Supporting Information for

Highly Diastereo- and Enantioselective Construction of Spiro[cyclopenta[*b*]indole-1,3'-oxindole] Scaffold via Catalytic Asymmetric Formal [3+2] Cycloadditions

Wei Tan, Xin Li, Yu-Xin Gong, Meng-Di Ge and Feng Shi*

School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou, 221116, China

Email: fshi@jsnu.edu.cn

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1. General method

NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a micrOTOF-QⅡ HRMS/MS instrument (Bruker). Enantiomeric excesses (*ee*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric excesses by chiral HPLC were Chiralpak IC and IA columns. Optical rotation values were measured with instruments operating at $\lambda = 589$ nm, corresponding to the sodium D line at the temperatures indicated. Analytic grade solvents for the column chromatography and commercially available reagents were used as received. Substrates **1** and **2** were synthesized according to the literature methods.[1]

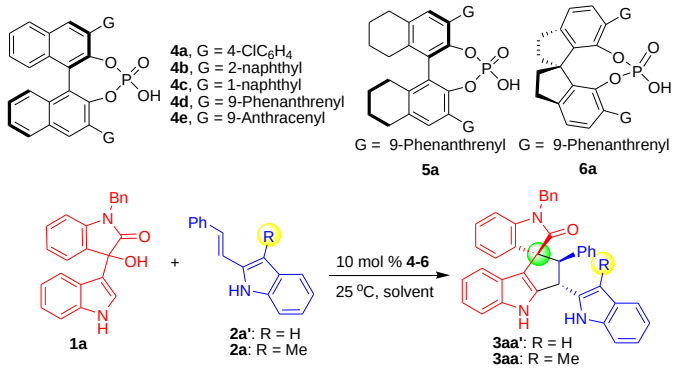
2. Screening of catalysts and optimization of conditions

To testify our hypothesis, isatin-derived 3-indolylmethanol **1a** was initially subjected to the reactions with 2-vinylindoles **2a'** and **2a**, respectively, in the presence of CPA **4a** (Table1, entries 1-2). As expected, 2-vinylindole **2a'** failed to afford the desired [3+2] cycloaddition product **3aa'** (entry 1), while 3-methyl-2-vinylindole **2a** successfully delivered the designed spiro[cyclopenta[*b*]indole-1,3'-oxindole] **3aa** in a high yield and good stereoselectivity within one hour (entry 2). These results demonstrated that the introduction of a methyl group to C3-position of 2-vinylindole greatly switched its reactivity, leading to the desired [3+2] cycloaddition with 3-indolylmethanol. So, substrate **2a** was utilized to the experiments on screening of BINOL-derived CPAs **4** (entries 2-6), which revealed that 3,3'-(9-phenanthrenyl)-substituted CPA **4d** delivered the reaction in the highest stereoselectivity (entry 5). Then, the BINOL backbone of catalyst **4d** was changed to structurally more rigid H_8-BINOL and SPINOL backbones, leading to further improved enantioselectivities (entries 7-8 *vs* 5) but with a decrease of the yield (entry

1. (a) Q.−X. Guo, Y.−G. Peng, J.−W. Zhang, L. Song, Z. Feng, L.−Z. Gong, *Org. Lett.* **2009**, *11*, 4620; (b) L. Song, Q.−X. Guo, X.−C. Li, J. Tian, Y.−G. Peng , *Angew. Chem. Int. Ed.* **2012**, *51*, 1899; (c) C. Zheng, Y. Lu, J. Zhang, X. Chen, Z. Chai, W. Ma, G. Zhao, *Chem. Eur. J.* **2010**, *16*, 5853.

8 *vs* 5). In the presence of spiro-CPA **6a**, different types of solvents were tested for the aim to increase the yield without sacrifice of the stereoselectivity (entry 8-12). Although chloroform greatly enhanced the yield, the enantioselectivity was decreased to the same level as CPA **4a** offered (entry 9 *vs* 5). Considering the excellent catalytic activity and synthetic simplicity of H_8-BINOL derived CPA **5a** (entry 7), this catalyst was finally chosen as the most suitable one for further evaluation on the reaction temperature (entries 13-14). The results disclosed that elevating the temperature was detrimental to the enantioselectivity (entry 13 *vs* 7), while properly lowering the temperature to 0^oC led to a higher enantioselectivity of 98% *ee* albeit with a prolonged reaction time (entry 14 *vs* 7).

Table 1. Screening of catalysts and optimization of conditions[a]

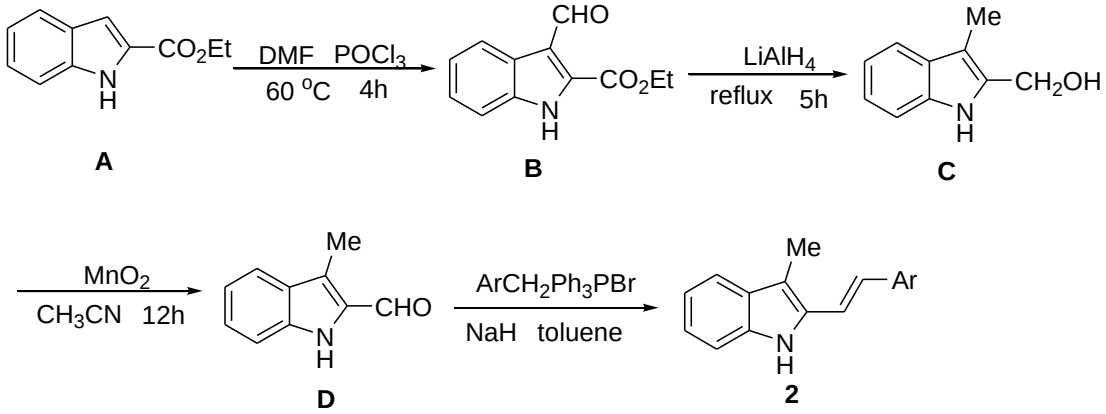


Entry	**3**	Cat.	solvent	yield (%)[b]	dr[c]	ee (%)[d]
1	**3aa'**	**4a**	toluene	trace	-	-
2	**3aa**	**4a**	toluene	91	88:12	79
3	**3aa**	**4b**	toluene	99	75:15	50
4	**3aa**	**4c**	toluene	97	87:13	76
5	**3aa**	**4d**	toluene	99	>95:5	94
6	**3aa**	**4e**	toluene	99	95:5	90
7	**3aa**	**5a**	toluene	99	>95:5	95
8	**3aa**	**6a**	toluene	72	>95:5	97
9	**3aa**	**6a**	$CHCl_3$	99	>95:5	94
10	**3aa**	**6a**	CH_3CN	33	>95:5	71

11	**3aa**	**6a**	AcOEt	trace	-	-
12	**3aa**	**6a**	1,4-dioxane	trace	-	-
13[e]	**3aa**	**5a**	toluene	99	>95:5	78
14[f]	**3aa**	**5a**	toluene	97	>95:5	98

[a] Unless indicated otherwise, the reaction was carried out in 0.05 mmol scale catalyzed by 10 mol % **4**-**6** in solvent (0.5 mL) at 25^{o}C for 1 h, and the mole ratio of **1a**:**2a** was 1:1.2. [b] Isolated yield. [c] The *dr* value was determined by ^{1}H MMR. [d] The *ee* value was determined by HPLC. [e] Performed at 50^{o}C. [f] Performed at 0^{o}C for 12 h.

3. General procedure for the synthesis of substrates 2



A to **B**: Under argon atmosphere, 2.7 mL anhydrous DMF (35 mmol) was added to a dried flask and cooled to 0 ^{o}C. Then, 1 mL $POCl_3$ (11 mmol) was added dropwise to the reaction system and stirred for 5 min at 0 ^{o}C. Substrate **A** (10 mmol) was dissolved in 4 mL anhydrous DMF and was added to the reaction system. Then, the reaction mixture was stirred at rt for 30 min and was warmed to 60 ^{o}C to react for 4 h. After stopping the reaction, NaOH aqueous solution (2 M) was added to the reaction mixture at 0 ^{o}C and modulated the pH to 7. Subsequently, a large amount of water was added to the reaction mixture and stirred for 5 min to generate a yellow solid (compound **B**), which was filtered and subjected to the next step.

B to **C**: Under argon atmosphere, compound **B** (5 mmol) was added to a dried flask and dissolved in 40 mL anhydrous THF. Then, $LiAlH_4$ (25 mmol) was added to the reaction system by many portions at 0 ^{o}C and stirred for 10 min at rt, which was

further refluxed at 80 ^{o}C for 5 h. After completing the reaction, NaOH aqueous solution (1 M) was added to the reaction mixture at 0 ^{o}C and modulated the pH to 7. Subsequently, the resultant reaction mixture was extracted by EtOAc and the organic layer was further purified by flash column chromatography (petroleum ether/ethyl acetate = 2/1) to obtain compound **C**.

C to **D**: To a stirred solution of compound **C** (5 mmol) in CH_3CN (40 mL), MnO_2 (30 mmol) was added by many portions and then reacted at rt for 15 h, which indicated the completion of the reaction by TLC. Then, the reaction mixture was filtered and the filtrate was condensed, which was purified by flash column chromatography (petroleum ether/ethyl acetate = 15/1) to give compound **D**.

D to substrates **2**: Under argon atmosphere, $ArCH_2Ph_3PBr$ (0.96 mmol) was added to a dried flask and dissolved in 3 mL anhydrous toluene. Then, NaH (1.6 mmol) was added to the reaction system at 0 ^{o}C and stirred for 20 min at rt. Subsequently, the solution of compound **D** (0.8 mmol) in anhydrous toluene (3 mL) was added to the reaction system, which was reacted at 80 ^{o}C for 2 h. After completing the reaction, saturated NH_4Cl aqueous solution was added to the reaction mixture, which was extracted by EtOAc. The resultant organic layer was dried by anhydrous Na_2SO_4 and purified by flash column chromatography (petroleum ether/ethyl acetate = 50/1) to afford substrates **2**.

(*E*)-3-methyl-2-styryl-1H-indole (2a): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.56 – 7.52 (m, 3H), 7.40 – 7.28 (m, 4H), 7.28 – 7.18 (m, 3H), 7.14 – 7.07 (m, 1H), 6.80 (d, *J* = 16.5, 1H), 2.42 (s, 3H).

(*E*)-3-methyl-2-(2-methylstyryl)-1H-indole (2b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.24 – 7.19 (m, 3H), 7.18 – 7.10 (m, 2H), 7.01 (d, *J* = 16.3 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H).

(*E*)-2-(2-fluorostyryl)-3-methyl-1H-indole (2c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.64 (td, *J* = 7.7, 1.7 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.24 – 7.19 (m, 2H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.95 (d, *J* = 16.6 Hz, 1H), 2.42 (s, 3H).

(*E*)-3-methyl-2-(3-methylstyryl)-1H-indole (2d): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (s, 1H), 7.54 (d, *J* = 7.9, 1H), 7.36 – 7.29 (m, 3H), 7.28 (d, *J* = 7.5, 1H), 7.25 – 7.17 (m, 2H), 7.14 – 7.06 (m, 2H), 6.78 (d, *J* = 16.5, 1H), 2.42 (s, 3H), 2.40 (s, 3H).

(*E*)-2-(3-chlorostyryl)-3-methyl-1H-indole (2e): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.55 (d, *J* = 7.9, 1H), 7.50 (t, *J* = 1.8, 1H), 7.37 (d, *J* = 7.7, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 7.15 – 7.08 (m, 1H), 6.71 (d, *J* = 16.4, 1H), 2.42 (s, 3H).

(*E*)-3-methyl-2-(4-methylstyryl)-1H-indole (2f): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.56 (d, *J* = 7.9, 1H), 7.51 – 7.44 (m, 2H), 7.31 (d, *J* = 8.0, 1H), 7.25 – 7.19 (m, 1H), 7.18 – 7.05 (m, 4H), 6.74 (d, *J* = 16.5, 1H), 2.42 (s, 3H).

(*E*)-2-(4-fluorostyryl)-3-methyl-1H-indole (2g): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.55 (d, *J* = 7.8, 1H), 7.43 (d, *J* = 8.1, 2H), 7.31 (d, *J* = 8.0, 1H), 7.24 – 7.15 (m, 4H), 7.14 – 7.08 (m, 1H), 6.78 (d, *J* = 16.5, 1H), 2.42 (s, 3H), 2.38 (s, 3H).

4. General procedure for the synthesis of products 3 and control experiments

Toluene (0.5 mL) was added to the mixture of 3-indolylmethanols **1** (0.05 mmol), 3-methyl-2-vinylindoles **2** (0.06 mmol) and the catalyst **5a** (0.005 mmol). The resultant reaction mixture was stirred at rt or 0 ^{o}C for a given time, which was purified through flash column chromatography to afford pure products **3**.

5. Characterization data of products 3

(1R,2R,3R)-1'-benzyl-5'-methyl-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ba):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 91% (26.7 mg); >95:5 dr; white solid; m.p. 169–170 ^{o}C; $[\alpha]_D^{20}$ = –56.0 (c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.93 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 7.27 – 7.25 (m, 1H), 7.25 – 7.19 (m, 4H), 7.19 – 7.13 (m, 4H), 7.13 – 7.06 (m, 4H), 7.02 – 6.93 (m, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 7.1 Hz, 2H), 6.43 (d, *J* = 7.9 Hz, 1H), 5.89 (d, *J* = 9.7 Hz, 1H), 4.97 (d, *J* = 16.0 Hz, 1H), 4.56 (d, *J* = 9.7 Hz, 1H), 4.36 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H), 2.17 (s,

3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.2, 144.6, 140.8, 140.5, 135.6, 135.4, 135.4, 132.5, 132.3, 130.8, 129.4, 129.3, 128.8, 128.5, 128.2, 127.7, 127.0, 126.5, 124.2, 123.0, 121.9, 120.1, 119.3, 118.8, 118.5, 118.1, 112.2, 110.6, 109.7, 109.0, 70.6, 60.4, 43.6, 41.1, 21.2, 8.7. IR (KBr): 3544, 3494, 3029, 2920, 2361, 2342, 1698, 1496, 1340, 741, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O\text{-}H)^-$ requires m/z 582.2545, found m/z 582.2575. Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.287 min (minor), t_R = 4.927 min (major).

(1R,2R,3R)-1'-benzyl-5'-chloro-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ca):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 6 h ; yield: 74% (22.2 mg); >95:5 dr; white solid; m.p. 160–161 ^oC; $[\alpha]_D^{20}$ = –122.2 (c 0.248, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.89 (s, 1H), 7.48 – 7.44 (m, 2H), 7.32 – 7.30 (m, 1H), 7.28 – 7.27 (m, 1H), 7.26 – 7.21 (m, 3H), 7.20 – 7.18 (m, 2H), 7.17 – 7.12 (m, 4H), 7.11 – 7.07 (m, 3H), 7.03 – 6.97 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.2 Hz, 2H), 6.44 (d, *J* = 8.3 Hz, 1H), 5.88 (d, *J* = 9.7 Hz, 1H), 4.98 (d, *J* = 16.0 Hz, 1H), 4.52 (d, *J* = 9.7 Hz, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.7 144.7, 141.8, 140.4, 135.6, 134.9, 134.8 132.6 131.9, 129.3 129.2, 128.7 128.6 128.3, 128.3 127.9, 127.2, 126.5 123.9 122.8, 122.1, 122.1 120.4 119.4, 118.6 118.1 118.0, 112.2, 110.6, 110.3, 110.1, 70.7, 60.5, 43.7, 41.0, 8.7. IR (KBr): 3524, 3493, 3294, 2960, 2922, 2853, 2360, 2341, 1715, 1698, 1487, 1456, 1170, 1028, 741, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{32}ClN_3O\text{-}H)^-$ requires m/z 602.1998, found m/z 602.2010. Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 3.943 min (minor), t_R = 4.300 min (major).

(1R,2R,3R)-1'-benzyl-6'-methoxy-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3da):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 97% (29 mg); >95:5 dr; white solid; m.p. 158–159 ^{o}C; $[\alpha]_D^{20}$ = –216.0 (c 0.488, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.95 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.21 (m, 5H), 7.19 – 7.13 (m, 4H), 7.12 – 7.09 (m, 3H), 7.08 – 7.07 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 2H), 6.13 (d, *J* = 2.2 Hz, 1H), 5.87 (d, *J* = 9.7 Hz, 1H), 4.95 (d, *J* = 16.0 Hz, 1H), 4.53 (d, *J* = 9.8 Hz, 1H), 4.34 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.7, 160.2, 144.5, 144.4, 140.4, 135.6, 135.4, 135.3, 132.5, 129.4, 129.3, 128.6, 128.2, 127.7, 127.1, 126.5, 124.1, 123.0, 122.5, 121.9, 121.8, 120.2, 119.3, 118.9, 118.5, 118.1, 112.1, 110.6, 109.7, 106.6, 97.3, 70.6, 59.9, 55.3, 43.6, 40.87, 8.7. IR (KBr): 3534, 3488, 3309, 3199, 2921, 2361, 2343, 1699, 1503, 1377, 1161, 1031, 742, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O\text{-}H)^-$ requires m/z 598.2494, found m/z 598.2515. Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.333 min (minor), t_R = 4.820 min (major)

(1R,2R,3R)-1'-benzyl-6'-bromo-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ea):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 97% (31.4 mg); >95:5 dr; white solid; m.p. 186–187 ^{o}C; $[\alpha]_D^{20}$ = -155.7 (c 0.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.91 (s, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.22 (m, 4H), 7.19 – 7.16 (m, 4H), 7.14 – 7.09 (m, 4H), 7.09 – 7.07 (m, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.68 (s, 1H), 6.49 (d, *J* = 7.5 Hz, 2H), 5.86 (d, *J* = 9.7 Hz, 1H), 4.94 (d, *J* = 16.1 Hz, 1H), 4.52 (d, *J* = 9.7 Hz, 1H), 4.32 (d, *J* = 16.1 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.1, 144.7, 144.6, 140.4, 135.6, 135.0, 134.6, 132.1, 129.8, 129.4, 129.2, 128.7, 128.4, 127.9, 127.3, 126.4, 125.8, 124.8, 122.8, 122.0, 122.0, 122.0, 120.3, 119.4, 118.5, 118.0, 117.9, 112.6, 112.2, 110.7, 109.9, 70.5, 60.1, 43.6, 41.01, 8.7. IR (KBr): 3546, 3494, 2921, 2361, 2342,

1699, 1603, 1487, 1456, 1260, 1171, 740, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{30}BrN_3O\text{-}H)^-$ requires m/z 646.1493, found m/z 646.1508. Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak IA, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 19.683 min (minor), t_R = 26.087 min (major).

(1R,2R,3R)-1'-benzyl-7'-methyl-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro -2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3fa):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 95% (27.8 mg); >95:5 dr; white solid; m.p. 184–185 ^oC; $[\alpha]_D^{20}$ = –861.4 (c 0.51, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.96 (s, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 6.2 Hz, 1H), 7.23 (s, 1H), 7.22 – 7.17 (m, 4H), 7.16 – 7.12 (m, 3H), 7.12 – 7.08 (m, 4H), 7.07 – 7.05 (m, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.41 (d, *J* = 7.1 Hz, 2H), 5.87 (d, *J* = 9.8 Hz, 1H), 5.13 (d, *J* = 17.0 Hz, 1H), 4.72 (d, *J* = 17.0 Hz, 1H), 4.58 (d, *J* = 9.8 Hz, 1H), 2.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.1, 144.5, 141.4, 140.4, 137.4, 135.6, 135.4, 132.5, 131.5, 129.4, 129.4, 128.7, 128.3, 127.8, 126.6, 125.3, 122.9, 122.9, 121.8, 121.8, 121.7, 120.1, 119.7, 119.3, 119.1, 118.5, 118.0, 112.2, 110.7, 109.7, 70.9, 59.8, 44.9, 41.1, 18.7, 8.7. IR (KBr): 3564, 3498, 2971, 2360, 2341, 1683, 1540, 1456, 1339, 742, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O\text{-}H)^-$ requires m/z 582.2545, found m/z 582.2566. Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 24.543 min (major), t_R = 39.460 min (minor).

(1R,2R,3R)-1'-benzyl-7'-bromo-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro -2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ga):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 97% (31.5 mg); >95:5 dr; white solid; m.p. 178–179 ^oC; $[\alpha]_D^{20}$ = -165.2 (c 0.488, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.95 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.40 (dd, *J* = 8.2, 1.1 Hz, 1H),

7.26 – 7.22 (m, 1H), 7.22 – 7.19 (m, 2H), 7.19 – 7.13 (m, 5H), 7.12 – 7.06 (m, 5H), 7.02 – 6.97 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.48 (d, *J* = 7.1 Hz, 2H), 5.84 (d, *J* = 9.7 Hz, 1H), 5.14 (dd, *J* = 37.8, 16.7 Hz, 2H), 4.55 (d, *J* = 9.7 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.9, 144.6, 140.8, 140.4, 137.2, 135.6, 134.9, 134.5, 134.2, 132.1, 129.4, 129.2, 128.4, 128.4, 128.1, 126.5, 125.7, 124.2, 122.9, 122.7, 122.0, 122.0, 120.3, 119.4, 118.5, 118.4, 117.9, 112.2, 110.7, 109.8, 102.4, 71.0, 60.1, 44.4, 41.16, 8.7. IR (KBr): 3554, 3493, 3307, 2923, 2855, 2360, 2341, 1698, 1450, 1339, 1116, 1021, 739, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{30}BrN_3O\text{-}H)^-$ requires m/z 646.1493, found m/z 646.1468. Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 9.717 min (major), t_R = 28.957 min (minor).

(1R,2R,3R)-1'-benzyl-7-methoxy-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ha):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 92% (27.5 mg); >95:5 dr; white solid; m.p. 173–174 ^oC; $[\alpha]_D^{20}$ = –191.3 (c 0.424, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.97 (s, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.18 (m, 3H), 7.15 (s, 2H), 7.14 – 7.12 (m, 2H), 7.12-7.10 (m, 2H), 7.10 – 7.09 (m, 2H), 7.08 – 7.07 (m, 1H), 6.74 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 3H), 6.24 (d, *J* = 2.4 Hz, 1H), 5.86 (d, *J* = 9.8 Hz, 1H), 4.98 (d, *J* = 16.0 Hz, 1H), 4.55 (d, *J* = 9.8 Hz, 1H), 4.41 (d, *J* = 16.0 Hz, 1H), 3.65 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.3, 154.3, 145.6, 143.2, 135.6, 135.6, 135.3, 132.4, 130.5, 129.4, 129.2, 128.6, 128.5, 128.2, 127.7, 127.1, 126.5, 123.5, 123.5, 122.9, 121.9, 119.3, 118.5, 118.3, 112.6, 110.8, 110.6, 109.7, 109.3, 101.2, 70.6, 60.3, 55.9, 43.6, 41.0, 8.7. IR (KBr): 3565, 3413, 3236, 2360, 2341, 1715, 1697, 1637, 1615, 1488, 1456, 1170, 744, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O_2\text{-}H)^-$ requires m/z 598.2494, found m/z 598.2516. Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC,

hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.643 min (minor), t_R = 6.027 min (major).

(1R,2R,3R)-1'-benzyl-7-bromo-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ia):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 7 h ; yield: 79% (25.8 mg); >95:5 dr; white solid; m.p. 153–155 ^{o}C; $[\alpha]_D^{20}$ = 703.7 (c 0.428, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.93 (s, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.43 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.24 – 7.23 (m, 1H), 7.21 – 7.19 (m, 1H), 7.19 – 7.18 (m, 1H), 7.18 – 7.16 (m, 2H), 7.16 – 7.14 (m, 2H), 7.13 – 7.12 (m, 1H), 7.12 – 7.09 (m, 1H), 7.07 – 7.01 (m, 4H), 6.97 (t, *J* = 7.7 Hz, 2H), 6.63 – 6.54 (m, 4H), 5.85 (d, *J* = 9.6 Hz, 1H), 4.91 (d, *J* = 15.9 Hz, 1H), 4.53 (d, *J* = 9.6 Hz, 1H), 4.48 (d, *J* = 16.0 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.8, 145.1, 143.0, 141.2, 135.5, 135.1, 135.1, 132.0, 130.5, 129.6, 129.0, 128.7, 128.7, 128.3, 127.8, 127.2, 126.5, 123.5, 123.3, 123.1, 122.0, 121.4, 119.4, 118.6, 118.1, 115.2, 115.1, 110.7, 109.6, 109.5, 70.5, 60.5, 43.7, 41.6, 8.8. IR (KBr): 3555, 3423, 2924, 2360, 2341, 1715, 1696, 1684, 1614, 1456, 1173, 746, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{30}BrN_3O\text{-}H)^-$ requires m/z 646.1493, found m/z 646.1480. Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 3.690 min (minor), t_R = 4.067 min (major).

(1R,2R,3R)-1'-benzyl-6-methyl-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ja):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 83% (24.3 mg); >95:5 dr; white solid; m.p. 167–168 ^{o}C; $[\alpha]_D^{20}$ = –991.2 (c 0.306, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.97 (s, 1H), 7.50 – 7.44 (m, 2H), 7.25 – 7.21 (m, 2H), 7.19 – 7.16 (m, 4H), 7.15 – 7.10 (m, 5H), 7.10 – 7.06 (m, 2H), 6.96 (s, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 3H), 5.87 (d, *J* = 9.6 Hz, 1H), 4.96 (d, *J* = 16.0 Hz, 1H), 4.54 (d, *J*

= 9.6 Hz, 1H), 4.41 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.4, 143.8, 143.2, 141.0, 135.6, 135.4, 135.3, 132.6, 131.6, 130.8, 129.5, 129.2, 128.6, 128.4, 128.2, 127.7, 127.1, 126.5, 123.5, 122.8, 121.8, 121.7, 120.7, 119.3, 118.5, 118.4, 117.5, 112.2, 110.6, 109.6, 109.2, 70.6, 60.5, 43.6, 41.2, 21.7, 8.7. IR (KBr): 3565, 3433, 3291, 3057, 2920, 2857, 1696, 1611, 1488, 1465, 1174, 803, 741, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O\text{-}H)^-$ requires m/z 582.2545, found m/z 582.2569. Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.227 min (minor), t_R = 5.860 min (major).

(1R,2R,3R)-1'-benzyl-6-bromo-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ka):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 7 h ; yield: 81% (26.3 mg); >95:5 dr; white solid; m.p. 157–158 ^oC; $[\alpha]_D^{20}$ = –494.8 (c 0.426, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.92 (s, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 6.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.18 (m, 2H), 7.17 – 7.13 (m, 4H), 7.11 – 7.10 (m, 2H), 7.05 – 7.03 (m, 4H), 6.99 – 6.95 (m, 2H), 6.64 – 6.52 (m, 4H), 5.85 (d, *J* = 9.6 Hz, 1H), 4.91 (d, *J* = 15.9 Hz, 1H), 4.53 (d, *J* = 9.6 Hz, 1H), 4.48 (d, *J* = 15.9 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.8, 145.2, 143.0, 141.2, 135.5, 135.1, 135.1, 132.0, 130.5, 129.6, 129.0, 128.7, 128.7, 128.3, 127.8, 127.2, 126.5, 123.5, 123.3, 123.1, 121.0, 122.4, 119.4, 118.6, 118.1, 115.2, 115.1, 110.7, 109.6, 109.5, 70.4, 60.5, 43.7, 41.6, 8.8. IR (KBr): 3545, 3493, 3274, 3057, 2921, 2361, 1687, 1606, 1457, 1261, 1173, 802, 746, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{30}BrN_3O\text{-}H)^-$ requires m/z 646.1493, found m/z 646.1483. Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 3.693 min (minor), t_R = 4.067 min (major).

(1R,2R,3R)-1'-benzyl-5-methyl-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3la):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 88% (25.6 mg); >95:5 dr; white solid; m.p. 176–178 ^{o}C; $[\alpha]_D^{20}$ = –166.9 (c 0.528, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.00 (s, 1H), 7.50 (t, *J* = 6.7 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.26 – 7.21 (m, 3H), 7.21 – 7.15 (m, 4H), 7.14 – 7.12 (d, *J* = 7.1 Hz, 3H), 7.10 – 7.09 (m, 2H), 6.95 – 6.86 (m, 2H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.54 (t, *J* = 7.2 Hz, 3H), 5.96 (d, *J* = 9.7 Hz, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.60 (d, *J* = 9.7 Hz, 1H), 4.42 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.2, 144.2, 143.3, 140.0, 135.6, 135.4, 135.3, 132.6, 130.7, 129.4, 129.2, 128.6, 128.5, 128.2, 127.7, 127.0, 126.5, 123.5, 122.8, 122.7, 122.5, 122.0, 121.3, 120.4, 119.4, 119.3, 118.5, 115.8, 110.7, 109.9, 109.3, 70.6, 60.5, 43.6, 41.1, 16.8, 8.7. IR (KBr): 3552, 3416, 3236, 2919, 1694, 1638, 1616, 1465, 1383, 1299, 1080, 741, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O\text{-}H)^-$ requires m/z 582.2545, found m/z 582.2584. Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.010 min (major), t_R = 4.483 min (minor).

(1R,2R,3R)-1'-benzyl-5-bromo-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ma):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 9 h ; yield: 72% (23.3 mg); >95:5 dr; white solid; m.p. 150–151 ^{o}C; $[\alpha]_D^{20}$ = –97.1 (c 0.344, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.95 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.25 – 7.23 (m, 1H), 7.22 – 7.20 (m, 2H), 7.20 – 7.16 (m, 3H), 7.16 – 7.13 (m, 2H), 7.12 – 7.10 (m, 2H), 7.07 – 7.07 (m, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.55 – 6.50 (m, 3H), 5.95 (d, *J* = 9.8 Hz, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.59 (d, *J* = 9.9 Hz, 1H), 4.41 (d, *J* = 16.0 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.7, 145.2, 143.3, 138.9, 135.7, 135.2, 134.9, 131.8, 130.3, 129.3, 129.2, 128.7, 128.6, 128.3, 127.87, 127.1, 126.5, 124.4, 124.2, 123.4, 122.9, 122.2, 121.5, 120.0, 119.5, 118.6, 117.3, 110.7, 110.2, 109.4, 105.3, 70.6, 60.3, 43.7, 40.9, 8.7. IR (KBr): 3542, 3466, 2923, 2854, 2360, 1697, 1488, 1456, 1418, 1362, 741, 697 cm^{-1};

ESI FTMS exact mass calcd for $(C_{40}H_{30}BrN_3O\text{-}H)^-$ requires m/z 646.1493, found m/z 646.1467. Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IA, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 18.930 min (minor), t_R = 44.390 min (major).

(1R,2R,3R)-1'-benzyl-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3aa):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 12 h ; yield: 97% (27.6 mg); >95:5 dr; white solid; m.p. 171–173 ^oC; $[\alpha]_D^{20}$ = –195.7 (c 0.506, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.98 (s, 1H), 7.48 (t, *J* = 6.4 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.25 – 7.23 (m, 2H), 7.22 – 7.19 (m, 3H), 7.18 – 7.16 (m, 2H), 7.16 – 7.14 (m, 2H), 7.13 – 7.12 (m, 2H), 7.11 – 7.09 (m, 2H), 7.09 – 7.05 (m, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.53 (dd, *J* = 10.0, 7.7 Hz, 3H), 5.90 (d, *J* = 9.7 Hz, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.58 (d, *J* = 9.8 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.2, 144.7, 143.2, 140.5, 135.6, 135.3, 135.3, 132.4, 130.7, 129.4, 129.2, 128.6, 128.5, 128.3, 127.7, 127.1, 126.5, 123.5, 123.0, 122.9, 121.9, 120.2, 119.3, 118.6, 118.5, 118.0, 112.2, 110.7, 109.7, 109.3, 70.6, 60.4, 43.6, 41.0, 8.7. IR (KBr): 3525, 3443, 3277, 3029, 2918, 1695, 1608, 1488, 1353, 1173, 1080, 1012, 740, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{31}N_3O\text{-}H)^-$ requires m/z 568.2388, found m/z 568.2399. Enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.273 min (minor), t_R = 4.870 min (major).

(1R,2R,3R)-1'-benzyl-3-(3-methyl-1H-indol-2-yl)-2-(o-tolyl)-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ab):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 12 h ; yield: 93% (27.1 mg); >95:5 dr; white solid; m.p. 167–168 ^oC; $[\alpha]_D^{20}$ = –197.2 (c 0.608, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.08 (d, *J* = 7.0 Hz, 1H), 7.97 (s, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.21 – 7.20 (m,

1H), 7.19 – 7.17 (m, 3H), 7.15 – 7.12 (m, 4H), 7.11 – 7.09 (m, 1H), 7.08 – 7.05 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.59 – 6.54 (m, 3H), 5.75 (d, *J* = 9.5 Hz, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 5.06 (d, *J* = 9.5 Hz, 1H), 4.43 (d, *J* = 16.0 Hz, 1H), 2.05 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.7, 144.6, 143.1, 140.6, 137.7, 135.6, 135.4, 134.3, 132.6, 131.2, 130.2, 129.7, 129.5, 128.6, 128.5, 127.3, 127.1, 126.6, 126.1, 124.0, 122.9, 122.6, 121.9, 121.8, 120.1, 119.3, 118.6, 118.5, 118.1, 112.2, 110.7, 109.6, 109.3, 65.2, 60.4, 43.8, 43.7, 20.0, 8.4. IR (KBr): 3544, 3423, 3292, 3055, 3030, 2922, 2855, 2360, 2341, 1697, 1610, 1488, 1171, 740, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O\text{-}H)^-$ requires m/z 582.2545, found m/z 582.2587. Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.420 min (minor), t_R = 5.213 min (major).

(1R,2S,3R)-1'-benzyl-2-(2-fluorophenyl)-3-(3-methyl-1H-indol-2-yl)-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ac):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 12 h ; yield: 81% (23.9 mg); >95:5 dr; white solid; m.p. 156–157 ^oC; $[\alpha]_D^{20}$ = –652.3 (c 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.00 (s, 1H), 7.97 – 7.93 (m, 1H), 7.49 (dd, *J* = 7.2, 4.5 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.21 – 7.20 (m, 1H), 7.19 – 7.17 (m, 1H), 7.17 – 7.15 (m, 1H), 7.15 – 7.13 (m, 1H), 7.12 – 7.08 (m, 6H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.79 – 6.74 (m, 2H), 6.61 – 6.56 (m, 3H), 5.89 (d, *J* = 9.8 Hz, 1H), 5.07 (d, *J* = 9.8 Hz, 1H), 5.01 (d, *J* = 9.8 Hz, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.3, 162.5, 160.0, 144.4, 142.8, 140.4, 135.6, 135.4, 132.0, 130.9, 130.9, 130.2, 129.3, 129.0, 129.0, 128.6, 128.5, 127.1, 126.5, 124.2, 124.0, 124.0, 122.9, 122.9, 122.8, 122.7, 122.0, 121.9, 120.2, 119.3, 118.7, 118.5, 118.0, 115.4, 115.2, 112.1, 110.7, 109.9, 109.1, 60.6, 60.0, 43.6, 41.3, 8.6. IR (KBr): 3545, 3413, 3307, 3196, 3056, 2921, 2359, 1697, 1608, 1489, 1384, 740 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{30}FN_3O\text{-}H)^-$ requires m/z 586.2294, found m/z 586.2335. Enantiomeric excess: 97%, determined by HPLC

(Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.227 min (minor), t_R = 4.673 min (major).

(1R,2R,3R)-1'-benzyl-3-(3-methyl-1H-indol-2-yl)-2-(m-tolyl)-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ad):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 12 h ; yield: 83% (24.2 mg); >95:5 dr; white solid; m.p. 168–170 ^{o}C; $[\alpha]_D^{20}$ = –205.9 (c 0.544, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.94 (s, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.25 – 7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 7.18 – 7.14 (m, 2H), 7.13 – 7.08 (m, 5H), 7.05 (s, 3H), 6.97 – 6.93 (m, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.55 – 6.50 (m, 3H), 5.89 (d, *J* = 9.8 Hz, 1H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.54 (d, *J* = 9.8 Hz, 1H), 4.36 (d, *J* = 16.0 Hz, 1H), 2.20 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.2, 144.8, 143.3, 140.4, 137.6, 135.6, 135.4, 135.2, 132.5, 130.8, 129.9, 129.4, 128.5, 128.5, 128.1, 127.1, 126.5, 126.2, 123.5, 123.0, 122.8, 121.9, 121.8, 120.1, 119.3, 118.6, 118.5, 118.0, 112.1, 110.6, 109.8, 109.2, 70.6, 60.3, 43.6, 40.9, 21.3, 8.7. IR (KBr): 3515, 3433, 3293, 3197, 3055, 2918, 2359, 1697, 1608, 1488, 1384, 1173, 739, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O\text{-}H)^-$ requires m/z 582.2545, found m/z 582.2578. Enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.037 min (minor), t_R = 4.760 min (major).

(1R,2R,3R)-1'-benzyl-2-(3-chlorophenyl)-3-(3-methyl-1H-indol-2-yl)-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ae):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 12 h ; yield: 96% (28.9 mg); >95:5 dr; white solid; m.p. 164–165 ^{o}C; $[\alpha]_D^{20}$ = –223.6 (c 0.602, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.94 (s, 1H), 7.47 (dd, *J* = 17.5, 7.4 Hz, 2H), 7.25 – 7.22 (m, 3H), 7.22 – 7.21 (m, 1H), 7.20 – 7.18 (m, 1H), 7.18 – 7.14 (m, 4H), 7.13 – 7.11 (m, 3H), 7.10 – 7.08 (m, 1H), 7.06 – 7.04 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 3H), 5.83 (d, *J* = 9.7 Hz, 1H), 4.97 (d, *J* = 15.9 Hz, 1H), 4.52 (d, *J* = 9.7 Hz, 1H), 4.41 (d, *J*

= 15.9 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.9, 144.3, 143.2, 140.5, 137.5, 135.6, 135.3, 134.0, 131.9, 130.2, 129.5, 129.3, 129.3, 128.8, 128.6, 128.0, 127.4, 127.3, 126.6, 123.5, 123.0, 122.9, 122.1, 122.0, 120.3, 119.4, 118.6, 118.1, 112.2, 110.68, 109.9, 109.4, 69.9, 60.2, 43.64, 4.03, 8.7. IR (KBr): 3515, 3453, 3293, 3199, 3057, 2921, 1699, 1459, 1431, 1363, 1173, 740, 696 cm-1; ESI FTMS exact mass calcd for $(C_{40}H_{30}ClN_3O\text{-}H)^-$ requires m/z 602.1998, found m/z 602.2024. Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 3.853 min (minor), t_R = 4.260 min (major).

(1R,2R,3R)-1'-benzyl-3-(3-methyl-1H-indol-2-yl)-2-(p-tolyl)-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3af):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 12 h ; yield: 99% (29.1 mg); >95:5 dr; white solid; m.p. 176–177 ^oC; $[\alpha]_D^{20}$ = –524.5 (c 0.548, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.96 (s, 1H), 7.47 (t, *J* = 8.2 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.18 – 7.13 (m, 2H), 7.13 – 7.05 (m, 7H), 6.96 – 6.93 (m, 3H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.54 (dd, *J* = 7.6, 2.8 Hz, 3H), 5.86 (d, *J* = 9.8 Hz, 1H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.55 (d, *J* = 9.8 Hz, 1H), 4.37 (d, *J* = 16.0 Hz, 1H), 2.31 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.3, 144.8, 143.2, 140.4, 137.2, 135.6, 135.3, 132.5, 132.3, 130.8, 129.4, 129.1, 128.9, 128.4, 127.0, 126.6, 123.5, 123.0, 122.8, 121.8, 120.1, 119.3, 118.6, 118.5, 118.0, 112.1, 110.6, 109.7, 109.2, 70.3, 60.4, 43.6, 41.1, 21.2, 8.7. IR (KBr): 3552, 3475, 3414, 3236, 3056, 2919, 1697, 1638, 1616, 1488, 1464, 1172, 1012, 740, 621 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{33}N_3O\text{-}H)^-$ requires m/z 582.2545, found m/z 582.2563. Enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.453 min (minor), t_R = 5.453 min (major).

(1R,2R,3R)-1'-benzyl-2-(4-fluorophenyl)-3-(3-methyl-1H-indol-2-yl)-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ag):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 12 h ; yield: 99% (29.2 mg); >95:5 dr; white solid; m.p. 188–189 ^{o}C; $[\alpha]_D^{20}$ = –355.9 (c 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.95 (s, 1H), 7.47 (dd, *J* = 18.3, 7.4 Hz, 2H), 7.26 – 7.24 (m 1H), 7.24 – 7.20 (m, 3H), 7.18 – 7.17 (m, 2H), 7.16 – 7.13 (m, 3H), 7.13 – 7.10 (m, 2H), 7.09 – 7.07 (m, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.82 (t, *J* = 8.5 Hz, 3H), 6.63 – 6.54 (m, 3H), 5.82 (d, *J* = 9.7 Hz, 1H), 4.99 (d, *J* = 15.9 Hz, 1H), 4.52 (d, *J* = 9.7 Hz, 1H), 4.40 (d, *J* = 16.0 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.2, 163.7, 161.3, 144.4, 143.2, 140.5, 135.6, 135.2, 132.16, 131.17, 131.14, 130.89, 130.81, 130.46, 129.36, 128.66, 128.54, 127.29, 126.51, 123.49, 122.0, 123.9, 122.0, 122.0, 120.2, 119.4, 118.6, 118.5, 118.0, 115.2, 115.0, 112.2, 110.7, 109.8, 109.3, 69.8, 60.3, 43.6, 41.3, 8.7. IR (KBr): 3428, 3266, 3056, 2922, 2360, 2341, 1694, 1609, 1509, 1458, 1216, 739, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{30}FN_3O\text{-}H)^-$ requires m/z 586.2294, found m/z 586.2329. Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.037 min (minor), t_R = 4.467 min (major).

(1R,2R,3R)-1'-benzyl-4-methyl-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3na):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 4 h ; yield: 70.5% (20.6 mg); >95:5 dr; white solid; m.p. 210–212 ^{o}C; $[\alpha]_D^{20}$ = –190.3 (c 0.412, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.51 (t, *J* = 8.1 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.26 – 7.21 (m, 3H), 7.21 – 7.14 (m, 5H), 7.13 – 7.08 (m, 5H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.64 – 6.44 (m, 3H), 5.94 (d, *J* = 8.8 Hz, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.61 (d, *J* = 9.0 Hz, 1H), 4.42 (d, *J* = 16.0 Hz, 1H), 3.40 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.2, 145.7, 143.2, 141.4, 135.3, 132.5, 130.9, 129.2, 128.6, 128.5, 128.2, 127.7, 127.0, 126.5, 123.5, 122.8, 122.6, 121.8, 121.4, 119.8, 119.3, 118.5, 118.1, 110.61, 109.9, 109.2, 70.5, 60.2, 43.6, 30.1, 8.6. IR (KBr): 3419, 3383, 2923, 1645, 1616, 1456, 1416, 1340, 1261, 1158, 1080, 1029, 741 cm^{-1}; ESI FTMS exact mass calcd for

($C_{41}H_{33}N_3O$-H)$^-$ requires m/z 582.2545, found m/z 582.2579. Enantiomeric excess: 73%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.553 min (major), t_R = 5.123 min (minor).

1'-benzyl-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (3ai):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); Reaction time = 16 h ; yield: 29% (8.4 mg); >95:5 dr; white solid; m.p. 170–172 ^oC; $[\alpha]_D^{20}$ = –46.4 (c 0.168, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.31 (s, 1H), 8.00 (s, 1H), 7.47 (t, *J*=7.9, 2H), 7.32 (d, *J*=8.2, 1H), 7.25 – 7.22 (m, 2H), 7.21 – 7.19 (m, 2H), 7.18 – 7.16 (m, 2H), 7.16 – 7.14 (m, 2H), 7.14 – 7.10 (m, 3H), 7.10 – 7.04 (m, 3H), 6.95 (t, *J*=7.5, 1H), 6.79 (d, *J*=7.9, 1H), 6.51 (t, *J*=8.3, 3H), 5.91 (d, *J*=9.8, 1H), 5.01 (d, *J*=16.0, 1H), 4.57 (d, *J*=9.8, 1H), 4.40 (d, *J*=16.0, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.0, 144.7, 143.3, 140.4, 135.6, 135.3, 132.4, 130.6, 129.3, 129.2, 128.6, 128.2, 127.7, 127.0, 126.5, 123.5, 123.0, 122.8, 121.9, 120.2, 119.3, 118.5, 118.11, 112.07, 110.6, 109.9, 109.2, 70.6, 60.3, 43.6, 40.9, 8.6. IR (KBr): 3544, 3385, 2961, 2922, 1698, 1614, 1456, 1363, 1261, 1157, 1082, 1030, 803, 742 cm^{-1}; ESI FTMS exact mass calcd for ($C_{40}H_{31}N_3O$-H)$^-$ requires m/z 568.2388, found m/z 568.2416. Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.333 min (minor), t_R = 4.950 min (major).

6. Procedure and characterization data for the derivation of product 3ea

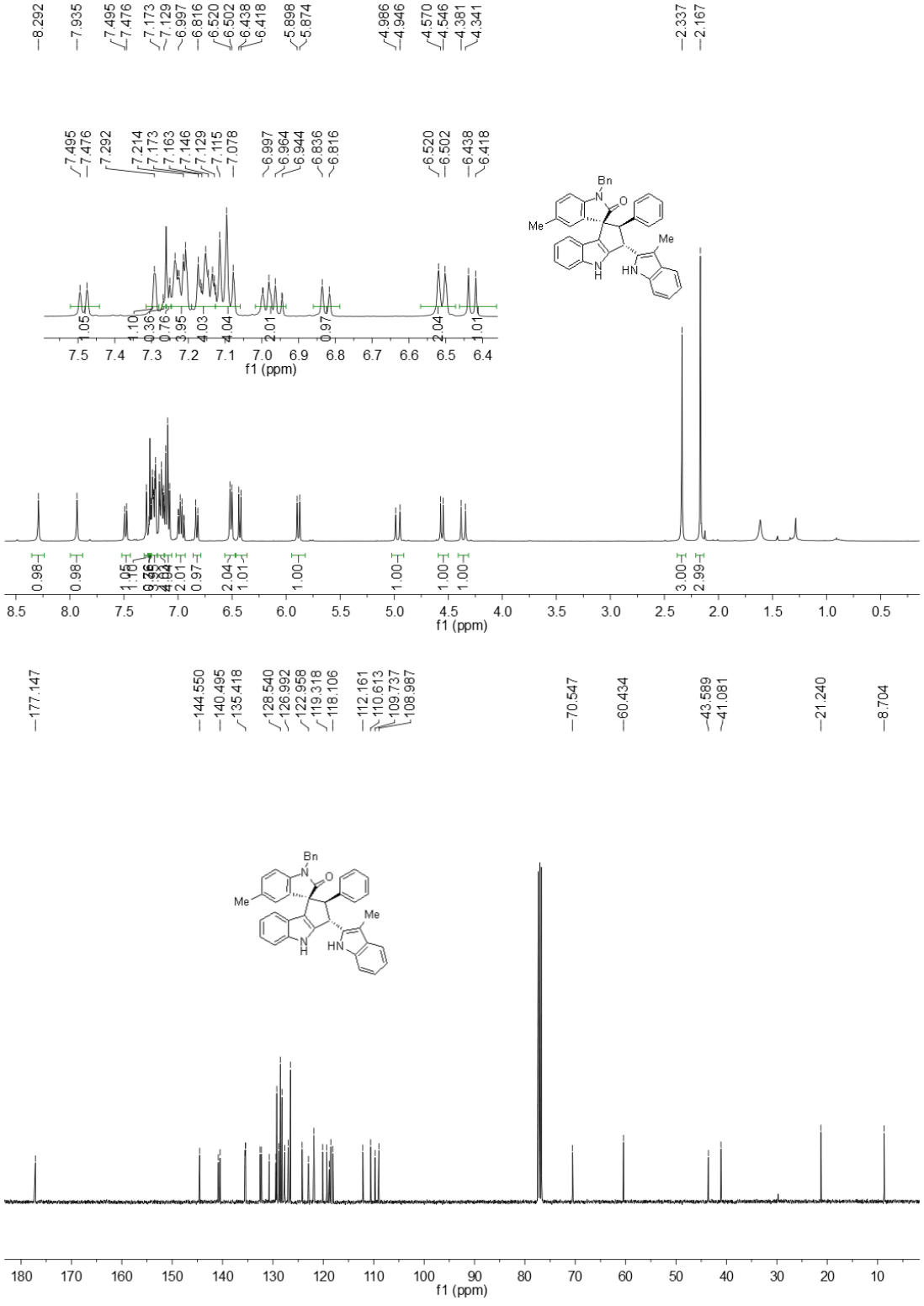
Under argon atmosphere, compound **3ea** (0.05 mmol), 4-chlorophenylboronic acid (0.075 mmol), $CsCO_3$ (0.1 mmol), $Pd(OAc)_2$ (0.0025 mmol) and butyldi-1-adamantylphosphine (0.003 mmol) were added to a dried tube. After adding DME (0.6 mL) to the reaction system, the reaction mixture was stirred at 80 ^oC for 15 h. Then, the reaction mixture was subjected to flash column chromatography (petroleum ether/ethyl acetate = 6/1) to give pure product **7**.

(1R,2R,3R)-1'-benzyl-6'-(4-chlorophenyl)-3-(3-methyl-1H-indol-2-yl)-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one (7):

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1); Reaction time = 15 h ; yield: 92% (31.2 mg); white solid; m.p. 141–143 ^{o}C; $[\alpha]_D^{20}$ = -91.3 (c 0.624, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.41 (s, 1H), 7.64 – 7.51 (m, 2H), 7.47 – 7.40 (m, 2H), 7.37 (d, *J* = 4.5 Hz, 3H), 7.28 (s, 1H), 7.26 – 7.21 (m, 4H), 7.19 – 7.12 (m, 4H), 7.12-7.05 (m, 4H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 8.7 Hz, 1H), 6.68 (s, 1H), 6.54 (d, *J* = 7.2 Hz, 2H), 5.90 (d, *J* = 9.8 Hz, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.62 (d, *J* = 9.7 Hz, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.3, 145.0, 143.9, 140.6, 140.4, 139.3, 135.7, 135.4, 135.2, 133.5, 132.6, 130.3, 129.4, 129.3, 129.0, 128. 9, 128.6, 128.3, 128.3, 127.7, 127.1, 126.5, 123.9, 123.0, 121.8, 121.7, 121.6, 120.1, 119.2, 118.4, 118.3, 118.0, 112.3, 110.7, 109.6, 107.6, 70.5, 60.2, 43.6, 41.0, 8.7. IR (KBr): 3375, 3030, 2963, 2852, 1714, 1617, 1485, 1449, 1376, 1261, 1093, 1009, 810, 741, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{46}H_{34}ClN_3O\text{-}H)^-$ requires m/z 678.2311, found m/z 678.2308.

7. Copies of NMR spectra for products 3 and 7

3ba



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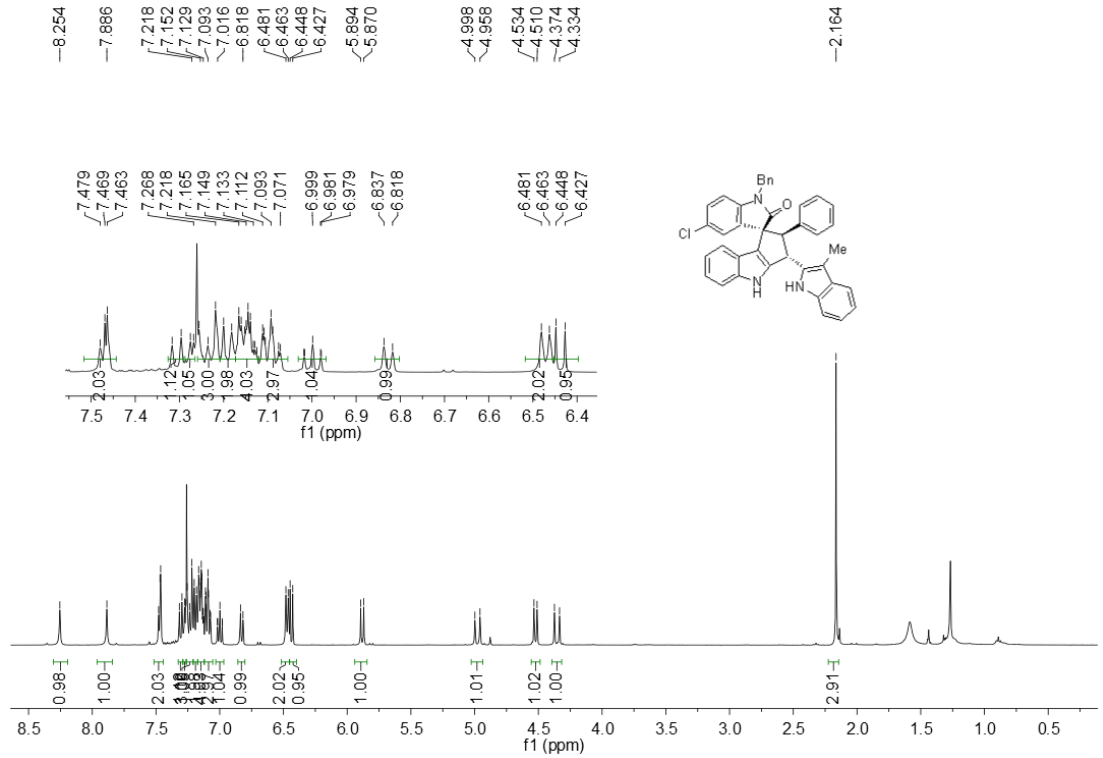
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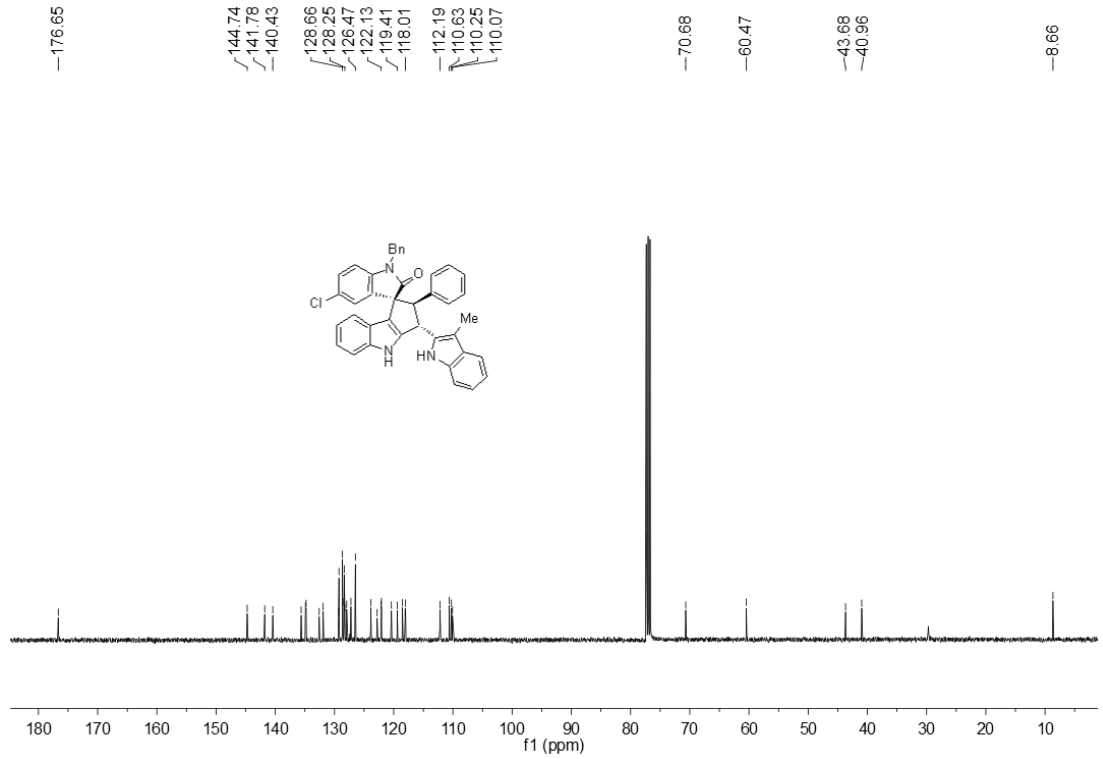
f1 (ppm)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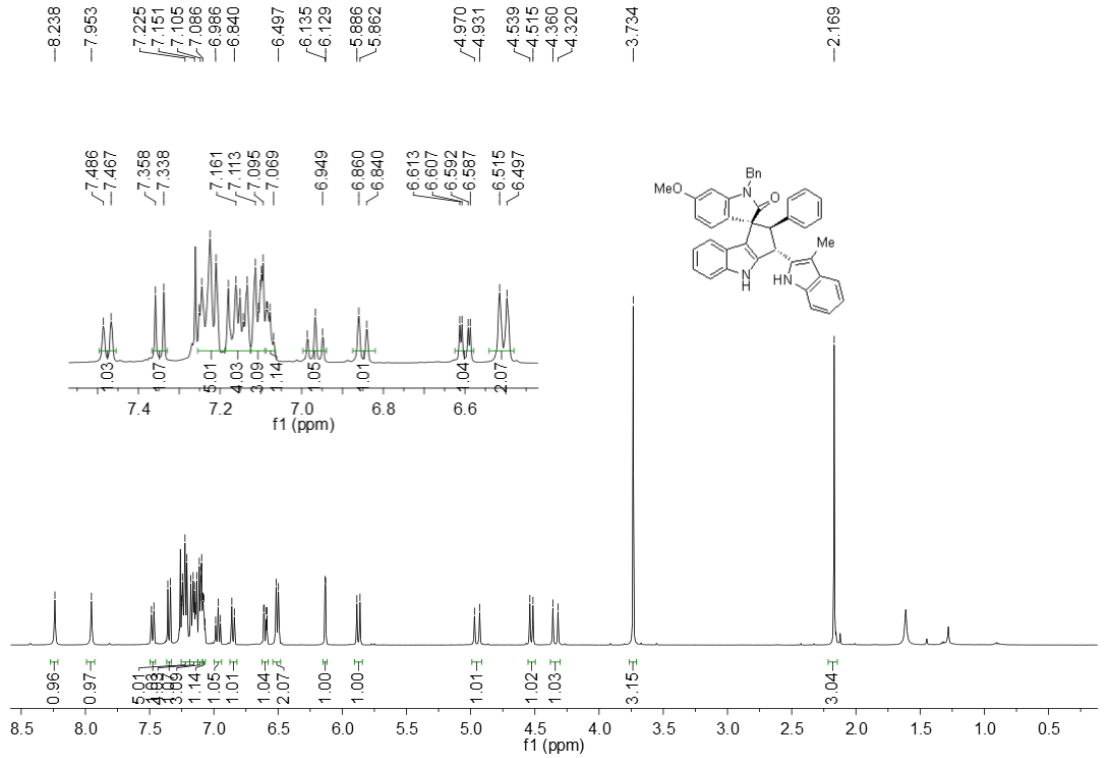
3da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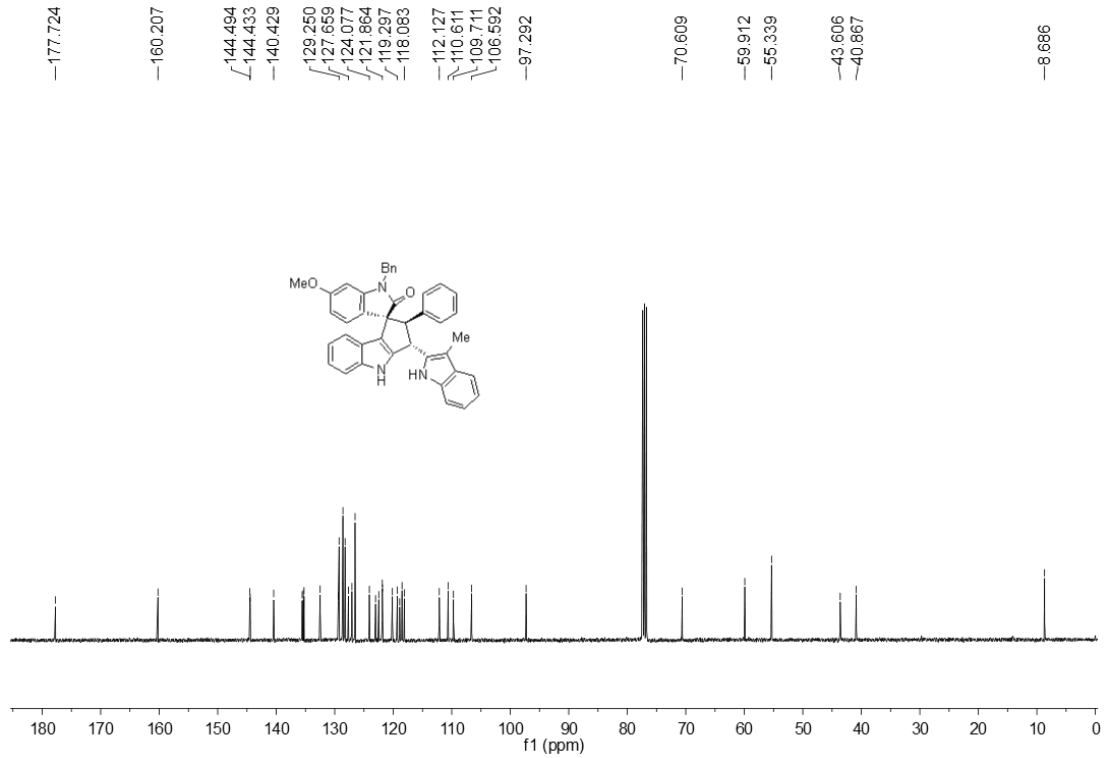
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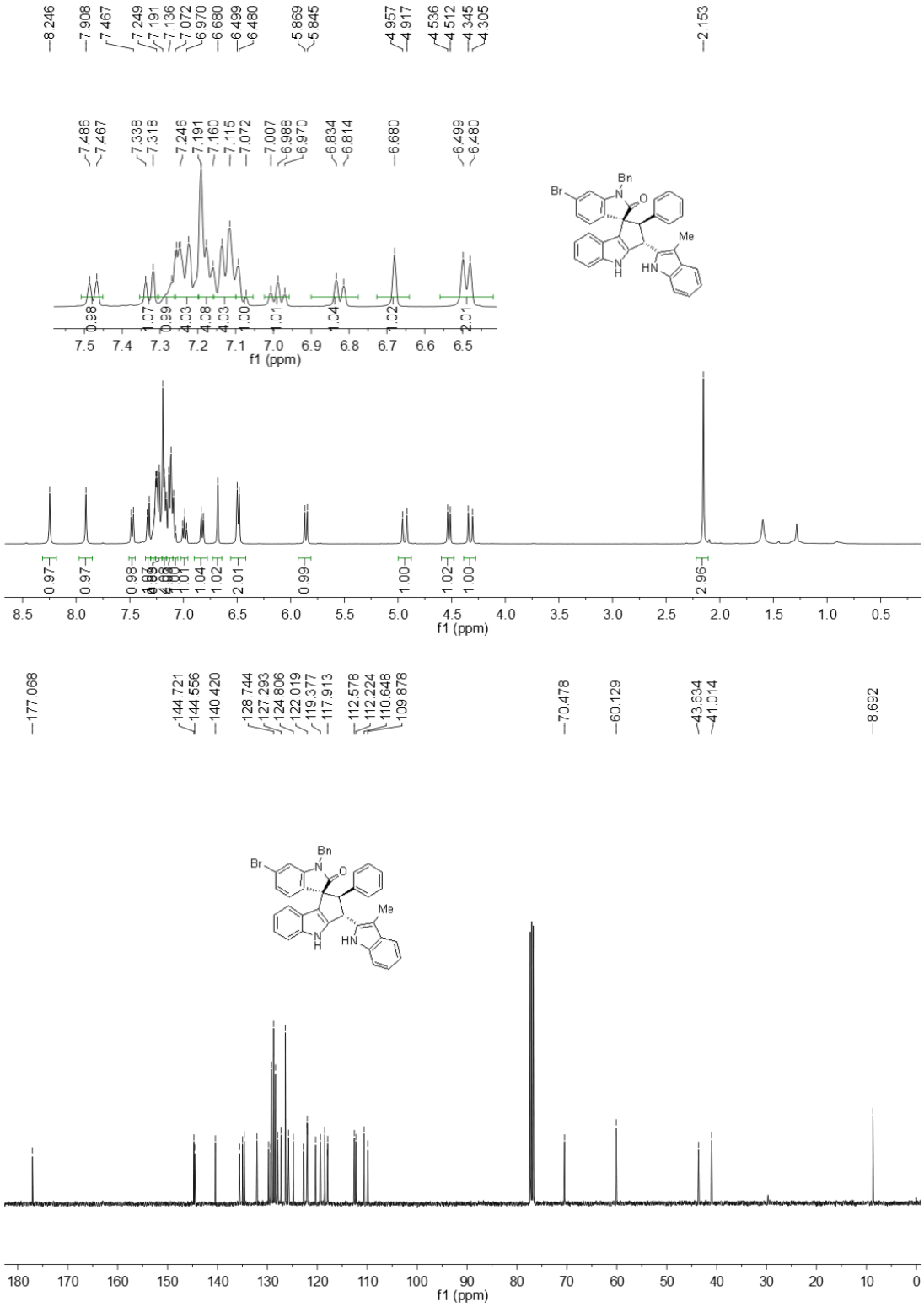
f1 (ppm)

3ea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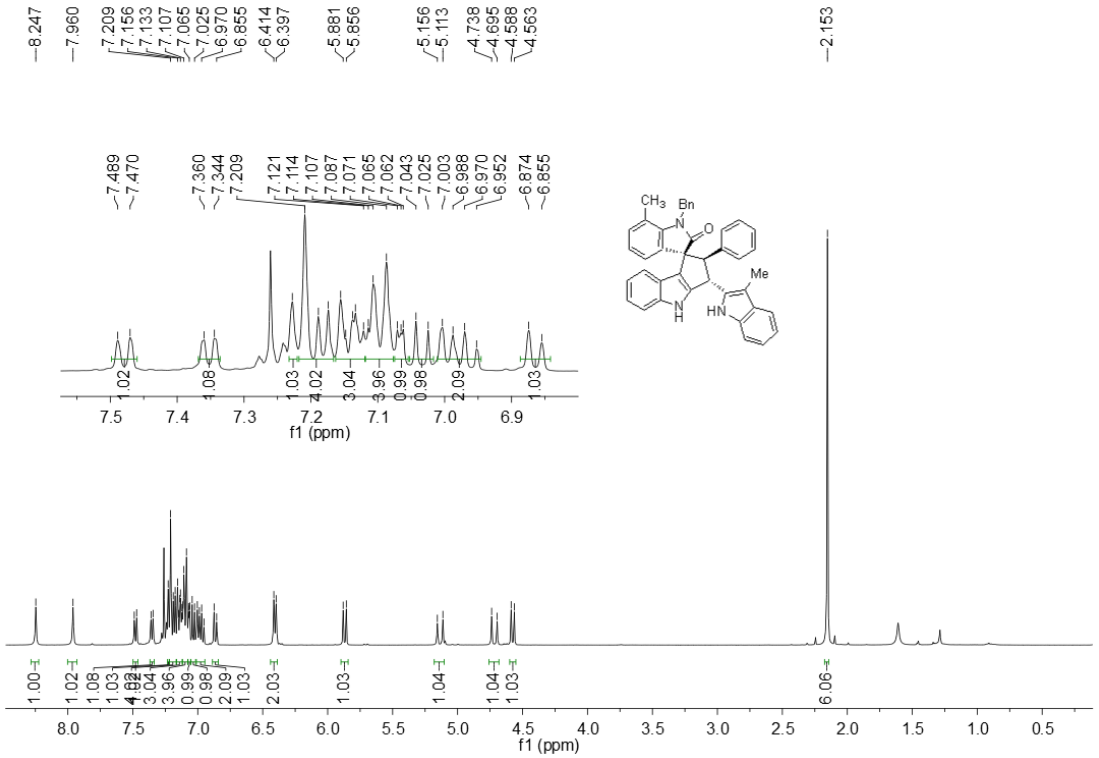
3fa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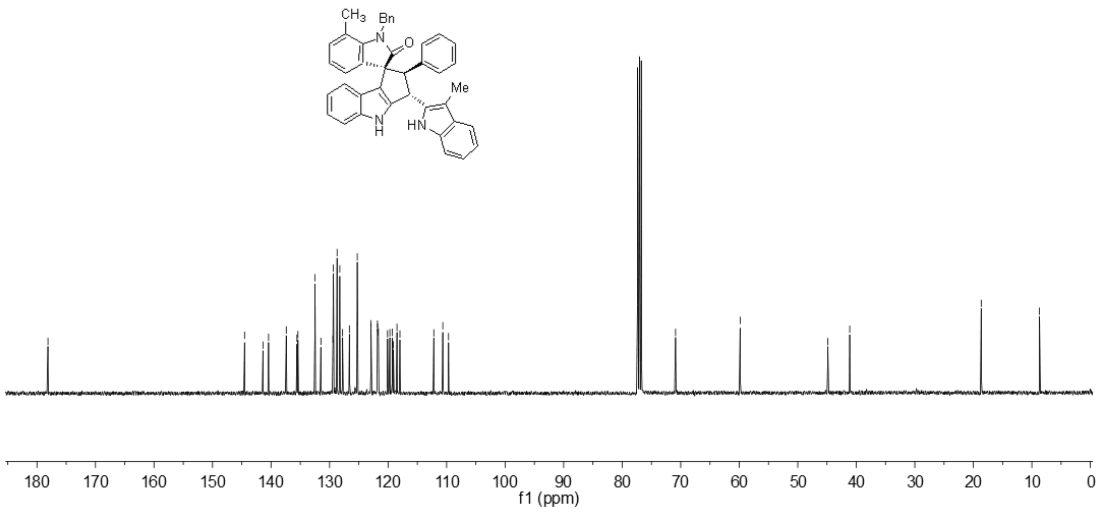
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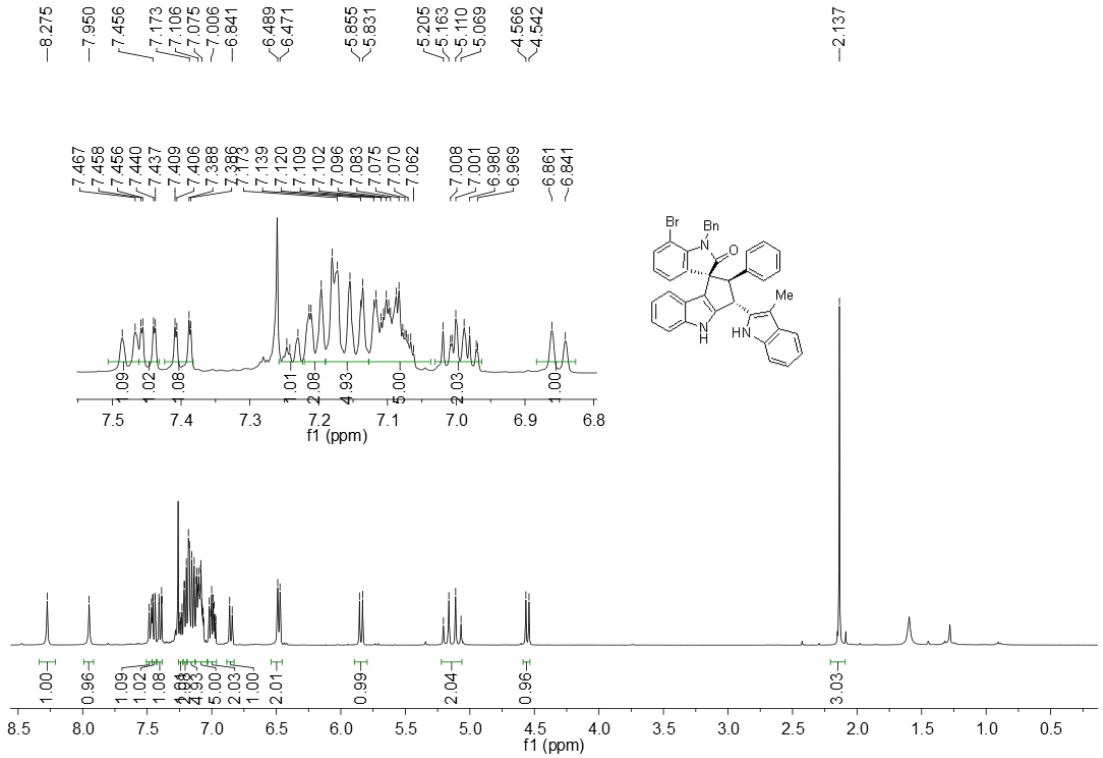
f1 (ppm)

3ga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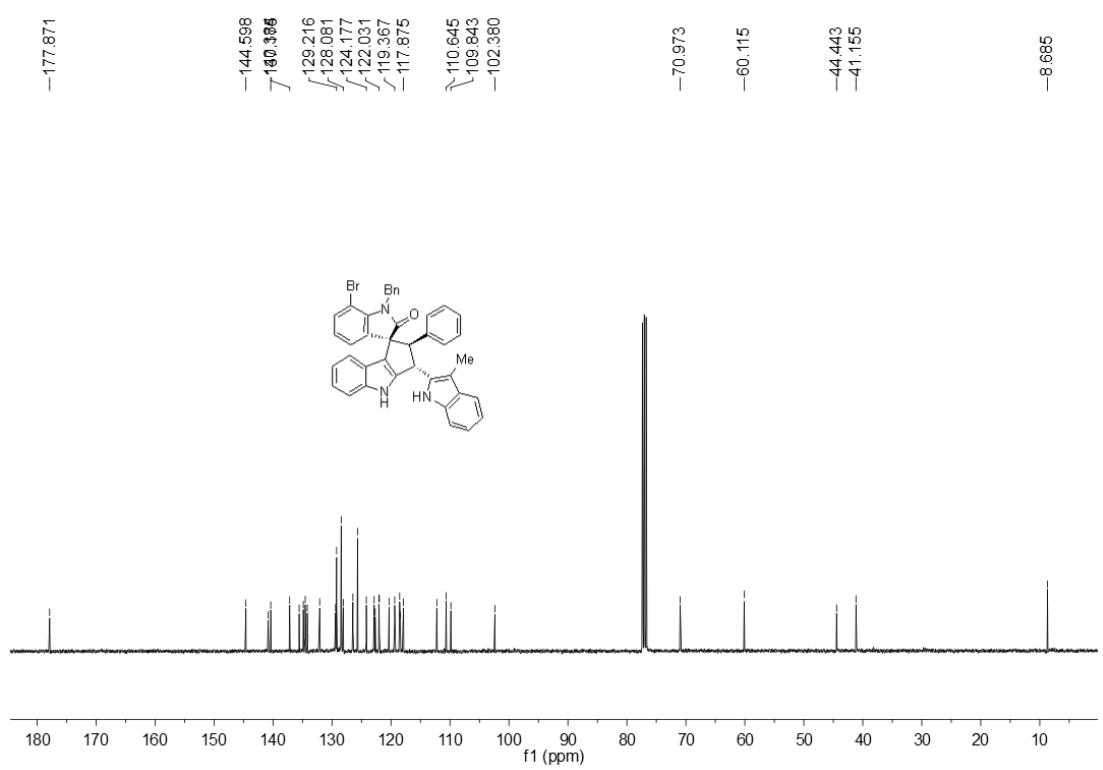
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Bn
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O
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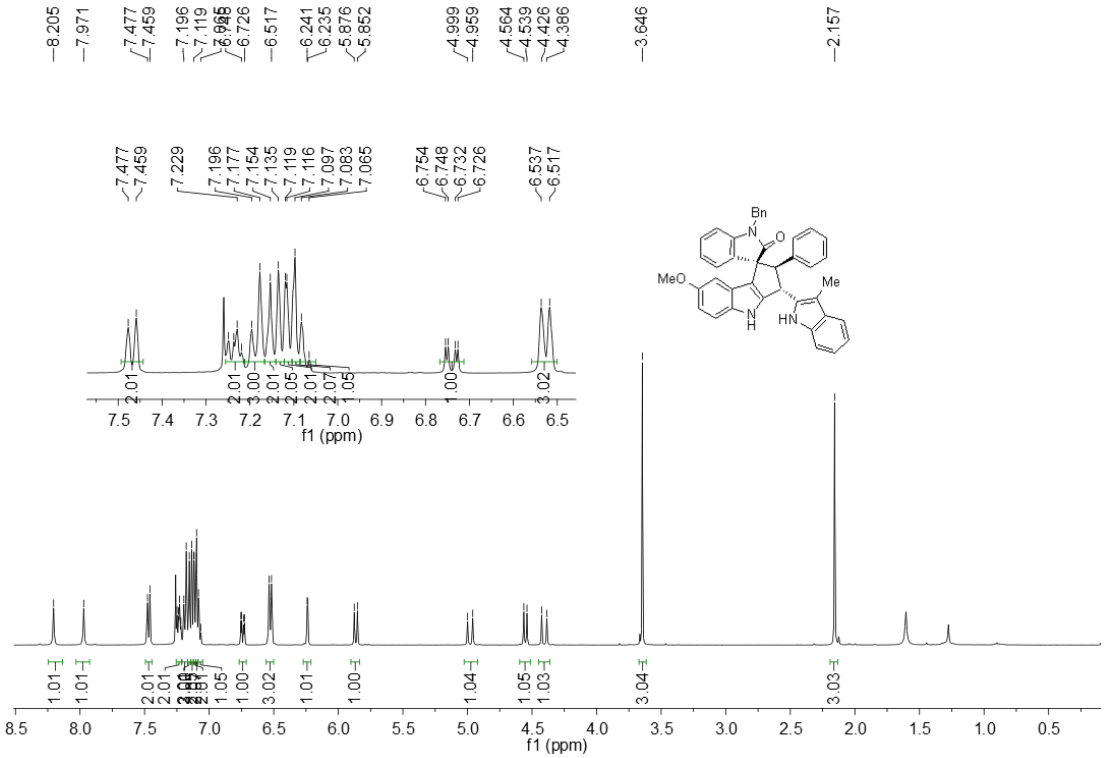
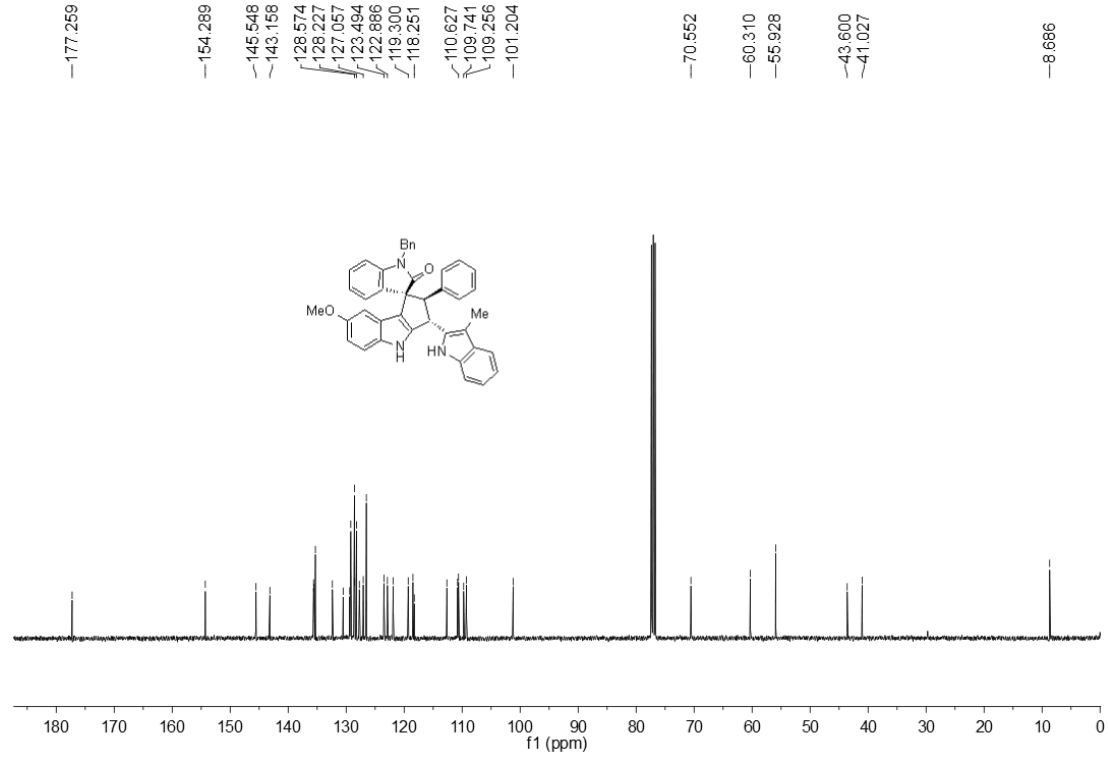
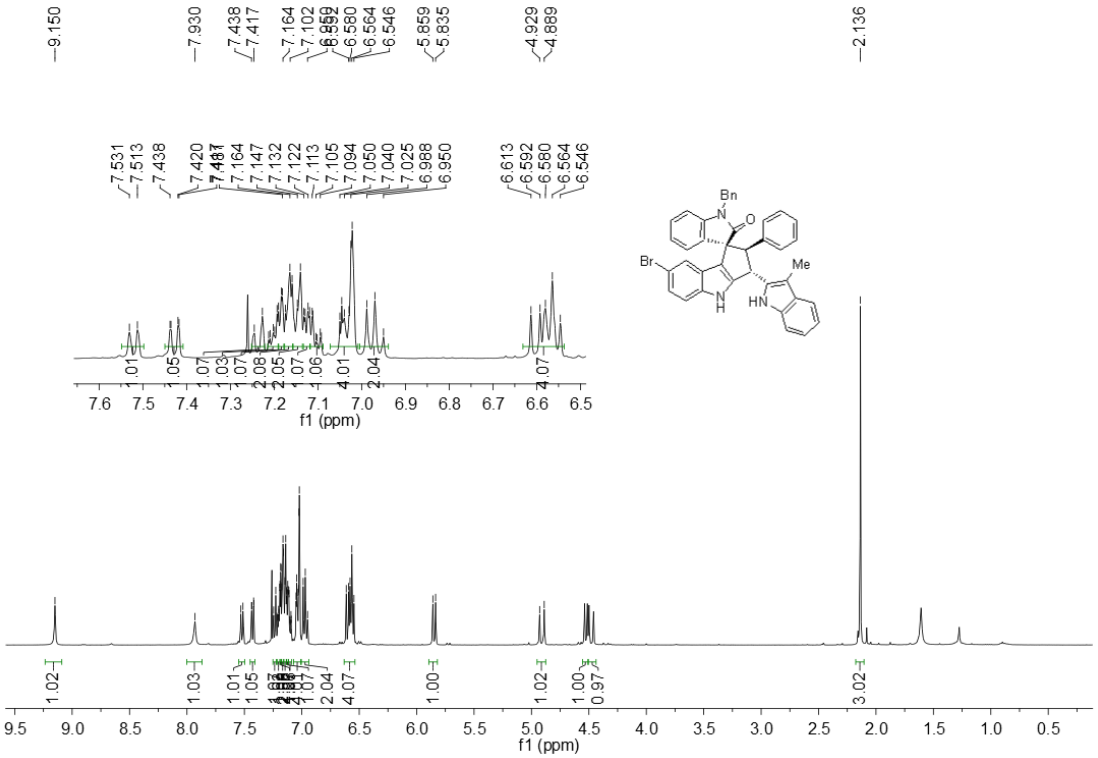
HN
H
f1 (ppm)

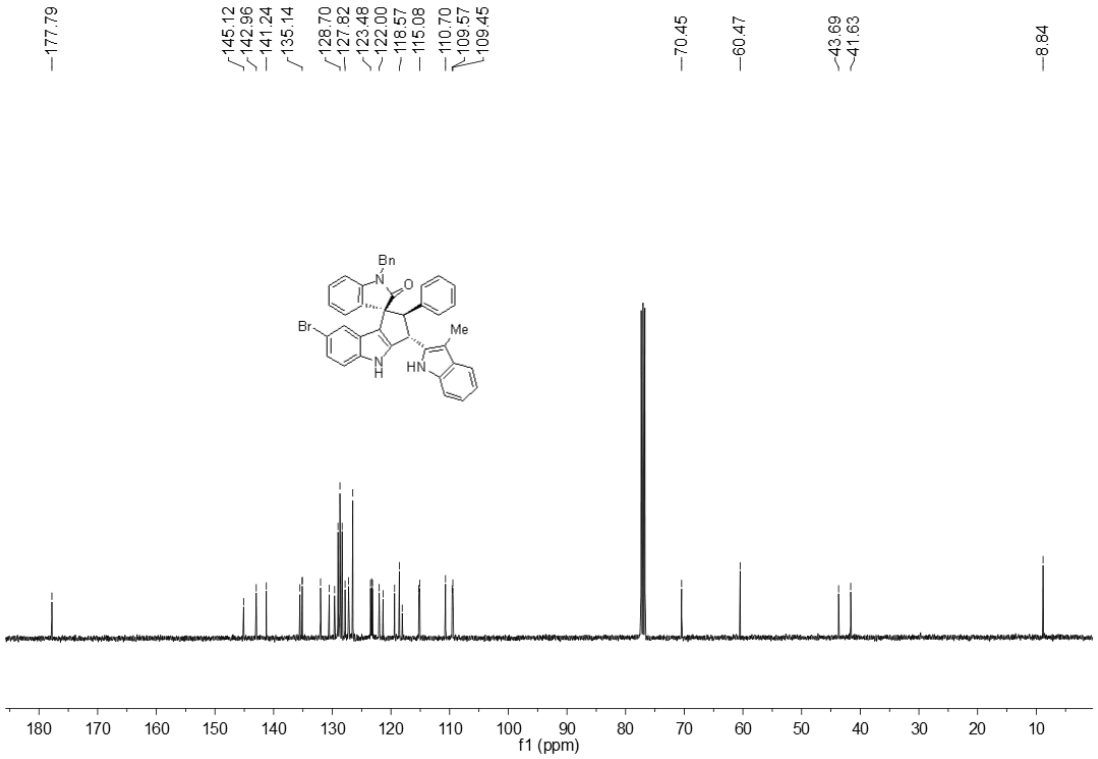
3ha


8.205
7.971
7.477
7.459
7.196
7.119
6.726
6.517
6.241
6.235
5.876
5.852
4.999
4.959
4.564
4.539
4.426
4.386
3.646
2.157
Bn
MeO
Me
HN
f1 (ppm)

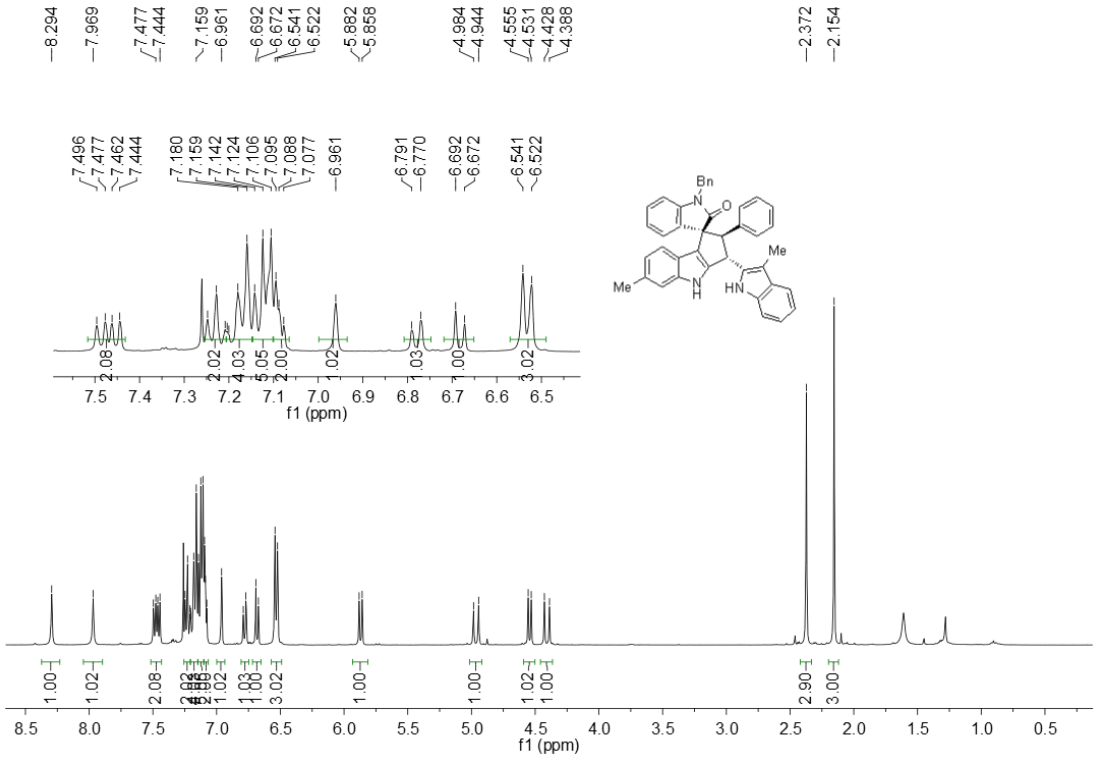

177.259
154.289
145.548
143.158
128.574
128.227
127.057
123.494
122.886
119.300
118.251
110.627
109.741
109.256
101.204
70.552
60.310
55.928
43.600
41.027
8.686
Bn
MeO
Me
HN
f1 (ppm)

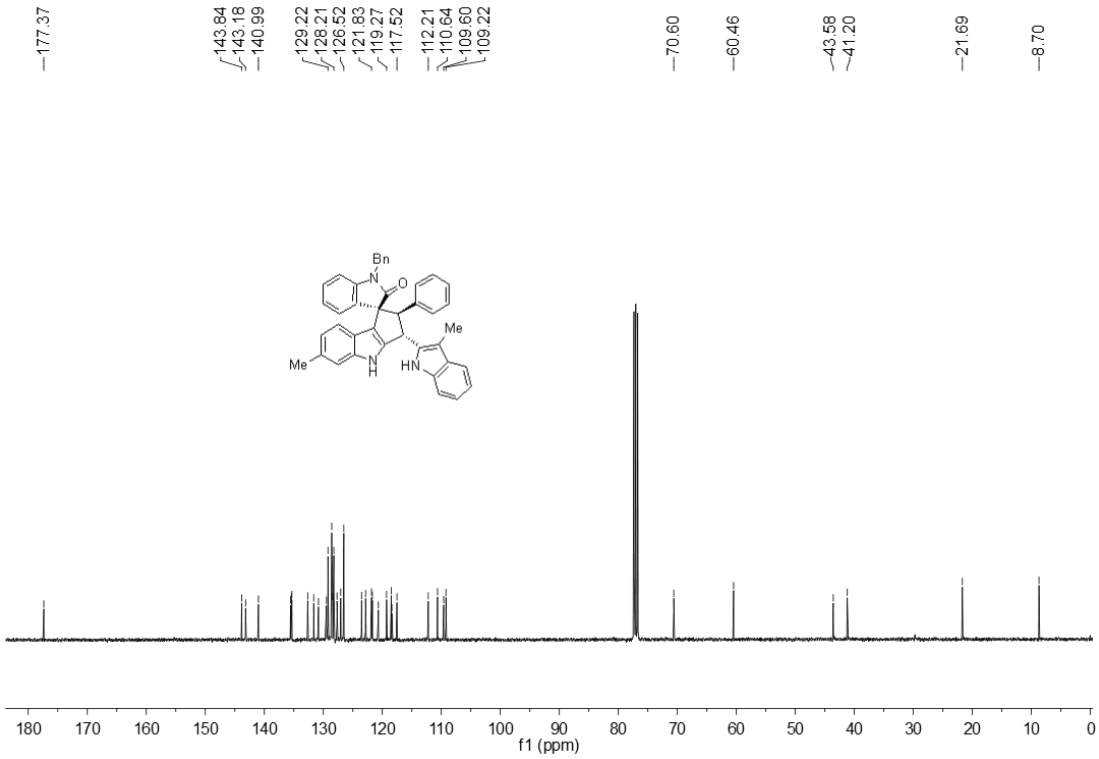
3ia


9.150
7.930
7.438
7.417
7.164
7.102
6.580
6.564
6.546
5.859
5.835
4.929
4.889
2.136
Bn
Br
Me
HN
f1 (ppm)

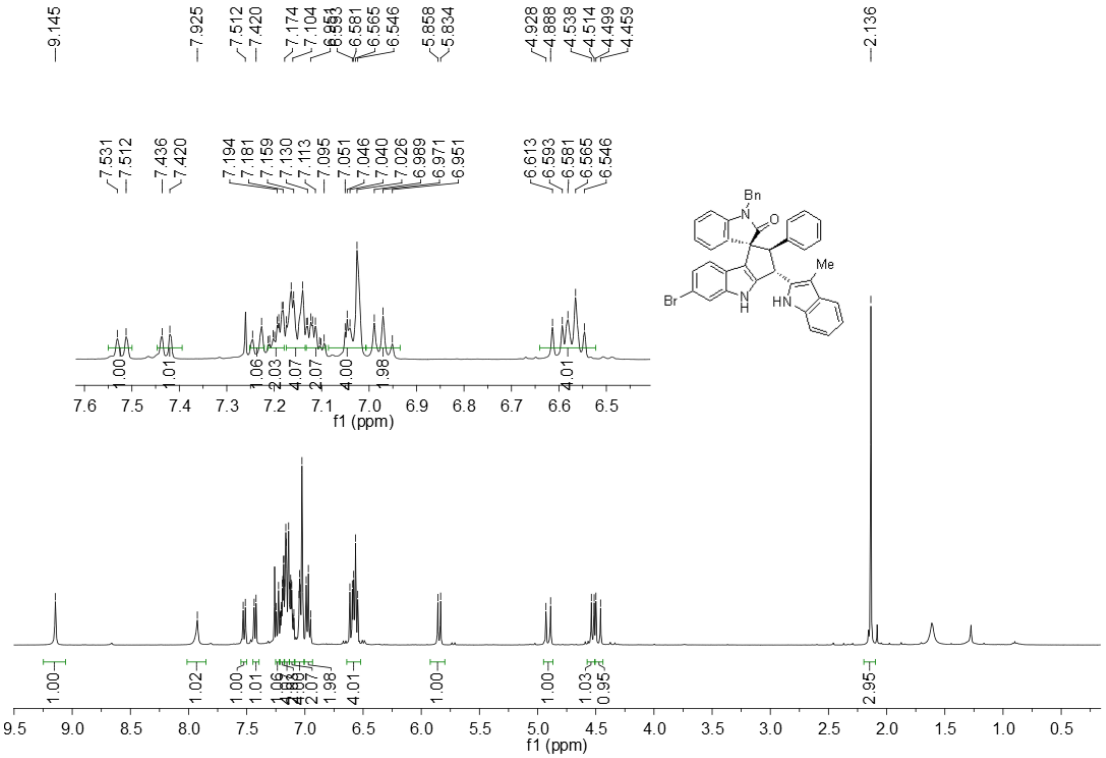

177.79
145.12
142.96
141.24
135.14
128.70
127.82
123.48
122.00
118.57
115.08
110.70
109.57
109.45
70.45
60.47
43.69
41.63
8.84
Bn
Br
Me
HN
f1 (ppm)

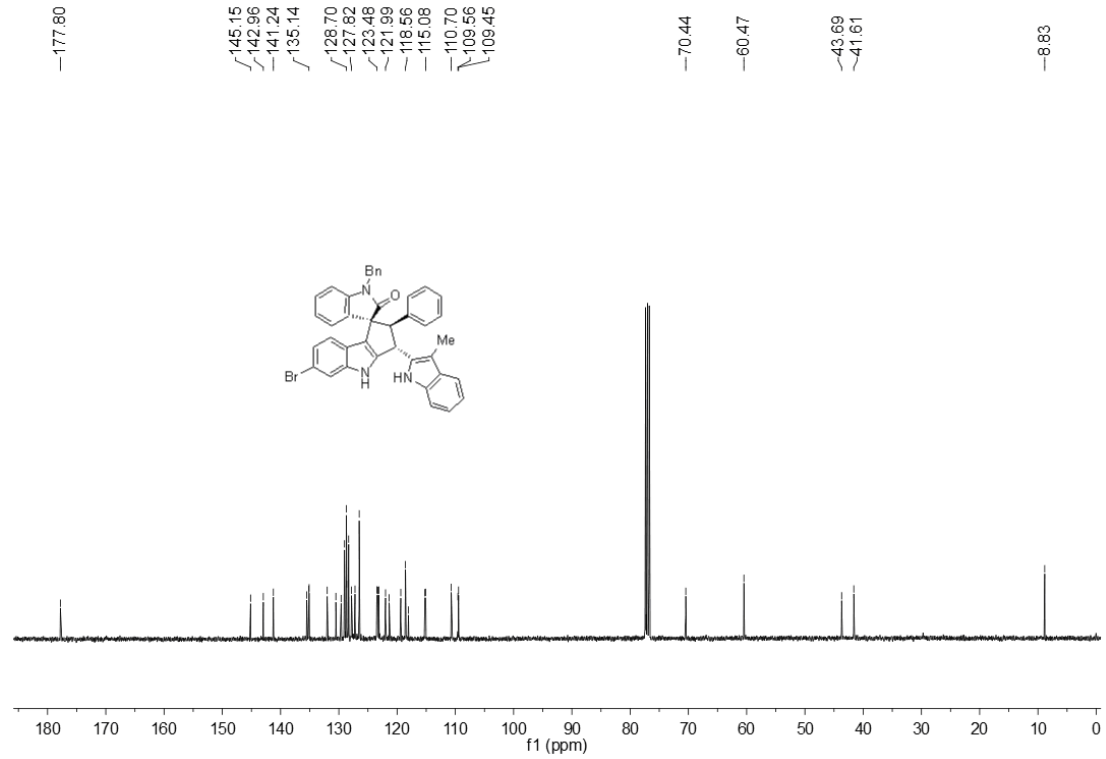
3ja


8.294
7.969
7.477
7.444
7.159
6.961
6.692
6.672
6.541
6.522
5.882
5.858
4.984
4.944
4.555
4.531
4.428
4.388
2.372
2.154
Bn
Me
Me
HN
f1 (ppm)

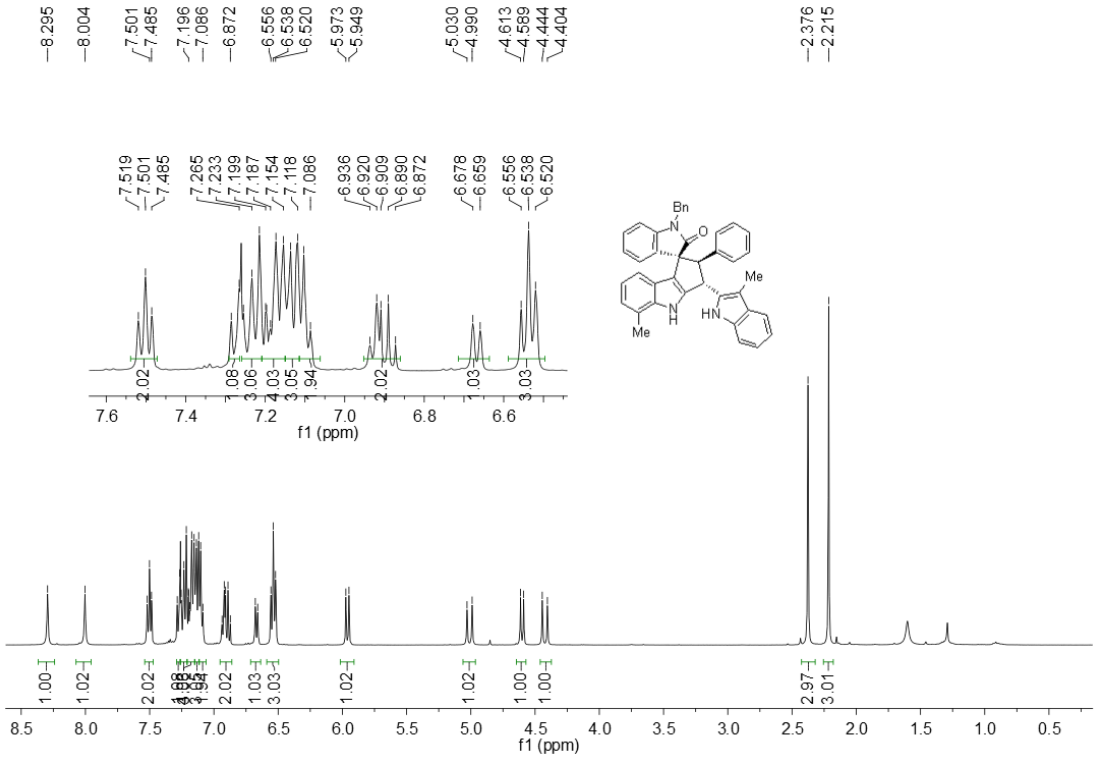

177.37
143.84
143.18
140.99
129.22
128.21
126.52
121.83
119.27
117.52
112.21
110.64
109.60
109.22
70.60
60.46
43.58
41.20
21.69
8.70
Bn
Me
Me
HN
f1 (ppm)

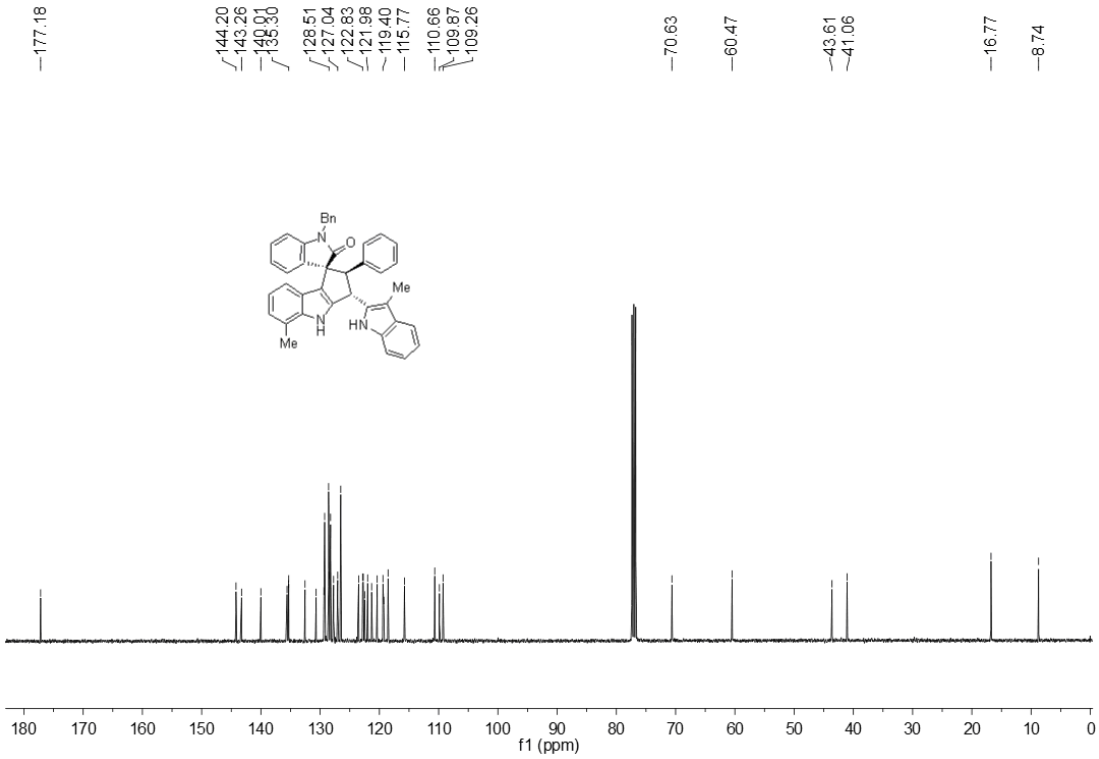
3ka


9.145
7.925
7.512
7.420
7.174
7.104
6.581
6.565
6.546
5.858
5.834
4.928
4.888
4.538
4.514
4.499
4.459
2.136
Bn
N
O
Me
Br
H
HN
f1 (ppm)

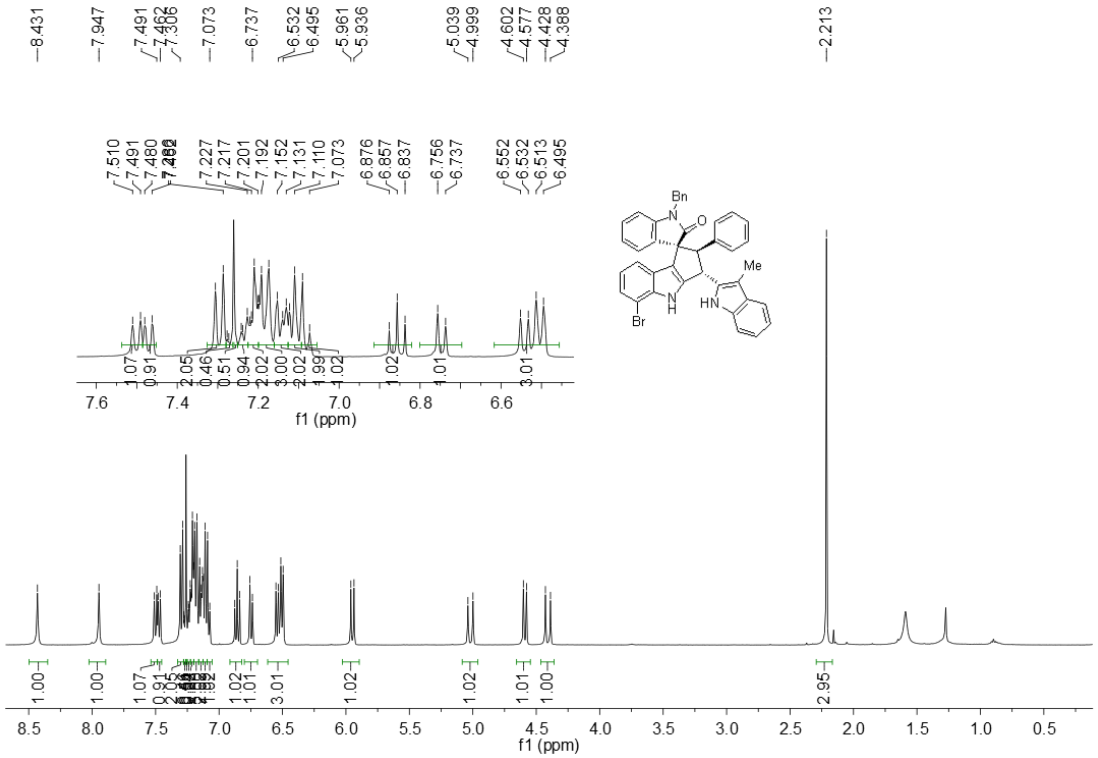

177.80
145.15
142.96
141.24
135.14
128.70
127.82
123.48
121.99
118.56
115.08
110.70
109.56
109.45
70.44
60.47
43.69
41.61
8.83
Bn
N
O
Me
Br
H
HN
f1 (ppm)

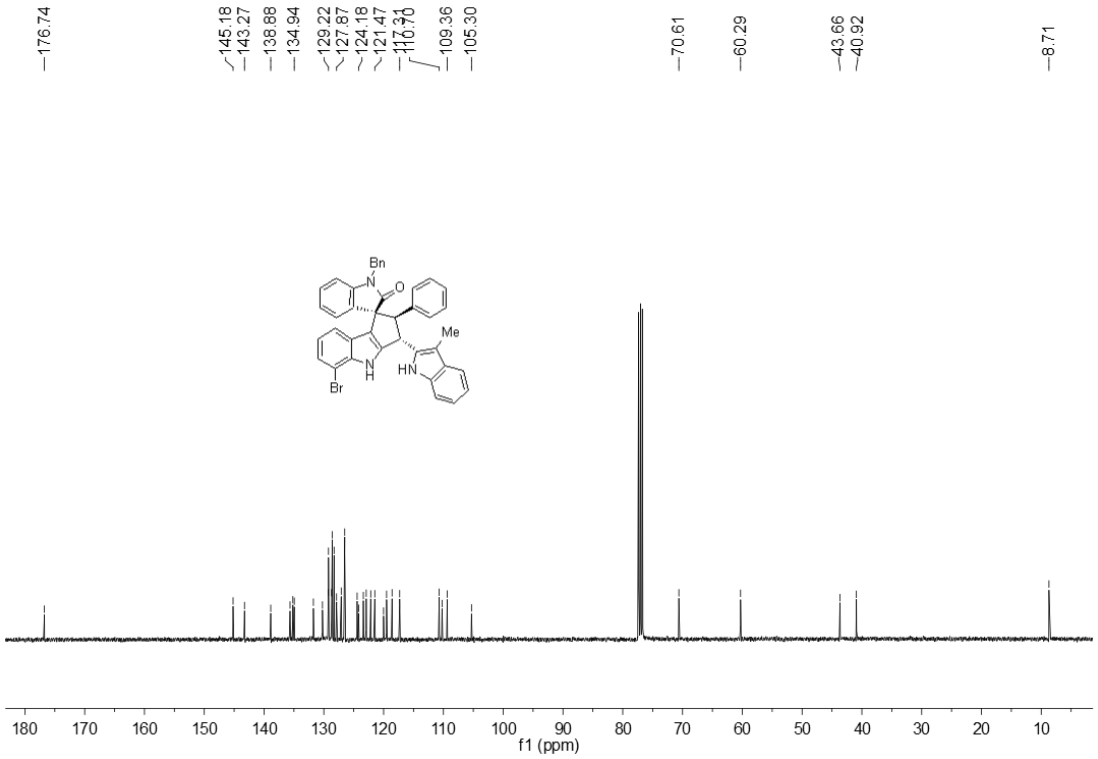
3la


8.295
8.004
7.501
7.485
7.196
7.086
6.872
6.556
6.538
6.520
5.973
5.949
5.030
4.990
4.613
4.589
4.444
4.404
2.376
2.215
Bn
Me
HN
Me
f1 (ppm)

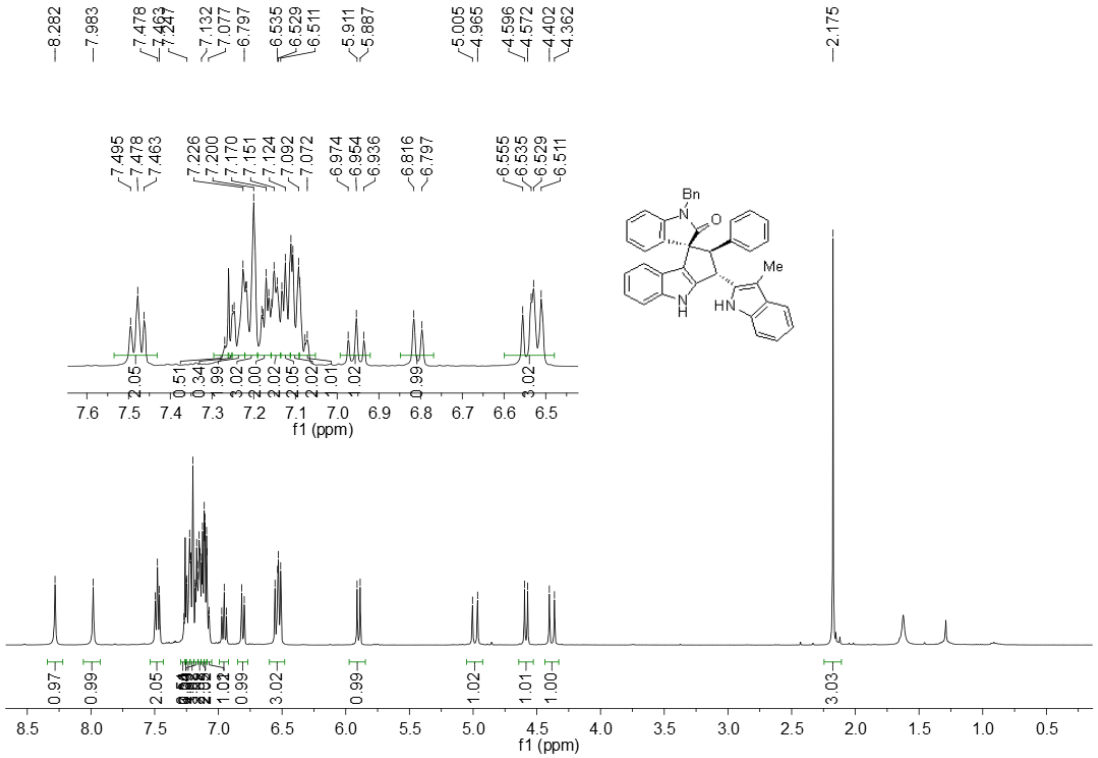

177.18
144.20
143.26
140.01
135.30
128.51
127.04
122.83
121.98
119.40
115.77
110.66
109.87
109.26
70.63
60.47
43.61
41.06
16.77
8.74
Bn
Me
HN
Me
f1 (ppm)

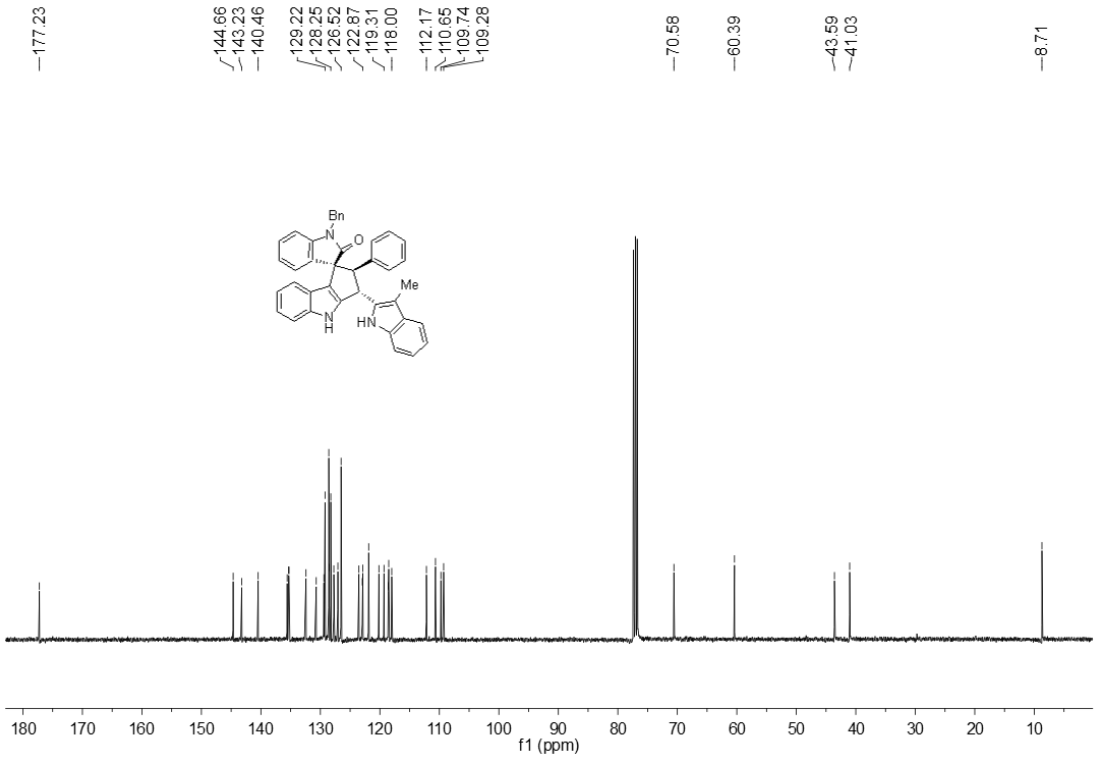
3ma


8.431
7.947
7.491
7.462
7.306
7.073
6.737
6.532
6.495
5.961
5.936
5.039
4.999
4.602
4.577
4.428
4.388
2.213
Bn
N
O
Me
HN
H
N
Br
f1 (ppm)

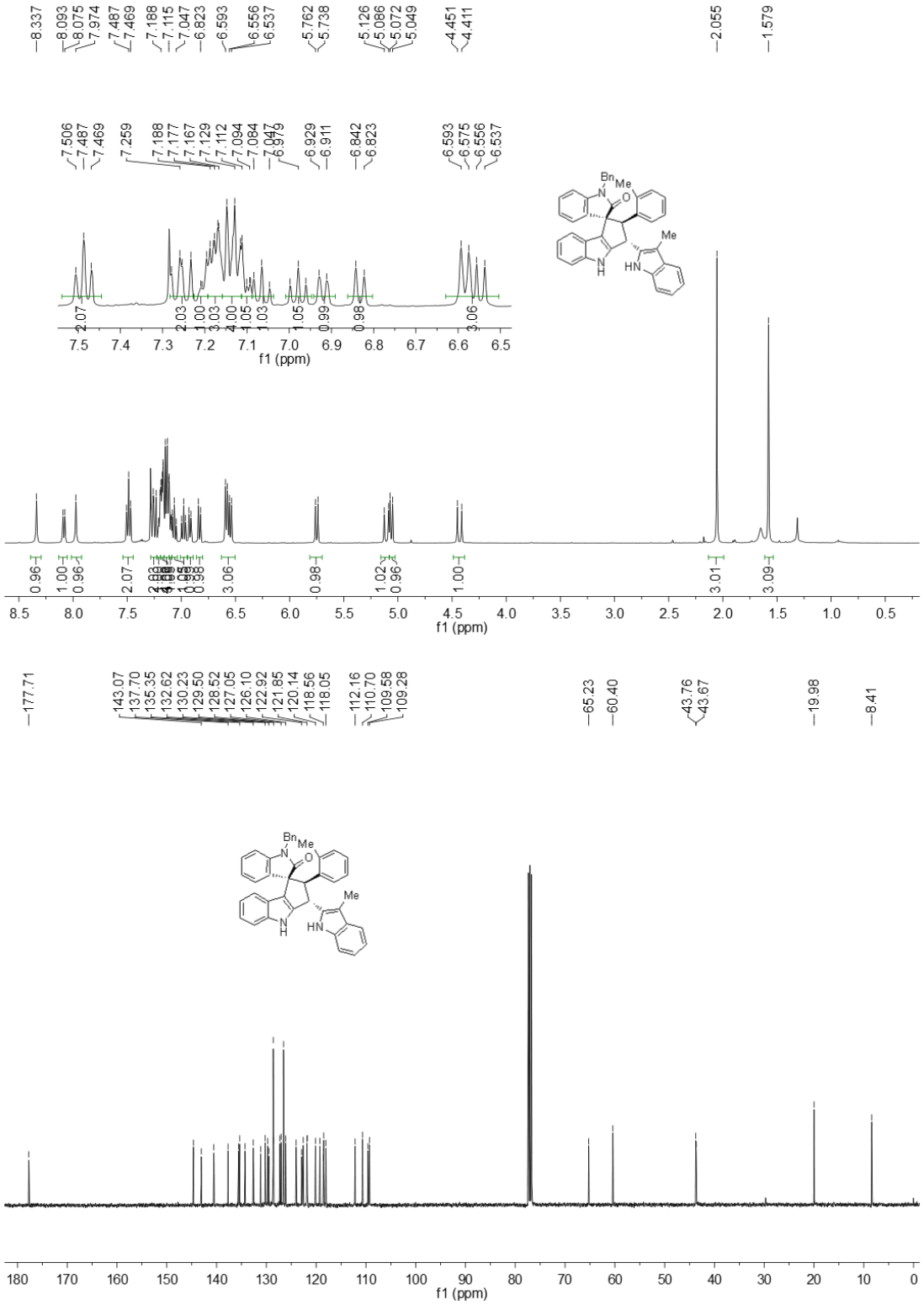

176.74
145.18
143.27
138.88
134.94
129.22
127.87
124.18
121.47
117.31
110.70
109.36
105.30
70.61
60.29
43.66
40.92
8.71
Bn
N
O
Me
HN
H
N
Br
f1 (ppm)

3aa

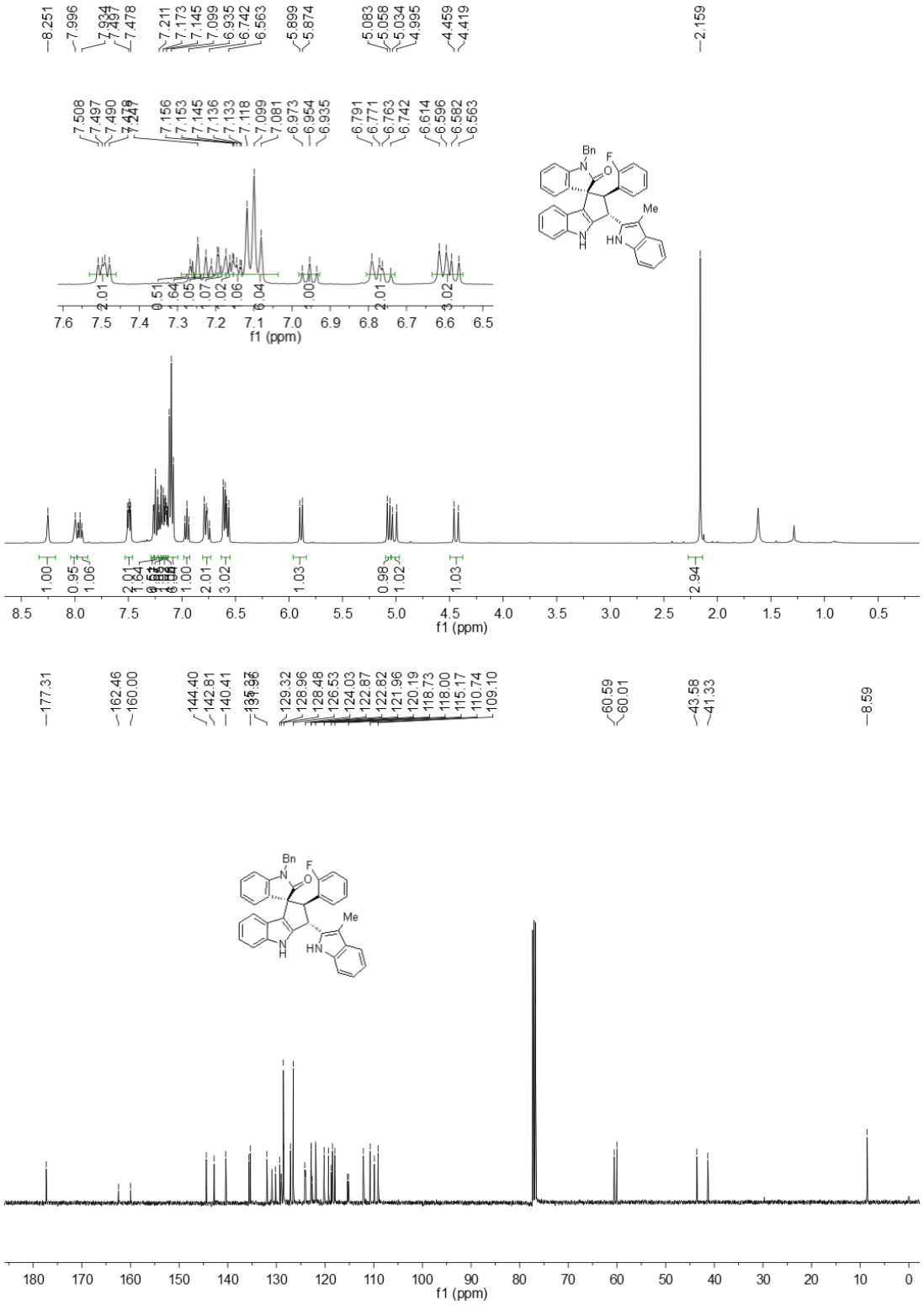

8.282
7.983
7.478
7.463
7.247
7.132
7.077
6.797
6.535
6.529
6.511
5.911
5.887
5.005
4.965
4.596
4.572
4.402
4.362
2.175
Bn
N
O
Me
HN
H
f1 (ppm)


177.23
144.66
143.23
140.46
129.22
128.25
126.52
122.87
119.31
118.00
112.17
110.65
109.74
109.28
70.58
60.39
43.59
41.03
8.71
Bn
N
O
Me
HN
H
f1 (ppm)

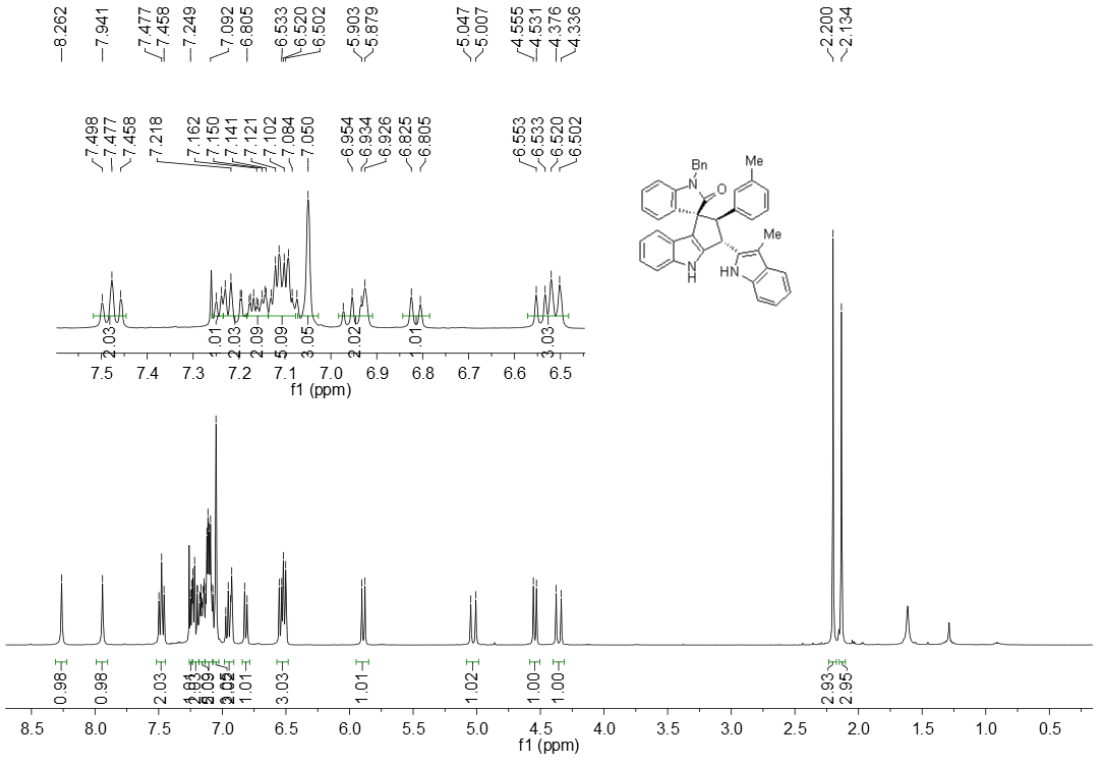
3ab

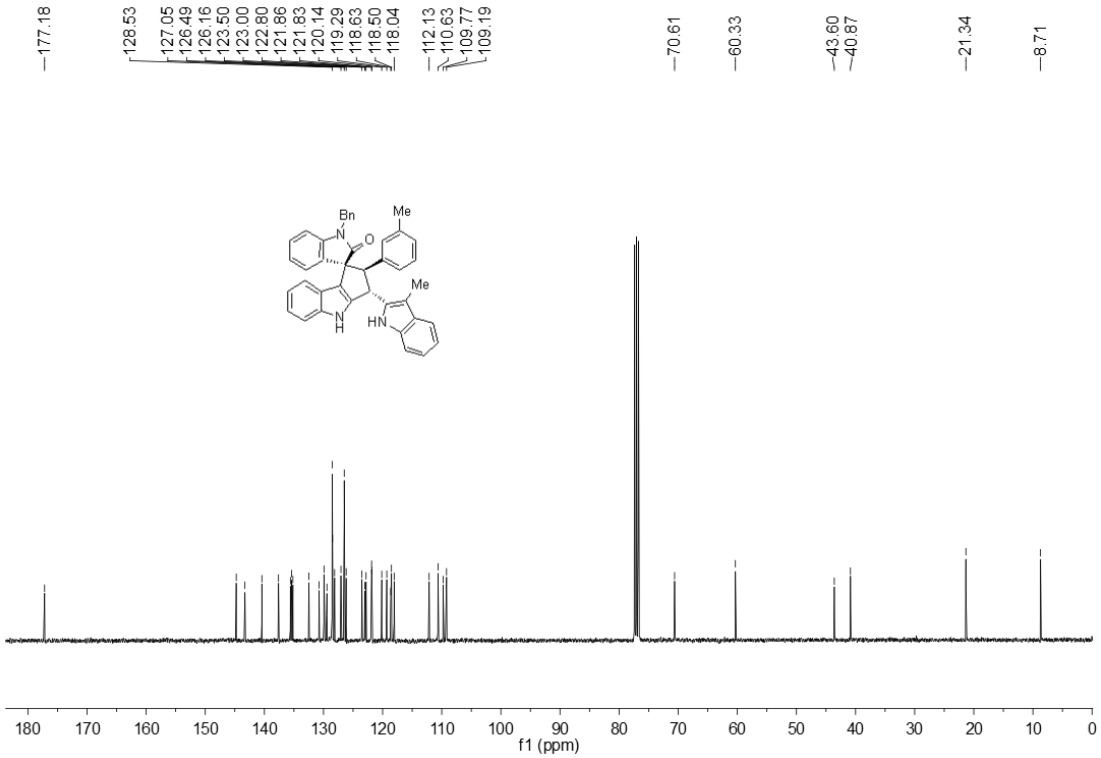

8.337
8.093
8.075
7.974
7.487
7.469
7.188
7.115
7.047
6.823
6.593
6.556
6.537
5.762
5.738
5.126
5.086
5.072
5.049
4.451
4.411
2.055
1.579
f1 (ppm)
177.71
143.07
137.70
135.35
132.62
130.23
129.50
128.52
127.05
126.10
122.92
121.85
120.14
118.56
118.05
112.16
110.70
109.58
109.28
65.23
60.40
43.76
43.67
19.98
8.41
f1 (ppm)

3ac

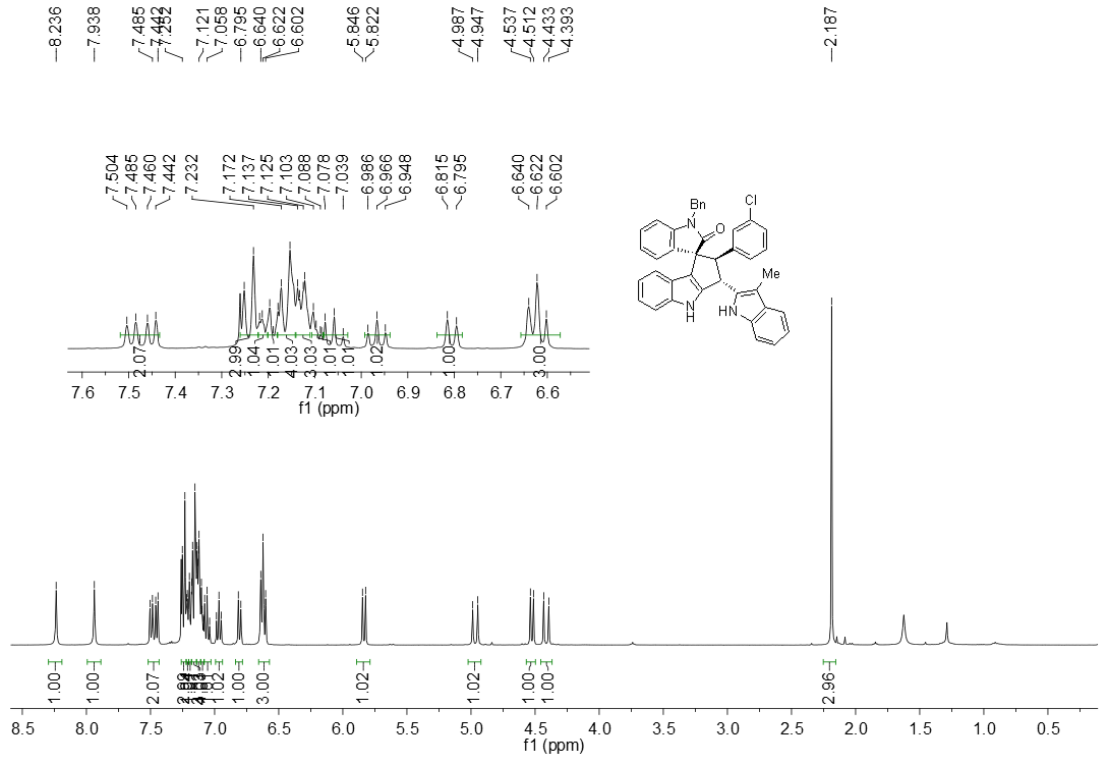

8.251
7.996
7.934
7.497
7.478
7.211
7.173
7.145
7.099
6.935
6.742
6.563
5.899
5.874
5.083
5.058
5.034
4.995
4.459
4.419
2.159
Bn
F
O
Me
HN
f1 (ppm)
177.31
162.46
160.00
144.40
142.81
140.41
129.32
128.96
128.48
126.53
124.03
122.87
122.82
121.96
120.19
118.73
118.00
115.17
110.74
109.10
60.59
60.01
43.58
41.33
8.59

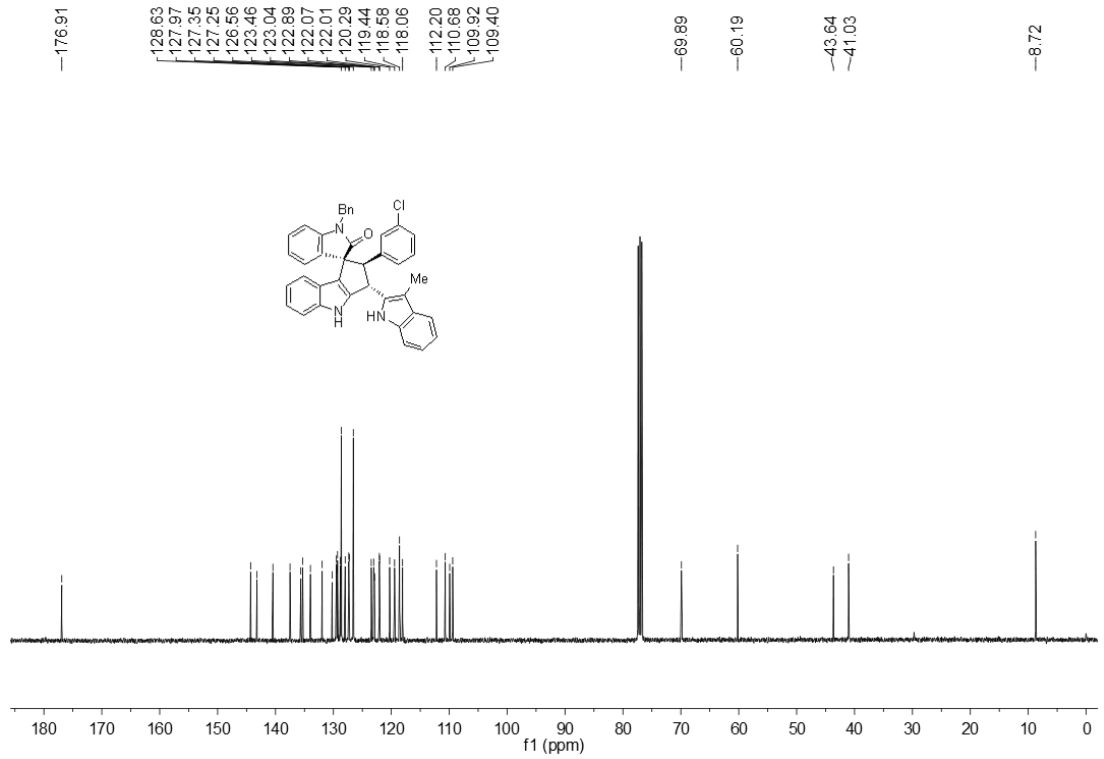
3ad


8.262
7.941
7.498
7.477
7.458
7.477
7.458
7.249
7.218
7.162
7.150
7.141
7.121
7.102
7.092
7.084
7.050
6.954
6.934
6.926
6.825
6.805
6.805
6.553
6.533
6.520
6.502
6.533
6.520
6.502
5.903
5.879
5.047
5.007
4.555
4.531
4.376
4.336
2.200
2.134
Bn
Me
Me
HN
f1 (ppm)

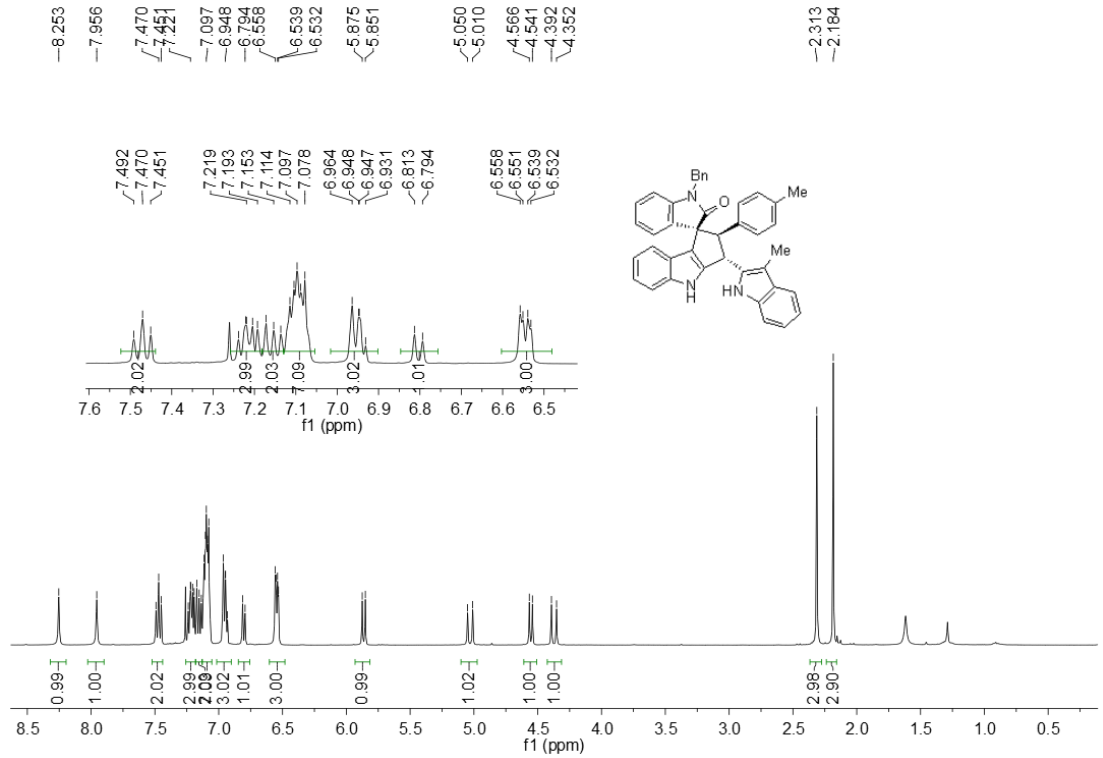

177.18
128.53
127.05
126.49
126.16
123.50
123.00
122.80
121.86
121.83
120.14
119.29
118.63
118.50
118.04
112.13
110.63
109.77
109.19
70.61
60.33
43.60
40.87
21.34
8.71
Bn
Me
Me
HN
f1 (ppm)

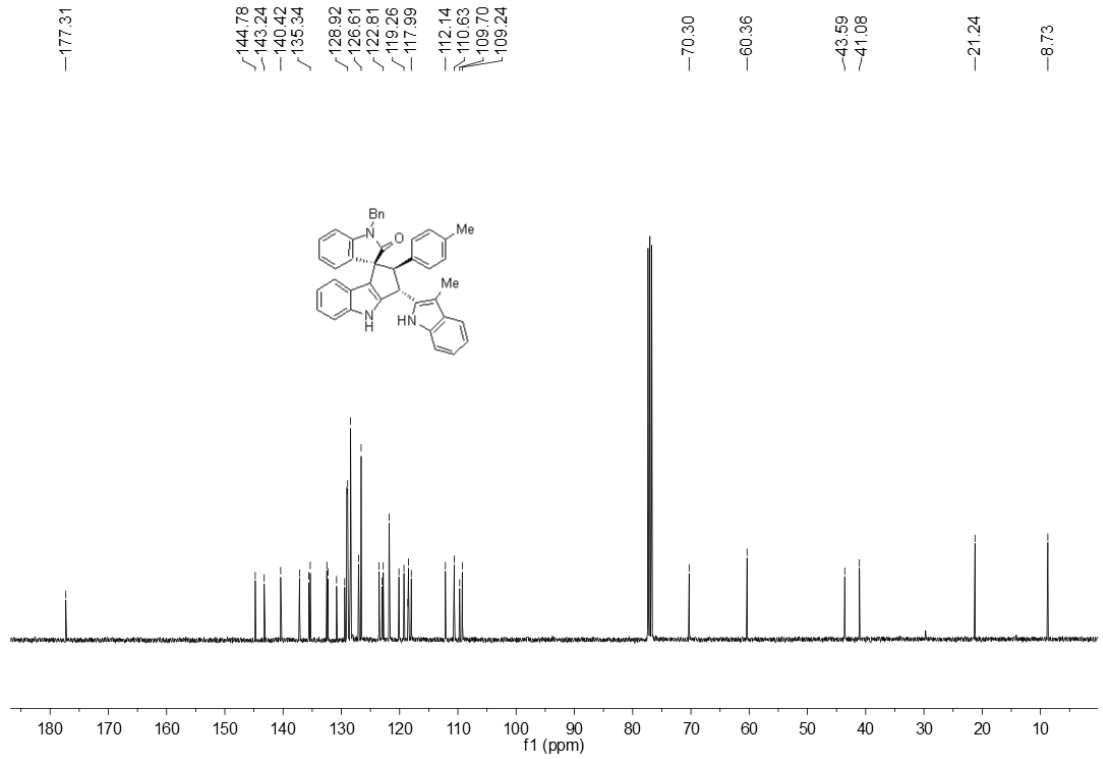
3ae


8.236
7.938
7.485
7.460
7.442
7.292
7.121
7.058
6.795
6.640
6.622
6.602
5.846
5.822
4.987
4.947
4.537
4.512
4.433
4.393
2.187
Bn
Cl
Me
HN
f1 (ppm)

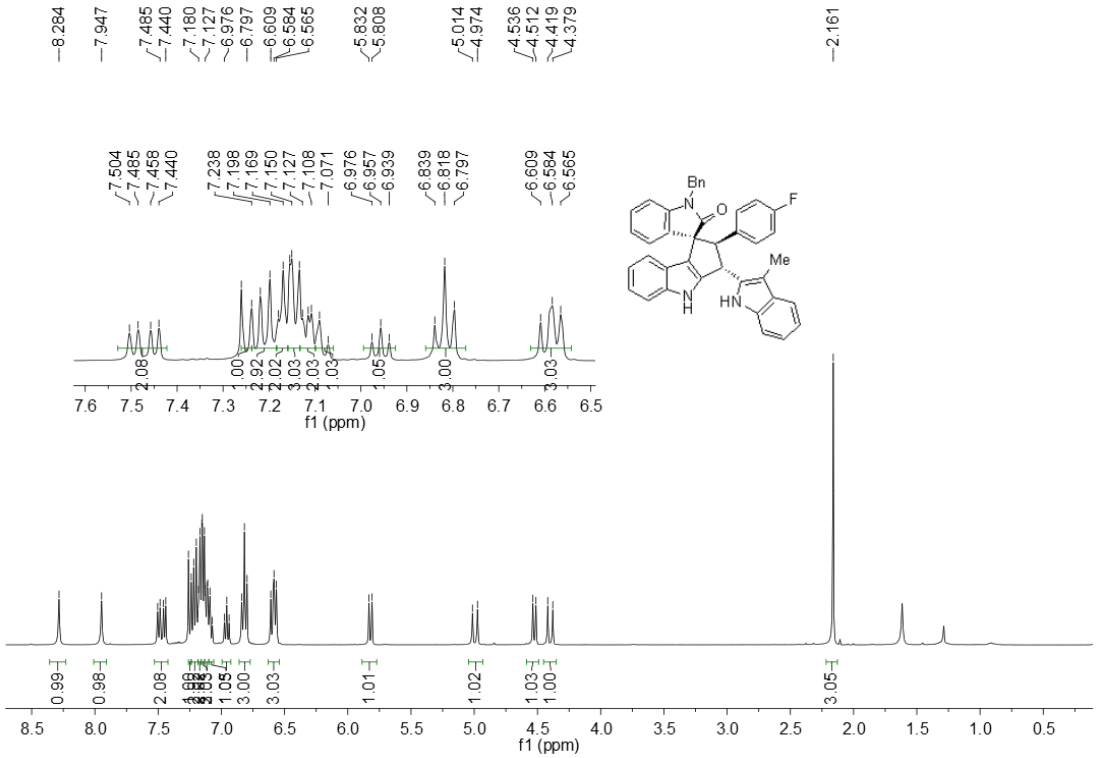

176.91
128.63
127.97
127.35
127.25
126.56
123.46
123.04
122.89
122.07
122.01
120.29
119.44
118.58
118.06
112.20
110.68
109.92
109.40
69.89
60.19
43.64
41.03
8.72
Bn
Cl
Me
HN
f1 (ppm)

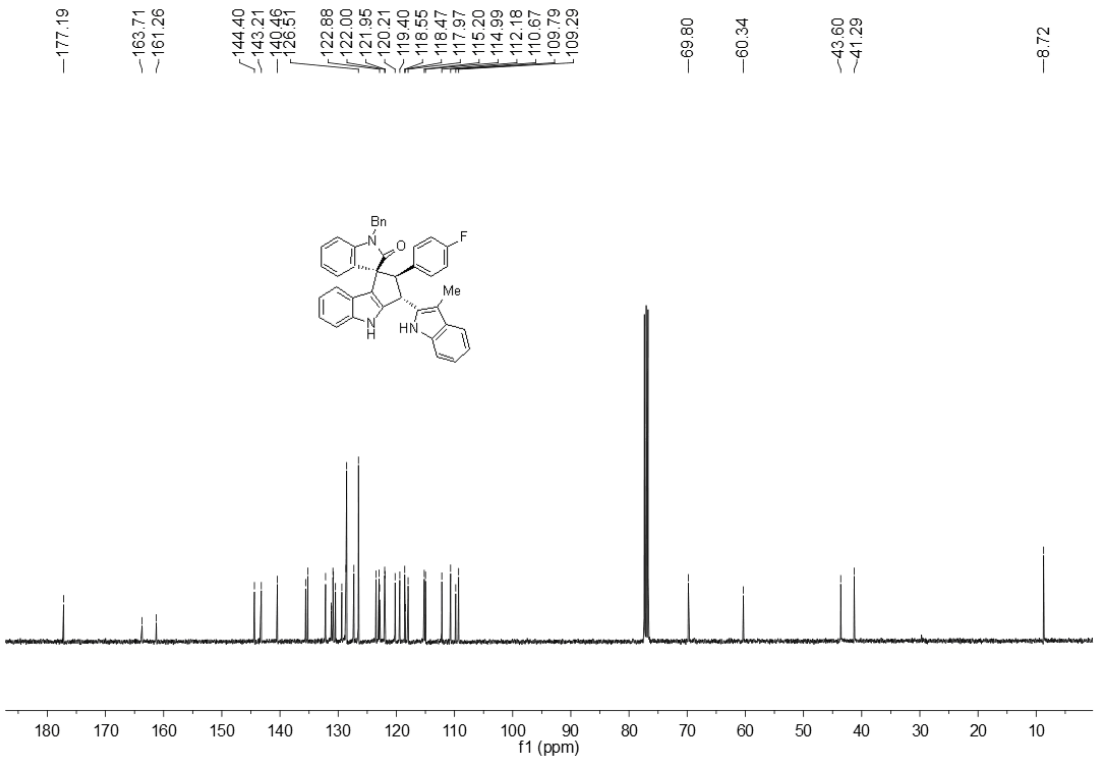
3af


8.253
7.956
7.470
7.451
7.221
7.097
6.948
6.794
6.558
6.539
6.532
5.875
5.851
5.050
5.010
4.566
4.541
4.392
4.352
2.313
2.184
Bn
Me
Me
HN
f1 (ppm)

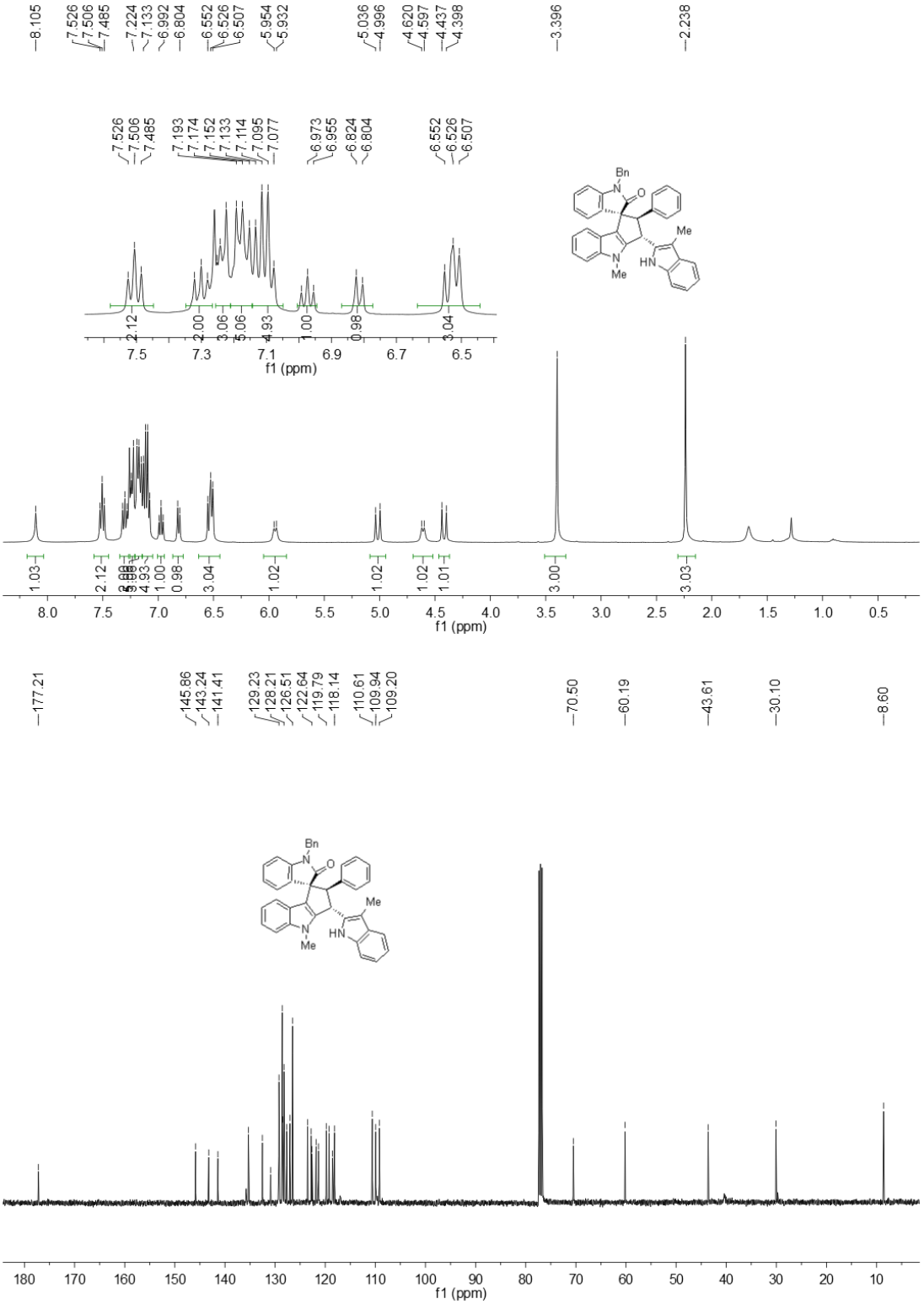

177.31
144.78
143.24
140.42
135.34
128.92
126.61
122.81
119.26
117.99
112.14
110.63
109.70
109.24
70.30
60.36
43.59
41.08
21.24
8.73
Bn
Me
Me
HN
f1 (ppm)

3ag

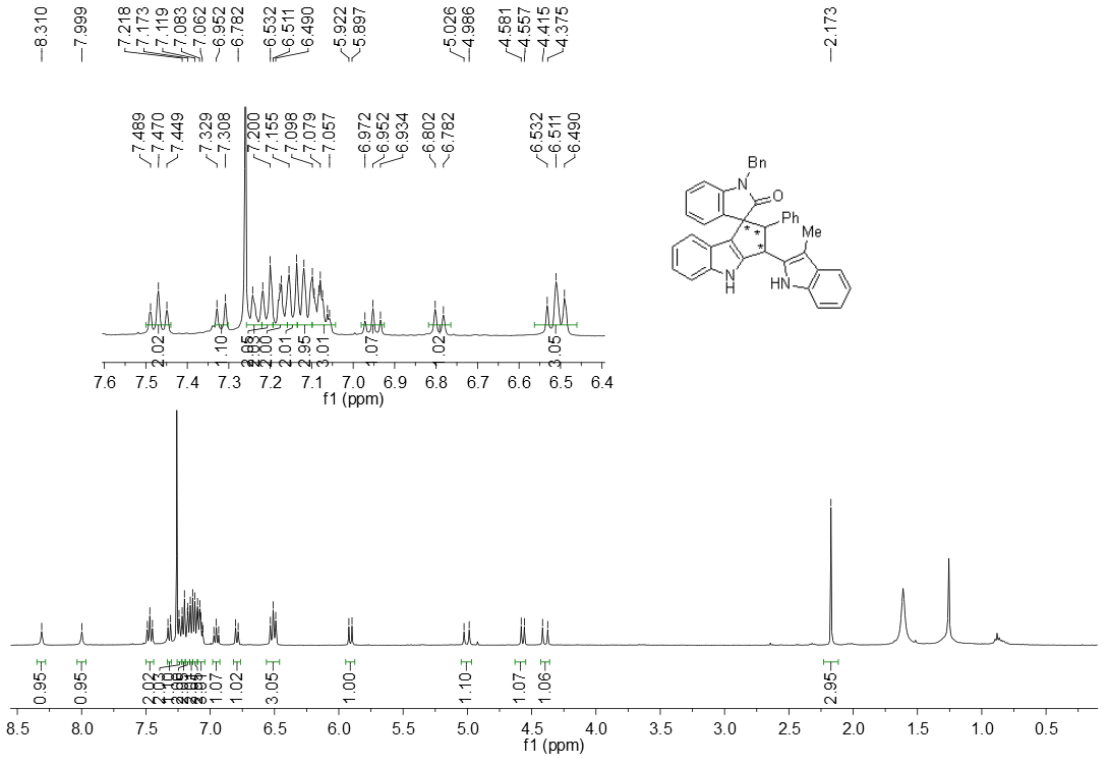

8.284
7.947
7.485
7.440
7.180
7.127
6.976
6.797
6.609
6.584
6.565
5.832
5.808
5.014
4.974
4.536
4.512
4.419
4.379
2.161
Bn
N
O
F
Me
HN
H
f1 (ppm)

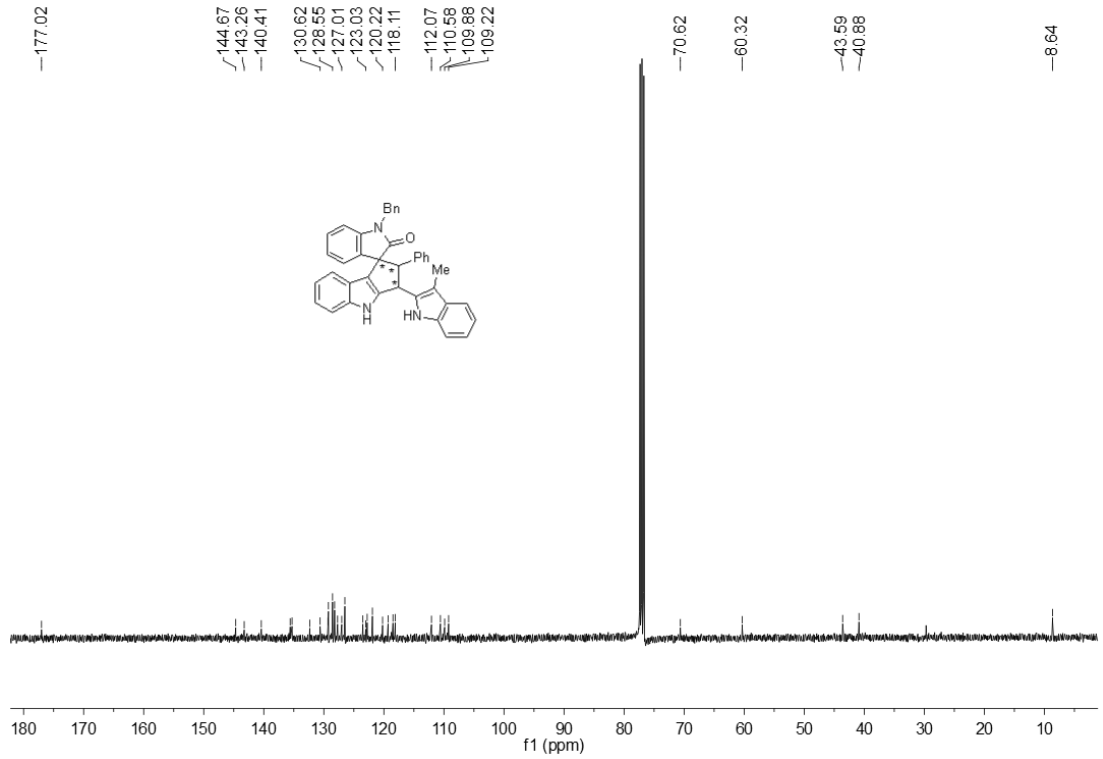

177.19
163.71
161.26
144.40
143.21
140.46
126.51
122.88
122.00
121.95
120.21
119.40
118.55
118.47
117.97
115.20
114.99
112.18
110.67
109.79
109.29
69.80
60.34
43.60
41.29
8.72
Bn
N
O
F
Me
HN
H
f1 (ppm)

3na

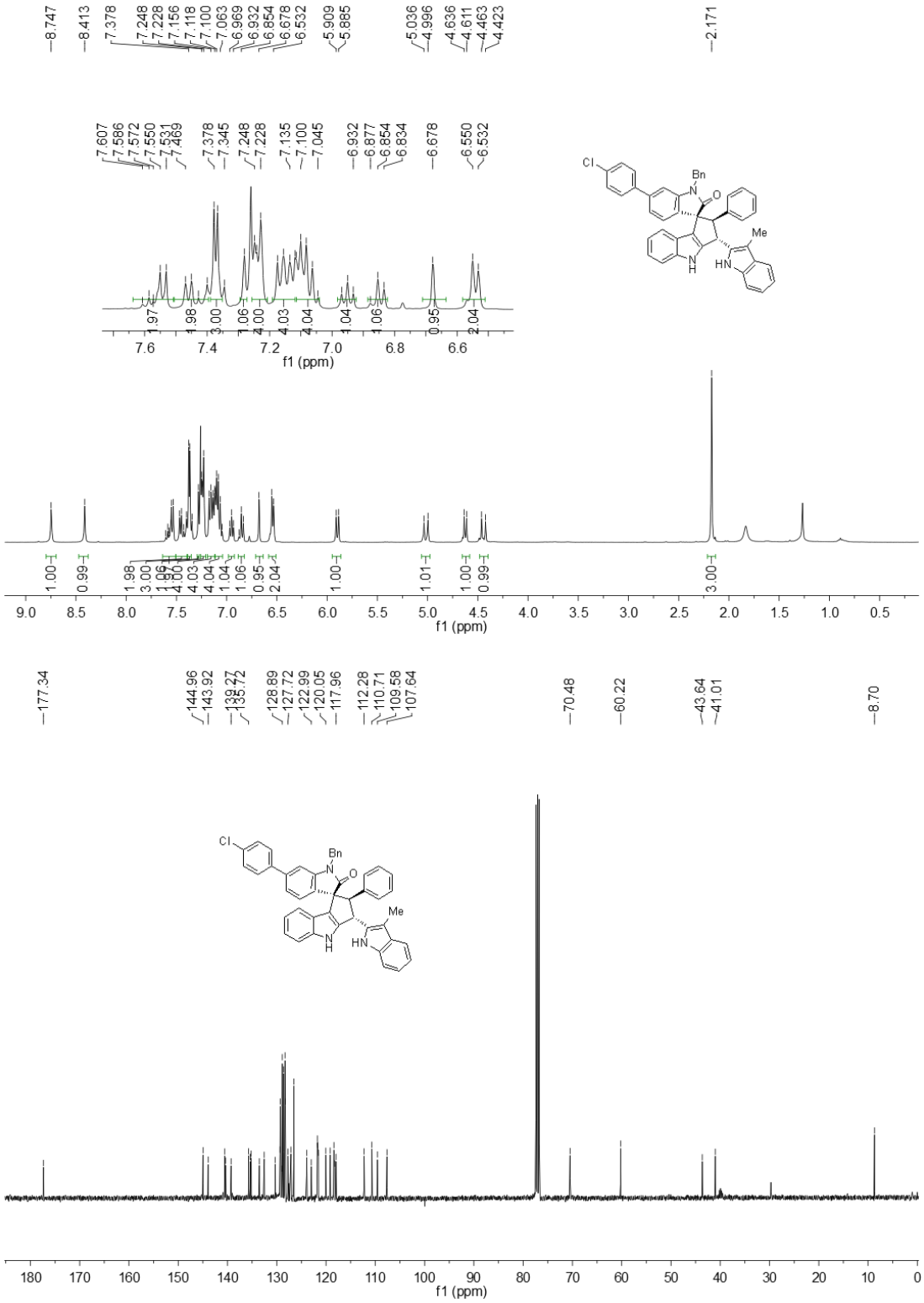

8.105
7.526
7.506
7.485
7.224
7.133
6.992
6.804
6.552
6.526
6.507
5.954
5.932
5.036
4.996
4.620
4.597
4.437
4.398
3.396
2.238
Bn
N
O
Me
N
Me
HN
f1 (ppm)
177.21
145.86
143.24
141.41
129.23
128.21
126.51
122.64
119.79
118.14
110.61
109.94
109.20
70.50
60.19
43.61
30.10
8.60
f1 (ppm)

3ai


8.310
7.999
7.218
7.173
7.119
7.083
7.062
6.952
6.782
6.532
6.511
6.490
5.922
5.897
5.026
4.986
4.581
4.557
4.415
4.375
2.173
Bn
Ph
Me
HN
f1 (ppm)

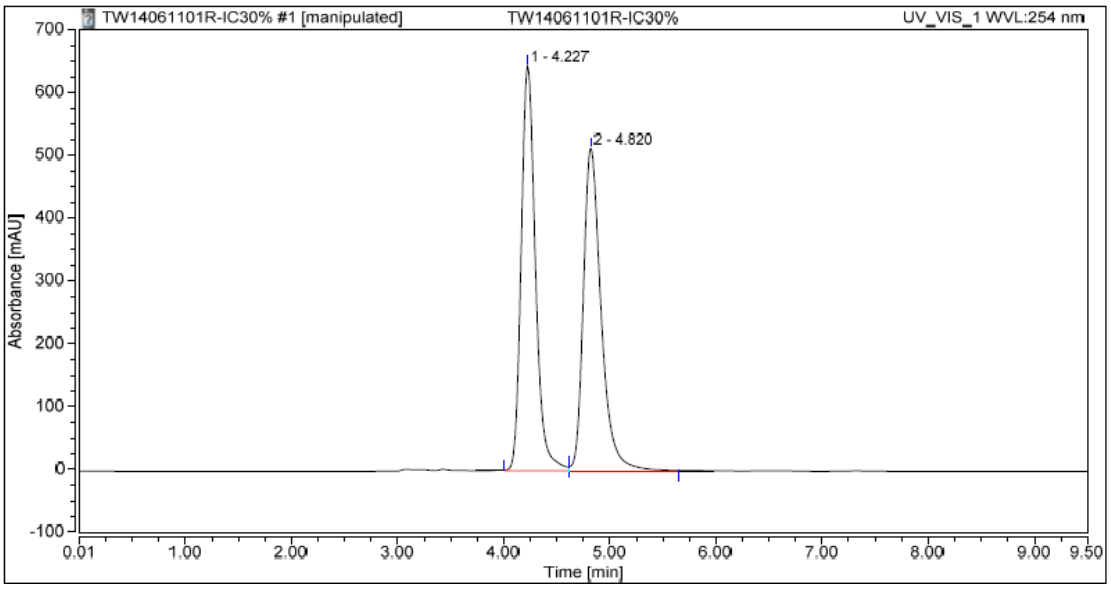

177.02
144.67
143.26
140.41
130.62
128.55
127.01
123.03
120.22
118.11
112.07
110.58
109.88
109.22
70.62
60.32
43.59
40.88
8.64
Bn
Ph
Me
HN
f1 (ppm)

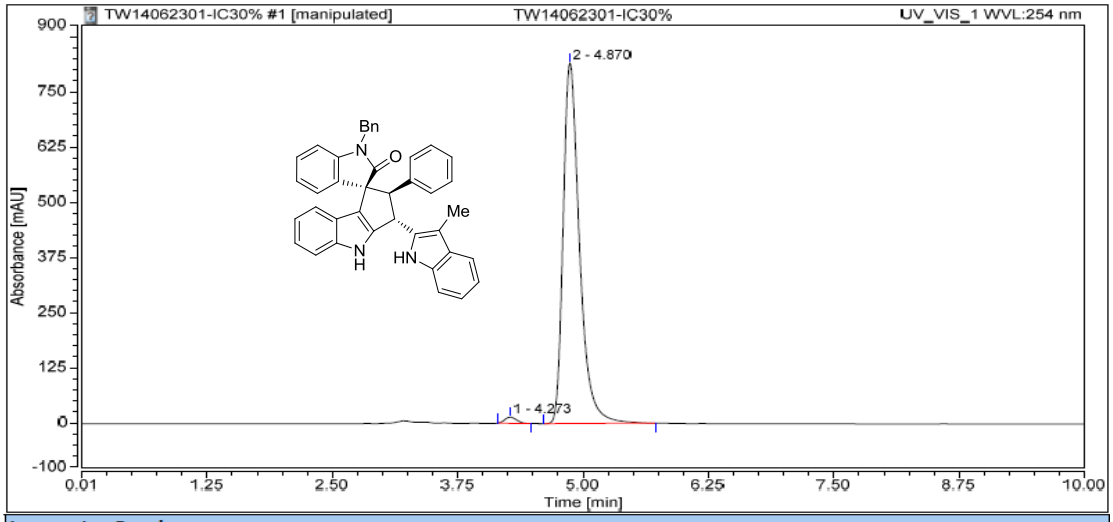
Compound 7


8.747
8.413
7.378
7.248
7.228
7.156
7.118
7.100
7.063
6.969
6.932
6.854
6.678
6.532
5.909
5.885
5.036
4.996
4.636
4.611
4.463
4.423
2.171
7.607
7.586
7.572
7.550
7.531
7.469
7.378
7.345
7.248
7.228
7.135
7.100
7.045
6.932
6.877
6.854
6.834
6.678
6.550
6.532
Cl
Bn
N
O
Me
HN
H
f1 (ppm)
177.34
144.96
143.92
139.27
135.72
128.89
127.72
122.99
120.05
117.96
112.28
110.71
109.58
107.64
70.48
60.22
43.64
41.01
8.70

8. Chiral HPLC analyses of products 3

3aa

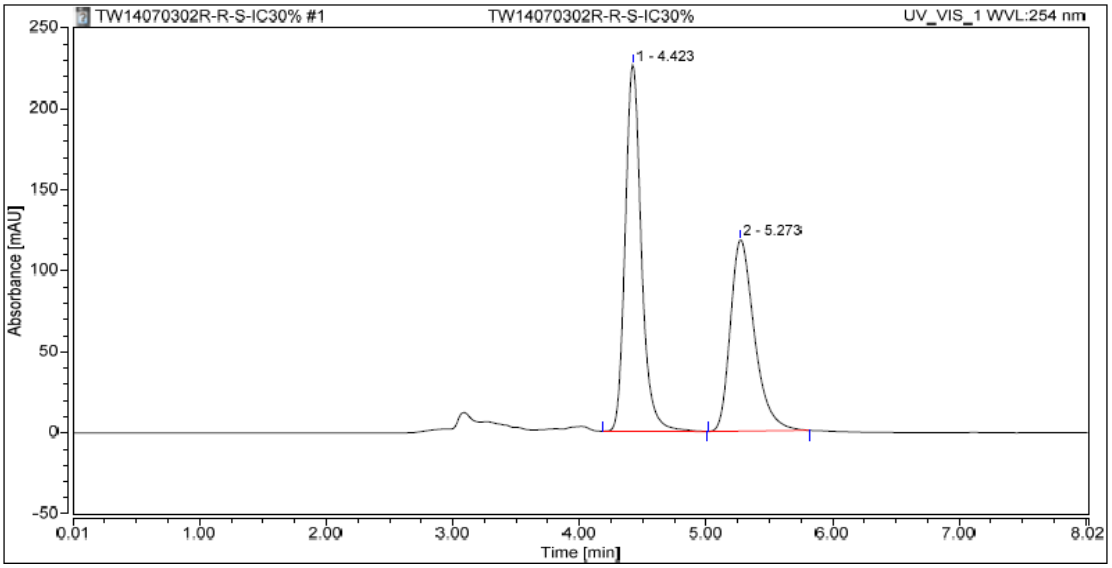


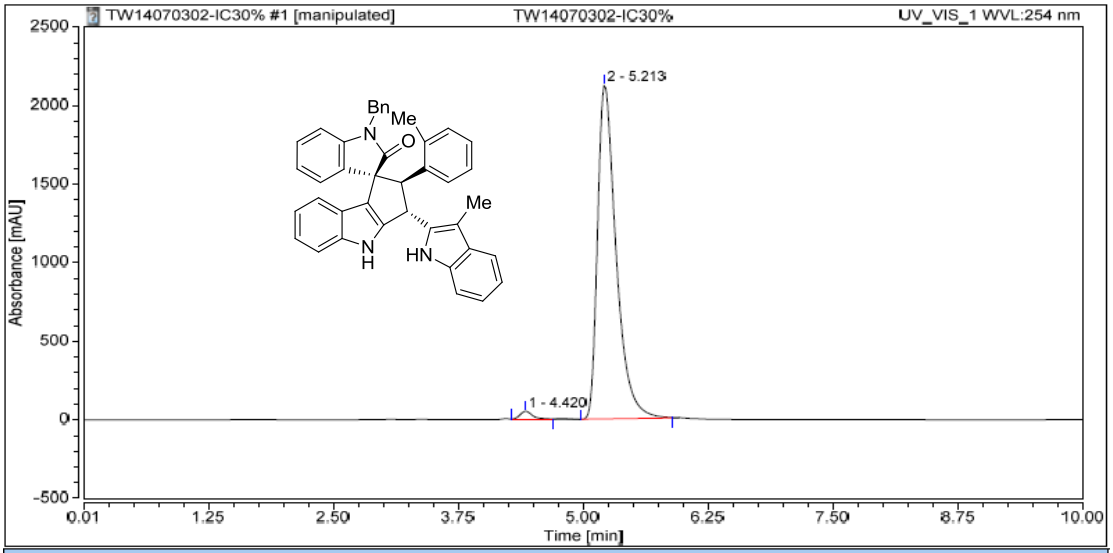


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.273	1.909	14.016	1.22	1.69	n.a.
2		4.870	154.275	815.632	98.78	98.31	n.a.
Total:			**156.184**	**829.648**	**100.00**	**100.00**	

3ab

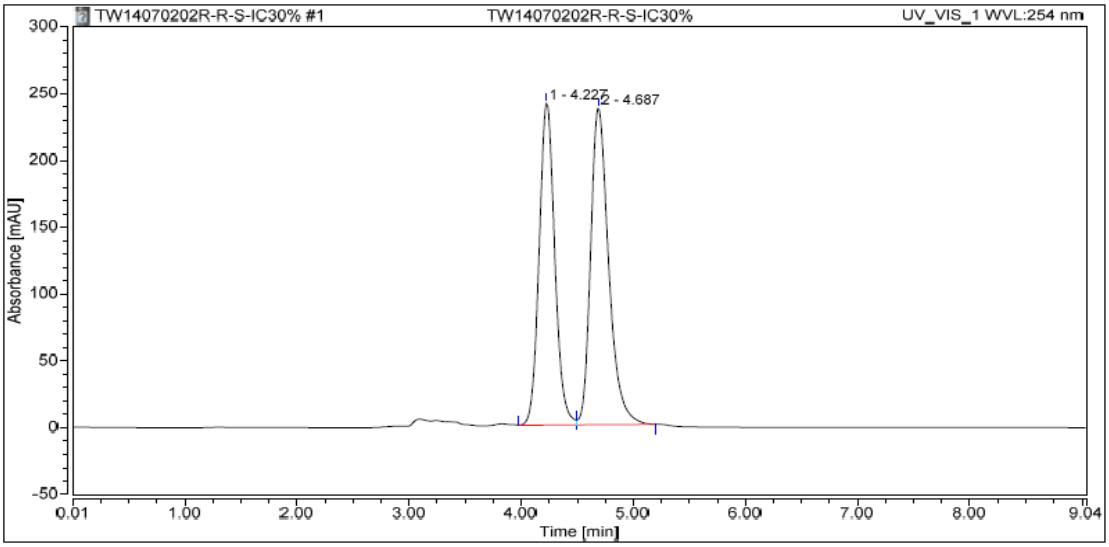


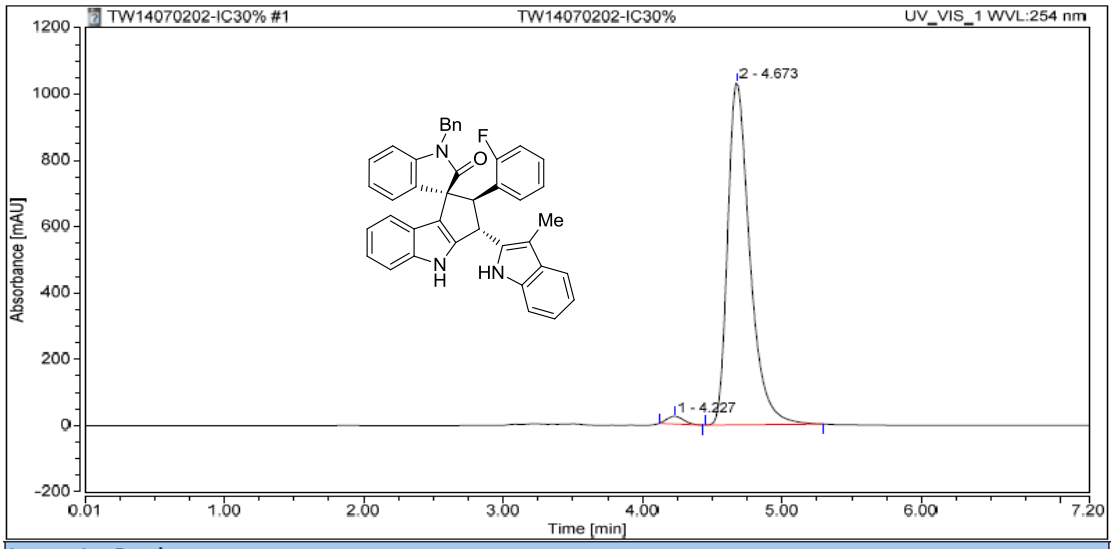


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.420	7.228	50.359	1.56	2.31	n.a.
2		5.213	457.310	2126.785	98.44	97.69	n.a.
Total:			**464.539**	**2177.144**	**100.00**	**100.00**	

3ac

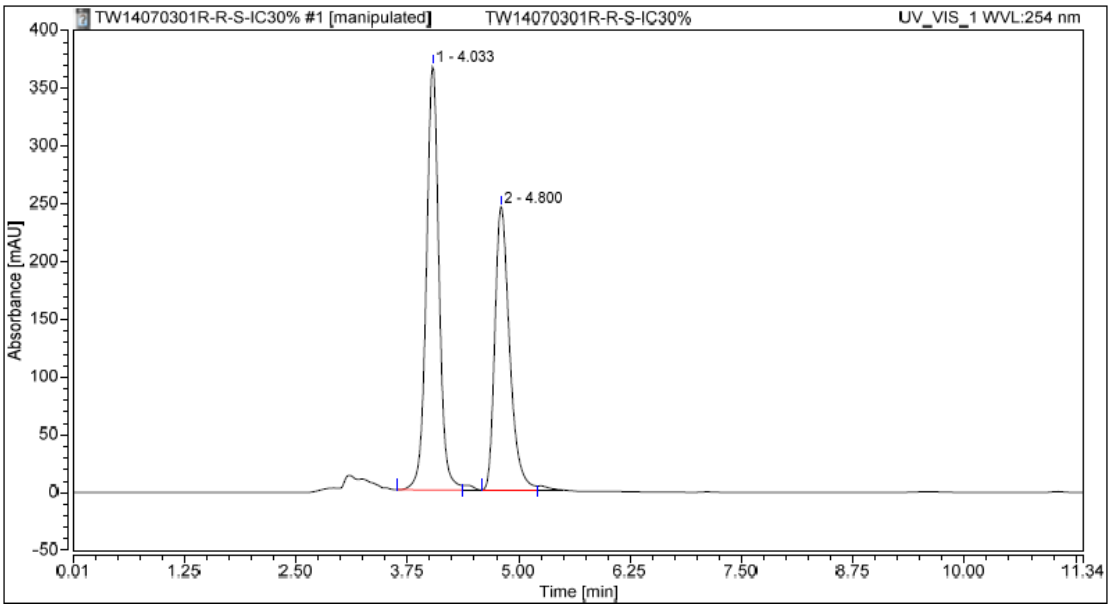


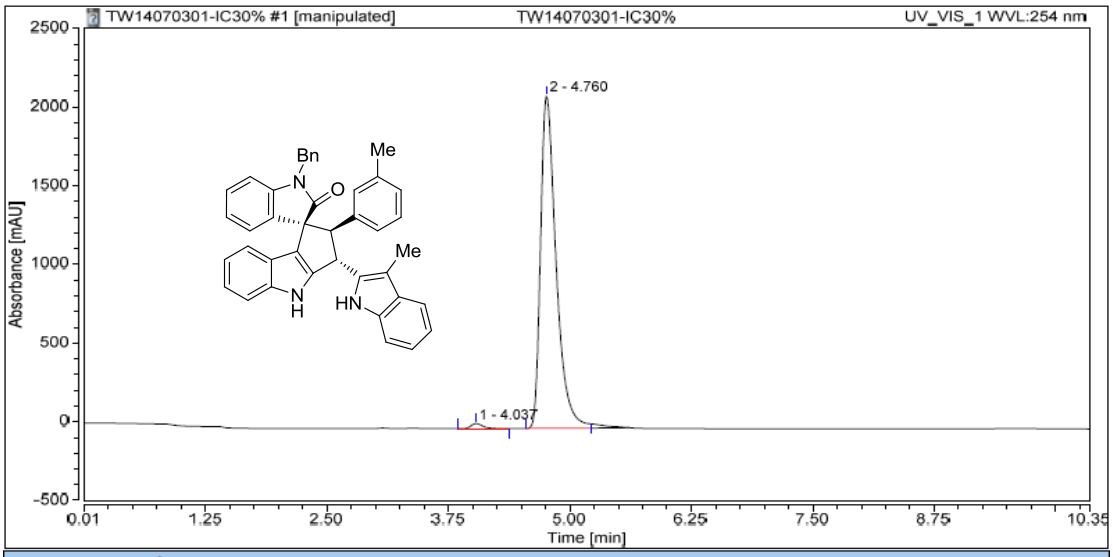


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.227	3.226	23.167	1.67	2.20	n.a.
2		4.673	189.980	1031.769	98.33	97.80	n.a.
Total:			**193.206**	**1054.936**	**100.00**	**100.00**	

3ad

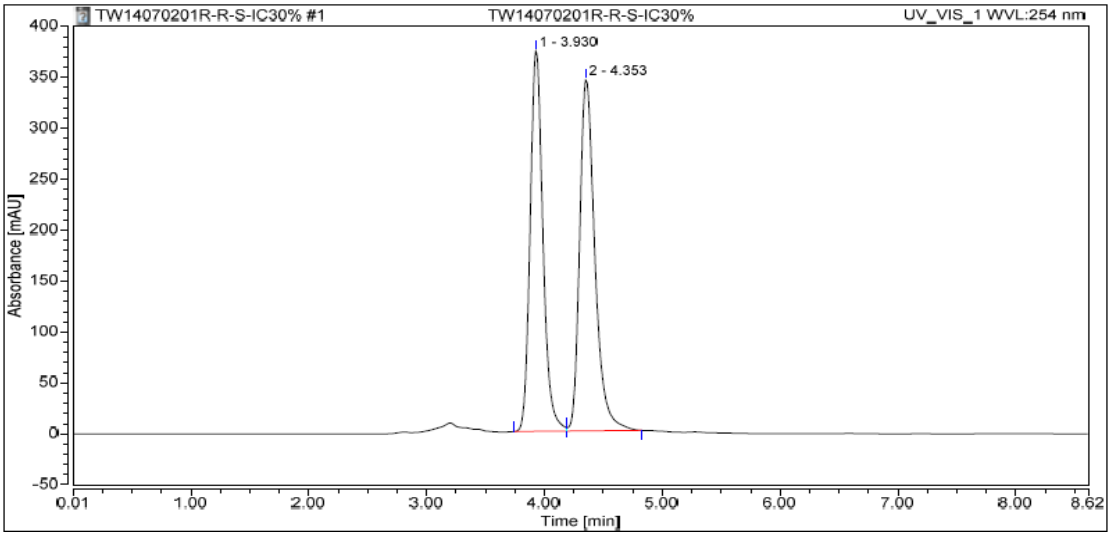


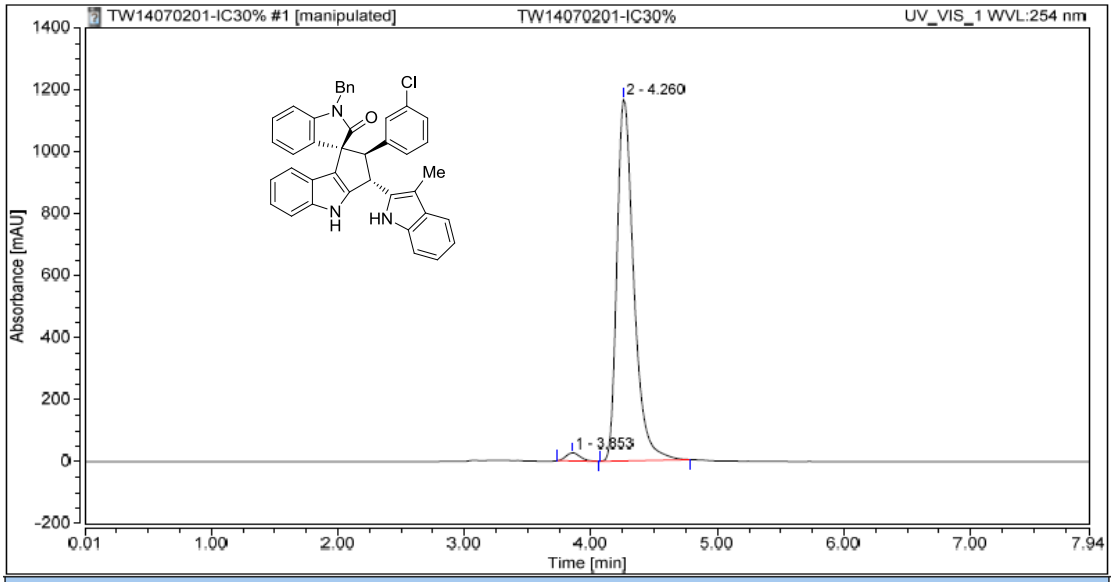


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.037	4.603	32.182	1.16	1.50	n.a.
2		4.760	390.868	2113.672	98.84	98.50	n.a.
Total:			**395.470**	**2145.855**	**100.00**	**100.00**	

3ae

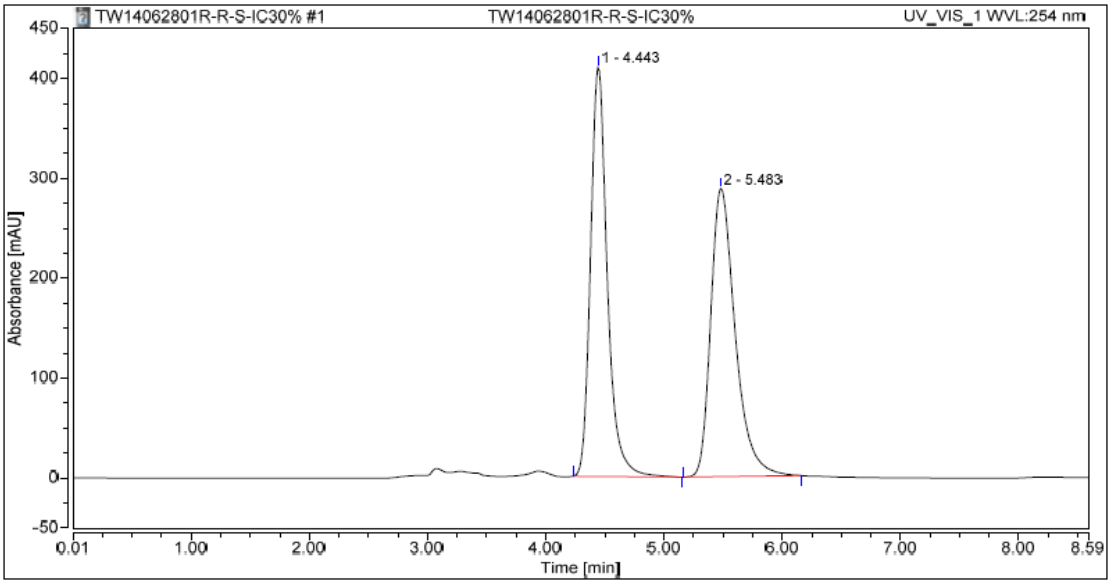


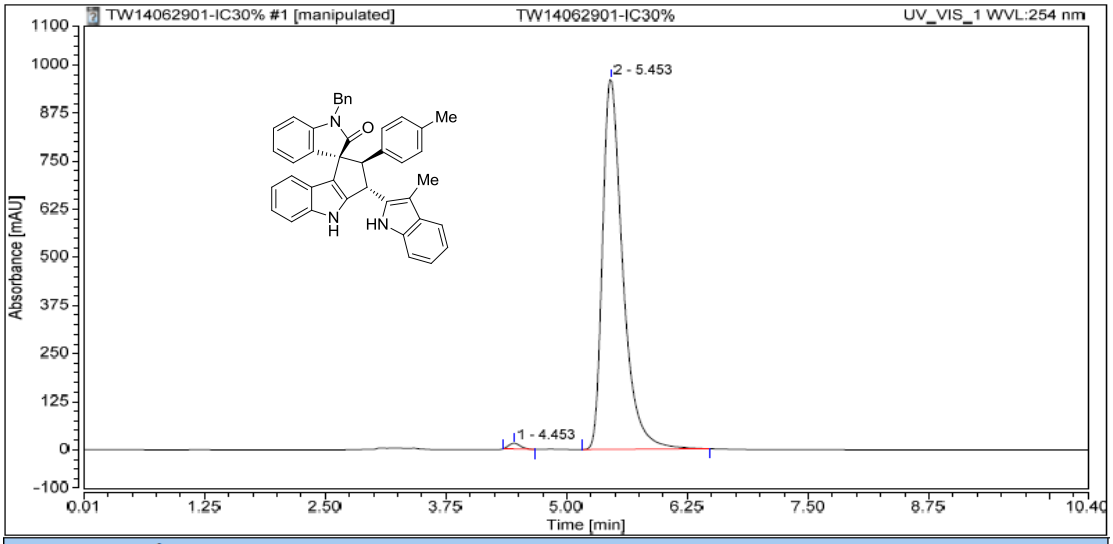


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.853	3.336	26.057	1.82	2.18	n.a.
2		4.260	180.372	1169.192	98.18	97.82	n.a.
Total:			**183.708**	**1195.249**	**100.00**	**100.00**	

3af

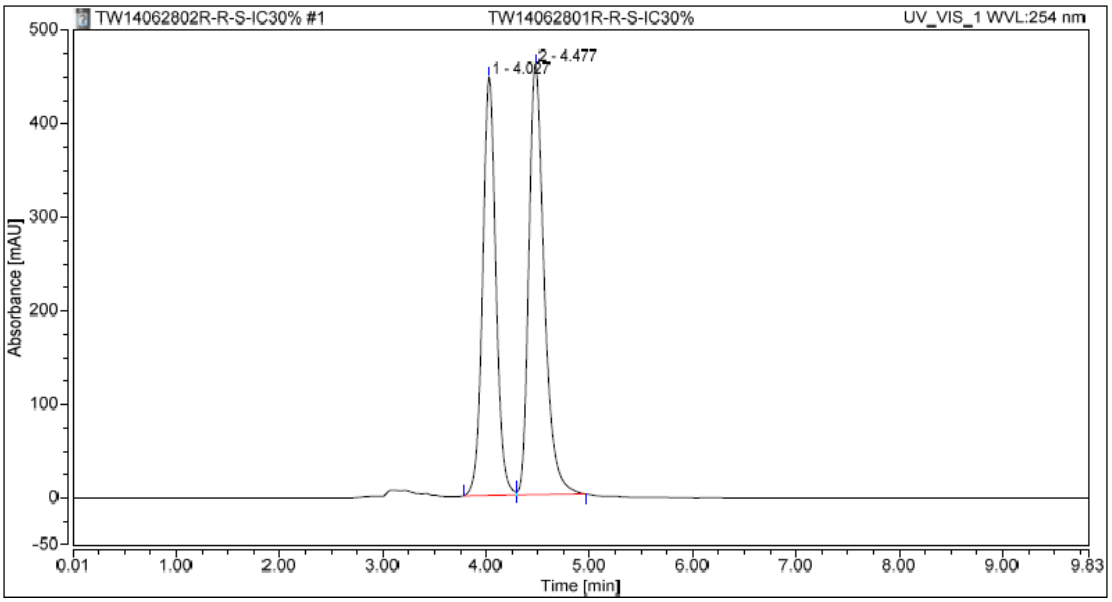


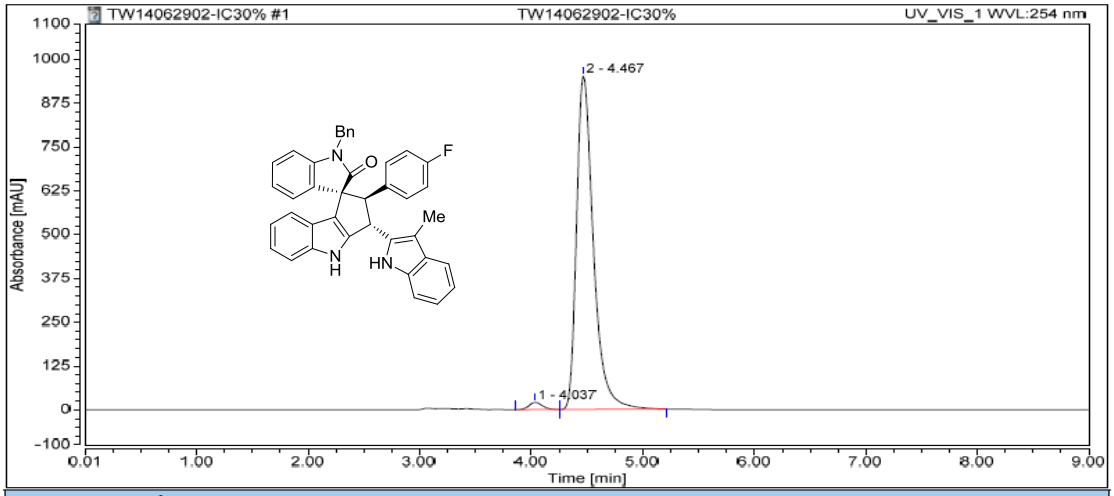


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.453	2.030	14.845	0.86	1.52	n.a.
2		5.453	233.847	963.210	99.14	98.48	n.a.
Total:			**235.877**	**978.055**	**100.00**	**100.00**	

3ag

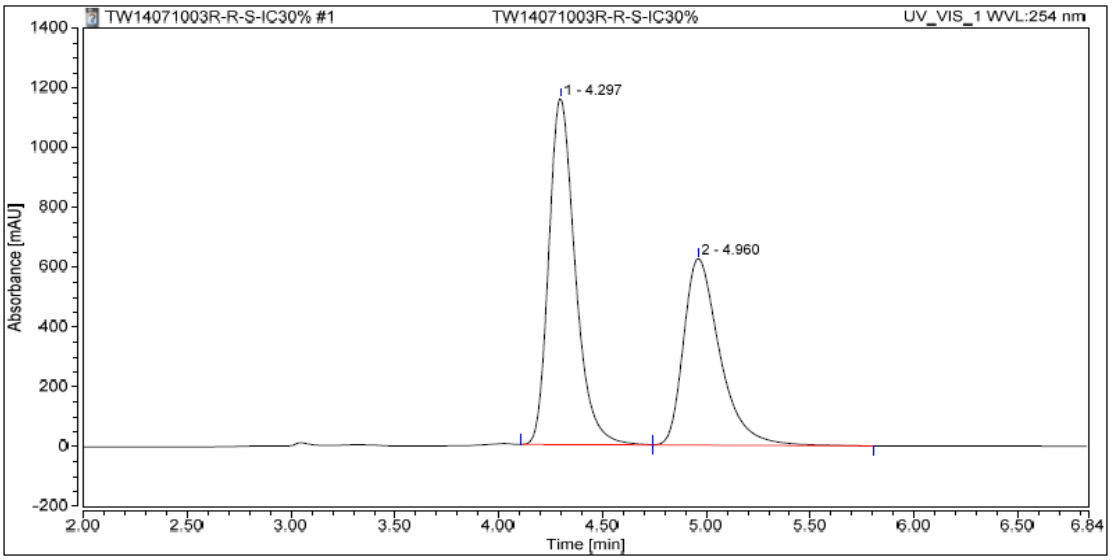


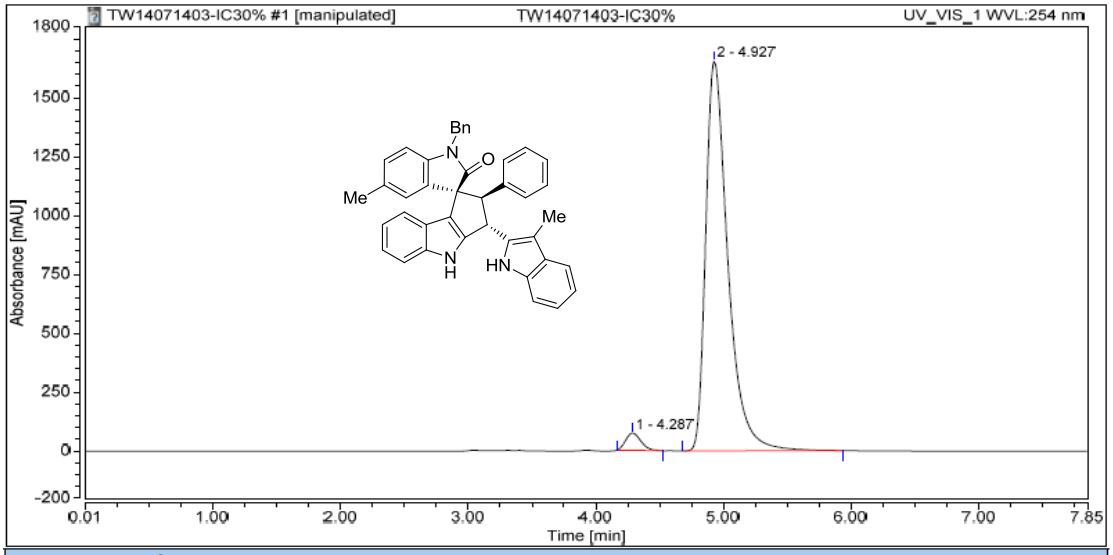


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.037	2.865	20.631	1.69	2.12	n.a.
2		4.467	166.539	952.476	98.31	97.88	n.a.
Total:			**169.405**	**973.107**	**100.00**	**100.00**	

3ba

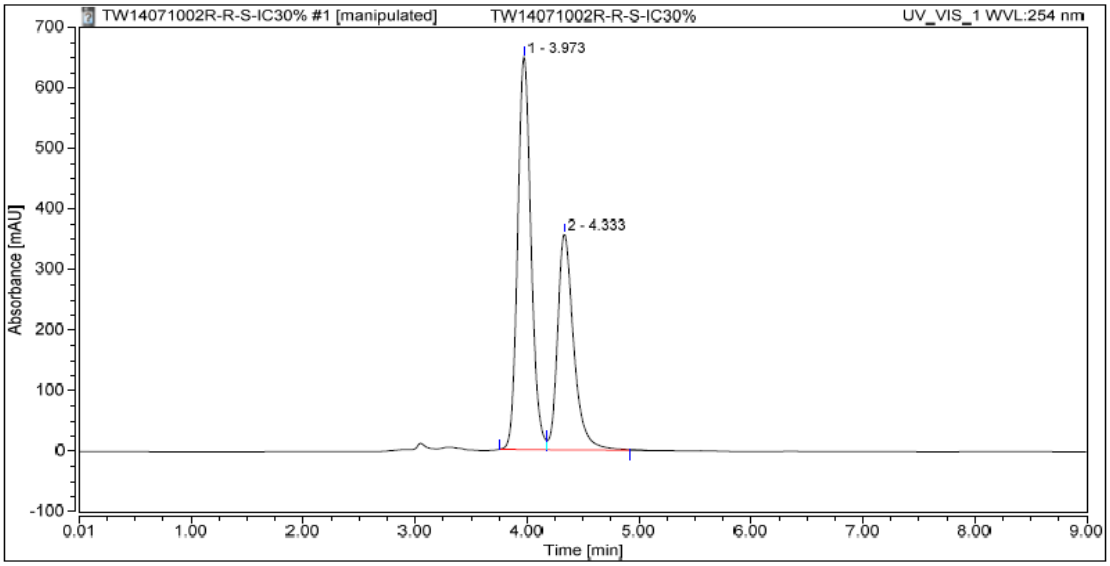


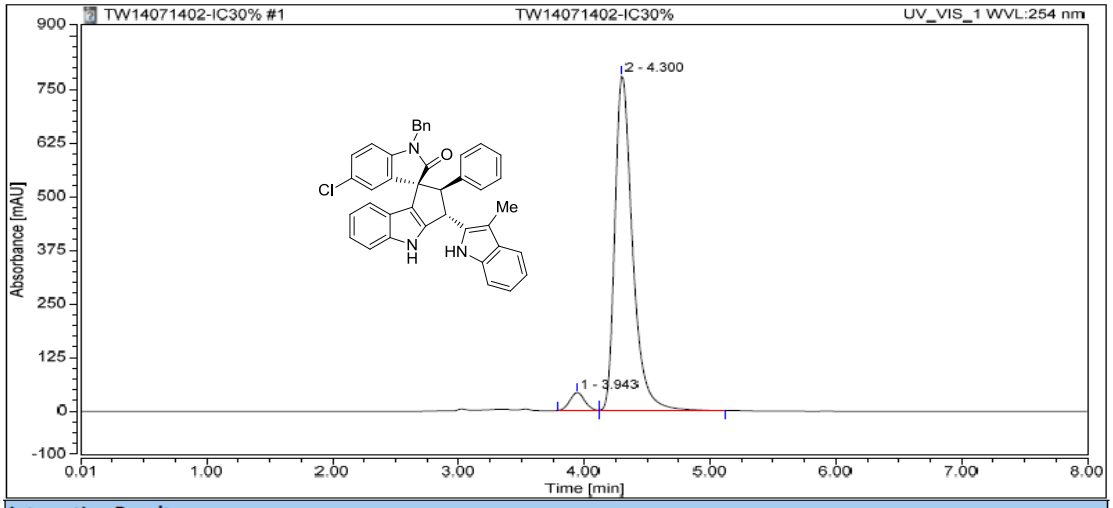


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.287	10.041	73.458	2.94	4.25	n.a.
2		4.927	332.013	1654.237	97.06	95.75	n.a.
Total:			**342.054**	**1727.695**	**100.00**	**100.00**	

3ca

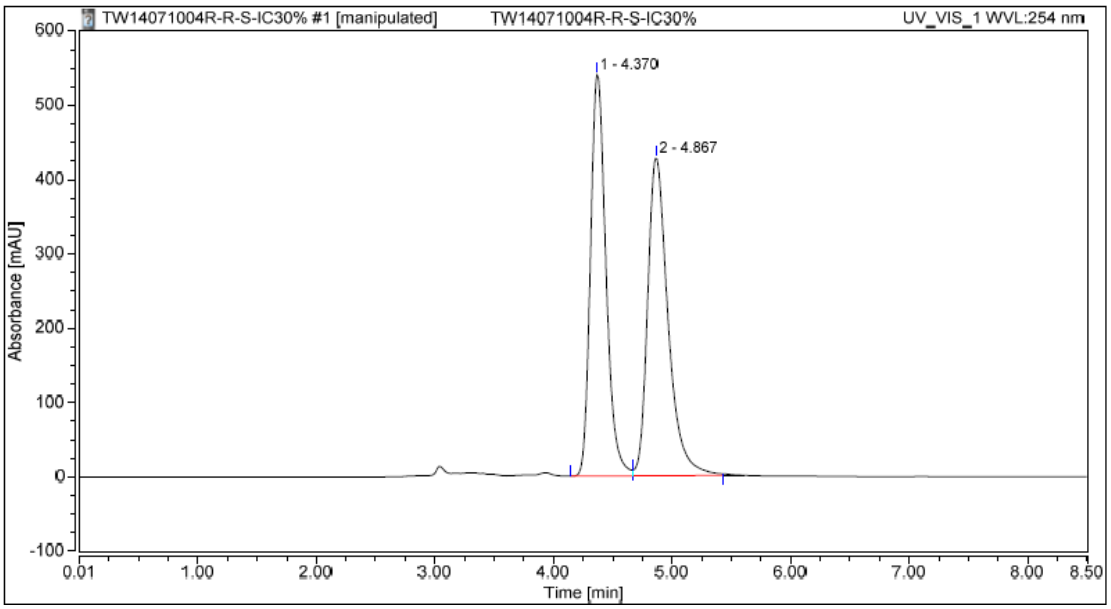


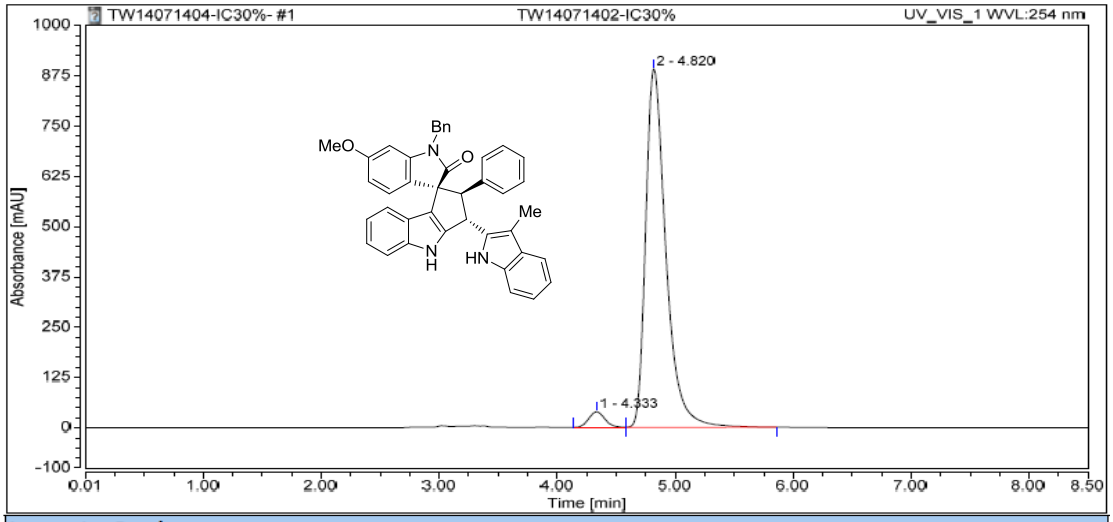


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.943	5.745	41.919	4.32	5.10	n.a.
2		4.300	127.195	780.464	95.68	94.90	n.a.
Total:			**132.940**	**822.384**	**100.00**	**100.00**	

3da

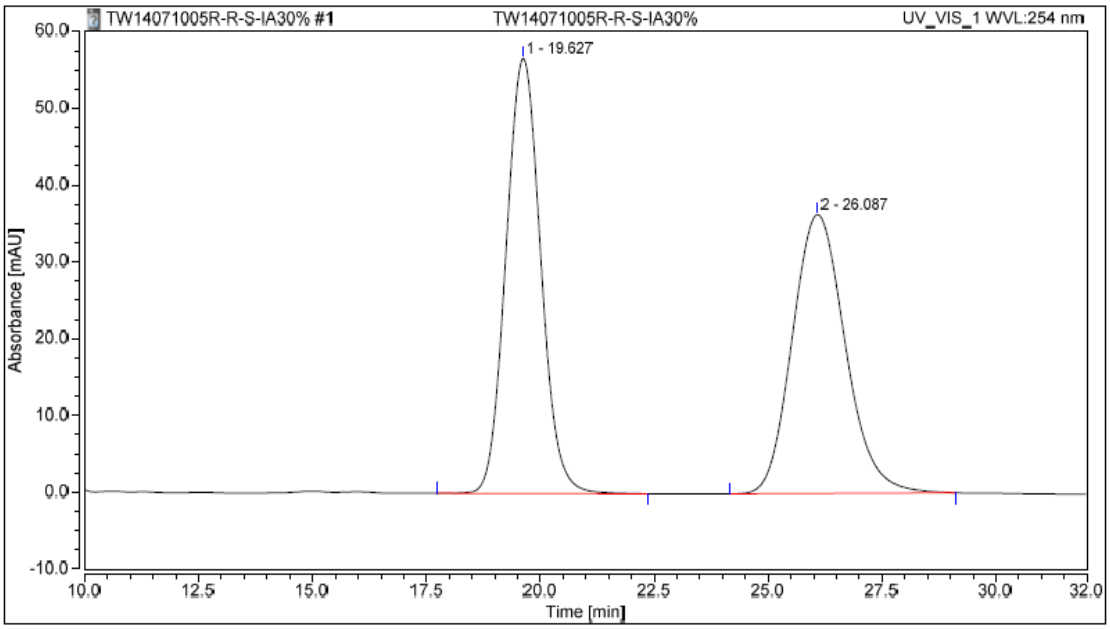


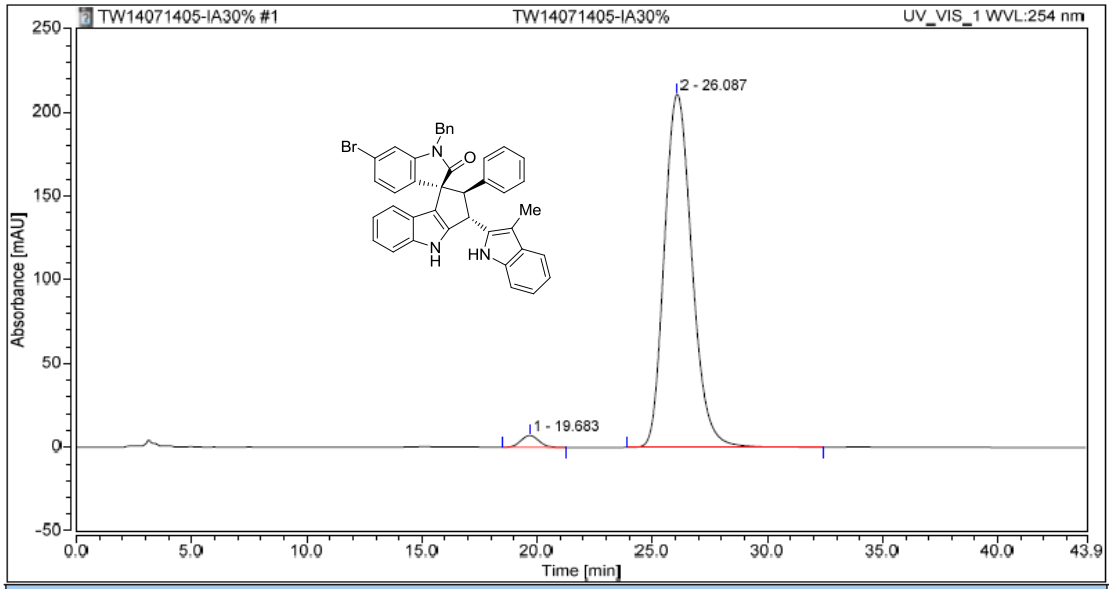


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.333	6.115	38.600	3.33	4.15	n.a.
2		4.820	177.252	890.830	96.67	95.85	n.a.
Total:			**183.367**	**929.430**	**100.00**	**100.00**	

3ea

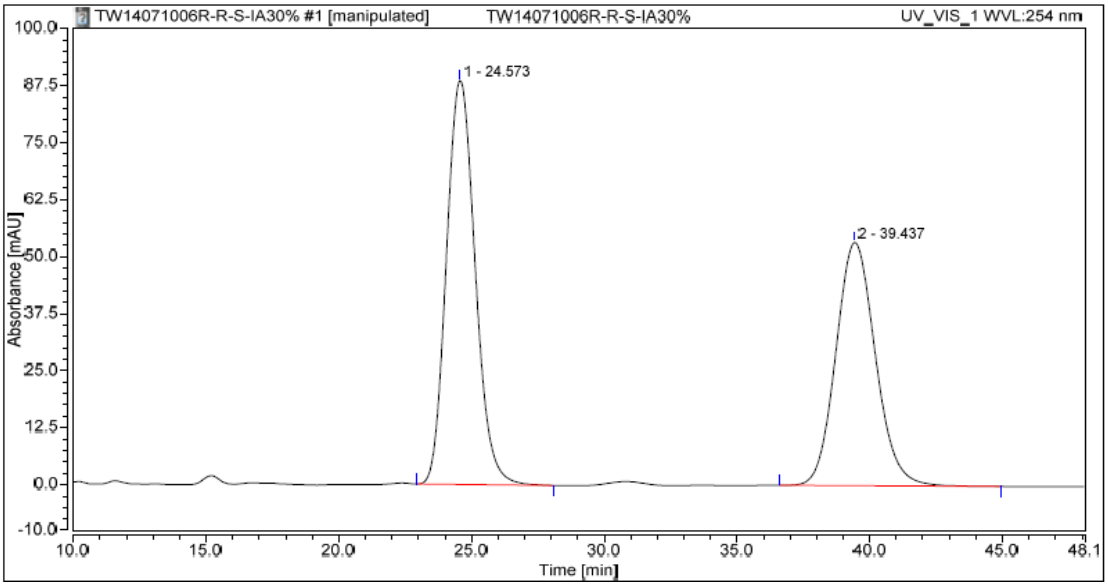


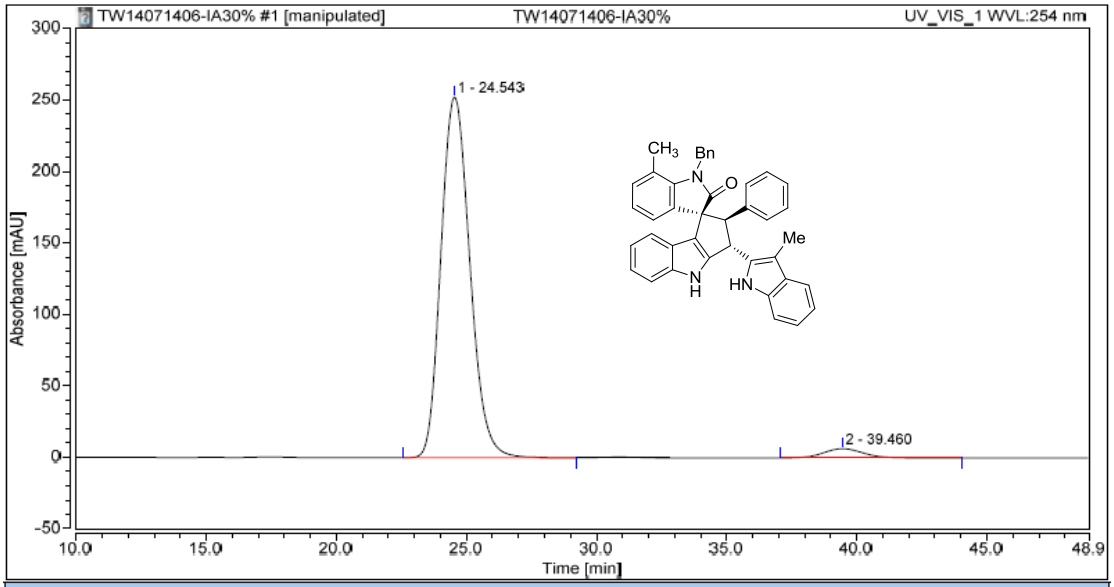


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.683	6.329	7.006	2.12	3.21	n.a.
2		26.087	292.672	211.003	97.88	96.79	n.a.
Total:			**299.001**	**218.009**	**100.00**	**100.00**	

3fa

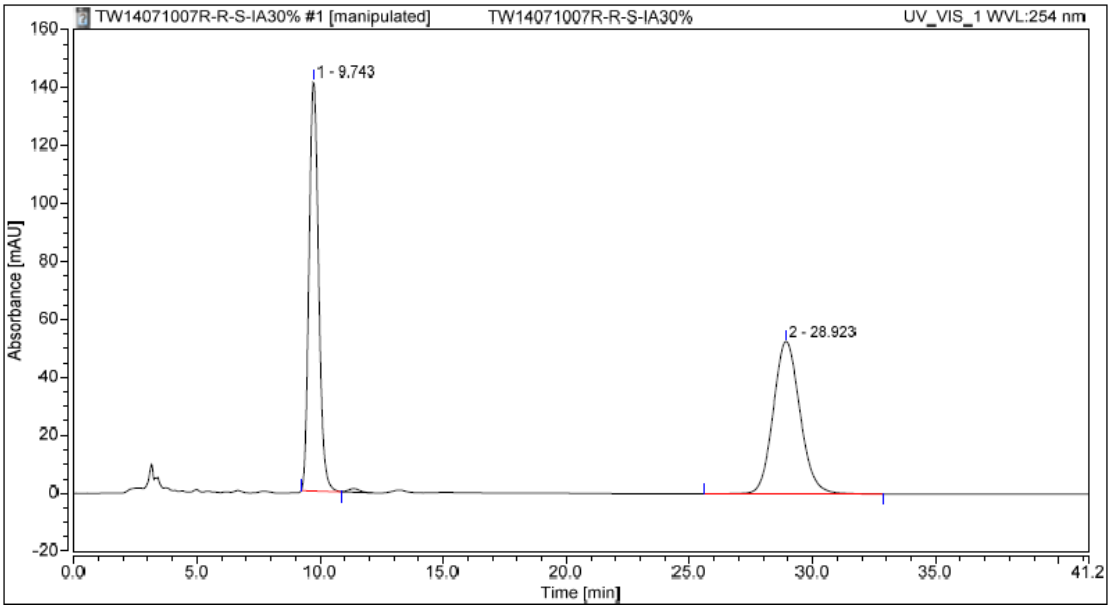


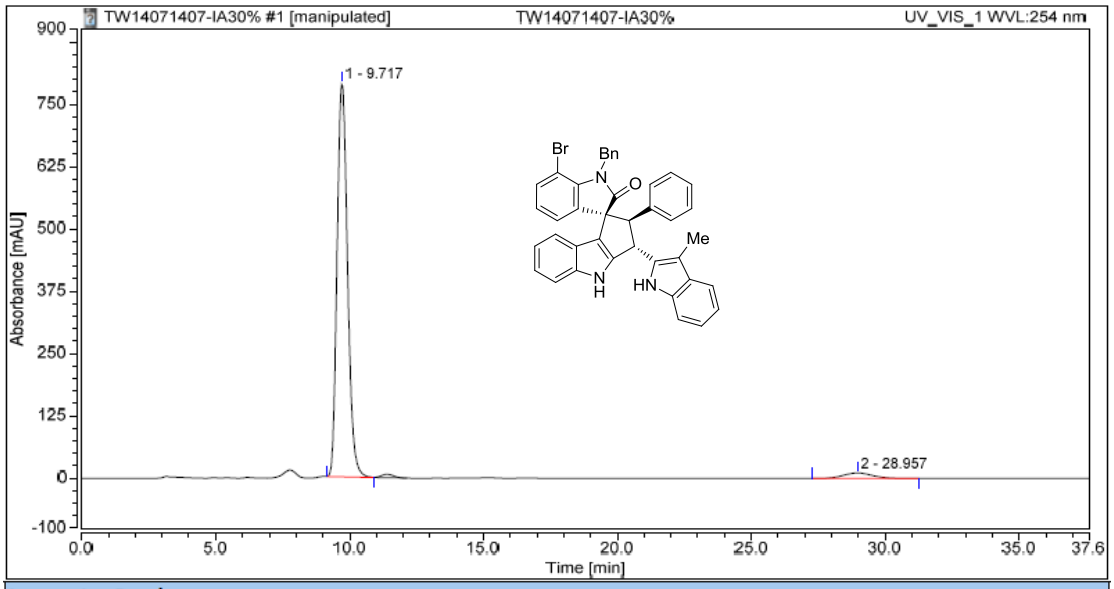


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.543	324.684	252.375	96.66	97.52	n.a.
2		39.460	11.225	6.405	3.34	2.48	n.a.
Total:			**335.908**	**258.780**	**100.00**	**100.00**	

3ga

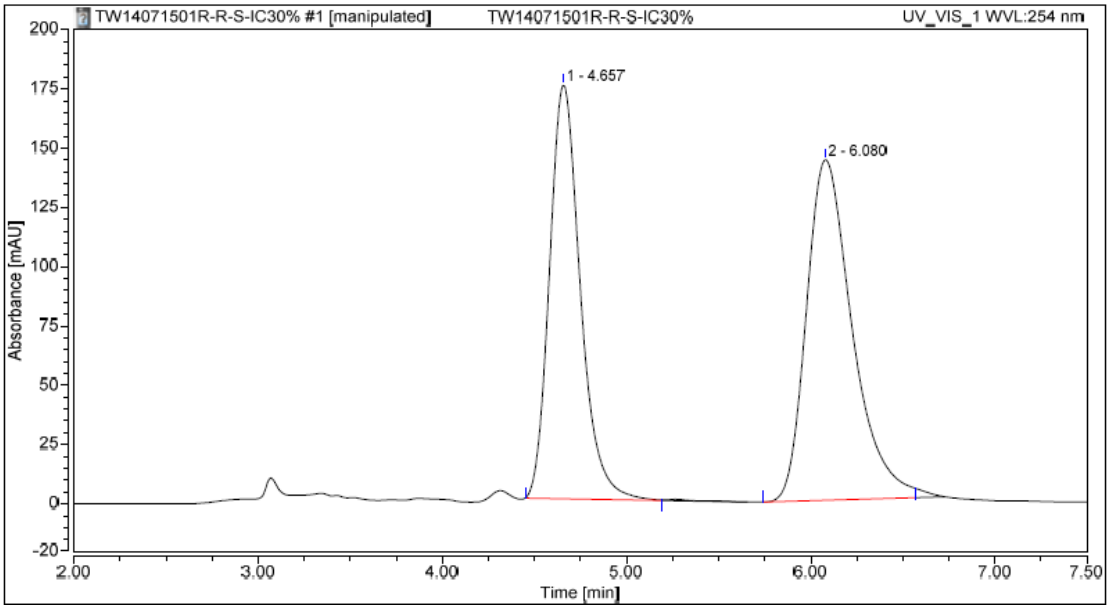


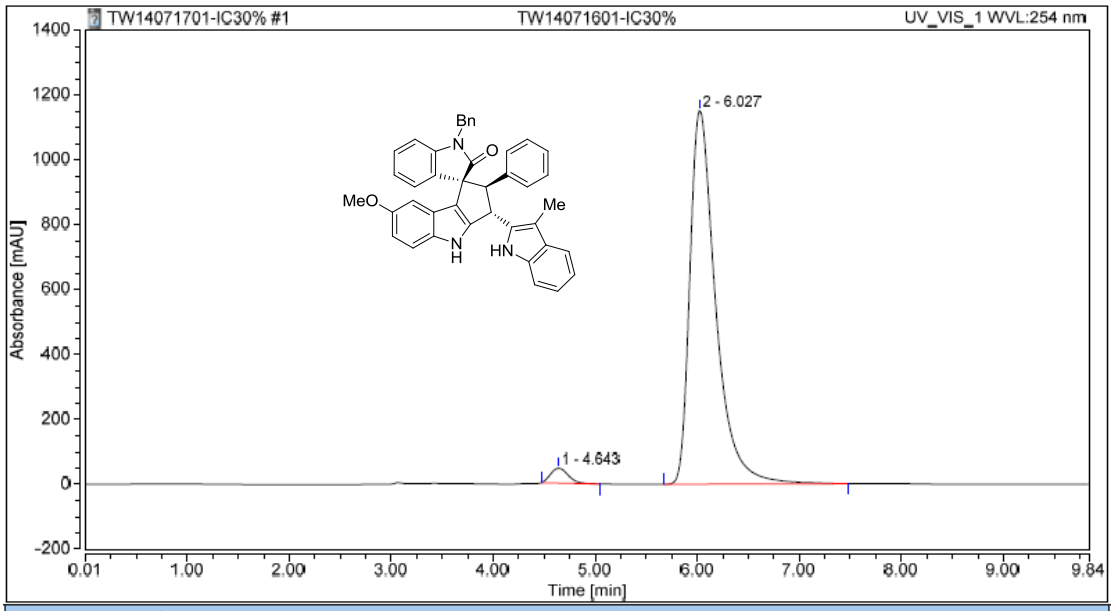


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.717	357.168	789.598	96.35	98.65	n.a.
2		28.957	13.538	10.804	3.65	1.35	n.a.
Total:			**370.706**	**800.401**	**100.00**	**100.00**	

3ha

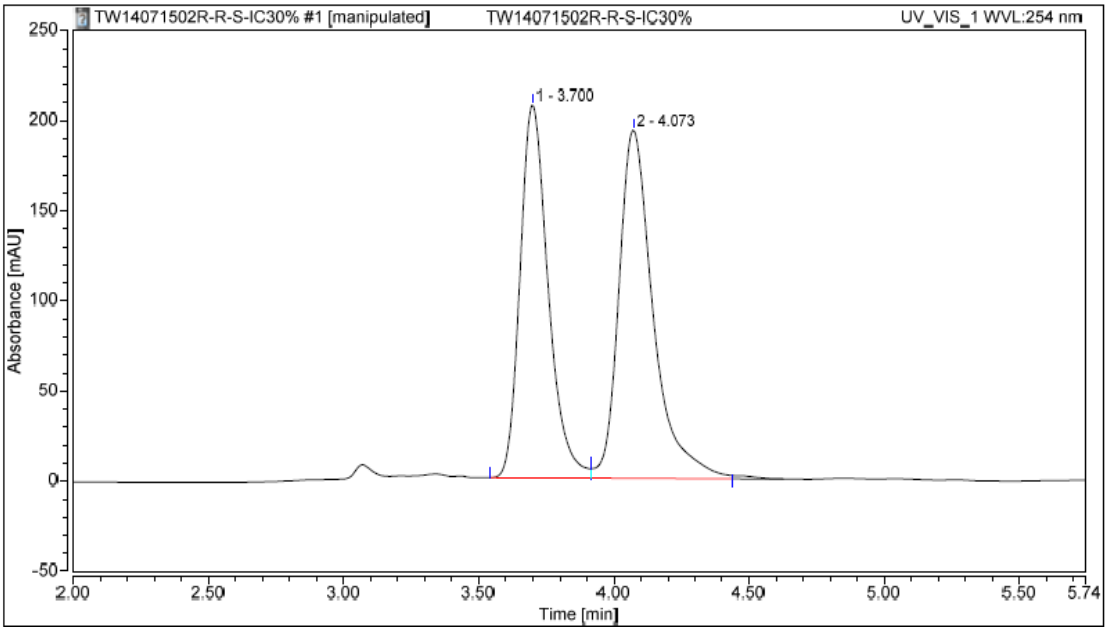


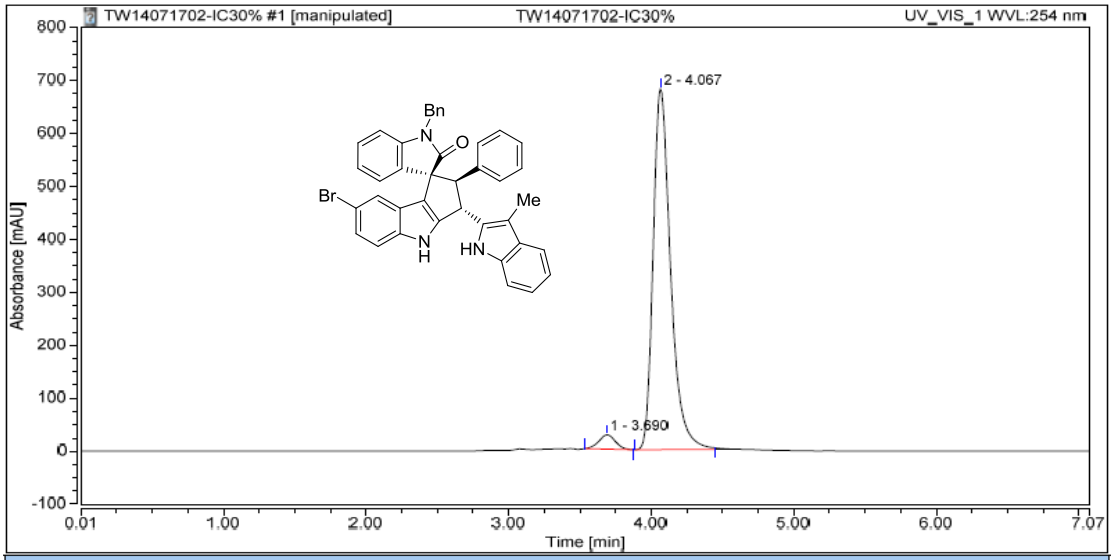


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.643	9.213	46.195	2.65	3.85	n.a.
2		6.027	338.085	1153.024	97.35	96.15	n.a.
Total:			**347.298**	**1199.218**	**100.00**	**100.00**	

3ia

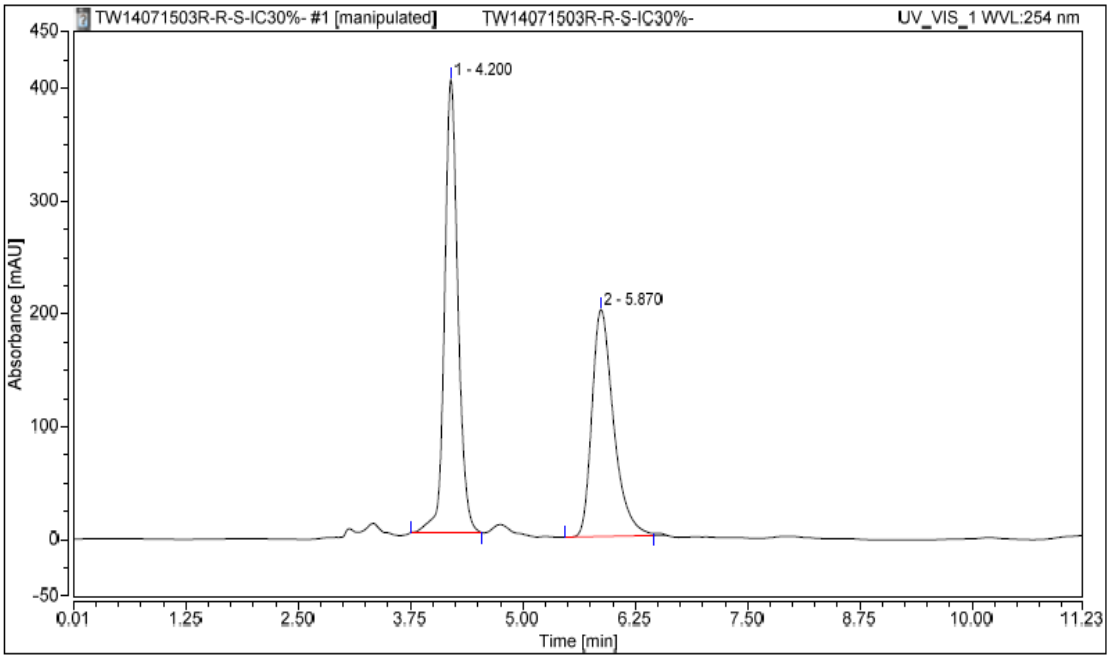


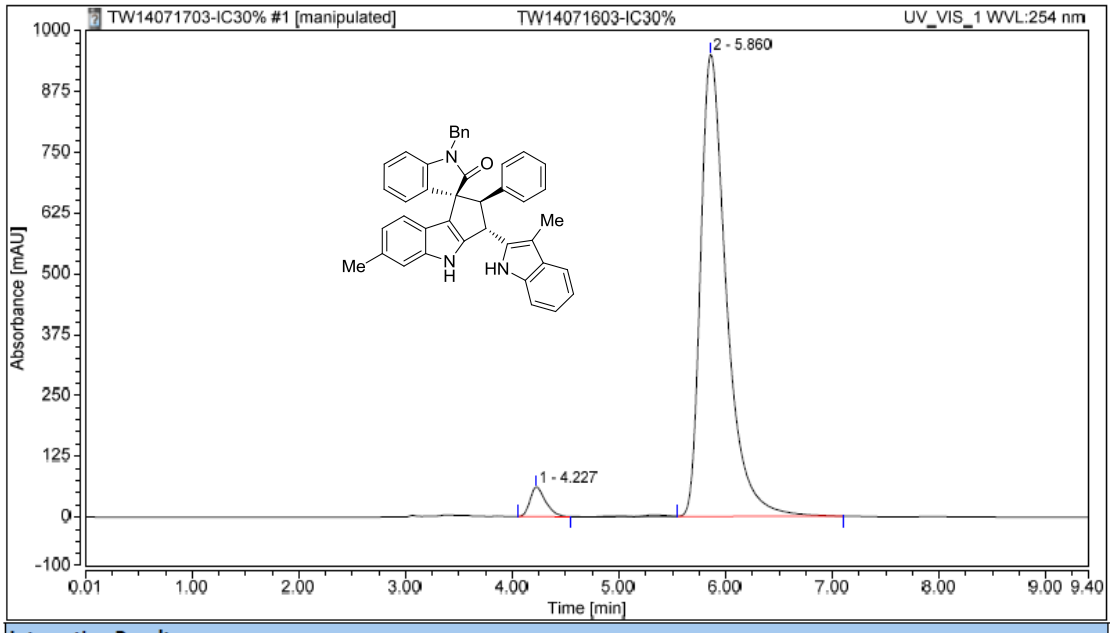


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.690	3.634	27.072	3.63	3.82	n.a.
2		4.067	96.579	680.721	96.37	96.18	n.a.
Total:			**100.213**	**707.793**	**100.00**	**100.00**	

3ja

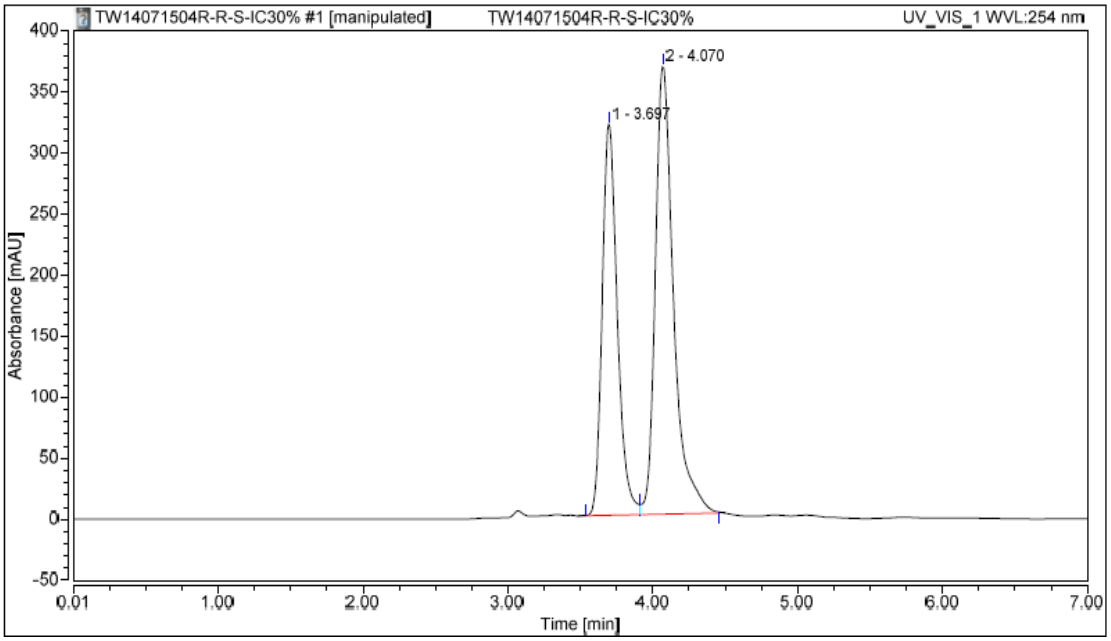


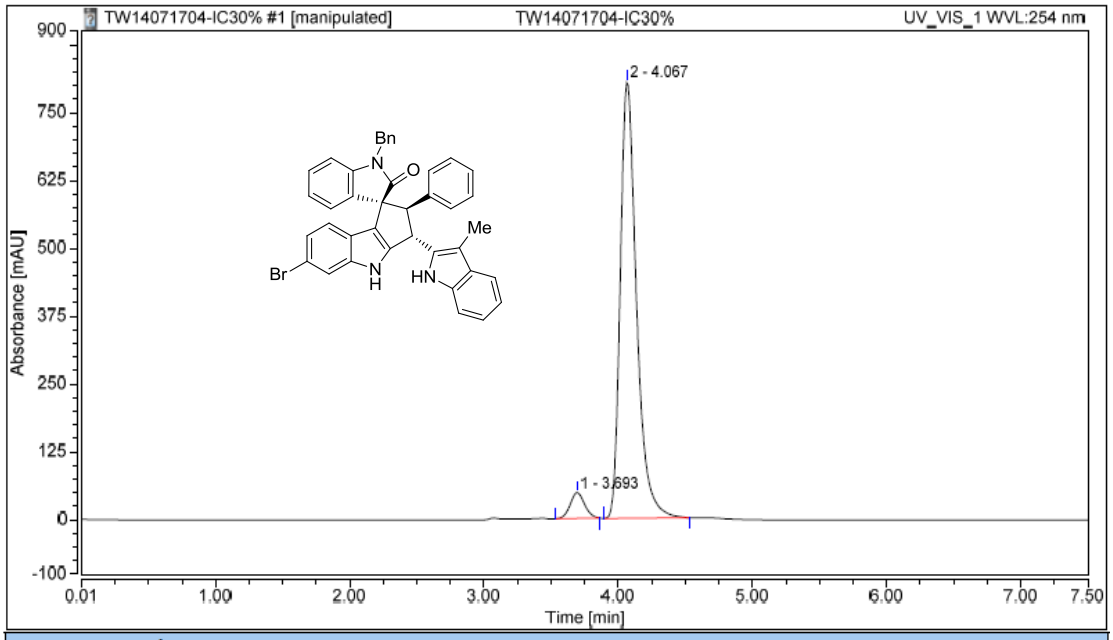


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.227	10.353	61.020	3.75	6.03	n.a.
2		5.860	265.600	950.337	96.25	93.97	n.a.
Total:			**275.953**	**1011.358**	**100.00**	**100.00**	

3ka

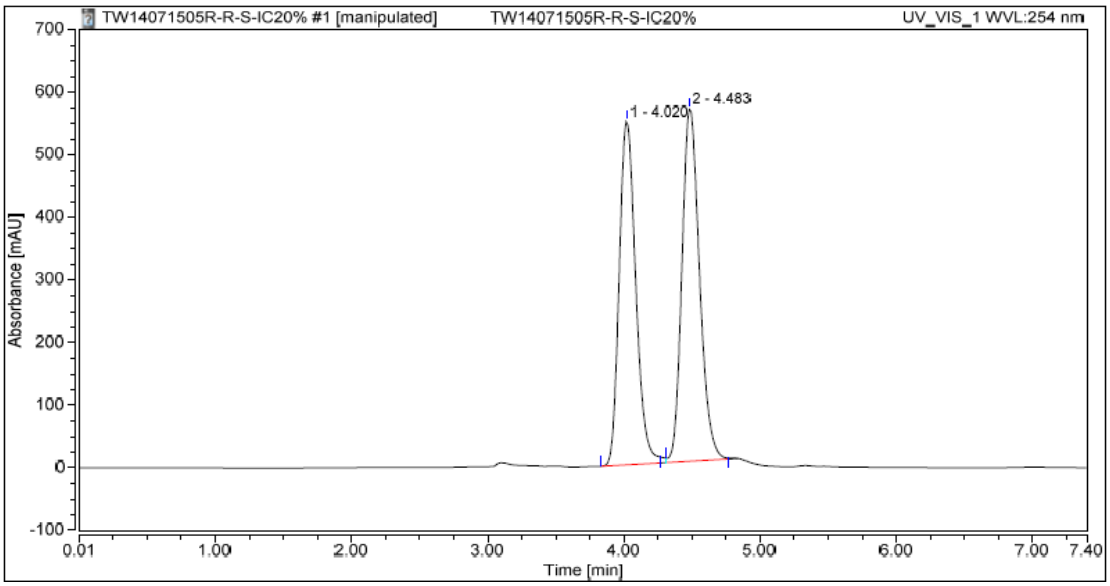


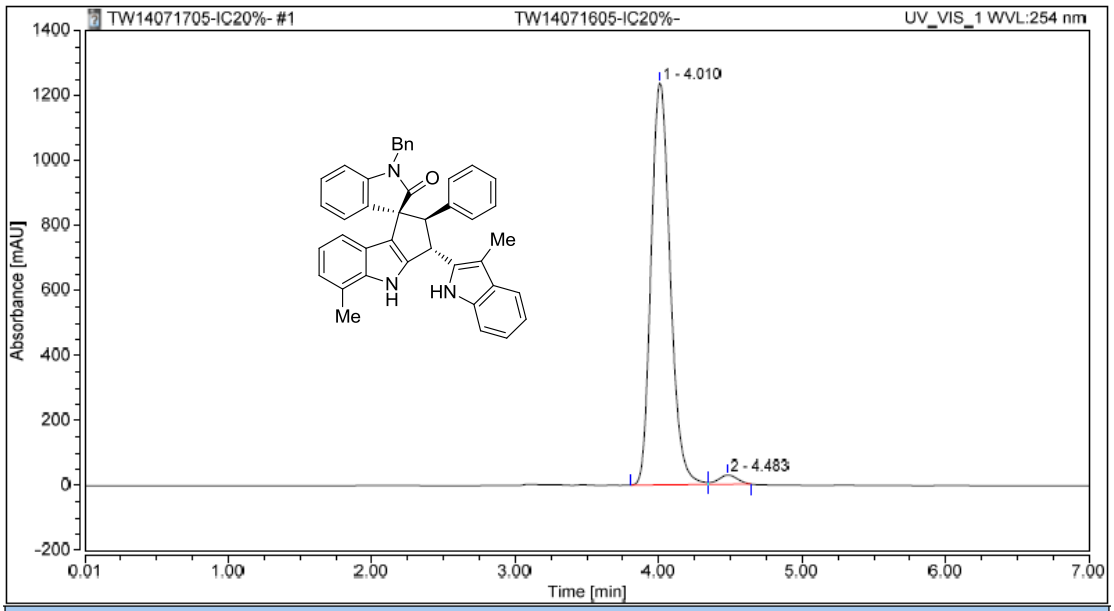


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.693	5.853	47.443	4.95	5.58	n.a.
2		4.067	112.474	803.501	95.05	94.42	n.a.
Total:			118.327	850.944	100.00	100.00	

3la

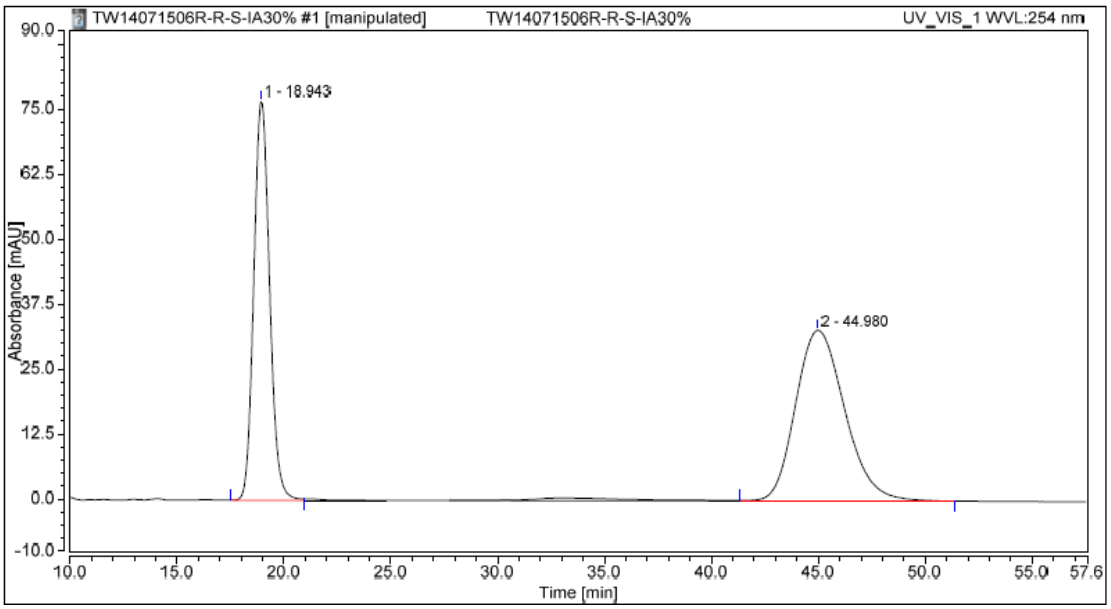


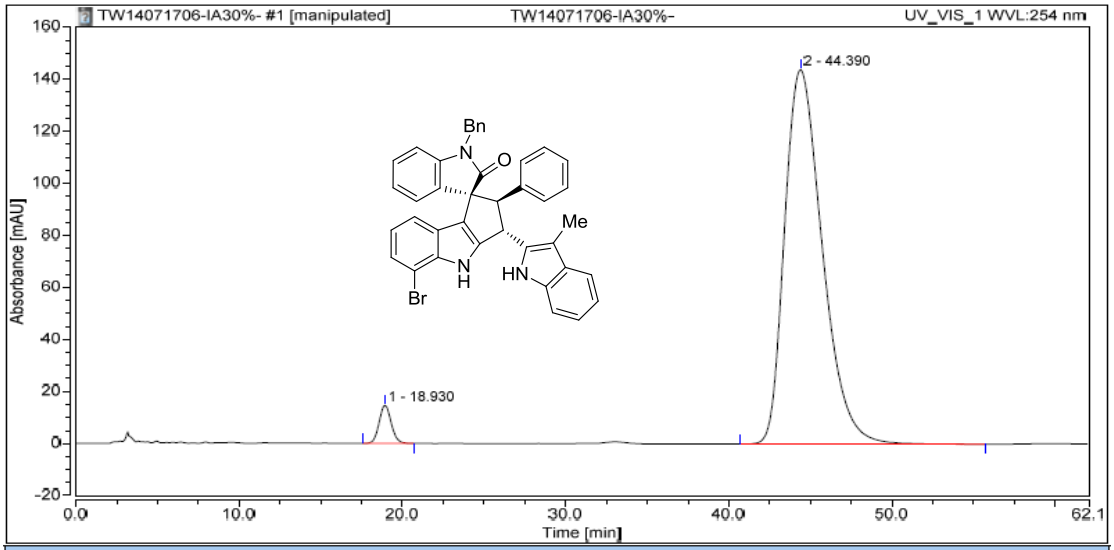


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.010	190.790	1238.389	97.74	97.74	n.a.
2		4.483	4.404	28.578	2.26	2.26	n.a.
Total:			**195.193**	**1266.967**	**100.00**	**100.00**	

3ma

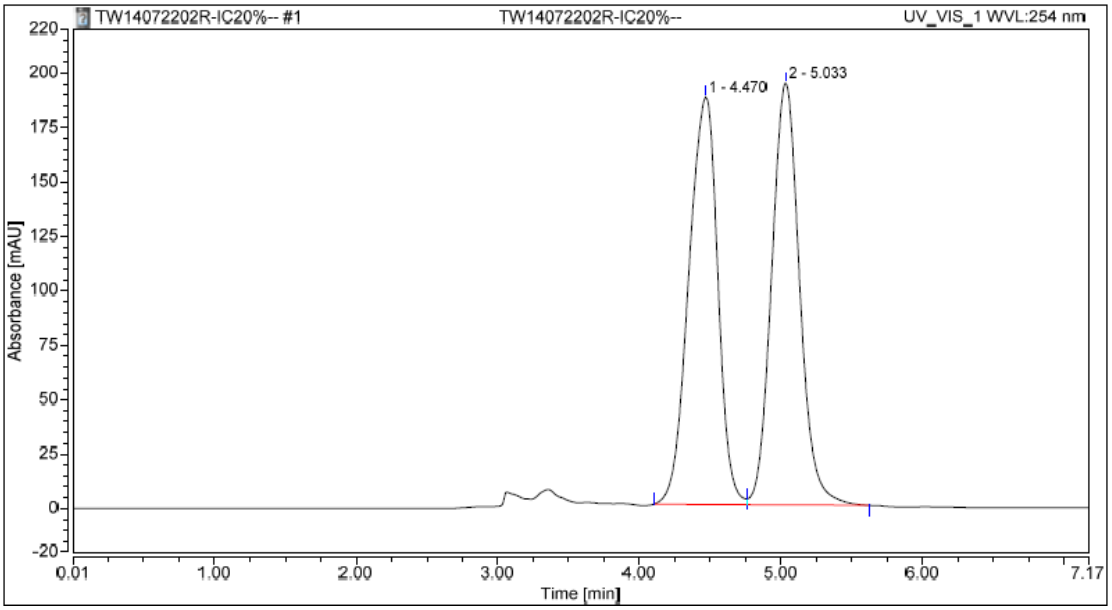


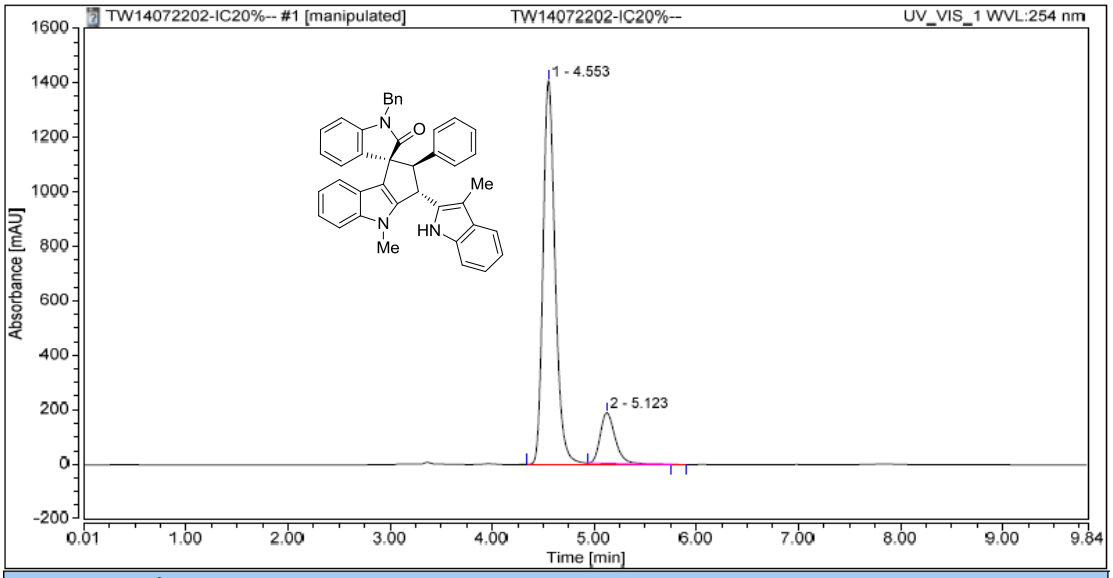


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.930	12.563	14.614	3.16	9.22	n.a.
2		44.390	384.506	143.850	96.84	90.78	n.a.
Total:			**397.069**	**158.463**	**100.00**	**100.00**	

3na

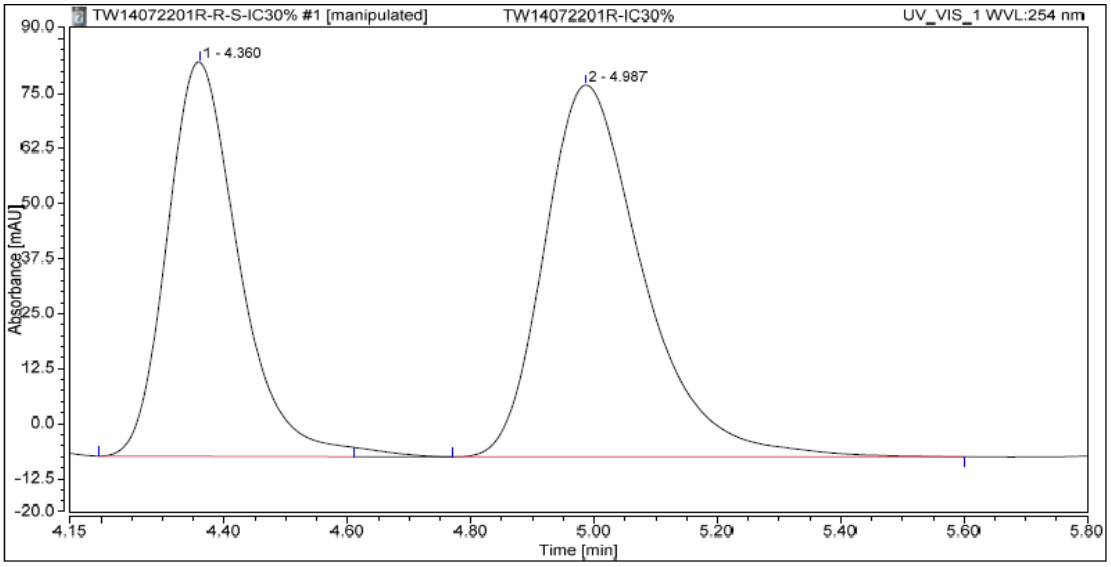


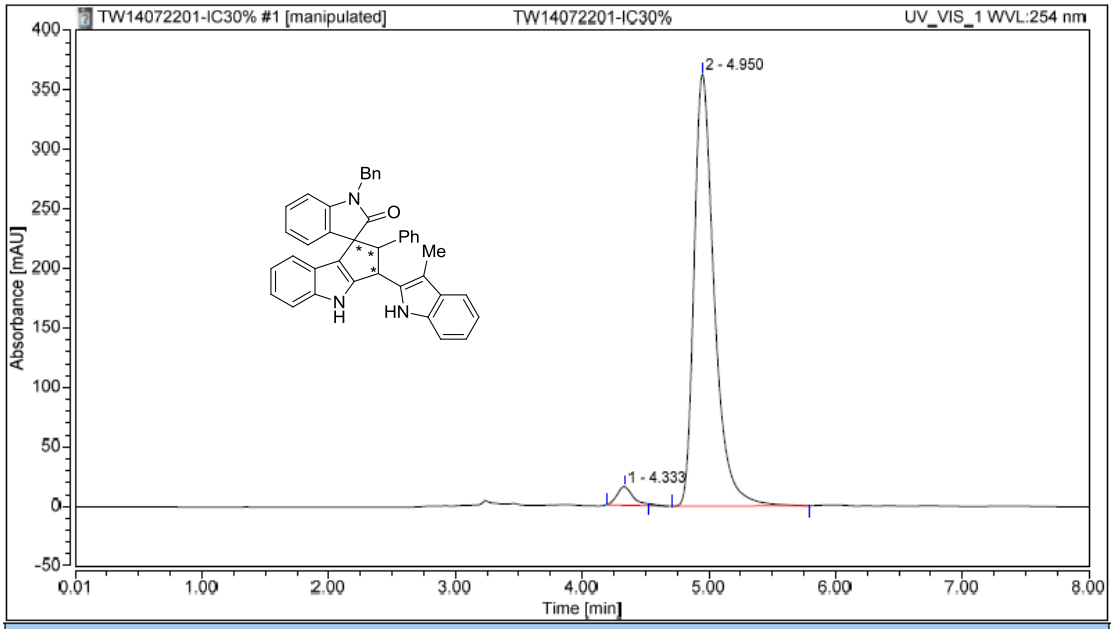


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.553	196.534	1408.765	86.29	88.31	n.a.
2		5.123	31.223	186.478	13.71	11.69	n.a.
Total:			**227.756**	**1595.243**	**100.00**	**100.00**	

3ai

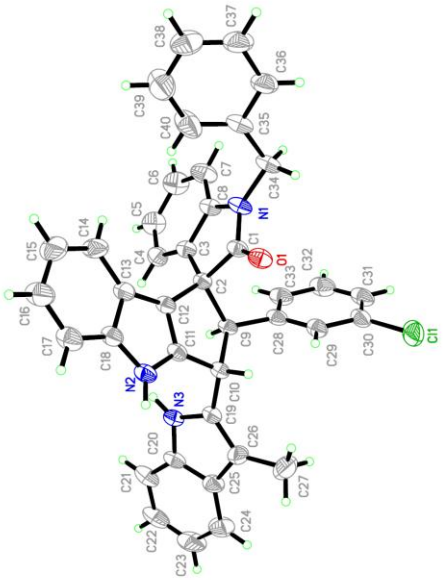


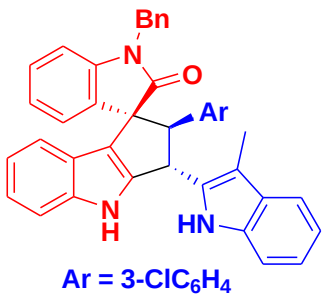


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.333	2.275	15.711	3.28	4.15	n.a.
2		4.950	66.975	362.886	96.72	95.85	n.a.
Total:			**69.250**	**378.597**	**100.00**	**100.00**	

9. X-ray single crystal data for product 3ae





Ar = 3-ClC$_6$H$_4$

(1*R*,2*R*,3*R*)-3ae

_chemical_formula_sum	'C40 H30 Cl N3 O'
_chemical_formula_weight	604.12
_symmetry_cell_setting	Orthorhombic
_symmetry_space_group_name_H-M	P2(1)2(1)2(1)
_cell_length_a	12.3755(14)
_cell_length_b	12.5125(15)
_cell_length_c	22.536(3)
_cell_angle_alpha	90.00
_cell_angle_beta	90.00
_cell_angle_gamma	90.00
_cell_volume	3489.7(7)
_cell_formula_units_Z	4
_cell_measurement_temperature	296(2)
_cell_measurement_reflns_used	9919
_cell_measurement_theta_min	2.31
_cell_measurement_theta_max	22.93
_diffrn_ambient_temperature	296(2)
_diffrn_radiation_wavelength	0.71073

_diffrn_radiation_type MoK\a

_diffrn_radiation_source 'fine-focus sealed tube'

_diffrn_radiation_monochromator graphite

_diffrn_measurement_device_type 'CCD area detector'

_diffrn_measurement_method 'phi and omega scans'

_diffrn_reflns_number 47288

_diffrn_reflns_av_R_equivalents 0.0338

_diffrn_reflns_av_sigmaI/netI 0.0296

_diffrn_reflns_theta_min 1.81

_diffrn_reflns_theta_max 27.94

_reflns_number_total 8144

_reflns_number_gt 5829

_reflns_threshold_expression >2sigma(I)

_refine_ls_abs_structure_details

'Flack H D (1983), Acta Cryst. A39, 876-881'

_refine_ls_abs_structure_Flack 0.03(8)

_chemical_absolute_configuration ad

_refine_ls_number_reflns 8144

_refine_ls_number_parameters 407

_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.0757

_refine_ls_R_factor_gt 0.0534

_refine_ls_wR_factor_ref 0.1593

_refine_ls_wR_factor_gt 0.1489

_refine_ls_goodness_of_fit_ref 1.079

_refine_ls_restrained_S_all 1.079

_refine_ls_shift/su_max 0.040

_refine_ls_shift/su_mean 0.006