

## Supporting Information

### **Deep eutectic solvent promoted synthesis of structurally diverse hybrid molecules with privileged heterocyclic substructures**

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- **Experimental Section**

## General procedure

The melting points of all the synthesized compounds were determined on electric melting point apparatus and are uncorrected. The aldehydes, 1,3-diketones and hydantoin used in the synthesis of heterocycles were purchased from the commercial sources and were used as such. The purity of all the synthesized compounds was checked by TLC. The solid compound was purified by recrystallization from absolute ethanol without using any column chromatography.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on JEOL 400MHz and 100MHz NMR spectrometer, respectively. Analytical and spectral data of the synthesized heterocycles are also included.

**Synthesis of deep eutectic solvents based on guanidine salt and urea:** Deep eutectic solvent based on guanidine salt and urea was prepared according to literature procedure<sup>1</sup>. A mixture of GuHCl (100 mmol) and urea (200 mmol) at 70 °C until homogenous liquid was formed. The resulting eutectic solvent was then allowed to cool at room temperature and was used for the synthesis of the desired product without further purification.

**Typical procedure for synthesis of heterocycles:** A mixture of aldehyde (1 mmol), 1,3-diketone (1 mmol) and hydantoin (1 mmol) in deep eutectic solvent (2 ml) was stirred on a magnetic stirrer at 80°C for nearly 30–38 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched by pouring it on crushed ice. The deep eutectic solvent remained in the water and the solid product was separated by filtration. The deep eutectic solvent was recovered from the filtrate by evaporation. The recovered deep eutectic solvent was reused.

## Reference

1. J. Parnica and M. Antalík, *Journal of Molecular Liquids*, 2014, **197**, 23-26.

- **Spectral details**

**10-(1H-indol-3-yl)indeno[2',1':4,5]pyrrolo[1,2-c]imidazole-1,3,9(2H)-trione (4aa):** Yield: 95%, Musturd yellow solid, mp (149-151°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.28 (bs, 1H, NH), 10.05 (s, 1H, NH), 6.99-8.01 (m, 8H, ArH), 8.32 (s, 1H, ArH). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 94.59, 111.64, 113.70, 119.78, 120.63, 121.21, 121.65, 122.06, 124.49, 128.04, 128.85, 129.48, 130.02, 133.41, 133.223, 136.73, 137.30, 140.05, 149.14, 167.50, 185.27. Anal. calculated for C<sub>21</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub> : C 71.39, H 3.14, N 11.89, O 13.58%; found: C 71.60, H 3.11, N 11.87, O 13.56 %.

**10-(naphthalen-1-yl)indeno[2',1':4,5]pyrrolo[1,2-c]imidazole-1,3,9(2H)-trione (4ab):** Yield: 92%, Light brown liquid, <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.23 (bs, 1H, NH), 7.53-8.36 (m, 11H, ArH). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 110.70, 115.42, 121.56, 123.48, 124.98, 125.25, 127.07, 127.76, 128.73, 129.19, 131.48, 132.18, 133.81, 134.56, 135.42, 135.58, 136.83, 140.06, 140.15, 149.29, 167.36, 186.30. Anal. calculated for C<sub>23</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub> : C 75.82, H 3.32, N 7.69, O 13.17%; found: C 75.80, H 3.31, N 7.67, O 13.16 %.

**10-(pyridin-3-yl)indeno[2',1':4,5]pyrrolo[1,2-c]imidazole-1,3,9(2H)-trione (4ac):** Yield: 92%, Light brown solid, mp (110-112°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.25 (bs, 1H, NH), 9.16-9.18(d,1H, ArH), 8.71-8.72 (m, 1H, ArH), 7.45-8.04 (m, 6H, ArH). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 113.65, 121.27, 121.86, 123.70, 124.26, 129.16, 131.45, 133.16, 133.33, 135.75, 135.86, 139.91, 140.30, 147.57, 148.25, 149.26, 167.31, 188.91. Anal. calculated for C<sub>18</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub> : C 68.57, H 2.88, N 13.33, O 15.22%; found: C 68.55, H 2.86, N 13.31, O 15.21 %.

**10-(thiophen-3-yl)indeno[2',1':4,5]pyrrolo[1,2-c]imidazole-1,3,9(2H)-trione (4ad):** Yield: 94%, Dark green solid, mp (128-130°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.26 (bs, 1H, NH), 7.77-8.05(m, 6H, ArH), 7.22-7.25 (m, 1H, ArH), <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 113.58,

121.37, 121.97, 123.23, 124.83, 128.14, 128.45, 128.72, 130.52, 135.06, 135.29, 138.40, 140.48, 141.86, 149.17, 167.21, 186.59. Anal. calculated for C<sub>17</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>S: C 63.74, H 2.52, N 8.75, O 14.98; found: C 63.73, H 2.51, N 8.71, O 14.97.

**10-(3-bromo-4-hydroxy-5-methoxyphenyl)indeno[2',1':4,5]pyrrolo[1,2-c]imidazole-**

**1,3,9(2H)-trione (4ae):** Yield: 91%, Mahroon solid, mp (135-137°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.52 (bs, 1H, NH), 9.76 (bs, 1H, OH), 7.71-7.97 (m, 4H, ArH), 7.34 (s, 1H, ArH), 7.48 (s, 1H, ArH), 3.93 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 56.70, 108.92, 114.49, 115.12, 121.97, 123.23, 126.17, 126.69, 128.15, 132.20, 134.37, 135.24, 137.96, 140.01, 140.68, 142.50, 150.20, 154.41, 167.24, 189.84. Anal. calculated for C<sub>20</sub>H<sub>11</sub>BrN<sub>2</sub>O<sub>5</sub>: C 54.69, H 2.52, N 6.38, O 18.21%; found: C 54.67, H 2.51, N 6.37, O 18.20 %.

**9-(1H-indol-3-yl)-6,6-dimethyl-6,7-dihydro-1H-imidazo[1,5-a]indole-1,3,8(2H,5H)-trione**

**(4ba):** Yield: 94%, Yellow solid, (134-136°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.22 (bs, 1H, NH), 10.04 (s, 1H, NH), 8.75 (s, 1H, ArH), 7.31-7.99 (m, 4H, ArH), 2.92 (s, 2H, CH<sub>2</sub>), 2.60 (s, 2H, CH<sub>2</sub>), 1.11 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 28.67, 35.49, 43.77, 54.00, 94.49, 111.70, 113.58, 118.85, 121.44, 121.83, 122.03, 128.26, 128.85, 129.99, 135.69, 136.29, 149.82, 167.58, 197.78. Anal. calculated for C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>: C 69.15, H 4.93, N 12.10, O 13.82%; found: C 69.14, H 4.91, N 12.07, O 13.86 %.

**6,6-dimethyl-9-(naphthalen-1-yl)-6,7-dihydro-1H-imidazo[1,5-a]indole-1,3,8(2H,5H)-trione**

**(4bb):** Yield: 91%, Light brown liquid, <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ = 11.26 (bs, 1H, NH), 7.25-8.06 (m, 7H, ArH), 2.89 (s, 2H, CH<sub>2</sub>), 2.48 (s, 2H, CH<sub>2</sub>), 1.08 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 28.74, 35.36, 43.26, 54.18, 113.55, 124.20, 125.73, 127.07, 127.50, 128.59, 129.18, 131.45, 134.27, 134.39, 136.85, 138.40, 149.04, 167.26, 193.72. Anal. calculated

for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub> : C 73.73, H 5.06, N 7.82, O 13.39%; found: C 73.71, H 5.04, N 13.37, O 13.36 %.

**6,6-dimethyl-9-(pyridin-3-yl)-6,7-dihydro-1H-imidazo[1,5-a]indole-1,3,8(2H,5H)-trione**

**(4bc):** Yield 93%, Light brown, mp (112-115°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.26 (s, 1H, NH), 8.97 (s, 1H, ArH), 7.66-8.54 (m, 3H, ArH), 2.88 (s, 2H, CH<sub>2</sub>), 2.58 (s, 2H, CH<sub>2</sub>), 1.09 (s, 6H, CH<sub>3</sub>). Anal. calculated for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: C 66.01, H 4.89, N 13.58, O 15.52%; found: C 66.00, H 4.88, N 13.57, O 15.50 %.

**6,6-dimethyl-9-(thiophen-3-yl)-6,7-dihydro-1H-imidazo[1,5-a]indole-1,3,8(2H,5H)-trione**

**(4bd):** Yield 95%, Violet solid, mp (129-131°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.89 (s, 1H, NH), 7.12-7.37 (m, 3H, ArH), 2.90 (s, 2H, CH<sub>2</sub>), 2.59 (s, 2H, CH<sub>2</sub>), 1.12 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 29.08, 32.15, 45.21, 52.60, 115.77, 123.88, 126.52, 127.74, 129.47, 130.42, 133.59, 136.69, 151.65, 166.92, 189.76. Anal. calculated for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S: C 61.13, H 4.49, N 8.91, O 15.27, S 10.20%; found: C 61.11, H 4.47, N 8.89, O 15.24, S 10.18 %.

**9-(3-bromo-4-hydroxy-5-methoxyphenyl)-6,6-dimethyl-6,7-dihydro-1H-imidazo[1,5-**

**a]indole-1,3,8(2H,5H)-trione (4be):** Yield 91%, Off-white solid, mp (133-135°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.58 (bs, 1H, NH), 9.76 (s, 1H, OH), 7.62 (s, 1H, ArH), 7.34 (s, 1H, ArH), 3.95 (s, 3H, CH<sub>3</sub>), 2.92 (s, 2H, CH<sub>2</sub>), 2.50 (s, 2H, CH<sub>2</sub>), 1.13 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 28.38, 35.46, 43.33, 54.34, 56.13, 109.15, 113.26, 115.34, 123.09, 126.62, 130.83, 135.30, 137.38, 141.11, 148.98, 154.23, 167.24, 196.19. Anal. calculated for C<sub>19</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>5</sub>: C 52.67, H 3.96, N 6.47, O 18.46%; found: C 52.66, H 3.94, N 6.45, O 18.44 %.

**7-(1H-indol-3-yl)-6H,8H-chromeno[3',4':4,5]pyrrolo[1,2-c]imidazole-6,8,10(9H)-trione**

**(4ca):** Yield 93%, Orange solid, mp (119-121°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.22 (bs, 1H,

NH), 10.04 (s, 1H, NH), 7.78 (s, 1H, ArH), 7.18-8.30 (m, 8H, ArH).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 94.40, 111.66, 118.48, 119.72, 121.28, 122.04, 123.09, 124.46, 126.50, 126.92, 128.56, 128.90, 129.67, 130.50, 131.00, 136.75, 139.20, 149.37, 158.35, 158.85, 167.22. Anal. calculated for  $\text{C}_{21}\text{H}_{11}\text{N}_3\text{O}_4$  : C 68.29, H 3.00, N 11.38, O 17.33%; found: C 68.27, H 2.99, N 11.36, O 17.31 %.

**7-(pyridin-3-yl)-6H,8H-chromeno[3',4':4,5]pyrrolo[1,2-c]imidazole-6,8,10(9H)-trione (4cc):** Yield 92%, Greenish black solid, mp (129-131°C);  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 11.24 (bs, 1H, NH), 7.06-8.02 (m, 8H, ArH).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 115.87, 120.26, 123.06, 123.65, 124.52, 124.93, 125.30, 126.65, 128.53, 129.23, 131.50, 133.44, 134.70, 140.69, 142.64, 152.75, 153.96, 167.66. Anal. calculated for  $\text{C}_{18}\text{H}_9\text{N}_3\text{O}_4$  : C 65.26, H 2.74, N 12.68, O 19.32%; found: C 65.24, H 2.73, N 12.66, O 19.30 %.

**7-(thiophen-3-yl)-6H,8H-chromeno[3',4':4,5]pyrrolo[1,2-c]imidazole-6,8,10(9H)-trione (4cd):** Yield 91%, Rust brown solid, mp (122-123°C);  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 11.27 (s, 1H, NH), 7.08-8.04 (m, 7H, ArH). Anal. calculated for  $\text{C}_{17}\text{H}_8\text{N}_2\text{O}_4\text{S}$ : C 60.71, H 2.40, N 8.33, O 19.03, S 9.53%; found: C 60.69, H 2.37, N 8.31, O 19.01, S 9.51 %.

**7-(3-bromo-4-hydroxy-5-methoxyphenyl)-6H,8H-chromeno[3',4':4,5]pyrrolo[1,2-c]imidazole-6,8,10(9H)-trione (4ce):** Yield 92%, Rust brown solid, mp (130-132°C);  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 11.53 (bs, 1H, NH), 9.77 (s, 1H, OH), 7.34-8.05 (m, 5H, ArH), 6.90 (s, 1H, ArH), 3.97 (s, 3H, CH<sub>3</sub>),  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 56.87, 112.84, 113.83, 116.64, 122.95, 126.13, 126.64, 126.98, 127.51, 129.15, 129.98, 132.72, 137.46, 139.21, 141.33, 149.62, 151.74, 153.36, 156.22, 167.53. Anal. Calculated for  $\text{C}_{20}\text{H}_{11}\text{BrN}_2\text{O}_6$ : C 52.77, H 2.44, N 6.15, O 21.09%; found: C 52.76, H 2.42, N 6.12, O 21.08 %.

**5-(1H-indol-3-yl)-1,3-dimethyl-2H-imidazo[1',5':1,5]pyrrolo[2,3-d]pyrimidine-**

**2,4,6,8(1H,3H,7H)-tetraone (4da):** Yield 95%, Orange solid, mp (120-122°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.23 (bs, 1H, NH), 10.08 (bs, 1H, NH), 7.99 (s, 1H, ArH), 7.33-7.49 (m, 4H, ArH), 3.18 (s, 3H, CH<sub>3</sub>), 3.02 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 27.98, 30.35, 101.65, 113.62, 115.24, 120.25, 121.63, 121.86, 122.06, 129.12, 129.86, 130.36, 138.28, 143.61, 151.43, 153.74, 157.32, 167.82. Anal. calculated for C<sub>18</sub>H<sub>13</sub>N<sub>5</sub>O<sub>4</sub> : C 59.50, H 3.61, N 19.28, O 17.61%; found: C 59.49, H 3.59, N 19.25, O 17.59 %.

**1,3-dimethyl-5-(naphthalen-1-yl)-2H-imidazo[1',5':1,5]pyrrolo[2,3-d]pyrimidine-**

**2,4,6,8(1H,3H,7H)-tetraone (4db):** Yield 92%, Yellow liquid; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.23 (s, 1H, NH), 7.50-8.06 (m, 7H, ArH), 3.43 (s, 3H, CH<sub>3</sub>), 3.28 (s, 3H, CH<sub>3</sub>). Anal. calculated for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>: C 64.17, H 3.77, N 14.97, O 17.09%; found: C 64.16, H 3.76, N 14.95, O 17.07 %.

**1,3-dimethyl-5-(pyridin-3-yl)-2H-imidazo[1',5':1,5]pyrrolo[2,3-d]pyrimidine-**

**2,4,6,8(1H,3H,7H)-tetraone (4dc):** Yield 93%, Mahroon solid, mp (130-132°C); <sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>): 27.49, 28.52, 113.68, 123.48, 124.35, 131.78, 136.02, 137.50, 143.85, 147.31, 148.20, 148.66, 151.89, 158.86, 166.80. Anal. calculated for C<sub>15</sub>H<sub>11</sub>N<sub>5</sub>O<sub>4</sub> : C 55.39, H 3.41, N 21.53, O 19.67%; found: C 55.36, H 3.40, N 21.51, O 19.65 %.

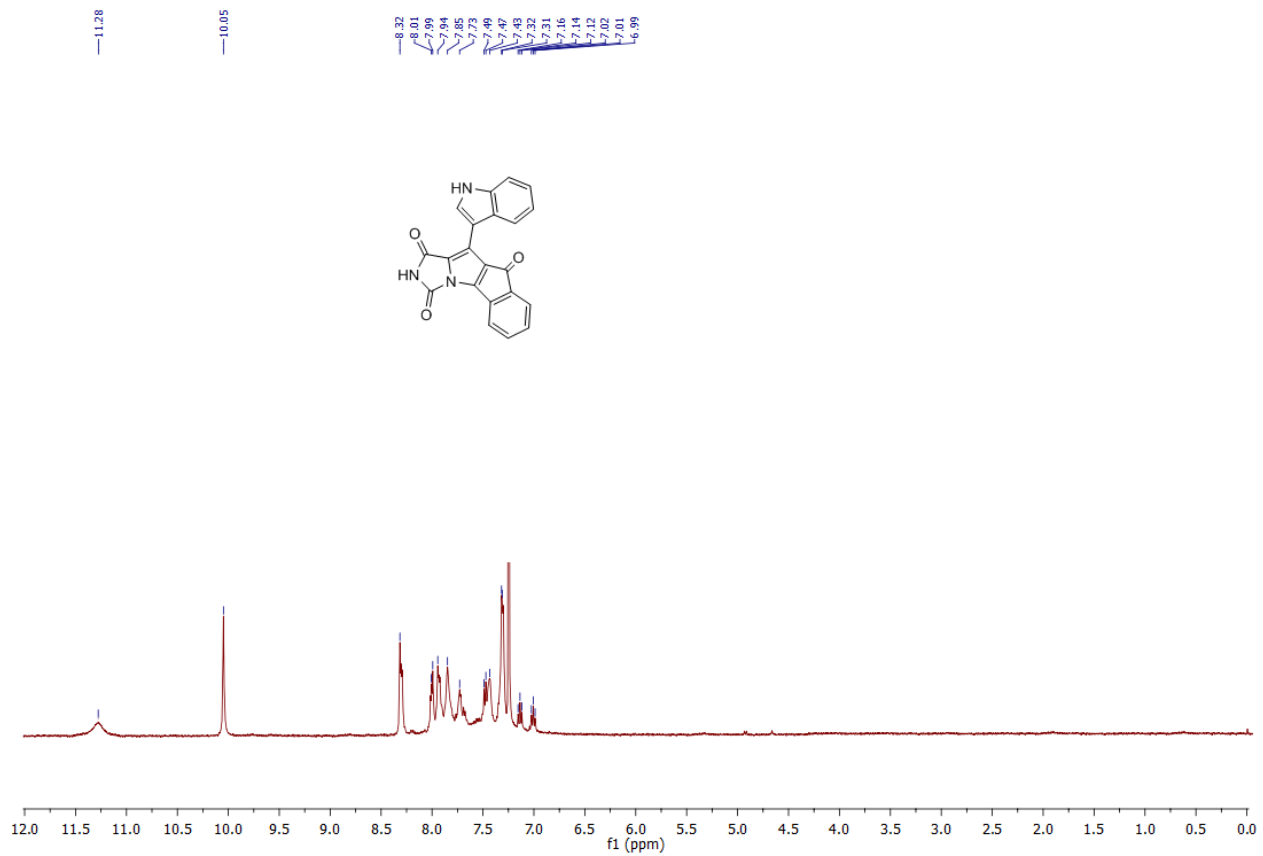
**1,3-dimethyl-5-(thiophen-3-yl)-2H-imidazo[1',5':1,5]pyrrolo[2,3-d]pyrimidine-**

**2,4,6,8(1H,3H,7H)-tetraone (4dd):** Yield 94%, Brown solid, mp (119-121°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.28 (s, 1H, NH), 7.27-8.00 (m, 3H, ArH), 3.41 (s, 3H, CH<sub>3</sub>), 3.18 (s, 3H, CH<sub>3</sub>). Anal. Calculated for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>S: C 50.91, H 3.05, N 16.96, O 19.37, S 9.71%; found: C 50.90, H 3.04, N 16.94, O 19.35, S 9.70 %.

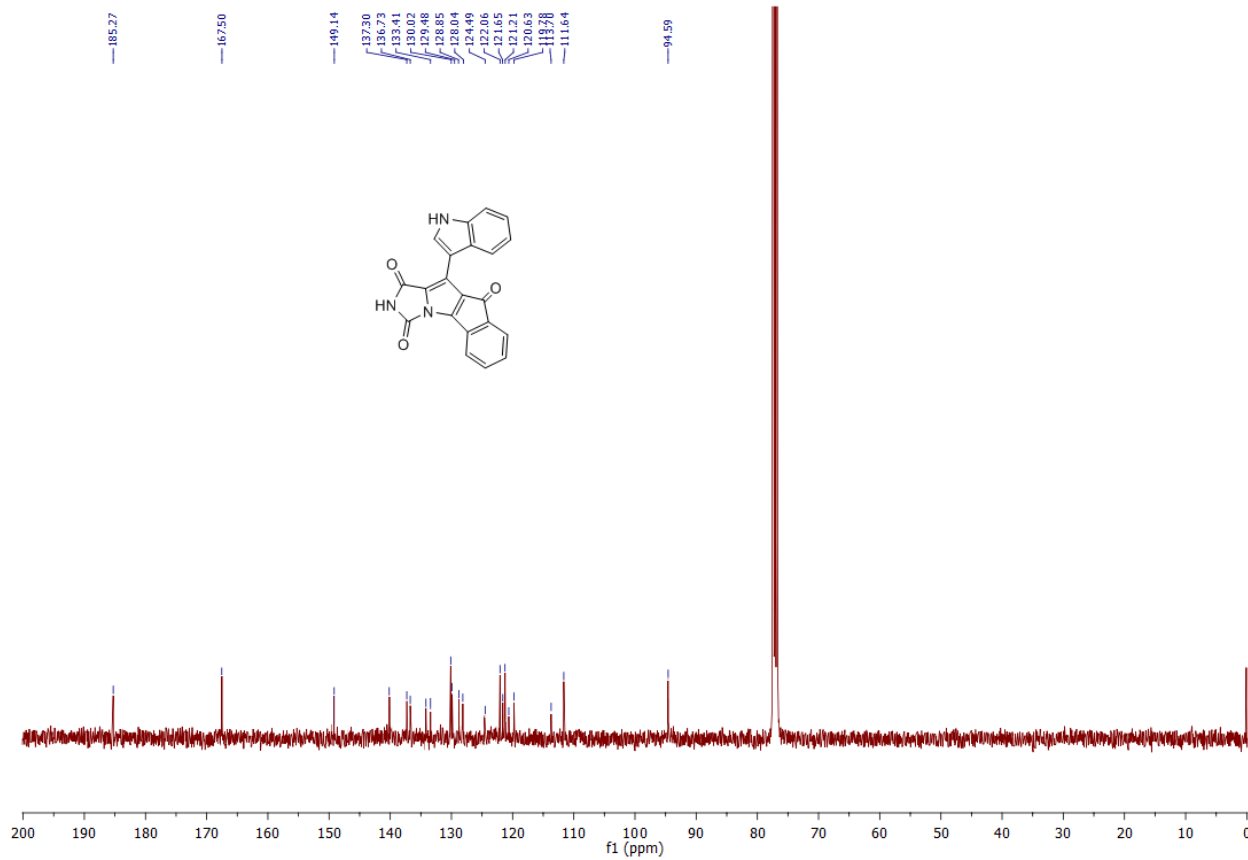


**5-(3-bromo-4-hydroxy-5-methoxyphenyl)-1,3-dimethyl-2H-imidazo[1',5':1,5]pyrrolo[2,3-d]pyrimidine-2,4,6,8(1H,3H,7H)-tetraone (4de):** Yield 92%, Yellowish green solid, mp (120-122°C); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 11.55 (bs, 1H, NH), 9.73 (bs, 1H, OH), 7.68 (s, 1H, ArH), 7.37 (s, 1H, ArH), 3.87 (s, 3H, CH<sub>3</sub>), 3.18 (s, 3H, CH<sub>3</sub>), 3.03 (s, 3H, CH<sub>3</sub>), <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 24.87, 29.14, 56.90, 109.71, 110.03, 116.13, 118.13, 125.09, 129.26, 129.42, 133.18, 138.40, 149.14, 150.29, 155.42, 158.85, 168.62. Anal. Calculated for C<sub>17</sub>H<sub>13</sub>BrN<sub>4</sub>O<sub>6</sub>: C 45.45, H 2.92, N 12.47, O 21.37%; found: C 45.43, H 2.90, N 12.44, O 21.36 %.

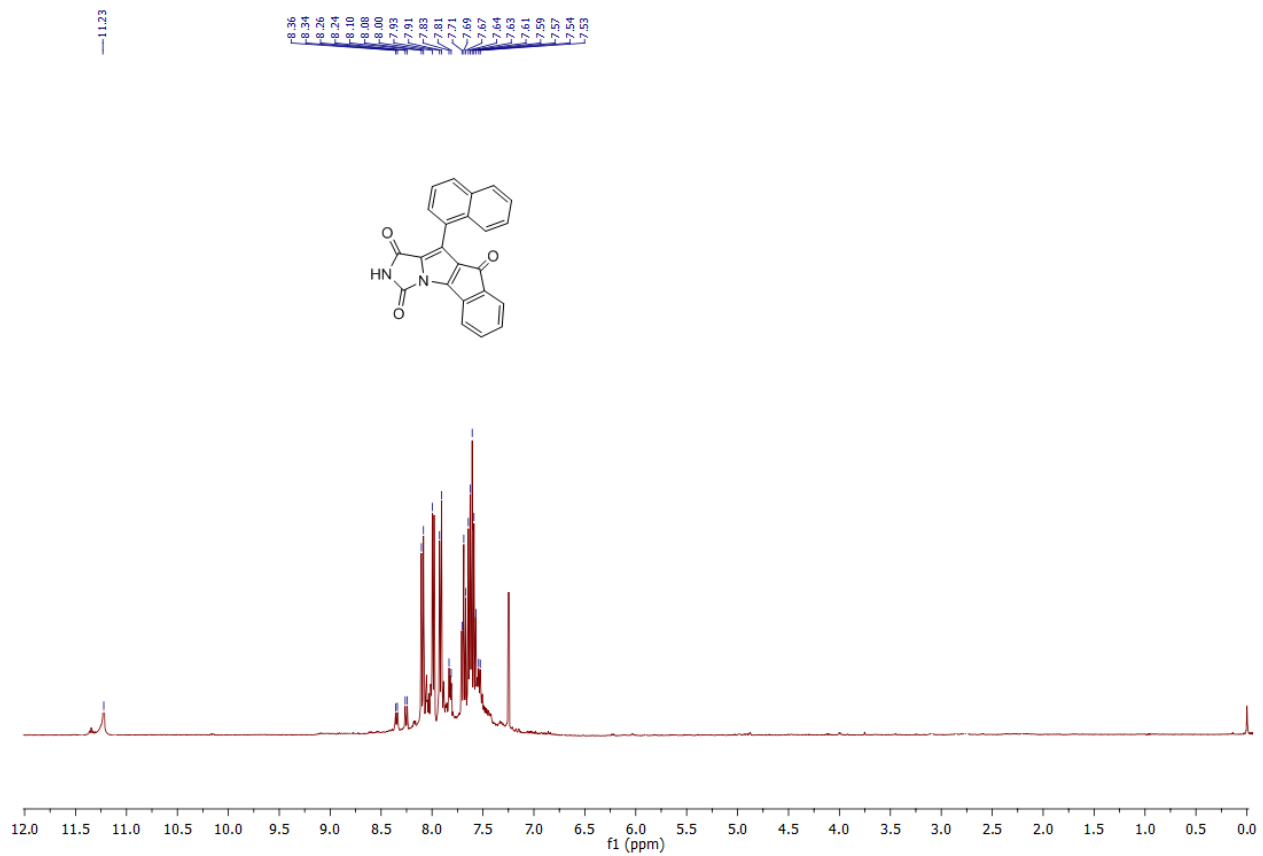
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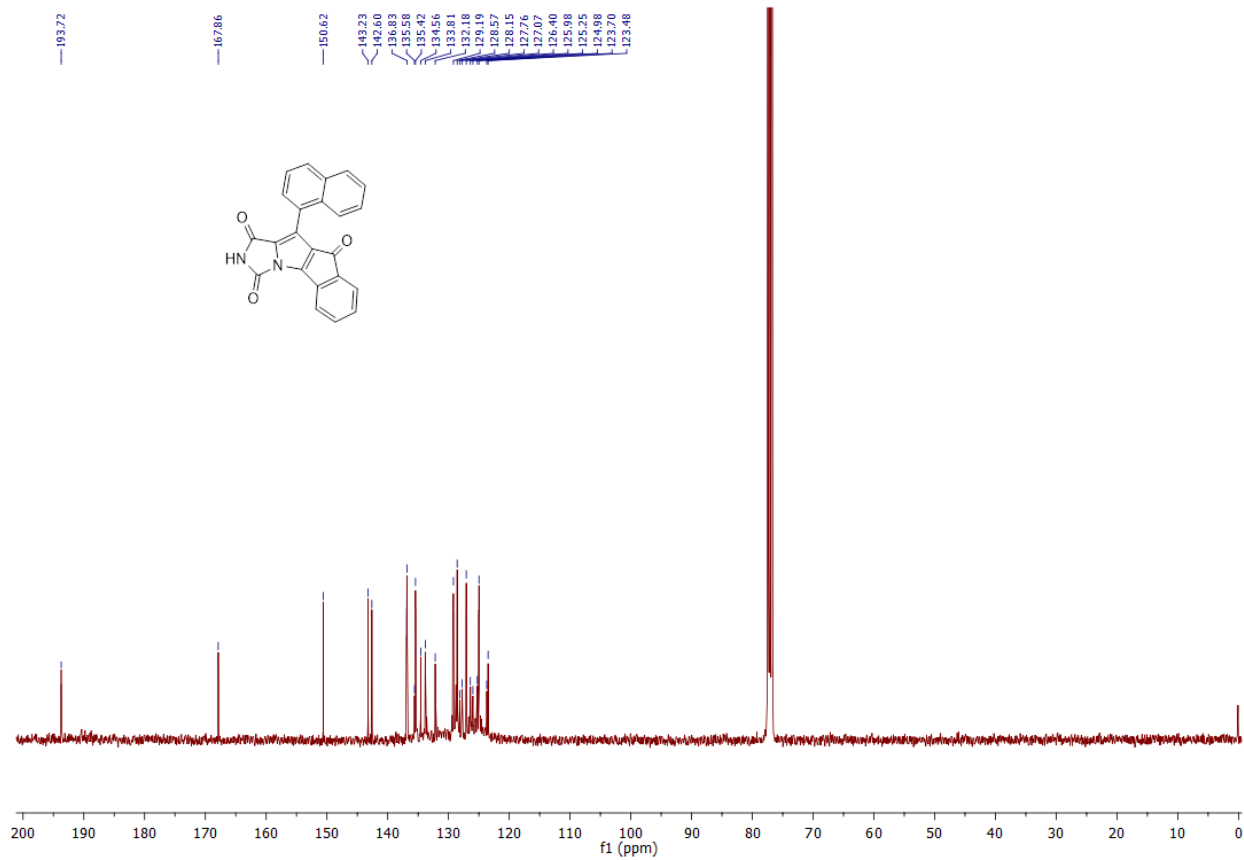
<sup>1</sup>H spectra of (4aa)



<sup>13</sup>C spectra of (4aa)



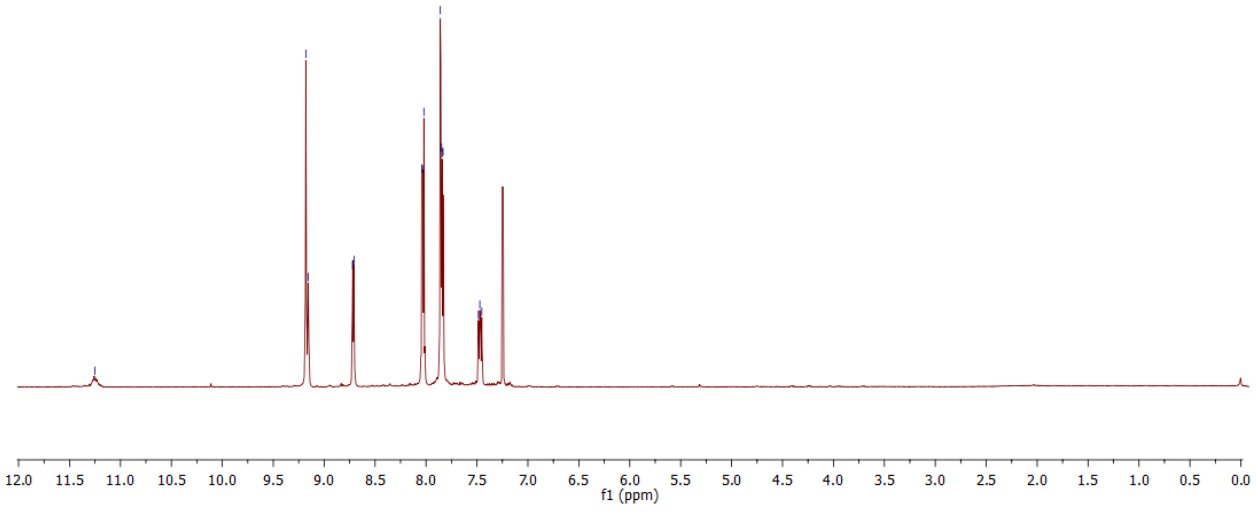
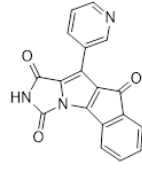
**<sup>1</sup>H spectra of (4ab)**



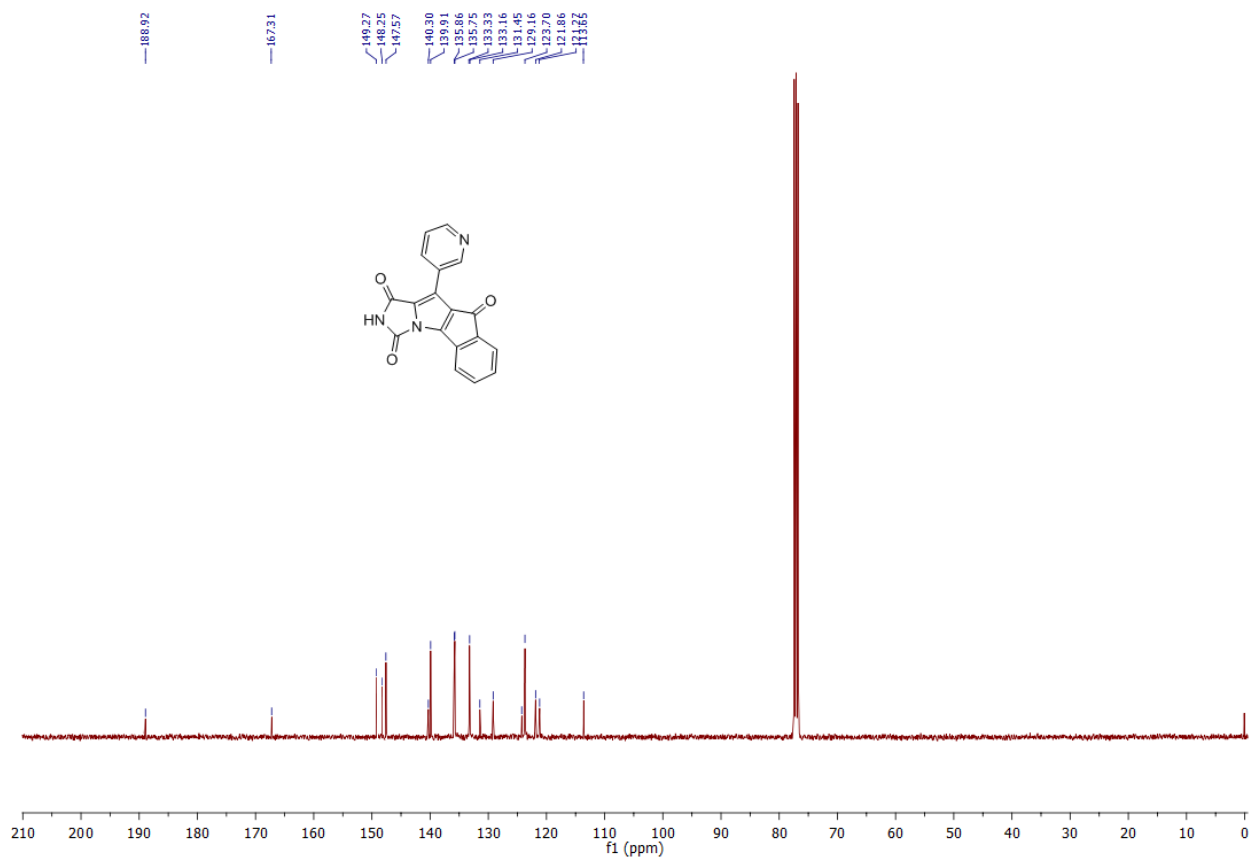
<sup>13</sup>C spectra of (4ab)

—11.25

9.18  
9.16  
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8.71  
8.04  
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7.85  
7.84  
7.83  
7.47  
7.45



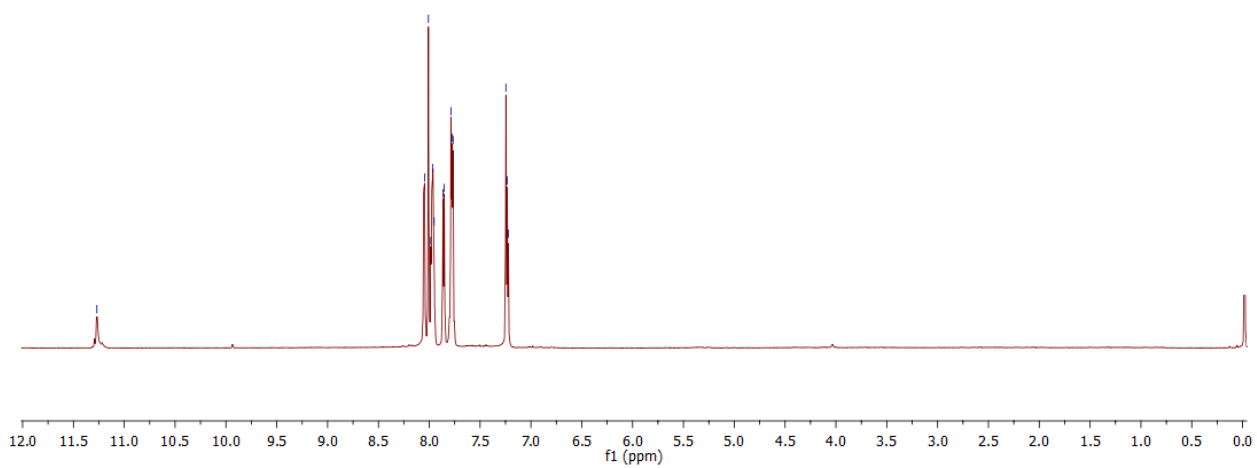
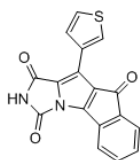
**<sup>1</sup>H spectra of (4ac)**



<sup>13</sup>C spectra of (4ac)

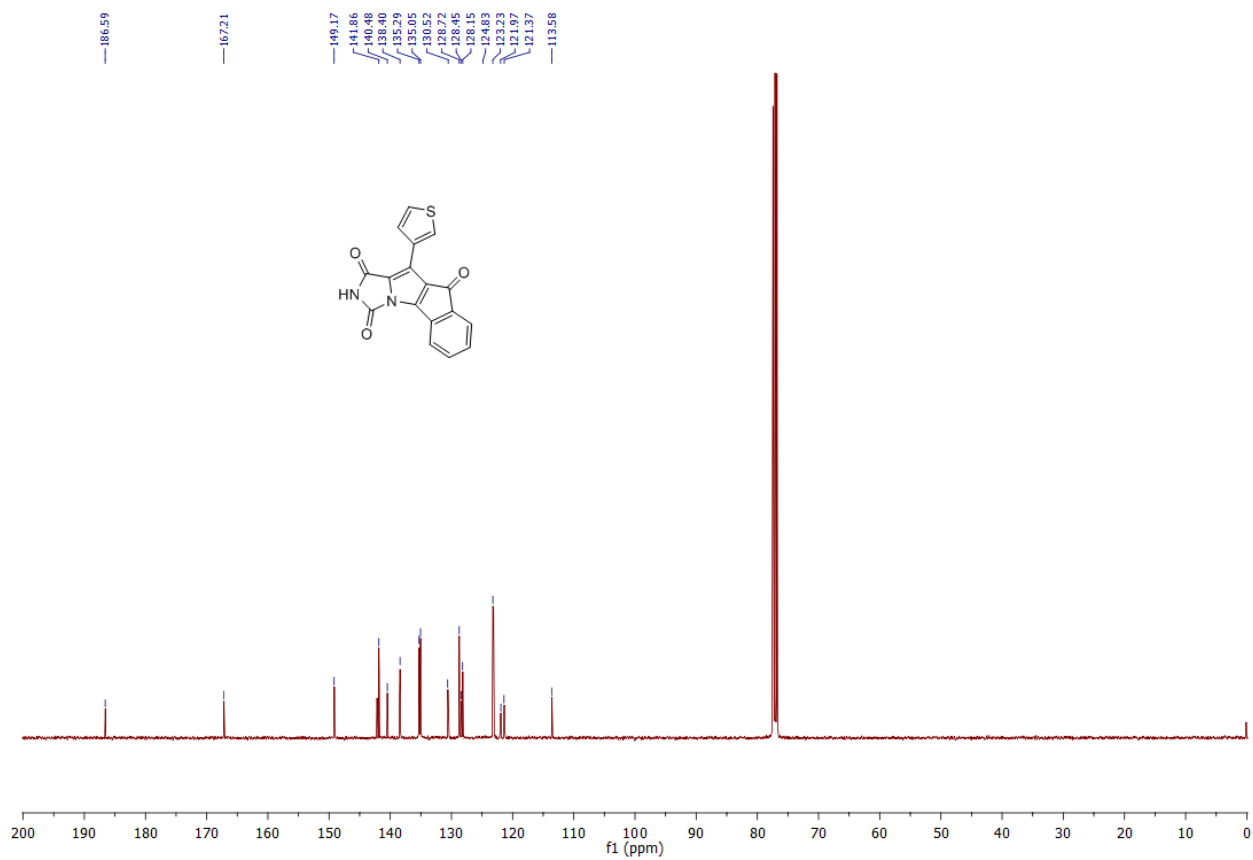
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8.05  
7.97  
7.95  
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7.77  
7.25  
7.22

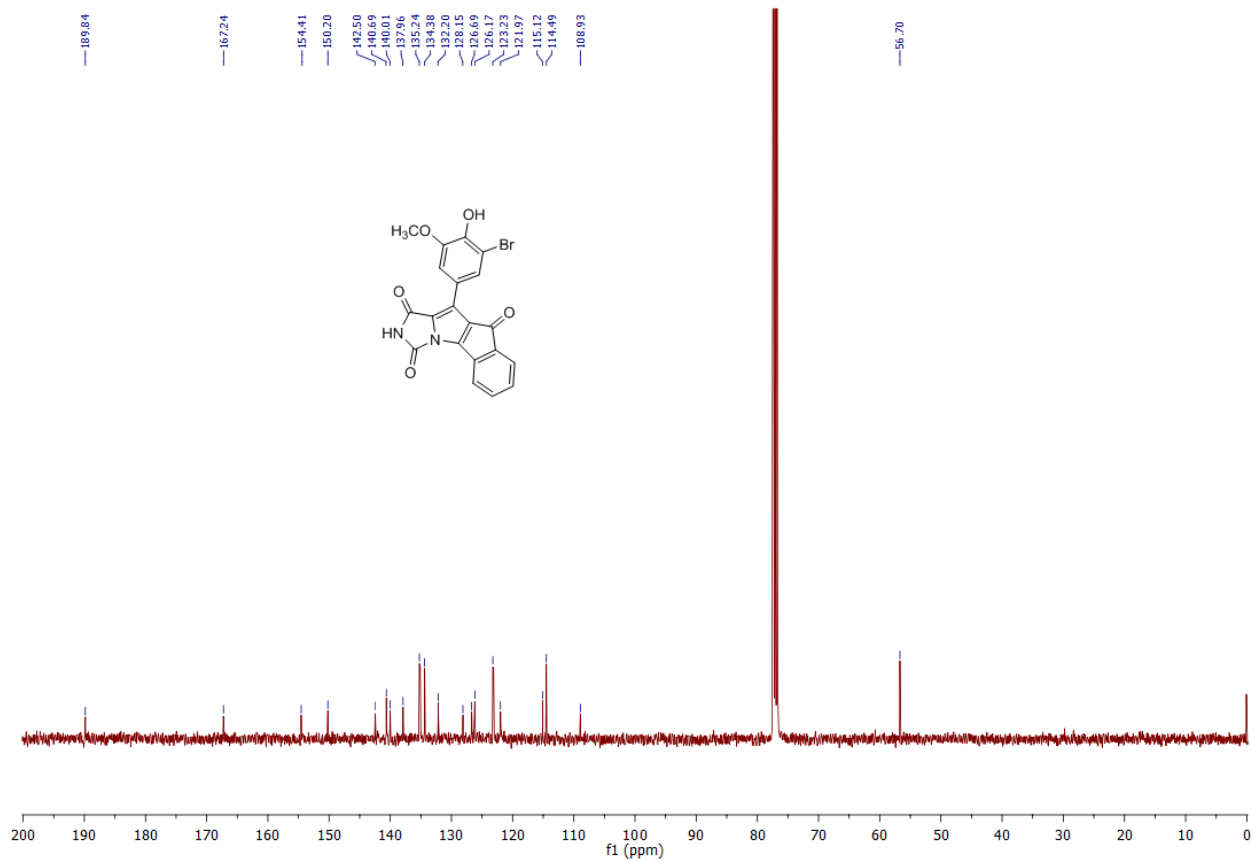


**<sup>1</sup>H spectra of (4ad)**

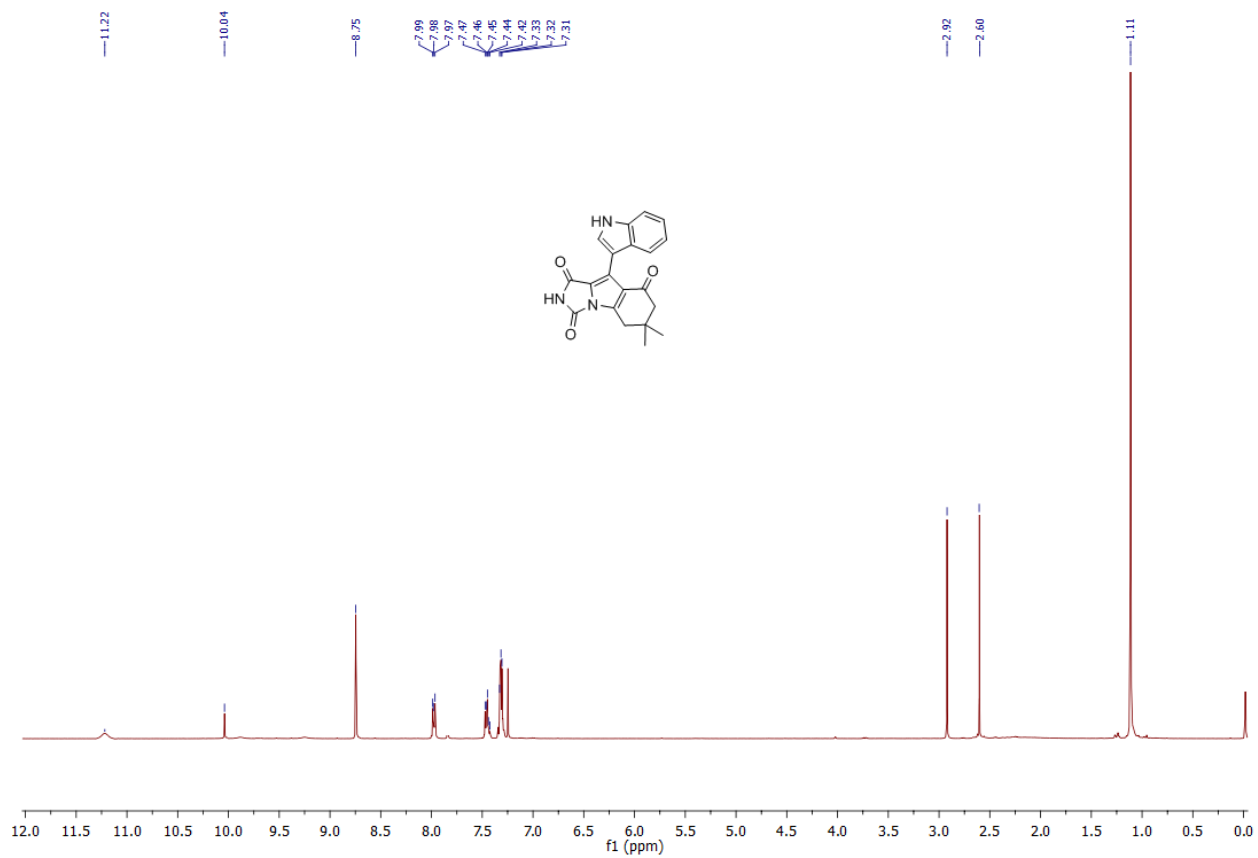




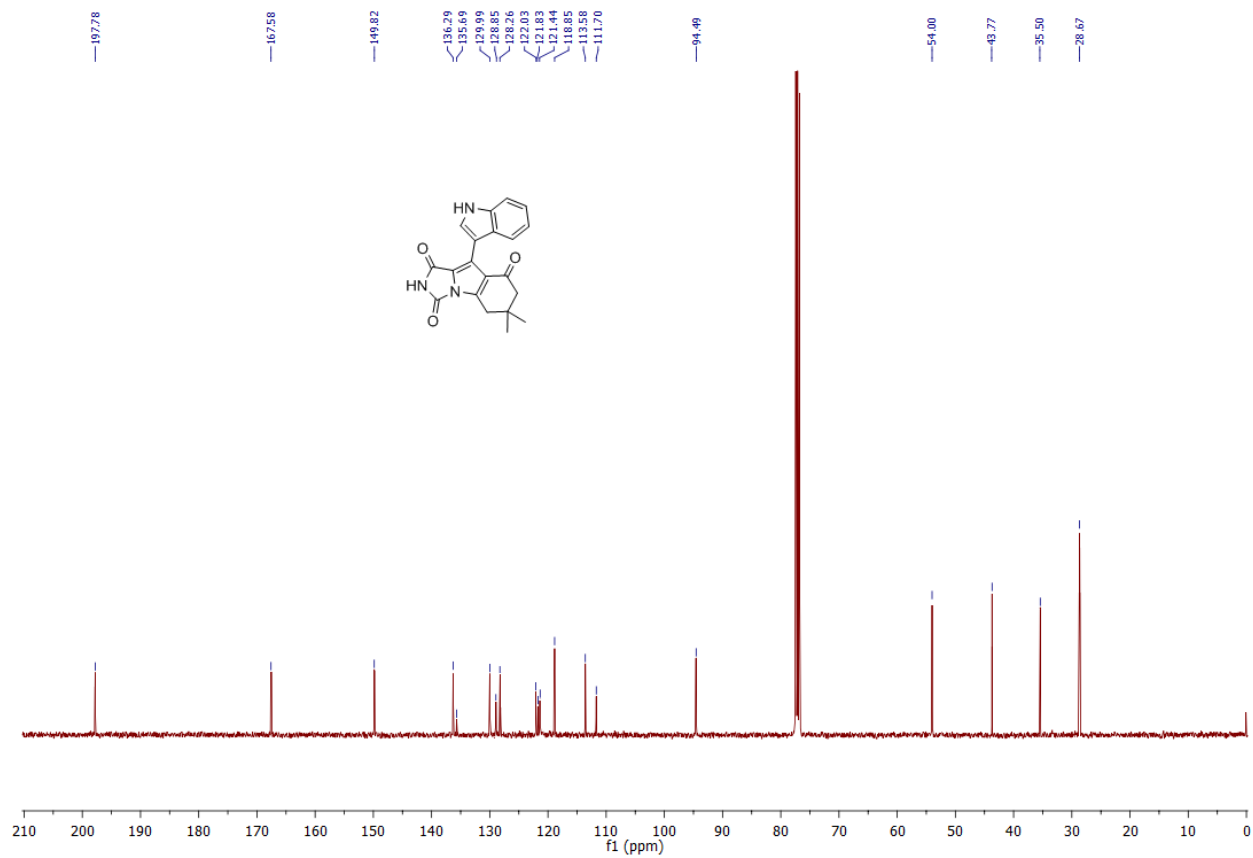
<sup>13</sup>C spectra of (4ad)



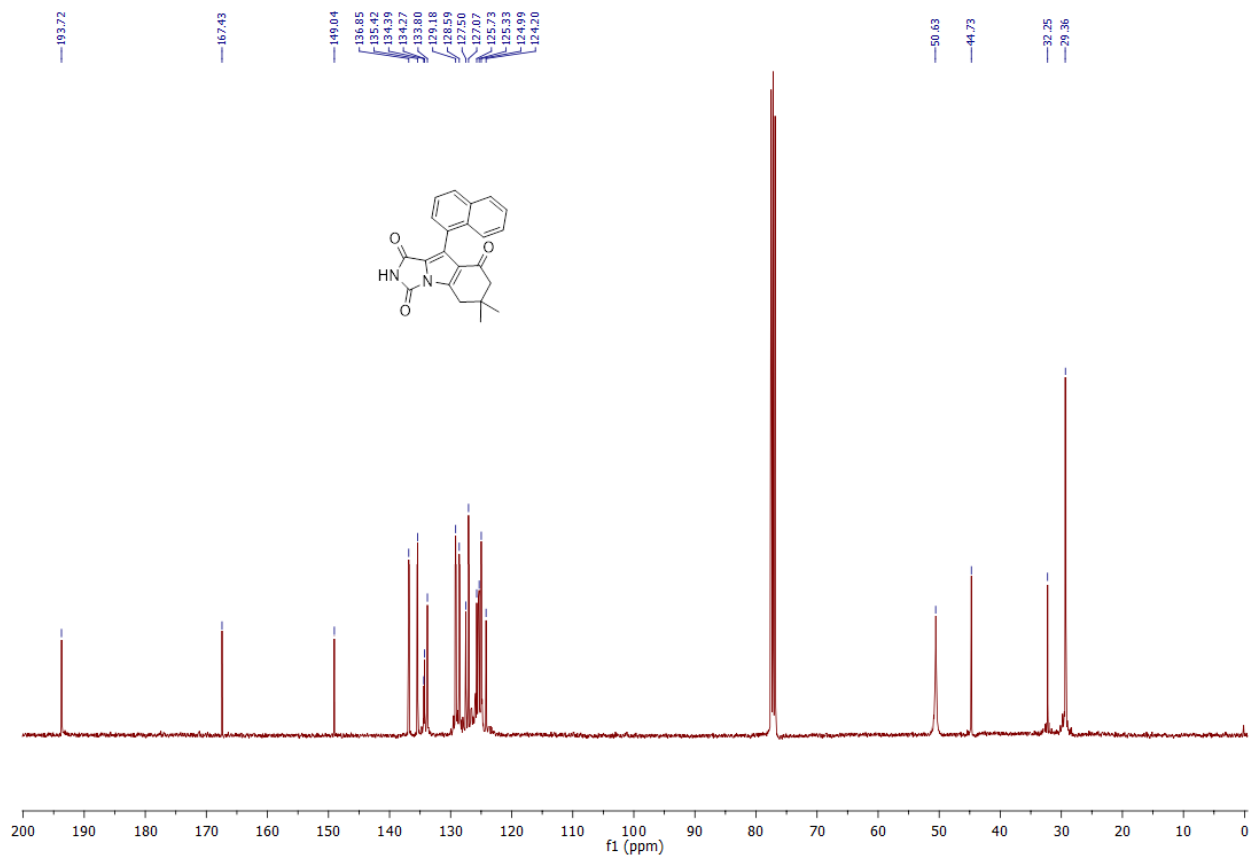
<sup>13</sup>C spectra of (4ae)



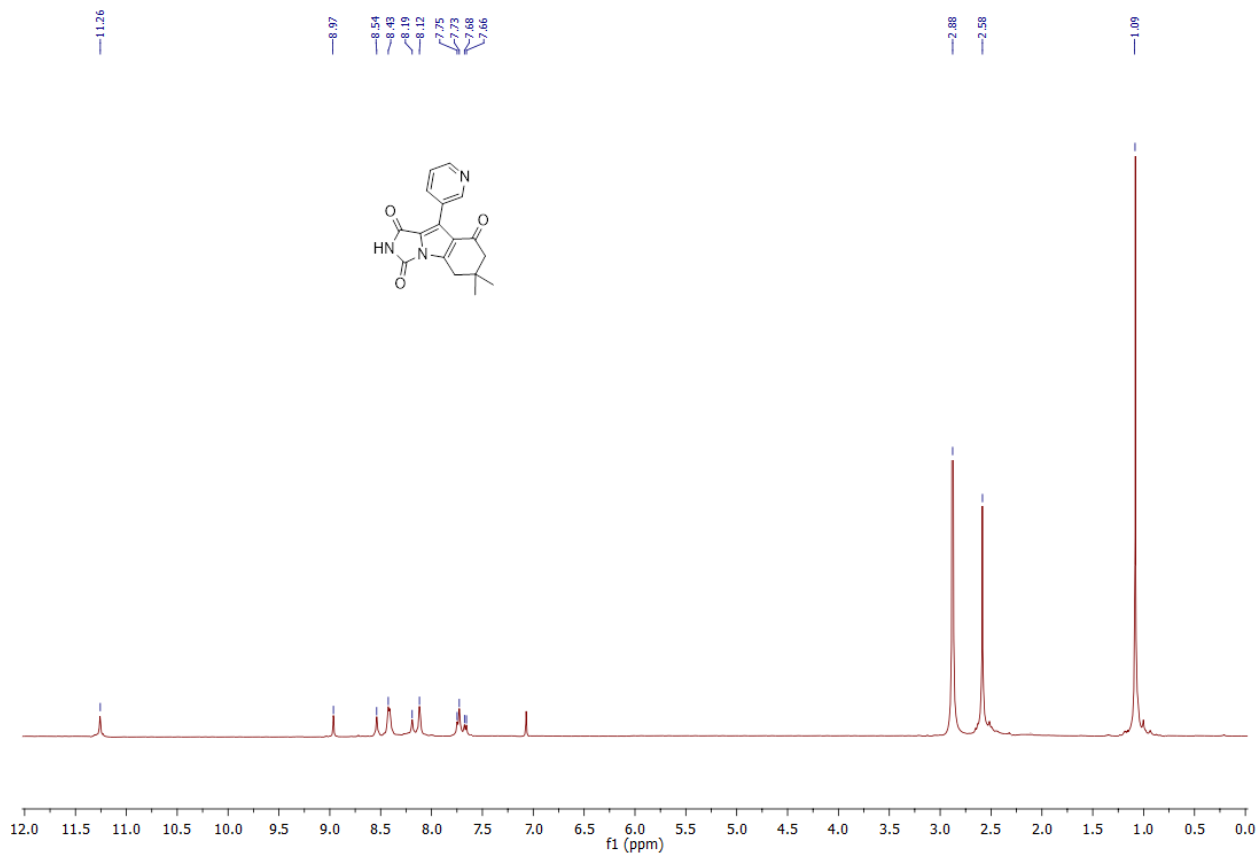
**<sup>1</sup>H spectra of (4ba)**



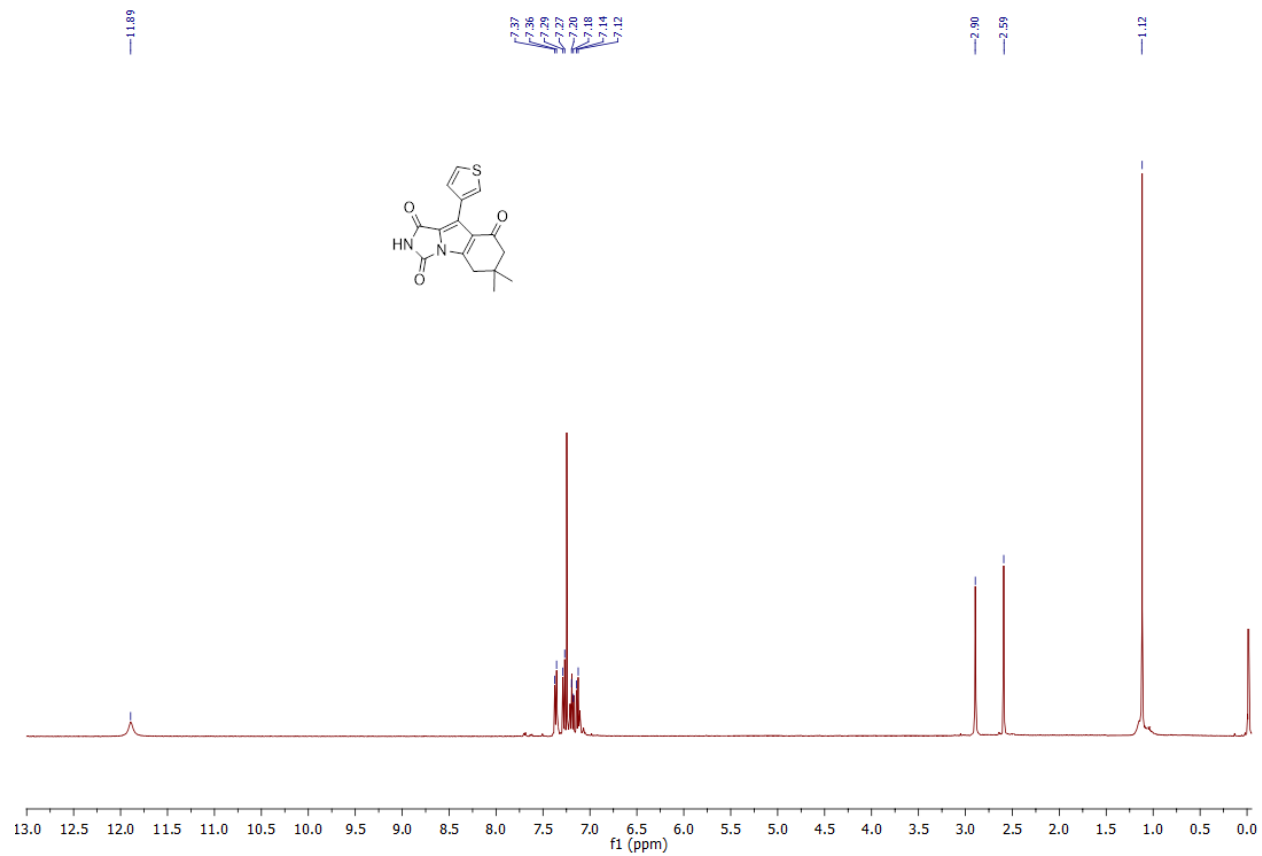
$^{13}\text{C}$  spectra of (4ba)



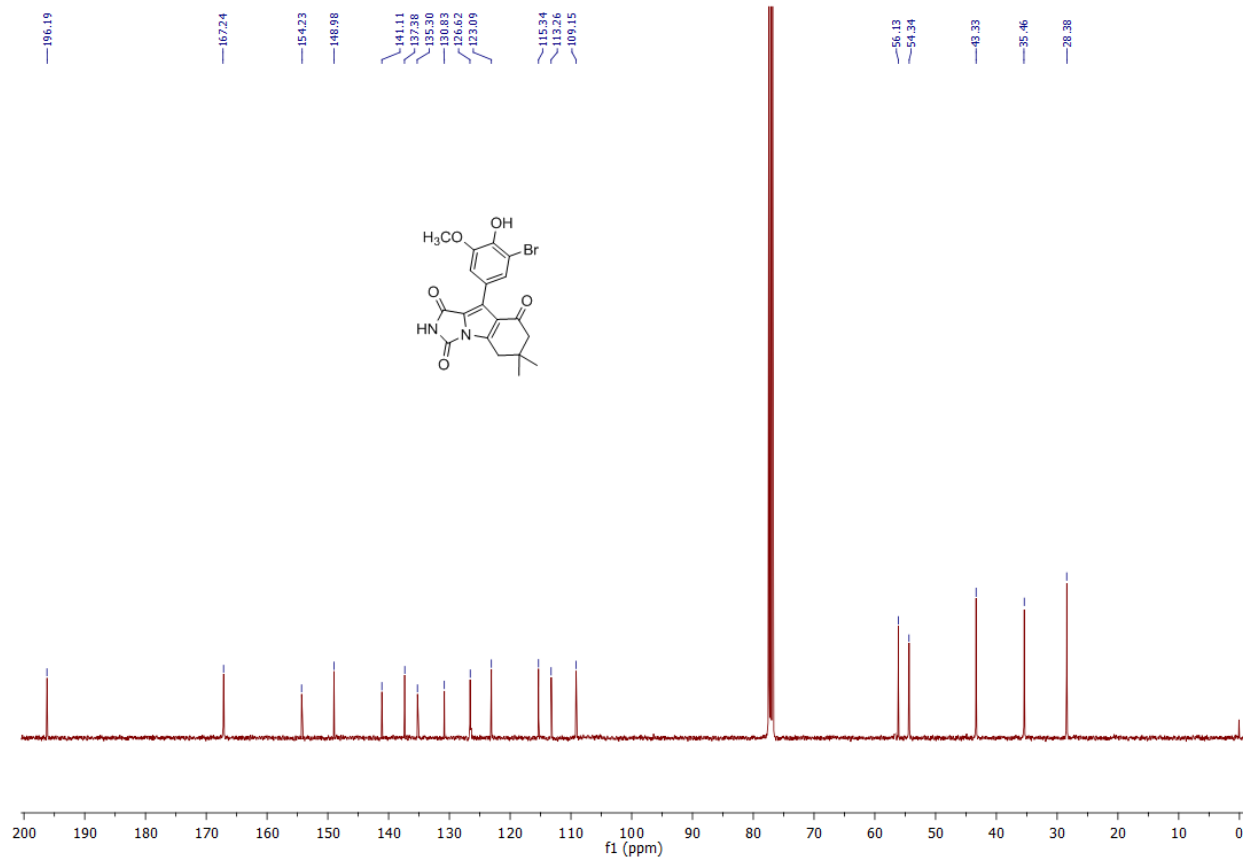
<sup>13</sup>C spectra of (4bb)



**<sup>1</sup>H spectra of (4bc)**

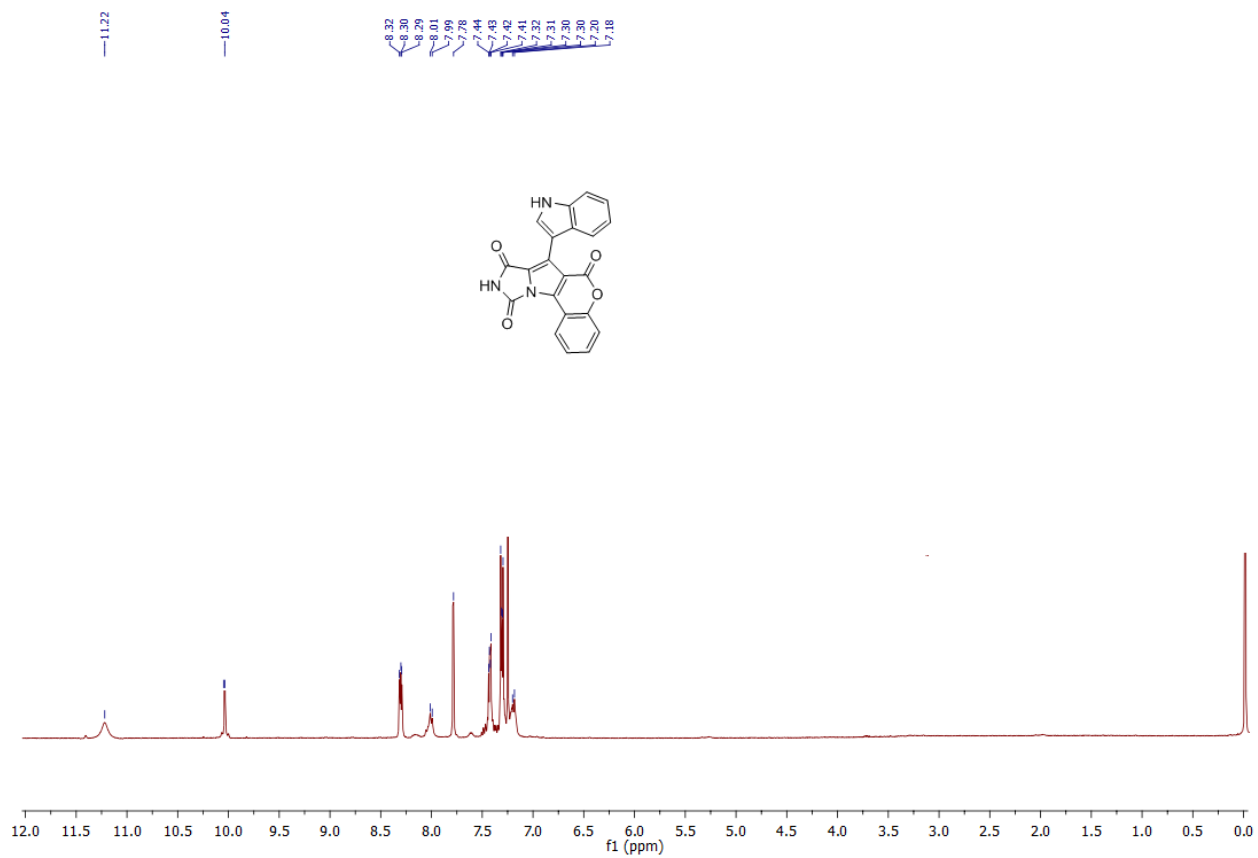


<sup>1</sup>H spectra of (4bd)

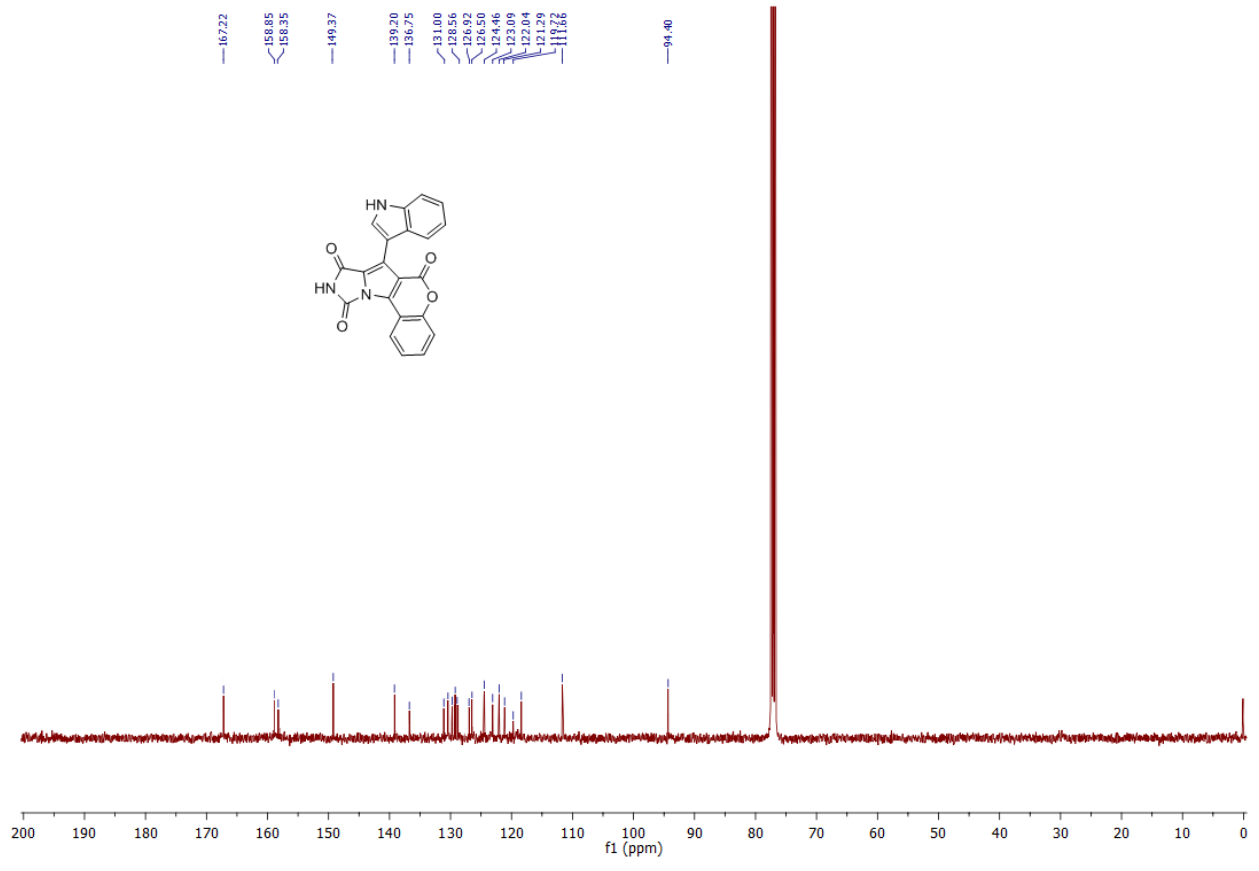


<sup>13</sup>C spectra of (4be)

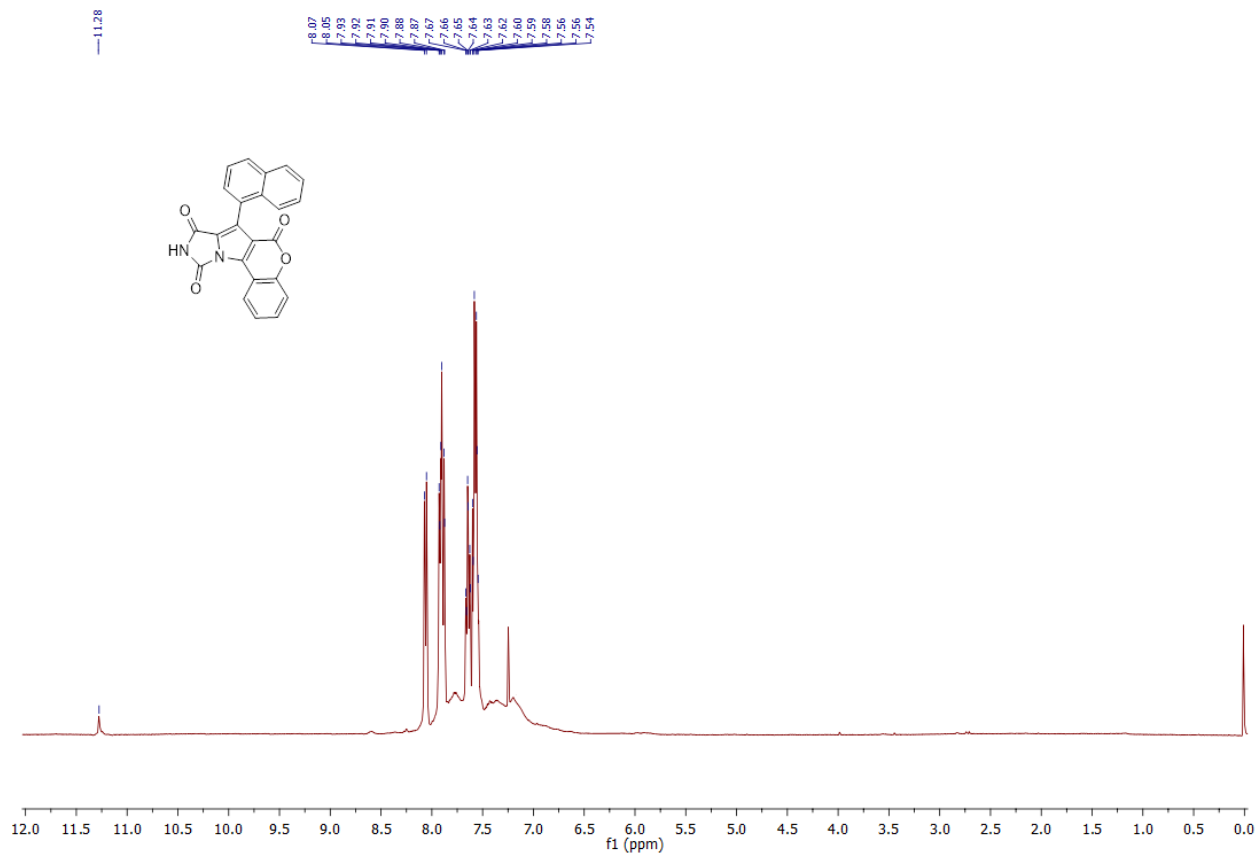




<sup>1</sup>H spectra of (4ca)



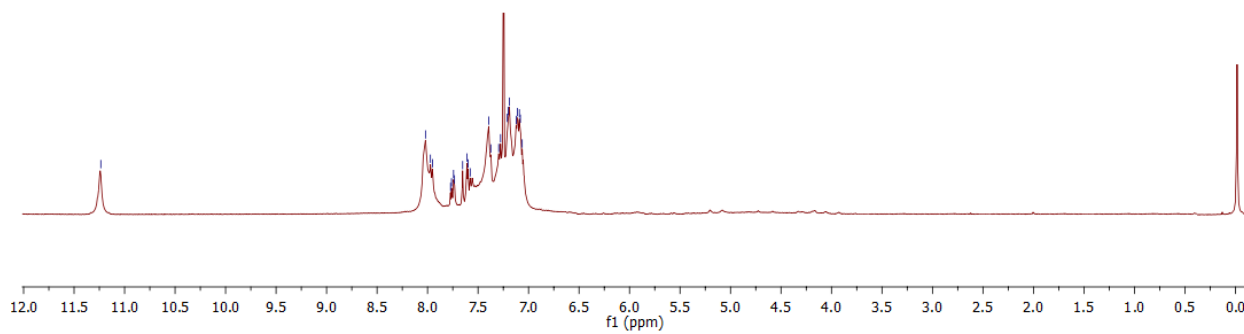
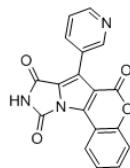
<sup>13</sup>C spectra of (4ca)



<sup>1</sup>H spectra of (4cb)

—11.24

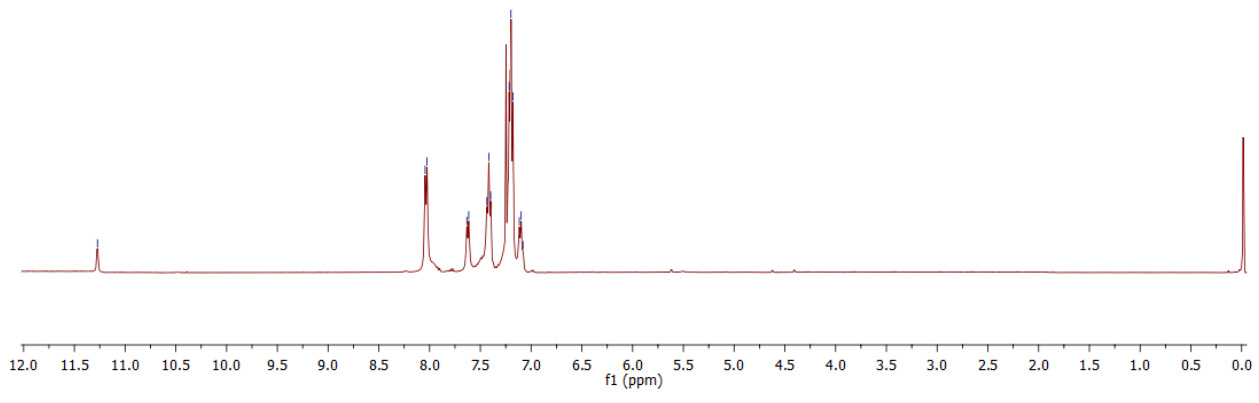
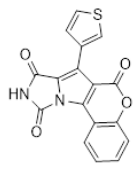
8.02  
7.90  
7.85  
7.77  
7.76  
7.74  
7.73  
7.65  
7.61  
7.60  
7.58  
7.39  
7.30  
7.28  
7.21  
7.20  
7.19  
7.12  
7.11  
7.09  
7.08  
7.06



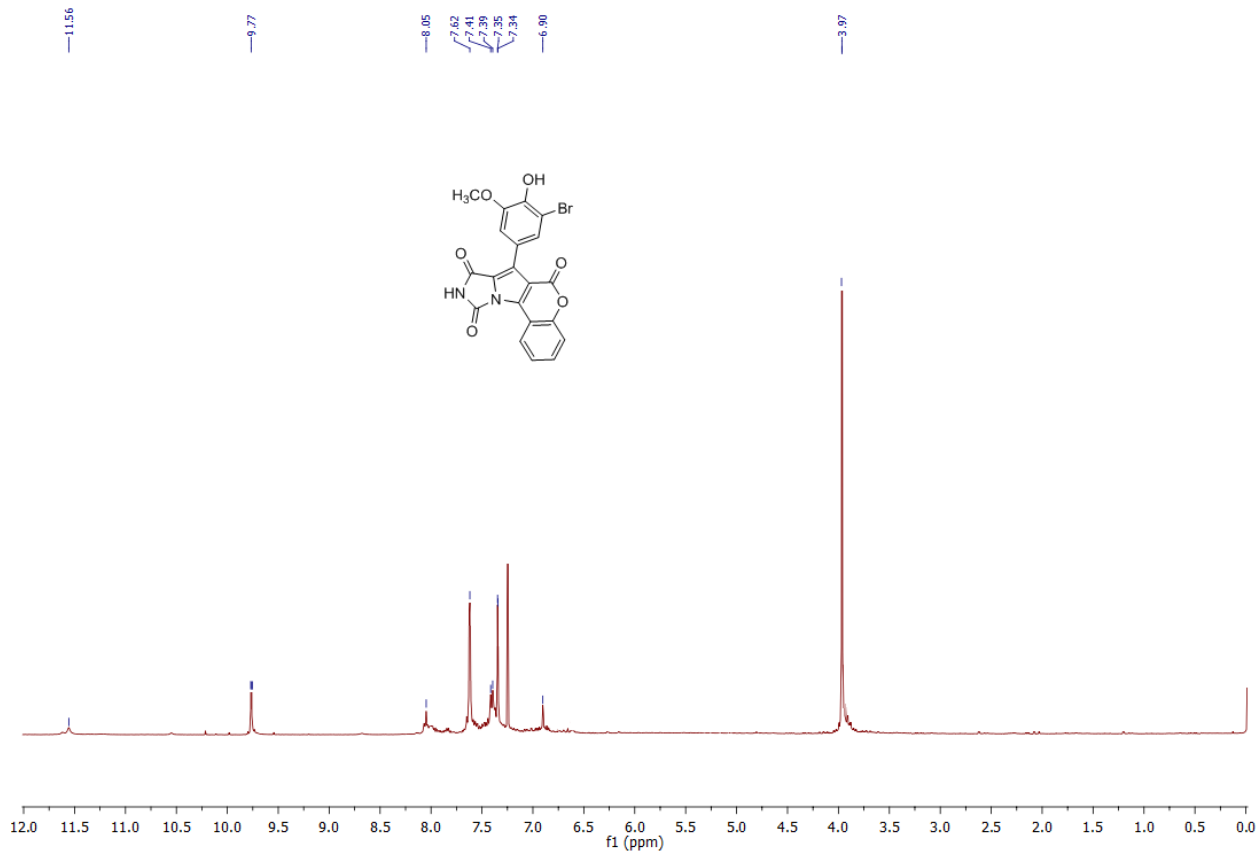
<sup>1</sup>H spectra of (4cc)

—11.27

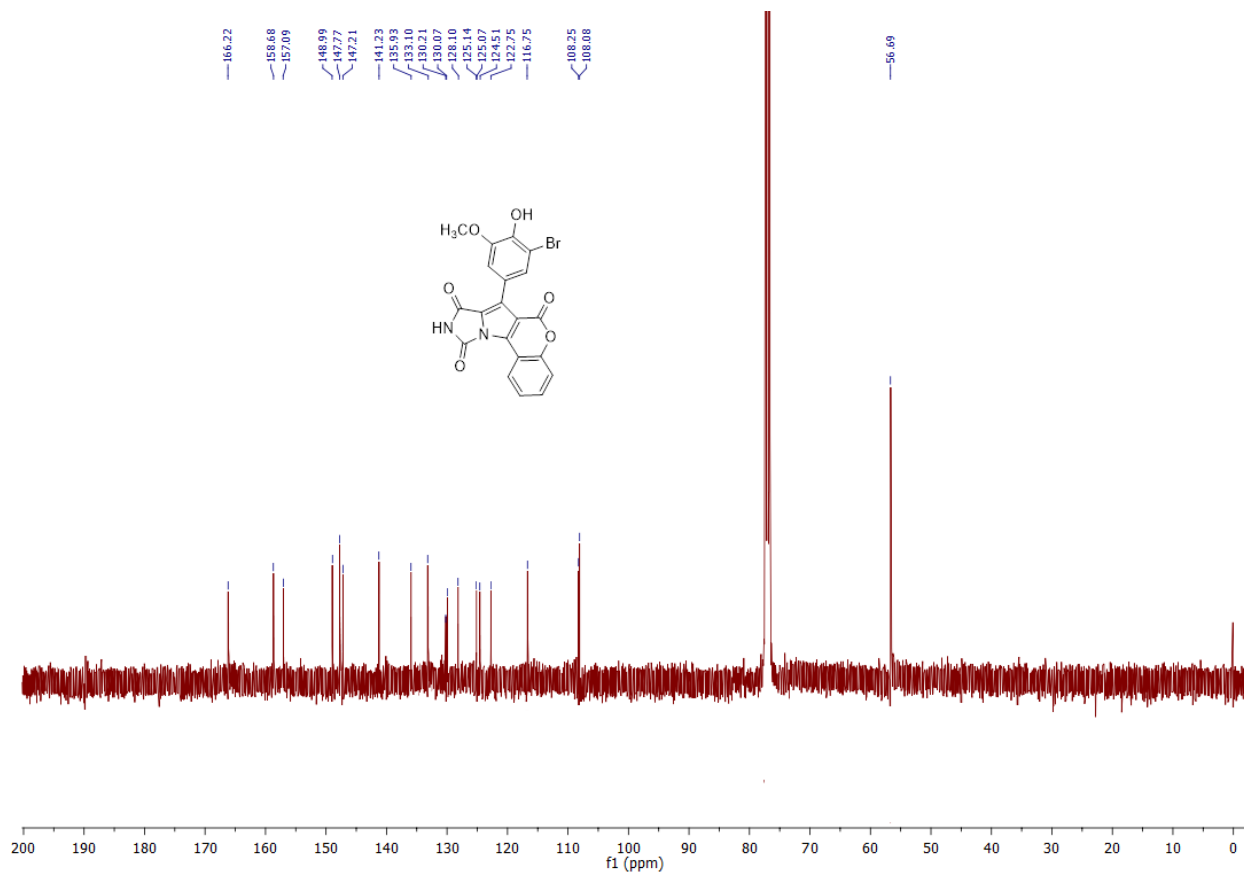
8.04  
7.63  
7.61  
7.44  
7.42  
7.40  
7.22  
7.20  
7.18  
7.12  
7.10  
7.08



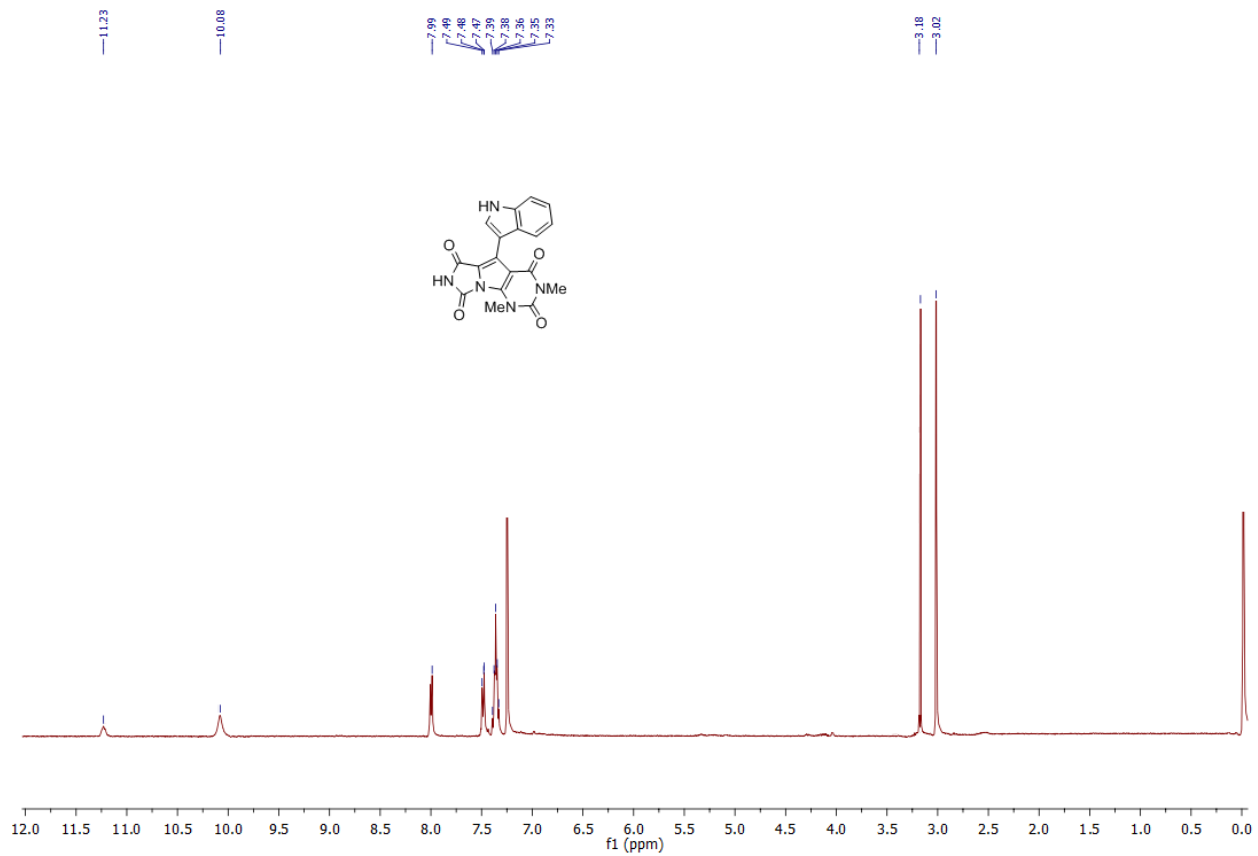
**<sup>1</sup>H spectra of (4cd)**



<sup>1</sup>H spectra of (4ce)

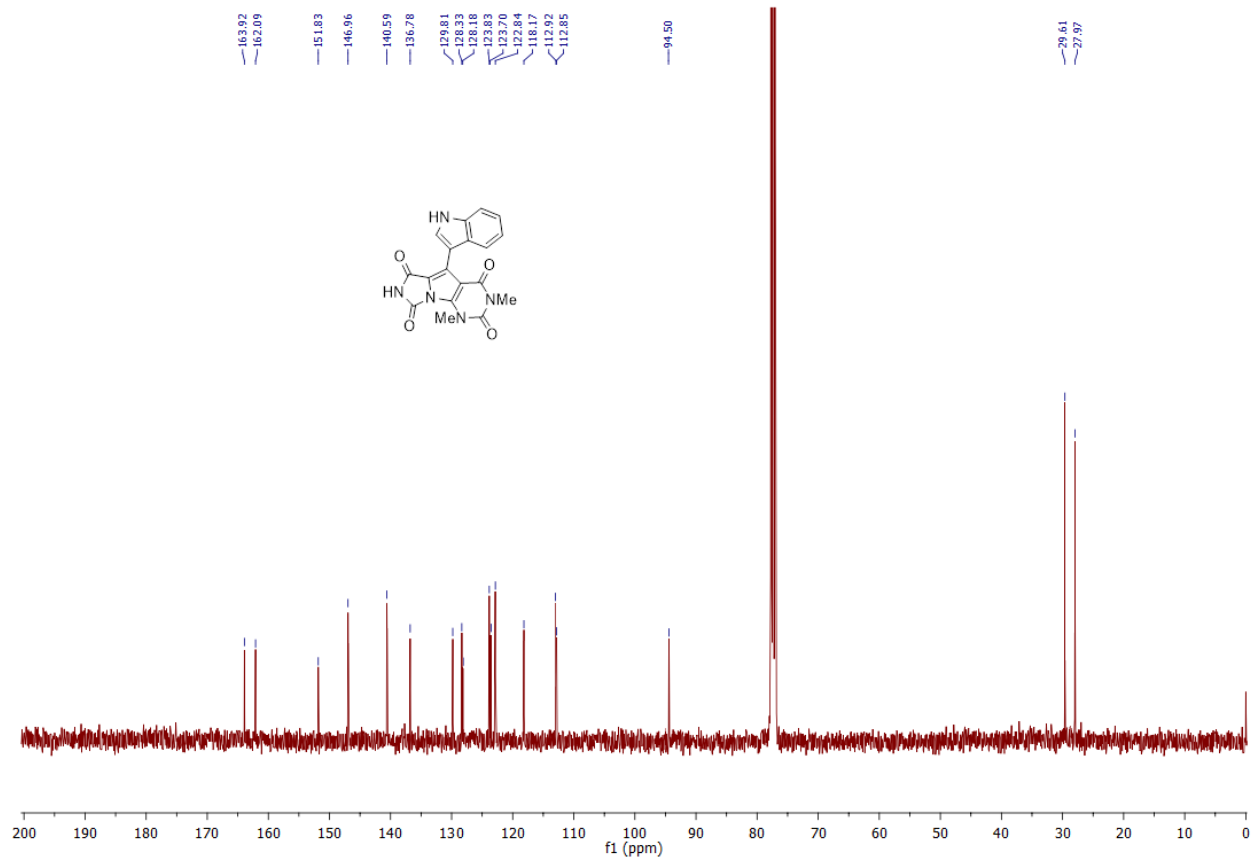


$^{13}\text{C}$  spectra of (4ce)

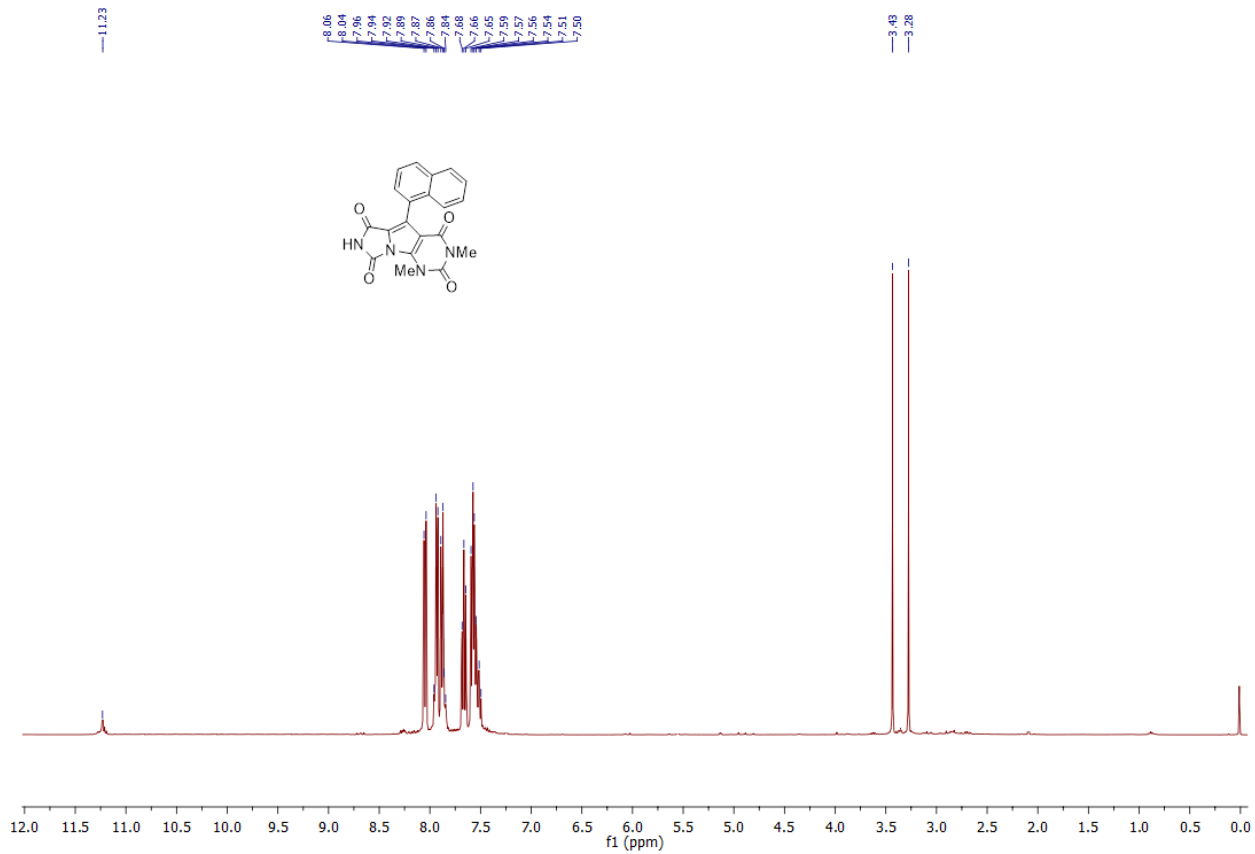


<sup>1</sup>H spectra of (4da)

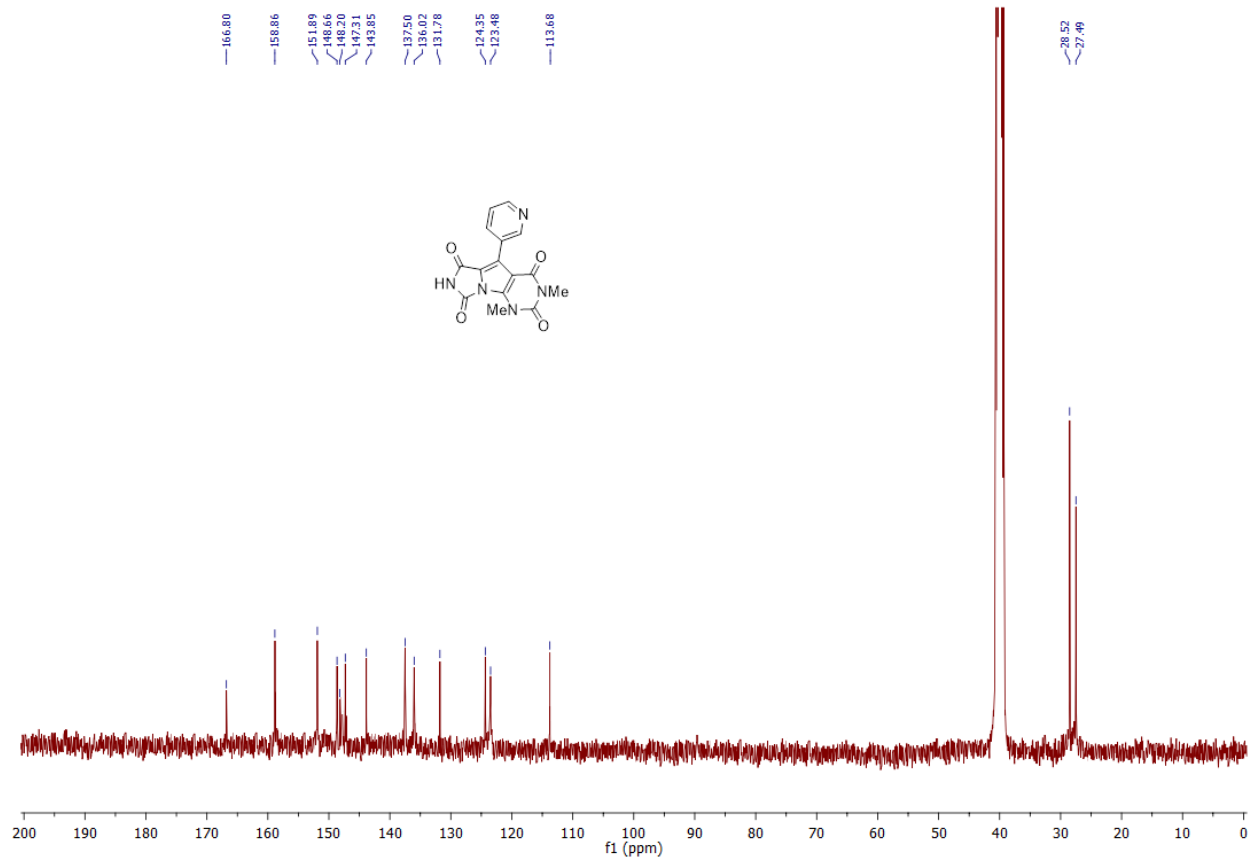




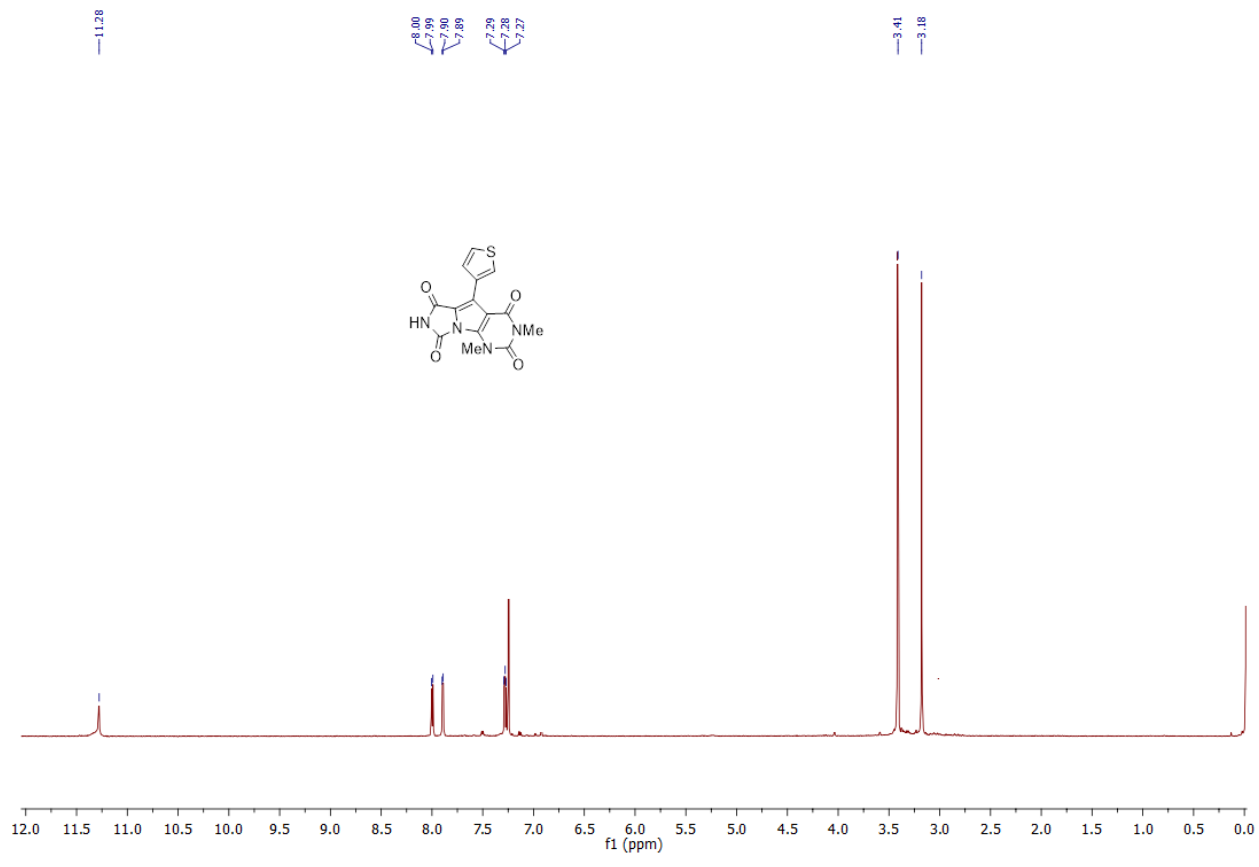
<sup>13</sup>C spectra of (4da)



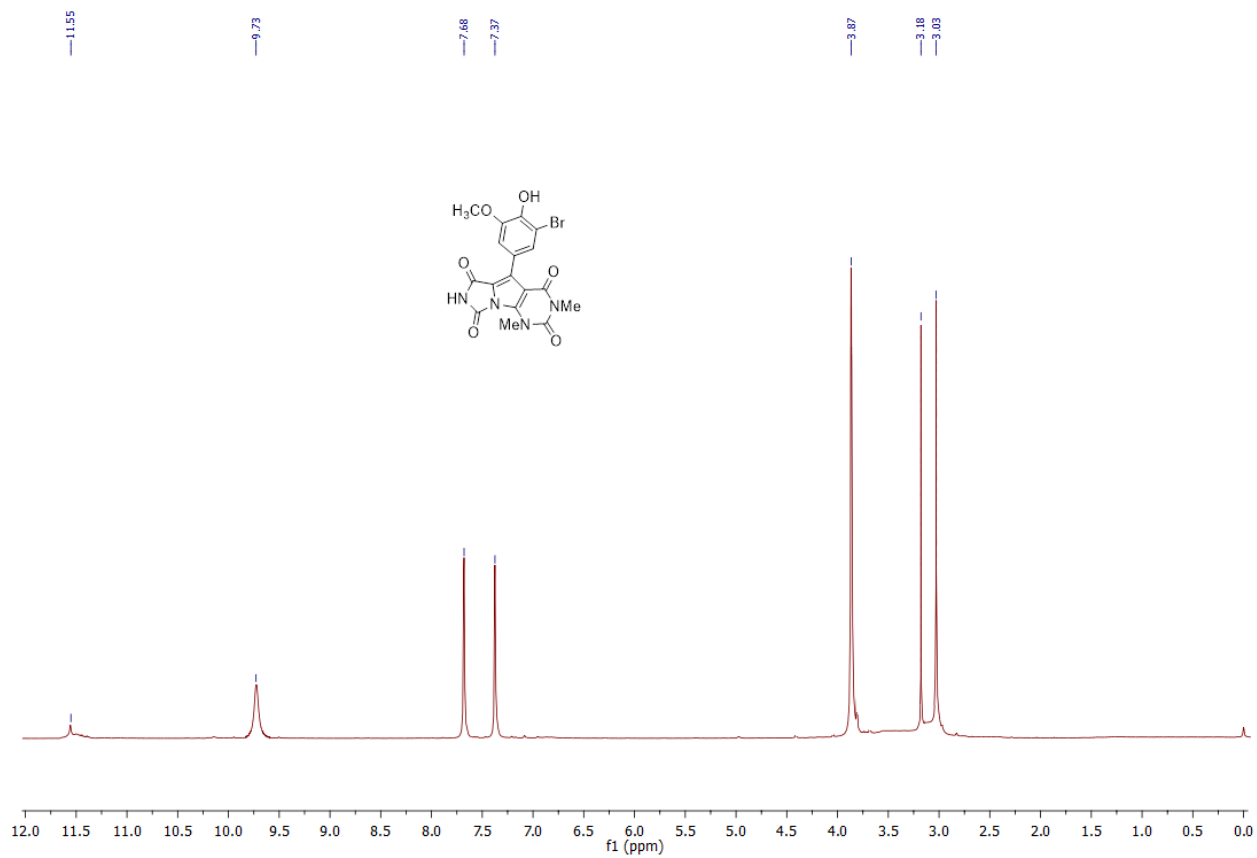
<sup>1</sup>H spectra of (4db)



<sup>13</sup>C spectra of (4dc)



<sup>1</sup>H spectra of (4dd)



$^1\text{H}$  spectra of (4de)