Supporting Information for

Brønsted Acid-Catalyzed Regioselective Reactions of 2-Indolylmethanols with Cyclic Enaminone and Anhydride Leading to C3-Functionalized Indole Derivatives

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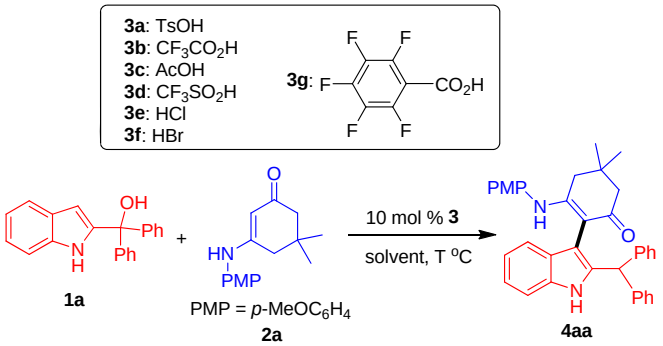
1. General information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured respectively at 400 MHz, 100 MHz and 376 MHz, respectively. The solvents used for NMR spectroscopy were $CDCl_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Analytical grade solvents for the column chromatography were used after distillation. 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 optimization of reaction conditions

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

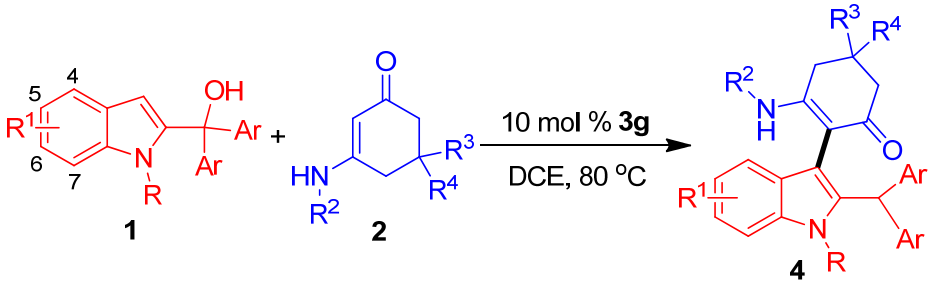


entry	**Cat.**	solvent	T (^{o}C)	yield (%)[b]
1	**3a**	toluene	80	49
2	**3b**	toluene	80	58
3	**3c**	toluene	80	No reaction
4	**3d**	toluene	80	Trace
5	**3e**	toluene	80	68
6	**3f**	toluene	80	50
7	**3g**	toluene	80	77
8	**3g**	$ClCH_2CH_2Cl$	80	96
9	**3g**	CH_3CN	80	17
10	**3g**	AcOEt	80	Trace
11	**3g**	1,4-dioxane	80	Trace
12	**3g**	ethanol	80	Trace
13	**3g**	$ClCH_2CH_2Cl$	100	82
14	**3g**	$ClCH_2CH_2Cl$	60	77
15	**3g**	$ClCH_2CH_2Cl$	50	70

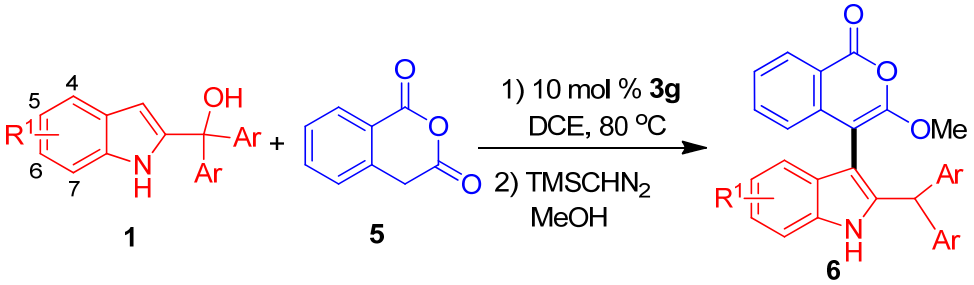
1. a) A. R. Katritzky, P. Lue, Y. X. Chen, *J. Org. Chem.* **1990**, *55*, 3688; b) K.-S. Cao, H.-X. Bian, W.-H. Zheng, *Org. Biomol. Chem.* **2015**, *13*, 6449; c) L. Wang, X. Lu, L. An, J. Zou, *Chin. J. Chem.* **2009**, *27*, 1353.

[a]Unless indicated otherwise, the reaction was carried out at the 0.1 mmol scale catalyzed by 10 mol% **3** in a solvent (1 mL) at T [o]C for 12 h, and the mole ratio of **1a**:**2a** was 1:1.2. [b]Isolated yield.

3. General procedure for the synthesis of products 4 and 6



To the mixture of 2-indolylmethanols **1** (0.1 mmol), enaminones **2** (0.12 mmol) and the catalyst **3g** (0.01 mmol), was added 1,2-dicholoroethane (1 mL). After being stirred at 80 [o]C for 12 h, the reaction mixture was directly purified through flash column chromatography on silica gel to afford pure products **4**.



To the mixture of 2-indolylmethanols **1** (0.1 mmol), homophthalic anhydride **5** (0.12 mmol) and the catalyst **3g** (0.01 mmol), was added 1,2-dicholoroethane (1 mL). After being stirred at 80 [o]C for 12 h, $TMSCHN_2$ (0.1 mL) and methanol (0.1 mL) was added to the reaction mixture, which was stirred for 5 min at room temperature. Then, the resultant solution was directly purified through flash column chromatography on silica gel to afford pure products **6**.

4. Characterization data of products 4 and 6

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4aa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 96% (50.6 mg); yellow solid; m.p. 88.8-90.2 [o]C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.39 – 7.31 (m, 5H), 7.29 – 7.26 (m, 2H), 7.26 – 7.18 (m, 5H), 7.15 – 7.07 (m, 2H), 6.79 – 6.74 (m, 2H), 6.63 – 6.56 (m, 2H), 6.33 (s, 1H), 5.76 (s, 1H), 3.78 (s, 3H), 2.39 (dd, *J* = 16.1, 1.0 Hz, 1H), 2.33 – 2.23 (m, 2H), 2.07 (d, *J* = 16.6 Hz, 1H), 1.14 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 193.7, 160.1, 157.8, 142.7, 141.8, 139.9, 135.8, 131.0, 129.3, 128.8, 128.7, 128.5, 128.1, 127.5, 127.0, 126.5, 121.6, 119.9, 119.1, 114.2, 111.2, 105.1, 103.9, 55.5, 50.9, 49.4, 40.0, 32.4, 28.4, 28.3; IR (KBr): 3341, 3056, 2955, 1575, 1540, 1452, 1383, 1321, 1298, 1245, 1219, 1155, 1077, 1031, 908, 829, 762, 743, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_2O_2+Na)^+$ requires m/z 549.2512, found m/z 549.2524.

2-(2-(bis(2-methoxyphenyl)methyl)-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethyl cyclohex-2-enone (4ba): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 90% (52.8 mg); yellow solid; m.p. 96.2-97.2 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.38 – 7.33 (m, 1H), 7.26 – 7.17 (m, 3H), 7.13 – 7.05 (m, 3H), 6.98 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.89 – 6.80 (m, 8H), 6.73 (s, 1H), 6.33 (s, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.44 (s, 3H), 2.35 (d, *J* = 16.0 Hz, 1H), 2.28 (d, *J* = 16.7 Hz, 1H), 2.18 – 2.10 (m, 2H), 1.08 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 158.9, 157.7, 157.2, 157.0, 138.3, 135.5, 131.7, 130.5, 130.2, 130.1, 129.6, 129.4, 127.9, 127.8, 121.1, 120.7, 120.6, 119.8, 119.6, 114.1, 110.7, 110.6, 105.6, 104.1, 55.7, 55.5, 55.4, 50.9, 40.2, 37.5, 32.2, 29.0, 27.2; IR (KBr): 3335, 2953, 2835, 2347, 2232, 1589, 1542, 1490, 1382, 1322, 1290, 1167, 1105, 1030, 902, 830, 754 cm^{-1}; ESI FTMS exact mass calcd for $(C_{38}H_{38}N_2O_4+Na)^+$ requires m/z 609.2724, found m/z 609.2739.

2-(2-(bis(3-fluorophenyl)methyl)-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcy clohex-2-enone (4ca): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 80% (45.0 mg); yellow solid; m.p. 169.7-171.0 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 5.4 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.34 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 – 7.08 (m, 3H), 7.02 – 6.87 (m, 5H), 6.82 – 6.75 (m, 2H), 6.72 – 6.65 (m, 2H), 6.37 (s, 1H), 5.78 (s, 1H), 3.78 (s, 3H), 2.42 – 2.29 (m, 2H), 2.25 (d, *J* = 16.2 Hz, 1H), 2.09 (d, *J* = 16.7 Hz, 1H), 1.13 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 163.1 (d, *J* = 245.2 Hz), 162.9 (d, *J* = 244.7 Hz), 160.2, 158.0, 144.8 (d, *J* = 6.7 Hz), 143.7 (d, *J* = 6.9 Hz), 138.4, 135.9, 130.8, 130.4 (d, *J* = 8.2 Hz), 130.0 (d, *J* = 8.2 Hz), 127.7, 127.6, 125.1 (d, *J* = 2.8 Hz), 124.5 (d, *J* = 2.8 Hz), 121.9, 120.1, 119.2, 116.2, 116.0, 115.6, 115.3, 114.3, 114.1, 113.8, 113.6, 111.4, 105.6, 103.6, 55.5, 50.8, 48.8(t, *J* = 2.6 Hz), 40.0, 32.4, 28.3, 28.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ

-112.0, -112.7; IR (KBr): 3649, 3056, 2956, 2349, 2282, 1611, 1588, 1485, 1452, 1392, 1298, 1246, 1145, 1032, 971, 896, 829, 803, 762, 744, 684 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{32}F_2N_2O_2+Na)^+$ requires m/z 585.2324, found m/z 585.2328.

2-(2-(di-*p*-tolylmethyl)-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4da): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 81% (45.0 mg); yellow solid; m.p. 90.6-91.4 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.36 – 7.33 (m, 1H), 7.28 – 7.24 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.10 (m, 3H), 7.09 – 7.01 (m, 5H), 6.78 – 6.73 (m, 2H), 6.57 – 6.52 (m, 2H), 6.29 (s, 1H), 5.64 (s, 1H), 3.78 (s, 3H), 2.39 (d, *J* = 16.3 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.30 – 2.24 (m, 2H), 2.07 (d, *J* = 16.6 Hz, 1H), 1.14 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 160.3, 157.8, 140.3, 139.8, 138.9, 136.4, 135.9, 135.8, 131.0, 129.4, 129.1, 128.5, 128.3, 127.5, 121.5, 119.8, 119.1, 114.1, 111.1, 104.9, 103.9, 55.5, 50.8, 48.5, 40.0, 32.4, 28.5, 28.2, 21.1, 21.0; IR (KBr): 3651, 3336, 3051, 2956, 2362, 2342, 1735, 1576, 1540, 1455, 1392, 1321, 1298, 1246, 1180, 1106, 1032, 819, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{38}H_{38}N_2O_2+Na)^+$ requires m/z 577.2826, found m/z 577.2837.

2-(2-(bis(4-fluorophenyl)methyl)-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ea): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 68% (38.3 mg); yellow solid; m.p. 212.5-213.9 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.38 – 7.33 (m, 1H), 7.29 – 7.23 (m, 3H), 7.16 – 7.08 (m, 4H), 7.04 – 6.98 (m, 2H), 6.97 – 6.91 (m, 2H), 6.81 – 6.76 (m, 2H), 6.66 – 6.61 (m, 2H), 6.32 (s, 1H), 5.73 (s, 1H), 3.78 (s, 3H), 2.41 – 2.34 (m, 1H), 2.31 (d, *J* = 16.7 Hz, 1H), 2.25 (d, *J* = 16.2 Hz, 1H), 2.10 (d, *J* = 16.7 Hz, 1H), 1.14 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 161.9 (d, *J* = 244.4 Hz), 161.6 (d, *J* = 244.1 Hz), 160.1, 158.0, 139.4, 138.4 (d, *J* = 3.3 Hz), 137.3 (d, *J* = 3.1 Hz), 135.9, 130.8, 130.7, 130.1, 127.9, 127.4, 121.8, 120.1, 119.1, 115.7, 115.5, 115.4, 115.2, 114.3, 111.3, 105.2, 103.8, 55.5, 50.9, 47.8, 40.0, 32.4, 28.4, 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6, -116.1; IR (KBr): 3302, 3058, 2958, 1574, 1540, 1455, 1383, 1321, 1299, 1246, 1220, 1157, 1095, 1033, 1013, 837, 796, 763, 742 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{32}F_2N_2O_2+Na)^+$ requires m/z 585.2324, found m/z 585.2329.

2-(2-(bis(4-chlorophenyl)methyl)-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4fa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 52% (31.0 mg); yellow solid; m.p. 102.8-103.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.37 – 7.33 (m, 1H), 7.32 – 7.26 (m, 3H), 7.25 – 7.19 (m, 4H), 7.15 – 7.08 (m, 4H), 6.82 – 6.77 (m, 2H), 6.64 – 6.58 (m, 2H), 6.28 (s, 1H), 5.70 (s, 1H), 3.79 (s, 3H), 2.36 (d, *J* = 16.2 Hz, 1H), 2.31 – 2.21 (m, 2H), 2.09 (d, *J* = 16.7 Hz, 1H), 1.13 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 160.2, 158.0, 140.8, 139.7, 138.8, 135.9, 133.1, 132.5, 130.7, 130.6, 130.0, 128.9, 128.6, 127.8, 127.4, 121.9, 120.2, 119.1, 114.3, 111.3, 105.5, 103.7, 55.5, 50.8, 48.1, 40.0, 32.4, 28.6, 28.0; IR (KBr): 3339, 3216, 2955, 2927, 1577, 1540, 1490, 1454, 1383, 1321, 1288, 1246, 1218, 1179, 1090, 1032, 1013, 829, 744 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{32}Cl_2N_2O_2+Na)^+$ requires m/z 617.1733, found m/z 617.1725.

2-(2-benzhydryl-5-bromo-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ga): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 97% (58.8 mg); yellow solid; m.p. 112.9-113.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.33 – 7.22 (m, 8H), 7.20 – 7.16 (m, 3H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.79 – 6.75 (m, 2H), 6.60 – 6.55 (m, 2H), 6.21 (s, 1H), 5.70 (s, 1H), 3.78 (s, 3H), 2.37 (d, *J* = 16.2 Hz, 1H), 2.31 – 2.20 (m, 2H), 2.04 (d, *J* = 16.7 Hz, 1H), 1.11 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 160.5, 158.0, 142.3, 141.4, 141.3, 134.4, 130.7, 130.0, 129.2, 128.8, 128.6, 127.6, 127.1, 126.7, 124.4, 121.5, 114.2, 113.3, 112.7, 105.0, 103.1, 55.5, 50.7, 49.3, 39.9, 32.3, 28.5, 28.2; IR (KBr): 3855, 3753, 3651, 3025, 2954, 2927, 2244, 1576, 1536, 1450, 1383, 1294, 1245, 1218, 1154, 1031, 963, 903, 829, 797, 730, 698, 642 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}BrN_2O_2+Na)^+$ requires m/z 629.1604, found m/z 629.1608.

2-(2-benzhydryl-6-methoxy-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ha): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 99% (55.1 mg); yellow solid; m.p. 117.9-118.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.34 – 7.29 (m, 4H), 7.28 – 7.26 (m, 0H), 7.26 – 7.18 (m, 7H), 6.80 – 6.73 (m, 4H), 6.60 – 6.55 (m, 2H), 6.33 (s, 1H), 5.69 (s, 1H), 3.78 (d, *J* = 2.9 Hz, 6H), 2.38 (d, *J* =

16.5 Hz, 1H), 2.31 – 2.22 (m, 2H), 2.05 (d, *J* = 16.6 Hz, 1H), 1.12 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 159.9, 157.8, 156.3, 142.8, 142.0, 138.3, 136.5, 131.0, 129.2, 128.7, 128.4, 127.4, 126.9, 126.4, 122.3, 119.7, 114.1, 109.8, 105.0, 104.0, 95.0, 55.7, 55.5, 50.9, 49.3, 39.9, 32.4, 28.4, 28.2; IR (KBr): 3334, 3025, 2954, 2833, 1626, 1591, 1542, 1453, 1383, 1298, 1245, 1157, 1104, 1031, 951, 828, 802, 729, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{36}N_2O_3+Na)^+$ requires m/z 579.2618, found m/z 579.2624.

2-(2-benzhydryl-6-chloro-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ia): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 99% (55.5 mg); yellow solid; m.p. 108.4-109.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.34 – 7.27 (m, 5H), 7.25 – 7.21 (m, 5H), 7.19 – 7.15 (m, 2H), 7.04 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.78 – 6.74 (m, 2H), 6.60 – 6.54 (m, 2H), 6.23 (s, 1H), 5.70 (s, 1H), 3.78 (s, 3H), 2.35 (dd, *J* = 16.2, 1.0 Hz, 1H), 2.30 – 2.20 (m, 2H), 2.04 (d, *J* = 16.7 Hz, 1H), 1.11 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 160.3, 157.9, 142.3, 141.4, 140.6, 136.0, 130.7, 129.2, 128.8, 128.6, 128.5, 127.4, 127.1, 126.7, 126.6, 120.6, 119.8, 114.2, 111.2, 105.4, 103.3, 55.5, 50.7, 49.3, 39.9, 32.4, 28.4, 28.2; IR (KBr): 3752, 3713, 3677, 3650, 3630, 3059, 2956, 2347, 2244, 1578, 1540, 1451, 1383, 1298, 1246 1218, 1155, 1060, 1031, 912, 829, 803, 730, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{33}ClN_2O_2+Na)^+$ requires m/z 583.2123, found m/z 583.2115.

2-(2-benzhydryl-7-bromo-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ja): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 84% (50.9 mg); yellow solid; m.p. 153.1-154.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.38 – 7.26 (m, 8H), 7.26 – 7.19 (m, 4H), 7.00 – 6.95 (m, 1H), 6.79 – 6.73 (m, 2H), 6.61 – 6.54 (m, 2H), 6.22 (s, 1H), 5.74 (s, 1H), 3.78 (s, 3H), 2.39 (dd, *J* = 16.3, 1.1 Hz, 1H), 2.32 – 2.23 (m, 2H), 2.06 (d, *J* = 16.6 Hz, 1H), 1.13 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 160.2, 157.9, 142.3, 141.2, 140.5, 134.4, 130.8, 129.4, 129.1, 128.9, 128.6, 127.4, 127.2, 126.7, 124.0, 121.2, 118.3, 114.2, 106.8, 104.8, 103.5, 55.5, 50.8, 49.4, 39.9, 32.4, 28.4, 28.2; IR (KBr): 3331, 3151, 3059, 2954, 1612, 1578, 1560, 1539, 1493, 1452, 1393, 1344, 1317, 1299, 1247, 1183, 1168, 1118, 1031, 829, 776, 750, 735, 698 cm^{-1}; ESI FTMS exact mass calcd for

$(C_{36}H_{33}BrN_2O_2+Na)^+$ requires m/z 629.1604, found m/z 629.1614.

2-(2-benzhydryl-1-methyl-1*H*-indol-3-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ka): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 85% (46.0 mg); yellow solid; m.p. 84.5-85.4 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 7H), 7.26 – 7.16 (m, 6H), 7.13 – 7.08 (m, 1H), 6.75 – 6.69 (m, 2H), 6.51 – 6.45 (m, 2H), 6.18 (s, 1H), 5.83 (s, 1H), 3.77 (s, 3H), 3.42 (s, 3H), 2.32 (dd, *J* = 16.1, 1.4 Hz, 1H), 2.24 – 2.15 (m, 2H), 2.00 (d, *J* = 16.6 Hz, 1H), 1.15 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 160.0, 157.6, 141.5, 140.8, 139.6, 137.9, 131.0, 129.4, 128.7, 128.0, 127.5, 127.1, 126.6, 126.4, 121.7, 119.6, 119.2, 114.1, 109.1, 106.5, 104.5, 55.4, 51.0, 48.9, 39.8, 32.5, 31.4, 29.5, 27.5; IR (KBr): 3346, 3054, 2955, 1579, 1536, 1467, 1394, 1379, 1288, 1245, 1218, 1167, 1149, 1105, 1031, 894, 829, 742, 701 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{36}N_2O_2+Na)^+$ requires m/z 563.2669, found m/z 563.2657.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((4-ethoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ab): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 82% (44.4 mg); yellow solid; m.p. 84.5-85.4 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.37 – 7.31 (m, 5H), 7.29 – 7.17 (m, 7H), 7.14 – 7.07 (m, 2H), 6.77 – 6.72 (m, 2H), 6.60 – 6.54 (m, 2H), 6.31 (s, 1H), 5.76 (s, 1H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.39 (dd, *J* = 16.1, 1.1 Hz, 1H), 2.32 – 2.23 (m, 2H), 2.05 (d, *J* = 16.6 Hz, 1H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.13 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 160.2, 157.2, 142.7, 141.8, 139.8, 135.8, 130.8, 129.3, 128.8, 128.7, 128.4, 128.1, 127.5, 126.9, 126.5, 121.5, 119.9, 119.1, 114.6, 111.2, 105.1, 103.8, 63.7, 50.8, 49.3, 39.9, 32.4, 28.4, 28.2, 14.8; IR (KBr): 3341, 3056, 2926, 2360, 1575 , 1540, 1509, 1450, 1391, 1320, 1300, 1243, 1217, 1168, 1114, 1028, 1011, 826, 744, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{37}H_{36}N_2O_2+Na)^+$ requires m/z 563.2669, found m/z 563.2681.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((4-isopropoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ac): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 99% (54.9 mg); yellow solid; m.p.95.4-96.7 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.36 – 7.29 (m, 5H), 7.28 – 7.26 (m, 1H), 7.26 – 7.17 (m, 6H), 7.14 – 7.06 (m, 2H), 6.76 –

6.70 (m, 2H), 6.60 – 6.52 (m, 2H), 6.31 (s, 1H), 5.74 (s, 1H), 4.48 (p, *J* = 6.1 Hz, 1H), 2.36 (dd, *J* = 16.1, 1.0 Hz, 1H), 2.30 (d, *J* = 16.7 Hz, 1H), 2.23 (d, *J* = 16.2 Hz, 1H), 2.06 (d, *J* = 16.6 Hz, 1H), 1.32 (dd, *J* = 6.0, 1.5 Hz, 6H), 1.13 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 160.2, 156.1, 142.7, 141.8, 139.8, 135.8, 130.7, 129.2, 128.8, 128.7, 128.4, 128.1, 127.4, 127.0, 126.5, 121.6, 119.9, 119.1, 116.0, 105.1, 103.8, 70.2, 50.8, 49.3, 39.9, 32.4, 28.4, 28.2, 22.0; IR (KBr): 3351, 3057, 2959, 2359, 2340, 1683, 1652, 1573, 1540, 1508, 1449, 1392, 1323, 1243, 1219, 1116, 1027, 952, 742, 701 cm^{-1}; ESI FTMS exact mass calcd for $(C_{38}H_{38}N_2O_2+Na)^+$requires m/z 577.2826, found m/z 577.2840.

2-(2-benzhydryl-1*H*-indol-3-yl)-5,5-dimethyl-3-(*p*-tolylamino)cyclohex-2-enone (4ad): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 99% (51.0 mg); yellow solid; m.p. 85.1-86.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.38 – 7.31 (m, 5H), 7.29 – 7.18 (m, 7H), 7.15 – 7.07 (m, 2H), 7.06 – 7.02 (m, 2H), 6.60 – 6.53 (m, 2H), 6.41 (s, 1H), 5.76 (s, 1H), 2.43 – 2.34 (m, 2H), 2.31 (s, 3H), 2.27 (d, *J* = 16.2 Hz, 1H), 2.13 (d, *J* = 16.7 Hz, 1H), 1.14 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 159.6, 142.6, 141.8, 139.8, 135.8, 135.6, 129.6, 129.3, 128.8, 128.7, 128.4, 128.1, 127.0, 126.5, 125.5, 121.6, 119.9, 119.1, 111.2, 105.1, 104.4, 50.9, 49.4, 40.0, 32.5, 28.4, 28.2, 20.9; IR (KBr): 3340, 3056, 3025, 2956, 2925, 2360, 2342, 1588, 1540, 1514, 1493, 1450, 1383, 1322, 1268, 1221, 1156, 1122, 1077, 1028, 899, 810, 763, 743, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_2O+Na)^+$ requires m/z 533.2563, found m/z 533.2571.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((4-(*tert*-butyl)phenyl)amino)-5,5-dimethylcyclohex-2-enone (4ae): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 82% (45.3 mg); yellow solid; m.p. 102.4-104.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.37 – 7.31 (m, 5H), 7.29 – 7.17 (m, 9H), 7.14 – 7.06 (m, 2H), 6.64 – 6.59 (m, 2H), 6.43 (s, 1H), 5.76 (s, 1H), 2.46 – 2.37 (m, 2H), 2.26 (d, *J* = 16.2 Hz, 1H), 2.16 (d, *J* = 16.6 Hz, 1H), 1.30 (s, 9H), 1.15 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 159.3, 148.7, 142.6, 141.8, 139.8, 135.8, 135.6, 129.3, 128.8, 128.7, 128.4, 128.0, 127.0, 126.5, 125.9, 124.8, 121.6, 119.9, 119.1, 111.2, 105.1, 104.5, 50.9, 49.4, 40.1, 34.5, 32.6, 31.3, 28.3, 28.2; IR (KBr): 3649, 3344, 3057, 2959, 2867, 2360, 1619, 1516, 1493, 1453, 1322, 1269, 1226, 1155, 1121, 1077,

1028, 898, 840, 762, 743, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{39}H_{40}N_2O+Na)^+$ requires m/z 575.3033, found m/z 575.3021.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((4-fluorophenyl)amino)-5,5-dimethylcyclohex-2-enone (4af): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 94% (48.4 mg); yellow solid; m.p. 88.7-89.8 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.37 – 7.18 (m, 12H), 7.15 – 7.07 (m, 2H), 6.95 – 6.89 (m, 2H), 6.62 – 6.54 (m, 2H), 6.29 (s, 1H), 5.73 (s, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 2.34 – 2.26 (m, 2H), 2.08 (d, *J* = 16.6 Hz, 1H), 1.15 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 160.6 (d, *J* = 244.5 Hz), 159.2, 142.6, 141.6, 139.9, 135.8, 134.2, 129.2, 128.8, 128.7, 128.5, 128.0, 127.6, 127.5, 127.0, 126.5, 121.7, 120.0, 119.0, 115.9, 115.7, 111.3, 104.9, 104.8, 50.9, 49.3, 40.0, 32.6, 28.4, 28.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.8; IR (KBr): 3648, 3341, 3058, 2957, 2360, 2341, 1585, 1541, 1452, 1383, 1321, 1269, 1229, 1210, 1152, 1027, 1012, 899, 835, 777, 762, 744, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{31}FN_2O+Na)^+$ requires m/z 537.2313, found m/z 537.2305.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((4-chlorophenyl)amino)-5,5-dimethylcyclohex-2-enone (4ag): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 79% (41.9 mg); yellow solid; m.p. 167.0-168.5 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.35 – 7.26 (m, 7H), 7.26 – 7.17 (m, 7H), 7.15 – 7.07 (m, 2H), 6.58 – 6.49 (m, 2H), 6.33 (s, 1H), 5.71 (s, 1H), 2.45 – 2.33 (m, 2H), 2.29 (d, *J* = 16.2 Hz, 1H), 2.14 (d, *J* = 16.5 Hz, 1H), 1.15 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.5, 142.5, 141.6, 139.9, 136.9, 135.8, 131.0, 129.2, 129.1, 128.8, 128.7, 128.5, 128.0, 127.0, 126.6, 126.4, 121.7, 120.1, 119.0, 111.3, 105.6, 104.8, 50.9, 49.3, 40.1, 32.7, 28.4, 28.2; IR (KBr): 3332, 3056, 2955, 2360, 2341, 1618, 1587, 1540, 1451, 1381, 1319, 1266, 1220, 1156, 1089, 1026, 1012, 743, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{31}ClN_2O+Na)^+$ requires m/z 553.2017, found m/z 553.2023.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((3-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ah): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 69% (36.4 mg); yellow solid; m.p. 127.4-128.5 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.35 – 7.27 (m, 6H), 7.25 – 7.06 (m, 9H), 6.69 – 6.65 (m, 1H), 6.42 (s, 1H), 6.28 (dd,

J = 7.9, 1.9 Hz, 1H), 6.21 – 6.16 (m, 1H), 5.72 (s, 1H), 3.75 (s, 3H), 2.46 – 2.37 (m, 2H), 2.26 (d, *J* = 16.2 Hz, 1H), 2.19 (d, *J* = 16.6 Hz, 1H), 1.15 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 160.0, 158.8, 142.6, 141.7, 139.8, 139.4, 135.7, 129.7, 129.2, 128.8, 128.7, 128.4, 128.0, 127.0, 126.5, 121.6, 120.0, 119.1, 117.5, 111.2, 111.1, 110.8, 105.1, 105.0, 55.4, 50.9, 49.4, 40.2, 32.7, 28.4, 28.2; IR (KBr): 3649, 3337, 3057, 2956, 2360, 2341, 1577, 1541, 1493, 1450, 1382, 1319, 1283, 1262, 1196, 1155, 1078, 1031, 744, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_2O_2+Na)^+$ requires m/z 549.2512, found m/z 549.2508.

2-(2-benzhydryl-1*H*-indol-3-yl)-5,5-dimethyl-3-(*m*-tolylamino)cyclohex-2-enone (4ai): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 91% (46.5 mg); yellow solid; m.p. 138.5-139.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.40 – 7.26 (m, 7H), 7.26 – 7.18 (m, 5H), 7.15 – 7.07 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.53 – 6.48 (m, 1H), 6.43 (s, 1H), 6.40 – 6.36 (m, 1H), 5.75 (s, 1H), 2.42 (d, *J* = 16.4 Hz, 2H), 2.32 – 2.26 (m, 4H), 2.21 – 2.14 (m, 1H), 1.16 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.2, 142.6, 141.8, 139.8, 139.0, 138.1, 135.8, 129.3, 128.8, 128.7, 128.5, 128.1, 127.0, 126.5, 126.4, 125.9, 122.3, 121.6, 120.0, 119.1, 111.2, 105.1, 104.7, 50.9, 49.4, 40.1, 32.6, 28.3, 21.3; IR (KBr): 3327, 3251, 3057, 2960, 2360, 2340, 1618, 1493, 1449, 1383, 1320, 1265, 1150, 1172, 1115, 1030, 1010, 786, 762, 730, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_2O+Na)^+$ requires m/z 533.2563, found m/z 533.2574.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((3-fluorophenyl)amino)-5,5-dimethylcyclohex-2-enone (4aj): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 61% (31.4 mg); yellow solid; m.p. 83.5-84.8 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.37 – 7.27 (m, 6H), 7.25 – 7.06 (m, 9H), 6.85 – 6.78 (m, 1H), 6.45 – 6.36 (m, 2H), 6.34 – 6.27 (m, 1H), 5.70 (s, 1H), 2.43 (dd, *J* = 16.3, 5.1 Hz, 2H), 2.29 (d, *J* = 16.2 Hz, 1H), 2.21 (d, *J* = 16.5 Hz, 1H), 1.17 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 162.7 (d, *J* = 245.6 Hz), 158.1, 142.0 (d, *J* = 88.7 Hz), 140.0, 139.9, 135.8, 130.1 (d, *J* = 9.4 Hz), 129.2, 128.8, 128.7, 128.5, 128.0, 127.0, 126.7, 121.8, 120.3 (d, *J* = 2.9 Hz), 120.1, 118.9, 112.1 (d, *J* = 20.9 Hz), 111.9 (d, *J* = 23.2 Hz), 111.3, 106.1, 104.7, 50.9, 49.4, 40.2, 32.8, 28.4, 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.5; IR (KBr): 3649, 3448, 3342, 3059, 2958, 2360, 2341, 1589, 1550, 1451,

1389, 1321, 1279, 1143, 1076, 1030, 1012, 926, 898, 864, 783, 764, 744, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{31}FN_2O+Na)^+$ requires m/z 537.2313, found m/z 537.2319.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((2-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (4ak): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 65% (34.2 mg); yellow solid; m.p. 136.7-138.1 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.42 – 7.39 (m, 1H), 7.37 – 7.31 (m, 4H), 7.29 – 7.22 (m, 2H), 7.22 – 7.14 (m, 5H), 7.13 – 7.04 (m, 3H), 6.89 – 6.84 (m, 1H), 6.81 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.53 (s, 1H), 5.78 (s, 1H), 3.64 (s, 3H), 2.40 – 2.32 (m, 2H), 2.17 (dd, *J* = 30.5, 16.3 Hz, 2H), 1.13 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 159.4, 153.3, 142.7, 141.9, 139.4, 135.6, 129.4, 128.7, 128.2, 128.1, 127.6, 126.9, 126.3, 126.3, 125.4, 121.4, 120.3, 119.7, 119.5, 111.1, 110.9, 105.2, 105.1, 55.3, 50.9, 49.7, 40.0, 32.4, 28.8, 27.9; IR (KBr): 3332, 3178, 3056, 2956, 1572, 1537, 1499, 1451, 1393, 1420, 1302, 1322, 1271, 1178, 1210, 1153, 1114, 1028, 742, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_2O_2+Na)^+$ requires m/z 549.2512, found m/z 549.2523.

2-(2-benzhydryl-1*H*-indol-3-yl)-5,5-dimethyl-3-(*o*-tolylamino)cyclohex-2-enone (4al): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 75% (38.4 mg); yellow solid; m.p. 159.5-160.2 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.41 – 7.38 (m, 1H), 7.36 – 7.31 (m, 4H), 7.29 – 7.27 (m, 1H), 7.26 – 7.16 (m, 6H), 7.13 – 7.05 (m, 5H), 6.66 – 6.60 (m, 1H), 6.14 (s, 1H), 5.79 (s, 1H), 2.41 (dd, *J* = 16.3, 1.1 Hz, 1H), 2.30 (d, *J* = 16.3 Hz, 1H), 2.17 (d, *J* = 16.6 Hz, 1H), 1.96 (d, *J* = 16.7 Hz, 1H), 1.88 (s, 3H), 1.13 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 160.4, 142.7, 141.9, 140.1, 136.9, 135.8, 135.3, 130.7, 129.3, 128.8, 128.6, 128.5, 127.9, 127.7, 127.0, 126.9, 126.5, 126.4, 121.5, 119.9, 119.2, 111.2, 104.9, 103.9, 100.0, 50.9, 49.2, 39.9, 32.4, 28.3, 17.9; IR (KBr): 3327, 3179, 3057, 2955, 2925, 1618, 1572, 1540, 1493, 1451, 1418, 1384, 1322, 1304, 1267, 1153, 1112, 741, 716, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_2O+Na)^+$ requires m/z 533.2563, found m/z 533.2563.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((2-fluorophenyl)amino)-5,5-dimethylcyclohex-2-enone

(4am): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 63% (32.4 mg); yellow solid; m.p. 210.4-211.1 ^{o}C; H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.40 – 7.37 (m, 1H), 7.35 – 7.31 (m, 4H), 7.29 – 7.27 (m, 1H), 7.25 – 7.15 (m, 6H), 7.15 – 7.00 (m, 5H), 6.75 – 6.69 (m, 1H), 6.20 (s, 1H), 5.76 (s, 1H), 2.42 – 2.33 (m, 2H), 2.25 (d, *J* = 16.1 Hz, 1H), 2.08 (d, *J* = 16.5 Hz, 1H), 1.15 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.0, 157.1 (d, *J* = 246.3 Hz), 142.5, 141.7, 139.8, 135.7, 129.3, 128.8, 128.6, 128.4, 127.9, 127.7, 127.4 (d, *J* = 7.5 Hz), 127.0, 126.5, 126.4 (d, *J* = 12.2 Hz), 124.3 (d, *J* = 3.9 Hz), 121.6, 120.0, 119.2, 116.2 (d, *J* = 19.9 Hz), 111.1, 105.8, 104.7, 50.9, 49.5, 39.6 (d, *J* = 1.8 Hz), 32.5, 28.3, 28.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.8; IR (KBr): 3330, 3178, 3058, 2958, 1618, 1580, 1535, 1499, 1420, 1322, 1272, 1153, 1103, 1031, 763, 742, 716, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{31}FN_2O+Na)^+$requires m/z 537.2313, found m/z 537.2315.

2-(2-benzhydryl-1*H*-indol-3-yl)-3-((2-fluorophenyl)amino)-5,5-dimethylcyclohex-2-enone

(4an): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 97% (51.5 mg); yellow solid; m.p. 205.6-206.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.43 – 7.40 (m, 1H), 7.36 – 7.30 (m, 5H), 7.29 – 7.26 (m, 1H), 7.26 – 7.24 (m, 1H), 7.23 – 7.14 (m, 6H), 7.13 – 7.05 (m, 3H), 6.77 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.38 (s, 1H), 5.76 (s, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 2.35 – 2.25 (m, 2H), 2.06 (d, *J* = 16.5 Hz, 1H), 1.16 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.5, 142.5, 141.8, 139.8, 135.7, 130.6, 130.0, 129.3, 128.8, 128.7, 128.5, 127.9, 127.2, 127.0, 126.9, 126.4, 121.6, 119.9, 119.4, 111.1, 106.2, 104.6, 51.0, 49.5, 40.0, 32.6, 28.4, 28.2; IR (KBr): 3338, 3176, 3058, 2956, 2926, 1619, 1481, 1417, 1321, 1276, 1227, 1155, 1061, 1030, 741, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{31}ClN_2O+Na)^+$ requires m/z 553.2017, found m/z 553.2019.

2-(2-benzhydryl-1*H*-indol-3-yl)-5,5-dimethyl-3-(phenylamino)cyclohex-2-enone (4ao): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 86% (42.7 mg); yellow solid; m.p. 177.2-178.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.38 – 7.31 (m, 5H), 7.30 – 7.18 (m, 9H), 7.15 – 7.07 (m, 3H), 6.70 – 6.62 (m, 2H), 6.47 (s, 1H), 5.75 (s, 1H), 2.46 – 2.37 (m, 2H), 2.28 (d, *J* = 16.1 Hz, 1H), 2.17 (d, *J* = 16.5 Hz, 1H), 1.15 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.0, 142.6, 141.7, 139.9, 138.3, 135.8,

129.3, 129.0, 128.8, 128.7, 128.5, 128.1, 127.0, 126.6, 125.6, 125.2, 121.6, 120.0, 119.1, 111.2, 105.0, 50.9, 49.4, 40.1, 32.6, 28.4, 28.2; IR (KBr): 3677 3651 3631, 3057, 2956, 2365, 2345, 1578, 1495, 1447, 1419, 1391, 1322, 1269, 1221, 1154, 1122, 1075, 1030, 1011, 900, 762, 741, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{32}N_2O+Na)^+$ requires m/z 519.2407, found m/z 519.2408.

2-(2-benzhydryl-1*H*-indol-3-yl)-5,5-dimethyl-3-((3,4,5-trimethoxyphenyl)amino)cyclohex-2-enone (4ap): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 69% (40.5 mg); yellow solid; m.p. 94.3-95.1 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.37 – 7.19 (m, 10H), 7.19 – 7.06 (m, 4H), 6.31 (s, 1H), 5.85 (s, 2H), 5.73 (s, 1H), 3.80 (s, 3H), 3.77 (s, 6H), 2.46 – 2.38 (m, 2H), 2.34 – 2.29 (m, 1H), 2.19 (d, *J* = 16.6 Hz, 1H), 1.17 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.4, 153.2, 142.7, 141.7, 139.8, 136.2, 135.9, 134.0, 129.2, 128.8, 128.7, 128.4, 128.1, 127.0, 126.4, 121.7, 119.9, 119.1, 111.3, 105.0, 104.8, 103.3, 61.0, 56.3, 50.9, 49.2, 40.1, 32.6, 28.3, 28.2; IR (KBr): 3345, 3057, 2957, 2247, 1588, 1506, 1451, 1382, 1319, 1263, 1231, 1181, 1128, 1050, 1030, 1011, 816, 745, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{38}H_{38}N_2O_4+Na)^+$ requires m/z 609.2724, found m/z 609.2729.

2-(2-benzhydryl-1*H*-indol-3-yl)-5,5-dimethyl-3-((3,4,5-trimethoxyphenyl)amino)cyclohex-2-enone (4aq): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 64% (32.7 mg); yellow solid; m.p. 139.7-140.5 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.33 – 7.28 (m, 5H), 7.27 – 7.22 (m, 5H), 7.22 – 7.18 (m, 3H), 7.18 – 7.14 (m, 2H), 7.13 – 7.09 (m, 1H), 7.09 – 7.05 (m, 1H), 6.88 – 6.80 (m, 2H), 5.73 (s, 1H), 5.24 (t, *J* = 6.8 Hz, 1H), 4.22 – 4.06 (m, 2H), 2.42 – 2.32 (m, 2H), 2.27 (d, *J* = 16.2 Hz, 1H), 2.10 (d, *J* = 16.4 Hz, 1H), 1.13 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 161.9, 142.7, 142.0, 139.9, 138.3, 135.9, 129.2, 128.7, 128.7, 128.4, 128.0, 127.2, 126.9, 126.5, 126.1, 121.5, 119.8, 119.3, 111.1, 105.1, 102.5, 50.5, 49.0, 46.3, 38.8, 32.0, 28.5, 28.4; IR (KBr): 3369, 3057, 2955, 2925, 2348, 2282, 1567, 1493, 1452, 1401, 1353, 1322, 1271, 1156, 1109, 1074, 1030, 736, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_2O+Na)^+$ requires m/z 533.2563, found m/z 533.2570.

4-(2-benzhydryl-1*H*-indol-3-yl)-5-((4-methoxyphenyl)amino)-1,6-dihydro-[1,1'-biphenyl]-3(2

***H*)-one (4ar):** Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 82% (47.2 mg); unseparated isomers with 1:1 molar ratio; yellow solid; m.p. 127.8-128.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.90 (m, 2H), 7.47 – 7.44 (m, 1H), 7.40 – 7.36 (m, 7H), 7.35 – 7.27 (m, 14H), 7.27 – 7.26 (m, 2H), 7.26 – 7.19 (m, 10H), 7.17 – 7.14 (m, 2H), 7.13 – 7.05 (m, 2H), 6.78 – 6.71 (m, 4H), 6.69 – 6.63 (m, 4H), 6.42 (d, *J* = 16.6 Hz, 2H), 5.76 (d, *J* = 22.0 Hz, 2H), 3.75 (s, 6H), 3.47 – 3.38 (m, 1H), 2.87 – 2.59 (m, 6H), 2.55 – 2.41 (m, 2H), 2.32 – 2.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 160.4, 157.9, 143.6, 143.5, 142.8, 142.7, 141.6, 139.8, 139.6, 135.6, 130.8, 130.7, 129.3, 128.9, 128.8, 128.7, 128.5, 128.3, 128.0, 127.4, 127.3, 127.1, 127.0, 126.9, 126.8, 126.7, 126.5, 121.6, 120.0, 119.1, 118.9, 114.3, 114.2, 111.2, 105.2, 105.1, 105.0, 55.5, 49.9, 44.1, 44.0, 39.8, 34.0, 33.9; IR (KBr): 3340, 3025, 2931, 2348, 2242, 1575, 1540, 1452, 1391, 1289, 1245, 1179, 1105, 1031, 911, 823, 774, 744, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{34}N_2O_2+Na)^+$ requires m/z 597.2512, found m/z 597.2526.

2-(2-benzhydryl-1*H*-indol-3-yl)-5,5-dimethyl-3-(methyl(phenyl)amino)cyclohex-2-enone (4as): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 40% (20.4 mg); yellow solid; m.p. 87.3-88.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.38 – 7.35 (m, 1H), 7.34 – 7.26 (m, 8H), 7.25 – 7.18 (m, 5H), 7.15 – 7.11 (m, 1H), 7.10 – 7.02 (m, 2H), 6.98 – 6.93 (m, 2H), 5.76 (s, 1H), 2.51 (s, 3H), 2.42 (d, *J* = 16.6 Hz, 1H), 2.39 – 2.30 (m, 2H), 2.21 – 2.14 (m, 1H), 1.10 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 162.5, 146.7, 142.5, 141.2, 137.7, 135.5, 129.8, 129.3, 129.0, 128.6, 126.7, 126.6, 125.1, 125.0, 121.3, 119.7, 119.4, 110.9, 109.7, 109.6, 51.5, 48.9, 45.2, 42.4, 31.9, 28.2, 27.9; IR (KBr): 3851, 3646, 3626, 3271, 3057, 2954, 2354, 1731, 1572, 1521, 1452, 1327, 1280, 1179, 1132, 1076, 1059, 1027, 897, 761, 743, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{34}N_2O+Na)^+$ requires m/z 533.2563, found m/z 533.2570.

4-(2-benzhydryl-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6a): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 92% (42.1 mg); yellow solid; m.p. 216.5-218.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 1H), 8.00 (s, 1H), 7.49 – 7.43 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.25 – 7.13 (m, 8H), 7.13 – 6.99 (m, 4H), 5.56 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 155.2,

141.8, 141.6, 141.5, 138.7, 135.7, 134.9, 129.7, 128.9, 128.9, 128.8, 128.6, 128.5, 126.9, 126.8, 125.1, 124.2, 122.0, 120.1, 119.3, 117.0, 111.0, 104.5, 87.8, 56.0, 49.1; IR (KBr): 3371, 3025, 2952, 1720, 1636, 1603, 1553, 1492, 1478, 1454, 1316, 1295, 1242, 1161, 1061, 1029, 762, 744, 712, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{23}NO_3+Na)^+$ requires m/z 480.1570, found m/z 480.1584.

4-(2-(bis(2-methoxyphenyl)methyl)-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6b): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 60% (31.1 mg); yellow solid; m.p. 128.7-130.0 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 1H), 8.06 (s, 1H), 7.45 – 7.40 (m, 1H), 7.34 – 7.31 (m, 1H), 7.29 – 7.23 (m, 1H), 7.20 – 7.13 (m, 4H), 7.10 – 7.07 (m, 1H), 7.06 – 7.01 (m, 1H), 7.01 – 6.97 (m, 2H), 6.85 – 6.79 (m, 2H), 6.78 – 6.75 (m, 1H), 6.71 – 6.67 (m, 1H), 6.08 (s, 1H), 3.51 (d, *J* = 1.5 Hz, 6H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 157.0, 156.9, 155.1, 141.7, 139.0, 135.2, 134.3, 130.3, 130.0, 129.6, 129.3, 129.2, 127.9, 127.7, 124.8, 124.7, 121.4, 120.3, 120.0, 119.7, 119.0, 117.0, 110.8, 110.6, 110.5, 103.8, 88.1, 55.6, 55.4, 55.3, 37.1; IR (KBr): 3313, 3002, 2933, 2835, 1638, 1604, 1554, 1489, 1456, 1434, 1374, 1313, 1185, 1157, 1102, 1063, 1051, 1029, 796, 752, 724, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{27}NO_5+Na)^+$ requires m/z 540.1781, found m/z 540.1795.

4-(2-(bis(3-methoxyphenyl)methyl)-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6c): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 76% (39.4 mg); yellow solid; m.p. 132.1-133.2 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.01 (s, 1H), 7.48 – 7.41 (m, 1H), 7.36 – 7.32 (m, 1H), 7.31 – 7.26 (m, 1H), 7.23 – 7.15 (m, 3H), 7.14 – 7.09 (m, 1H), 7.09 – 7.03 (m, 2H), 6.78 – 6.65 (m, 5H), 6.63 – 6.58 (m, 1H), 5.48 (s, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 159.7, 155.2, 143.2, 142.9, 141.6, 138.4, 135.6, 134.8, 129.6, 129.5, 129.4, 128.9, 125.0, 124.2, 122.0, 121.3, 121.2, 120.0, 119.3, 117.0, 115.3, 115.1, 111.7, 111.6, 111.1, 104.5, 87.8, 56.1, 55.2, 55.1, 49.1; IR (KBr): 3357, 2931, 2834, 1720, 1641, 1604, 1583, 1554, 1479, 1455, 1434, 1373, 1294, 1263, 1242, 1152, 1031, 764, 743, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{27}NO_5+Na)^+$ requires m/z 540.1781, found m/z 540.1771.

4-(2-(bis(3-fluorophenyl)methyl)-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6d): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 67% (33.1 mg); yellow solid; m.p. 154.7-155.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.98 (s, 1H), 7.50 – 7.44 (m, 1H), 7.41 – 7.36 (m, 1H), 7.32 – 7.28 (m, 1H), 7.27 – 7.16 (m, 4H), 7.11 – 7.06 (m, 1H), 7.05 – 7.01 (m, 1H), 6.97 – 6.84 (m, 5H), 6.81 – 6.76 (m, 1H), 5.55 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 245.4 Hz), 161.2, 155.2, 143.8, 143.7, 143.5, 143.4, 141.3, 137.2, 135.8, 135.0, 130.3, 130.2, 130.1, 130.0, 129.8, 128.7, 125.3, 124.5 (d, *J* = 11.3 Hz), 124.0, 122.4, 120.3, 119.5, 117.0, 116.1, 115.9, 115.6, 114.2 (d, *J* = 6.7 Hz), 114.0 (d, *J* = 6.8 Hz), 111.2, 105.1, 87.3, 56.0, 48.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.1, -112.3; IR (KBr): 3355, 3057, 2952, 2255, 1718, 1639, 1610, 1588, 1556, 1480, 1455, 1376, 1329, 1296, 1240, 1142, 1062, 1027, 969, 907, 881, 793, 768, 744, 686 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{21}F_2NO_3+Na)^+$ requires m/z 516.1382, found m/z 516.1390.

4-(2-(di-*p*-tolylmethyl)-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6e): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 91% (44.2 mg); yellow solid; m.p. 123.2-124.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.99 (s, 1H), 7.48 – 7.42 (m, 1H), 7.34 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.23 – 7.16 (m, 2H), 7.08 – 6.95 (m, 10H), 5.48 (s, 1H), 3.67 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 155.1, 141.6, 139.1, 139.0, 138.6, 136.4, 136.4, 135.6, 134.8, 129.6, 129.2, 129.0, 128.9, 128.8, 128.6, 125.0, 124.3, 121.9, 120.0, 119.3, 117.0, 111.0, 104.3, 87.9, 56.1, 48.4, 21.0, 21.0; IR (KBr): 3290, 3019, 2920, 1635, 1605, 1555, 1509, 1478, 1456, 1434, 1375, 1312, 1295, 1243, 1186, 1161, 1099, 1062, 1030, 820, 803, 762, 747, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{27}NO_3+Na)^+$ requires m/z 508.1883, found m/z 508.1870.

4-(2-(bis(4-fluorophenyl)methyl)-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6f): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 57% (28.2 mg); yellow solid; m.p. 128.2-129.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.93 (s, 1H), 7.48 – 7.43 (m, 1H), 7.38 – 7.35 (m, 1H), 7.32 – 7.28 (m, 1H), 7.23 – 7.18 (m, 2H), 7.12 – 7.05 (m, 3H), 7.04 – 6.99 (m, 3H), 6.99 – 6.94 (m, 2H), 6.93 – 6.87 (m, 2H), 5.53 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, *J* = 244.8 Hz), 161.2,

155.2, 141.3, 138.2, 137.4 (d, *J* = 3.2 Hz), 137.1 (d, *J* = 3.3 Hz), 135.7, 134.9, 130.4 (d, *J* = 8.8 Hz), 130.2 (d, *J* = 7.9 Hz), 129.8, 128.8, 125.2, 124.0, 122.3, 120.3, 119.4, 117.0, 115.5 (d, *J* = 17.8 Hz), 115.3 (d, *J* = 17.6 Hz), 111.1, 104.7, 87.5, 56.1, 47.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.4, -115.5; IR (KBr): 3373, 3062, 2951, 1722, 1643, 1604, 1556, 1505, 1479, 1455, 1434, 1373, 1324, 1296, 1224, 1158, 1097, 1062, 1017, 903, 835, 796, 767, 746, 713 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{21}F_2NO_3+Na)^+$ requires m/z 516.1382, found m/z 516.1375.

4-(2-(bis(4-chlorophenyl)methyl)-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6g): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 69% (36.3 mg); yellow solid; m.p. 189.3-190.5 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.92 (s, 1H), 7.48 – 7.43 (m, 1H), 7.38 – 7.35 (m, 1H), 7.32 – 7.28 (m, 1H), 7.25 – 7.16 (m, 6H), 7.10 – 7.04 (m, 3H), 7.02 – 6.96 (m, 3H), 5.51 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 155.1, 139.9, 139.5, 137.5, 135.8, 135.0, 133.0, 130.2, 130.0, 129.8, 128.9, 128.7, 125.3, 124.0, 122.4, 120.3, 119.5, 117.0, 111.1, 105.0, 87.4, 56.1, 47.7; IR (KBr): 3369, 3061, 2924, 1726, 1636, 1603, 1552, 1490, 1478, 1456, 1434, 1403, 1371, 1296, 1242, 1162, 1090, 1062, 1015, 826, 802, 790, 768, 745, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{21}Cl_2NO_3+Na)^+$ requires m/z 548.0791, found m/z 548.0795.

4-(2-benzhydryl-5-bromo-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6h): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 83% (44.5 mg); yellow solid; m.p. 157.4-158.1 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.18 (m, 1H), 8.07 (s, 1H), 7.46 (ddd, *J* = 8.3, 7.2, 1.5 Hz, 1H), 7.34 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.26 – 7.18 (m, 5H), 7.18 – 7.13 (m, 3H), 7.12 – 7.08 (m, 2H), 7.02 – 6.99 (m, 1H), 6.97 – 6.93 (m, 1H), 5.56 (s, 1H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 155.3, 141.3, 141.1, 139.4, 134.9, 134.4, 130.0, 129.8, 128.8, 128.7, 128.5, 127.1, 127.0, 125.2, 124.5, 123.9, 121.3, 118.5, 117.0, 106.0, 104.6, 87.3, 56.0, 49.2; IR (KBr): 3295, 3058, 3024, 2950, 1639, 1605, 1550, 1493, 1480, 1453, 1372, 1329, 1296, 1244, 1191, 1162, 1131, 1061, 1030, 779, 768, 737, 727, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{22}BrNO_3+Na)^+$ requires m/z 560.0660, found m/z 560.0666.

4-(2-benzhydryl-6-methoxy-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6i): Flash

column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 95% (46.4 mg); yellow solid; m.p. 115.6-116.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.91 (s, 1H), 7.49 – 7.44 (m, 1H), 7.32 – 7.26 (m, 2H), 7.25 – 7.14 (m, 7H), 7.12 – 7.06 (m, 4H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.74 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.51 (s, 1H), 3.82 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 156.5, 155.2, 142.0, 141.7, 141.6, 137.3, 136.4, 134.9, 129.7, 128.9, 128.8, 128.5, 128.4, 126.8, 126.7, 125.1, 124.2, 123.1, 119.9, 117.0, 109.8, 104.3, 94.9, 87.8, 56.0, 55.7, 49.1; IR (KBr): 3373, 3025, 2953, 1723, 1626, 1604, 1583, 1555, 1479, 1494, 1451, 1424, 1366, 1325, 1298, 1244, 1198, 1155, 1125, 1061, 1029, 766, 746, 729, 700 cm^{-1}; ESI FTMS exact mass calcd for $(C_{32}H_{25}NO_4+Na)^+$ requires m/z 510.1676, found m/z 510.1680.

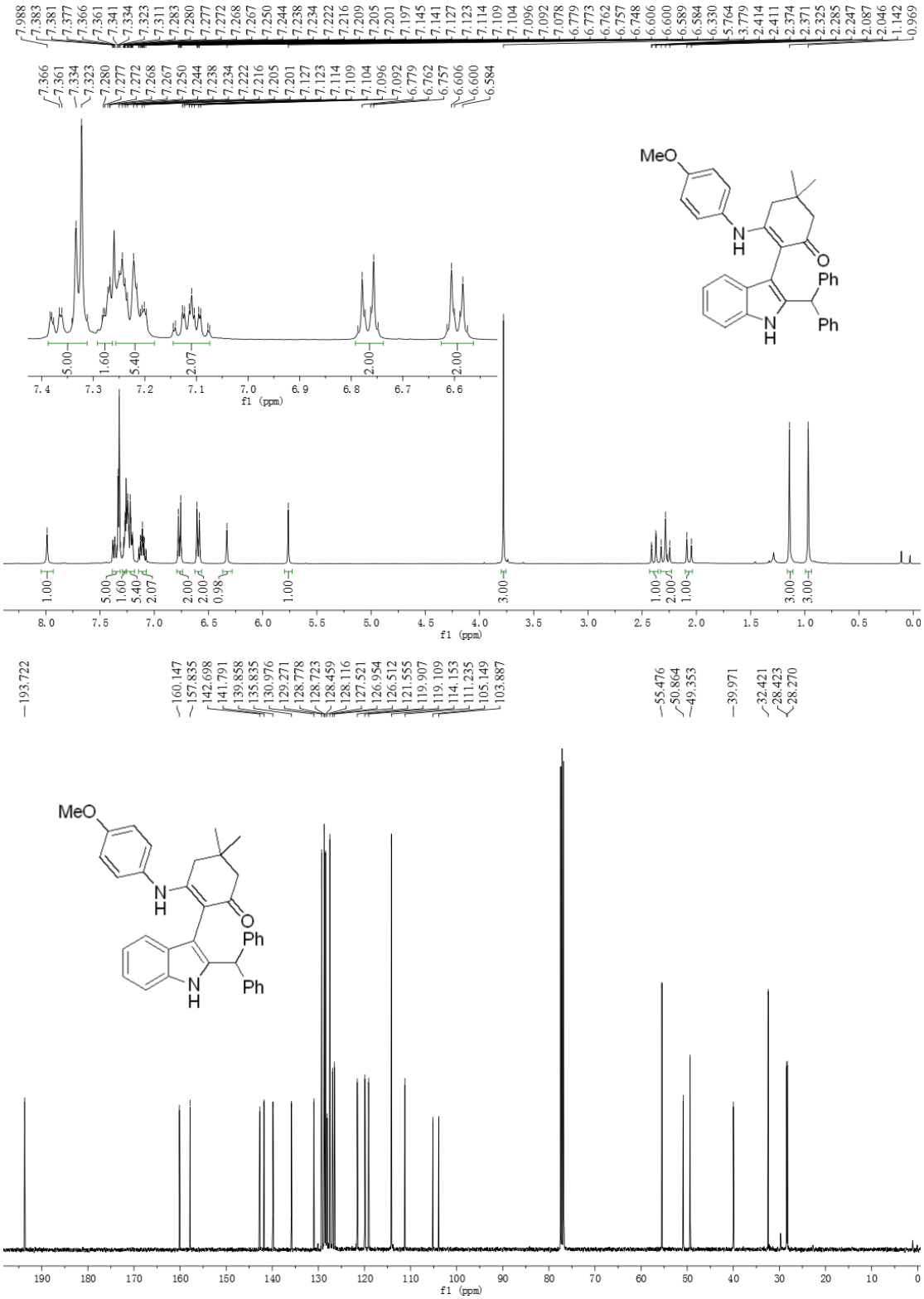
4-(2-benzhydryl-6-chloro-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6j): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 94% (46.2 mg); yellow solid; m.p. 138.5-139.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.01 (s, 1H), 7.49 – 7.44 (m, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.26 – 7.16 (m, 5H), 7.14 – 7.10 (m, 3H), 7.06 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.04 – 6.99 (m, 2H), 5.52 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 155.2, 141.5, 141.3, 141.2, 139.4, 136.0, 135.0, 129.8, 128.9, 128.7, 128.5, 127.9, 127.4, 127.0, 126.9, 125.2, 123.9, 120.8, 120.1, 117.0, 111.1, 104.7, 87.1, 56.0, 49.1; IR (KBr): 3355, 3060, 3025, 2951, 1722, 1642, 1605, 1556, 1493, 1478, 1451, 1363, 1323, 1297, 1241, 1161, 1060, 1029, 972, 936, 907, 802, 766, 730, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{22}ClNO_3+Na)^+$ requires m/z 514.1180, found m/z 514.1189.

4-(2-benzhydryl-7-bromo-1*H*-indol-3-yl)-3-methoxy-1*H*-isochromen-1-one (6k): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 12 h; yield: 84% (45.0 mg); yellow solid; m.p. 115.2-116.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.06 (s, 1H), 7.48 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.26 – 7.17 (m, 7H), 7.13 – 7.10 (m, 2H), 7.09 – 7.05 (m, 2H), 7.02 – 6.99 (m, 1H), 5.52 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 155.3, 141.4, 141.3, 141.1, 140.1, 135.0, 134.3, 130.7, 129.8, 128.9, 128.7, 128.5, 127.0, 125.2, 124.9, 123.8, 121.7, 116.9, 113.4, 112.5, 104.2, 86.9, 56.0, 49.1; IR (KBr): 3851, 3346, 3059, 3025, 2950, 1643, 1604, 1556, 1493, 1479,

1368, 1301, 1261, 1241, 1158, 1061, 1028, 944, 902, 799, 765, 730, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{22}BrNO_3+Na)^+$ requires m/z 560.0660, found m/z 560.0675.

5. NMR Spectra of products 4 and 6

4aa



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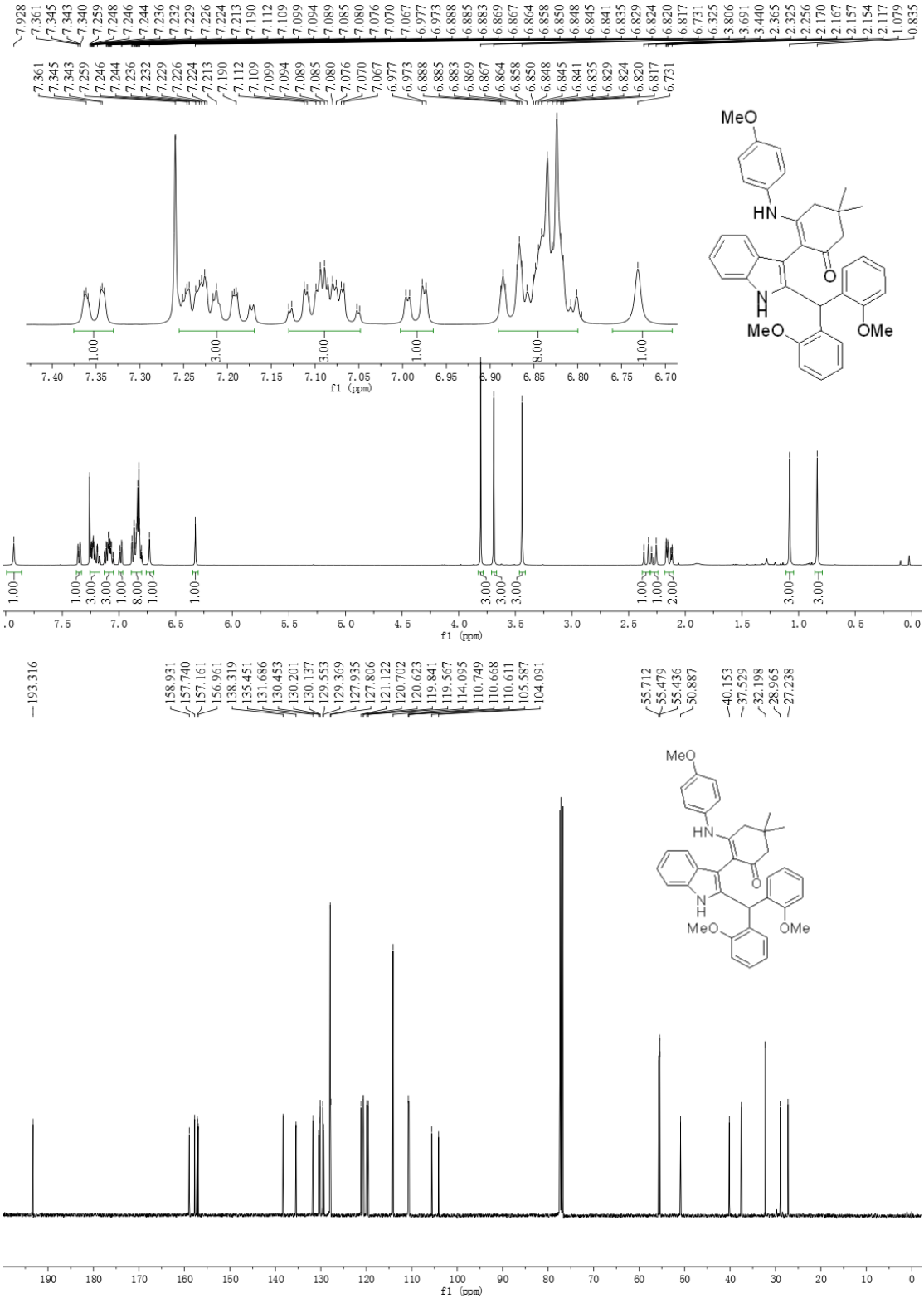

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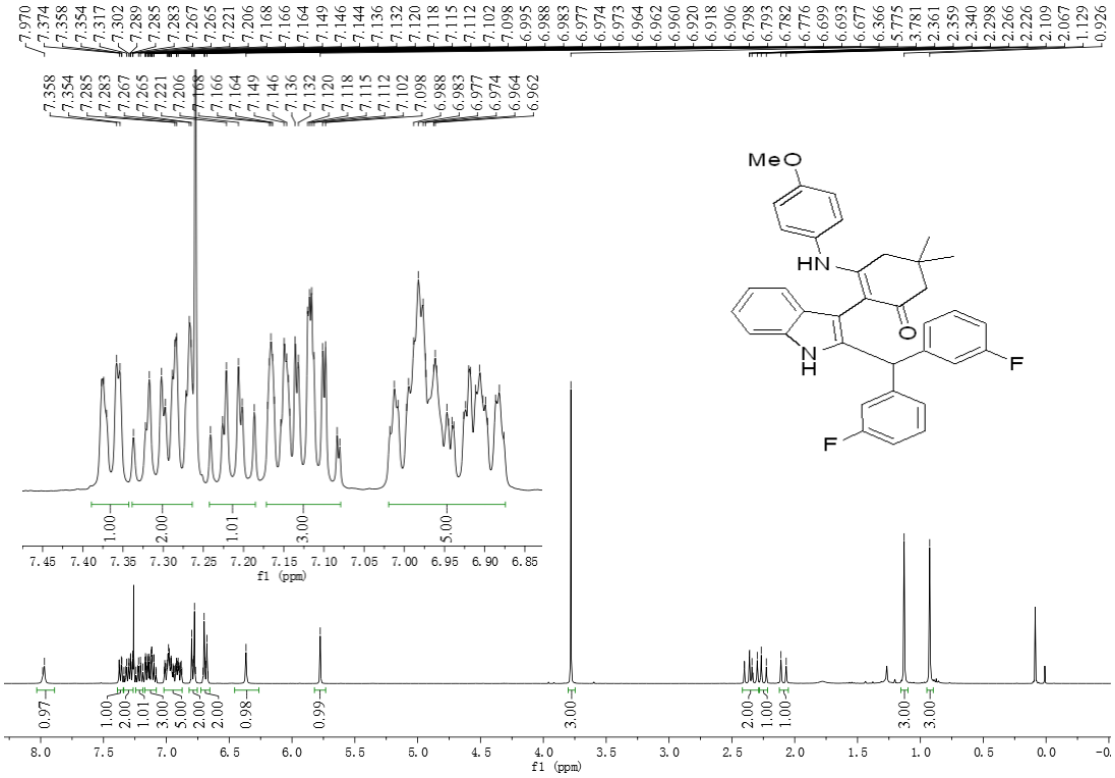

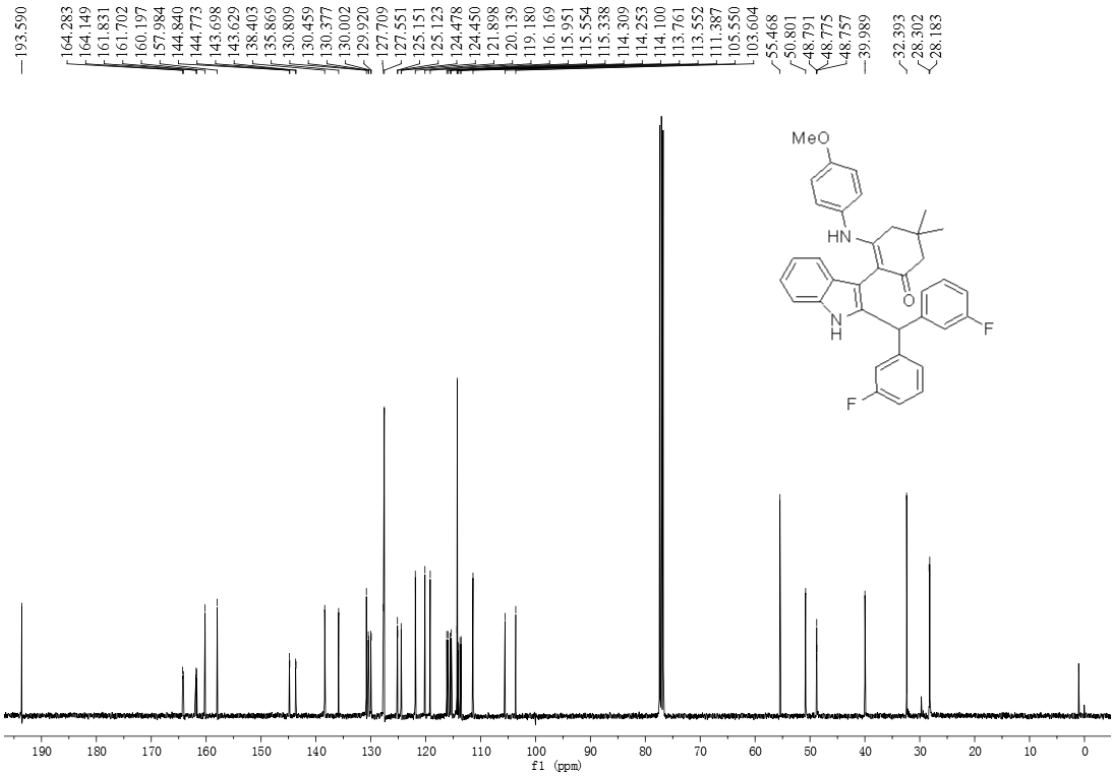

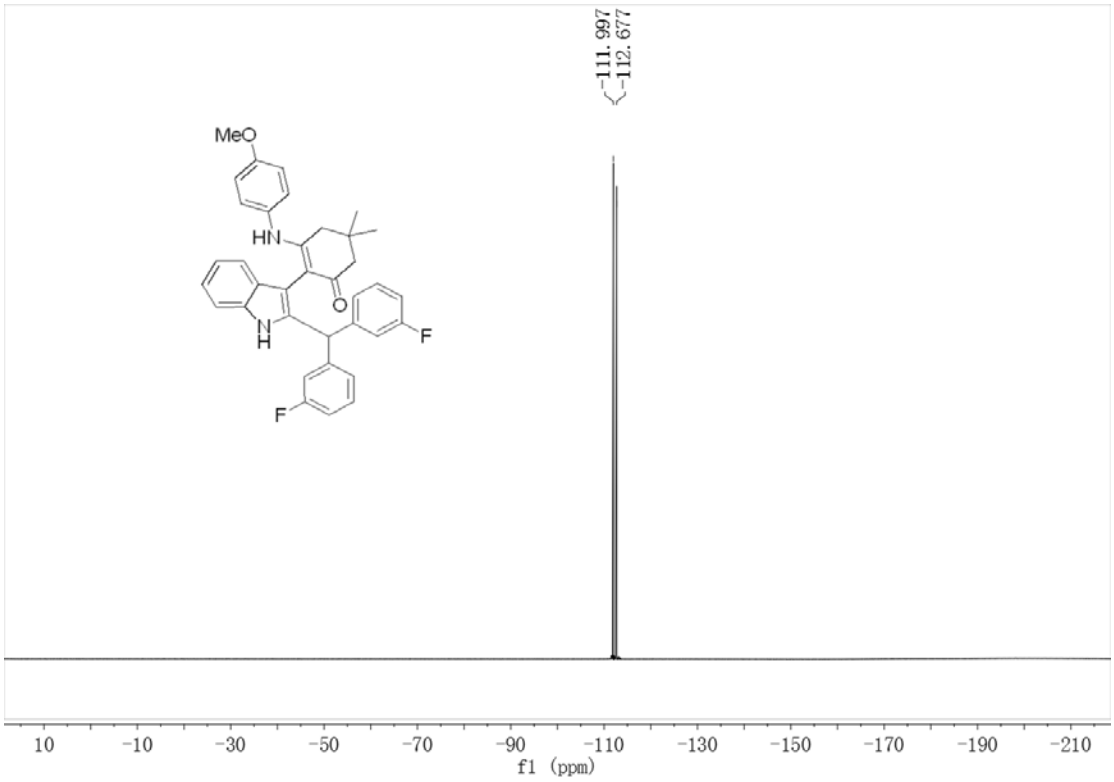
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O
N
H
F
F
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-130
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-170
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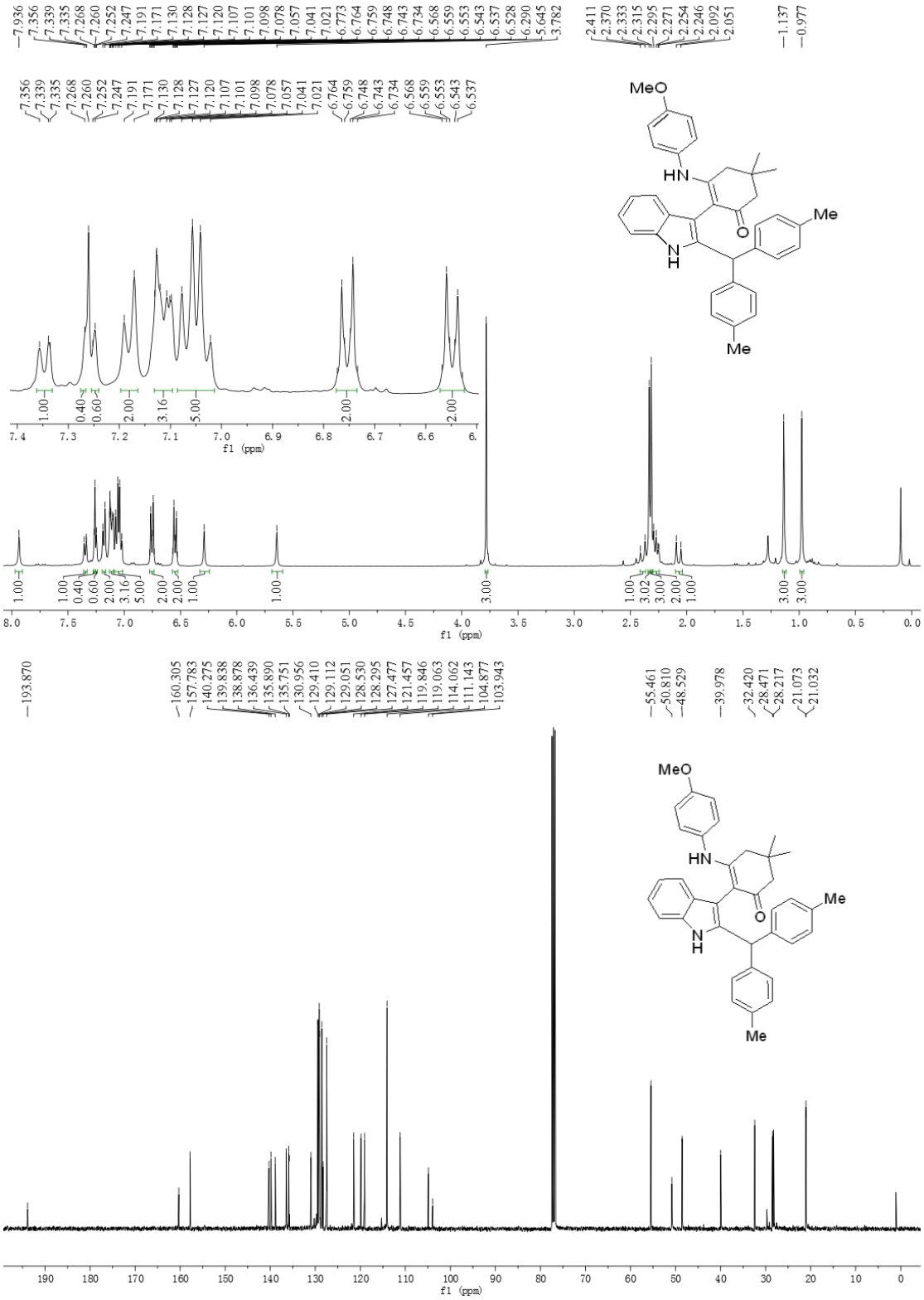
-210
f1 (ppm)

4da



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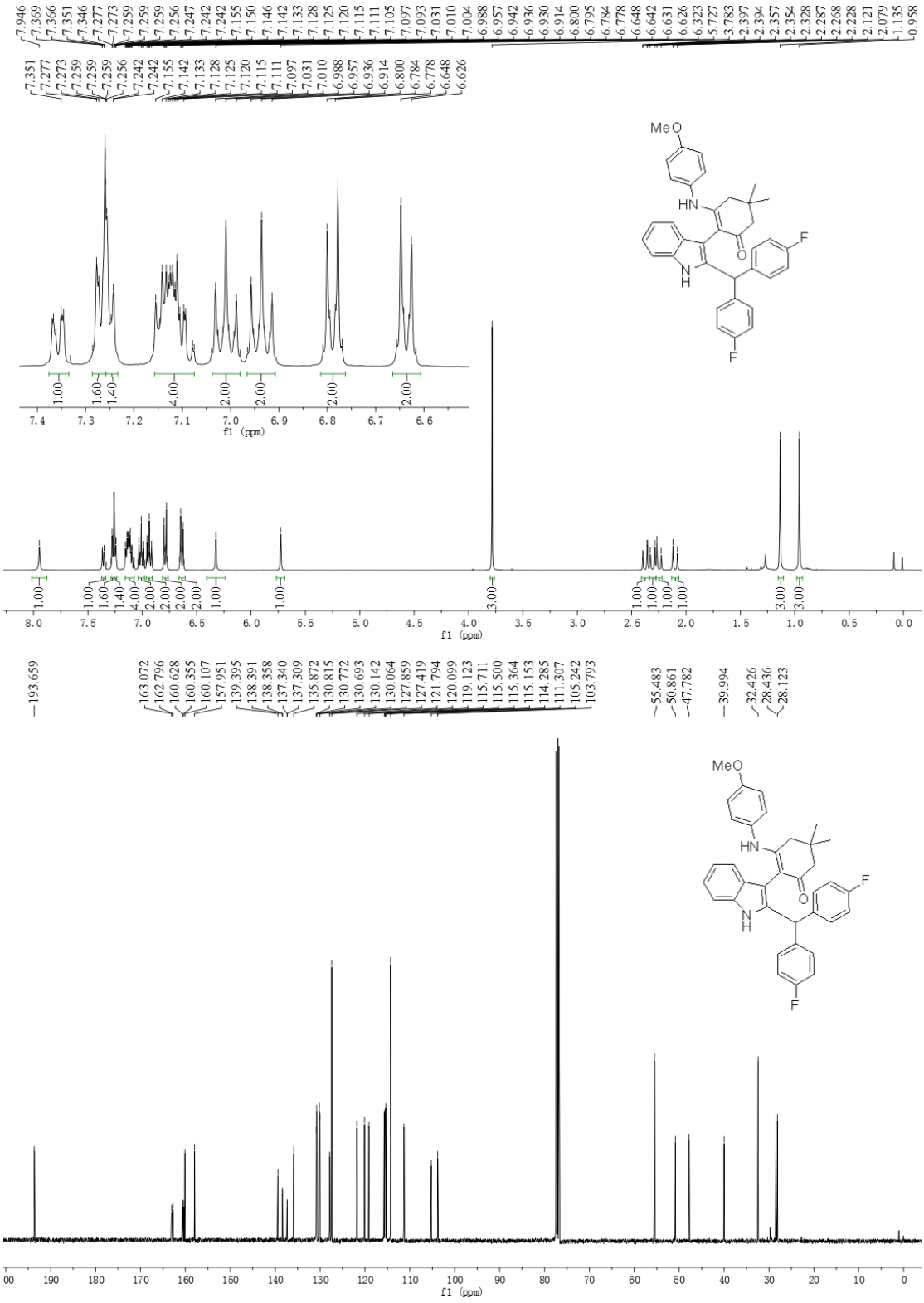

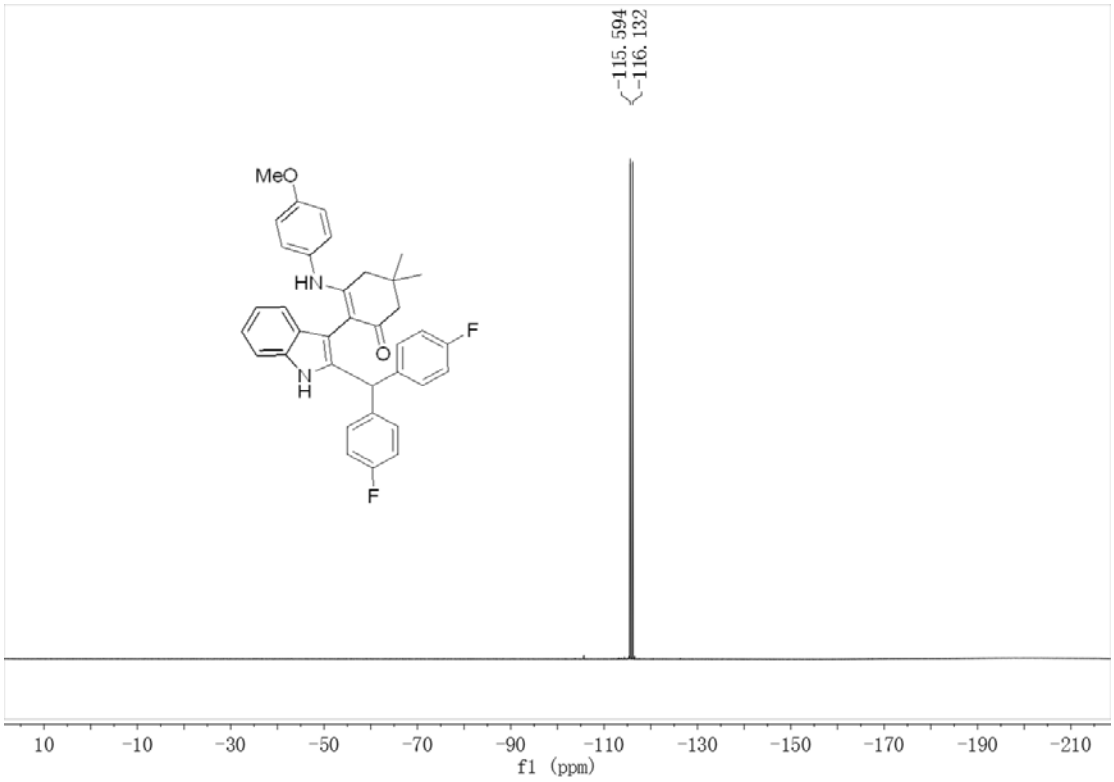
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H
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-70
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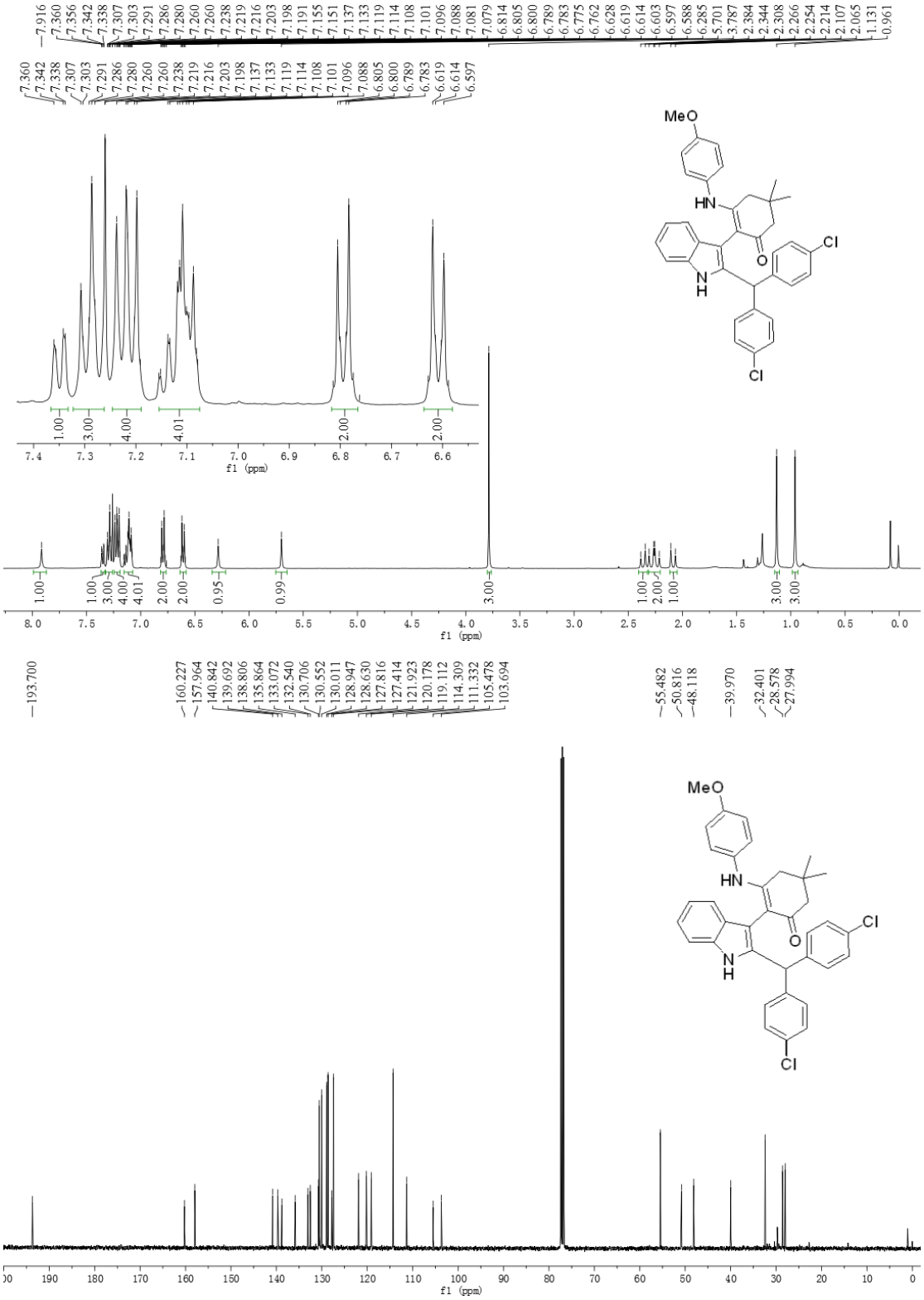
-190
-210
f1 (ppm)

4fa



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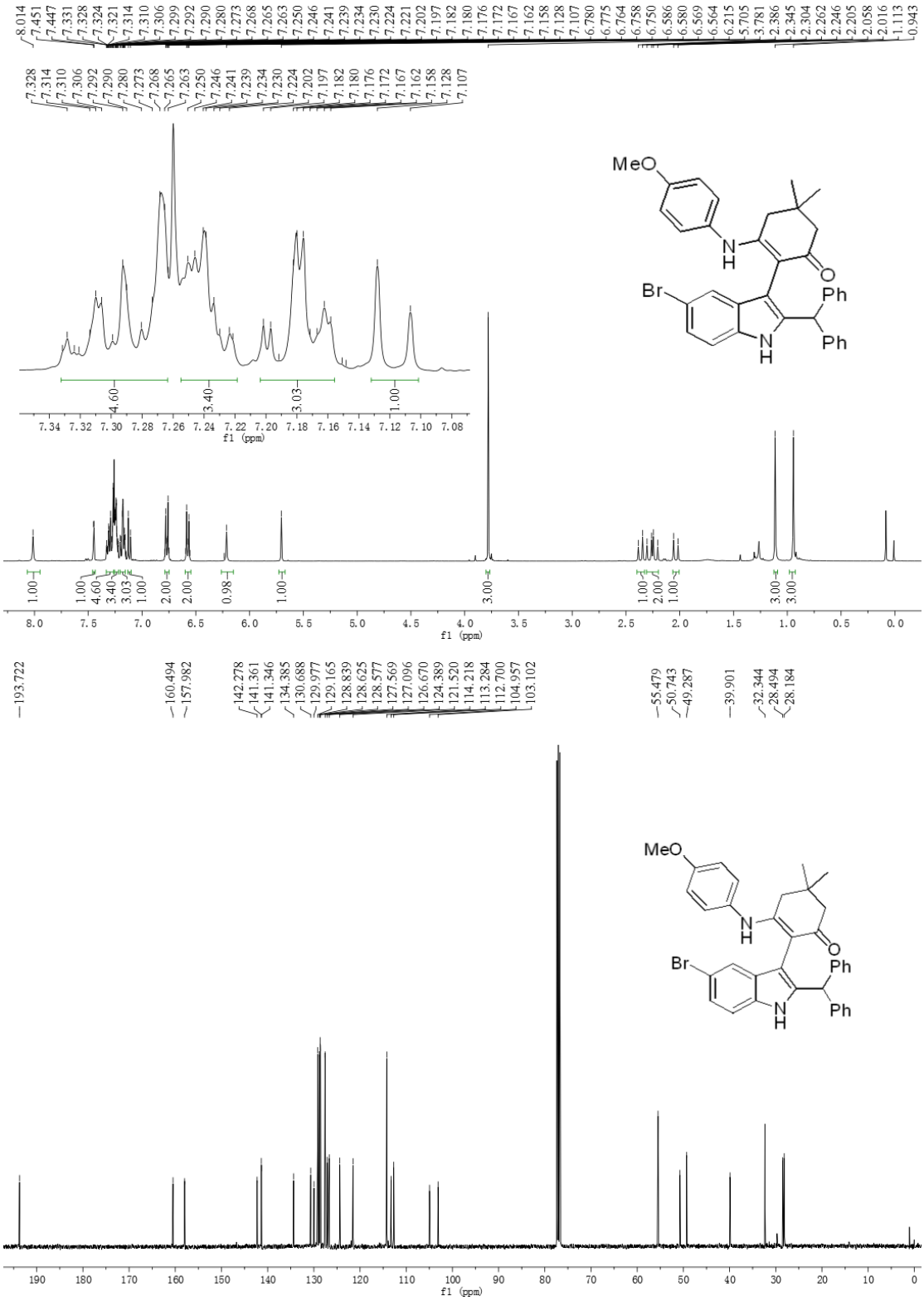

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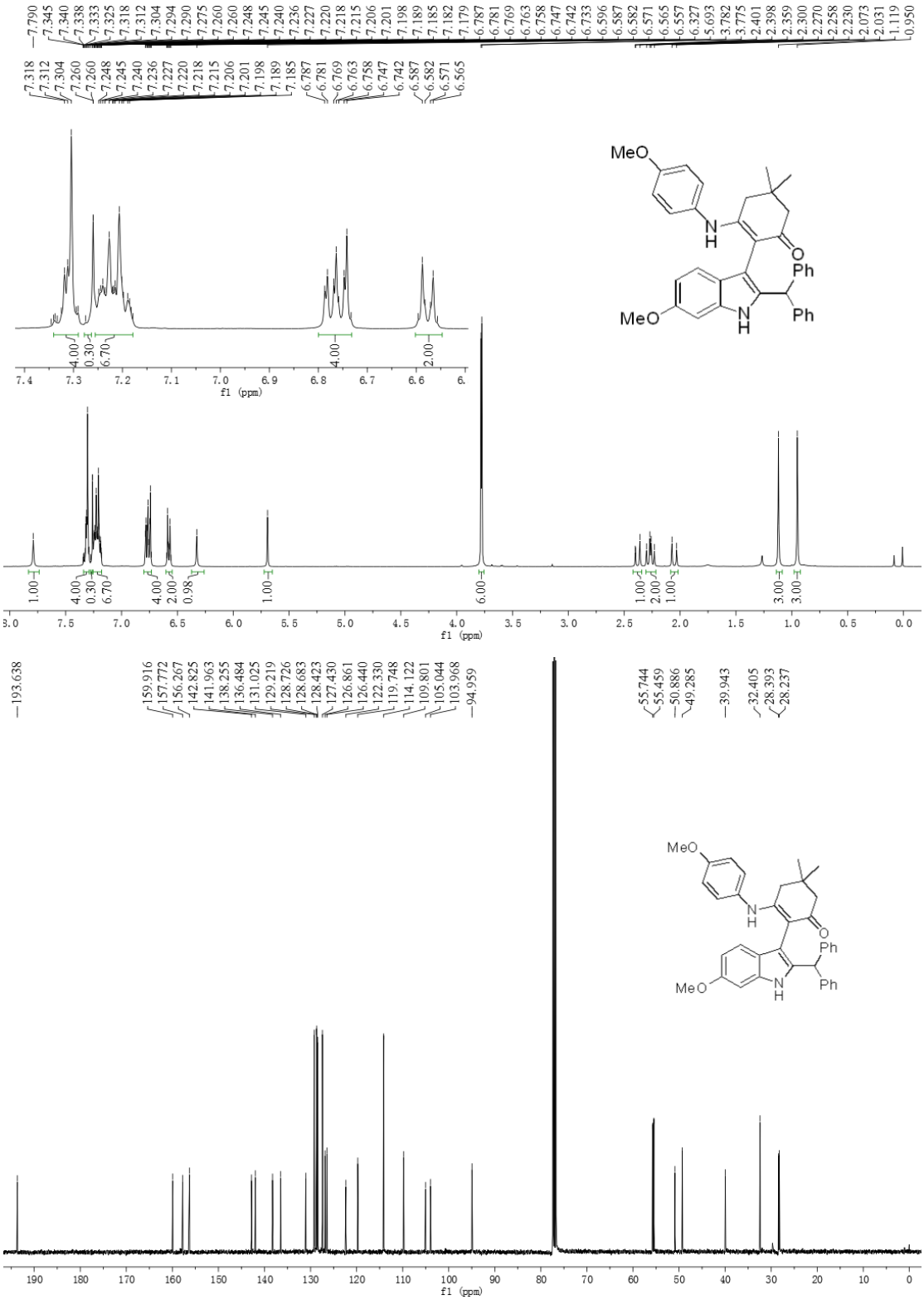

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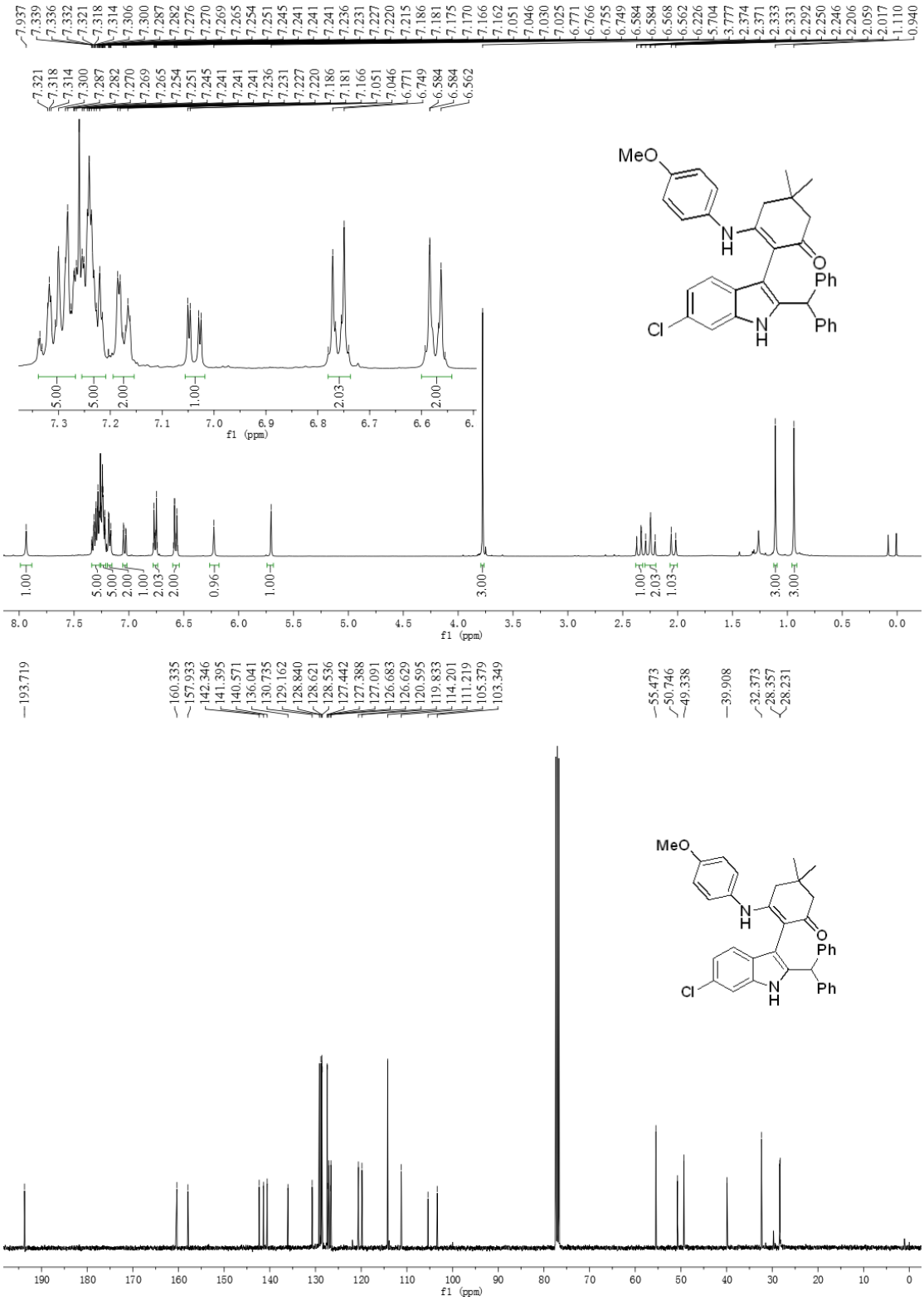

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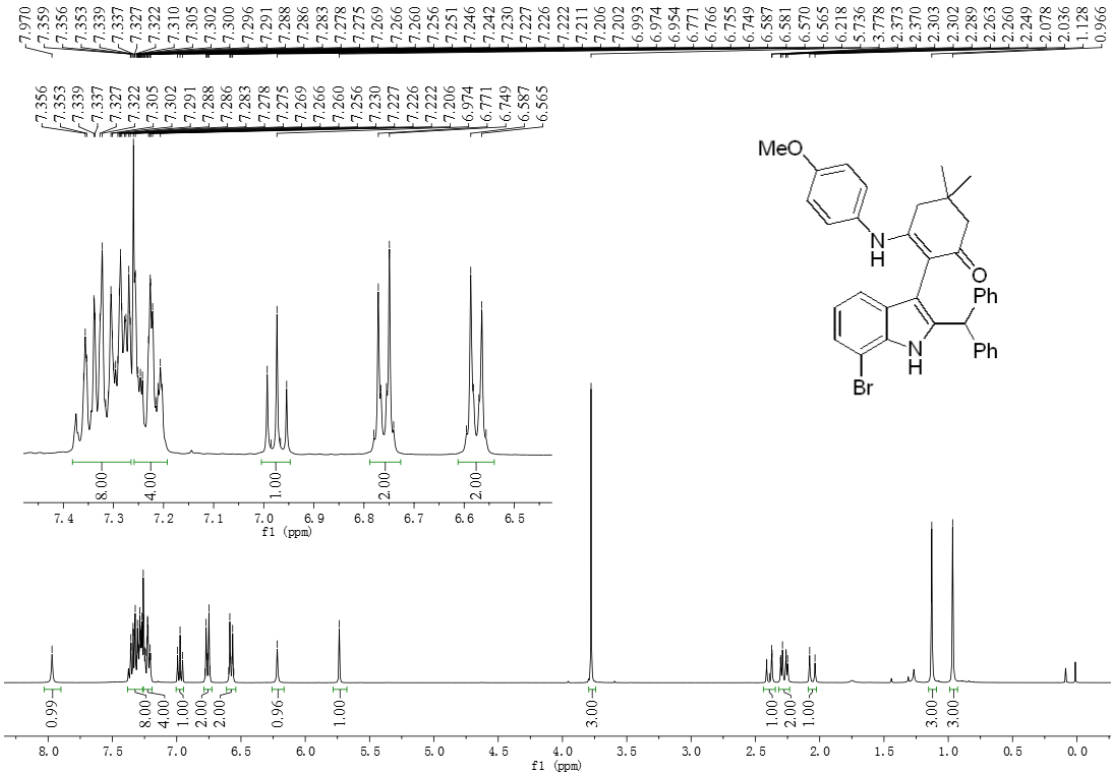

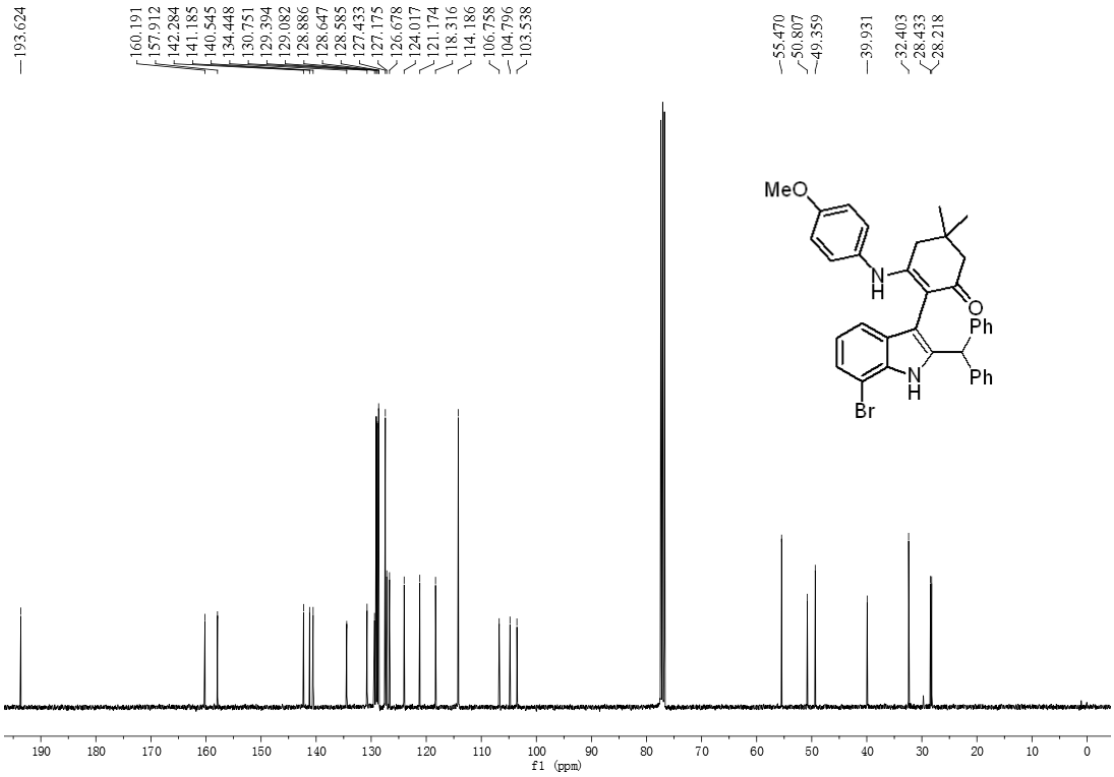

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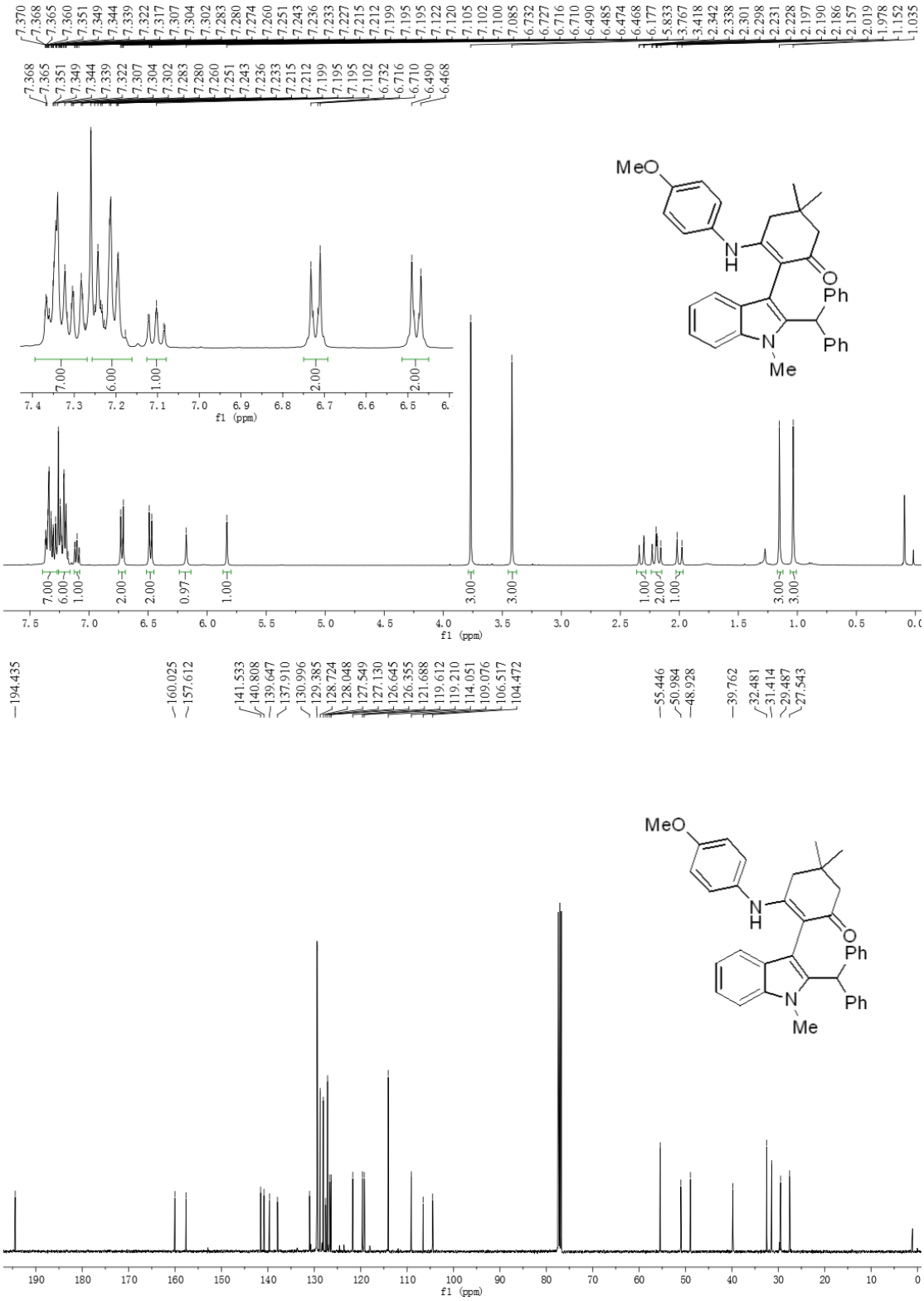

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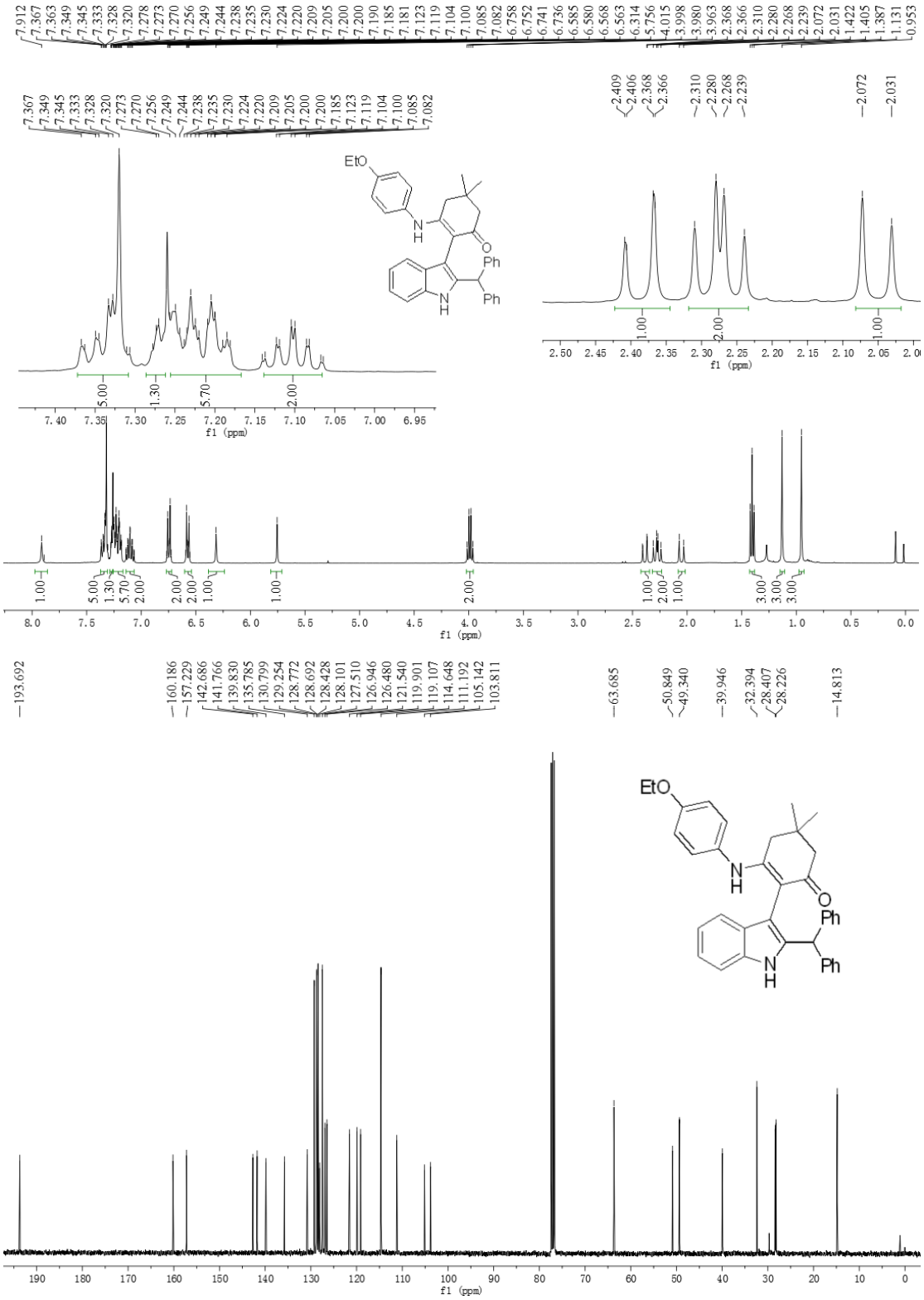

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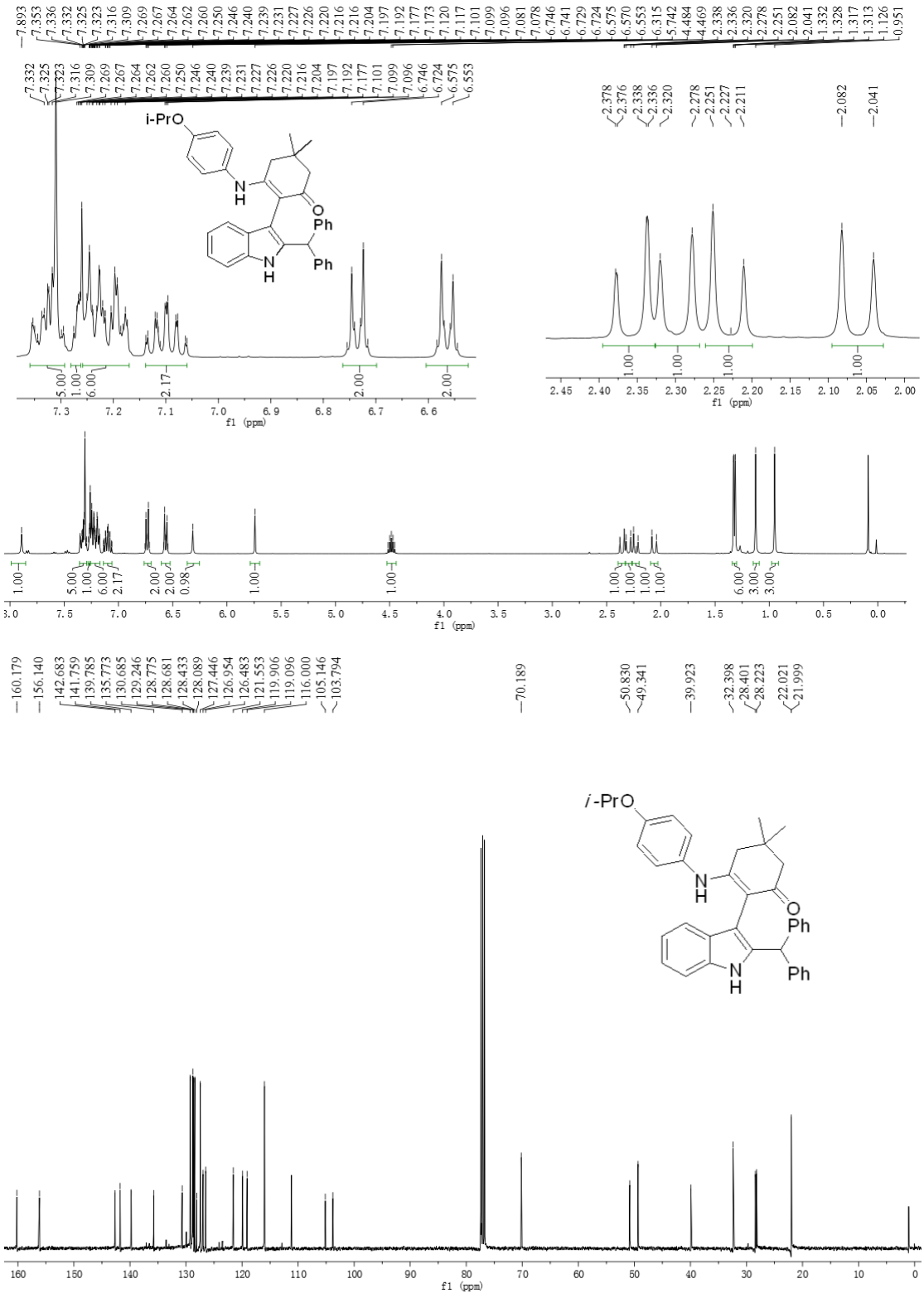

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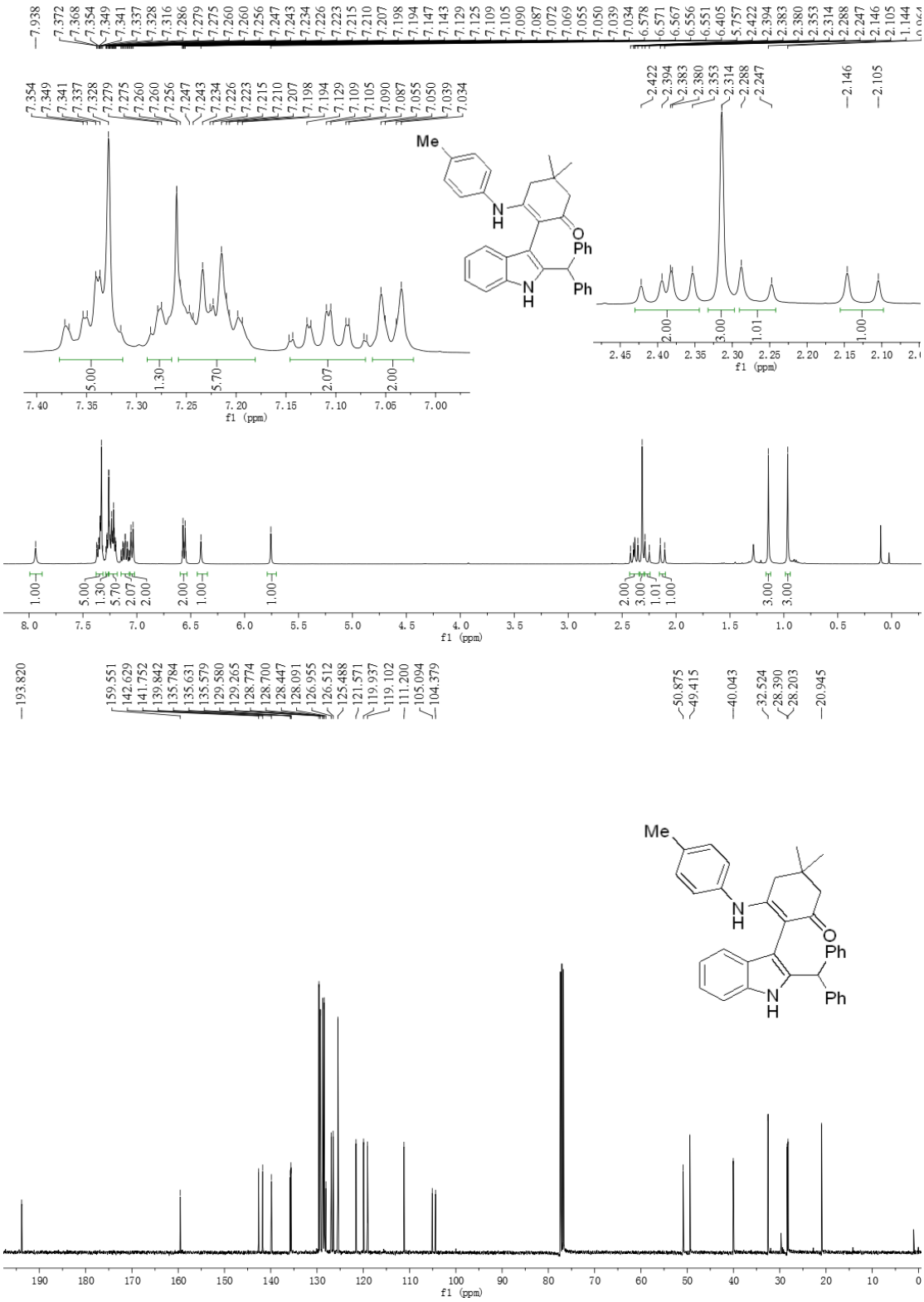

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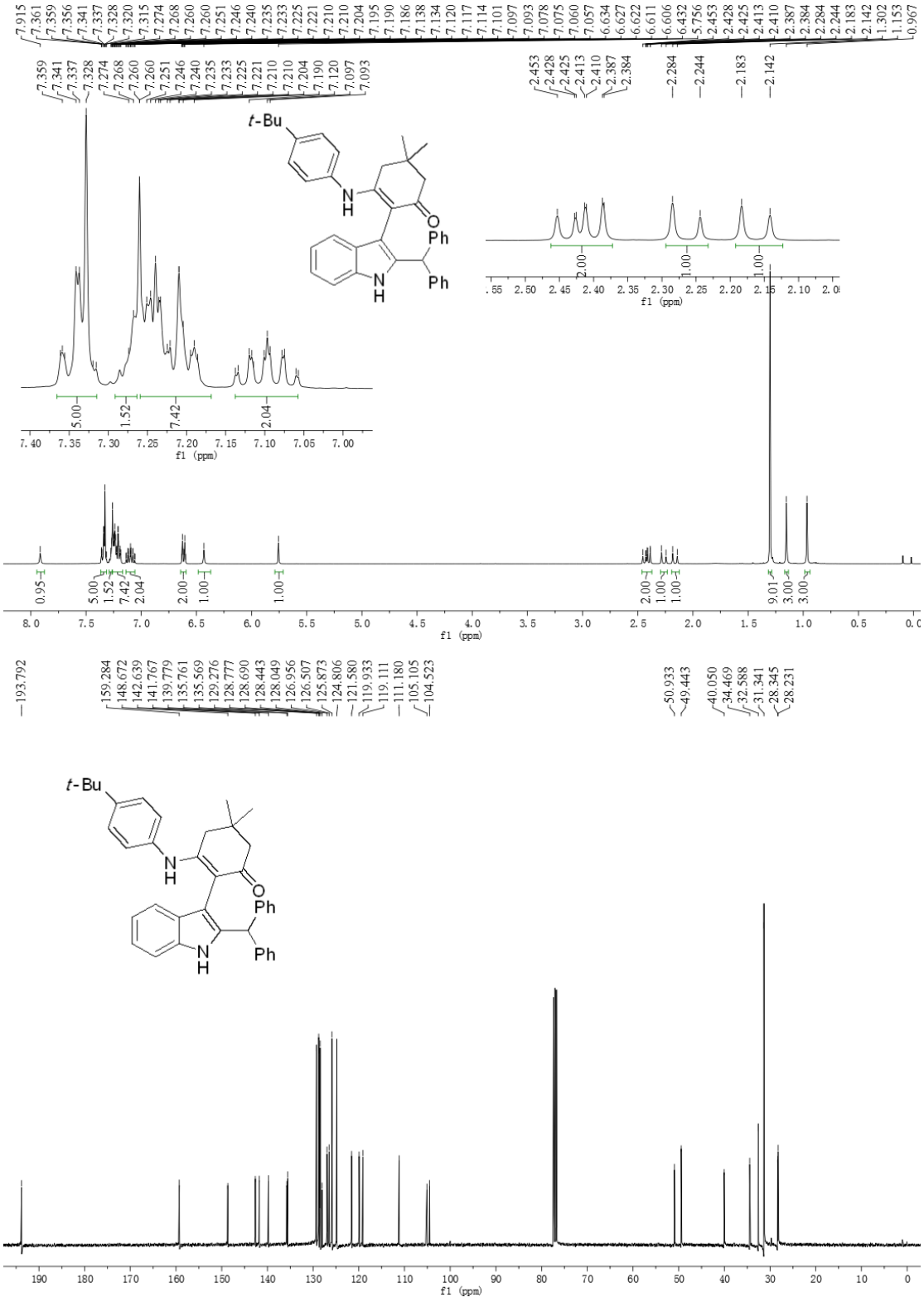

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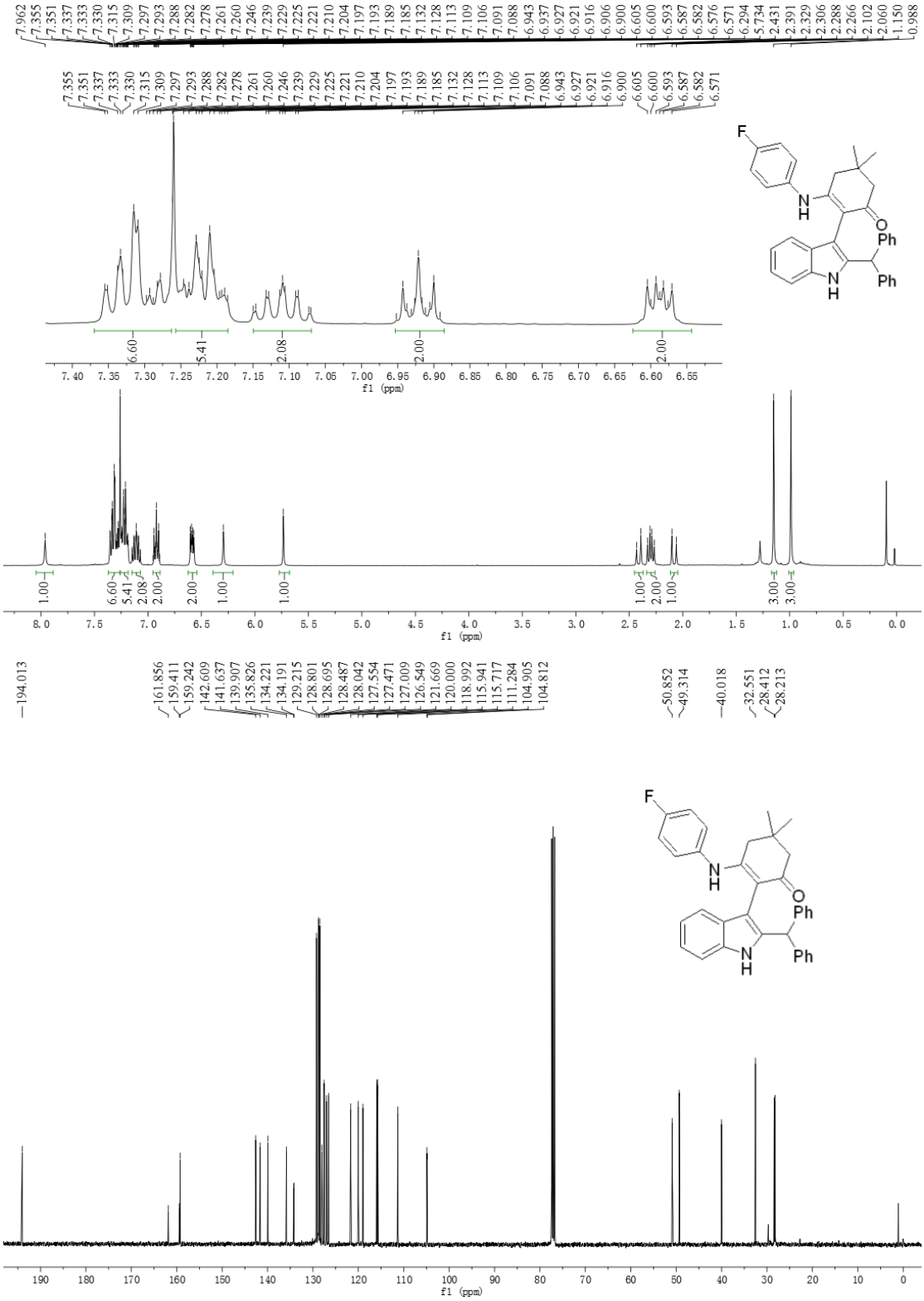

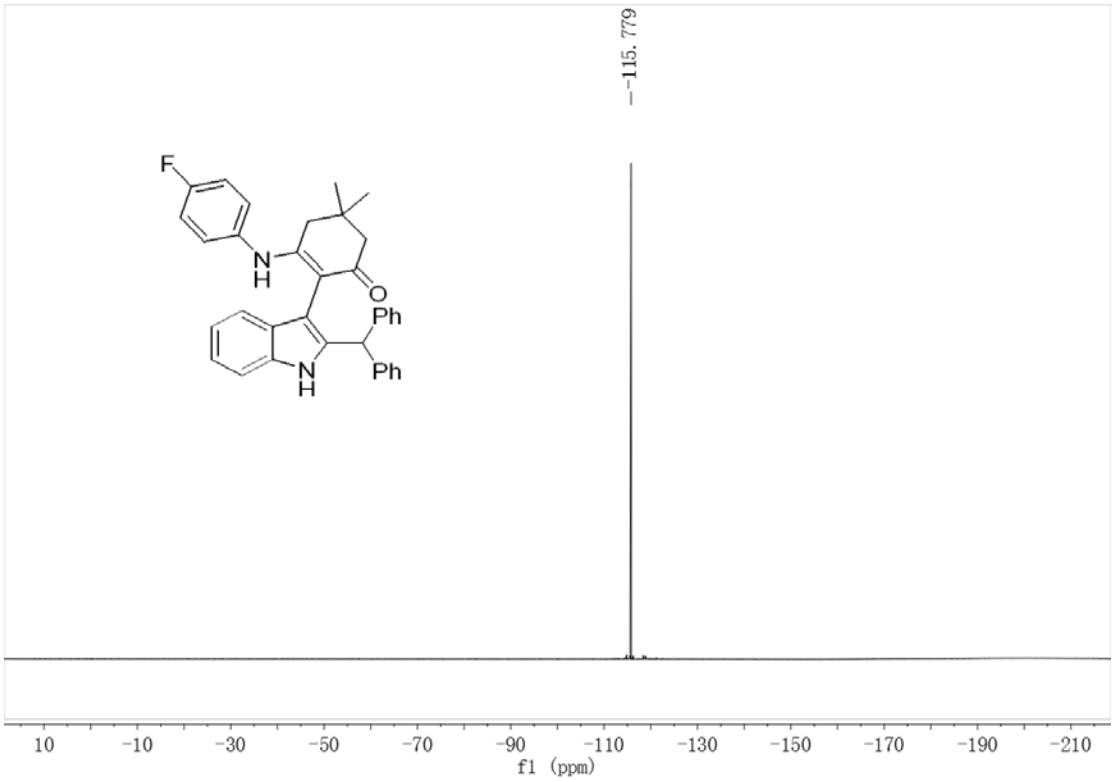
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Ph
Ph
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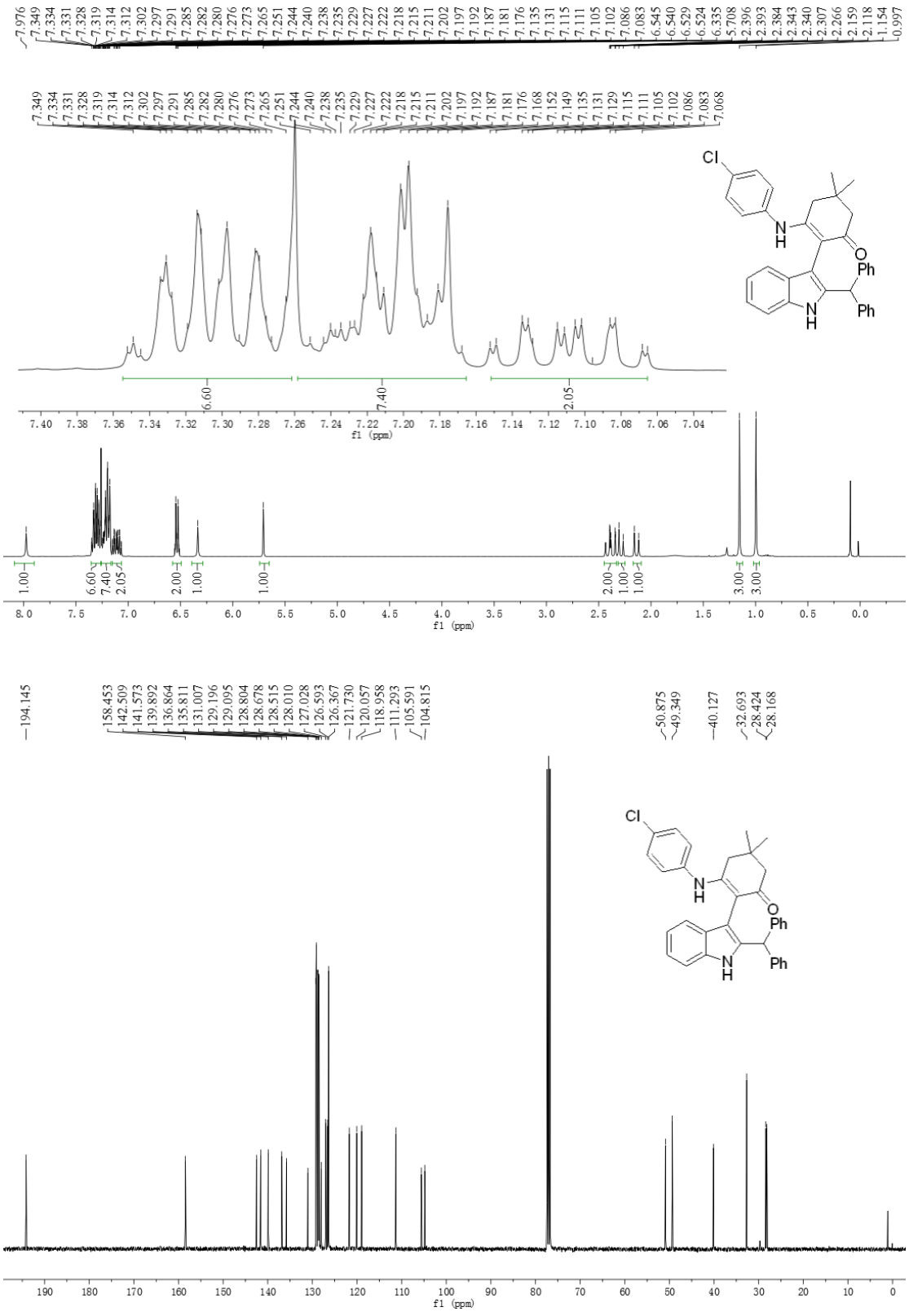
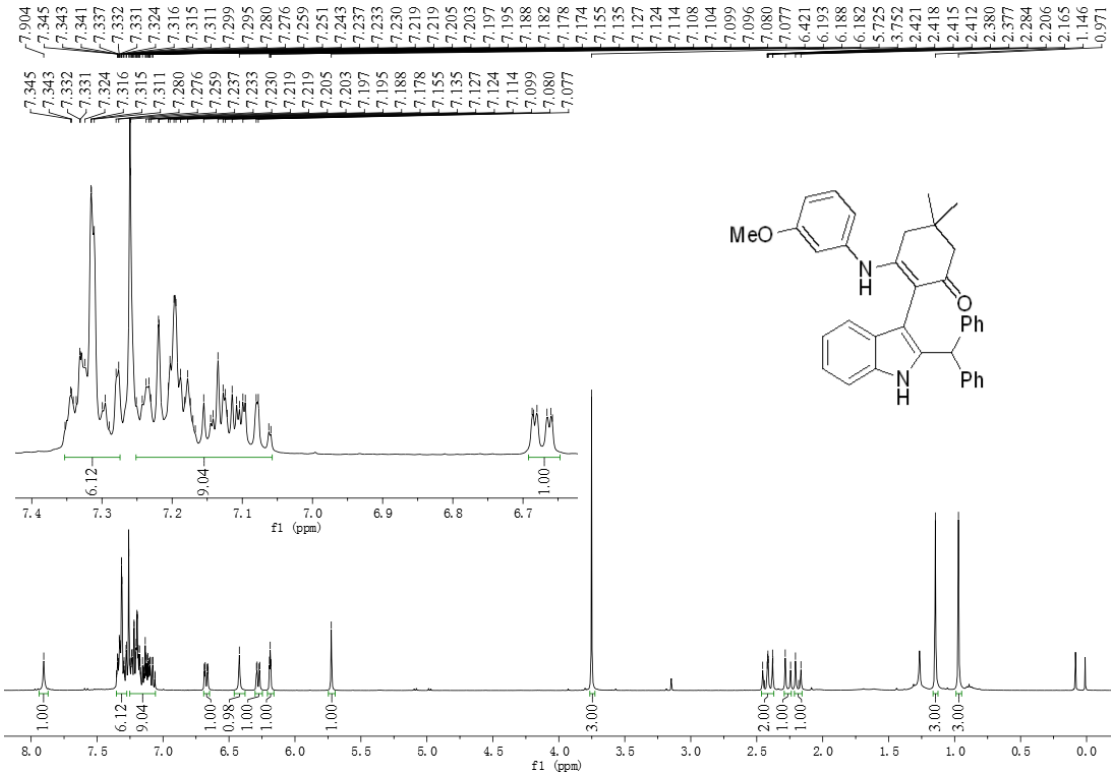
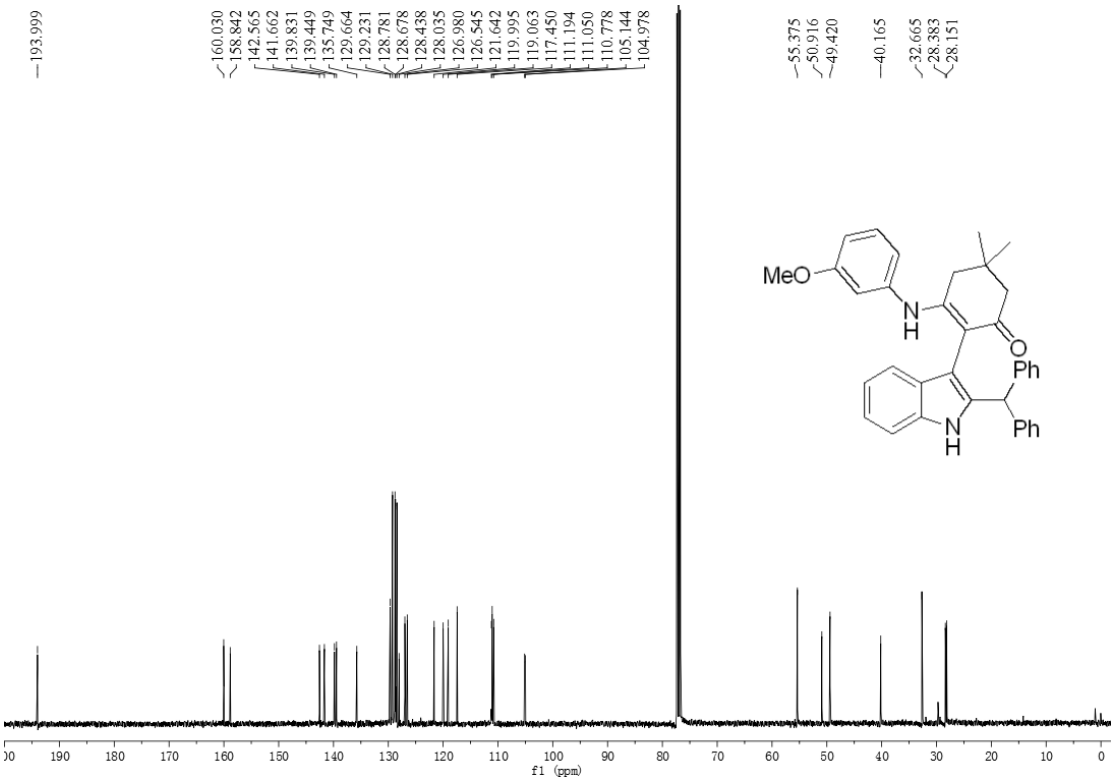
f1 (ppm)

4ag



4ah





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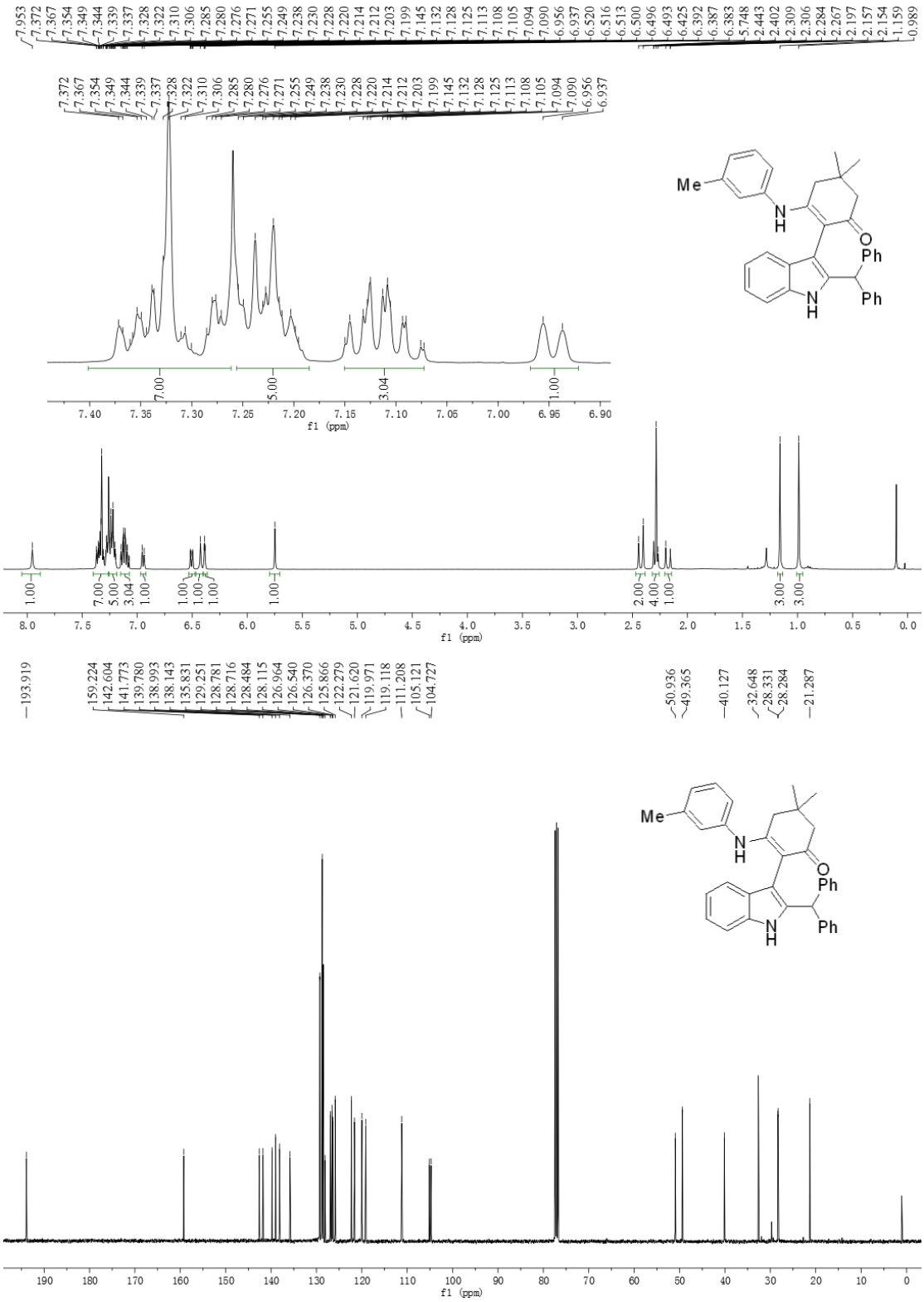
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Ph
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H
Ph
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3.04
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1.00
2.00
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3.00
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f1 (ppm)
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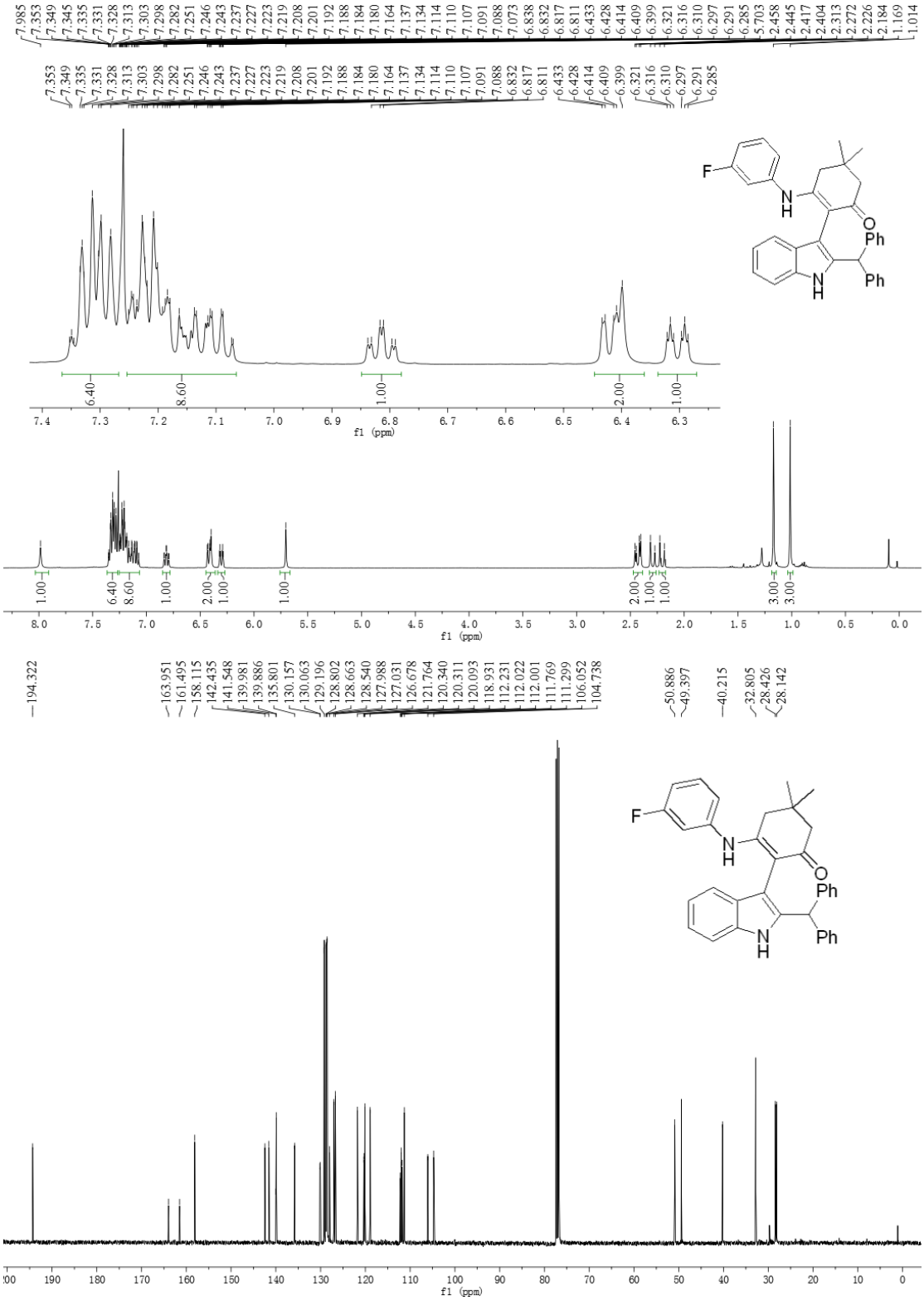
Ph
f1 (ppm)

4aj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3.00
f1 (ppm)
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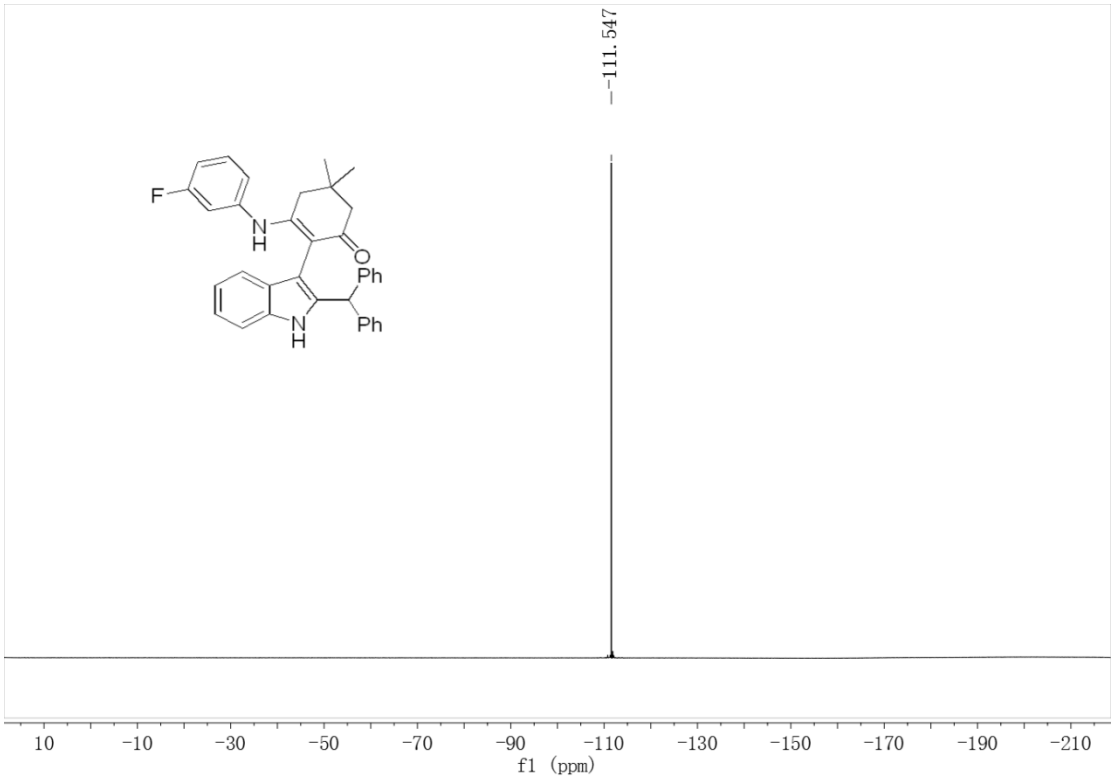
N
H
f1 (ppm)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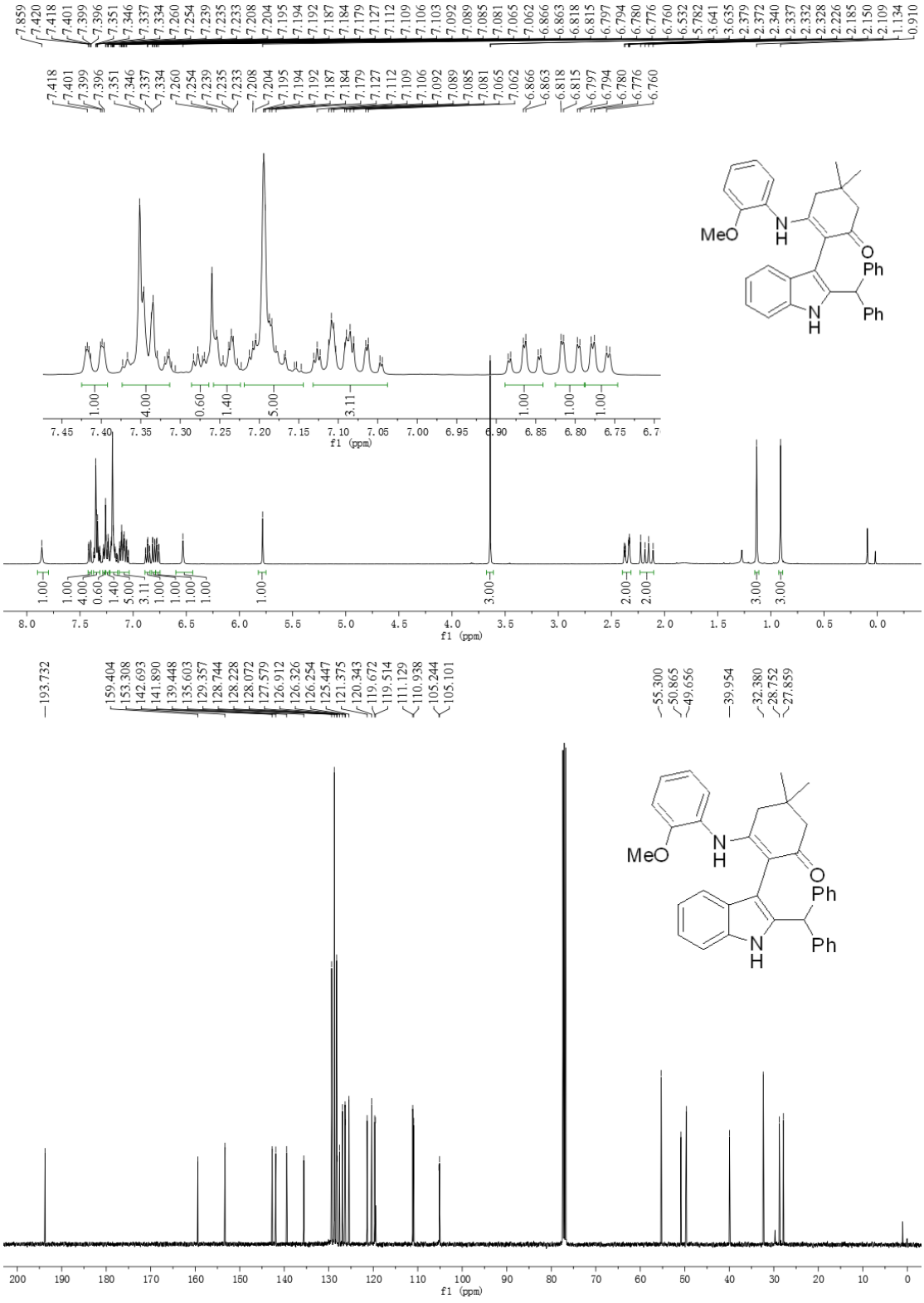
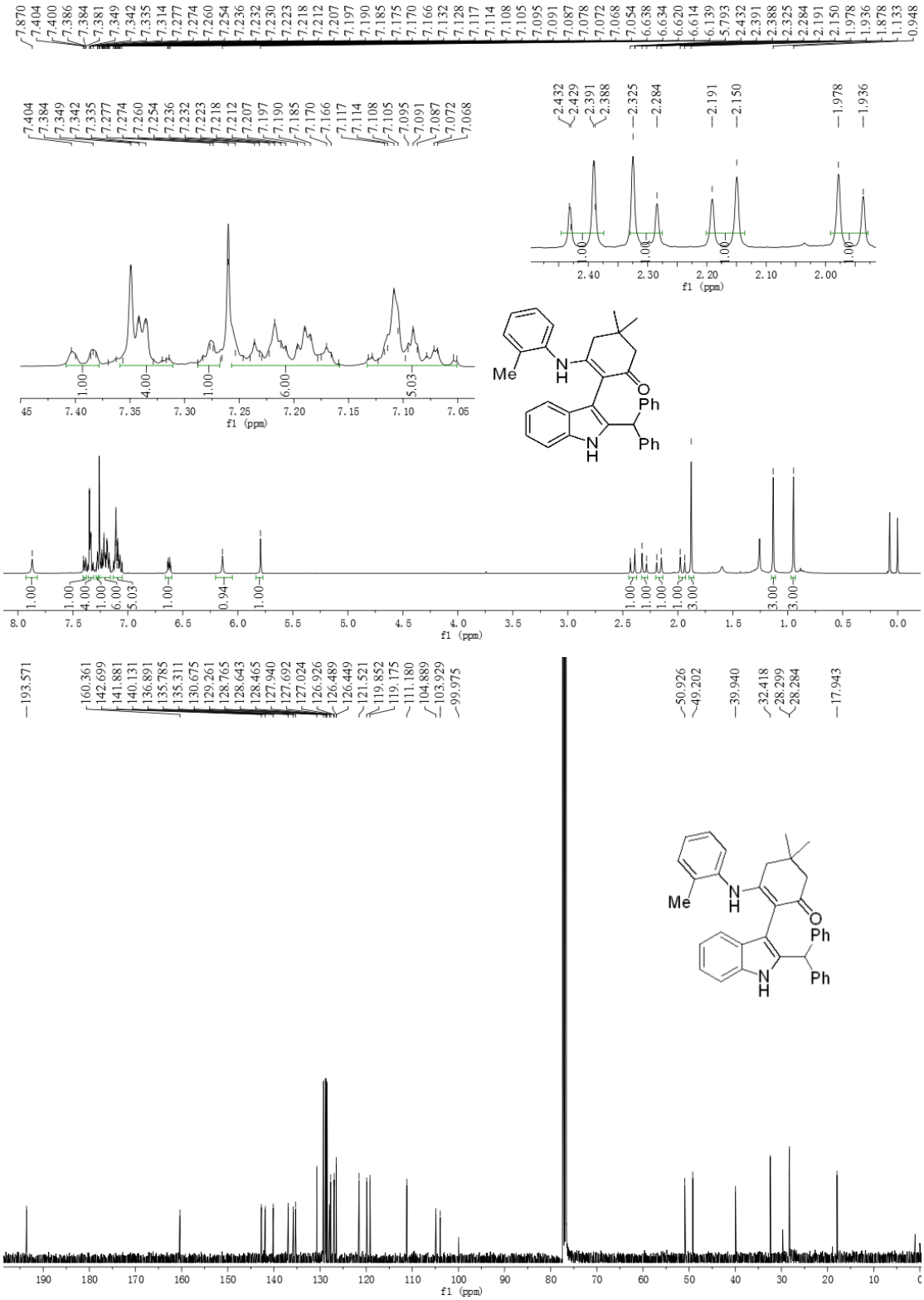
f1 (ppm)

4ak



4al



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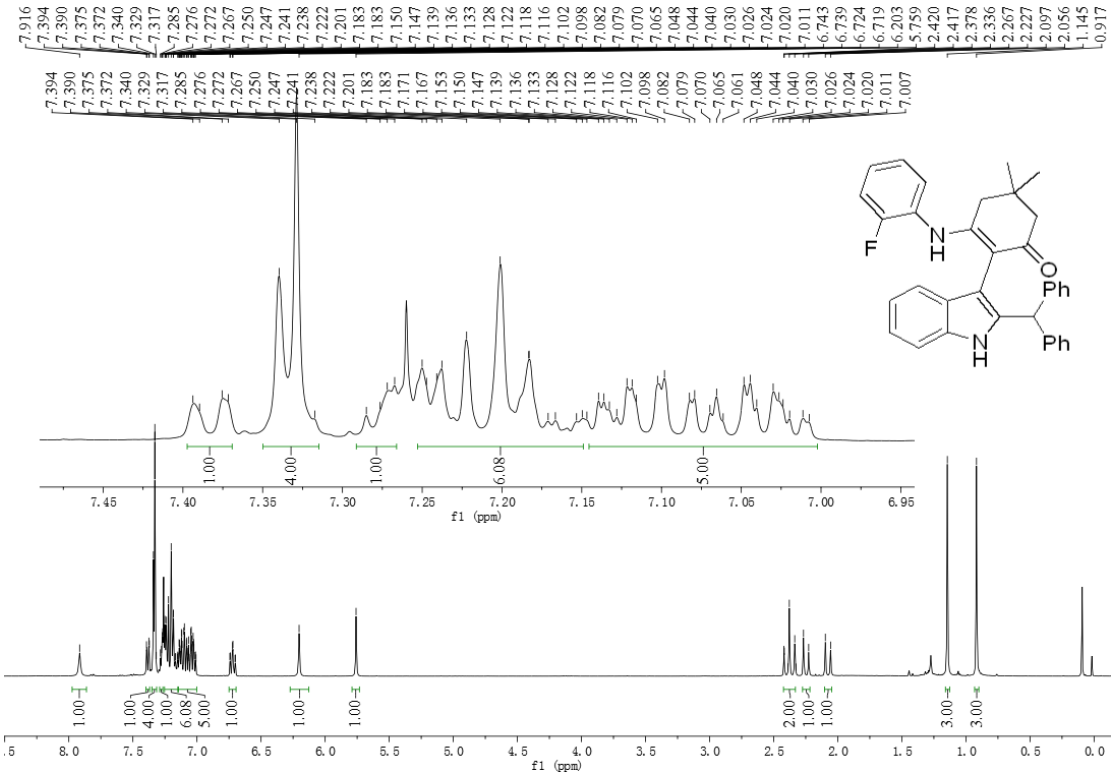
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7.238
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7.118
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2.417
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2.267
2.227
2.097
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H
O
Ph
Ph
N
H
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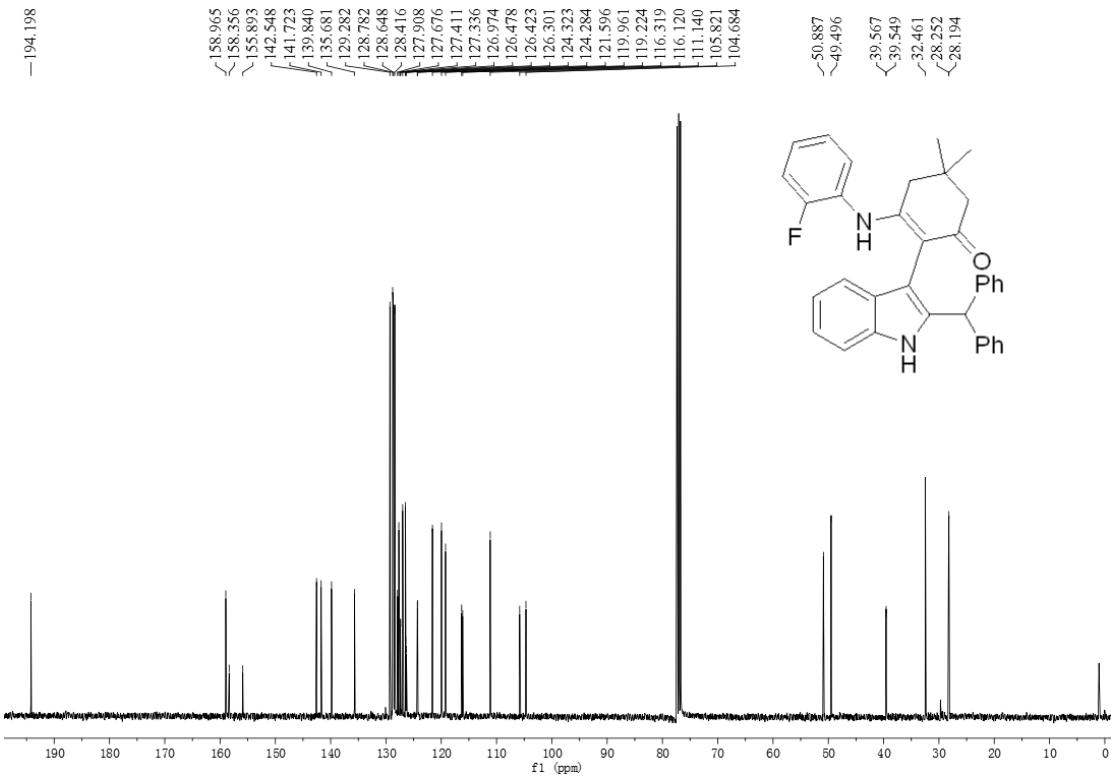
5.00
f1 (ppm)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127.676
127.411
127.336
126.974
126.478
126.423
126.301
124.323
124.284
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119.961
119.224
116.319
116.120
111.140
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104.684
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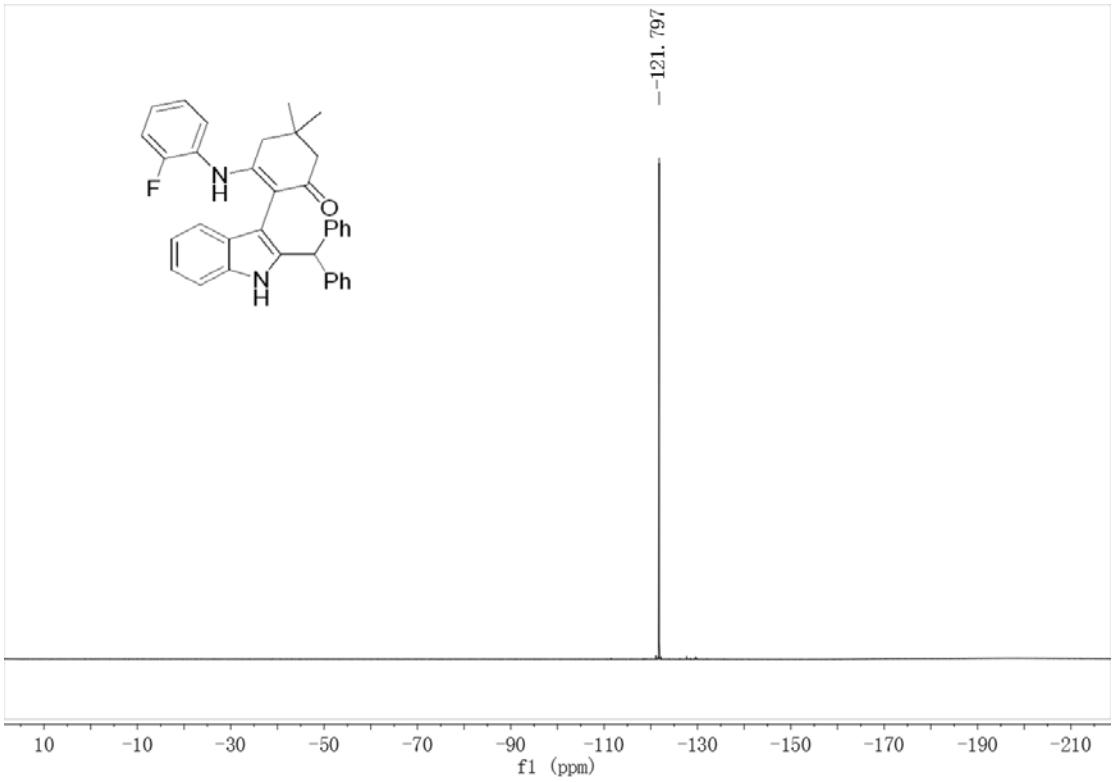
H
O
Ph
Ph
N
H
f1 (ppm)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Ph
Ph
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H
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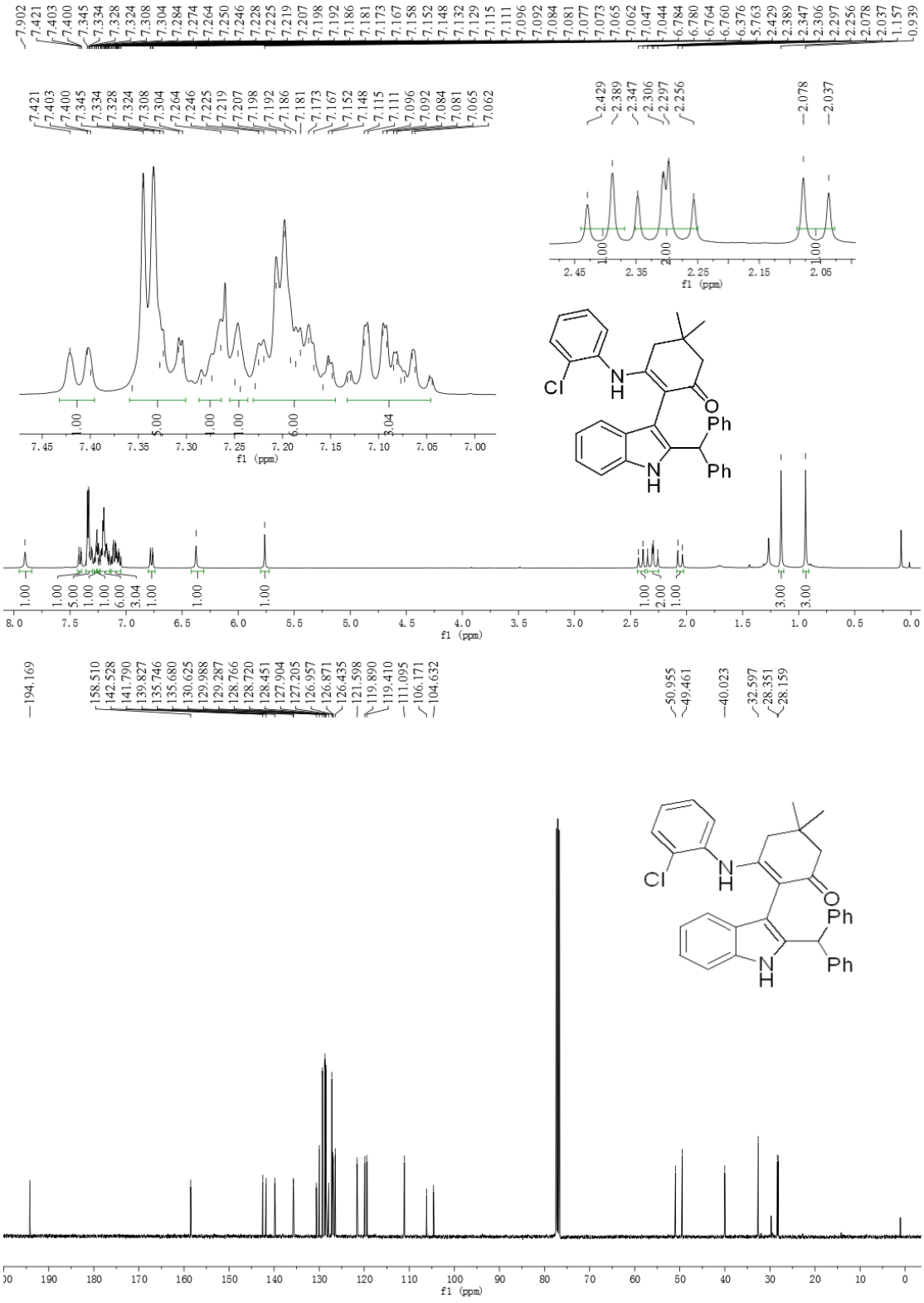
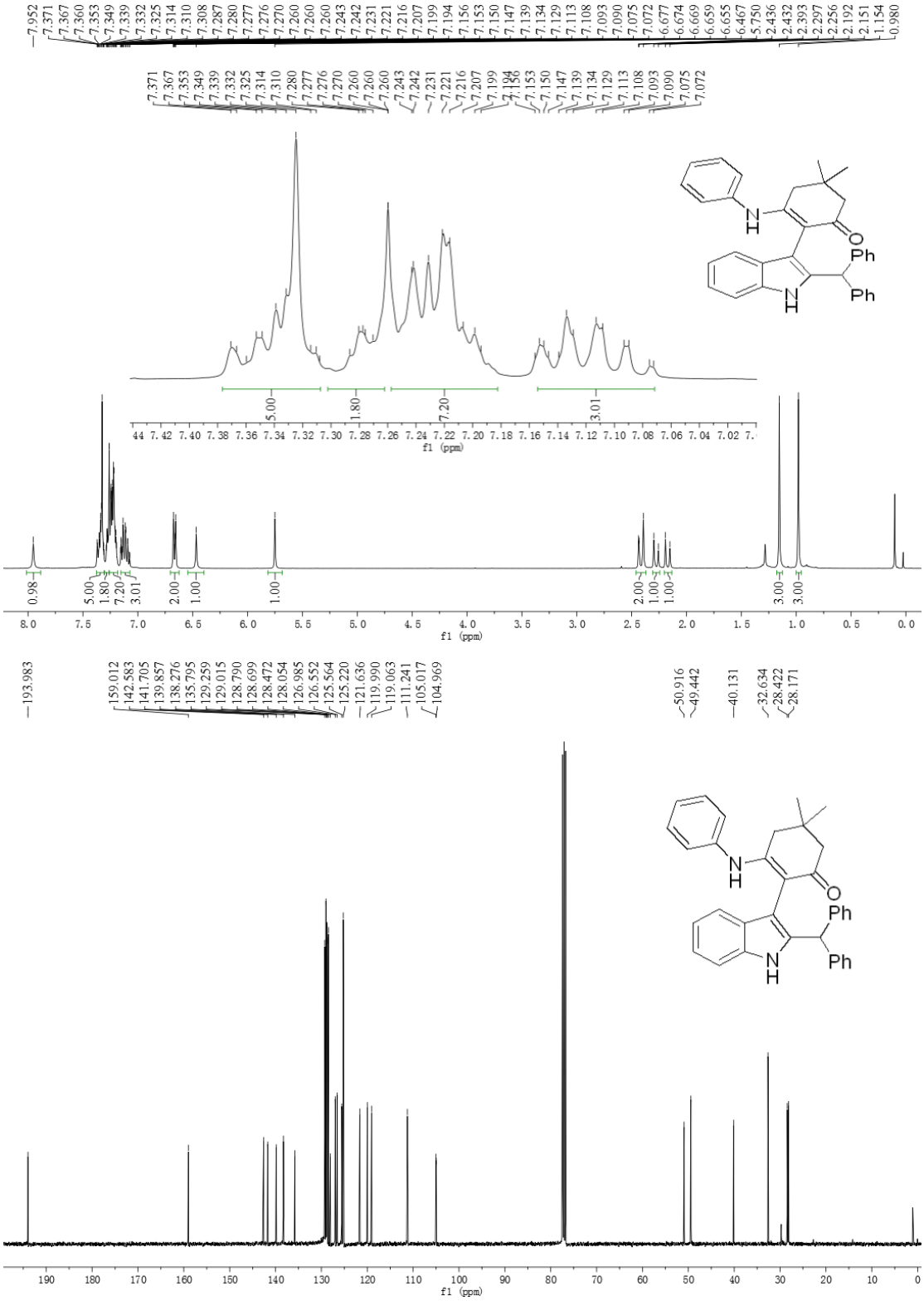
-170
-190
-210
f1 (ppm)

4an

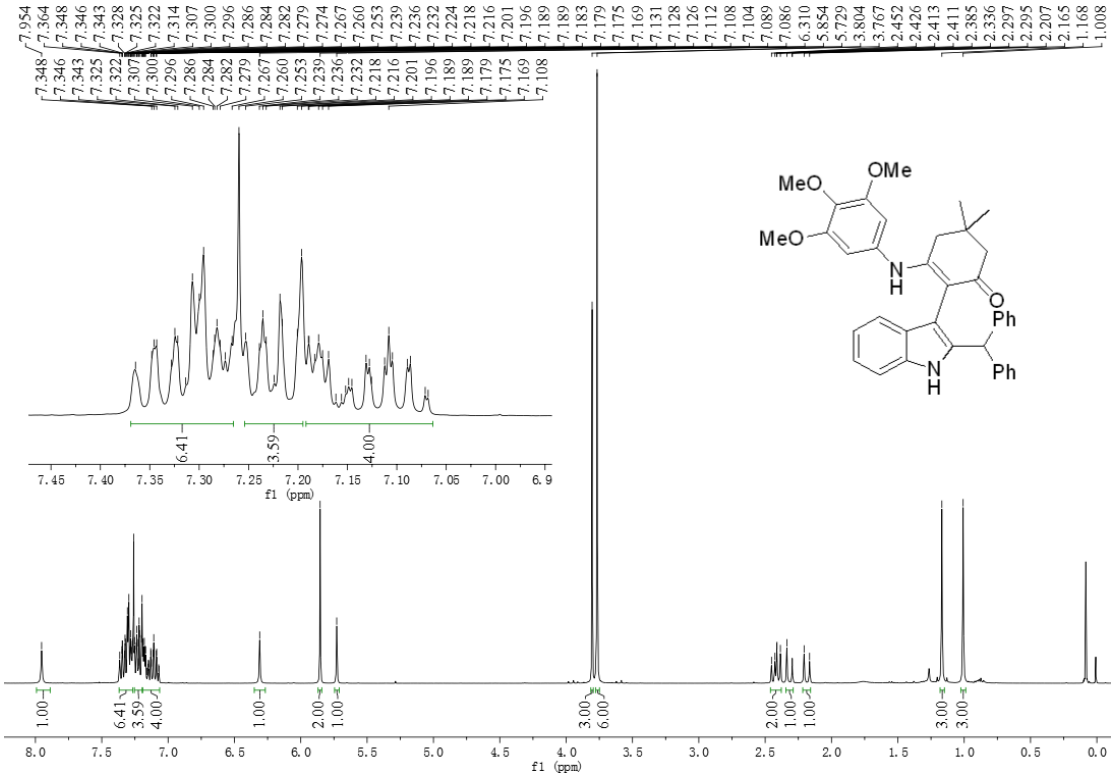

7.902 7.421 7.403 7.400 7.345 7.334 7.328 7.324 7.308 7.304 7.284 7.274 7.264 7.250 7.246 7.228 7.225 7.219 7.207 7.198 7.192 7.186 7.181 7.173 7.167 7.158 7.152 7.148 7.132 7.129 7.115 7.111 7.096 7.092 7.084 7.081 7.077 7.073 7.065 7.062 7.047 7.044 6.784 6.780 6.764 6.760 6.376 5.763 2.429 2.389 2.347 2.306 2.297 2.256 2.078 2.037 1.157 0.939
1.00 5.00 1.00 1.00 6.00 3.04 1.00 1.00 1.00 1.00 2.00 1.00 3.00 3.00
f1 (ppm)
Cl N H O Ph Ph N H

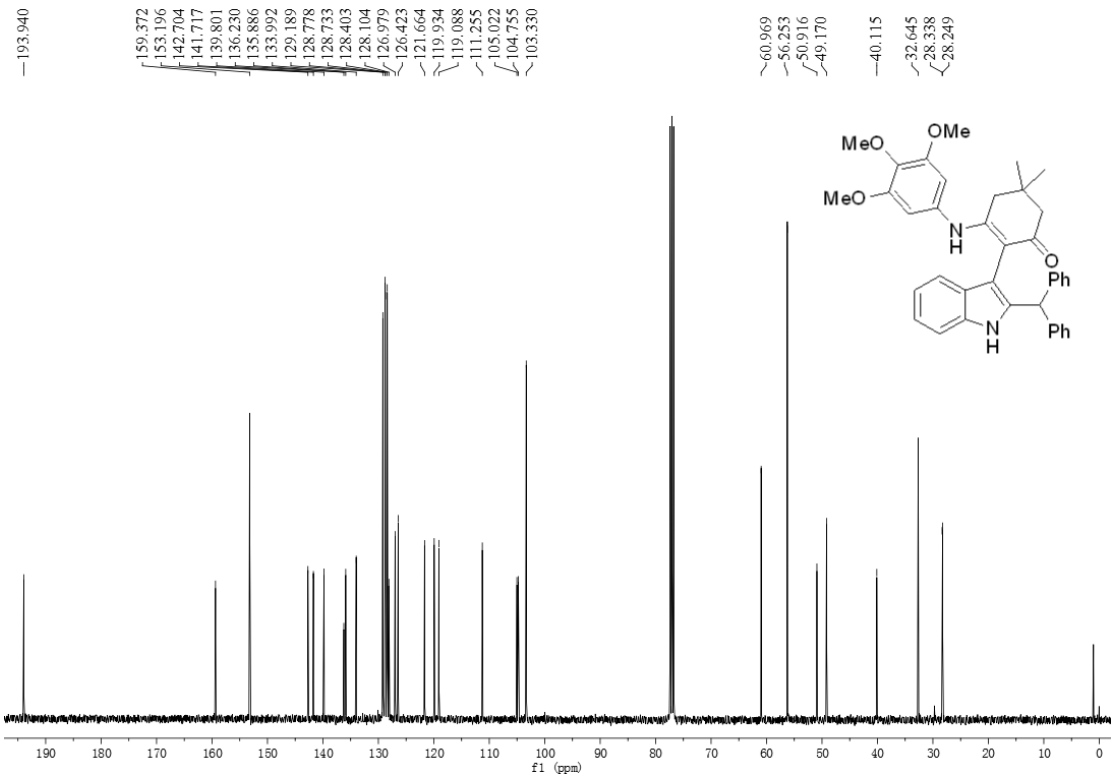
194.169 158.510 142.528 141.790 139.827 135.746 135.680 130.625 129.988 129.287 128.766 128.720 128.451 127.904 127.205 126.957 126.871 126.435 121.598 119.890 119.410 111.095 106.171 104.632 50.955 49.461 40.023 32.597 28.351 28.159
f1 (ppm)
Cl N H O Ph Ph N H

4ao

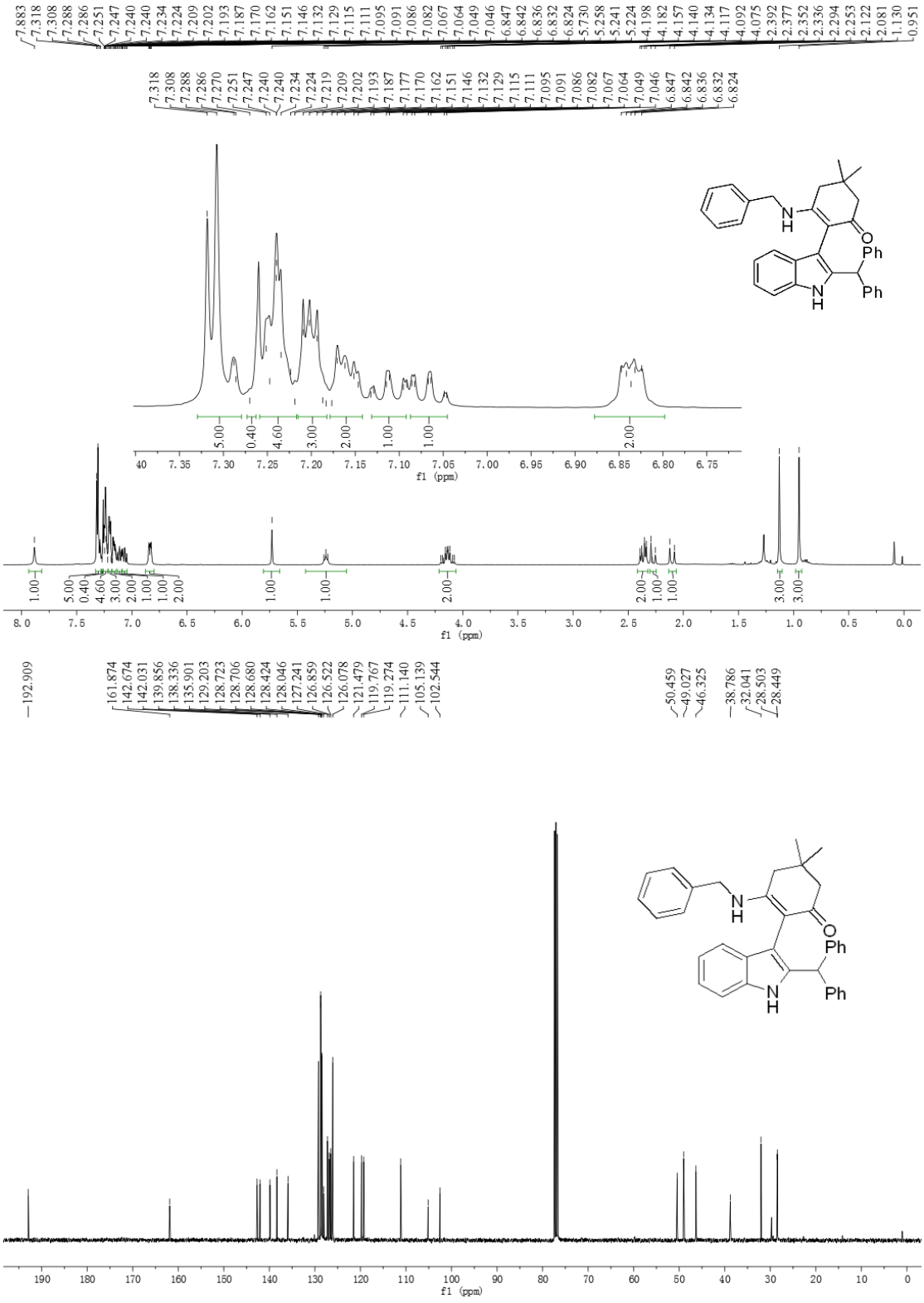


4ap

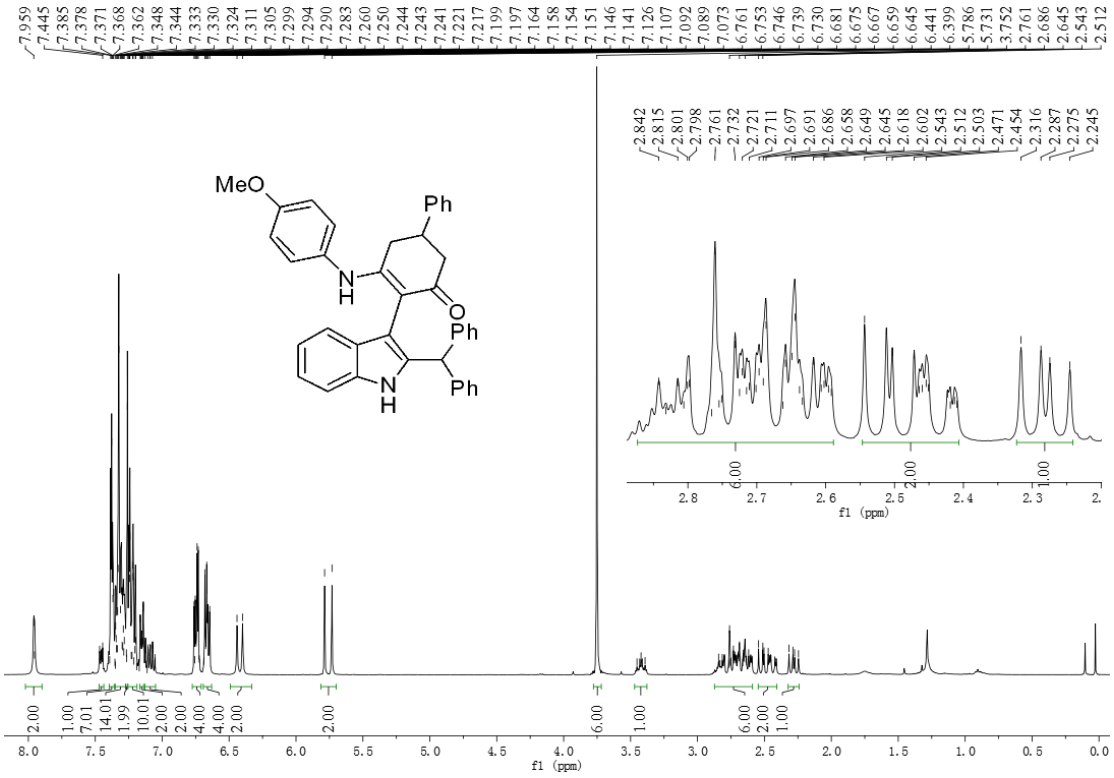


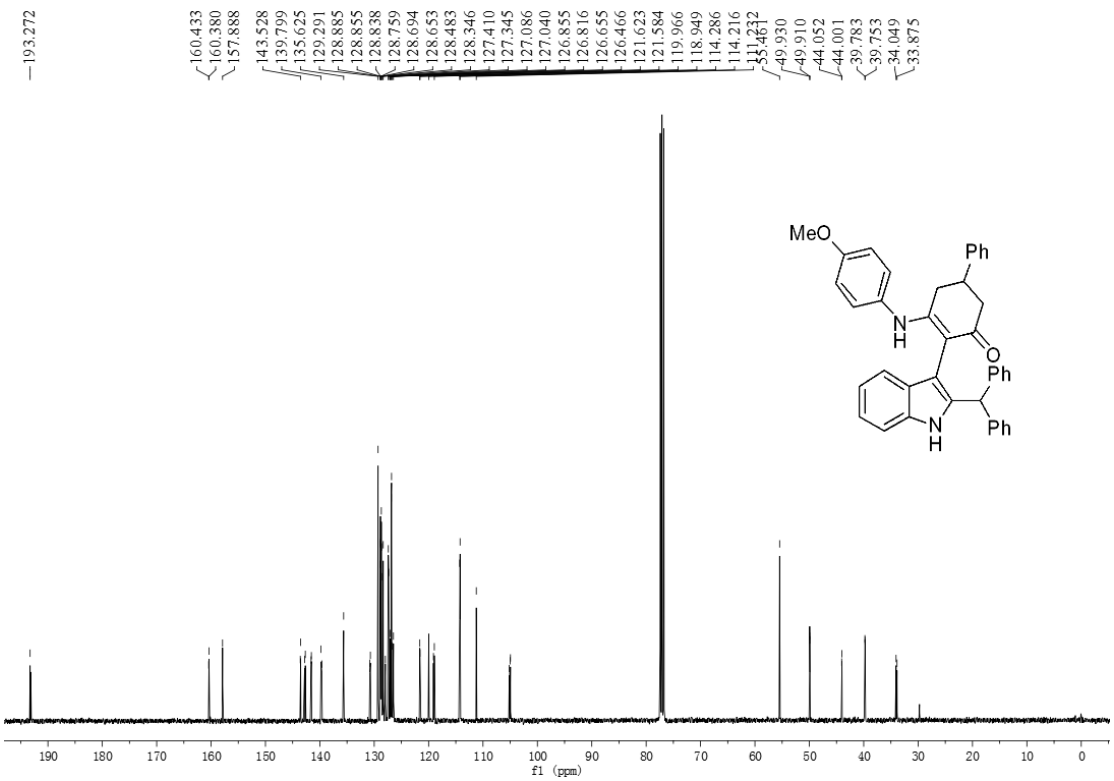


4aq

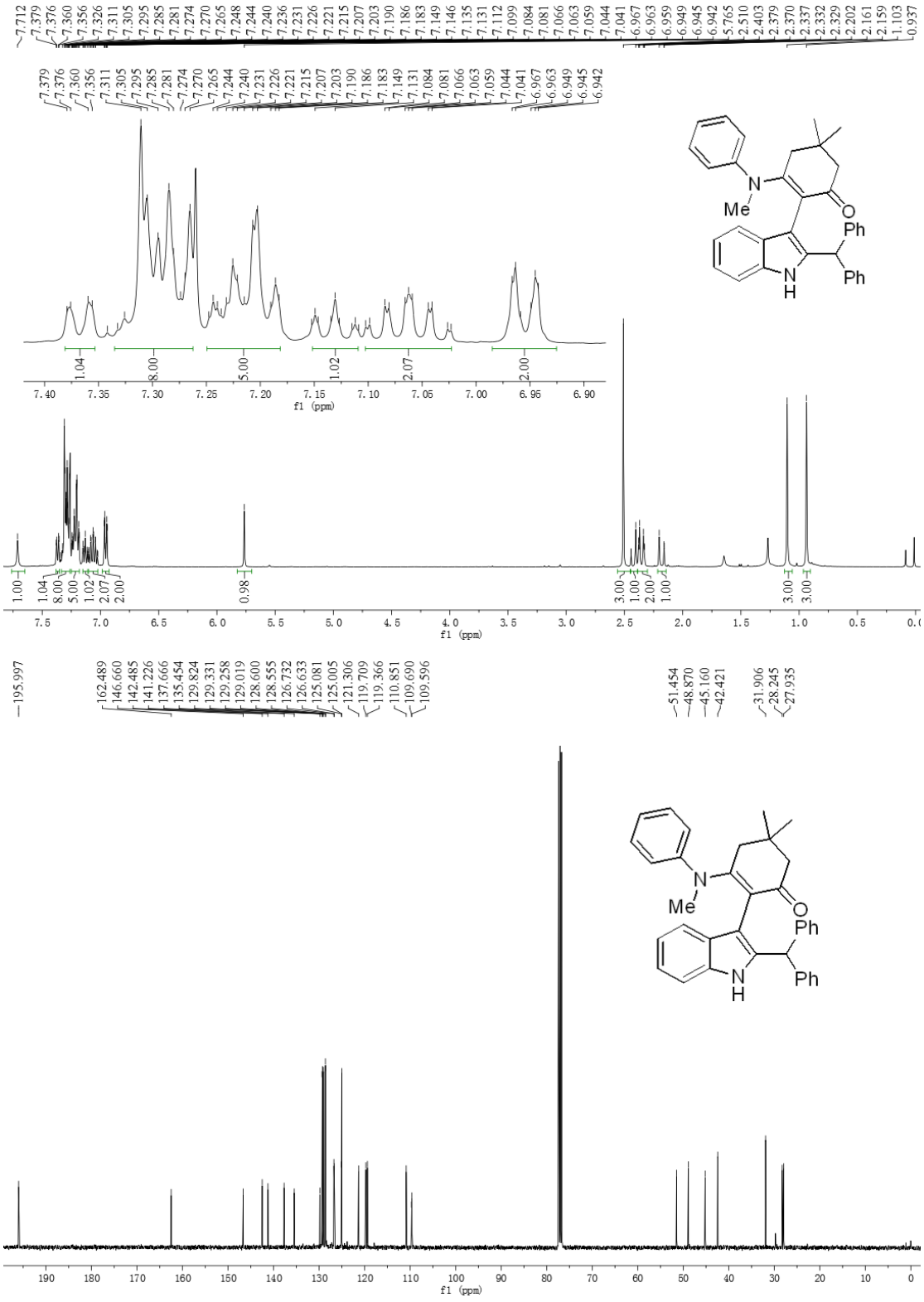

7.883 7.318 7.308 7.288 7.286 7.251 7.247 7.240 7.240 7.234 7.224 7.209 7.202 7.193 7.187 7.170 7.162 7.151 7.146 7.132 7.129 7.115 7.095 7.091 7.086 7.082 7.067 6.847 6.842 6.836 6.832 6.824 5.730 5.258 5.241 5.224 4.198 4.182 4.157 4.140 4.134 4.117 4.092 4.075 2.392 2.377 2.352 2.336 2.294 2.253 2.122 2.081 1.130 0.951
7.318 7.308 7.288 7.286 7.270 7.251 7.247 7.240 7.240 7.234 7.224 7.219 7.209 7.202 7.193 7.187 7.177 7.170 7.162 7.151 7.146 7.132 7.129 7.115 7.111 7.095 7.091 7.086 7.082 7.067 7.064 7.049 7.046 6.847 6.842 6.836 6.832 6.824
5.00 0.40 4.60 3.00 2.00 1.00 1.00 2.00
f1 (ppm)
1.00 5.00 0.40 4.60 3.00 2.00 1.00 1.00 2.00 1.00 1.00 2.00 2.00 1.00 1.00 3.00 3.00
f1 (ppm)
192.909 161.874 142.674 142.031 139.856 138.336 135.901 129.203 128.723 128.706 128.680 128.424 128.046 127.241 126.859 126.522 126.078 121.479 119.767 119.274 111.140 105.139 102.544 50.459 49.027 46.325 38.786 32.041 28.503 28.449
f1 (ppm)

4ar (unseparable isomers with 1:1 molar ratio)



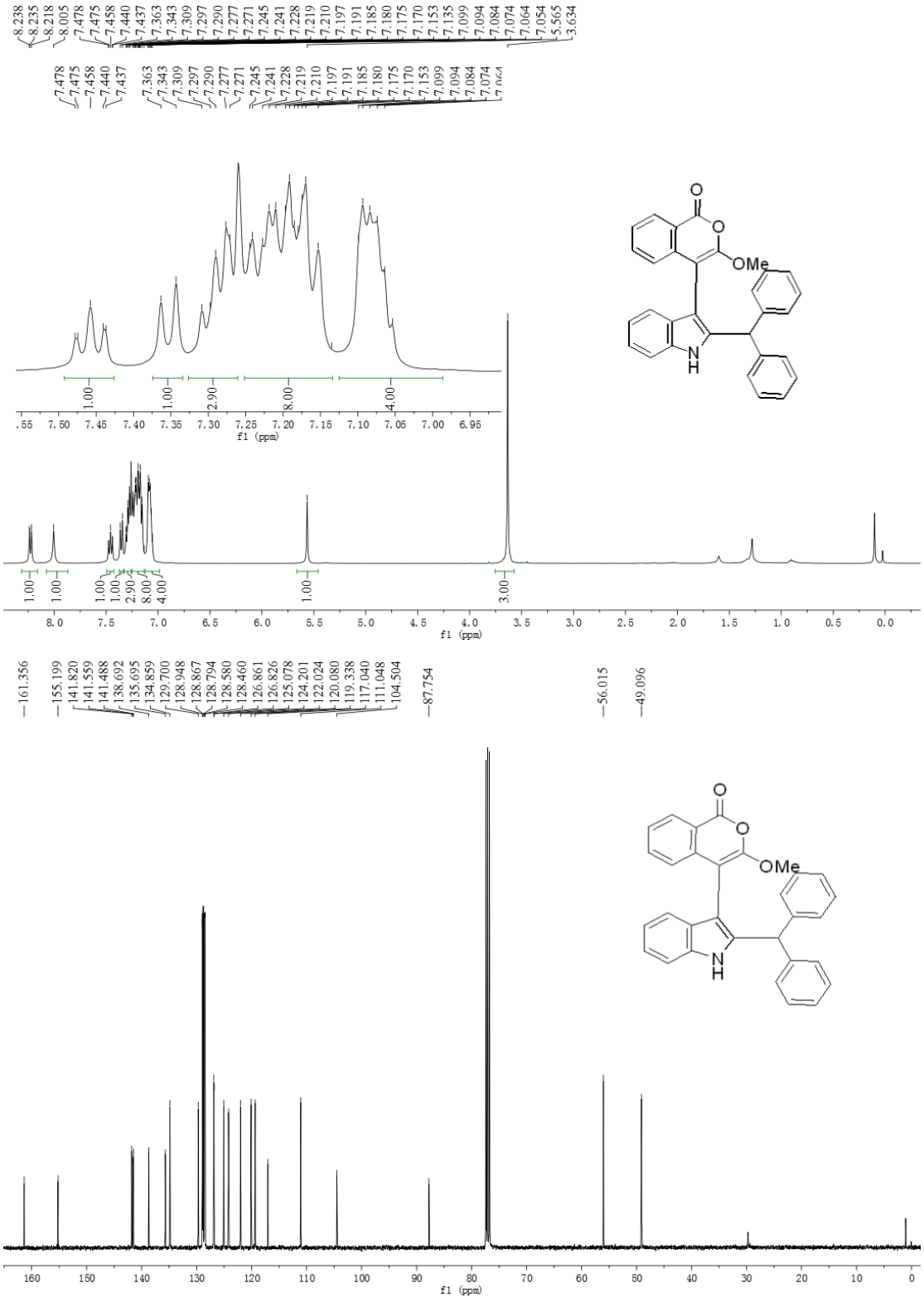


4as

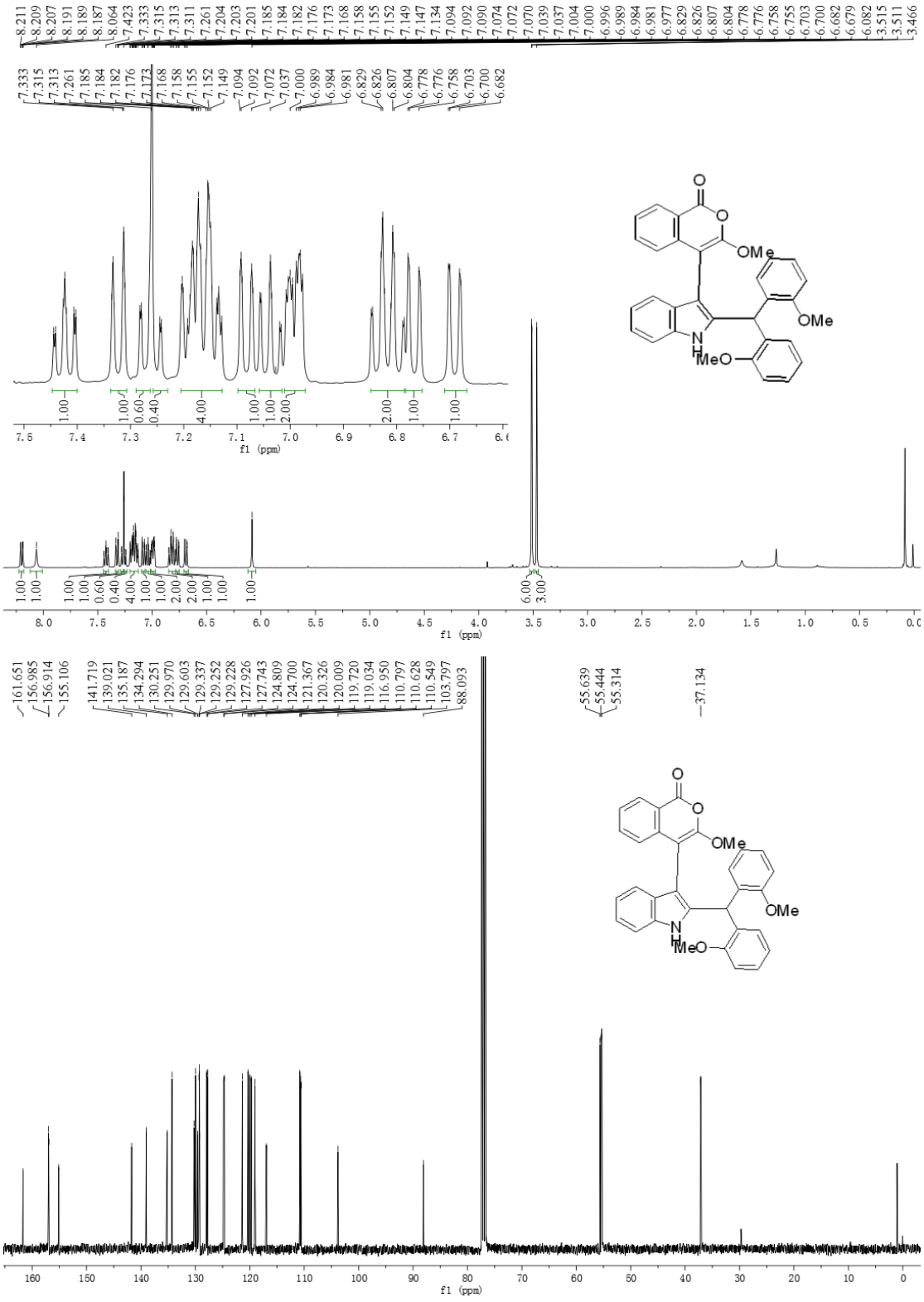

7.712 7.379 7.376 7.360 7.356 7.326 7.311 7.305 7.295 7.285 7.281 7.274 7.270 7.265 7.248 7.244 7.240 7.236 7.231 7.226 7.221 7.215 7.207 7.203 7.190 7.186 7.183 7.149 7.146 7.135 7.131 7.112 7.099 7.084 7.081 7.066 7.063 7.059 7.044 7.041 6.967 6.963 6.959 6.949 6.945 6.942 5.765 2.510 2.403 2.379 2.370 2.337 2.332 2.329 2.202 2.161 2.159 1.103 0.937
1.04 8.00 5.00 1.02 2.07 2.00
f1 (ppm)
1.00 1.04 8.00 5.00 1.02 2.07 2.00 0.98 3.00 1.00 2.00 1.00 3.00 3.00
f1 (ppm)
N
Me
O
Ph
N
H
Ph

195.997 162.489 146.660 142.485 141.226 137.666 135.454 129.824 129.331 129.258 129.019 128.600 128.555 126.732 126.633 125.081 125.005 121.306 119.709 119.366 110.851 109.690 109.596 51.454 48.870 45.160 42.421 31.906 28.245 27.935
f1 (ppm)
N
Me
O
Ph
N
H
Ph

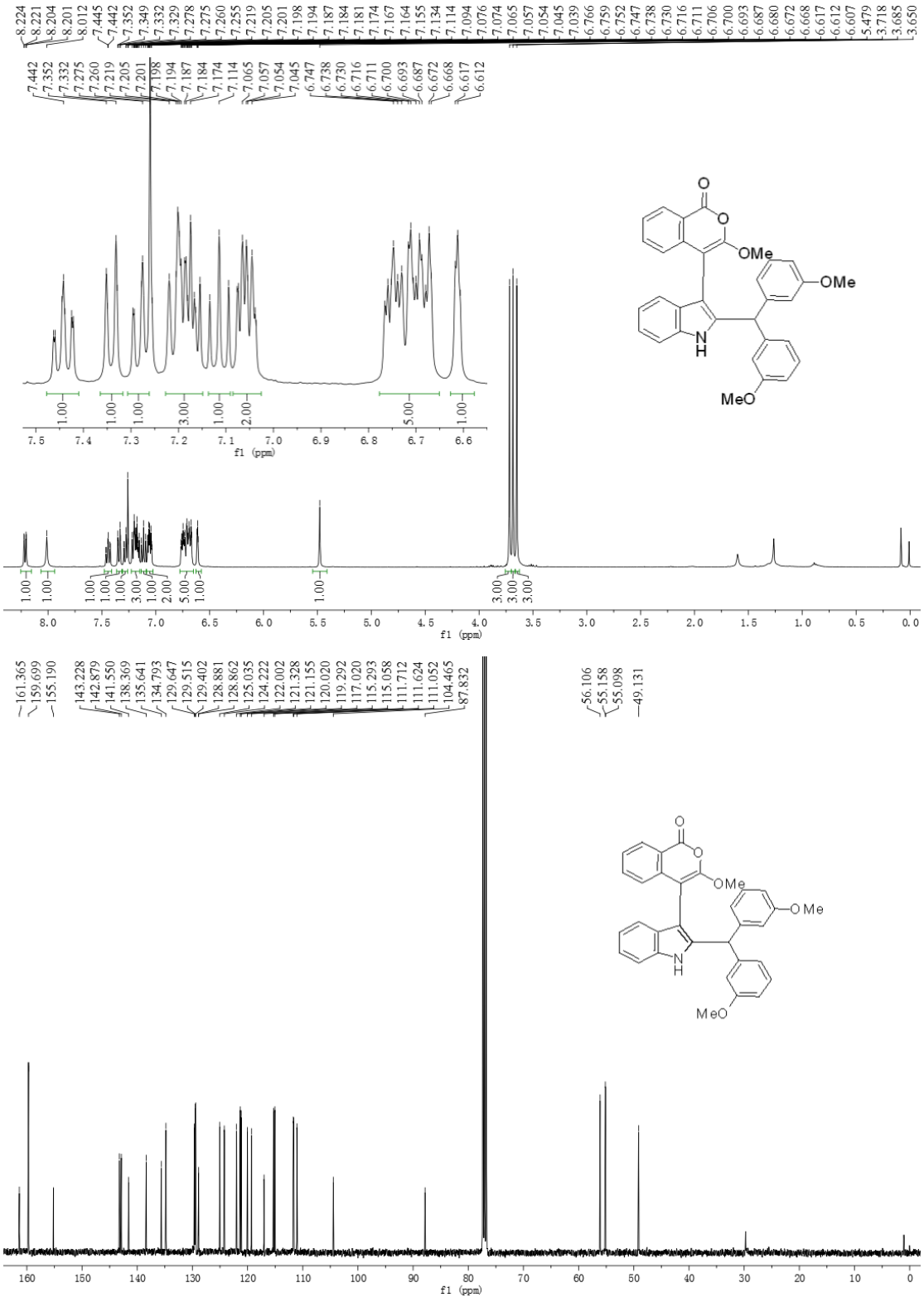
6a


8.238
8.235
8.218
8.005
7.478
7.475
7.458
7.440
7.437
7.363
7.343
7.309
7.297
7.290
7.277
7.271
7.245
7.241
7.228
7.219
7.210
7.197
7.191
7.185
7.180
7.175
7.170
7.153
7.135
7.099
7.094
7.084
7.074
7.064
7.054
5.565
3.634
1.00
1.00
2.90
8.00
4.00
f1 (ppm)
O
O
OMe
N
H
1.00
1.00
1.00
1.00
2.90
8.00
4.00
1.00
3.00
f1 (ppm)
161.356
155.199
141.820
141.559
141.488
138.692
135.695
134.859
129.700
128.948
128.867
128.794
128.580
128.460
126.861
126.826
125.078
124.201
122.024
120.080
119.338
117.040
111.048
104.504
87.754
56.015
49.096
O
O
OMe
N
H
f1 (ppm)

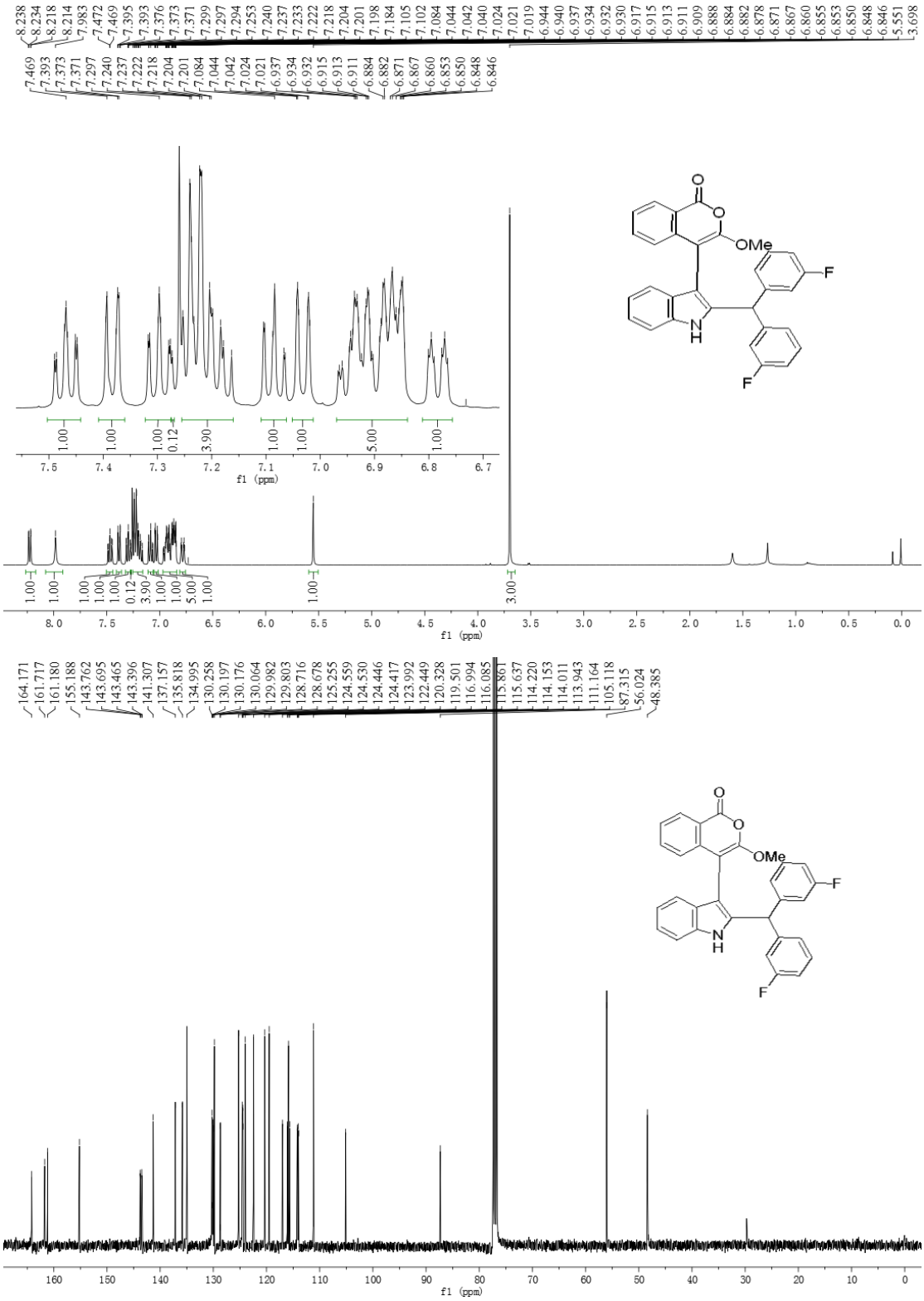
6b

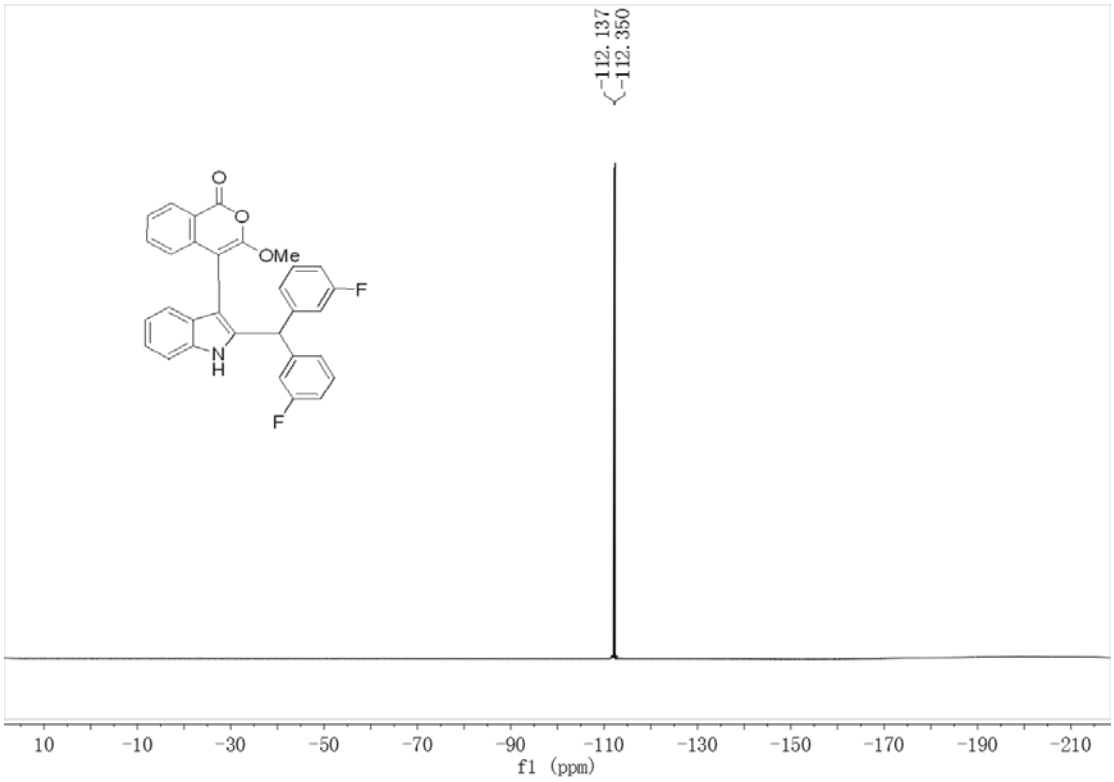


6c

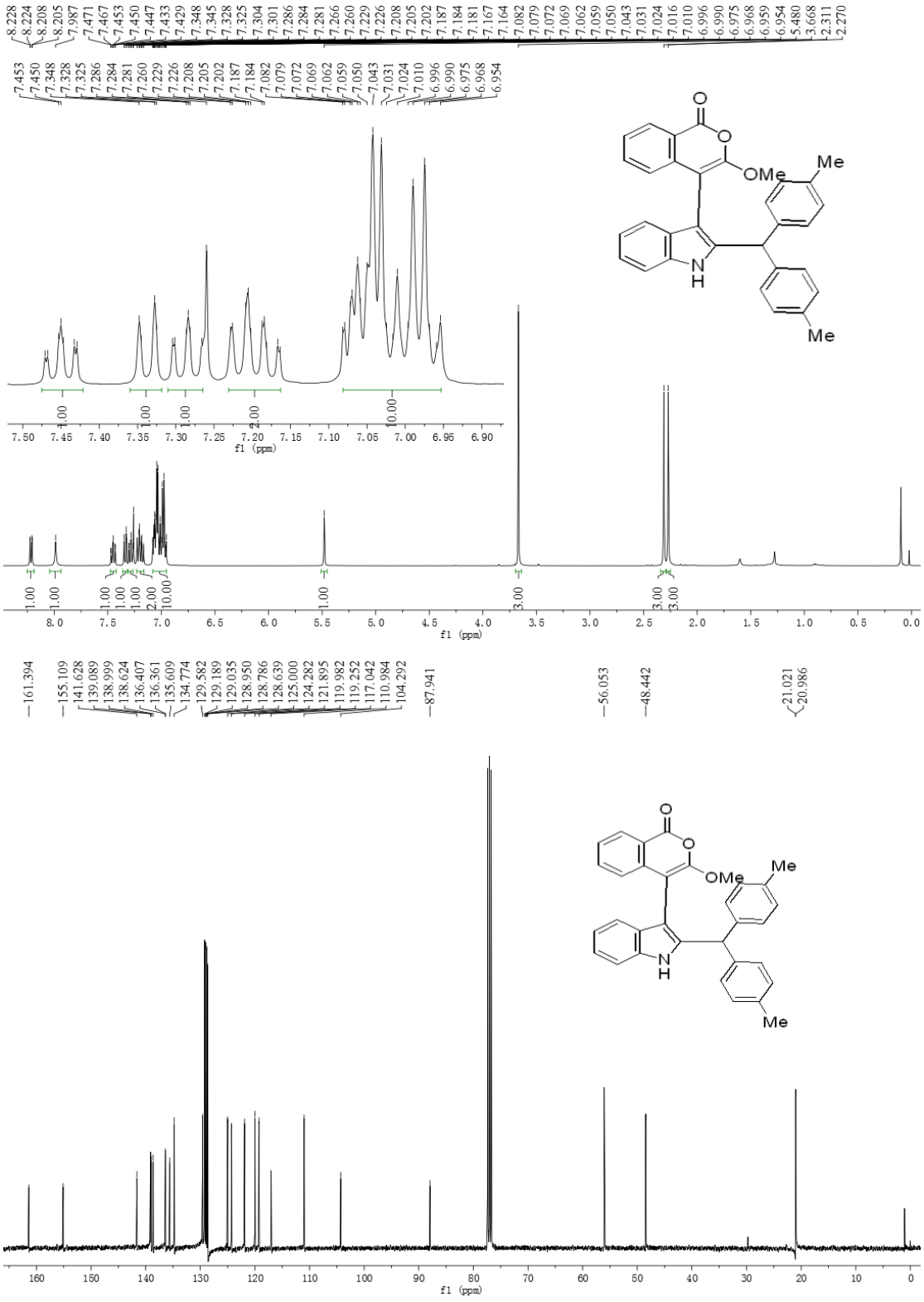


6d

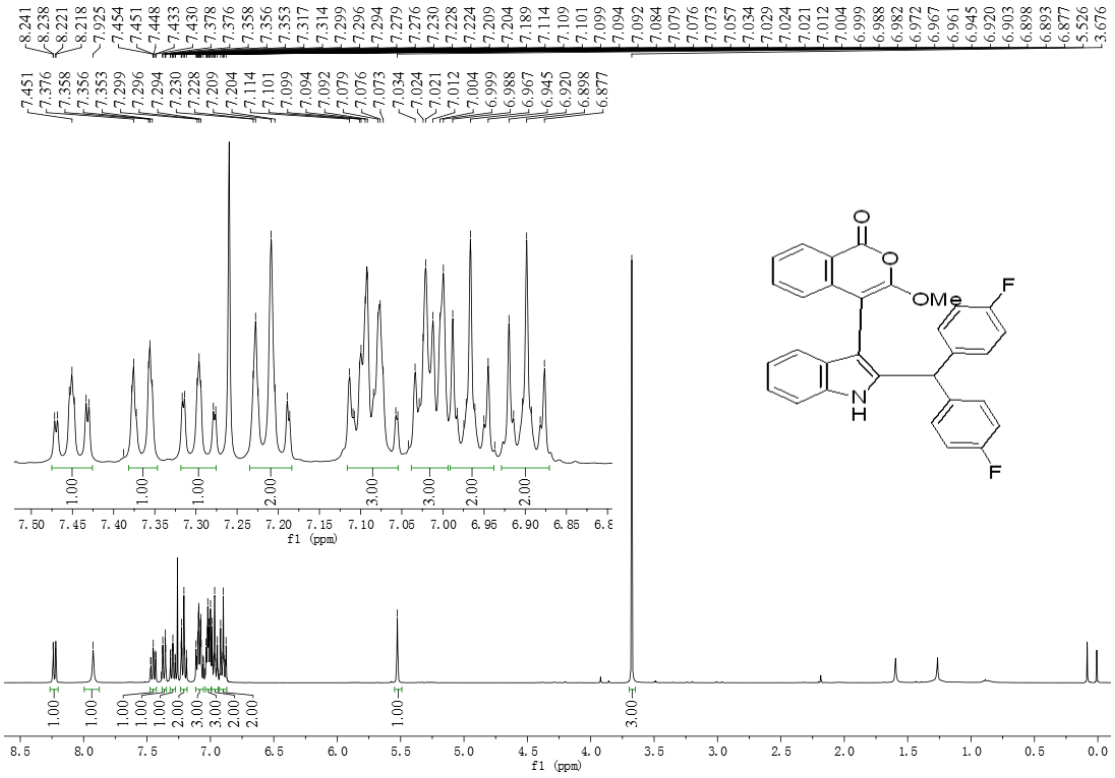


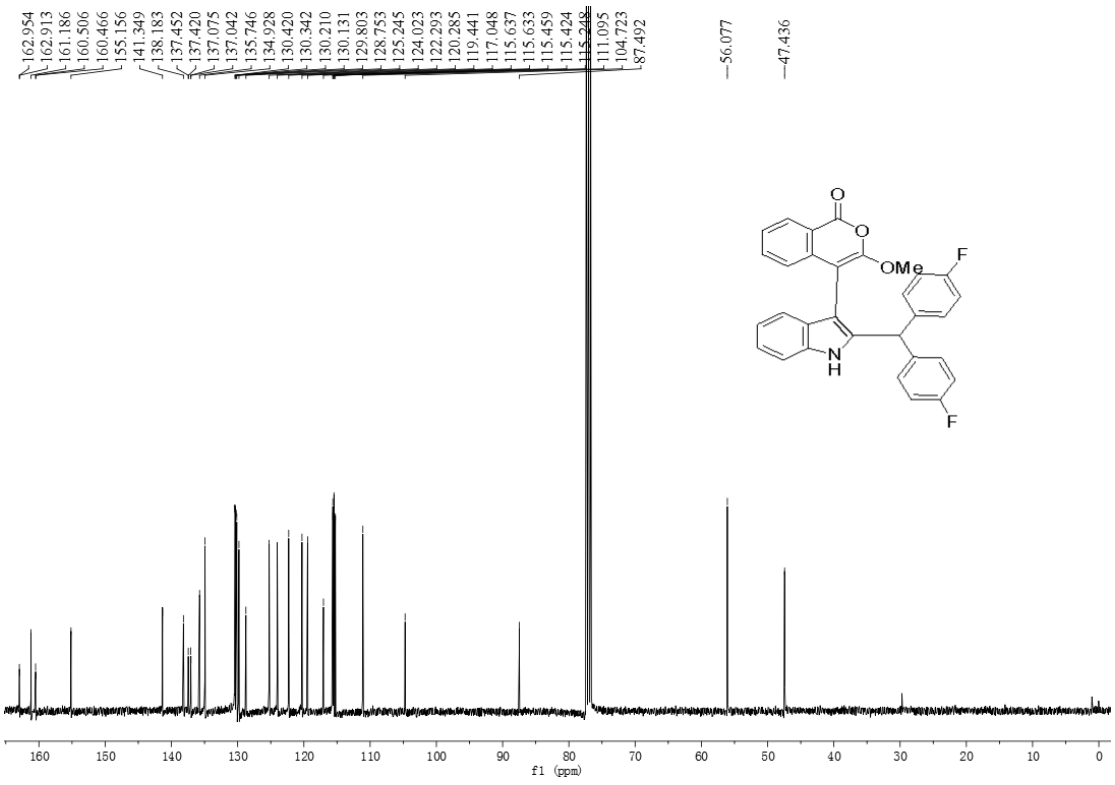

-112.137
-112.350
O
O
OMe
F
N
H
F
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

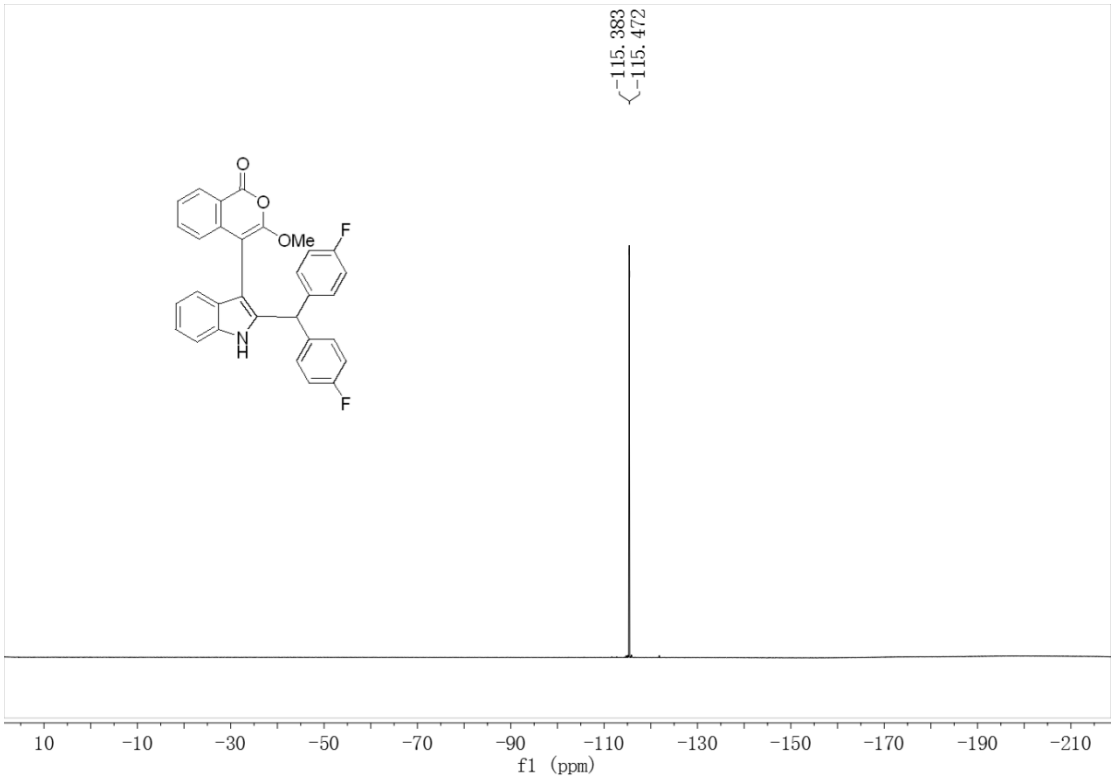
6e


8.228
8.224
8.208
8.205
7.987
7.471
7.467
7.453
7.450
7.447
7.433
7.429
7.348
7.345
7.328
7.325
7.304
7.301
7.286
7.284
7.281
7.266
7.260
7.229
7.226
7.208
7.205
7.202
7.187
7.184
7.181
7.167
7.164
7.082
7.079
7.072
7.069
7.062
7.059
7.050
7.043
7.031
7.024
7.016
7.010
6.996
6.990
6.975
6.968
6.959
6.954
5.480
3.668
2.311
2.270
O
O
OMe
Me
N
H
Me
f1 (ppm)
f1 (ppm)
161.394
155.109
141.628
139.089
138.999
138.624
136.407
136.361
135.609
134.774
129.582
129.189
129.035
128.950
128.786
128.639
125.000
124.282
121.895
119.982
119.252
117.042
110.984
104.292
87.941
56.053
48.442
21.021
20.986
f1 (ppm)

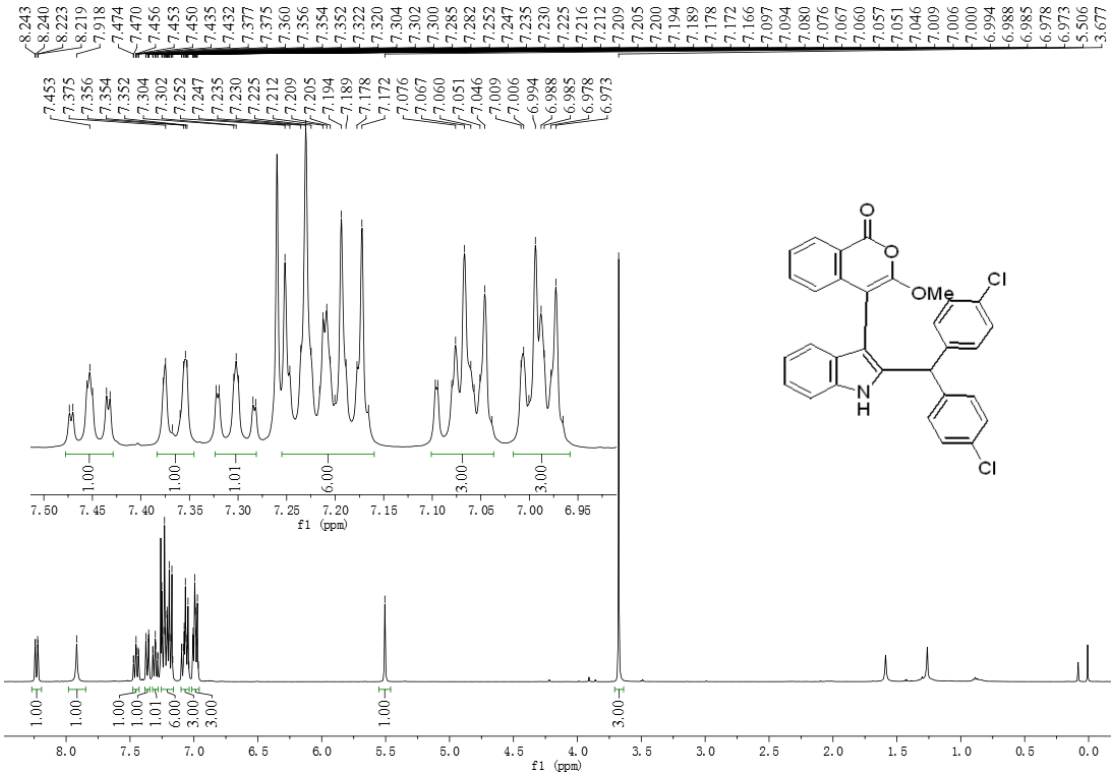
6f

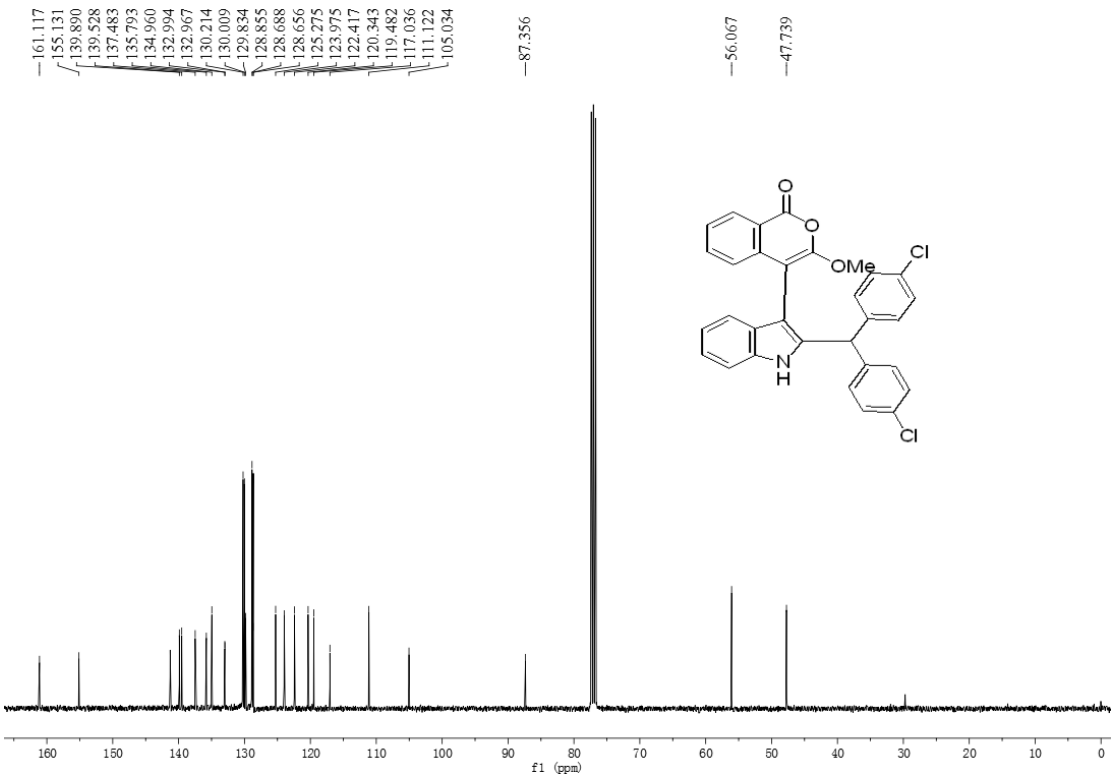

8.241
8.238
8.221
8.218
7.925
7.454
7.451
7.448
7.433
7.430
7.378
7.376
7.358
7.356
7.353
7.317
7.314
7.299
7.296
7.294
7.279
7.276
7.230
7.228
7.224
7.209
7.204
7.189
7.114
7.109
7.101
7.099
7.094
7.092
7.084
7.079
7.076
7.073
7.057
7.034
7.029
7.024
7.021
7.012
7.004
6.999
6.988
6.982
6.972
6.967
6.961
6.945
6.920
6.903
6.898
6.893
6.877
5.526
3.676
OMe
F
N
H
F
f1 (ppm)


162.954
162.913
161.186
160.506
160.466
155.156
141.349
138.183
137.452
137.420
137.075
137.042
135.746
134.928
130.420
130.342
130.210
130.131
129.803
128.753
125.245
124.023
122.293
120.285
119.441
117.048
115.637
115.633
115.459
115.424
115.248
111.095
104.723
87.492
56.077
47.436
OMe
F
N
H
F
f1 (ppm)

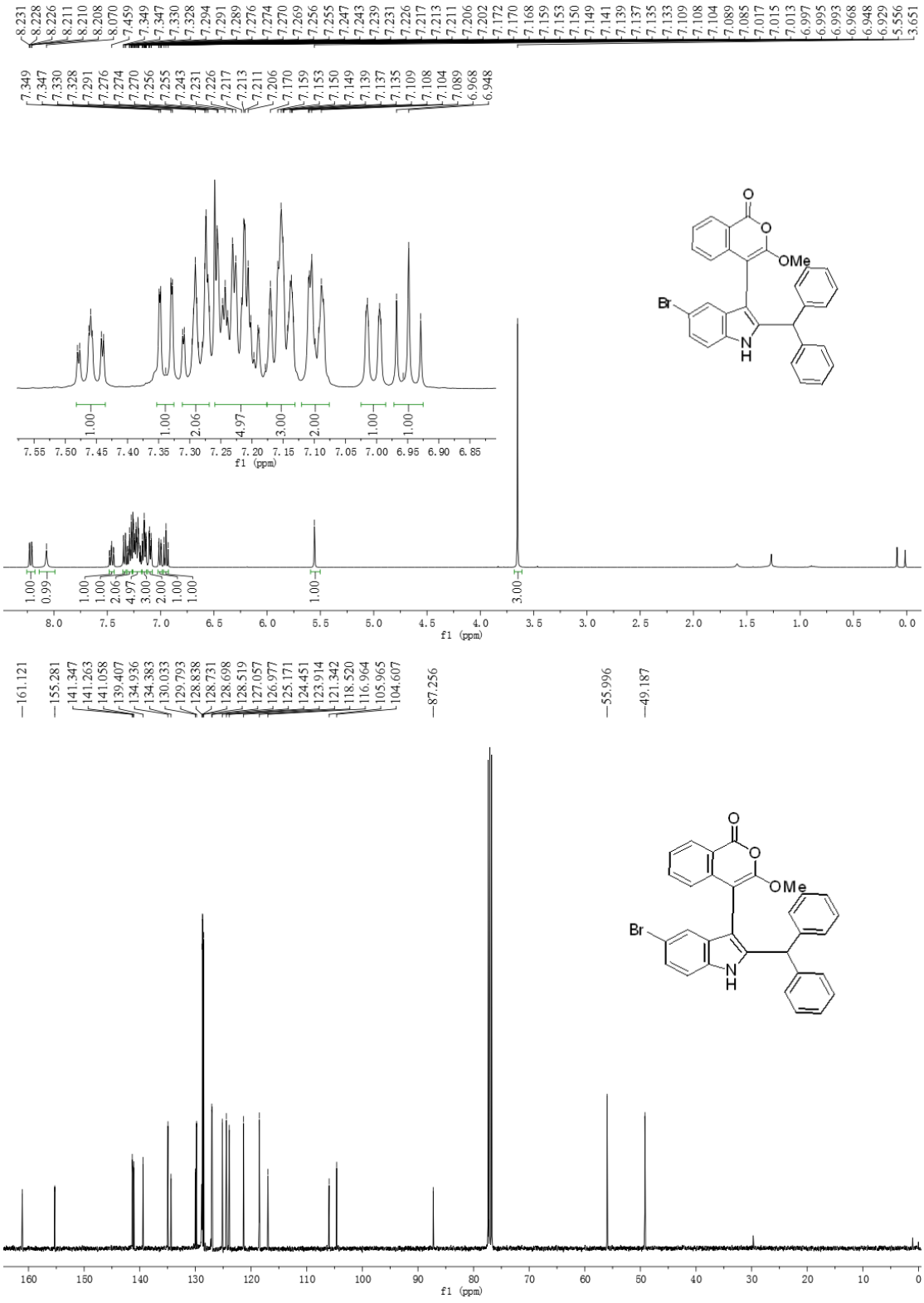

-115.383
-115.472
O
O
OMe
F
N
H
F
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

6g

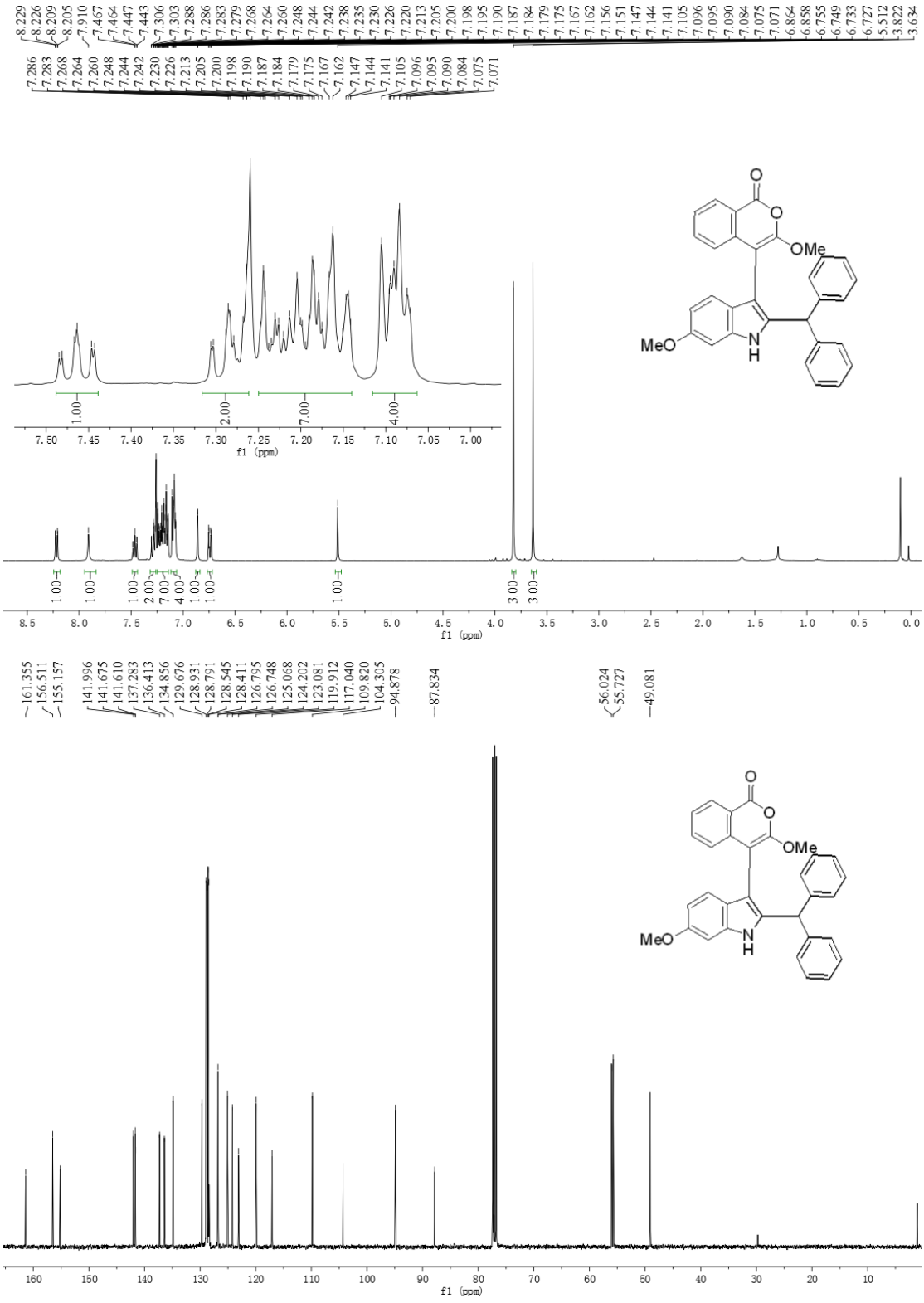

8.243
8.240
8.223
8.219
7.918
7.474
7.470
7.456
7.453
7.450
7.435
7.432
7.377
7.375
7.360
7.356
7.354
7.352
7.322
7.320
7.304
7.302
7.300
7.285
7.282
7.252
7.247
7.235
7.230
7.225
7.212
7.209
7.205
7.200
7.194
7.189
7.178
7.172
7.166
7.097
7.094
7.080
7.076
7.067
7.060
7.057
7.051
7.046
7.009
7.006
7.000
6.994
6.988
6.985
6.978
6.973
5.506
3.677
1.00
1.00
1.01
6.00
3.00
3.00
f1 (ppm)
OMe
Cl
Cl
N
H


161.117
155.131
139.890
139.528
137.483
135.793
134.960
132.994
132.967
130.214
130.009
129.834
128.855
128.688
128.656
125.275
123.975
122.417
120.343
119.482
117.036
111.122
105.034
87.356
56.067
47.739
f1 (ppm)
OMe
Cl
Cl
N
H

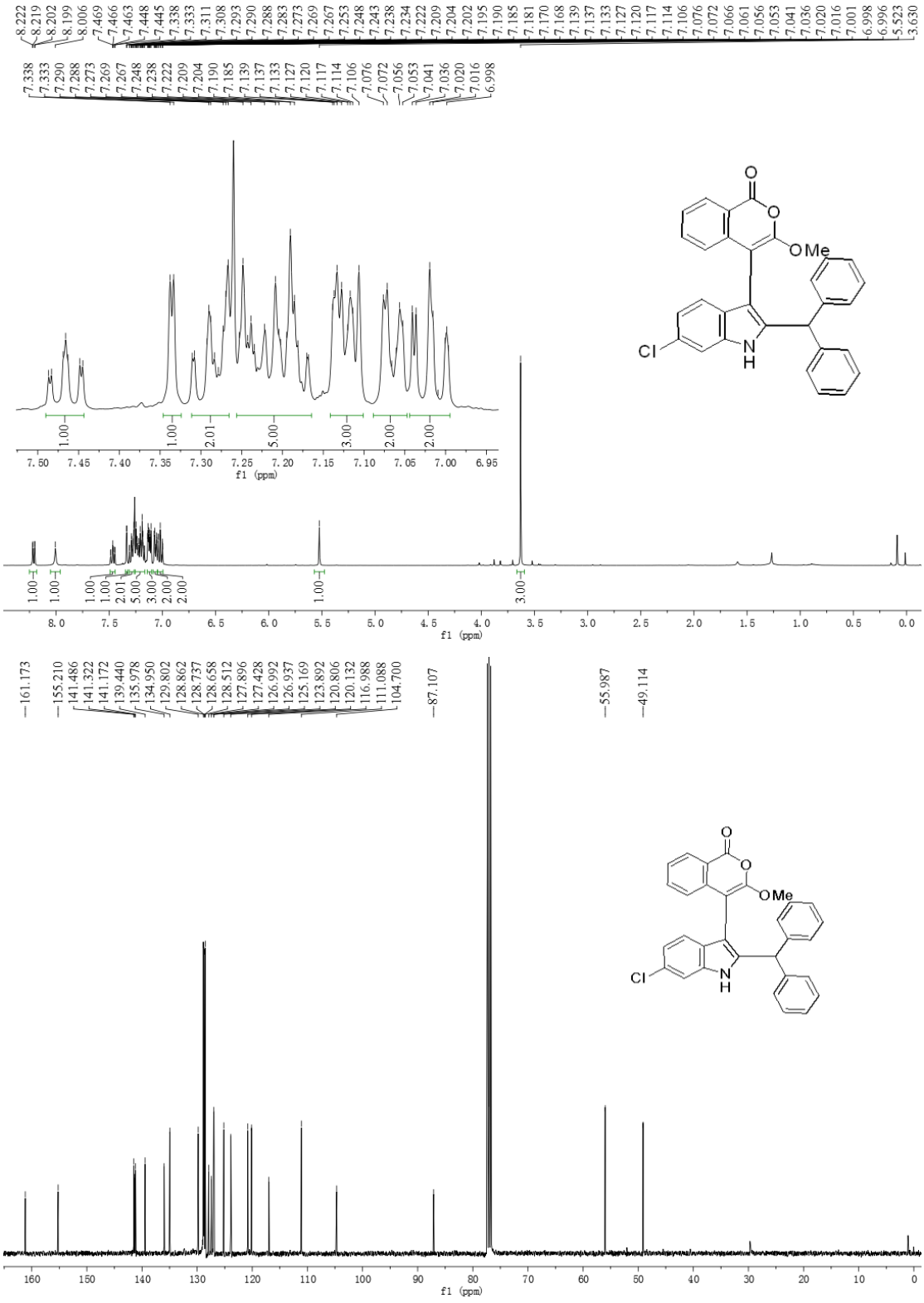
6h


8.231
8.228
8.226
8.211
8.210
8.208
8.070
7.459
7.349
7.347
7.330
7.328
7.294
7.291
7.289
7.276
7.274
7.270
7.269
7.256
7.255
7.247
7.243
7.239
7.231
7.226
7.217
7.213
7.211
7.206
7.202
7.172
7.170
7.168
7.159
7.153
7.150
7.149
7.141
7.139
7.137
7.135
7.133
7.109
7.108
7.104
7.089
7.085
7.017
7.015
7.013
6.997
6.995
6.993
6.968
6.948
6.929
5.556
3.651
O
O
OMe
Br
N
H
f1 (ppm)
161.121
155.281
141.347
141.263
141.058
139.407
134.936
134.383
130.033
129.793
128.838
128.731
128.698
128.519
127.057
126.977
125.171
124.451
123.914
121.342
118.520
116.964
105.965
104.607
87.256
55.996
49.187

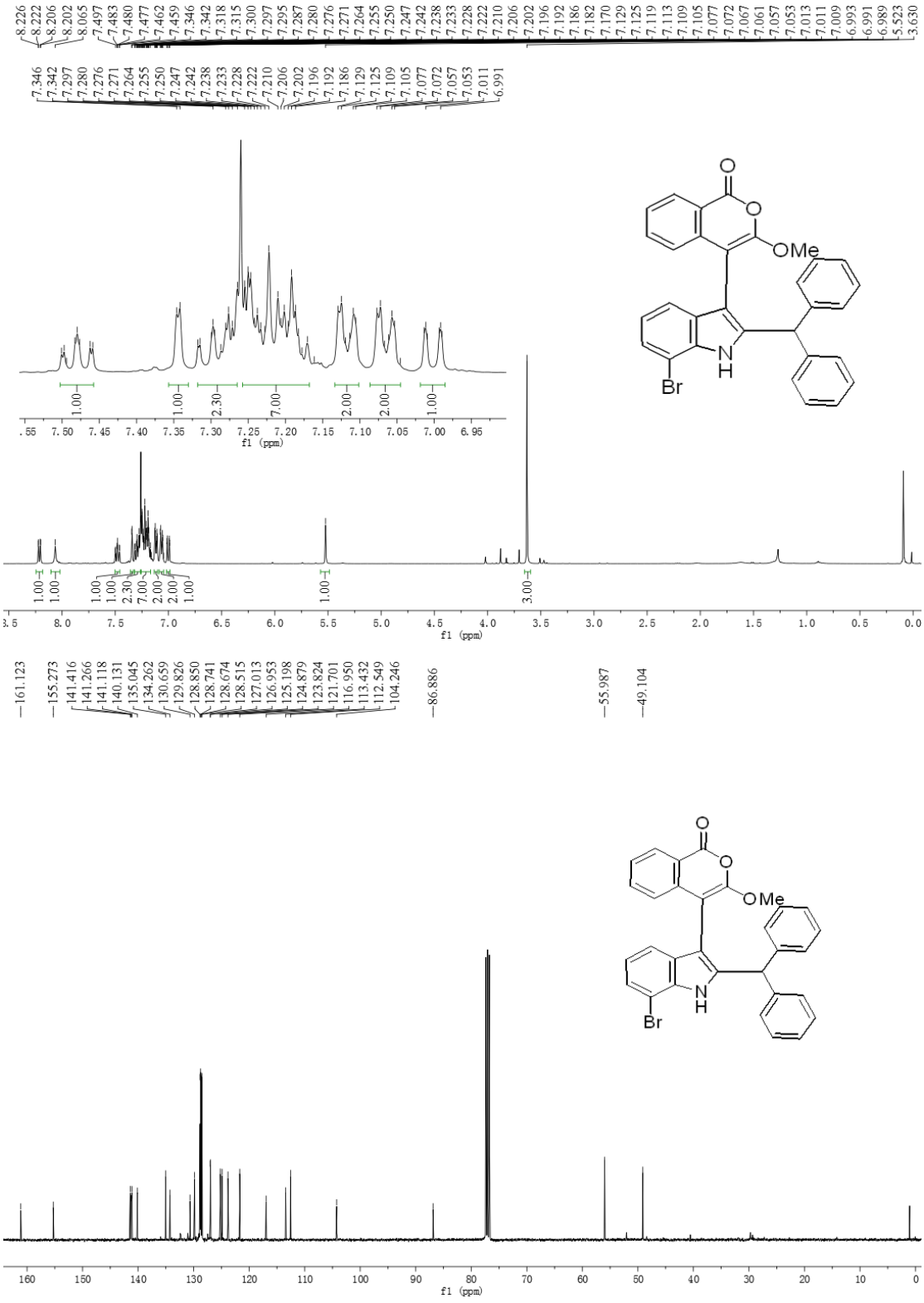
6i


8.229
8.226
8.209
8.205
7.910
7.467
7.464
7.447
7.443
7.306
7.303
7.288
7.286
7.283
7.279
7.268
7.264
7.260
7.248
7.244
7.242
7.230
7.226
7.213
7.205
7.200
7.198
7.190
7.187
7.184
7.179
7.175
7.167
7.162
7.147
7.144
7.141
7.105
7.096
7.095
7.090
7.084
7.075
7.071
6.864
6.858
6.755
6.749
6.733
6.727
5.512
3.822
3.634
O
O
OMe
MeO
N
H
1.00
2.00
7.00
4.00
f1 (ppm)
3.00
161.355
156.511
155.157
141.996
141.675
141.610
137.283
136.413
134.856
129.676
128.931
128.791
128.545
128.411
126.795
126.748
125.068
124.202
123.081
119.912
117.040
109.820
104.305
94.878
87.834
56.024
55.727
49.081

6j

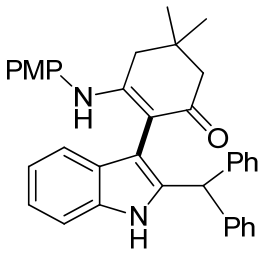

8.222
8.219
8.202
8.199
8.006
7.469
7.466
7.463
7.448
7.445
7.338
7.333
7.311
7.308
7.293
7.290
7.288
7.283
7.273
7.269
7.267
7.253
7.248
7.243
7.238
7.234
7.222
7.209
7.204
7.202
7.195
7.190
7.185
7.181
7.170
7.168
7.139
7.137
7.133
7.127
7.120
7.117
7.114
7.106
7.076
7.072
7.066
7.061
7.056
7.053
7.041
7.036
7.020
7.016
7.001
6.998
6.996
5.523
3.630
O
O
OMe
Cl
N
H
f1 (ppm)
161.173
155.210
141.486
141.322
141.172
139.440
135.978
134.950
129.802
128.862
128.737
128.658
128.512
127.896
127.428
126.992
126.937
125.169
123.892
120.806
120.132
116.988
111.088
104.700
87.107
55.987
49.114

6k

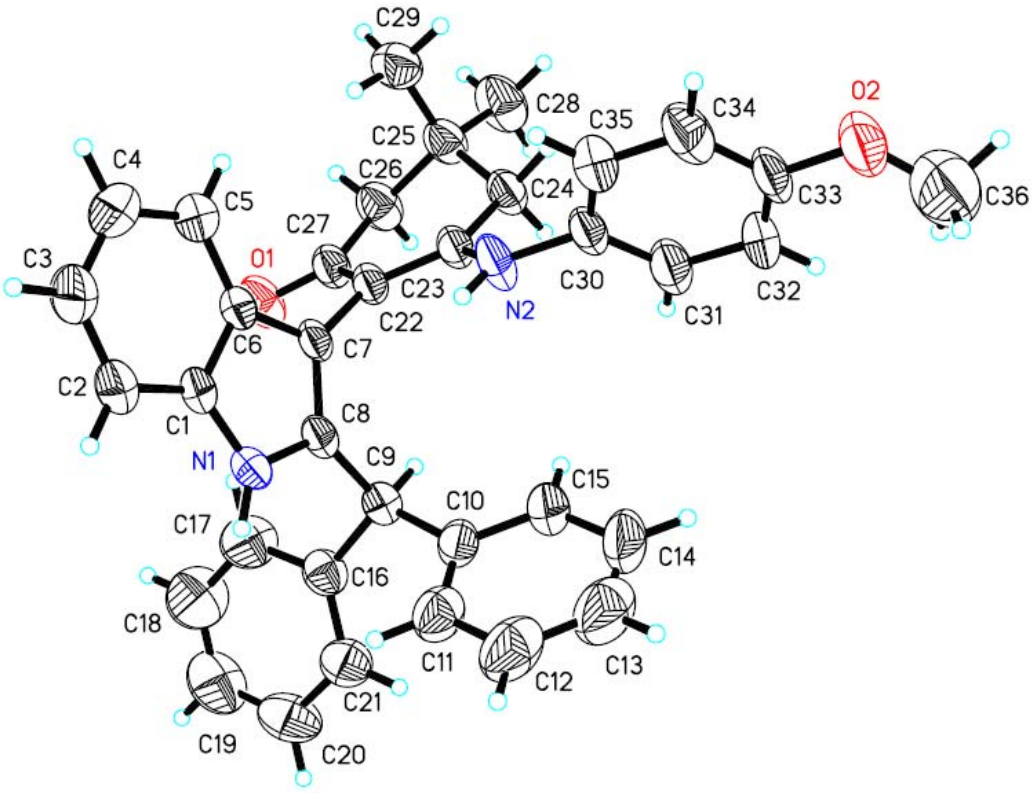

8.226
8.222
8.206
8.202
8.065
7.497
7.483
7.480
7.477
7.462
7.459
7.346
7.342
7.318
7.315
7.300
7.297
7.295
7.287
7.280
7.276
7.271
7.264
7.255
7.250
7.247
7.242
7.238
7.233
7.228
7.222
7.210
7.206
7.202
7.196
7.192
7.186
7.182
7.170
7.129
7.125
7.119
7.113
7.109
7.105
7.077
7.072
7.067
7.061
7.057
7.053
7.013
7.011
7.009
6.993
6.991
6.989
5.523
3.630
O
O
OMe
N
H
Br
f1 (ppm)
161.123
155.273
141.416
141.266
141.118
140.131
135.045
134.262
130.659
129.826
128.850
128.741
128.674
128.515
127.013
126.953
125.198
124.879
123.824
121.701
116.950
113.432
112.549
104.246
86.886
55.987
49.104

6. X-ray single crystal data for compounds 4aa and 6a

Compound 4aa:



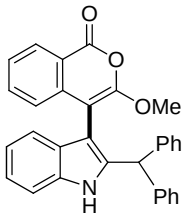
4aa



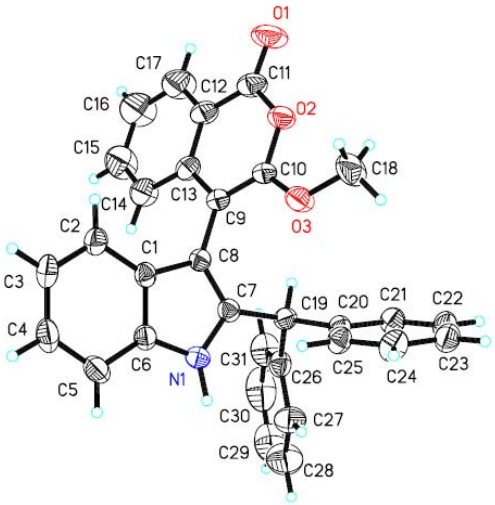
The thermal ellipsoid was drawn at the 30% probability level.

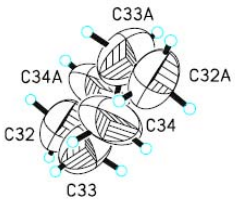
Empirical formula	C36 H34 N2 O2	
Formula weight	526.65	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 23.463(5) Å	α= 90°.
	b = 12.095(2) Å	β= 96.456(7)°.
	c = 20.499(5) Å	γ = 90°.
Volume	5781(2) $Å^3$	
Z	8	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	2240	
Crystal size	0.32 x 0.28 x 0.25 mm^3	
Theta range for data collection	1.747 to 25.497°.	
Index ranges	-28<=h<=24, -14<=k<=14, -24<=l<=24	
Reflections collected	19894	
Independent reflections	5384 [R(int) = 0.0466]	
Completeness to theta = 26.000°	94.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6262	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5384 / 26 / 364	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0784, wR2 = 0.2295	
R indices (all data)	R1 = 0.1521, wR2 = 0.2948	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.746 and -0.402 $e.Å^{-3}$	

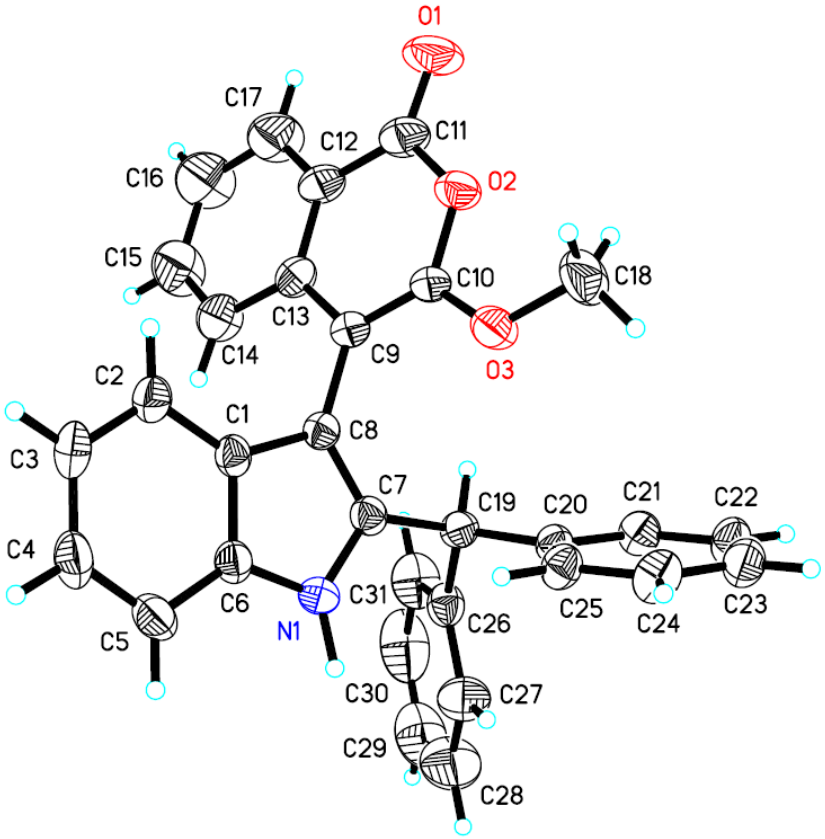
Compound 6a:



6a







The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C34 H30 N O3	
Formula weight	500.59	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.861(5) Å	α= 89.660(9)°.
	b = 10.455(5) Å	β= 76.844(9)°.
	c = 15.398(8) Å	γ = 63.337(8)°.
Volume	1373.0(12) $Å^3$	
Z	2	
Density (calculated)	1.211 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	530	
Crystal size	0.220 x 0.170 x 0.130 mm^3	
Theta range for data collection	2.193 to 25.096°.	
Index ranges	-11<=h<=7, -12<=k<=12, -18<=l<=18	
Reflections collected	9088	
Independent reflections	4857 [R(int) = 0.0466]	
Completeness to theta = 25.242°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5563	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4857 / 2 / 349	
Goodness-of-fit on F^2	0.959	
Final R indices [I>2sigma(I)]	R1 = 0.0805, wR2 = 0.2057	
R indices (all data)	R1 = 0.1495, wR2 = 0.2548	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.452 and -0.228 $e.Å^{-3}$	