Supporting Information

for

Phosphine-catalysed denitrative rearomatising (3+2) annulation of α,β-ynones and 3-nitroindoles

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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_2SO_4 (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 ν_{max} in inverse centimeters. Melting points were recorded on a digital melting point apparatus Stuart SMP30 and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) 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 $CDCl_3$ (δ 77.1 ppm) and $(CD_3)_2SO$ (δ 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.[1,2,3]

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.

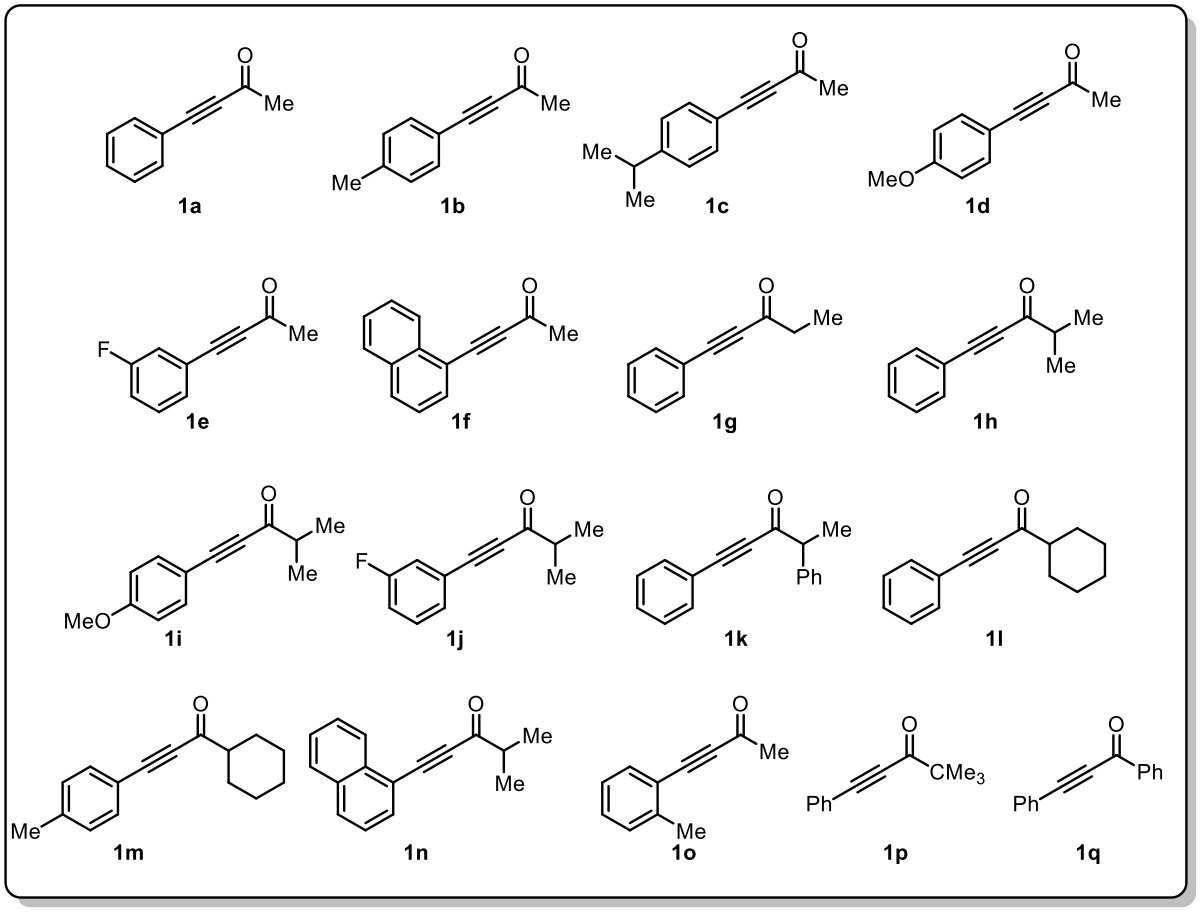


Figure 1S: Ynones employed during this study

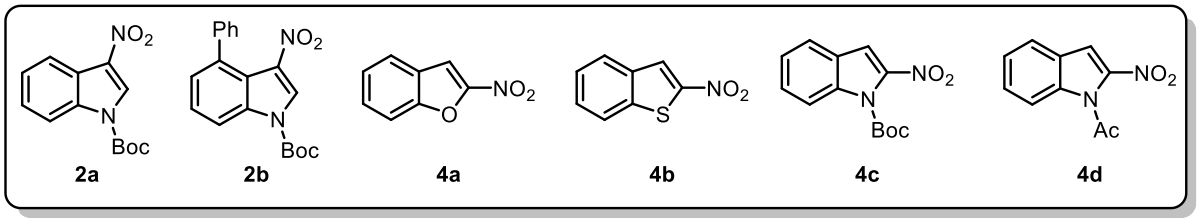
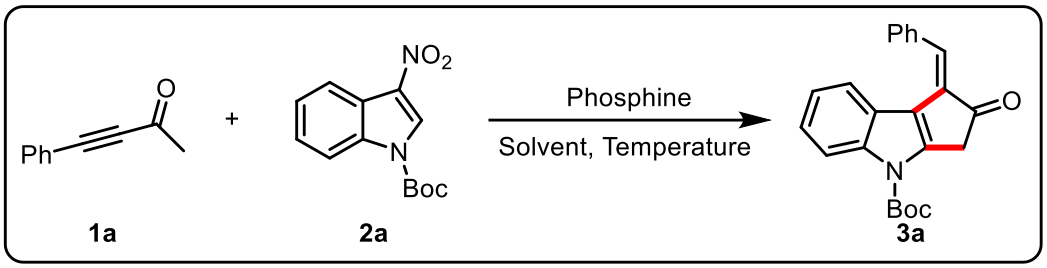


Figure 2S: Nitro-substituted heterocycles employed during this study

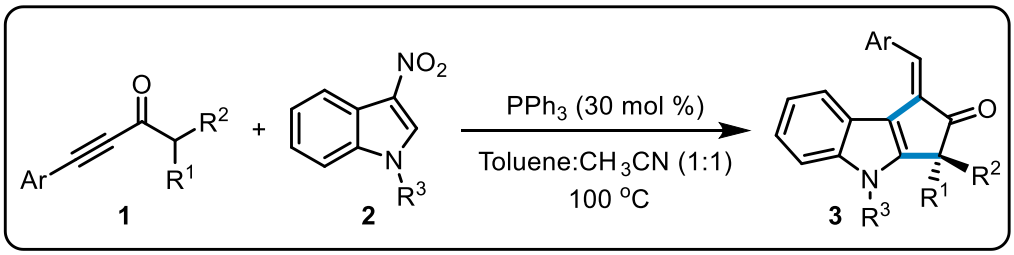
General procedure-1: Optimization of reaction parameters for 3a



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_2SO_4, 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

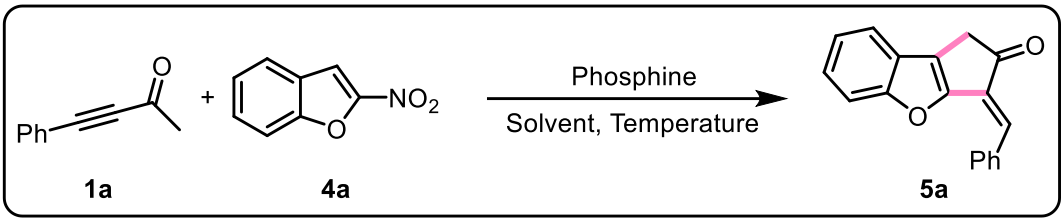


Scheme 2S: Synthesis of **3a-3o**

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_2SO_4, 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.



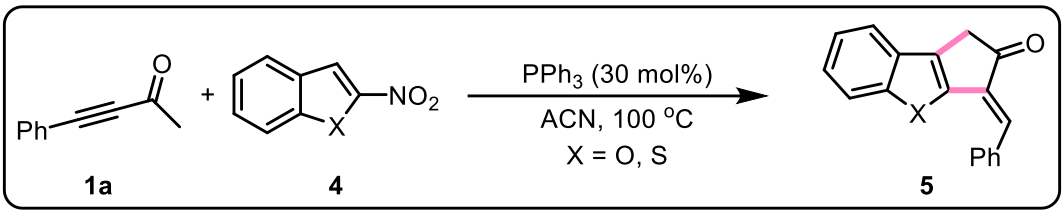
Scheme S3: Optimization of reaction parameters.

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_2SO_4, 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.

Sl No.	Phosphine (mol%)	Solvent	Temp (°C)	Time (h)	Yield (%)
1.	PPh_3 (30)	Toluene-ACN (1:1)	100	16	21
2.	PBu_3 (30)	Toluene-ACN (1:1)	100	7	10
3.	PCy_3 (30)	Toluene-ACN (1:1)	100	16	13
4.	PPh_3 (30)	Toluene	100	24	trace
5.	**PPh_3 (30)**	**ACN**	**100**	**18**	**63**
6.	PPh_3 (30)	1,4-Dioxane	100	24	decomposed
7.	PPh_3 (30)	DMF	100	24	decomposed
8.	PPh_3 (30)	DCM	50	24	trace

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

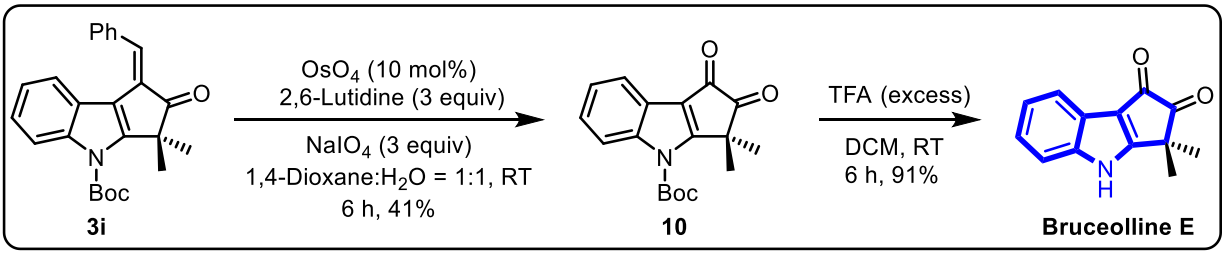
General procedure-4: Evaluating the substrate scope for 5



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_3 (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_2SO_4, 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.

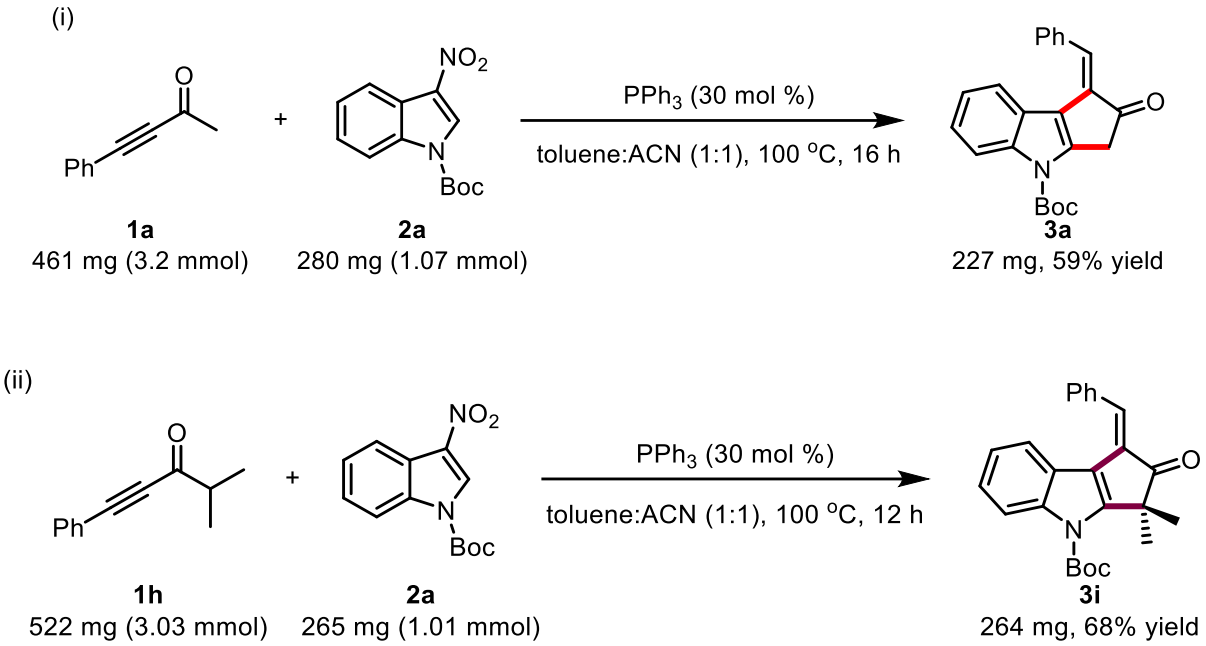
Step 1:

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_4 (0.1 equiv, 0.025 mmol) and $NaIO_4$ (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_2SO_4, 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 $NaHCO_3$ and extracted with DCM (2 x 2 mL). The organic extracts were combined, dried over Na_2SO_4, 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.

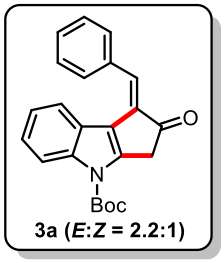
Scale-up reactions of 1a and 1h with 2a: The scale-up reactions were performed as described in the general procedure-2.



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

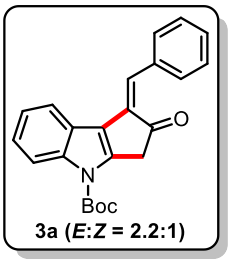
Spectroscopic data of the newly synthesized compounds during the present study

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



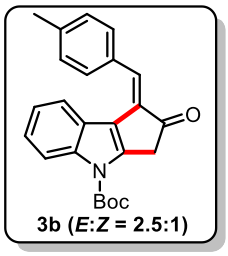
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 35 mg of **2a** afforded 37 mg of **3a** (77% yield). R_f = 0.5 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2984, 1740, 1373, 1242, 1046, 787. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.30 (d, *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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{23}H_{22}NO_3$ $(M+H)^+$: 360.1600, found: 360.1599.

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



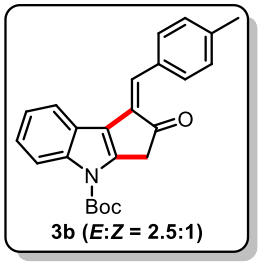
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29-8.26 (m, 1H), 7.57 (d, *J* = 7.96 Hz, 1H), 7.46-7.33 (m, 3H), 7.40-7.37 (m, 1H), 7.36-7.34 (m, 1H), 7.33-7.32 (m, 1H), 7.30-7.26 (m, 1H), 7.05 (dt, *J* = 8.08 and 0.88 Hz, 1H), 3.81 (s, 2H), 1.68 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 203.3, 149.0, 143.3, 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):**



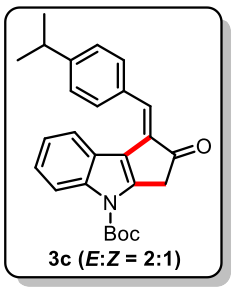
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 32 mg of **3b** (75% yield). R_f = 0.5 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2978, 1716, 1454, 1366, 1156, 751. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.29 (t, *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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{24}H_{23}NNaO_3$ $(M+Na)^+$: 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):**



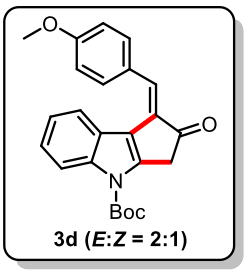
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.24-7.20 (m, 6H), 6.73 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 2H), 2.44 (s, 3H), 1.68 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 203.4, 149.1, 143.07, 138.5, 138.3, 133.6, 131.5, 130.0 (2C), 129.9, 128.99 (2C), 125.9, 124.5, 124.2, 123.4, 123.1, 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):**



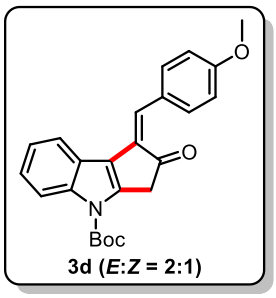
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 34 mg of **3c** (74% yield). R_f = 0.4 (EtOAc/ Hexane = 0.5/9.5). **M.P** = 148-150 °C. **IR (thin film, neat):** ν_{max}/cm^{-1} 2962, 1730, 1365, 1321, 1117, 746. **^{1}H NMR (400 MHz, $CDCl_3$)**: 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). **^{13}C NMR (100 MHz, $CDCl_3$)**: 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 $C_{26}H_{28}NO_3$ $(M+H)^+$: 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):**



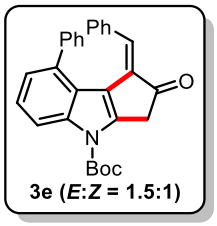
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 30 mg of **3d** (68% yield). R_f = 0.4 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3049, 2939, 1735, 1321, 1254, 1113, 736. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.02 (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). **^{13}C NMR (100 MHz, $CDCl_3$)**: 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 $C_{24}H_{24}NO_4$ $(M+H)^+$: 390.1705, found: 390.1690.

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



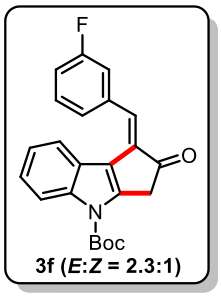
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.30-8.28 (m, 2H), 7.32-7.30 (m, 2H), 6.97-6.92 (m, 4H), 6.82 (d, *J* = 7.9 Hz, 1H), 3.86 (s, 3H), 3.74 (s, 2H), 1.67 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 201.8, 160.0, 149.2, 139.0, 138.3, 132.4 (2C), 130.4, 129.9, 128.0, 126.1, 124.8, 123.4, 124.33, 123.1, 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(1*H*)-carboxylate (major isomer) (3e):**



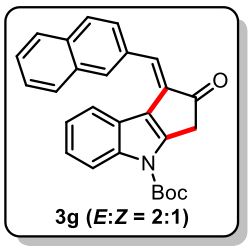
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 20 mg of **2b** afforded 11 mg of **3e** (43% yield). R_f = 0.6 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2977, 1732, 1344, 1252, 1123, 754. **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.39 (d, *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). **^{13}C NMR (100 MHz, CDCl$_3$)**: 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 $C_{29}H_{26}NO_3$ $(M+H)^+$: 436.1913, found: 436.1904.

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



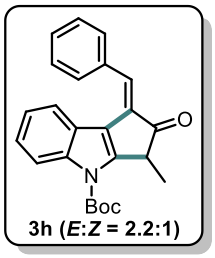
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 27 mg of **3f** (63% yield). R_f = 0.5 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2978, 1736, 1369, 1322, 1138, 760. **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.30 (d, *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). **^{13}C NMR (100 MHz, CDCl$_3$)**: 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). **^{19}F NMR (376.4 MHz, CDCl$_3$)**: δ -113.34. **HRMS (ESI)**: m/z calcd for $C_{18}H_{11}FNO$ $(M-Boc)^+$: 276.0825, found: 276.0818.

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



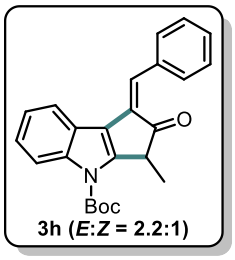
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 35 mg of **3g** (74% yield). R_f = 0.4 (EtOAc/ Hexane = 0.5/9.5). **M.P** = 168-170 ºC. **IR (thin film, neat):** ν_{max}/cm^{-1} 3055, 2978, 1731, 1369, 1352, 1111, 762. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{27}H_{23}NNaO_3$ $(M+Na)^+$: 432.1585, found: 432.1576.

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



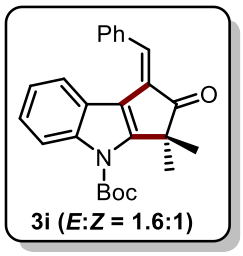
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 30 mg of **3h** (70% yield). R_f = 0.45 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2978, 1727, 1354, 1316, 1154, 1116, 736. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.20 (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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{24}H_{24}NO_3$ $(M+H)^+$: 374.1756, found: 374.1787.

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



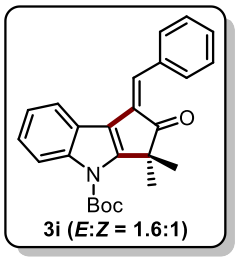
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.74-7.72 (m, 2H), 7.28-7.16 (m, 5H), 6.95 (t, *J* = 8.1 Hz, 1H), 6.48 (d, *J* = 7.9 HZ, 1H), 3.73 (q, *J* = 7.4 Hz, 1H), 1.62 (s, 9H), 1.47 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 206.8, 149.06, 148.9, 138.8, 136.8, 131.0, 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):**



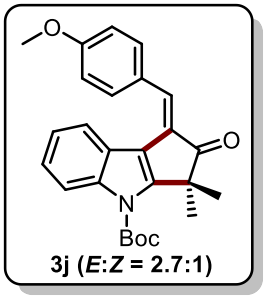
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 31 mg of **3i** (69% yield). R_f = 0.4 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2974, 1737, 1363, 1155, 1107, 760. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.23-8.20 (m, 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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{25}H_{26}NO_3$ $(M+H)^+$: 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):**



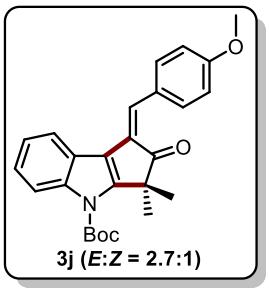
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.45-7.44 (m, 2H), 7.38-7.33 (m, 4H), 7.29-7.24 (m, 1H), 7.02 (dt, *J* = 8.0 and 0.8 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 1.74 (s, 9H), 1.59 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 207.8, 149.5, 149.3, 138.7, 135.1, 129.8, 129.74, 128.8, 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):**



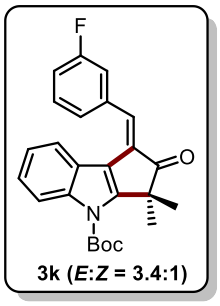
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 34 mg of **3j** (71% yield). R_f = 0.4 (EtOAc/ Hexane = 0.5/9.5). **M.P** = 150-152 ºC. **IR (thin film, neat):** ν_{max}/cm^{-1} 2970, 1730, 1300, 1251, 1151, 1104, 742. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{26}H_{28}NO_4$ $(M+H)^+$: 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):**



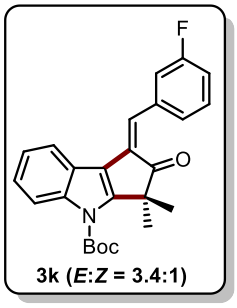
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.87-7.85 (m, 2H), 7.32 (s, 1H), 7.30-7.26 (m, 1H), 7.08 (dt, *J* = 8.0 and 0.8 Hz, 1H), 6.93-6.92 (m, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 3H), 1.75 (s, 9H), 1.58 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 209.8, 159.9, 152.2, 149.2, 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):**



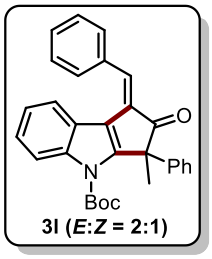
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 32 mg of **3k** (70% yield). R_f = 0.35 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} [1] 2975, 1736, 1358, 1303, 1153, 1109, 747. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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). **^{13}C NMR (100 MHz, $CDCl_3$)**: 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). **^{19}F NMR (376.4 MHz, $CDCl_3$)**: δ -113.44. **HRMS (ESI)**: m/z calcd for $C_{25}H_{24}FNNaO_3$ $(M+Na)^+$: 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):**



^{1}H NMR (400 MHz, $CDCl_3$): Peaks corresponding to the minor isomer are not clearly distinguishable. **^{13}C NMR (100 MHz, $CDCl_3$)**: 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* = 23.1Hz, 1C), 115.4 (d, *J* = 15.8 Hz, 1C), 85.4, 48.8, 28.2 (3C), 22.70 (2C). **^{19}F NMR (376.4 MHz, $CDCl_3$)**: δ -111.78.

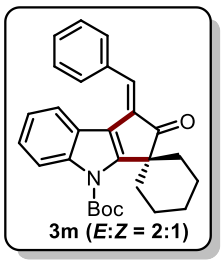
***tert*-Butyl (*E*)-1-benzylidene-3-methyl-2-oxo-3-phenyl-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (3l):**



3l (*E*:*Z* = 2:1)

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):** ν_{max}/cm^{-1} 2978, 1730, 1351, 1311, 1142, 745. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{30}H_{28}NO_3$ $(M+H)^+$: 450.2069, found: 450.2093.

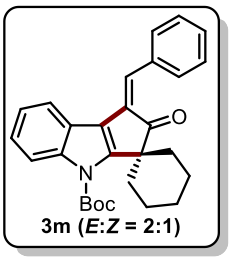
***tert*-Butyl (*E*)-1'-benzylidene-2'-oxo-1',2'-dihydro-4'*H*-spiro[cyclohexane-1,3'-cyclopenta[*b*]indole]-4'-carboxylate (major isomer) (3m):**



3m (*E*:*Z* = 2:1)

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):** ν_{max}/cm^{-1} 2931, 1732, 1359, 1301, 1152, 742. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{28}H_{29}NNaO_3$ $(M+Na)^+$: 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):**

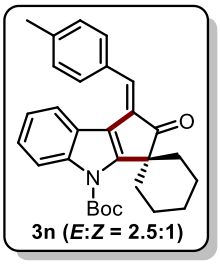


3m (*E*:*Z* = 2:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 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}C NMR (100 MHz, $CDCl_3$)**: δ 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).

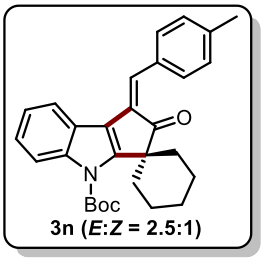
***tert*-Butyl (*E*)-1'-(4-methylbenzylidene)-2'-oxo-1',2'-dihydro-4'*H*-spiro[cyclohexane-1,3'-cyclopenta[*b*]indole]-4'-carboxylate (major isomer) (3n):**



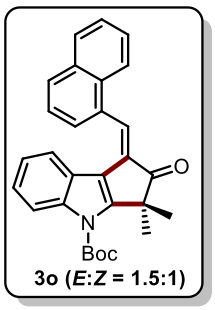
This compound was isolated as pale-yellow liquid. Following the general procedure-2, 30 mg of **2a** afforded 33 mg of **3n** (65% yield). R_f = 0.4 (EtOAc/ Hexane = 0.5/9.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2978, 1731, 1352, 1142, 745. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.14-8.12 (m, 1H), 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}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{29}H_{32}NO_3$ $(M+H)^+$: 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}H NMR (400 MHz, $CDCl_3$): δ 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}C NMR (100 MHz, $CDCl_3$)**: δ 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).



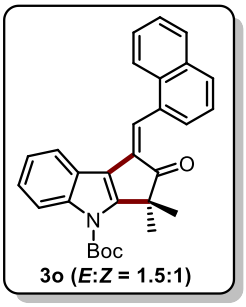
***tert*-Butyl (*E*)-3,3-dimethyl-1-(naphthalen-1-ylmethylene)-2-oxo-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (major isomer) (3o):**



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):** ν_{max}/cm^{-1} 2972, 1737, 1369, 1312, 1165, 1109. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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}C NMR**

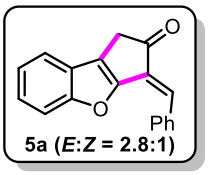
(100 MHz, $CDCl_3$): δ 209.5, 152.9, 149.2, 138.78, 134.4, 133.3, 132.3, 131.3, 129.0, 128.5, 127.7, 126.5, 126.30, 125.9, 125.4, 125.13, 124.5, 124.1, 123.71, 123.3, 121.5, 115.9, 85.2, 49.71, 28.2 (3C), 22.7 (2C). **HRMS (ESI)**: m/z calcd for $C_{29}H_{27}NNaO_3$ $(M+Na)^+$: 460.1889, found: 460.1906.

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



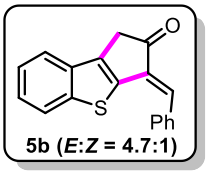
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.91 (m, 4H), 7.90-7.85 (m, 2H), 7.80 (s, 1H), 7.49-7.48 (m, 3H), 7.43-7.40 (m, 2H), 1.75 (s, 9H), 1.53 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 207.5, 150.0, 138.73, 134.5, 133.3, 131.7, 131.4, 130.8, 128.7, 128.2, 127.8, 126.6, 126.34, 126.27, 125.9, 125.7, 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 ºC. **IR (thin film, neat):** ν_{max}/cm^{-1} 2929, 1731, 1515, 1372, 1111, 750. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{18}H_{13}O_2$ $(M+H)^+$: 261.0916, found: 261.0912.

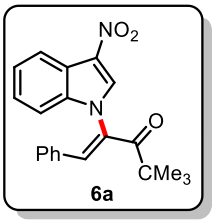
(*Z*)-3-Benzylidene-1,3-dihydro-2*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one (major isomer) (5b):



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):** ν_{max}/cm^{-1} 3058, 2926, 1732, 1617, 1190, 755. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 203.0, 141.7, 140.1, 140.0, 135.1, 134.7, 133.0, 129.5,

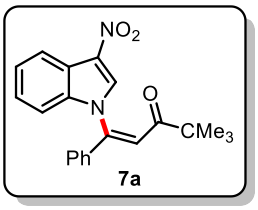
128.9 (2C), 128.8 (2C), 128.2, 126.2, 125.1, 123.0, 122.3, 38.4. **HRMS (ESI)**: m/z calcd for $C_{18}H_{13}OS$ $(M+H)^+$: 277.0687, found: 277.0685.

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



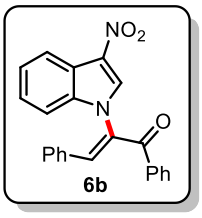
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 12 mg of **6a** (30% yield). R_f = 0.45 (EtOAc/ Hexane = 1/4). **M.P** = 164-166 ^oC. **IR (thin film, neat):** ν_{max}/cm^{-1} 2968, 1689, 1602, 1533, 1482, 1453, 1305, 1228, 751. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{21}H_{21}N_2O_3$ $(M+H)^+$: 349.1552, found: 349.1554.

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



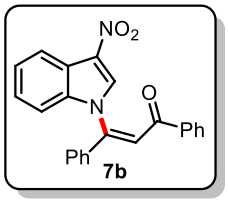
This compound was isolated as pale-yellow solid. Following the general procedure-2, 30 mg of **2a** afforded 11 mg of **7a** (27% yield). R_f = 0.45 (EtOAc/ Hexane = 1/4). **M.P** = 135-137 ^oC. **IR (thin film, neat):** ν_{max}/cm^{-1} 2968, 1689, 1600, 1536, 1482, 1450, 1228, 750. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 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). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{21}H_{21}N_2O_3$ $(M+H)^+$: 349.1552, found: 349.1546.

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



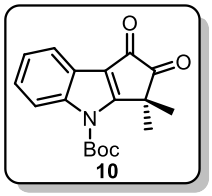
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 16 mg of **6b** (38% yield). R_f = 0.45 (EtOAc/ Hexane = 1/4). **IR (thin film, neat):** ν_{max}/cm^{-1} 2927, 1664, 1600, 1577, 1451, 1226, 751. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.24 (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). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 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 $C_{23}H_{17}N_2O_3$ $(M+H)^+$: 369.1239, found: 369.1249.

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



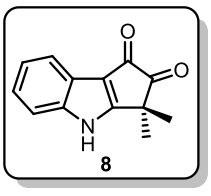
This compound was isolated as pale-yellow semi-solid. Following the general procedure-2, 30 mg of **2a** afforded 17 mg of **7b** (40% yield). R_f = 0.5 (EtOAc/ Hexane = 1/4). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1667, 1599, 1534, 1482, 1304, 1228, 751. **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 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}C NMR (100 MHz, CDCl$_3$)**: δ 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 $C_{23}H_{17}N_2O_3$ $(M+H)^+$: 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):** ν_{max}/cm^{-1} 2977, 1746, 1706, 1423, 1360, 1142, 765. **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 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}C NMR (100 MHz, CDCl$_3$)**: δ 205.2, 177.9, 170.7, 148.1, 138.7, 127.2, 126.7, 125.4, 122.0,4, 122.01, 116.4, 87.3, 45.8, 28.1 (3C), 22.2 (2C). **HRMS (ESI)**: m/z calcd for $C_{18}H_{19}NNaO_4$ $(M+Na)^+$: 336.1212, found: 336.1215.

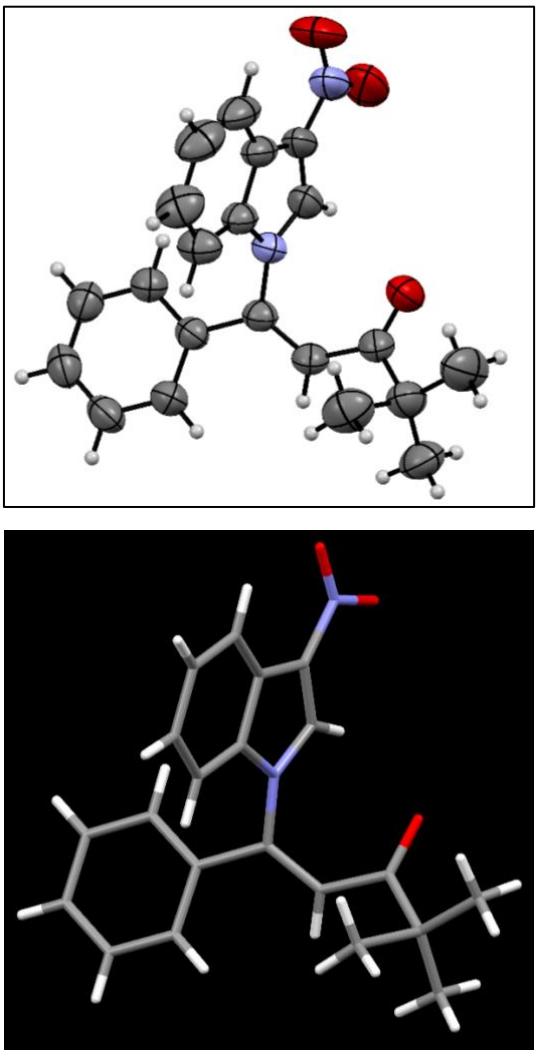
3,3-Dimethyl-3,4-dihydrocyclopenta[*b*]indole-1,2-dione (8):



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):** ν_{max}/cm^{-1} 3393, 1735, 1661, 1023, 996, 761. **^{1}H NMR (400 MHz, DMSO-*d*^{6})**: δ 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}C NMR (100 MHz, DMSO-*d*^{6})**: δ 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 $C_{13}H_{11}NNaO_2$ $(M+Na)^+$: 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.

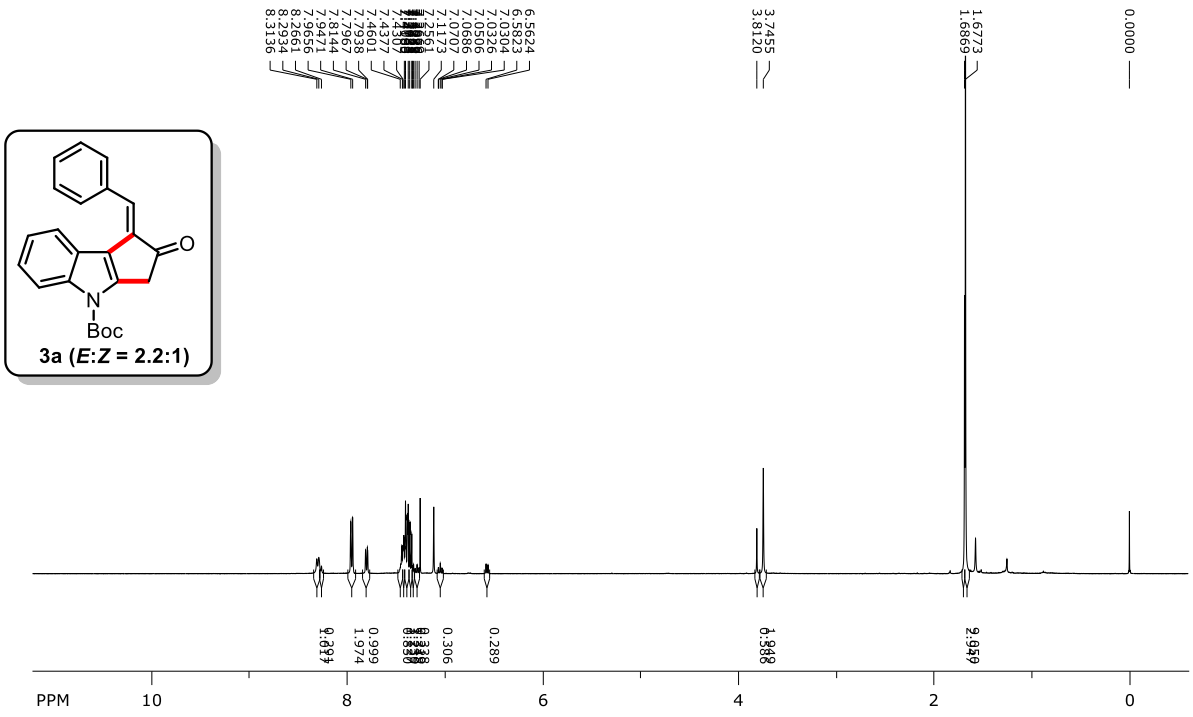
Crystal Data for $C_{21}H_{20}N_2O_3$ (M =348.39 g/mol): triclinic, space group P-1 (no. 2), a = 9.9977(7) Å, b = 10.0721(7) Å, c = 10.6301(8) Å, α = 73.343(7)°, β = 82.375(6)°, γ = 63.636(7)°, V = 918.83(11) Å^3, Z = 2, T = 293.0(10) K, μ(Mo Kα) = 0.085 mm^{-1}, *Dcalc* = 1.259 g/cm^3, 7049 reflections measured (5.32° ≤ 2Θ ≤ 65.48°), 5725 unique (R_{int} = 0.0197, R_{sigma} = 0.0459) which were used in all calculations. The final R_1 was 0.0648 (>2sigma(I)) and wR_2 was 0.2074

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

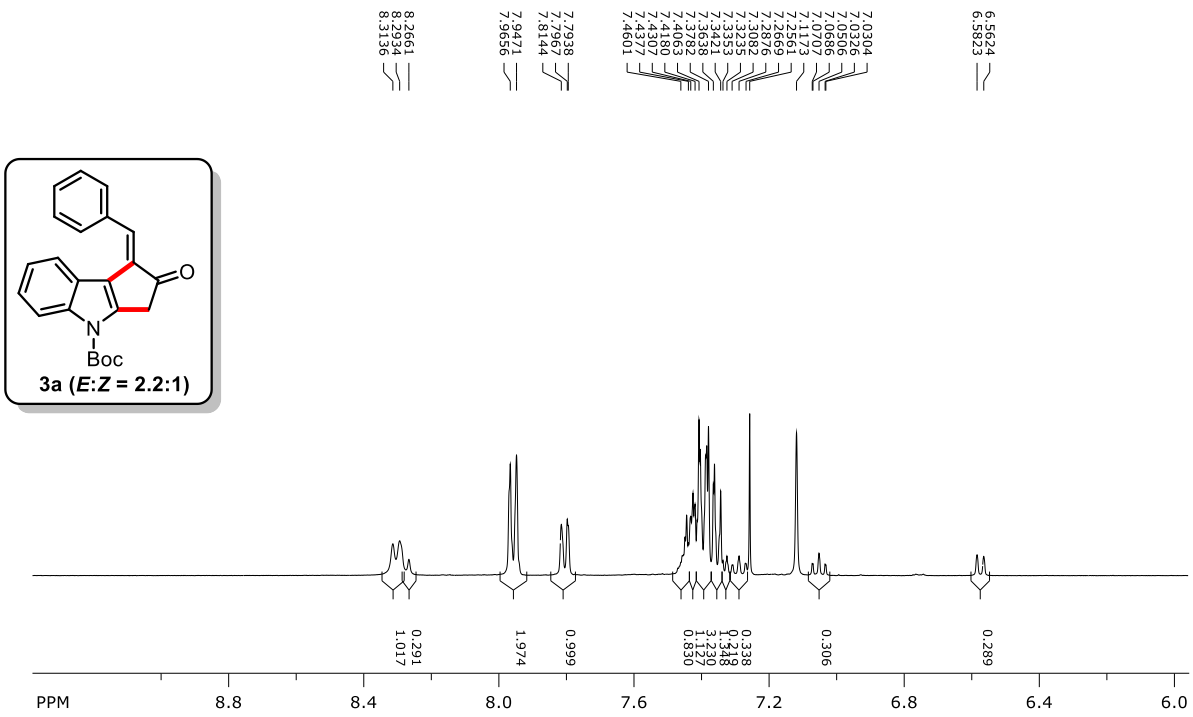
Identification code	7a
Empirical formula	$C_{21}H_{20}N_2O_3$
Formula weight	348.39
Temperature/K	293.0(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.9977(7)
b/Å	10.0721(7)
c/Å	10.6301(8)
α/°	73.343(7)
β/°	82.375(6)
γ/°	63.636(7)
Volume/Å^3	918.83(11)
Z	2
ρ_{calc}g/cm^3	1.259
μ/mm^{-1}	0.085
F(000)	368.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.32 to 65.48
Index ranges	$-14 \leq h \leq 14$, $-9 \leq k \leq 13$, $-16 \leq l \leq 15$
Reflections collected	7049
Independent reflections	5725 [R_{int} = 0.0197, R_{sigma} = 0.0459]
Data/restraints/parameters	5725/36/268
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0648, wR_2 = 0.1642
Final R indexes [all data]	R_1 = 0.1100, wR_2 = 0.2074
Largest diff. peak/hole / e Å^{-3}	0.27/-0.18

Copies of ^{1}H and ^{13}C-NMR spectra of all the newly synthesised compounds

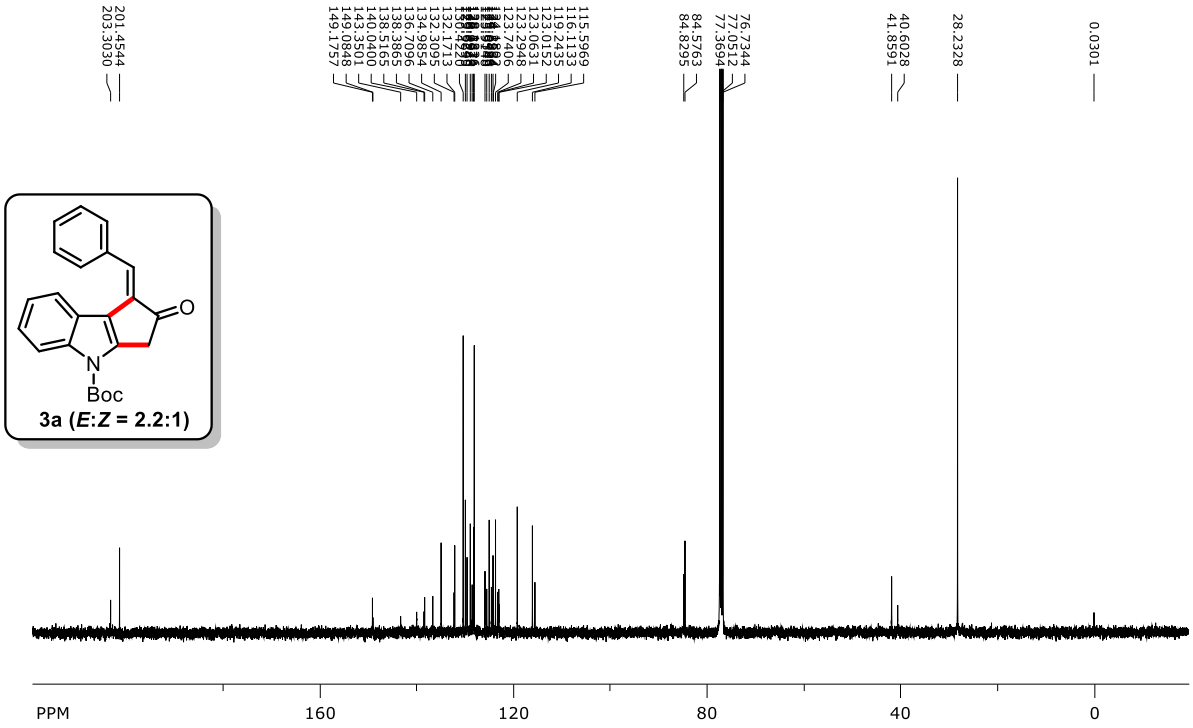
^{1}H NMR (400 MHz, $CDCl_3$):



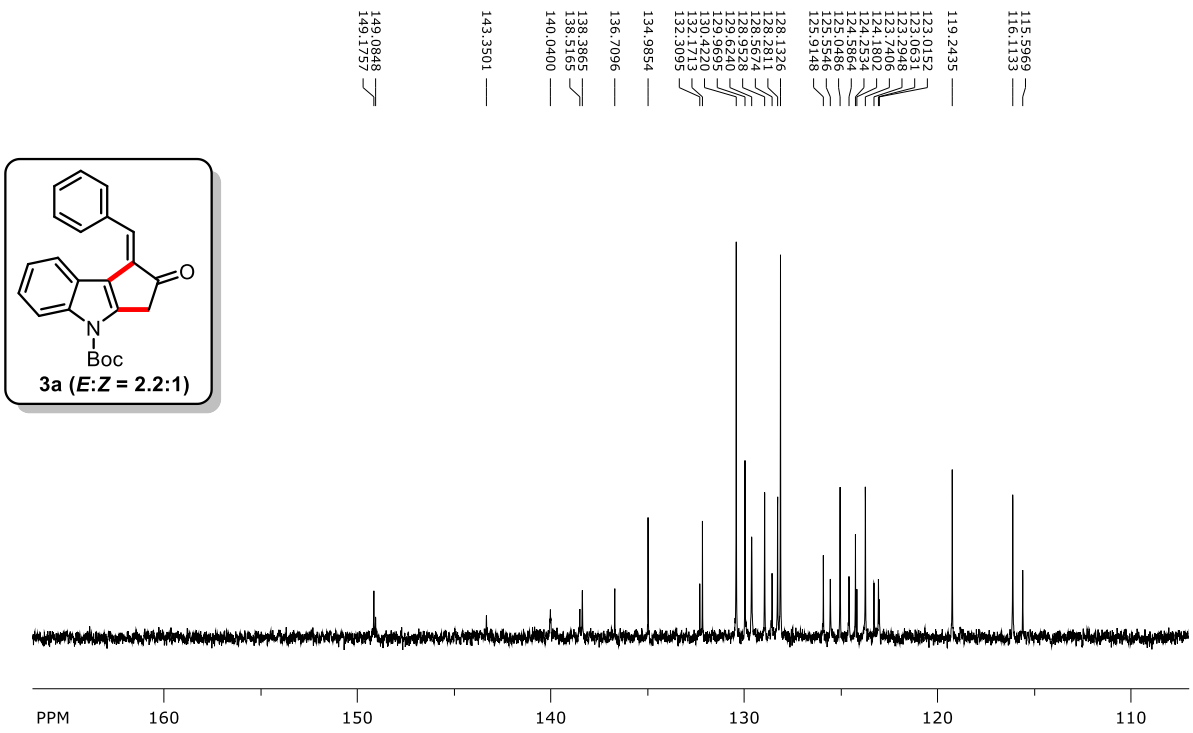
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.0-9.0 ppm region



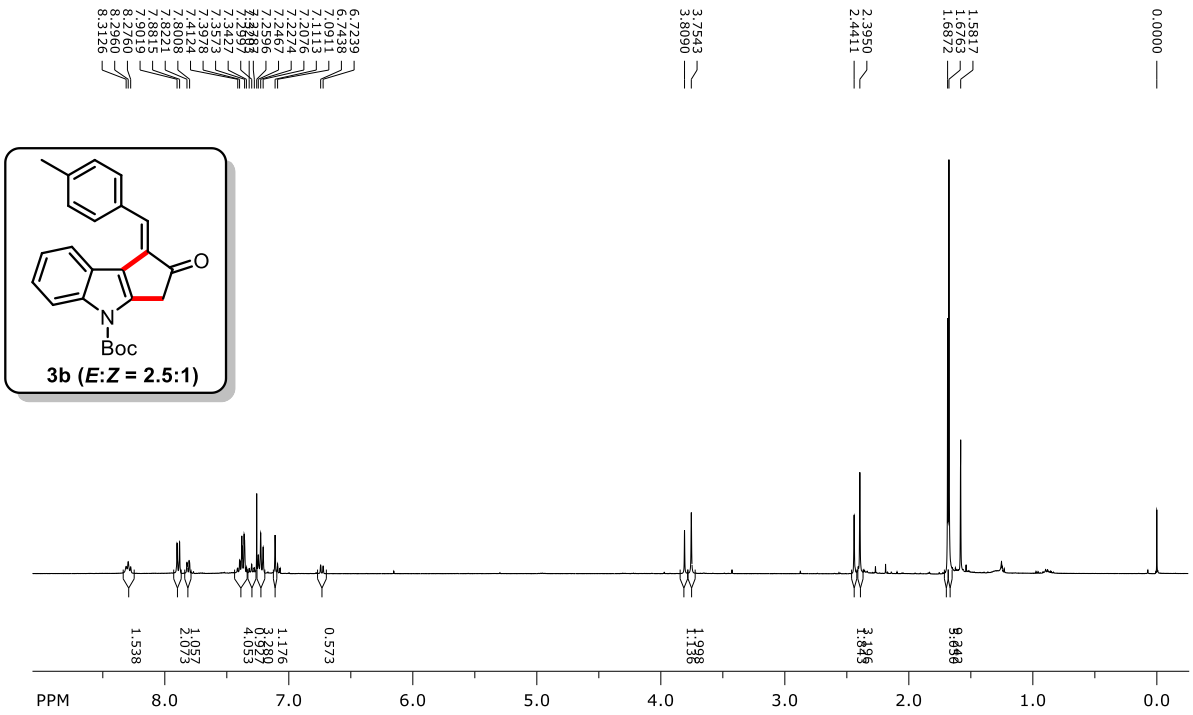
^{13}C NMR (100 MHz, $CDCl_3$):



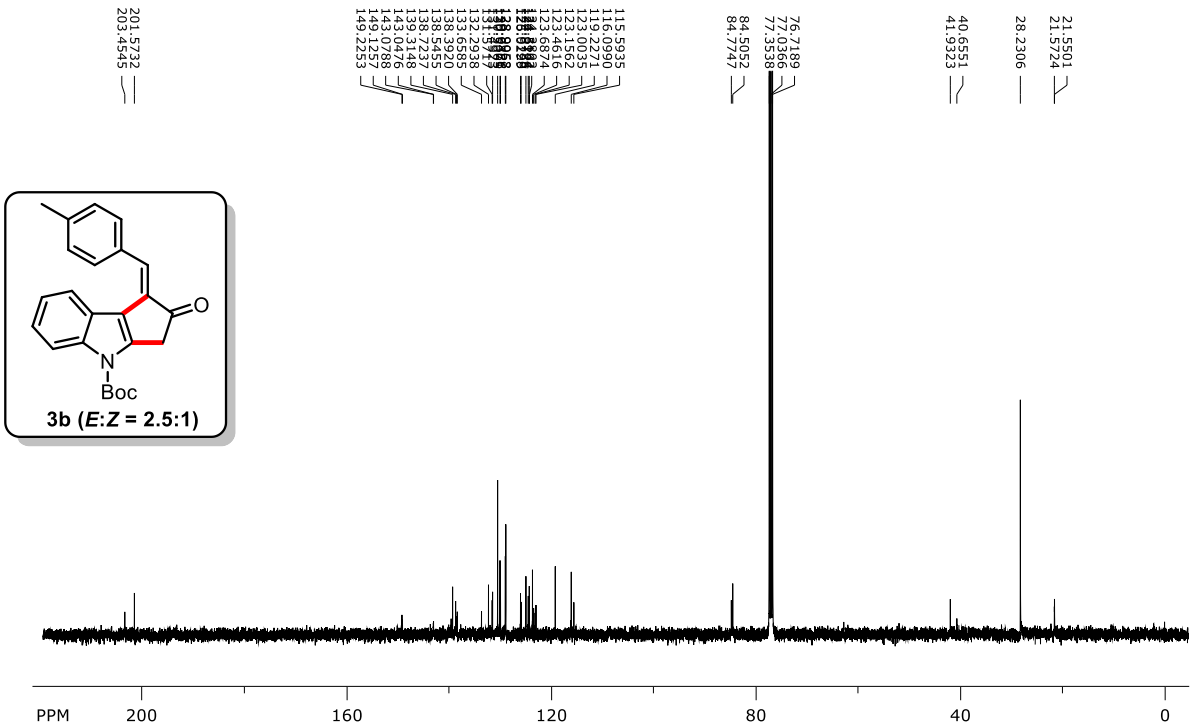
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-160 ppm region



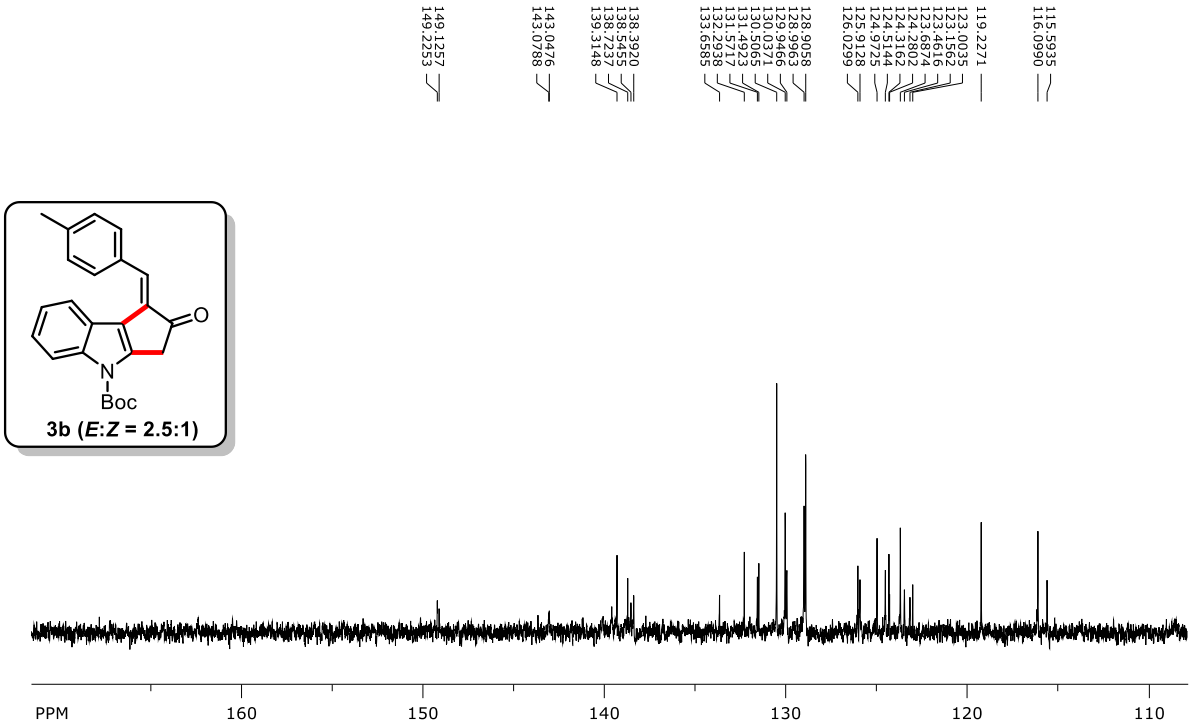
^{1}H NMR (400 MHz, $CDCl_3$):



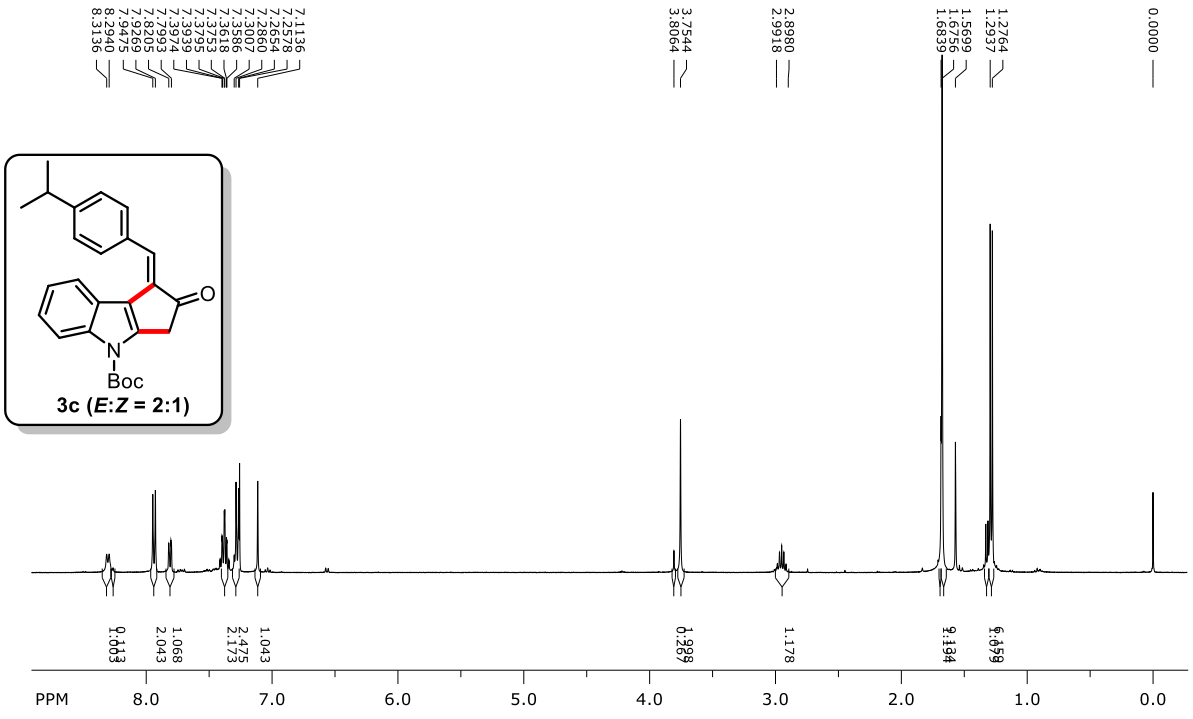
^{13}C NMR (100 MHz, $CDCl_3$):



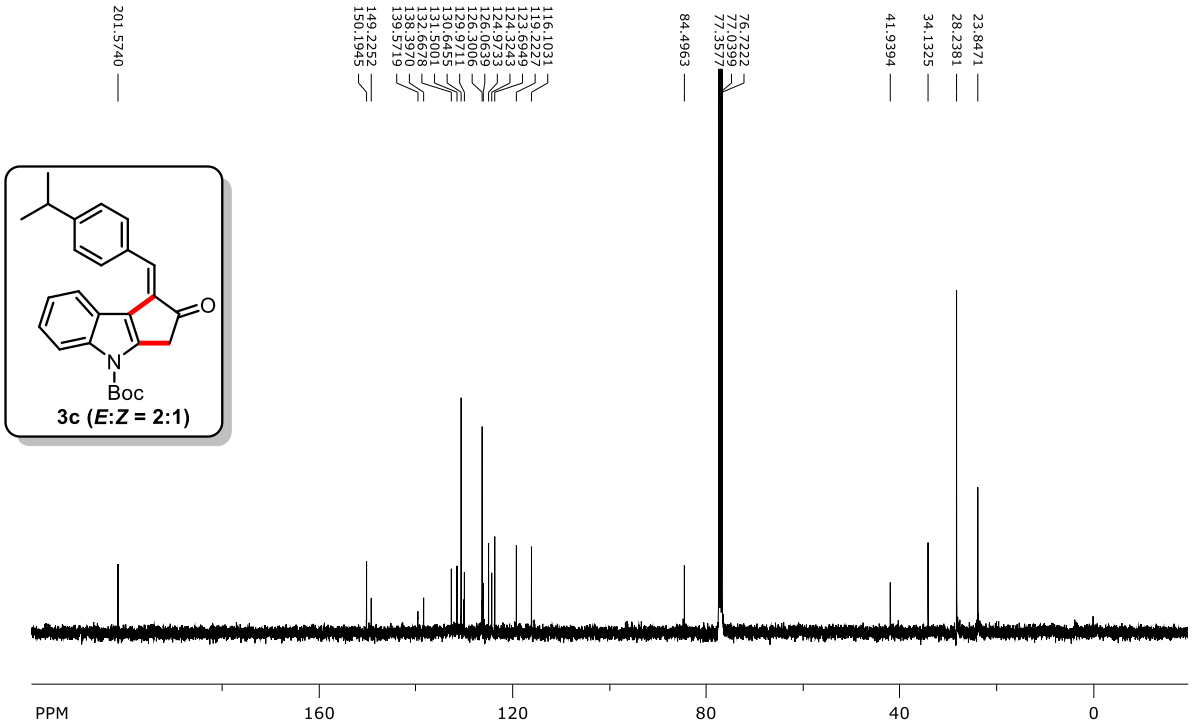
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-150 ppm region



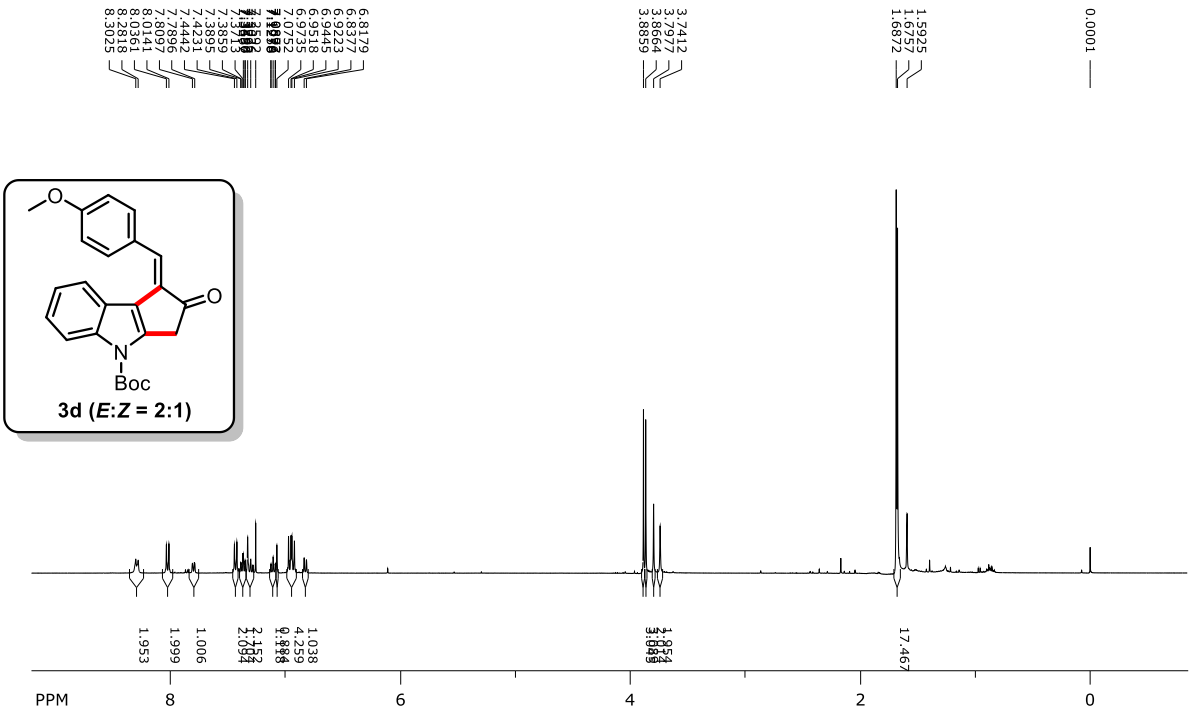
^{1}H NMR (400 MHz, $CDCl_3$):



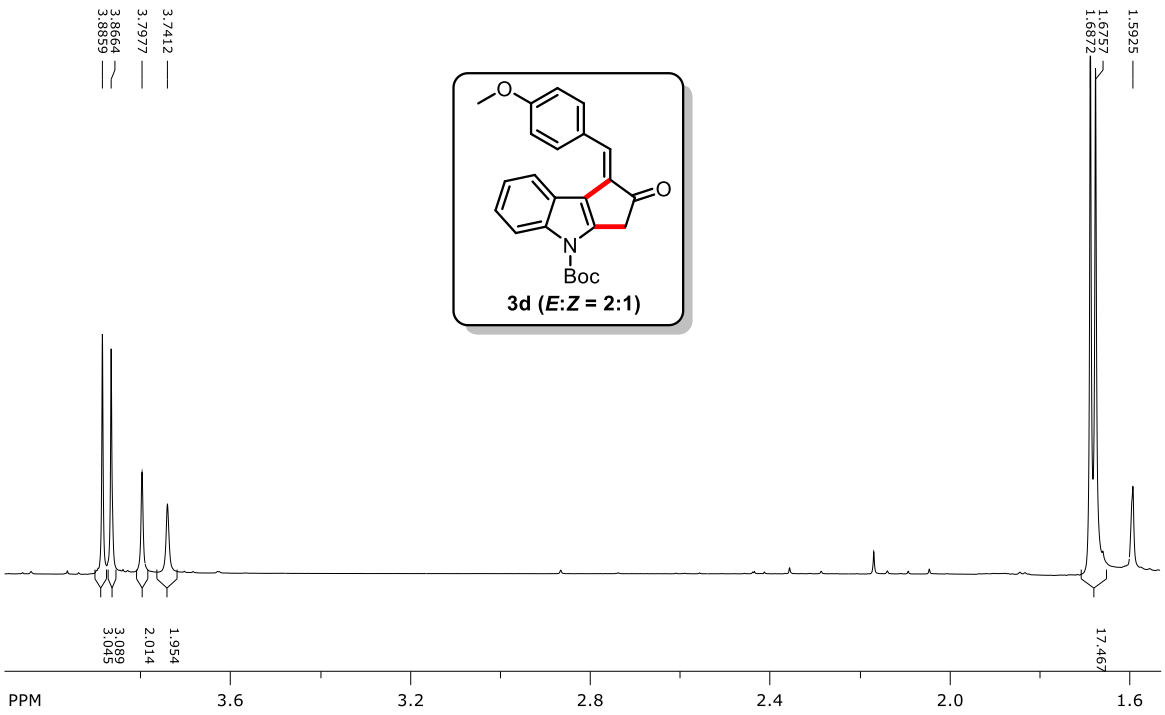
^{13}C NMR (100 MHz, $CDCl_3$):



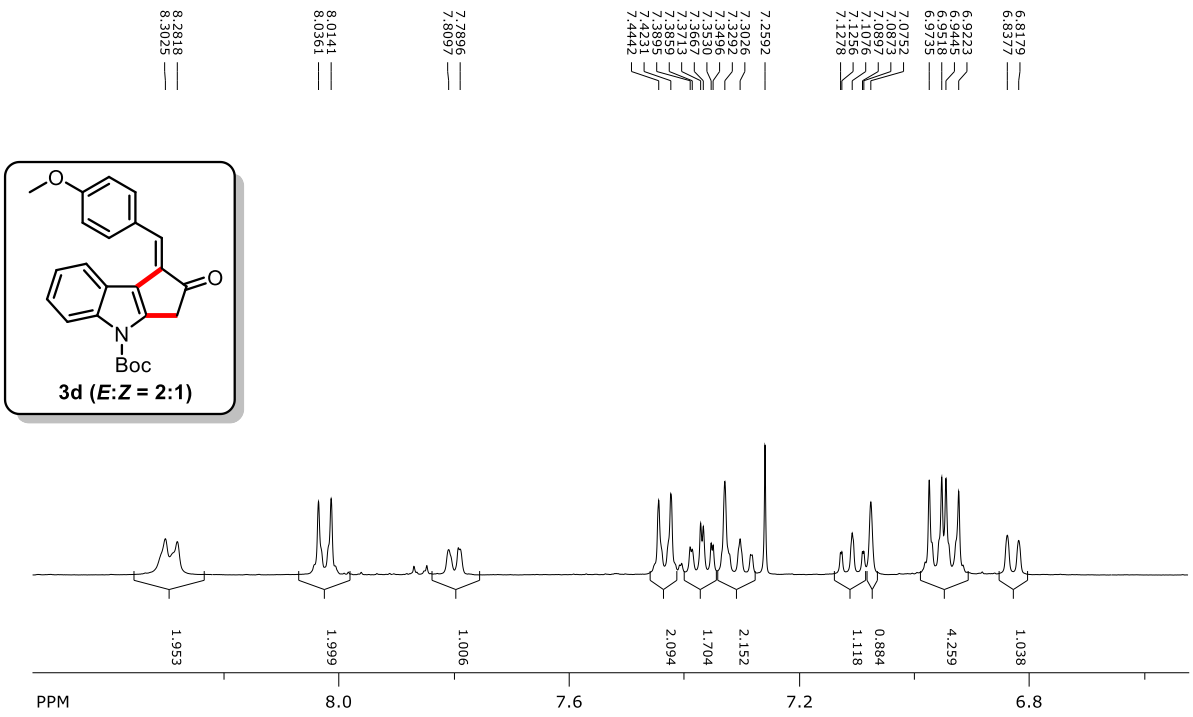
^{1}H NMR (400 MHz, $CDCl_3$):



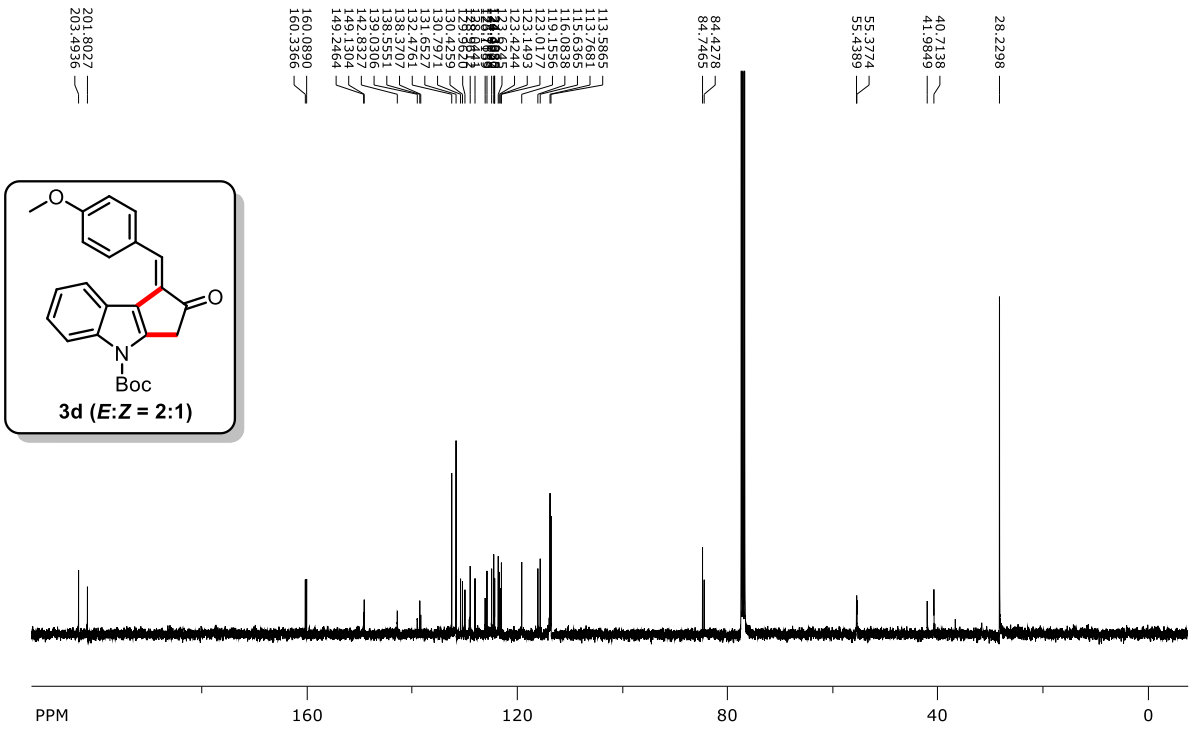
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 1.5-4 ppm region



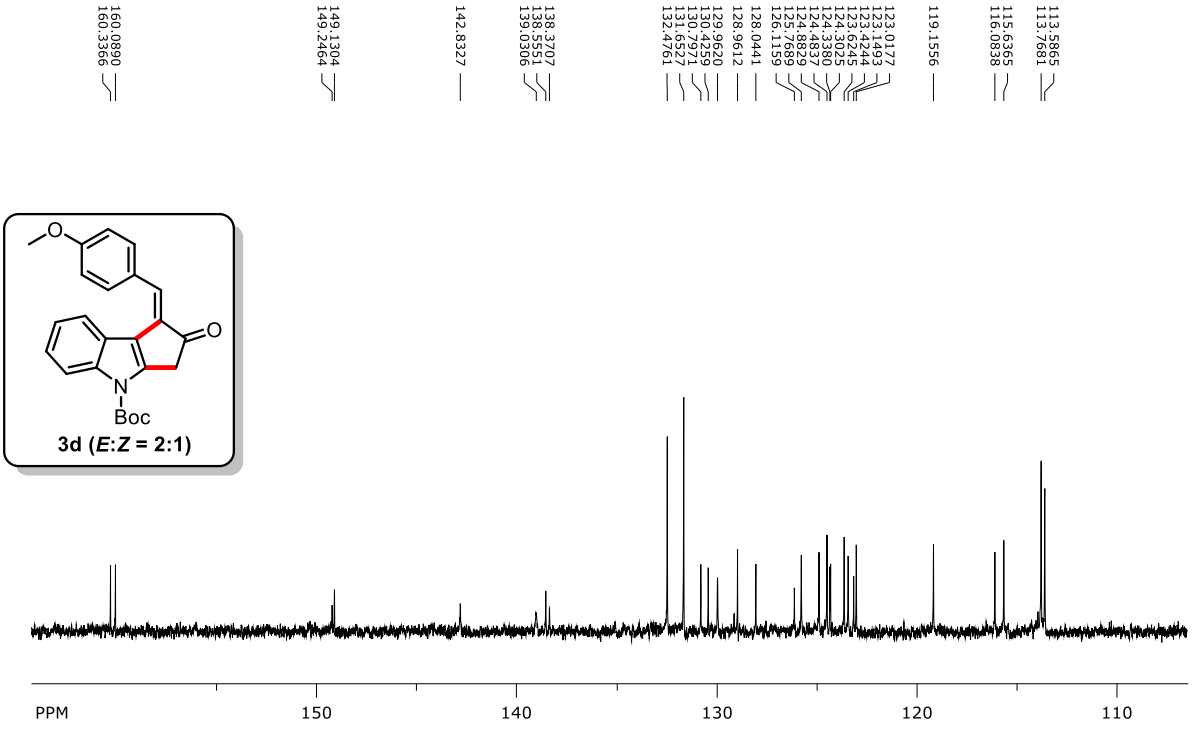
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.5-8.5 ppm region



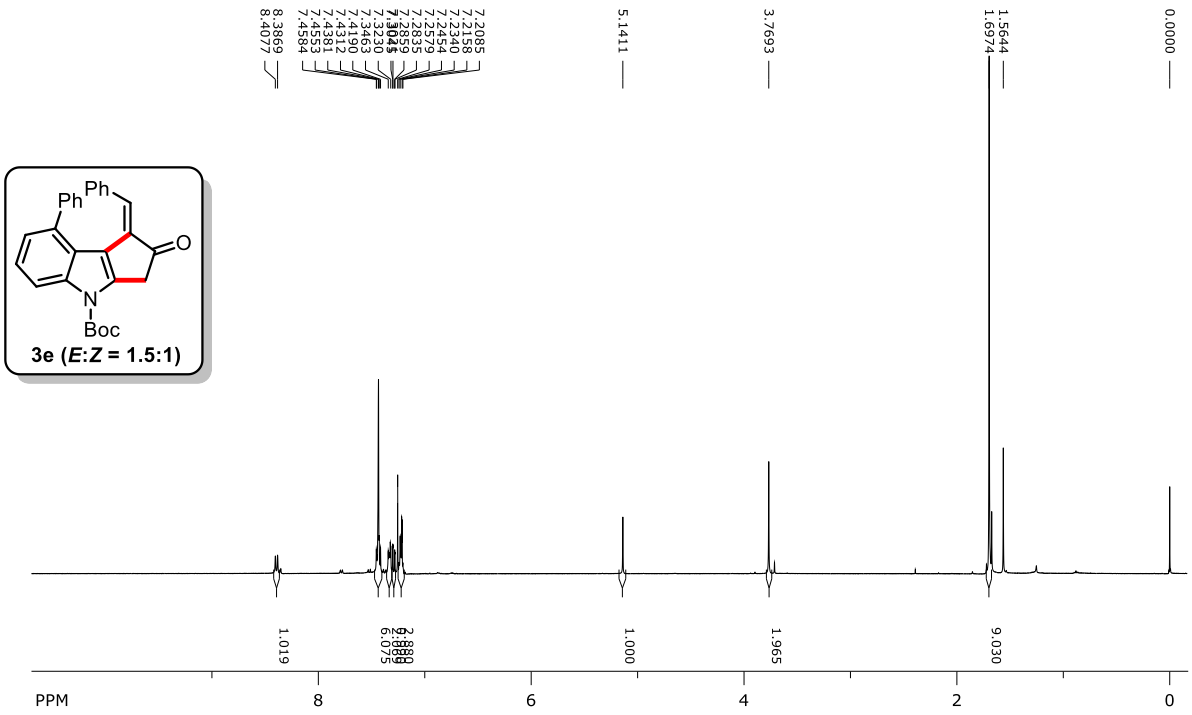
^{13}C NMR (100 MHz, $CDCl_3$):



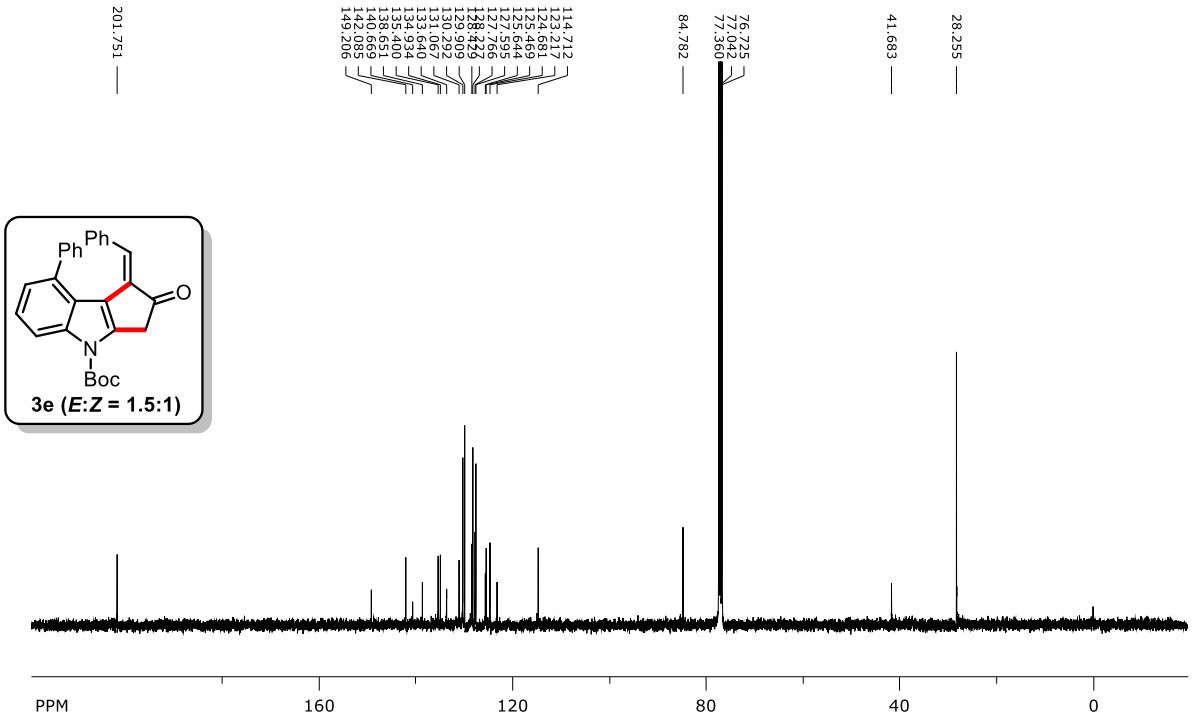
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-170 ppm region



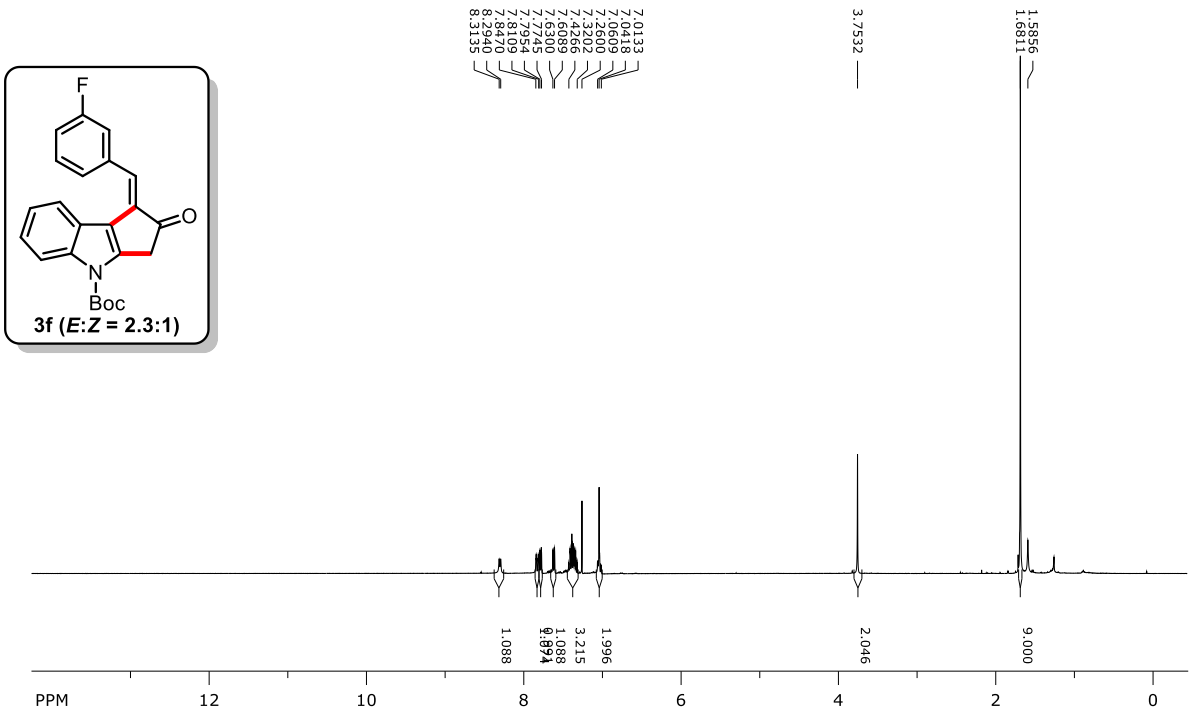
^{1}H NMR (400 MHz, $CDCl_3$):



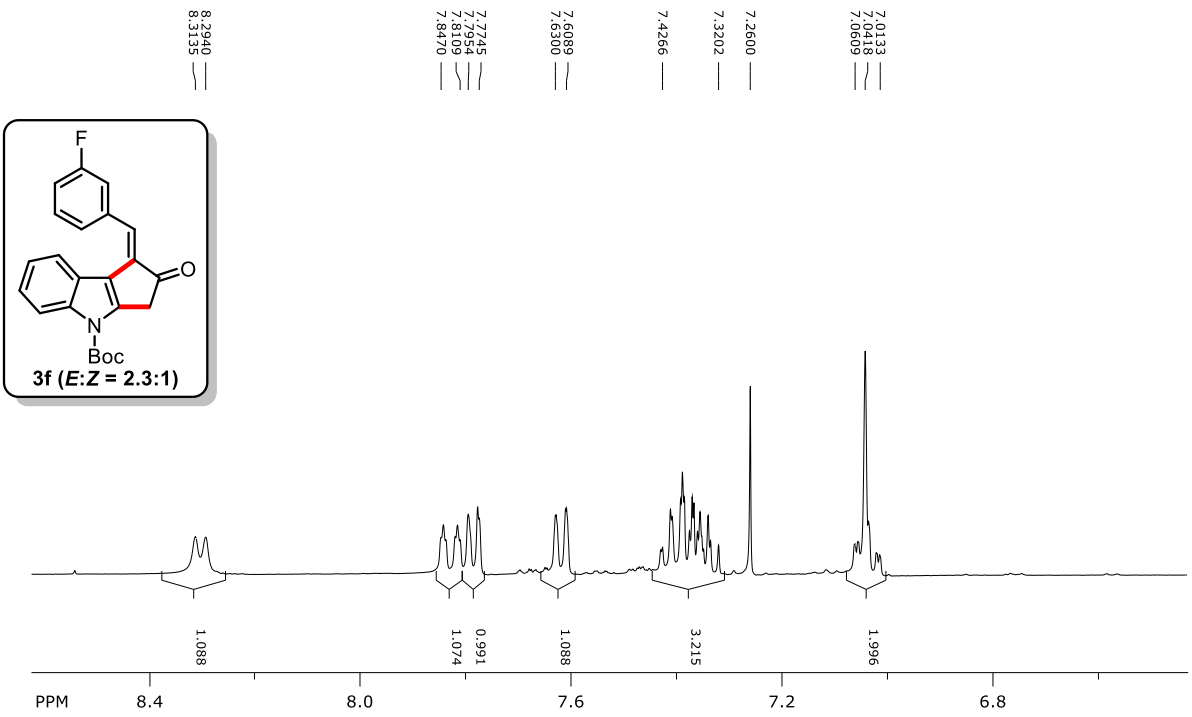
^{13}C NMR (100 MHz, $CDCl_3$):



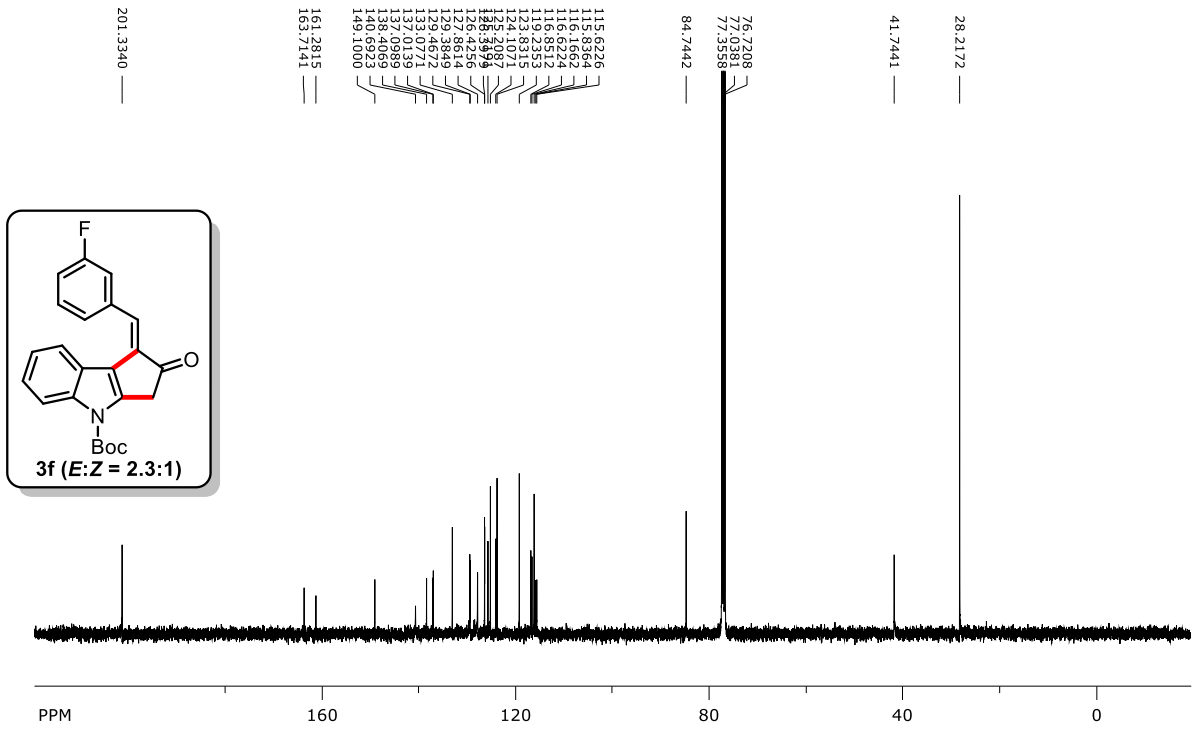
^{1}H NMR (400 MHz, $CDCl_3$):



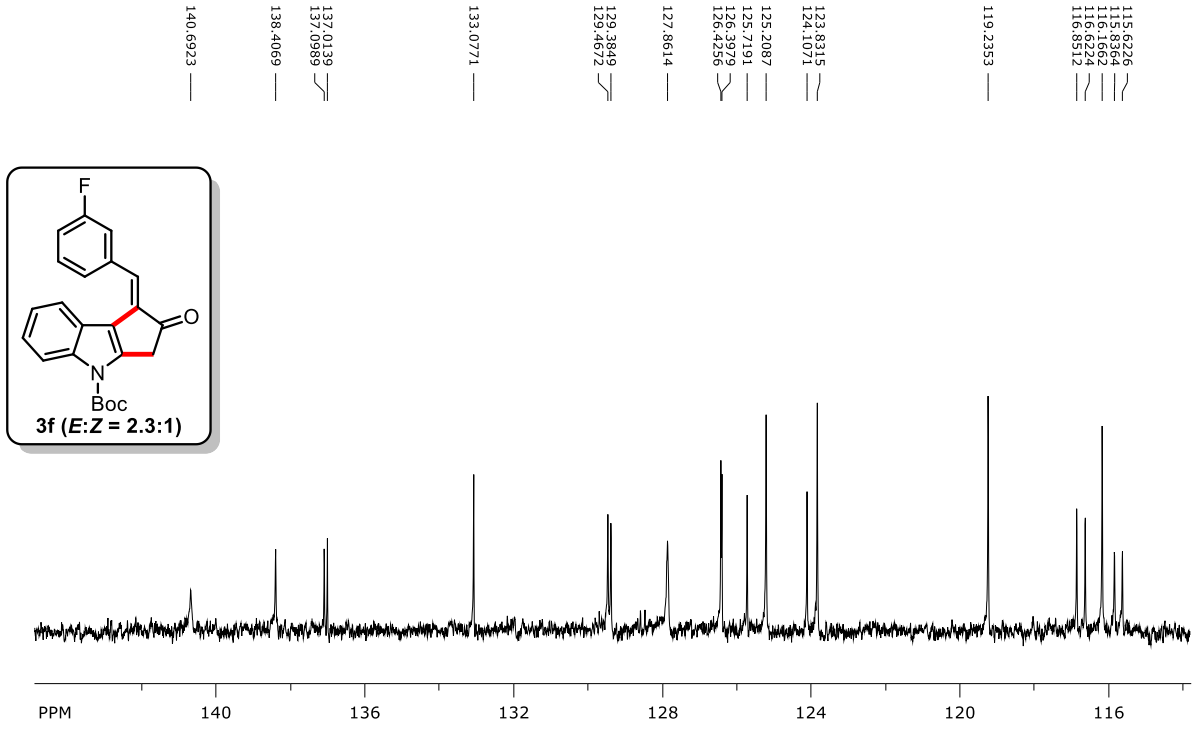
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.5-8.5 ppm region



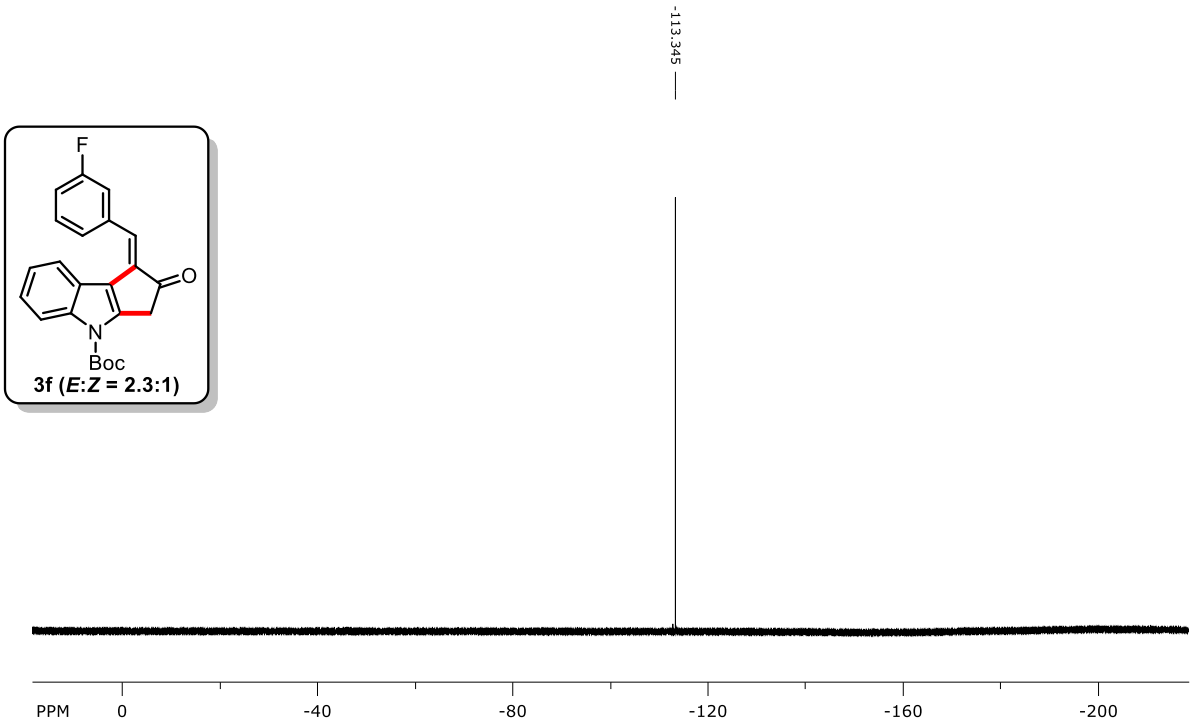
^{13}C NMR (100 MHz, $CDCl_3$):



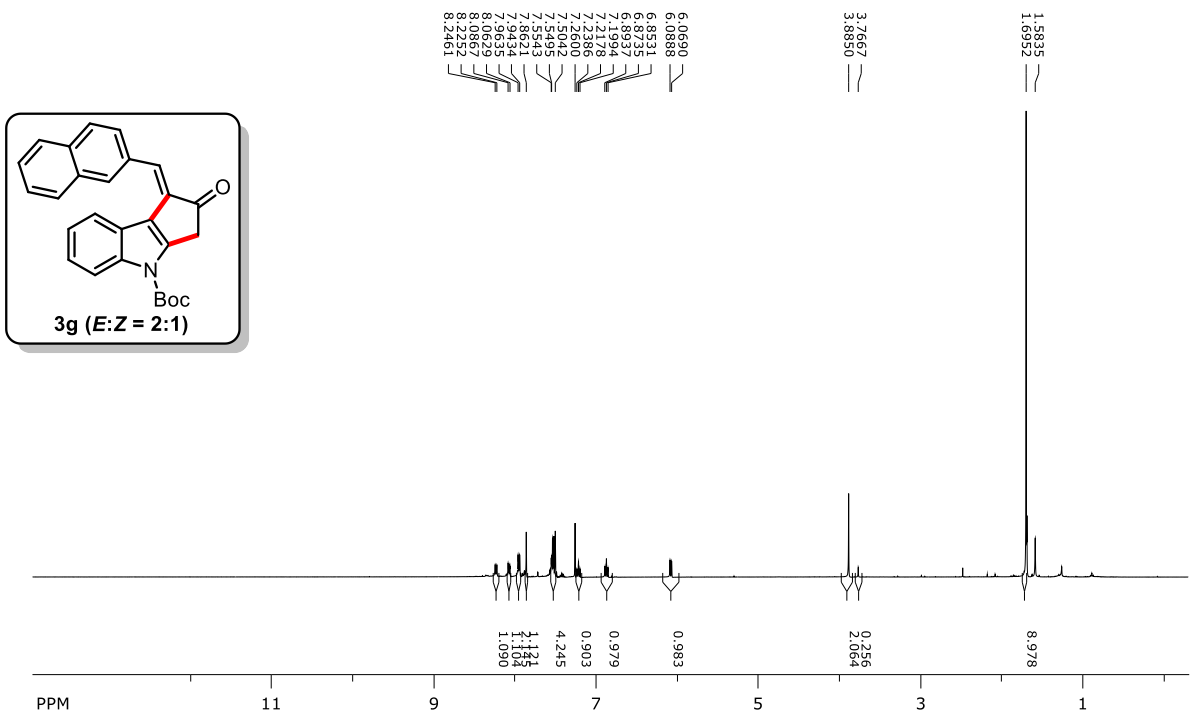
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-150 ppm region



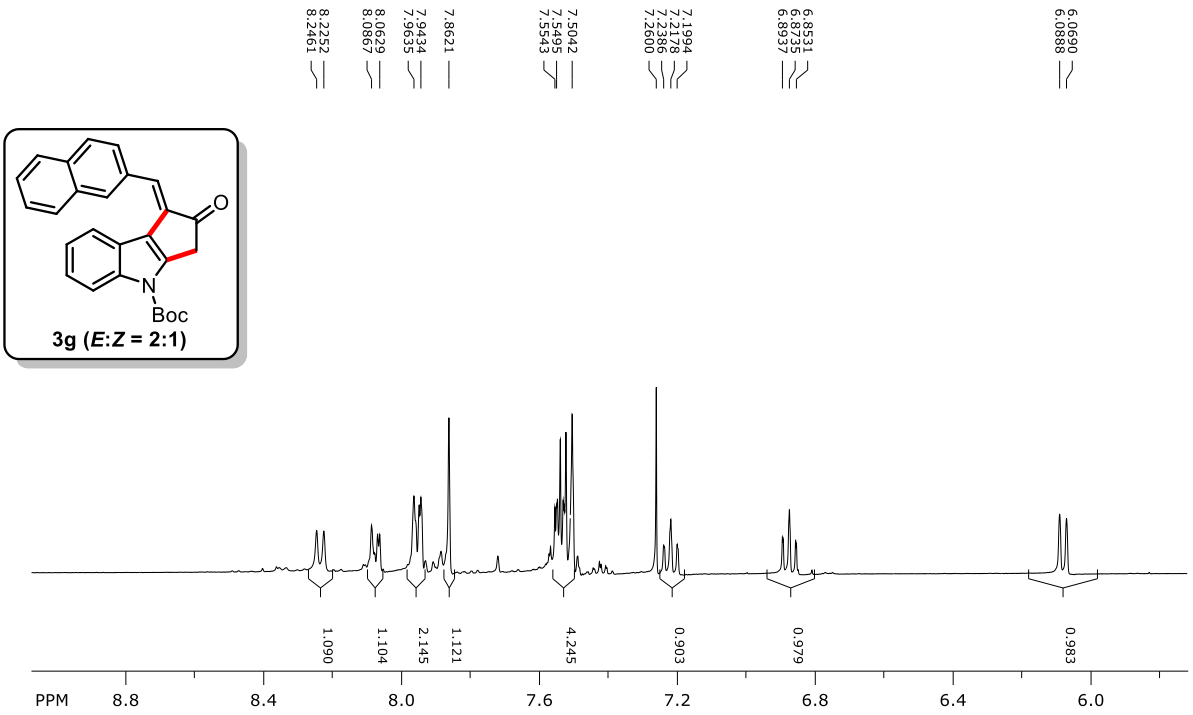
^{19}F NMR (376.5 MHz, $CDCl_3$):



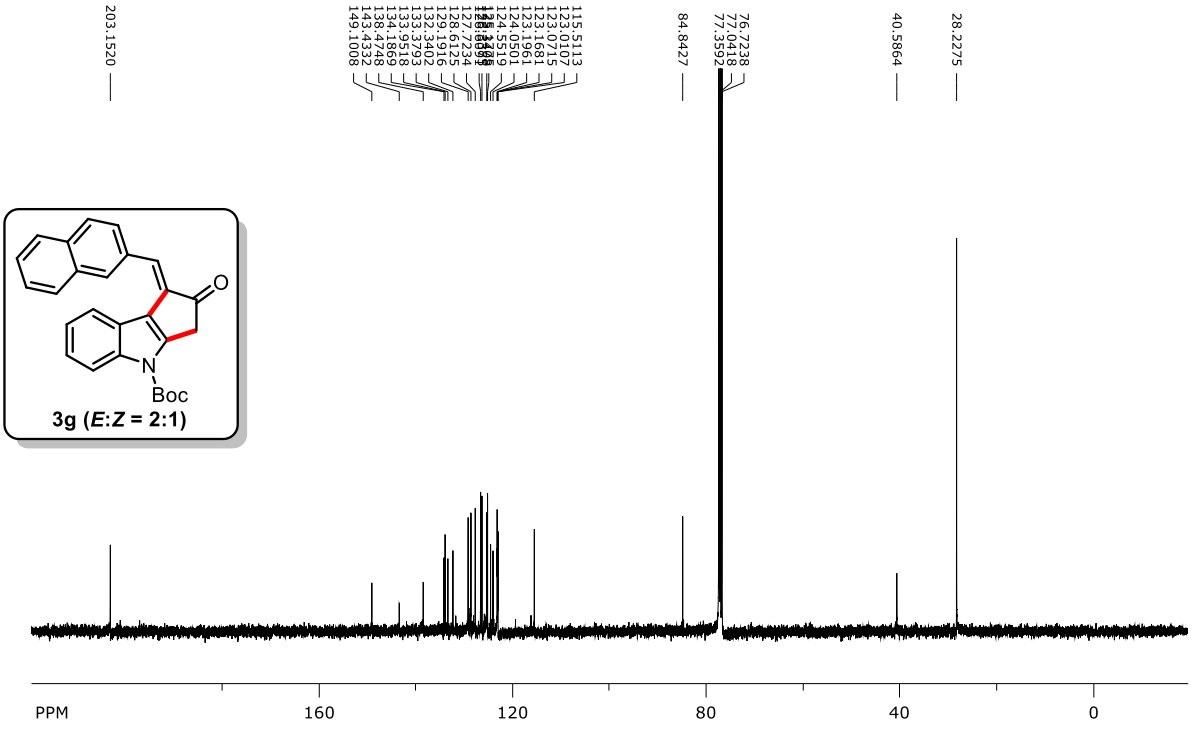
^{1}H NMR (400 MHz, $CDCl_3$):



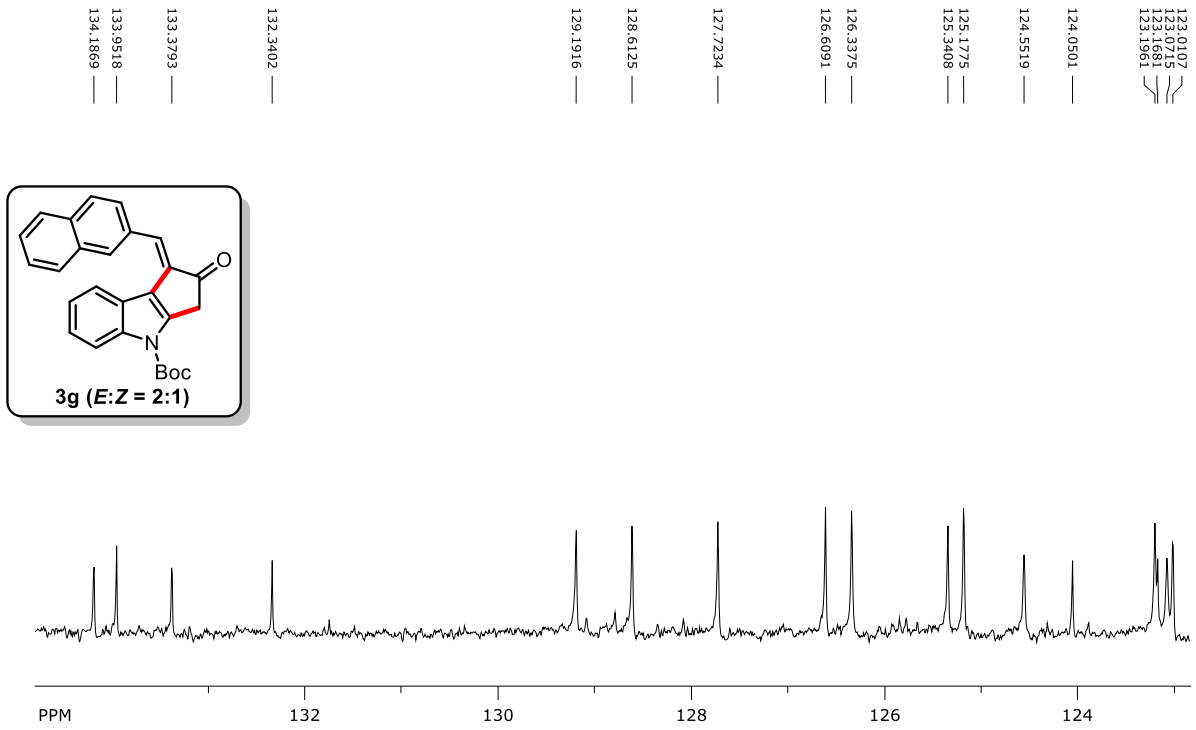
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.0-9.0 ppm region



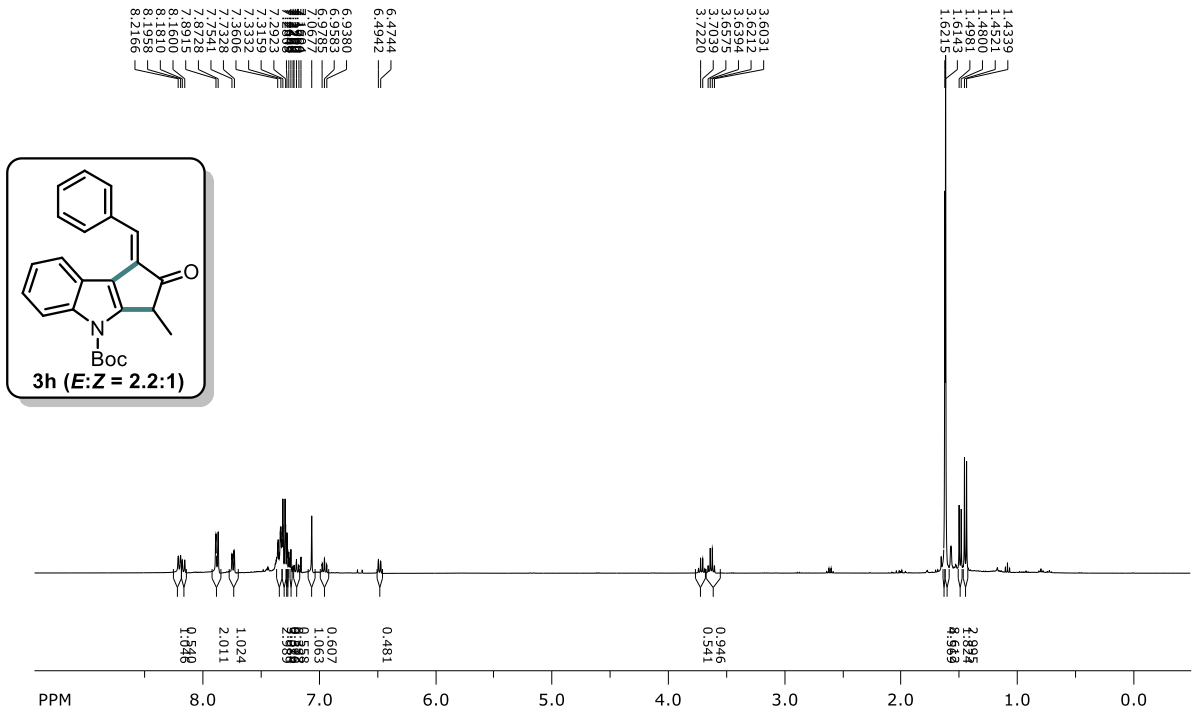
^{13}C NMR (100 MHz, $CDCl_3$):



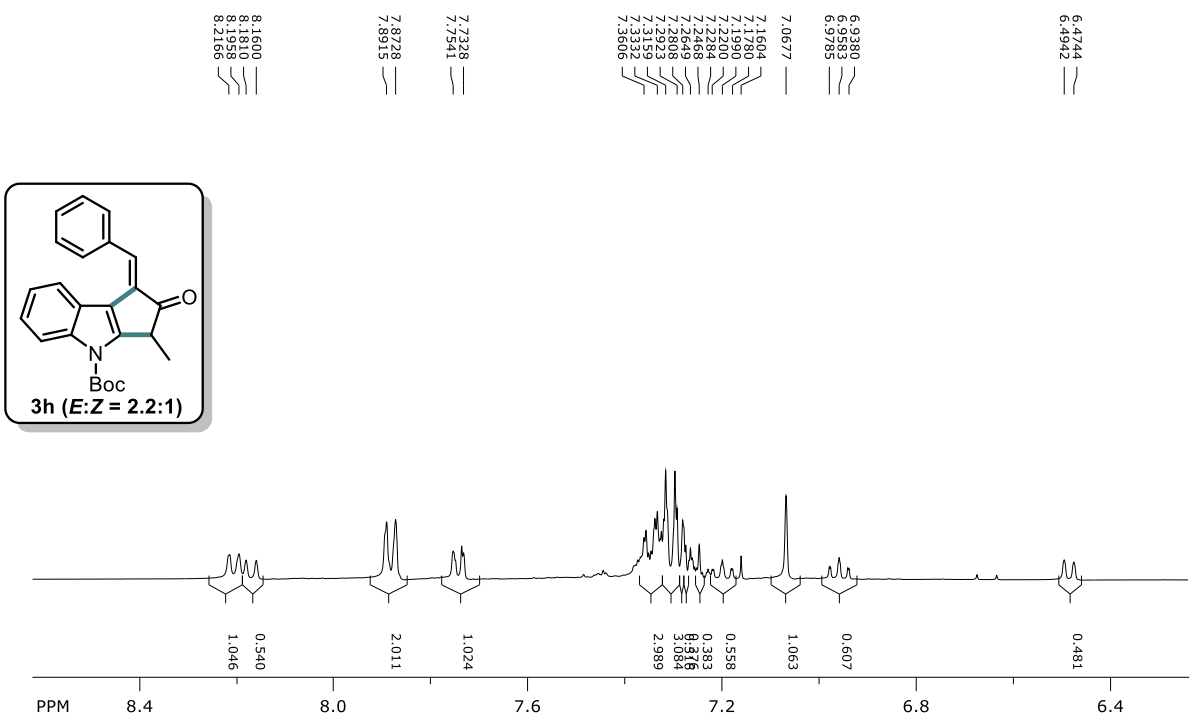
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 122-136 ppm region



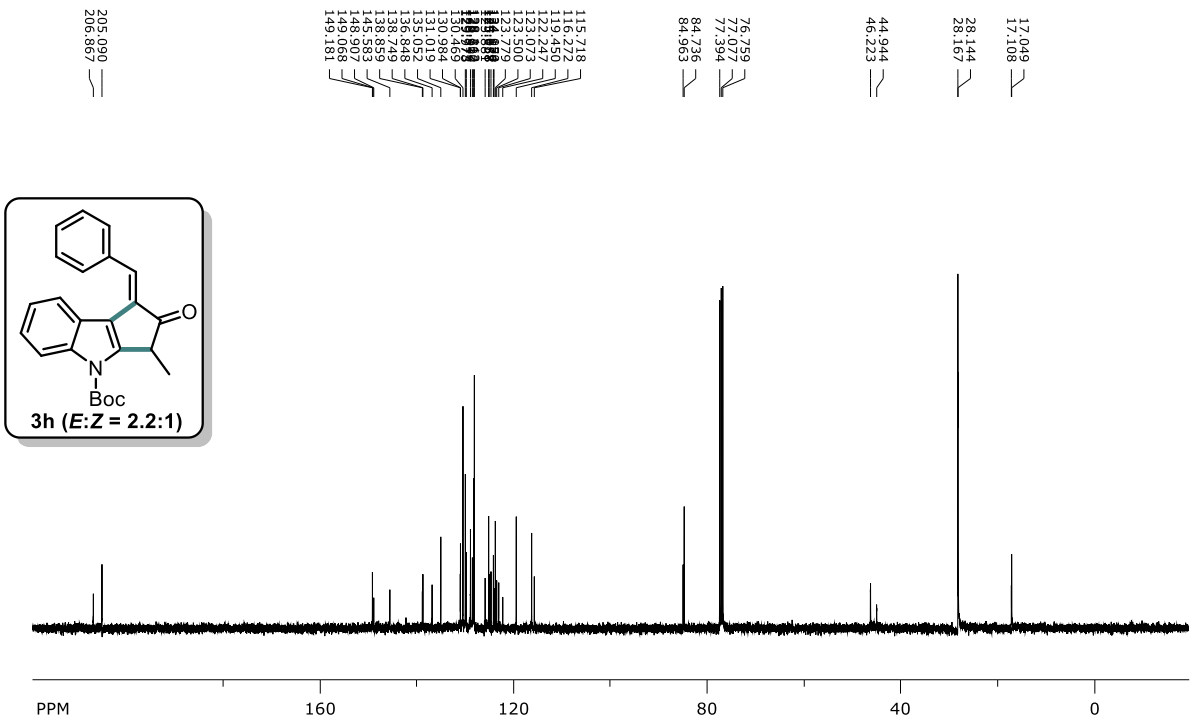
^{1}H NMR (400 MHz, $CDCl_3$):



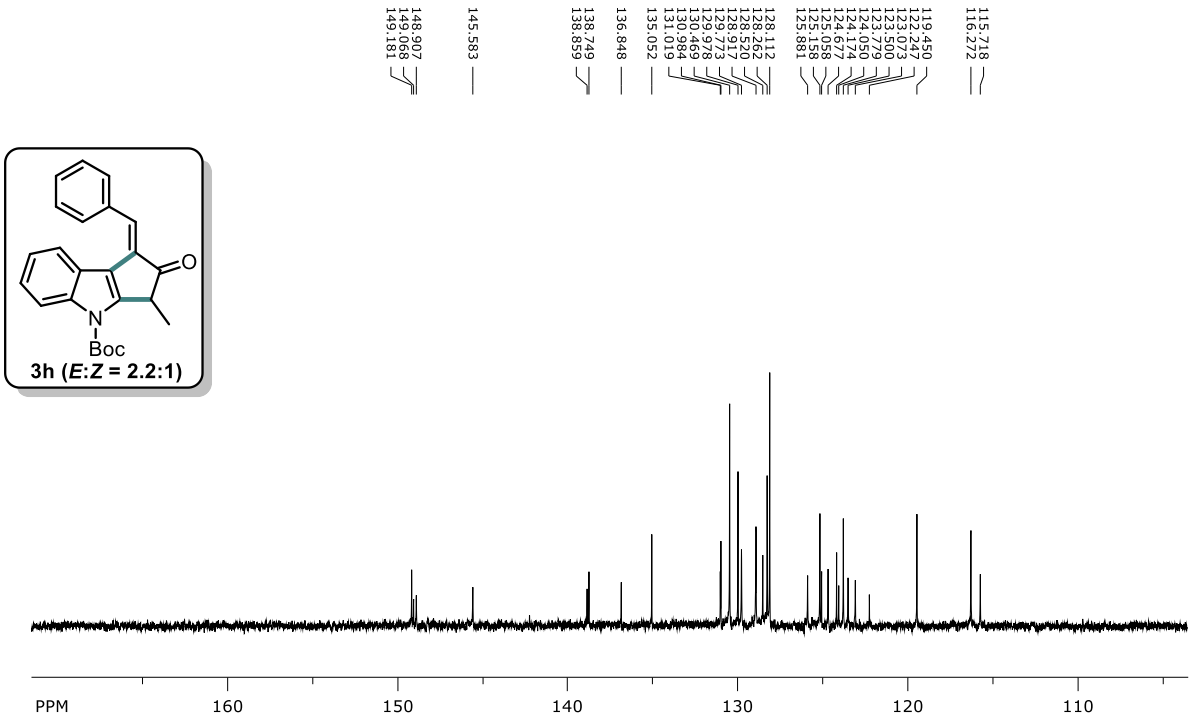
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.5-8.5 ppm region



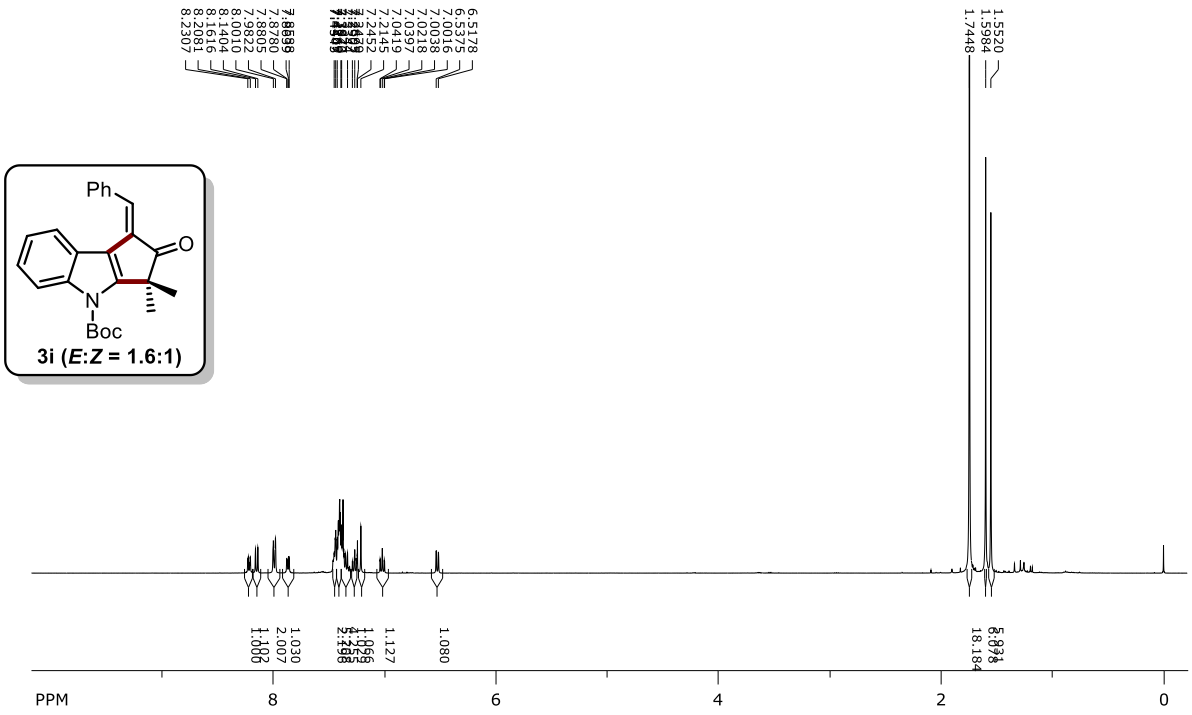
^{13}C NMR (100 MHz, $CDCl_3$):



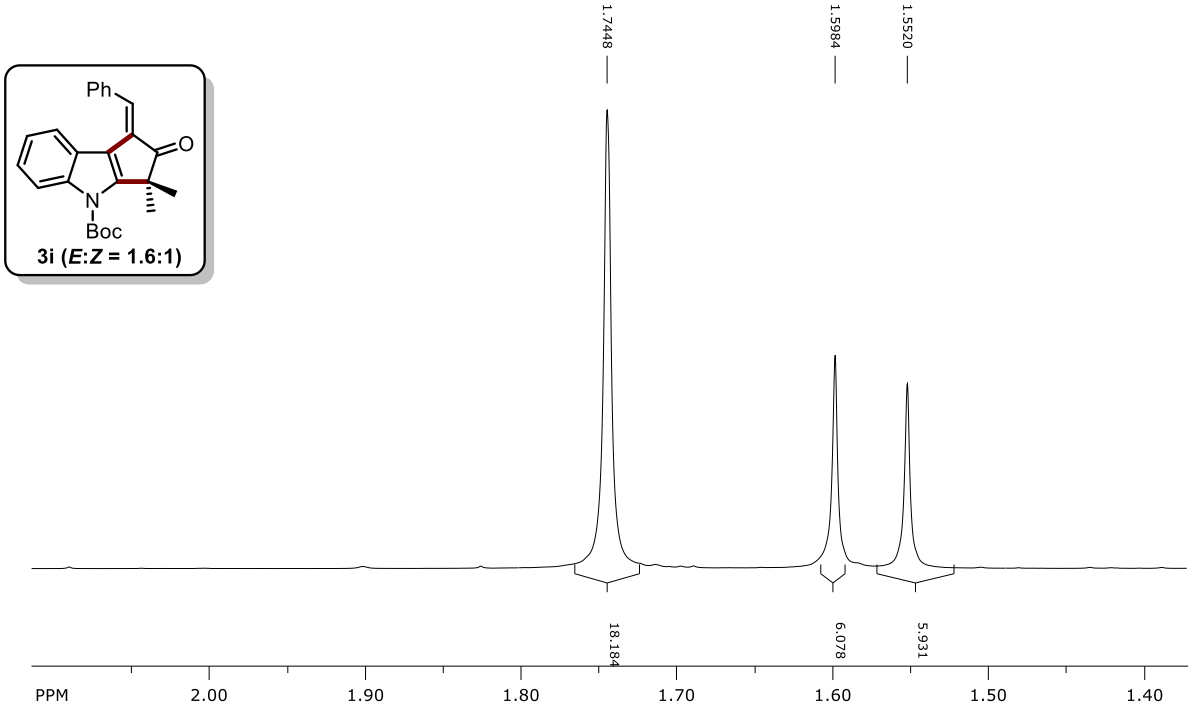
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-160 ppm region



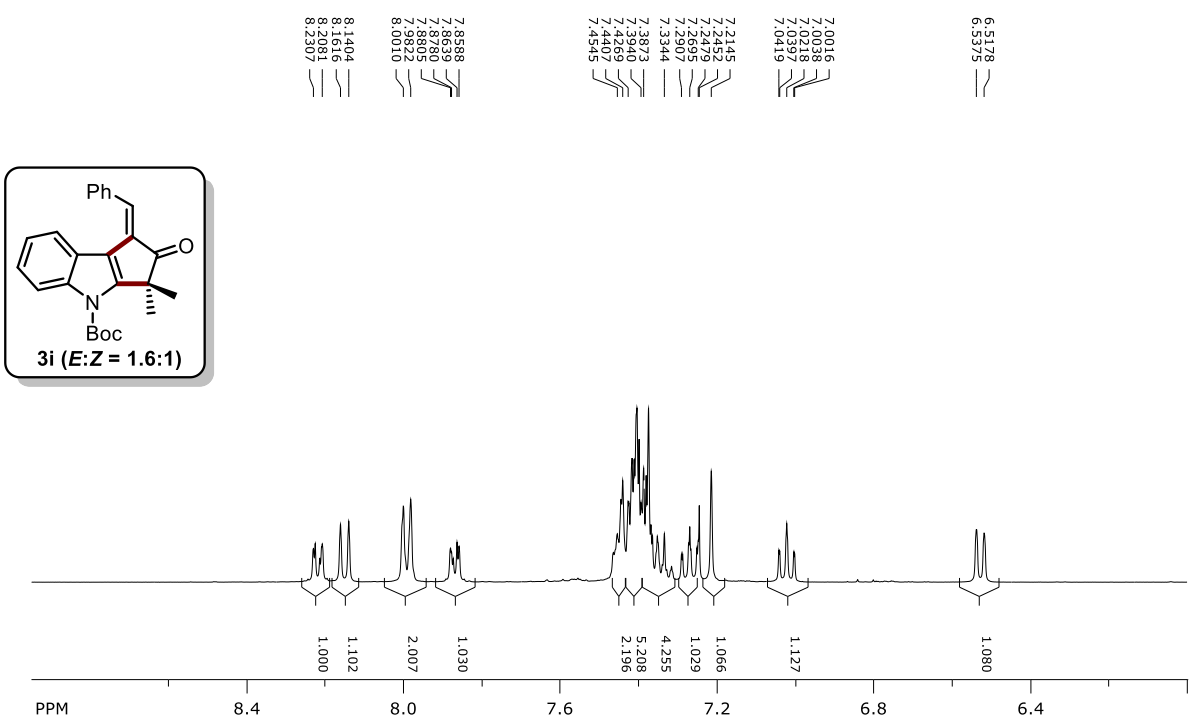
^{1}H NMR (400 MHz, $CDCl_3$):



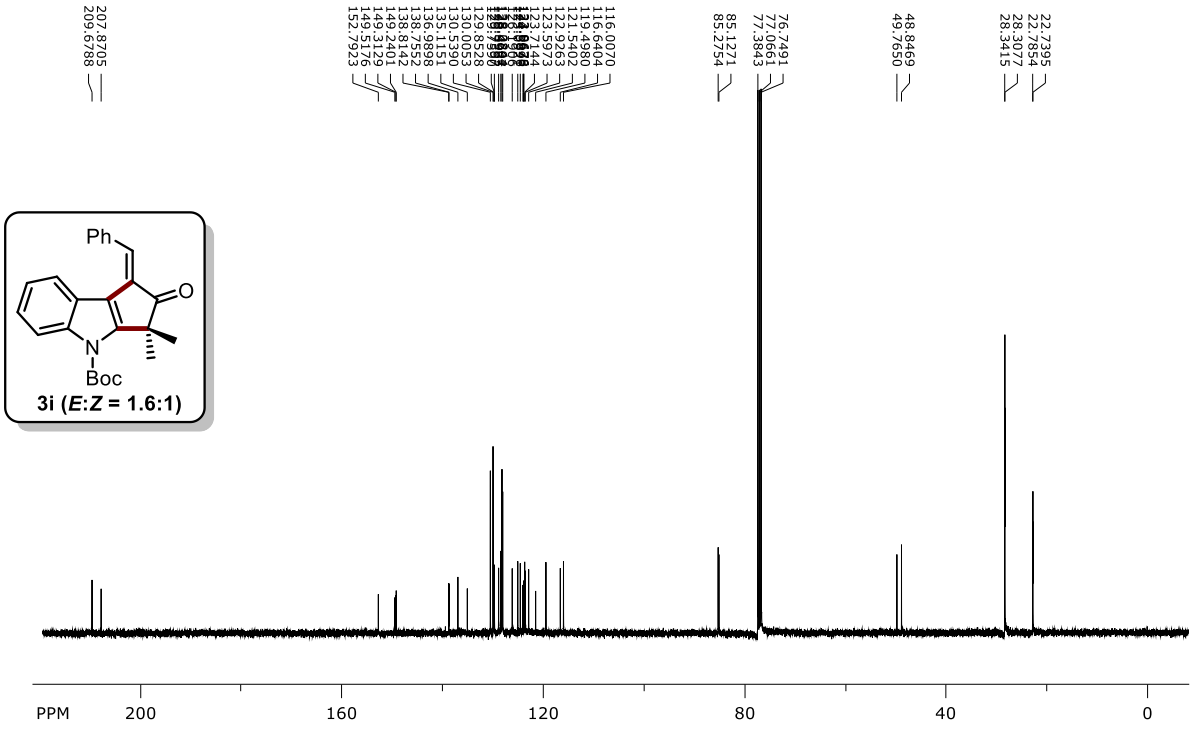
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 1.5-2.0 ppm region



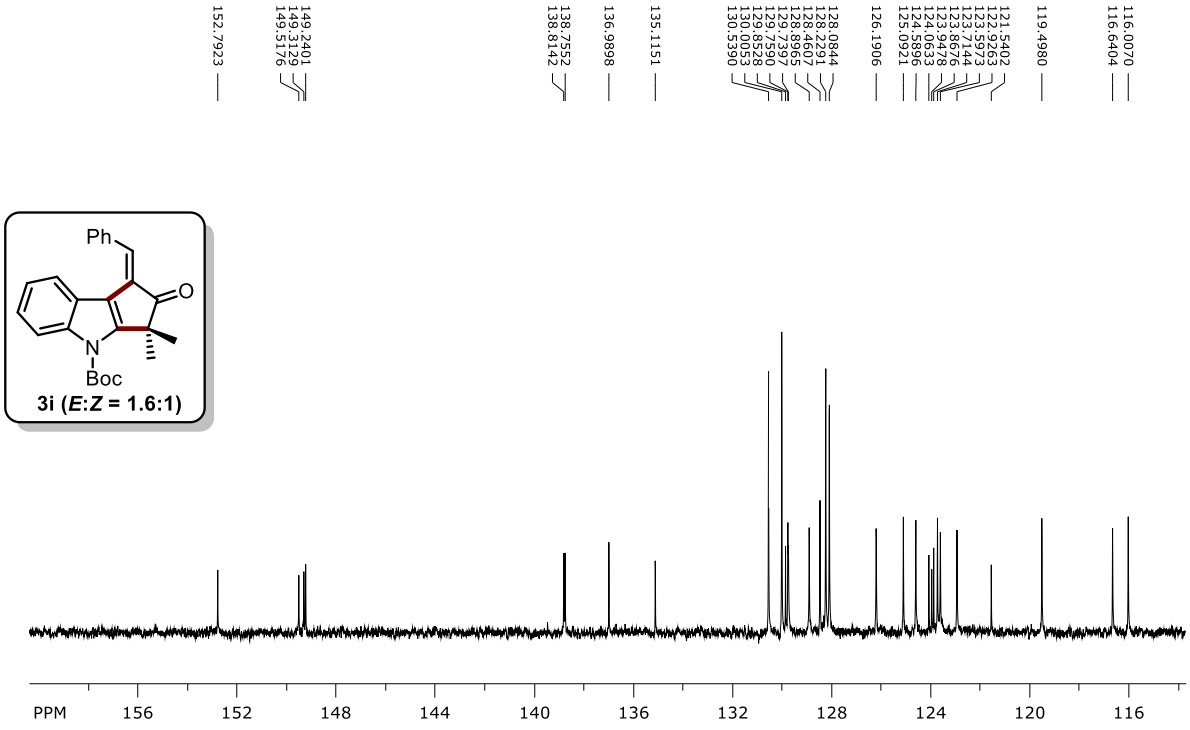
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.0-9.0 ppm region



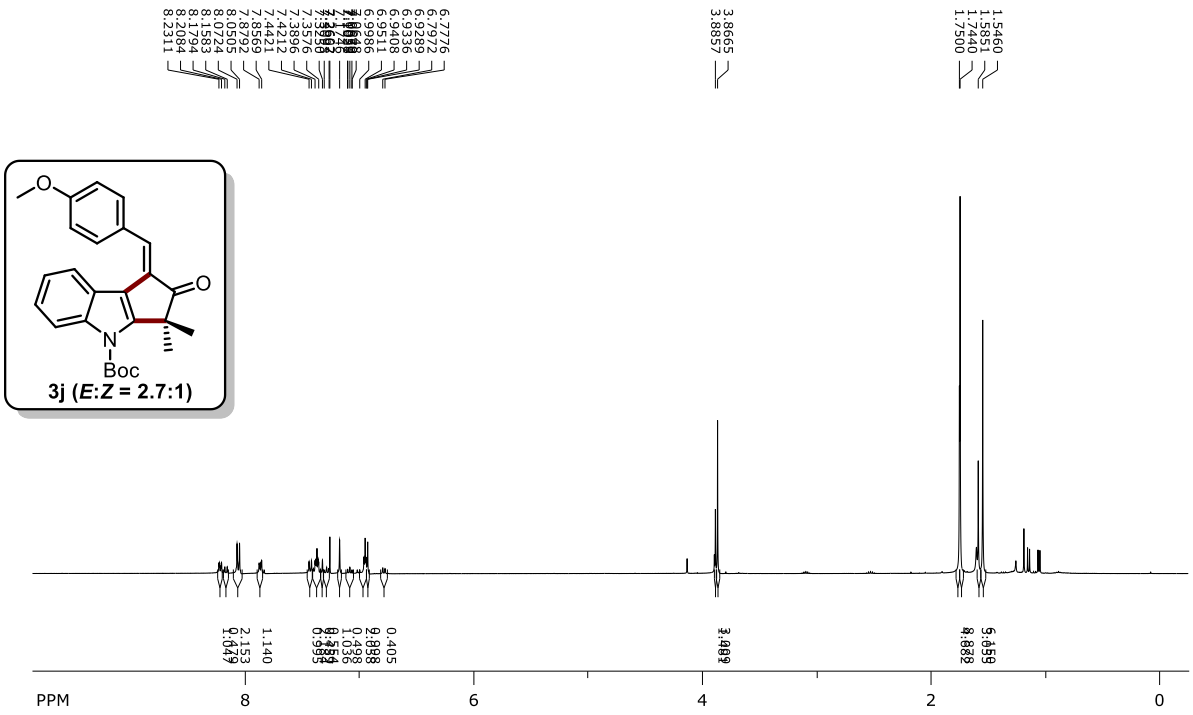
^{13}C NMR (100 MHz, $CDCl_3$):



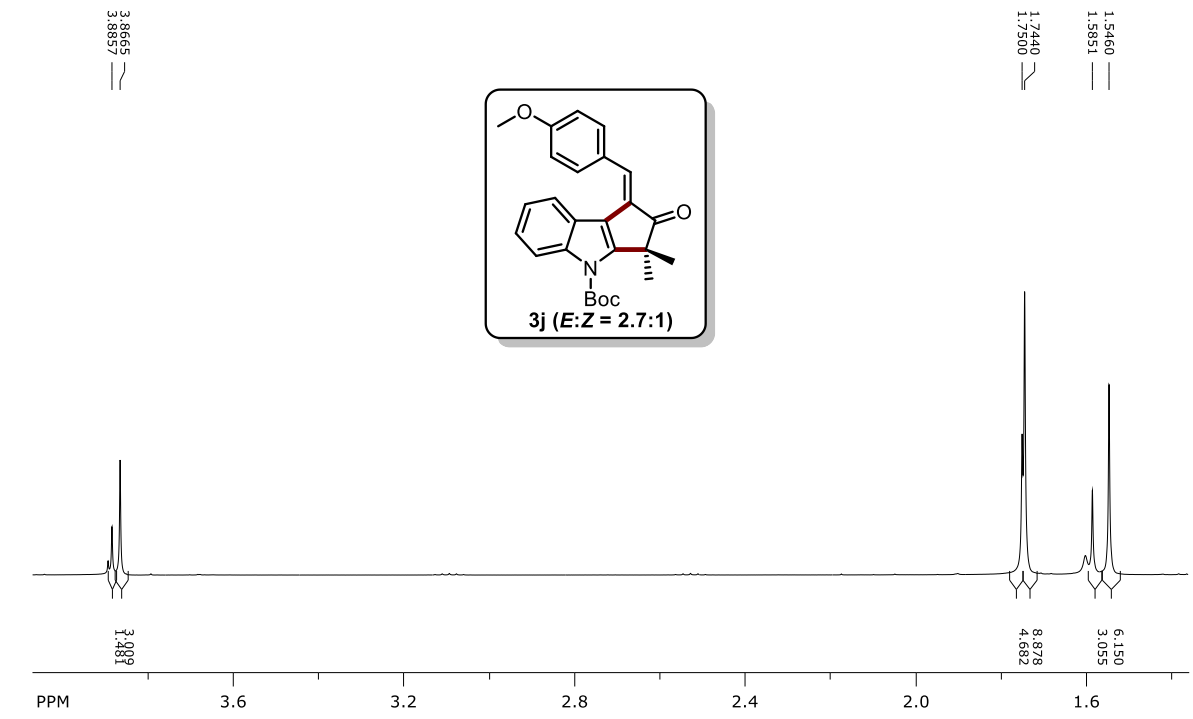
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 115-156 ppm region



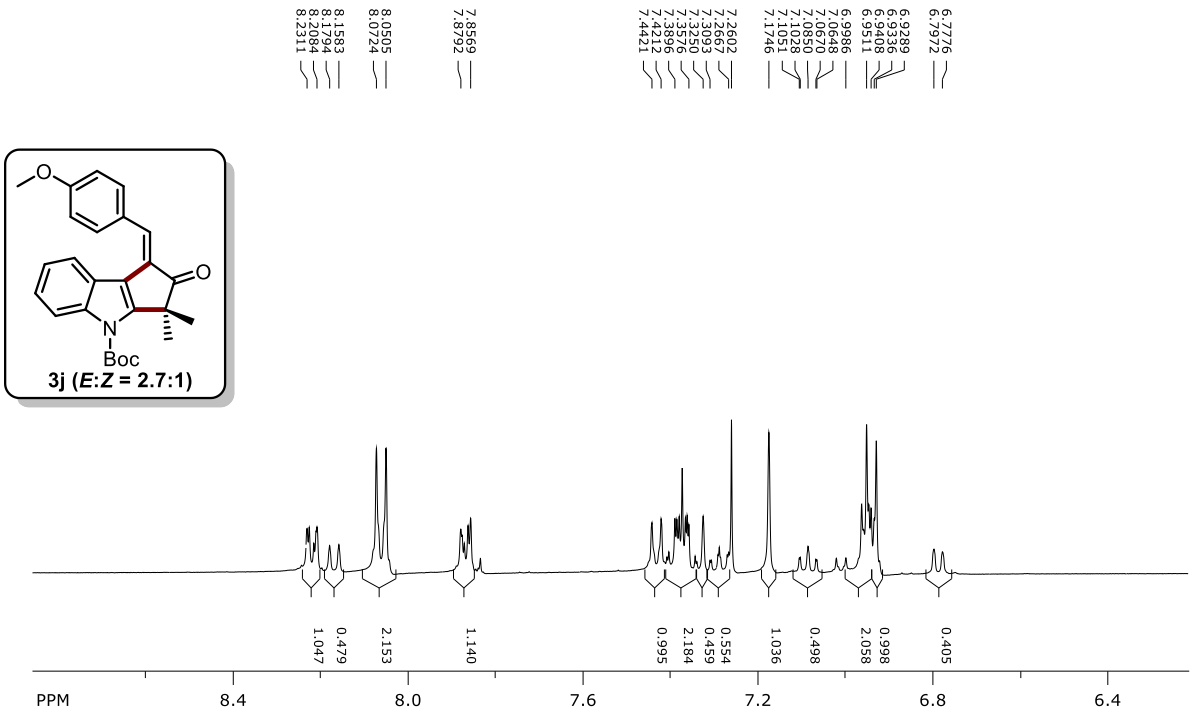
^{1}H NMR (400 MHz, $CDCl_3$):



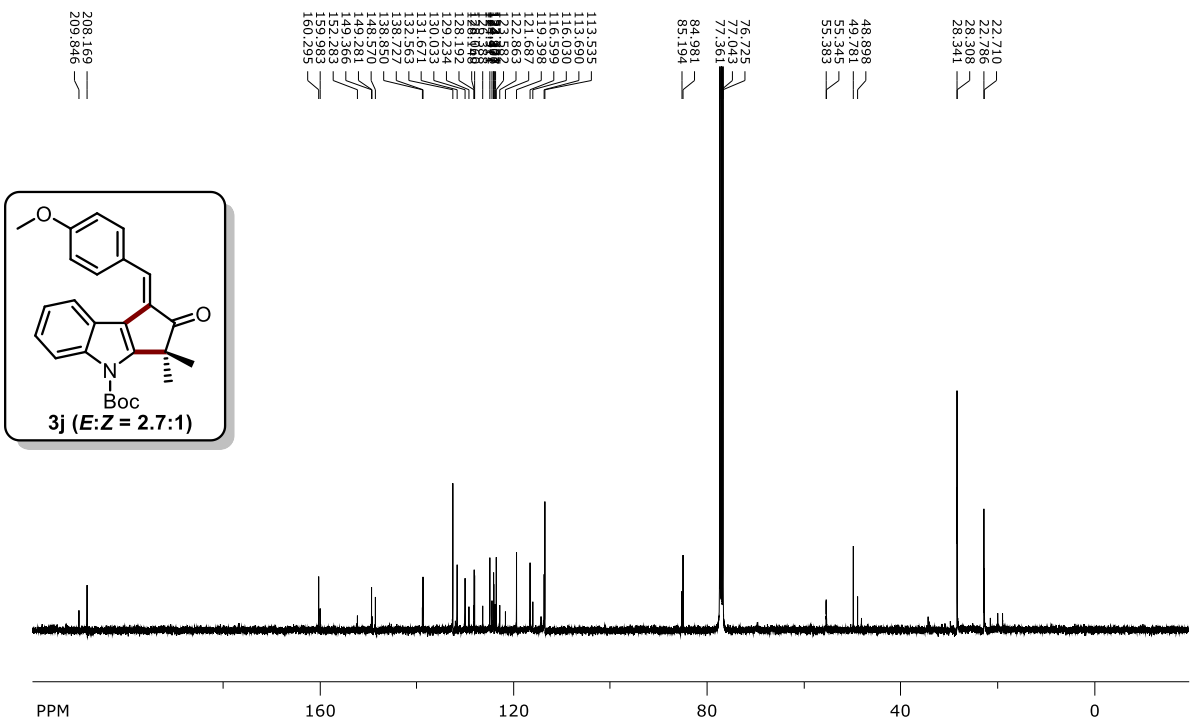
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 1.5-4.0 ppm region



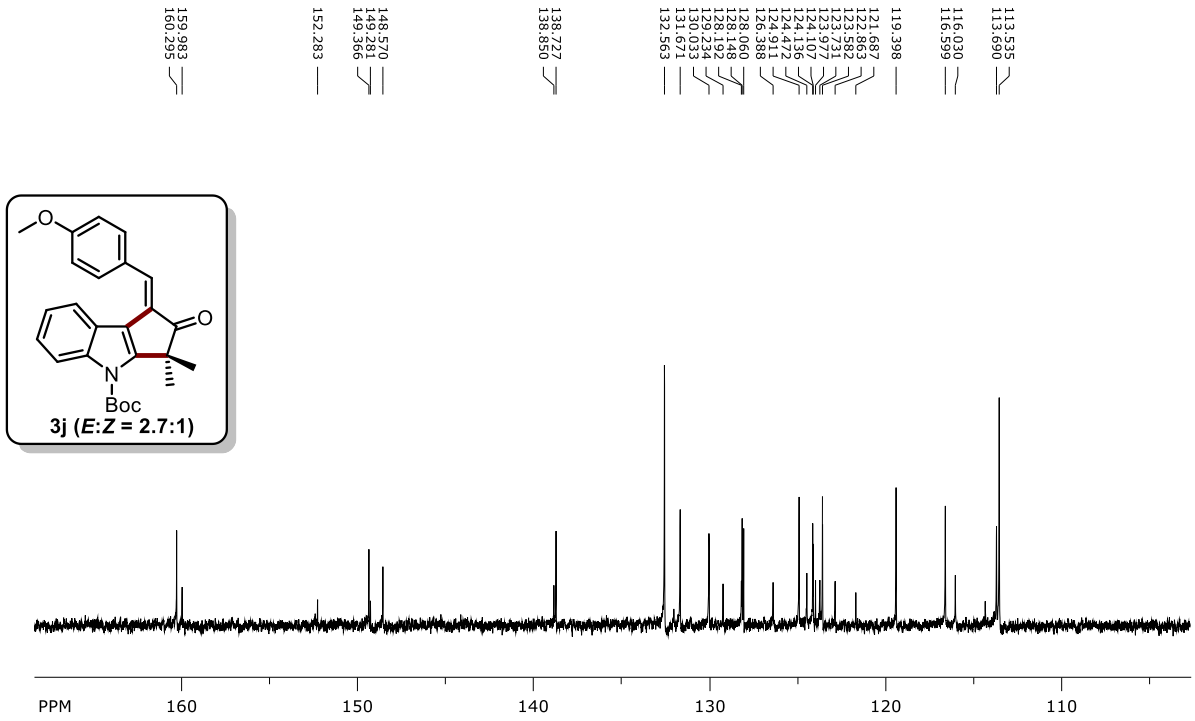
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.5-9.0 ppm region



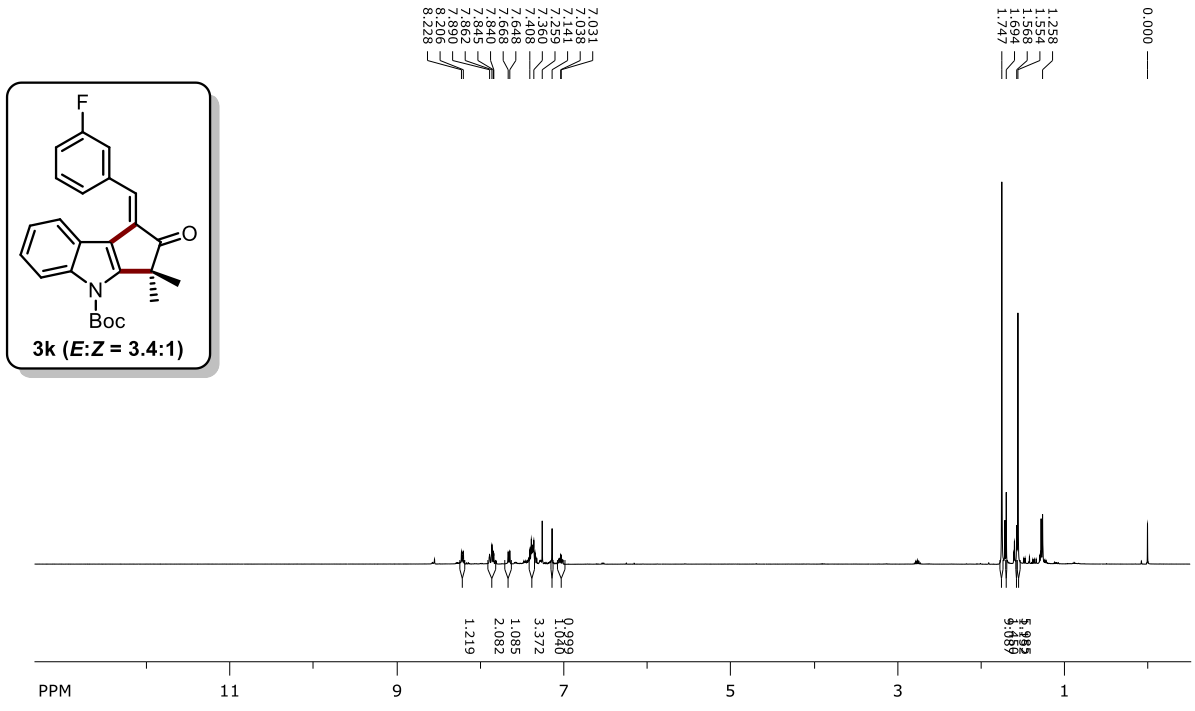
^{13}C NMR (100 MHz, $CDCl_3$):



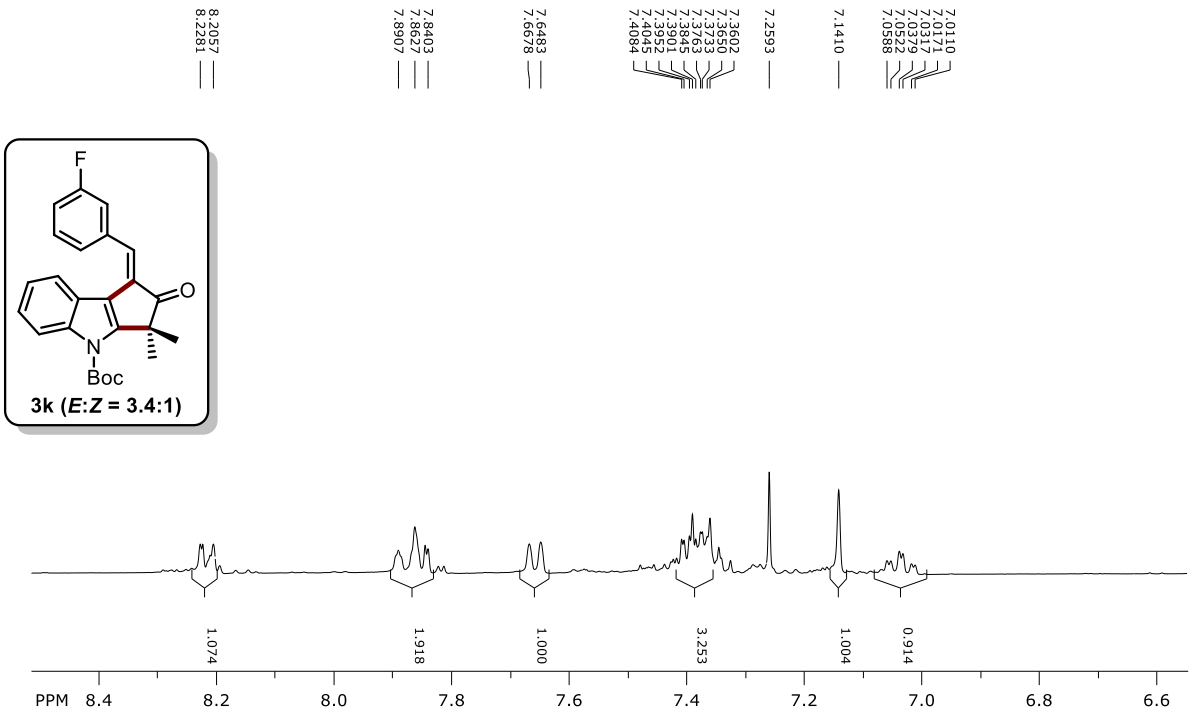
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-160 ppm region



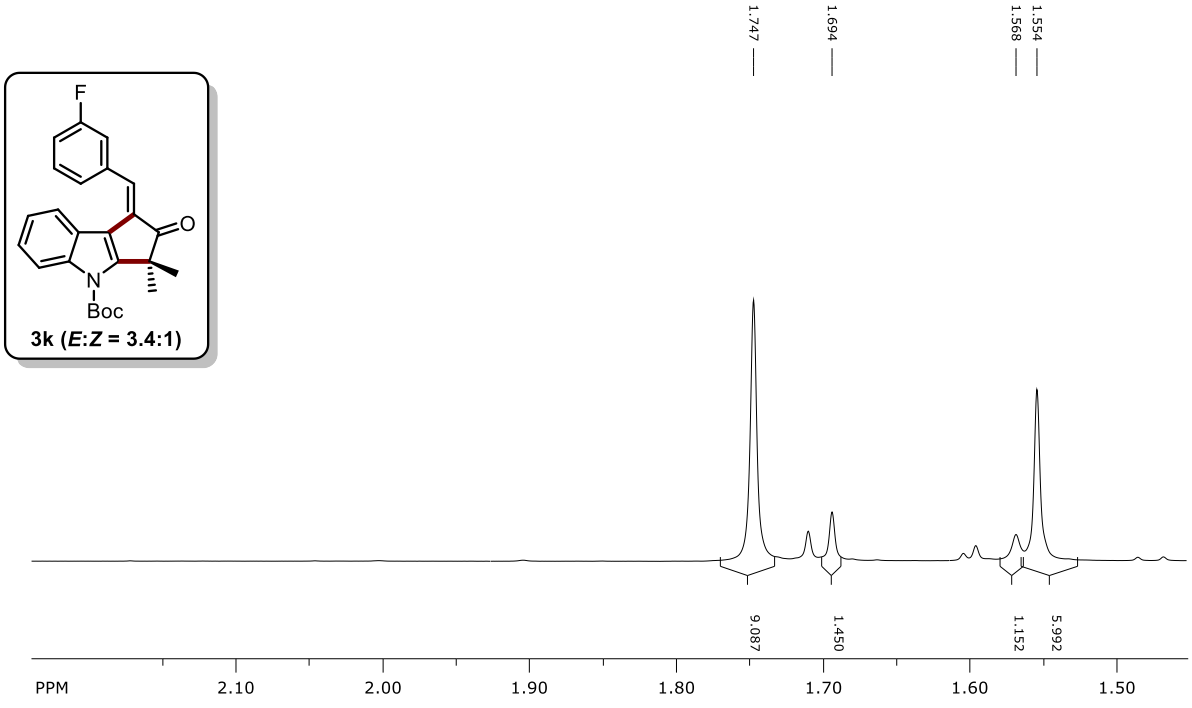
^{1}H NMR (400 MHz, $CDCl_3$):



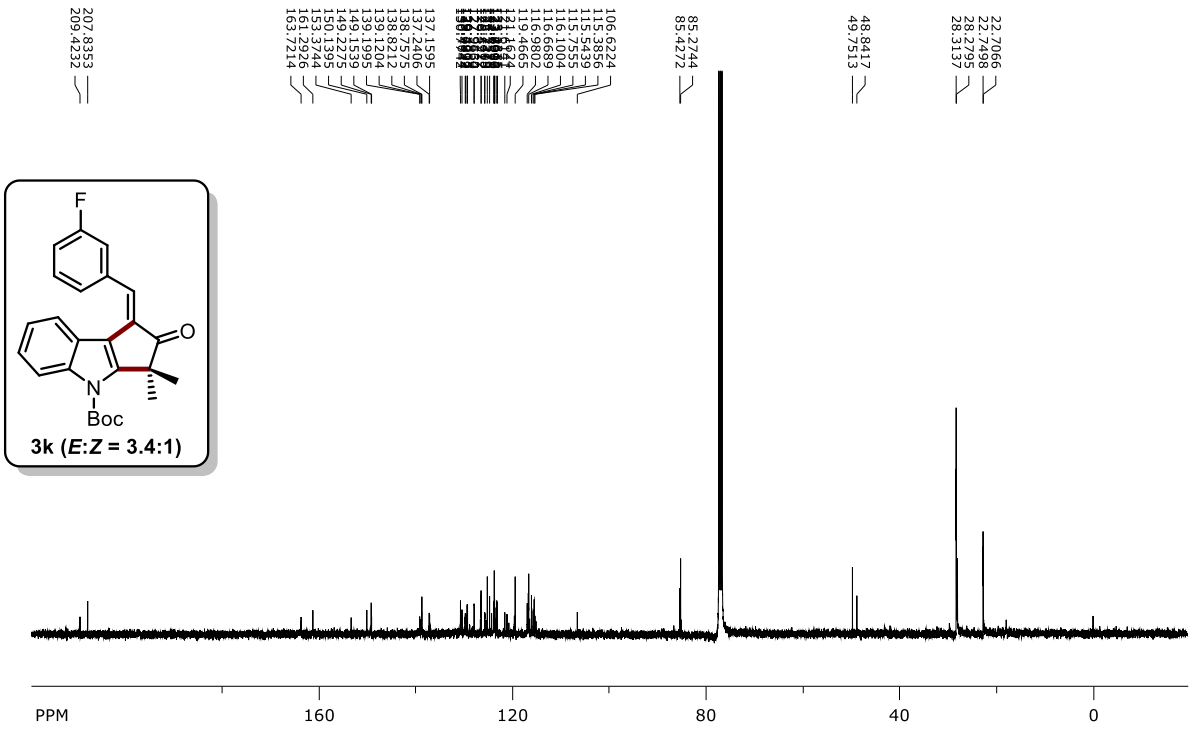
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.6-8.5 ppm region



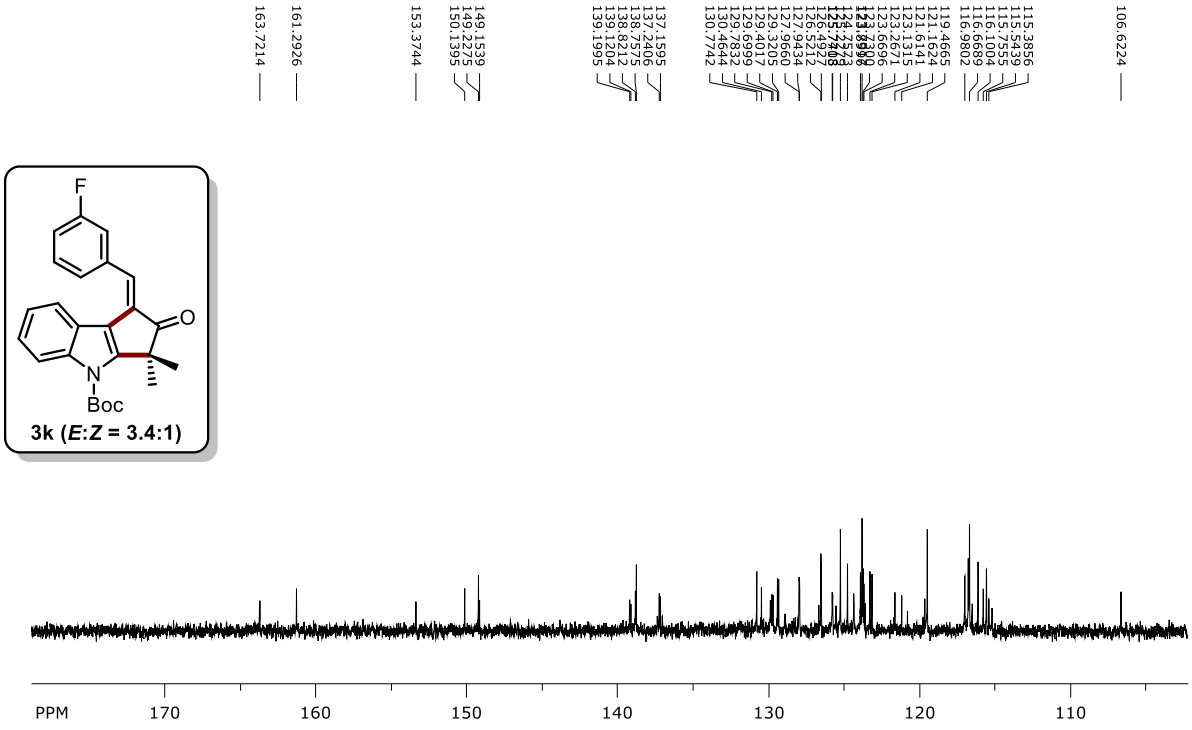
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 1.0-3.0 ppm region



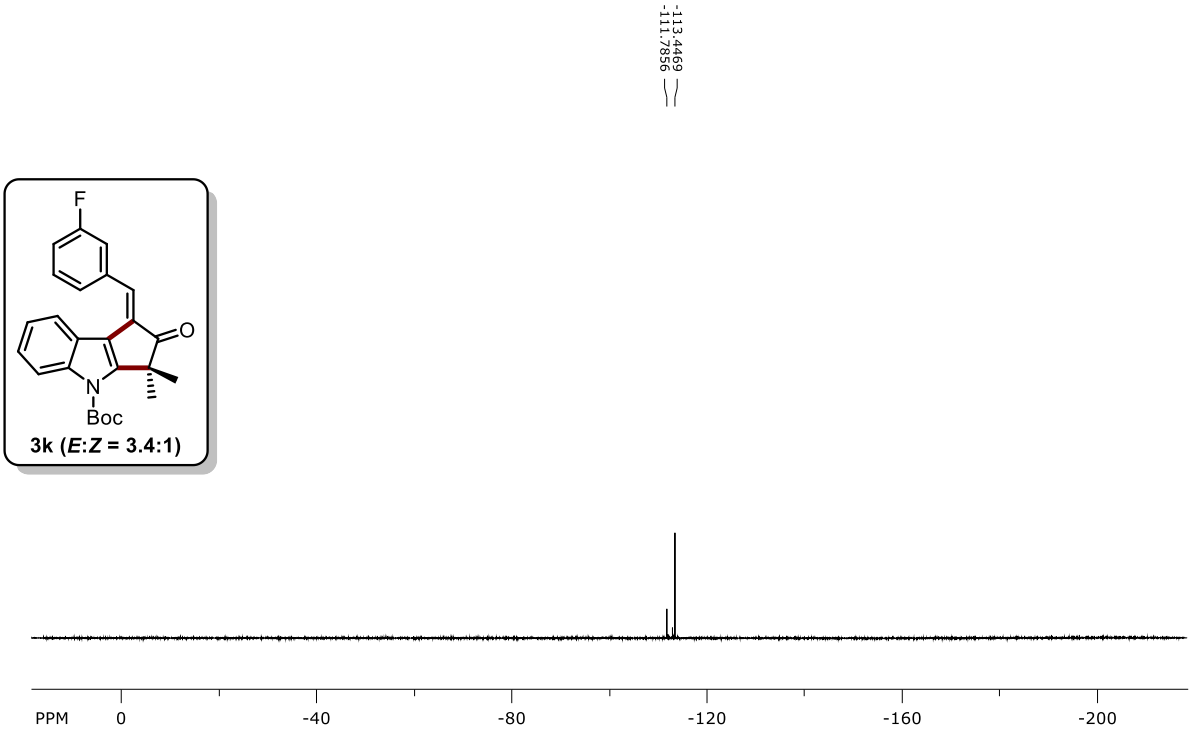
^{13}C NMR (100 MHz, $CDCl_3$):



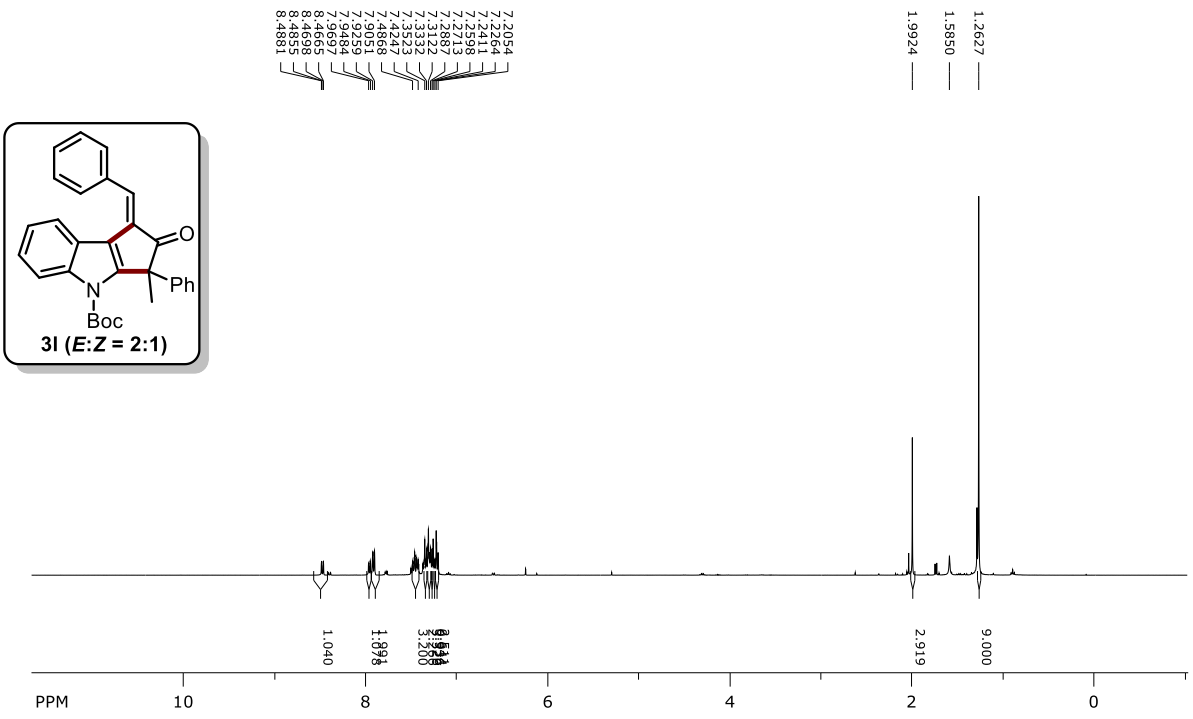
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 102-170 ppm region



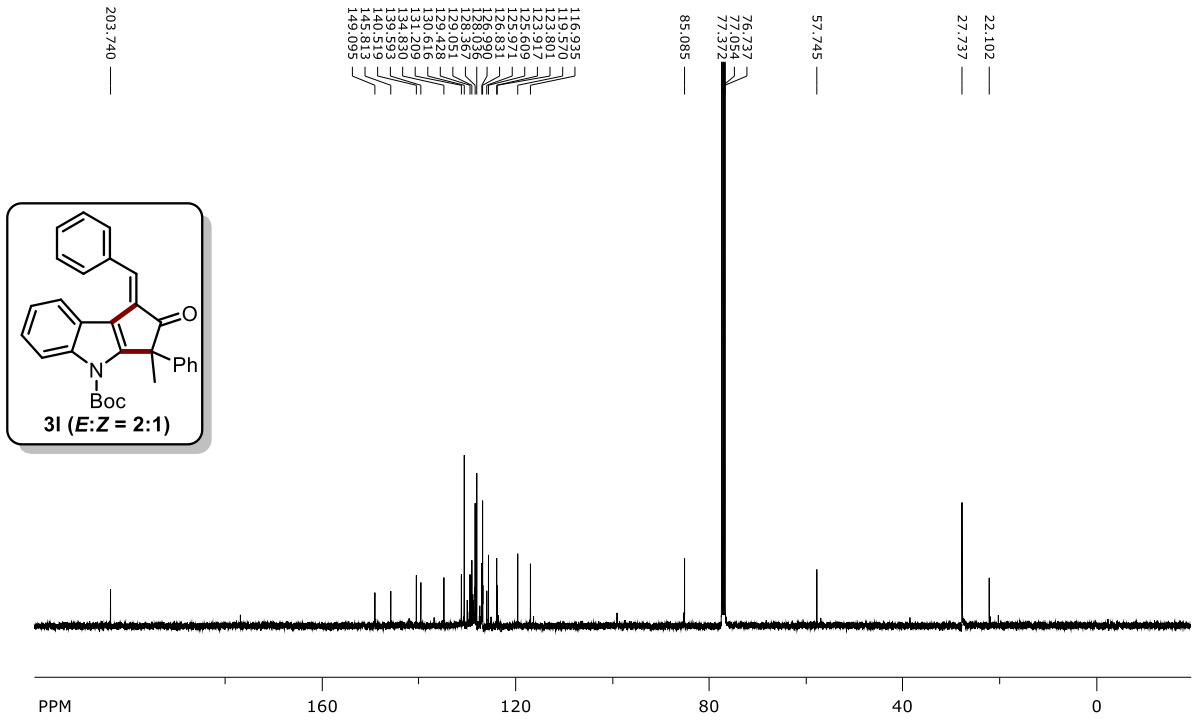
^{19}F NMR (376.5 MHz, $CDCl_3$):



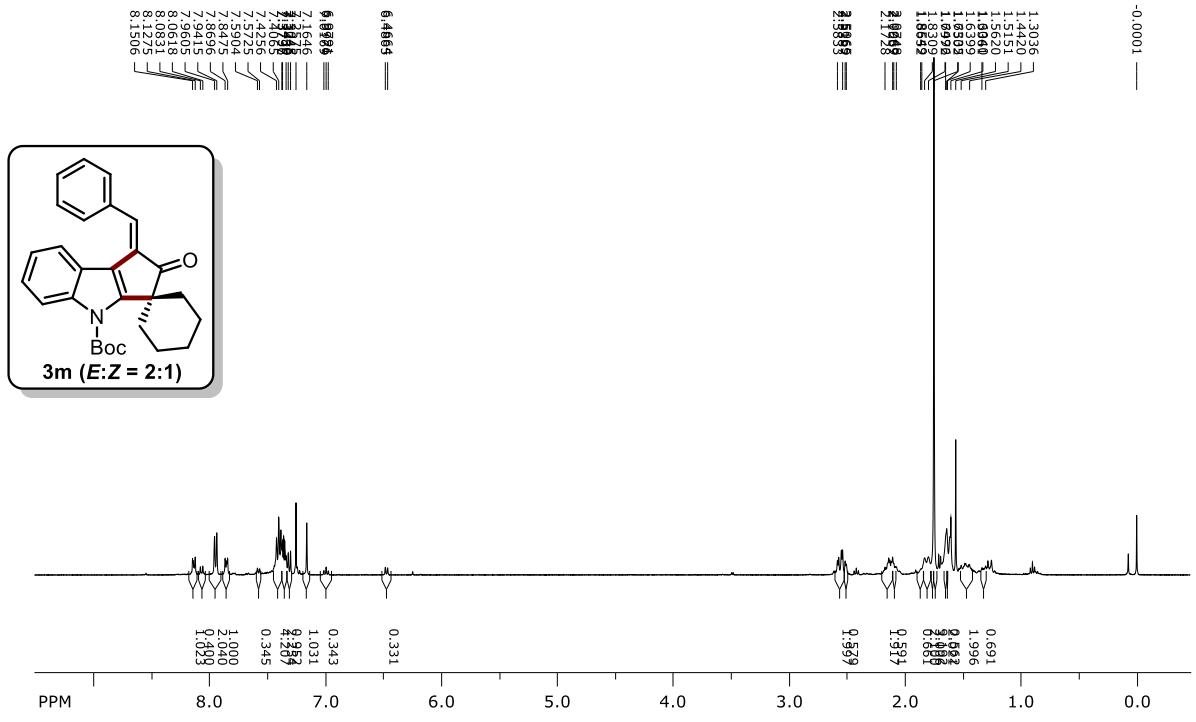
^{1}H NMR (400 MHz, $CDCl_3$):



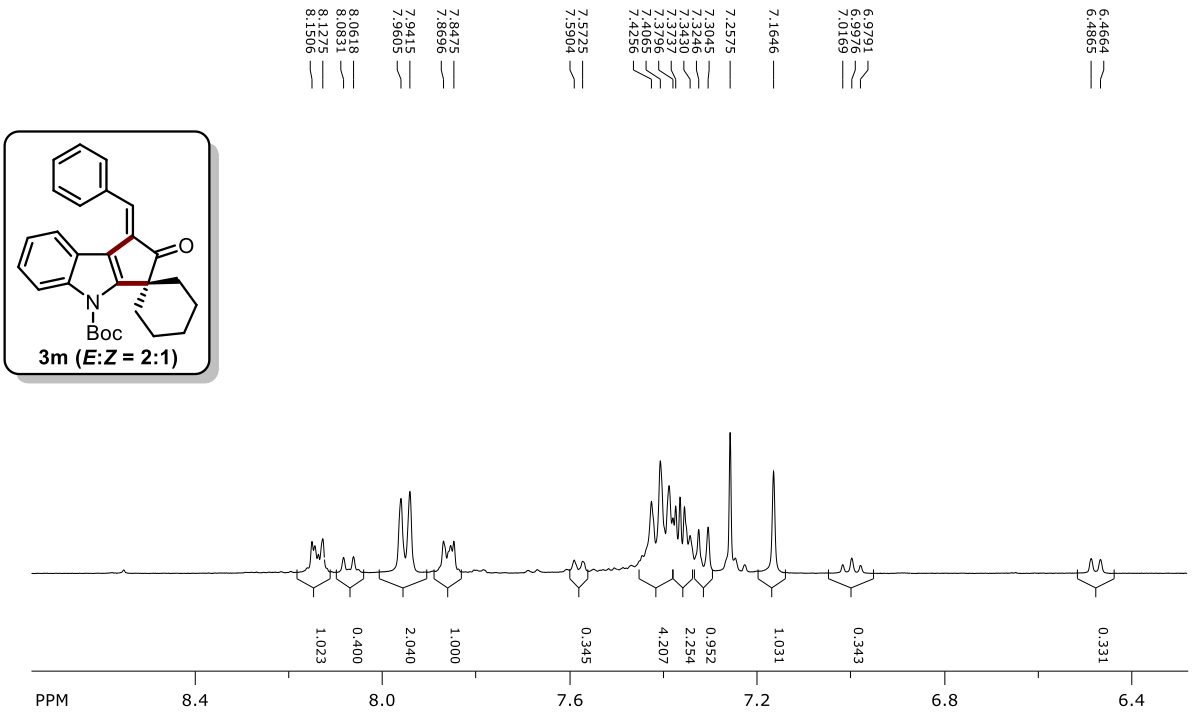
^{13}C NMR (100 MHz, $CDCl_3$):



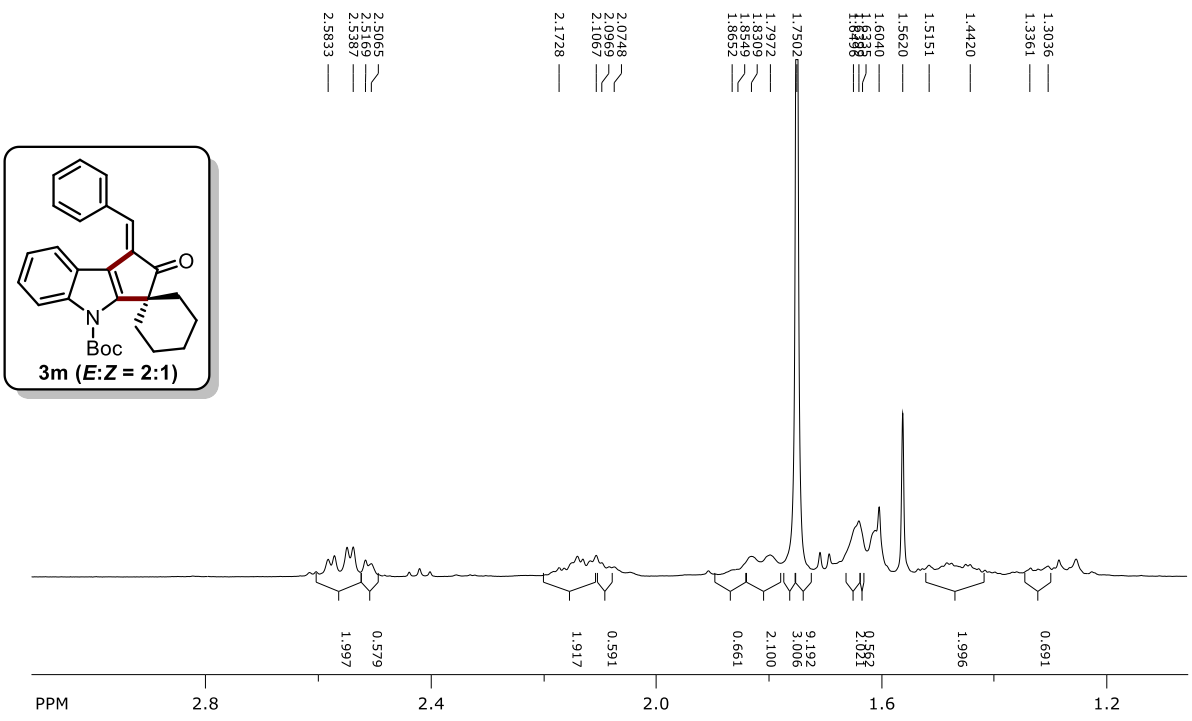
^{1}H NMR (400 MHz, $CDCl_3$):



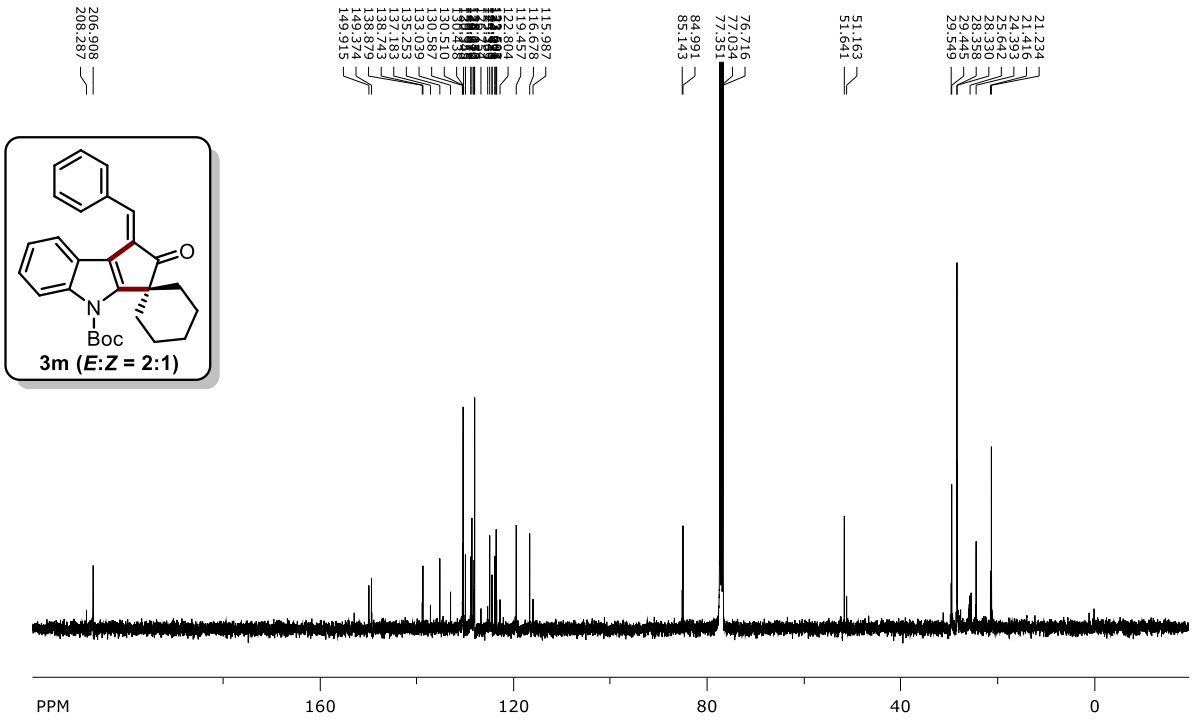
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.0-9.0 ppm region



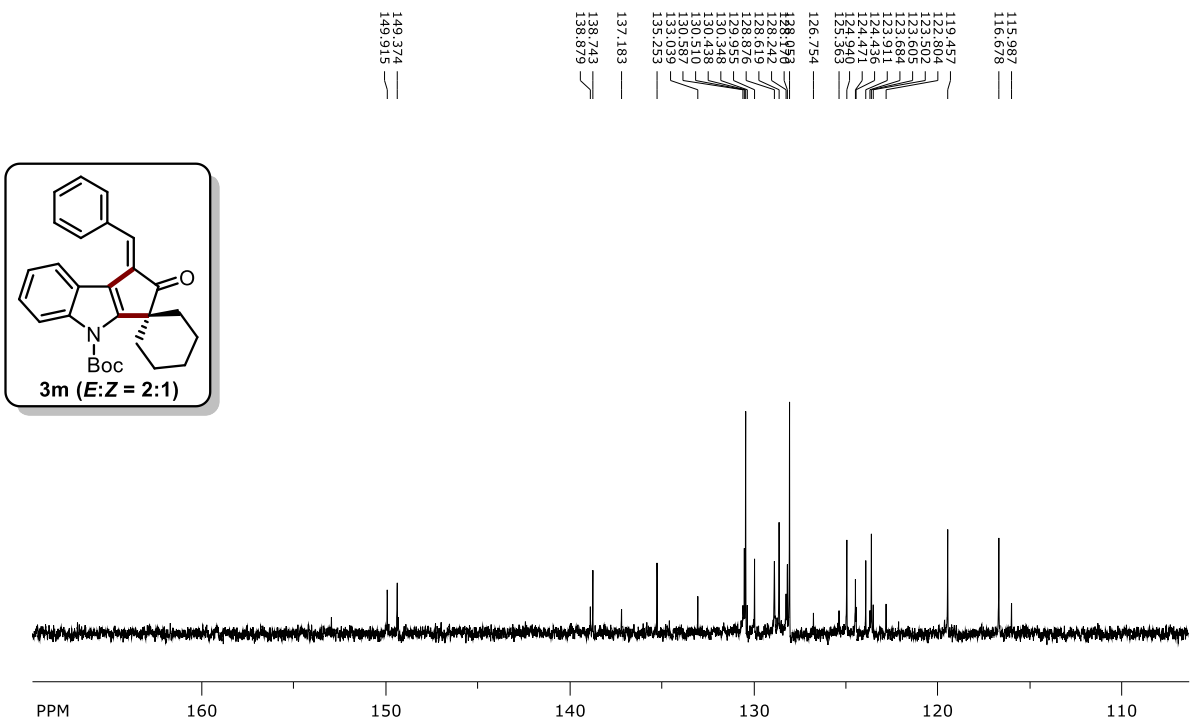
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 1.0-3.0 ppm region



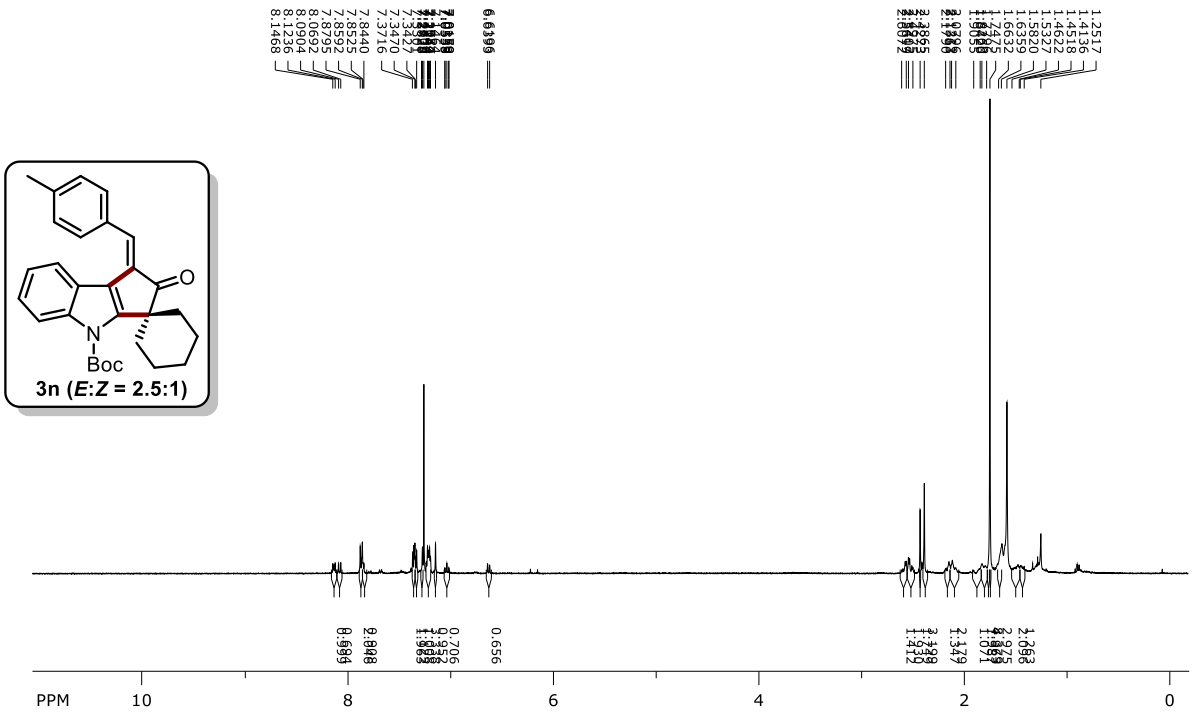
^{13}C NMR (100 MHz, $CDCl_3$):



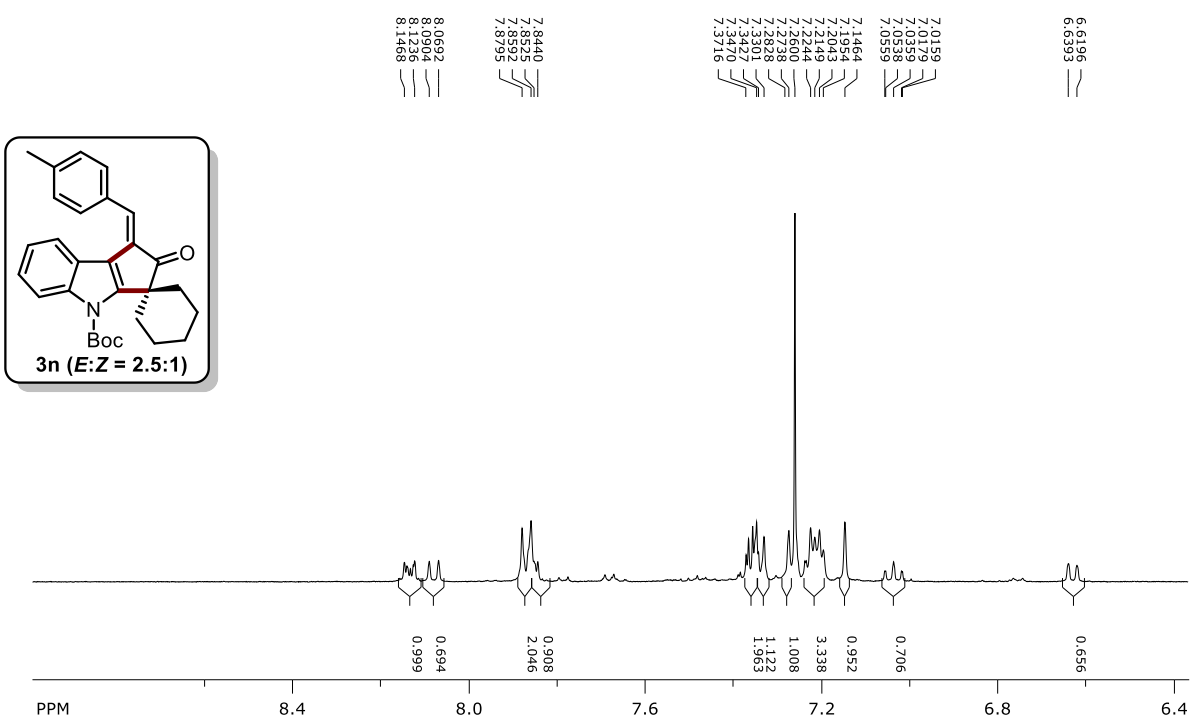
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-160 ppm region



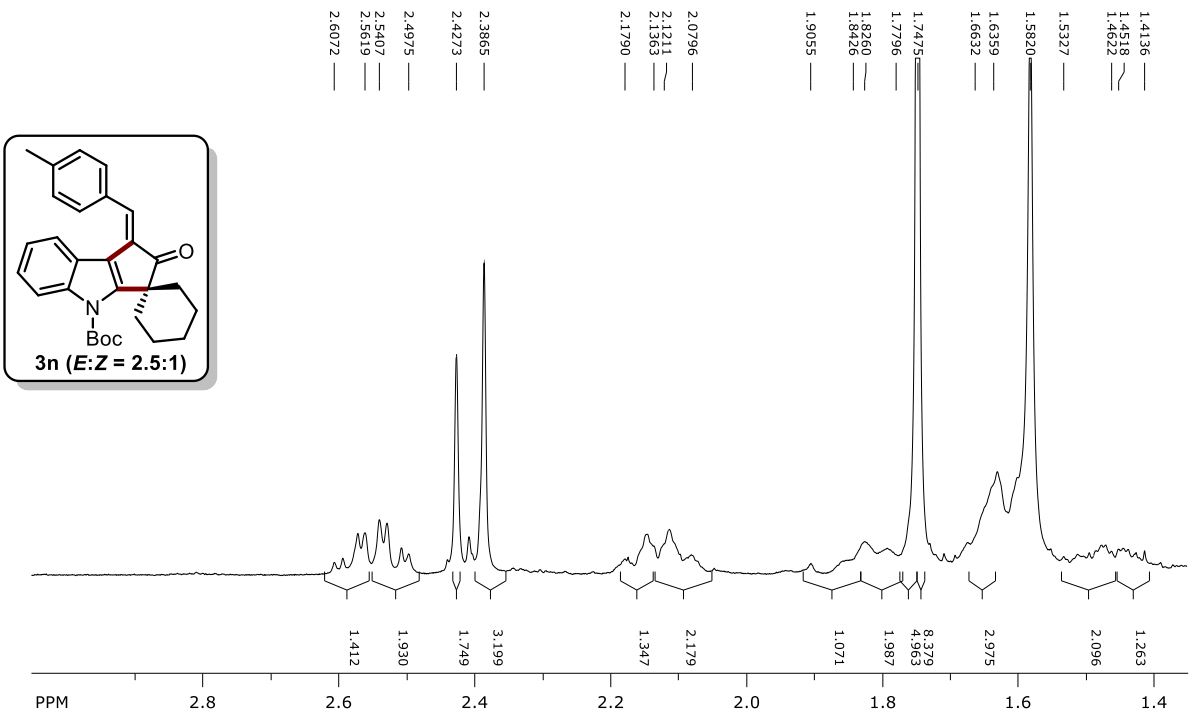
^{1}H NMR (400 MHz, $CDCl_3$):



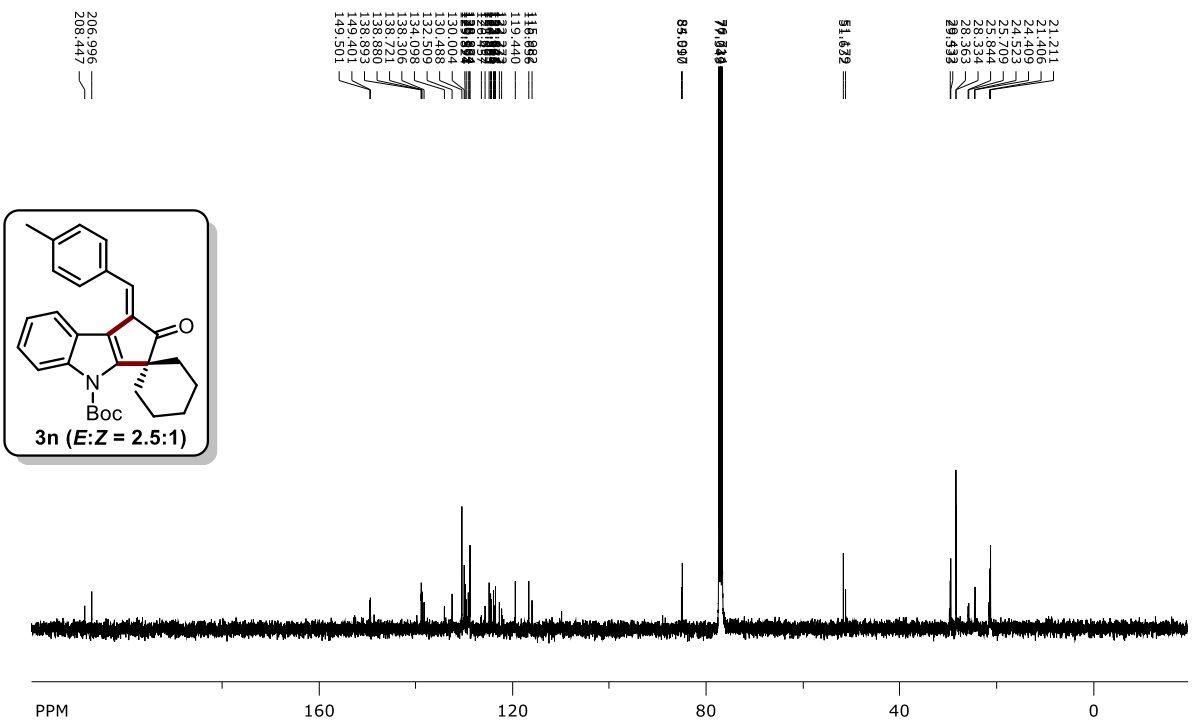
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.4-9.0 ppm region



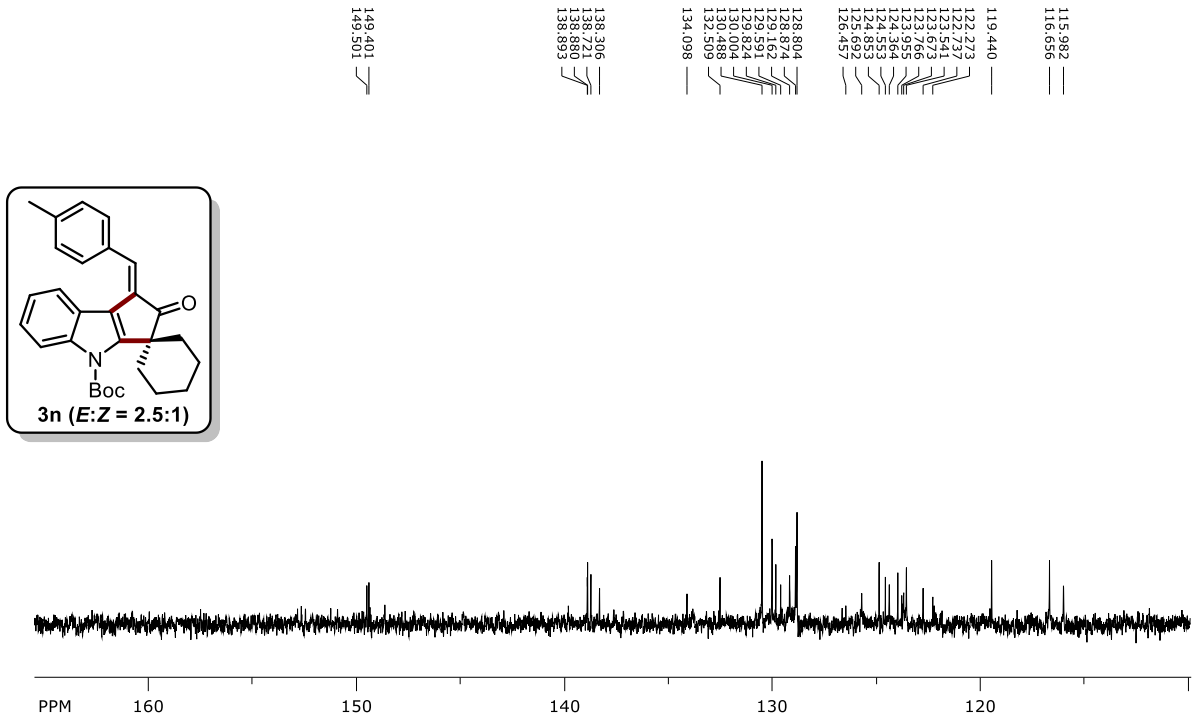
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 1.0-3.0 ppm region



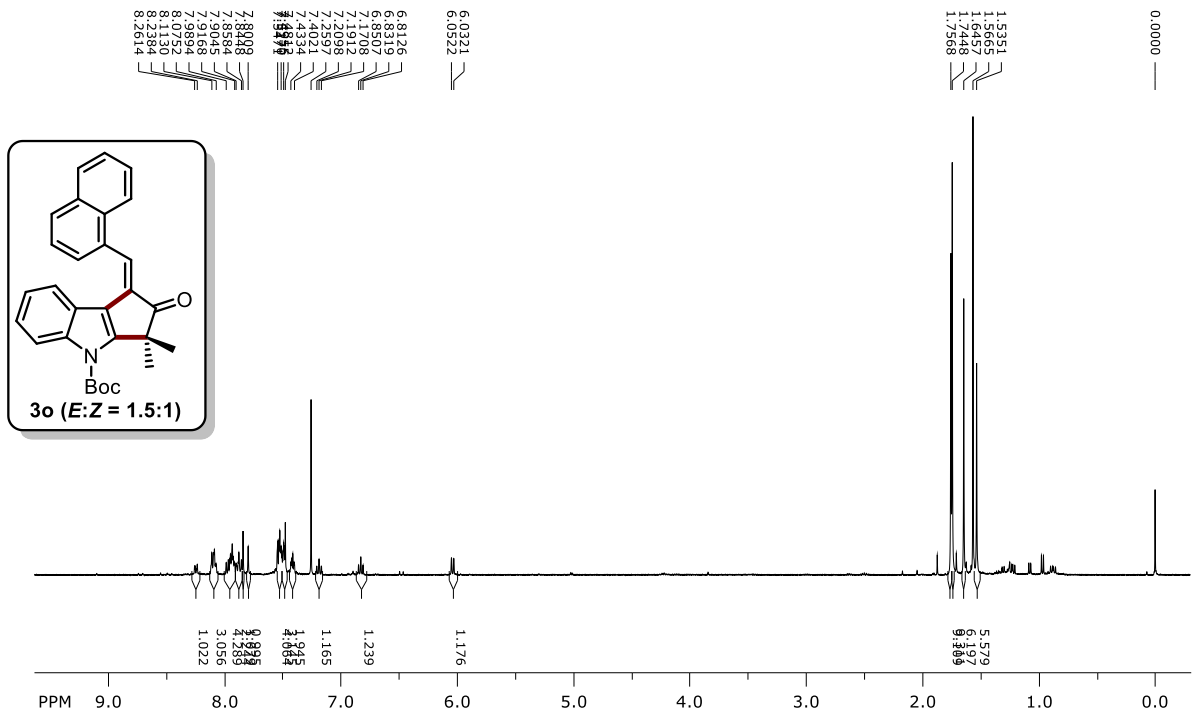
^{13}C NMR (100 MHz, $CDCl_3$):



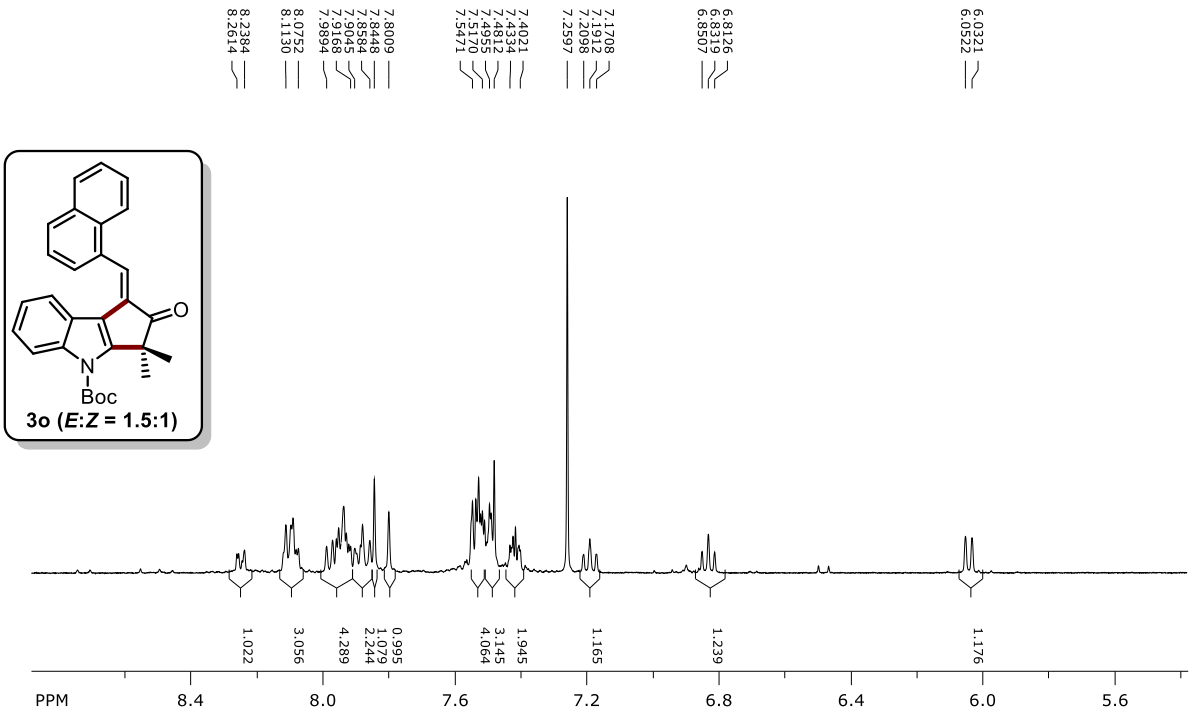
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-160 ppm region



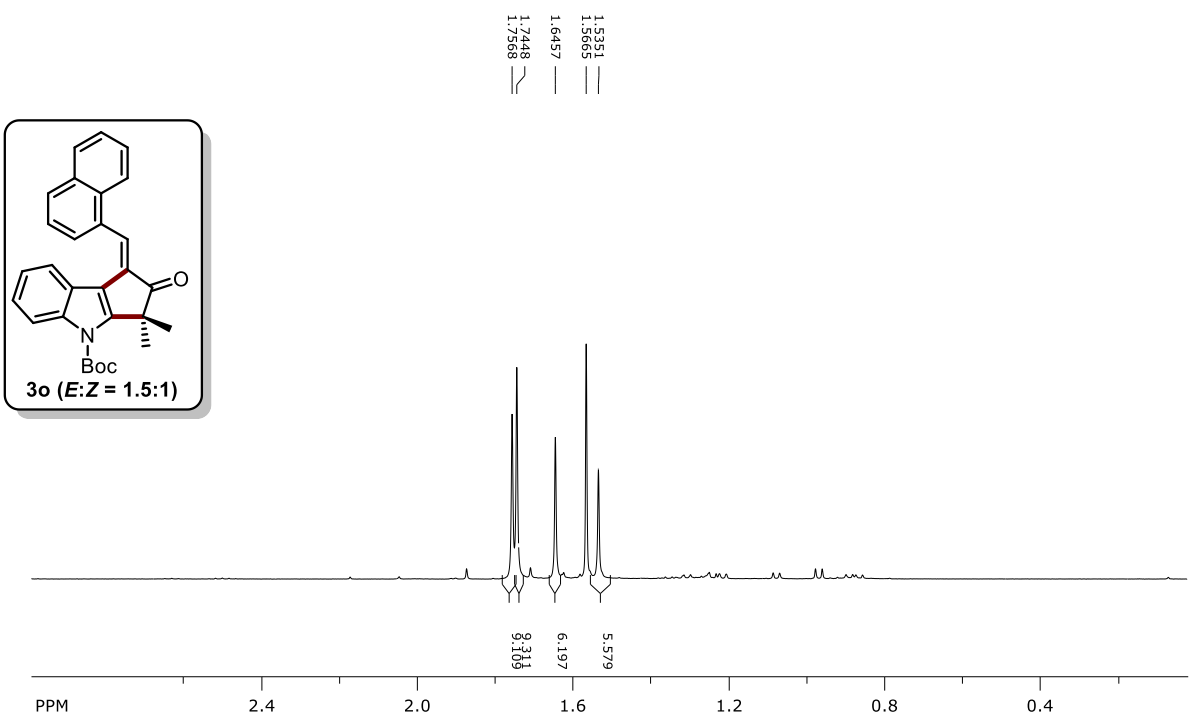
^{1}H NMR (400 MHz, $CDCl_3$):



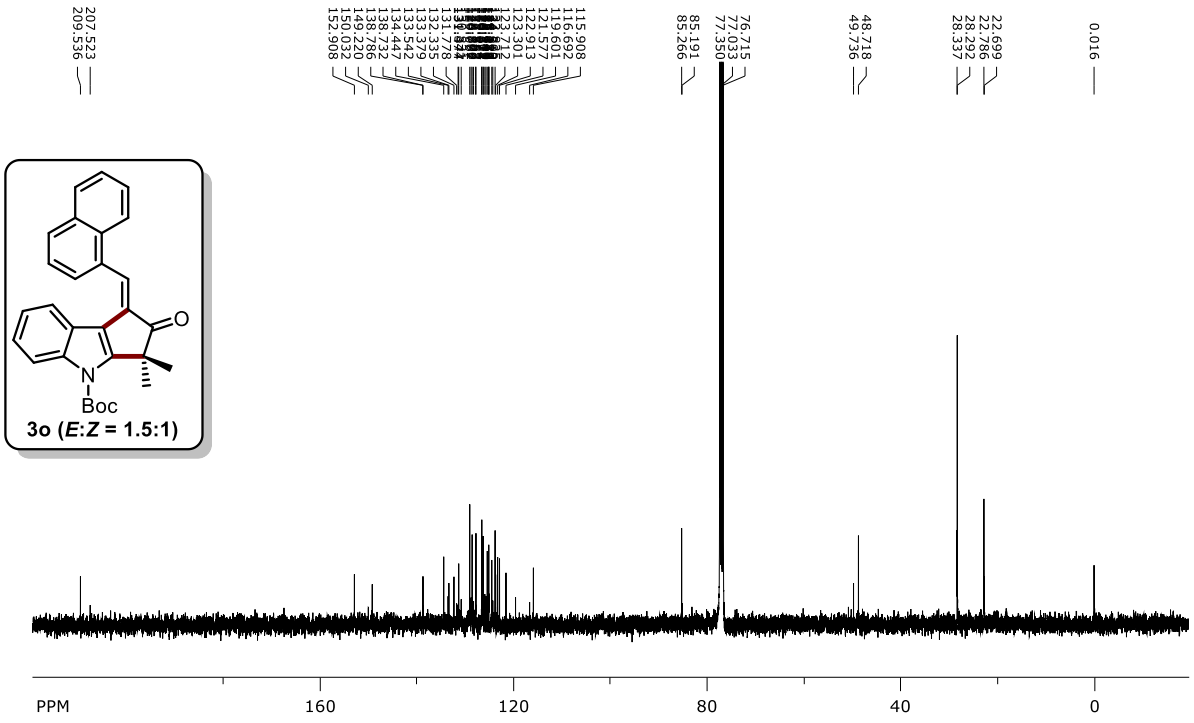
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 5.6-9.0 ppm region



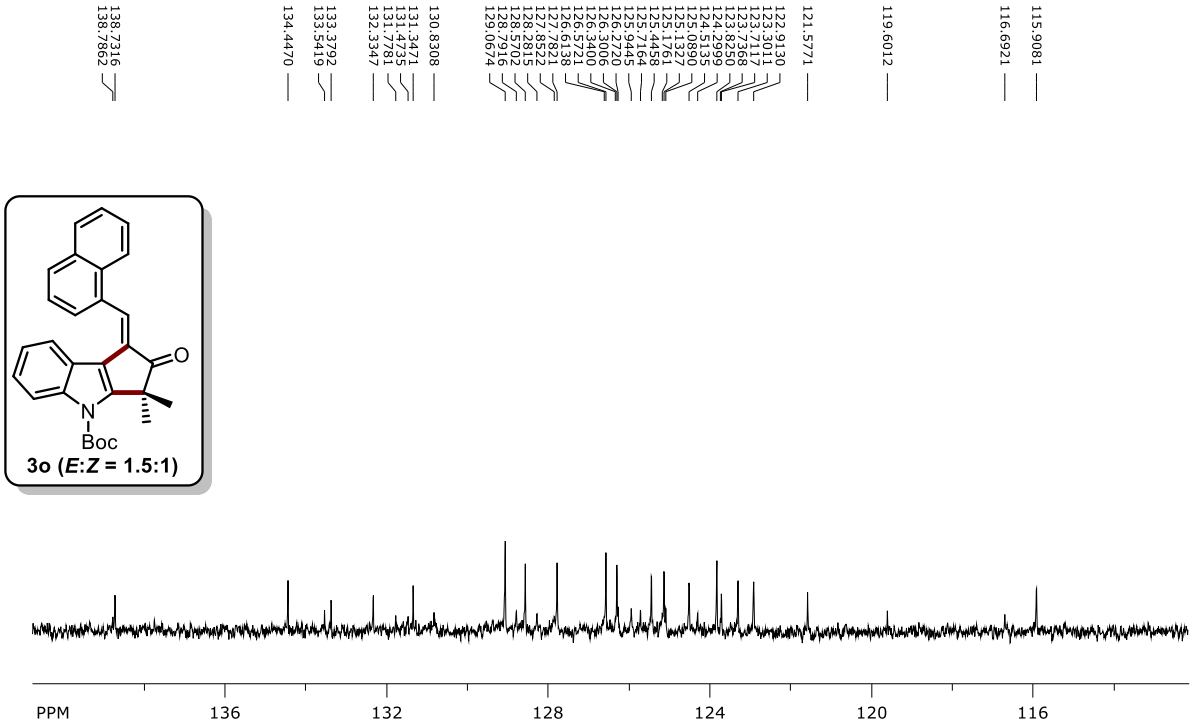
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 1.0-3.0 ppm region



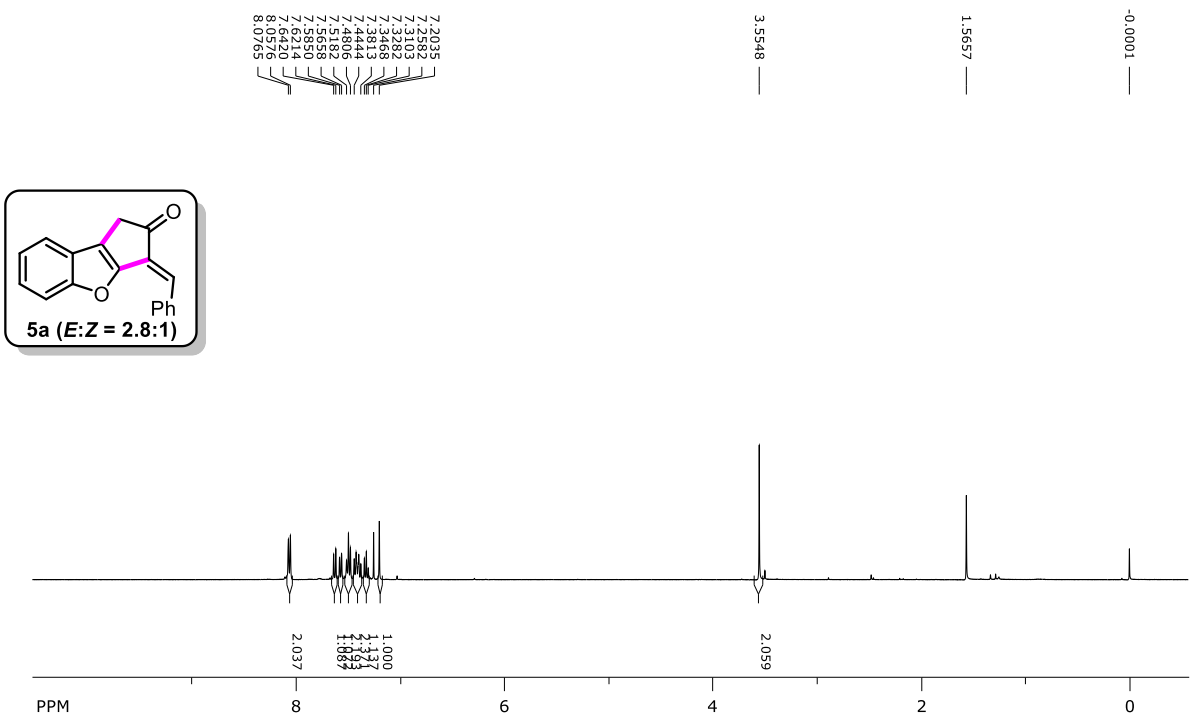
^{13}C NMR (100 MHz, $CDCl_3$):



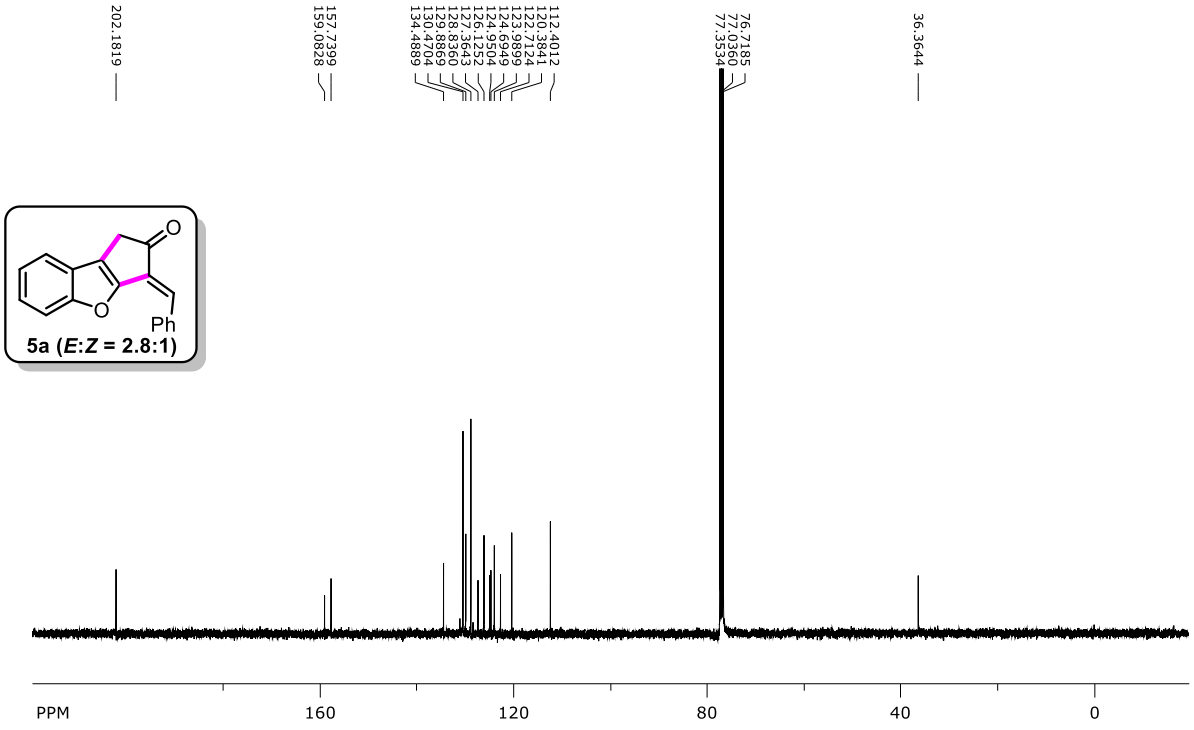
^{13}C NMR (100 MHz, $CDCl_3$): expansion of 110-140 ppm region



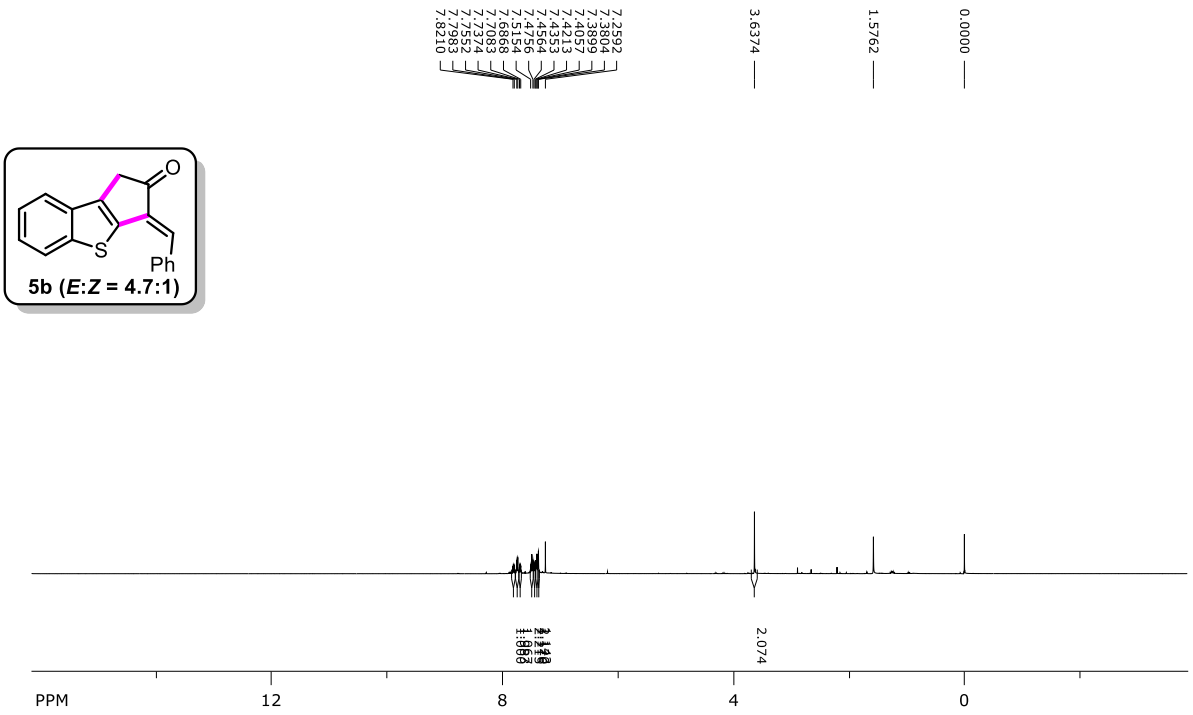
^{1}H NMR (400 MHz, $CDCl_3$):



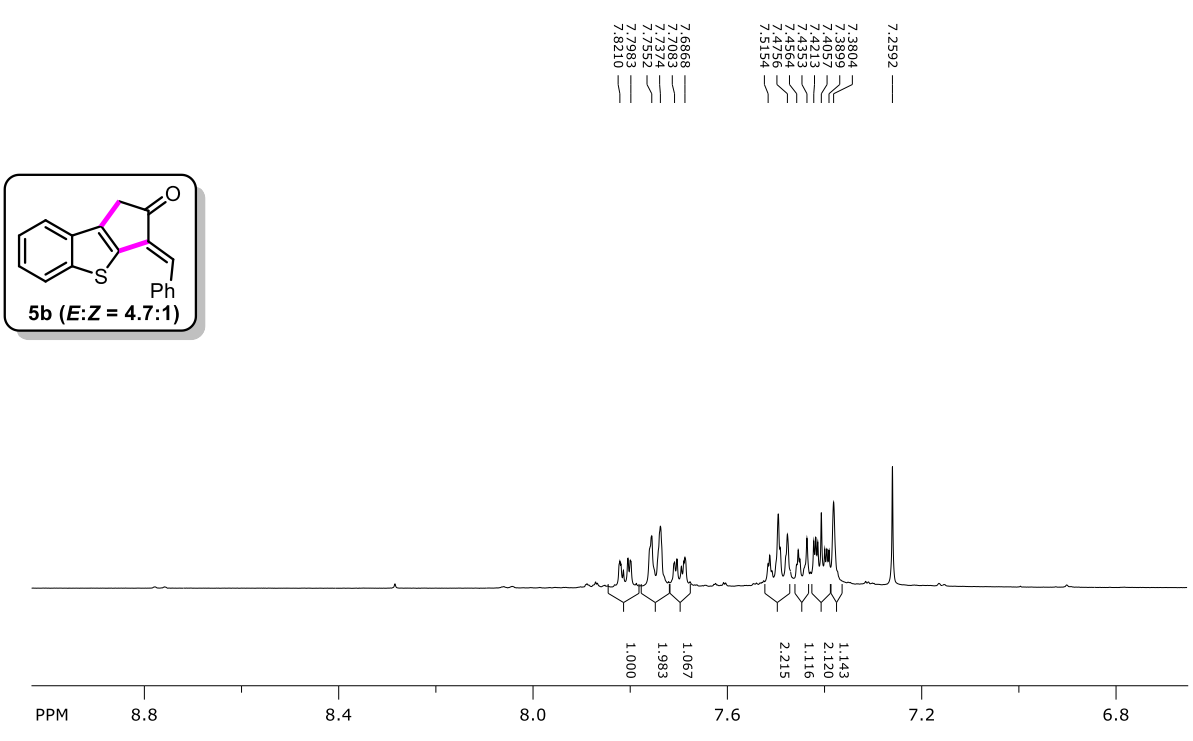
^{13}C NMR (100 MHz, $CDCl_3$):



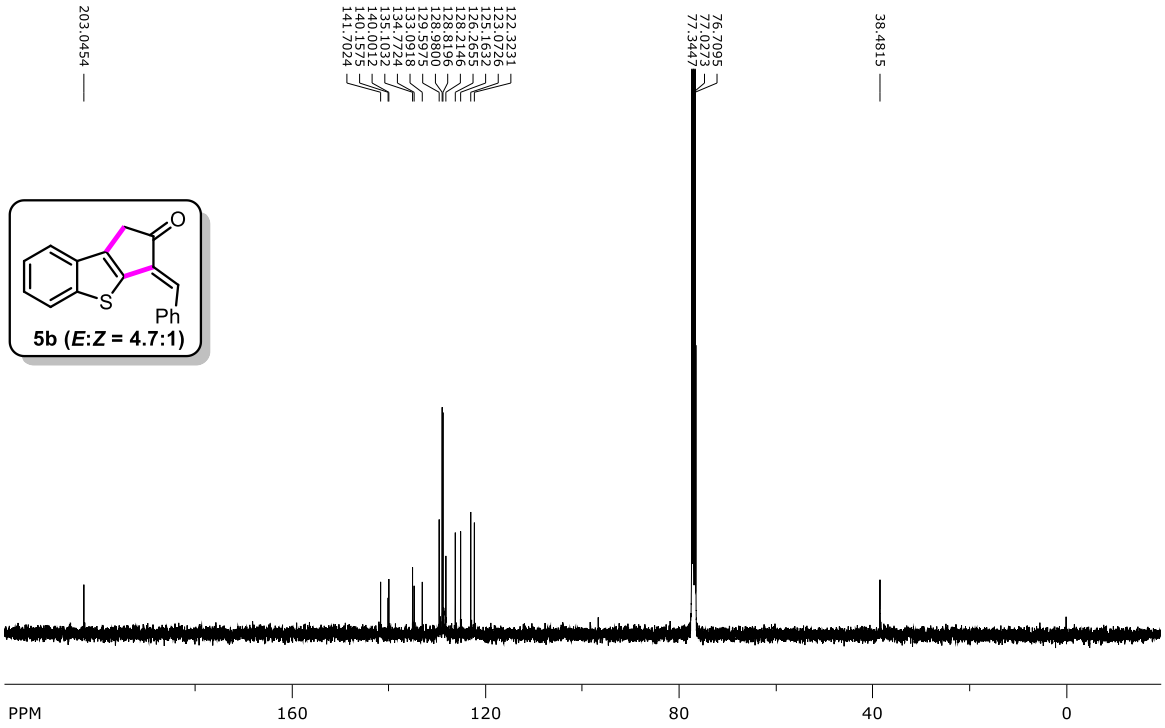
^{1}H NMR (400 MHz, $CDCl_3$):



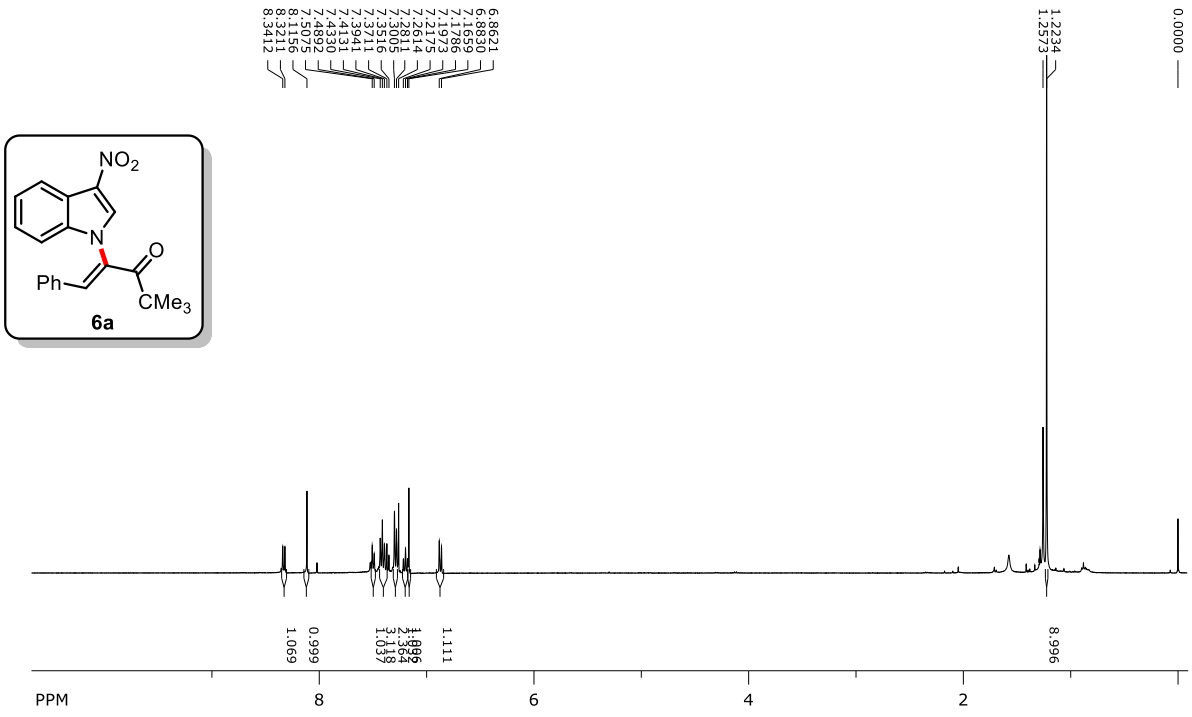
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.8-9.0 ppm region



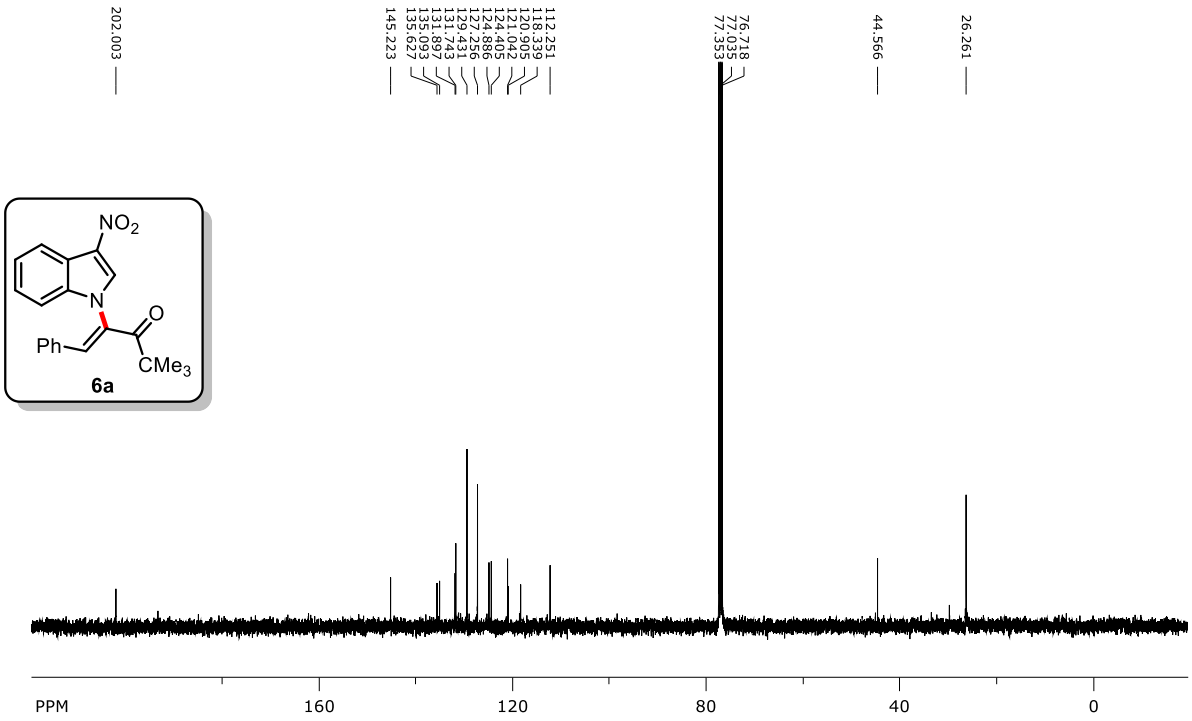
^{13}C NMR (100 MHz, $CDCl_3$):



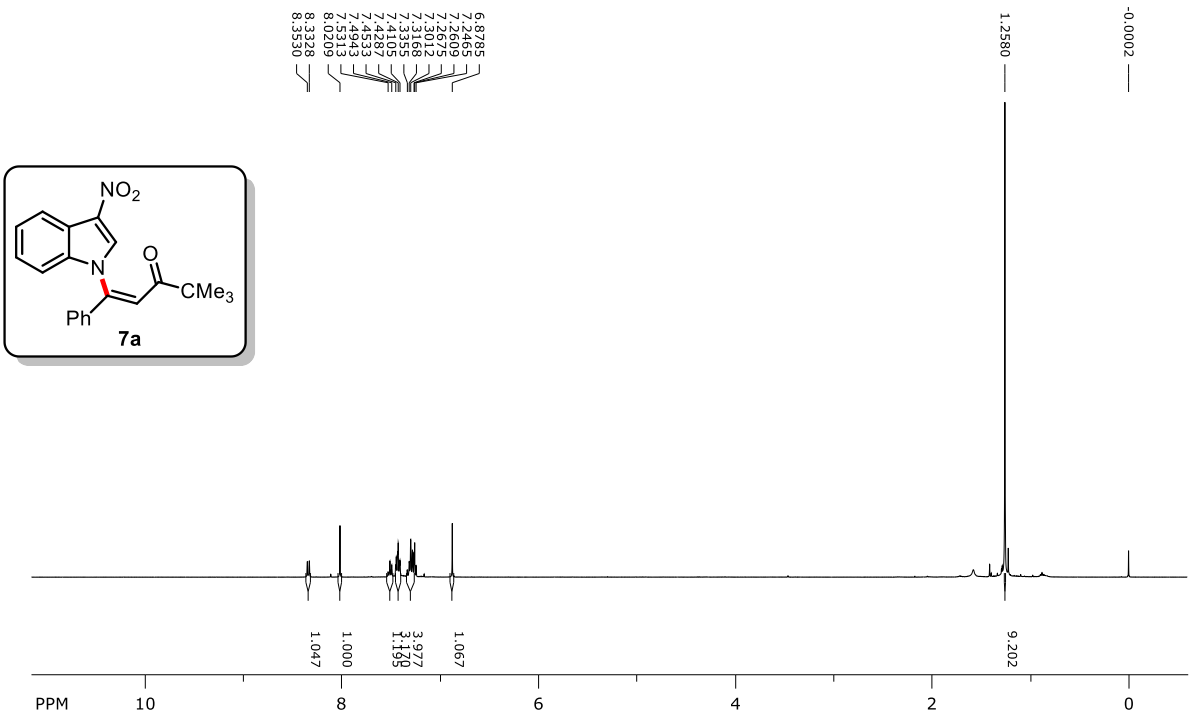
^{1}H NMR (400 MHz, $CDCl_3$):



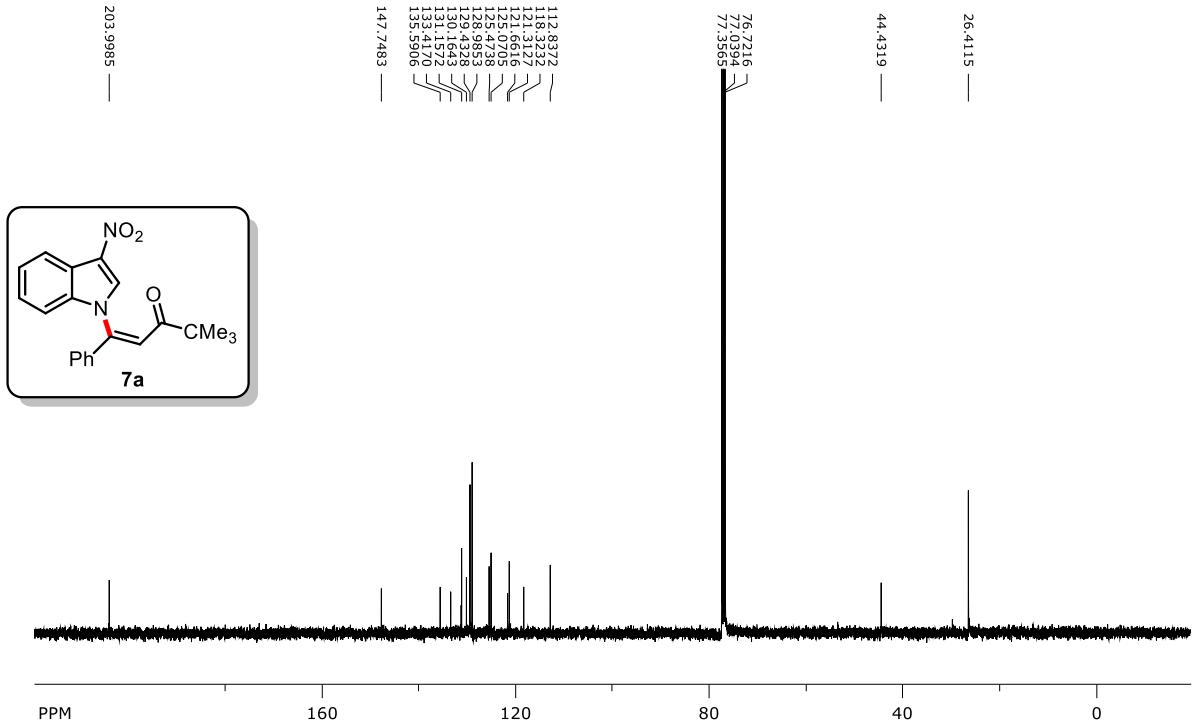
^{13}C NMR (100 MHz, $CDCl_3$):



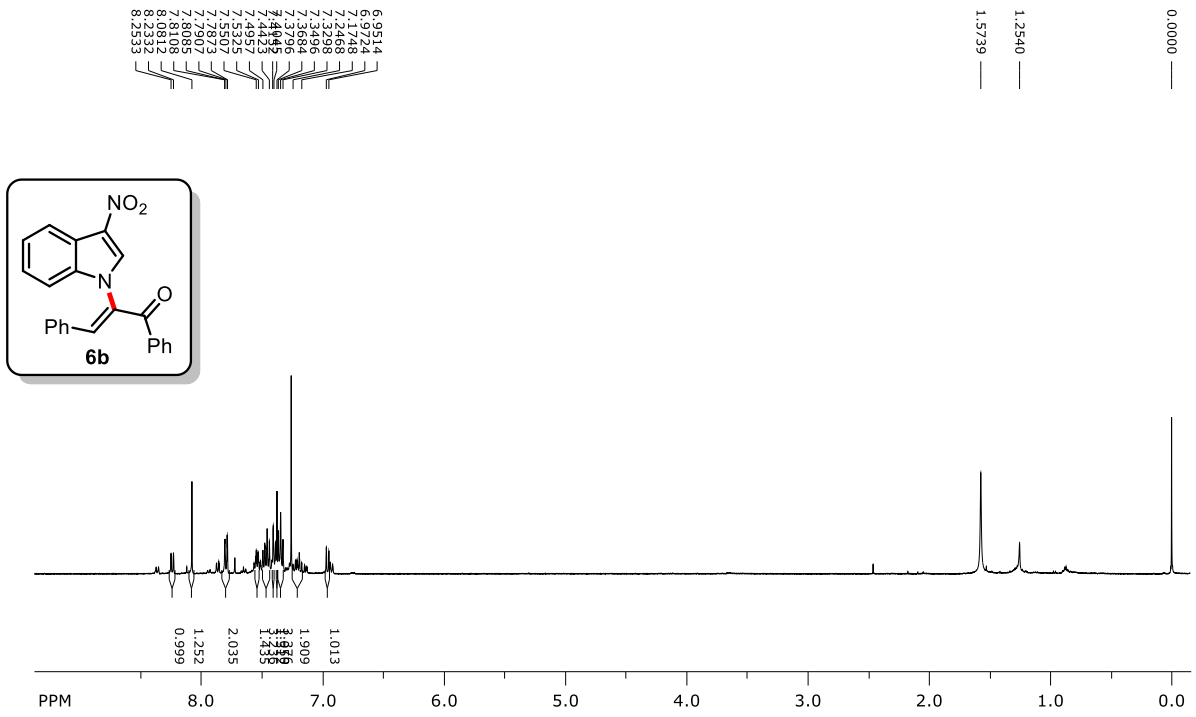
^{1}H NMR (400 MHz, $CDCl_3$):



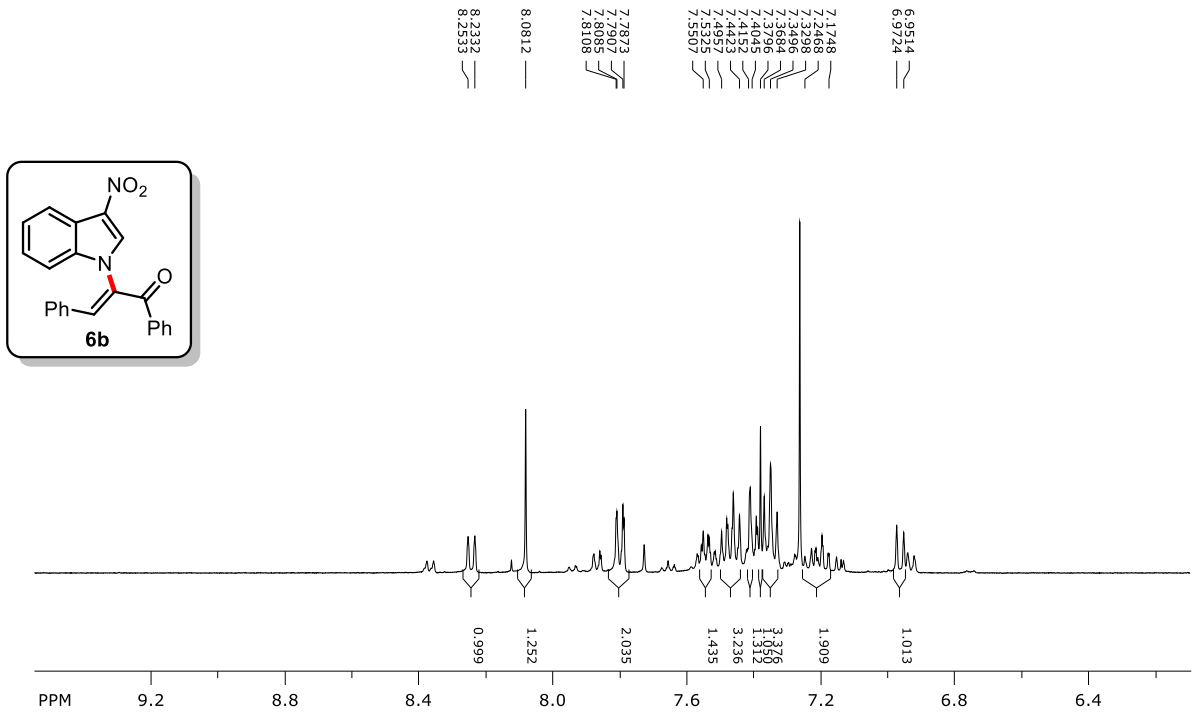
^{13}C NMR (100 MHz, $CDCl_3$):



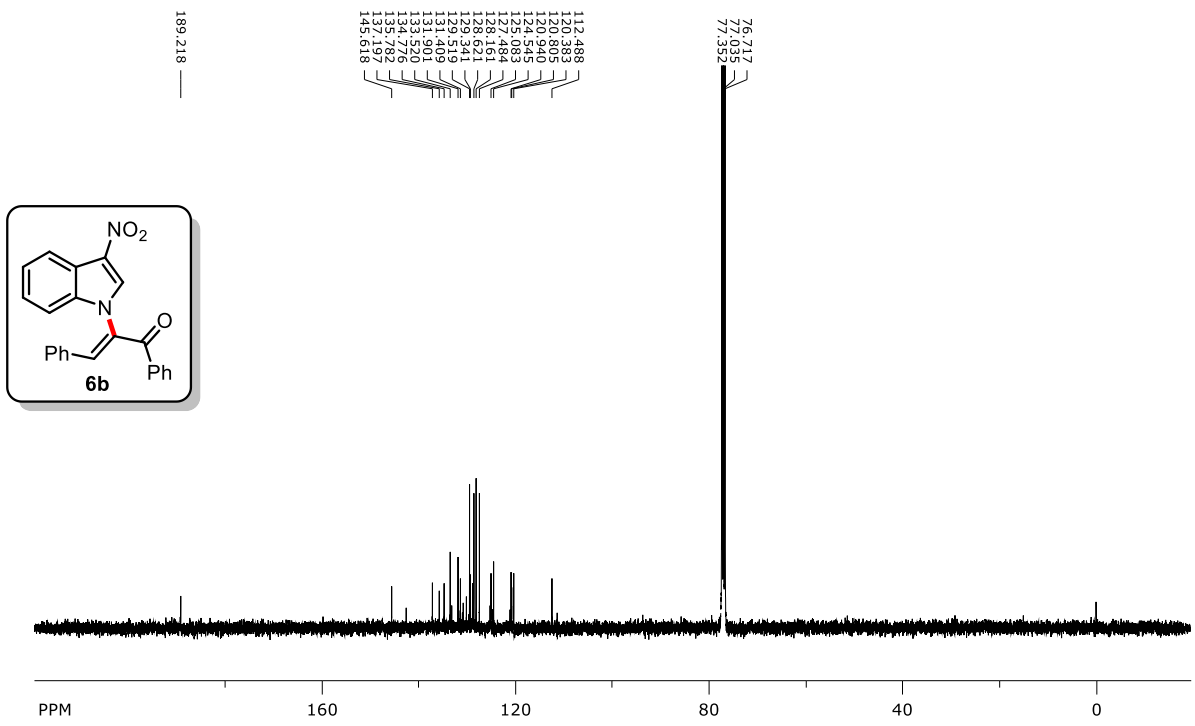
^{1}H NMR (400 MHz, $CDCl_3$):



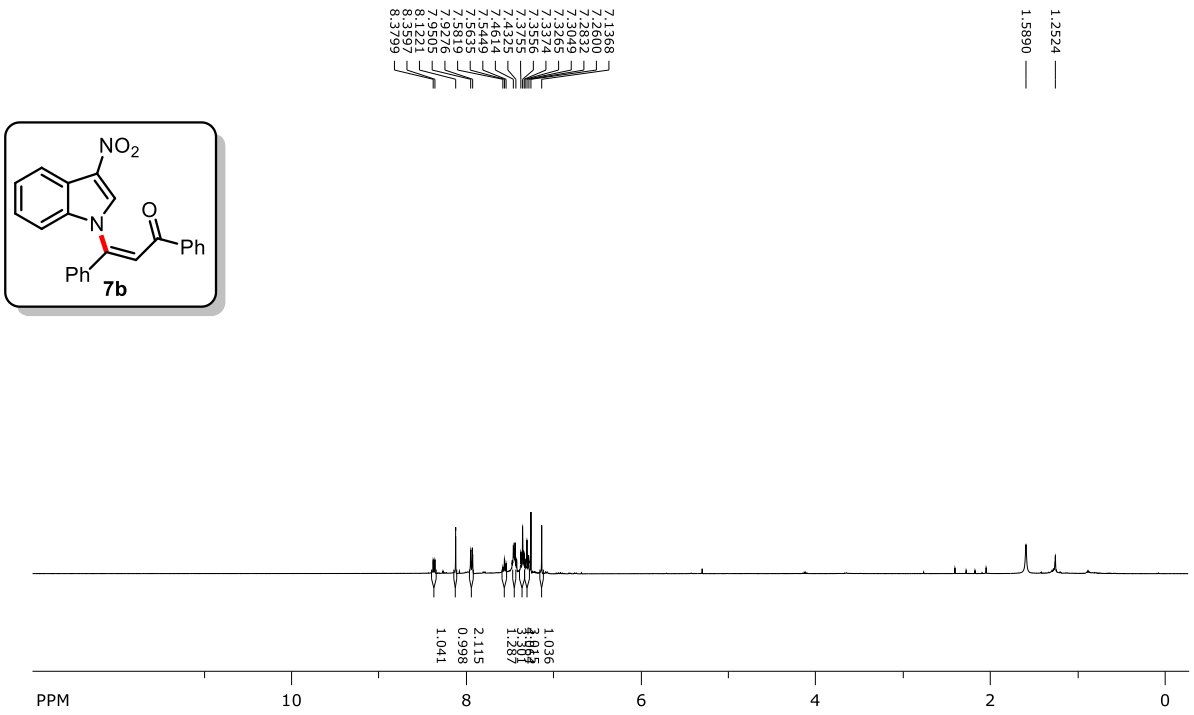
^{1}H NMR (400 MHz, $CDCl_3$): expansion of 6.5-9.0 ppm region



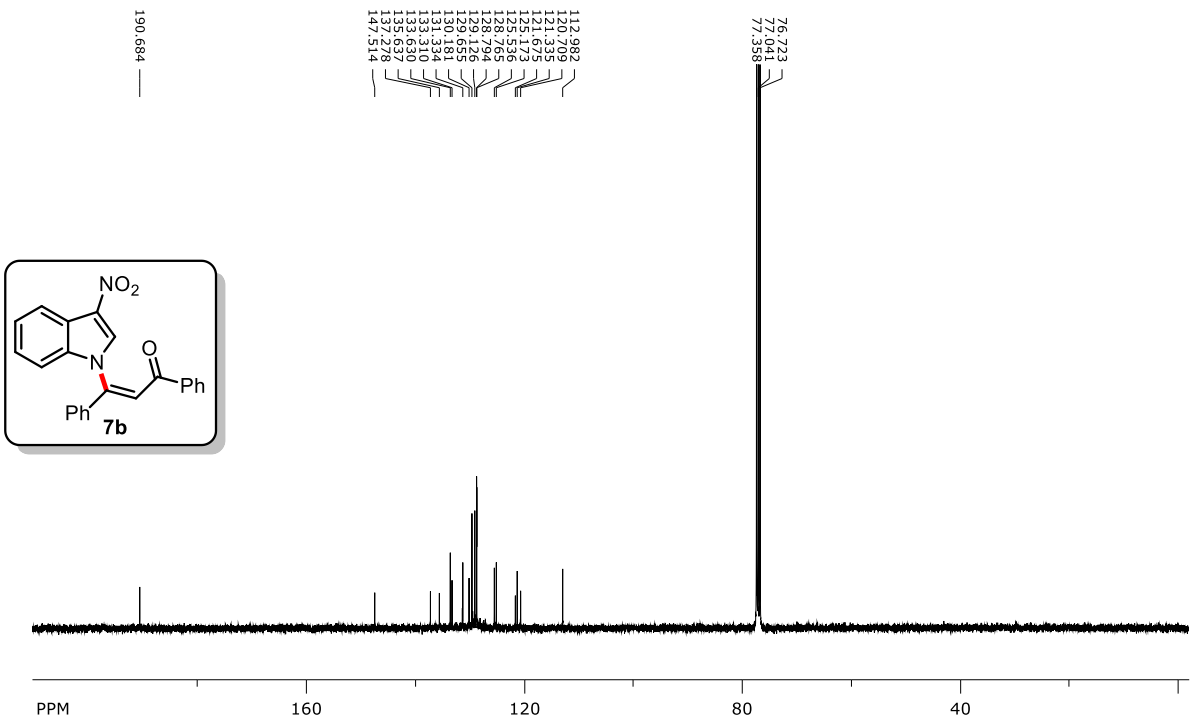
^{13}C NMR (100 MHz, $CDCl_3$):



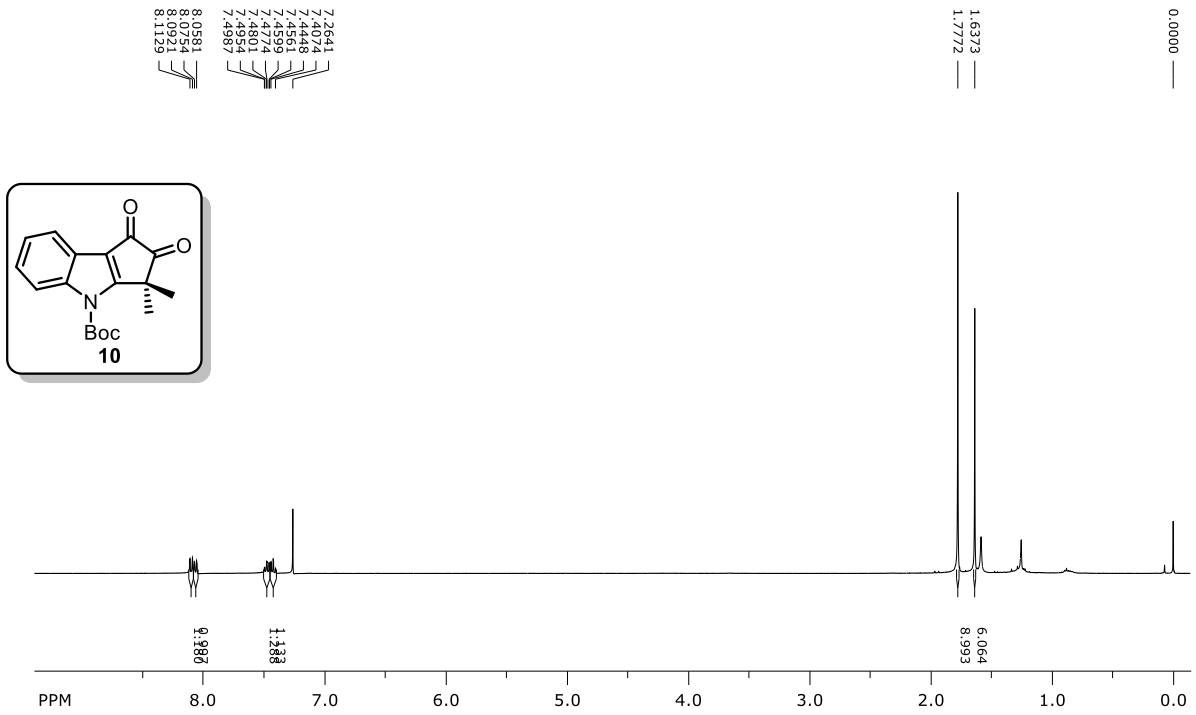
^{1}H NMR (400 MHz, $CDCl_3$):



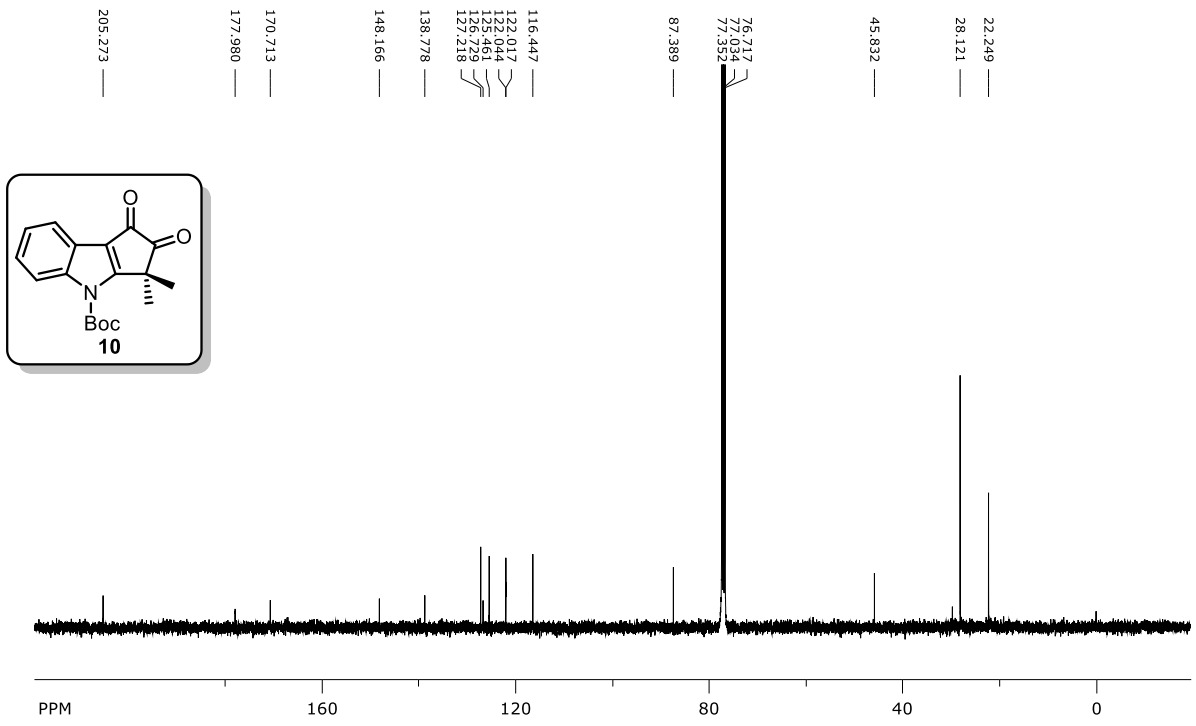
^{13}C NMR (100 MHz, $CDCl_3$):



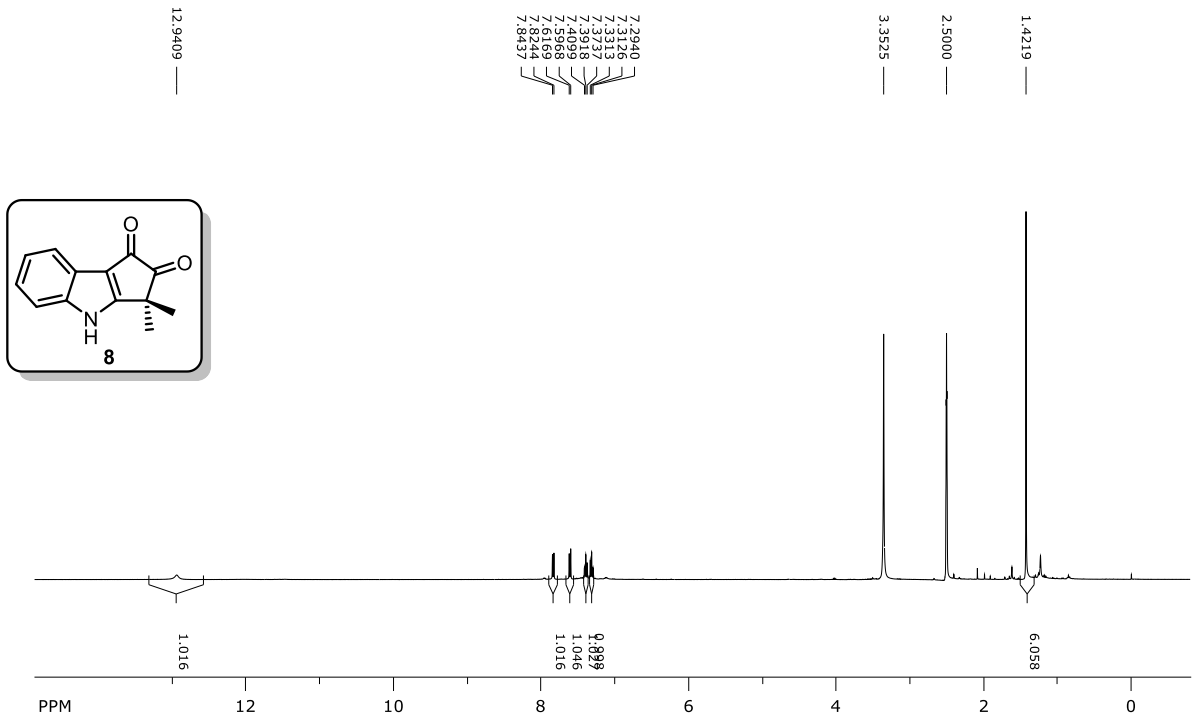
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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



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