

# Electronic Supplementary Information

## Rhodium Catalyzed Multicomponent Dehydrogenative Annulation: One-step Construction of Isoindole Derivatives

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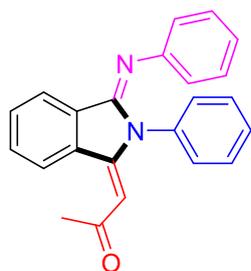
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## General Procedures

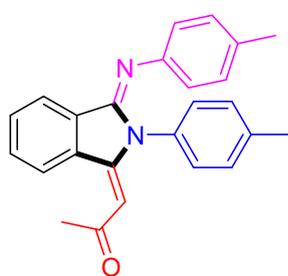
All reactions were carried out in flame-dried glassware using standard Schlenk techniques. All organic solvents were dried and distilled by standard methods prior to use.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{11}\text{B}$  NMR spectra were recorded on Bruker DPX 400/500 spectrometers at 400/500, 100/125, 128/160 MHz, respectively. All chemical shifts were reported in  $\delta$  units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external  $\text{BF}_3\cdot\text{OEt}_2$  (0.00 ppm) for boron chemical shifts. High resolution mass spectra (HRMS) were obtained on Thermo Q Exactive Focus Orbitrap APCI. GC-MS analyses were performed on Agilent GC-MS 6890N. Compounds **6a**,<sup>1</sup> **8a**<sup>2</sup> and **9a**<sup>3</sup> were prepared according to literature methods. Imines **1** were prepared by in-situ condensation of the corresponding aryl aldehydes and amines.<sup>4</sup> All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified.

**Preparation of isoindolin-1-imine-3-ylidene derivatives (4). A representative procedure.** In-situ condensation of the corresponding aryl aldehyde (0.1 mmol) and amine (0.1 mmol) generated imine **1**.<sup>4</sup> Imine **1** (1 equiv, 0.1 mmol), amine **2** (2 equiv, 0.2 mmol), vinyl ketone **3** (4 equiv, 0.4 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (1.2 mg, 2 mol%, 0.002 mmol) and  $\text{Cu}(\text{OAc})_2$  (127 mg, 7 equiv, 0.7 mmol) were mixed in DMF (2.0 mL). The resulting mixture was stirred at 110 °C under argon for 10 h. After cooling to room temperature, the reaction mixture was washed with water (3 x 3.0 mL) and extracted with diethyl ether (3 x 5.0 mL). The organic portions were combined. After removal of organic solvents under reduced pressure, the residue was subjected to flash column chromatography on silica gel (230-400 mesh) using dichloromethane and ethyl acetate (100/1 in V/V) as eluent to give the product **4**.



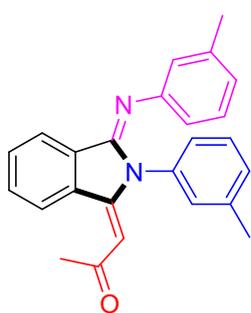
**4aa:** Yield 94%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.32 (d,  $J$  = 8.0 Hz, 1H), 7.56 (m, 3H), 7.49 (t,  $J$  = 7.6 Hz, 1H), 7.40 (d,  $J$  = 7.6 Hz, 2H), 7.31 (m, 2H), 7.26 (t,  $J$  = 7.6 Hz, 1H), 7.11 (t,  $J$  = 7.6 Hz, 1H), 6.90 (d,  $J$  = 7.6 Hz, 2H), 6.76 (d,  $J$  = 8.0 Hz, 1H) (aryl CH), 5.63 (s, 1H)

(alkenyl CH), 2.20 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2 (C=O), 153.3, 151.7, 149.6, 136.0, 134.8, 131.9, 131.1, 129.9, 129.7, 129.3, 128.9, 128.2, 128.0, 125.4, 123.5, 120.3, 103.5 (aryl C and alkenyl C), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 339.1492. Found: 339.1490.



**4ab:** Yield 93%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.33 (d,  $J$  = 8.0 Hz, 1H), 7.56 (d,  $J$  = 7.6 Hz, 1H), 7.39 (d,  $J$  = 8.0 Hz, 2H), 7.28 (m, 3H), 7.12 (d,  $J$  = 8.0 Hz, 2H), 6.80 (m, 3H) (aryl CH), 5.65 (s, 1H) (alkenyl CH), 2.46 (s, 3H), 2.37 (s, 3H), 2.22 (s, 3H) ( $\text{CH}_3$ ).

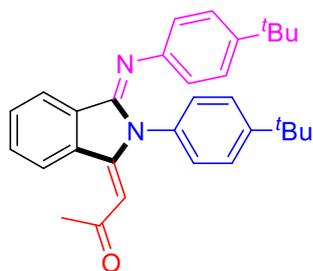
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2 (C=O), 153.6, 151.9, 147.1, 138.8, 134.8, 133.2, 132.8, 131.8, 131.1, 130.6, 129.8, 129.4, 128.1, 128.1, 125.4, 120.2, 103.3 (aryl C and alkenyl C), 32.5, 21.5, 21.1 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 367.1805. Found: 367.1802.



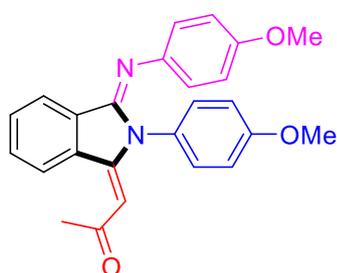
**4ac:** Yield 53%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.30 (d,  $J$  = 8.0 Hz, 1H), 7.55 (t,  $J$  = 7.6 Hz, 1H), 7.46 (t,  $J$  = 8.0 Hz, 1H), 7.27 (m, 2H), 7.19 (m, 3H), 6.92 (d,  $J$  = 7.6 Hz, 1H), 6.78 (d,  $J$  = 8.0 Hz, 1H), 6.71 (m, 2H) (aryl CH), 5.60 (s, 1H) (alkenyl CH), 2.46 (s, 3H), 2.31 (s, 3H), 2.20 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3 (C=O),

153.3, 151.9, 149.6, 139.9, 139.1, 135.9, 134.8, 131.8, 131.1, 130.3, 129.9, 129.6, 129.1, 128.2, 128.1, 126.7, 125.5, 124.3, 121.0, 117.4, 103.5 (aryl C and alkenyl C), 32.6, 21.6, 21.6 ( $\text{CH}_3$ ).

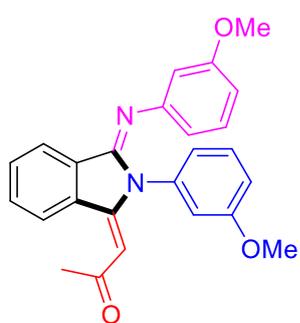
HRMS:  $m/z$  calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 367.1805. Found: 367.1805.



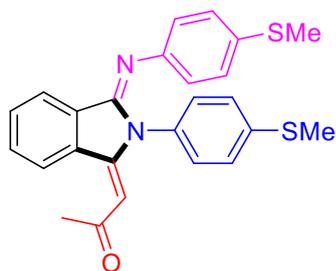
**4ad:** Yield 86%. Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.30 (d,  $J = 8.0$  Hz, 1H), 7.55 (m, 3H), 7.29 (m, 5H), 6.82 (m, 3H) (aryl CH), 5.66 (s, 1H) (alkenyl CH), 2.21 (s, 3H) ( $\text{CH}_3$ ), 1.39 (s, 9H), 1.33 (s, 9H) ( $^t\text{Bu}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.4 ( $\text{C}=\text{O}$ ), 153.3, 151.9, 151.5, 146.9, 146.5, 134.8, 133.2, 131.8, 131.1, 129.0, 128.1, 126.8, 126.1, 125.4, 119.8, 103.3 (aryl C and alkenyl C), 34.9, 34.5, 32.6, 31.7, 31.5 ( $\text{CH}_3$  and  $^t\text{Bu}$ ). HRMS:  $m/z$  calcd for  $\text{C}_{31}\text{H}_{35}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 451.2744. Found: 451.2743.



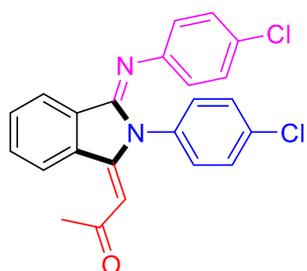
**4ae:** Yield 83%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.30 (d,  $J = 8.0$  Hz, 1H), 7.55 (d,  $J = 7.6$  Hz, 1H), 7.29 (m, 3H), 7.08 (m, 2H), 6.85 (m, 5H) (aryl CH), 5.62 (s, 1H) (alkenyl CH), 3.88 (s, 3H), 3.82 (s, 3H) ( $\text{OCH}_3$ ), 2.21 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3 ( $\text{C}=\text{O}$ ), 159.6, 156.1, 154.2, 152.1, 142.9, 134.7, 131.8, 131.1, 130.7, 128.4, 128.1, 128.0, 125.3, 121.3, 115.2, 114.5, 103.3 (aryl C and alkenyl C), 55.6 ( $\text{OCH}_3$ ), 32.5 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_3^+$   $[\text{M}+\text{H}]^+$ : 399.1703. Found: 399.1702.



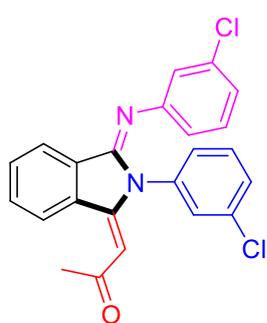
**4af:** Yield 60%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.29 (d,  $J = 8.0$  Hz, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.49 (t,  $J = 8.0$  Hz, 1H), 7.28 (t,  $J = 7.6$  Hz, 1H), 7.21 (t,  $J = 8.0$  Hz, 1H), 6.99 (m, 2H), 6.92 (m, 1H), 6.85 (d,  $J = 7.6$  Hz, 1H), 6.67 (m, 1H), 6.49 (m, 2H) (aryl CH), 5.65 (s, 1H) (alkenyl CH), 3.87 (s, 3H), 3.78 (s, 3H) ( $\text{OCH}_3$ ), 2.21 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3 ( $\text{C}=\text{O}$ ), 160.6, 153.3, 151.5, 150.9, 137.0, 134.7, 132.0, 131.2, 130.6, 130.1, 128.1, 127.9, 125.6, 121.9, 115.5, 114.6, 112.7, 109.6, 105.7, 103.8 (aryl C and alkenyl C), 55.6, 55.4 ( $\text{OCH}_3$ ), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_3^+$   $[\text{M}+\text{H}]^+$ : 399.1703. Found: 399.1701.



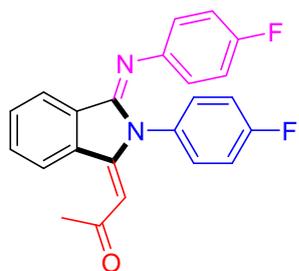
**4ag:** Yield 56%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.29 (d,  $J = 8.0$  Hz, 1H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.41 (m, 2H), 7.29 (m, 3H), 7.24 (m, 2H), 6.85 (m, 3H) (aryl CH), 5.64 (s, 1H) (alkenyl CH), 3.54 (s, 3H), 3.50 (s, 3H) ( $\text{OCH}_3$ ), 2.21 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3 (C=O), 153.6, 151.5, 147.3, 139.9, 134.7, 132.5, 132.1, 131.3, 130.0, 128.5, 128.2, 127.9, 127.2, 125.4, 121.1, 103.8 (aryl C and alkenyl C), 32.6 ( $\text{CH}_3$ ), 17.0, 15.6 ( $\text{SCH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{OS}_2^+$   $[\text{M}+\text{H}]^+$ : 431.1246. Found: 431.1244.



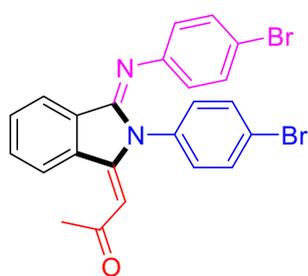
**4ah:** Yield 91%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.30 (d,  $J = 8.0$  Hz, 1H), 7.57 (m, 3H), 7.31 (m, 5H), 6.83 (m, 3H) (aryl CH), 5.63 (s, 1H) (alkenyl CH), 2.22 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1 (C=O), 153.5, 151.0, 147.9, 135.0, 134.6, 134.2, 132.3, 131.3, 131.1, 130.2, 129.4, 128.8, 128.3, 127.6, 125.3, 121.7, 104.1 (aryl C and alkenyl C), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{OCl}_2^+$   $[\text{M}+\text{H}]^+$ : 407.0713. Found: 407.0712.



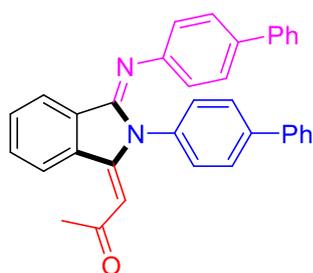
**4ai:** Yield 61%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.28 (d,  $J = 8.0$  Hz, 1H), 7.59 (t,  $J = 7.6$  Hz, 1H), 7.51 (m, 2H), 7.40 (m, 1H), 7.30 (m, 3H), 7.10 (d,  $J = 7.6$  Hz, 1H), 6.94 (m, 1H), 6.85 (d,  $J = 7.6$  Hz, 1H), 6.80 (d,  $J = 7.6$  Hz, 1H) (aryl CH), 5.62 (s, 1H) (alkenyl CH), 2.24 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3 (C=O), 153.4, 150.9, 150.6, 137.0, 135.4, 135.0, 134.6, 132.4, 131.5, 130.9, 130.4, 130.1, 129.5, 128.4, 128.1, 127.6, 125.4, 123.7, 120.7, 118.7, 104.4 (aryl C and alkenyl C), 32.7 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{OCl}_2^+$   $[\text{M}+\text{H}]^+$ : 407.0713. Found: 407.0715.



**4aj:** Yield 59%. Yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.30 (d,  $J = 8.0$  Hz, 1H), 7.58 (m, 1H), 7.33 (m, 5H), 7.02 (m, 2H), 6.84 (m, 2H), 6.79 (d,  $J = 8.0$  Hz, 1H) (aryl CH), 5.59 (s, 1H) (alkenyl CH), 2.22 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2 ( $\text{C}=\text{O}$ ), 162.6 (d,  $^1J_{\text{C-F}} = 248$  Hz), 159.7 (d,  $^1J_{\text{C-F}} = 240$  Hz), 154.0, 151.5, 145.5, 134.7, 132.2, 131.7, 131.5 (d,  $^3J_{\text{C-F}} = 8$  Hz), 131.3, 128.3, 127.8, 125.3, 121.6 (d,  $^3J_{\text{C-F}} = 8$  Hz), 117.1 (d,  $^2J_{\text{C-F}} = 23$  Hz), 116.2 (d,  $^2J_{\text{C-F}} = 22$  Hz), 103.9 (aryl C and alkenyl C), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{OF}_2^+$  [ $\text{M}+\text{H}$ ] $^+$ : 375.1304. Found: 375.1303.



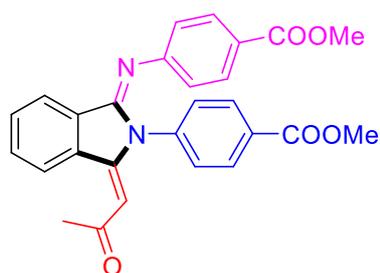
**4ak:** Yield 80%. Yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.29 (d,  $J = 8.0$  Hz, 1H), 7.71 (m, 2H), 7.58 (t,  $J = 7.6$  Hz, 1H), 7.43 (m, 2H), 7.30 (m, 3H), 6.85 (d,  $J = 8.0$  Hz, 1H), 6.78 (m, 2H) (aryl CH), 5.63 (s, 1H) (alkenyl CH), 2.22 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2 ( $\text{C}=\text{O}$ ), 153.3, 150.9, 148.4, 134.8, 134.6, 133.2, 132.3, 131.4, 128.4, 127.7, 125.3, 123.2, 122.2, 116.5, 104.1 (aryl C and alkenyl C), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{OBr}_2^+$  [ $\text{M}+\text{H}$ ] $^+$ : 496.9683. Found: 496.9682.



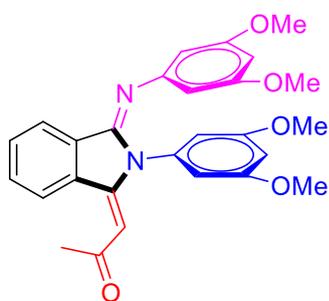
**4al:** Yield 41%. Yellow crystals.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.34 (d,  $J = 8.0$  Hz, 1H), 7.81 (m, 2H), 7.67 (m, 4H), 7.59 (m, 3H), 7.45 (m, 7H), 7.30 (m, 2H), 7.01 (m, 2H), 6.94 (d,  $J = 8.0$  Hz, 1H) (aryl CH), 5.74 (s, 1H) (alkenyl CH), 2.24 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.4 ( $\text{C}=\text{O}$ ), 153.4, 151.6, 149.0, 141.8, 140.8, 140.3, 136.3, 135.0, 134.8, 132.1, 131.3, 130.0, 129.1, 128.9, 128.6, 128.3, 128.1, 127.9, 127.4, 127.1, 126.8, 125.5, 120.9, 103.8 (aryl C and alkenyl C), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{35}\text{H}_{27}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 491.2118. Found: 491.2119.



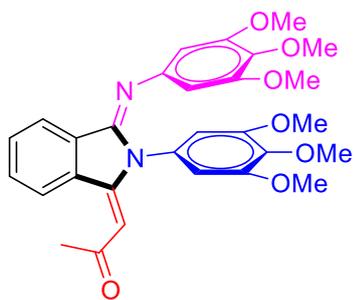
**Figure S1.** Molecular Structure of **4al**



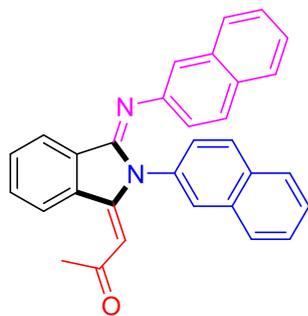
**4am:** Yield 35%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.28 (d,  $J = 8.0$  Hz, 1H), 8.26 (m, 2H), 8.01 (m, 2H), 7.59 (t,  $J = 8.0$  Hz, 1H), 7.49 (m, 2H), 7.28 (m, 1H), 7.95 (m, 2H), 6.79 (m, 1H) (aryl CH), 5.64 (s, 1H) (alkenyl CH), 3.96 (s, 3H), 3.92 (s, 3H) ( $\text{COOCH}_3$ ), 2.21 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2 ( $\text{C}=\text{O}$ ), 167.1, 166.4, 153.9, 152.9, 150.7, 134.0, 134.7, 132.5, 131.5, 131.3, 130.7, 129.9, 128.4, 127.7, 125.3, 120.3, 104.5 (aryl C and alkenyl C), 52.9, 52.1 ( $\text{COOCH}_3$ ), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_5^+$   $[\text{M}+\text{H}]^+$ : 455.1602. Found: 455.1600.



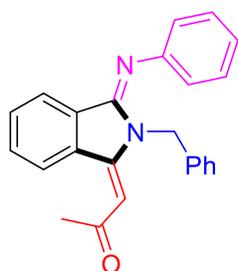
**4an:** Yield 48%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.28 (d,  $J = 8.0$  Hz, 1H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.31 (t,  $J = 7.6$  Hz, 1H), 6.97 (d,  $J = 7.6$  Hz, 1H), 6.57 (s, 1H), 6.51 (m, 2H), 6.24 (s, 1H), 6.10 (m, 2H) (aryl CH), 5.67 (s, 1H) (alkenyl CH), 3.84 (s, 6H), 3.74 (s, 6H) ( $\text{OCH}_3$ ), 2.23 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.4 ( $\text{C}=\text{O}$ ), 161.5, 153.1, 151.6, 151.3, 137.5, 134.6, 132.0, 131.3, 128.1, 127.8, 125.7, 108.0, 103.9, 101.1, 98.5, 96.2 (aryl C and alkenyl C), 55.7, 55.5 ( $\text{OCH}_3$ ), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}_5^+$   $[\text{M}+\text{H}]^+$ : 459.1915. Found: 459.1914.



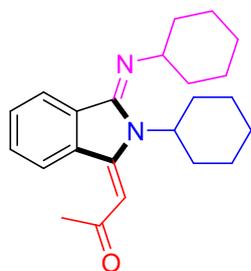
**4ao:** Yield 33%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.27 (d,  $J = 8.0$  Hz, 1H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.33 (t,  $J = 7.6$  Hz, 1H), 6.94 (d,  $J = 7.6$  Hz, 1H), 6.57 (s, 2H), 6.17 (s, 2H) (aryl CH), 5.62 (s, 1H) (alkenyl CH), 3.92 (s, 3H), 3.90 (s, 6H), 3.85 (s, 3H), 3.78 (s, 6H) ( $\text{OCH}_3$ ), 2.24 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.4 ( $\text{C}=\text{O}$ ), 154.1, 154.0, 153.9, 151.7, 145.7, 138.3, 134.61, 134.5, 132.1, 131.4, 128.1, 127.7, 125.7, 106.9, 104.1, 97.6 (aryl C and alkenyl C), 61.4, 61.0, 56.4, 56.2 ( $\text{OCH}_3$ ), 32.7 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{29}\text{H}_{31}\text{N}_2\text{O}_7^+$   $[\text{M}+\text{H}]^+$ : 519.2126. Found: 519.2127.



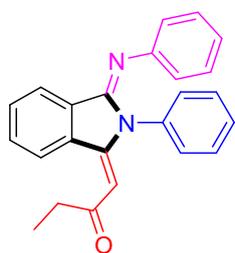
**4ap:** Yield 74%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.37 (d,  $J = 8.0$  Hz, 1H), 8.07 (d,  $J = 8.8$  Hz, 1H), 7.96 (m, 3H), 7.83 (m, 2H), 7.72 (d,  $J = 8.0$  Hz, 1H), 7.57 (m, 4H), 7.42 (m, 2H), 7.35 (s, 1H), 7.17 (m, 2H), 6.81 (d,  $J = 7.6$  Hz, 1H) (aryl CH), 5.72 (s, 1H) (alkenyl CH), 2.18 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.4 ( $\text{C}=\text{O}$ ), 153.7, 151.7, 147.2, 134.9, 134.4, 133.8, 133.4, 133.3, 132.1, 131.3, 130.6, 123.0, 129.2, 129.0, 128.4, 128.2, 128.1, 128.1, 127.9, 127.4, 127.8, 127.1, 126.8, 126.4, 125.5, 124.5, 121.7, 116.2, 104.0 (aryl C and alkenyl C), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{31}\text{H}_{23}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 439.1805. Found: 439.1803.



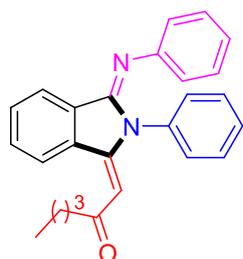
**4aq:** Yield 34%. Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.35 (d,  $J = 8.0$  Hz, 1H), 7.51 (m, 1H), 7.36 (m, 4H), 7.30 (m, 3H), 7.22 (m, 1H), 7.17 (t,  $J = 7.6$  Hz, 1H), 6.97 (m, 2H), 7.80 (d,  $J = 7.6$  Hz, 1H) (aryl CH), 5.25 (s, 1H) (alkenyl CH), 2.25 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.9 ( $\text{C}=\text{O}$ ), 152.3, 149.4, 149.2, 136.6, 135.1, 131.9, 130.8, 129.5, 128.9, 128.2, 128.0, 127.5, 126.9, 125.2, 123.8, 120.5, 103.0 (aryl C and alkenyl C), 44.5 ( $\text{CH}_3$ ) 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 353.1648. Found: 353.1647.



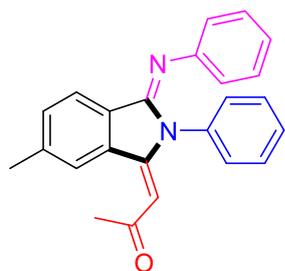
**4ar:** Yield 46%. Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.35 (m, 1H), 7.51 (m, 1H), 7.84 (m, 1H), 7.50 (m, 2H) (aryl *CH*), 5.94 (s, 1H) (alkenyl *CH*), 4.26 (m, 1H), 2.52 (m, 1H) (*CH*), 2.34 (s, 3H) ( $\text{CH}_3$ ), 1.87 (m, 7H), 1.64 (m, 5H), 1.41 (m, 6H), 1.24 (m, 2H) ( $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.4 ( $\text{C}=\text{O}$ ), 150.1, 135.6, 131.0, 130.8, 128.1, 128.0, 124.7 (aryl *C* and alkenyl *C*), 56.5, 34.7, 32.8, 28.9, 26.8, 26.1, 25.9, 24.5 (*CH*,  $\text{CH}_2$  and  $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 351.2431. Found: 351.2428.



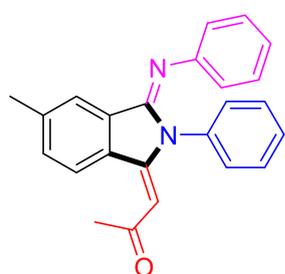
**4as:** Yield 80%. Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.36 (d,  $J = 8.0$  Hz, 1H), 7.56 (m, 3H), 7.49 (t,  $J = 7.6$  Hz, 1H), 7.28 (m, 3H), 7.26 (t,  $J = 7.6$  Hz, 1H), 7.11 (t,  $J = 7.6$  Hz, 1H), 6.90 (d,  $J = 7.6$  Hz, 2H), 6.75 (d,  $J = 8.0$  Hz, 1H) (aryl *CH*), 5.63 (s, 1H) (alkenyl *CH*), 2.46 (q,  $J = 7.6$  Hz, 2H), 1.09 (t,  $J = 7.6$  Hz, 2H) (Et).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.5 ( $\text{C}=\text{O}$ ), 153.3, 151.5, 149.7, 136.1, 134.9, 131.9, 131.1, 129.9, 129.8, 129.3, 128.9, 128.2, 128.0, 125.4, 123.5, 120.4, 103.1 (aryl *C* and alkenyl *C*), 28.1, 8.9 (Et). HRMS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 353.1648. Found: 353.1648.



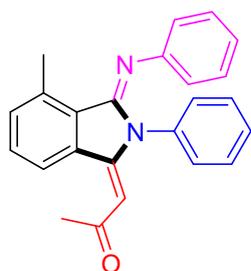
**4at:** Yield 80%. Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.35 (d,  $J = 8.0$  Hz, 1H), 7.64-7.44 (m, 4H), 7.40 (d,  $J = 7.2$  Hz, 2H), 7.35-7.20 (m, 3H), 7.10 (dd,  $J = 7.6, 7.2$  Hz, 1H), 6.90 (d,  $J = 7.6$  Hz, 2H), 6.74 (d,  $J = 7.6$  Hz, 1H) (aryl *CH*), 5.62 (s, 1H) (alkenyl *CH*), 2.42 (t,  $J = 7.6$  Hz, 2H), 1.66-1.51 (m, 2H), 1.35-1.20 (m, 4H), 0.87 (t,  $J = 6.8$  Hz, 3H) (*n*-pentyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.1 ( $\text{C}=\text{O}$ ), 153.2, 151.3, 149.6, 135.9, 134.7, 131.7, 130.9, 129.7, 129.6, 129.1, 128.7, 128.0, 127.9, 125.2, 123.3, 120.2, 103.3 (aryl *C* and alkenyl *C*), 44.9, 31.4, 24.6, 22.5, 13.9 (*n*-pentyl). HRMS:  $m/z$  calcd for  $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 395.2118. Found: 395.2112.



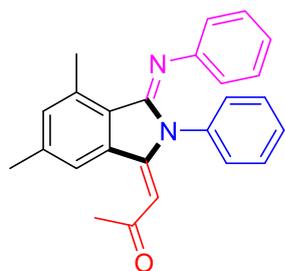
**4ba:** Yield 85%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.14 (s, 1H), 7.58 (t,  $J = 7.6$  Hz, 2H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.39 (d,  $J = 7.6$  Hz, 2H), 7.30 (t,  $J = 7.6$  Hz, 2H), 7.09 (m, 2H), 6.90 (d,  $J = 7.6$  Hz, 2H), 6.62 (d,  $J = 8.0$  Hz, 1H) (aryl CH), 5.61 (s, 1H) (alkenyl CH), 2.45, 2.20 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3 (C=O), 153.5, 152.0, 149.7, 142.7, 136.1, 135.1, 132.0, 129.9, 129.8, 129.3, 128.9, 128.5, 125.5, 125.2, 123.5, 120.5, 103.4 (aryl C and alkenyl C), 32.2, 22.2 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 353.1648. Found: 353.1648.



**4ca:** Yield 83%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.19 (d,  $J = 8.0$  Hz, 1H), 7.58 (t,  $J = 7.6$  Hz, 2H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.34 (m, 5H), 7.11 (t,  $J = 7.2$  Hz, 1H), 6.89 (d,  $J = 7.6$  Hz, 2H), 6.50 (s, 1H) (aryl CH), 5.58 (s, 1H) (alkenyl CH), 2.19 (s, 6H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2 (C=O), 153.5, 151.9, 149.7, 141.7, 136.1, 132.7, 132.3, 129.8, 129.8, 129.2, 128.9, 128.3, 128.0, 126.0, 123.5, 120.4, 103.0 (aryl C and alkenyl C), 32.5, 22.0 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 353.1648. Found: 353.1647.

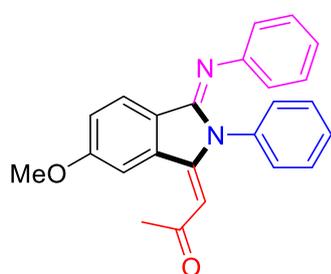


**4da:** Yield 83%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.12 (d,  $J = 7.6$  Hz, 1H), 7.53 (t,  $J = 7.6$  Hz, 1H), 7.44 (d,  $J = 7.2$  Hz, 1H), 7.10 (m, 3H), 6.96 (m, 2H), 6.84 (t,  $J = 7.6$  Hz, 2H), 6.61 (t,  $J = 7.2$  Hz, 1H), 6.44 (d,  $J = 7.6$  Hz, 2H) (aryl CH), 5.35 (s, 1H) (alkenyl CH), 2.79 (s, 3H), 2.12 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.4 (C=O), 153.5, 148.3, 147.7, 137.0, 136.9, 134.8, 133.7, 131.2, 130.9, 130.2, 129.2, 128.3, 127.9, 125.1, 121.6, 120.3, 103.3 (aryl C and alkenyl C), 32.6, 19.7 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 353.1648. Found: 353.1648.



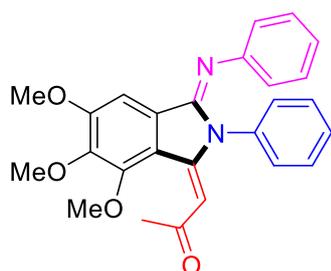
**4ea:** Yield 78%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.97 (s, 1H), 7.26 (s, 1H), 7.09 (m, 3H), 6.95 (m, 2H), 6.83 (t,  $J = 7.2$  Hz, 2H), 6.61 (t,  $J = 7.2$  Hz, 1H), 6.44 (d,  $J = 7.6$  Hz, 2H) (aryl CH), 5.33 (s, 1H) (alkenyl CH), 2.74 (s, 3H), 2.51 (s, 3H), 2.12 (s, 3H) ( $\text{CH}_3$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.4 ( $\text{C}=\text{O}$ ), 153.8, 148.3, 147.8, 141.6, 137.1, 136.5, 135.7, 133.9, 130.2, 129.1, 128.5, 128.2, 127.9, 125.4, 121.4, 120.4, 103.1 (aryl C and alkenyl C), 32.6, 22.0, 19.5 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 367.1805. Found: 367.1804.



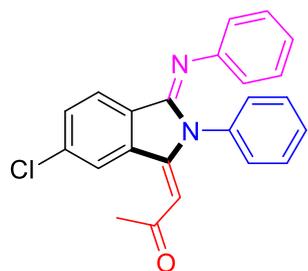
**4fa:** Yield 82%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.10 (s, 1H), 7.58 (t,  $J = 7.6$  Hz, 2H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.39 (d,  $J = 7.2$  Hz, 2H), 7.30 (t,  $J = 7.6$  Hz, 2H), 7.10 (t,  $J = 7.6$  Hz, 1H), 6.90 (d,  $J = 7.6$  Hz, 2H), 6.79 (m, 1H), 6.62 (d,  $J = 8.8$  Hz, 1H)

(aryl CH), 5.63 (s, 1H) (alkenyl CH), 3.93 (s, 3H) ( $\text{OCH}_3$ ), 2.20 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3 ( $\text{C}=\text{O}$ ), 162.7, 153.4, 152.2, 149.7, 136.9, 136.0, 129.8, 129.7, 129.3, 128.9, 126.5, 123.5, 120.6, 118.8, 111.5, 103.3 (aryl C and alkenyl C), 55.8 ( $\text{OCH}_3$ ), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_2^+$   $[\text{M}+\text{H}]^+$ : 369.1598. Found: 369.1596.

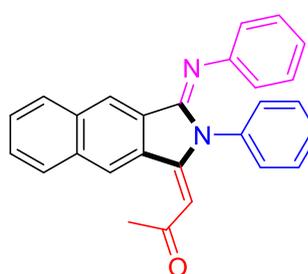


**4ga:** Yield 86%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42 (m, 4H), 7.31 (m, 3H), 7.07 (t,  $J = 7.2$  Hz, 1H), 6.89 (d,  $J = 7.6$  Hz, 2H), 6.62 (s, 1H) (aryl CH), 5.94 (s, 1H) (alkenyl CH), 4.01 (s, 3H), 3.87 (s, 3H), 3.39 (s, 3H) ( $\text{OCH}_3$ ), 1.97 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$

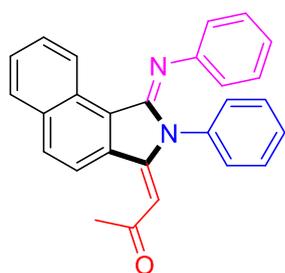
NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.8 ( $\text{C}=\text{O}$ ), 155.3, 153.7, 149.9, 145.4, 144.8, 139.4, 129.2, 128.6, 127.7, 127.2, 123.3, 123.3, 122.7, 120.5, 105.1, 102.6 (aryl C and alkenyl C), 61.2, 60.8, 55.6 ( $\text{OCH}_3$ ), 31.2 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_4^+$   $[\text{M}+\text{H}]^+$ : 429.1809. Found: 429.1808.



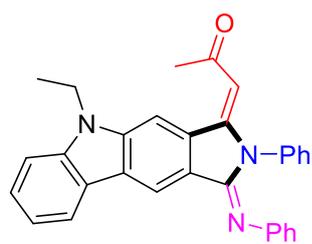
**4ha:** Yield 49%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.40 (s, 1H), 7.59 (t,  $J = 7.6$  Hz, 2H), 7.50 (t,  $J = 7.6$  Hz, 1H), 7.39 (d,  $J = 7.2$  Hz, 2H), 7.31 (t,  $J = 7.6$  Hz, 2H), 7.22 (t,  $J = 8.4$  Hz, 1H), 7.12 (d,  $J = 7.6$  Hz, 1H), 6.88 (d,  $J = 7.6$  Hz, 2H), 6.65 (d,  $J = 8.4$  Hz, 1H) (aryl CH), 5.64 (s, 1H) (alkenyl CH), 2.20 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2 (C=O), 152.4, 150.6, 149.3, 138.3, 136.3, 135.7, 131.3, 123.0, 129.6, 129.4, 129.1, 128.3, 126.3, 126.2, 123.8, 120.3, 104.2 (aryl C and alkenyl C), 32.5 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{OCl}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 373.1102. Found: 373.1102.



**4ia:** Yield 64%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.06 (s, 1H), 9.07 (d,  $J = 8.4$  Hz, 1H), 7.60 (m, 3H), 7.53 (m, 3H), 7.45 (d,  $J = 7.6$  Hz, 2H), 7.37 (t,  $J = 7.6$  Hz, 2H), 7.19 (m, 2H), 6.97 (d,  $J = 7.6$  Hz, 2H) (aryl CH), 5.66 (s, 1H) (alkenyl CH), 2.24 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2 (C=O), 153.4, 152.4, 150.0, 136.2, 134.8, 133.9, 130.6, 130.4, 130.0, 129.7, 129.6, 129.4, 129.4, 129.1, 128.1, 126.6, 124.8, 123.6, 120.5, 102.7 (aryl C and alkenyl C), 32.6 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{27}\text{H}_{21}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 389.1648. Found: 389.1649.

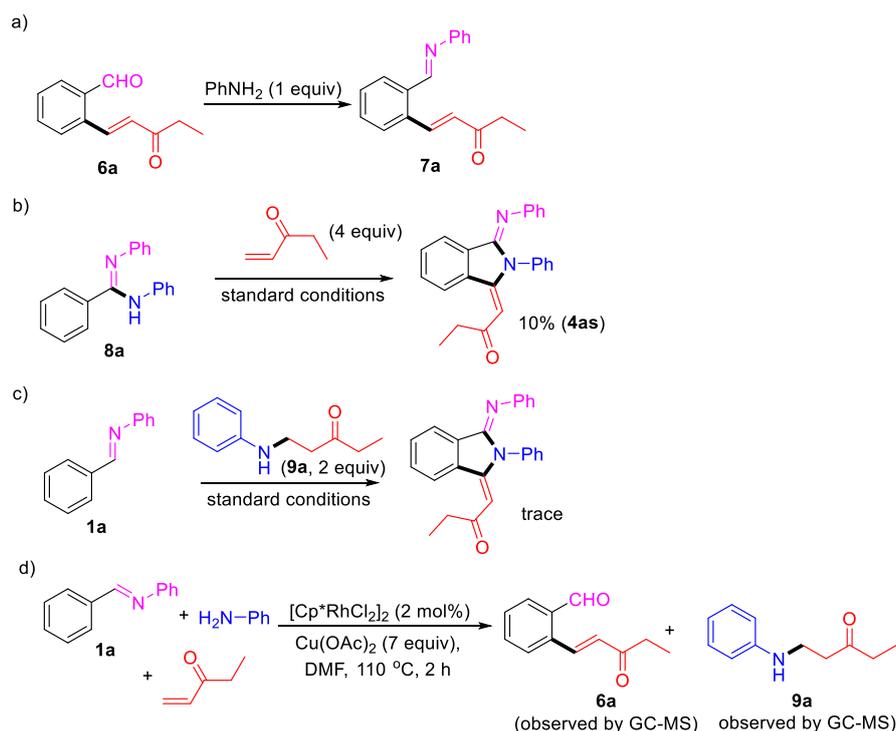


**4ja:** Yield 75%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.64 (m, 1H), 9.13 (d,  $J = 8.8$  Hz, 1H), 8.07 (d,  $J = 8.8$  Hz, 1H), 7.96 (m, 1H), 7.62 (m, 2H), 7.12 (m, 3H), 7.01 (m, 2H), 6.88 (m, 2H), 6.66 (t,  $J = 7.6$  Hz, 1H), 6.55 (d,  $J = 7.6$  Hz, 2H) (aryl CH), 5.48 (s, 1H) (alkenyl CH), 2.18 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.8 (C=O), 153.1, 149.1, 147.6, 137.0, 135.7, 133.1, 132.4, 130.3, 129.2, 128.7, 128.7, 128.3, 128.3, 127.7, 126.2, 123.2, 121.9, 120.5, 104.8 (aryl C and alkenyl C), 32.7 ( $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{27}\text{H}_{21}\text{N}_2\text{O}^+$  [ $\text{M}+\text{H}$ ] $^+$ : 389.1648. Found: 389.1646.



**4ka:** Yield 80%. Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.79 (s, 1H), 7.68 (d,  $J = 8.0$  Hz, 1H), 8.62 (d,  $J = 7.2$  Hz, 2H), 7.50 (m, 4H), 7.41 (m, 3H), 7.32 (s, 1H), 7.22 (m, 2H), 7.02 (d,  $J = 7.6$  Hz, 2H) (aryl CH), 5.67 (s, 1H) (alkenyl CH), 4.51 (q,  $J = 7.2$  Hz, 2H) ( $\text{CH}_2\text{CH}_3$ ), 2.25 (s, 3H) ( $\text{CH}_3$ ), 1.50 (t,  $J = 7.2$  Hz, 3H) ( $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3 (C=O), 154.4, 153.6, 141.7, 141.6, 136.3, 132.2, 129.9, 129.5, 128.9, 127.2, 124.8, 123.54, 122.8, 120.8, 119.9, 119.1, 118.1, 109.7, 109.0, 102.3 (aryl C and alkenyl C), 38.1, 32.7, 14.0 ( $\text{CH}_2$  and  $\text{CH}_3$ ). HRMS:  $m/z$  calcd for  $\text{C}_{31}\text{H}_{26}\text{N}_3\text{O}^+$   $[\text{M}+\text{H}]^+$ : 456.2070. Found: 456.2069.

### Control experiments.



**Scheme S1.** Control experiments.

**Reaction of 6a with aniline.** Compound **6a** (18.8 mg, 0.1 mmol), aniline (9.1  $\mu\text{L}$ , 1.0 equiv, 0.1 mmol) and molecular sieves (3 $\text{\AA}$ , 50 mg) were mixed in dichloromethane (1 mL). After stirred at room temperature under argon for 12 h, all the solvent was removed under

reduced pressure to give **7a** (26 mg, 99%).

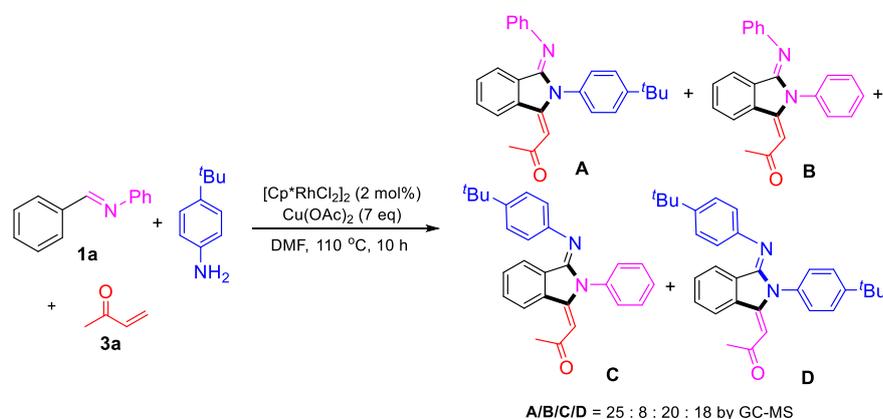
**Reaction of 8a with ethyl vinyl ketone.** Compound **8a** (27.2 mg, 0.1 mmol), ethyl vinyl ketone (39.8  $\mu$ L, 4 equiv, 0.4 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (1.2 mg, 2 mol%, 0.002 mmol) and Cu(OAc)<sub>2</sub> (127 mg, 7 equiv, 0.7 mmol) were mixed in DMF (2.0 mL). The resulting mixture was stirred at 110 °C under argon for 12 h. After cooling to room temperature, the reaction mixture was washed with water (3 x 3.0 mL) and extracted with diethyl ether (3 x 5.0 mL). The organic portions were combined. The mixture was analyzed by GC-MS using diphenylacetylene as an internal standard.

**Reaction of 1a with 9a.** Compound **1a** (18.1 mg, 0.1 mmol), **9a** (35.4 mg, 0.2 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (1.2 mg, 2 mol%, 0.002 mmol) and Cu(OAc)<sub>2</sub> (127 mg, 7 equiv, 0.7 mmol) were mixed in DMF (2.0 mL). The resulting mixture was stirred at 110 °C under argon for 12 h. After cooling to room temperature, the reaction mixture was washed with water (3 x 3.0 mL) and extracted with diethyl ether (3 x 5.0 mL). The organic portions were combined. The mixture was analyzed by GC-MS using diphenylacetylene as an internal standard.

**Detection of reaction intermediates.** Compound **1a** (18.1 mg, 0.1 mmol), aniline (18.2  $\mu$ L, 2 equiv, 0.2 mmol), ethyl vinyl ketone **3b** (39.5  $\mu$ L, 4 equiv, 0.4 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (1.2 mg, 2 mol%, 0.002 mmol) and Cu(OAc)<sub>2</sub> (127 mg, 7 equiv, 0.7 mmol) were mixed in DMF (2.0 mL). The resulting mixture was stirred at 110 °C under argon for 2 h. The reaction mixture was washed with water (3 x 3.0 mL) and extracted with diethyl ether (3 x 5.0 mL). The organic portions were combined. The mixture was analyzed by GC-MS.

**Cross-Over Experiment.** Compound **1a** (18.1 mg, 0.1 mmol), 4-(*tert*-butyl)aniline (32  $\mu$ L, 2 equiv, 0.2 mmol), methyl vinyl ketone **3a** (33  $\mu$ L, 4 equiv, 0.4 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (1.2 mg, 2 mol%, 0.002 mmol) and Cu(OAc)<sub>2</sub> (127 mg, 7 equiv, 0.7 mmol) were mixed in DMF (2.0 mL). The resulting mixture was stirred at 110 °C under argon for 10 h. After cooling to

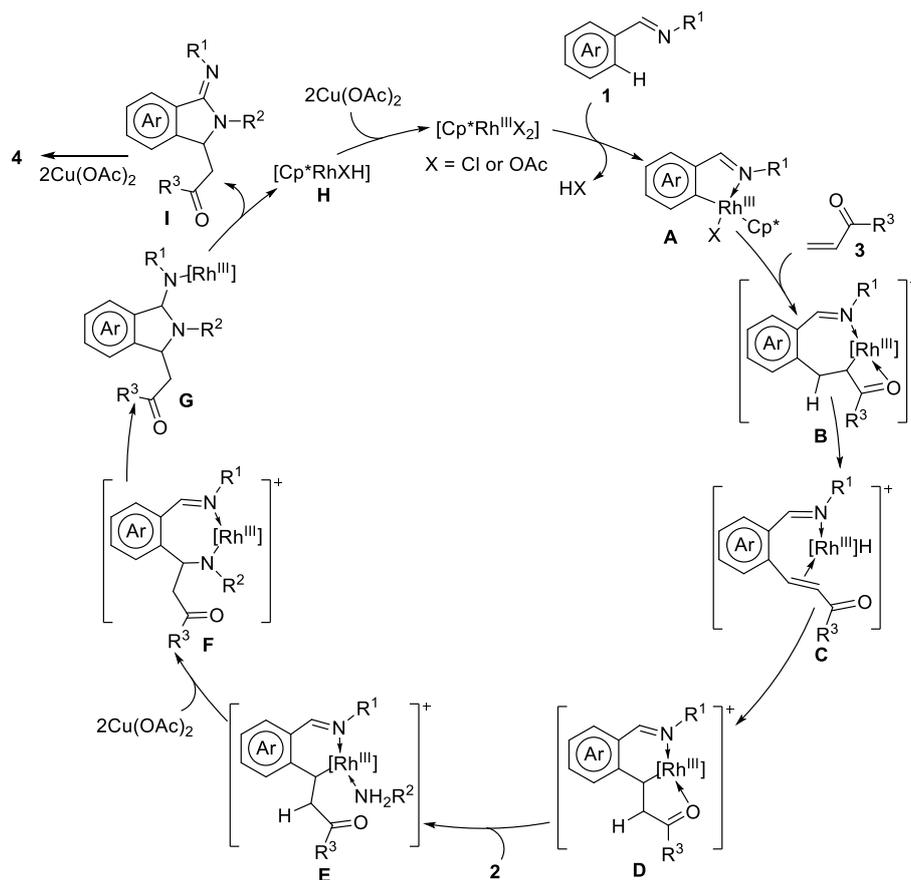
room temperature, the reaction mixture was analyzed by GC-MS using diphenylacetylene as an internal standard to determine the molar ratio of 4 isomers, **A/B/C/D** = 25:8:20:18.



**Scheme S2.** Cross-over experiment

### Proposed Catalytic Cycle

Although the above control experiments cannot lead to a solid conclusion, a plausible catalytic cycle is proposed in Scheme S3 on the basis of these observations and literature works.<sup>5-8</sup> Chelation of imine to Rh(III) center followed by C-H bond activation generates an intermediate **A**.<sup>5</sup> Alkene insertion into C-Rh bond gives the intermediate **B**, which undergoes  $\beta$ -H elimination to produce the complex **C** bearing the Rh-H bond. A rapid alkene insertion into Rh-H bond affords the key intermediate **D**. The coordination of amine yields **E**. Oxidation (generation of nitrene) and subsequent nitrene insertion give the seven-membered rhodacycle **F**.<sup>6,7</sup> Intramolecular nucleophilic cyclization affords **G**.  $\beta$ -H elimination, followed by oxidation generates the cyclic compound **4** and catalyst Rh(III) to finish the catalytic cycle.<sup>8</sup> Accordingly, a total amount of 6 equivalents of Cu(OAc)<sub>2</sub> oxidant is required to complete this catalytic cycle.



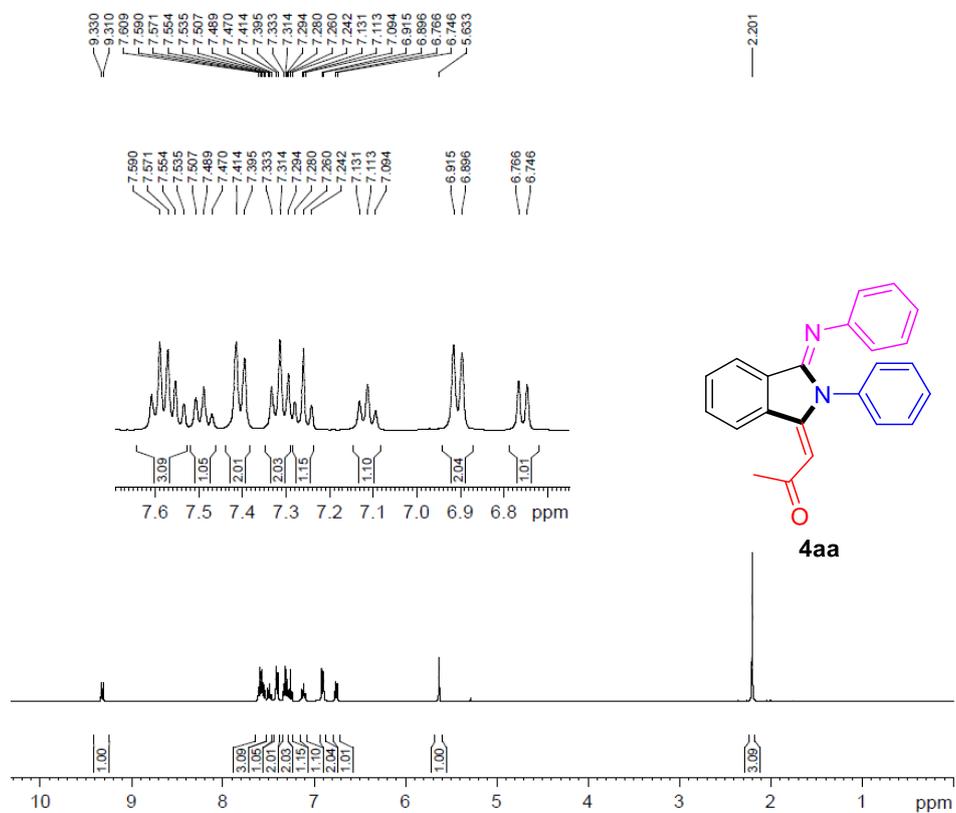
**Scheme S3** Proposed reaction mechanism.

**X-ray Structure Determination.** X-ray data of **4al** were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-K $\alpha$  radiation. An empirical absorption correction was applied using the SADABS program.<sup>8</sup> The structure was solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on  $F^2$  using the SHELXTL program package.<sup>10</sup> All hydrogen atoms were geometrically fixed using the riding model.

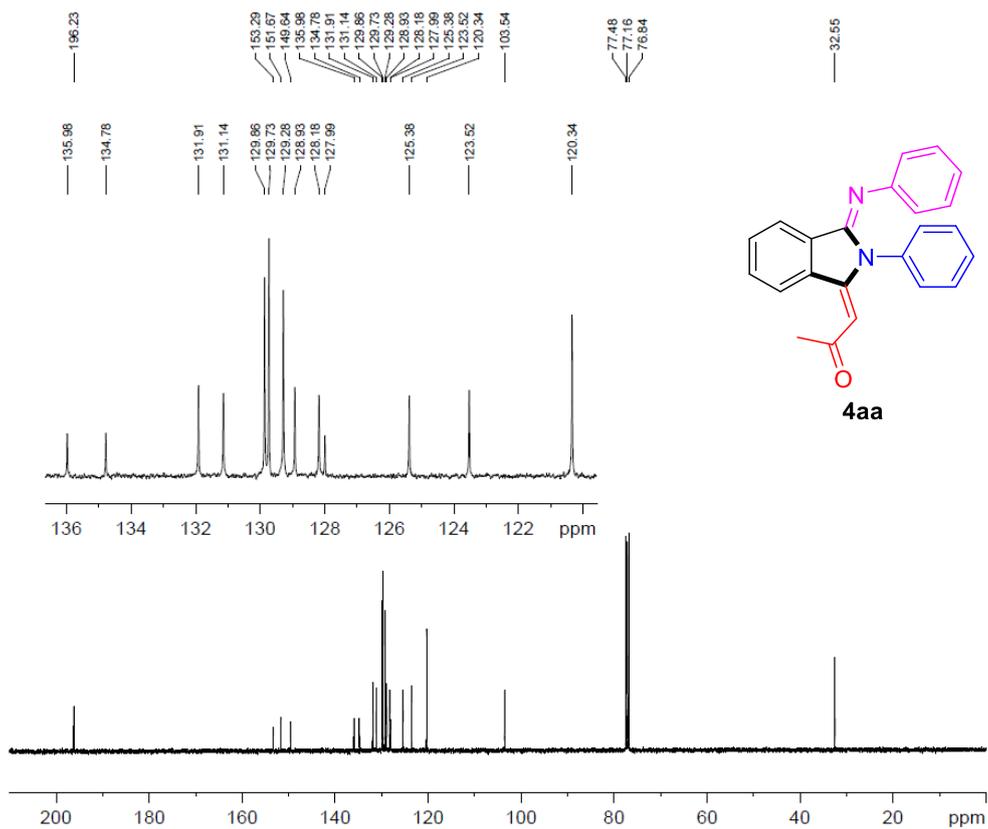
CCDC 2058196 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## References

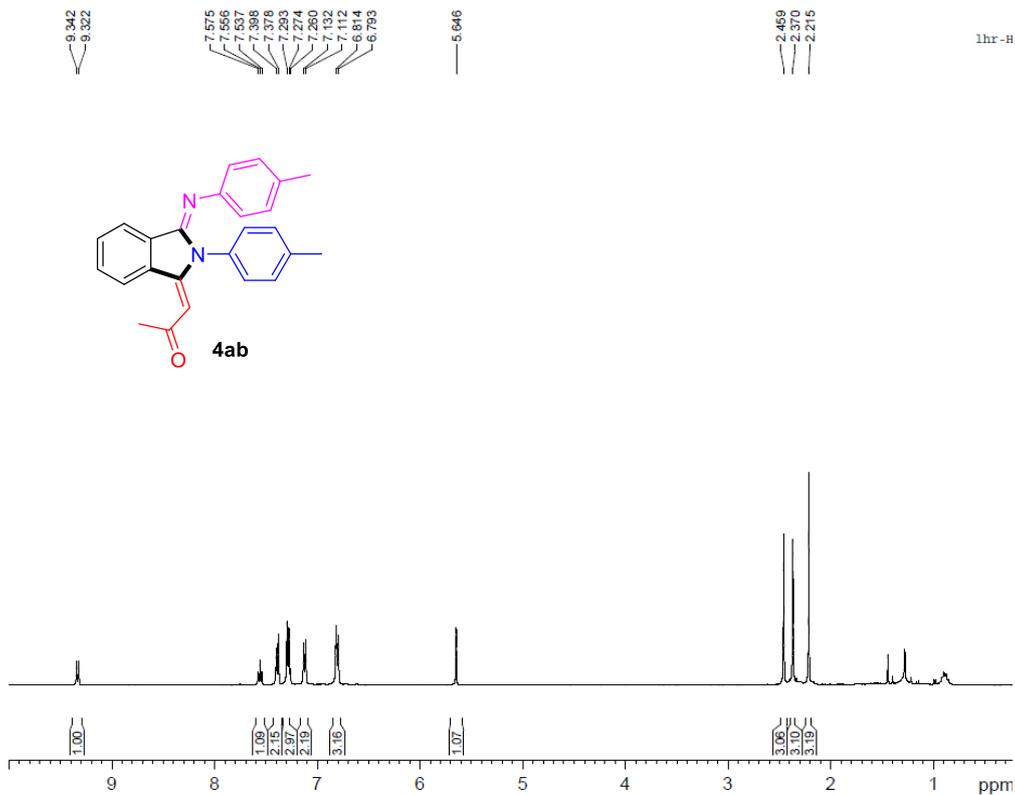
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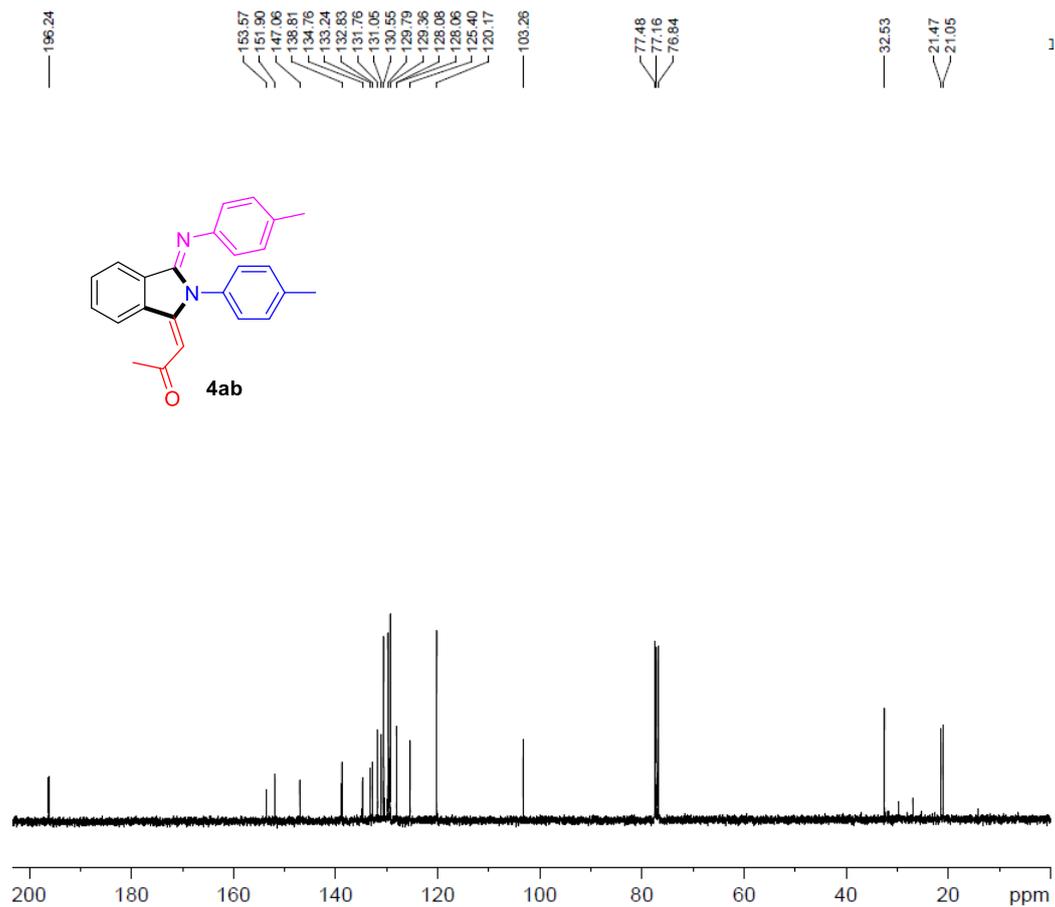
<sup>1</sup>H NMR spectrum of **4aa** in CDCl<sub>3</sub>, 400 MHz.



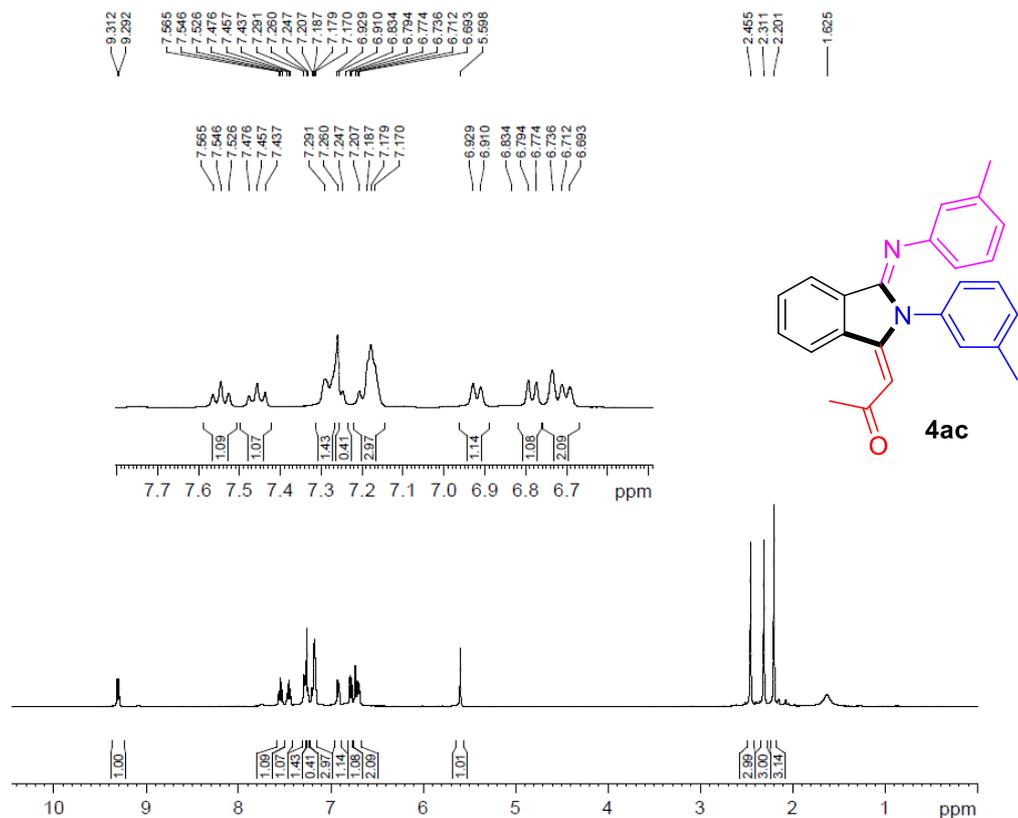
<sup>13</sup>C NMR spectrum of **4aa** in CDCl<sub>3</sub>, 100 MHz.



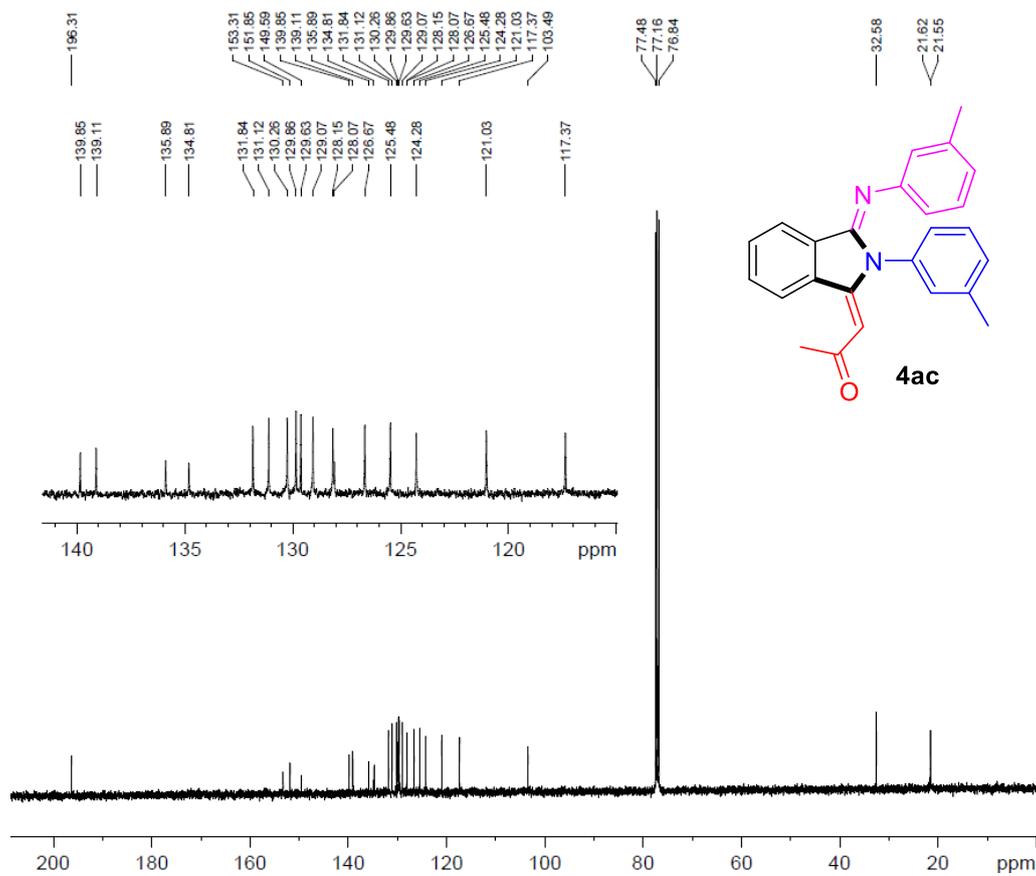
<sup>1</sup>H NMR spectrum of **4ab** in CDCl<sub>3</sub>, 400 MHz.



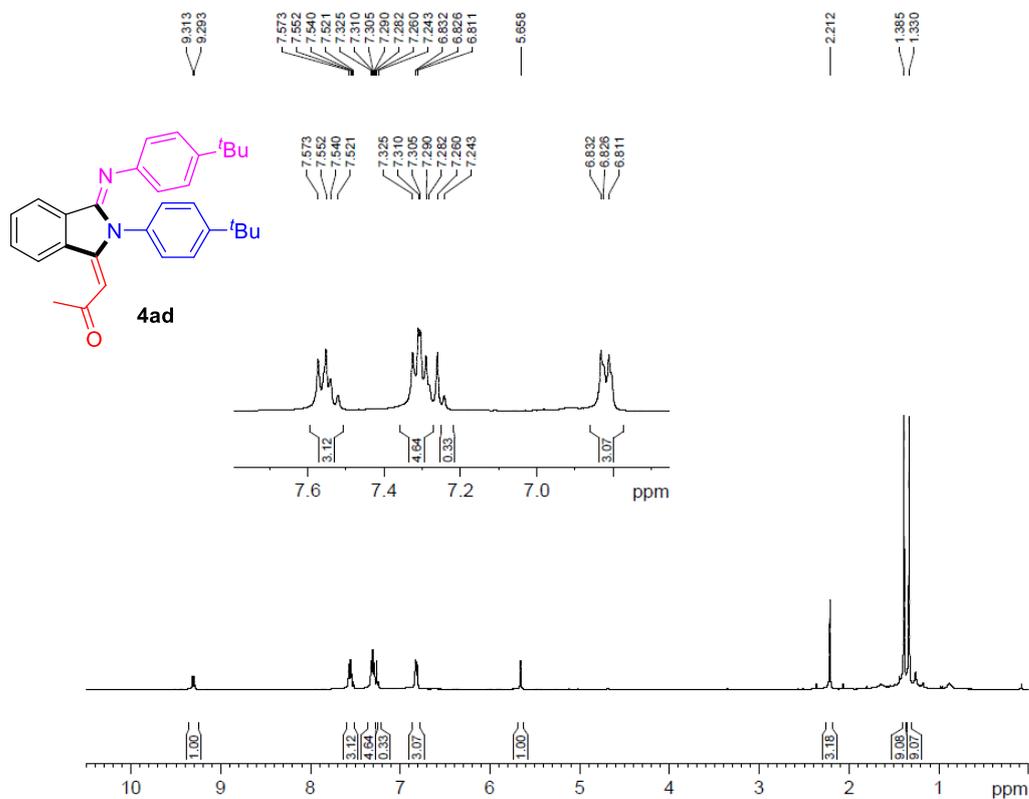
$^{13}\text{C}$  NMR spectrum of **4ab** in  $\text{CDCl}_3$ , 100 MHz.



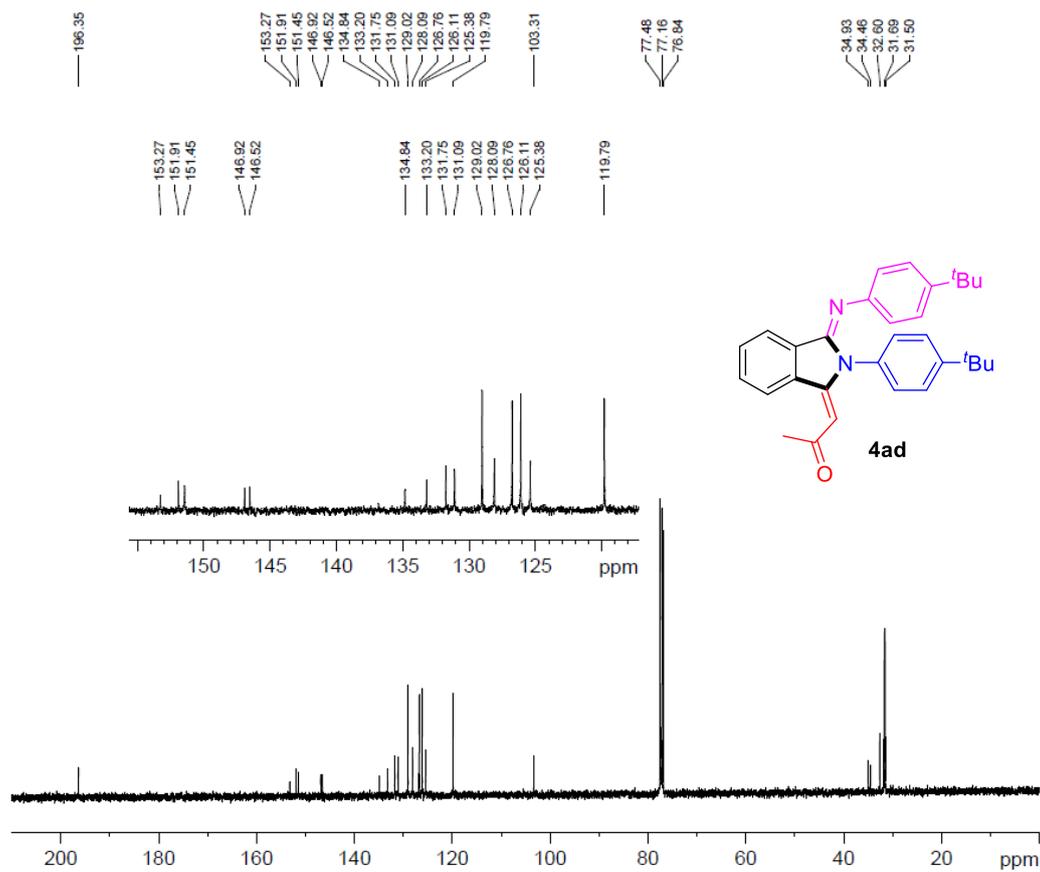
$^1\text{H}$  NMR spectrum of **4ac** in  $\text{CDCl}_3$ , 400 MHz.



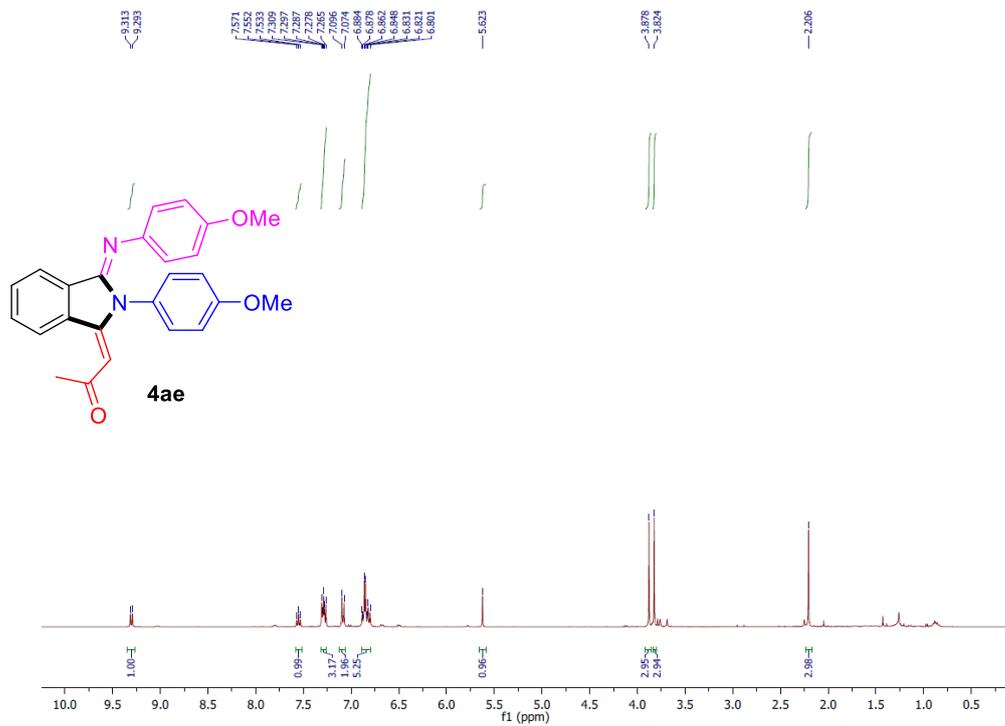
<sup>13</sup>C NMR spectrum of **4ac** in CDCl<sub>3</sub>, 100 MHz.



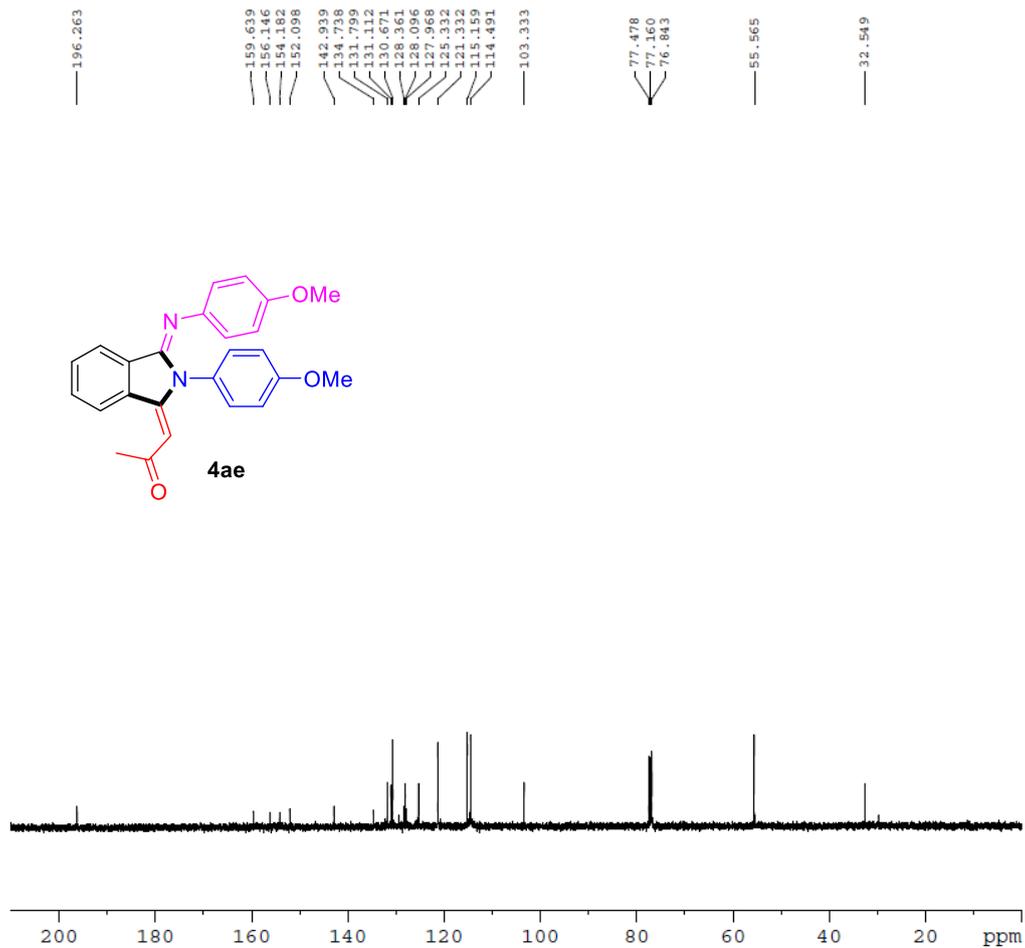
<sup>1</sup>H NMR spectrum of **4ad** in CDCl<sub>3</sub>, 400 MHz.



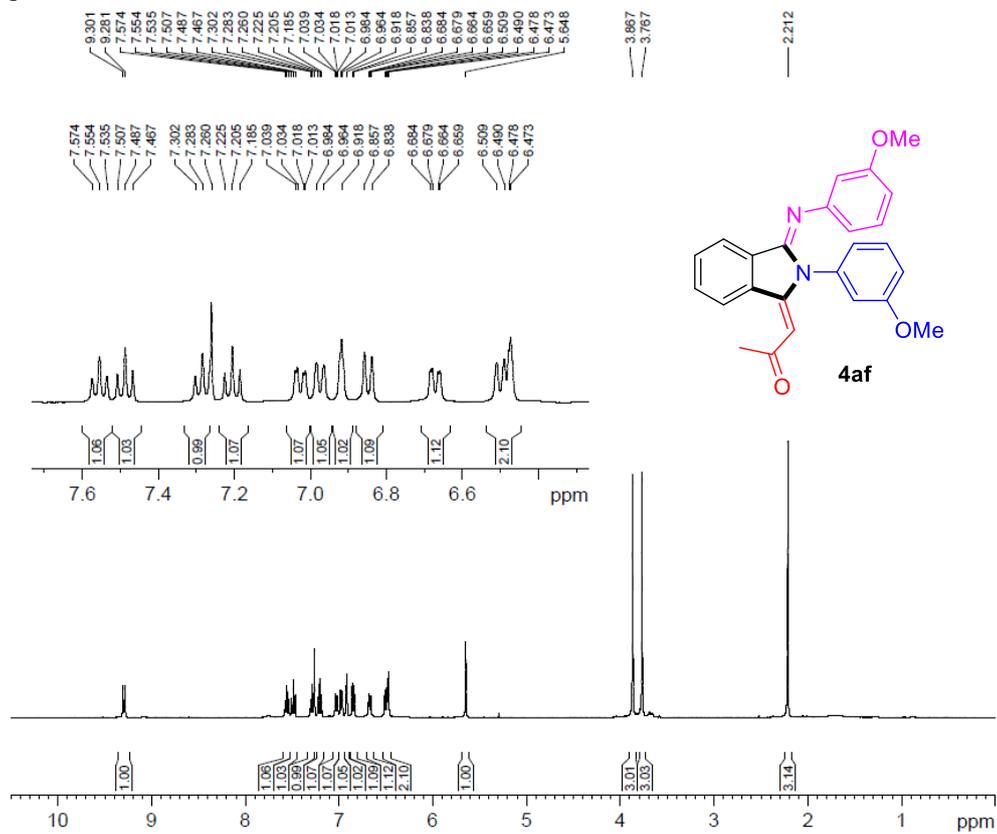
<sup>13</sup>C NMR spectrum of **4ad** in CDCl<sub>3</sub>, 100 MHz.



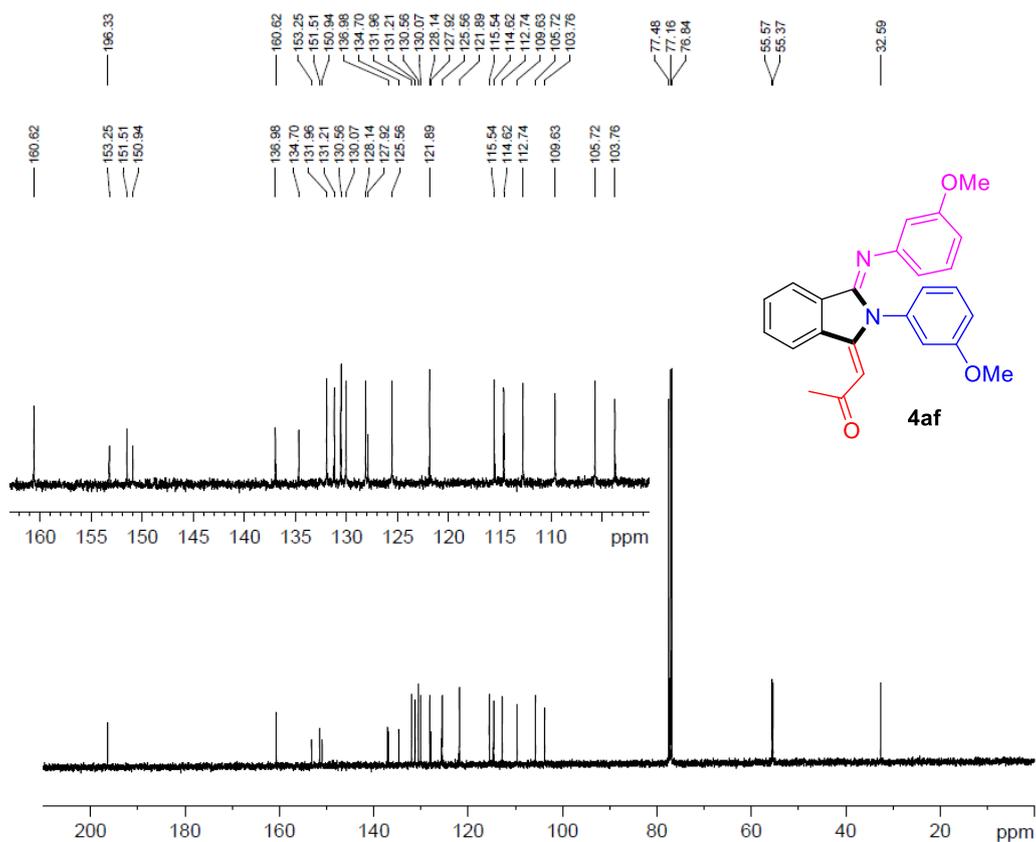
<sup>1</sup>H NMR spectrum of **4ae** in CDCl<sub>3</sub>, 400 MHz.



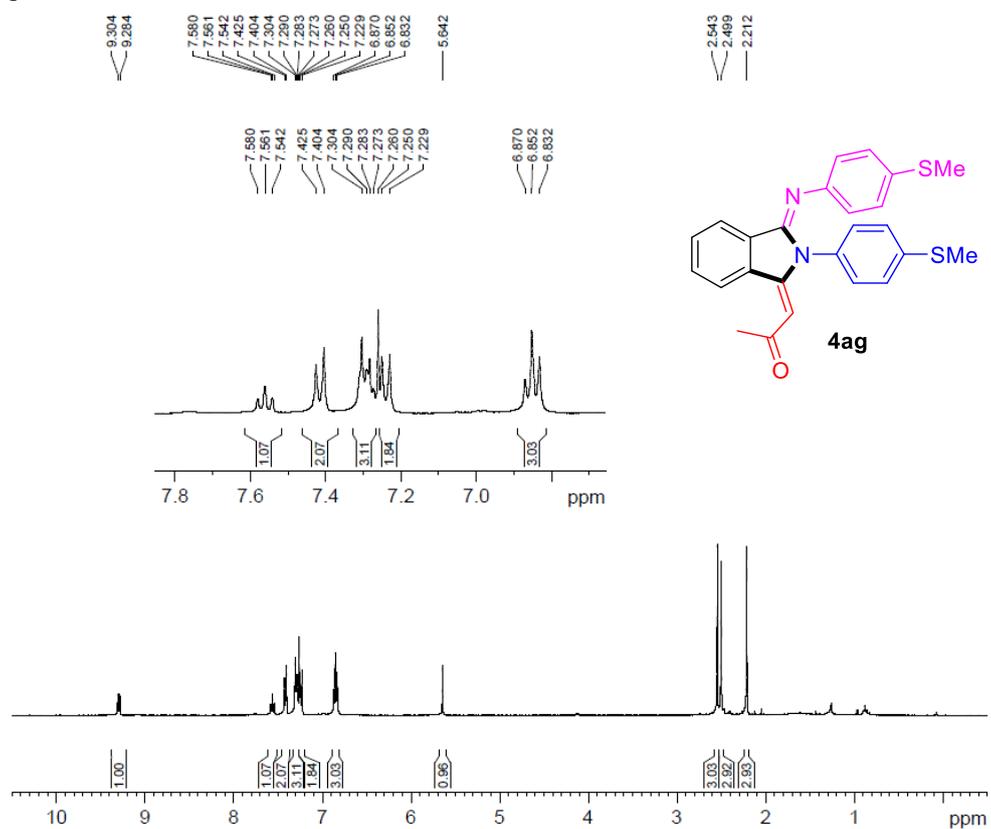
$^{13}\text{C}$  NMR spectrum of **4ae** in  $\text{CDCl}_3$ , 100 MHz.



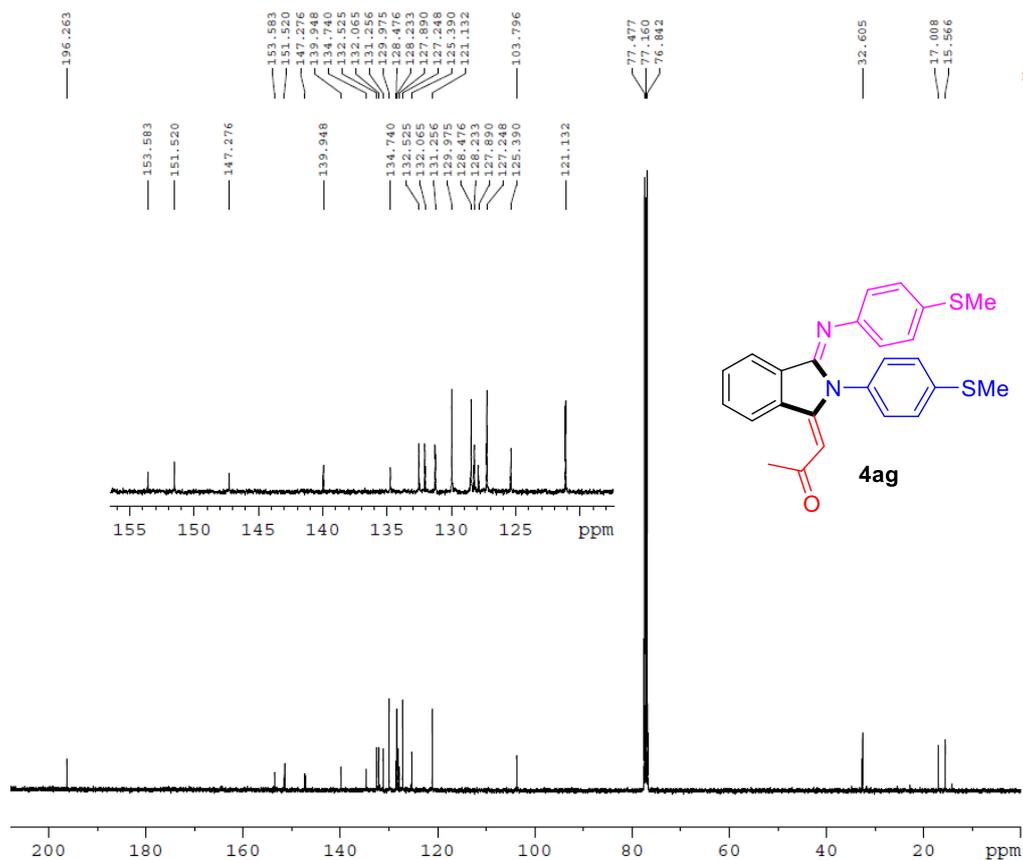
$^1\text{H}$  NMR spectrum of **4af** in  $\text{CDCl}_3$ , 400 MHz.



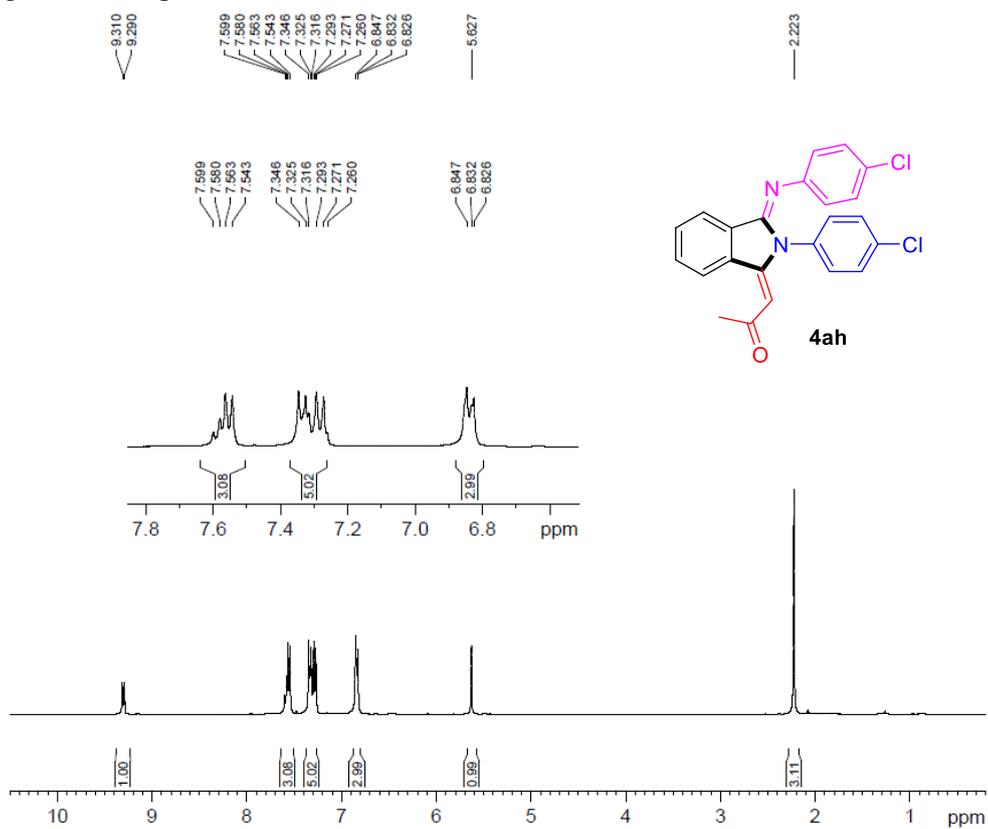
$^1\text{H}$  NMR spectrum of **4ag** in  $\text{CDCl}_3$ , 400 MHz.



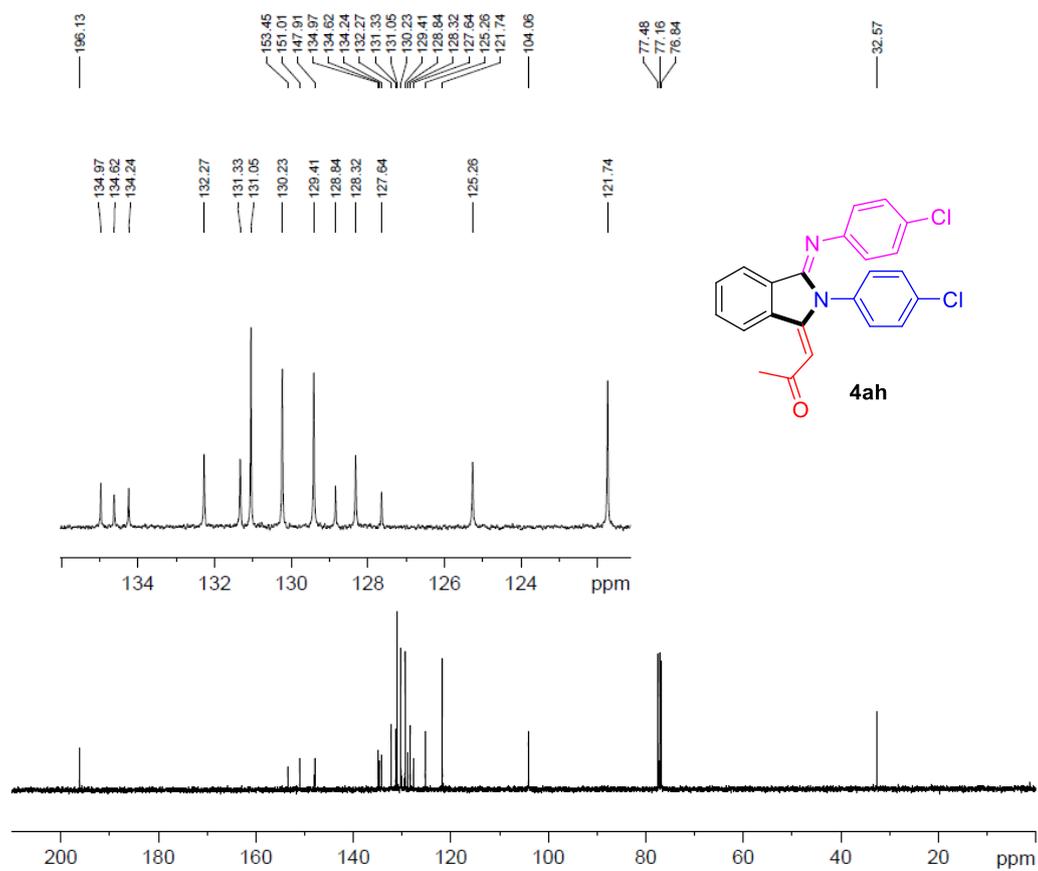
$^1\text{H}$  NMR spectrum of **4ag** in  $\text{CDCl}_3$ , 400 MHz.



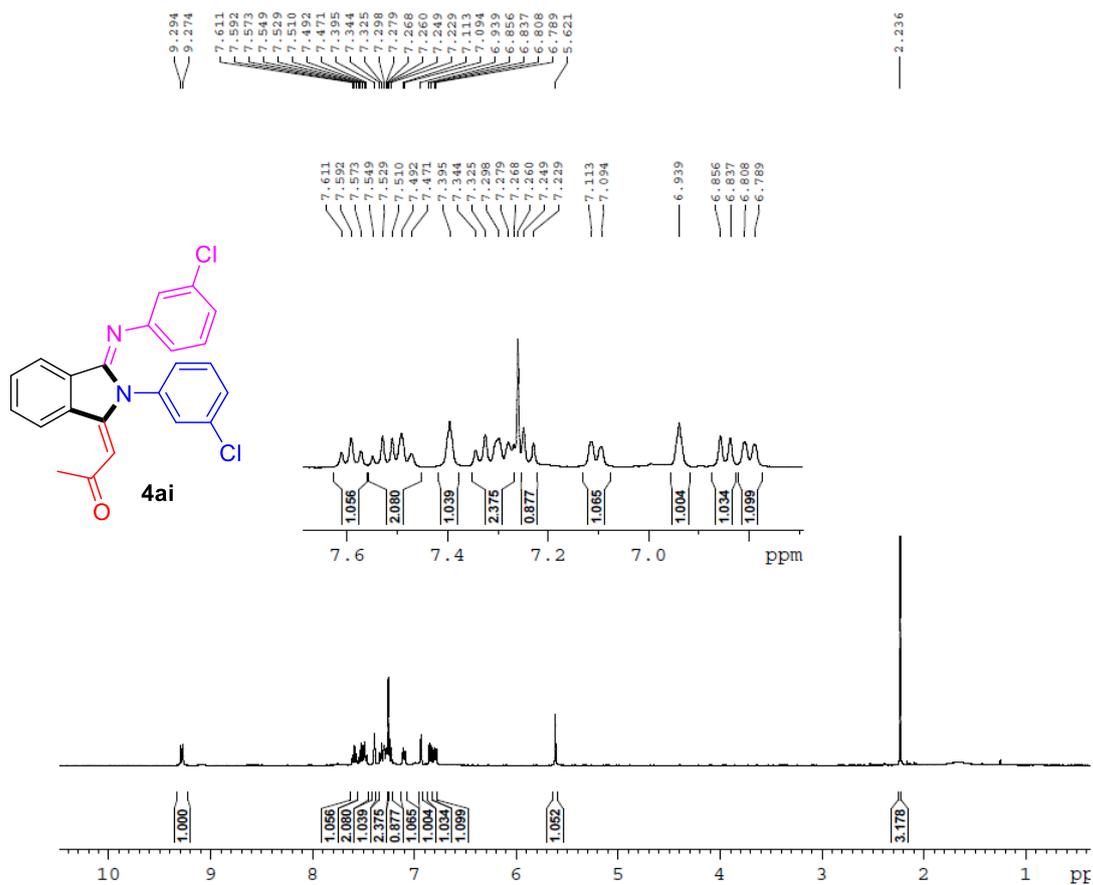
$^1\text{H}$  NMR spectrum of **4ah** in  $\text{CDCl}_3$ , 400 MHz.



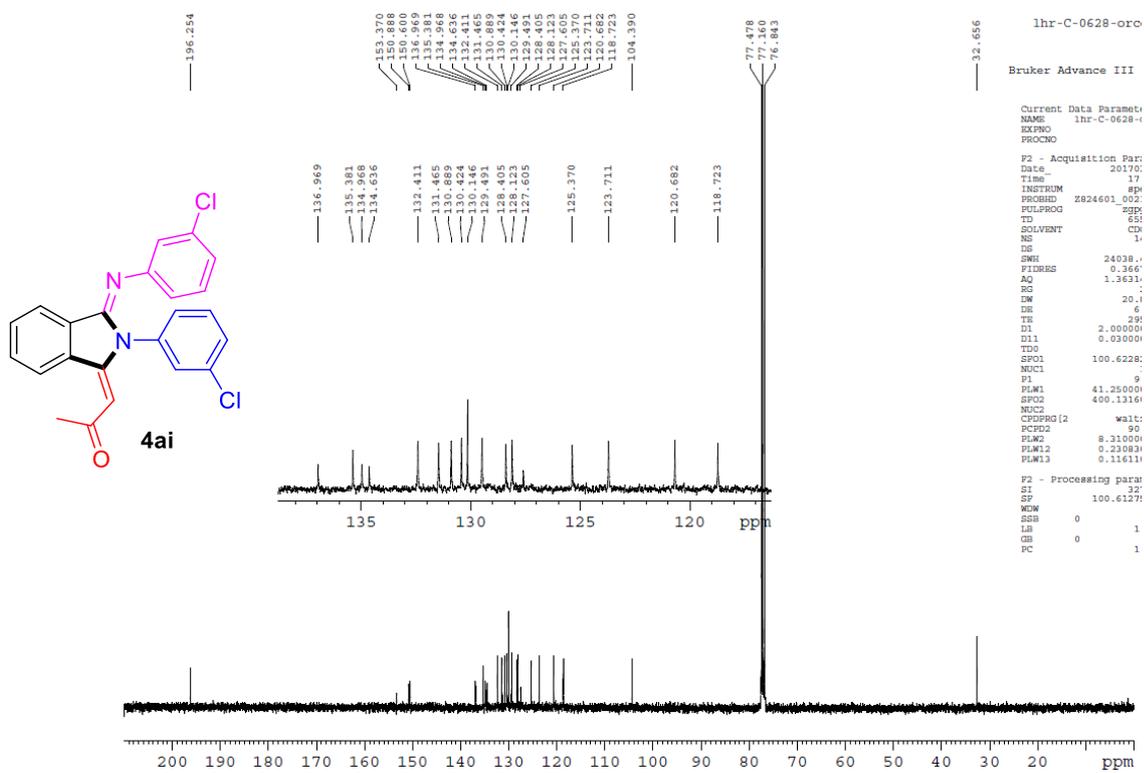
$^1\text{H}$  NMR spectrum of **4ah** in  $\text{CDCl}_3$ , 400 MHz.



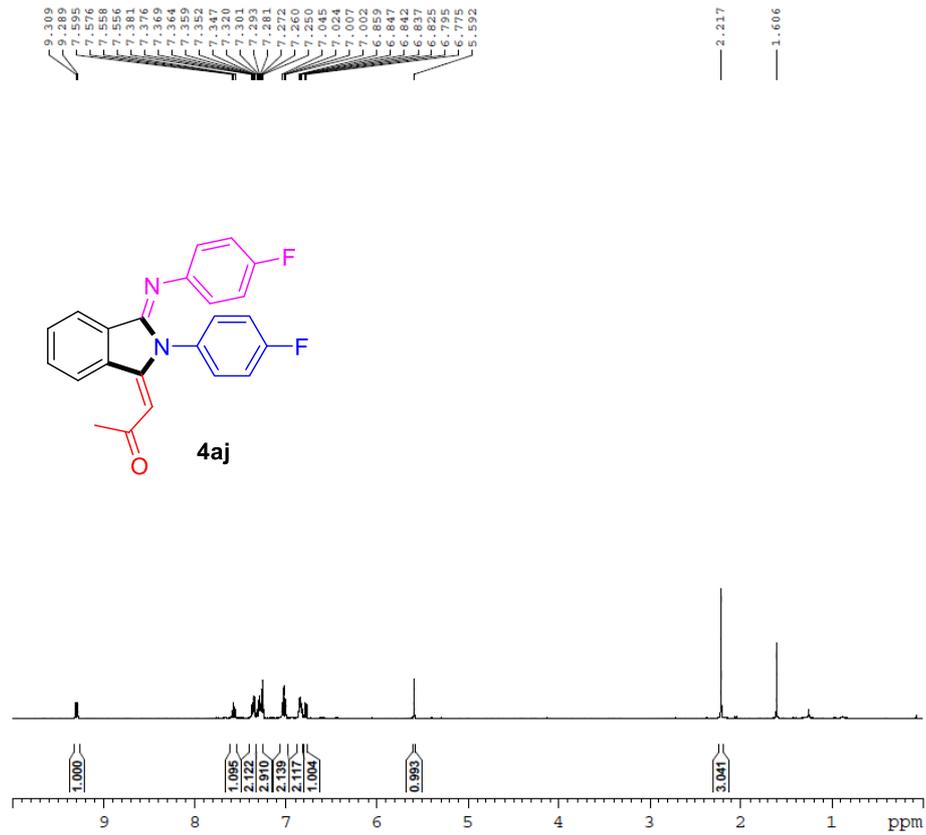
$^{13}\text{C}$  NMR spectrum of **4ah** in  $\text{CDCl}_3$ , 100 MHz.



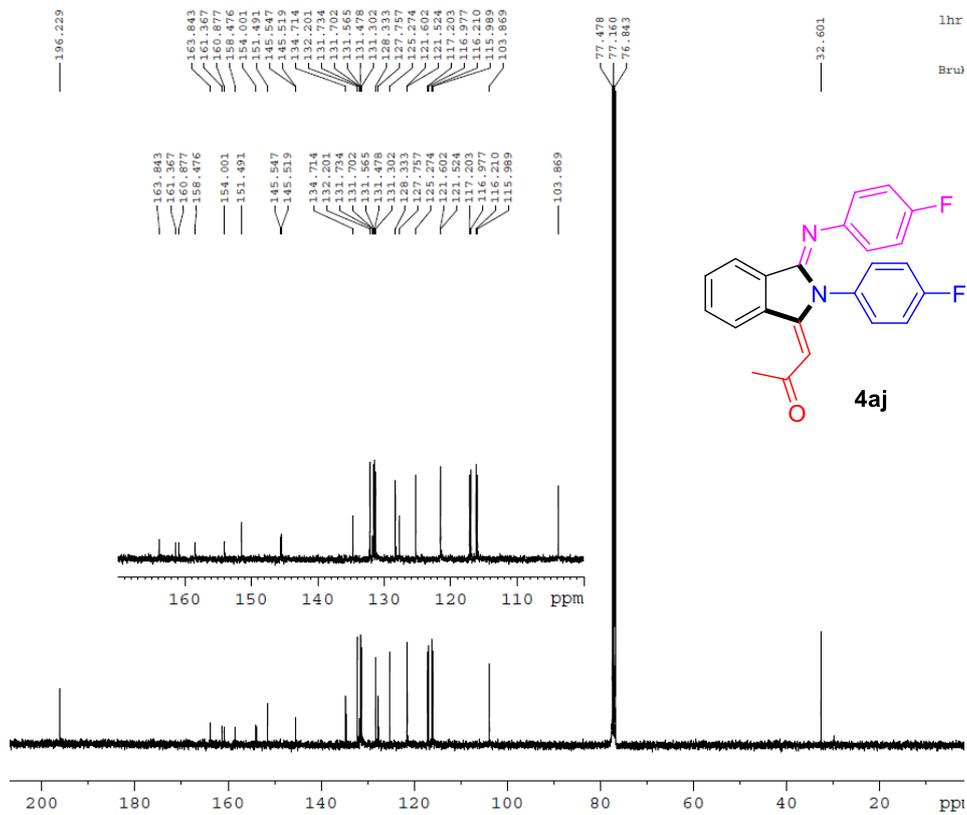
<sup>1</sup>H NMR spectrum of **4ai** in CDCl<sub>3</sub>, 400 MHz.



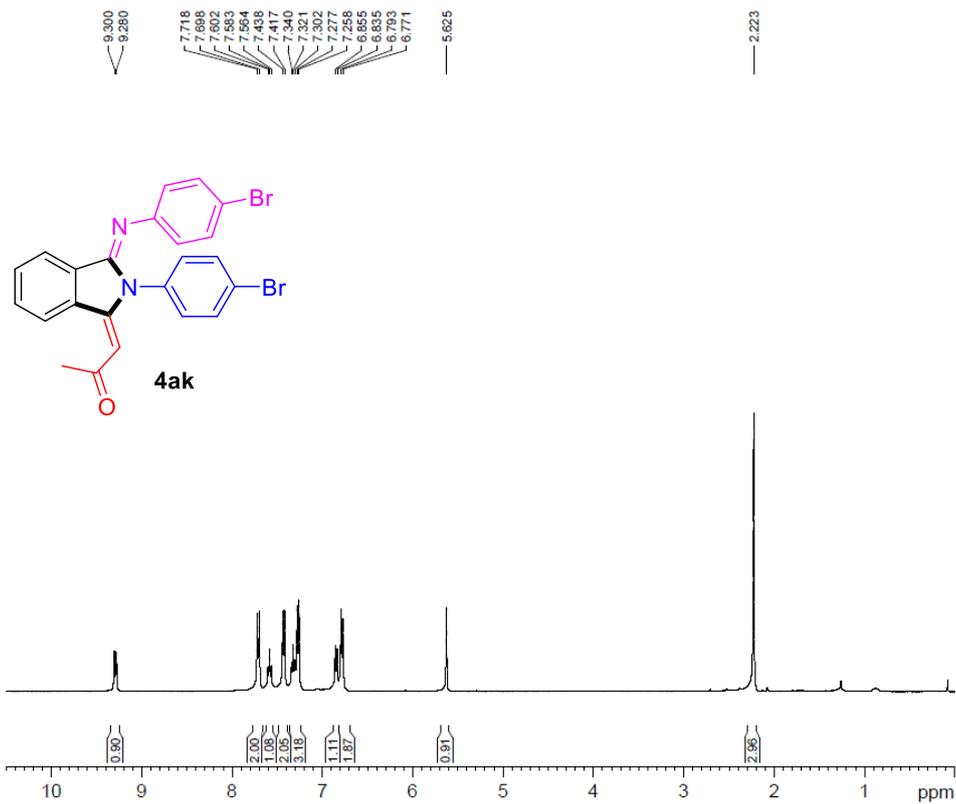
<sup>13</sup>C NMR spectrum of **4ai** in CDCl<sub>3</sub>, 100 MHz.



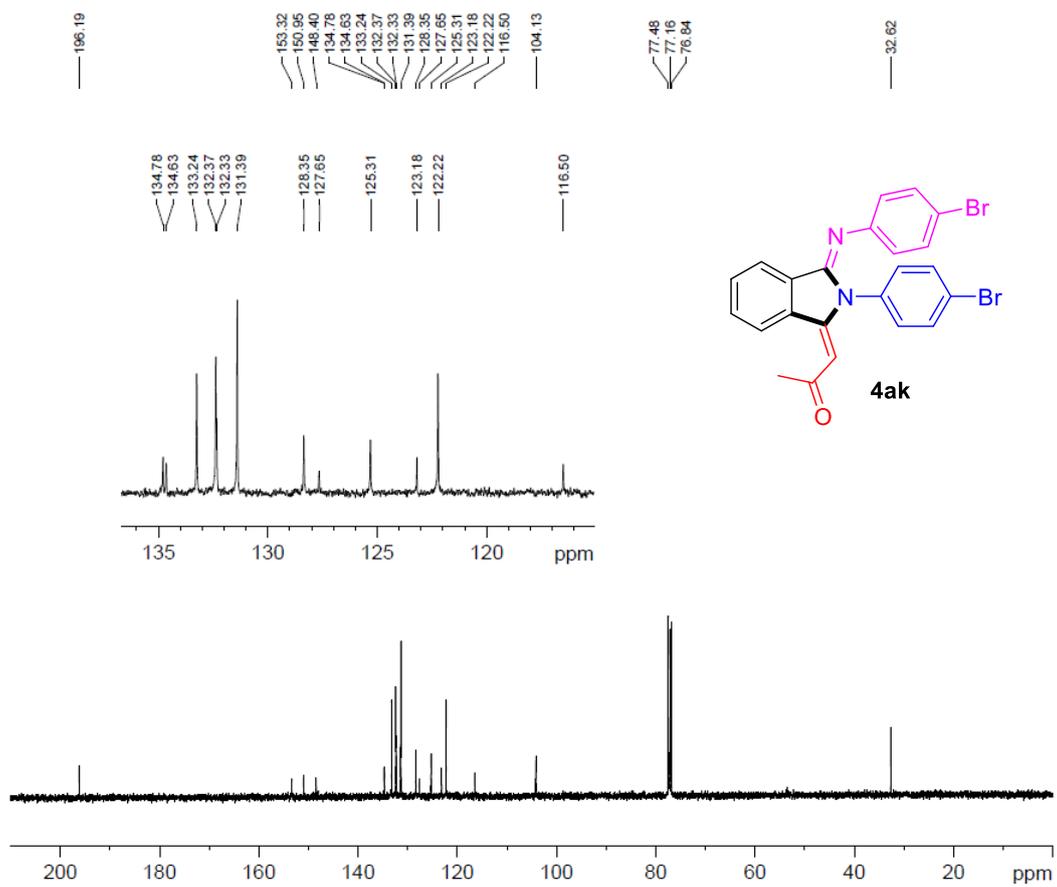
<sup>1</sup>H NMR spectrum of **4aj** in CDCl<sub>3</sub>, 400 MHz.



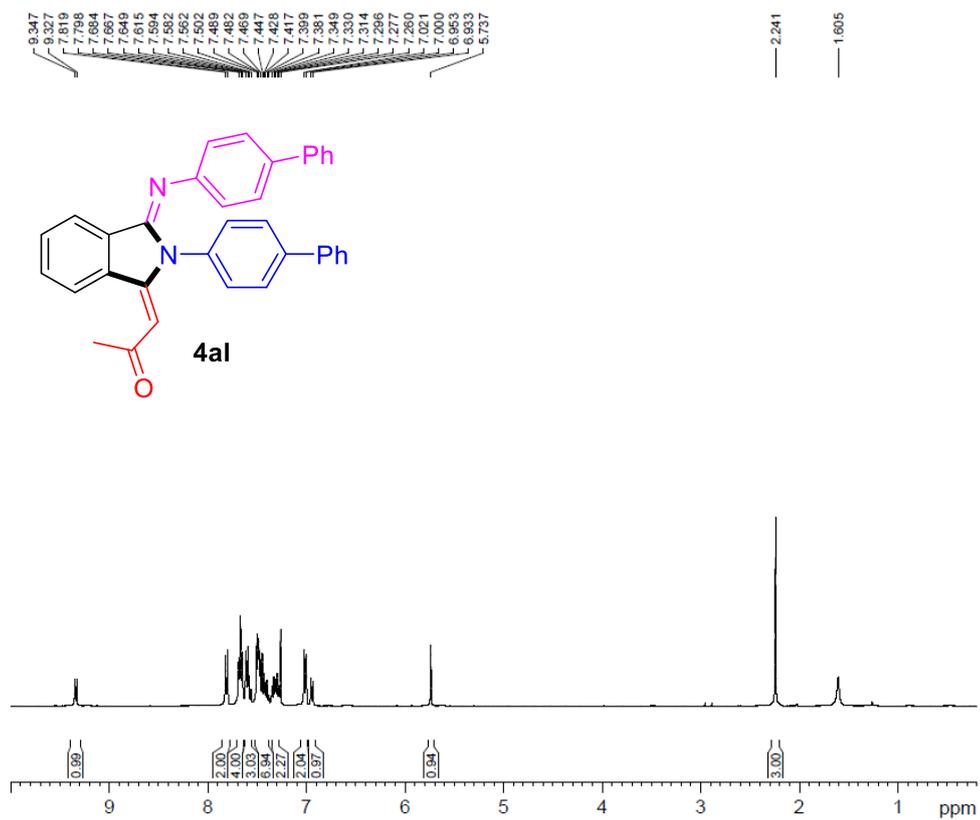
<sup>13</sup>C NMR spectrum of **4aj** in CDCl<sub>3</sub>, 100 MHz.



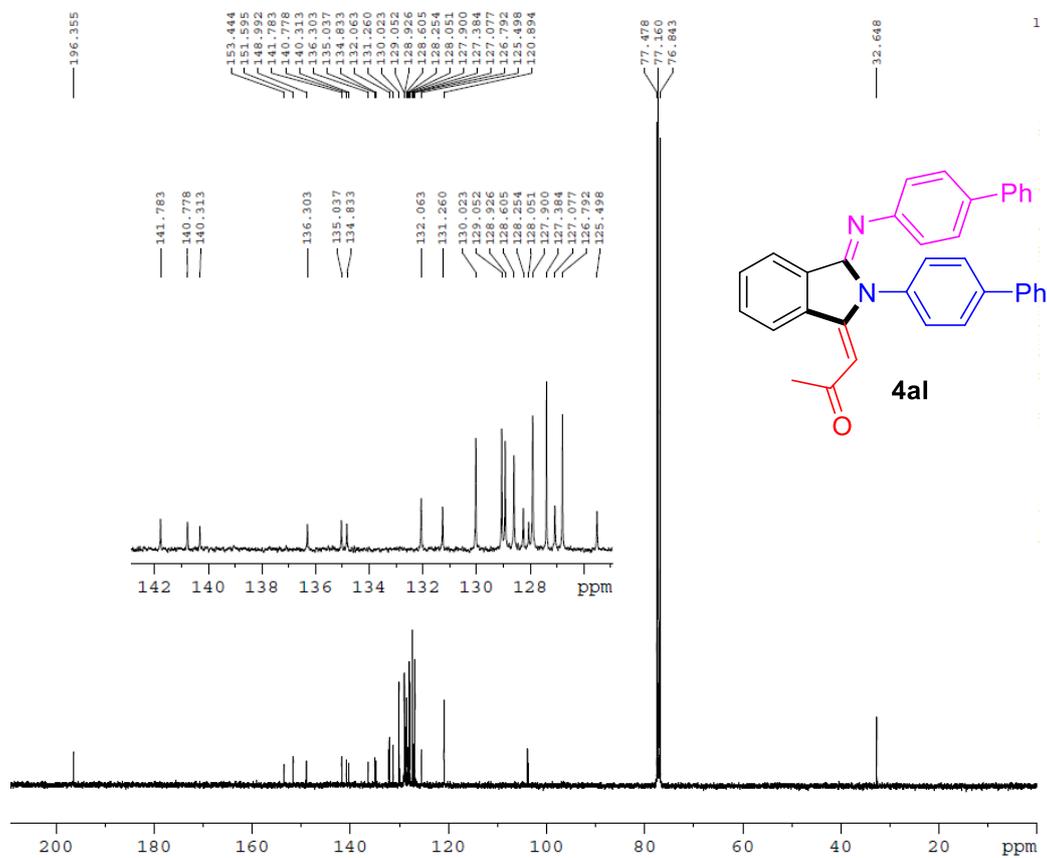
<sup>1</sup>H NMR spectrum of **4ak** in CDCl<sub>3</sub>, 400 MHz.



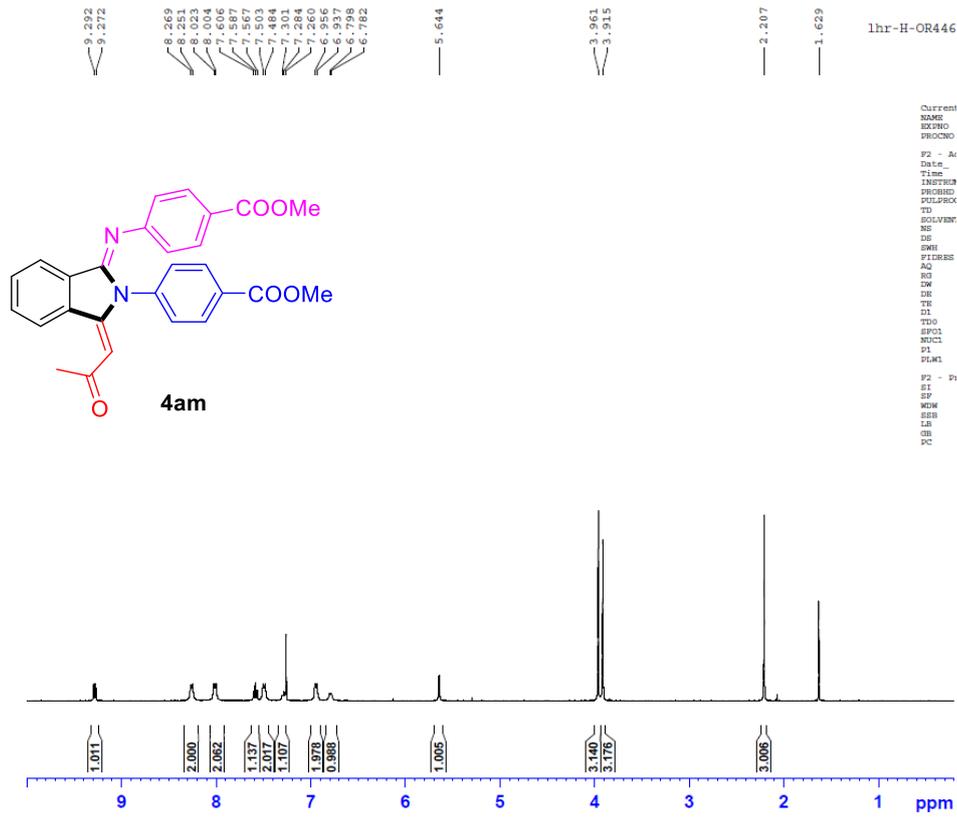
<sup>13</sup>C NMR spectrum of **4ak** in CDCl<sub>3</sub>, 100 MHz.



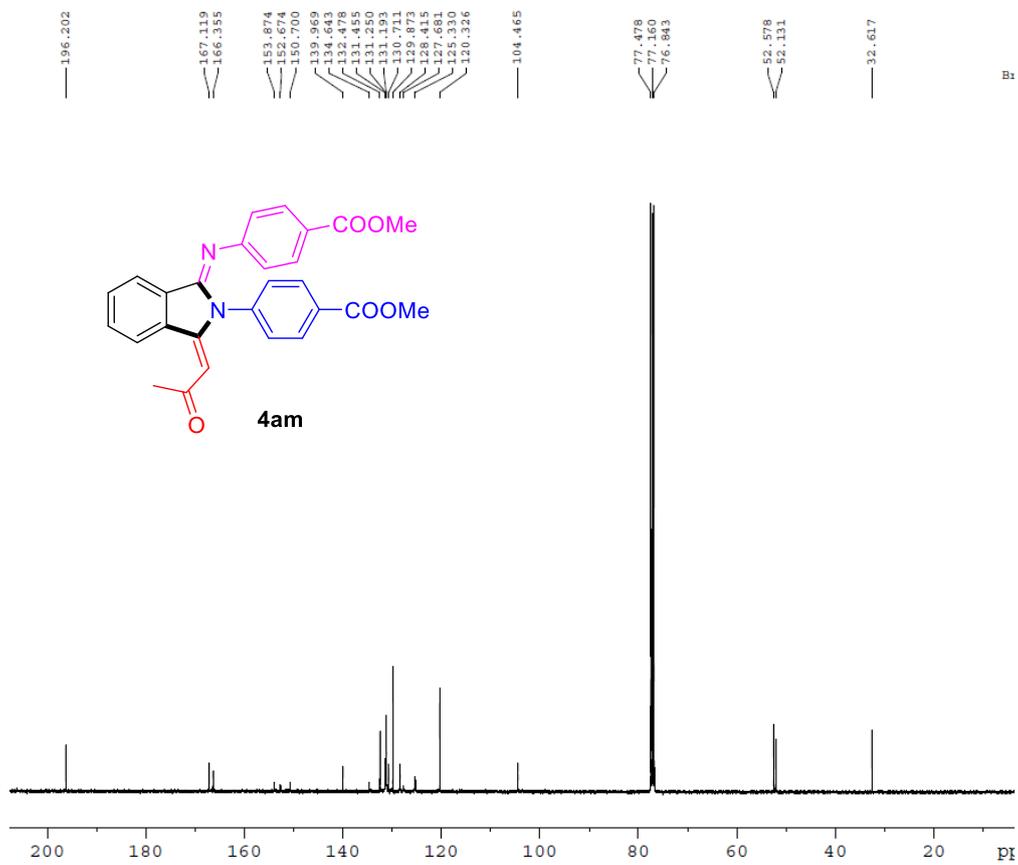
<sup>1</sup>H NMR spectrum of **4al** in CDCl<sub>3</sub>, 400 MHz.



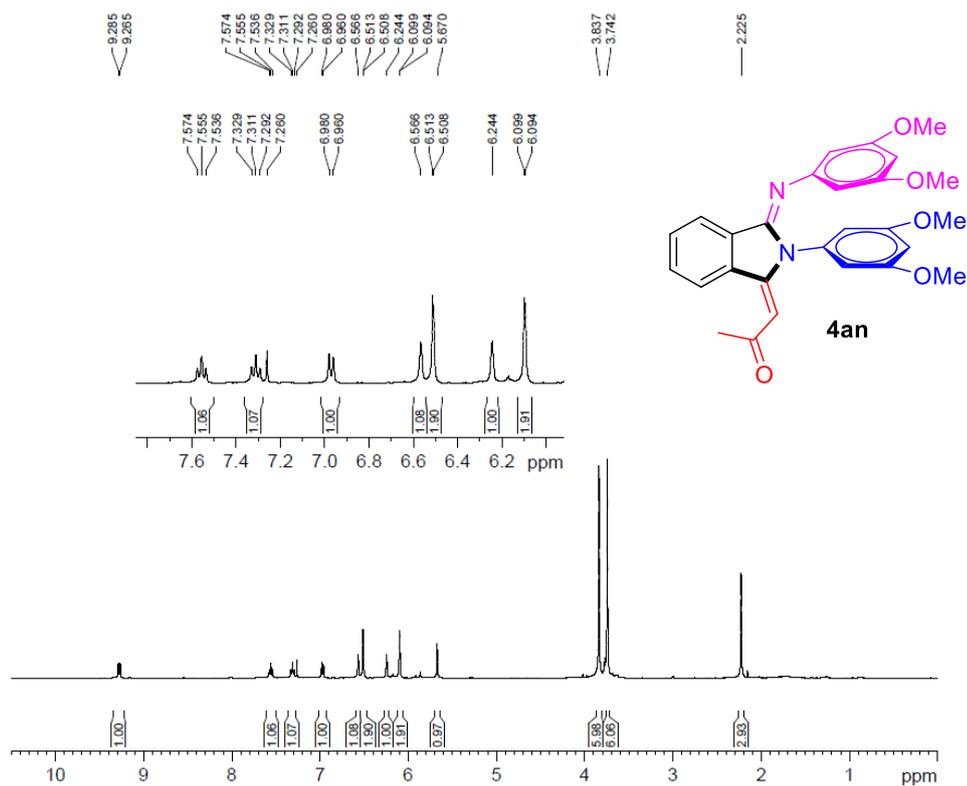
<sup>13</sup>C NMR spectrum of **4al** in CDCl<sub>3</sub>, 100 MHz.



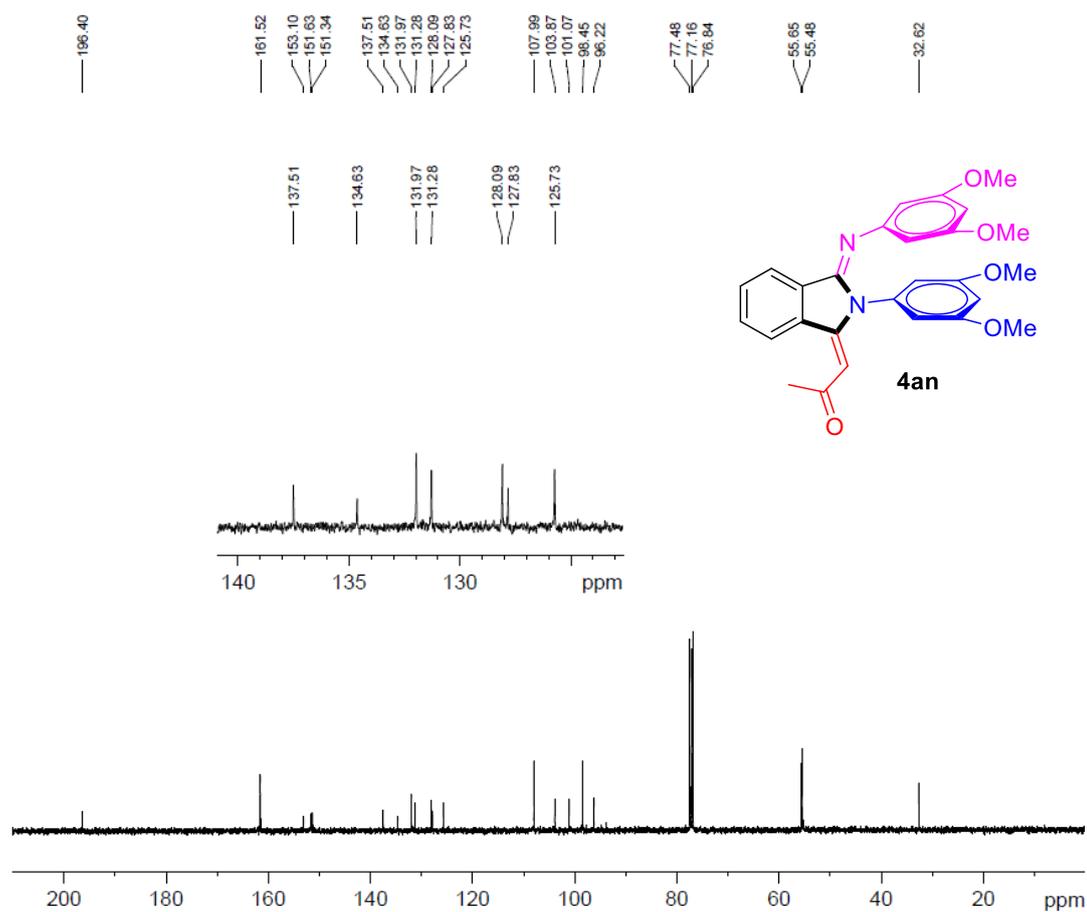
<sup>1</sup>H NMR spectrum of **4am** in CDCl<sub>3</sub>, 400 MHz.



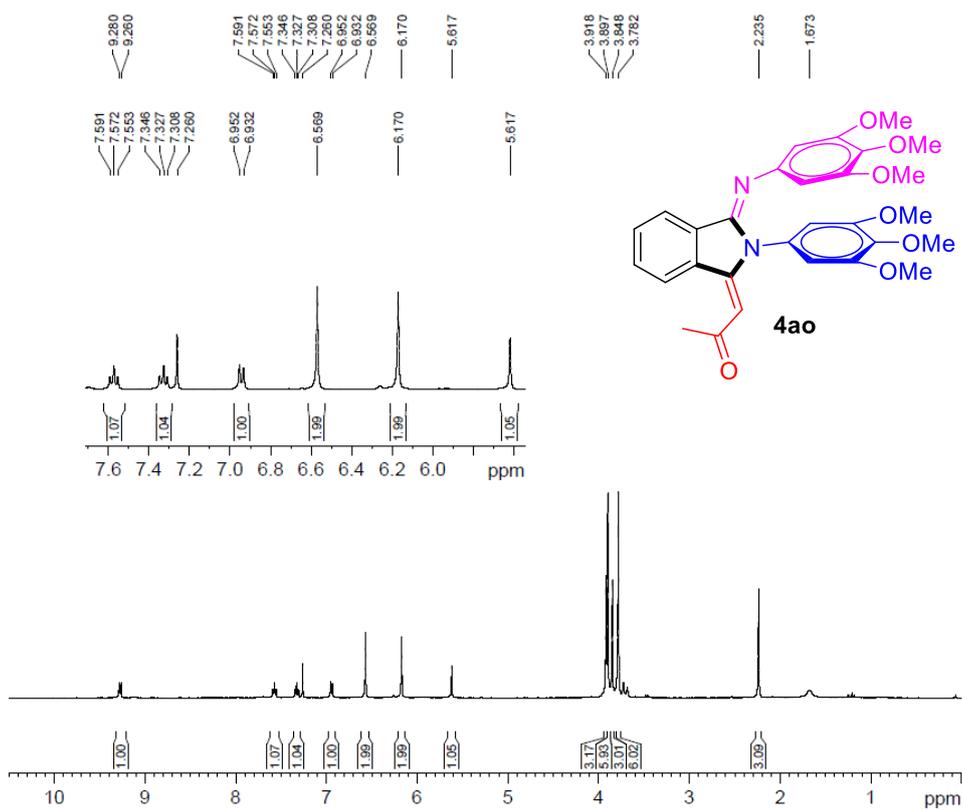
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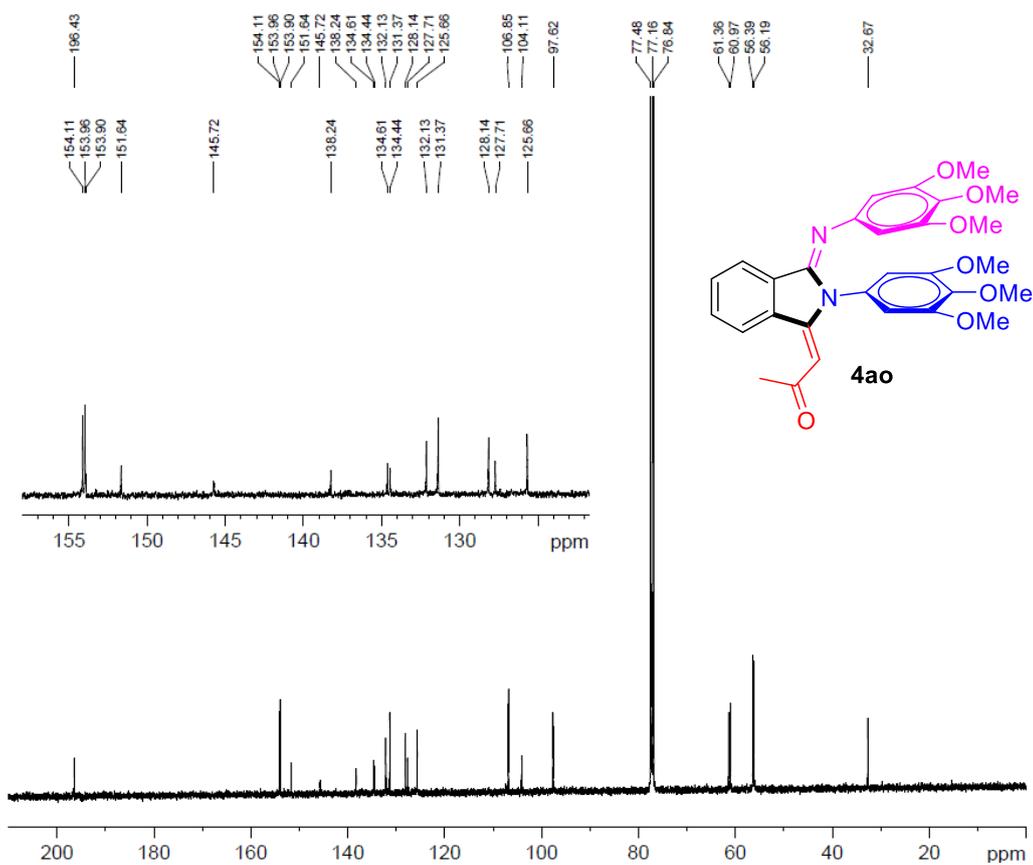
<sup>1</sup>H NMR spectrum of **4an** in CDCl<sub>3</sub>, 400 MHz.



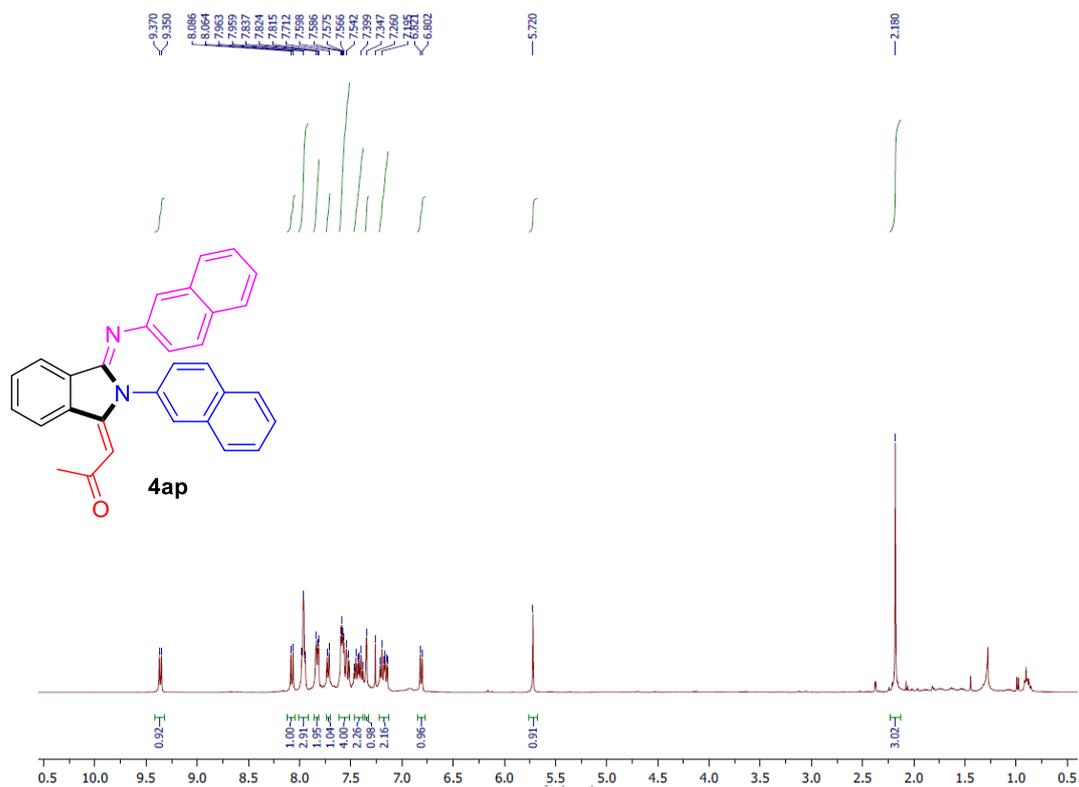
<sup>13</sup>C NMR spectrum of **4an** in CDCl<sub>3</sub>, 100 MHz.



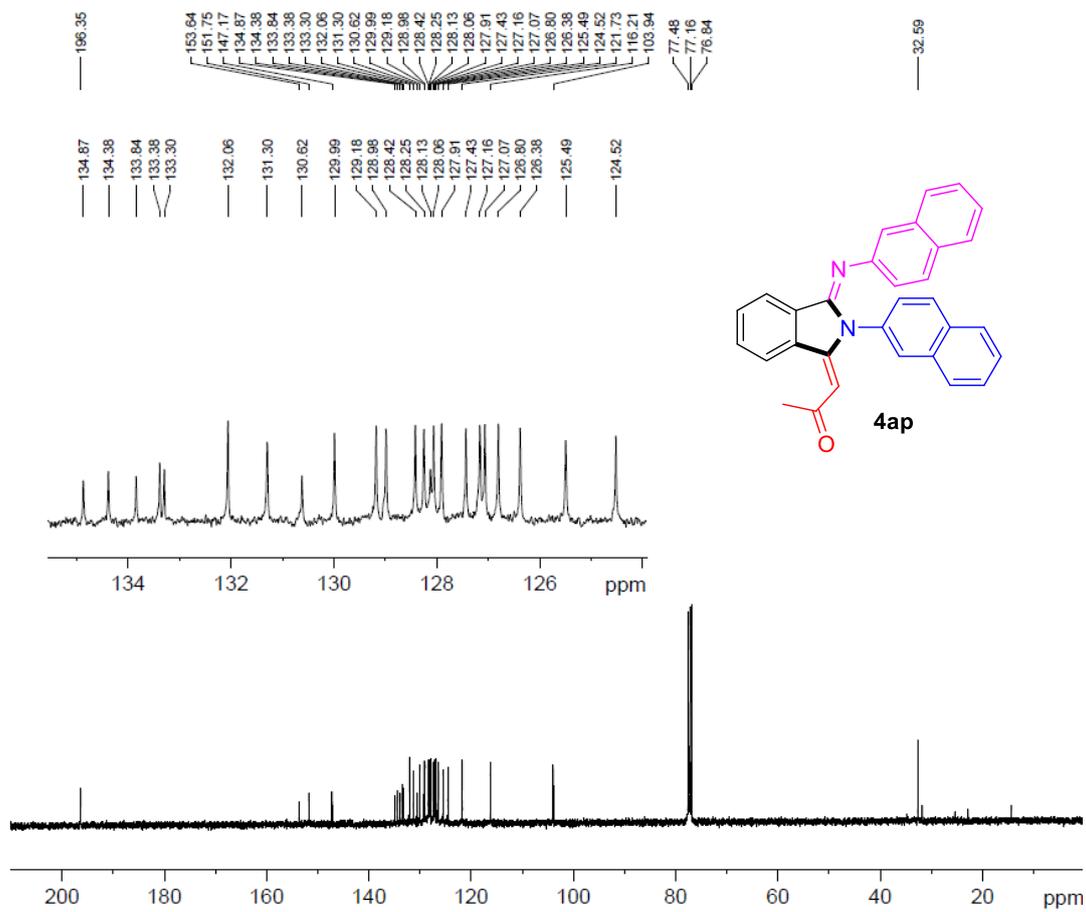
<sup>1</sup>H NMR spectrum of **4ao** in CDCl<sub>3</sub>, 400 MHz.



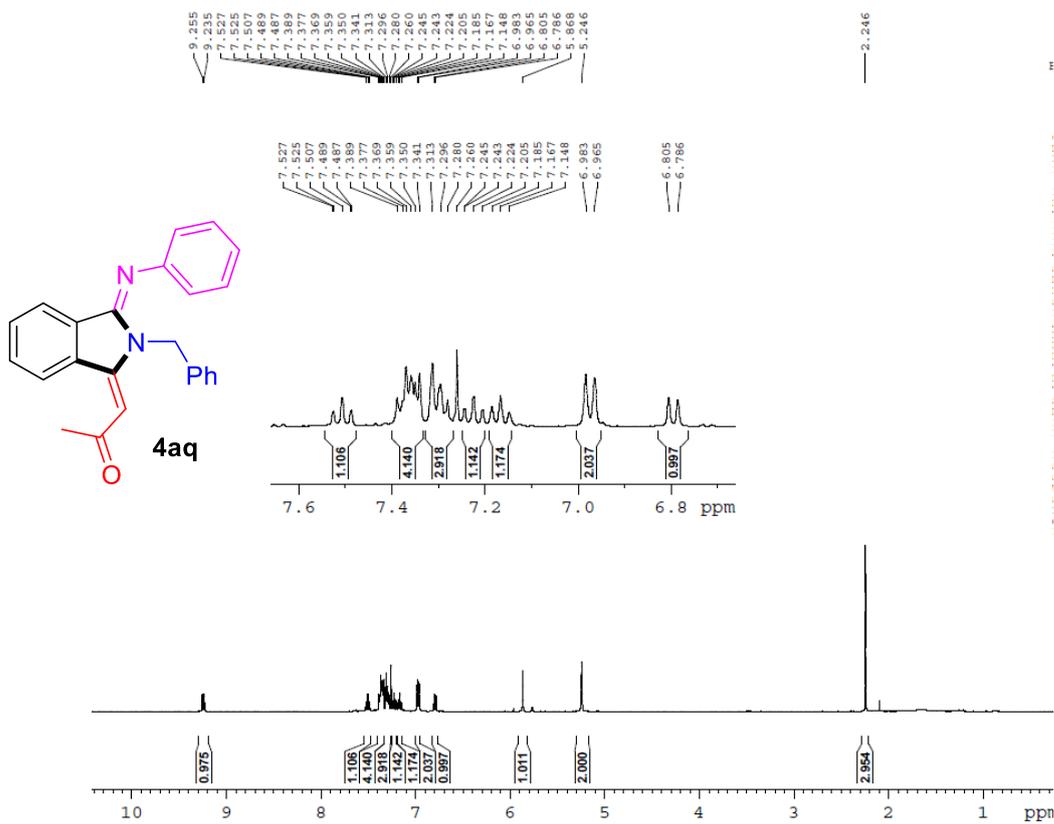
<sup>13</sup>C NMR spectrum of **4ao** in CDCl<sub>3</sub>, 100 MHz.



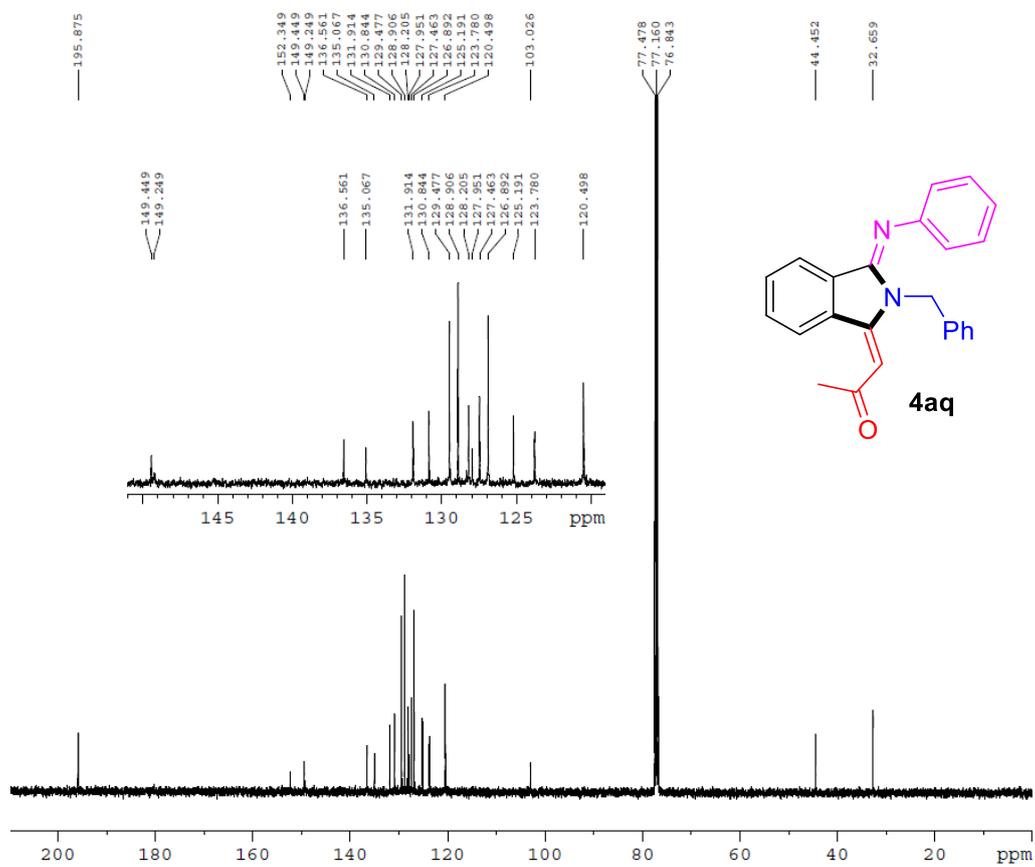
<sup>1</sup>H NMR spectrum of **4ap** in CDCl<sub>3</sub>, 400 MHz.



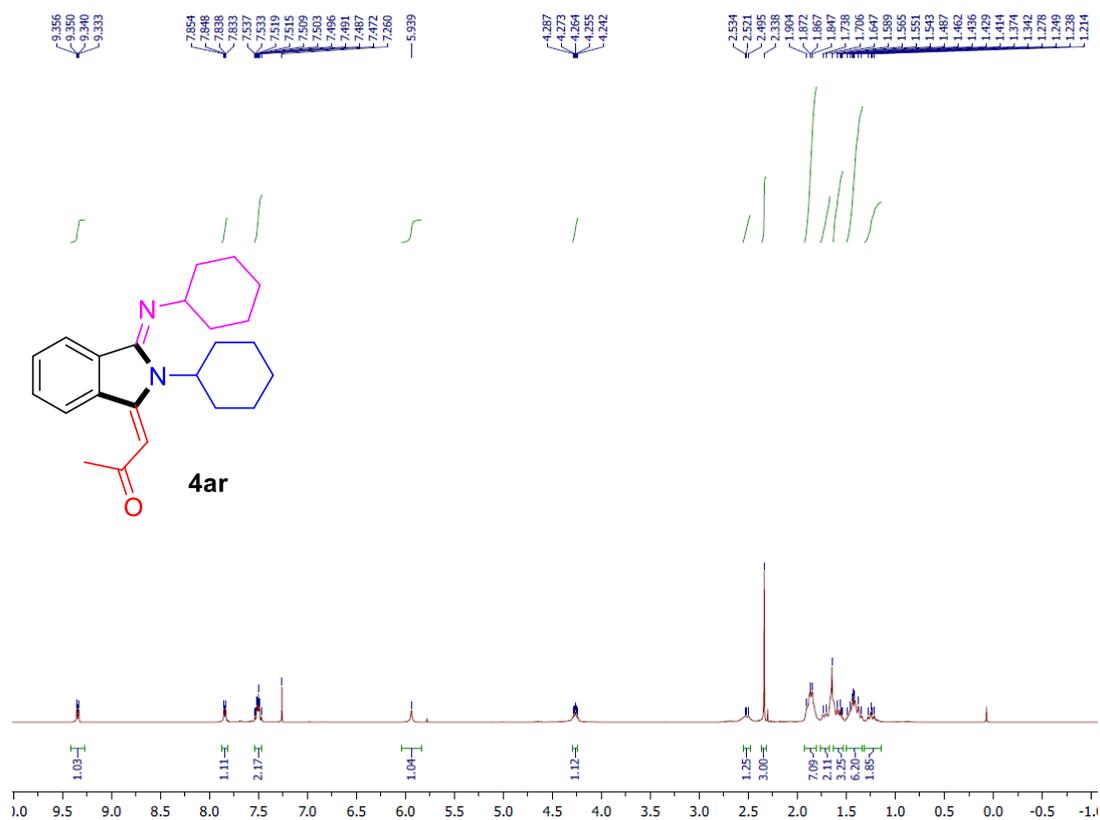
<sup>13</sup>C NMR spectrum of **4ap** in CDCl<sub>3</sub>, 100 MHz.



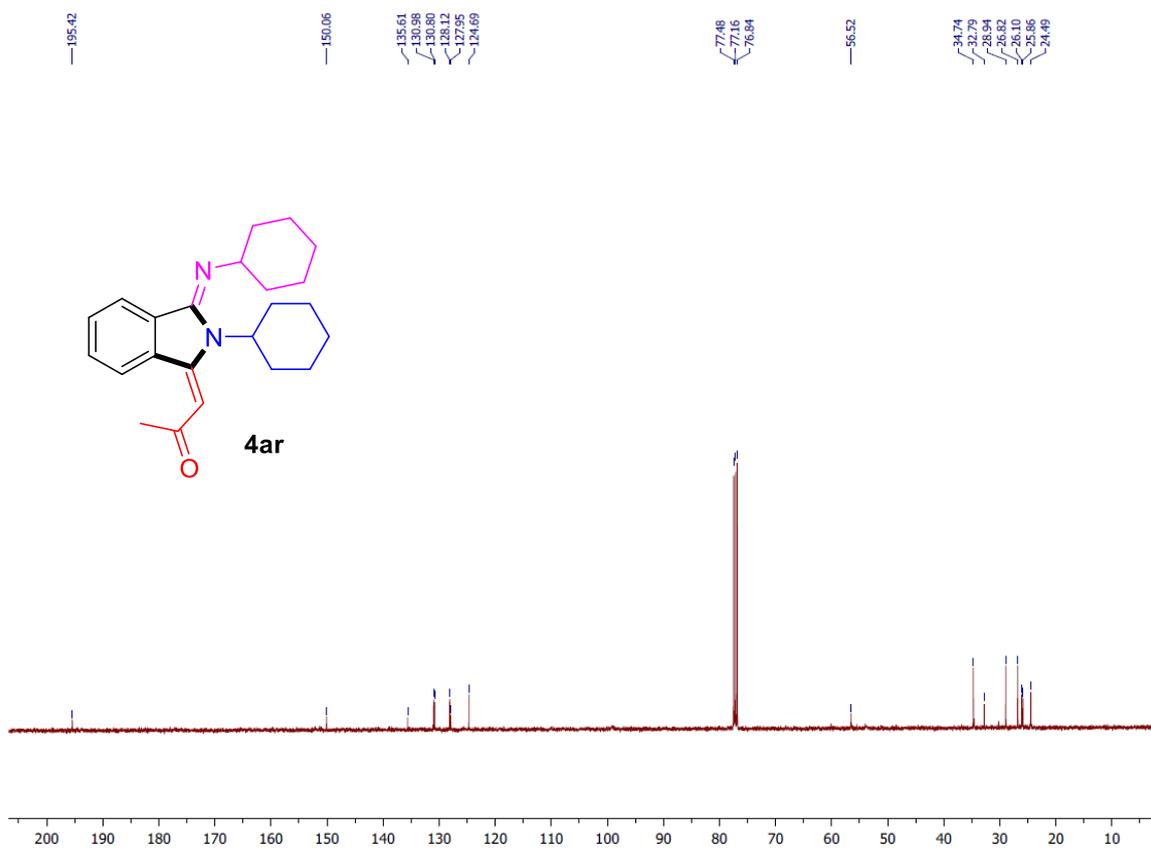
<sup>1</sup>H NMR spectrum of 4aq in CDCl<sub>3</sub>, 400 MHz.



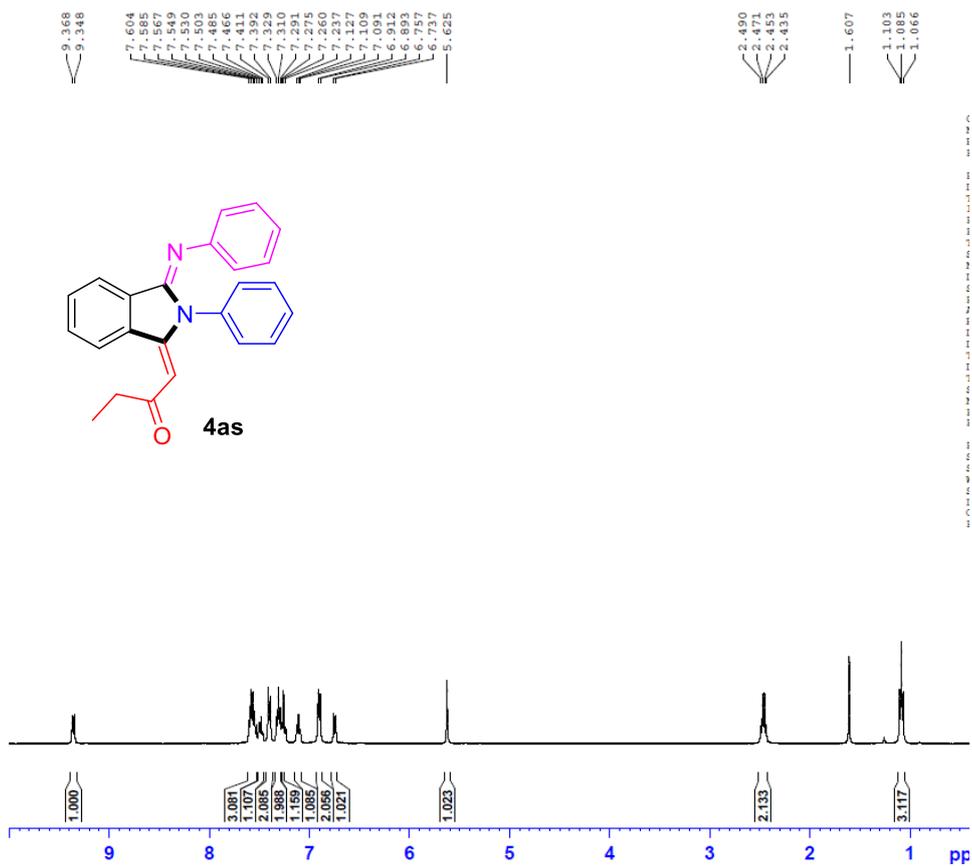
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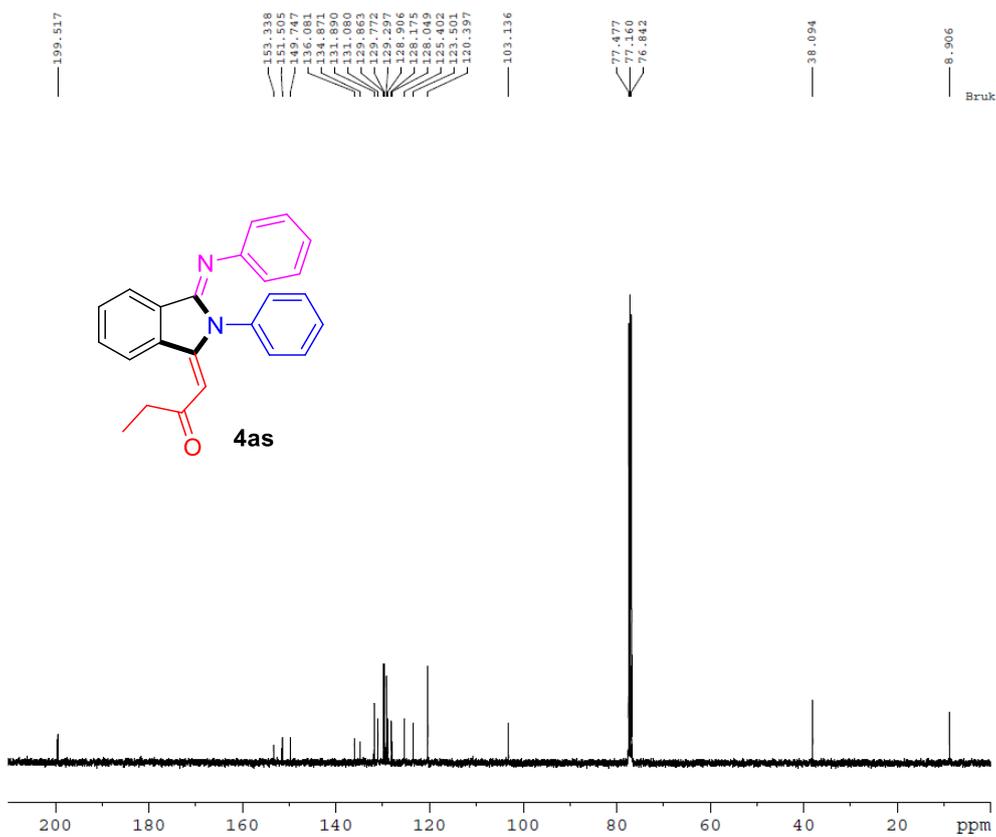
<sup>1</sup>H NMR spectrum of **4ar** in CDCl<sub>3</sub>, 400 MHz.



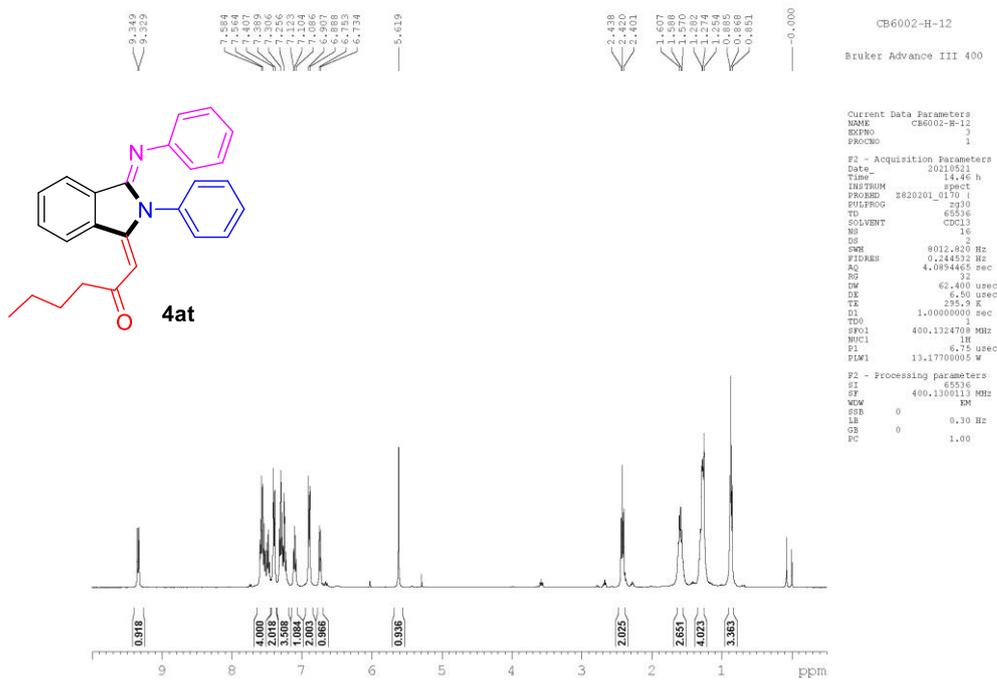
<sup>13</sup>C NMR spectrum of **4ar** in CDCl<sub>3</sub>, 100 MHz.



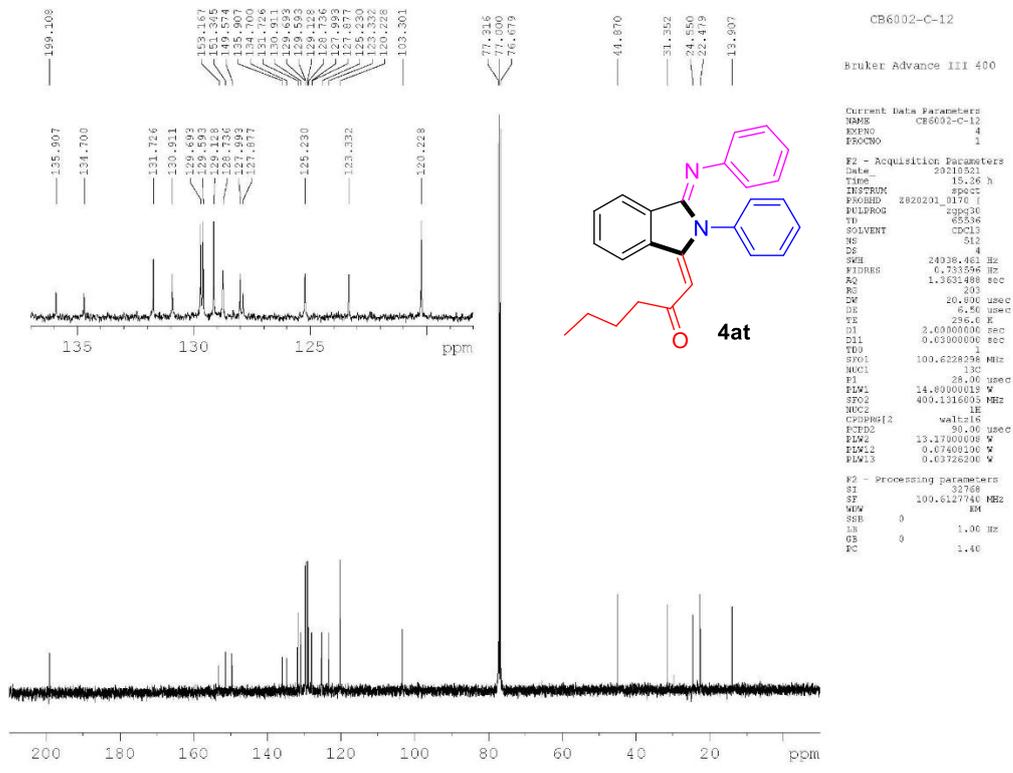
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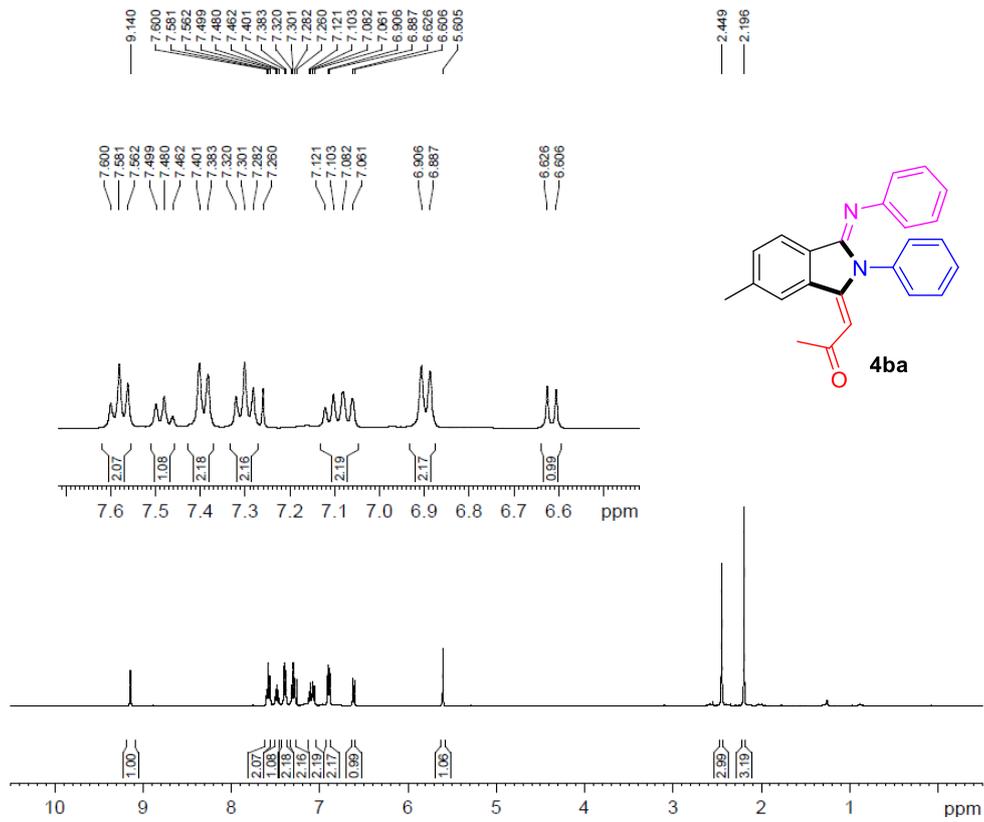
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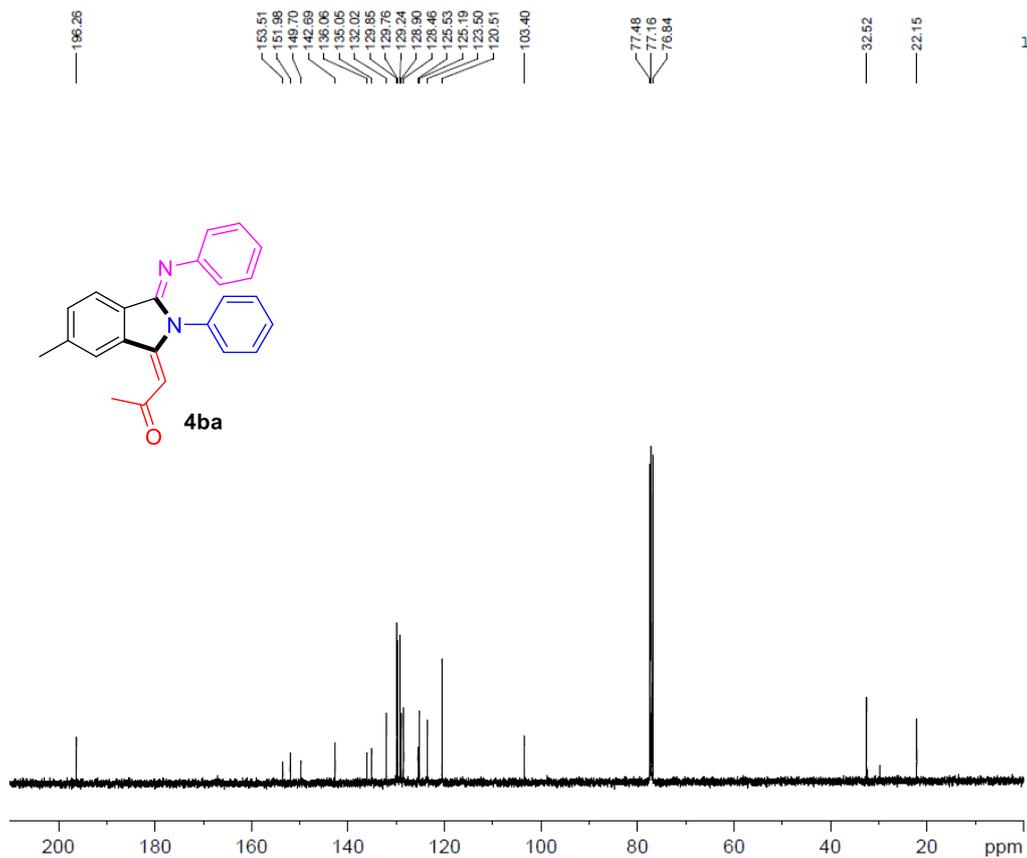
<sup>1</sup>H NMR spectrum of **4at** in CDCl<sub>3</sub>, 400 MHz.



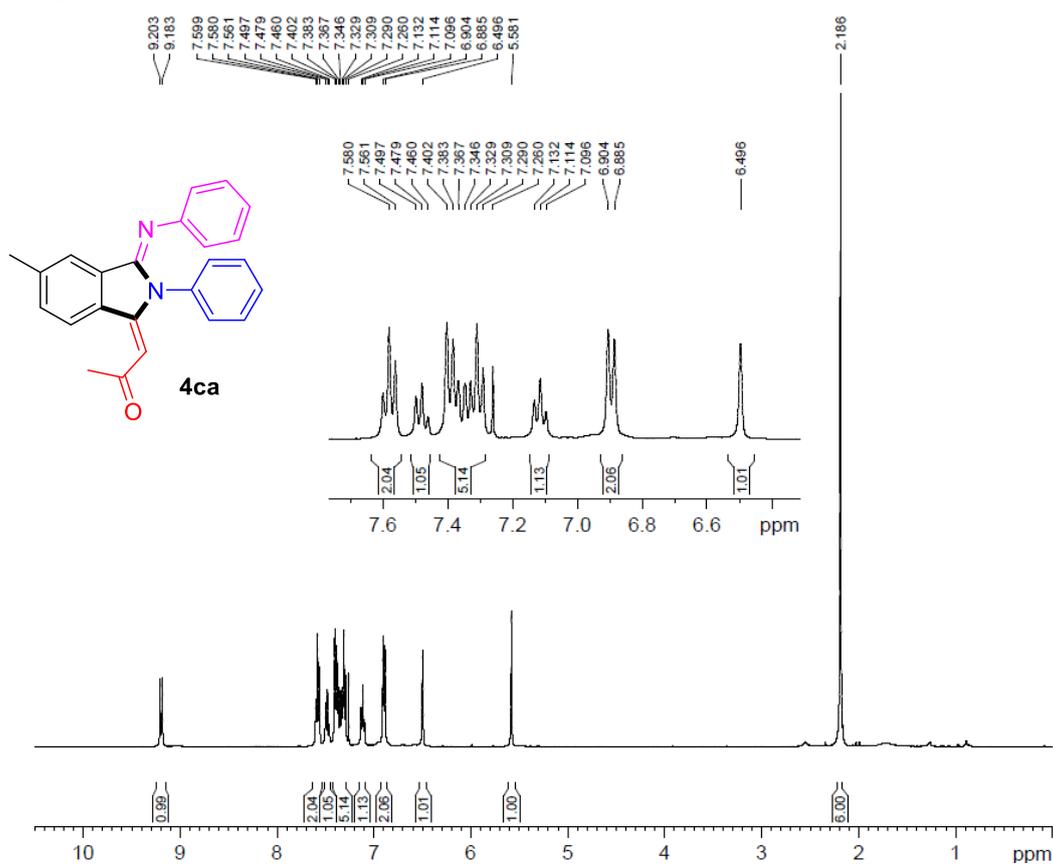
<sup>13</sup>C NMR spectrum of **4at** in CDCl<sub>3</sub>, 400 MHz.



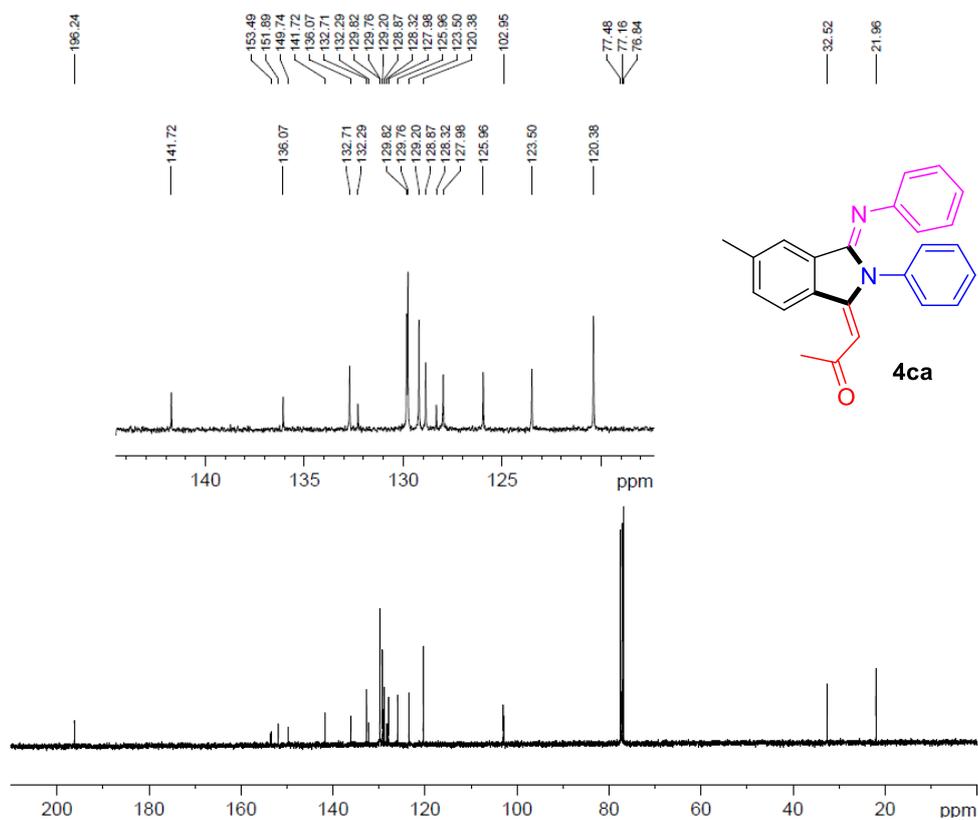
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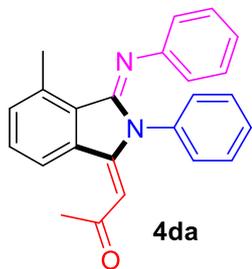
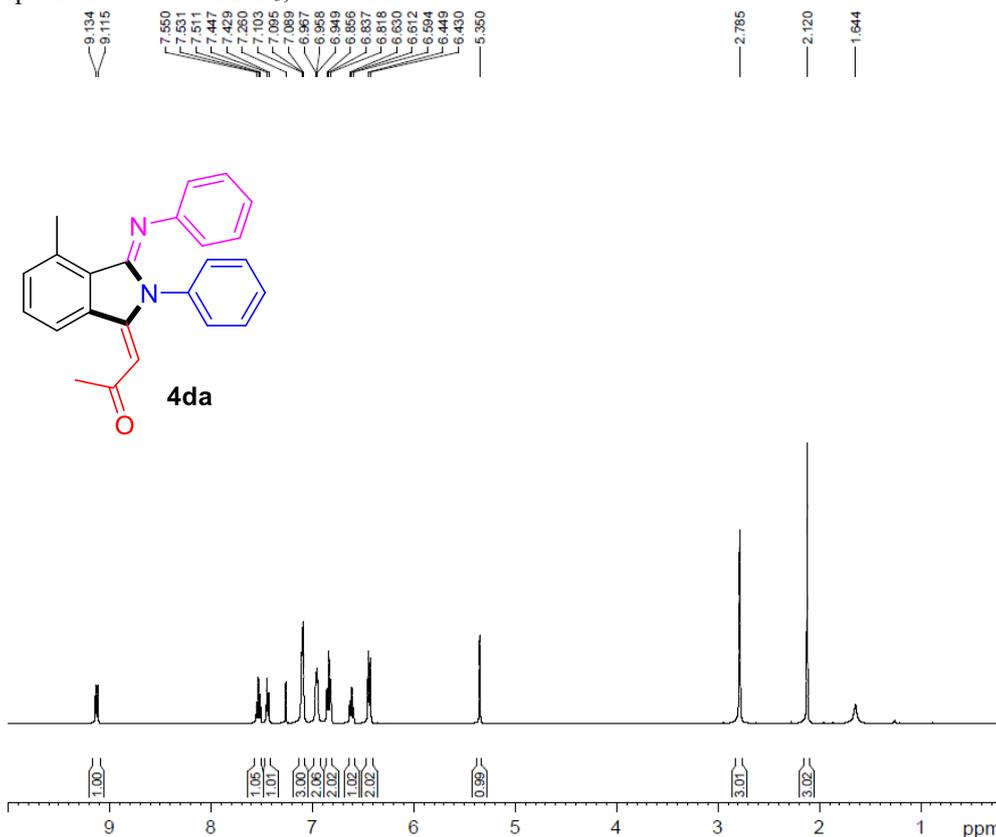
$^{13}\text{C}$  NMR spectrum of **4ba** in  $\text{CDCl}_3$ , 100 MHz.



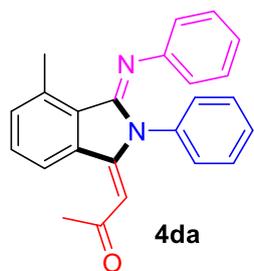
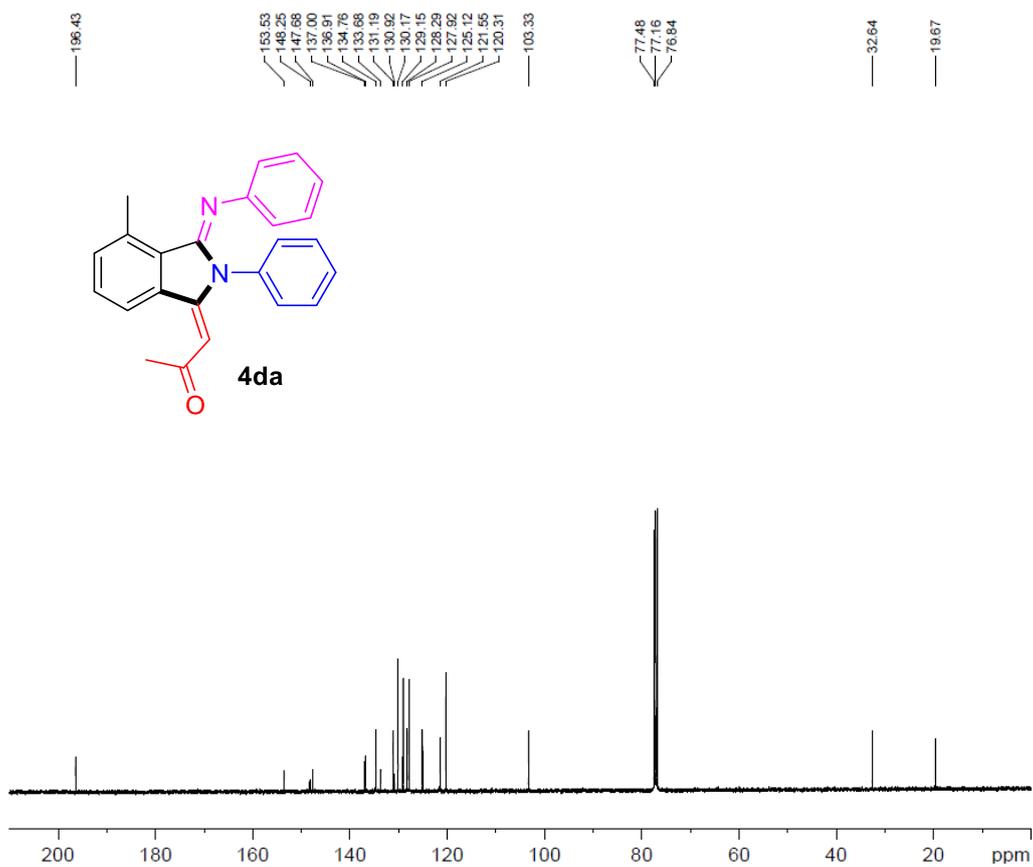
$^1\text{H}$  NMR spectrum of **4ca** in  $\text{CDCl}_3$ , 400 MHz.



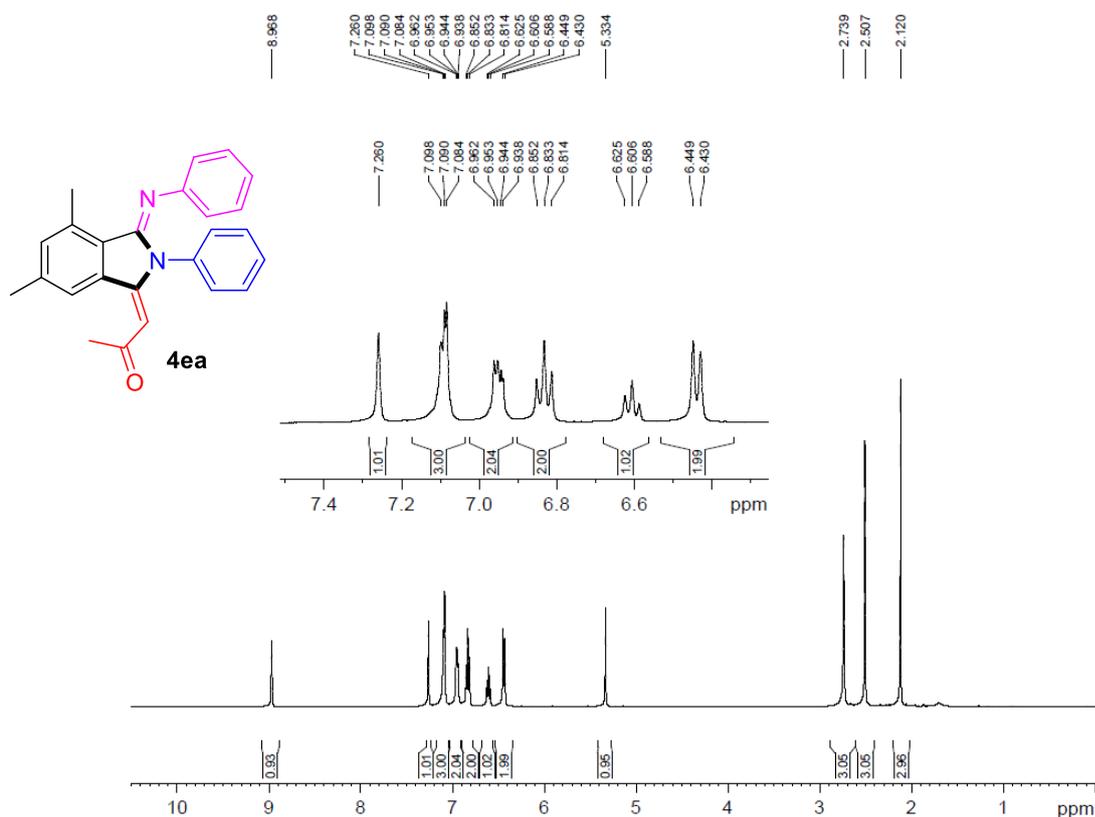
$^{13}\text{C}$  NMR spectrum of **4ca** in  $\text{CDCl}_3$ , 100 MHz.



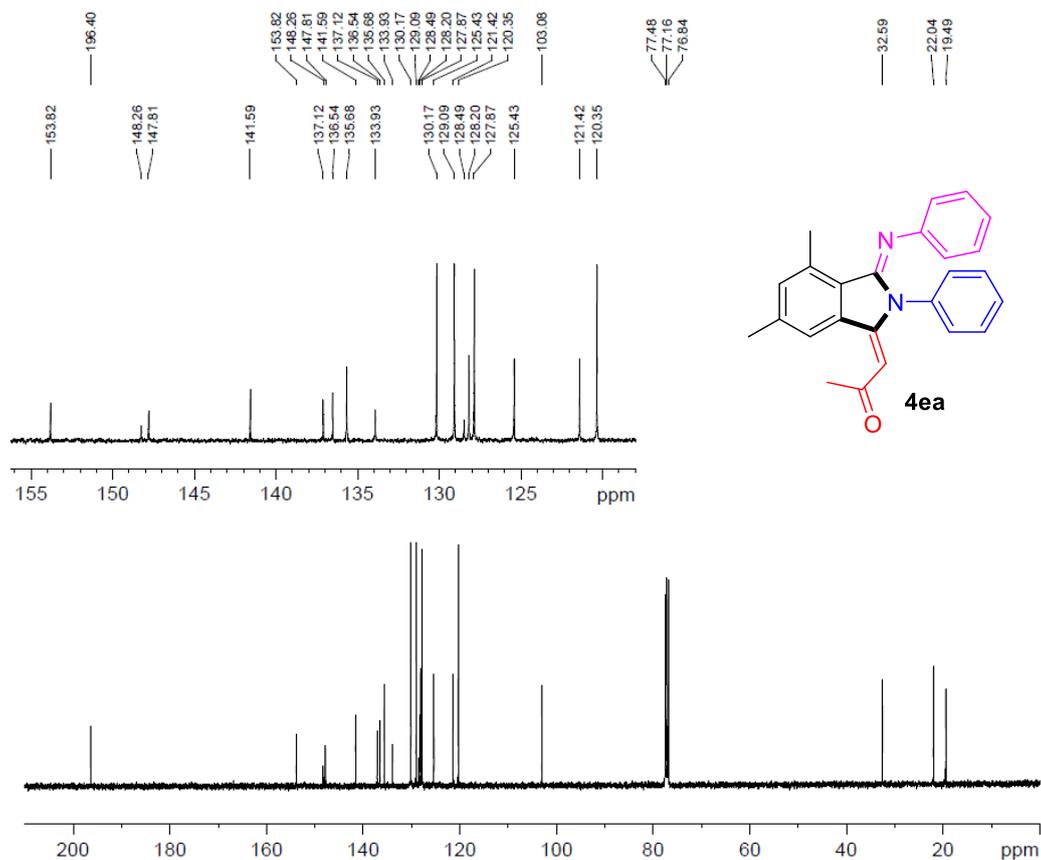
$^1\text{H}$  NMR spectrum of **4da** in  $\text{CDCl}_3$ , 400 MHz.



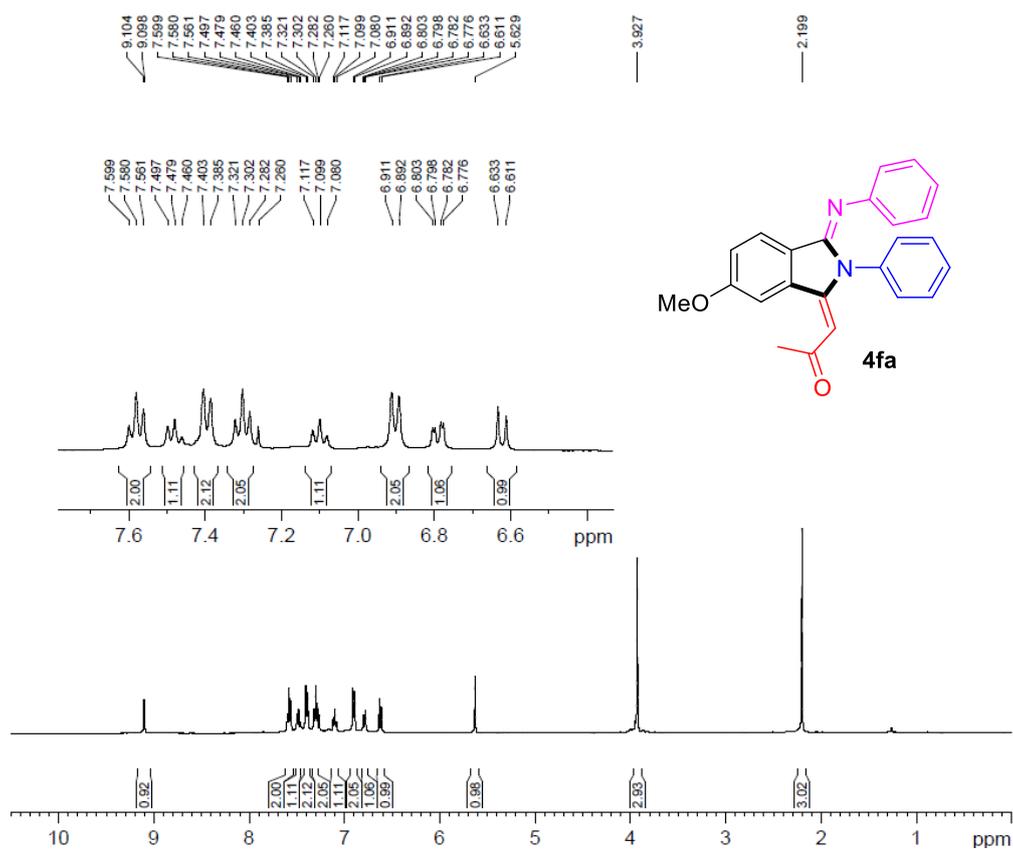
$^{13}\text{C}$  NMR spectrum of **4da** in  $\text{CDCl}_3$ , 100 MHz.



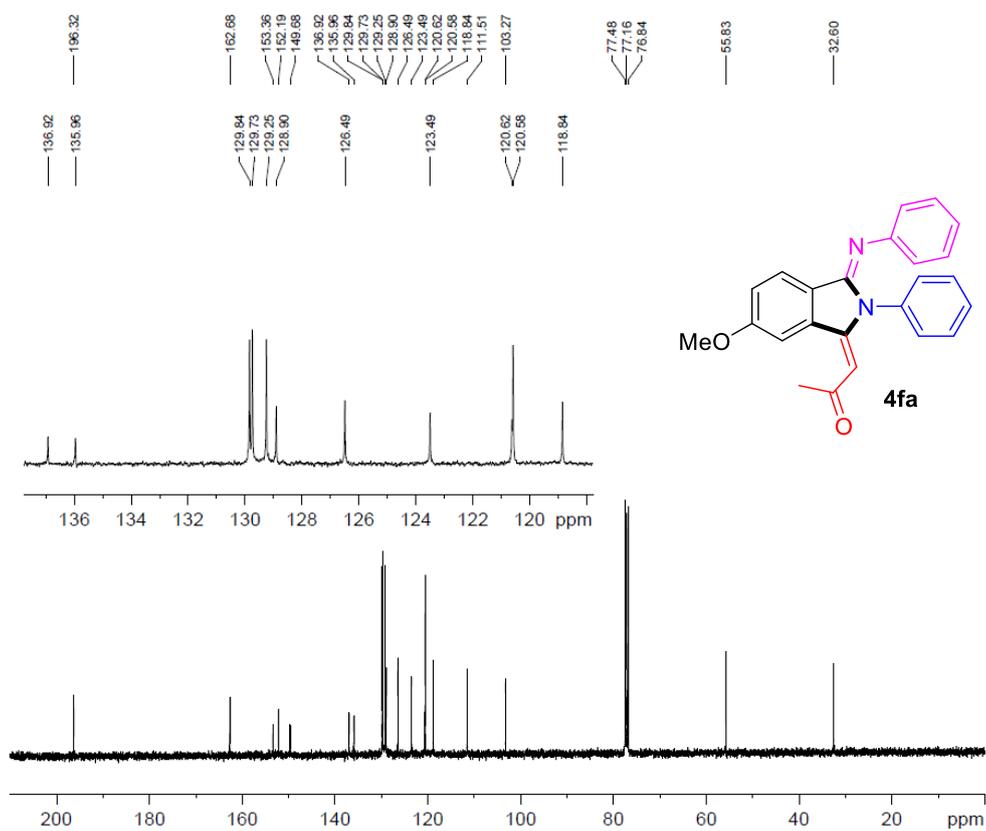
$^1\text{H}$  NMR spectrum of **4ea** in  $\text{CDCl}_3$ , 400 MHz.



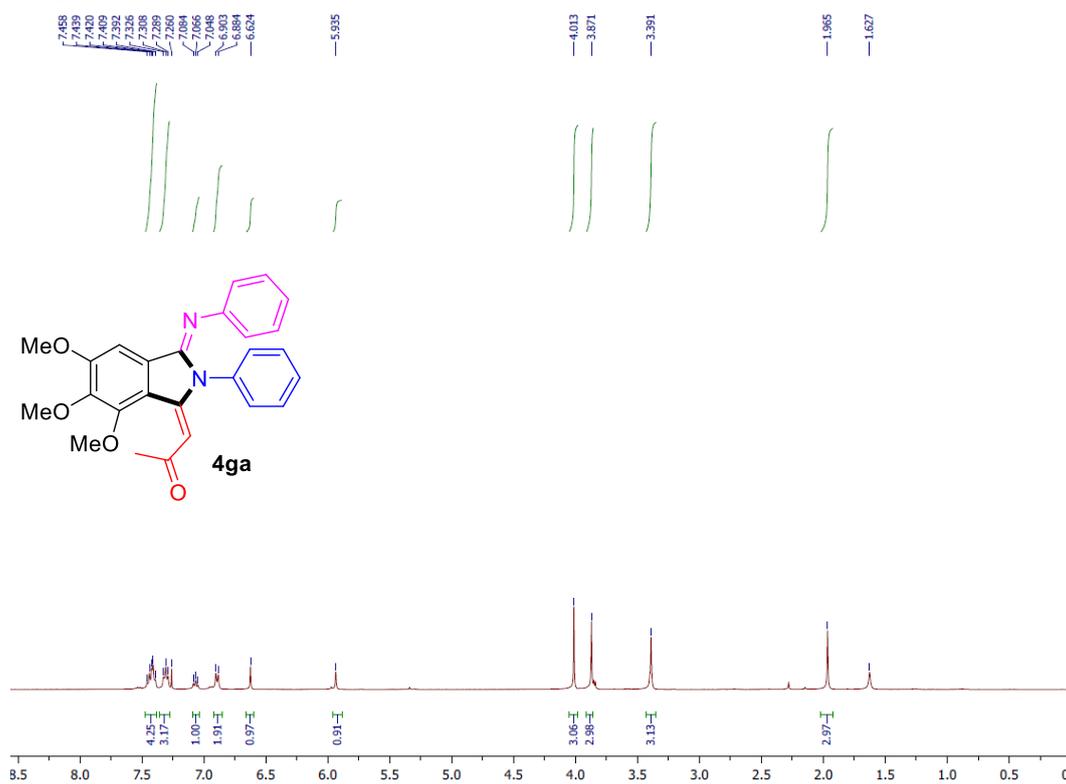
$^{13}\text{C}$  NMR spectrum of **4fa** in  $\text{CDCl}_3$ , 100 MHz.



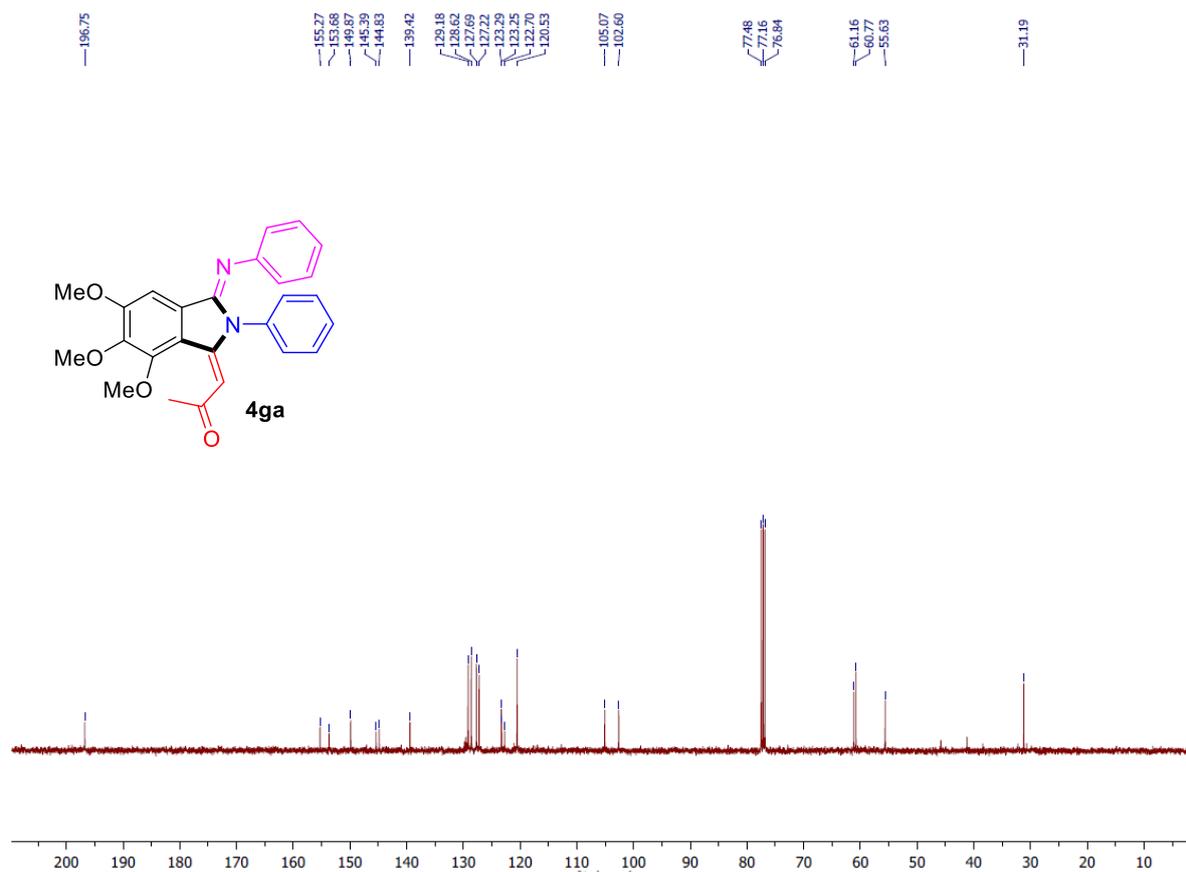
$^1\text{H}$  NMR spectrum of **4fa** in  $\text{CDCl}_3$ , 400 MHz.



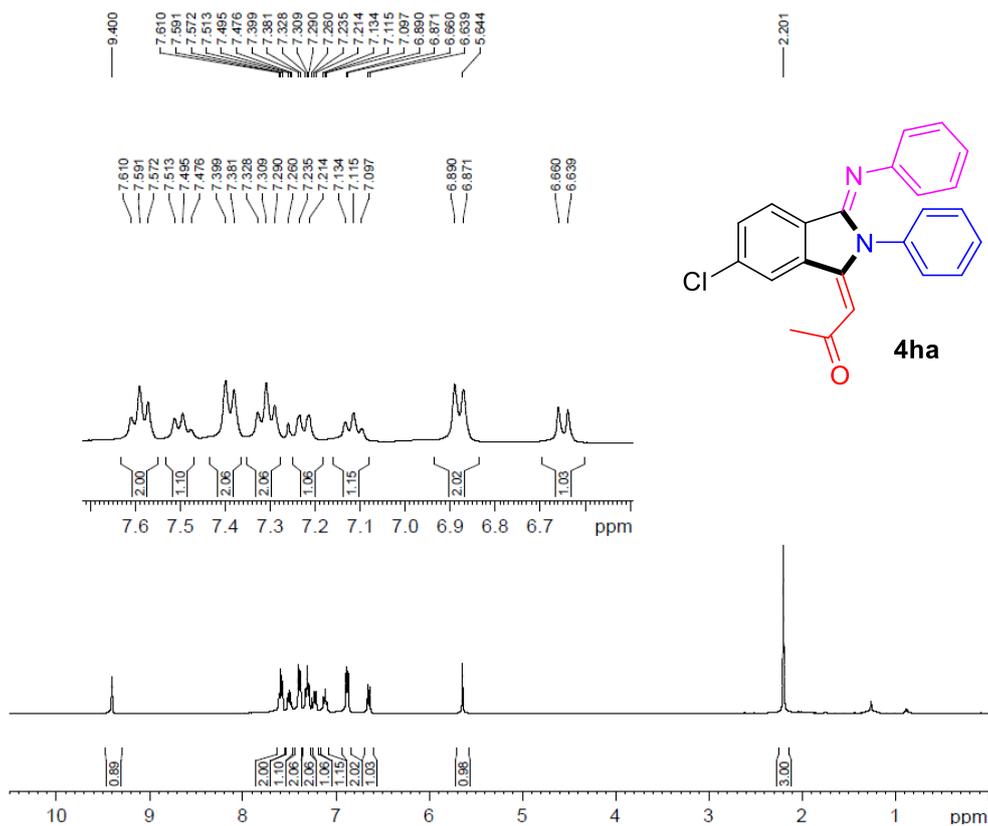
$^{13}\text{C}$  NMR spectrum of **4fa** in  $\text{CDCl}_3$ , 100 MHz.



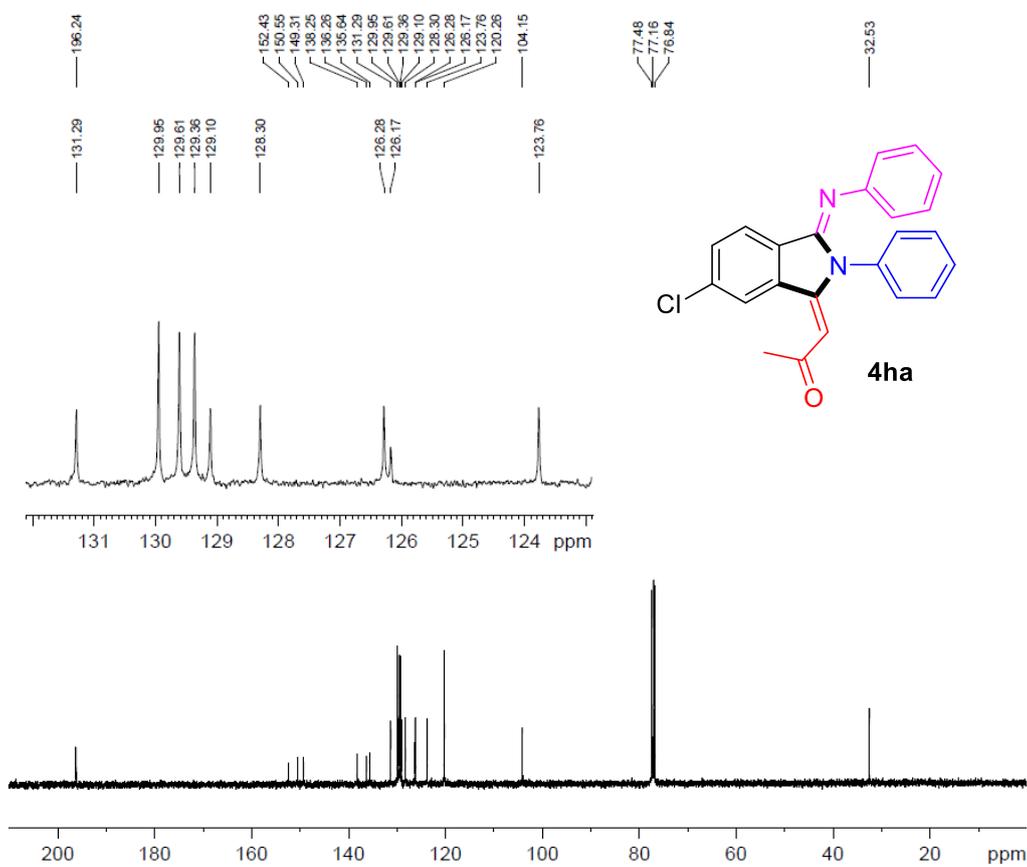
$^1\text{H}$  NMR spectrum of **4ga** in  $\text{CDCl}_3$ , 400 MHz.



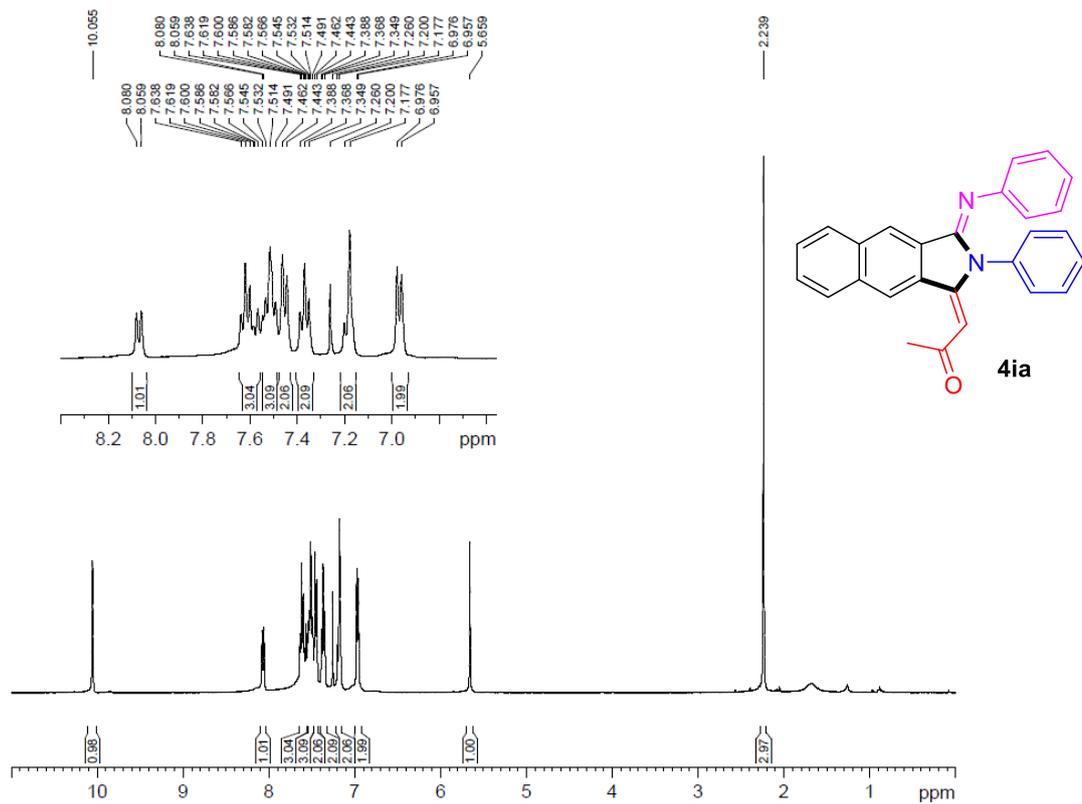
$^{13}\text{C}$  NMR spectrum of **4ga** in  $\text{CDCl}_3$ , 100 MHz.



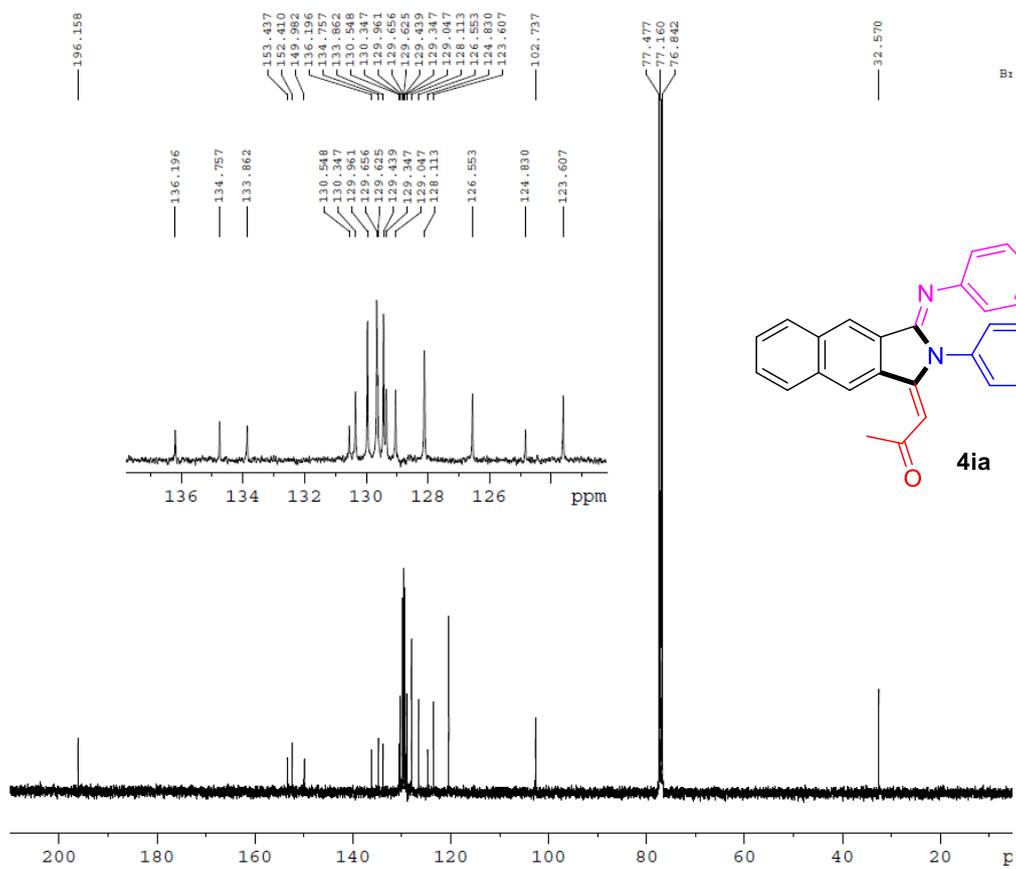
<sup>1</sup>H NMR spectrum of **4ha** in CDCl<sub>3</sub>, 400 MHz.



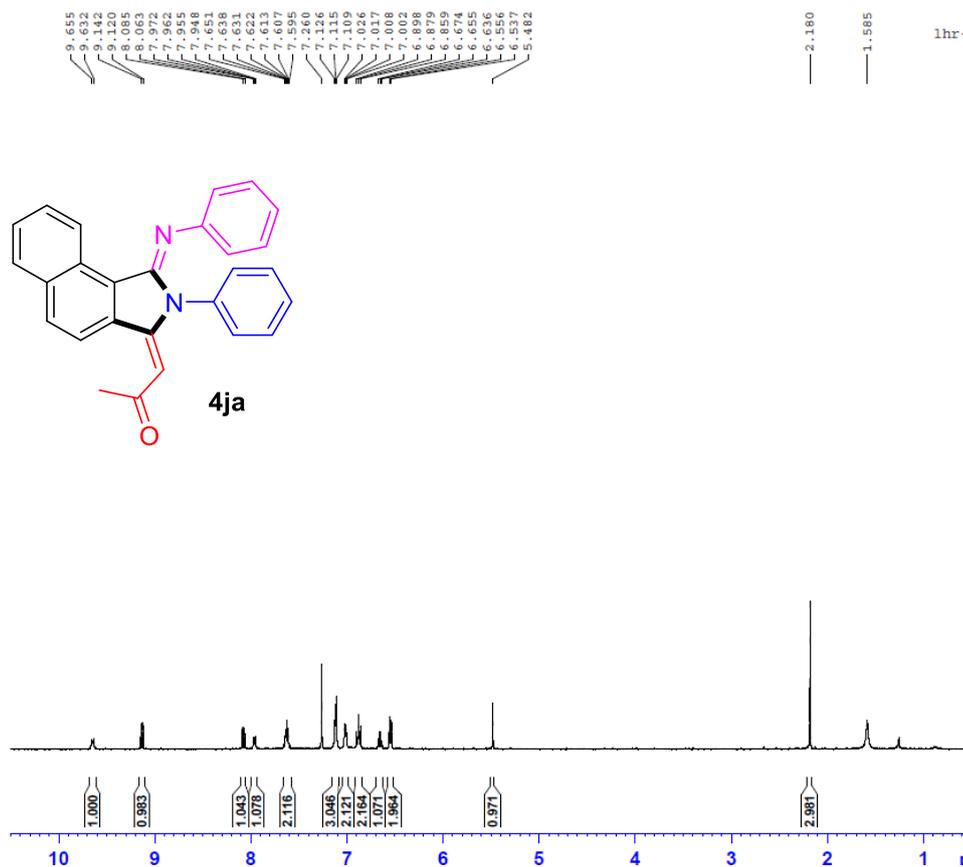
<sup>13</sup>C NMR spectrum of **4ha** in CDCl<sub>3</sub>, 100 MHz.



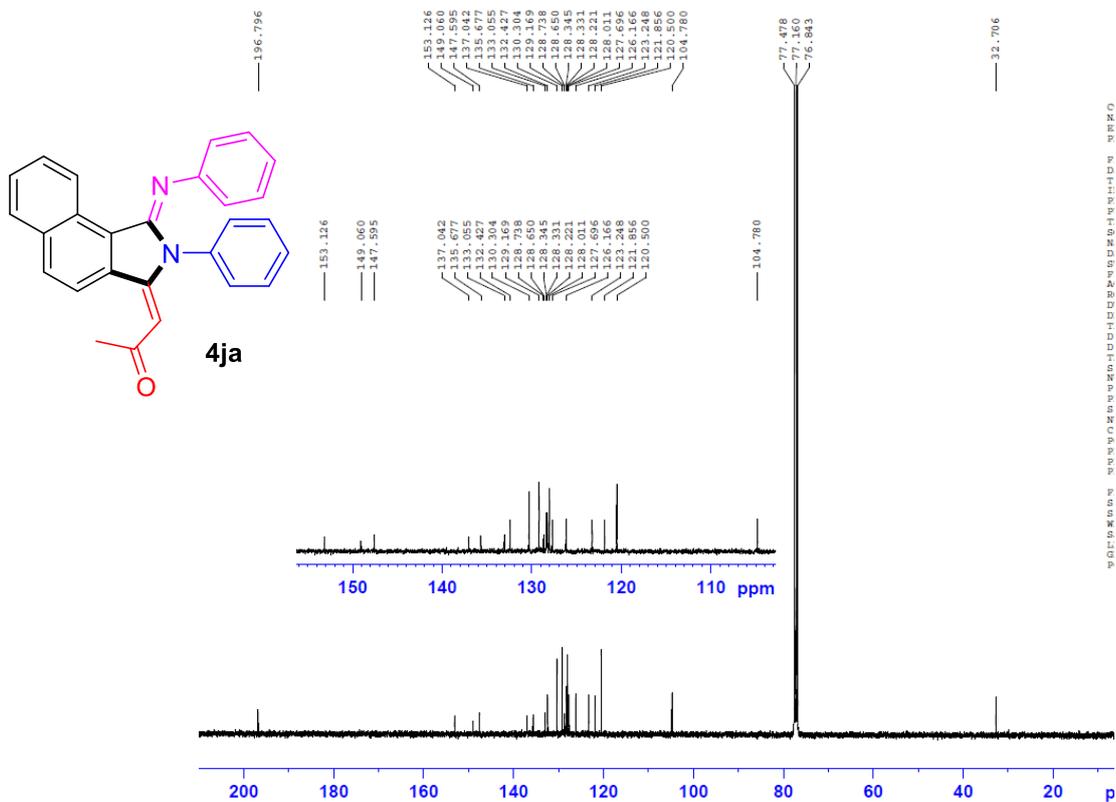
<sup>1</sup>H NMR spectrum of **4ia** in CDCl<sub>3</sub>, 400 MHz.



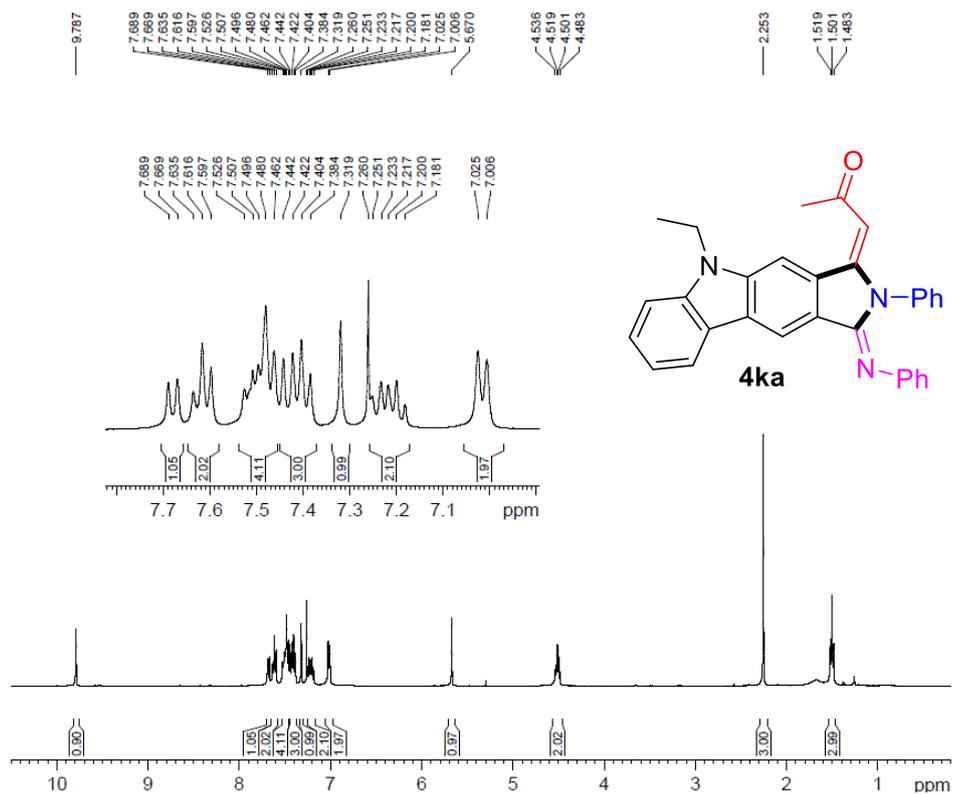
<sup>13</sup>C NMR spectrum of **4ia** in CDCl<sub>3</sub>, 100 MHz.



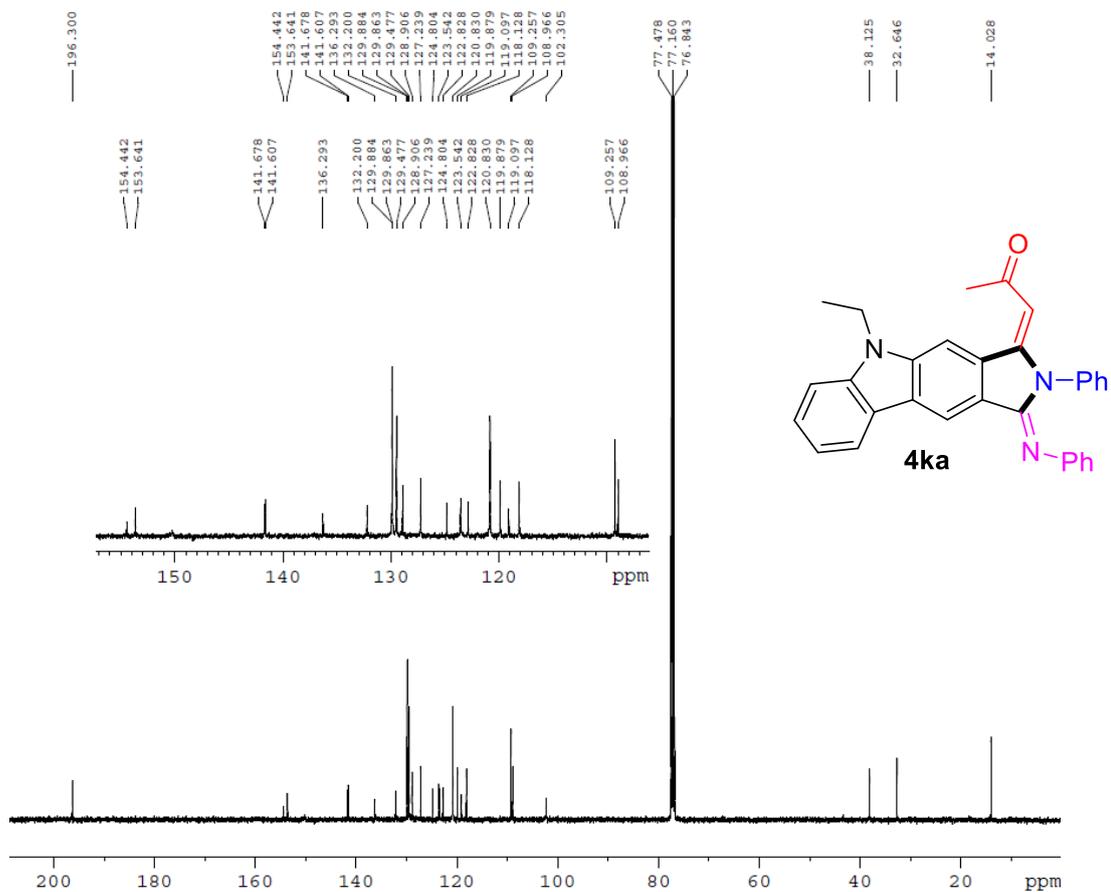
<sup>1</sup>H NMR spectrum of **4ja** in CDCl<sub>3</sub>, 400 MHz.



<sup>13</sup>C NMR spectrum of **4ja** in CDCl<sub>3</sub>, 100 MHz.



<sup>1</sup>H NMR spectrum of **4ka** in CDCl<sub>3</sub>, 400 MHz.



<sup>13</sup>C NMR spectrum of **4ka** in CDCl<sub>3</sub>, 100 MHz.