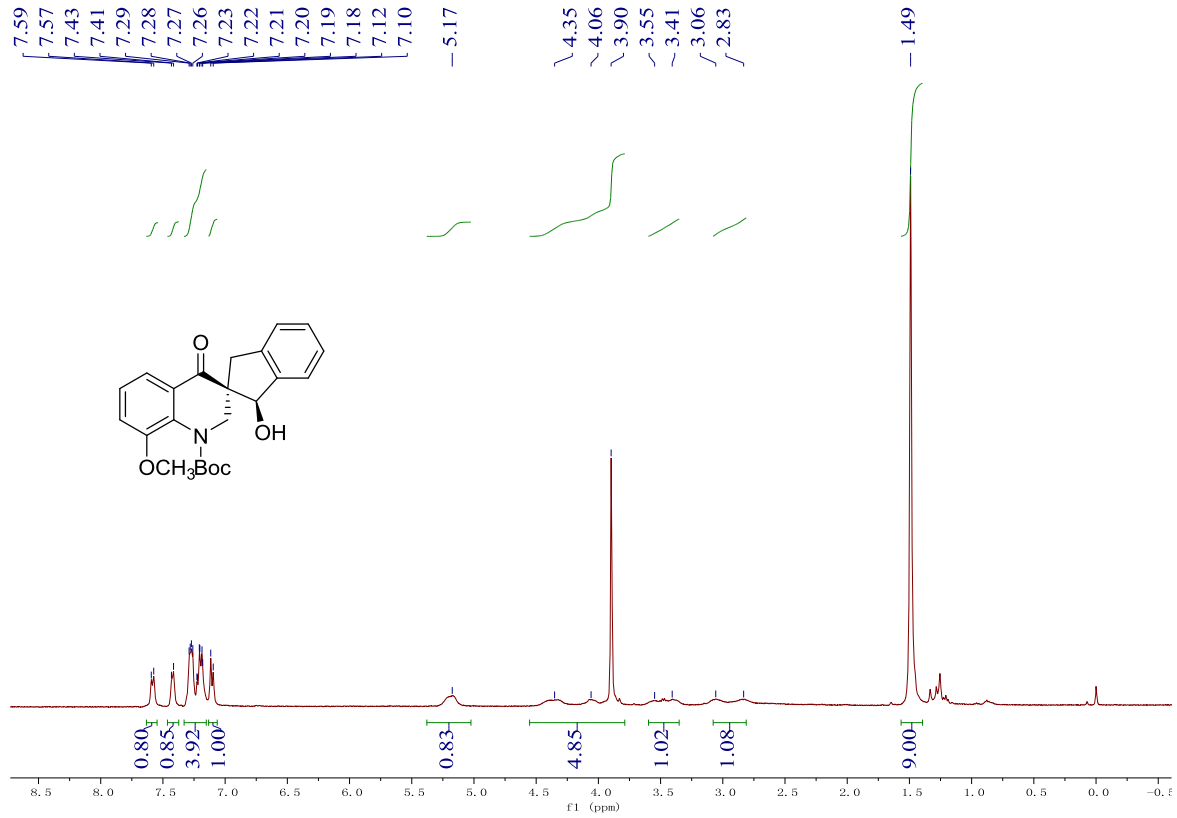
^{1}H NMR Spectrum of **6d**



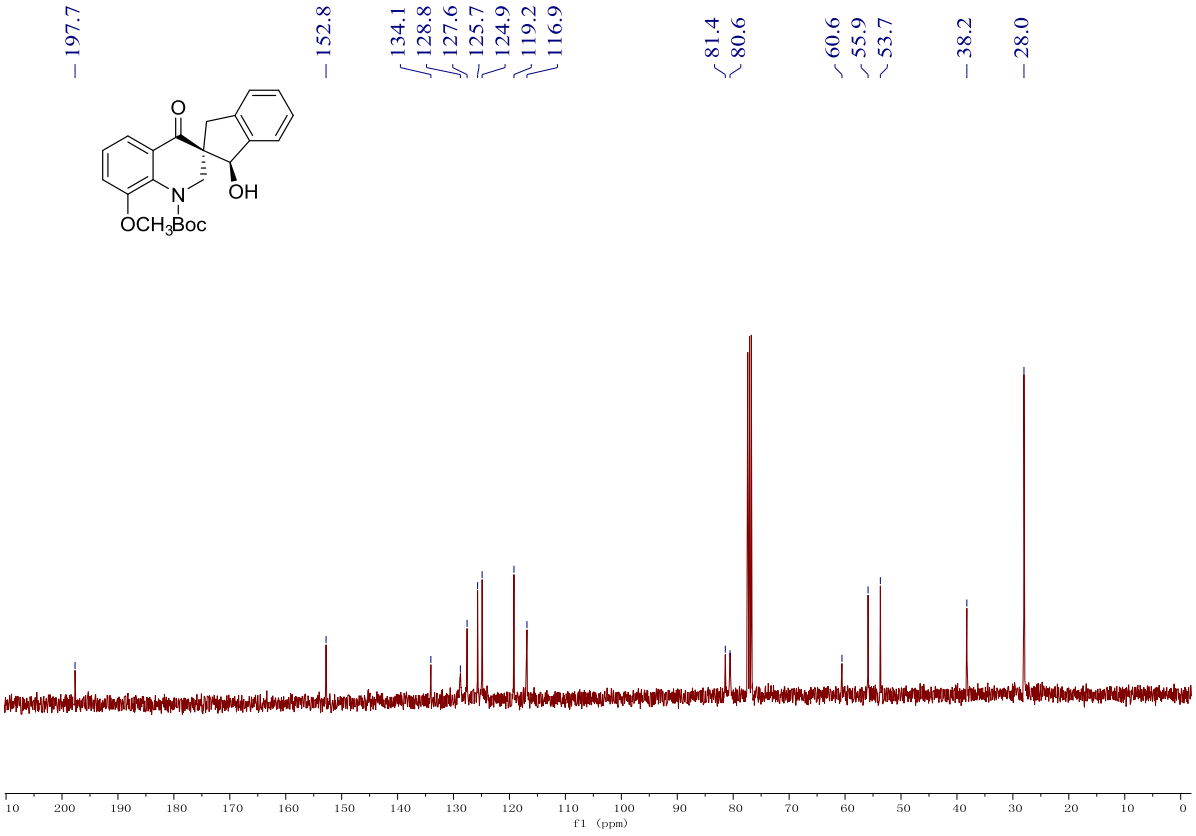
^{13}C NMR Spectrum of **6d**



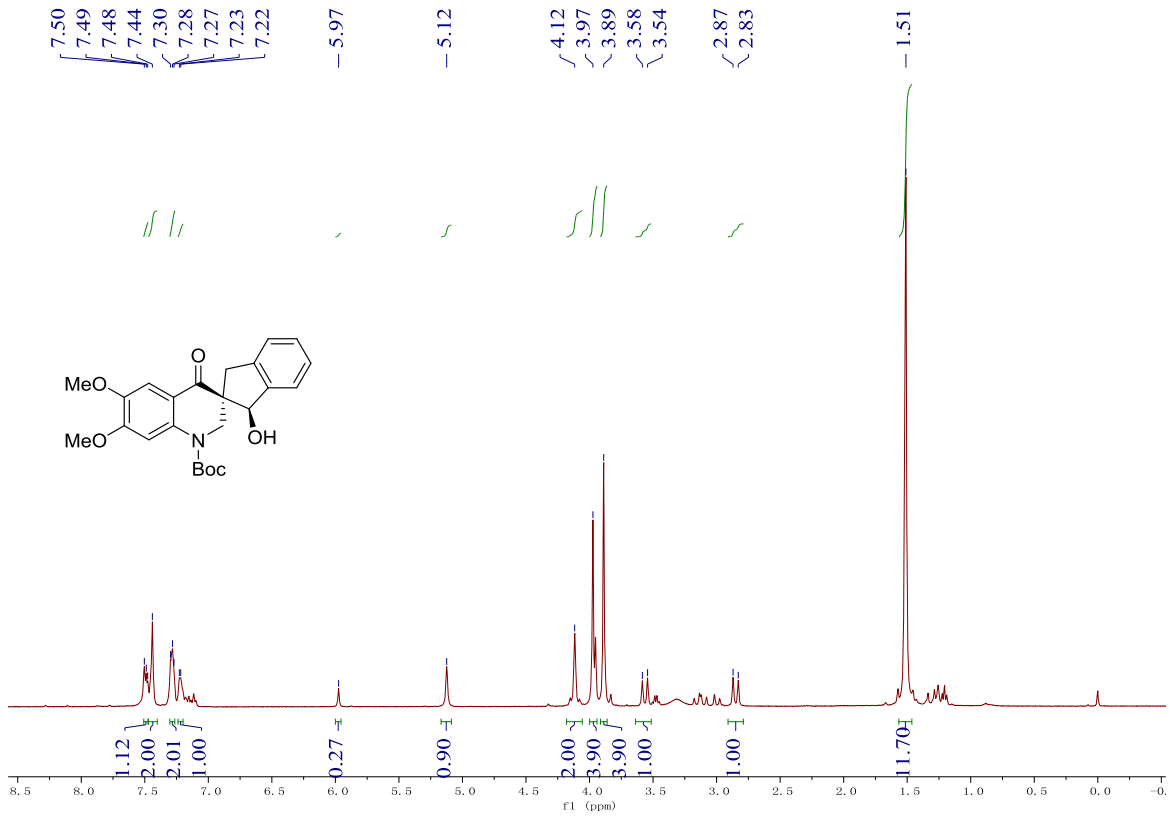
^{1}H NMR Spectrum of **6e**



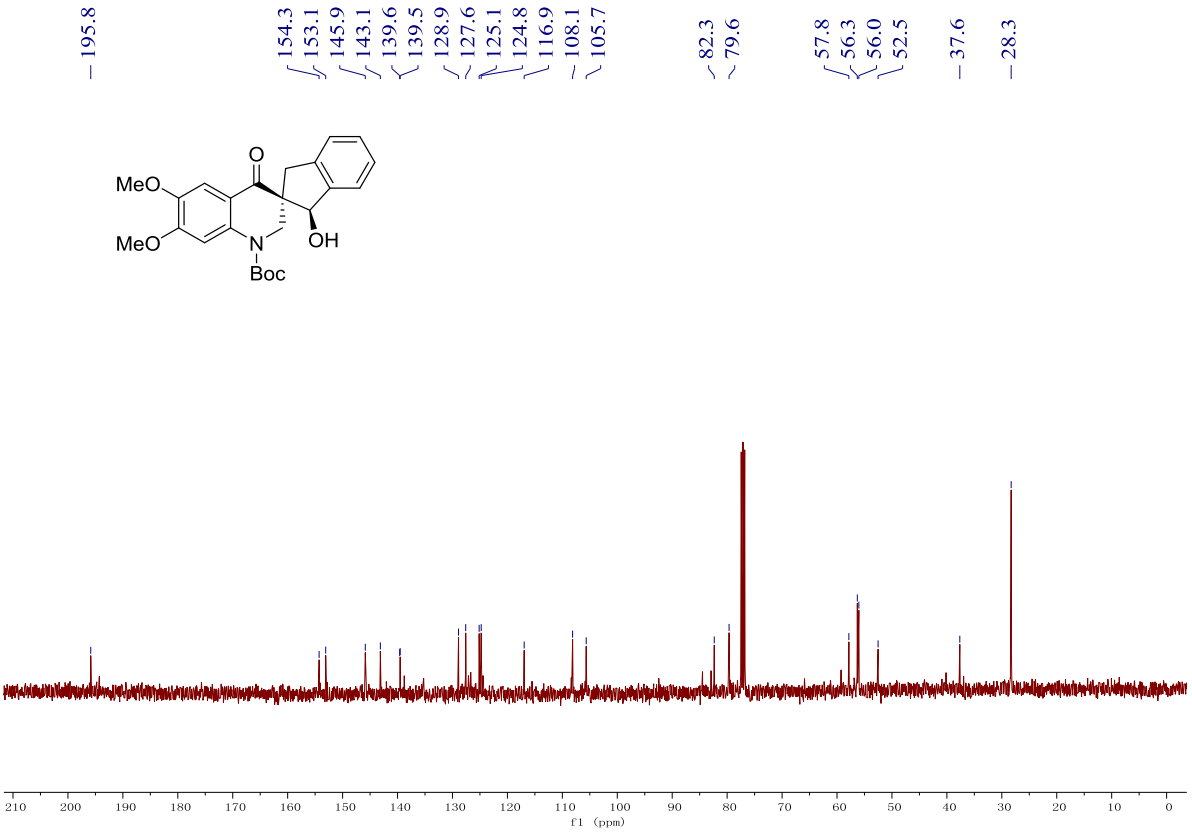
^{13}C NMR Spectrum of **6e**



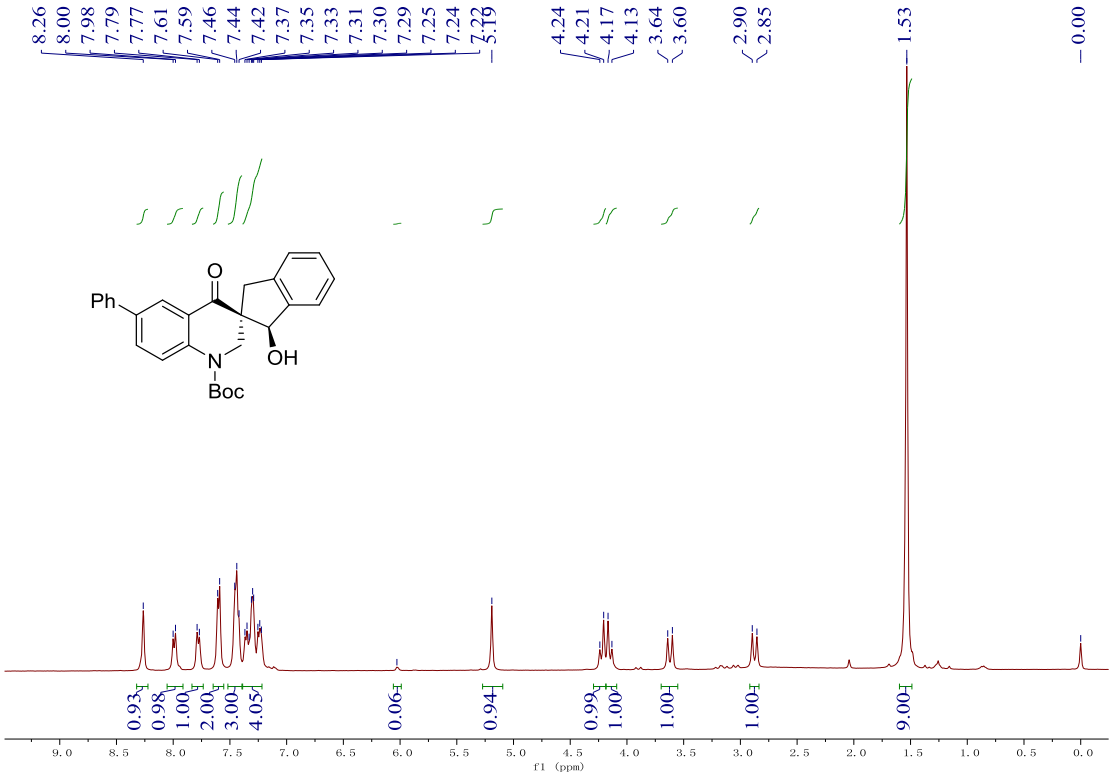
^{1}H NMR Spectrum of **6f**



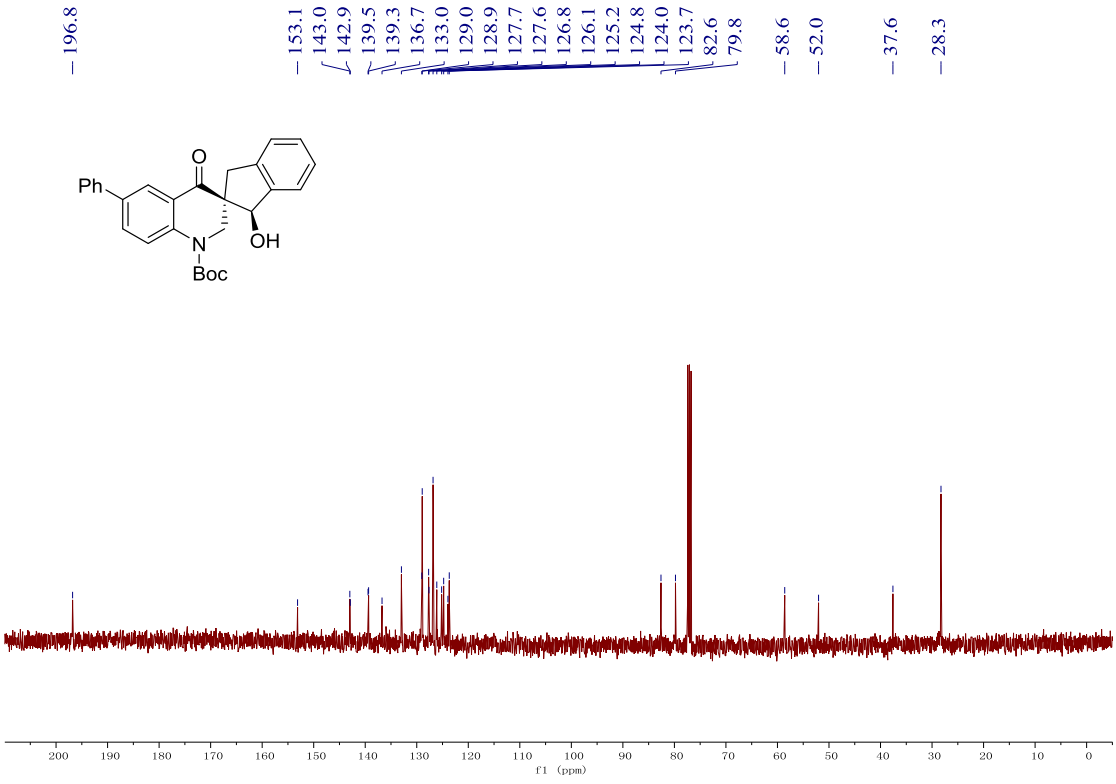
^{13}C NMR Spectrum of **6f**



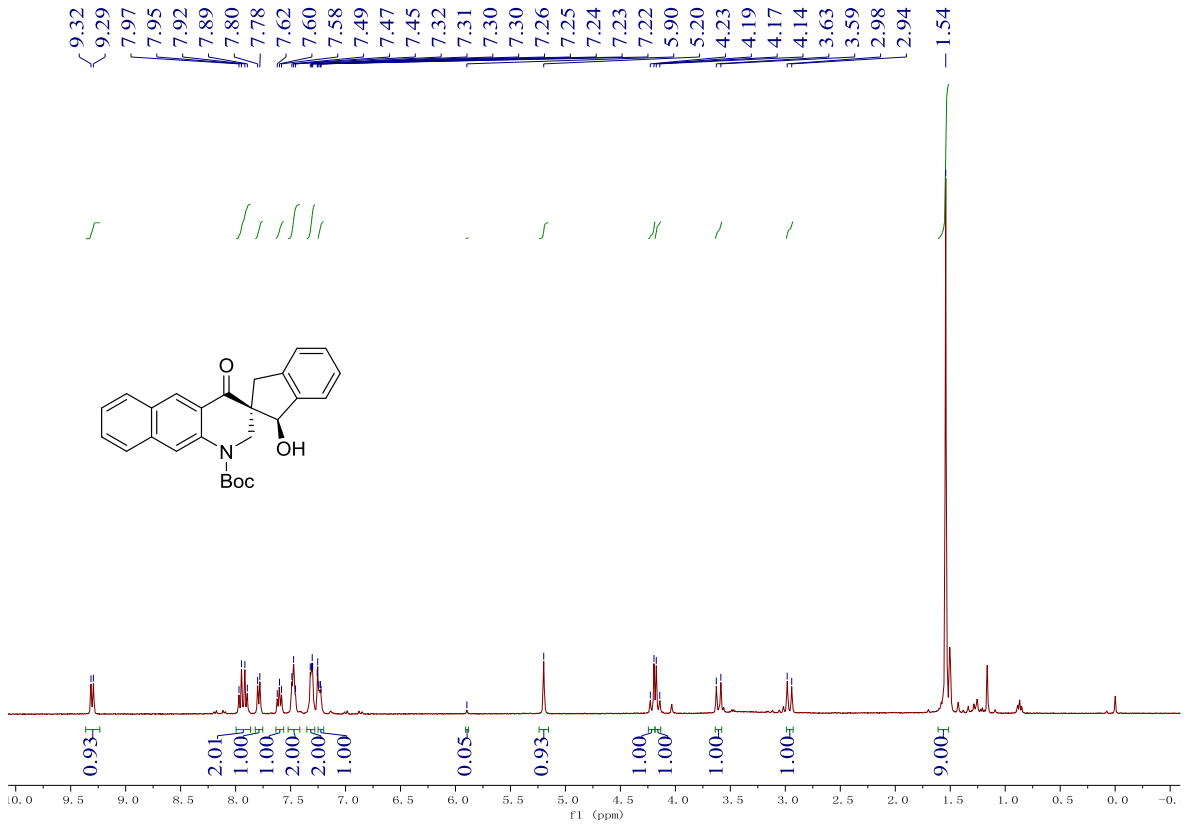
^{1}H NMR Spectrum of **6g**



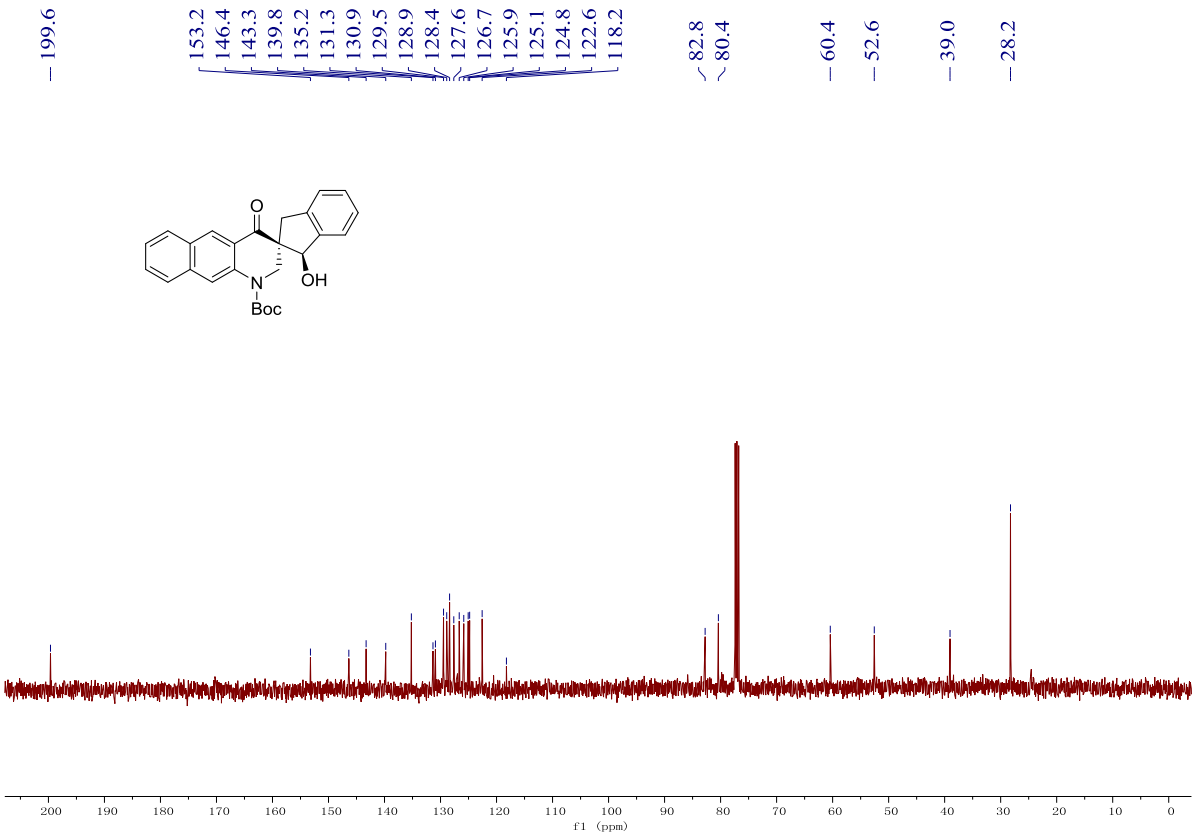
^{13}C NMR Spectrum of **6g**



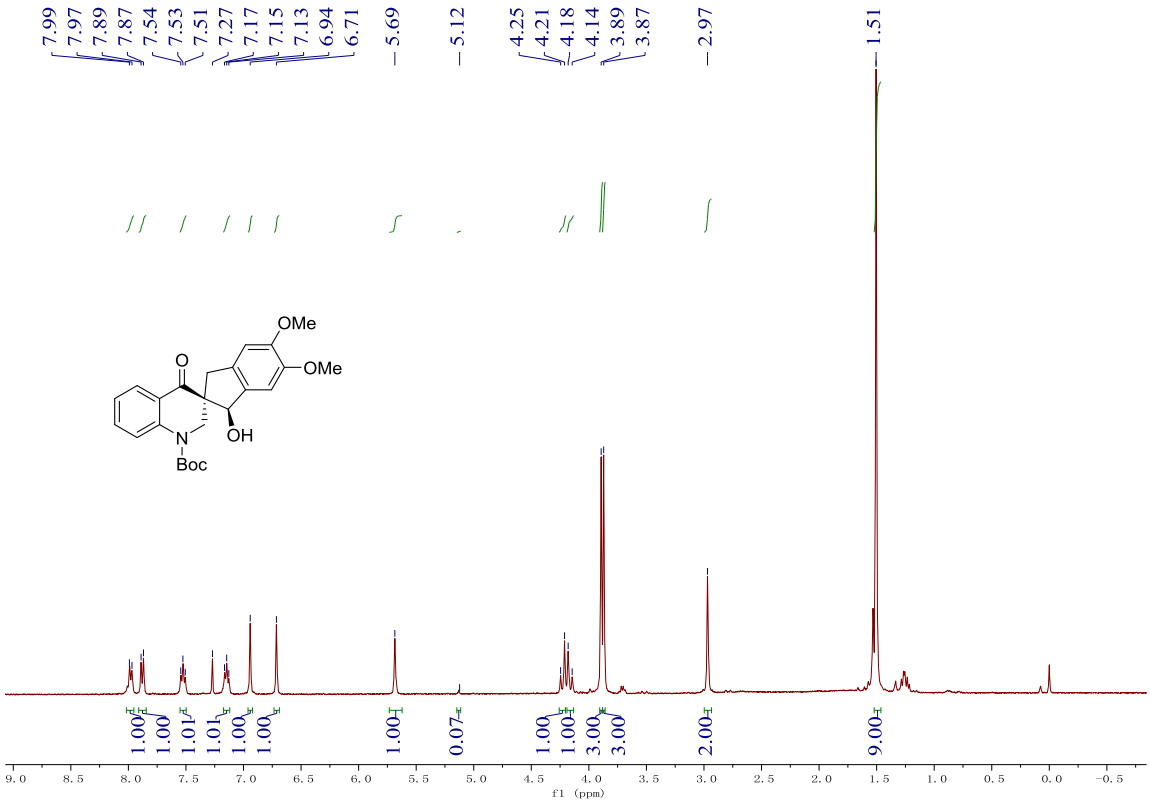
^{1}H NMR Spectrum of **6h**



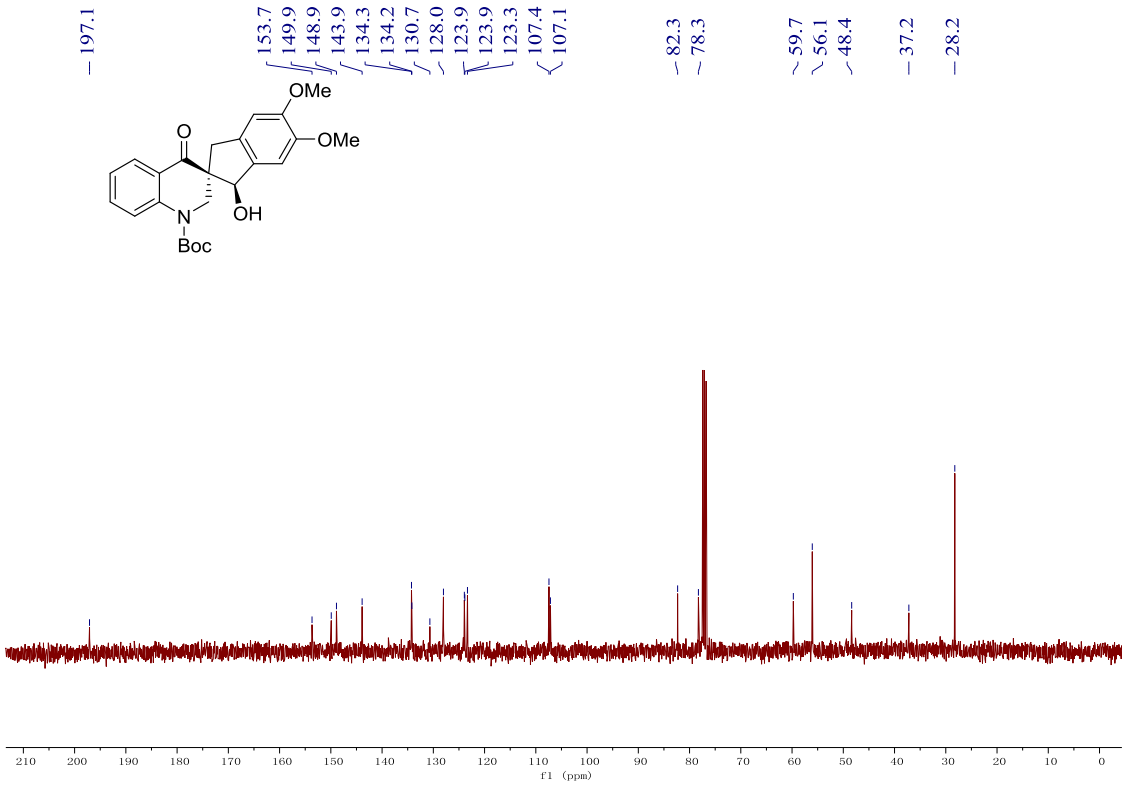
^{13}C NMR Spectrum of **6h**



^{1}H NMR Spectrum of **6i**

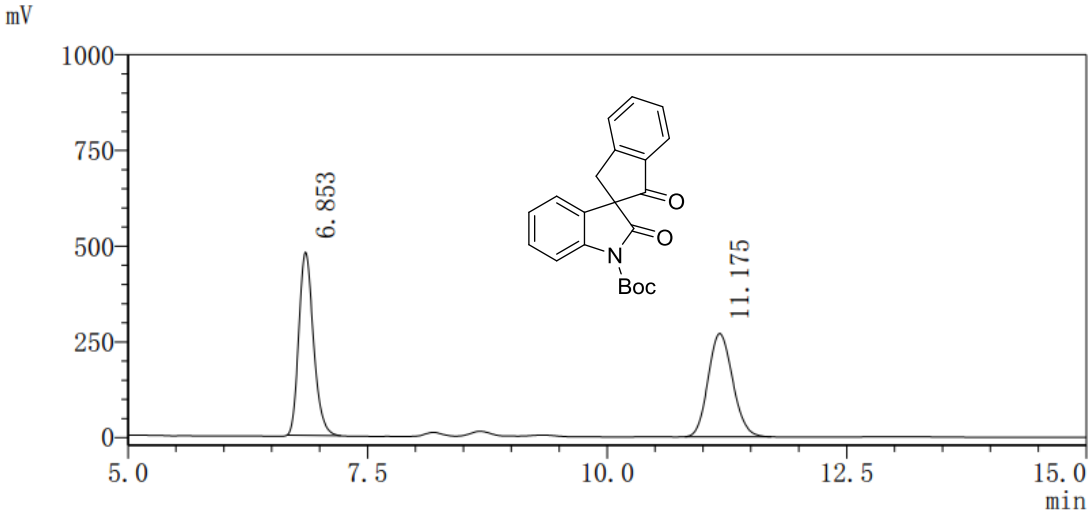


^{13}C NMR Spectrum of **6i**



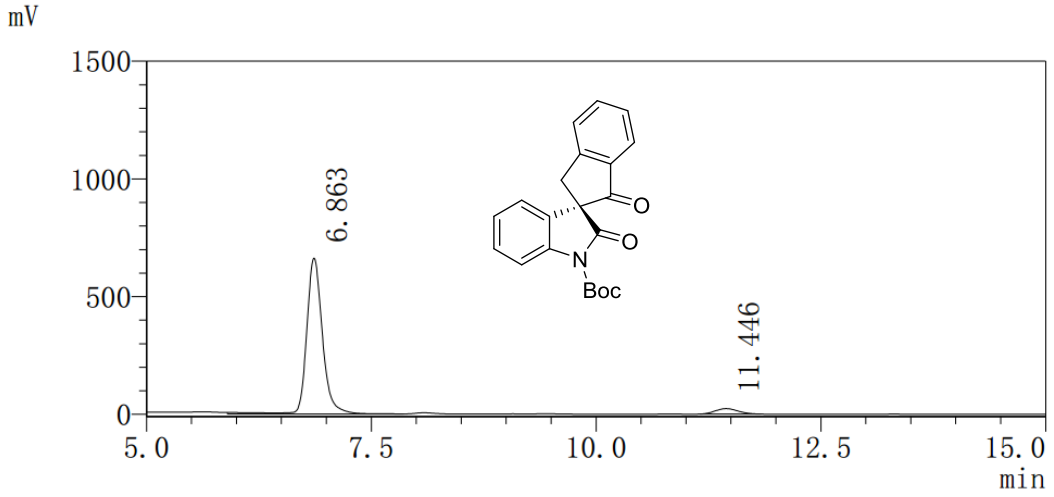
Copies of HPLC spectra of spirocyclic products

Racemic **2a**



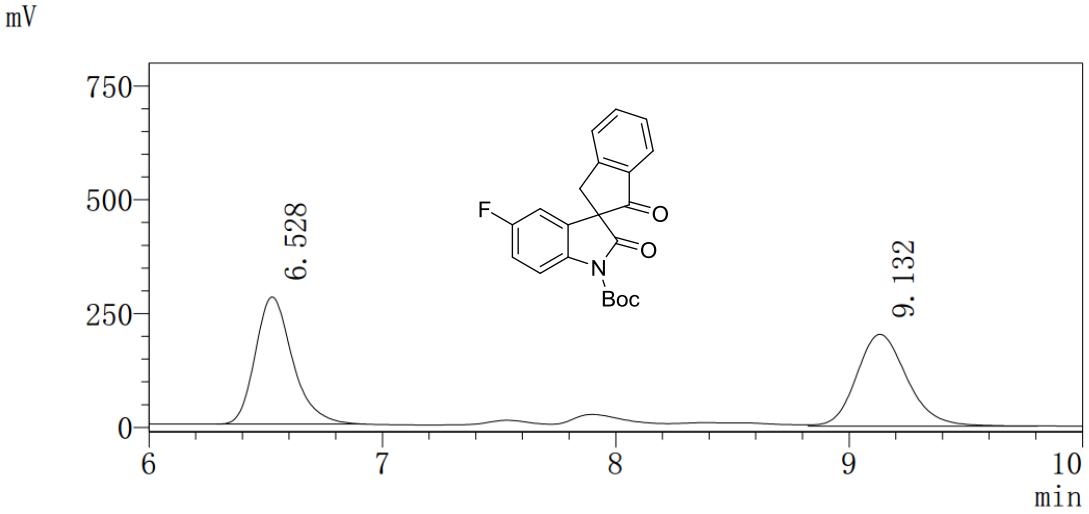
Peak	Ret.Time	Area	Area %	Height	Height %
1	6.853	5087767	51.470	478127	63.946
2	11.175	4797074	48.530	269573	36.054

Chiral **2a,** 91% ee



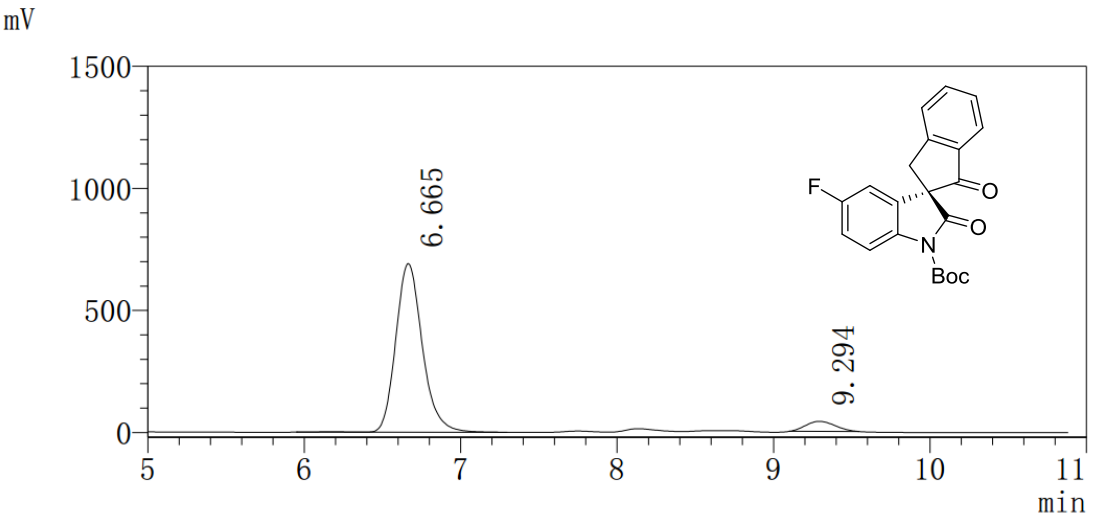
Peak	Ret.Time	Area	Area %	Height	Height %
1	6.863	8159260	95.277	661668	96.642
2	11.446	404428	4.723	22991	3.358

Racemic **2b**



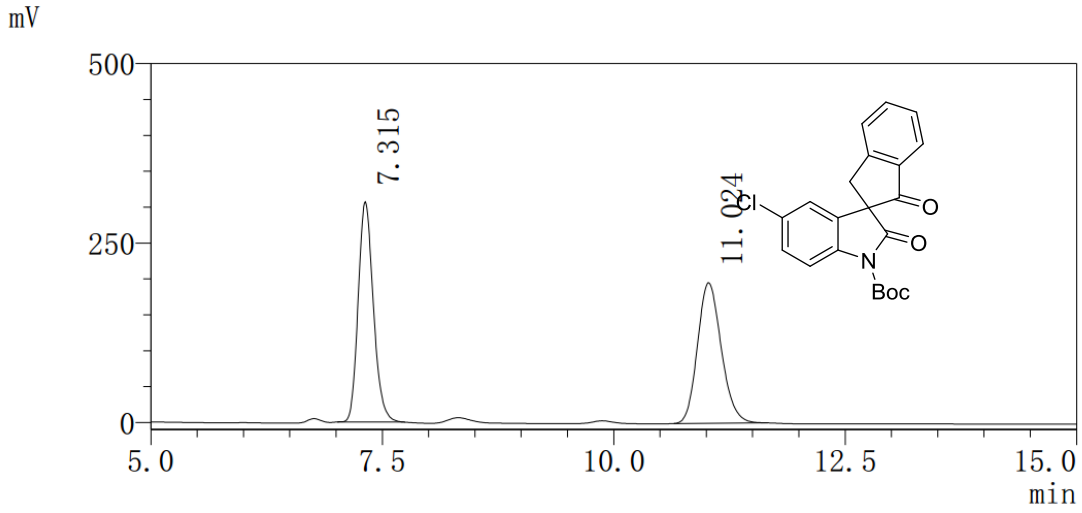
Peak	Ret.Time	Area	Area %	Height	Height %
1	6.528	3102790	50.676	279371	58.101
2	9.132	3020031	49.324	201463	41.899

Chiral **2b,** 88% ee



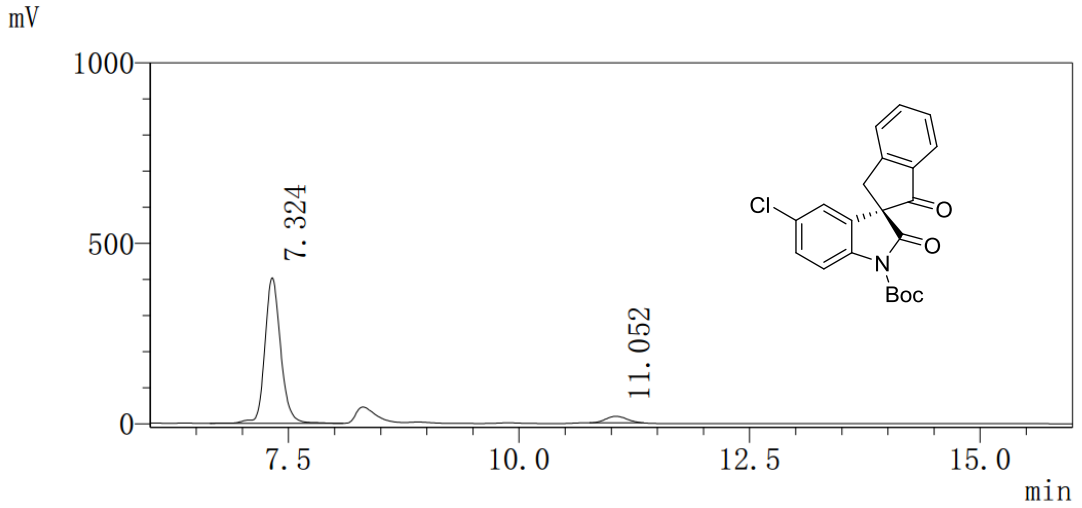
Peak	Ret.Time	Area	Area %	Height	Height %
1	6.665	8166280	93.818	691540	94.382
2	9.294	538131	6.182	41165	5.618

Racemic **2c**



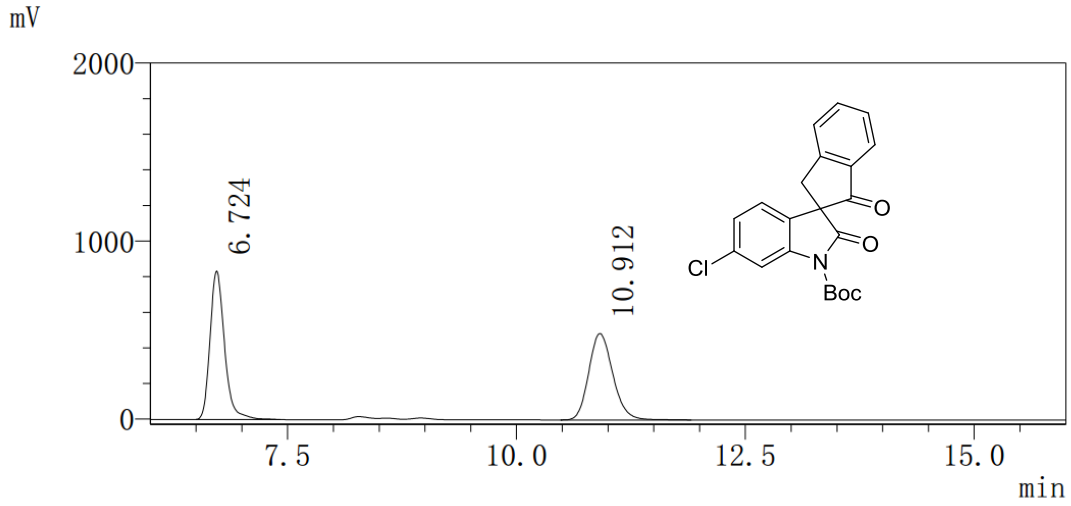
Peak	Ret.Time	Area	Area %	Height	Height %
1	7.315	3507157	50.044	306621	61.020
2	11.024	3500974	49.956	195871	38.980

Chiral 2c, 89% ee



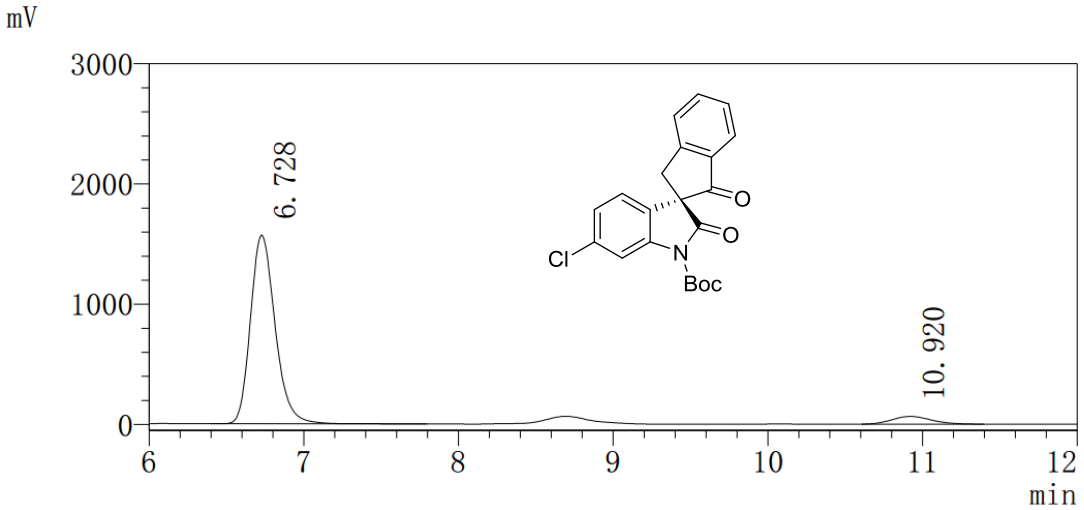
Peak	Ret.Time	Area	Area %	Height	Height %
1	7.324	4812807	94.342	403001	95.710
2	11.052	288637	5.658	18065	4.290

Racemic **2d**



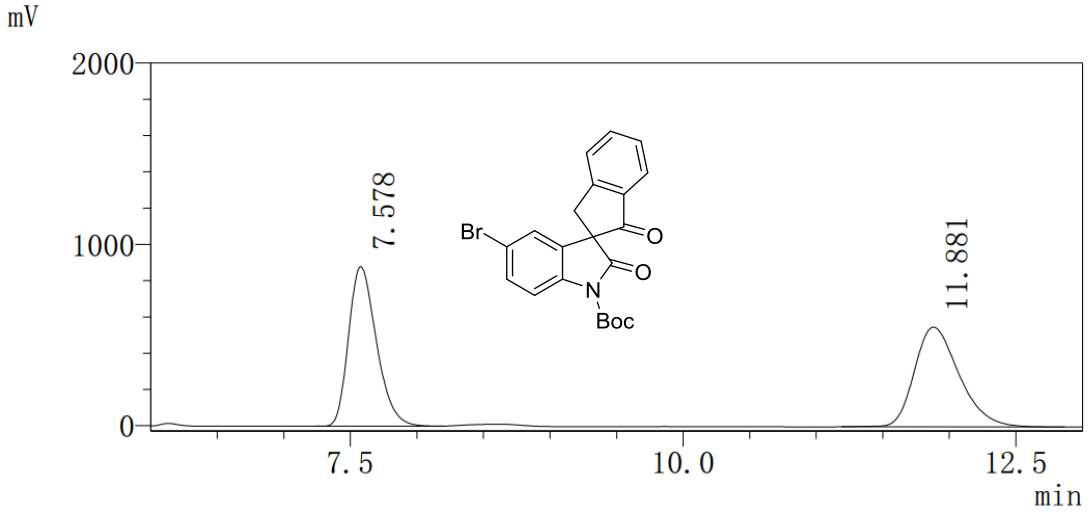
Peak	Ret.Time	Area	Area %	Height	Height %
1	6.724	9189907	50.896	833500	63.188
2	10.912	8866216	49.104	485590	36.812

Chiral **2d**, 88% ee



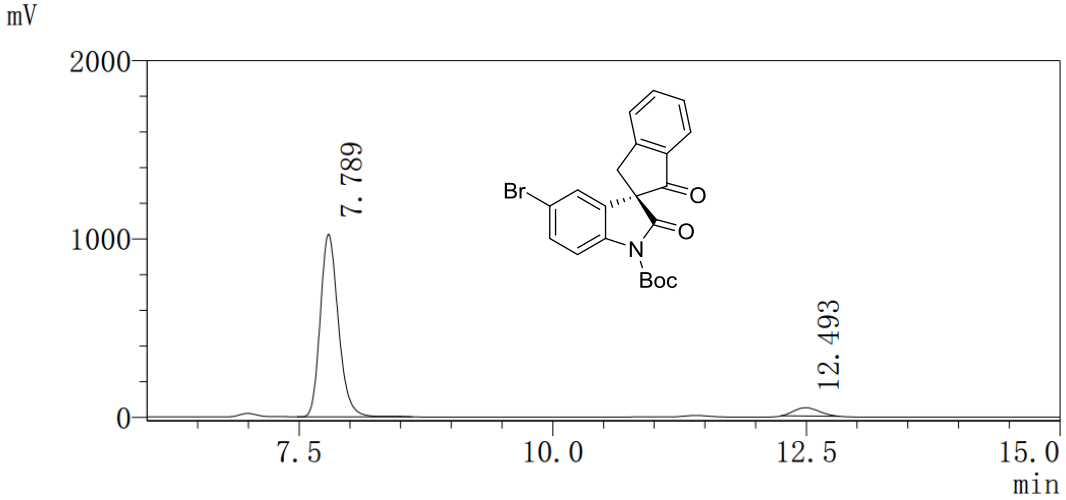
Peak	Ret.Time	Area	Area %	Height	Height %
1	6.728	17375302	93.858	1569123	96.077
2	10.920	1137040	6.142	64069	3.923

Racemic **2e**



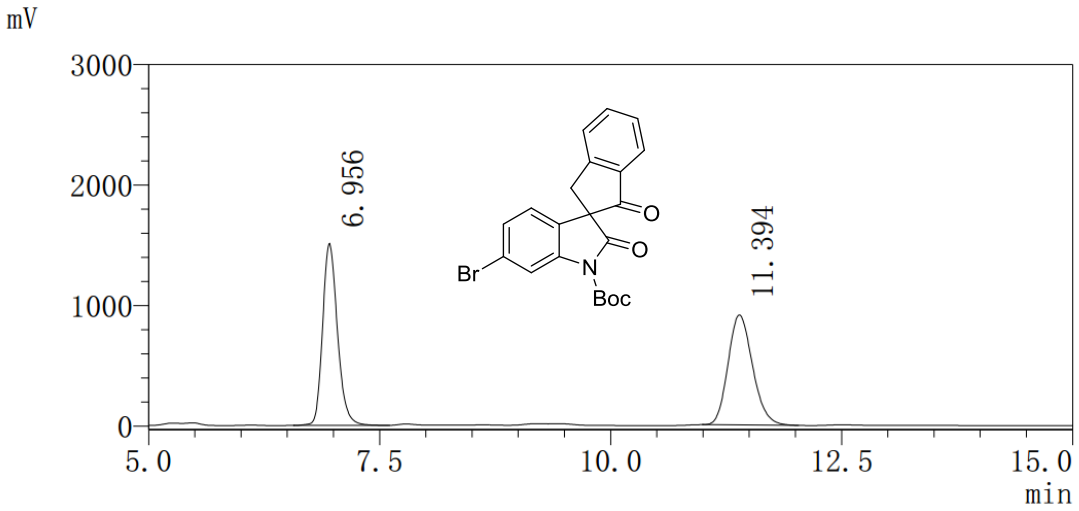
Peak	Ret.Time	Area	Area %	Height	Height %
1	7.578	12810189	49.904	880676	61.550
2	11.881	12859721	50.096	550143	38.450

Chiral **2e**, 88% ee



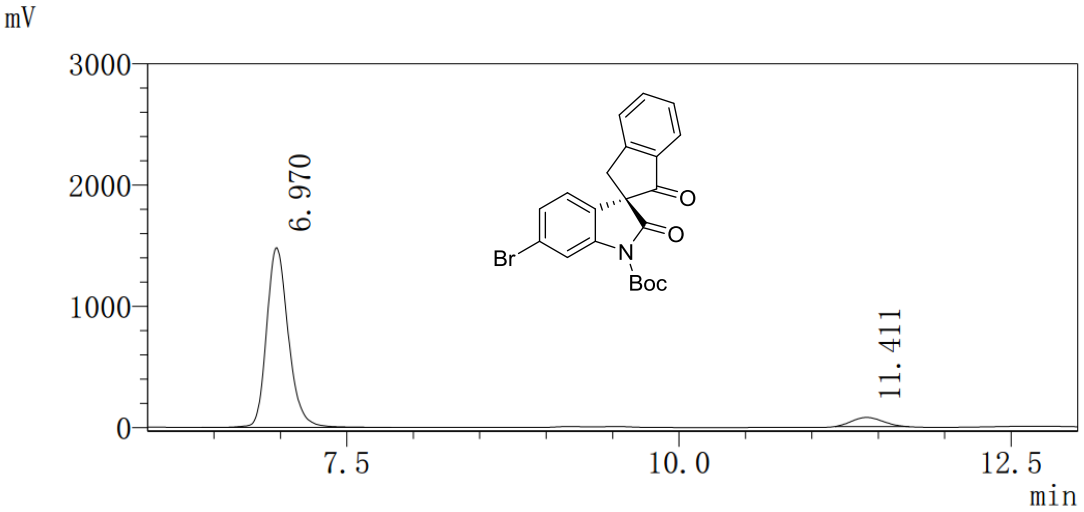
Peak	Ret.Time	Area	Area %	Height	Height %
1	7.789	12742345	94.033	1025114	95.642
2	12.493	808640	5.967	46711	4.358

Racemic **2f**



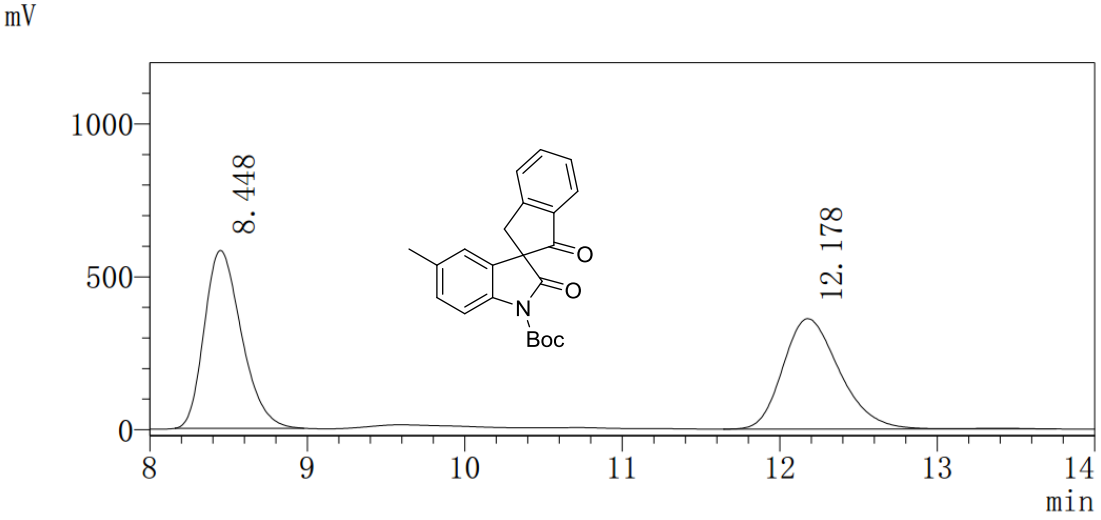
Peak	Ret.Time	Area	Area %	Height	Height %
1	6.956	16902787	50.064	1508903	62.307
2	11.394	16859655	49.936	912813	37.693

Chiral **2f**, 87% ee



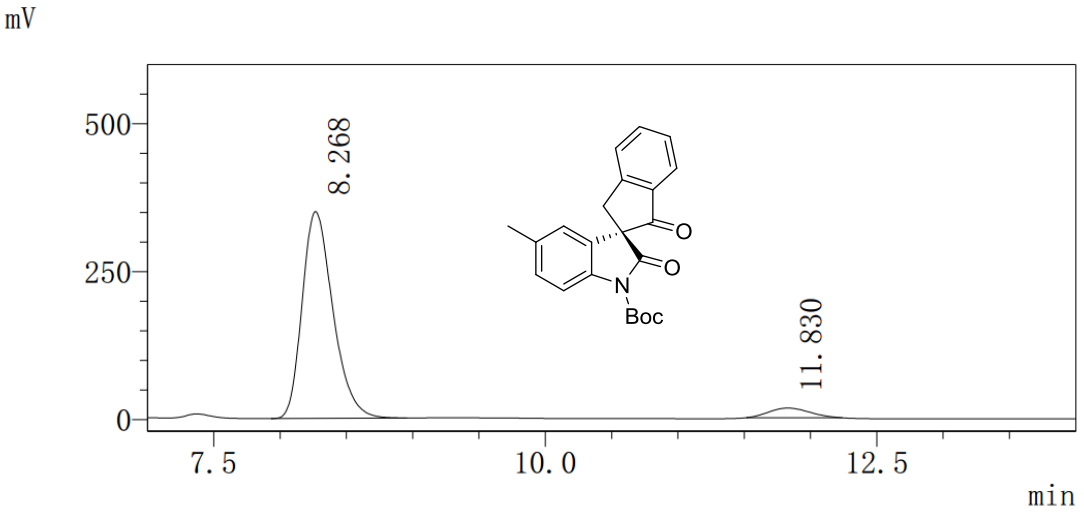
Peak	Ret.Time	Area	Area %	Height	Height %
1	6.970	16836337	93.283	1481195	95.195
2	11.411	1212366	6.717	74761	4.805

Racemic **2g**



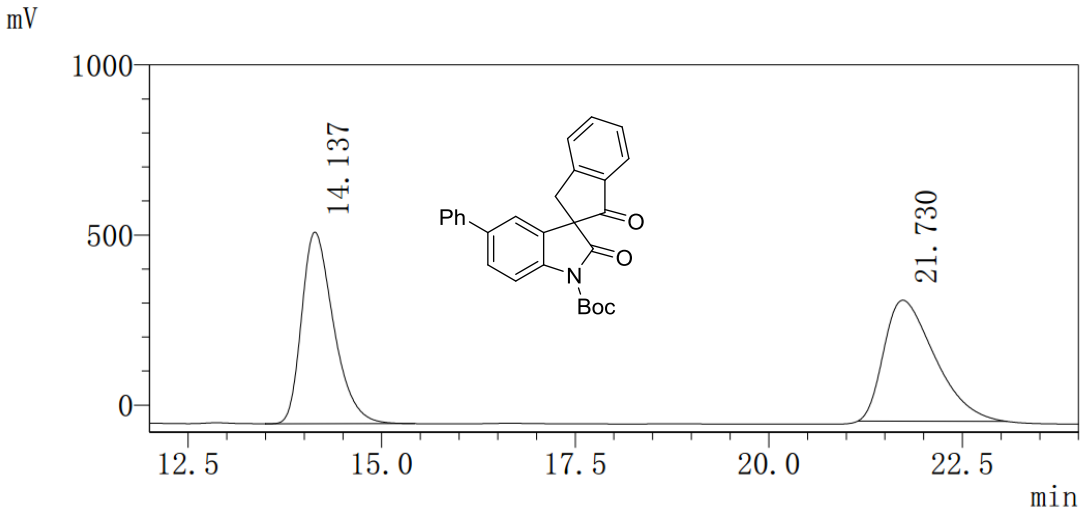
Peak	Ret.Time	Area	Area %	Height	Height %
1	8.448	9550360	51.316	582004	61.720
2	12.178	9060417	48.684	360973	38.280

Chiral **2g**, 88% ee



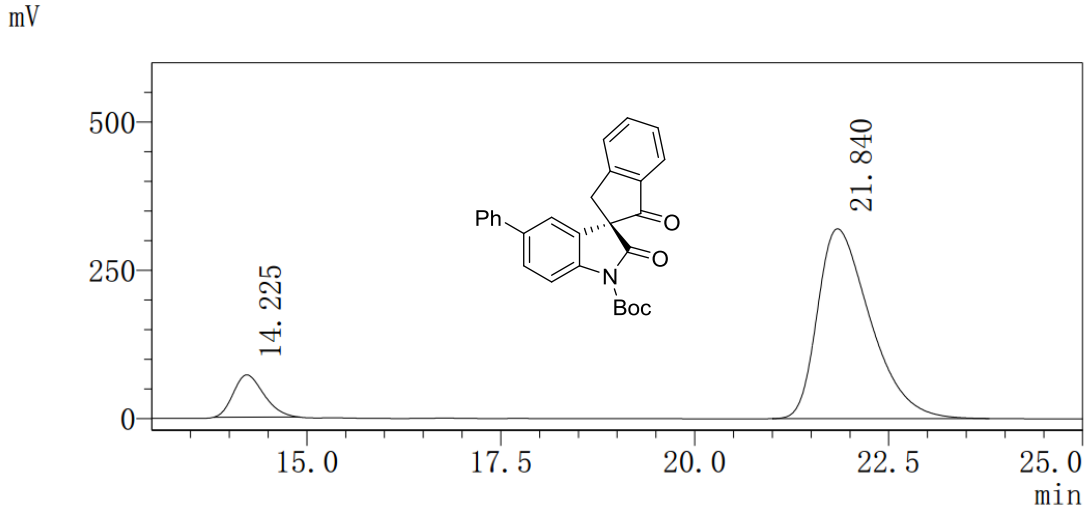
Peak	Ret.Time	Area	Area %	Height	Height %
1	8.268	5650363	94.200	349902	95.537
2	11.830	347896	5.800	16344	4.463

Racemic **2h**



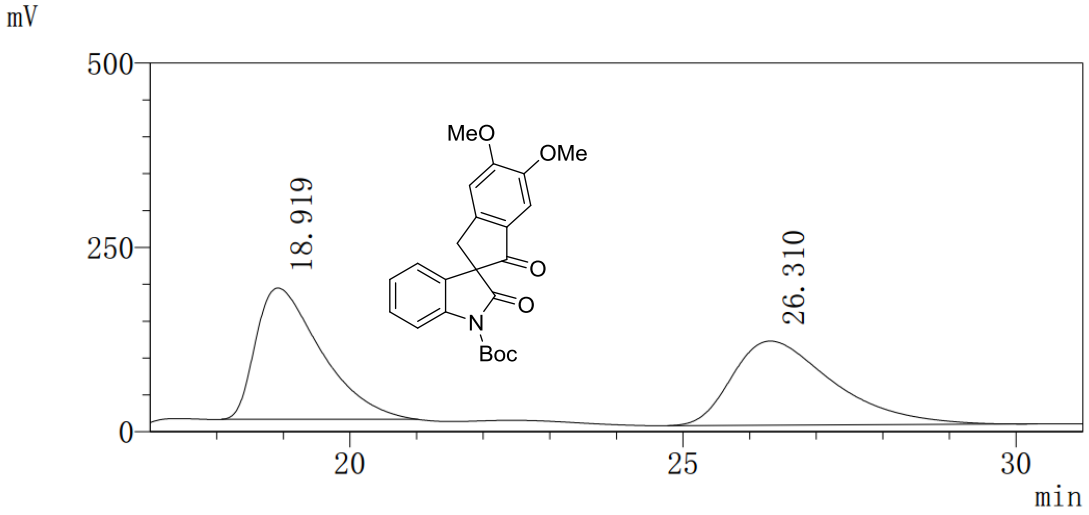
Peak	Ret.Time	Area	Area %	Height	Height %
1	14.137	16184453	49.823	563501	61.314
2	21.730	16299704	50.177	355541	38.686

Chiral **2h**, 77% ee



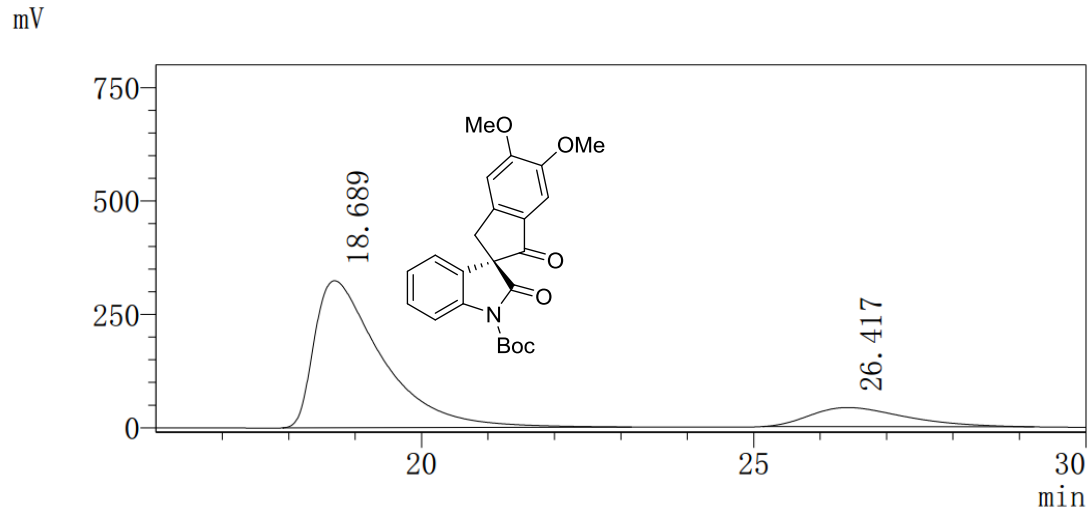
Peak	Ret.Time	Area	Height	Area %	Height %
1	14.225	1952585	71386	11.410	18.224
2	21.840	15159746	320331	88.590	81.776

Racemic **2i**



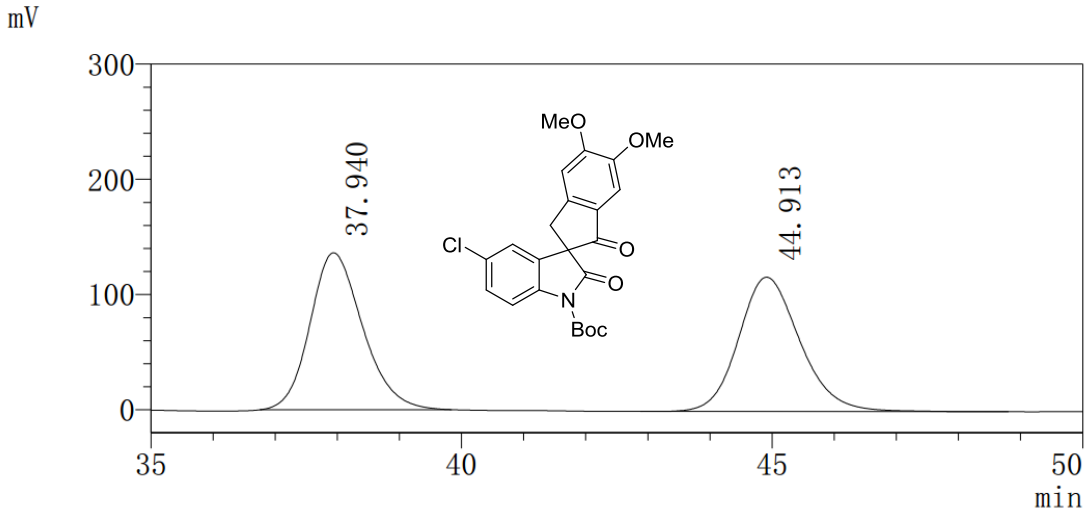
Peak	Ret.Time	Area	Area %	Height	Height %
1	18.919	12158828	50.174	178129	60.950
2	26.310	12074382	49.826	114125	39.050

Chiral **2i**, 69% ee



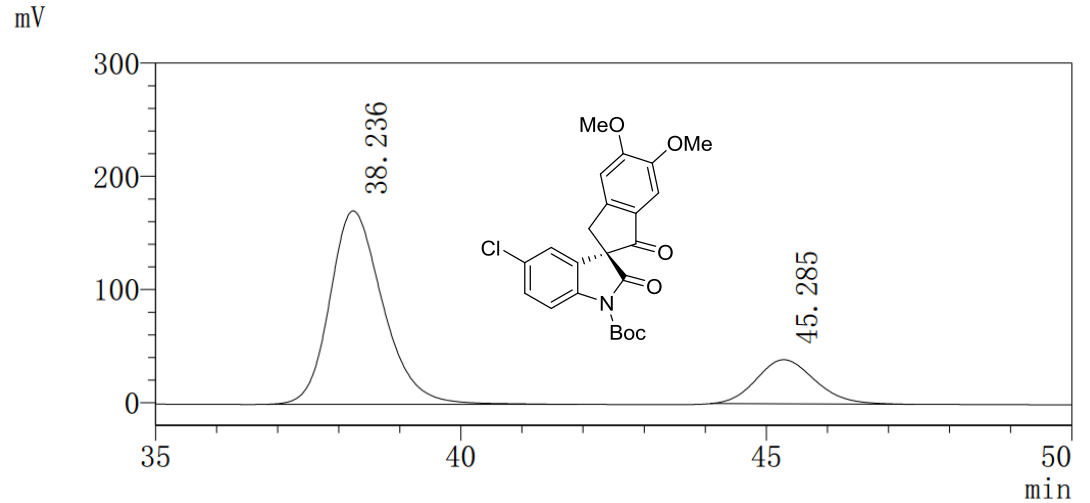
Peak	Ret.Time	Area	Area %	Height	Height %
1	18.689	22985665	84.518	324184	88.507
2	26.417	4210490	15.482	42097	11.493

Racemic **2j**



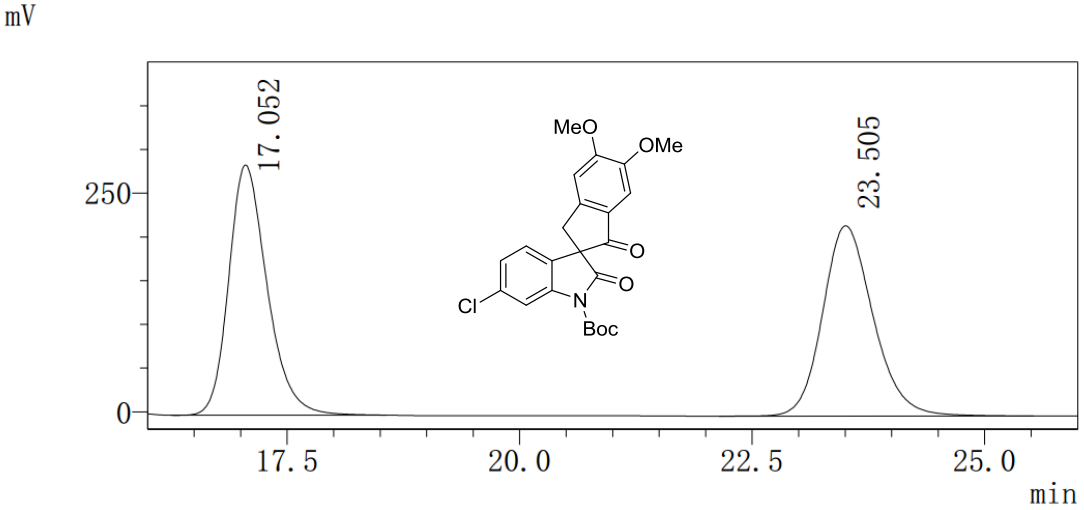
Peak	Ret.Time	Area	Area %	Height	Height %
1	37.940	8035707	50.042	136174	53.880
2	44.913	8022348	49.958	116564	46.120

Chiral **2j,** 60% ee



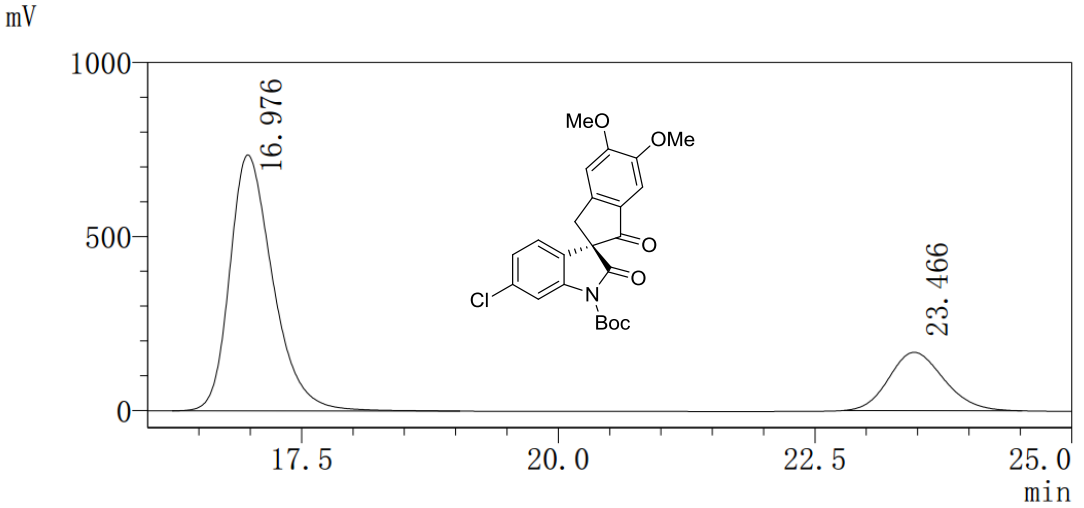
Peak	Ret.Time	Area	Area %	Height	Height %
1	38.236	10316801	79.808	170803	81.412
2	45.285	2610249	20.192	38998	18.588

Racemic **2k**



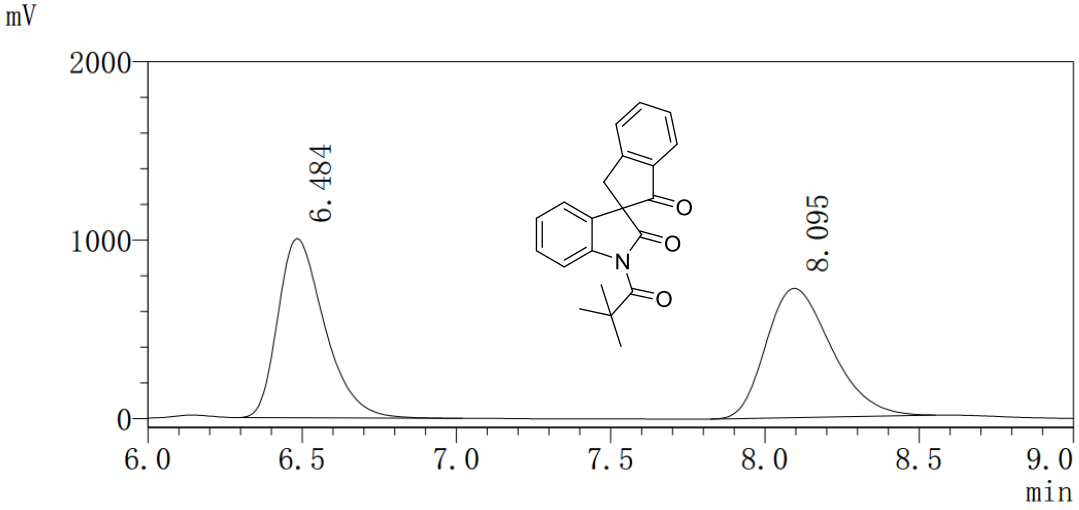
Peak	Ret.Time	Area	Area %	Height	Height %
1	17.052	8228461	50.003	286158	56.790
2	23.505	8227490	49.997	217729	43.210

Chiral **2k,** 55% ee



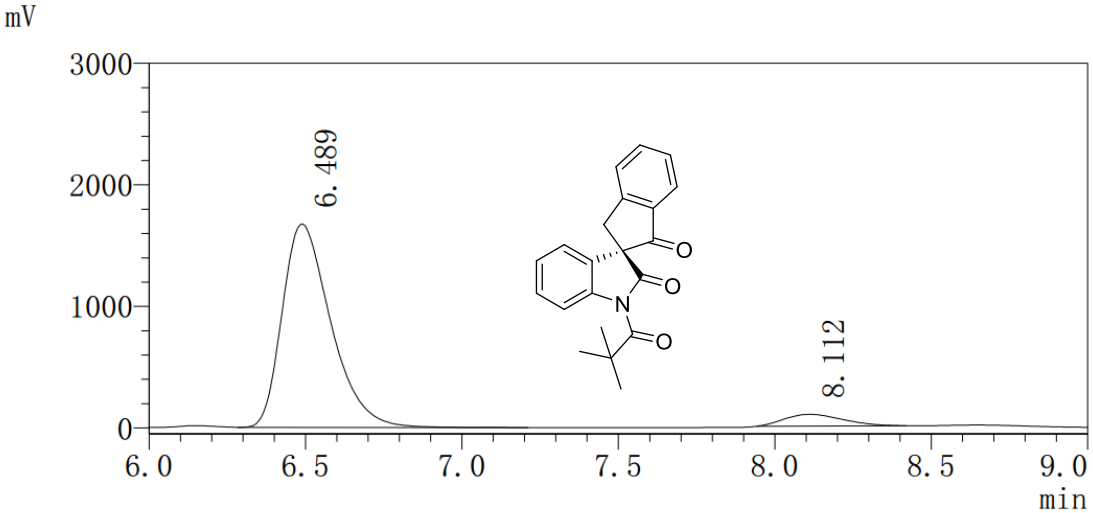
Peak	Ret.Time	Area	Area %	Height	Height %
1	16.976	21548019	77.547	736103	81.471
2	23.466	6239008	22.453	167411	18.529

Racemic **2l**



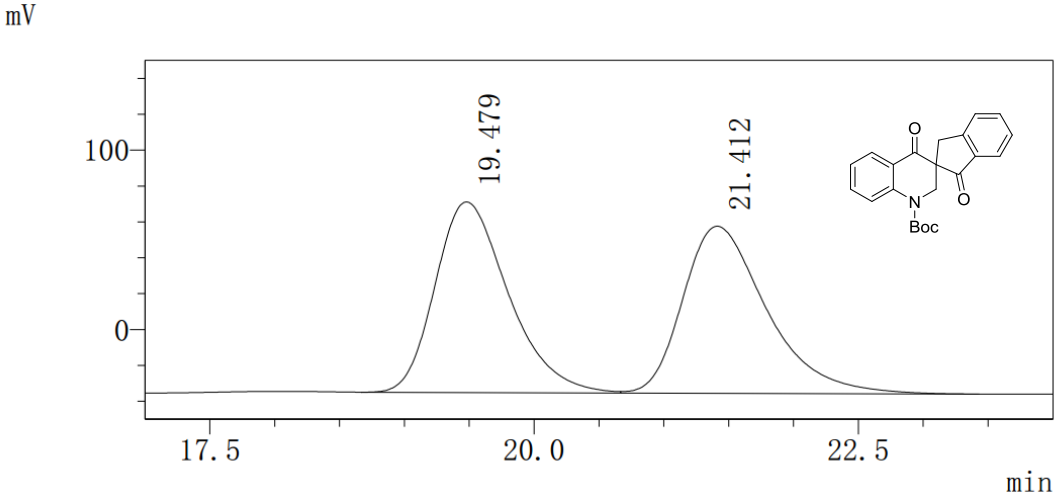
Peak	Ret. Time	Area	Area %	Height	Height %
1	6.484	10577629	49.777	1004982	58.136
2	8.095	10672529	50.223	723679	41.864

Chiral **2l**, 87% ee



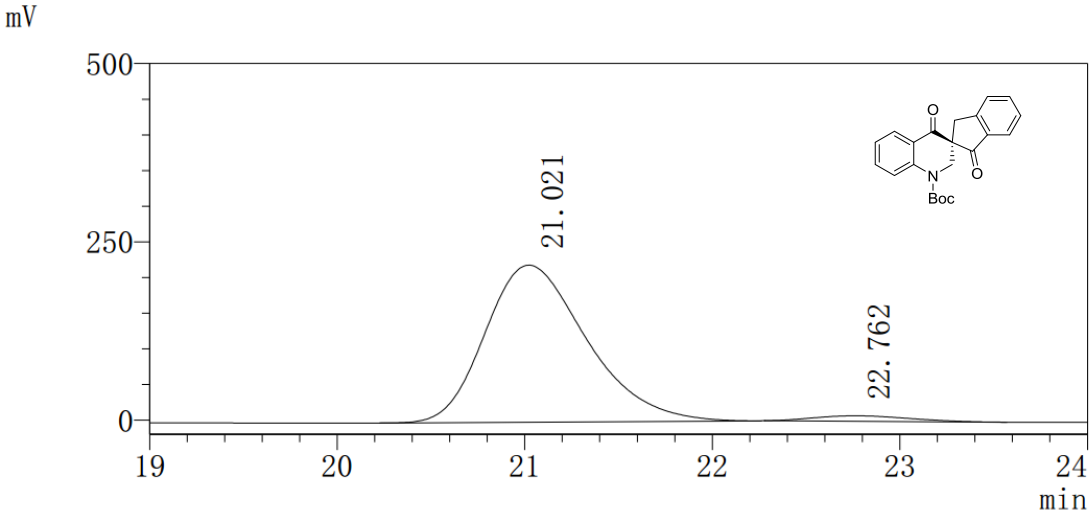
Peak	Ret. Time	Area	Area %	Height	Height %
1	6.489	18074416	93.531	1673387	94.570
2	8.112	1250060	6.469	96086	5.430

Racemic **5a**



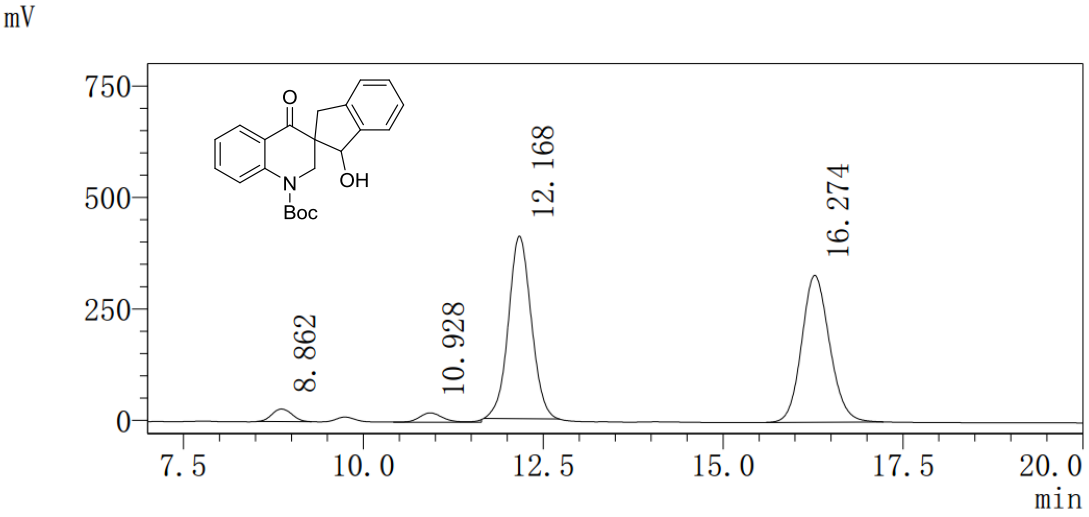
Peak	Ret.Time	Area	Area %	Height	Height %
1	19.479	4172924	49.941	106255	53.298
2	21.412	4182766	50.059	93105	46.702

Chiral **2m,** 94% ee



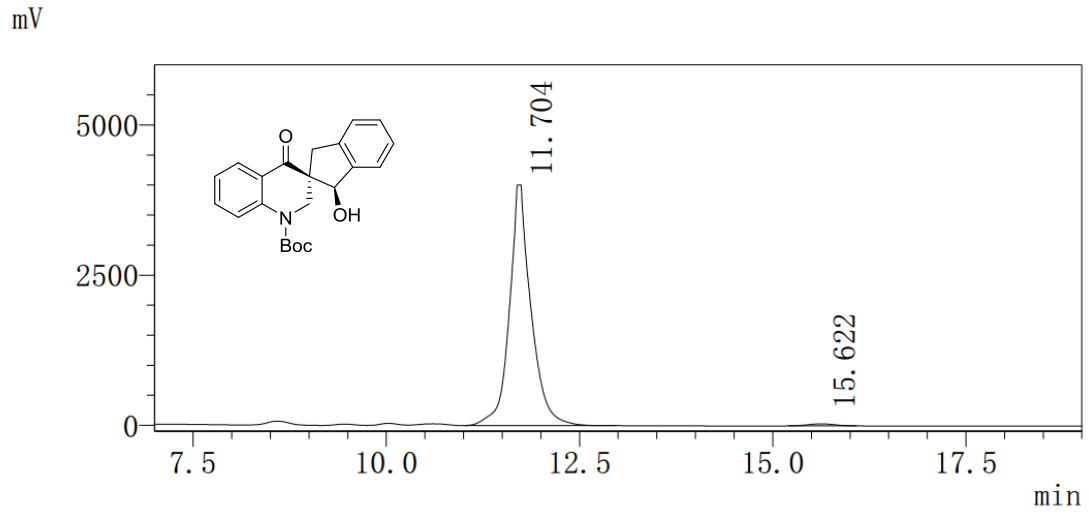
Peak	Ret.Time	Area	Area %	Height	Height%
1	21.021	8284890	96.790	220102	96.597
2	22.762	274752	3.210	7754	3.403

Racemic **6a**



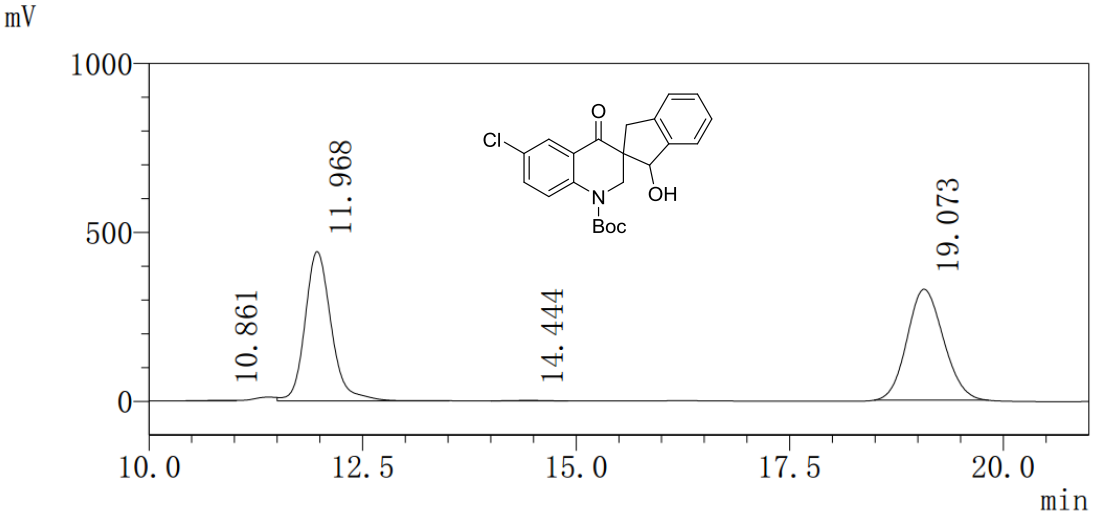
Peak	Ret. Time	Area	Area %	Height	Height %
1	8.862	542941	2.857	28082	3.563
2	10.928	501265	2.638	20986	2.663
3	12.168	9058811	47.673	409513	51.964
4	16.274	8898963	46.832	329489	41.810

Chiral **6a,** 98% ee



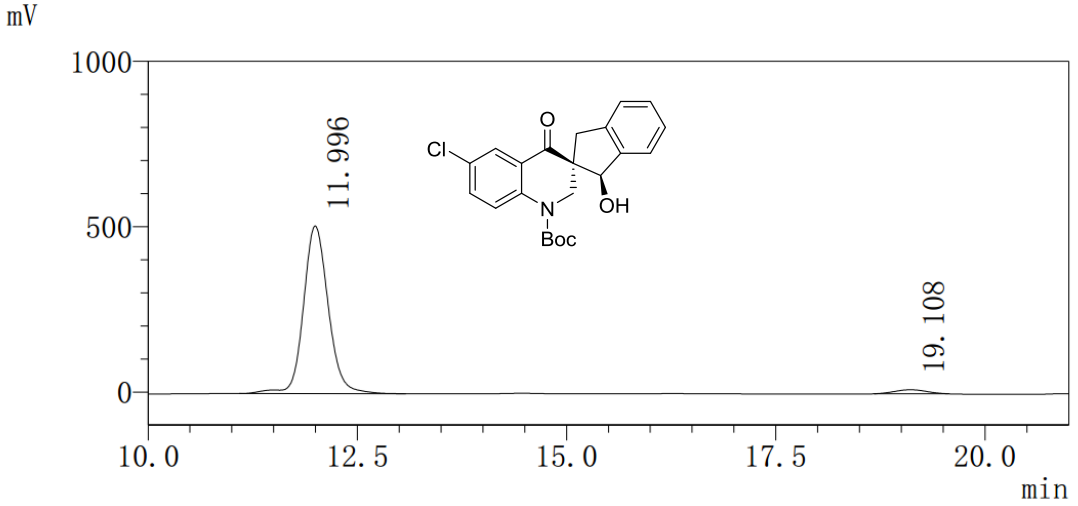
Peak	Ret. Time	Area	Area %	Height	Height %
1	11.704	77992648	98.965	4003642	99.165
2	15.622	815683	1.035	33717	0.835

Racemic **6b**



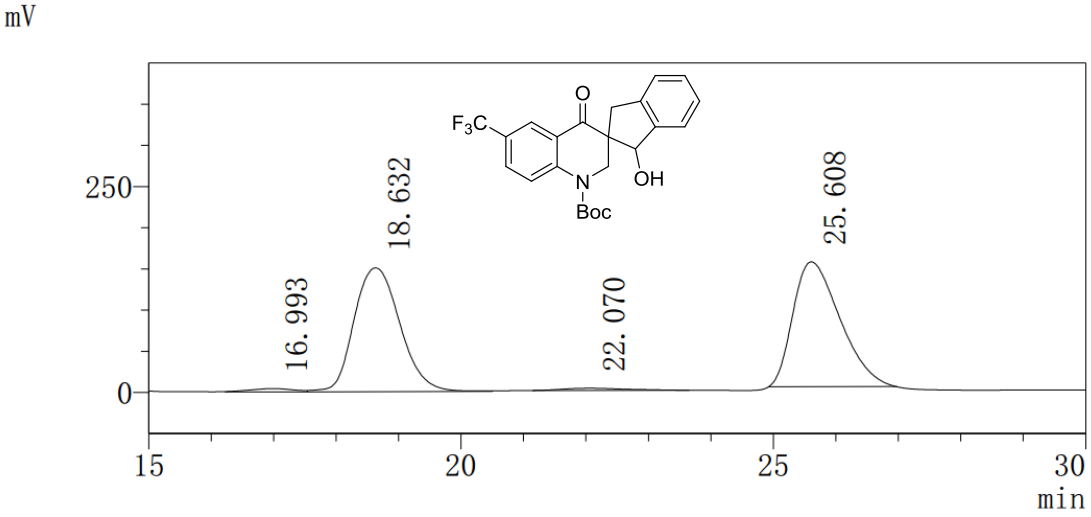
Peak	Ret.Time	Area	Area %	Height	Height %
1	10.861	33072	0.171	1593	0.206
2	11.968	9477293	49.134	442417	57.177
3	14.444	32712	0.170	1255	0.162
4	19.073	9745632	50.525	328503	42.455

Chiral **6a,** 94% ee



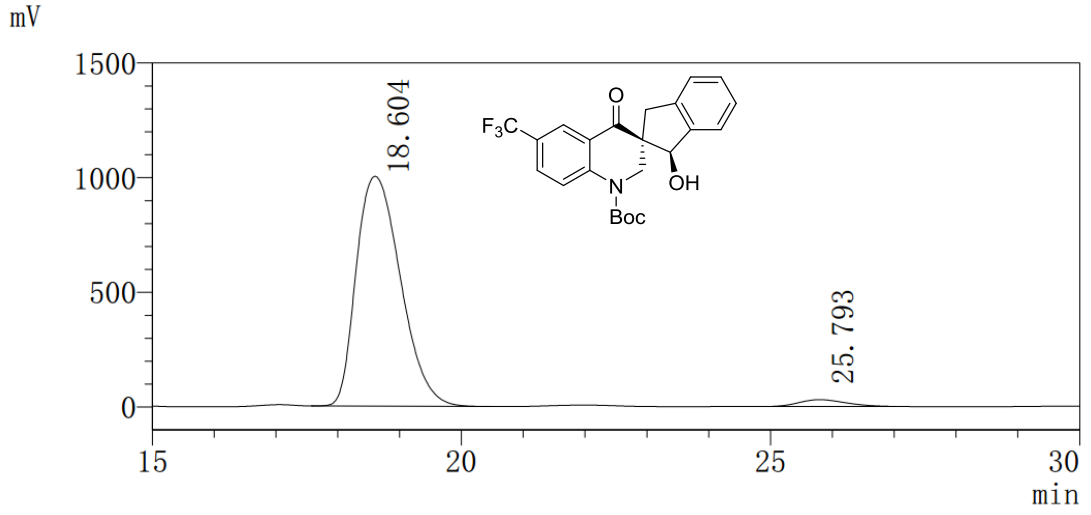
Peak	Ret.Time	Area	Area %	Height	Height %
1	11.996	10501358	97.007	507033	97.638
2	19.108	323998	2.993	12266	2.362

Racemic **6c**



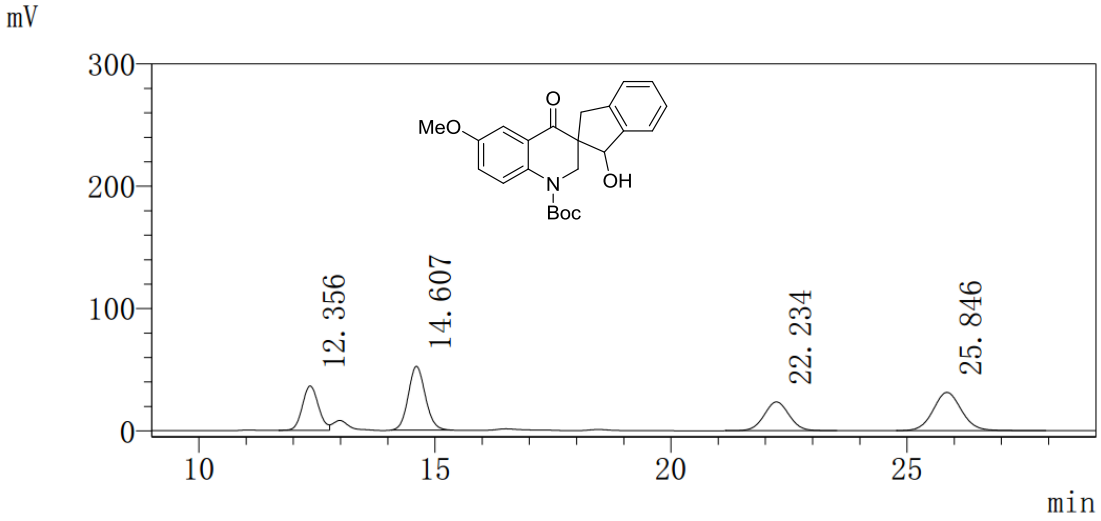
Peak	Ret.Time	Area	Area %	Height	Height %
1	16.993	187013	1.170	3924	1.272
2	18.632	7664734	47.955	150267	48.705
3	22.070	187550	1.173	2644	0.857
4	25.608	7943830	49.701	151691	49.166

Chiral **6c**, 94% ee



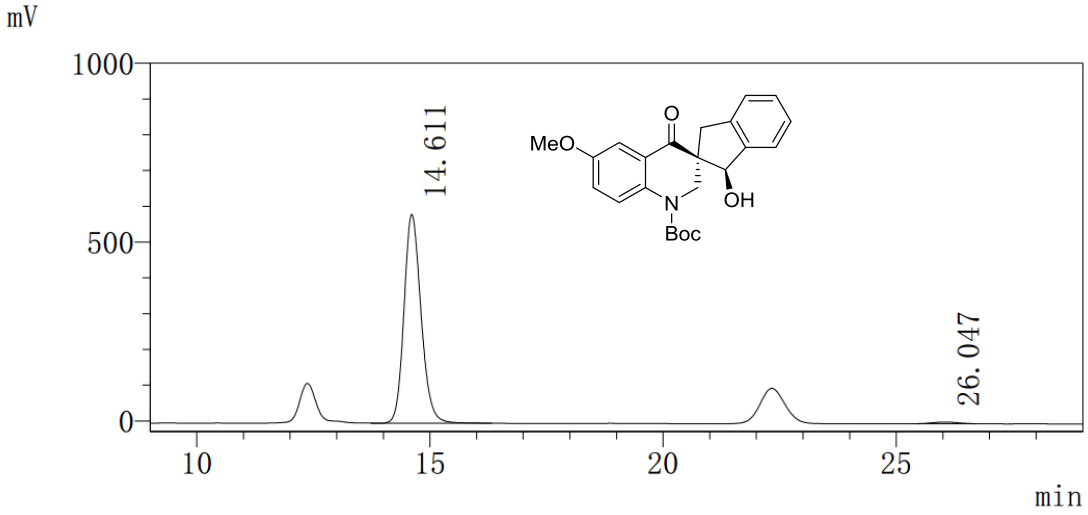
Peak	Ret.Time	Area	Area %	Height	Height %
1	18.604	49937203	97.057	1002009	97.151
2	25.793	1514117	2.943	29380	2.849

Racemic **6d**



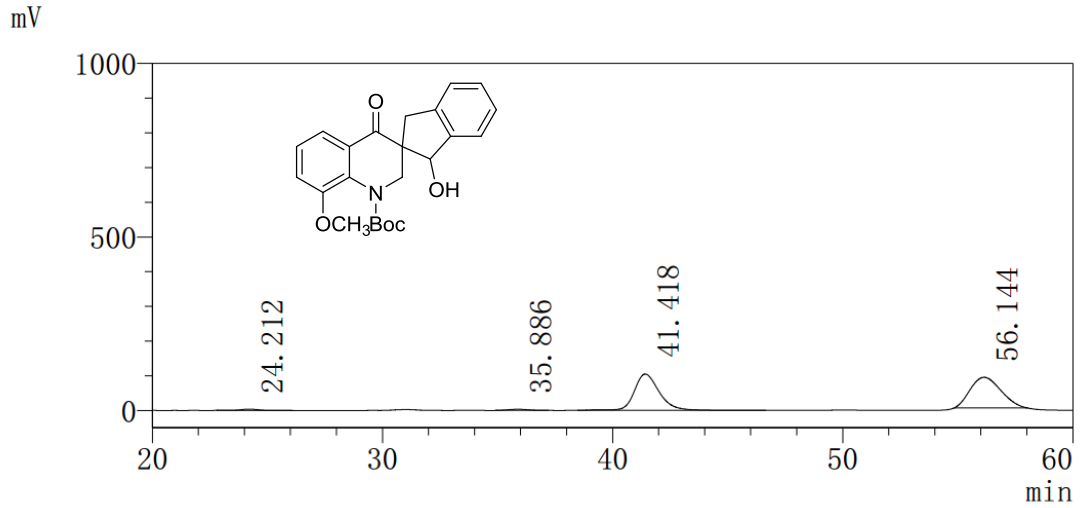
Peak	Ret.Time	Area	Area %	Height	Height %
1	12.356	865889	19.900	36371	25.372
2	14.607	1309610	30.098	52173	36.394
3	22.234	866180	19.907	23543	16.423
4	25.846	1309438	30.094	31267	21.811

Chiral **6d**, 98% ee



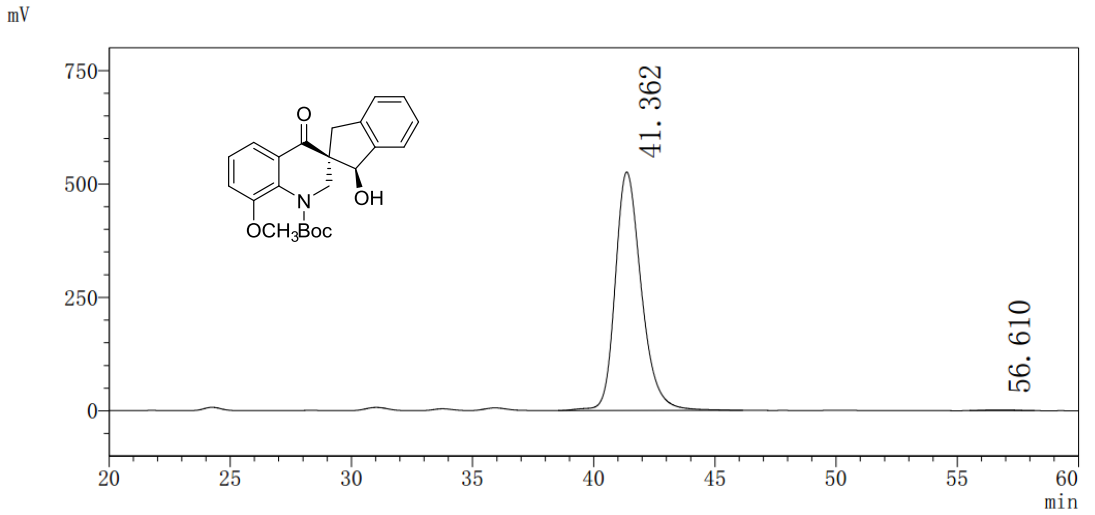
Peak	Ret.Time	Area	Area %	Height	Height %
1	14.611	14883308	98.835	583715	99.199
2	26.047	175374	1.165	4711	0.801

Racemic **6e**



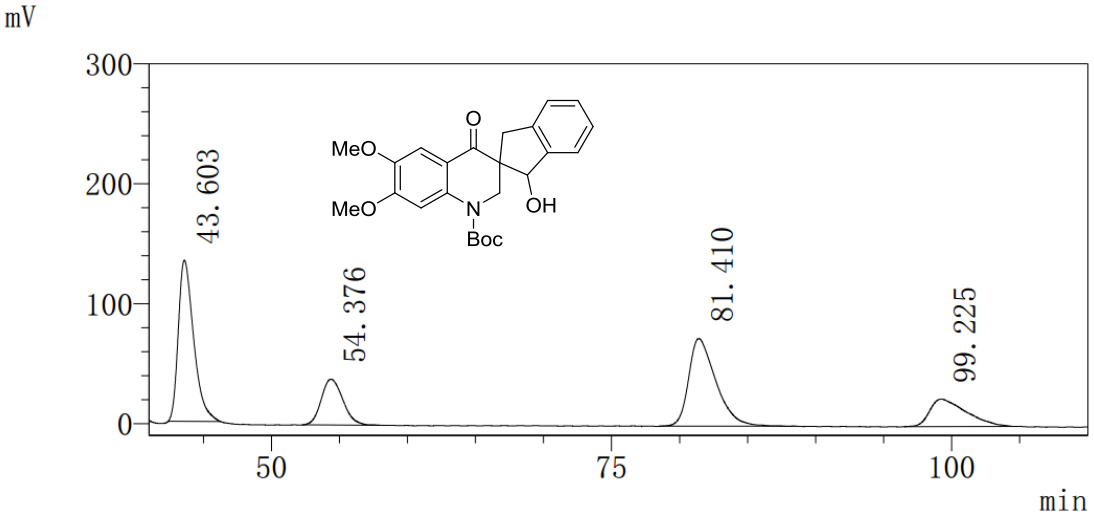
Peak	Ret. Time	Area	Area %	Height	Height %
1	24.212	191592	1.163	3694	1.849
2	35.886	192342	1.168	3289	1.646
3	41.418	7947014	48.240	104727	52.408
4	56.144	8142995	49.430	88121	44.098

Chiral **6e**, 99% ee



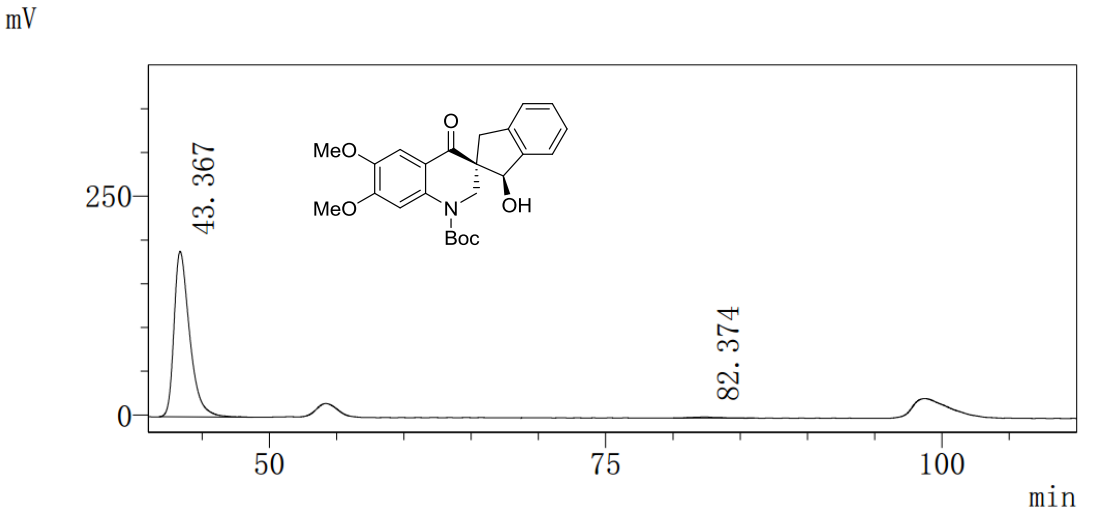
Peak	Ret. Time	Area	Area %	Height	Height %
1	41.362	39424560	99.683	525713	99.720
2	56.610	125215	0.317	1477	0.280

Racemic **6f**



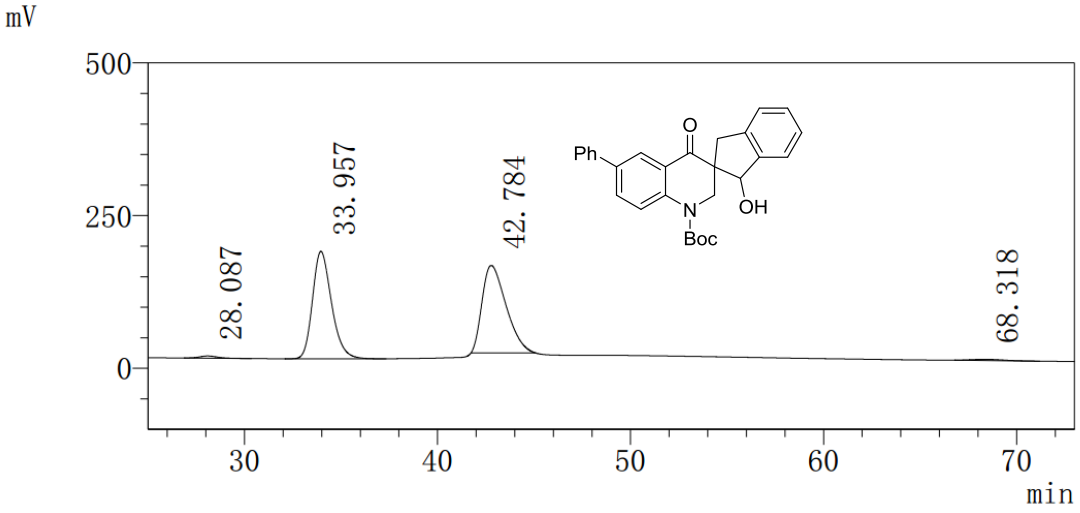
Peak	Ret. Time	Area	Area %	Height	Height %
1	43.603	10564681	36.078	134518	50.027
2	54.376	4241355	14.484	38217	14.213
3	81.410	10186663	34.787	73161	27.209
4	99.225	4290086	14.651	22994	8.551

Chiral **6f,** 98% ee



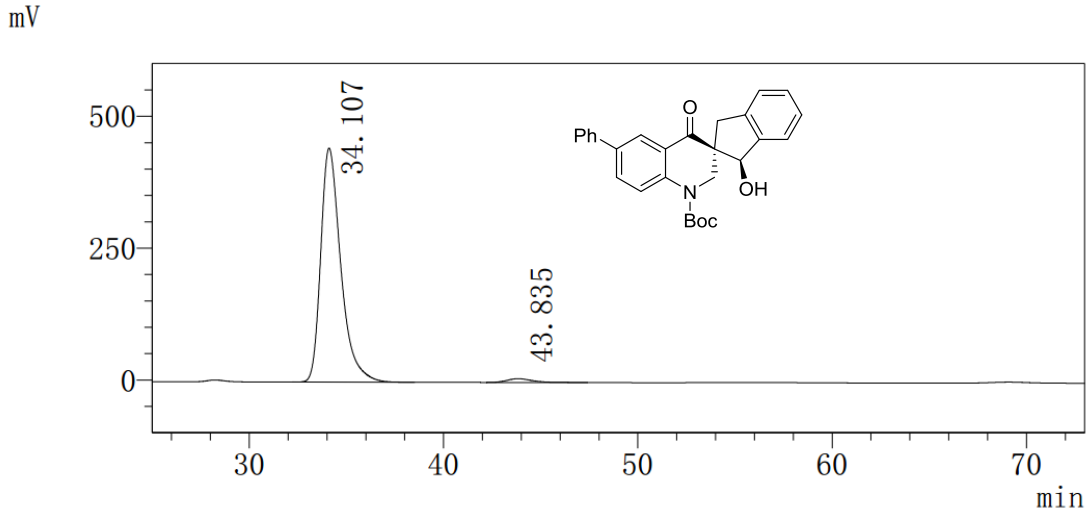
Peak	Ret. Time	Area	Area %	Height	Height %
1	43.367	15282119	99.256	189193	99.390
2	82.374	114525	0.744	1161	0.610

Racemic **6g**



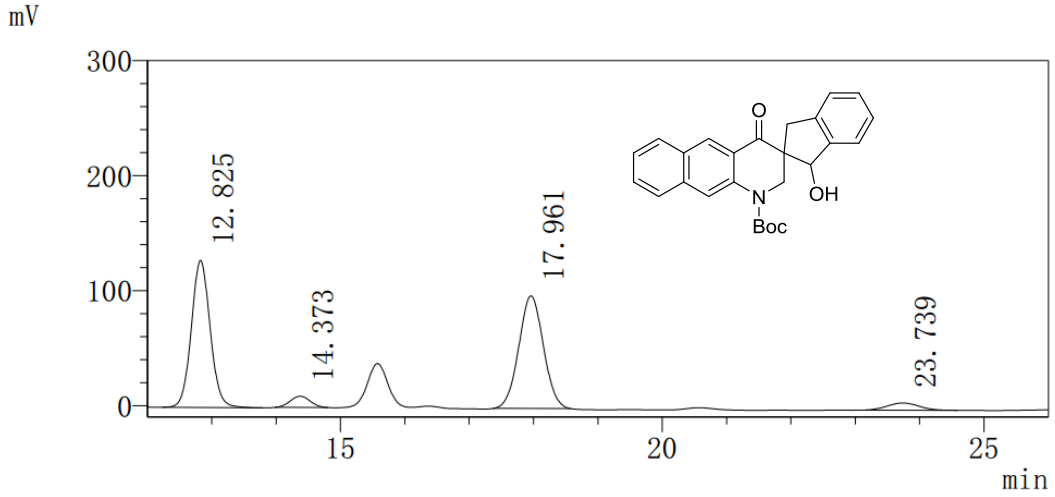
Peak	Ret.Time	Area	Area %	Height	Height %
1	28.087	240109	0.966	3639	1.121
2	33.957	12039960	48.442	175811	54.152
3	42.784	12332859	49.620	143148	44.092
4	68.318	241641	0.972	2061	0.635

Chiral **6g**, 96% ee



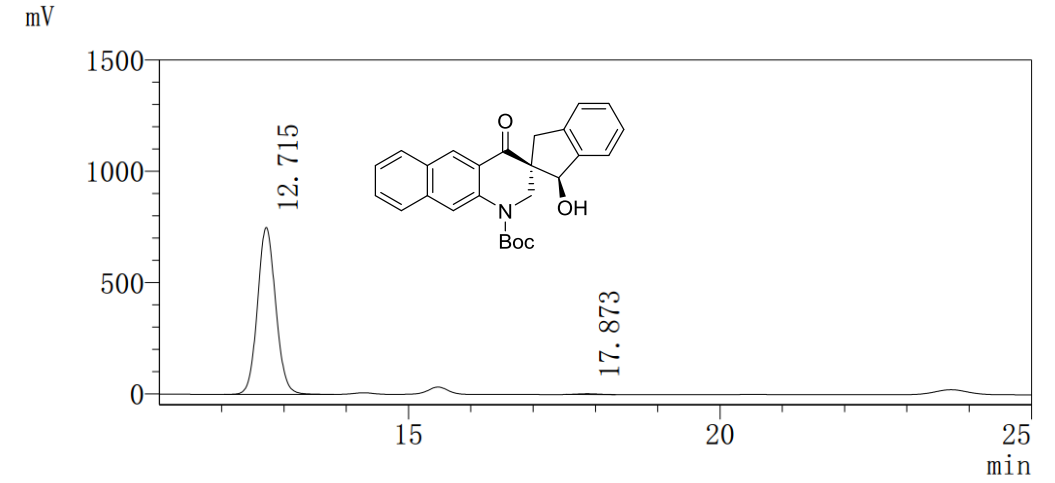
Peak	Ret.Time	Area	Area %	Height	Height %
1	34.107	31858712	98.004	443694	98.423
2	43.835	648752	1.996	7110	1.577

Racemic **6h**



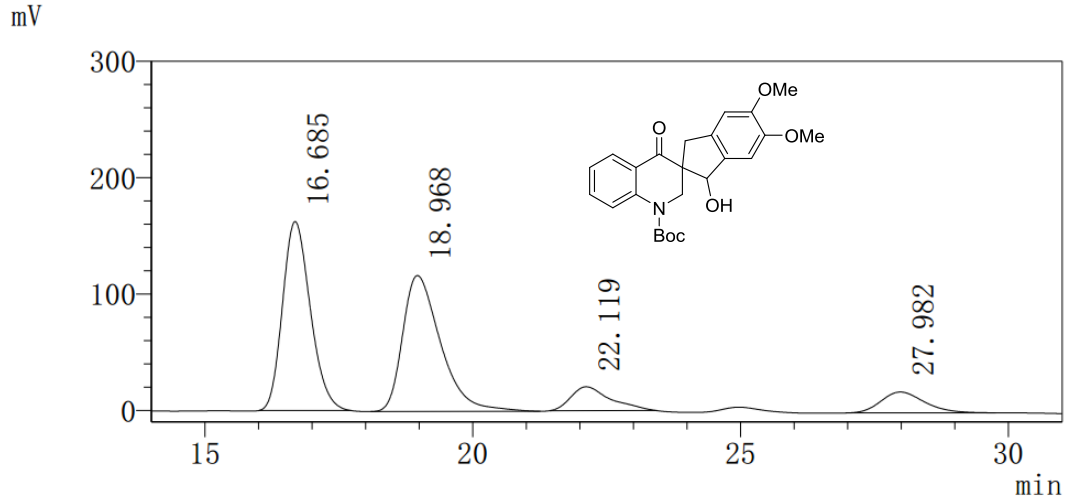
Peak	Ret.Time	Area	Area %	Height	Height %
1	12.825	2607135	46.255	127951	52.888
2	14.373	209425	3.716	9756	4.033
3	17.961	2605702	46.230	97924	40.477
4	23.739	214119	3.799	6296	2.602

Chiral **6h**, 99% ee



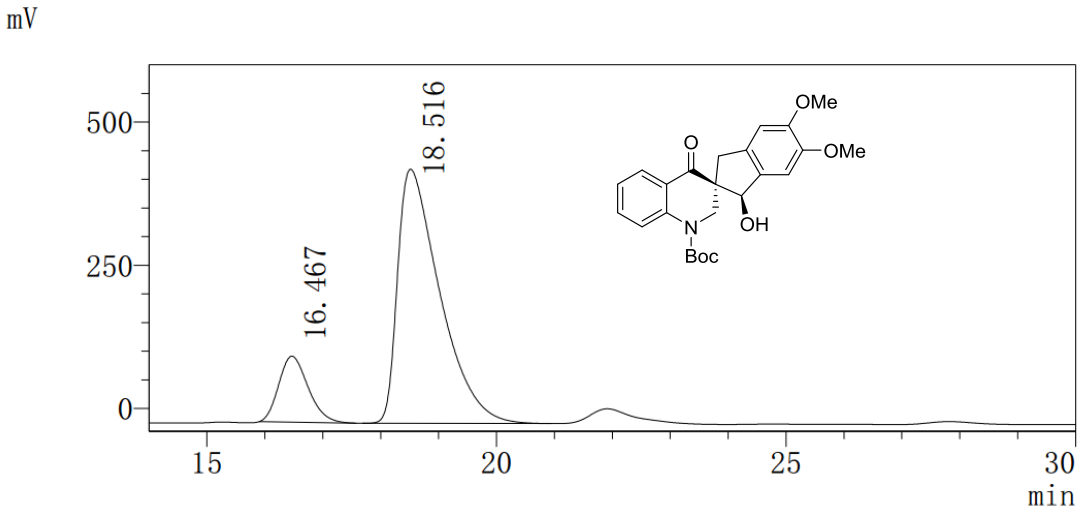
Peak	Ret.Time	Area	Area %	Height	Height %
1	12.715	15274697	99.469	750845	99.542
2	17.873	81616	0.531	3458	0.458

Racemic **6i**



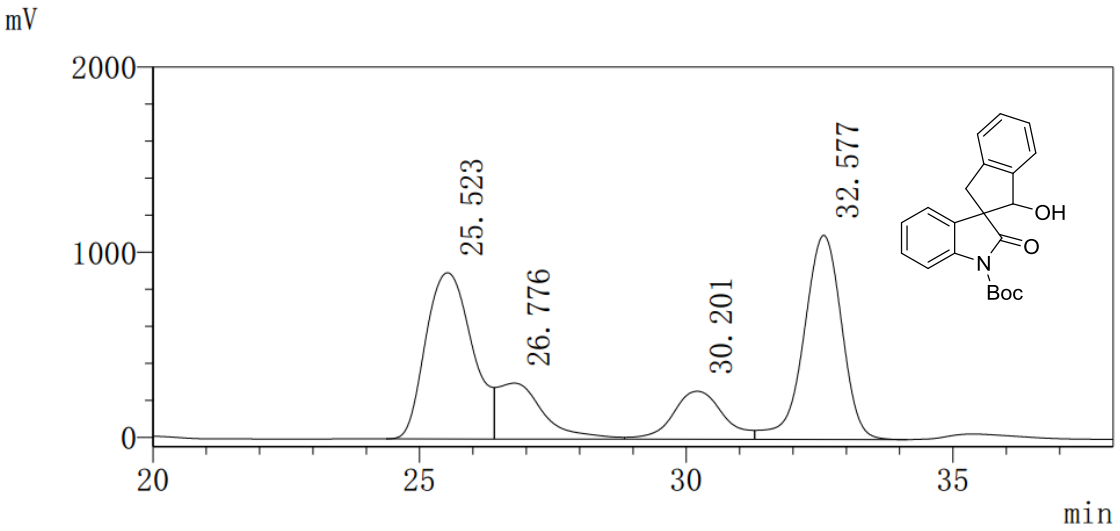
Peak	Ret. Time	Area	Area %	Height	Height %
1	16.685	5854156	42.792	162432	51.104
2	18.968	5757185	42.083	116925	36.787
3	22.119	1052912	7.696	20514	6.454
4	27.982	1016324	7.429	17972	5.654

Chiral **6i**, 70% ee



Peak	Ret. Time	Area	Area %	Height	Height %
1	16.467	4043620	15.228	114975	20.576
2	18.516	22510016	84.772	443816	79.424

Racemic **3a**



Peak	Ret.Time	Area	Area %	Height	Height %
1	25.523	54533520	37.844	897210	35.023
2	26.776	18158675	12.601	301673	11.776
3	30.201	16997389	11.795	259601	10.134
4	32.577	54411198	37.759	1103260	43.067