

## *Supporting Information for*

### A one-pot regioselective synthesis of benzo[*d*]imidazo[2,1-*b*]thiazoles

Xinhai Zhang, Jiong Jia and Chen Ma\*

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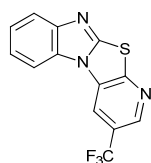
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Table 1 X-ray structure data of compound **3a**

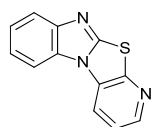
Compound reference	<b>3a</b>
Chemical formula	C <sub>13</sub> H <sub>6</sub> F <sub>3</sub> N <sub>5</sub> S
Formula Mass	293.27
Crystal system	Orthorhombic
<i>a</i> /Å	17.790(4)
<i>b</i> /Å	20.166(4)
<i>c</i> /Å	6.7371(13)
$\alpha$ /°	90.00
$\beta$ /°	90.00
$\gamma$ /°	90.00
Unit cell volume/Å <sup>3</sup>	2417.0(8)
Temperature/K	273(2)
Space group	<i>Aba2</i>
No. of formula units per unit cell, <i>Z</i>	8
No. of reflections measured	5767
No. of independent reflections	2104
<i>R</i> <sub>int</sub>	0.0257
Final <i>R</i> <sub><i>I</i></sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0317
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0760
Final <i>R</i> <sub><i>I</i></sub> values (all data)	0.0450
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0841

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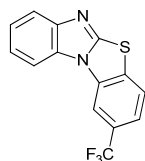
3a

**3-(Trifluoromethyl)benzo[4',5']imidazo[2',1':2,3]thiazolo[5,4-*b*]pyridine (3a)** white solid (64%), mp 270-271°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.76 (s, 1H), 8.25 (s, 1H), 7.88-7.94 (m, 2H), 7.44-7.52 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 110.50 114.62 (d, *J* = 3.5 Hz) 120.31 121.99 123.15 124.36 124.72 128.57 130.19 141.71 (t, *J* = 3.3 Hz) 147.24 152.82 156.71. HRMS calcd for (M+H<sup>+</sup>) 294.0268; found: 294.0292.



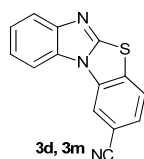
3b

**Benzo[4',5']imidazo[2',1':2,3]thiazolo[5,4-*b*]pyridine (3b)** light yellow solid (67%), mp 183-186°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.48 (dd, *J* = 1.2, 1.5 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 1.8 Hz, 1H), 7.36-7.49 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 110.31 118.22 119.77 121.02 122.50 124.07 128.78 130.23 145.16 146.91 152.53 153.02. HRMS calcd for (M+H<sup>+</sup>) 226.0394; found: 226.0427.



3c

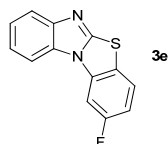
**2-(Trifluoromethyl)benzo[*d*]benzo[4,5]imidazo[2,1-*b*]thiazole (3c)** white solid (72%), mp 211-213°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.13 (s, 1H), δ 7.95-7.99 (m, 1H), 7.58-7.88 (m, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.41-7.49 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 112.78 115.91 118.80 122.73 123.82 124.16 124.48 (d, *J* = 3.75 Hz) 129.94 (d, *J* = 1.5 Hz) 133.62 144.19 (t, *J* = 4 Hz) 145.51 147.34 147.86 156.43. HRMS calcd for (M+H<sup>+</sup>) 293.0316; found: 293.0372.



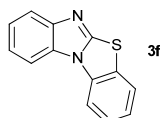
3d, 3m

**Benzo[*d*]benzo[4,5]imidazo[2,1-*b*]thiazole-2-carbonitrile (3d, 3m)** white solid (68%, 43%), mp 274-276 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.17(d, *J* = 1.2 Hz, 1H), 7.94-7.97 (m, 1H), 7.85-7.88 (m, 2H), 7.66 (dd, *J* = 1.5, 1.2 Hz, 1H), 7.43-7.51 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 112.78 115.89 118.79 121.71 123.80 124.13 124.46 129.94 133.59 144.16 145.45 147.31 147.82 156.43. HRMS calcd for (M+H<sup>+</sup>) 250.0394; found: 250.0434.

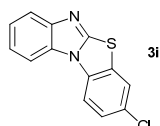
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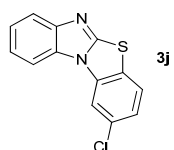
**2-Fluorobenzo[d]benzo[4,5]imidazo[2,1-b]thiazole (3e)** white solid (54%), mp 163-166 °C.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.32-8.46 (m, 2H), 8.06-8.14 (m, 1H), 7.76 (dd,  $J = 2.4$ , 2.1 Hz, 1H), 7.13-7.52 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  106.54 (d,  $J = 28.5$  Hz) 117.03 (t,  $J = 16.2$  Hz) 123.93 127.15 128.65 (d,  $J = 2.4$  Hz) 131.45 (d,  $J = 9.7$  Hz) 135.08 (d,  $J = 12$  Hz) 152.75 160.90 165.48 167.90. HRMS calcd for ( $\text{M}+\text{H}^+$ ) 243.0348; found: 243.0375.



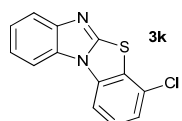
**Benzo[d]benzo[4,5]imidazo[2,1-b]thiazole (3f, 3g, 3h)** white solid (62%, 77%, 71%), mp 139-141 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.36$  Hz, 2H), 7.85 (dd,  $J = 1.36$ , 1.28 Hz, 1H), 7.76 (d,  $J = 8$  Hz, 1H), 7.54-7.58 (m, 1H), 7.37-7.46 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  110.62 112.41 119.45 122.02 123.68 124.35 124.46 126.74 129.05 130.44 133.22 147.94 155.35. HRMS calcd for ( $\text{M}+\text{H}^+$ ) 225.0442; found: 225.0468.



**3-Chlorobenzo[d]benzo[4,5]imidazo[2,1-b]thiazole (3i)** white solid (69%), mp 210-212 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 7.32$  Hz, 1H), 7.83 (d,  $J = 8.56$  Hz, 2H), 7.72 (d,  $J = 1.96$  Hz, 1H), 7.51 (dd,  $J = 2$  Hz, 1H), 7.36-7.45 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  110.37 112.81 119.68 122.19 123.79 124.07 126.94 129.82 130.25 130.49 131.71 148.08 154.89. HRMS calcd for ( $\text{M}+\text{H}^+$ ) 259.9989; found: 259.0087.



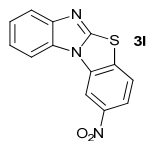
**2-Chlorobenzo[d]benzo[4,5]imidazo[2,1-b]thiazole (3j)** white solid (85%), mp 233-236 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (dd,  $J = 1.92$ , 1.32 Hz, 2H), 7.84 (dd,  $J = 1.32$ , 1.48 Hz, 1H),  $\delta$  7.65 (d,  $J = 8.52$  Hz, 1H),  $\delta$  7.37-7.45 (m, 2H), 7.36 (dd,  $J = 1.92$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  110.64 112.84 119.63 122.40 124.10 124.65 124.99 127.35 130.21 132.88 133.83 147.89 155.54. HRMS calcd for ( $\text{M}+\text{H}^+$ ) 259.9989; found: 259.0087.



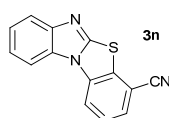
**4-Chlorobenzo[d]benzo[4,5]imidazo[2,1-b]thiazole (3k)** white solid (83%), mp 198-201 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 8.04$  Hz, 1H), 7.84 (t,  $J = 6.2$ , 7.64 Hz, 2H), 7.50 (t,  $J = 8$  Hz, 1H)  $\delta$  7.34-7.44 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  110.27 110.51 119.73 122.27 123.90

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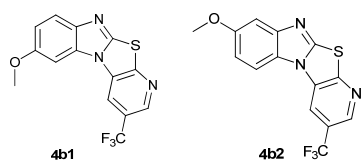
124.17 127.60 128.92 129.28. 130.36 134.07 148.05 154.63. HRMS calcd for (M+H<sup>+</sup>) 259.9989;  
found: 259.0083.



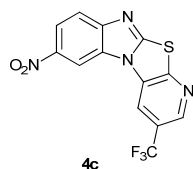
**2-Nitrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazole (3l)** yellow solid (54%), mp 274-277°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.75 (s, 1H), 8.30 (d, *J* = 8.32 Hz, 1H), 8.05 (d, *J* = 4.72 Hz, 1H), 7.87-7.92 (m, 2H), 7.50 (d, *J* = 3.72 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 107.31 110.82 119.44 120.06 123.15 124.54 124.67 130.32 133.27136.75 146.70 147.91 154.95. HRMS calcd for (M+H<sup>+</sup>) 270.0293; found: 270.0333.



**Benzo[d]benzo[4,5]imidazo[2,1-b]thiazole-4-carbonitrile (3n)** light yellow solid (53%), mp 232-234°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.05 (d, *J* = 8 Hz, 1H), 7.34 (dd, *J* = 1.24 Hz, 1H), 7.82 (m, 2H), 7.39-7.48 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 97.56 114.46 119.10 119.54 122.85 124.28 124.71 128.90 131.21 131.33 132.88 134.91 148.26 154.91. HRMS calcd for (M+H<sup>+</sup>) 250.0394; found: 250.0433.

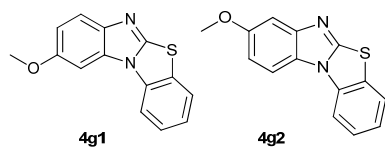


**7-Methoxy-3-(trifluoromethyl)benzo[4',5']imidazo[2',1':2,3]thiazolo[5,4-b]pyridine (4b1), 8-methoxy-3-(trifluoromethyl)benzo[4',5']imidazo[2',1':2,3]thiazolo[5,4-b]pyridine (4b2)** white solid (81%), mp 225-227°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.75 (s, 1H), 8.14 (d, *J* = 1.5 Hz), 7.77 (dd, *J* = 4.2 Hz, 1H), 7.35 (dd, *J* = 2.4 Hz, 1H), 7.09 (dd, *J* = 2.4 Hz, 1H), 3.97(s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 56.29 95.09 102.89 110.78 112.56 114.40 (q, *J* = 3.75 Hz) 120.45 124.57 128.41 130.57 141.66 (t, *J* = 4.5 Hz) 151.17 156.66 157.82. HRMS calcd for (M+H<sup>+</sup>) 324.0374; found: 324.0406.

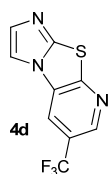


**7-Nitro-3-(trifluoromethyl)benzo[4',5']imidazo[2',1':2,3]thiazolo[5,4-b]pyridine (4c)** yellow solid (27%), mp 241-244°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.85 (d, *J* = 0.88 Hz, 1H), 8.75 (d, *J* = 2.04 Hz, 1H), 8.51 (d, *J* = 8.84 Hz, 1H), 7.39-7.48 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 112.78 115.91 118.80 121.73 123.82 124.53 (d, *J* = 8.4 Hz) 129.94 (d, *J* = 3.4 Hz) 133.62 144.19 (t) 145.51 147.34 147.86 156.43. HRMS calcd for (M+H<sup>+</sup>) 339.0119; found: 339.0151.

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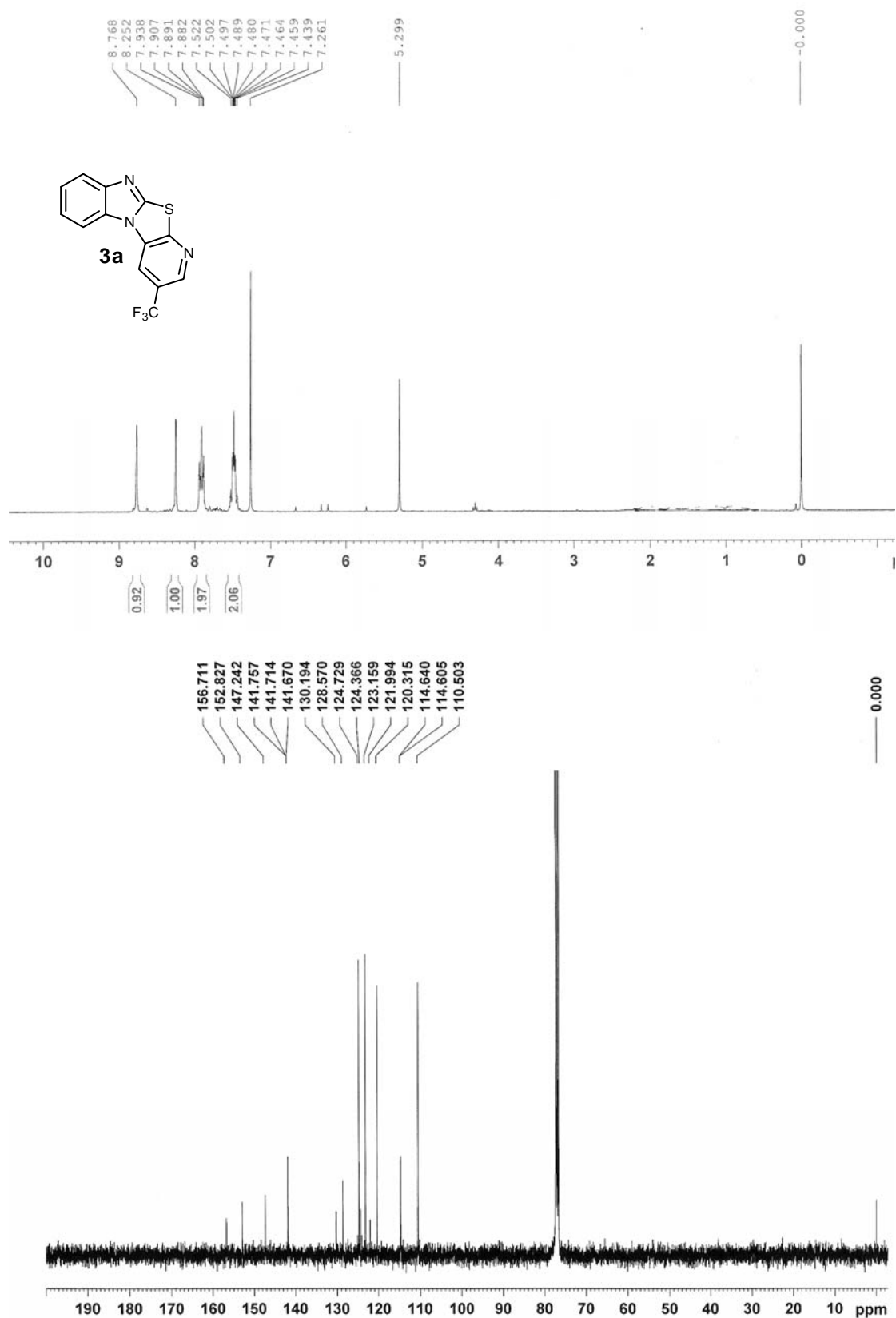


**9-Methoxybenzo[*d*]benzo[4,5]imidazo[2,1-*b*]thiazole (4g1), 8-methoxybenzo[*d*]benzo[4,5]imidazo[2,1-*b*]thiazole (4g2)** white solid (79%), mp 123-125°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (dd,  $J = 3.2$  Hz, 2H), 8.75 (d,  $J = 4.8$  Hz, 1H), 7.69- 7.72 (m, 3H), 7.52 (t, 2H)  $\delta$  7.41 (d,  $J = 2.24$  Hz, 1H), 7.31-7.36 (m, 3H), 6.97-7.05 (m, 2H), 3.92 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  56.13 95.62 102.28 110.77 111.18 111.59 112.14 119.72 124.25 126.58 128.09 133.08 155.74 156.89. HRMS calcd for ( $\text{M}+\text{H}^+$ ) 255.0547; found: 255.0614.

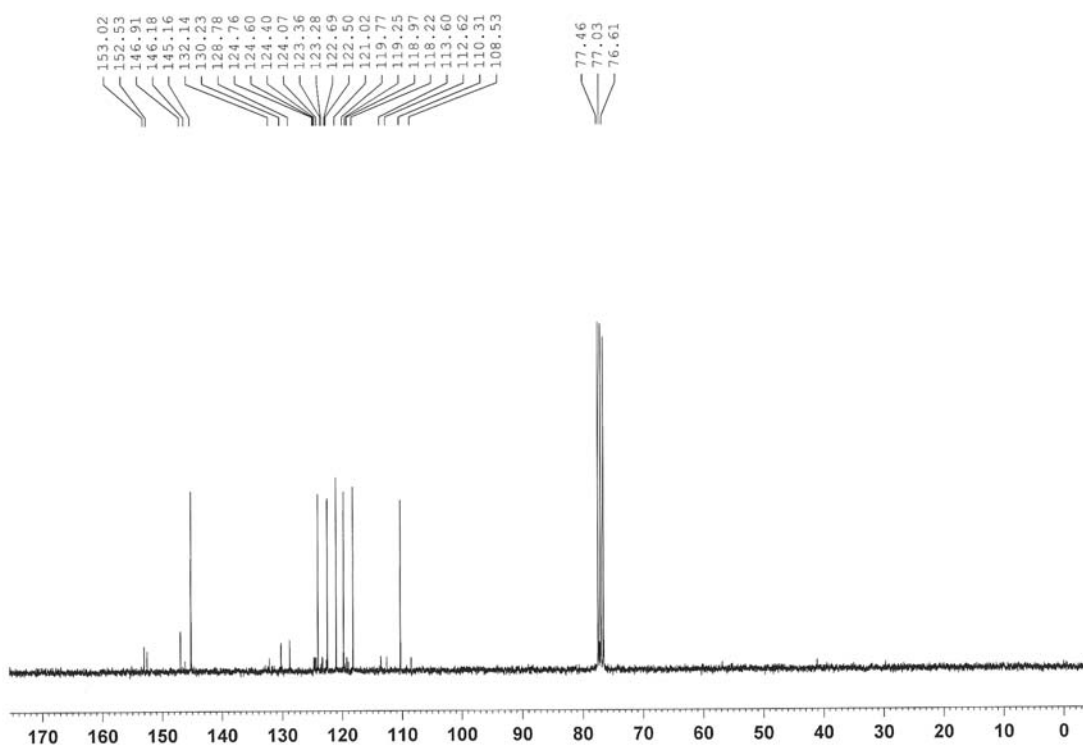
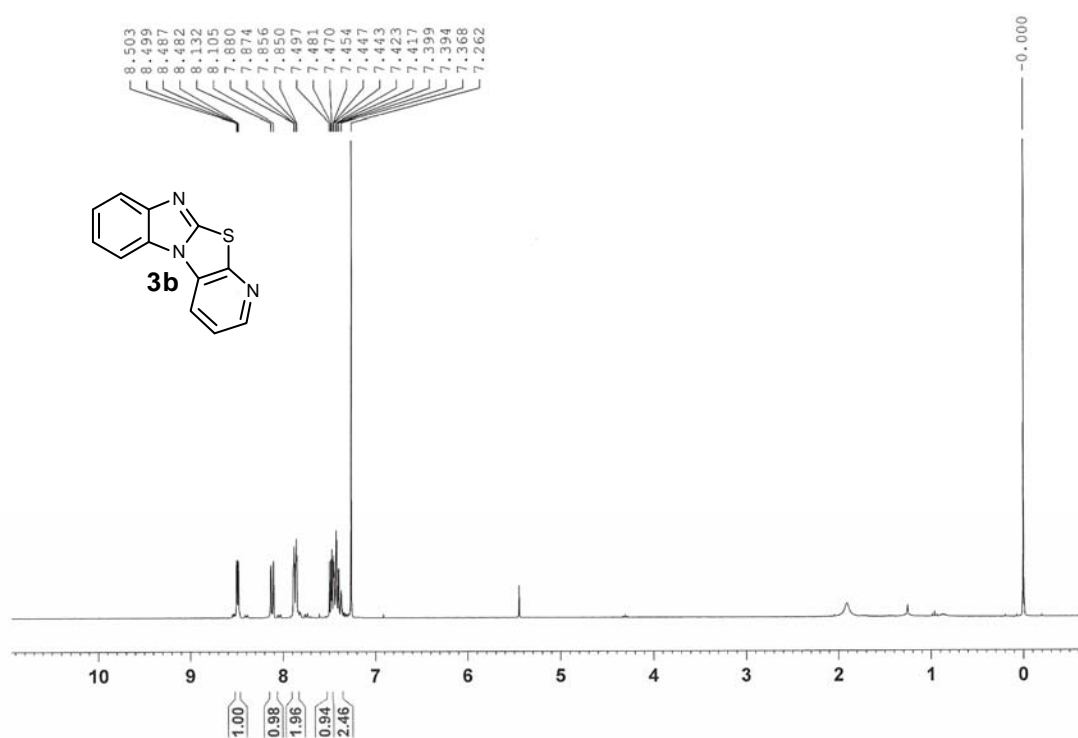


**6-(Trifluoromethyl)imidazo[2',1':2,3]thiazolo[5,4-*b*]pyridine (4d)** white solid (67%), mp 128-130°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (s, 1H), 8.28(s, 1H), 7.99 (s, 1H), 7.46 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  112.67 121.40 123.72 125.87 129.89 (q,  $J = 3.75$  Hz) 135.96 143.22 (q,  $J = 4.5$  Hz) 146.32 146.95. HRMS calcd for ( $\text{M}+\text{H}^+$ ) 244.0112; found: 244.0187.

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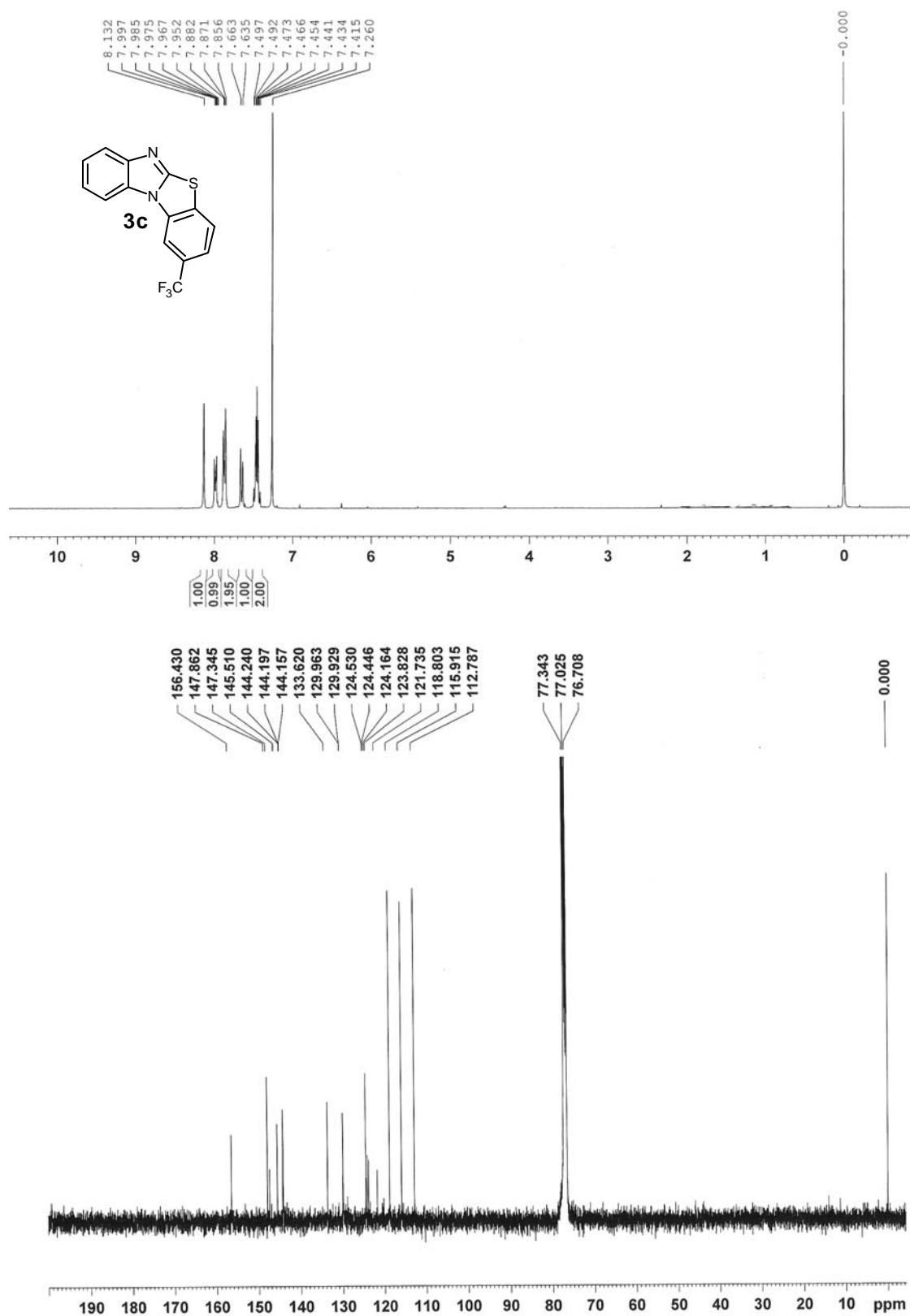


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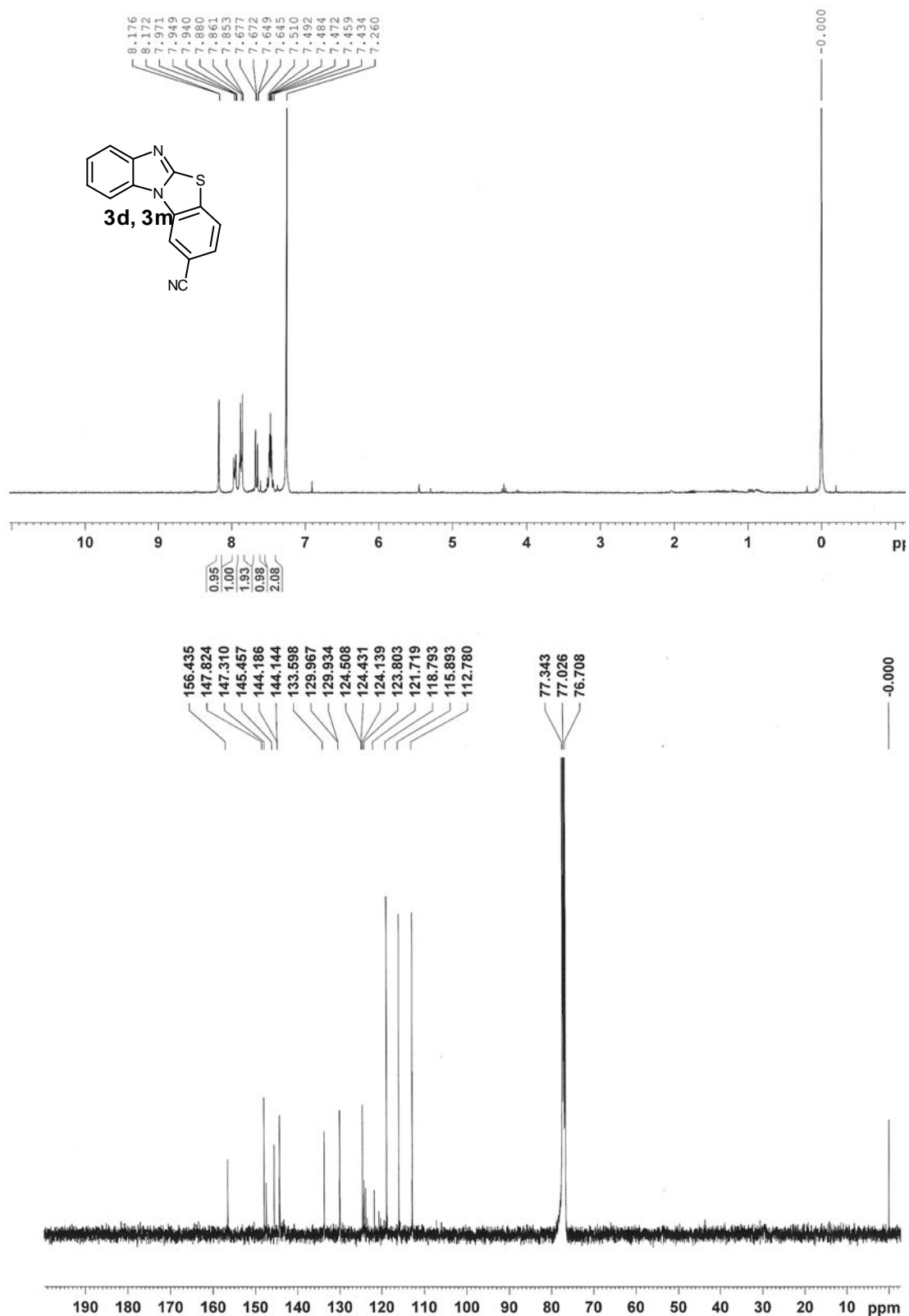




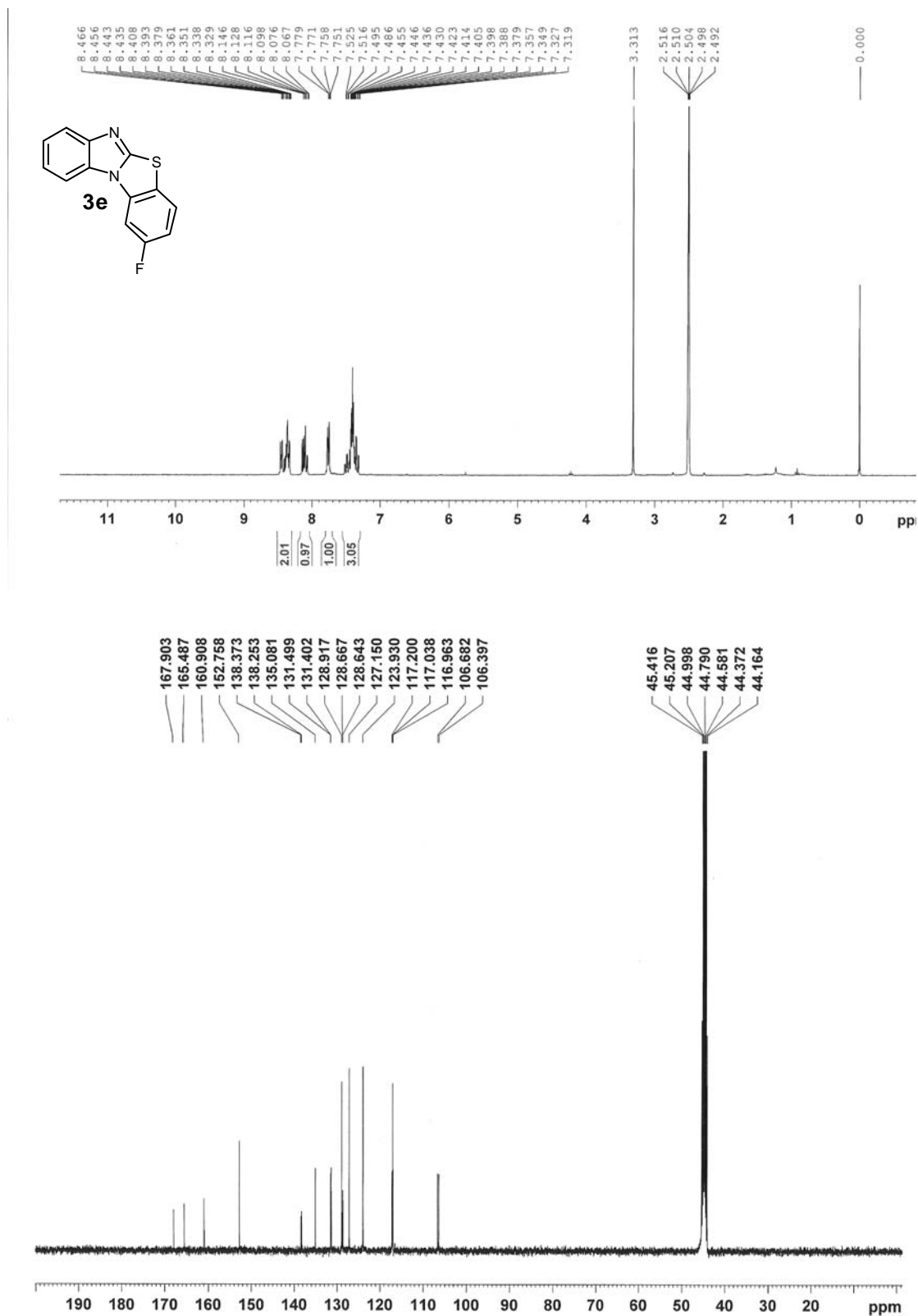
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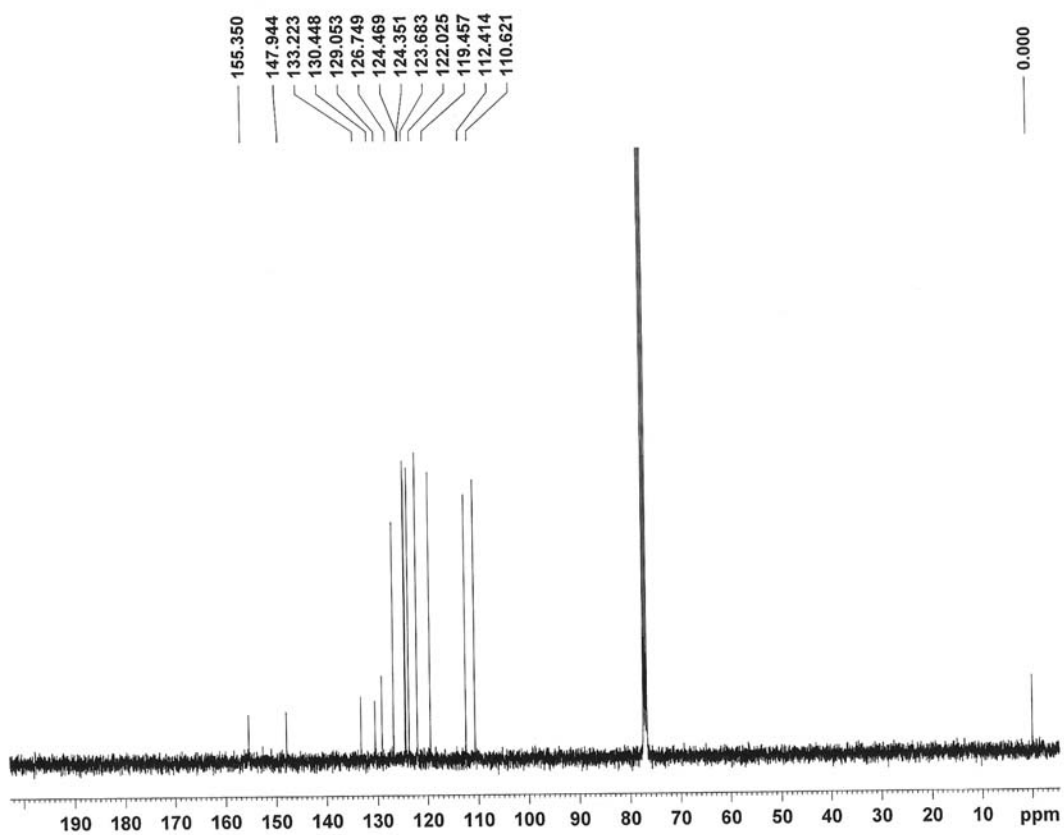
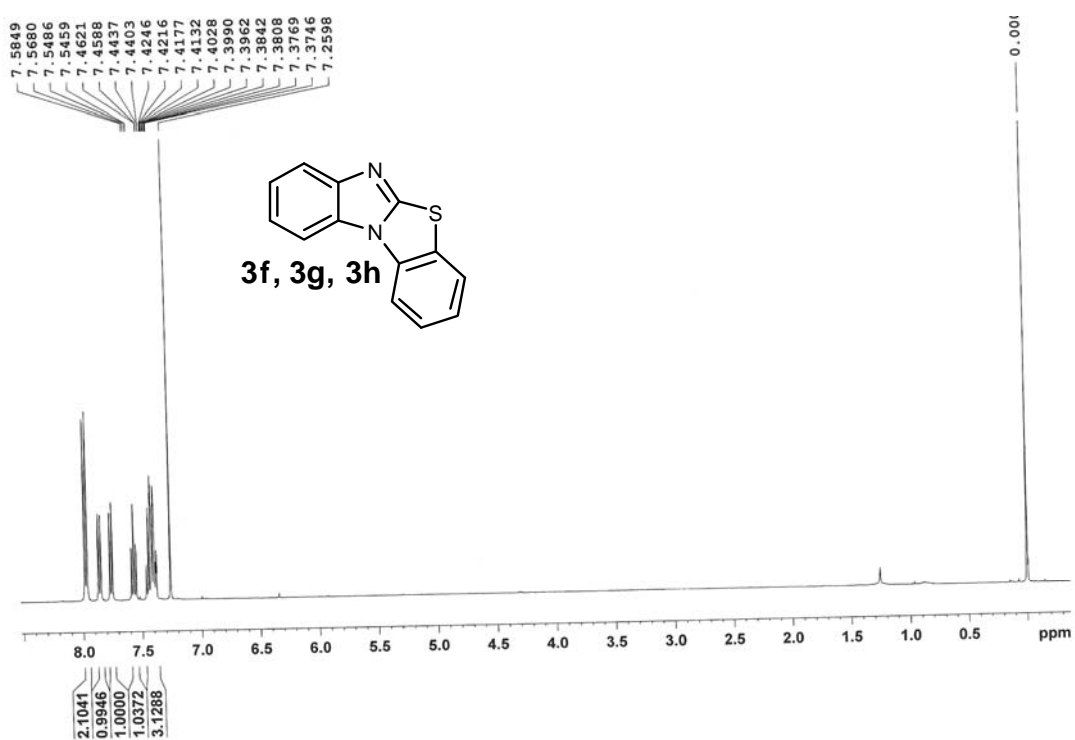
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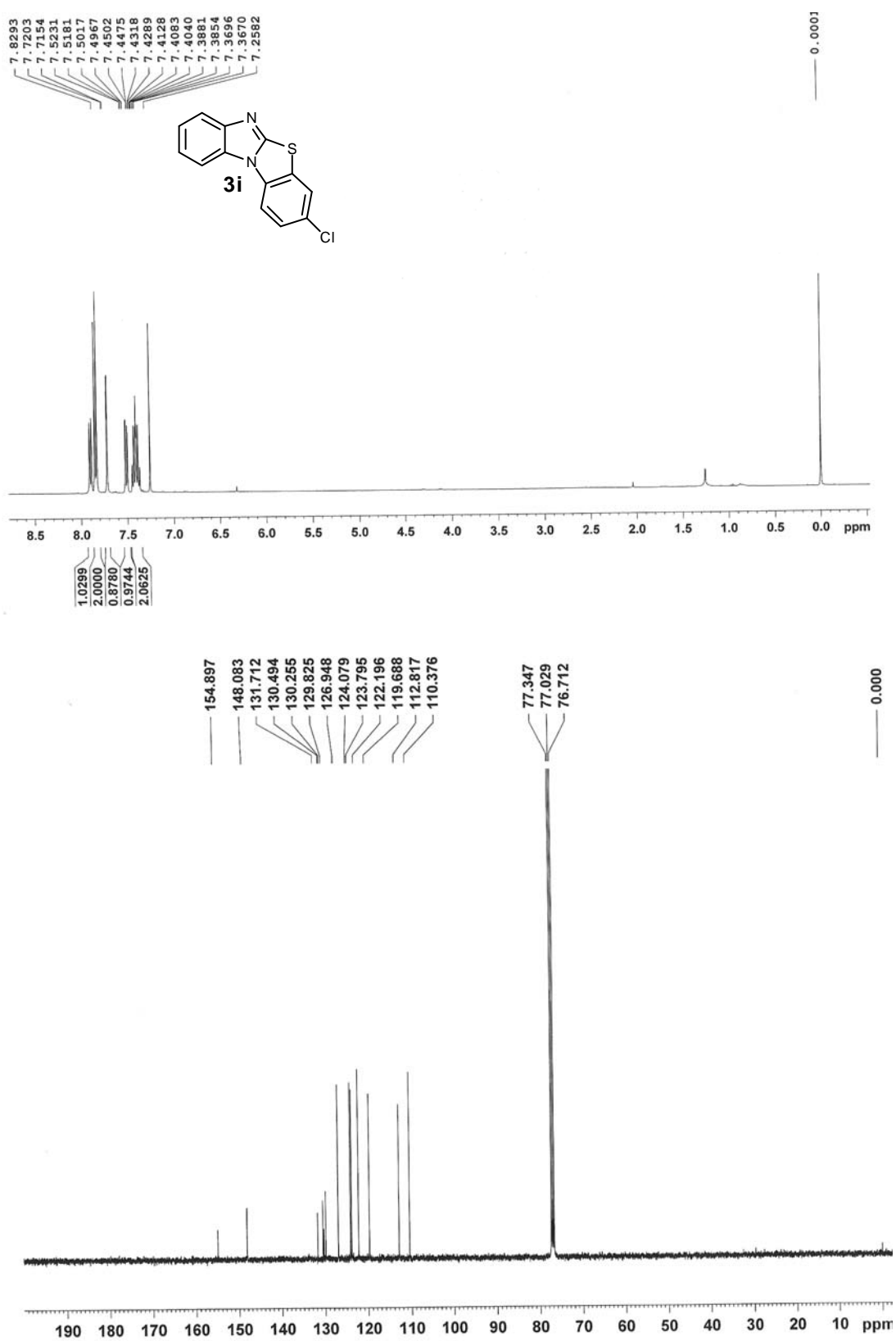
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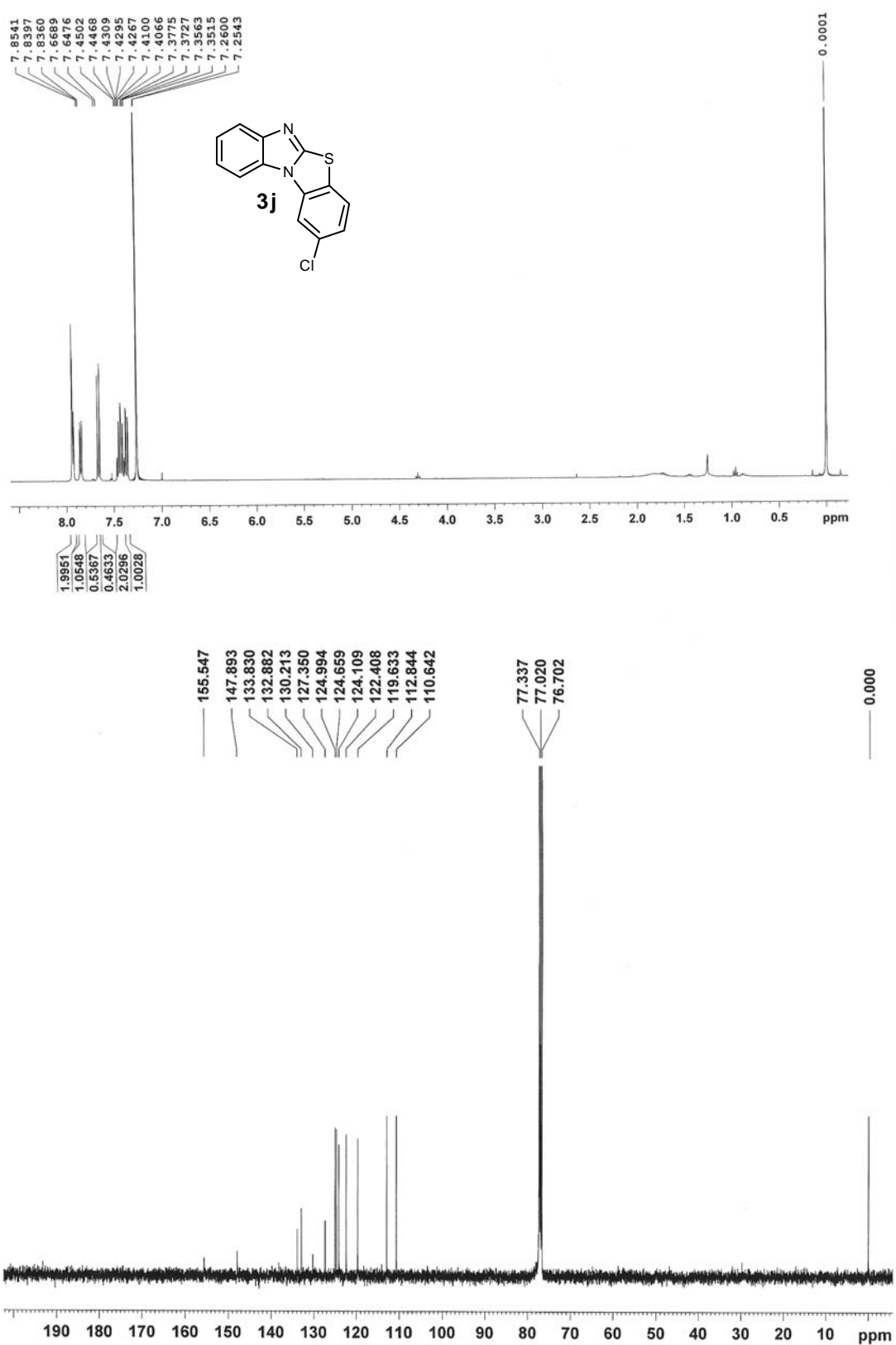
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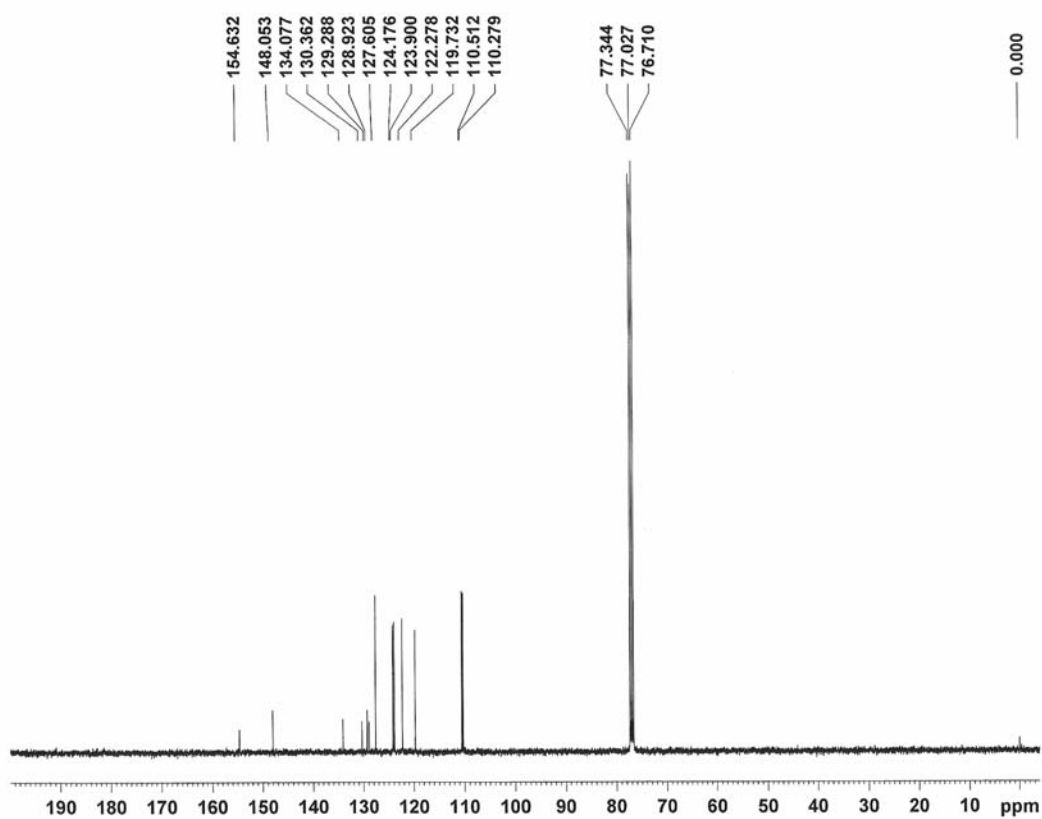
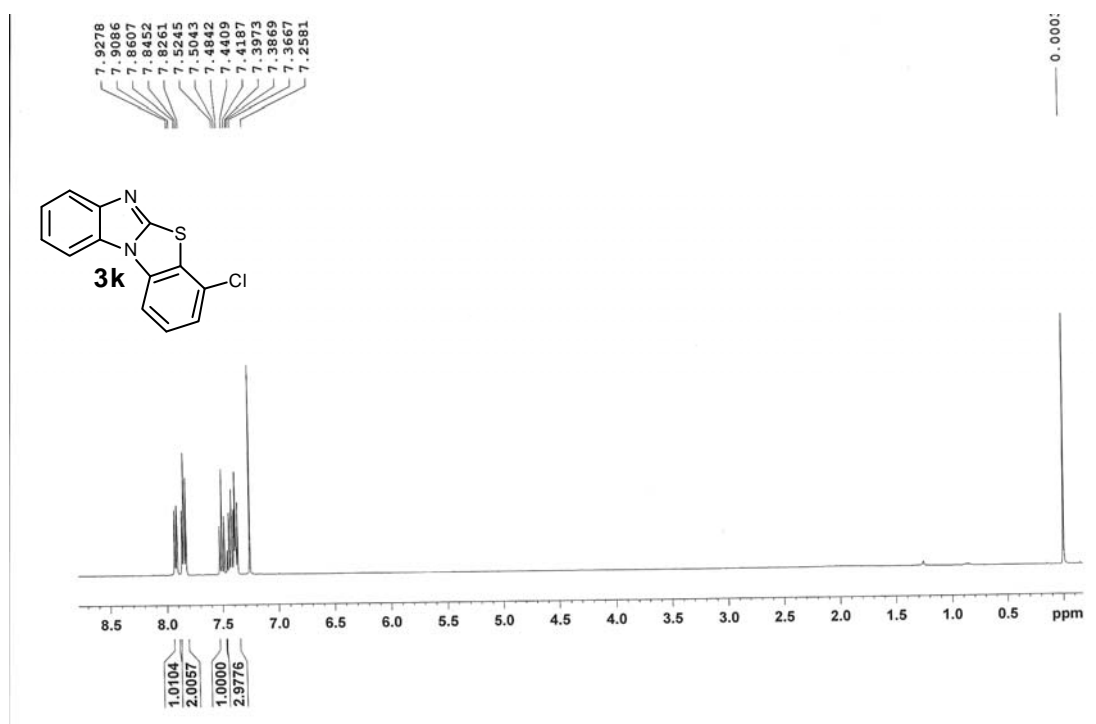
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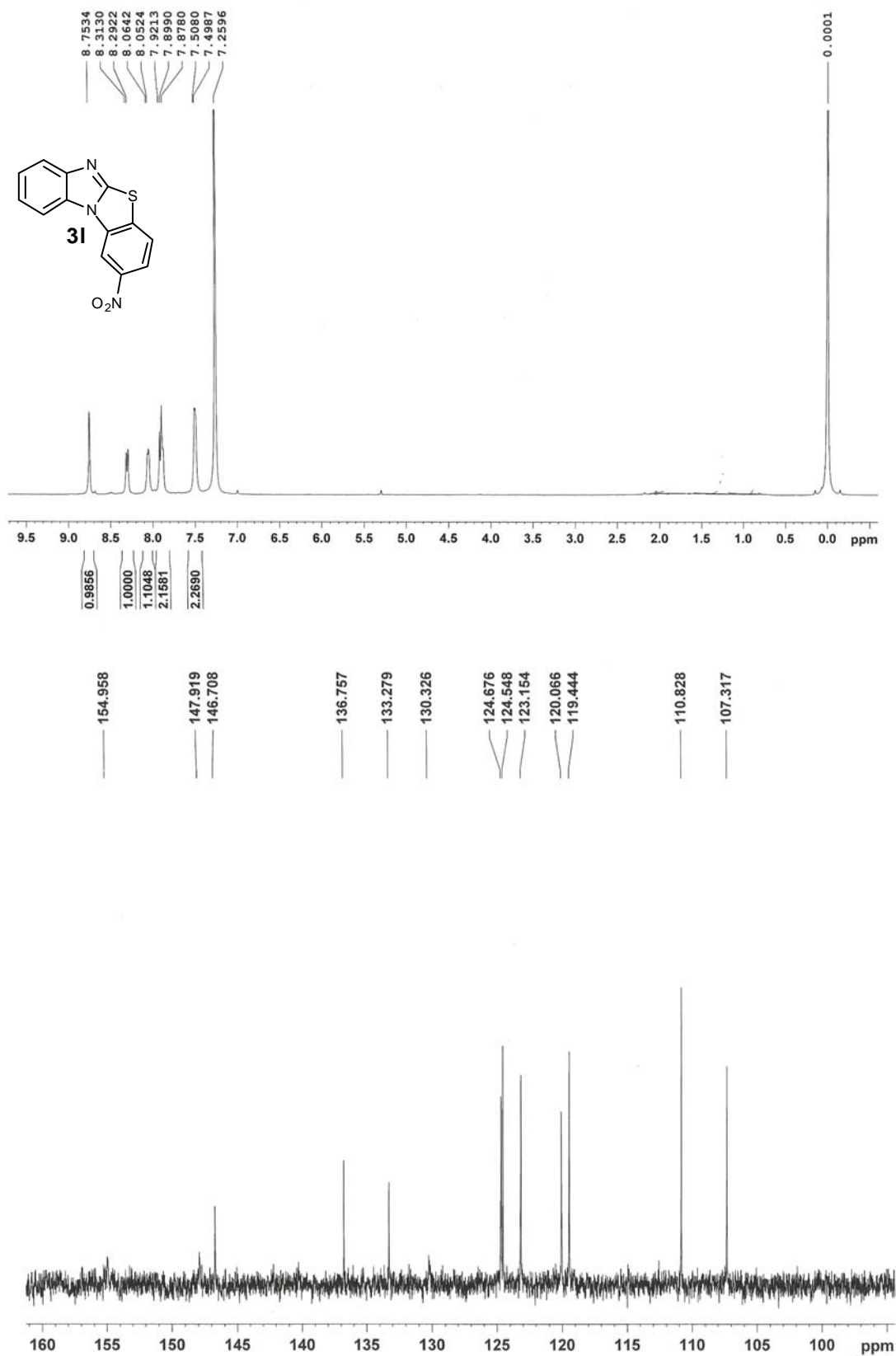
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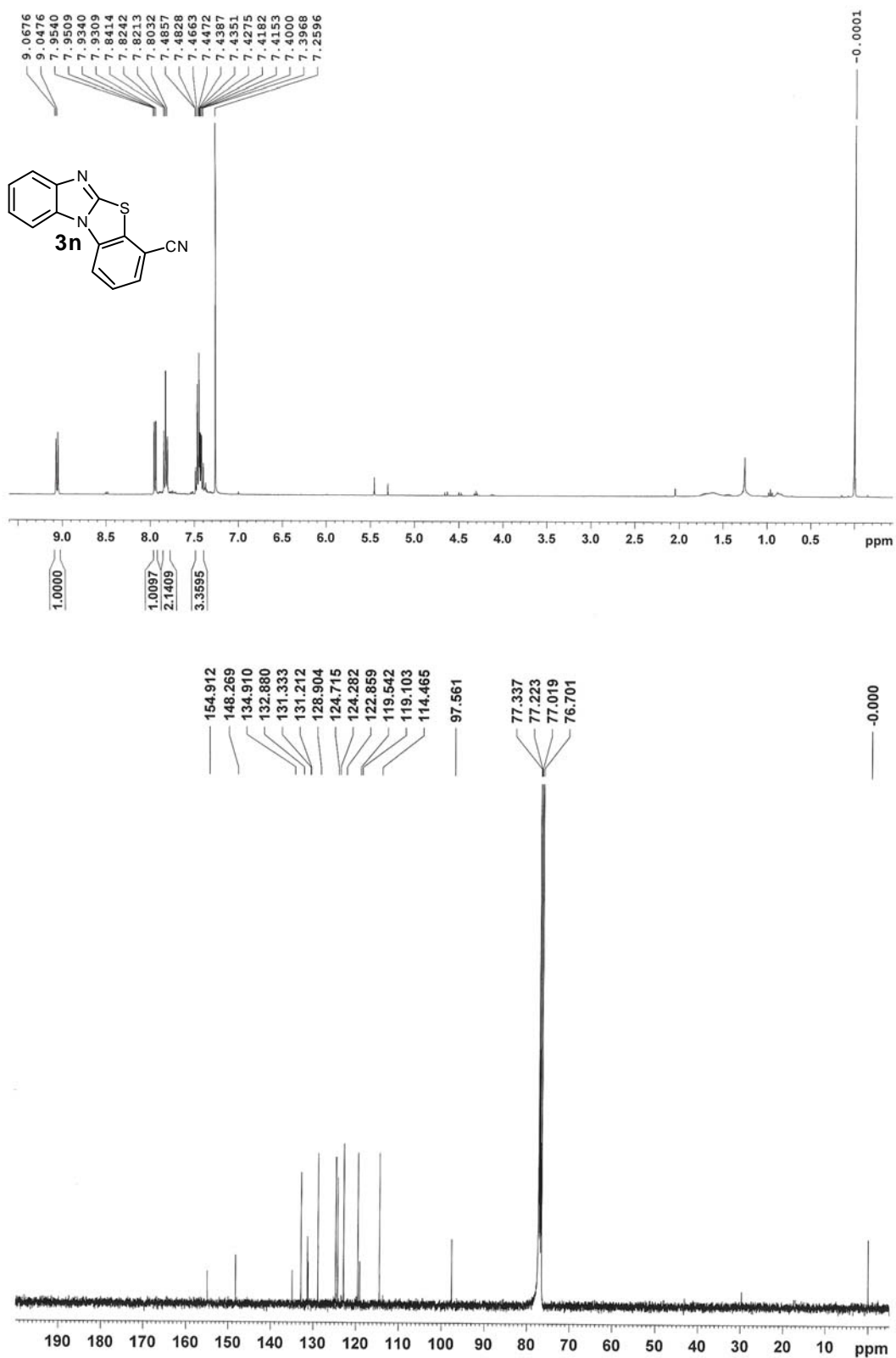
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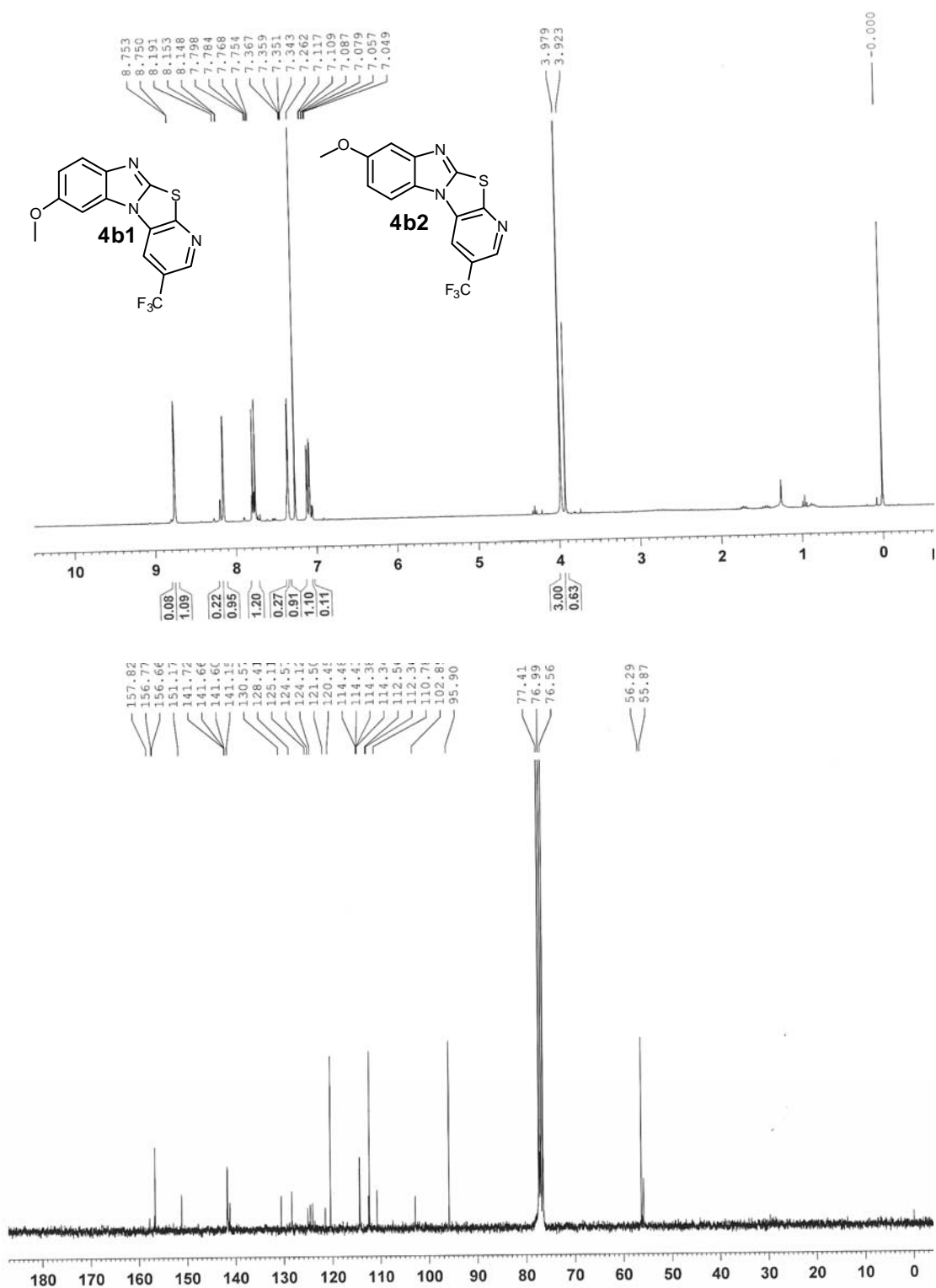


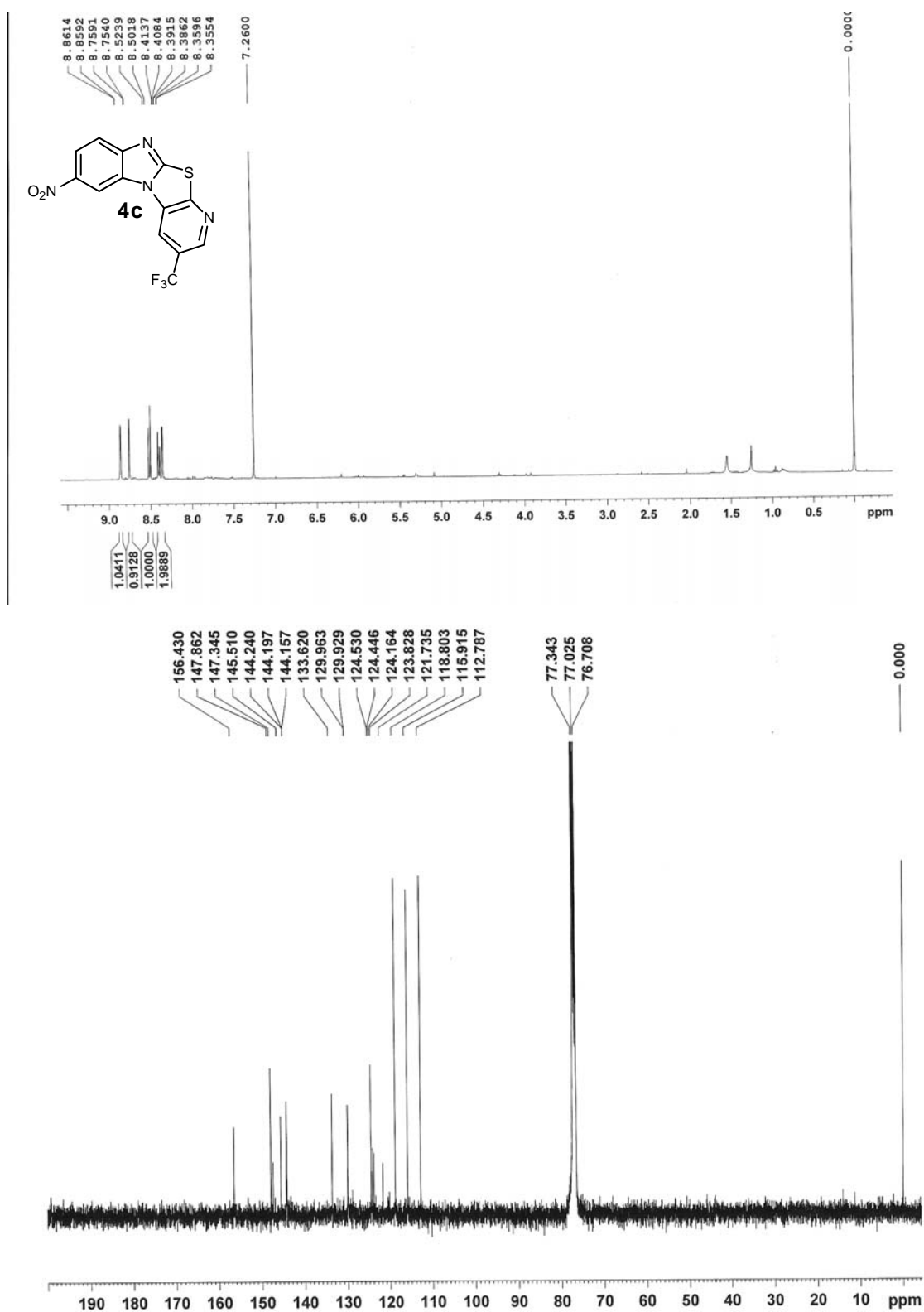
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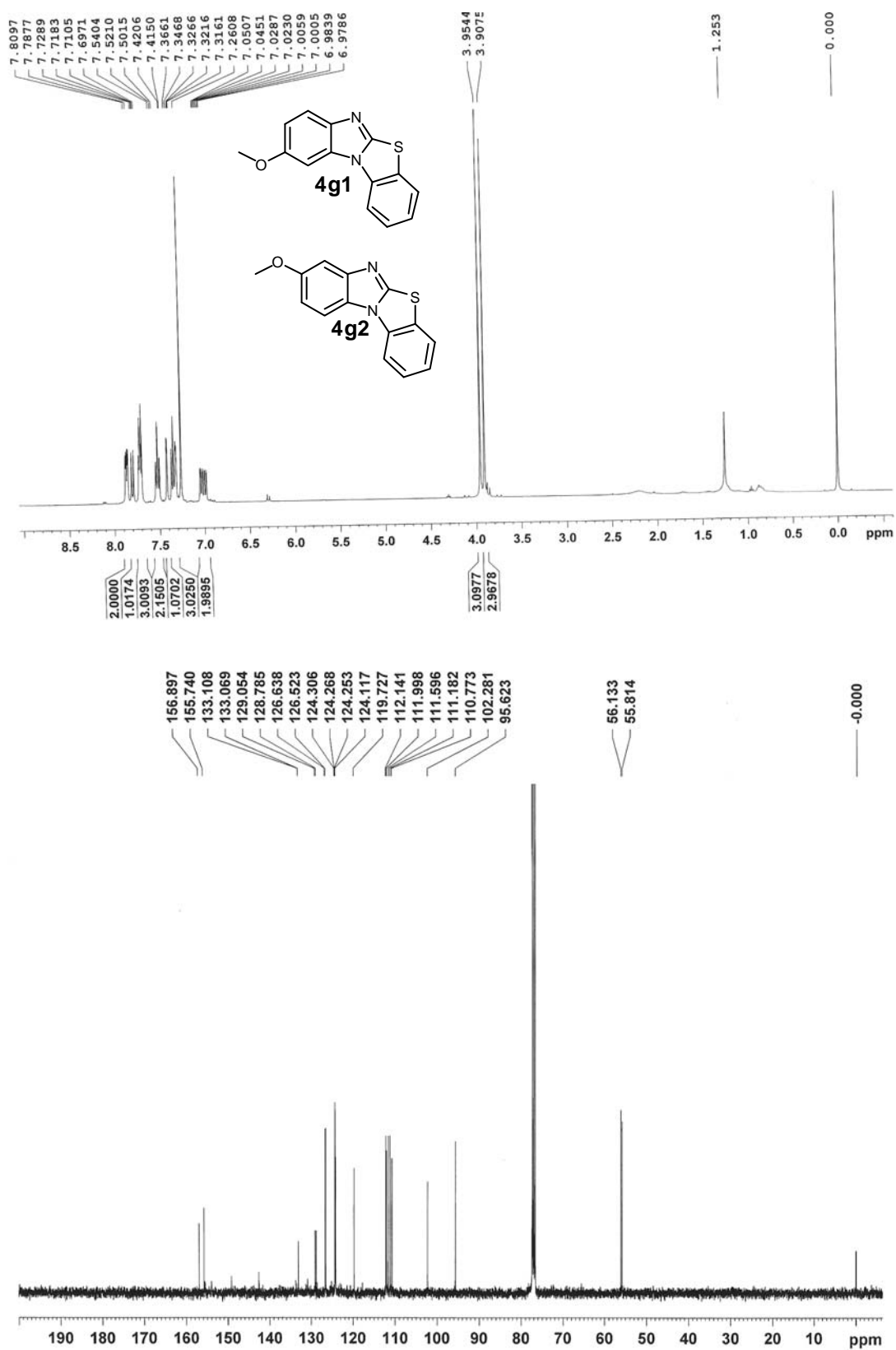








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