Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Asymmetric *N*-alkylation of indoles with isatins catalyzed by *N*-heterocyclic carbene: efficient synthesis of functionalized cyclic *N,O*-aminal indole derivatives

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Contents

1. General information

Optical rotation was measured by the Perkin Elmer 341 polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400spectrometer using tetramethylsilane (TMS) as internal reference, and chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The HRMS analysis was obtained on a Bruker ApexII FT-ICR mass spectrometer with ESI ionization method. The *ee* value determination was carried out using chiral HPLC with Chirapak AD–H, OD–H and OJ column on Agilent 1260 with a UV-detector. Melting points were determined on an XT–4 melting point apparatus and were uncorrected. All syntheses and manipulations were carried out under a dry nitrogen atmosphere. DCM was freshly distilled from phosphorous pentoxide. Toluene and THF were freshly distilled from a deep-blue solution of sodium-benzophenone under nitrogen. Other chemicals were purchased from commercial suppliers and used directly. Flash column chromatography was carried out utilizing 200–300 mesh silica gel.

N-Heterocyclic carbene precatalyst **3a** was commercially available from TCI. Precatalysts **3b**–**3e** were synthesized according to the literature,[1-4] respectively. 1*H*-Indole-2-carb-aldehydes **1** were synthesized according to the literature.[5]

2. Optimization of reaction conditions

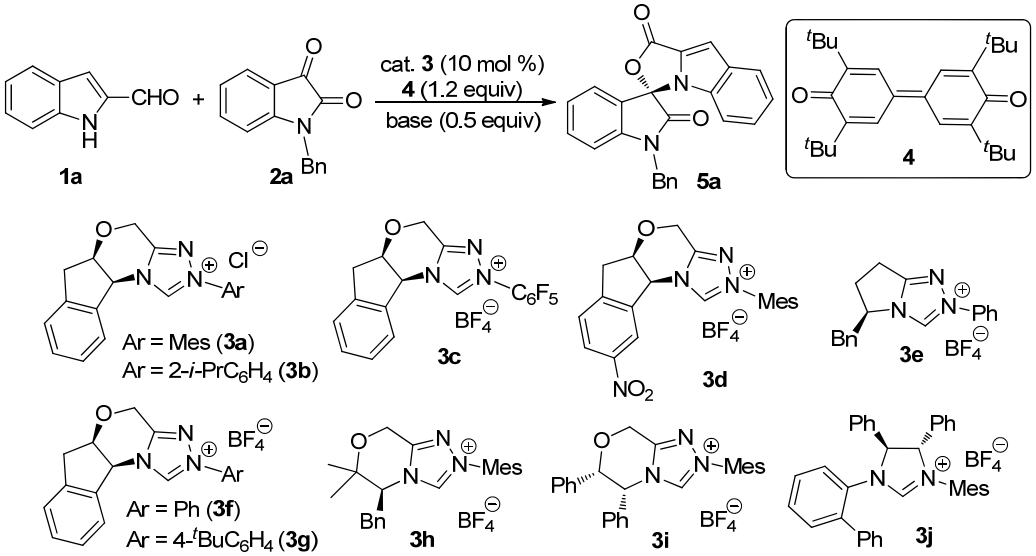
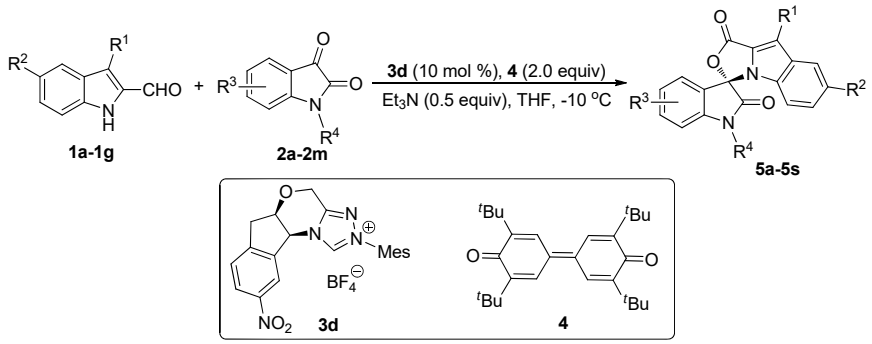


Table S1. Optimization of reaction conditions[a]

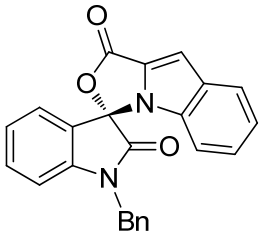
entry	cat.	base	solvent	temp (^{o}C)	time (h)	yield (%)[b]	ee (%)[c]
1	**3a**	DBU	THF	30	0.5	58	77
2	**3b**	DBU	THF	30	0.5	58	62
3	**3c**	DBU	THF	30	0.5	58	0
4	**3d**	DBU	THF	30	0.5	58	78
5	**3e**	DBU	THF	30	12	trace	-
6	**3f**	DBU	THF	30	12	47	0
7	**3g**	DBU	THF	30	12	trace	-
8	**3h**	DBU	THF	30	12	10	59
9	**3i**	DBU	THF	30	24	nr	-
10	**3j**	DBU	THF	30	12	nr	-
11	**3a**	DABCO	THF	30	0.5	79	77
12	**3a**	DIPEA	THF	30	0.5	81	77
13	**3a**	Et_3N	THF	30	0.5	84	77
14	**3b**	Et_3N	THF	30	0.5	79	66
15	**3c**	Et_3N	THF	30	0.5	76	9
16	**3d**	Et_3N	THF	30	0.5	83	84
17	**3d**	Et_3N	$PhCH_3$	30	2	74	85
18	**3d**	Et_3N	DCM	30	22	71	64
19	**3d**	Et_3N	THF	0	11	82	88
20	**3d**	Et_3N	THF	-10	5	71	90
21[d]	**3d**	Et_3N	THF	-10	12	81	90
22[e]	**3d**	Et_3N	THF	-10	12	87	90
23[f]	**3d**	Et_3N	THF	-10	12	94	90

[a]Reaction conditions: **1a** (0.2 mmol, 2 equiv), **2a** (0.1 mmol), cat. **3** (0.01 mmol, 0.1 equiv), base (0.05 mmol, 0.5 equiv), quinone **4** (0.12 mmol, 1.2 equiv), solvent (1 mL). [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Quinone **4** (1.5 equiv) was used. [e]Quinone **4** (1.7 equiv) was used. [f]Quinone **4** (2 equiv) was used.

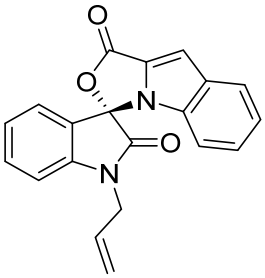
3. General procedure for NHC-catalyzed annulation of indole-2-formaldehydes with isatins



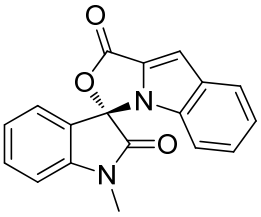
To a dry Schlenk tube with a magnetic stirring bar was charged indole-2-formaldehyde **1** (0.2 mmol), isatin **2** (0.1 mmol), NHC precatalyst **3d** (0.01 mmol, 4.6 mg), and quinone **4** (0.2 mmol, 81.8 mg), a solution of Et_3N (0.05 mmol) in dry THF (1 mL) was added under nitrogen atmosphere. The reaction mixture was stirred at –10 °C for 12 h (monitored by TLC). The solvent was removed in *vacuo* and the residue was purified by chromatography on silica gel using hexanes/EtOAc (6:1) as eluent to afford the desired products **5**.



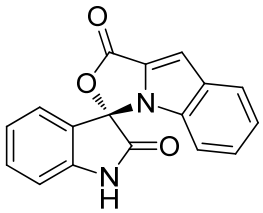
(*S*)-1-benzyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5a). Yield 94%, white solid, m.p. 194–196°C, $[\alpha]_D^{20}$ +7.000 (1.00 mg/mL in CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.36 – 7.33 (m, 5H), 7.28 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.16 – 7.08 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 5.11 (d, J = 15.6 Hz, 1H), 4.82 (d, J = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 159.3, 143.8, 134.5, 133.5, 133.2, 132.2, 129.1, 128.3, 127.7, 126.1, 125.9, 124.8, 124.4, 124.3, 122.4, 120.6, 110.7, 110.2, 103.2, 88.1, 44.7. HRMS (ESI): Exact mass calcd for $C_{24}H_{17}N_2O_3$ $[M+H]^+$: 381.1234, Found: 381.1245. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 60.971 min, t_{major} = 67.970 min, 90% ee).



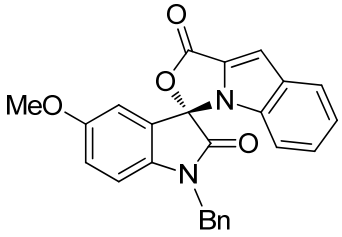
(*S*)-1-allyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5b). Yield 94%, white solid, m.p. 168–170°C, $[\alpha]_D^{20}$ +21.500 (2.70 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 1H), 7.56 – 7.52 (m, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.24 (s, 1H), 7.22 – 7.17 (m, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.62 (dd, J = 6.0, 3.2 Hz, 1H), 5.92 – 5.83 (m, 1H), 5.40 – 5.33 (m, 2H), 4.49 – 4.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 159.3, 143.9, 133.5, 133.2, 132.3, 130.3, 126.2, 126.1, 124.9, 124.4, 124.3, 122.4, 120.6, 119.1, 110.6, 110.0, 103.2, 88.1, 43.2. HRMS (ESI): Exact mass calcd for $C_{20}H_{15}N_2O_3$ $[M+H]^+$: 331.1077, Found: 331.1087. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major}= 37.469 min, t_{minor} = 46.961 min, 92% ee).



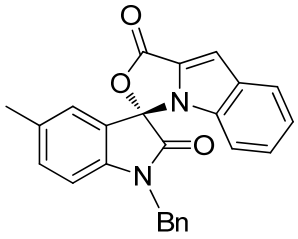
(*S*)-1-methyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5c). Yield: 87%, white solid, m.p. 205–207°C, $[\alpha]_D^{20}$ +20.000 (2.10 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 2.4 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.28 – 7.26 (m, 1H), 7.23 (s, 1H), 7.21 – 7.13 (m, 3H), 7.08 (d, J = 8.0 Hz, 1H), 6.62 – 6.59 (m, 1H), 3.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 159.3, 144.7, 133.6, 133.1, 132.2, 126.0, 126.0, 124.8, 124.3, 124.3, 122.4, 120.5, 110.0, 109.7, 103.1, 88.1, 27.0. HRMS (ESI): Exact mass calcd for $C_{18}H_{13}N_2O_3$ $[M+H]^+$: 305.0921, Found: 305.0929. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, retention time: t_{minor} = 34.650 min, t_{major}= 40.478 min, 89% ee).



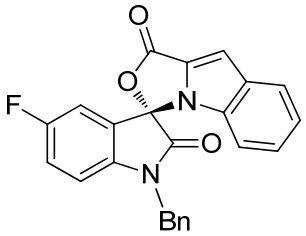
(*S*)-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5d). Yield: 79%, white solid, m.p. 319–321°C, $[\alpha]_D^{20}$ +11.712 (2.22 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (br s, 1H), 7.79 – 7.77 (m, 1H), 7.50 – 7.46 (m, 1H), 7.25 (d, J = 3.6 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.12 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.69 – 6.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 159.4, 141.7, 133.7, 133.1, 132.3, 126.4, 126.2, 124.6, 124.4, 124.3, 122.5, 120.6, 112.0, 110.2, 103.3, 88.4. HRMS (ESI): Exact mass calcd for $C_{17}H_{11}N_2O_3$ $[M+H]^+$: 291.0764, Found: 291.0768. HPLC (Chiralpak OJ column, *n*-hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, retention time: t_{minor} = 65.836 min, t_{major}= 100.513 min, 81% ee).



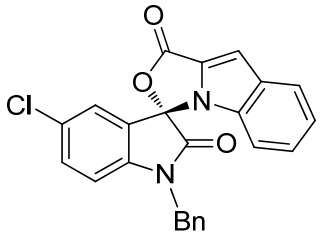
(*S*)-1-benzyl-5-methoxy-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5e). Yield 95%, white solid, m.p. 79–81°C, $[\alpha]_D^{20}$ +17.200 (2.50 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 1H), 7.34 (s, 5H), 7.25 (s, 1H), 7.23 – 7.13 (m, 2H), 6.96 (dd, J = 8.8, 2.4 Hz, 1H), 6.88 (d, J = 8.8 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 6.55 (d, J = 8.4 Hz, 1H), 5.08 (d, J = 15.6 Hz, 1H), 4.79 (d, J = 15.6 Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 159.3, 157.0, 136.7, 134.6, 133.2, 132.2, 129.0, 128.3, 127.7, 125.9, 124.7, 124.3, 122.4, 121.6, 118.6, 112.1, 111.6, 110.3, 103.1, 88.4, 55.8, 44.8. HRMS (ESI): Exact mass calcd for $C_{25}H_{19}N_2O_4$ $[M+H]^+$: 411.1339, Found: 411.1345. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 36.245 min, t_{major}= 43.935 min, 91% ee).



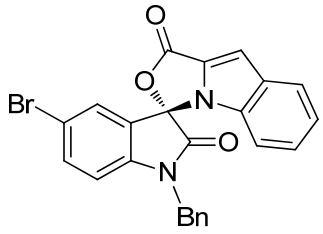
(*S*)-1-benzyl-5-methyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5f). Yield 86%, white solid, m.p. 126–128°C, $[\alpha]_D^{20}$ +18.667 (1.50 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 1H), 7.35 – 7.32 (m, 5H), 7.25 (s, 1H), 7.22 – 7.18 (m, 2H), 7.16 – 7.12 (m, 1H), 7.09 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 8.4 Hz, 1H), 5.08 (d, J = 15.2 Hz, 1H), 4.80 (d, J = 15.2 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 159.4, 141.3, 134.7, 134.2, 133.7, 133.2, 132.2, 129.0, 128.3, 127.7, 126.6, 125.9, 124.8, 124.3, 122.4, 120.5, 110.5, 110.3, 103.0, 88.3, 44.7, 20.8. HRMS (ESI): Exact mass calcd for $C_{25}H_{19}N_2O_3$ $[M+H]^+$: 395.1390, Found: 395.1398. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 51.752 min, t_{major}= 58.528 min, 89% ee).



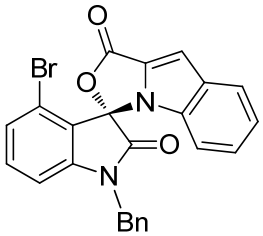
(*S*)-1-benzyl-5-fluoro-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5g). Yield 89%, white solid, m.p. 138–139°C, $[\alpha]_D^{20}$ +8.065 (3.10 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 7.35 (s, 5H), 7.25 – 7.13 (m, 4H), 7.03 (dd, J = 6.8, 2.4 Hz 1H), 6.92 (dd, J = 8.4, 4.0 Hz, 1H), 6.53 (d, J = 8.0 Hz, 1H), 5.11 (d, J = 15.2 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 159.6 (d, J = 244.4 Hz), 158.9, 139.6, 134.2, 133.2, 132.2, 129.2, 128.5, 127.7, 126.2, 124.5 (d, J = 14.4 Hz), 122.6, 122.2 (d, J = 7.6 Hz), 120.0 (d, J = 23.4 Hz), 114.1 (d, J = 25.1 Hz), 111.8 (d, J = 7.6 Hz), 110.1, 103.6, 87.7, 44.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ 116.8. HRMS (ESI): Exact mass calcd for $C_{24}H_{16}FN_2O_3$ $[M+H]^+$: 399.1139, Found: 399.1143. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 76.054 min, t_{major}= 86.255 min, 95% ee).



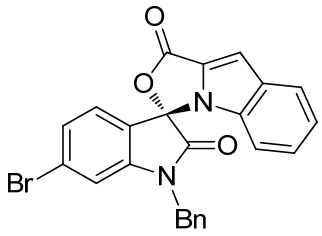
(*S*)-1-benzyl-5-chloro-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5h). Yield 77%, white solid, m.p. 173–175°C, $[\alpha]_D^{20}$ +21.250 (3.20 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 1H), 7.41 (dd, J = 8.4, 2.4 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.27 – 7.16 (m, 4H), 6.91 (d, J = 8.4 Hz, 1H), 6.53 (dd, J = 8.0, 0.8 Hz, 1H), 5.11 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 158.8, 142.2, 134.1, 133.4, 133.3, 132.2, 130.0, 129.2, 128.5, 127.7, 126.4, 126.2, 124.5, 124.5, 122.6, 122.3, 111.9, 110.1, 103.6, 87.6, 44.9. HRMS (ESI): Exact mass calcd for $C_{24}H_{16}ClN_2O_3$ $[M+H]^+$: 415.0844, Found: 415.0852. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major}= 35.290 min, t_{minor}= 40.449 min, 92% ee).



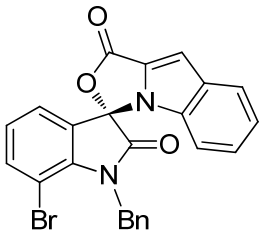
(*S*)-1-benzyl-5-bromo-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5i). Yield 76%, white solid, m.p. 204–206°C, $[\alpha]_D^{20}$ +22.400 (2.50 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.0, 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.27 – 7.16 (m, 3H), 6.86 (d, J = 8.4 Hz, 1H), 6.53 (d, J = 8.4 Hz, 1H), 5.10 (d, J = 15.2 Hz, 1H), 4.80 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 158.8, 142.7, 136.3, 134.1, 133.2, 132.2, 129.2, 128.5, 127.7, 126.2, 124.5, 124.5, 122.6, 122.6, 117.0, 112.3, 110.1, 103.6, 87.5, 44.8. HRMS (ESI): Exact mass calcd for $C_{24}H_{16}BrN_2O_3$ $[M+H]^+$: 459.0339, Found: 459.0350. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 35.104 min, t_{minor} = 43.441 min, 91% ee).



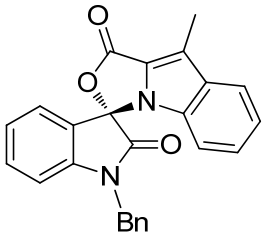
(*S*)-1-benzyl-4-bromo-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*α*]indole]-1',2-dione (5j). Yield 84%, white solid, m.p. 209–211°C, $[\alpha]_D^{20}$ +5.814 (4.30 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 7.36 – 7.30 (m, 5H), 7.28 – 7.23 (m, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.17 – 7.14 (m, 2H), 6.93 (d, J = 8.0 Hz, 1H), 6.52 (d, J = 8.4 Hz, 1H), 5.12 (d, J = 15.6 Hz, 1H), 4.85 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 159.2, 145.6, 134.4, 134.2, 133.0, 132.0, 129.2, 128.5, 128.1, 127.6, 126.0, 125.1, 124.5, 122.4, 121.4, 119.1, 109.7, 109.6, 103.3, 88.2, 44.8. HRMS (ESI): Exact mass calcd for $C_{24}H_{16}BrN_2O_3$ $[M+H]^+$: 459.0339, Found: 459.0345. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 55.242 min, t_{minor}= 60.951 min, 98% ee).



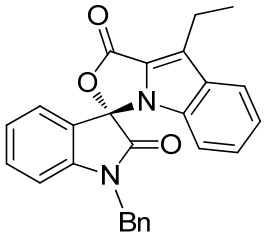
(*S*)-1-benzyl-6-bromo-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*α*]indole]-1',2-dione (5k). Yield 97%, white solid, m.p. 179–181°C, $[\alpha]_D^{20}$ +8.056 (3.60 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 7.45 – 7.33 (m, 5H), 7.28 – 7.24 (m, 2H), 7.22 – 7.13 (m, 4H), 6.53 (d, J = 8.4 Hz, 1H), 5.09 (d, J = 15.6 Hz, 1H), 4.79 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 159.0, 145.0, 134.0, 133.2, 132.2, 129.3, 128.6, 127.7, 127.6, 127.4, 127.344, 126.2, 124.6, 124.5, 122.6, 119.5, 114.3, 110.1, 103.6, 87.6, 44.9. HRMS (ESI): Exact mass calcd for $C_{24}H_{16}BrN_2O_3$ $[M+H]^+$: 459.0339, Found: 459.0344. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 38.879 min, t_{minor} = 46.936 min, 93% ee).



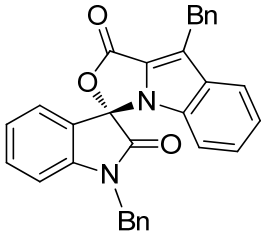
(*S*)-1-benzyl-7-bromo-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5l). Yield 60%, white solid, m.p. 204–206°C, $[\alpha]_D^{20}$ –4.516 (3.10 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 6.4, 2.4 Hz, 1H), 7.62 (dd, J = 8.4, 1.2 Hz, 1H), 7.33 – 7.28 (m, 5H), 7.26 – 7.17 (m, 4H), 6.99 (dd, J = 8.0, 7.6 Hz, 1H), 6.61 – 6.59 (m, 1H), 5.51 (d, J = 16.0 Hz, 1H), 5.42 (d, J = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 158.9, 141.5, 139.4, 135.9, 133.2, 132.2, 128.8, 127.8, 126.9, 126.2, 125.6, 125.4, 124.6, 124.5, 124.0, 122.6, 110.2, 104.0, 103.6, 87.0, 45.4. HRMS (ESI): Exact mass calcd for $C_{24}H_{16}BrN_2O_3$ $[M+H]^+$: 459.0339, Found: 459.0342. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{minor}= 16.816 min, t_{major} =33.712 min, 95% ee).



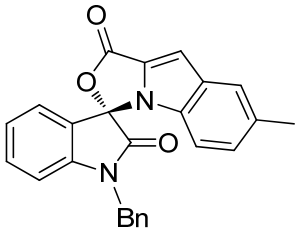
(*S*)-1-benzyl-9'-methyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5m). Yield 79%, white solid, m.p. 181–183°C, $[\alpha]_D^{20}$ +11.538 (2.60 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.35 – 7.34 (m, 5H), 7.28 (dd, J = 7.2, 0.8 Hz, 1H), 7.21 – 7.07 (m, 3H), 6.96 (d, J = 7.6 Hz, 1H), 6.47 (d, J = 8.4 Hz, 1H), 5.09 (d, J = 15.2 Hz, 1H), 4.82 (d, J = 15.6 Hz, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 159.8, 143.7, 134.6, 133.7, 133.3, 132.1, 129.0, 128.3, 127.6, 126.1, 126.0, 124.2, 122.4, 121.6, 121.5, 121.0, 115.8, 110.6, 110.2, 87.8, 44.6, 8.7. HRMS (ESI): Exact mass calcd for $C_{25}H_{19}N_2O_3$ $[M+H]^+$: 395.1390, Found: 395.1399. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{minor} = 9.828 min, t_{major}= 13.057 min, 90% ee).



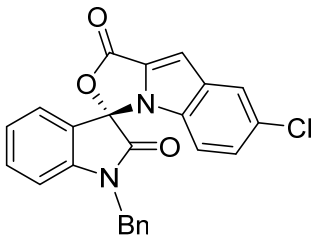
(*S*)-1-benzyl-9'-ethyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5n). Yield 98%, white solid, m.p. 193–195°C, $[\alpha]_D^{20}$ +11.786 (2.80 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.35 – 7.34 (m, 5H), 7.29 (dd, J = 7.6, 0.8 Hz, 1H), 7.19 – 7.07 (m, 3H), 6.96 (d, J = 8.0 Hz, 1H), 6.47 (d, J = 8.4 Hz, 1H), 5.10 (d, J = 15.2 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 3.14 – 3.08 (m, 2H), 1.48 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 159.7, 143.7, 134.6, 133.2, 132.9, 132.1, 129.0, 128.3, 127.7, 126.1, 125.9, 124.2, 122.7, 122.6, 121.6, 121.0, 121.0, 110.6, 110.2, 87.8, 44.6, 17.6, 14.9. HRMS (ESI): Exact mass calcd for $C_{26}H_{21}N_2O_3$ $[M+H]^+$: 409.1547, Found: 409.1558. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{minor} = 8.304 min, t_{major} = 10.102 min, 93% ee).



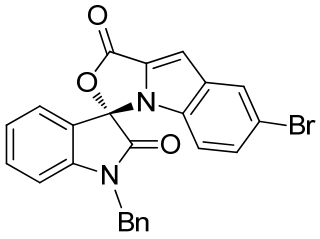
(*S*)-1,9'-dibenzyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5o). Yield 96%, white solid, m.p. 124–126°C, $[\alpha]_D^{20}$ +9.474 (1.90 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 1H), 7.45 – 7.39 (m, 3H), 7.35 – 7.24 (m, 8H), 7.21 – 7.17 (m, 1H), 7.12 – 7.07 (m, 3H), 6.96 (d, J = 8.0 Hz, 1H), 6.48 – 6.46 (m, 1H), 5.10 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.2 Hz, 1H), 4.48 (d, J = 15.6 Hz, 1H), 4.42 (d, J = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 159.7, 143.8, 139.6, 134.6, 133.3, 132.9, 132.4, 129.1, 128.7, 128.6, 128.3, 127.7, 126.3, 126.2, 126.0, 124.2, 122.9, 121.9, 120.8, 118.7, 110.7, 110.3, 88.0, 44.7, 30.1. HRMS (ESI): Exact mass calcd for $C_{31}H_{23}N_2O_3$ $[M+H]^+$: 471.1703, Found: 471.1712. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major}= 21.576 min, t_{minor} = 23.632 min, 93% ee).



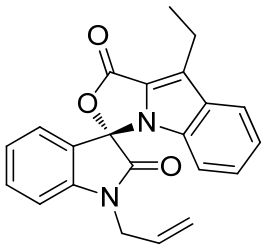
(*S*)-1-benzyl-7'-methyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5p). Yield 69%, white solid, m.p. 185–187°C, $[\alpha]_D^{20}$ +11.765 (1.70 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.46 – 7.41 (m, 1H), 7.36 – 7.35 (m, 5H), 7.27 (d, J = 0.4 Hz, 1H), 7.16 (d, J = 0.4 Hz, 1H), 7.11 – 7.07 (m, 1H), 6.97 (d, J = 8.0 Hz, 2H), 6.41 (d, J = 8.4 Hz, 1H), 5.11 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 159.4, 143.7, 134.6, 133.5, 133.4, 132.0, 130.7, 129.1, 128.3, 127.9, 127.6, 126.1, 124.8, 124.2, 123.6, 120.7, 110.7, 109.8, 102.6, 88.1, 44.7, 21.4. HRMS (ESI): Exact mass calcd for $C_{25}H_{19}N_2O_3$ $[M+H]^+$: 395.1390, Found: 395.1394. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major}= 66.593 min, t_{minor}= 87.849 min, 84% ee).



(*S*)-1-benzyl-7'-chloro-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5q). Yield 59%, white solid, mp 182–183.7 °C, $[\alpha]_D^{20}$ +122 (10 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.35 (m, 5H), 7.28 – 7.26 (m, 1H), 7.19 (s, 1H), 7.14 – 7.07 (m, 2H), 7.00 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 8.8 Hz, 1H), 5.12 (d, J = 15.2 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 158.8, 143.8, 134.5, 134.0, 133.7, 129.2, 128.5, 128.4, 127.7, 126.6, 126.1, 124.4, 123.6, 120.3, 111.2, 110.9, 102.5, 88.2, 44.8. HRMS (ESI): Exact mass calcd for $C_{24}H_{16}ClN_2O_3$ [M+H]: 415.0844, Found: 415.0848. HPLC (Chiralpak IA column, *n*-hexane/PrOH = 85/15, flow rate = 0.5 mL/min, retention time: t_{major} = 52.448 min, t_{minor}= 67.889 min, 90% ee).

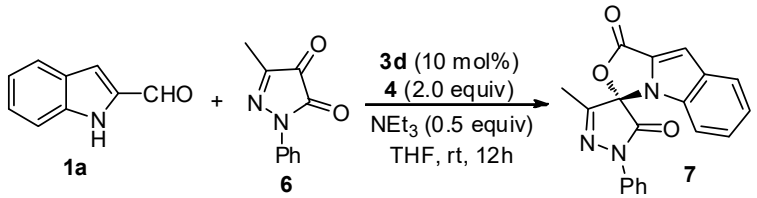


(*S*)-1-benzyl-7'-bromo-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5r). Yield 41%, white solid, m.p. 170–172 °C, $[\alpha]_D^{20}$ +12.857 (2.10 mg/mL in CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 1.6 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.36 – 7.35 (m, 5H), 7.28 (d, J = 0.04 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.18 (s, 1H), 7.14 – 7.10 (m, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.36 (d, J = 8.8 Hz, 1H), 5.12 (d, J = 15.2 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 158.8, 143.7, 134.6, 134.4, 133.7, 130.7, 129.1, 129.0, 128.5, 127.7, 126.8, 126.1, 125.9, 124.4, 120.2, 115.8, 111.5, 110.8, 102.3, 88.2, 44.8. HRMS (ESI): Exact mass calcd for $C_{24}H_{16}BrN_2O_3$ $[M+H]^+$: 459.0339, Found: 459.0345. HPLC (Chiralpak AD–H column, *n*-hexane/PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 82.805 min, t_{minor}= 92.921 min, 93% ee).



(*S*)-1-allyl-9'-ethyl-1'*H*-spiro[indoline-3,3'-oxazolo[3,4-*a*]indole]-1',2-dione (5s). Yield 97%, white solid, m.p. 124–126 °C, $[\alpha]_D^{20}$ +15.714 (2.80 mg/mL in CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.75 (m, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.18 – 7.11 (m, 3H), 7.06 (d, J = 8.0 Hz, 1H), 6.58 – 6.55 (m, 1H), 5.92 – 5.82 (m, 1H), 5.39 – 5.32 (m, 2H), 4.45 (dd, J = 16.4, 4.8 Hz, 1H), 4.35 (dd, J = 16.4, 5.6 Hz, 1H), 3.15 – 3.05 (m, 2H), 1.47 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 159.6, 143.9, 133.3, 132.9, 132.1, 130.3, 126.1, 126.0, 124.1, 122.6, 122.6, 121.5, 121.0, 121.0, 118.9, 110.5, 110.0, 87.7, 43.1, 17.6, 14.9. HRMS (ESI): Exact mass calcd for $C_{22}H_{19}N_2O_3$ $[M+H]^+$: 359.1390, Found: 359.1395. HPLC (Chiralpak AD–H column, *n*-hexane/ *i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{minor}= 12.810 min, t_{major} = 22.446 min, 94% ee).

4. General procedure for NHC-catalyzed annulation of indole-2-formaldehydes with 3-methyl-1-phenyl-1H-pyrazole-4,5-dione



To a dry Schlenk tube with a magnetic stirring bar was charged 1*H*-indole-2-carbaldehyde (**1a**) (0.2 mmol), 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dione (**6**) (0.1 mmol), NHC precatalyst **3d** (0.01 mmol, 4.6 mg), and quinone **4** (0.2 mmol, 81.8 mg), a solution of Et_3N (0.05 mmol) in dry THF (1 mL) was added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h (monitored by TLC). The solvent was removed in *vacuo* and the residue was purified by chromatography on silica gel using hexanes/EtOAc (6:1) as eluent to afford the desired product **7**.

(*S*)-3'-methyl-1'-phenyl-1*H*-spiro[oxazolo[3,4-*a*]indole-3,4'-pyrazole]-1,5'(1'*H*)-dione (**7**). Yield 51%, white solid, m.p. 129.5–130.2°C, $[\alpha]_D^{20}$ –107.00 (10 mg/mL in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.83 (d, J = 8.4 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.39 – 7.35 (m, 1H), 7.32 – 7.28 (m, 3H), 7.04 (dd, J = 8.4, 0.8 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 157.9, 154.1, 136.9, 133.1, 132.1, 129.2, 127.2, 126.3, 124.7, 123.2, 122.8, 118.6, 109.5, 104.7, 87.3, 12.2. HRMS (ESI): Exact mass calcd for $C_{19}H_{13}N_3O_3$ $[M+H]^+$: 332.1030, Found: 332.1039. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 12.980 min, t_{minor}= 15.910 min, 43% ee).

5. References

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(2) Vora, H. U.; Lathrop, S. P.; Reynolds, N. T.; Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *Org. Synth.* **2010**, *87*, 350.

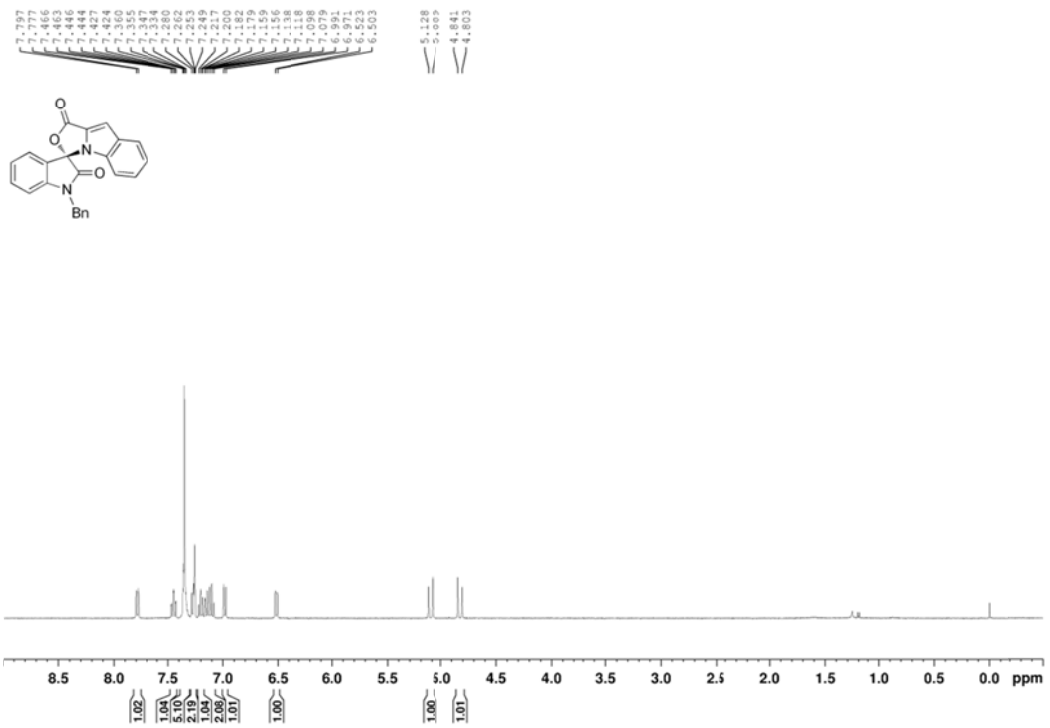
(3) Zhao, C.; Li, F.; Wang, J. *Angew. Chem., Int. Ed.* **2016**, *55*, 1820

(4) Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *J. Org. Chem.* **2005**, *70*, 5725.

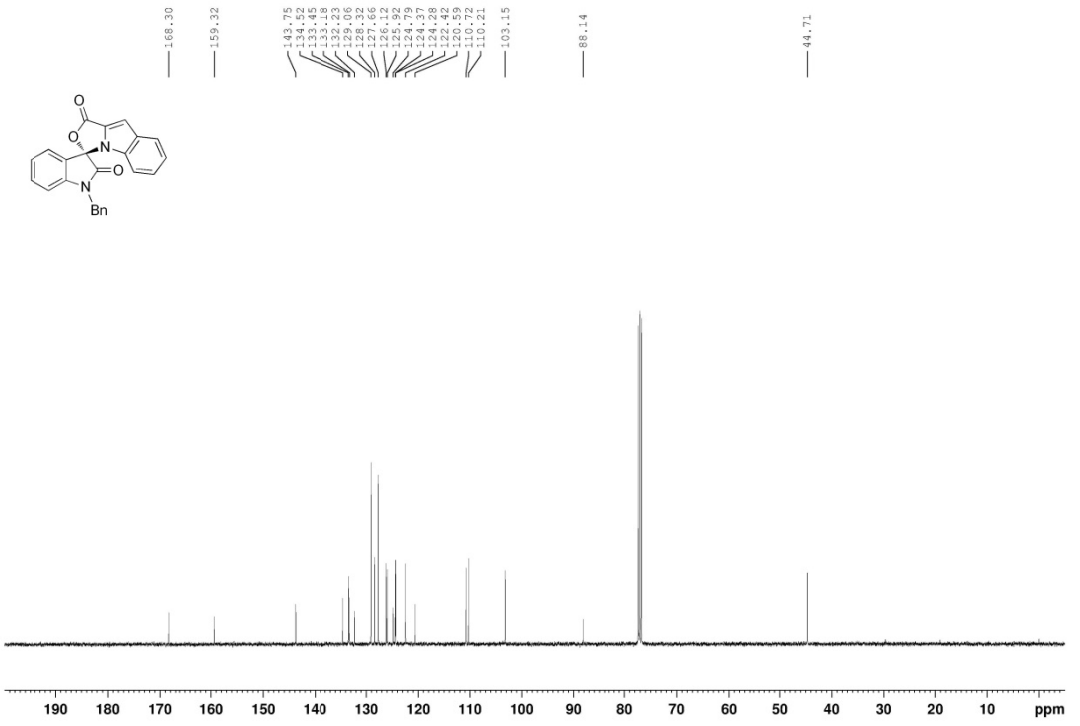
(5) Zheng, C.; Lu, Y.; Zhang, J.; Chen, X.; Chai, Z.; Ma, W.; Zhao, G. *Chem. Eur. J.* **2010**, *16*, 5853.

6. NMR spectra of the compounds 5a−5s and 7

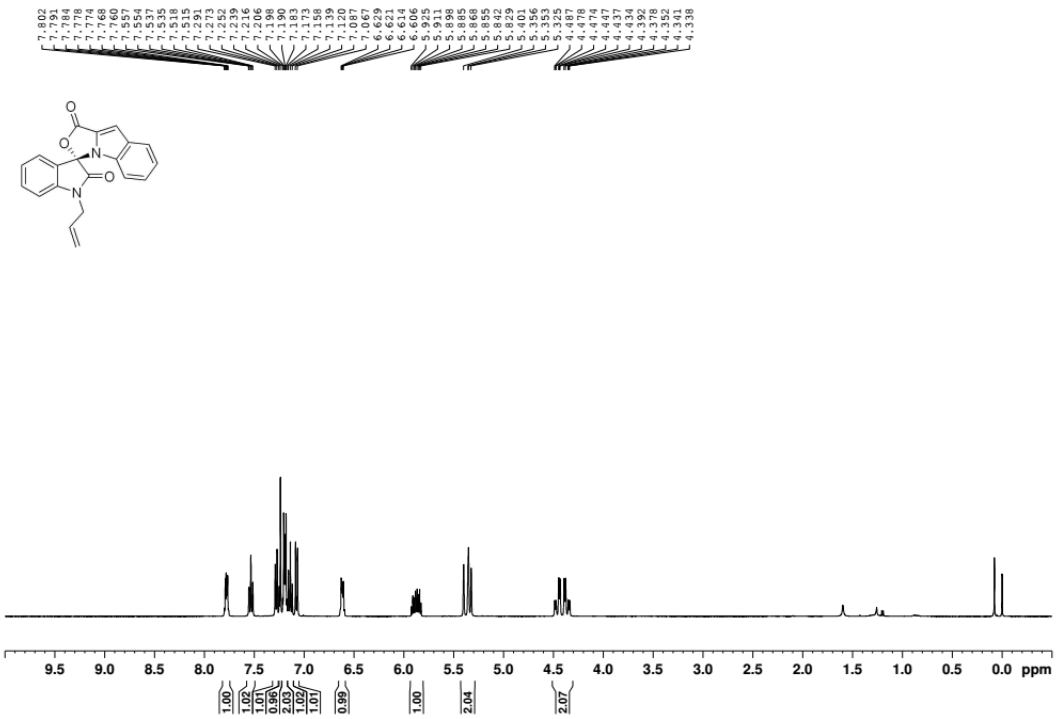
^{1}H NMR spectrum of compound **5a** ($CDCl_3$, 400 MHz)



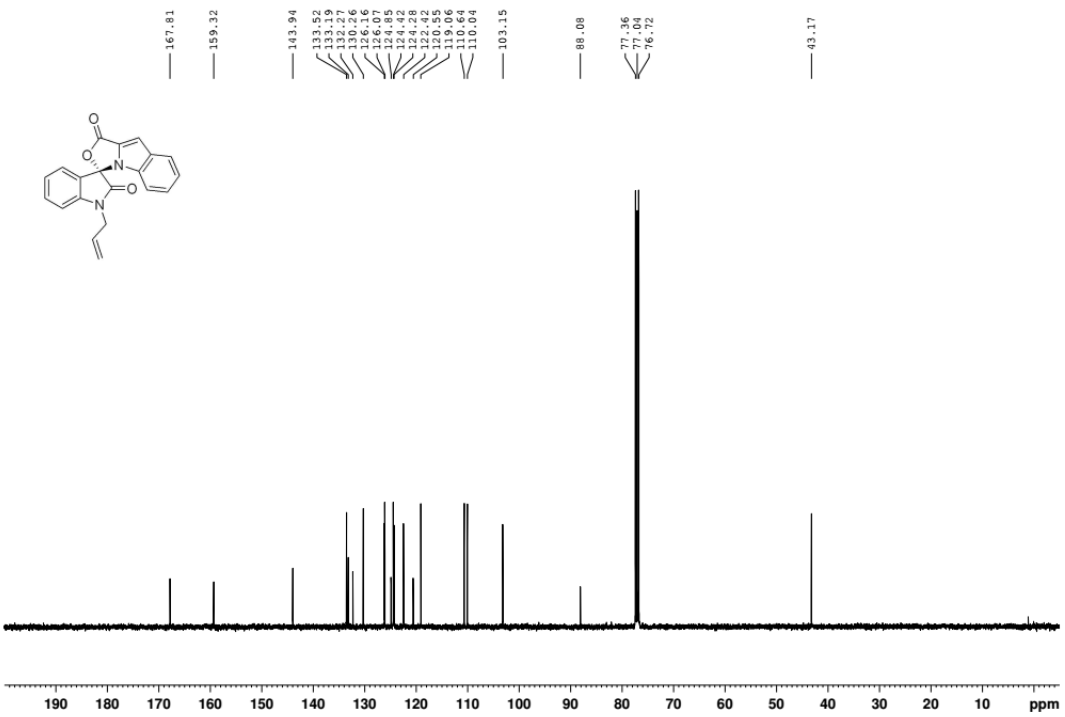
^{13}C NMR spectrum of compound **5a** ($CDCl_3$, 100 MHz)



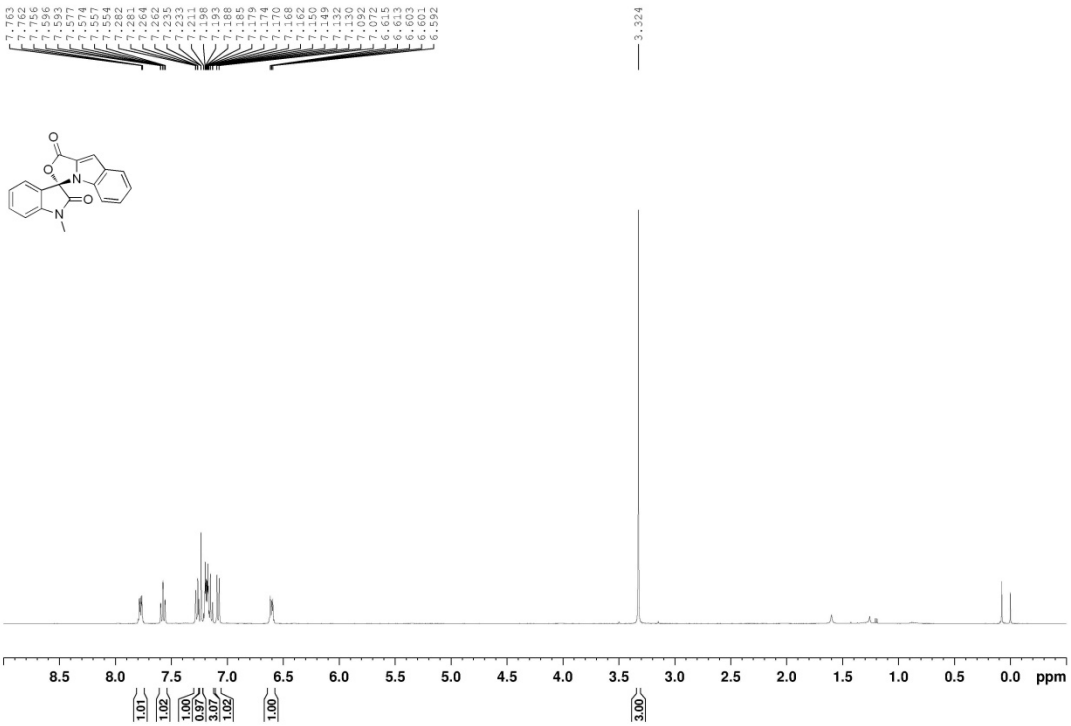
^{1}H NMR spectrum of compound **5b** ($CDCl_3$, 400 MHz)



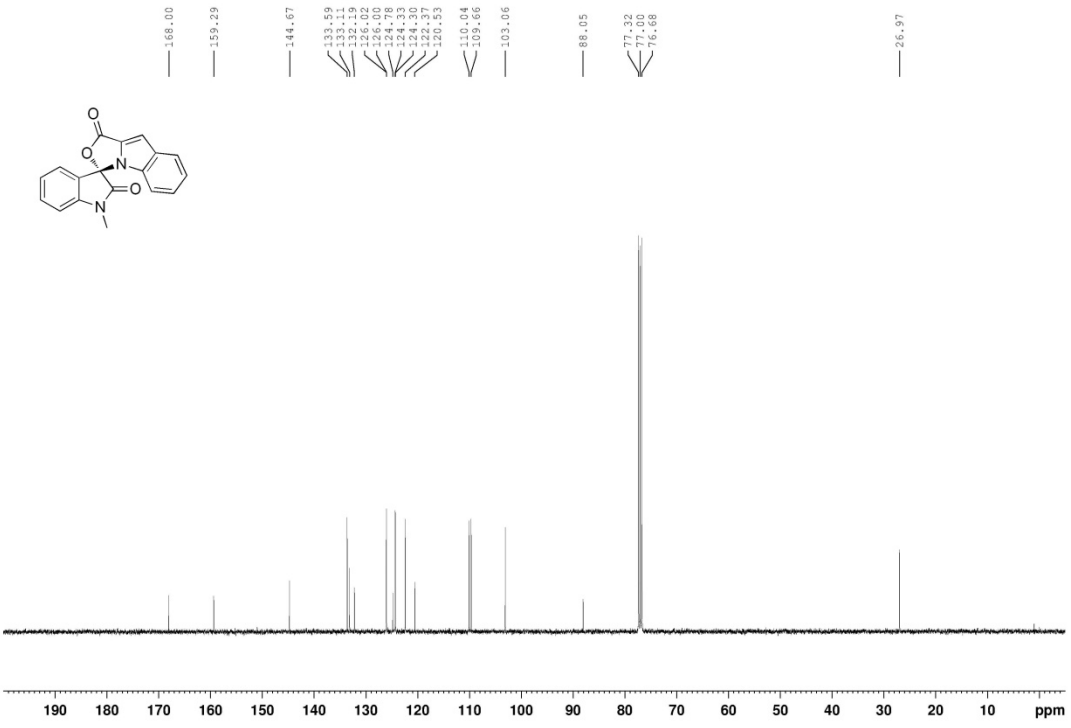
^{13}C NMR spectrum of compound **5b** ($CDCl_3$, 100 MHz)



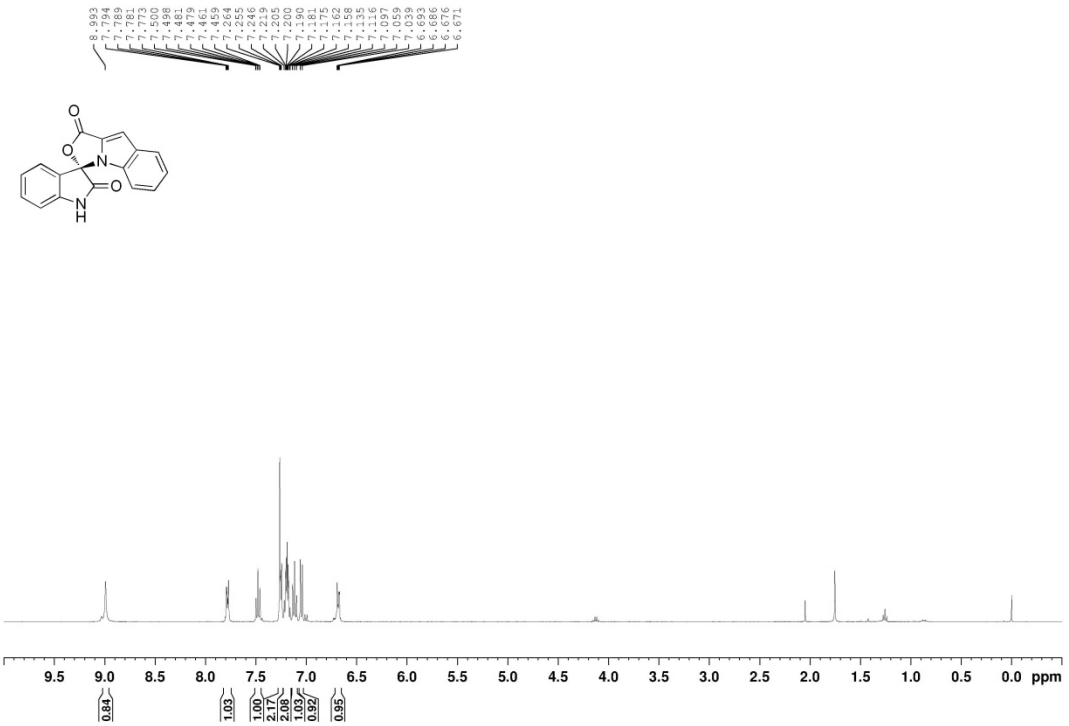
^{1}H NMR spectrum of compound **5c** ($CDCl_3$, 400 MHz)



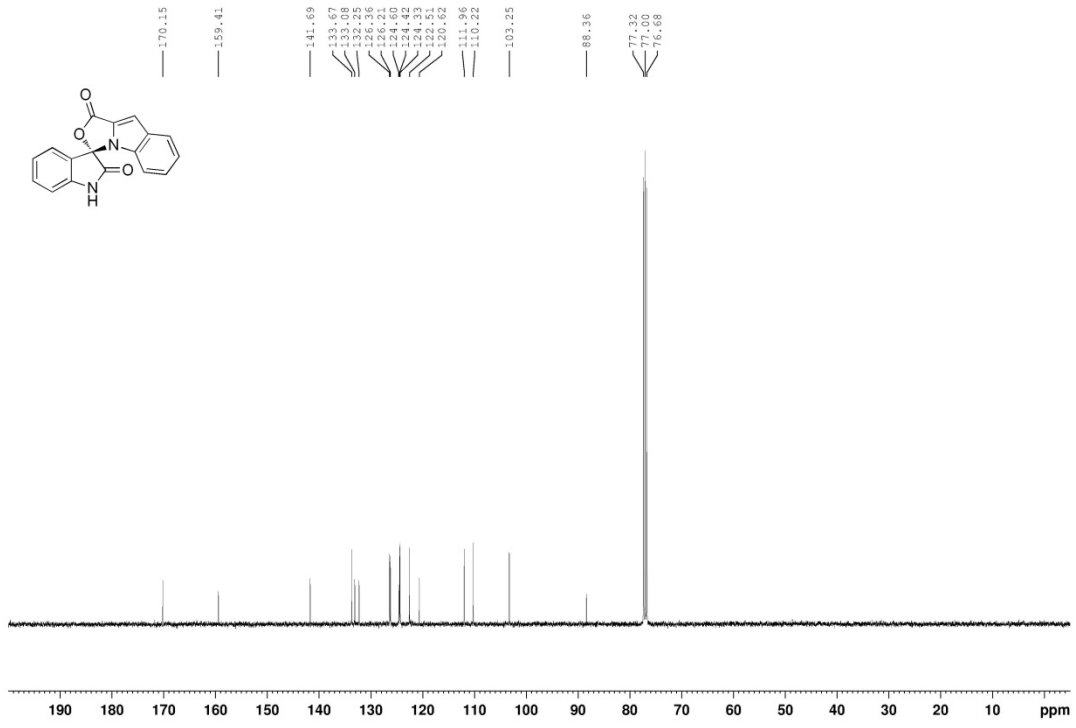
^{13}C NMR spectrum of compound **5c** ($CDCl_3$, 100 MHz)



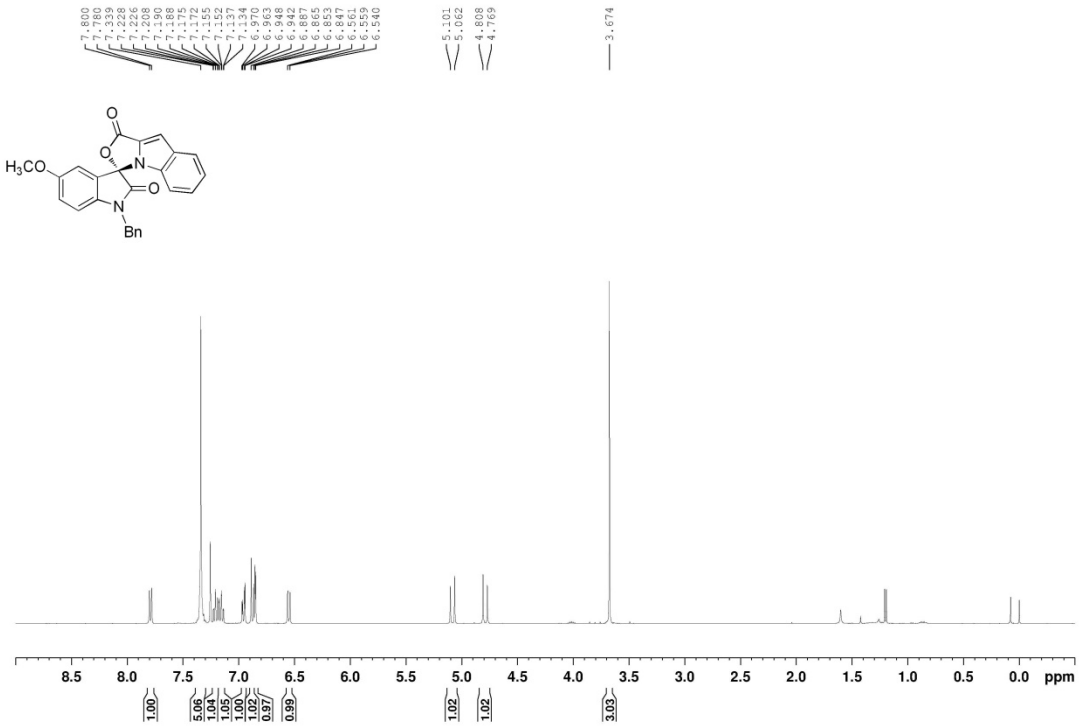
^{1}H NMR spectrum of compound **5d** ($CDCl_3$, 400 MHz)



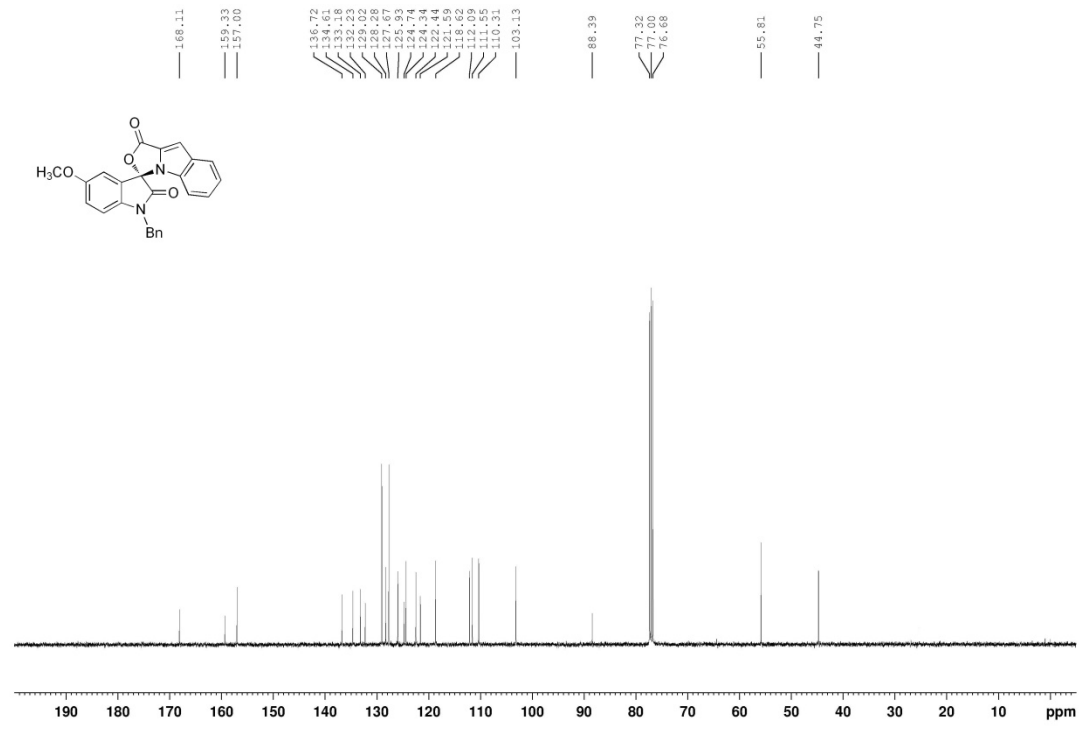
^{13}C NMR spectrum of compound **5d** ($CDCl_3$, 100 MHz)



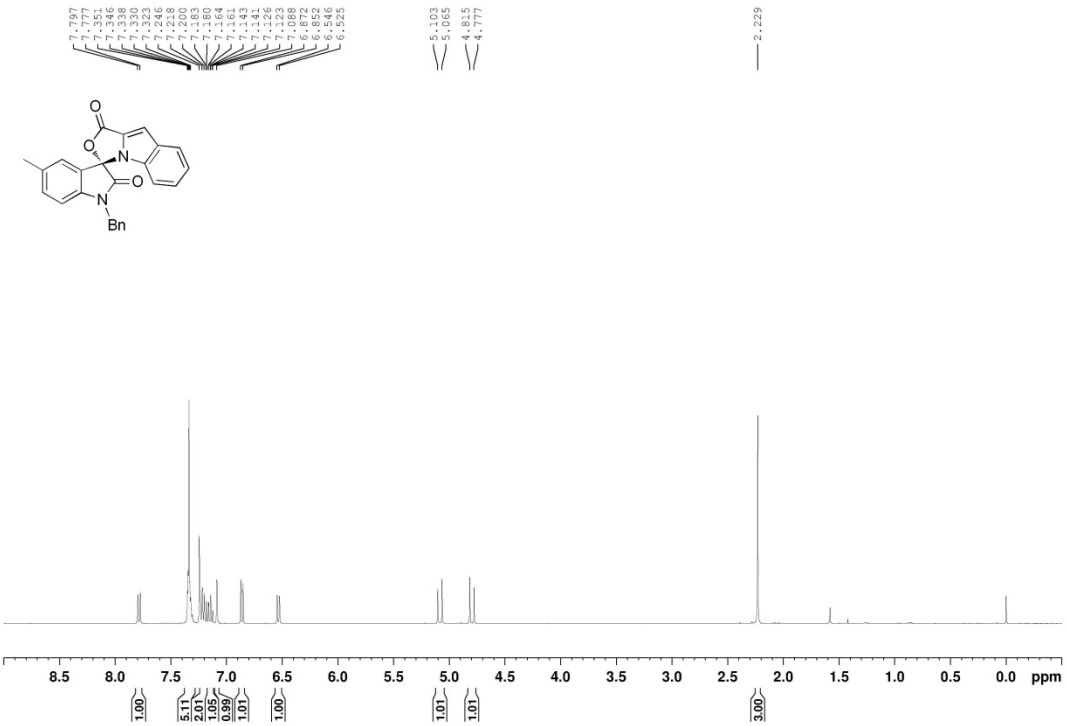
^{1}H NMR spectrum of compound **5e** ($CDCl_3$, 400 MHz)



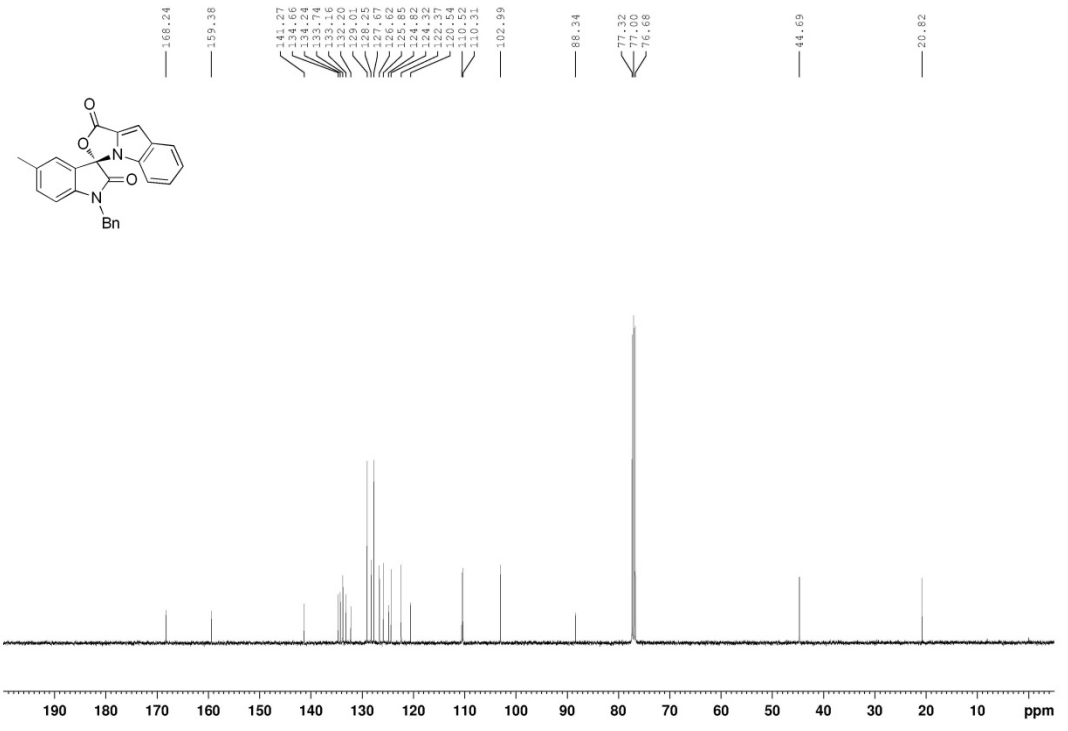
^{13}C NMR spectrum of compound **5e** ($CDCl_3$, 100 MHz)



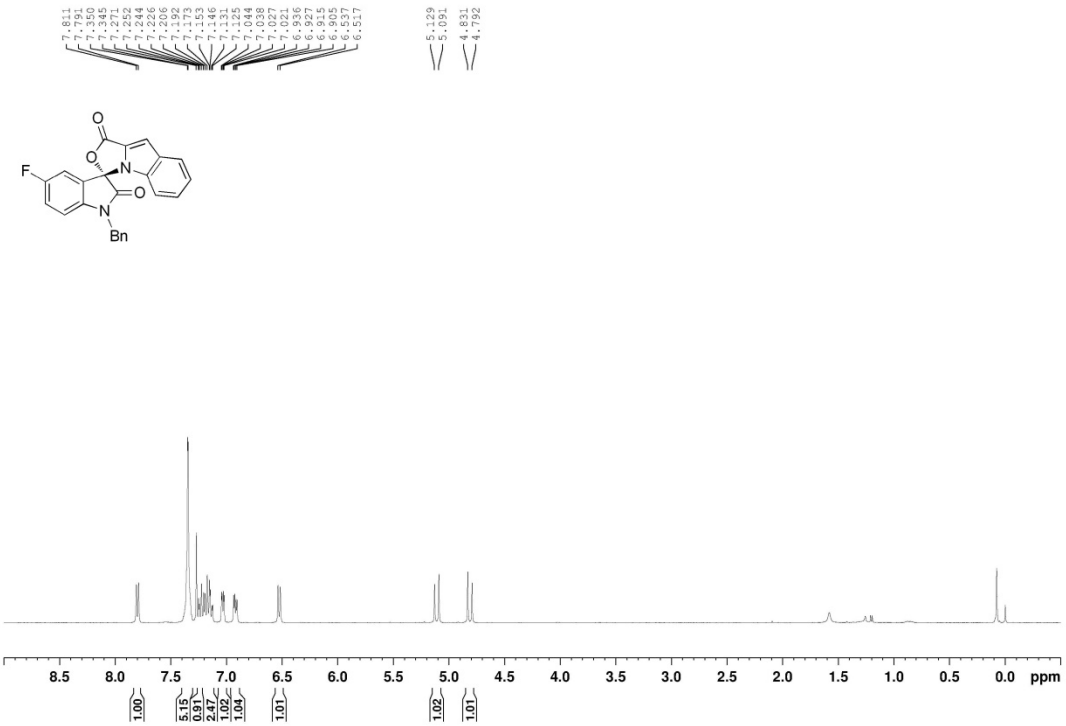
^{1}H NMR spectrum of compound **5f** ($CDCl_3$, 400 MHz)



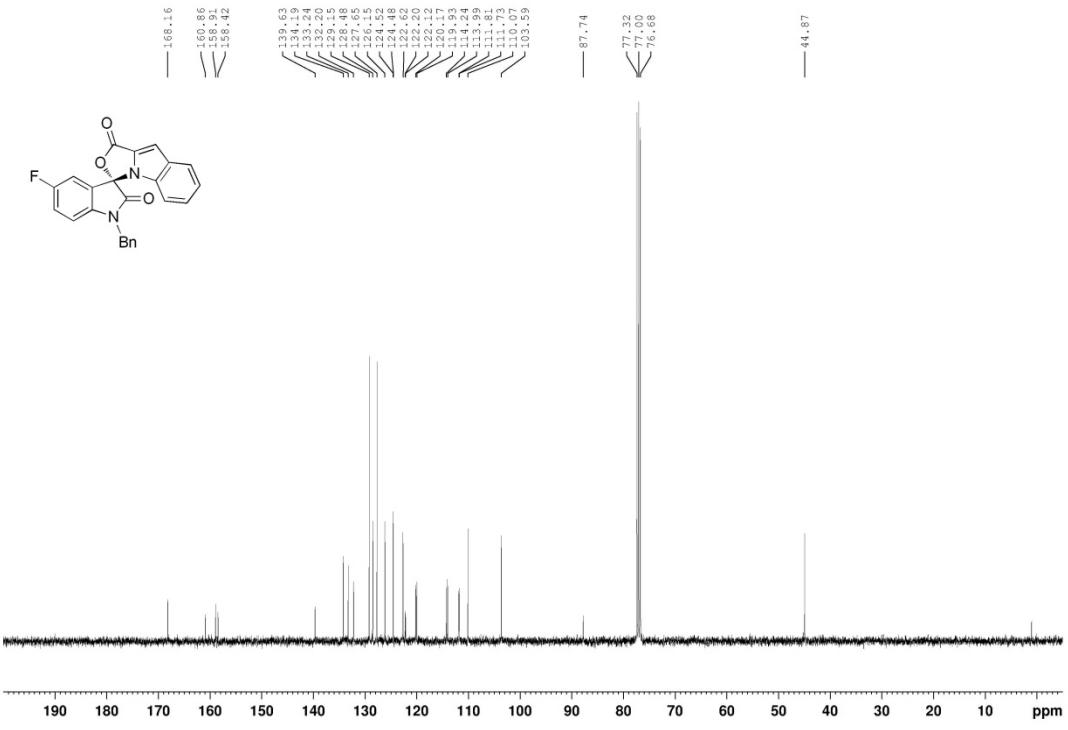
^{13}C NMR spectrum of compound **5f** ($CDCl_3$, 100 MHz)



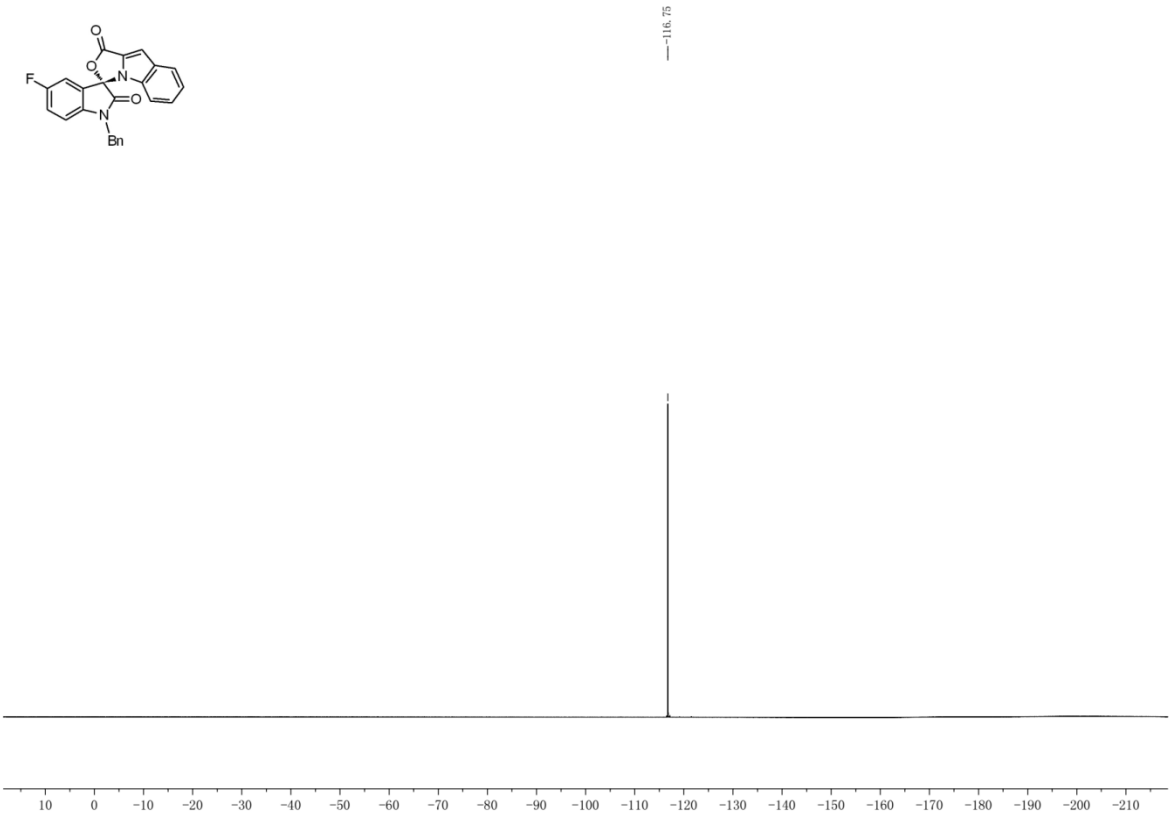
^{1}H NMR spectrum of compound **5g** ($CDCl_3$, 400 MHz)



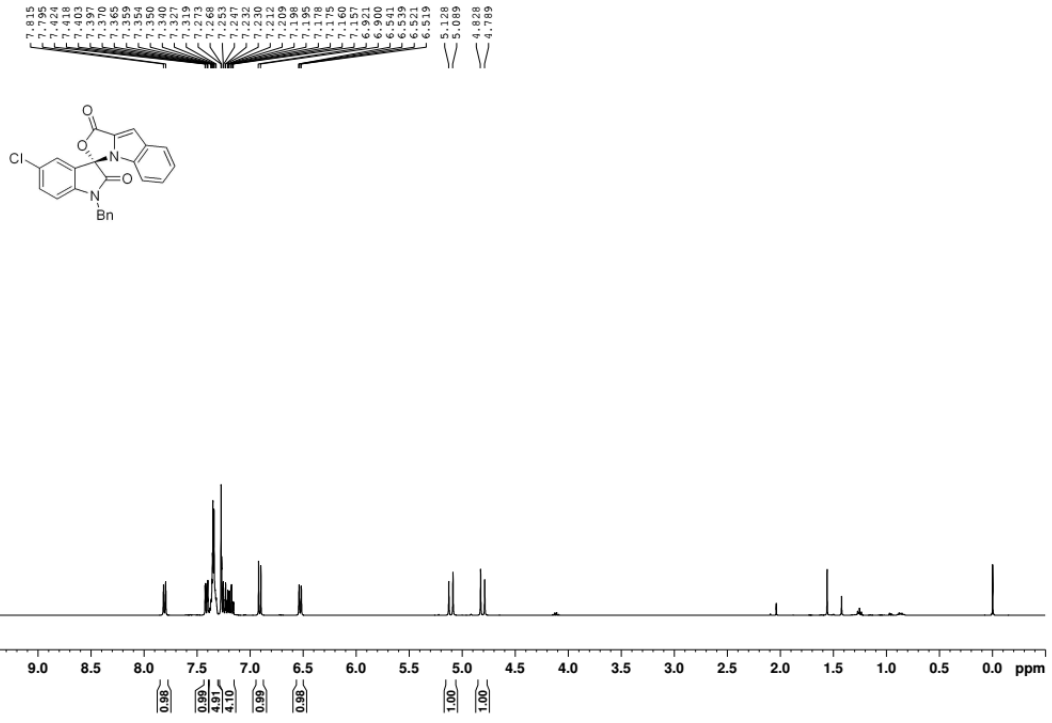
^{13}C NMR spectrum of compound **5g** ($CDCl_3$, 100 MHz)



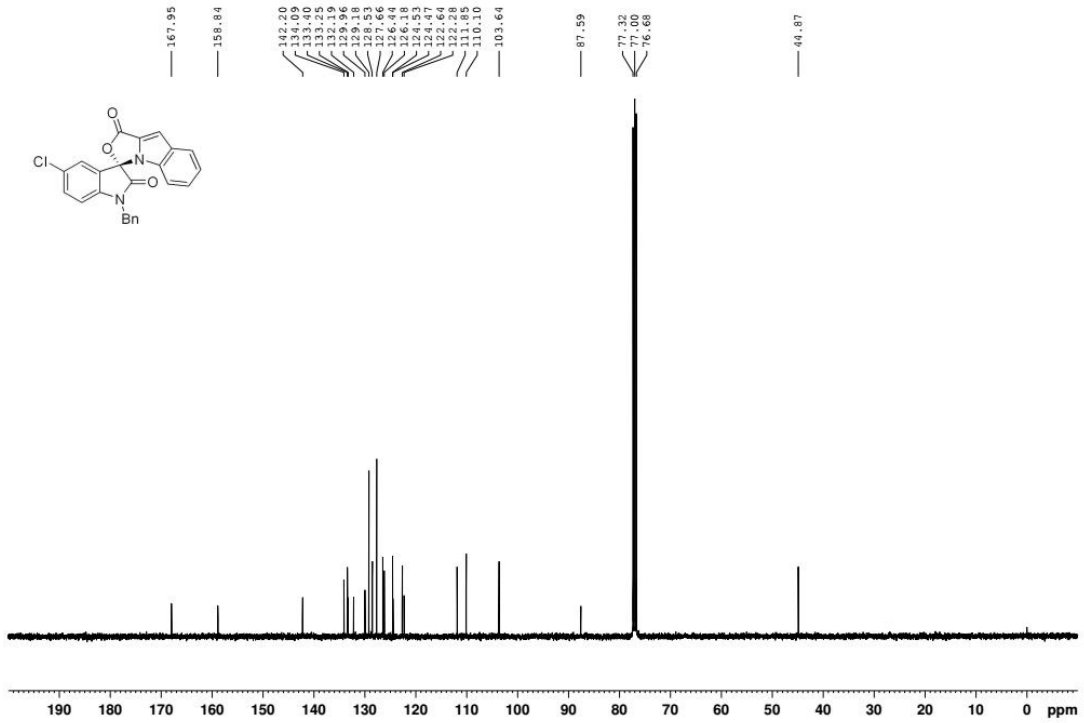
^{19}F NMR spectrum of compound **5g** ($CDCl_3$, 376 MHz)



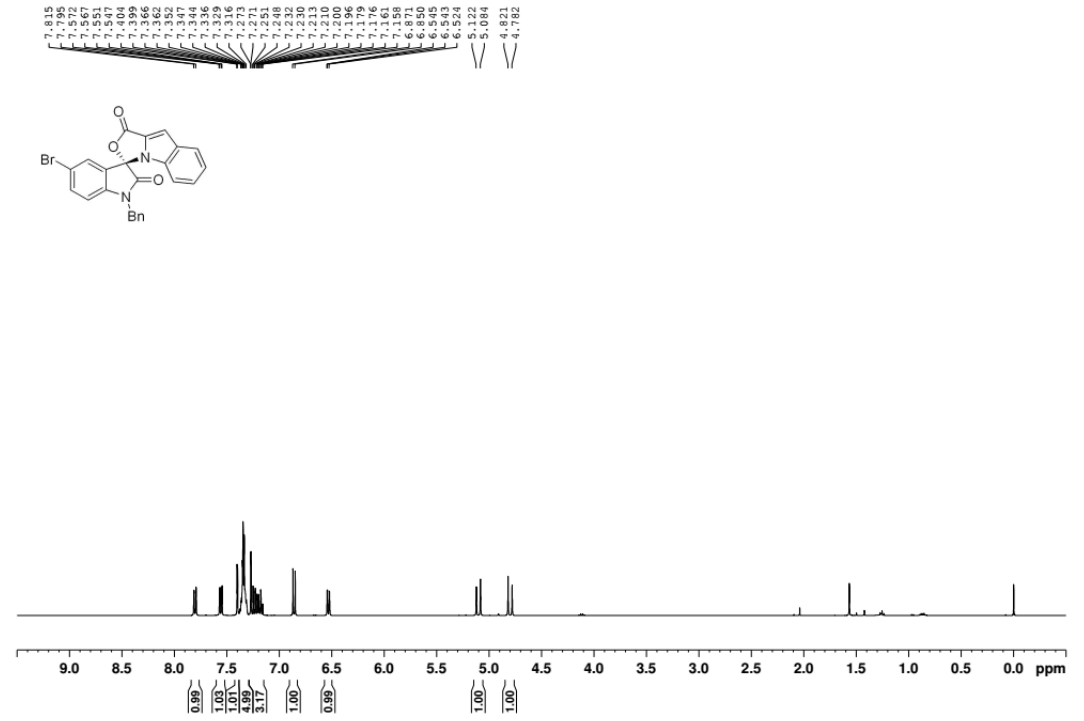
^{1}H NMR spectrum of compound **5h** ($CDCl_3$, 400 MHz)



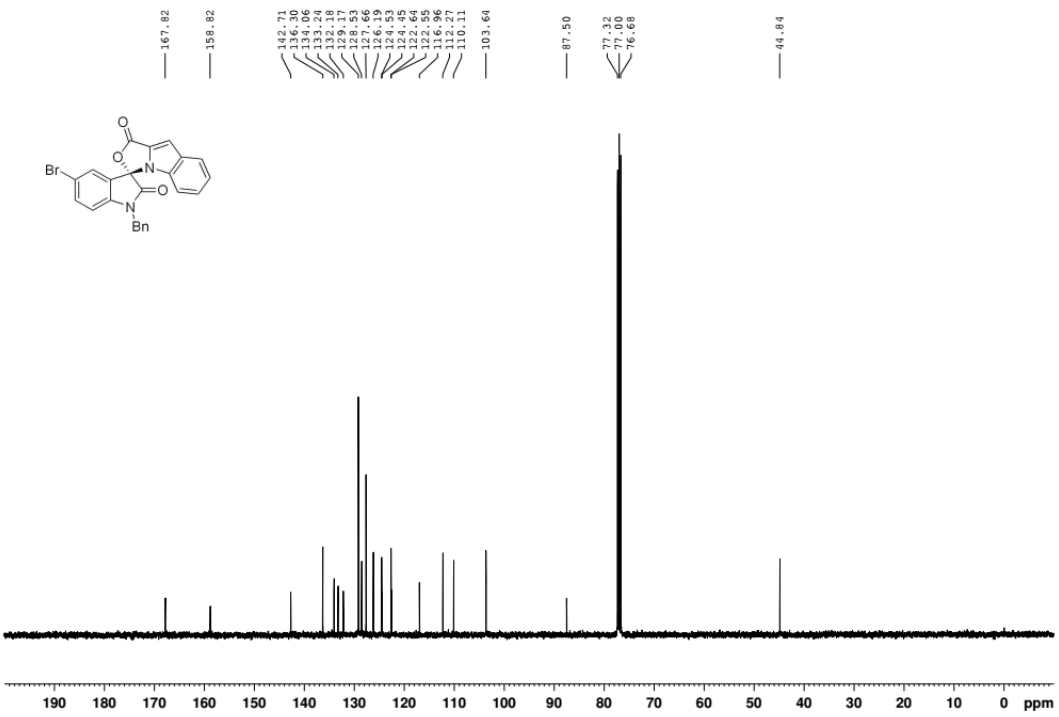
^{13}C NMR spectrum of compound **5h** ($CDCl_3$, 100 MHz)



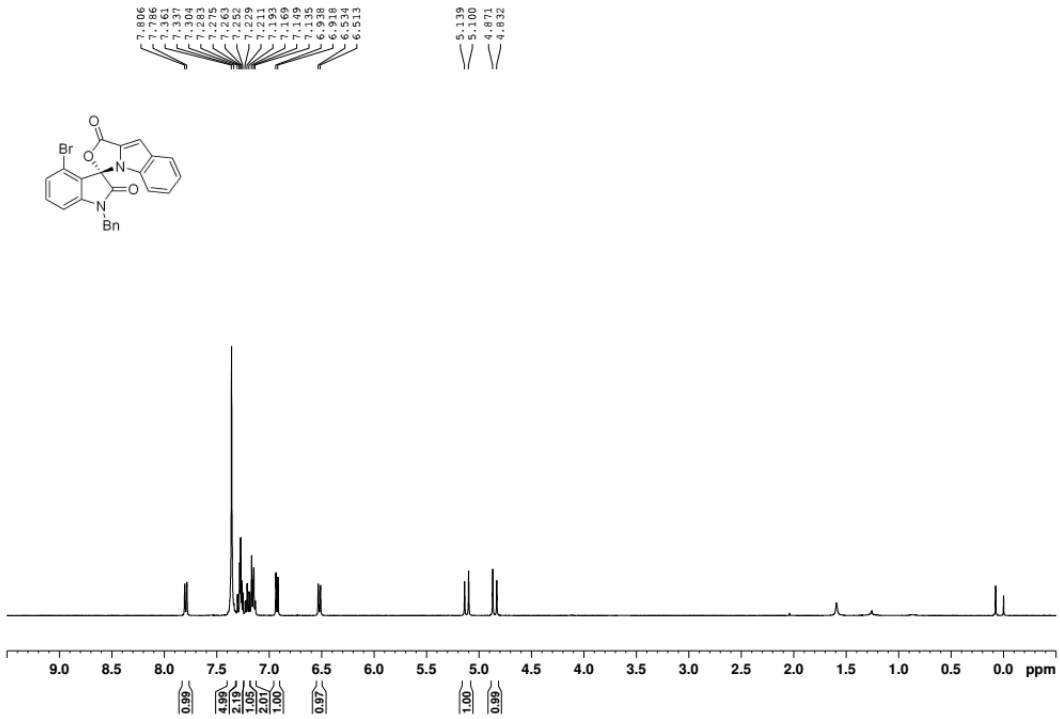
^{1}H NMR spectrum of compound **5i** ($CDCl_3$, 400 MHz)



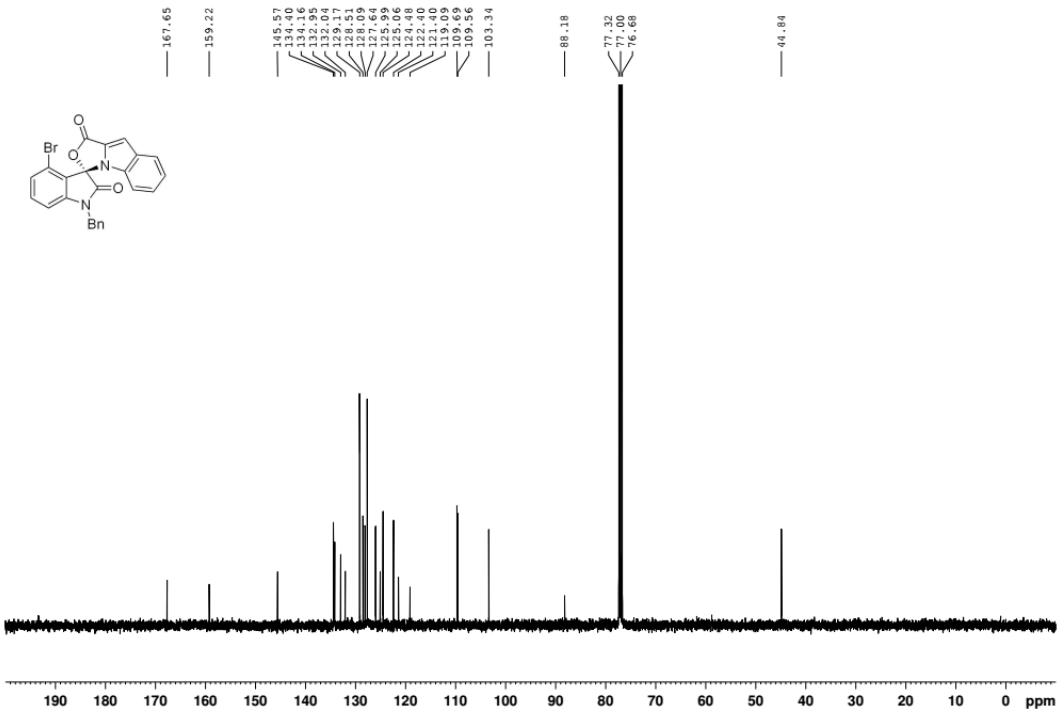
^{13}C NMR spectrum of compound **5i** ($CDCl_3$, 100 MHz)



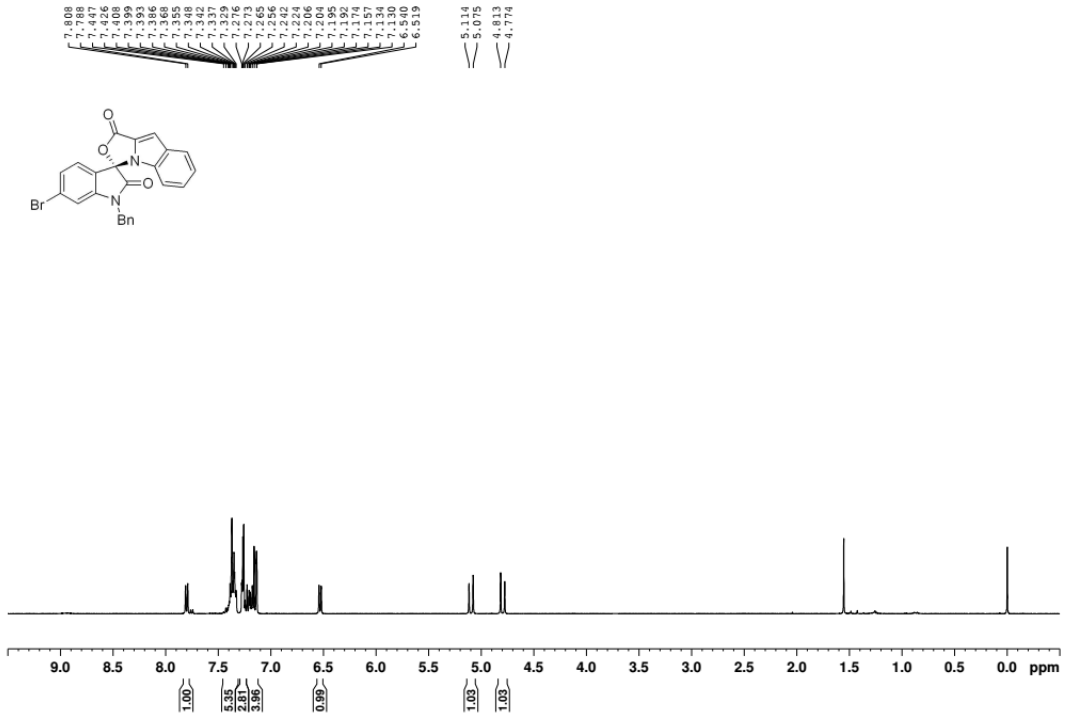
^{1}H NMR spectrum of compound **5j** ($CDCl_3$, 400 MHz)



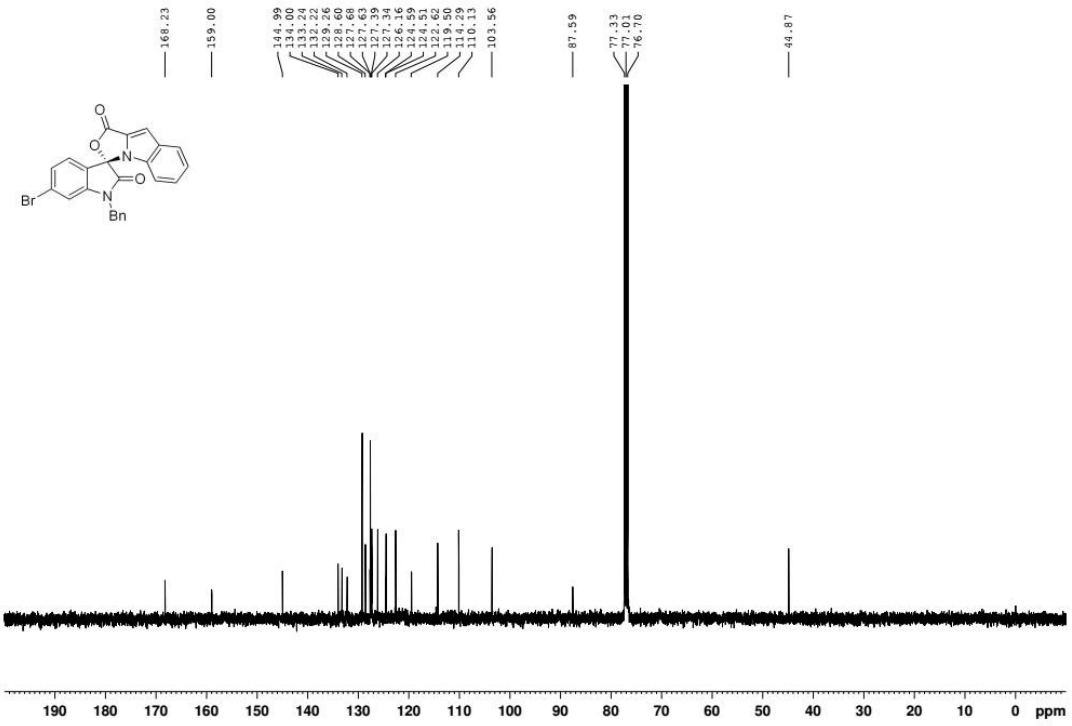
^{13}C NMR spectrum of compound **5j** ($CDCl_3$, 100 MHz)



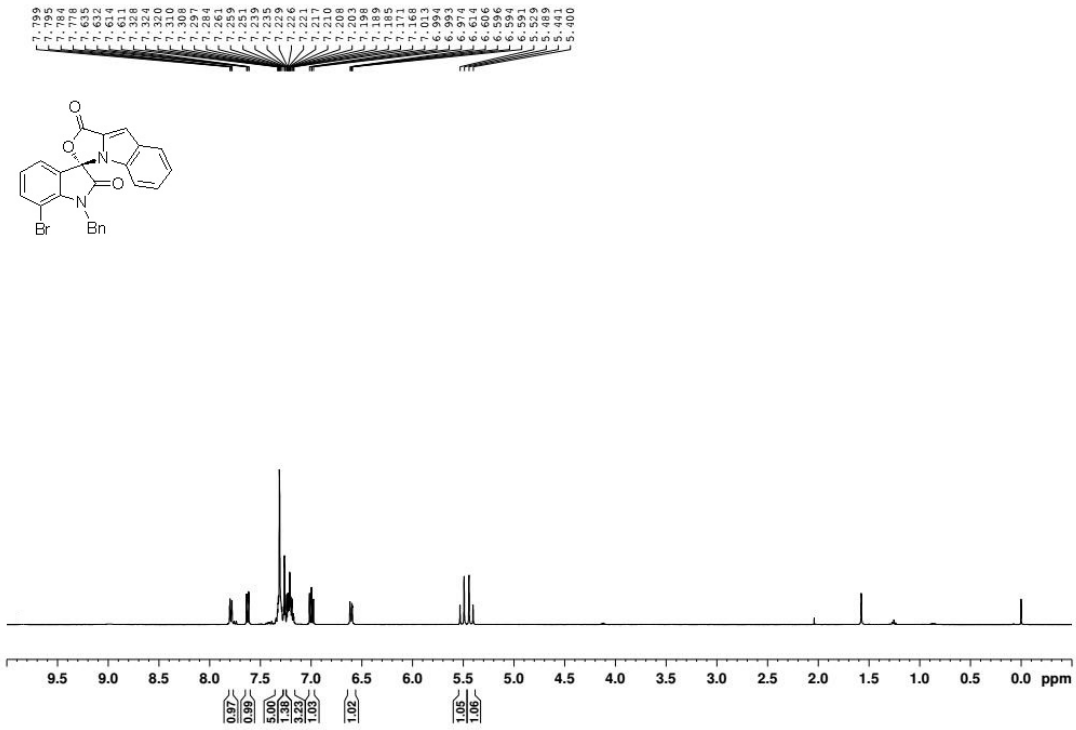
^{1}H NMR spectrum of compound **5k** ($CDCl_3$, 400 MHz)



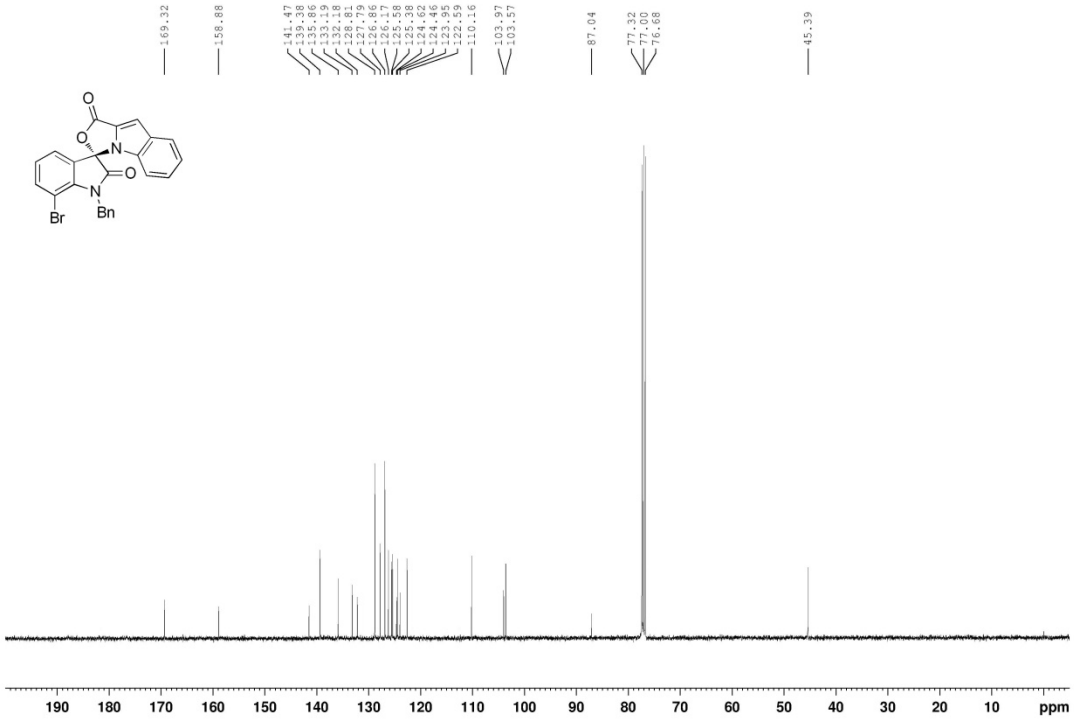
^{13}C NMR spectrum of compound **5k** ($CDCl_3$, 100 MHz)



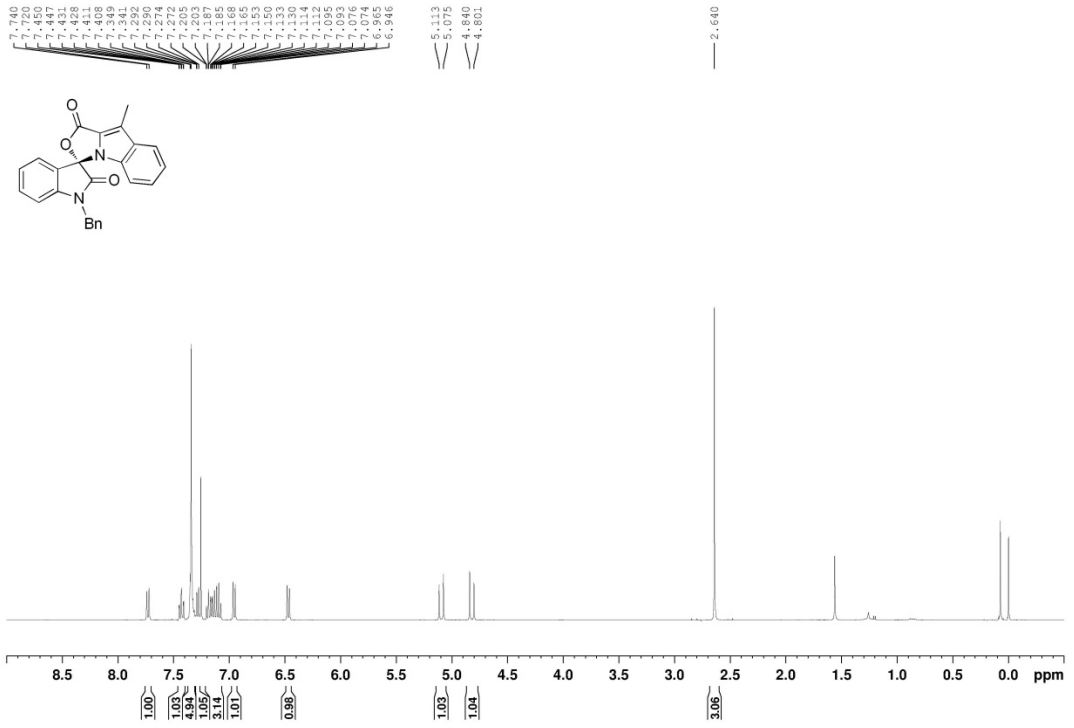
^{1}H NMR spectrum of compound **5l** ($CDCl_3$, 400 MHz)



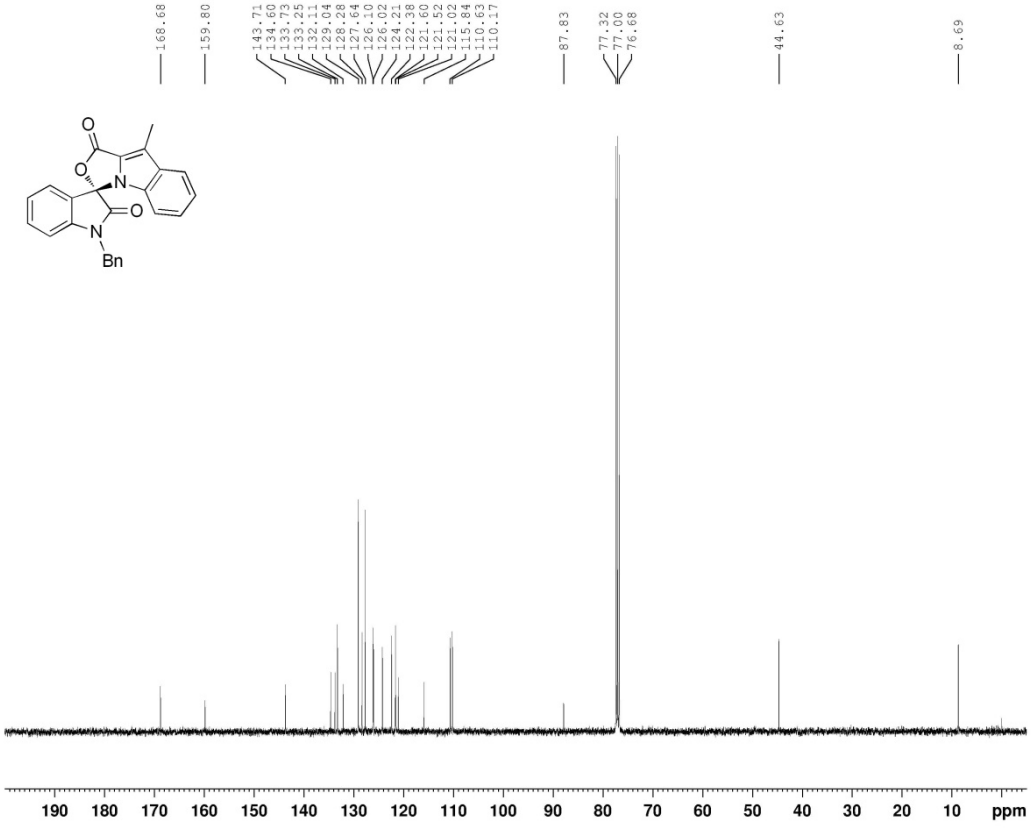
^{13}C NMR spectrum of compound **5l** ($CDCl_3$, 100 MHz)



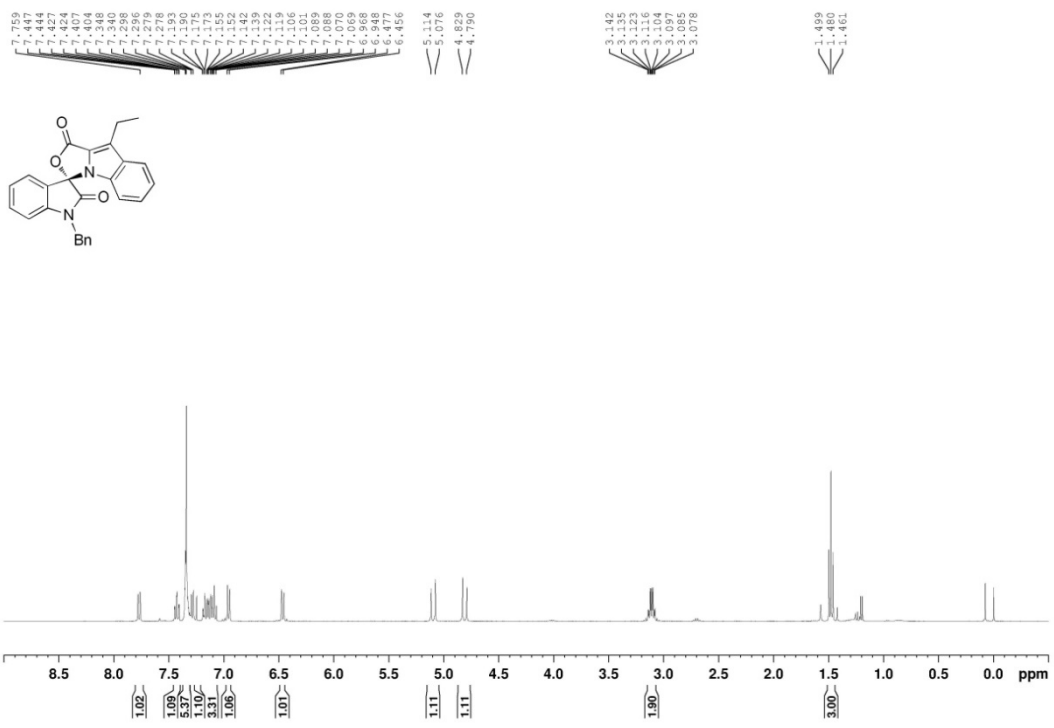
^{1}H NMR spectrum of compound **5m** ($CDCl_3$, 400 MHz)



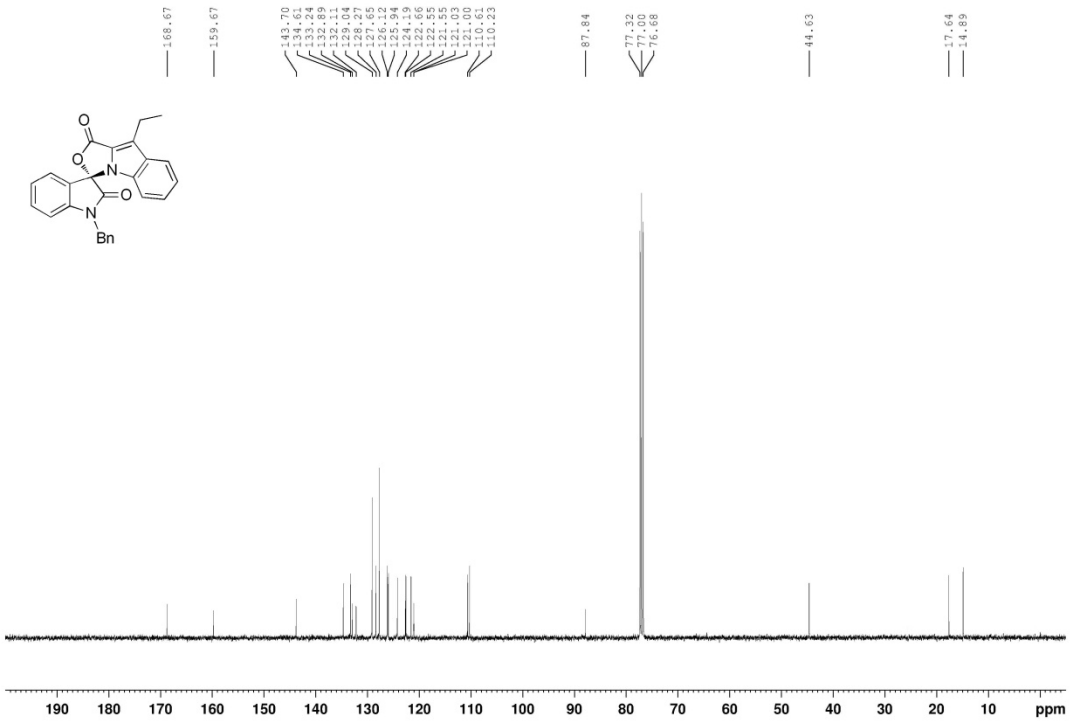
^{13}C NMR spectrum of compound **5m** ($CDCl_3$, 100 MHz)



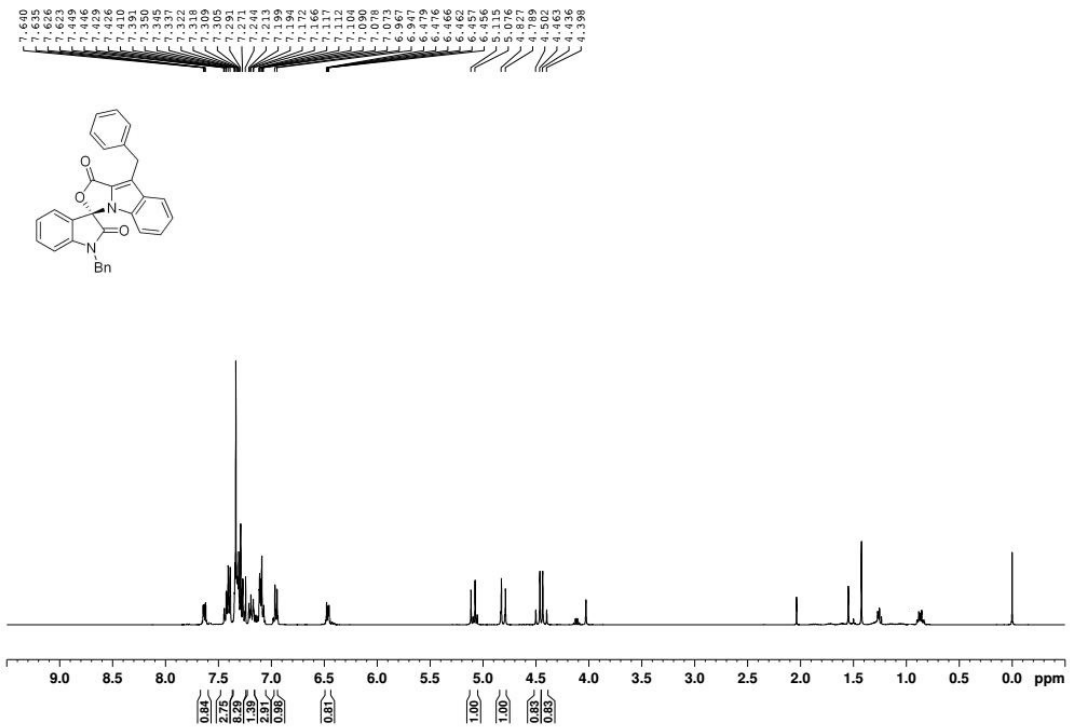
^{1}H NMR spectrum of compound **5n** ($CDCl_3$, 400 MHz)



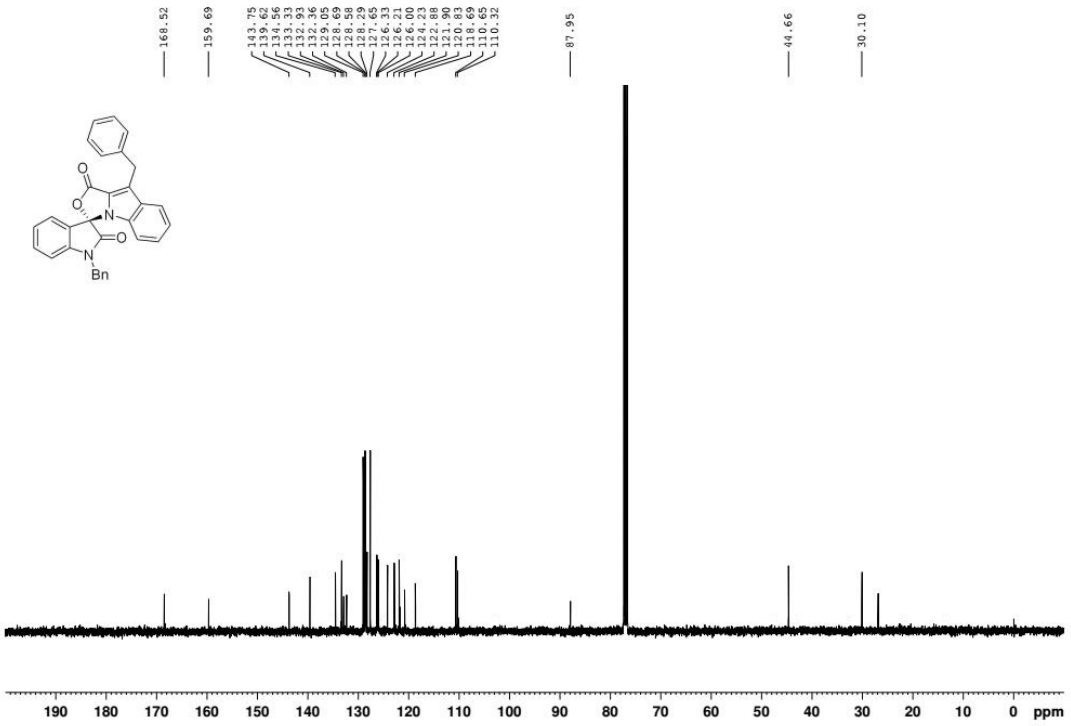
^{13}C NMR spectrum of compound **5n** ($CDCl_3$, 100 MHz)



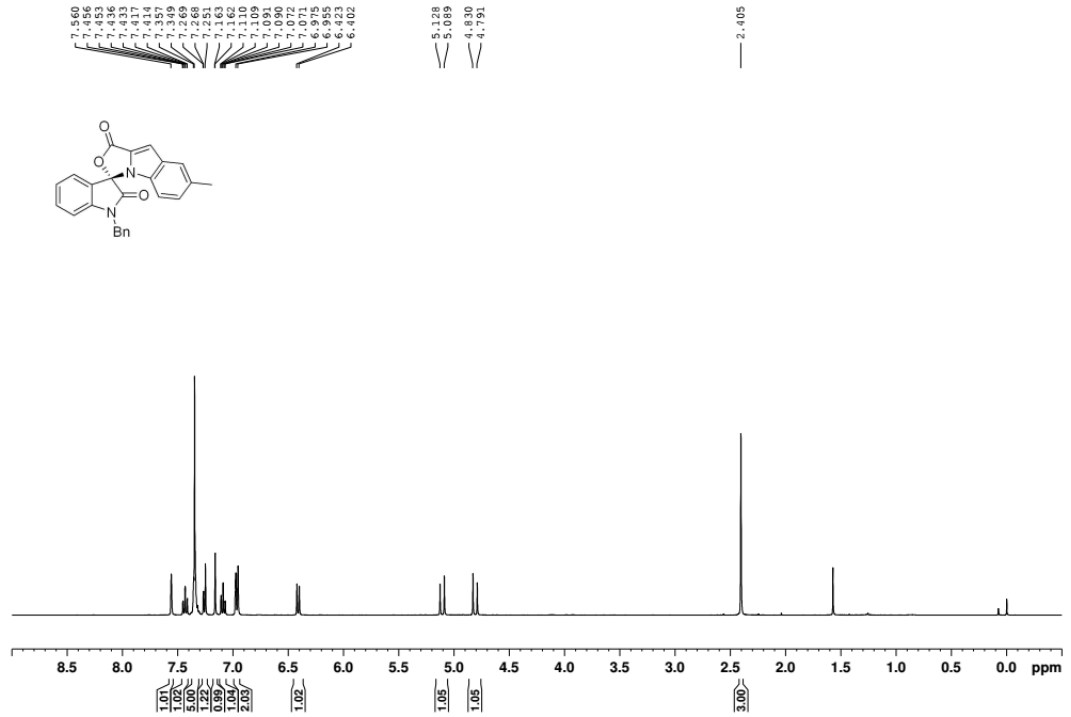
^{1}H NMR spectrum of compound **5o** ($CDCl_3$, 400 MHz)



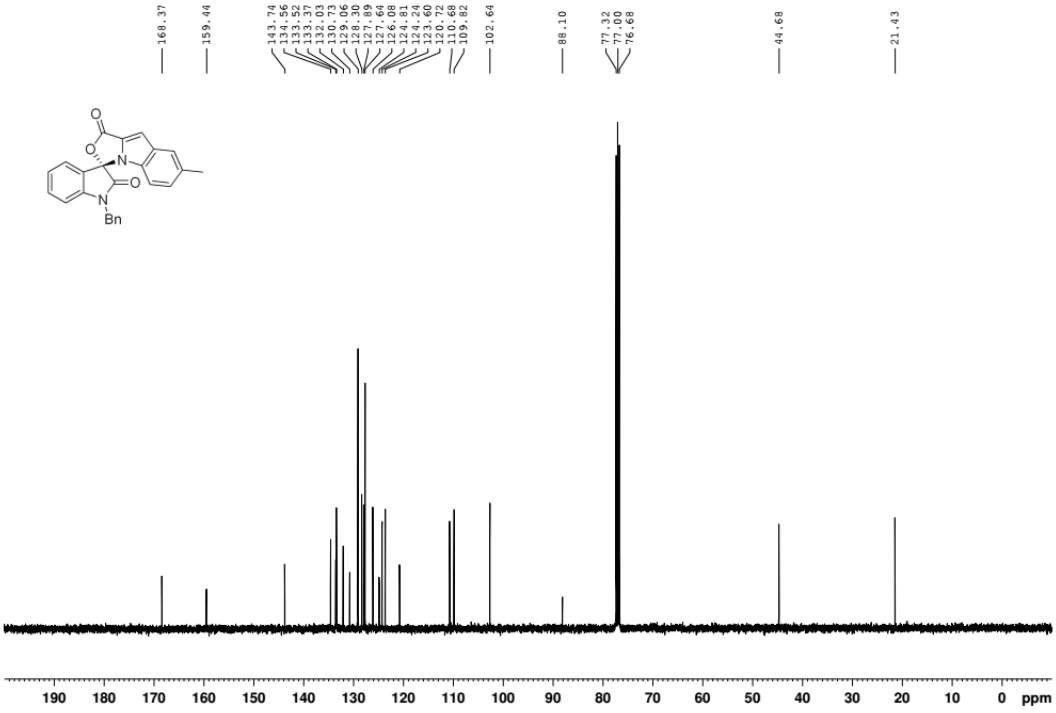
^{13}C NMR spectrum of compound **5o** ($CDCl_3$, 100 MHz)



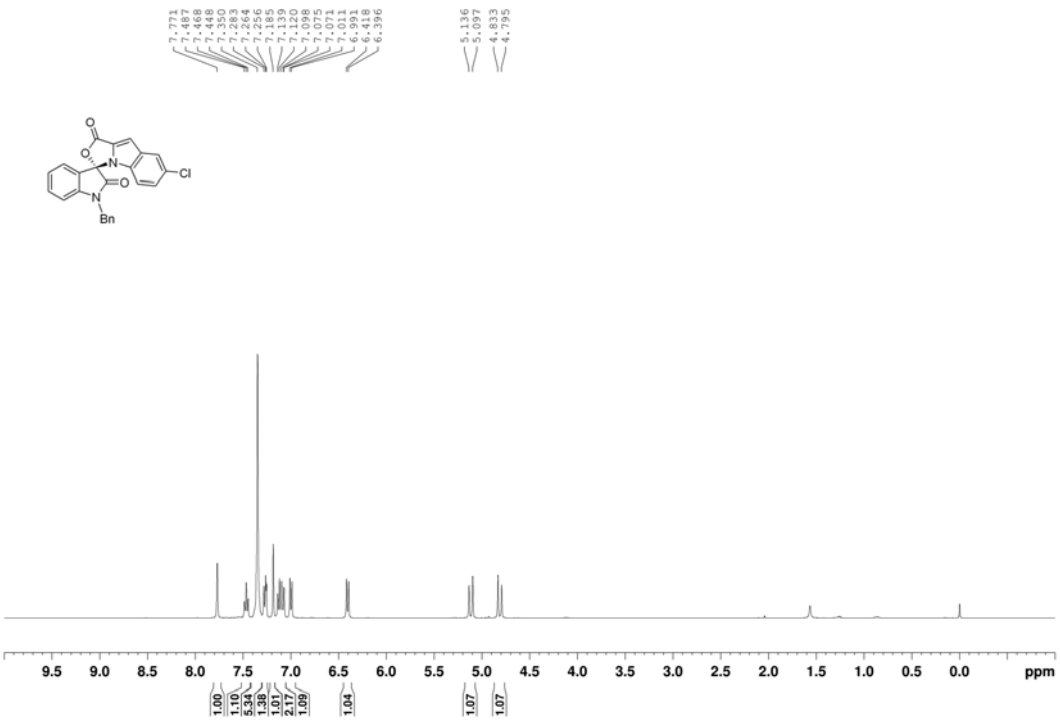
^{1}H NMR spectrum of compound **5p** ($CDCl_3$, 400 MHz)



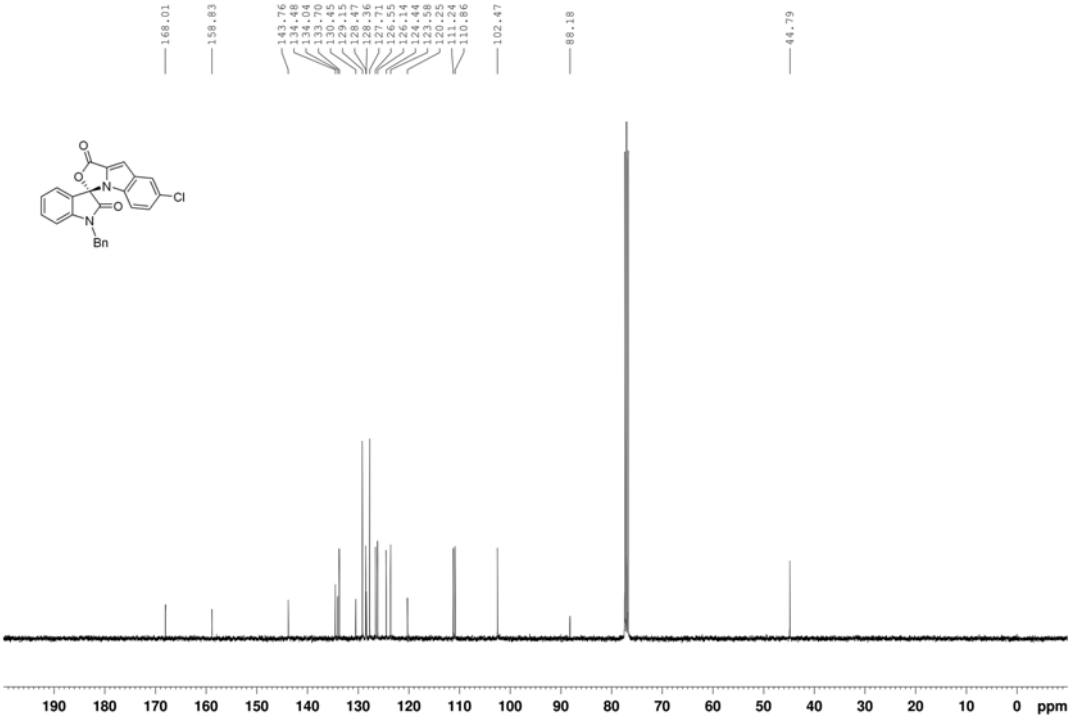
^{13}C NMR spectrum of compound **5p** ($CDCl_3$, 100 MHz)



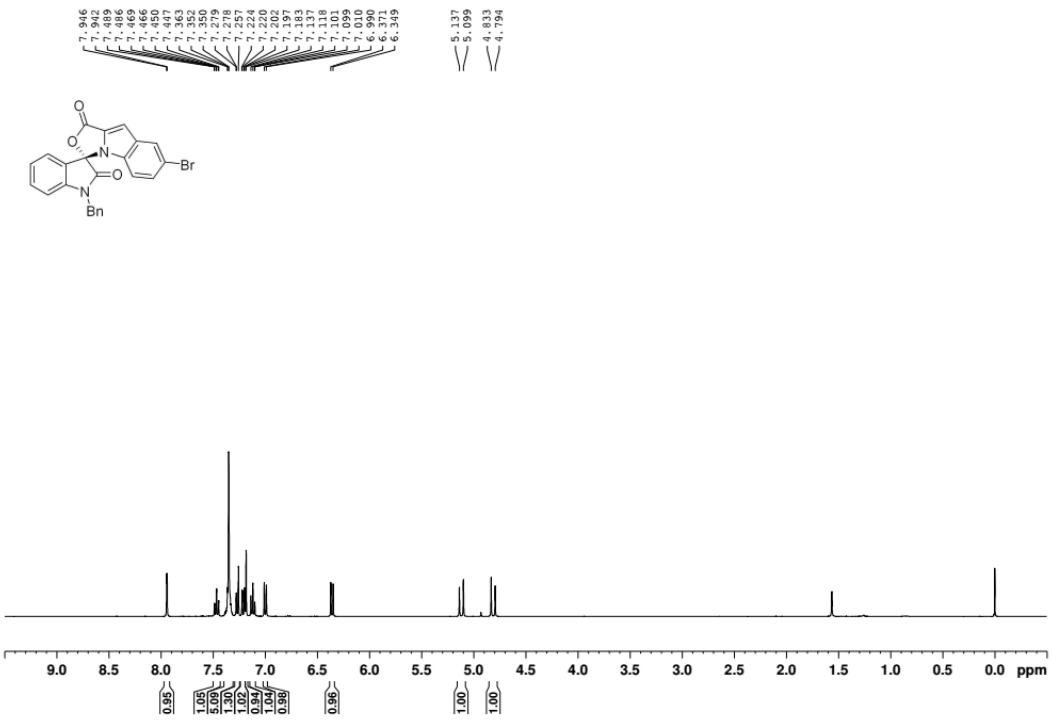
^{1}H NMR spectrum of compound **5q** ($CDCl_3$, 400 MHz)



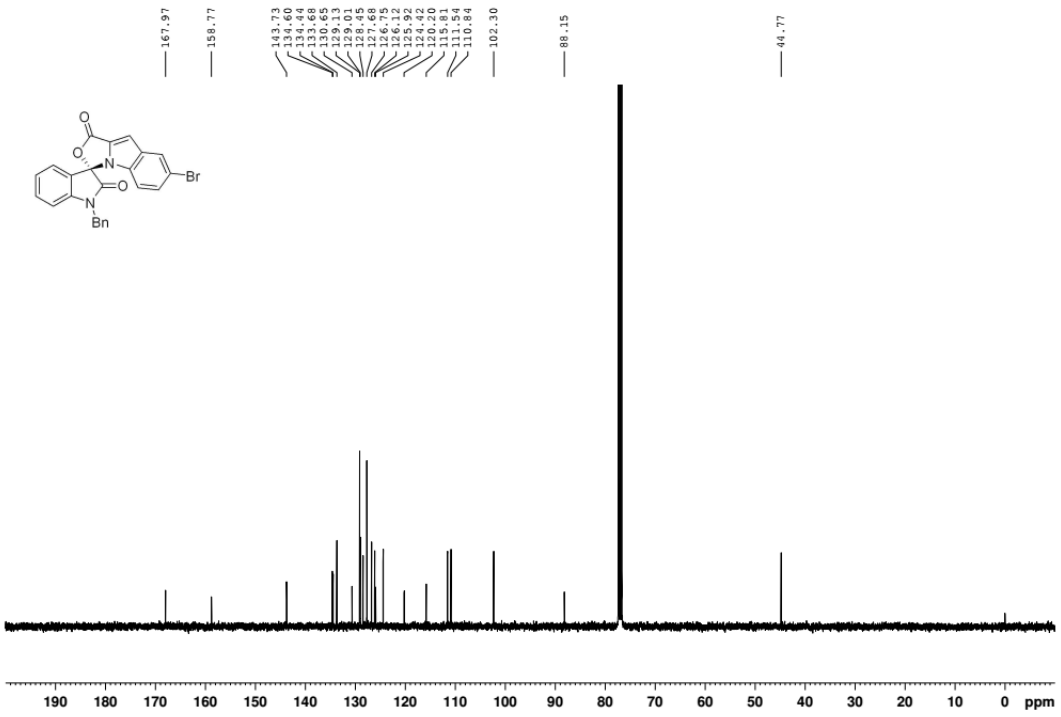
^{13}C NMR spectrum of compound **5q** ($CDCl_3$, 100 MHz)



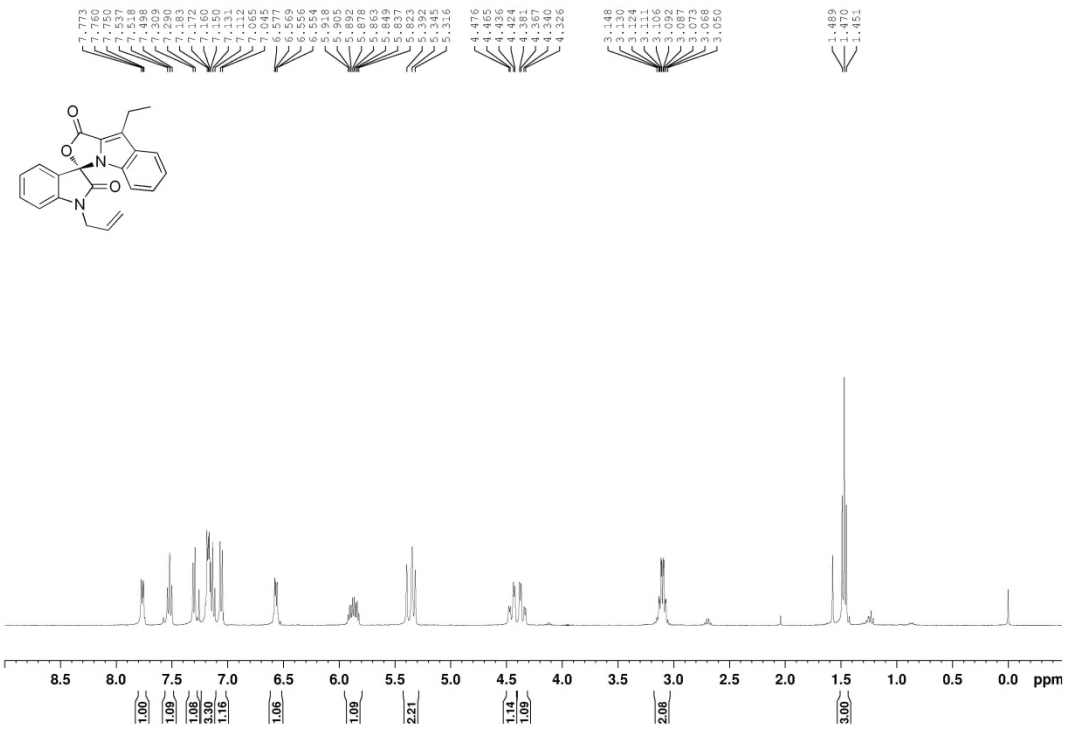
^{1}H NMR spectrum of compound **5r** ($CDCl_3$, 400 MHz)



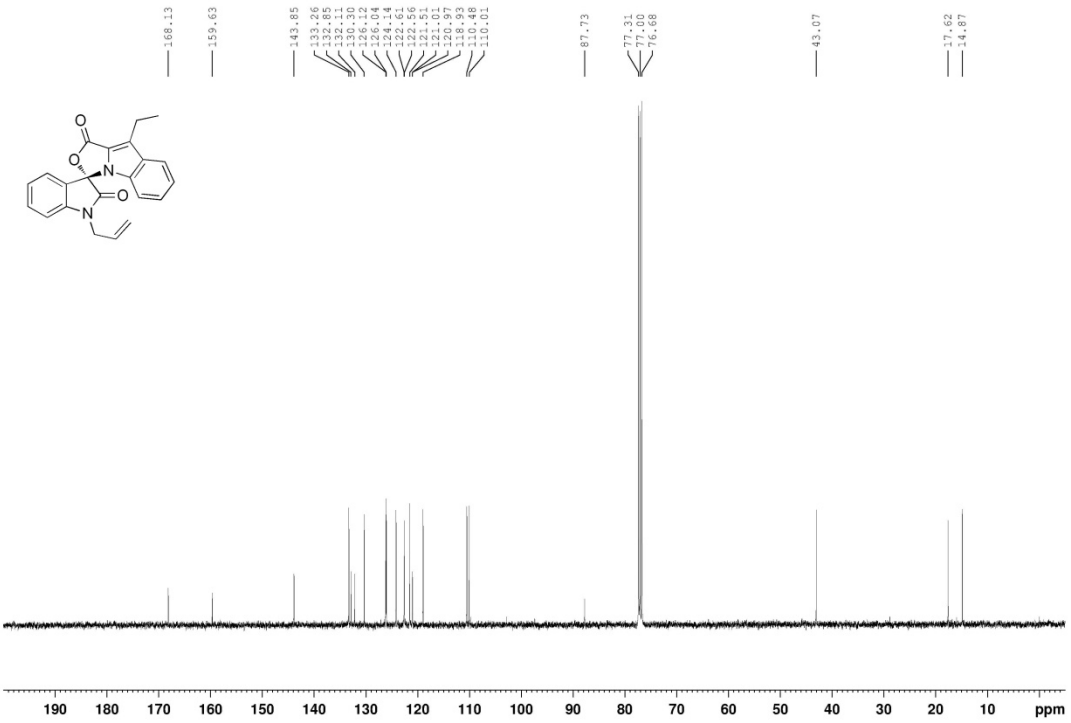
^{13}C NMR spectrum of compound **5r** ($CDCl_3$, 100 MHz)



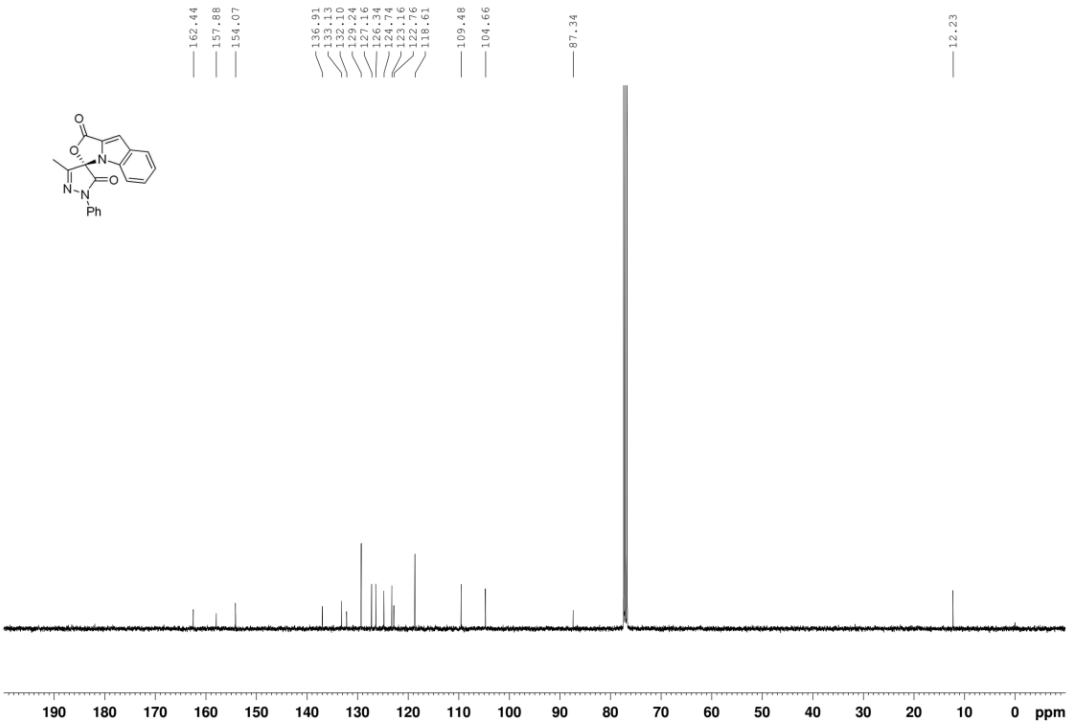
^{1}H NMR spectrum of compound **5s** ($CDCl_3$, 400 MHz)



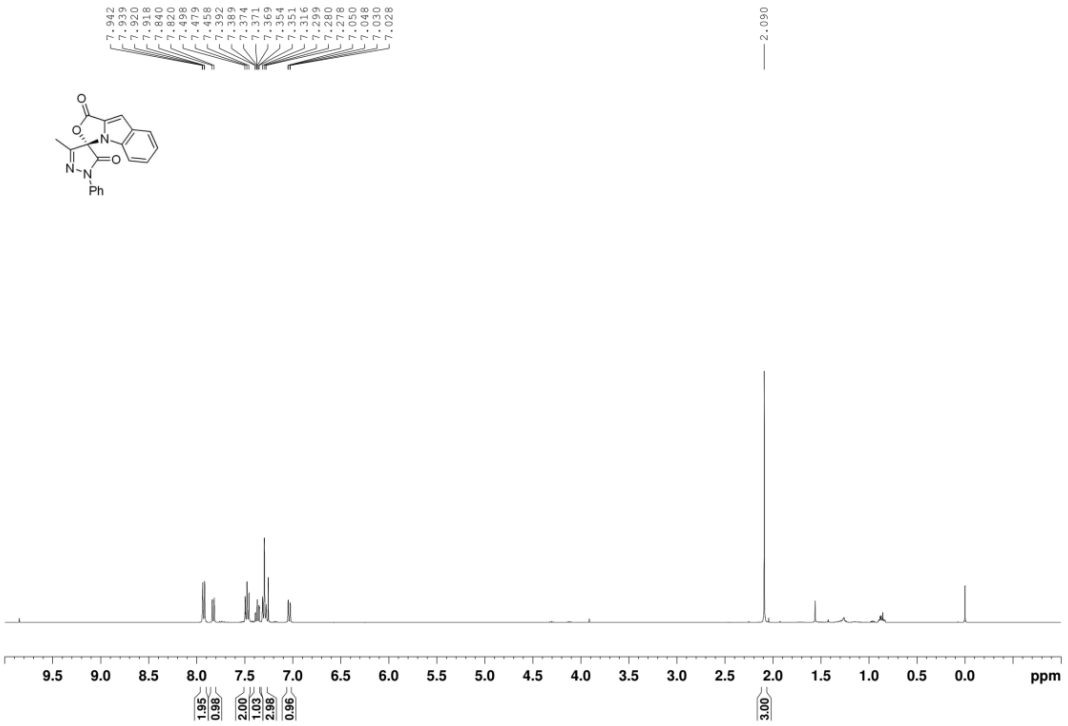
^{13}C NMR spectrum of compound **5s** ($CDCl_3$, 100 MHz)



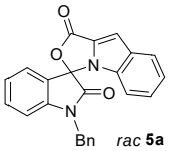
^{1}H NMR spectrum of compound **7** ($CDCl_3$, 400 MHz)



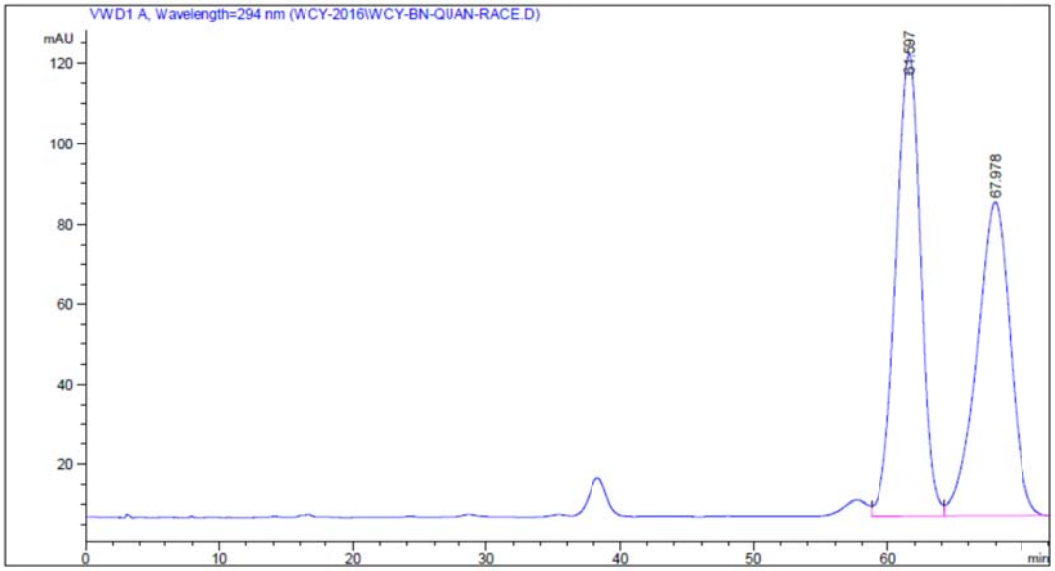
^{13}C NMR spectrum of compound **7** ($CDCl_3$, 100 MHz)



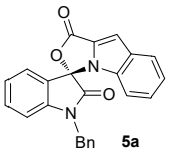
7. HPLC spectra of the compounds 5a−5s and 7



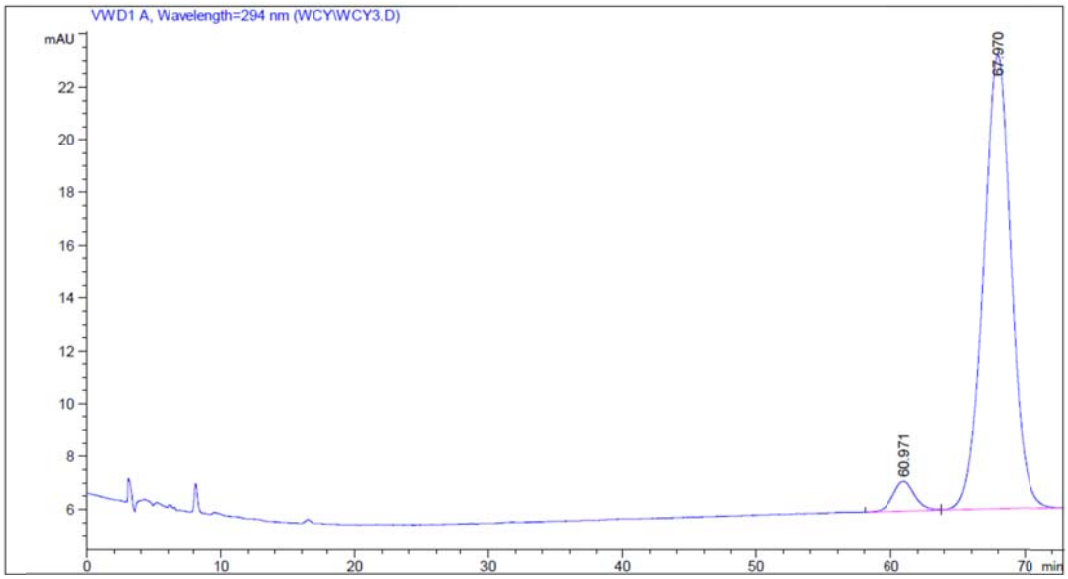
rac **5a**



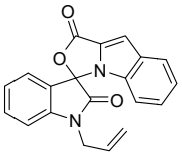
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	61.597	1.49424e4	115.11676	52.4798
2	PDA 294.0 nm	67.978	1.35303e4	78.13834	47.5202



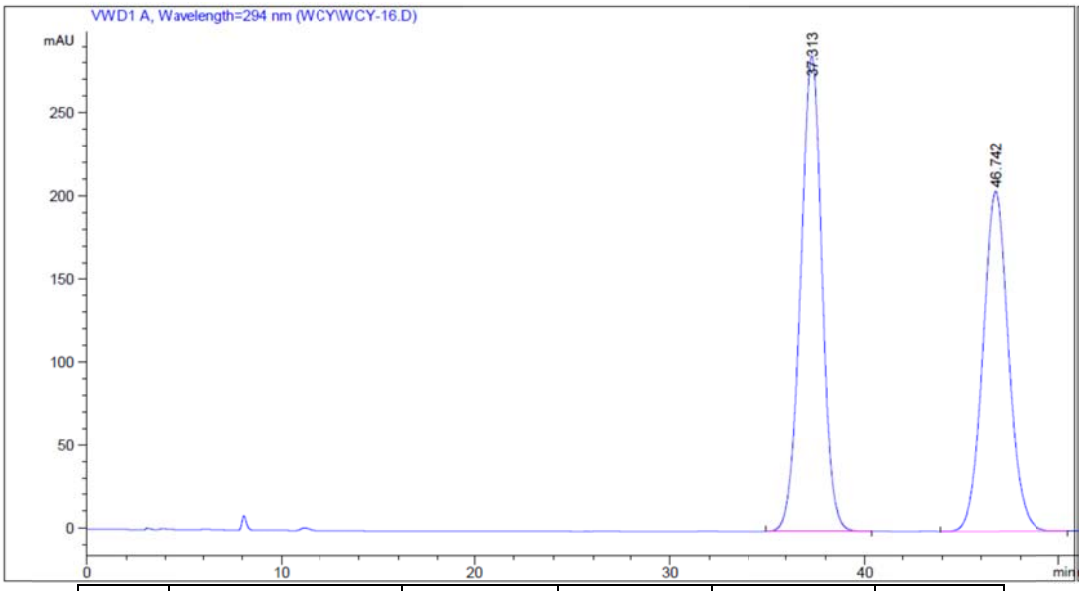
5a



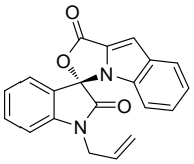
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	60.971	130.18935	1.13687	4.9741
2	PDA 294.0 nm	67.970	2487.13257	17.19423	95.0259



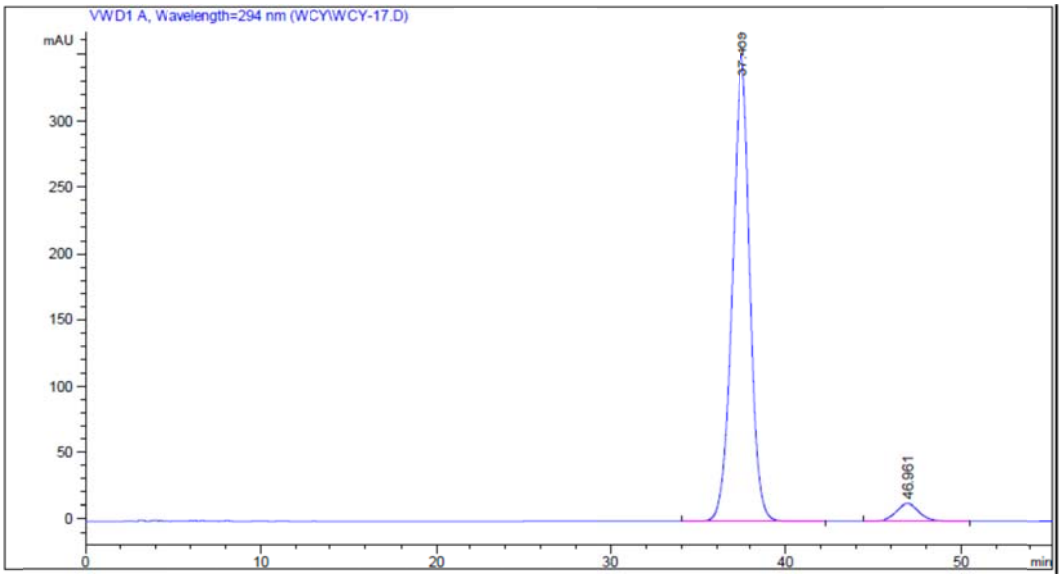
rac **5b**



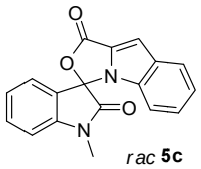
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	37.313	2.15194e4	285.90811	53.6338
2	PDA 294.0 nm	46.742	1.86035e4	204.31013	46.3662



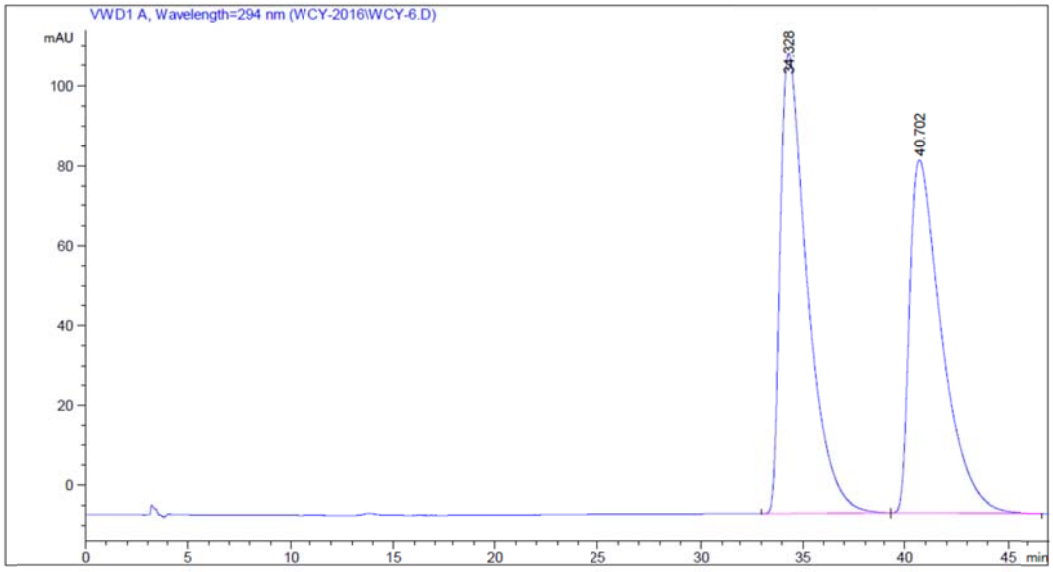
5b



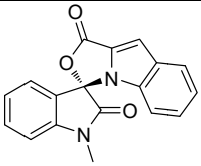
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	37.469	2.66289e4	350.35040	95.7544
2	PDA 294.0 nm	46.961	1180.67224	12.99745	4.2456



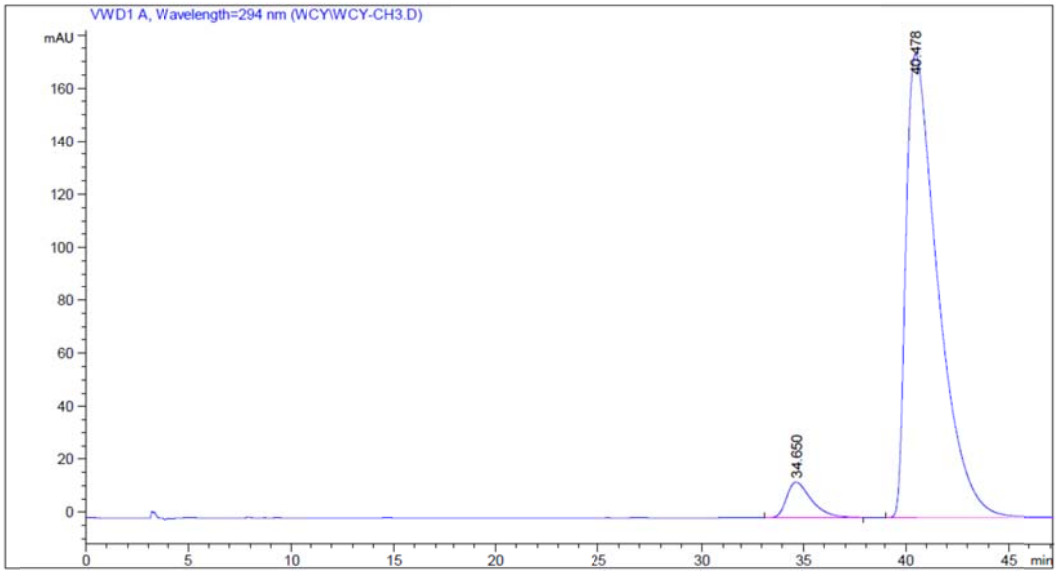
rac **5c**



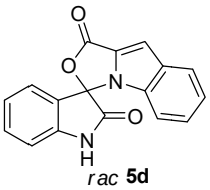
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	34.328	1.04430e4	114.99951	52.1907
2	PDA 294.0 nm	40.702	9566.28320	88.38822	47.8093



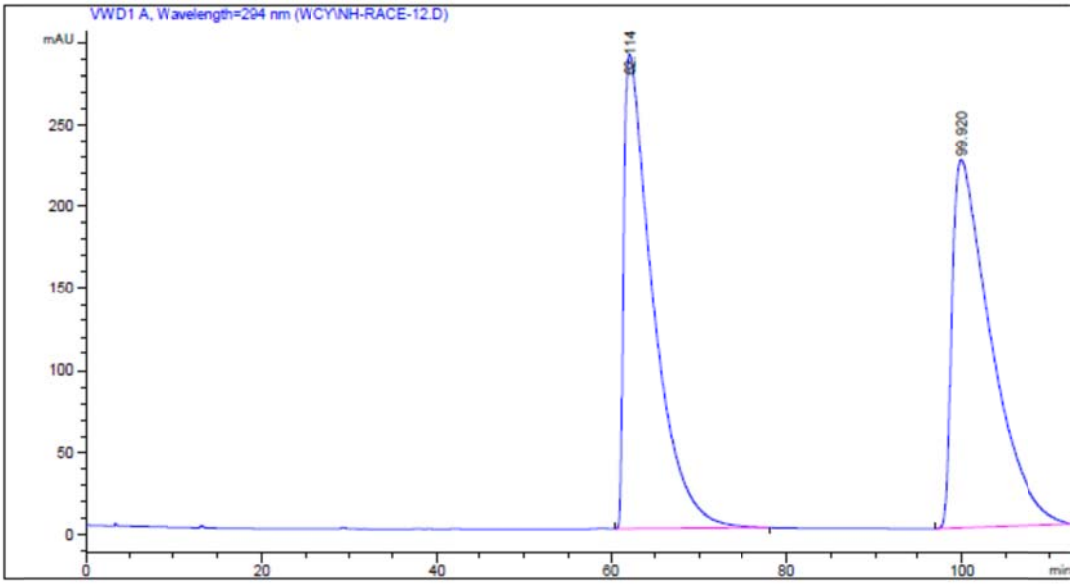
5c



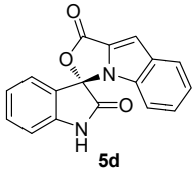
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	34.650	1099.81250	13.33855	5.5591
2	PDA 294.0 nm	40.478	1.86840e4	174.77658	94.4409



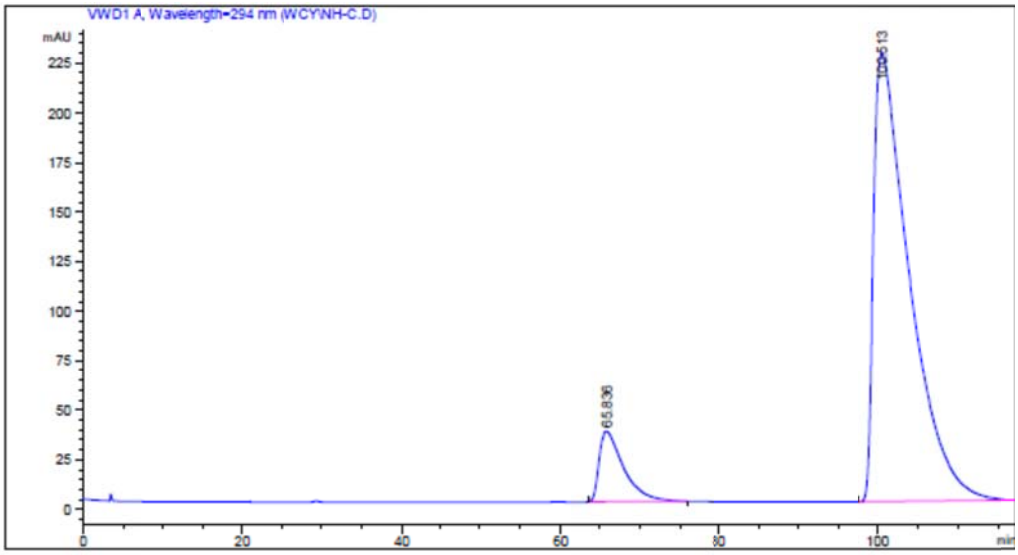
rac **5d**



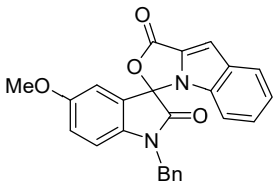
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	62.114	6.54116e4	288.70721	48.9070
2	PDA 294.0 nm	99.920	6.83354e4	223.84796	51.0930



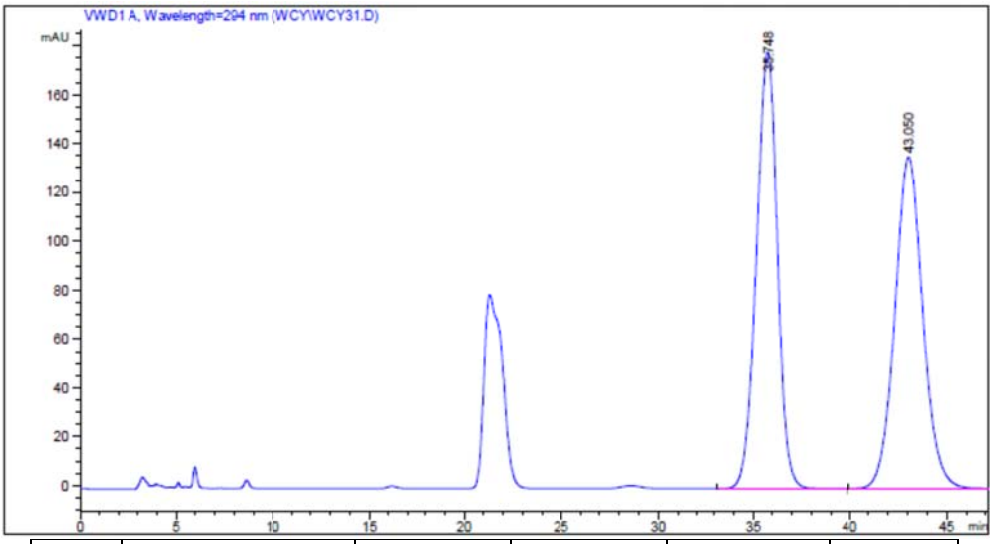
5d



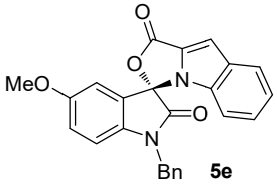
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	65.836	7414.70264	35.33968	9.5695
2	PDA 294.0 nm	100.513	7.00679e4	226.05521	90.4305



rac **5e**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	35.748	1.33497e4	178.45653	49.6395
2	PDA 294.0 nm	43.050	1.35436e4	135.54822	50.3605



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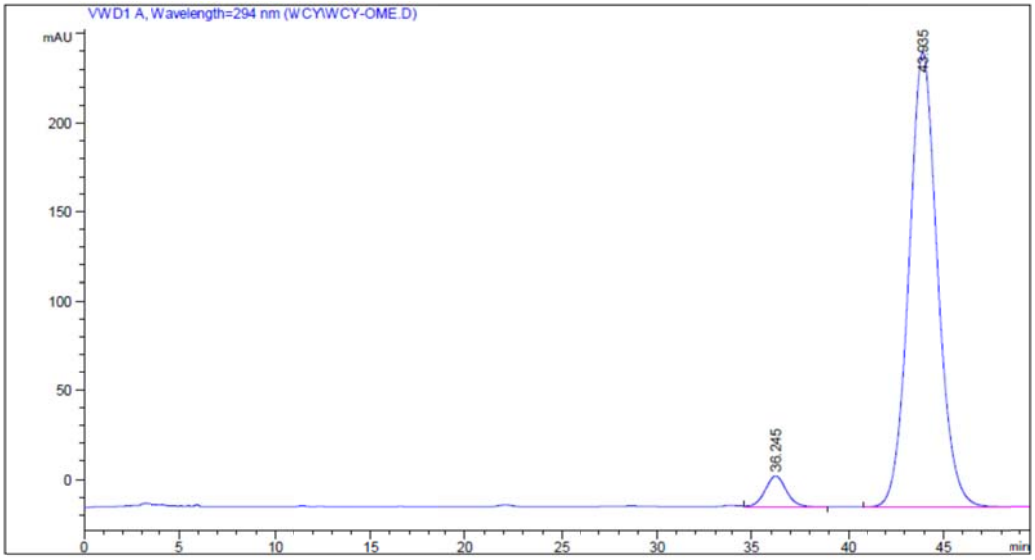
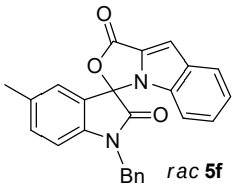
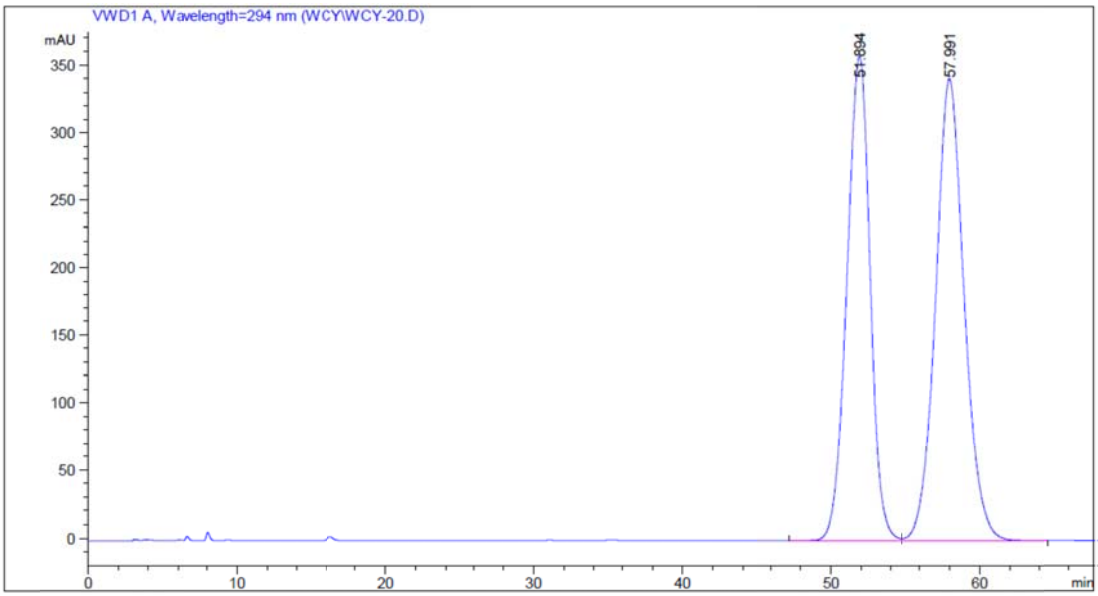


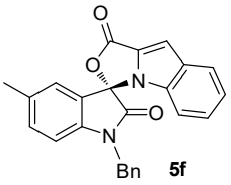
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	36.245	1303.65552	17.24951	4.7390
2	PDA 294.0 nm	43.935	2.62057e4	254.83798	95.2610



rac **5f**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	51.894	3.82382e4	357.92993	45.8574
2	PDA 294.0 nm	57.991	4.51468e4	341.38016	54.1426



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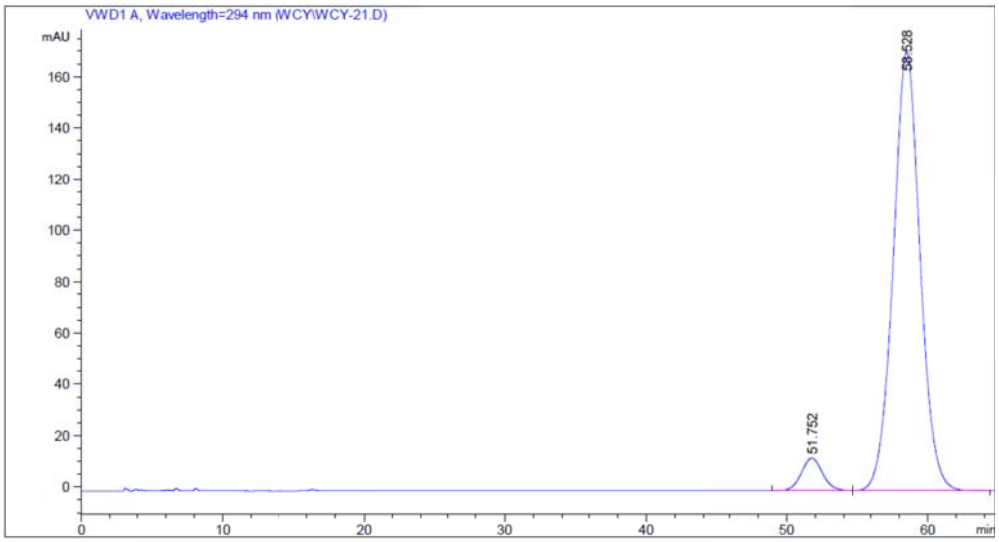
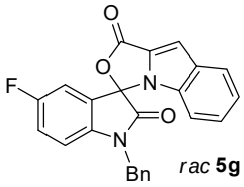
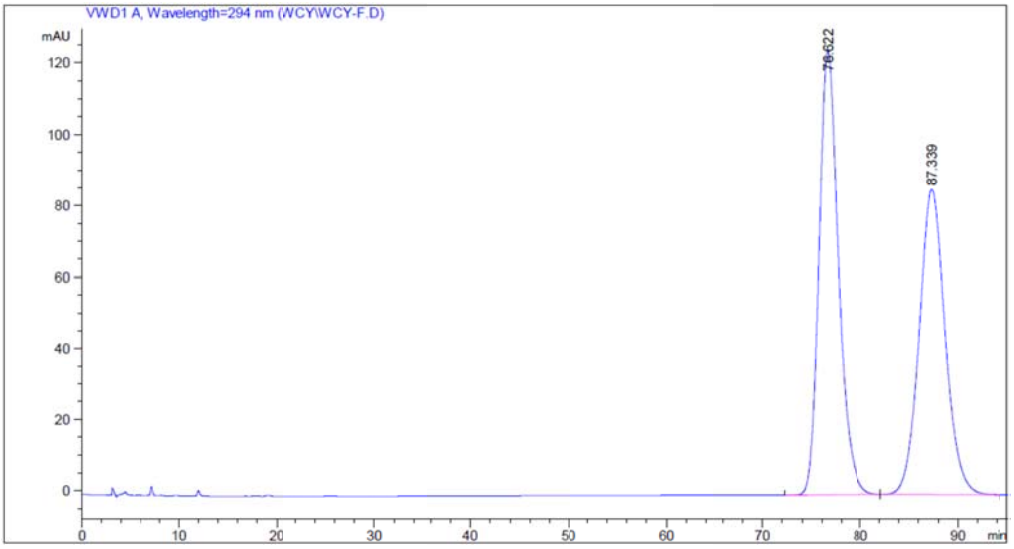


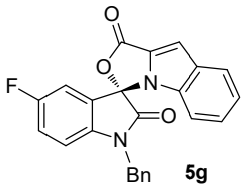
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	51.752	1294.78870	12.63601	5.4683
2	PDA 294.0 nm	58.528	2.23832e4	171.22549	94.5317



rac **5g**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	76.622	1.71976e4	124.42851	52.1967
2	PDA 294.0 nm	87.339	1.57501e4	85.62537	47.8033



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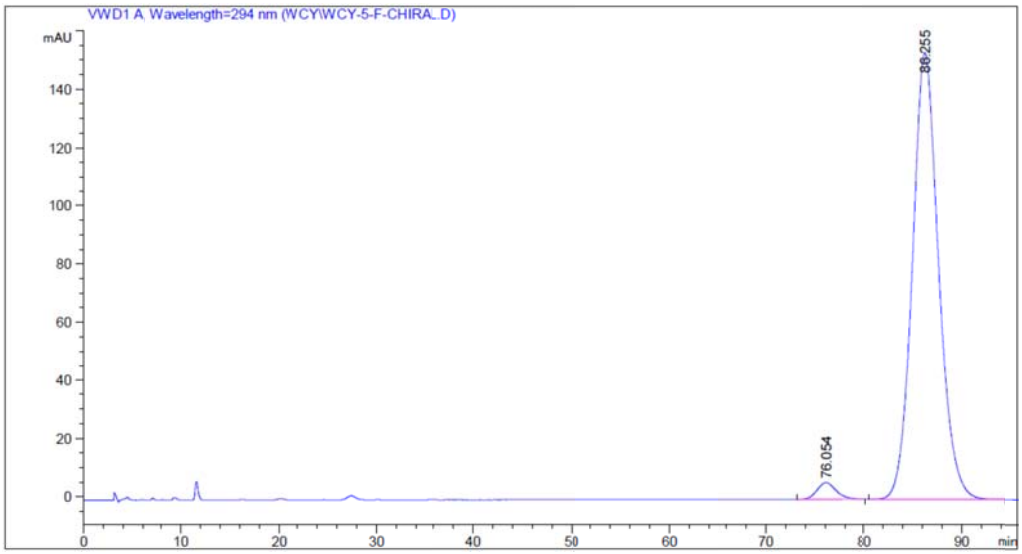
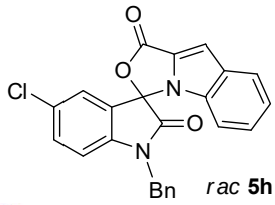
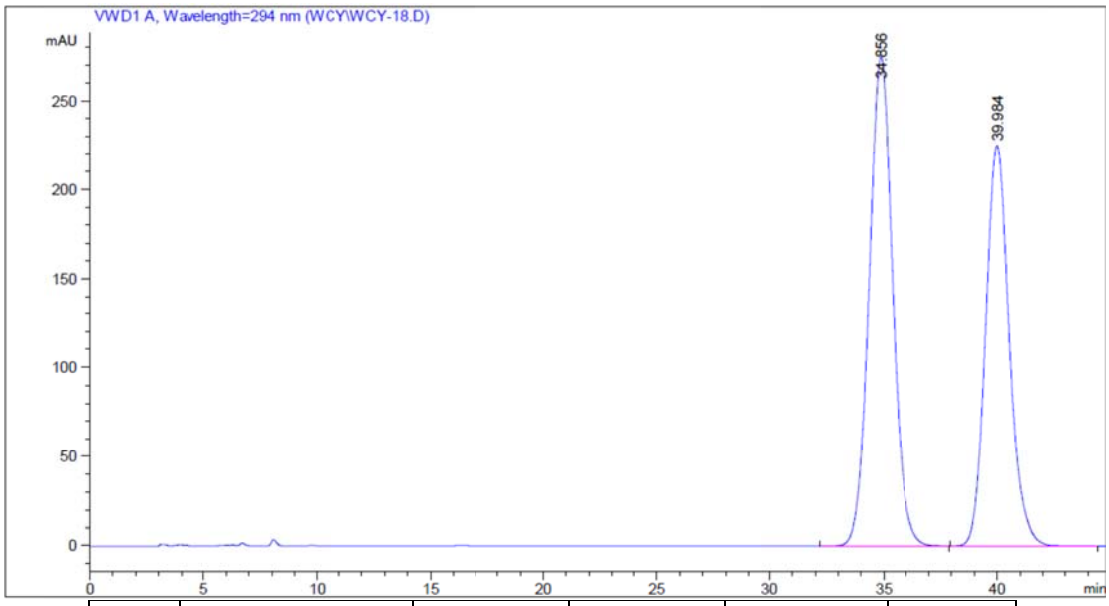


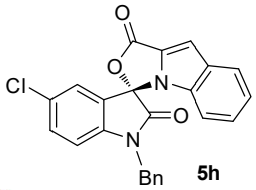
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	76.054	766.01086	5.71267	2.6385
2	PDA 294.0 nm	86.255	2.82658e4	153.24281	97.3615



rac **5h**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	34.856	1.96477e4	274.40750	54.9019
2	PDA 294.0 nm	39.984	1.61392e4	224.96971	45.0981



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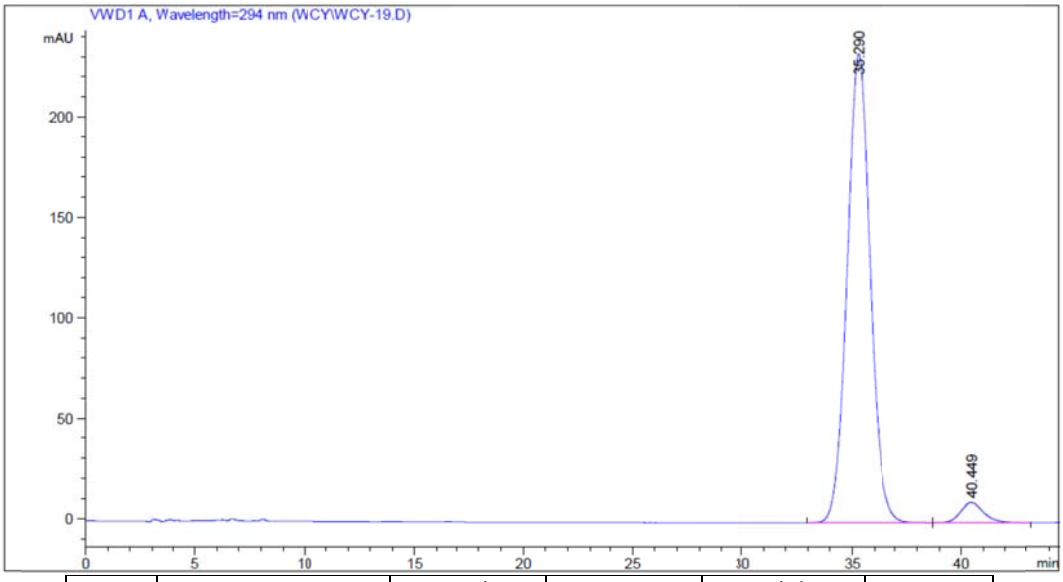
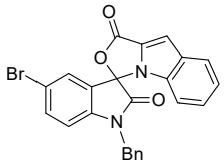
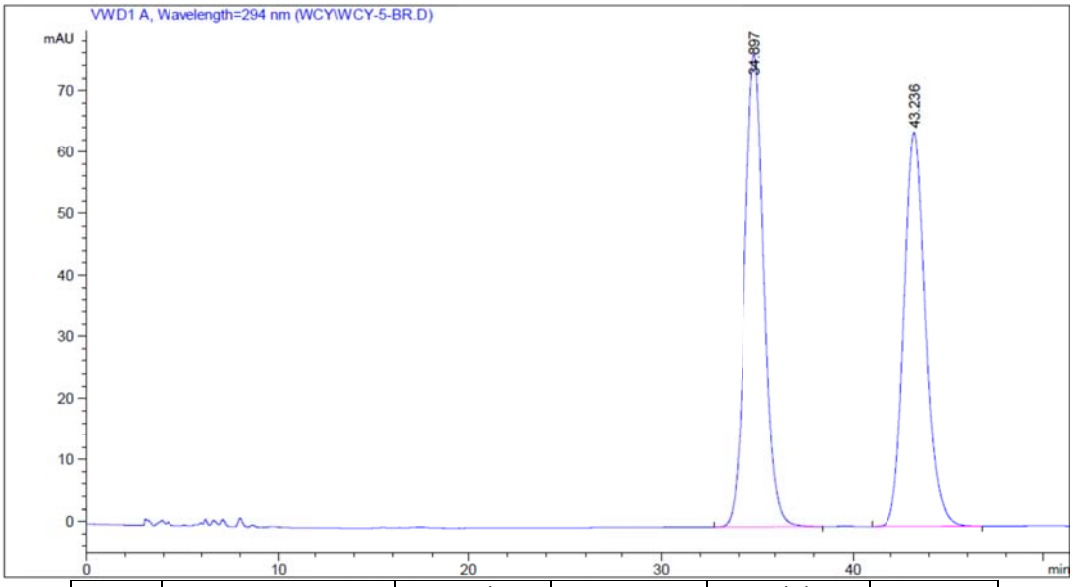


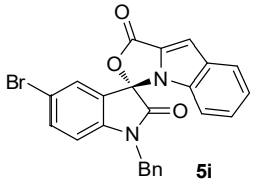
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	35.290	1.69711e4	233.08875	95.9717
2	PDA 294.0 nm	40.449	712.34857	9.72455	4.0283



rac **5i**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	34.897	5493.46240	76.65495	52.1803
2	PDA 294.0 nm	43.236	5034.38574	63.98945	47.8197



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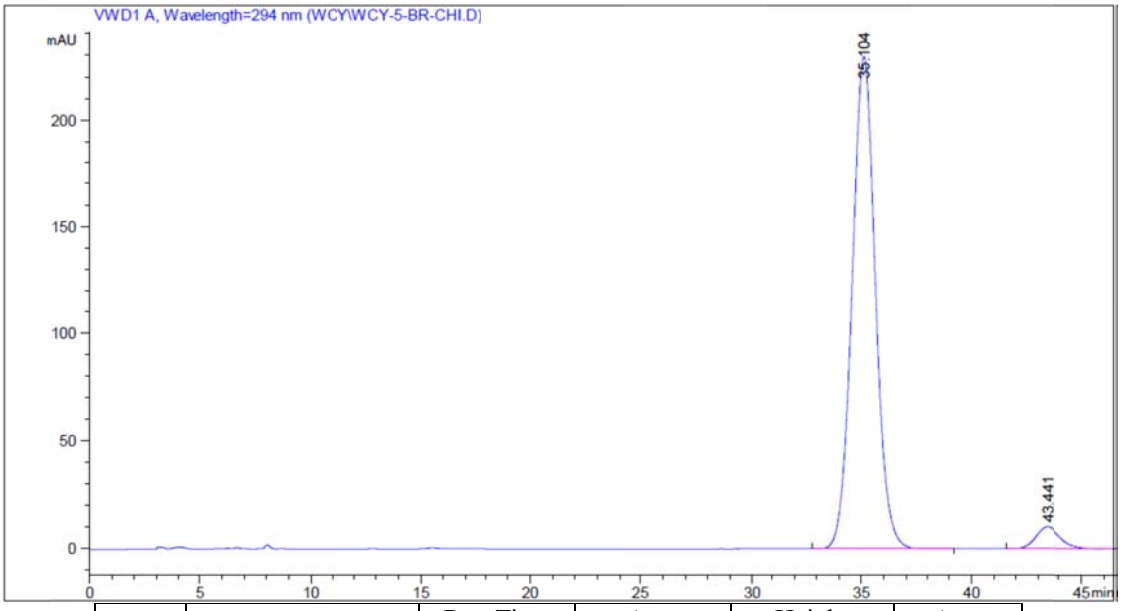
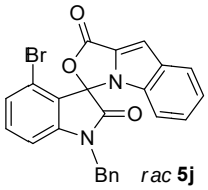
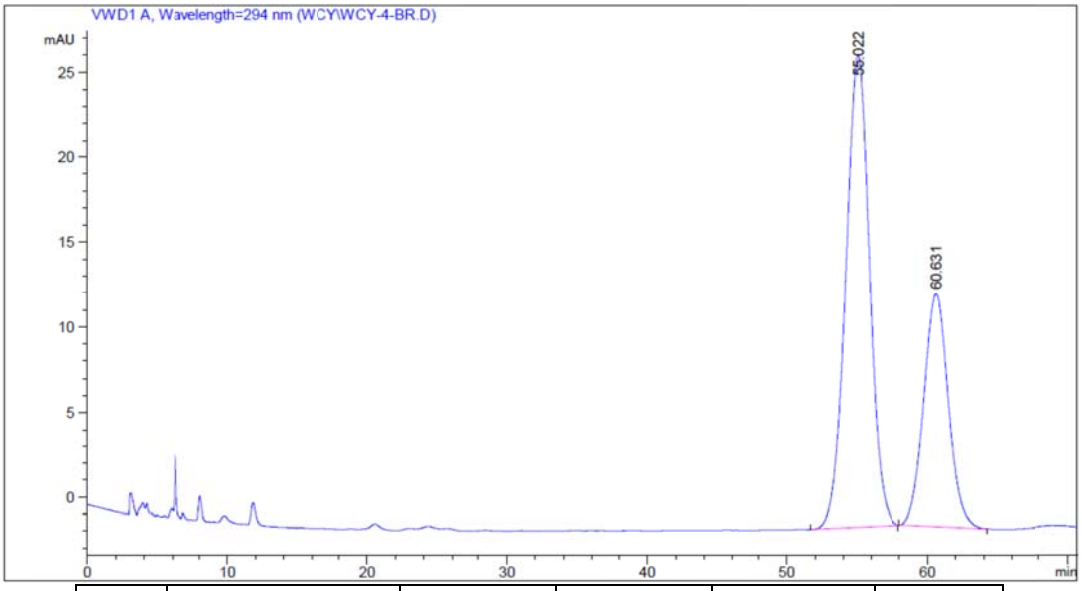


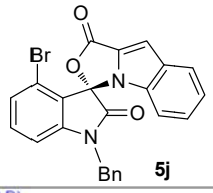
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	35.104	1.65311e4	229.60469	95.3296
2	PDA 294.0 nm	43.441	809.89655	10.21602	4.6704



rac **5j**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	55.022	3250.98999	27.77894	66.0611
2	PDA 294.0 nm	60.631	1670.19910	13.69331	33.9389



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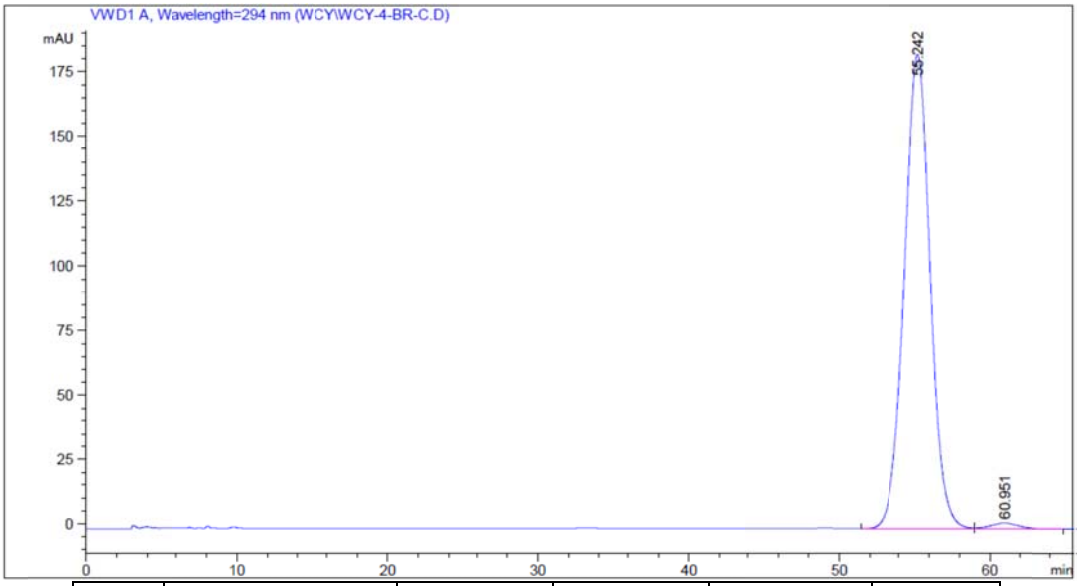
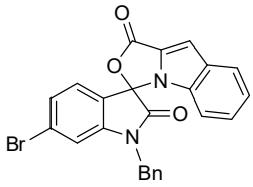
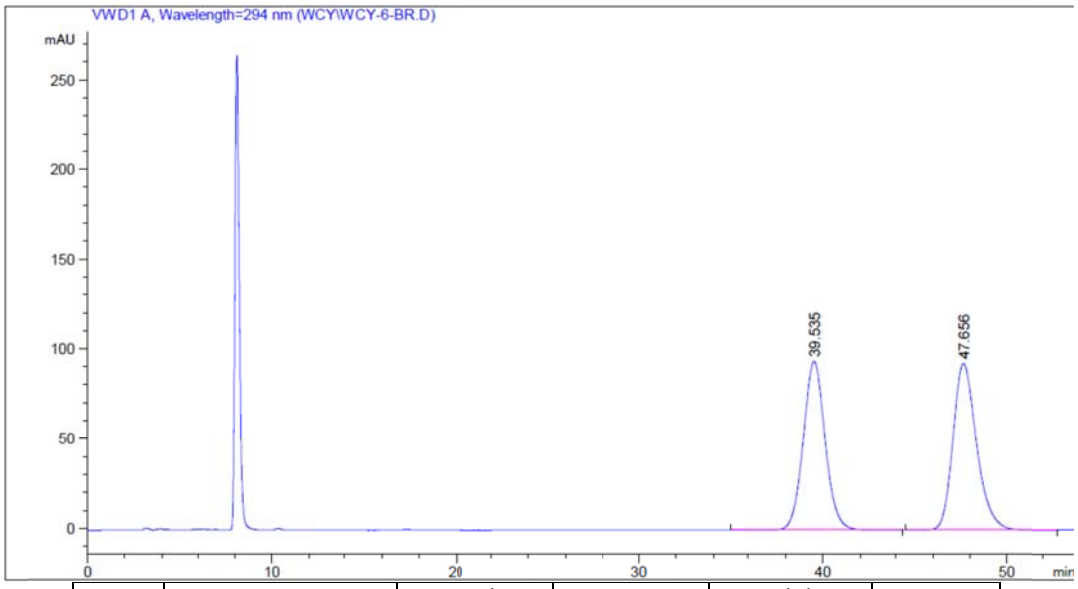


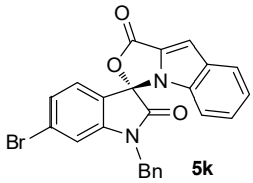
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	55.242	2.19329e4	183.43774	98.7887
2	PDA 294.0 nm	60.951	268.93335	2.14819	1.2113



rac **5k**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	39.535	7666.39160	93.93566	48.3137
2	PDA 294.0 nm	47.656	8201.56445	92.66058	51.6863



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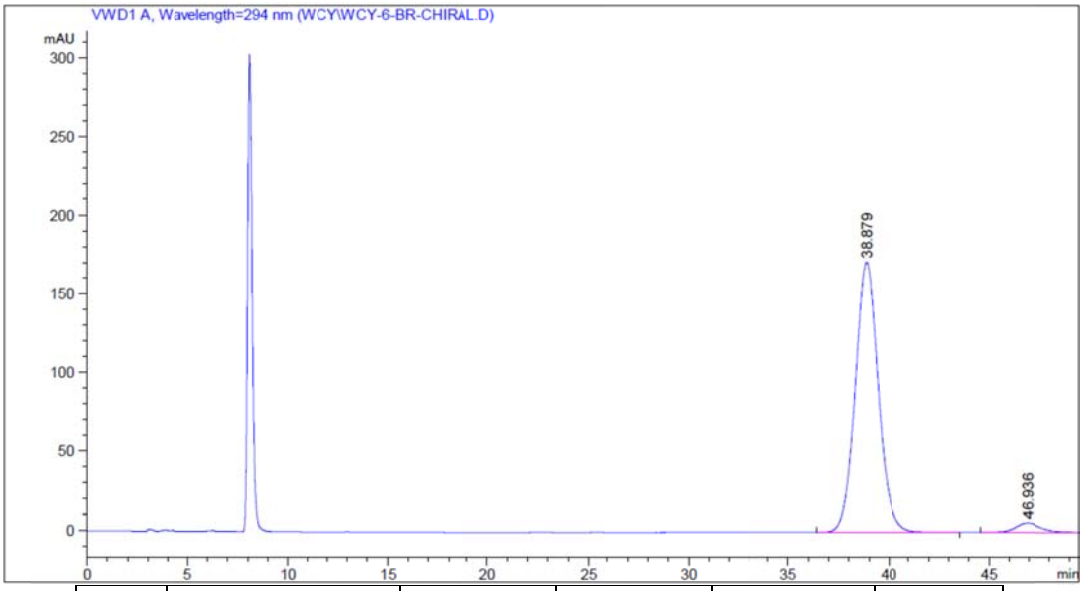
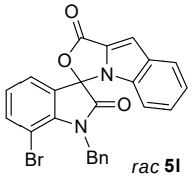
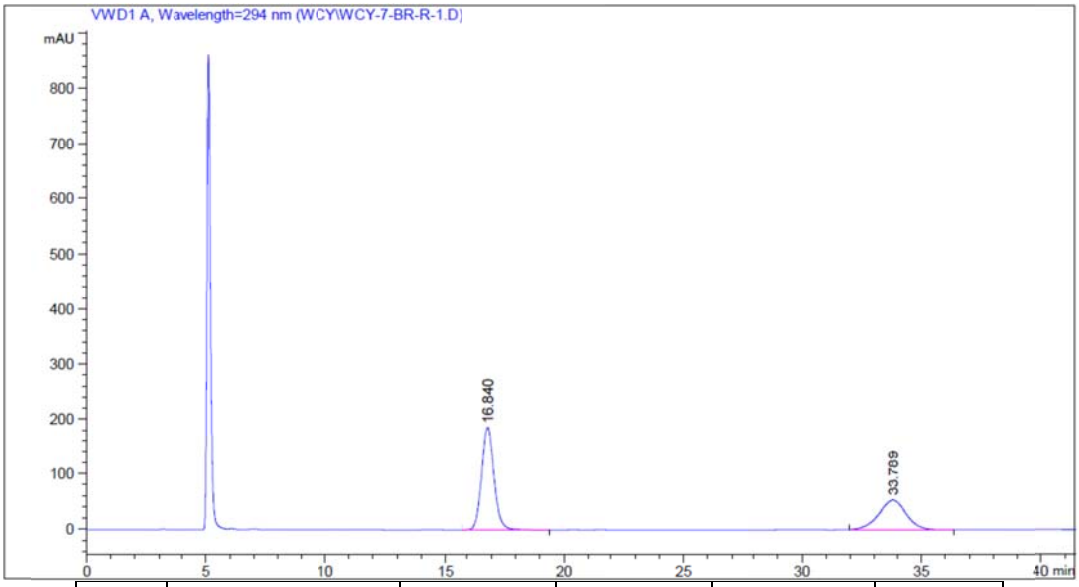


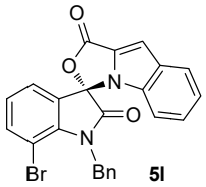
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	38.879	1.36627e4	171.46104	96.5172
2	PDA 294.0 nm	46.936	493.02011	5.85665	3.4828



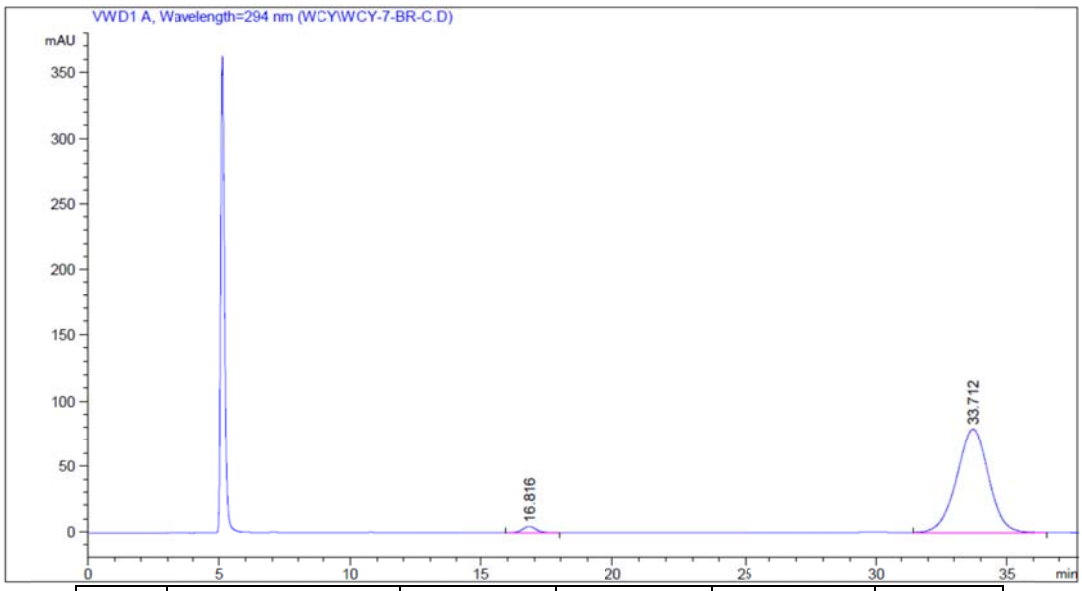
rac **5l**



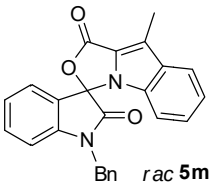
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	16.840	6621.51270	185.89731	60.2188
2	PDA 294.0 nm	33.789	4374.24414	53.12273	39.7821



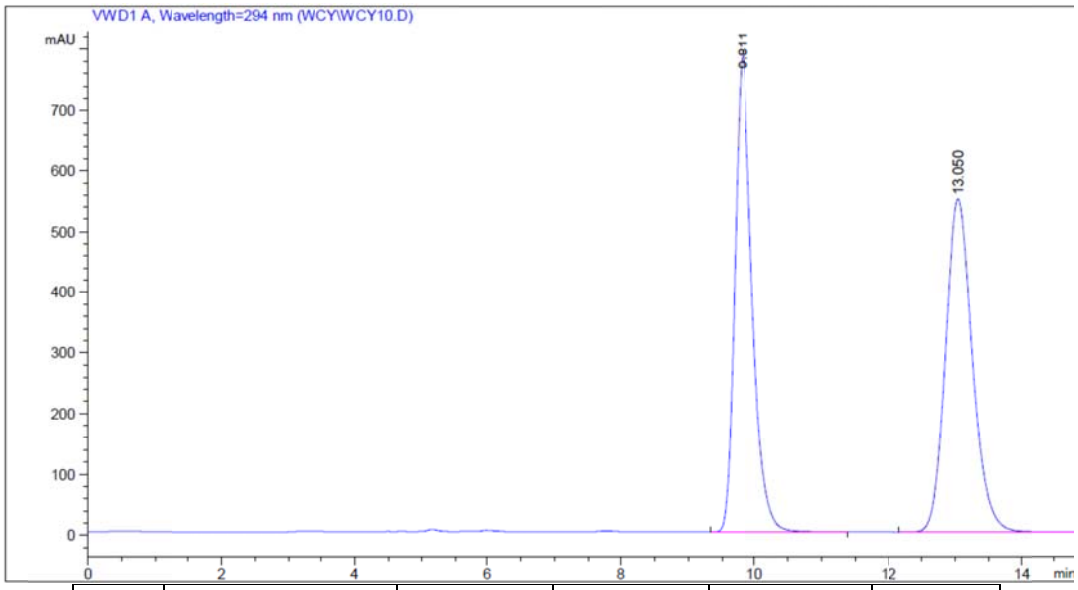
5l



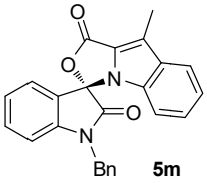
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	16.816	169.54294	4.84452	2.5007
2	PDA 294.0 nm	33.712	6610.35938	79.23486	97.4993



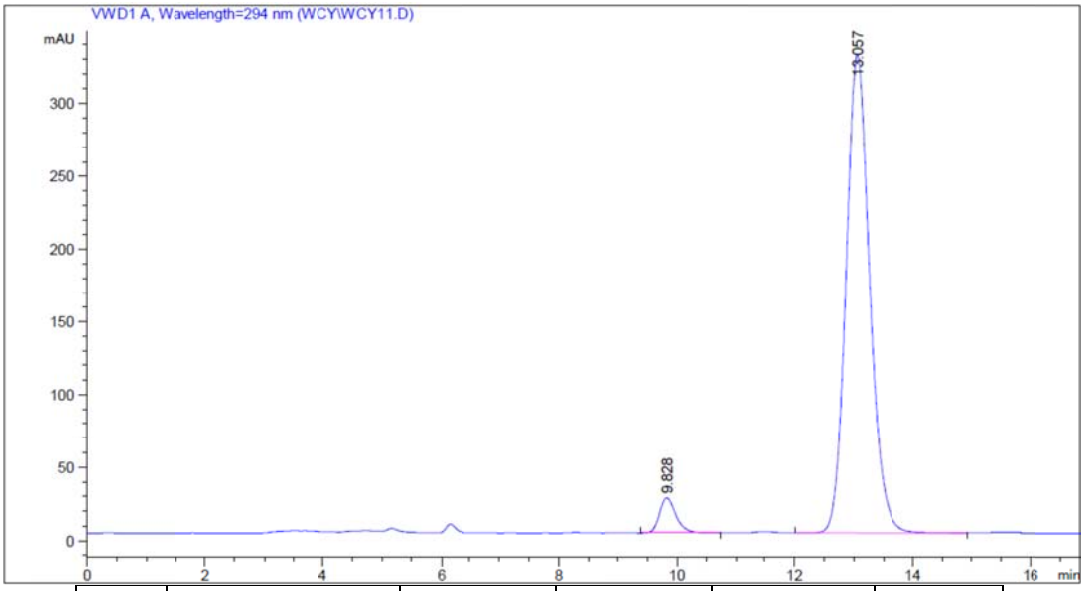
rac **5m**



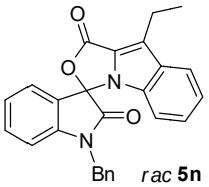
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	9.811	1.52269e4	784.05084	50.0451
2	PDA 294.0 nm	13.050	1.51995e4	547.58832	49.9549



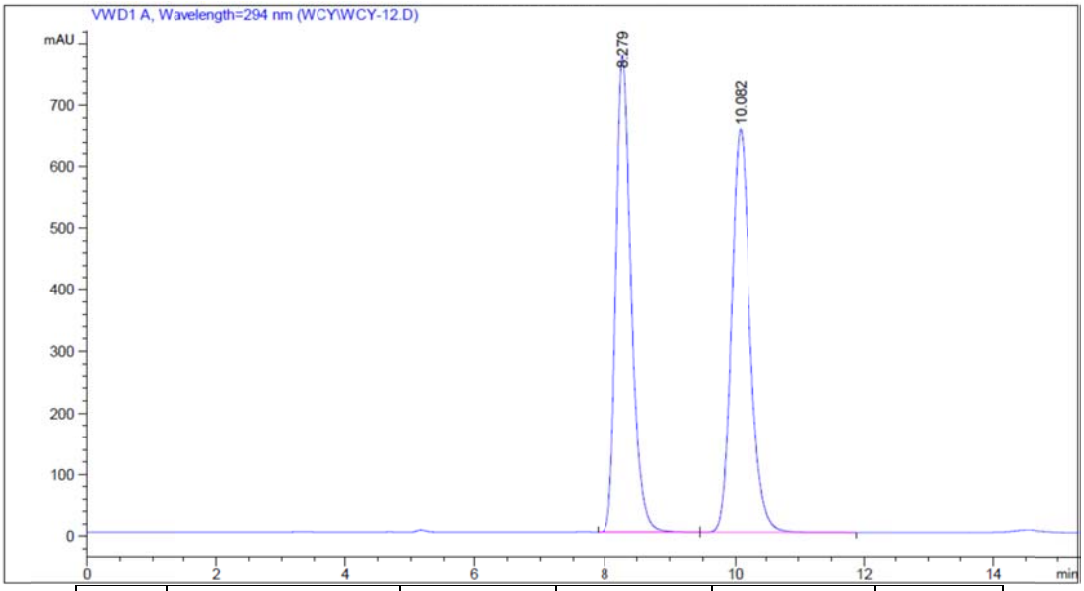
5m



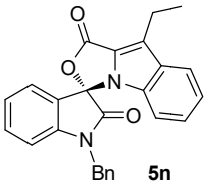
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	9.828	452.51416	23.45523	4.7588
2	PDA 294.0 nm	13.057	9056.49219	327.27692	95.2412



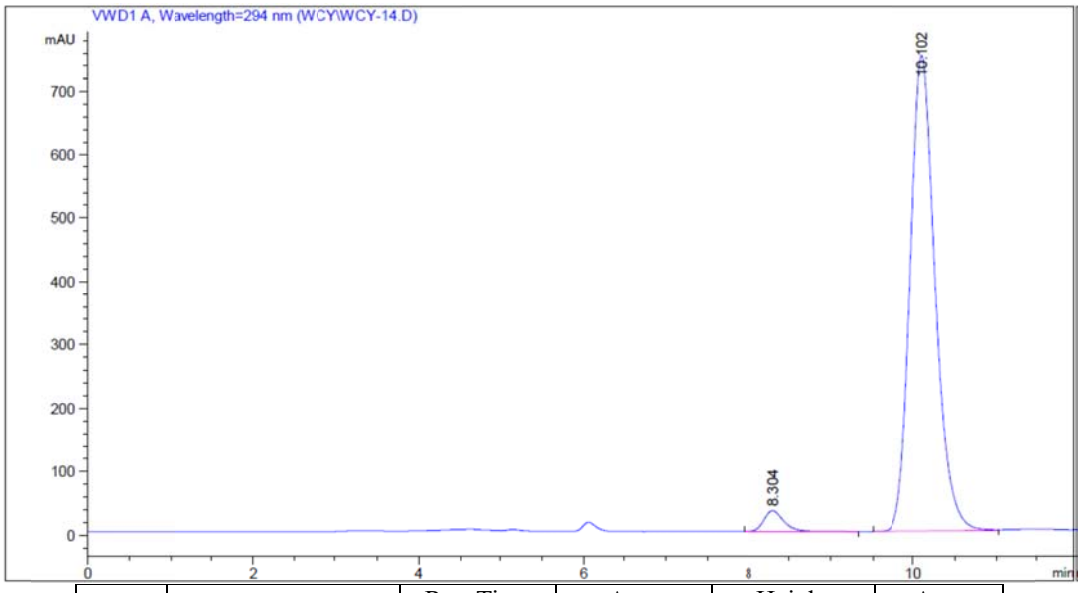
rac **5n**



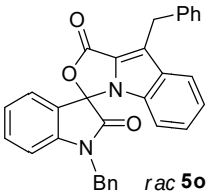
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	8.279	1.27214e4	775.79187	48.0893
2	PDA 294.0 nm	10.082	1.37323e4	655.54846	51.9107



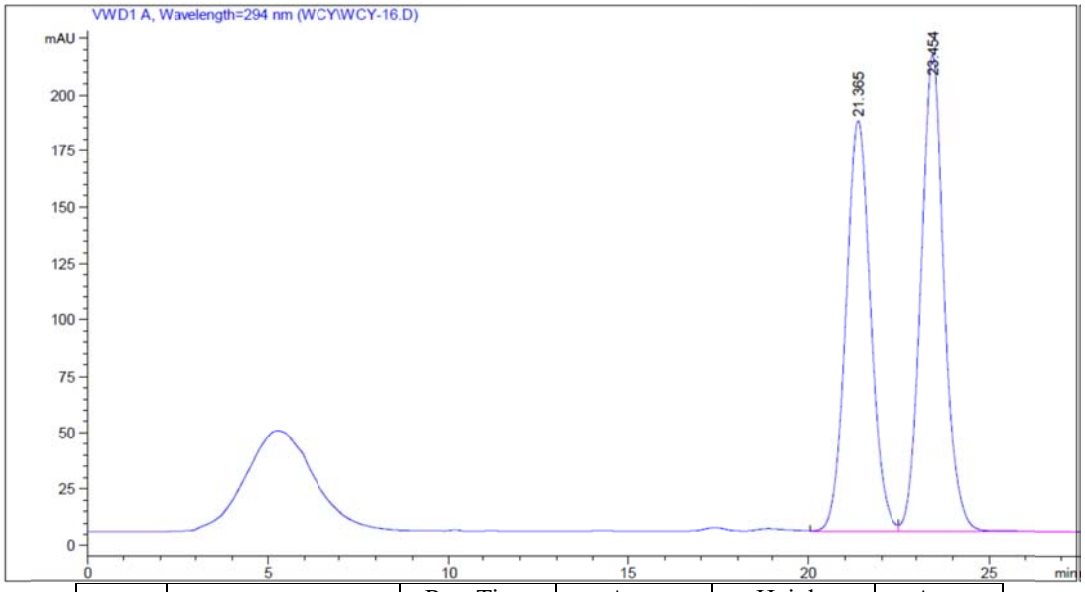
5n



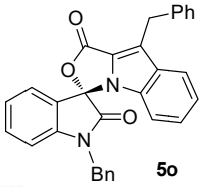
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	8.304	544.82556	32.78666	3.3423
2	PDA 294.0 nm	10.102	1.57559e4	749.38763	96.6577



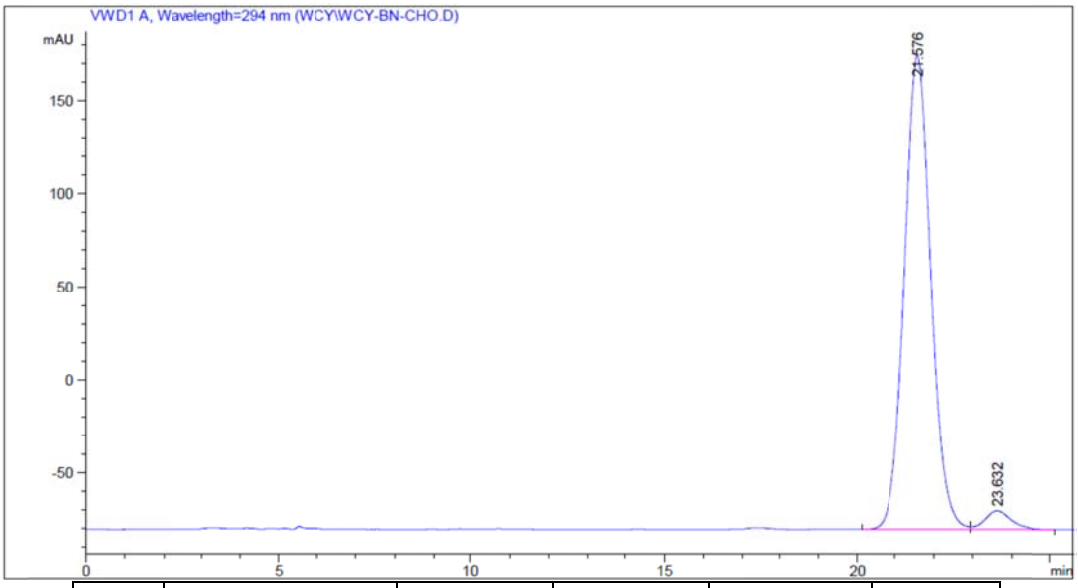
rac **5o**



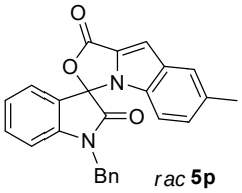
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	21.365	8605.78516	182.16986	47.8269
2	PDA 294.0 nm	23.454	9387.81250	211.21138	52.1731



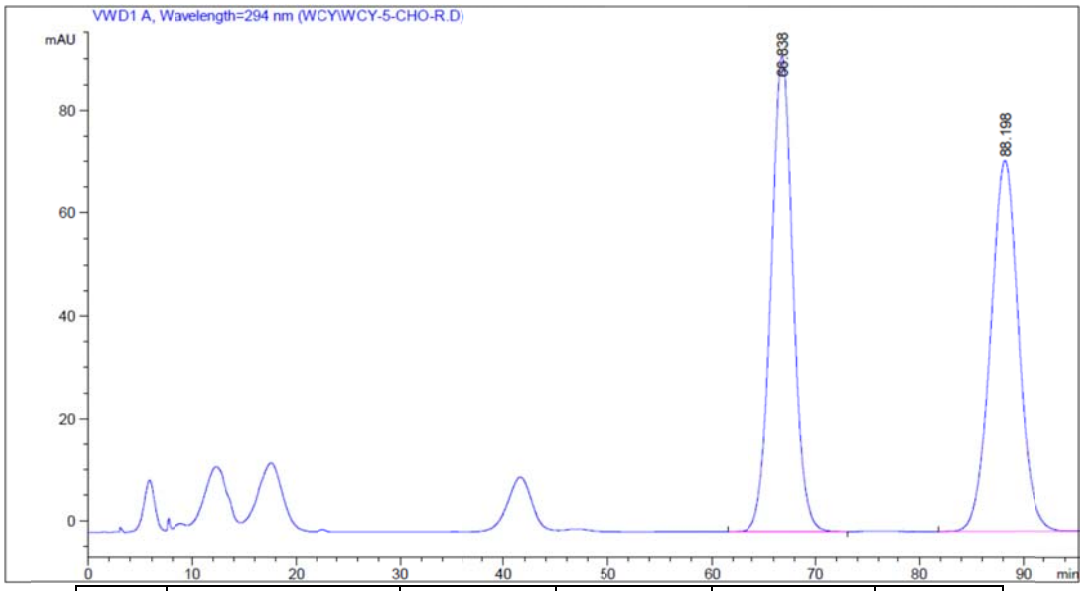
5o



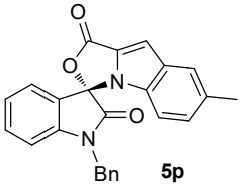
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	21.576	1.22341e4	254.47762	96.3819
2	PDA 294.0 nm	23.632	459.25220	9.92803	3.6181



rac **5p**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	66.838	1.34698e4	92.41288	49.9162
2	PDA 294.0 nm	88.198	1.35151e4	72.04472	50.0838



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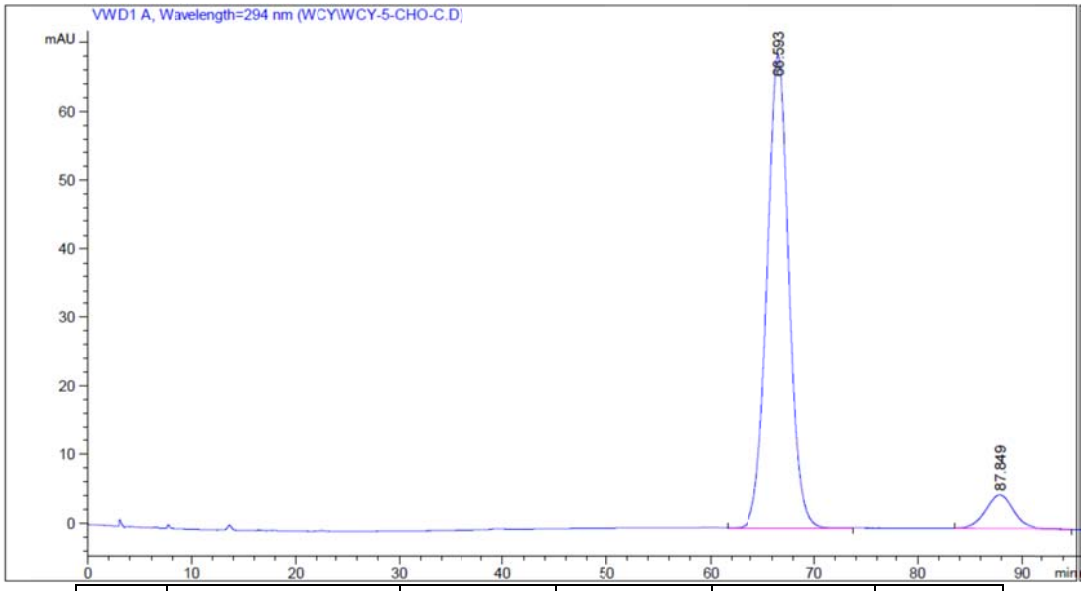
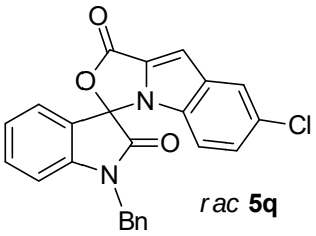
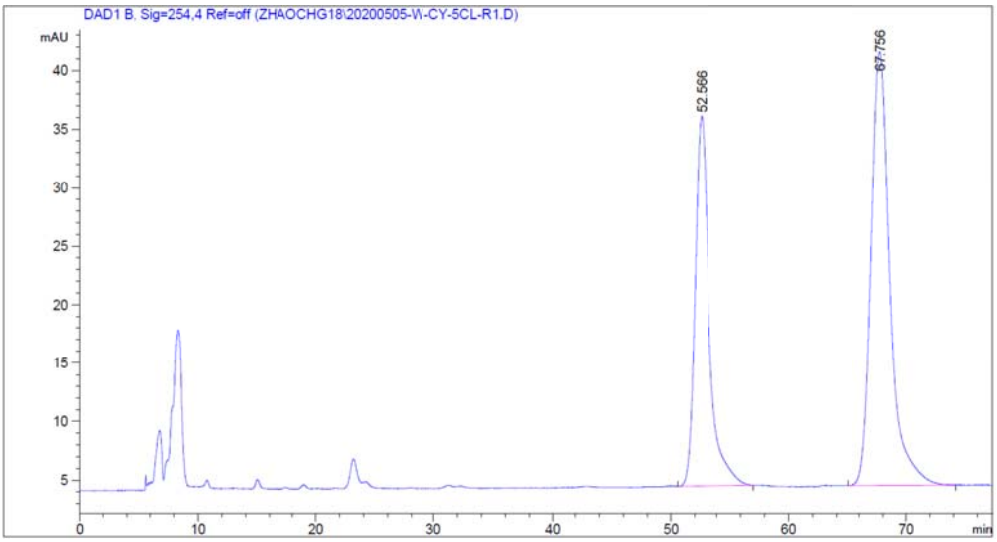


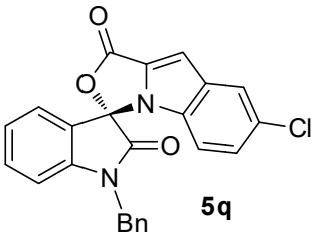
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	66.593	9988.19922	68.87824	91.7623
2	PDA 294.0 nm	87.849	896.65869	4.83905	8.2377



rac **5q**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	52.566	2783.06982	31.62564	40.4818
2	PDA 254.0 nm	67.756	4091.79248	37.03612	59.5182



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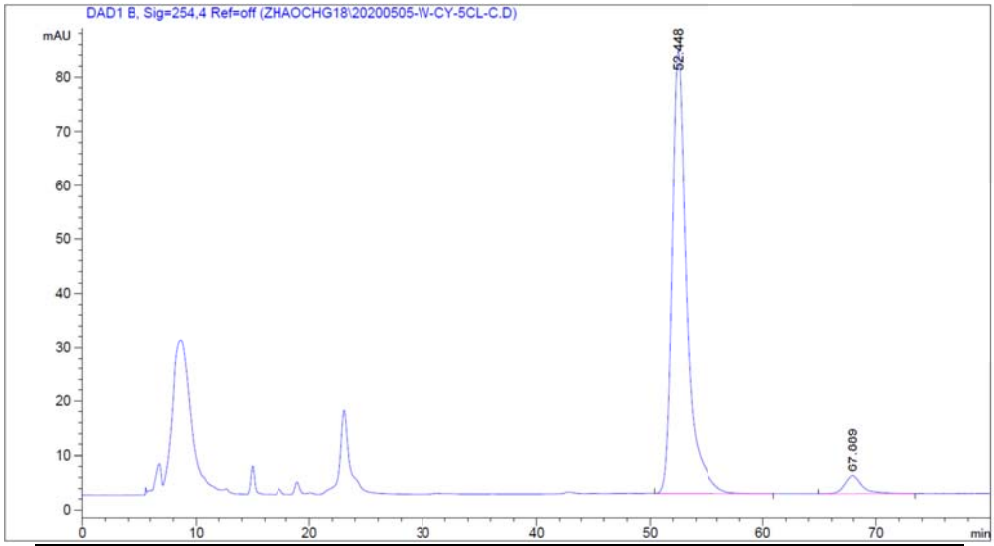
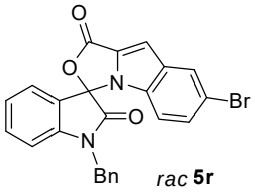
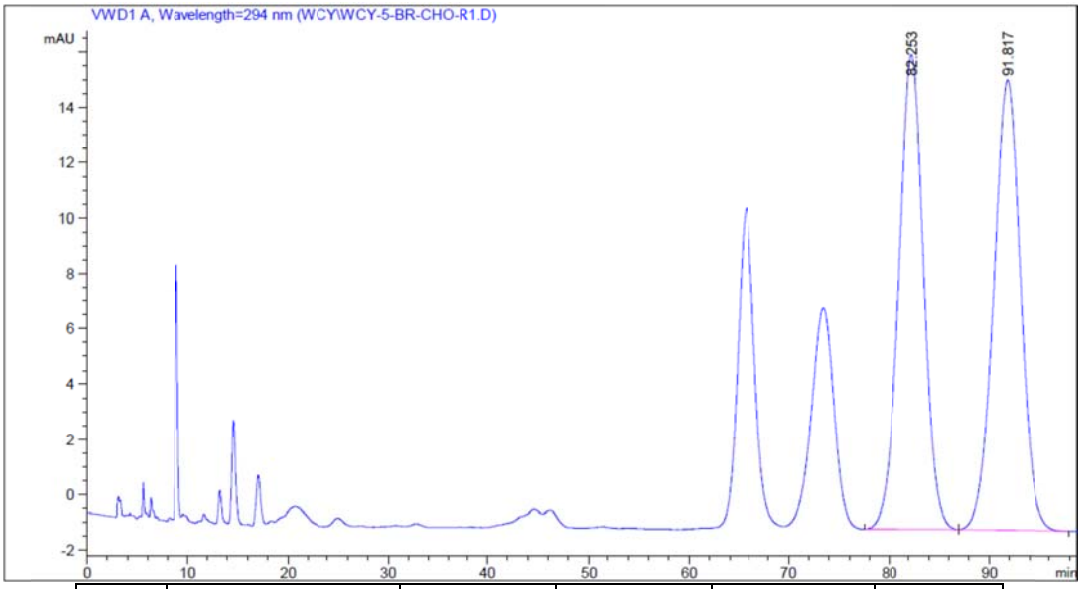


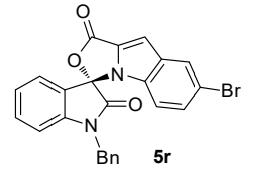
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	52.448	7294.73828	87.78465	95.0363
2	PDA 254.0 nm	67.889	381.00415	3.38533	4.9637



rac **5r**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	82.253	2951.16162	17.14303	49.2568
2	PDA 294.0 nm	91.817	3040.22070	16.28676	50.7432



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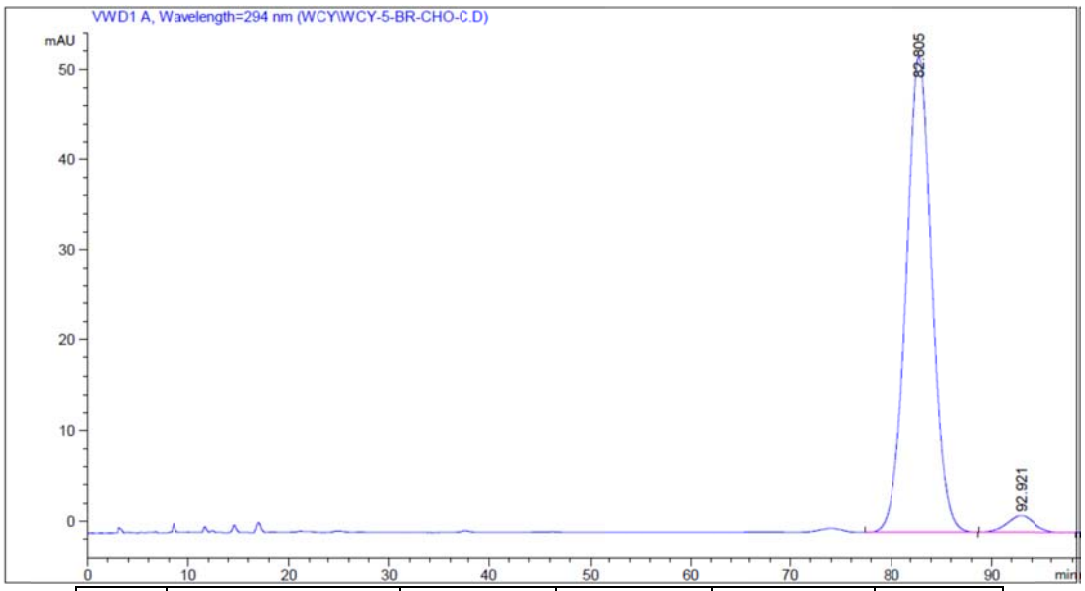
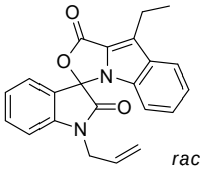
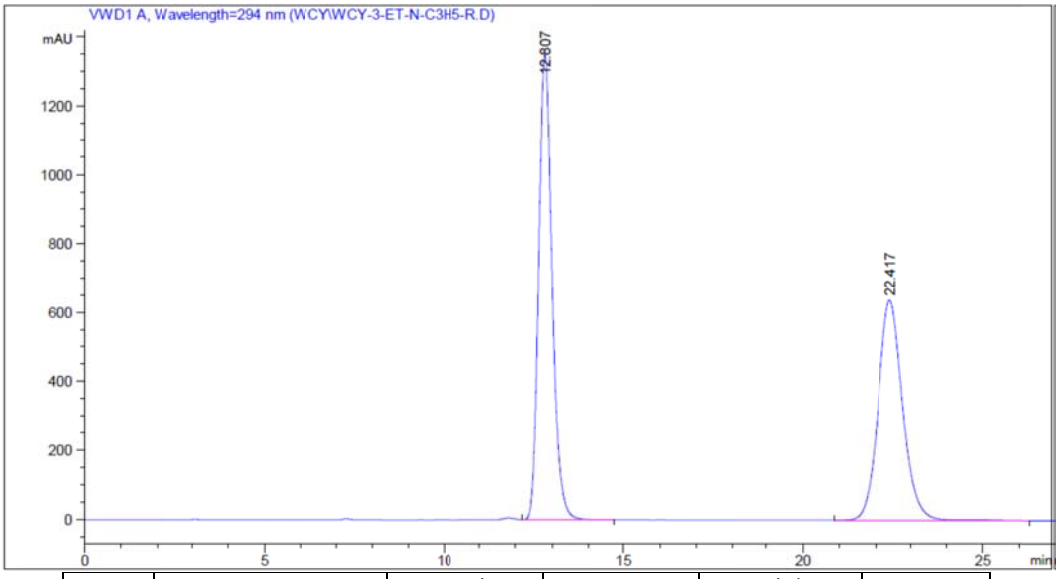


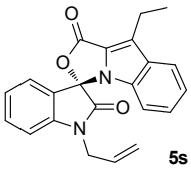
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	82.805	9420.01465	52.62624	96.2964
2	PDA 294.0 nm	92.921	362.29788	1.86916	3.7036



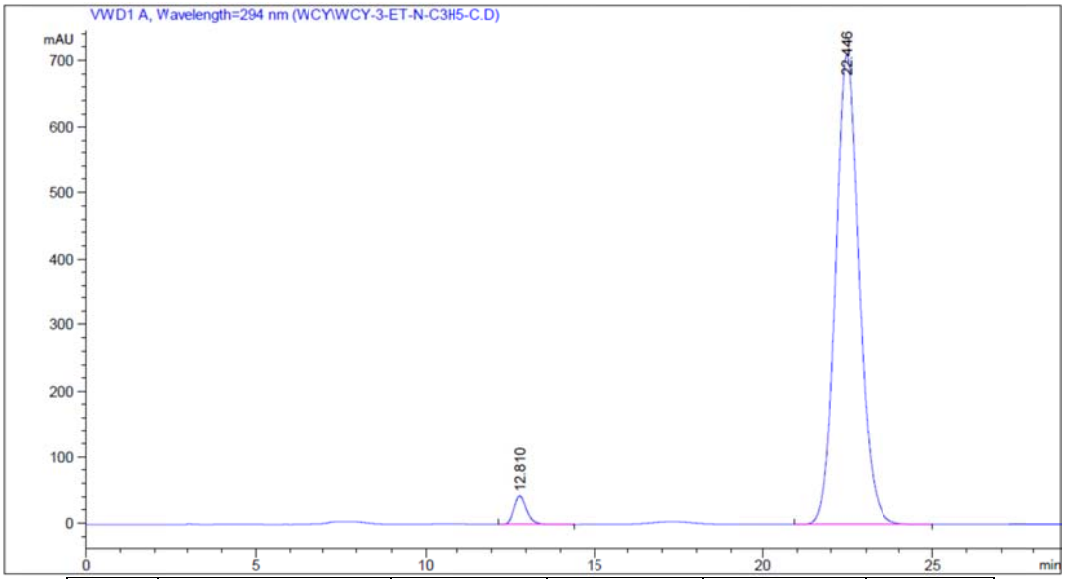
rac **5s**



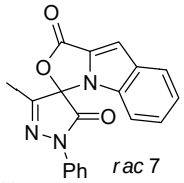
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	12.807	3.46980e4	1351.60425	53.2062
2	PDA 294.0 nm	22.417	3.05163e4	637.57477	46.7938



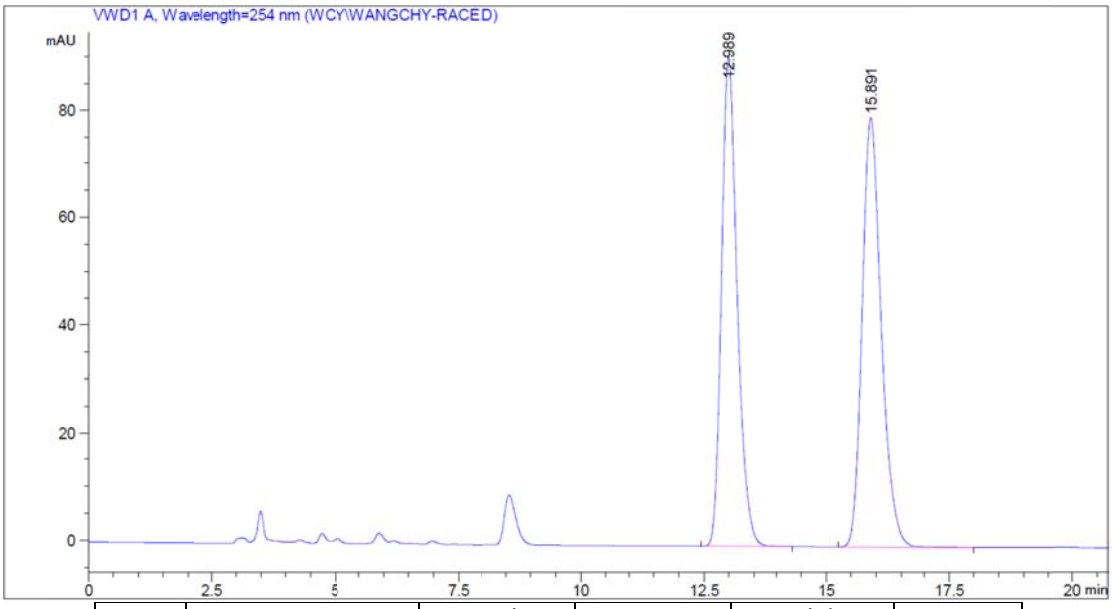
5s



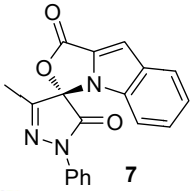
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 294.0 nm	12.810	1105.50500	43.19627	3.1356
2	PDA 294.0 nm	22.446	3.41506e4	710.54584	96.8644



rac 7



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	12.989	1979.45972	90.92188	48.2861
2	PDA 254.0 nm	15.891	2119.97681	79.88206	51.7139



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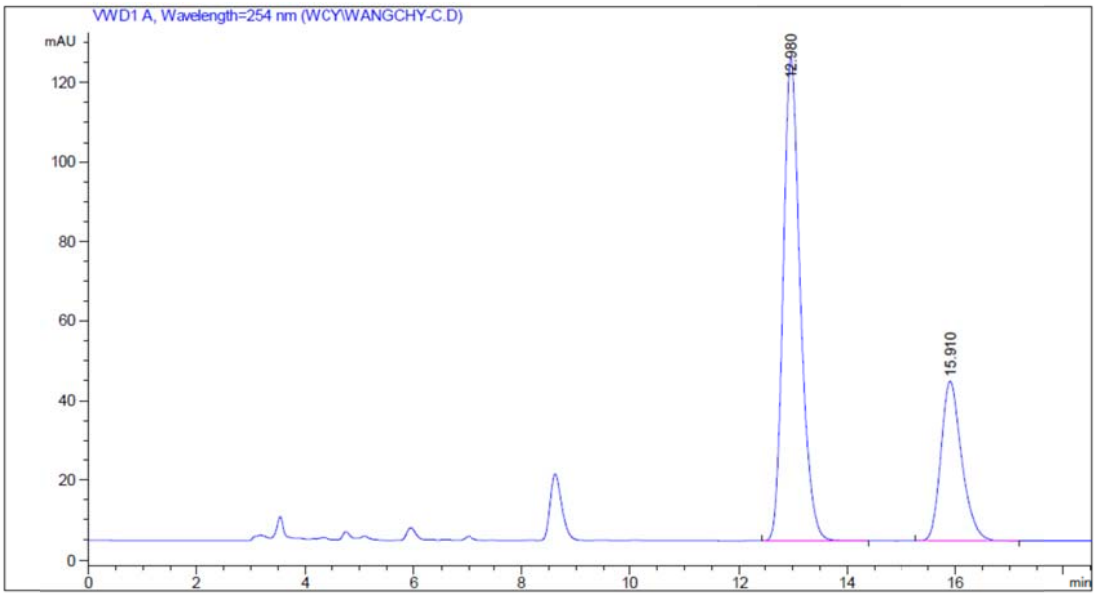

Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	12.980	2621.02124	121.33563	71.3508
2	PDA 254.0 nm	15.910	1052.41016	39.99773	28.6492