

## Supporting Information

### Synthesis of Benzimidazole Fused Poly-heterocycles *via* Oxidant Free Cu-Catalyzed Dehydrogenative C-N Coupling and Photophysical Studies

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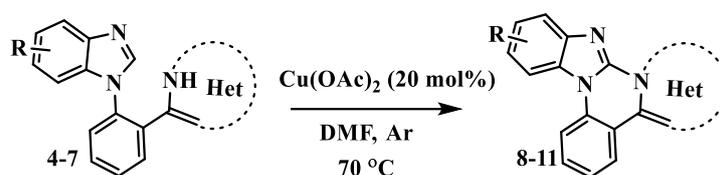
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## 1. General Information

The use of all chemicals was done without additional purification and they were all purchased from commercial providers. Silica gel with a mesh size of 100–200 was used for column chromatography purifications. Air and Moisture sensitive reaction were carried out in oven-dried glassware sealed with rubber septum under the positive pressure of argon/nitrogen gas. Reactions were stirred using magnetic bar over magnetic stirrer. Solvents were dried as per standard procedure. Analytical thin-layer chromatography (TLC) was done using Merck 60 F<sub>254</sub> precoated silica gel plates (0.2 mm thickness). Plates were viewed using UV light (254 nm) on a Spectroline Model ENF-24061/F 254 nm after elution. NMR Spectra were measured on Bruker 400 NMR spectrometer (<sup>1</sup>H at 400 MHz, <sup>13</sup>C at 101 MHz). Data for <sup>1</sup>H spectra are as reported as follows: Chemical shift (ppm, reference to (CH<sub>3</sub>)<sub>4</sub>Si; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = double of triplet, ddd = doublet of doublet of doublet, m = multiplet), coupling constant (Hz), and Integration data for <sup>13</sup>C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl<sub>3</sub>: 77.0 ppm, DMSO-d<sub>6</sub>: 39.9). High-resolution mass spectral analysis (HRMS) was performed on a Bruker Daltonics MicroTOF-Q-II mass spectrometer and ThermoFinnigan Exactive Plus ORBITRAP mass spectrometer using MeOH as a solvent with an electrospray ionization (ESI) positive method.

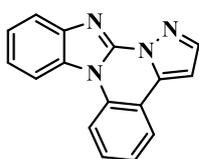
## 2. Experimental Procedure

### 2.1 General procedure for the synthesis of compounds (8-11):



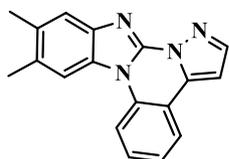
An oven dried schlenk tube was filled with compound (**4-7**) (0.5 mmol), and  $\text{Cu}(\text{OAc})_2$  (20 mol%) in dry DMF solvent. The schlenk tube was flush with argon gas and maintain the inert atmosphere. The reaction mixture was stirred at 70 °C for 12 hours until the substrate was completely consumed (reaction monitor by TLC). After full conversion of starting material, the reaction mixture was brought to room temperature. Then solvent of reaction mixture was evaporated and extracted with ethyl acetate. The organic layer was washed with water and brine solution. The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure then the crude product was purified by column chromatography over silica gel using a mixture of hexane/ ethyl acetate (4:1) as the eluent to afford cyclized product (**8-11**).

#### 2.1.1 Characterization data for products (8-11)



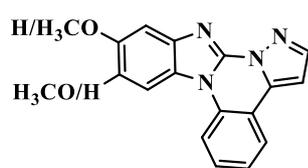
##### Benzo[4,5]imidazo[1,2-a]pyrazolo[1,5-c]quinazoline (**8a**)

The compound **8a** was synthesized by the procedure as described general procedure above and obtained as a white solid: yield 85%; mp: 192 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J = 8.4$  Hz, 1H), 8.06 (d,  $J = 1.8$  Hz, 1H), 8.01 (d,  $J = 8.1$  Hz, 1H), 7.89 (d,  $J = 7.9$  Hz, 2H), 7.59 – 7.52 (m, 1H), 7.40 (dd,  $J = 11.1, 4.1$  Hz, 1H), 7.38 – 7.31 (m, 2H), 6.90 (d,  $J = 1.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.46, 142.53, 141.94, 137.20, 132.03, 130.90, 130.30, 125.35, 125.25, 124.48, 123.21, 120.71, 115.29, 115.19, 112.92, 101.16, 77.37, 77.05, 76.73. HRMS (ESI-ORBITRAP) Calculated for  $\text{C}_{16}\text{H}_{11}\text{N}_4$  [ $\text{M} + \text{H}$ ] $^+$  259.2840, found 259.0974.



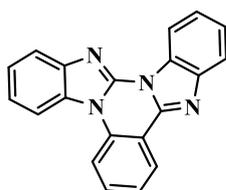
##### 10,11-Dimethylbenzo[4,5]imidazo[1,2-a]pyrazolo[1,5-c]quinazoline (**8b**)

The compound **8b** was synthesized by the procedure as described above and obtained as a white solid: yield 82 %; mp: > 280 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 8.4$  Hz, 1H), 8.09 (d,  $J = 1.6$  Hz, 1H), 7.99 (d,  $J = 7.8$  Hz, 1H), 7.82 (s, 1H), 7.65 (dd,  $J = 15.1, 6.9$  Hz, 2H), 7.43 (t,  $J = 7.6$  Hz, 1H), 6.96 (d,  $J = 1.5$  Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.12, 141.35, 140.81, 137.05, 133.35, 132.17, 132.09, 130.15, 129.21, 125.19, 124.88, 120.72, 115.22, 115.02, 113.25, 100.88, 77.37, 77.05, 76.73, 20.88, 20.30. HRMS (ESI-ORBITRAP) Calculated for  $\text{C}_{18}\text{H}_{15}\text{N}_4$  [ $\text{M} + \text{H}$ ] $^+$  287.3380, found 287.1297.



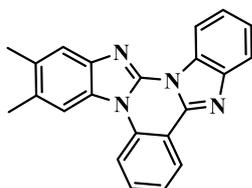
**11(10)-Methoxybenzo[4,5]imidazo[1,2-a]pyrazolo[1,5-c]quinazoline (8c, d)**

The compounds (**8c, d**) were synthesized by the procedure as described above and obtained as an inseparable mixture of white solid: yield 80 %; mp: 177 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 – 8.60 (m, 2H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.66 (dd, *J* = 10.0, 5.0 Hz, 2H), 7.50 (dd, *J* = 5.4, 3.7 Hz, 2H), 7.43 (dd, *J* = 9.6, 5.5 Hz, 2H), 6.94 (dd, *J* = 8.8, 2.1 Hz, 1H), 3.87 (d, *J* = 8.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.03, 156.33, 144.37, 143.70, 140.95, 136.58, 134.02, 133.83, 131.93, 131.85, 130.45, 130.26, 126.55, 126.50, 125.29, 125.21, 125.17, 125.11, 124.29, 124.24, 124.17, 120.06, 119.56, 114.87, 114.63, 114.54, 114.46, 112.96, 111.87, 111.18, 102.68, 98.57, 77.35, 77.03, 76.71, 56.05, 55.62. HRMS (ASAP/Q-TOF) Calculated for C<sub>17</sub>H<sub>13</sub>N<sub>4</sub>O [M + H]<sup>+</sup> 289.3100, found 289.1086.



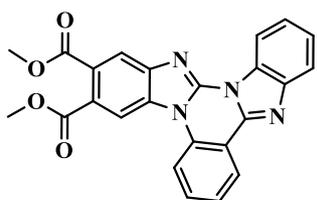
**Benzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[1,2-c]quinazoline (9a)**

The compound **9a** was synthesized by the procedure as described above and obtained as a white solid: yield 80 %; mp: 230 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.74 – 8.69 (m, 1H), 8.66 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.86 – 7.80 (m, 1H), 7.74 – 7.67 (m, 1H), 7.55 – 7.49 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (dd, *J* = 11.3, 3.9 Hz, 1H), 7.36 – 7.31 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.53, 143.80, 142.52, 141.65, 134.08, 131.99, 130.34, 130.07, 126.59, 125.34, 125.33, 124.39, 124.25, 123.08, 120.04, 119.63, 114.99, 114.92, 114.50, 112.65, 77.35, 77.03, 76.72. HRMS (ESI-ORBITRAP) Calculated for C<sub>20</sub>H<sub>13</sub>N<sub>4</sub> [M + H]<sup>+</sup> 309.1062, found 309.1139.



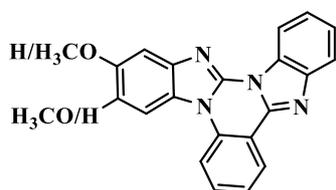
**12,13-Dimethylbenzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[1,2-c]quinazoline (9b)**

The compound **9b** was synthesized by the procedure as described above and obtained as a white solid: yield 78 %; mp: 145 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 8.0 Hz, 2H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.92 (s, 1H), 7.83 (s, 1H), 7.70 (s, 1H), 7.57 (m, 3H), 2.50 (s, 3H), 2.45 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.58, 141.03, 134.41, 133.28, 132.16, 132.08, 130.45, 128.60, 126.68, 125.31, 125.17, 124.34, 120.38, 119.62, 115.47, 115.07, 114.57, 114.51, 113.61, 113.25, 77.34, 77.02, 76.70, 20.87, 20.29. HRMS (ESI-ORBITRAP) Calculated for C<sub>22</sub>H<sub>17</sub>N<sub>4</sub> [M + H]<sup>+</sup> 337.1375, found 337.1444.



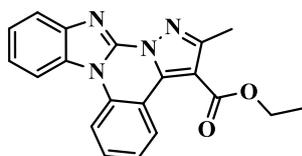
**Dimethyl benzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[1,2-c]quinazoline-12,13-dicarboxylate (9c)**

The compound **9c** was synthesized by the procedure as described above and obtained as a white solid: yield 79 %; mp: 244 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.72 (dd, *J* = 6.4, 2.8 Hz, 1H), 8.57 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 7.99 – 7.93 (m, 1H), 7.90 – 7.83 (m, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.58 – 7.51 (m, 2H), 4.02 (s, 3H), 4.01 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.21, 167.96, 144.54, 144.42, 144.19, 143.93, 133.51, 132.56, 131.19, 130.29, 129.15, 126.99, 126.49, 126.39, 125.89, 124.96, 120.82, 119.96, 115.34, 115.01, 114.93, 114.24, 77.34, 77.02, 76.70, 53.02, 52.91. HRMS (ESI-ORBITRAP) Calculated for C<sub>24</sub>H<sub>17</sub>N<sub>4</sub>O<sub>4</sub> [M + H]<sup>+</sup> 425.1172, found 425.1250.



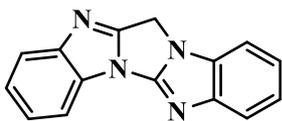
**13(12)-Methoxybenzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[1,2-c]quinazoline (9d, e)**

The compound (**9d, e**) was synthesized by the procedure as described above and obtained as an inseparable mixture of a white solid: yield 75 %; mp: 172 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 – 8.59 (m, 2H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.96 – 7.88 (m, 1H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.50 (dd, *J* = 5.4, 3.7 Hz, 2H), 7.47 – 7.39 (m, 2H), 6.94 (dd, *J* = 8.8, 2.1 Hz, 1H), 3.88 (s, 2H), 3.86 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.03, 156.33, 144.37, 143.70, 140.95, 136.58, 134.02, 133.83, 131.93, 131.85, 130.45, 130.26, 126.55, 126.50, 125.29, 125.21, 125.17, 125.11, 124.29, 124.24, 124.17, 120.06, 119.56, 114.87, 114.63, 114.54, 114.46, 112.96, 111.87, 111.18, 102.68, 98.57, 77.35, 77.03, 76.71, 56.05. HRMS (ESI-ORBITRAP) Calculated for C<sub>21</sub>H<sub>15</sub>N<sub>4</sub>O [M + H]<sup>+</sup> 339.1168, found 339.1239.



**Ethyl 2-methylbenzo[4,5]imidazo[1,2-a]pyrazolo[1,5-c]quinazoline-3-carboxylate (10)**

The compound **10** was synthesized by the procedure as described above and obtained as a white solid: yield 71 %; mp: 220 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.58 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.45 (d, *J* = 7.8 Hz, 1H), 8.22 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.03 – 7.96 (m, 1H), 7.81 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.61 – 7.44 (m, 3H), 4.50 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.19, 156.68, 142.78, 141.09, 138.57, 132.97, 131.60, 130.79, 129.17, 125.22, 124.85, 123.36, 120.85, 114.90, 114.65, 113.26, 110.01, 77.34, 77.02, 76.71, 61.13, 15.71, 14.34. HRMS (ASAP/Q-TOF) Calculated for C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>Na [M + Na]<sup>+</sup> 367.3638, found 367.1172.



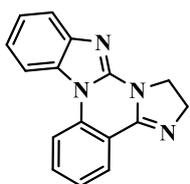
### Bis-benzimidazole (11)

The compound **11** was synthesized by the procedure as described above and obtained as a white solid: yield 58 %; mp: > 250 °C; <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.62 (dd, *J* = 6.2, 2.9 Hz, 1H), 7.54 (dd, *J* = 5.8, 3.3 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 3.6 Hz, 1H), 7.17 (d, *J* = 3.2 Hz, 1H), 7.13 (d, *J* = 4.8 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 1H), 5.68 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 145.55, 143.44, 136.58, 123.21, 122.78, 122.78, 122.42, 122.42, 121.89, 121.89, 119.15, 118.75, 111.92, 110.92, 45.25, 40.57, 40.36, 40.15, 39.94, 39.74, 39.53, 39.32. HRMS (ESI-ORBITRAP) Calculated for C<sub>20</sub>H<sub>17</sub>N<sub>4</sub>O<sub>2</sub> [M + H]<sup>+</sup> 247.0905, found 247.0984.

## 2.2 General procedure for the synthesis of compounds (10aa-ac):

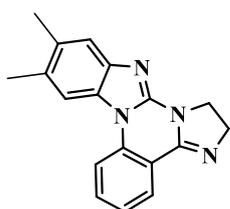
An oven dried schlenk tube was filled with compound **3a** (0.5 mmol), ethylenediamine (0.5 mmol) and K<sub>2</sub>CO<sub>3</sub> in dry DMF solvent. The schlenk tube was flush with argon gas and maintain the inert atmosphere. The reaction mixture was stirred at 70 °C for 5 hours. After full conversion of starting material, Cu(OAc)<sub>2</sub> (20 mol%) was added in reaction mixture and further stirred at 70 °C for 12 hours until the substrate was completely consumed (reaction monitor by TLC). Then DMF solvent of evaporated DMF and extracted with ethyl acetate. The organic layer was washed with water and brine solution. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure then the crude product was purified by column chromatography over silica gel using a mixture of hexane/ethyl acetate (1:99) as the eluent to afford solid product **10aa-ac**.

### 2.2.1 Characterization data for products (10aa-ac)



#### 1,2-dihydrobenzo[4,5]imidazo[1,2-a]imidazo[1,2-c]quinazoline (10aa)

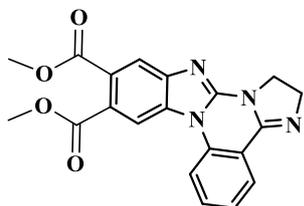
The compound **10aa** was synthesized by the procedure as described above and obtained as a white solid: yield 85 %; mp: 222 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.61 (dd, *J* = 15.4, 7.7 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 4.21 (s, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.44, 145.66, 143.11, 136.27, 133.33, 130.88, 127.82, 124.81, 123.64, 121.59, 118.46, 114.62, 114.32, 111.56, 77.38, 77.06, 76.74, 54.36, 46.16. HRMS (ESI-ORBITRAP) Calculated for C<sub>16</sub>H<sub>13</sub>N<sub>4</sub> [M + H]<sup>+</sup> 261.1062, found 261.1130.



#### 10,11-dimethyl-1,2-dihydrobenzo[4,5]imidazo[1,2-a]imidazo[1,2-c]quinazoline (10ab)

The compound **10ab** was synthesized by the procedure as described above and obtained as a white solid: yield 81 %; mp: 239 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.63 (m, 1H),

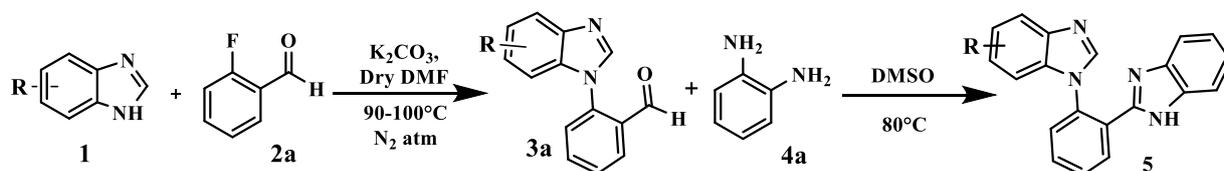
7.53 (s, 1H), 7.35 (s, 1H), 7.31 (t,  $J = 7.5$  Hz, 1H), 4.23 (s, 4H), 2.39 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.69, 145.18, 141.36, 136.44, 133.26, 132.16, 130.12, 129.20, 127.77, 124.48, 118.95, 114.58, 114.18, 112.31, 77.36, 77.04, 76.73, 54.27, 46.20, 20.61, 20.18. HRMS (ESI-ORBITRAP) Calculated for  $\text{C}_{18}\text{H}_{17}\text{N}_4$   $[\text{M} + \text{H}]^+$  289.1375, found 289.1453.



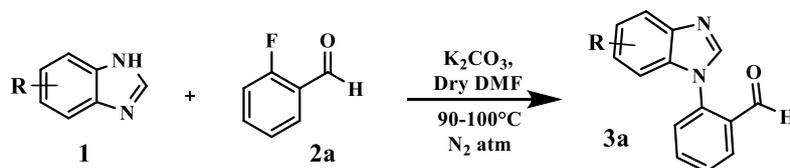
### Dimethyl 1,2-dihydrobenzo[4,5]imidazo[1,2-a]imidazo[1,2-c]quinazoline-10,11-dicarboxylate (**10ac**)

The compound **10ac** was synthesized by the procedure as described above and obtained as a white solid: yield 79 %; mp: 248 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 4.8$  Hz, 2H), 8.07 (d,  $J = 8.4$  Hz, 1H), 7.86 (s, 1H), 7.76 (t,  $J = 7.8$  Hz, 1H), 7.42 (t,  $J = 7.5$  Hz, 1H), 4.29 (s, 4H), 3.96 (d,  $J = 6.1$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.57, 167.98, 151.83, 148.02, 145.48, 135.55, 133.78, 131.91, 128.90, 128.13, 125.89, 124.55, 118.71, 114.99, 114.62, 112.78, 77.35, 77.03, 76.71, 54.57, 52.81, 52.78, 46.18. HRMS (ESI-ORBITRAP) Calculated for  $\text{C}_{20}\text{H}_{17}\text{N}_4\text{O}_4$   $[\text{M} + \text{H}]^+$  377.1172, found 377.1250.

## 2.3 General procedure for synthesizing compound type (5)

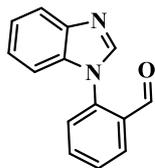


### 2.3.1 General procedure for synthesizing compound type (3a)<sup>1</sup>:



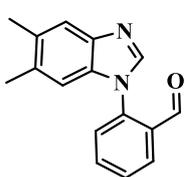
An oven dried 25 ml round-bottom flask was taken benzimidazole (1.0 equiv, 6.8 mmol), 2-fluorobenzaldehyde (2.0 equiv, 13.6 mmol), and  $\text{K}_2\text{CO}_3$  (2.0 equiv, 13.6 mmol) in DMF (5.0 ml) were added, and the reaction was stirred at 90 °C for 16 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound of type **3a**.

### 2.3.1.1 Characterization data for products (3aa-ag)



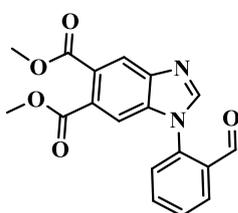
#### 2-(1H-Benzo[d]imidazol-1-yl) benzaldehyde (3aa)

The compound **3aa** was synthesized by the procedure as described above and obtained as a yellow sticky compound: yield 75 %;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.69 (s, 1H), 8.12 (d,  $J = 7.8$  Hz, 1H), 8.08 (d,  $J = 5.6$  Hz, 1H), 7.87 (dd,  $J = 8.2, 7.4$  Hz, 1H), 7.81 (dd,  $J = 14.7, 7.1$  Hz, 1H), 7.67 (dd,  $J = 11.2, 4.0$  Hz, 1H), 7.48 (d,  $J = 7.9$  Hz, 1H), 7.31 (tt,  $J = 13.4, 6.7$  Hz, 2H), 7.21 (d,  $J = 7.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  188.42, 143.35, 143.29, 137.82, 135.75, 135.53, 131.60, 129.68, 129.63, 127.96, 124.45, 123.33, 120.71, 110.00, 77.47, 77.15, 76.84. HRMS (ESI-ORBITRAP) Calculated for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}$   $[\text{M} + \text{H}]^+$  223.0793, found 223.0862.



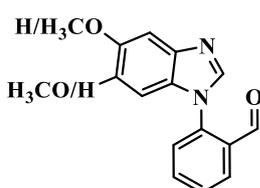
#### 2-(5,6-Dimethyl-1H-benzo[d]imidazol-1-yl)benzaldehyde (3ab)

The compound **3ab** was synthesized by the procedure as described above and obtained as a white solid: 64% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.69 (s, 1H), 8.11 (dd,  $J = 7.8, 1.5$  Hz, 1H), 7.94 (s, 1H), 7.79 (td,  $J = 7.7, 1.6$  Hz, 1H), 7.70–7.58 (m, 2H), 7.47 (dd,  $J = 7.9, 0.8$  Hz, 1H), 6.98 (s, 1H), 2.37 (s, 3H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  188.5, 142.5, 141.9, 138.3, 135.4, 134.4, 133.8, 132.3, 131.6, 129.4, 129.3, 127.8, 120.6, 110.0, 77.47, 77.15, 76.83, 20.5, 20.2; HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}$  251.1179, found 251.1181.



#### Dimethyl 1-(2-formylphenyl)-1H-benzo[d]imidazole-5,6-dicarboxylate (3ac)

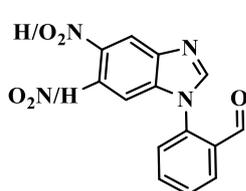
The compound **3ac** was synthesized by the procedure as described above and obtained as a colourless sticky compound: yield 55 %;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.74 (s, 1H), 8.30 (s, 1H), 8.21 (s, 1H), 8.16 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.87 (td,  $J = 7.7, 1.6$  Hz, 1H), 7.77 (t,  $J = 7.5$  Hz, 1H), 7.57 (s, 1H), 7.52 (dd,  $J = 7.8, 0.8$  Hz, 1H), 3.95 (s, 3H), 3.88 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  187.88, 168.21, 168.02, 146.45, 144.49, 136.53, 136.05, 135.62, 131.70, 131.16, 130.50, 128.65, 128.34, 127.43, 122.41, 111.59, 77.47, 77.15, 76.83, 52.85, 52.82. HRMS (ESI-ORBITRAP) Calculated for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_5$   $[\text{M} + \text{H}]^+$  339.0903, found 339.0970.



#### 2-(5(6)-methoxy-1H-benzo[d]imidazol-1-yl) benzaldehyde (3ad, ae)

The compound (**3ad, ae**) was synthesized by the procedure as described above and obtained as an inseparable mixture yellow sticky compound, 68% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.78–9.69 (s, 1H), 8.13 (ddd,  $J = 7.9, 6.6, 1.5$  Hz, 1H), 7.99 (d,  $J = 21.6$  Hz, 1H), 7.81 (qd,  $J = 7.6, 1.6$  Hz, 1H), 7.76, 7.11 (d, 1H), 7.67 (q,  $J = 7.4$  Hz, 1H), 7.50 (d,  $J = 7.9$  Hz, 1H), 6.64 (d, 1H), 6.96 (td,  $J = 9.1, 2.4$  Hz, 1H), 3.82 (s, 3H);  $^{13}\text{C}$

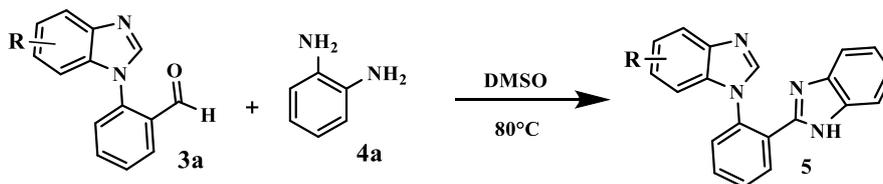
NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  188.4, 188.8, 157.8, 156.8, 144.3, 143.5, 142.4, 138.0, 137.7, 136.4, 135.5, 135.4, 131.6, 131.5, 130.4, 129.6, 129.5, 127.8, 127.7, 121.2, 114.5, 112.7, 110.4, 102.6, 93.1, 77.43, 77.11, 76.79, 55.8; HRMS (ESI-ORBITRAP)  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> 253.0972, found 253.0976.



### 2-(5(6)-Nitro-1H-benzo[d]imidazol-1-yl) benzaldehyde (3af, ag)

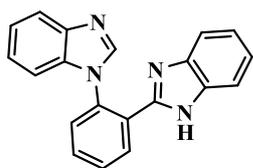
The compound (3af, ag) was synthesized by the procedure as described above and obtained as an inseparable mixture of yellow solid, 63% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.77 (s, 1H), 8.77 (d, *J* = 2.1 Hz, 1H), 8.29–8.19 (m, 2H), 8.18–8.09 (m, 1H), 7.93–7.85 (m, 1H), 7.80 (td, *J* = 8.4, 0.6 Hz, 1H), 7.57–7.52 (m, *J* = 7.8, 4.8, 0.9 Hz, 1H), 7.29–7.22 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  188.0, 188.0, 147.7, 147.6, 146.5, 144.7, 144.3, 142.8, 139.3, 135.6, 135.3, 134.8, 132.0, 131.6, 131.5, 130.7, 130.6, 128.4, 128.3, 121.0, 119.9, 118.8, 117.4, 110.2, 107.1, 77.40, 77.09, 76.77; HRMS (ESI-ORBITRAP)  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>10</sub>N<sub>3</sub>O<sub>3</sub> 268.0717, found 268.0719.

## 2.3.2 General procedure for synthesizing compound (5):



An oven dried 25 ml round-bottom flask was taken compound **3a** (1.0 equiv, 3.2 mmol), and benzene-1,2-diamine (1.0 equiv, 3.2 mmol) in DMSO (3.0 ml) were added, and the reaction was stirred at 80 °C for 8 hours. Upon the completion of the reaction (confirm by TLC), and the reaction mixture was dissolved in ethyl acetate. Then the organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound of type **5**.

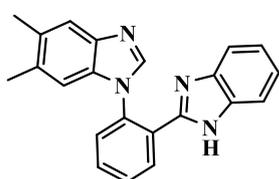
### 2.3.2.1 Characterization data for products (5a-g)



#### 2-(2-(1H-benzo[d]imidazol-1-yl)phenyl)-1H-benzo[d]imidazole (5a)

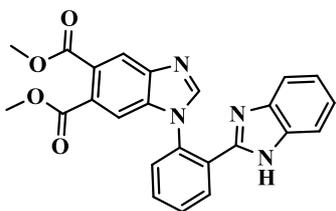
The compound **5a** was synthesized by the procedure as described above and obtained as a white solid: yield 78 %; mp: 198 °C; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>)  $\delta$  12.56 (s, 1H), 8.25 (s, 1H), 8.07 – 7.99 (m, 1H), 7.79 – 7.71 (m, 2H), 7.67 (dd, *J* = 9.6, 4.9 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.18 – 7.05 (m, 5H). <sup>13</sup>C NMR (101 MHz, DMSO *d*<sub>6</sub>)  $\delta$  149.23, 144.98, 143.92, 143.59, 134.90, 134.75, 134.49,

131.96, 131.53, 129.44, 128.66, 128.30, 123.42, 123.04, 122.36, 121.94, 120.01, 119.50, 111.86, 110.49, 40.62, 40.41, 40.20, 39.99, 39.78, 39.58, 39.37. HRMS (ESI-ORBITRAP)  $m/z$   $[M + H]^+$  calculated for  $C_{20}H_{15}N_4$  311.1218, found 311.1297.



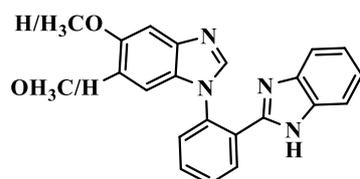
**1-(2-(1H-benzo[d]imidazol-2-yl)phenyl)-5,6-dimethyl-1H-benzimidazole (5b)**

The compound **5b** was synthesized by the procedure as described above and obtained as a white solid: yield 75 %; mp: 201 °C;  $^1H$  NMR (400 MHz, DMSO  $d_6$ )  $\delta$  12.51 (s, 1H), 8.02 (s, 1H), 7.98 (dd,  $J = 7.4, 1.7$  Hz, 1H), 7.77 – 7.68 (m, 2H), 7.63 (dd,  $J = 7.5, 1.3$  Hz, 1H), 7.44 (d,  $J = 7.8$  Hz, 1H), 7.40 (d,  $J = 7.9$  Hz, 1H), 7.36 (d,  $J = 7.7$  Hz, 1H), 7.13 (t,  $J = 7.6$  Hz, 1H), 7.08 (t,  $J = 7.5$  Hz, 1H), 6.92 (s, 1H), 2.23 (s, 3H), 2.15 (s, 3H).  $^{13}C$  NMR (101 MHz, DMSO  $d_6$ )  $\delta$  149.34, 143.97, 143.90, 142.06, 134.90, 134.78, 133.30, 132.10, 132.00, 131.53, 130.78, 129.23, 128.46, 128.33, 123.03, 121.94, 120.02, 119.47, 111.87, 110.66, 40.56, 40.35, 40.14, 39.93, 39.72, 39.51, 39.31, 20.38, 20.23. HRMS (ESI-ORBITRAP)  $m/z$   $[M + H]^+$  calculated for  $C_{22}H_{19}N_4$  339.1531, found 339.1597.



**Dimethyl 1-(2-(1H-benzo[d]imidazol-2-yl)phenyl)-1H-benzimidazole-5,6-dicarboxylate (5c)**

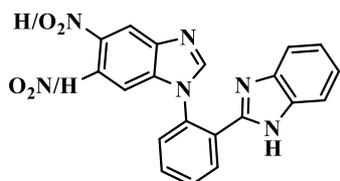
The compound **5c** was synthesized by the procedure as described above and obtained as a white solid: yield 75 %; mp: 165 °C;  $^1H$  NMR (400 MHz, DMSO  $d_6$ )  $\delta$  12.72 (s, 1H), 8.52 (s, 1H), 8.09 (dd,  $J = 5.8, 2.9$  Hz, 1H), 8.03 (s, 1H), 7.82 – 7.76 (m, 3H), 7.43 (s, 1H), 7.40 (d,  $J = 7.9$  Hz, 1H), 7.32 (d,  $J = 8.0$  Hz, 1H), 7.16 – 7.10 (m, 1H), 7.08 – 7.02 (m, 1H), 3.79 (s, 3H), 3.72 (s, 3H).  $^{13}C$  NMR (101 MHz, DMSO  $d_6$ )  $\delta$  168.20, 167.87, 148.96, 148.65, 144.65, 143.90, 136.18, 134.79, 133.37, 131.60, 131.48, 130.33, 129.24, 128.33, 126.92, 126.45, 123.27, 122.06, 120.98, 119.53, 111.94, 111.84, 52.97, 52.95, 40.61, 40.40, 40.19, 39.91, 39.77, 39.56, 39.35. HRMS (ASAP/Q-TOF)  $m/z$   $[M + Na]^+$  calculated for  $C_{24}H_{18}N_4O_4Na$  449.1226, found 449.1226.



**1-(2-(1H-benzo[d]imidazol-2-yl)phenyl)-5(6)-methoxy-1H-benzimidazole (5d, e)**

The compound (**5d**, **e**) was synthesized by the procedure as described above and obtained as an inseparable mixture of white solid: yield 69 %; mp: 197 °C;  $^1H$  NMR (400 MHz, DMSO  $d_6$ )  $\delta$  12.51 (s, 2H), 8.15 (d,  $J = 7.5$  Hz, 2H), 8.00 (dd,  $J = 7.3, 1.8$  Hz, 2H), 7.71 (dtdd,  $J = 19.8, 12.4, 7.2, 1.4$  Hz, 6H), 7.51 (d,  $J = 8.8$  Hz, 1H), 7.45 (d,  $J = 7.7$  Hz, 2H), 7.36 (t,  $J = 7.6$  Hz, 2H), 7.18 (d,  $J = 2.3$  Hz, 1H), 7.09 (dd,  $J = 16.8, 8.3$  Hz, 4H), 6.97 (d,  $J = 8.8$  Hz, 1H), 6.71 (dd,  $J = 8.7, 2.2$  Hz, 2H), 6.51

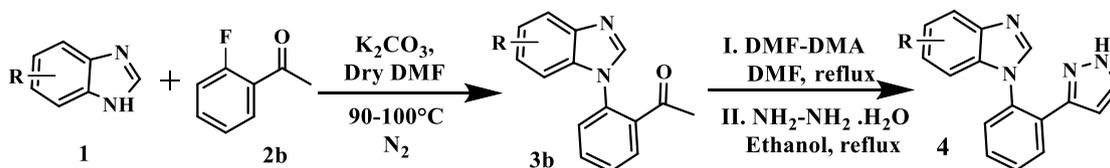
(d,  $J = 2.3$  Hz, 1H), 3.73 (s, 2H), 3.54 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz, DMSO  $d_6$ )  $\delta$  156.68, 155.97, 149.45, 149.29, 145.11, 144.46, 143.92, 143.86, 137.83, 135.11, 134.92, 134.66, 134.62, 132.14, 132.03, 131.64, 131.54, 129.27, 128.45, 128.35, 128.19, 128.08, 123.03, 121.94, 120.44, 119.51, 119.43, 112.97, 112.01, 111.88, 111.83, 110.83, 102.54, 93.55, 55.90, 55.69, 40.61, 40.45, 40.40, 40.21, 39.99, 39.78, 39.57. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{17}\text{N}_4\text{O}$  341.1324, found 341.1397.



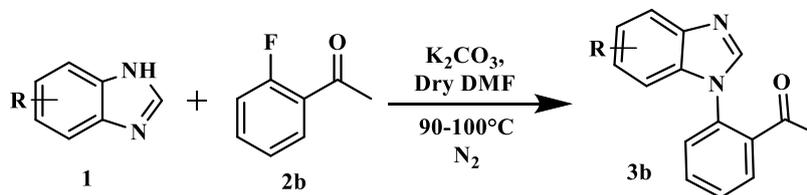
### 1-(2-(1H-benzo[d]imidazol-2-yl)phenyl)-5(6)-nitro-1H-benzo[d]imidazole (**5f, g**)

The compound (**5f, g**) was synthesized by the procedure as described above and obtained as an inseparable mixture of white solid: yield 63 %; mp: 169 °C;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ )  $\delta$  12.76 (s, 1H), 8.59 (d,  $J = 3.3$  Hz, 1H), 8.16 – 7.99 (m, 2H), 7.89 (dd,  $J = 5.2, 3.4$  Hz, 1H), 7.85 – 7.72 (m, 3H), 7.35 (d,  $J = 35.1$  Hz, 2H), 7.30 – 7.24 (m, 1H), 7.08 (d,  $J = 31.7$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz, DMSO  $d_6$ )  $\delta$  150.38, 149.22, 148.61, 148.11, 143.35, 142.92, 139.50, 133.31, 131.59, 131.40, 130.45, 129.31, 128.23, 123.28, 122.09, 119.13, 116.21, 111.88, 111.19, 107.19, 40.59, 40.38, 40.17, 39.96, 39.75, 39.55, 39.34. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{20}\text{H}_{14}\text{N}_5\text{O}_2$  356.1069, found 356.1140.

## 2.4 General procedure for synthesizing compound type (**4**)<sup>1</sup>:



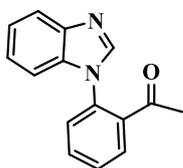
### 2.4.1 General procedure for synthesizing compound type (**3b**)<sup>1</sup>:



An oven dried 25 ml round-bottom flask was taken benzimidazole (1.0 equiv, 6.8 mmol), 2-fluoroacetophenone (2.0 equiv, 13.6 mmol), and  $\text{K}_2\text{CO}_3$  (2.0 equiv, 13.6 mmol) in DMF (5.0 ml) were added, and the reaction was stirred at 90 °C for 16 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under

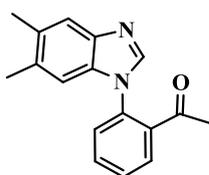
the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compounds of type **3b**.

#### 2.4.1.1 Characterization data for products (3ba-bd)



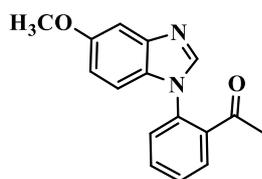
##### 1-(2-(1H-benzo[d]imidazol-1-yl)phenyl)ethan-1-one (**3ba**)

The compound **3ba** was synthesized by the procedure as described above and obtained as a colourless sticky liquid: yield 70%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (s, 1H), 7.88 (d,  $J = 7.6$  Hz, 1H), 7.82 (d,  $J = 7.7$  Hz, 1H), 7.69 (t,  $J = 7.6$  Hz, 1H), 7.60 (t,  $J = 7.6$  Hz, 1H), 7.45 (d,  $J = 7.8$  Hz, 1H), 7.37 – 7.27 (m, 2H), 7.22 (d,  $J = 7.7$  Hz, 1H), 1.92 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.68, 137.31, 133.67, 132.88, 130.03, 129.42, 127.97, 124.21, 123.12, 120.69, 110.06, 77.43, 77.11, 76.79, 28.80. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}$  237.0950, found 237.1019.



##### 1-(2-(5,6-dimethyl-1H-benzo[d]imidazol-1-yl)phenyl)ethan-1-one (**3bb**)

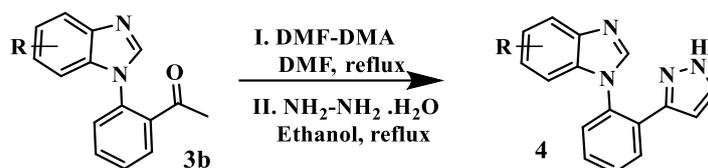
The compound **3bb** was synthesized by the procedure as described above and obtained as a colourless sticky liquid: yield 62%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (s, 1H), 7.81 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.70 (td,  $J = 7.7, 1.6$  Hz, 1H), 7.64 (s, 1H), 7.60 (td,  $J = 7.6, 1.0$  Hz, 1H), 7.46 (d,  $J = 7.8$  Hz, 1H), 7.01 (s, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 1.89 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.03, 142.08, 137.42, 134.07, 133.63, 133.36, 132.80, 132.20, 129.96, 129.18, 127.78, 127.79, 120.63, 110.09, 77.37, 77.05, 76.73, 28.80, 20.61, 20.32. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}$  265.1263, found 265.1333.



##### 1-(2-(5-methoxy-1H-benzo[d]imidazol-1-yl)phenyl)ethan-1-one (**3bc**)

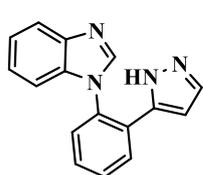
The compound (**3bc**) was synthesized by the procedure as described above and obtained as colourless sticky liquid: yield 68%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (s, 1H), 7.86 – 7.80 (m, 1H), 7.75 (d,  $J = 8.9$  Hz, 1H), 7.71 (dd,  $J = 8.3, 7.1$  Hz, 1H), 7.62 (t,  $J = 7.3$  Hz, 1H), 7.47 (d,  $J = 7.8$  Hz, 1H), 6.98 (dd,  $J = 8.8, 2.2$  Hz, 1H), 6.64 (d,  $J = 2.0$  Hz, 1H), 3.78 (s, 3H), 1.93 (s,  $J = 10.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.86, 157.75, 137.46, 133.77, 132.87, 130.04, 129.37, 127.80, 121.25, 112.76, 93.16, 77.34, 77.02, 76.71, 55.84, 28.80. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_2$  267.1055, found 267.1123.

## 2.4.2 General procedure for synthesizing compound (4):



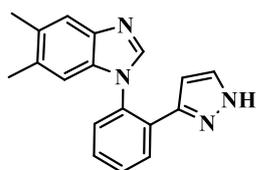
An oven dried 25 ml round-bottom flask was taken compound **3b** (1.0 equiv, 0.84 mmol), and DMF-DMA (1.5 equiv, 1.26 mmol) in DMF solvent were added, and the reaction was stirred to reflux overnight. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was again treated with hydrazine hydrate (2.0 equiv, 0.49 mmol) in ethanol under reflux condition for 4 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound of type **4**.

### 2.4.2.1 Characterization data for products (4a-d)



#### 1-(2-(1H-pyrazol-5-yl)phenyl)-1H-benzo[d]imidazole (**4a**)

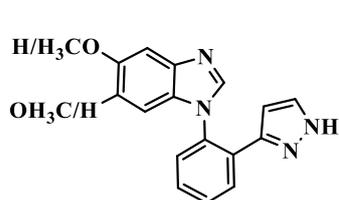
The compound **4a** was synthesized by the procedure as described above and obtained as a white solid: yield 75%; mp: 188 – 190 °C; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>) δ 12.88 (s, 1H), 8.22 (s, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.1 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 10.2 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 5.26 (s, 1H). <sup>13</sup>C NMR (101 MHz, DMSO *d*<sub>6</sub>) δ 147.01, 144.58, 143.41, 135.15, 132.94, 132.23, 130.07, 130.04, 129.93, 129.18, 129.12, 123.55, 122.37, 120.04, 110.77, 103.47, 40.61, 40.45, 40.40, 40.24, 40.20, 39.99, 39.78. HRMS (ESI-ORBITRAP) *m/z* [M + H]<sup>+</sup> calculated for C<sub>16</sub>H<sub>13</sub>N<sub>4</sub> 261.1062, found 261.1130.



#### 1-(2-(1H-pyrazol-3-yl)phenyl)-5,6-dimethyl-1H-benzo[d]imidazole (**4b**)

The compound **4b** was synthesized by the procedure as described above and obtained as a white solid: yield 73%; mp: 193 °C; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>) δ 12.88 (s, 1H), 8.01 (s, 2H), 7.58 (d, *J* = 31.3 Hz, 4H), 7.48 (s, 2H), 6.81 (s, 1H), 2.29 (s, 3H), 2.20 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO *d*<sub>6</sub>) δ 143.58, 143.10, 141.88, 134.56, 133.73, 133.14, 132.76, 132.37, 130.90, 130.87, 129.86, 129.23, 120.05, 113.04, 110.68,

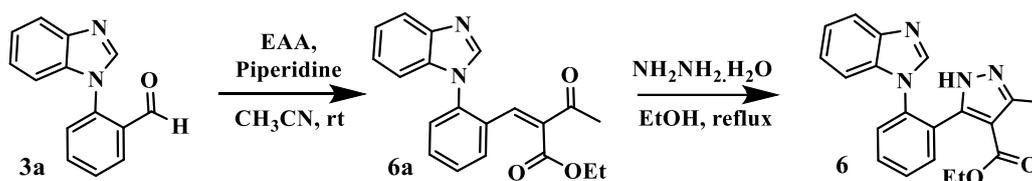
103.45, 40.54, 40.33, 40.12, 39.91, 39.71, 39.50, 39.29, 20.40, 20.30. HRMS (ESI-ORBITRAP)  $m/z$   $[M + H]^+$  calculated for  $C_{18}H_{17}N_4$  289.1375, found 289.1453.



### 1-(2-(1H-pyrazol-3-yl)phenyl)-5(6)-methoxy-1H-benzo[d]imidazole (**4c, d**)

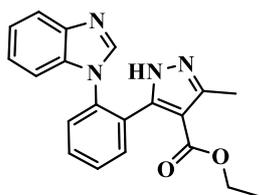
The compound (**4c, d**) was synthesized by the procedure as described above and obtained as an inseparable mixture of white solid: yield 65%; mp: 196 °C;  $^1H$  NMR (400 MHz, DMSO  $d_6$ )  $\delta$  12.87 (s, 1H), 8.10 – 7.97 (m, 2H), 7.58 (dd,  $J = 17.8, 9.0$  Hz, 3H), 7.50 (s, 2H), 6.82 (d,  $J = 8.7$  Hz, 1H), 6.43 (s, 1H), 5.29 (s, 1H), 3.78 (s, 1H), 3.61 (s, 3H).  $^{13}C$  NMR (101 MHz, DMSO  $d_6$ )  $\delta$  156.89, 147.14, 143.56, 137.73, 135.66, 133.07, 132.10, 130.17, 129.94, 129.83, 129.21, 129.01, 120.56, 111.99, 103.57, 93.70, 55.85, 40.61, 40.40, 40.19, 39.98, 39.78, 39.57, 39.36. HRMS (ESI-ORBITRAP)  $m/z$   $[M + H]^+$  calculated for  $C_{17}H_{15}N_4O$  291.1168, found 291.1248.

## 2.5 Synthetic procedure for compound (**6**):



An oven dried 25 ml round-bottom flask was taken compound **3a** (1.0 equiv, 1.12 mmol), EAA (1.1 equiv, 1.23 mmol), and piperidine (0.05 equiv, 0.05 mmol) in  $CH_3CN$  were added and stirred the reaction mixture at room temperature overnight. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $Na_2SO_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **6a**.

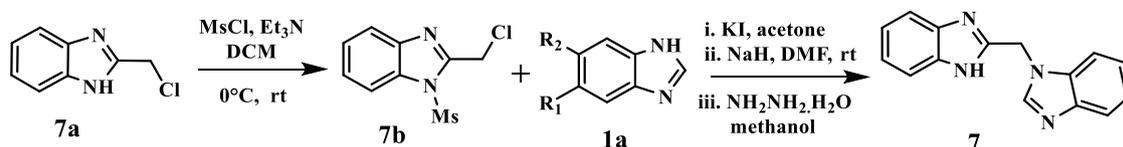
The compound **6a** was again treated with hydrazine hydrate (2.0 equiv, 1.79 mmol) in ethanol solvent under reflux condition for 6 hours. Upon the completion of the compound **6a** (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $Na_2SO_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **6**.



### Ethyl 5-(2-(1H-benzo[d]imidazol-1-yl)phenyl)-3-methyl-1H-pyrazole-4-carboxylate (**6**)

The compound **6** was synthesized by the procedure as described above and obtained as a white solid: yield 61 %; mp: 190 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 5.8 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.63 – 7.56 (m, 2H), 7.55 – 7.48 (m, 2H), 7.32 (td, *J* = 7.4, 2.9 Hz, 2H), 7.24 – 7.19 (m, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.18, 149.65, 145.16, 144.00, 134.93, 134.03, 132.19, 131.31, 130.11, 129.61, 128.28, 126.41, 123.33, 122.50, 119.59, 110.86, 109.79, 77.35, 77.04, 76.72, 59.60, 13.94, 11.75. HRMS (ESI-ORBITRAP) *m/z* [M + H]<sup>+</sup> calculated for C<sub>20</sub>H<sub>19</sub>N<sub>4</sub>O<sub>2</sub> 347.3900, found 347.1508.

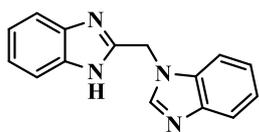
## 2.6 Synthetic procedure for compound (**7**)<sup>2</sup>:



An oven dried 25 ml round-bottom flask was taken compound **7a** (1.0 equiv, 1.20 mmol), NEt<sub>3</sub> (4.0 equiv, 4.81 mmol), and MsCl (3.0 equiv, 3.61 mmol) in dry DCM were added under nitrogen atmosphere, and the reaction was stirred to 0 °C at room temperature for 4 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **7b**.

The compound **7b** was again treated with KI (3.0 equiv, 4.79 mmol) in acetone under reflux condition for 4 hours. Upon the completion of the compound **7b** (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure.

The crude was again treated with benzimidazole **1a** (1.1 equiv, 1.75 mmol), and NaH (1.1 equiv, 1.75 mmol) in DMF at room temperature. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was further treated with hydrazine hydrate (1.5 equiv, 2.41 mmol) in methanol solvent under reflux condition for 6 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **7**.

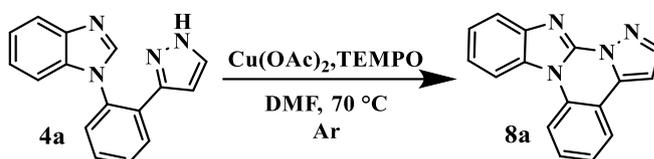


### 2-((1H-benzo[d]imidazol-1-yl)methyl)-1H-benzo[d]imidazole (**7**)

The compound **7** was synthesized by the procedure as described above and obtained as a white solid: yield 65%; mp: > 260 °C; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>) δ 12.76 (s, 1H), 8.40 (s, 1H), 7.65 (dd, *J* = 5.7, 3.3 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.24 – 7.09 (m, 5H), 5.74 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO *d*<sub>6</sub>) δ 150.11, 144.96, 143.90, 134.34, 122.96, 122.15, 119.92, 111.03, 42.84, 40.62, 40.41, 40.20, 39.99, 39.78, 39.57, 39.36. HRMS (ASAP/Q-TOF) *m/z* [M + H]<sup>+</sup> calculated for C<sub>15</sub>H<sub>13</sub>N<sub>4</sub> 249.1062, found 249.1103.

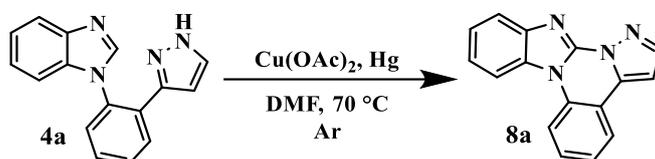
## 3. Experimental procedure for control experiments

### 3.1 Reaction to test the radical formation:



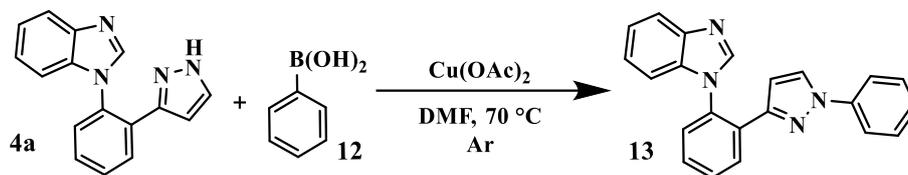
An oven dried schlenk tube was taken with compound **4a** (1.0 equiv, 0.38 mmol), TEMPO (1.0 equiv, 0.38 mmol), and Cu(OAc)<sub>2</sub> (20 mol%) in DMF solvent. The schlenk tube was flush with argon gas and maintain the inert argon atmosphere. The reaction mixture was stirred at 70 °C for 12 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **8a** with 82% yield.

### 3.2 Reaction to test the Cu-nanoparticle formation:



An oven dried schlenk tube was taken with compound **4a** (1.0 equiv, 0.38 mmol), Hg (10 mol%), and Cu(OAc)<sub>2</sub> (20 mol%) in DMF solvent. The schlenk tube was flush with argon gas and maintain the inert argon atmosphere. The reaction mixture was stirred at 70 °C for 12 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **8a** with 80% yield.

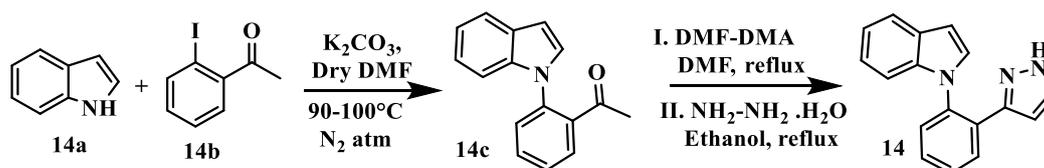
### 3.3 Intermolecular C-N coupling with Phenyl boronic acid:



An oven dried schlenk tube was taken with compound **4a** (1.0 equiv, 0.38 mmol), phenyl boronic acid **12** (1.0 equiv, 0.38 mmol), and  $\text{Cu}(\text{OAc})_2$  (1.0 equiv, 0.38 mmol) in DMF solvent. The schlenk tube was flush with argon gas and maintain the inert argon atmosphere. The reaction mixture was stirred at 70 °C for 12 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid with 69% yield (mp: 192 °C) of target compound **13**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.96 (s, 1H), 7.89 (d,  $J = 8.0$  Hz, 1H), 7.67 – 7.60 (m, 2H), 7.57 – 7.47 (dtd,  $J = 15.7, 7.8, 1.3$  Hz, 4H), 7.40 (t,  $J = 7.9$  Hz, 2H), 7.35 – 7.29 (m, 1H), 7.23 (dd,  $J = 14.2, 7.0$  Hz, 3H), 5.56 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.92, 143.48, 143.25, 139.77, 135.03, 133.11, 131.36, 130.21, 129.57, 129.39, 129.08, 128.40, 127.79, 126.58, 123.57, 122.48, 120.20, 118.97, 110.63, 106.59, 77.35, 77.03, 76.71. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{22}\text{H}_{17}\text{N}_4$  337.1375, found 337.1439.

### 3.4 Synthetic procedure for 1-(2-(1H-pyrazol-3-yl)phenyl)-1H-indole (**14**):



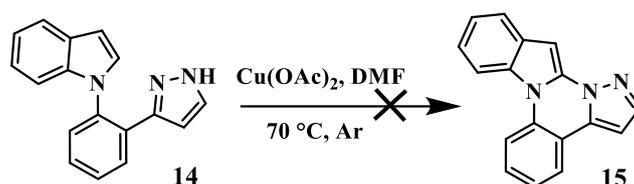
An oven dried 25 ml round-bottom flask was taken indole **14a** (1.0 equiv, 2.56 mmol), 2-iodoacetophenone **14b** (0.8 equiv, 2.12 mmol)  $\text{CuI}$  (0.25 equiv, 0.64 mmol), and  $\text{K}_2\text{CO}_3$  (2.5 equiv, 6.40 mmol) in DMF (3.0 ml) were added, and the reaction was stirred at 90-100 °C for 24 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **14c**<sup>3</sup>.

An oven dried 25 ml round-bottom flask was taken compound **14c** (1.0 equiv, 1.06 mmol), and DMF-

DMA (2.5 equiv, 2.65 mmol) in DMF solvent were added, and the reaction was stirred to reflux overnight. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was again treated with hydrazine hydrate (2 equiv, 2.06 mmol) in ethanol under reflux condition for 4 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the colorless sticky liquid with 68% yield of target compound **14**.

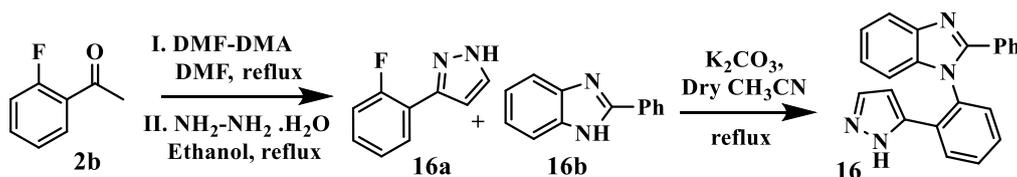
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.95 (m, 1H), 7.74 (t,  $J = 11.1$  Hz, 1H), 7.71 – 7.65 (m, 1H), 7.52 (ddd,  $J = 10.6, 8.0, 1.5$  Hz, 2H), 7.48 – 7.38 (m, 2H), 7.17 – 7.11 (m, 2H), 7.10 (t,  $J = 3.2$  Hz, 1H), 7.07 (t,  $J = 3.9$  Hz, 1H), 6.66 (d,  $J = 3.1$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.91, 136.31, 130.28, 129.52, 129.15, 128.95, 128.84, 128.69, 128.66, 128.39, 128.08, 125.75, 122.40, 120.91, 120.24, 110.49, 103.32, 77.35, 77.04, 76.72. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{17}\text{H}_{14}\text{N}_3$  260.1109, found 260.1180.

### 3.5 Reaction to test the role of benzimidazole nitrogen:



An oven dried schlenk tube was taken with compound **14** (1.0 equiv, 0.5 mmol), and  $\text{Cu}(\text{OAc})_2$  (20 mol%) in DMF solvent. The schlenk tube was flush with argon gas and maintain the inert argon atmosphere. The reaction mixture was stirred at 70 °C for 12 hours even then no cyclization product **15** was form.

### 3.6 Synthetic procedure for 1-(2-(1H-pyrazol-3-yl)phenyl)-2-phenyl-1H-benzo [d]imidazole (16):



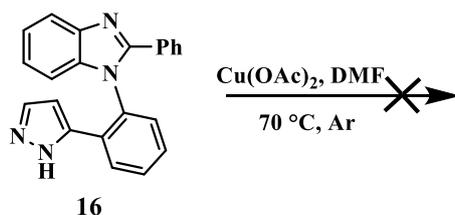
An oven dried 25 ml round-bottom flask was taken compound **2b** (1.0 equiv, 1.56 mmol), and DMF-

DMA (2.5 equiv, 3.90 mmol) in DMF solvent were added, and the reaction was stirred to reflux overnight. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was again treated with hydrazine hydrate (2.0 equiv, 3.12 mmol) in ethanol under reflux condition for 4 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **16a**.

An oven dried 25 ml round-bottom flask was taken compound **16a** (1.0 equiv, 1.23 mmol), compound **16b** (1.0 equiv, 1.23 mmol), and  $\text{K}_2\text{CO}_3$  (2.0 equiv, 2.46 mmol) in  $\text{CH}_3\text{CN}$  (5.0 ml) were added, and the reaction was stirred at reflux for 19 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the pale yellow sticky liquid with yield 45% of target compound **16**.

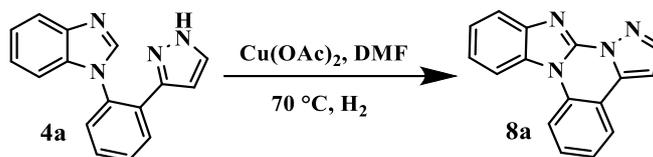
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (dt,  $J = 4.4, 2.5$  Hz, 3H), 7.82 (td,  $J = 7.7, 1.7$  Hz, 1H), 7.67 – 7.64 (m, 3H), 7.48 (t,  $J = 5.7$  Hz, 4H), 7.28 (d,  $J = 3.2$  Hz, 1H), 7.22 (dt,  $J = 6.5, 3.3$  Hz, 1H), 7.20 – 7.14 (m, 1H), 6.74 (dd,  $J = 5.0, 2.9$  Hz, 1H).

### 3.7. Intramolecular C-N coupling with 2-phenyl benzimidazole:



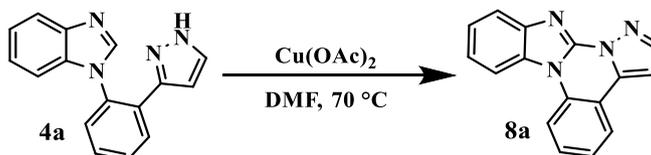
An oven dried schlenk tube was taken with compound **16** (1.0 equiv, 0.5 mmol), and  $\text{Cu}(\text{OAc})_2$  (20 mol%) in DMF solvent. The schlenk tube was flush with argon gas and maintain the inert argon atmosphere. The reaction mixture was stirred at 70  $^\circ\text{C}$  for 12 hours even then no cyclized product form.

### 3.8 Reaction in hydrogen atmosphere:



An oven dried schlenk tube was taken with compound **4a** (1.0 equiv, 0.5 mmol), and  $\text{Cu}(\text{OAc})_2$  (20 mol%) in DMF solvent. The schlenk tube was flush with hydrogen gas and maintain the hydrogen atmosphere. The reaction mixture was stirred at  $70\text{ }^\circ\text{C}$ . After 12 hours solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the target compound **8a** with 55% yield.

### 3.9 Headspace GC analysis:



An oven dried schlenk tube was filled with compound (**4a**) (5.0 mmol), and  $\text{Cu}(\text{OAc})_2$  (20 mol%) in dry DMF solvent. The schlenk tube was taken under vacuum to make the reaction moisture free atmosphere. The reaction mixture was stirred at  $70\text{ }^\circ\text{C}$  for 5 hours. After 5 hours, the gas was taken out with the help of gas trap syringe and injected to GC.

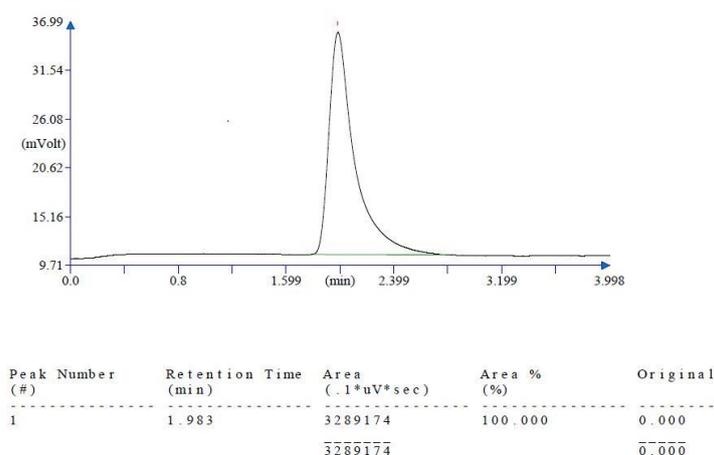
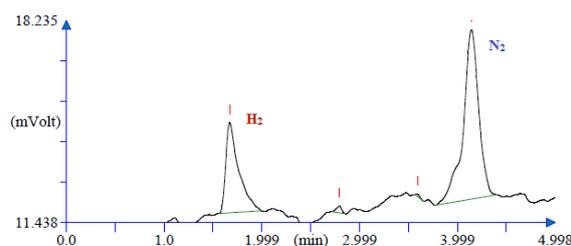


Figure S1. Hydrogen gas analysis by GC

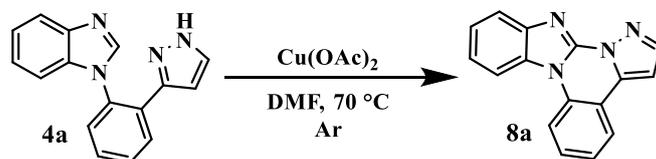


Peak Number (#)	Retention Time (min)	Area (.1* $\mu$ V*sec)	Area % (%)	Original
1	1.672	277882	30.444	0.000
2	4.142	634890	69.556	0.000
		912772		0.000

Figure S2. Reaction Headspace GC analysis

## 4. Gram Scale and Synthetic Versatility

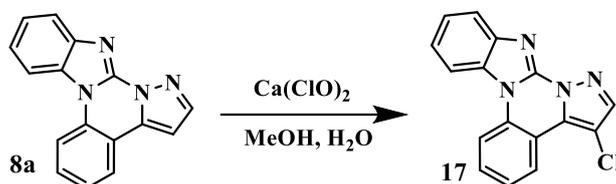
### 4.1 Gram Scale procedure for Synthesis of compound (8a):



An oven dried RB was filled with compound **4a** (3.84 mmol) (1.0 gm) and  $\text{Cu}(\text{OAc})_2$  (20 mol%) in dry DMF solvent. The RB was flush with argon gas and maintain the inert atmosphere. The reaction mixture was stirred at 70 °C for 14 hours until the substrate was completely consumed (reaction monitor by TLC). After full conversion of starting material cool the reaction mixture to room temperature. The reaction mixture allows to rotary evaporator to evaporate solvent and extracted with ethyl acetate. The organic layer was washed with water and brine solution. The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure then the crude product was purified by column chromatography over silica gel using a mixture of hexane/ ethyl acetate (4:1) as the eluent to afford cyclized product **8a** with 82% (813mg) yield.

## 4.2 Synthetic Versatility of compound (8a):

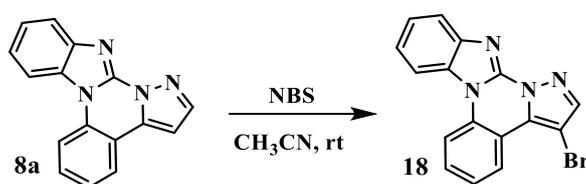
### 4.2.1 Synthetic procedure for 3-Chlorobenzo[4,5]imidazo[1,2-a]pyrazolo [1,5-c] quinazoline (17):



An oven dried 25 ml round-bottom flask was taken compound **8a** (1.0 equiv, 0.8 mmol), and  $\text{Ca}(\text{ClO})_2$  (1.0 equiv, 0.8 mmol), in methanol: water (1:1) (2.0 ml) were added, and the reaction was stirred at room temperature for 10 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid with 68% yield (mp: 200 °C) of target compound **17**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (dd,  $J = 8.0, 1.3$  Hz, 1H), 8.39 (d,  $J = 8.4$  Hz, 1H), 8.18 – 8.13 (m, 1H), 8.07 (s, 1H), 7.96 (dd,  $J = 7.2, 1.6$  Hz, 1H), 7.78 – 7.71 (m, 1H), 7.57 – 7.52 (m, 1H), 7.46 (ddd,  $J = 15.7, 7.6, 1.3$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.66, 142.48, 141.29, 132.06, 131.08, 130.87, 130.63, 125.29, 124.95, 124.73, 123.49, 120.85, 115.15, 114.81, 113.04, 107.49, 77.34, 77.03, 76.71. HRMS (ASAP/Q-TOF)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{16}\text{H}_{10}\text{N}_4\text{Cl}$  293.7260, found 293.0544.

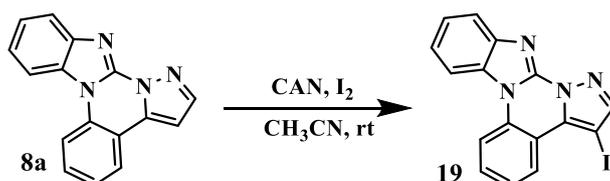
### 4.2.2 Synthetic procedure for 3-Bromobenzo[4,5]imidazo[1,2-a]pyrazolo [1,5-c] quinazoline (18):



An oven dried 25 ml round-bottom flask was taken compound **8a** (1.0 equiv, 0.8 mmol), and NBS (1.0 equiv, 0.8 mmol), in  $\text{CH}_3\text{CN}$  (2.0 ml) were added, and the reaction was stirred at room temperature for 12 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid with 64% yield (mp: 205 °C) of target compound **18**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (dd,  $J = 8.0, 1.3$  Hz, 1H), 8.39 (d,  $J = 8.4$  Hz, 1H), 8.18 – 8.13 (m, 1H), 8.07 (s, 1H), 7.96 (dd,  $J = 7.2, 1.6$  Hz, 1H), 7.78 – 7.71 (m, 1H), 7.57 – 7.52 (m, 1H), 7.46 (ddd,  $J = 15.7, 7.6, 1.3$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.66, 142.48, 141.29, 132.06, 131.08, 130.87, 130.63, 125.29, 124.95, 124.73, 123.49, 120.85, 115.15, 114.81, 113.04, 107.49, 77.34, 77.03, 76.71. HRMS (ASAP/Q-TOF)  $m/z$   $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{16}\text{H}_{10}\text{N}_4\text{Br}$  337.0011, found 337.9977.

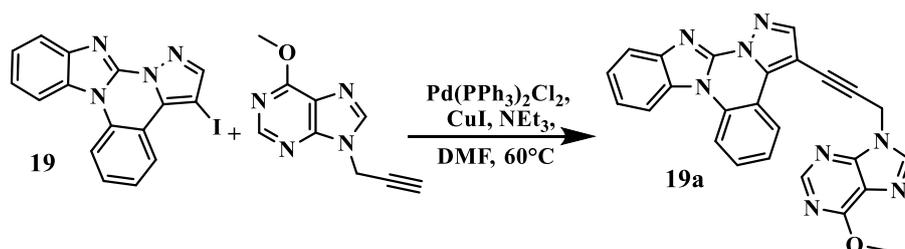
#### 4.2.3 Synthetic procedure for 3-Iodobenzo[4,5]imidazo[1,2-a]pyrazolo[1,5-c]quinazoline (**19**)<sup>4</sup>:



An oven dried 25 ml round-bottom flask was taken compound **8a** (1.0 equiv, 0.8 mmol), CAN (1.0 equiv, 0.8 mmol), and  $\text{I}_2$  (1.0 equiv, 0.8 mmol), in  $\text{CH}_3\text{CN}$  (2.0 ml) were added, and the reaction was stirred at room temperature for 8 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid with 72% yield (mp:  $>260$  °C) of target compound **19**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.19 (dd,  $J = 8.1, 1.3$  Hz, 1H), 8.45 (d,  $J = 8.3$  Hz, 1H), 8.24 – 8.17 (m, 1H), 8.15 (s, 1H), 8.02 – 7.95 (m, 1H), 7.85 – 7.76 (m, 1H), 7.62 – 7.55 (m, 1H), 7.55 – 7.44 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.84, 144.92, 130.94, 129.58, 124.92, 124.92, 124.86, 124.81, 123.95, 123.49, 123.49, 122.08, 120.89, 116.59, 115.33, 113.13, 77.34, 77.02, 76.70. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{16}\text{H}_9\text{N}_4\text{I}$  385.9872, found 384.9937.

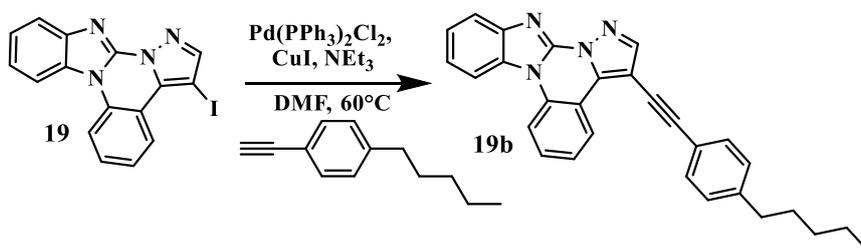
#### 4.2.4 Synthetic procedure for 3-(3-(6-methoxy-9H-purin-9-yl) prop-1-yn-1-yl) benzo [4,5] imidazo[1,2-a] pyrazolo[1,5-c] quinazoline (**19a**):



An oven dried 25 ml round-bottom flask was taken compound **19** (1.0 equiv, 0.8 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%), CuI (10 mol%), phenyl acetylene (1.0 equiv, xmmol) and NEt<sub>3</sub> (2.5 equiv, 2.0 mmol), in DMF (2.0 ml) were added, and the reaction was stirred at 60 °C for 10 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid with 48% yield (mp: 197 °C) of target compound **19a**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.77 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.66 (s, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 8.26 (s, 1H), 8.20 (d, *J* = 6.7 Hz, 2H), 8.03 – 7.96 (m, 1H), 7.82 – 7.74 (m, 1H), 7.54 – 7.45 (m, 3H), 5.45 (s, 2H), 4.23 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.31, 152.55, 152.24, 151.69, 147.32, 142.45, 141.95, 141.37, 141.21, 137.03, 132.31, 131.33, 130.85, 125.41, 124.89, 123.66, 120.95, 115.23, 114.99, 113.09, 98.22, 96.13, 87.41, 77.34, 77.02, 76.70, 54.41, 29.70. HRMS (ESI-ORBITRAP) *m/z* [M + H]<sup>+</sup> calculated for C<sub>25</sub>H<sub>16</sub>N<sub>8</sub>O 445.1447, found 445.2563.

#### 4.2.5 Synthetic procedure for 3-((4-Pentylphenyl) ethynyl) benzo [4,5] imidazo [1,2-a] pyrazolo [1, 5-c] quinazoline (**19b**):

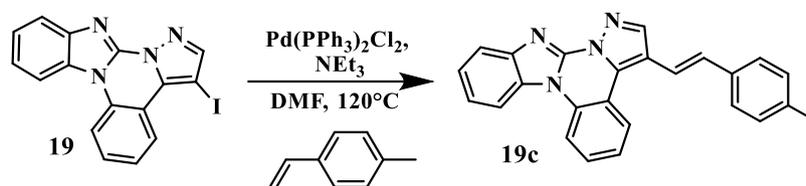


An oven dried 25 ml round-bottom flask was taken compound **19** (1.0 equiv, 0.8 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%), CuI (10 mol%), phenyl acetylene (1.0 equiv, 0.8 mmol) and NEt<sub>3</sub> (2.5 equiv, 2.0 mmol), in DMF (2.0 ml) were added, and the reaction was stirred at 60 °C for 10 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid 61% yield (mp: 215 °C) of target compound **19b**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.04 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.26 (s, 1H), 8.24 – 8.19 (m, 1H), 8.03 – 7.97 (m, 1H), 7.82 – 7.75 (m, 1H), 7.57 (dd, *J* = 10.8, 8.2 Hz, 3H), 7.54 – 7.45 (m, 2H), 7.24 (s, 2H), 2.72 – 2.63 (m, 2H), 1.67 (dd, *J* = 15.0, 7.6 Hz, 2H), 1.36 (dd, *J* = 7.2, 3.8 Hz, 4H), 0.92 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.15, 144.14, 142.59, 141.53, 135.94, 132.25, 131.44, 130.95, 130.83, 128.73, 125.58, 125.43, 124.73, 123.45, 120.84, 119.99, 115.65,

115.11, 113.06, 100.41, 95.68, 79.59, 77.34, 77.02, 76.70, 35.95, 31.46, 30.98, 22.54, 14.03. HRMS (ESI-ORBITRAP)  $m/z$   $[M + H]^+$  calculated for  $C_{29}H_{24}N_4$  429.5390, found 429.2064.

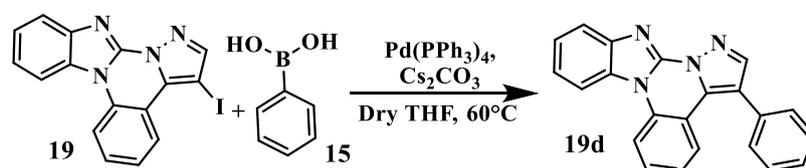
#### 4.2.6 Synthetic procedure for (E)-3-(4-Methylstyryl) benzo [4,5] imidazo[1,2-a] pyrazolo[1,5-c] quinazoline (19c):



An oven dried 25 ml round-bottom flask was taken compound **19** (1.0 equiv, 0.8 mmol),  $Pd(PPh_3)_2Cl_2$  (10 mol%),  $NEt_3$  (2.0 equiv, 1.6 mmol), and phenyl styrene (1.0 equiv, 0.8 mmol) in DMF (2.0 ml) were added, and the reaction was stirred at 120 °C for 12 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $Na_2SO_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid with 58% yield (mp: 210 °C) of target compound **19c**.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.42 (d,  $J = 8.3$  Hz, 1H), 8.36 – 8.29 (m, 2H), 8.18 (d,  $J = 7.8$  Hz, 1H), 7.99 – 7.95 (m, 1H), 7.75 – 7.68 (m, 1H), 7.53 (dd,  $J = 9.0, 5.6$  Hz, 1H), 7.50 – 7.40 (m, 5H), 7.24 (d,  $J = 8.0$  Hz, 2H), 7.13 (d,  $J = 16.1$  Hz, 1H), 2.40 (d,  $J = 5.1$  Hz, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  143.24, 142.08, 138.17, 136.90, 132.28, 129.85, 129.59, 128.40, 126.45, 125.44, 125.34, 124.54, 123.14, 121.07, 120.66, 119.57, 118.09, 118.01, 116.54, 116.38, 115.44, 112.98, 77.34, 77.02, 76.70, 21.34. HRMS (ASAP/Q-TOF)  $m/z$   $[M + H]^+$  calculated for  $C_{25}H_{19}N_4$  375.4470, found 375.1531.

#### 4.2.7 Synthetic procedure for 3-phenylbenzo [4,5] imidazo[1,2-a] pyrazolo[1,5-c] quinazoline (19d):

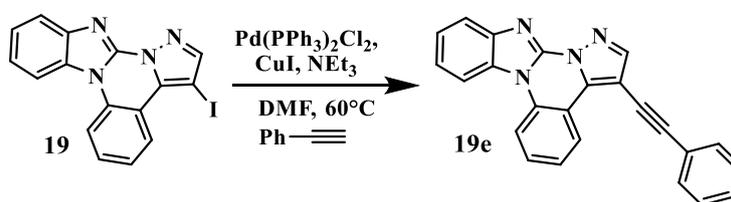


An oven dried 25 ml round-bottom flask was taken compound **19** (1.0 equiv, 0.8 mmol),  $Pd(PPh_3)_4$  (0.05 mol%),  $Cs_2CO_3$  (2.0 equiv, 1.6 mmol), and phenyl boronic acid (1.2 equiv, 0.96 mmol) in dry THF (2.0 ml) were added, and the reaction was stirred at 60 °C for 8 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $Na_2SO_4$ , and

removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid with 55% yield (mp: 245°C) of target compound **19d**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (d,  $J = 8.4$  Hz, 1H), 8.19 (d,  $J = 7.6$  Hz, 1H), 8.08 (s, 1H), 8.03 (dd,  $J = 8.1, 1.3$  Hz, 1H), 7.99 (dd,  $J = 7.9, 1.0$  Hz, 1H), 7.69 – 7.64 (m, 1H), 7.60 – 7.54 (m, 4H), 7.49 (dddd,  $J = 14.1, 12.4, 5.3, 3.7$  Hz, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.48, 142.80, 142.05, 132.24, 132.10, 130.98, 130.10, 129.75, 129.10, 128.30, 124.91, 124.89, 124.54, 123.17, 120.71, 120.21, 115.91, 115.36, 113.01, 77.34, 77.03, 76.71. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{22}\text{H}_{14}\text{N}_4$  335.1218, found 335.1283.

#### 4.2.8 Synthetic procedure for 3-(phenylethynyl) indolo[1,2-a] pyrazolo [1,5-c] quinazoline (**19e**):



An oven dried 25 ml round-bottom flask was taken compound **19** (1.0 equiv, 0.8 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (10 mol%),  $\text{CuI}$  (10 mol%), phenyl acetylene (1.0 equiv, 0.8 mmol) and  $\text{NEt}_3$  (2.5 equiv, 2.0 mmol), in DMF (2.0 ml) were added, and the reaction was stirred at 60 °C for 10 hours. Upon the completion of the reaction (confirm by TLC), the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under the reduced pressure. The crude was purified with silica gel column chromatography to afford the white solid with 68% yield (mp: 250 °C) of target compound **19e**.

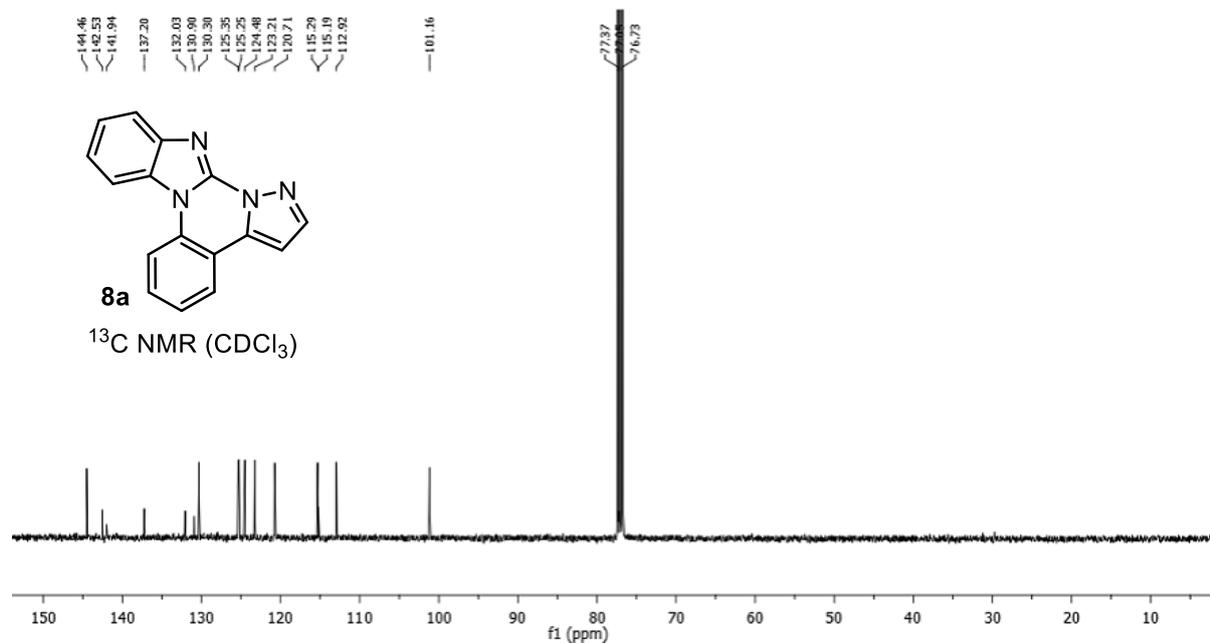
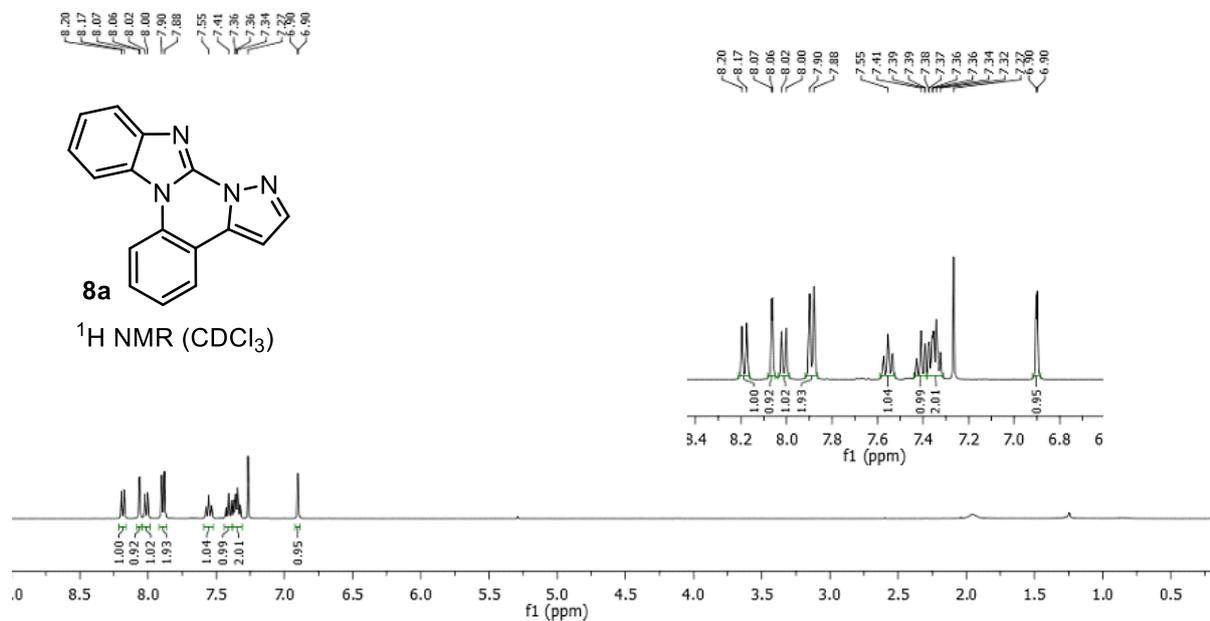
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.02 (dd,  $J = 8.0, 1.3$  Hz, 1H), 8.44 (d,  $J = 8.4$  Hz, 1H), 8.27 (s, 1H), 8.22 – 8.19 (m, 1H), 8.01 – 7.97 (m, 1H), 7.80 – 7.75 (m, 1H), 7.64 (dd,  $J = 7.4, 2.2$  Hz, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.50 (td,  $J = 7.2, 1.4$  Hz, 2H), 7.46 – 7.41 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.13, 142.57, 141.45, 136.04, 132.26, 131.49, 130.92, 130.87, 128.78, 128.60, 125.53, 125.40, 124.73, 123.46, 122.88, 120.85, 115.54, 115.10, 113.04, 100.15, 95.41, 80.30, 77.33, 77.01, 76.70. HRMS (ESI-ORBITRAP)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{24}\text{H}_{14}\text{N}_4$  359.1218, found 359.1286.

## 5. References

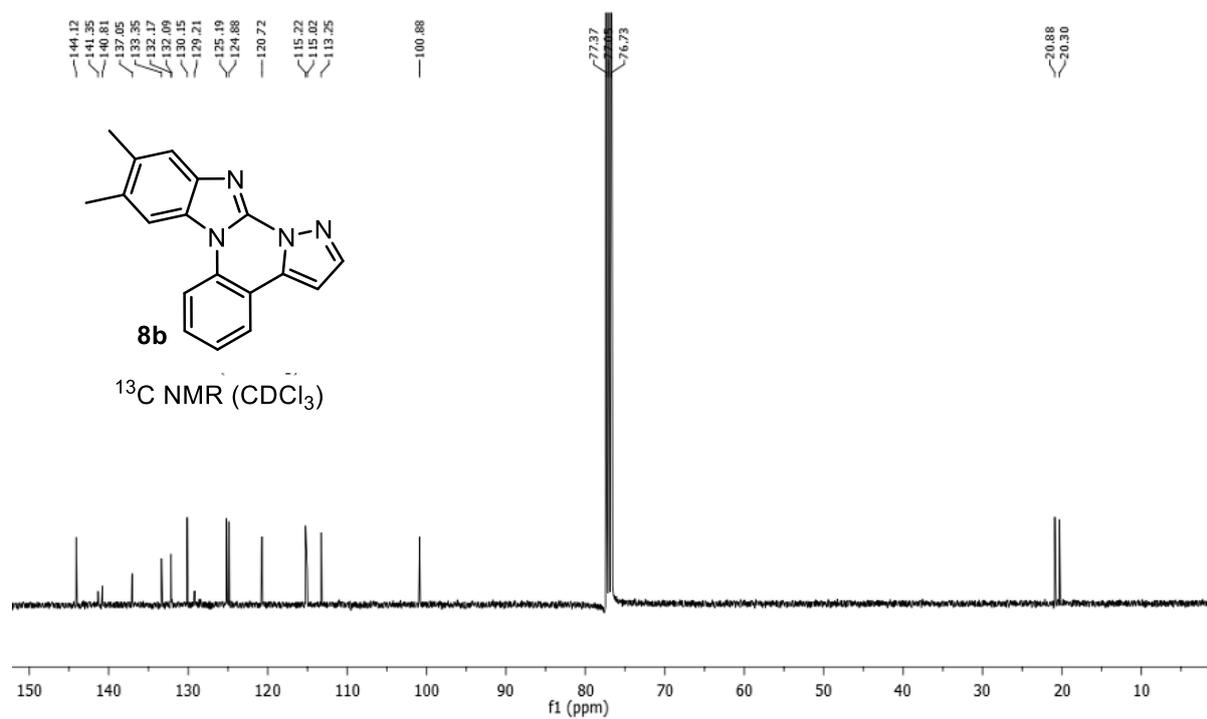
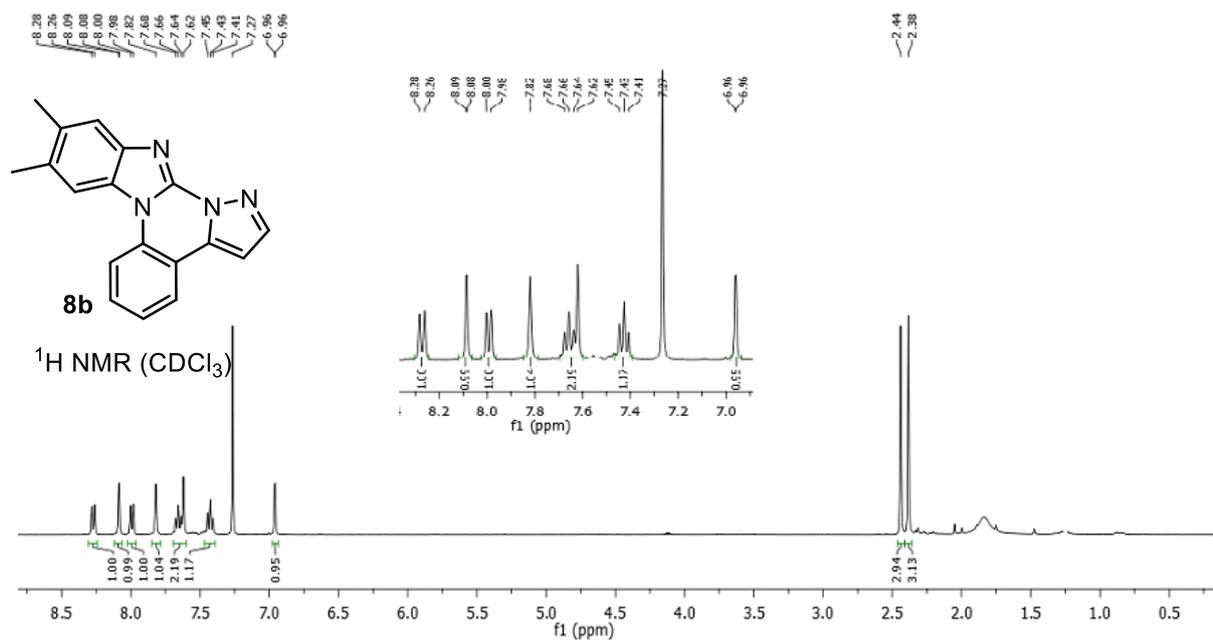
1. S. Sahoo, S. Pal, *J. Org. Chem.*, 2021, **86**, 4081–4097.
2. K. L. Yu, R. L. Civiello, K. D. Combrink, H. B. Gulgeze, N. Sin, X. Wang, N. Meanwell, B. L. Venables, Y. Zhang, B. C. Pearce, Z. Yin, J. W. Thuring, United States Patent Application Publication US 2002/0099208 A1, 2002, **09**, 994,012.
3. Y. Mu, Y. Yuan, Y. Wang, M. Xu, Y. Feng, Y. Zhao, Y. Li, *Org. Biomol. Chem.*, 2020, **18**, 6916.
4. M. I. R. Franco, I. Dorronsoro, A. I. H. Higuera, G. Antequera, *Tetrahedron Lett.*, 2001, **42**, 863–865.

## 6. Copy of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

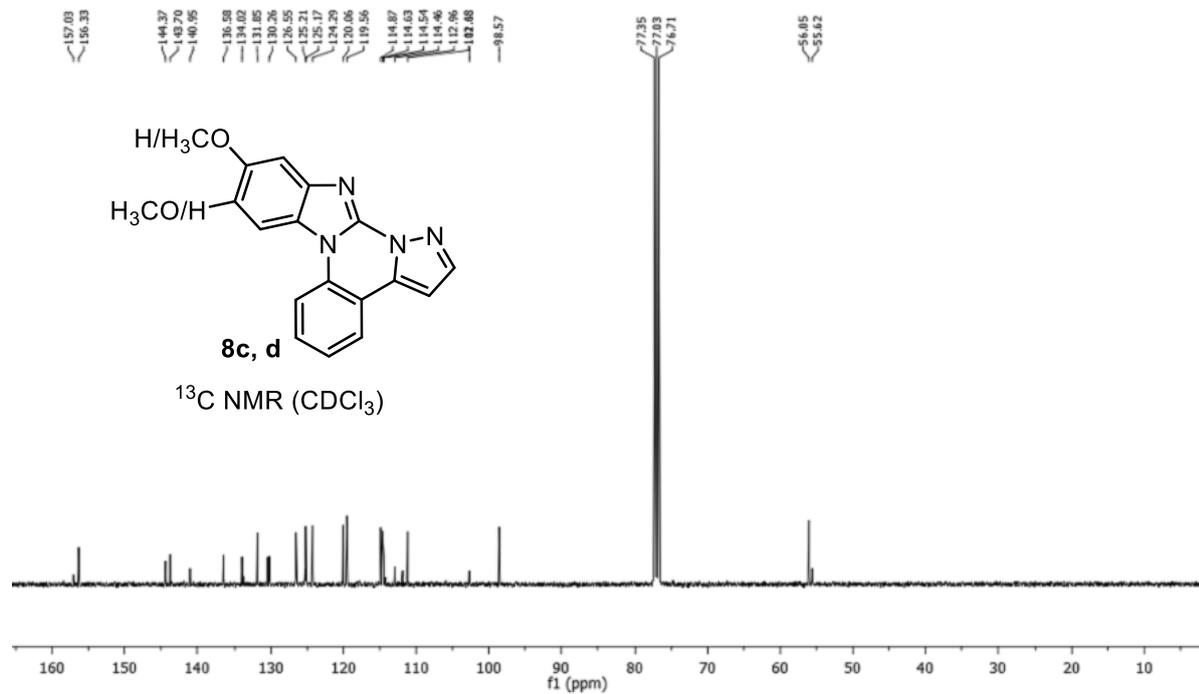
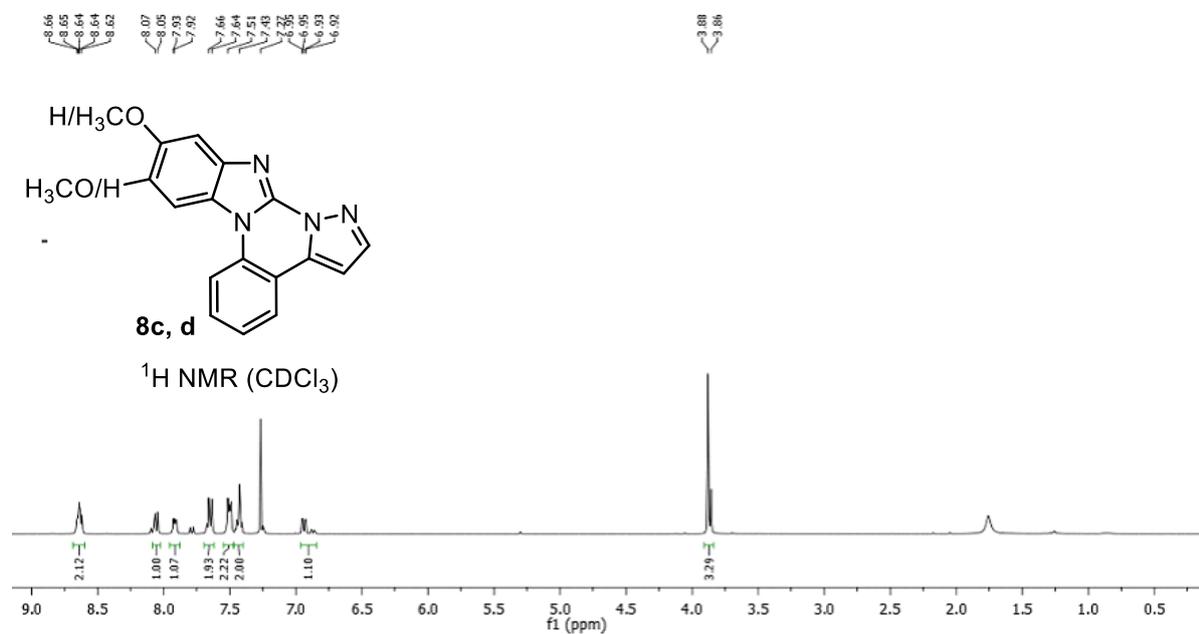
### 6.1 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 8a:



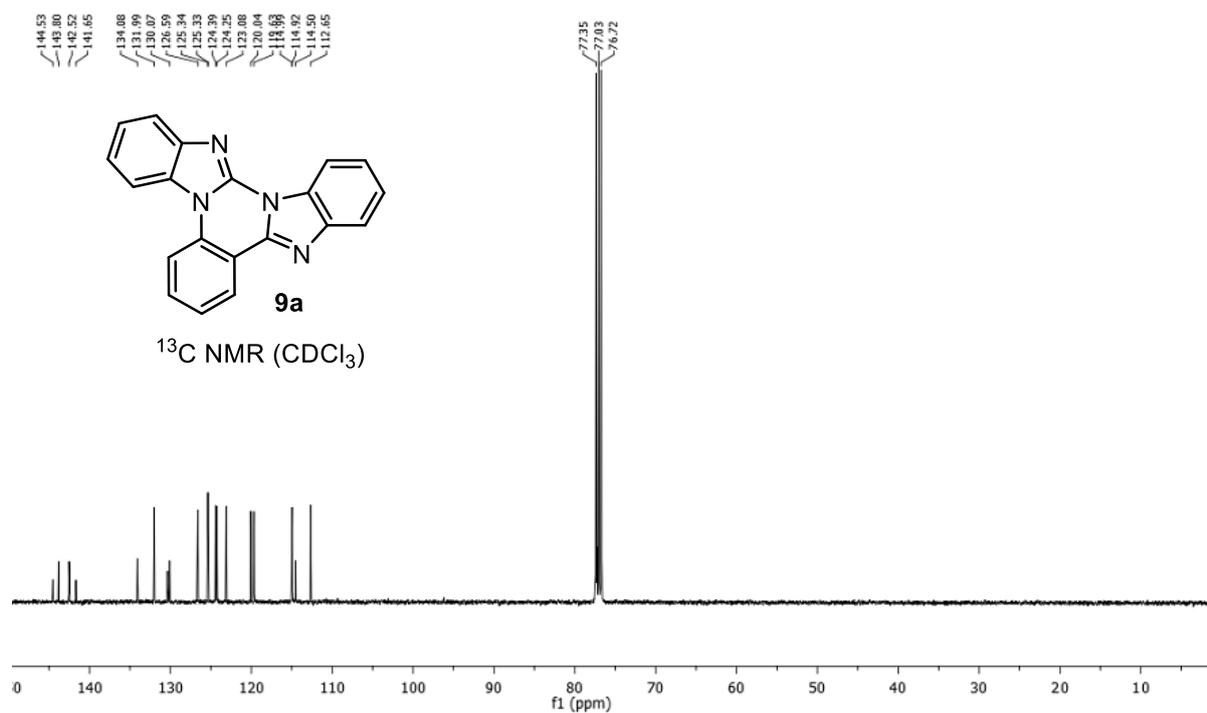
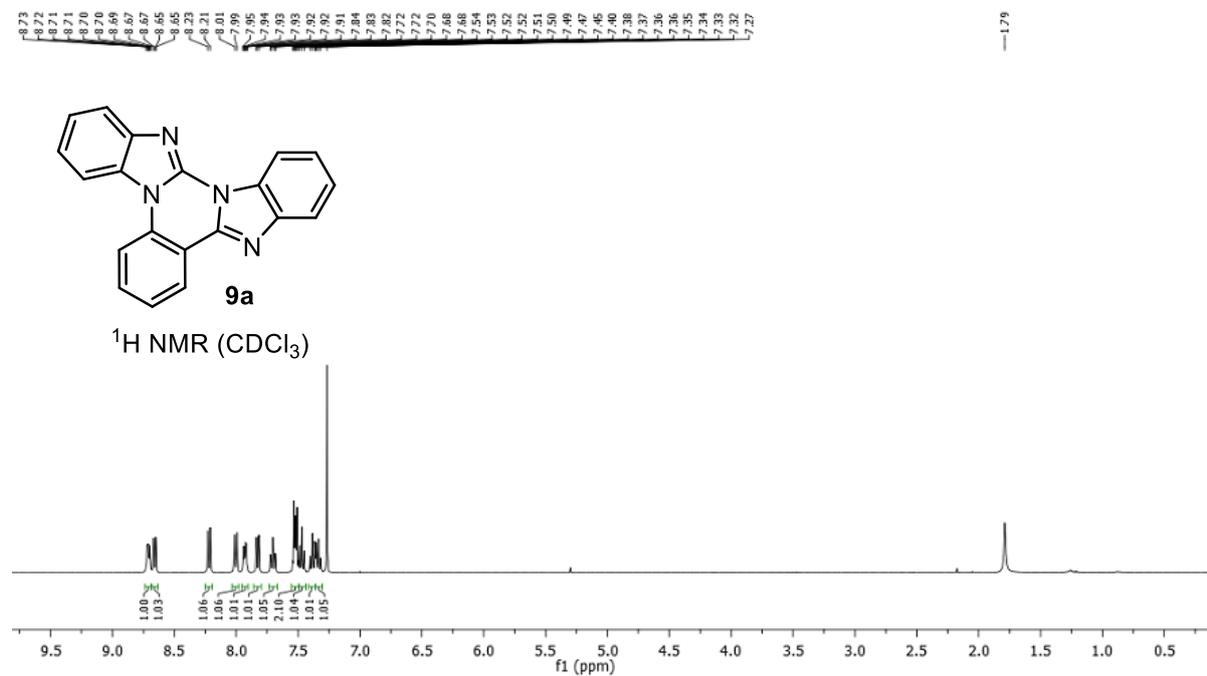
## 6.2 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 8b:



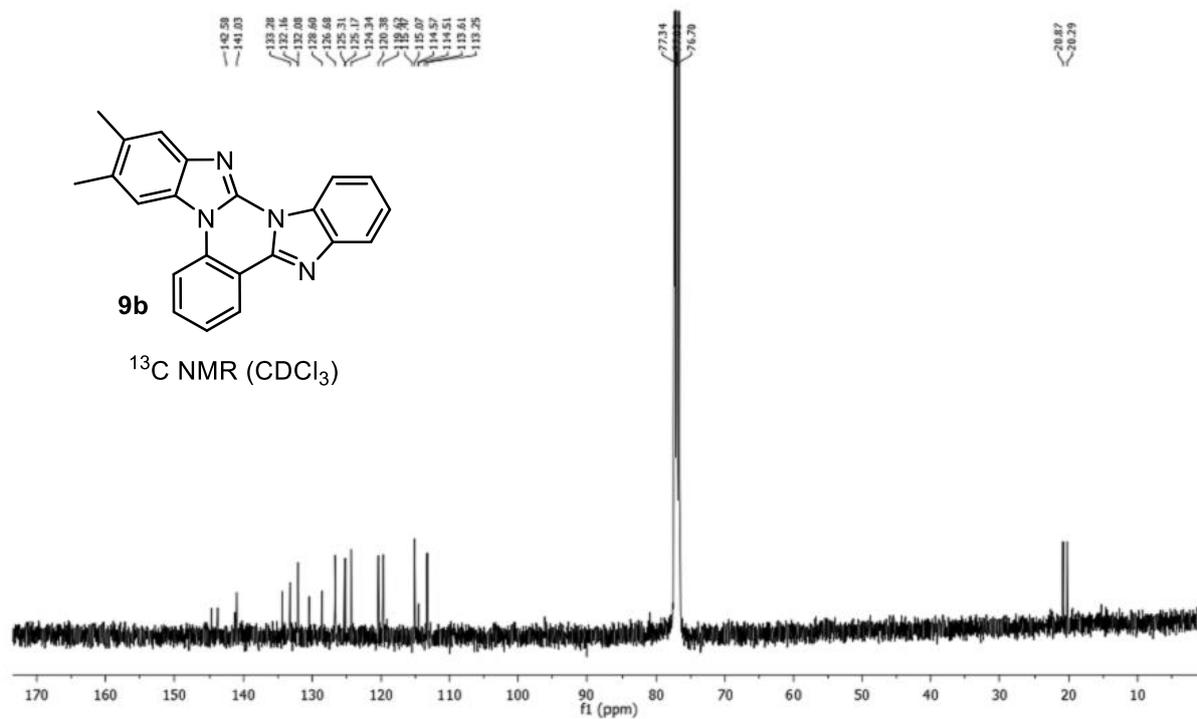
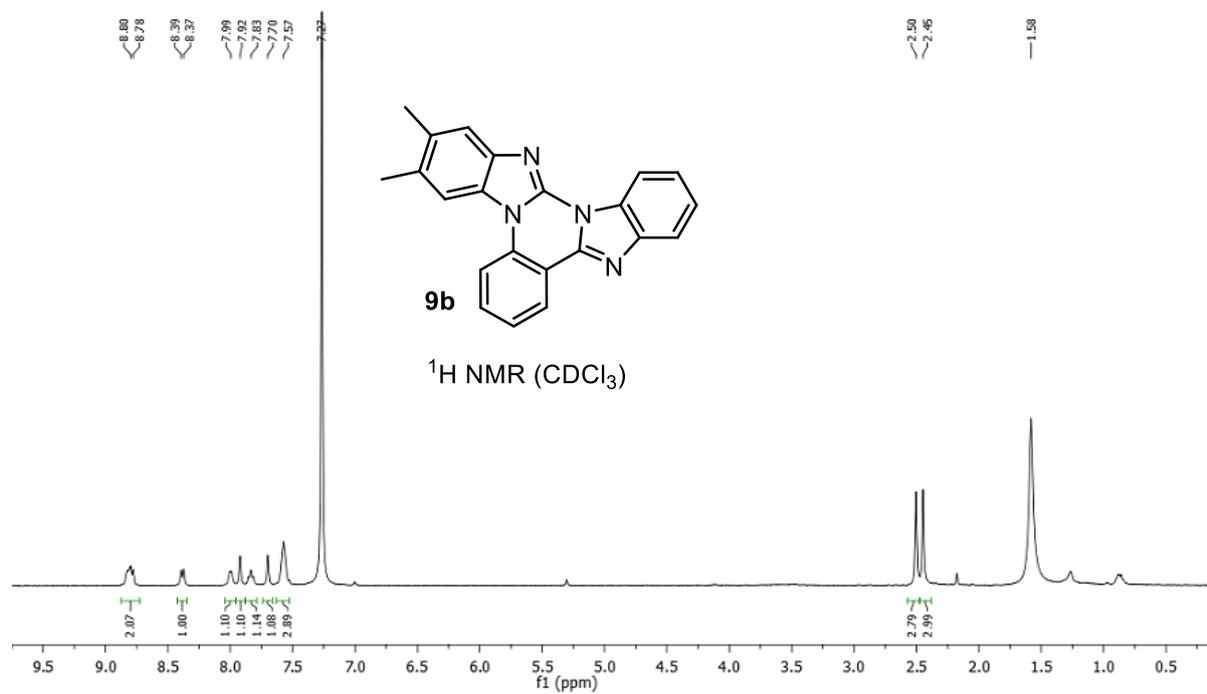
### 6.3 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 8c-d:



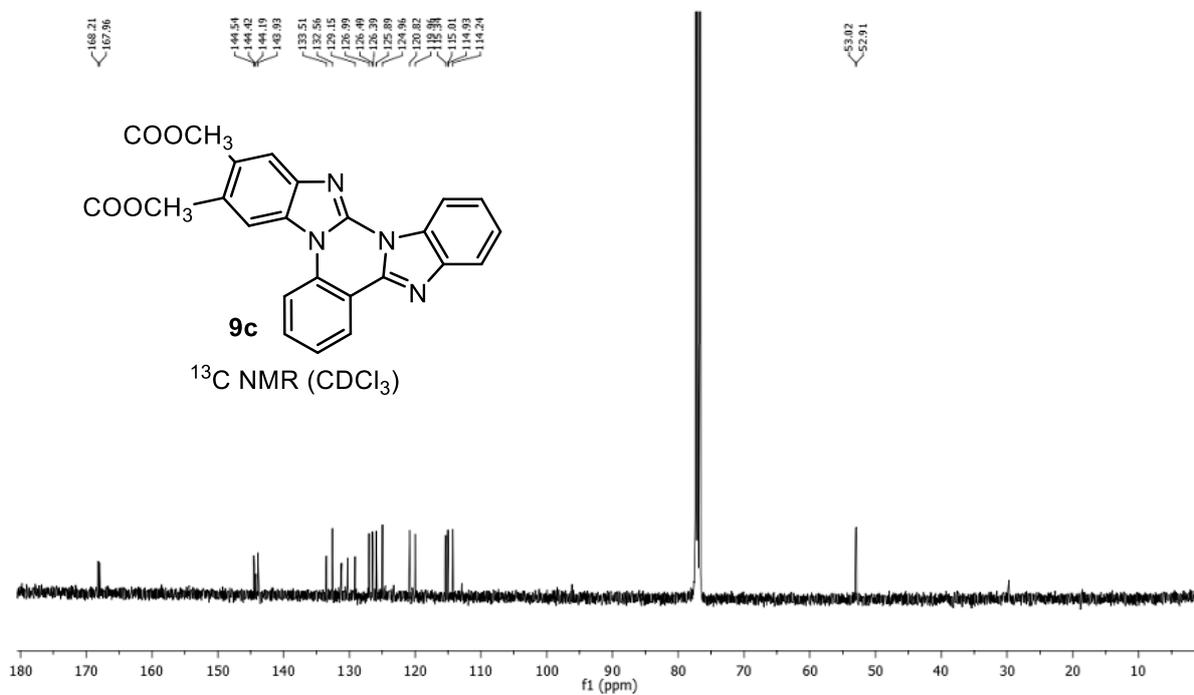
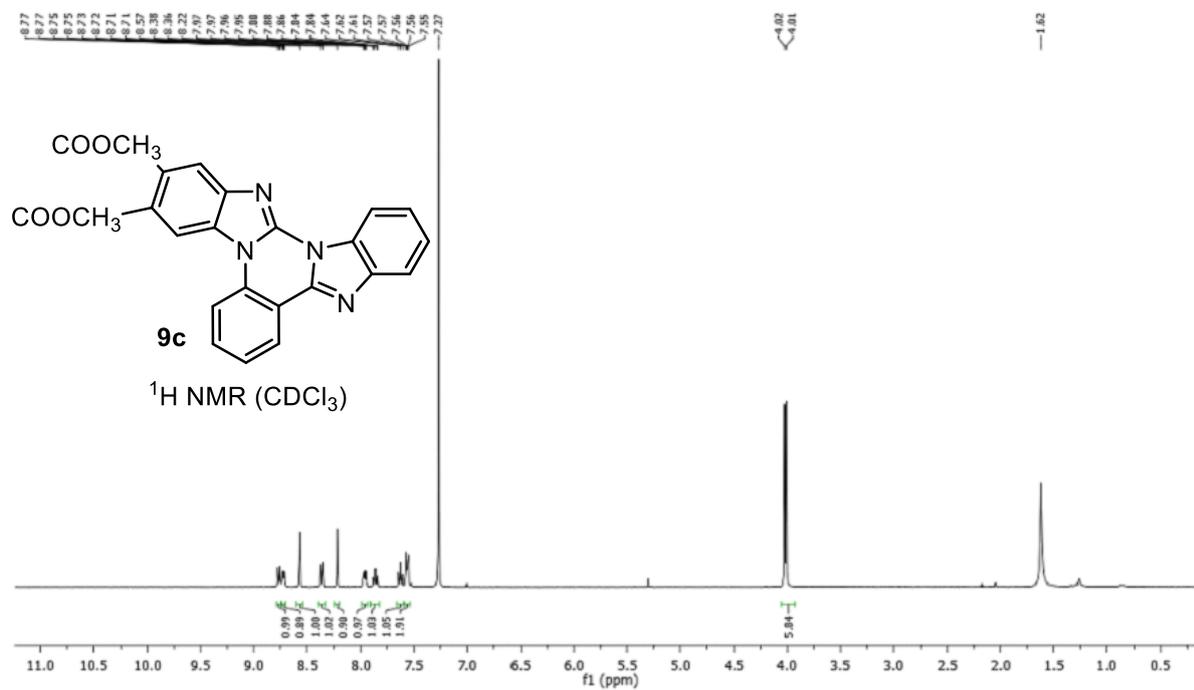
## 6.4 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 9a:



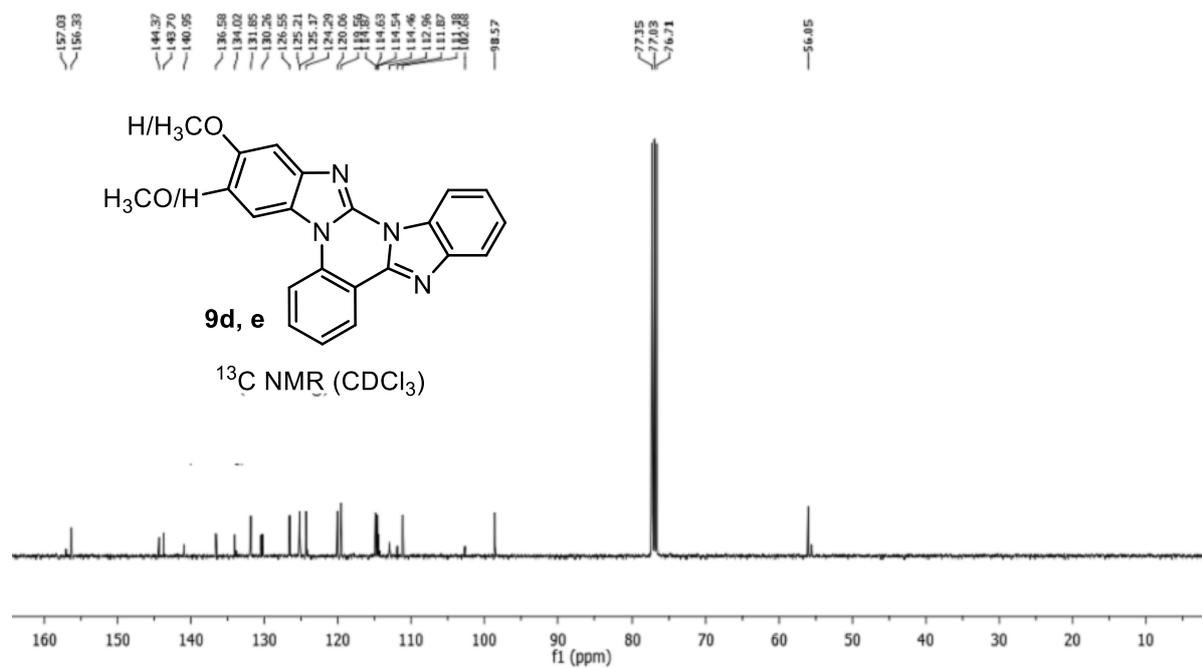
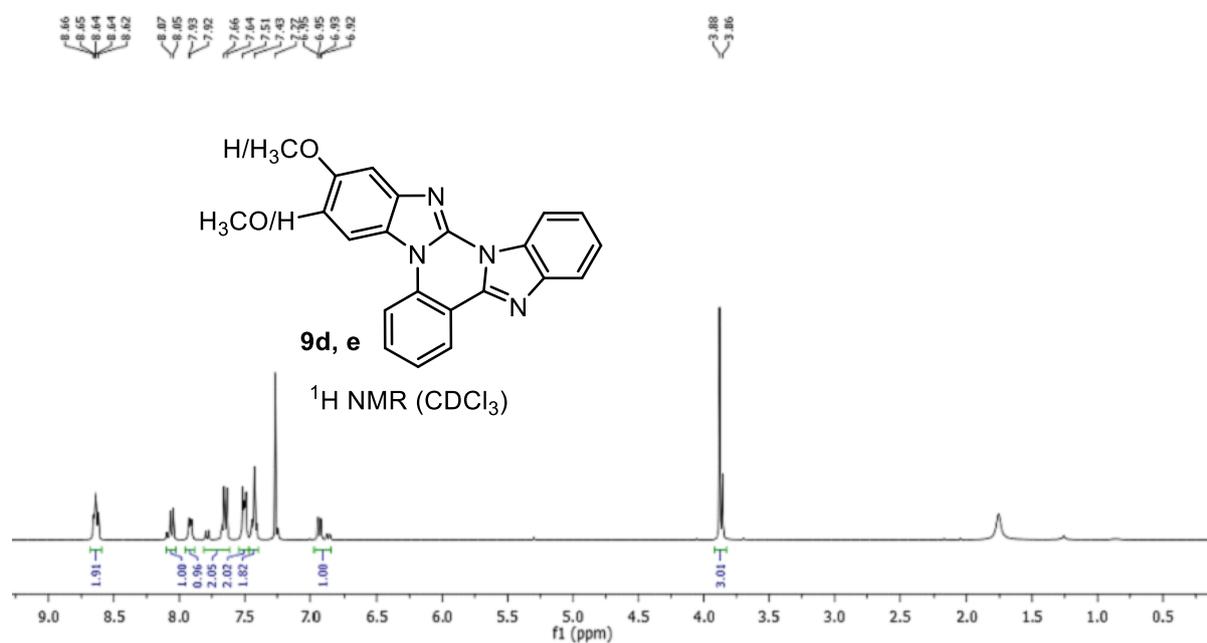
## 6.5 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 9b:



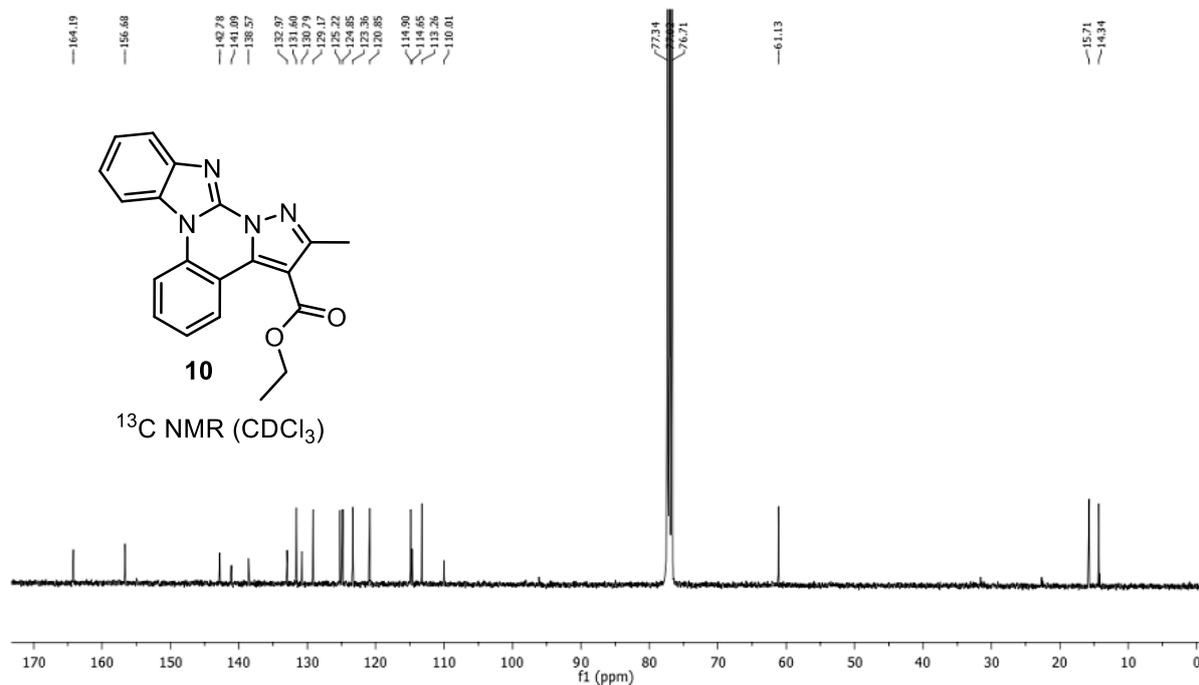
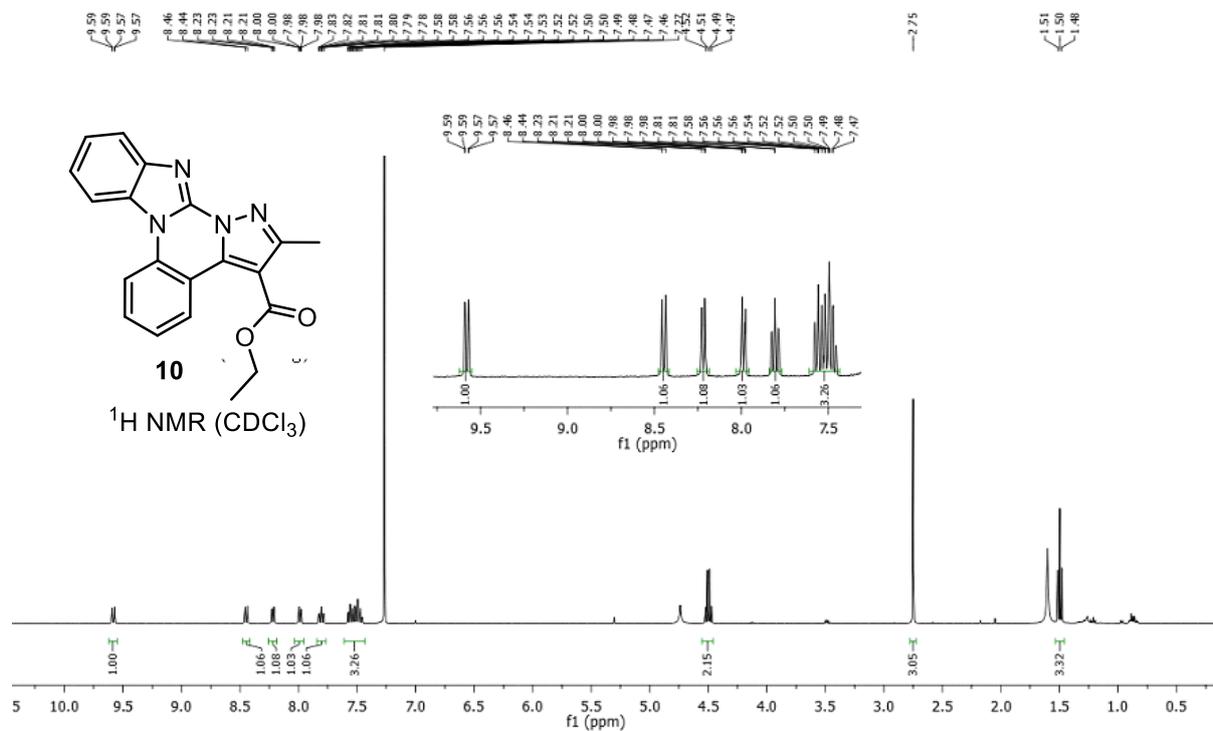
## 6.6 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 9c:



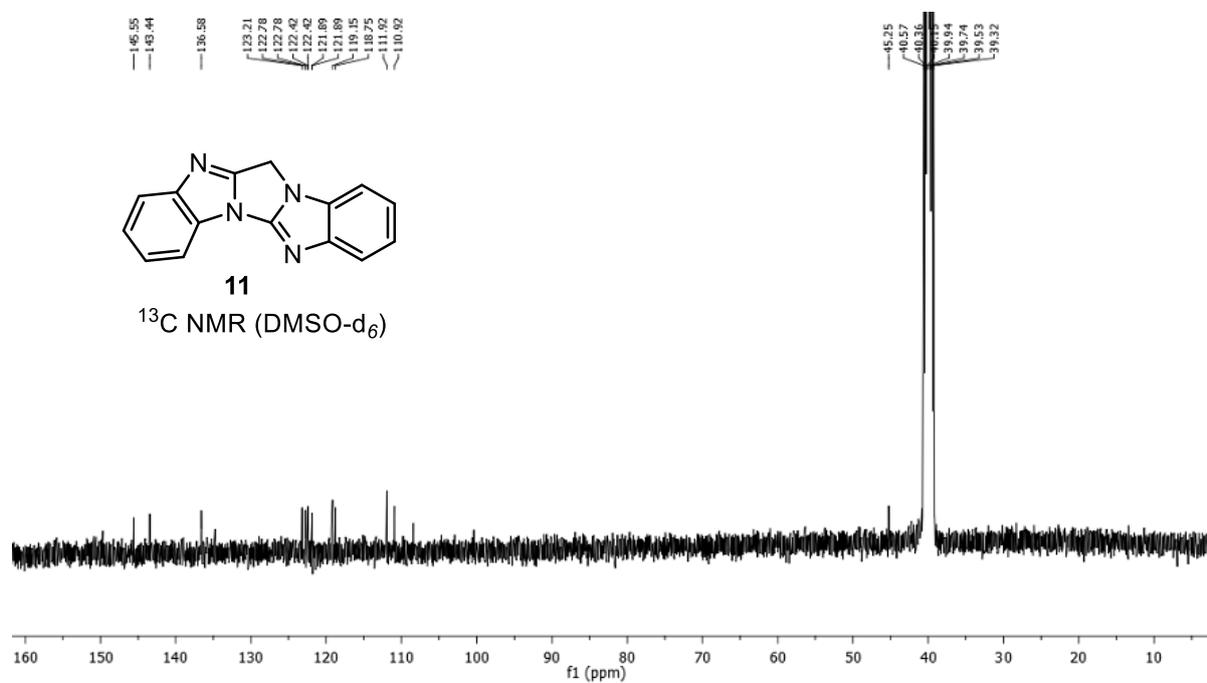
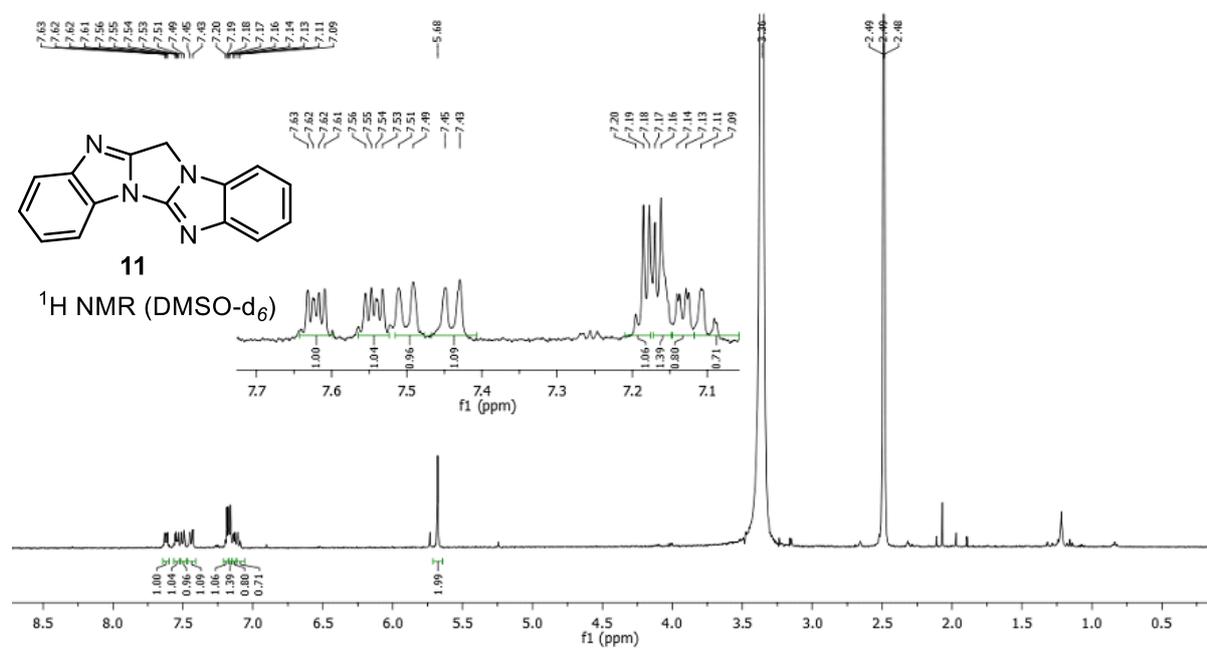
## 6.7 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 9d-e:



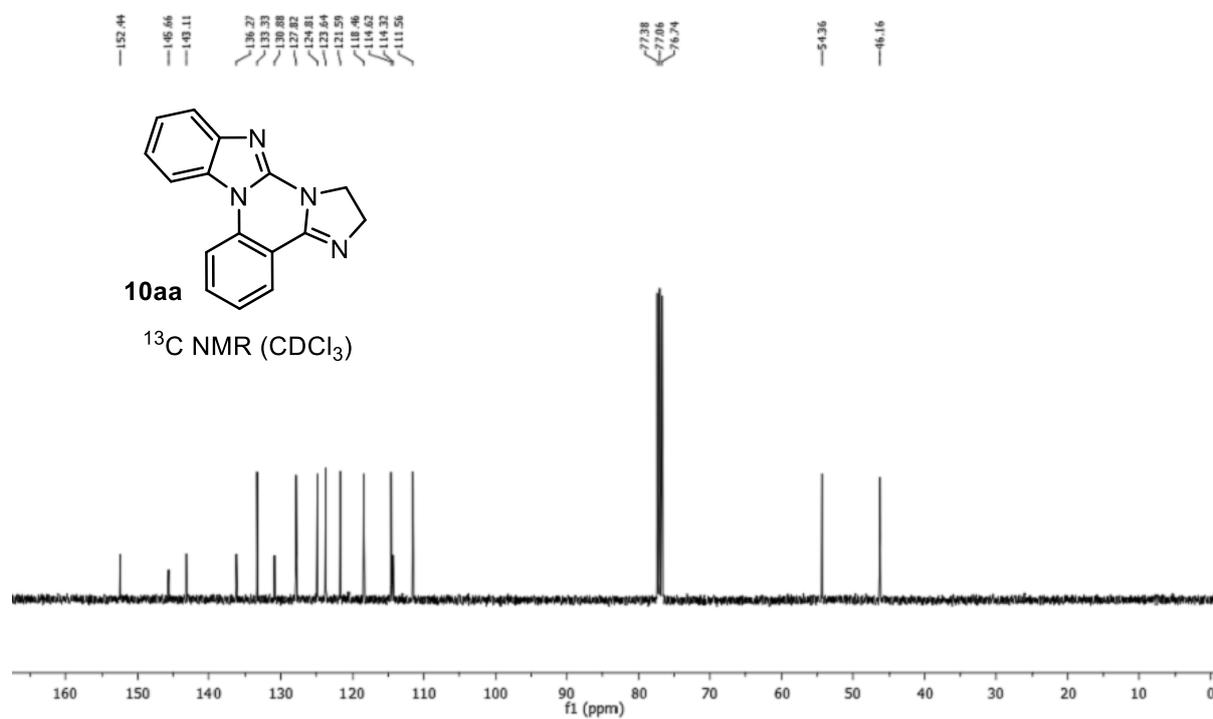
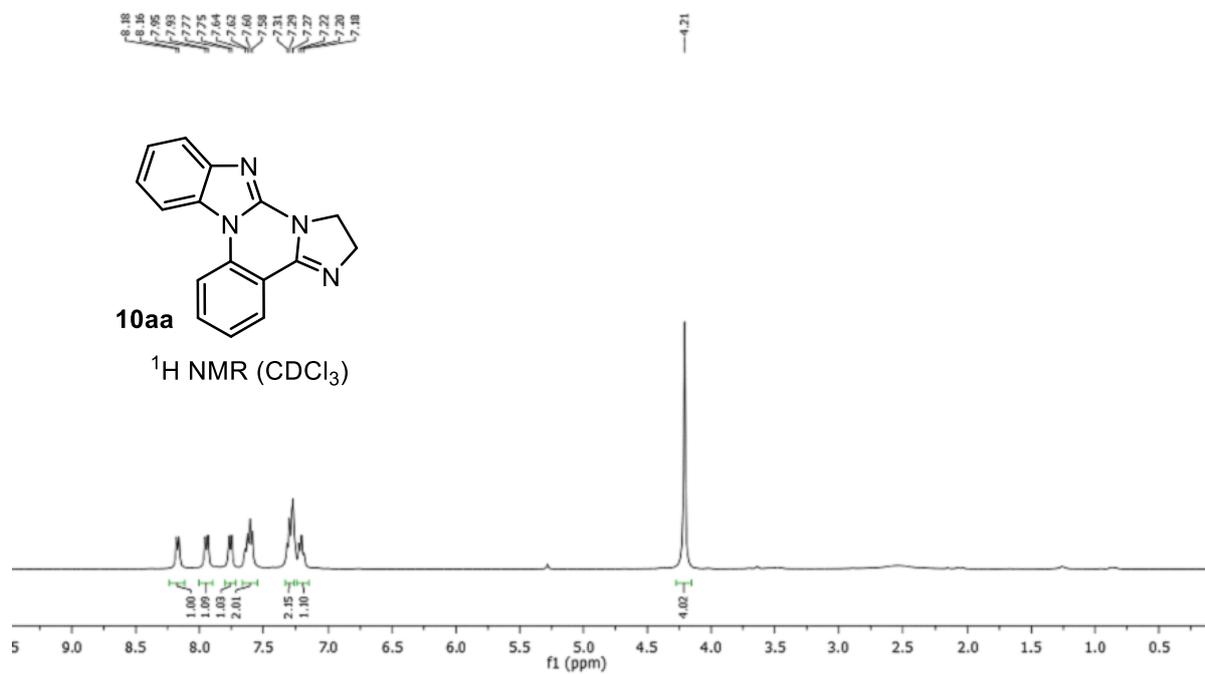
## 6.8 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 10:



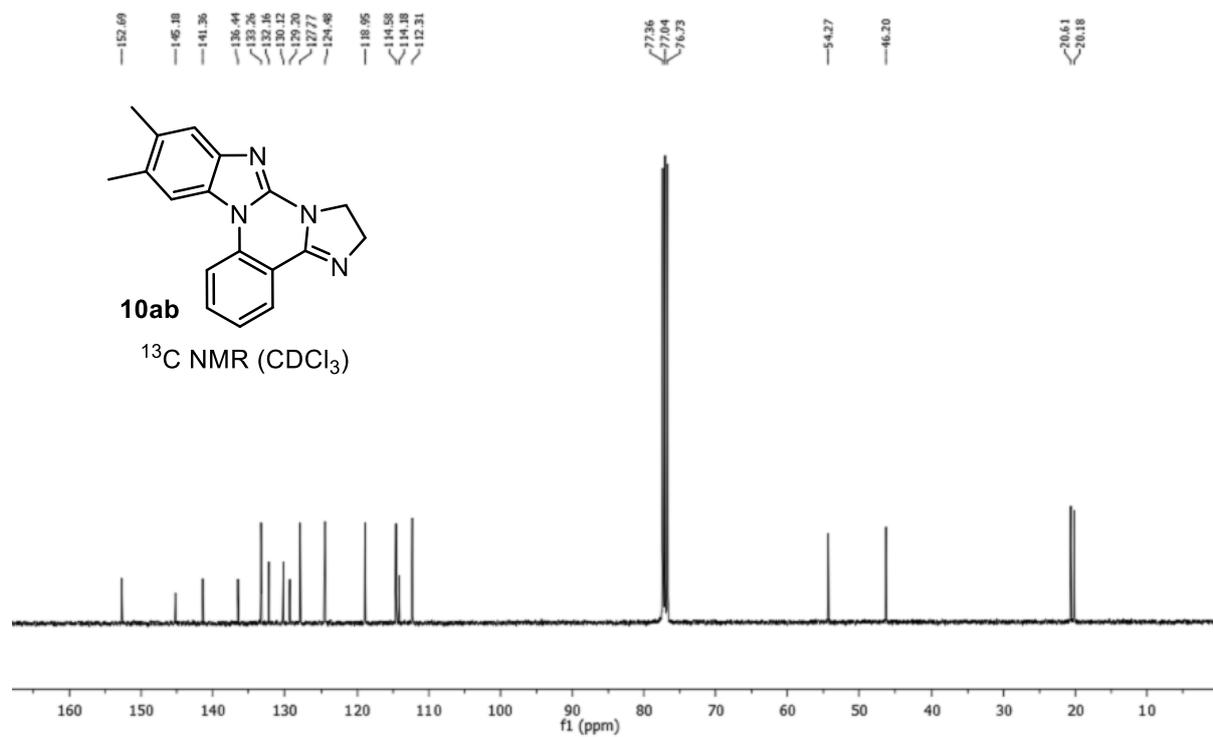
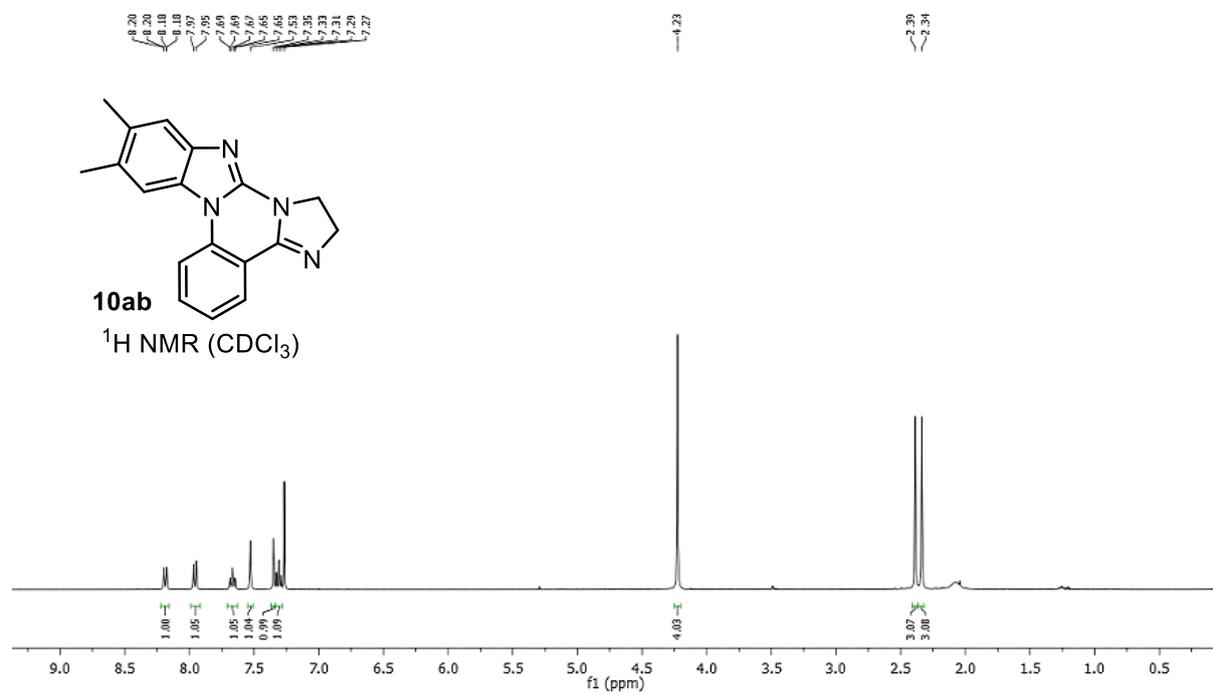
## 6.9 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 11:



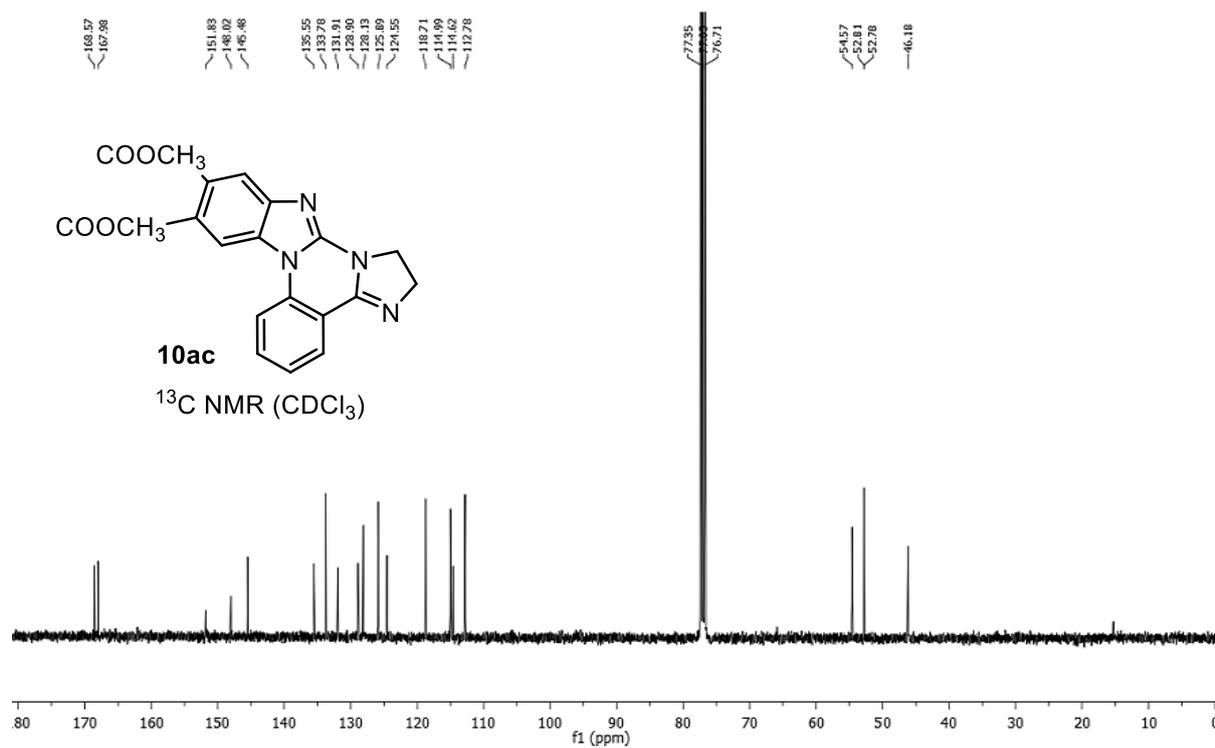
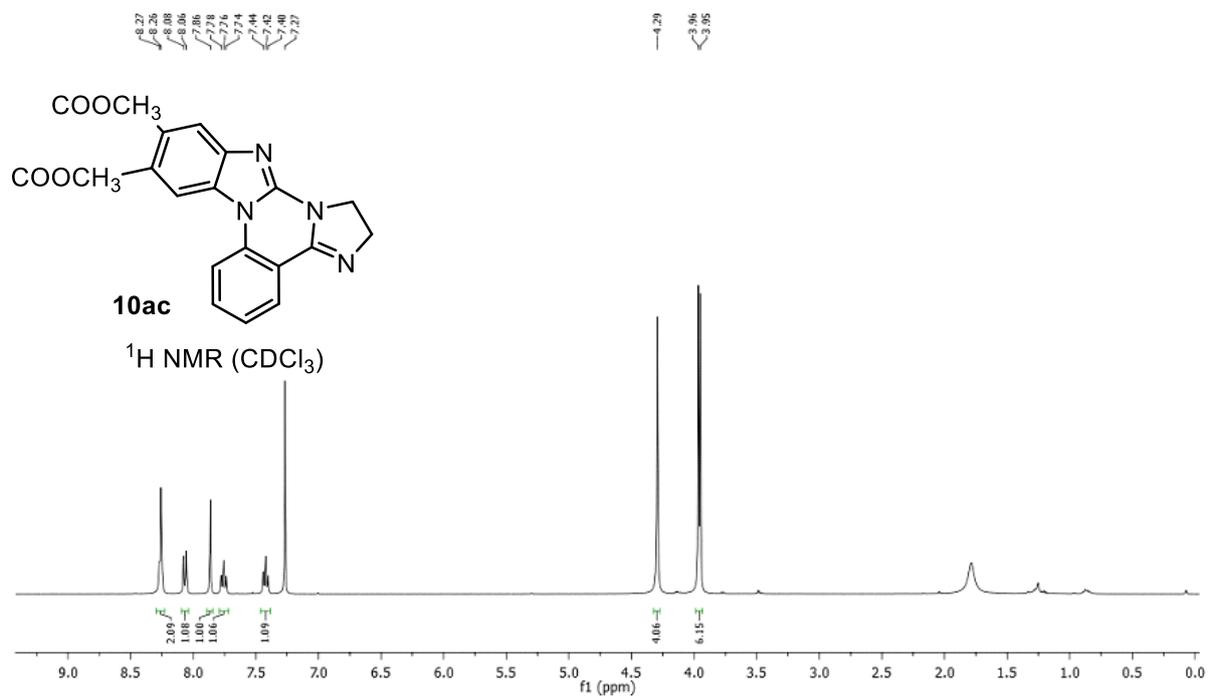
## 6.10 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 10aa:



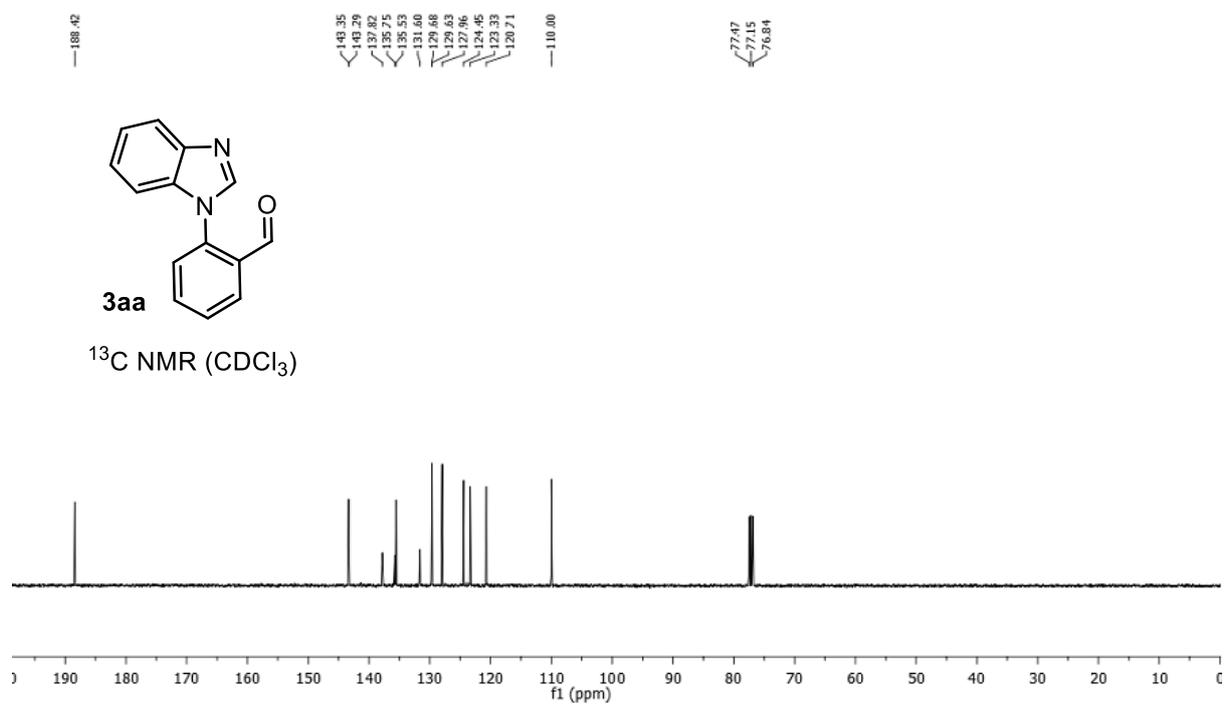
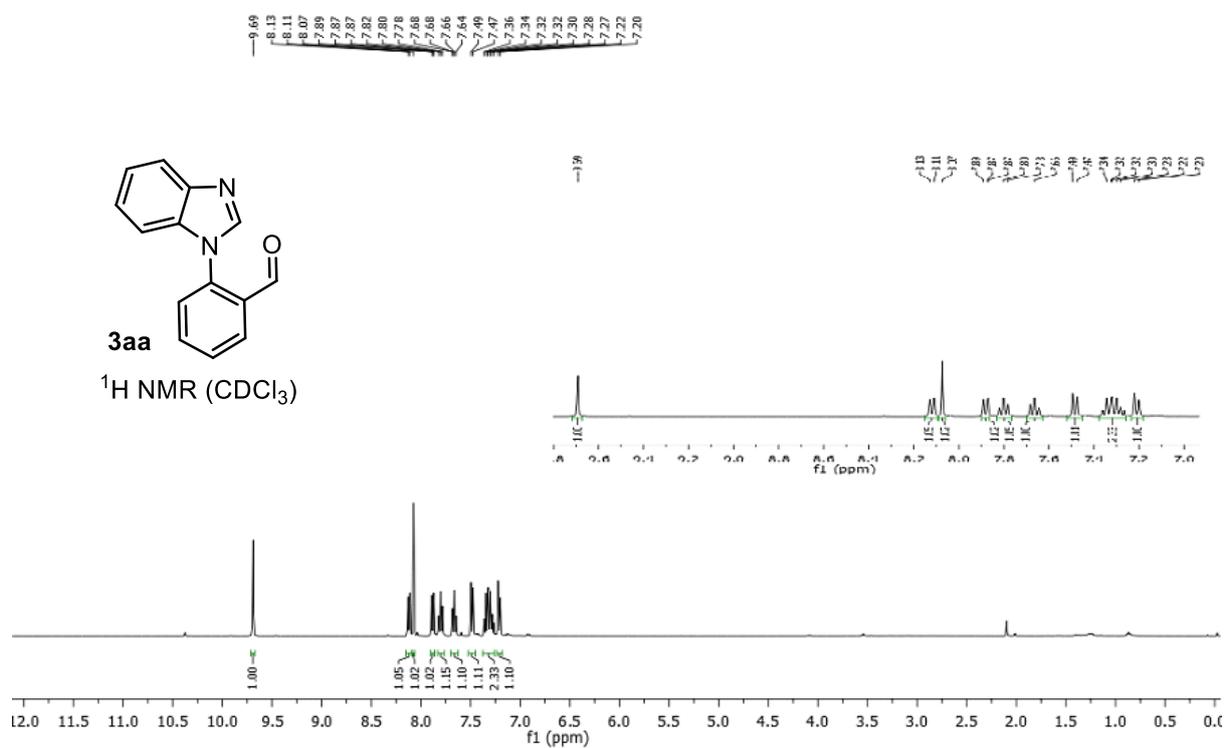
## 6.11 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 10ab:



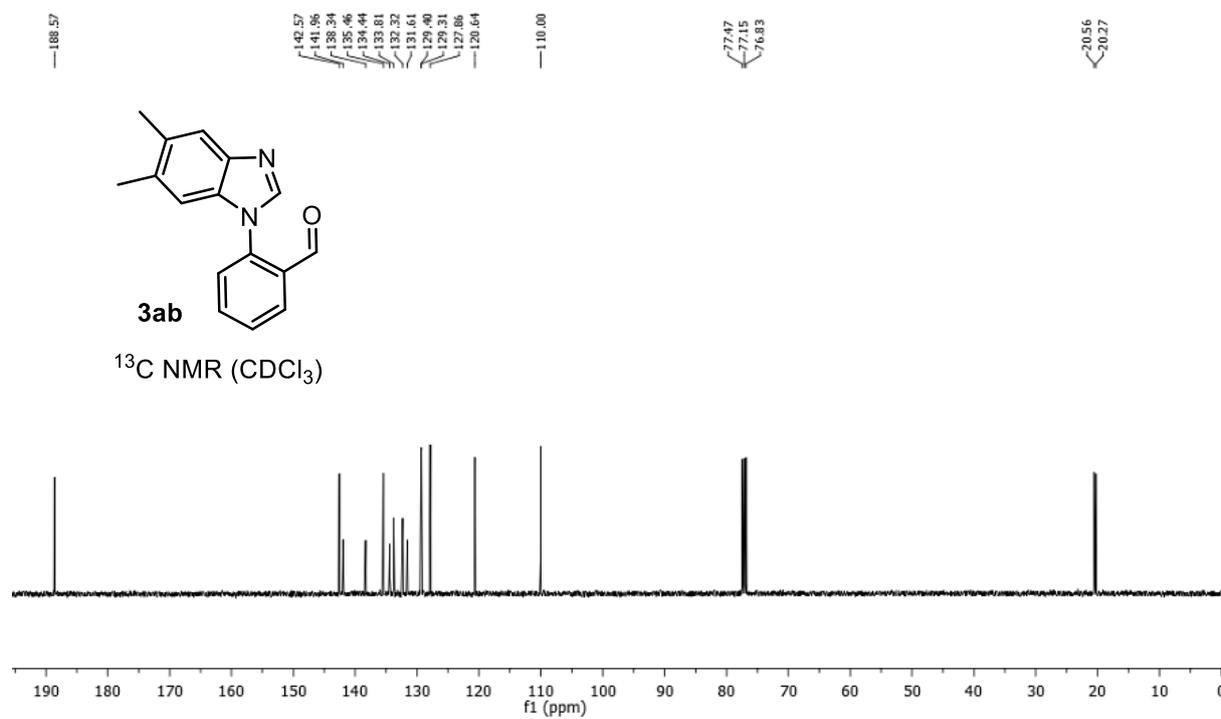
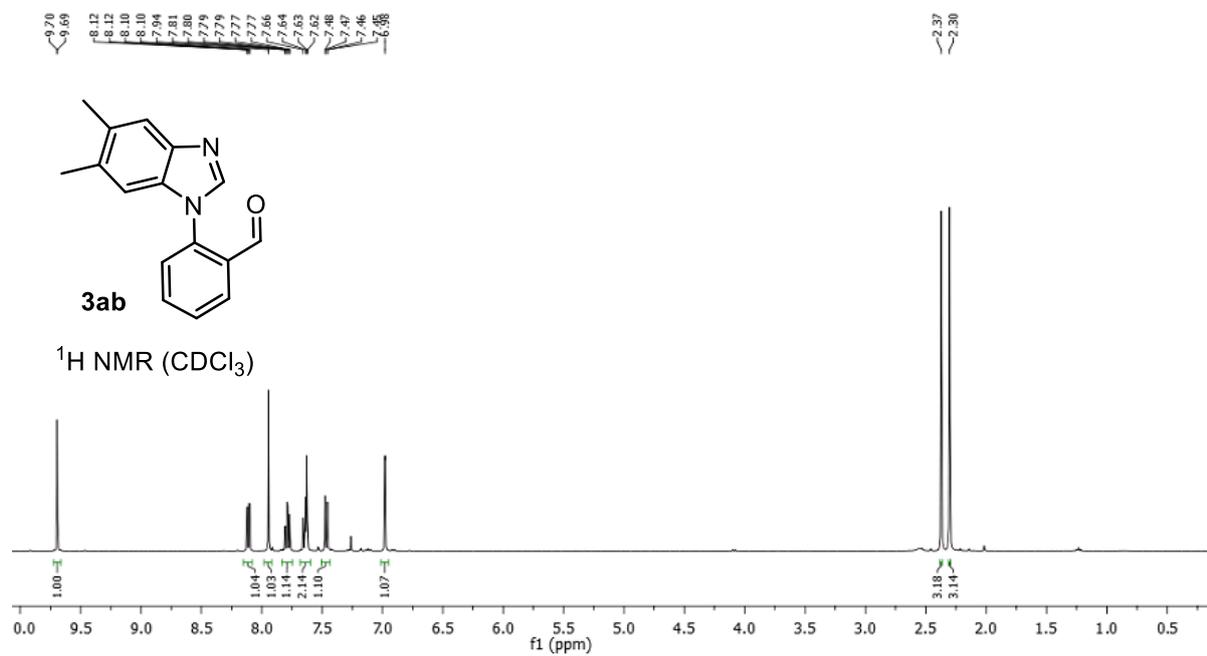
## 6.12 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 10ac:



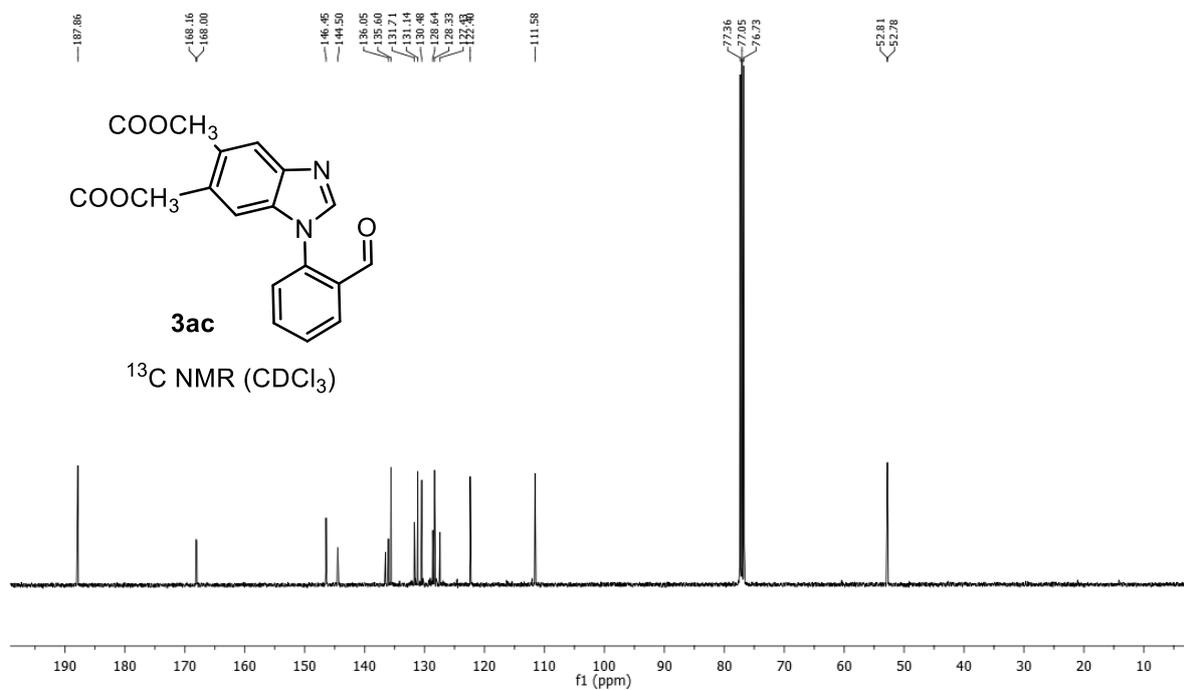
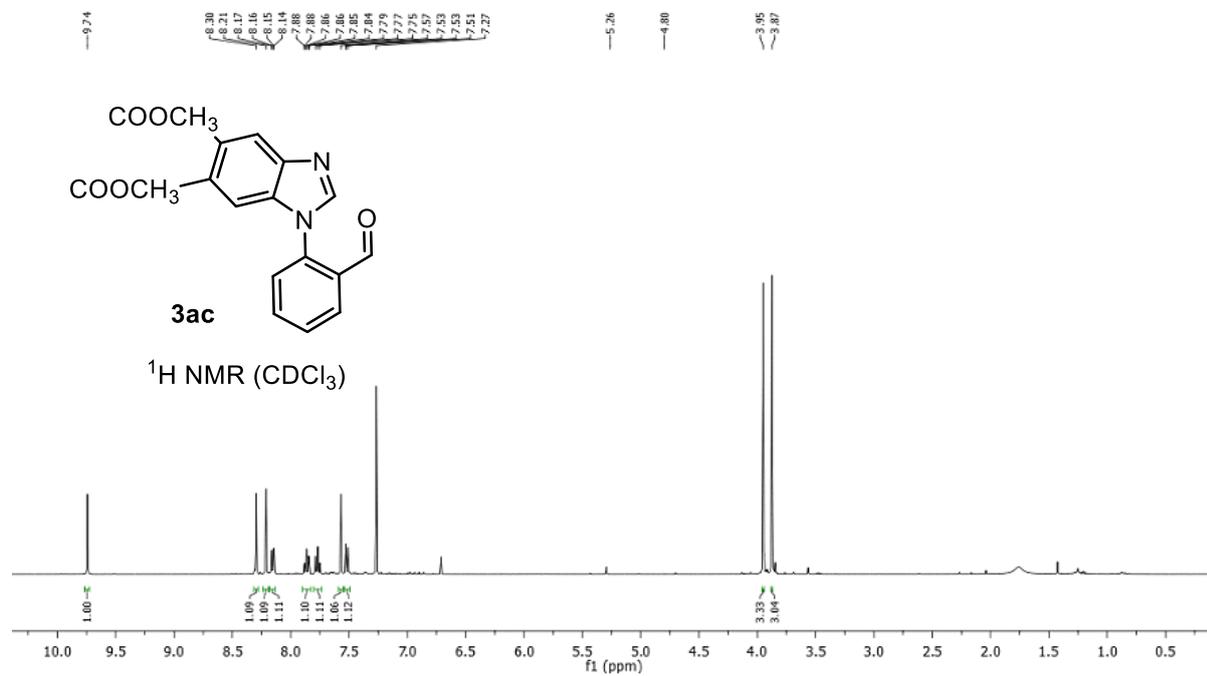
### 6.13 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3aa:



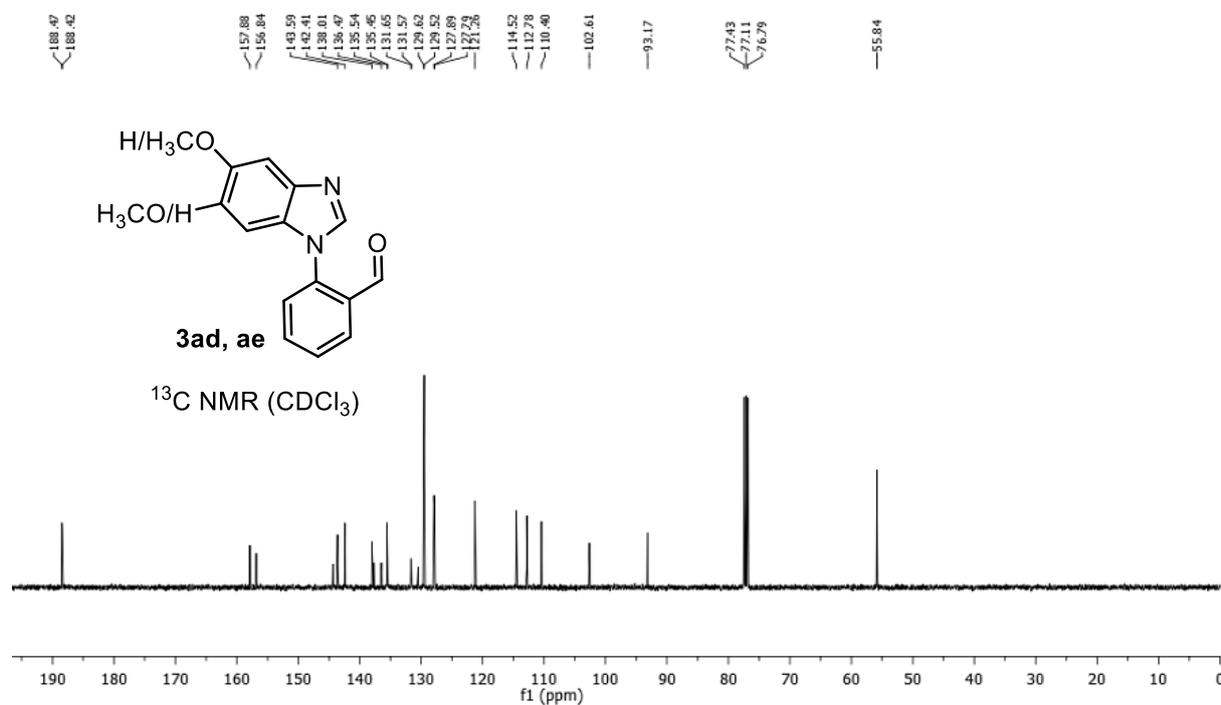
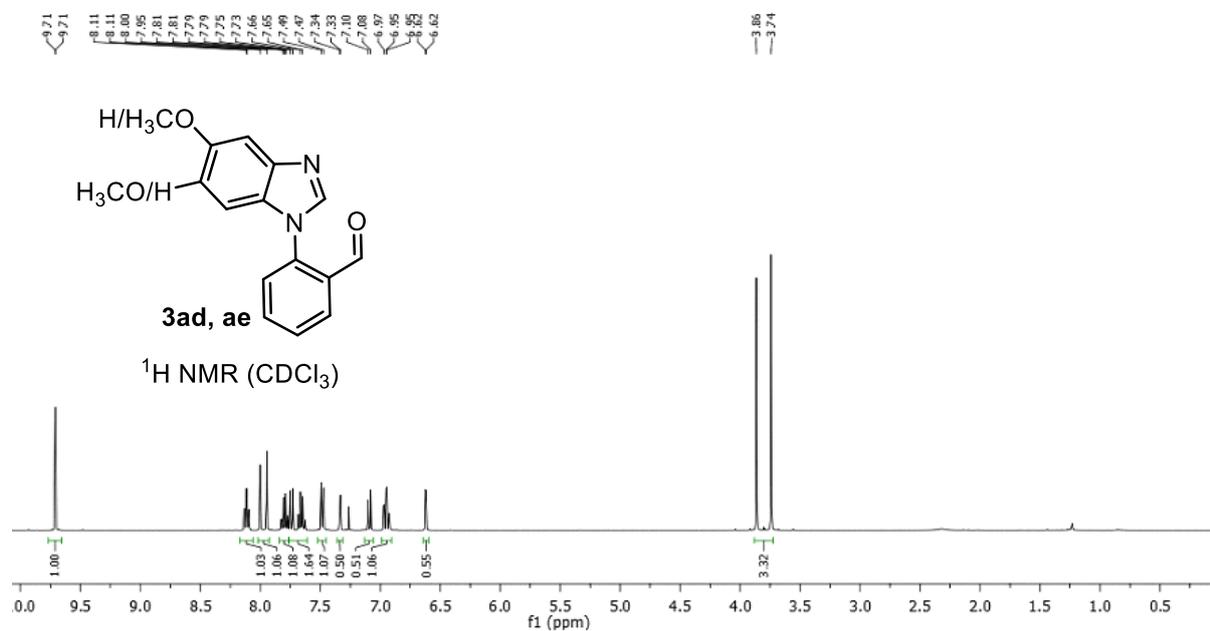
## 6.14 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3ab:



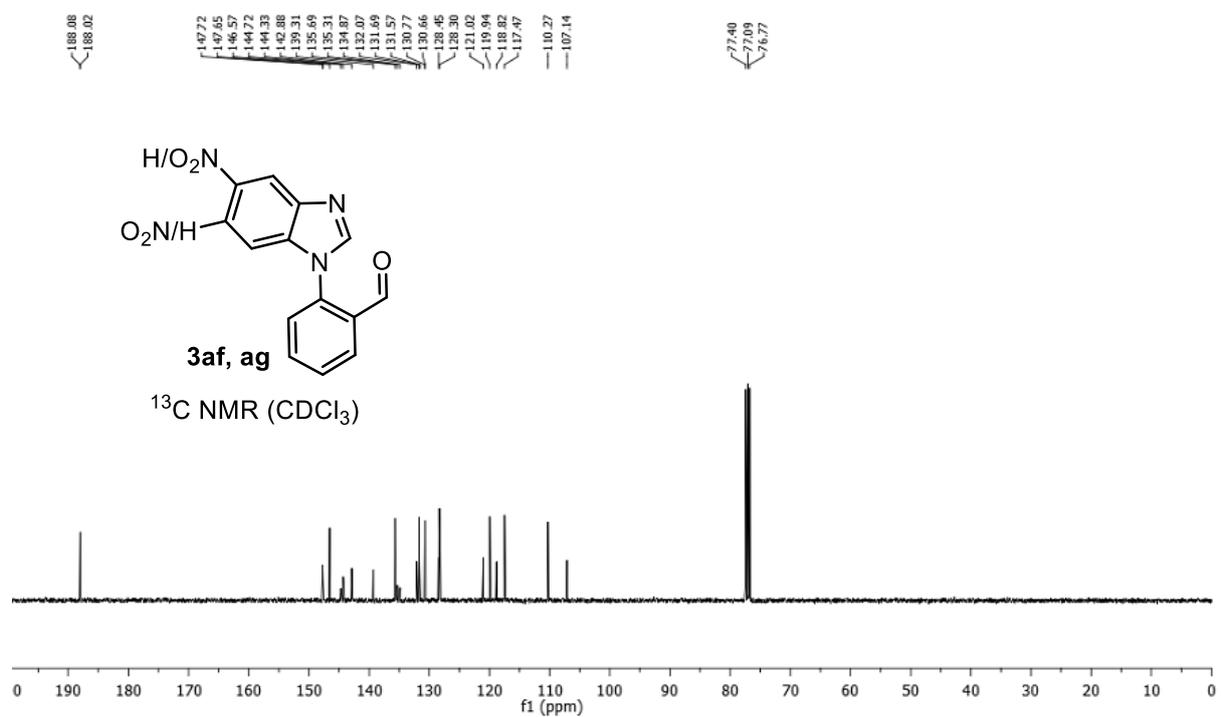
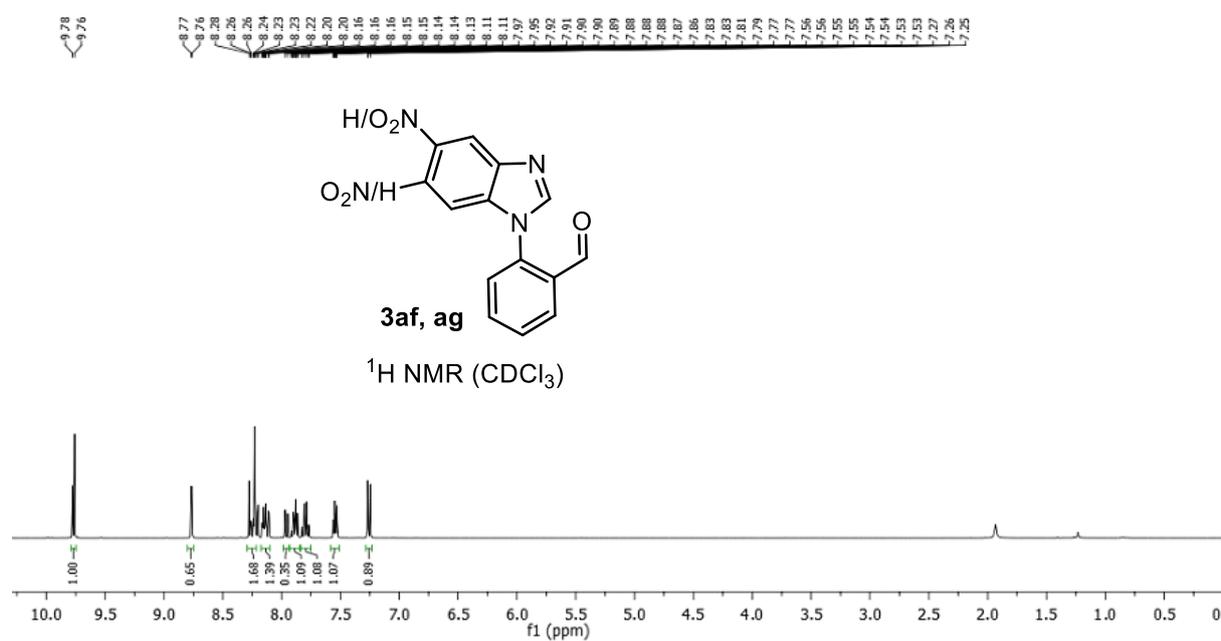
## 6.15 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3ac:



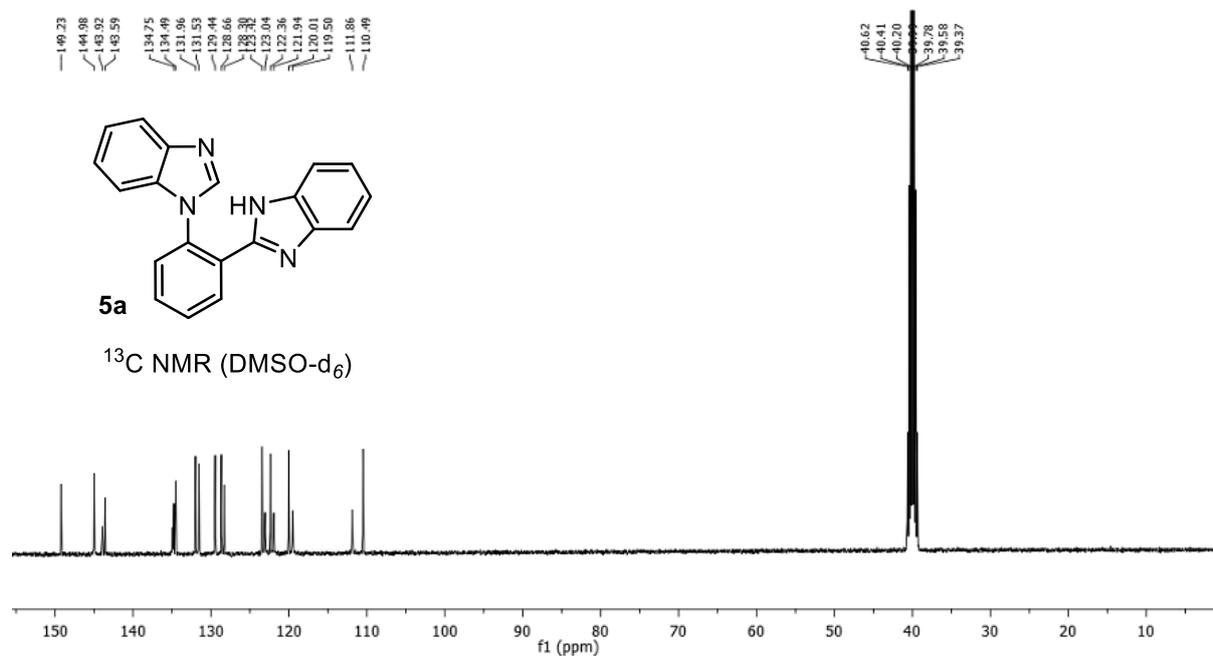
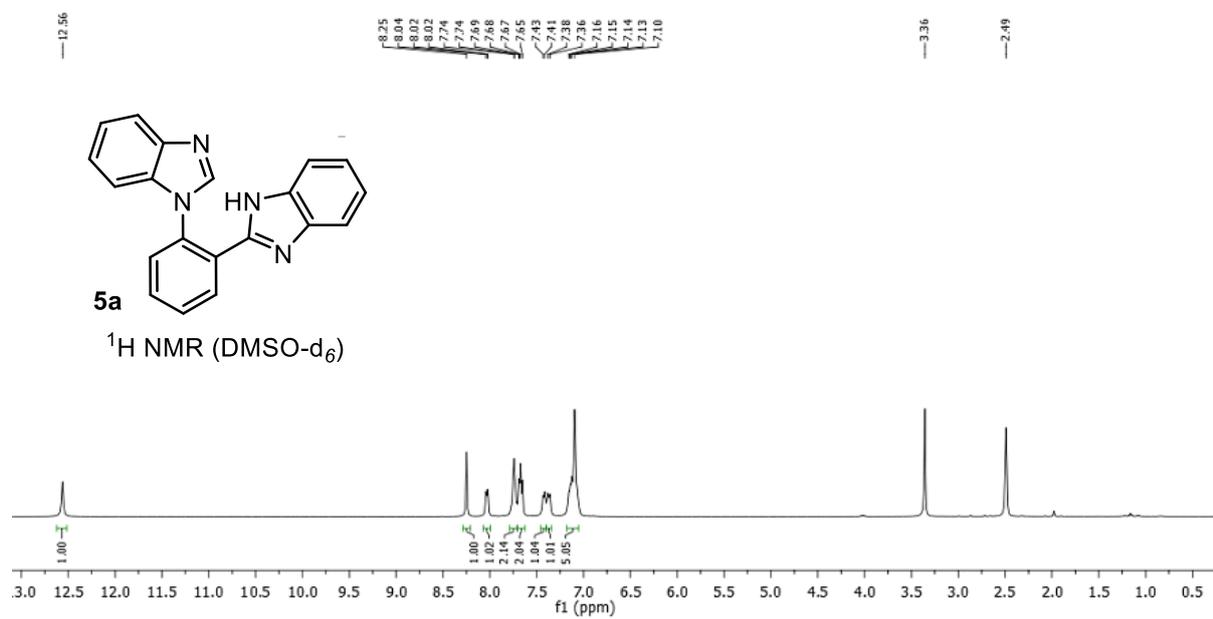
## 6.16 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3ad-ae:



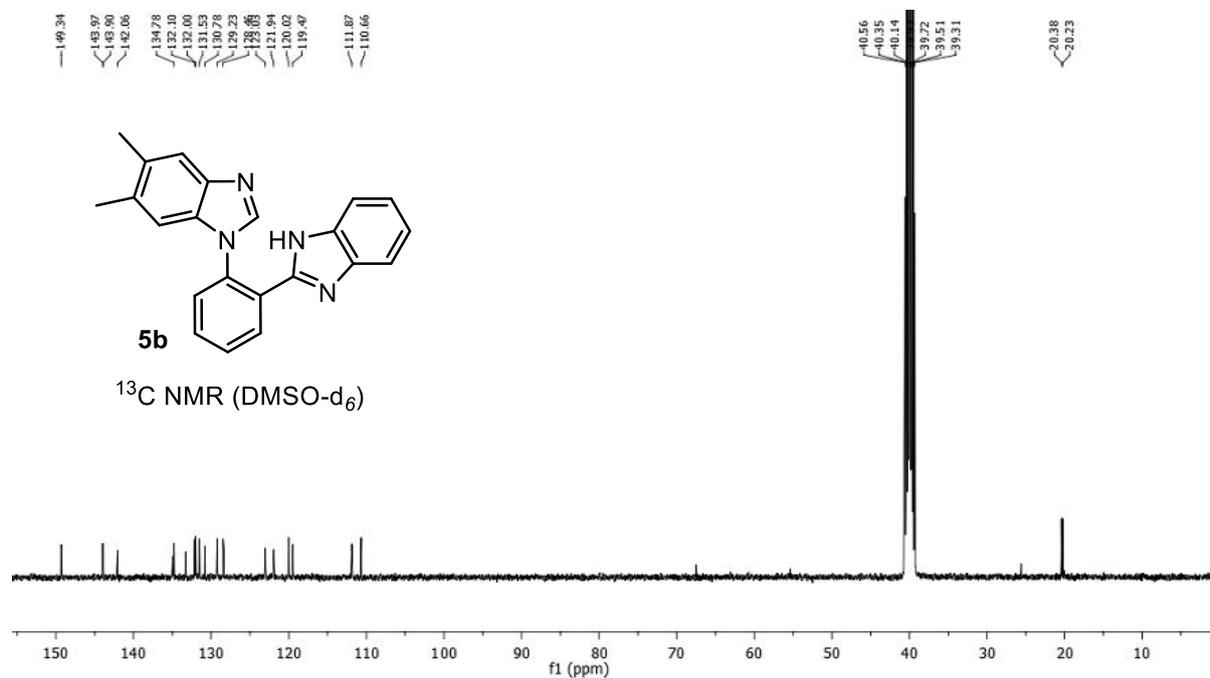
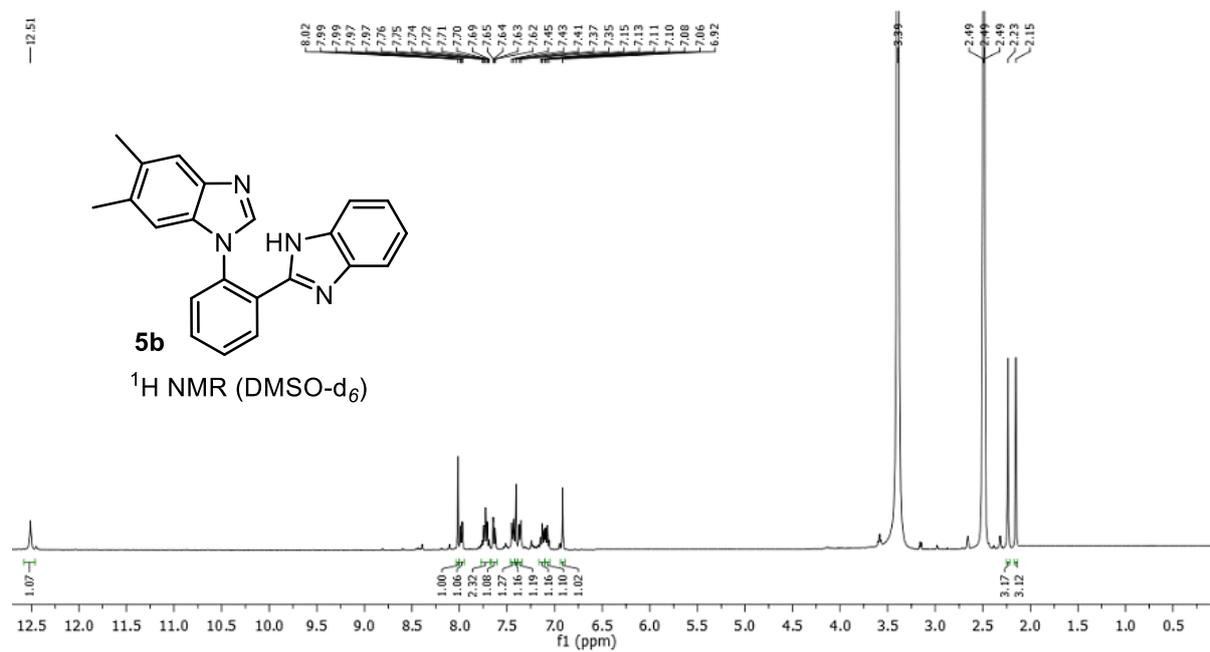
## 6.17 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3af-ag:



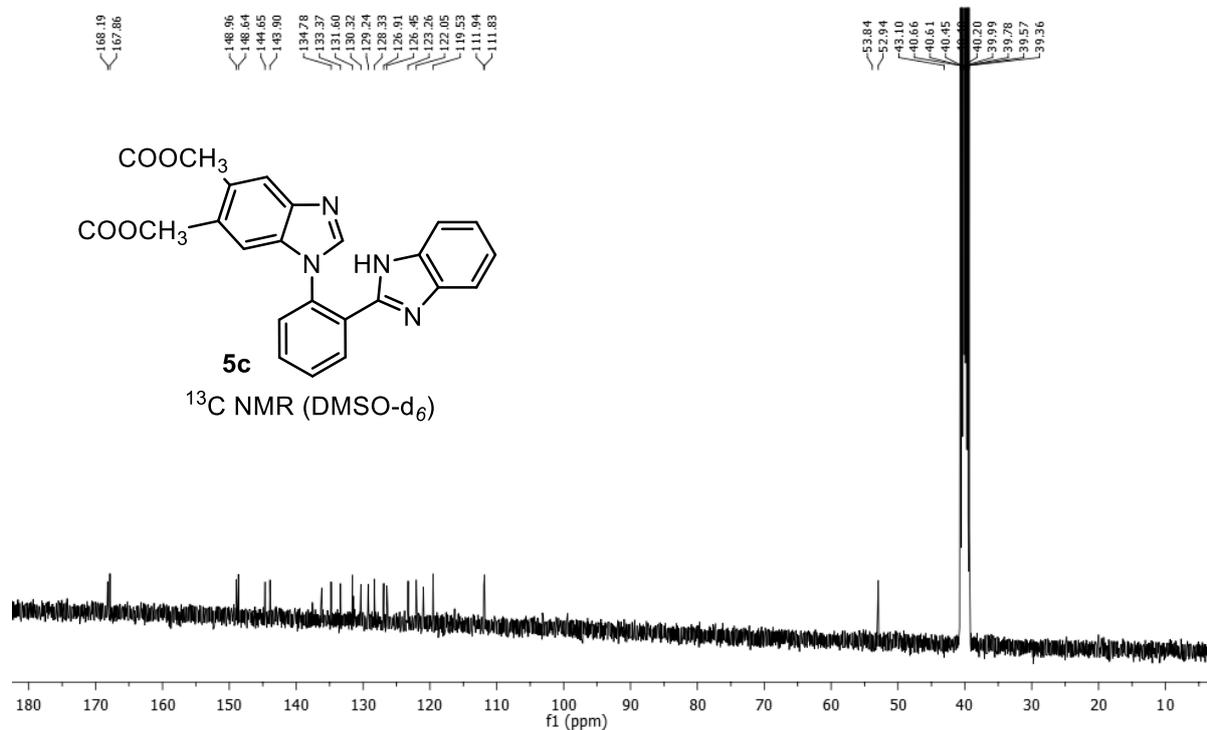
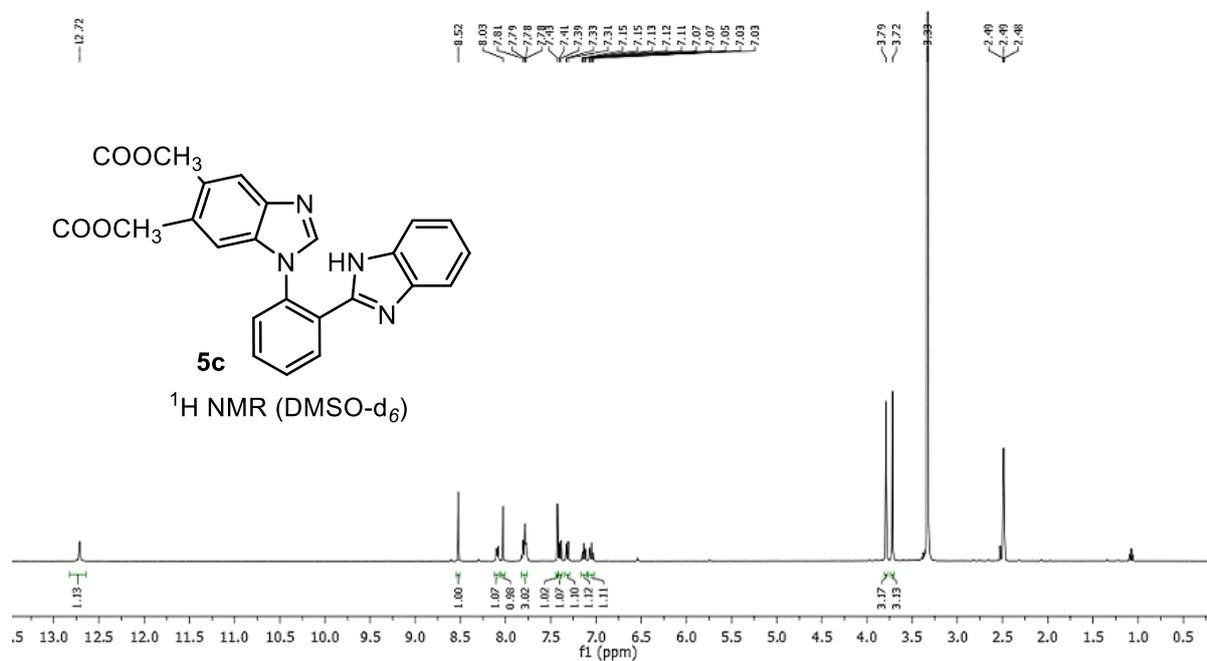
## 6.18 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 5a:



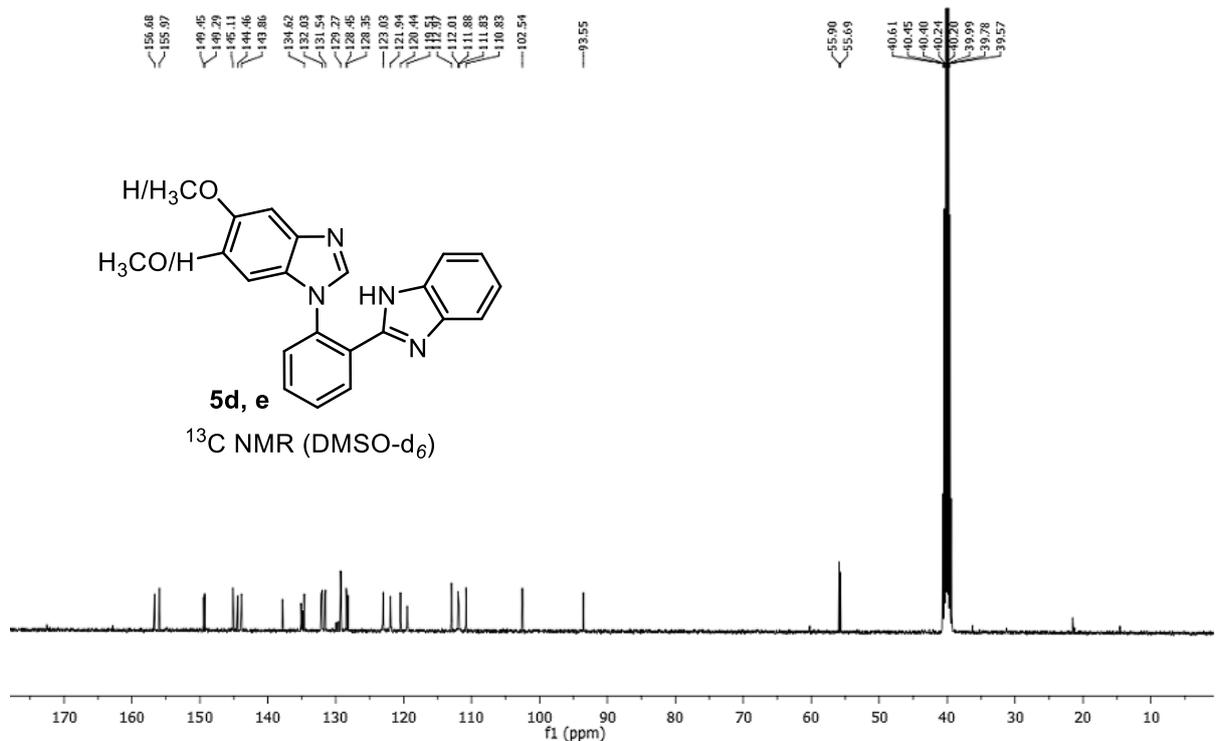
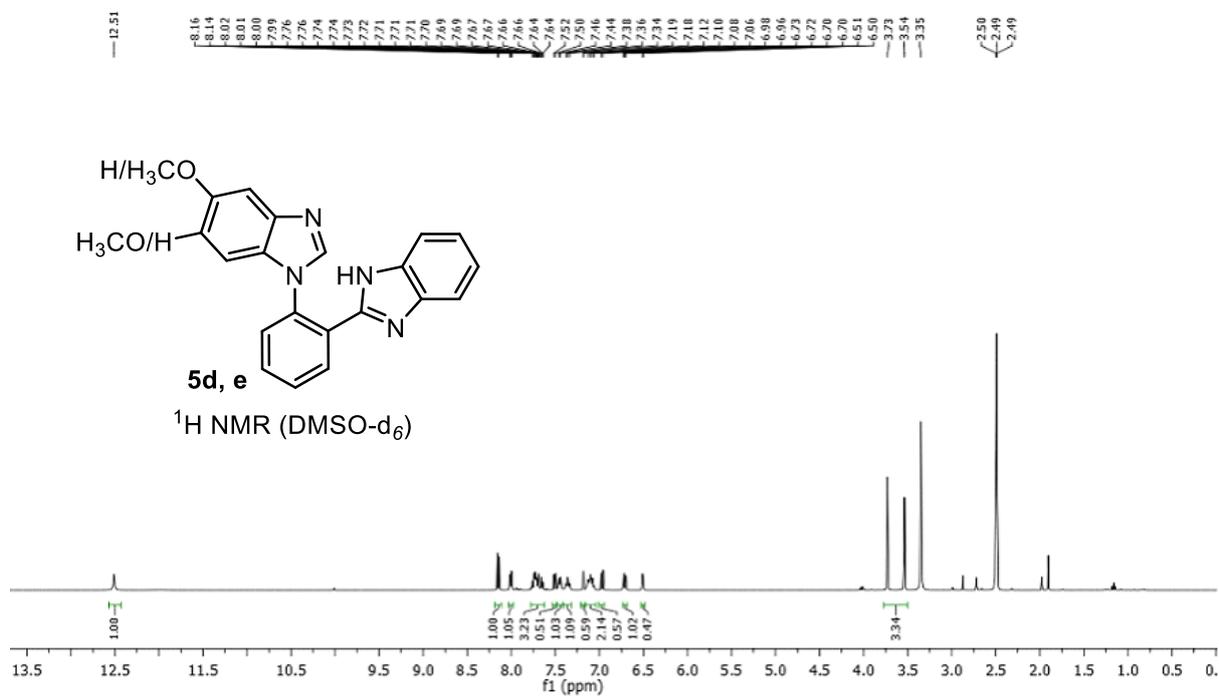
## 6.19 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 5b:



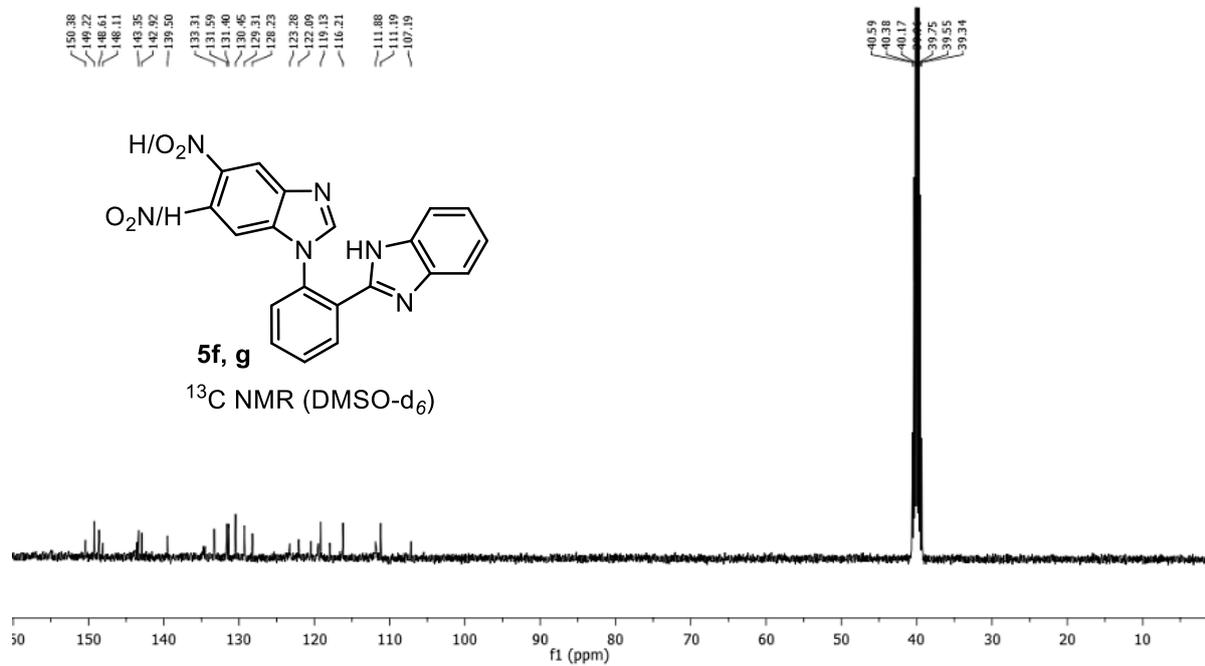
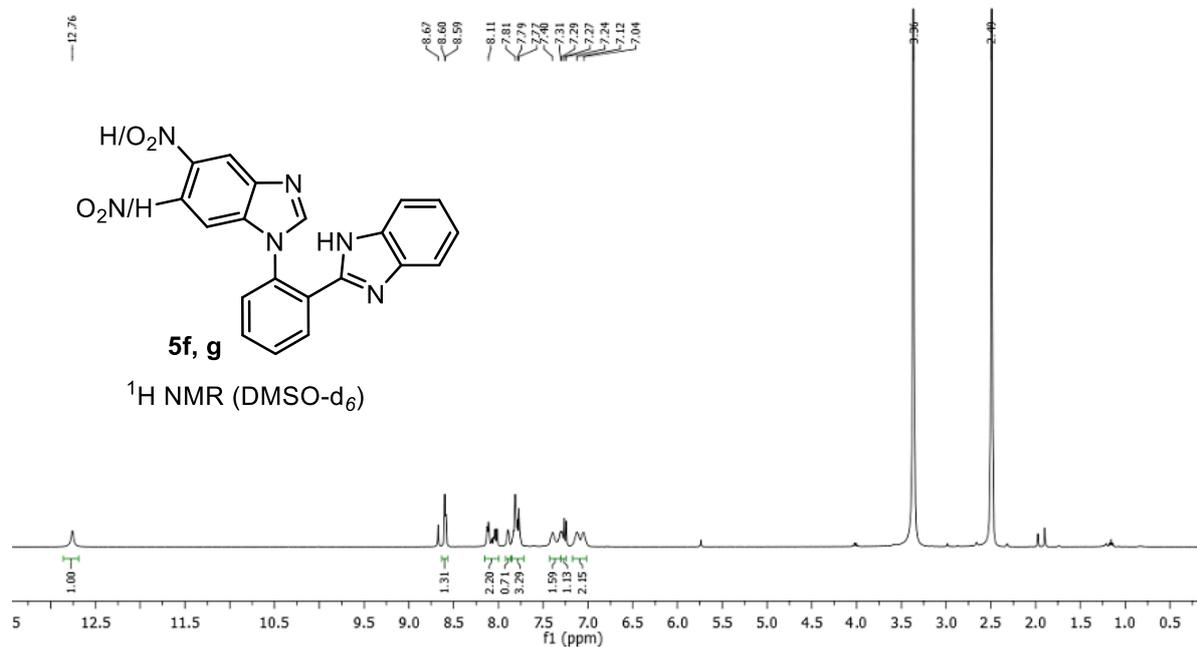
## 6.20 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 5c:



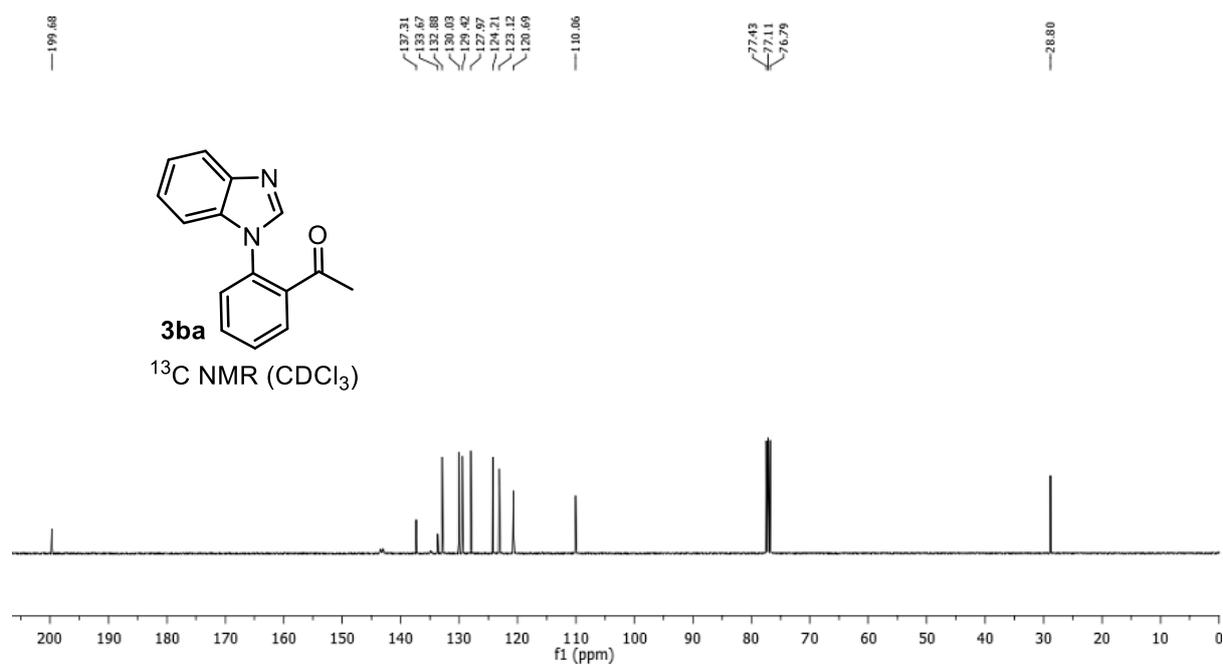
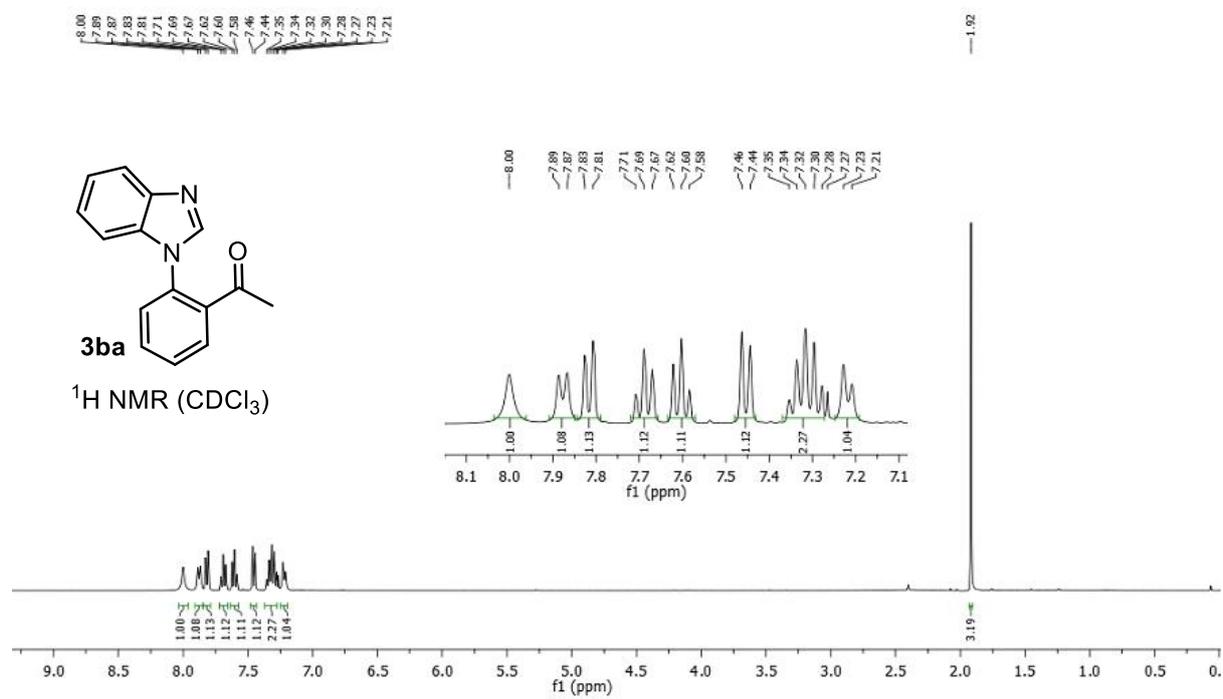
## 6.21 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 5d-e:



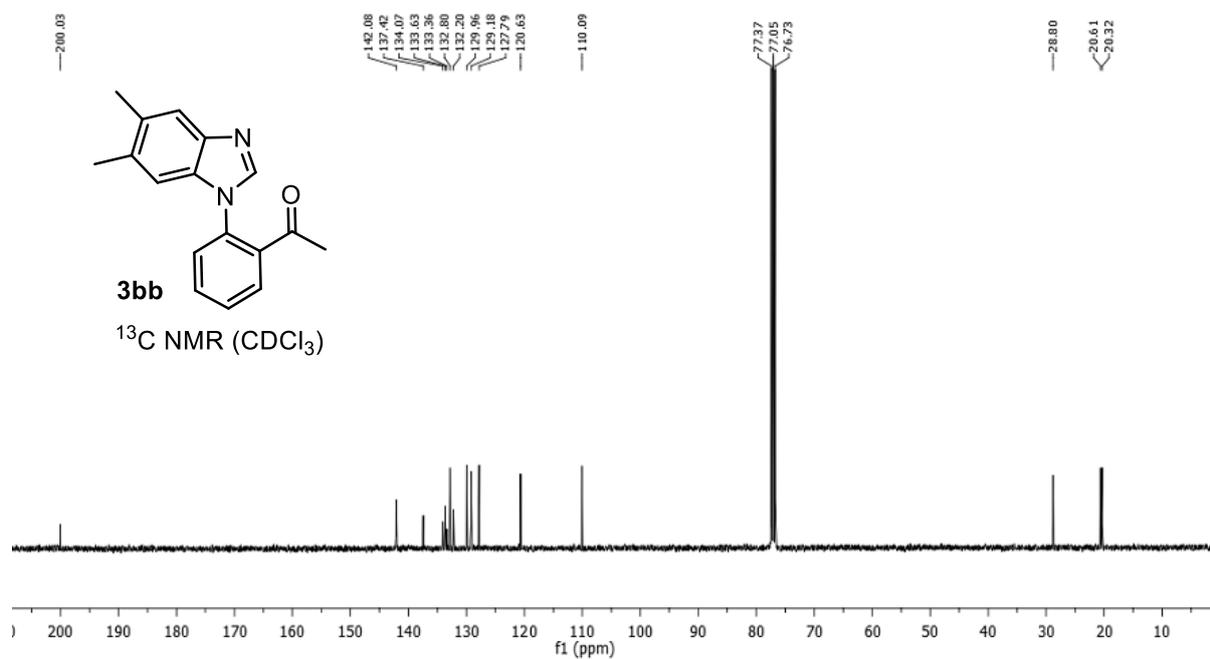
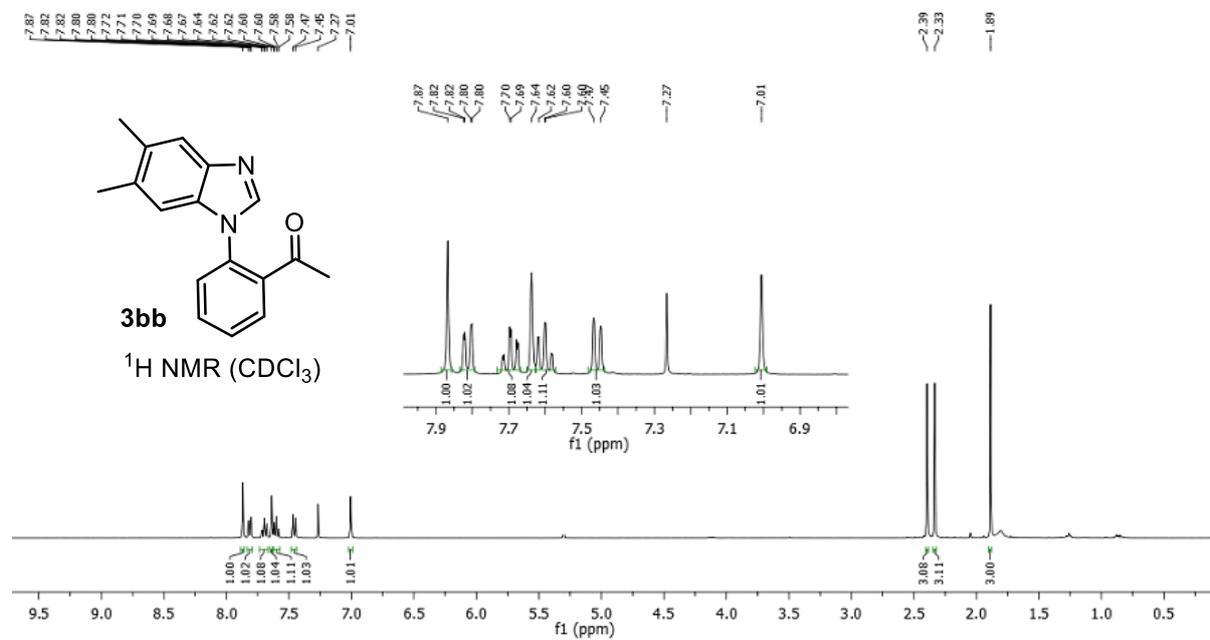
## 6.22 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 5f-g:



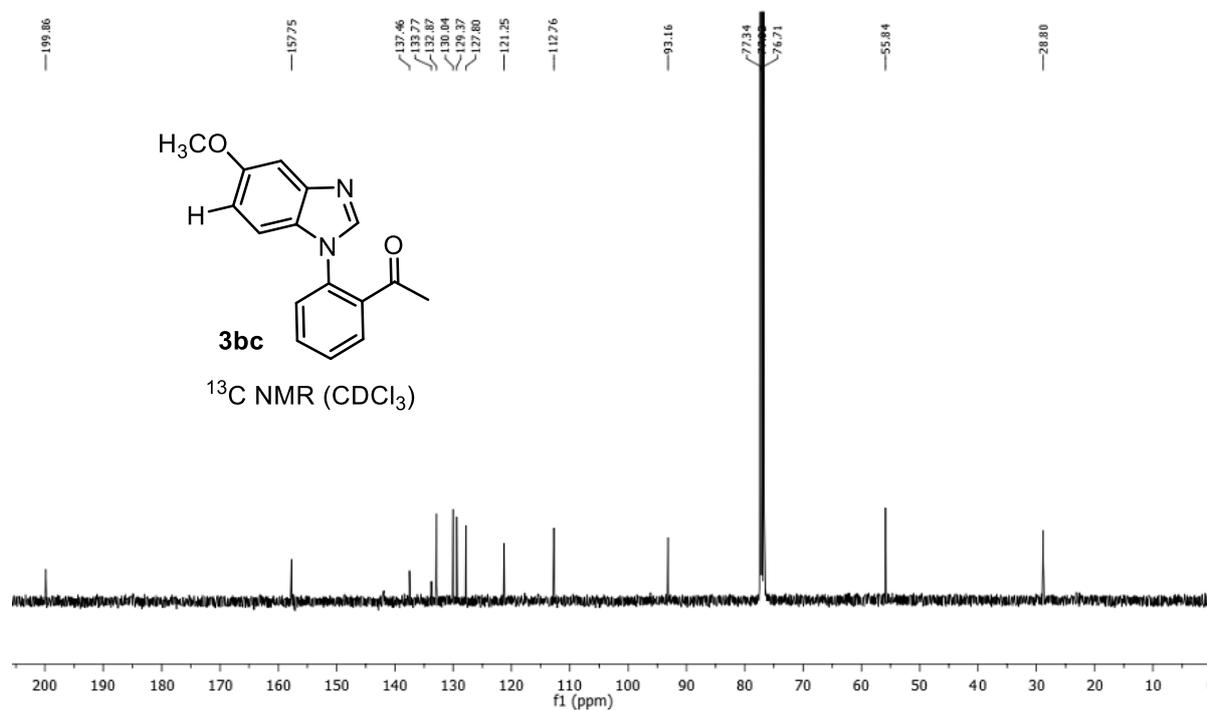
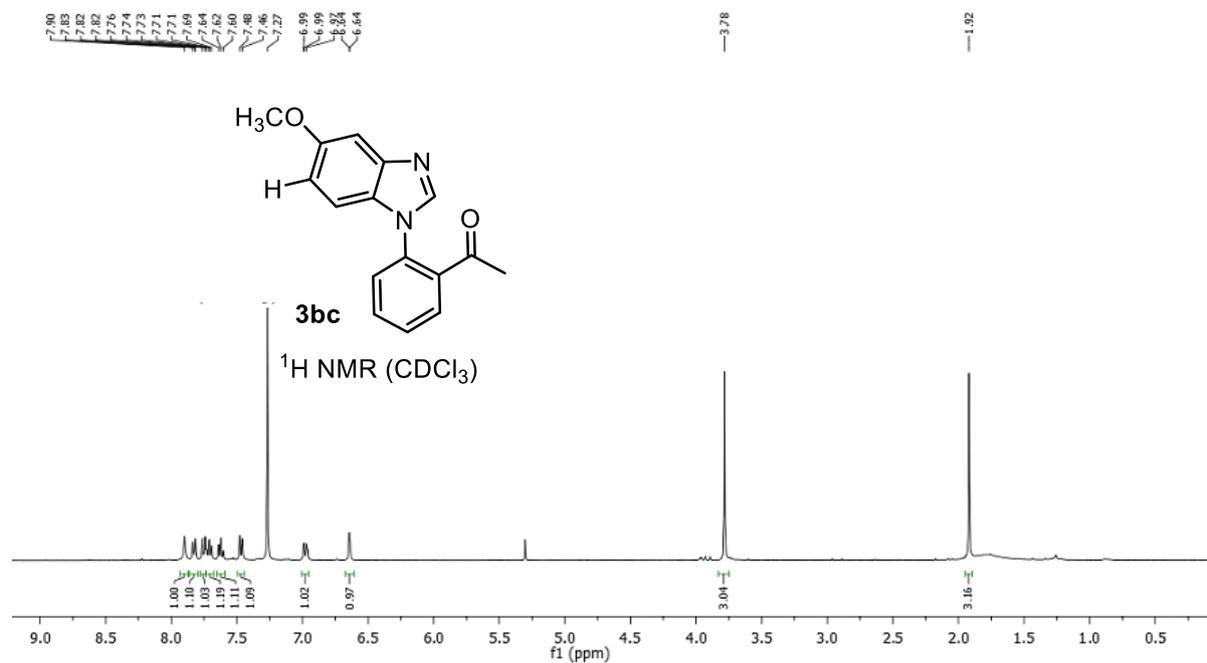
## 6.23 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3ba:



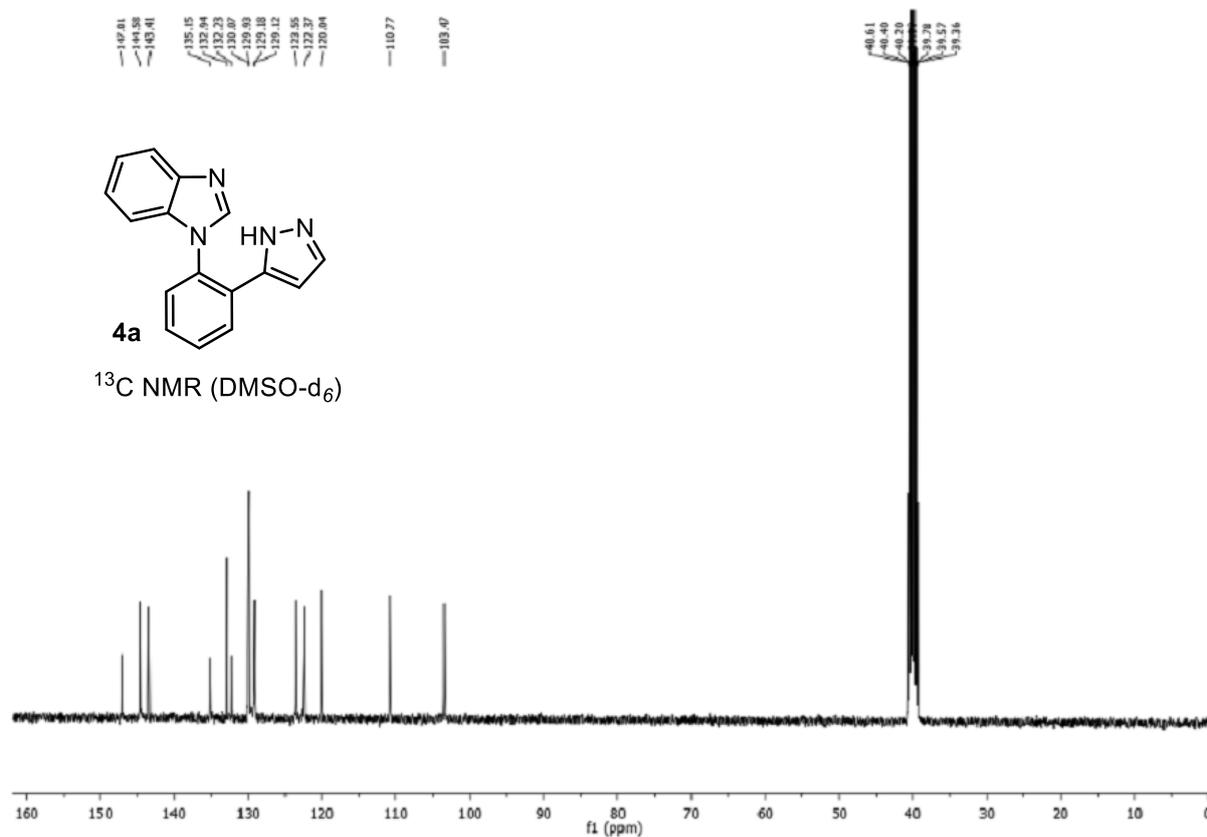
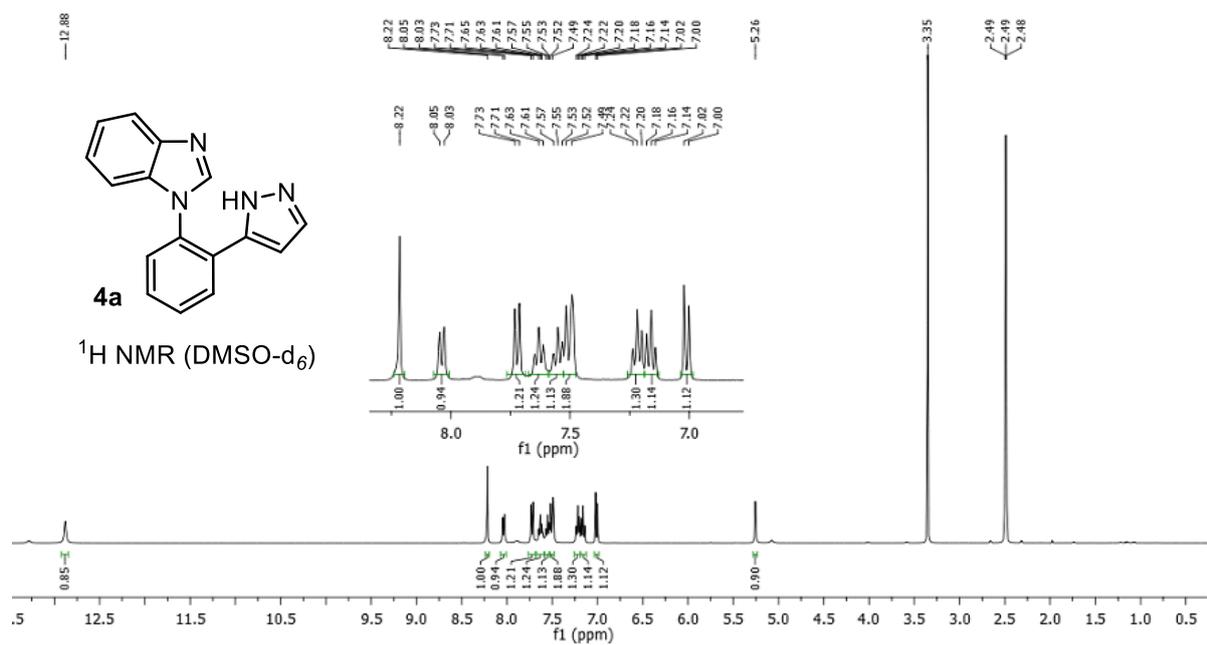
## 6.24 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3bb:



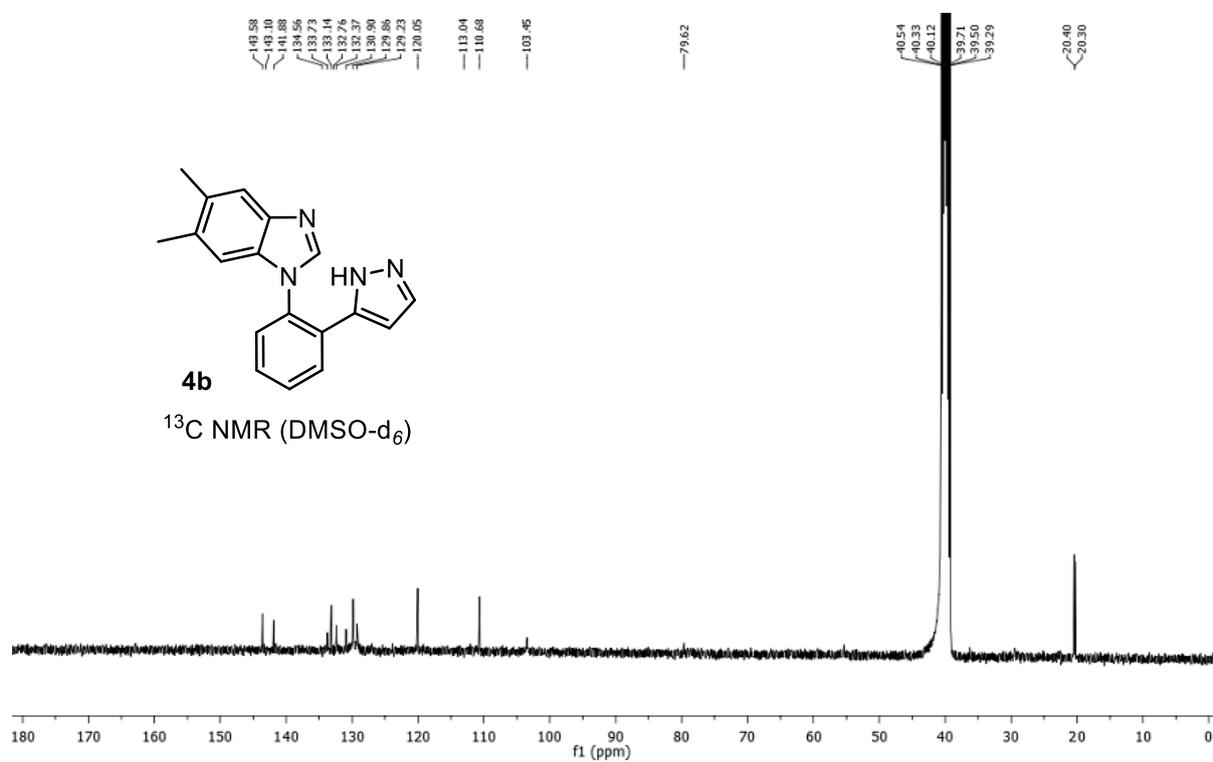
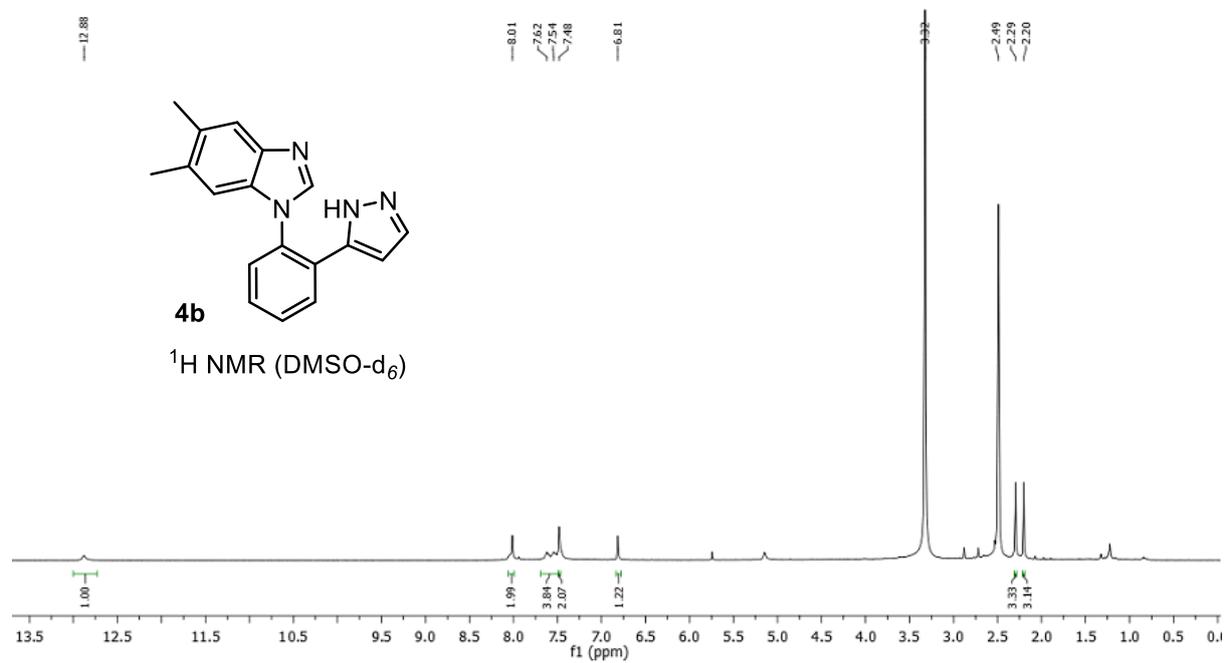
## 6.25 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3bc:



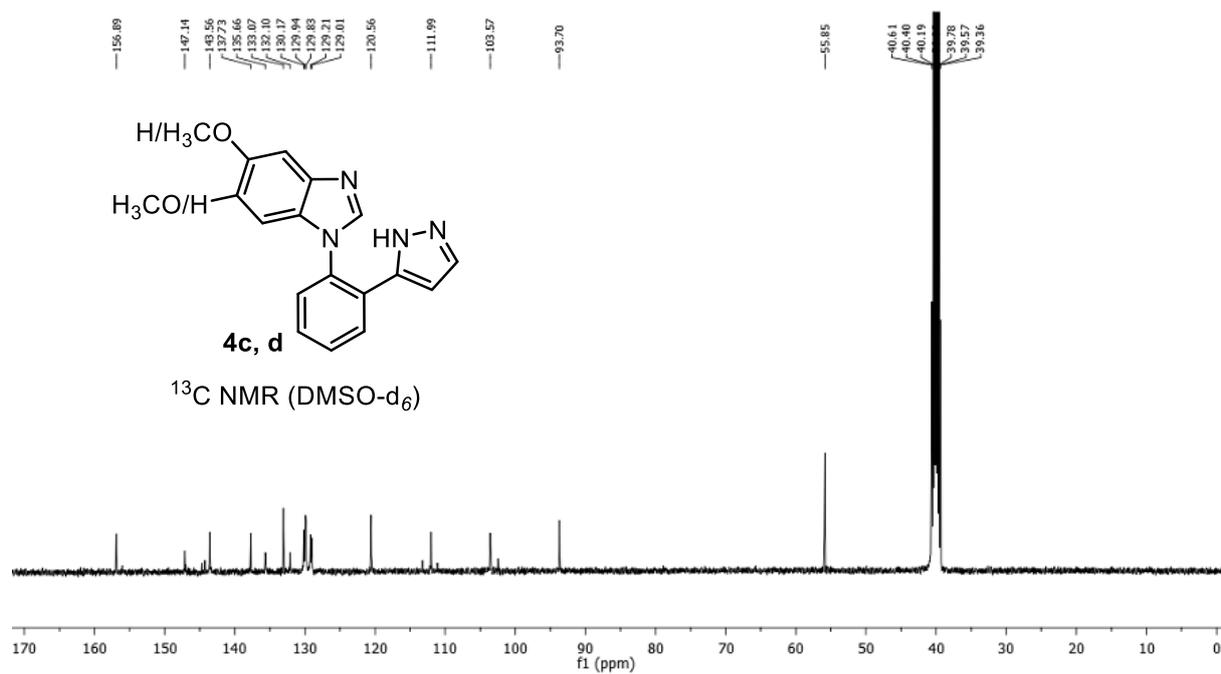
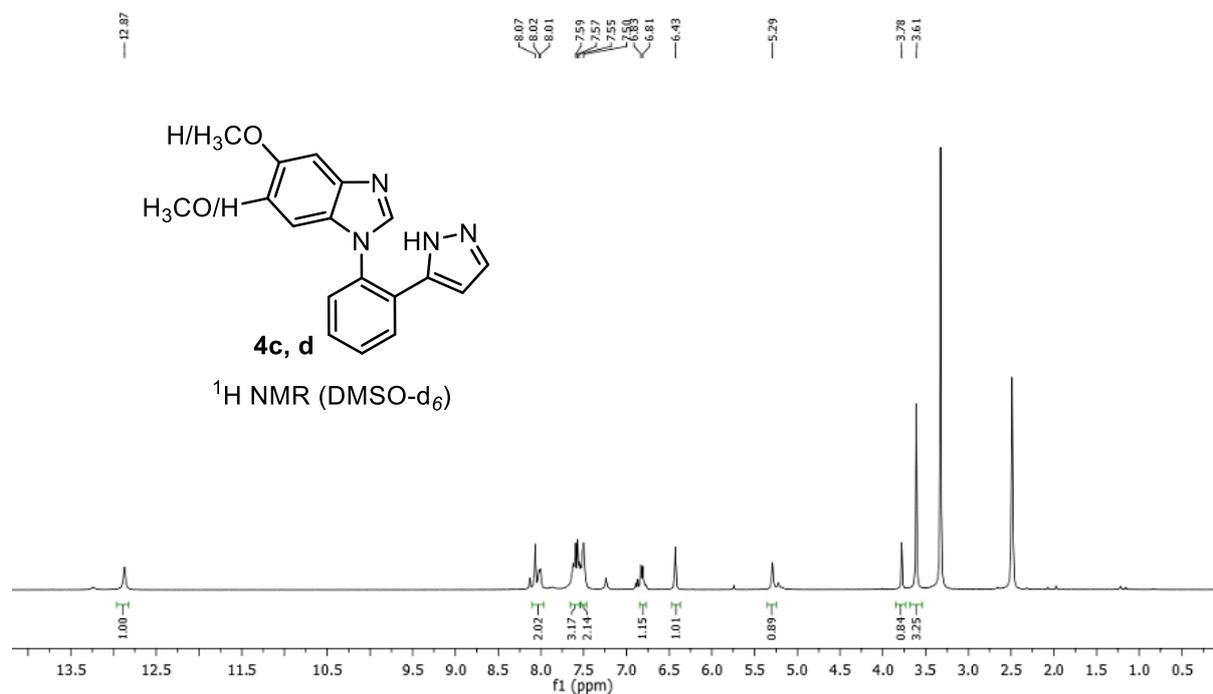
## 6.26 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 4a:



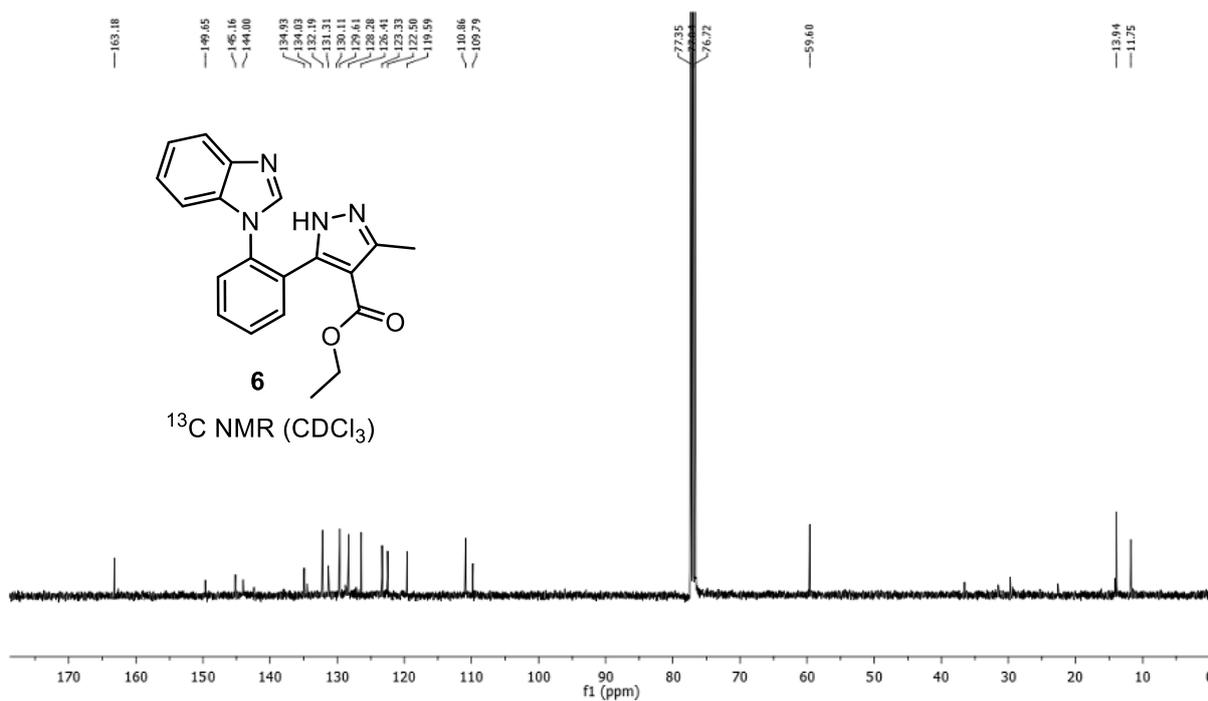
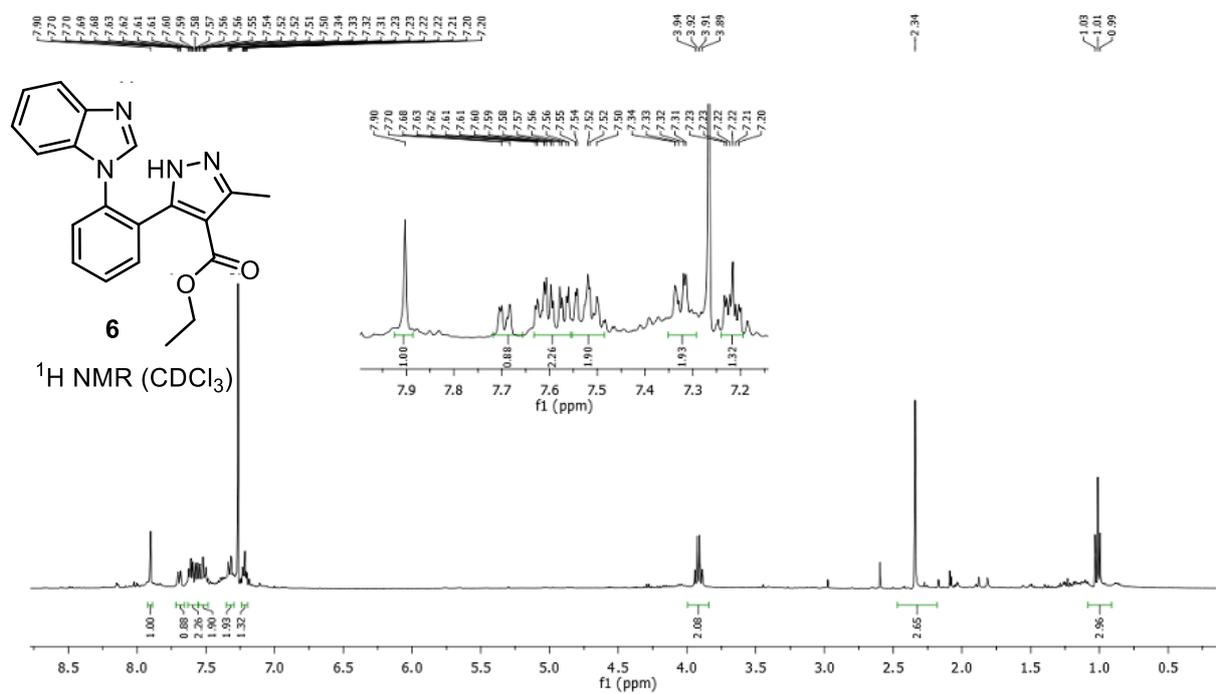
## 6.27 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 4b:



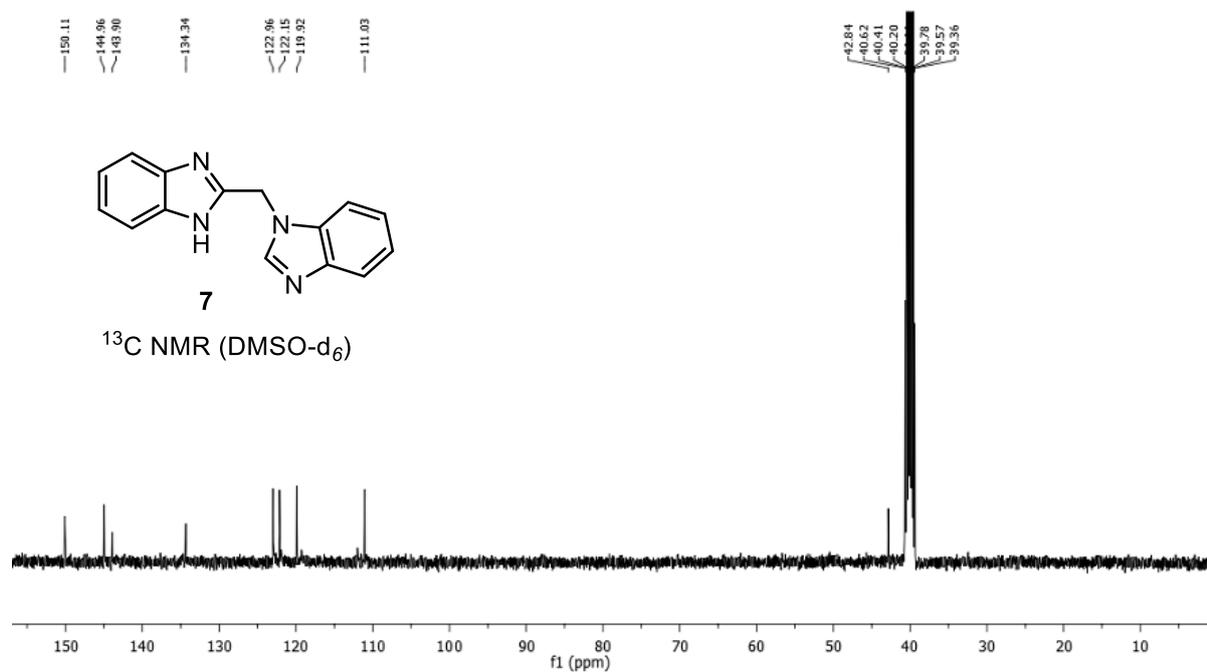
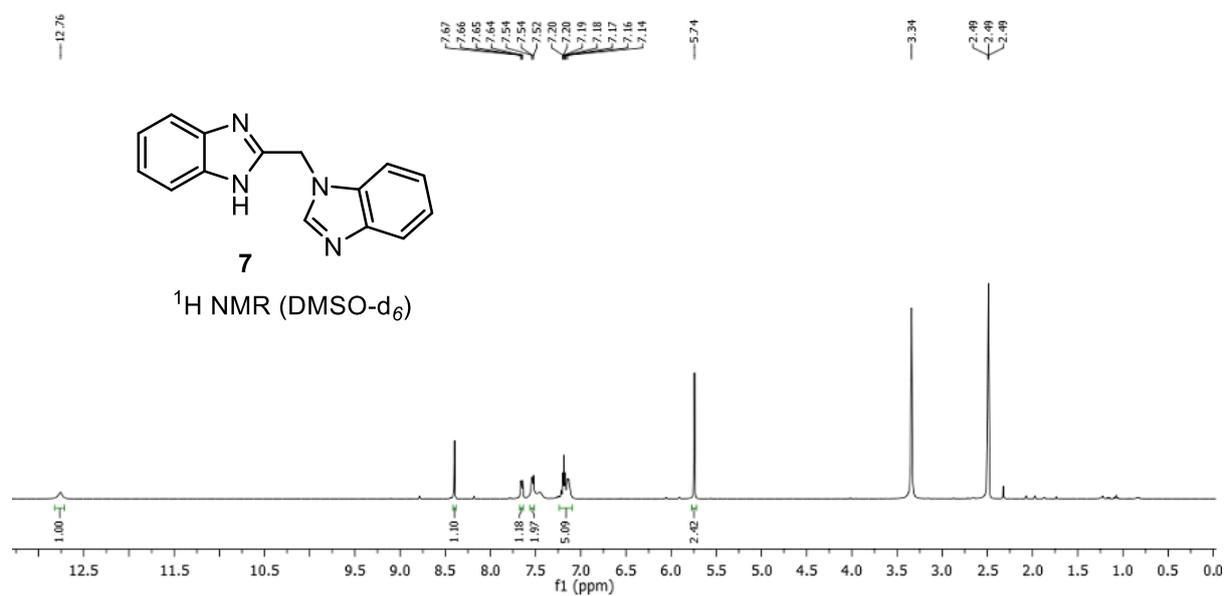
## 6.28 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 4c-d:



## 6.29 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 6:

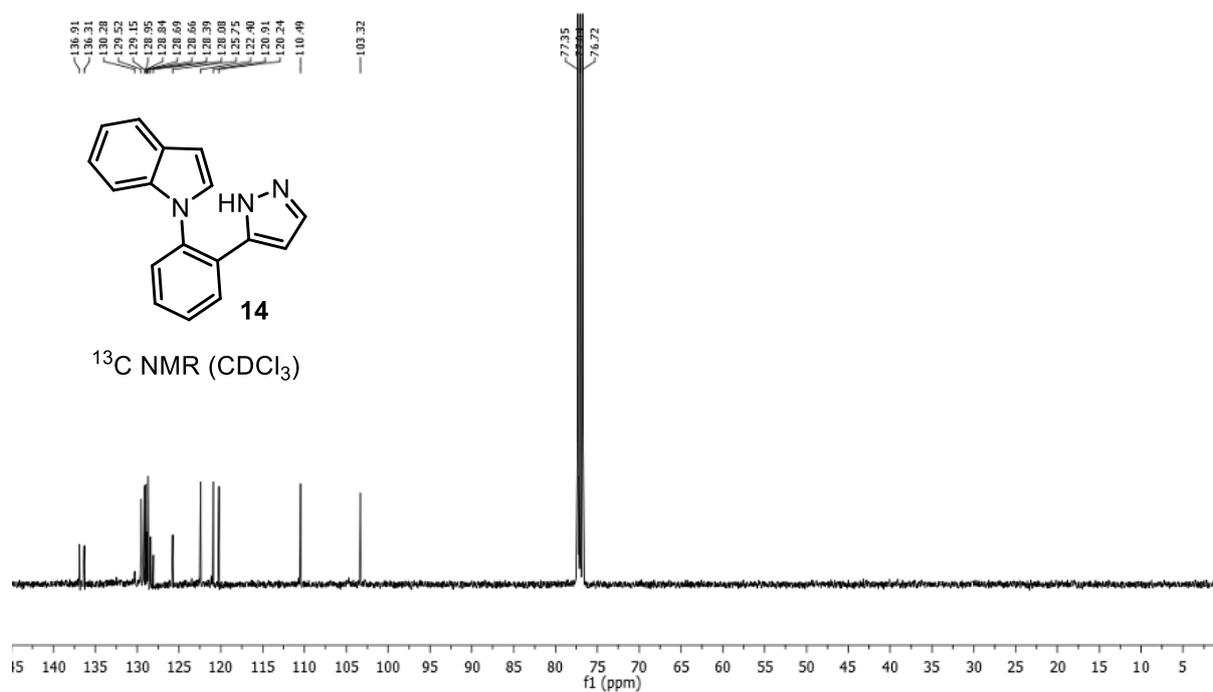
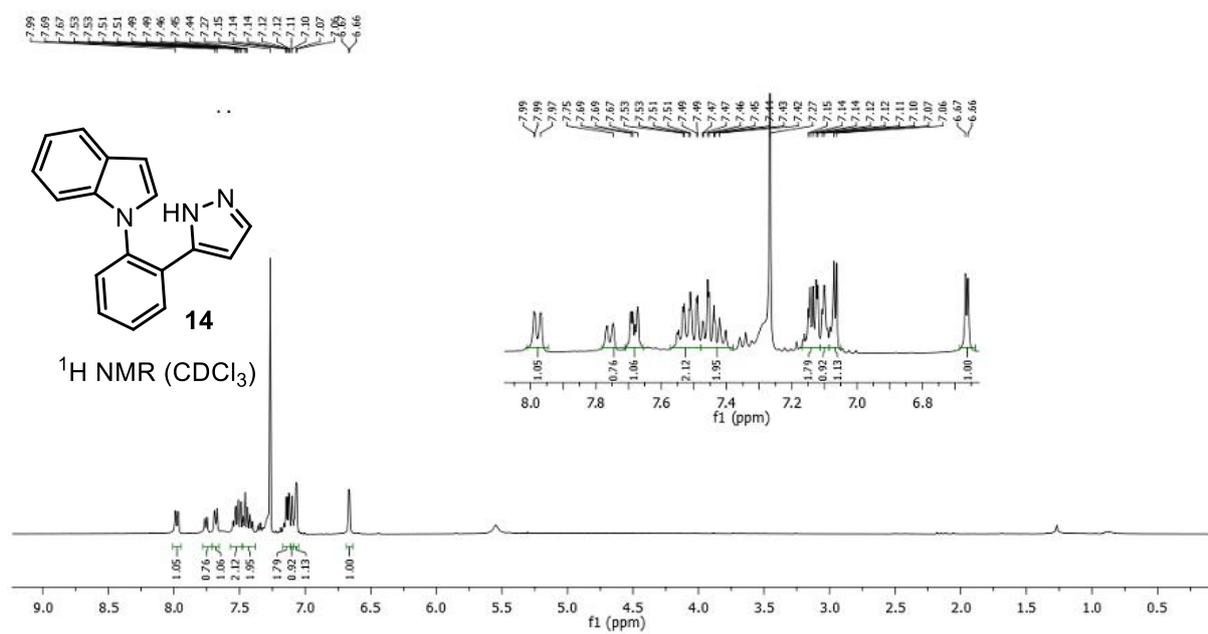


### 6.30 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 7:

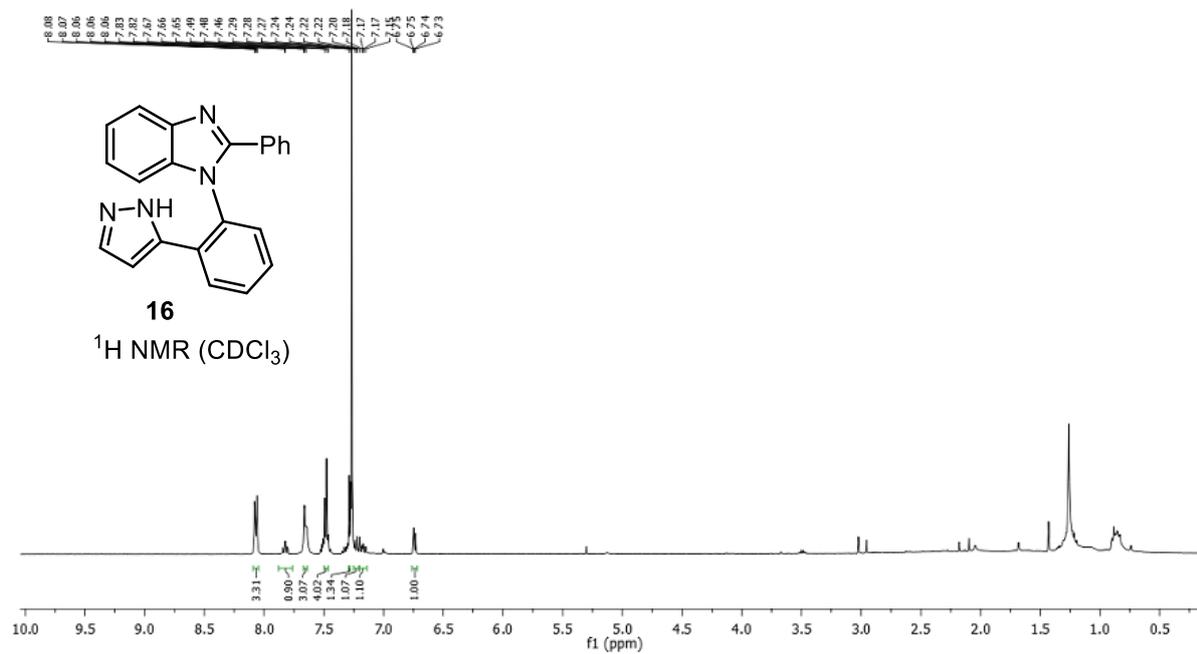




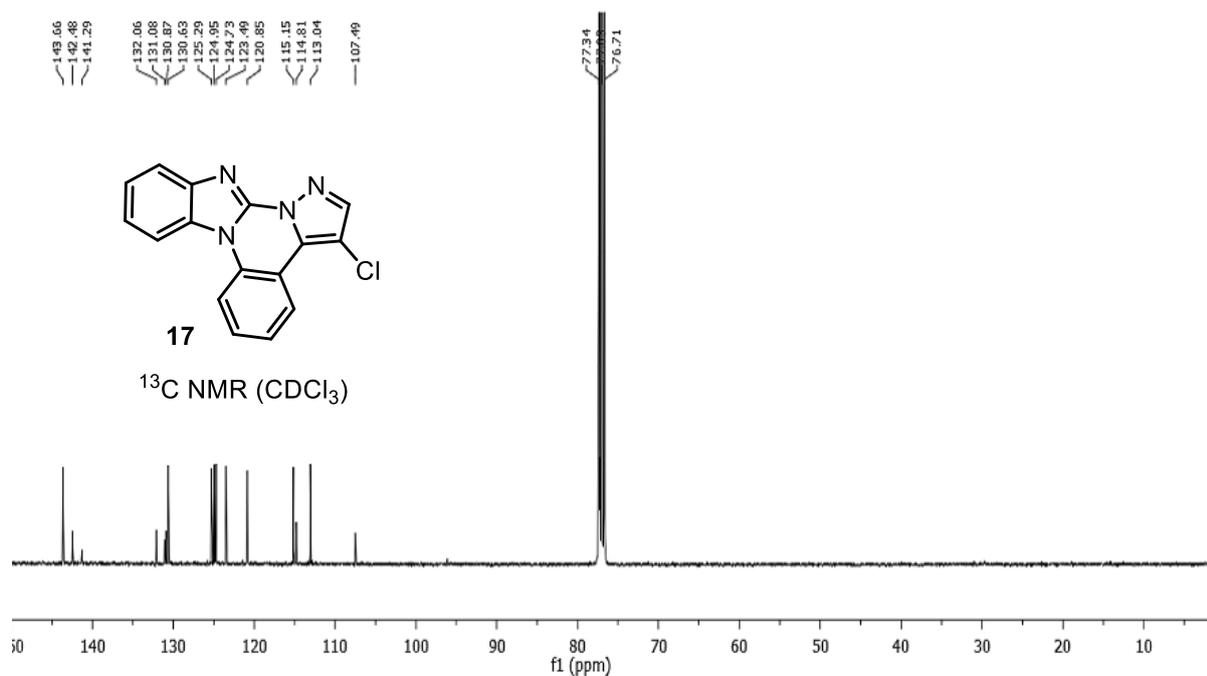
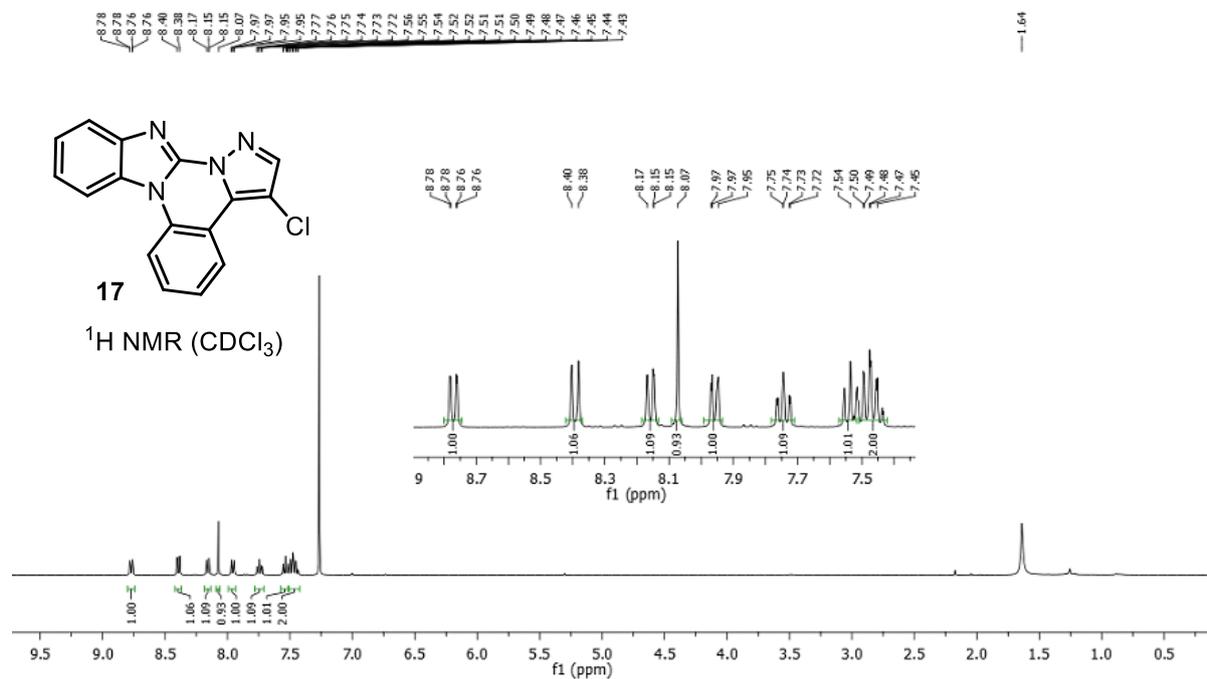
### 6.32 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 14:



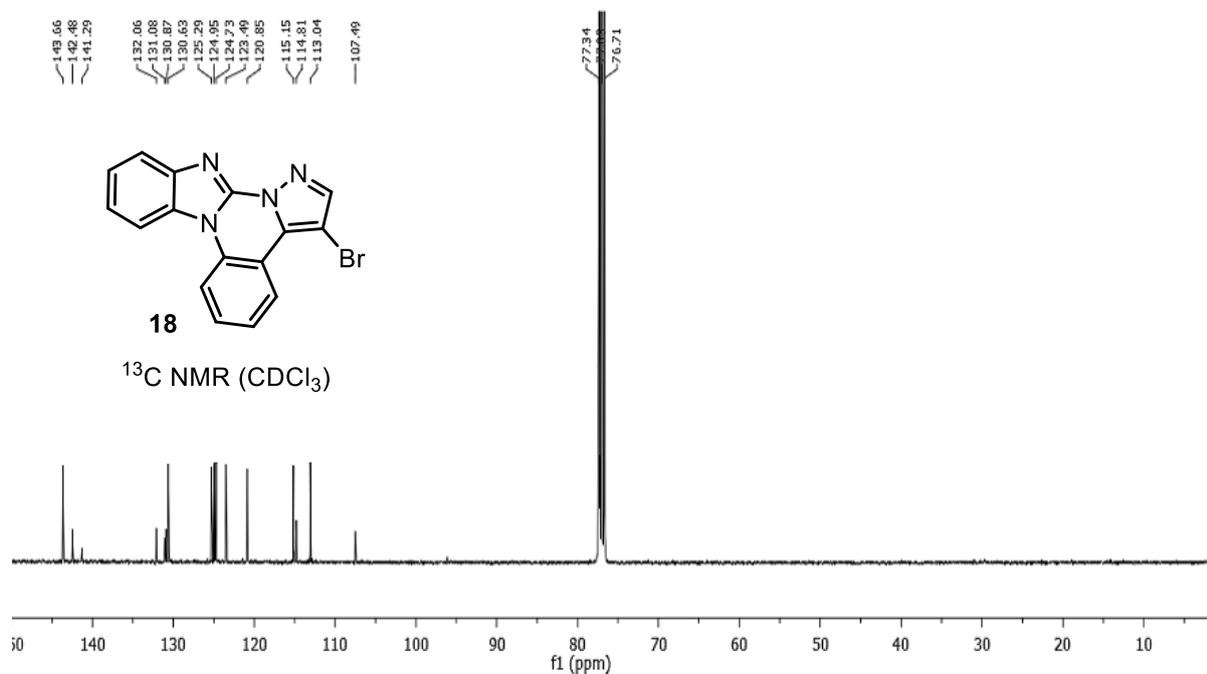
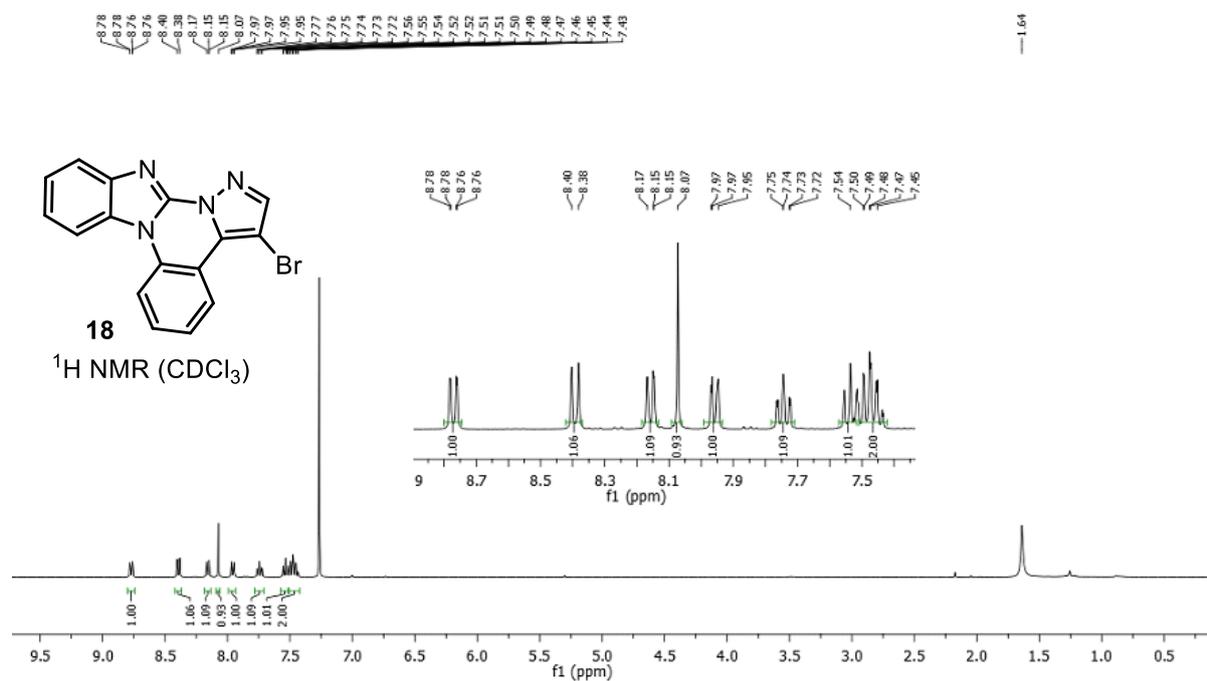
### 6.33 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 16:



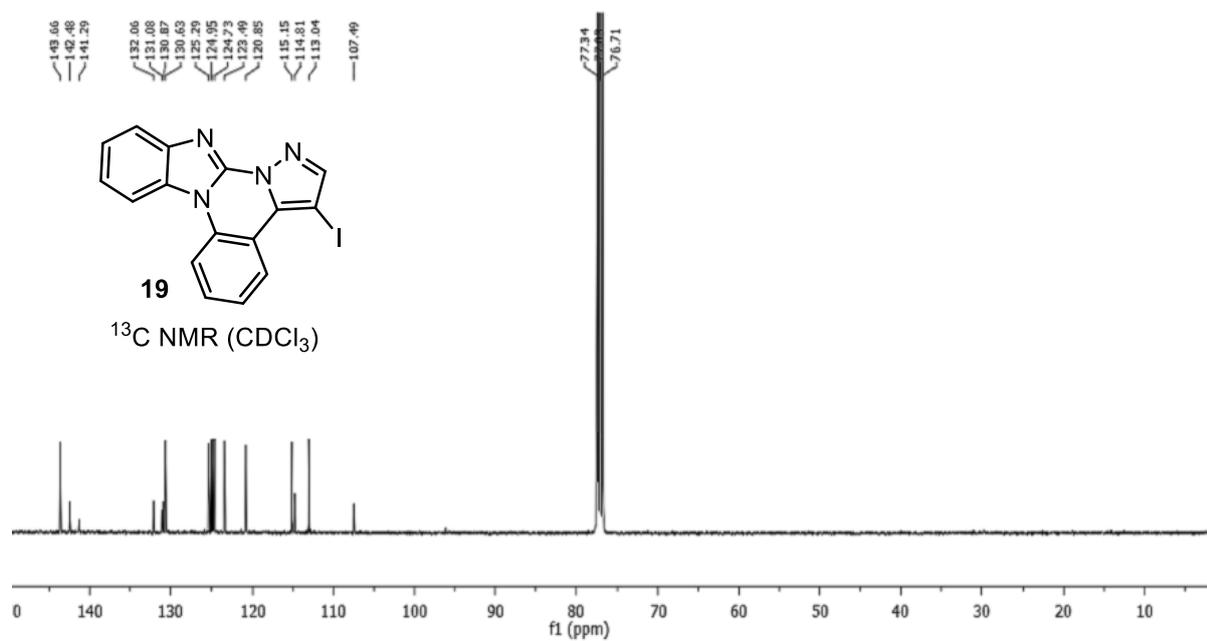
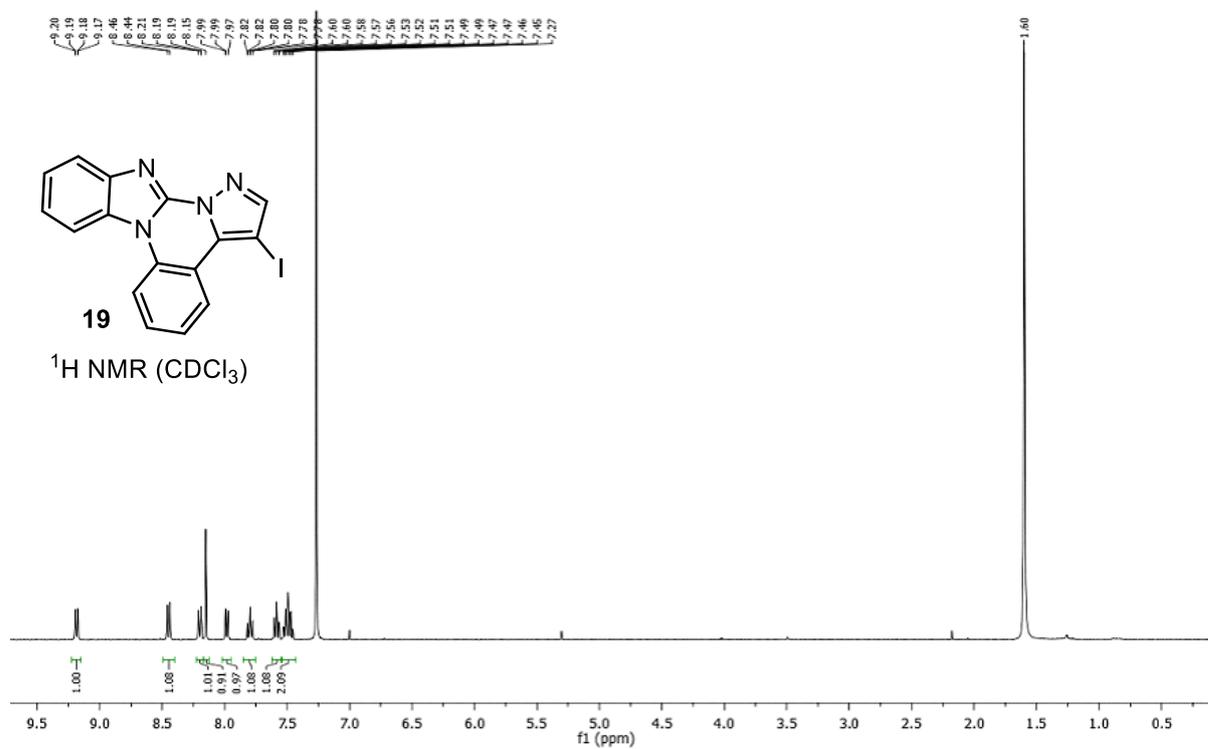
### 6.34 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 17:



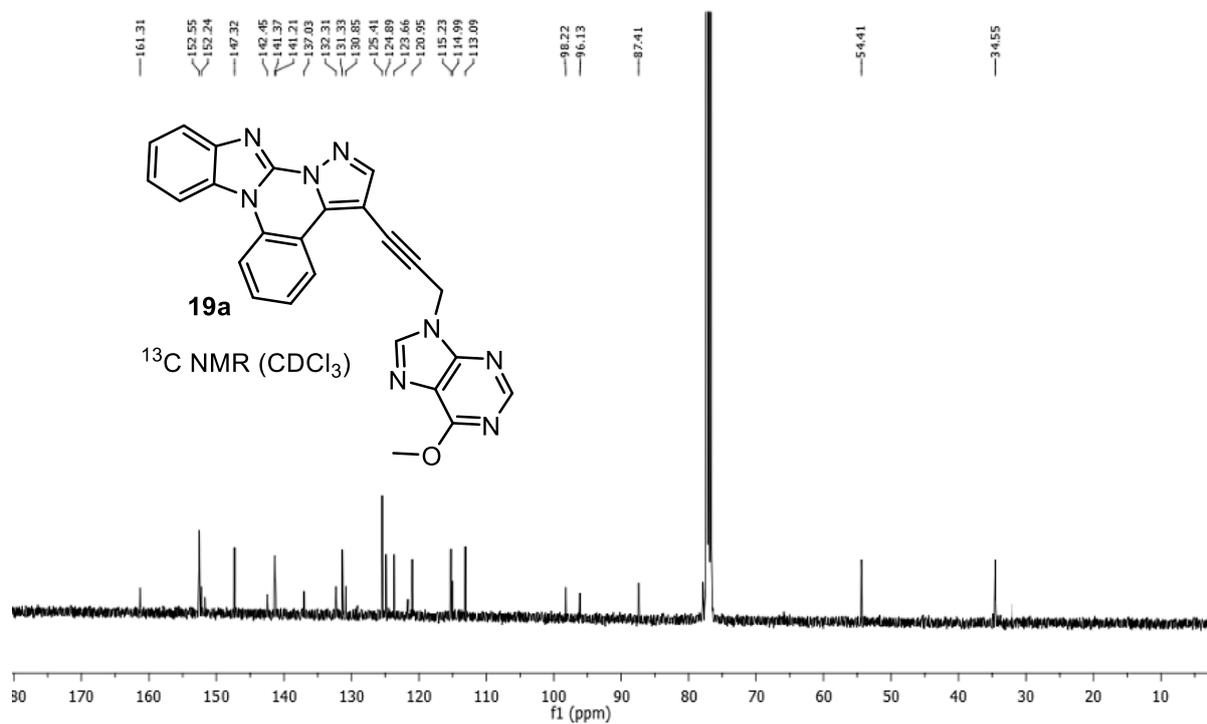
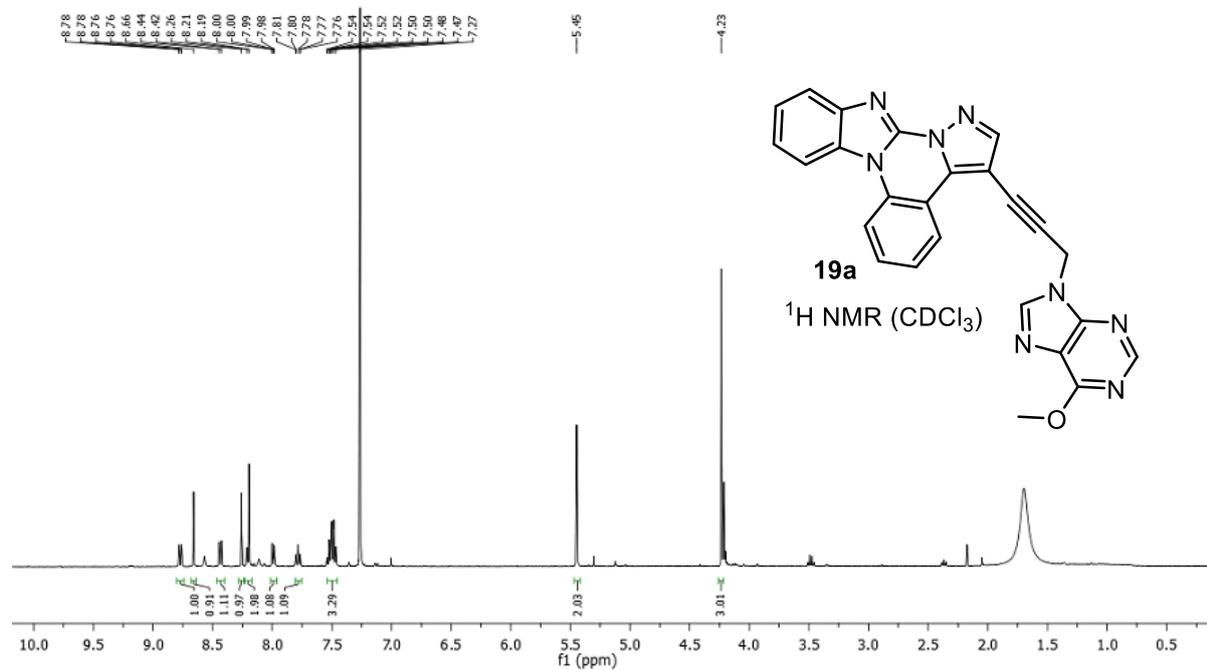
## 6.35 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 18:



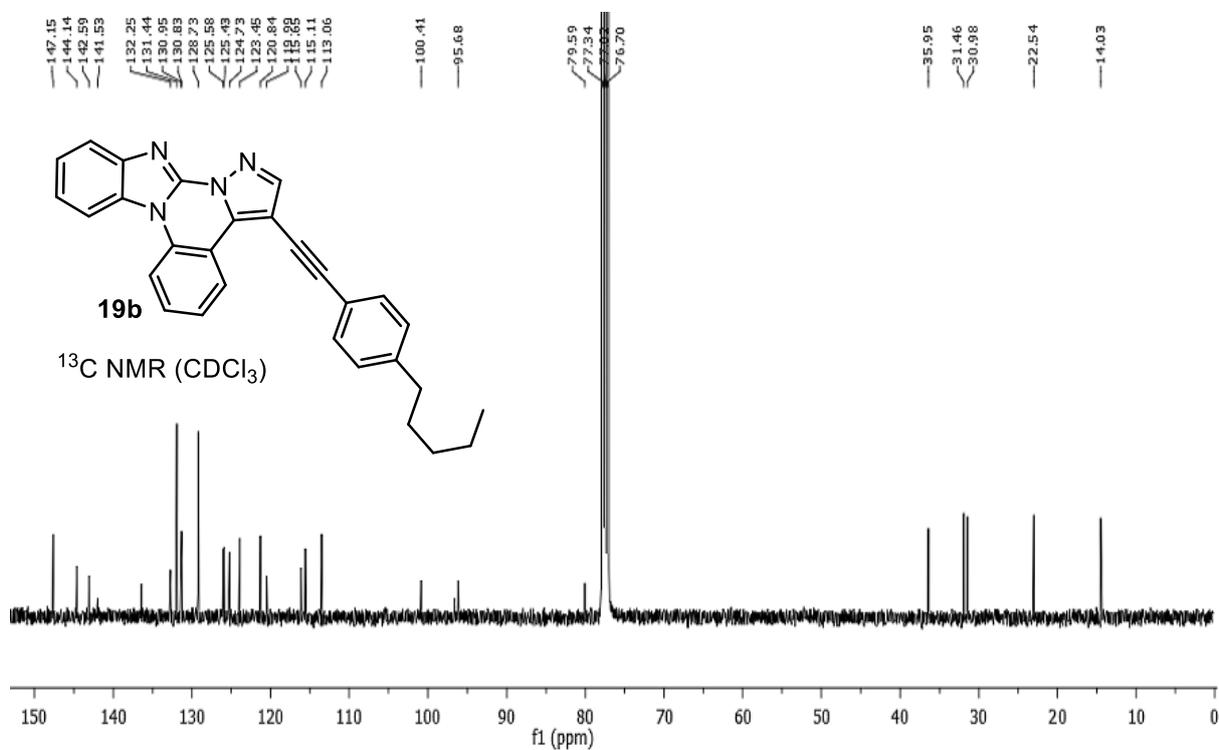
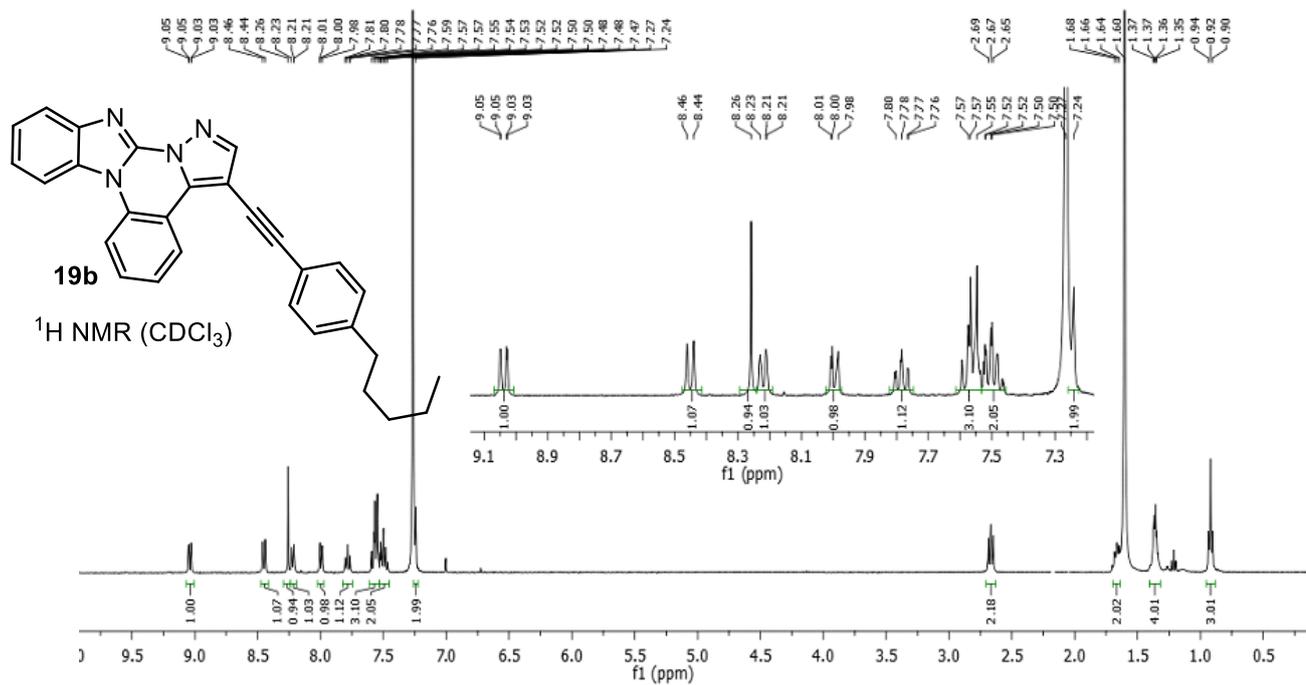
### 6.36 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 19:



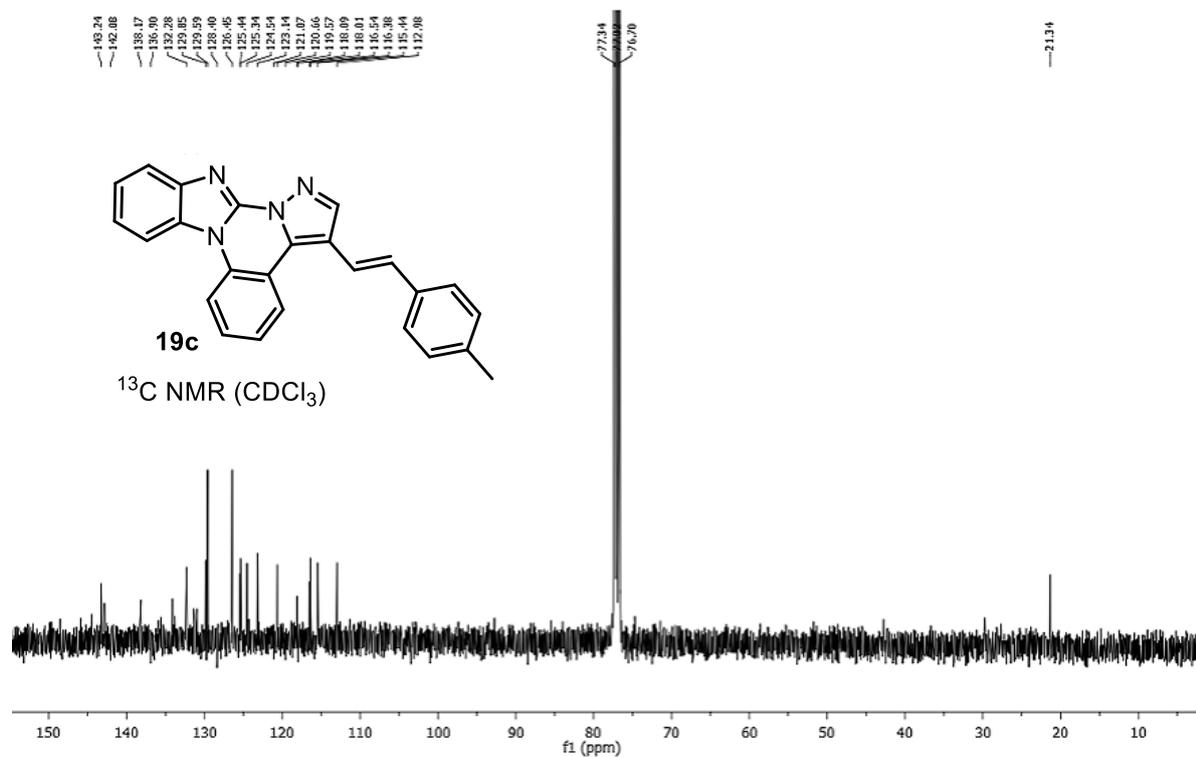
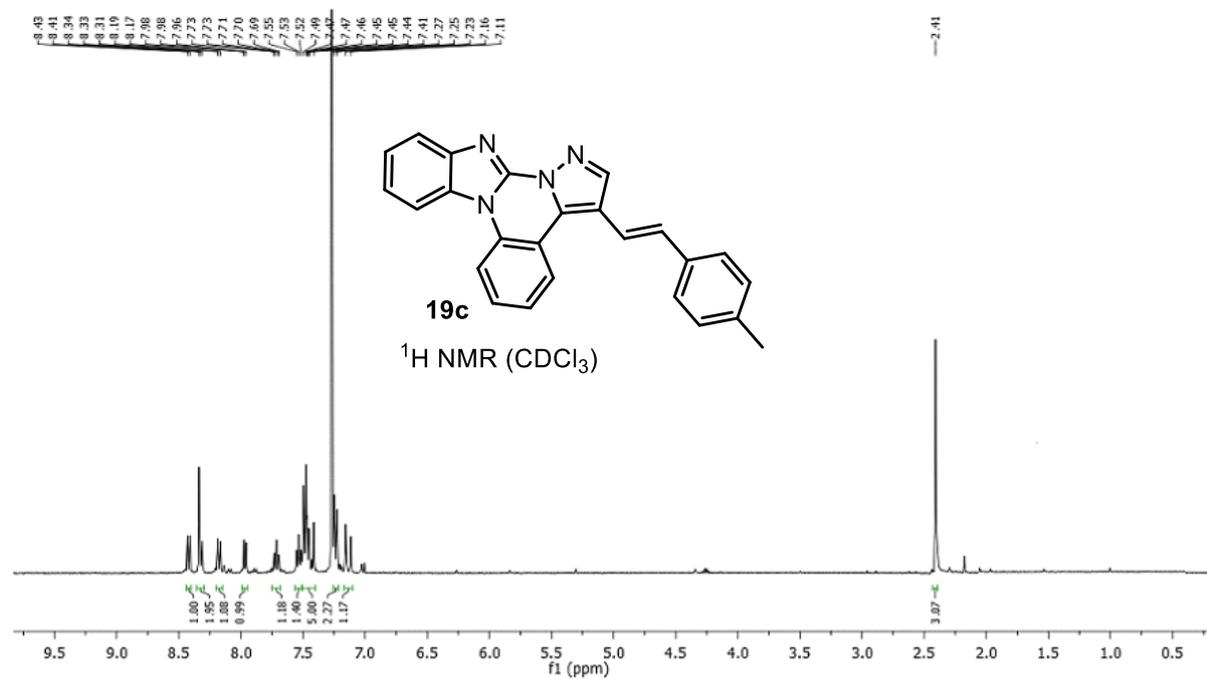
### 6.37 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 19a:



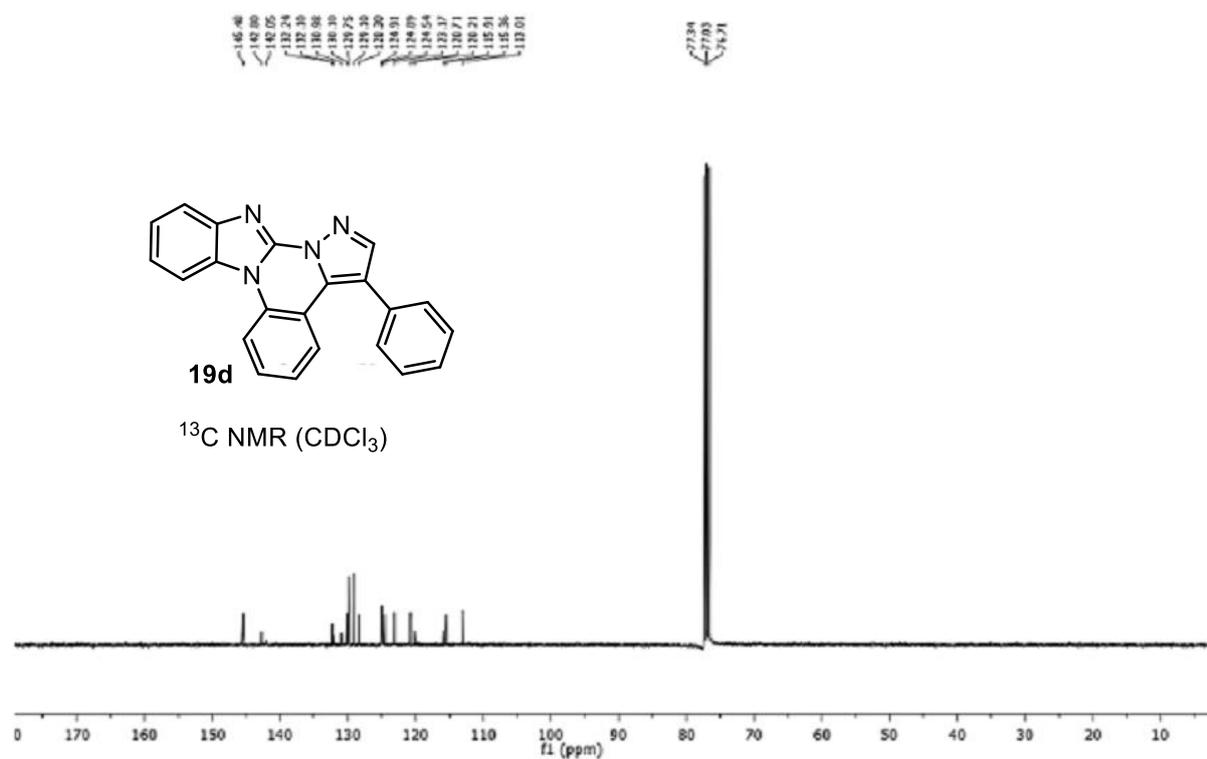
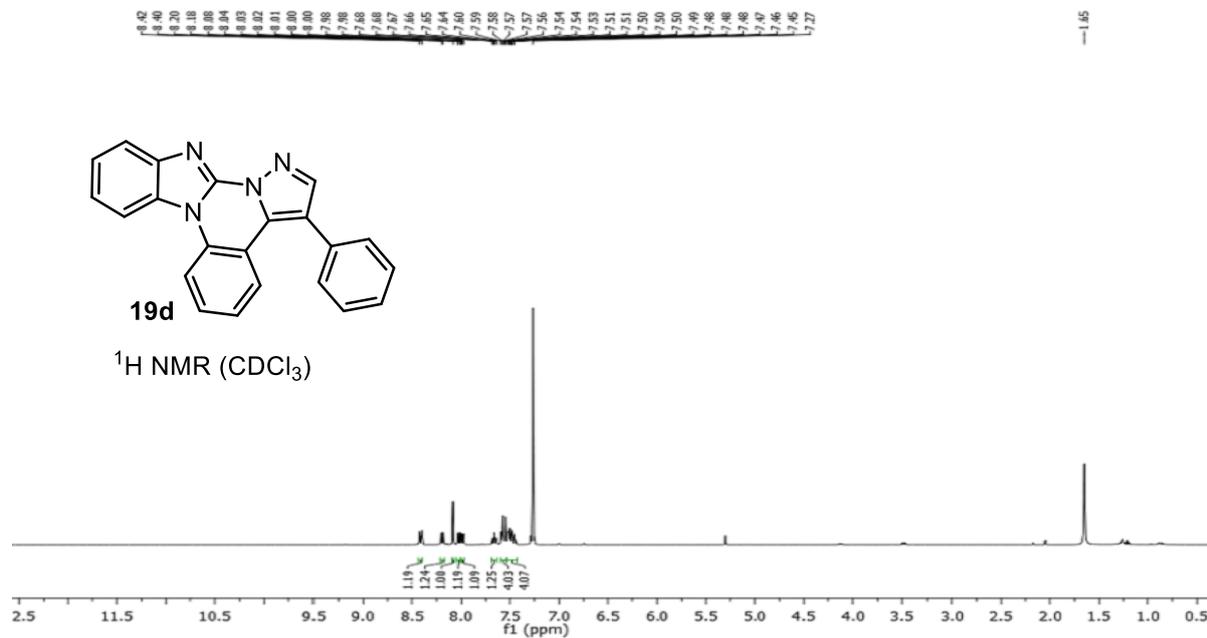
### 6.38 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 19b:



### 6.39 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 19c:



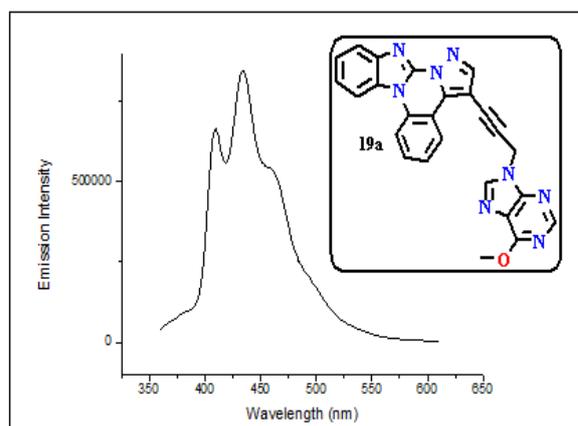
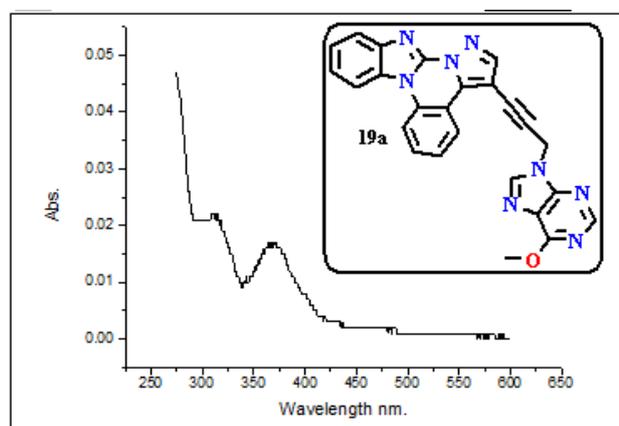
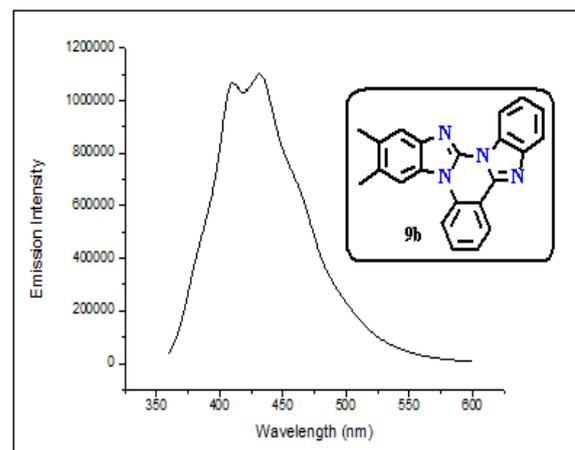
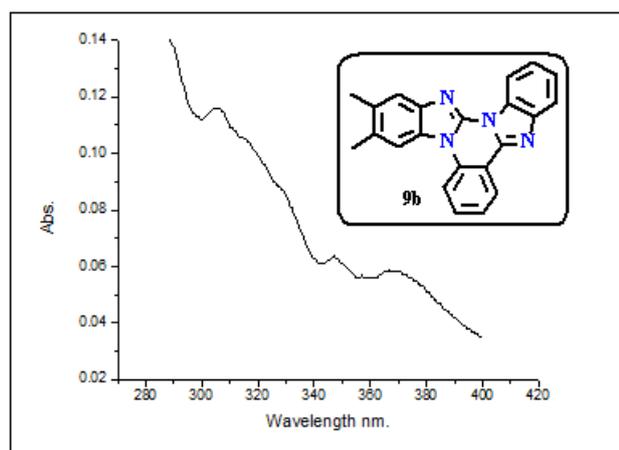
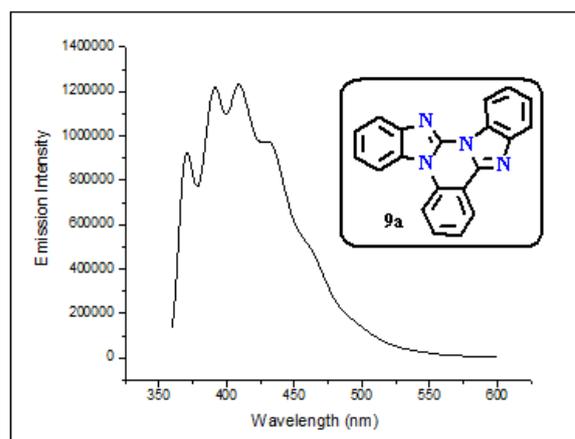
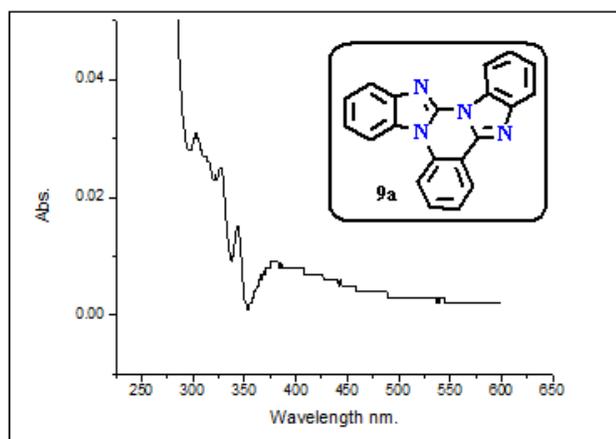
## 6.40 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 19d:

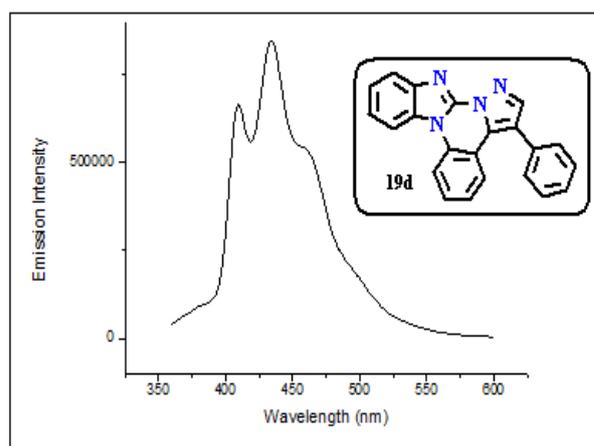
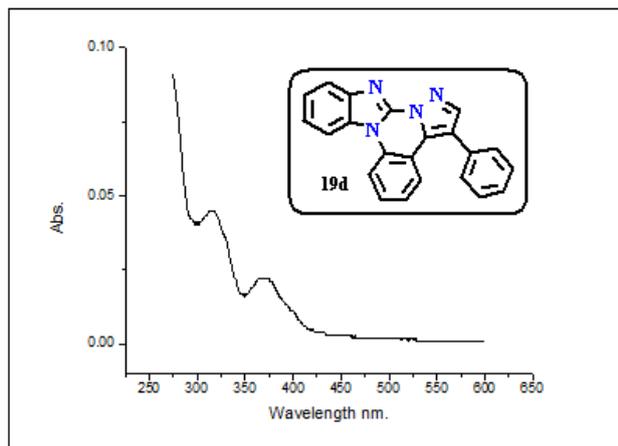
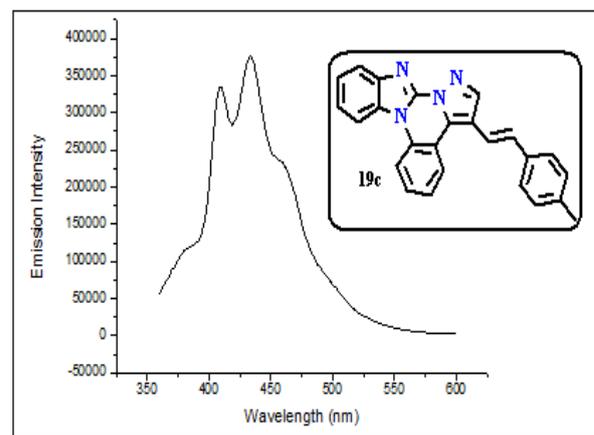
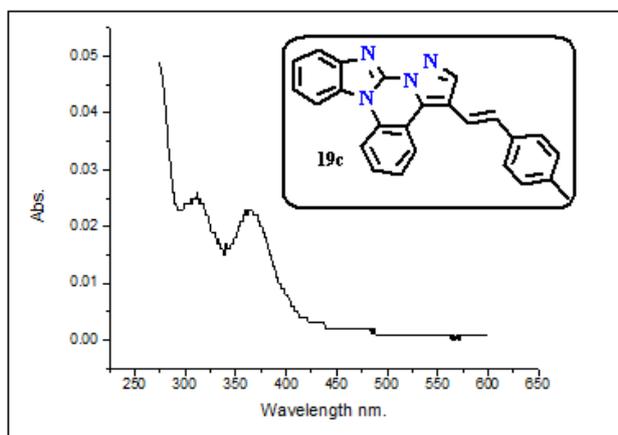
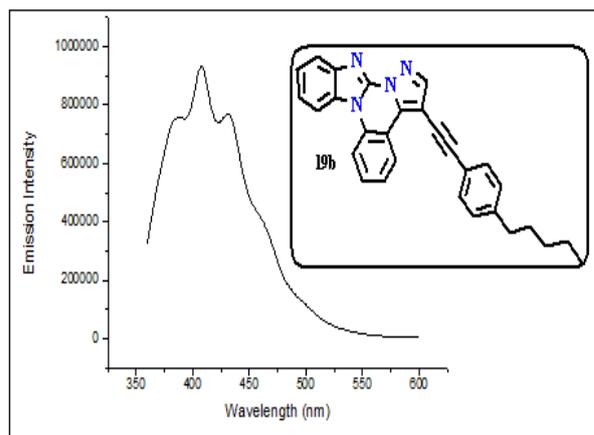
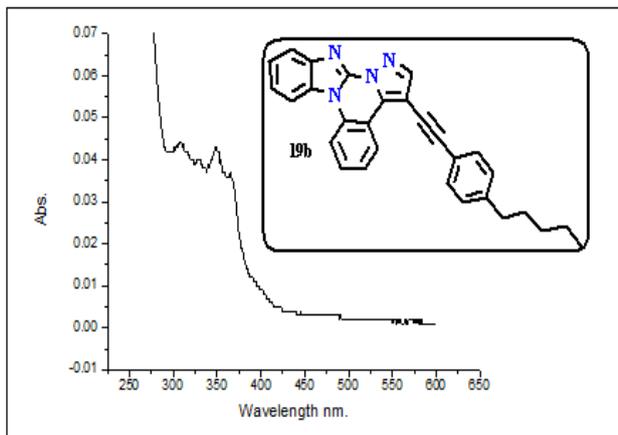




## 7. Photophysical Studies

UV-Vis and Emission spectres:





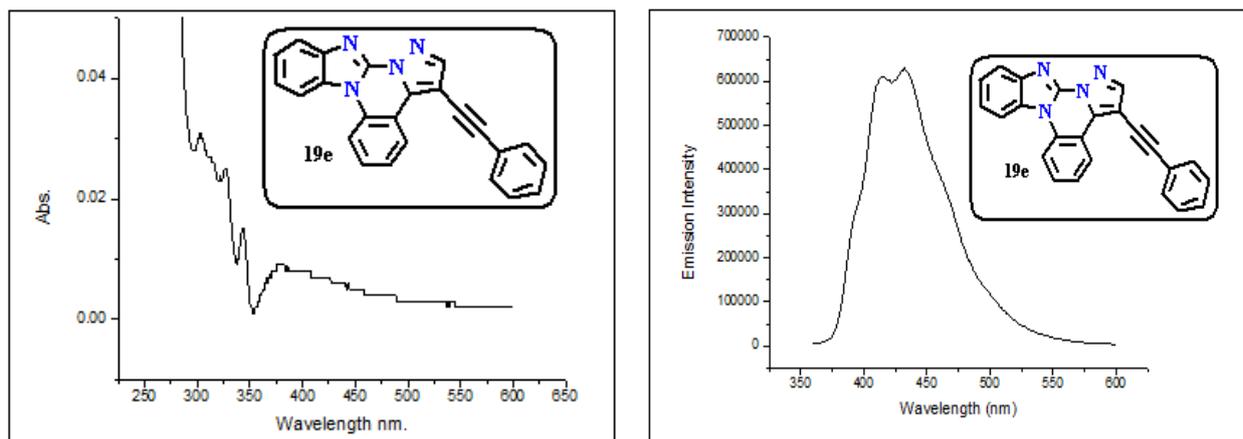


Figure S5 Absorption and fluorescence emission spectra in  $\text{CHCl}_3$  at  $5 \times 10^{-6}$  mol/L.