

**Electronic Supplementary Information**

**Copper-catalyzed cascade C–N coupling/C–H amination: One pot synthesis of imidazo[1,2-*b*]indazole**

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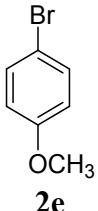
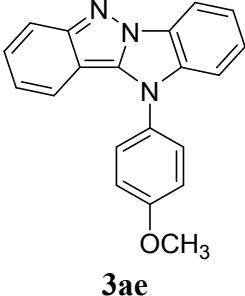
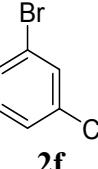
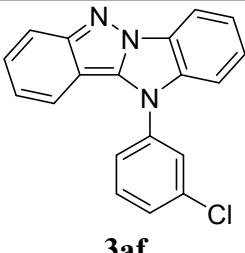
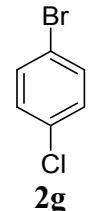
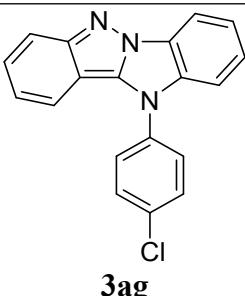
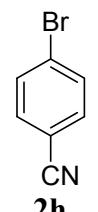
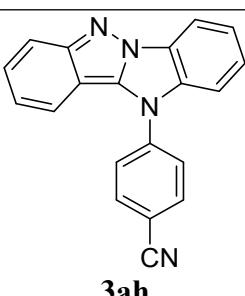
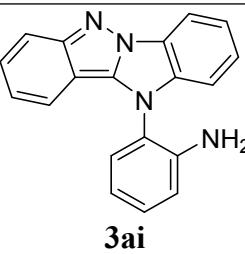
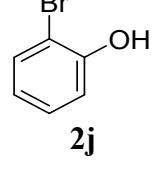
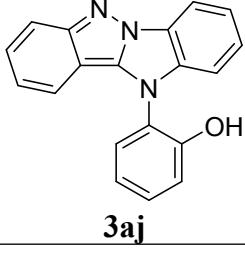
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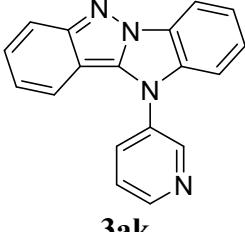
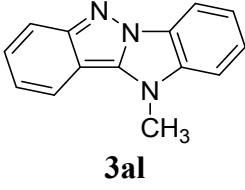
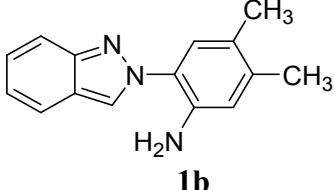
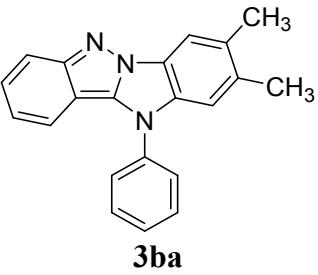
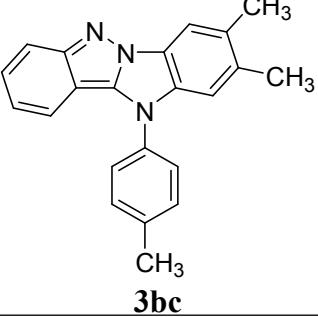
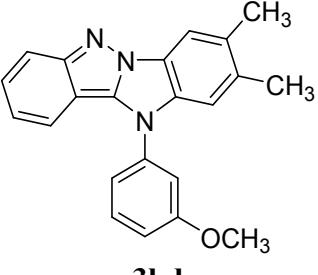
**Table S1: Copper-catalyzed one pot cascade synthesis of imidazo[1,2-*b*]indazole (3).<sup>a</sup>**

The reaction scheme illustrates the synthesis of imidazo[1,2-*b*]indazoles (3) from two starting materials, 1 and 2. Reagent 1 is 2-(2*H*-indazol-2-yl)aniline, which reacts with reagent 2 (aryl/heteroaryl/aliphatic halides) in the presence of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  and X-Phos catalyst in DMF at  $100^\circ\text{C}$  for 8 hours to yield the final product 3.

**Table S1: Copper-catalyzed one pot cascade synthesis of imidazo[1,2-*b*]indazole (3).<sup>a</sup>**

S.No	2-(2 <i>H</i> -Indazol-2-yl)aniline (1)	Aryl/heteroaryl/aliphatic halides (2)	Imidazo[1,2- <i>b</i> ]indazoles (3)	Yield <sup>b</sup> (%)
1				72
2	<b>1a</b>			68
3	<b>1a</b>			70
4	<b>1a</b>			72

5	<b>1a</b>			70
6	<b>1a</b>			70
7	<b>1a</b>			68
8	<b>1a</b>			70
9	<b>1a</b>			65
10	<b>1a</b>			65

11	<b>1a</b>	<b>2k</b>		68
12	<b>1a</b>	<b>2l</b>		65
13	 <b>1b</b>	<b>2a</b>		71
14	<b>1b</b>	<b>2c</b>		70
15	<b>1b</b>	<b>2d</b>		69

16	<b>1b</b>	<b>2e</b>	 <b>3be</b>	70
17	<b>1b</b>	<b>2g</b>	 <b>3bg</b>	70
18	<b>1b</b>	<b>2j</b>	 <b>3bj</b>	66
19	<b>1b</b>	<b>2l</b>	 <b>3bl</b>	65

20	 <b>1c</b>	<b>2a</b>	 <b>3ca</b>	70
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<sup>a</sup>All the reactions were carried out using compound **1** (0.47 mmol), **2** (0.71 mmol) and

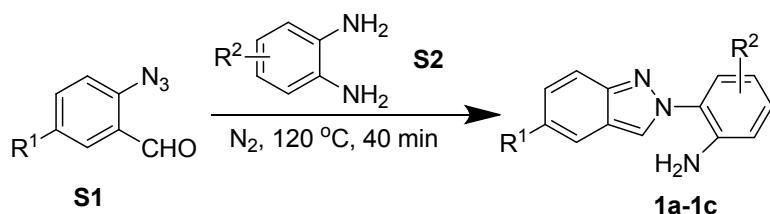
Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (20 mol%), X-Phos (5 mol%) in DMF (3 mL) at 100 °C for 8 h in seal tube.

<sup>b</sup>Isolated yield.

## Chemistry

**General methods:** Unless stated otherwise, solvents and chemicals were obtained from commercial sources and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. Flash chromatography was performed on silica gel (100-200 mesh) using hexane and ethyl acetate. <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> solutions by using 400 or 100 MHz spectrometers, respectively. Proton chemical shifts ( $\delta$ ) are relative to tetramethylsilane (TMS,  $\delta$  = 0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as b (broad). Coupling constants ( $J$ ) are given in hertz. Melting points were determined using a melting point apparatus and are uncorrected. MS spectra were obtained on a mass spectrometer. HRMS data were recorded by electrospray ionization with a Q-TOF mass analyzer. 2-azidobenzaldehyde<sup>1</sup>,2-azido-5-bromobenzaldehyde<sup>1</sup>was prepared according to the known procedure.

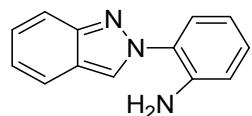
### General procedure for the synthesis of indazol-2-ylanilines (**1**):<sup>2</sup>



2-Azidobenzaldehyde (**S1**) (3.39 mmol), *o*-phenylenediamine (**S2**) (3.39 mmol) were taken in a oven dried schlenck tube and it was closed with nitrogen balloon and stirred for 40 min at 120 °C. After completion of the reaction was monitored by TLC. The reaction mixture was cool to

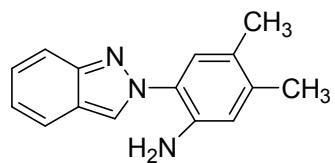
room temperature, diluted with DCM and was purified using column chromatography over silica gel with EtOAc / hexane to give desired product of **1a-c**.

**2-(2*H*-Indazol-2-yl)aniline (**1a**):**



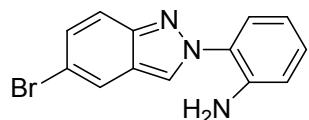
Off white solid; Yield: 65 %; mp: 78-80 °C (76-78 °C lit<sup>3</sup>);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.22 (s, 1H), 7.75 (t,  $J = 7.8$  Hz, 2H), 7.34 (t,  $J = 7.8$  Hz, 2H), 7.25-7.21 (m, 1H), 7.13 (t,  $J = 7.6$  Hz, 1H), 6.88 (d,  $J = 8.0$  Hz, 1H), 6.84 (t,  $J = 7.6$  Hz, 1H), 4.86 (s, 2H).

**2-(2*H*-Indazol-2-yl)-4,5-dimethylaniline (**1b**):**



Off white solid; Yield: 55%; mp: 147-151 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.19 (d,  $J = 0.8$  Hz, 1H), 7.76-7.71 (m, 2H), 7.34-7.30(m, 1H), 7.14-7.10 (m, 2H), 6.69 (s, 1H), 4.62 (s, 2H), 2.24 (s, 3H), 2.22 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.4, 138.9, 138.1, 126.4 (2C), 125.7, 124.5, 123.5, 122.0, 121.8, 120.3, 118.8, 117.5, 19.6 18.7; HR-MS(ESI+) m/z calculated for  $[\text{C}_{15}\text{H}_{16}\text{N}_3]^+ = [\text{M} + \text{H}]^+$  238.1344, found 238.1343.

**2-(5-Bromo-2*H*-indazol-2-yl)aniline(**1c**):**

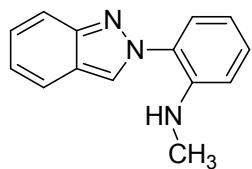


Brown solid; Yield: 75%; mp: 86-88 °C (88-90 °C lit<sup>3</sup>);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (d,  $J = 0.4$  Hz, 1H), 7.89 (d,  $J = 1.2$  Hz, 1H), 7.63 (d,  $J = 8.8$  Hz, 1H), 7.39 (dd,  $J = 9.2$  & 8.0 Hz, 1H), 7.31 (dd,  $J = 8.0$  & 7.5 Hz, 1H), 7.25-7.21 (m, 1H), 6.89-6.81 (m, 2H), 4.87 (s, 2H).

**Procedure for the synthesis of 2-(2*H*-indazol-2-yl)-*N*-methylaniline (**1A**)**

To a mixture of NaH (1.25 equiv) and indazol-2-ylanilines (1 equiv) in DMF was added MeI (1.10 equiv) dropwise at 0 °C and stirred at 0 °C for 12 h under nitrogen atmosphere. After completion of the reaction (confirmed by TLC), the mixture was diluted with ice water and extracted with ethyl acetate (20 mL × 3). The organic layers were collected, combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under low vacuum. The residue was purified

by column chromatography using hexane-ethyl acetate as an eluent to afford the title compound.

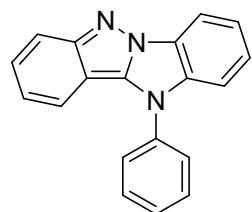


Gray solid; Yield: 52%; mp: 136-140 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.17 (s, 1H), 7.74 (dd, *J* = 10.0 & 8.8 Hz, 2H), 7.35-7.28 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.00 (s, 1H), 2.85 (d, *J* = 4.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 149.5, 143.6, 129.9, 126.7, 126.2, 124.8, 124.0, 122.2, 121.8, 120.4, 117.5, 115.9, 111.6, 30.0; HR-MS(ESI+) m/z calculated for [C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>]<sup>+</sup> = [M + H]<sup>+</sup> 224.1187, found 224.1187.

#### General procedure for the synthesis of imidazo[1,2-*b*]indazoles (3):

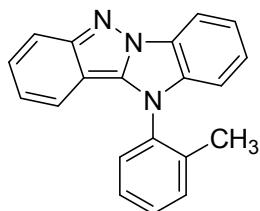
To an ovendried sealtube was added 2-(2*H*-indazol-2-yl)aniline (**1**) (0.478 mmol), aryl/heteroaryl/aliphatic halide (**2**) (0.717 mmol), Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (20 mol %) and X-Phos (5 mol %) were also added to the seal tube, then DMF (3 mL) was added. The mixture was stirred at 100 °C for 8 h in an oil bath. After completion of the reaction, the mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (2×15 mL). The organic layers were collected, combined and washed by saturated sodium bicarbonate, brine and dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue obtained was purified by column chromatography using ethylacetate/hexane to give the desired product.

#### 11-Phenyl-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole(3aa):



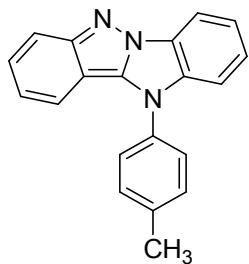
Gray solid; Yield: 72%; mp: 172-174 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21-8.18 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 3H), 7.70-7.63 (m, 3H), 7.56-7.52 (m, 2H), 7.47-7.44 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 153.6, 136.7, 135.8, 135.0, 130.2 (2C), 128.1, 127.1, 126.1, 124.9, 124.7 (2C), 122.3, 119.2, 118.1, 116.6, 112.3, 110.9, 102.9; HR-MS(ESI+) m/z calculated for [C<sub>19</sub>H<sub>14</sub>N<sub>3</sub>]<sup>+</sup> = [M + H]<sup>+</sup> 284.1187, found 284.1210.

#### 11-(*o*-Tolyl)-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3ab):



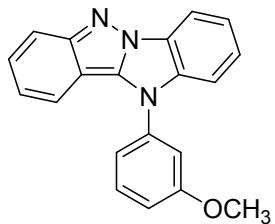
Gray solid; Yield: 68%; mp: 152-154 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.20 (t,  $J = 8.8$  Hz, 1H), 7.75 (d,  $J = 8.8$  Hz, 1H), 7.52 (t,  $J = 5.2$  Hz, 3H), 7.47-7.40 (m, 3H), 7.35 (t,  $J = 7.6$  Hz, 1H), 7.25-7.18 (m, 2H), 6.86 (t,  $J = 7.6$  Hz, 1H), 2.16 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6, 137.6, 136.4, 135.8, 134.1, 132.0, 129.7, 128.1, 127.6, 127.2, 125.7, 124.8, 121.9, 118.7, 118.0, 116.4, 112.3, 111.1, 103.0, 17.8; HR-MS(ESI+) m/z calculated for  $[\text{C}_{20}\text{H}_{16}\text{N}_3]^+ = [\text{M} + \text{H}]^+$  298.1344, found 298.1372.

**11-(*p*-Tolyl)-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3ac):**



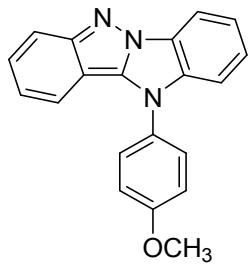
Off white solid; Yield: 70%; mp: 156-158 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.19-8.17 (m, 1H), 7.75 (d,  $J = 9.2$  Hz, 1H), 7.63-7.58 (m, 3H), 7.53 (d,  $J = 8.4$  Hz, 1H), 7.47-7.42 (m, 4H), 7.38-7.36 (m, 1H), 6.94-6.92 (m, 1H), 2.51(s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6, 138.3, 136.9, 135.2, 133.2, 130.8 (2C), 127.1, 126.0, 124.8, 124.7 (2C), 122.1, 119.3, 117.9, 116.5, 112.3, 110.9, 102.9, 21.2; HR-MS(ESI+) m/z calculated for  $[\text{C}_{20}\text{H}_{16}\text{N}_3]^+ = [\text{M} + \text{H}]^+$  298.1339, found 298.1338.

**11-(3-Methoxyphenyl)-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3ad):**



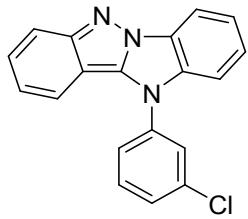
Gray solid; Yield: 72%; mp: 200-202 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18 (t,  $J = 4.6$  Hz, 1H), 7.76 (d,  $J = 9.2$  Hz, 1H), 7.67 (t,  $J = 4.4$  Hz, 1H), 7.61-7.55 (m, 2H), 7.44 (t,  $J = 4.4$  Hz, 2H), 7.39-7.33 (m, 2H), 7.29 (s, 1H), 7.06 (d,  $J = 8.4$  Hz, 1H), 6.95 (t,  $J = 7.4$  Hz, 1H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.0, 153.7, 136.9, 136.6, 135.0, 130.9, 127.1, 126.1, 124.9, 122.3, 119.3, 118.1, 116.8, 116.6, 113.7, 112.3, 111.1, 110.4, 102.9, 55.6; HR-MS(ESI+) m/z calculated for  $[\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}]^+ = [\text{M} + \text{H}]^+$  314.1288, found 314.1286.

**11-(4-Methoxyphenyl)-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3ae):**



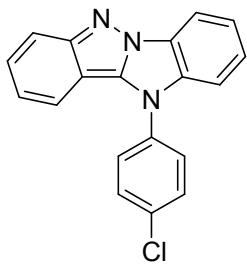
Brown solid; Yield: 70%; mp: 155-157 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18 (t,  $J = 4.6$  Hz, 1H), 7.75 (d,  $J = 8.8$  Hz, 1H), 7.65 (d,  $J = 8.8$  Hz, 2H), 7.55-7.37 (m, 5H), 7.18 (d,  $J = 8.8$  Hz, 2H), 6.92 (t,  $J = 7.6$  Hz, 1H), 3.95 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.4, 153.6, 137.2, 135.5, 128.4, 127.1, 126.5 (2C), 125.9, 124.8, 122.0, 119.1, 117.9, 116.5, 115.3 (2C), 112.2, 110.8, 102.8, 55.7; HR-MS(ESI+) m/z calculated for  $[\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}]^+ = [\text{M} + \text{H}]^+$  314.1288, found 314.1288.

**11-(3-Chlorophenyl)-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3af):**



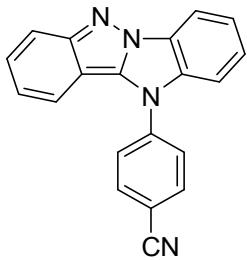
Gray solid; Yield: 70%; mp: 189-191 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.21-8.18 (m, 1H), 7.79-7.77 (m, 2H), 7.69-7.60 (m, 3H), 7.55-7.44 (m, 4H), 7.39 (t,  $J = 7.4$  Hz, 1H), 6.98 (t,  $J = 7.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6, 137.0, 135.9, 134.7, 131.2, 128.2, 127.2, 126.2, 125.1, 124.8 (2C), 122.7 (2C), 118.9, 118.5, 116.8, 112.5, 110.8, 102.8; HR-MS (ESI+) m/z calculated for  $[\text{C}_{19}\text{H}_{13}\text{ClN}_3]^+ = [\text{M} + \text{H}]^+$  318.0798, found 318.0796.

**11-(4-Chlorophenyl)-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3ag):**



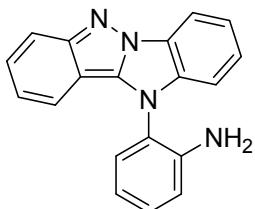
Off white solid; Yield: 68%; mp: 220-224 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.20-8.18 (m, 1H), 7.77 (d,  $J$  = 8.8 Hz, 1H), 7.71 (d,  $J$  = 8.8 Hz, 2H), 7.65 (d,  $J$  = 8.4 Hz, 2H), 7.61-7.58 (m, 1H), 7.52 (d,  $J$  = 8.4 Hz, 1H), 7.47-7.45 (m, 2H), 7.38 (t,  $J$  = 7.6 Hz, 1H), 6.95 (t,  $J$  = 7.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6, 134.9, 134.4, 133.8, 130.5 (2C), 130.2, 127.2, 126.1, 126.0 (2C), 125.0, 122.6, 118.9, 118.4, 116.8, 112.4, 110.7, 102.8; HR-MS (ESI+) m/z calculated for  $[\text{C}_{19}\text{H}_{13}\text{ClN}_3]^+ = [\text{M} + \text{H}]^+$  318.0793, found 318.0794.

**4-(11*H*-Benzo[4,5]imidazo[1,2-*b*]indazol-11-yl)benzonitrile (3ah):**



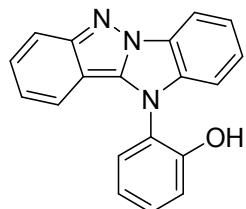
Brown solid; Yield: 70%; mp: 201-205 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.20 (t,  $J$  = 4.6 Hz, 1H), 8.00 (d,  $J$  = 8.4 Hz, 2H), 7.94 (d,  $J$  = 8.4 Hz, 2H), 7.79 (d,  $J$  = 9.2 Hz, 1H), 7.67 (t,  $J$  = 4.4 Hz, 1H), 7.54-7.49 (m, 3H), 7.40 (t,  $J$  = 7.6 Hz, 1H), 7.01 (t,  $J$  = 7.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6, 139.8, 134.3 (2C), 135.5, 134.2, 127.3, 126.5, 125.4, 124.6 (2C), 123.4, 119.0, 118.7, 117.9, 117.1, 112.7, 111.2, 110.8, 102.9; HR-MS(ESI+) m/z calculated for  $[\text{C}_{20}\text{H}_{13}\text{N}_4]^+ = [\text{M} + \text{H}]^+$  309.1135, found 309.1135.

**2-(11*H*-Benzo[4,5]imidazo[1,2-*b*]indazol-11-yl)aniline (3ai):**



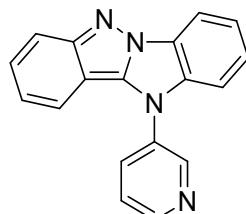
Brown solid; Yield: 65%; mp: 207-209 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.12 (d,  $J = 5.2$  Hz, 1H), 7.60 (d,  $J = 7.6$  Hz, 1H), 7.49-7.45(m, 2H), 7.34-7.30 (m, 5H), 7.06 (d,  $J = 6.4$  Hz, 1H), 6.85-6.76 (m, 2H), 5.44 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  153.0, 146.0, 137.6, 135.8, 130.6, 128.5, 127.0, 125.9, 125.1, 122.0, 119.8, 119.1, 117.6, 116.8, 116.7, 116.2, 112.2, 112.1, 103.1; HR-MS(ESI+) m/z calculated for  $[\text{C}_{19}\text{H}_{15}\text{N}_4]^+ = [\text{M} + \text{H}]^+$  299.1296, found 299.1304.

**2-(11*H*-Benzo[4,5]imidazo[1,2-*b*]indazol-11-yl)phenol (3aj):**



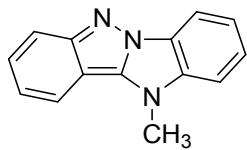
Off white solid; Yield: 65%; mp: 301-305 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  10.35 (s, 1H), 8.14 (d,  $J = 6.8$  Hz, 1H), 7.66-7.63 (m, 2H), 7.49 (t,  $J = 7.0$  Hz, 3H), 7.42 (d,  $J = 6.4$  Hz, 1H), 7.31-7.27 (m, 3H), 7.12 (t,  $J = 7.6$  Hz, 1H), 6.88 (t,  $J = 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  153.1, 152.6, 137.1, 135.3, 130.4, 128.1, 126.7, 124.9 (2C), 121.8, 121.7, 119.9, 119.2, 117.5, 117.4, 115.9, 111.9, 111.5, 102.6; HR-MS(ESI+) m/z calculated for  $[\text{C}_{19}\text{H}_{14}\text{N}_3\text{O}]^+ = [\text{M} + \text{H}]^+$  300.1137, found 300.1140.

**11-(Pyridin-3-yl)-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3ak):**



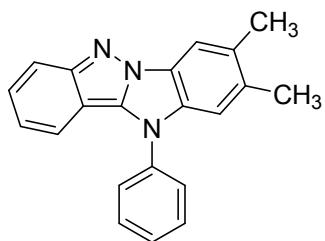
Off white solid; Yield: 68%; mp: 193-195 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.13 (s, 1H), 8.81 (d,  $J = 1.2$  Hz, 1H), 8.22 (d,  $J = 2.4$  Hz, 1H), 8.12 (d,  $J = 6.0$  Hz, 1H), 7.78 (d,  $J = 8.4$  Hz, 1H), 7.66-7.62 (m, 2H), 7.53-7.46 (m, 3H), 7.39 (t,  $J = 6.6$  Hz, 1H), 6.98 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6, 149.1, 146.1, 136.1, 134.8, 132.9, 131.9, 127.3, 126.3, 125.2, 124.6, 123.0, 118.7, 118.6, 116.9, 112.6, 110.5, 102.7; HR-MS (ESI+) m/z calculated for  $[\text{C}_{18}\text{H}_{13}\text{N}_4]^+ = [\text{M} + \text{H}]^+$  285.1140, found 285.1146.

**11-Methyl-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3al):**



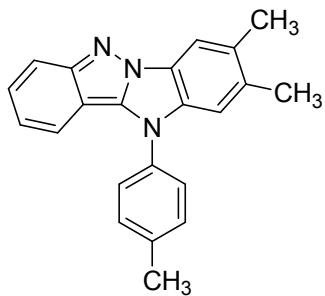
Brown solid; Yield: 65%; mp: 153-157 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11 (d,  $J = 8.0$  Hz, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.73 (d,  $J = 8.8$  Hz, 1H), 7.45 (s, 2H), 7.37 (t,  $J = 6.8$  Hz, 2H), 7.00 (t,  $J = 7.6$  Hz, 1H), 4.09 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.3, 138.1, 135.7, 127.1, 125.4, 124.4, 121.3, 118.4, 117.9, 116.3, 112.1, 109.7, 102.8, 31.1; HR-MS(ESI+) m/z calculated for  $[\text{C}_{14}\text{H}_{12}\text{N}_3]^+ = [\text{M} + \text{H}]^+$  222.1031, found 222.1061.

**2,3-Dimethyl-11-phenyl-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3ba):**



Gray solid; Yield: 71%; mp: 169-171 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (s, 1H), 7.75 (d,  $J = 8.4$  Hz, 3H), 7.67 (t,  $J = 8.0$  Hz, 2H), 7.53 (d,  $J = 8.0$  Hz, 2H), 7.40 (s, 1H), 7.35 (t,  $J = 7.6$  Hz, 1H), 6.92 (t,  $J = 7.4$  Hz, 1H), 2.47 (s, 3H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.4, 136.3, 136.1, 134.1, 133.4, 131.4, 130.1 (2C), 127.8, 126.8, 124.6 (2C), 124.4, 119.1, 117.8, 116.5, 112.6, 111.4, 103.1, 20.6, 20.3; HR-MS(ESI+) m/z calculated for  $[\text{C}_{21}\text{H}_{18}\text{N}_3]^+ = [\text{M} + \text{H}]^+$  312.1495, found 312.1493.

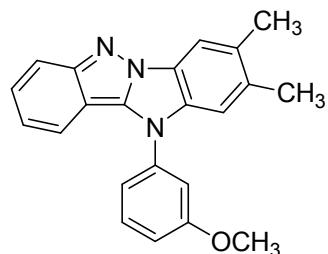
**2,3-Dimethyl-11-(*p*-tolyl)-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3bc):**



Gray solid; Yield: 70%; mp: 222-224 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (s, 1H), 7.73 (d,  $J = 8.8$  Hz, 1H), 7.60 (d,  $J = 8.0$  Hz, 2H), 7.52 (d,  $J = 8.4$  Hz, 1H), 7.45 (d,  $J = 8.0$  Hz, 2H), 7.34 (t,  $J = 7.4$  Hz, 2H), 6.89 (t,  $J = 7.4$  Hz, 1H), 2.50 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.3, 137.9, 136.6, 134.0, 133.6, 133.5, 131.2, 130.7 (2C), 126.7, 124.6

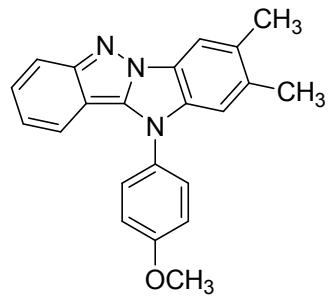
(2C), 124.3, 119.2, 117.6, 116.4, 112.6, 111.4, 103.1, 21.2, 20.6, 20.2; HR-MS(ESI+) m/z calculated for  $[C_{22}H_{20}N_3]^+ = [M + H]^+$  326.1657, found 326.1663.

**11-(3-Methoxyphenyl)-2,3-dimethyl-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3bd):**



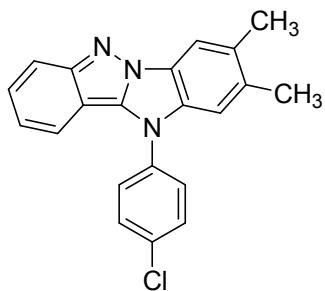
Off white solid; Yield: 69%; mp 226-228 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.94 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.60-7.54 (m, 2H), 7.43 (s, 1H), 7.37-7.32 (m, 2H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 3.91 (s, 3H), 2.46 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.9, 153.4, 137.2, 136.3, 134.1, 133.4, 131.4, 130.9, 126.7, 124.4, 119.2, 117.8, 116.7, 116.5, 113.3, 112.6, 111.6, 110.3, 103.1, 55.6, 20.6, 20.2; HR-MS(ESI+) m/z calculated for  $[C_{22}H_{20}N_3O]^+ = [M + H]^+$  342.1606, found 342.1606.

**11-(4-Methoxyphenyl)-2,3-dimethyl-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3be):**



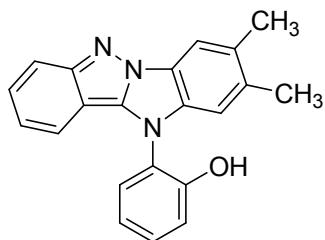
Off white solid; Yield: 70%; mp: 111-115 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.93 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.63-7.60 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.36-7.31 (m, 1H), 7.28 (s, 1H), 7.17-7.14 (m, 2H), 6.91-6.87 (m, 1H), 3.93 (s, 3H), 2.45 (s, 3H), 2.39 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.1, 153.3, 136.8, 134.0, 133.9, 131.1, 128.7, 126.7, 126.3 (2C), 124.2, 119.0, 117.6, 116.3, 115.2 (2C), 112.5, 111.2, 103.0, 55.6, 20.6, 20.2; HR-MS(ESI+) m/z calculated for  $[C_{22}H_{20}N_3O]^+ = [M + H]^+$  342.1601, found 342.1599.

**11-(4-Chlorophenyl)-2,3-dimethyl-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole (3bg):**



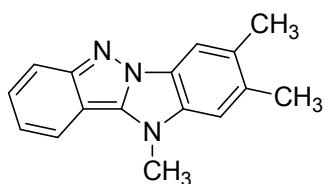
Brown solid; Yield: 70%; mp 252-254 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (s, 1H), 7.74 (d,  $J$  = 8.8 Hz, 1H), 7.70-7.68 (m, 2H), 7.65-7.63 (m, 2H), 7.50 (d,  $J$  = 8.4 Hz, 1H), 7.37-7.33 (m, 2H), 6.93 (t,  $J$  = 7.4 Hz, 1H), 2.46 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.3, 136.0, 134.7, 134.3, 133.4, 133.3, 131.7, 130.4 (2C), 126.8, 125.8 (2C), 124.5, 118.8, 118.1, 116.6, 112.7, 111.2, 102.9, 20.6, 20.2; HR-MS(ESI+) m/z calculated for  $[\text{C}_{21}\text{H}_{17}\text{ClN}_3]^+ = [\text{M} + \text{H}]^+$  346.1106, found 346.1107.

**2-(2,3-Dimethyl-11H-benzo[4,5]imidazo[1,2-b]indazol-11-yl)phenol (3bj):**



Off white solid; Yield: 66%; mp: 226-230 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  10.28 (s, 1H), 7.91 (s, 1H), 7.61 (dd,  $J$  = 23.0 & 6.4 Hz, 2H), 7.47 (t,  $J$  = 7.2 Hz, 1H), 7.27-7.20 (m, 4H), 7.11 (t,  $J$  = 7.2 Hz, 1H), 6.84 (t,  $J$  = 7.0 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  153.0, 152.2, 136.8, 134.0, 133.8, 130.8, 130.4, 128.1, 126.6, 123.1, 121.8, 120.1, 118.9, 117.4, 117.3, 115.5, 112.0, 111.7, 102.8, 19.9, 19.6; HR-MS(ESI+) m/z calculated for  $[\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}]^+ = [\text{M} + \text{H}]^+$  328.1450, found 328.1451.

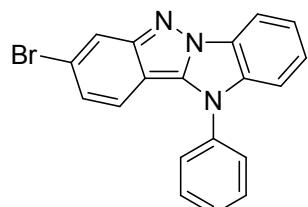
**2,3,11-Trimethyl-11H-benzo[4,5]imidazo[1,2-b]indazole (3bl):**



Brown solid; Yield: 65%; mp: 157-159 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (s, 1H), 7.81 (d,  $J$  = 8.4 Hz, 1H), 7.70 (d,  $J$  = 8.8 Hz, 1H), 7.35 (t,  $J$  = 7.6 Hz, 1H), 7.20 (s, 1H), 6.98 (t,  $J$  = 7.2 Hz, 1H), 4.03 (s, 3H), 2.44 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.1, 137.9, 134.2, 133.7,

130.3, 126.7, 123.8, 118.3, 117.6, 116.2, 112.4, 110.2, 103.1, 31.0, 20.6, 20.2; HR-MS(ESI+) m/z calculated for  $[C_{16}H_{16}N_3]^+ = [M + H]^+$  250.1344, found 250.1368.

**8-Bromo-11-phenyl-11*H*-benzo[4,5]imidazo[1,2-*b*]indazole(3ca):**

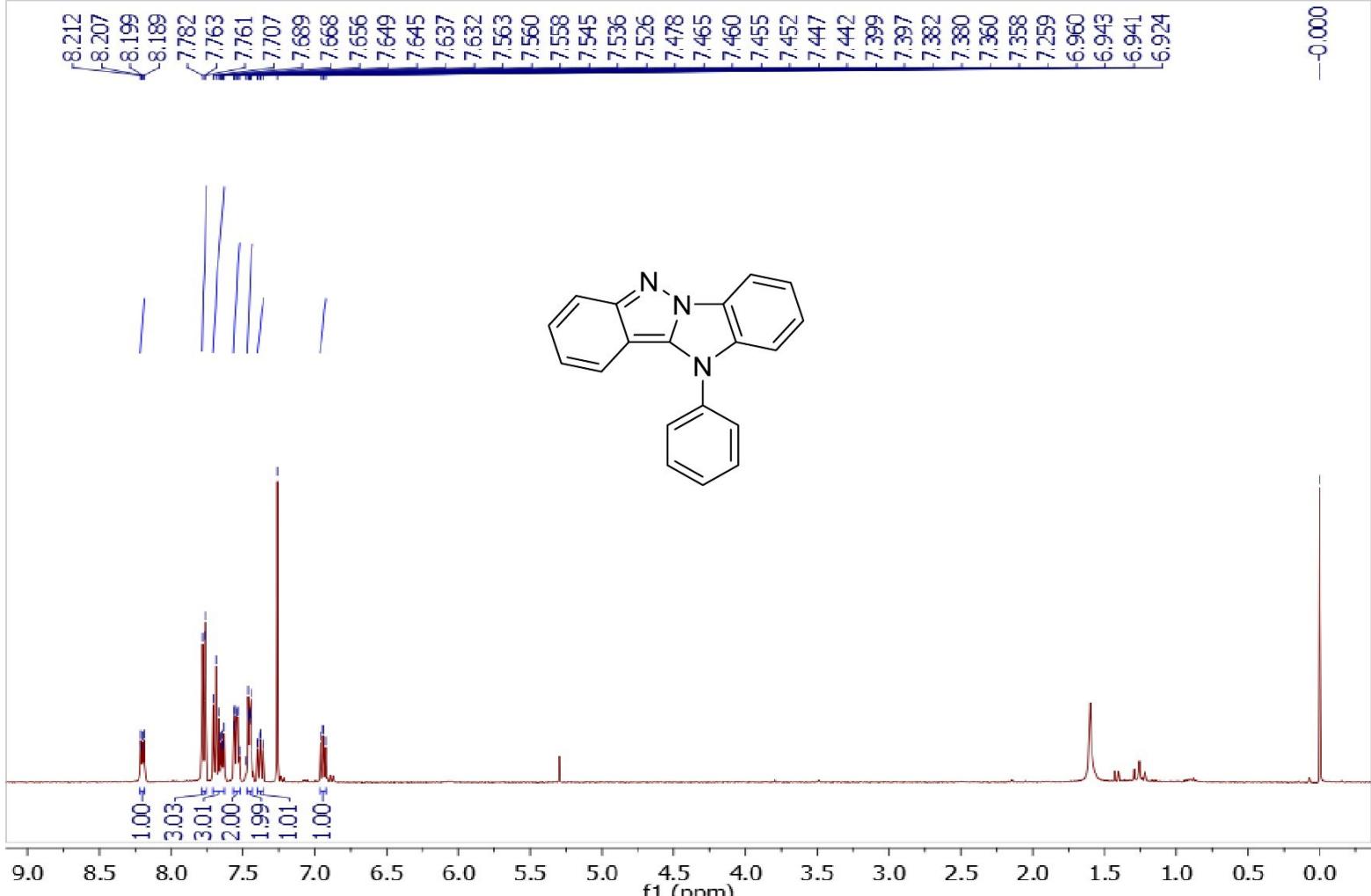


Brown solid; Yield: 70%; mp: 170-174 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.17 (t,  $J = 4.2$  Hz, 1H), 7.70 (t,  $J = 7.4$  Hz, 4H), 7.65-7.62 (m, 3H), 7.59-7.54 (m, 1H), 7.49-7.42 (m, 2H), 7.41 (d,  $J = 10.4$  Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  151.8, 135.8, 135.5, 135.1, 130.5, 130.4, 128.5, 128.4, 127.8, 125.8, 125.3, 124.7, 122.6, 121.2, 118.3, 112.4, 111.1, 110.5, 103.9; HR-MS(ESI+) m/z calculated for  $[C_{19}H_{13}BrN_3]^+ = [M + H]^+$  362.0293, found 362.0294.

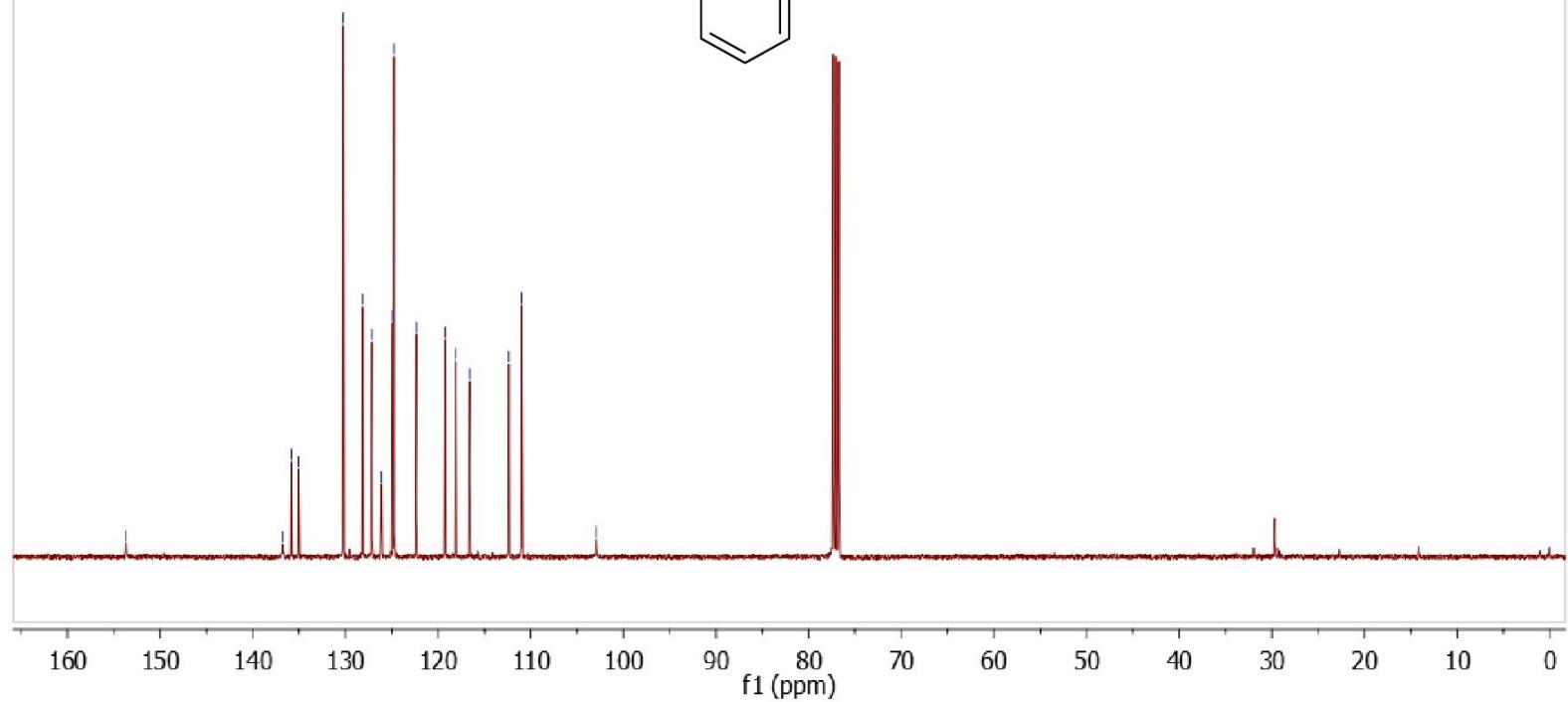
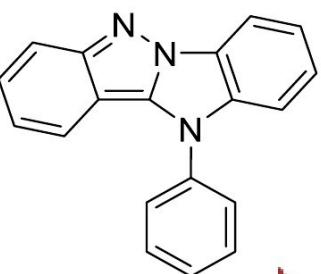
**References:**

1. J. Hu, Y. Cheng, Y. Yang and Y. Rao, *Chem. Commun.*, 2011, **47**, 10133;
2. S. Vidyacharan, A. Murugan and D. S. Sharada, *J. Org. Chem.*, 2016, **81**, 2837.
3. S. Vidyacharan, A. Sagar, N. C. Chaitra, D. S. Sharada, *RSC Adv.*, 2014, **4**, 34232.

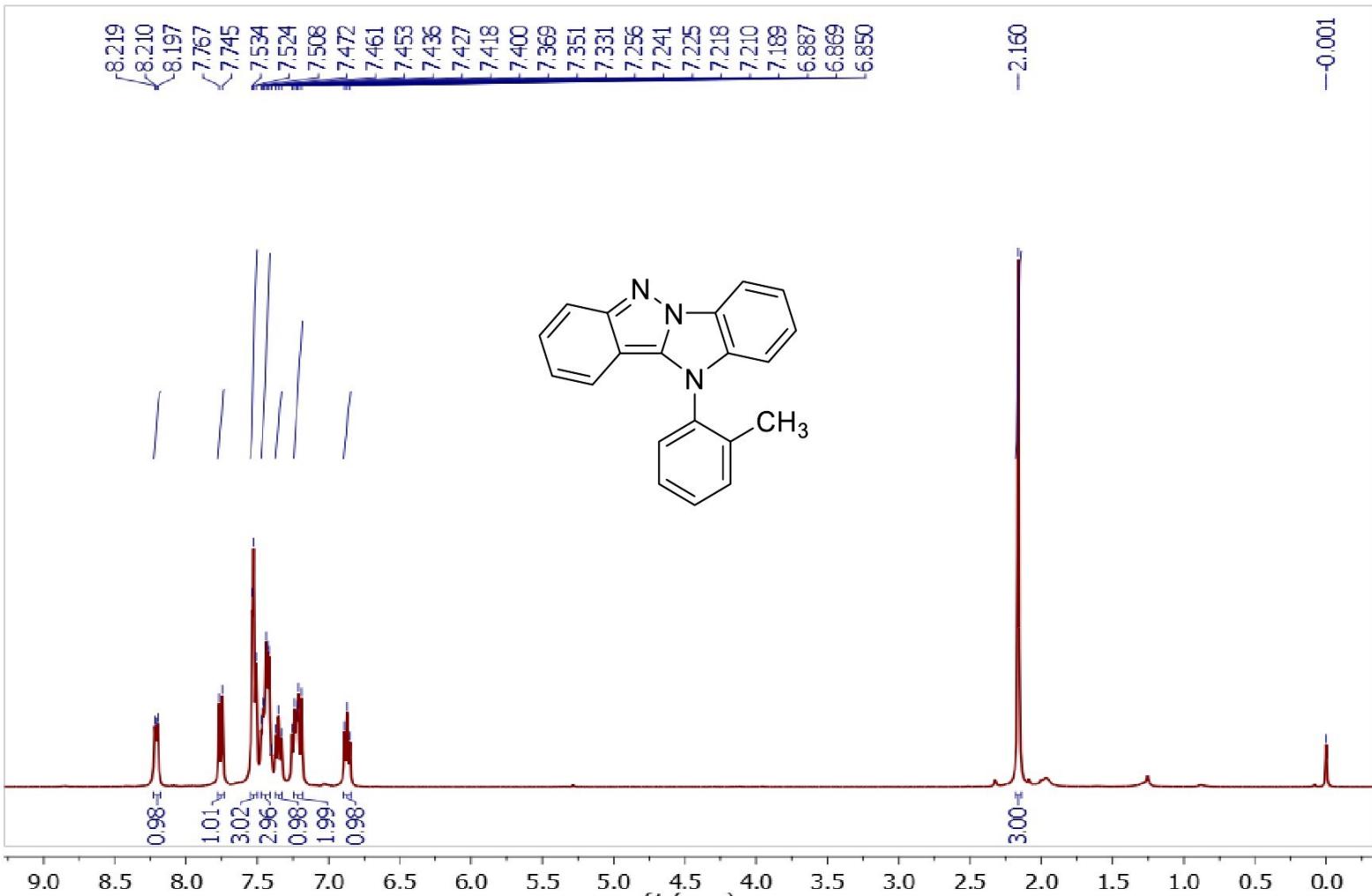
# Compound-3aa



— 153.67  
— 136.75  
— 135.84  
— 135.04  
— 130.24  
— 128.14  
— 127.15  
— 126.08  
— 124.91  
— 124.76  
— ~ 122.35  
— ~ 119.24  
— 118.11  
— 116.60  
— 112.35  
— 110.97  
— 102.94

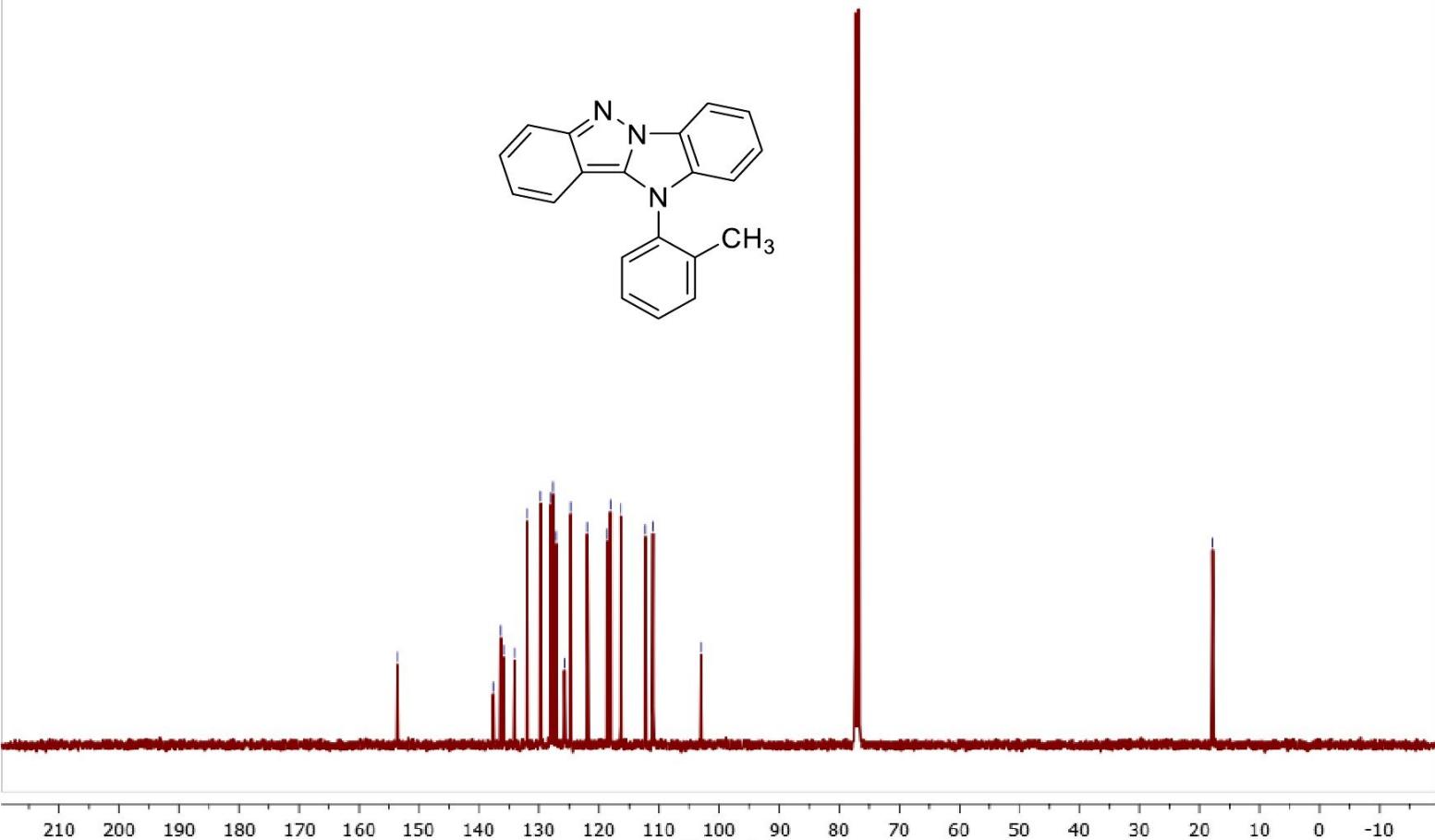
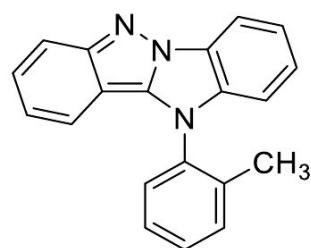


## Compound-3ab



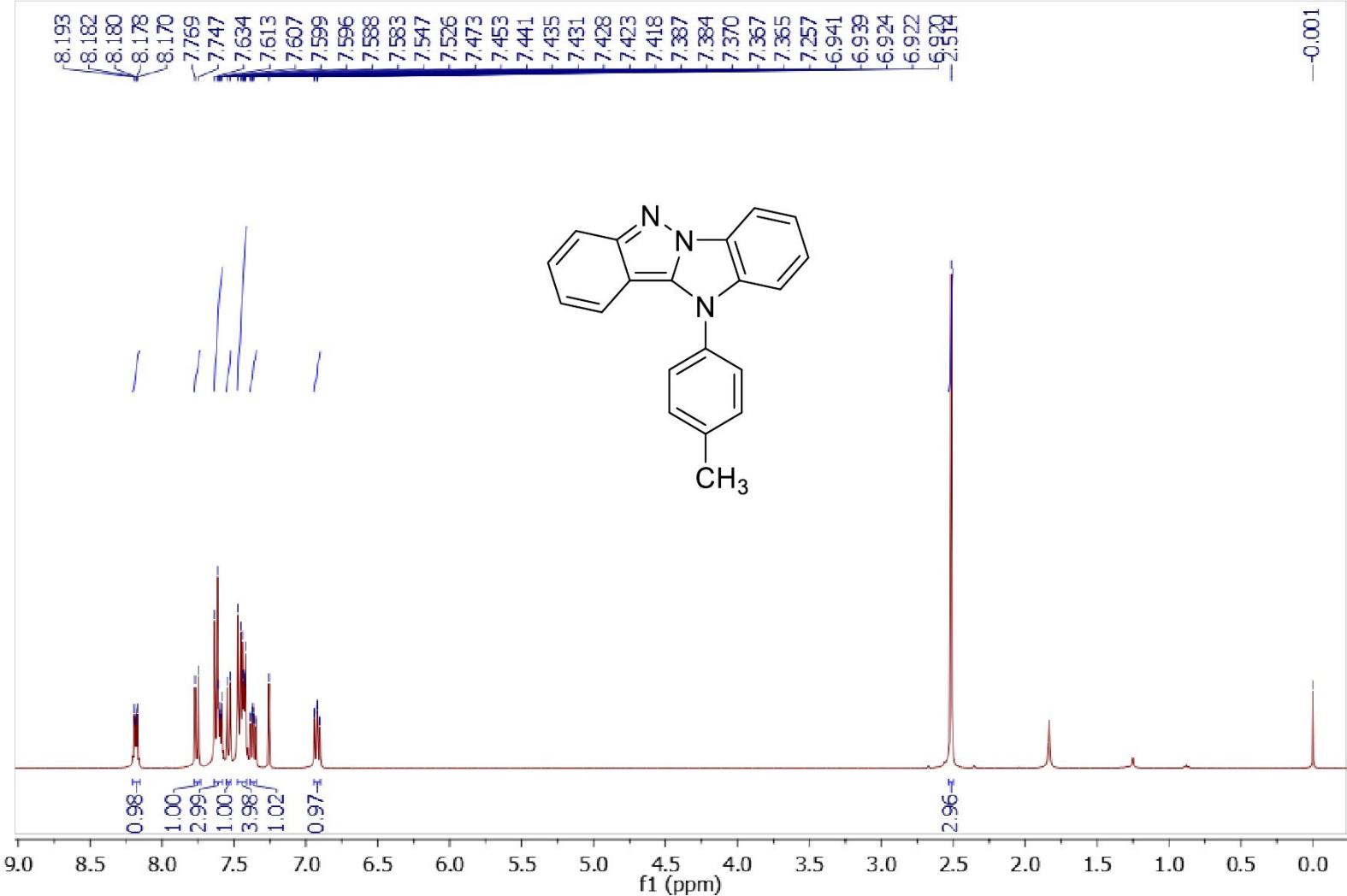
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-135.44  
-135.86  
-134.08  
-132.02  
-129.75  
-128.11  
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-127.18  
-125.75  
-124.78  
-121.96  
-118.71  
-118.07  
-116.41  
-112.28  
-111.08  
-103.01

-1781



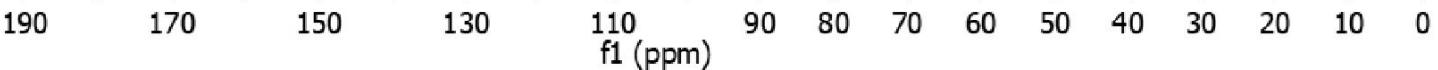
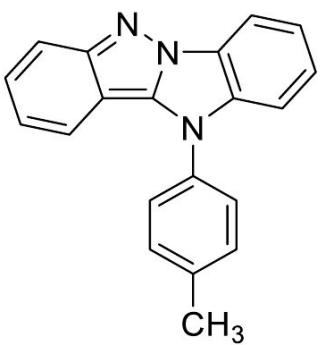
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

# Compound-3ac

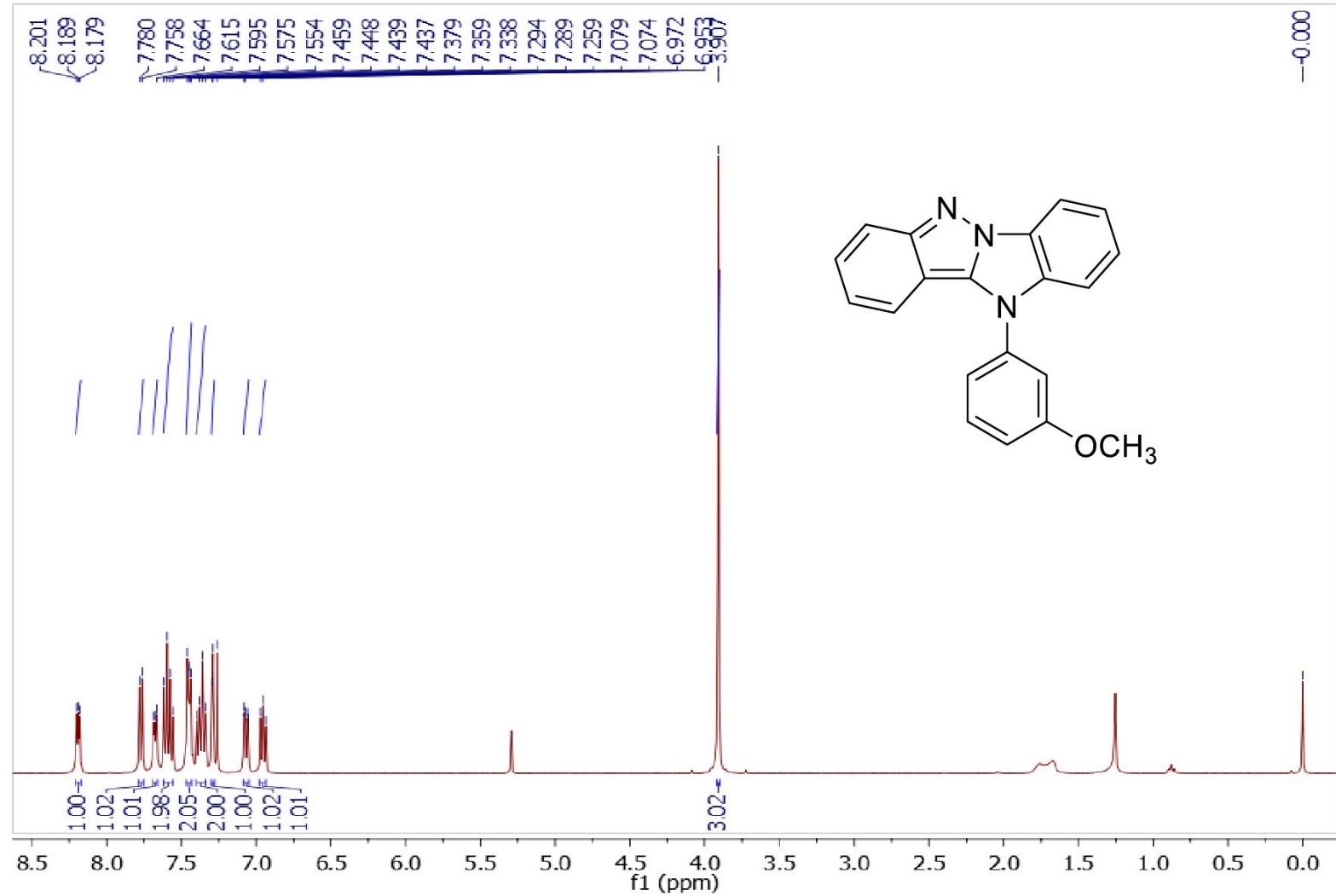


-21.27

— 153.65  
— 138.29  
— 136.96  
— 135.24  
— 133.19  
— 130.78  
— 127.11  
— 126.01  
— 124.82  
— 124.73  
— 122.17  
— 119.28  
— 117.96  
— 116.54  
— 112.31  
— 110.97  
— 102.90

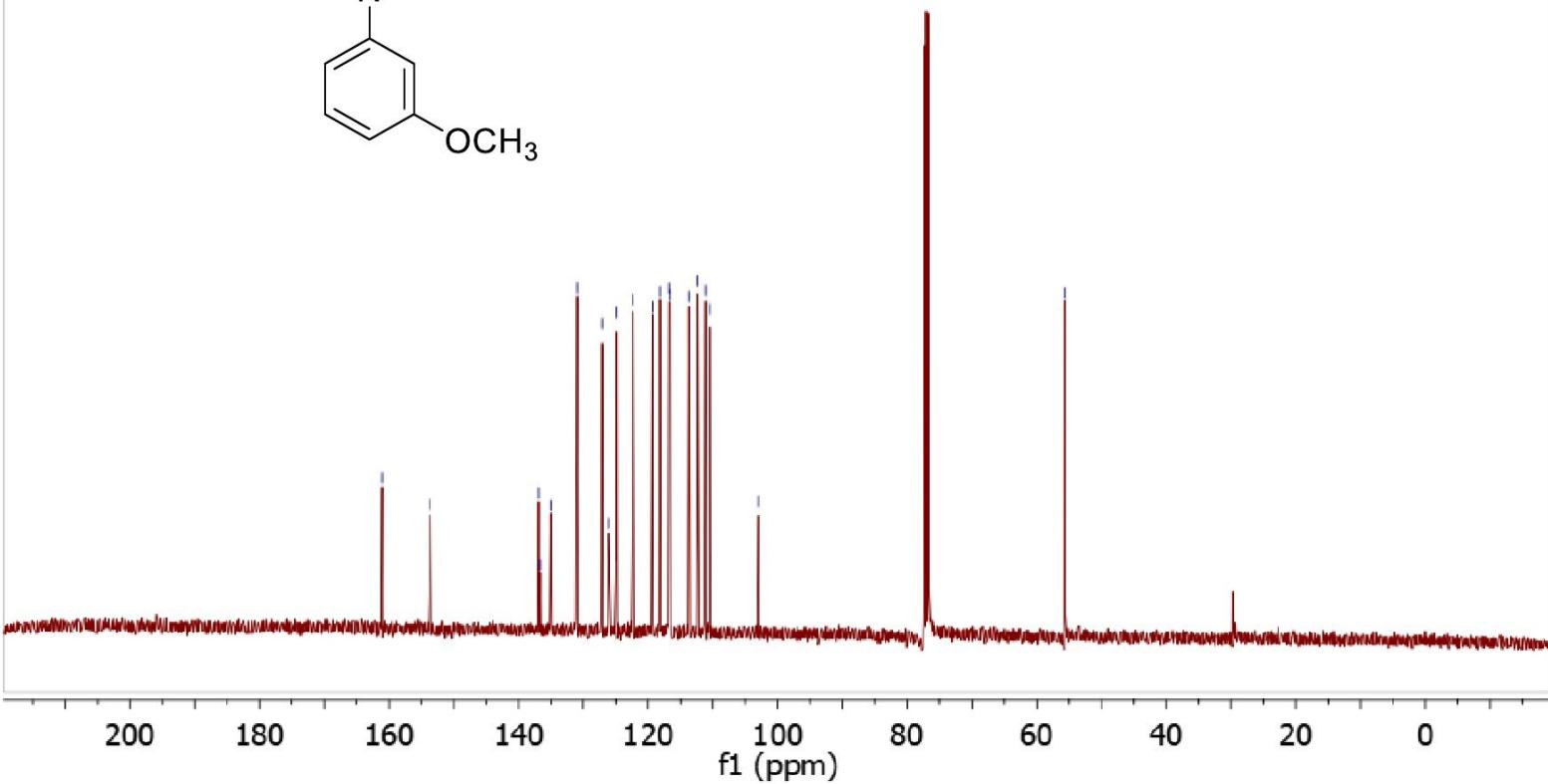
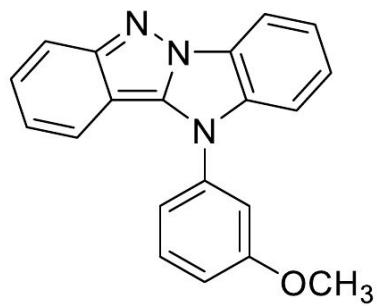


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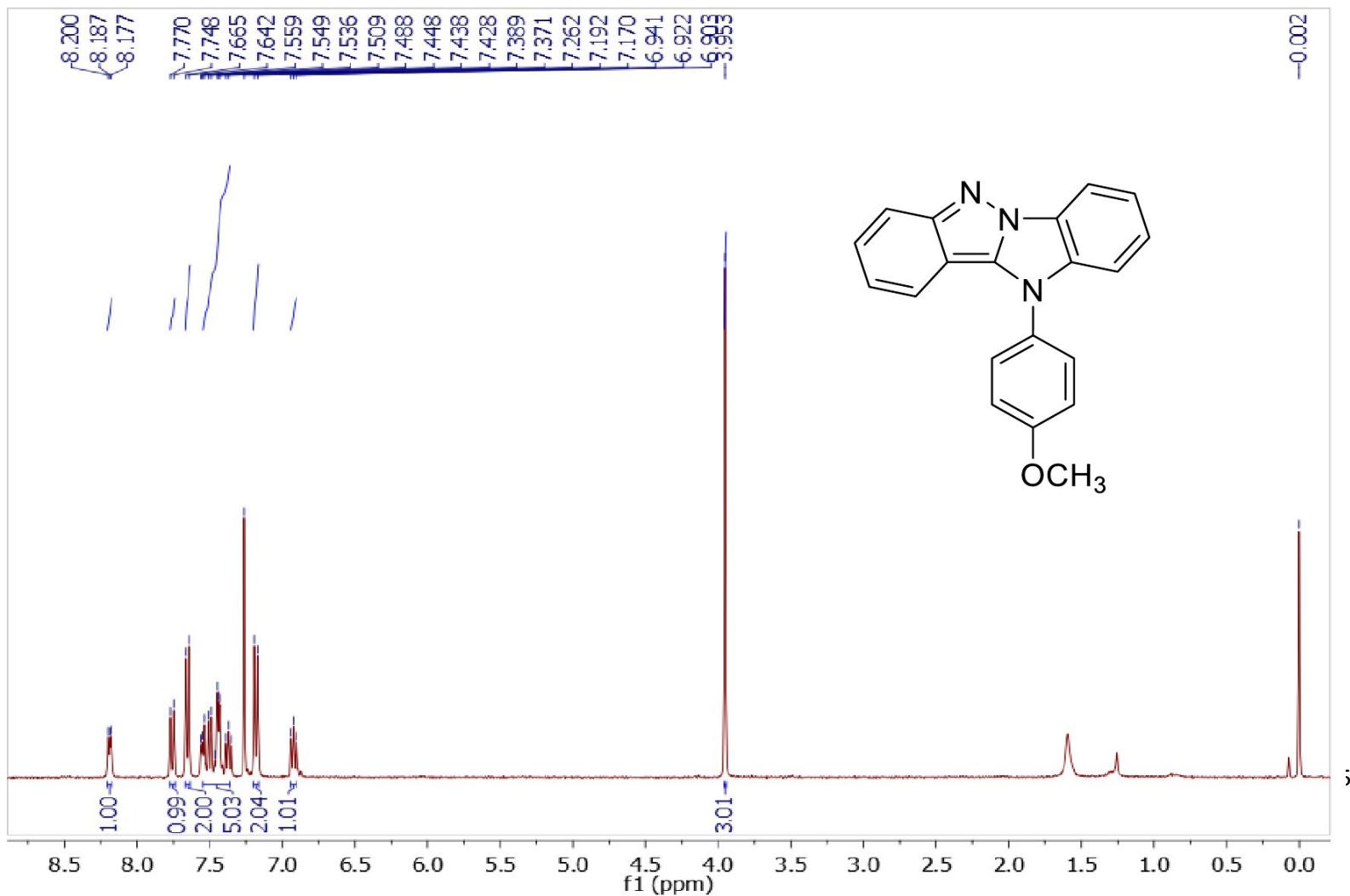


-161.03  
-153.69  
-136.91  
136.67  
135.02  
130.97  
127.10  
126.11  
124.90  
122.35  
119.31  
118.13  
116.81  
116.65  
113.71  
112.33  
111.16  
110.47  
102.96

-55.65

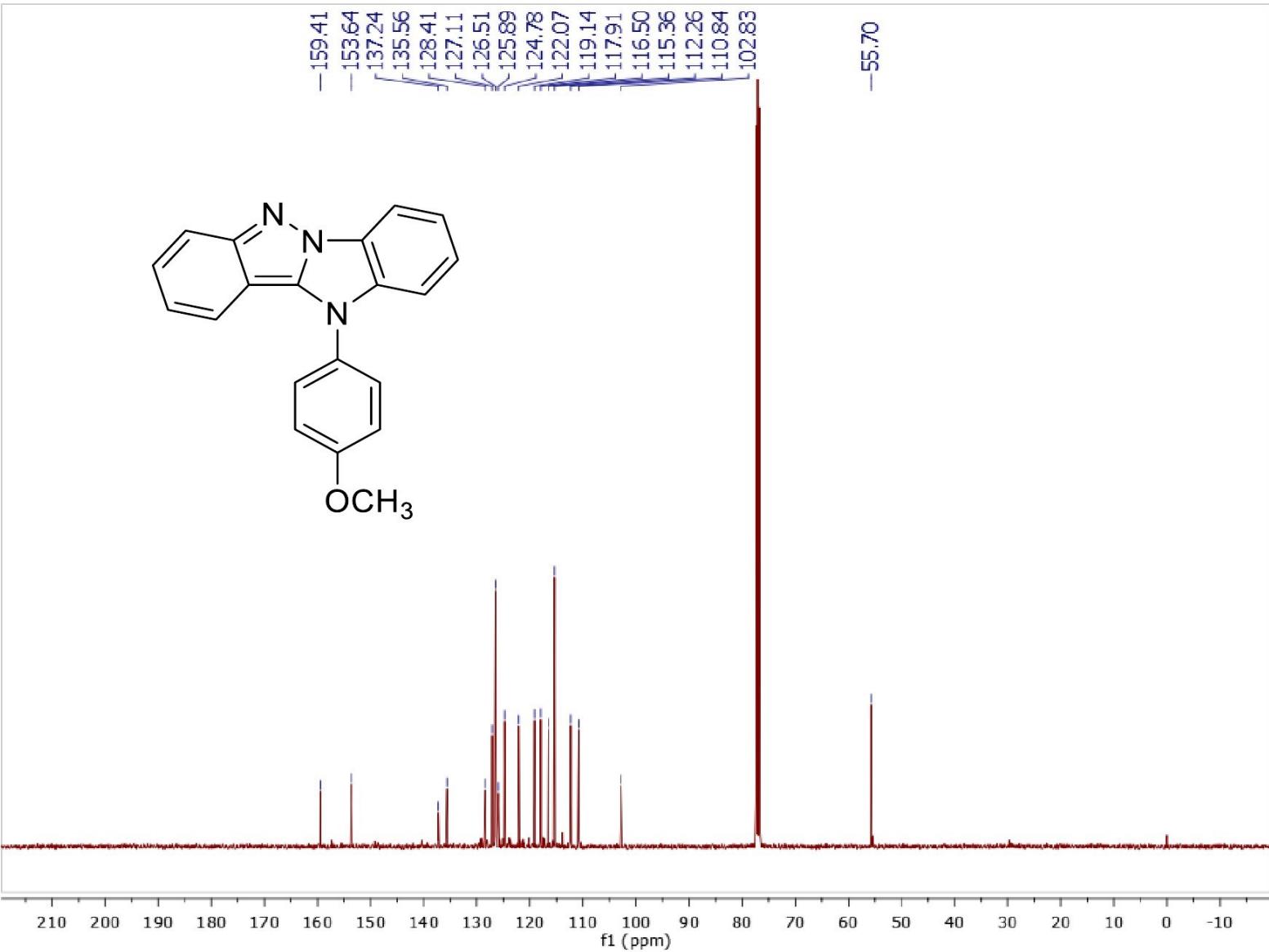
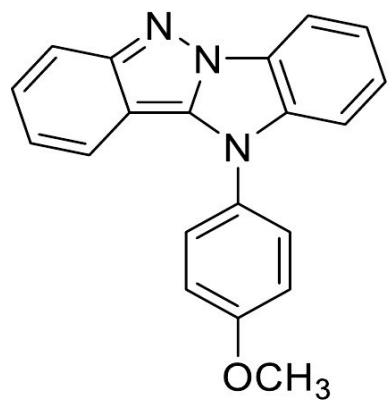


# Compound-3ae

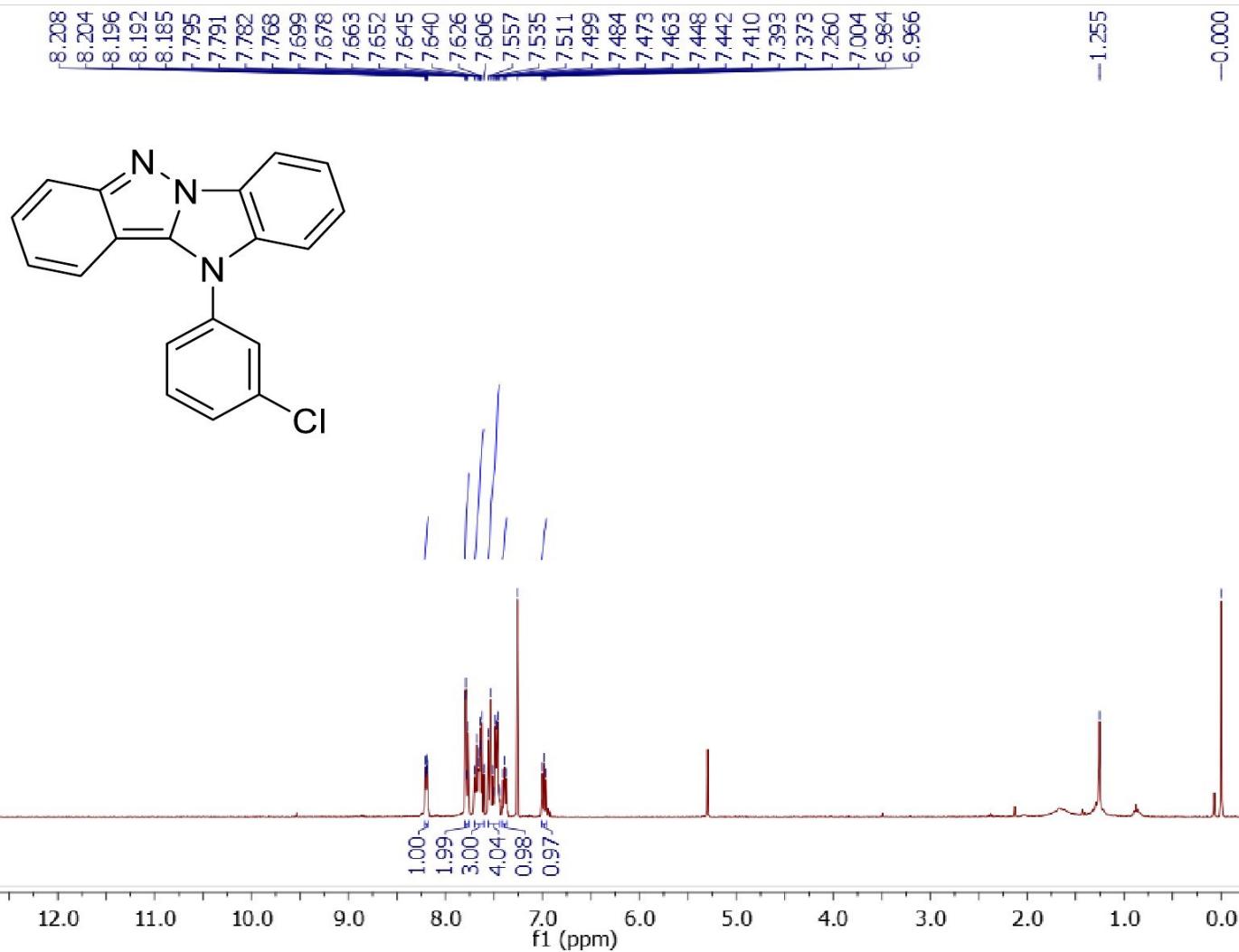


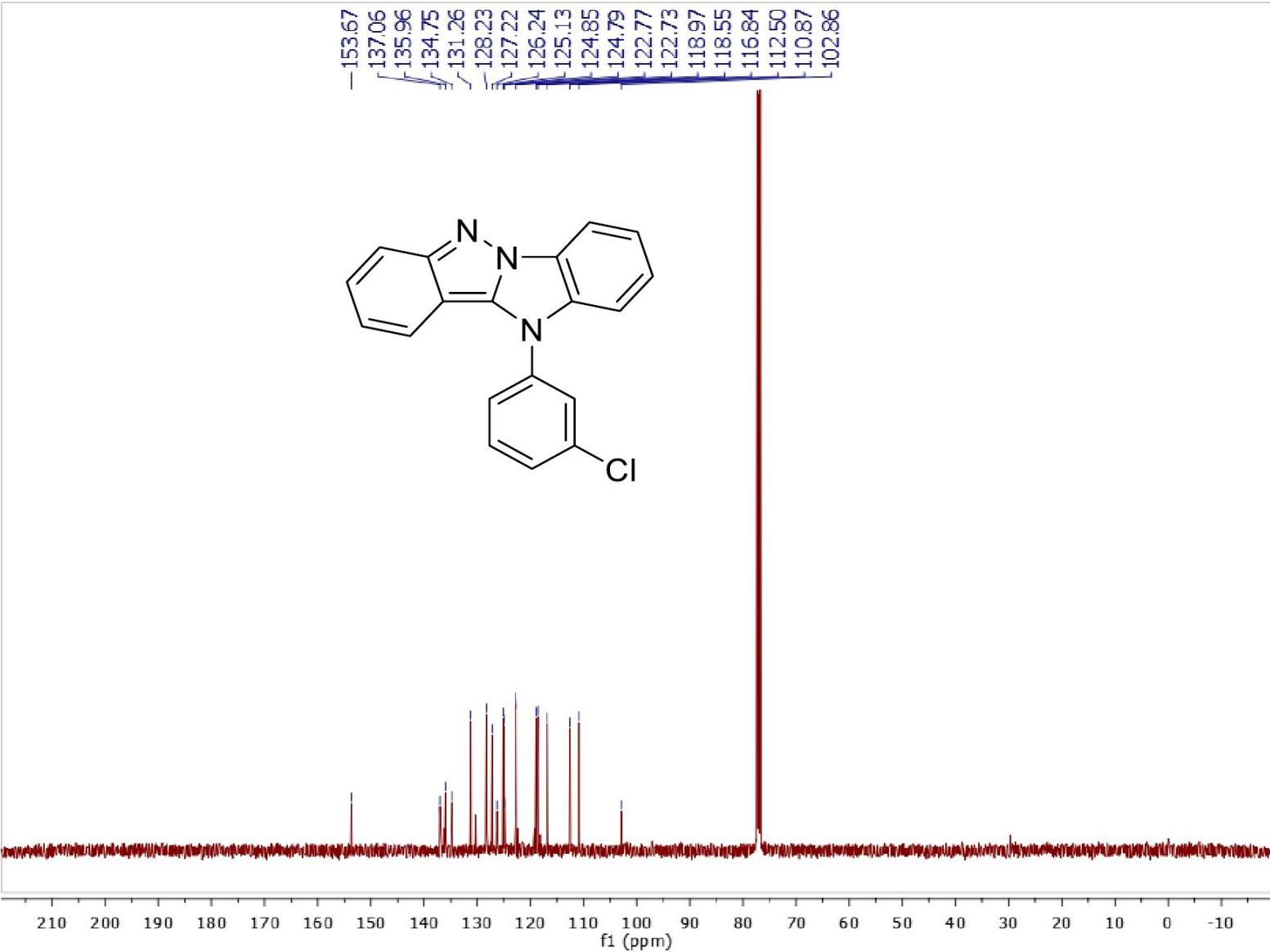
-159.41  
-153.64  
-137.24  
135.56  
135.56  
128.41  
127.11  
126.51  
125.89  
124.78  
122.07  
119.14  
117.91  
116.50  
115.36  
112.26  
110.84  
102.83

-55.70



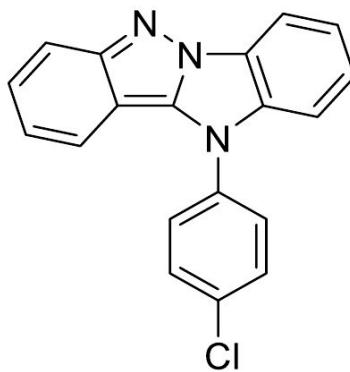
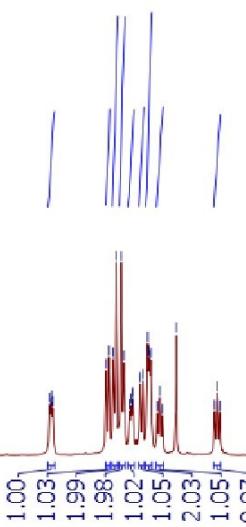
# Compound-3af





# Compound-3ag

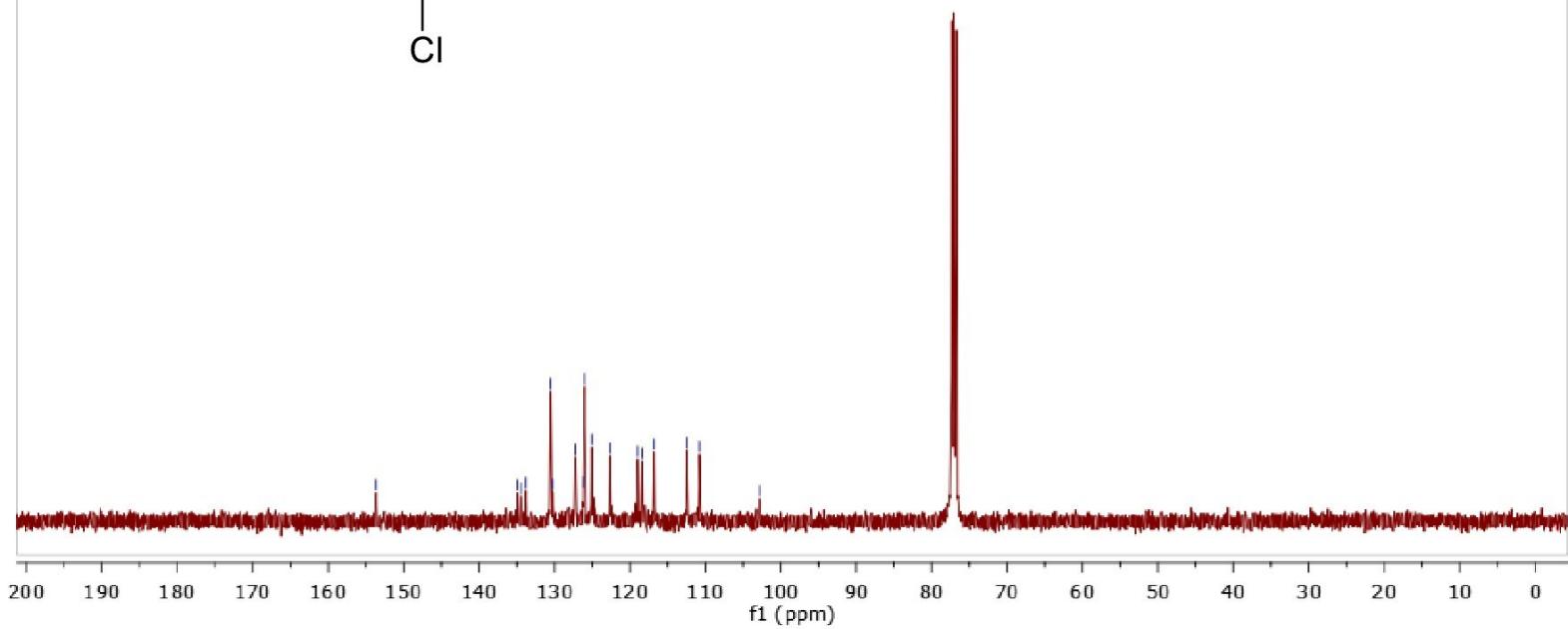
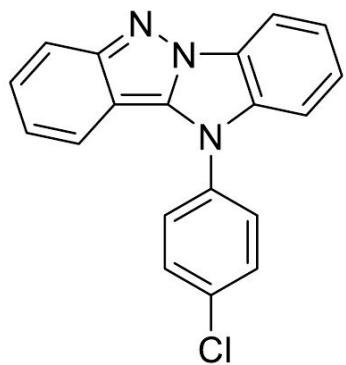
8.200  
8.194  
8.185  
8.178  
7.781  
7.759  
7.729  
7.707  
7.670  
7.649  
7.608  
7.600  
7.590  
7.585  
7.530  
7.509  
7.472  
7.465  
7.458  
7.449  
7.402  
7.384  
7.364  
7.261  
6.978  
6.959  
6.940



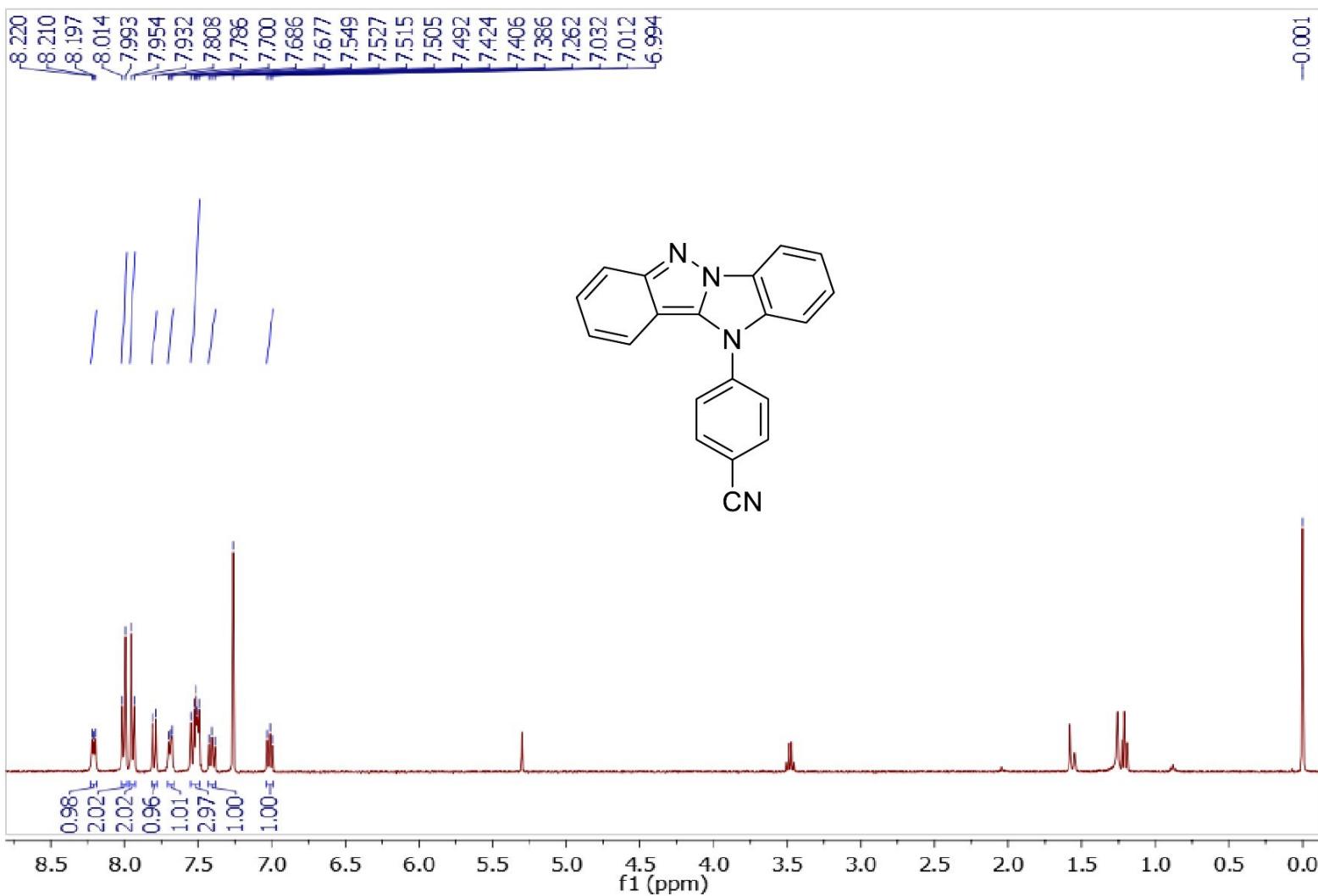
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

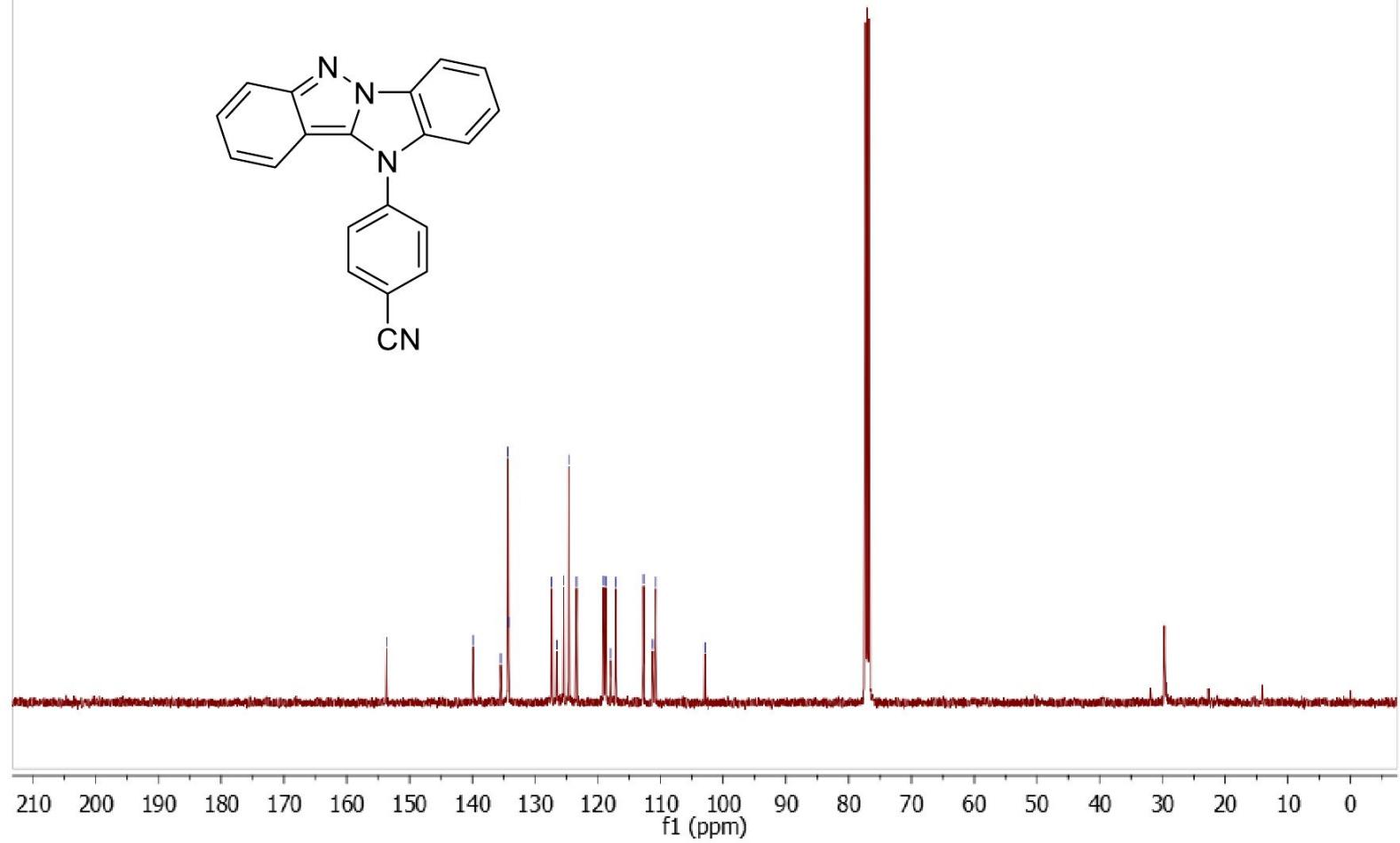
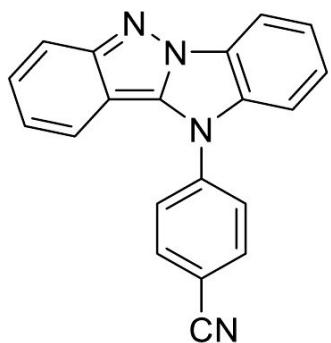
-153.66  
-134.91  
-134.41  
-133.78  
-130.49  
-130.24  
-127.20  
-126.17  
-126.01  
-125.05  
-122.62  
-118.94  
-118.39  
-116.79  
-112.46  
-110.74  
-102.78



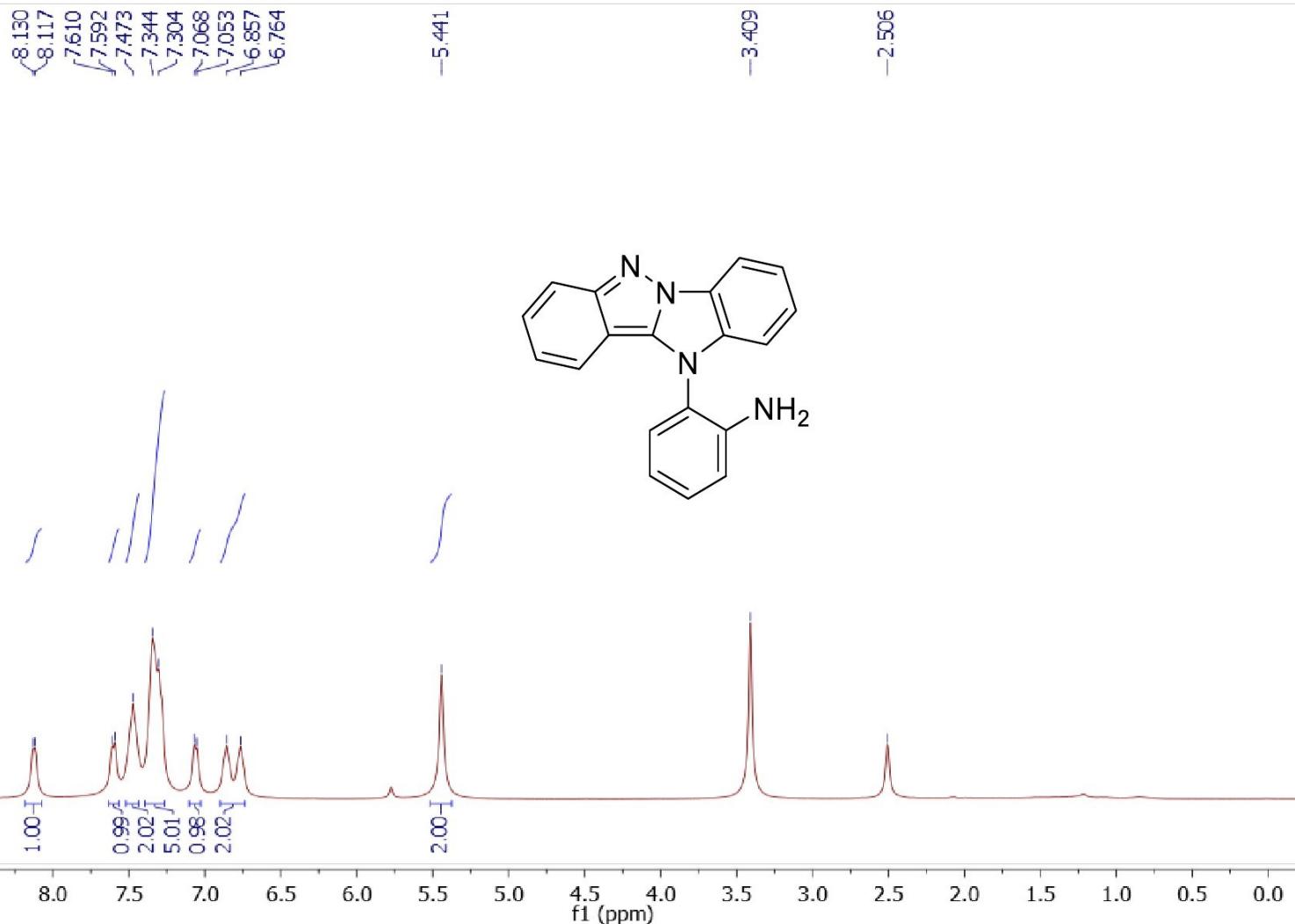
# Compound-3ah



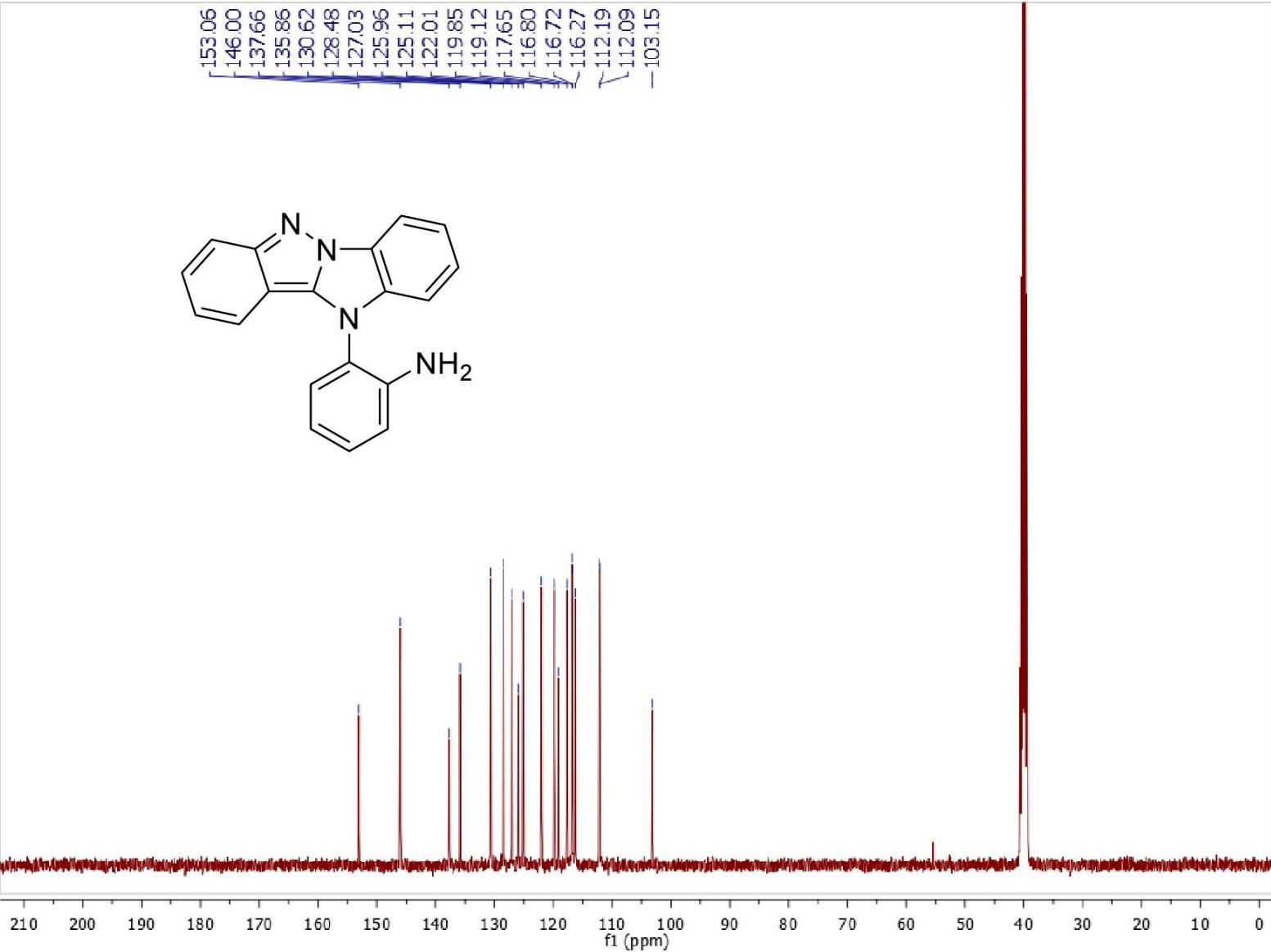
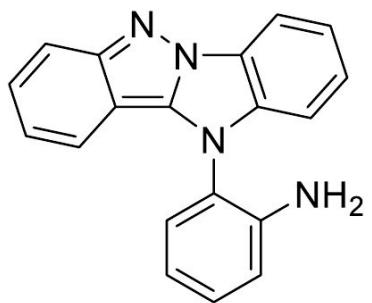
— 153.63  
— 139.84  
— 135.49  
— 134.29  
— 134.22  
— 127.33  
— 126.53  
— 125.40  
— 124.58  
— 123.38  
— 119.03  
— 118.75  
— 117.92  
— 117.11  
— 112.70  
— 111.23  
— 110.80  
— 102.90



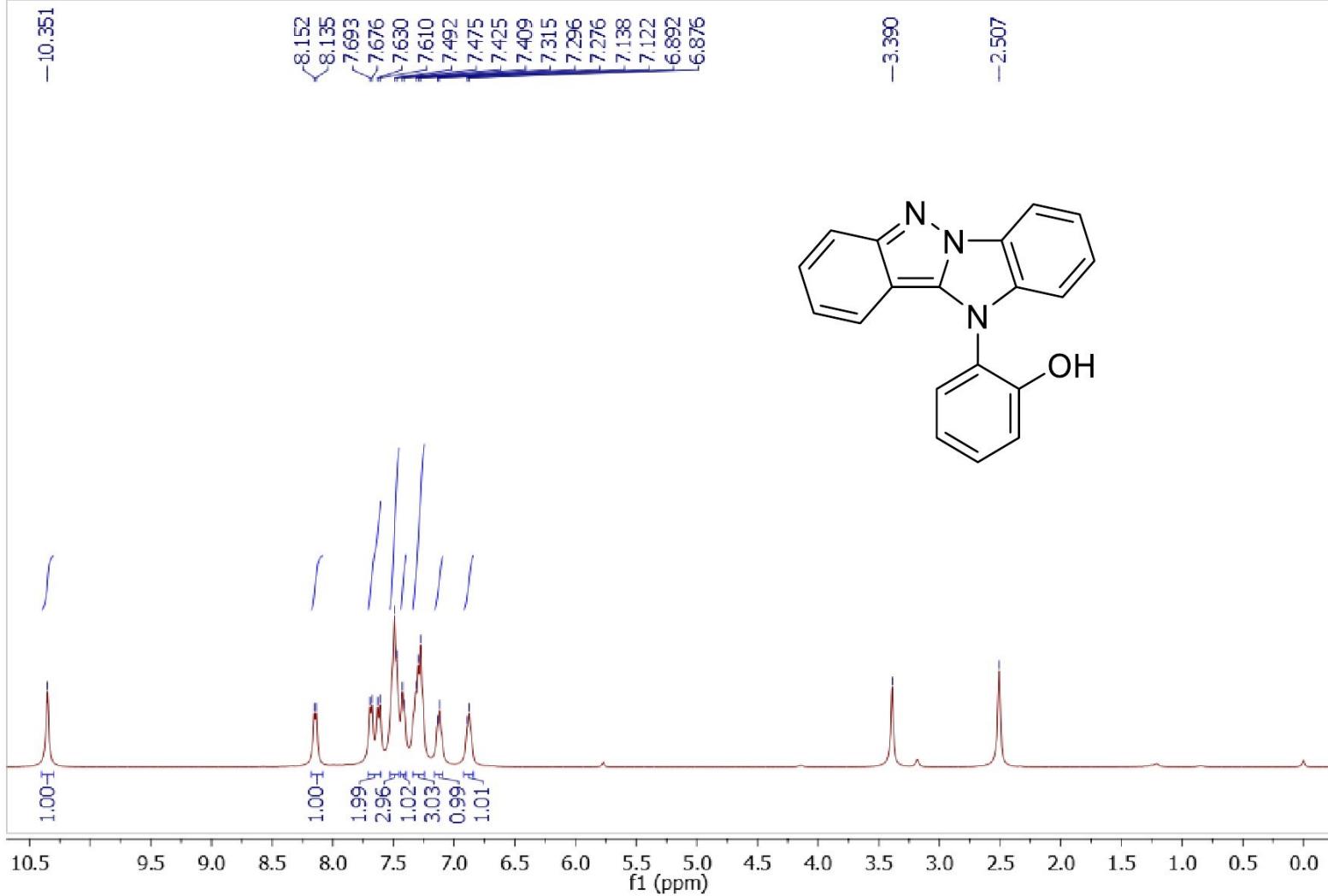
# Compound-3ai



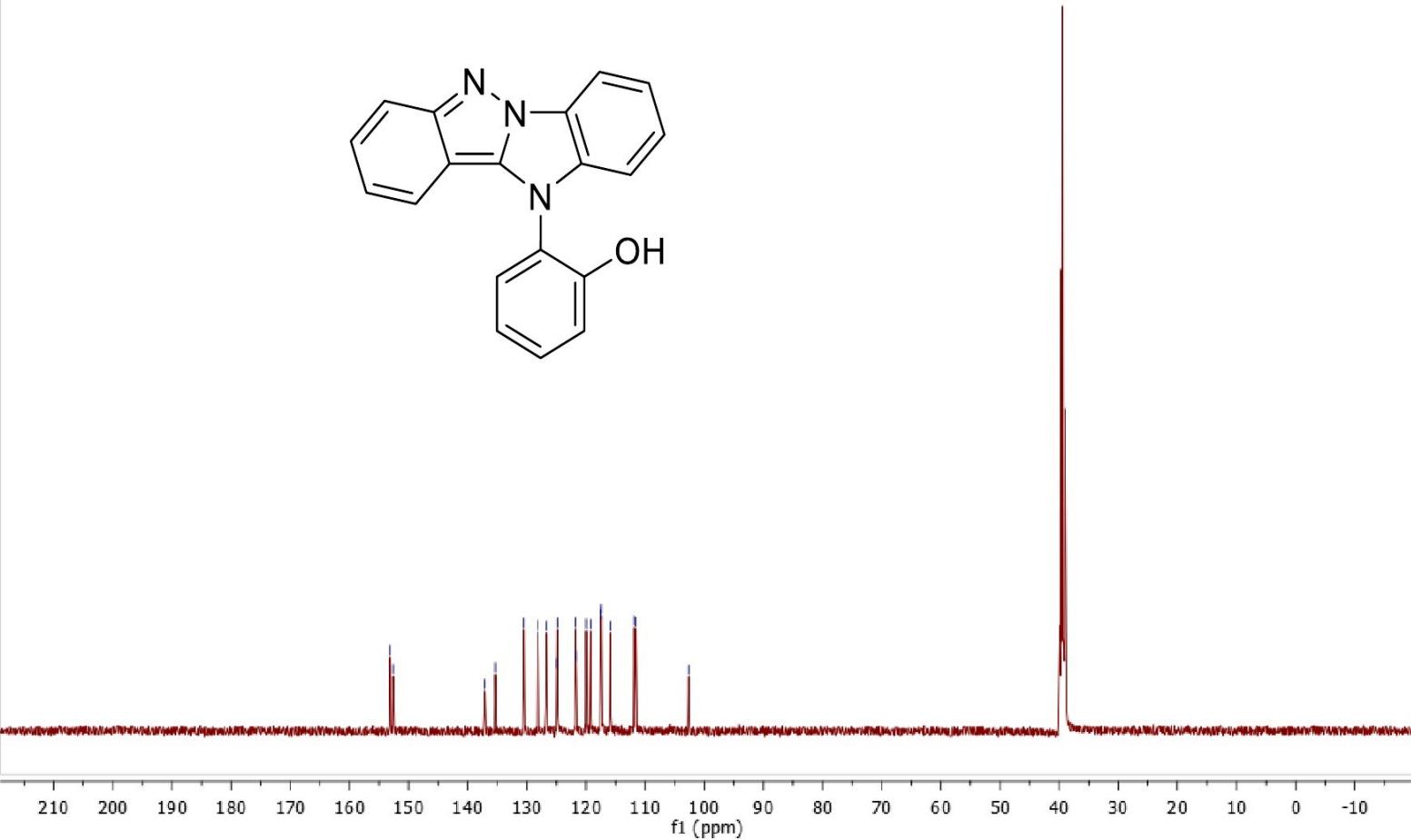
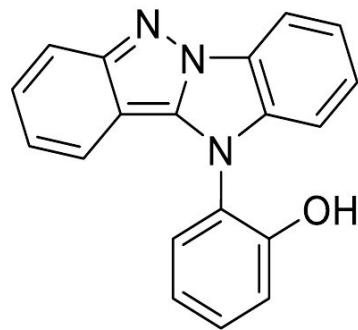
153.06  
146.00  
137.66  
135.86  
130.62  
128.48  
127.03  
125.96  
125.11  
122.01  
119.85  
119.12  
117.65  
116.80  
116.72  
116.27  
112.19  
112.09  
—103.15



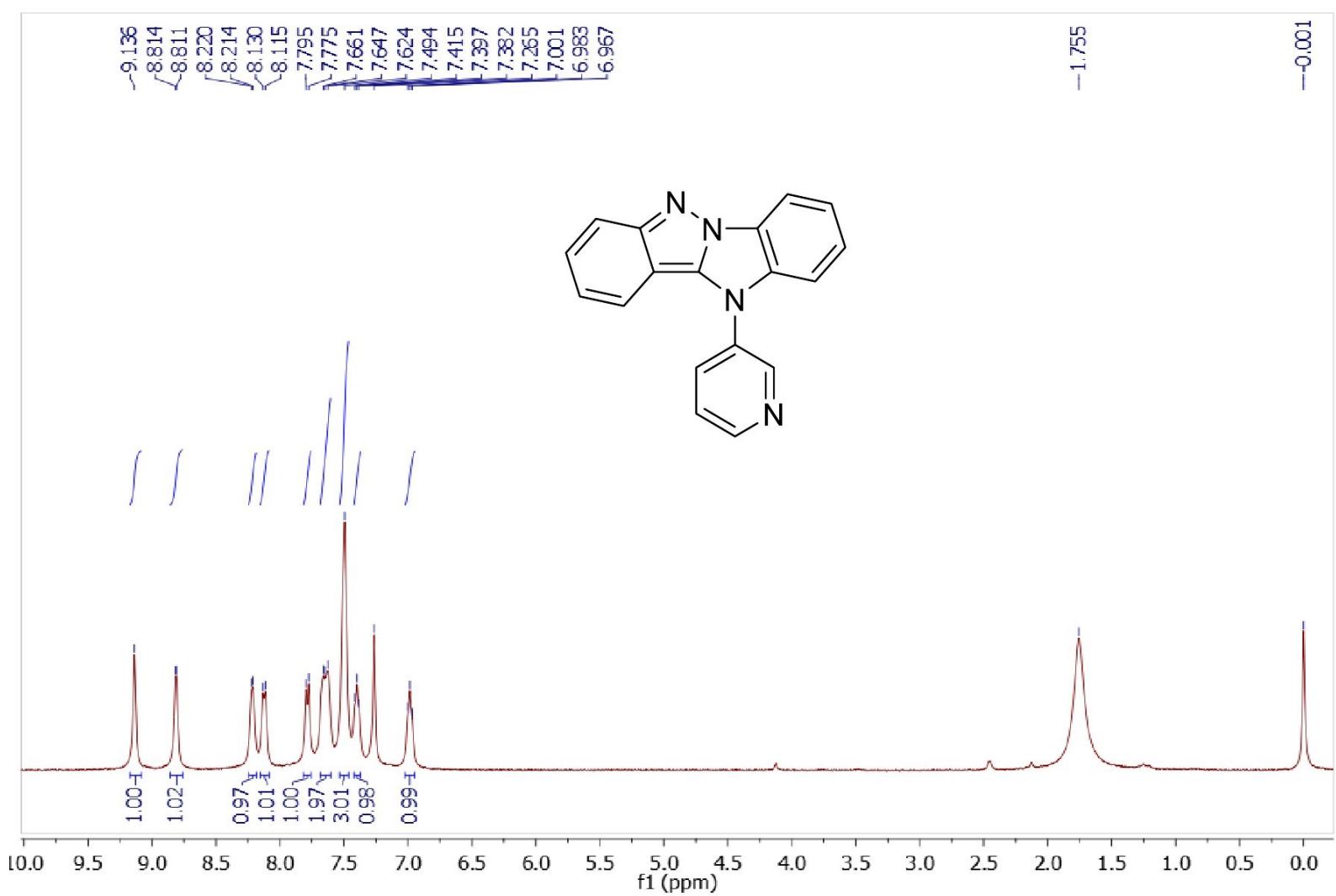
# Compound-3aj

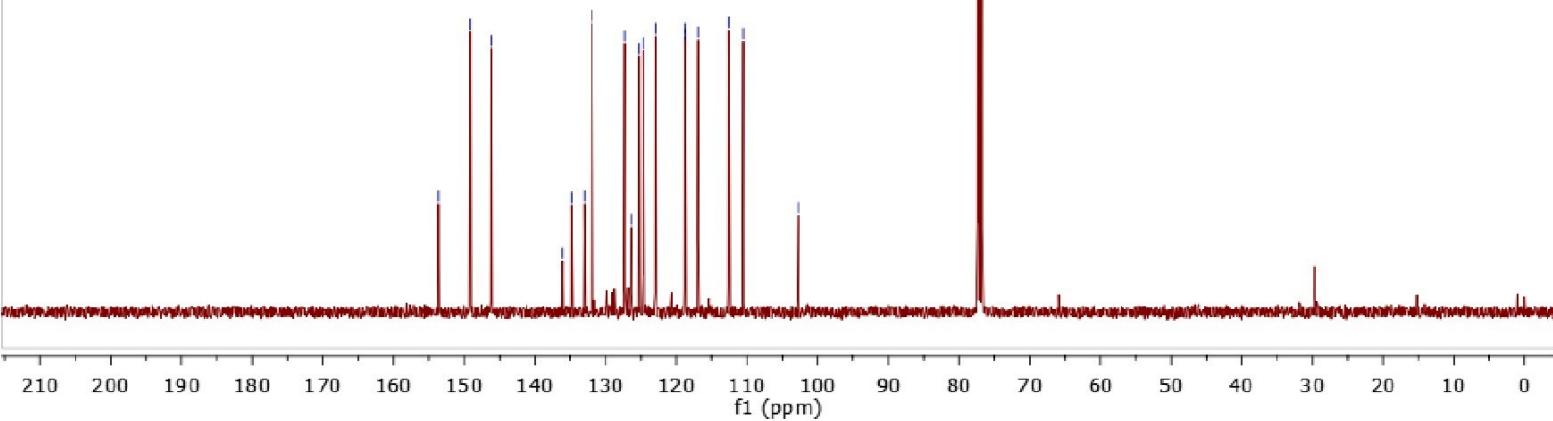
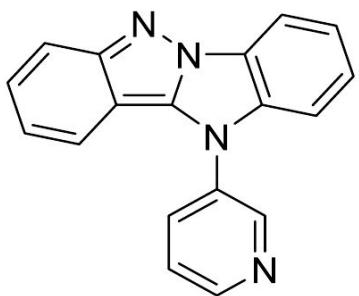


152.60  
137.11  
135.35  
130.47  
128.13  
126.68  
124.95  
124.88  
121.78  
121.70  
119.98  
119.19  
117.48  
117.43  
115.89  
111.90  
111.57  
102.66

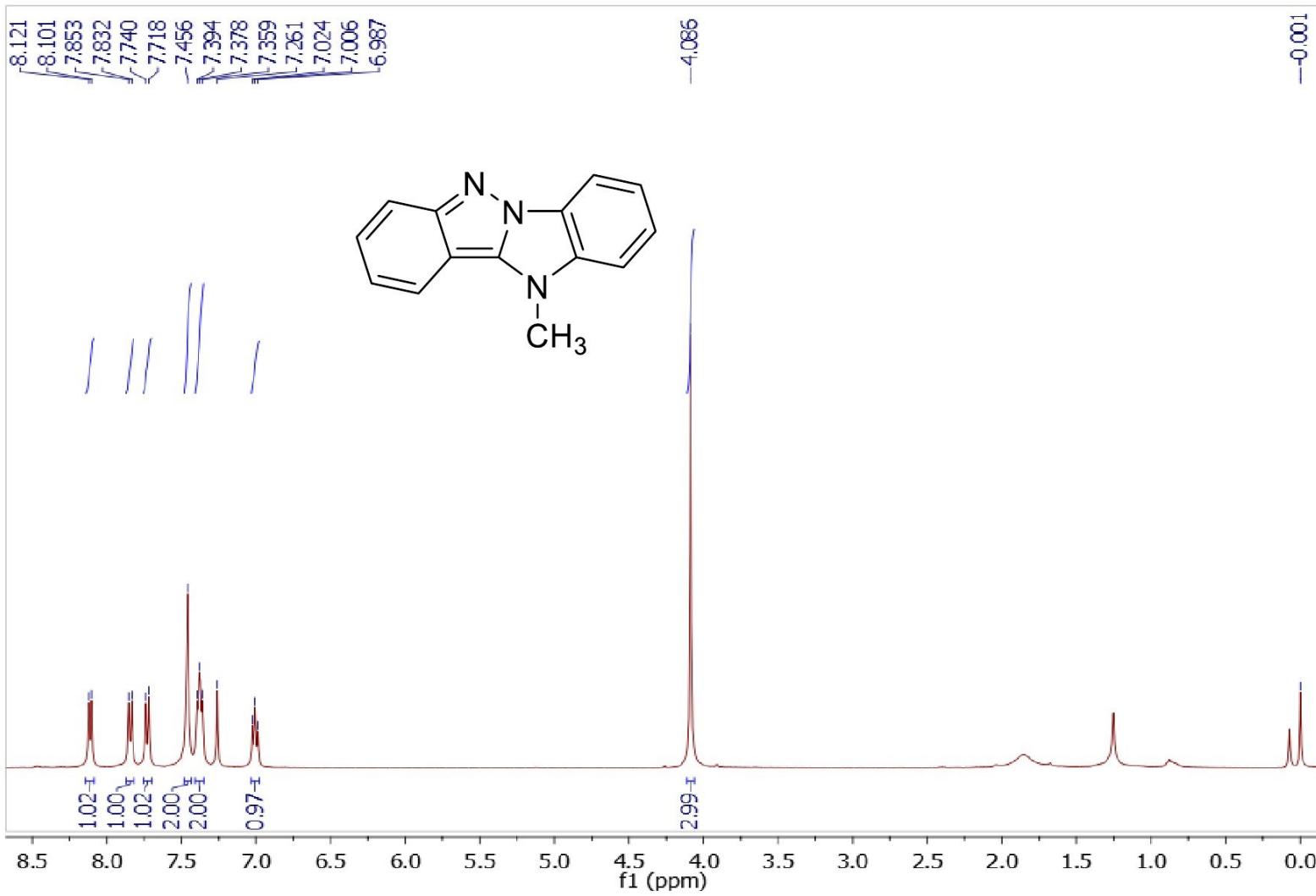


# Compound-3ak





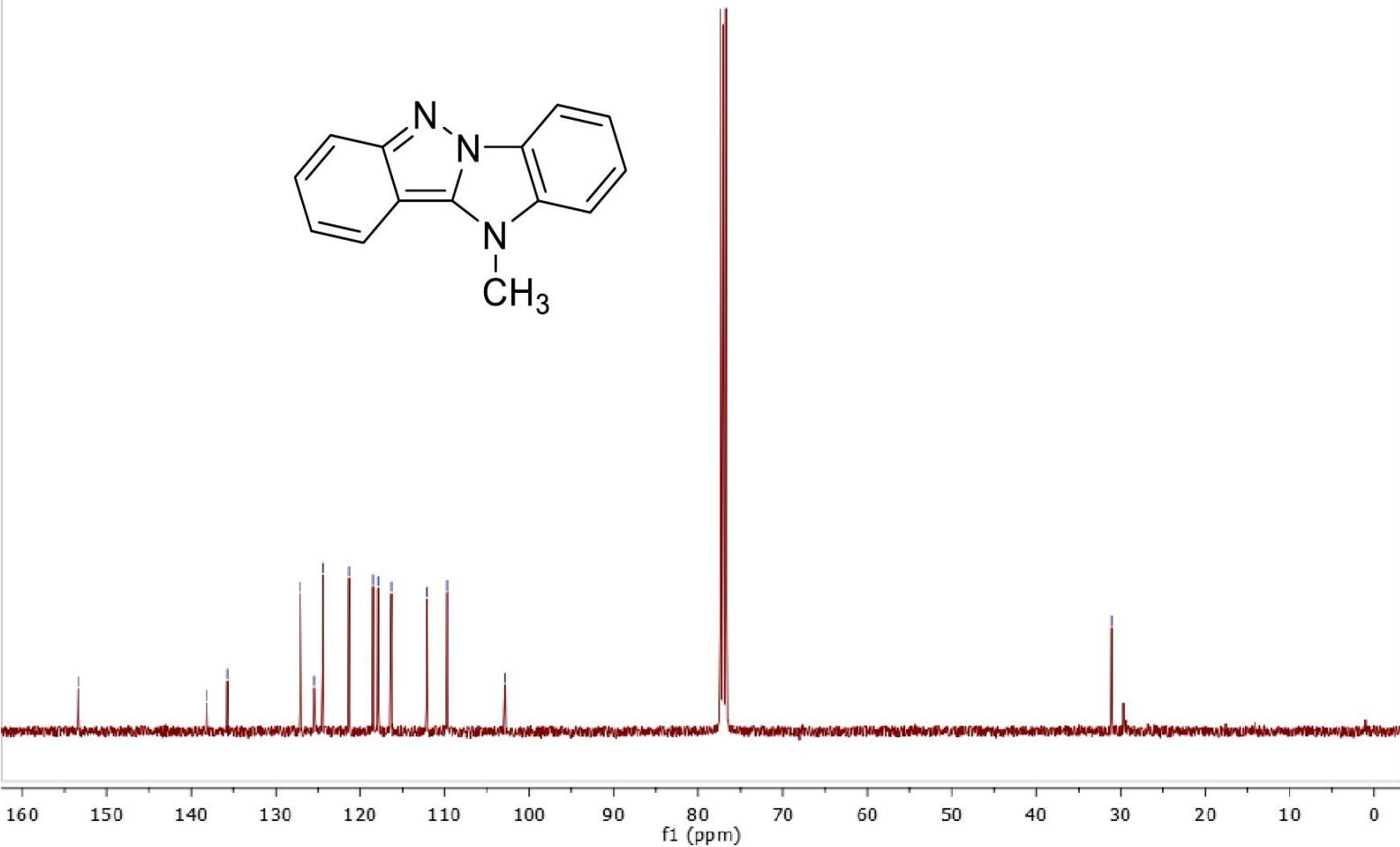
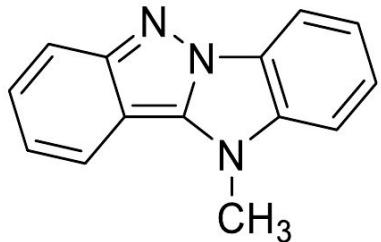
# Compound-3al



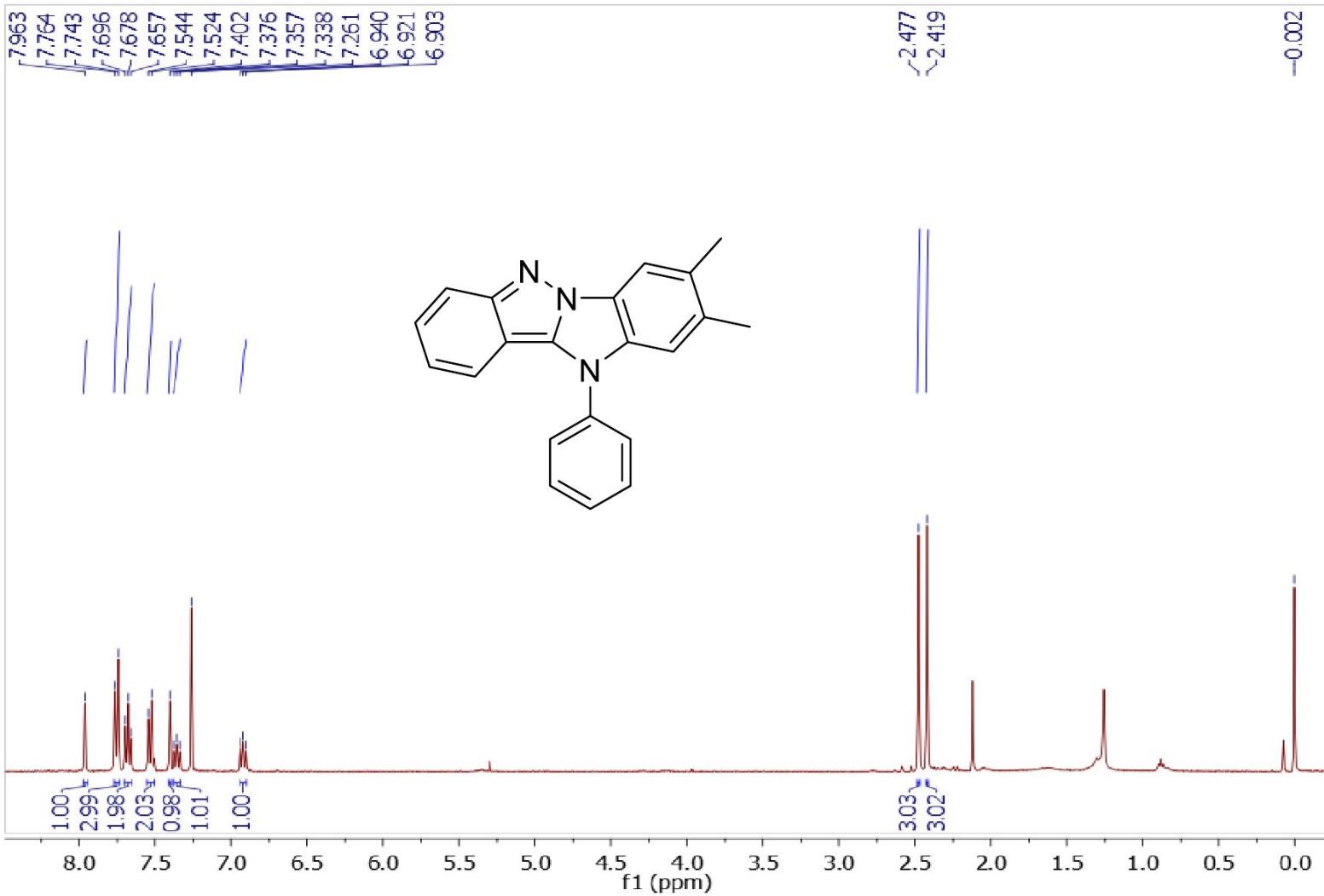
-153.35

-138.17  
-135.74  
-127.10  
-125.42  
-124.45  
-121.30  
-118.46  
-117.89  
-116.33  
-112.14  
-109.72  
-102.85

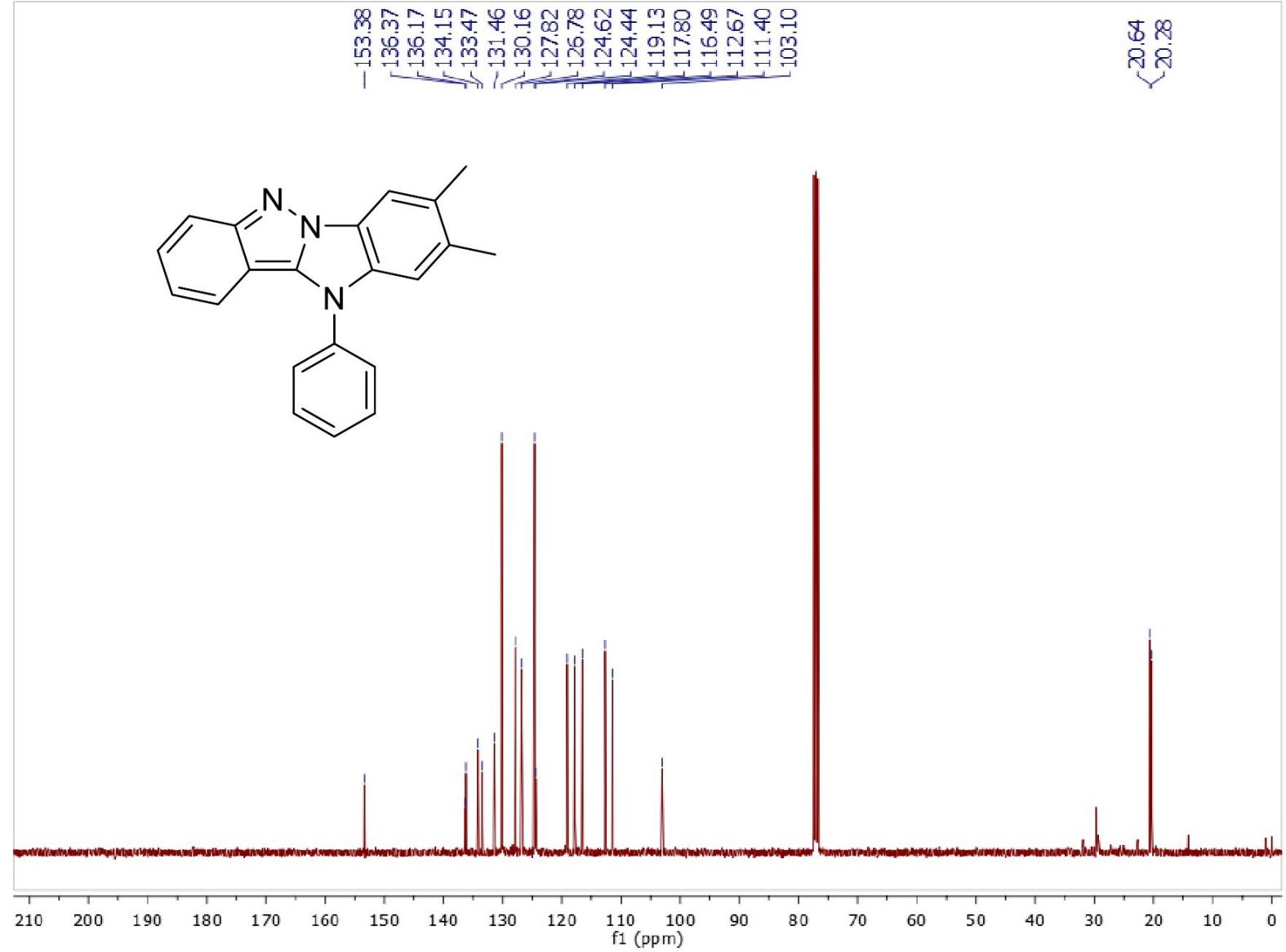
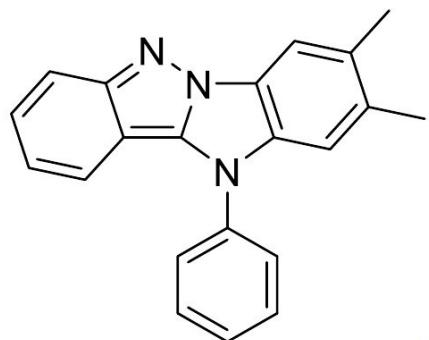
-31.10



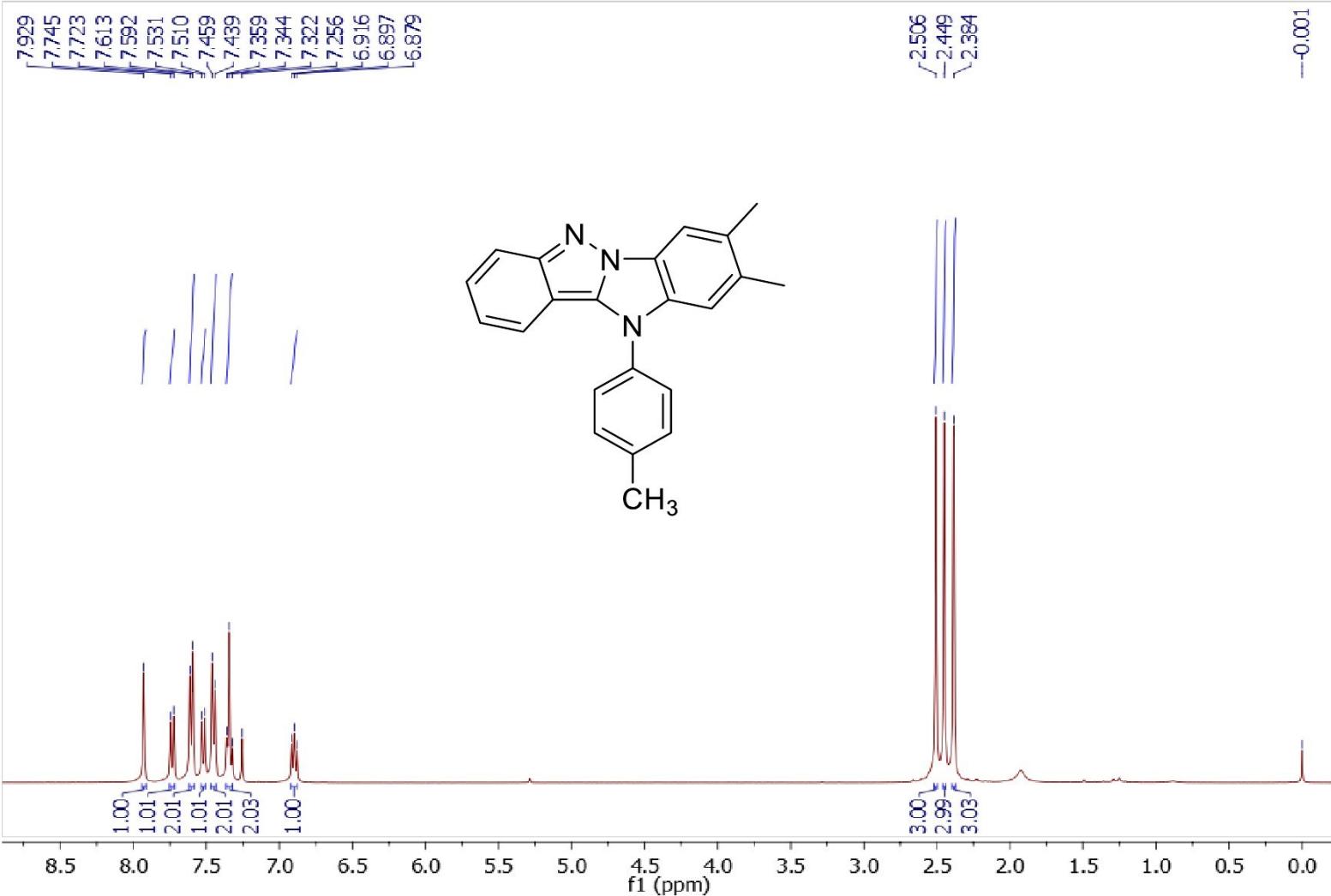
# Compound-3ba



<20.64  
<20.28

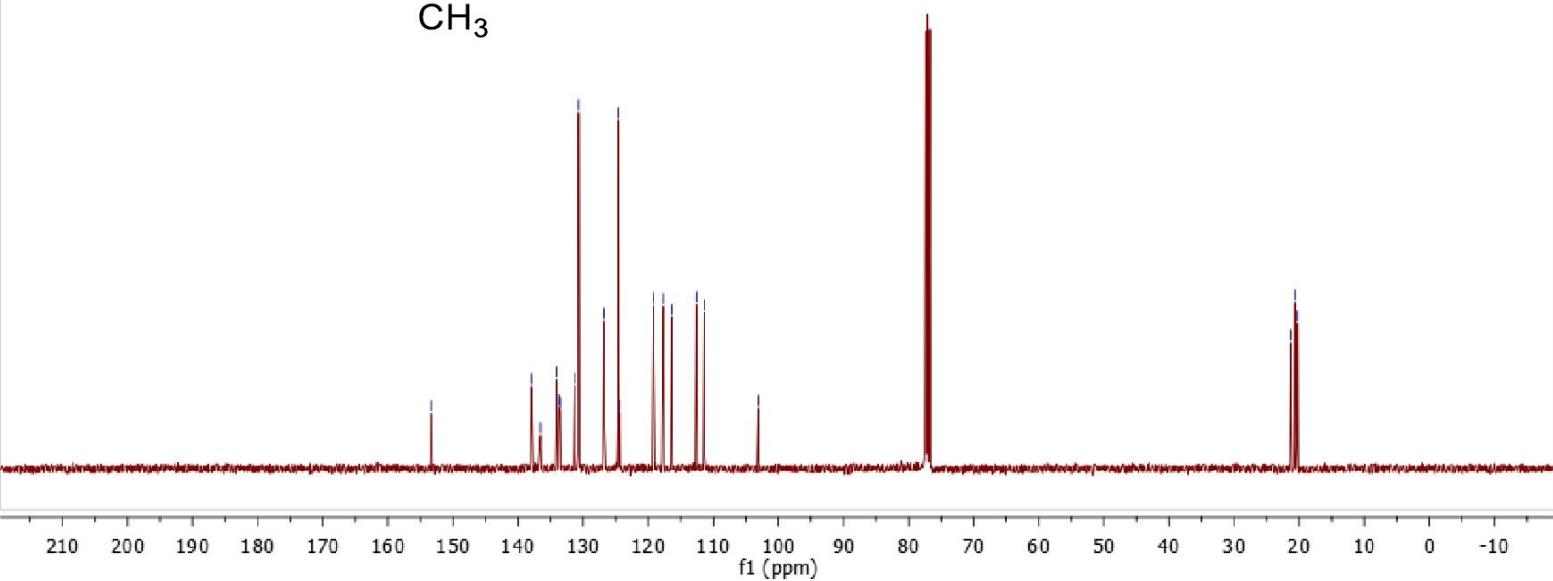
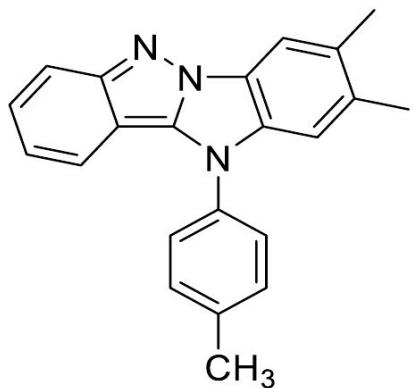


# Compound-3bc



{  
21.25  
20.62  
20.27

-153.35  
-137.94  
-136.58  
-134.06  
-133.66  
-133.49  
-131.27  
-130.70  
-126.75  
-124.59  
-124.34  
-119.18  
-117.67  
-116.39  
-112.61  
-111.40  
-103.11



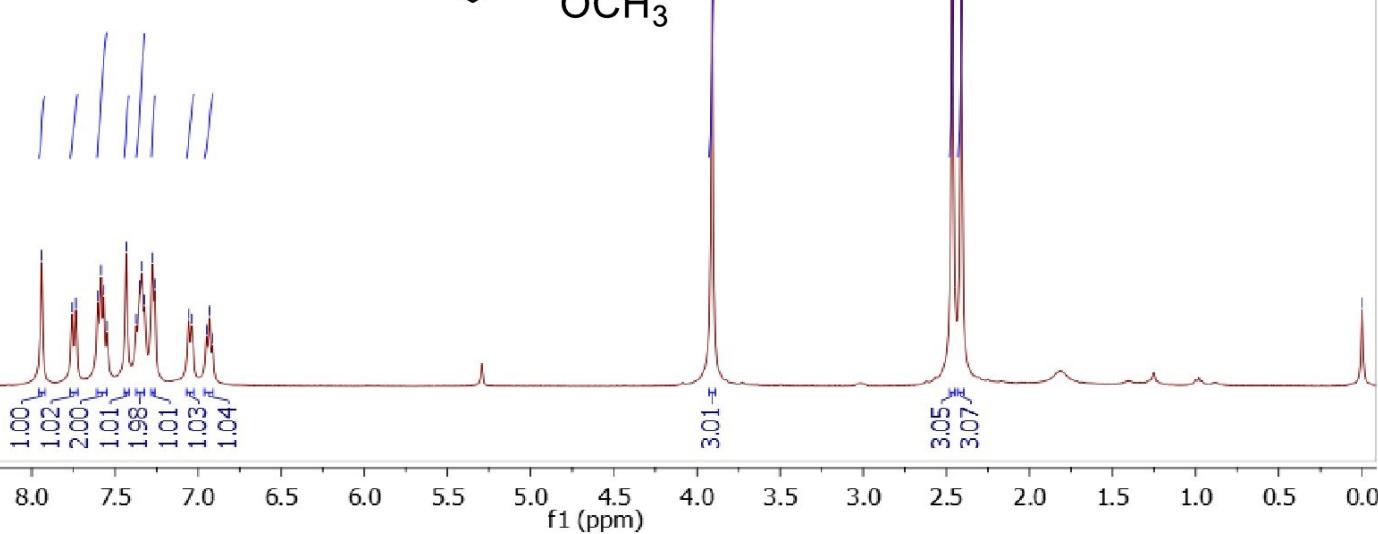
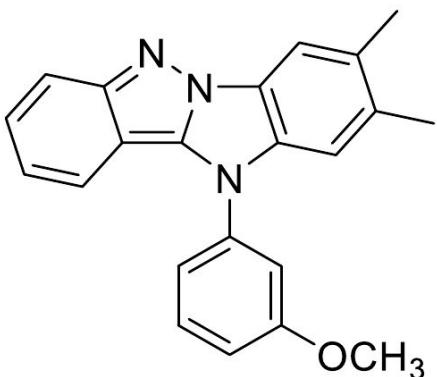
# Compound-3bd

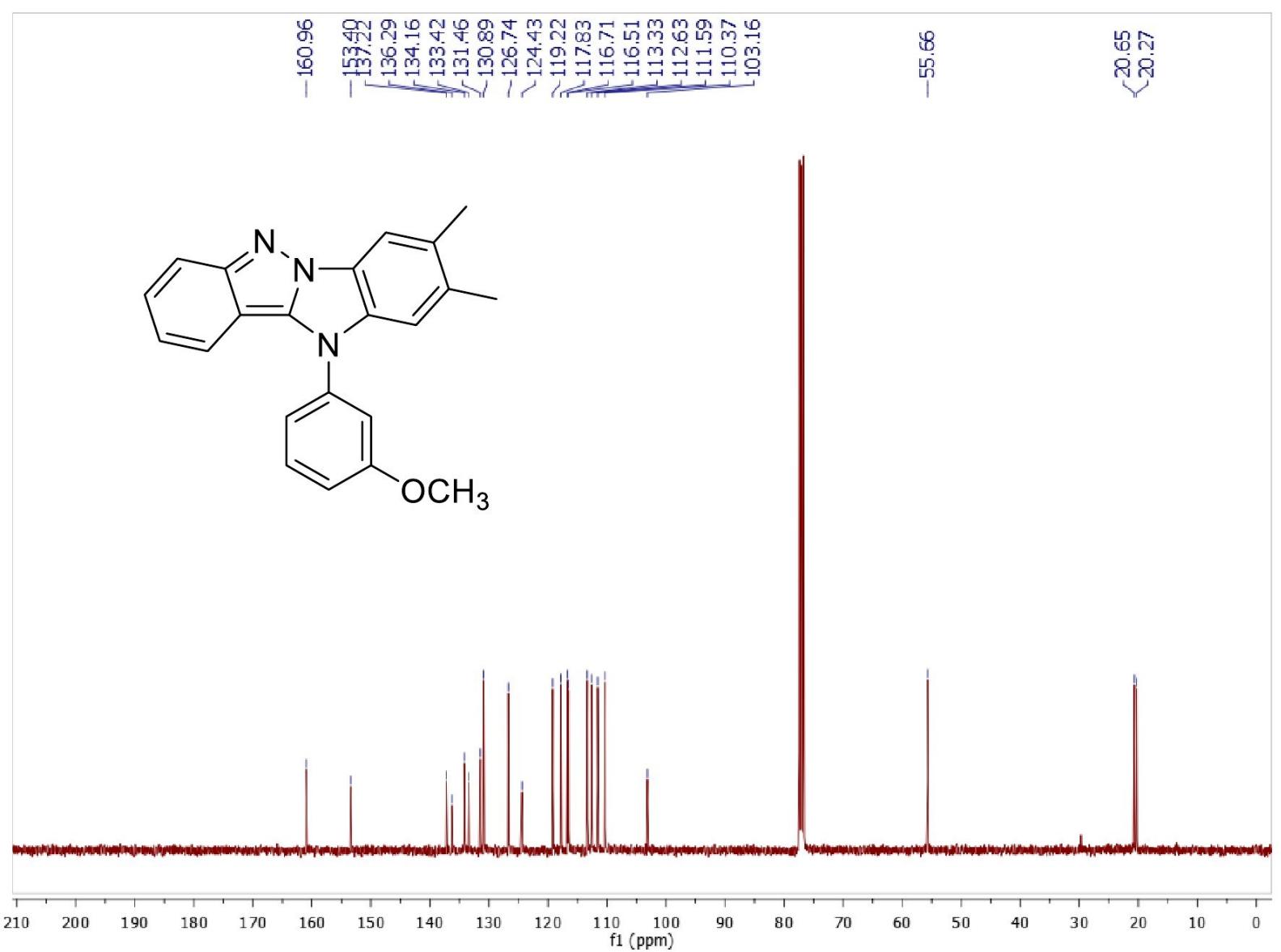
7.941  
7.757  
7.735  
7.602  
7.583  
7.556  
7.546  
7.431  
7.372  
7.351  
7.338  
7.322  
7.274  
7.260  
7.056  
7.038  
6.949  
6.931  
6.913

-3.908

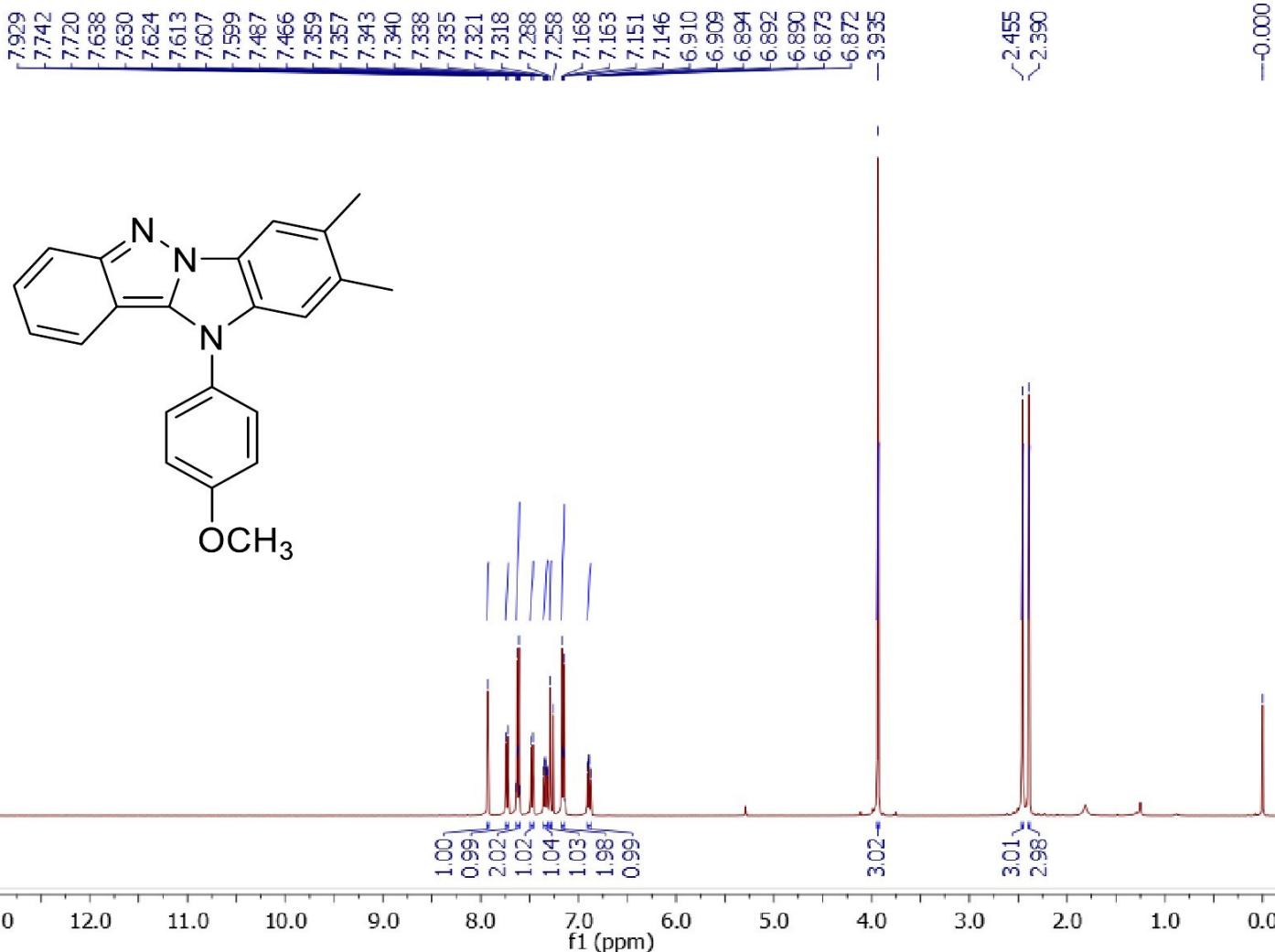
2.464  
2.410

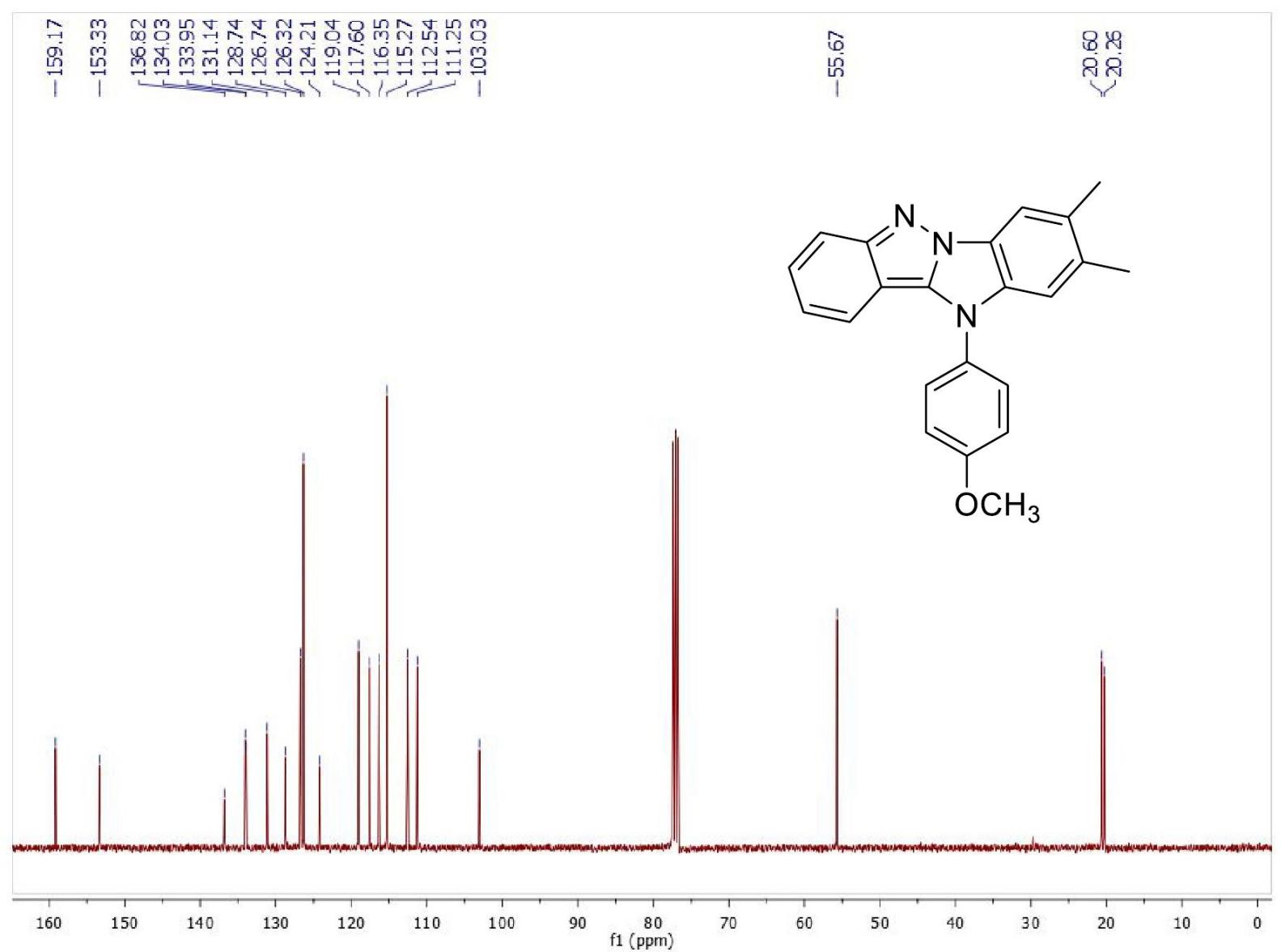
-0.001



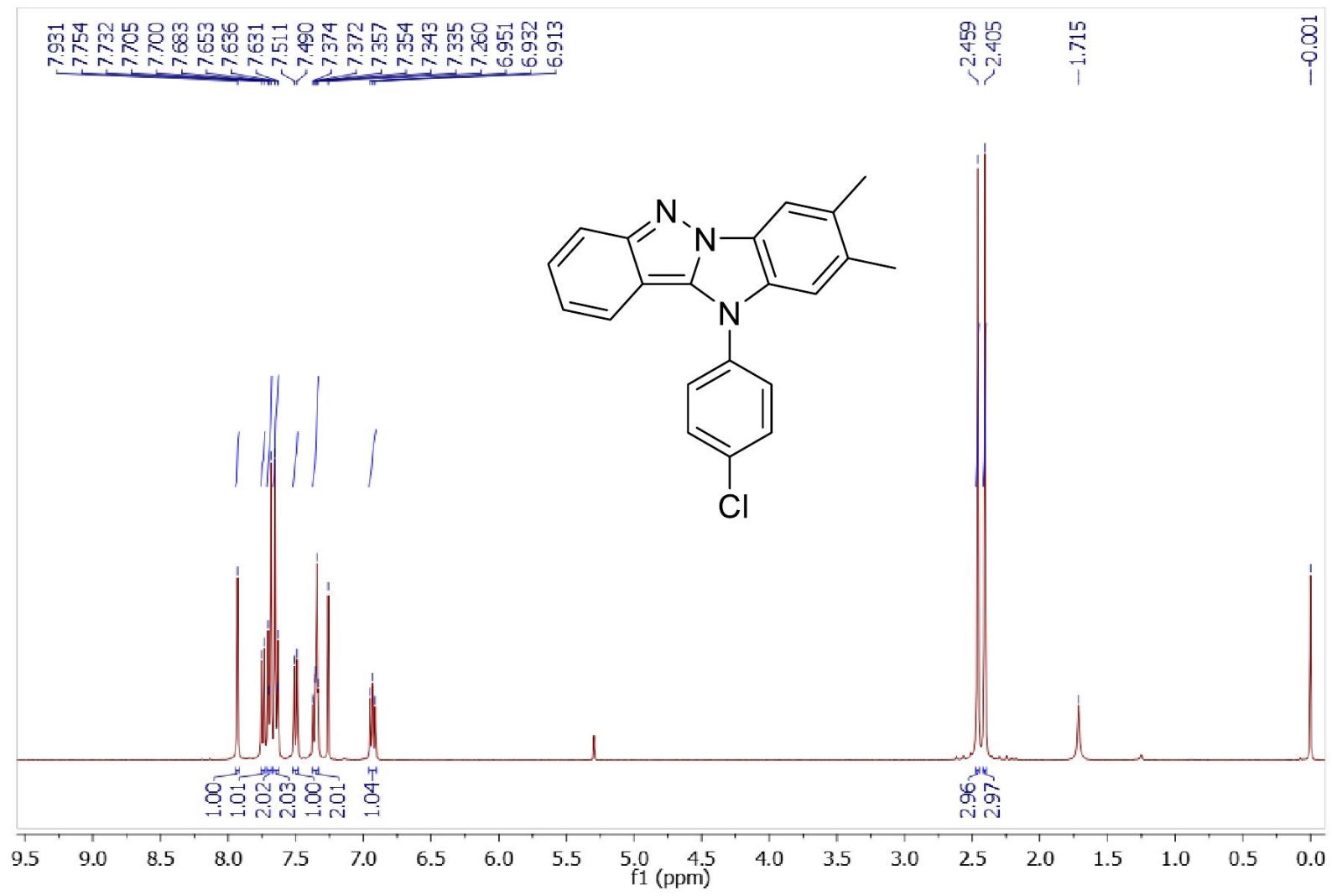


## Compound-3be

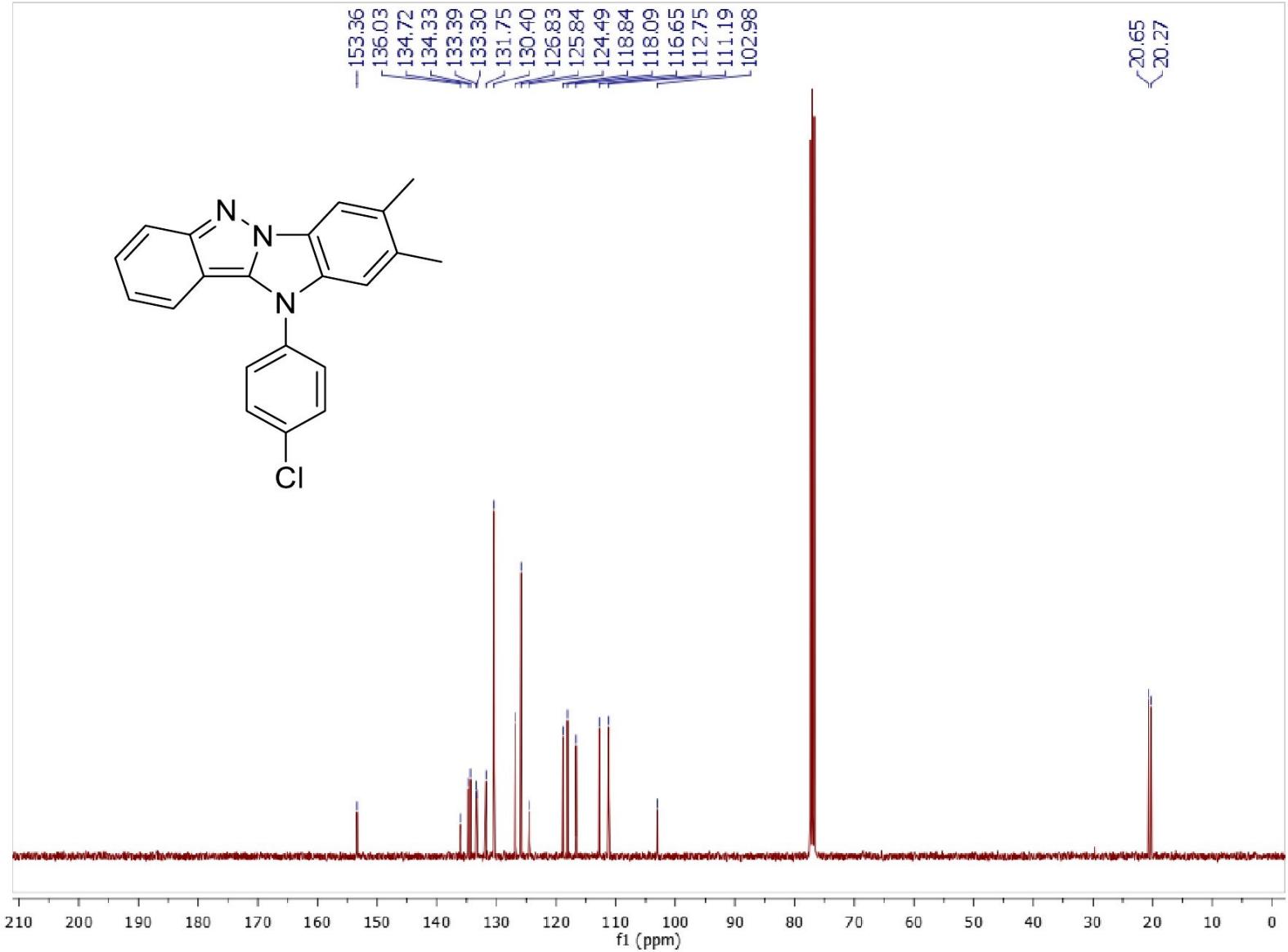
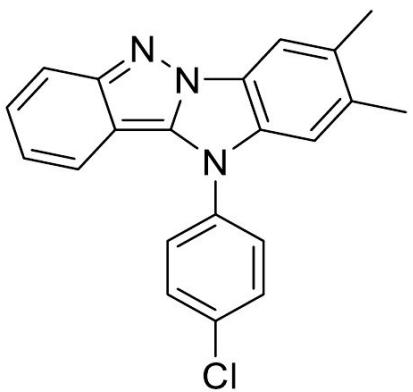




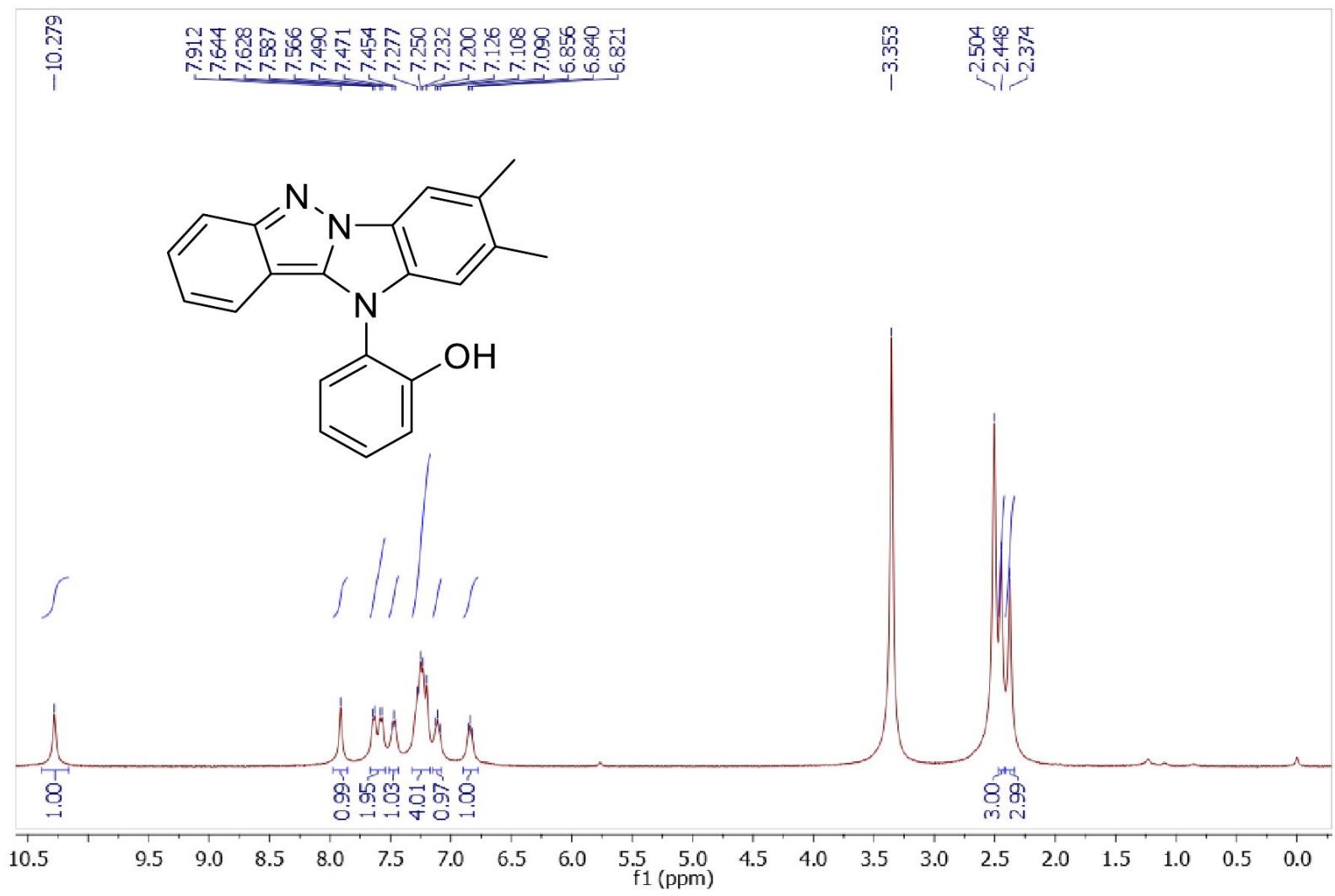
# Compound-3bg

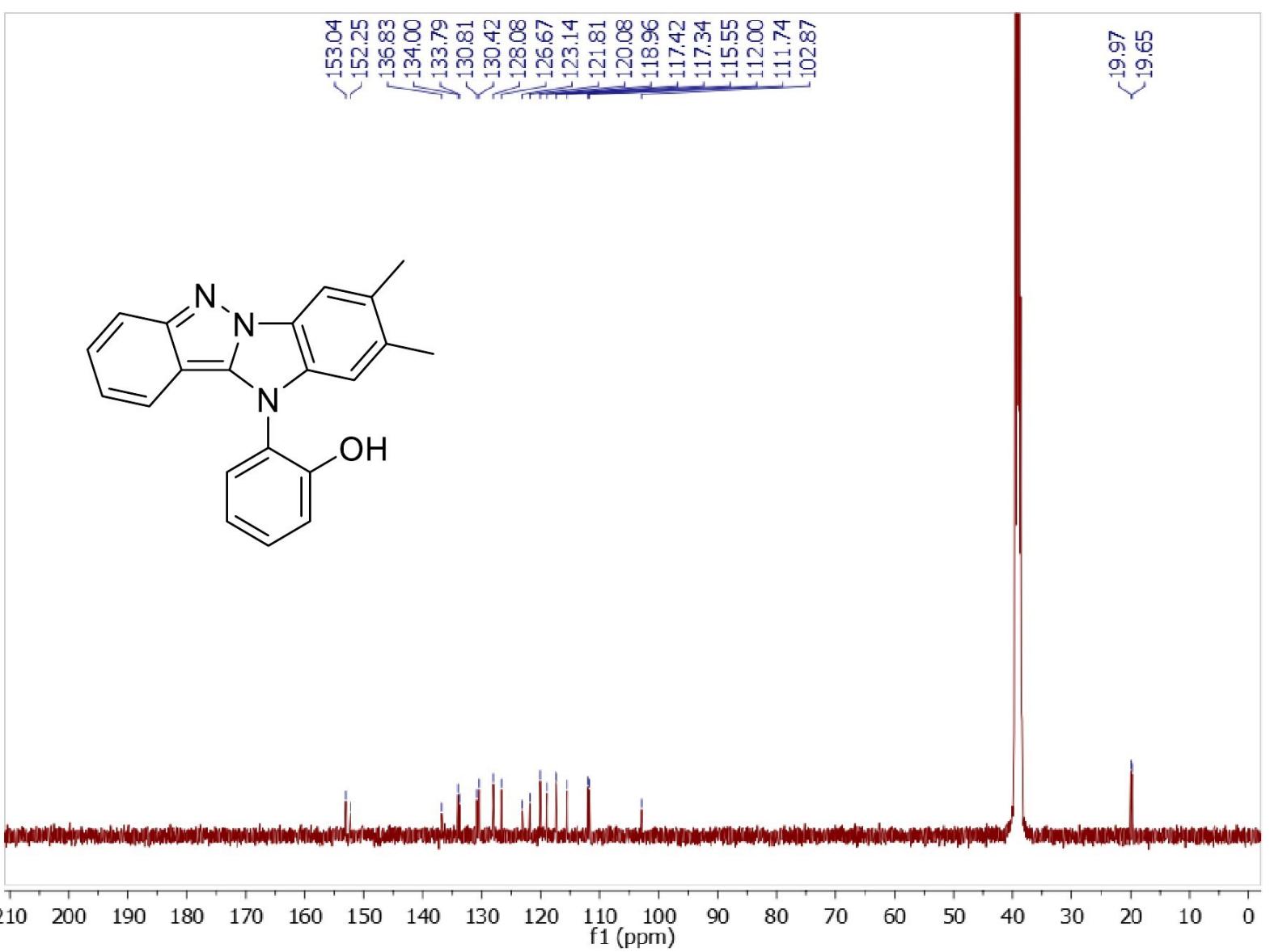


<20.65  
<20.27

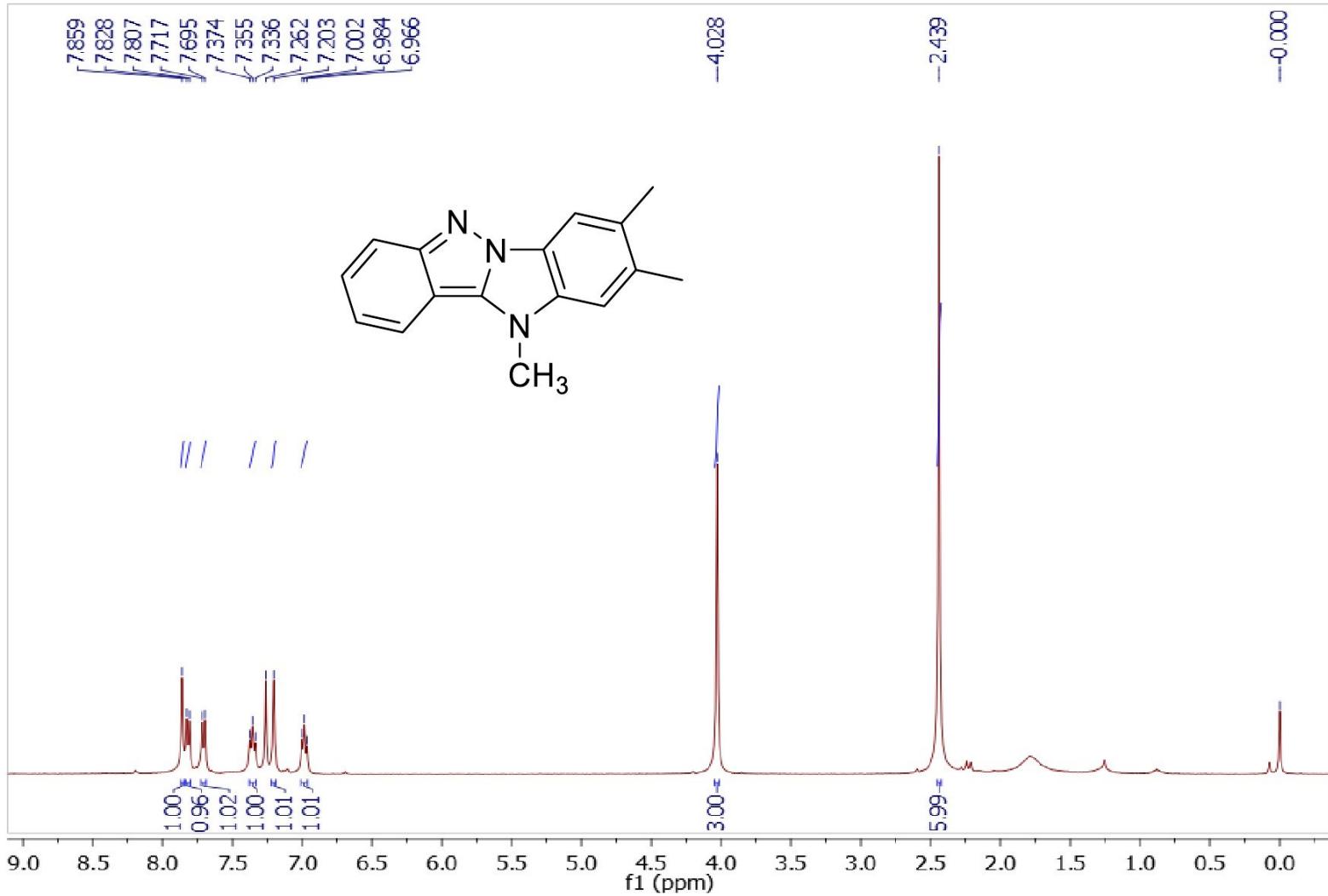


# Compound-3bj





# Compound-3bl

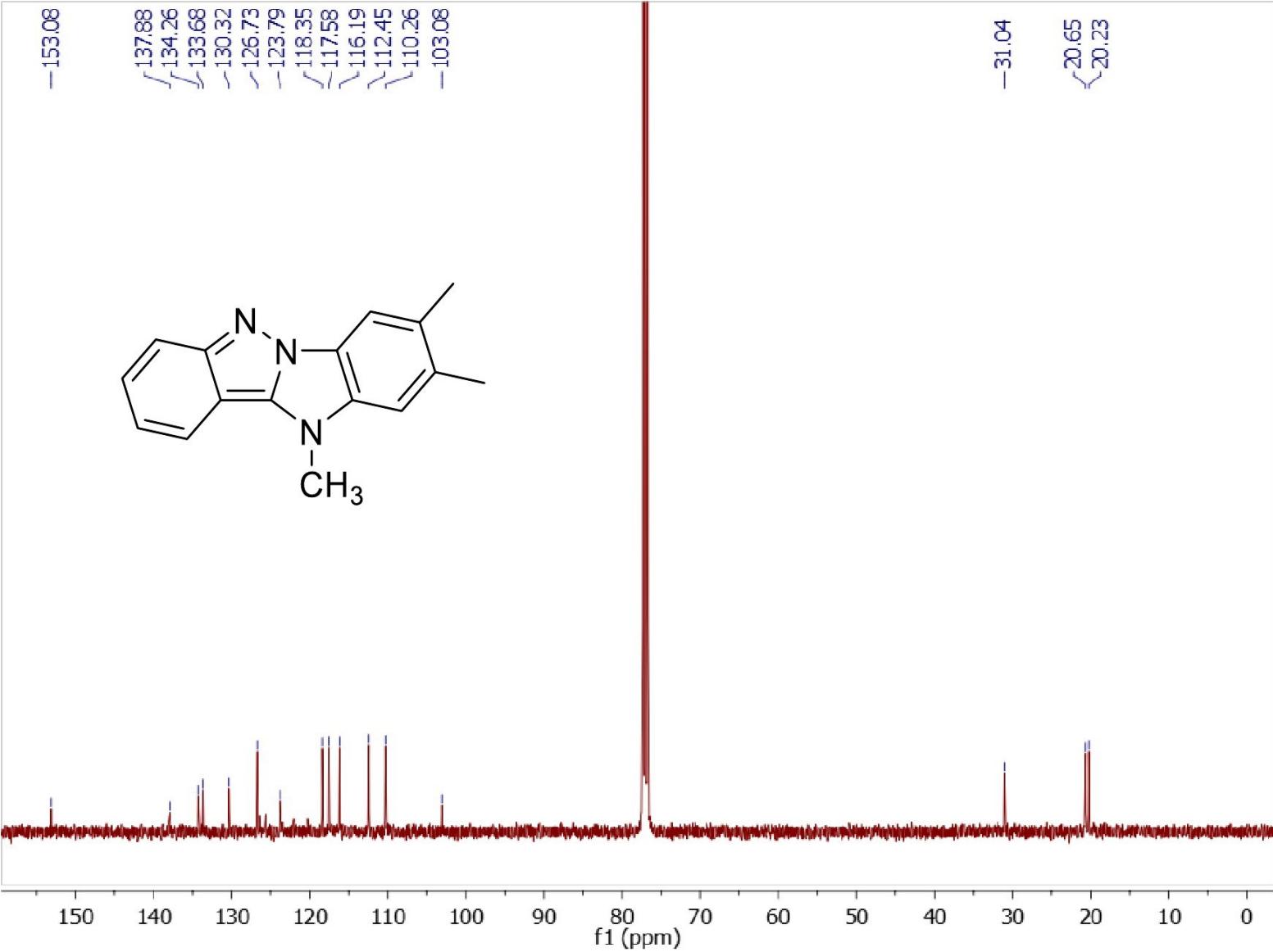
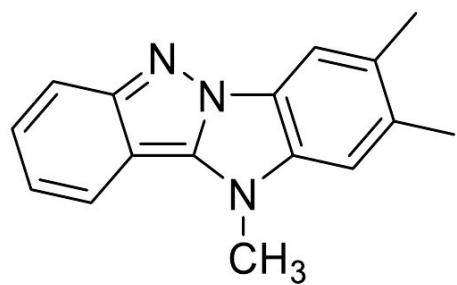


-153.08

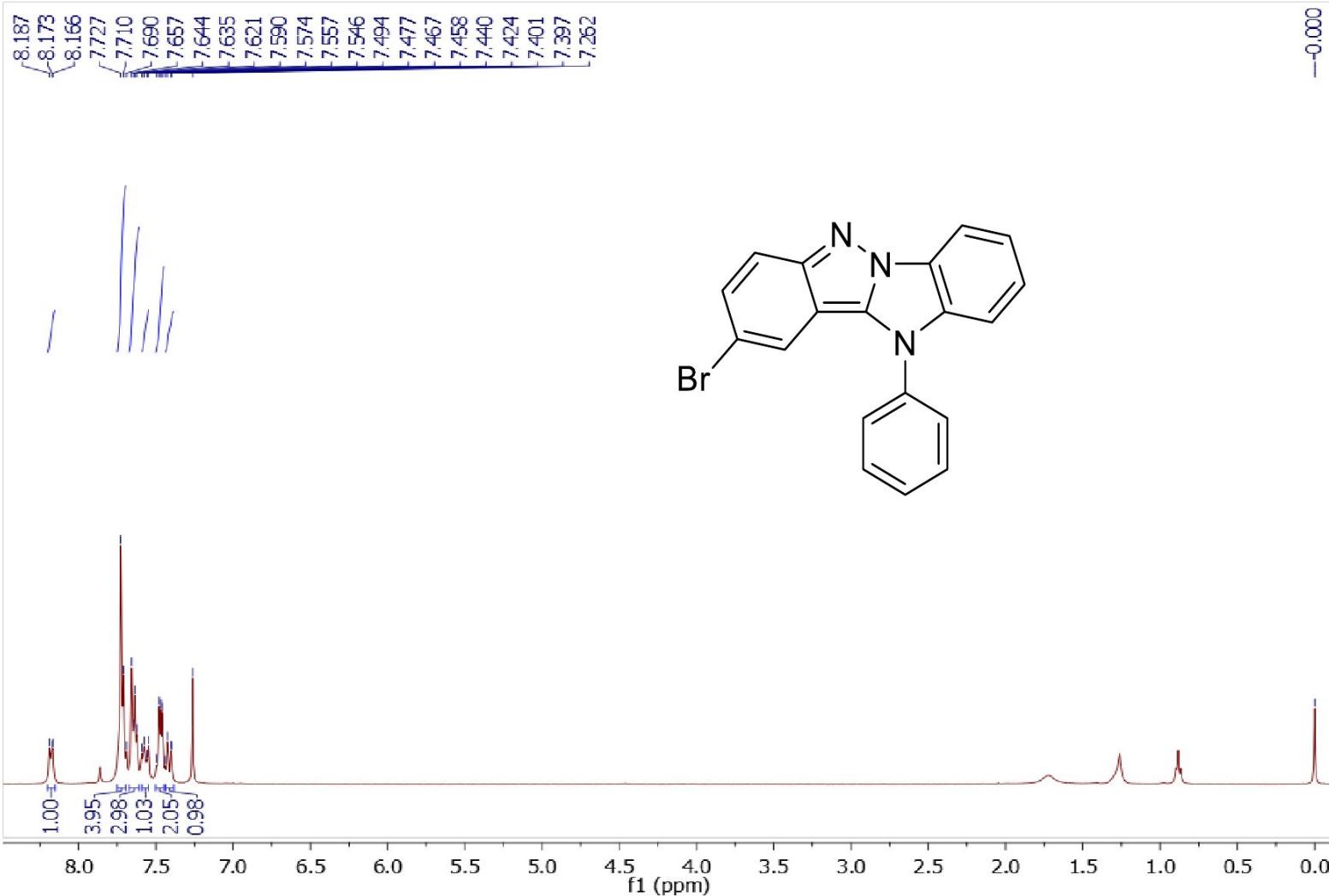
/ 137.88  
/ 134.26  
/ 133.68  
-130.32  
-126.73  
-123.79  
/ 118.35  
/ 117.58  
\ 116.19  
\ 112.45  
\ 110.26  
-103.08

-31.04

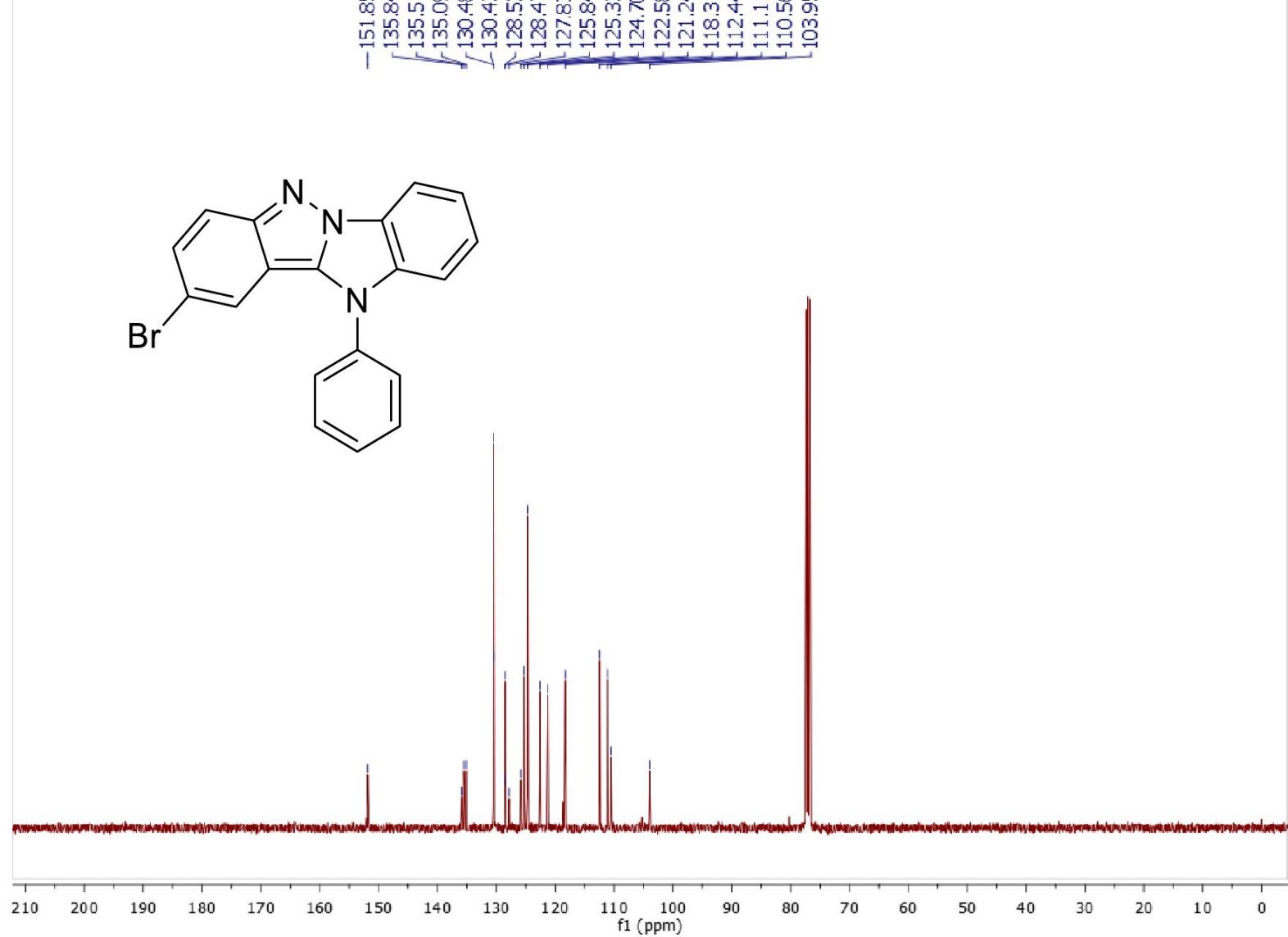
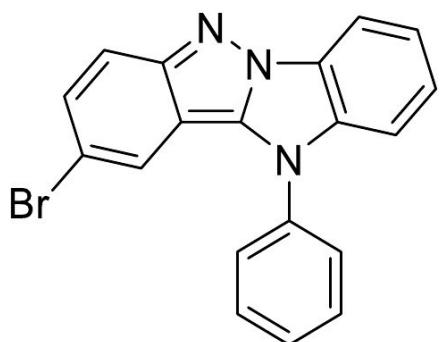
< 20.65  
< 20.23



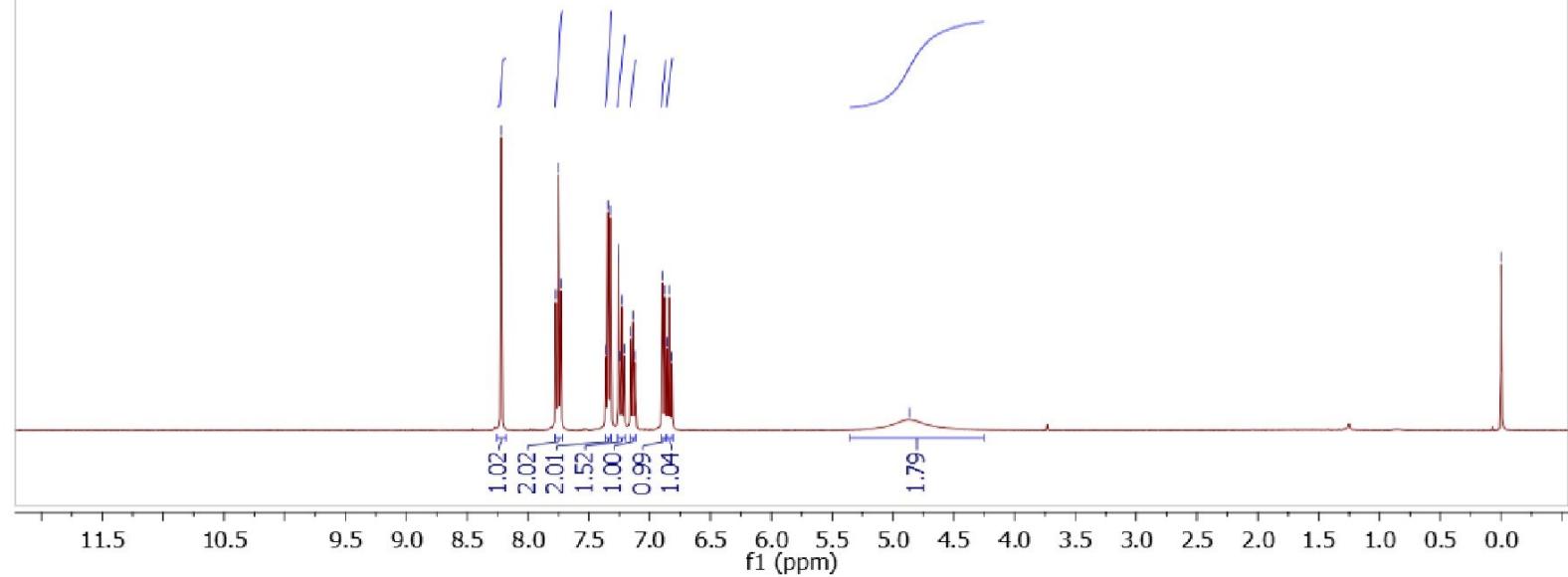
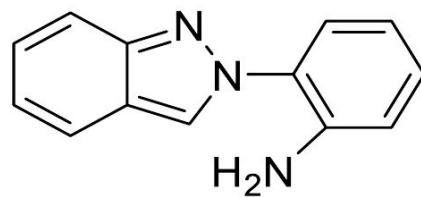
# Compound-3ca



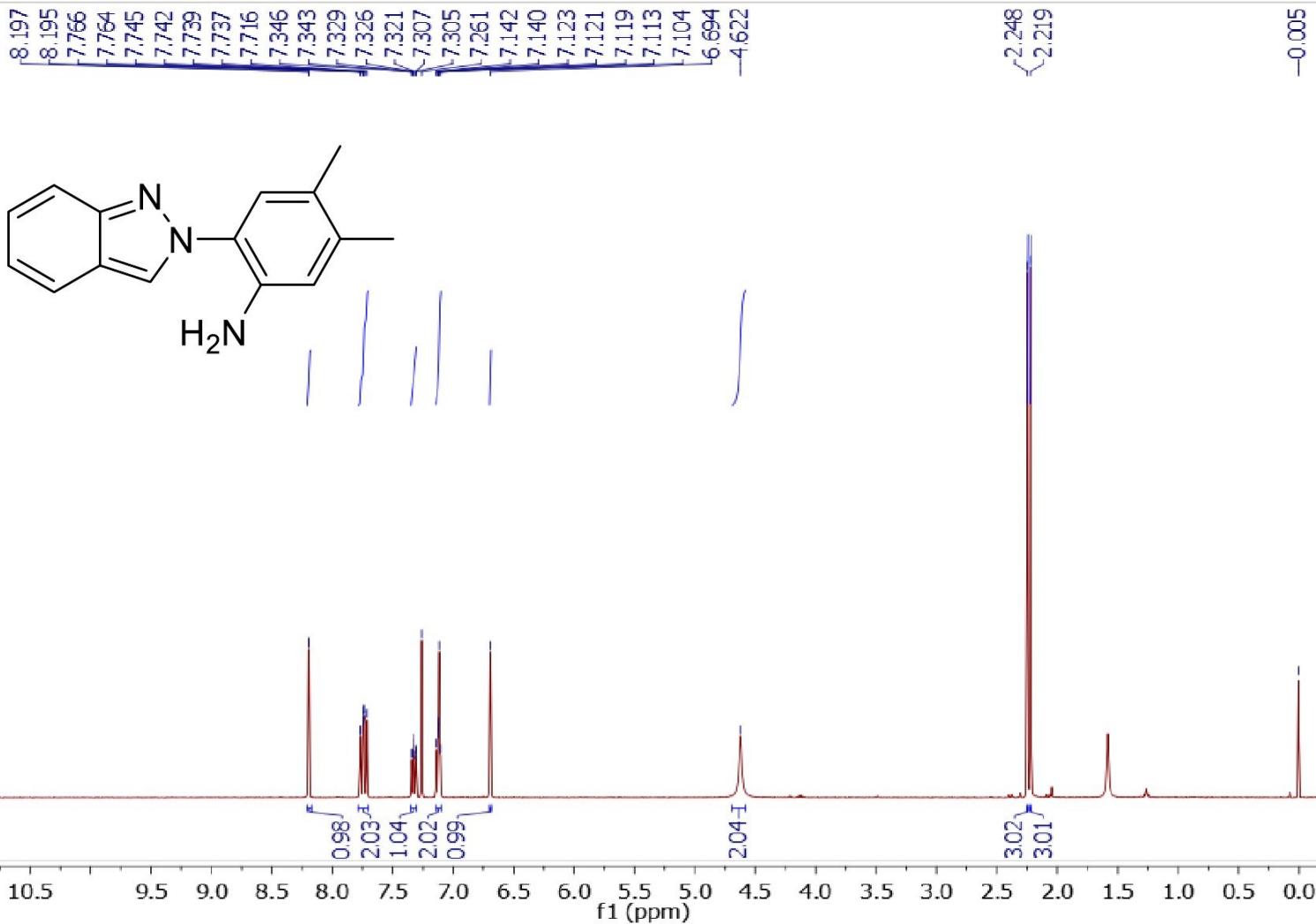
-151.85  
-135.84  
-135.51  
-135.09  
-130.48  
-130.43  
-128.52  
-128.47  
-127.83  
-125.84  
-125.33  
-124.70  
-122.58  
-121.24  
-118.31  
-112.44  
-111.11  
-110.56  
103.95



# Compound-1a



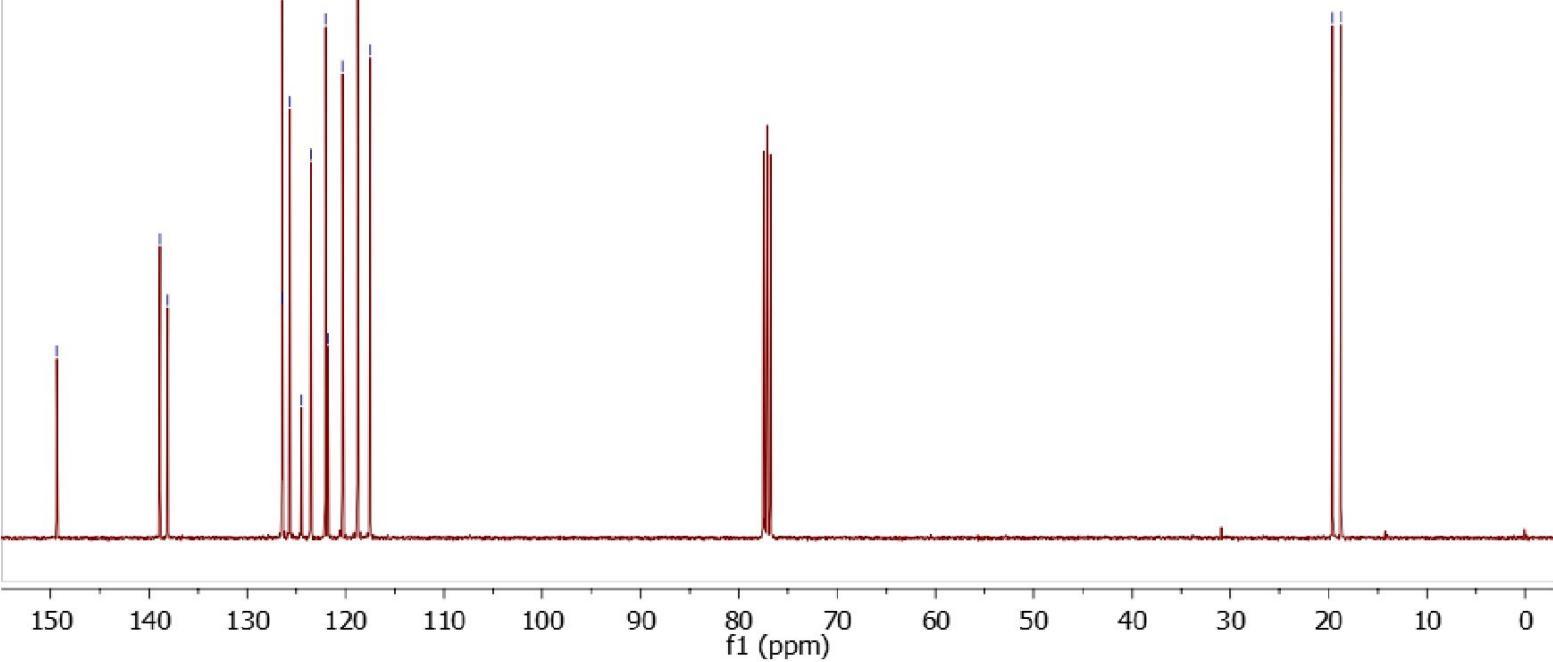
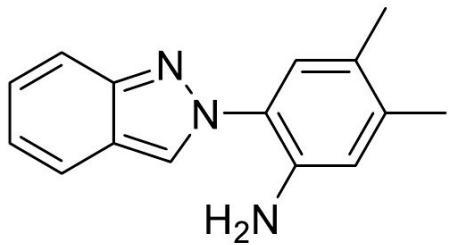
# Compound-1b



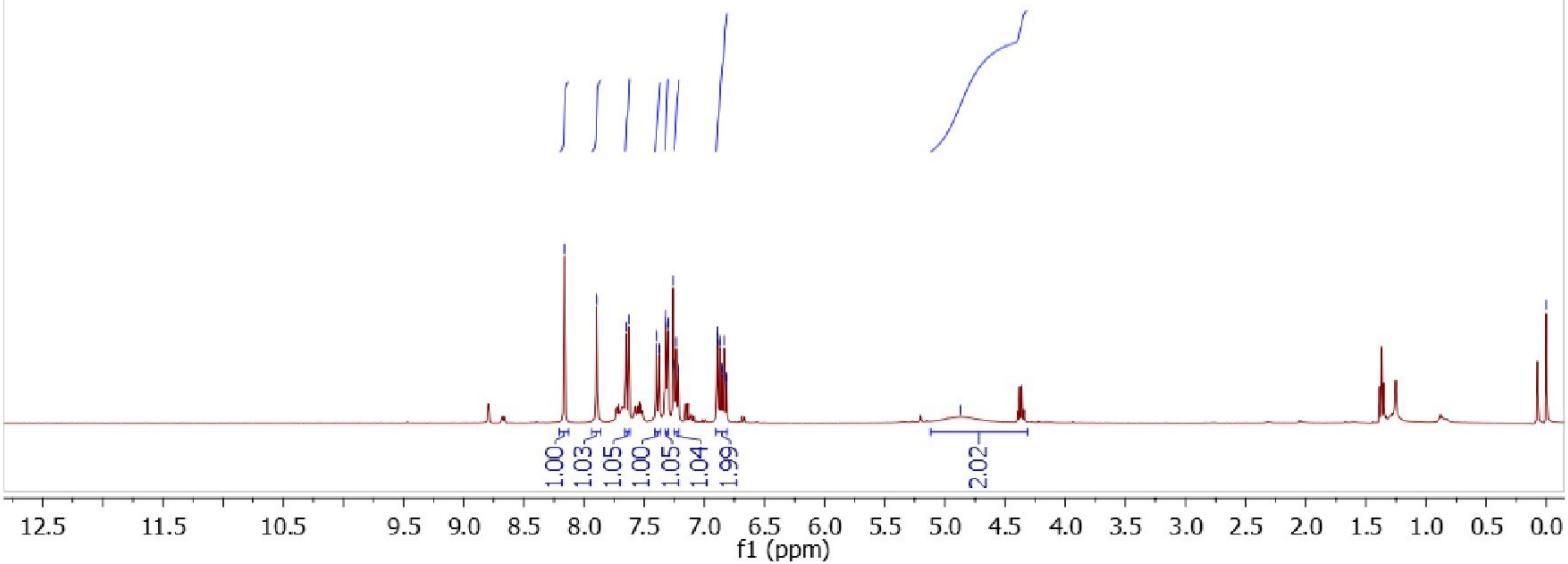
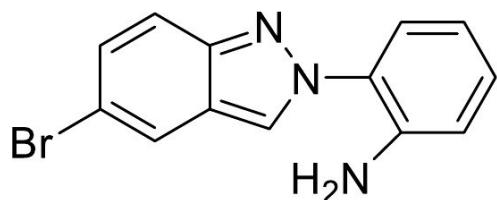
-149.41

~138.90  
~138.06  
126.46  
126.40  
~125.69  
~124.50  
~123.52  
122.03  
121.82  
120.34  
118.81  
117.51

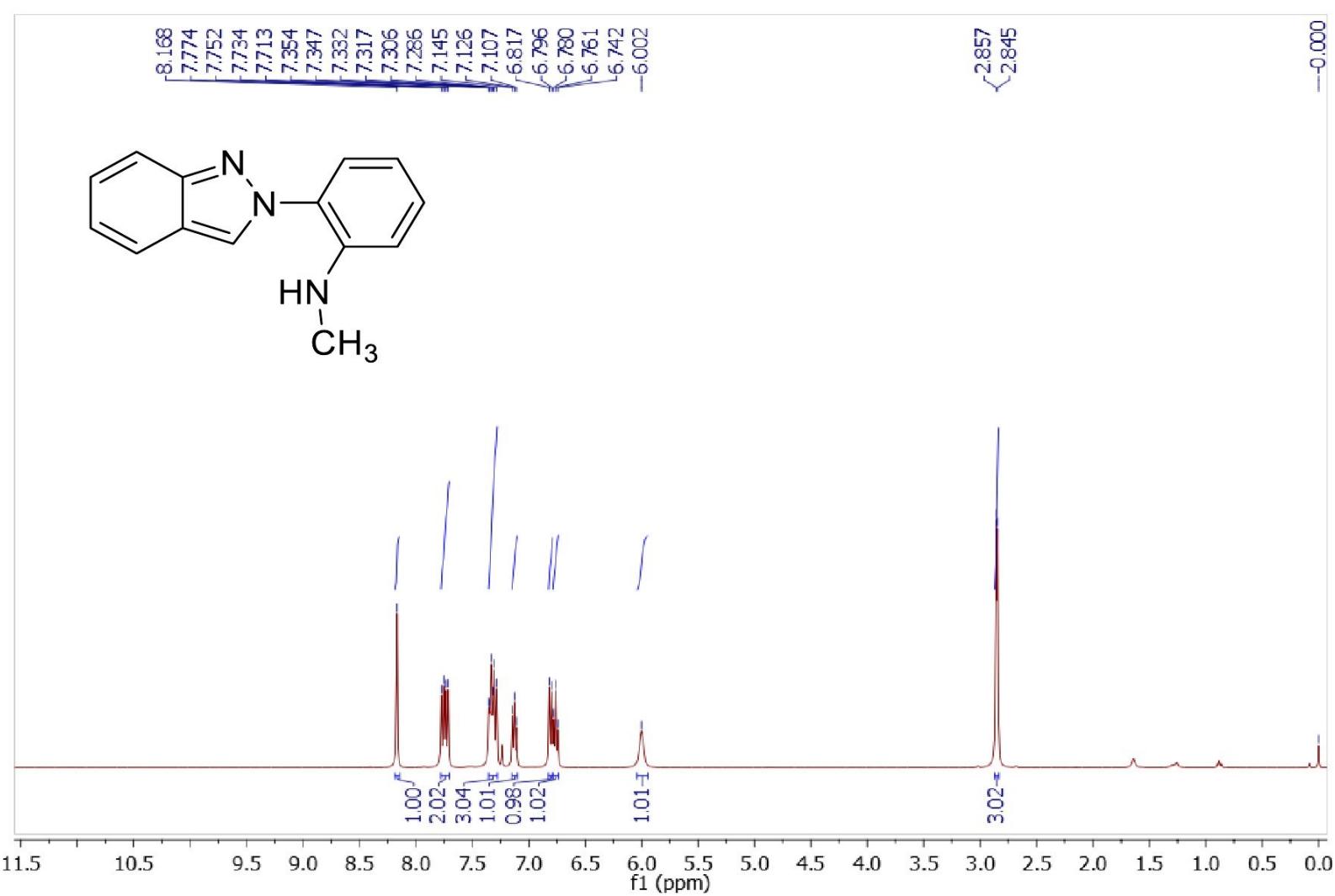
~19.60  
~18.74



# Compound-1c



# Compound-1A



-149.54  
-143.64  
-129.89  
-126.69  
-126.22  
-124.87  
-124.06  
-122.20  
-121.83  
-120.40  
-117.48  
-115.97  
-111.61

-30.01

