

## Supporting Information

for

### Phosphine-catalysed denitrative rearomatising (3+2) annulation of $\alpha,\beta$ -ynones and 3-nitroindoles

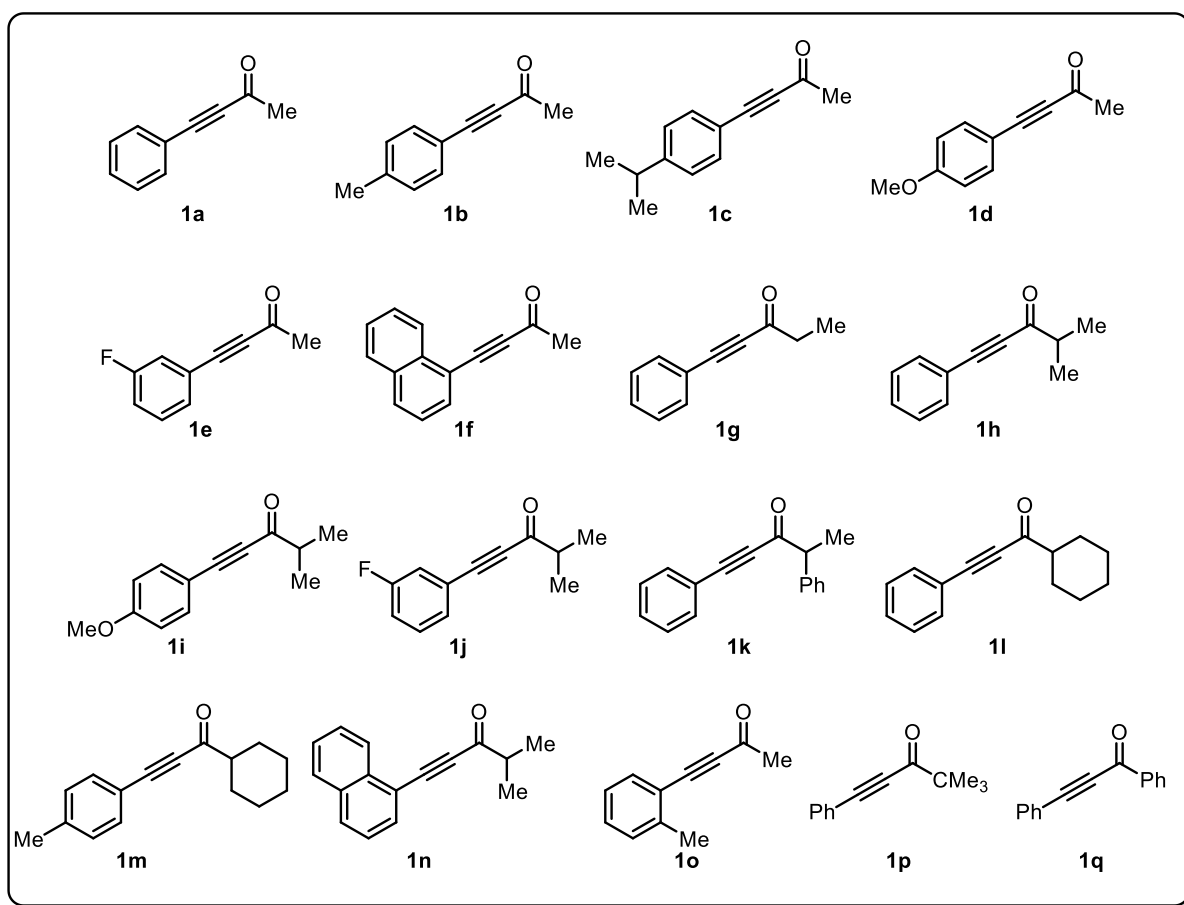
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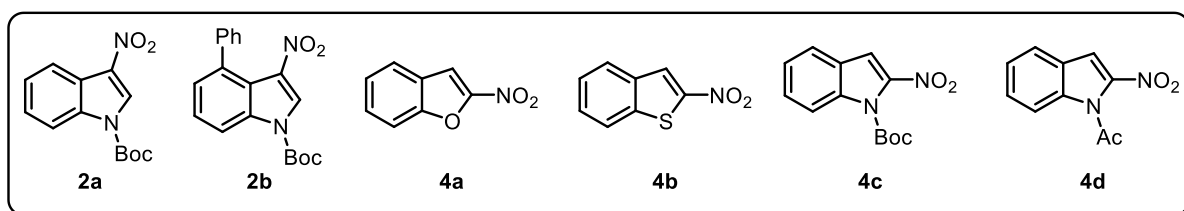
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**General experimental methods:** All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin-layer chromatography (TLC), silica aluminium foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H<sub>2</sub>SO<sub>4</sub> (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating (using a hot air gun). Column chromatography was performed using SD Fine silica gel 100-200 mesh (approximately 15-20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. DCM was obtained by distillation over calcium hydride and stored with 4 Å molecular sieves. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer as thin films or KBr pellet, as indicated, with  $\nu_{\text{max}}$  in inverse centimeters. Melting points were recorded on a digital melting point apparatus Stuart SMP30 and were uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. NMR shifts are reported as delta ( $\delta$ ) units in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Carbon chemical shifts are internally referenced to the deuterated solvent signals in CDCl<sub>3</sub> ( $\delta$  77.1 ppm) and (CD<sub>3</sub>)<sub>2</sub>SO ( $\delta$  39.5 ppm). Single crystal X-ray analysis was carried on a Rigaku XtaLAB mini-X-ray diffractometer. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. Nitro-substituted heterocycles **2a**, **2b**, **4a**, **4b**, **4c**, **4d** and ynones **1a-1q** were synthesized according to the literature procedures.<sup>1,2,3</sup>

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1. N. Nowrouzi, A. M. Mehranpour, E. Bashiri and Z. Shayan, *Tetrahedron Lett.*, 2012, **53**, 4841-4842.
  2. (a) Q. Yao, L. Kong, F. Zhang, X. Tao and Y. Li, *Adv. Synth. Catal.*, 2017, **359**, 3079-3084; (b) Y. M. Zhang, M. L. Yuan, W. P. Liu, J. H. Xie and Q. Zhou, *Org. Lett.*, 2018, **20**, 4486-4489; (c) Z. Li, H. Yu, Y. Liu, L. Zhou, Z. Sun and H. Guo, *Adv. Synth. Catal.*, 2016, **358**, 1880-1885.
  3. (a) E. T. Pelkey and G. W. Gribble, *Tetrahedron Lett.*, 1997, **38**, 5603-5606; (b) H. Zhang, J. He, Y. Chen, C. Zhuang, C. Jiang, K. Xiao, Z. Su, X. Ren and T. Wang, *Angew. Chem. Int. Ed.*, 2021, **60**, 19860-19870.

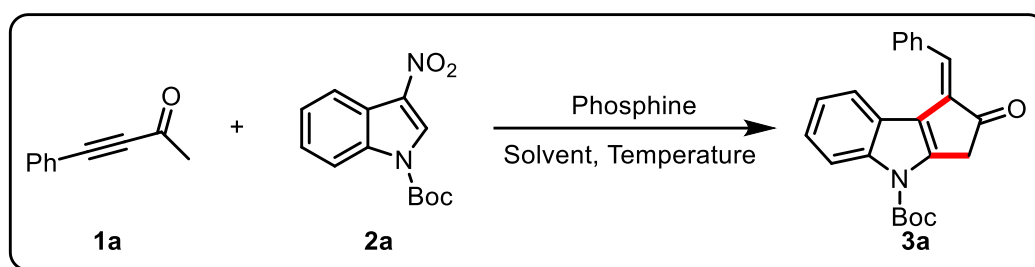


**Figure 1S:** Yrones employed during this study



**Figure 2S:** Nitro-substituted heterocycles employed during this study

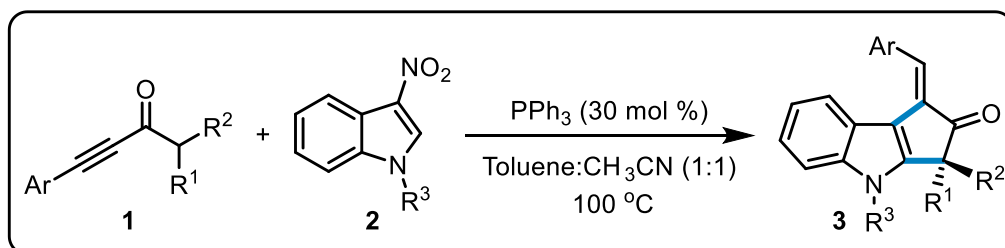
### General procedure-1: Optimization of reaction parameters for **3a**



**Scheme S1:** General reaction for the optimization of reaction parameters.

An oven-dried 10 mL glass vial was charged with 3-nitroindole **2a** (1.0 equiv, 0.1 mmol) and ynone **1a**. An appropriate solvent (1.0 mL) and phosphine were introduced. The reaction mixture was stirred until **2a** disappeared (as detected by TLC). The reaction was quenched with water and extracted with EtOAc (2 x 2 mL). The organic extracts were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as an eluent (49:1) to afford **3a** as a pale yellow semi-solid.

### General procedure-2: Evaluating the substrate scope



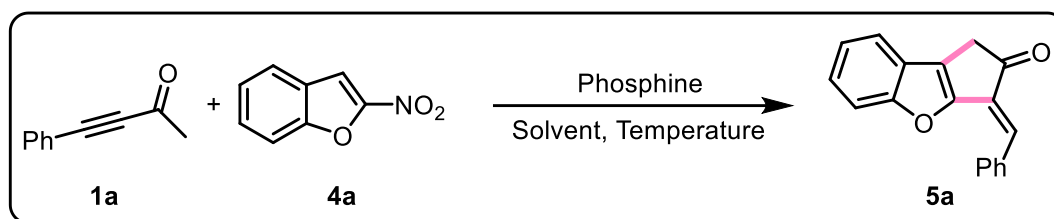
**Scheme 2S:** Synthesis of **3a-3o**

An oven-dried 10 mL glass vial was charged with **2** (1.0 equiv) and **1** (3 equiv). Toluene (0.5 mL) and acetonitrile (0.5 mL) were introduced. Then, triphenylphosphine (30 mol%) was added into the reaction mixture. The reaction mixture was stirred at 100 °C (in a heating block) until **2** disappeared (as detected by TLC). The reaction was quenched with water and extracted with EtOAc (2 x 2 mL). The organic extracts were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as an eluent (49:1), to afford **3** in 43-77% yield.

The same procedure was employed to synthesize **6a**, **7a**, **6b**, **7b**.



### General procedure-3: Optimization of reaction parameters for **5a**.



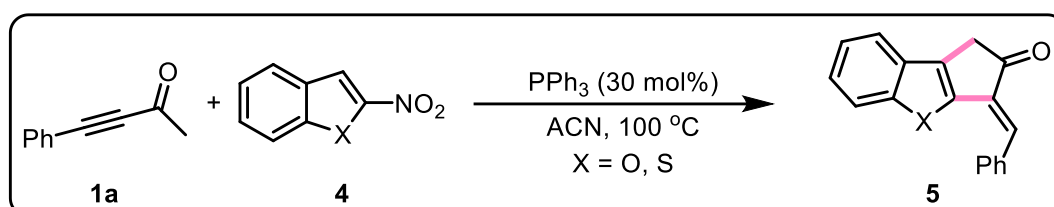
**Scheme S3:** Optimization of reaction parameters.

An oven-dried 10 mL glass vial was charged with **4a** (1.0 equiv, 0.1 mmol) and ynone **1a** (3.0 equiv, 0.3 mmol). An appropriate solvent (1.0 mL) and phosphine were introduced. The reaction mixture was stirred until **4a** disappeared (as detected by TLC). The reaction was quenched with water and extracted with EtOAc (2 x 2 mL). The organic extracts were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as an eluent (49:1) to afford **5a** as pale-yellow solid.

SI No.	Phosphine (mol%)	Solvent	Temp (°C)	Time (h)	Yield (%)
1.	PPh <sub>3</sub> (30)	Toluene-ACN (1:1)	100	16	21
2.	PBu <sub>3</sub> (30)	Toluene-ACN (1:1)	100	7	10
3.	PCy <sub>3</sub> (30)	Toluene-ACN (1:1)	100	16	13
4.	PPh <sub>3</sub> (30)	Toluene	100	24	trace
<b>5.</b>	<b>PPh<sub>3</sub> (30)</b>	<b>ACN</b>	<b>100</b>	<b>18</b>	<b>63</b>
6.	PPh <sub>3</sub> (30)	1,4-Dioxane	100	24	decomposed
7.	PPh <sub>3</sub> (30)	DMF	100	24	decomposed
8.	PPh <sub>3</sub> (30)	DCM	50	24	trace

**Table 1S:** Optimization of the reaction parameters for **5a**

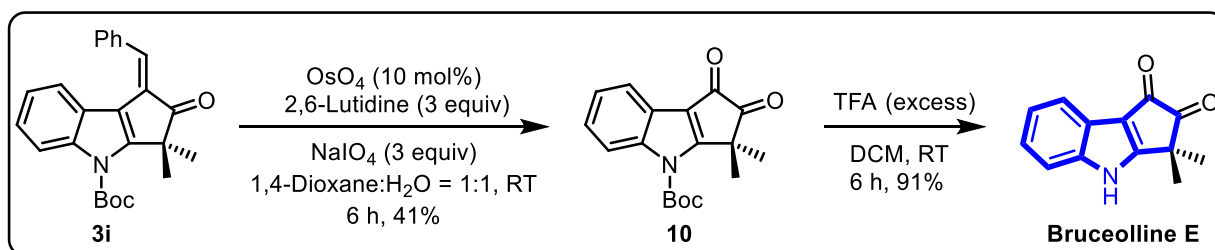
### General procedure-4: Evaluating the substrate scope for **5**



**Scheme S4:** Synthesis of **5**

An oven-dried 10 mL glass vial was charged with **4** (1.0 equiv), ynone **1a** (3.0 equiv) and ACN (1.0 mL). Then, PPh<sub>3</sub> (30 mol%) was introduced. The progress of the reaction was detected by TLC. Upon completion, the reaction was quenched with water and extracted with EtOAc (2 x 2 mL). The organic extracts were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as an eluent (49:1) to afford **5**.

#### General procedure-5: Synthesis of Bruceolline E



**Scheme S5:** Synthesis of Bruceolline E.

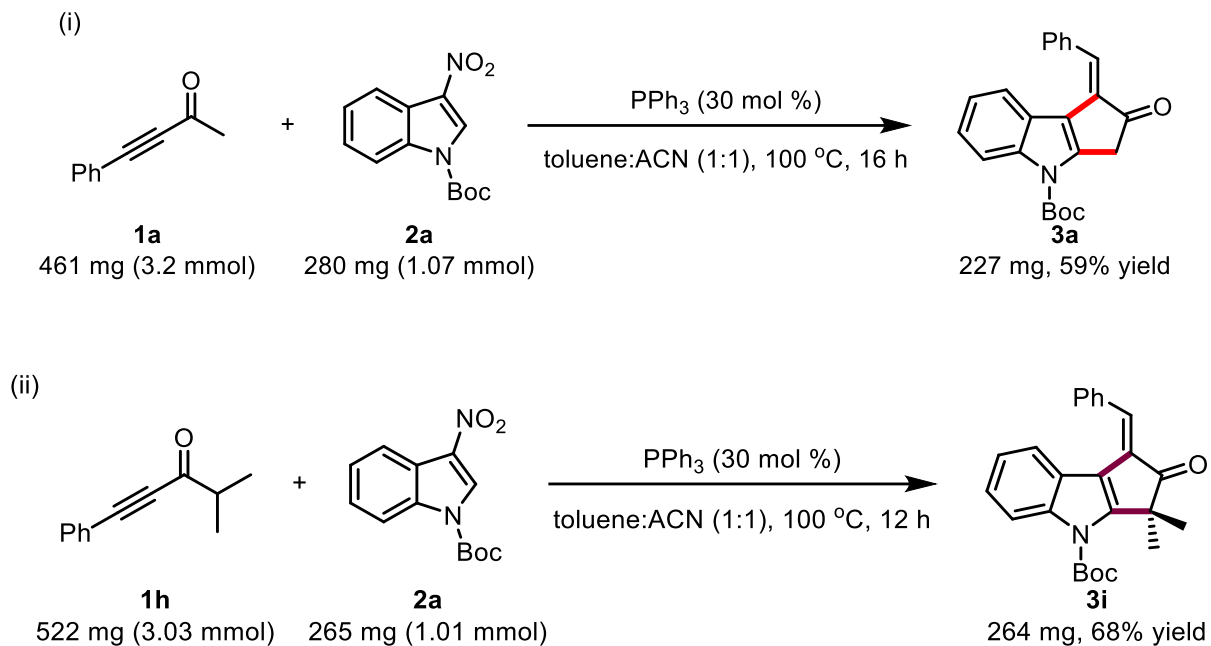
#### Step 1:

To a solution of **3i** (1 equiv, 0.25 mmol) in 1,4-dioxane-water (1:1, 4 mL) were added 2,6-lutidine (3 equiv, 0.77 mmol), OsO<sub>4</sub> (0.1 equiv, 0.025 mmol) and NaIO<sub>4</sub> (3 equiv, 0.77 mmol) sequentially. The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion, reaction was quenched with water and extracted with DCM (2 x 5 mL). The organic extracts were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as an eluent (3:2) to afford **10** in 41% yield.

#### Step 2:

To a solution of **10** (1 equiv, 0.09 mmol) in DCM (3 mL), TFA (0.1 mL) was added and the reaction mixture was stirred at room temperature until the complete consumption of the starting material. After 6 h, the solution was quenched with NaHCO<sub>3</sub> and extracted with DCM (2 x 2 mL). The organic extracts were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as an eluent (3:2) to afford **8** in 91% yield.

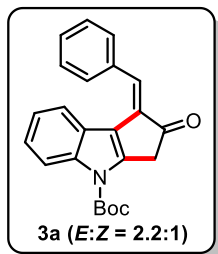
**Scale-up reactions of 1a and 1h with 2a:** The scale-up reactions were performed as described in the general procedure-2.



**Scheme S6:** Scale-up reaction for **3a** and **3i**

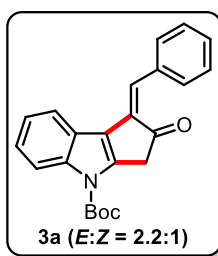
## Spectroscopic data of the newly synthesized compounds during the present study

### *tert*-Butyl (*E*)-1-benzylidene-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (**3a**):



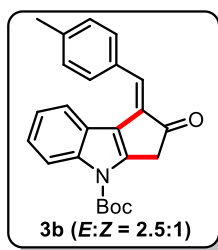
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 35 mg of **2a** afforded 37 mg of **3a** (77% yield).  $R_f = 0.5$  (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2984, 1740, 1373, 1242, 1046, 787.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.30 (d,  $J = 8.0$  Hz, 1H), 7.95 (d,  $J = 7.4$  Hz, 2H), 7.80 (d,  $J = 8.2$  Hz, 1H), 7.43-7.41 (m, 1H), 7.40-7.37 (m, 3H), 7.36-7.34 (m, 1H), 7.11 (s, 1H), 3.74 (s, 2H), 1.67 (s, 9H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  201.4, 149.1, 140.0, 138.3, 134.9, 132.1, 130.4 (2C), 128.2, 128.1 (2C), 125.9, 125.0, 124.5, 123.7, 123.06, 119.2, 116.1, 84.5, 41.8, 28.2 (3C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 360.1600, found: 360.1599.

### *tert*-Butyl (*Z*)-1-benzylidene-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (minor isomer) (**3a**):



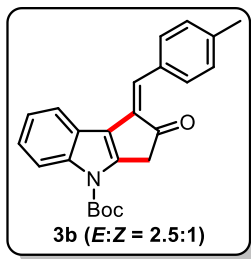
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.29-8.26 (m, 1H), 7.57 (d,  $J = 7.96$  Hz, 1H), 7.46-7.33 (m, 3H), 7.40-7.37 (m, 1H), 7.36-7.34 (m, 1H), 7.33-7.32 (m, 1H), 7.30-7.26 (m, 1H), 7.05 (dt,  $J = 8.08$  and  $0.88$  Hz, 1H), 3.81 (s, 2H), 1.68 (s, 9H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  203.3, 149.0, 143.3, 138.5, 136.7, 132.3, 129.9 (2C), 129.6, 128.9 (2C), 128.5, 125.5, 124.2, 124.1, 123.2, 123.01, 115.9, 84.8, 40.6, 28.2 (3C).

### *tert*-Butyl (*E*)-1-(4-methylbenzylidene)-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (**3b**):



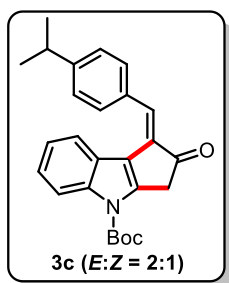
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 32 mg of **3b** (75% yield).  $R_f = 0.5$  (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2978, 1716, 1454, 1366, 1156, 751.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.29 (t,  $J = 6.6$  Hz, 1H), 8.89 (d,  $J = 8.1$  Hz, 2H), 7.41-7.34 (m, 4H), 7.33- 7.27 (m, 1H), 7.11 (s, 1H), 3.75 (s, 2H), 2.39 (s, 3H), 1.67 (s, 9H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  201.5, 149.2, 143.04, 139.3, 138.7, 132.2, 131.4, 130.5 (2C), 128.90 (2C), 126.0, 124.9, 124.3, 123.6, 123.0, 119.2, 116.0, 84.5, 41.9, 28.2 (3C), 21.5. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{24}\text{H}_{23}\text{NNaO}_3$  ( $\text{M}+\text{Na}$ ) $^+$ : 396.1576, found: 396.1569.

***tert*-Butyl (Z)-1-(4-methylbenzylidene)-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (minor isomer) (3b):**



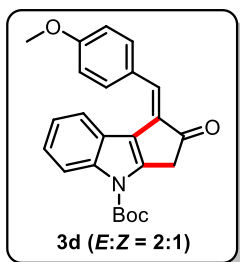
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.24-7.20 (m, 6H), 6.73 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 2H), 2.44 (s, 3H), 1.68 (s, 9H).  
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 203.4, 149.1, 143.07, 138.5, 138.3, 133.6, 131.5, 130.0 (2C), 129.9, 128.99 (2C), 125.9, 124.5, 124.2, 123.4, 123.1, 115.9, 84.7, 40.6, 28.2 (3C), 21.57.

***tert*-Butyl (E)-1-(4-isopropylbenzylidene)-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (3c):**



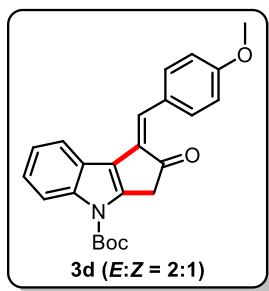
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 34 mg of **3c** (74% yield). *R<sub>f</sub>* = 0.4 (EtOAc/ Hexane = 0.5/9.5). **M.P** = 148-150 °C. **IR (thin film, neat):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2962, 1730, 1365, 1321, 1117, 746. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.31-8.29 (m, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.37 (dt, *J* = 7.1 and 1.6 Hz, 2H), 7.30-7.26 (m, 2H), 7.11 (s, 1H), 3.75 (s, 2H), 2.99-2.89 (m, 1H), 1.67 (s, 9H), 1.28 (d, *J* = 6.9 Hz, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 201.5, 150.1, 149.2, 139.5, 138.3, 132.6, 131.5, 130.6 (2C), 129.9, 126.3 (2C), 126.0, 124.9, 124.3, 123.6, 119.2, 116.1, 84.4, 41.9, 34.1, 28.2 (3C), 23.8 (2C). **HRMS (ESI):** *m/z* calcd for C<sub>26</sub>H<sub>28</sub>NO<sub>3</sub> (M+H)<sup>+</sup>: 402.2069, found: 402.2061.

***tert*-Butyl (E)-1-(4-methoxybenzylidene)-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (3d):**



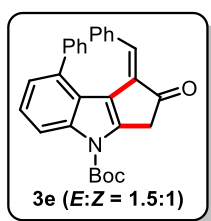
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 30 mg of **3d** (68% yield). *R<sub>f</sub>* = 0.4 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):**  $\nu_{\text{max}}/\text{cm}^{-1}$  3049, 2939, 1735, 1321, 1254, 1113, 736. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.44-7.42 (m, 2H), 7.38-7.34 (m, 2H), 7.10 (dt, *J* = 7.1, 0.88 Hz, 1H), 7.07 (s, 1H), 3.88 (s, 3H), 3.79 (s, 2H), 1.68 (s, 9H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 203.4, 160.3, 149.1, 142.8, 138.5, 131.6 (2C), 130.7, 128.9, 125.7, 124.4, 124.30, 123.6, 123.0, 119.1, 115.6, 113.7 (2C), 84.7, 55.4, 40.7, 28.2 (3C). **HRMS (ESI):** *m/z* calcd for C<sub>24</sub>H<sub>24</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 390.1705, found: 390.1690.

**tert-Butyl (Z)-1-(4-methoxybenzylidene)-2-oxo-2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate (minor isomer) (3d):**



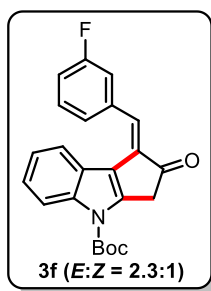
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.30-8.28 (m, 2H), 7.32-7.30 (m, 2H), 6.97-6.92 (m, 4H), 6.82 (d, *J* = 7.9 Hz, 1H), 3.86 (s, 3H), 3.74 (s, 2H), 1.67 (s, 9H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 201.8, 160.0, 149.2, 139.0, 138.3, 132.4 (2C), 130.4, 129.9, 128.0, 126.1, 124.8, 123.4, 124.33, 123.1, 116.0, 113.5 (2C), 84.4, 55.3, 41.9, 28.2 (3C).

**tert-Butyl (E)-1-benzylidene-2-oxo-8-phenyl-2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate (major isomer) (3e):**



This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 20 mg of **2b** afforded 11 mg of **3e** (43% yield). *R<sub>f</sub>* = 0.6 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** *v*<sub>max</sub>/cm<sup>-1</sup> 2977, 1732, 1344, 1252, 1123, 754. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.39 (d, *J* = 8.3 Hz, 1H), 7.45-7.41 (m, 6H), 7.34-7.32 (m, 2H), 7.29 (dd, *J* = 7.4 and 0.9 Hz, 1H), 7.24-7.20 (m, 3H), 5.14 (s, 1H), 3.76 (s, 2H), 1.69 (s, 9H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 201.7, 149.2, 142.0, 140.6, 138.6, 135.4, 134.9, 133.6, 131.0, 130.2 (2C), 129.9 (2C), 128.4, 128.2 (2C), 127.7, 127.5 (2C), 125.6, 125.4, 124.6, 123.2, 114.7, 84.7, 41.6, 28.2 (3C). **HRMS (ESI):** *m/z* calcd for C<sub>29</sub>H<sub>26</sub>NO<sub>3</sub> (M+H)<sup>+</sup>: 436.1913, found: 436.1904.

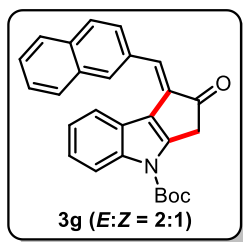
**tert-Butyl (E)-1-(3-fluorobenzylidene)-2-oxo-2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate (major isomer) (3f):**



This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 27 mg of **3f** (63% yield). *R<sub>f</sub>* = 0.5 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** *v*<sub>max</sub>/cm<sup>-1</sup> 2978, 1736, 1369, 1322, 1138, 760. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.30 (d, *J* = 7.8 Hz, 1H), 7.84-7.81 (m, 1H), 7.79-7.77 (m, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.42-7.32 (m, 3H), 7.06-7.01 (m, 2H), 3.75 (s, 2H), 1.68 (s, 9H). **<sup>13</sup>C NMR (100**

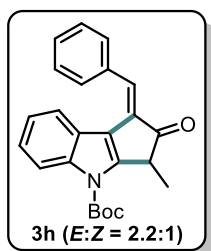
**MHz, CDCl<sub>3</sub>):** δ 203.3, 162.4 (d, *J* = 243.2 Hz, 1C), 149.1, 140.6, 138.4, 137.0 (d, *J* = 8.5 Hz, 1C), 133.0, 129.4 (d, *J* = 8.2 Hz, 1C), 127.8, 126.4 (d, *J* = 2.7 Hz, 1C), 125.7, 125.2, 124.1, 123.8, 119.2, 116.7 (d, *J* = 22.8 Hz, 1C), 116.1, 115.7 (d, *J* = 21.3 Hz, 1C), 84.7, 41.7, 28.2 (3C). **<sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>):** δ -113.34. **HRMS (ESI):** *m/z* calcd for C<sub>18</sub>H<sub>11</sub>FN<sub>2</sub>O (M-Boc)<sup>+</sup>: 276.0825, found: 276.0818.

**tert-Butyl (E)-1-(naphthalen-2-ylmethylene)-2-oxo-2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate (major isomer) (3g):**



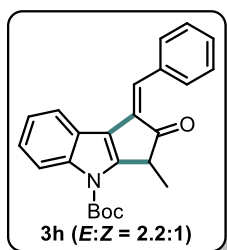
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 35 mg of **3g** (74% yield).  $R_f = 0.4$  (EtOAc/ Hexane = 0.5/9.5). **M.P** = 168-170 °C. **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  3055, 2978, 1731, 1369, 1352, 1111, 762.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.23 (d,  $J = 8.3$  Hz, 1H), 8.08-8.06 (m, 1H), 7.96-7.94 (m, 2H), 7.86 (s, 1H), 7.55-7.50 (m, 4H), 7.21 (t,  $J = 8.3$  Hz, 1H), 6.87 (t,  $J = 8.1$  Hz, 1H), 6.07 (d,  $J = 7.9$  Hz, 1H), 3.88 (s, 2H), 1.69 (s, 9H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  203.1, 149.1, 143.1, 138.4, 134.1, 133.9, 133.3, 132.2, 129.1, 128.6, 127.7, 126.9, 126.3, 125.3, 125.1, 124.5, 124.0, 123.18, 123.16, 123.07, 123.01, 115.5, 84.8, 40.5, 28.2 (3C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{27}\text{H}_{23}\text{NNaO}_3$  ( $\text{M}+\text{Na}$ ) $^+$ : 432.1585, found: 432.1576.

**tert-Butyl (E)-1-benzylidene-3-methyl-2-oxo-2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate (major isomer) (3h):**



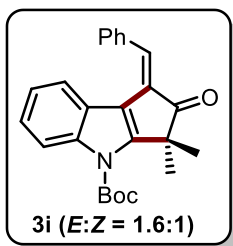
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 30 mg of **3h** (70% yield).  $R_f = 0.45$  (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2978, 1727, 1354, 1316, 1154, 1116, 736.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.20 (d,  $J = 8.3$  Hz, 1H), 7.89-7.87 (m, 2H), 7.36-7.33 (m, 3H), 7.31-7.29 (m, 3H), 7.06 (s, 1H), 3.63 (q,  $J = 7.2$  Hz, 1H), 1.61 (s, 9H), 1.44 (d,  $J = 7.2$  Hz, 3H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  205.0, 149.1, 145.5, 138.7, 135.0, 130.9, 130.4 (2C), 128.9, 128.5, 128.1 (2C), 125.1, 124.1, 123.7, 123.0, 119.4, 116.2, 84.7, 46.2, 28.16 (3C), 17.0. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{24}\text{H}_{24}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 374.1756, found: 374.1787.

**tert-Butyl (Z)-1-benzylidene-3-methyl-2-oxo-2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate (minor isomer) (3h):**



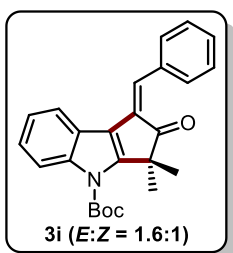
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.16 (d,  $J = 8.4$  Hz, 1H), 7.74-7.72 (m, 2H), 7.28-7.16 (m, 5H), 6.95 (t,  $J = 8.1$  Hz, 1H), 6.48 (d,  $J = 7.9$  Hz, 1H), 3.73 (q,  $J = 7.4$  Hz, 1H), 1.62 (s, 9H), 1.47 (d,  $J = 7.2$  Hz, 3H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  206.8, 149.06, 148.9, 138.8, 136.8, 131.0, 129.9 (2C), 129.7, 128.2 (2C), 125.8, 125.0, 124.6, 124.0, 123.5, 122.2, 115.7, 84.9, 44.9, 28.14 (3C), 17.1.

***tert*-Butyl (E)-1-benzylidene-3,3-dimethyl-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (3i):**



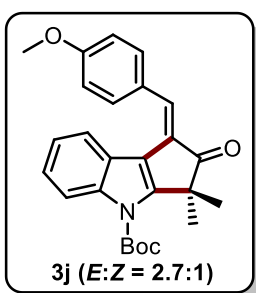
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 31 mg of **3i** (69% yield).  $R_f = 0.4$  (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2974, 1737, 1363, 1155, 1107, 760.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.23-8.20 (m, 1H), 8.00-7.98 (d,  $J = 7.5$  Hz, 2H), 7.88-7.85 (m, 1H), 7.42-7.39 (m, 5H), 7.216 (s, 1H), 1.74 (s, 9H), 1.55 (s, 6H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  209.6, 152.7, 149.2, 138.8, 136.9, 130.5 (2C), 130.0 (2C), 129.76, 128.4, 125.0, 124.5, 123.8, 123.7, 122.9, 119.4, 116.0, 85.2, 48.8, 28.30 (3C), 22.73 (2C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{25}\text{H}_{26}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 388.1893, found: 388.1913.

***tert*-Butyl (Z)-1-benzylidene-3,3-dimethyl-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (minor isomer) (3i):**



**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.15 (d,  $J = 8.4$  Hz, 1H), 7.45-7.44 (m, 2H), 7.38-7.33 (m, 4H), 7.29-7.24 (m, 1H), 7.02 (dt,  $J = 8.0$  and 0.8 Hz, 1H), 6.52 (d,  $J = 7.8$  Hz, 1H), 1.74 (s, 9H), 1.59 (s, 6H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  207.8, 149.5, 149.3, 138.7, 135.1, 129.8, 129.74, 128.8, 128.2 (2C), 128.0 (2C), 126.1, 124.0, 123.9, 123.5, 121.5, 126.6, 85.2, 49.7, 28.34 (3C), 22.78 (2C).

***tert*-Butyl (E)-1-(4-methoxybenzylidene)-3,3-dimethyl-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (3j):**



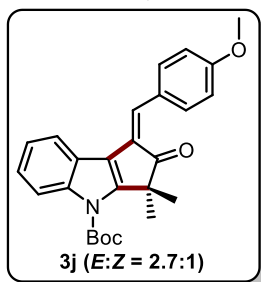
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 34 mg of **3j** (71% yield).  $R_f = 0.4$  (EtOAc/ Hexane = 0.5/9.5). **M.P** = 150-152 °C. **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2970, 1730, 1300, 1251, 1151, 1104, 742.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.23-8.20 (m, 1H), 8.06 (d,  $J = 8.7$  Hz, 2H), 7.44-7.42 (m, 1H), 7.38-7.35 (m, 2H), 7.17 (s, 1H), 6.99-6.94 (m, 2H), 3.86 (s, 3H), 1.74 (s, 9H), 1.54 (s, 6H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  208.1, 160.2, 149.3, 148.5, 138.7, 132.5 (2C), 130.0, 128.19, 128.0, 124.9, 124.13, 123.9, 123.5, 119.3, 116.0, 113.5 (2C), 84.9, 55.38, 49.7, 28.33 (3C), 22.78 (2C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{26}\text{H}_{28}\text{NO}_4$  ( $\text{M}+\text{H}$ ) $^+$ : 418.2018, found: 418.2018.



*tert*-Butyl

**(Z)-1-(4-methoxybenzylidene)-3,3-dimethyl-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (minor isomer) (3j):**

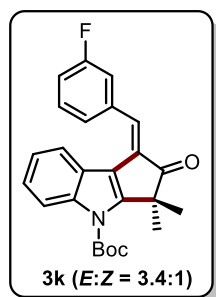
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.87-7.85 (m, 2H), 7.32 (s, 1H), 7.30-



7.26 (m, 1H), 7.08 (dt, *J* = 8.0 and 0.8 Hz, 1H), 6.93-6.92 (m, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 3H), 1.75 (s, 9H), 1.58 (s, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 209.8, 159.9, 152.2, 149.2, 138.8, 131.6 (2C), 129.2, 128.14, 126.3, 124.4, 124.10, 123.7, 122.8, 121.6, 116.5 (2C), 113.6, 85.1, 55.34, 48.8, 28.30 (3C), 22.71 (2C).

*tert*-Butyl

**(E)-1-(3-fluorobenzylidene)-3,3-dimethyl-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (3k):**



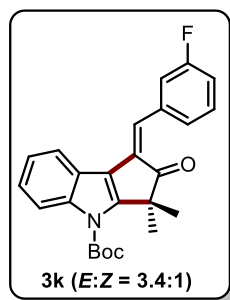
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 32 mg of **3k** (70% yield). *R<sub>f</sub>* = 0.35 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** *v*<sub>max</sub>/cm<sup>-1</sup> 2975, 1736, 1358, 1303, 1153, 1109, 747. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.21 (d, *J* = 8.9 Hz, 1H), 7.89-7.83 (m, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.40-7.34 (m, 4H), 7.14 (s, 1H), 7.03 (dt, *J* = 8.3 Hz and 7.4 Hz, 1H), 1.74 (s, 9H), 1.55 (s, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 207.8, 162.5 (d, *J* = 242.8 Hz, 1C), 150.1, 149.2, 138.7, 137.20 (d, *J* = 8.1 Hz, 1C), 130.7, 129.36 (d, *J* = 8.1 Hz, 1C), 126.50 (d, *J* = 2.8 Hz, 1C), 125.2, 123.7, 123.1 (d, *J* = 13.5 Hz, 1C), 121.6, 119.4, 115.9 (d, *J* = 34.4 Hz, 1C), 116.6, 115.5, 106.6, 85.2, 49.7, 28.3 (3C), 22.74 (2C). **<sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>):** δ -113.44. **HRMS (ESI):** *m/z* calcd for C<sub>25</sub>H<sub>24</sub>FNNaO<sub>3</sub> (M+Na)<sup>+</sup>: 428.1638, found: 428.1623.

*tert*-Butyl

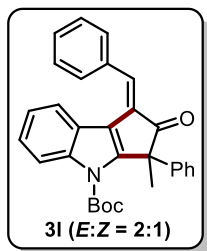
**(Z)-1-(3-fluorobenzylidene)-3,3-dimethyl-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (minor isomer) (3k):**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** Peaks corresponding to the minor isomer are not clearly



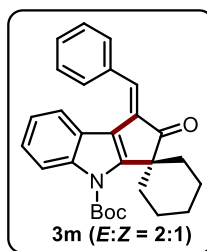
distinguishable. **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 209.4, 162.5 (d, *J* = 245.6 Hz, 1C), 153.3, 149.1, 139.1 (d, *J* = 7.8 Hz, 1C), 138.8, 130.4, 129.74 (d, *J* = 8.3 Hz, 1C), 127.95 (d, *J* = 2.3 Hz, 1C), 125.7, 124.7, 124.3, 123.9, 123.73, 123.67, 121.1, 116.8 (d, *J* = 23.1 Hz, 1C), 115.4 (d, *J* = 15.8 Hz, 1C), 85.4, 48.8, 28.2 (3C), 22.70 (2C). **<sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>):** δ -111.78.

**tert-Butyl (E)-1-benzylidene-3-methyl-2-oxo-3-phenyl-2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate (major isomer) (3l):**



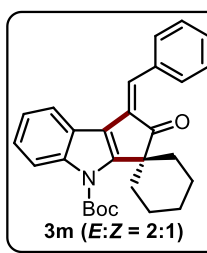
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 37 mg of **3l** (72% yield).  $R_f = 0.45$  (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2978, 1730, 1351, 1311, 1142, 745.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.47 (dd,  $J = 7.6$  and 1.7 Hz, 1H), 7.96-7.94 (m, 1H), 7.92-7.90 (m, 2H), 7.48-7.42 (m, 3H), 7.35-7.33 (m, 2H), 7.31-7.28 (m, 3H), 7.27 (s, 1H), 7.22-7.20 (m, 2H), 1.99 (s, 3H), 1.26 (s, 9H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  203.7, 149.0, 145.8, 140.5, 139.5, 134.8, 131.2, 130.6 (2C), 129.4, 129.0, 128.3 (2C), 128.0 (2C), 126.9, 126.8 (2C), 125.9, 125.6, 123.9, 123.8, 119.5, 116.9, 85.0, 57.7, 27.7 (3C), 22.1. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{30}\text{H}_{28}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 450.2069, found: 450.2093.

**tert-Butyl (E)-1'-benzylidene-2'-oxo-1',2'-dihydro-4'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-4'-carboxylate (major isomer) (3m):**



This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 30 mg of **3m** (62% yield).  $R_f = 0.4$  (EtOAc/ Hexane = 0.5/9.5). **M.P** = 158-161 °C. **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2931, 1732, 1359, 1301, 1152, 742.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.15-8.12 (m, 1H), 7.95 (d,  $J = 7.6$  Hz, 2H), 7.42-7.379 (m, 4H), 7.373-7.343 (m, 2H), 7.16 (s, 1H), 2.58-2.53 (m, 2H), 2.17-2.10 (m, 2H), 1.83-1.79 (m, 2H), 1.75 (s, 9H), 1.64-1.63 (m, 2H), 1.51-1.44 (m, 2H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  206.9, 149.3, 138.7, 135.2, 133.0, 130.4 (2C), 129.9, 128.6, 128.0 (2C), 126.7, 125.3, 124.47, 123.9, 123.60, 119.4, 116.6, 84.9, 51.6, 29.4, 28.33 (3C), 24.3 (2C), 21.2 (2C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{28}\text{H}_{29}\text{NNaO}_3$  ( $\text{M}+\text{Na}$ ) $^+$ : 450.2045, found: 450.2045.

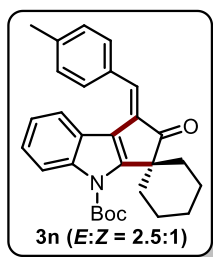
**tert-Butyl (Z)-1'-benzylidene-2'-oxo-1',2'-dihydro-4'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-4'-carboxylate (minor isomer) (3m):**



**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.08-8.06 (m, 1H), 7.86-7.84 (m, 3H), 7.59-7.57 (m, 1H), 7.32-7.30 (m, 3H), 6.99 (t,  $J = 7.7$  Hz, 1H), 6.47 (d,  $J = 8.0$  Hz, 1H), 2.51-2.50 (m, 2H), 2.09-2.07 (m, 2H), 1.86-1.85 (m, 2H), 1.75 (s, 9H), 1.639-1.633 (m, 2H), 1.33-1.30 (m, 2H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  208.2, 149.9, 138.8, 137.1, 130.58, 130.51 (2C), 130.34,

128.8, 128.2, 128.1 (2C), 124.9, 124.43, 123.68, 123.5, 122.8, 115.9, 85.9, 51.6, 29.5, 28.35 (3C), 25.6 (2C), 21.4 (2C).

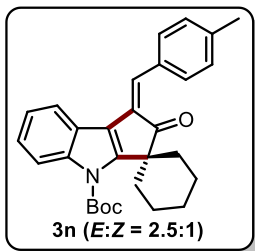
***tert*-Butyl (*E*)-1'-(4-methylbenzylidene)-2'-oxo-1',2'-dihydro-4'*H*-spiro[cyclohexane-1,3'-cyclopenta[*b*]indole]-4'-carboxylate (major isomer) (3n):**



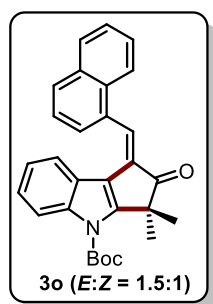
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 33 mg of **3n** (65% yield).  $R_f$  = 0.4 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2978, 1731, 1352, 1142, 745.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.14-8.12 (m, 1H), 7.87-7.85 (m, 2H), 7.37-7.34 (m, 2H), 7.22-7.19 (m, 3H), 7.14 (s, 1H), 2.54-2.49 (m, 2H), 2.38 (s, 3H), 2.12-2.07 (m, 2H), 1.82-1.79 (m, 2H), 1.66-1.63 (m, 2H), 1.53-1.46 (m, 2H), 1.74 (s, 9H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  206.9, 149.4, 138.89, 138.7, 132.5, 130.4 (2C), 129.8, 128.1, 128.80 (2C), 125.6, 124.8, 123.9, 123.5, 122.7, 119.4, 116.6, 84.9, 51.6, 29.4, 28.36 (3C), 25.7, 24.4 (2C), 21.2 (2C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{29}\text{H}_{32}\text{NO}_3(\text{M}+\text{H})^+$ : 442.2382, found: 442.2382.

***tert*-Butyl (*Z*)-1'-(4-methylbenzylidene)-2'-oxo-1',2'-dihydro-4'*H*-spiro[cyclohexane-1,3'-cyclopenta[*b*]indole]-4'-carboxylate (minor isomer) (3n):**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.07 (d,  $J$  = 8.4 Hz, 1H), 7.85-7.84 (m 2H), 7.342-7.33 (m, 2H), 7.28-7.27 (m, 2H), 7.03 (dt,  $J$  = 7.1 and 0.8 Hz, 1H), 6.62 (d,  $J$  = 7.8 Hz, 1H), 2.60-2.56 (m, 2H), 2.42 (s, 3H), 2.17-2.13 (m, 2H), 1.90-1.84 (m, 2H), 1.74 (s, 9H), 1.66-1.63 (m, 2H), 1.45-1.41 (m, 2H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  208.4, 149.5, 138.88, 138.3, 134.0, 132.5, 130.0, 129.5, 128.87 (2C), 126.4, 124.5, 124.3 (2C), 123.7, 123.6, 122.2, 115.9, 85.0, 51.1, 29.5, 28.33 (3C), 25.8, 24.5 (2C), 21.4 (2C).



***tert*-Butyl (*E*)-3,3-dimethyl-1-(naphthalen-1-ylmethylene)-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (3o):**



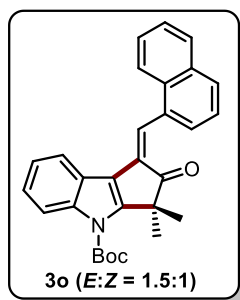
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 5 mg of **3o** (11% yield).  $R_f$  = 0.4 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2972, 1737, 1369, 1312, 1165, 1109.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.26-8.23 (m, 1H), 8.11-8.07 (m, 3H), 7.84 (s, 1H), 7.54-7.51 (m, 4H), 7.19 (t,  $J$  = 8.4 Hz, 1H), 6.83 (t,  $J$  = 7.9 Hz, 1H), 6.04 (d,  $J$  = 7.9 Hz, 1H), 1.74 (s, 9H), 1.64 (s, 6H).  **$^{13}\text{C}$  NMR**

(100 MHz, CDCl<sub>3</sub>):  $\delta$  209.5, 152.9, 149.2, 138.78, 134.4, 133.3, 132.3, 131.3, 129.0, 128.5, 127.7, 126.5, 126.30, 125.9, 125.4, 125.13, 124.5, 124.1, 123.71, 123.3, 121.5, 115.9, 85.2, 49.71, 28.2 (3C), 22.7 (2C). **HRMS (ESI)**:  $m/z$  calcd for C<sub>29</sub>H<sub>27</sub>NNaO<sub>3</sub> (M+Na)<sup>+</sup>: 460.1889, found: 460.1906.

**tert-Butyl**

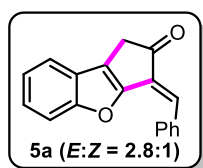
**(Z)-3,3-dimethyl-1-(naphthalen-1-ylmethylene)-2-oxo-2,3-**

**dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (minor isomer) (3o):**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  7.98-7.91 (m, 4H), 7.90-7.85 (m, 2H), 7.80 (s, 1H), 7.49-7.48 (m, 3H), 7.43-7.40 (m, 2H), 1.75 (s, 9H), 1.53 (s, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  207.5, 150.0, 138.73, 134.5, 133.3, 131.7, 131.4, 130.8, 128.7, 128.2, 127.8, 126.6, 126.34, 126.27, 125.9, 125.7, 125.17, 125.0, 124.2, 123.73, 119.6, 116.6, 85.1, 49.73, 28.3 (3C), 22.6 (2C).

**(E)-3-Benzylidene-1,3-dihydro-2*H*-cyclopenta[*b*]benzofuran-2-one (major isomer) (5a):**

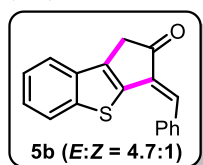


This compound was isolated as pale-yellow solid. Following the general procedure-4, 30 mg of **4a** afforded 30 mg of **5a** (63% yield).  $R_f$  = 0.45 (EtOAc/ Hexane = 0.5/9.5). **M.P** = 108-110 °C. **IR (thin film, neat)**:  $\nu_{\max}/\text{cm}^{-1}$  2929, 1731, 1515, 1372, 1111, 750. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:

$\delta$  8.06 (d,  $J$  = 7.5 Hz, 2H), 7.63 (d,  $J$  = 8.2 Hz, 1H), 7.57 (d,  $J$  = 7.6 Hz, 1H), 7.51-7.48 (m, 2H), 7.44-7.38 (m, 2H), 7.34-7.31 (m, 1H), 7.20 (s, 1H), 3.55 (s, 2H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  202.1, 159.0, 157.7, 134.4, 130.4 (2C), 129.8, 128.8 (2C), 127.3, 126.1, 124.9, 124.6, 123.9, 122.7, 120.3, 112.4, 36.3. **HRMS (ESI)**:  $m/z$  calcd for C<sub>18</sub>H<sub>13</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 261.0916, found: 261.0912.

**(Z)-3-Benzylidene-1,3-dihydro-2*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one (major isomer)**

**(5b):**

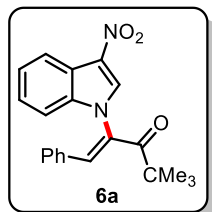


This compound was isolated as pale-yellow semi-solid. Following the general procedure-4, 30 mg of **4b** afforded 20 mg of **5b** (43% yield).  $R_f$  = 0.45 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat)**:  $\nu_{\max}/\text{cm}^{-1}$  3058, 2926,

1732, 1617, 1190, 755. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  7.82-7.79 (m, 1H), 7.75-7.73 (m, 2H), 7.70-7.68 (m, 1H), 7.51-7.47 (m, 2H), 7.45-7.43 (m, 1H), 7.42-7.38 (m, 2H), 7.38 (s, 1H), 3.63 (s, 2H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  203.0, 141.7, 140.1, 140.0, 135.1, 134.7, 133.0, 129.5,

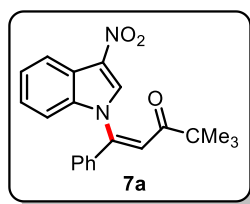
128.9 (2C), 128.8 (2C), 128.2, 126.2, 125.1, 123.0, 122.3, 38.4. **HRMS (ESI):**  $m/z$  calcd for  $C_{18}H_{13}OS$  ( $M+H$ )<sup>+</sup>: 277.0687, found: 277.0685.

**(Z)-4,4-Dimethyl-2-(3-nitro-1H-indol-1-yl)-1-phenylpent-1-en-3-one (6a):**



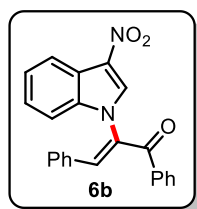
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 12 mg of **6a** (30% yield).  $R_f$  = 0.45 (EtOAc/ Hexane = 1/4). **M.P** = 164-166 °C. **IR (thin film, neat):**  $\nu_{max}/cm^{-1}$  2968, 1689, 1602, 1533, 1482, 1453, 1305, 1228, 751. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.33 (d,  $J$  = 8.0 Hz, 1H), 8.11 (s, 1H), 7.50-7.49 (m, 1H), 7.43-7.37 (m, 3H), 7.30-7.28 (m, 2H), 7.21-7.17 (m, 1H), 7.16 (s, 1H), 6.88-6.86 (m, 1H), 1.22 (s, 9H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  202.0, 145.2, 135.6, 135.0, 131.8, 131.7, 129.4 (3C), 127.2 (2C), 124.8, 124.4, 121.0, 120.9, 118.3, 112.2, 44.5, 26.2 (3C). **HRMS (ESI):**  $m/z$  calcd for  $C_{21}H_{21}N_2O_3$  ( $M+H$ )<sup>+</sup>: 349.1552, found: 349.1554.

**(Z)-4,4-Dimethyl-1-(3-nitro-1H-indol-1-yl)-1-phenylpent-1-en-3-one (7a):**



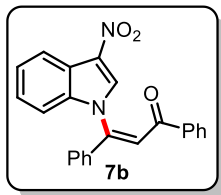
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 11 mg of **7a** (27% yield).  $R_f$  = 0.45 (EtOAc/ Hexane = 1/4). **M.P** = 135-137 °C. **IR (thin film, neat):**  $\nu_{max}/cm^{-1}$  2968, 1689, 1600, 1536, 1482, 1450, 1228, 750. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.34 (d,  $J$  = 8.0 Hz, 1H), 8.02 (s, 1H), 7.53-7.49 (m, 1H), 7.45-7.41 (m, 3H), 7.33-7.26 (m, 4H), 6.87 (s, 1H), 1.25 (s, 9H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  203.9, 147.7, 135.5, 133.4, 131.1, 130.1, 129.4 (2C), 128.9 (3C), 125.4, 125.0, 121.6, 121.3, 118.3, 112.8, 44.3, 26.4 (3C). **HRMS (ESI):**  $m/z$  calcd for  $C_{21}H_{21}N_2O_3$  ( $M+H$ )<sup>+</sup>: 349.1552, found: 349.1546.

**(Z)-2-(3-Nitro-1H-indol-1-yl)-1,3-diphenylprop-2-en-1-one (6b):**



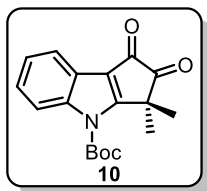
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 16 mg of **6b** (38% yield).  $R_f$  = 0.45 (EtOAc/ Hexane = 1/4). **IR (thin film, neat):**  $\nu_{max}/cm^{-1}$  2927, 1664, 1600, 1577, 1451, 1226, 751. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.24 (d,  $J$  = 8.0 Hz, 1H), 8.08 (s, 1H), 7.81-7.78 (m, 2H), 7.55-7.53 (m, 1H), 7.49-7.44 (m, 3H), 7.41-7.40 (m, 1H), 7.37 (s, 1H), 7.36-7.32 (m, 3H), 7.24-7.17 (m, 2H), 6.96 (d,  $J$  = 8.4 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  189.2, 145.6, 137.1, 135.7, 134.7, 133.5, 131.9, 131.4, 129.5 (2C), 129.3, 128.6 (2C), 128.1 (2C), 127.4 (2C), 125.0, 124.5, 120.9, 120.8, 120.3, 112.4. **HRMS (ESI):**  $m/z$  calcd for  $C_{23}H_{17}N_2O_3$  ( $M+H$ )<sup>+</sup>: 369.1239, found: 369.1249.

**(Z)-3-(3-Nitro-1*H*-indol-1-yl)-1,3-diphenylprop-2-en-1-one (7b):**



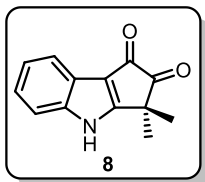
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 17 mg of **7b** (40% yield).  $R_f = 0.5$  (EtOAc/ Hexane = 1/4). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2928, 1667, 1599, 1534, 1482, 1304, 1228, 751.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.36 (d,  $J = 8.0$  Hz, 1H), 8.12(s, 1H), 7.95-7.92 (m, 2H), 7.58-7.54 (m, 1H), 7.46-7.43 (m, 3H), 7.37-7.33 (m, 4H), 7.32-7.28 (m, 3H), 7.13 (s, 1H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  190.6, 147.5, 137.2, 135.6, 133.6, 133.3, 131.3, 130.1, 129.6 (2C), 129.1 (2C), 128.79 (3C), 128.76 (2C), 125.5, 125.1, 121.6, 121.3, 120.7, 112.9. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_3$  ( $\text{M}+\text{H}^+$ ): 369.1239, found: 369.1237.

***tert*-Butyl 3,3-dimethyl-1,2-dioxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (10):**



This compound was isolated as pale-yellow solid. Following the general procedure-5, 30 mg of **3i** afforded 10 mg of **10** (41% yield).  $R_f = 0.5$  (EtOAc/ Hexane = 1/4). **M.P** = 295-297 °C. **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2977, 1746, 1706, 1423, 1360, 1142, 765.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.10 (d,  $J = 8.3$  Hz, 1H), 8.07-8.05 (m, 1H), 7.47 (dt,  $J = 8.5$  and 1.0 Hz, 1H), 7.44-7.40 (m, 1H), 1.77 (s, 9H), 1.63 (s, 6H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  205.2, 177.9, 170.7, 148.1, 138.7, 127.2, 126.7, 125.4, 122.0, 122.01, 116.4, 87.3, 45.8, 28.1 (3C), 22.2 (2C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{18}\text{H}_{19}\text{NNaO}_4$  ( $\text{M}+\text{Na}^+$ ): 336.1212, found: 336.1215.

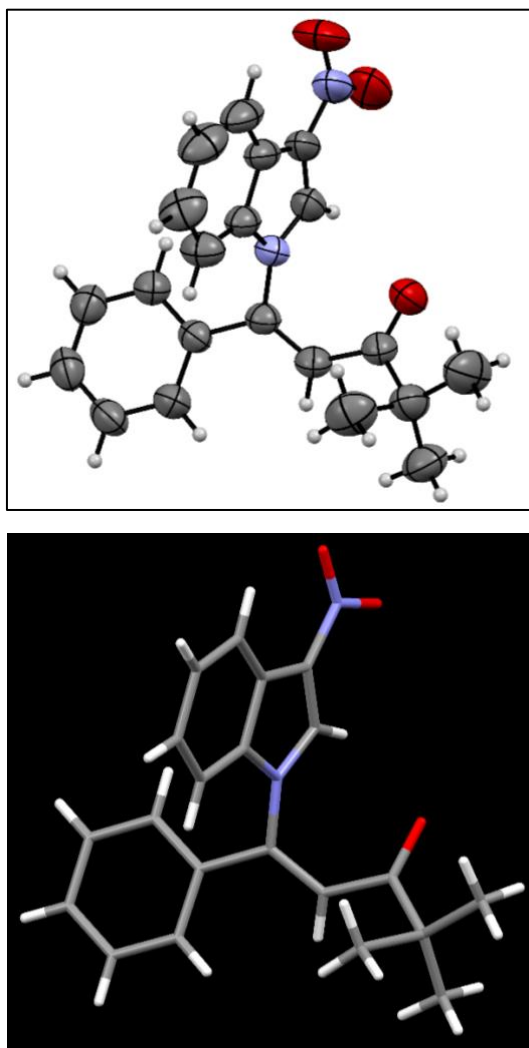
**3,3-Dimethyl-3,4-dihydrocyclopenta[*b*]indole-1,2-dione (8):**



This compound was isolated as pale-yellow solid. Following the general procedure-5, 50 mg of **10** afforded 31 mg of **8** (91% yield).  $R_f = 0.3$  (EtOAc/ Hexane = 2/3). **M.P** = 288-290 °C. **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  3393, 1735, 1661, 1023, 996, 761.  **$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):**  $\delta$  12.94 (s, 1H), 7.83 (d,  $J = 7.8$  Hz, 1H), 7.60 (d,  $J = 8.0$  Hz, 1H), 7.39 (t,  $J = 7.2$  Hz, 1H), 7.33-7.29 (m, 1H), 1.42 (s, 6H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):**  $\delta$  206.9, 175.6, 171.3, 140.3, 125.7, 123.8, 121.9, 121.5, 121.4, 114.0, 42.0, 23.3 (2C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{NNaO}_2$  ( $\text{M}+\text{Na}^+$ ): 236.0687, found: 236.0693.

**Crystal structure of 7a (CCDC- 2214774):** The structure of **7a** was confirmed by single-crystal X-ray diffraction analysis.

**Crystallization procedure of 7a:** In a 5 mL glass vial, **7a** was dissolved in EtOAc (2.5 mL) and hexane (0.5 mL) and the solution were kept at room temperature for slow evaporation. After 4-6 days, suitable single crystals were obtained.



ORTEP diagram of **7a** with 50% ellipsoidal probability.

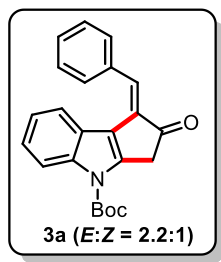
**Crystal Data** for  $C_{21}H_{20}N_2O_3$  ( $M = 348.39$  g/mol): triclinic, space group P-1 (no. 2),  $a = 9.9977(7)$  Å,  $b = 10.0721(7)$  Å,  $c = 10.6301(8)$  Å,  $\alpha = 73.343(7)^\circ$ ,  $\beta = 82.375(6)^\circ$ ,  $\gamma = 63.636(7)^\circ$ ,  $V = 918.83(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 293.0(10)$  K,  $\mu(\text{Mo K}\alpha) = 0.085$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.259$  g/cm<sup>3</sup>, 7049 reflections measured ( $5.32^\circ \leq 2\theta \leq 65.48^\circ$ ), 5725 unique ( $R_{\text{int}} = 0.0197$ ,  $R_{\text{sigma}} = 0.0459$ ) which were used in all calculations. The final  $R_1$  was 0.0648 ( $>2\sigma(I)$ ) and  $wR_2$  was 0.2074

Table 2S: Crystal data and structure refinement for 7a.

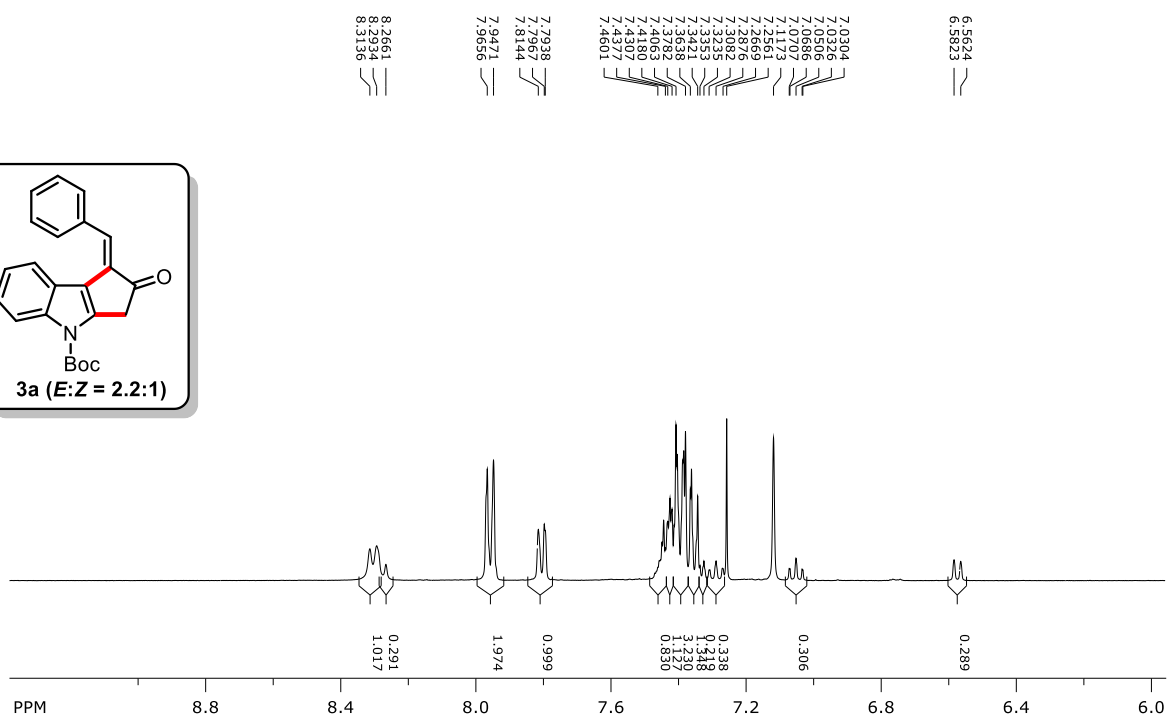
Identification code	7a
Empirical formula	C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>
Formula weight	348.39
Temperature/K	293.0(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.9977(7)
b/Å	10.0721(7)
c/Å	10.6301(8)
$\alpha$ /°	73.343(7)
$\beta$ /°	82.375(6)
$\gamma$ /°	63.636(7)
Volume/Å <sup>3</sup>	918.83(11)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.259
$\mu/\text{mm}^{-1}$	0.085
F(000)	368.0
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.2
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	5.32 to 65.48
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 13, -16 ≤ l ≤ 15
Reflections collected	7049
Independent reflections	5725 [R <sub>int</sub> = 0.0197, R <sub>sigma</sub> = 0.0459]
Data/restraints/parameters	5725/36/268
Goodness-of-fit on F <sup>2</sup>	1.024
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0648, wR <sub>2</sub> = 0.1642
Final R indexes [all data]	R <sub>1</sub> = 0.1100, wR <sub>2</sub> = 0.2074
Largest diff. peak/hole / e Å <sup>-3</sup>	0.27/-0.18



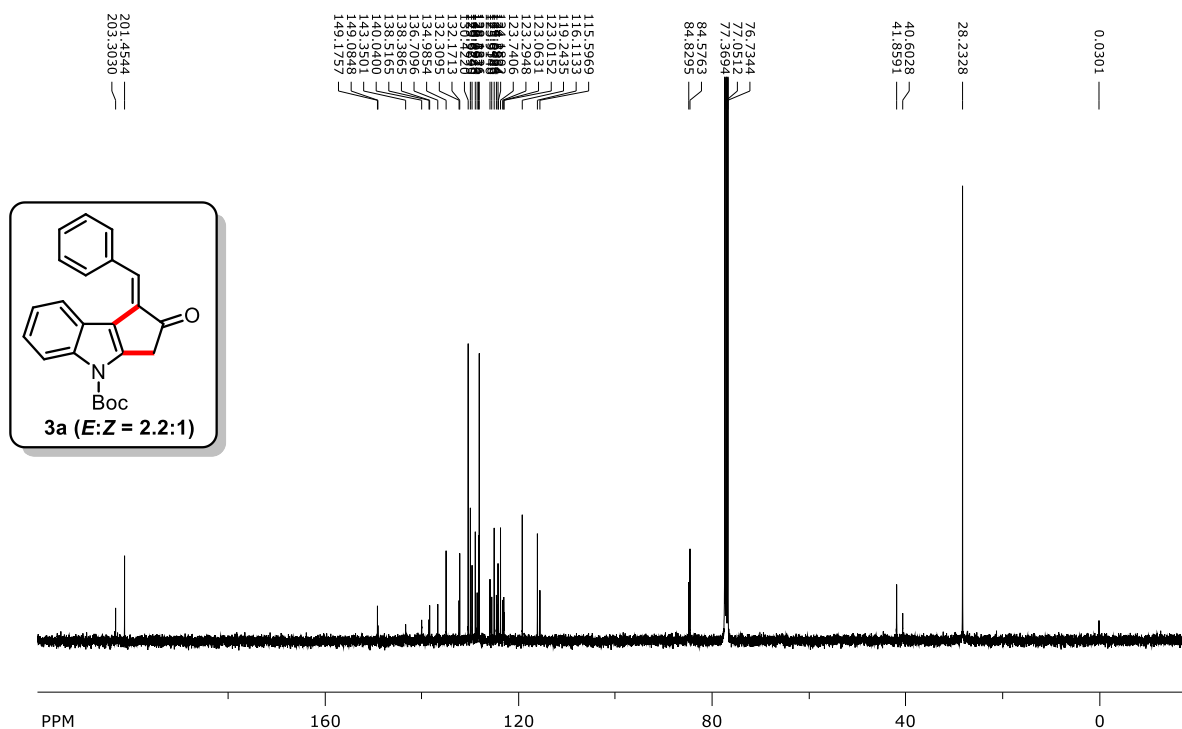
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



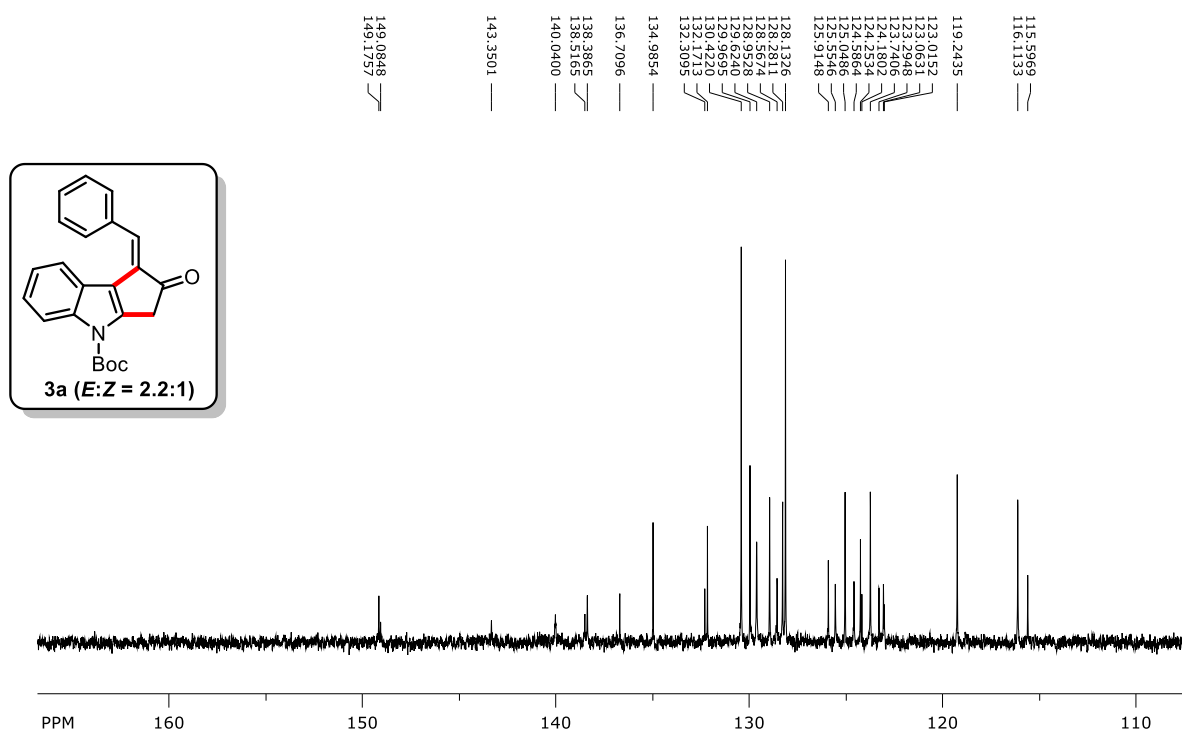
**3a** (*E:Z* = 2.2:1)



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): expansion of 110-160 ppm region**



Chemical structure of **3b** (*E:Z* = 2.5:1) is shown in the inset. The structure is a 1-Boc-2-(4-phenylbut-3-en-1-yl)indole derivative, with the indole ring highlighted in red.

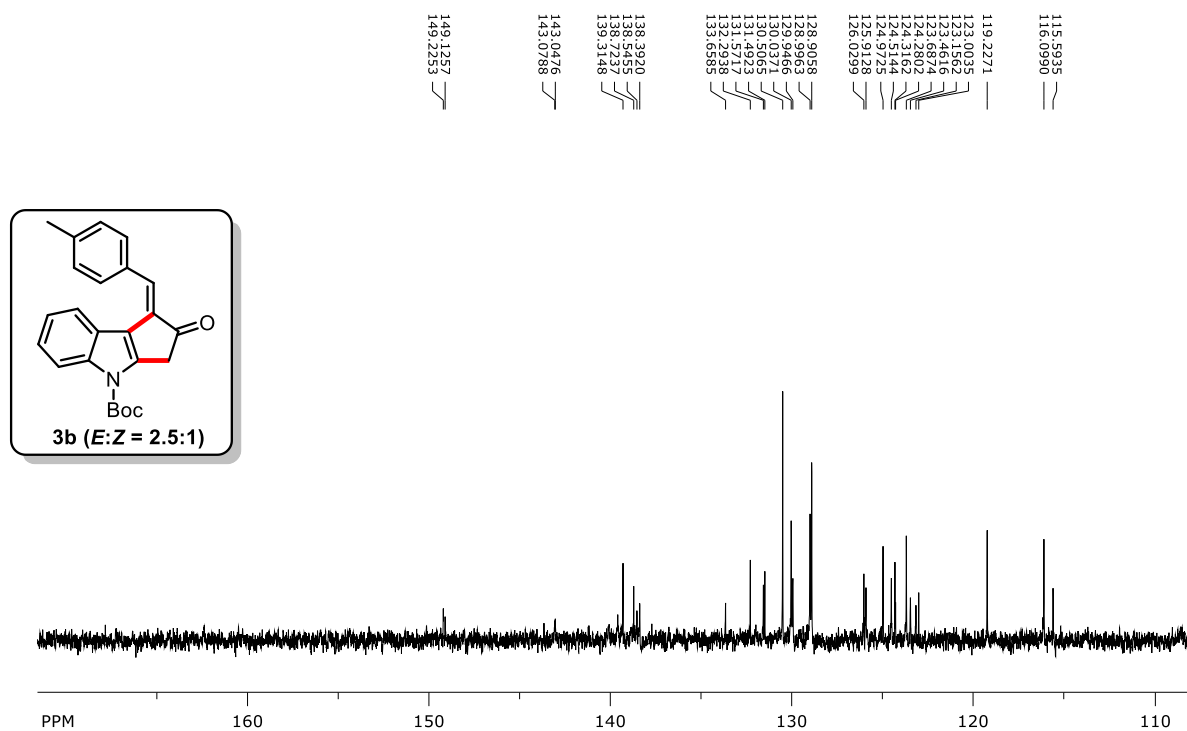
The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) shows the following peaks (ppm) and integration values:

Peak (ppm)	Integration
0.000	0.573
1.5817, 1.6763, 1.6872	1.176
2.3950, 2.4411	1.176
3.7563, 3.8090	4.053
7.0911, 7.1113, 7.1133, 7.2274, 7.2467, 7.2596, 7.3183, 7.3437, 7.3573, 7.3978, 7.4054, 7.8221, 7.8815, 7.9019, 8.2600, 8.3126	1.097
7.6239, 6.7438, 7.0911, 7.1113, 7.1133, 7.2274, 7.2467, 7.2596, 7.3183, 7.3437, 7.3573, 7.3978, 7.4054, 7.8221, 7.8815, 7.9019, 8.2600, 8.3126	1.538
7.6239, 6.7438, 7.0911, 7.1113, 7.1133, 7.2274, 7.2467, 7.2596, 7.3183, 7.3437, 7.3573, 7.3978, 7.4054, 7.8221, 7.8815, 7.9019, 8.2600, 8.3126	1.198
7.6239, 6.7438, 7.0911, 7.1113, 7.1133, 7.2274, 7.2467, 7.2596, 7.3183, 7.3437, 7.3573, 7.3978, 7.4054, 7.8221, 7.8815, 7.9019, 8.2600, 8.3126	1.345
7.6239, 6.7438, 7.0911, 7.1113, 7.1133, 7.2274, 7.2467, 7.2596, 7.3183, 7.3437, 7.3573, 7.3978, 7.4054, 7.8221, 7.8815, 7.9019, 8.2600, 8.3126	1.298
7.6239, 6.7438, 7.0911, 7.1113, 7.1133, 7.2274, 7.2467, 7.2596, 7.3183, 7.3437, 7.3573, 7.3978, 7.4054, 7.8221, 7.8815, 7.9019, 8.2600, 8.3126	9.343

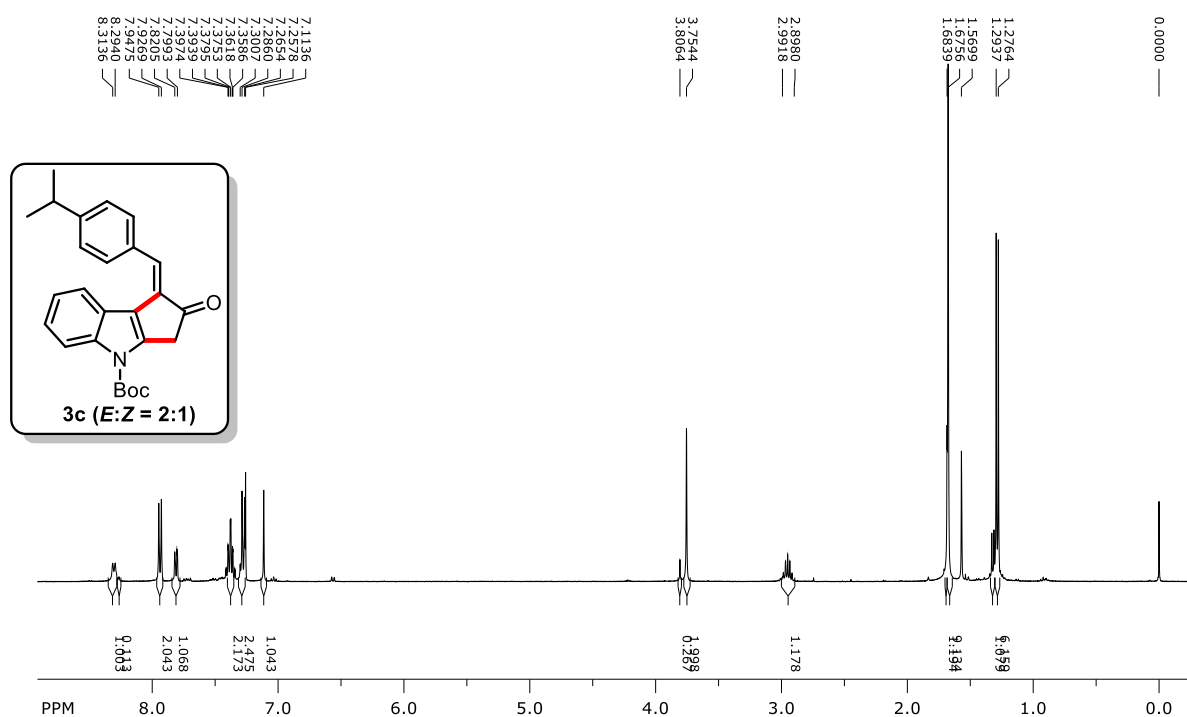
**3b** (*E:Z* = 2.5:1)

Chemical structure of **3b** (*E:Z* = 2.5:1) is shown above the spectrum.

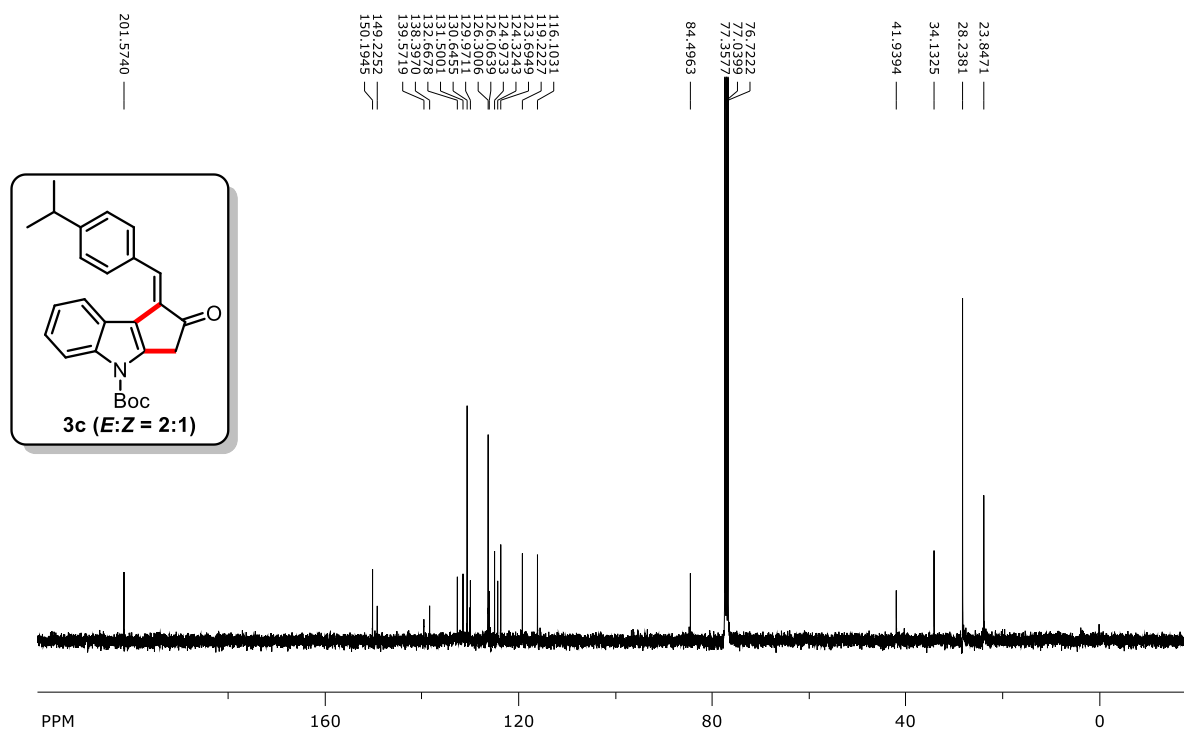
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): expansion of 110-150 ppm region**



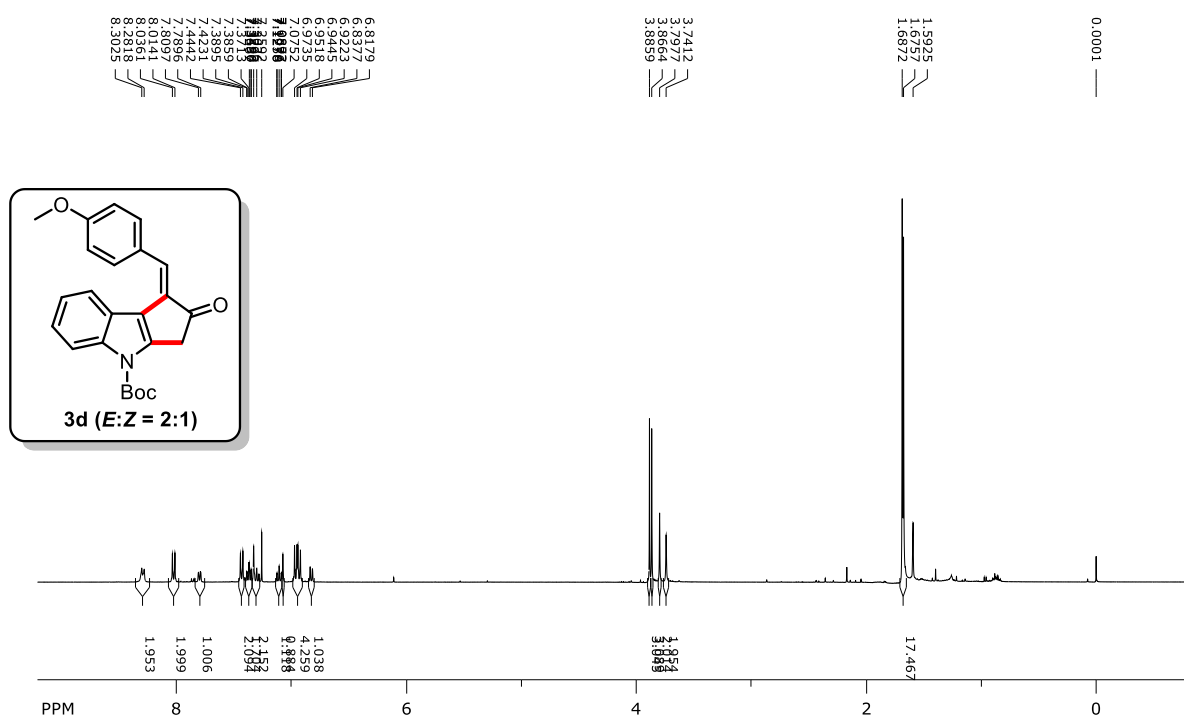
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



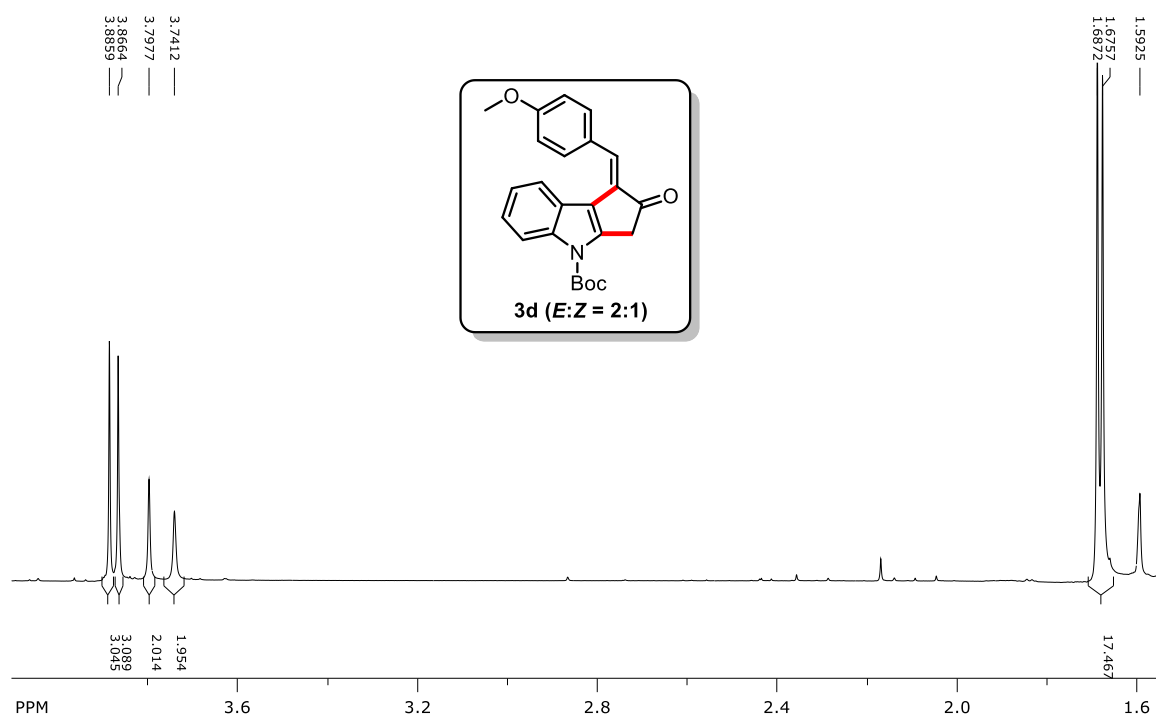
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



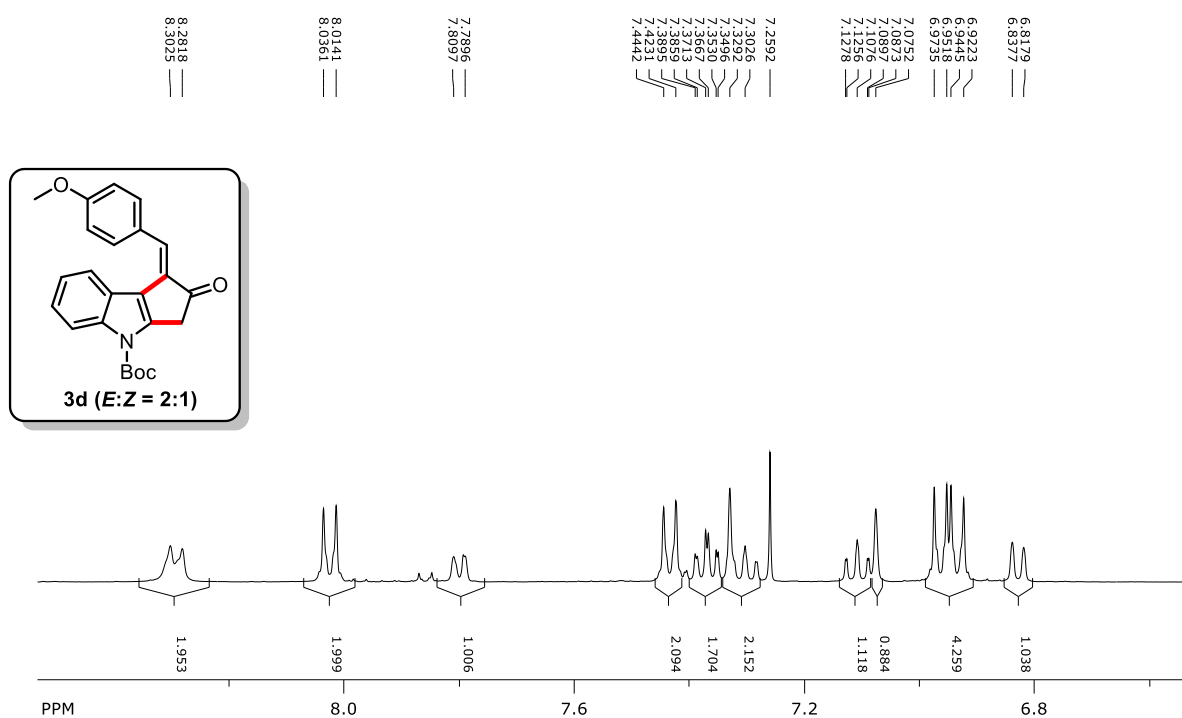
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



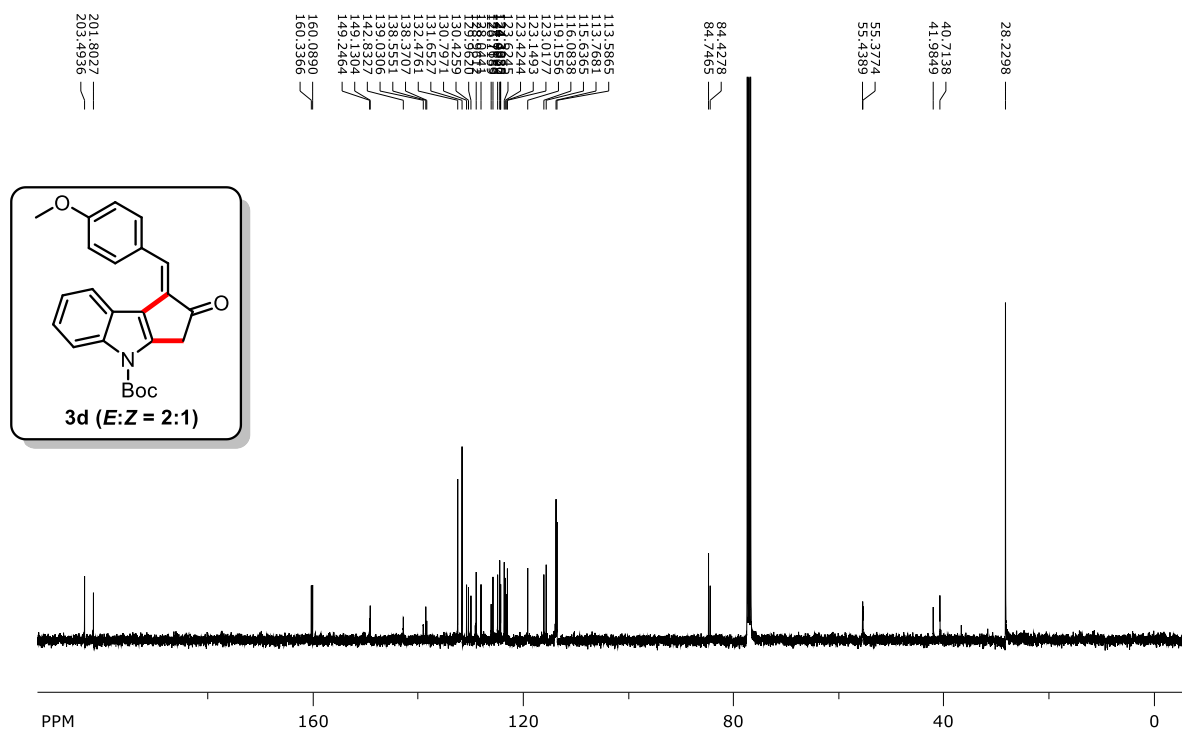
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): expansion of 1.5-4 ppm region**



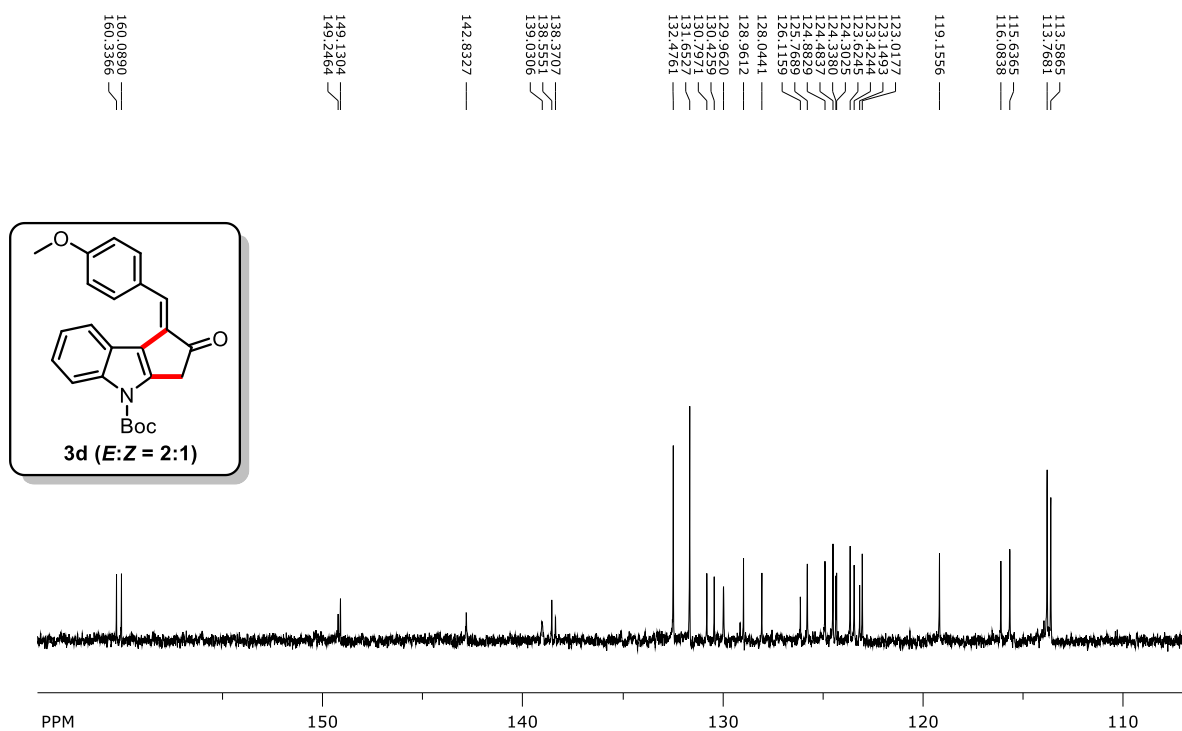
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): expansion of 6.5-8.5 ppm region**



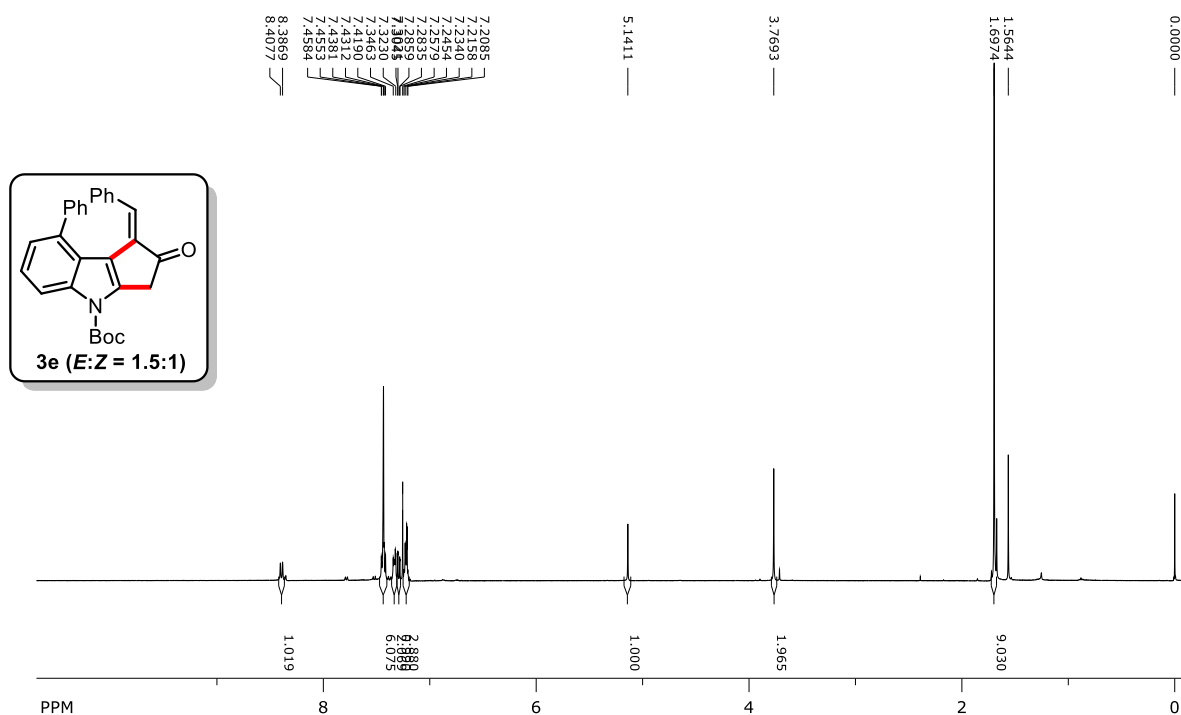
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



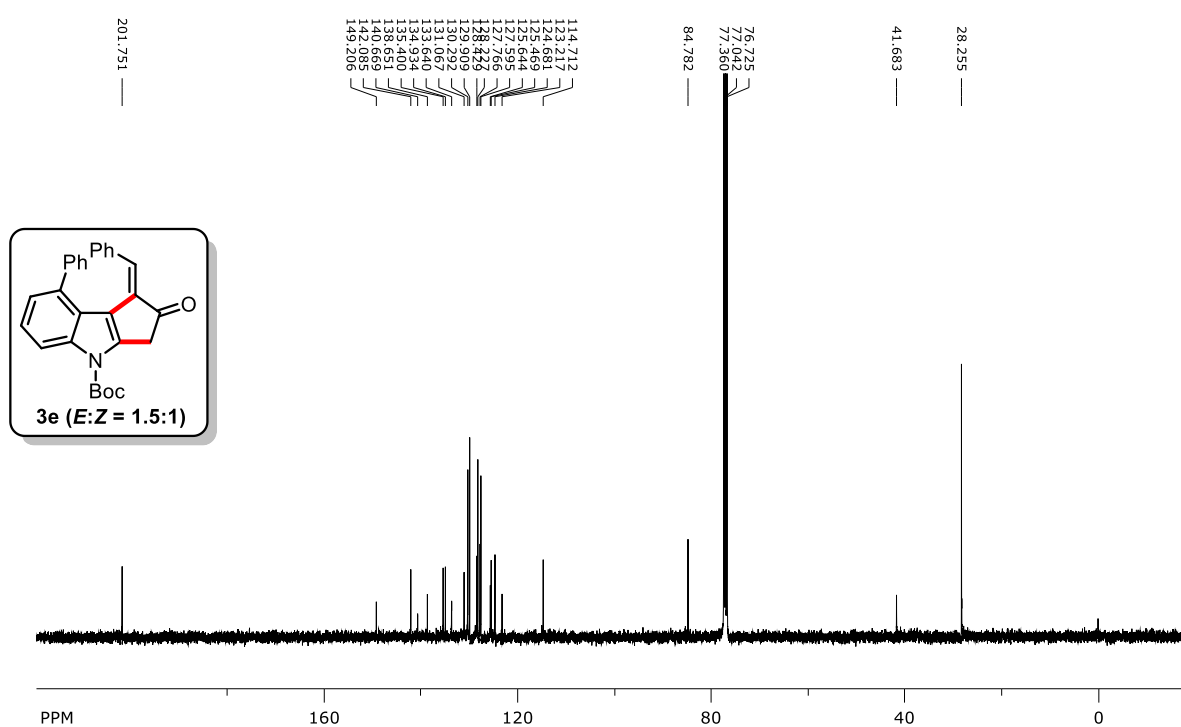
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): expansion of 110-170 ppm region**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**

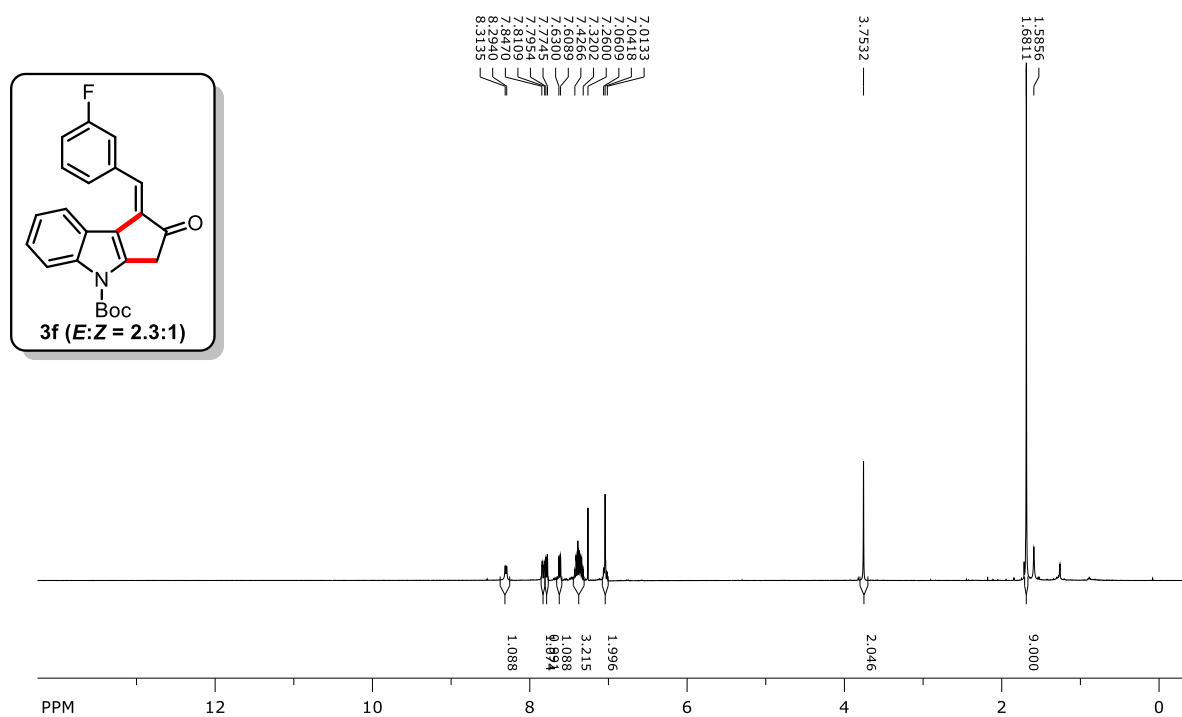


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**

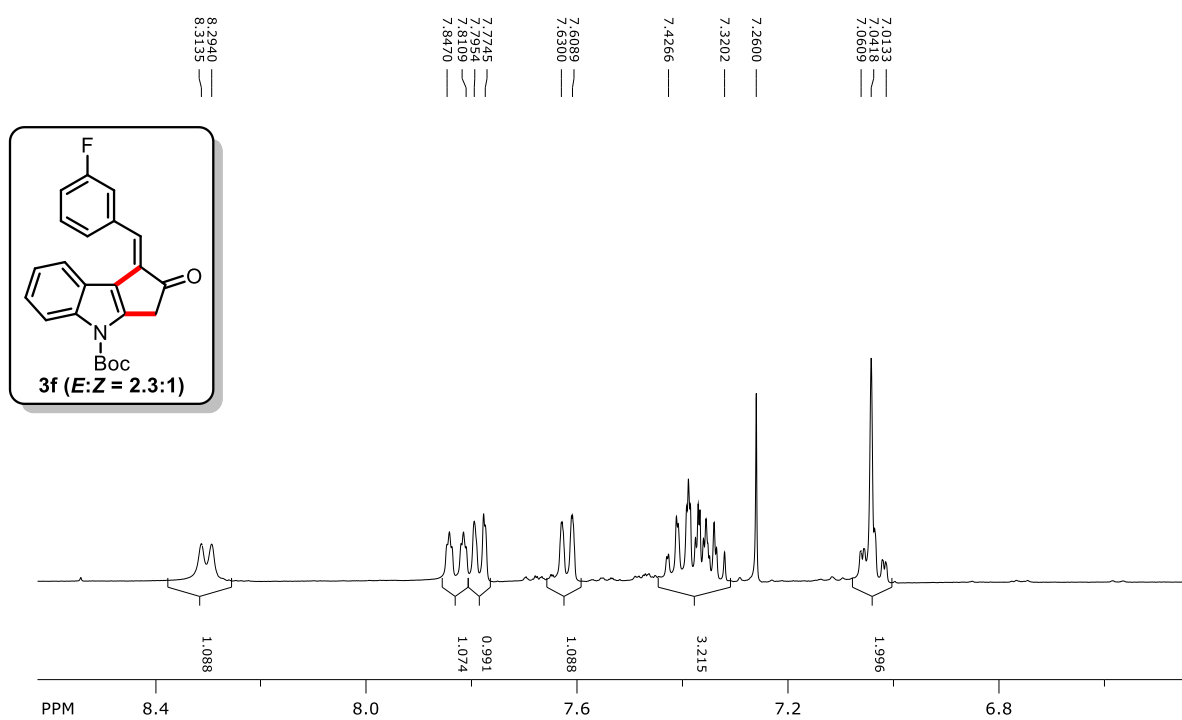




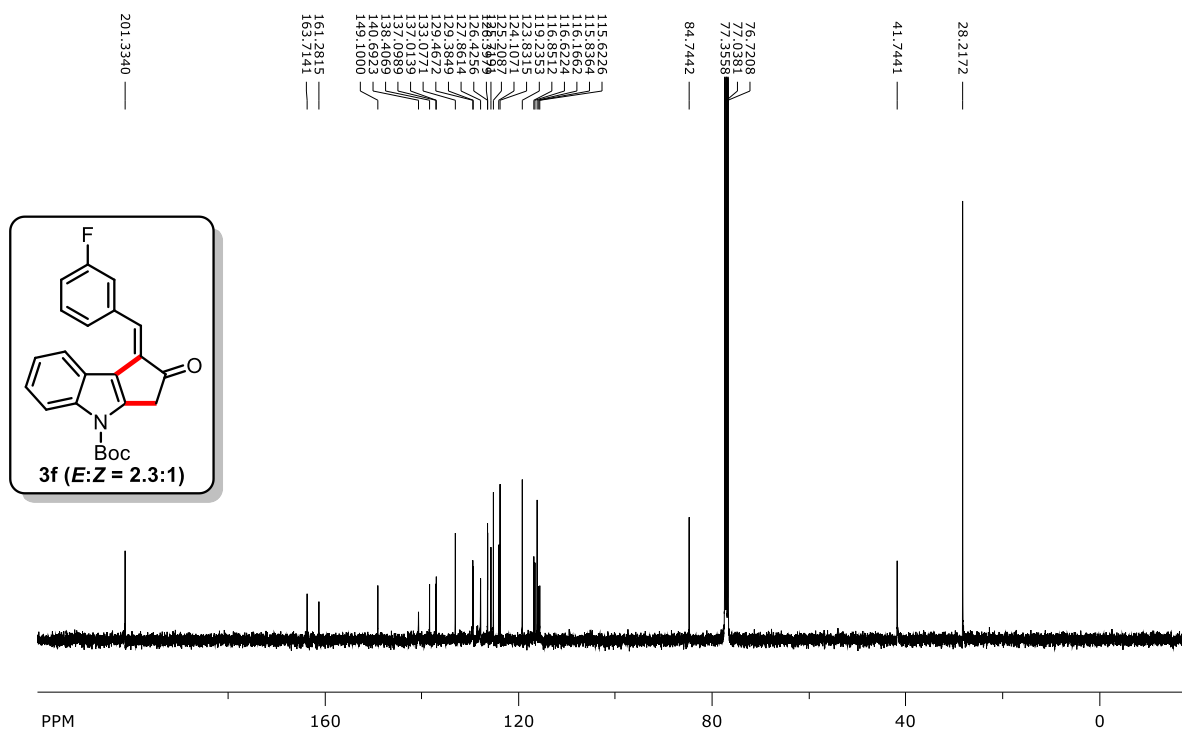
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



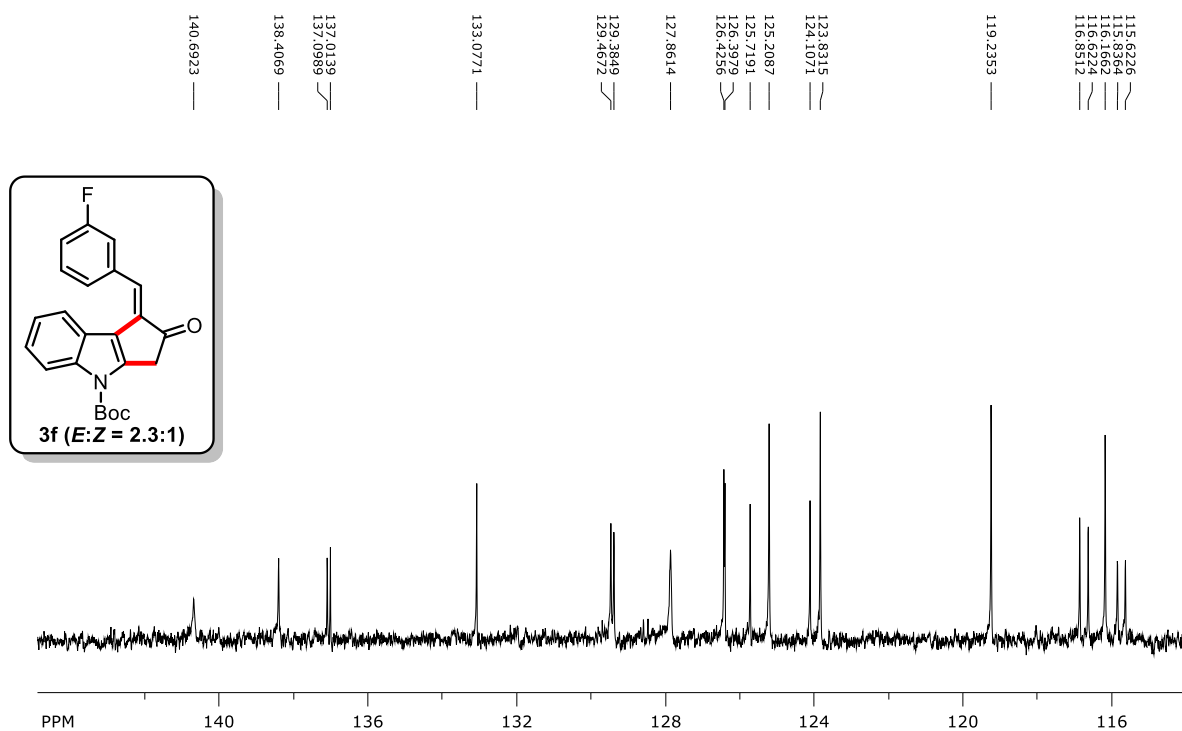
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): expansion of 6.5-8.5 ppm region**



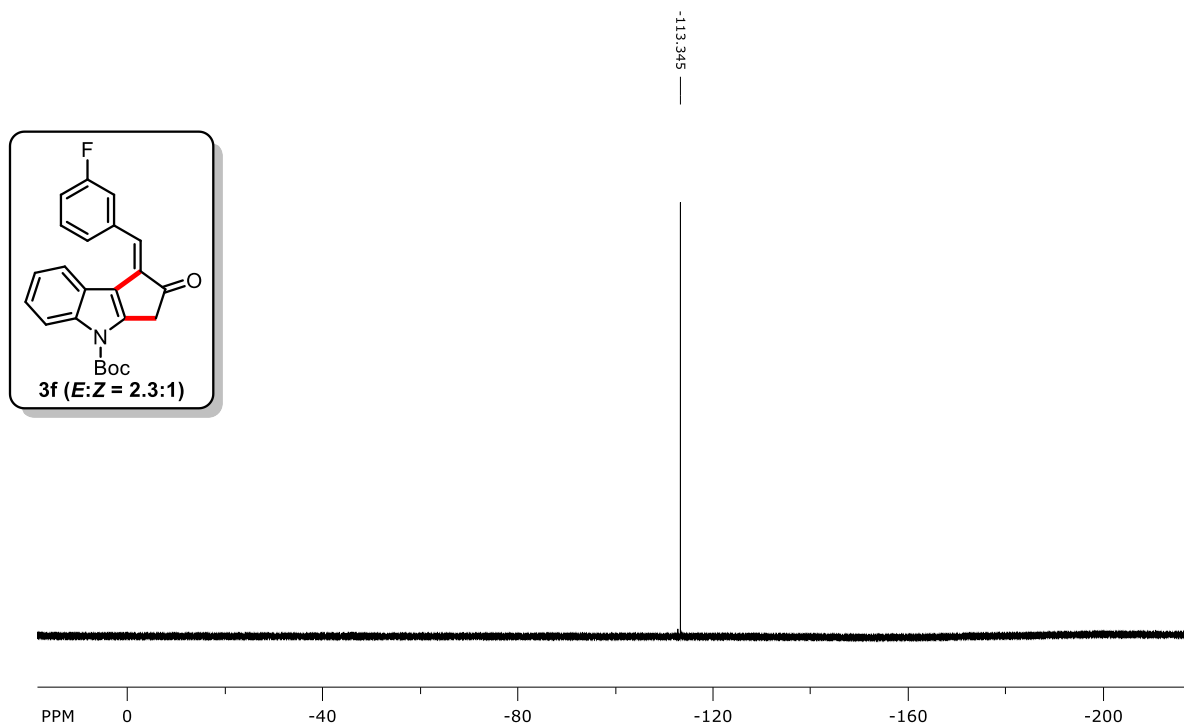
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



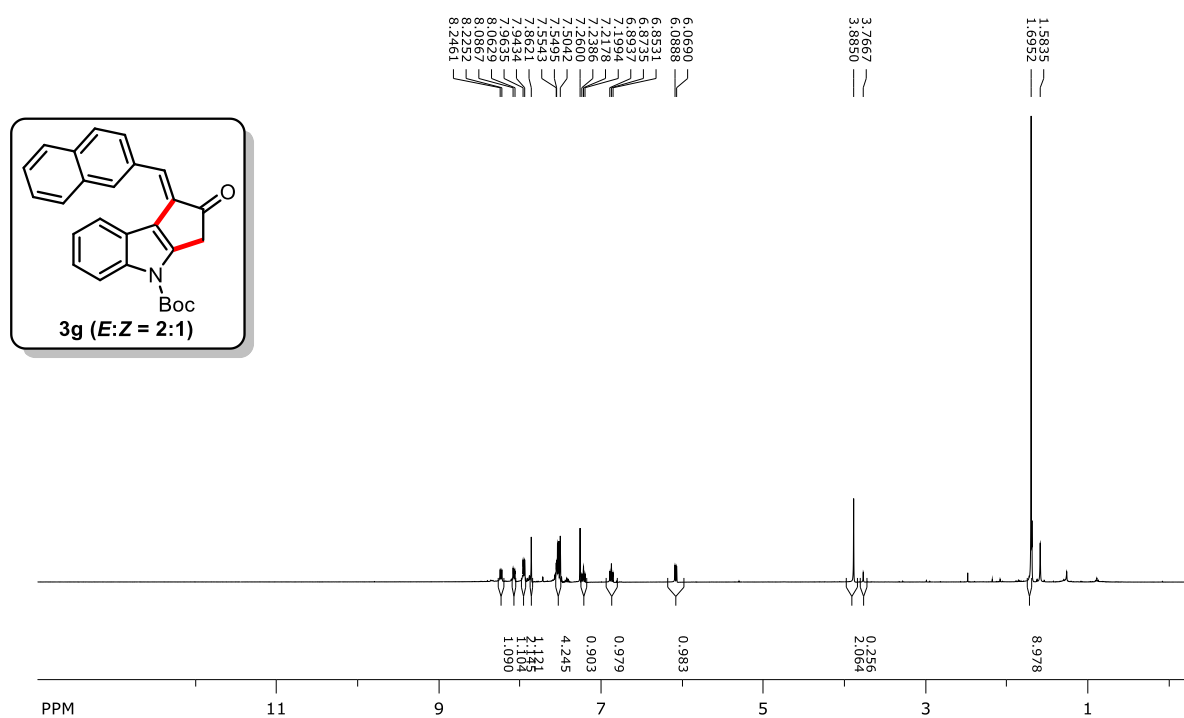
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): expansion of 110-150 ppm region**



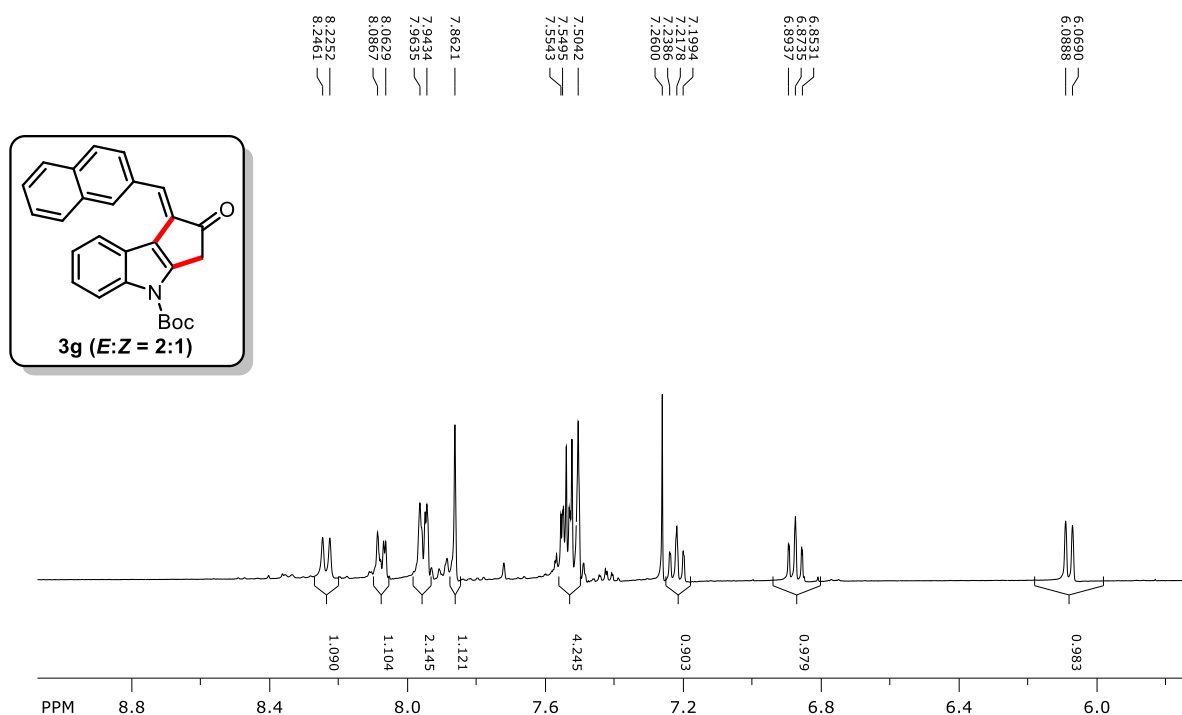
**$^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ ):**



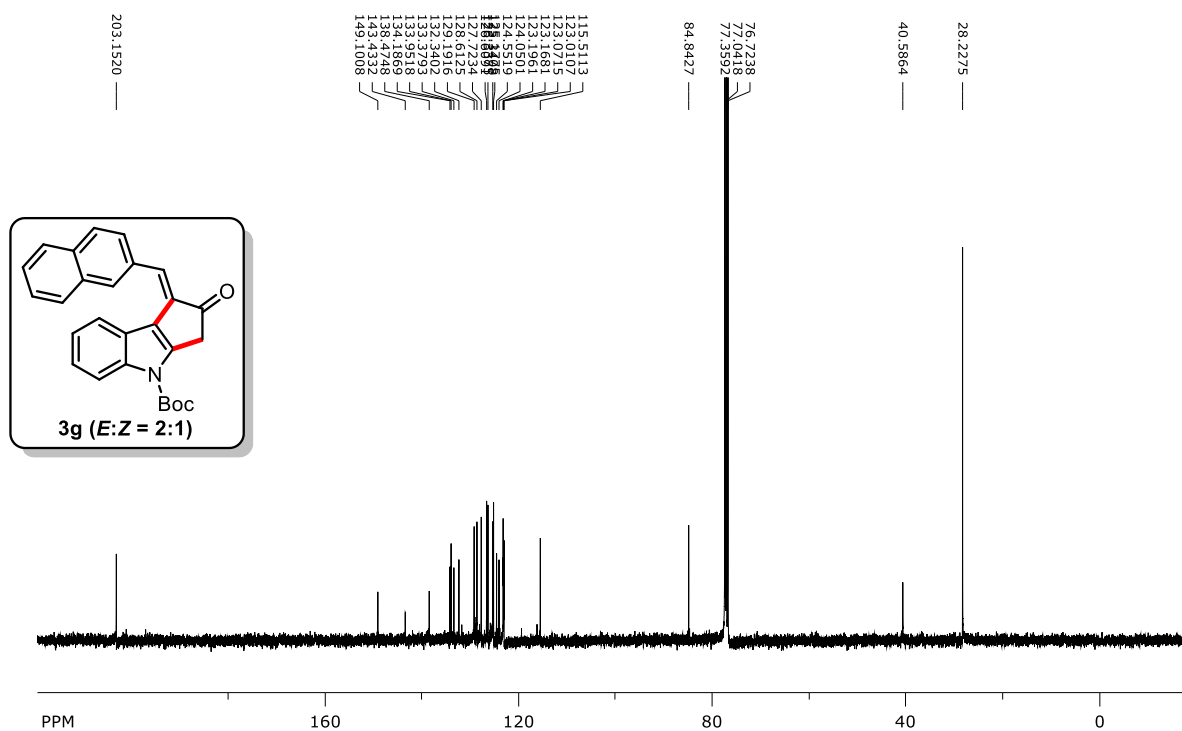
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



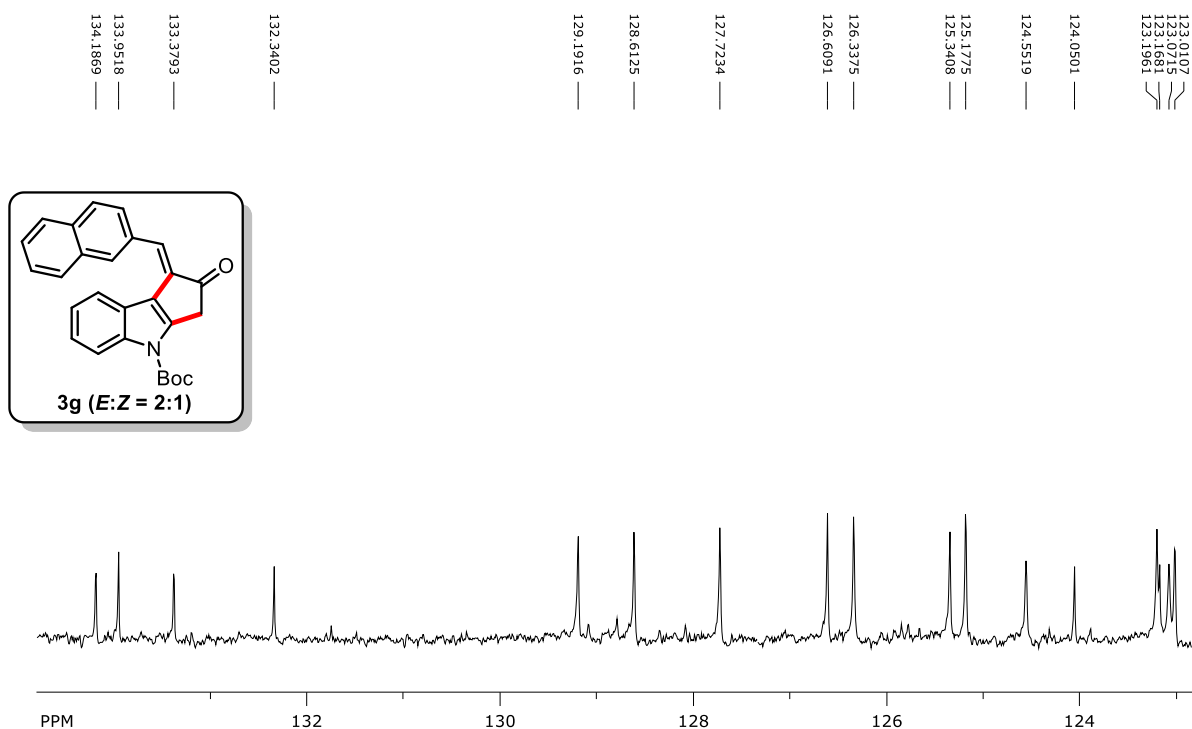
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 6.0-9.0 ppm region**



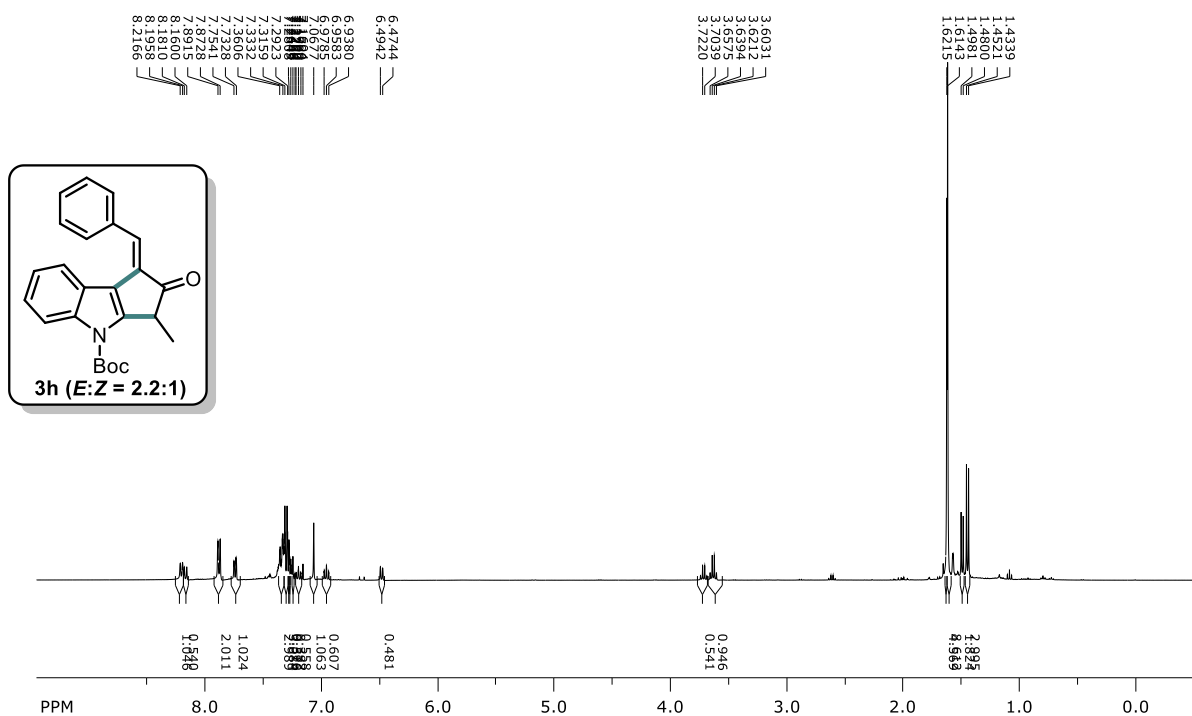
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



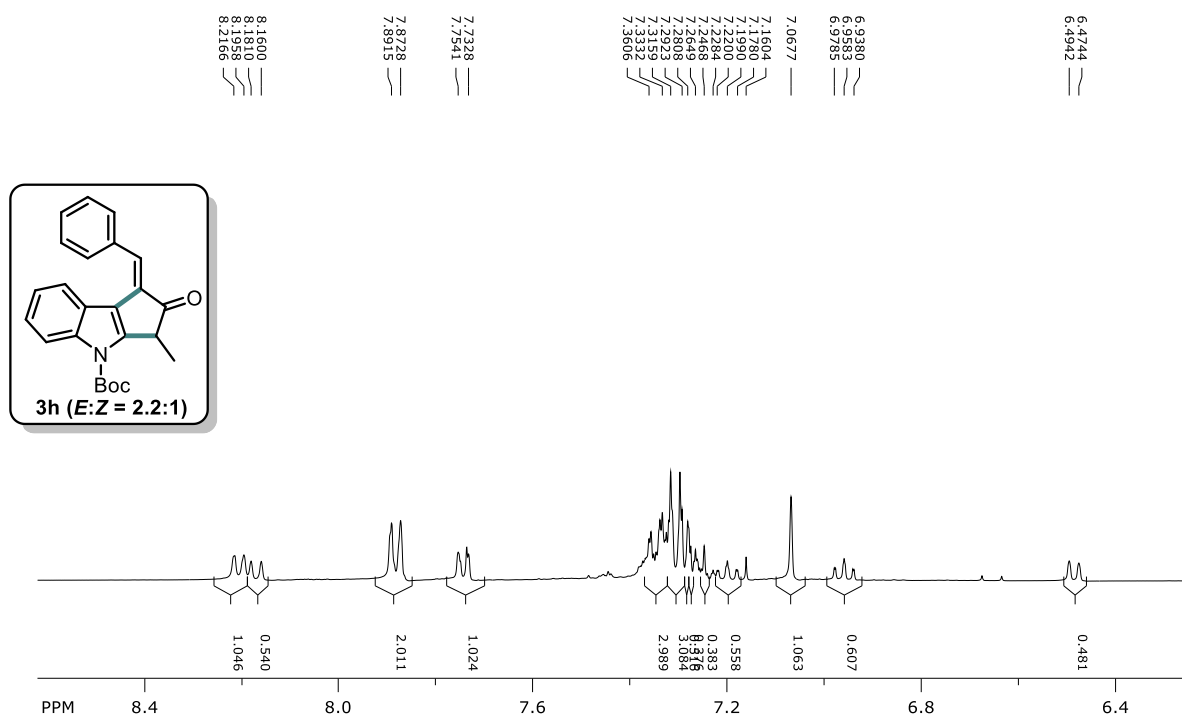
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): expansion of 122-136 ppm region**



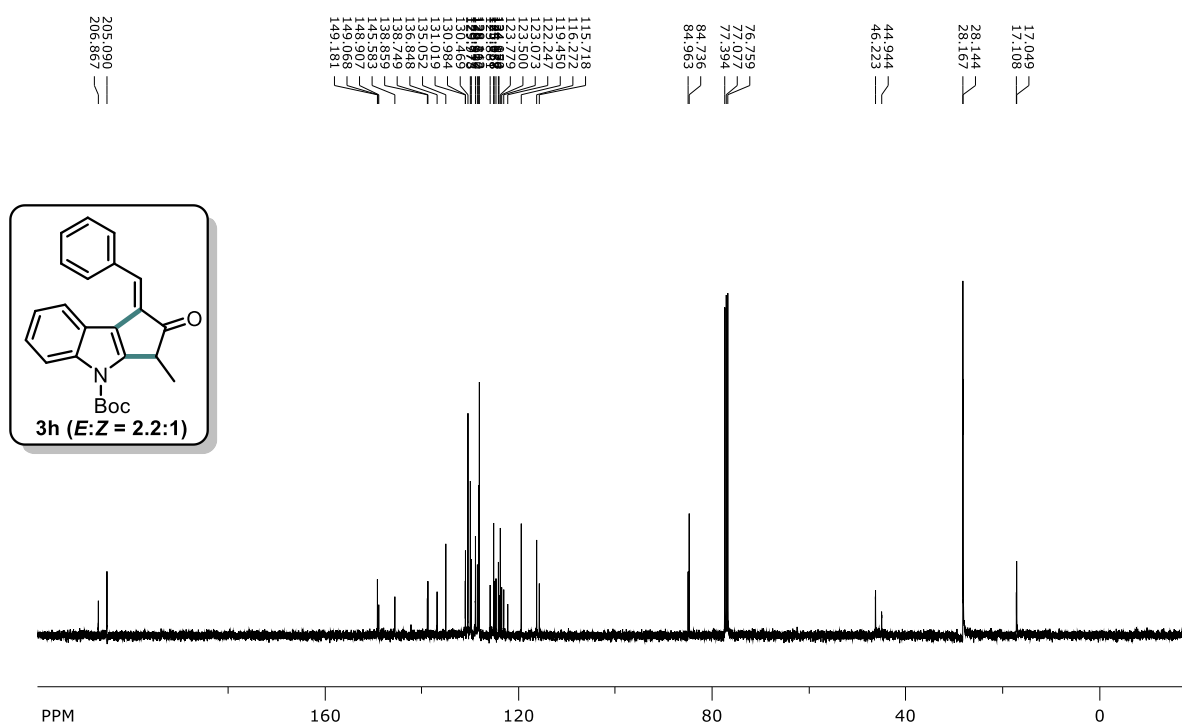
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



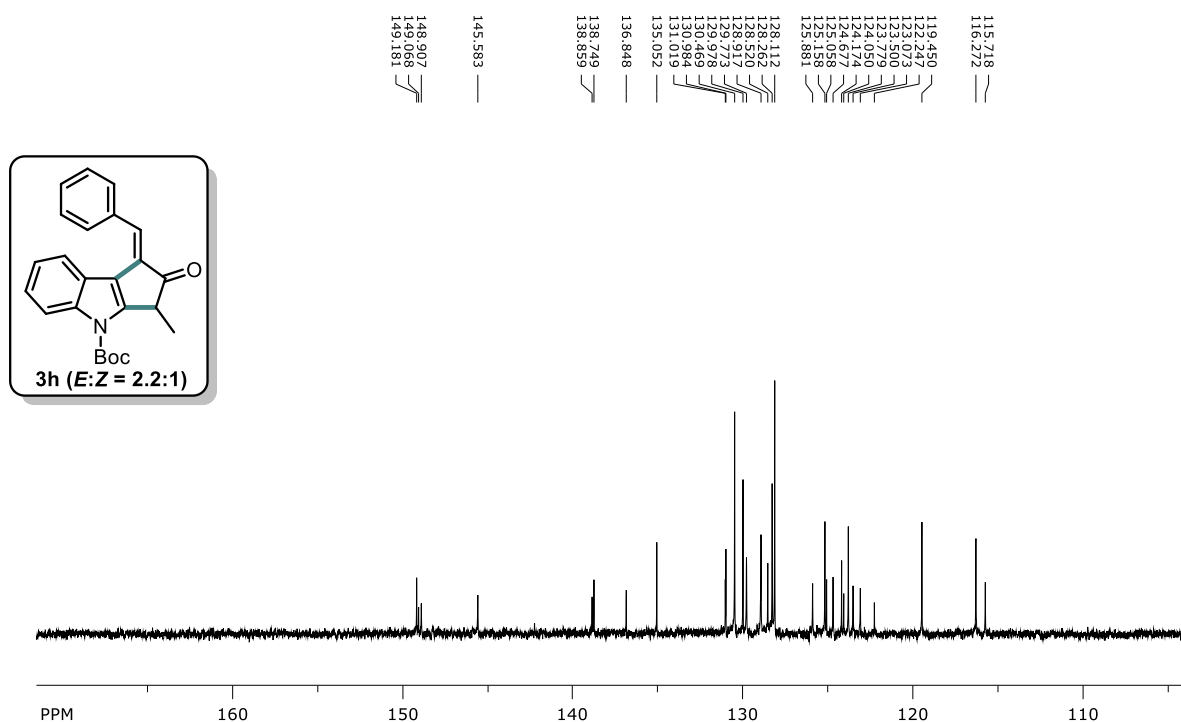
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 6.5-8.5 ppm region**



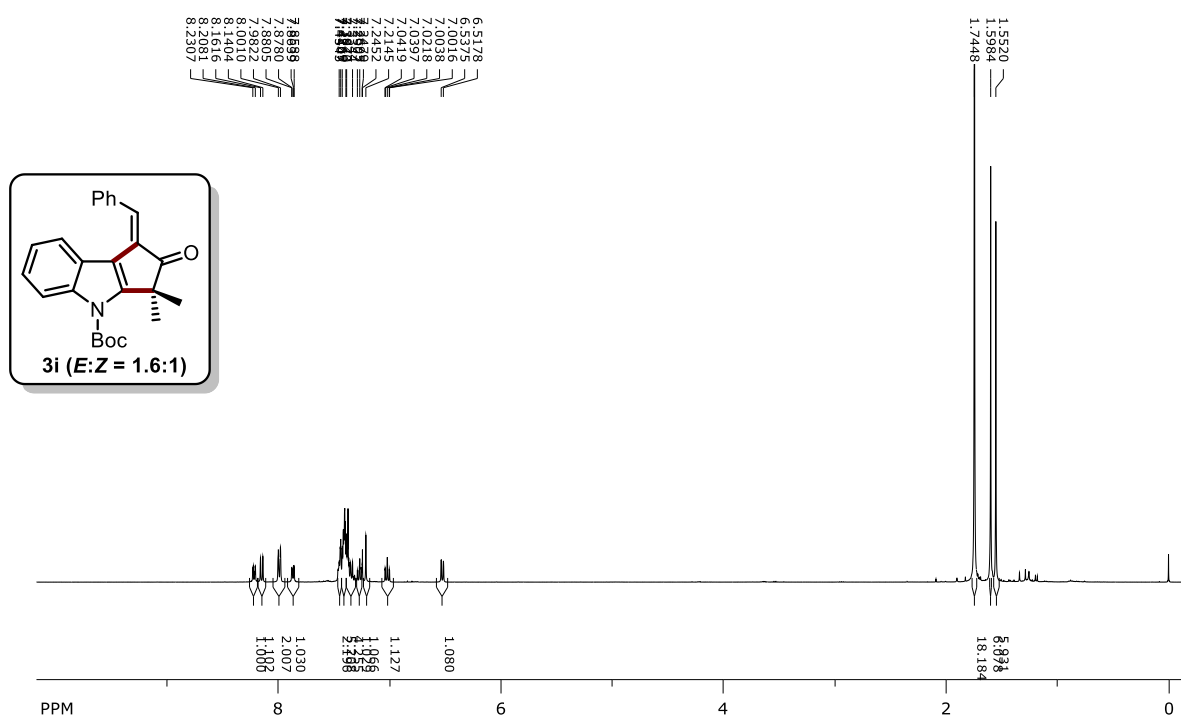
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



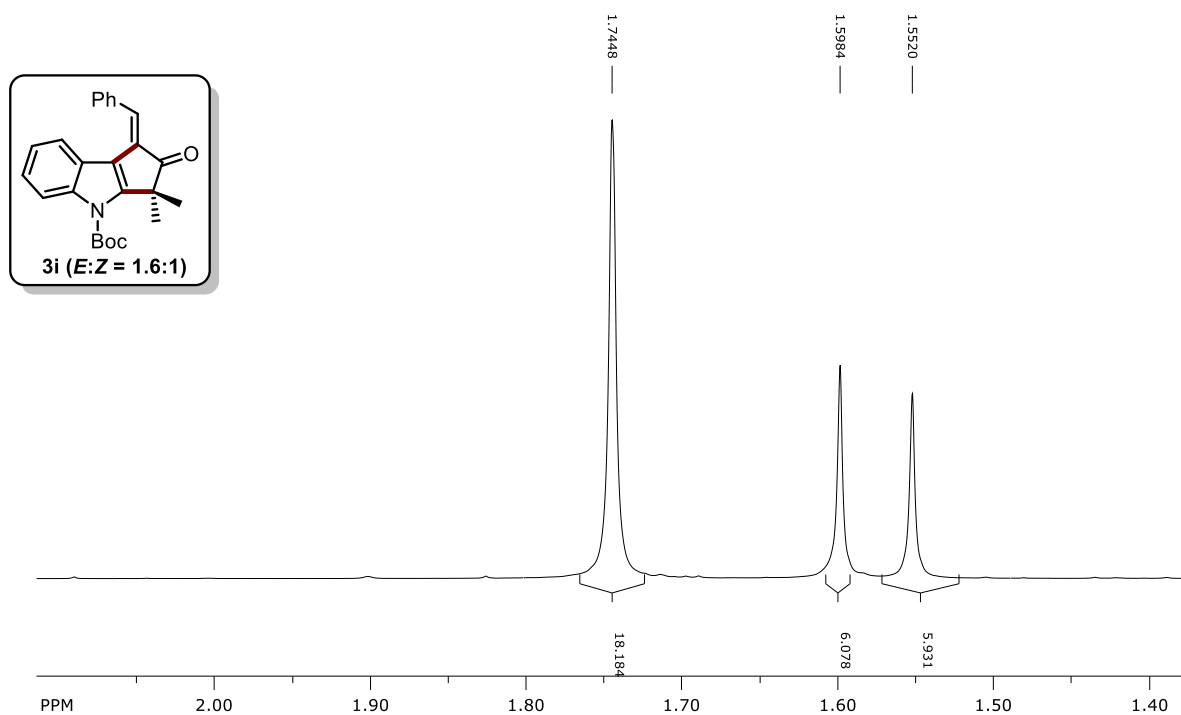
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): expansion of 110-160 ppm region**



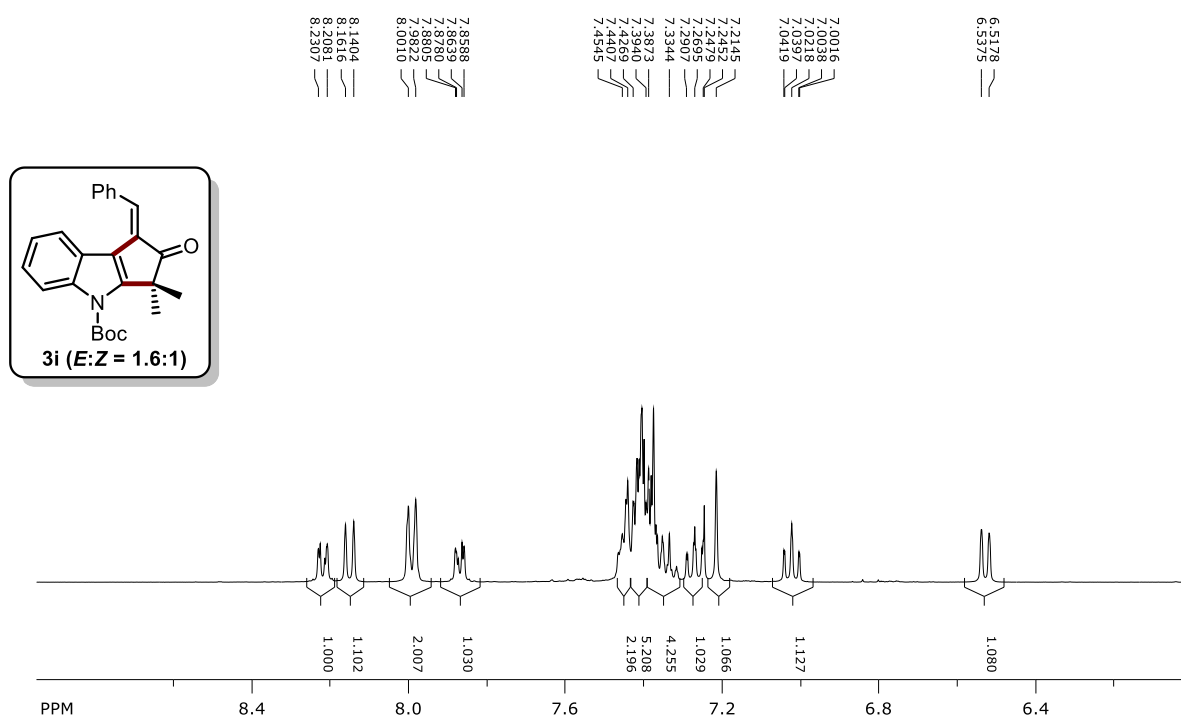
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 1.5-2.0 ppm region**

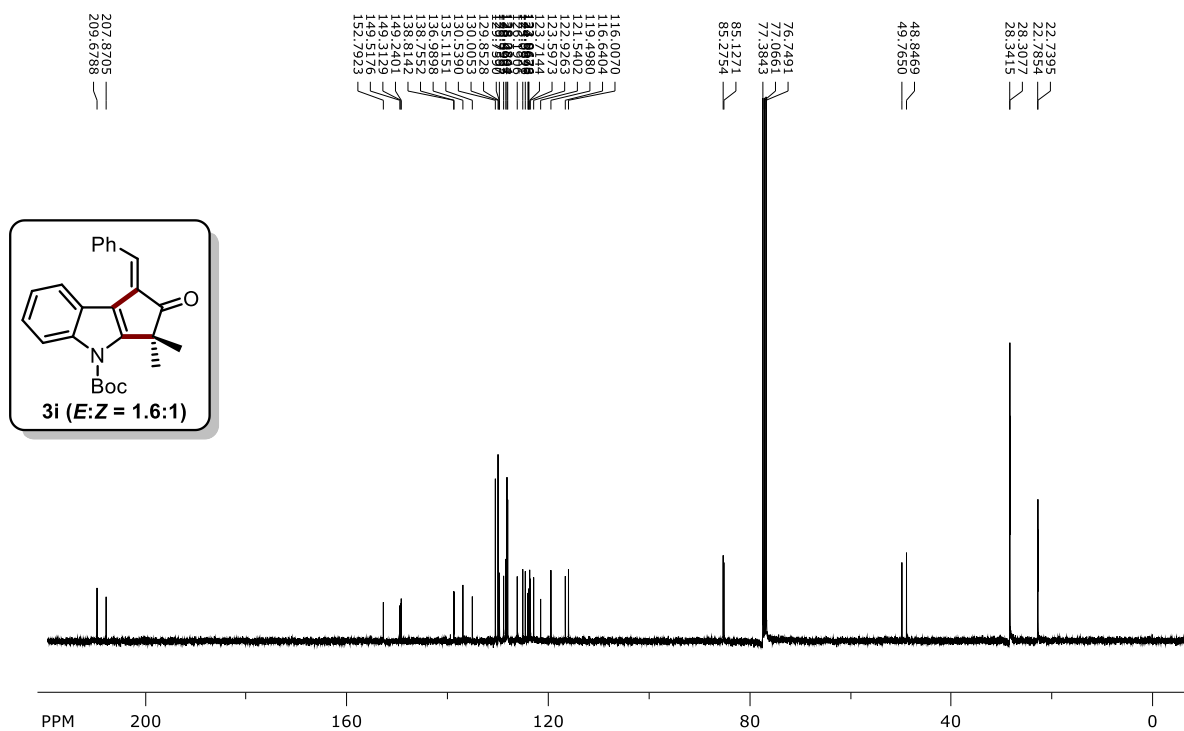


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 6.0-9.0 ppm region**

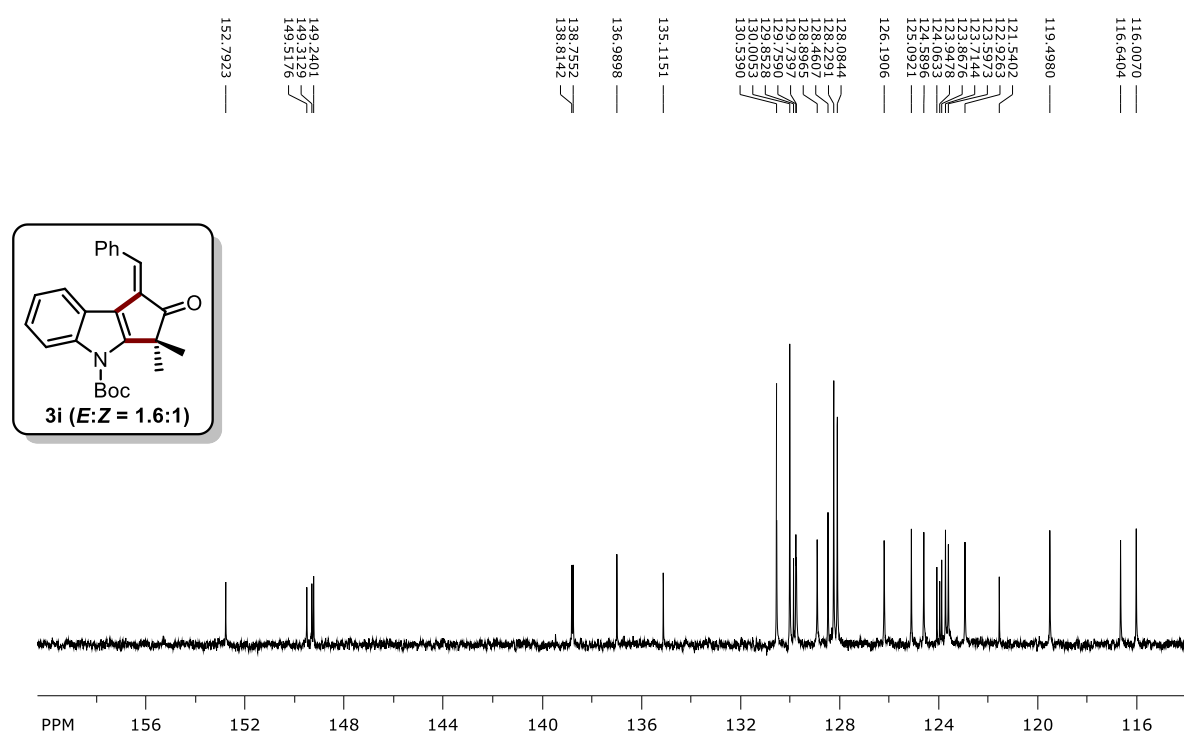




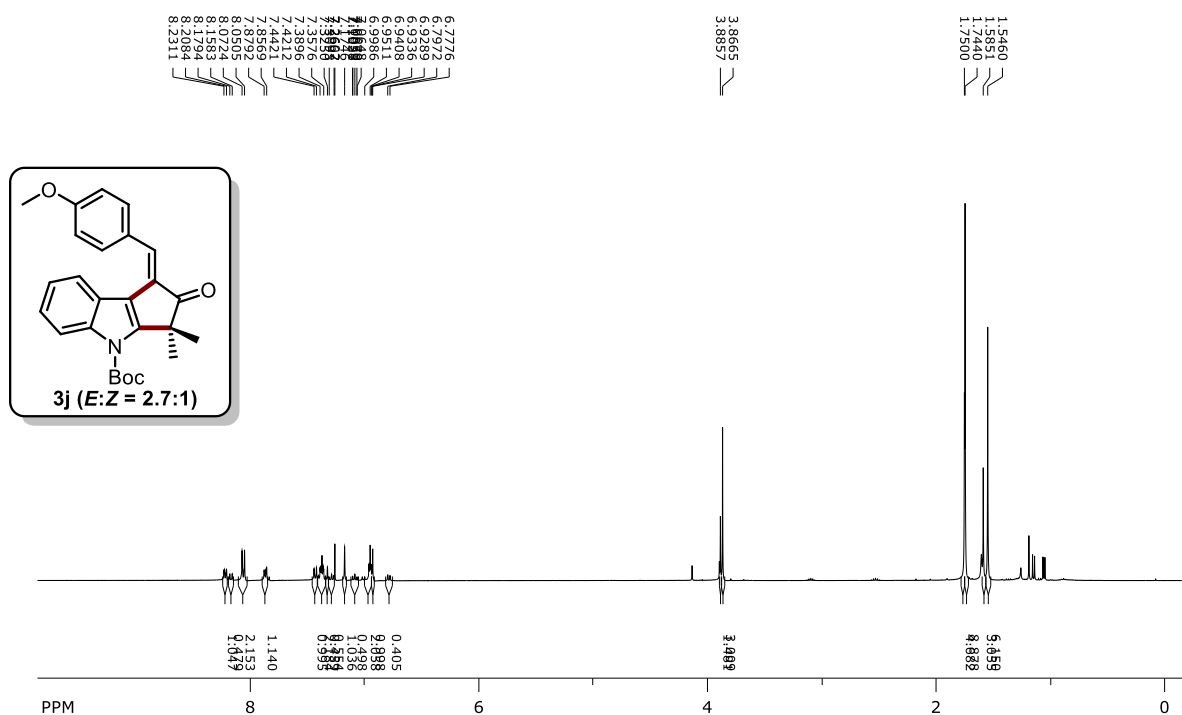
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



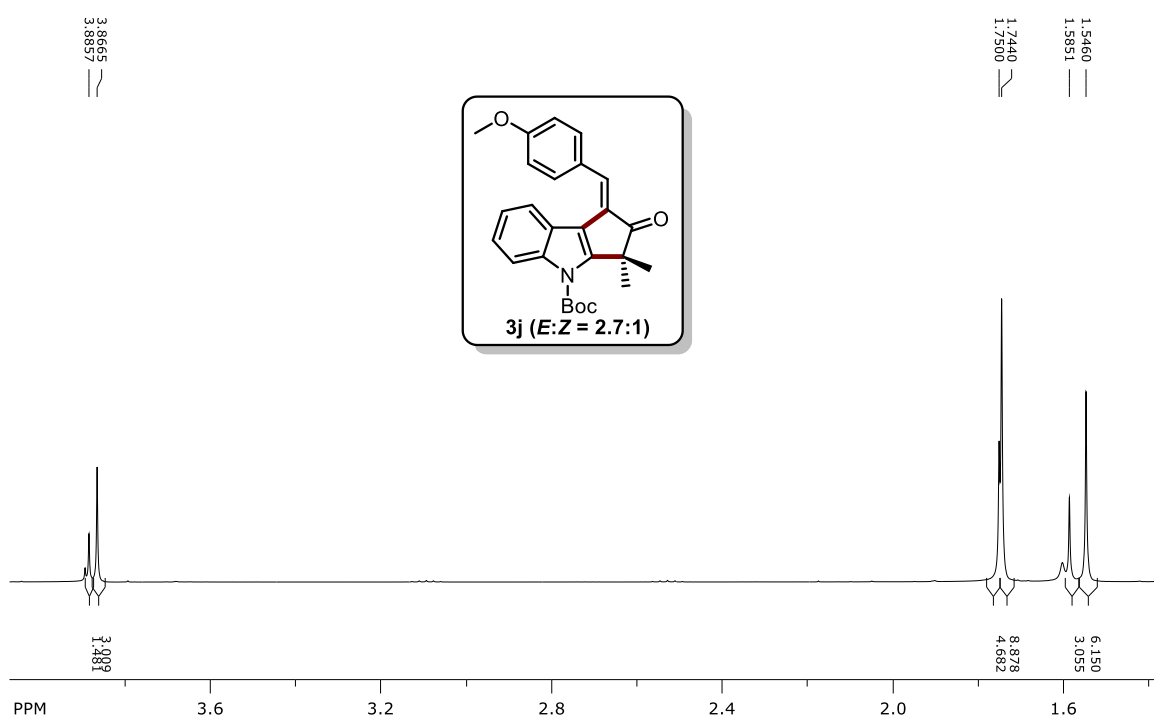
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): expansion of 115-156 ppm region**



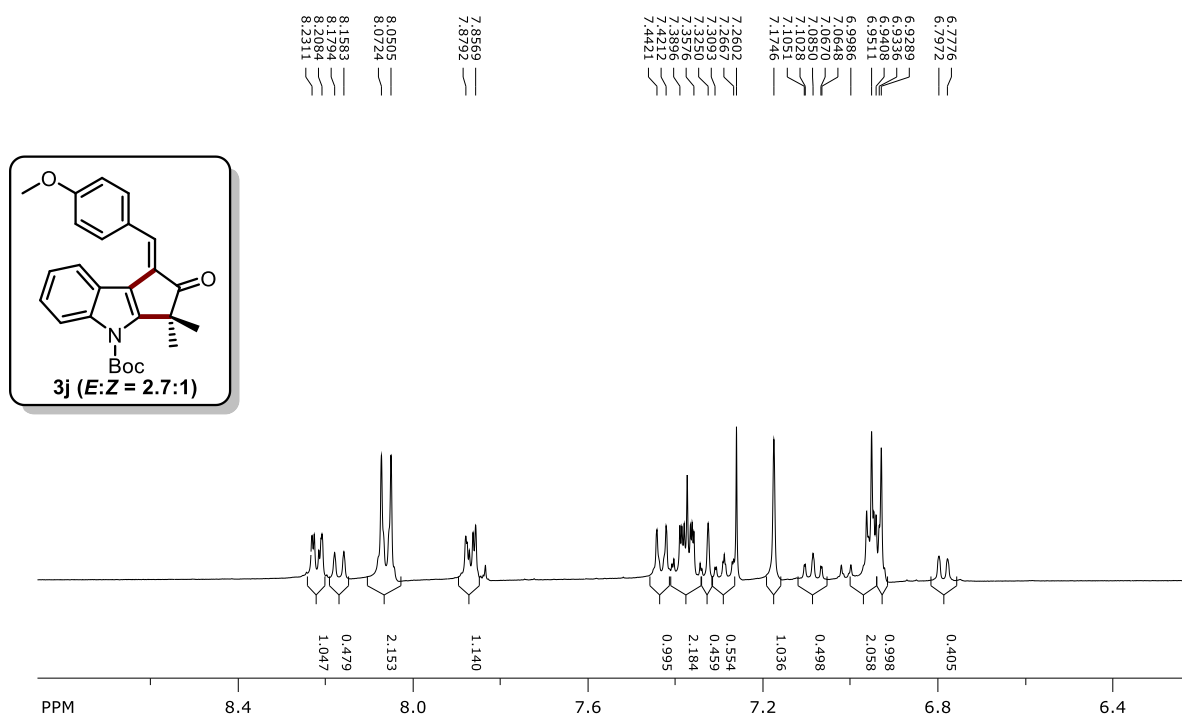
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



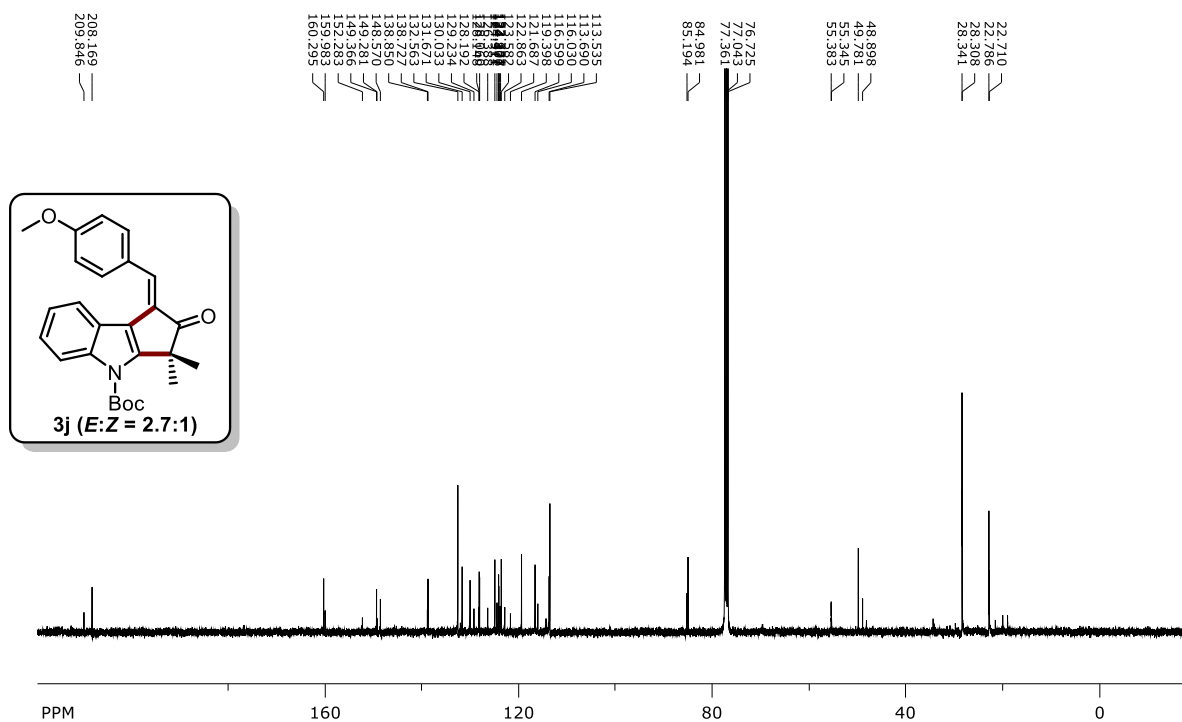
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 1.5-4.0 ppm region**



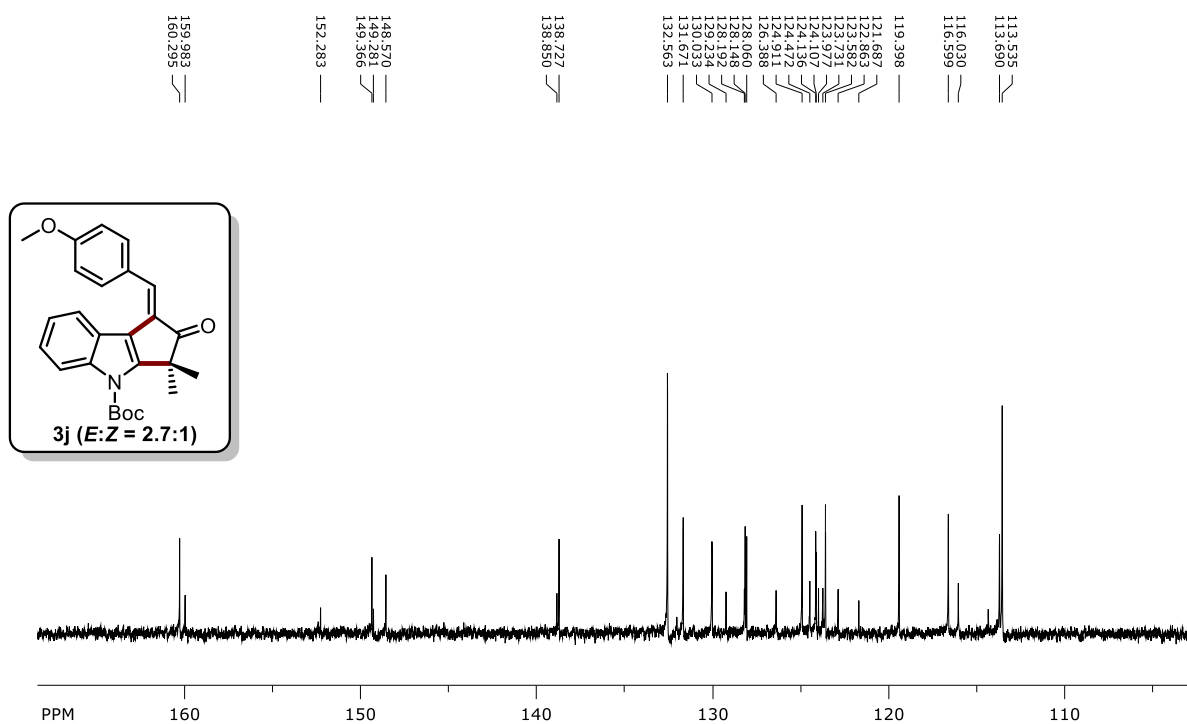
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 6.5-9.0 ppm region**



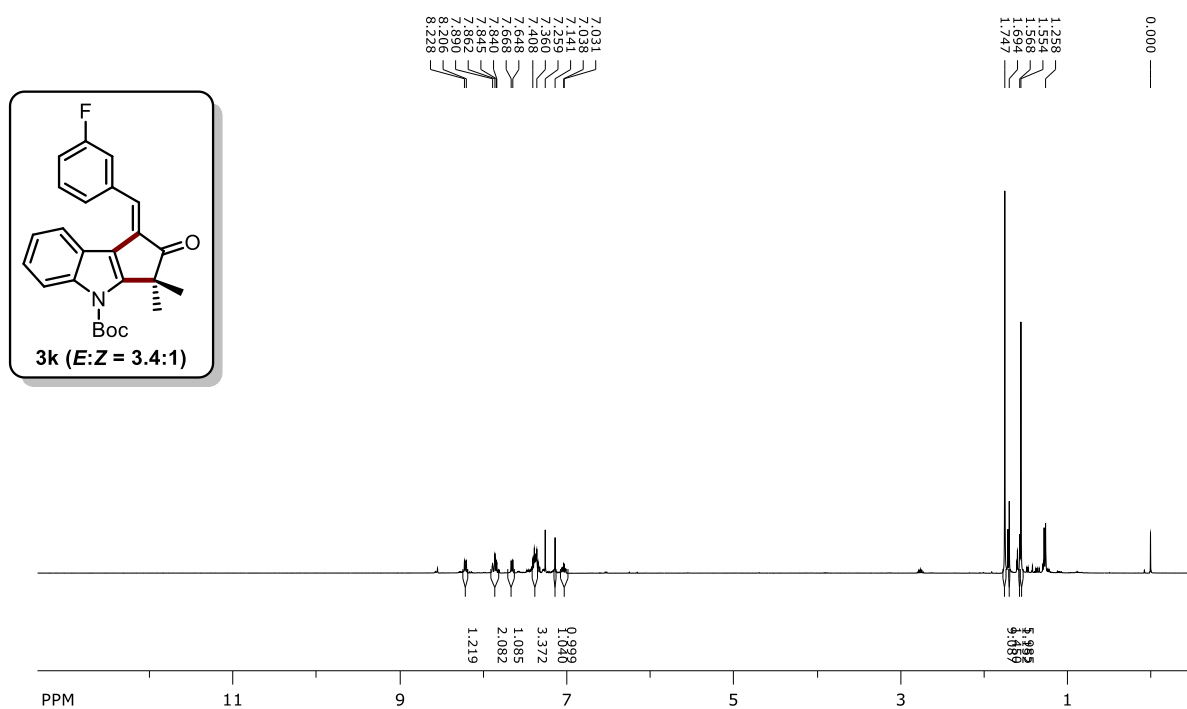
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



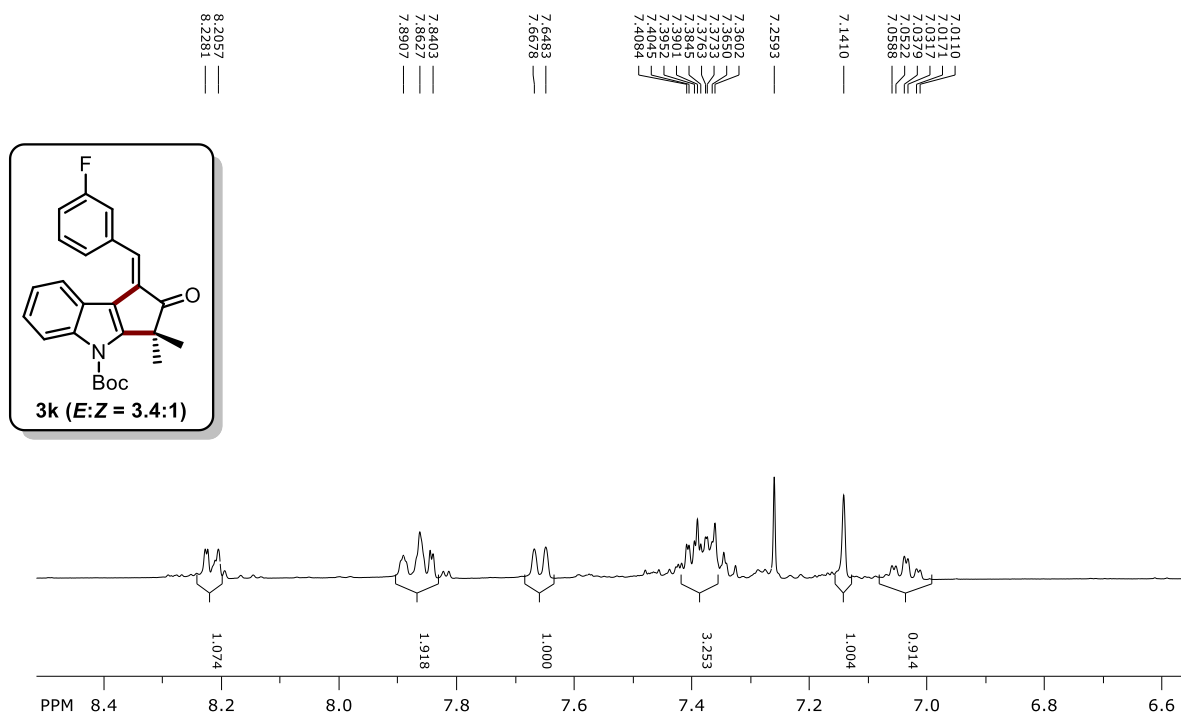
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): expansion of 110-160 ppm region**



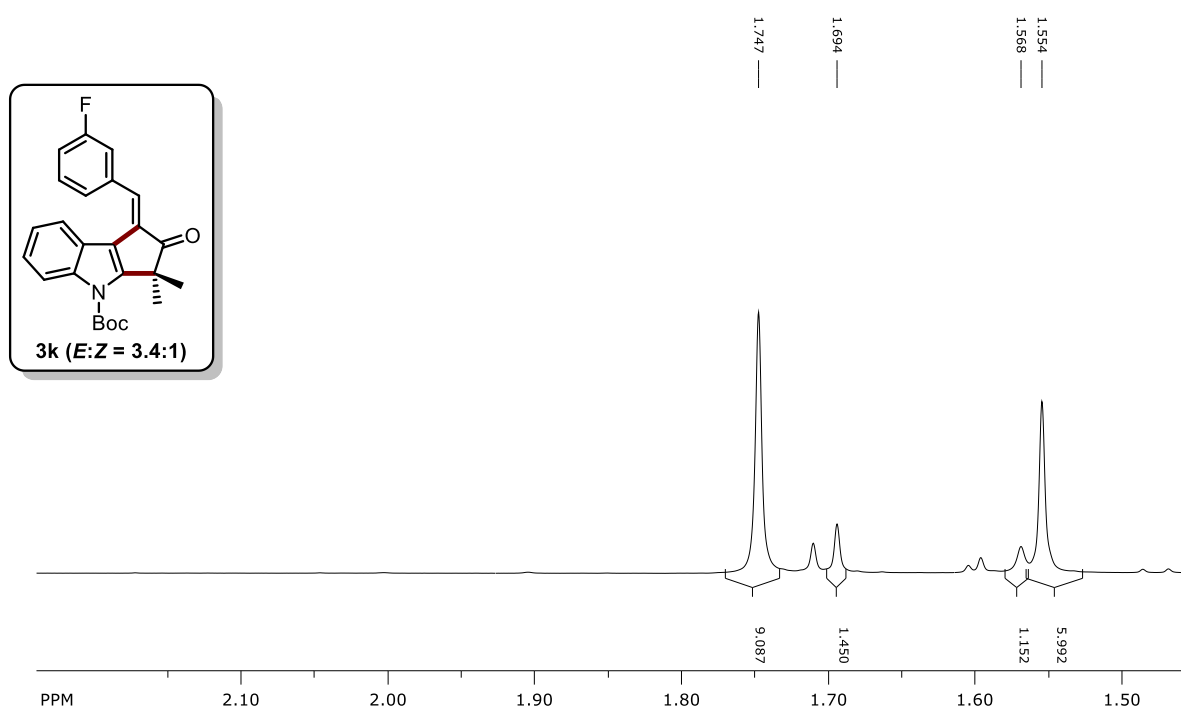
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



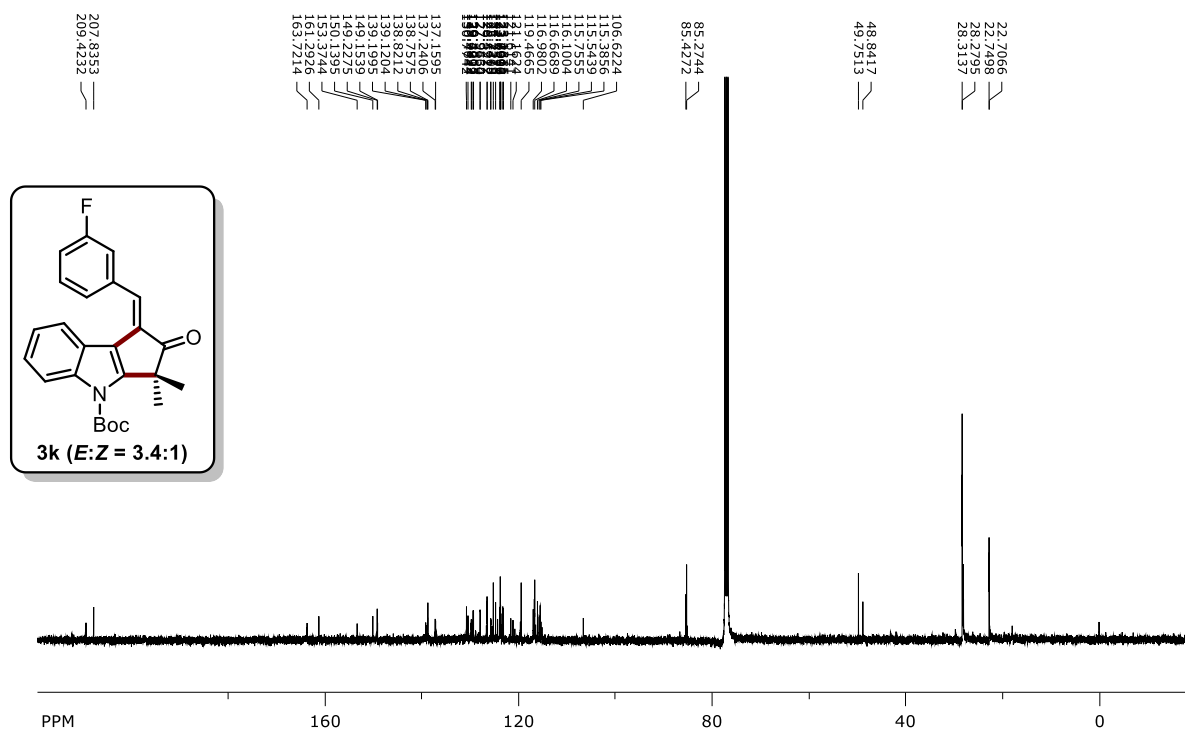
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 6.6-8.5 ppm region**



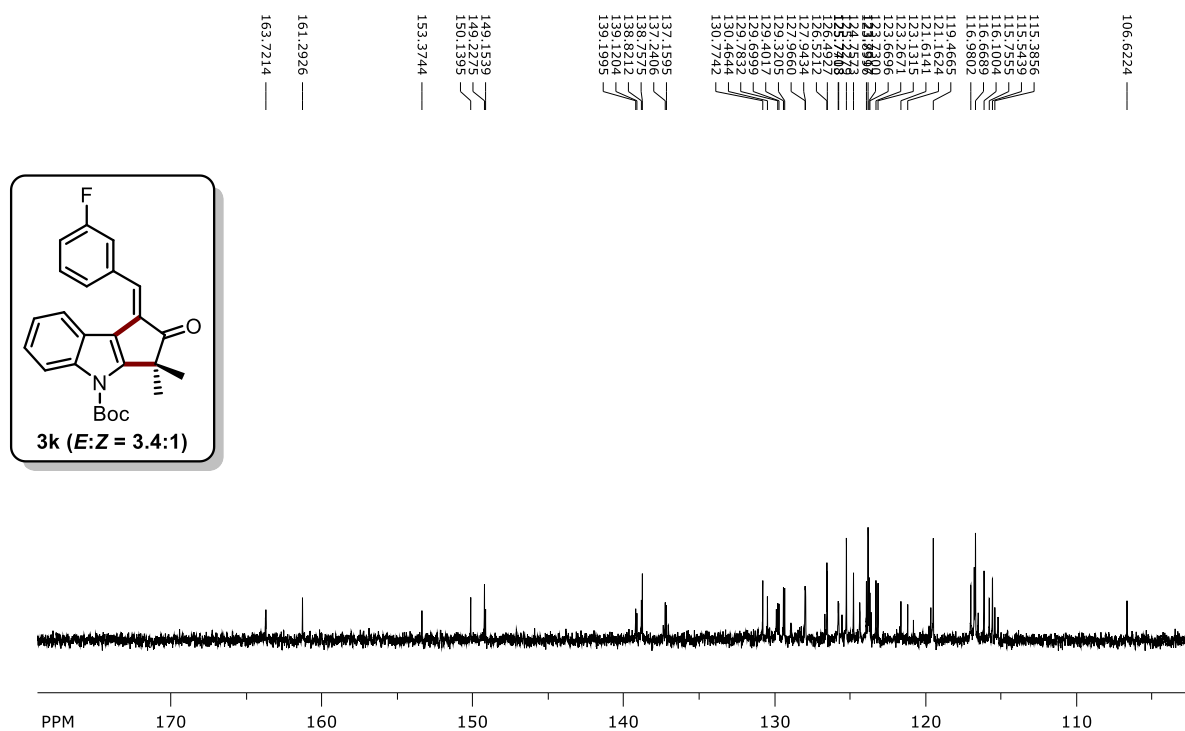
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 1.0-3.0 ppm region**



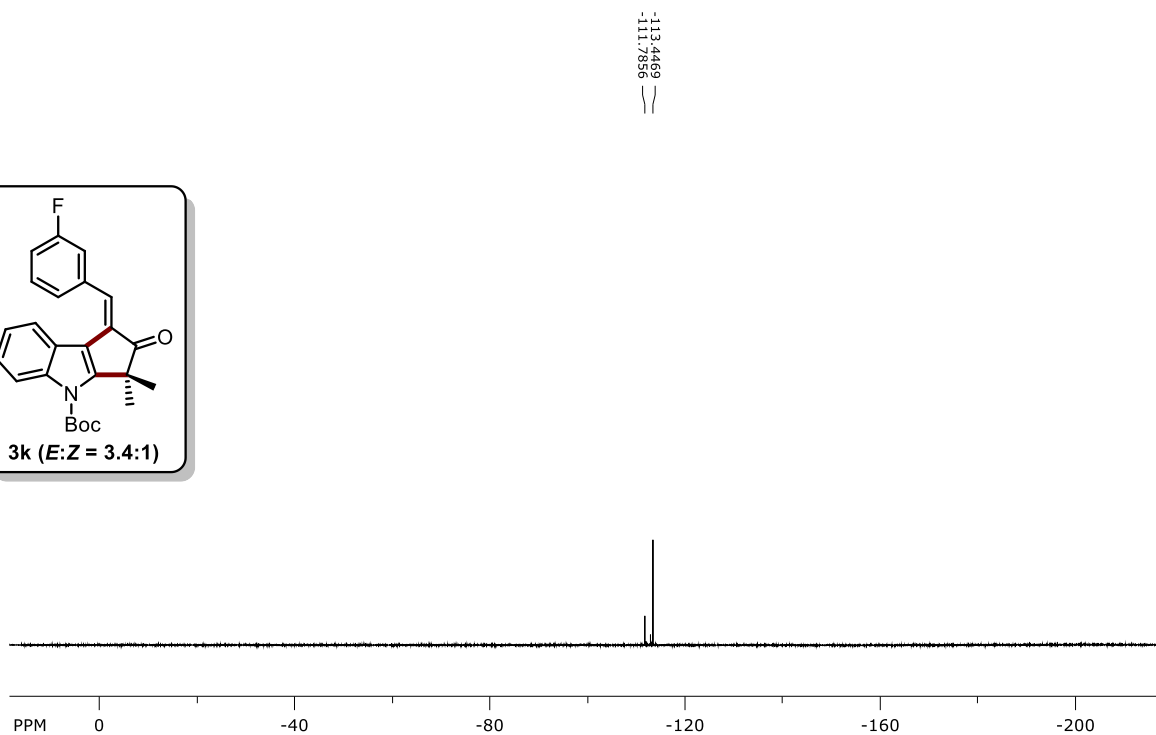
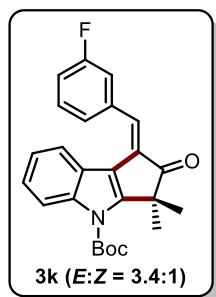
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



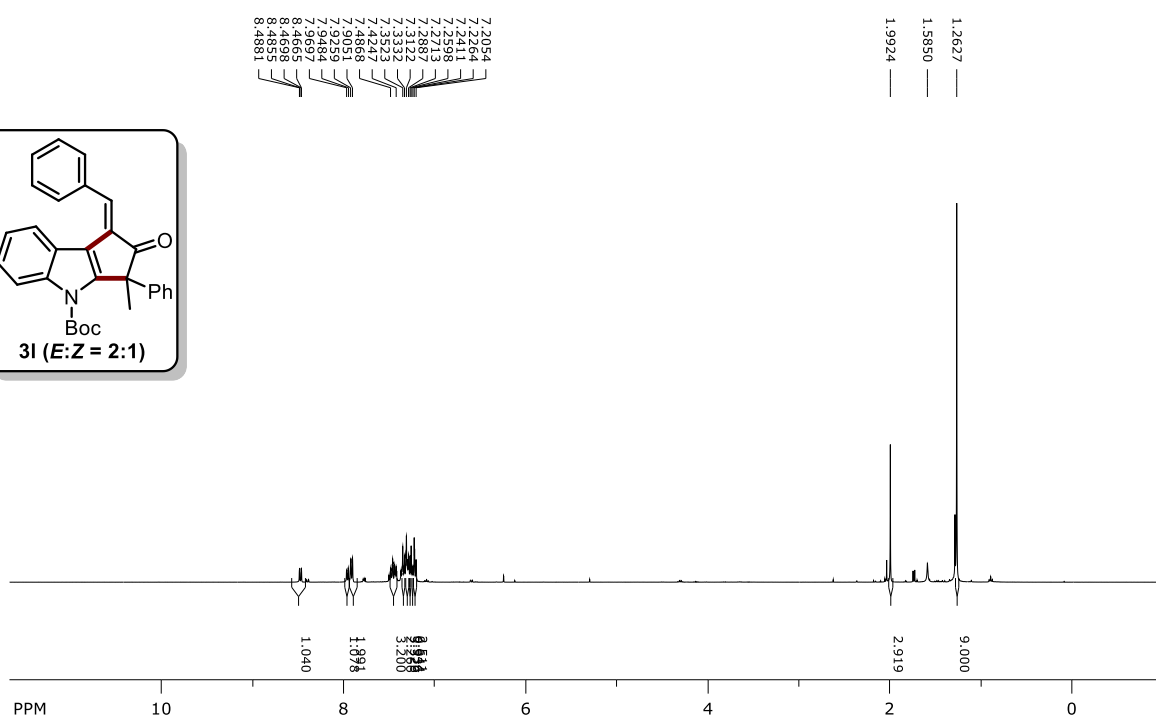
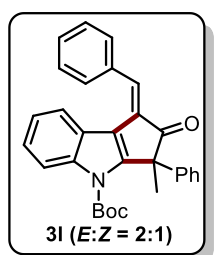
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): expansion of 102-170 ppm region**



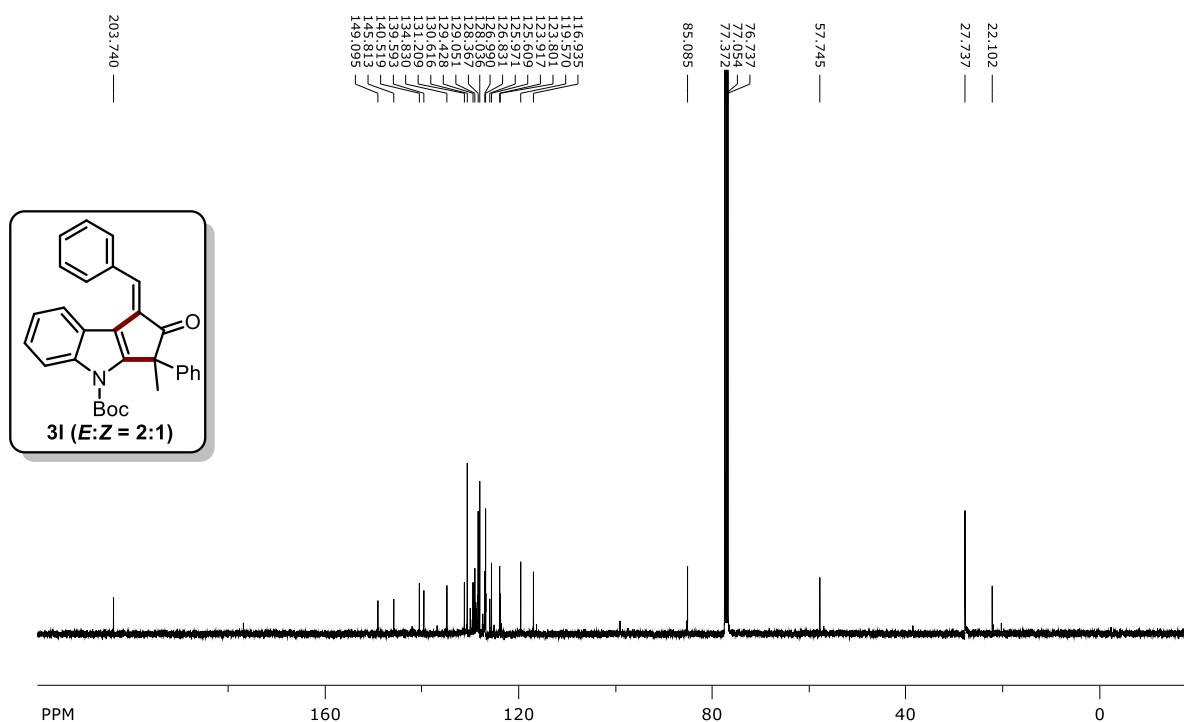
**$^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ ):**



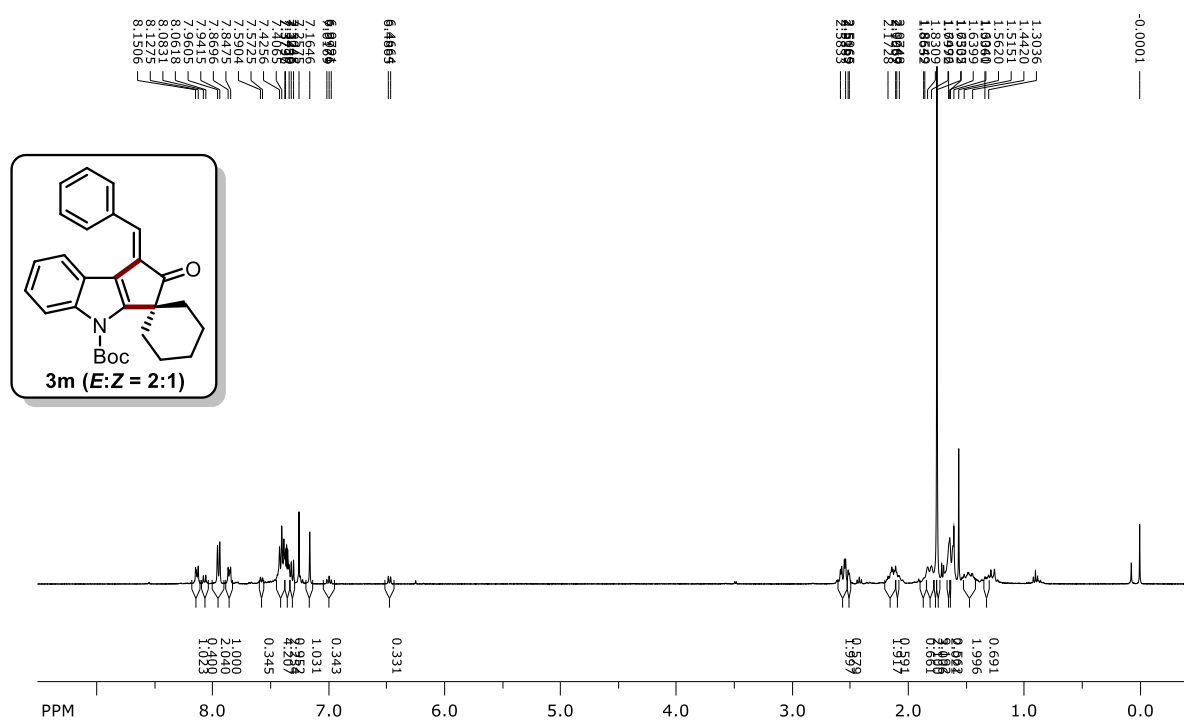
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**

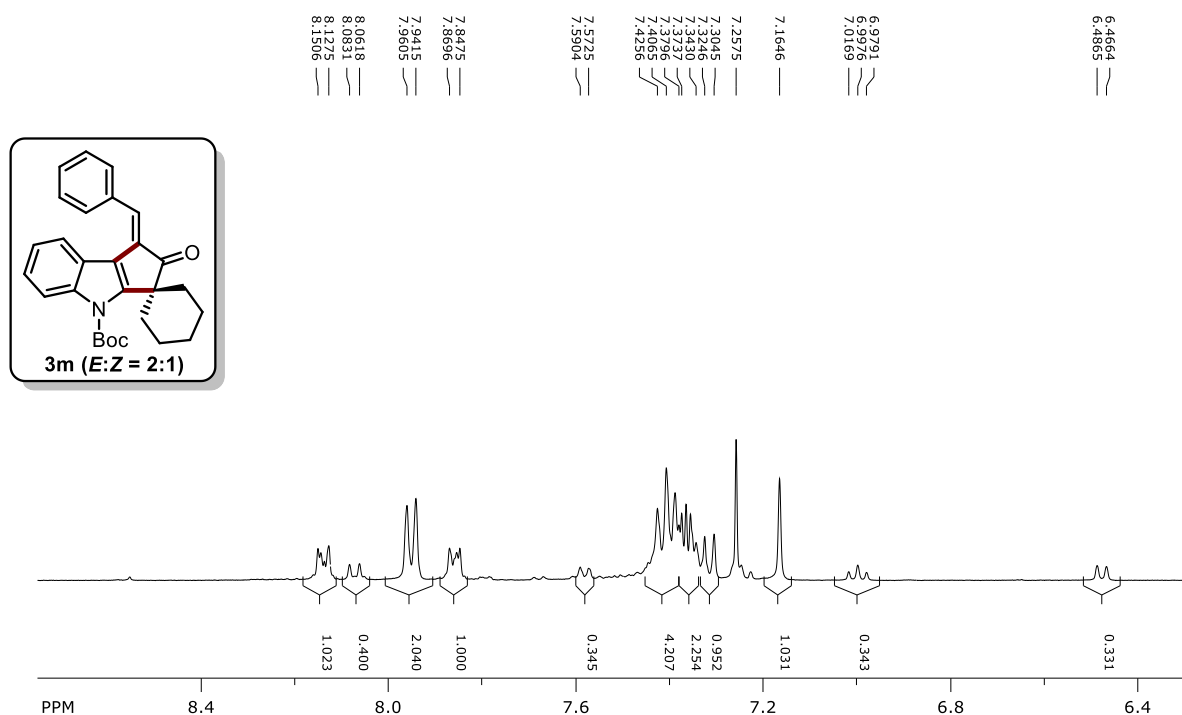


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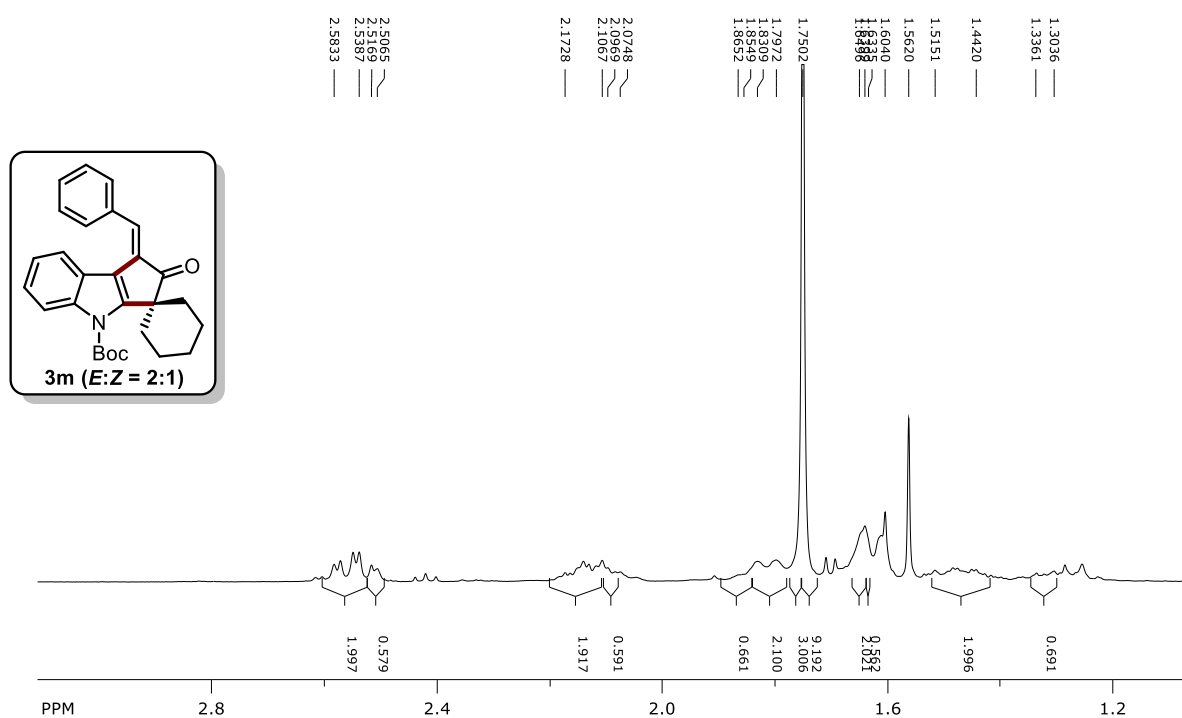




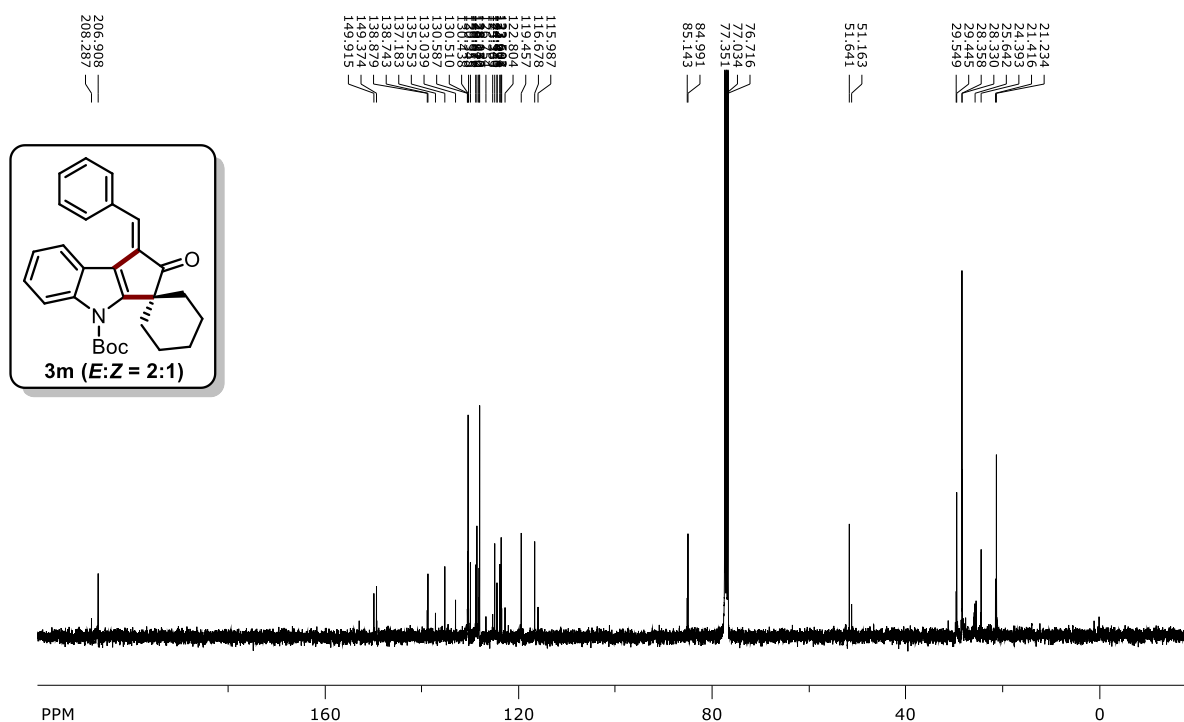
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): expansion of 6.0-9.0 ppm region**



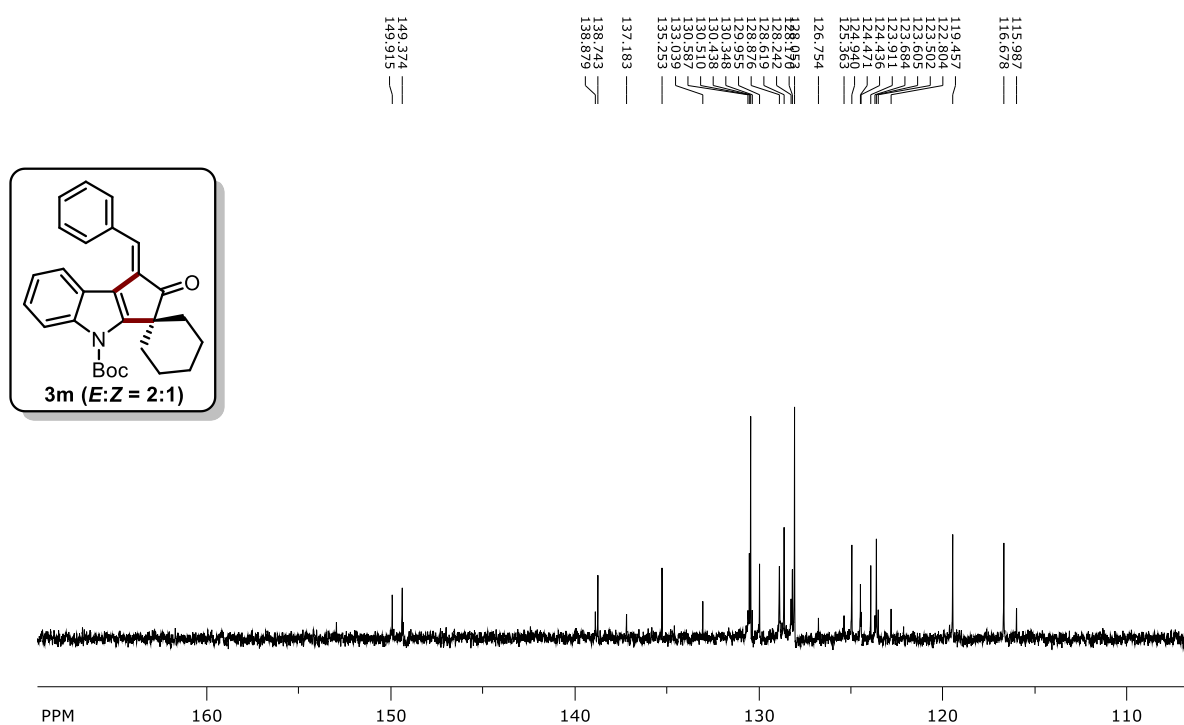
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): expansion of 1.0-3.0 ppm region**



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): expansion of 110-160 ppm region**



CC1=CC=C(C=C1)/C=C2C(=O)C3CC[C@H]3N(C2)c4ccccc4C(=O)OC(C)(C)C

**3n (*E*:*Z* = 2.5:1)**

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 1.5172  
 1.5165  
 1.5158  
 1.5151  
 1.5144  
 1.5137  
 1.5130  
 1.5123  
 1.5116  
 1.5109  
 1.5102  
 1.5095  
 1.5088  
 1.5081  
 1.5074  
 1.5067  
 1.5060  
 1.5053  
 1.5046  
 1.5039  
 1.5032  
 1.5025  
 1.5018  
 1.5011  
 1.5004  
 1.4997  
 1.4990  
 1.4983  
 1.4976  
 1.4969  
 1.4962  
 1.4955  
 1.4948

Chemical structure of **3n** (*E:Z* = 2.5:1) is shown. The structure is a complex molecule featuring a bicyclic system with a Boc-protected amine and a cyclohexyl group. The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) is displayed below the structure, showing peaks in the aromatic region (6.4-8.1 ppm) and aliphatic region (1.0-1.7 ppm). Integration values are provided for several peaks.

<sup>1</sup>H NMR peaks (ppm) and integration values:

Peak (ppm)	Integration
8.0692	0.694
8.0904	0.999
8.1236	0.999
8.1466	0.999
7.8844	0.908
7.8852	0.908
7.8795	2.046
7.3710	1.963
7.3477	1.122
7.3391	1.122
7.2828	1.008
7.2598	3.338
7.2434	0.952
7.2149	0.706
7.2043	0.952
7.1464	0.952
7.1454	0.952
7.0159	0.656
7.0137	0.656
7.0359	0.656
7.0538	0.656
7.0559	0.656

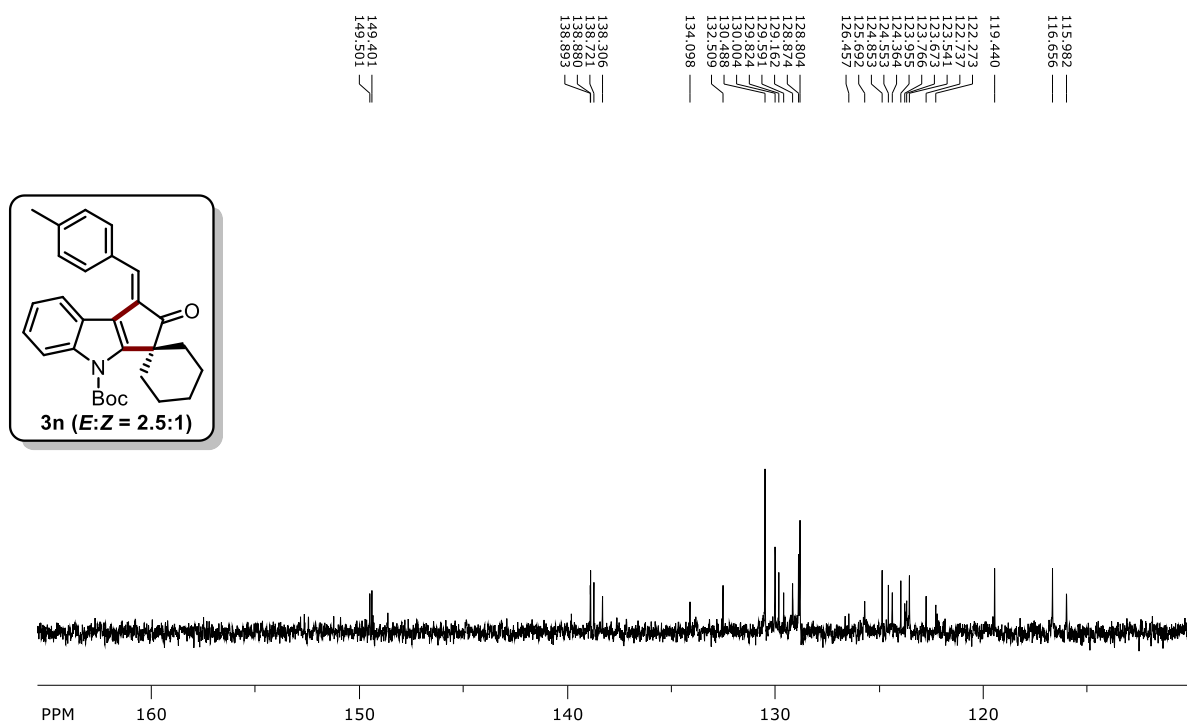
**3n (E:Z = 2.5:1)**

Chemical Shift (ppm)	Integration
1.4136, 1.4518, 1.4622	1.263
1.5327	2.096
1.5820	2.975
1.6359, 1.6632	2.975
1.7475, 1.7796	8.379, 4.563
1.8260, 1.8426	1.987
1.9055	1.071
2.0796, 2.1211, 2.1363, 2.1790	2.179
2.3865, 2.4273	1.749
2.4975, 2.5407, 2.5619, 2.6072	1.930
2.6072	1.412

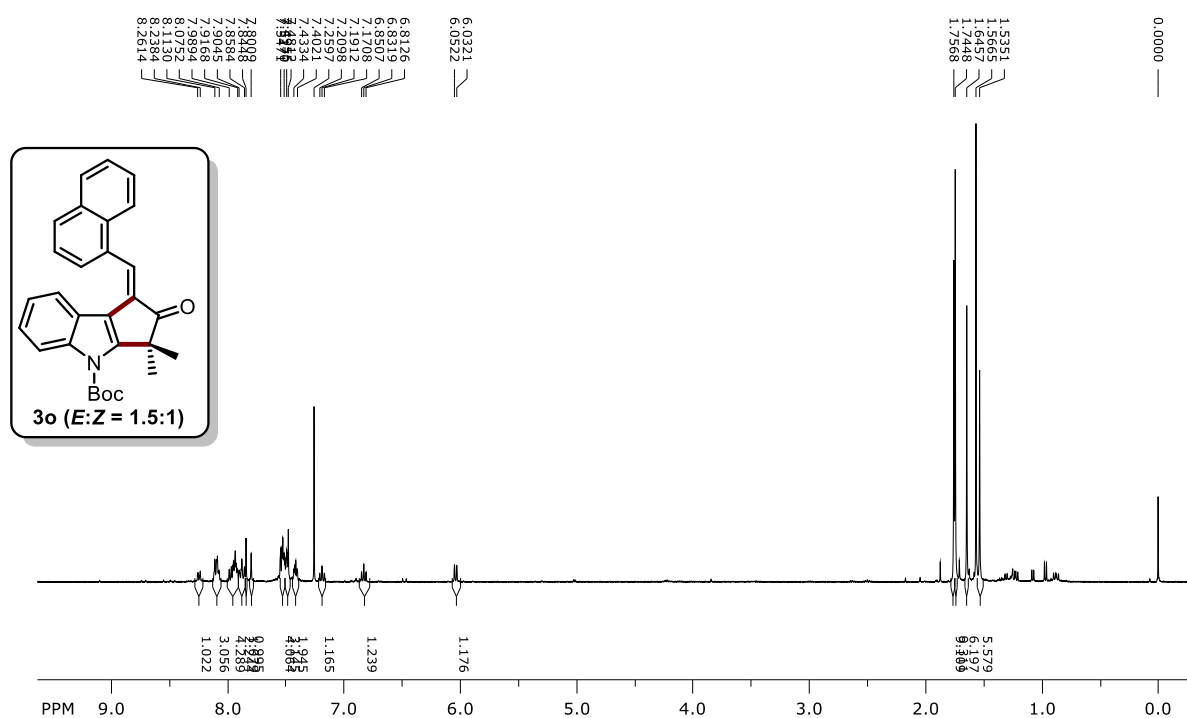
CC1=CC=C(C=C1)/C=C2C(=O)C3CCCC[C@H]3C2=C1c1ccccc1N(C2)C(=O)OC(C)(C)C  
**3n (E:Z = 2.5:1)**

Chemical Shift (ppm)	Integration
7.26	1.00
7.19	0.10
7.14	0.10
7.09	0.10
7.04	0.10
6.99	0.10
6.94	0.10
6.89	0.10
6.84	0.10
6.79	0.10
6.74	0.10
6.69	0.10
6.64	0.10
6.59	0.10
6.54	0.10
6.49	0.10
6.44	0.10
6.39	0.10
6.34	0.10
6.29	0.10
6.24	0.10
6.19	0.10
6.14	0.10
6.09	0.10
6.04	0.10
5.99	0.10
5.94	0.10
5.89	0.10
5.84	0.10
5.79	0.10
5.74	0.10
5.69	0.10
5.64	0.10
5.59	0.10
5.54	0.10
5.49	0.10
5.44	0.10
5.39	0.10
5.34	0.10
5.29	0.10
5.24	0.10
5.19	0.10
5.14	0.10
5.09	0.10
5.04	0.10
4.99	0.10
4.94	0.10
4.89	0.10
4.84	0.10
4.79	0.10
4.74	0.10
4.69	0.10
4.64	0.10
4.59	0.10
4.54	0.10
4.49	0.10
4.44	0.10
4.39	0.10
4.34	0.10
4.29	0.10
4.24	0.10
4.19	0.10
4.14	0.10
4.09	0.10
4.04	0.10
3.99	0.10
3.94	0.10
3.89	0.10
3.84	0.10
3.79	0.10
3.74	0.10
3.69	0.10
3.64	0.10
3.59	0.10
3.54	0.10
3.49	0.10
3.44	0.10
3.39	0.10
3.34	0.10
3.29	0.10
3.24	0.10
3.19	0.10
3.14	0.10
3.09	0.10
3.04	0.10
2.99	0.10
2.94	0.10
2.89	0.10
2.84	0.10
2.79	0.10
2.74	0.10
2.69	0.10
2.64	0.10
2.59	0.10
2.54	0.10
2.49	0.10
2.44	0.10
2.39	0.10
2.34	0.10
2.29	0.10
2.24	0.10
2.19	0.10
2.14	0.10
2.09	0.10
2.04	0.10
1.99	0.10
1.94	0.10
1.89	0.10
1.84	0.10
1.79	0.10
1.74	0.10
1.69	0.10
1.64	0.10
1.59	0.10
1.54	0.10
1.49	0.10
1.44	0.10
1.39	0.10
1.34	0.10
1.29	0.10
1.24	0.10
1.19	0.10
1.14	0.10
1.09	0.10
1.04	0.10
0.99	0.10
0.94	0.10
0.89	0.10
0.84	0.10
0.79	0.10
0.74	0.10
0.69	0.10
0.64	0.10
0.59	0.10
0.54	0.10
0.49	0.10
0.44	0.10
0.39	0.10
0.34	0.10
0.29	0.10
0.24	0.10
0.19	0.10
0.14	0.10
0.09	0.10
0.04	0.10

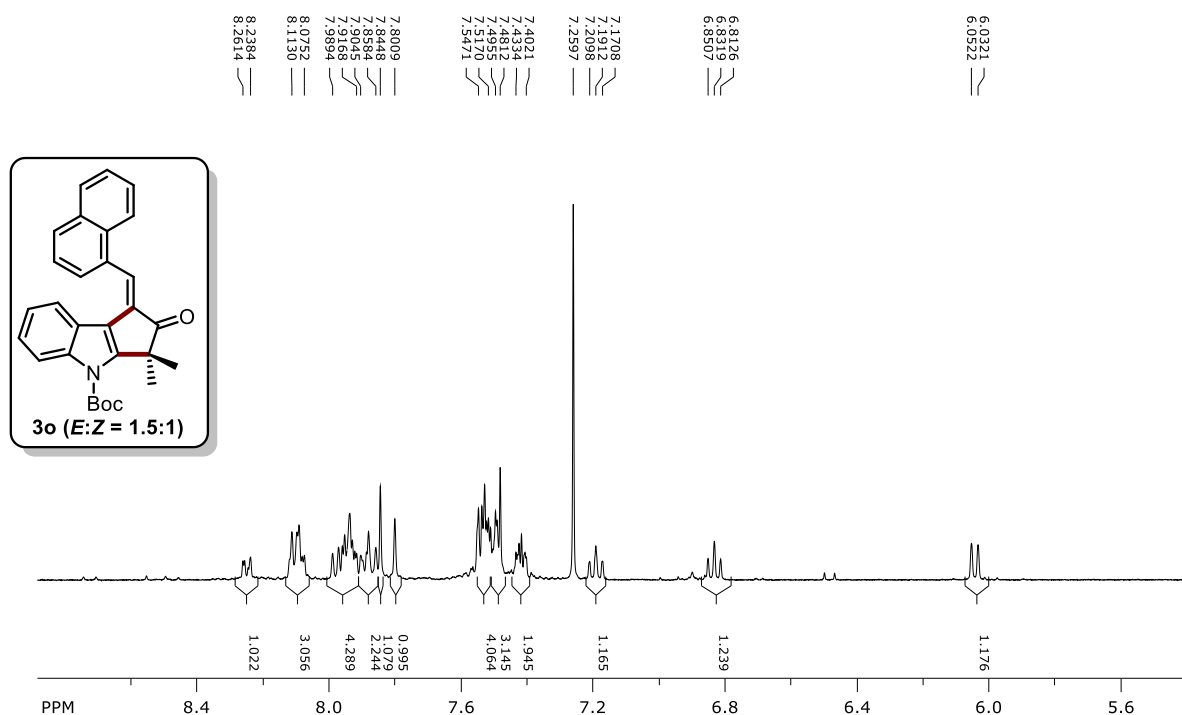
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): expansion of 110-160 ppm region**



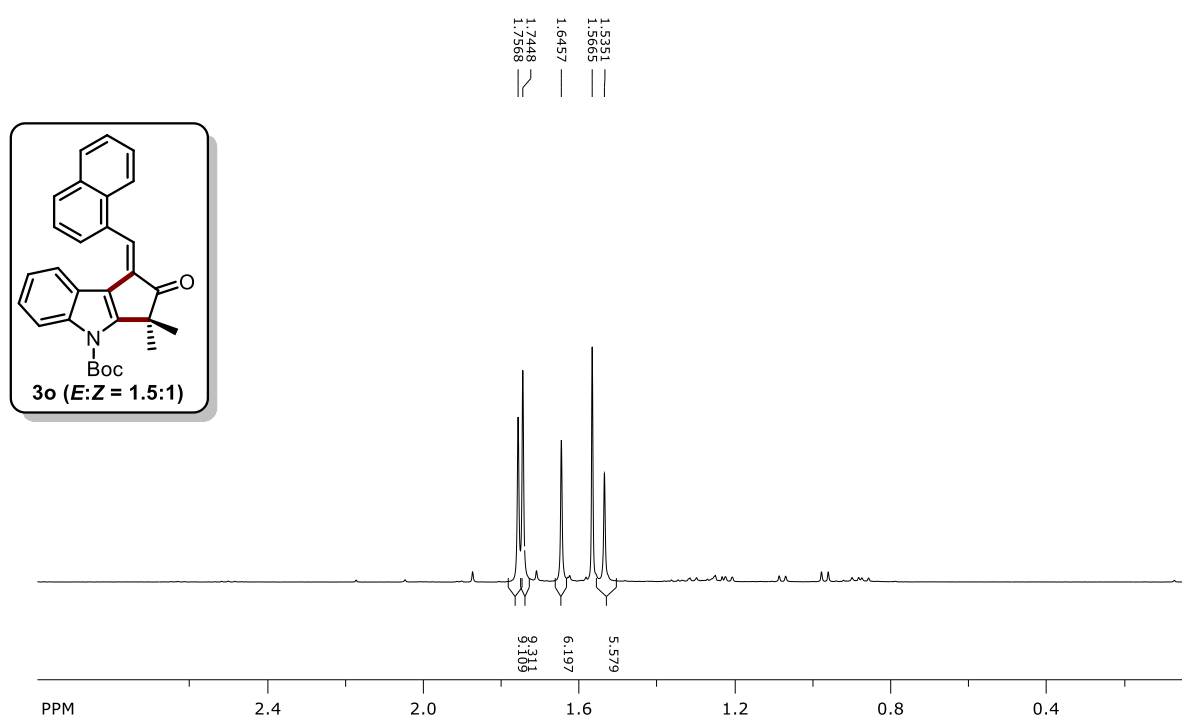
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



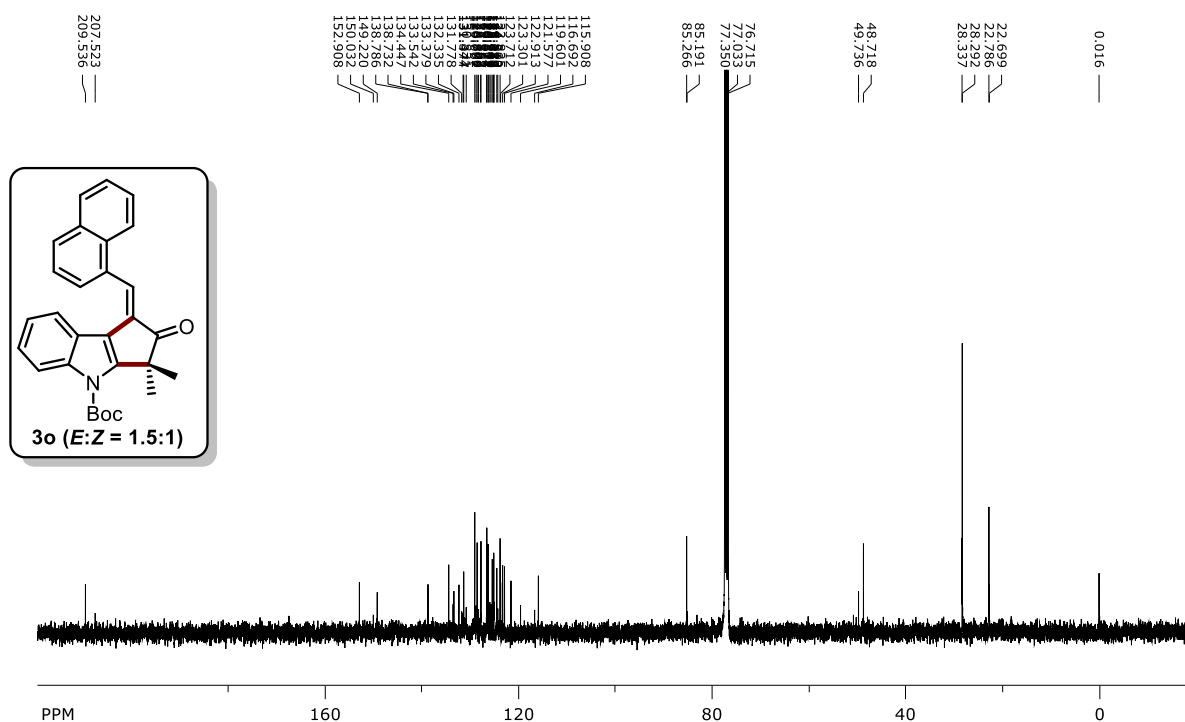
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 5.6-9.0 ppm region**



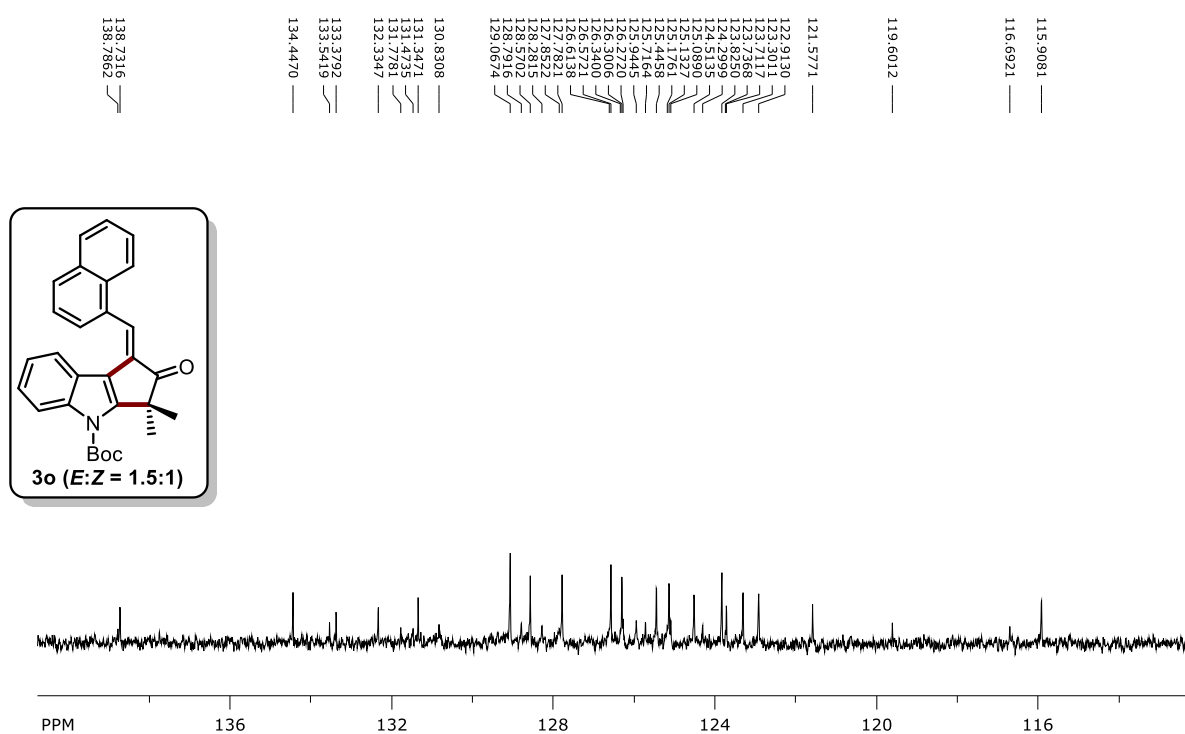
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 1.0-3.0 ppm region**



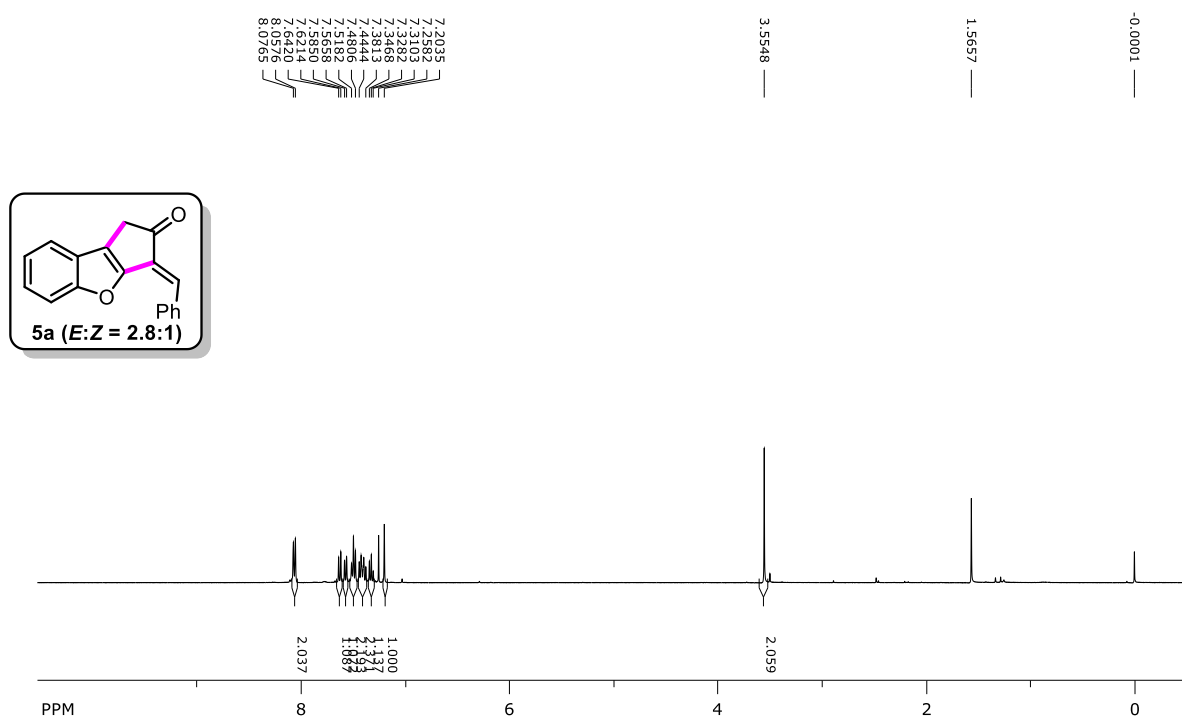
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



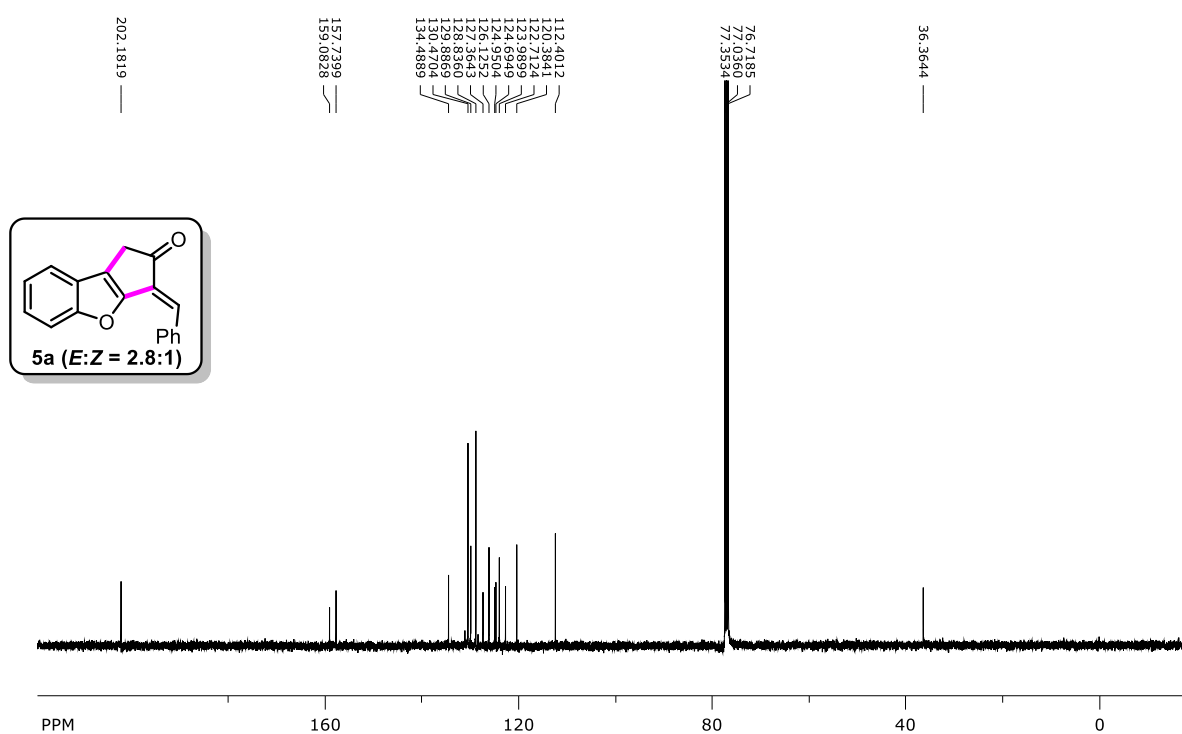
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): expansion of 110-140 ppm region**



**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**

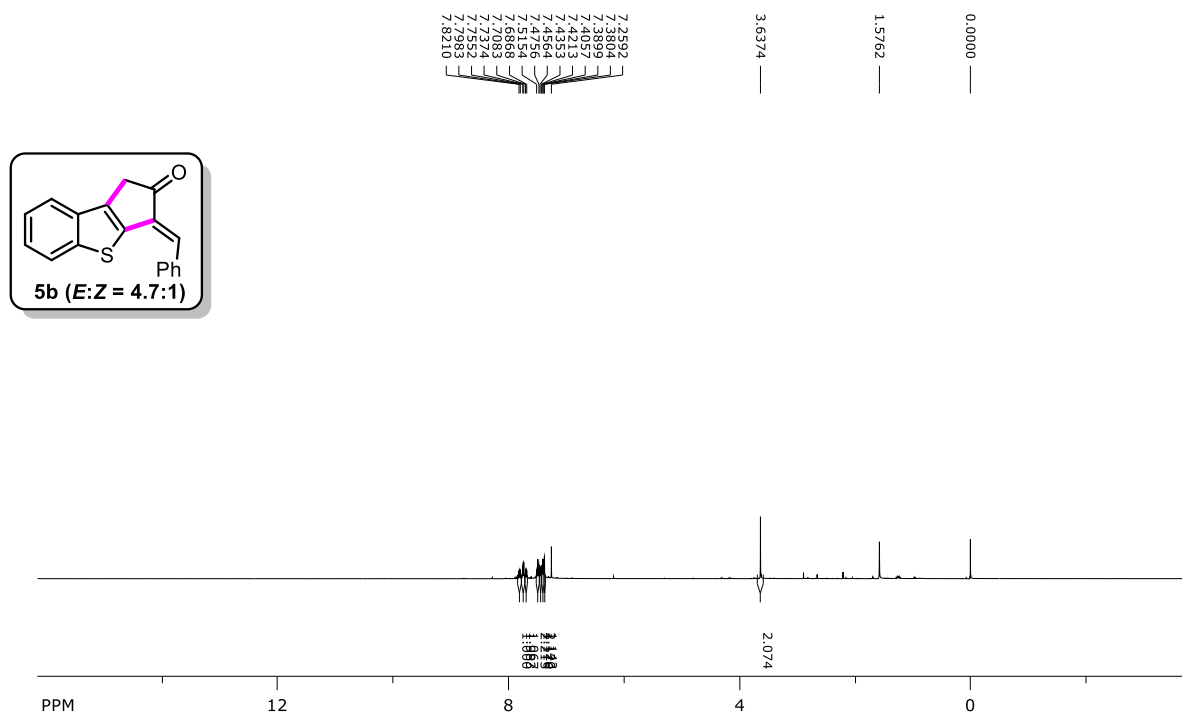


**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**

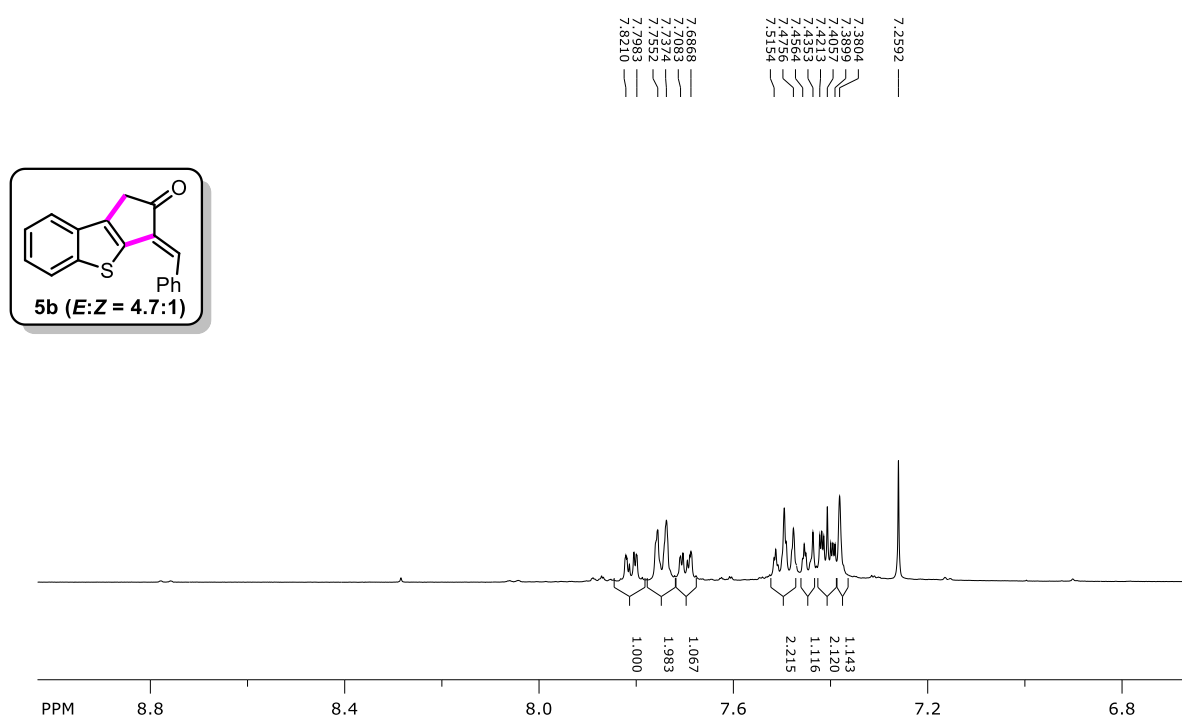




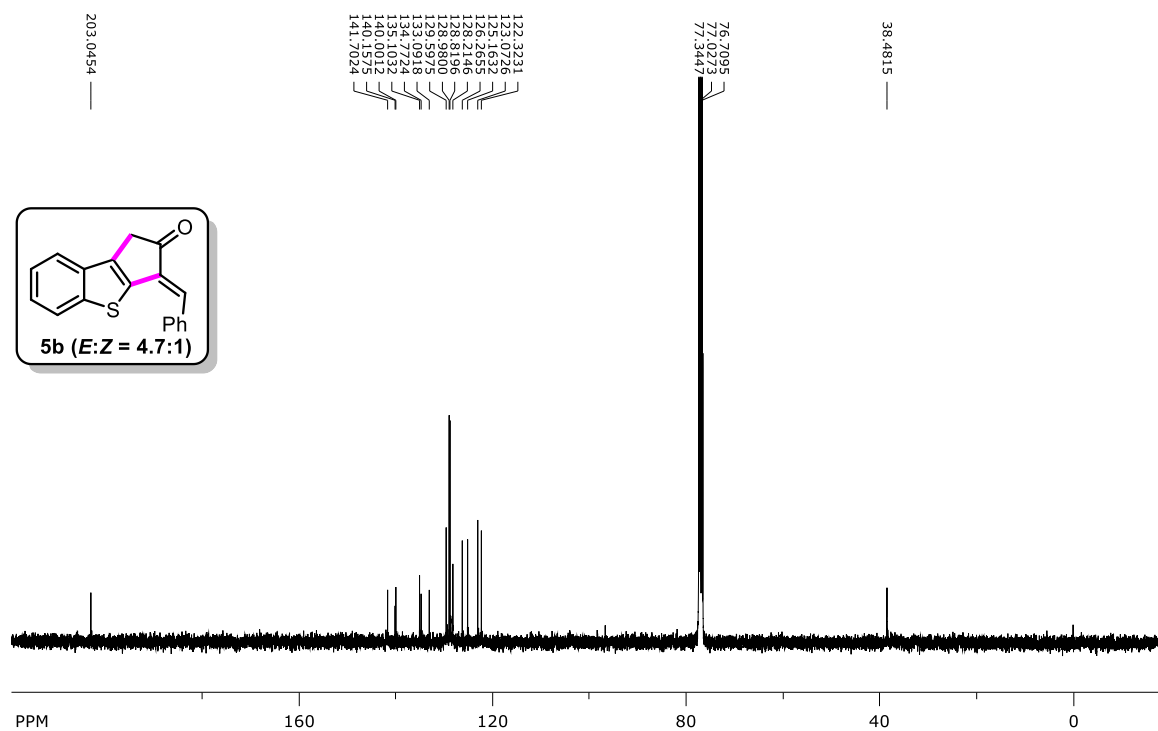
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



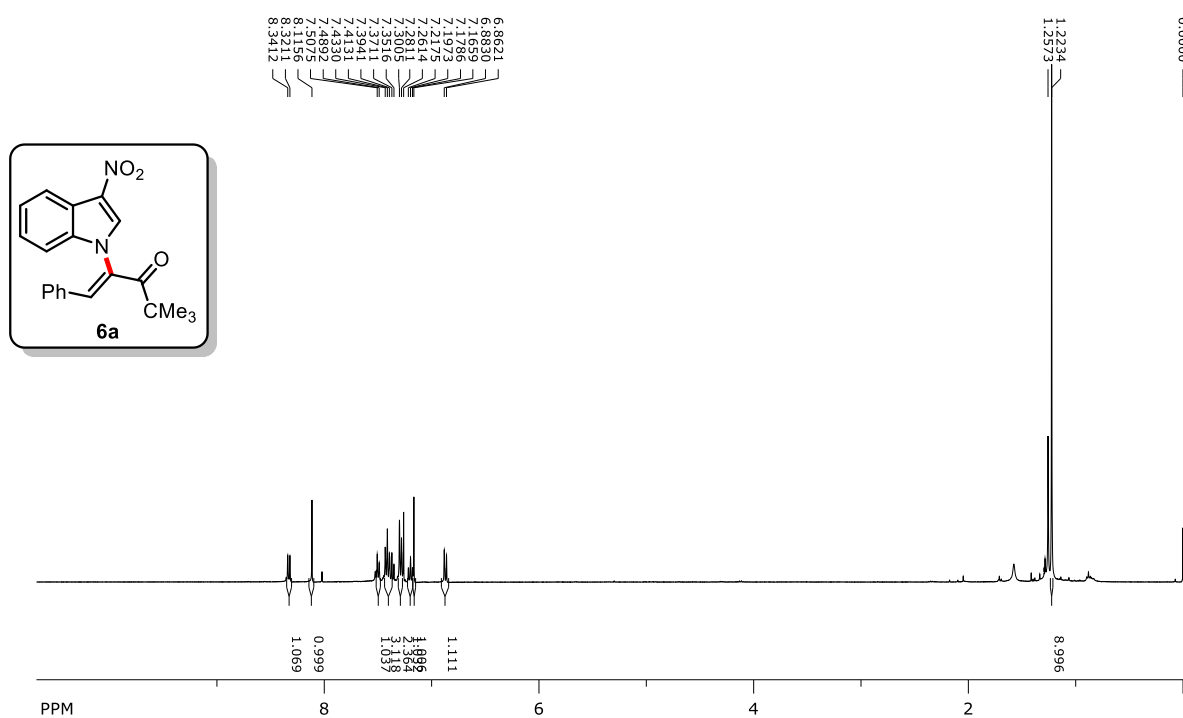
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): expansion of 6.8-9.0 ppm region**



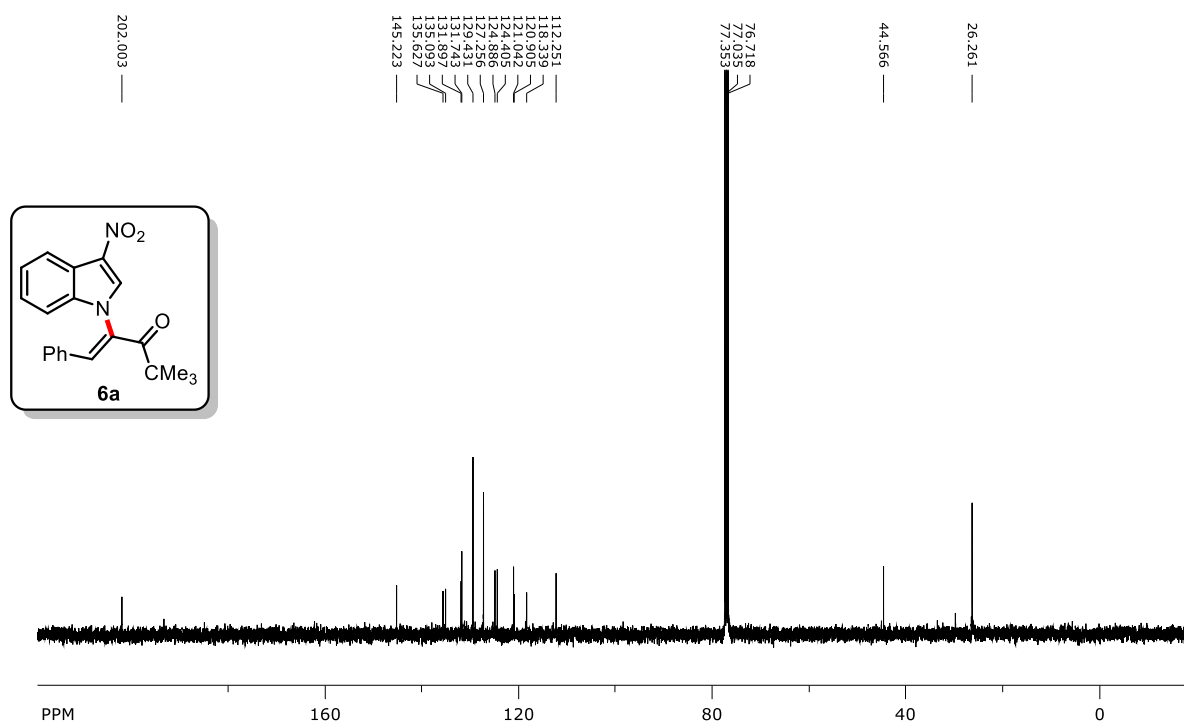
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



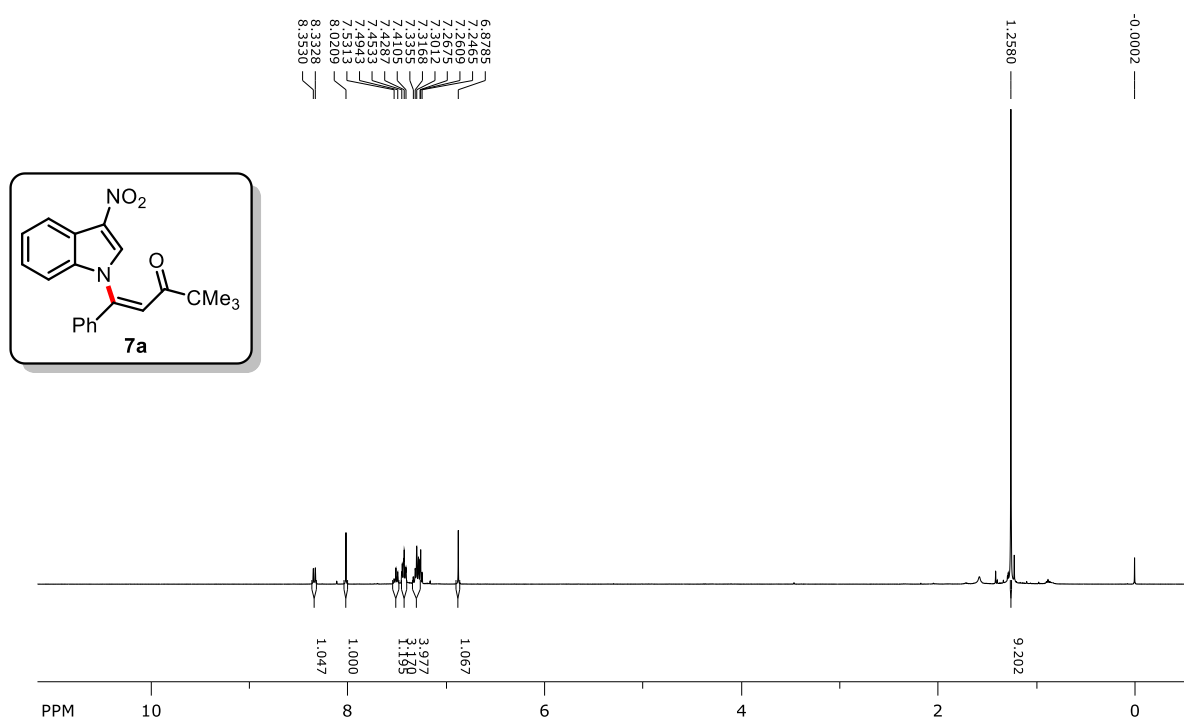
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



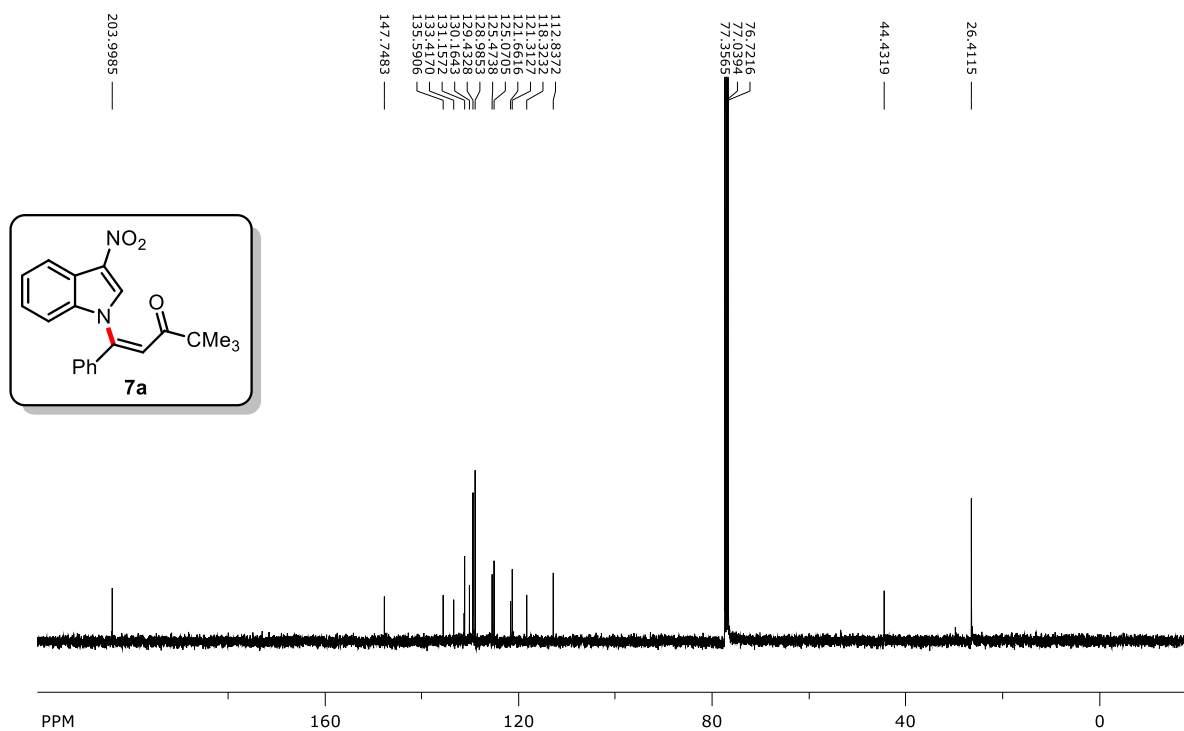
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



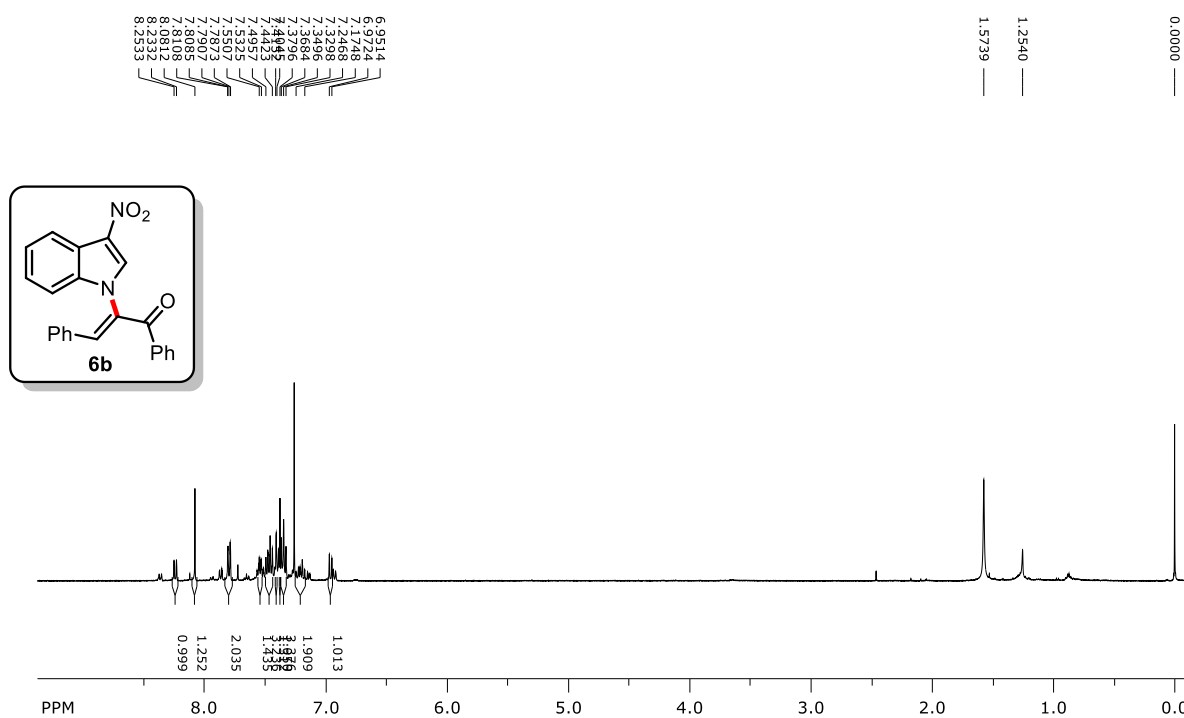
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



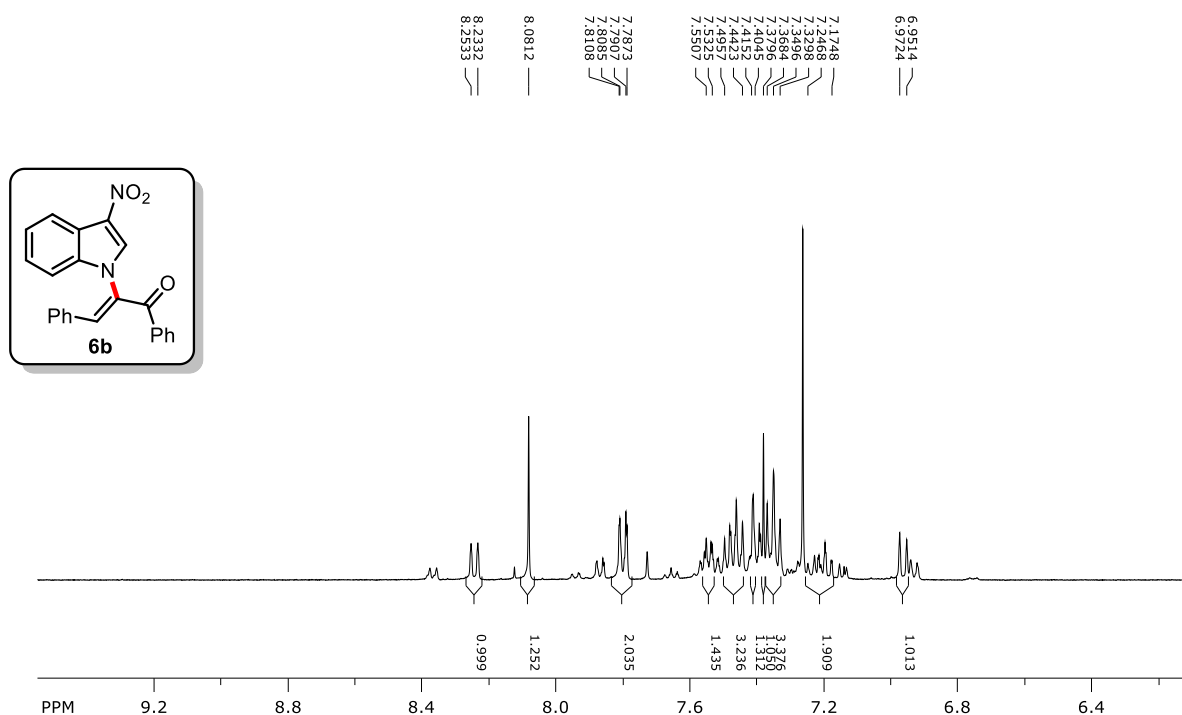
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



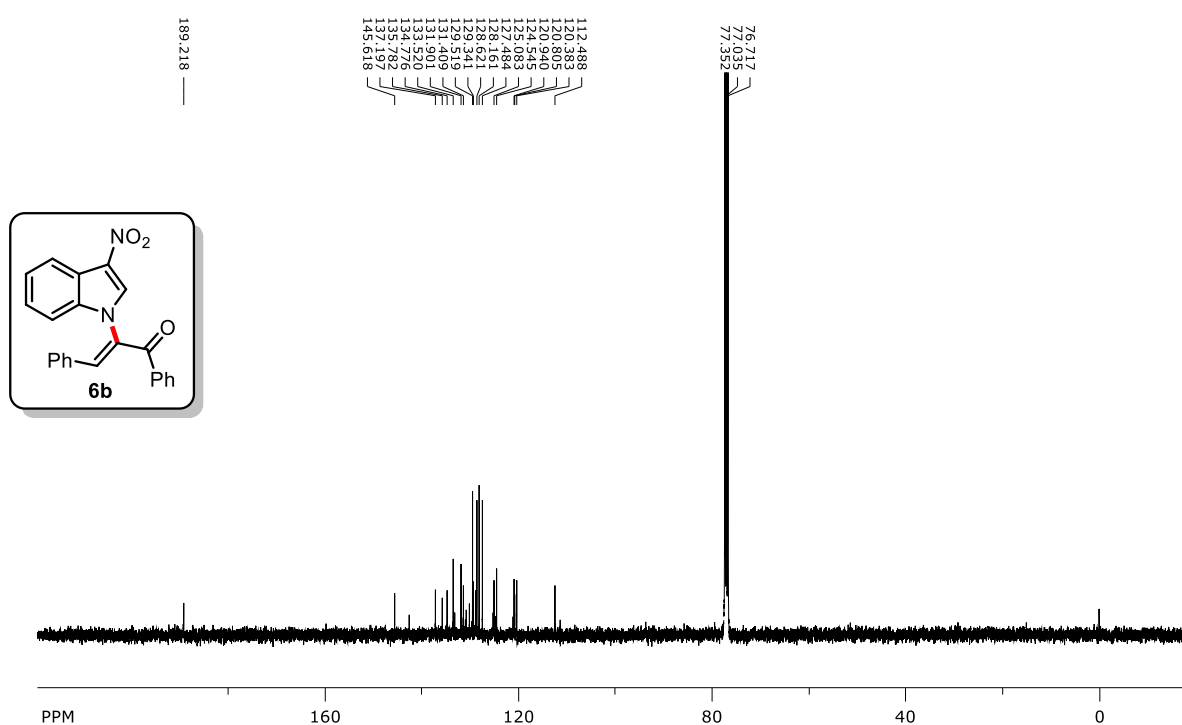
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



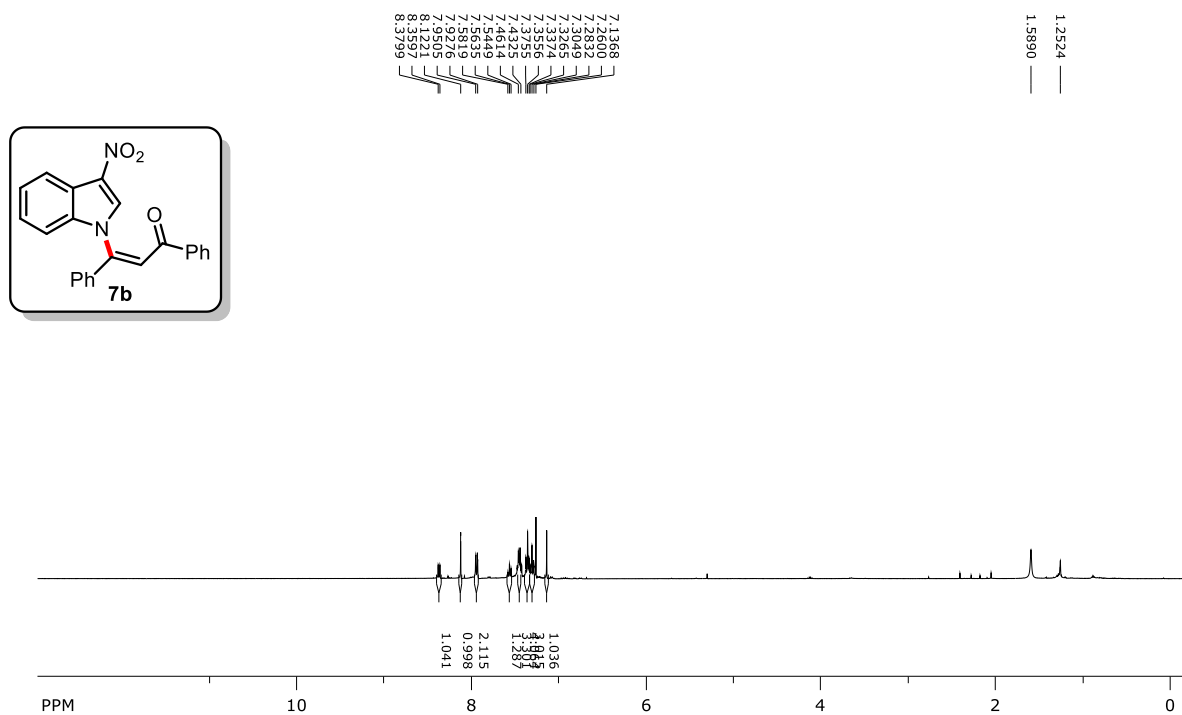
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): expansion of 6.5-9.0 ppm region**



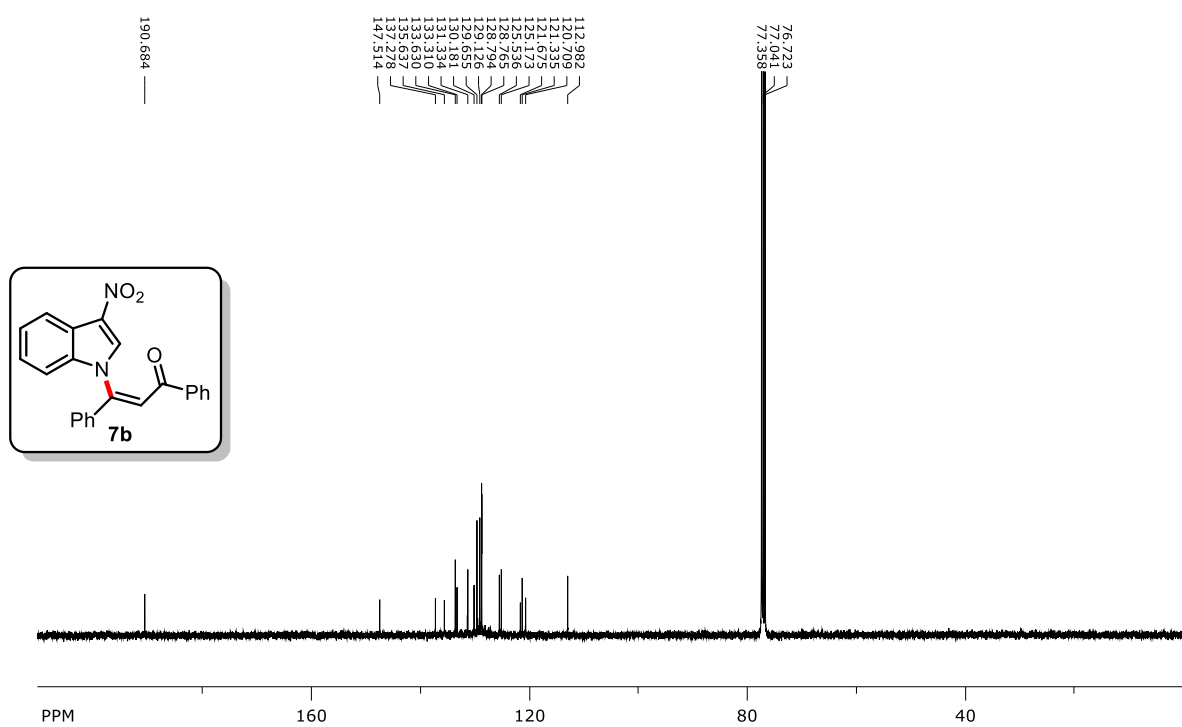
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



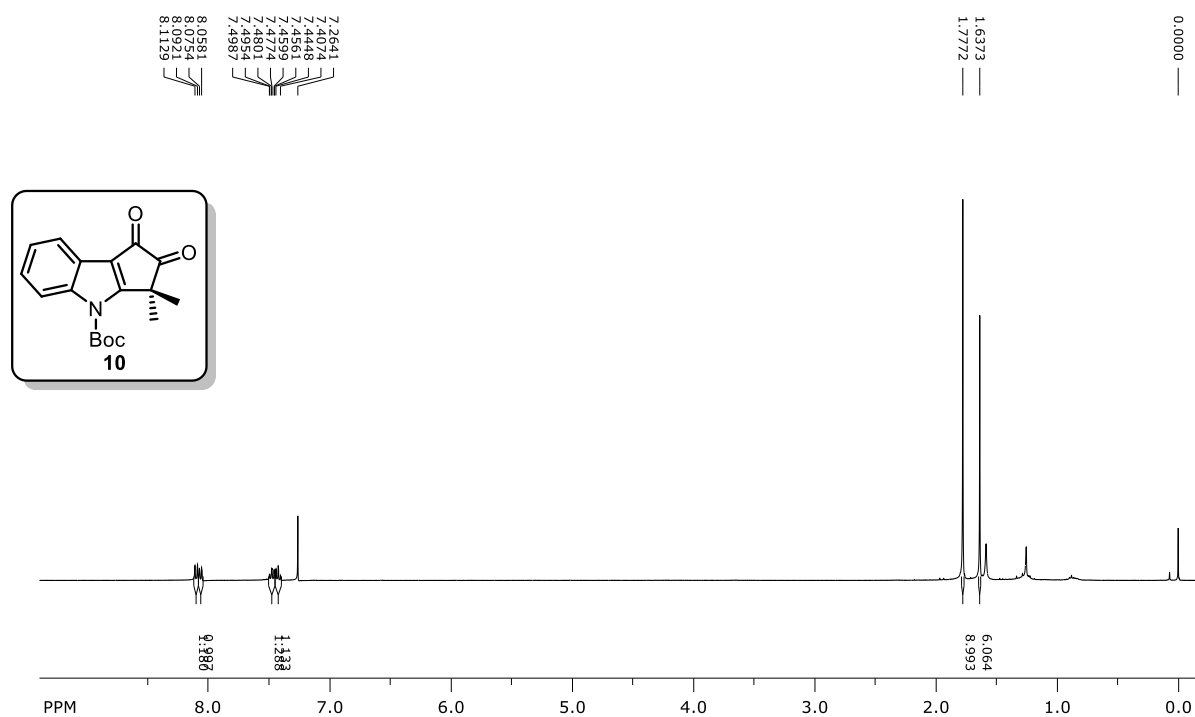
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



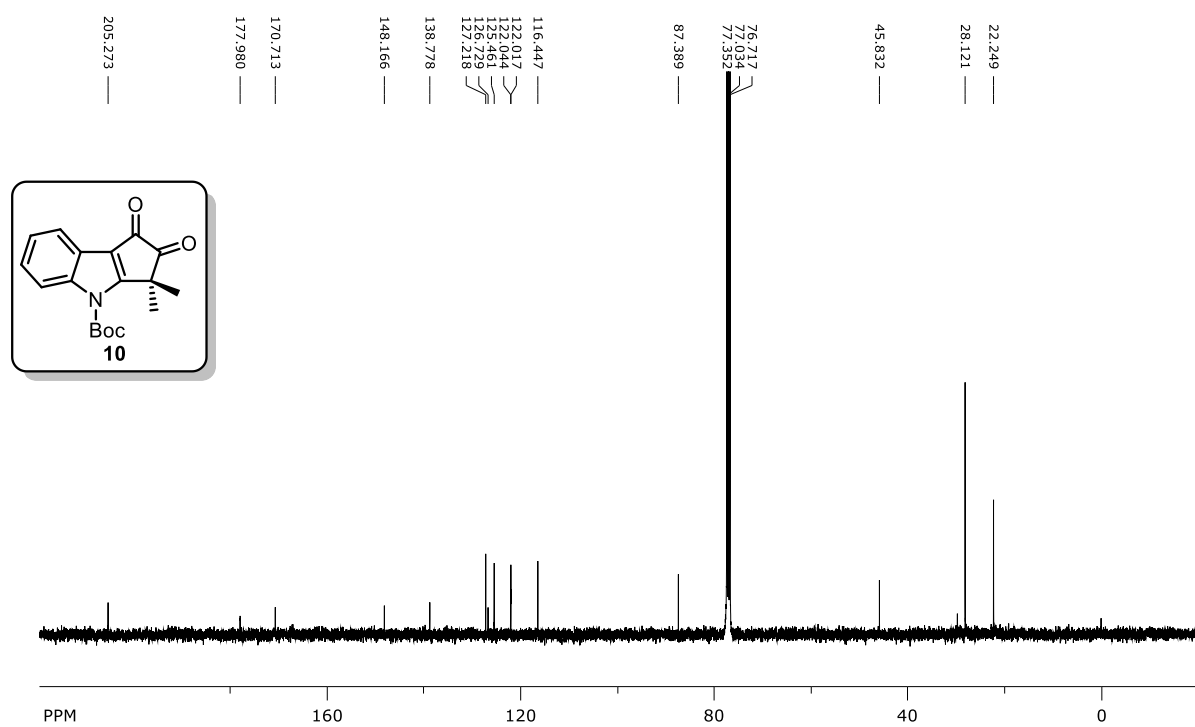
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



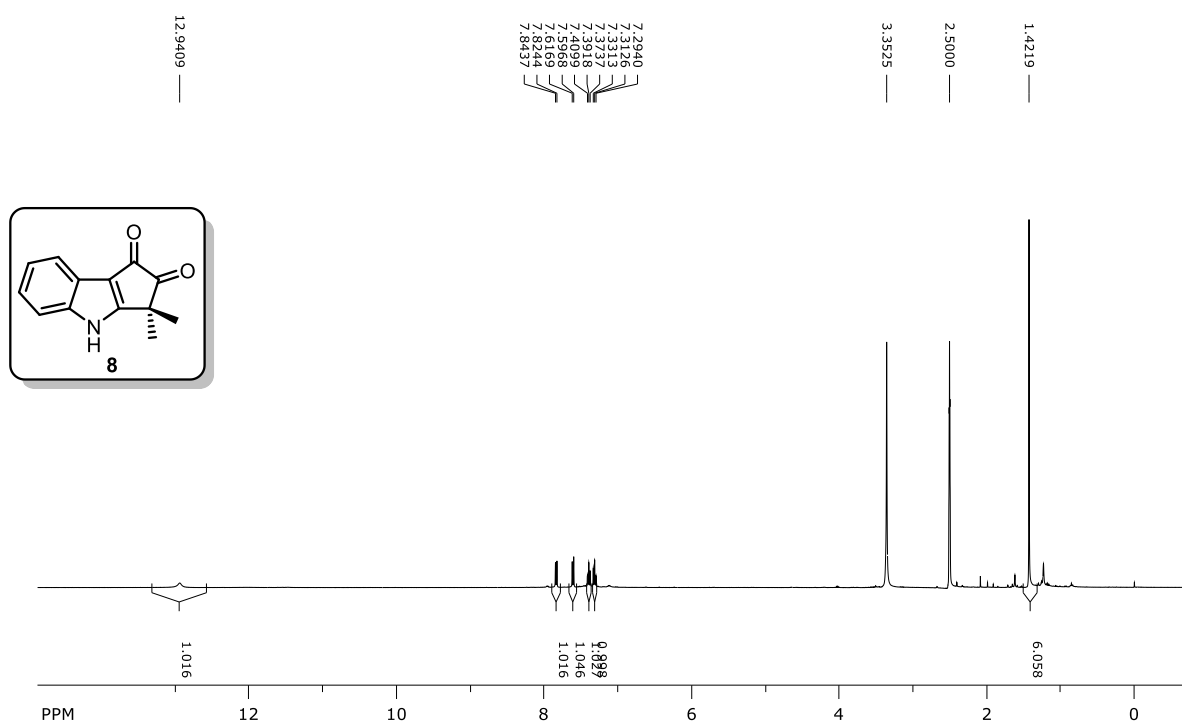
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**



**$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d^6$ ):**



**$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d^6$ ):**

