

## *Supporting Information*

# **Mn(I)-Catalyzed Nucleophilic Addition/Ring Expansion via C-H Activation and C-C Cleavage**

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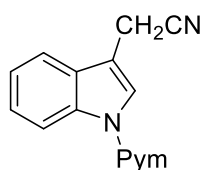
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## Experimental Section:

**General Considerations:** All the reactions were carried out under argon atmosphere using standard Schlenk technique. The  $^1\text{H}$  NMR spectra were recorded at 400 MHz or 600 MHz. The  $^{13}\text{C}$  NMR spectra were recorded at 150 MHz. The  $^{19}\text{F}$  NMR spectra were recorded at 565 MHz. Chemical shifts were expressed in parts per million ( $\delta$ ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), etc. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ( $\text{CDCl}_3$ :  $\delta$  H = 7.26 ppm,  $\delta$  C = 77.00 ppm). The coupling constants  $J$  were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using a MicroTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm). Column chromatography was performed on silica gel 200-300 mesh. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available. Commercial reagents were used without further purification. All the substrates *N*-pyrimidinylindoles<sup>1</sup> (**1a-1ba**), *N*-pyridinylindoles<sup>2</sup> (**1ca-1ea**), 2-benzofuranyl-pyridines<sup>3</sup> (**1fa** and **1ga**), propargy-1-3-diones<sup>4</sup> (**2a-2h**, **2n** and **2o**), ethyl 2-oxo-1-(prop-2-yn-1-yl)cyclopentane-1-carboxylate<sup>5</sup> (**2i**) were prepared according to the literatures.

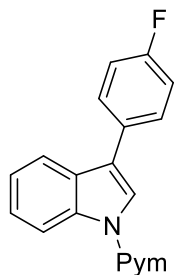
### Preparation of the Substrates



#### 2-(1-(pyrimidin-2-yl)-1H-indol-3-yl)acetonitrile (**1e**)

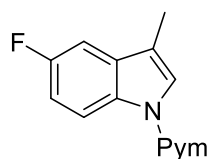
The title compound was isolated as a white solid. M.p.: 123-124 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J$  = 8.4 Hz, 1H), 8.71 (d,  $J$  = 4.8 Hz, 2H), 8.36 (s, 1H), 7.58 (d,  $J$  = 7.8 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.34 – 7.29 (m, 1H), 7.09 (t,  $J$  = 4.8 Hz, 1H), 3.86 (d,  $J$  = 1.2 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 157.4, 135.7, 129.2, 124.6, 124.4, 122.5, 118.1,

117.4, 116.7, 116.5, 108.9, 14.5. **HRMS (ESI):** Calcd for Chemical Formula: C<sub>14</sub>H<sub>10</sub>N<sub>4</sub> [M+H]<sup>+</sup> 235.0978, Found: 235.0976.



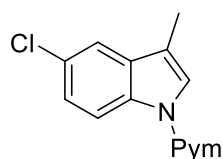
### 3-(4-fluorophenyl)-1-(pyrimidin-2-yl)-1H-indole (1d)

The title compound was isolated as a white solid. M.p.: 86-87 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.90 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 2H), 8.40 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.44 – 7.38 (m, 1H), 7.35 – 7.28 (m, 1H), 7.22 – 7.14 (m, 2H), 7.08 (t, *J* = 4.8 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 162.0 (d, *J* = 246.4 Hz), 158.1, 157.6, 136.0, 130.5 (d, *J* = 4.0 Hz), 129.4 (d, *J* = 8.0 Hz), 124.1, 122.9, 122.5, 120.9, 119.52, 116.6, 116.2, 115.8, 115.6. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -115.64 – -115.71 (m). **HRMS (ESI):** Calcd for Chemical Formula: C<sub>18</sub>H<sub>12</sub>N<sub>3</sub>F [M+H]<sup>+</sup> 290.1088, Found: 290.1082.



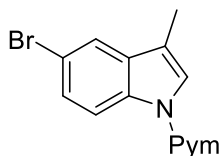
### 5-fluoro-3-methyl-1-(pyrimidin-2-yl)-1H-indole (1w)

The title compound was isolated as a white solid. M.p.: 67-68 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.72 (dd, *J* = 9.1, 4.8 Hz, 1H), 8.66 (d, *J* = 4.8 Hz, 2H), 8.07 (s, 1H), 7.19 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.08 – 7.03 (m, 1H), 7.01 (t, *J* = 4.8 Hz, 1H), 2.32 (d, *J* = 1.1 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 158.1, 157.5, 133.0 (*J* = 9.0 Hz), 132.0, 124.5, 117.2 (*J* = 9.0), 115.8 (*J* = 4.0 Hz), 115.7, 111.4, 111.1, 104.4, 104.1, 9.7. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -121.91 – -121.99 (m). **HRMS (ESI):** Calcd for Chemical Formula: C<sub>13</sub>H<sub>10</sub>FN<sub>3</sub> [M+H]<sup>+</sup> 228.0932, Found: 228.0939.



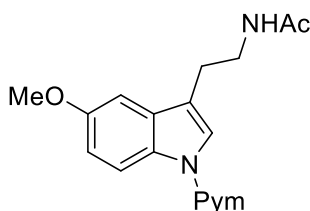
### 5-chloro-3-methyl-1-(pyrimidin-2-yl)-1H-indole (1x)

The title compound was isolated as a white solid. M.p.: 94-95 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.71 – 8.67 (m, 3H), 8.06 (s, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.29 (d, *J* = 1.8 Hz, 1H), 7.02 (t, *J* = 4.8 Hz, 1H), 2.32 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.1, 157.4, 133.9, 133.3, 127.4, 124.2, 123.7, 118.4, 117.3, 115.9, 115.4, 9.6. HRMS (ESI): Calcd for Chemical Formula: C<sub>13</sub>H<sub>10</sub>N<sub>3</sub>Cl [M+H]<sup>+</sup> 244.0636, Found: 244.0640.



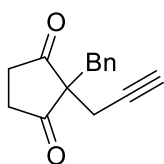
### 5-bromo-3-methyl-1-(pyrimidin-2-yl)-1H-indole (1y)

The title compound was isolated as a white solid. M.p.: 86-87 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 – 8.64 (m, 3H), 8.04 (d, *J* = 1.0 Hz, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.03 (t, *J* = 4.8 Hz, 1H), 2.31 (d, *J* = 1.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.1, 157.4, 134.3, 133.8, 126.3, 124.0, 121.5, 117.7, 115.9, 115.33, 115.1, 9.6. HRMS (ESI): Calcd for Chemical Formula: C<sub>13</sub>H<sub>10</sub>N<sub>3</sub>Br [M+H]<sup>+</sup> 288.0131, Found: 288.0135.



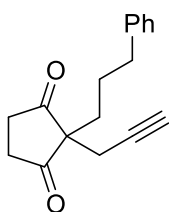
### N-(2-(5-methoxy-1-(pyrimidin-2-yl)-1H-indol-3-yl)ethyl)acetamide (1z)

The title compound was isolated as a white solid. M.p.: 136-137 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.69 – 8.64 m, 3H), 8.07 (m, 1H), 7.04 (m, 1H), 7.02 – 6.94 (m, 2H), 5.65 (m, 1H), 3.89 (m, 3H), 3.64 – 3.61 (m, 2H), 2.97 – 2.94 (m, 2H), 1.94 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.1, 158.1, 157.4, 155.5, 131.8, 130.6, 123.7, 117.3, 117.1, 115.7, 112.8, 101.2, 55.7, 39.2, 25.2, 23.4. HRMS (ESI): Calcd for Chemical Formula: C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>N<sub>4</sub> [M+H]<sup>+</sup> 311.1503, Found: 311.1500.



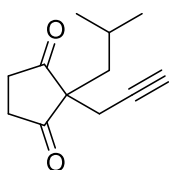
### 2-benzyl-2-(prop-2-yn-1-yl)cyclopentane-1,3-dione (2c)

The title compound was isolated as a white solid from 2-benzylcyclopentane-1,3-dione and propargyl bromide. M.p.: 48-50 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 7.20 (m, 3H), 7.02 (dd,  $J = 7.5, 1.7$  Hz, 2H), 2.93 (s, 2H), 2.58 (d,  $J = 2.6$  Hz, 2H), 2.55 (d,  $J = 7.0$  Hz, 1H), 2.52 (d,  $J = 6.6$  Hz, 1H), 2.04 (d,  $J = 6.5$  Hz, 1H), 2.01 (d,  $J = 7.0$  Hz, 1H), 1.95 (t,  $J = 2.6$  Hz, 1H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  216.1, 134.8, 129.6, 128.7, 127.4, 78.6, 70.9, 61.5, 41.8, 37.0, 24.2. **HRMS (ESI)**: Calcd for Chemical Formula:  $\text{C}_{15}\text{H}_{14}\text{O}_2$   $[\text{M}+\text{H}]^+$  227.1067, Found: 227.1066.



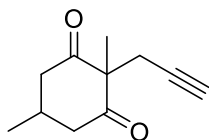
### 2-(3-phenylpropyl)-2-(prop-2-yn-1-yl)cyclopentane-1,3-dione (2d)

The title compound was isolated as a white solid from 2-(3-phenylpropyl)cyclopentane-1,3-dione and propargyl bromide. M.p.: 64-65 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (t,  $J = 7.5$  Hz, 2H), 7.17 (t,  $J = 7.4$  Hz, 1H), 7.08 (d,  $J = 7.2$  Hz, 2H), 2.80 – 2.67 (m, 4H), 2.51 (t,  $J = 7.7$  Hz, 2H), 2.43 (d,  $J = 2.6$  Hz, 2H), 1.96 (t,  $J = 2.6$  Hz, 1H), 1.68 – 1.63 (m, 2H), 1.46 – 1.39 (m, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  215.6, 140.9, 126.0, 78.6, 70.8, 59.4, 36.6, 35.8, 34.6, 26.4, 23.7. **HRMS (ESI)**: Calcd for Chemical Formula:  $\text{C}_{17}\text{H}_{18}\text{O}_2$   $[\text{M}+\text{H}]^+$  255.1380, Found: 255.1381.



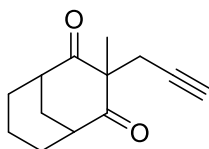
### 2-isobutyl-2-(prop-2-yn-1-yl)cyclopentane-1,3-dione (2e)

The title compound was isolated as a white solid from 2-isobutylcyclopentane-1,3-dione and propargyl bromide. M.p.: 43-44 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  2.70 (s, 4H), 2.29 (d,  $J = 2.6$  Hz, 2H), 1.92 (t,  $J = 2.6$  Hz, 1H), 1.53 (d,  $J = 6.8$  Hz, 2H), 1.42 (dt,  $J = 13.4, 6.7$  Hz, 1H), 0.65 (d,  $J = 6.7$  Hz, 6H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  215.8, 78.2, 70.9, 59.0, 43.9, 36.4, 25.9, 24.9, 23.4. **HRMS (ESI)**: Calcd for Chemical Formula:  $\text{C}_{12}\text{H}_{16}\text{O}_2$   $[\text{M}+\text{H}]^+$  193.1223, Found: 193.1223.



### 2,5-dimethyl-2-(prop-2-yn-1-yl)cyclohexane-1,3-dione (2g)

The title compound (dr = 1:1.1) was isolated as a white solid from 2,5-dimethylcyclohexane-1,3-dione and propargyl bromide. M.p.: 40-42 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  2.85 (dd,  $J = 15.8, 4.5$  Hz, 1H), 2.71 (dd,  $J = 15.3, 3.9$  Hz, 1H), 2.63 (s, 2H), 2.52 – 2.40 (m, 2H), 2.30 – 2.07 (m, 1H), 1.96 (d,  $J = 24.4$  Hz, 1H), 1.31 (d,  $J = 15.0$  Hz, 3H), 1.09 (dd,  $J = 20.6, 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  208.7, 208.5, 80.7, 80.1, 70.9, 70.3, 63.3, 63.2, 46.2, 46.1, 25.0, 25.0, 24.8, 23.7, 23.1, 21.9, 21.4, 20.8. HRMS (ESI): Calcd for Chemical Formula:  $\text{C}_{10}\text{H}_{12}\text{O}_2$   $[\text{M}+\text{H}]^+$  165.0910, Found: 165.1908.



### 3-methyl-3-(prop-2-yn-1-yl)bicyclo[3.3.1]nonane-2,4-dione (2h)

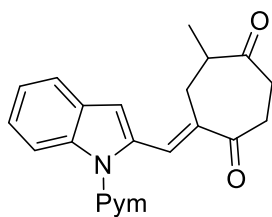
The title compound was isolated as a white solid from 2,5-dimethylcyclohexane-1,3-dione and propargyl bromide. M.p.: 40-42 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.77 – 2.65 (m, 3H), 2.54 (d,  $J = 2.7$  Hz, 2H), 2.04 – 1.95 (m, 1H), 1.83 – 1.68 (m, 2H), 1.66 – 1.57 (m, 1H), 1.24 (s, 3H), 1.19 – 1.13 (m, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  214.7, 79.0, 71.9, 60.7, 43.4, 31.4, 28.6, 26.3, 20.7, 19.6. HRMS (ESI): Calcd for Chemical Formula:  $\text{C}_{13}\text{H}_{16}\text{O}_2$   $[\text{M}+\text{H}]^+$  205.1223, Found: 205.1222.

## General Procedure for Mn(I) catalyzed ring expansion cascade

Conditions A (Standard conditions): A mixture of substituted *N*-pyrimidinylindoles or 2-benzofuranyl-pyridines **1** (0.2 mmol, 1 equiv), propargyl-1-3-diones **2** (0.4 mmol, 2.0 equiv), MnBr(CO)<sub>5</sub> (5.5 mg, 10.0 mol %), KOH (2.8 mg, 25.0 mol %) were weighted in a Schlenk tube equipped with a stir bar. TFE (2.0 mL) was added and the mixture was stirred at 120 °C for 15 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:2 and EtOAc/DCM = 1:20).

Conditions B: A mixture of *N*-pyrimidinylindoles **1** (0.2 mmol, 1 equiv), **2** (0.4 mmol, 2.0 equiv), MnBr(CO)<sub>5</sub> (5.5 mg, 10.0 mol %) were weighted in a Schlenk tube equipped with a stir bar. TFE (0.50 mL), DCM (1.50 mL) and Cy<sub>2</sub>NH (9.1 mg, 25 mol %) was added and the mixture was stirred at 100 °C for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:2 and EtOAc/DCM = 1:20).

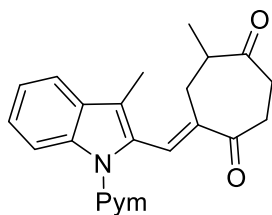
## Preparation and Characterization of Products



**(E)-5-methyl-7-((1-(pyrimidin-2-yl)-1*H*-indol-2-yl)methylene)cycloheptane-1,4-dione (3aa)**

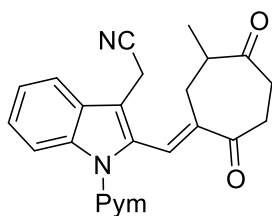
The title compound was isolated as a pale yellow solid (conditions A: 42.1 mg, 60%). M.p.: 152-153 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.94 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.35 (m, 1H), 7.29 – 7.25 (m, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 6.80 (s, 1H), 3.25 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.82 – 2.64 (m, 4H), 1.27 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.1, 201.1, 158.3, 157.4, 137.1, 134.4, 134.0, 131.3, 128.7, 125.1, 122.6, 121.1, 117.5, 114.3, 110.6, 46.6, 38.31, 37.6,

32.3, 16.0. **HRMS (ESI):** Calcd for Chemical Formula: C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 346.1550, Found: 346.1552.



**(E)-5-methyl-7-((3-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ba)**

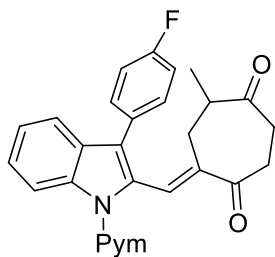
The title compound was isolated as a white solid (conditions A: 55.0 mg, 77%). M.p.: 84-85 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.67 (d, *J* = 4.8 Hz, 2H), 8.56 (d, *J* = 8.3 Hz, 1H), 7.83 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.30 – 7.25 (m, 1H), 7.06 (t, *J* = 4.8 Hz, 1H), 2.87 2.74 (m, 4H), 2.71 2.64 (m, 2H), 2.52 (dd, *J* = 14.8, 9.9 Hz, 1H), 2.23 (d, *J* = 0.9 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 211.5, 201.2, 157.9, 157.8, 136.7, 135.4, 133.7, 131.1, 130.4, 124.7, 122.1, 119.1, 116.7, 116.5, 114.9, 46.3, 37.96, 37.7, 32.4, 16.4, 10.1. **HRMS (ESI):** Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub> [M+Na]<sup>+</sup> 360.1707, Found: 360.1705.



**(E)-2-(2-((6-methyl-2,5-dioxocycloheptylidene)methyl)-1-(pyrimidin-2-yl)-1H-indol-3-yl)acetonitrile (3ca)**

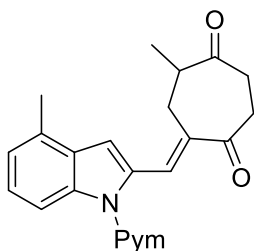
The title compound was isolated as a pale yellow solid (conditions A: 31.2 mg, 41%). M.p.: 120-121 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.72 (d, *J* = 4.8 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.74 (m, 2H), 7.46 – 7.40 (m, 1H), 7.39 – 7.34 (m, 1H), 7.16 (t, *J* = 4.8 Hz, 1H), 3.70 (s, 2H), 2.90 – 2.84 (m, 2H), 2.80 – 2.75 (m, 2H), 2.69 – 2.61 (m, 2H), 2.52 (dd, *J* = 14.8, 9.8 Hz, 1H), 0.95 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C (151 MHz, CDCl<sub>3</sub>) δ 210.8, 200.7, 158.1, 157.4, 138.3, 136.5, 132.3, 131.5, 127.9, 125.3, 123.0, 118.6, 117.5, 116.6, 115.3, 108.1, 46.1, 37.6, 37.5, 32.2, 16.3, 14.0. **HRMS (ESI):** Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub> [M+H]<sup>+</sup> 385.1659 Found: 385.1658.





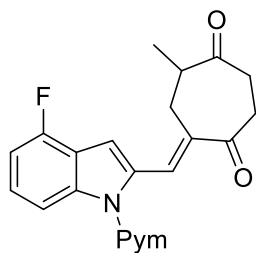
**(E)-5-((3-(4-fluorophenyl)-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3da)**

The title compound was isolated as a white solid (conditions A: 60.6 mg, 69%, *E/Z* = 7.8:1). M.p.: 98-99 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.55 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 7.32 – 7.27 (m, 1H), 7.18 – 7.11 (m, 3H), 2.71 – 2.55 (m, 3H), 2.52 – 2.42 (m, 1H), 2.40 – 2.29 (m, 1H), 2.11 – 1.92 (m, 2H), 1.15 (d, *J* = 6.6 Hz, 0.35H, minor), 0.77 (d, *J* = 6.2 Hz, 2.72H, major). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) for the major *E* isomer: δ 211.2, 201.0, 159.4 (d, *J* = 282.3 Hz), 158.1, 158.0, 157.7, 136.8, 136.4, 132.2, 131.3 (d, *J* = 7.9 Hz), 130.8, 129.84, 129.8 (d, *J* = 3.5 Hz), 128.7, 124.9, 122.8, 121.2, 119.4, 117.3, 115.9, 115.7, 114.8, 45.3, 37.9, 37.5, 32.3, 16.3. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -114.10 – -114.15 (m). HRMS (ESI): Calcd for C<sub>27</sub>H<sub>22</sub>FN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 440.1769, Found: 440.1769.



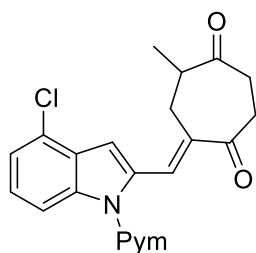
**(E)-5-methyl-7-((4-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ea)**

The title compound was isolated as a white solid (conditions A: 41.1 mg, 57%, *E/Z* = 13.2:1). M.p.: 90-91 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.88 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.03 (s, 1H), 7.34 (dd, *J* = 9.7, 6.0 Hz, 1H), 7.26 (t, *J* = 4.8 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.89 (s, 1H), 3.34 (dd, *J* = 15.2, 2.5 Hz, 1H), 3.03 – 2.92 (m, 2H), 2.90 – 2.78 (m, 3H), 2.78 – 2.71 (m, 1H), 2.66 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.0, 201.0, 158.3, 157.5, 137.0, 134.21, 133.5, 131.4, 130.5, 128.5, 125.2, 122.9, 117.5, 111.8, 109.1, 46.7, 38.4, 37.7, 32.3, 18.5, 15.7. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 360.1707, Found: 360.1705.



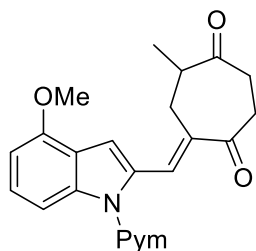
**(E)-5-((4-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3fa)**

The title compound was isolated as a pale yellow solid (conditions A: 43.7 mg, 60%). M.p.: 152-153 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.90 (s, 1H), 7.30 – 7.26 (m, 1H), 7.24 (t, *J* = 4.8 Hz, 1H), 6.94 (dd, *J* = 9.3, 8.2 Hz, 1H), 6.87 (s, 1H), 3.24 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.96 – 2.84 (m, 2H), 2.84 – 2.71 (m, 3H), 2.71 – 2.65 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 210.9, 201.0, 158.4, 156.8, 156.3 (d, *J* = 249.2 Hz), 139.2 (d, *J* = 9.1 Hz), 135.3, 134.2, 130.8, 125.6 (d, *J* = 9.1 Hz), 118.2, 118.1, 117.9, 110.5 (d, *J* = 4.5 Hz), 107.4 (d, *J* = 18.1 Hz), 105.7, 46.6, 38.3, 37.7, 32.3, 15.9. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -121.80 – -121.82 (m). HRMS (ESI): Calcd for C<sub>21</sub>H<sub>18</sub>FN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 364.1456, Found:364.1457.



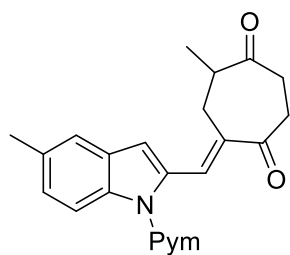
**(E)-5-((4-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3ga)**

The title compound was isolated as a white solid (conditions A: 31.5 mg, 42%, *E/Z* = 17.2:1). M.p.: 167-168 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.33 – 8.25 (m, 1H), 7.92 (s, 1H), 7.28 – 7.23 (m, 3H), 6.90 (s, 1H), 3.26 (dd, *J* = 15.0, 2.4 Hz, 1H), 2.99 – 2.85 (m, 2H), 2.84 – 2.75 (m, 2H), 2.74 – 2.64 (m, 2H), 1.30 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 210.8, 201.0, 158.5, 157.3, 137.7, 135.5, 134.7, 130.7, 127.6, 126.2, 125.5, 122.3, 118.0, 113.0, 108.4, 46.7, 38.4, 37.7, 32.3, 15.7. HRMS (ESI): Calcd for C<sub>21</sub>H<sub>18</sub>ClN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 380.1160, Found: 380.1160.



**(E)-5-((4-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3ha)**

The title compound was isolated as a pale yellow solid (conditions A: 45.1 mg, 60%, *E/Z* = 5:1). M.p.: 67-70 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.77 (d, *J* = 4.8 Hz, 0.39H, minor), 7.95 – 7.93 (m, 2H), 7.31 – 7.26 (m, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.15 (t, *J* = 4.8 Hz, 0.21H, minor), 6.99 (s, 0.19H, minor), 6.96 (s, 1H), 6.83 (s, 0.18H, minor), 6.67 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 0.20H, minor), 3.98 (s, 3H), 3.94 (s, 0.63H, minor), 3.27 (dd, *J* = 15.1, 2.4 Hz, 1H), 2.96 – 2.84 (m, 2H), 2.82 – 2.73 (m, 3H), 2.72 – 2.65 (m, 1H), 1.29 (d, *J* = 6.7 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 0.61H, minor). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for the *E* isomer (major) δ 211.2, 201.1, 158.3, 157.6, 153.3, 138.5, 134.1, 132.7, 131.2, 126.1, 125.2, 119.6, 117.6, 107.9, 107.2, 107.2, 102.3, 55.4, 46.6, 38.3, 37.7, 32.3, 15.9. for the *Z* isomer (minor) δ 212.0, 206.0, 158.1, 157.9, 153.1, 138.1, 137.3, 132.4, 125.2, 117.1, 107.9, 102.4, 55.3, 46.2, 38.5, 38.1, 37.3, 15.5. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 376.1656, Found: 376.1646.

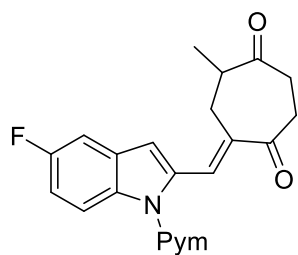


**(E)-5-methyl-7-((5-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ia)**

The title compound was isolated as a white solid (conditions A: 41.0 mg, 57%). M.p.: 140-141 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 8.6 Hz, 1H), 7.96 (s, 1H), 7.44 (s, 1H), 7.21 – 7.15 (m, 2H), 6.72 (s, 1H), 3.23 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.94 – 2.82 (m, 2H), 2.81 – 2.74 (m, 2H), 2.74 – 2.64 (m, 2H), 2.47 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.2, 201.1, 158.3, 157.5, 135.5, 134.1, 134.0,

132.1, 131.6, 129.0, 126.7, 120.8, 117.3, 114.1, 110.5, 46.6, 38.4, 37.6, 32.3, 21.3, 15.9.

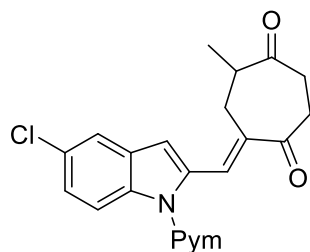
**HRMS (ESI):** Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 360.1707, Found: 360.1705



**(E)-5-((5-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-me**

**thylcycloheptane-1,4-dione (3ja)**

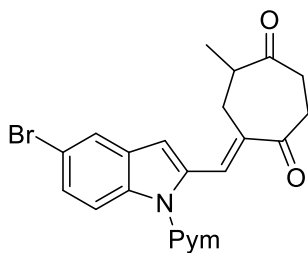
The title compound was isolated as a white solid (conditions A: 47.1 mg, 65%). M.p.: 147-148 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.38 (dd, *J* = 9.1, 4.6 Hz, 1H), 7.92 (s, 1H), 7.30 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.22 (t, *J* = 4.8 Hz, 1H), 7.09 (td, *J* = 9.1, 2.6 Hz, 1H), 6.73 (s, 1H), 3.22 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.95 – 2.84 (m, 2H), 2.83 – 2.77 (m, 2H), 2.75 – 2.65 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.0, 201.1, 159.1 (d, *J* = 238.6 Hz), 158.3, 157.3, 135.5, 134.9, 133.5, 131.2, 129.4 (d, *J* = 10.1 Hz), 117.6, 115.7 (d, *J* = 7.6 Hz), 113.2, 112.0, 110.0 (d, *J* = 4.5 Hz), 105.9 (d, *J* = 22.7 Hz), 46.6, 38.3, 37.6, 32.2, 16.0. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -120.79 – -120.85 (m). **HRMS (ESI):** Calcd for C<sub>21</sub>H<sub>18</sub>FN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 364.1456, Found: 364.1457



**4(E)-5-((5-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-**

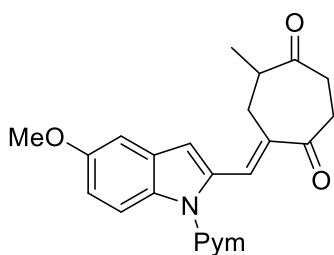
**methylcycloheptane-1,4-dione (3ka)**

The title compound was isolated as a white solid (conditions A: 36.0 mg, 47%). M.p.: 170-171 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.36 (d, *J* = 8.9 Hz, 1H), 7.91 (s, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.30 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.22 (t, *J* = 4.8 Hz, 1H), 6.71 (s, 1H), 3.21 (dd, *J* = 15.2, 2.7 Hz, 1H), 2.94 – 2.89 (m, 1H), 2.88 – 2.76 (m, 3H), 2.74 – 2.65 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 210.9, 201.0, 158.4, 157.3, 135.4, 135.3, 135.1, 131.1, 129.8, 128.1, 125.1, 120.4, 117.8, 115.7, 109.5, 46.6, 38.3, 37.6, 32.3, 16.0. **HRMS (ESI):** Calcd for C<sub>21</sub>H<sub>18</sub>ClN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 380.1160, Found: 380.1159.



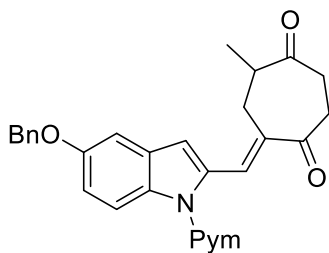
**(E)-5-((5-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3la)**

The title compound was isolated as a white solid (conditions A: 51.7mg, 61%). M.p.: 99-100 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 4.7 Hz, 2H), 8.28 (d, *J* = 8.9 Hz, 1H), 7.89 (s, 1H), 7.76 (d, *J* = 1.8 Hz, 1H), 7.41 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.21 (t, *J* = 4.7 Hz, 1H), 6.68 (s, 1H), 3.18 (dd, *J* = 15.2, 2.5 Hz, 1H), 2.93 – 2.88 (m, 1H), 2.86 – 2.74 (m, 3H), 2.72 – 2.64 (m, 2H), 1.24 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 210.9, 201.0, 158.4, 157.2, 135.7, 135.1, 130.9, 130.4, 127.7, 123.4, 117.8, 116.0, 115.7, 109.3, 46.5, 38.2, 37.6, 32.2, 16.0. HRMS (ESI): Calcd for C<sub>21</sub>H<sub>18</sub>BrN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 424.0655, Found: 424.0647.



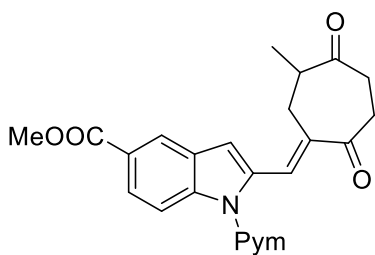
**(E)-5-((5-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3ma)**

The title compound was isolated as a pale yellow solid (conditions A: 41.7 mg, 56%). M.p.: 110-111 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.32 (d, *J* = 9.1 Hz, 1H), 7.95 (s, 1H), 7.16 (t, *J* = 4.8 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.99 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.71 (s, 1H), 3.87 (s, 3H), 3.22 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.94 – 2.82 (m, 2H), 2.80 – 2.74 (m, 2H), 2.74 – 2.63 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.1, 201.1, 158.2, 157.4, 155.8, 134.4, 134.1, 132.1, 131.5, 129.4, 117.2, 115.5, 114.9, 110.4, 102.3, 55.6, 46.6, 38.3, 37.6, 32.2, 16.0. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 376.1656, Found: 376.1656



**(E)-5-((5-(benzyloxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3na)**

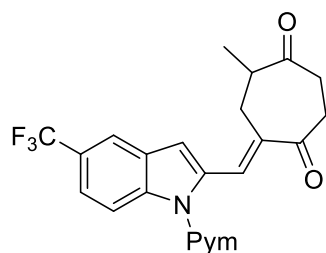
The title compound was isolated as a pale yellow solid (conditions A: 52.4 mg, 58%, E/Z = 7.7:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.73 (d, *J* = 4.8 Hz, 0.30H, minor), 8.34 (d, *J* = 9.1 Hz, 1H), 7.96 (s, 1H), 7.47 (t, *J* = 6.3 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 7.17 – 7.14 (m, 2H), 7.11 – 7.05 (m, 1H), 7.00 (dd, *J* = 9.1, 2.6 Hz, 0.15H, minor), 6.87 (s, 0.13H, minor), 6.80 (s, 0.13H, minor), 6.71 (s, 1H), 5.14 (s, 2H), 5.11 (s, 0.27H, minor), 3.22 (dd, *J* = 15.0, 2.5 Hz, 1H), 2.96 – 2.81 (m, 2H), 2.80 – 2.73 (m, 2H), 2.73 – 2.62 (m, 2H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.21 (d, *J* = 6.6 Hz, 0.43H, minor). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) for the E isomer (major): δ 211.1, 201.1, 158.2, 158.0, 157.5, 155.0, 137.2, 134.6, 134.2, 132.3, 131.6, 129.4, 128.5, 127.9, 127.4, 117.3, 115.6, 115.55, 110.5, 103.9, 70.5, 46.6, 38.3, 37.6, 32.3, 16.0. for the Z isomer (minor): δ 212.0, 206.2, 154.8, 137.4, 137.3, 134.4, 132.0, 129.7, 128.5, 127.8, 125.3, 116.8, 115.5, 111.0, 104.2, 70.5, 46.1, 38.5, 38.1, 37.3, 15.5. HRMS (ESI): Calcd for C<sub>28</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 452.1969, Found: 452.1972.



**methyl (E)-2-((6-methyl-2,5-dioxocycloheptylidene)methyl)-1-(pyrimidin-2-yl)-1H-indole-5-carboxylate (30a)**

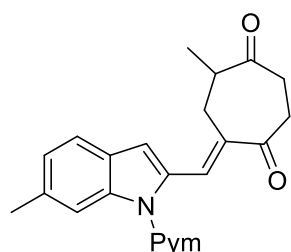
The title compound was isolated as a white solid (conditions A: 48.6 mg, 60%, E/Z = 20:1). M.p.: 77-78 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.40 – 8.35 (m, 2H), 8.02 (dd, *J* = 9.0, 1.6 Hz, 1H), 7.88 (s, 1H), 7.25 (t, *J* = 4.9 Hz, 1H), 6.84 (s, 1H), 3.94 (s, 3H), 3.21 (dd, *J* = 15.1, 2.5 Hz, 1H), 2.95 – 2.82 (m, 2H), 2.81 – 2.73 (m, 2H), 2.73 – 2.62 (m, 2H), 1.26 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 210.8, 200.9, 167.4, 158.5, 157.2,

139.5, 135.5, 135.4, 130.7, 128.4, 126.0, 124.5, 123.6, 118.1, 114.1, 110.8, 52.0, 46.5, 38.2, 37.6, 32.3, 16.0. **HRMS (ESI):** Calcd for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup> 404.1605, Found: 404.1603



**(E)-5-methyl-7-((1-(pyrimidin-2-yl)-5-(trifluoromethyl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3pa)**

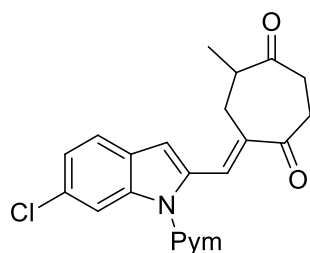
The title compound was isolated as a white solid (conditions A: 52.2 mg, 63%). M.p.: 118-119 °C. **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.84 (d, *J* = 4.6 Hz, 2H), 8.47 (d, *J* = 8.8 Hz, 1H), 7.95 (s, 1H), 7.90 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.26 (m, 1H), 6.83 (s, 1H), 3.21 (d, *J* = 13.9 Hz, 1H), 2.98 – 2.77 (m, 4H), 2.75 – 2.66 (m, 2H), 1.27 (d, *J* = 6.7 Hz, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 210.8, 201.0, 158.5, 157.1, 138.3, 135.8, 135.6, 130.6, 128.2, 124.8 (q, *J* = 31.7 Hz), 124.7 ((q, *J* = 271.8 Hz)), 121.4 (q, *J* = 3.0 Hz), 118.6 (q, *J* = 4.5 Hz), 118.1, 114.8, 110.2, 46.5, 38.2, 37.6, 32.2, 16.0. **<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)** δ -60.97. **HRMS (ESI):** Calcd for C<sub>22</sub>H<sub>18</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 414.1424, Found: 414.1422.



**(E)-5-methyl-7-((6-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3qa)**

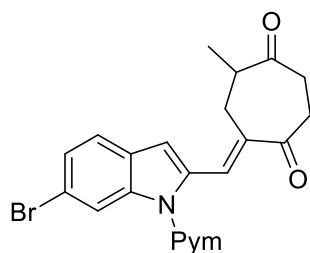
The title compound was isolated as a white solid (conditions A: 44.3mg, 62%, E/Z = 5.9:1). M.p.: 129-130 °C. **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.17 (s, 1H), 7.92 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 4.8 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.78 (s, 1H), 3.25 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.82 – 2.74 (m, 2H), 2.72 – 2.64 (m, 2H), 2.51 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** for the E isomer (major): δ 211.2, 201.1, 158.3, 157.5, 137.6, 135.4, 133.9, 133.5, 131.4, 126.6, 124.4, 120.8, 117.5, 114.0, 110.7, 46.5, 38.3, 37.6, 32.3, 22.2, 16.0. for the Z isomer (minor): δ 212.1, 206.3,

158.1, 137.2, 137.1, 134.5, 133.2, 126.7, 125.1, 124.0, 120.7, 116.9, 111.1, 46.1, 38.5, 38.1, 37.3, 22.2, 15.5. **HRMS (ESI):** Calcd for C<sub>22</sub>H<sub>21</sub>O<sub>2</sub>N<sub>3</sub> [M+H]<sup>+</sup> 360.1707, Found: 360.1702.



**(E)-5-((6-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3ra)**

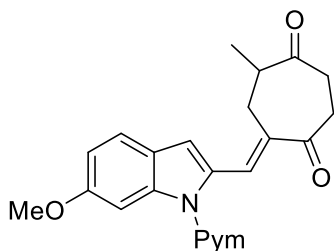
The title compound was isolated as a pale yellow solid (conditions A: 43.0 mg, 57%). M.p.: 167-168 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.45 (d, *J* = 1.7 Hz, 1H), 7.90 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.74 (s, 1H), 3.21 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.95 – 2.88 (m, 1H), 2.88 – 2.75 (m, 3H), 2.75 – 2.64 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.0, 201.0, 158.4, 157.2, 137.3, 134.8, 134.8, 131.0, 130.94, 127.2, 123.3, 121.8, 117.8, 114.6, 110.2, 46.5, 38.3, 37.6, 32.3, 16.0. **HRMS (ESI):** Calcd for C<sub>21</sub>H<sub>18</sub>ClN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 380.1160, Found: 380.1159



**(E)-5-((6-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3sa)**

The title compound was isolated as a pale yellow solid (conditions A: 54.7 mg, 65%, E/Z = 12.8:1). M.p.: 143-144 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.61 (d, *J* = 1.1 Hz, 1H), 7.89 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.23 (t, *J* = 4.8 Hz, 1H), 6.74 (s, 1H), 3.20 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.97 – 2.76 (m, 4H), 2.74 – 2.65 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 210.9, 201.0, 158.4, 158.2, 157.1, 137.6, 134.9, 134.6, 130.9, 127.5, 125.9, 122.1, 118.8, 117.8, 117.5, 110.2, 46.5, 38.2, 37.6, 32.2, 16.0. **HRMS (ESI):** Calcd for C<sub>21</sub>H<sub>18</sub>BrN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 424.0655, Found: 424.0647.

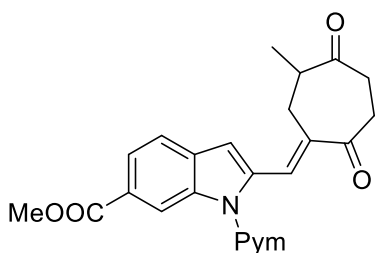




**(E)-5-((6-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-**

**7-methylcycloheptane-1,4-dione (3ta)**

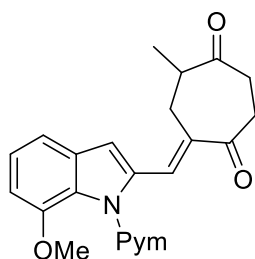
The title compound was isolated as a pale yellow solid (conditions A: 45.1 mg, 60%, E/Z = 14.7:1). M.p.: 120-121 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.81 (d, *J* = 4.8 Hz, 2H), 7.94 (d, *J* = 2.2 Hz, 1H), 7.92 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 6.92 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.76 (s, 1H), 3.89 (s, 3H), 3.23 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.80 – 2.74 (m, 2H), 2.74 – 2.63 (m, 2H), 1.28 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.2, 201.1, 158.6, 158.3, 157.5, 138.3, 133.1, 133.1, 131.4, 122.8, 121.7, 117.4, 112.4, 111.0, 98.0, 55.6, 46.5, 38.4, 37.6, 32.4, 16.0. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 376.1656, Found: 376.1656.



**methyl (E)-2-((6-methyl-2,5-dioxocycloheptylidene)methyl)-**

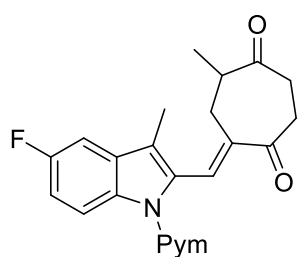
**1-(pyrimidin-2-yl)-1H-indole-6-carboxylate (3ua)**

The title compound was isolated as a white solid (conditions A: 33.3 mg, 41%). M.p.: 125-126 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.04 (s, 1H), 8.85 (t, *J* = 4.9 Hz, 2H), 7.94 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.89 (s, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.26 (dd, *J* = 5.9, 3.7 Hz, 1H), 6.79 (s, 1H), 3.94 (s, 3H), 3.21 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.94 – 2.84 (m, 2H), 2.83 – 2.75 (m, 2H), 2.75 – 2.64 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 210.8, 201.0, 167.7, 158.6, 157.1, 136.9, 136.4, 135.8, 132.2, 130.6, 126.4, 123.5, 120.7, 118.0, 116.4, 109.9, 52.1, 46.5, 38.2, 37.6, 32.2, 16.0. HRMS (ESI): Calcd for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup> 404.1605, Found: 404.1604.



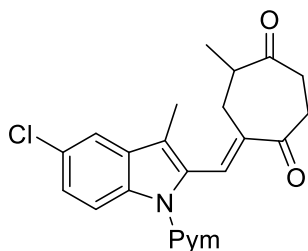
**(E)-5-((7-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3va)**

The title compound was isolated as a yellow solid (conditions A: 26.4 mg, 35%). M.p.: 117-118 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.87 (d, *J* = 4.9 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.32 – 7.28 (m, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.84 (s, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 3.64 (s, 3H), 3.21 (dd, *J* = 15.3, 2.5 Hz, 1H), 2.92 – 2.78 (m, 2H), 2.77 – 2.67 (m, 3H), 2.67 – 2.57 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 210.9, 200.9, 158.1, 158.0, 147.0, 136.9, 134.5, 130.2, 128.1, 127.4, 122.4, 119.7, 114.0, 108.3, 106.0, 55.7, 46.0, 38.1, 37.5, 32.6, 16.0. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 376.1656, Found: 376.1656.



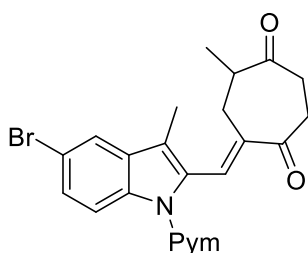
**(E)-5-((5-fluoro-3-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3wa)**

The title compound was isolated as an off-white solid (conditions A: 52.8 mg, 70%). M.p.: 129-130 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.67 (d, *J* = 4.8 Hz, 2H), 8.53 (dd, *J* = 9.1, 4.6 Hz, 1H), 7.80 (s, 1H), 7.21 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.11 – 7.03 (m, 2H), 2.90 – 2.73 (m, 4H), 2.73 – 2.62 (m, 2H), 2.51 (dd, *J* = 14.7, 9.8 Hz, 1H), 2.18 (d, *J* = 1.0 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 211.4, 201.1, 159.0 (d, *J* = 357.9 Hz), 157.9, 157.6, 135.8, 133.4, 133.0, 132.6, 131.3 (d, *J* = 13.6 Hz), 116.7, 116.2 (d, *J* = 13.6 Hz), 116.15 (d, *J* = 6.0 Hz), 112.4 (d, *J* = 37.8 Hz), 104.3 (d, *J* = 36.2 Hz), 46.3, 37.9, 37.7, 32.4, 16.4, 10.1. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -121.09. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>20</sub>FN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 378.1612, Found: 378.1610



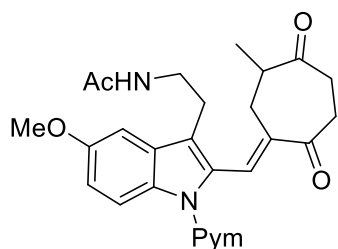
**(E)-5-((5-chloro-3-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3xa)**

The title compound was isolated as a yellow oil (conditions A: 55.2 mg, 70%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.67 (d, *J* = 4.8 Hz, 2H), 8.49 (d, *J* = 8.9 Hz, 1H), 7.78 (s, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.28 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.08 (t, *J* = 4.8 Hz, 1H), 2.88 – 2.82 (m, 2H), 2.80 – 2.74 (m, 2H), 2.68 – 2.64 (m, 2H), 2.50 (dd, *J* = 14.9, 9.9 Hz, 1H), 2.18 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.3, 201.0, 157.9, 157.6, 135.9, 134.9, 133.2, 132.3, 131.6, 127.7, 124.6, 118.6, 116.8, 116.3, 115.7, 46.3, 37.9, 37.6, 32.4, 16.4, 10.0. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 394.1317, Found: 394.1312.



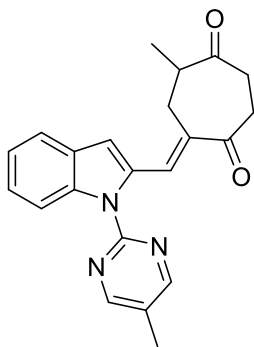
**(E)-5-((5-bromo-3-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3ya)**

The title compound was isolated as a brown solid (conditions A: 56.6 mg, 65%). M.p.: 84–85 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 4.7 Hz, 2H), 8.46 (d, *J* = 8.9 Hz, 1H), 7.80 (s, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.10 (t, *J* = 4.7 Hz, 1H), 2.89 – 2.81 (m, 2H), 2.79 – 2.75 (m, 2H), 2.69 – 2.65 (m, 2H), 2.51 (dd, *J* = 14.9, 9.9 Hz, 1H), 2.19 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.3, 201.0, 158.0, 157.6, 136.0, 135.3, 133.1, 132.2, 127.3, 121.7, 116.9, 116.7, 115.6, 115.4, 46.3, 37.9, 37.7, 32.4, 16.4, 10.0. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>20</sub>BrN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 438.0812, Found: 438.0808.



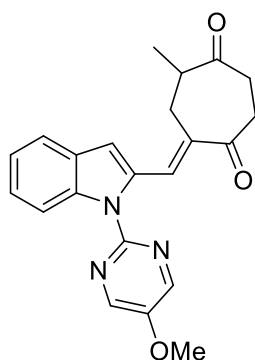
**(E)-N-(2-(5-methoxy-2-((6-methyl-2,5-dioxocycloheptylidene)methyl)-1-(pyrimidin-2-yl)-1H-indol-3-yl)ethyl)acetamide (3za)**

The title compound was isolated as yellow oil (conditions A: 39.5 mg, 40%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.68 (d,  $J = 4.7$  Hz, 2H), 8.47 (d,  $J = 9.1$  Hz, 1H), 7.77 (s, 1H), 7.13 (d,  $J = 2.5$  Hz, 1H), 7.09 (t,  $J = 4.8$  Hz, 1H), 7.00 (dd,  $J = 9.1, 2.5$  Hz, 1H), 5.54 (m, 1H), 3.91 (s, 3H), 3.53 – 3.41 (m, 2H), 2.93 – 2.83 (m, 4H), 2.82 – 2.70 (m, 2H), 2.70 – 2.59 (m, 2H), 2.48 (dd,  $J = 14.7, 9.9$  Hz, 1H), 1.92 (s, 3H), 0.94 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  211.4, 201.1, 170.3, 158.0, 157.6, 155.9, 132.1, 131.7, 130.1, 117.3, 116.7, 116.2, 114.0, 101.1, 55.8, 46.1, 39.4, 37.9, 37.6, 32.3, 24.8, 23.3, 16.4. **HRMS (ESI):** Calcd for  $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_4$   $[\text{M}+\text{H}]^+$  461.2183, Found:461.2174.



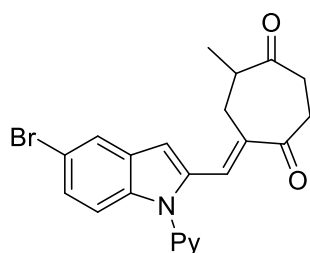
**(E)-5-methyl-7-((1-(5-methylpyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3aaa)**

The title compound was isolated as a white solid (conditions A: 56.7 mg, 83%). M.p.:130-131 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63 (s, 2H), 8.25 (d,  $J = 8.4$  Hz, 1H), 7.89 (s, 1H), 7.65 (d,  $J = 7.8$  Hz, 1H), 7.35 – 7.33 (m, 1H), 7.26 – 7.22 (m, 1H), 6.80 (s, 1H), 3.24 (dd,  $J = 15.2, 2.6$  Hz, 1H), 2.93 – 2.82 (m, 2H), 2.81 – 2.74 (m, 2H), 2.74 – 2.62 (m, 2H), 2.36 (s, 3H), 1.27 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  211.1, 201.1, 158.3, 155.4, 137.1, 134.5, 133.8, 130.9, 128.50, 127.1, 124.9, 122.3, 121.1, 113.8, 109.9, 46.4, 38.3, 37.6, 32.3, 15.9, 15.1. **HRMS (ESI):** Calcd for  $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  360.1707, Found: 360.1707.



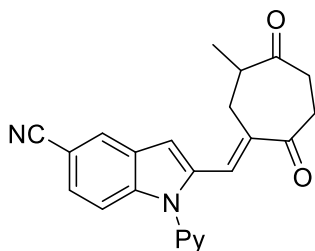
**(E)-5-((1-(5-methoxypyrimidin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3baa)**

The title compound was isolated as a white solid (conditions A: 38.1 mg, 51%). M.p.: 135-136 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.50 (s, 2H), 8.11 (d,  $J = 8.4$  Hz, 1H), 7.84 (s, 1H), 7.66 (d,  $J = 7.8$  Hz, 1H), 7.36 – 7.31 (m, 1H), 7.26 – 7.22 (m, 1H), 6.81 (s, 1H), 3.99 (s, 3H), 3.26 (dd,  $J = 15.3, 2.6$  Hz, 1H), 2.94 – 2.85 (m, 2H), 2.81 – 2.63 (m, 4H), 1.29 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  211.1, 201.1, 151.0, 150.8, 144.5, 137.2, 134.9, 133.8, 130.5, 128.3, 124.9, 122.2, 121.1, 113.2, 109.4, 56.3, 46.5, 38.3, 37.6, 32.4, 16.0. **HRMS (ESI)**: Calcd for  $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_3$   $[\text{M}+\text{H}]^+$  376.1656, Found: 376.1657.



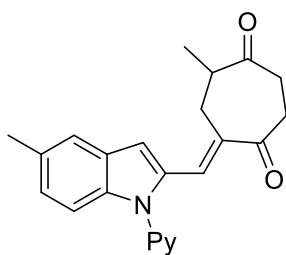
**(E)-5-((5-bromo-1-(pyridin-2-yl)-1H-indol-2-yl)methylene)-7-methylcycloheptane-1,4-dione (3caa)**

The title compound was isolated as an off-white solid (conditions A: 50.5 mg, 60%). M.p.: 167-168 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (dd,  $J = 4.8, 1.3$  Hz, 1H), 7.93 (td,  $J = 7.7, 1.9$  Hz, 1H), 7.82 (d,  $J = 1.8$  Hz, 1H), 7.44 (s, 1H), 7.43 – 7.37 (m, 2H), 7.33 (dd,  $J = 8.7, 1.6$  Hz, 2H), 6.78 (s, 1H), 3.22 (dd,  $J = 15.3, 2.6$  Hz, 1H), 2.92 – 2.83 (m, 2H), 2.80 – 2.68 (m, 3H), 2.68 – 2.60 (m, 1H), 1.30 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  210.7, 200.8, 150.0, 149.9, 138.7, 137.3, 136.3, 134.6, 129.6, 127.6, 127.4, 123.7, 122.8, 121.2, 114.8, 112.8, 107.0, 46.0, 38.1, 37.5, 32.5, 16.1. **HRMS (ESI)**: Calcd for  $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_2\text{Br}$   $[\text{M}+\text{H}]^+$  423.0703, Found: 423.0704.



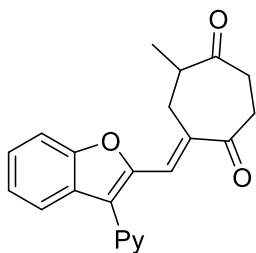
**(E)-2-((6-methyl-2,5-dioxocycloheptylidene)methyl)-1-(pyridin-2-yl)-1H-indole-5-carbonitrile (3daa)**

The title compound was isolated as a white solid (conditions A: 28.6 mg, 39%). M.p.: 173-174 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.71 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.05 (s, 1H), 7.97 (td, *J* = 7.7, 1.9 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.47 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.45 (dd, *J* = 7.2, 5.2 Hz, 1H), 7.39 (s, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 6.90 (s, 1H), 3.21 (dd, *J* = 15.4, 2.7 Hz, 1H), 2.94 – 2.84 (m, 2H), 2.81 – 2.70 (m, 3H), 2.67 – 2.62 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 210.4, 200.7, 150.1, 149.5, 139.0, 138.9, 138.5, 135.8, 127.7, 127.0, 126.8, 126.7, 123.4, 121.4, 120.0, 112.3, 107.5, 104.9, 45.9, 38.0, 37.4, 32.5, 16.1. HRMS (ESI): Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 370.1550, Found: 370.1552.



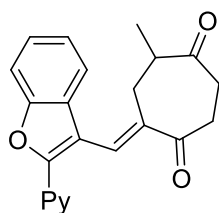
**(E)-5-methyl-7-((5-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3eaa)**

The title compound was isolated as a pale yellow solid (conditions A: 31.7 mg, 44%, E/Z = 12.5:1). M.p.: 138-139 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.71 – 8.66 (m, 1H), 7.90 (td, *J* = 7.8, 1.9 Hz, 1H), 7.53 (s, 1H), 7.48 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.10 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.81 (s, 1H), 3.26 (dd, *J* = 15.3, 2.6 Hz, 1H), 2.93 – 2.82 (m, 2H), 2.78 – 2.71 (m, 3H), 2.69 – 2.59 (m, 1H), 2.46 (s, 3H), 1.31 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.0, 200.9, 150.6, 149.8, 138.5, 136.1, 135.9, 133.6, 131.2, 128.5, 128.4, 126.5, 122.3, 121.1, 120.9, 110.9, 107.9, 46.0, 38.2, 37.5, 32.6, 21.4, 16.1. HRMS (ESI): Calcd for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 359.1754, Found: 359.1754.



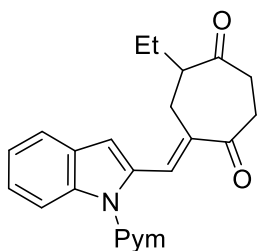
**(E)-5-methyl-7-((3-(pyridin-2-yl)benzofuran-2-yl)methylene)cycloheptane-1,4-dione (3faa)**

The title compound was isolated as a pale yellow solid (condition A: 40.0 mg, 58%). M.p.: 175-176 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.82 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.35 – 7.31 (m, 2H), 3.68 (dd, *J* = 14.7, 2.6 Hz, 1H), 2.95 – 2.88 (m, 2H), 2.86 – 2.82 (m, 1H), 2.80 – 2.70 (m, 2H), 2.68 – 2.61 (m, 1H), 1.34 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 211.3, 201.1, 154.3, 151.2, 150.0, 149.3, 139.1, 136.5, 131.9, 127.9, 125.9, 123.5, 122.8, 121.4, 120.8, 114.7, 111.8, 46.4, 38.2, 37.7, 32.7, 16.1. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>19</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 346.1438, Found: 346.1431.



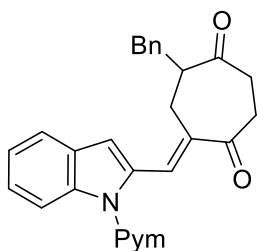
**(E)-5-methyl-7-((2-(pyridin-2-yl)benzofuran-3-yl)methylene)cycloheptane-1,4-dione (3gaa)**

The title compound was isolated as an off-white solid (conditions A: 32.0 mg, 46%). M.p.: 109-110 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.71 – 8.66 (m, 1H), 8.02 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.78 (td, *J* = 7.8, 1.8 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.34 – 7.27 (m, 1H), 7.23 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1H), 2.93 – 2.84 (m, 2H), 2.84 – 2.70 (m, 3H), 2.69 – 2.61 (m, 1H), 2.49 (dd, *J* = 15.0, 10.2 Hz, 1H), 0.88 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.2, 201.9, 154.8, 151.3, 150.4, 150.3, 137.8, 136.8, 126.9, 126.1, 124.5, 123.9, 122.5, 121.5, 111.3, 47.5, 38.2, 37.2, 32.2, 16.2. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>19</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 346.1438, Found: 346.1432.



**(E)-5-ethyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ab)**

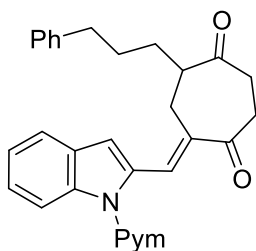
The title compound was isolated as a white solid (conditions B: 29.5 mg, 41%). M.p.: 125-126 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.41 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 4.8 Hz, 1H), 6.82 (s, 1H), 3.23 (dd, *J* = 15.3, 3.0 Hz, 1H), 2.95 – 2.75 (m, 4H), 2.72 – 2.60 (m, 2H), 1.91 – 1.81 (m, 1H), 1.62 – 1.53 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.3, 201.1, 158.3, 157.6, 137.1, 134.2, 134.2, 131.8, 128.8, 125.0, 122.6, 121.1, 117.4, 114.4, 110.6, 53.8, 38.1, 37.8, 30.2, 24.1, 11.8. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 360.1707, Found: 360.1701.



**(E)-5-benzyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ac)**

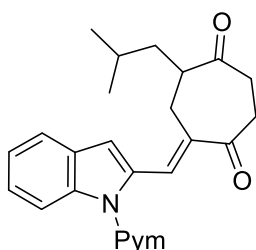
The title compound was isolated as a white solid (condition A: 40.0 mg, 47%). M.p.: 170-171 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 4.8 Hz, 2H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.16 (m, 7H), 6.02 (s, 1H), 3.42 (dd, *J* = 15.2, 2.7 Hz, 1H), 3.35 (dd, *J* = 14.1, 4.7 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.98 – 2.90 (m, 1H), 2.84 – 2.77 (m, 2H), 2.75 – 2.69 (m, 1H), 2.68 – 2.62 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 210.5, 201.1, 158.3, 157.4, 139.1, 137.1, 133.7, 133.5, 131.8, 129.4, 128.7, 128.6, 126.7, 125.0, 122.3, 121.5, 117.4, 114.1, 53.8, 38.8, 37.6, 36.4, 29.4. HRMS (ESI): Calcd for C<sub>28</sub>H<sub>24</sub>N<sub>3</sub>O<sub>2</sub> [M+Na]<sup>+</sup> 422.1863, Found: 422.1866.





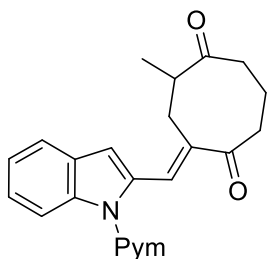
**(E)-5-(3-phenylpropyl)-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ad)**

The title compound was isolated as a pale yellow solid (condition A: 49.7 mg, 56%). M.p.: 63-64 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.78 (d, *J* = 4.0 Hz, 2H), 8.43 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 – 7.17 (m, 3H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.77 (s, 1H), 3.20 (d, *J* = 13.9 Hz, 1H), 2.94 – 2.85 (m, 2H), 2.83 – 2.74 (m, 3H), 2.66 – 2.60 (m, 1H), 2.59 – 2.53 (m, 2H), 1.88 – 1.84 (m, 1H), 1.65 – 1.52 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.2, 201.0, 158.2, 157.5, 141.8, 137.1, 134.1, 134.0, 132.1, 128.7, 128.22, 128.18, 125.7, 125.0, 122.6, 121.1, 117.4, 114.5, 110.6, 52.2, 38.0, 37.7, 35.6, 30.3, 30.1, 28.9. HRMS (ESI): Calcd for C<sub>30</sub>H<sub>29</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 450.2176, Found: 450.2169.



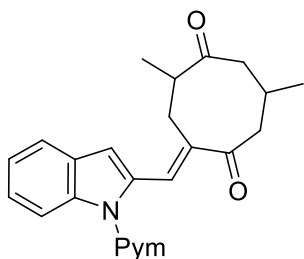
**(E)-5-isobutyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ae)**

The title compound was isolated as a pale yellow solid (condition A: 41.4 mg, 58%). M.p.: 74-75 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.71 (d, *J* = 4.7 Hz, 2H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 4.7 Hz, 1H), 6.72 (s, 1H), 3.08 (d, *J* = 12.6 Hz, 1H), 2.86 – 2.68 (m, 5H), 2.58 – 2.54 (m, 1H), 1.72 – 1.68 (dt, *J* = 14.1, 7.2 Hz, 1H), 1.51 – 1.46 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.24 – 1.17 (m, 1H), 0.79 – 0.77 (m, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 211.6, 201.1, 158.2, 157.6, 137.1, 134.2, 134.2, 132.1, 128.8, 125.0, 122.6, 121.0, 117.4, 114.5, 110.6, 50.2, 40.0, 37.9, 30.7, 25.6, 22.7, 22.3. HRMS (ESI): Calcd for C<sub>25</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 388.2020, Found: 388.2016.



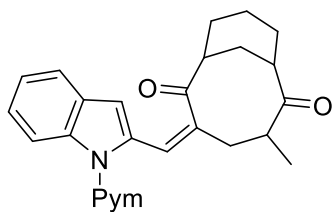
**(E)-2-methyl-4-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cyclooctane-1,5-dione (3af)**

The title compound was isolated as a pale yellow solid (condition A: 40.0 mg, 47%). M.p.: 114-115 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.37 – 8.30 (m, 1H), 7.88 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.28 – 7.22 (m, 1H), 7.16 (t, *J* = 4.8 Hz, 1H), 6.81 (s, 1H), 3.31 (dd, *J* = 14.2, 3.3 Hz, 1H), 2.96 – 2.83 (m, 2H), 2.80 – 2.74 (m, 1H), 2.68 – 2.56 (m, 1H), 2.52 – 2.44 (m, 2H), 2.22 – 2.08 (m, 1H), 2.00 – 1.86 (m, 1H), 1.24 (d, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 215.2, 203.1, 158.2, 157.4, 137.2, 135.0, 134.3, 130.8, 128.7, 125.0, 122.5, 121.1, 117.5, 114.1, 110.2, 48.9, 38.6, 37.7, 32.7, 24.7, 15.8. HRMS (ESI): Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 360.1707, Found: 360.1703.



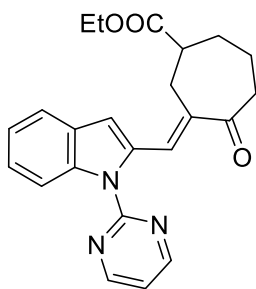
**(E)-2,7-dimethyl-4-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cyclooctane-1,5-dione (3ag)**

The title compound was isolated as a pale yellow solid (condition A: 41.0 mg, 56%, E/Z = 9:1). M.p.: 53-54 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.73 (d, *J* = 4.8 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 3.7 Hz, 1H), 7.13 (t, *J* = 4.8 Hz, 1H), 6.79 (s, 1H), 3.29 (dd, *J* = 14.5, 3.9 Hz, 1H), 2.97 (dd, *J* = 11.8, 5.4 Hz, 1H), 2.90 – 2.86 (m, 1H), 2.63 – 2.54 (m, 3H), 2.45 – 2.38 (m, 1H), 2.29 – 2.22 (m, 2H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 214.5, 201.5, 158.3, 157.5, 137.2, 135.8, 134.4, 130.9, 128.9, 125.1, 122.6, 121.2, 117.6, 114.2, 110.0, 48.6, 47.4, 43.6, 33.1, 31.1, 20.7, 15.4. HRMS (ESI): Calcd for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 374.1863, Found: 374.1857.



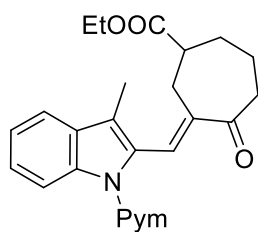
**(Z)-3-methyl-5-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)bi-cyclo[5.3.1]undecane-2,6-dione (3ah')**

The title compound was isolated as a white solid (condition A: 61.1 mg, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.42 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.80 (s, 1H), 6.45 (s, 1H), 3.37 – 3.19 (m, 2H), 2.66 – 2.53 (m, 2H), 2.49 – 2.45 (m, 2H), 2.19 (dd, *J* = 32.3, 13.1 Hz, 2H), 1.86 (dt, *J* = 14.8, 5.4 Hz, 1H), 1.66 – 1.59 (m, 1H), 1.34 – 1.26 (m, 2H), 1.17 – 1.09 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 215.5, 212.4, 158.2, 141.7, 136.7, 134.9, 129.2, 124.1, 122.4, 120.8, 120.0, 117.1, 114.5, 109.5, 47.1, 44.6, 43.9, 43.3, 27.6, 25.1, 24.2, 18.1, 17.7. HRMS (ESI): Calcd for C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 400.2020, Found: 400.2020.



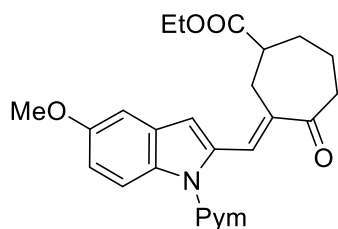
**(E)-5-benzyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ai)**

The title compound was isolated as a pale yellow solid (condition B: 55.1 mg, 71%). M.p.: 111-112 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 4.8 Hz, 2H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.90 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 7.09 (s, 1H), 4.31 – 4.19 (m, 2H), 3.62 (d, *J* = 13.6 Hz, 1H), 2.85 (t, *J* = 12.3 Hz, 1H), 2.77 – 2.61 (m, 3H), 2.26 (d, *J* = 12.0 Hz, 1H), 2.12 – 2.09 (m, 1H), 1.98 – 1.88 (m, 1H), 1.65 – 1.55 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 202.5, 174.8, 158.3, 157.5, 137.1, 134.6, 134.2, 129.8, 128.9, 124.8, 122.4, 121.0, 117.4, 114.1, 110.8, 60.7, 45.8, 42.7, 33.3, 31.1, 23.3, 14.3. HRMS (ESI): Calcd for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 390.1812, Found: 390.1816.



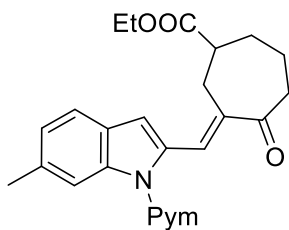
**(E)-5-benzyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3aj)**

The title compound was isolated as a pale yellow solid (condition B: 64.5 mg, 80%). M.p.: 99-101 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.59 (d, *J* = 4.7 Hz, 2H), 8.45 (d, *J* = 8.3 Hz, 1H), 7.71 (s, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 4.7 Hz, 1H), 3.96 – 3.84 (m, 2H), 3.00 (d, *J* = 14.7 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.64 (dd, *J* = 12.7, 7.2 Hz, 1H), 2.48 (dd, *J* = 14.6, 10.8 Hz, 1H), 2.37 (t, *J* = 10.3 Hz, 1H), 2.16 (s, 3H), 2.13 – 2.08 (m, 1H), 2.05 – 2.01 (m, 1H), 1.74 – 1.66 (m, 1H), 1.61 – 1.55 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 202.7, 175.0, 157.91, 157.87, 136.7, 136.0, 132.4, 131.4, 130.6, 124.4, 122.0, 119.0, 116.42, 116.39, 114.8, 60.4, 45.3, 43.0, 33.8, 30.8, 23.8, 13.9, 10.2. HRMS (ESI): Calcd for C<sub>24</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 404.1969, Found: 404.1975.



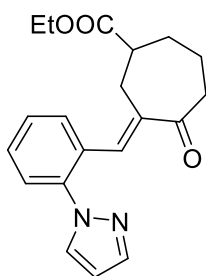
**(E)-5-benzyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3ak)**

The title compound was isolated as a pale yellow solid (condition B: 59.6 mg, 71%). M.p.: 122-123 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.77 (d, *J* = 4.5 Hz, 2H), 8.29 (d, *J* = 9.1 Hz, 1H), 7.92 (s, 1H), 7.15 (t, *J* = 4.4 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 1H), 7.02 – 6.95 (m, 2H), 4.28 – 4.19 (m, 2H), 3.87 (s, 3H), 3.61 (d, *J* = 14.3 Hz, 1H), 2.85 (t, *J* = 12.7 Hz, 1H), 2.76 – 2.61 (m, 3H), 2.26 (d, *J* = 12.7 Hz, 1H), 2.16 – 2.08 (m, 1H), 1.96 – 1.89 (m, 1H), 1.64 – 1.58 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 202.6, 174.9, 158.2, 157.5, 155.7, 134.7, 134.4, 132.2, 130.1, 129.7, 117.2, 115.3, 114.5, 110.7, 102.6, 60.7, 55.6, 45.9, 42.7, 33.4, 31.1, 23.4, 14.2. HRMS (ESI): Calcd for C<sub>24</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup> 420.1918, Found: 420.1918.



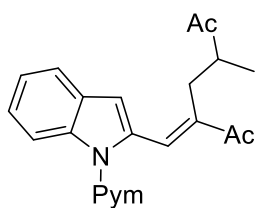
**(E)-5-benzyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3al)**

The title compound was isolated as a pale yellow solid (condition B: 58.1 mg, 72%). M.p.: 123-125 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.78 (d, *J* = 4.6 Hz, 2H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.92 (s, 1H), 7.41 (s, 1H), 7.15 (dd, *J* = 8.9, 4.5 Hz, 2H), 7.00 (s, 1H), 4.30 – 4.20 (m, 2H), 3.61 (d, *J* = 14.3 Hz, 1H), 2.85 (t, *J* = 12.4 Hz, 1H), 2.75 – 2.61 (m, 3H), 2.46 (s, 3H), 2.26 (d, *J* = 12.4 Hz, 1H), 2.15 – 2.09 (m, 1H), 1.96 – 1.89 (m, 1H), 1.64 – 1.57 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 202.6, 174.8, 158.2, 157.5, 135.5, 134.3, 134.2, 131.8, 130.1, 129.2, 126.4, 120.7, 117.2, 113.9, 110.6, 60.7, 45.8, 42.7, 33.4, 31.1, 23.3, 21.3, 14.3. HRMS (ESI): Calcd for C<sub>24</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 404.1969, Found: 404.1964.



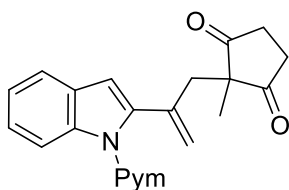
**(E)-5-benzyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (3am)**

The title compound was isolated as a pale yellow oil (condition B: 9.9 mg, 15%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 1.5 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.49 (s, 1H), 7.47 – 7.44 (m, 1H), 7.41 – 7.37 (m, 2H), 6.42 (t, *J* = 2.0 Hz, 1H), 4.15 – 4.07 (m, 2H), 3.13 (d, *J* = 14.8 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.69 – 2.64 (m, 1H), 2.53 (dd, *J* = 14.7, 10.7 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.21 – 2.14 (m, 1H), 2.11 – 2.02 (m, 1H), 1.86 – 1.78 (m, 1H), 1.63 – 1.55 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 202.3, 174.6, 141.1, 139.9, 138.3, 135.2, 130.9, 123.0, 129.6, 129.4, 127.3, 125.2, 107.1, 60.7, 45.8, 42.7, 33.3, 30.2, 23.4, 14.2. HRMS (ESI): Calcd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 339.1703, Found: 339.1699.



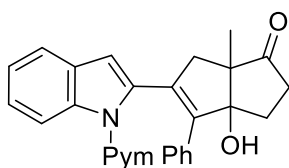
**(E)-3-methyl-5-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)heptane-2,6-dione (3ao)**

The title compound was isolated as a pale yellow solid (condition B: 10.5 mg, 15%). M.p.: 138-139 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.8$  Hz, 2H), 8.45 (d,  $J = 8.4$  Hz, 1H), 7.97 (s, 1H), 7.65 (d,  $J = 7.8$  Hz, 1H), 7.35 (t,  $J = 7.7$  Hz, 1H), 7.28 – 7.25 (m, 1H), 7.19 (t,  $J = 4.8$  Hz, 1H), 6.98 (s, 1H), 3.01 (dd,  $J = 12.9, 5.7$  Hz, 1H), 2.89 – 2.86 (m, 1H), 2.85 – 2.81 (m, 1H), 2.41 (s, 3H), 2.13 (s, 3H), 1.04 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  212.2, 199.9, 158.2, 158.1, 157.9, 137.5, 137.1, 134.5, 134.0, 129.1, 124.9, 122.7, 121.2, 117.3, 114.7, 111.0, 46.0, 29.1, 28.0, 26.1, 15.9. **HRMS (ESI):** Calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  346.1550, Found: 346.1553.



**(E)-5-benzyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methylene)cycloheptane-1,4-dione (4aa)**

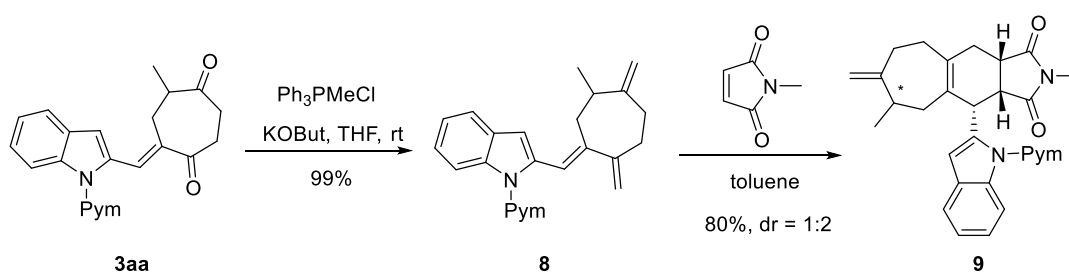
The title compound was isolated as a white solid (condition A: 15.2 mg, 22%). M.p.: 86-89 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (d,  $J = 4.8$  Hz, 2H), 8.33 (d,  $J = 8.4$  Hz, 1H), 7.46 (d,  $J = 7.7$  Hz, 1H), 7.21 (t,  $J = 7.3$  Hz, 1H), 7.13 (t,  $J = 7.4$  Hz, 1H), 7.09 (t,  $J = 4.8$  Hz, 1H), 6.42 (s, 1H), 5.09 – 5.08 (m, 2H), 2.72 (s, 2H), 2.45 (dd,  $J = 19.1, 6.6$  Hz, 2H), 2.19 (dd,  $J = 19.1, 6.6$  Hz, 2H), 0.94 (s, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  215.9, 158.0, 157.8, 139.3, 137.9, 137.6, 128.4, 124.2, 122.3, 120.5, 118.8, 117.2, 114.5, 110.1, 56.0, 42.6, 34.9, 22.2. **HRMS (ESI):** Calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  346.1550, Found: 346.1548.



**3a-hydroxy-6a-methyl-4-phenyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)-1,3,3a,6,6a-tetrahydropentalen-1(2H)-one (5an)**

The title compound was isolated as a pale yellow solid (condition A: 11.8 mg, 14%). M.p.: 112-113 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (d,  $J = 4.8$  Hz, 2H), 8.00 (dd,  $J = 6.9, 1.5$  Hz, 1H), 7.82 (dd,  $J = 7.3, 1.2$  Hz, 1H), 7.39 – 7.24 (m, 6H), 7.21 (d,  $J = 7.4$  Hz, 2H), 5.99 (s, 1H), 3.13 (dd,  $J = 13.8, 0.8$  Hz, 1H), 2.87 – 2.80 (m, 1H), 2.74 (dd,  $J = 13.8, 1.1$  Hz, 1H), 2.71 – 2.64 (m, 1H), 2.62 – 2.54 (m, 1H), 2.46 (s, 1H), 2.32 – 2.24 (m, 1H), 1.15 (s, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  219.3, 158.8, 158.7, 134.0, 136.5, 135.8, 130.1, 128.8, 128.2, 127.0, 126.4, 125.1, 124.5, 122.2, 120.8, 120.8, 118.8, 111.9, 78.0, 55.7, 35.8, 33.3, 32.8, 16.6. **HRMS (ESI)**: Calcd for  $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  422.1863, Found: 422.1856.

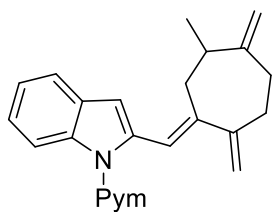
### Derivatization reaction:



### General procedure:

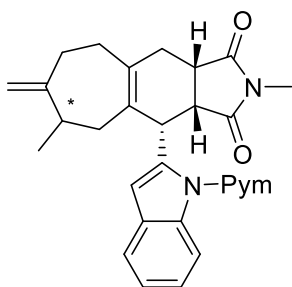
Methyl(triphenyl)phosphonium chloride (248 mg, 8 equiv) was dissolved in THF (2 mL),  $t\text{BuOK}$  (0.8 mL, 1M in THF) was added slowly at room temperature and stirred for 30 min. **3aa** (0.1 mmol, 34.5 mg) was then added and the mixtures were allowed to be stirred for another 30 min. After the removal of the solvents, the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:10).

A mixture of **8** (0.1 mmol, 1 equiv), *N*-methylsuccinimide (0.15 mmol, 1.5 equiv), were weighted in a Schlenk tube equipped with a stir bar. Toluene (2.0 mL) and DCE (0.2 mL) was added and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:4).



**(E)-2-((6-methyl-2,5-dimethylenecycloheptylidene)methyl)-1-(pyrimidin-2-yl)-1H-indole (8)**

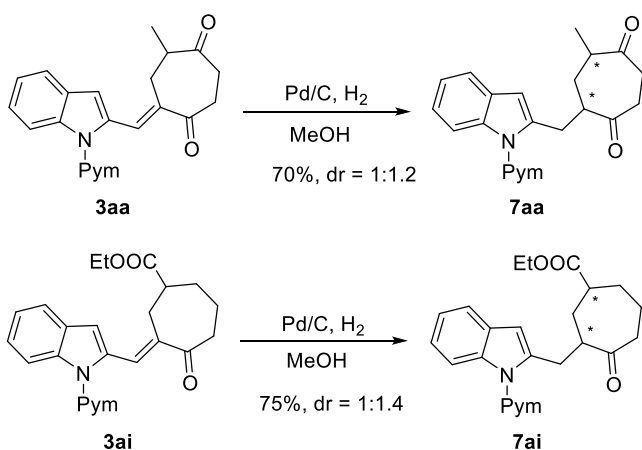
The title compound was isolated as a pale yellow oil (34.0 mg, 99%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.16 (m, 3H), 6.95 (s, 1H), 6.66 (s, 1H), 5.19 (d, *J* = 2.0 Hz, 1H), 4.82 (s, 1H), 4.75 (d, *J* = 1.0 Hz, 1H), 4.73 (s, 1H), 2.85 (dd, *J* = 14.5, 2.1 Hz, 1H), 2.55 – 2.44 (m, 4H), 2.39 (dd, *J* = 14.5, 10.0 Hz, 1H), 2.23 (td, *J* = 13.8, 5.6 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz): δ 158.8, 158.5, 156.3, 154.0, 143.4, 137.3, 137.0, 129.9, 123.7, 122.5, 120.7, 118.7, 118.0, 114.3, 110.6, 108.7, 108.0, 40.3, 38.2, 37.2, 36.8, 20.3. HRMS (ESI): Calcd for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub> [M+H]<sup>+</sup> 342.1965, Found: 342.1958.



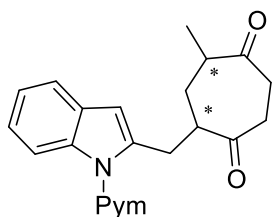
**(3aR,4S,10aS)-2,6-dimethyl-7-methylene-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)-4,5,6,7,8,9,10,10a-octahydro-6H-cyclohepta[f]isoindole-1,3-dione (9)**

The title compound was isolated as a pale yellow solid (37.7 mg, 83%). M.p.: 163-165 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.81 – 8.71 (m, 2H), 8.11 (dd, *J* = 8.1, 5.3 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.39 (m, 1H), 5.33 (m, 1H), 4.60 (m, 2H), 3.10 – 2.99 (m, 1H), 2.98 – 2.82 (m, 2H), 2.44 – 2.36 (m, 2H), 2.35 – 2.21 (m, 7H), 2.21 – 2.10 (m, 2H), 0.92 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 179.5, 179.4, 177.9, 177.8, 158.3, 158.0, 157.95, 155.8, 155.3, 137.8, 137.7, 137.4, 137.3, 132.8, 132.3, 132.0, 128.1, 128.0, 123.4, 123.3, 121.9, 120.3, 120.3, 117.3, 117.25, 113.5, 110.0, 109.9, 108.3, 108.0, 44.8, 44.4, 40.8, 40.5, 39.5, 39.4, 39.2, 38.3, 38.2, 37.9, 35.5, 35.3, 34.2, 32.7, 28.6, 27.9, 24.1, 24.0, 21.2, 19.7. HRMS (ESI): Calcd for C<sub>28</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub> [M+H]<sup>+</sup> 453.2285, Found: 453.2287.



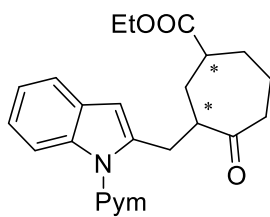


General procedure: A mixture of **3aa** (34.5 mg, 0.1 mmol) or **3ai** (39 mg, 0.1 mmol) and Pd/C (5% w/w, 5.4 mg) in MeOH (2 mL) was stirred for 18 hours at rt under a hydrogen atmosphere. After the reaction was completed, the solid was filtered out. The filtrate was concentrated in vacuo and the residue was purified by silica gel column chromatography to afford **7aa** (25.0 mg, 72%) or **7ai** (29.3 mg, 75%).



**5-methyl-7-((1-(pyrimidin-2-yl)-1H-indol-2-yl)methyl)-5,13,7,13-cycloheptane-1,4-dione (7aa)**

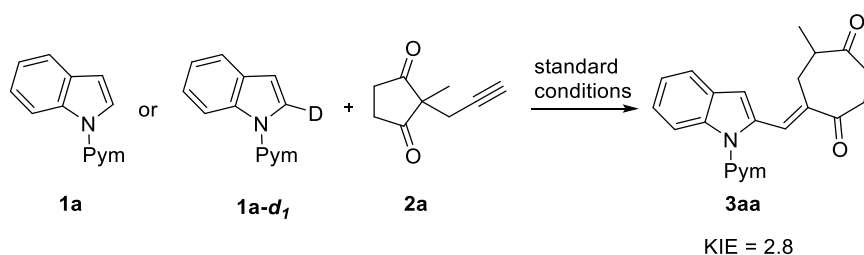
The title compound was isolated as a colorless oil (25.0 mg, 72%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.77 – 8.74 (m, 2H), 8.31 (t,  $J = 9.0$  Hz, 1H), 7.56 – 7.49 (m, 1H), 7.26 – 7.13 (m, 3H), 6.47 – 6.46 (m, 1H), 3.76 – 3.71 (m, 1H), 3.41 – 3.35 (m, 1H), 3.05 – 2.93 (m, 1H), 2.80 – 2.77 (m, 1H), 2.75 – 2.64 (m, 2H), 2.63 – 2.55 (m, 2H), 2.08 (dt,  $J = 14.4, 3.7$  Hz, 0.48H), 1.85 – 1.76 (m, 1H), 1.42 (dt,  $J = 14.4, 11.9$  Hz, 0.51H), 1.06 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  212.2, 211.8, 211.2, 210.9, 158.1, 158.1, 138.9, 138.6, 136.9, 136.8, 129.1, 129.06, 122.9, 122.1, 122.0, 119.8, 117.1, 117.05, 114.3, 108.0, 107.7, 51.8, 48.3, 46.5, 42.7, 38.2, 38.0, 37.4, 37.35, 36.3, 34.9, 30.4, 29.7, 16.5, 15.5. HRMS (ESI): Calcd for  $\text{C}_{23}\text{H}_{25}\text{N}_3$   $[\text{M}+\text{H}]^+$  348.1707, Found: 348.1704.



**4-(1,2,3,4-tetrahydroquinolin-8-yl)butan-1-ol (7ai)**

The title compound was isolated as a colorless oil (29.3 mg, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.81 – 8.74 (m, 2H), 8.30 – 8.28 (m, 1H), 7.52 (t, *J* = 8.2 Hz, 1H), 7.24 – 7.13 (m, 3H), 6.49 (s, 0.37H, minor), 6.46 (s, 0.52H, major), 4.09 (q, *J* = 7.1 Hz, 1H), 4.06 – 3.92 (m, 1H), 3.85 – 3.68 (m, 1H), 3.31 – 3.11 (m, 1H), 3.05 – 2.93 (m, 1H), 2.59 – 2.54 (m, 1H), 2.51 – 2.49 (m, 1H), 2.48 – 2.39 (m, 1H), 2.25 – 1.90 (m, 3H), 1.87 – 1.72 (m, 1H), 1.71 – 1.39 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 1.94H, major), 1.09 (t, *J* = 7.1 Hz, 1.12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 213.9, 175.0, 174.8, 158.1, 158.11, 139.2, 139.1, 136.9, 129.1, 122.8, 122.7, 121.9, 121.8, 119.8, 119.7, 117.1, 117.0, 114.19, 114.18, 107.9, 107.5, 60.5, 49.8, 48.4, 46.9, 43.1, 43.1, 41.9, 33.6, 31.8, 31.4, 31.1, 30.7, 30.1, 22.4, 21.8, 14.1, 14.0. HRMS (ESI): Calcd for C<sub>23</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 392.1969, Found: 392.1962.

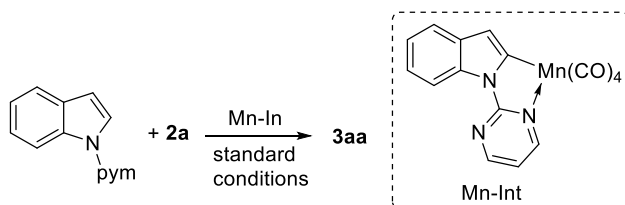
## KIE experiments:



A mixture of **1a** (0.2 mmol, 1 equiv), or **1a-d<sub>1</sub>** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2.0 equiv), MnBr(CO)<sub>5</sub> (5.5 mg, 10.0 mol %), KOH (2.8 mg, 25.0 mol %) were weighted in a Schlenk tube equipped with a stir bar. TFE (2.0 mL) was added and the mixture was stirred at 120 °C for 16 h under Ar atmosphere. Afterwards, the two independent reactions were poured into different round flasks, 5 mL H<sub>2</sub>O and 20 mL *n*-pentane was added, the organic phase was separated and evaporated under reduced pressure, the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:2 and EtOAc/DCM = 1:20). The products were isolated giving the yield of 21% (14.4 mg, for **1a**) and 7% (5.1 mg, for **1a-d<sub>1</sub>**).

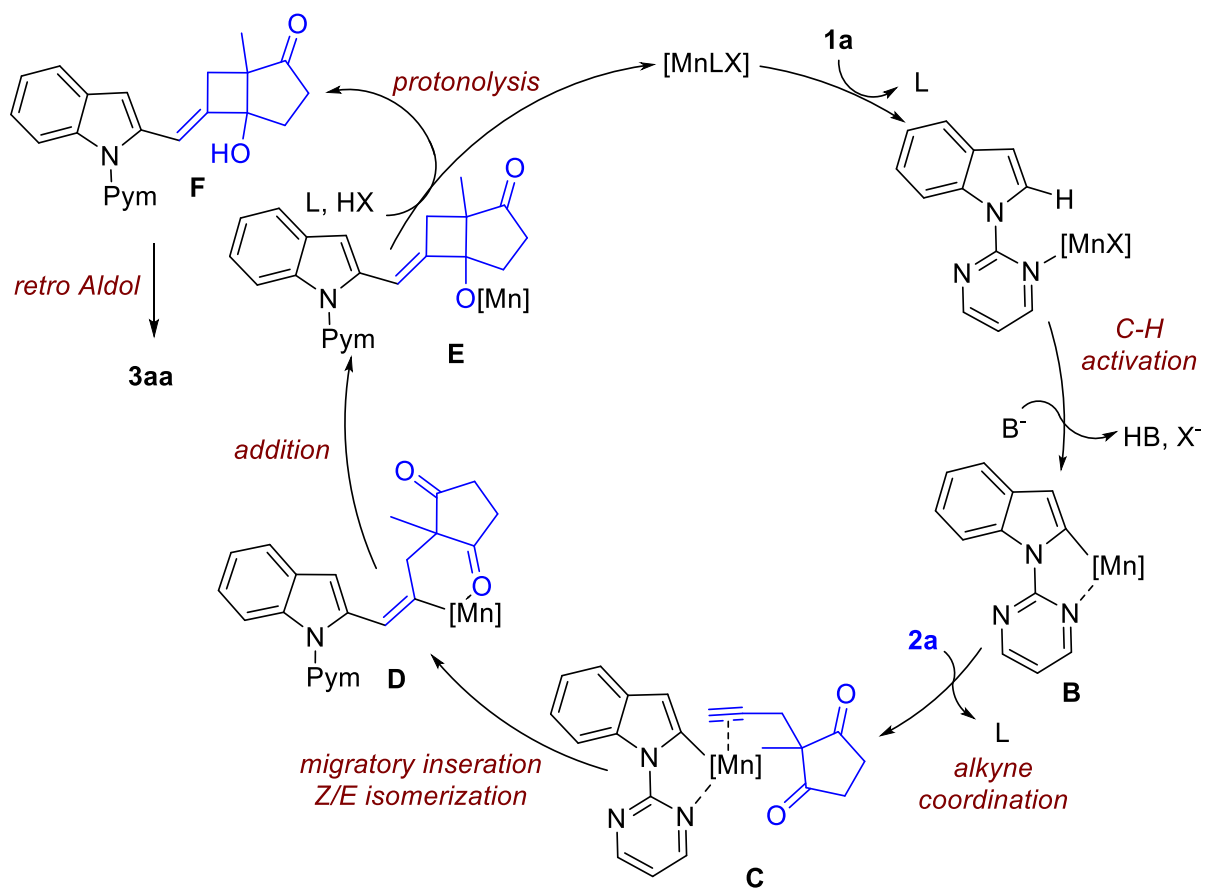
## Cascade catalyzed by Mn-Int:

Intermediate Mn-Int **A** was synthesized according to the literature reports.<sup>6</sup>

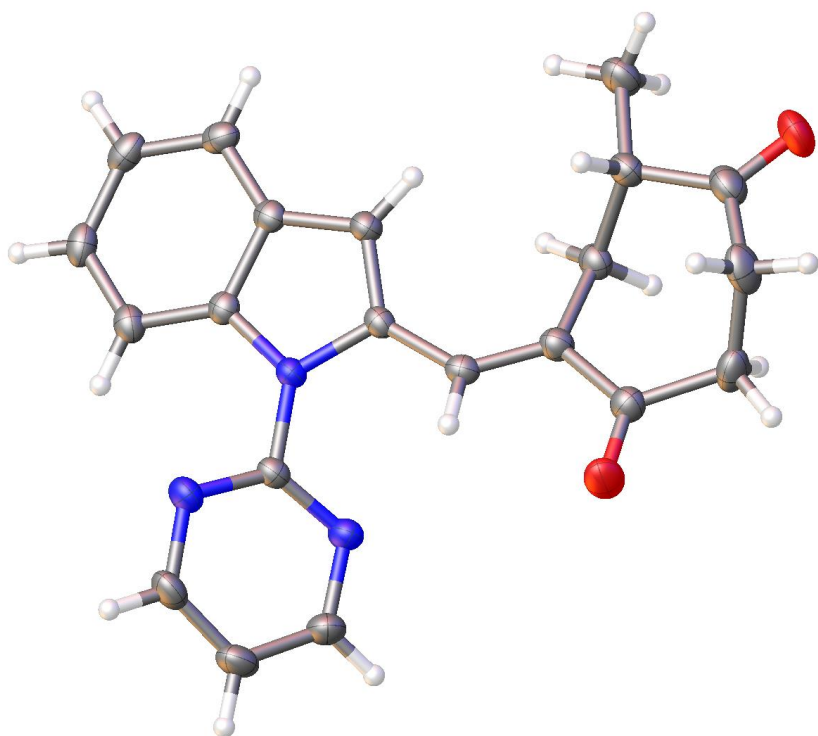


A mixture of **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2.0 equiv), Mn-Int (10 mol %), KOH (25 mol %), were weighted to a Schlenk tube equipped with a stir bar. TFE (2.0 mL) was added and the mixture was stirred at 120 °C for 15 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel using EA/PE as eluent to give **3aa** (36.6 mg, 53%).

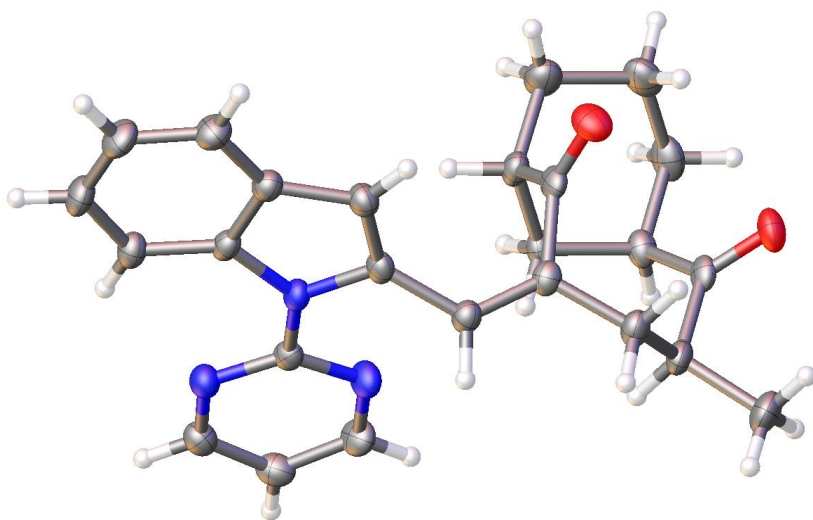
## Proposed Mechanism



**Crystal structure of 3aa**

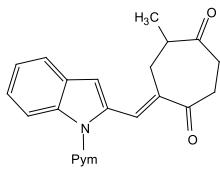


**Crystal structure of 3ah'**

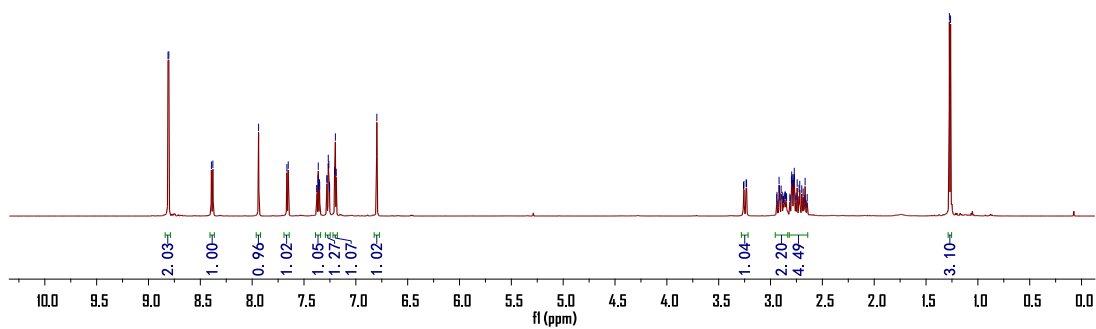


< 8.81  
 < 8.80  
 < 8.39  
 < 8.38  
 — 7.94  
 — 7.65  
 > 7.35  
 > 7.26  
 > 7.19  
 — 6.80

> 3.26  
 > 3.26  
 > 3.24  
 > 3.23  
 > 2.91  
 > 2.86  
 > 2.80  
 > 2.77  
 > 2.72  
 > 2.67  
 < 1.27  
 < 1.26



3aa



— 211.08

— 201.08

< 158.32

< 157.43

> 137.09

> 134.42

> 134.02

> 131.34

> 128.71

> 125.09

> 122.63

> 121.10

> 117.51

> 114.29

— 110.60

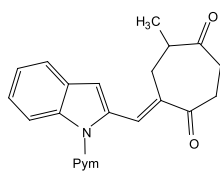
— 46.57

> 38.31

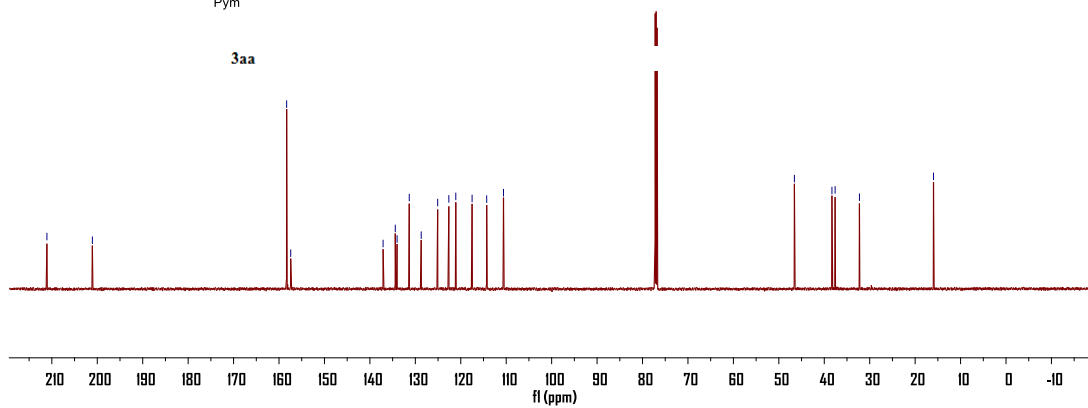
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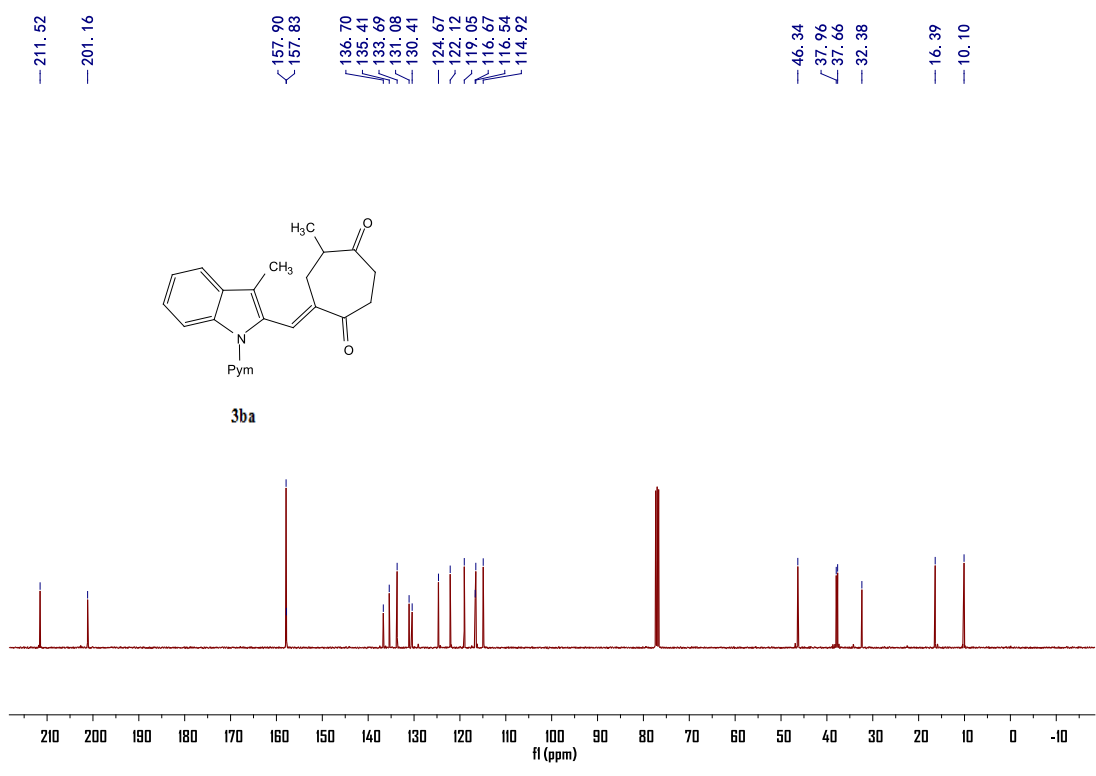
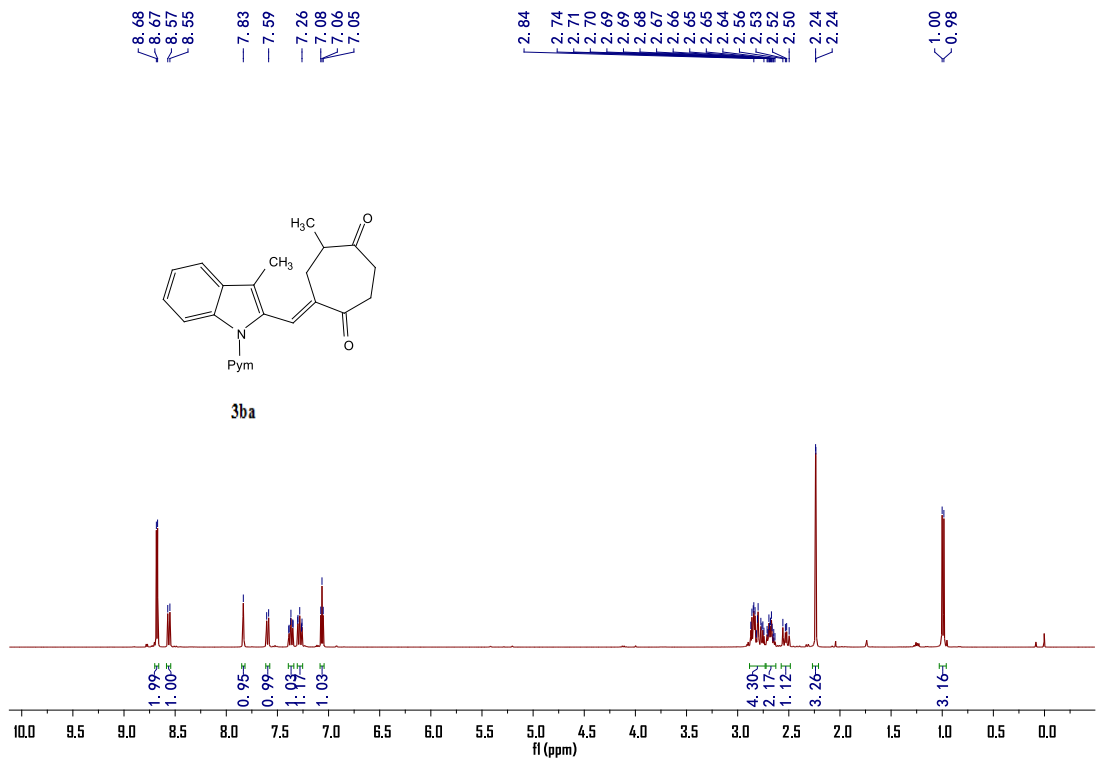
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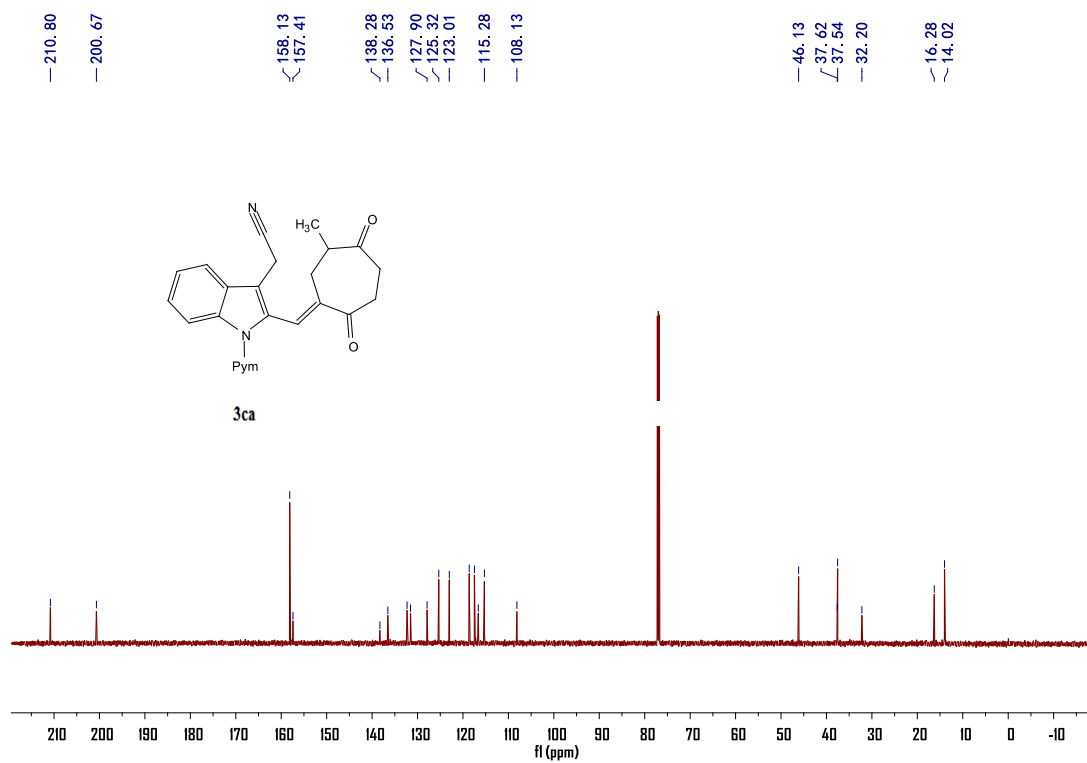
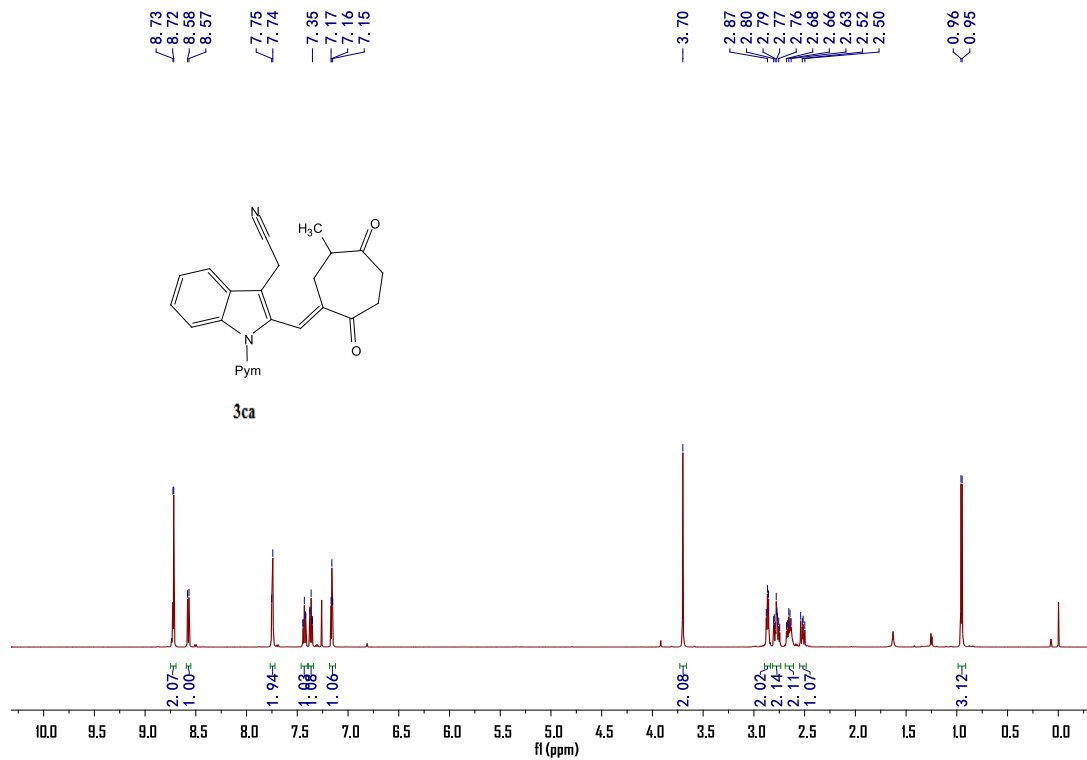
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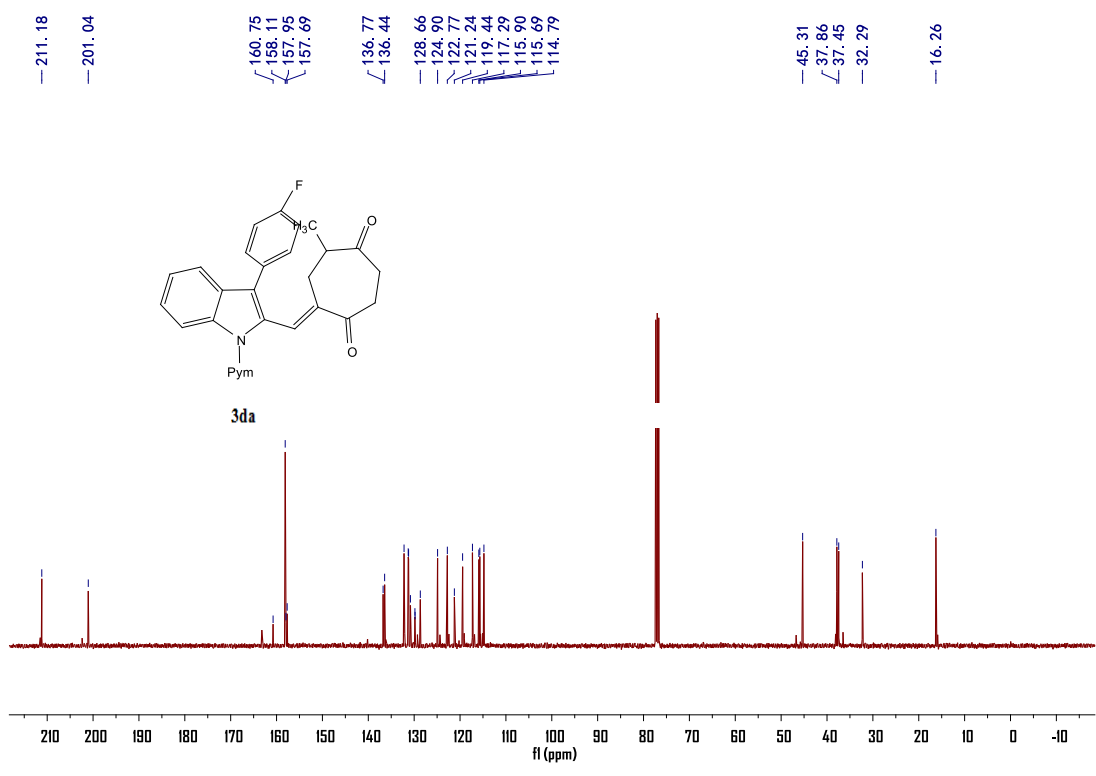
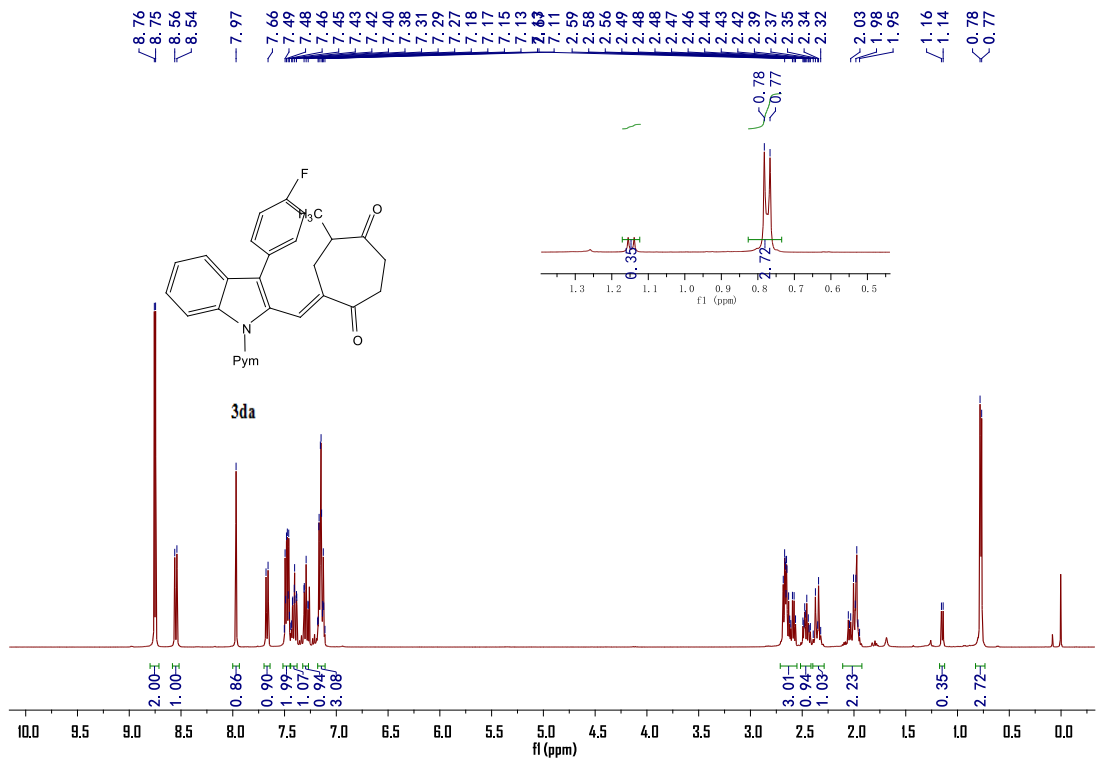
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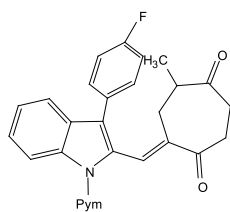




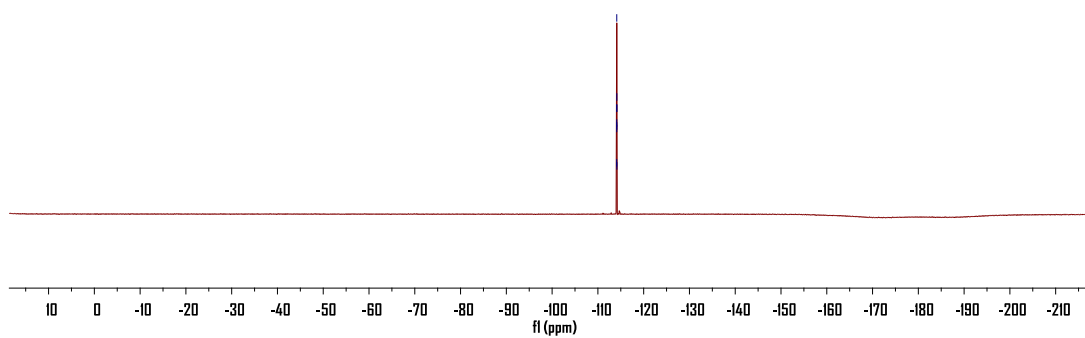








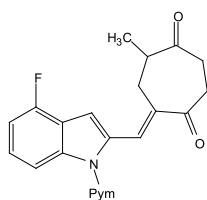
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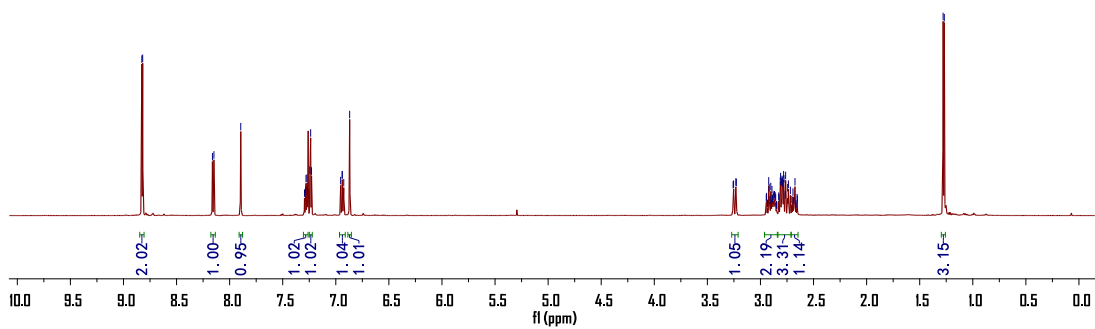
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6.87

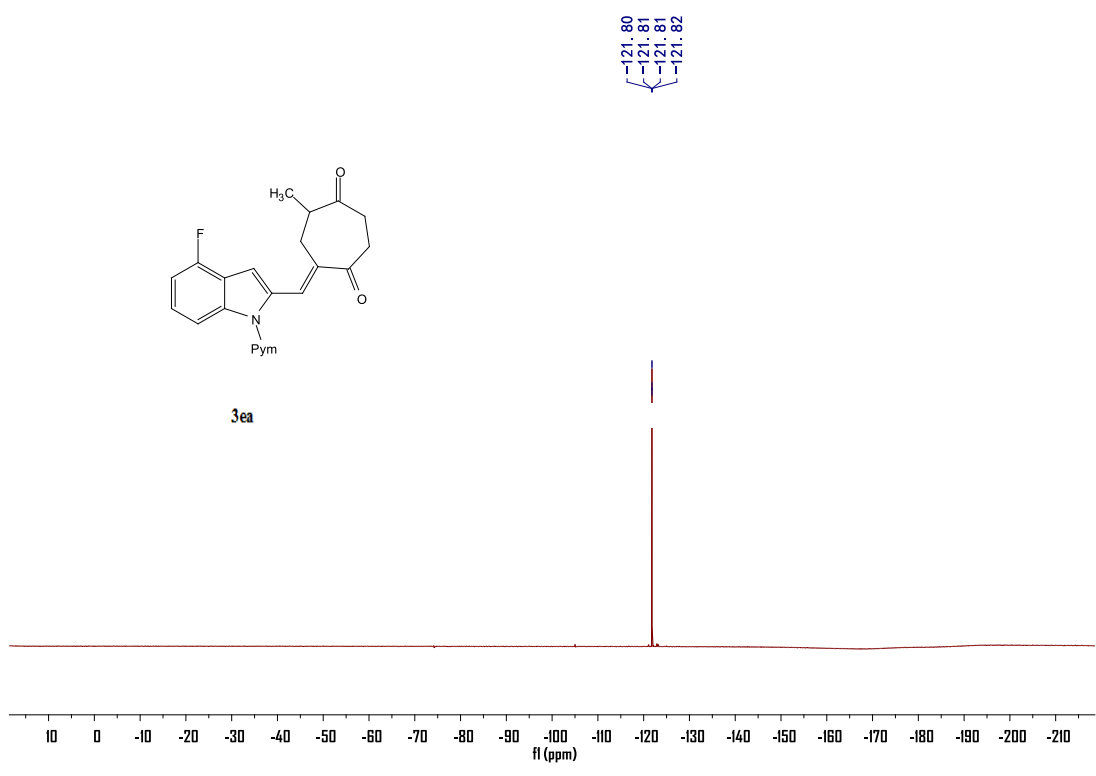
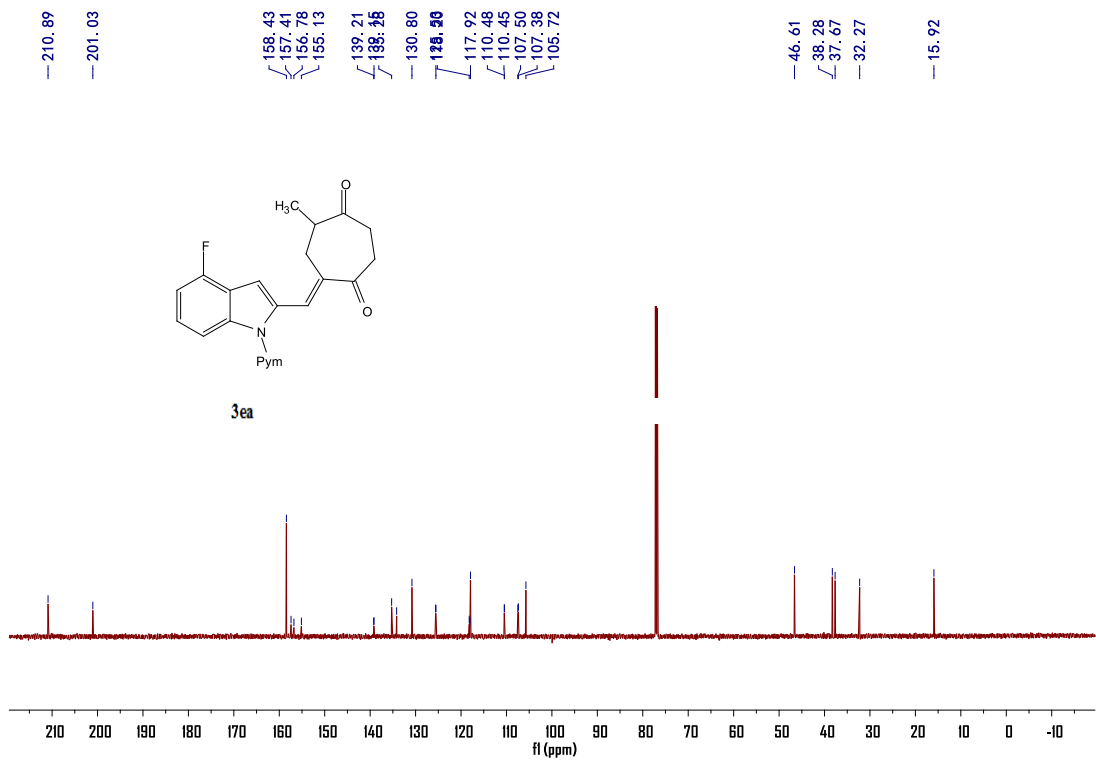
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2.69  
2.66

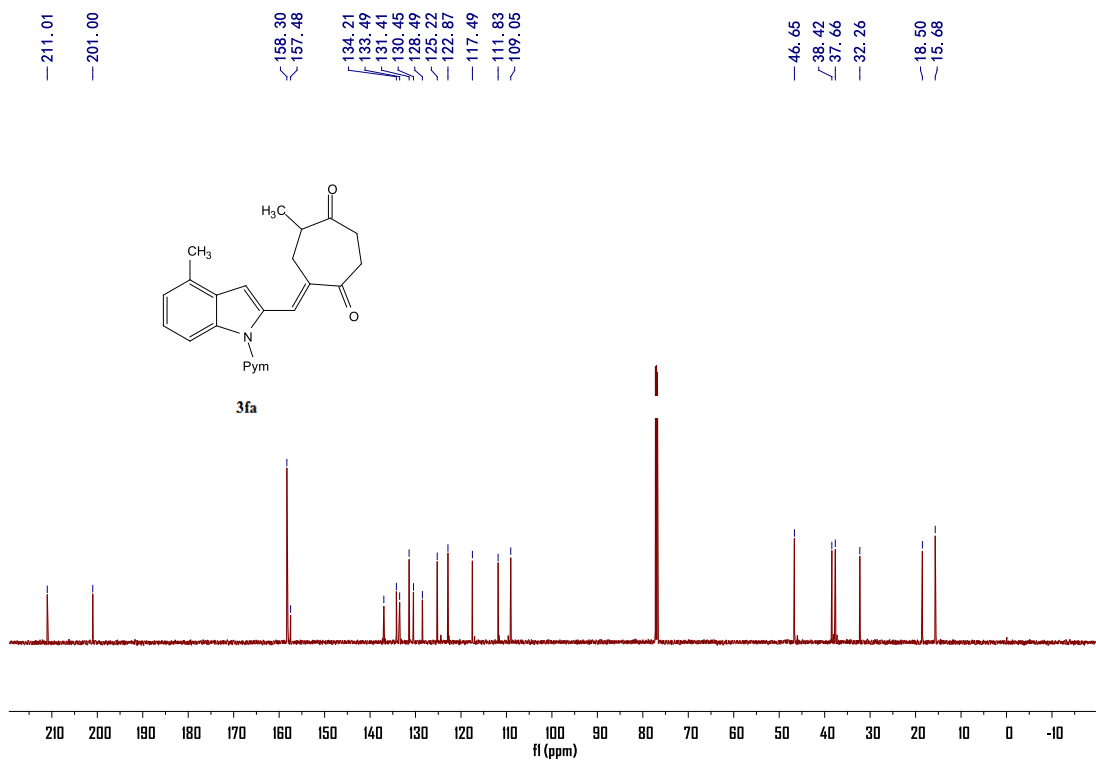
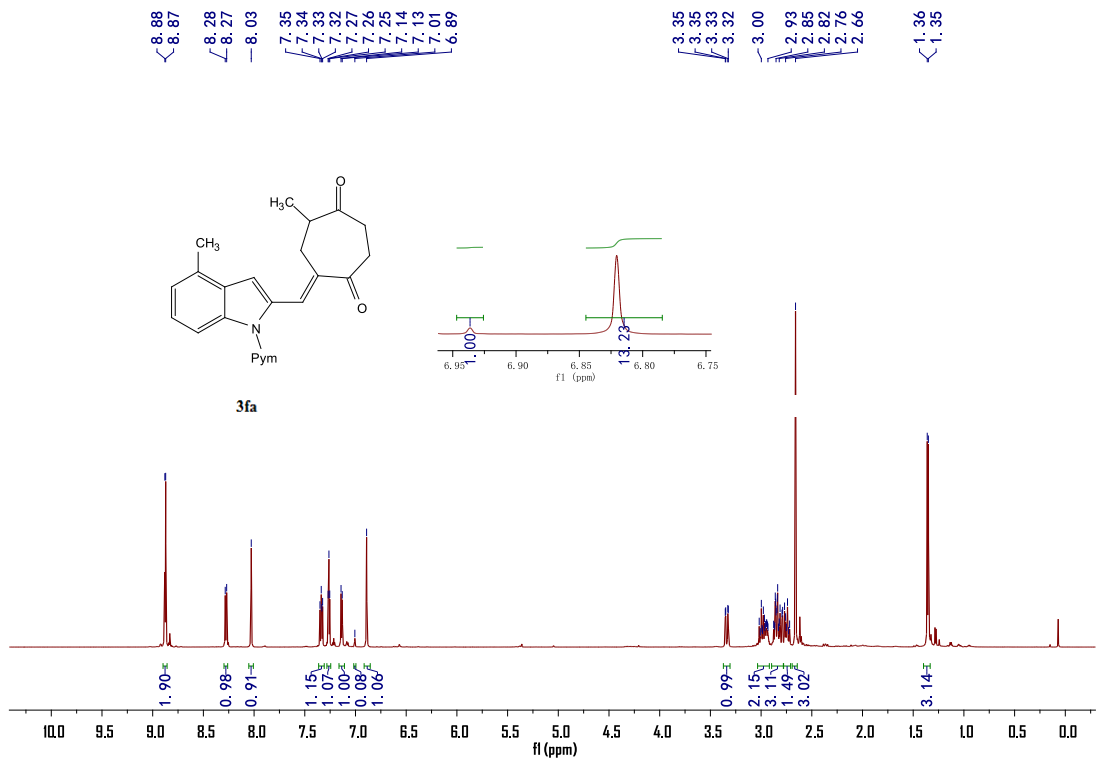
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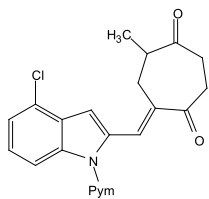
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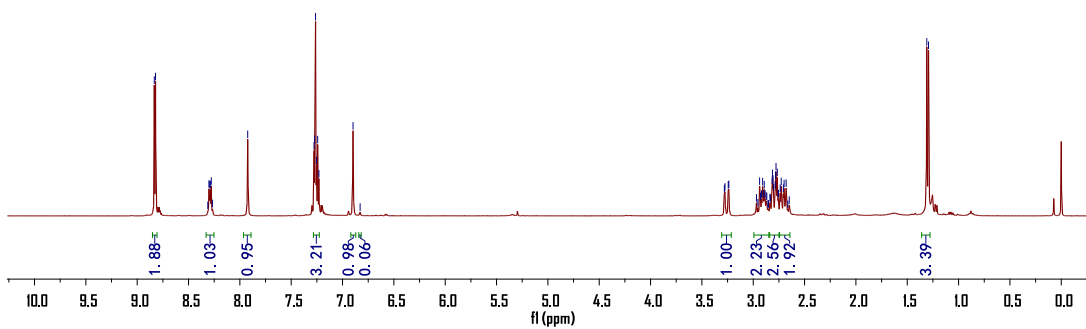
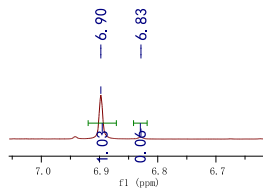




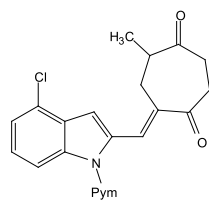
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 7.23  
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 6.83  
 3.28  
 3.28  
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 3.24  
 2.90  
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 2.81  
 2.78  
 2.73  
 2.68  
 1.31



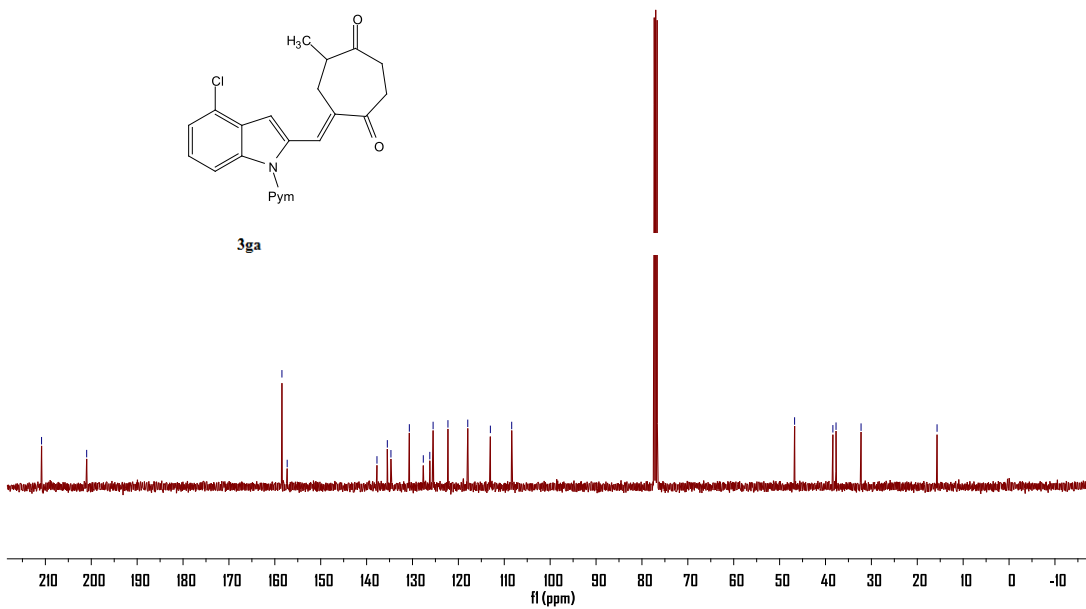
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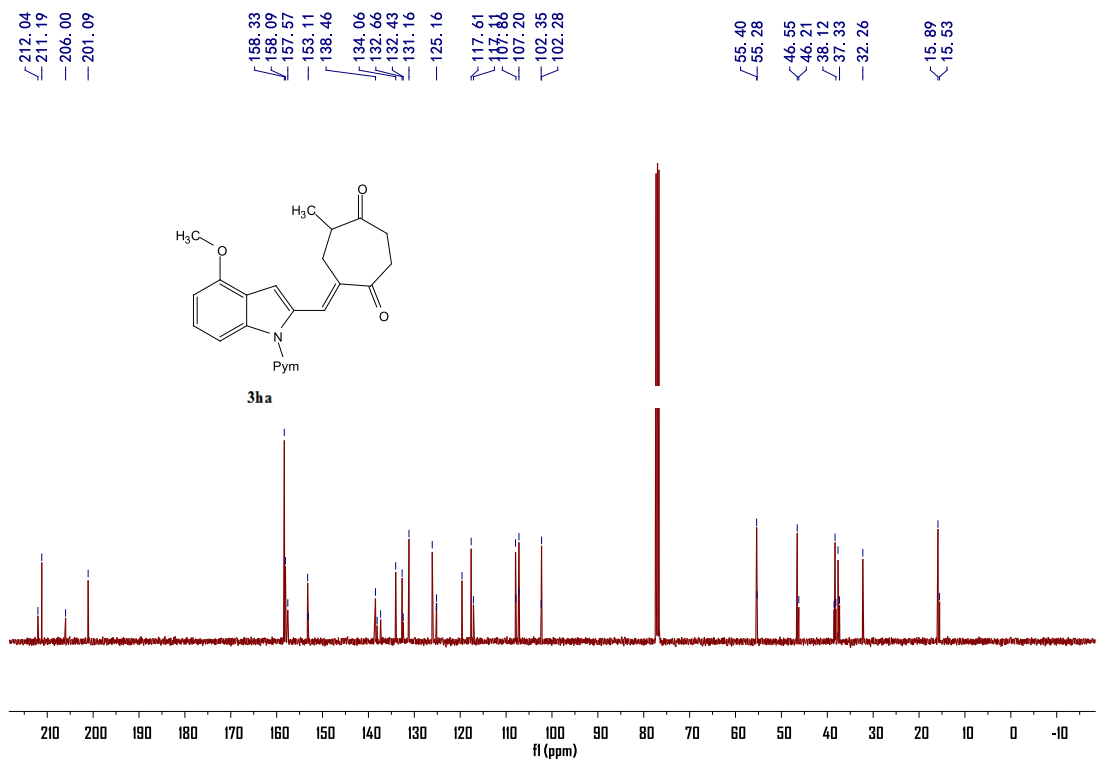
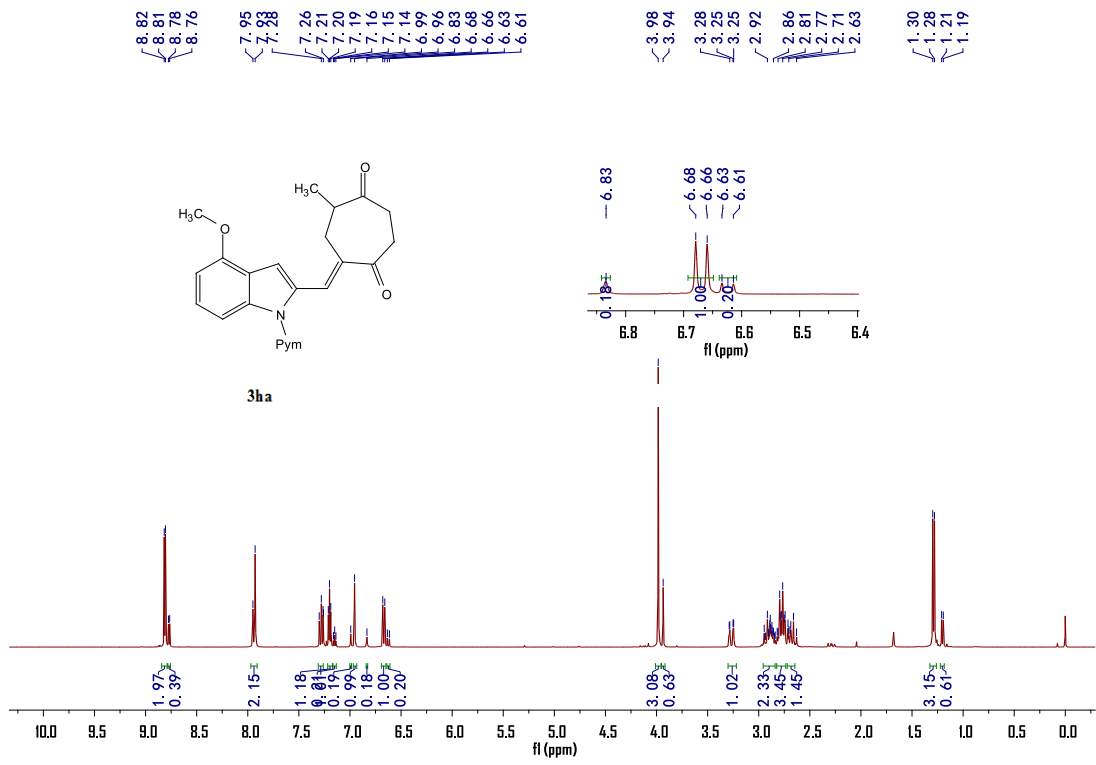


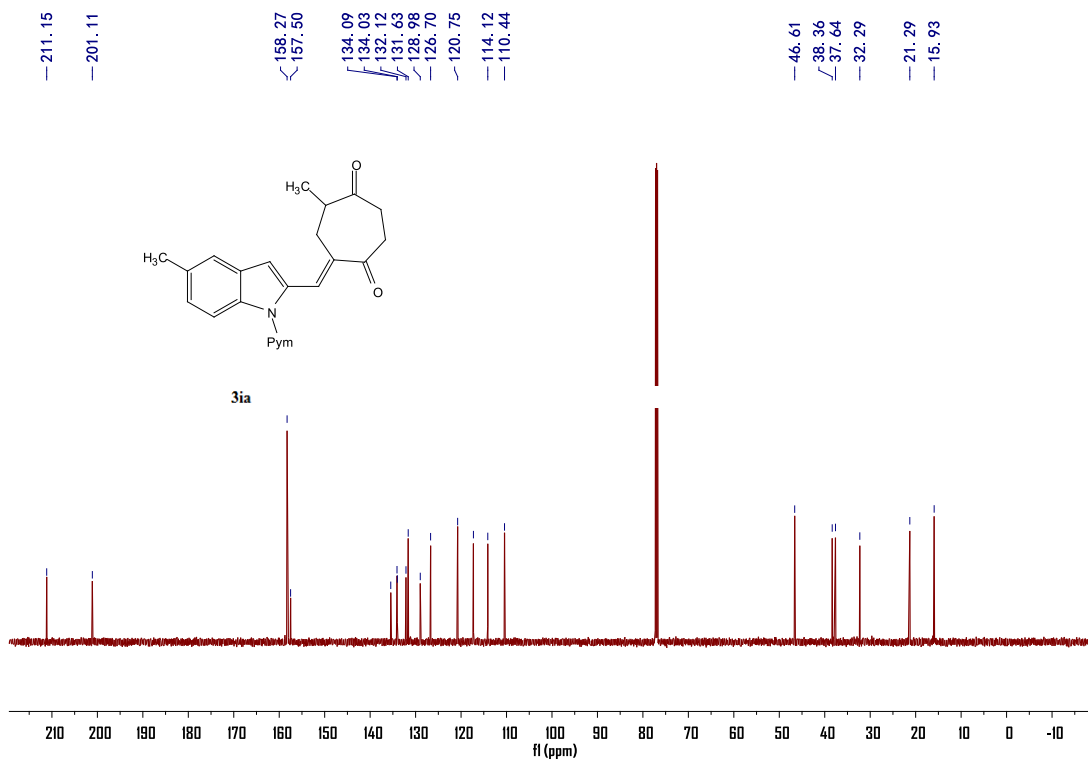
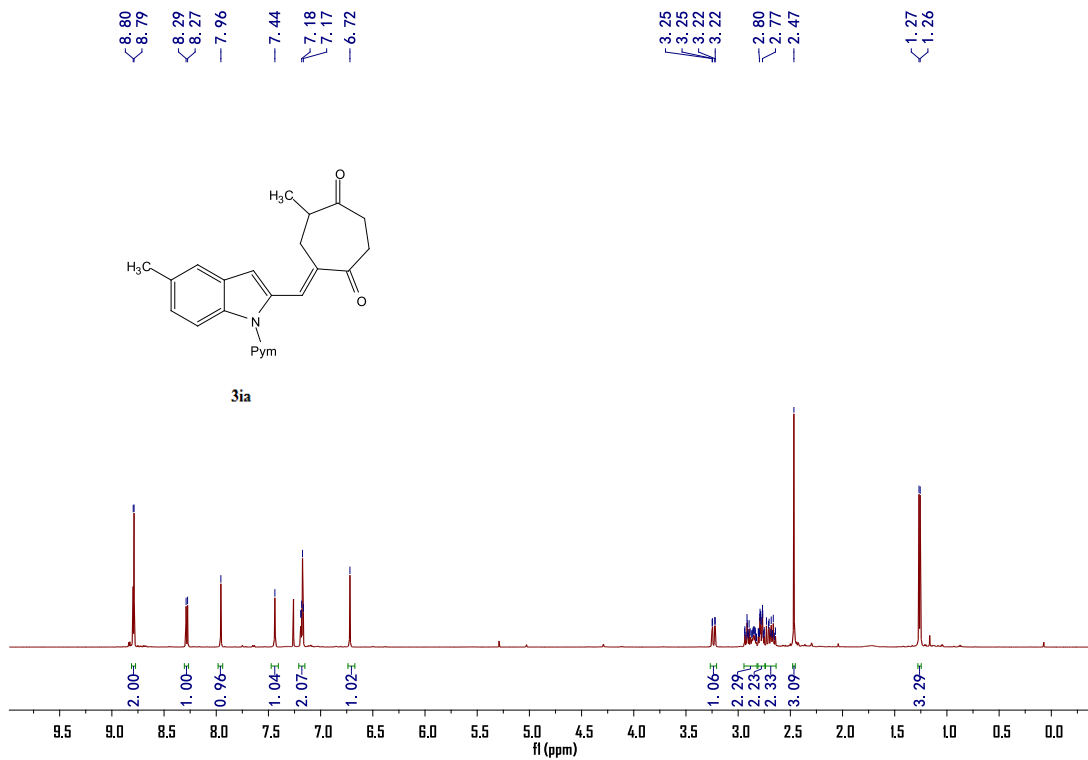
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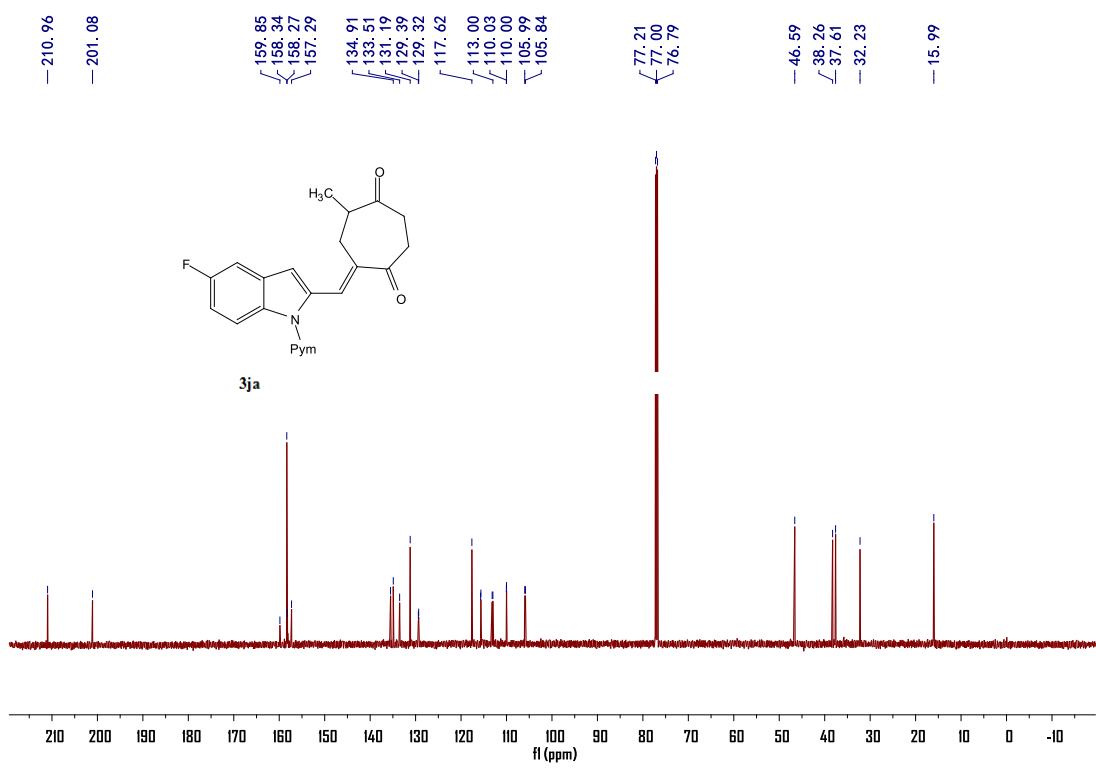
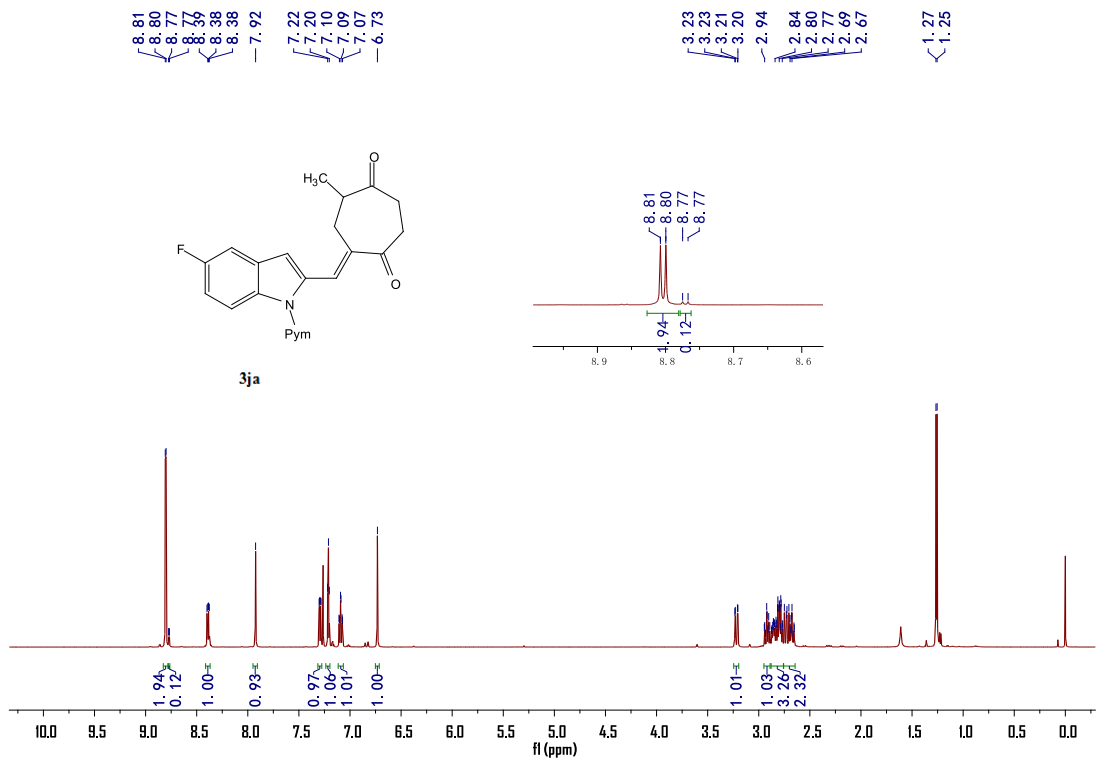


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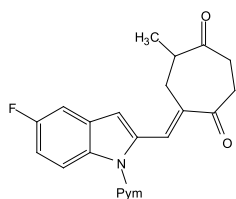






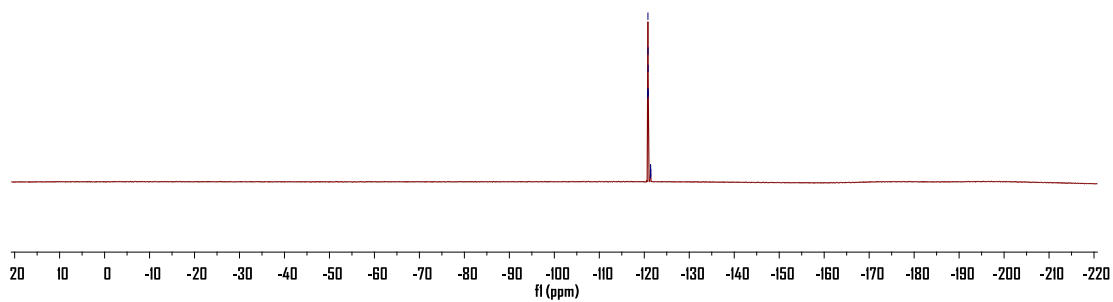






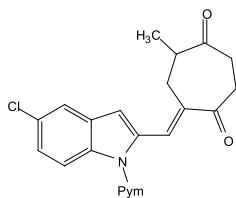
3ja

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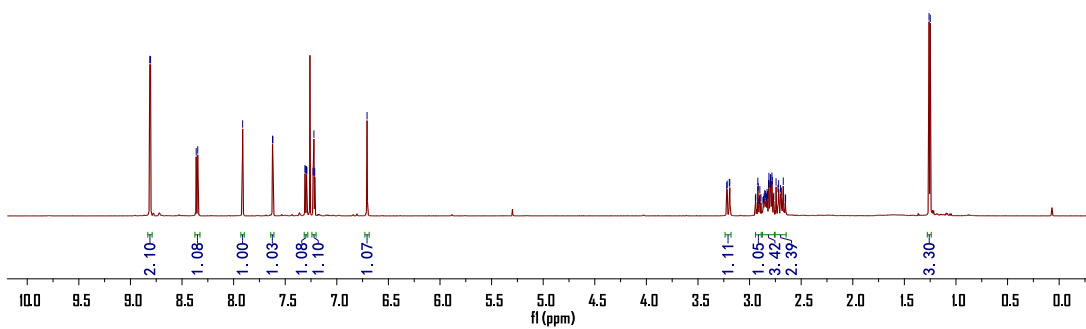


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7.23  
7.21  
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3.22  
3.22  
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2.72  
2.67  
1.26  
1.25



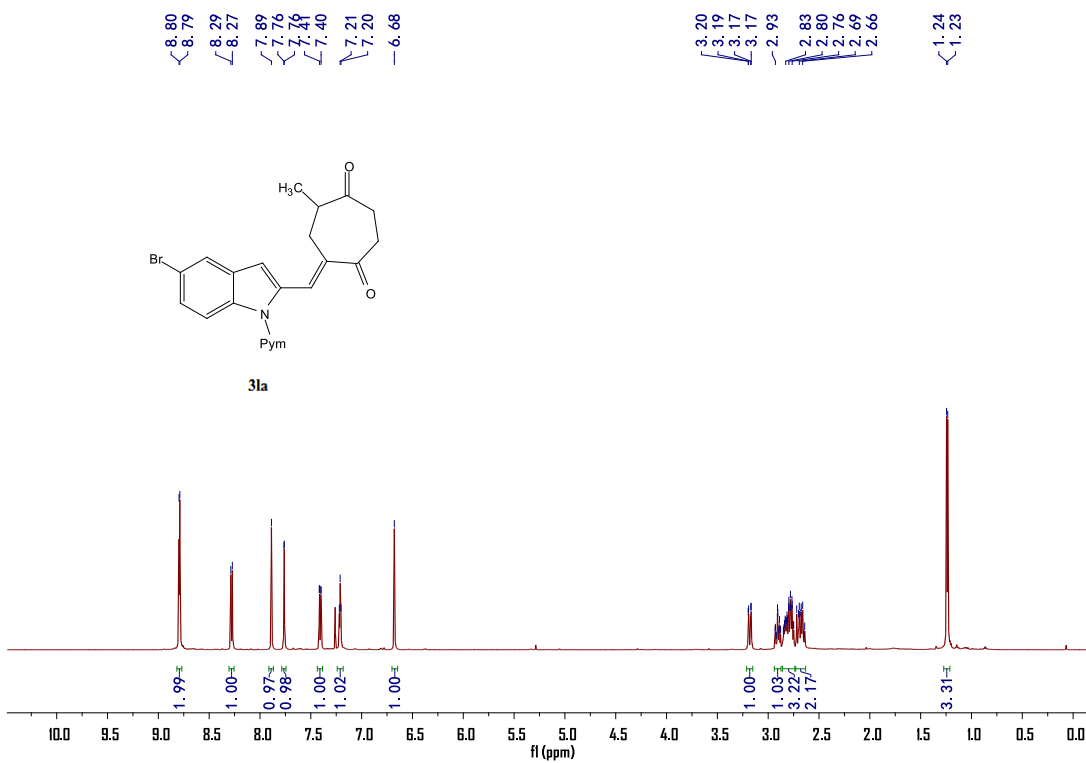
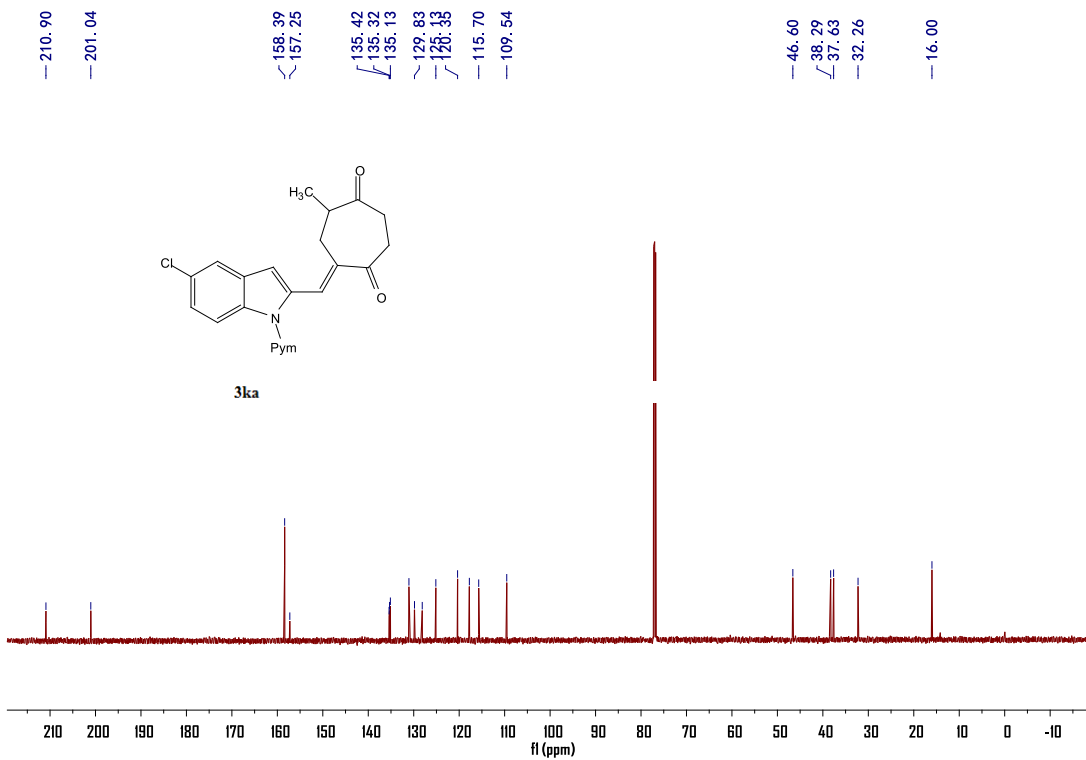
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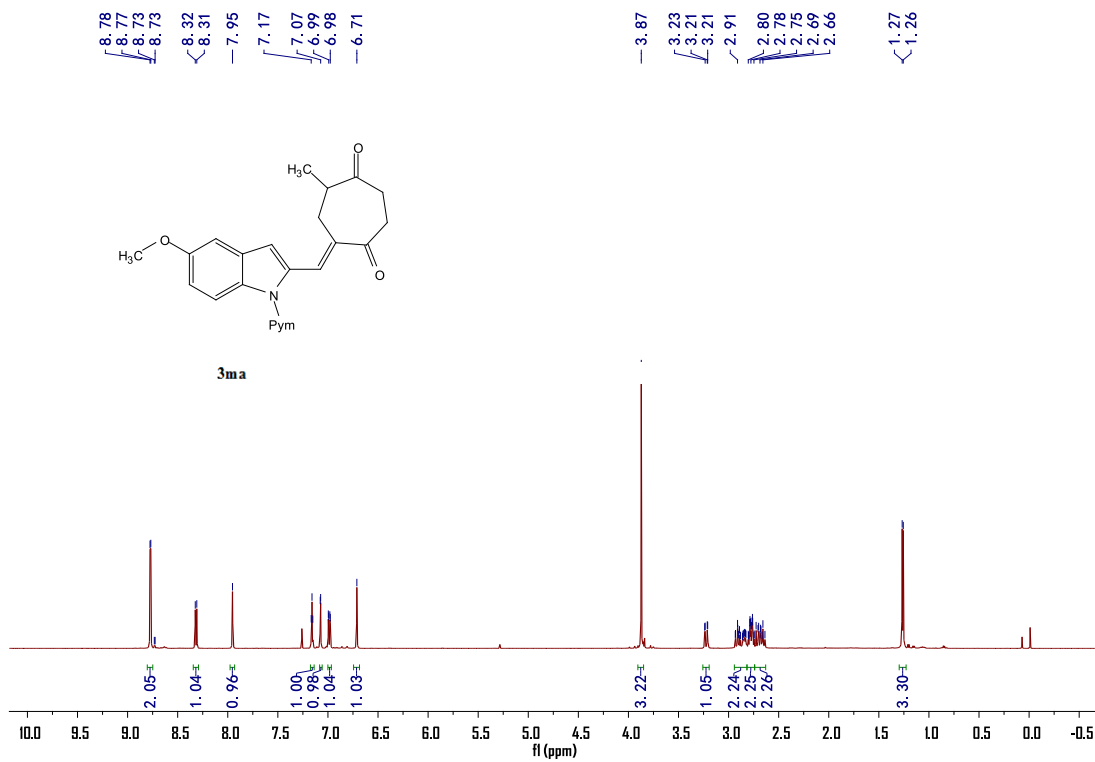
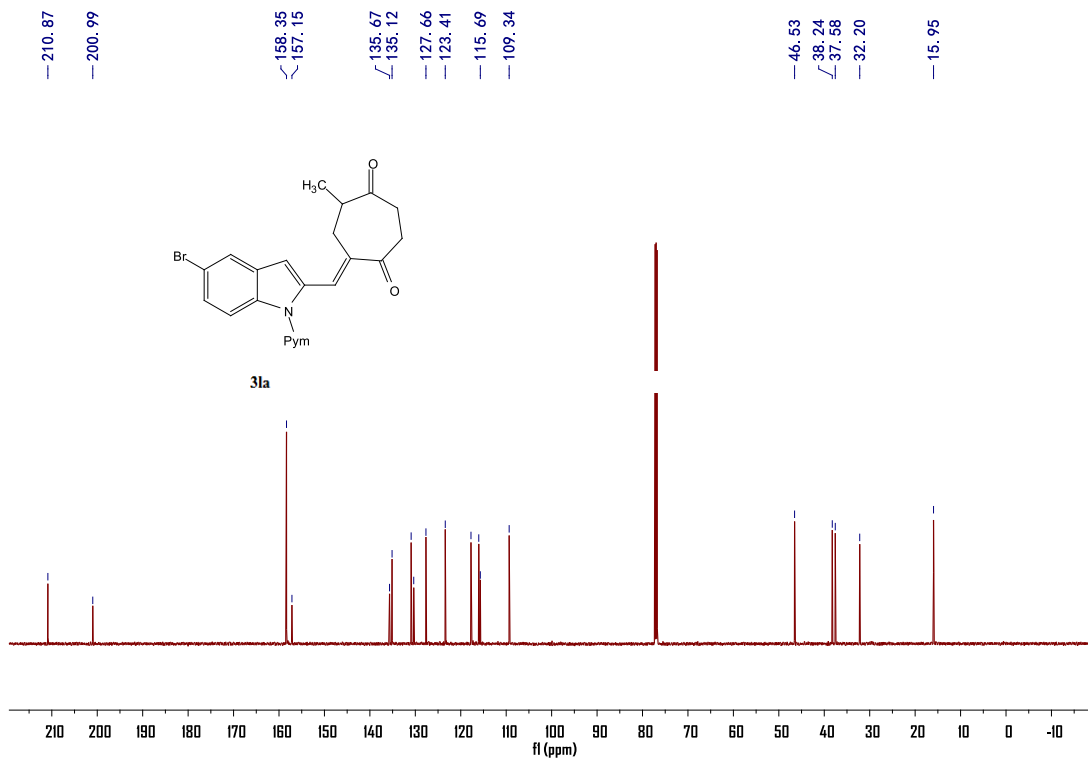


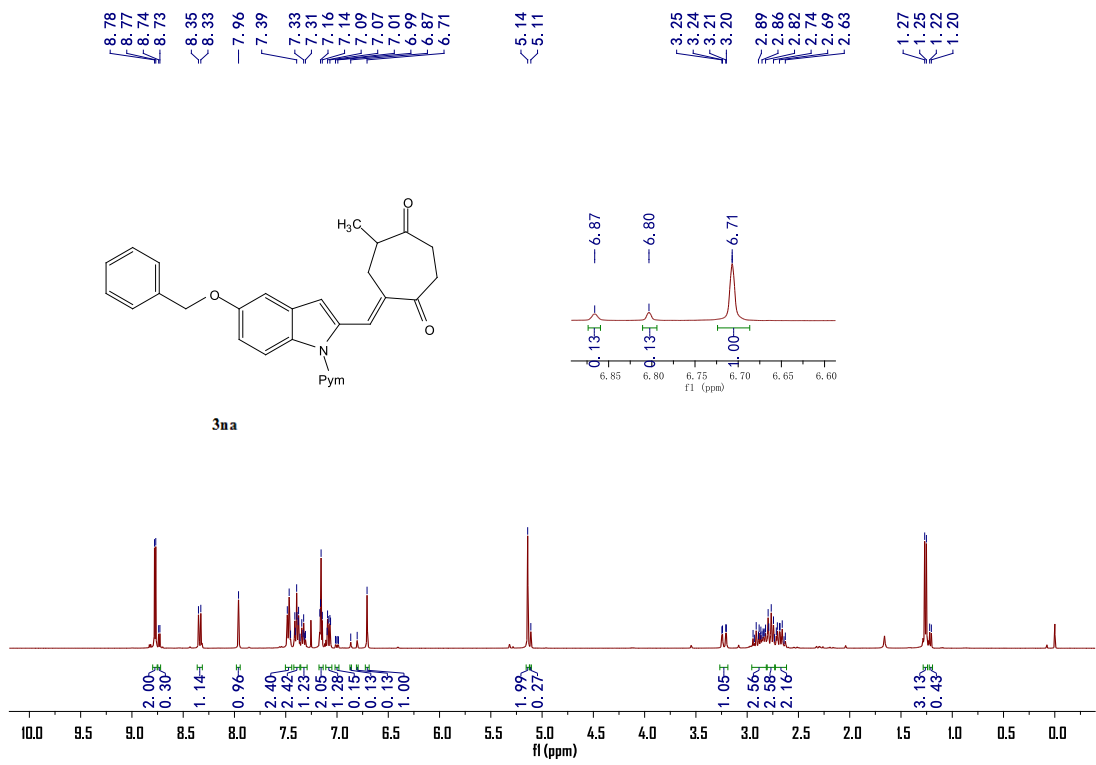
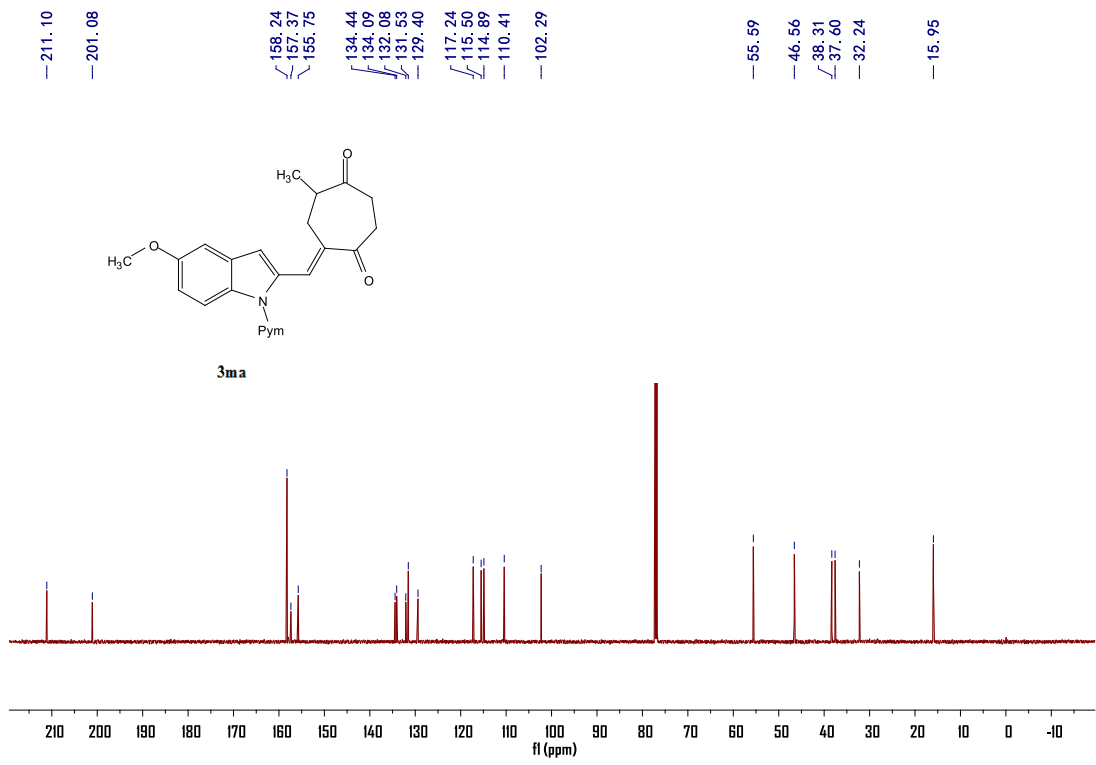
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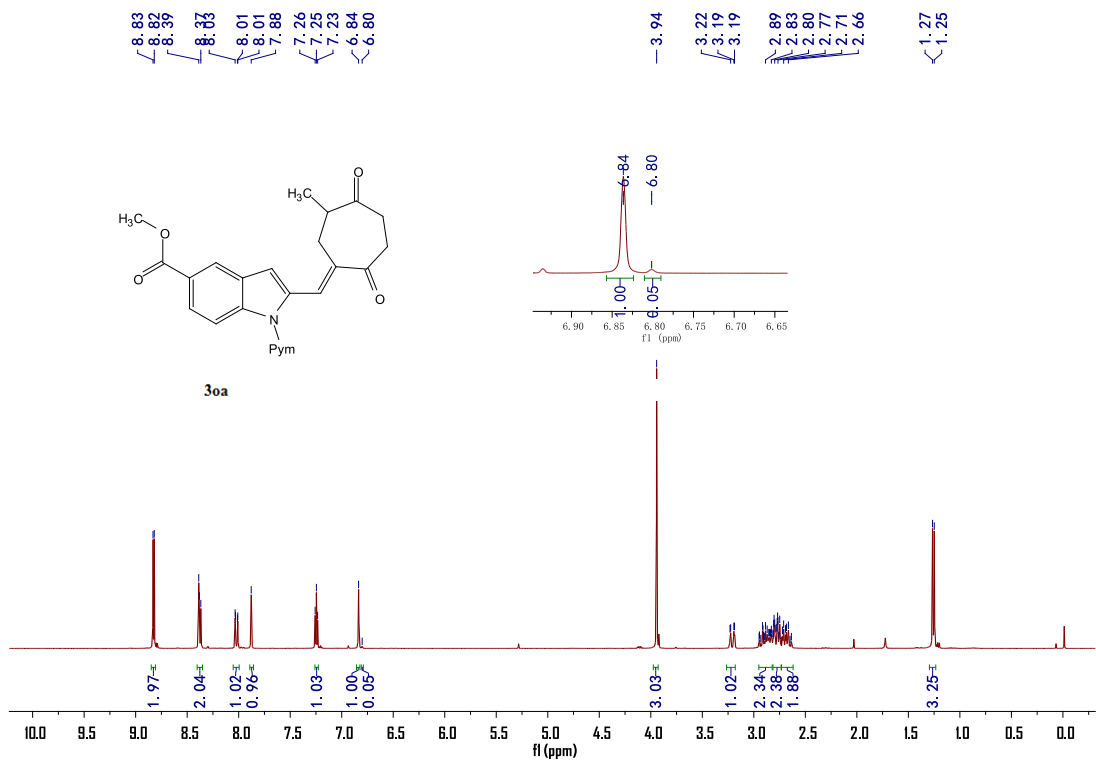
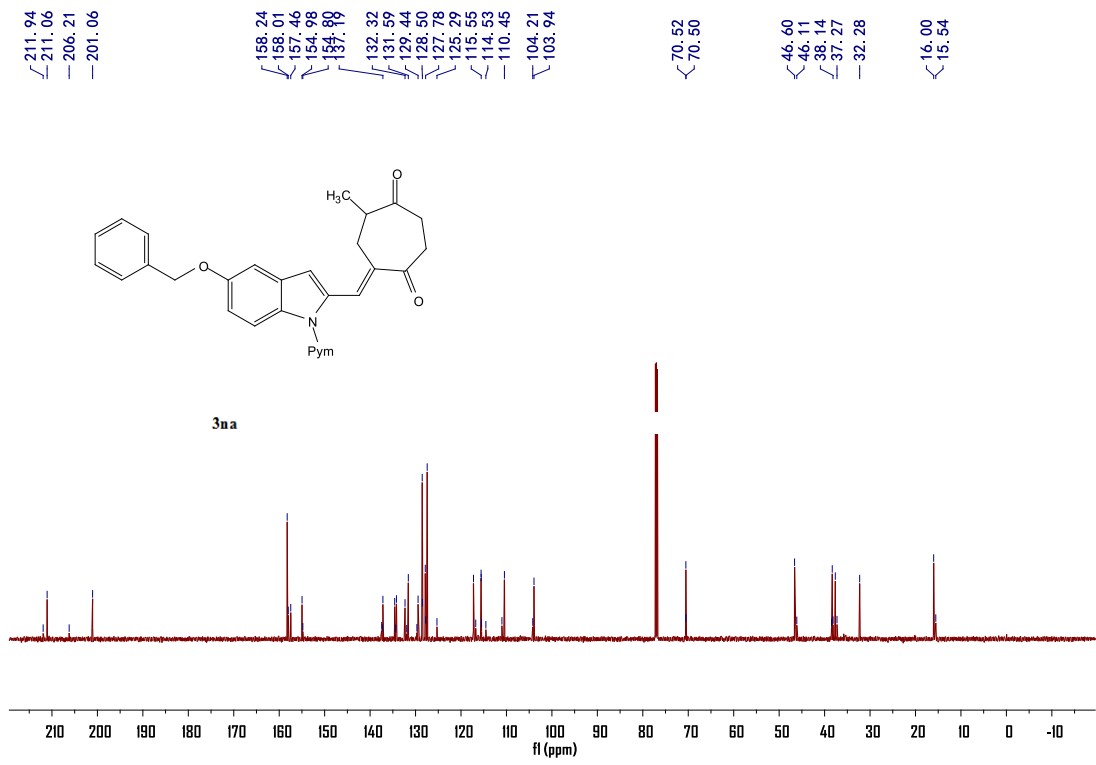
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3.30





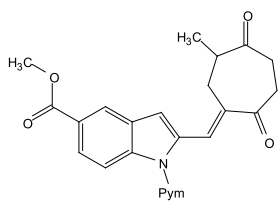




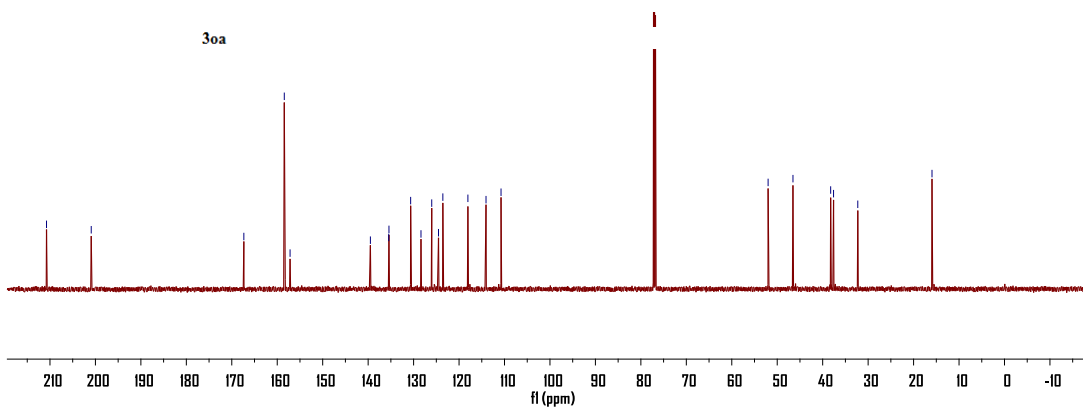
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— 200.92

— 167.35  
— 158.45  
— 157.18  
— 139.51  
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— 130.65  
— 123.56  
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— 114.07  
— 110.76

— 52.01  
— 46.54  
— 38.24  
— 37.61  
— 32.27  
— 15.95

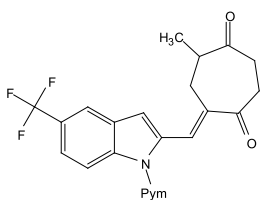


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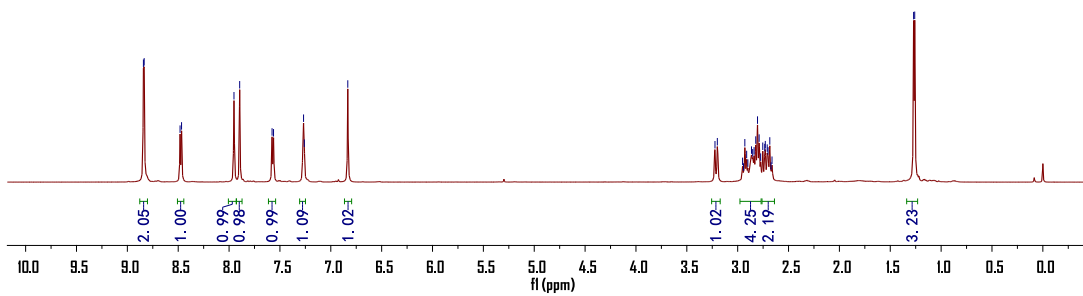


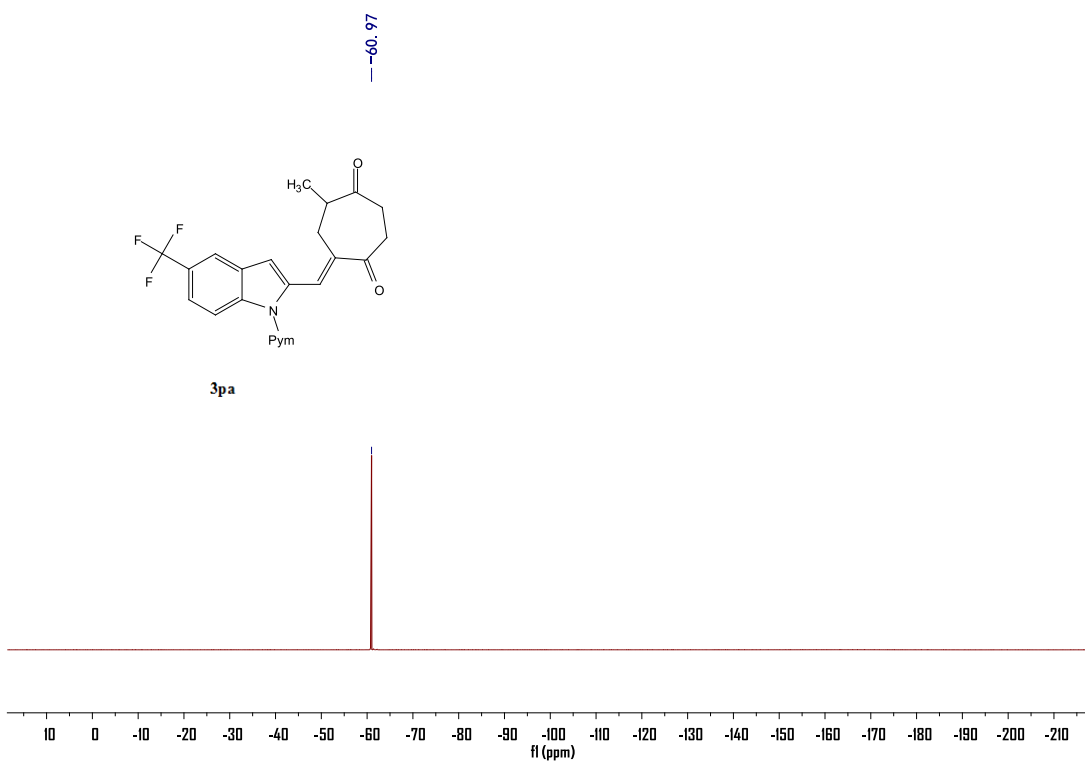
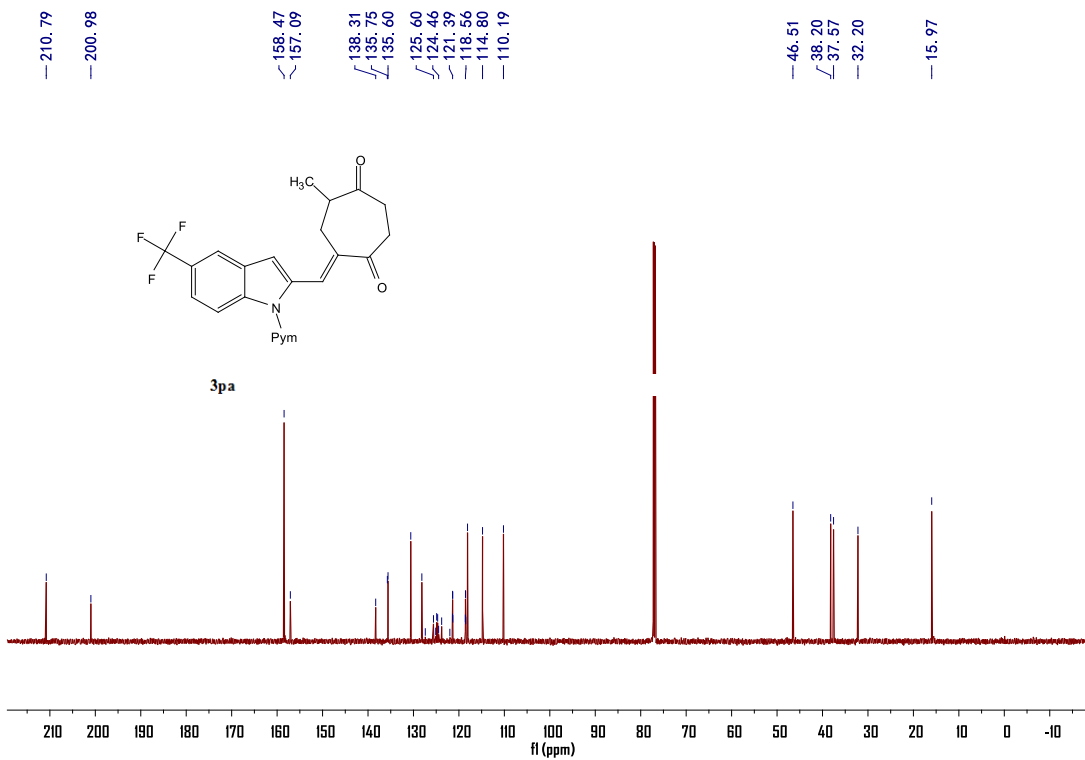
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— 8.47  
— 7.95  
— 7.90  
— 7.56  
— 7.27  
— 7.26  
— 6.83

— 3.22  
— 3.20  
— 2.95  
— 2.84  
— 2.79  
— 2.73  
— 2.70  
— 2.66  
— 1.27  
— 1.26

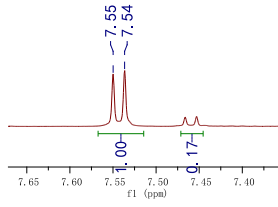
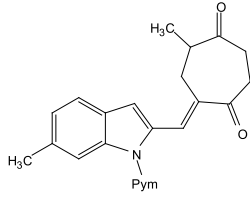


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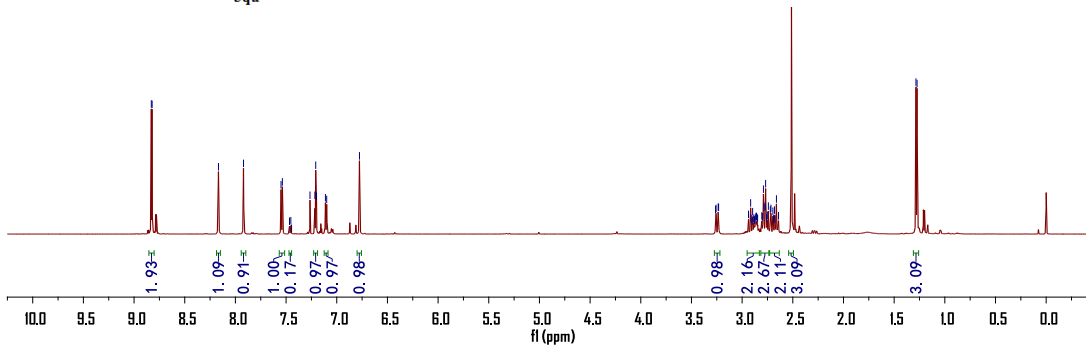




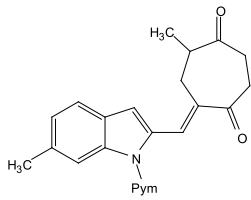
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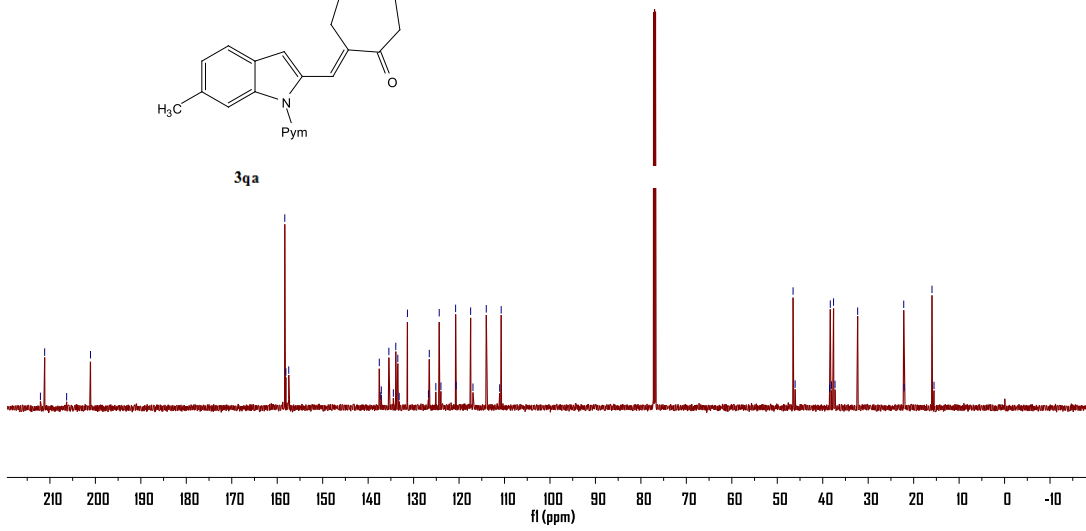
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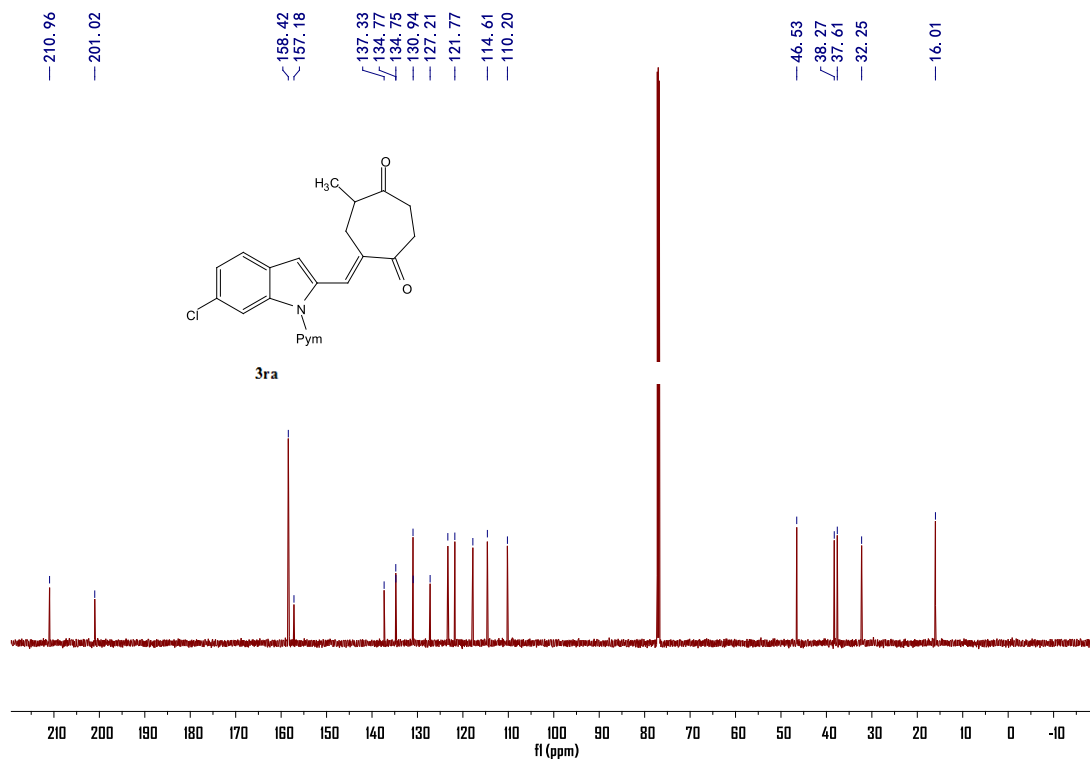
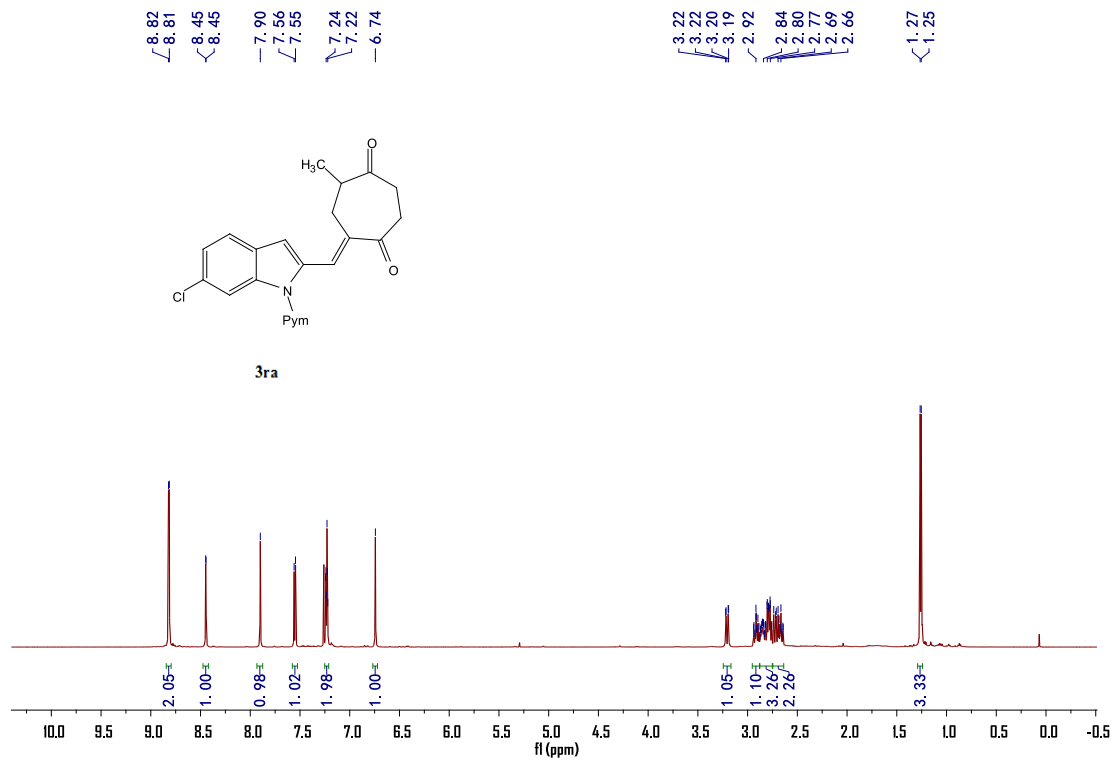
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 111.06  
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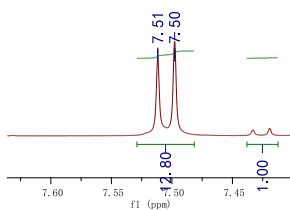
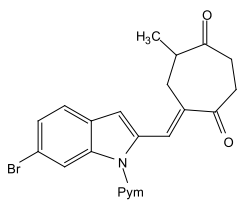
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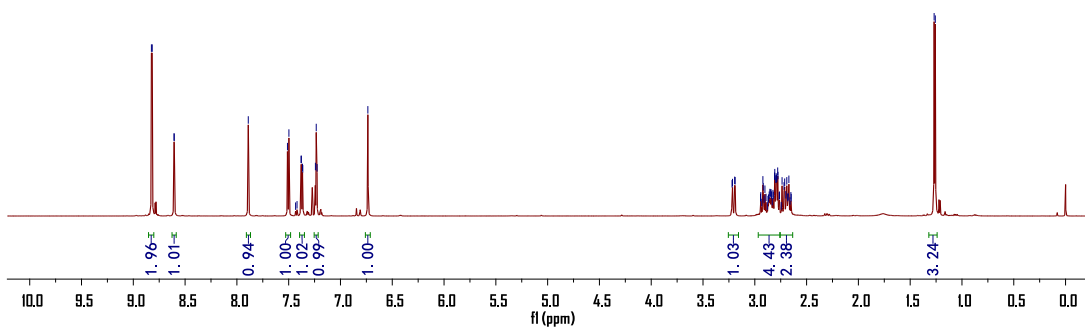




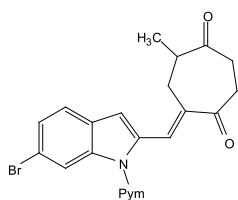
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 1.26



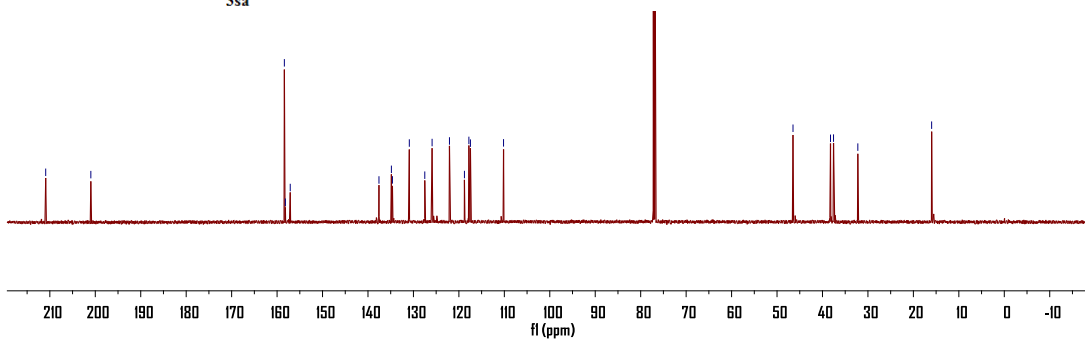
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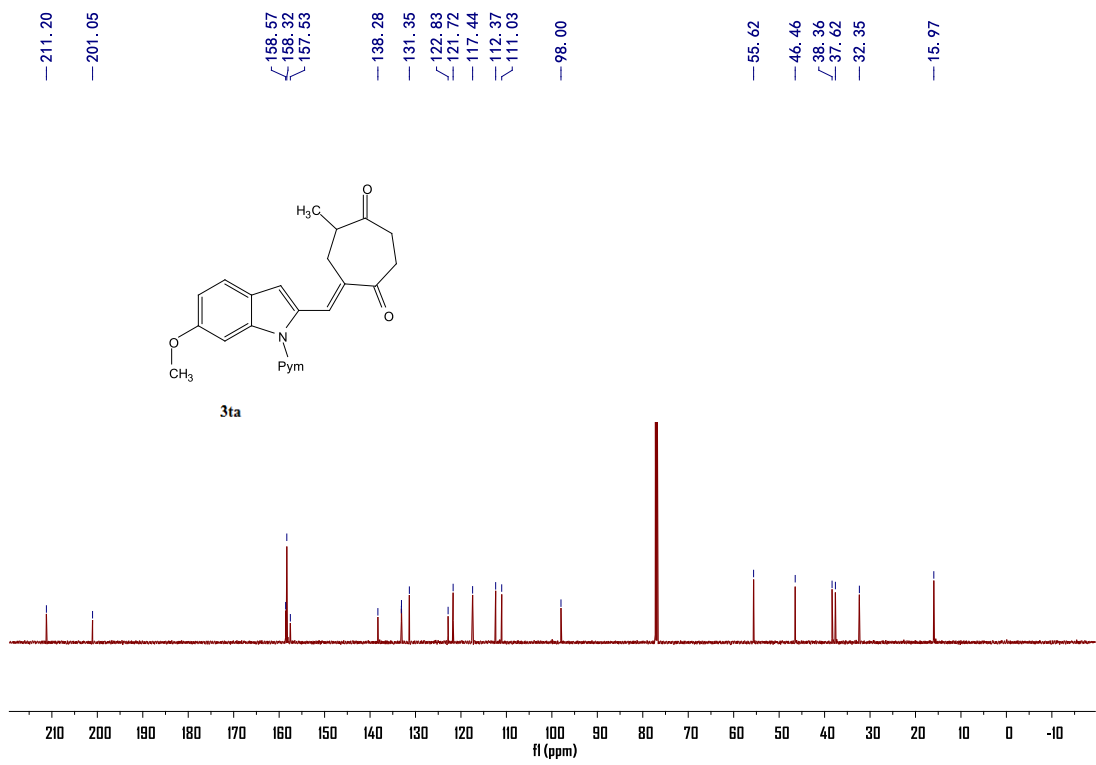
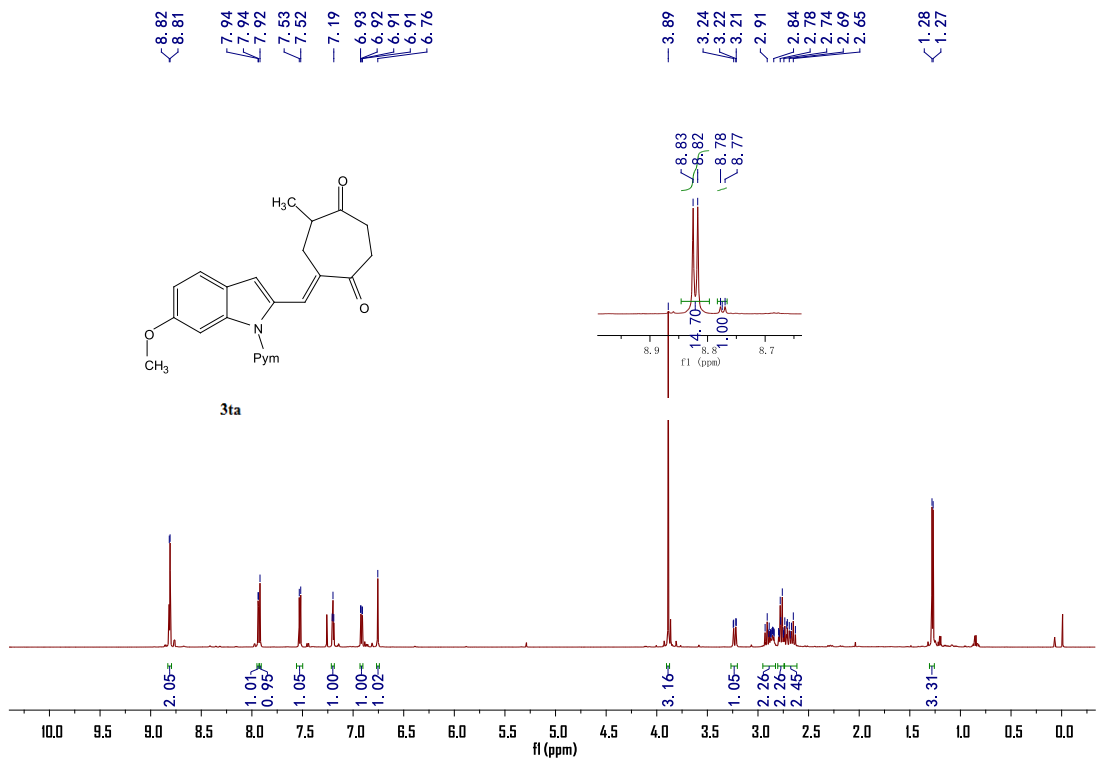


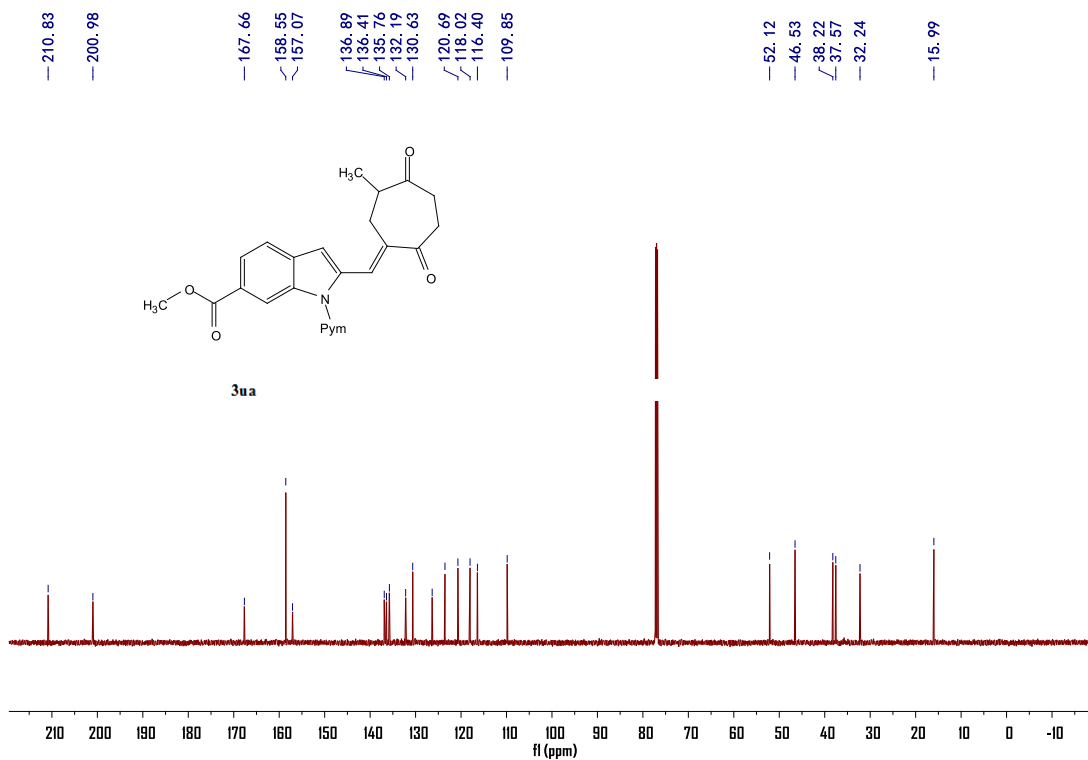
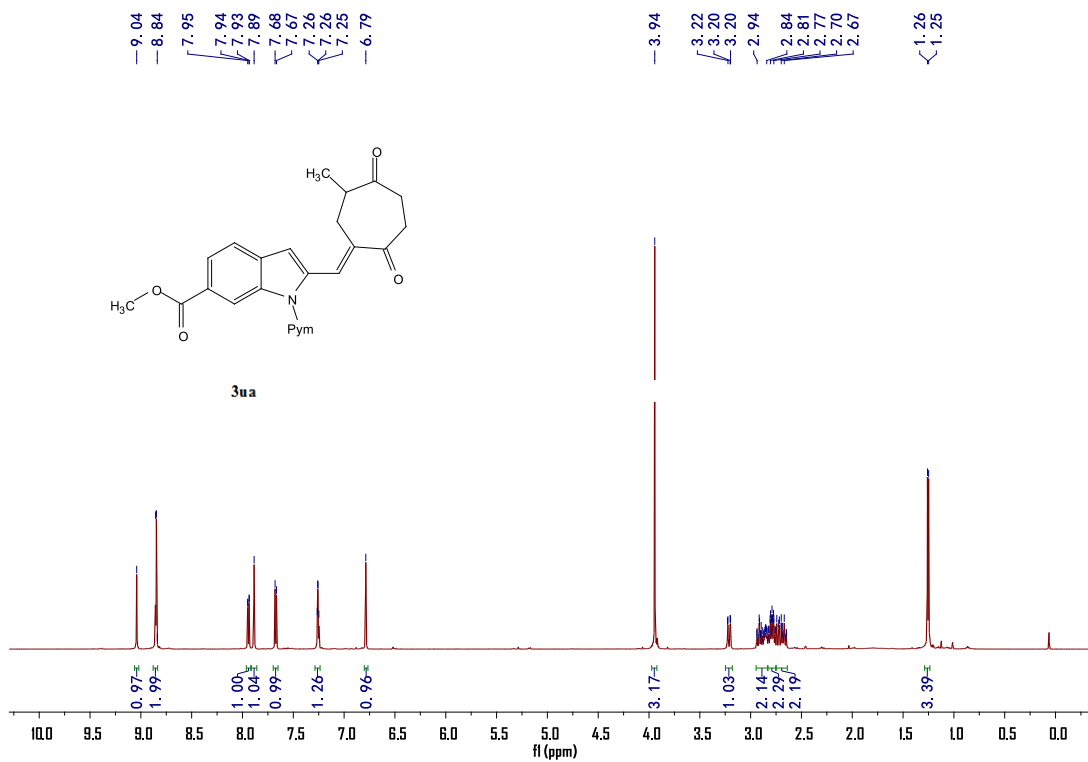
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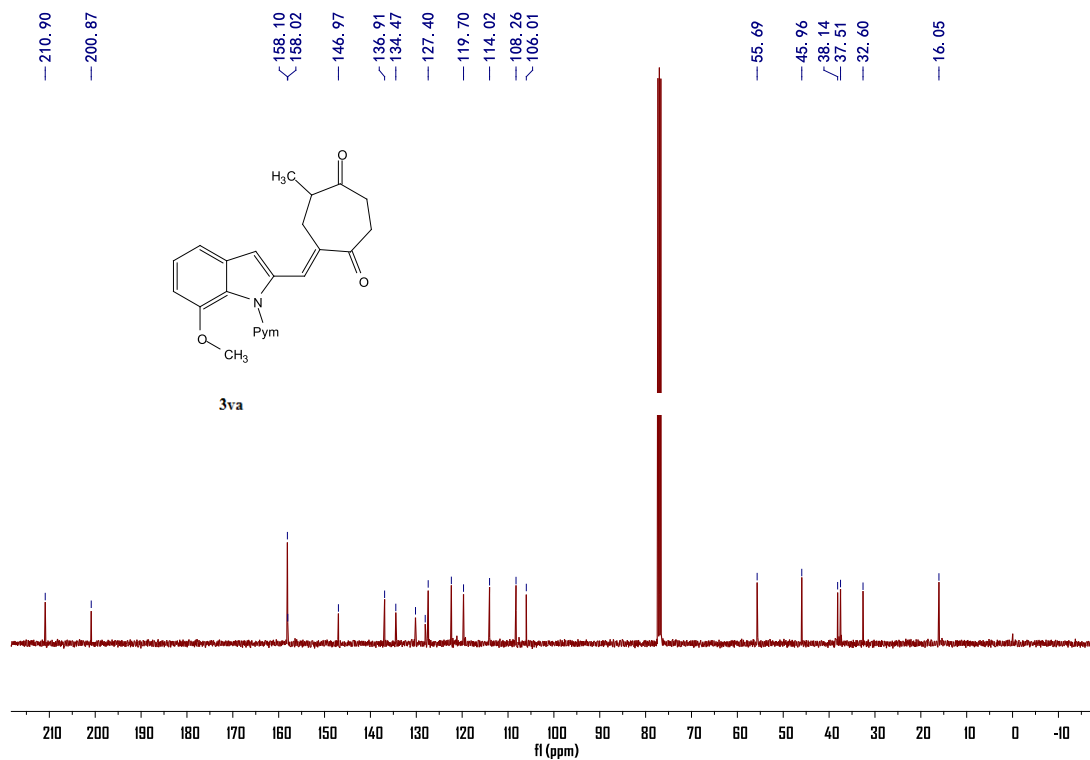
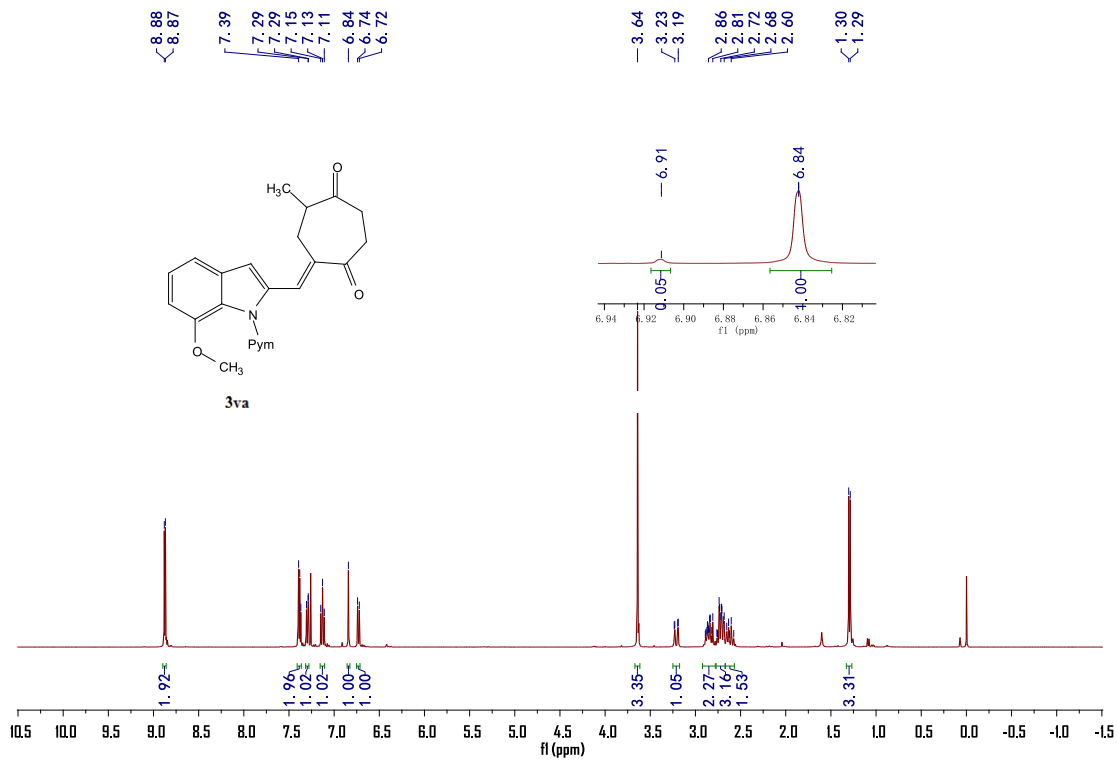


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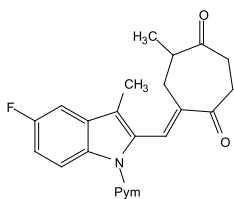




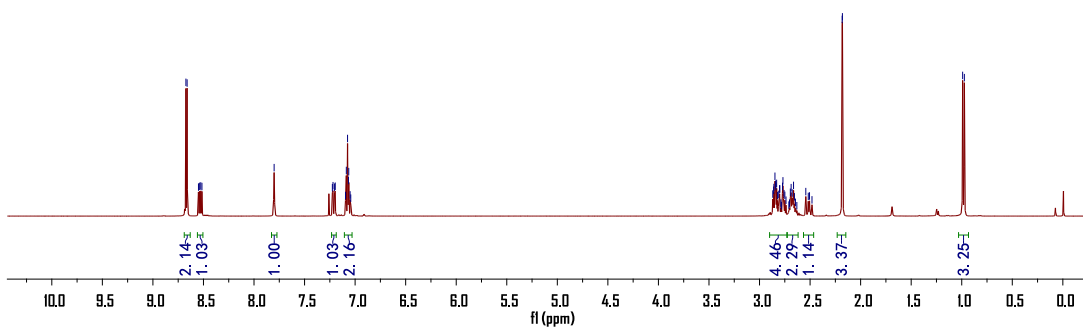




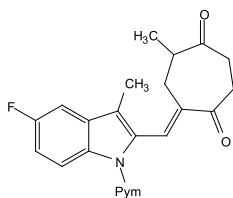
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 7.06  
 7.05  
 7.04  
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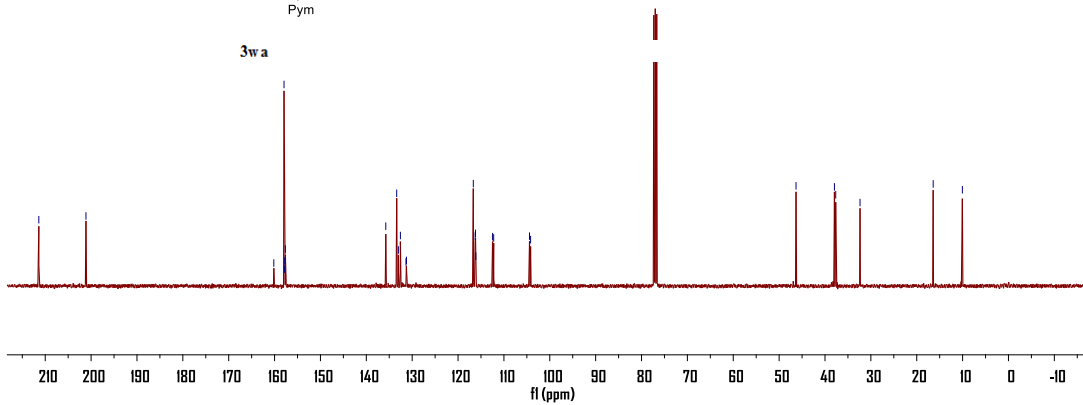
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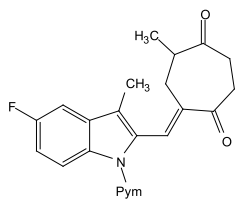


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 131.25  
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 116.19  
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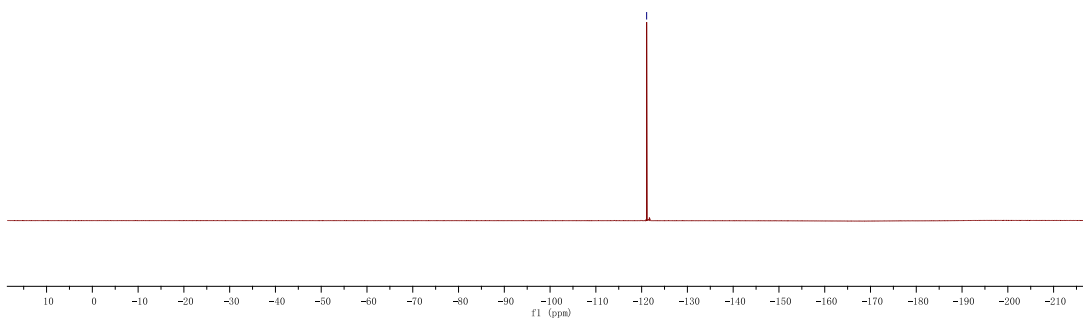


3wa





3wa



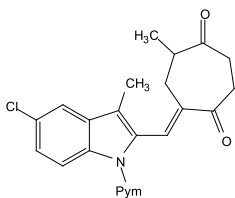
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8.48

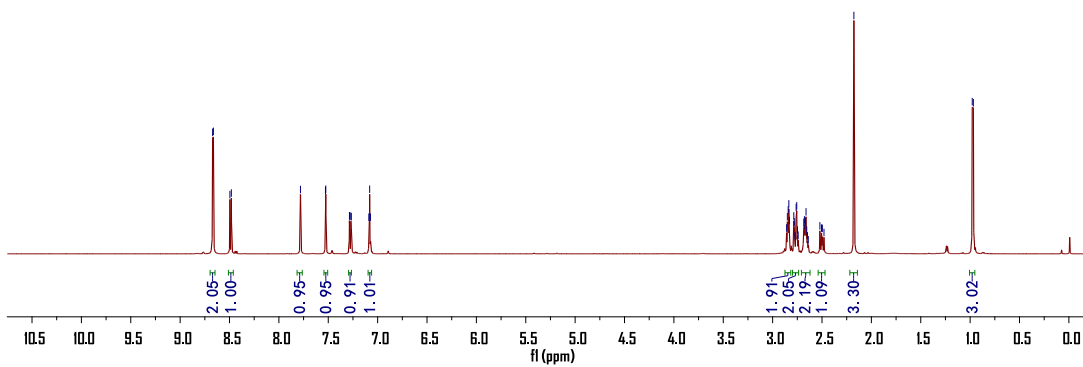
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7.52  
7.27  
7.09  
7.08  
7.07

2.84  
2.75  
2.74  
2.68  
2.67  
2.66  
2.65  
2.64  
2.52  
2.50  
2.48

0.98  
0.97



3xa



2.05  
1.00

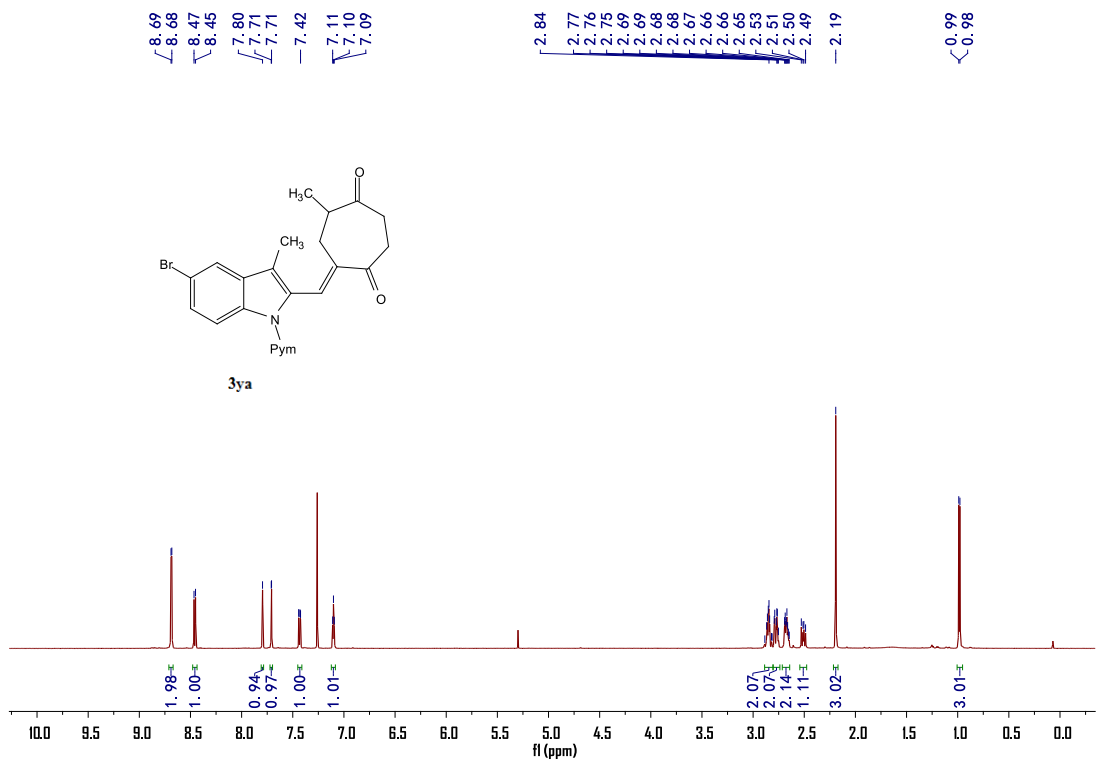
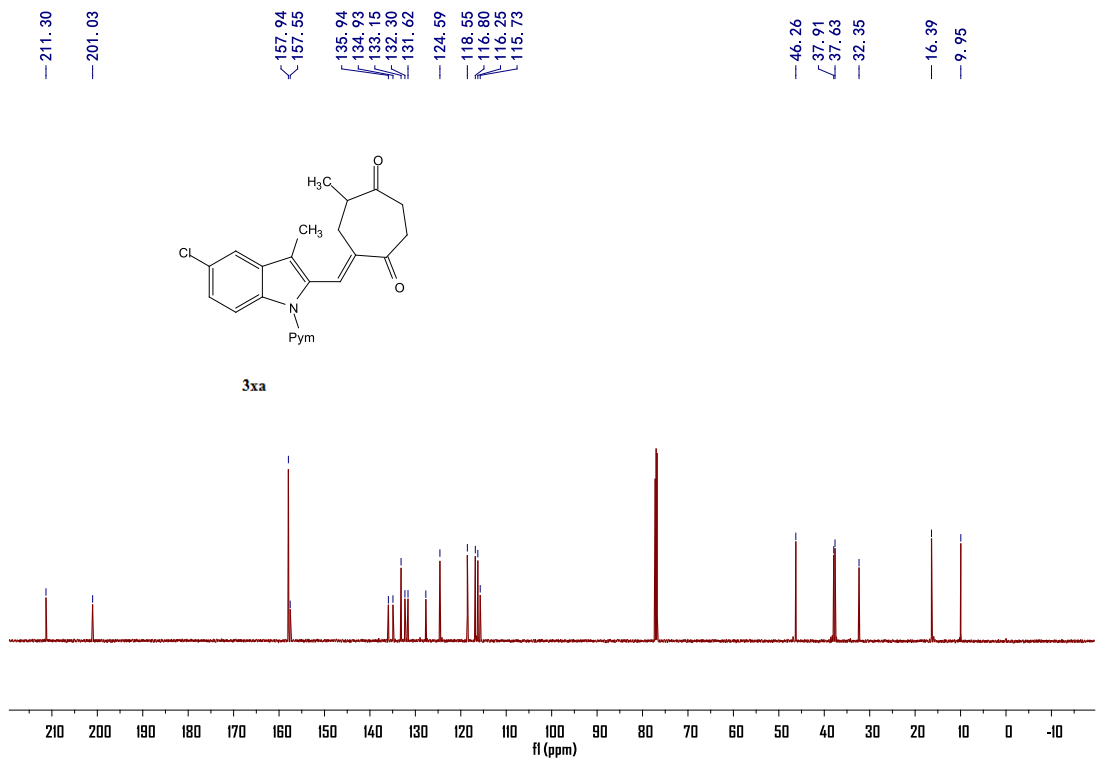
0.95  
0.95

0.91  
1.01

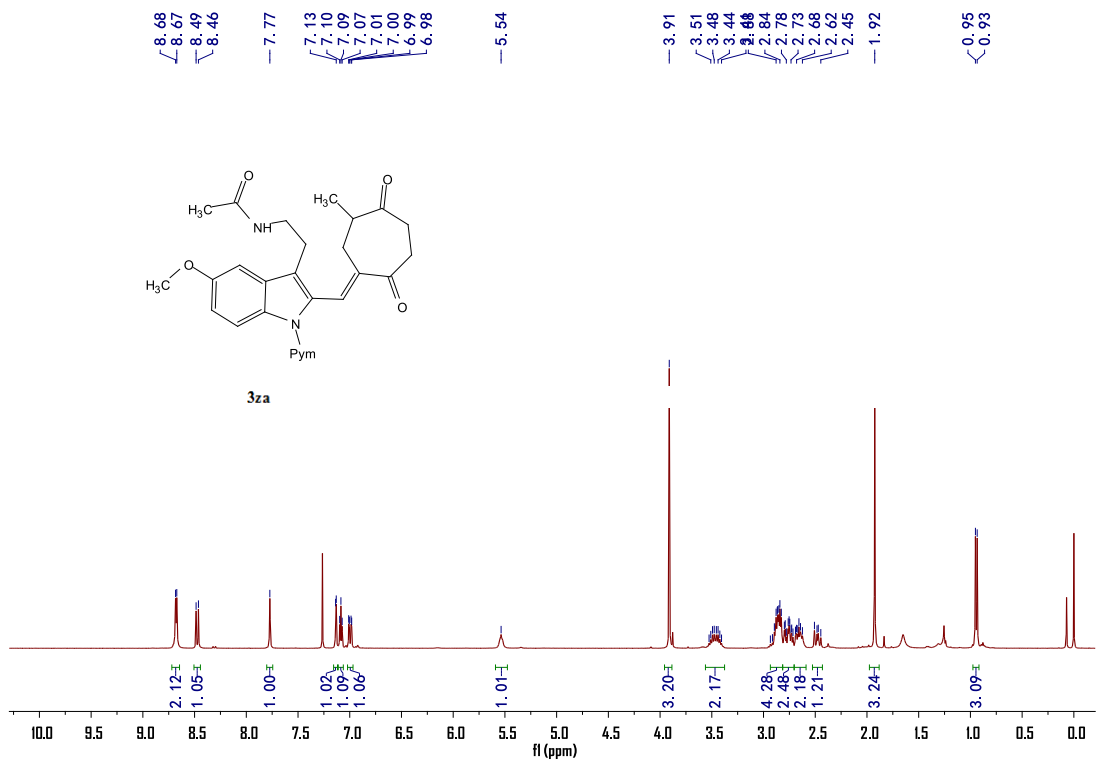
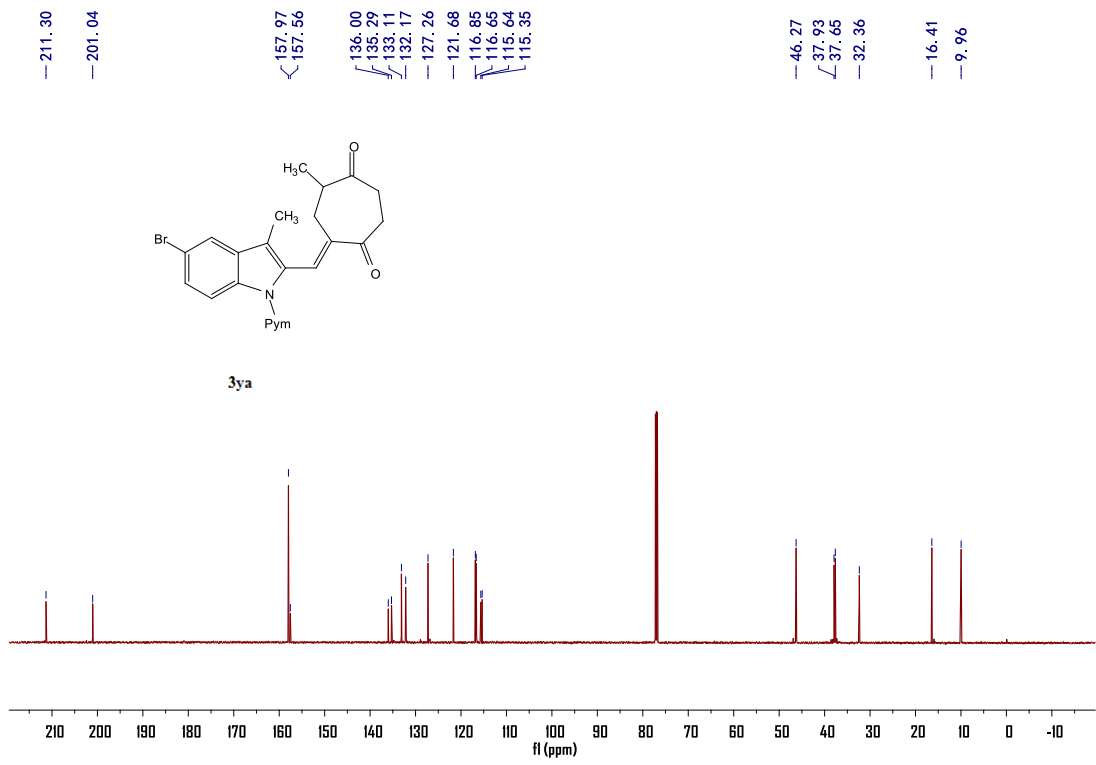
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1.09

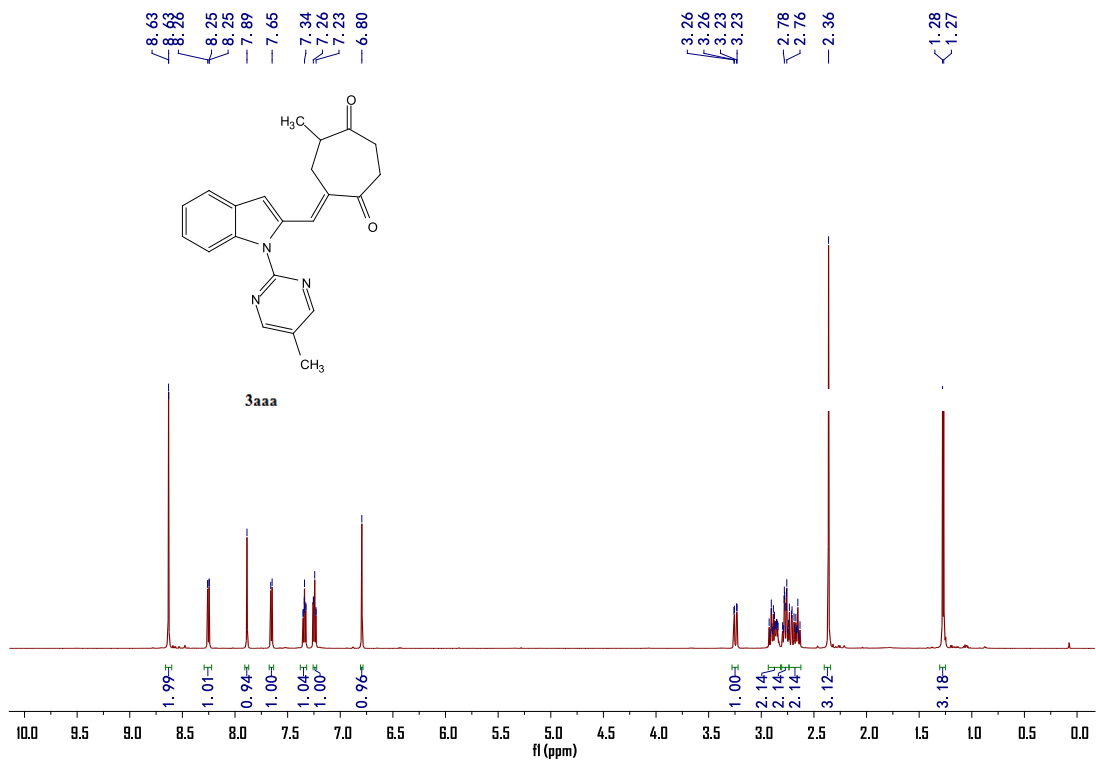
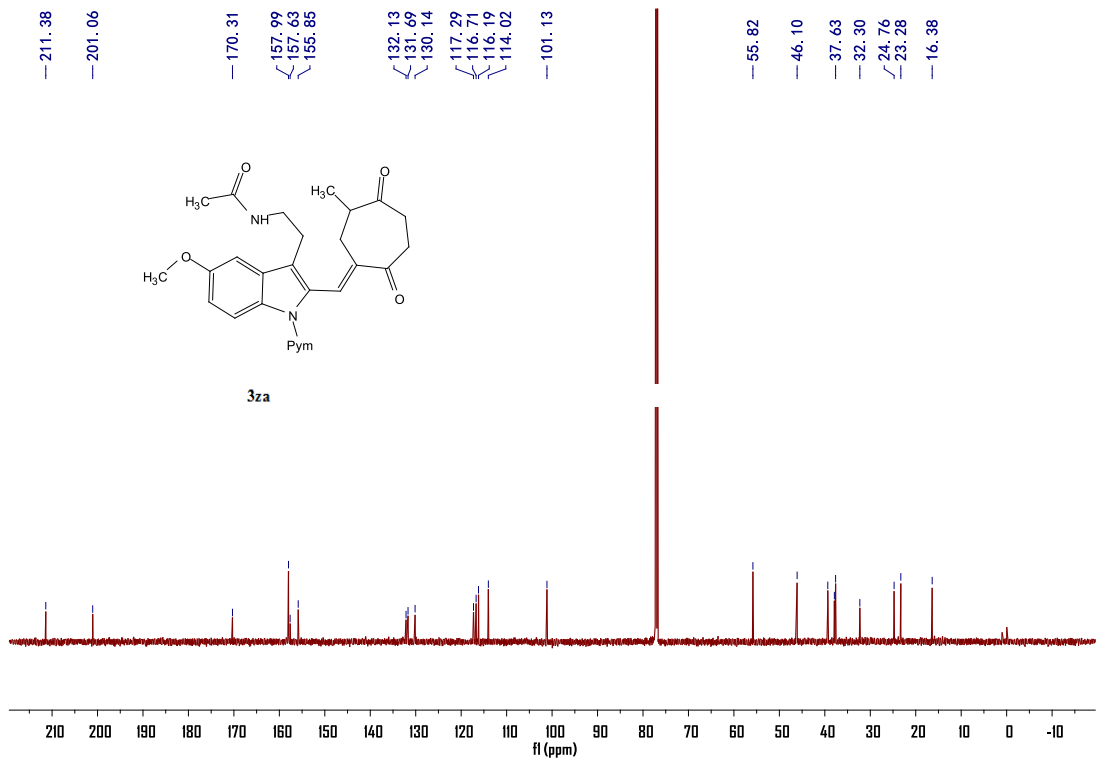
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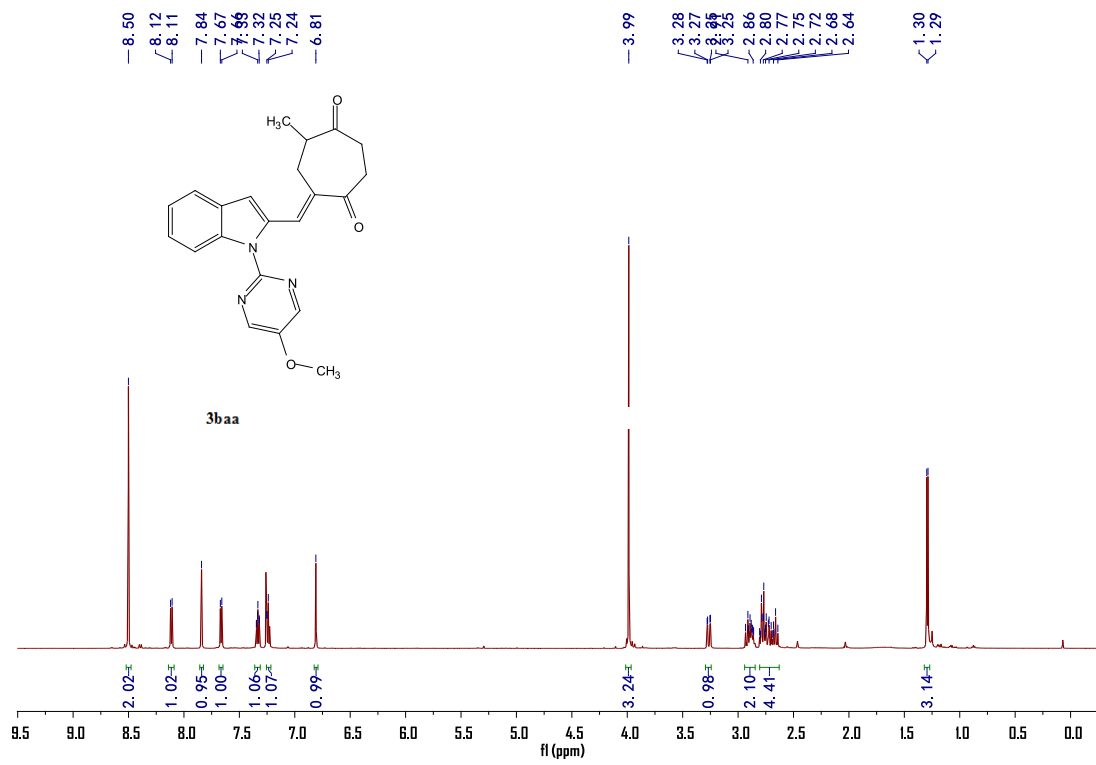
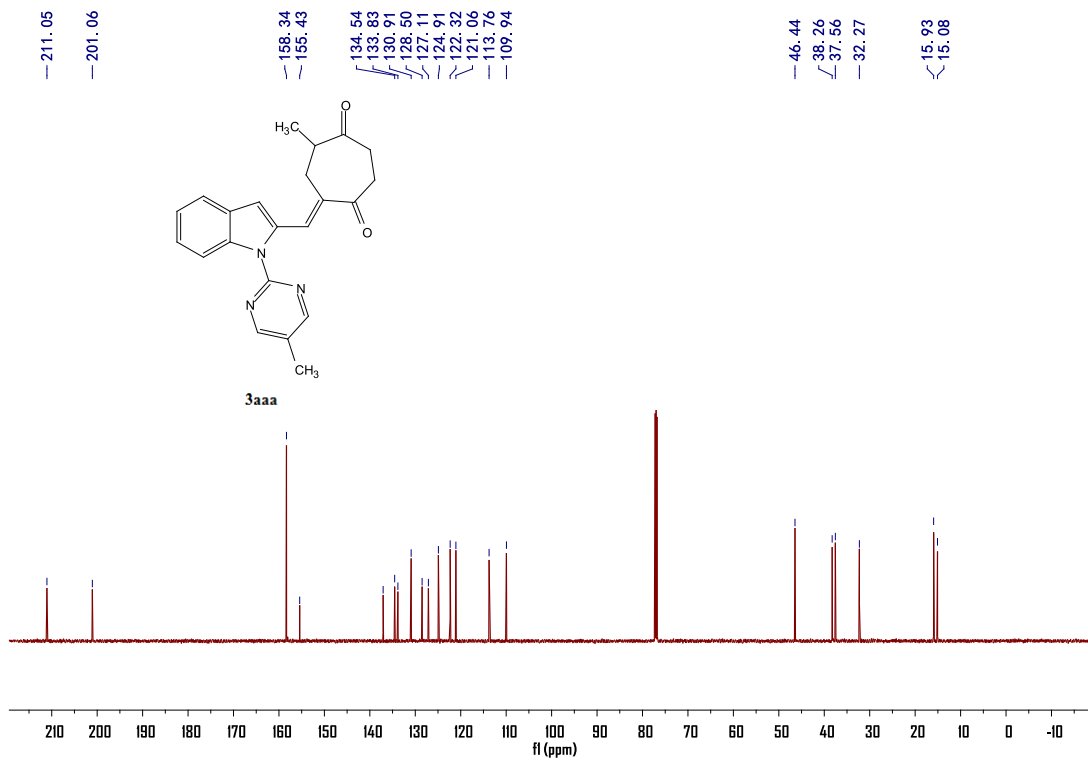
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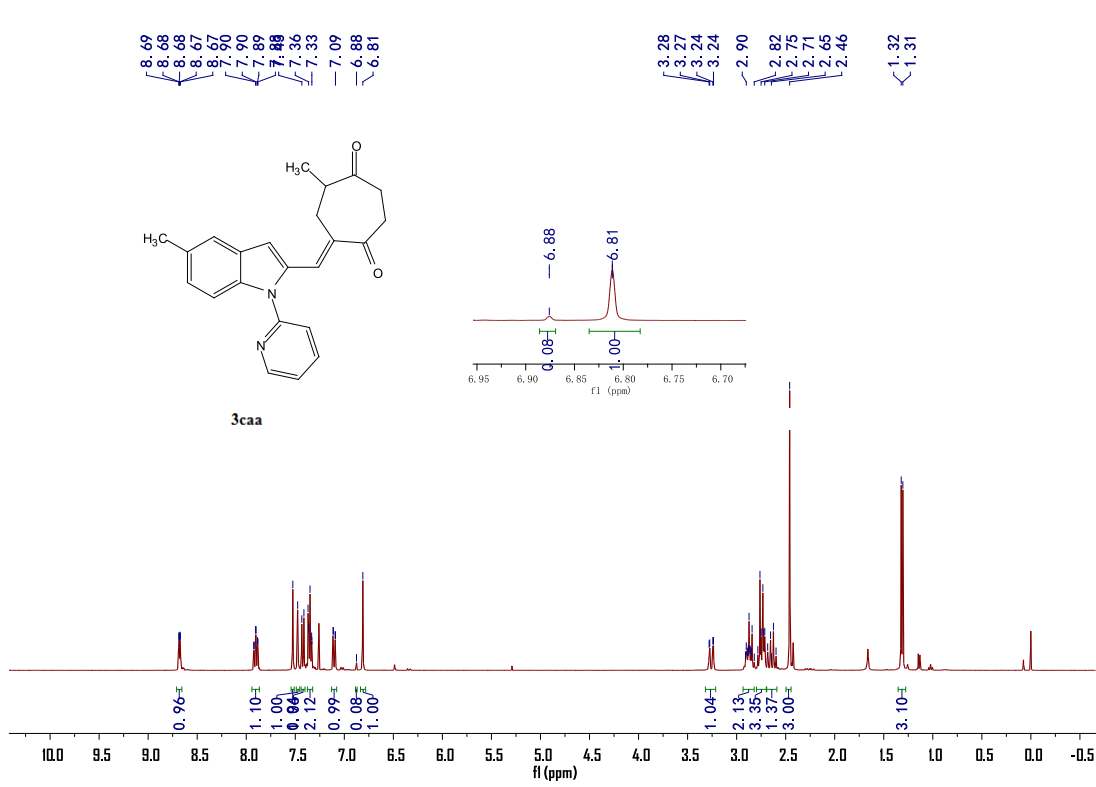
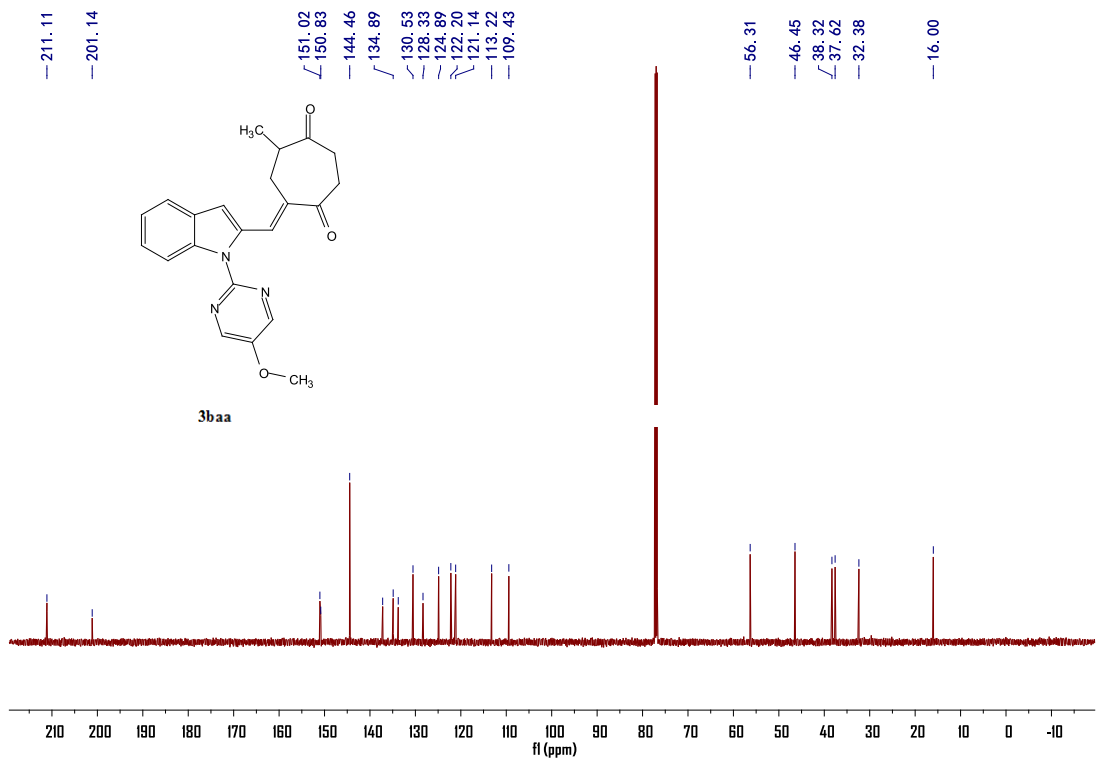


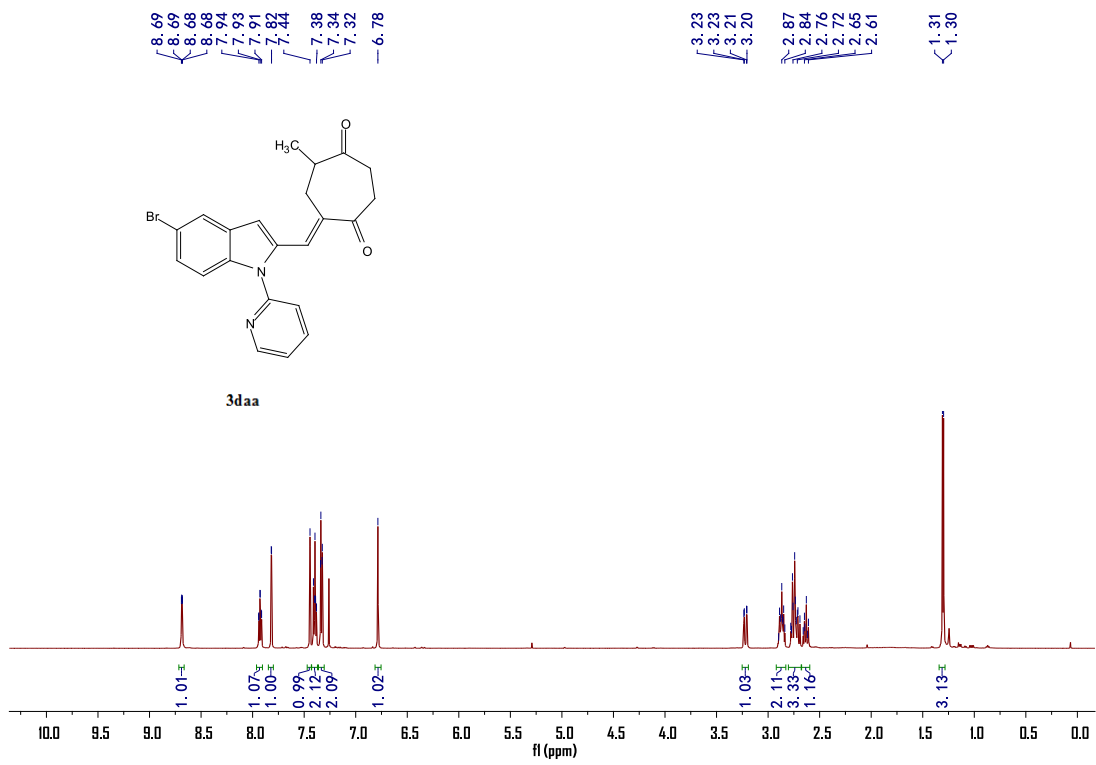
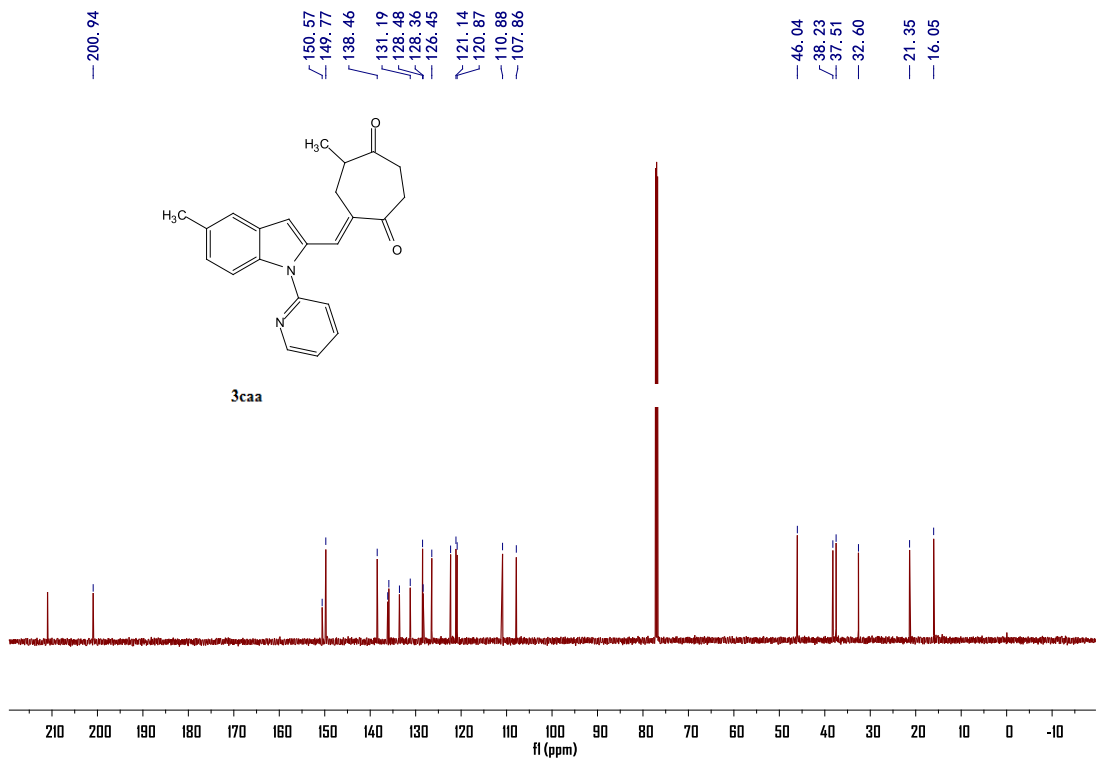


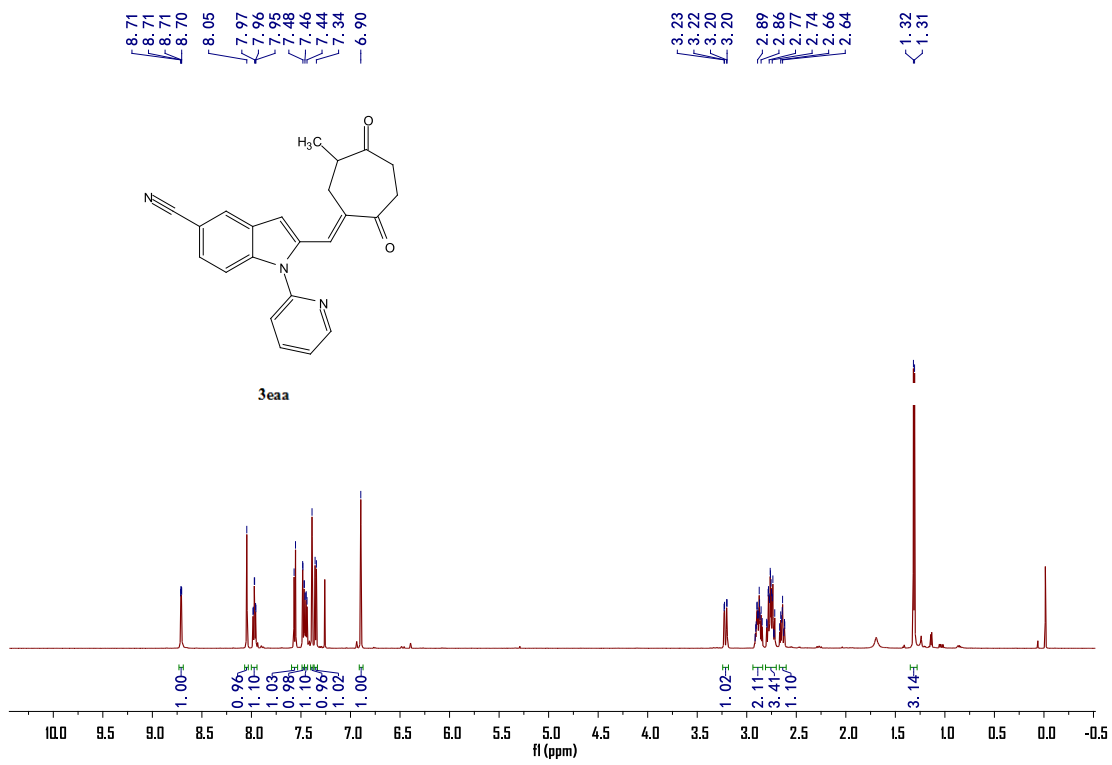
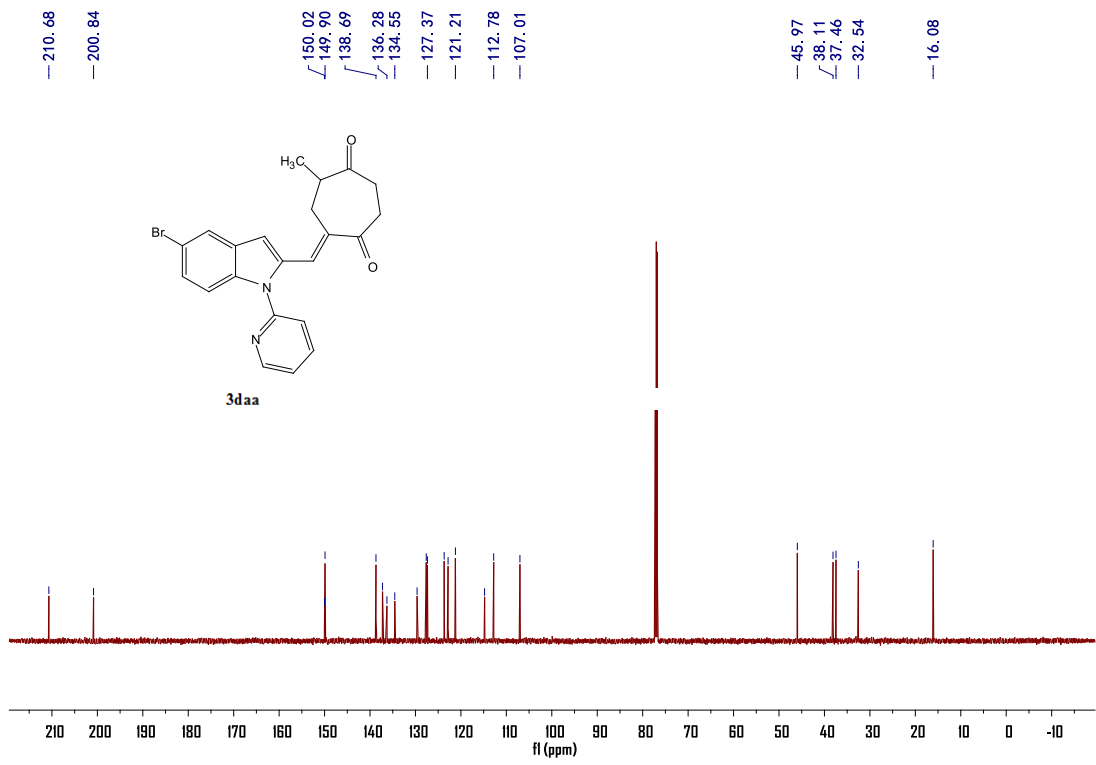


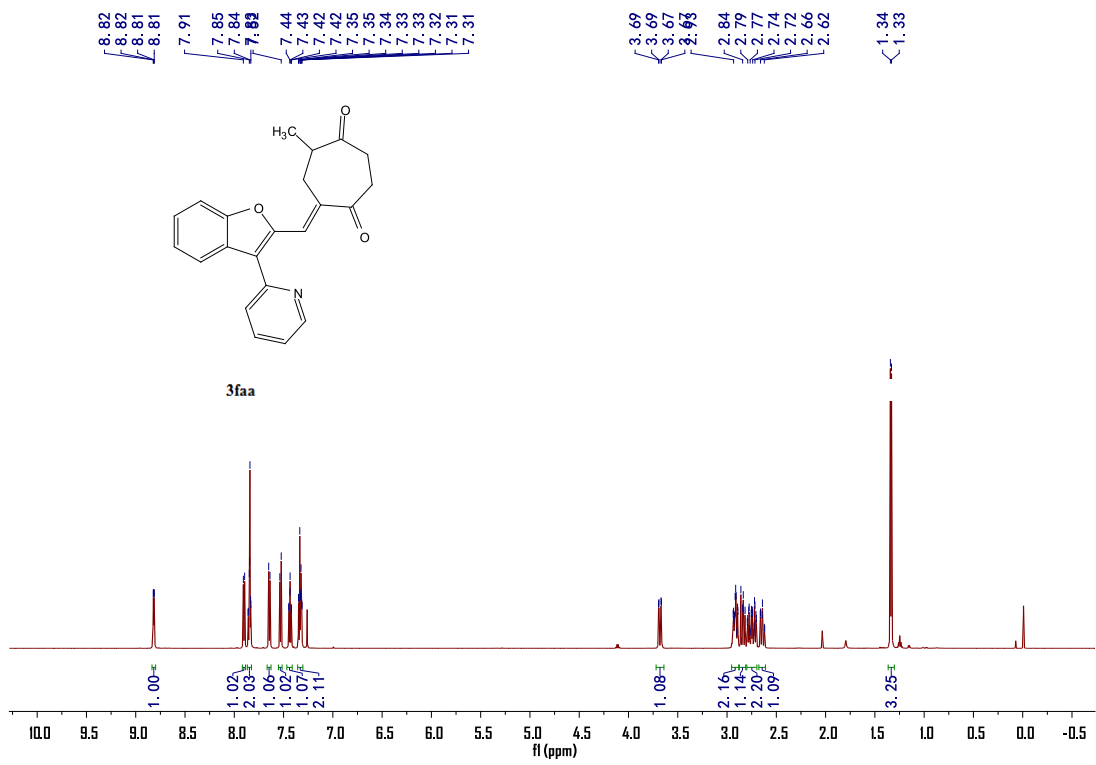
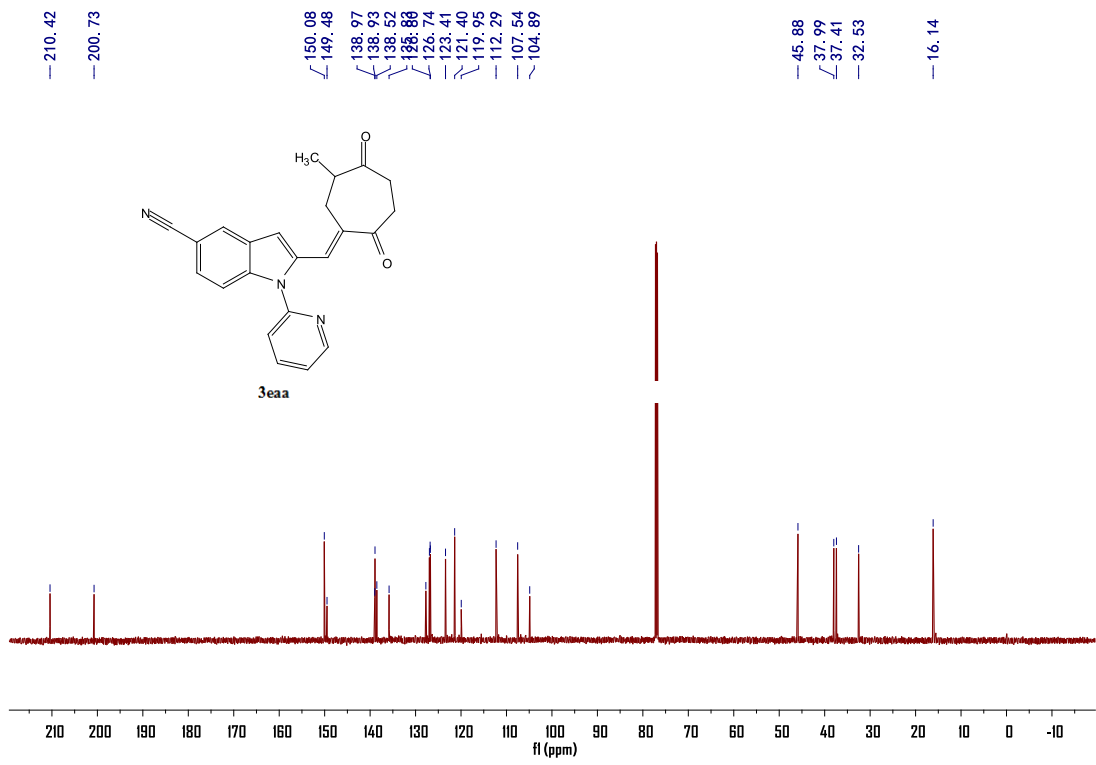






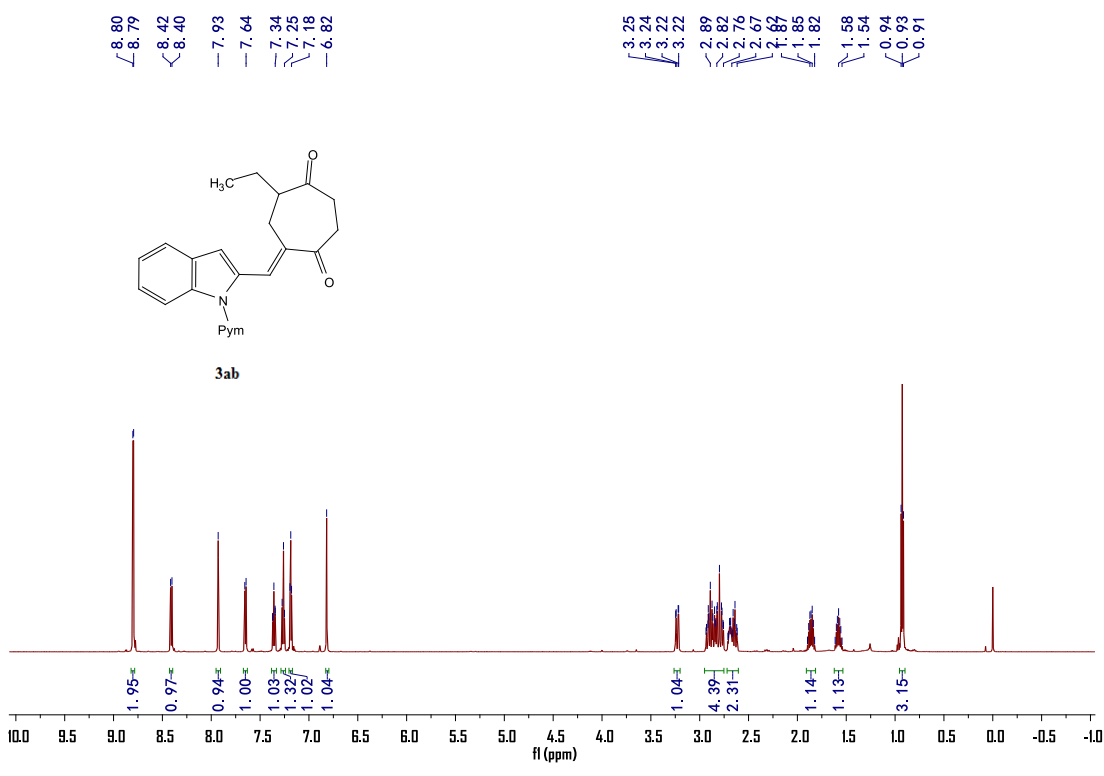
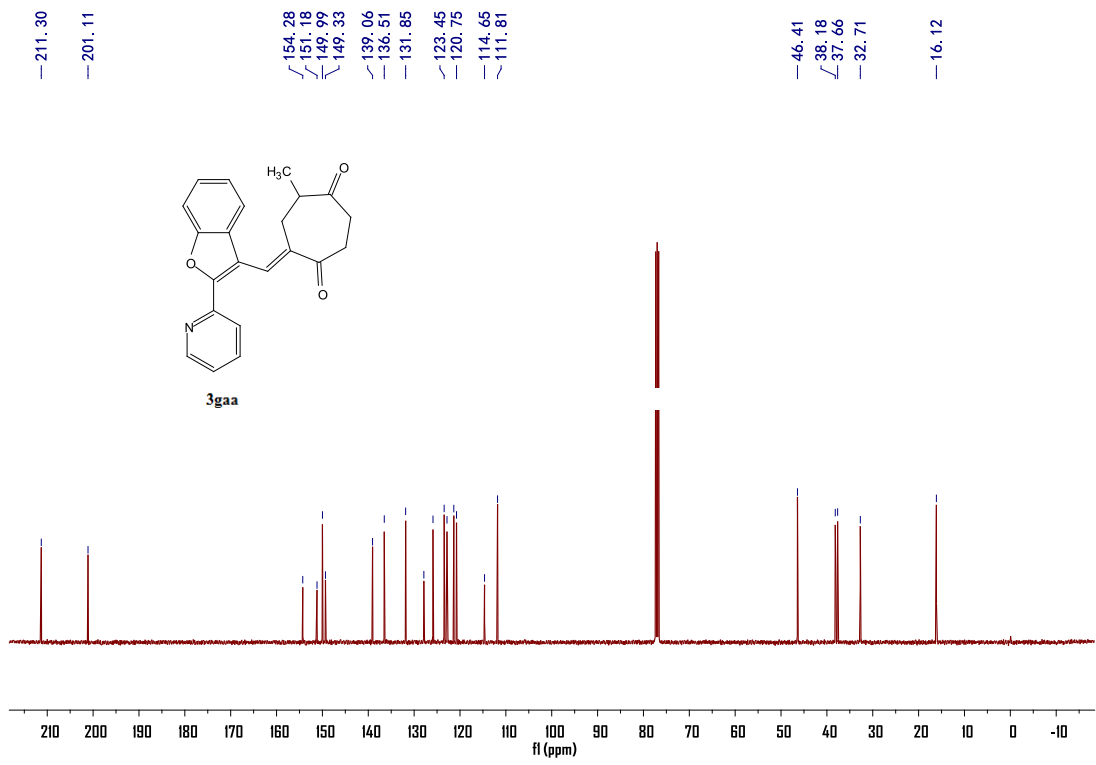


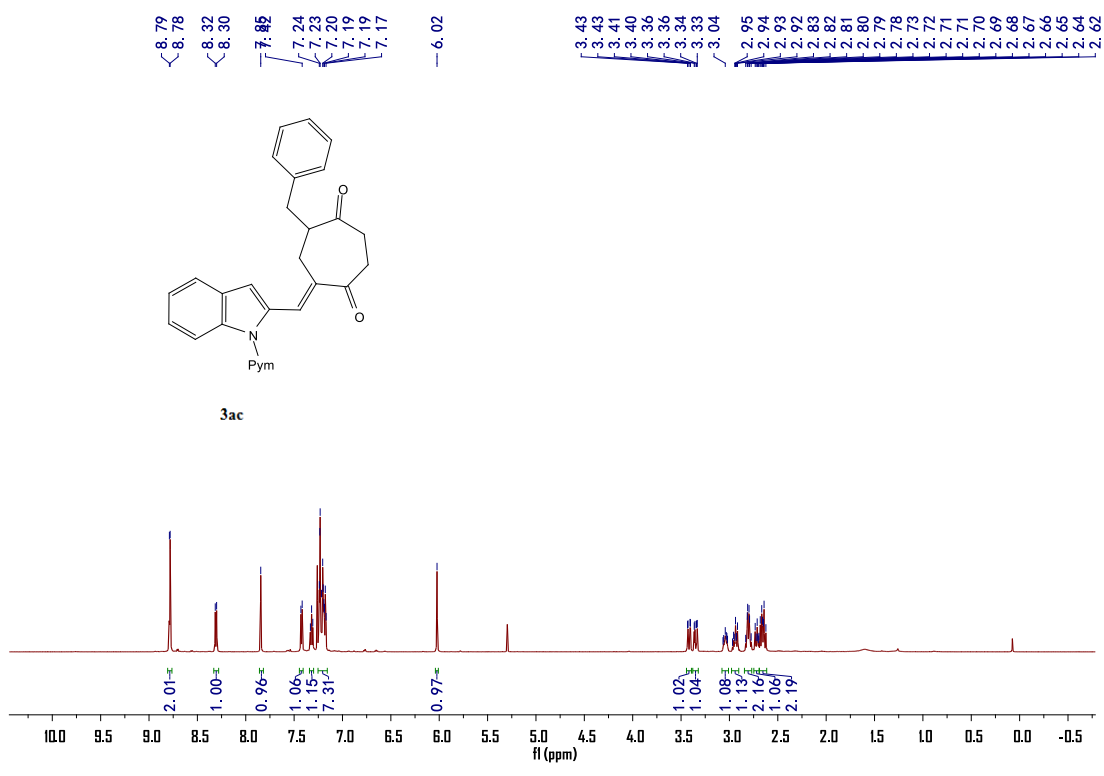
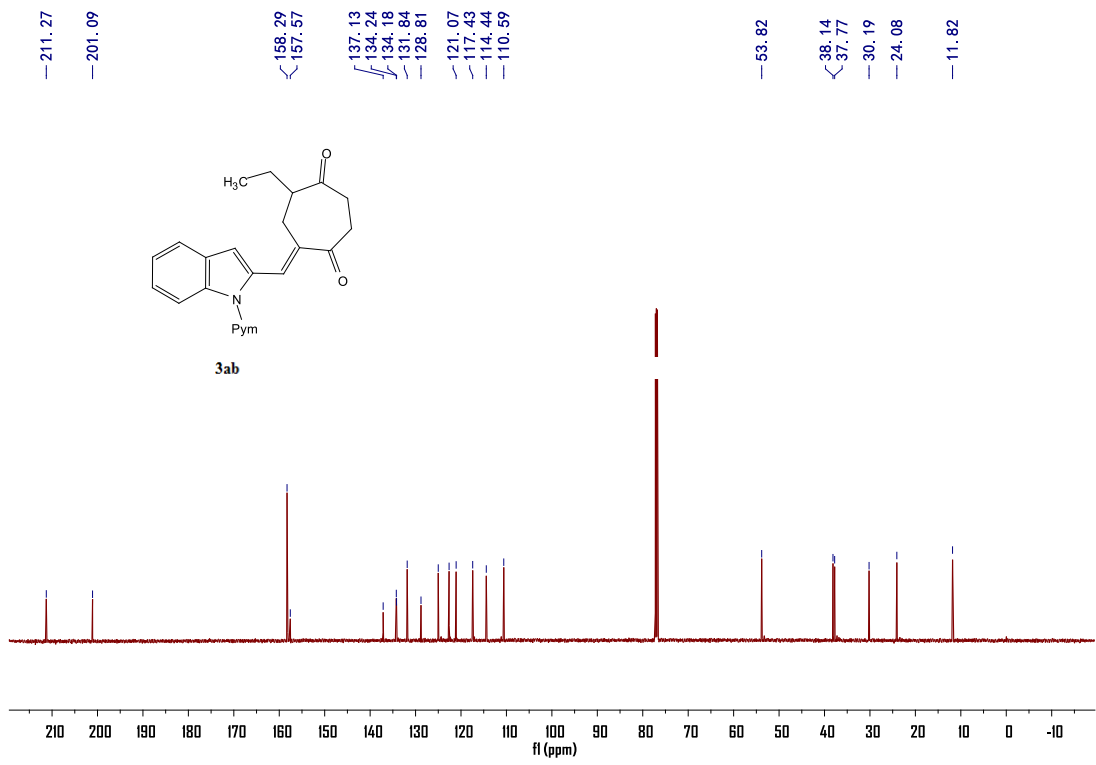


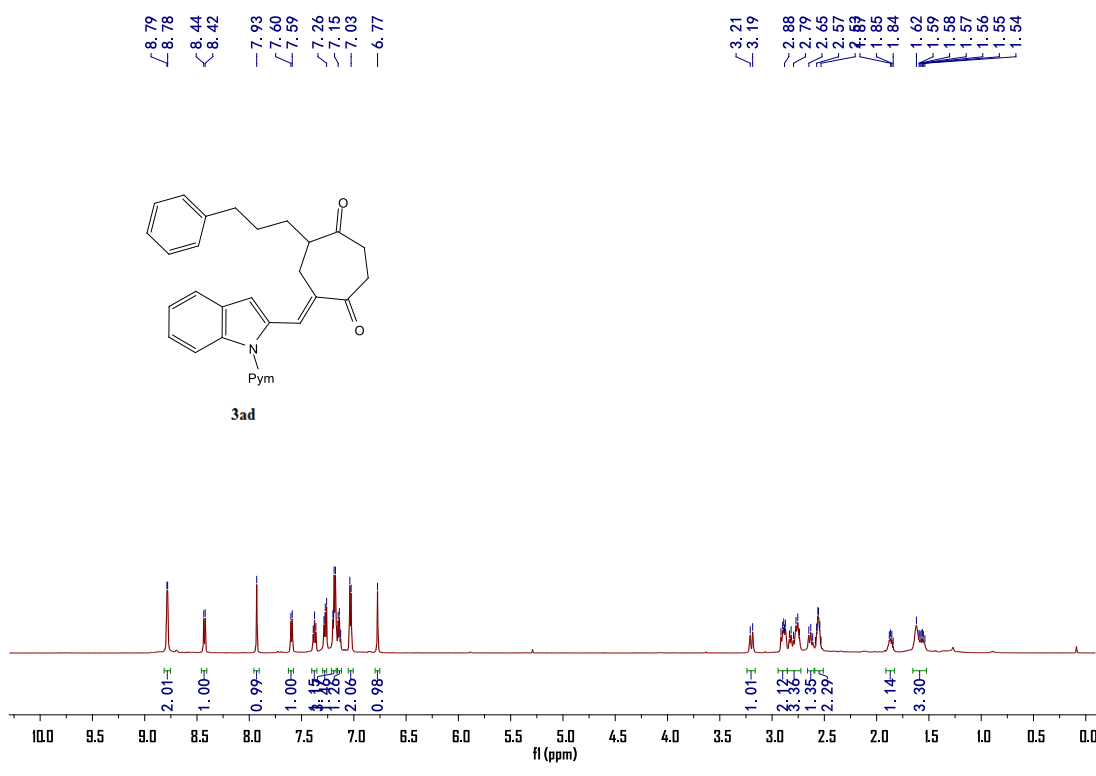
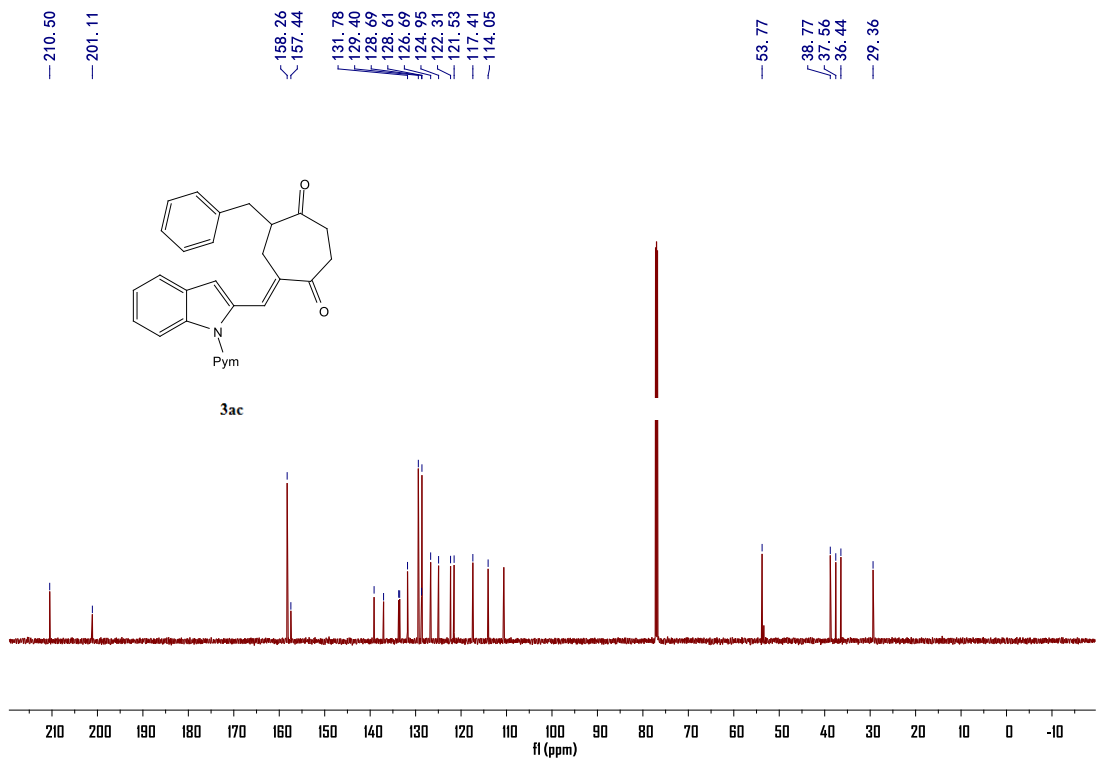


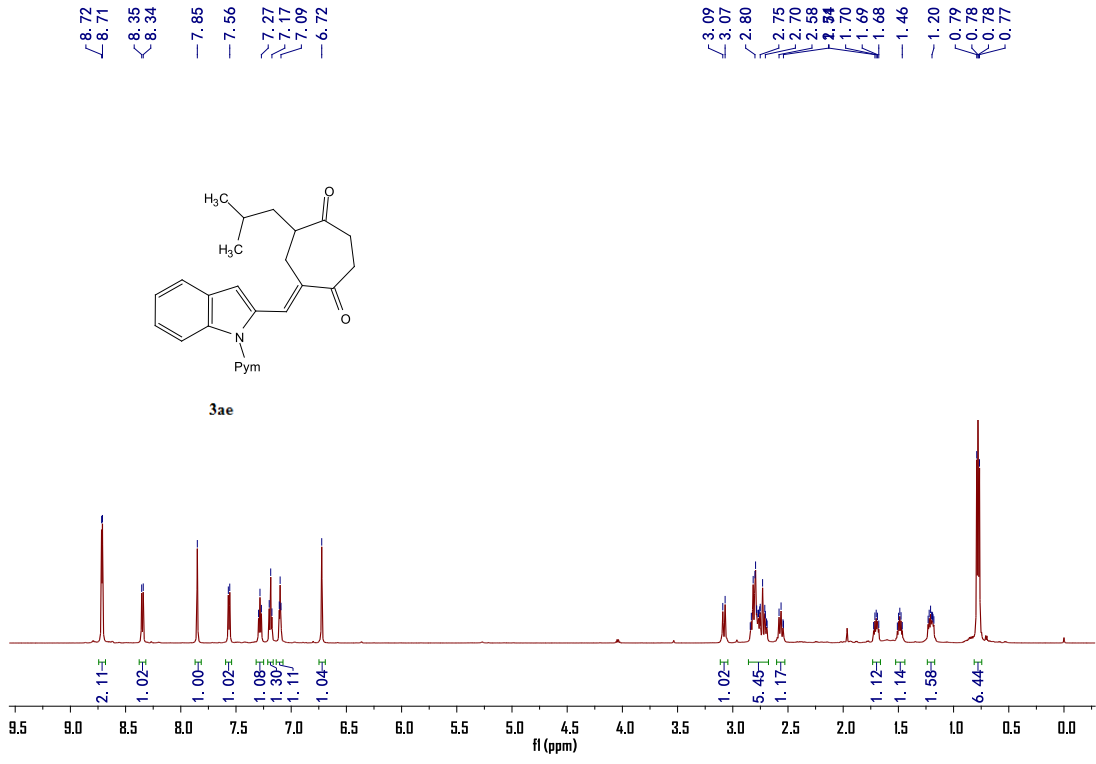
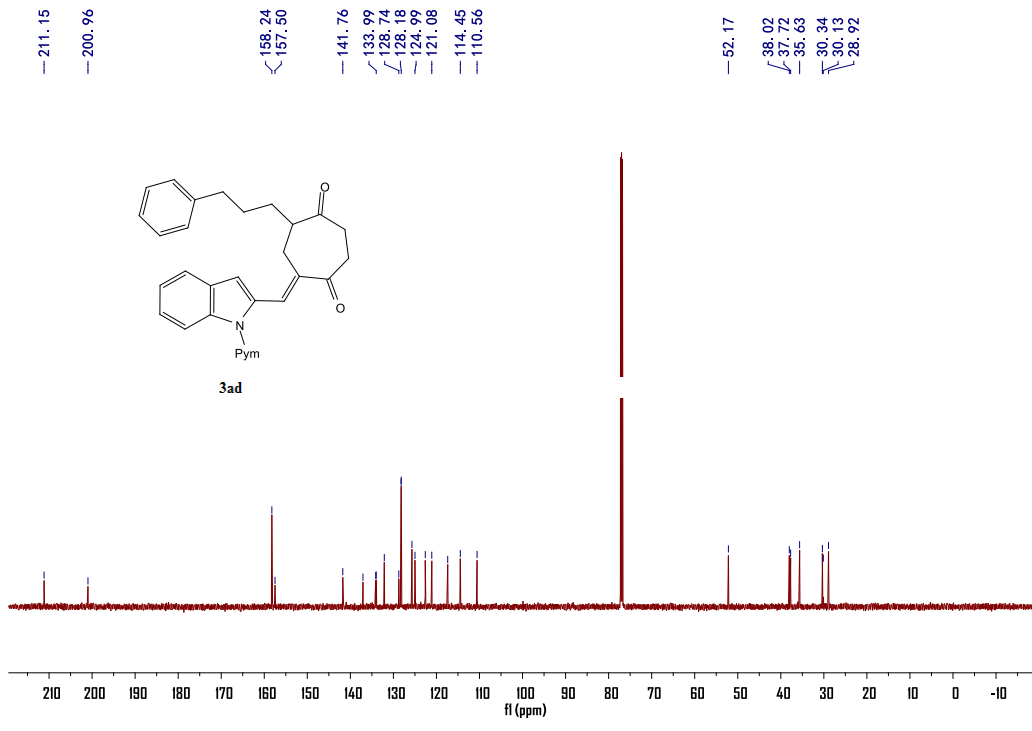


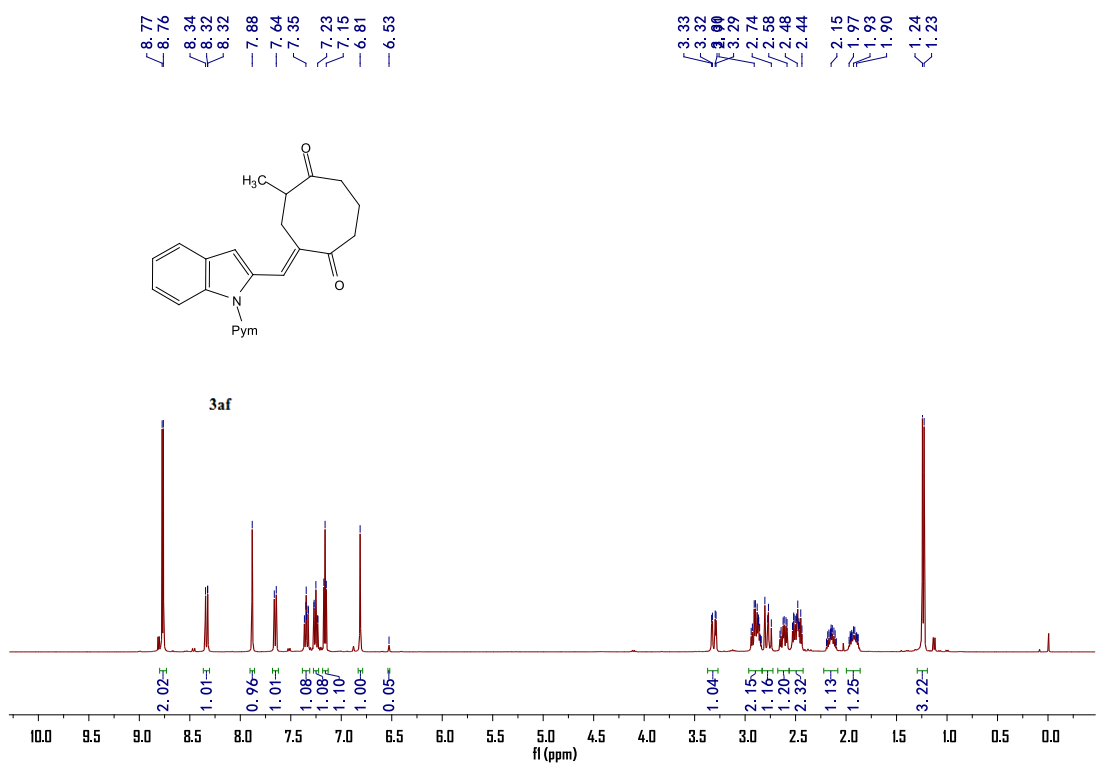
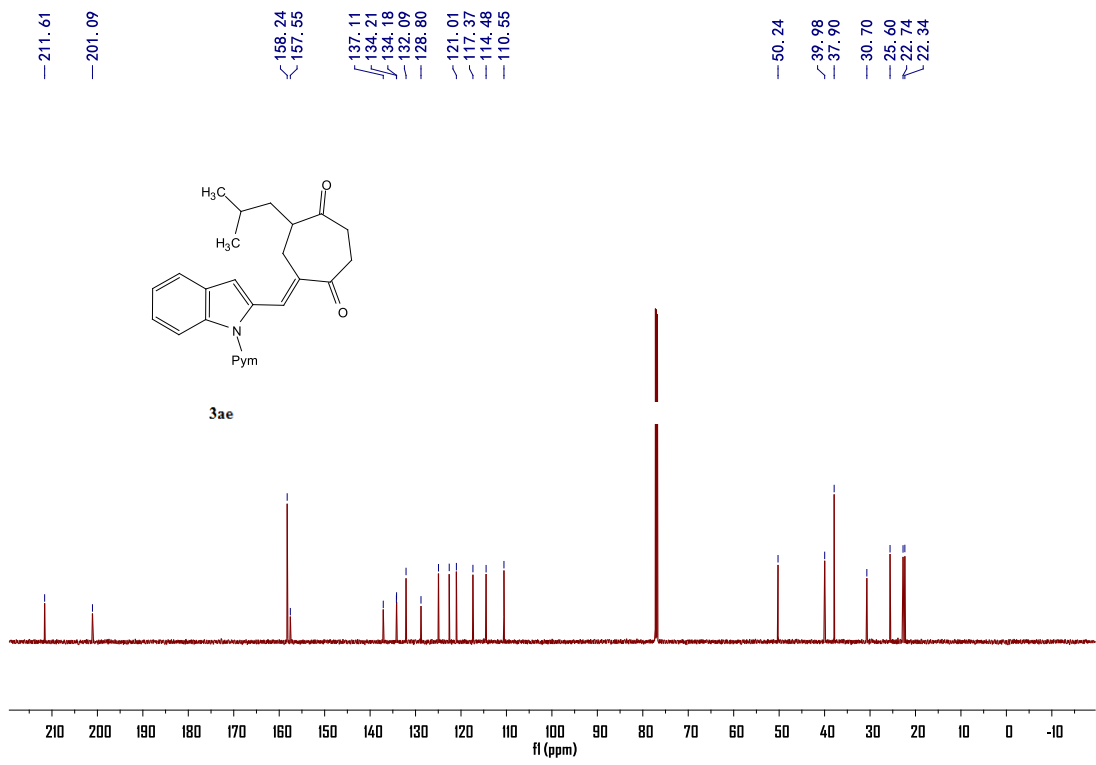


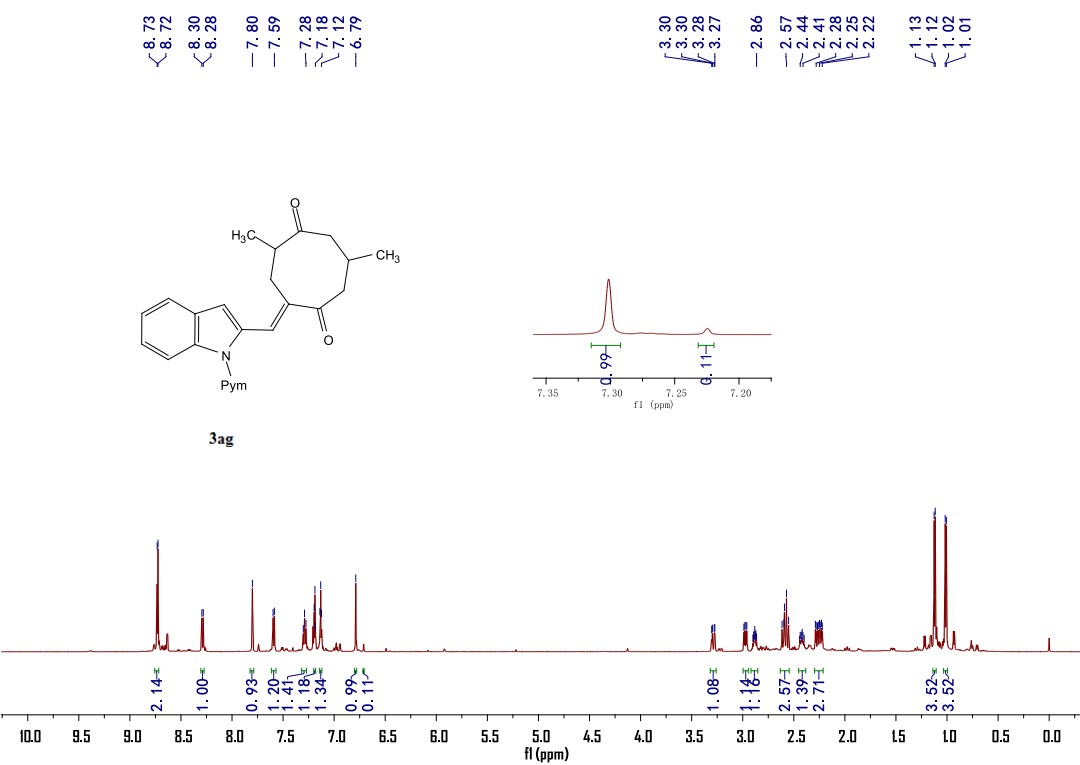
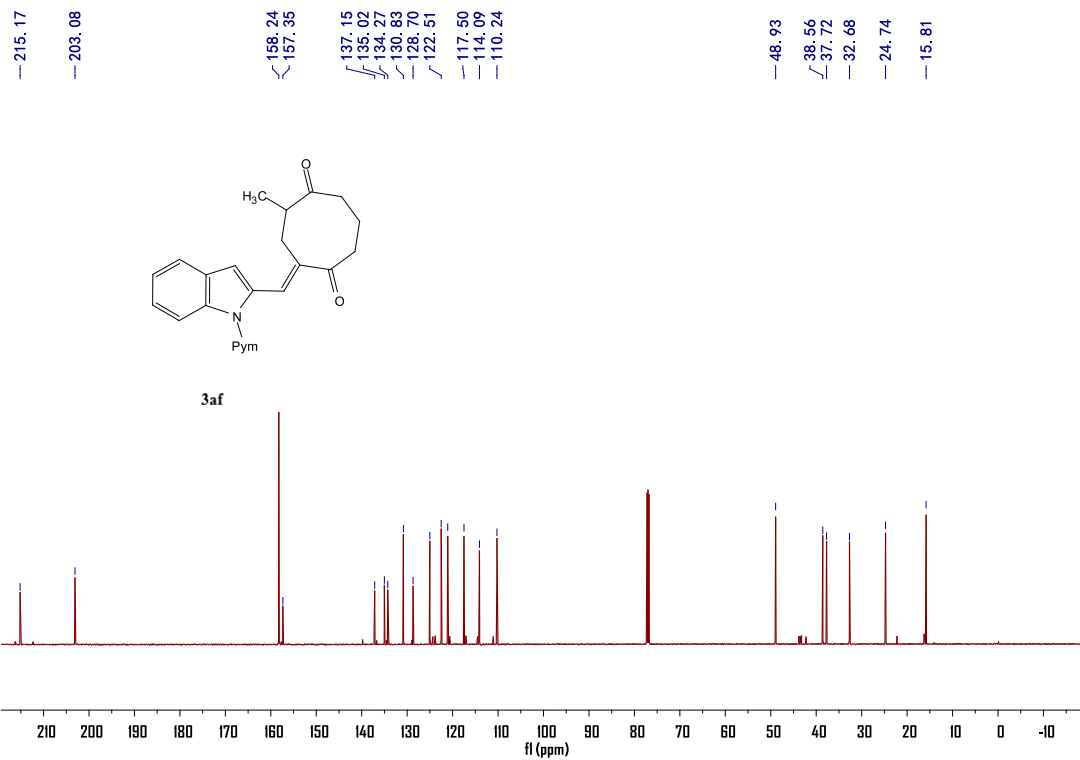


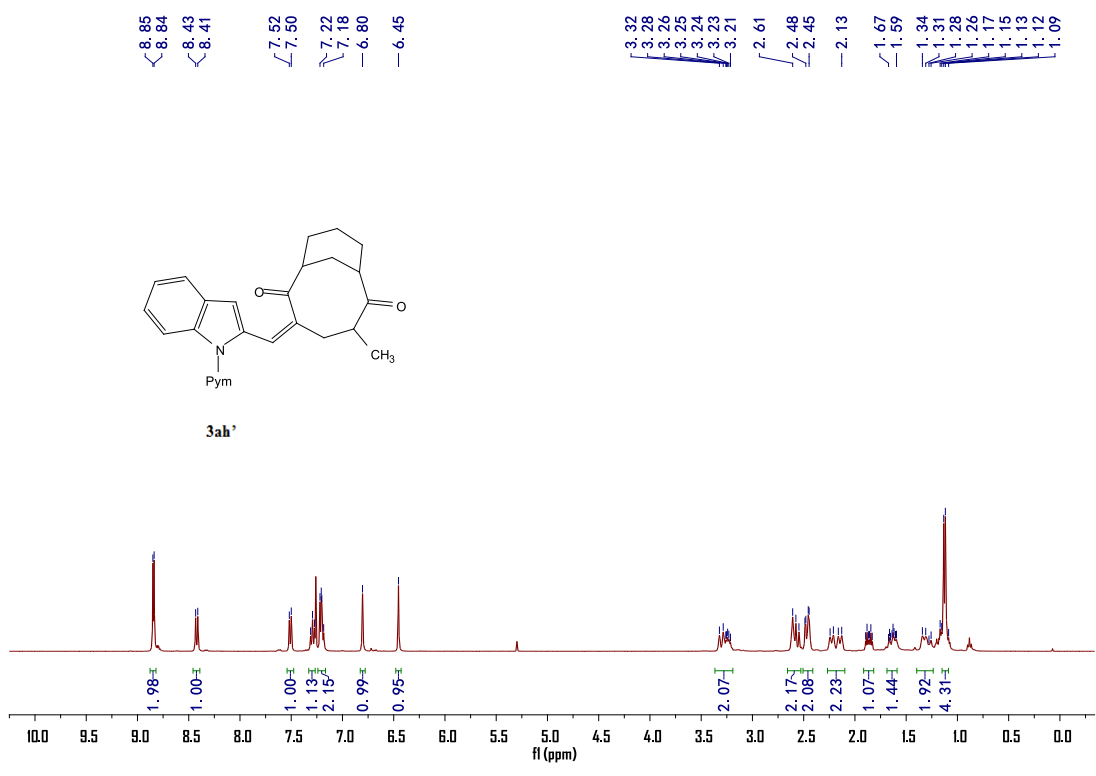
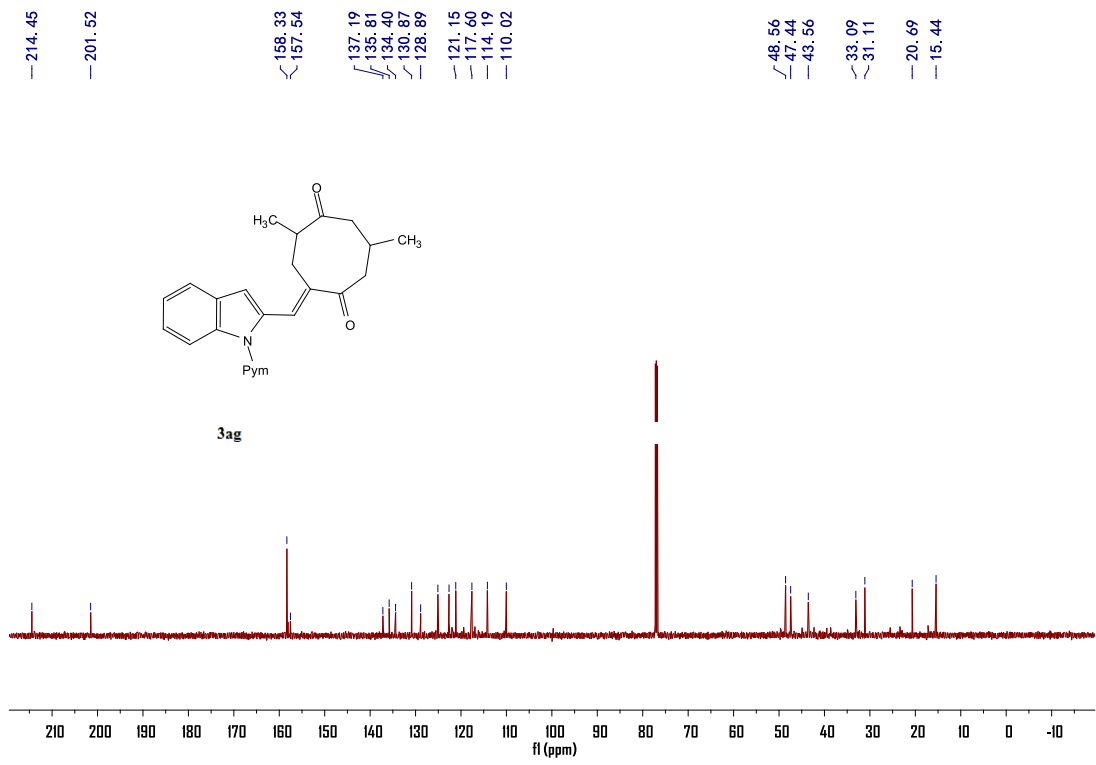


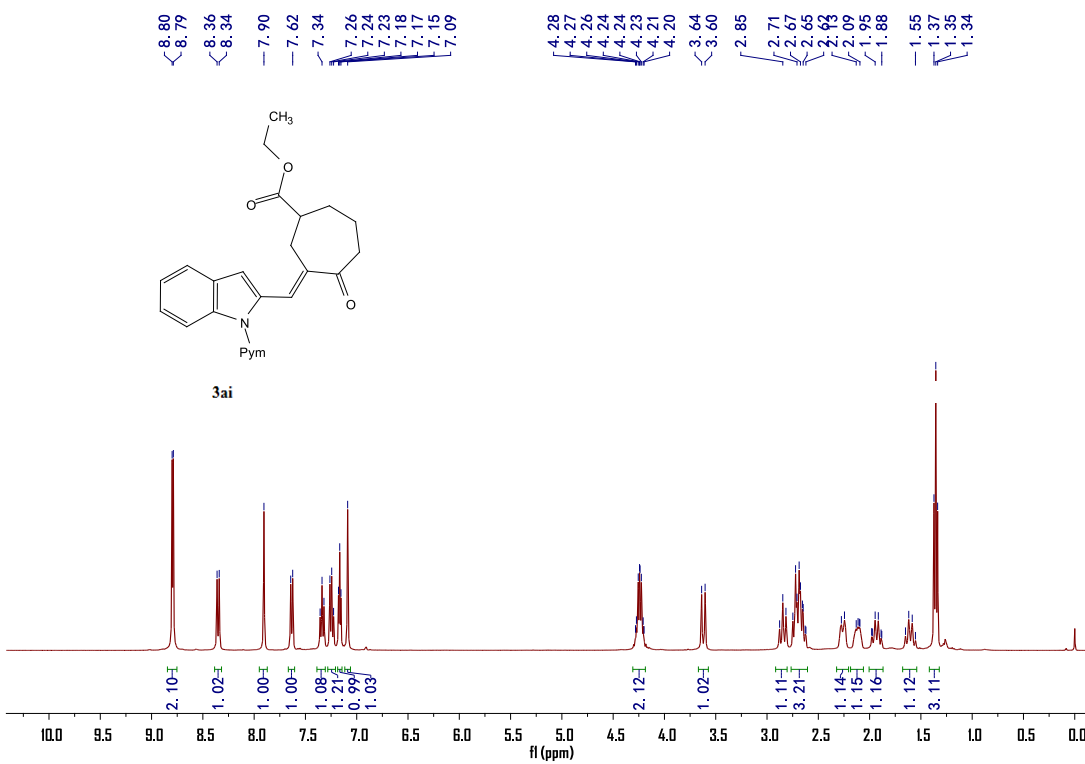
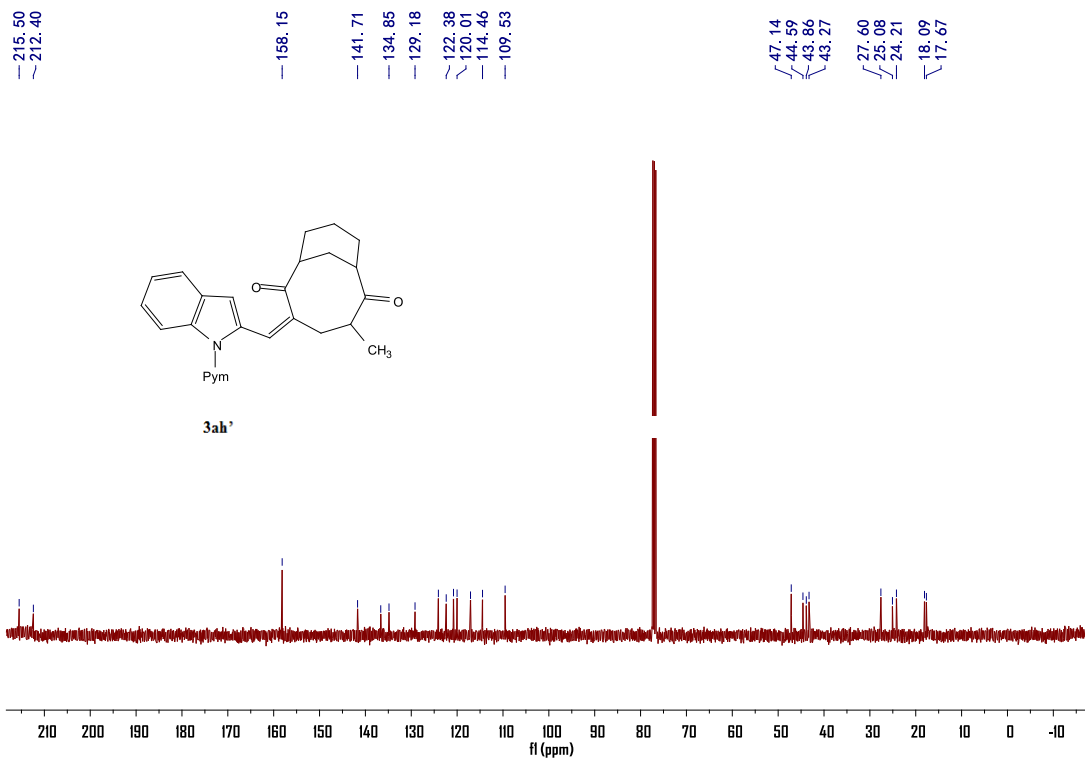




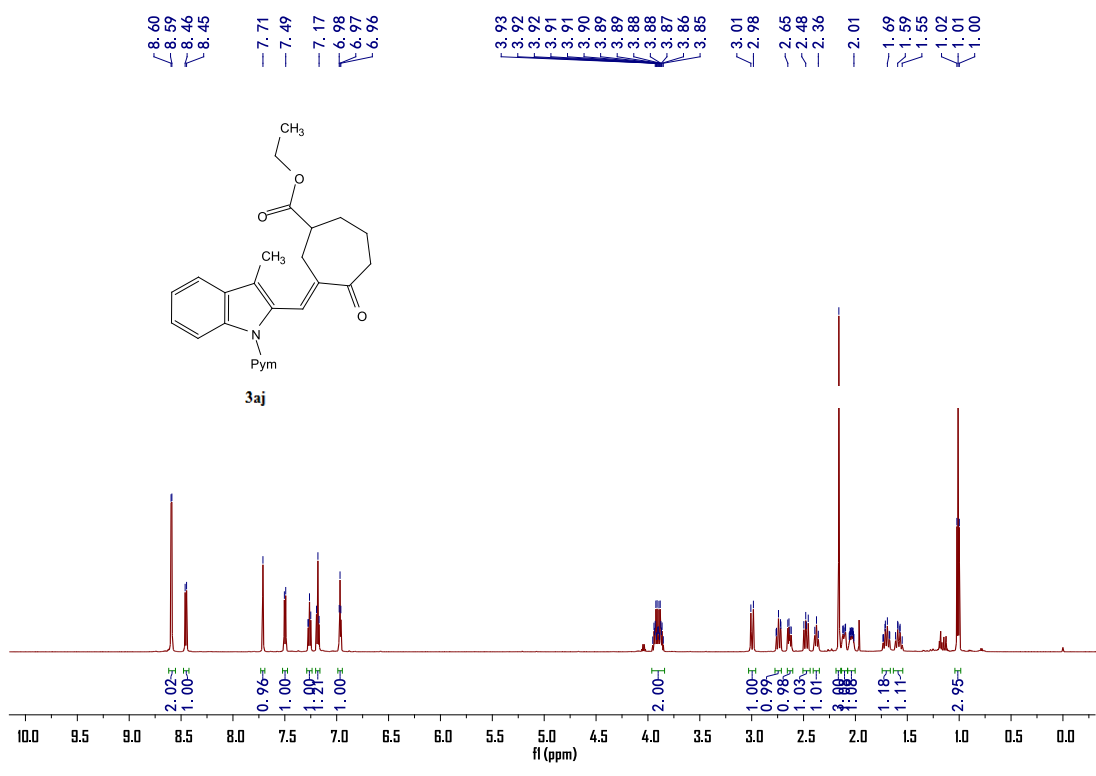
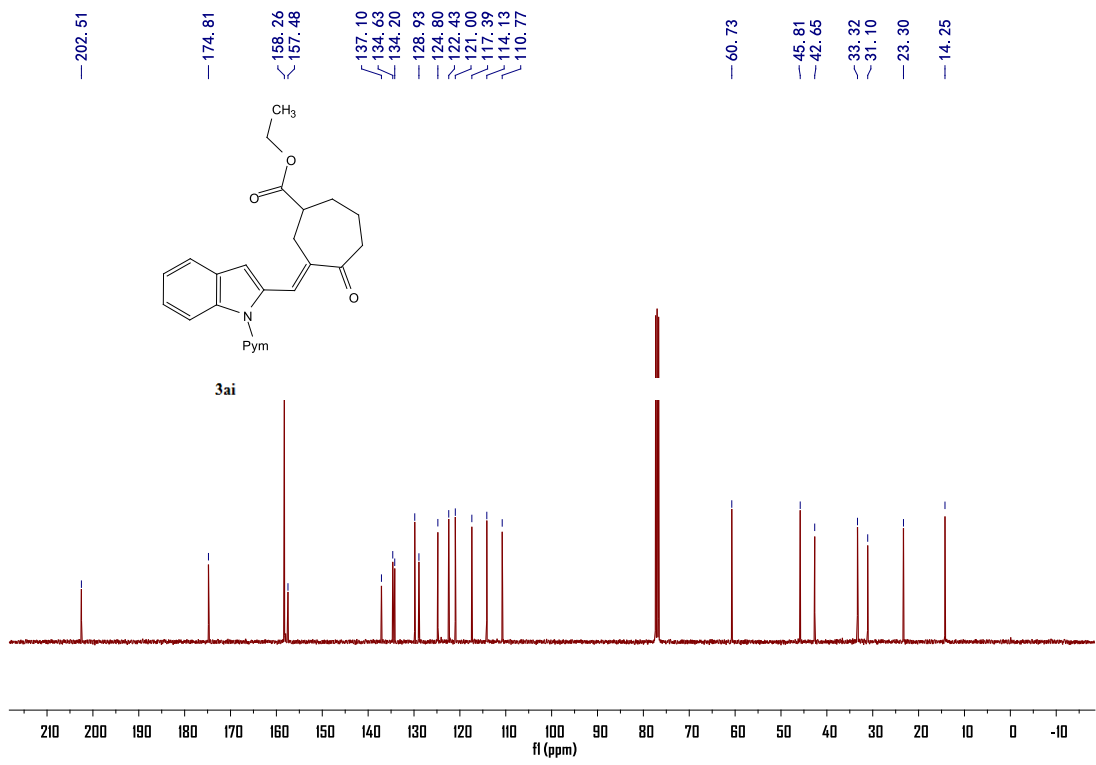


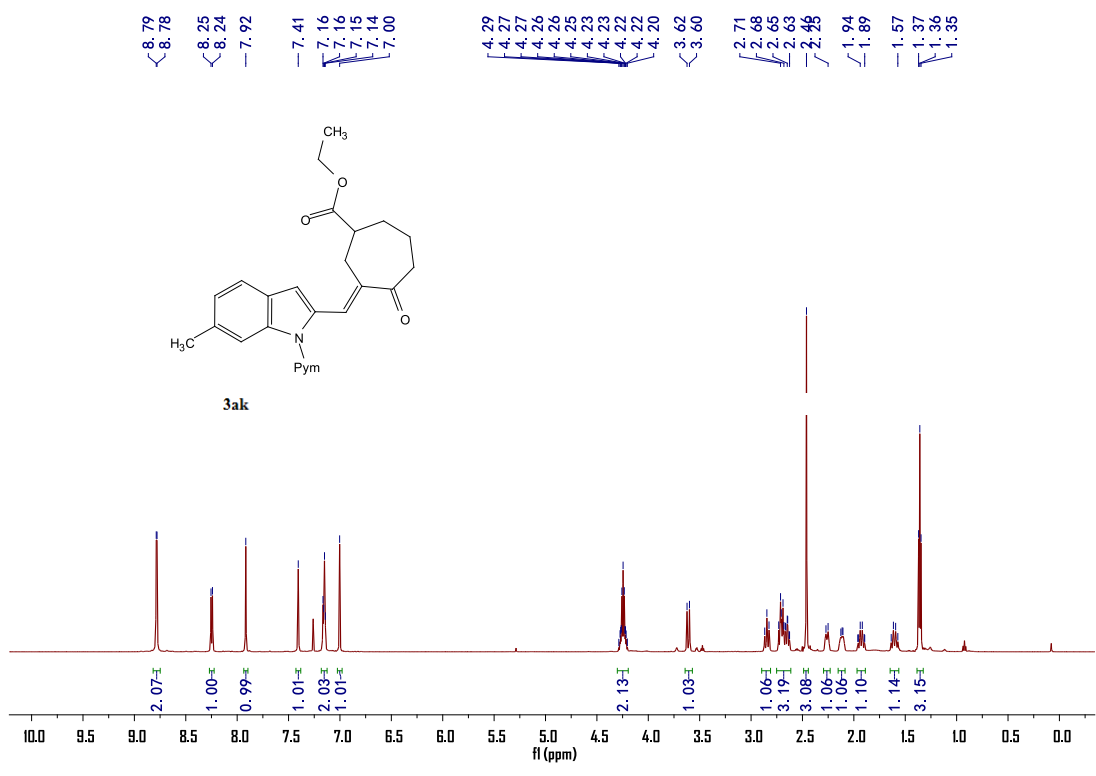
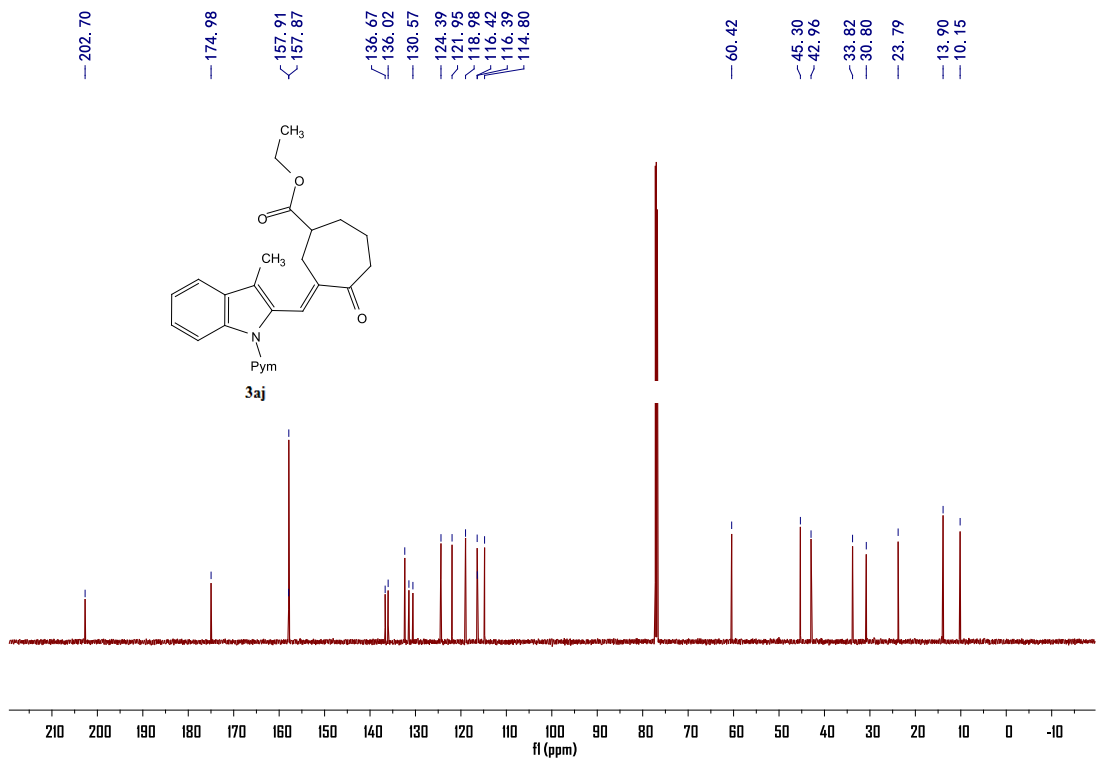


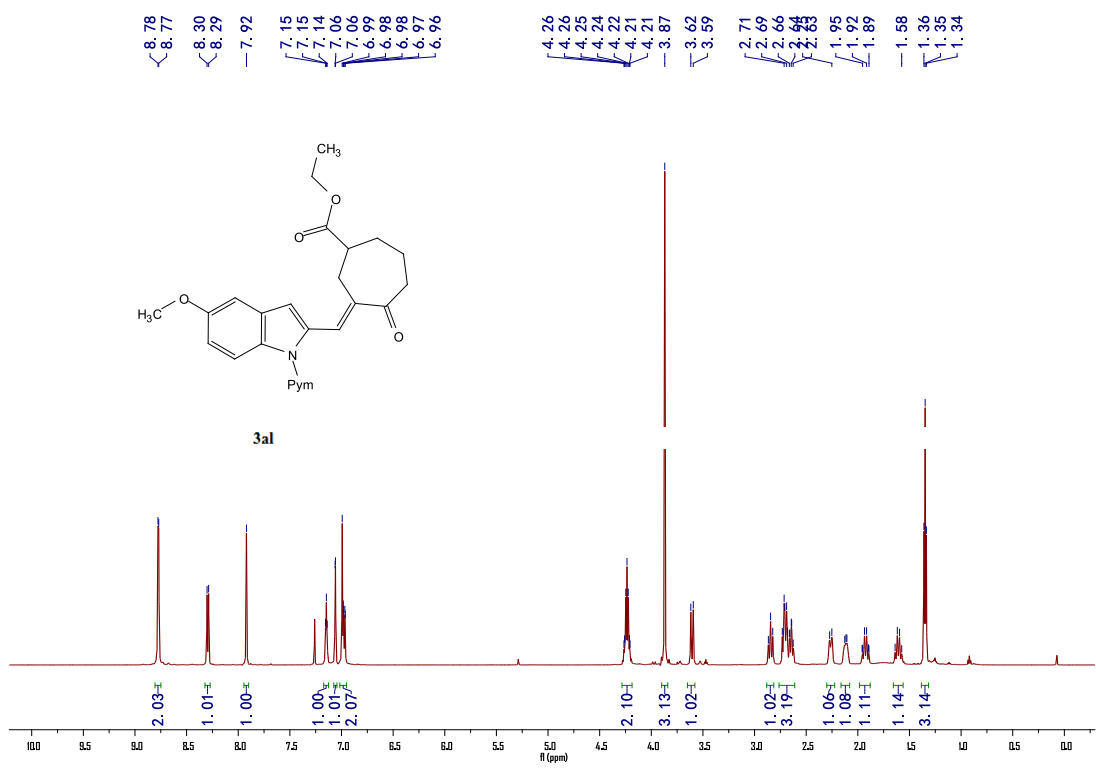
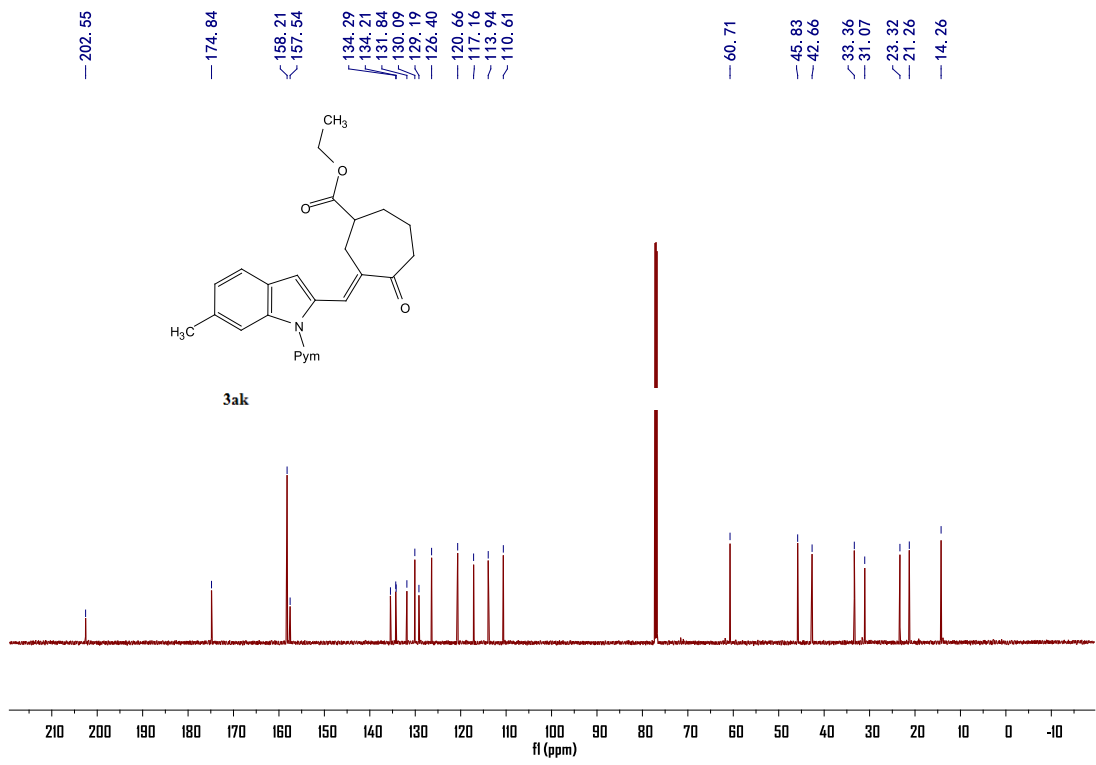


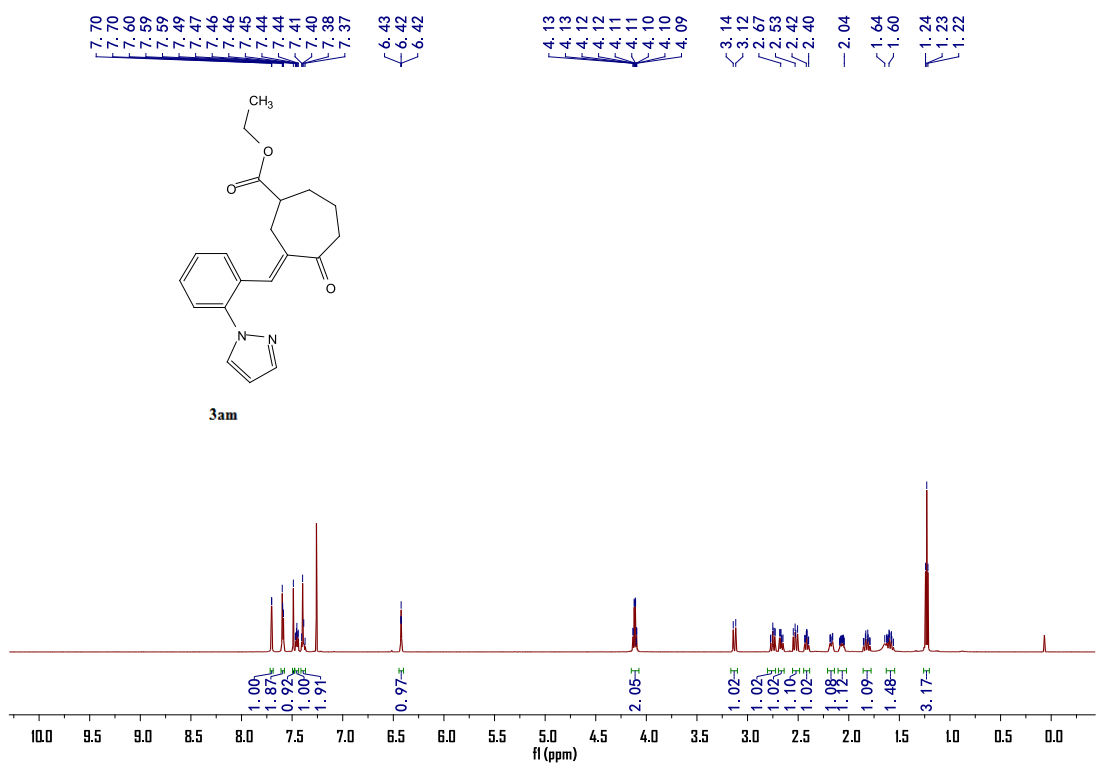
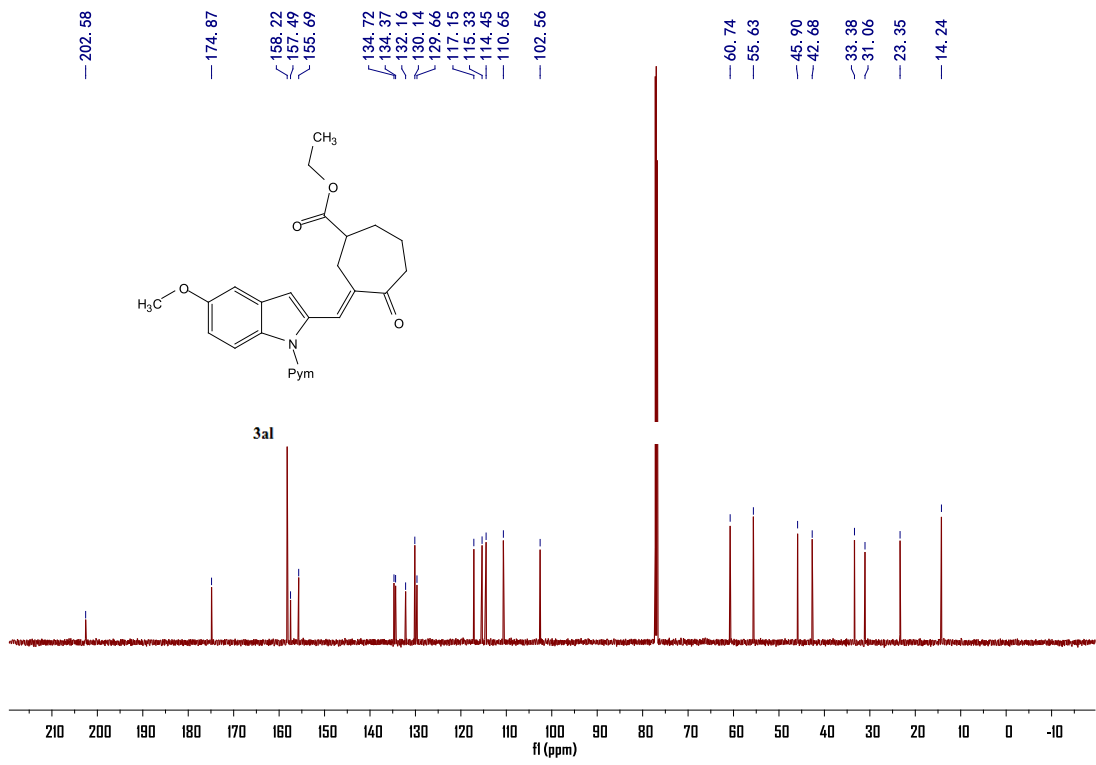


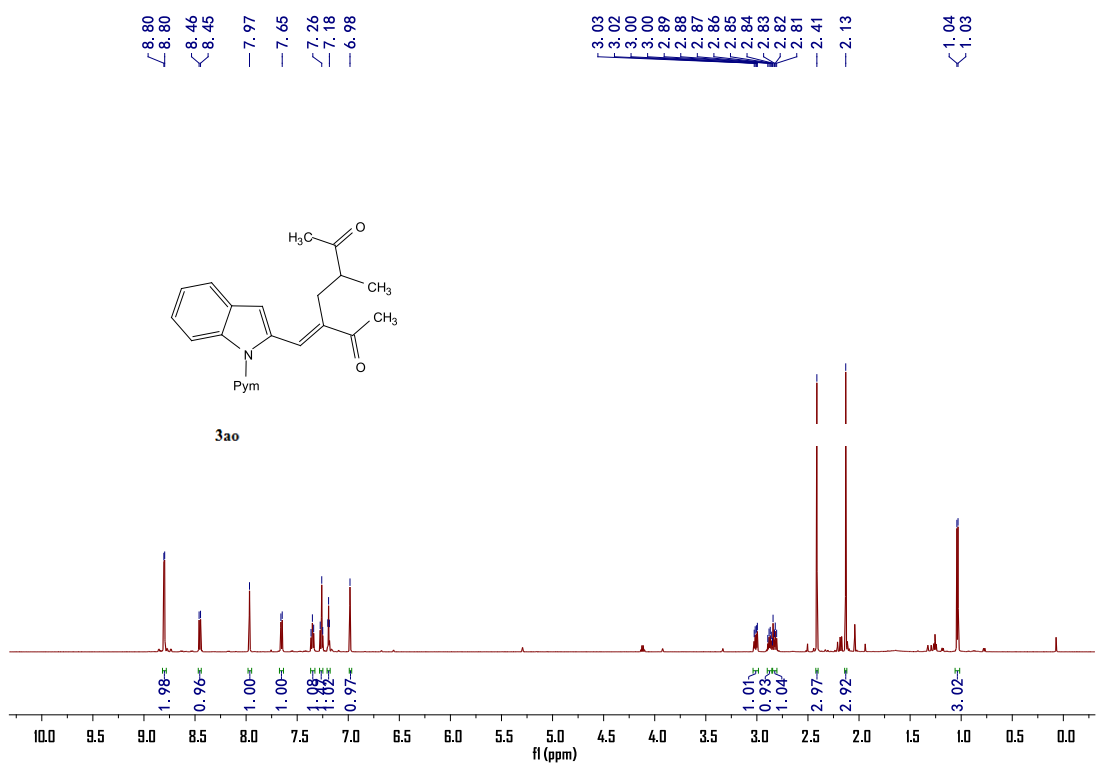
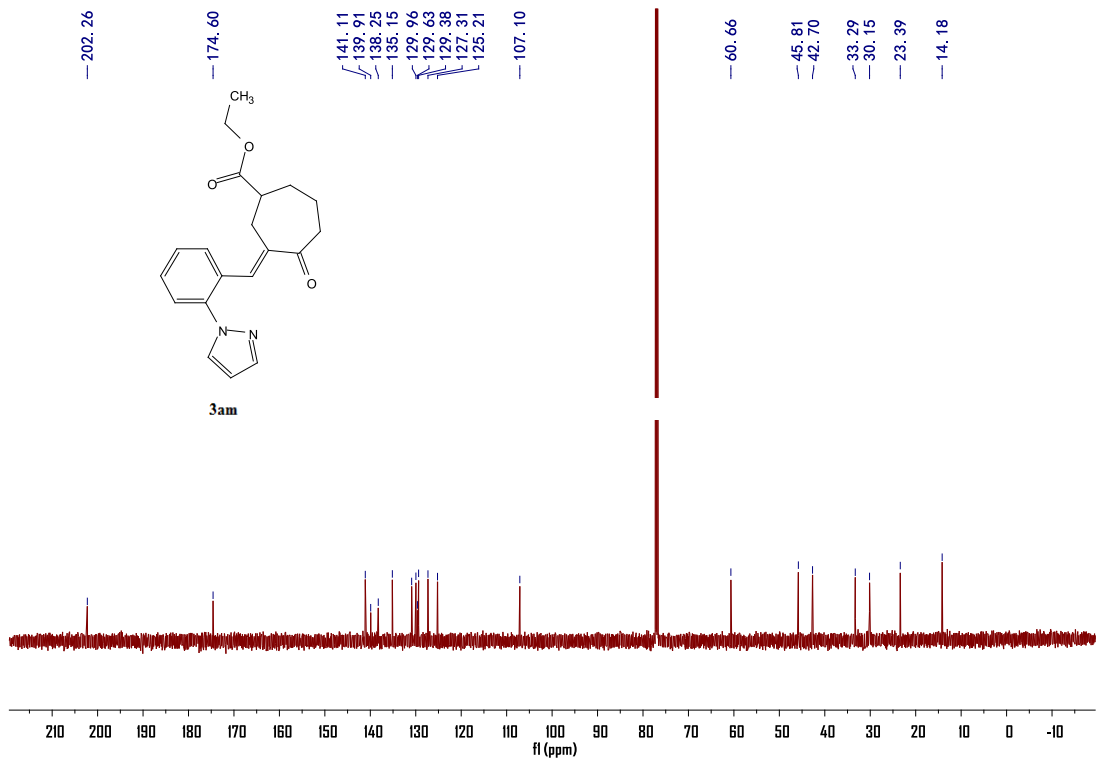


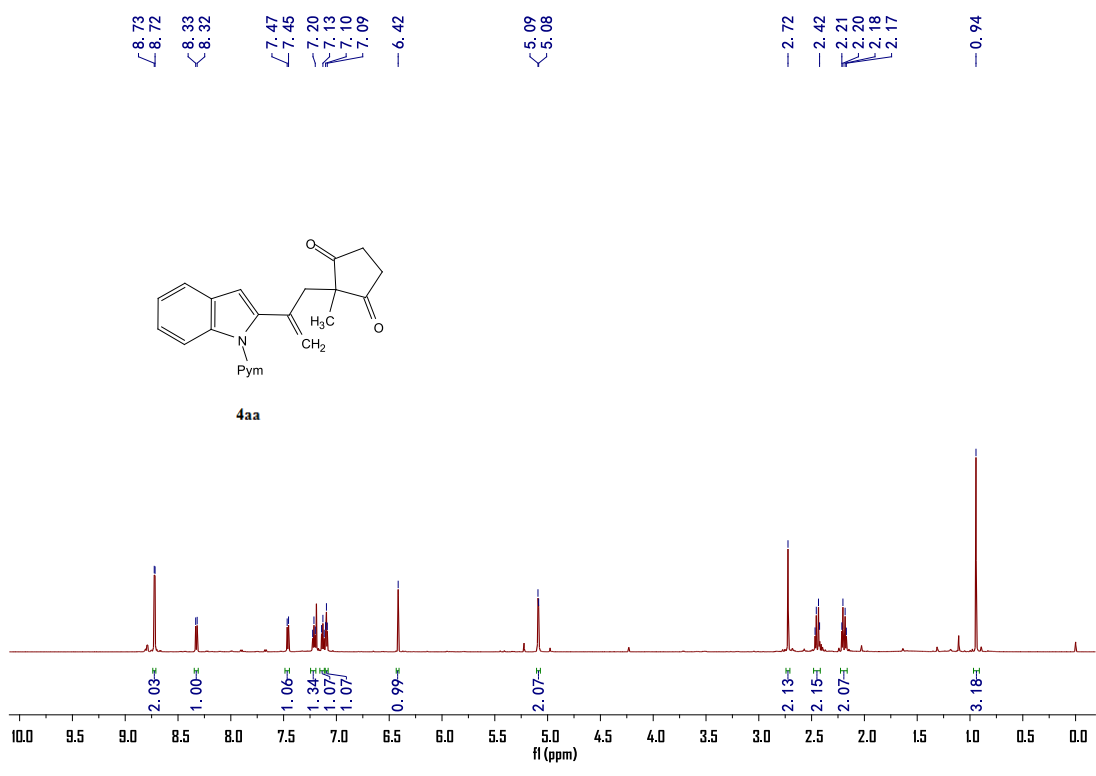
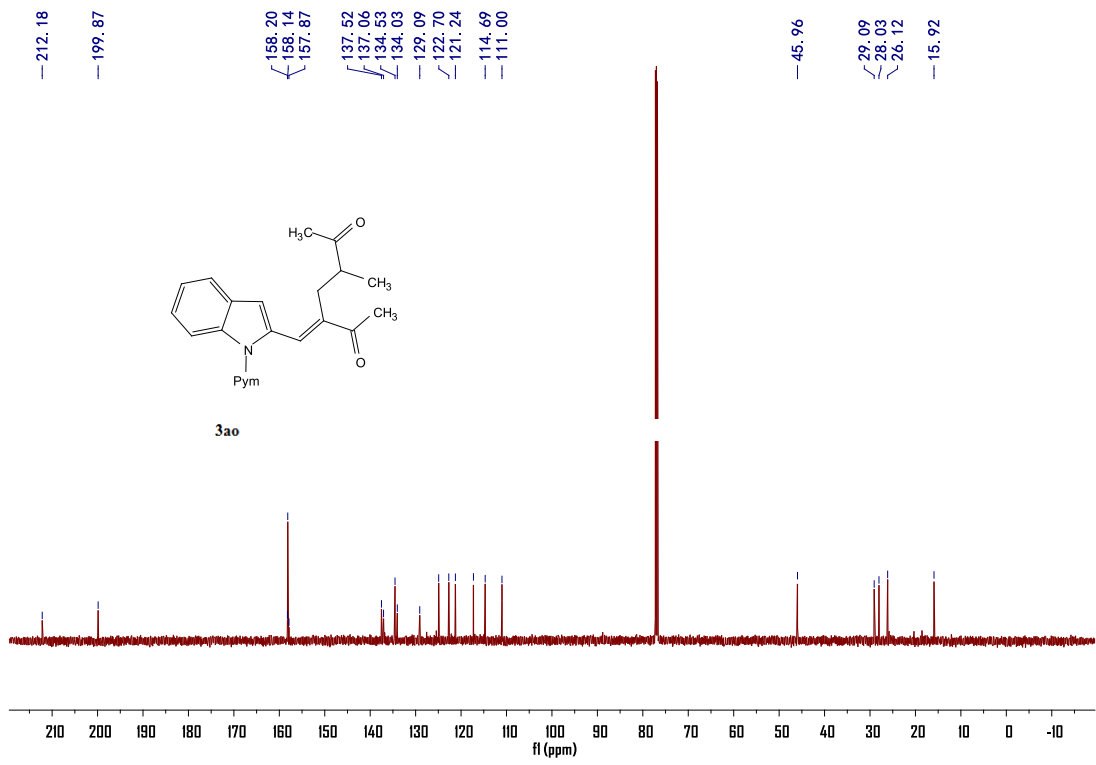


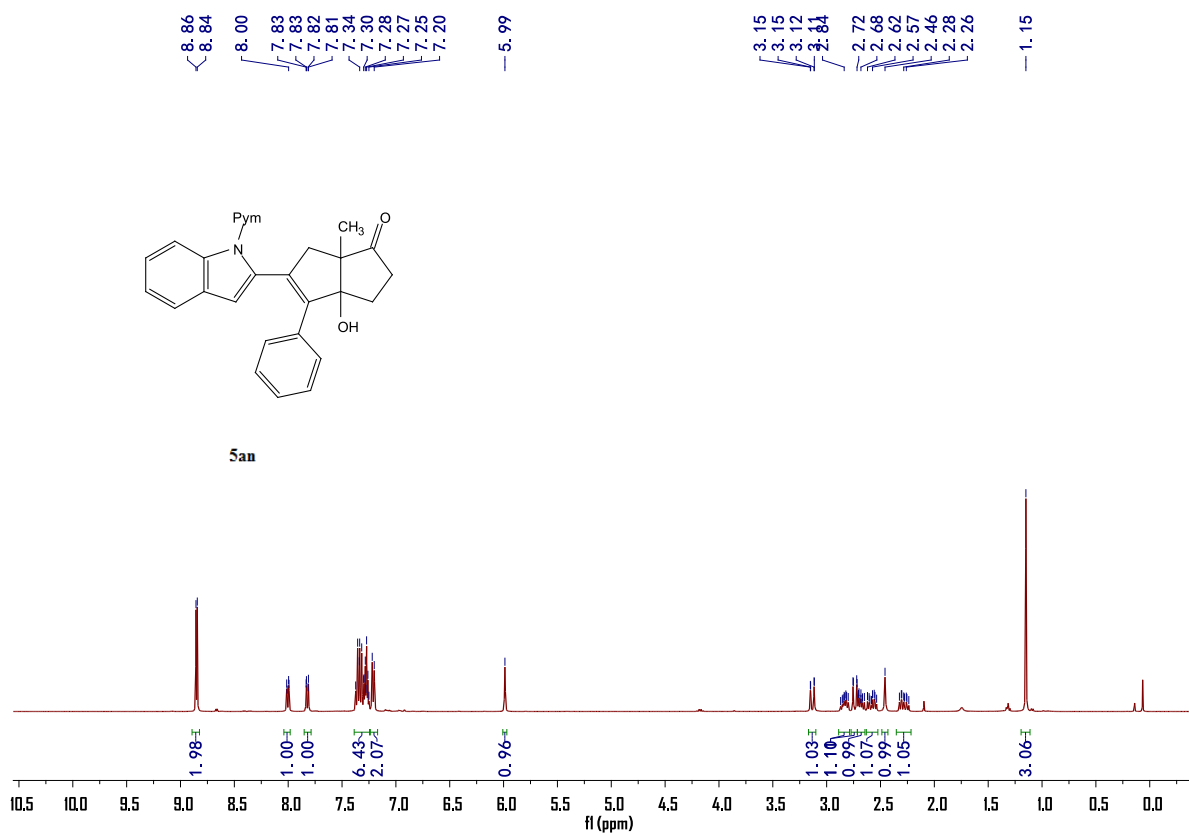
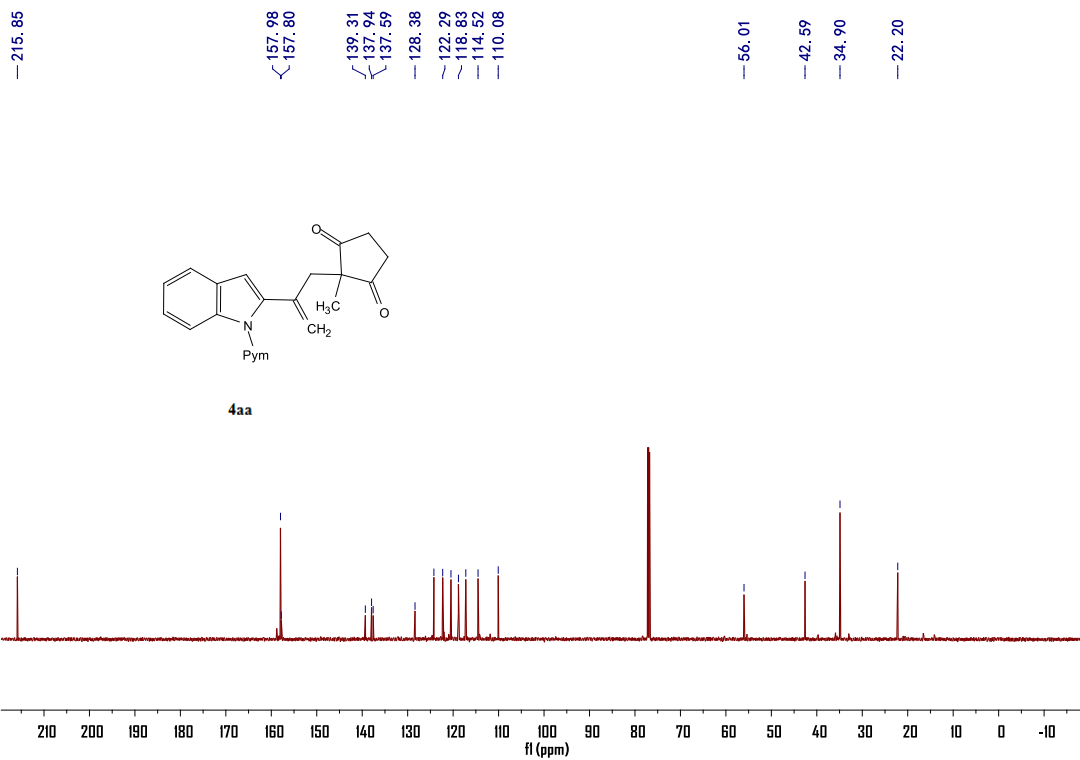












— 219.32

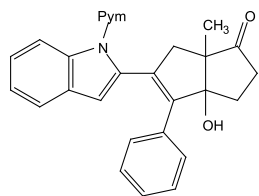
158.83  
158.68  
139.96  
136.46  
135.78  
128.78  
122.17  
118.80  
111.87

— 78.02

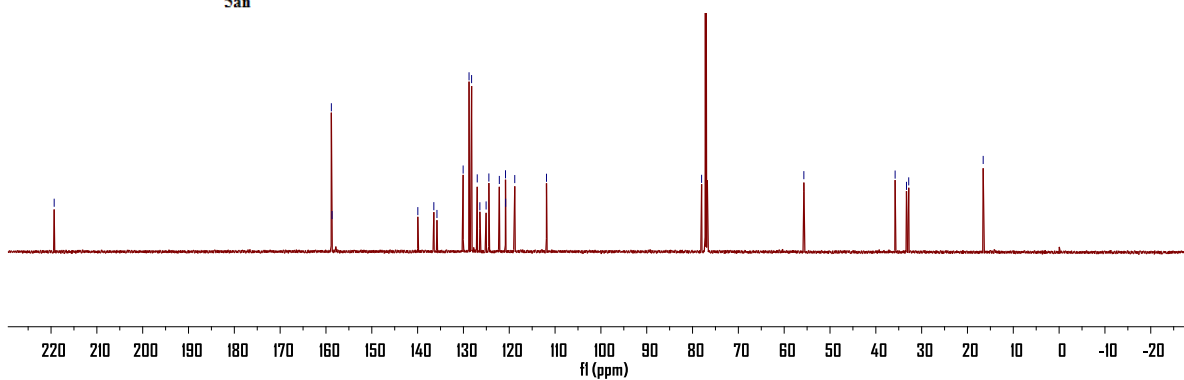
— 55.71

35.79  
33.31  
32.82

— 16.57



5an



8.81  
8.80  
8.23  
8.22  
7.61  
7.60  
7.21  
7.17  
6.95  
6.66

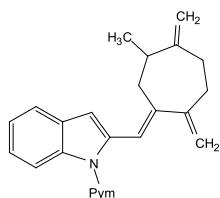
5.20  
5.19  
4.82  
4.75  
4.75  
4.73

2.86  
2.86  
2.84  
2.84

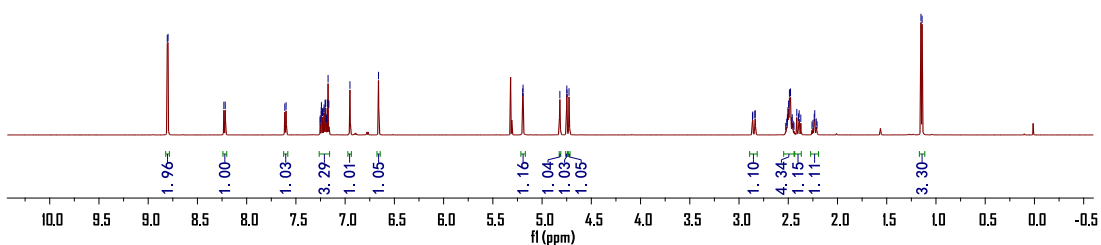
2.49  
2.46  
2.40  
2.25  
2.22

1.15  
1.14

<sup>1</sup>H NMR(600MHz, CDCl<sub>3</sub>)

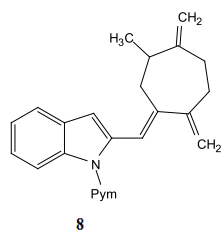


8



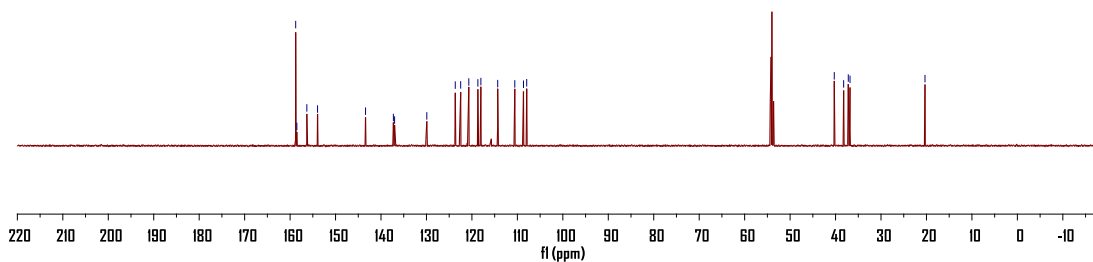


<sup>1</sup>H NMR(600MHz CDCl<sub>3</sub>)

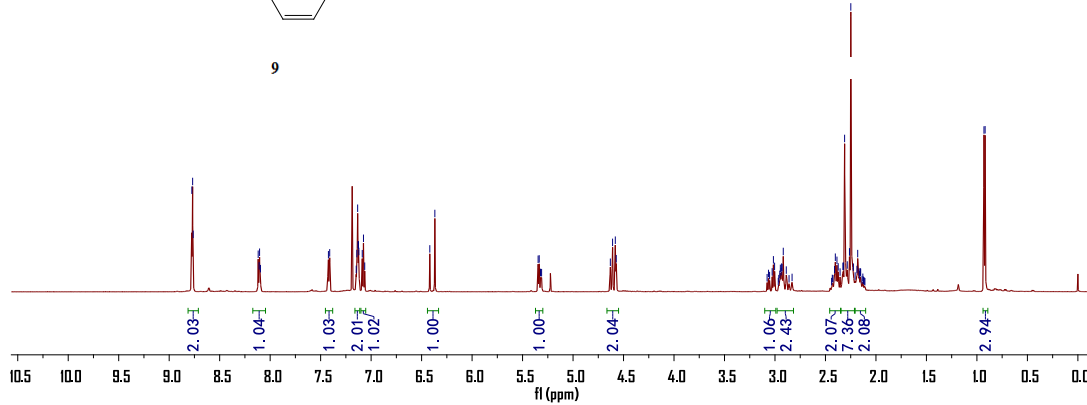
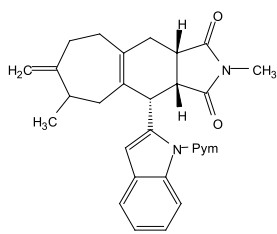


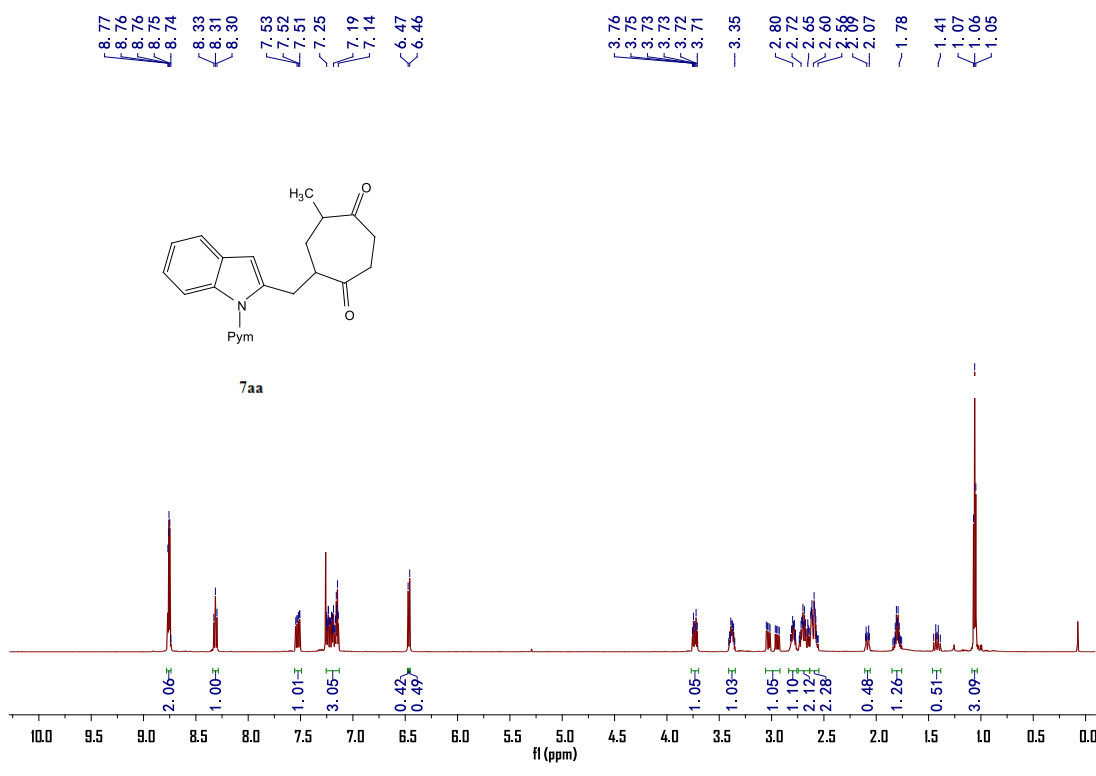
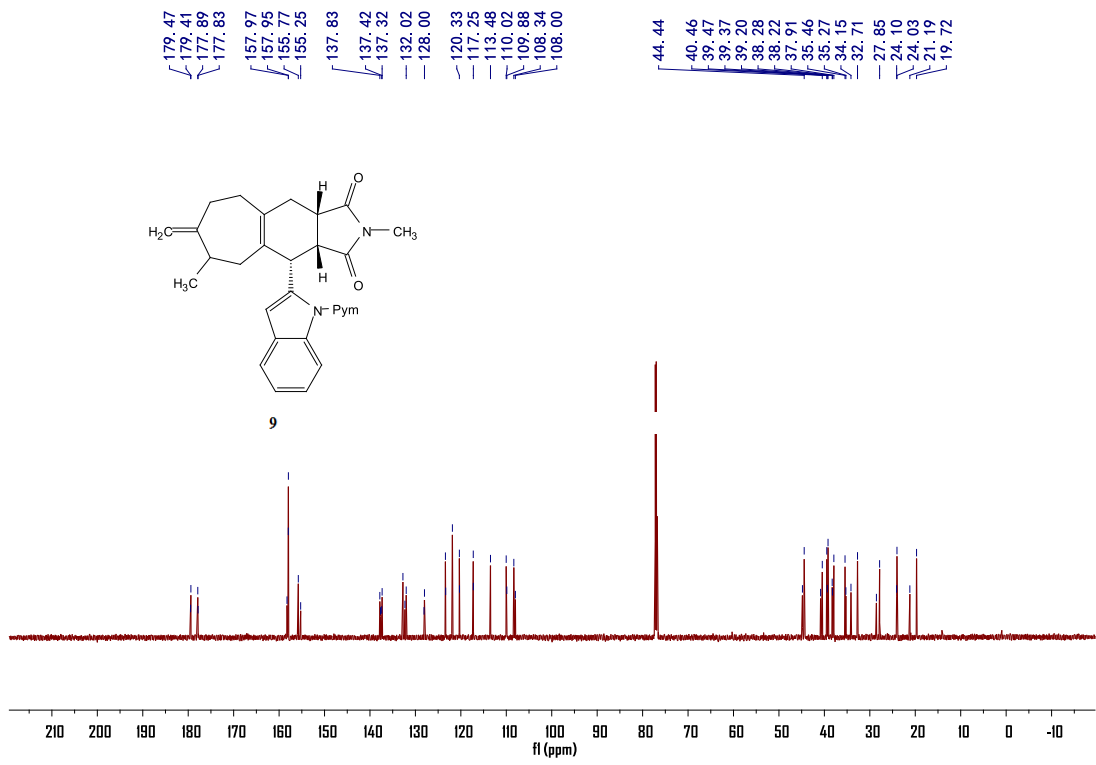
158.77  
158.51  
156.32  
153.96  
143.40  
137.01  
129.92  
120.68  
118.03  
114.33  
110.57  
108.66  
107.95

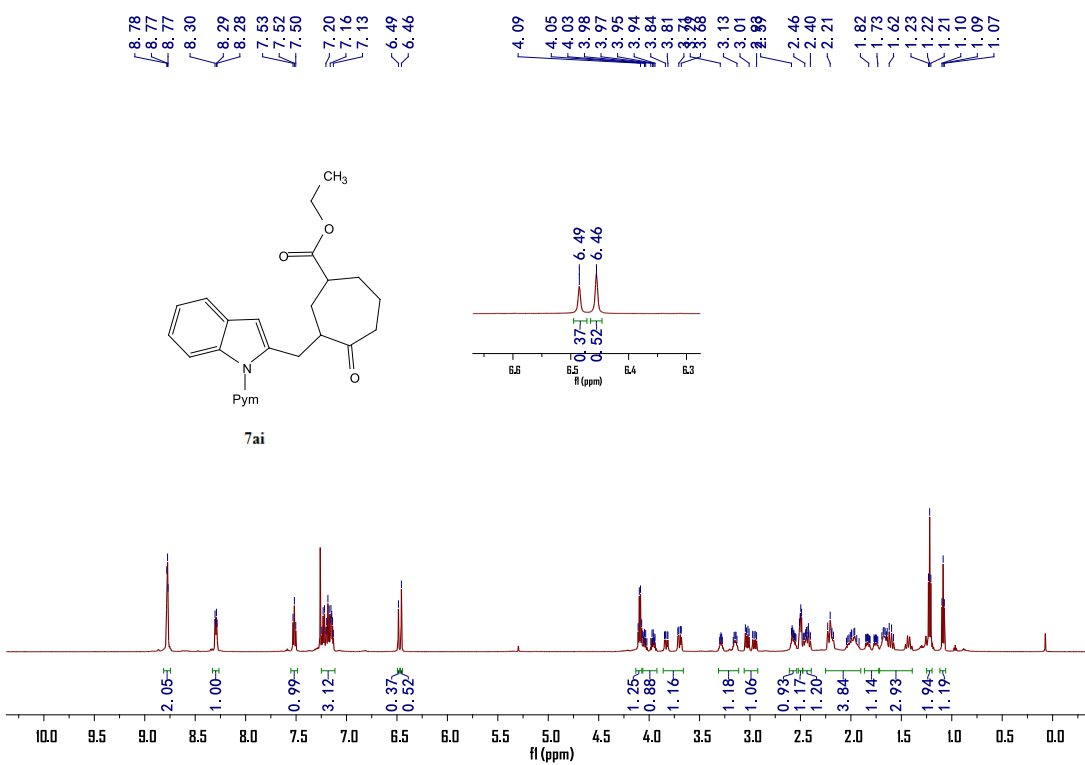
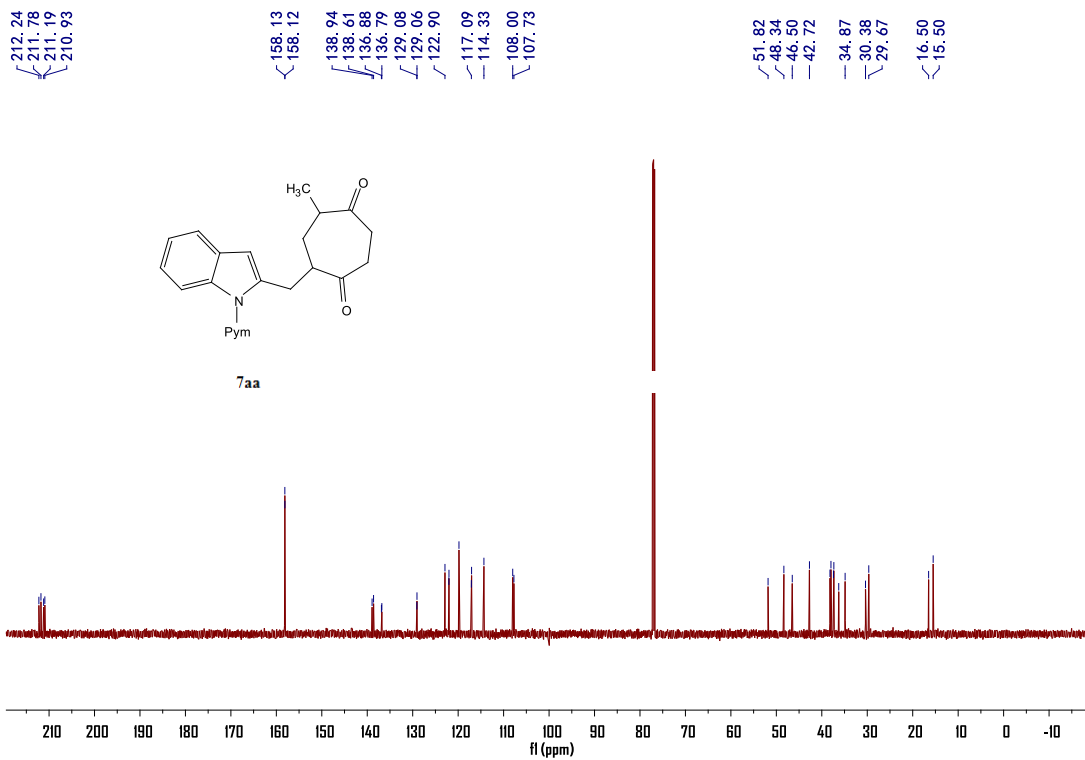
40.28  
38.22  
37.20  
36.82  
20.32

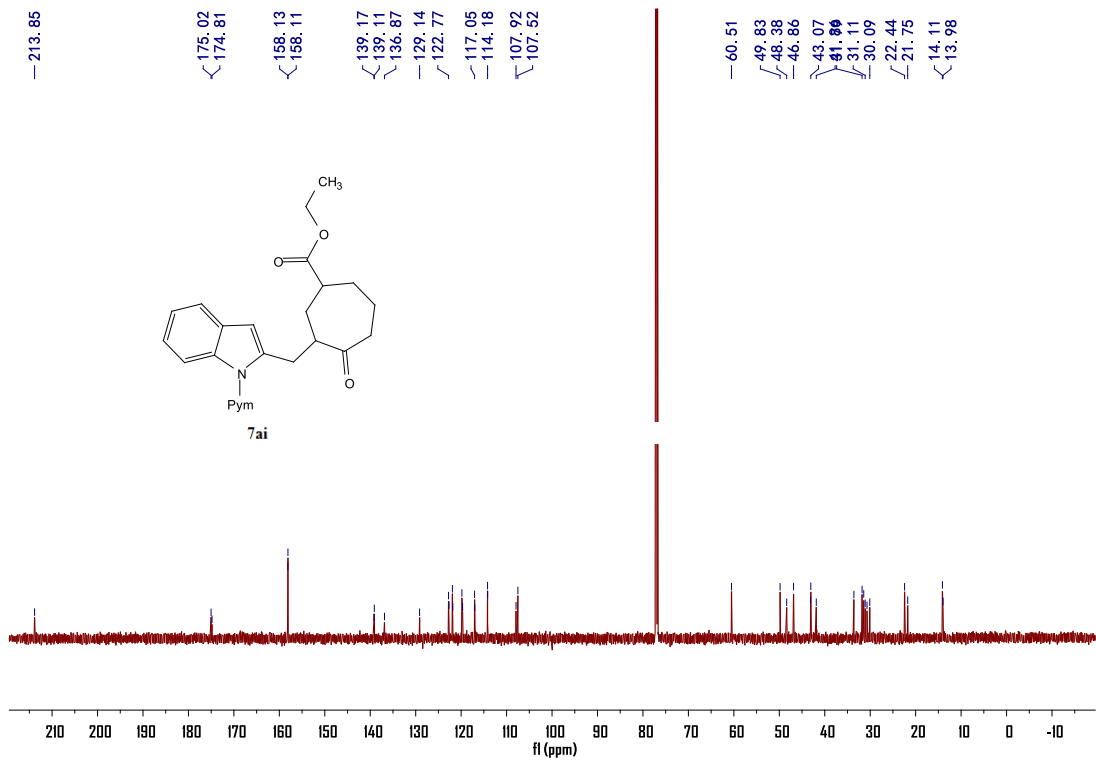


8.78  
8.77  
8.76  
8.11  
8.10  
8.10  
7.42  
7.41  
7.13  
7.12  
7.06  
6.42  
6.37  
5.35  
5.34  
5.32  
5.31  
4.63  
4.61  
4.58  
4.57  
3.05  
2.97  
2.95  
2.94  
2.93  
2.89  
2.88  
2.28  
2.22  
2.18  
2.15  
2.13  
2.11  
0.93  
0.92









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