Supporting Information for

Catalytic Asymmetric Chemoselective 1,3-Dipolar Cycloadditions of Azomethine Ylide with Isatin-derived Imines: Diastereo- and Enantioselective Construction of Spiro[imidazolidine-2,3'-oxindole] Framework

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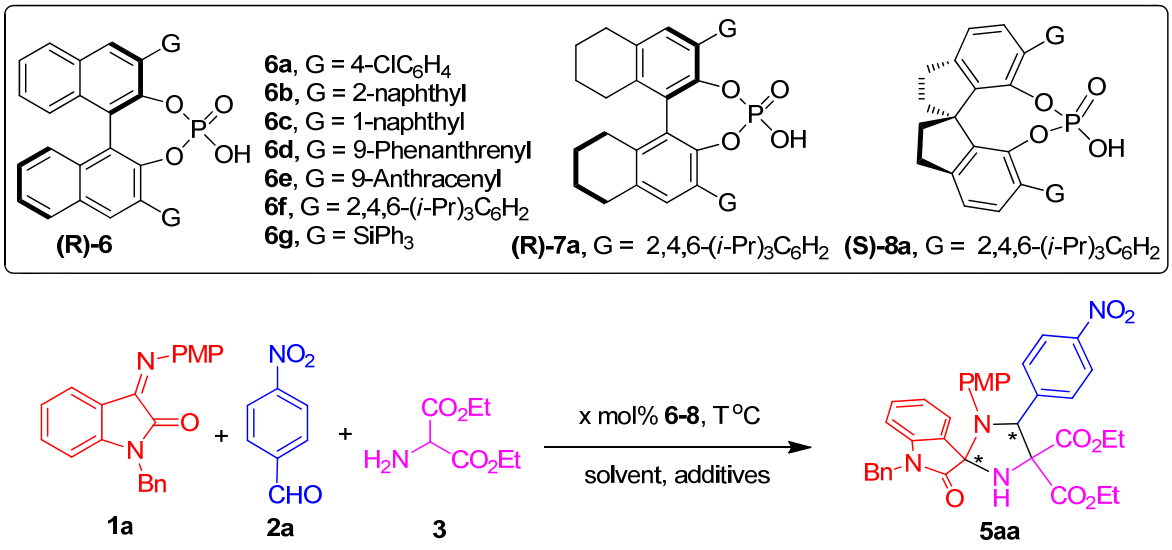
1. General information

^{1}H and ^{13}C NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Enantiomeric ratio (*er*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral column used for the determination of enantiomeric ratio by chiral HPLC was Chiralpak IC and IA 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 **5aa** 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** were synthesized according to the literature method.[1]

2. Screening of catalysts and optimization of conditions

Table 1. Screening of Catalysts and optimization of reaction conditions[a]



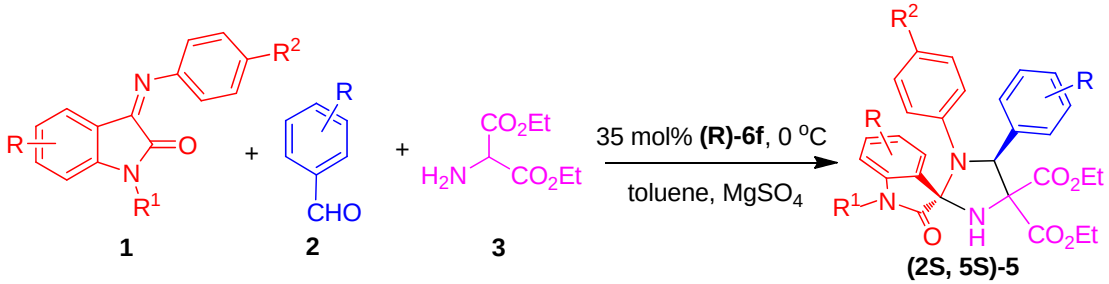
[1] C. Gioia, A. Hauville, L. Bernardi, F. Fini, A. Ricci, *Angew. Chem. Int. Ed.* **2008**, *47*, 9236.

entry	**Cat.** (x)	solvent	reaction time	T (^{o}C)	additives	yield (%)[b]	dr[c]	er[d]
1	**(R)-6a** (10)	toluene	1day	25	-	51	>95:5	60:40
2	**(R)-6b** (10)	toluene	1day	25	-	61	>95:5	58:42
3	**(R)-6c** (10)	toluene	1day	25	-	54	>95:5	58:42
4	**(R)-6d** (10)	toluene	1day	25	-	68	>95:5	69:31
5	**(R)-6e** (10)	toluene	1day	25	-	55	>95:5	61:39
6	**(R)-6f** (10)	toluene	1day	25	-	69	>95:5	75:25
7	**(R)-6g** (10)	toluene	1day	25	-	49	>95:5	55:45
8	**(R)-7a** (10)	toluene	1day	25	-	61	>95:5	74:26
9	**(S)-8a** (10)	toluene	1day	25	-	63	>95:5	68:32
10	**(S)-6f** (10)	EtOAc	1day	25	-	73	>95:5	57:43
11	**(S)-6f** (10)	CH_3CN	1day	25	-	68	>95:5	51:49
12	**(S)-6f** (10)	1,4-dioxane	1day	25	-	57	>95:5	60:40
13	**(S)-6f** (10)	CH_2ClCH_2Cl	1day	25	-	58	>95:5	51:49
14	**(S)-6f** (10)	*o*-xylene	1day	25	-	71	>95:5	67:33
15	**(S)-6f** (10)	*m*-xylene	1day	25	-	66	>95:5	68:32
16	**(S)-6f** (10)	*p*-xylene	1day	25	-	64	>95:5	57:43
17	**(S)-6f** (10)	Br-Ph	1day	25	-	64	>95:5	56:34
18	**(S)-6f** (10)	F-Ph	1day	25	-	63	>95:5	55:45
19	**(S)-6f** (10)	Cl-Ph	1day	25	-	60	>95:5	54:46
20	**(S)-6f** (10)	toluene	1day	25	3 Å	63	>95:5	65:35
21	**(S)-6f** (10)	toluene	1day	25	4 Å	66	>95:5	61:39
22	**(S)-6f** (10)	toluene	1day	25	5 Å	64	>95:5	54:46
23	**(S)-6f** (10)	toluene	1day	25	Na_2SO_4	68	>95:5	70:30
24	**(S)-6f** (10)	toluene	1day	25	$MgSO_4$	71	>95:5	79:21
25	**(S)-6f** (10)	toluene	1day	30	$MgSO_4$	68	>95:5	77:24
26	**(S)-6f** (10)	toluene	1day	50	$MgSO_4$	63	>95:5	70:30
27	**(S)-6f** (10)	toluene	1day	0	$MgSO_4$	48	>95:5	85:15
28	**(S)-6f** (10)	toluene	1day	-10	$MgSO_4$	43	>95:5	85:15
29	**(S)-6f** (10)	toluene	2days	0	$MgSO_4$	69	>95:5	91:9
30	**(S)-6f** (10)	toluene	2days	-10	$MgSO_4$	70	>95:5	91:9
31[e]	**(S)-6f** (10)	toluene	2days	0	$MgSO_4$	48	>95:5	67:33
32[f]	**(S)-6f** (10)	toluene	2days	0	$MgSO_4$	64	>95:5	85:15
33	**(S)-6f** (20)	toluene	2days	0	$MgSO_4$	70	>95:5	91:9
34	**(S)-6f** (30)	toluene	2days	0	$MgSO_4$	68	>95:5	94:6
35	**(S)-6f** (35)	toluene	2days	0	$MgSO_4$	72	>95:5	95:5
36	**(S)-6f** (50)	toluene	2days	0	$MgSO_4$	68	>95:5	95:5
37	**(R)-6f** (35)	toluene	2days	0	$MgSO_4$	72	>95:5	95:5

[a] Unless otherwise indicated, the reaction was carried out at 0.1 mmol scale in a solvent (1 mL) with additives (100 mg), and the mole ratio of **1a:2a:3** was 1:1.2:1.1. [b] Isolated yield. [c] The *dr* value was determined by HPLC and ^{1}H NMR. [d] The *er* value was determined by HPLC. [e] The

mole ratio of **1a:2a:3** was 1:2.4:2.2. [f] The mole ratio of **1a:2a:3** was 2:1.2:1.1. PMP = *p*-methoxyphenyl.

3. General procedure for the catalytic asymmetric synthesis of products 5



After a solution of aldehyde **2** (0.12 mmol), amino-ester **3** (0.11 mmol), the catalyst **6f** (0.035 mmol), and magnesium sulfate (100 mg) in toluene (0.5 mL) was stirred at room temperature for 30 mins, the solution of isatin-derived imine **1** (0.1 mmol) in toluene (0.5 mL) was added. After being stirred at 0 °C for 48 h, the reaction mixture was filtered to remove magnesium sulfate 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 flash column chromatography on silica gel to afford products **5**.

4. Characterization of products 5

(2*R*,5*R*)-diethyl 1'-benzyl-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (*ent*-5aa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48h; yield: 72% (47.2 mg); >95:5 dr; colorless solid, m.p. 143.8-145.1 °C; $[\alpha]_D^{20}$ = 202.7 (c 0.30, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 2H), 8.01 – 7.94 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.14 – 7.09 (m, 1H), 7.08 – 6.99 (m, 2H), 6.79 – 6.70 (m, 3H), 6.54 – 6.46 (m, 4H), 6.46 – 6.38 (m, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 4.59 – 4.37 (m, 1H), 4.34 – 4.24 (m, 2H), 4.17 (d, *J* = 16.0 Hz, 1H), 3.98 – 3.78 (m, 1H), 3.63 (s, 3H), 3.51 – 3.33 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 169.6, 169.2, 156.9, 147.5, 145.2, 144.0, 134.8, 133.9,

131.2, 128.4, 127.2, 126.7, 126.5, 125.7, 124.9, 123.4, 123.2, 114.0, 109.8, 82.8, 75.0, 66.4, 62.8, 62.4, 55.1, 43.2, 14.0, 13.4; IR (KBr): 3734, 3368, 3328, 3295, 3109, 3062, 2980, 2956, 2934, 2836, 1734, 1614, 1510, 1492, 1469, 1456, 1442, 1366, 1347, 1283, 1243, 1220, 1177, 1135, 1109, 1081, 1046, 1014, 954, 919, 906, 869, 853, 802 , 756, 696, 671, 611, 594, 552, 527 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_4O_8+Na)^+$ requires m/z 673.2269, found m/z 673.2269; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 11.19 min (minor), t_R = 15.41 min (major).

(2*S*,5*S*)-diethyl 1'-benzyl-1-(4-methoxyphenyl)-5'-methyl-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ba): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 61% (40.3 mg); >95:5 dr; colorless solid, m.p. 69.8-71.1 ^oC; $[\alpha]_D^{20}$ = -96.0 (c 0.05, Acetone); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.78 – 7.74 (m, 1H), 7.14 – 7.09 (m, 1H), 7.07 – 7.00 (m, 3H), 6.78 – 6.73 (m, 2H), 6.73 (s, 1H), 6.52 – 6.45 (m, 4H), 6.32 (d, *J* = 7.9 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.50 – 4.41 (m, 1H), 4.34 – 4.27 (m, 1H), 4.25 (s, 1H), 4.14 (d, *J* = 16.0 Hz, 1H), 3.94 – 3.85 (m, 1H), 3.64 (s, 3H), 3.48 – 3.39 (m, 1H), 2.44 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 169.7, 169.2, 156.8, 147.5, 145.4, 141.6, 134.9, 134.1, 133.1, 131.5, 128.4, 127.2, 126.7, 126.6, 125.5, 125.3, 123.2, 114.0, 109.6, 83.0, 75.0, 66.4, 62.8, 62.4, 55.1, 43.2, 21.2, 14.0, 13.4; IR (KBr): 2967, 2938, 1731, 1717, 1605, 1520, 1498, 1457, 1365, 1347, 1298, 1269, 1243, 1215, 1174, 1144, 1104, 1080, 1043, 1013, 863, 853, 816, 695 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{36}N_4O_8+Na)^+$ requires m/z 687.2425, found m/z 687.2452; Enantiomeric ratio: 86:14, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 9.29 min (major), t_R = 15.52 min (minor).

(2*S*,5*S*)-diethyl

1'-benzyl-5'-fluoro-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ca): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 63% (42.4 mg); >95:5 dr; colorless solid, m.p. 175.9-176.5 ^{o}C; $[\alpha]_D^{20}$ = -49.1 (c 0.11, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.1 Hz, 2H), 7.83 – 7.74 (m, 3H), 7.15 – 7.11 (m, 1H), 7.08 – 7.02 (m, 2H), 6.96 – 6.90 (m, 1H), 6.82 – 6.77 (m, 2H), 6.70 (s, 1H), 6.55 – 6.50 (m, 2H), 6.48 – 6.42 (m, 2H), 6.96 – 6.90 (m, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 4.49 – 4.41 (m, 1H), 4.33 – 4.25 (m, 1H), 4.18 (s, 1H), 4.14 (d, *J* = 16.1 Hz, 1H), 3.95 – 3.86 (m, 1H), 3.65 (s, 3H), 3.49 – 3.41 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 169.6, 168.9, 159.6 (d, *J* = 241.5 Hz), 157.1, 147.6, 144.7, 139.9(d, *J* = 2.0 Hz), 134.4, 133.6, 128.5, 127.3, 126.5, 125.9, 123.2, 117.6 (d, *J* = 23.3 Hz), 114.1, 113.0 (d, *J* = 24.6 Hz), 110.6(d, *J* = 7.6 Hz), 82.7(d, *J* = 1.7 Hz), 74.9, 66.4, 62.8, 62.4, 55.1, 43.3, 14.0, 13.4; IR (KBr): 3376, 2994, 2954, 2927, 2853, 2837, 1752, 1731, 1608, 1597, 1519, 1460, 1445, 1381, 1366, 1346, 1301, 1265, 1244, 1187, 1141, 1104, 1092, 1042, 1015, 968 878, 865, 856, 841, 820, 806, 780, 696, 682, 596 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}FN_4O_8+Na)^+$ requires m/z 691.2175, found m/z 691.2178; Enantiomeric ratio: 87:13, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 8.60 min (major), t_R = 10.41 min (minor).

(2*S*,5*S*)-diethyl

1'-benzyl-6'-bromo-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5da): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 61% (44.5 mg); >95:5 dr; colorless solid, m.p. 101.7-102.4 ^{o}C; $[\alpha]_D^{20}$ = -254.3 (c 0.05, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.17 – 7.12 (m, 1H), 7.09 – 7.04 (m, 2H), 6.79 – 6.74 (m, 2H), 6.69 (s, 1H), 6.57 (d, *J* = 1.5 Hz, 1H), 6.55 – 6.50 (m, 2H), 6.48 – 6.43 (m, 2H), 5.08 (d, *J* = 16.1 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.33 – 4.25 (m, 1H), 4.17 (s, 1H), 4.13 (d, *J* = 16.1 Hz, 1H), 3.94 – 3.85 (m, 1H), 3.65 (s, 3H), 3.47 – 3.39

(m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 169.7, 169.0, 157.1, 147.6, 145.3, 144.8, 134.2, 133.5, 128.6, 127.5, 126.4, 126.4, 126.3, 125.9, 125.8, 125.0, 123.2, 114.2, 113.1, 82.4, 74.8, 66.4, 62.8, 62.4, 55.1, 43.2, 14.0, 13.4; IR (KBr): 3750, 3735, 3649, 2963, 2930, 2850, 1734, 1607, 1522, 1509, 1489, 1456, 1370, 1347, 1262, 1242, 1218, 1175, 1135, 1106, 1082, 1061, 1043, 951, 853, 802, 739, 720, 695 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}BrN_4O_8+Na)^+$ requires m/z 753.1361, found m/z 753.1356; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 10.44 min (minor), t_R = 13.90 min (major).

(2*S*,5*S*)-diethyl 1'-benzyl-1-(4-methoxyphenyl)-7'-methyl-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ea): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 72% (48.2 mg); >95:5 dr; colorless solid, m.p. 96.4-97.2 ^{o}C; $[\alpha]_D^{20}$ = -87.8 (c 0.60, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H), 7.89 – 7.86 (m, 1H), 7.84 – 7.77 (m, 2H), 7.17 – 7.12 (m, 1H), 7.12 – 7.07 (m, 1H), 7.04 – 6.99 (m, 3H), 6.84 – 6.79 (m, 2H), 6.74 (s, 1H), 6.55 – 6.50 (m, 2H), 6.35 – 6.30 (m, 2H), 5.25 (d, *J* = 17.0 Hz, 1H), 4.58 (d, *J* = 17.1 Hz, 1H), 4.47 – 4.39 (m, 1H), 4.33 – 4.25 (m, 2H), 3.92 – 3.83 (m, 1H), 3.65 (s, 3H), 3.46 – 3.38 (m, 1H), 2.06 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 169.6, 169.3, 156.9, 147.5, 145.4, 142.1, 136.8, 135.1, 134.0, 128.5, 127.4, 126.8, 126.0, 125.2, 123.5, 123.2, 122.9, 120.5, 114.1, 82.1, 75.0, 66.6, 62.8, 62.3, 55.1, 44.4, 18.5, 14.0, 13.4; IR (KBr): 3066, 2980, 2954, 2932, 2905, 2835, 1733, 1605, 1510, 1473, 1454, 1419, 1347, 1299, 1281, 1245 ,1216, 1148, 1134, 1111, 1095, 1044, 1013, 970, 860, 841,799, 778, 748, 729, 721, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{36}N_4O_8+Na)^+$ requires m/z 687.2425, found m/z 687.2433; Enantiomeric ratio: 94:6, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 10.85 min (major), t_R = 14.52 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-7'-fluoro-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5fa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 71% (47.4 mg); >95:5 dr; colorless solid, m.p. 151.1-152.2 ^{o}C; $[\alpha]_D^{20}$ = -79.4 (c 0.57, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.85 – 7.76 (m, 3H), 7.21 – 7.15 (m, 1H), 7.14 – 7.09 (m, 1H), 7.06 – 6.98 (m, 3H), 6.78 – 6.73 (m, 2H), 6.72 (s, 1H), 6.55 (d, *J* = 7.5 Hz, 2H), 6.51 – 6.46 (m, 2H), 5.08 (d, *J* = 15.7 Hz, 1H), 4.51 – 4.40 (m, 2H), 4.34 – 4.26 (m, 1H), 4.23 (s, 1H), 3.94 – 3.83 (m, 1H), 3.63 (s, 3H), 3.47 – 3.38 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 169.5, 169.1, 157.0, 147.6, 147.3 (d, *J* = 244.7 Hz), 145.0, 136.1, 133.6, 130.6(d, *J* = 9.2 Hz), 129.7(d, *J* = 3.2 Hz), 128.2, 127.1, 126.5, 125.7, 124.2(d, *J* = 6.2 Hz), 123.2, 120.9(d, *J* = 3.3 Hz), 119.4 (d, *J* = 19.4 Hz), 114.1, 82.6(d, *J* = 2.6 Hz), 74.9, 66.5, 62.8, 62.4, 55.1, 44.8(d, *J* = 4.3 Hz), 14.0, 13.4; IR (KBr): 2980, 2953, 2932, 2836, 1733, 1633, 1605, 1585, 1510, 1455, 1444, 1420, 1349, 1301, 1282, 1218, 1169, 1133, 1111, 1096, 1083, 1044, 1013, 972, 886, 869, 853, 797, 781, 735, 720, 710, 692, 661, 590, 564 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}FN_4O_8+Na)^+$ requires m/z 691.2175, found m/z 691.2169; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 7.75 min (major), t_R = 9.52 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-7'-bromo-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ga): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 64% (46.9 mg); >95:5 dr; colorless solid, m.p. 172.3-172.9 ^{o}C; $[\alpha]_D^{20}$ = -72.2 (c 0.42, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 8.03 – 7.97 (m, 1H), 7.83 – 7.73 (m, 2H), 7.45 – 7.41 (m, 1H), 7.14 – 7.07 (m, 2H), 7.04 – 6.98 (m, 2H), 6.84 – 6.78 (m, 2H), 6.70 (s, 1H), 6.55 – 6.49 (m, 2H), 6.42 – 6.35 (m, 2H), 5.18 (d, *J* = 16.7 Hz, 1H), 5.06 (d, *J* = 16.7 Hz, 1H), 4.47 – 4.38 (m, 1H), 4.33 – 4.25 (m, 1H), 4.21 (s, 1H),

3.93 – 3.84 (m, 1H), 3.65 (s, 3H), 3.47 – 3.38 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 169.6, 169.0, 157.2, 147.6, 144.9, 141.7, 137.1, 136.6, 133.4, 130.1, 128.2, 126.6, 126.2, 125.6, 124.7, 124.3, 123.2, 114.2, 103.0, 81.9, 74.9, 66.7, 62.9, 62.4, 55.1, 43.9, 14.0, 13.4; IR (KBr):3336, 2979, 2953, 2932, 2835, 1734, 1607, 1578, 1510, 1454, 1346, 1298, 1276, 1244, 1216, 1168, 1144, 1109, 1037, 1014, 960, 872, 855, 841, 798, 780, 737, 720, 695 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}BrN_4O_8+Na)^+$ requires m/z 753.1361, found m/z 753.1362; Enantiomeric ratio: 89:11, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 8.96 min (major),t_R = 9.69 min (minor).

(2*S*,5*S*)-diethyl 1-(4-methoxyphenyl)-1'-(4-methylbenzyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ha): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 68% (45.0 mg); >95:5 dr; colorless solid, m.p. 154.9-156.4 ^{o}C; $[\alpha]_D^{20}$ = -106.5 (c 0.26, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 2H), 7.99 – 7.94 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.17 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 2H), 6.77 – 6.72 (m, 3H), 6.50 – 6.46 (m, 2H), 6.46 – 6.42 (m, 1H), 6.39 (d, *J* = 7.9 Hz, 2H), 5.06 (d, *J* = 15.9 Hz, 1H), 4.51 – 4.40 (m, 1H), 4.34 – 4.27 (m, 1H), 4.26 (s, 1H), 4.13 (d, *J* = 15.9 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.64 (s, 3H), 3.47 – 3.39 (m, 1H), 2.23 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 169.6, 169.2, 156.8, 147.5, 145.3, 144.1, 136.8, 134.0, 131.8, 131.2, 129.1, 126.7, 126.6, 125.6, 124.8, 123.3, 123.2, 114.0, 109.8, 82.8, 75.1, 66.5, 62.7, 62.4, 55.0, 42.9, 21.0, 14.0, 13.4; IR (KBr): 3300, 3104, 3050, 2983, 2930, 2856, 2838, 1733, 1613, 1510, 1490, 1470, 1443, 1420, 1347, 1283, 1243, 1178, 1136, 1110, 1046, 1012, 956, 941, 912, 867, 853, 802, 755, 728, 696, 670, 606, 594, 558 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{36}N_4O_8+Na)^+$ requires m/z 687.2425, found m/z 687.2425; Enantiomeric ratio: 94:6, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 12.19 min (major), t_R = 15.61 min

(minor).

(2*S*,5*S*)-diethyl 1'-(4-bromobenzyl)-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ia): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 69% (50.4 mg); >95:5 dr; colorless solid, m.p. 177.2-178.0 ^{o}C; $[\alpha]_D^{20}$ = -113.7 (c 0.33, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 2H), 8.01 – 7.96 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.18 – 7.11 (m, 2H), 6.75 – 6.69 (m, 3H), 6.50 – 6.45 (m, 2H), 6.41 (d, *J* = 7.1 Hz, 1H), 6.32 (d, *J* = 8.2 Hz, 2H), 5.05 (d, *J* = 16.1 Hz, 1H), 4.49 – 4.41 (m, 1H), 4.33 – 4.23 (m, 2H), 4.09 (d, *J* = 16.1 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.64 (s, 3H), 3.47 – 3.39 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 169.6, 169.1, 156.9, 147.5, 145.1, 143.7, 133.9, 133.8, 131.5, 131.3, 128.3, 126.7, 125.7, 125.1, 123.6, 123.2, 121.1, 82.8, 75.0, 66.3, 62.8, 62.4, 55.1, 42.5, 14.0, 13.4; IR (KBr): 3852, 2962, 2923, 2853, 1760, 1735, 1509, 1489, 1469, 1346, 1279, 1261, 1242, 1203, 1047, 1032, 1012, 1107, 803 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}BrN_4O_8+Na)^+$ requires m/z 753.1361, found m/z 753.1359; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 10.69 min (major), t_R = 15.93 min (minor).

(2*S*,5*S*)-diethyl1'-(3-chlorobenzyl)-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ja): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 73% (50.2 mg); >95:5 dr; colorless solid, m.p. 188.6-189.4 ^{o}C; $[\alpha]_D^{20}$ = -32.8 (c 0.88, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 8.01 – 7.97 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.19 (m, 2H), 7.03 – 6.97 (m, 2H), 6.75 – 6.70 (m, 3H), 6.50 – 6.45 (m, 2H), 6.43 – 6.36 (m, 3H), 5.07 (d, *J* = 16.1 Hz, 1H), 4.50 – 4.41 (m, 1H), 4.33 – 4.22 (m, 2H), 4.11 (d, *J* = 16.1 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.63 (s, 3H), 3.47 – 3.39 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.1 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.2, 156.8, 147.5, 145.2, 143.7, 137.1, 134.3, 133.8, 131.3, 129.8, 129.5, 127.6, 127.0, 126.7, 125.6, 125.0, 124.6, 123.6, 123.2, 114.0, 109.6, 82.7, 75.0, 66.6, 62.8, 62.4, 55.0, 42.7, 14.0, 13.4; IR (KBr): 2961, 2925, 2854, 1735, 1613, 1523, 1509, 1469, 1443, 1347, 1262, 1279, 1242, 1218, 1178, 1137, 1095, 1044, 1015, 956, 853, 801, 754, 695 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}ClN_4O_8+Na)^+$ requires m/z 707.1879, found m/z 707.1879; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 10.29 min (major), t_R = 15.48 min (minor).

(2*S*,5*S*)-diethyl 1'-(2-chlorobenzyl)-1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ka): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 62% (42.7 mg); >95:5 dr; colorless solid, m.p. 152.1-153.4 ^{o}C; $[\alpha]_D^{20}$ = -75.7 (c 0.96, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 8.03 – 7.99 (m, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.22 (m, 1H), 7.09 – 7.04 (m, 1H), 6.81 – 6.76 (m, 2H), 6.72 (s, 1H), 6.72 – 6.68 (m, 1H), 6.53 – 6.48 (m, 2H), 6.46 – 6.38 (m, 1H), 5.61 – 5.51 (m, 1H), 5.04 (d, *J* = 17.0 Hz, 1H), 4.49 – 4.41 (m, 2H), 4.34 – 4.26 (m, 2H), 3.93 – 3.84 (m, 1H), 3.63 (s, 3H), 3.44 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 169.6, 169.1, 157.0, 145.1, 133.9, 132.5, 132.0, 131.4, 129.2, 128.4, 127.1, 126.8, 126.6, 126.0, 125.0, 123.6, 123.2, 114.1, 109.5, 82.9, 75.0, 66.4, 62.8, 62.4, 55.1, 40.6, 14.0, 13.4; IR (KBr): 2988, 2962, 2931, 2853, 1728, 1614, 1605, 1558, 1512, 1489, 1471, 1444, 1420, 1379, 1347, 1308, 1269, 1244, 1226, 1179, 1136, 1102, 1076, 1049, 1032, 1011, 959, 940, 916, 868, 851, 804, 753, 722, 697, 670 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}ClN_4O_8+Na)^+$ requires m/z 707.1879, found m/z 707.1875; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 85/ 15, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 16.16 min (major), t_R = 17.37 min (minor).

(2*S*,5*S*)-diethyl 1-(4-methoxyphenyl)-5-(4-nitrophenyl)-2'-oxo-1'-phenylspiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5la): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 71% (45.0 mg); >95:5 dr; colorless solid, m.p. 98.2-99.5 ^{o}C; $[\alpha]_D^{20}$ = -22.1 (c 0.86, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 2H), 8.07 – 7.95 (m, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 7.02 – 6.86 (m, 2H), 6.85 – 6.69 (m, 2H), 6.66 – 6.58 (m, 2H), 6.55 – 6.47 (m, 2H), 4.48 – 4.38 (m, 1H), 4.32 (d, *J* = 6.1 Hz, 1H), 4.31 – 4.21 (m, 1H), 3.96 – 3.84 (m, 1H), 3.61 (s, 3H), 3.49 – 3.38 (m, 1H), 1.29 (d, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 169.6, 169.1, 147.5, 145.2, 145.0, 133.8, 133.6, 131.2, 129.4, 128.0, 126.4, 126.3, 125.6, 125.1, 123.8, 123.2, 113.8, 109.8, 82.9, 75.2, 66.4, 62.8, 62.4, 55.2, 14.0, 13.4; IR (KBr): 3343, 3056, 2988, 2919, 2850, 1792, 1736, 1685, 1636, 1613, 1597, 1558, 1510, 1468, 1447, 1419, 1370, 1347, 1297, 1282, 1243, 1214, 1174, 1142, 1111, 1092, 1043, 943, 870, 854, 827, 758, 699cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{32}N_4O_8+Na)^+$ requires m/z 659.2112, found m/z 659.2108; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 10.25 min (minor), t_R = 10.99 min (major).

(2*S*,5*S*)-diethyl 1'-benzyl-5-(4-nitrophenyl)-2'-oxo-1-(4-phenoxyphenyl)spiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ma): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 67% (47.6 mg); >95:5 dr; colorless solid, m.p. 103.2-104.8 ^{o}C; $[\alpha]_D^{20}$ = -106.6 (c 0.68, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 2H), 7.96 – 7.92 (m, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.28 – 7.19 (m, 4H), 7.19 – 7.16 (m, 3H), 7.06 – 7.02 (m, 1H), 6.88 – 6.84 (m, 2H), 6.72 – 6.65 (m, 5H), 6.61 – 6.56 (m, 2H), 6.51 (d, *J* = 7.4 Hz, 1H), 5.11 (d, *J* = 15.9 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.35 – 4.27 (m, 2H), 4.25 (d, *J* = 15.9 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.48 – 3.40 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 169.3, 169.1, 156.5, 154.1, 147.6, 145.3, 143.9, 136.5, 134.9, 131.3, 129.7, 128.6, 127.4, 126.7, 124.7, 124.5, 123.5, 123.3, 119.1, 118.5, 110.0, 82.8, 75.2, 66.6, 62.9, 62.5, 43.4, 14.0, 13.4; IR (KBr): 3031, 2983, 2915, 1792, 1731, 1684, 1648, 1614, 1589, 1558, 1540, 1520, 1506, 1489, 1469, 1456, 1394, 1347, 1308, 1274, 1236, 1171, 1132, 1046, 1013, 954, 870, 850, 807, 797, 753, 723, 693, 670 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{36}N_4O_8+Na)^+$ requires m/z 735.2425, found m/z 735.2425; Enantiomeric ratio: 91:9, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 9.38 min (major), t_R = 12.87 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-5-(4-nitrophenyl)-2'-oxo-1-(p-tolyl)spiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate(5na):Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 71% (45.2 mg); >95:5 dr; colorless solid, m.p. 195.1-196.4 ^oC; $[\alpha]_D^{20}$ = -74.2 (c 0.64, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.9 Hz, 2H), 7.99 – 7.93 (m, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.18 (m, 2H), 7.16 – 7.10 (m, 1H), 7.08 – 7.01 (m, 2H), 6.78 – 6.72 (m, 3H), 6.67 – 6.61 (m, 2H), 6.60 – 6.53 (m, 2H), 6.51 – 6.44 (m, 1H), 5.10 (d, *J* = 15.9 Hz, 1H), 4.50 – 4.41 (m, 1H), 4.35 – 4.26 (m, 2H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.48 – 3.39 (m, 1H), 2.16 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 169.4, 169.2, 147.5, 145.4, 143.9, 138.8, 134.9, 133.9, 131.2, 129.5, 129.4, 128.4, 127.2, 126.8, 126.7, 124.8, 123.4, 123.3, 109.9, 82.7, 75.1, 66.3, 62.8, 62.4, 43.3, 20.8, 14.0, 13.4; IR (KBr): 3334, 2979, 2963, 2921, 2854, 1736, 1616, 1605, 1515, 1492, 1471, 1455, 1420, 1379, 1366, 1344, 1312, 1266, 1251, 1218, 1180, 1138, 1105, 1081, 1045, 1015, 952, 901, 871, 854, 801, 758, 728, 713, 694, 677, 649 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_4O_7+Na)^+$ requires m/z 657.2320, found m/z 657.2300; Enantiomeric ratio: 92:8, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 9.37 min (major), t_R = 12.87 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-1-(4-fluorophenyl)-5-(4-nitrophenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5oa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 76% (48.5 mg); >95:5 dr; colorless solid, m.p. 174.2-175.7 ^{o}C; $[\alpha]_D^{20}$ = -76.2 (c 0.29, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ8.11 (d, *J* = 8.9 Hz, 2H), 7.99 – 7.95 (m, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.25 (m, 1H), 7.25 – 7.20 (m, 1H), 7.18 – 7.13 (m, 1H), 7.12 – 7.07 (m, 2H), 6.77 – 6.70 (m, 3H), 6.67 – 6.61 (m, 2H), 6.57 – 6.52 (m, 2H), 6.50 (d, *J* = 7.2 Hz, 1H), 5.09 (d, *J* = 15.9 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.34 – 4.26 (m, 2H), 4.20 (d, *J* = 15.9 Hz, 1H), 3.94 – 3.85 (m, 1H), 3.48 – 3.40 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 169.2 (d, *J* = 39.2 Hz), 159.3 (d, *J* = 243.0 Hz), 147.7, 144.8, 144.0, 137.3 (d, *J* = 2.8 Hz), 134.8, 131.4, 129.4, 128.5, 127.4, 126.6, 126.5, 125.4 (d, *J* = 7.9 Hz), 124.8, 123.5, 123.3, 115.6 (d, *J* = 22.2 Hz), 109.9, 82.8, 75.0, 66.5, 62.9, 62.5, 43.3, 14.0, 13.4; IR (KBr): 3065, 3030, 2982, 2964, 2919, 2851, 1734, 1615, 1522, 1508, 1490, 1469, 1456, 1366, 1346, 1262, 1279, 1217, 1177, 1139, 1095, 1045, 1015, 954, 918, 906, 853, 799, 755, 733, 696, 675 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{31}FN_4O_7+Na)^+$ requires m/z 661.2069, found m/z 661.2059; Enantiomeric ratio: 87:13, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 8.08 min (major), t_R = 10.77 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-5-(4-cyanophenyl)-1-(4-methoxyphenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ab): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 62% (39.1 mg); >95:5 dr; colorless solid, m.p. 142.2-143.6 ^{o}C; $[\alpha]_D^{20}$ = -92.5 (c 0.31, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 1H), 7.77 – 7.72 (m, 2H), 7.55 – 7.50 (m, 2H), 7.25 – 7.17 (m, 2H), 7.14 – 7.09 (m, 1H), 7.07 – 7.01 (m, 2H), 6.77 – 6.72 (m, 2H), 6.67 (s, 1H), 6.51 – 6.46 (m, 4H), 6.44 – 6.39 (m, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 4.49 – 4.41 (m, 1H), 4.33 – 4.25 (m, 2H), 4.16 (d, *J* = 16.0 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.63 (s,

3H), 3.46 – 3.38 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 169.6, 169.2, 156.8, 144.0, 143.2, 134.8, 134.0, 131.8, 131.2, 128.4, 127.2, 126.8, 126.5, 125.6, 124.8, 123.3, 118.7, 114.0, 111.6, 109.8, 82.8, 75.1, 66.6, 62.7, 62.3, 55.1, 43.2, 14.0, 13.4; IR (KBr): 2982, 2955, 2933, 2908, 2227, 1751, 1732, 1614, 1512, 1491, 1468, 1444, 1427, 1417, 1362, 1336, 1284, 1245, 1222, 1181, 1155, 1134, 1110, 1082, 1047, 1035, 1016, 998, 954, 908, 860, 844, 816, 792, 758, 741, 731, 698, 558 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{34}N_4O_6+Na)^+$ requires m/z 653.2370, found m/z 653.2371; Enantiomeric ratio: 89:11, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 12.77 min (major), t_R = 18.37 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-5-(4-(methoxycarbonyl)phenyl)-1-(4-methoxyphenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ac): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 62% (41.3 mg); >95:5 dr; colorless solid, m.p. 101.0-102.4 °C; $[\alpha]_D^{20}$ = -108.1 (c 0.43, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.14 – 7.09 (m, 1H), 7.08 – 7.02 (m, 2H), 6.77 – 6.71 (m, 2H), 6.66 (s, 1H), 6.51 – 6.44 (m, 4H), 6.44 – 6.39 (m, 1H), 5.12 (d, *J* = 16.0 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.34 – 4.25 (m, 2H), 4.16 (d, *J* = 16.0 Hz, 1H), 3.89 – 3.81 (m, 4H), 3.62 (s, 3H), 3.42 – 3.34 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 169.8, 169.3, 166.9, 156.5, 144.0, 142.9, 134.9, 134.5, 131.0, 129.6, 129.3, 128.4, 127.2, 127.1, 126.6, 125.4, 124.9, 123.3, 113.9, 109.7, 82.7, 75.1, 66.8, 62.6, 62.2, 55.1, 52.0, 43.2, 14.0, 13.3; IR (KBr): 3735, 3336, 3031, 2988, 2953, 2938, 2839, 1736, 1685, 1614, 1541, 1509, 1490, 1470, 1432, 1377, 1361, 1339, 1283, 1241, 1177, 1158, 1138, 1110, 1086, 1029, 1020, 948, 872, 845, 788, 760, 732, 720, 695 cm^{-1}; ESI FTMS exact mass calcd for $(C_{38}H_{37}N_3O_8+Na)^+$ requires m/z 686.2473, found m/z 686.2471; Enantiomeric ratio: 92:8, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.88 min (major), t_R = 19.59 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-5-(3-cyanophenyl)-1-(4-methoxyphenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ad): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 52% (32.9 mg); >95:5 dr; colorless solid, m.p. 105.8-107.5 ^{o}C; $[\alpha]_D^{20}$ = -126.4 (c 0.46, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.38 – 7.32 (m, 1H), 7.25 – 7.19 (m, 2H), 7.14 – 7.09 (m, 1H), 7.07 – 7.02 (m, 2H), 6.78 – 6.73 (m, 2H), 6.64 (s, 1H), 6.52 – 6.46 (m, 4H), 6.44 – 6.39 (m, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.50 – 4.41 (m, 1H), 4.34 – 4.27 (m, 1H), 4.25 (s, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.64 (s, 3H), 3.49 – 3.41 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 169.6, 169.2, 156.8, 144.0, 139.3, 134.8, 133.9, 131.5, 131.2, 128.9, 128.4, 127.2, 126.7, 126.5, 125.7, 124.9, 123.4, 118.8, 114.0, 112.2, 109.8, 82.8, 75.0, 66.3, 62.7, 62.3, 55.1, 43.1, 14.0, 13.4; IR (KBr): 3303, 3065, 3052, 3036, 2987, 2962, 2933, 2911, 2838, 2228, 1822, 1756, 1735, 1652, 1614, 1581, 1510, 1479, 1456, 1444, 1366, 1349, 1323, 1296, 1283, 1262, 1243, 1215, 1173, 1131, 1112, 1096, 1082, 1048, 1028, 992, 958, 938, 912, 861, 843, 832, 805, 760, 705, 694, 667, 622, 549, 526 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{34}N_4O_6+Na)^+$ requires m/z 653.2370, found m/z 653.2381; Enantiomeric ratio: 88:12, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 11.67 min (major), t_R = 15.47 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-1-(4-methoxyphenyl)-2'-oxo-5-(3-(trifluoromethyl)phenyl)spiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ae): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 60% (40.6 mg); >95:5 dr; colorless solid, m.p. 148.1-148.7 ^{o}C; $[\alpha]_D^{20}$ = -135.9 (c 0.37, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 1H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.15 – 7.10 (m, 1H), 7.09 – 7.00 (m, 2H), 6.80 –

6.74 (m, 2H), 6.68 (s, 1H), 6.53 – 6.46 (m, 4H), 6.46 – 6.40 (m, 1H), 5.12 (d, *J* = 16.0 Hz, 1H), 4.51 – 4.40 (m, 1H), 4.34 – 4.24 (m, 2H), 4.16 (d, *J* = 16.0 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.64 (s, 3H), 3.45 – 3.36 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 169.8, 169.3, 156.7, 144.0, 141.7, 134.9, 134.3, 131.1, 130.0 (d, *J* = 32.2 Hz), 128.4, 127.0, 126.6, 126.0 (d, *J* = 232.2 Hz),125.5, 124.9(d, *J* = 4.2 Hz), 123.3, 113.9, 109.7, 82.8, 75.1, 66.6, 62.7, 62.2, 55.1, 43.2, 14.0, 13.1; IR (KBr): 2963, 2933, 2840, 1758, 1733, 1615, 1582, 1541, 1509, 1490, 1471, 1444, 1420, 1370, 1351, 1326, 1284, 1244, 1218, 1163, 1130, 1110, 1084, 1066, 1047, 1018, 953, 861, 840, 819, 806, 792, 762, 733, 722, 704, 666, 552 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{34}F_3N_3O_6+Na)^+$ requires m/z 696.2292, found m/z 696.2292; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.47 min (major), t_R = 8.30 min (minor).

(2*S*,5*S*)-diethyl 1'-benzyl-5-(4-chloro-3-fluorophenyl)-1-(4-methoxyphenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5af): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 65% (43.8 mg); >95:5 dr; colorless solid, m.p. 86.4-88.1 °C; $[\alpha]_D^{20}$ = -107.1 (c 0.65, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 1H), 7.44 – 7.35 (m, 2H), 7.28 – 7.23 (m, 1H), 7.23 – 7.16 (m, 2H), 7.14 – 7.10 (m, 1H), 7.07 – 7.02 (m, 2H), 6.78 – 6.73 (m, 2H), 6.58 (s, 1H), 6.53 – 6.47 (m, 4H), 6.44 – 6.39 (m, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.34 – 4.23 (m, 2H), 4.16 (d, *J* = 16.0 Hz, 1H), 3.97 – 3.88 (m, 1H), 3.65 (s, 3H), 3.61 – 3.53 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 169.7, 169.3, 157.9 (d, *J* = 246.9 Hz), 156.7, 144.0, 138.6(d, *J* = 6.2 Hz), 134.9, 134.1, 131.1, 130.1, 128.4, 127.2, 126.9, 126.6, 125.6, 124.9, 123.3, 120.1 (d, *J* = 17.8 Hz), 114.0, 109.7, 82.7, 75.0, 66.1(d, *J* = 1.7 Hz), 62.8, 62.3, 55.1, 43.1, 14.0, 13.3; IR (KBr): 3749, 3725, 3690, 3675, 3649, 3629, 2958, 2925, 2854, 1771, 1734, 1684, 1648, 1615, 1578, 1558, 1541, 1509, 1489, 1471, 1428, 1363, 1279, 1243, 1216, 1178, 1134, 1080, 1047, 977, 949, 754 cm^{-1}; ESI

FTMS exact mass calcd for $(C_{36}H_{33}ClFN_3O_6+Na)^+$ requires m/z 680.1934, found m/z 680.1935; Enantiomeric ratio: 90:10, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 6.02 min (major), t_R = 8.67 min (minor).

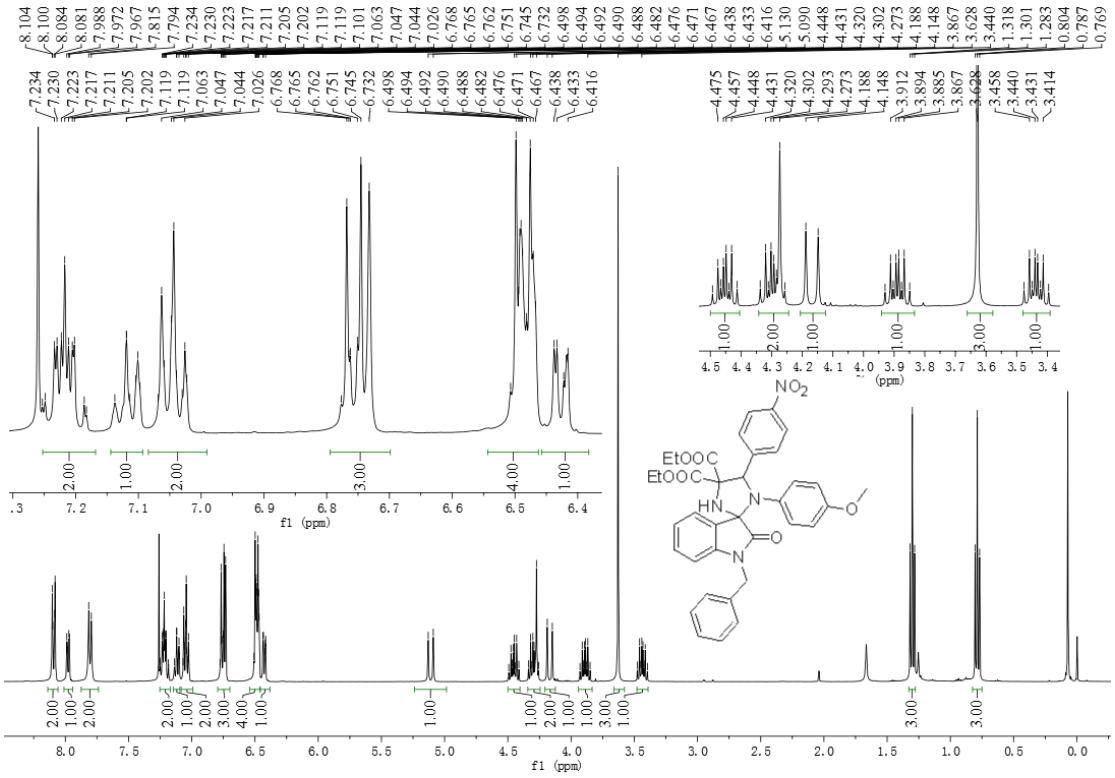
(2*S*,5*S*)-diethyl 1'-benzyl-5-(3-chloro-4-fluorophenyl)-1-(4-methoxyphenyl)-2'-oxospiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ag): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 71% (47.6 mg); >95:5 dr; colorless solid, m.p. 151.4-152.9 ^oC; $[\alpha]_D^{20}$ = -115.7 (c 0.65, Acetone); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 1H), 7.64 (d, *J* = 6.4 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.24 – 7.17 (m, 2H), 7.15 – 7.10 (m, 1H), 7.08 – 6.98 (m, 3H), 6.78 – 6.73 (m, 2H), 6.56 (s, 1H), 6.53 – 6.47 (m, 4H), 6.44 – 6.39 (m, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 4.50 – 4.39 (m, 1H), 4.35 – 4.26 (m, 1H), 4.24 (s, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 3.96 – 3.86 (m, 1H), 3.65 (s, 3H), 3.60 – 3.51 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 169.8, 169.3, 157.5 (d, *J* = 247.4 Hz), 156.7, 144.0, 134.9, 134.5(d, *J* = 3.7 Hz), 134.2, 131.1, 128.4, 127.2, 126.9, 126.6, 125.6, 124.8, 123.3, 120.7 (d, *J* = 17.5 Hz), 116.1 (d, *J* = 20.8 Hz), 113.9, 109.7, 82.7, 75.0, 66.0, 62.8, 62.3, 55.1, 43.1, 14.0, 13.4; IR (KBr): 3750, 3735, 3690, 3649, 2961, 2925, 2854, 1731, 1685, 1615, 1541, 1509, 1497, 1470, 1457, 1439, 1417, 1367, 1351, 1281, 1261, 1244, 1216, 1177, 1107, 1082, 1060, 1045, 955, 860, 793, 755, 669, 661 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}ClFN_3O_6+Na)^+$ requires m/z 680.1934, found m/z 680.1937; Enantiomeric ratio: 88:12, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 6.07 min (major), t_R = 9.77 min (minor).

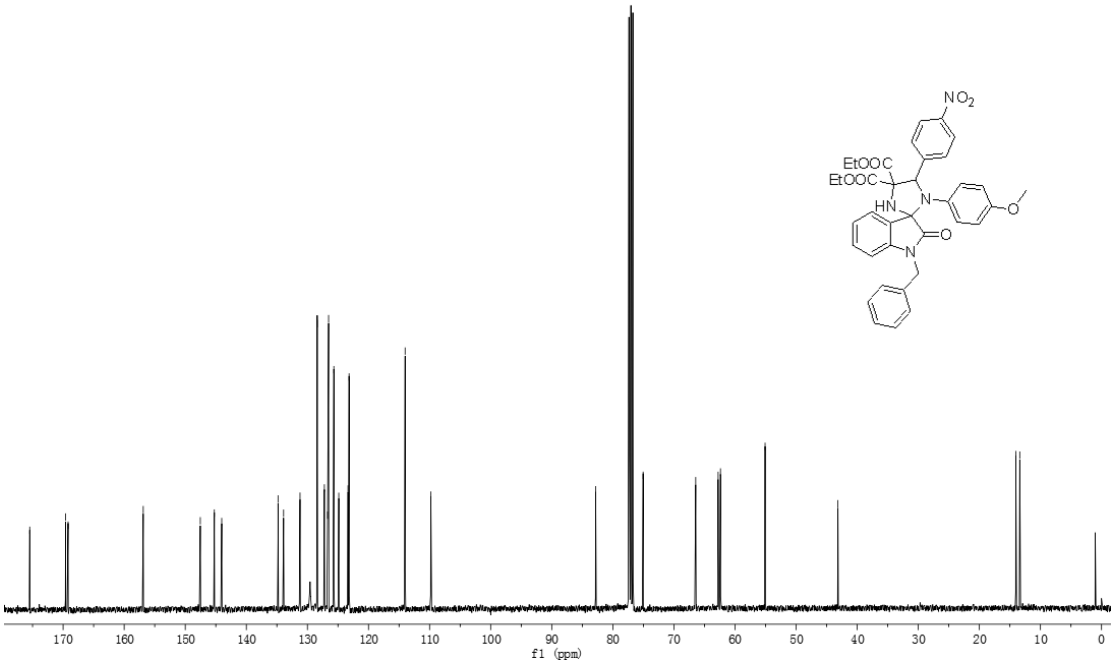
(2*S*,5*S*)-diethyl 1'-benzyl-1-(4-methoxyphenyl)-2'-oxo-5-phenylspiro[imidazolidine-2,3'-indoline]-4,4-dicarboxylate (5ah): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 48 h; yield: 43% (26.2 mg); >95:5 dr;

colorless sticky oil; $[\alpha]_D^{20}$ = -120.9 (c 0.41, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.26 – 7.15 (m, 5H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 2H), 6.78 – 6.73 (m, 2H), 6.60 (s, 1H), 6.53 (d, *J* = 7.3 Hz, 2H), 6.50 – 6.45 (m, 2H), 6.45 – 6.40 (m, 1H), 5.13 (d, *J* = 16.0 Hz, 1H), 4.50 – 4.41 (m, 1H), 4.33 – 4.25 (m, 2H), 4.17 (d, *J* = 16.0 Hz, 1H), 3.88 – 3.80 (m, 1H), 3.62 (s, 3H), 3.41 – 3.33 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 170.0, 169.5, 156.2, 144.0, 137.4, 135.0, 130.9, 128.5, 128.4, 128.0, 127.8, 127.4, 127.2, 126.7, 125.1, 124.8, 123.2, 113.8, 109.6, 82.6, 75.3, 67.1, 62.5, 62.0, 55.0, 43.2, 14.0, 13.3; IR (KBr): 3734, 3031, 2981, 2902, 1991, 1967, 1942, 1921, 1868, 1828, 1792, 1771, 1755, 1733, 1698, 1616, 1557, 1541, 1509, 1495, 1472, 1456, 1368, 1346, 1281, 1248, 1218, 1177, 1133, 1109, 1078, 1047 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{35}N_3O_6+Na)^+$ requires m/z 628.2418, found m/z 628.2419; Enantiomeric ratio: 72:28, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 7.67 min (major), t_R = 14.60 min (minor).

5. NMR spectra of products 5

5aa





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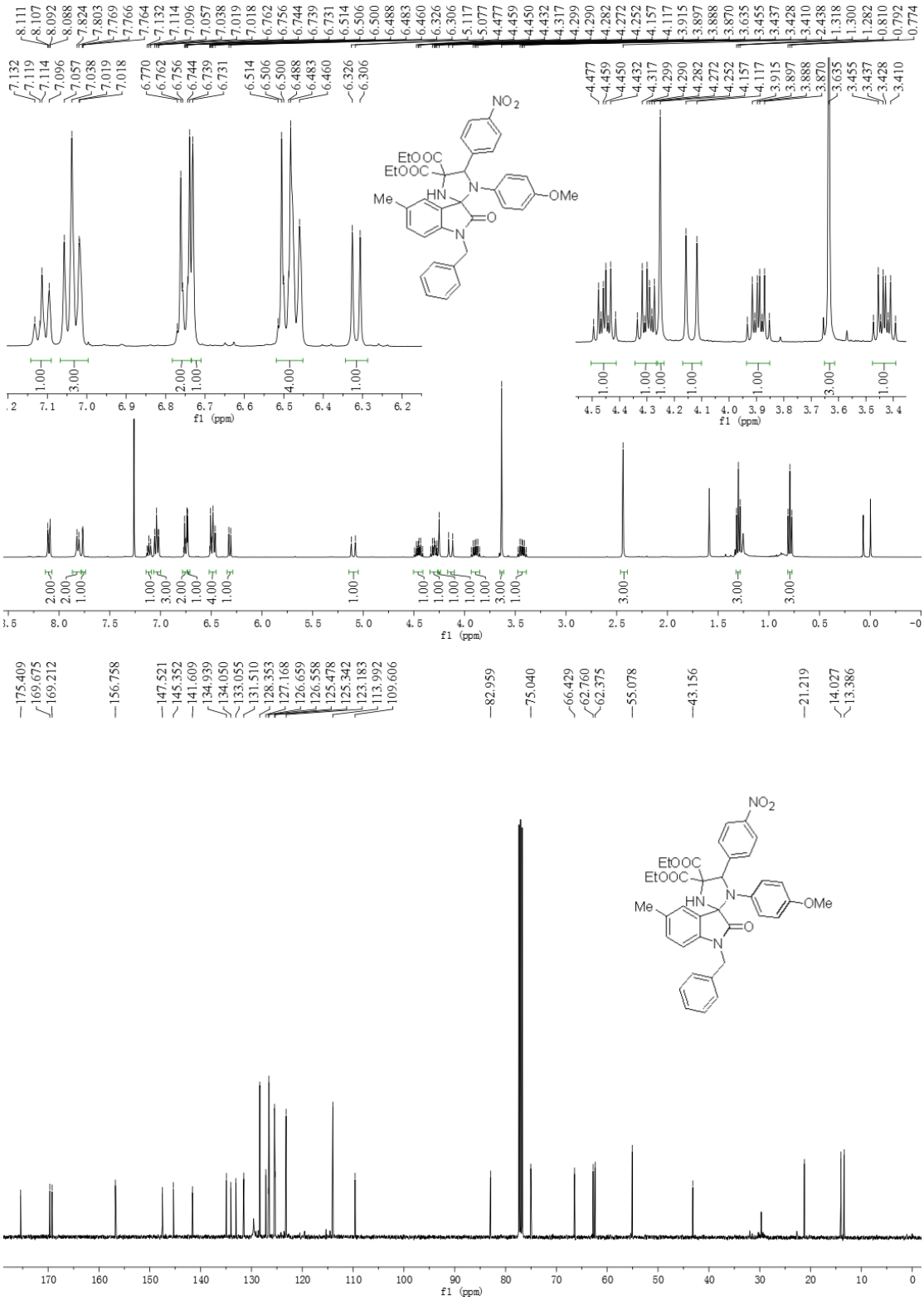

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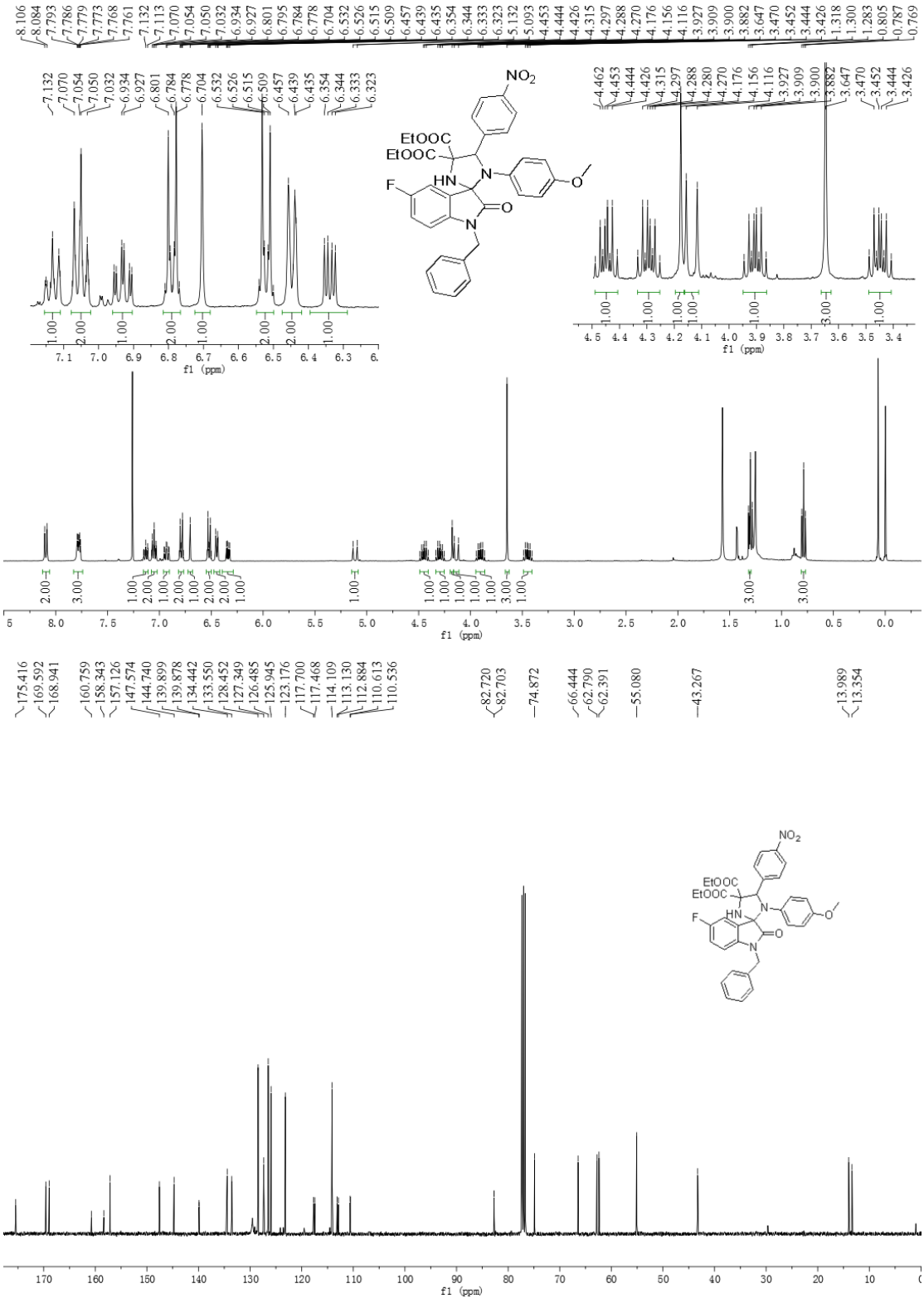

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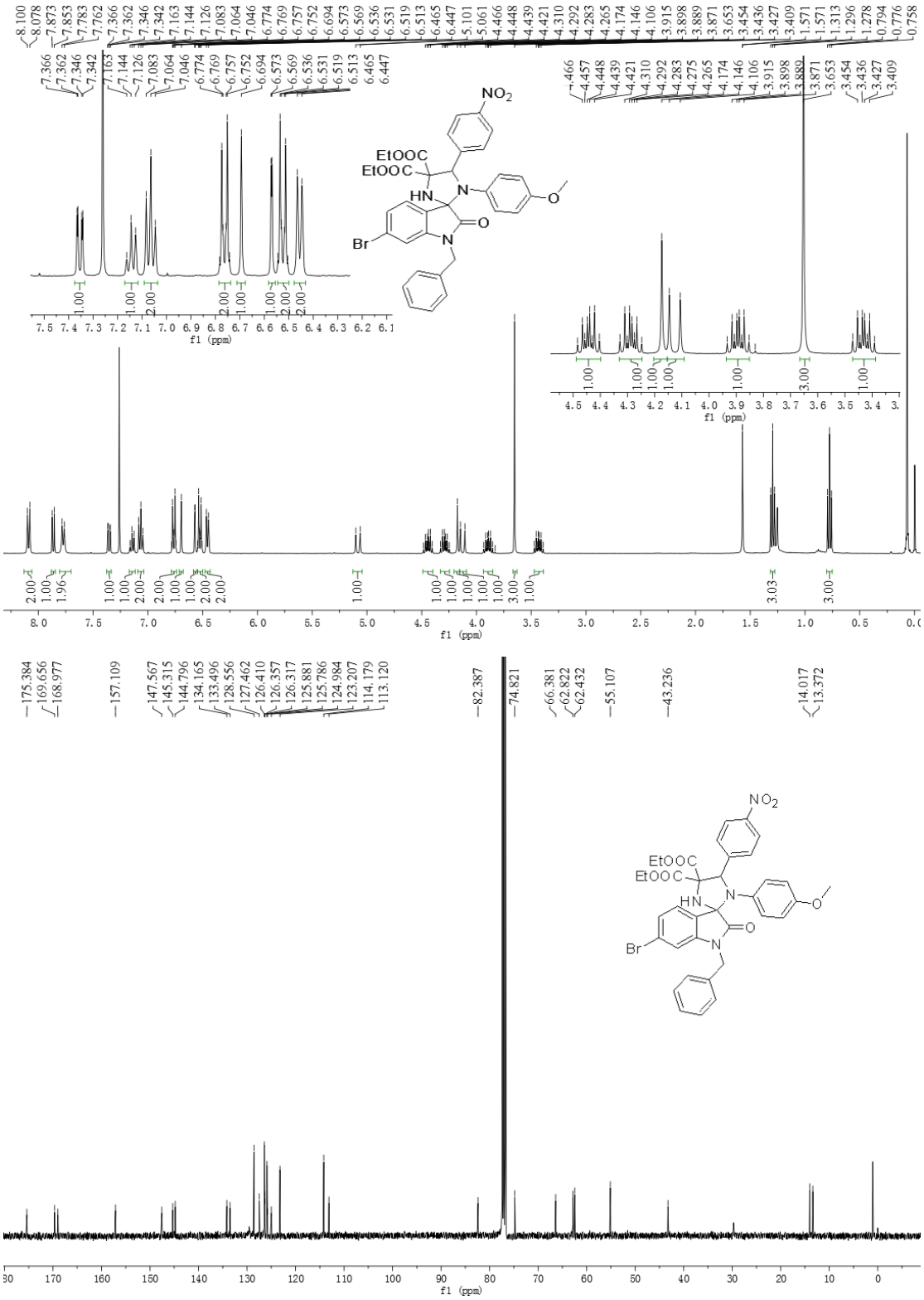
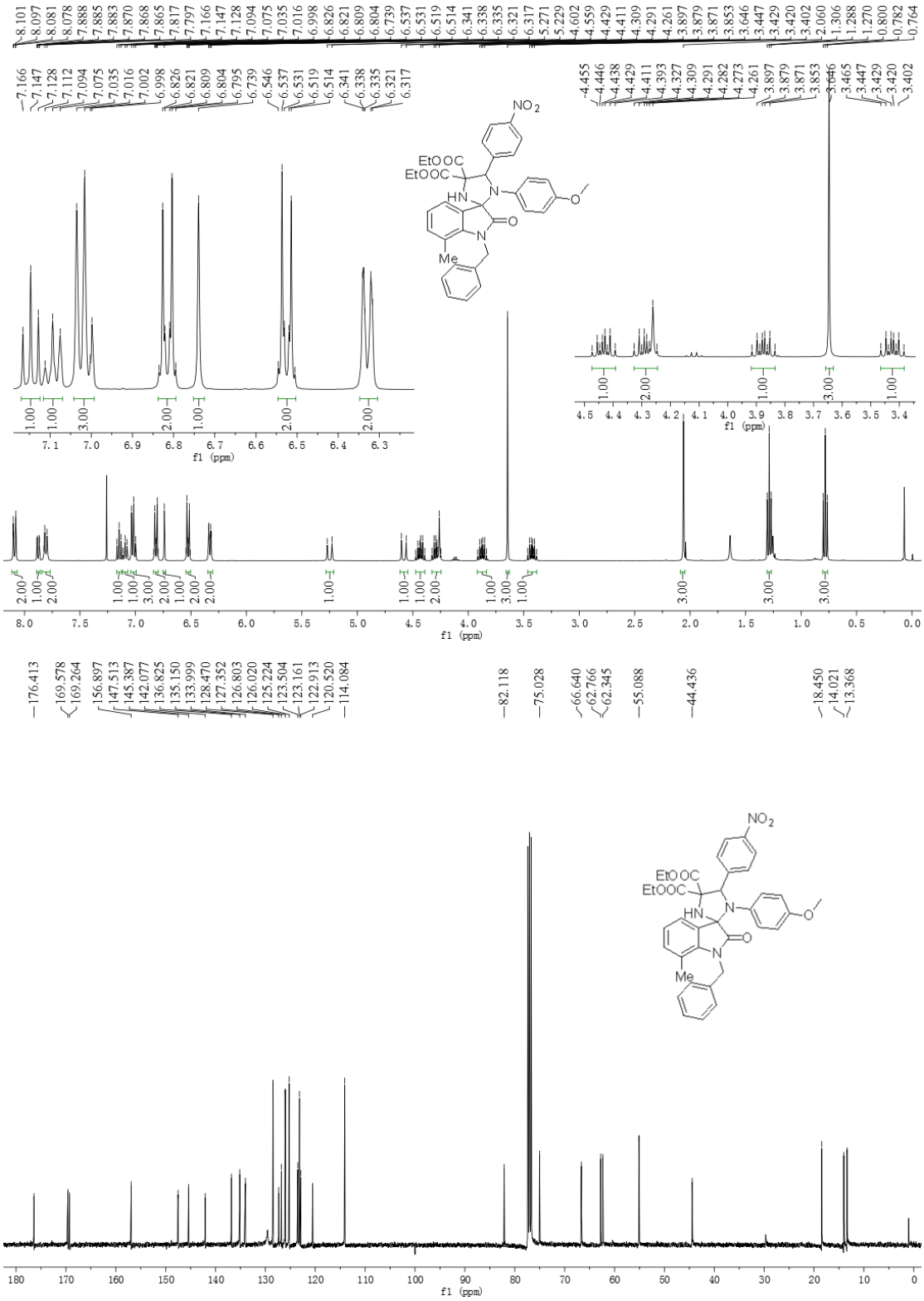


5ea



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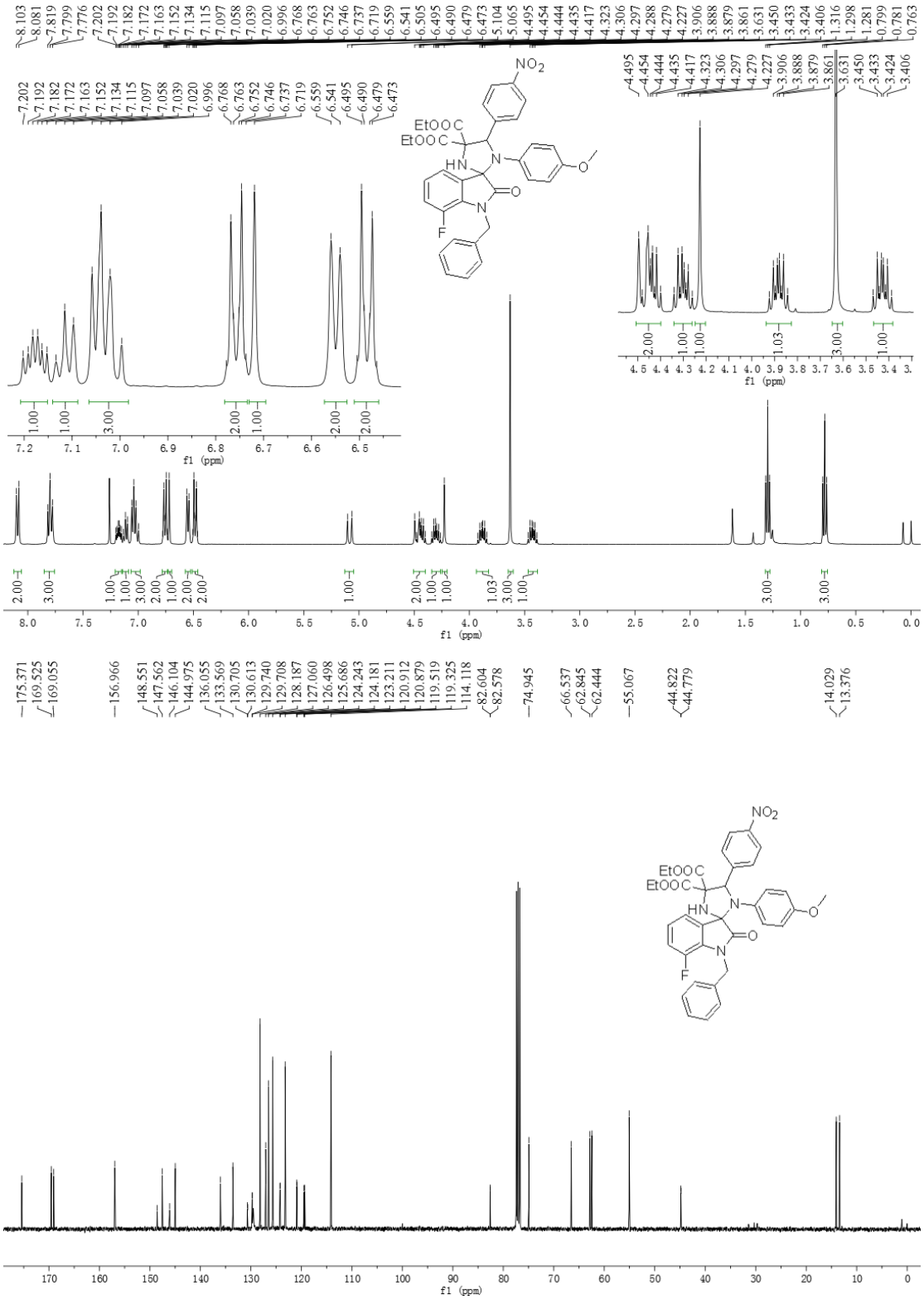

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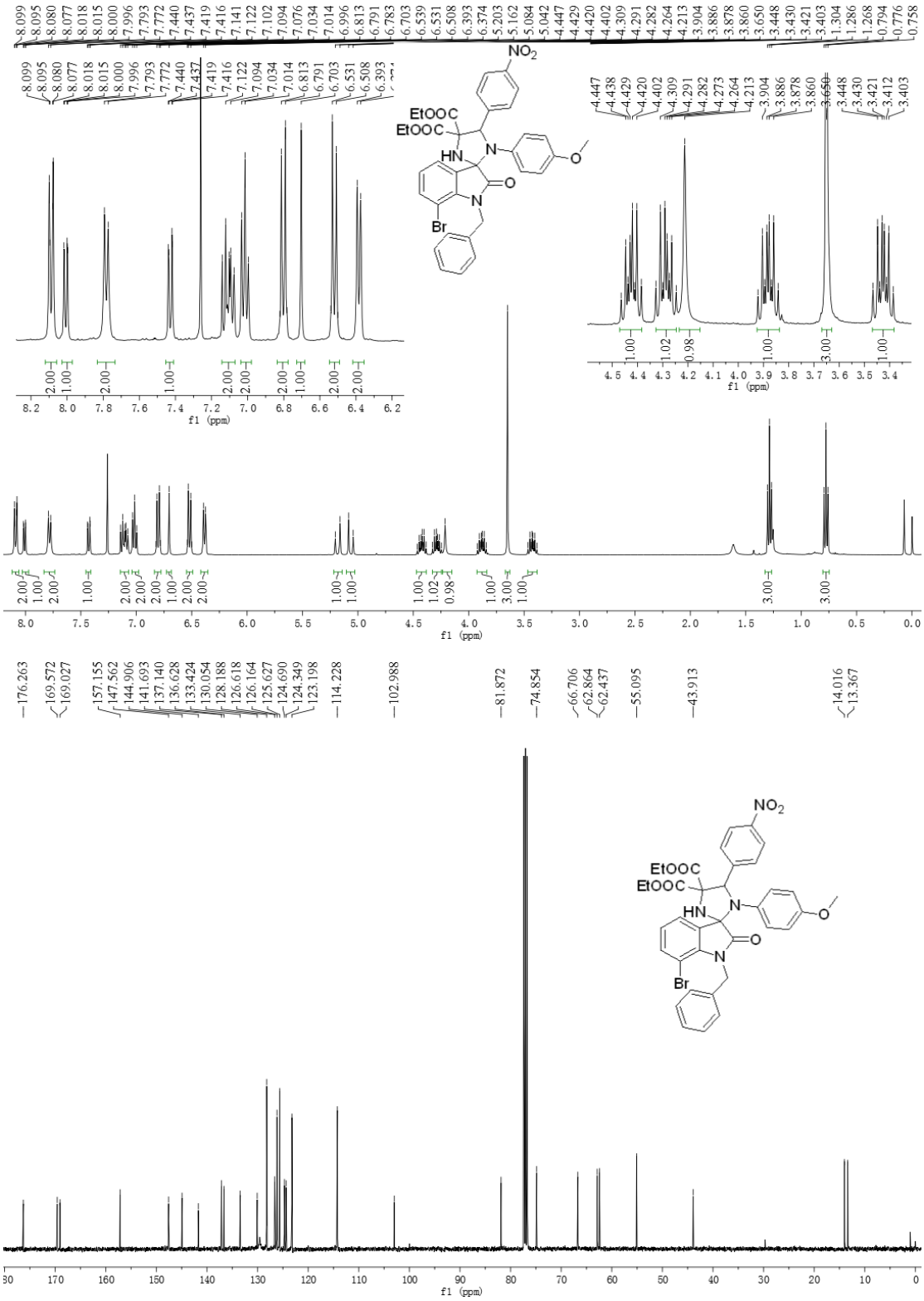

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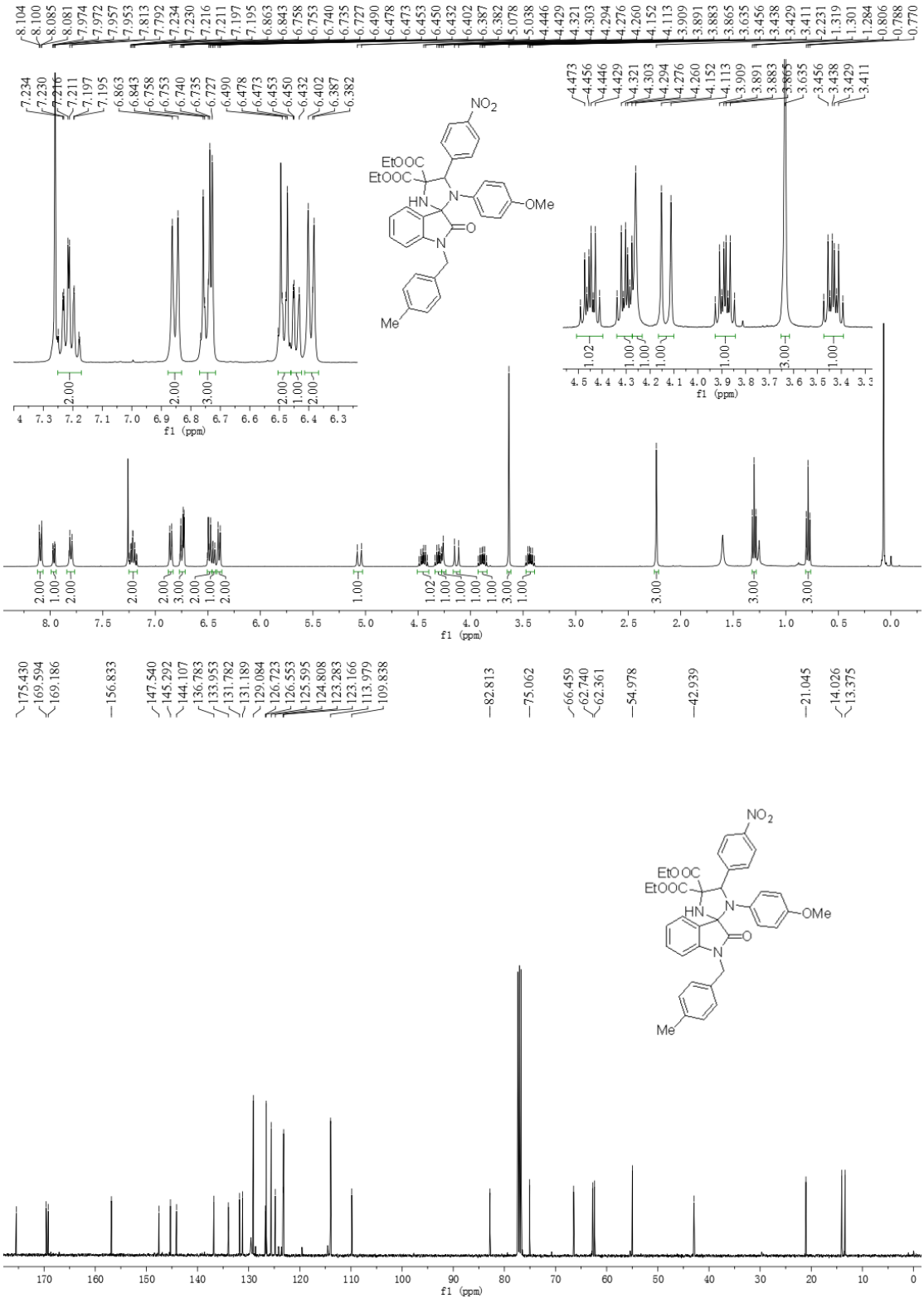

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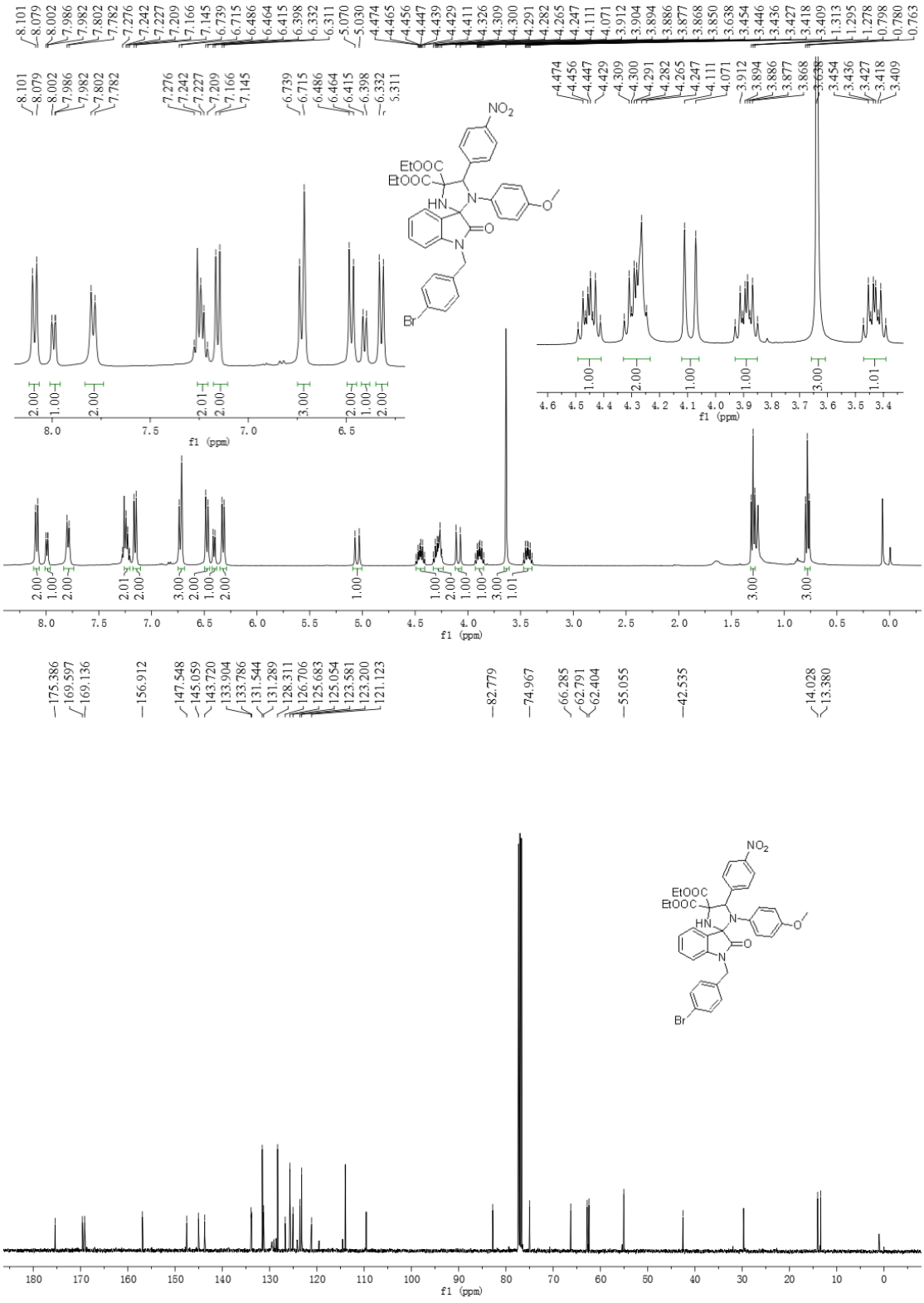

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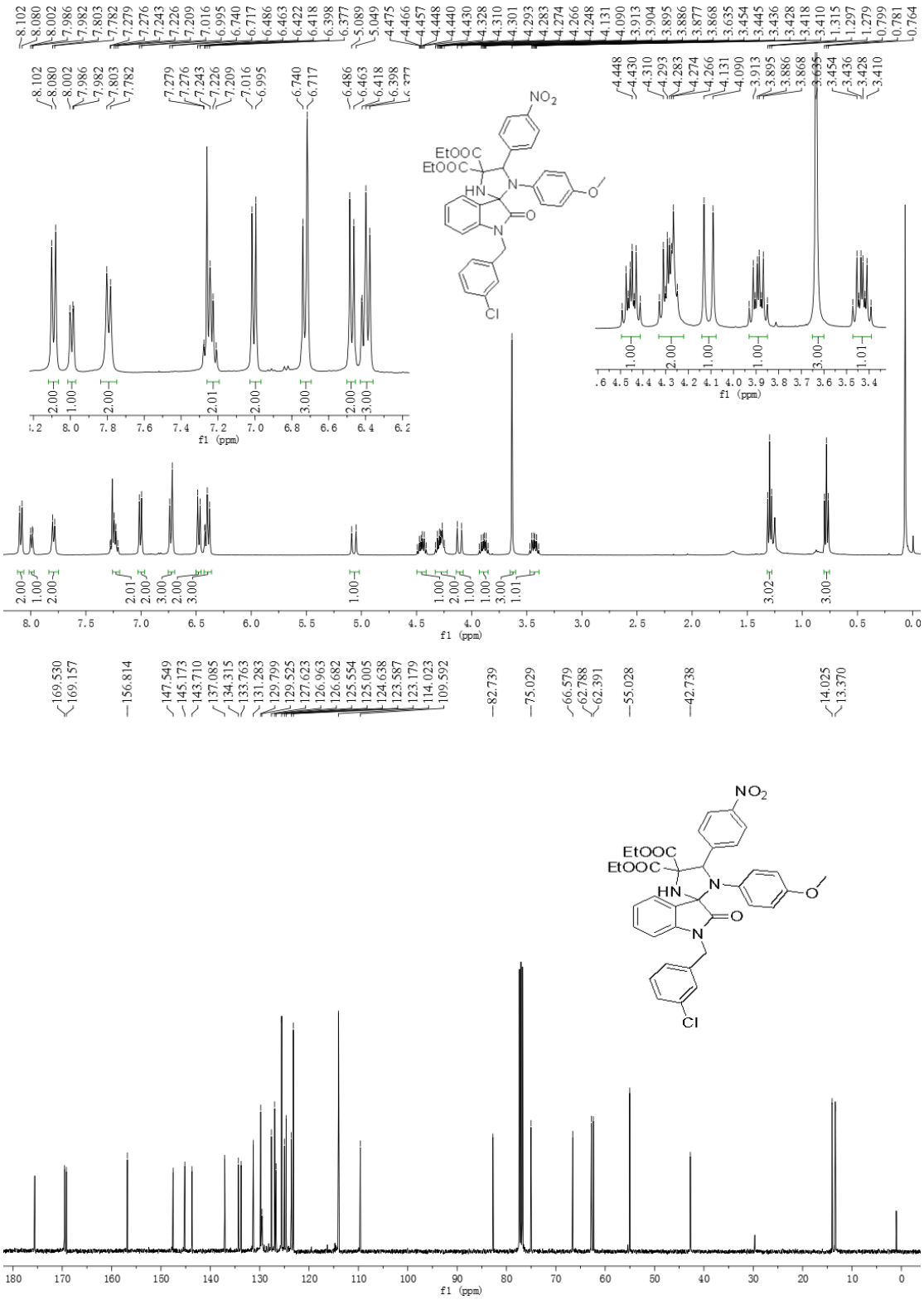

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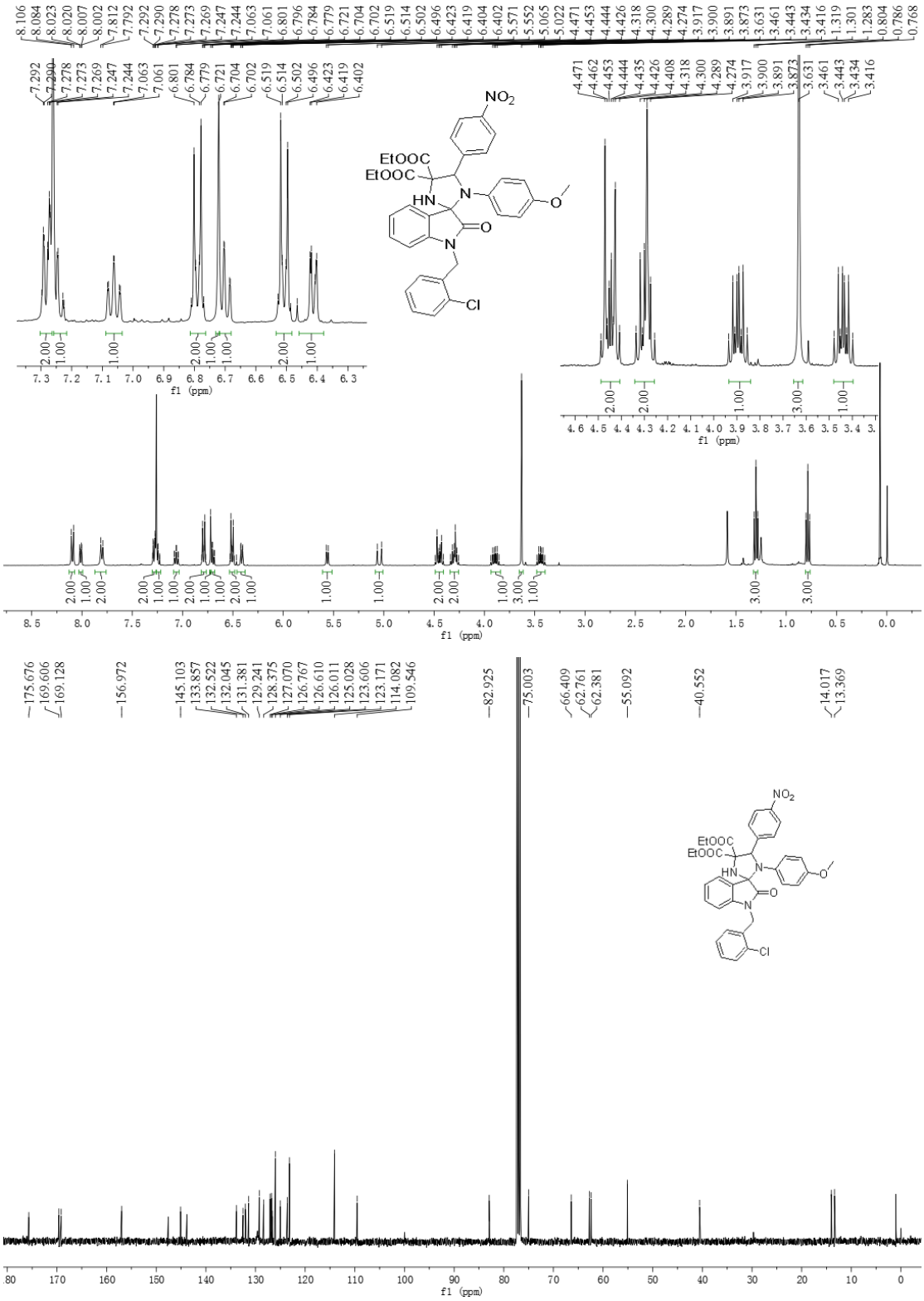

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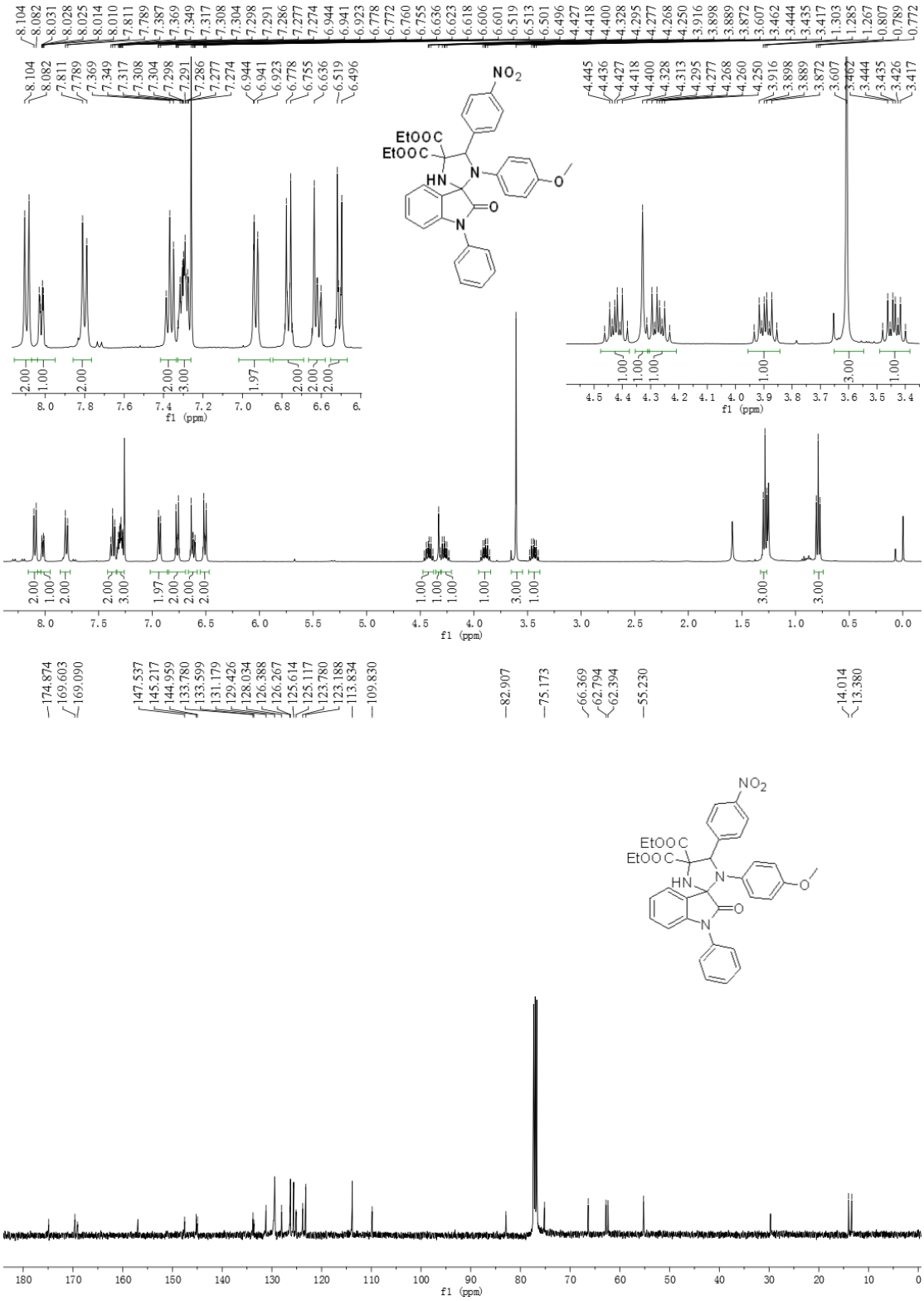

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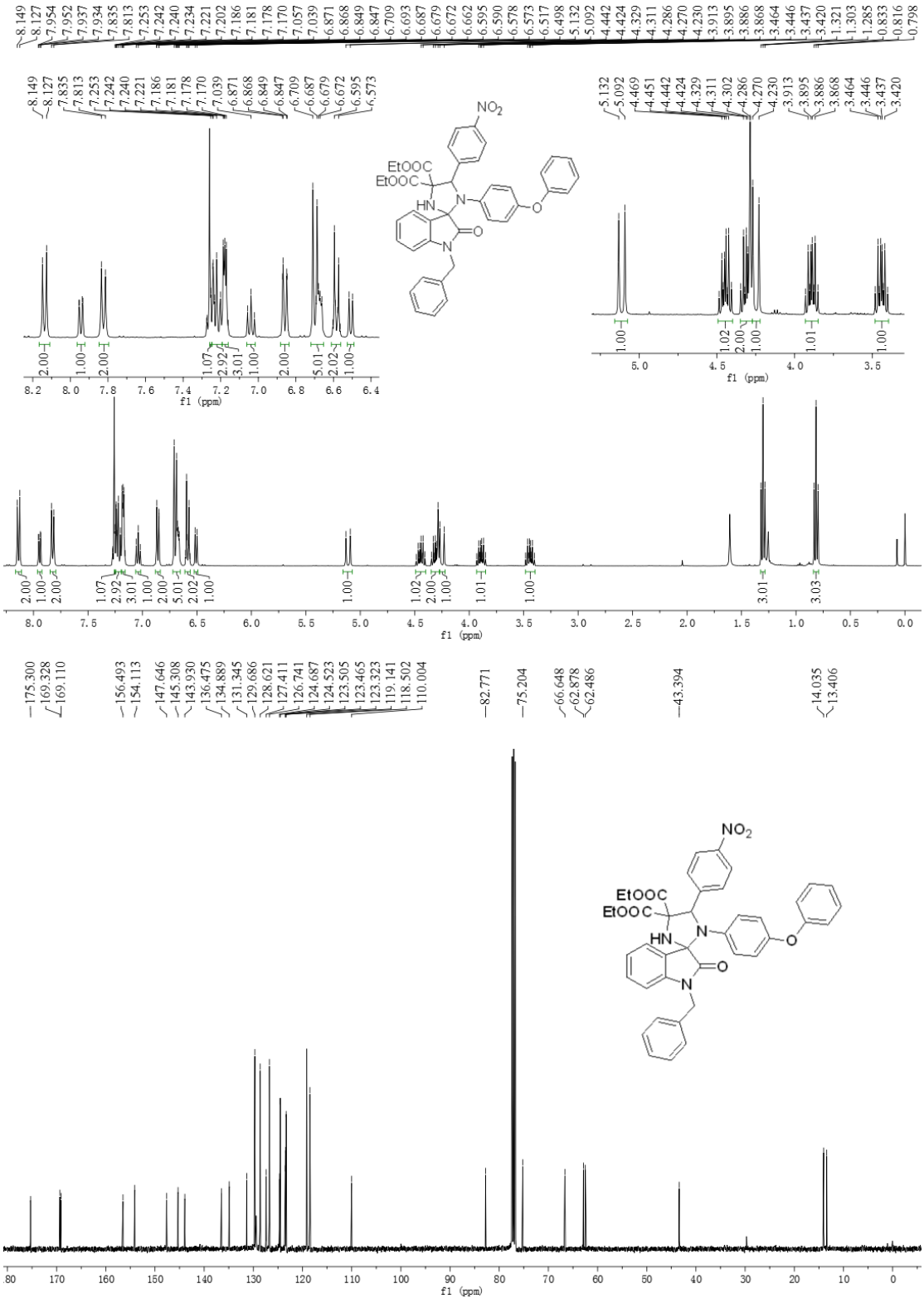

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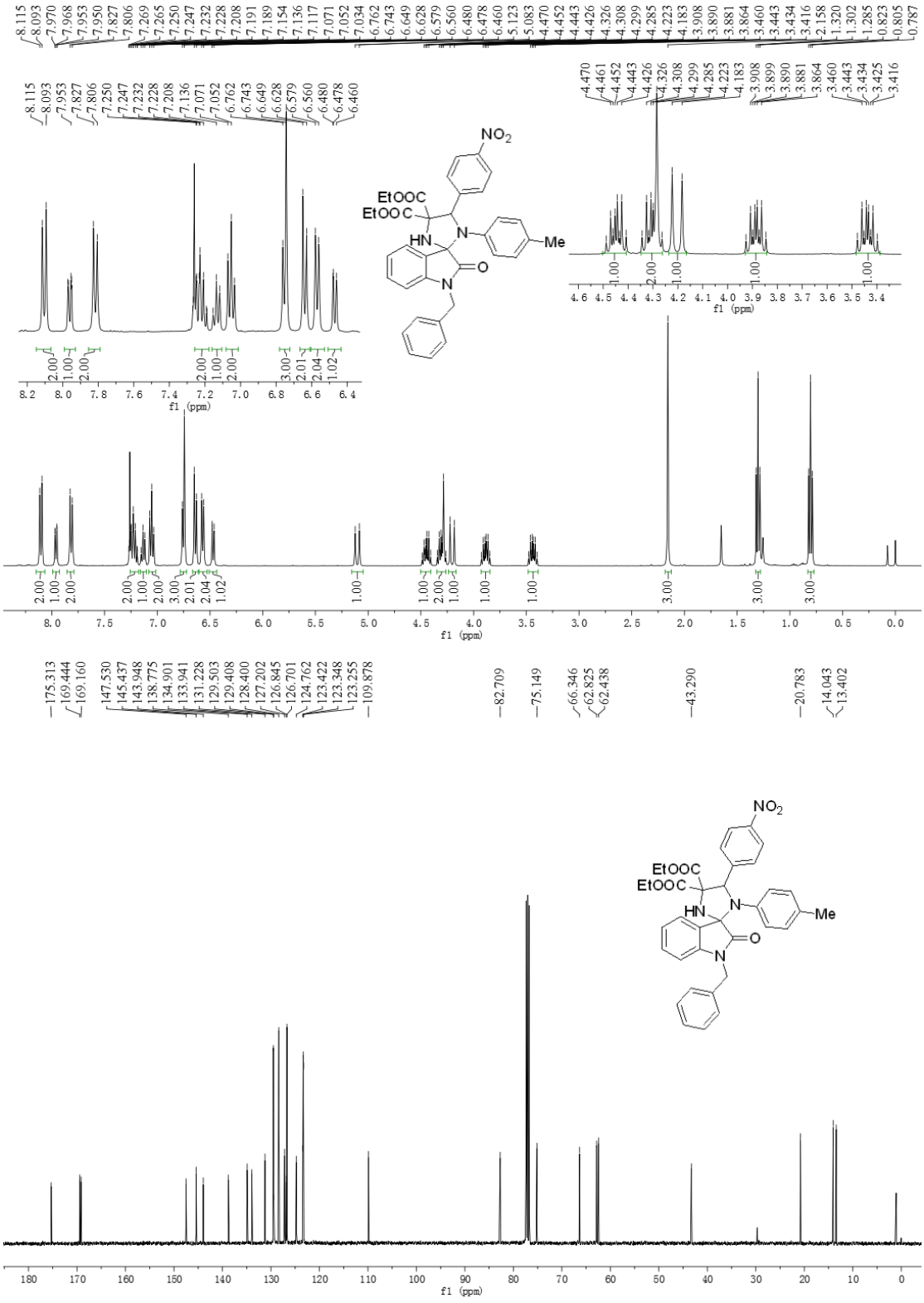

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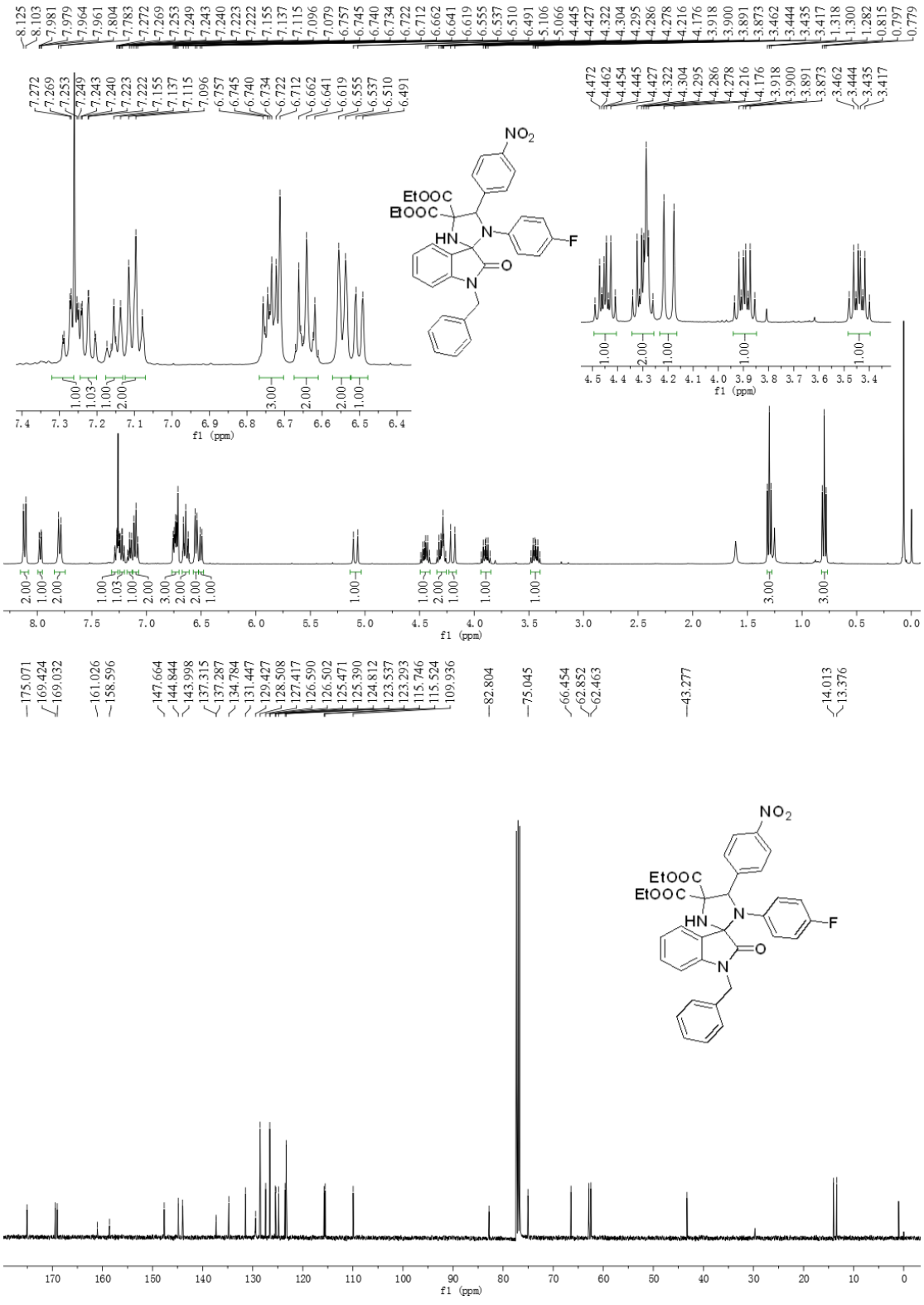

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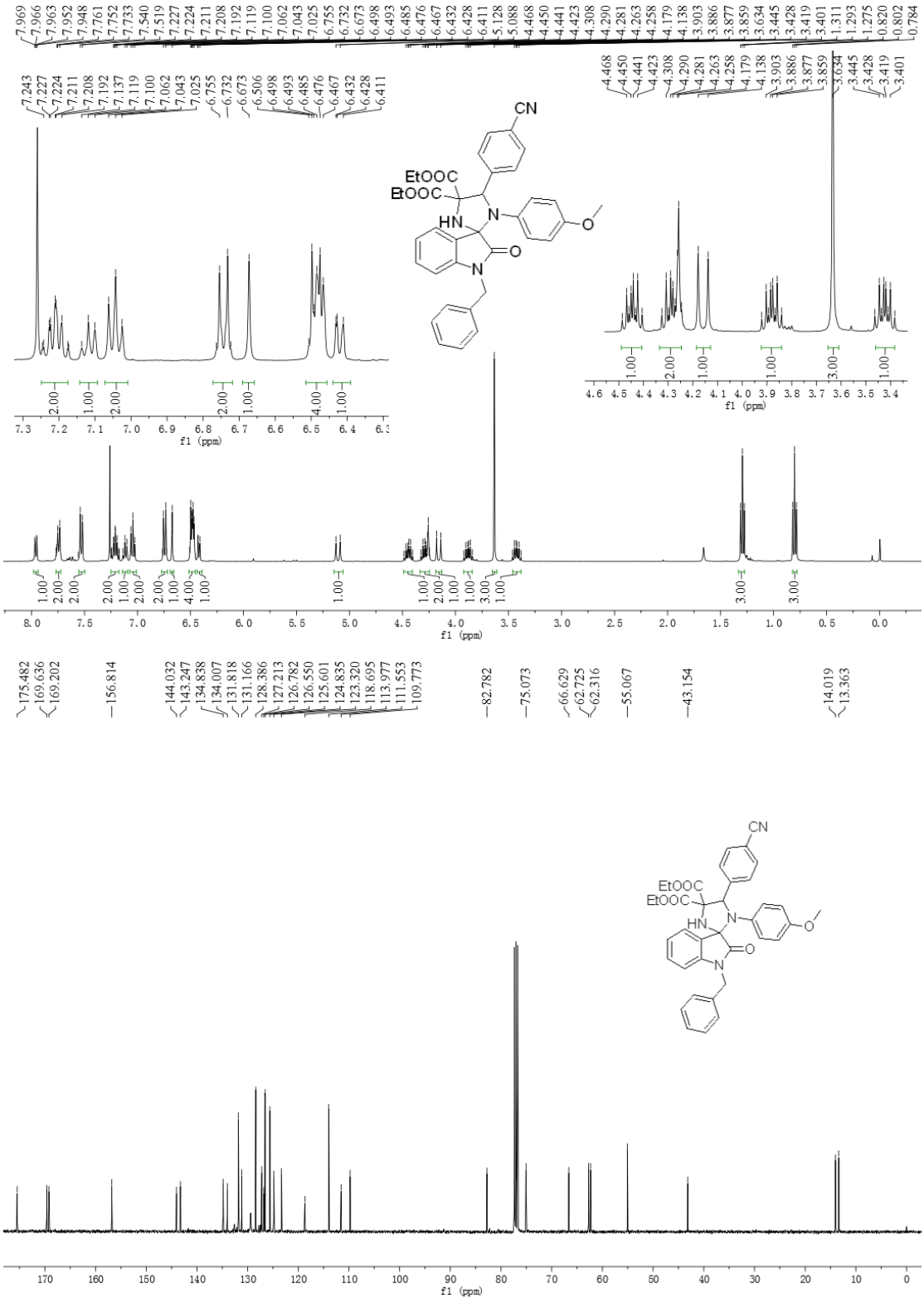

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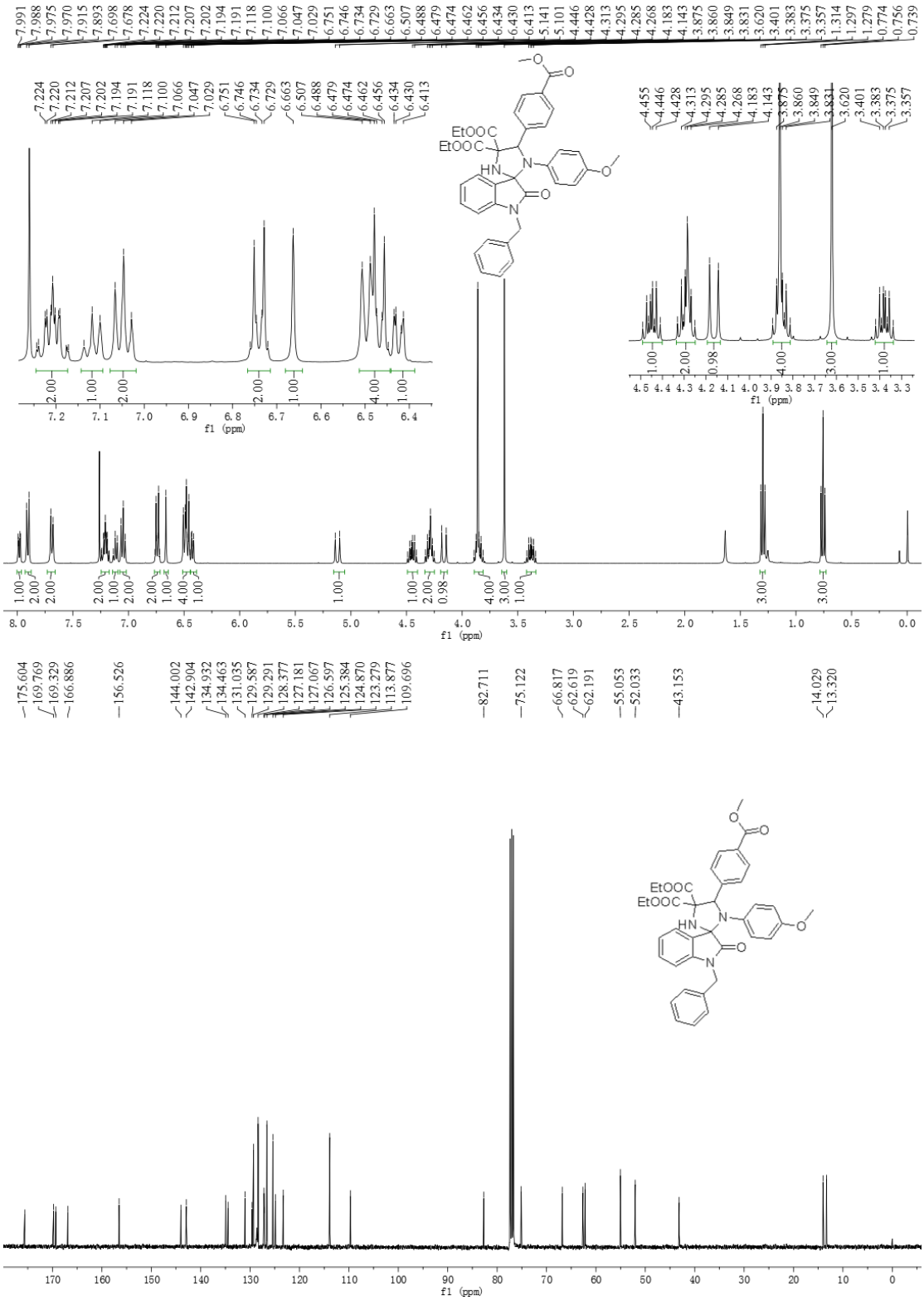

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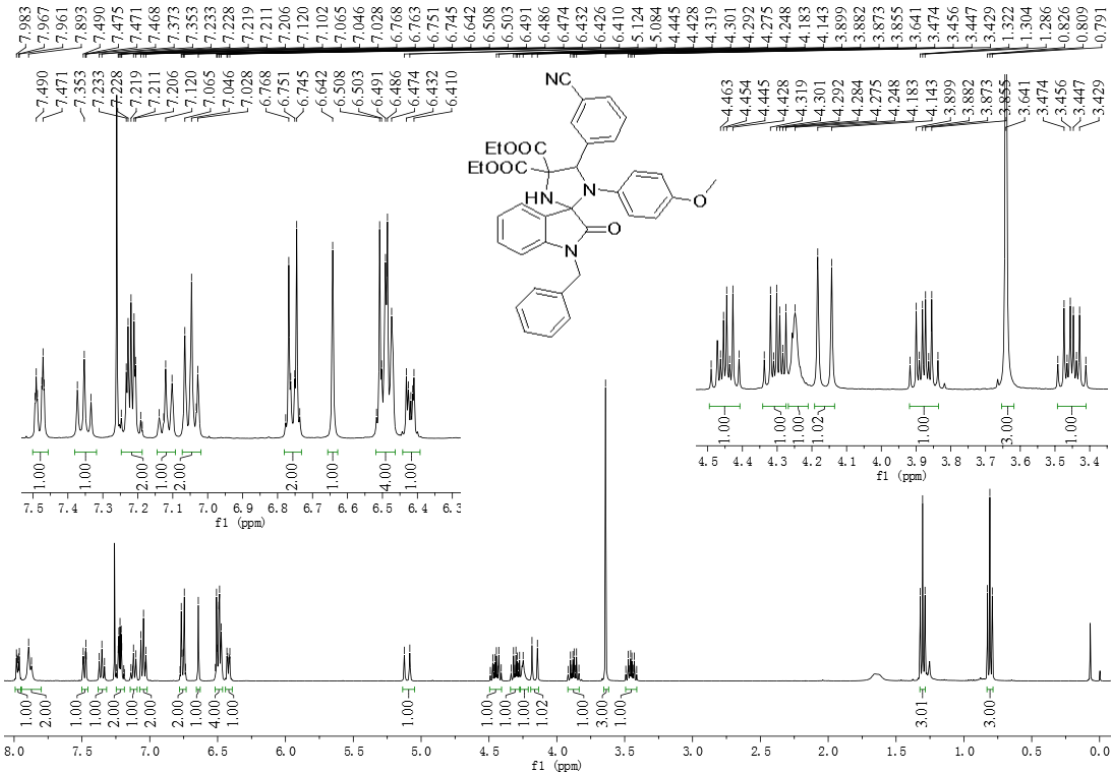

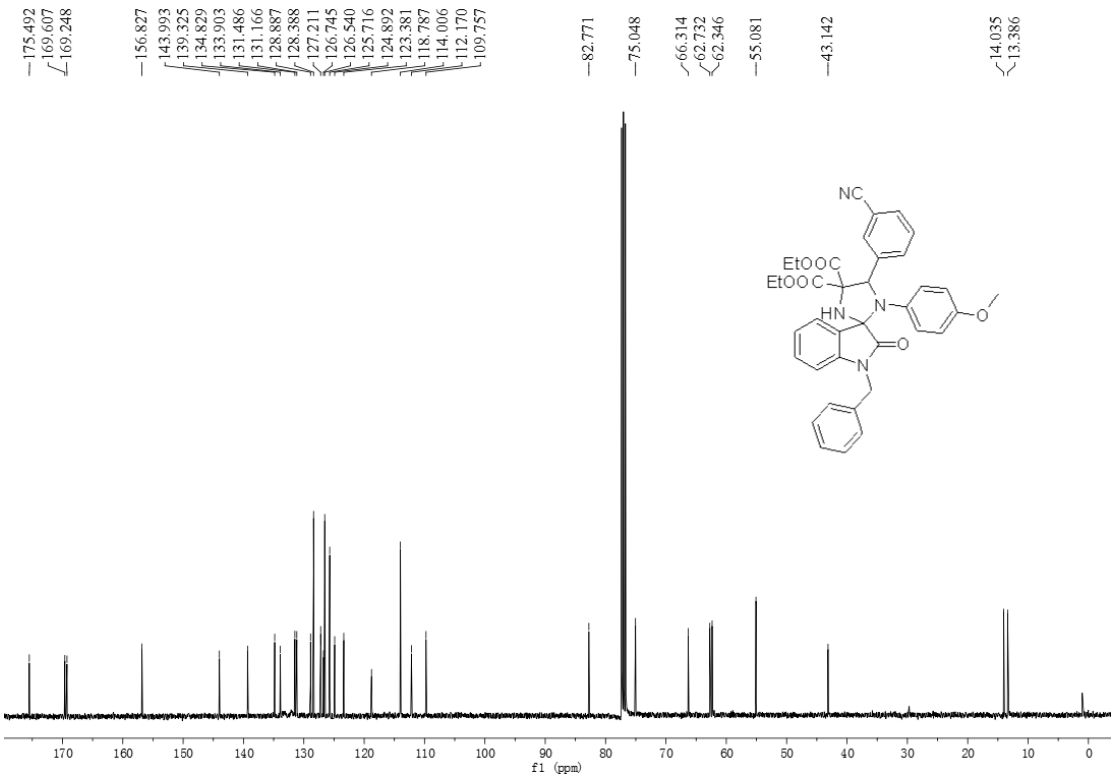

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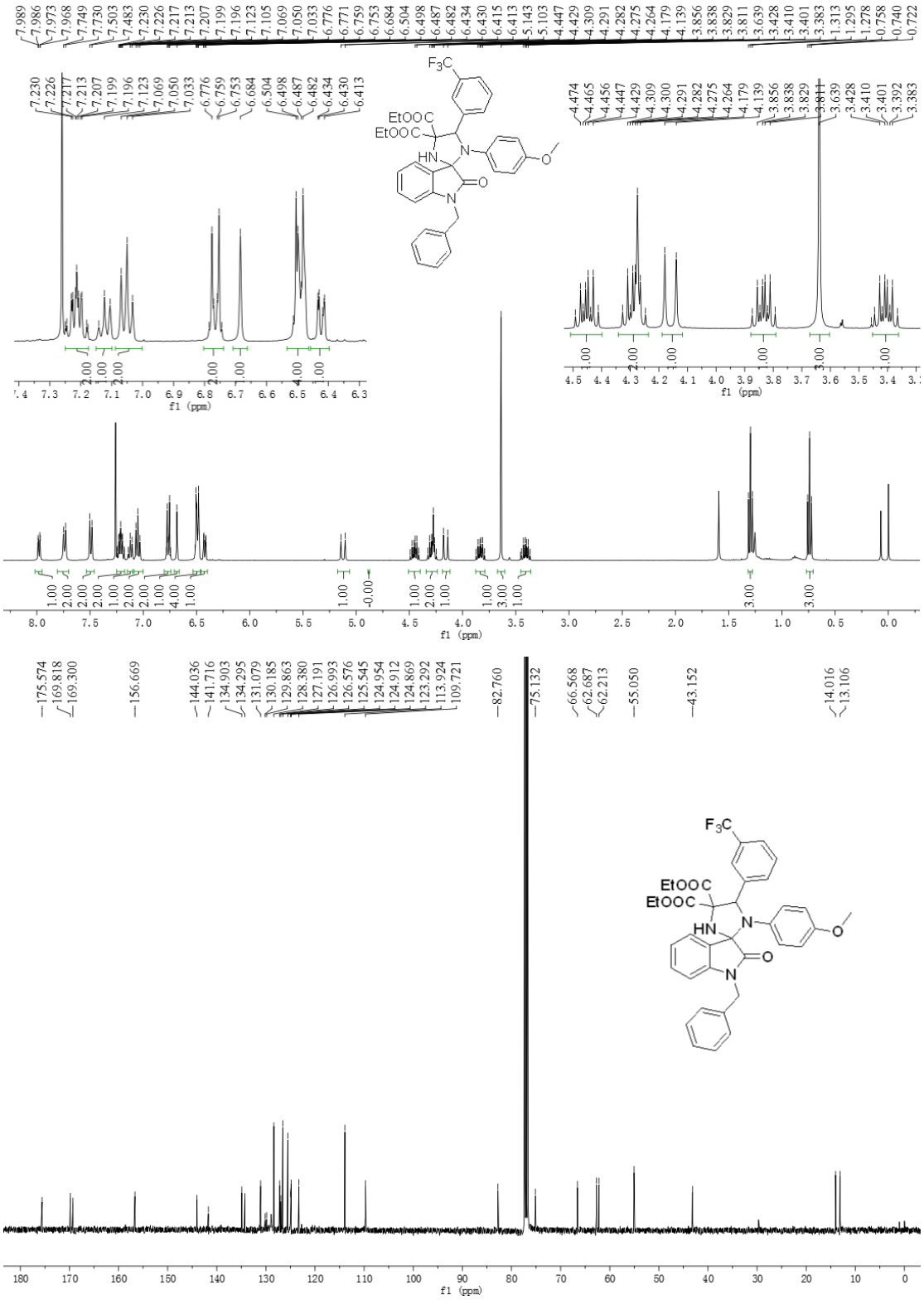

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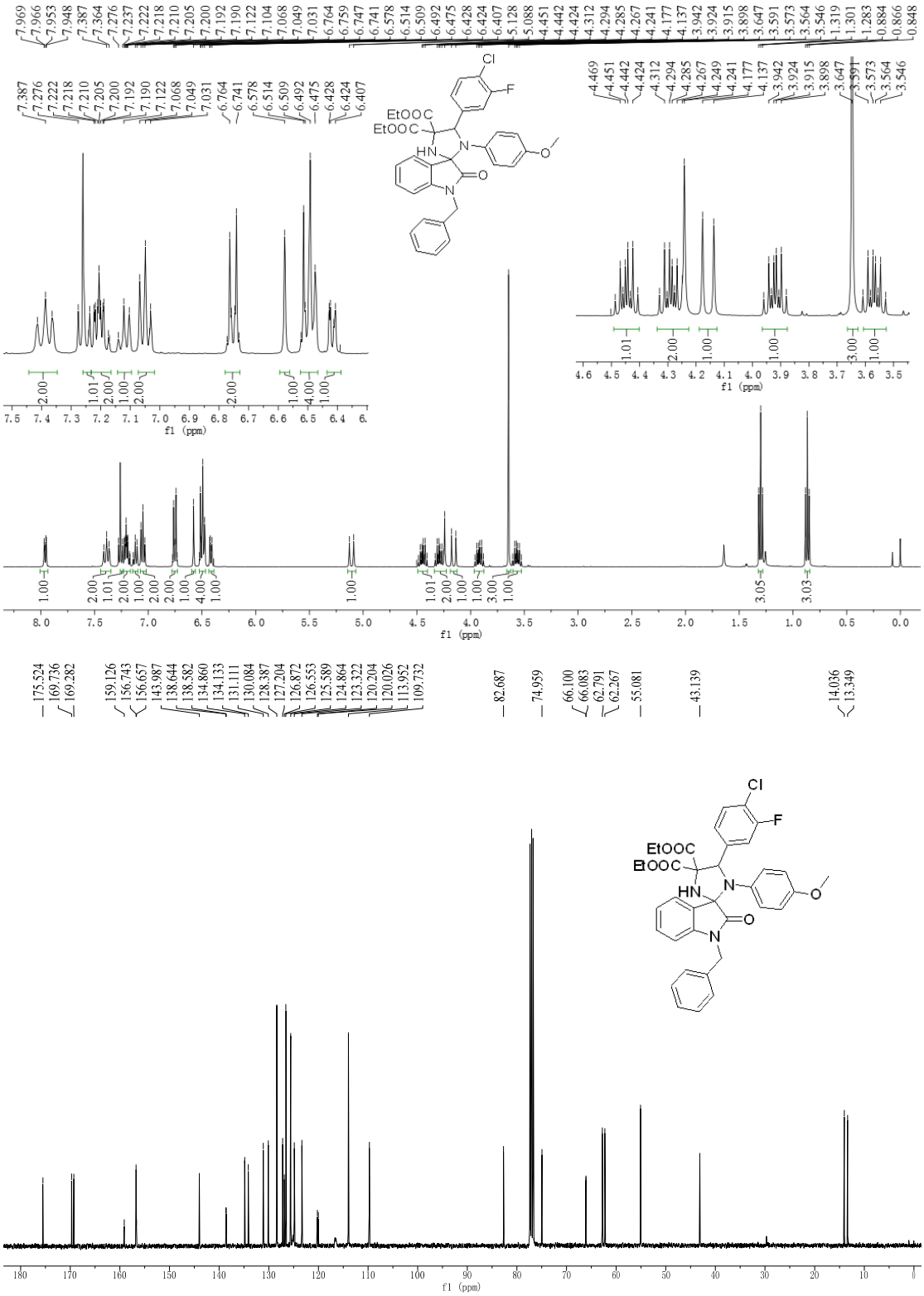

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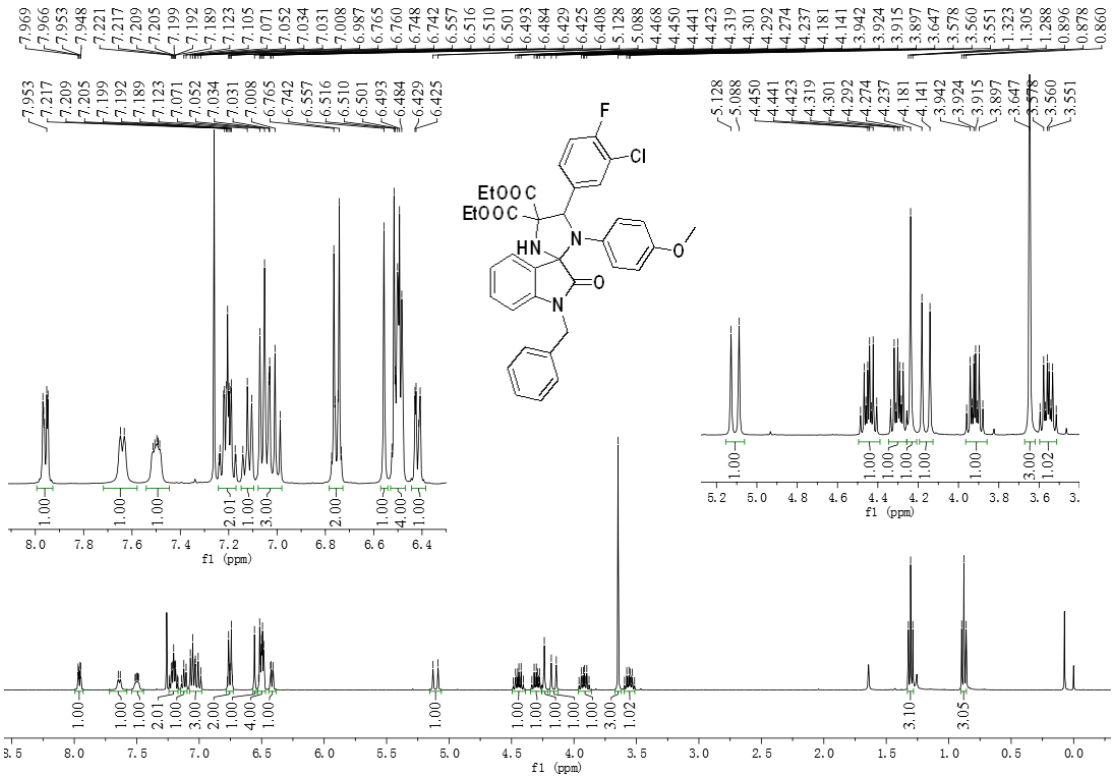
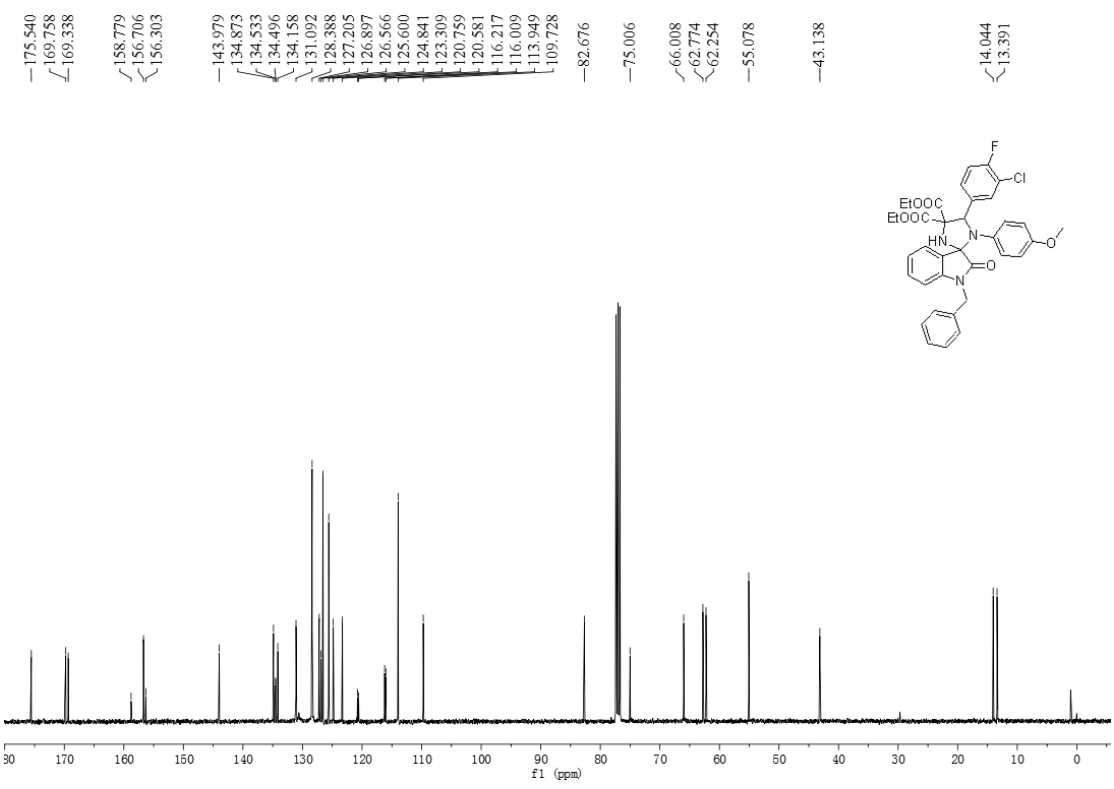

F
Cl
EtOOC
EtOOC
HN
N
O
O
N
f1 (ppm)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134.873
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134.496
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126.897
126.566
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124.841
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120.759
120.581
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116.009
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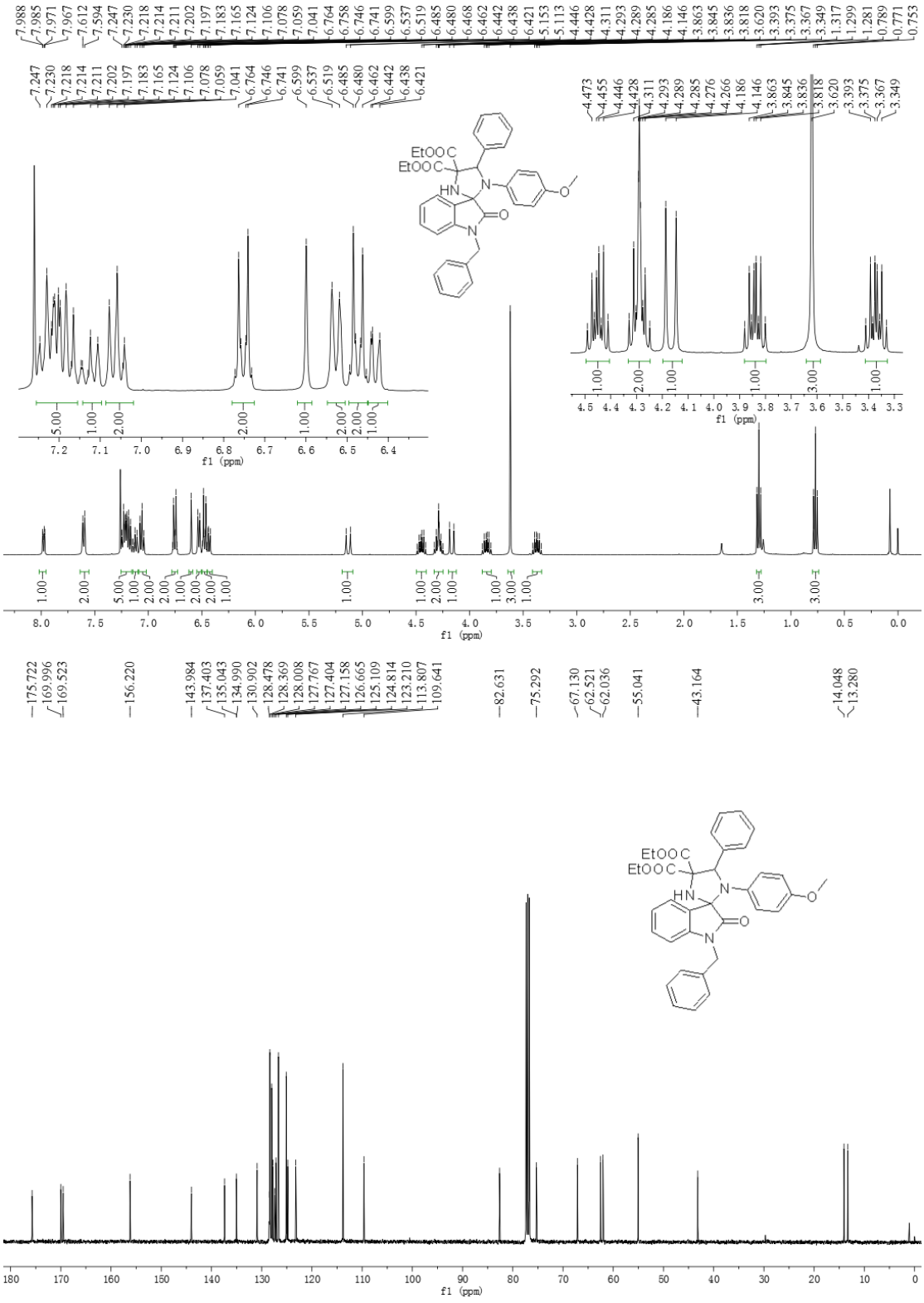
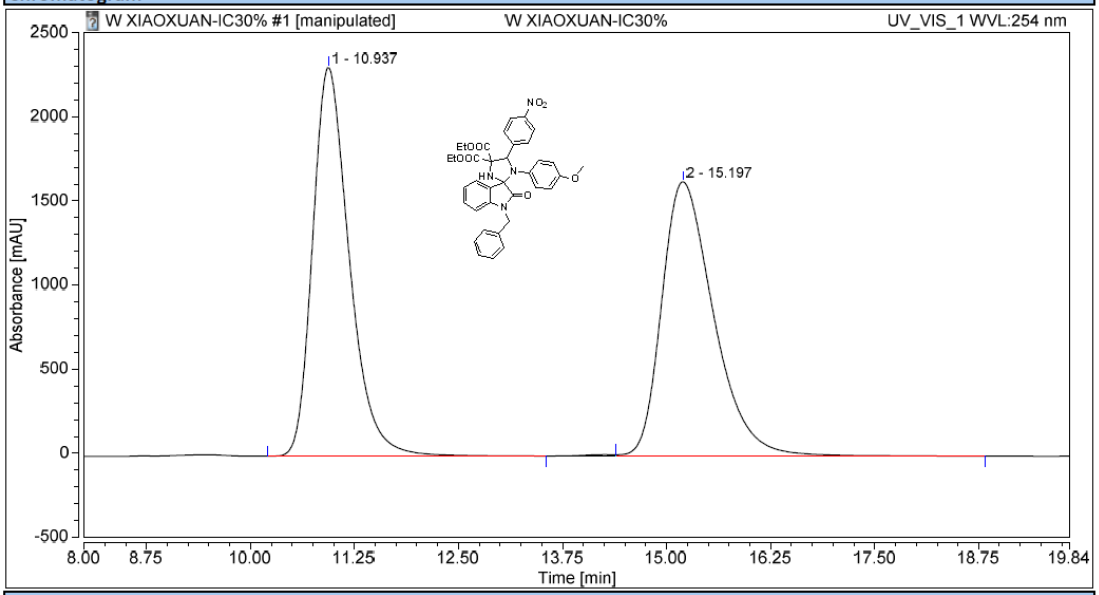
5ah



6. HPLC spectra of products 5

ent-5aa

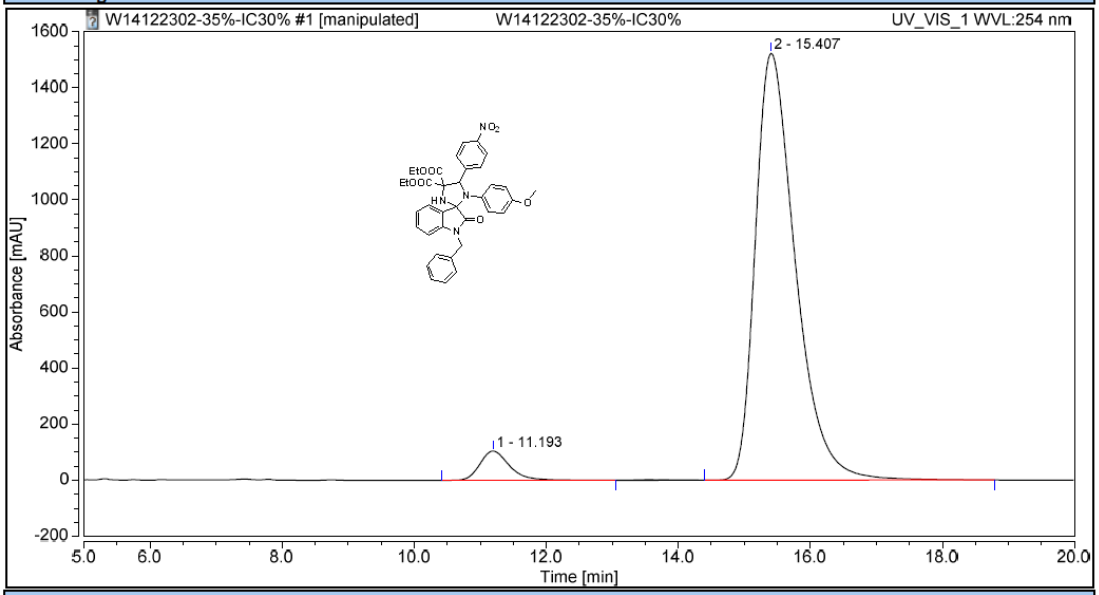
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.937	1183.498	2312.137	50.06	58.62	n.a.
2		15.197	1180.766	1632.047	49.94	41.38	n.a.
Total:			**2364.264**	**3944.184**	**100.00**	**100.00**	

Chromatogram

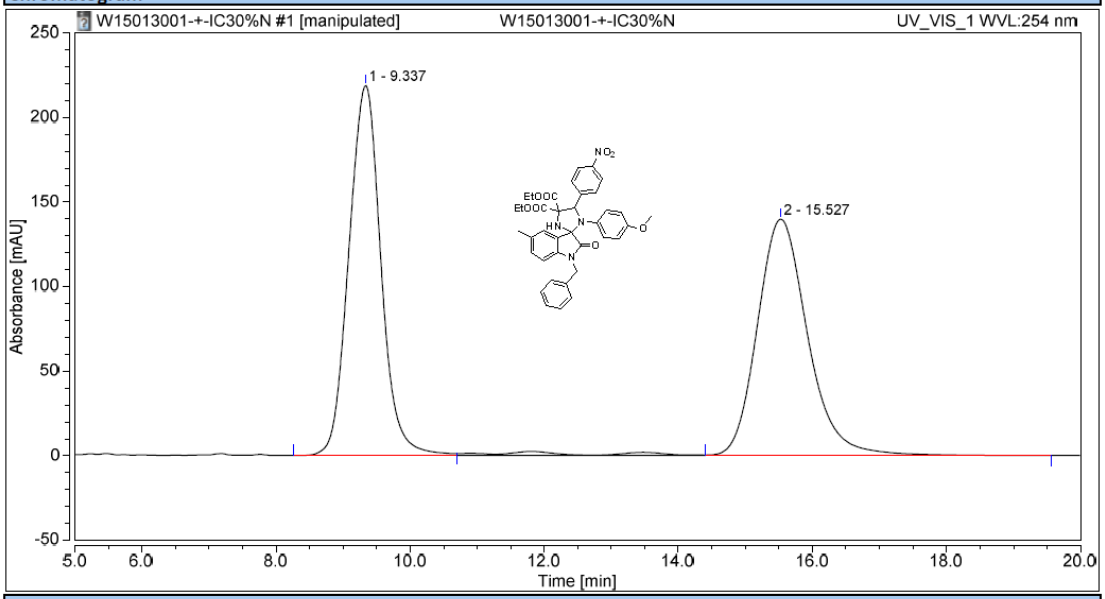


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.193	54.462	104.350	4.84	6.41	n.a.
2		15.407	1071.576	1523.380	95.16	93.59	n.a.
Total:			**1126.038**	**1627.730**	**100.00**	**100.00**	

5ba

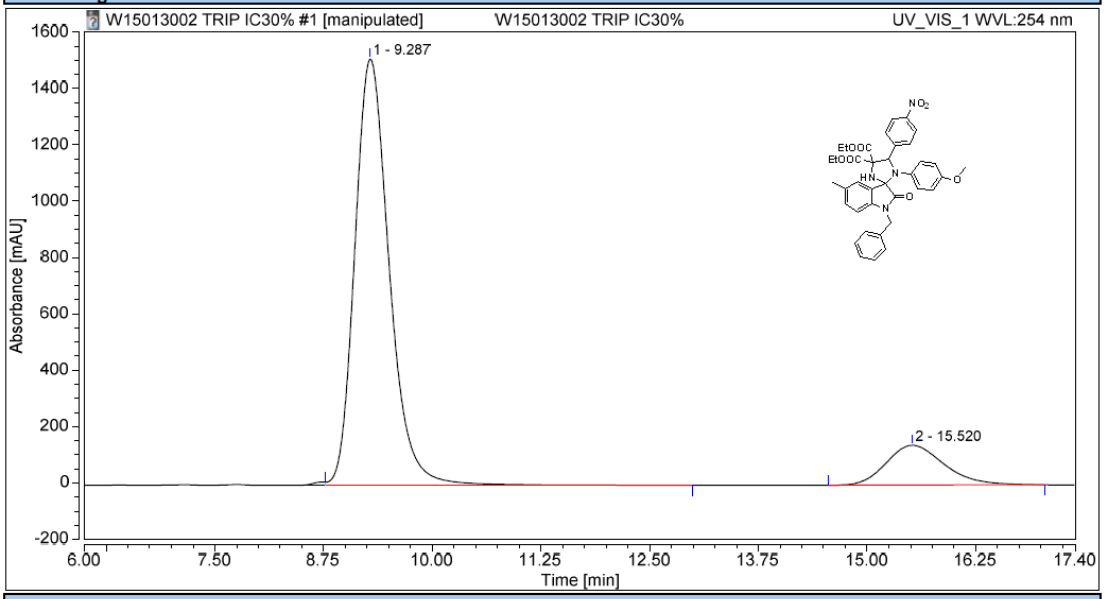
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.337	121.023	218.785	50.00	61.01	n.a.
2		15.527	121.047	139.798	50.00	38.99	n.a.
Total:			**242.070**	**358.583**	**100.00**	**100.00**	

Chromatogram

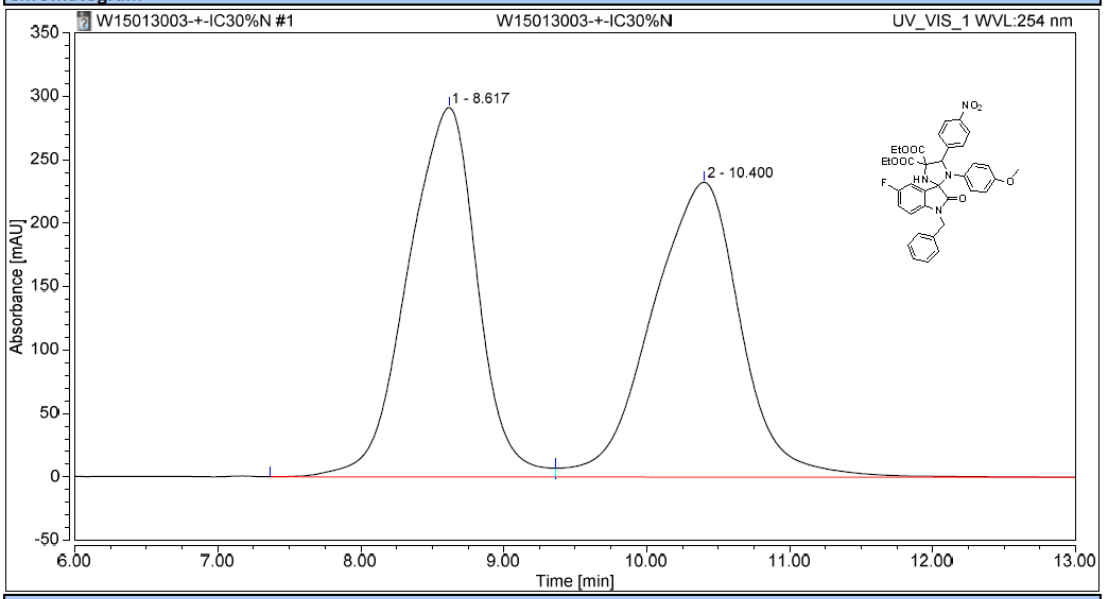


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.287	693.332	1512.733	86.45	91.48	n.a.
2		15.520	108.703	140.822	13.55	8.52	n.a.
Total:			**802.035**	**1653.555**	**100.00**	**100.00**	

5ca

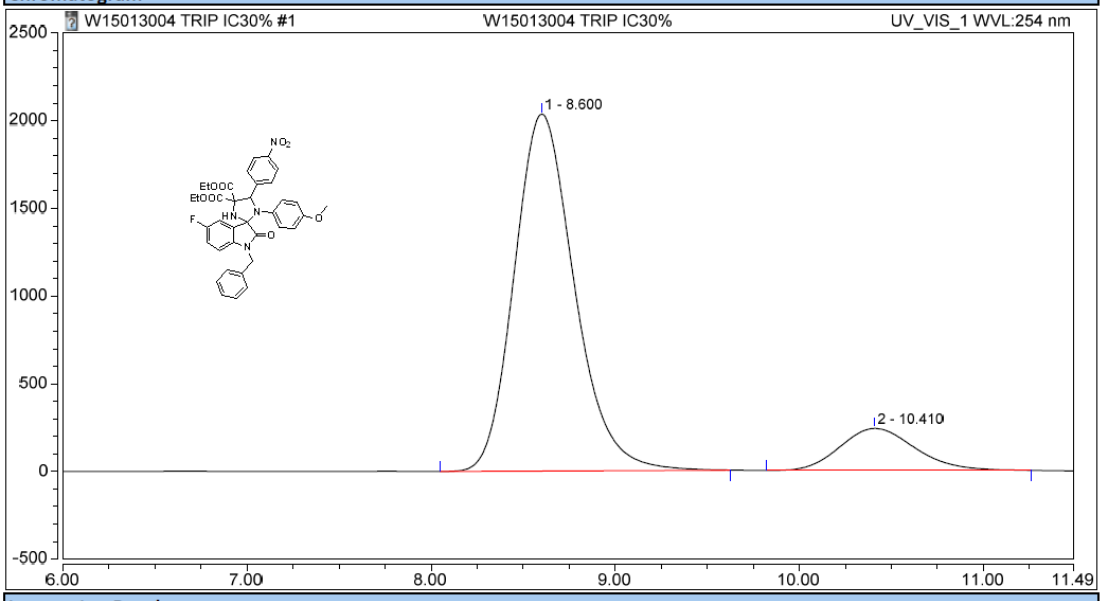
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.617	163.524	291.300	49.42	55.61	n.a.
2		10.400	167.376	232.527	50.58	44.39	n.a.
Total:			**330.900**	**523.828**	**100.00**	**100.00**	

Chromatogram

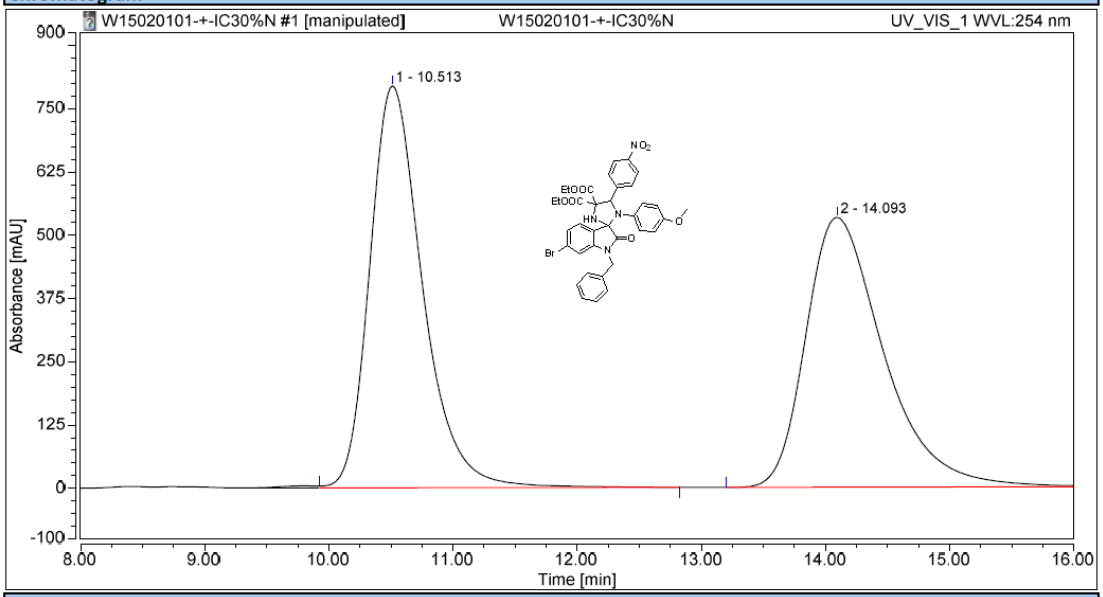


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.600	770.475	2035.448	87.11	89.46	n.a.
2		10.410	114.003	239.864	12.89	10.54	n.a.
Total:			**884.478**	**2275.312**	**100.00**	**100.00**	

5da

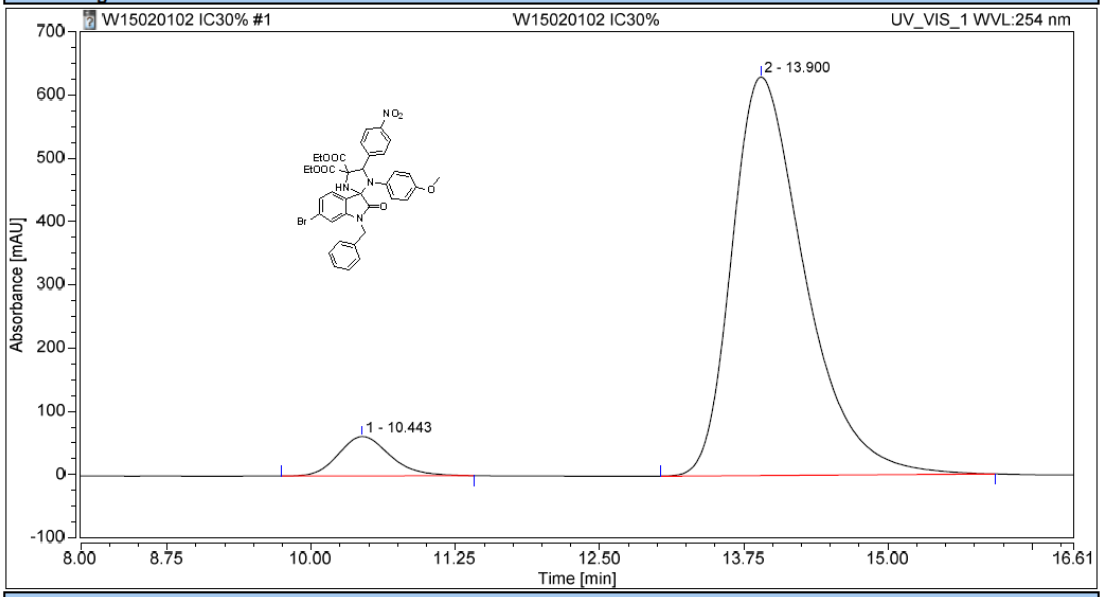
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.513	391.341	794.180	50.30	59.83	n.a.
2		14.093	386.740	533.233	49.70	40.17	n.a.
Total:			**778.081**	**1327.413**	**100.00**	**100.00**	

Chromatogram

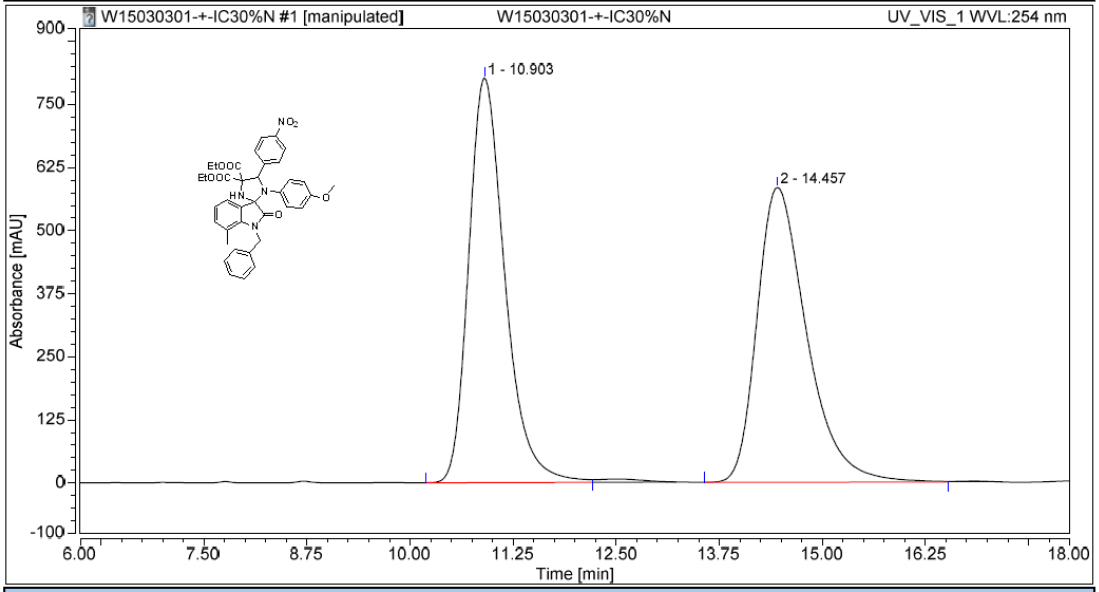


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.443	32.160	62.227	6.51	8.99	n.a.
2		13.900	462.078	630.249	93.49	91.01	n.a.
Total:			**494.238**	**692.476**	**100.00**	**100.00**	

5ea

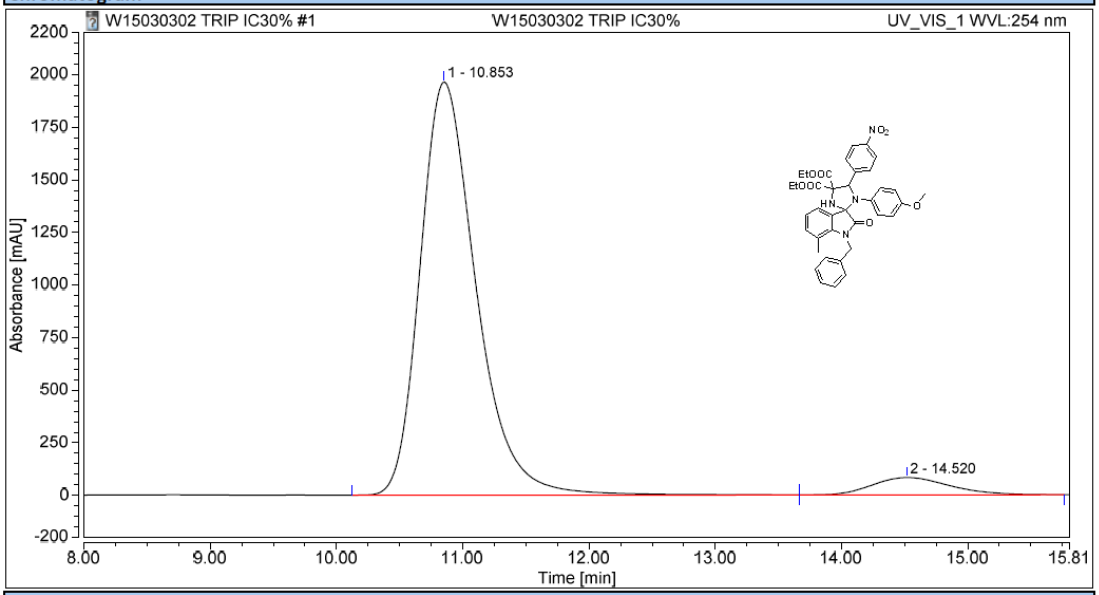
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.903	408.629	801.471	50.10	57.84	n.a.
2		14.457	407.020	584.180	49.90	42.16	n.a.
Total:			**815.649**	**1385.651**	**100.00**	**100.00**	

Chromatogram

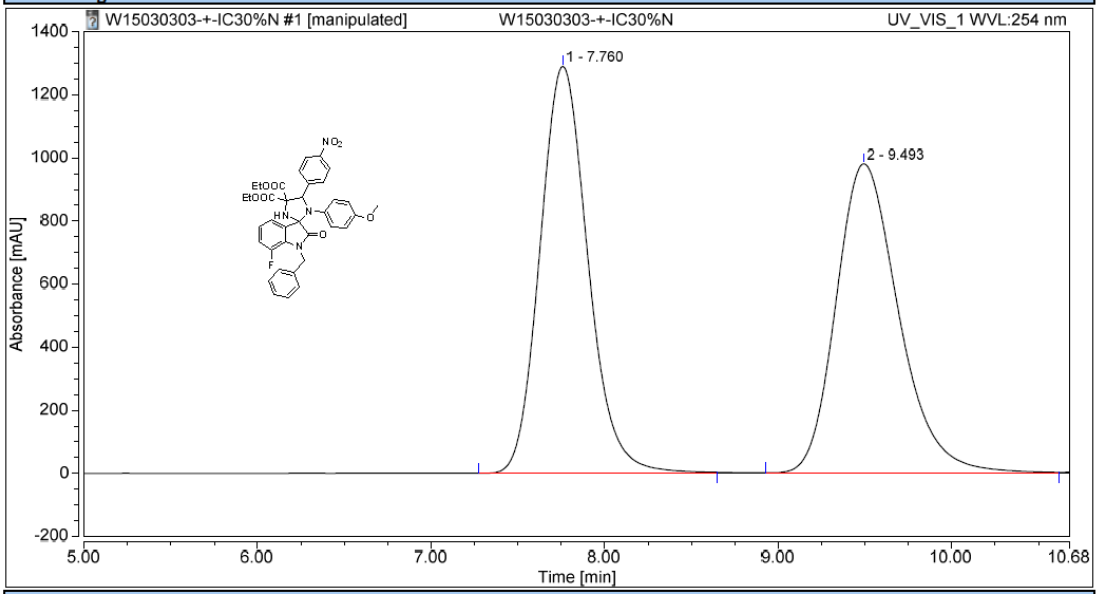


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.853	1008.288	1964.906	94.47	95.96	n.a.
2		14.520	59.065	82.770	5.53	4.04	n.a.
Total:			**1067.353**	**2047.675**	**100.00**	**100.00**	

5fa

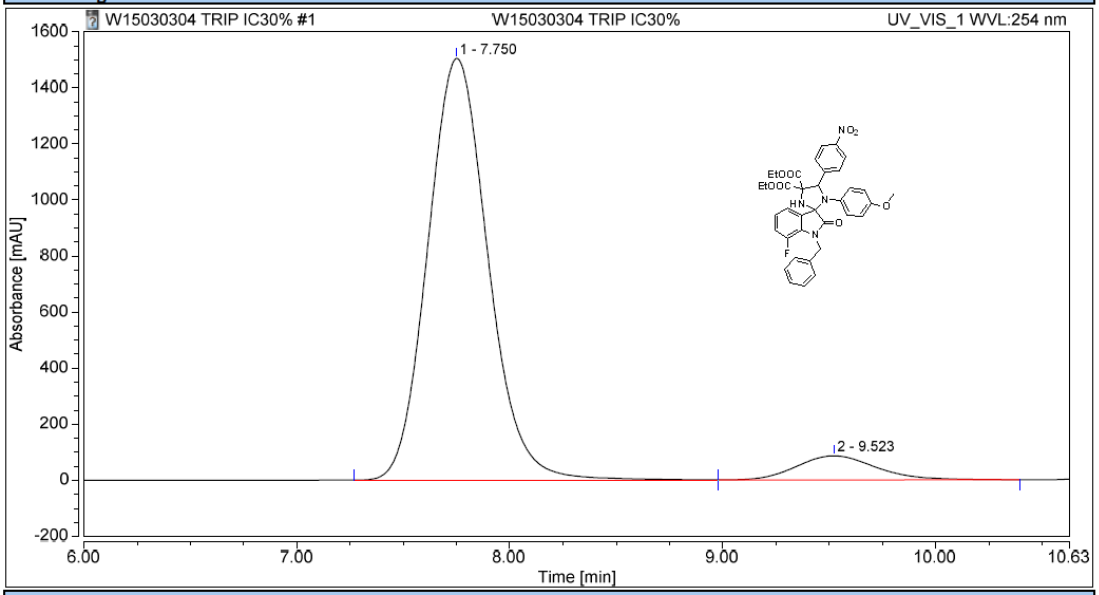
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.760	414.015	1290.922	50.13	56.80	n.a.
2		9.493	411.823	981.764	49.87	43.20	n.a.
Total:			**825.838**	**2272.686**	**100.00**	**100.00**	

Chromatogram

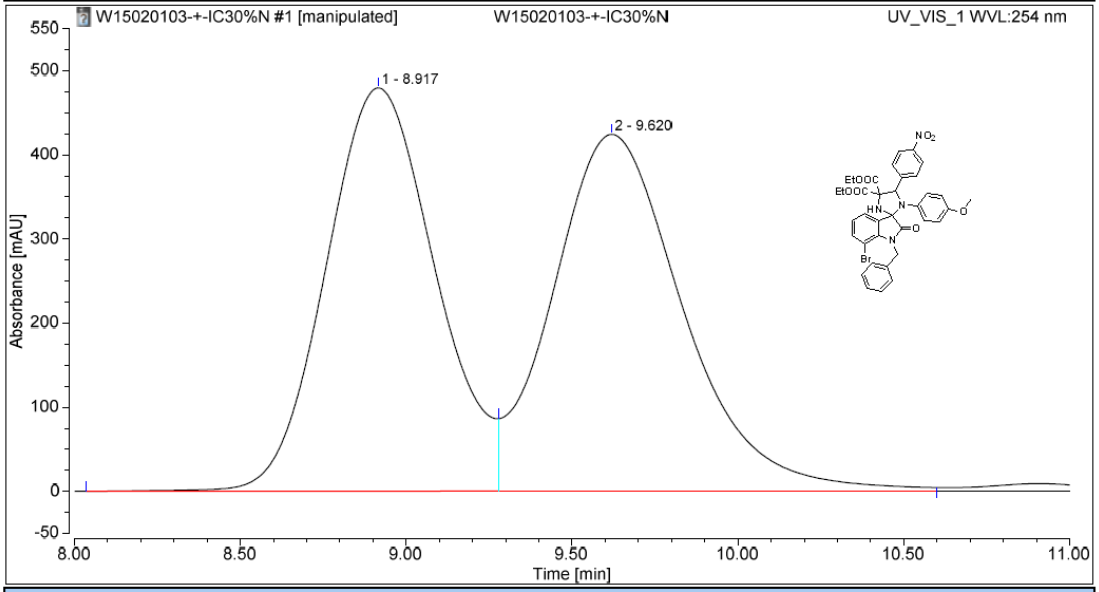


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.750	492.200	1504.405	93.01	94.61	n.a.
2		9.523	37.004	85.696	6.99	5.39	n.a.
Total:			**529.204**	**1590.101**	**100.00**	**100.00**	

5ga

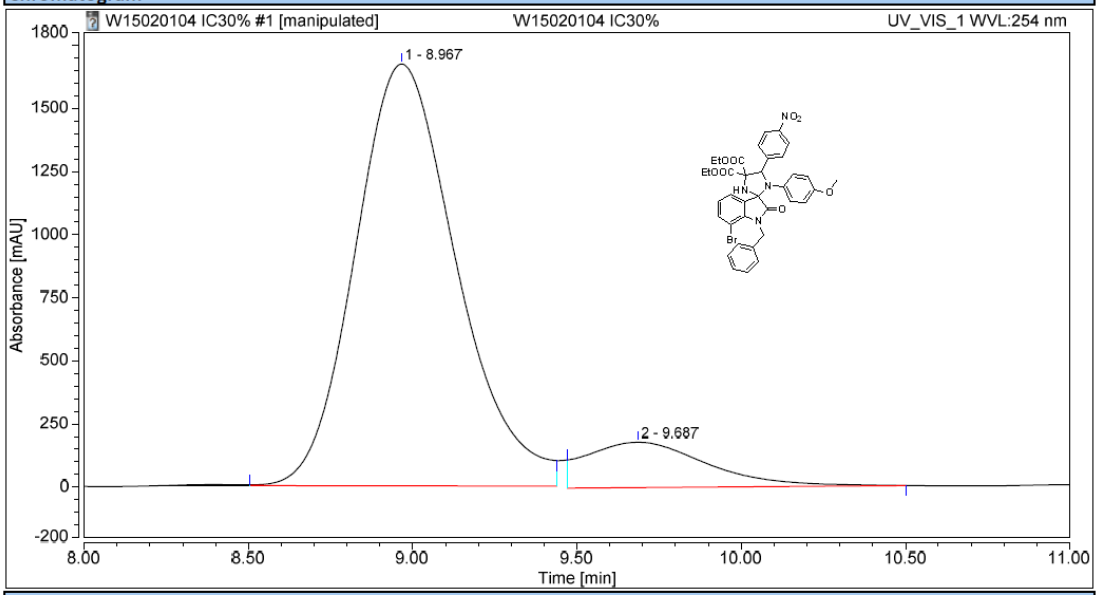
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.917	182.734	479.555	48.64	53.06	n.a.
2		9.620	192.959	424.191	51.36	46.94	n.a.
Total:			**375.693**	**903.746**	**100.00**	**100.00**	

Chromatogram

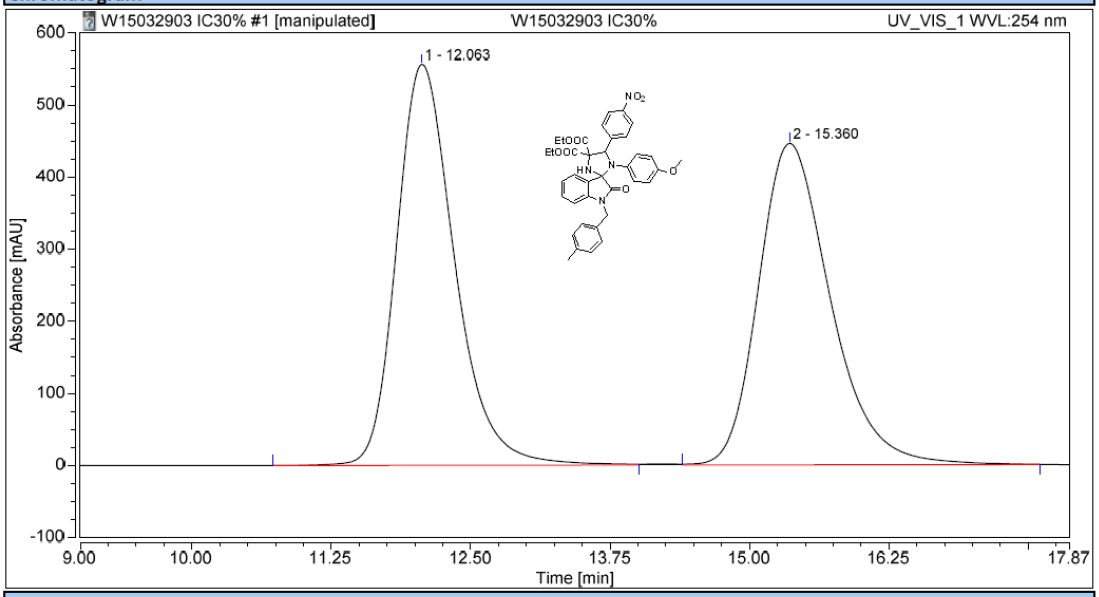


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.967	597.711	1672.578	88.65	90.31	n.a.
2		9.687	76.541	179.469	11.35	9.69	n.a.
Total:			**674.252**	**1852.048**	**100.00**	**100.00**	

5ha

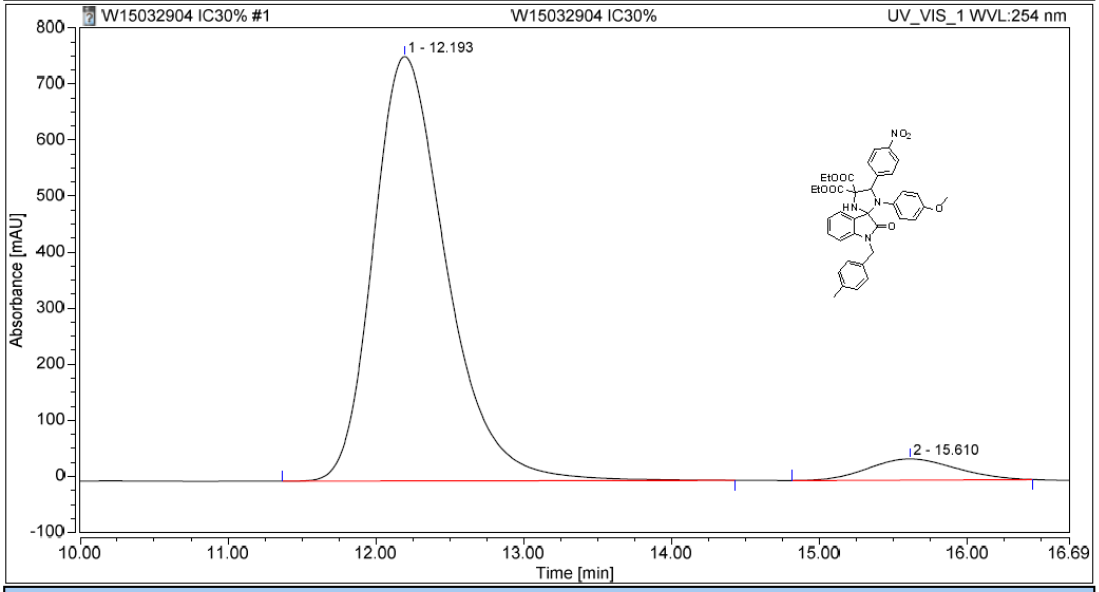
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.063	335.872	556.533	50.21	55.52	n.a.
2		15.360	333.080	445.924	49.79	44.48	n.a.
Total:			**668.952**	**1002.457**	**100.00**	**100.00**	

Chromatogram

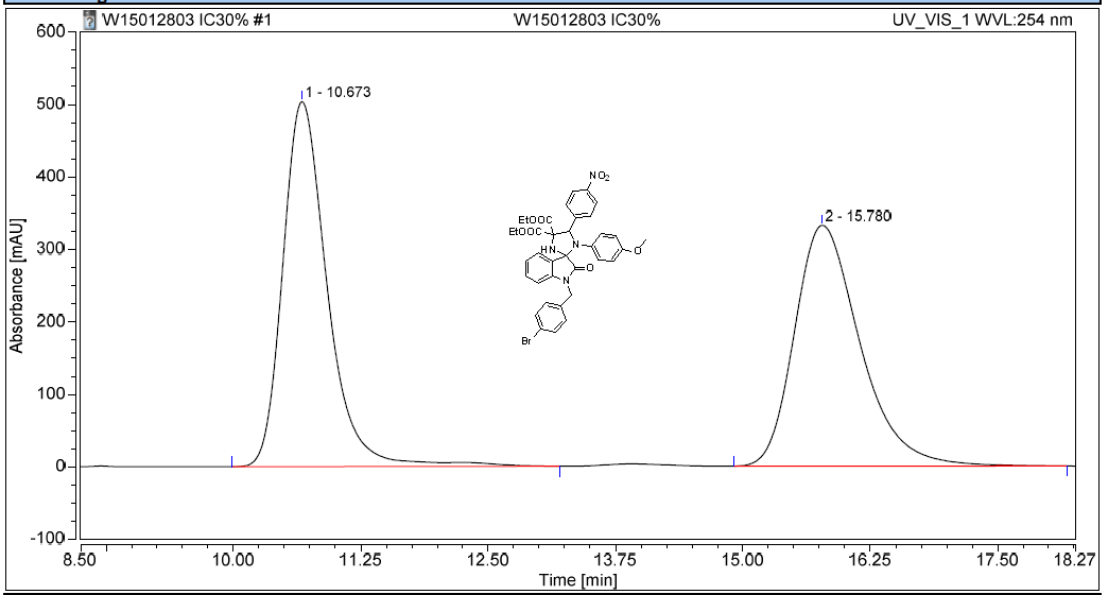


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.193	433.597	757.099	94.42	95.27	n.a.
2		15.610	25.625	37.620	5.58	4.73	n.a.
Total:			**459.223**	**794.719**	**100.00**	**100.00**	

5ia

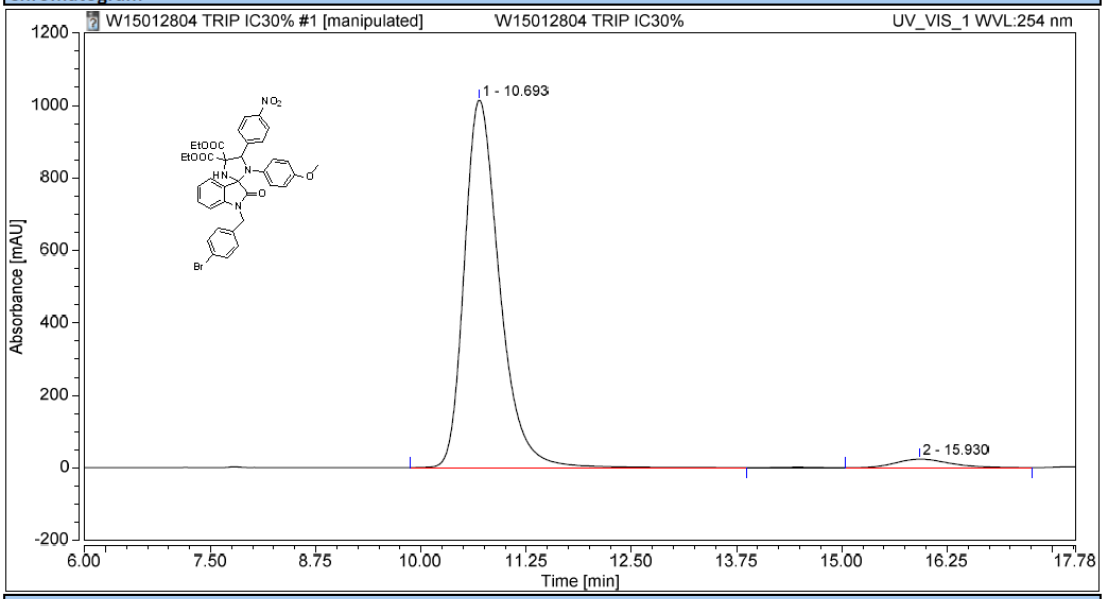
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.673	255.627	504.001	50.77	60.24	n.a.
2		15.780	247.893	332.605	49.23	39.76	n.a.
Total:			**503.519**	**836.606**	**100.00**	**100.00**	

Chromatogram

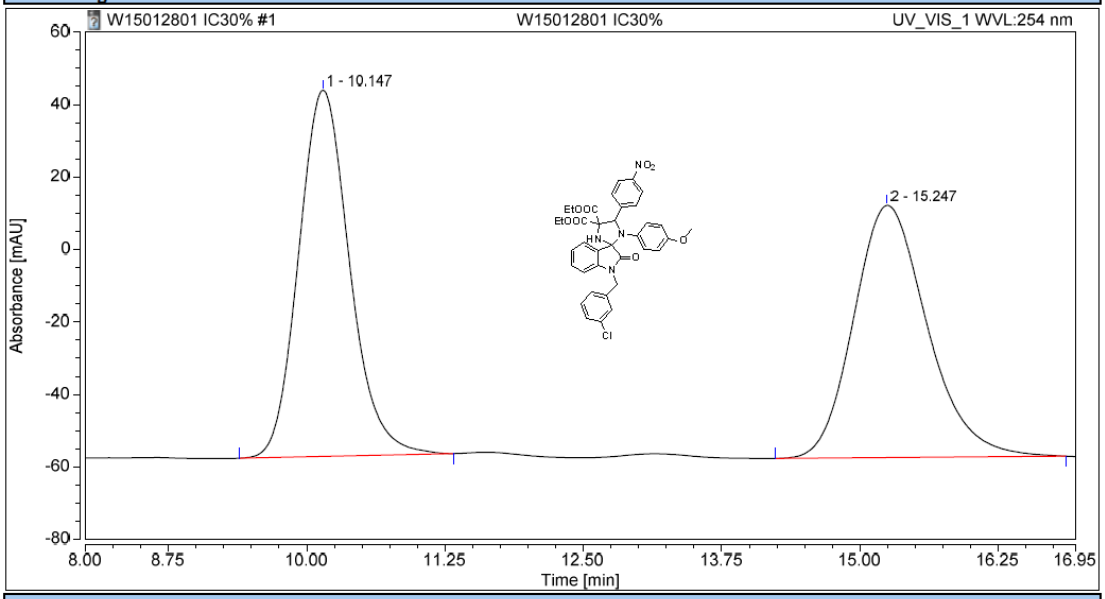


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.693	492.102	1014.945	96.56	97.72	n.a.
2		15.930	17.551	23.646	3.44	2.28	n.a.
Total:			**509.653**	**1038.591**	**100.00**	**100.00**	

5ja

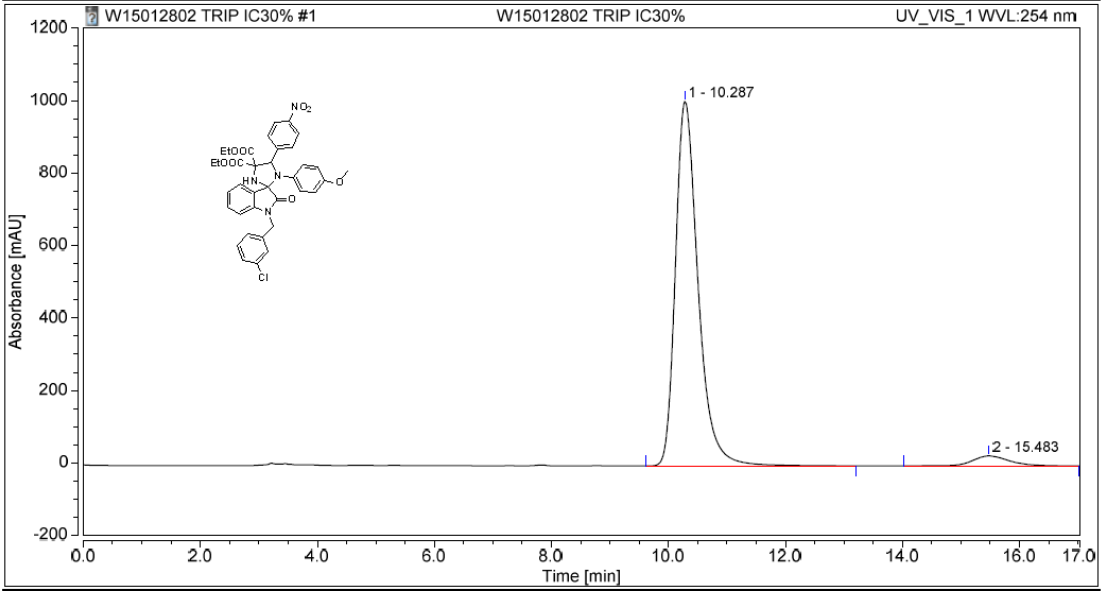
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.147	53.855	101.078	50.16	59.22	n.a.
2		15.247	53.517	69.598	49.84	40.78	n.a.
Total:			**107.372**	**170.676**	**100.00**	**100.00**	

Chromatogram

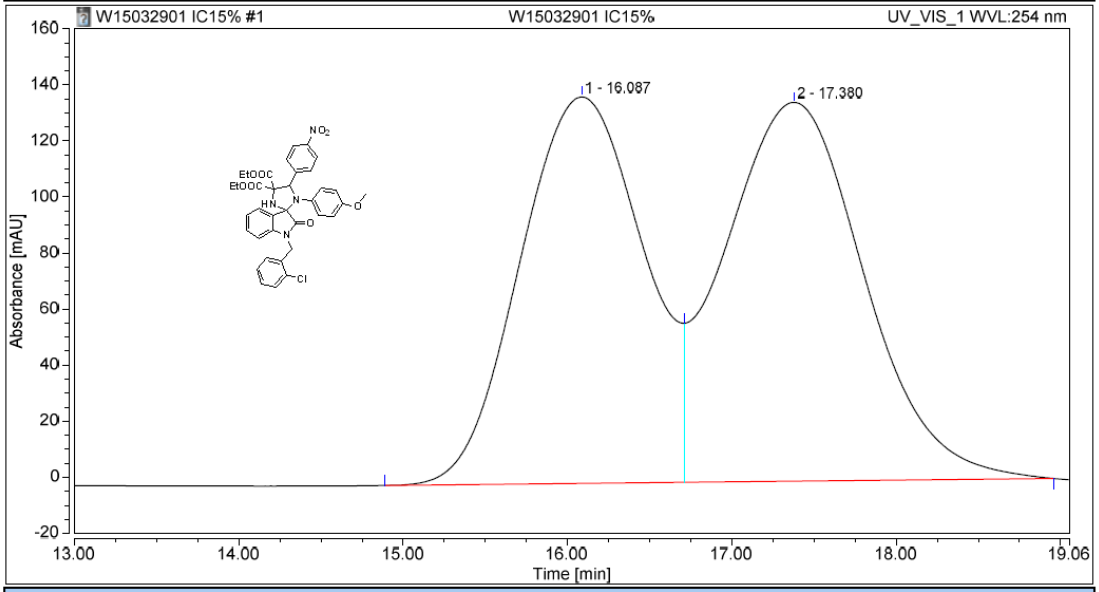


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.287	450.692	1005.795	95.80	97.37	n.a.
2		15.483	19.780	27.158	4.20	2.63	n.a.
Total:			**470.472**	**1032.954**	**100.00**	**100.00**	

5ka

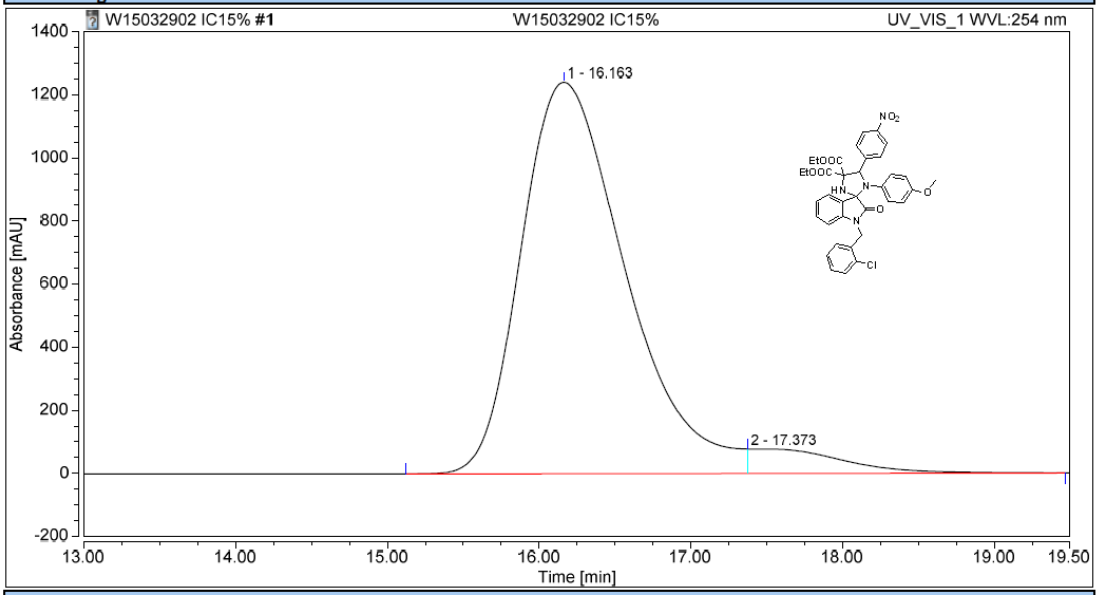
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.087	119.575	137.872	47.37	50.50	n.a.
2		17.380	132.868	135.152	52.63	49.50	n.a.
Total:			**252.442**	**273.024**	**100.00**	**100.00**	

Chromatogram

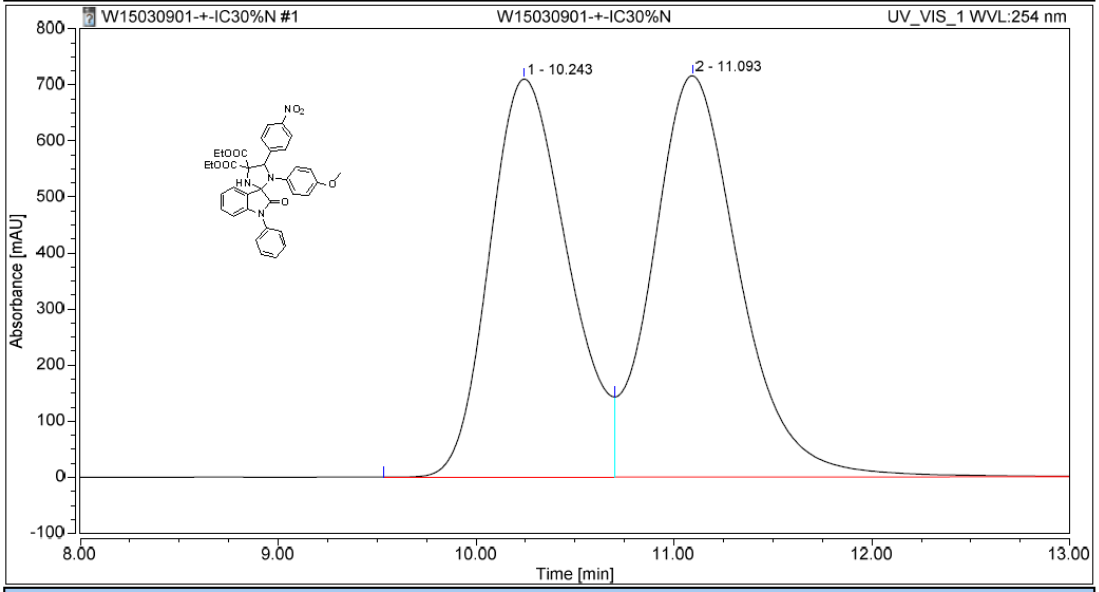


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.163	989.838	1241.379	94.70	94.12	n.a.
2		17.373	55.392	77.504	5.30	5.88	n.a.
Total:			**1045.230**	**1318.883**	**100.00**	**100.00**	

5la

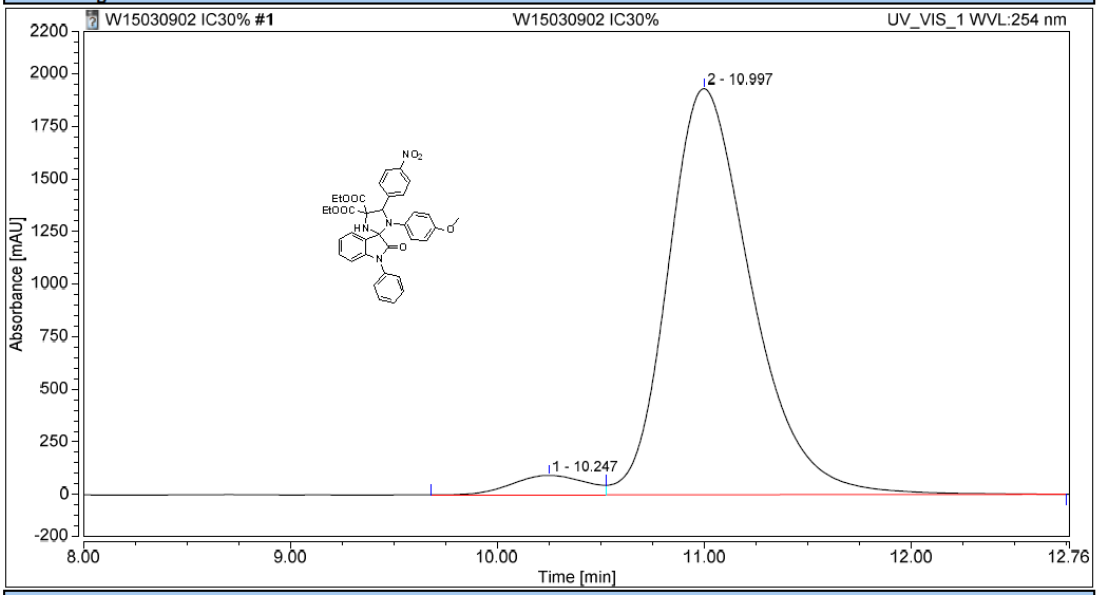
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.243	326.351	710.086	47.22	49.80	n.a.
2		11.093	364.843	715.811	52.78	50.20	n.a.
Total:			**691.194**	**1425.897**	**100.00**	**100.00**	

Chromatogram

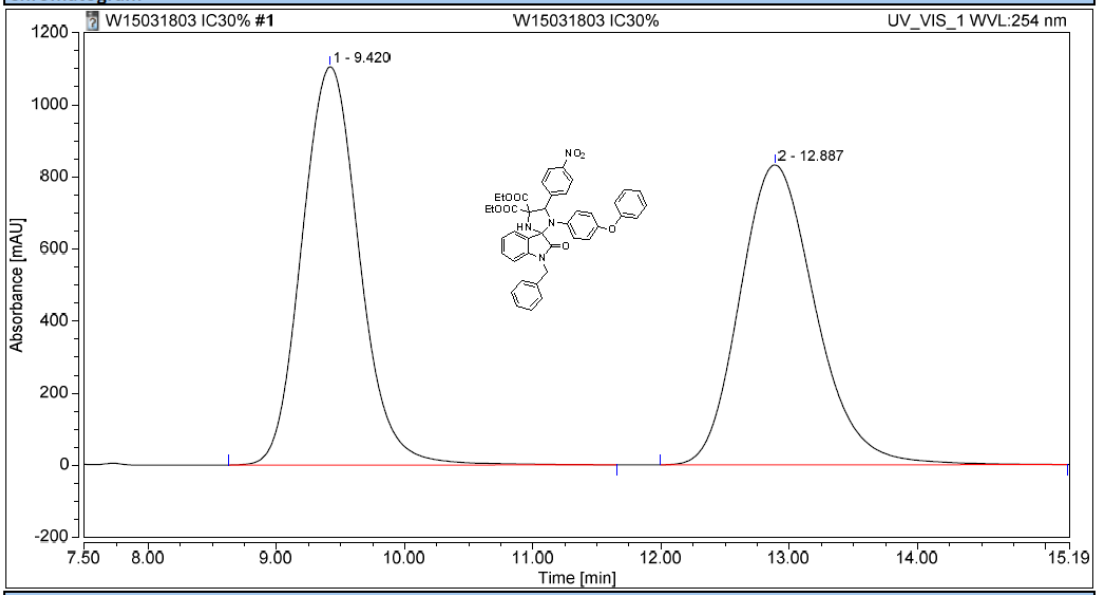


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.247	38.238	92.510	4.06	4.57	n.a.
2		10.997	902.709	1931.634	95.94	95.43	n.a.
Total:			**940.947**	**2024.144**	**100.00**	**100.00**	

5ma

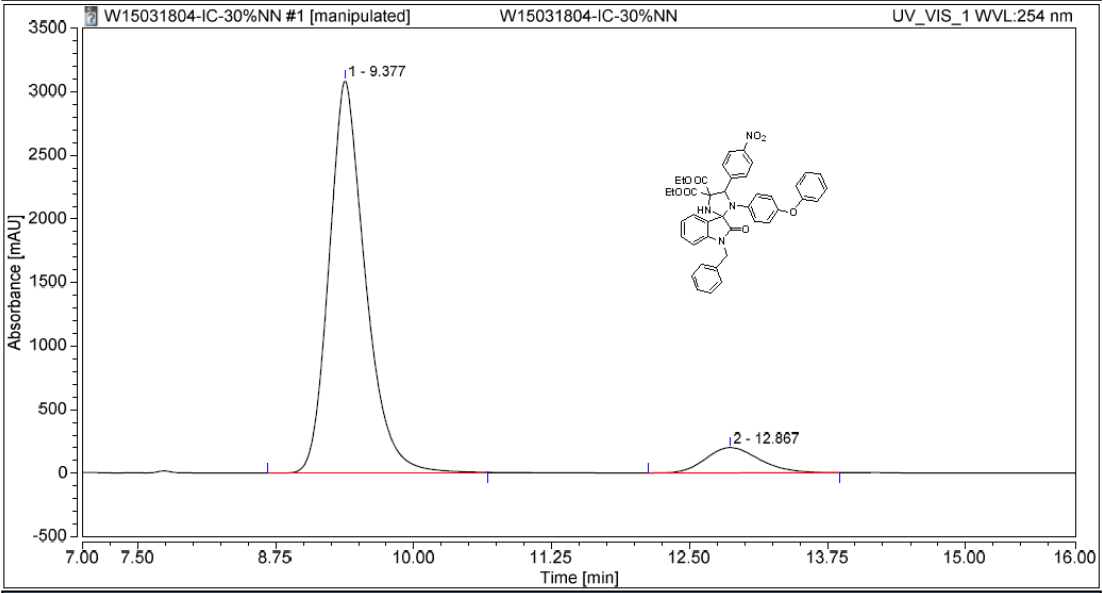
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.420	573.794	1104.913	50.23	57.04	n.a.
2		12.887	568.641	832.057	49.77	42.96	n.a.
Total:			**1142.435**	**1936.970**	**100.00**	**100.00**	

Chromatogram

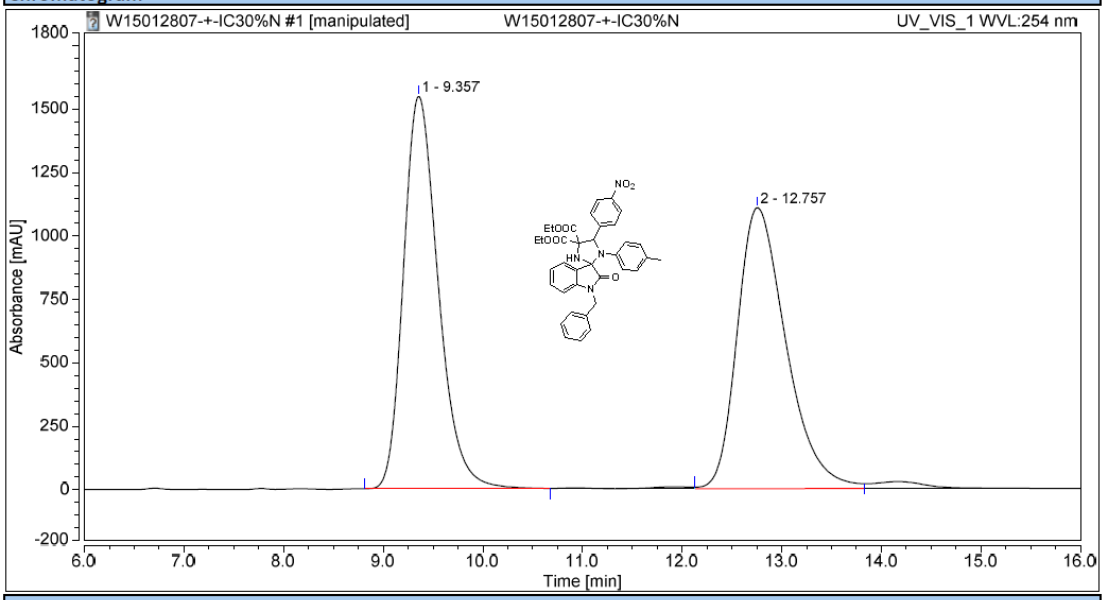


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.377	1176.209	3085.330	91.26	93.95	n.a.
2		12.867	112.685	198.811	8.74	6.05	n.a.
Total:			**1288.894**	**3284.141**	**100.00**	**100.00**	

5na

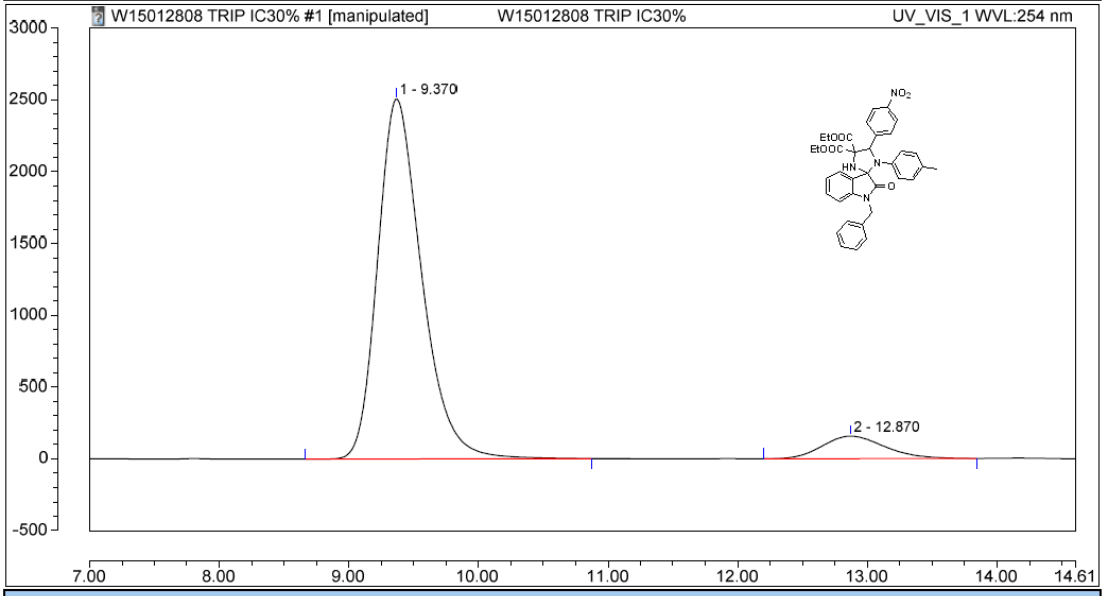
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.357	626.537	1547.711	49.92	58.27	n.a.
2		12.757	628.570	1108.300	50.08	41.73	n.a.
Total:			**1255.107**	**2656.010**	**100.00**	**100.00**	

Chromatogram

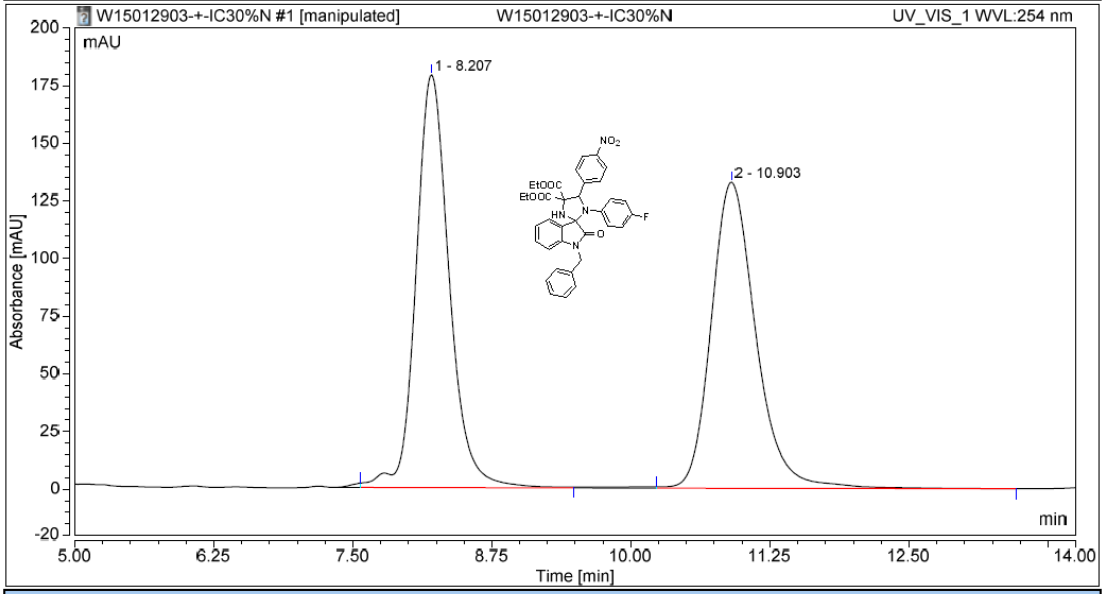


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.370	988.815	2508.476	91.90	94.14	n.a.
2		12.870	87.204	156.267	8.10	5.86	n.a.
Total:			**1076.020**	**2664.742**	**100.00**	**100.00**	

5oa

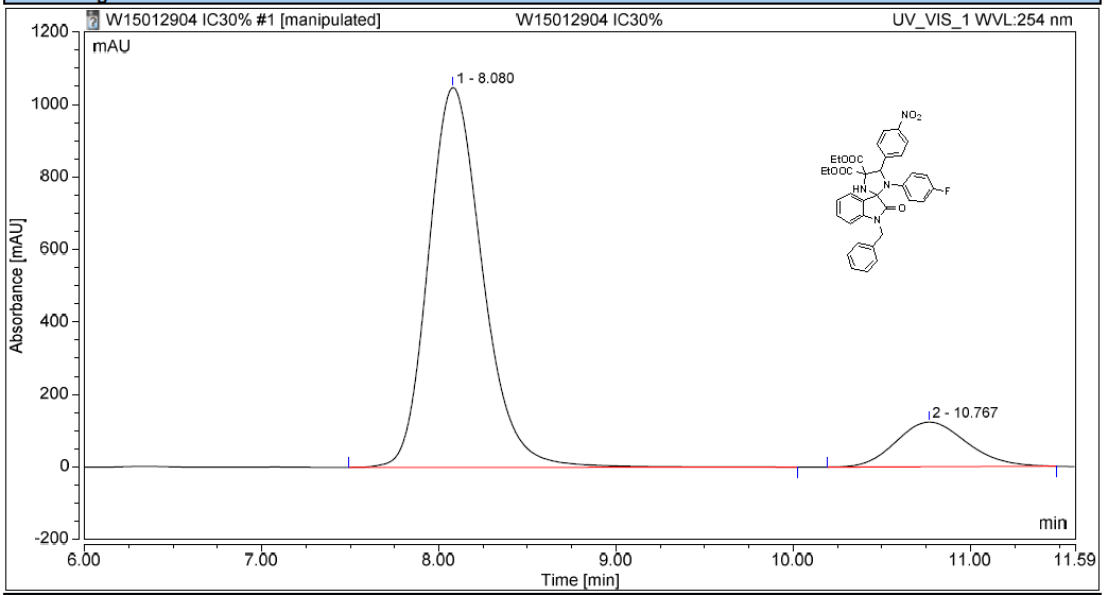
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.207	62.259	179.127	50.24	57.43	n.a.
2		10.903	61.664	132.763	49.76	42.57	n.a.
Total:			**123.923**	**311.891**	**100.00**	**100.00**	

Chromatogram

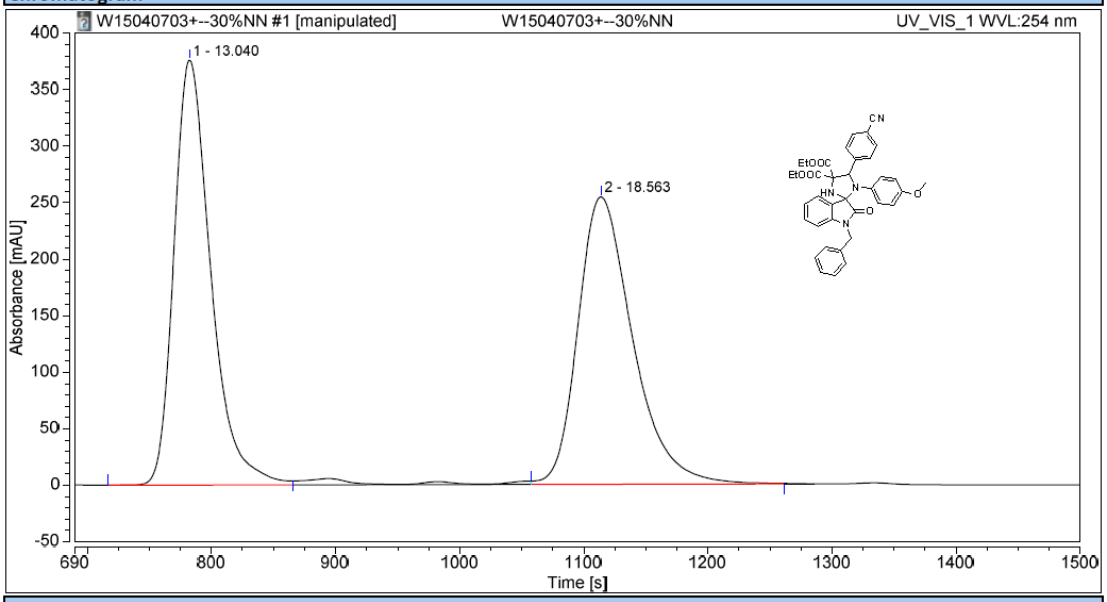


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.080	370.647	1048.220	86.66	89.47	n.a.
2		10.767	57.068	123.305	13.34	10.53	n.a.
Total:			**427.714**	**1171.525**	**100.00**	**100.00**	

5ab

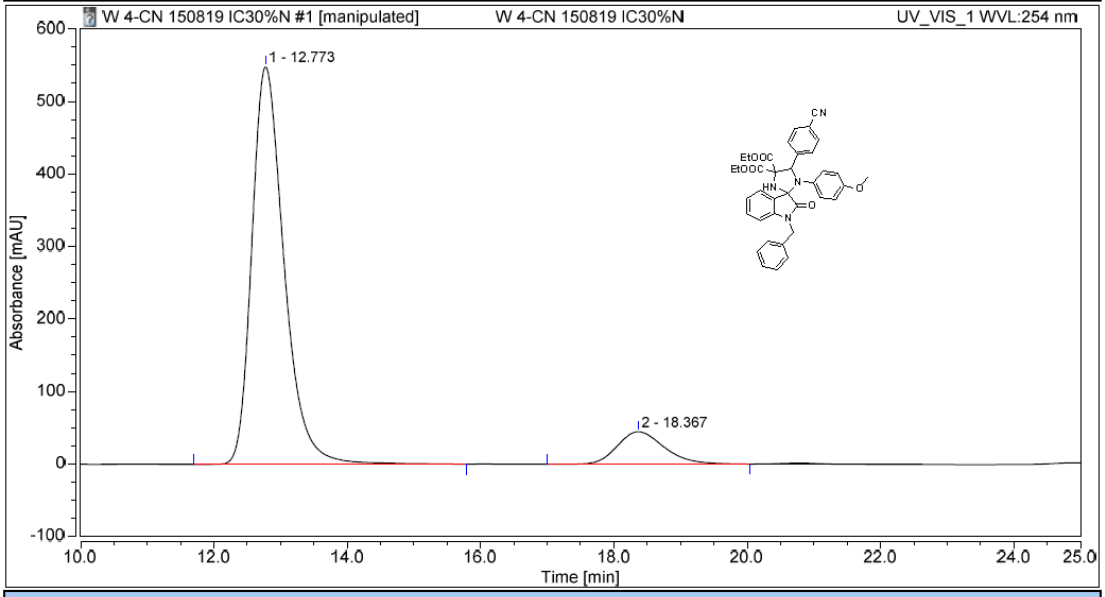
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.040	214.920	376.050	49.82	59.64	n.a.
2		18.563	216.434	254.432	50.18	40.36	n.a.
Total:			**431.354**	**630.482**	**100.00**	**100.00**	

Chromatogram

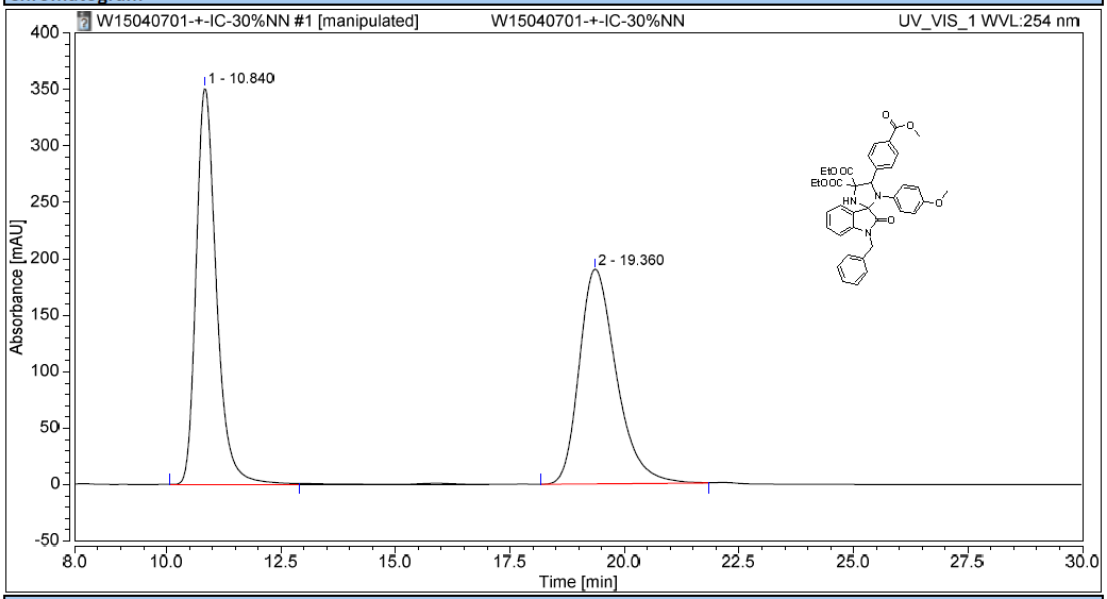


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.773	308.263	548.847	89.03	92.39	n.a.
2		18.367	37.998	45.231	10.97	7.61	n.a.
Total:			**346.261**	**594.078**	**100.00**	**100.00**	

5ac

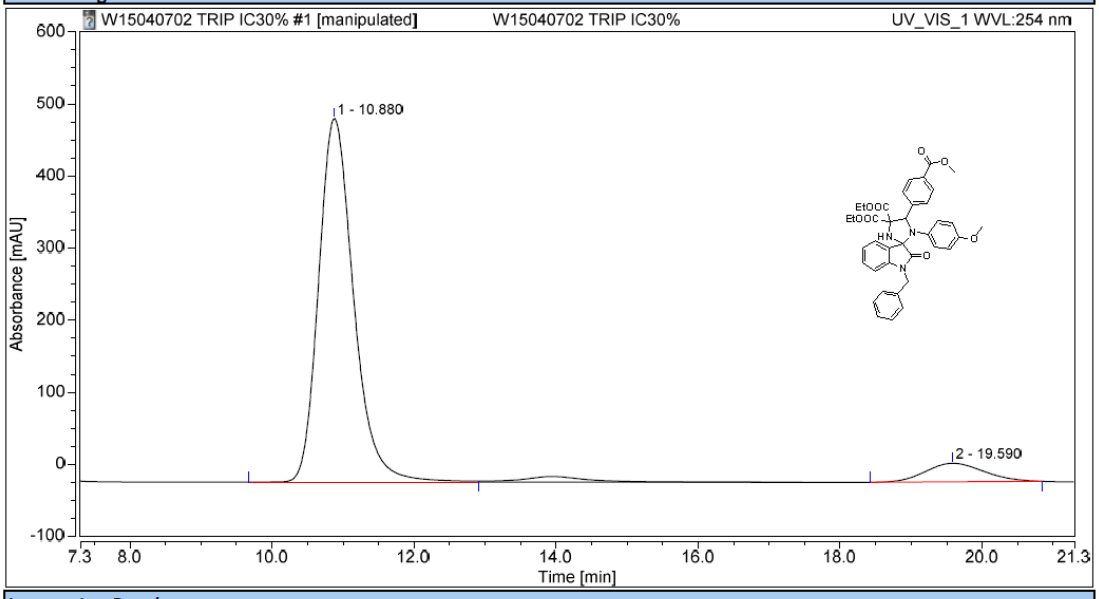
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.840	179.835	351.304	50.17	64.86	n.a.
2		19.360	178.647	190.291	49.83	35.14	n.a.
Total:			**358.482**	**541.595**	**100.00**	**100.00**	

Chromatogram

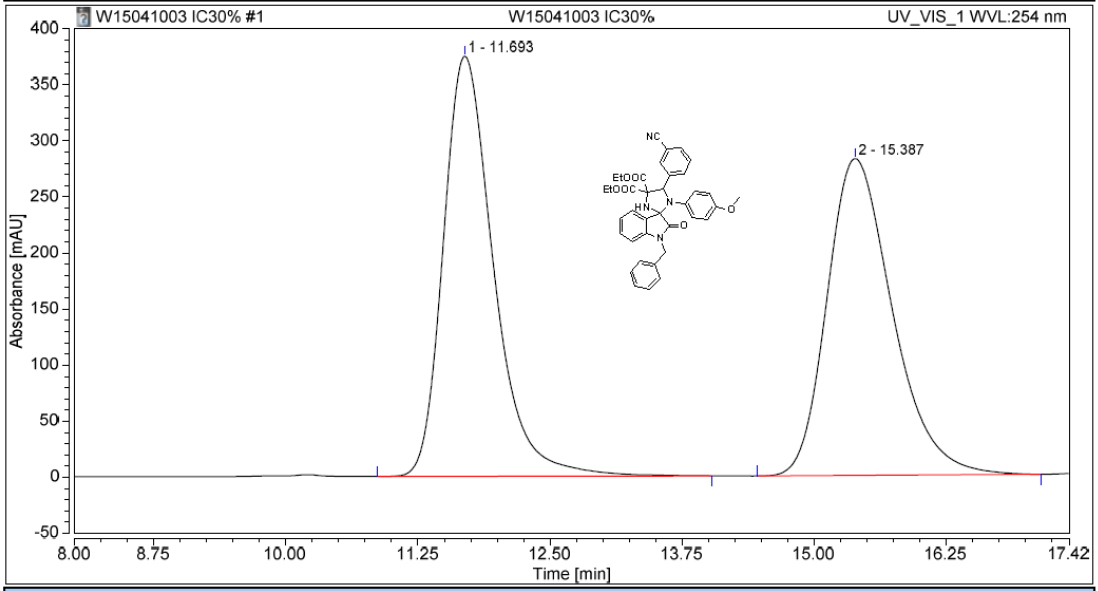


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.880	288.058	504.399	92.15	95.16	n.a.
2		19.590	24.523	25.639	7.85	4.84	n.a.
Total:			**312.581**	**530.037**	**100.00**	**100.00**	

5ad

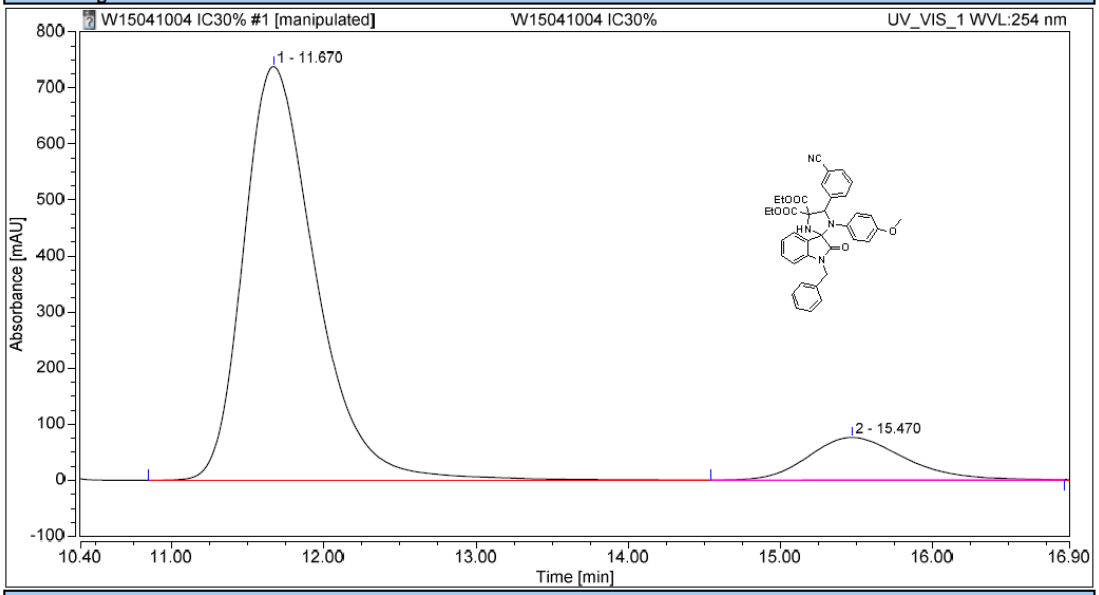
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.693	206.531	374.841	50.48	57.01	n.a.
2		15.387	202.597	282.653	49.52	42.99	n.a.
Total:			**409.129**	**657.494**	**100.00**	**100.00**	

Chromatogram

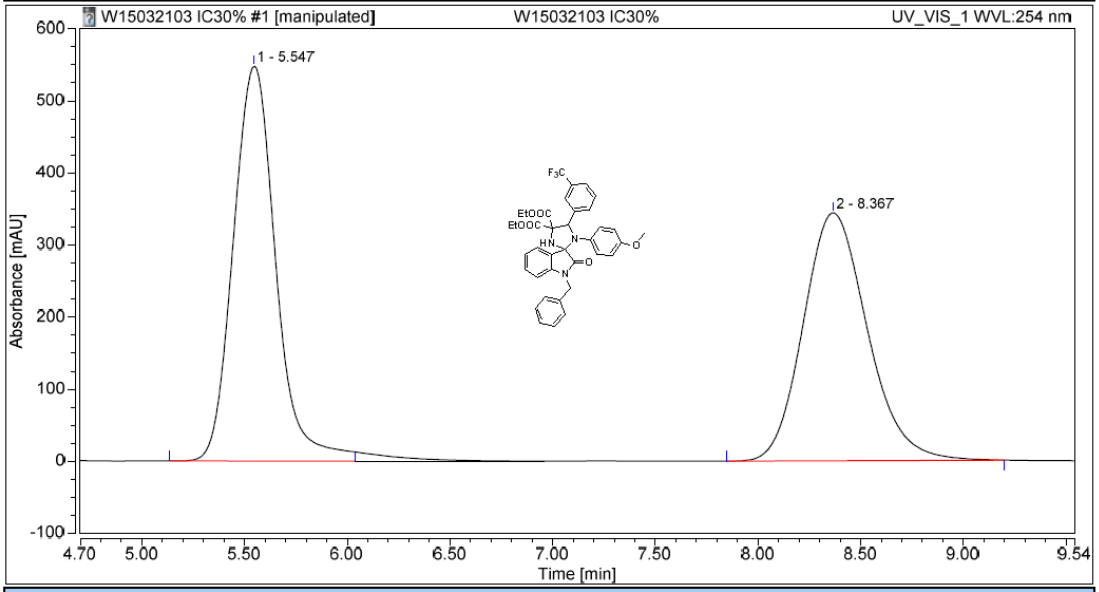


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.670	407.224	738.027	88.13	90.72	n.a.
2		15.470	54.848	75.471	11.87	9.28	n.a.
Total:			**462.072**	**813.499**	**100.00**	**100.00**	

5ae

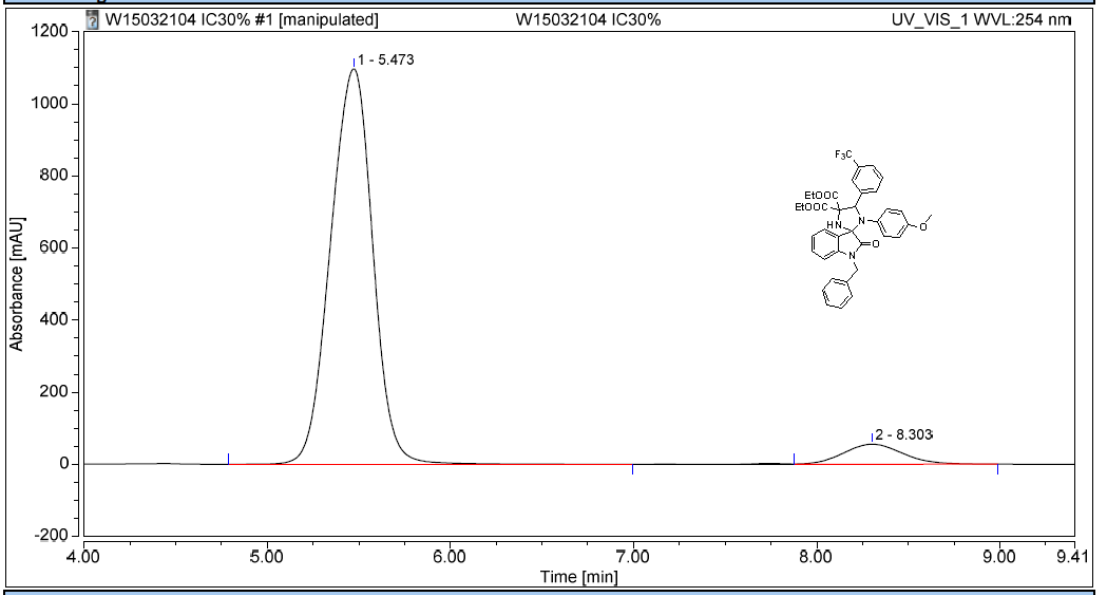
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.547	130.818	547.871	51.28	61.43	n.a.
2		8.367	124.284	344.019	48.72	38.57	n.a.
Total:			**255.103**	**891.890**	**100.00**	**100.00**	

Chromatogram

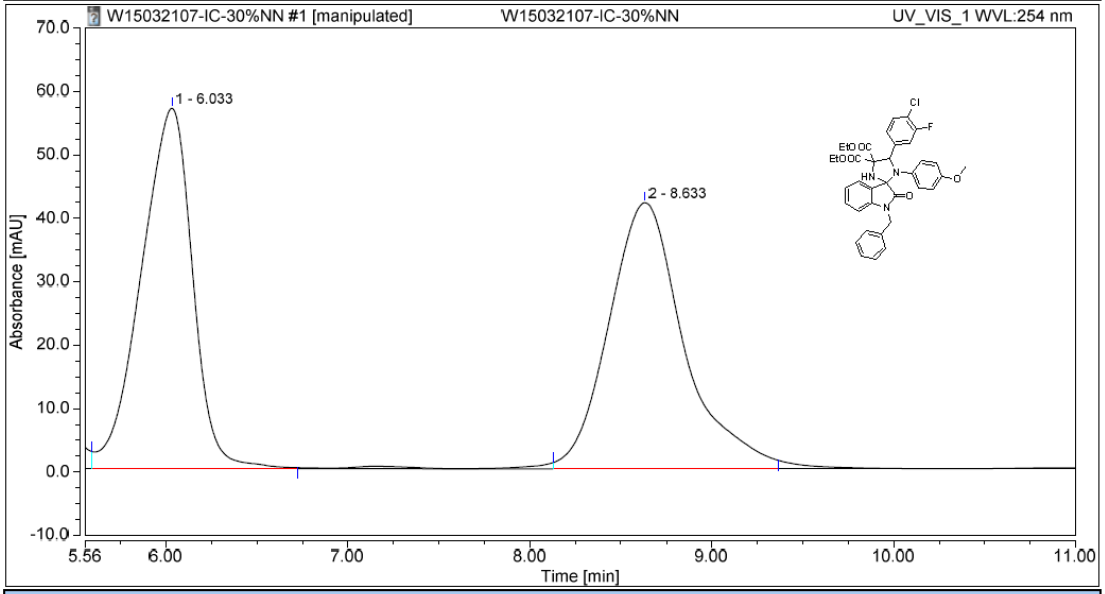


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.473	292.975	1097.986	93.34	95.18	n.a.
2		8.303	20.898	55.586	6.66	4.82	n.a.
Total:			**313.873**	**1153.572**	**100.00**	**100.00**	

5af

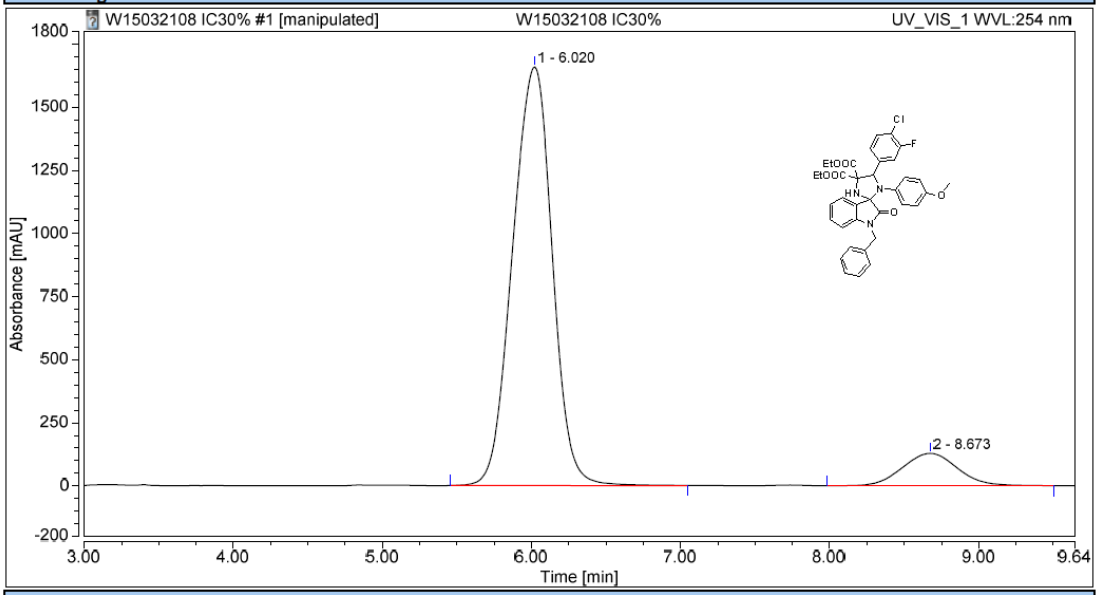
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.033	18.621	56.842	48.23	57.51	n.a.
2		8.633	19.985	41.993	51.77	42.49	n.a.
Total:			**38.605**	**98.835**	**100.00**	**100.00**	

Chromatogram

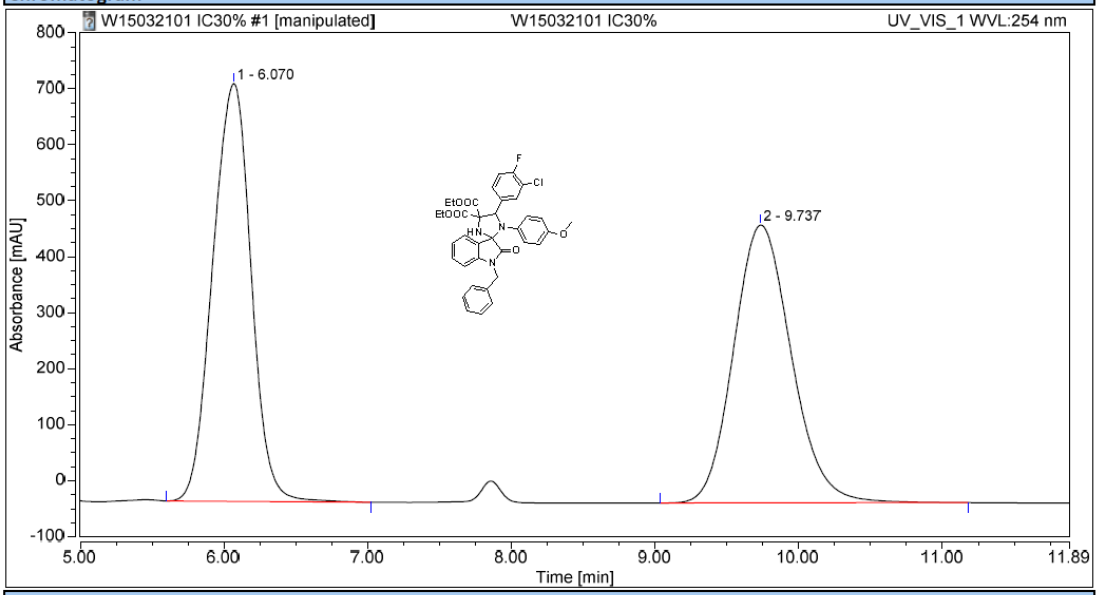


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.020	511.565	1659.741	90.35	92.85	n.a.
2		8.673	54.625	127.889	9.65	7.15	n.a.
Total:			**566.190**	**1787.630**	**100.00**	**100.00**	

5ag

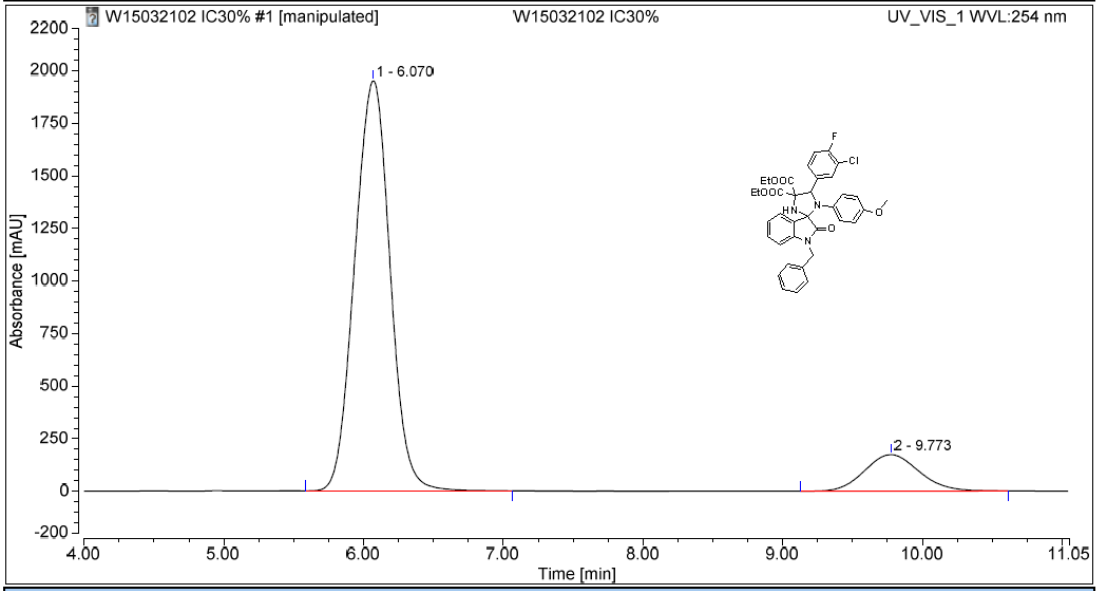
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.070	231.302	746.428	50.09	60.07	n.a.
2		9.737	230.441	496.090	49.91	39.93	n.a.
Total:			**461.743**	**1242.517**	**100.00**	**100.00**	

Chromatogram

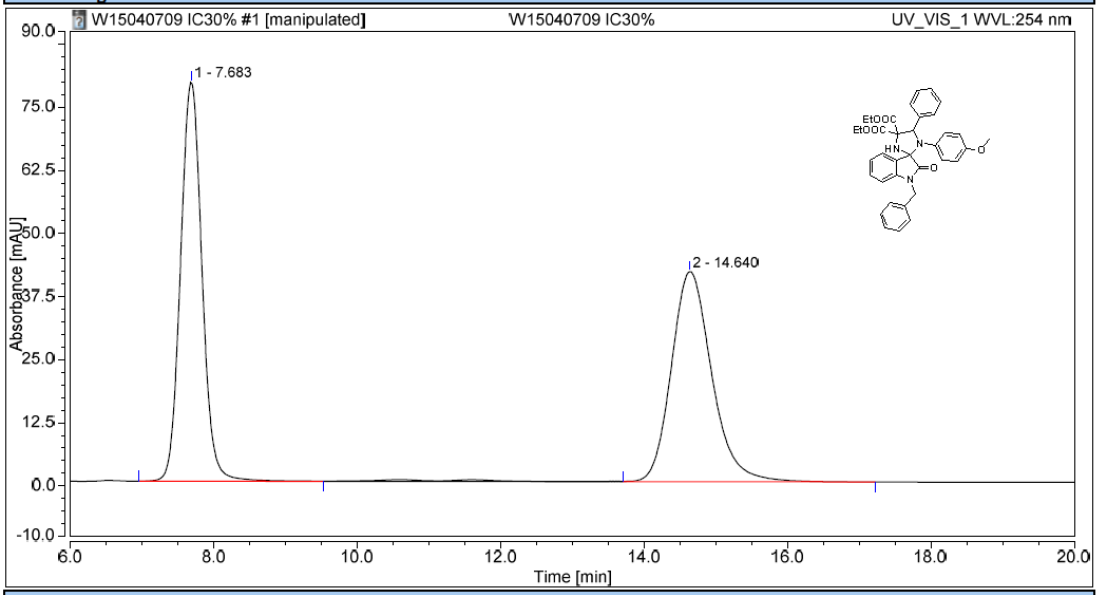


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.070	572.123	1952.350	87.94	91.84	n.a.
2		9.773	78.488	173.498	12.06	8.16	n.a.
Total:			**650.610**	**2125.848**	**100.00**	**100.00**	

5ah

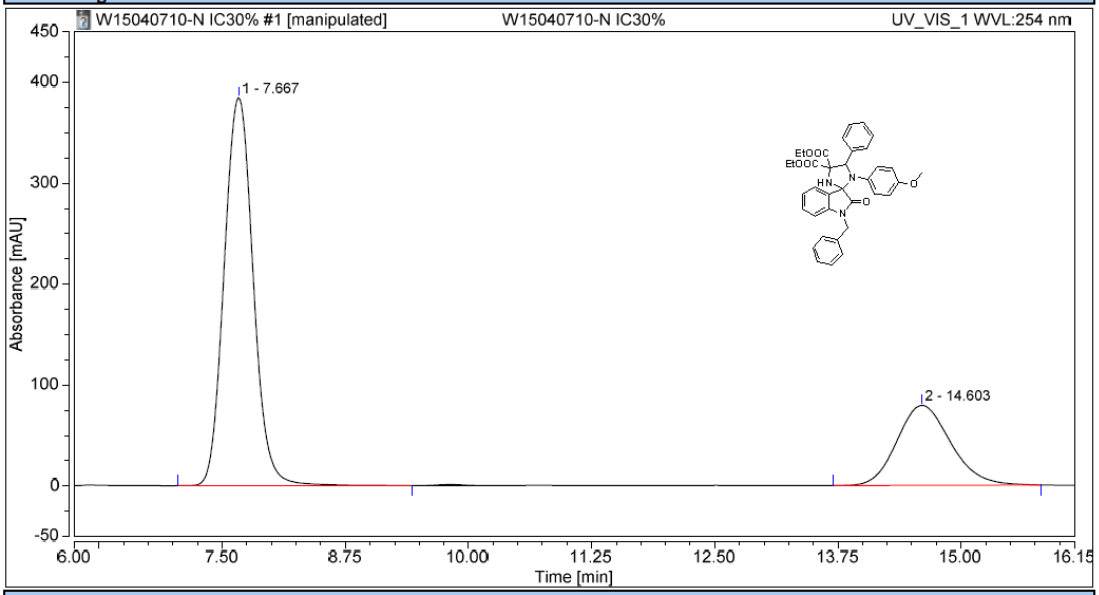
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.683	27.416	79.156	50.22	65.51	n.a.
2		14.640	27.174	41.669	49.78	34.49	n.a.
Total:			**54.589**	**120.825**	**100.00**	**100.00**	

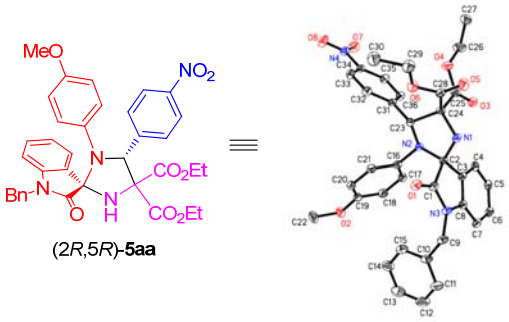
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.667	131.321	384.456	72.41	82.91	n.a.
2		14.603	50.047	79.232	27.59	17.09	n.a.
Total:			**181.369**	**463.688**	**100.00**	**100.00**	

7. X-ray single crystal data for product *ent*-5aa



Empirical formula	C36 H34 N4 O8	
Formula weight	650.67	
Temperature	130 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 7.96120(10) Å	α= 90°.
	b = 24.5627(4) Å	β= 90.8230(10)°.
	c = 16.5897(3) Å	γ = 90°.
Volume	3243.76(9) $Å^3$	
Z	4	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.787 mm^{-1}	
F(000)	1368	
Crystal size	0.3 x 0.12 x 0.05 mm^3	
Theta range for data collection	3.215 to 70.178°.	
Index ranges	-9<=h<=8, -29<=k<=29, -20<=l<=19	
Reflections collected	24751	
Independent reflections	10598 [R(int) = 0.0466]	
Completeness to theta = 67.679°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5580	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10598 / 1 / 871	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1173	
R indices (all data)	R1 = 0.0567, wR2 = 0.1245	
Absolute structure parameter	0.00(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.376 and -0.328 $e.Å^{-3}$	