Supporting Information for

Diastereo- and Enantioselective Construction of Indole-based 2,3-Dihydrobenzofuran Scaffold via Catalytic Asymmetric [3+2] Cyclizations of Quinone Monoimides with 3-Vinylindoles

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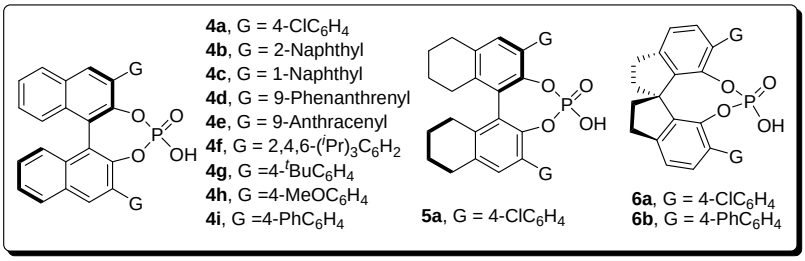
1. General information

^{1}H and ^{13}C NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy were $CDCl_3$, using tetramethylsilane as the internal reference. HRMS spectra were recorded on a LTQ-Orbitrap mass spectrometer. Enantiomeric ratios (*er*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of Enantiomeric ratios by chiral HPLC were Chiralpak IA, IC and AD-H columns. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. The X-ray source used for the single crystal X-ray diffraction analysis of compound **3da** was CuKα (λ = 1.54178), and the thermal ellipsoid was drawn at the 30% probability level. Analytical grade solvents for the column chromatography and commercially available reagents were used as received. All starting materials commercially available were used directly. Substrates **1** and **2** were synthesized according to the literature method.[1]

2. Screening of catalysts and condition optimization

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



entry	**Cat.**	solvent	T (°C)	**1a**:**2a**	additives (100mg)	yield (%)[b]	dr[c]	er[d]
1	**4a**	toluene (1ml)	25	1:1.2	-	67	>95:5	55:45
2	**4b**	toluene (1ml)	25	1:1.2	-	65	>95:5	55:45
3	**4c**	toluene (1ml)	25	1:1.2	-	60	>95:5	53:47

1. (a) D. Xia, Y. Wang, Z. Du, Q.-Y. Zheng, C. Wang, *Org. Lett.* **2012**, *14*, 588. (b) A. B. Leduc, M. A. Kerr, *Eur. J. Org. Chem.* **2007**, 237.

4	**4d**	toluene (1ml)	25	1:1.2	-	53	>95:5	55:45
5	**4e**	toluene (1ml)	25	1:1.2	-	57	>95:5	55:45
6	**4f**	toluene (1ml)	25	1:1.2	-	28	>95:5	54:46
7	**4a**	EtOAc (1mL)	25	1:1.2	-	53	>95:5	56:44
8	**4a**	CH_3CN (1mL)	25	1:1.2	-	58	>95:5	58:42
9	**4a**	1,4-dioxane (1mL)	25	1:1.2	-	56	>95:5	63:37
10	**4a**	CH_2ClCH_2Cl (1mL)	25	1:1.2	-	60	>95:5	58:42
11	**4a**	acetone (1mL)	25	1:1.2	-	44	>95:5	58:42
12	**4g**	1,4-dioxane (1mL)	25	1:1.2	-	60	>95:5	61:39
13	**4h**	1,4-dioxane (1mL)	25	1:1.2	-	79	>95:5	57:43
14	**4i**	1,4-dioxane (1mL)	25	1:1.2	-	92	>95:5	63:37
15	**5a**	1,4-dioxane (1mL)	25	1:1.2	-	74	>95:5	57:43
16	**6a**	1,4-dioxane (1mL)	25	1:1.2	-	74	>95:5	80:20
17	**6b**	1,4-dioxane (1mL)	25	1:1.2	-	72	>95:5	81:19
18	**6b**	toluene (1ml)	25	1:1.2	-	44	>95:5	59:41
19	**6b**	EtOAc (1mL)	25	1:1.2	-	77	>95:5	68:32
20	**6b**	CH_3CN (1mL)	25	1:1.2	-	99	>95:5	84:16
21	**6b**	CH_2ClCH_2Cl (1mL)	25	1:1.2	-	62	>95:5	71:29
22	**6b**	acetone (1mL)	25	1:1.2	-	99	>95:5	86:14
23	**6b**	acetone (1mL)	40	1:1.2	-	99	>95:5	85:15
24	**6b**	acetone (1mL)	0	1:1.2	-	90	>95:5	88:12
25	**6b**	acetone (1mL)	-10	1:1.2	-	94	>95:5	86:14
26	**6b**	acetone (1mL)	0	1:1.2	3 Å MS	83	>95:5	91:9
27	**6b**	acetone (1mL)	0	1:1.2	4 Å MS	84	>95:5	91:9
28	**6b**	acetone (1mL)	0	1:1.2	5 Å MS	88	>95:5	92:8
29	**6b**	acetone (1mL)	0	1:1.2	Na_2SO_4	95	>95:5	87:13
30	**6b**	acetone (1mL)	0	1:1.2	$MgSO_4$	82	>95:5	88:12
31	**6b**	acetone (2mL)	0	1:1.2	5 Å MS	89	>95:5	93:7
32	**6b**	acetone (4mL)	0	1:1.2	5 Å MS	73	>95:5	92:8
33	**6b**	acetone (2mL)	0	1:2	5 Å MS	96	>95:5	92:8
34	**6b**	acetone (2mL)	0	1:3	5 Å MS	99	>95:5	91:9
35	**6b**	acetone (2mL)	0	1.2:1	5 Å MS	99	>95:5	93:7
36	**6b**	acetone (2mL)	0	2:1	5 Å MS	96	>95:5	92:8
37	**6a**	acetone (2mL)	0	1.2:1	5 Å MS	99	>95:5	93:7

[a] Unless otherwise indicated, the reaction was carried out at the 0.05 mmol scale and catalyzed by 10 mol% **4-6** in a solvent for 15 h. [b] Isolated yield. [c] The *dr* value was determined by HPLC and ^{1}H NMR. [d] The *er* value was determined by HPLC.

3. General procedure for the synthesis of products 3

To the mixture of quinone monoimides **1** (0.06 mmol), 3-vinylindoles **2** (0.05 mmol),

catalyst **6a** (0.005 mmol) and 5 Å molecular sieves (100 mg), was added pre-cooled acetone (2 mL) at 0^{o}C. After the reaction mixture was stirred at 0^{o}C for 15 hours, the reaction mixture was filtered to remove molecular sieves and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through preparative thin layer chromatography on silica gel to afford pure products **3**.

4. Characterization data of products 3

4-methyl-N-((2*S*,3*S*)-2-(1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)benzenesulfonamide-(3aa): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 99% (24.4 mg); yellow solid; m.p. 127-129 ^{o}C; $[\alpha]_D^{20}$ = +85.0 (c 0.47, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.03 (m, 4H), 6.96 – 6.90 (m, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.69 (s, 1H), 6.38 (s, 1H), 5.75 (d, *J* = 8.3 Hz, 1H), 4.83 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 143.6, 141.8, 137.8, 135.9, 131.6, 129.5, 129.0, 128.7, 128.2, 127.6, 127.4, 127.2, 125.9, 125.7, 122.2, 122.1, 119.8, 119.7, 113.2, 109.9, 109.7, 88.9, 55.1, 32.8, 21.6; IR (KBr): 3278, 2923, 1597, 1546, 1484, 1459, 1334, 1159, 1088, 958, 810, 742 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{26}N_2O_3S\text{-}H)^-$ requires m/z 493.1580, found m/z 493.1588; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 13.85 min (major), t_R =16.91 min (minor).

N-((2*S*,3*S*)-2-(1,4-dimethyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3ba): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 93% (23.6 mg); yellow solid; m.p. 129-131 ^{o}C; $[\alpha]_D^{20}$ = +97.3 (c 0.55, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.31 – 7.28 (m, 1H), 7.28 – 7.26 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.12 (m, 4H), 7.12 – 7.08 (m, 1H), 6.91 – 6.86 (m, 2H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 1.2 Hz, 1H), 6.45 (s, 1H), 6.04 (d, *J* = 9.0 Hz, 1H), 4.74 (d, *J* =

8.9 Hz, 1H), 3.74 (d, *J* = 3.6 Hz, 3H), 2.49 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 143.5, 141.3, 137.9, 135.9, 131.8, 130.8, 129.5, 129.0, 128.7, 128.2, 127.7, 127.4, 127.3, 125.7, 125.7, 122.2, 122.1, 121.7, 113.2, 110.1, 107.3, 88.4, 55.5, 33.0, 21.60, 20.7; IR (KBr): 3279, 2962, 1889, 1461, 1335, 1310, 1235, 1159, 1088, 939, 812, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{28}N_2O_3S\text{-}H)^-$ requires m/z 507.1737, found m/z 507.1736; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 91:9, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 12.47 min (major), t_R =15.28 min (minor).

N-((2*S*,3*S*)-2-(5-methoxy-1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide (3ca): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 94% (24.7 mg); yellow solid; m.p. 59-61 ^{o}C; $[\alpha]_D^{20}$ = +79.4 (c 0.47, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.22 – 7.17 (m, 3H), 7.11 – 7.06 (m, 2H), 7.03 (s, 1H), 6.94 – 6.87 (m, 2H), 6.80 – 6.75 (m, 2H), 6.70 (d, *J* = 1.2 Hz, 1H), 6.44 (s, 1H), 5.75 (d, *J* = 8.4 Hz, 1H), 4.79 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 154.1, 143.6, 141.8, 136.0, 133.0, 131.7, 129.5, 129.0, 128.8, 128.2, 127.8, 127.4, 127.2, 126.3, 125.7, 122.0, 112.7, 112.3, 110.4, 109.9, 101.8, 88.9, 55.8, 55.1, 33.0, 21.6; IR (KBr): 3248, 2959, 2923, 2852, 1720, 1489, 1399, 1260, 1091, 1037, 965, 819 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{28}N_2O_4S\text{-}H)^-$ requires m/z 523.1686, found m/z 523.1685; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 89:11, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 26.34 min (major), t_R =42.08 min (minor).

N-((2*S*,3*S*)-2-(5-fluoro-1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3da): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 87% (22.3 mg); yellow solid; m.p. 136-138 ^{o}C; $[\alpha]_D^{20}$ = +80.4 (c 0.45, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.25 – 7.22 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.09 – 7.04 (m, 3H), 7.03 – 6.96 (m, 2H), 6.93 – 6.89 (m, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 1.2 Hz, 1H), 6.44 (s, 1H), 5.69 (d, *J* = 8.4 Hz, 1H), 4.77 (d, *J* = 8.4 Hz, 1H), 3.74 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 157.8 (*J* = 233.9 Hz), 143.6, 141.6, 135.8, 134.4, 131.4, 129.5, 129.2, 129.1, 128.8, 128.1, 127.4, 127.3, 126.1 (*J* = 9.9 Hz), 125.8, 122.1, 113.2, 113.1, 110.7 (*J* = 26.3 Hz), 110.4 (*J* = 9.8 Hz), 109.9,

104.8 (J = 23.8 Hz), 88.6, 55.1, 33.1, 21.6; IR (KBr): 3255, 2924, 1660, 1595, 1487, 1407, 1260, 1151, 1089, 946, 804, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{25}FN_2O_3S\text{-}H)^-$ requires m/z 511.1486, found m/z 511.1486; Diastereomeric ratio: >95:5, determined by ^1H NMR; Enantiomeric ratio: 91:9, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 14.35 min (major), t_R =16.24 min (minor).

N-((2*S*,3*S*)-2-(5-chloro-1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3ea): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 85% (22.4 mg); yellow solid; m.p. 142-144 ^oC; $[\alpha]_D^{20}$ = +87.8 (c 0.54, Acetone); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 1.8 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.23 (t, J = 5.2 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.08 – 7.02 (m, 3H), 6.94 – 6.89 (m, 1H), 6.78 (d, J = 8.5 Hz, 1H), 6.71 (s, 1H), 6.46 (d, J = 11.7 Hz, 1H), 5.68 (d, J = 8.8 Hz, 1H), 4.78 (d, J = 8.8 Hz, 1H), 3.73 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.6, 141.3, 136.1, 135.8, 131.4, 129.5, 129.2, 128.8, 128.8, 128.2, 127.4, 127.4, 126.9, 125.7, 125.6, 122.6, 122.1, 119.3, 112.7, 110.8, 110.0, 88.5, 55.2, 33.1, 21.6; IR (KBr): 3275, 2923, 1597, 1489, 1388, 1258, 1158, 1018, 966, 807, 794, 695 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{25}ClN_2O_3S\text{-}H)^-$ requires m/z 527.1191, found m/z 527.1185; Diastereomeric ratio: >95:5, determined by ^1H NMR; Enantiomeric ratio: 92:8, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 14.95 min (major), t_R =17.00 min (minor).

N-((2*S*,3*S*)-2-(5-bromo-1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3fa): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 87% (24.9 mg); yellow solid; m.p. 146-148 ^oC; $[\alpha]_D^{20}$ = +83.3 (c 0.60, Acetone); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 1.4 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.19 (t, J = 9.1 Hz, 3H), 7.10 – 7.04 (m, 2H), 7.03 (s, 1H), 6.94 – 6.88 (m, 1H), 6.78 (d, J = 8.5 Hz, 1H), 6.71 (s, 1H), 6.45 (s, 1H), 5.68 (d, J = 8.9 Hz, 1H), 4.77 (d, J = 8.9 Hz, 1H), 3.72 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.6, 141.2, 136.4, 135.9, 131.4, 129.5, 129.2, 128.8, 128.6, 128.2, 127.6, 127.4, 125.7, 125.2, 122.30, 122.1, 113.2, 112.6, 111.2, 110.0, 88.5, 55.2, 33.0, 21.6; IR (KBr): 3272, 2923, 1597, 1489, 1388, 1322, 1258, 1158, 1088, 965, 793, 695 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{25}BrN_2O_3S\text{-}H)^-$ requires m/z 571.0686, found m/z 571.0687; Diastereomeric ratio: >95:5, determined by ^1H NMR; Enantiomeric ratio:

92:8, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 15.49 min (major), t_R =17.40 min (minor).

N-((2*S*,3*S*)-2-(1,6-dimethyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methyl benzenesulfonamide-(3ga): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 84% (21.3 mg); yellow solid; m.p. 92-94 ^{o}C; $[\alpha]_D^{20}$ = +88.6 (c 0.27, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 7.08 – 7.03 (m, 2H), 6.97 (s, 1H), 6.95 – 6.91 (m, 1H), 6.91 – 6.87 (m, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 1.2 Hz, 1H), 6.43 (s, 1H), 5.72 (d, *J* = 8.3 Hz, 1H), 4.82 (d, *J* = 8.3 Hz, 1H), 3.71 (s, 3H), 2.49 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 143.5, 141.8, 138.2, 135.9, 132.1, 131.6, 129.5, 128.9, 128.7, 128.1, 127.4, 127.2, 127.1, 125.8, 123.7, 122.1, 121.4, 119.4, 113.0, 109.9, 109.6, 88.9, 55.1, 32.7, 21.9, 21.6; IR (KBr): 3254, 2923, 1598, 1559, 1483, 1330, 1261, 1161, 1090, 909, 800, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{28}N_2O_3S\text{-}H)^-$ requires m/z 507.1737, found m/z 507.1737; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 92:8, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 12.14 min (minor), t_R =13.89 min (major).

N-((2*S*,3*S*)-2-(6-fluoro-1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-m ethylbenzenesulfonamide-(3ha): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 90% (23.1 mg); yellow solid; m.p. 147-149 ^{o}C; $[\alpha]_D^{20}$ = +88.0 (c 0.56, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 1.7 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 2H), 7.25 (d, *J* = 5.2 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.04 (m, 2H), 7.02 (s, 1H), 7.01 – 6.97 (m, 1H), 6.95 – 6.90 (m, 1H), 6.84 – 6.79 (m, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.71 (d, *J* = 1.2 Hz, 1H), 6.47 (s, 1H), 5.71 (d, *J* = 8.5 Hz, 1H), 4.77 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (*J* = 237.3 Hz), 158.3, 143.6, 141.5, 137.9 (*J* = 11.9 Hz), 135.9, 131.5, 129.5, 129.2, 128.8, 128.2, 127.8 (*J* = 3.3 Hz), 127.4, 127.3, 125.7, 122.4, 122.0, 120.6 (*J* = 10.1 Hz), 113.5, 110.0, 108.4 (*J* = 24.4 Hz), 96.1 (*J* = 26.0 Hz), 88.6, 55.2, 33.0, 21.6; IR (KBr): 3238, 2924, 1597,1562, 1482, 1397, 1324, 1261, 1154, 1091, 799, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{25}FN_2O_3S\text{-}H)^-$ requires m/z 511. 1486, found m/z 511.1487; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 94:6, determined by

HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 16.77 min (minor), t_R =18.03 min (major).

N-((2*S*,3*S*)-2-(6-chloro-1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3ia): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 80% (21.2 mg); yellowish solid; m.p. 76-78 ^{o}C; $[\alpha]_D^{20}$ = +75.2 (c 0.47, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.28 (d, *J* = 2.1 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.07 – 7.02 (m, 3H), 7.02 – 6.98 (m, 1H), 6.94 – 6.89 (m, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.70 (d, *J* = 1.1 Hz, 1H), 6.40 (s, 1H), 5.70 (d, *J* = 8.5 Hz, 1H), 4.75 (d, *J* = 8.5 Hz, 1H), 3.71 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.6, 141.4, 138.1, 135.9, 131.4, 129.5, 129.2, 128.8, 128.4, 128.1, 128.1, 127.4, 127.3, 125.7, 124.4, 121.9, 120.7, 120.4, 113.5, 109.9, 109.7, 88.5, 55.3, 32.9, 21.6; IR (KBr): 3269, 2962, 1597, 1481, 1389, 1326, 1261, 1159, 1088, 959, 800, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{25}ClN_2O_3S\text{-}H)^-$ requires m/z 527.1191, found m/z 527.1184; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 15.45 min (minor), t_R =17.55 min (major).

N-((2*S*,3*S*)-2-(1,7-dimethyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3ja): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 95% (24.2 mg); yellow solid; m.p. 91-93 ^{o}C; $[\alpha]_D^{20}$ = +79.6 (c 0.62, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.22 – 7.16 (m, 3H), 7.09 – 7.03 (m, 2H), 6.92 (d, *J* = 5.2 Hz, 3H), 6.90 (d, *J* = 7.1 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 1.2 Hz, 1H), 6.43 (d, *J* = 3.7 Hz, 1H), 5.73 (d, *J* = 8.3 Hz, 1H), 4.80 (d, *J* = 8.3 Hz, 1H), 4.00 (s, 3H), 2.75 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 143.5, 141.9, 136.5, 135.9, 131.6, 129.5, 129.2, 129.0, 128.7, 128.2, 127.4, 127.2, 127.1, 125.7, 124.9, 122.1, 121.7, 120.0, 117.8, 112.8, 109.9, 88.8, 55.0, 36.9, 21.6, 19.7; IR (KBr): 3277, 2924, 1598, 1483, 1459, 1389, 1317, 1261, 1160, 1089, 810, 703 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{28}N_2O_3S\text{-}H)^-$ requires m/z 507.1737, found m/z 507.1736; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 91:9, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 13.83 min (major), t_R =20.80 min (minor).

N-((2*S*,3*S*)-2-(7-chloro-1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3ka): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 90% (23.8 mg); yellow solid; m.p. 93-95 ^{o}C; $[\alpha]_D^{20}$ = +55.4 (c 0.54, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 6.3 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.25 – 7.22 (m, 1H), 7.22 – 7.14 (m, 3H), 7.09 – 7.02 (m, 2H), 6.99 (d, *J* = 1.8 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.81 – 6.75 (m, 1H), 6.69 (s, 1H), 6.35 (s, 1H), 5.75 – 5.67 (m, 1H), 4.76 (d, *J* = 8.4 Hz, 1H), 4.10 (d, *J* = 2.3 Hz, 3H), 2.40 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.6, 141.4, 135.9, 133.0, 131.4, 130.1, 129.5, 129.2, 129.1, 128.8, 128.2, 127.4, 127.3, 125.7, 123.8, 122.0, 120.5, 118.5, 117.4, 113.3, 110.0, 88.4, 55.2, 36.8, 21.6; IR (KBr): 3293, 2918, 1879, 1488, 1412, 1324, 1257, 1161, 1083, 909, 810, 707 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{25}ClN_2O_3S\text{-}H)^-$ requires m/z 527.1191, found m/z 527.1194; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 11.88 min (major), t_R =16.23 min (minor).

4-methyl-N-((2*S*,3*S*)-2-(1-methyl-1H-indol-3-yl)-3-(o-tolyl)-2,3-dihydrobenzofuran-5-yl)benzenesulfonamide-(3la): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 80% (20.4 mg); yellow solid; m.p. 71-73 ^{o}C; $[\alpha]_D^{20}$ = +131.4 (c 0.24, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.27 – 7.22 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.12 (m, 2H), 7.12 – 7.08 (m, 1H), 7.08 – 7.04 (m, 1H), 7.03 (s, 1H), 6.97 – 6.90 (m, 2H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 1.2 Hz, 1H), 6.42 (s, 1H), 5.75 (d, *J* = 7.9 Hz, 1H), 5.15 (d, *J* = 7.9 Hz, 1H), 3.74 (s, 3H), 2.40 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 143.6, 140.4, 137.7, 136.6, 135.8, 132.0, 130.5, 129.5, 129.0, 128.1, 127.7, 127.4, 127.0, 126.5, 125.8, 125.6, 122.2, 121.8, 119.7, 119.7, 113.7, 109.9, 109.7, 88.5, 51.4, 32.8, 21.6, 19.8; IR (KBr): 3243, 2925, 2854, 1546, 1469, 1396, 1319, 1161, 1090, 1019, 817, 741 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{28}N_2O_3S\text{-}H)^-$ requires m/z 507.1737, found m/z 507.1737; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 16.63 min (major), t_R =30.31 min (minor).

N-((2*S*,3*S*)-3-(3-bromophenyl)-2-(1-methyl-1H-indol-3-yl)-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3ma): Preparative thin layer chromatography: pure

dichloromethane; Reaction time = 15 h; yield: 63% (18.1 mg); yellow solid; m.p. 71-73 ^{o}C; $[\alpha]_D^{20}$ = +77.4 (c 0.36, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.28 (s, 1H), 7.25 (d, *J* = 1.7 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.04 (s, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.93 – 6.88 (m, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.74 (s, 1H), 6.40 (s, 1H), 5.73 (d, *J* = 8.1 Hz, 1H), 4.79 (d, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 144.3, 143.7, 137.8, 135.9, 131.0, 130.9, 130.4, 130.3, 129.5, 129.2, 127.7, 127.4, 126.9, 125.9, 125.7, 122.9, 122.3, 121.8, 119.8, 119.6, 112.8, 110.1, 109.8, 88.6, 54.9, 32.9, 21.6; IR (KBr): 3252, 2923, 1593, 1485, 1379, 1330, 1260, 1159, 1090, 898, 811, 740 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{25}BrN_2O_3S\text{-}H)^-$ requires m/z 571.0686, found m/z 571.0686; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 90:10, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 14.45 min (minor), t_R =23.36 min (major).

N-((2*S*,3*S*)-3-(4-(tert-butyl)phenyl)-2-(1-methyl-1H-indol-3-yl)-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3na): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 73% (20.1 mg); yellow solid; m.p. 90-92 ^{o}C; $[\alpha]_D^{20}$ = +45.3 (c 0.54, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.91 – 6.86 (m, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 1.2 Hz, 1H), 6.28 (d, *J* = 5.2 Hz, 1H), 5.72 (d, *J* = 8.3 Hz, 1H), 4.79 (d, *J* = 8.3 Hz, 1H), 3.74 (s, 3H), 2.39 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 150.0, 143.5, 138.6, 137.8, 136.0, 131.7, 129.5, 128.9, 127.7, 127.6, 127.4, 126.0, 125.7, 125.6, 122.2, 122.2, 119.8, 119.6, 113.3, 109.9, 109.6, 88.8, 54.5, 34.5, 32.8, 31.4, 21.6; IR (KBr): 3256, 2960, 1598, 1484, 1394, 1331, 1261, 1161, 1090, 1017, 811, 740, 705 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{34}N_2O_3S\text{-}H)^-$ requires m/z 549.2206, found m/z 549.2206; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 90:10, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 12.86 min (minor), t_R =19.35 min (major).

N-((2*S*,3*S*)-3-(4-bromophenyl)-2-(1-methyl-1H-indol-3-yl)-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3oa): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 83% (23.8 mg); yellow solid; m.p. 115-117 ^{o}C; $[\alpha]_D^{20}$ = +76.3 (c 0.55,

Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 5.4 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.29 – 7.23 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.09 – 7.05 (m, 1H), 7.03 (s, 1H), 6.96 – 6.89 (m, 3H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.67 (s, 1H), 6.56 – 6.48 (m, 1H), 5.68 (d, *J* = 8.4 Hz, 1H), 4.80 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 143.7, 140.8, 137.8, 135.9, 131.9, 131.0, 129.9, 129.5, 129.2, 127.7, 127.4, 126.0, 125.8, 122.3, 121.9, 121.2, 119.8, 119.7, 112.7, 110.1, 109.8, 88.7, 54.7, 32.9, 21.6; IR (KBr): 3278, 2922, 1546, 1486, 1391, 1317, 1233, 1160, 1012, 813, 735, 688 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{25}BrN_2O_3S\text{-}H)^-$ requires m/z 571.0686, found m/z 571.0689; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 92:8, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 14.58 min (major), t_R =20.34 min (minor).

N-((2*S*,3*S*)-2-(1H-indol-3-yl)-3-methyl-2,3-dihydrobenzofuran-5-yl)-4-methylbenzenesulfonamide-(3pa): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 48% (10.1 mg); yellow oil; $[\alpha]_D^{20}$ = +46.5 (c 0.21, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.19 (m, 4H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.95 (s, 1H), 6.74 – 6.70 (m, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.47 (s, 1H), 5.45 (d, *J* = 8.9 Hz, 1H), 3.78 – 3.68 (m, 1H), 2.40 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 143.7, 136.9, 136.1, 133.6, 129.5, 128.7, 127.4, 125.7, 125.0, 122.8, 122.7, 121.2, 120.1, 119.7, 114.9, 111.5, 109.6, 100.0, 98.2, 87.9, 42.7, 21.6, 18.2; IR (KBr): 3406, 3265, 2960, 2924, 2850, 1707, 1483, 1333, 1901,1021, 813, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{22}N_2O_3S\text{-}H)^-$ requires m/z 417.1267, found m/z 417.1267; Diastereomeric ratio: 93:7, determined by ^{1}H NMR; Enantiomeric ratio: 82:18, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 12.95 min (major), t_R =15.81 min (minor).

4-(tert-butyl)-N-((2*S*,3*S*)-2-(1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl) benzenesulfonamide-(3ab): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 91% (24.4 mg); yellow solid; m.p. 160-162 ^{o}C; $[\alpha]_D^{20}$ = +145.0 (c 0.33, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.43 – 7.37 (m, 3H), 7.35 – 7.29 (m, 2H), 7.28 (t, *J* = 1.9 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.12 – 7.08 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.94 – 6.88 (m, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.76 (s, 1H), 6.43 (s, 1H), 5.77 (d, *J* = 8.4

Hz, 1H), 4.84 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 1.30 (d, *J* = 9.9 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 156.6, 141.8, 137.8, 136.1, 131.6, 129.1, 128.8, 128.2, 127.6, 127.3, 127.2, 125.9, 125.8, 125.5, 122.2, 121.9, 119.8, 119.7, 113.1, 109.9, 109.7, 88.9, 55.2, 35.1, 32.8, 31.1; IR (KBr): 3238, 2958, 1589, 1483, 1394, 1328, 1237, 1162, 1110, 965, 740, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{32}N_2O_3S\text{-}H)^-$ requires m/z 535.2050, found m/z 535.2050; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 92:8, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 14.14 min (minor), t_R =18.44 min (major).

4-methoxy-N-((2*S*,3*S*)-2-(1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)benzenesulfonamide-(3ac): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 98% (25.1 mg); yellow solid; m.p. 161-163 ^{o}C; $[\alpha]_D^{20}$ = +70.1 (c 0.54, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.26 – 7.22 (m, 1H), 7.09 – 7.03 (m, 4H), 6.97 – 6.92 (m, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 1.2 Hz, 1H), 6.35 (d, *J* = 5.9 Hz, 1H), 5.74 (d, *J* = 8.4 Hz, 1H), 4.83 (d, *J* = 8.4 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 158.5, 141.7, 137.8, 131.6, 130.4, 129.6, 129.1, 128.7, 128.2, 127.6, 127.2, 125.9, 125.8, 122.2, 122.0, 119.8, 119.7, 114.0, 113.1, 110.0, 109.7, 88.9, 55.6, 55.1, 32.8; IR (KBr): 3272, 2921, 1597, 1544, 1485, 1459, 1389, 1264, 1160, 1022, 828, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{26}N_2O_4S\text{-}H)^-$ requires m/z 509.1530, found m/z 509.1533; Diastereomeric ratio: >95:5, determined by ^{1}H NMR; Enantiomeric ratio: 88:12, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 21.32 min (minor), t_R =29.22 min (major).

2-methyl-N-((2*S*,3*S*)-2-(1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)benzenesulfonamide-(3ad): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 97% (24.1 mg); yellow solid; m.p. 58-60 ^{o}C; $[\alpha]_D^{20}$ = +73.5 (c 0.20, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 1H), 7.44 – 7.39 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.26 (m, 3H), 7.26 – 7.22 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.08 – 7.05 (m, 1H), 7.05 – 7.01 (m, 3H), 6.92 – 6.86 (m, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.67 (s, 1H), 6.45 (s, 1H), 5.73 (d, *J* = 8.4 Hz, 1H), 4.82 (d, *J* = 8.4 Hz, 1H), 3.74 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 141.7, 137.8, 137.2, 137.1, 132.9, 132.4, 131.6, 130.2, 128.8,

128.7, 128.1, 127.6, 127.2, 126.2, 125.9, 125.4, 122.2, 121.8, 119.8, 119.7, 113.1, 109.9, 109.7, 55.1, 32.8, 20.6; IR (KBr): 3273, 2924, 2854, 1601, 1555, 1466, 1377, 1261, 1159, 1064, 804, 741 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{26}N_2O_3S\text{-}H)^-$ requires m/z 493.1580, found m/z 493.1580; Diastereomeric ratio: >95:5, determined by ^1H NMR; Enantiomeric ratio: 87:13, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 12.73 min (minor), t_R =23.00 min (major).

N-((2*S*,3*S*)-2-(1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofuran-5-yl)benzenesulfonamide-(3ae): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 98% (23.6 mg); yellow solid; m.p. 121-123 ^oC; $[\alpha]_D^{20}$ = +173.9 (c 0.22, Acetone); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.26 – 7.22 (m, 1H), 7.10 – 7.06 (m, 1H), 7.06 – 7.02 (m, 3H), 6.97 – 6.92 (m, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 1.2 Hz, 1H), 6.42 (s, 1H), 5.75 (d, *J* = 8.4 Hz, 1H), 4.83 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 141.7, 138.8, 137.8, 132.8, 131.6, 128.9, 128.8, 128.8, 128.1, 127.6, 127.4, 127.3, 125.9, 125.9, 122.2, 122.1, 119.8, 119.7, 113.1, 110.0, 109.7, 88.9, 55.1, 32.8; IR (KBr): 3235, 2923, 1601, 1547, 1465, 1330, 1261, 1157, 1090, 896, 820, 741 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{24}N_2O_3S\text{-}H)^-$ requires m/z 479.1424, found m/z 479.1429; Diastereomeric ratio: >95:5, determined by ^1H NMR; Enantiomeric ratio: 90:10, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 19.86 min (major), t_R =25.47 min (minor).

5. Synthetic procedure and characterization data of compound 7

Under argon atmosphere, to the mixture of compound **3fa** (0.05 mmol), 4-chlorophenylboronic acid (0.12 mmol) and $Pd(PPh_3)_4$ (0.005 mmol), was added degassed K_2CO_3 aqueous solution (1 M, 0.33 mL) and degassed THF (1 mL). After being stirred at 65^oC for 13 h, the reaction mixture was extinguished by saturated aqueous solution of ammonia chloride, which was extracted by ethyl acetate for three times. The combined organic layer was concentrated under the reduced pressure to give the residue, which was subjected to flash column chromatography to give pure product **7**.

N-((2*S*,3*S*)-2-(5-(4-chlorophenyl)-1-methyl-1H-indol-3-yl)-3-phenyl-2,3-dihydrobenzofura

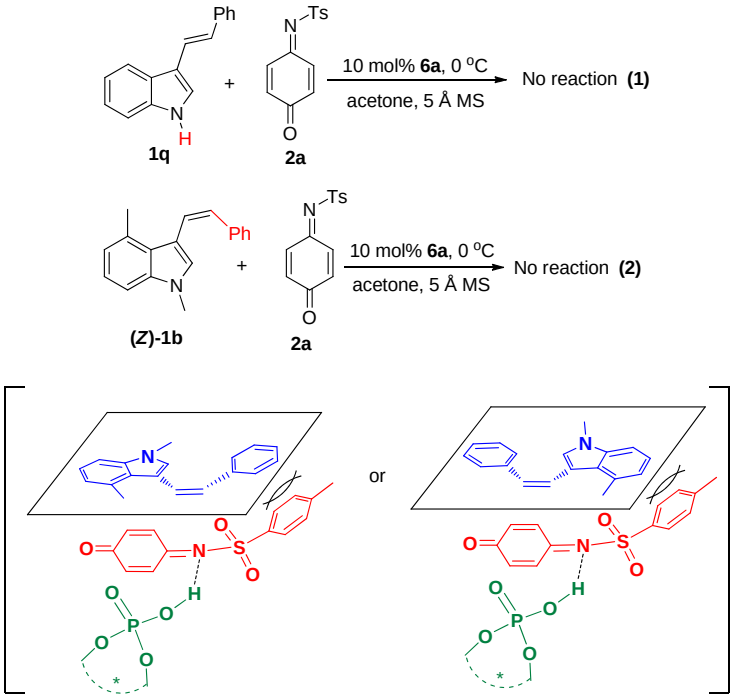
n-5-yl)-4-methylbenzenesulfonamide (7): Preparative thin layer chromatography: pure dichloromethane; Reaction time = 15 h; yield: 67% (20.4 mg); yellow solid; m.p. 124-126 ^{o}C; $[\alpha]_D^{20}$ = -27.8 (c 0.17, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.48 (s, 1H), 7.43 (t, *J* = 8.5 Hz, 3H), 7.36 (t, *J* = 8.2 Hz, 3H), 7.32 – 7.27 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.1 Hz, 3H), 6.92 (d, *J* = 7.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.68 (s, 1H), 6.28 (s, 1H), 5.81 (d, *J* = 8.7 Hz, 1H), 4.81 (d, *J* = 8.6 Hz, 1H), 3.78 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 143.6, 141.5, 140.7, 137.3, 135.9, 132.4, 131.9, 131.7, 129.5, 129.1, 128.8, 128.7, 128.5, 128.3, 128.1, 127.4, 127.3, 126.5, 125.8, 122.1, 121.8, 118.1, 113.7, 110.0, 110.0, 88.7, 55.4, 33.0, 21.6; IR (KBr): 3278, 2969, 2924, 2853, 1710, 1479, 1261, 1162, 1091, 1021, 810, 701 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{29}ClN_2O_3S\text{-}H)^-$ requires m/z 603.1503, found m/z 603.1503; Enantiomeric ratio: 92:8, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 36.66 min (major), t_R =46.45 min (minor).

6. Control experiments and a preliminary derivation

In order to further investigate the reactivity of different types of 3-vinylindoles, we performed some control experiments under the standard conditions (Scheme 1). Firstly, when 3-vinylindole **1q** with a free N-H group was employed to the reaction, no reaction occurred (eq. 1). This phenomenon is very interesting because previous reports on CPA-catalyzed reaction always found that such an N-H group in indole moiety was essential or favourable for both the reactivity and the enantioselectivity by generating a hydrogen bond with CPA. So, this result indicated that an ion pair interaction between the *N*-substituted indole imine cation with the CPA anion was beneficial to the designed [3+2] cyclization. Secondly, 3-vinylindole (*Z*)-**1b** was utilized to the reaction but it failed to participate in the reaction (eq. 2). This outcome implied that the *Z*/*E* configuration of 3-vinylindoles played a crucial role in the reactivity, and the poor reactivity of (*Z*)-isomer might be ascribed to the steric repulsion between the two reaction components.

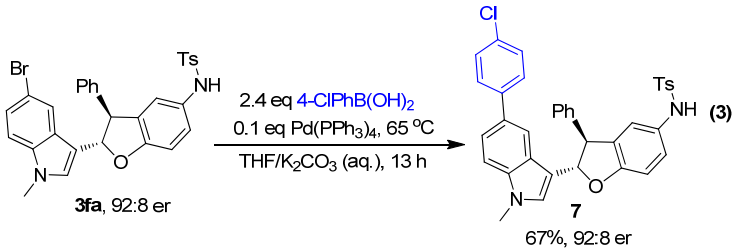
In the suggested transition state involving (*Z*)-vinylindole **1b**, the indole moiety or the phenyl group in the structure of (*Z*)-**1b** had a high possibility to be overlapped with the benzenesulfonyl group of substrate **2a**. This overlapped orientation might result in a steric repulsion between the

two reaction components, thus leading to the observed poor reactivity of (*Z*)-**1b**.



Scheme 1. Control experiments

Besides, a preliminary derivation of product **3fa** was carried out by Suzuki coupling with 4-chlorophenylboronic acid to generate compound **7** with maintained enantioselectivity of 92:8 er (eq. 3).



7. NMR spectra of products 3 and compound 7

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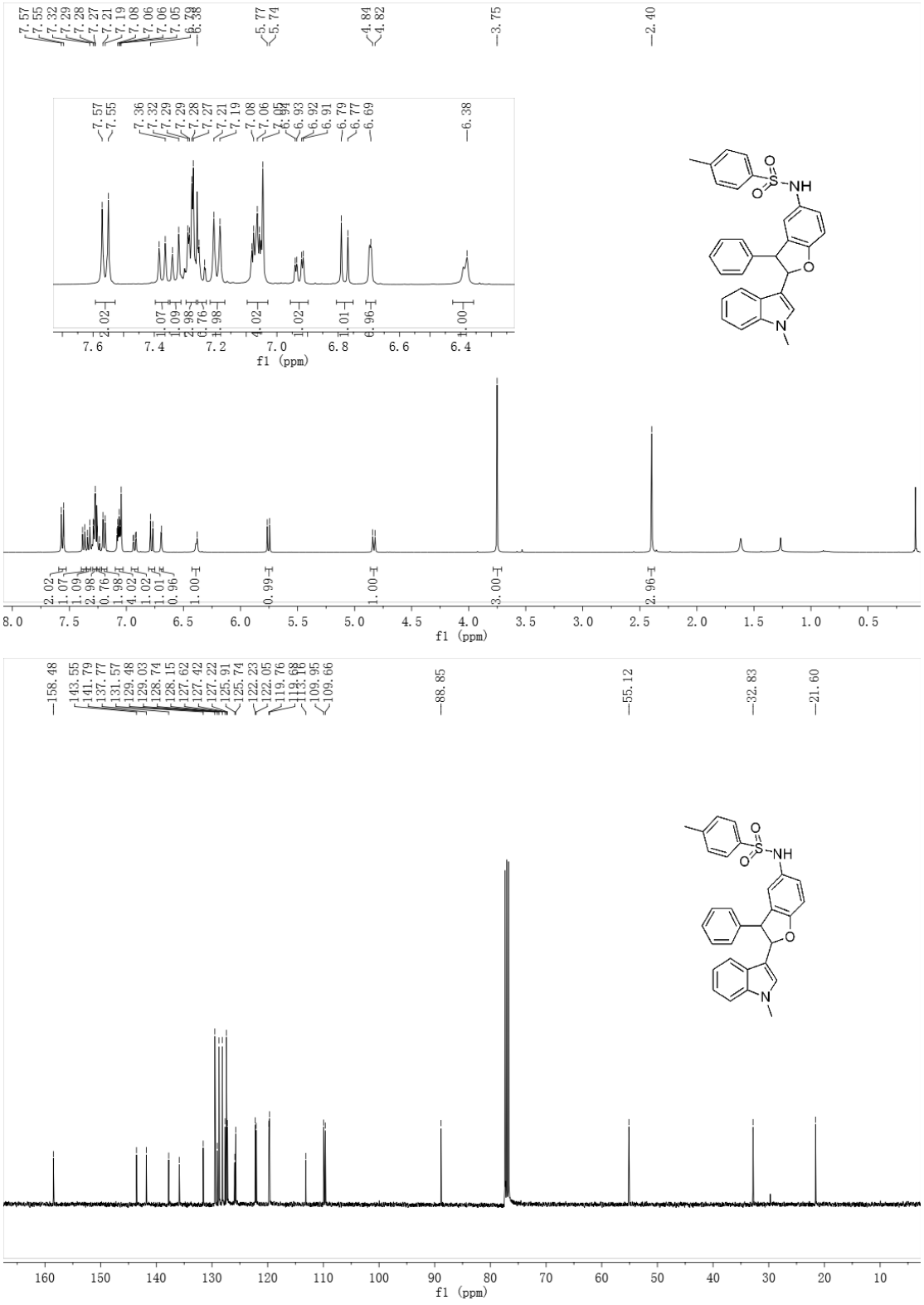

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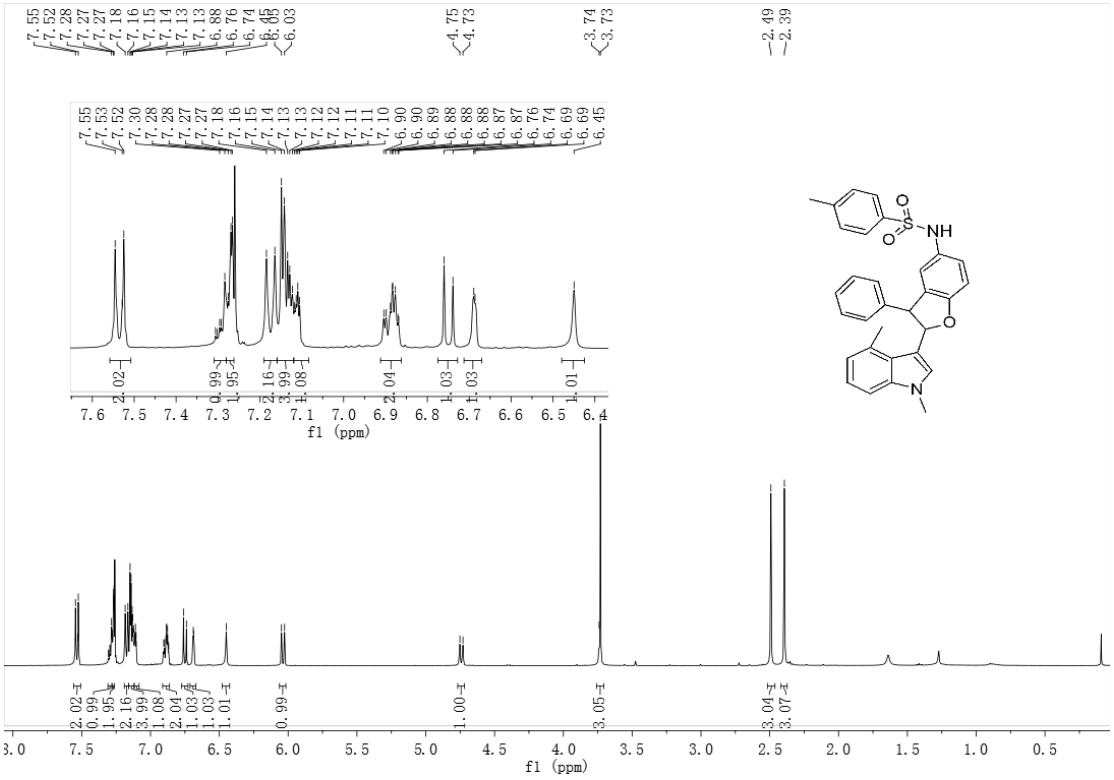

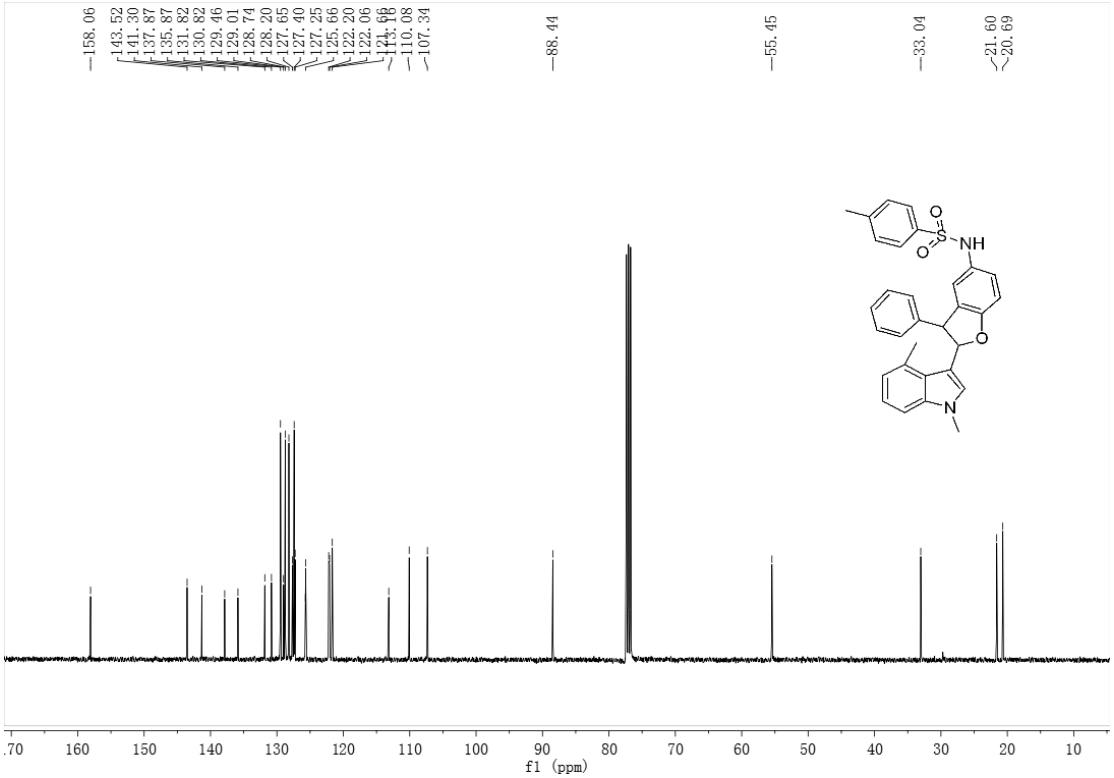

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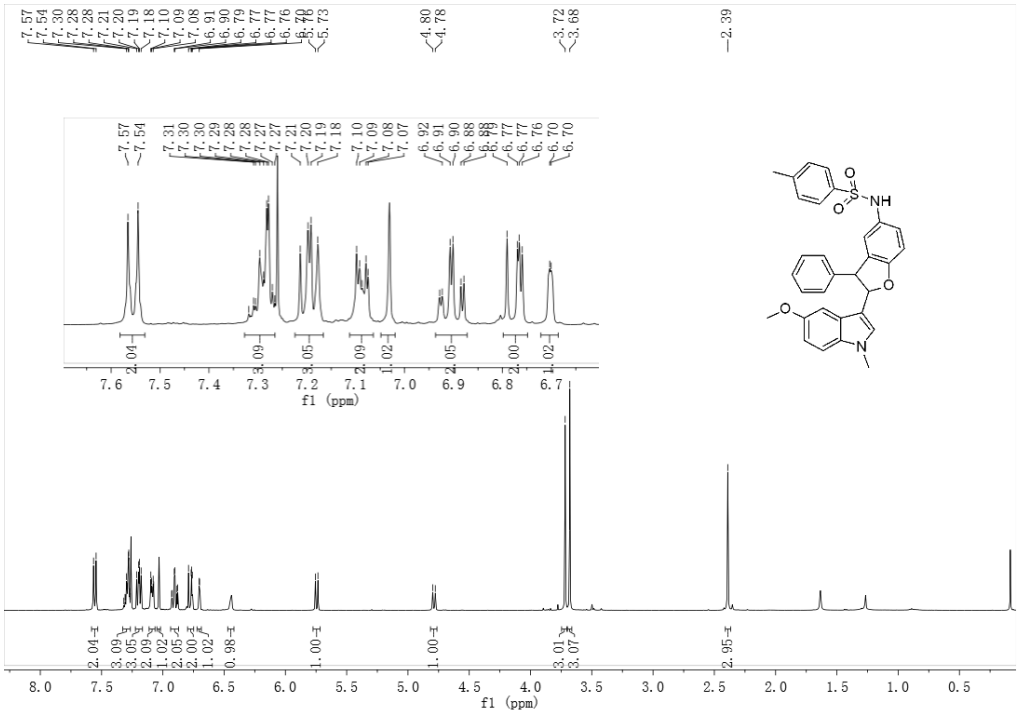

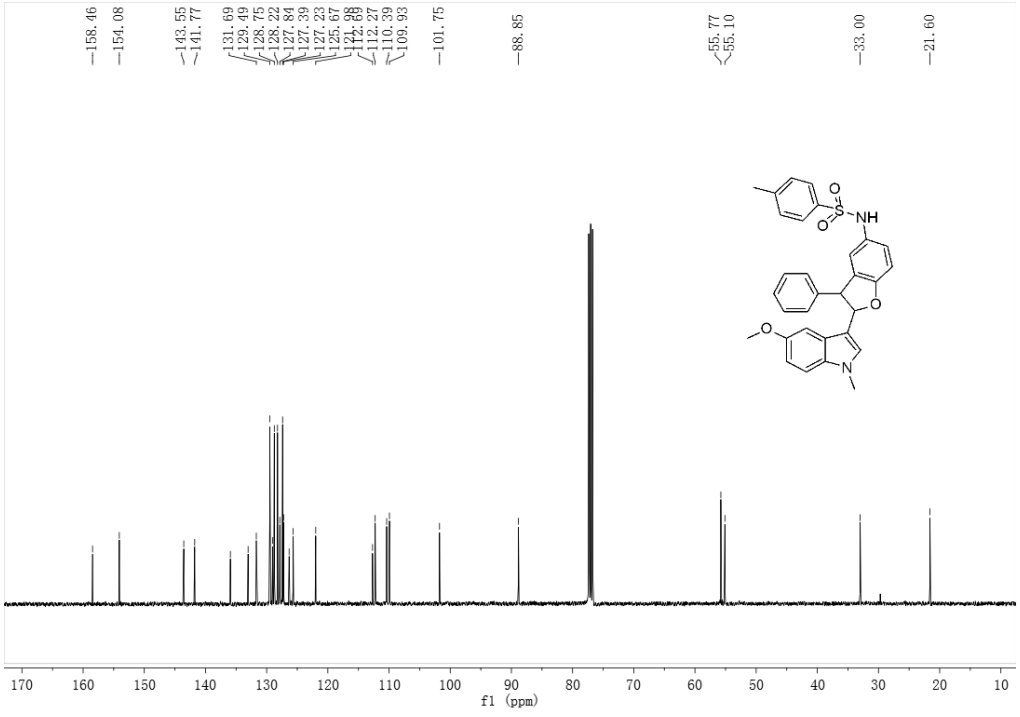

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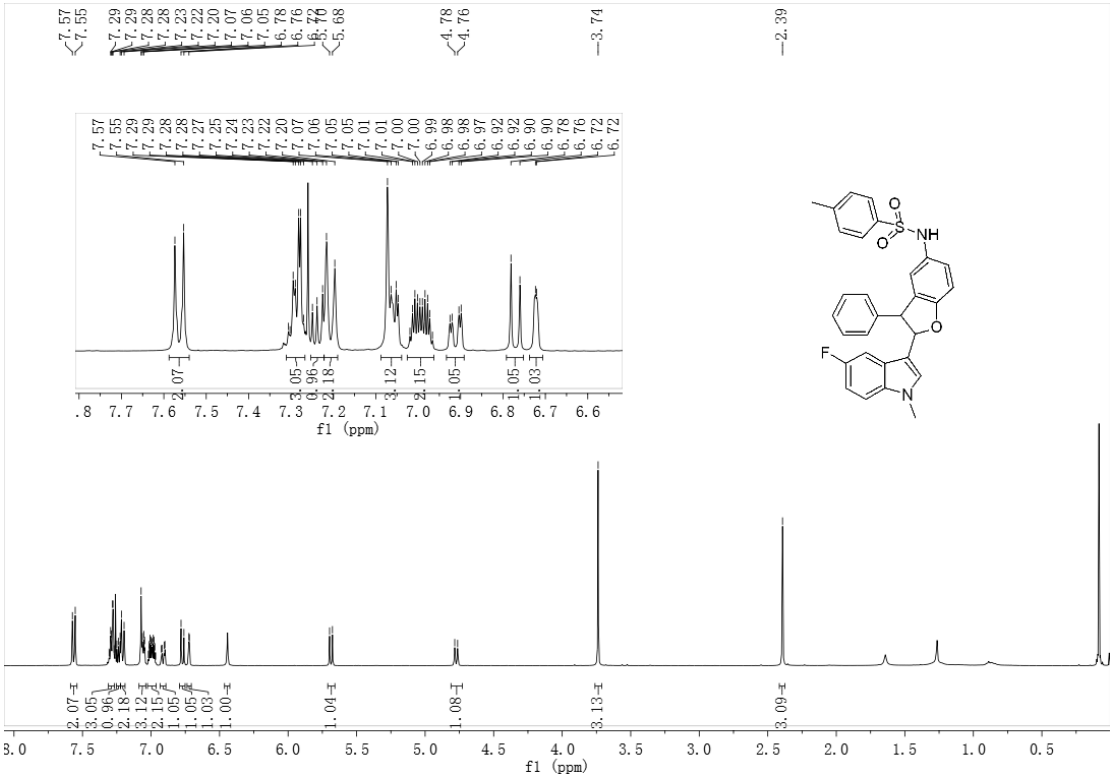
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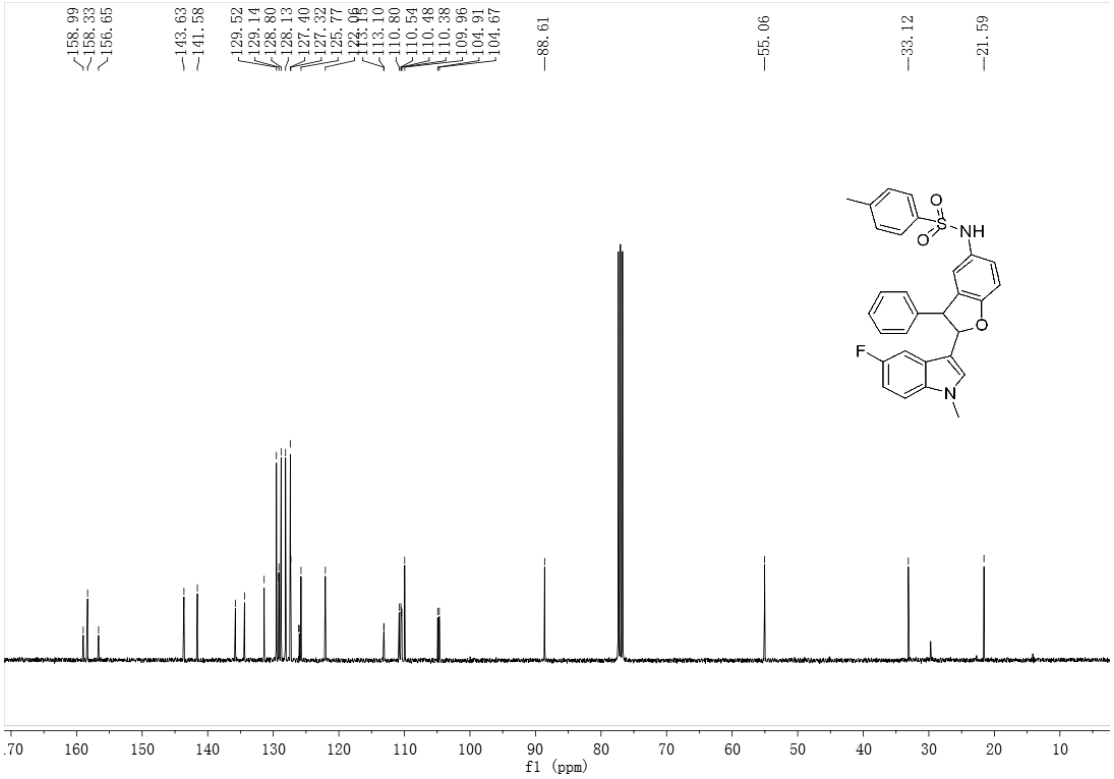
F
N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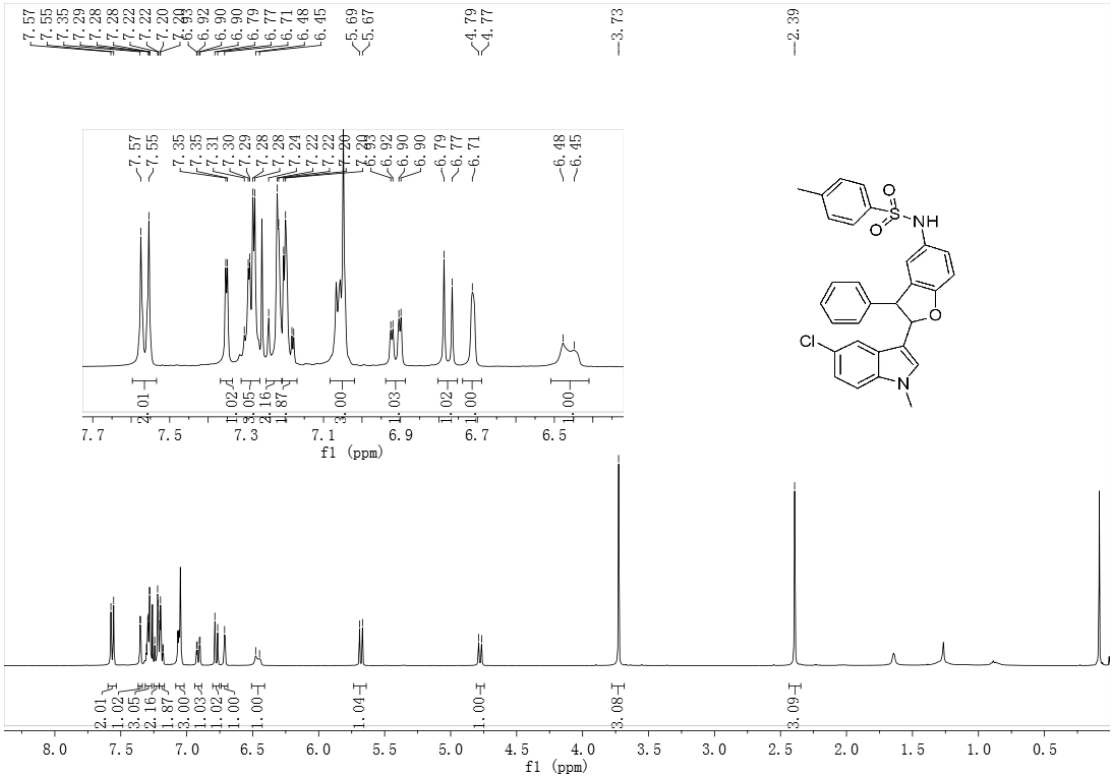
S
F
N

3ea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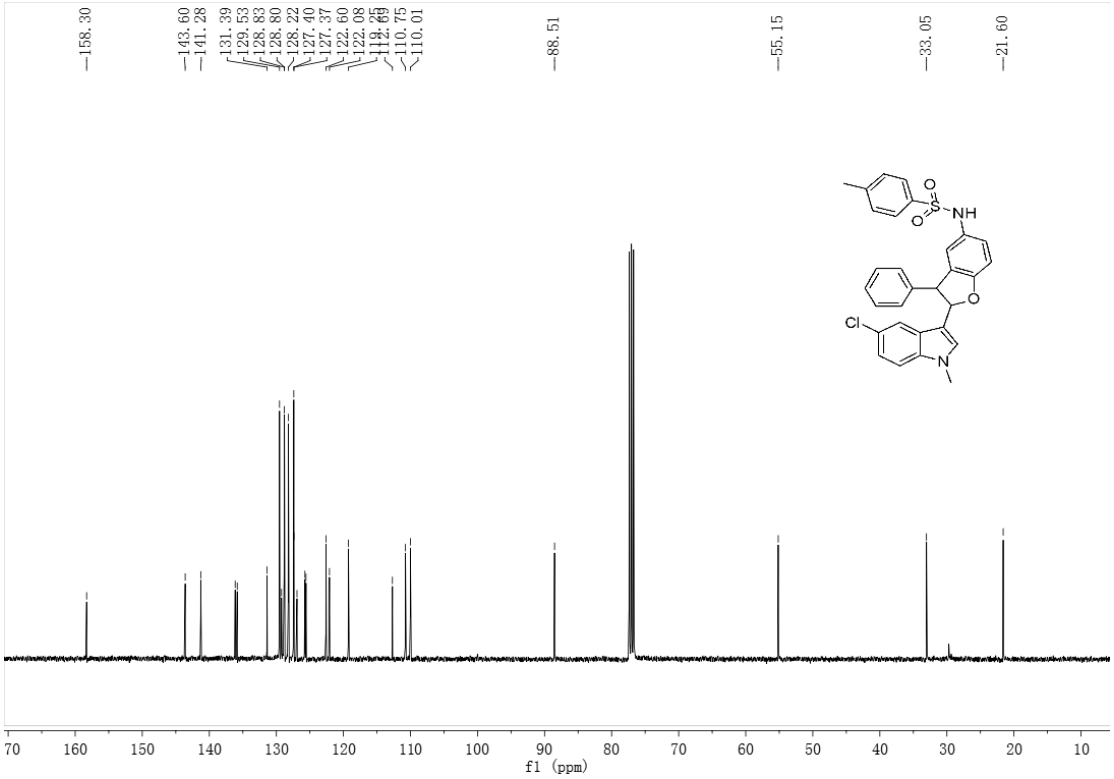
f1 (ppm)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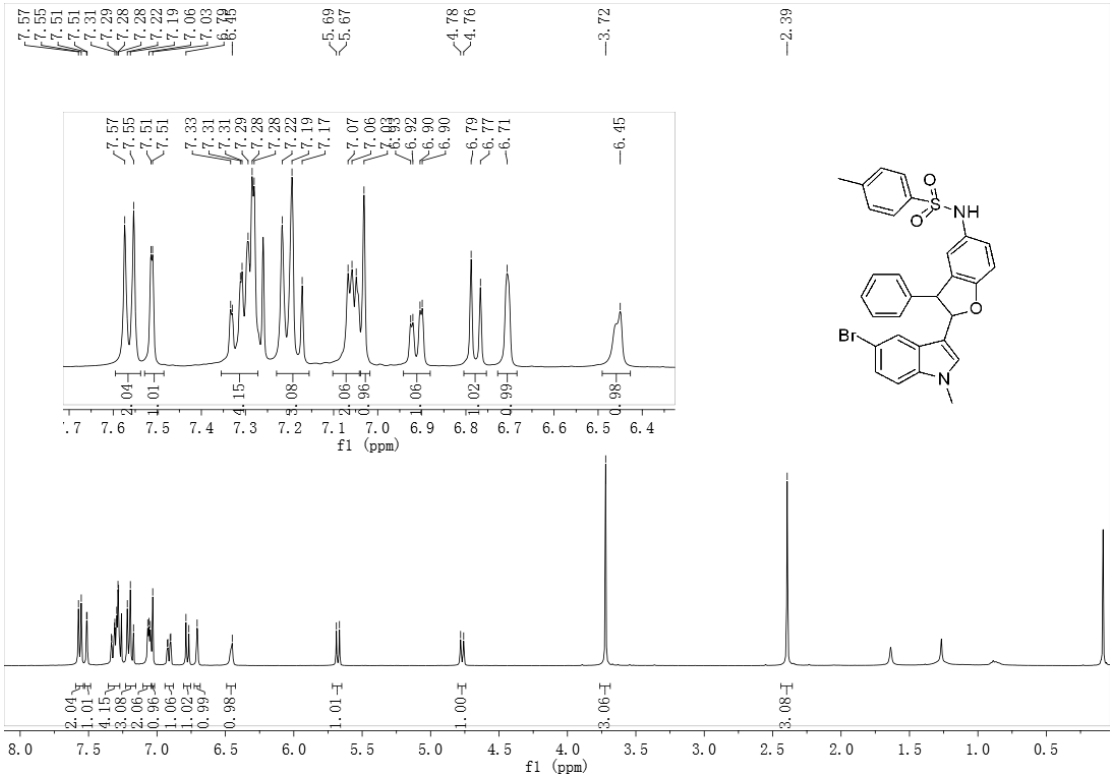
f1 (ppm)

3fa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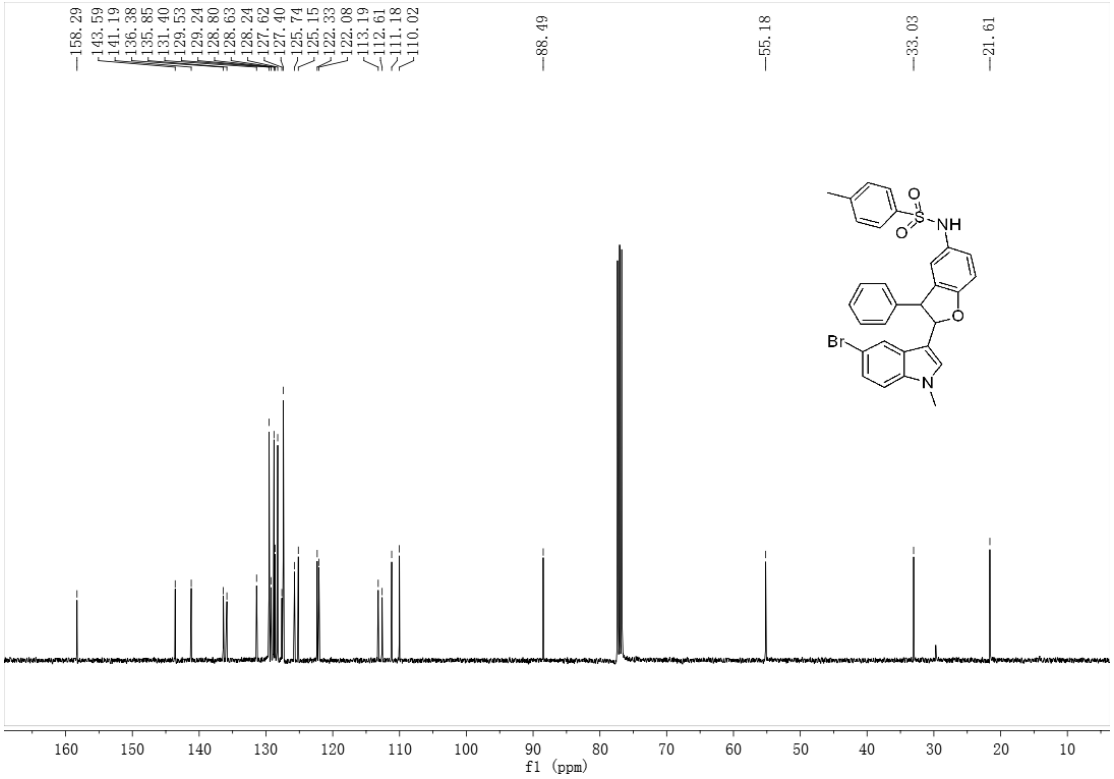
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N
f1 (ppm)

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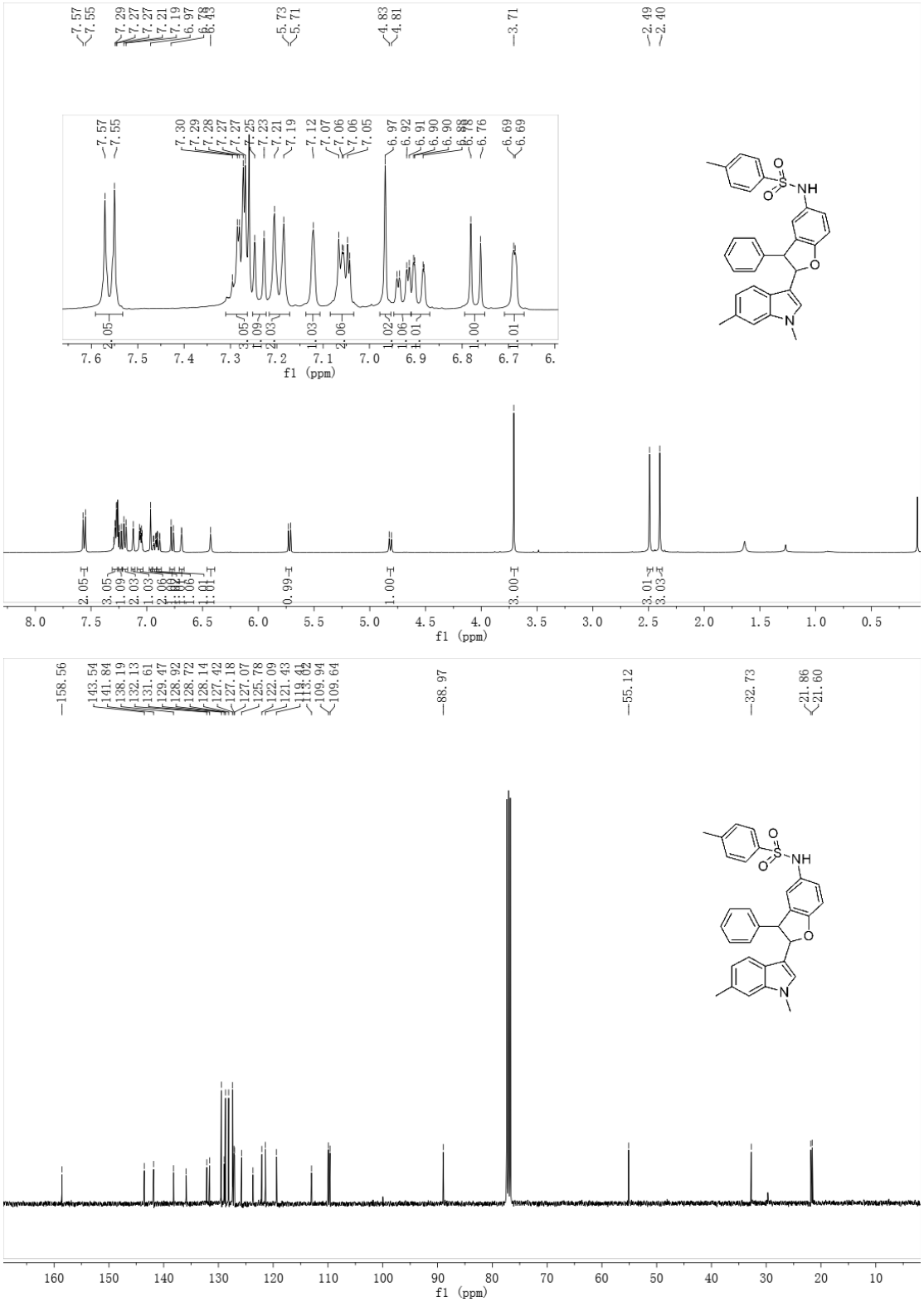

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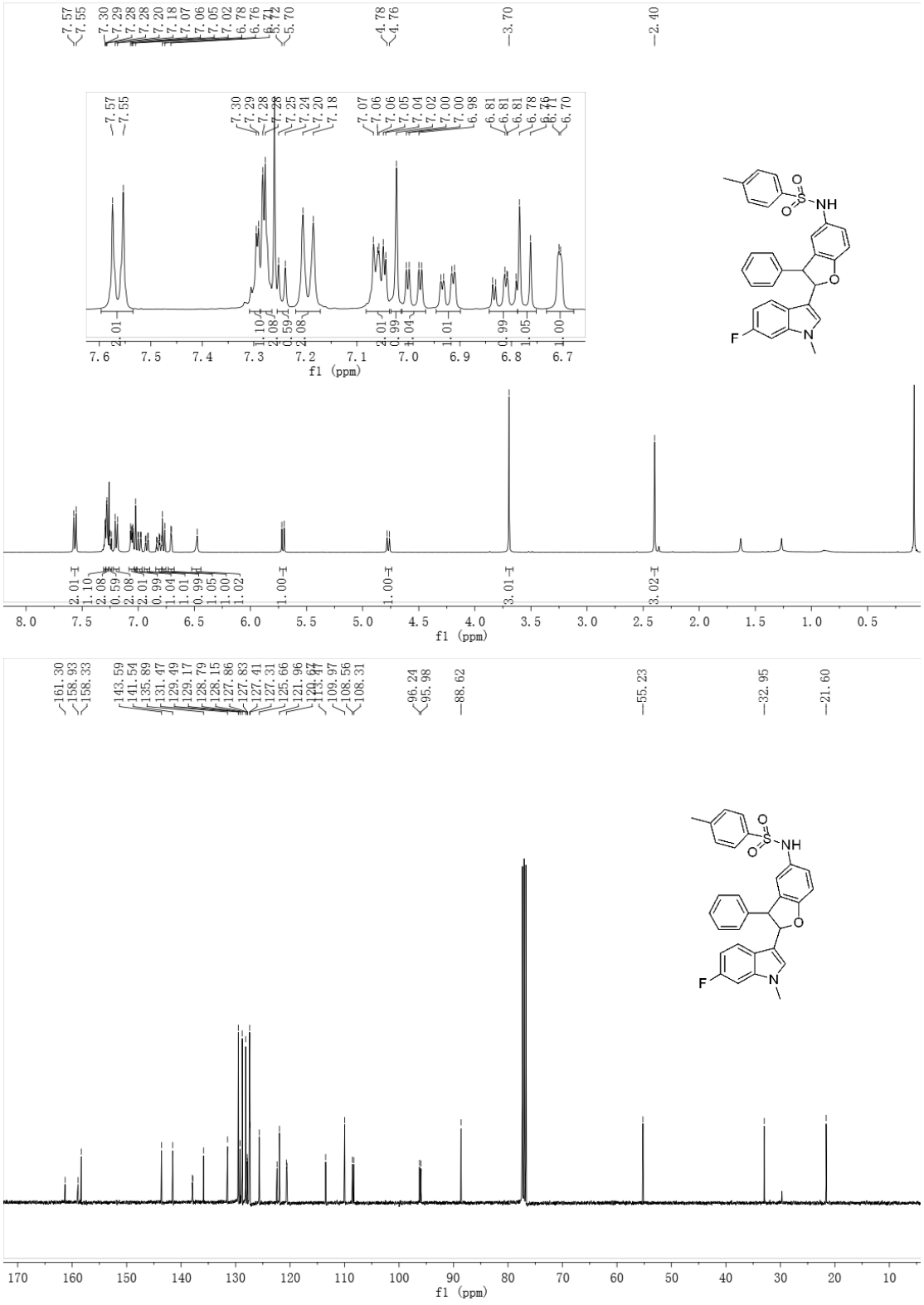

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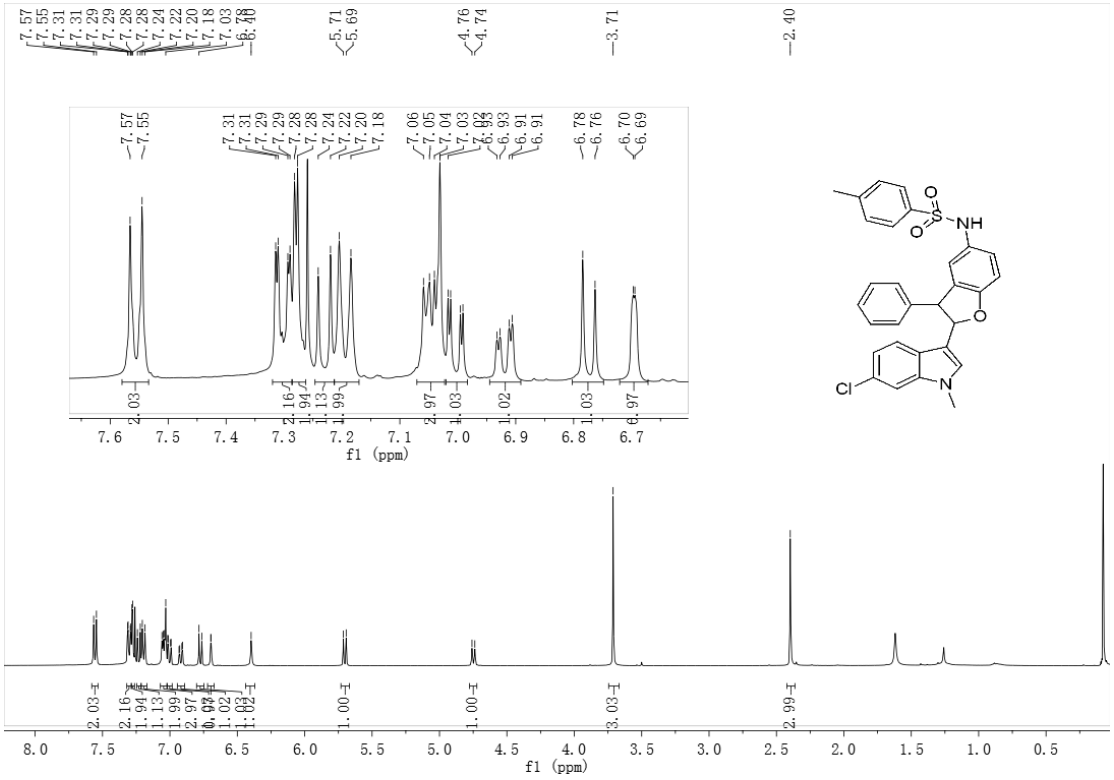
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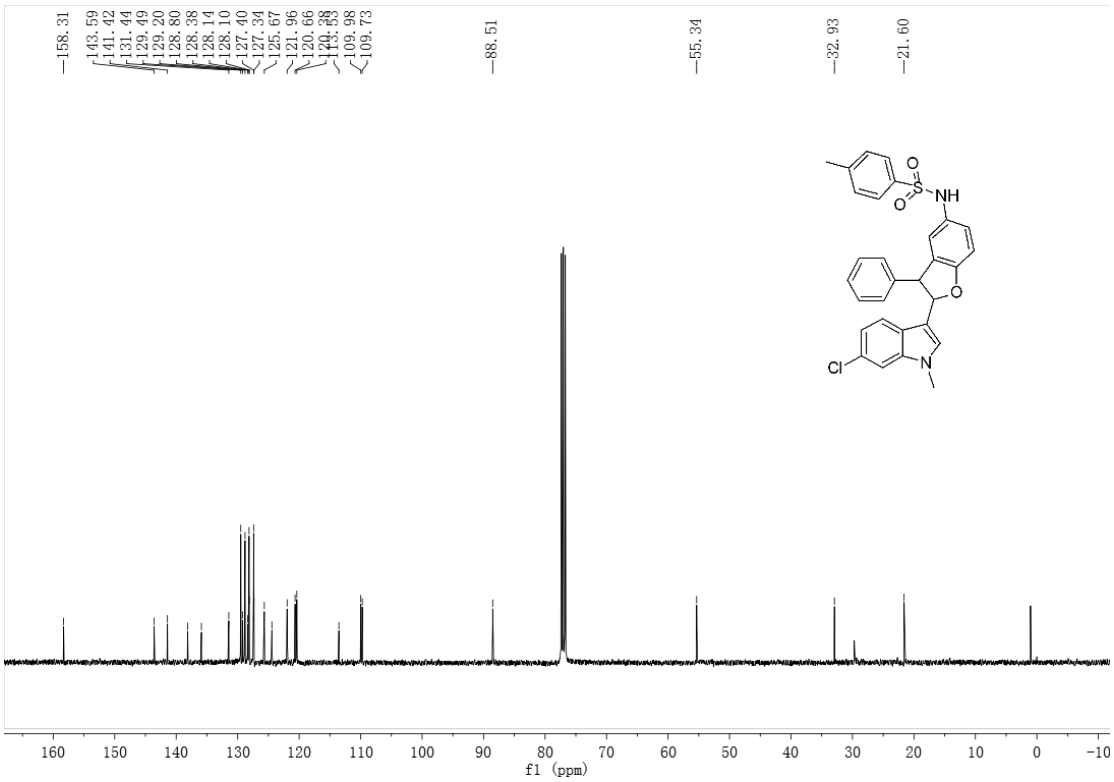
f1 (ppm)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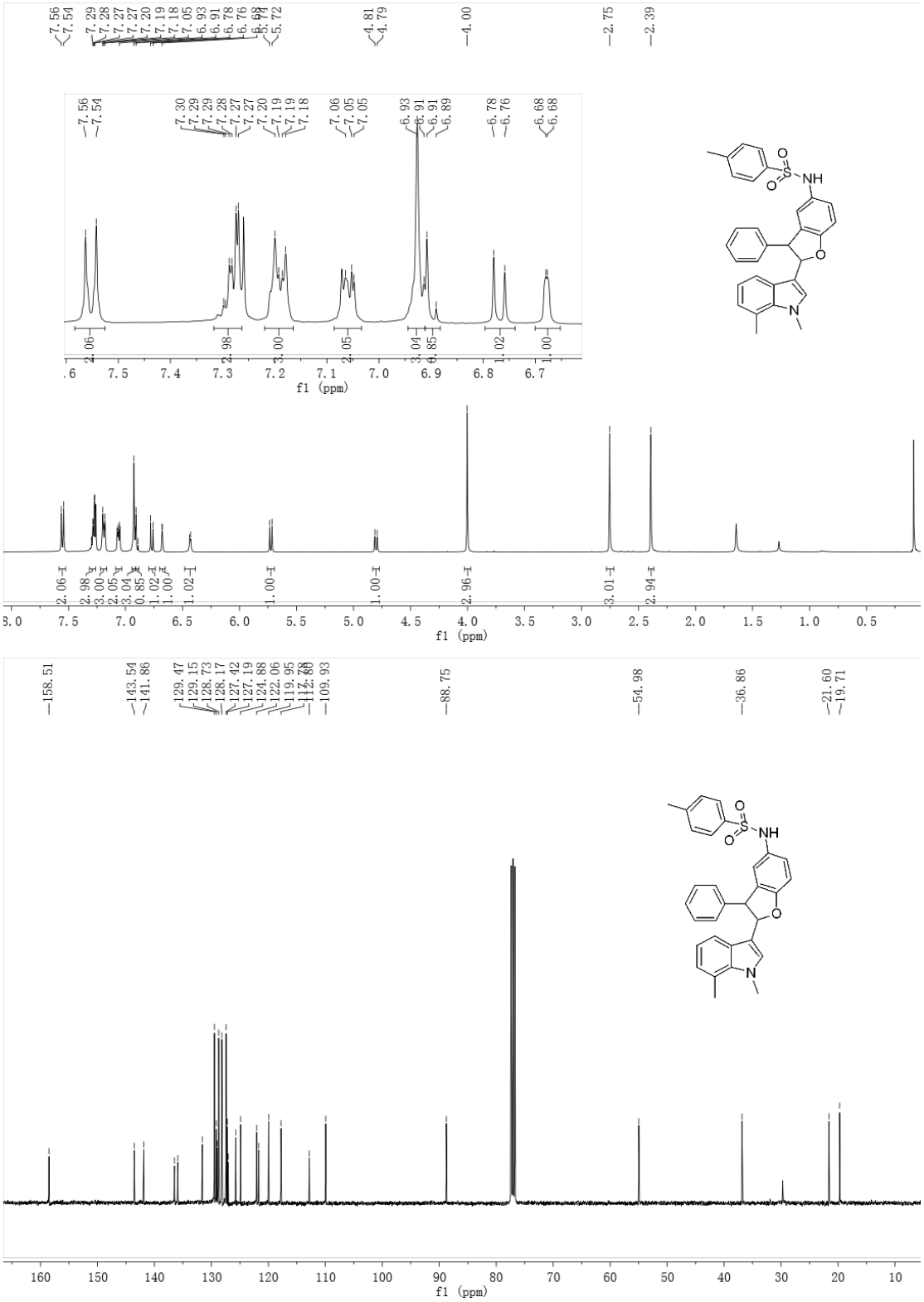
N
f1 (ppm)

3ja



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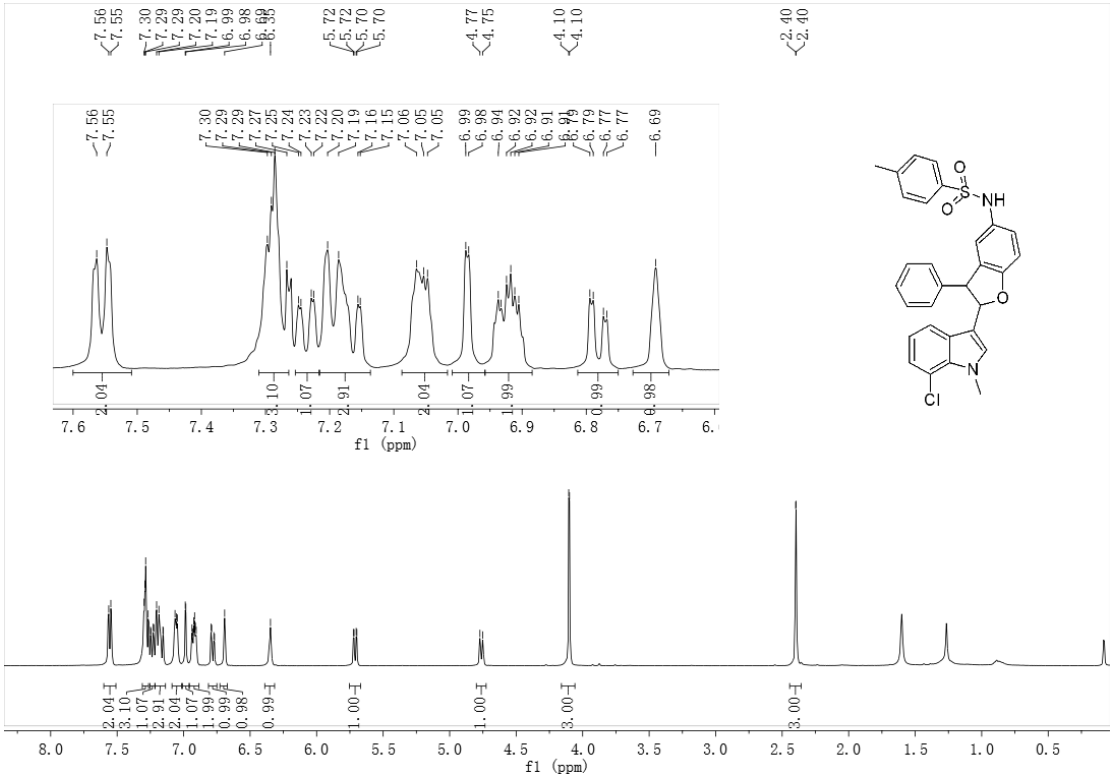
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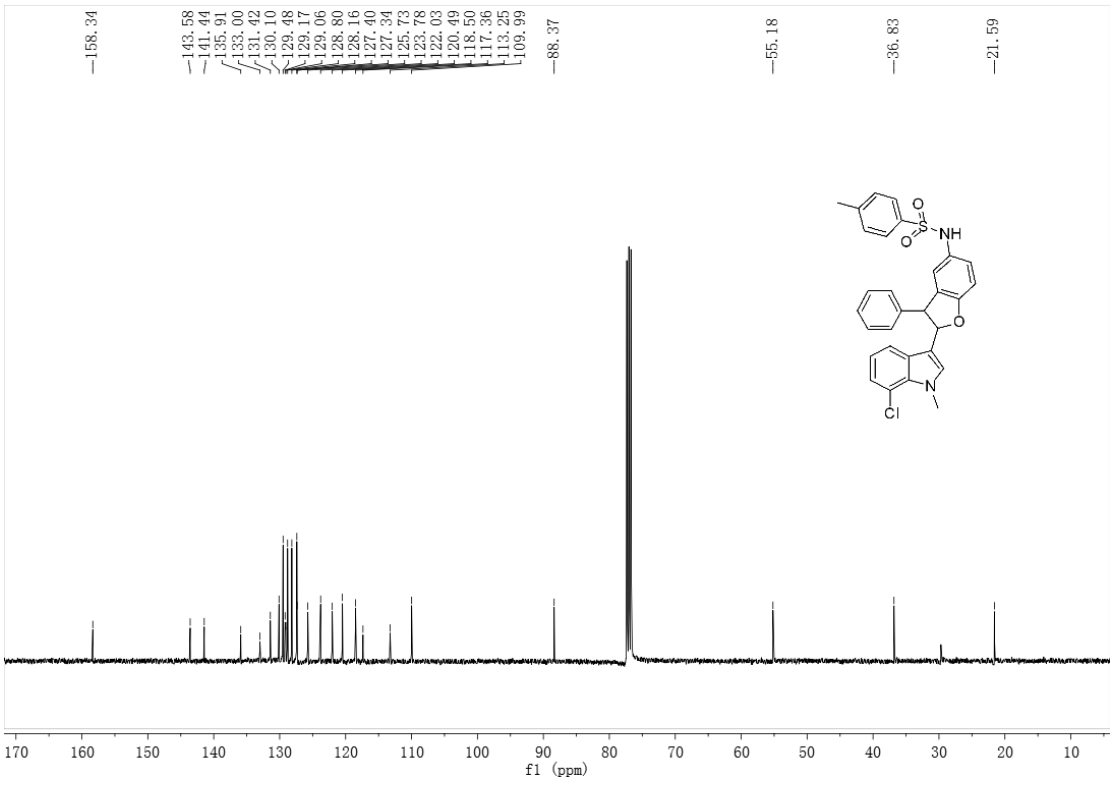
O
N
Cl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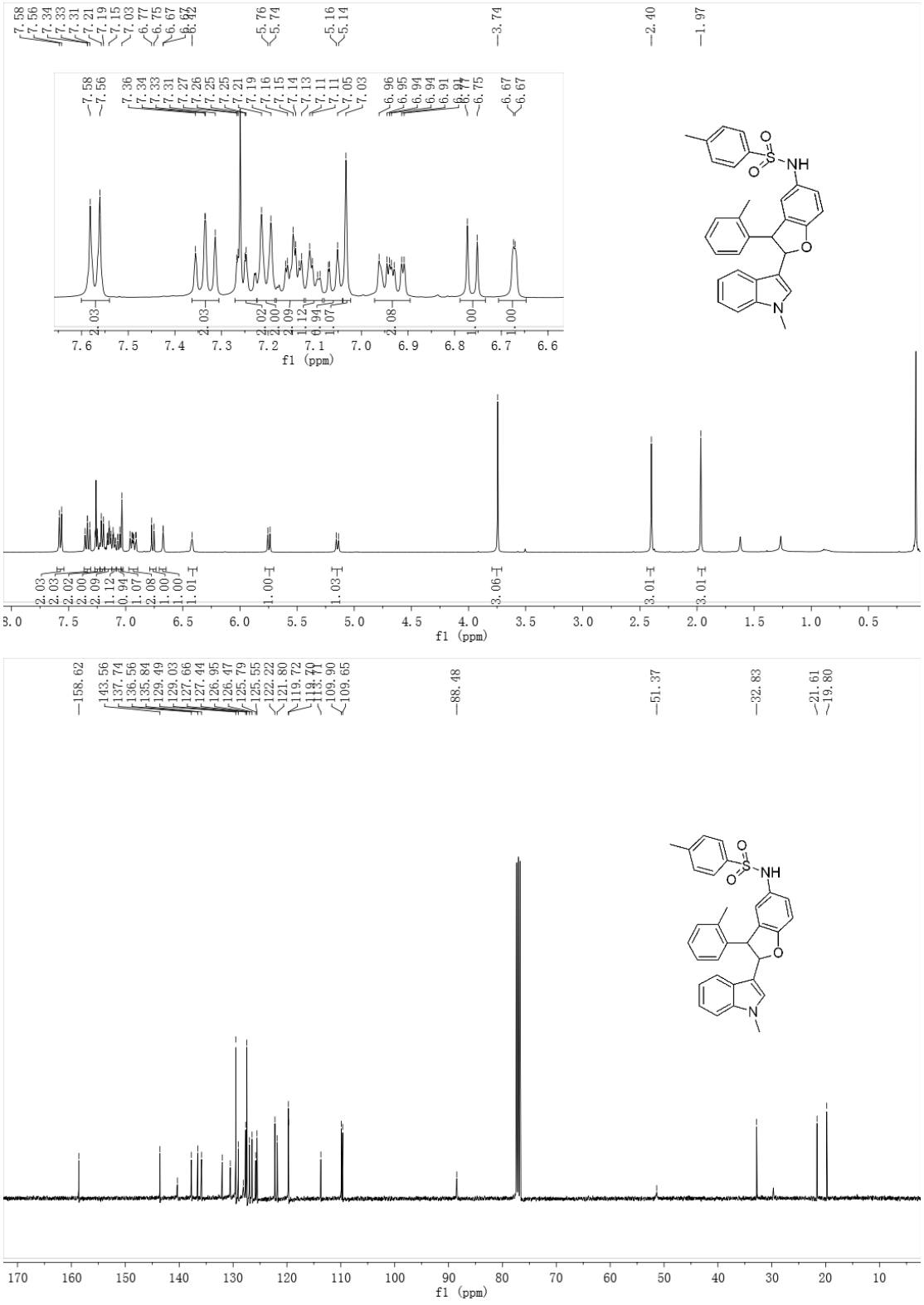
f1 (ppm)
NH
O
S
O
O
N
Cl

3la



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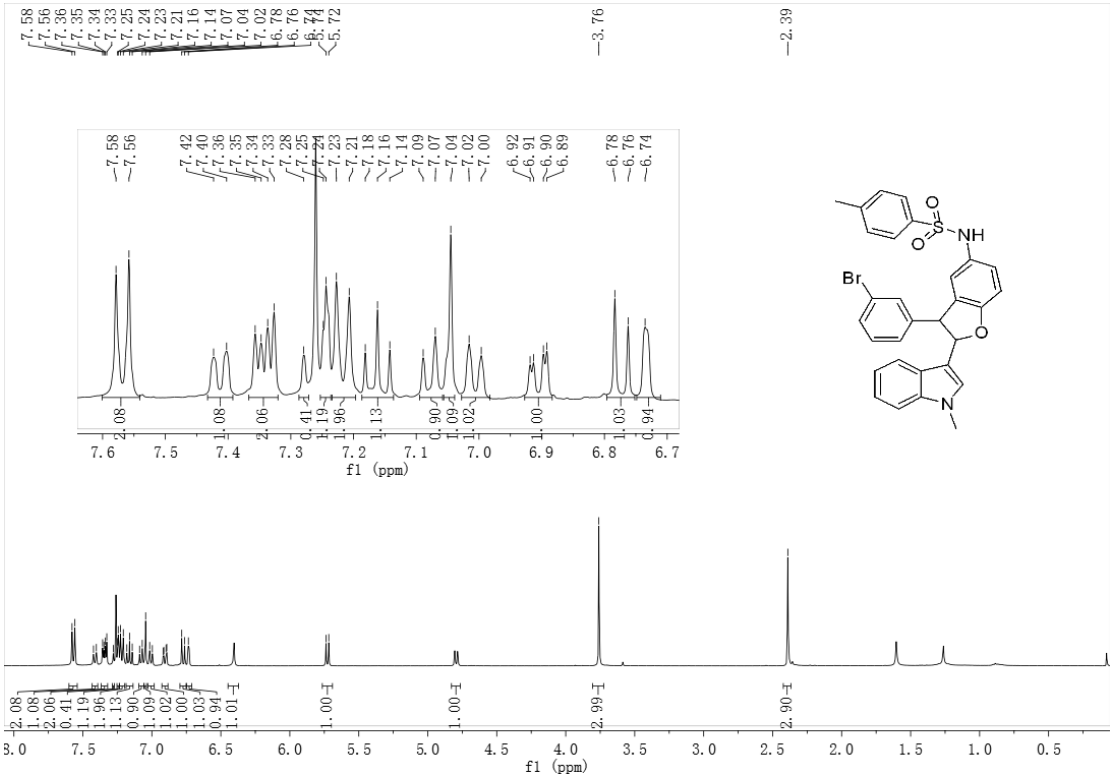
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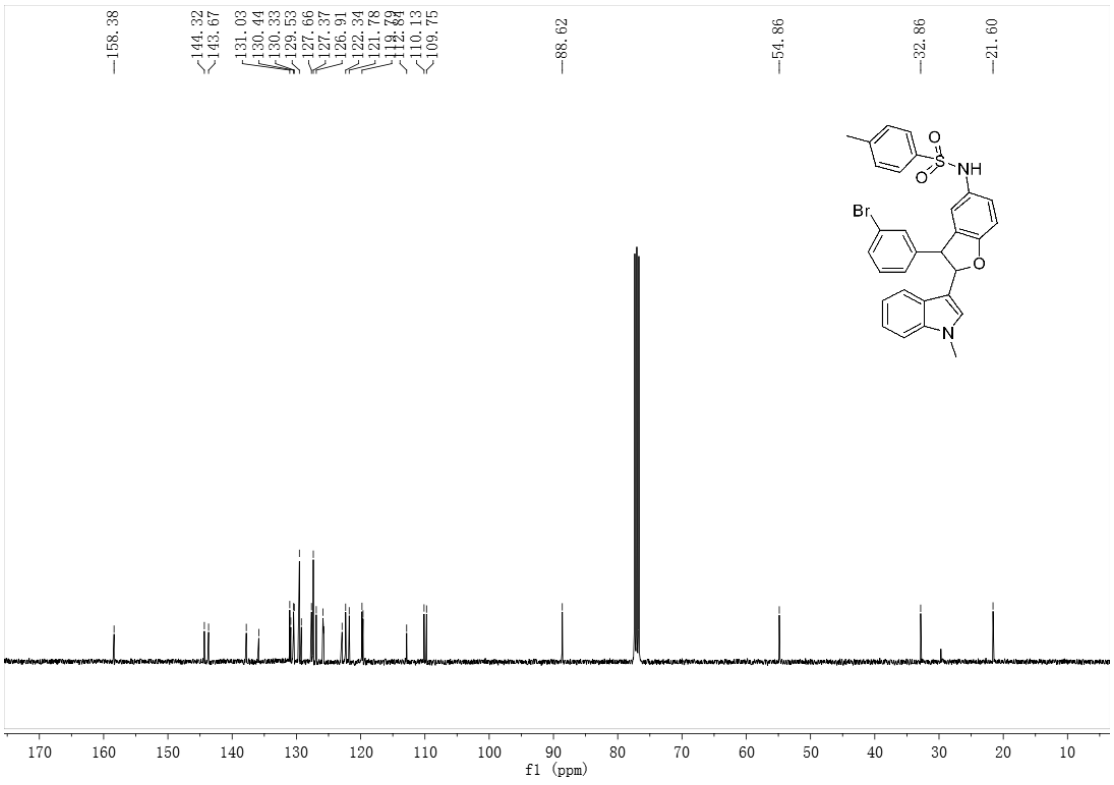
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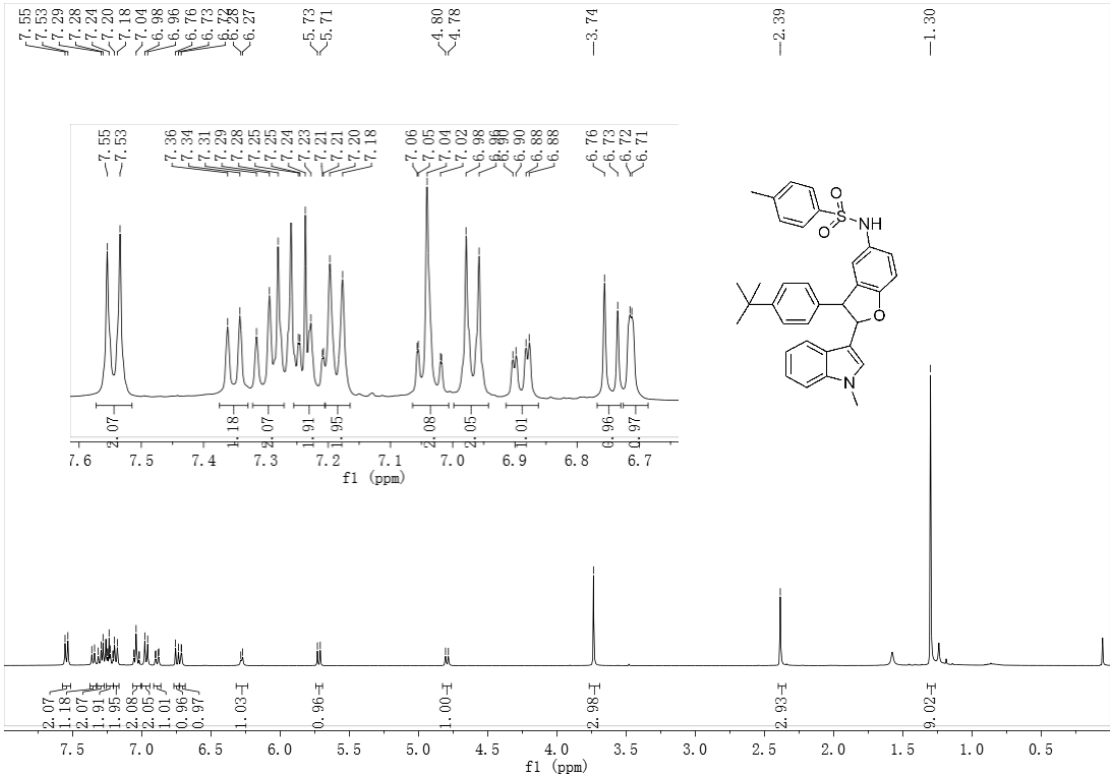
32.86
21.60
f1 (ppm)
NH
Br
O
N

3na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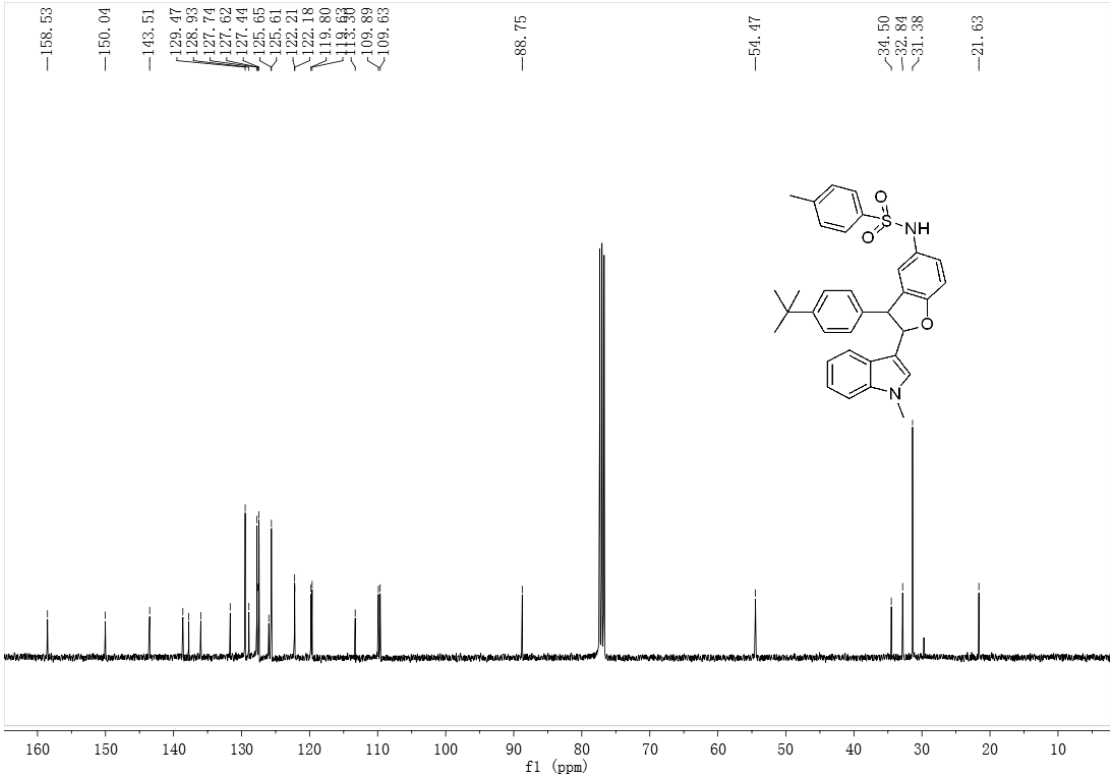
NH
f1 (ppm)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NH
f1 (ppm)

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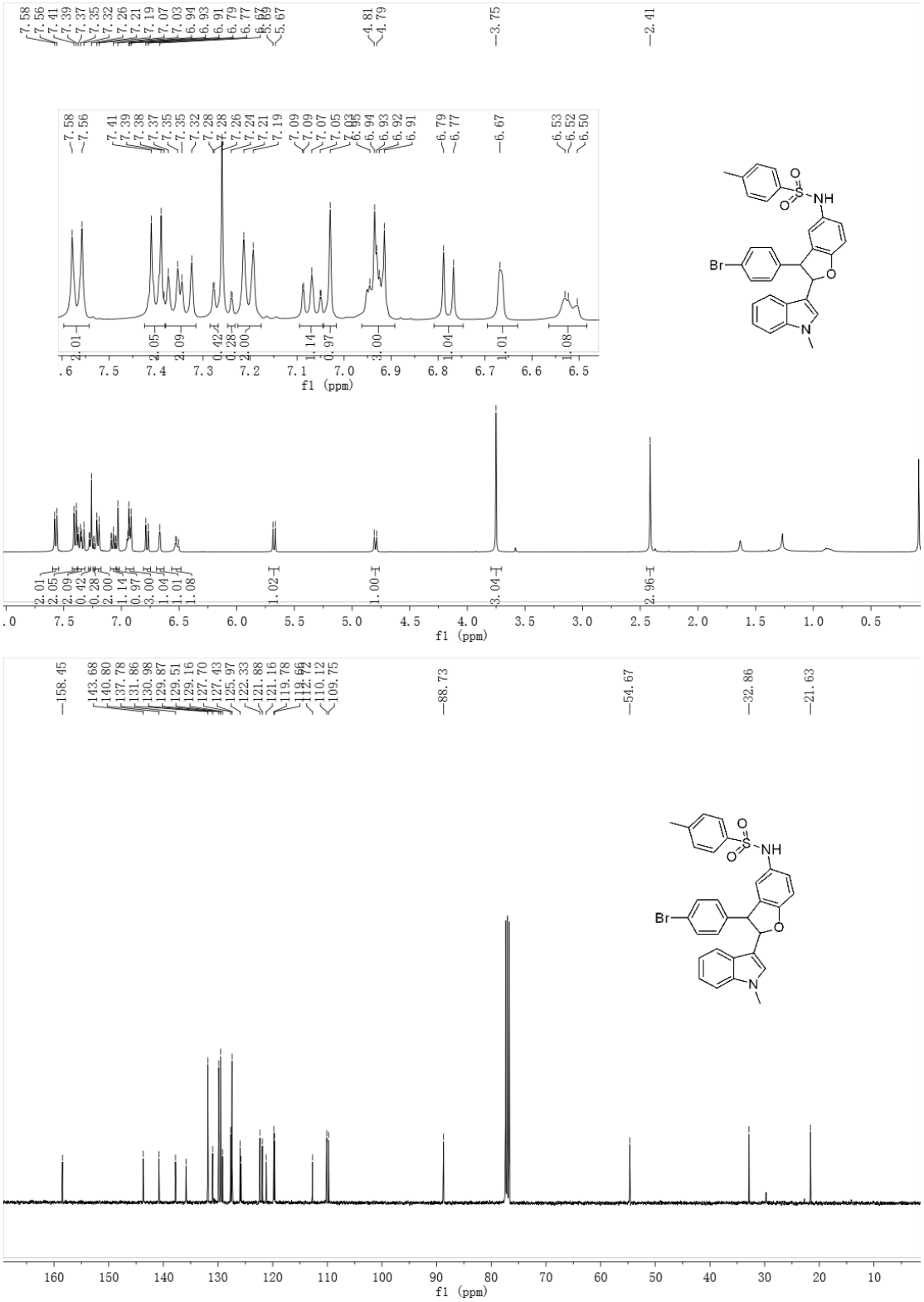

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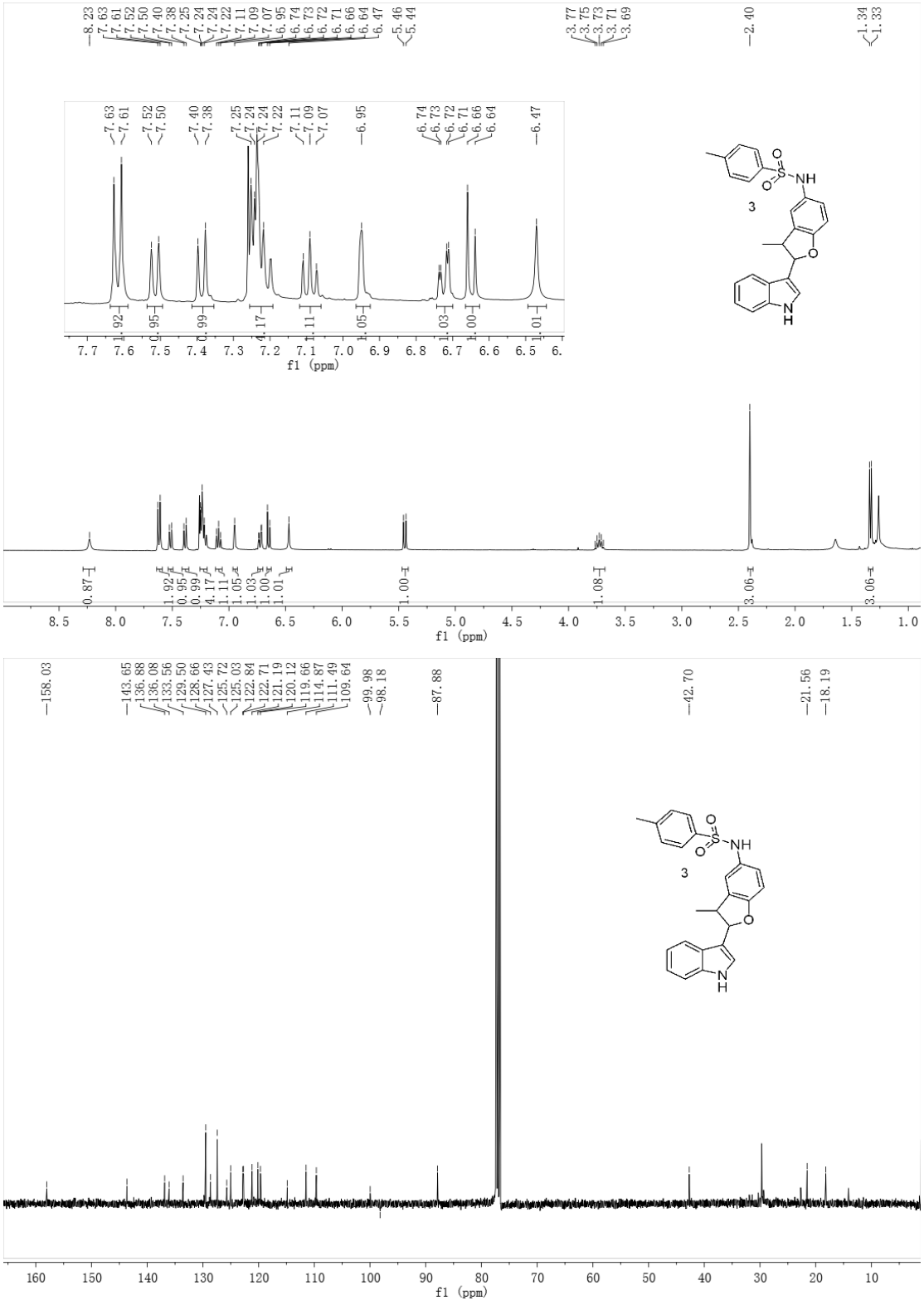
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3.71
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1.33
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0.99
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1.11
1.05
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1.01
f1 (ppm)
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0.95
0.99
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1.00
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f1 (ppm)
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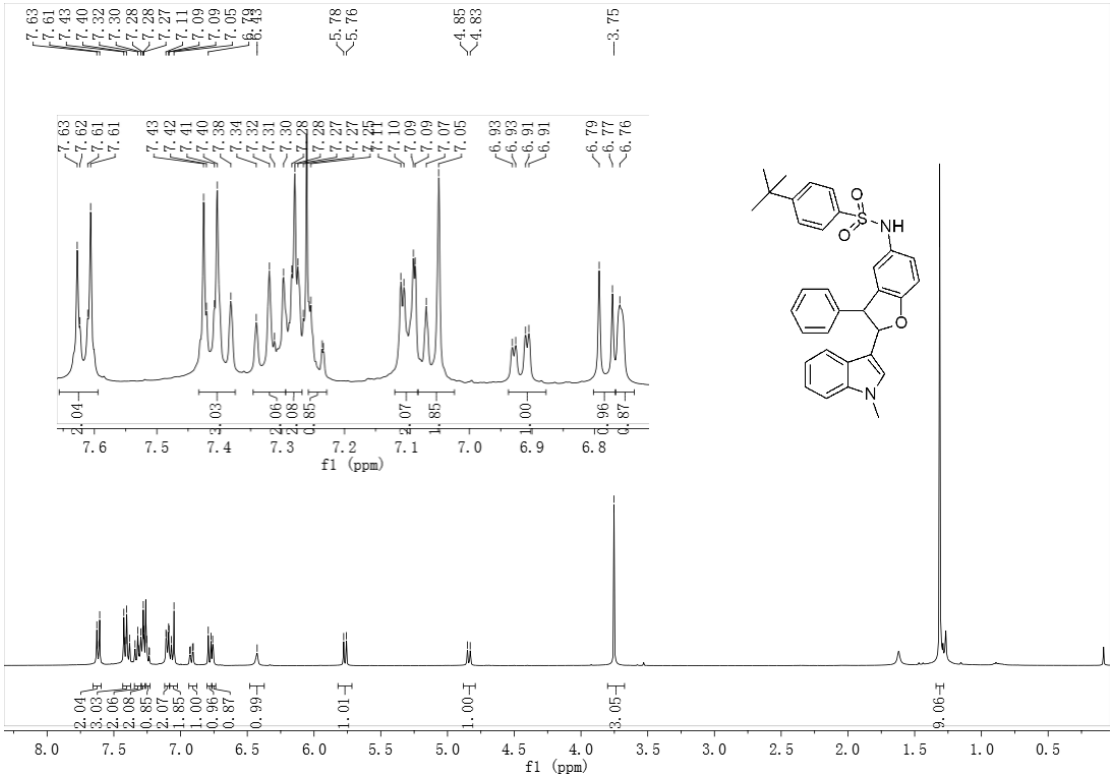
3ab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5.76
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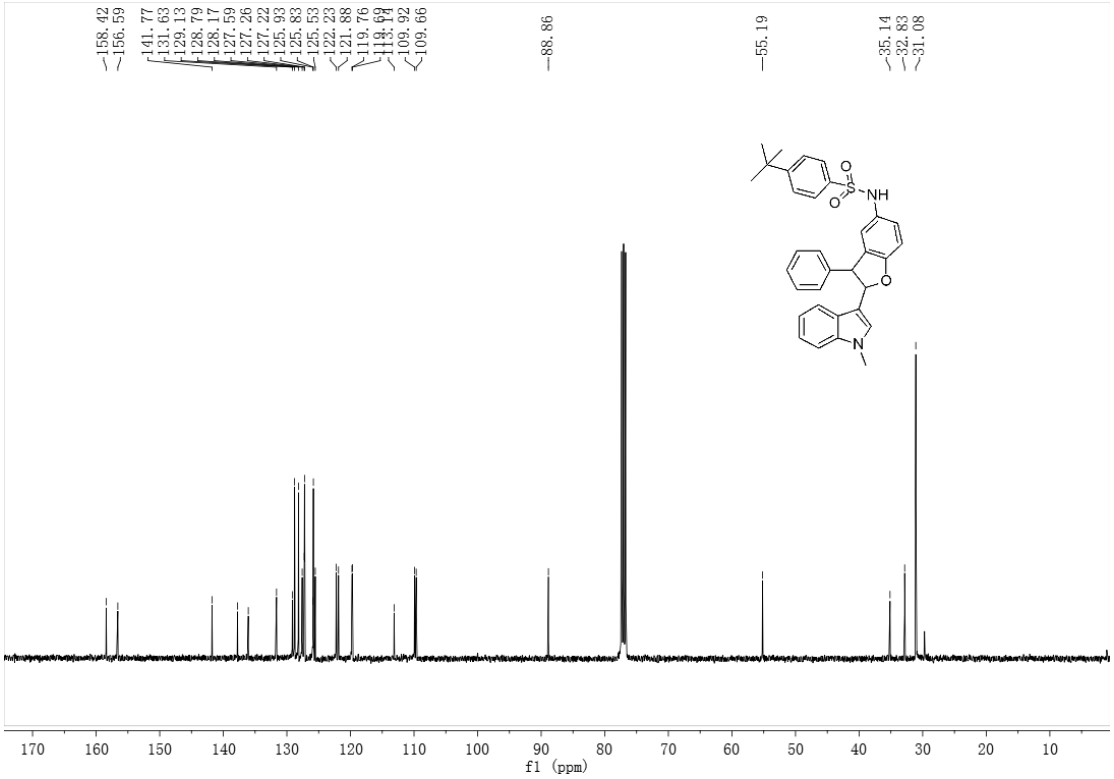
3.75
f1 (ppm)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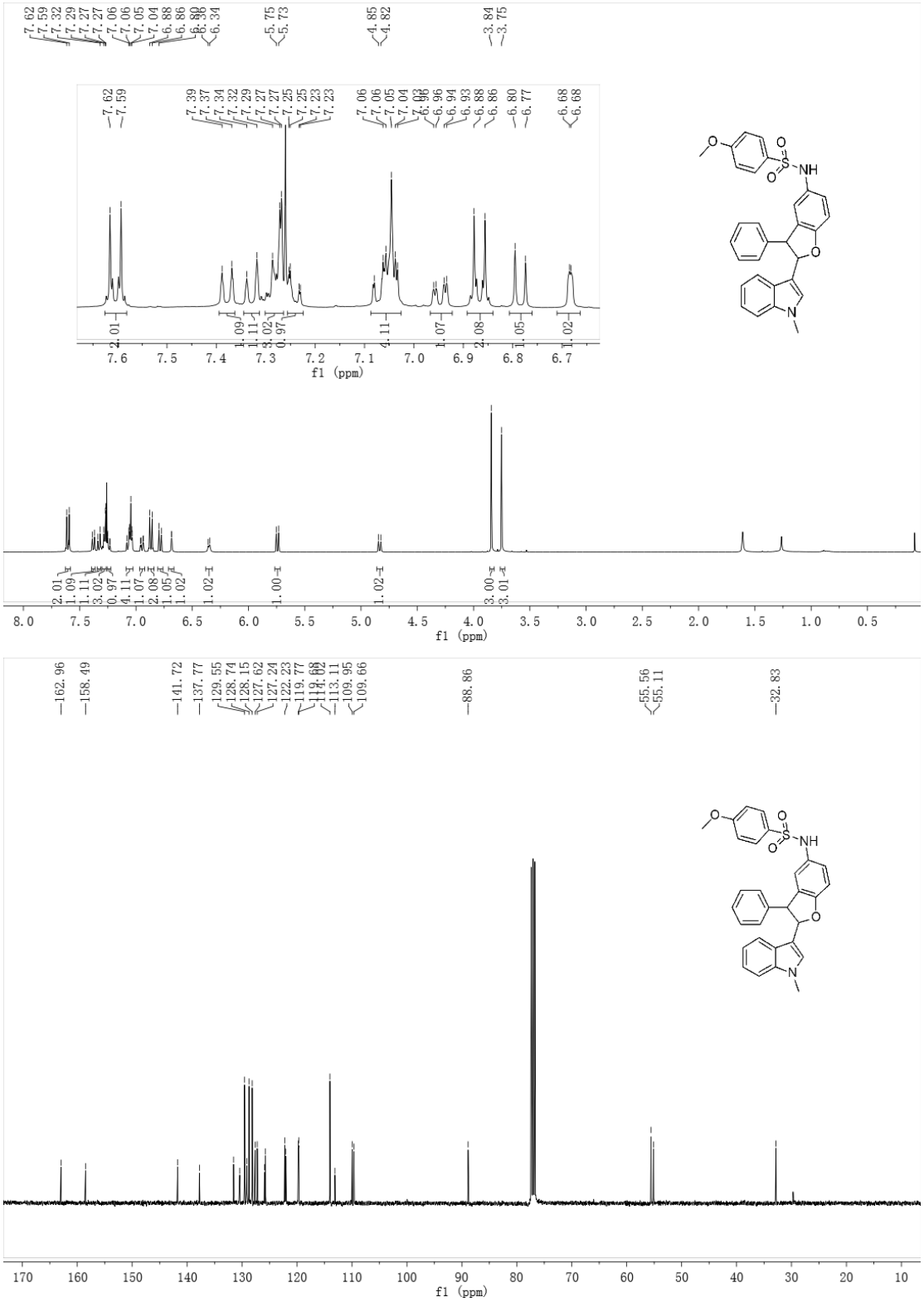
31.08
f1 (ppm)

3ac



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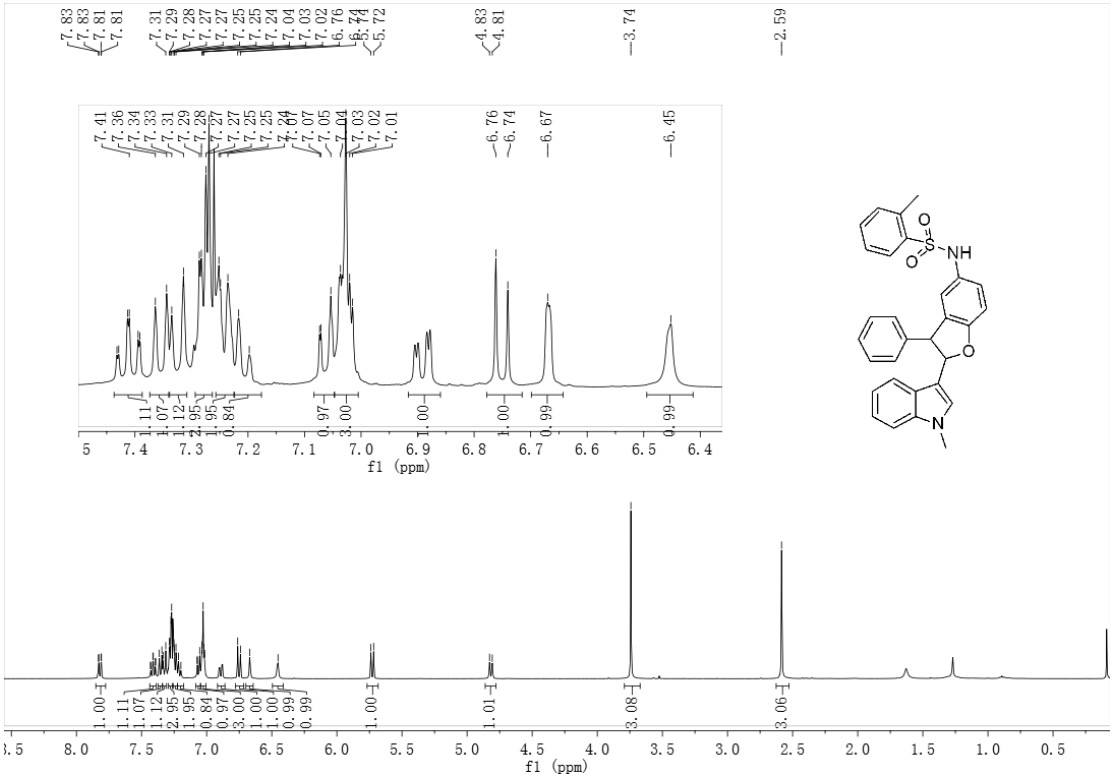
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7.36
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7.24
7.07
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6.45
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1.07
1.12
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0.97
3.00
1.00
1.00
0.99
0.99
f1 (ppm)
NH
O
N
1.00
1.11
1.07
1.12
2.95
1.95
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1.01
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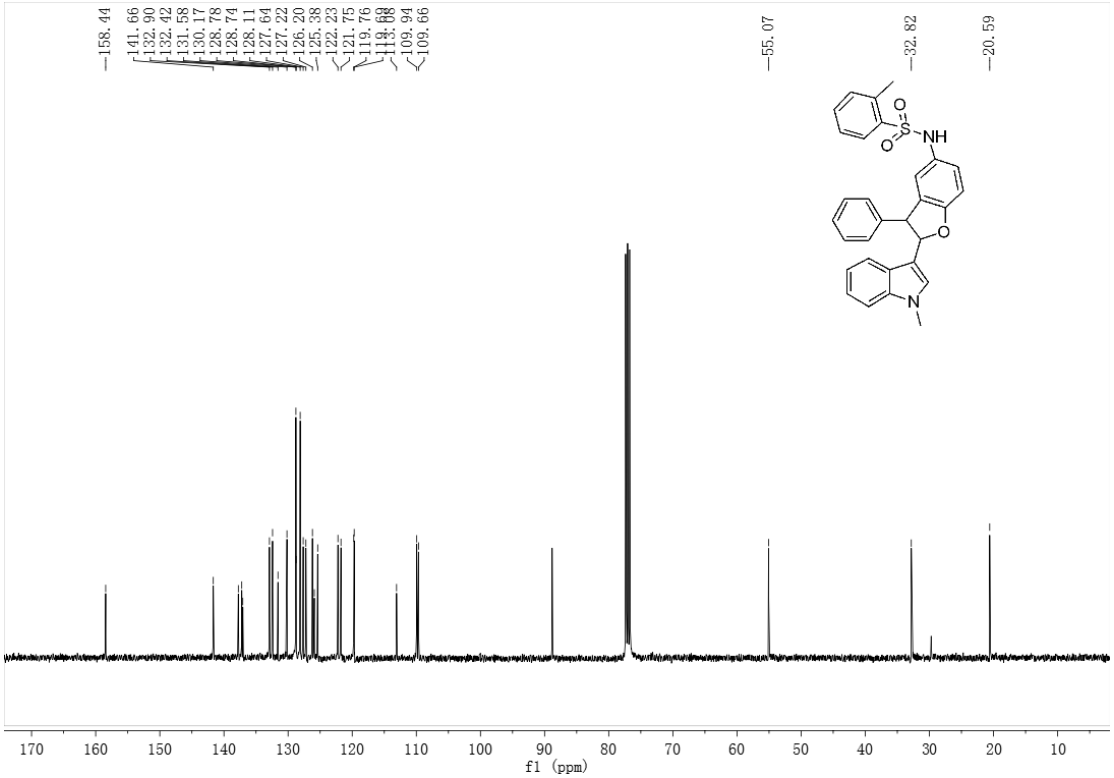
f1 (ppm)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55.07
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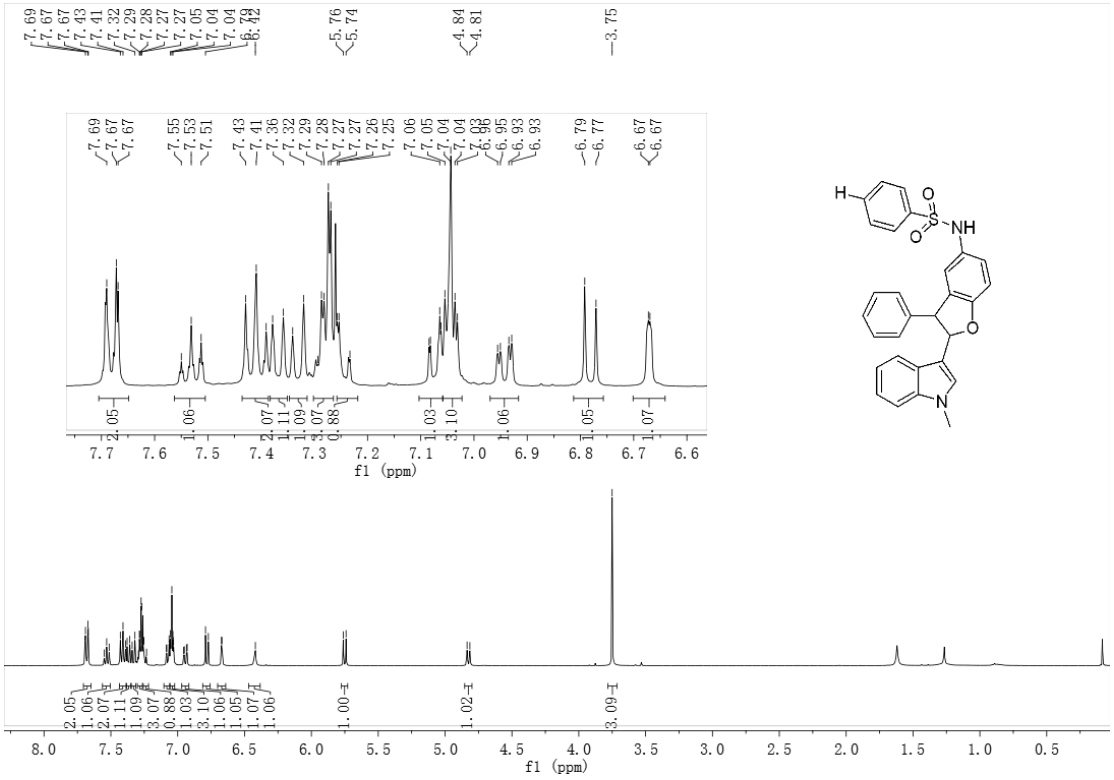
20.59
NH
O
N
f1 (ppm)

3ae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4.81
3.75
7.55
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7.51
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7.03
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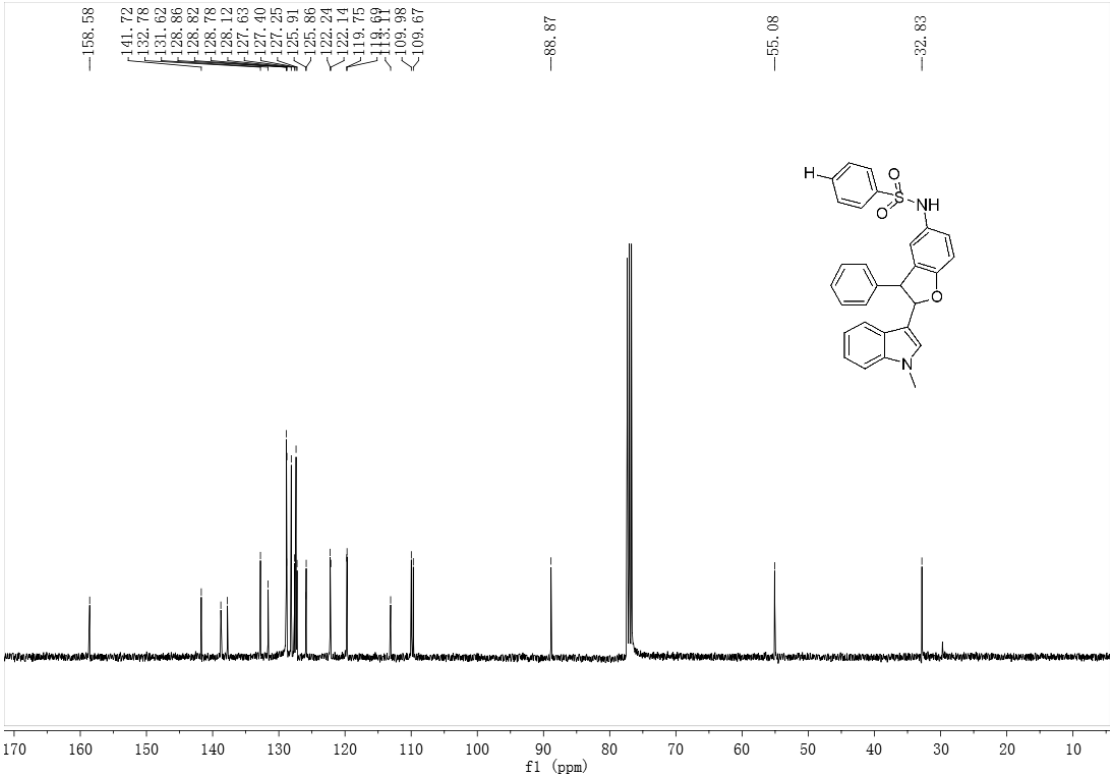
6.93
6.93
6.79
6.77
6.67
6.67
2.05
1.06
2.07
1.11
1.09
3.07
0.88
1.03
3.10
1.06
1.05
1.07
f1 (ppm)
H
O
S
O
NH
O
N
2.05
1.06
2.07
1.11
1.09
3.07
0.88
1.03
3.10
1.06
1.05
1.07
1.06
1.00
1.02
3.09
f1 (ppm)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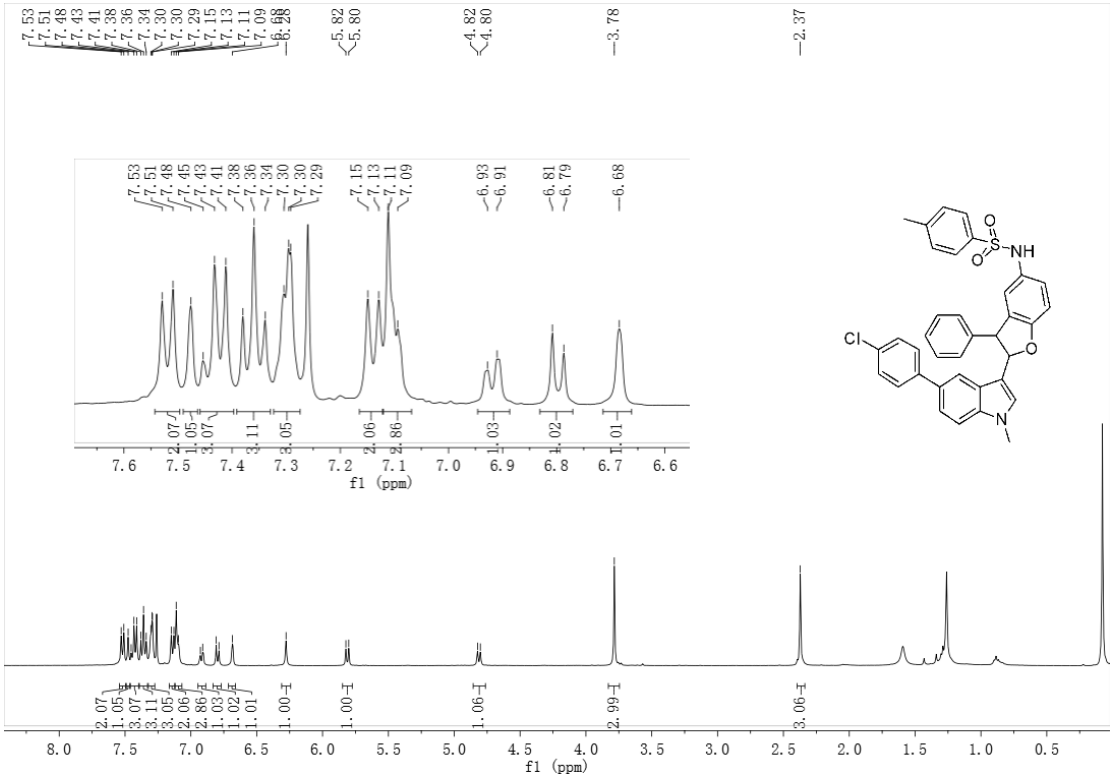
122.14
119.75
119.69
113.11
109.98
109.67
88.87
55.08
32.83
H
O
S
O
NH
O
N
f1 (ppm)

Compound 7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7.30
7.29
7.15
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7.11
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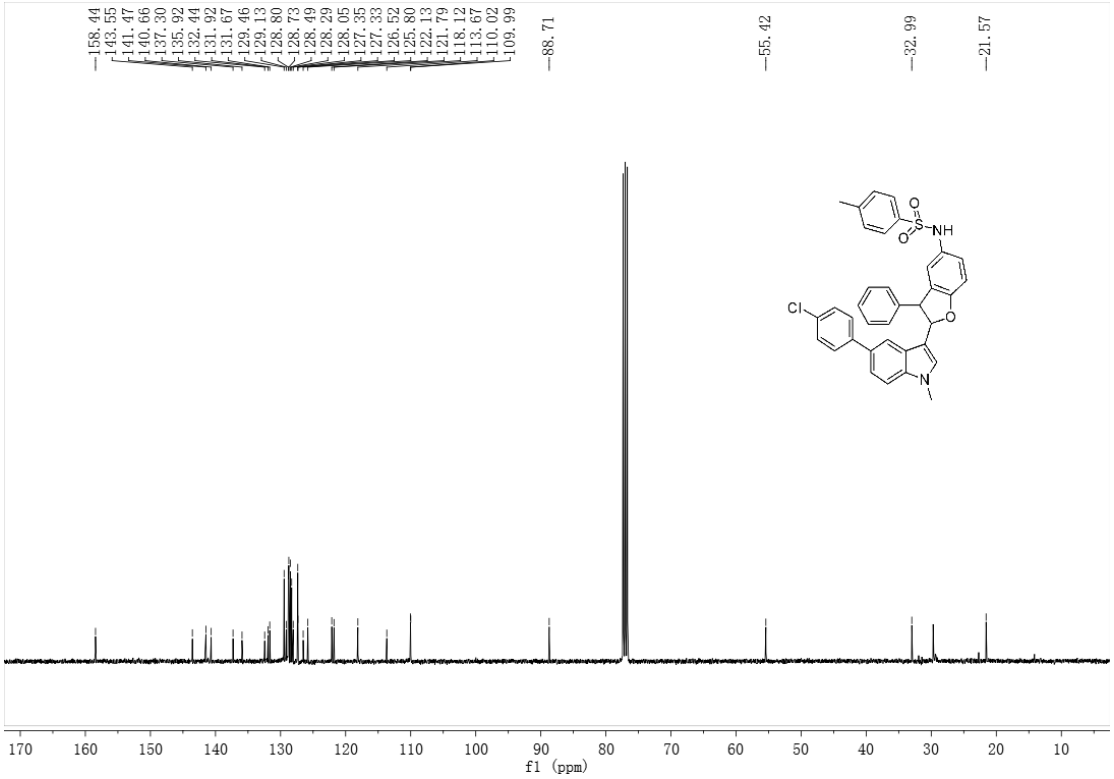
5.82
5.80
4.82
4.80
3.78
2.37
f1 (ppm)
NH
Cl
O
N


158.44
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140.66
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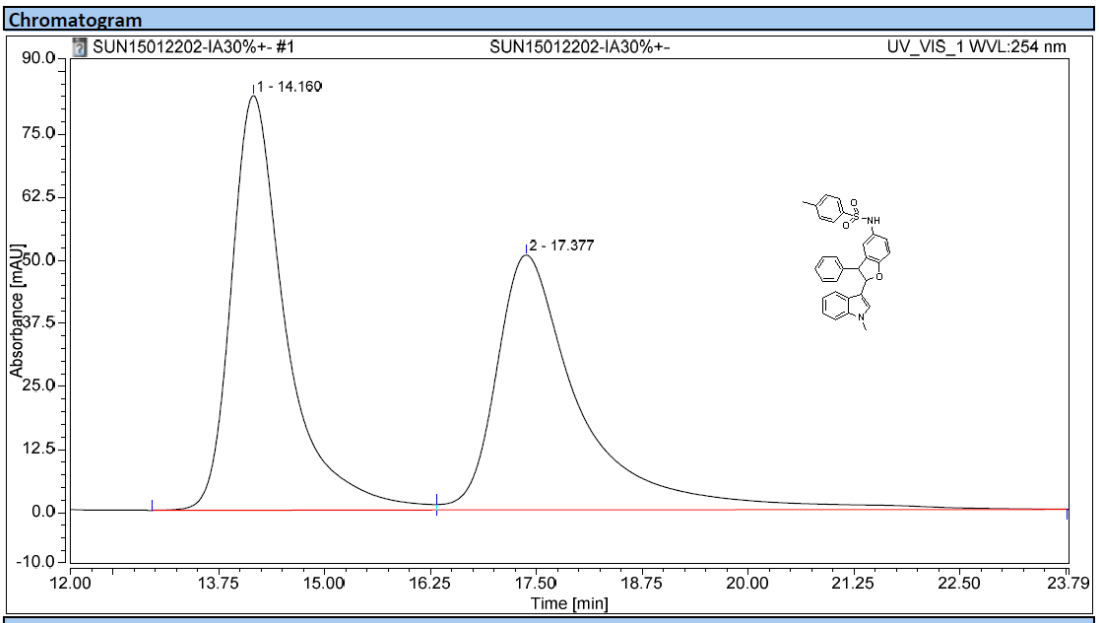
135.92
132.44
131.92
131.67
129.46
129.13
128.80
128.73
128.49
128.29
128.05
127.35
127.33
126.52
125.80
122.13
121.79
118.12
113.67
110.02
109.99
88.71
55.42
32.99
21.57
f1 (ppm)
NH
Cl
O
N

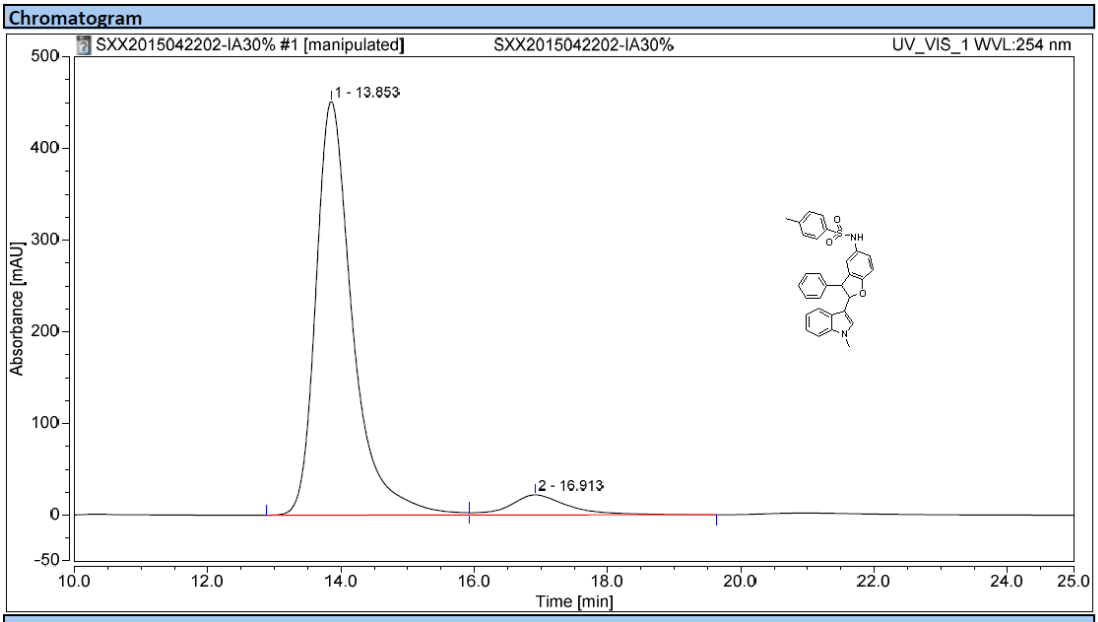
8. HPLC spectra of products 3 and compound 7

3aa



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.160	61.261	82.230	51.16	61.93	n.a.
2		17.377	58.481	50.539	48.84	38.07	n.a.
Total:			**119.742**	**132.769**	**100.00**	**100.00**	

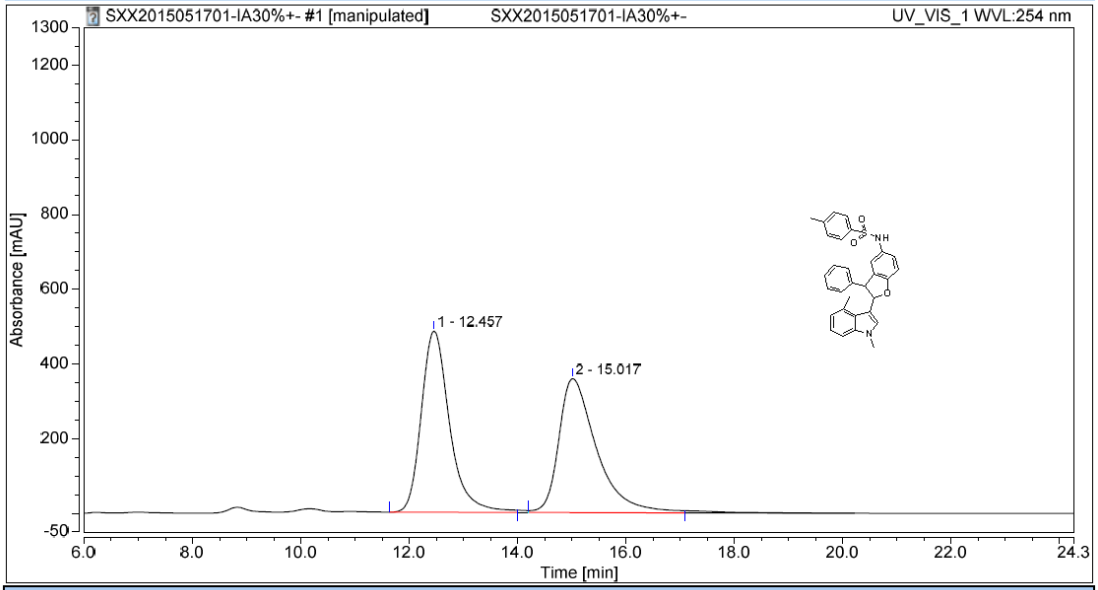


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.853	287.298	451.246	92.88	95.39	n.a.
2		16.913	22.033	21.791	7.12	4.61	n.a.
Total:			**309.331**	**473.037**	**100.00**	**100.00**	

3ba

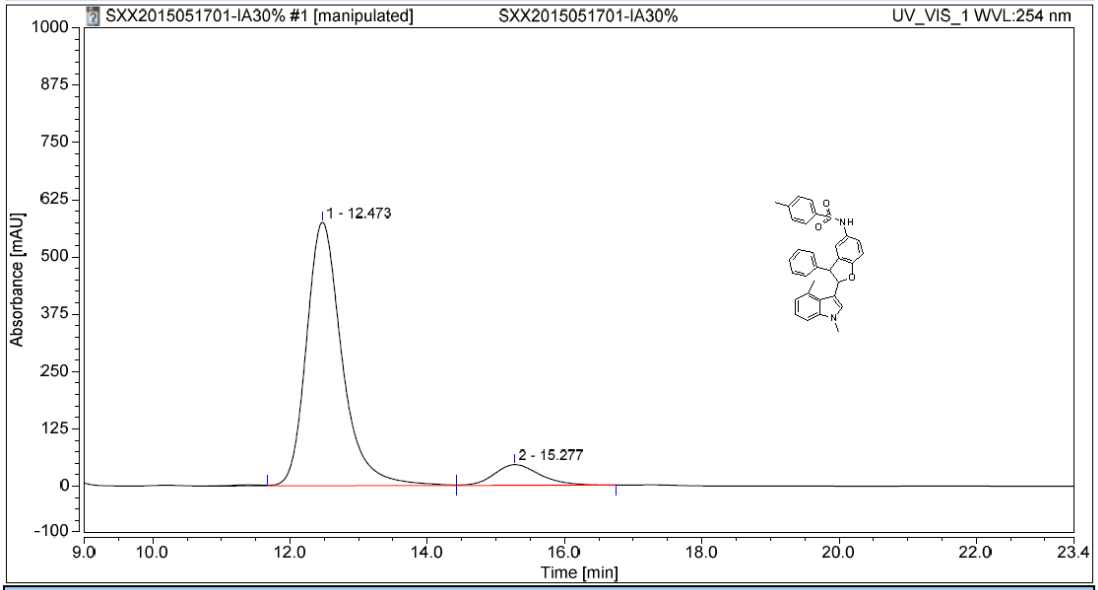
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.457	293.958	485.088	50.38	57.48	n.a.
2		15.017	289.473	358.833	49.62	42.52	n.a.
Total:			**583.431**	**843.920**	**100.00**	**100.00**	

Chromatogram

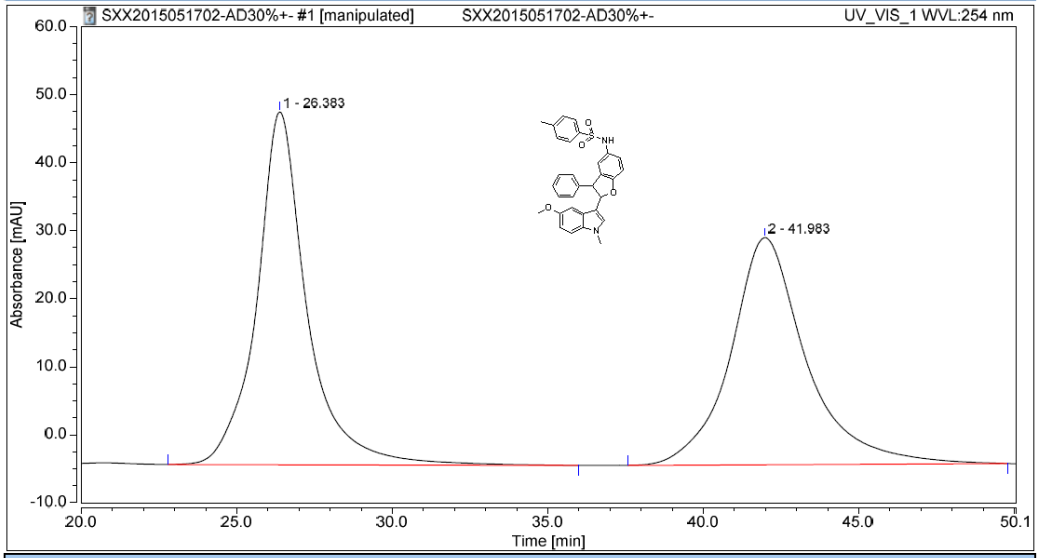


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.473	344.311	574.761	90.79	92.71	n.a.
2		15.277	34.937	45.184	9.21	7.29	n.a.
Total:			**379.247**	**619.945**	**100.00**	**100.00**	

3ca

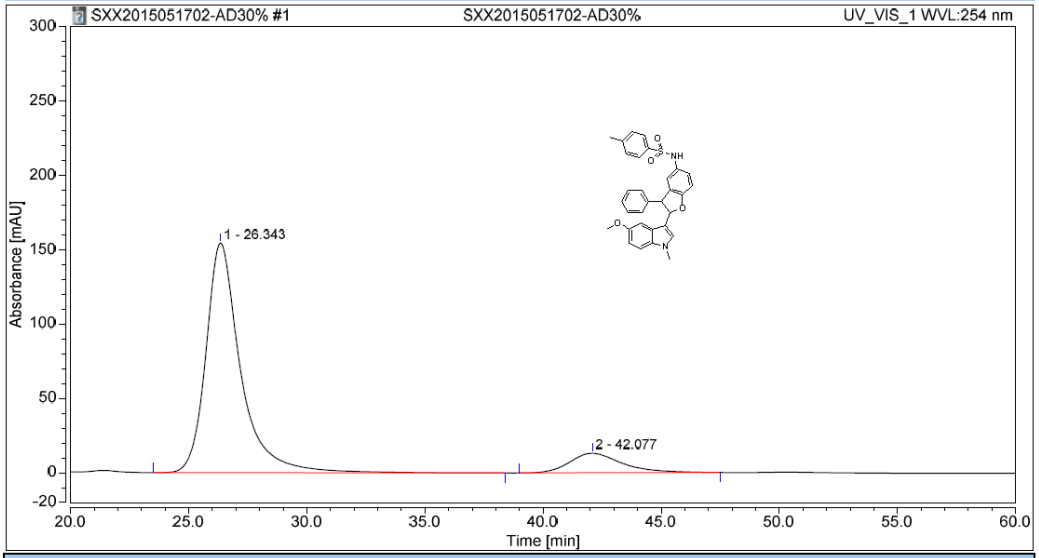
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.383	97.218	51.881	50.79	60.84	n.a.
2		41.983	94.198	33.397	49.21	39.16	n.a.
Total:			**191.417**	**85.278**	**100.00**	**100.00**	

Chromatogram

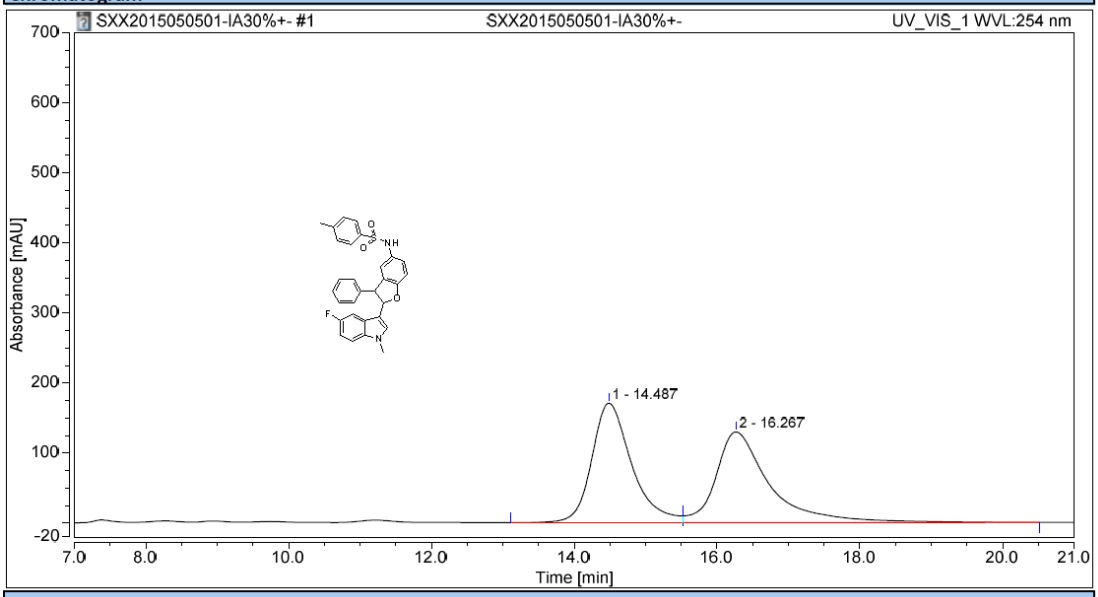


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.343	263.106	154.316	88.61	92.16	n.a.
2		42.077	33.822	13.125	11.39	7.84	n.a.
Total:			**296.927**	**167.441**	**100.00**	**100.00**	

3da

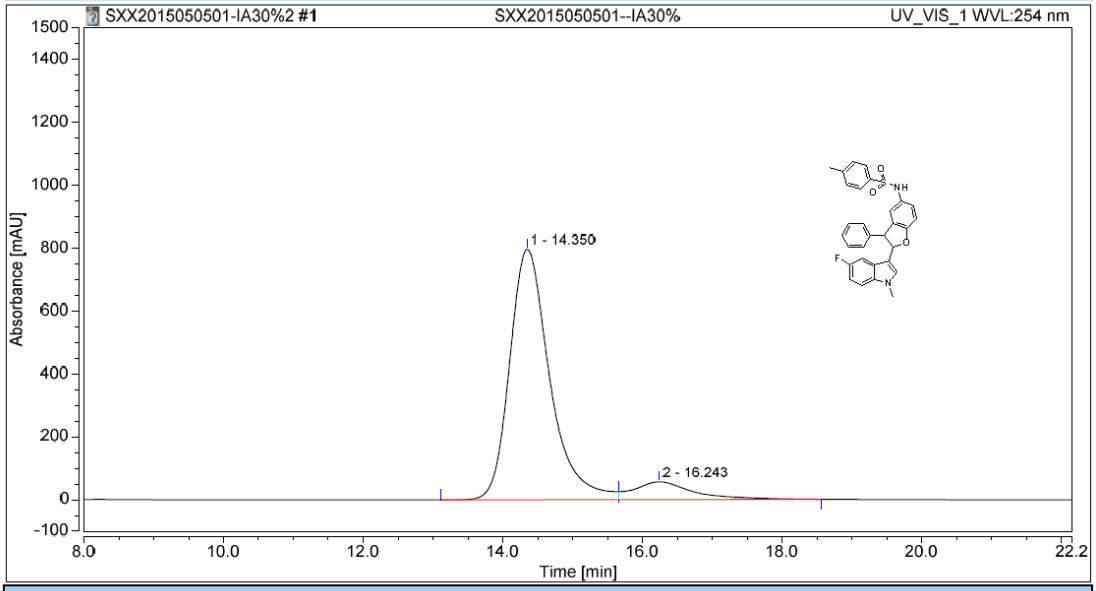
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.487	110.566	170.583	49.57	56.84	n.a.
2		16.267	112.465	129.514	50.43	43.16	n.a.
Total:			**223.031**	**300.097**	**100.00**	**100.00**	

Chromatogram

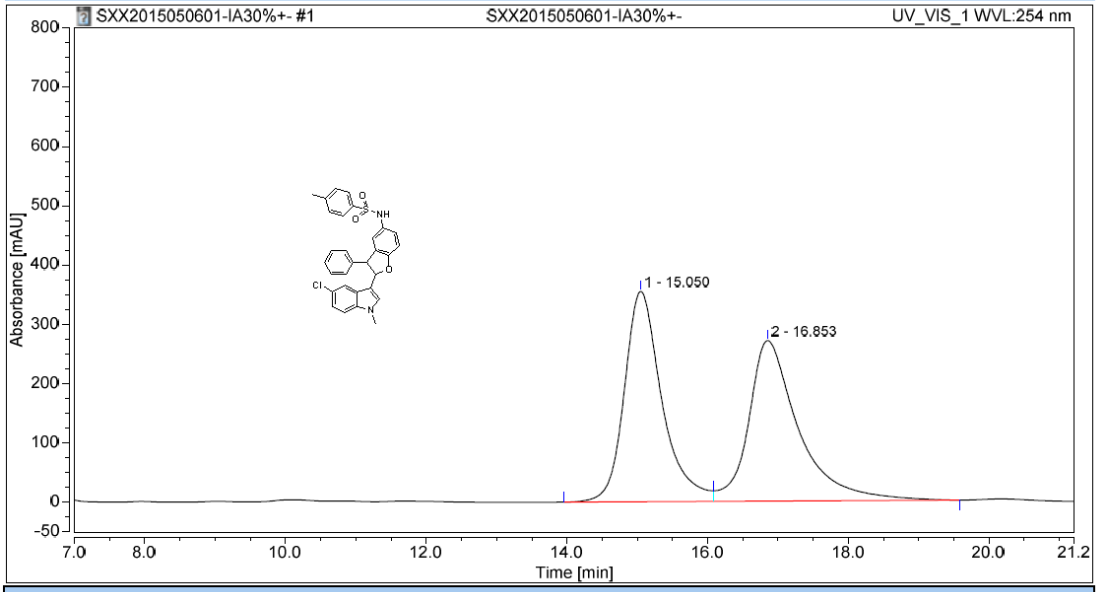


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.350	527.621	795.562	90.52	93.39	n.a.
2		16.243	55.258	56.298	9.48	6.61	n.a.
Total:			**582.879**	**851.860**	**100.00**	**100.00**	

3ea

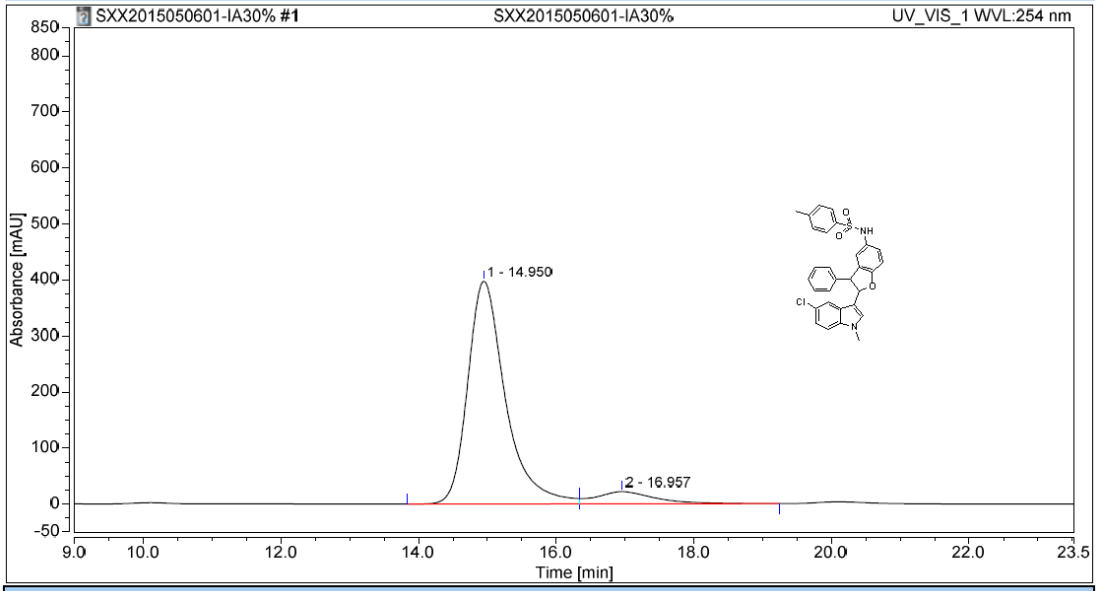
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.050	219.043	354.637	49.72	56.72	n.a.
2		16.853	221.548	270.621	50.28	43.28	n.a.
Total:			**440.591**	**625.258**	**100.00**	**100.00**	

Chromatogram

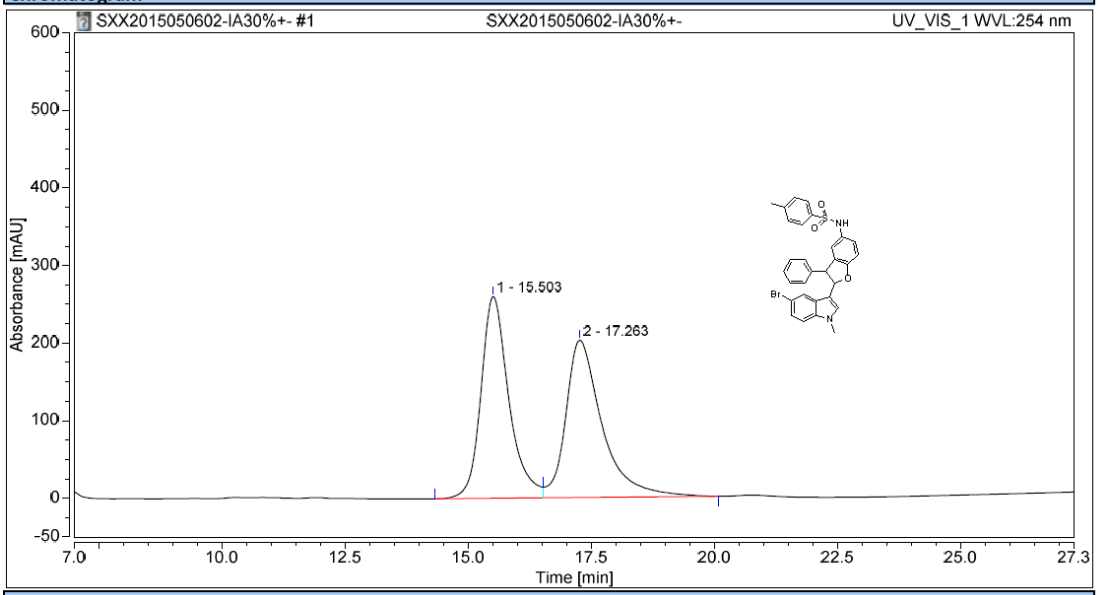


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.950	252.843	397.617	92.15	94.80	n.a.
2		16.957	21.548	21.815	7.85	5.20	n.a.
Total:			**274.391**	**419.432**	**100.00**	**100.00**	

3fa

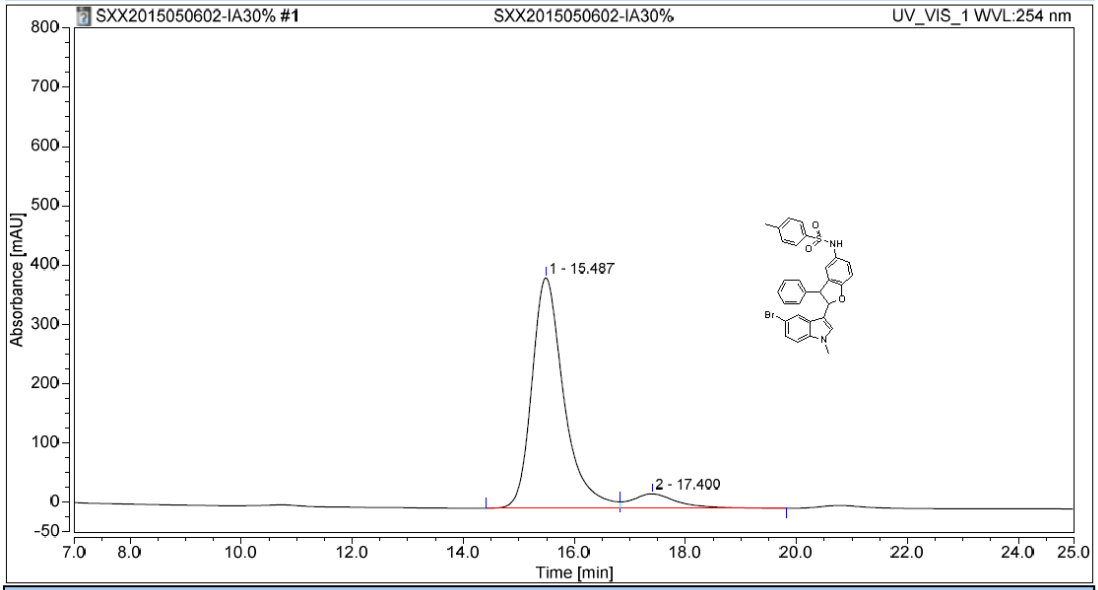
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.503	170.688	259.959	49.62	56.16	n.a.
2		17.263	173.304	202.896	50.38	43.84	n.a.
Total:			**343.992**	**462.854**	**100.00**	**100.00**	

Chromatogram

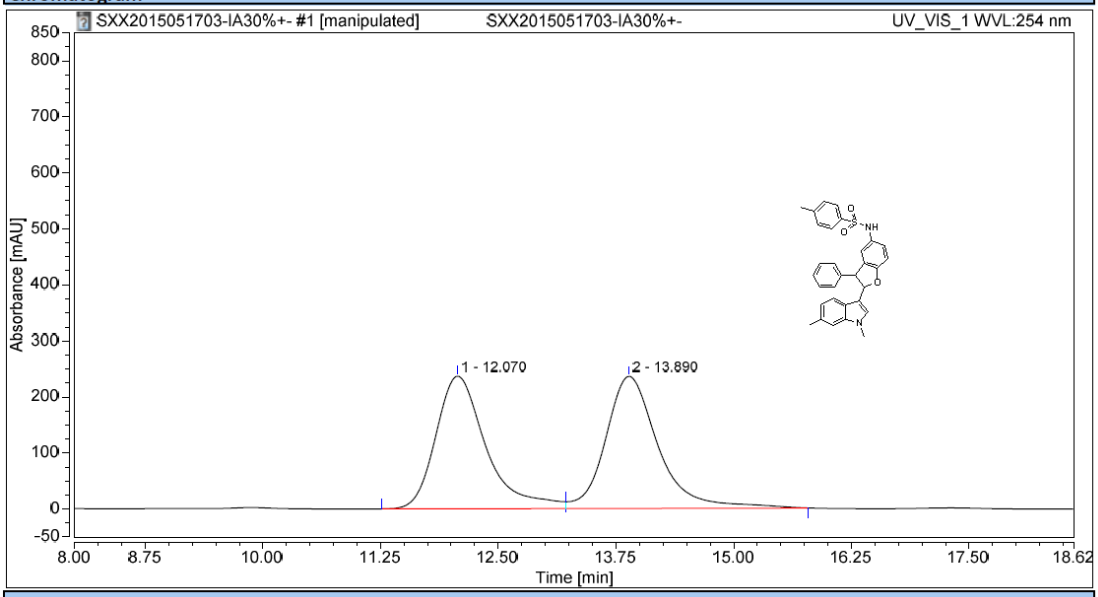


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.487	259.117	388.422	91.91	94.11	n.a.
2		17.400	22.813	24.324	8.09	5.89	n.a.
Total:			**281.930**	**412.746**	**100.00**	**100.00**	

3ga

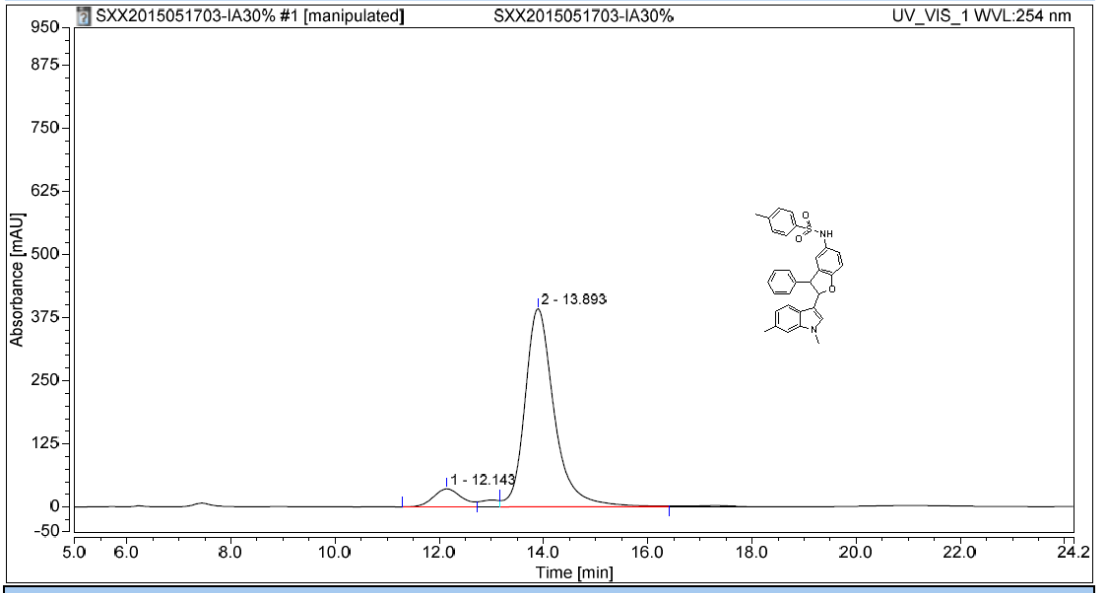
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.070	146.475	236.706	49.06	50.12	n.a.
2		13.890	152.096	235.559	50.94	49.88	n.a.
Total:			**298.571**	**472.265**	**100.00**	**100.00**	

Chromatogram

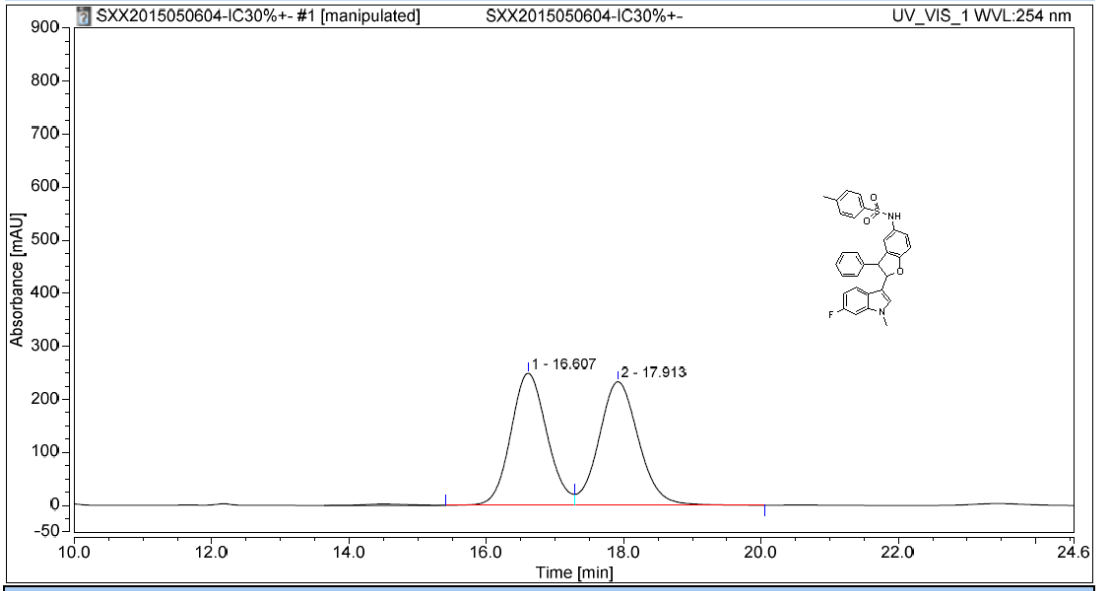


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.143	22.313	35.535	8.02	8.30	n.a.
2		13.893	255.878	392.706	91.98	91.70	n.a.
Total:			**278.191**	**428.241**	**100.00**	**100.00**	

3ha

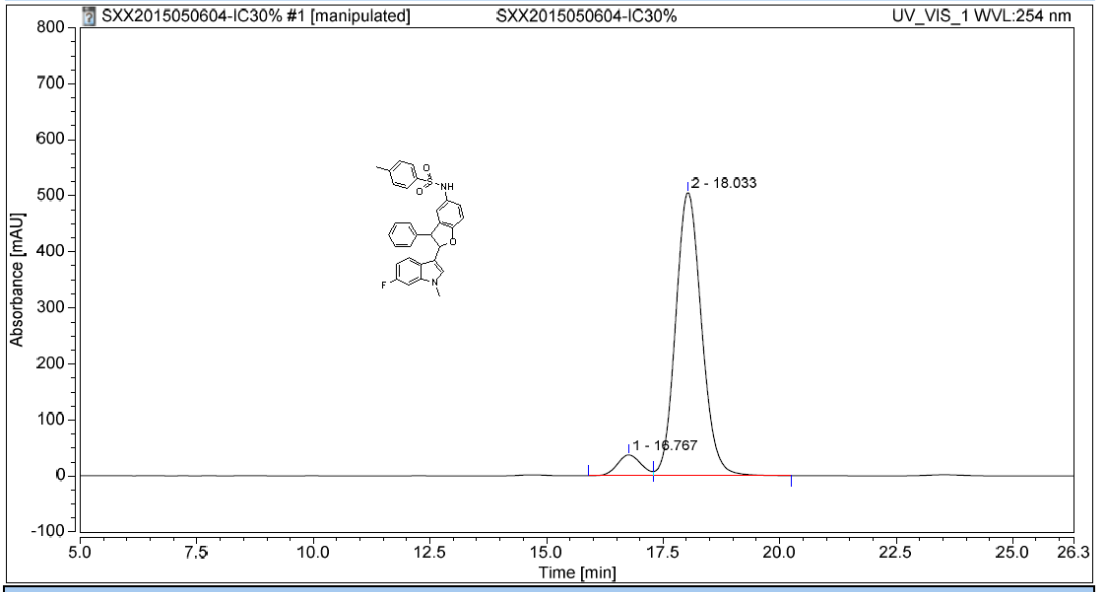
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.607	151.905	249.090	49.40	51.67	n.a.
2		17.913	155.580	232.986	50.60	48.33	n.a.
Total:			**307.486**	**482.076**	**100.00**	**100.00**	

Chromatogram

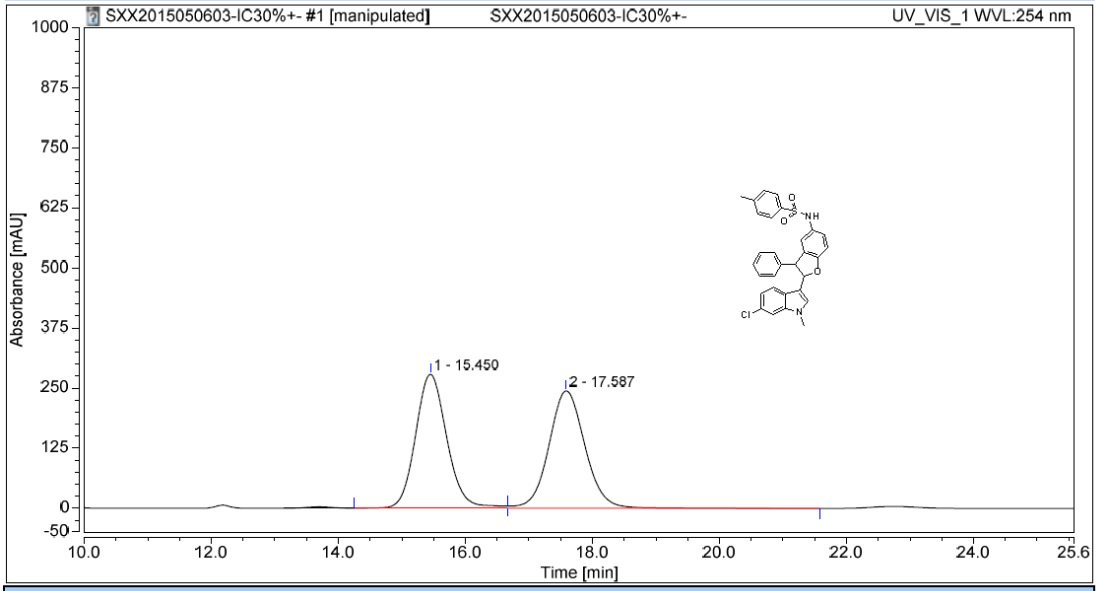


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.767	21.799	37.214	6.28	6.86	n.a.
2		18.033	325.120	505.405	93.72	93.14	n.a.
Total:			**346.919**	**542.619**	**100.00**	**100.00**	

3ia

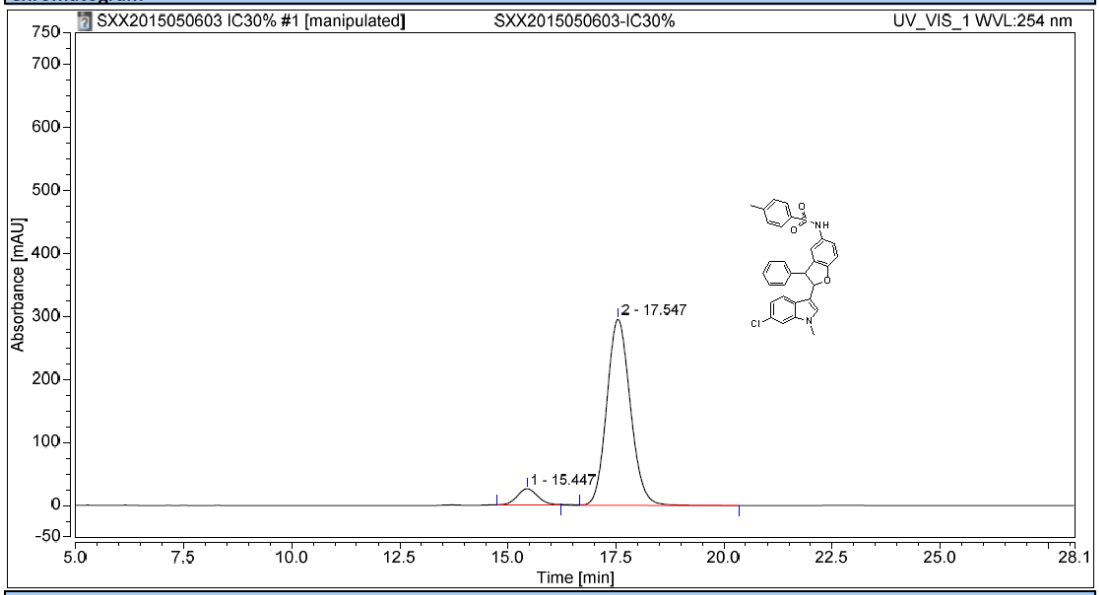
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.450	159.199	278.959	49.70	53.29	n.a.
2		17.587	161.135	244.551	50.30	46.71	n.a.
Total:			**320.334**	**523.511**	**100.00**	**100.00**	

Chromatogram

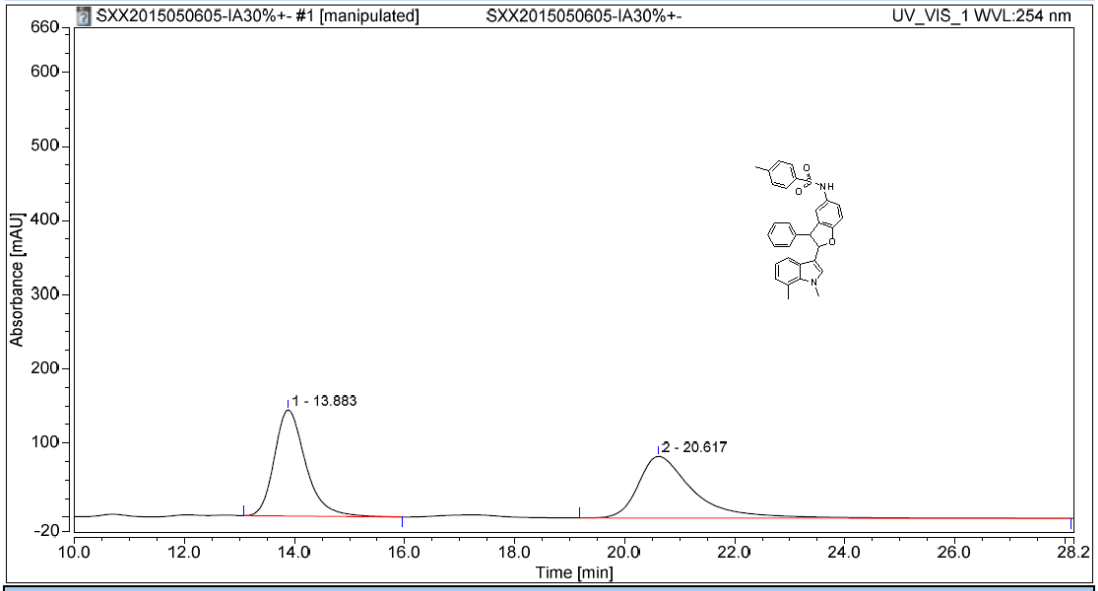


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.447	14.670	25.910	7.30	8.07	n.a.
2		17.547	186.213	295.057	92.70	91.93	n.a.
Total:			**200.883**	**320.967**	**100.00**	**100.00**	

3ja

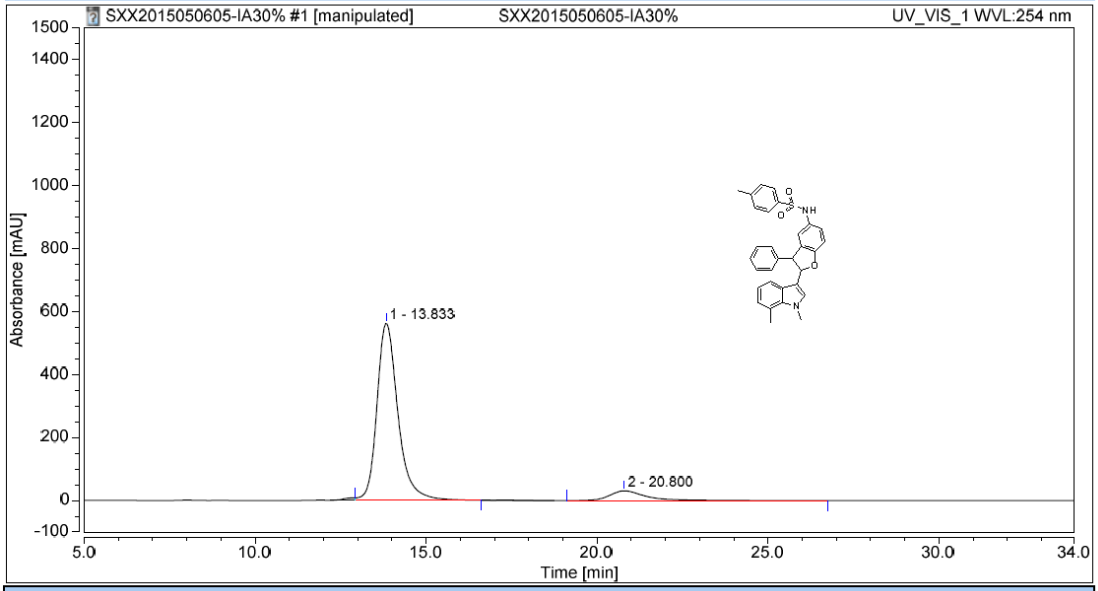
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.883	94.579	143.082	49.47	63.24	n.a.
2		20.617	96.625	83.164	50.53	36.76	n.a.
Total:			**191.204**	**226.246**	**100.00**	**100.00**	

Chromatogram

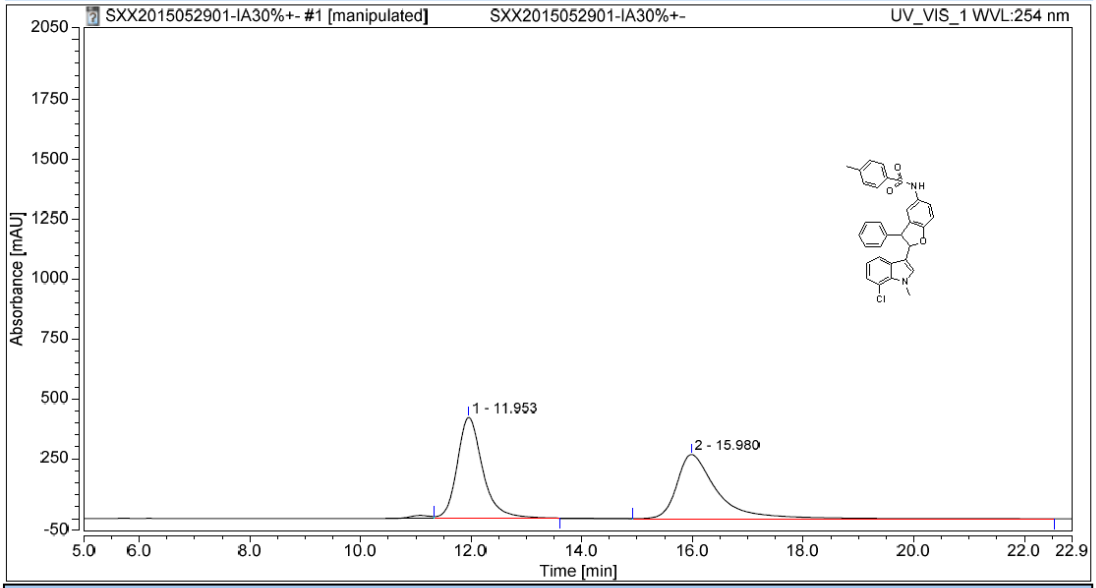


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.833	400.877	561.810	91.27	94.85	n.a.
2		20.800	38.363	30.496	8.73	5.15	n.a.
Total:			**439.239**	**592.306**	**100.00**	**100.00**	

3ka

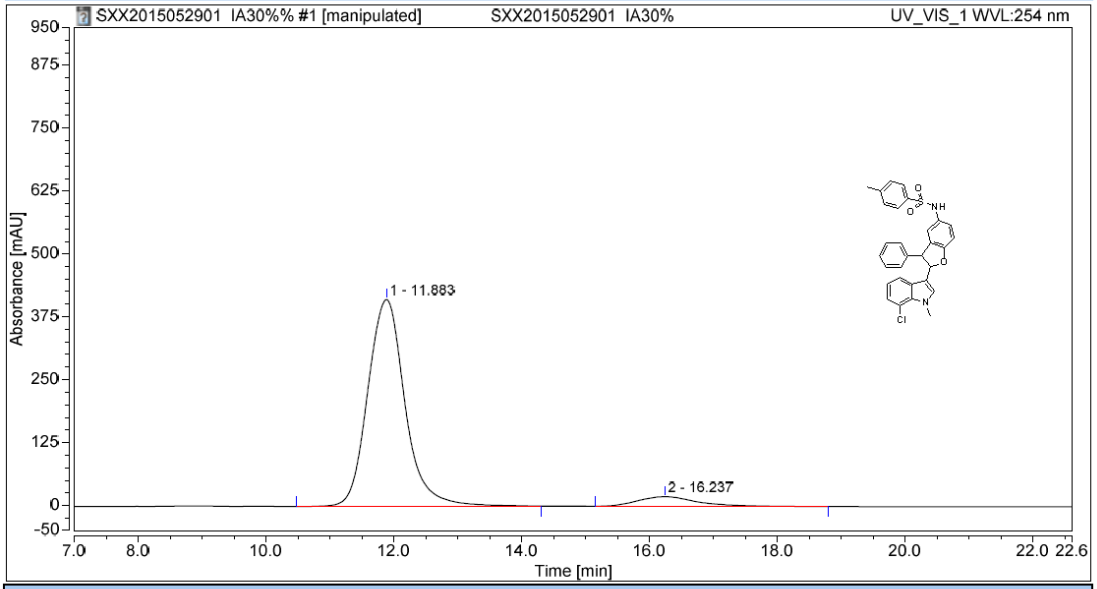
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.953	227.170	422.440	50.51	61.24	n.a.
2		15.980	222.590	267.385	49.49	38.76	n.a.
Total:			**449.759**	**689.825**	**100.00**	**100.00**	

Chromatogram

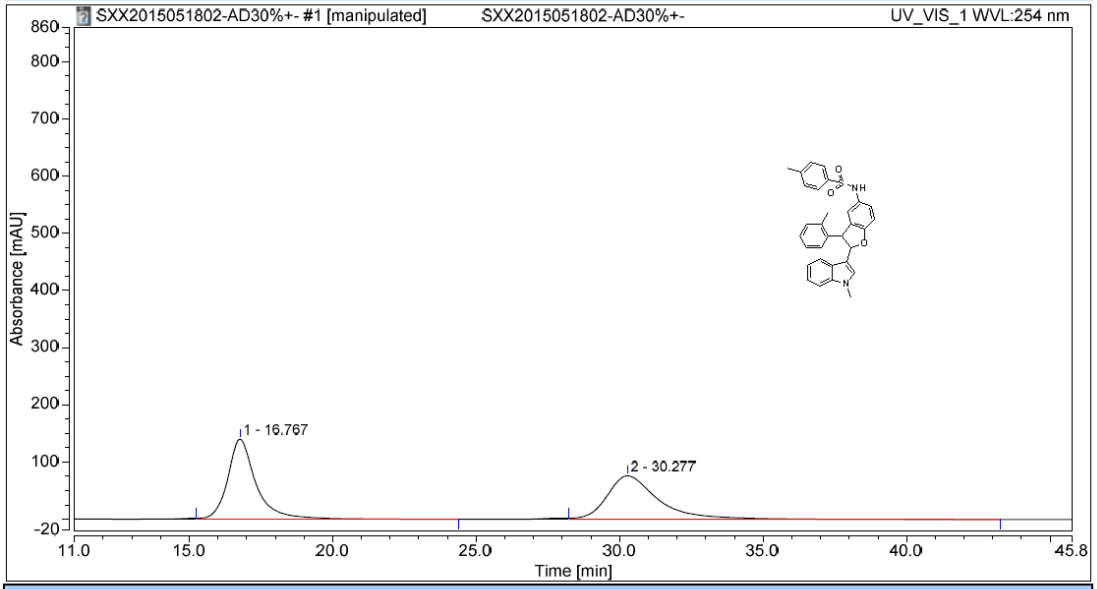


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.883	279.013	411.538	92.81	95.48	n.a.
2		16.237	21.626	19.489	7.19	4.52	n.a.
Total:			**300.638**	**431.027**	**100.00**	**100.00**	

3la

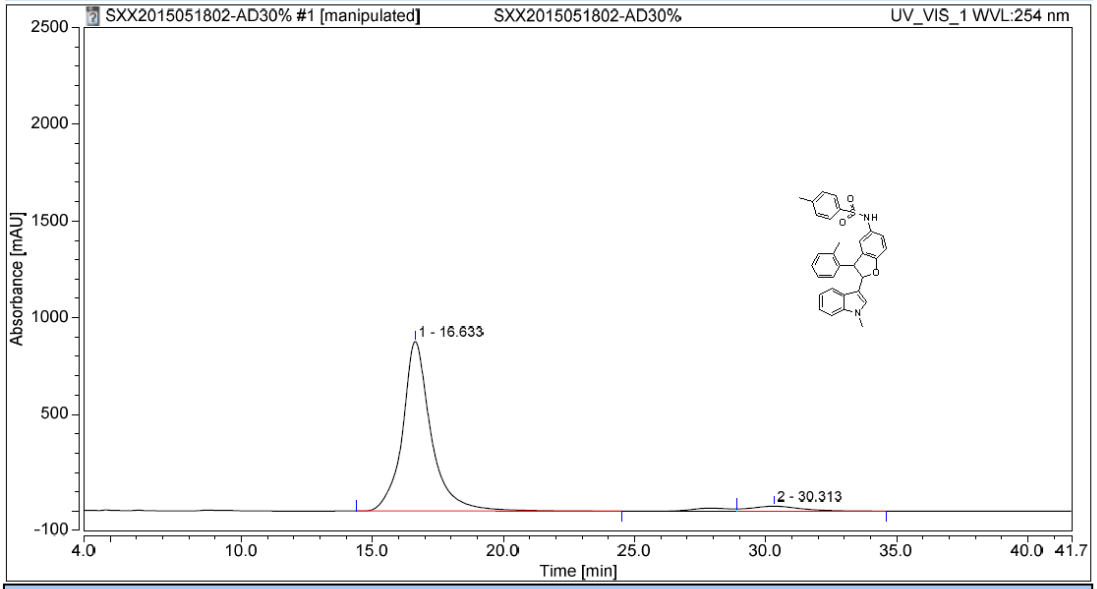
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.767	160.953	139.834	50.40	64.79	n.a.
2		30.277	158.371	75.986	49.60	35.21	n.a.
Total:			**319.324**	**215.820**	**100.00**	**100.00**	

Chromatogram

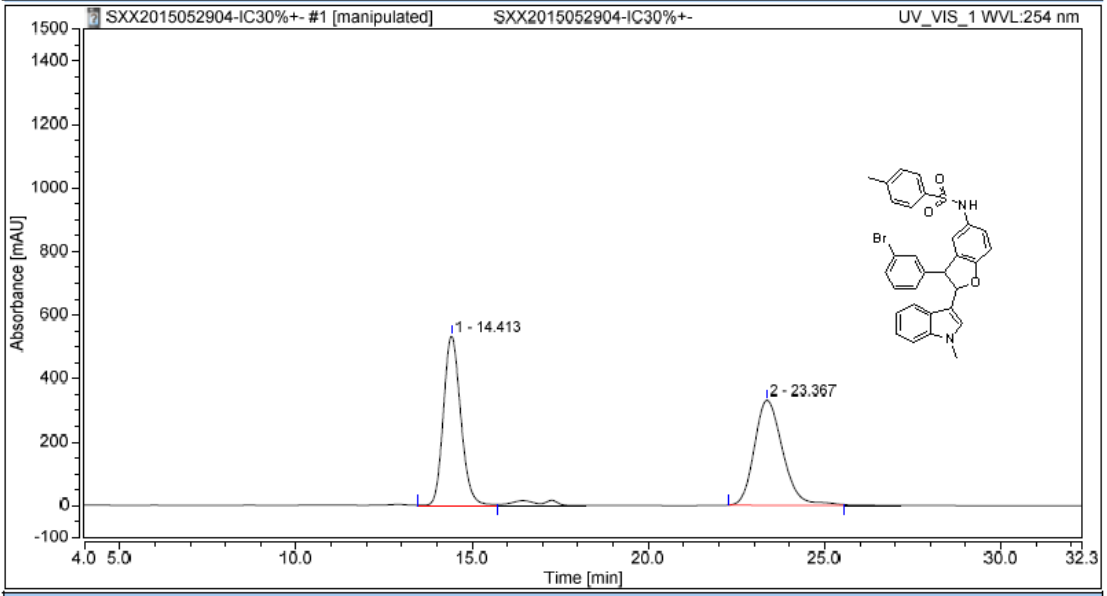


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.633	1109.946	877.131	95.14	97.16	n.a.
2		30.313	56.685	25.636	4.86	2.84	n.a.
Total:			**1166.631**	**902.768**	**100.00**	**100.00**	

3ma

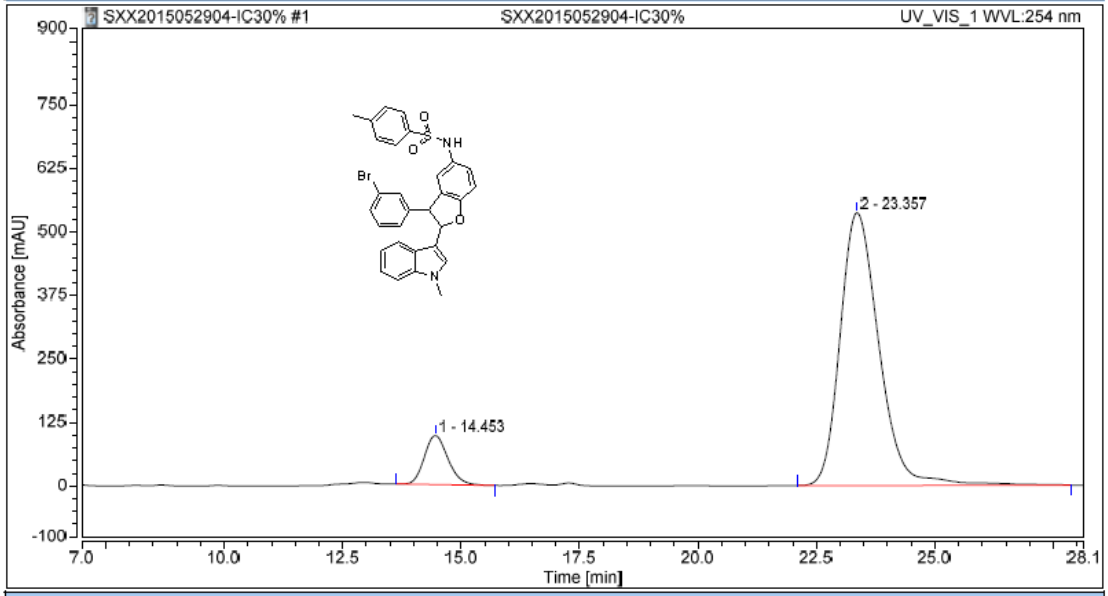
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.413	303.126	533.995	49.58	61.75	n.a.
2		23.367	308.258	330.824	50.42	38.25	n.a.
Total:			**611.383**	**864.819**	**100.00**	**100.00**	

Chromatogram

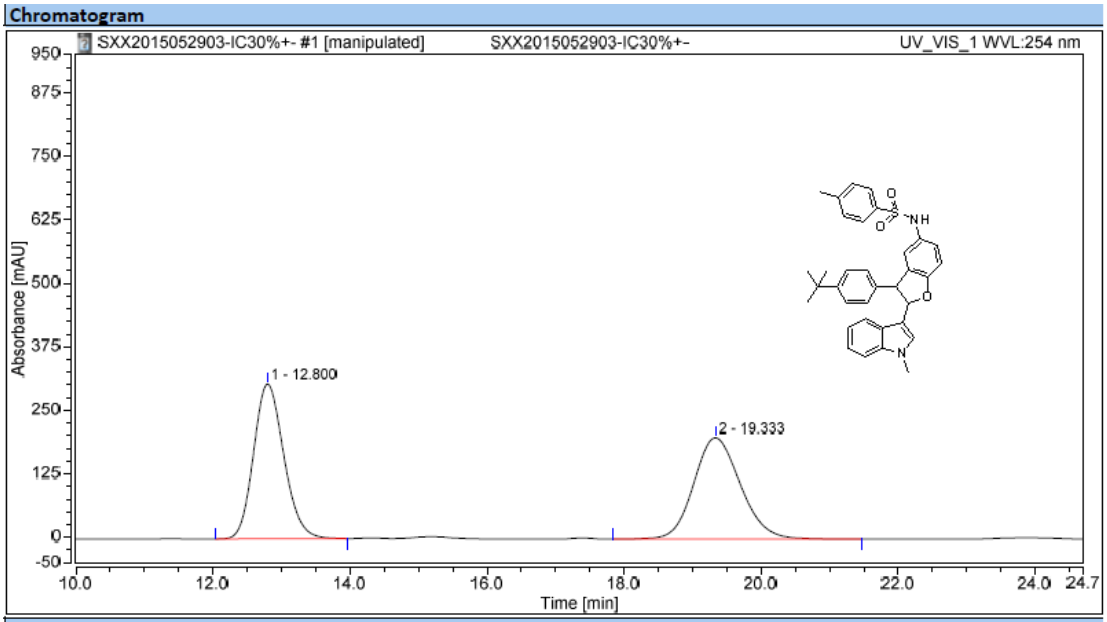


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.453	56.000	96.622	9.88	15.25	n.a.
2		23.357	510.960	536.973	90.12	84.75	n.a.
Total:			**566.960**	**633.595**	**100.00**	**100.00**	

3na

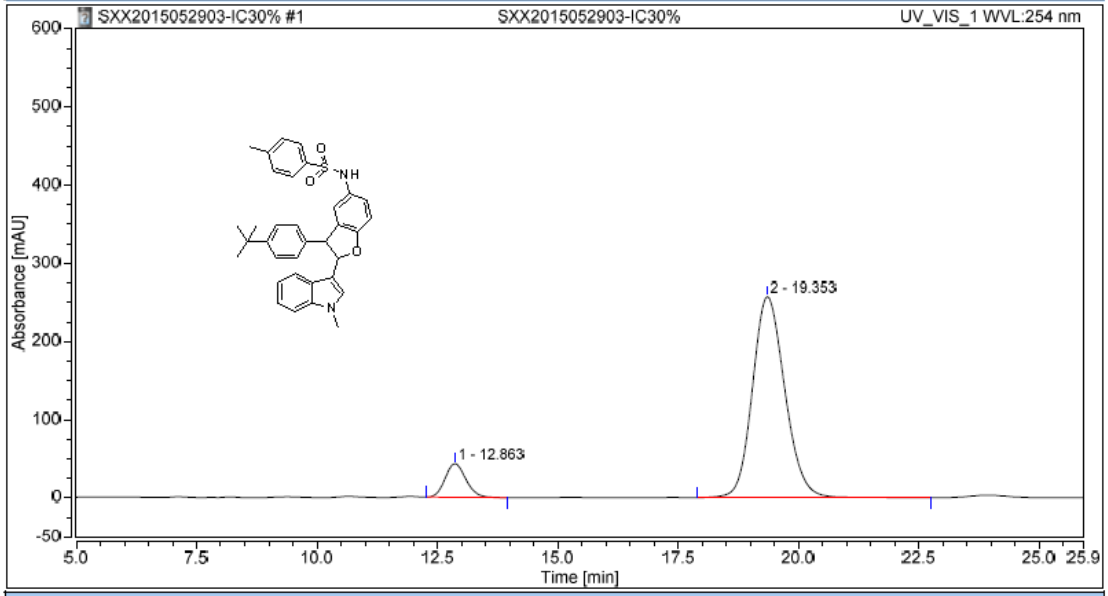
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.800	155.754	304.777	49.77	60.47	n.a.
2		19.333	157.169	199.217	50.23	39.53	n.a.
Total:			**312.923**	**503.995**	**100.00**	**100.00**	

Chromatogram

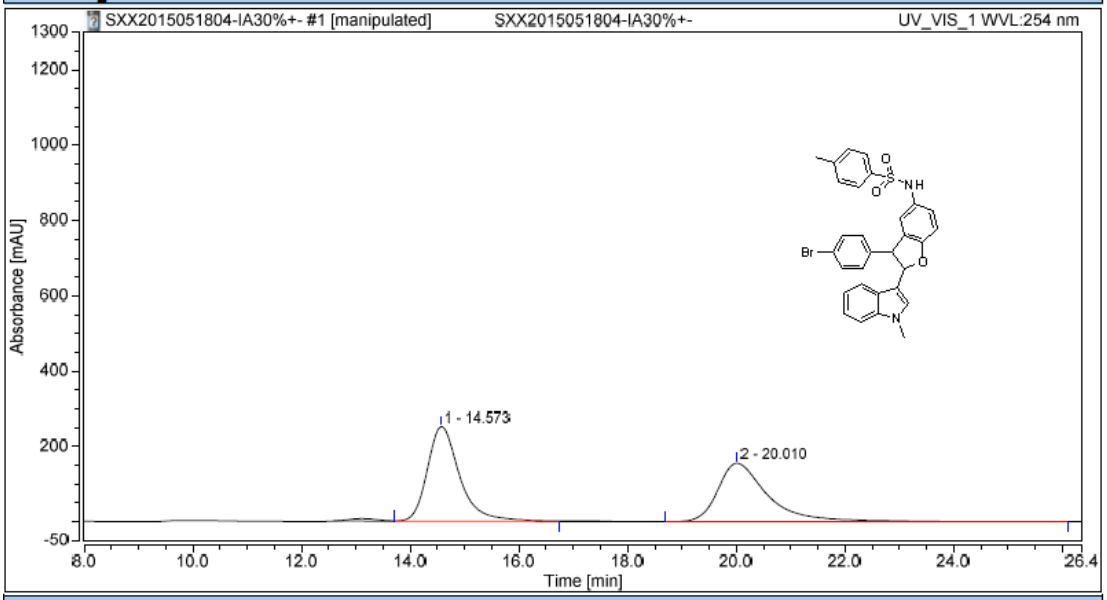


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.863	21.405	42.868	9.64	14.29	n.a.
2		19.353	200.712	257.072	90.36	85.71	n.a.
Total:			**222.117**	**299.941**	**100.00**	**100.00**	

3oa

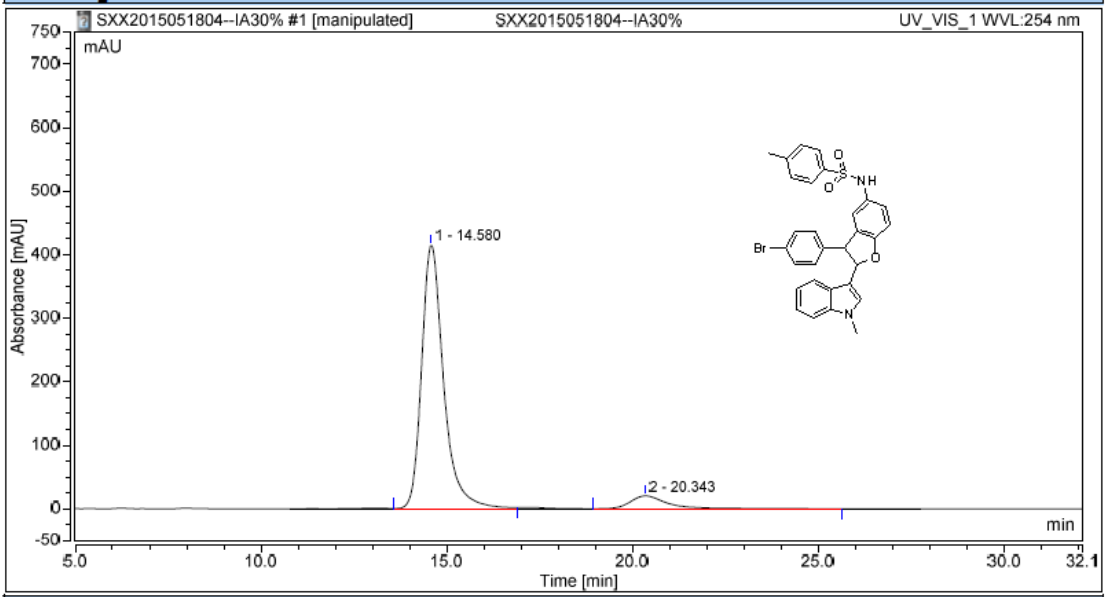
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.573	174.047	251.364	51.13	61.81	n.a.
2		20.010	166.380	155.300	48.87	38.19	n.a.
Total:			340.427	406.664	100.00	100.00	

Chromatogram

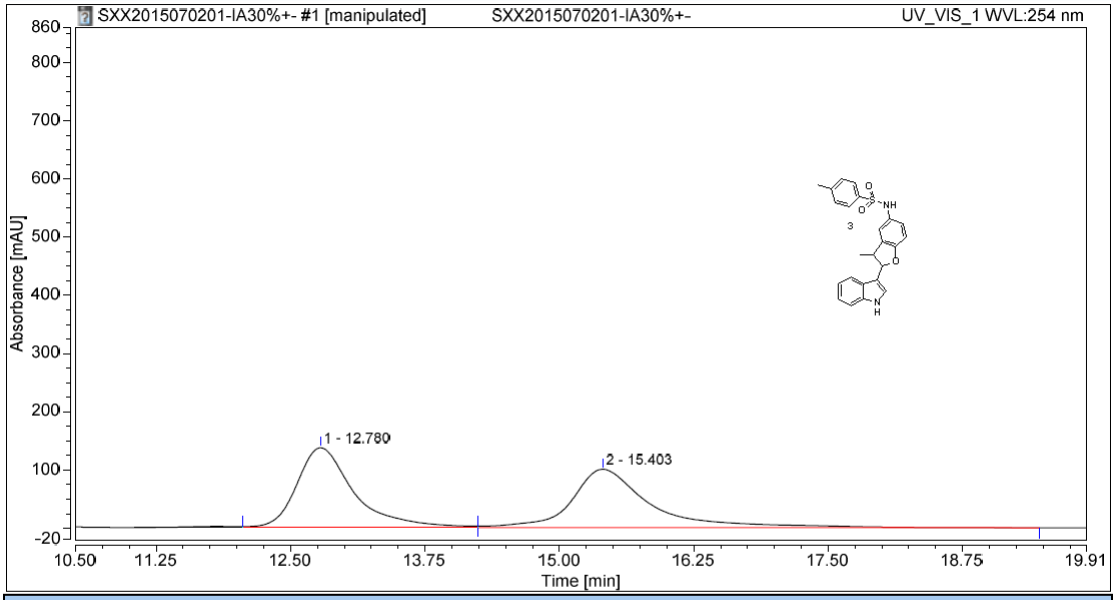


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.580	285.597	415.438	92.24	95.36	n.a.
2		20.343	24.017	20.225	7.76	4.64	n.a.
Total:			309.615	435.664	100.00	100.00	

3pa

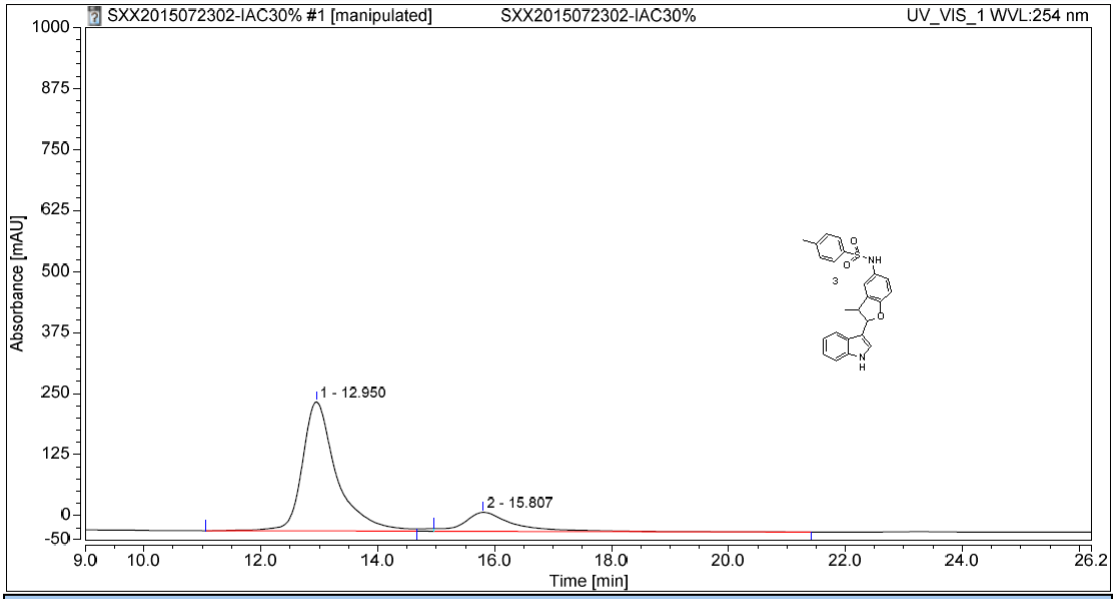
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.780	84.171	137.014	49.83	57.77	n.a.
2		15.403	84.742	100.148	50.17	42.23	n.a.
Total:			**168.914**	**237.162**	**100.00**	**100.00**	

Chromatogram

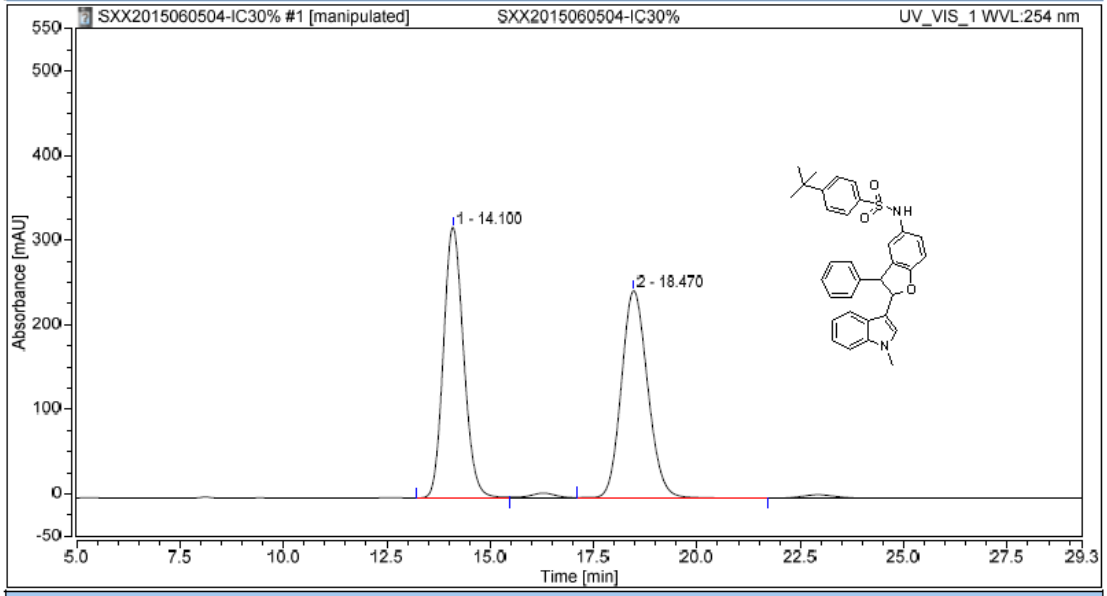


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.950	180.180	264.583	82.46	87.20	n.a.
2		15.807	38.336	38.826	17.54	12.80	n.a.
Total:			**218.517**	**303.409**	**100.00**	**100.00**	

3ab

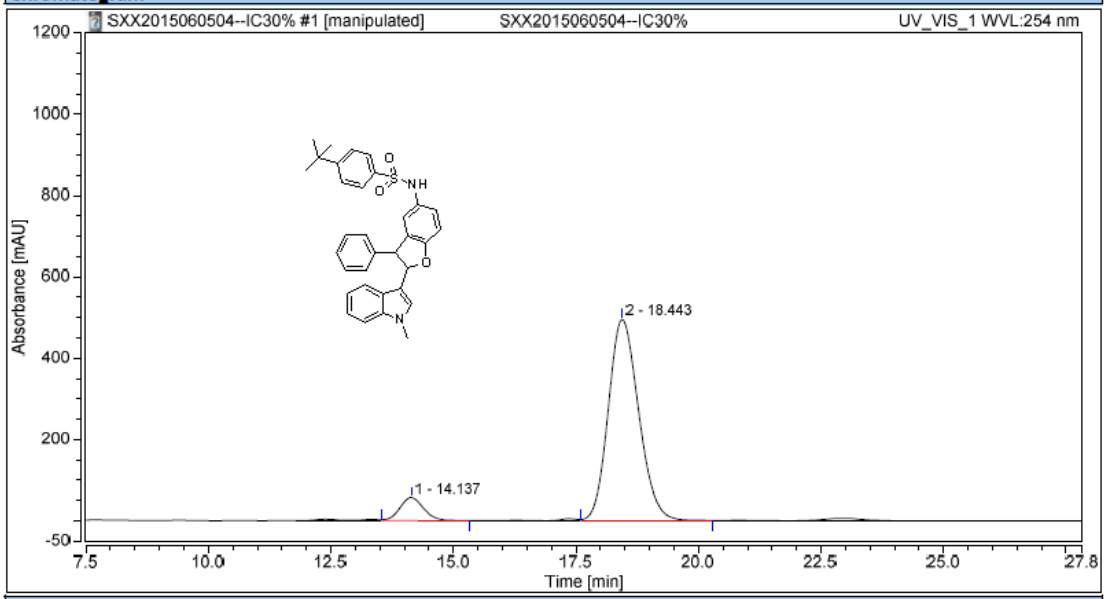
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.100	180.557	319.877	49.88	56.60	n.a.
2		18.470	181.416	245.239	50.12	43.40	n.a.
Total:			**361.973**	**565.116**	**100.00**	**100.00**	

Chromatogram

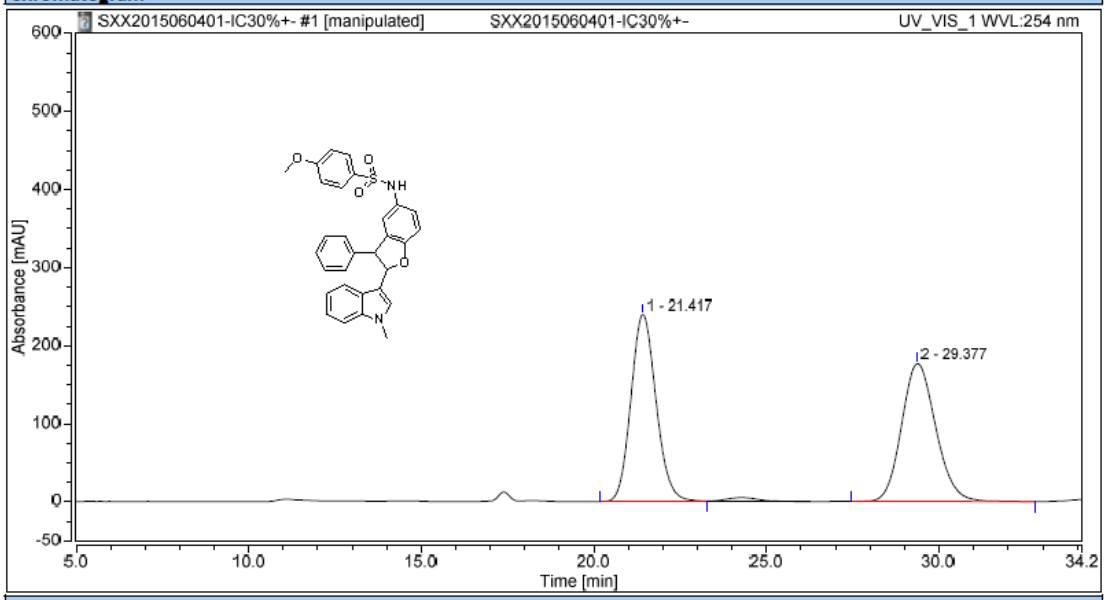


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.137	32.095	56.843	8.26	10.30	n.a.
2		18.443	356.326	495.014	91.74	89.70	n.a.
Total:			**388.420**	**551.857**	**100.00**	**100.00**	

3ac

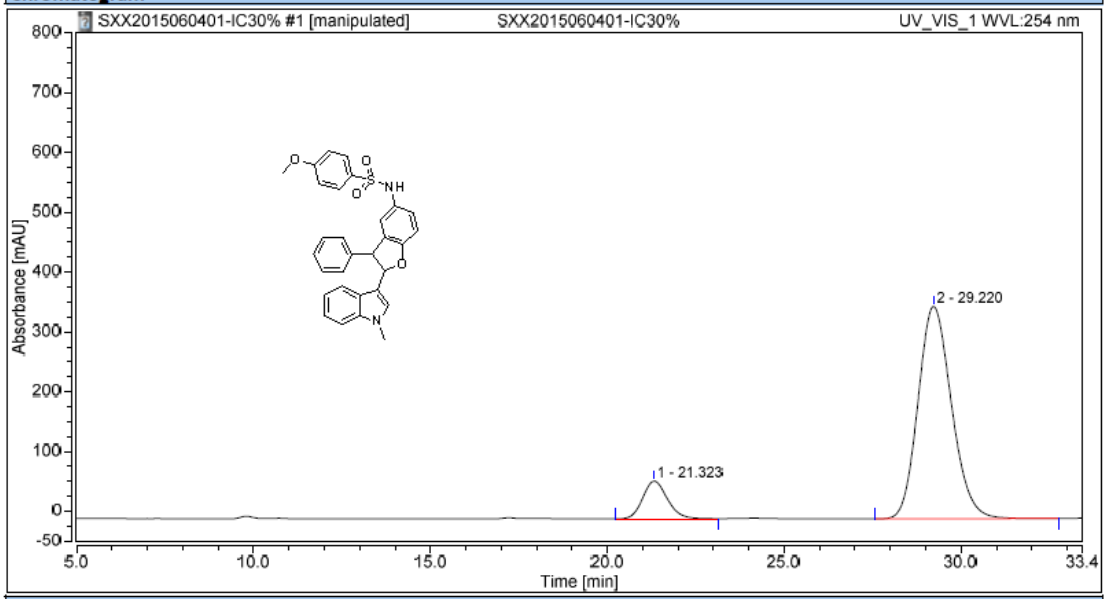
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.417	202.231	239.642	49.98	57.56	n.a.
2		29.377	202.401	176.681	50.02	42.44	n.a.
Total:			404.632	416.323	100.00	100.00	

Chromatogram

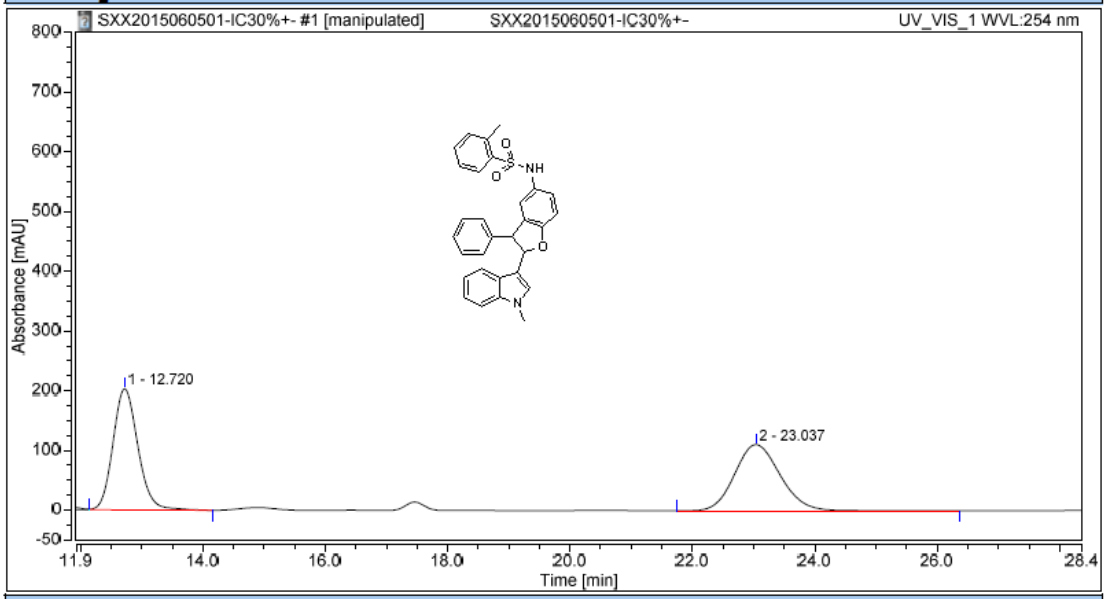


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.323	50.775	62.999	11.53	15.06	n.a.
2		29.220	389.720	355.288	88.47	84.94	n.a.
Total:			440.495	418.287	100.00	100.00	

3ad

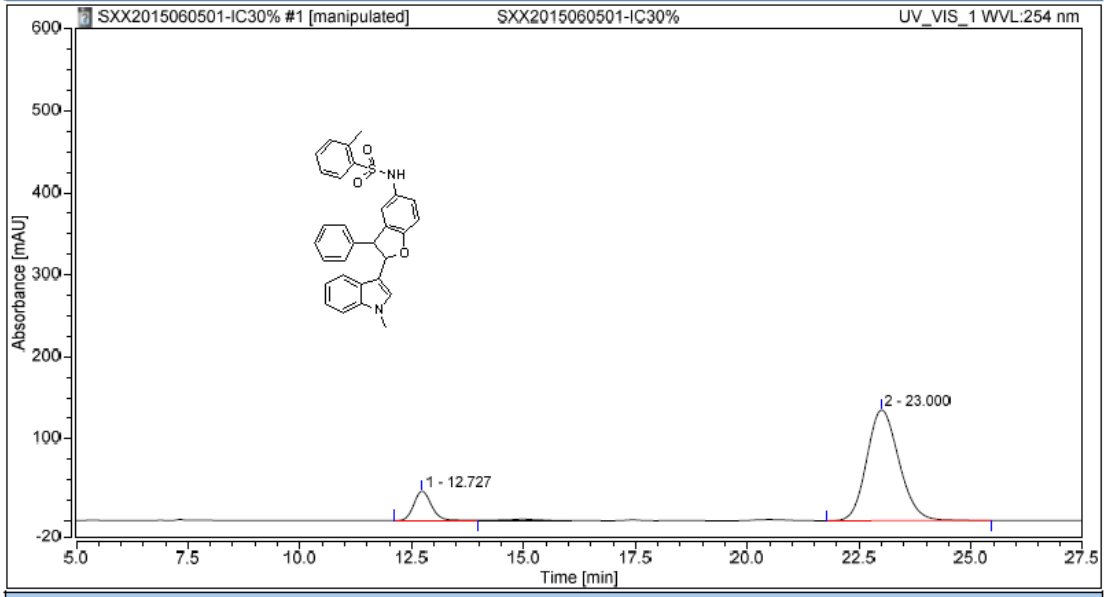
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.720	95.827	202.959	50.02	64.64	n.a.
2		23.037	95.763	111.014	49.98	35.36	n.a.
Total:			**191.590**	**313.974**	**100.00**	**100.00**	

Chromatogram

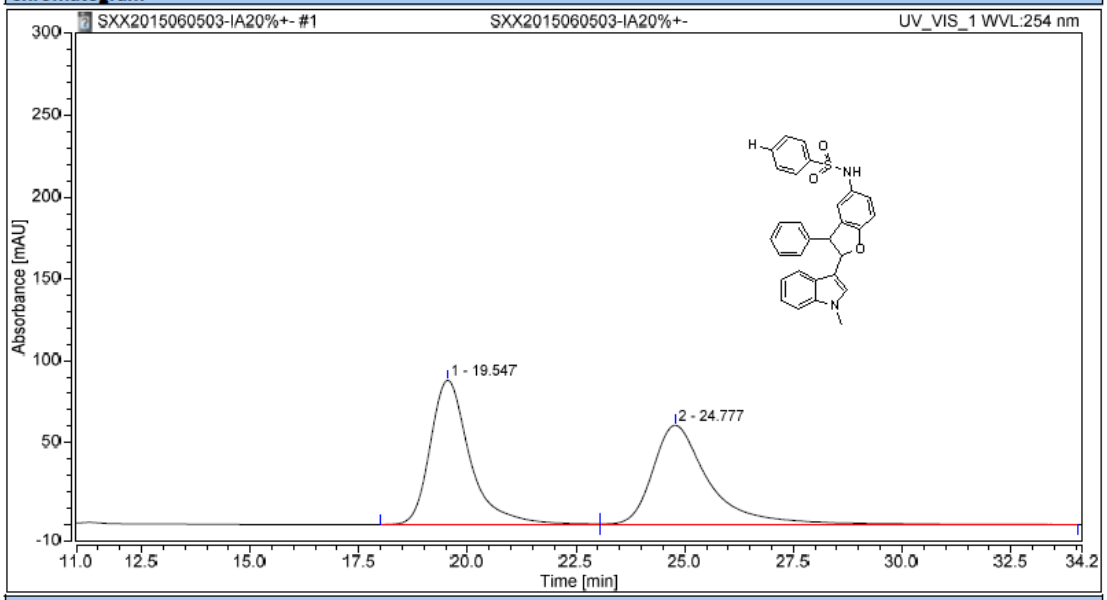


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.727	16.480	35.864	12.77	20.99	n.a.
2		23.000	112.578	135.020	87.23	79.01	n.a.
Total:			**129.058**	**170.883**	**100.00**	**100.00**	

3ae

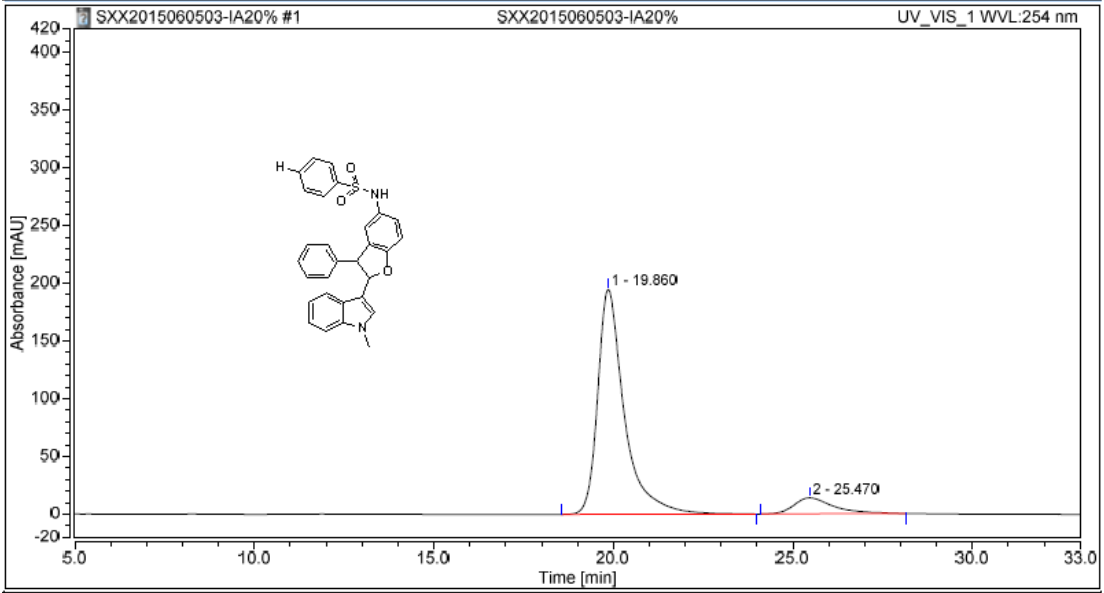
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.547	93.468	88.104	50.70	59.23	n.a.
2		24.777	90.883	60.644	49.30	40.77	n.a.
Total:			**184.351**	**148.747**	**100.00**	**100.00**	

Chromatogram

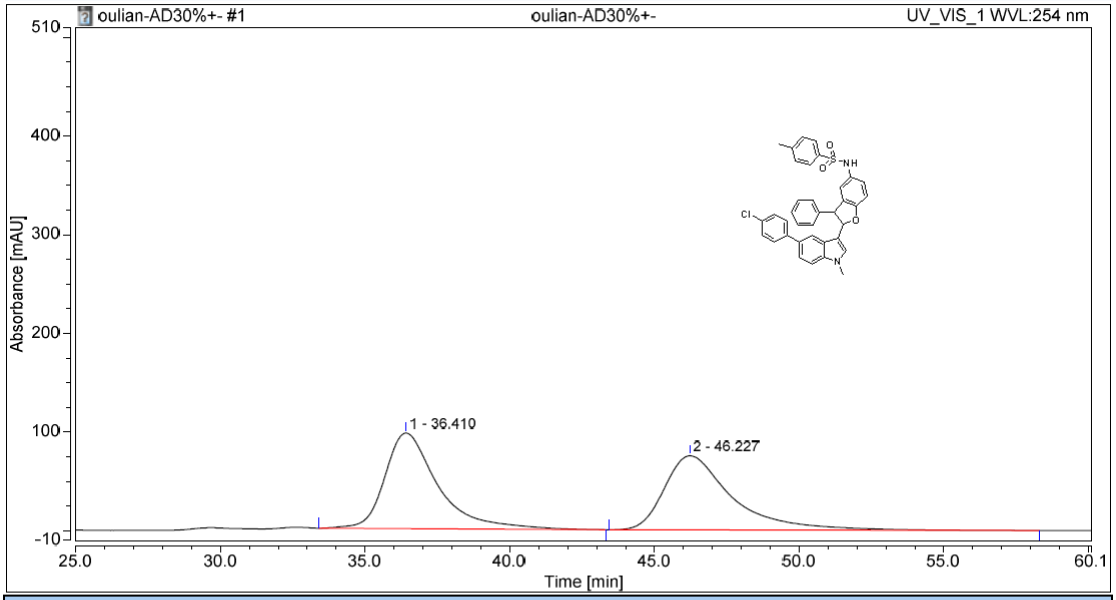


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.860	167.417	194.688	90.43	93.34	n.a.
2		25.470	17.714	13.886	9.57	6.66	n.a.
Total:			**185.131**	**208.574**	**100.00**	**100.00**	

Compound 7:

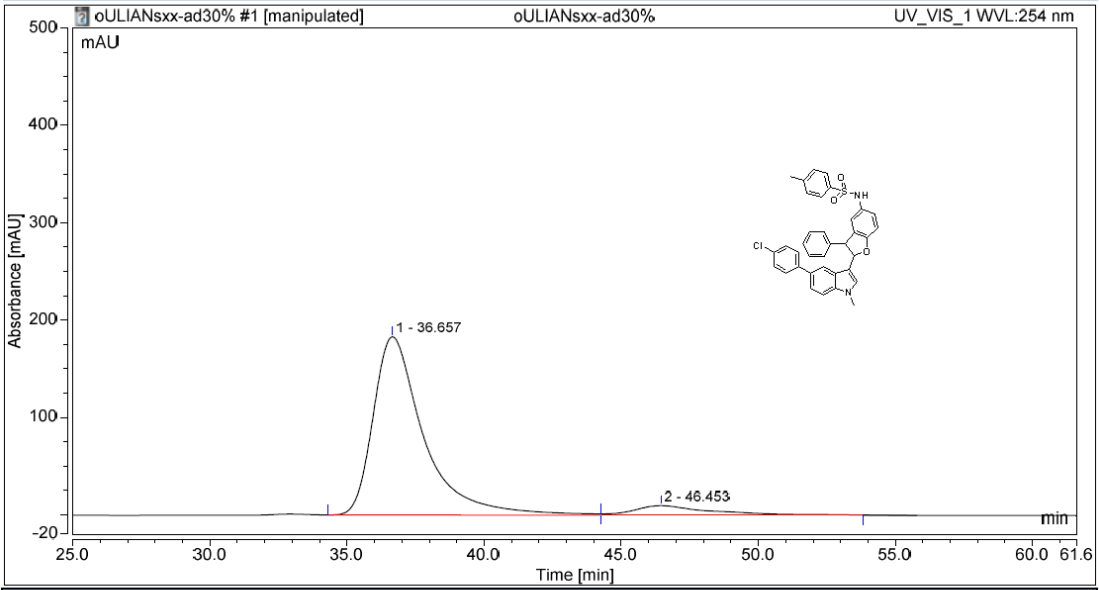
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		36.410	205.588	96.836	50.30	56.34	n.a.
2		46.227	203.135	75.027	49.70	43.66	n.a.
Total:			**408.723**	**171.863**	**100.00**	**100.00**	

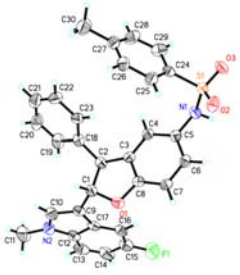
Chromatogram

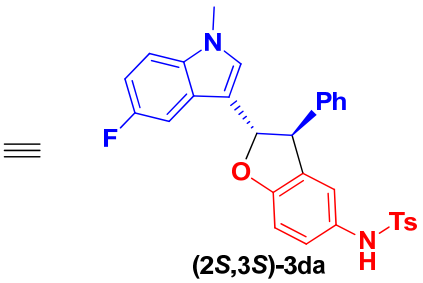


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		36.657	390.657	182.981	92.27	94.95	n.a.
2		46.453	32.718	9.733	7.73	5.05	n.a.
Total:			**423.375**	**192.714**	**100.00**	**100.00**	

9. X-ray single crystal data for compound 3da



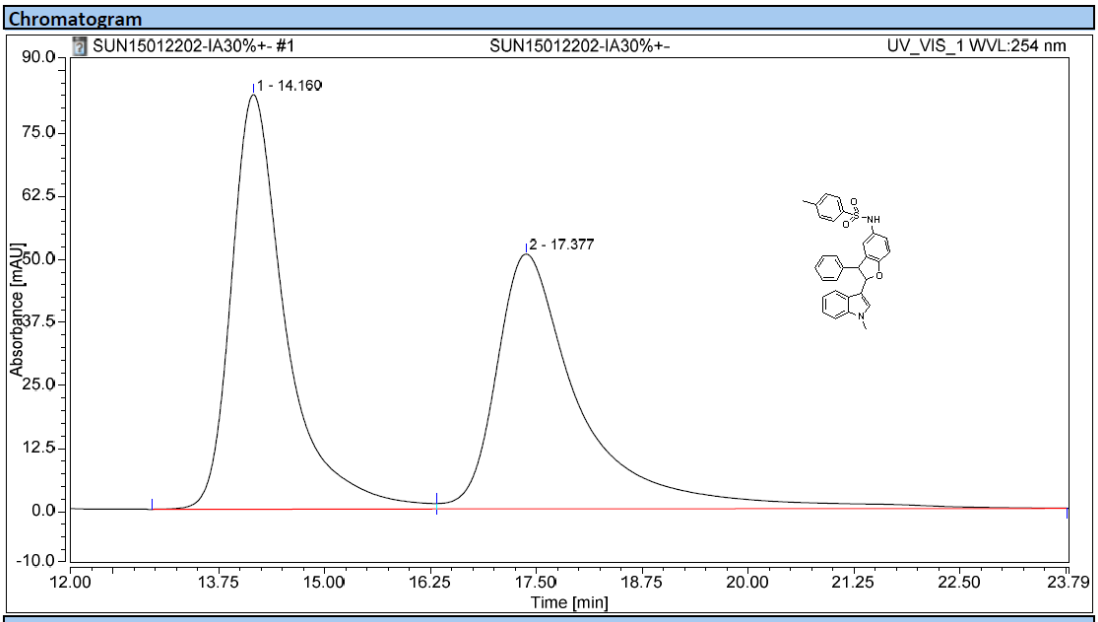


(2S,3S)-3da

Empirical formula	C30 H25 F N2 O3 S	
Formula weight	512.58	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 5.552(3) Å	α= 90°.
	b = 17.133(8) Å	β= 93.446(7)°.
	c = 13.413(6) Å	γ = 90°.
Volume	1273.7(11) $Å^3$	
Z	2	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.170 mm^{-1}	
F(000)	536	
Crystal size	0.31 x 0.3 x 0.25 mm^3	
Theta range for data collection	1.930 to 27.643°.	
Index ranges	-7<=h<=6, -22<=k<=21, -17<=l<=16	
Reflections collected	7137	
Independent reflections	5119 [R(int) = 0.0256]	
Completeness to theta = 26.000°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6064	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5119 / 1 / 337	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0785, wR2 = 0.2076	
R indices (all data)	R1 = 0.1099, wR2 = 0.2371	
Absolute structure parameter	0.03(7)	
Extinction coefficient	0.026(8)	
Largest diff. peak and hole	0.896 and -0.337 $e.Å^{-3}$	

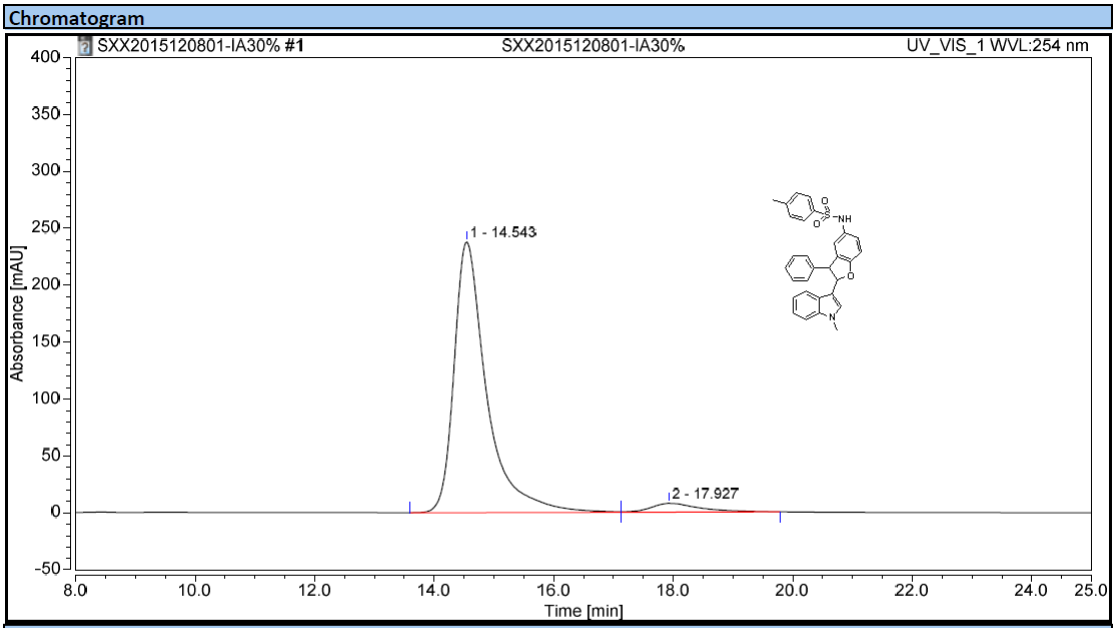
10. HPLC spectra of products 3 generated by large scale reactions

3aa (0.5 mmol scale)



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.160	61.261	82.230	51.16	61.93	n.a.
2		17.377	58.481	50.539	48.84	38.07	n.a.
Total:			**119.742**	**132.769**	**100.00**	**100.00**	

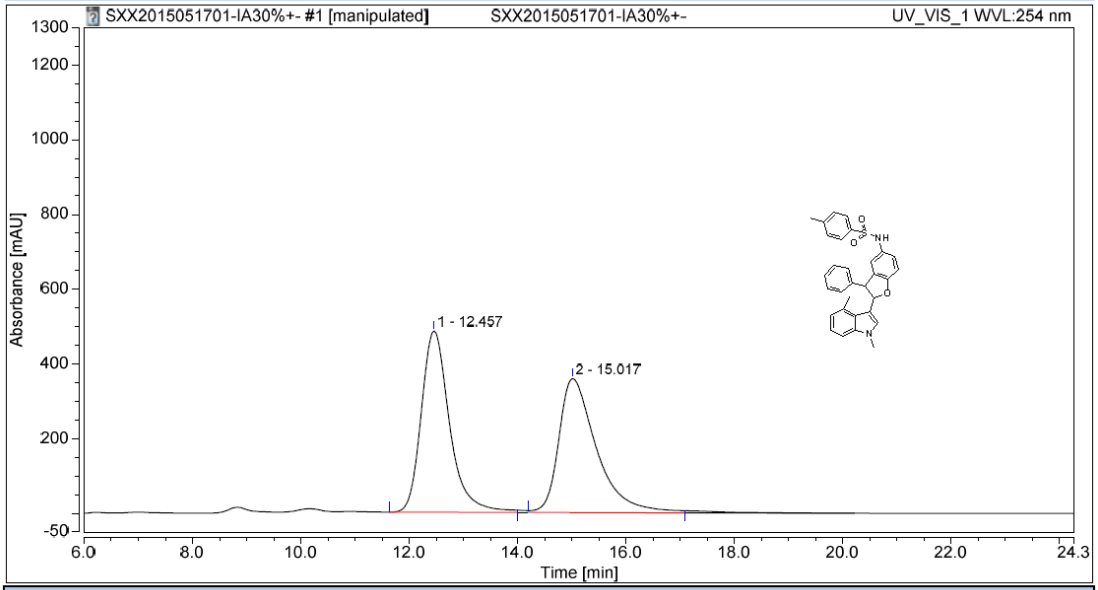


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.543	150.252	237.844	95.37	96.83	n.a.
2		17.927	7.294	7.774	4.63	3.17	n.a.
Total:			**157.546**	**245.619**	**100.00**	**100.00**	

3ba (0.5 mmol scale)

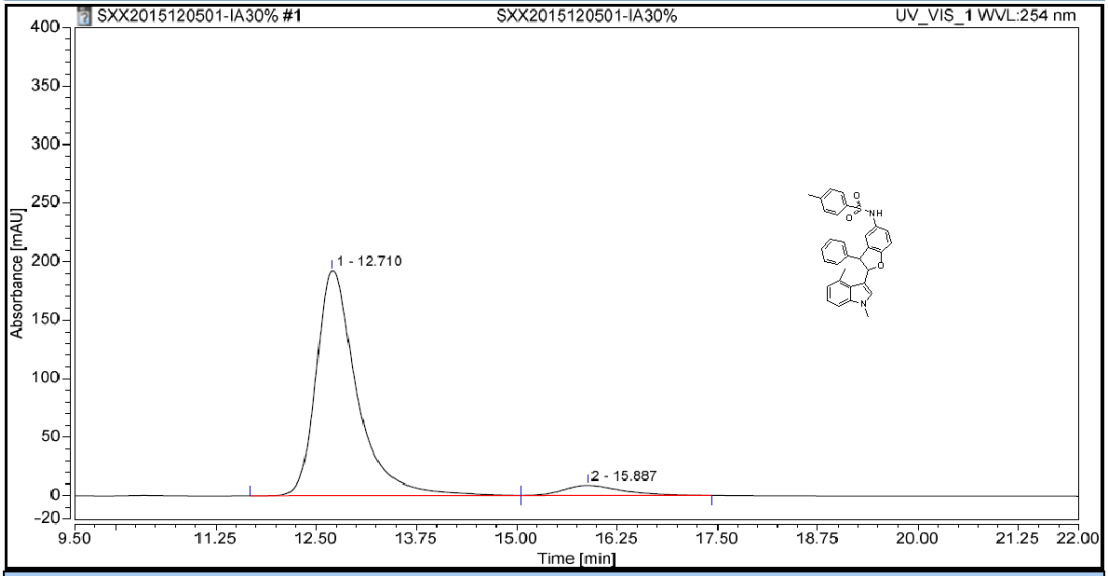
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.457	293.958	485.088	50.38	57.48	n.a.
2		15.017	289.473	358.833	49.62	42.52	n.a.
Total:			**583.431**	**843.920**	**100.00**	**100.00**	

Chromatogram

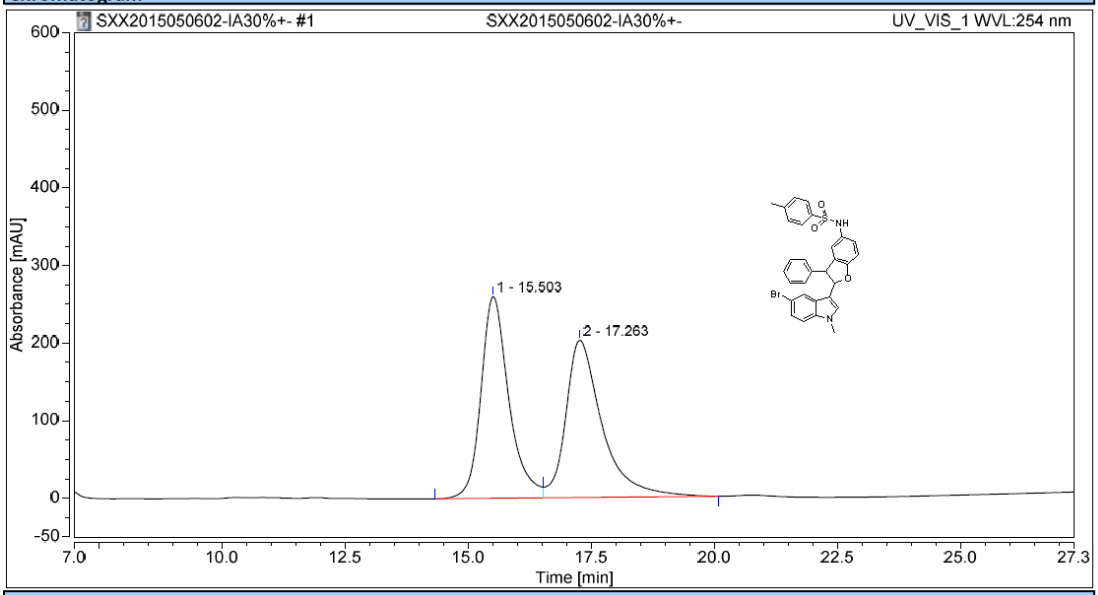


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.710	112.797	192.311	93.89	95.70	n.a.
2		15.887	7.342	8.646	6.11	4.30	n.a.
Total:			**120.138**	**200.958**	**100.00**	**100.00**	

3fa (0.5 mmol scale)

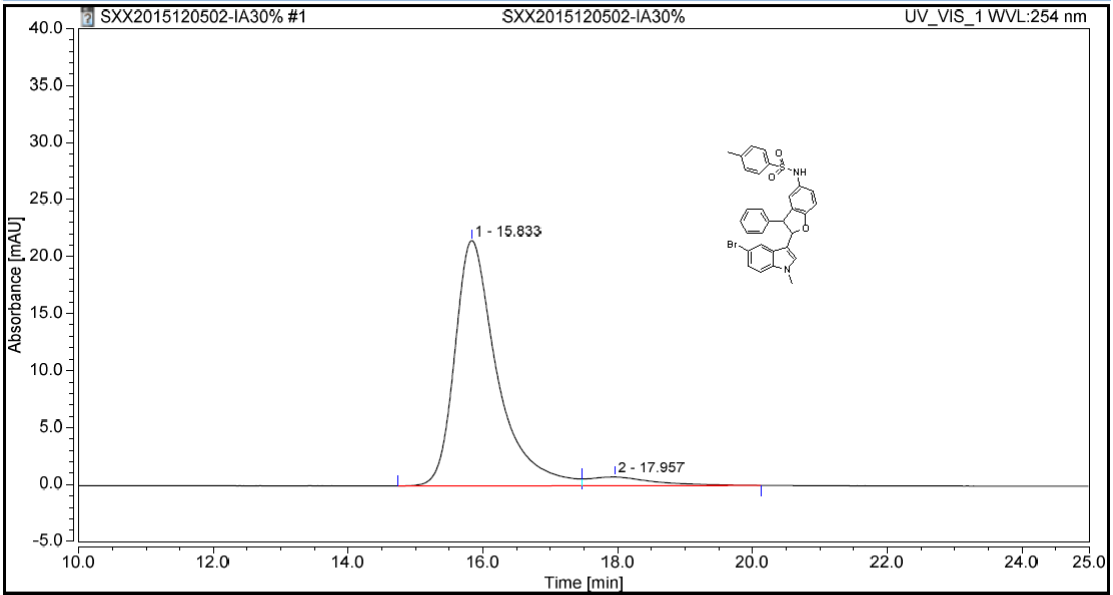
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.503	170.688	259.959	49.62	56.16	n.a.
2		17.263	173.304	202.896	50.38	43.84	n.a.
Total:			**343.992**	**462.854**	**100.00**	**100.00**	

Chromatogram

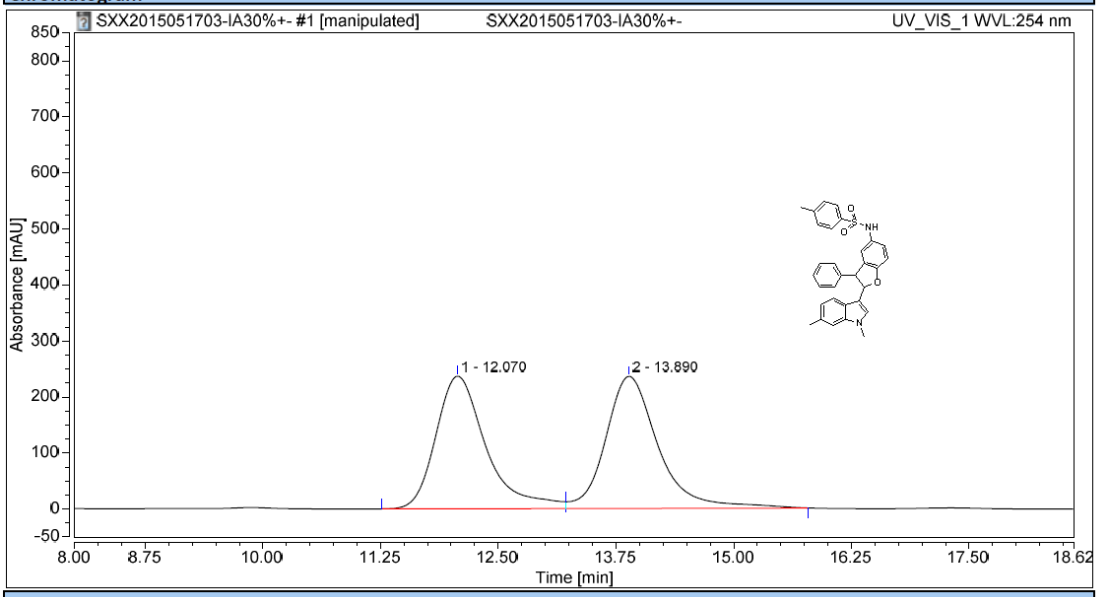


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.833	15.671	21.527	94.81	96.55	n.a.
2		17.957	0.858	0.770	5.19	3.45	n.a.
Total:			**16.528**	**22.298**	**100.00**	**100.00**	

3ga (0.5 mmol scale)

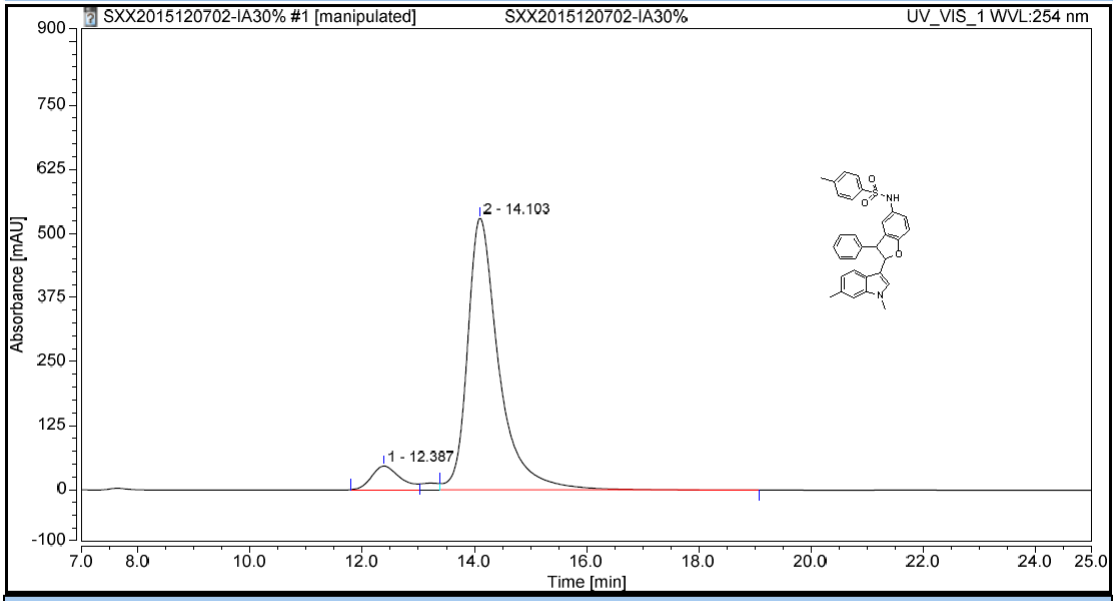
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.070	146.475	236.706	49.06	50.12	n.a.
2		13.890	152.096	235.559	50.94	49.88	n.a.
Total:			**298.571**	**472.265**	**100.00**	**100.00**	

Chromatogram

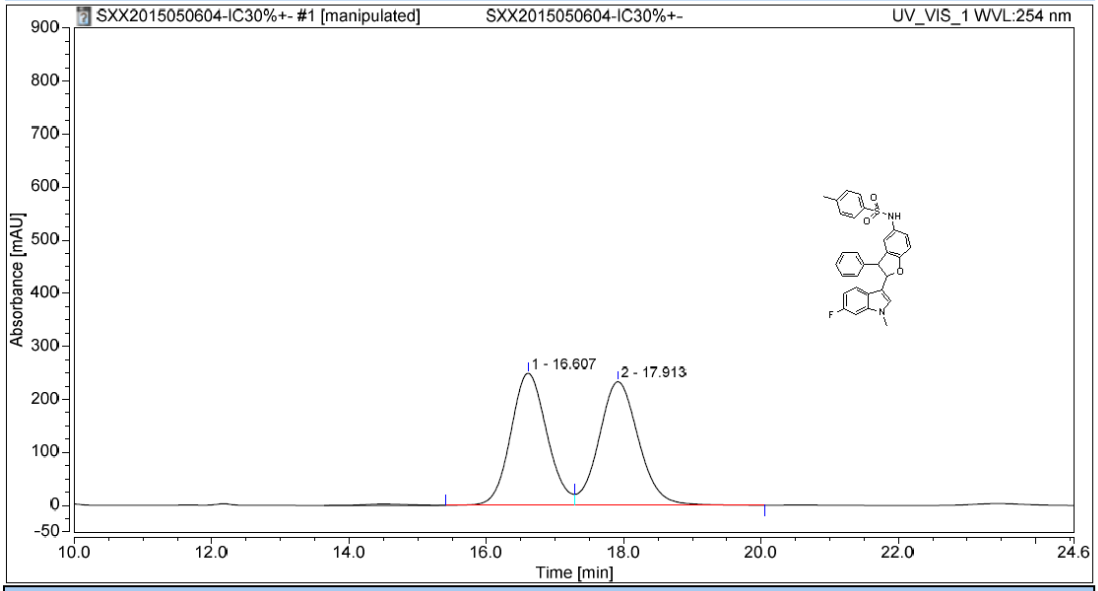


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.387	27.279	46.158	7.35	8.01	n.a.
2		14.103	343.658	530.218	92.65	91.99	n.a.
Total:			**370.937**	**576.376**	**100.00**	**100.00**	

3ha (0.5 mmol scale)

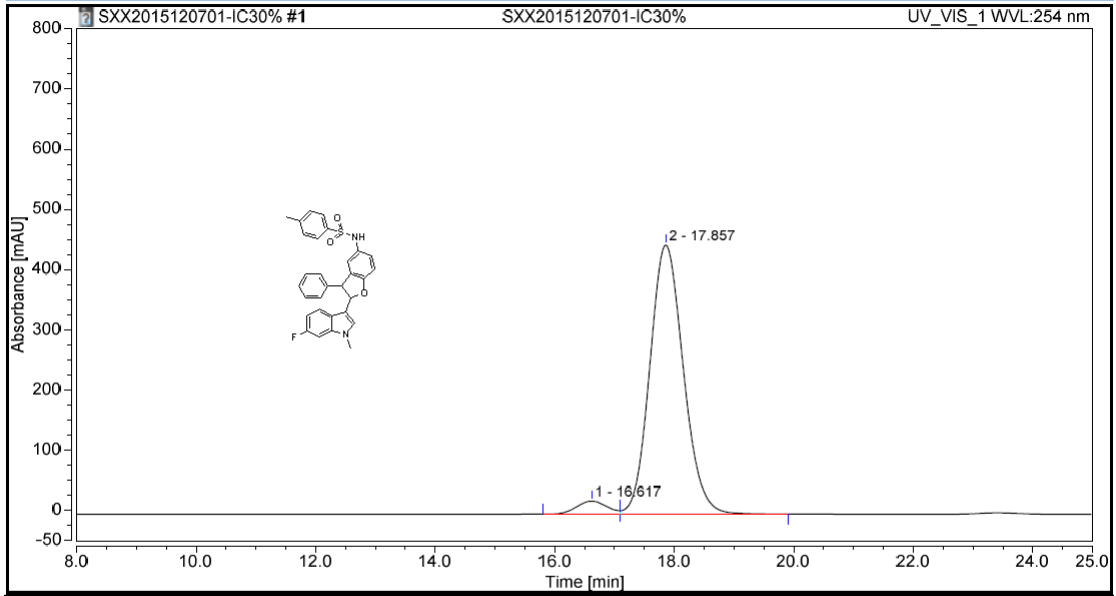
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.607	151.905	249.090	49.40	51.67	n.a.
2		17.913	155.580	232.986	50.60	48.33	n.a.
Total:			**307.486**	**482.076**	**100.00**	**100.00**	

Chromatogram

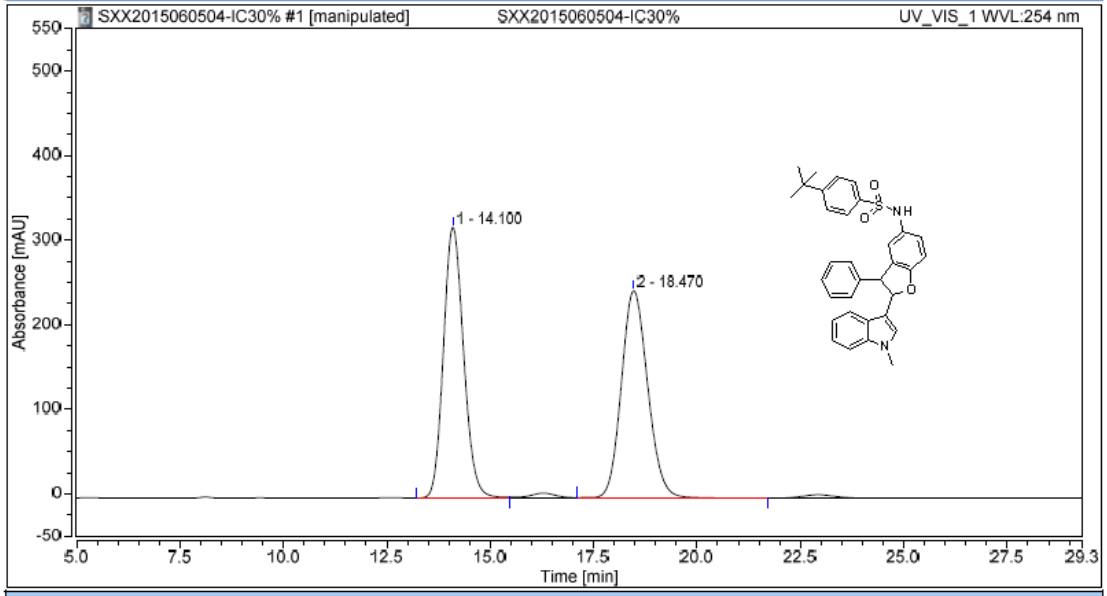


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.617	12.918	21.854	4.26	4.66	n.a.
2		17.857	290.434	446.958	95.74	95.34	n.a.
Total:			**303.352**	**468.812**	**100.00**	**100.00**	

3ab (0.5 mmol scale)

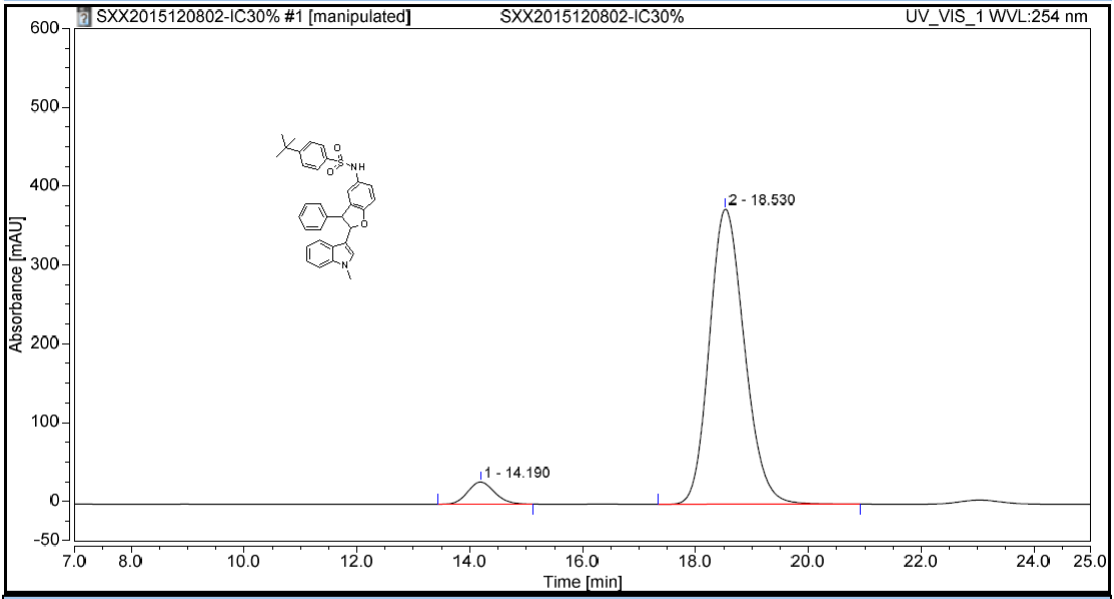
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.100	180.557	319.877	49.88	56.60	n.a.
2		18.470	181.416	245.239	50.12	43.40	n.a.
Total:			**361.973**	**565.116**	**100.00**	**100.00**	

Chromatogram

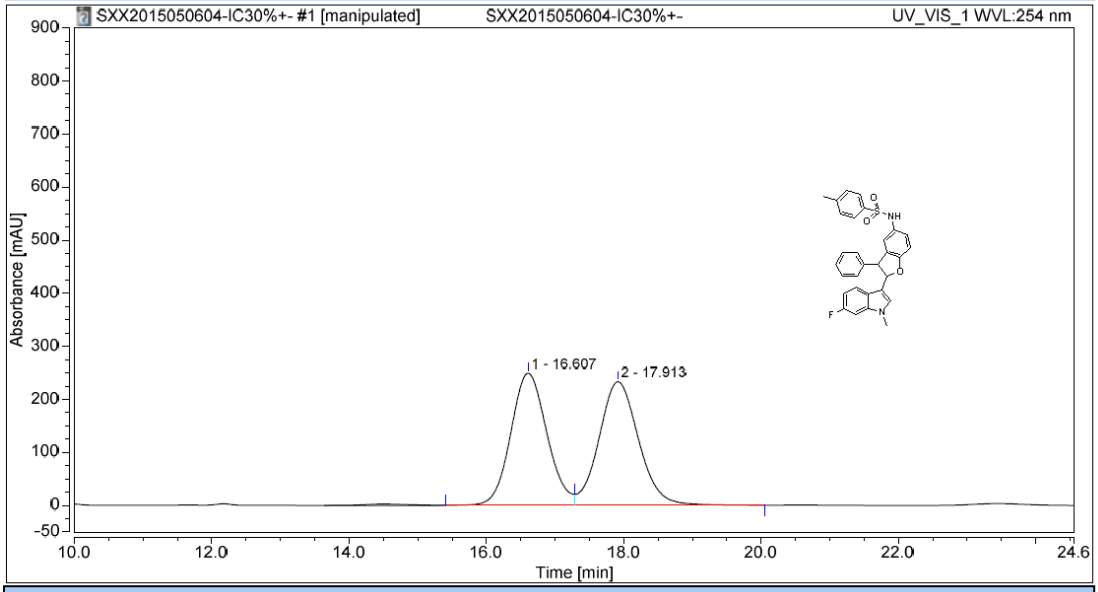


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.190	15.653	28.244	5.48	7.01	n.a.
2		18.530	269.797	374.592	94.52	92.99	n.a.
Total:			**285.451**	**402.836**	**100.00**	**100.00**	

3ha (3.5 mmol scale, 1.71 g)

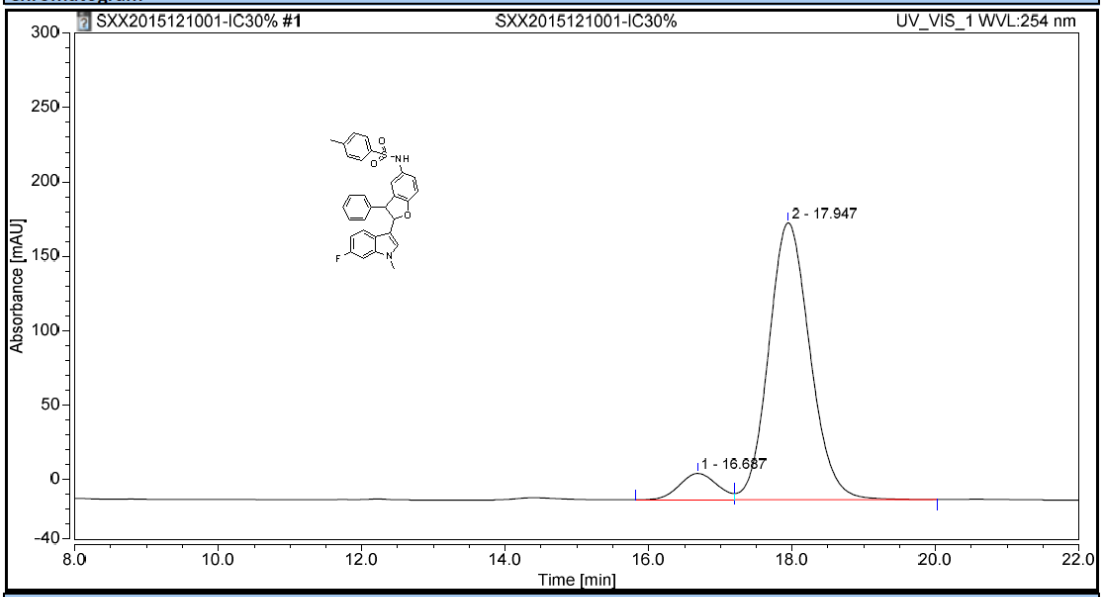
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.607	151.905	249.090	49.40	51.67	n.a.
2		17.913	155.580	232.986	50.60	48.33	n.a.
Total:			**307.486**	**482.076**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.687	10.727	17.688	7.98	8.69	n.a.
2		17.947	123.646	185.961	92.02	91.31	n.a.
Total:			**134.374**	**203.650**	**100.00**	**100.00**	