Supporting Information

The synthesis of diverse benzazepinoindoles via gold-catalyzed post-Ugi alkyne hydroarylation/Michael addition sequence

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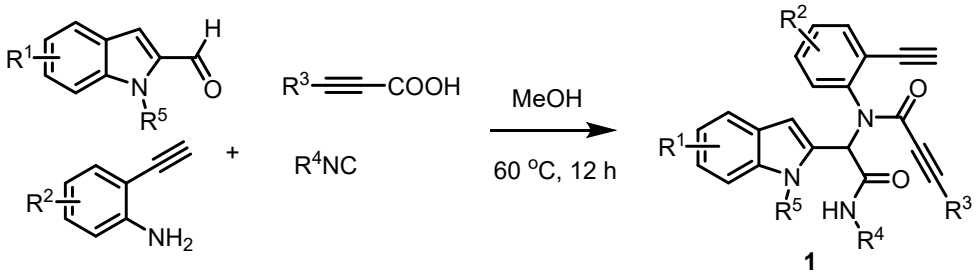
Contents

1. General information

Commercially available reagents were used without additional purification. Column chromatography was performed with silica gel (70-230 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM (400 MHz) spectrometer at ambient temperature using $CDCl_3$ or DMSO-d_6 as solvent. HRMS (ESI) spectrometry data were acquired on a quadrupole orthogonal acceleration time-of-flight mass spectrometer [Synapt G2 high definition mass spectrometer (HDMS), Waters, Milford, MA]. Samples were infused at 3 μL min^{-1}, and spectra were obtained in the positive ionization mode with a resolution of 15000 [full width at half maximum (FWHM)] with leucine encephalin as lock mass. Melting points were recorded on a Reichert Thermovar apparatus and were uncorrected.

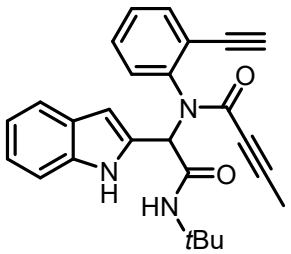
2. General procedure for the synthesis of Ugi adducts



1

To a solution of aldehyde (1.0 mmol) in methanol (2 mL) were added successively amine (1.2 equiv), acid (1.2 equiv) and isonitrile (1.2 equiv) in a screw capped vial equipped with a magnetic stir bar. The reaction mixture was stirred in an oil bath at 60 °C for 12 h in closed vial. After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with EtOAc (3×10 mL), Organic layer was dried over magnesium sulfate and evaporated under reduced pressure to obtained residue which was subjected to silica gel column chromatography (eluent: EtOAc/*n*-heptane 1:2 v/v) affording the desired product **1**.

3. Characterization of Ugi adducts



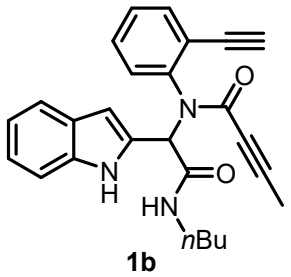
1a

1a was obtained as a brown solid. Yield 70%. Melting point 230 – 232 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 7.89 – 7.85 (m, 2H), 7.31 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.21 – 7.18 (m, 1H), 7.12 – 7.08 (m, 1H), 6.95 – 6.90 (m, 1H), 6.85 – 6.80 (m, 1H), 6.13 (d, J = 2.2 Hz, 1H), 6.05 (s, 1H), [4.28 (s), 4.23 (s), 1H], [1.66 (s), 1.65 (s), 3H], [1.27 (s), 1.22 (s), 9H]. Mixture of rotamers (~4:1).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.2, 154.0, 141.8, 136.9, 132.5, 132.0, 131.2, 129.4, 128.8, 127.4, 124.4, 121.7, 120.4, 119.3, 112.3, 104.5, 89.5, 85.2, 81.2, 75.1, 59.8, 51.2, 29.1, 3.7. Major rotamer.

HRMS (ESI, m/z) calcd for $C_{26}H_{25}N_3O_2$ ([M+H]$^+$): 412.2020, found 412.2022.



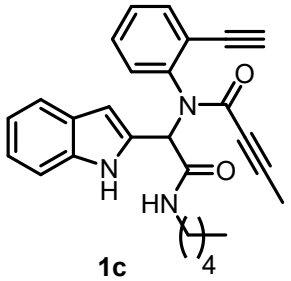
1b

1b was obtained as a yellow solid. Yield 60 %. Melting point 172 – 174°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.78 (s), 9.13 (s), 1H], 7.61 – 7.53 (m, 1H), 7.52 – 7.44 (m, 1H), 7.44 – 7.34 (m, 2H), 7.34 – 7.27 (m, 1H), [7.25 – 6.99 (m), 6.88 – 6.75 (m), 3H], [6.69 – 6.62 (m), 5.96 – 5.85 (m), 1H], [6.54 – 6.45 (m), 6.44 – 6.39 (m), 1H], [5.81 (s), 5.35 (s), 1H], [3.80 – 3.73 (m), 3.39 – 3.30 (m), 1H], [3.30 (s), 2.56 (s), 1H], 3.29 – 3.12 (m, 1H), [1.70 (s), 1.70 (s), 3H], 1.59 – 1.18 (m, 4H), 0.98 – 0.77 (m, 3H). Mixture of rotamers (~7:3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.8, 156.2, 155.3, 144.4, 142.1, 136.7, 136.5, 133.4, 133.1, 132.6, 130.5, 130.1, 130.1, 129.7, 129.5, 128.7, 128.7, 127.3, 127.2, 123.1, 123.1, 122.8, 122.5, 120.8, 120.7, 119.9, 119.7, 111.7, 111.4, 105.7, 105.5, 91.6, 91.1, 82.6, 81.4, 80.8, 79.3, 73.9, 73.9, 63.2, 60.1, 40.0, 39.8, 31.5, 20.1, 13.8, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{26}H_{25}N_3O_2$ ([M+H]$^+$): 412.2020, found 412.2023.



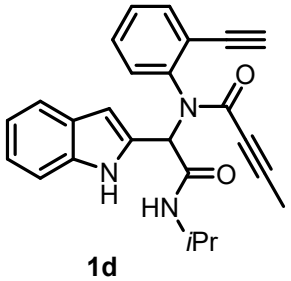
1c

1c was obtained as a white solid. Yield 56 %. Melting point 181 – 183 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.78 (s), 9.13 (s), 1H], 7.59 – 7.55 (m, 1H), 7.51 – 7.45 (m, 1H), 7.43 – 7.27 (m, 3H), 7.25 – 7.00 (m, 3H), [6.68 – 6.62 (m), 5.95 – 5.86 (m), 1H], [6.49 – 6.46 (m), 6.43 – 6.41 (m), 1H], [5.82 (s), 5.35 (s), 1H], [3.35 – 3.30 (m), 3.28 – 3.13 (m), 2H], [3.29 (s),2.57 (s), 1H], [1.70 (s), 1.70 (s), 3H], 1.57 – 1.40 (m, 2H), 1.33 – 1.27 (m, 2H), 1.26 – 1.18 (m, 2H), 0.90 – 0.83 (m, 3H). Mixture of rotamers (~7:3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.8, 156.2, 155.3, 144.4, 142.1, 136.7, 136.5, 133.4, 133.1, 132.6, 130.5, 130.1, 130.1, 129.7, 129.5, 128.7, 128.7, 127.3, 127.2, 123.1, 123.1, 122.8, 122.5, 120.8, 120.7, 119.9, 119.7, 111.7, 111.4, 105.7, 105.5, 91.6, 91.1, 82.5, 81.4, 80.7, 79.3, 73.9, 63.2, 60.1, 40.3, 40.1, 29.1, 29.1, 29.1, 22.4, 14.1, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ([M+H]$^+$): 426.2176, found 426.2161.



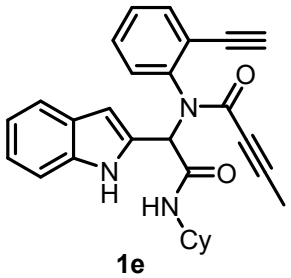
1d

1d was obtained as a brown solid. Yield 50 %. Melting point 174 – 176 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.74 (s), 9.11 (s), 1H], 7.60 – 7.53 (m, 1H), 7.52 – 7.45 (m, 1H), 7.41 – 7.26 (m, 3H), 7.26 – 7.00 (m, 3H), [6.49 – 6.47 (m), 6.42 – 6.40 (m), 1H], [5.75 (s), 5.34 (s), 1H], 5.72 (d, *J* = 7.9 Hz, 1H), 4.20 – 4.04 (m, 1H), [3.30 (s), 2.56 (s), 1H], [1.70 (s), 1.70 (s), 3H], [1.23 (d, *J* = 6.6 Hz), 1.13 (d, *J* = 6.6 Hz), 3H], [1.16 (d, *J* = 6.6 Hz), 1.07 (d, *J* = 6.6 Hz), 3H]. Mixture of rotamers (~7:3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.0, 156.2, 155.3, 144.3, 142.1, 136.7, 136.6, 133.4, 133.1, 132.6, 130.6, 130.1, 129.7, 129.4, 128.7, 128.7, 127.4, 127.2, 123.2, 123.0, 122.8, 122.5, 120.8, 120.7, 119.9, 119.7, 111.7, 111.4, 105.7, 105.5, 91.5, 91.1, 82.7, 81.4, 80.8, 79.3, 73.9, 63.2, 60.3, 42.4, 42.3, 22.7, 22.4, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{25}H_{23}N_3O_2$ ($[M+H]^+$): 398.1863, found 398.1864.



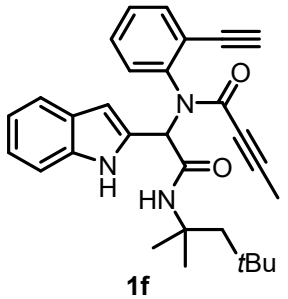
1e

1e was obtained as a brown solid. Yield 85 %. Melting point 215 – 217 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.74 (s), 9.08 (s), 1H], 7.59 – 7.47 (m, 2H), 7.46 – 7.34 (m, 2H), 7.34 – 7.27 (m, 1H), 7.25 – 6.99 (m, 3H), [6.50 (s), 5.73 (s), 1H], [6.49 – 6.47 (m), 6.42 – 6.41 (m), 1H], [5.76 (s), 5.33 (s), 1H], 3.89 – 3.71 (m, 1H), [3.29 (s), 2.55 (s), 1H], 1.99 – 1.75 (m, 2H), [1.71 (s), 1.70 (s), 3H], 1.61 – 1.52 (m, 2H), 1.42 – 0.97 (m, 6H). Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 165.9, 156.2, 155.4, 144.4, 142.1, 136.8, 136.6, 133.4, 133.1, 132.6, 130.6, 130.1, 129.7, 129.5, 128.8, 128.7, 127.4, 127.2, 123.2, 123.0, 122.8, 122.5, 120.8, 120.7, 119.9, 119.7, 111.7, 111.4, 105.7, 105.5, 91.5, 91.1, 82.7, 81.5, 80.8, 79.3, 73.9, 63.4, 60.2, 49.3, 49.2, 33.0, 32.7, 25.7, 25.5, 25.0, 24.9, 4.1. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{28}H_{27}N_3O_2$ ($[M+H]^+$): 438.2176, found 438.2180.



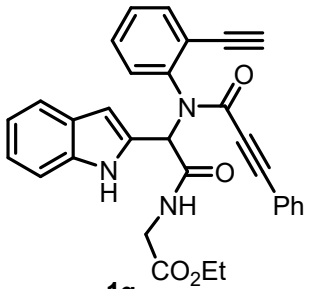
1f

1f was obtained as a yellow solid. Yield 58%. Melting point 109 – 101°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.77 (s), 9.07 (s), 1H], 7.72 – 7.68 (m, 1H), 7.57 – 7.53 (m, 1H), 7.49 – 7.38 (m, 2H), 7.37 – 7.26 (m, 2H), 7.21 – 7.14 (m, 1H), 7.11 – 6.98 (m, 1H), 6.43 – 6.42 (m, 1H), [6.41 (s), 5.75 (s), 1H], [5.86 (s), 5.11 (s), 1H], [3.24 (s), 2.47 (s), 1H], [1.83 – 1.71 (m), 1.62 – 1.52 (m), 2H], [1.69 (s) 1.69 (s), 3H], [1.46 (d, J = 3.3 Hz), 1.39 (d, J = 5.0 Hz), 6H], [0.96 (s,), 0.82 (s), 9H]. Mixture of rotamers (~7:3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 165.2, 156.2, 155.3, 144.9, 141.7, 136.8, 136.4, 133.3, 133.0, 133.0, 130.3, 130.1, 130.1, 129.4, 129.4, 128.6, 128.6, 127.3, 127.1, 123.3, 123.1, 122.7, 122.3, 120.7, 119.8, 119.5, 111.5, 111.2, 105.9, 105.4, 91.5, 90.9, 82.5, 81.4, 80.6, 79.2, 74.0, 73.9, 65.1, 59.9, 55.9, 52.8, 52.1, 31.5, 31.5, 31.3, 28.9, 28.9, 28.5, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{30}H_{33}N_3O_2$ ($[M+H]^+$): 468.2646, found 468.2633.



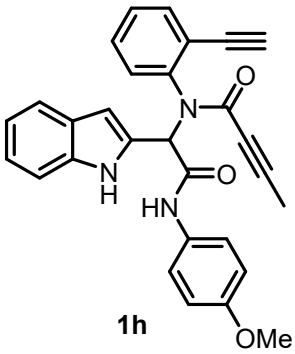
1g

1g was obtained as a brown solid. Yield 78 %. Melting point 207 – 209 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.80 (s), 9.14 (s), 1H], [7.69 – 7.63 (m), 7.54 – 7.52 (m), 1H], [7.61 – 7.56 (m), 7.52 – 7.50 (m), 1H], 7.50 – 7.26 (m, 5H), 7.25 – 7.00 (m, 6H), [6.57 – 6.54 (m), 6.50 – 6.46 (m), 1H], 6.43 – 6.37 (m, 1H), [5.94 (s), 5.48 (s), 1H], 4.26 – 4.16 (m, 2H), 4.16 – 4.12 (m, 1H), [4.12 – 4.06 (m), 4.01 – 3.89 (m), 1H], [3.44 (s), 2.60 (s), 1H], 1.30 – 1.18 (m, 3H). Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 169.3, 168.0, 167.1, 156.2, 155.6, 144.4, 142.1, 136.9, 136.8, 133.5, 133.2, 132.7, 131.9, 130.4, 130.4, 130.3, 130.2, 129.8, 129.6, 129.0, 129.0, 128.5, 128.5, 127.3, 127.2, 123.4, 123.2, 123.0, 122.7, 120.9, 120.8, 120.1, 120.0, 120.0, 119.8, 111.7, 111.5, 106.0, 105.9, 92.5, 92.1, 83.5, 82.3, 81.8, 80.4, 79.2, 63.4, 61.7, 60.3, 42,0 41.9, 14.2. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{31}H_{25}N_3O_4$ ([M+H]+): 504.1918, found 504.1918.



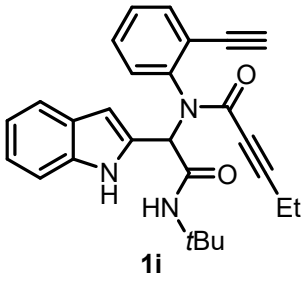
1h

1h was obtained as a brown solid. Yield 30 %. Melting point 176 – 178 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.72 (s), 9.08 (s), 1H], [8.45 (s), 7.82 (s), 1H], 7.57 – 7.53 (m, 1H), 7.47 – 7.42 (m, 1H), 7.38 – 7.34 (m, 1H), 7.33 – 7.30 (m, 1H), 7.29 – 7.24 (m, 2H), 7.23 – 7.21 (m, 1H), 7.19 – 7.13 (m, 1H), 7.10 – 6.95 (m, 2H), 6.78 – 6.74 (m, 2H), [6.55 – 6.53 (m), 6.41 – 6.40 (m), 1H], [5.90 (s), 5.72 (s), 1H], [3.71 (s), 3.70 (s), 3H], [3.26 (s), 2.50 (s), 1H], 1.65 (s, 3H). Mixture of rotamers (~7:3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.1, 156.8, 156.2, 155.6, 143.2, 142.1, 136.8, 136.7, 133.5, 133.2, 131.6, 130.6, 130.5, 130.2, 130.2, 130.0, 129.8, 129.6, 128.9, 128.9, 127.3, 127.2, 123.4, 123.0, 122.7, 122.4, 122.2, 120.9, 120.8, 120.1, 119.8, 114.2, 114.1, 111.8, 111.5, 106.0, 105.8, 92.0, 91.7, 82.9, 81.7, 80.8, 79.3, 73.8, 62.1, 61.0, 55.6, 4.1. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{29}H_{23}N_3O_3$ ($[M+H]^+$): 462.1812, found 462.1815.



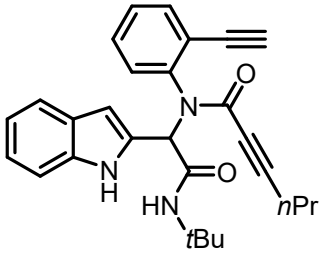
1i

1i was obtained as a brown solid. Yield 25 %. Melting point 171 – 173 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.75 (s), 9.06 (s), 1H] 7.59 – 7.55 (m, 1H), 7.50 – 7.42 (m, 1H), 7.41 – 7.33 (m, 2H), 7.32 – 7.26 (m, 1H), 7.25 – 7.19 (m, 1H), 7.19 – 6.98 (m, 2H), [6.48 (s), 5.74 (s), 1H], [6.47 – 6.46 (m), 6.42 – 6.41 (m), 1H], [5.80 (s), 5.30 (s), 1H], [3.26 (s), 2.54 (s), 1H], 2.08 – 1.98 (m, 2H), [1.40 (s), 1.30 (s), 9H], 0.84 – 0.79 (m, 3H). Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 165.9, 156.2, 155.4, 144.5, 142.1, 136.7, 136.5, 133.3, 133.0, 132.9, 130.5, 130.3, 130.0, 129.5, 129.5, 128.6, 128.6, 127.4, 127.2, 123.3, 123.2, 122.7, 122.4, 120.8, 120.7, 119.9, 119.6, 111.7, 111.3, 105.8, 105.4, 96.6, 96.2, 82.5, 81.5, 80.8, 79.4, 74.2, 74.1, 63.9, 60.3, 52.1, 52.0, 28.7, 28.7, 12.5, 12.5, 12.5, 12.5. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ($[M+H]^+$): 426.2176, found 426.2162.



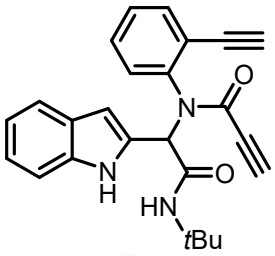
1j

1j was obtained as a brown solid. Yield 67 %. Melting point 127 – 129 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.74 (s), 9.04 (s), 1H], 7.60 – 7.55 (m, 1H), 7.50 – 7.35 (m, 3H), 7.34 – 7.27 (m, 1H), 7.25 – 7.11 (m, 2H), 7.11 – 6.99 (m, 1H), [6.48 (s), 5.73 (s), 1H], [6.47 – 6.46 (m), 6.42 – 6.40 (m), 1H], [5.79 (s), 5.29 (s), 1H], [3.26 (s), 2.54 (s), 1H], 2.07 – 2.00 (m, 2H), [1.40 (s), 1.30 (s), 9H], 1.24 – 1.16 (m, 2H), 0.68 – 0.62 (m, 3H). Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 165.9, 156.2, 155.4, 144.6, 142.1, 136.8, 136.5, 133.3, 133.1, 133.0, 130.5, 130.3, 130.0, 129.6, 129.5, 128.7, 128.6, 127.4, 127.2, 123.3, 123.3, 122.7, 122.4, 120.8, 120.7, 119.9, 119.6, 111.7, 111.3, 105.8, 105.4, 95.4, 95.1, 82.5, 81.5, 80.8, 79.4, 75.0, 74.9, 63.9, 60.3, 52.1, 52.0, 28.7, 28.7, 21.0, 21.0, 20.8, 13.2. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{28}H_{29}N_3O_2$ ($[M+H]^+$): 440.2333, found 440.2331.



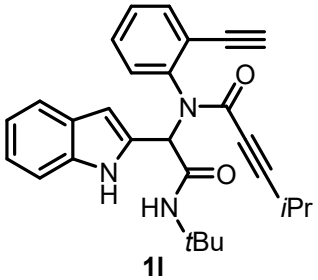
1k

1k was obtained as a yellow solid. Yield 40 %. Melting point 132 – 134 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.64 (s), 8.97 (s), 1H], 7.59 – 7.53 (m, 1H), 7.53 – 7.46 (m, 1H), 7.40 – 7.26 (m, 3H), 7.24 – 7.12 (m, 2H), 7.12 – 6.99 (m, 1H), [6.50 – 6.48 (m), 6.43 – 6.41 (m), 1H], [6.35 (s), 5.74 (s), 1H], [5.89 (s), 5.33 (s), 1H], [3.27 (s), 2.81 (s), 1H], [2.79 (s), 2.58 (s), 1H], [1.40 (s), 1.31 (s), 9H]. Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 165.5, 154.8, 154.0, 143.6, 141.0, 136.8, 136.5, 133.3, 133.3, 132.3, 130.4, 130.2, 129.6, 129.4, 129.1, 129.0, 127.3, 127.2, 123.4, 123.3, 122.9, 122.6, 120.8, 120.8, 120.0, 119.7, 111.7, 111.3, 106.1, 105.8, 82.8, 81.9, 80.5, 80.3, 79.9, 79.2, 76.1, 76.0, 64.0, 60.1, 52.2, 52.1, 28.7. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{25}H_{23}N_3O_2$ ($[M+H]^+$): 398.1863, found 398.1855.



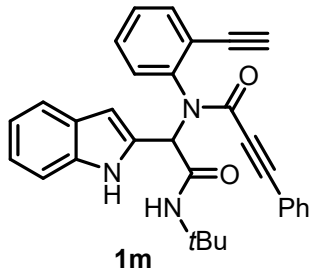
1l

1l was obtained as a brown solid. Yield 24 %. Melting point 120 – 122 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.75 (s) 9.07 (s), 1H], 7.59 – 7.55 (m, 1H), 7.50 – 7.43 (m, 1H), 7.43 – 7.36 (m, 1H), 7.36 – 7.26 (m, 2H), 7.25 – 7.11 (m, 2H), 7.11 – 6.99 (m, 1H), [6.49 (s), 5.75 (s), 1H], [6.48 – 6.46 (m), 6.43 – 6.41 (m), 1H] [5.80 (s), 5.31 (s), 1H], [3.25 (s), 2.54 (s), 1H], 2.42 – 2.31 (m, 1H), [1.40 (s), 1.30 (s), 9H], 0.87 – 0.83 (m, 6H). Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 165.9, 156.2, 155.4, 144.6, 142.2, 136.8, 136.5, 133.2, 133.0, 132.9, 130.6, 130.3, 130.0, 129.5, 128.6, 128.5, 127.4, 127.2, 123.4, 123.3, 122.7, 122.4, 120.8, 120.7, 119.9, 119.6, 111.7, 111.4, 105.8, 105.4, 100.1, 99.7, 82.5, 81.4, 80.8, 79.4, 74.1, 74.0, 63.8, 60.3, 52.1, 52.0, 28.7, 28.7, 21.5, 20.5, 20.5. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{28}H_{29}N_3O_2$ ($[M+H]^+$): 440.2333, found 440.2319.



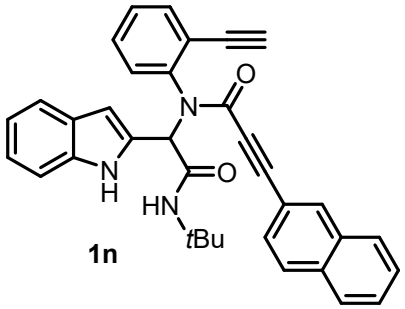
1m

1m was obtained as a yellow solid. Yield 45 %. Melting point 175 – 177 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.81 (s), 9.20 (s), 1H] 7.69 – 7.47 (m, 3H), 7.44 – 7.26 (m, 4H), 7.26 – 7.19 (m, 3H), 7.14 – 7.09 (m, 1H), 7.09 – 7.06 (m, 1H), 7.06 – 7.00 (m, 1H), [6.54 – 6.52 (m), 6.47 – 6.46 (m), 1H], [6.55 (s), 5.85 (s), 1H], [5.99 (s), 5.45 (s), 1H], [3.27 (s), 2.61 (s), 1H], [1.43 (s,), 1.34 (s), 9H]. Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 165.8, 156.1, 155.3, 144.3, 141.8, 136.8, 136.5, 133.2, 133.1, 132.8, 132.7, 132.6, 130.6, 130.3, 130.3, 130.2, 130.1, 129.6, 129.6, 128.8, 128.8, 128.4, 128.4, 127.4, 127.2, 123.6, 123.5, 122.7, 122.4, 120.8, 120.7, 120.1, 120.1, 119.9, 119.6, 111.7, 111.4, 105.8, 105.5, 92.1, 91.6, 82.7, 82.4, 82.3, 81.8, 80.6, 79.3, 63.7, 60.1, 52.1, 52.0, 28.7, 28.7. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{31}H_{27}N_3O_2$ ($[M+H]^+$): 474.2176, found 474.2175.



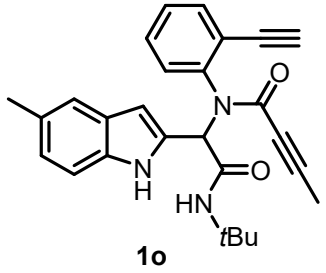
1n

1n was obtained as a yellow solid. Yield 49 %. Melting point 169 – 171 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.88 (s), 9.29 (s), 1H], 7.75 – 7.66 (m, 3H), 7.65 – 7.50 (m, 4H), 7.49 – 7.41 (m, 4H), 7.40 – 7.31 (m, 1H), [7.30 – 7.27 (m), 7.25 – 7.22 (m), 1H], 7.16 – 7.12 (m, 1H), 7.06 – 7.02 (m, 1H), [6.62 (s), 5.92 (s), 1H], [6.57 (d, J = 2.0 Hz), 6.50 (d, J = 2.0 Hz), 1H] ,[6.06 (s), 5.51 (s), 1H], [3.30 (s), 2.66 (s), 1H], [1.46 (s), 1.37 (s), 9H]. Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 165.8, 156.1, 155.3, 144.4, 141.9, 136.8, 136.5, 133.8, 133.7, 133.6, 133.3, 133.2, 132.8, 132.5, 130.6, 130.3, 130.2, 129.7, 129.7, 128.9, 128.8, 128.2, 128.2, 128.1, 128.1, 128.1, 127.8, 127.8, 127.8, 127.4, 127.2, 126.9, 126.9, 123.6, 123.5, 122.8, 122.5, 120.8, 120.7, 119.9, 119.6, 117.3, 117.2, 111.7, 111.4, 105.9, 105.5, 92.7, 92.2, 82.8, 82.7, 82.6, 81.8, 80.7, 79.4, 63.8, 60.3, 52.2, 52.1, 28.7, 28.7. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{35}H_{29}N_3O_2$ ([M+H]$^+$): 524.2333, found 524.2313.



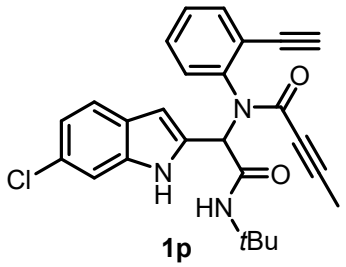
1o

1o was obtained as a yellow solid. Yield 73 %. Melting point 160 – 162 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.63 (s), 8.91 (s), 1H], [7.61 – 7.55 (m), 7.44 – 7.41 (m), 1H], [7.48 – 7.44 (m), 7.39 – 7.36 (m), 1H], 7.36 – 7.33 (m, 1H), 7.32 – 7.24 (m, 2H), 7.21 – 7.06 (m, 1H), [7.05 – 7.00 (m), 6.95 – 6.84 (m), 1H], [6.41 (s), 5.72 (s), 1H], [6.39 – 6.35 (m), 6.33 – 6.31 (m), 1H], [5.79 (s), 5.24 (s), 1H], [3.26 (s), 2.55 (s), 1H], [2.44 (s), 2.37 (s), 3H], 1.69 (s, 3H), [1.39 (s), 1.30 (s), 9H]. Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 165.9, 156.1, 155.3, 144.5, 141.8, 135.1, 134.9, 133.3, 133.1, 132.9, 130.4, 130.3, 130.1, 129.5, 129.4, 129.0, 128.7, 128.7, 128.6, 127.7, 127.4, 124.4, 124.1, 123.2, 120.3, 120.2, 111.3, 111.0, 105.3, 104.9, 91.3, 90.9, 82.5, 81.5, 80.7, 79.4, 74.0, 64.1, 60.3, 52.0, 28.7, 28.7, 21.6, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ([M+H]$^+$): 426.2176, found 426.2174.



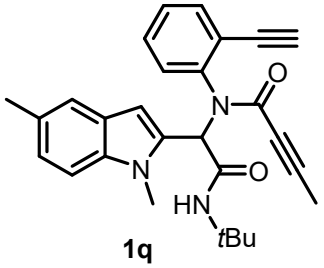
1p

1p was obtained as a yellow solid. Yield 20 %. Melting point 200 – 202 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.53 (s, 1H), 7.91 (s, 1H), 7.85 – 7.81 (m, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.22 – 7.19 (m, 1H), 7.13 – 7.08 (m, 1H), 6.85 – 6.81 (m, 1H), 6.18 (d, J = 2.0 Hz, 1H), 6.04 (s, 1H), 4.29 (s, 1H), 1.66 (s, 3H), 1.26 (s, 9H). Mixture of rotamers (~10:1).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.0, 153.9, 141.6, 137.3, 132.6, 132.3, 132.0, 129.5, 128.9, 126.4, 126.0, 124.4, 121.8, 119.6, 111.8, 104.7, 89.6, 85.3, 81.1, 75.0, 59.5, 51.2, 29.1, 3.7. Major rotamer.

HRMS (ESI, m/z) calcd for $C_{26}H_{24}ClN_3O_2$ ([M+H]$^+$): 446.1630, found 446.1638.



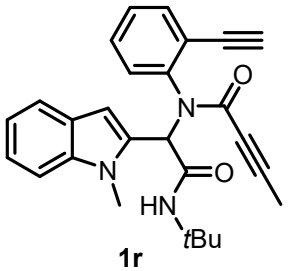
1q

1q was obtained as a yellow solid. Yield 35 %. Melting point 243 – 245 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [7.93 – 7.89 (m), 7.54 – 7.49 (m), 1H], 7.34 – 7.28 (m, 1H), 7.25 – 7.18 (m, 2H), 7.16 – 7.09 (m, 2H), 7.08 – 6.99 (m, 1H), [6.69 (d, J = 6.9 Hz), 6.63 (d, J = 4.5 Hz), 1H], [6.18 (s), 5.90 (s), 1H], [6.04 (s), 5.98 (s), 1H], [3.73 (s), 3.61 (s), 3H], [3.00 (s), 2.93 (s), 1H], [2.43 (s), 2.37 (s), 3H], [1.68 (s), 1.67 (s), 3H], [1.36 (s), 1.32 (s), 9H]. Mixture of rotamers (~4:1).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 165.3, 155.2, 154.9, 141.8, 140.3, 136.2, 136.0, 133.5, 133.1, 132.9, 131.6, 130.9, 129.2, 128.8, 128.3, 127.7, 127.4, 124.3, 124.0, 124.0, 124.0, 120.9, 120.6, 109.2, 105.0, 104.8, 90.3, 82.1, 81.0, 80.3, 74.0, 58.3, 56.3, 52.0, 51.8, 30.5, 30.1, 28.7, 28.5, 21.4, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{28}H_{29}N_3O_2$ ([M+H]$^+$): 440.2333, found 440.2334.



1r

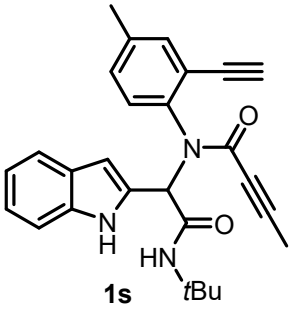
1r was obtained as a yellow solid. Yield 44 %. Melting point 202 – 204°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [7.91 – 7.86 (m), 7.53 – 7.49 (m), 1H], [7.57 – 7.54 (m),7.43 – 7.39 (m), 1H], 7.33 –

7.28 (m, 1H), 7.26 – 7.18 (m, 3H), 7.17 – 7.11 (m, 1H), [7.11 – 7.07 (m), 7.05 – 7.00 (m), 1H], [6.73 (s), 6.63 (s), 1H], [6.14 (s), 6.09 (s), 1H], [6.05 (s), 5.88 (s), 1H], [3.76 (s), 3.64 (s), 3H], [3.00 (s), 2.93 (s), 1H], [1.70 (s), 1.68 (s), 3H], [1.37 (s), 1.31 (s), 9H]. Mixture of rotamers (~4:1).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 155.3, 140.3, 137.5, 132.9, 131.6, 130.9, 129.3, 128.3, 127.2, 124.0, 122.4, 121.1, 119.6, 109.6, 105.6, 90.4, 81.0, 80.3, 74.0, 56.3, 52.1, 30.5, 28.8, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ([M+H]$^+$): 426.2176, found 426.2173.



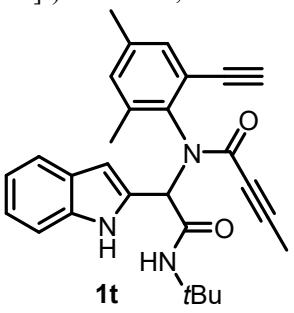
1s

1s was obtained as a brown solid. Yield 40 %. Melting point 98 – 100 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.74 (s), 9.10 (s), 1H], [7.58 – 7.55 (m), 7.50 – 7.47 (m), 1H] 7.42 – 7.35 (m, 1H), 7.26 – 6.99 (m, 5H), [6.51 (s), 5.28 (s), 1H], [6.47 – 6.44 (m), 6.40 – 6.38 (m),1H], 5.75 (s, 1H), [3.22 (s), 2.52 (s), 1H], [2.32 (s), 2.24 (s), 3H], 1.71 (s, 3H), [1.40 (s), 1.30 (s), 9H]. Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 165.9, 156.2, 155.5, 141.8, 139.3, 138.7, 138.6, 136.7, 136.5, 133.8, 133.5, 133.0, 130.9, 130.8, 130.4, 129.9, 129.0, 127.4, 127.2, 122.7, 122.6, 122.5, 122.3, 120.7, 120.6, 119.8, 119.5, 111.6, 111.4, 105.6, 105.3, 91.2, 90.9, 82.1, 81.0, 80.9, 79.6, 74.1, 73.9, 63.9, 60.5, 52.0, 51.9, 28.7, 28.7, 21.0, 4.1. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ([M+H]$^+$): 426.2176, found 426.2162.



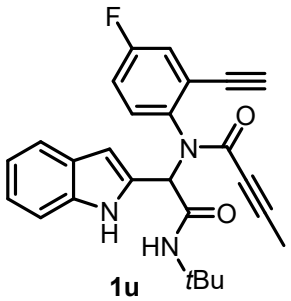
1t

1t was obtained as a brown solid. Yield 48 %. Melting point 108 – 110 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.55 – 7.52 (m, 1H), 7.37 – 7.33 (m, 1H), 7.21 – 7.17 (m, 1H), 7.10 – 7.07 (m, 2H), 7.06 – 7.03 (m, 1H), 6.38 – 6.35 (m, 1H), 5.79 (s, 1H), 4.91 (s, 1H), 2.53 (s, 3H), 2.27 (s, 3H), 2.20 (s, 1H), 1.70 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 156.5, 139.4, 138.5, 137.8, 137.0, 132.9, 132.9, 131.7, 127.5, 123.7, 122.7, 120.8, 119.7, 111.4, 105.8, 89.6, 79.5, 79.5, 73.9, 63.8, 51.8, 28.7, 20.9, 18.3, 4.0.

HRMS (ESI, m/z) calcd for $C_{28}H_{29}N_3O_2$ ([M+H]$^+$): 440.2333, found 440.2319.



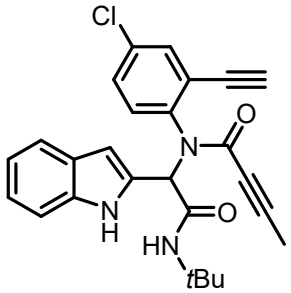
1u

1u was obtained as a brown solid. Yield 33%. Melting point 212 – 214 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.70 (s), 9.03 (s), 1H], 7.59 – 7.52 (m, 1H), 7.52 – 7.46 (m, 1H), 7.40 – 7.33 (m, 1H), 7.24 – 7.18 (m, 1H), 7.16 – 7.11 (m, 1H), 7.11 – 7.03 (m, 1H), 7.02 – 6.94 (m, 1H), [6.49 – 6.46 (m), 6.41 – 6.40 (m), 1H], [6.36 (s), 5.75 (s), 1H], [5.92 (s), 5.28 (s), 1H], [3.26 (s), 2.59 (s), 1H], 1.72 (s, 3H), [1.39 (s), 1.30 (s), 9H]. Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 165.8, 162.9 (d, J = 10.9 Hz), 160.4 (d, J = 11.0 Hz), 156.1, 155.2, 140.6 (d, J = 3.3 Hz), 137.8 (d, J = 3.4 Hz), 136.7, 136.4, 132.6, 132.4, 132.3, 131.5, 131.4, 129.7, 127.4, 127.2, 125.4 (d, J = 10.3 Hz), 125.1 (d, J = 10.4 Hz), 122.8, 122.6, 120.8, 120.7, 120.0, 119.8, 119.8, 119.6, 119.5, 117.3 (d, J = 22.7 Hz), 116.7 (d, J = 22.4 Hz), 111.7, 111.3, 106.0, 105.5, 91.8, 91.2, 83.2, 82.5, 79.5, 78.4, 73.9, 73.8, 63.8, 59.6, 52.1, 52.0, 28.7, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{26}H_{24}FN_3O_2$ ($[M+H]^+$): 430.1925, found 430.1909.



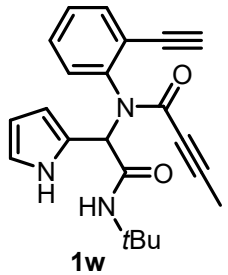
1v

1v was obtained as a brown solid. Yield 40 %. Melting point 145 – 147 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.68 (s), 9.00 (s), 1H], 7.64 – 7.29 (m, 4H), 7.25 – 6.99 j(m, 3H), [6.52 – 6.44 (m), 6.42 – 6.38 (m), 1H], [6.30 (s), 5.70 (s), 1H], [5.88 (s), 5.25 (s), 1H], [3.27 (s), 2.60 (s), 1H], [1.74 (s), 1.74 (s), 3H], [1.39 (s), 1.30 (s), 9H]. Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 165.7, 155.9, 155.1, 142.9, 140.2, 136.8, 136.5, 134.4, 132.9, 132.8, 132.6, 131.7, 130.8, 130.3, 129.8, 129.8, 127.4, 127.2, 125.0, 124.8, 122.9, 122.6, 120.8, 120.8, 120.0, 119.8, 111.7, 111.4, 106.0, 105.6, 91.9, 91.4, 83.5, 82.7, 79.4, 78.2, 73.9, 73.8, 63.8, 59.7, 53.6, 52.2, 52.1, 28.7, 4.1, 4.1. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{26}H_{24}ClN_3O_2$ ($[M+H]^+$): 446.1630, found 446.1636.



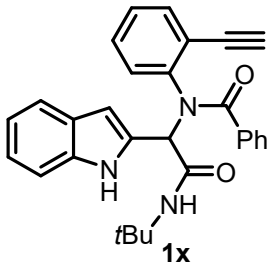
1w

1w was obtained as a yellow solid. Yield 52 %. Melting point 110 – 112 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.68 (s), 9.03 (s), 1H], 7.48 – 7.44 (m, 1H), 7.41 – 7.33 (m, 1H), 7.32 – 7.28 (m, 1H), 7.27 – 7.17 (m, 1H), [6.74 – 6.71 (m), 6.52 – 6.49 (m), 1H], [6.38 (s), 5.72 (s), 1H], [6.11 – 6.09 (m), 6.07 – 6.05 (m), 1H], [6.09 – 6.07 (m), 5.93 – 5.90 (m), 1H], [5.82 (s), 5.19 (s), 1H], [3.20 (s), 2.86 (s), 1H], 1.67 (s, 3H), [1.37 (s), 1.29 (s), 9H]. Mixture of rotamers (~9:8).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 166.8, 155.7, 155.0, 144.1, 141.7, 133.0, 132.9, 130.4, 129.8, 129.4, 129.3, 128.4, 128.4, 125.5, 123.8, 123.2, 122.6, 119.2, 119.0, 111.8, 111.2, 107.9, 107.7, 90.8, 90.3, 82.0, 81.3, 80.6, 79.6, 74.0, 74.0, 62.8, 58.6, 51.8, 51.6, 28.7, 28.7, 4.0. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{22}H_{23}N_3O_2$ ($[M+Na]^+$): 384.1682, found 384.1680.



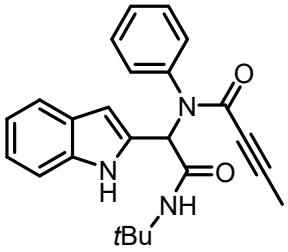
1x

1x was obtained as a brown solid. Yield 30 %. Melting point 76 – 78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ [10.08 (s), 9.44 (s), 1H], 7.68 – 7.56 (m, 1H), 7.51 – 7.41 (m, 3H), 7.40 – 7.27 (m, 2H), 7.26 – 7.04 (m, 6H), 7.03 – 6.91 (m, 1H), 6.53 – 6.42 (m, 1H), [6.30 (s), 5.78 (s), 1H], [5.80 (s), 5.41 (s), 1H], [3.46 (s),2.67 (s), 1H], [1.41 (s), 1.33 (s), 9H]. Mixture of rotamers (~3:2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 172.3, 166.9, 166.3, 145.9, 143.9, 136.8, 136.6, 135.5, 135.4, 133.8, 133.3, 133.2, 131.5, 130.7, 130.5, 130.2, 130.1, 129.6, 129.2, 128.9, 128.6, 127.9, 127.8, 127.5, 127.2, 122.7, 122.5, 122.4, 121.3, 120.8, 120.6, 119.8, 119.5, 111.7, 111.5, 105.6, 105.6, 83.8, 81.9, 81.0, 79.8, 65.9, 62.5, 51.9, 28.8. Mixture of rotamers.

HRMS (ESI, m/z) calcd for $C_{29}H_{27}N_3O_2$ ($[M+H]^+$): 450.2176, found 450.2172.



1y

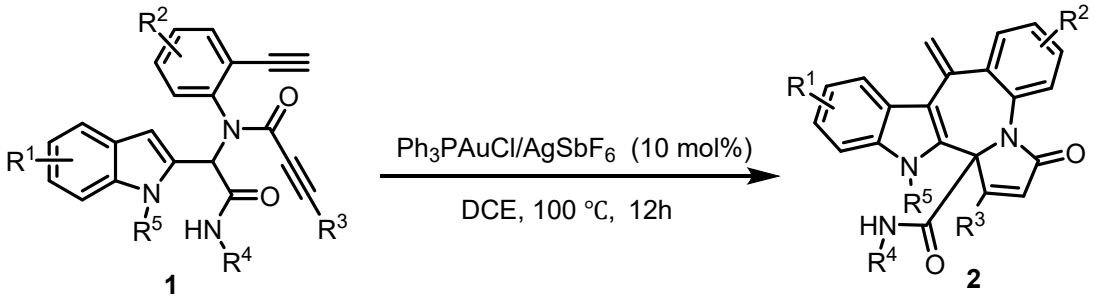
1y was obtained as a brown solid. Yield 42 %. Melting point 178 – 180 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.61 – 7.54 (m, 1H), 7.34 – 7.26 (m, 4H), 7.26 – 7.16 (m, 3H), 7.13 – 7.07 (m, 1H), 6.62 – 6.43 (m, 1H), 5.90 (s, 1H), 5.61 (s, 1H), 1.70 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 155.5, 141.4, 136.6, 132.0, 129.0, 128.8, 128.5, 127.1, 122.7, 120.6, 119.9, 111.7, 105.0, 92.3, 73.8, 61.8, 51.9, 28.6, 3.9.

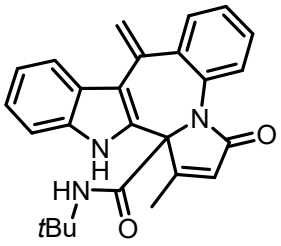
HRMS (ESI, m/z) calcd for $C_{24}H_{25}N_3O_2$ ([M+H]$^+$): 388.2020, found 388.2016.

4. General procedure for $Ph_3PAuCl/AgSbF_6$ catalyzed intramolecular cascade reaction



To a glass vial, Ph_3PAuCl (10 mol%) and $AgSbF_6$ (10 mol%) were loaded along with dry DCE (2 mL). Ugi product **1** (0.1 mmol) was added. The reaction vial was evacuated, backfilled with argon and was heated in oil bath at 100 °C for 12 hours. After completion, the mixture was loaded to silica gel column chromatography (eluent: EtOAc/*n*-heptane 1:1 v/v) to afford desired product **2.**

5. Characterization of products



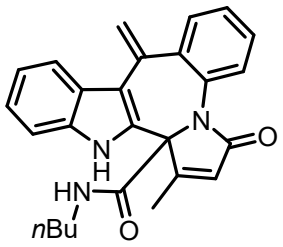
2a

2a was obtained as a yellow solid. Yield 88 %. Melting point 216 – 218 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.83 – 7.79 (m, 1H), 7.59 – 7.56 (m, 1H), 7.45 – 7.41 (m, 1H), 7.41 – 7.37 (m, 2H), 7.29 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.14 (m, 1H), 6.55 (s, 1H), 6.07 – 6.05 (m, 1H), 5.67 (dd, *J* = 8.3, 1.4 Hz, 2H), 2.31 (d, J = 1.6 Hz, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 167.2, 161.6, 145.0, 139.2, 136.5, 133.0, 129.9, 129.4, 129.2, 128.5, 128.2, 125.9, 123.1, 121.9, 120.5, 119.9, 117.7, 114.3, 111.6, 75.8, 52.5, 28.6, 15.0.

HRMS (ESI, m/z) calcd for $C_{26}H_{25}N_3O_2$ ([M+H]$^+$): 412.2020, found 412.2013.



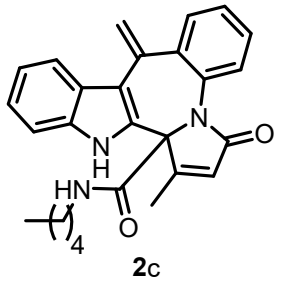
2b

2b was obtained as a brown solid. Yield 92 %. Melting point 188 – 200 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.47 – 7.31 (m, 4H), 7.26 – 7.13 (m, 2H), 7.05 – 6.90 (m, 1H), 6.18 – 5.92 (m, 1H), 5.68 (dd, *J* = 9.5, 1.4 Hz, 2H), 3.44 – 3.12 (m, 2H), 2.31 (d, *J* = 1.6 Hz, 3H), 1.55 – 1.30 (m, 2H), 1.28 – 1.18 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 168.0, 161.4, 144.9, 139.3, 136.6, 133.0, 130.1, 129.3, 129.0, 128.5, 128.1, 125.9, 123.1, 121.9, 120.5, 119.9, 117.6, 114.4, 111.6, 75.7, 40.0, 31.3, 20.0, 15.0, 13.7.

HRMS (ESI, m/z) calcd for $C_{26}H_{25}N_3O_2$ ([M+H]$^+$): 412.2020, found 412.2011.



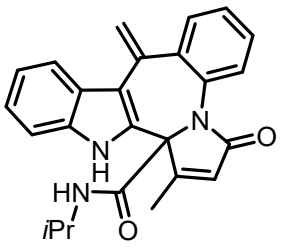
2c

2c was obtained as a brown solid. Yield 82 %. Melting point 230 – 232 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.85 – 7.80 (m, 1H), 7.59 – 7.55 (m, 1H), 7.49 – 7.27 (m, 4H), 7.26 – 7.21 (m, 1H), 7.20 – 7.15 (m, 1H), 7.13 (d, *J* = 5.9 Hz, 1H), 6.03 – 6.01 (m, 1H), 5.69 (dd, *J* = 10.2, 1.4 Hz, 2H), 3.32 – 3.19 (m, 2H), 2.31 (d, *J* = 1.6 Hz, 3H), 1.51 – 1.43 (m, 2H), 1.30 – 1.27 (m, 2H), 1.25 – 1.19 (m, 2H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 170.0, 161.4, 144.9, 139.4, 136.6, 133.0, 130.3, 129.3, 128.9, 128.5, 128.2, 125.9, 123.1, 121.9, 120.5, 119.8, 117.5, 114.4, 111.6, 75.8, 40.3, 29.0, 28.9, 22.3, 15.0, 14.1.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ([M+H]$^+$): 426.2176, found 426.2165.



2d

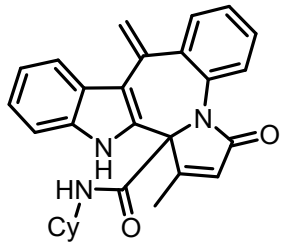
2d was obtained as a brown solid. Yield 84%. Melting point 252 – 254 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.85 – 7.78 (m, 1H), 7.60 – 7.55 (m, 1H), 7.42 – 7.38 (m, 3H), 7.37 – 7.34

(m, 1H), 7.25 – 7.21 (m, 1H), 7.19 – 7.15 (m, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.06 – 6.02 (m, 1H), 5.68 (dd, *J* = 9.3, 1.4 Hz, 2H), 4.09 – 3.95 (m, 1H), 2.31 (d, *J* = 1.6 Hz, 3H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 167.1, 161.3, 145.0, 139.3, 136.6, 133.0, 130.0, 129.3, 129.1, 128.5, 128.1, 125.9, 123.1, 121.9, 120.5, 119.8, 117.6, 114.4, 111.6, 75.6, 42.6, 22.3, 14.9.

HRMS (ESI, m/z) calcd for $C_{25}H_{23}N_3O_2$ ([M+H]$^+$): 398.1863, found 398.1852.



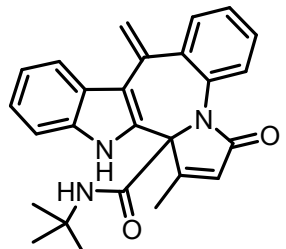
2e

2e was obtained as a yellow solid. Yield 98 %. Melting point 186 – 188 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.85 – 7.79 (m, 1H), 7.59 – 7.55 (m, 1H), 7.44 – 7.39 (m, 2H), 7.39 – 7.34 (m, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.14 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.06 – 6.03 (m, 1H), 5.68 (dd, *J* = 9.6, 1.4 Hz, 2H), 3.76 – 3.64 (m, 1H), 2.30 (d, *J* = 1.6 Hz, 3H), 1.97 – 1.84 (m, 1H), 1.80 – 1.67 (m, 3H), 1.66 – 1.58 (m, 1H), 1.43 – 1.21 (m, 3H), 1.19 – 1.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 167.0, 161.3, 144.9, 139.2, 136.5, 132.9, 130.0, 129.2, 128.9, 128.4, 128.1, 125.8, 123.0, 121.8, 120.4, 119.7, 117.4, 114.3, 111.5, 75.5, 49.4, 32.5, 25.3, 24.7, 14.9.

HRMS (ESI, m/z) calcd for $C_{28}H_{27}N_3O_2$ ([M+H]$^+$): 438.2176, found 438.2165.



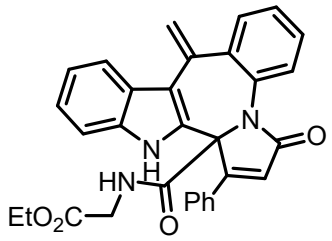
2f

2f was obtained as a yellow solid. Yield 98 %. Melting point 214 – 216 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.85 – 7.80 (m, 1H), 7.60 – 7.55 (m, 1H), 7.47 – 7.42 (m, 1H), 7.42 – 7.37 (m, 2H), 7.34 – 7.31 (m, 1H), 7.26 – 7.21 (m, 1H), 7.20 – 7.15 (m, 1H), 6.58 (s, 1H), 6.08 – 6.05 (m, 1H), 5.67 (dd, *J* = 14.9, 1.4 Hz, 2H), 2.33 (d, *J* = 1.6 Hz, 3H), 1.82 – 1.66 (m, 2H), 1.39 (d, *J* = 3.2 Hz, 6H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.7, 161.2, 144.9, 139.2, 136.5, 133.0, 130.0, 129.4, 129.2, 128.5, 128.2, 125.9, 123.1, 121.9, 120.5, 119.9, 117.7, 114.2, 111.5, 75.9, 56.5, 51.4, 31.4, 29.6, 28.6, 15.2.

HRMS (ESI, m/z) calcd for $C_{30}H_{33}N_3O_2$ ([M+H]$^+$): 468.2646, found 468.2634.



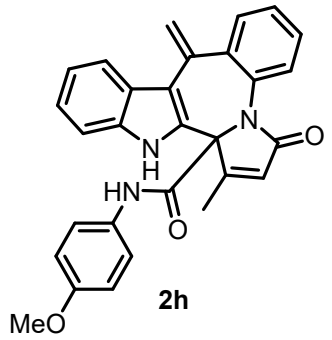
2g

2g was obtained as a brown solid. Yield 80%. Melting point 207 – 209 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.15 (m, 1H), 7.90 – 7.82 (m, 1H), 7.63 – 7.35 (m, 10H), 7.19 – 7.12 (m, 2H), 7.10 – 7.02 (m, 1H), 6.48 (s, 1H), 5.82 (d, *J* = 1.3 Hz, 1H), 5.70 (d, *J* = 1.3 Hz, 1H), 4.23 – 4.13 (m, 2H), 4.09 – 3.98 (m, 1H), 3.87 – 3.72 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 169.2, 167.2, 160.4, 143.2, 139.5, 136.2, 132.6, 132.2, 130.4, 130.1, 129.4, 129.2, 128.8, 128.5, 128.2, 127.4, 125.3, 125.2, 123.4, 120.7, 120.4, 118.4, 114.9, 111.4, 75.7, 61.8, 41.9, 14.2.

HRMS (ESI, m/z) calcd for $C_{31}H_{25}N_3O_4$ ($[M+H]^+$): 504.1918, found 504.1915.



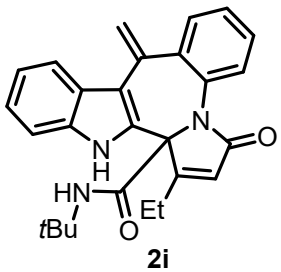
2h

2h was obtained as a yellow solid. Yield 72 %. Melting point 178 – 180 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.84 (s, 1H), 7.86 – 7.82 (m, 1H), 7.62 – 7.58 (m, 1H), 7.53 – 7.50 (m, 1H), 7.41 – 7.37 (m, 5H), 7.25 – 7.16 (m, 2H), 6.86 – 6.82 (m, 2H), 6.11 – 6.05 (m, 1H), 5.75 – 5.68 (m, 2H), 3.79 (s, 3H), 2.33 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 166.2, 161.2, 157.4, 145.1, 139.3, 136.6, 133.0, 130.2, 129.6, 129.5, 129.0, 128.8, 127.8, 125.9, 123.3, 122.4, 122.3, 120.6, 119.9, 117.6, 114.8, 114.4, 111.6, 76.0, 55.6, 15.0.

HRMS (ESI, m/z) calcd for $C_{29}H_{23}N_3O_3$ ($[M+H]^+$): 462.1812, found 462.1801.



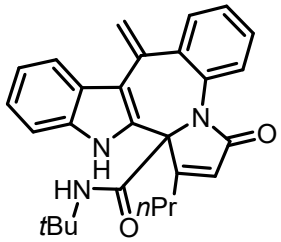
2i

2i was obtained as a brown solid. Yield 87 %. Melting point 258 – 260 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.86 – 7.77 (m, 1H), 7.61 – 7.56 (m, 1H), 7.46 – 7.37 (m, 3H), 7.31 – 7.28 (m, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.14 (m, 1H), 6.59 (s, 1H), 6.09 – 6.05 (m, 1H), 5.69 – 5.66 (m, 2H), 2.79 – 2.56 (m, 2H), 1.35 (s, 9H), 1.19 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 167.6, 167.3, 145.1, 139.3, 136.5, 133.0, 129.9, 129.4, 129.1, 128.5, 128.3, 125.9, 123.1, 120.5, 119.8, 119.5, 117.6, 114.4, 111.5, 75.8, 52.4, 28.6, 21.4, 11.4.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ($[M+H]^+$): 426.2176, found 426.2161.



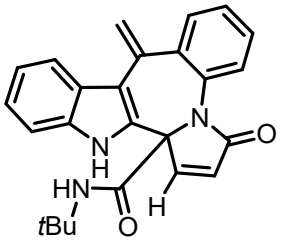
2j

2j was obtained as a brown solid. Yield 77 %. Melting point 266 – 268 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.83 – 7.78 (m, 1H), 7.60 – 7.56 (m, 1H), 7.46 – 7.36 (m, 3H), 7.30 – 7.27 (m, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.14 (m, 1H), 6.59 (s, 1H), 6.07 – 6.05 (m, 1H), 5.69 – 5.65 (m, 2H), 2.71 – 2.51 (m, 2H), 1.65 – 1.56 (m, 2H), 1.35 (s, 9H), 1.00 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 167.3, 166.1, 145.2, 139.3, 136.5, 133.0, 129.9, 129.4, 129.1, 128.5, 128.3, 125.9, 123.0, 120.5, 120.0, 119.8, 117.6, 114.4, 111.5, 75.8, 52.4, 29.9, 28.6, 20.3, 13.8.

HRMS (ESI, m/z) calcd for $C_{28}H_{29}N_3O_2$ ($[M+H]^+$): 440.2333, found 440.2318.



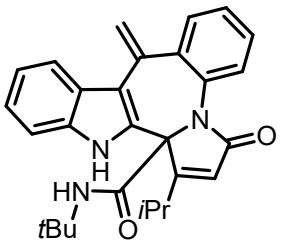
2k

2k was obtained as a yellow solid. Yield 68 %. Melting point 198 – 200 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.87 – 7.83 (m, 1H), 7.67 – 7.63 (m, 1H), 7.61 (d, *J* = 5.8 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.36 (m, 2H), 7.25 – 7.15 (m, 2H), 6.37 (d, *J* = 5.8 Hz, 1H), 6.26 (s, 1H), 5.77 (d, *J* = 1.2 Hz, 1H), 5.62 (d, *J* = 1.2 Hz, 1H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 167.3, 150.5, 143.7, 139.0, 136.8, 132.5, 129.9, 129.5, 129.4, 128.7, 128.7, 125.9, 125.7, 123.3, 120.6, 120.2, 118.6, 112.9, 111.5, 74.4, 52.6, 28.5.

HRMS (ESI, m/z) calcd for $C_{25}H_{23}N_3O_2$ ($[M+H]^+$): 398.1863, found 398.1848.



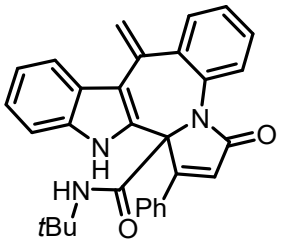
2l

2l was obtained as a yellow solid. Yield 84%. Melting point 268 – 270 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.83 – 7.79 (m, 1H), 7.59 – 7.55 (m, 1H), 7.45 – 7.40 (m, 1H), 7.40 – 7.36 (m, 2H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.24 – 7.14 (m, 2H), 6.61 (s, 1H), 6.14 (d, *J* = 0.7 Hz, 1H), 5.67 (s, 2H), 3.30 – 3.18 (m, 1H), 1.36 (s, 9H), 1.27 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 173.2, 167.0, 145.4, 139.3, 136.5, 133.0, 129.9, 129.4, 129.0, 128.4, 128.2, 126.0, 123.0, 120.4, 119.8, 119.4, 117.5, 114.5, 111.5, 75.3, 52.5, 28.6, 27.2, 23.8.

HRMS (ESI, m/z) calcd for $C_{28}H_{29}N_3O_2$ ($[M+H]^+$): 440.2333, found 440.2323.



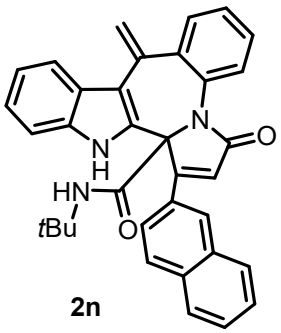
2m

2m was obtained as a yellow solid. Yield 96%. Melting point 182 – 184 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.90 – 7.85 (m, 1H), 7.61 – 7.58 (m, 1H), 7.55 – 7.52 (m, 1H), 7.52 – 7.48 (m, 2H), 7.48 – 7.45 (m, 2H), 7.44 – 7.37 (m, 3H), 7.18 – 7.13 (m, 2H), 7.07 – 7.03 (m, 1H), 6.49 (s, 1H), 5.89 (s, 1H), 5.83 (d, *J* = 1.3 Hz, 1H), 5.66 (d, *J* = 1.3 Hz, 1H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 165.5, 160.1, 143.0, 139.4, 136.2, 133.0, 132.4, 130.5, 129.6, 129.5, 129.2, 128.7, 128.6, 128.1, 127.9, 125.3, 125.3, 123.4, 120.8, 120.5, 118.5, 114.6, 111.3, 76.2, 52.5, 28.4.

HRMS (ESI, m/z) calcd for $C_{31}H_{27}N_3O_2$ ($[M+H]^+$): 474.2176, found 474.2172.



2n

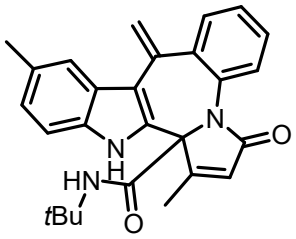
2n was obtained as a yellow solid. Yield 72%. Melting point 184 – 186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.03 – 7.96 (m, 2H), 7.95 – 7.92 (m, 1H), 7.90 – 7.85 (m, 2H), 7.66 – 7.57

(m, 3H), 7.55 – 7.52 (m, 1H), 7.48 – 7.38 (m, 3H), 7.17 – 7.08 (m, 2H), 6.98 – 6.95 (m, 1H), 6.59 (s, 1H), 5.91 (s, 1H), 5.86 (d, *J* = 1.3 Hz, 1H), 5.68 (d, *J* = 1.3 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 165.6, 159.9, 143.0, 139.5, 136.2, 133.9, 133.1, 132.4, 130.2, 129.7, 129.6, 129.2, 128.7, 128.6, 128.6, 128.2, 128.1, 127.8, 127.5, 127.4, 125.8, 125.3, 125.1, 123.4, 120.8, 120.5, 118.6, 114.8, 111.4, 76.3, 52.6, 28.4.

HRMS (ESI, m/z) calcd for $C_{35}H_{29}N_3O_2$ ($[M+H]^+$): 524.2333, found 524.2324.



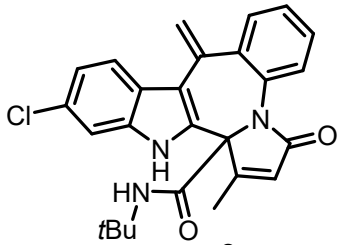
2o

2o was obtained as a brown solid. Yield 80%. Melting point 210 – 212 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.58 (d, *J* = 6.7 Hz, 2H), 7.47 – 7.34 (m, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.10 – 7.01 (m, 1H), 6.56 (s, 1H), 6.05 (s, 1H), 5.66 (d, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 2.35 – 2.25 (m, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 167.2, 161.6, 145.1, 139.3, 134.9, 133.0, 129.8, 129.8, 129.4, 129.1, 128.4, 128.2, 126.1, 124.7, 121.8, 119.4, 117.5, 113.8, 111.2, 75.9, 52.4, 28.6, 21.8, 15.0.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ($[M+H]^+$): 426.2176, found 426.2173.



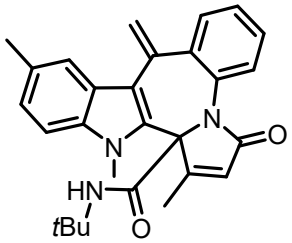
2p

2p was obtained as a brown solid. Yield 68 %. Melting point 166 – 168 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.45 – 7.39 (m, 2H), 7.36 (d, *J* = 1.8 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.14 – 7.10 (m, 1H), 6.56 (s, 1H), 6.08 – 6.05 (m, 1H), 5.67 – 5.61 (m, 2H), 2.29 (d, *J* = 1.6 Hz, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 167.1, 161.3, 144.7, 139.0, 136.8, 133.0, 129.9, 129.5, 129.2, 128.9, 128.9, 128.7, 124.5, 122.0, 121.2, 120.8, 118.0, 114.4, 111.4, 75.7, 52.6, 28.6, 14.9.

HRMS (ESI, m/z) calcd for $C_{29}H_{23}N_3O_3$ ($[M+H]^+$): 446.1630, found 446.1612.



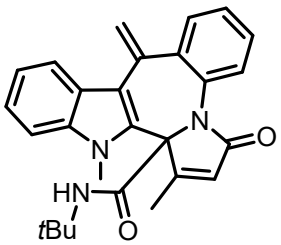
2q

2q was obtained as a brown solid. Yield 50%. Melting point 245 – 247 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.66 (m, 1H), 7.51 – 7.48 (m, 1H), 7.44 – 7.39 (m, 1H), 7.39 – 7.34 (m, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.16 (m, 2H), 6.11 – 6.09 (m, 1H), 5.70 – 5.66 (m, 2H), 4.81 (s, 1H), 3.76 (s, 3H), 2.51 (s, 3H), 2.34 (d, J = 1.6 Hz, 3H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 165.6, 160.3, 144.9, 139.1, 137.5, 132.7, 131.6, 130.6, 130.1, 129.4, 128.4, 127.9, 126.1, 125.3, 125.0, 120.0, 117.8, 116.0, 109.6, 76.4, 52.4, 33.7, 28.4, 21.6, 17.1.

HRMS (ESI, m/z) calcd for $C_{28}H_{29}N_3O_2$ ($[M+H]^+$): 440.2333, found 440.2325.



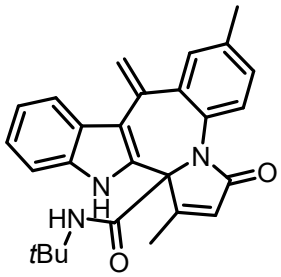
2r

2r was obtained as a brown solid. Yield 48 %. Melting point 268 – 270 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 1H), 7.52 – 7.48 (m, 1H), 7.44 – 7.40 (m, 1H), 7.40 – 7.37 (m, 1H), 7.36 – 7.34 (m, 2H), 7.33 – 7.30 (m, 1H), 7.29 – 7.25 (m, 1H), 6.13 – 6.10 (m, 1H), 5.71 – 5.66 (m, 2H), 4.84 (s, 1H), 3.79 (s, 3H), 2.35 (d, *J* = 1.6 Hz, 3H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 165.5, 160.2, 144.8, 139.1, 139.1, 132.7, 131.6, 130.1, 129.4, 128.5, 128.0, 126.0, 125.1, 123.7, 121.1, 120.5, 117.9, 116.5, 109.8, 76.4, 52.5, 33.7, 28.4, 17.1.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ($[M+H]^+$): 426.2176, found 426.2171.



2s

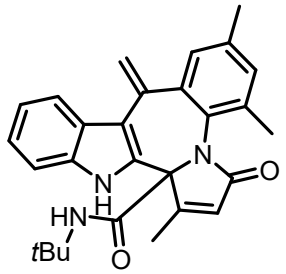
2s was obtained as a brown solid. Yield 80%. Melting point 209 – 211 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.84 – 7.77 (m, 1H), 7.42 – 7.37 (m, 2H), 7.25 – 7.20 (m, 2H), 7.19 – 7.14

(m, 2H), 6.59 (s, 1H), 6.08 – 6.03 (m, 1H), 5.66 (s, 2H), 2.39 (s, 3H), 2.30 (d, *J* = 1.6 Hz, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 167.3, 161.5, 144.7, 139.5, 139.3, 136.5, 130.3, 129.9, 129.6, 129.1, 128.3, 125.9, 123.0, 121.9, 120.4, 119.8, 117.4, 114.3, 111.5, 75.8, 52.4, 28.6, 21.3, 15.0.

HRMS (ESI, m/z) calcd for $C_{27}H_{27}N_3O_2$ ($[M+H]^+$): 426.2176, found 426.2160.



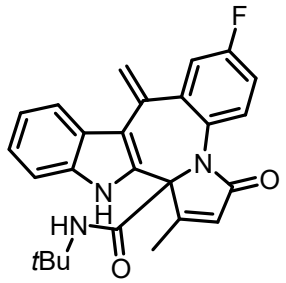
2t

2t was obtained as a brown solid. Yield 90%. Melting point 174 – 176 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.84 – 7.81 (m, 1H), 7.37 – 7.33 (m, 1H), 7.26 – 7.21 (m, 1H), 7.21 – 7.16 (m, 2H), 7.10 – 7.08 (m, 1H), 6.07 – 6.04 (m, 1H), 5.75 (s, 1H), 5.61 (dd, *J* = 15.5, 1.5 Hz, 2H), 2.37 (s, 3H), 2.34 (d, *J* = 1.6 Hz, 3H), 2.33 (s, 3H), 1.19 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 166.6, 161.1, 144.0, 139.8, 139.1, 137.7, 136.7, 131.4, 129.4, 128.6, 127.3, 125.8, 123.3, 122.9, 120.6, 120.1, 117.7, 114.7, 111.5, 76.2, 52.5, 28.4, 21.2, 19.3, 15.9.

HRMS (ESI, m/z) calcd for $C_{28}H_{29}N_3O_2$ ($[M+H]^+$): 440.2333, found 440.2324.



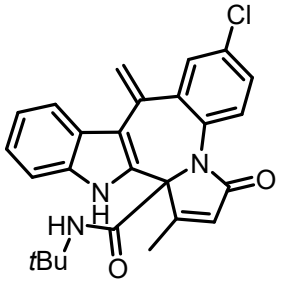
2u

2u was obtained as a brown solid. Yield 75%. Melting point 214 – 216 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.81 – 7.77 (m, 1H), 7.42 – 7.38 (m, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.08 (m, 4H), 6.51 (s, 1H), 6.06 – 6.04 (m, 1H), 5.69 (dd, *J* = 11.7, 1.2 Hz, 2H), 2.30 (d, *J* = 1.6 Hz, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 167.0, 162.45 (d, *J* = 250.1 Hz), 161.8, 147.20 (d, *J* = 8.5 Hz), 138.5, 138.4, 136.5, 131.57 (d, *J* = 9.2 Hz), 128.98 (d, *J* = 3.2 Hz), 128.3, 125.8, 123.2, 121.7, 120.6, 119.7, 118.2, 116.13 (d, *J* = 23.2 Hz), 115.20 (d, *J* = 22.8 Hz), 113.7, 111.6, 75.8, 52.5, 28.6, 14.9.

HRMS (ESI, m/z) calcd for $C_{26}H_{24}FN_3O_2$ ($[M+H]^+$): 430.1925, found 430.1919.



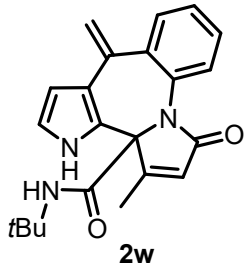
2v

2v was obtained as a yellow solid. Yield 78 %. Melting point 275 – 277 °C.

^{1}H NMR (400 MHz, 101 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.80 – 7.76 (m, 1H), 7.58 (d, J = 2.4 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.26 – 7.19 (m, 2H), 7.19 – 7.15 (m, 1H), 6.47 (s, 1H), 6.06 – 6.03 (m, 1H), 5.69 (dd, *J* = 8.8, 1.1 Hz, 2H), 2.30 (d, J = 1.6 Hz, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 167.0, 161.9, 146.5, 138.2, 136.5, 135.1, 131.6, 131.2, 129.2, 128.5, 128.1, 125.8, 123.3, 121.7, 120.7, 119.7, 118.3, 113.7, 111.6, 75.7, 52.5, 28.6, 14.9.

HRMS (ESI, m/z) calcd for $C_{26}H_{24}ClN_3O_2$ ($[M+H]^+$): 446.1630, found 446.1620.



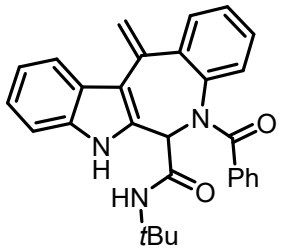
2w

2w was obtained as a brown solid. Yield 30 %. Melting point 183 – 185 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.59 – 7.49 (m, 1H), 7.46 – 7.32 (m, 2H), 7.26 – 7.15 (m, 1H), 6.78 (t, *J* = 2.7 Hz, 1H), 6.38 (s, 1H), 6.23 (t, *J* = 2.9 Hz, 1H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.42 (d, *J* = 1.5 Hz, 1H), 5.34 – 5.20 (m, 1H), 2.22 (d, *J* = 1.5 Hz, 3H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 167.4, 161.5, 143.9, 141.3, 133.0, 130.0, 129.4, 129.2, 128.4, 121.8, 121.6, 121.0, 119.2, 115.2, 108.6, 75.8, 52.3, 28.6, 14.8.

HRMS (ESI, m/z) calcd for $C_{22}H_{23}N_3O_2$ ($[M+H]^+$): 362.1863, found 362.1846.



2x

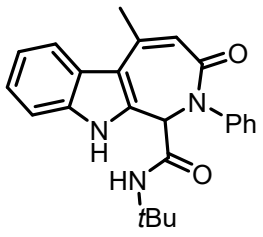
2x was obtained as a brown solid. Yield 45 %. Melting point 178 – 180 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.46 – 7.35 (m, 2H), 7.31

– 7.26 (m, 1H), 7.25 – 7.10 (m, 6H), 7.08 – 6.99 (m, 1H), 6.96 (s, 1H), 6.87 – 6.76 (m, 1H), 5.98 (d, *J* = 1.3 Hz, 2H), 5.64 (d, 1H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 167.1, 142.9, 141.3, 136.8, 135.0, 130.9, 130.6, 128.8, 128.8, 128.6, 128.0, 128.0, 125.8, 122.8, 120.5, 120.2, 116.1, 111.5, 58.5, 51.8, 28.7.

HRMS (ESI, m/z) calcd for $C_{29}H_{27}N_3O_2$ ([M+H]$^+$): 450.2176, found 450.2180.



2y

2y was obtained as a brown solid. Yield 99 %. Melting point 186 – 188 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.92 – 7.71 (m, 1H), 7.23 – 7.15 (m, 3H), 7.13 – 7.02 (m, 4H), 7.01 – 6.93 (m, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 5.53 (s, 1H), 5.21 (s, 1H), 2.45 (d, *J* = 1.3 Hz, 3H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 166.2, 143.8, 142.4, 136.3, 134.9, 129.2, 127.2, 127.0, 125.6, 122.8, 121.0, 120.4, 120.0, 112.9, 112.8, 61.8, 51.9, 28.4, 24.2.

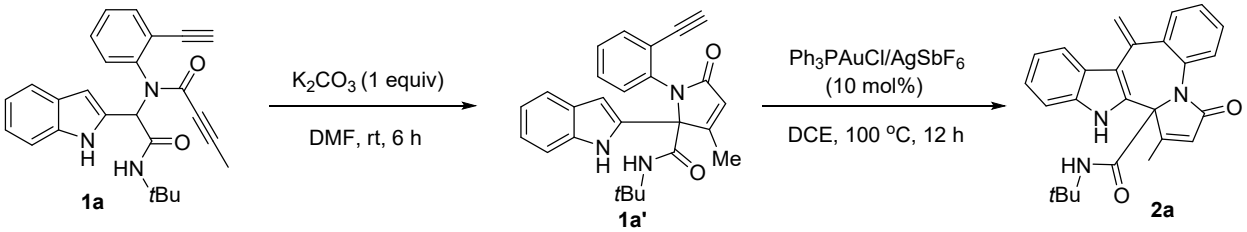
HRMS (ESI, m/z) calcd for $C_{24}H_{25}N_3O_2$ ([M+H]$^+$): 388.2020, found 388.2019.

Scale-up reaction for the synthesis of **2m**

To a glass vial, Ph_3PAuCl (10 mol%) and $AgSbF_6$ (10 mol%) were loaded along with dry DCE (20 mL). Ugi product **1m** (1.0 mmol) was added. The reaction vial was evacuated, backfilled with argon and was heated in oil bath at 100 °C for 12 hours. After completion, the mixture was loaded to silica gel column chromatography (eluent: EtOAc/*n*-heptane 1:1 v/v) to afford 446 mg **2m** in 94% yield.

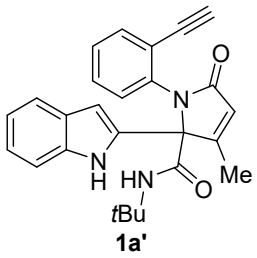
6. Control experiments.

Base-promoted reaction:



Ugi adduct **1a** (0.3 mmol) and K_2CO_3 (0.3 mmol) were placed in a screw-cap vial followed by addition of DMF (3 mL). The reaction mixture was sealed and stirred at rt for 6 hours. After completion, the resulting mixture was diluted with ethyl acetate and washed with water. The organic layer was dried with sodium sulfate and concentrated.the

mixture was loaded to silica gel column chromatography (eluent: EtOAc/*n*-heptane 1:1 v/v) to afford desired product **1a'**.



1a'

1a' was obtained as a brown solid. Yield 50 %. Melting point 140 – 142 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.63 – 7.53 (m, 2H), 7.46 – 7.38 (m, 1H), 7.26 – 7.01 (m, 5H), 6.64 – 6.56 (m, 1H), 6.51 (d, J = 8.2 Hz, 1H), 6.41 (s, 1H), 6.17 – 6.02 (m, 1H), 3.38 (s, 1H), 1.97 (d, J = 1.6 Hz, 3H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 162.4, 138.3, 136.0, 134.3, 133.0, 130.2, 127.8, 127.5, 125.6, 122.6, 121.4, 120.9, 120.9, 120.2, 111.8, 83.9, 82.4, 76.5, 52.7, 28.5, 13.8.

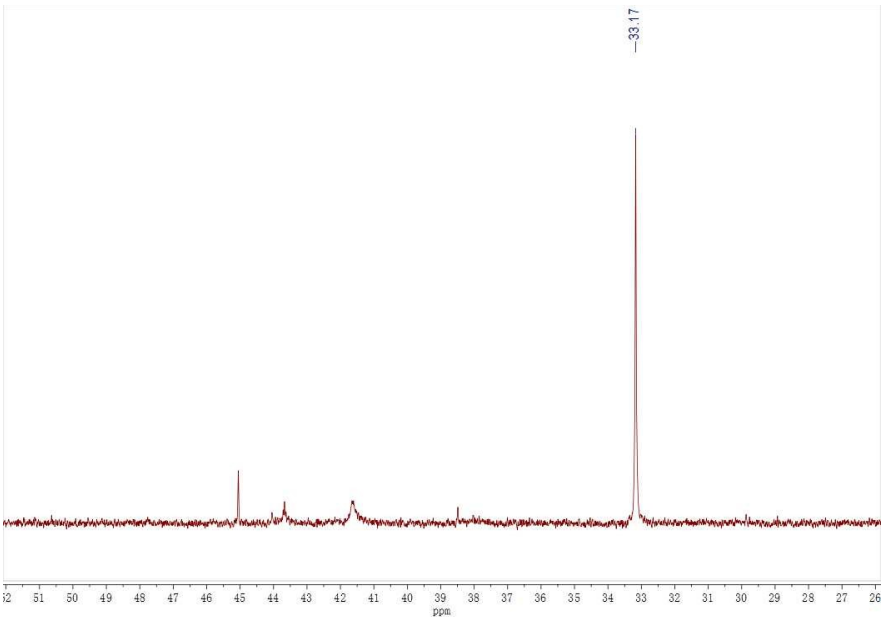
HRMS (ESI, m/z) calcd for $C_{26}H_{25}N_3O_2$ ($[M+H]^+$): 412.2020, found 412.2026.

To a glass vial, Ph_3PAuCl (10 mol%) and $AgSbF_6$ (10 mol%) were loaded along with dry DCE (2 mL). Ugi product **1a'** (0.1 mmol) was added. The reaction vial was evacuated, backfilled with argon and was heated in oil bath at 100 ^{o}C for 12 hours. After completion, the mixture was loaded to silica gel column chromatography (eluent: EtOAc/*n*-heptane 1:1 v/v) to afford desired product **2a** in 99% yield.

(a) ^{31}P NMR for $Ph_3PAuCl/AgSbF_6$ catalyzed intramolecular cascade reaction

To a glass vial, Ph_3PAuCl (10 mol%) and $AgSbF_6$ (10 mol%) were loaded along with dry DCE (2 mL). Then Ugi product **1a** (0.1 mmol) was added. The reaction vial was evacuated, backfilled with argon and was heated in oil bath at 100 ^{o}C for 12 hours. Through ^{31}P NMR study, the formation of different phosphine species could be observed via ^{31}P NMR. Results are shown in Figure **1**.

1) **1a** + $Ph_3PAuCl/AgSbF_6$ before reaction



2) **1a** + $Ph_3PAuCl/AgSbF_6$ after reaction

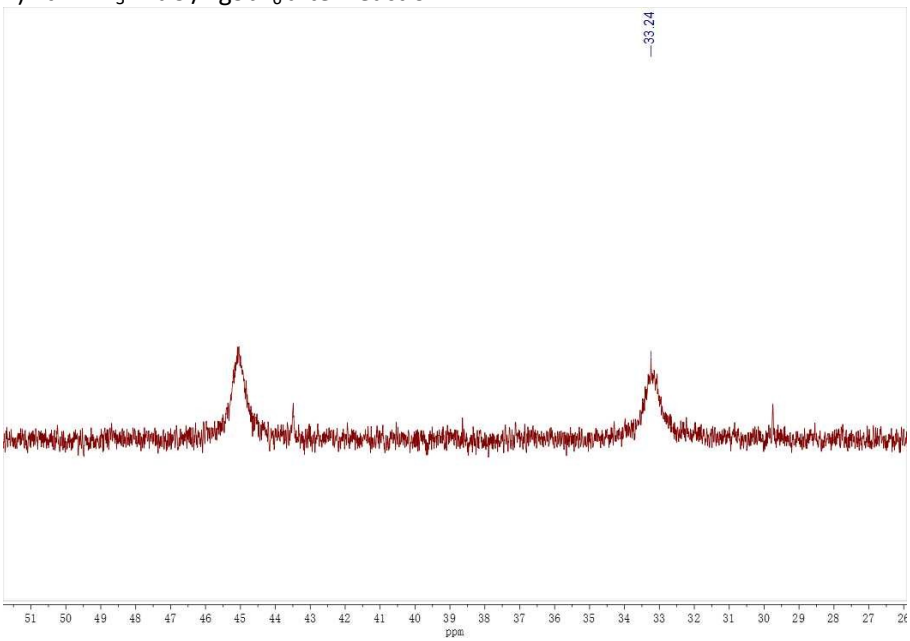
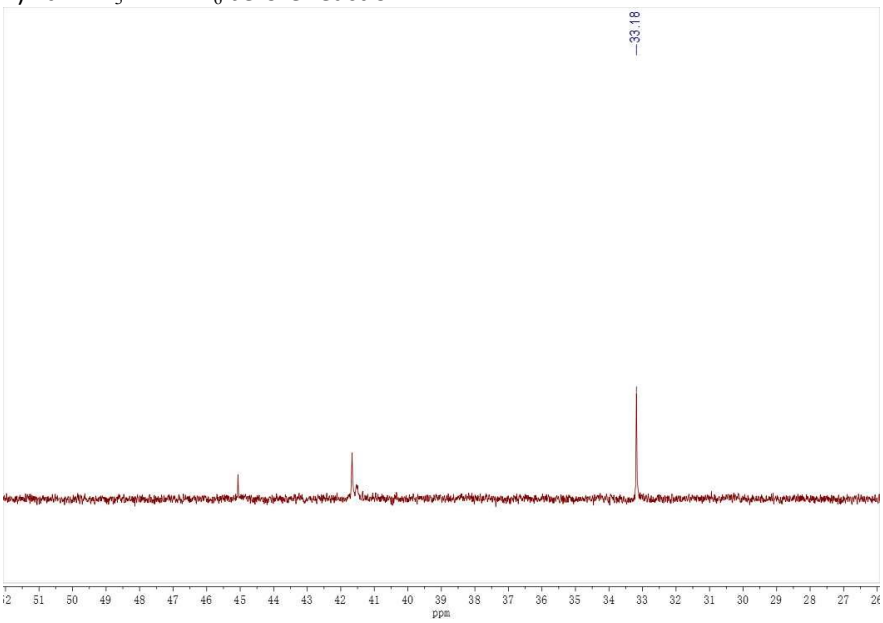


Figure **1.** ^{31}P NMR for $Ph_3PAuCl/AgSbF_6$

(b) ^{31}P NMR for $Ph_3PAuSbF_6$ catalyzed intramolecular cascade reaction

To a glass vial, $Ph_3PAuSbF_6$ (10 mol%) [Ph_3PAuCl (10 mol%) and $AgSbF_6$ (10 mol%) were loaded along with dry DCE (2 mL) under N_2 atmosphere, stirring at room temperature after 10 min, removal of AgCl by Celite filtration, the solvent was removed under reduced pressure to obtain $Ph_3PAuSbF_6$][1] was loaded along with dry DCE (2 mL). Then Ugi product **1a** (0.1 mmol) was added. The reaction vial was evacuated, backfilled with argon and was heated in oil bath at 100 ^oC for 12 hours. Through ^{31}P NMR study, the formation of different phosphine species could be observed via ^{31}P NMR. Results are shown in Figure **2**.

1) **1a** + $Ph_3PAuSbF_6$ before reaction



2) **1a** + $Ph_3PAuSbF_6$ after reaction

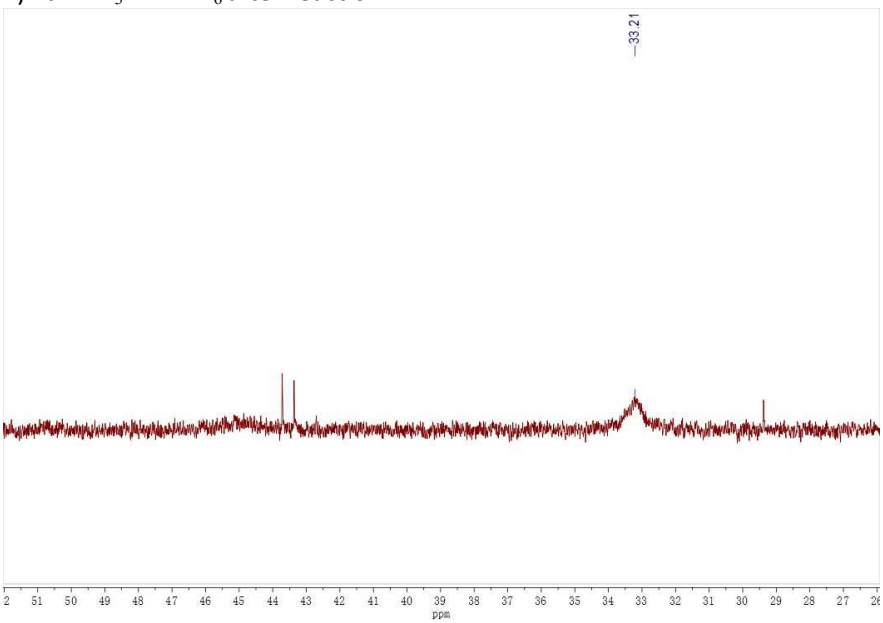


Figure **2.** ^{31}P NMR for $Ph_3PAuSbF_6$.

7. Single-crystal X-ray diffraction of 2a and 2m

Single crystals of **2a** and **2m** were obtained by slow diffusion from a solution of the compound in DCM layered with heptane at room temperature for several days. X-ray intensity data were collected at 293(2) K on an Agilent SuperNova diffractometer with Eos CCD detector using MoKα radiation. The images were processed (unit cell determination, intensity data integration, correction for Lorentz and polarization effects, and empirical absorption correction) using CrysAlisPRO[2]. Using Olex2[3], the structure was solved with the ShelXT[4] structure solution program using Intrinsic Phasing and refined with the ShelXL[5] refinement package using full-matrix least-squares minimization on F[3]. The asymmetric unit contains two molecules for **2a** and one molecule for **2m**. All H atoms were placed in idealized positions and refined in the riding mode, except for H2, H3, H5 and H6 in **2a** and H2, H3, H31A and H31B in **2m** which were located in F_o-F_c difference density maps, Non-hydrogen atoms were refined anisotropically and hydrogen atoms with isotropic temperature factors fixed at 1.2 times U_{eq} of the parent atoms (1.5 for methyl groups). Crystal data, data collection and structure refinement details for **2a** and **2m** are summarized in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2172861-2172862.

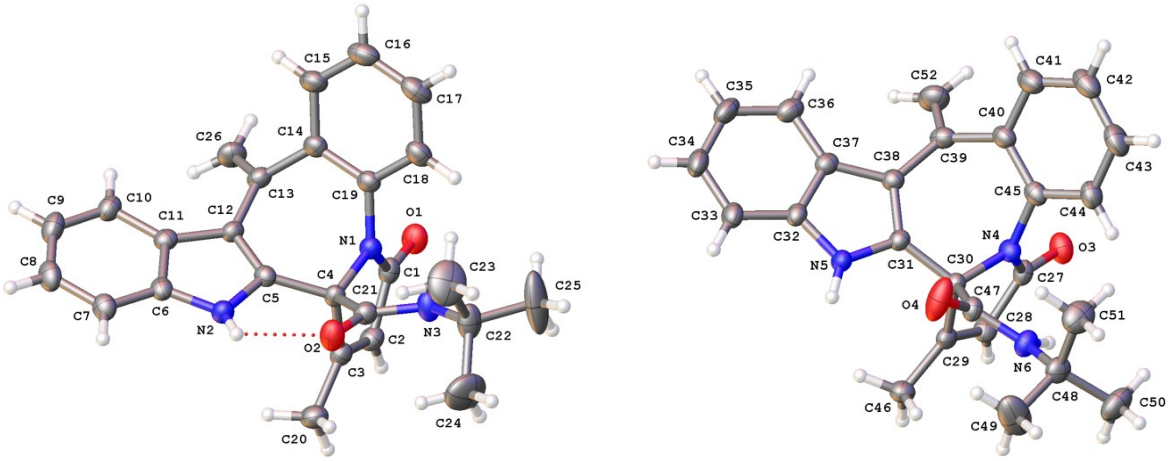


Figure S1. Molecular structure of **2a** showing both molecules in the asymmetric unit and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small circles of arbitrary radii.

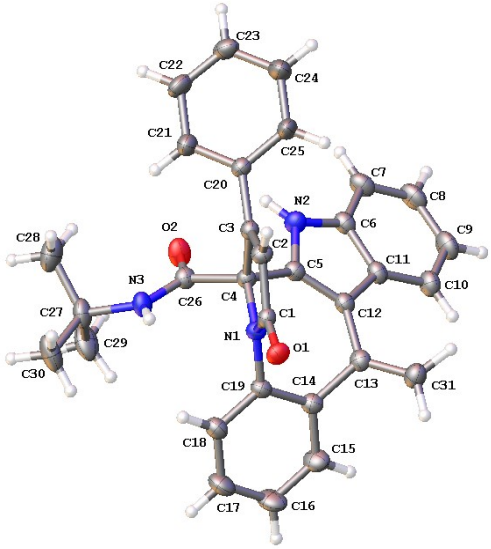


Figure S2. Molecular structure of **2m** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small circles of arbitrary radii.

Table S1. Crystal data, data collection and structure refinement details of compounds **2a** and **2m**

	2a	**2m**
Empirical formula	$C_{26}H_{25}N_3O_2$	$C_{31}H_{27}N_3O_2$
Formula weight	411.49	473.55
Temperature/K	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	13.9237(8)	10.2404(4)
b/Å	24.5877(7)	12.0290(4)
c/Å	14.3641(8)	21.4468(9)
α/°	90	90
β/°	115.433(7)	103.187(4)
γ/°	90	90
Volume/Å^3	4441.0(4)	2572.19(18)
Z	8	4
ρ_{calc}g/cm^3	1.231	1.223
μ/mm^{-1}	0.079	0.077
F(000)	1744.0	1000.0
Crystal size/mm^3	0.4 × 0.3 × 0.05	0.4 × 0.3 × 0.1
Radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
2Θ range for data collection/°	5.642 to 52.746	4.964 to 52.744
Index ranges	-17 ≤ h ≤ 17, -30 ≤ k ≤ 30, -17 ≤ l ≤ 17	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -26 ≤ l ≤ 26
Reflections collected	32259	41457
Independent reflections	9058 [R_{int} = 0.0637, R_{sigma} = 0.0957]	5255 [R_{int} = 0.0421, R_{sigma} = 0.0297]
Data/restraints/parameters	9058/0/583	5658/0/314
Goodness-of-fit on F^2	1.052	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0681, wR_2 = 0.1450	R_1 = 0.0510, wR_2 = 0.1200
Final R indexes [all data]	R_1 = 0.1459, wR_2 = 0.1893	R_1 = 0.0765, wR_2 = 0.1345
Largest diff. peak/hole / e Å^{-3}	0.22/-0.22	0.16/-0.20

8. References

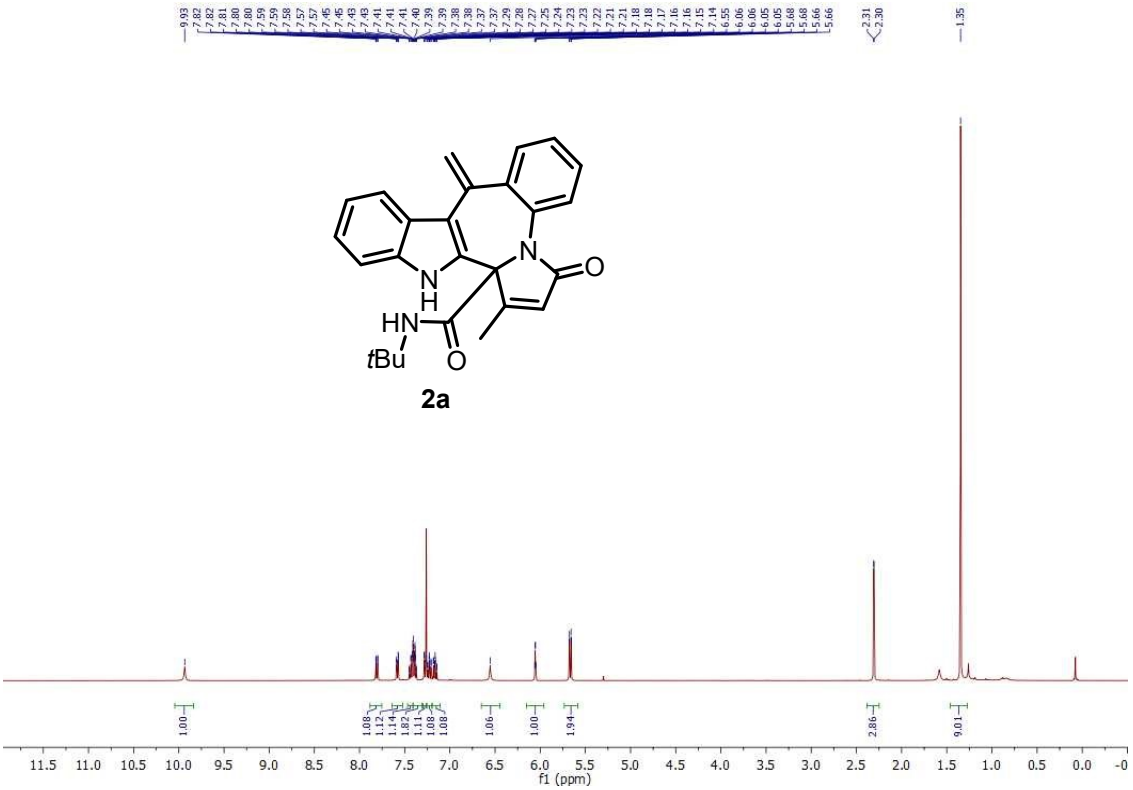
[1] D. Wang, R. Cai, S. Sharma, J. Jirak, S. K. Thummanapelli, N. G. Akhmedov, H. Zhang, X. Liu, J. L. Petersen, X. Shi, *J. Am. Chem. Soc*. 2012, **134**, 9012−9019.
[2] CrysAlis PRO (2012). Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.

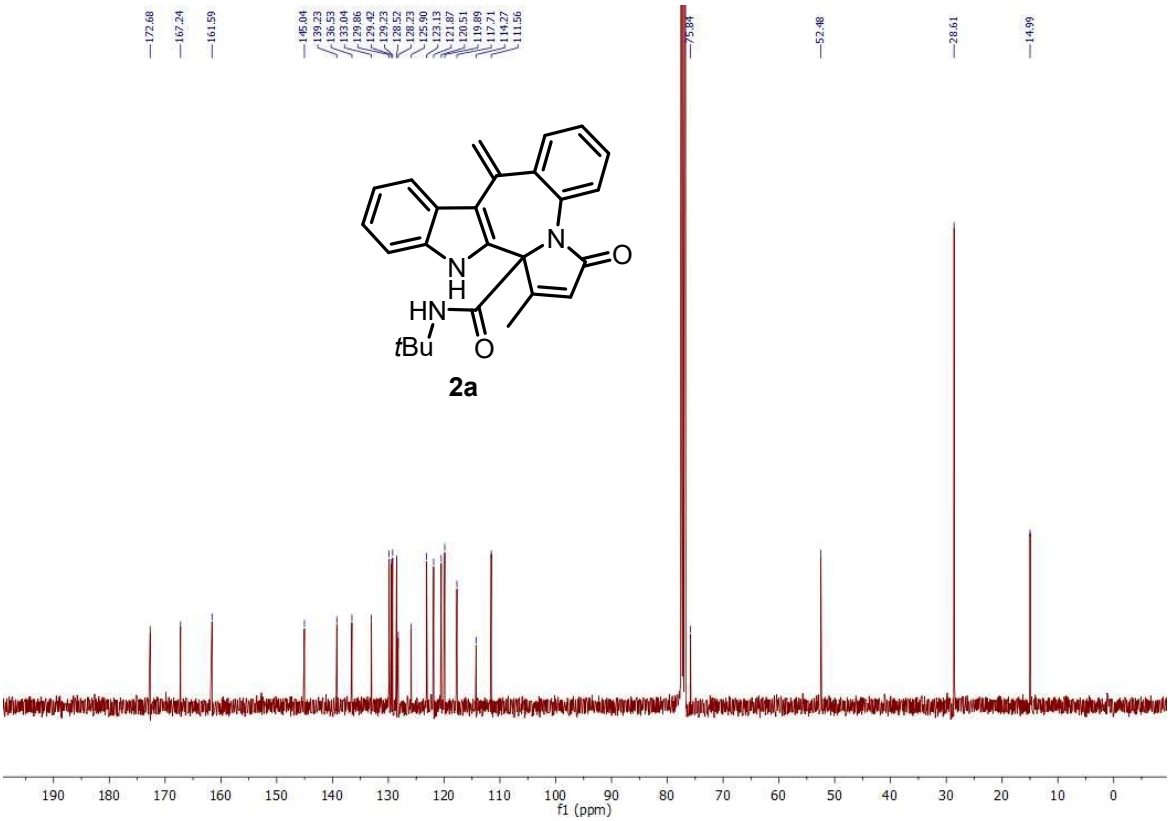
[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339-341.

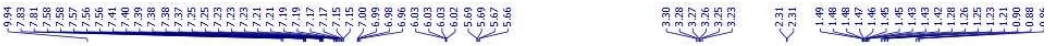
[4] G.M. Sheldrick, *Acta. Cryst.,* 2015, **A71**, 3-8.

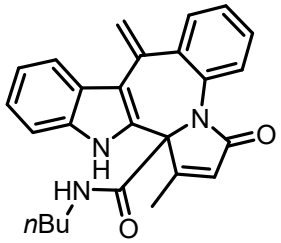
[5] G.M. Sheldrick, *Acta. Cryst.,* 2015, **C71**, 3-8

9. Copies of NMR spectrum





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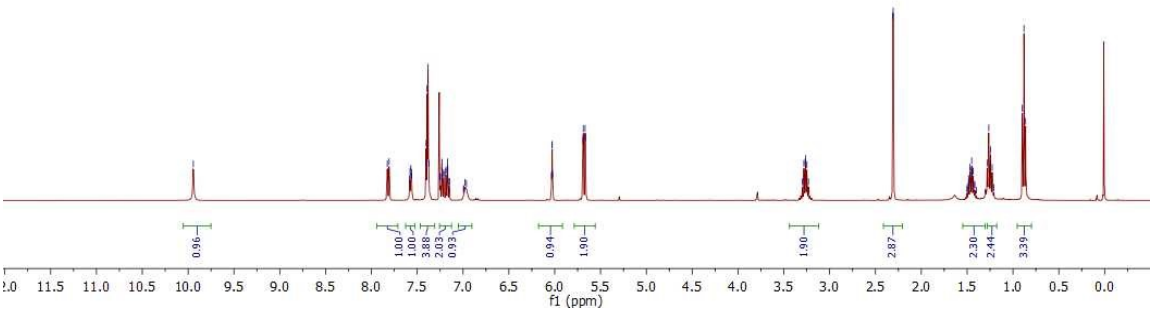
O
N
H
HN
O
nBu

2b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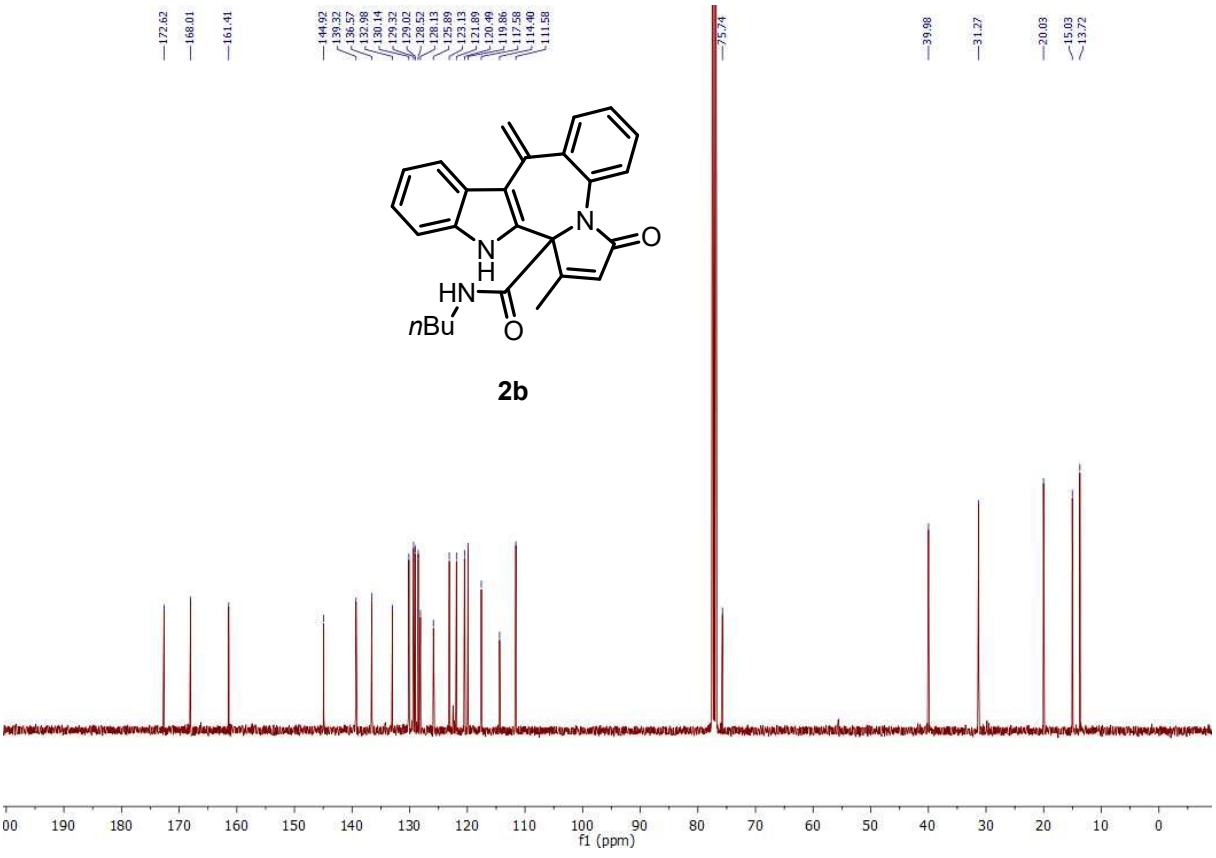
3.39
f1 (ppm)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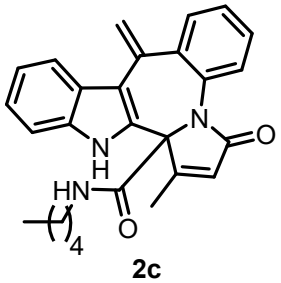
123.13
121.89
120.49
119.86
117.58
114.90
111.58
75.74
39.98
31.27
20.03
15.03
13.72
f1 (ppm)

N
O
N
H
HN
O
nBu

2b



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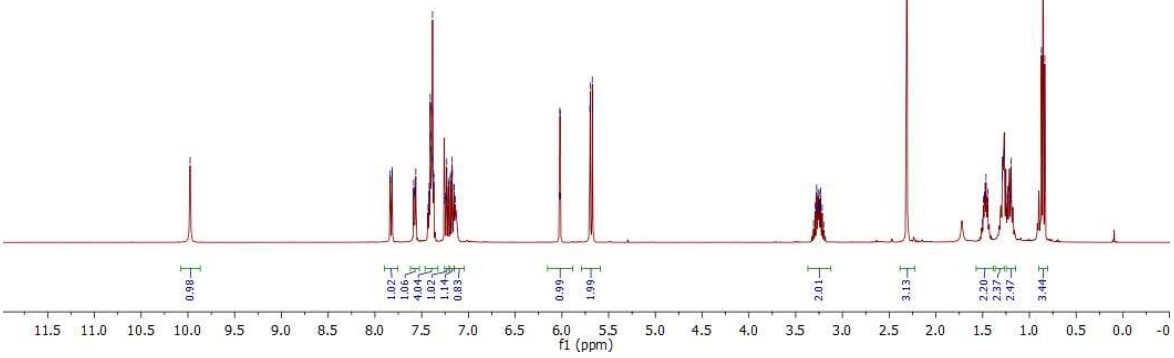
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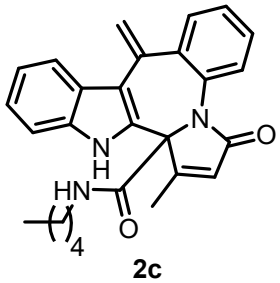
4.04
1.02
1.14
0.83
0.99
1.99
2.01
3.13
2.20
2.37
2.47
3.44
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)



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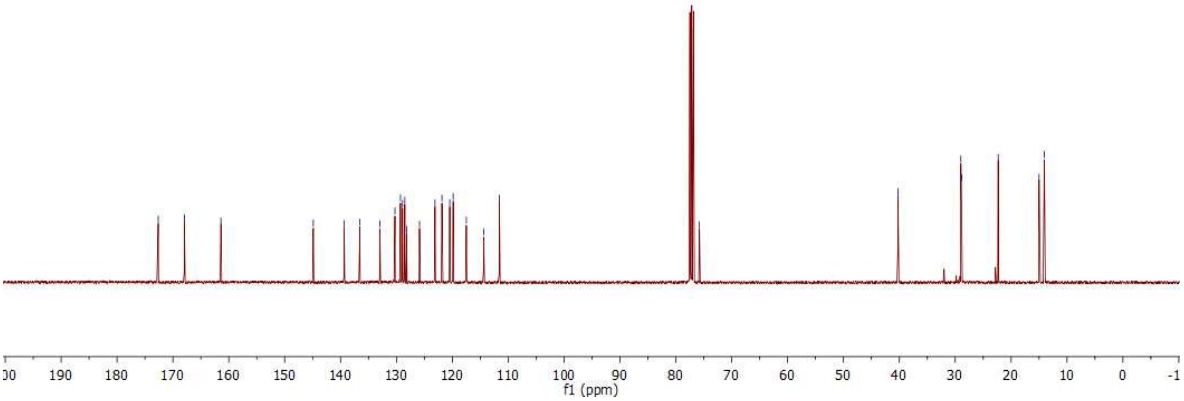
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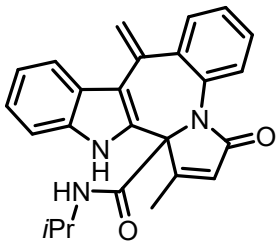

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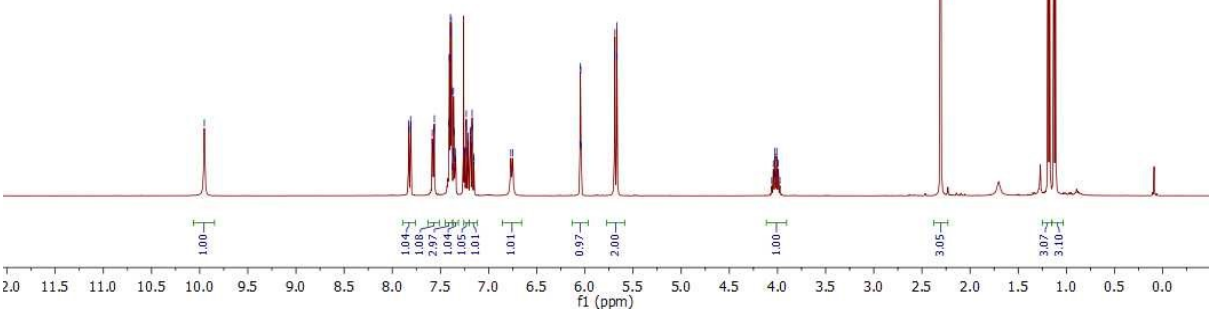

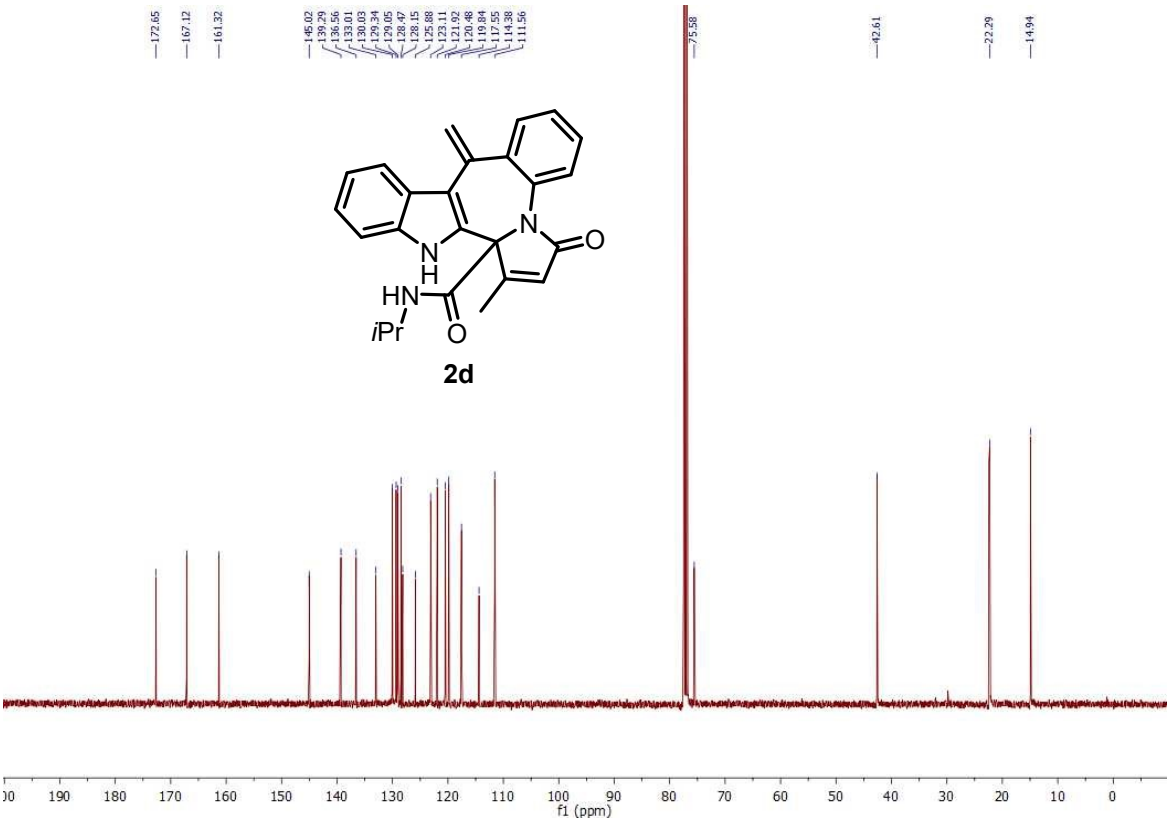

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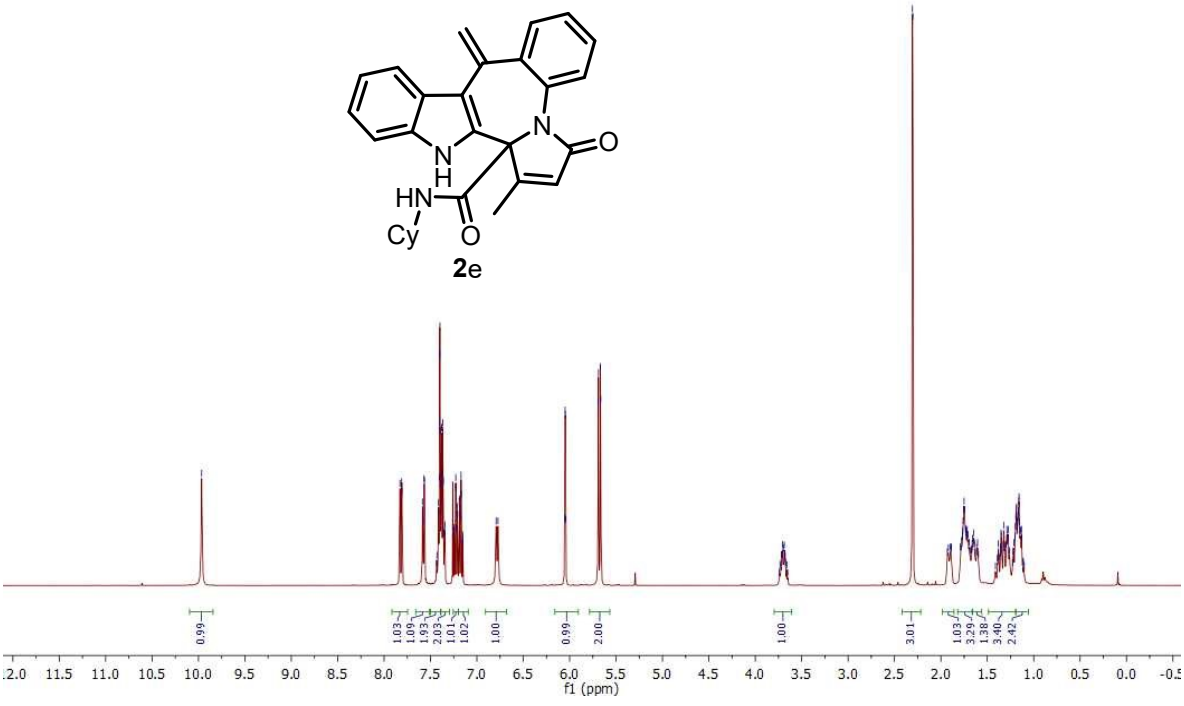
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H
HN
Cy
O
N
O
O

2e

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2.03
1.01
1.02
1.00
0.99
2.00
1.00
3.01
1.03
3.29
1.38
3.40
2.42
f1 (ppm)


172.58
166.97
161.28
144.93
139.22
136.45
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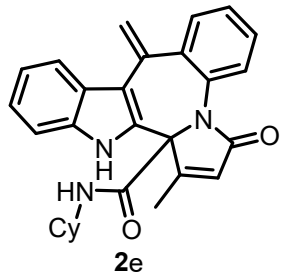
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Cy
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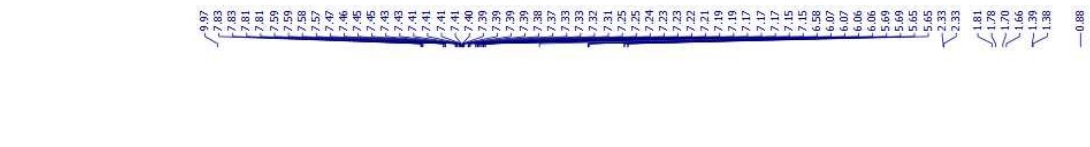
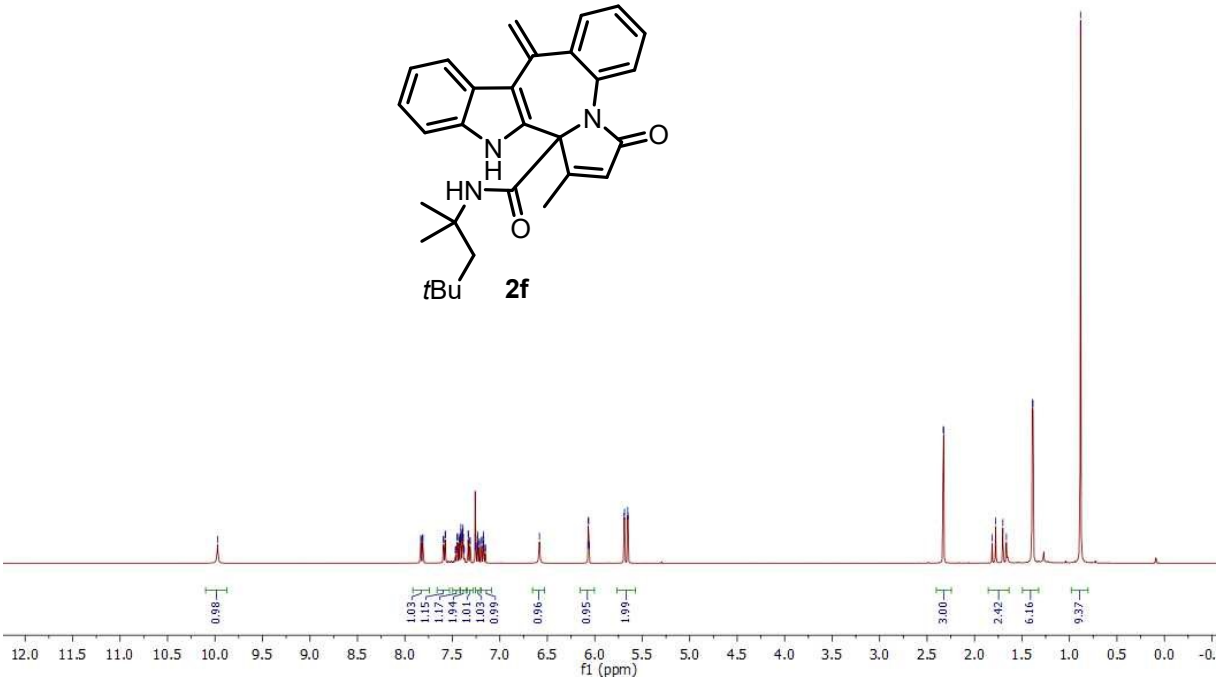
O

2e

f1 (ppm)

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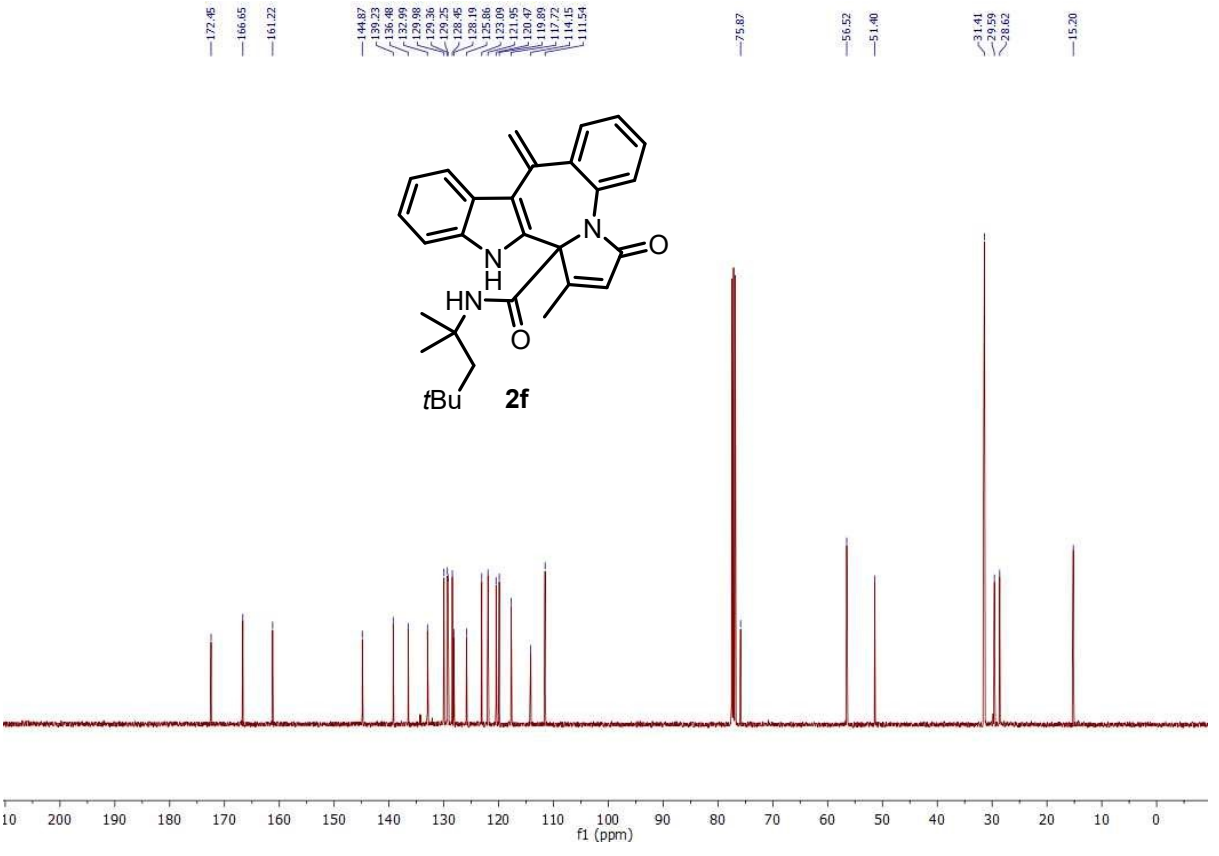
2f
f1 (ppm)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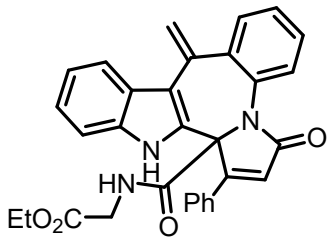
2f
f1 (ppm)



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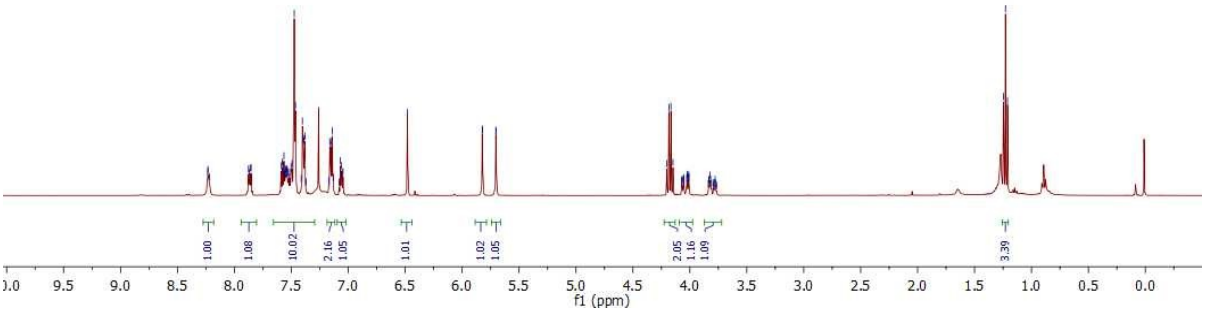

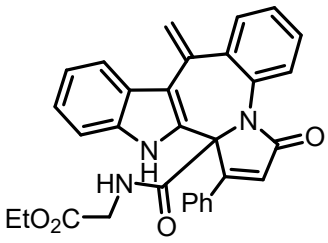

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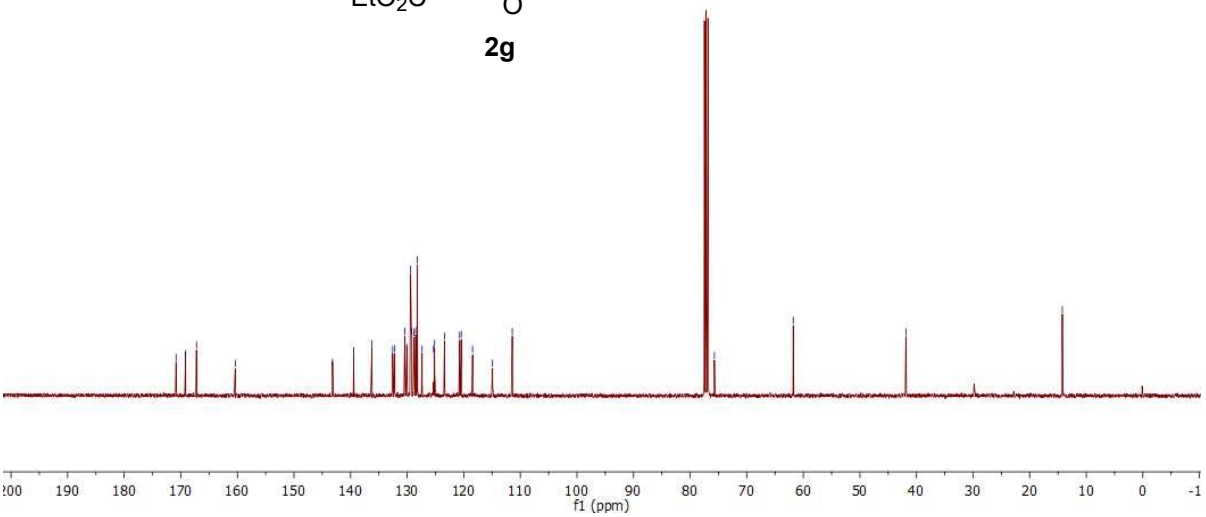

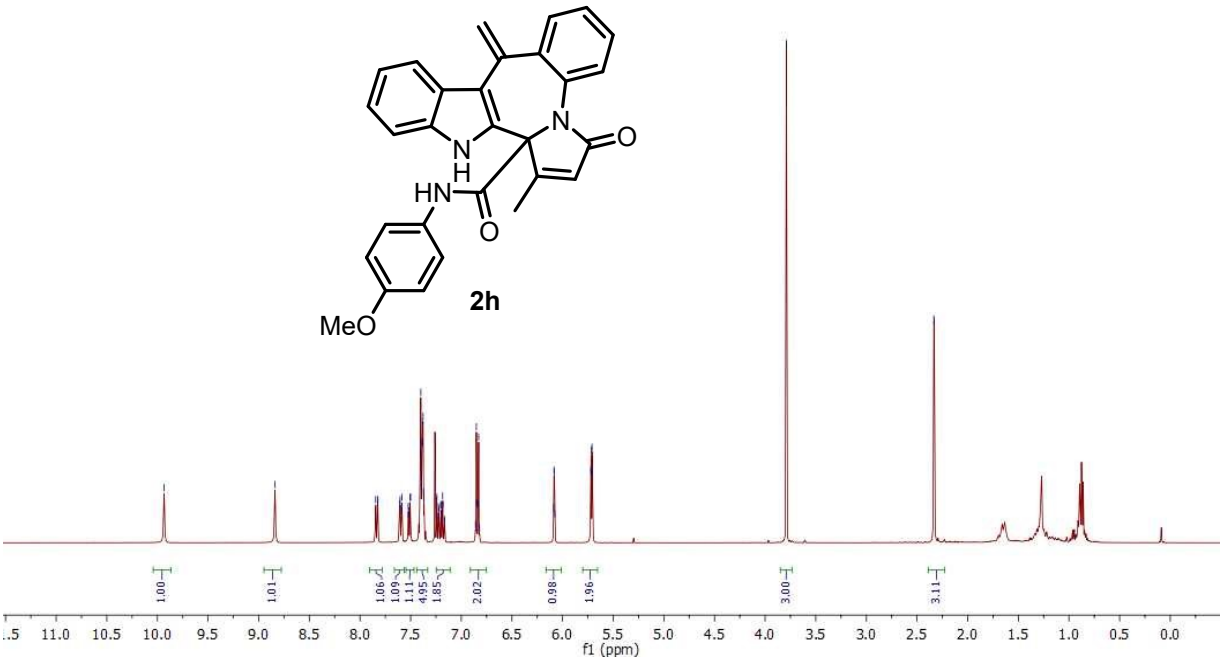
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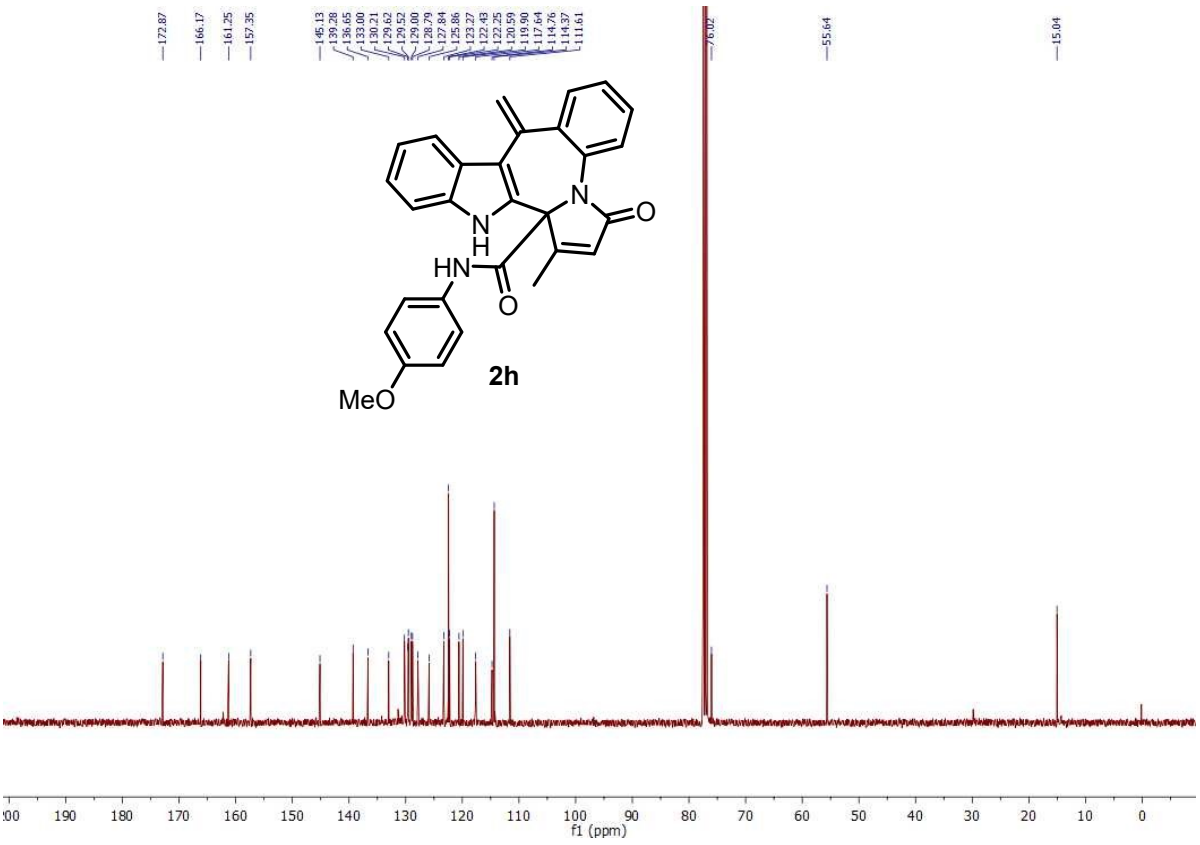
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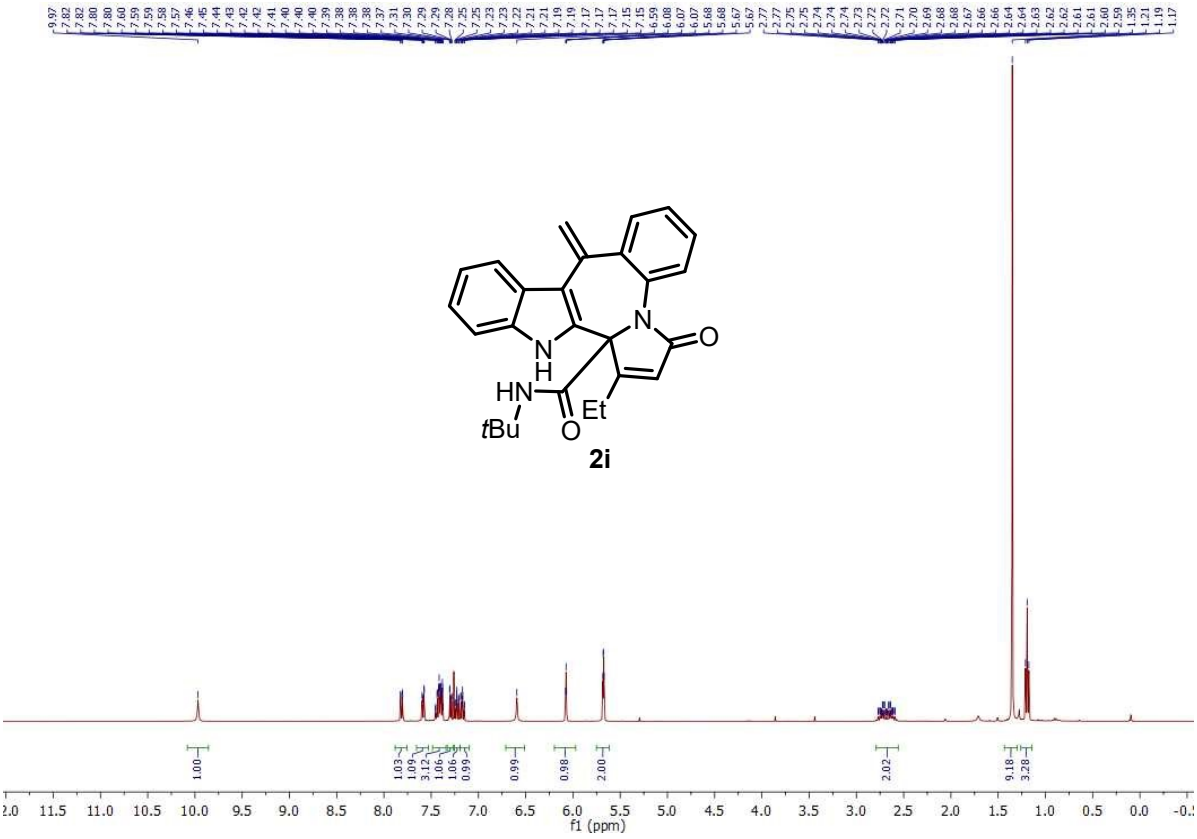
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O
2i
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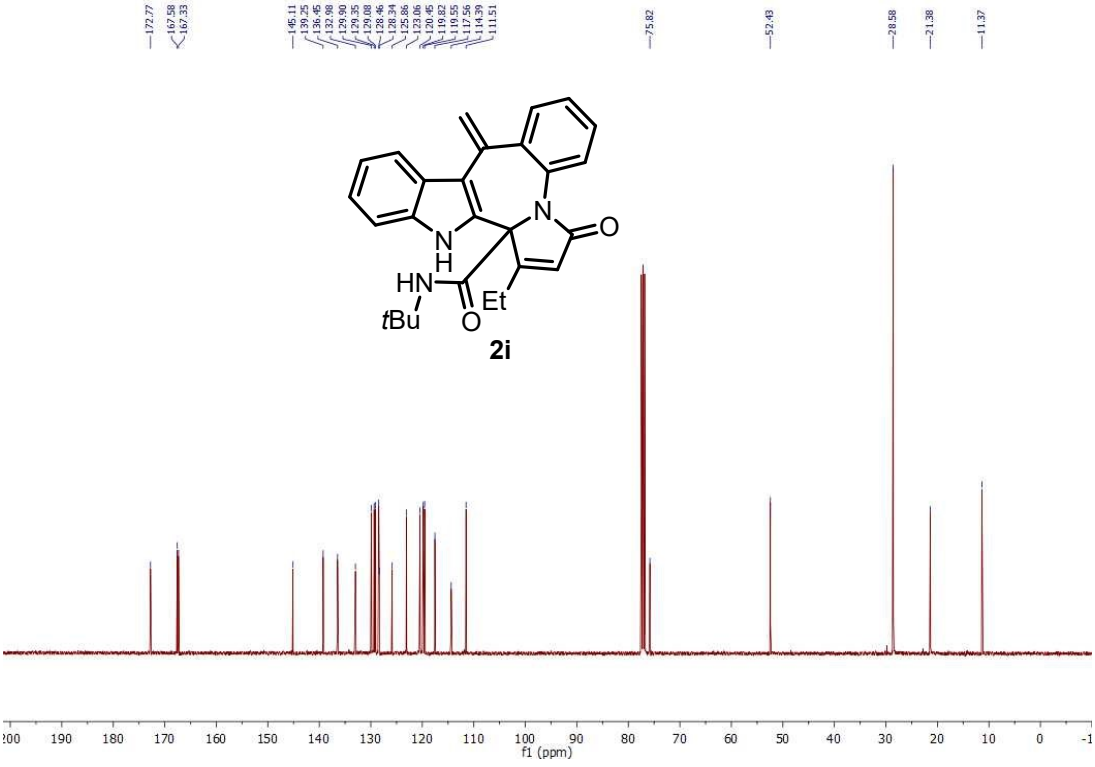
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2i
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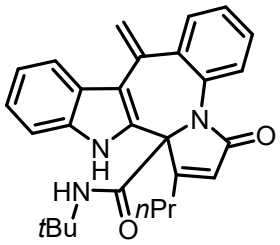

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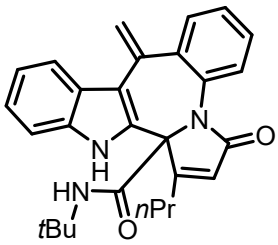

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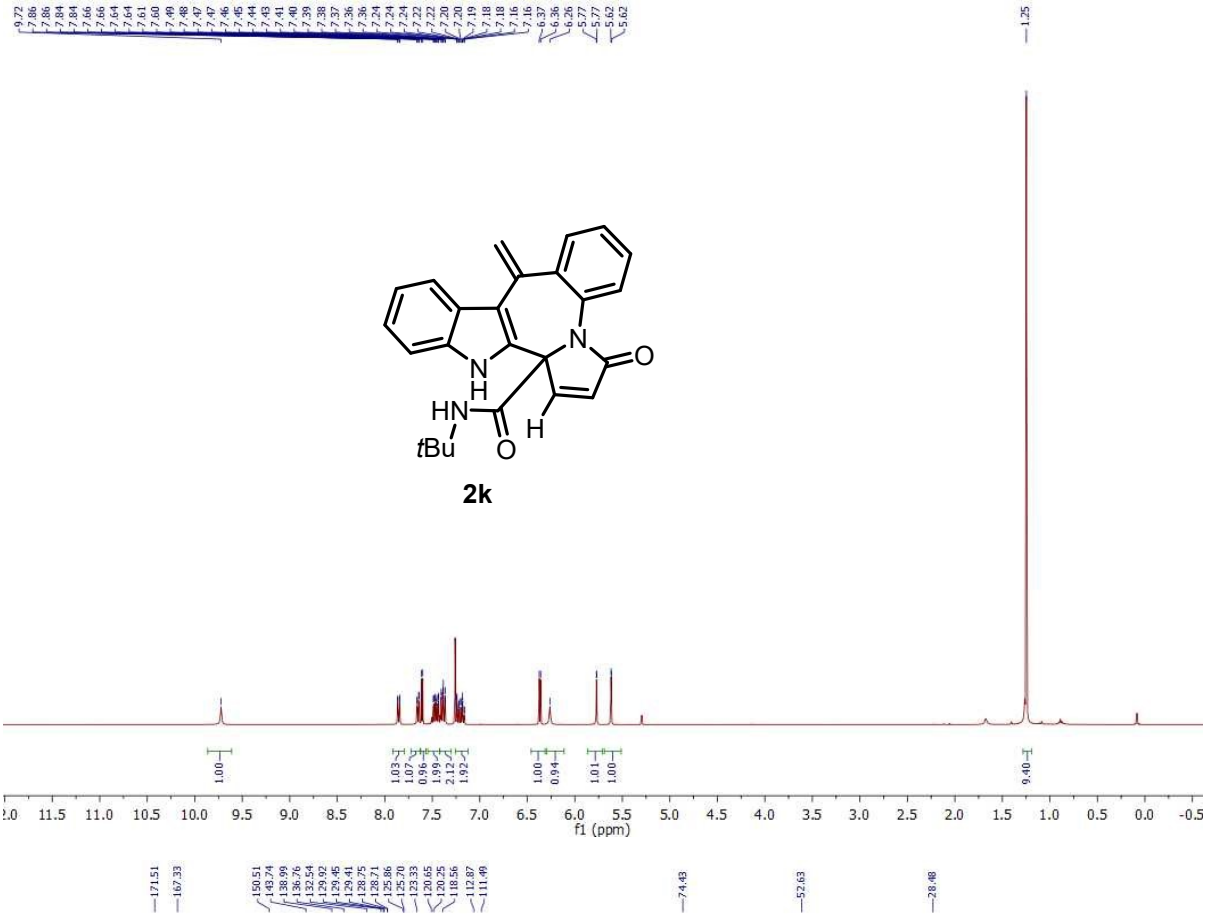
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O
tBu
O
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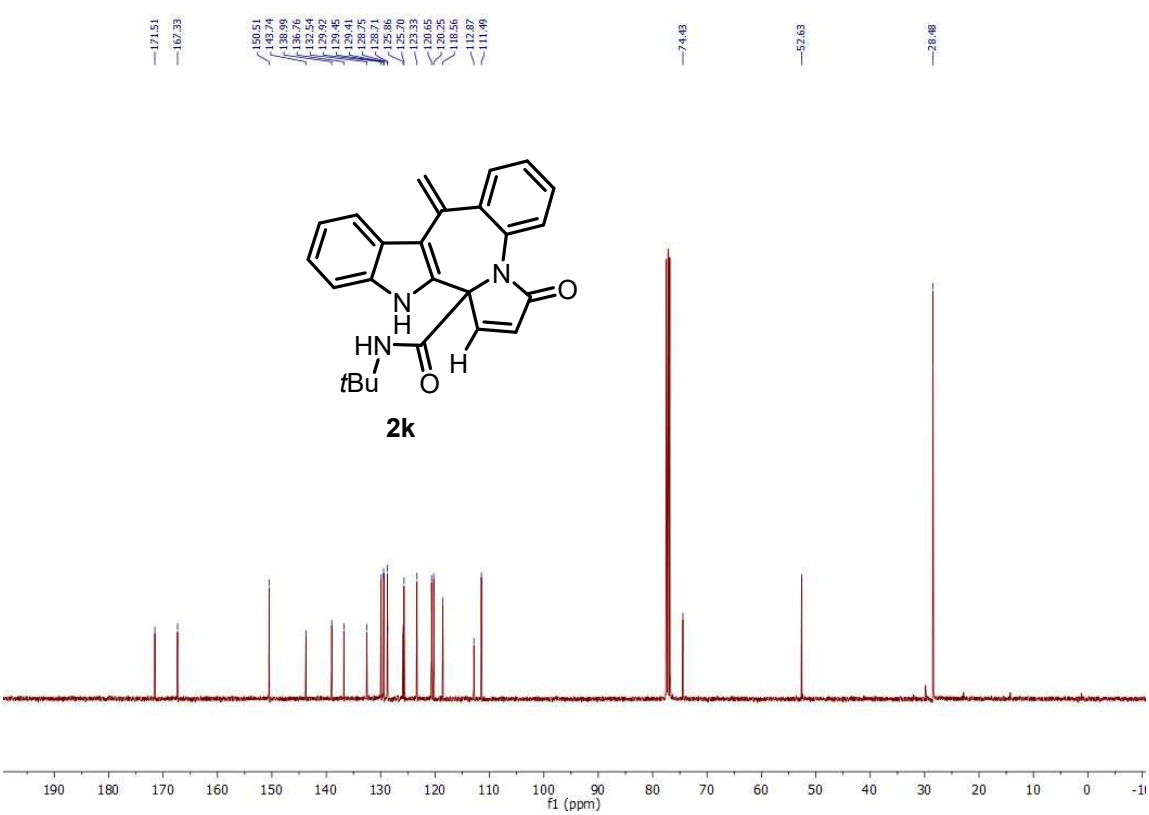
f1 (ppm)

2k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H
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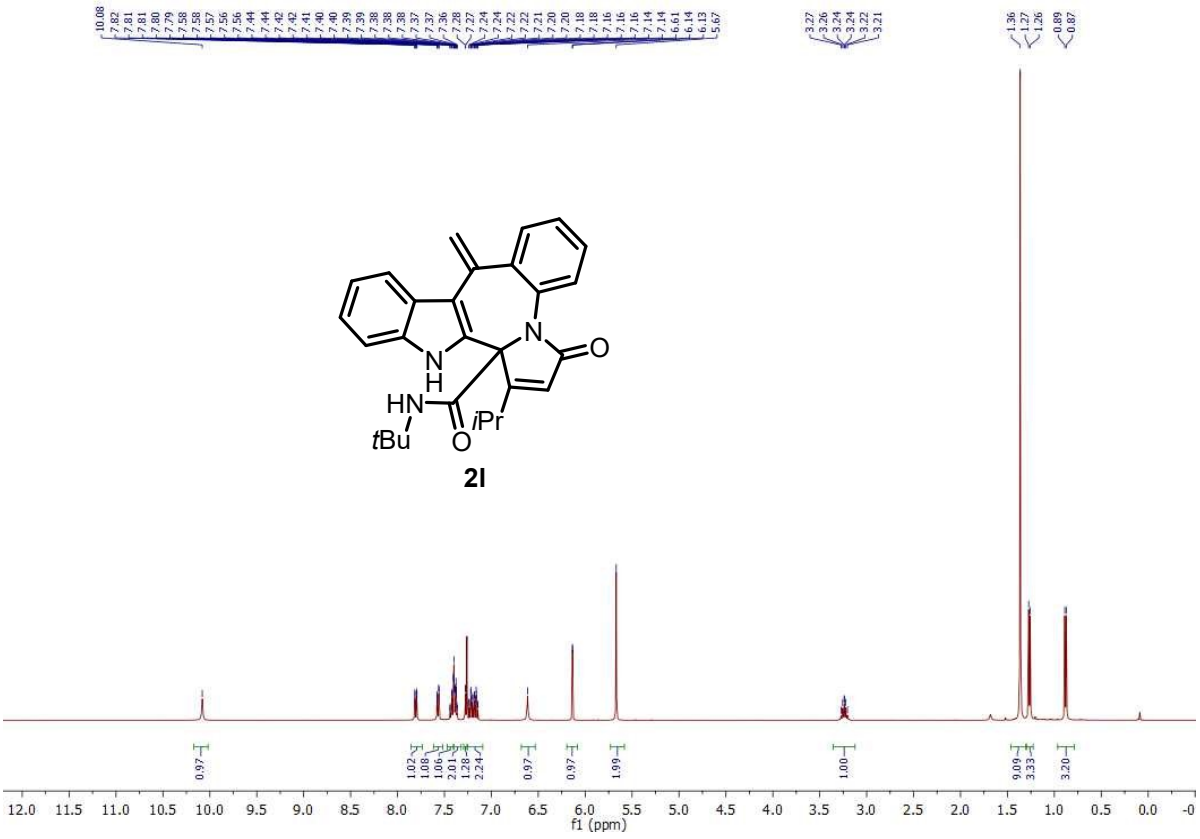
O
f1 (ppm)

2k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HN
tBu
O
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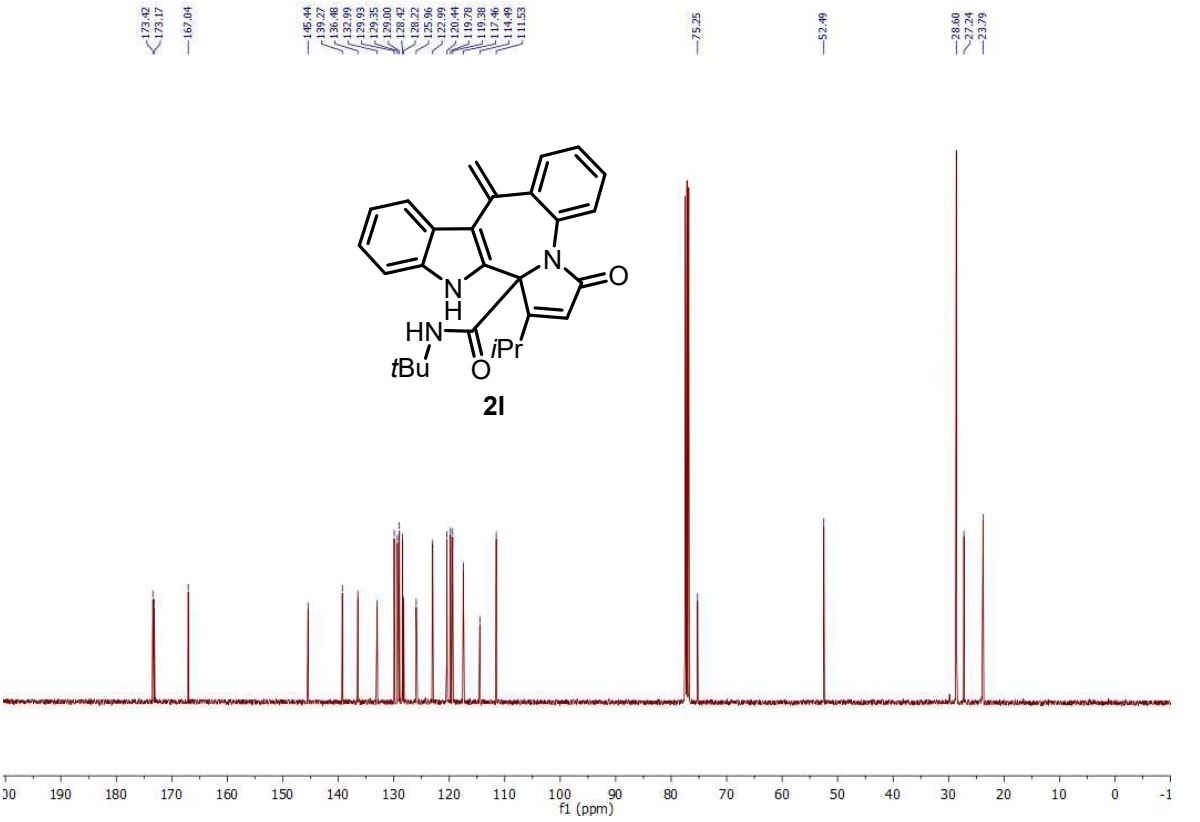
1.08
1.06
2.01
1.28
2.24
0.97
0.97
1.99
1.00
9.09
3.33
3.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

2l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28.60
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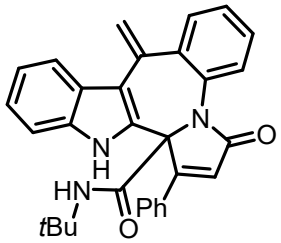
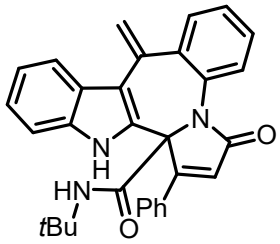
23.79
N
H
N
O
HN
tBu
O
iPr
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

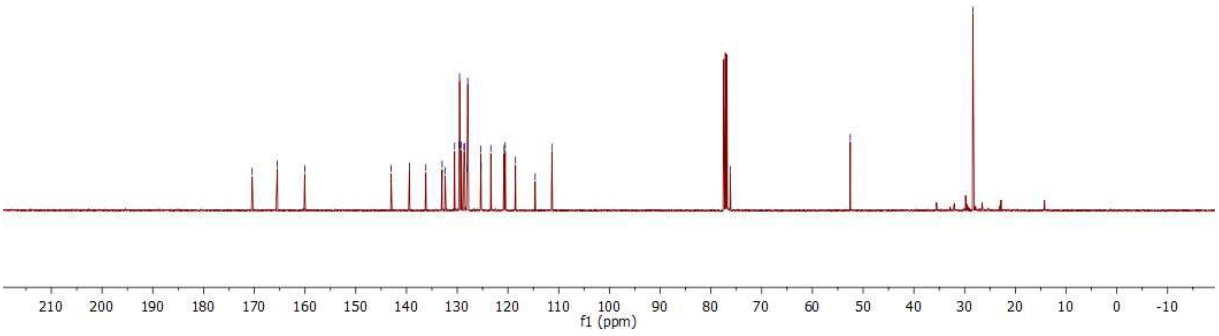
2l

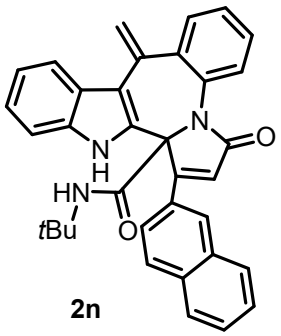


2m

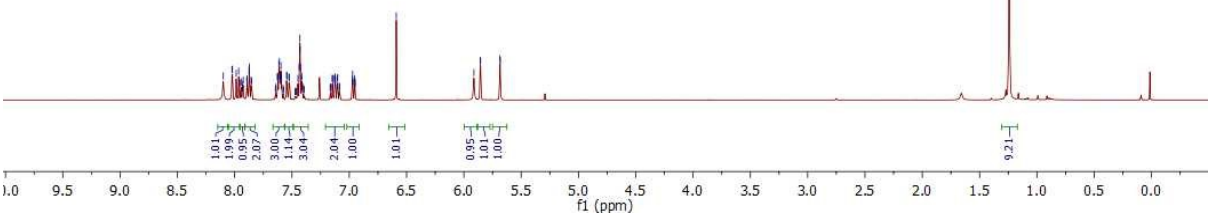


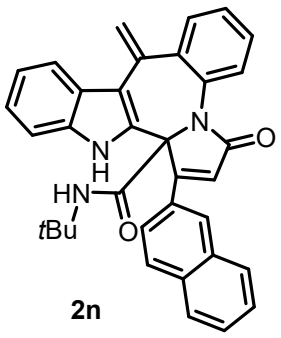
2m




N
O
N
H
HN
tBu
O

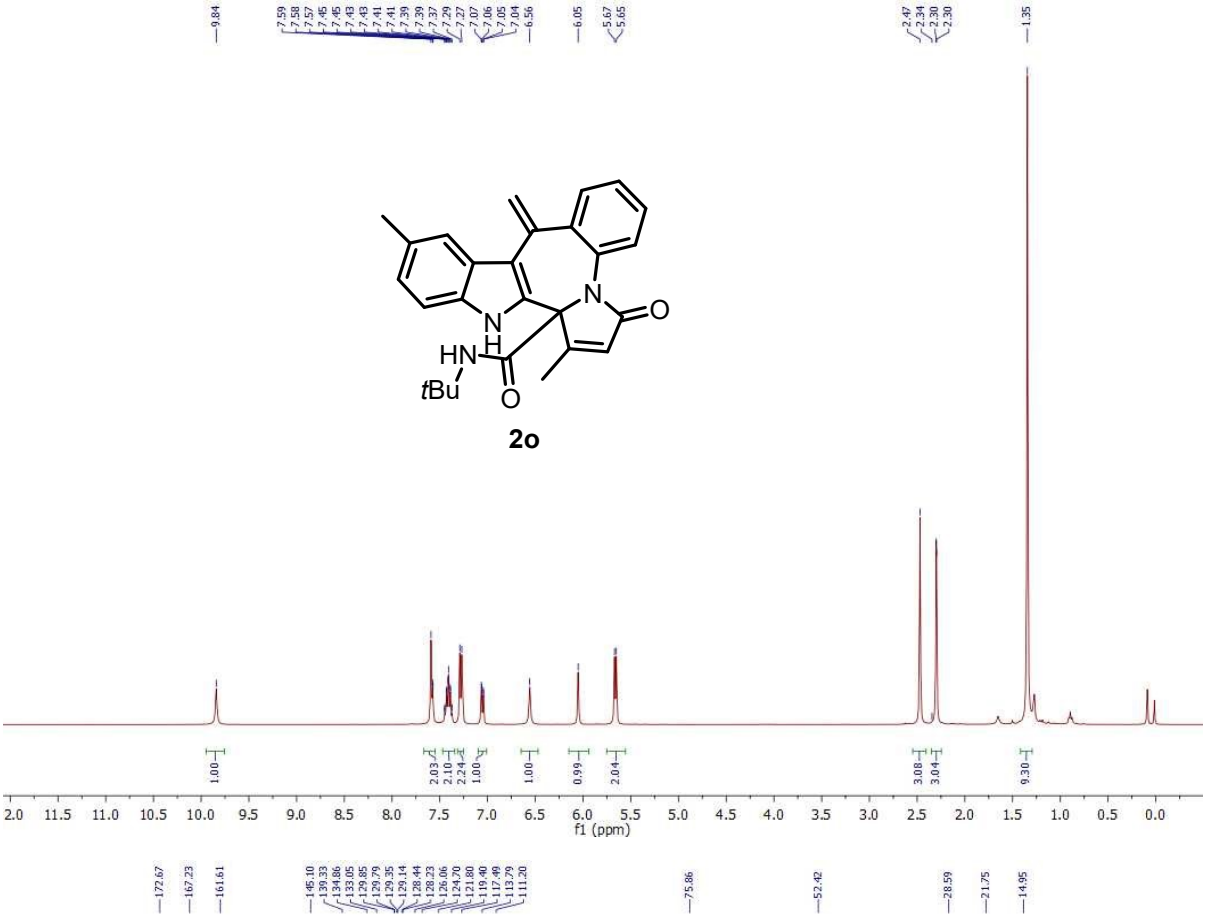
2n


1.01
1.99
0.95
2.07
3.00
1.14
3.04
2.04
1.00
1.01
0.95
1.01
1.00
9.21
f1 (ppm)

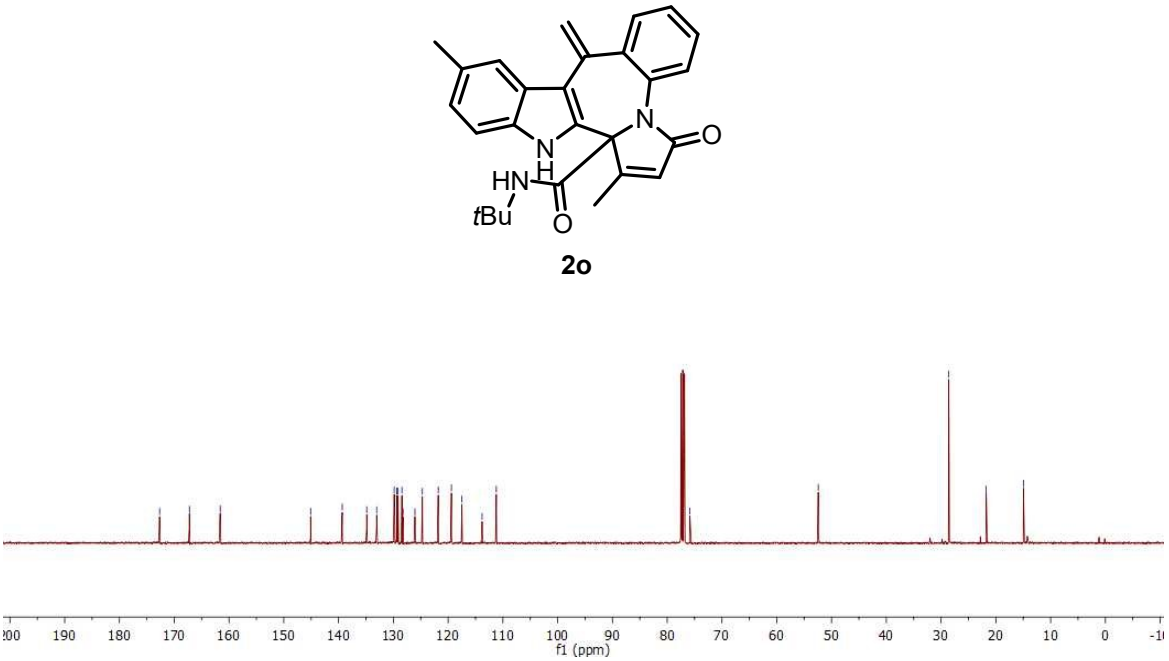

N
O
N
H
HN
tBu
O

2n

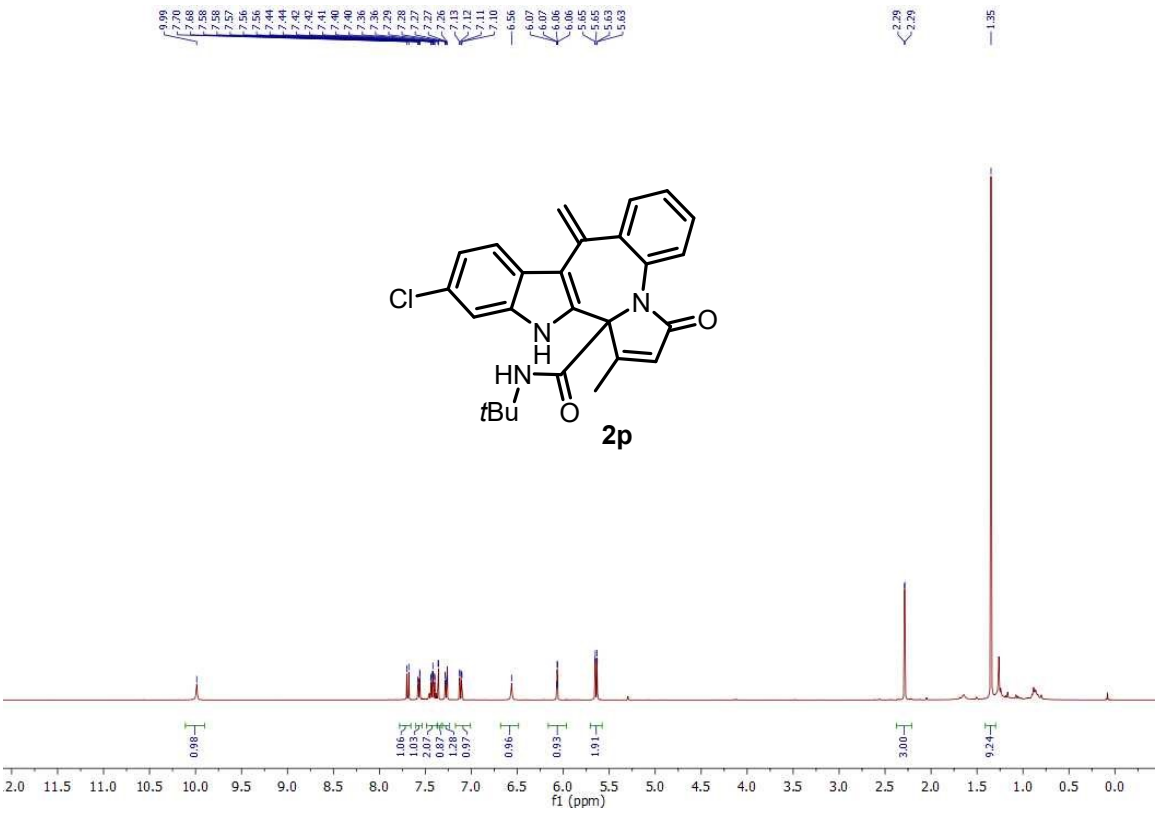
76.25
52.59
28.40
f1 (ppm)



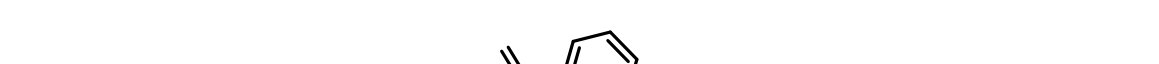
2o

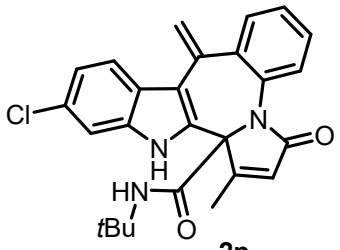


2o

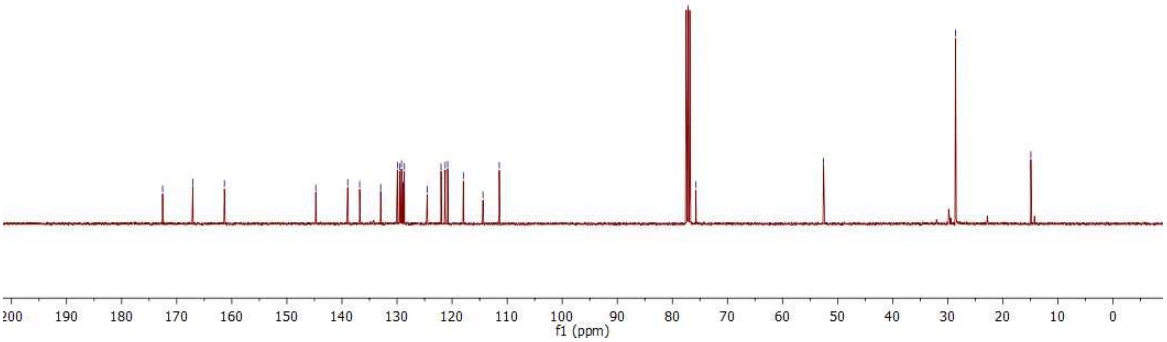


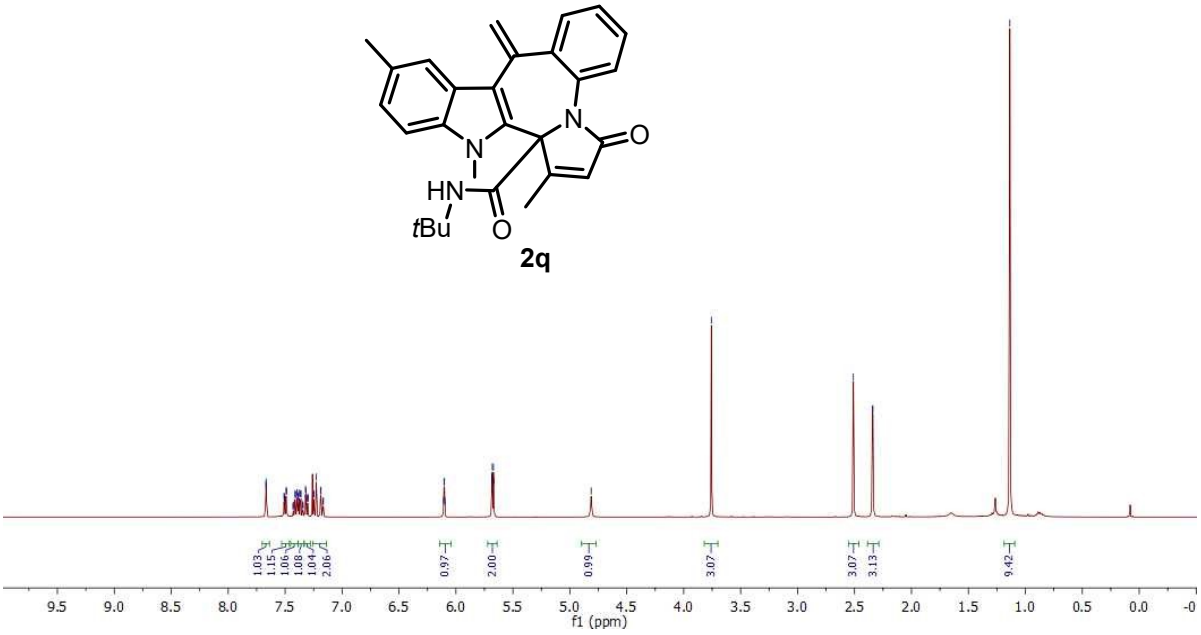
2p

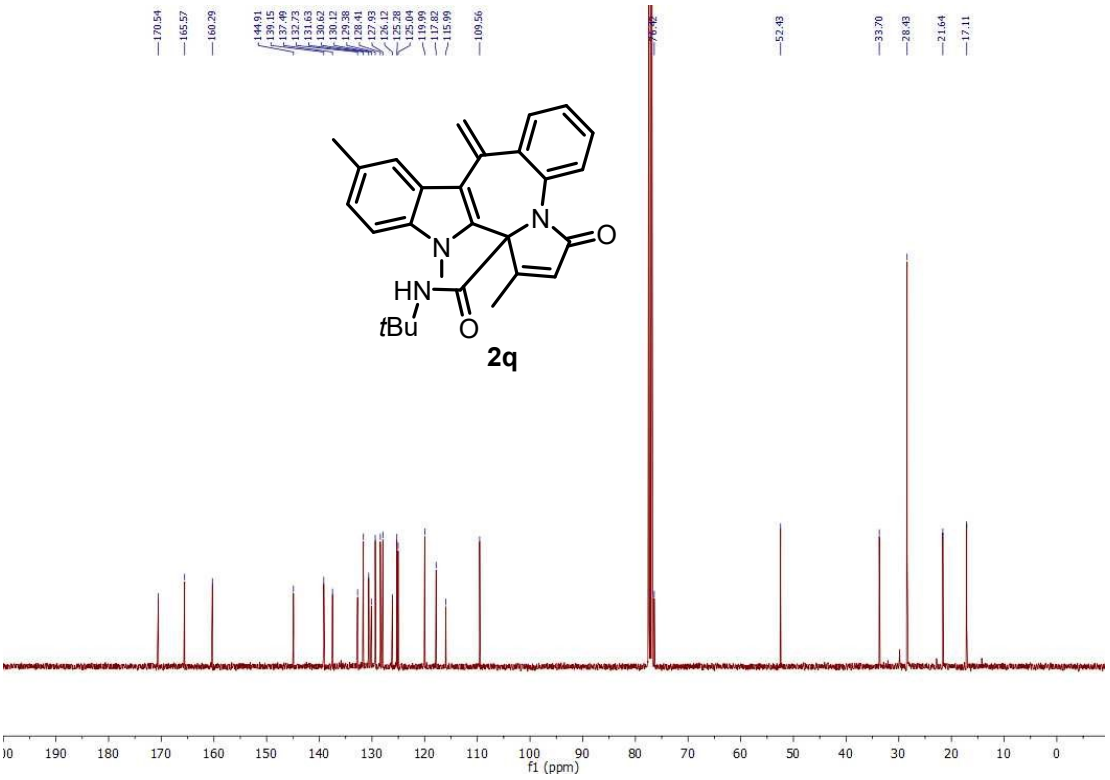


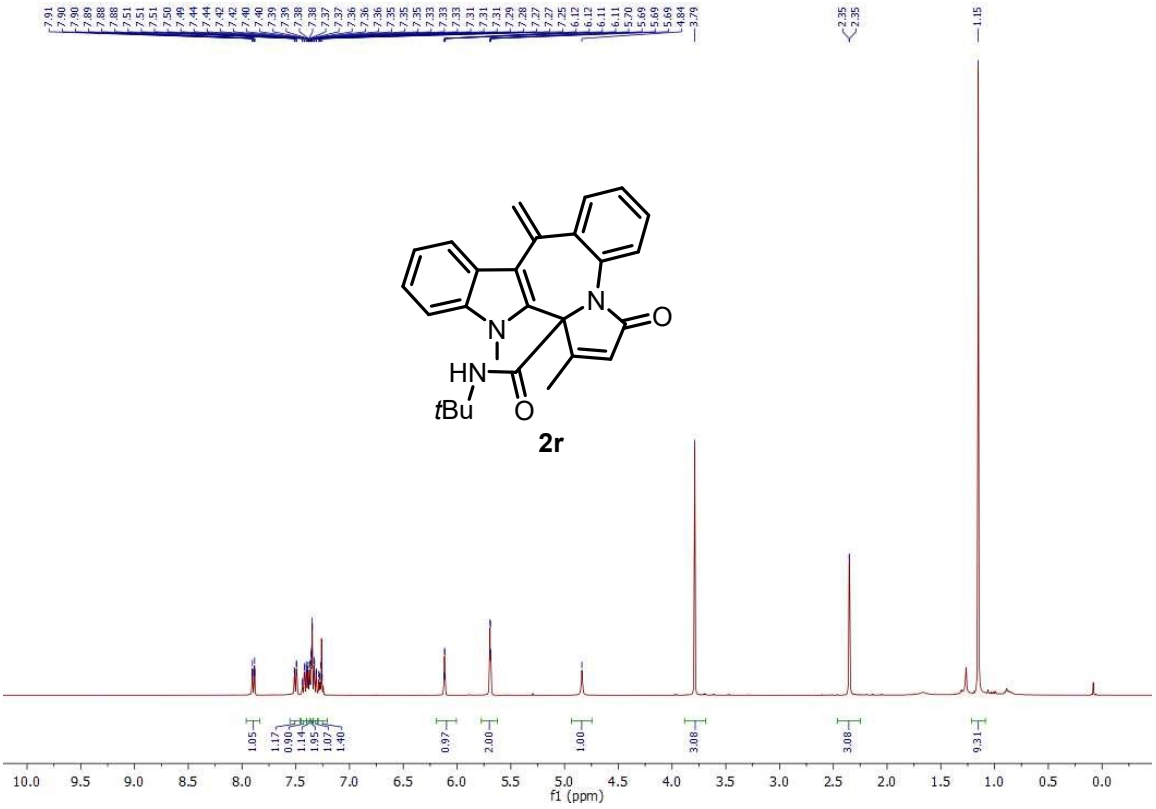


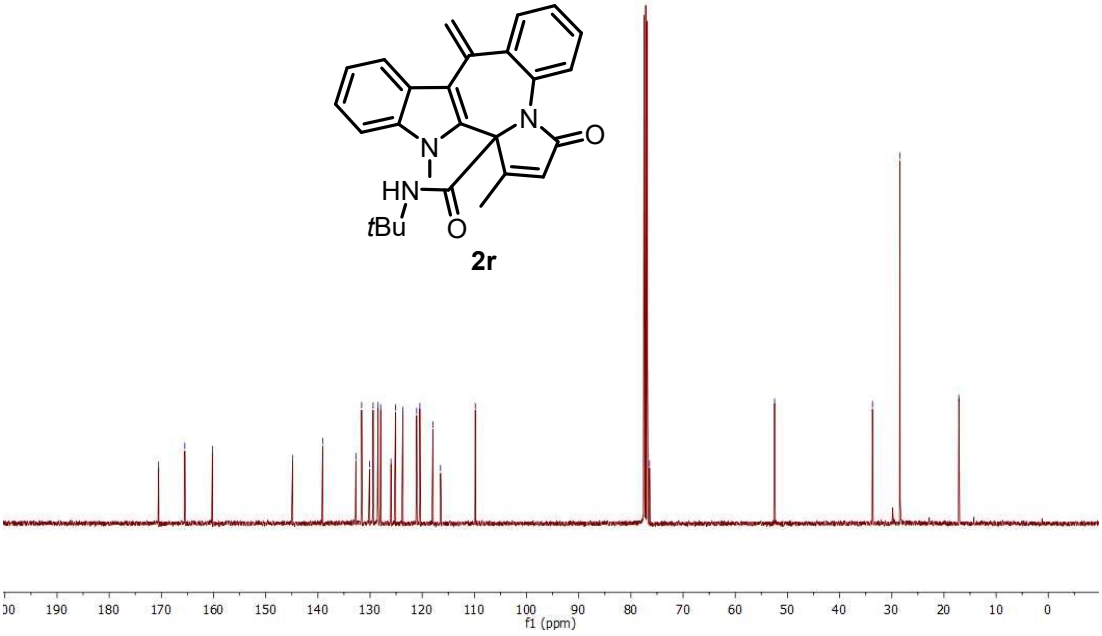
2p

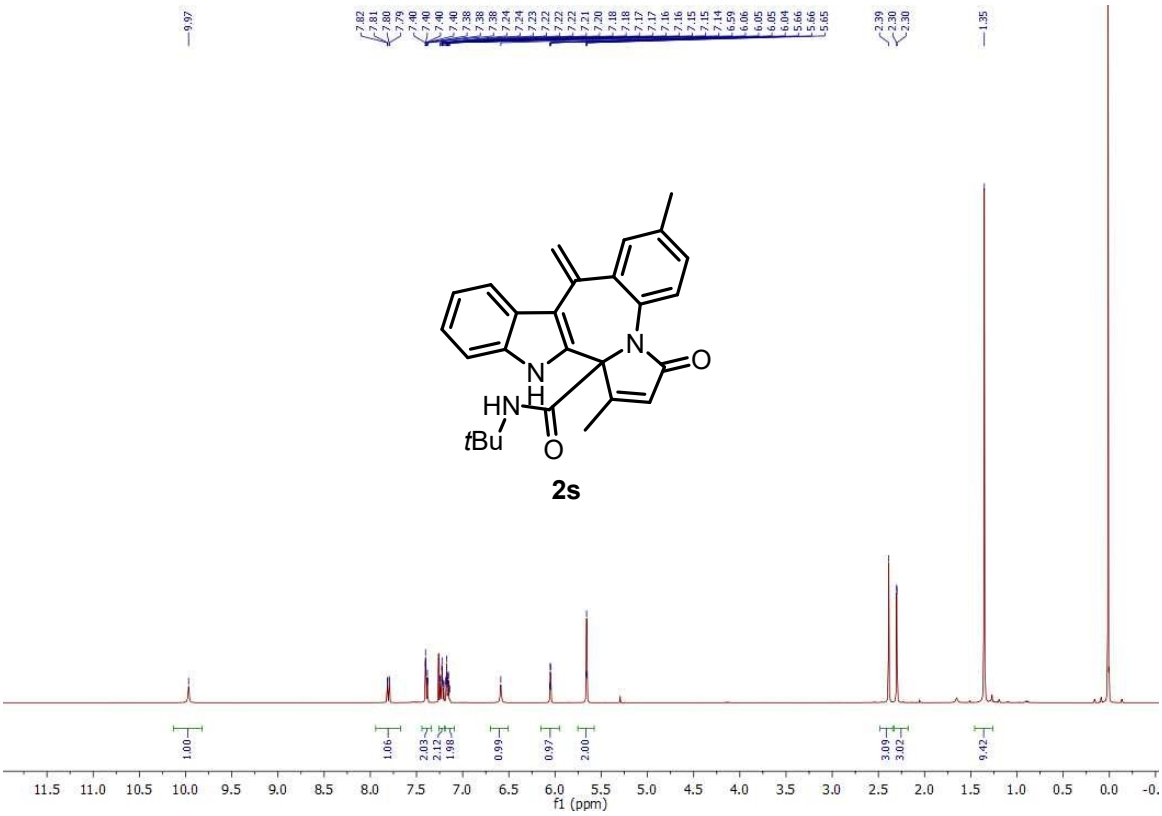



HN
tBu
O
N
O
2q
f1 (ppm)

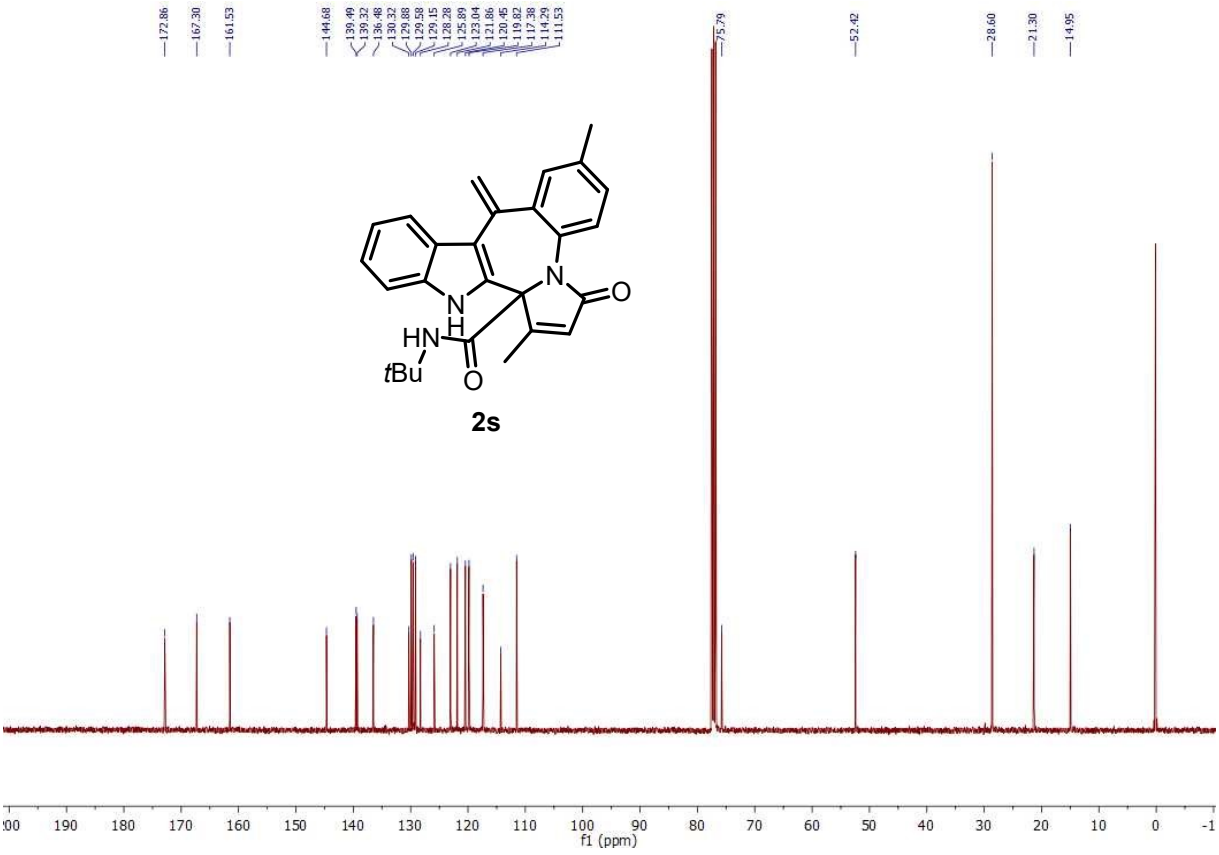

HN
tBu
O
N
O
2q
f1 (ppm)


HN
tBu
O
N
O
2r
f1 (ppm)

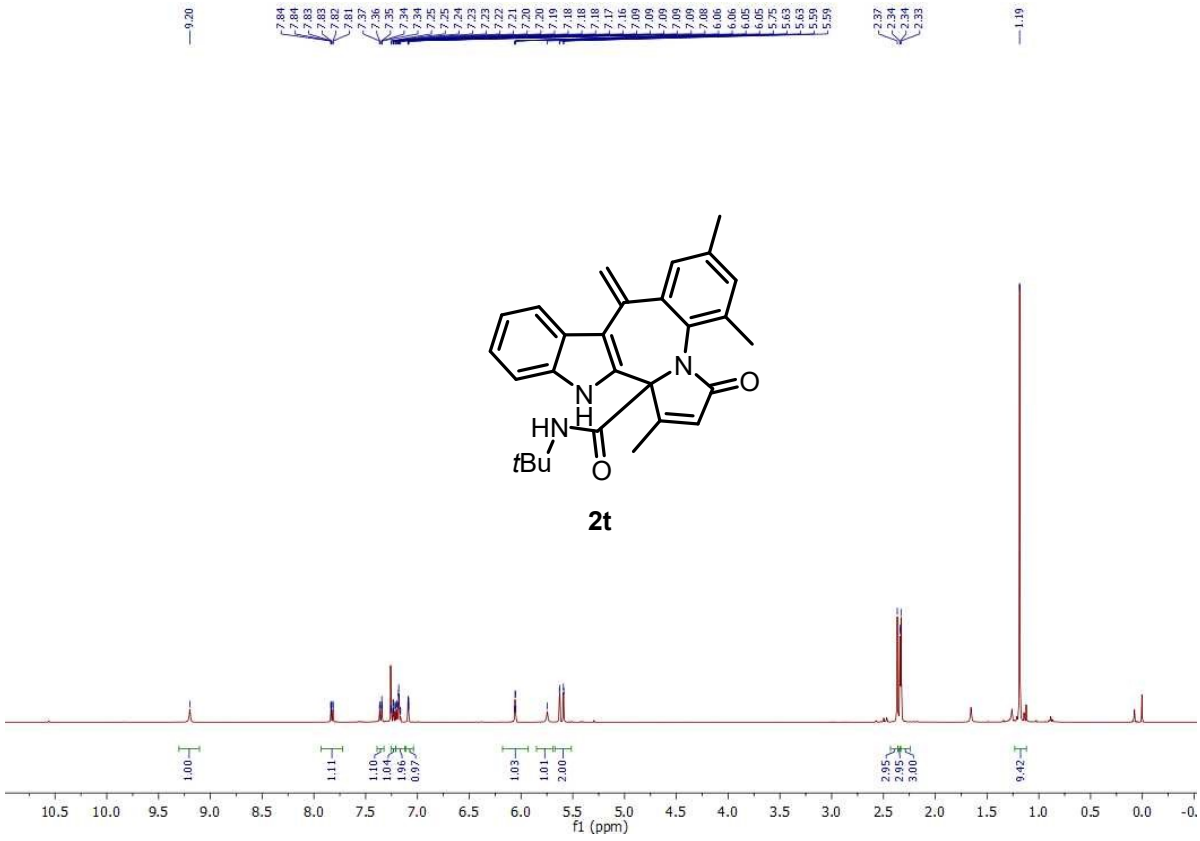

HN
tBu
O
N
O
2r
f1 (ppm)



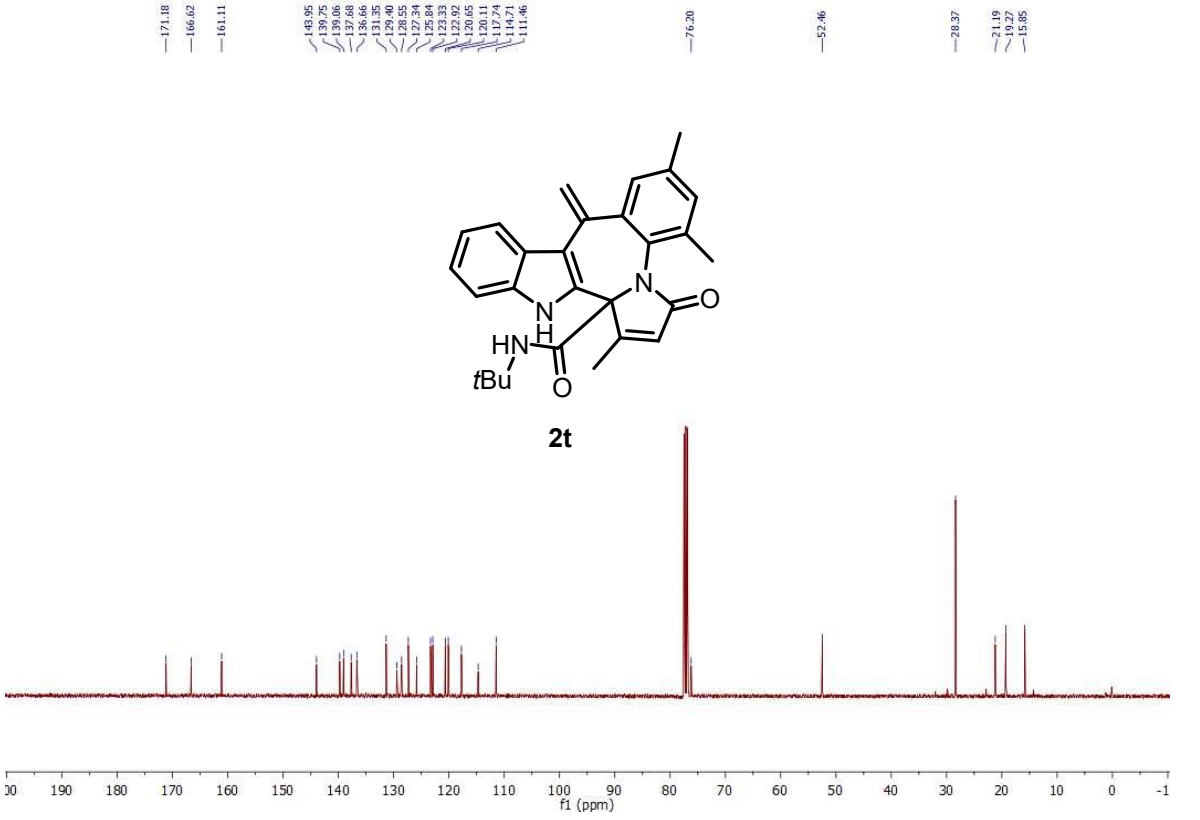
2s



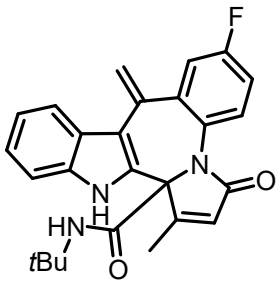
2s



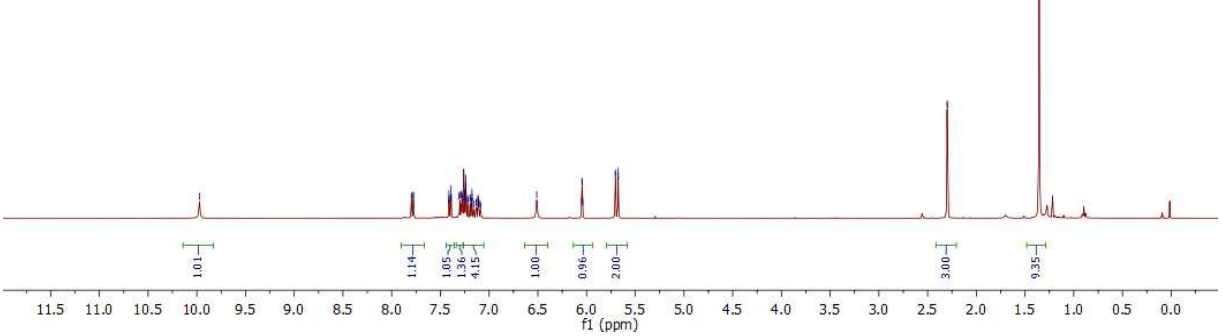
2t

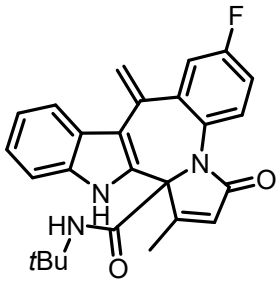


2t

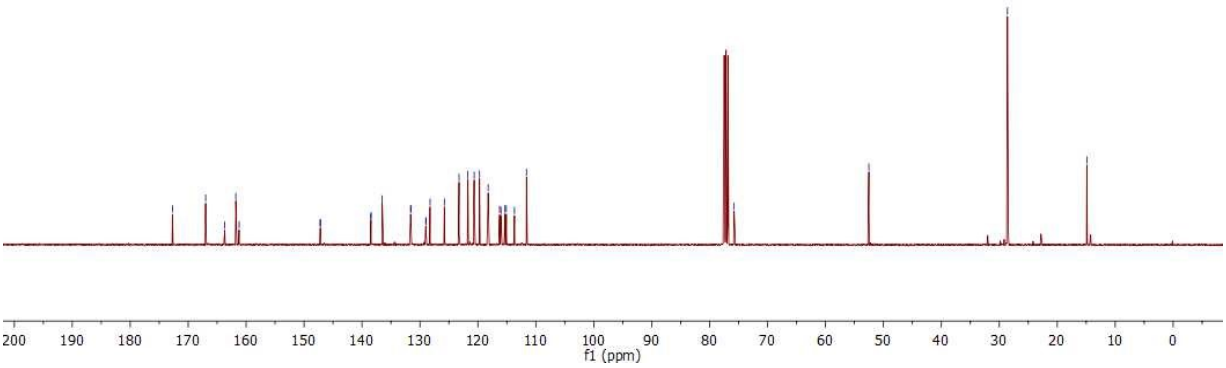

F
N
O
N
H
HN
tBu
O

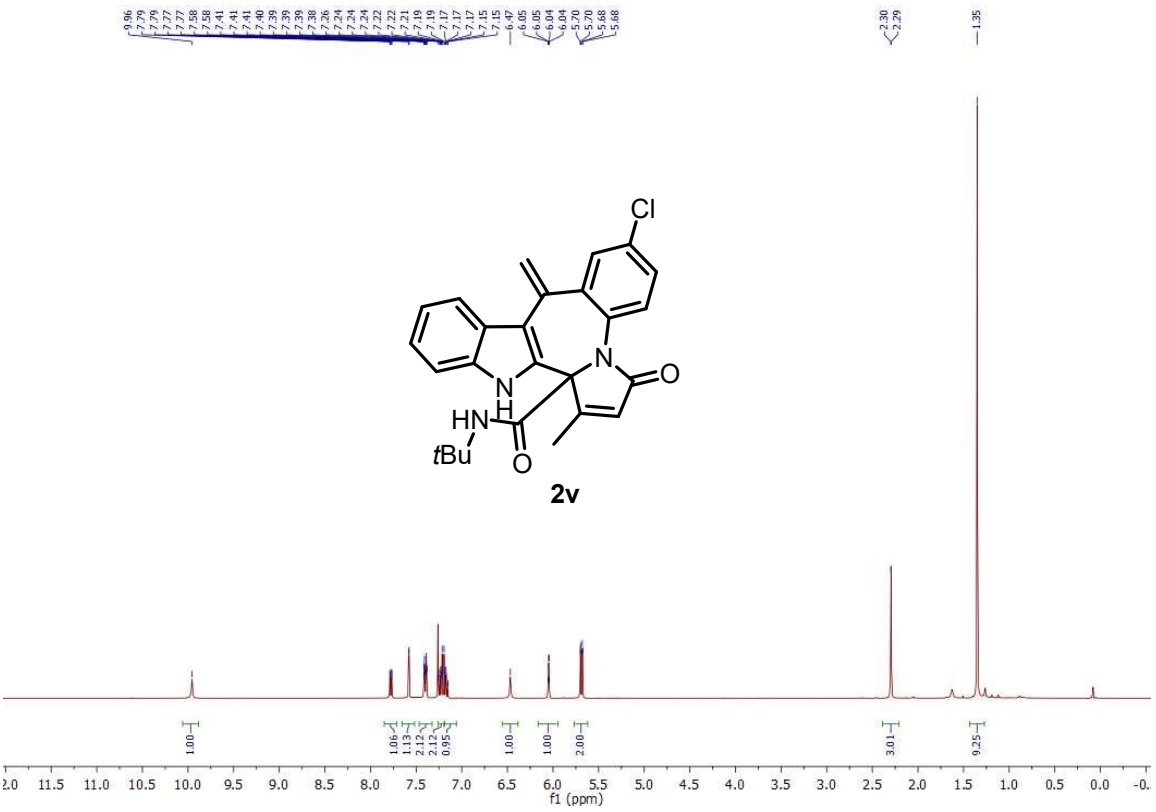
2u


1.01
1.14
1.05
1.36
4.15
1.00
0.96
2.00
3.00
9.35
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

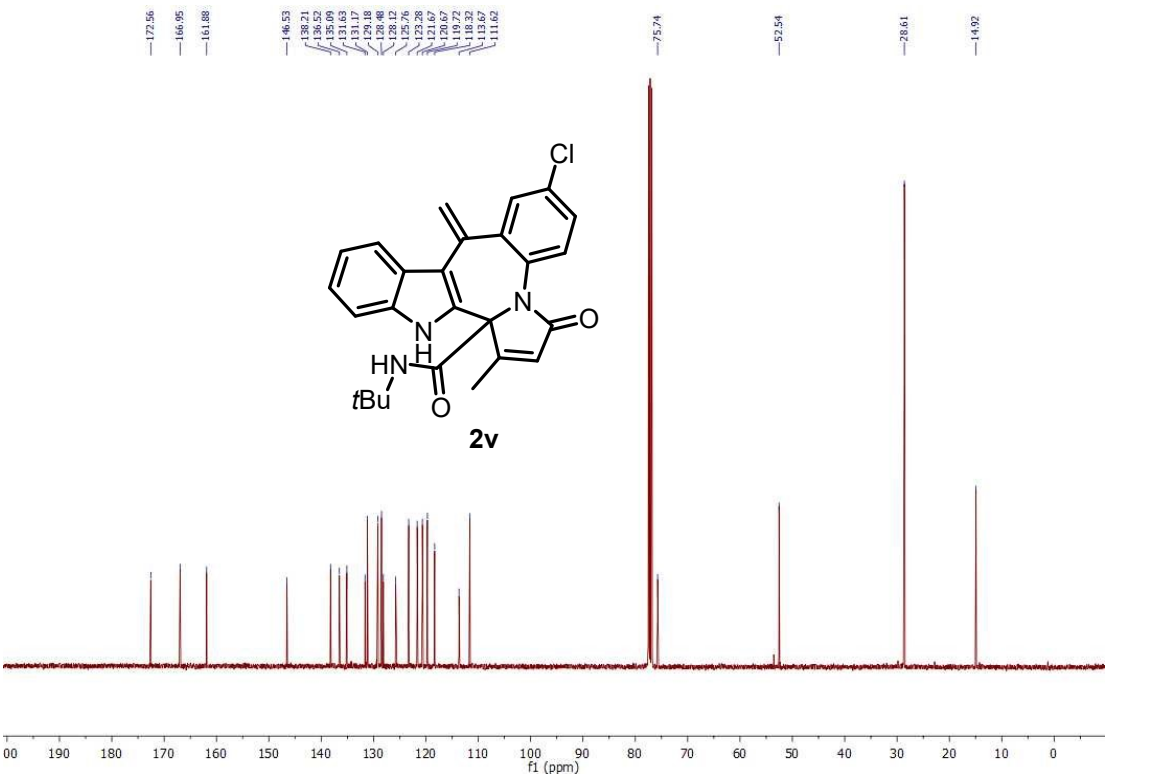

F
N
O
N
H
HN
tBu
O

2u

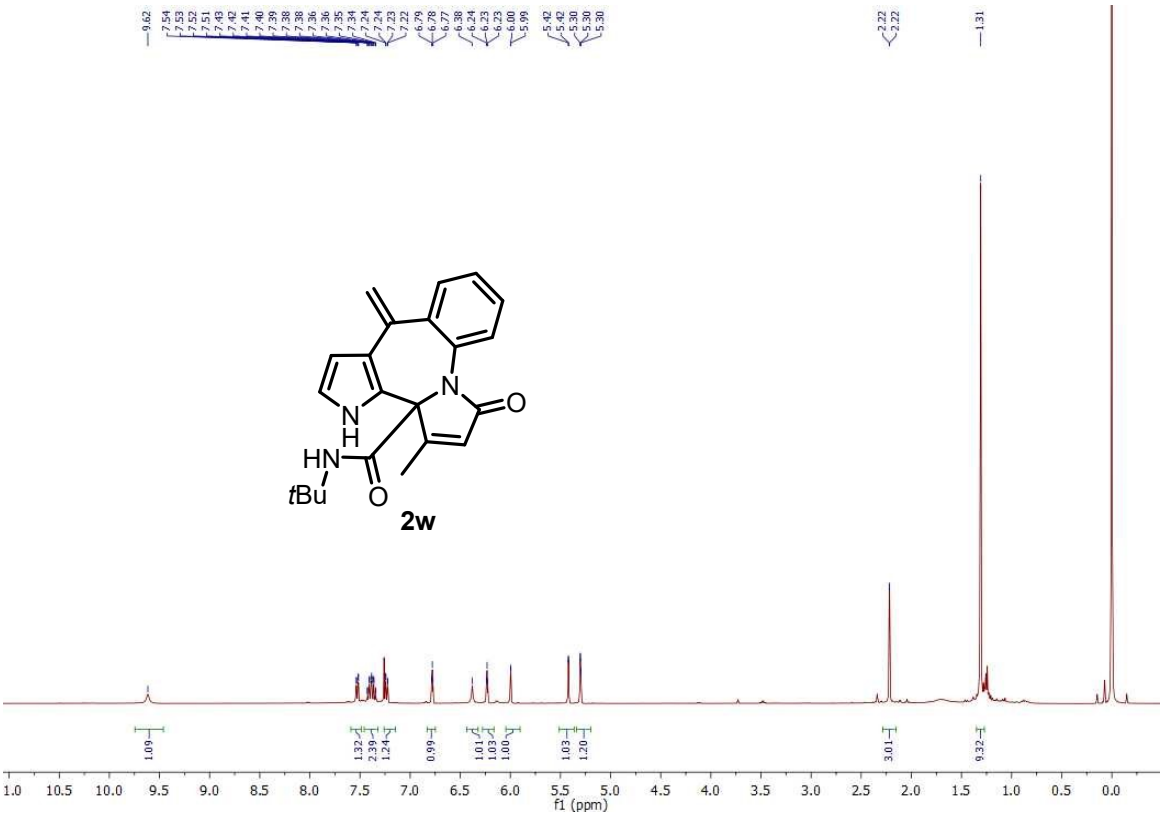

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

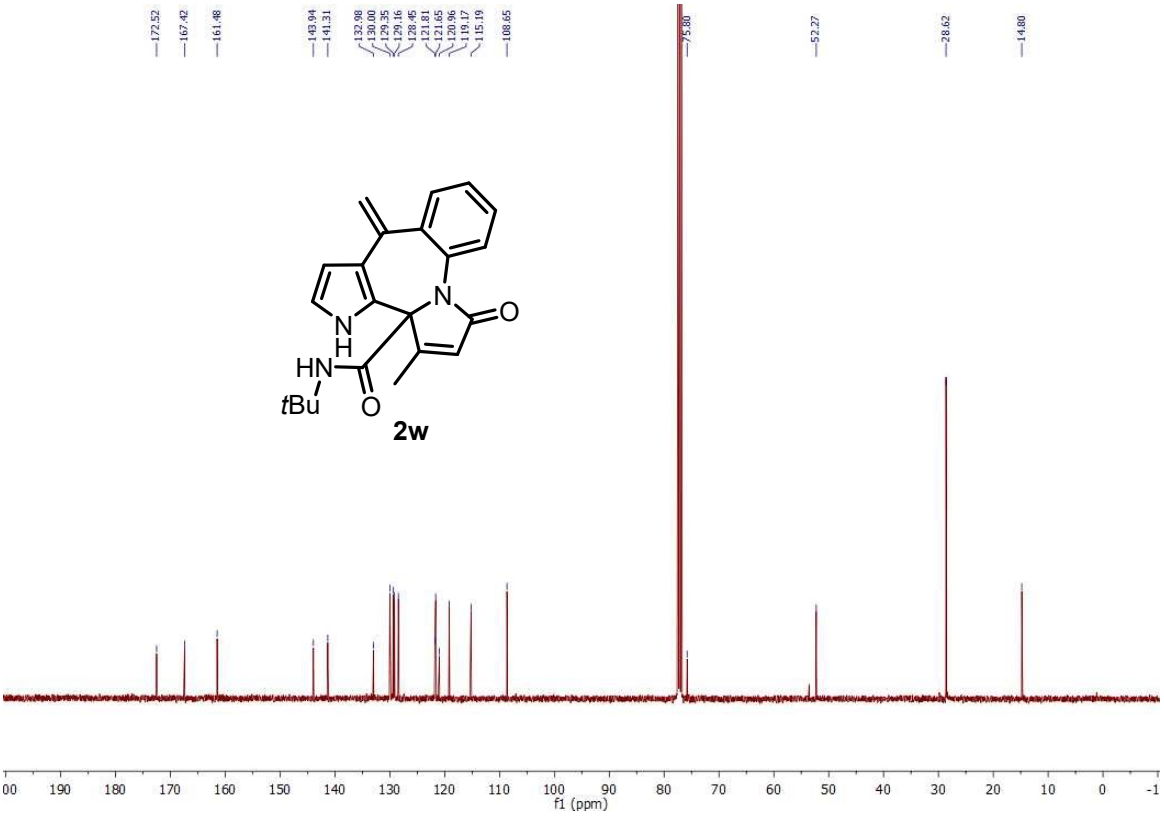


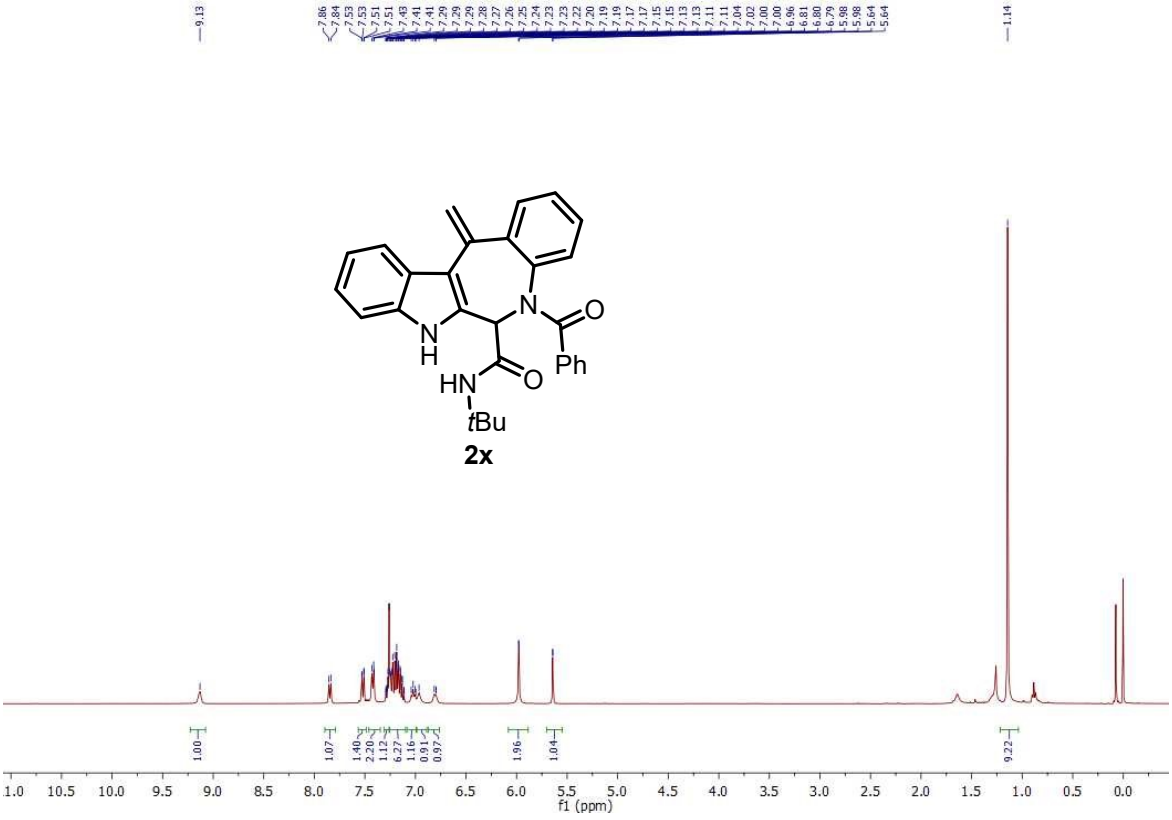
2v

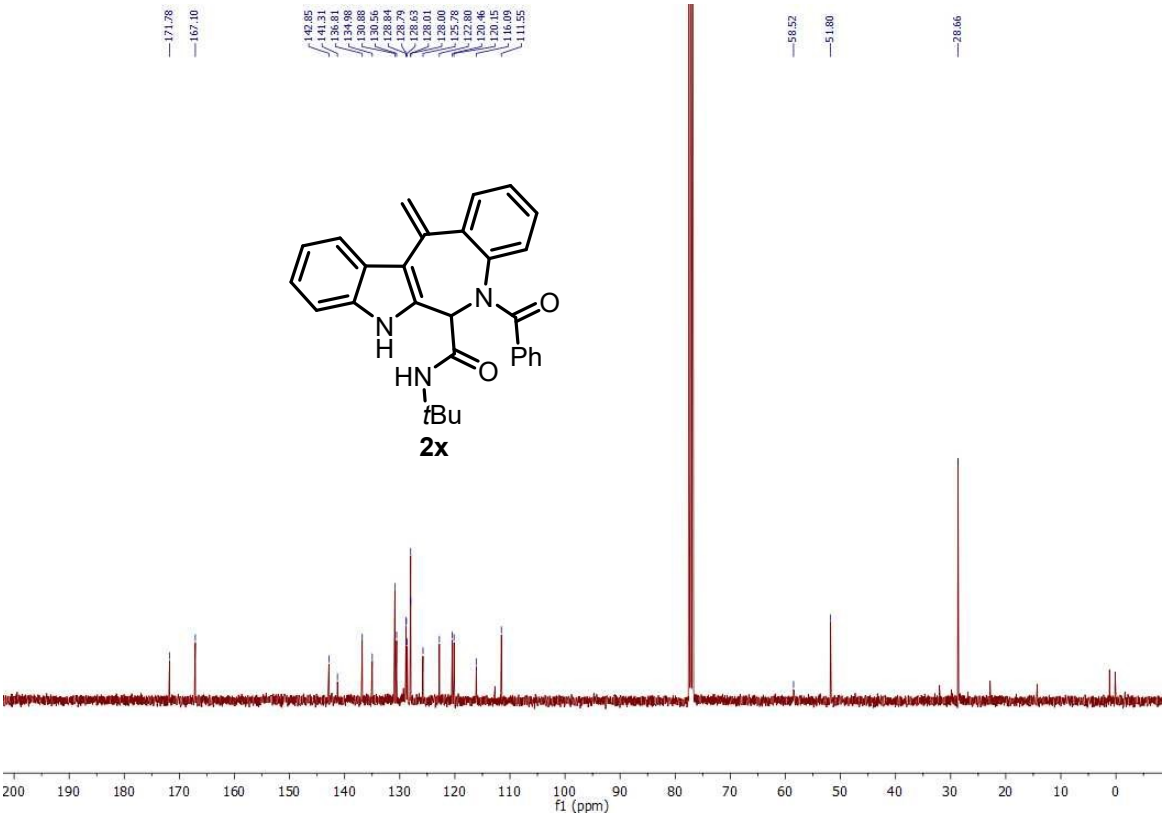


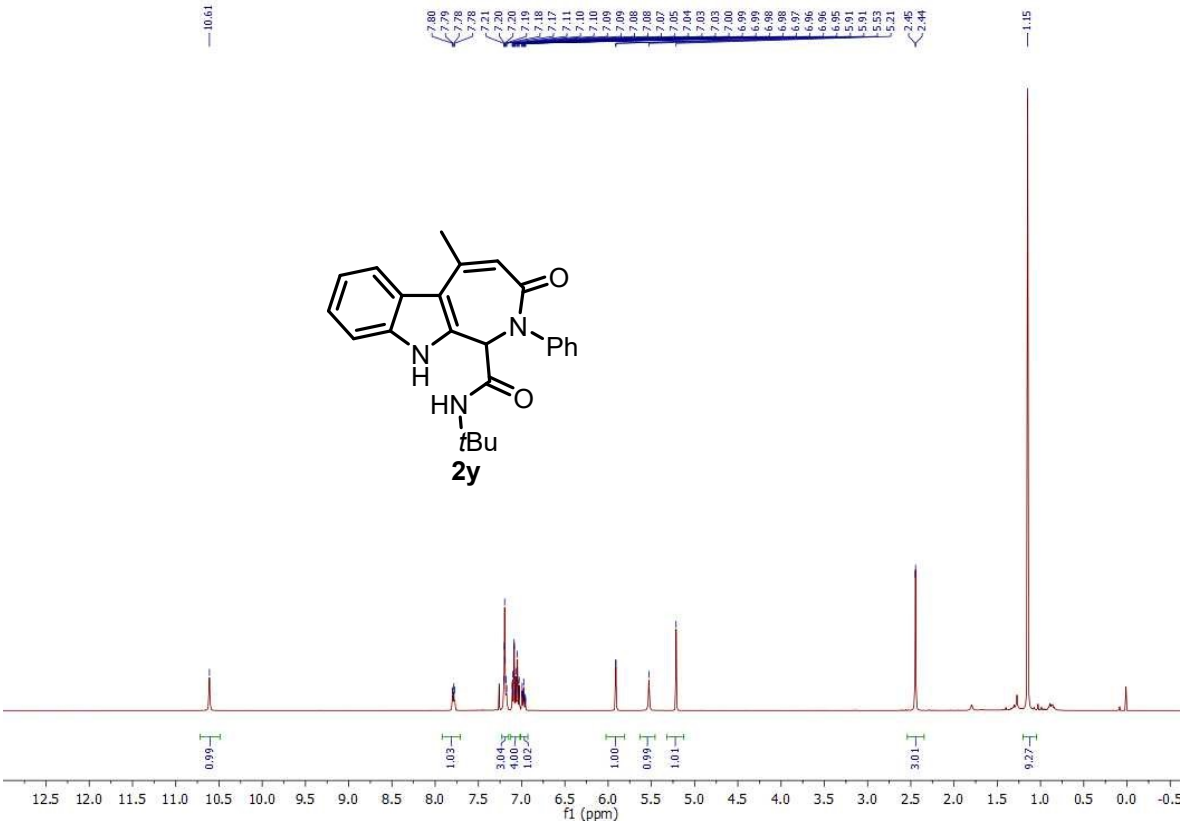
2v

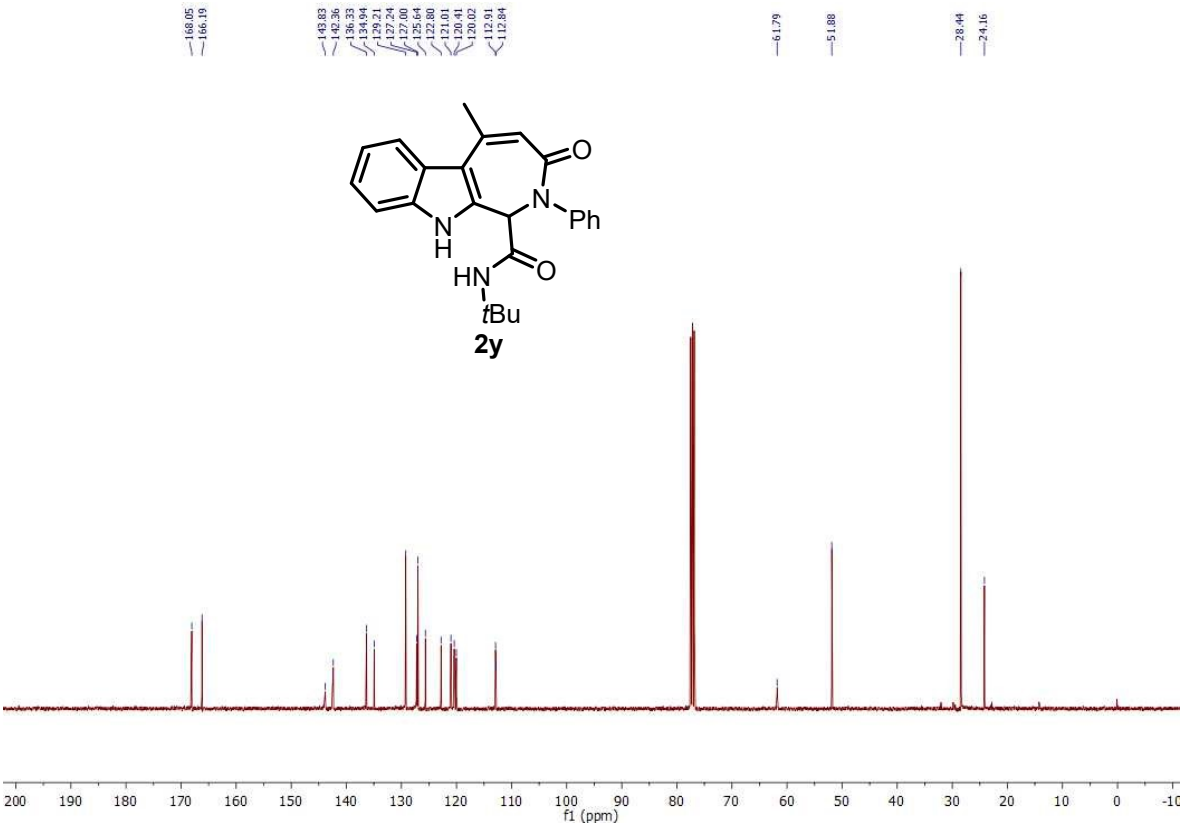

HN
tBu
O
N
H
N
O
2w
f1 (ppm)

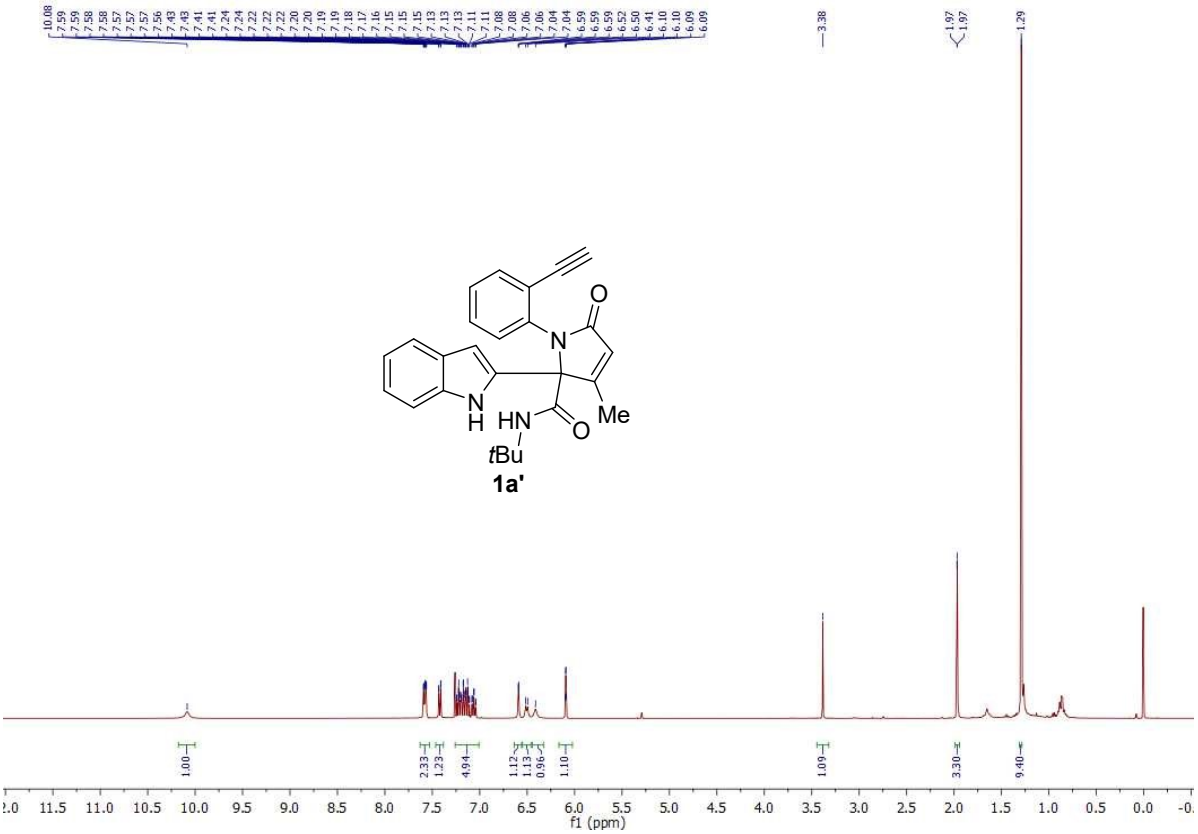

HN
tBu
O
N
H
N
O
2w
f1 (ppm)

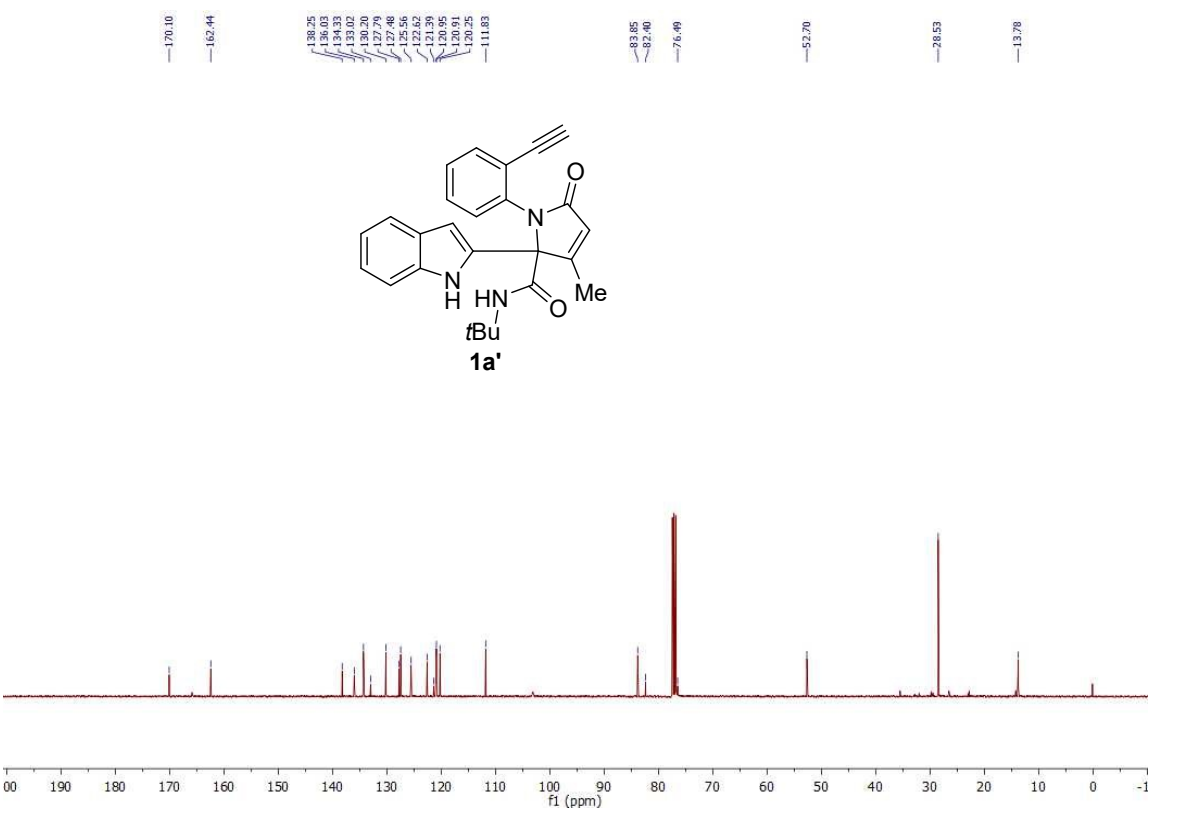

9.13
7.86
7.84
7.53
7.53
7.51
7.51
7.43
7.41
7.41
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.20
7.19
7.19
7.17
7.17
7.15
7.15
7.13
7.13
7.11
7.11
7.04
7.02
7.00
7.00
6.96
6.81
6.80
6.79
5.98
5.98
5.64
5.64
1.14
N
O
N
H
Ph
HN
O
tBu
2x
1.00
1.07
1.40
2.20
1.12
6.27
1.16
0.91
0.97
1.96
1.04
9.22
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.78
167.10
142.85
141.31
136.81
134.98
130.88
130.56
128.84
128.79
128.65
128.01
128.00
125.78
122.80
120.46
120.15
116.09
111.55
58.52
51.80
28.66
N
O
N
H
Ph
HN
O
tBu
2x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.61
7.80
7.79
7.78
7.78
7.21
7.20
7.20
7.19
7.18
7.17
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.05
7.04
7.03
7.03
7.00
6.99
6.99
6.98
6.98
6.97
6.96
6.96
6.95
5.91
5.91
5.53
5.21
2.45
2.44
1.15
O
N
Ph
N
H
O
HN
tBu
2y
0.99
1.03
3.04
4.00
1.02
1.00
0.99
1.01
3.01
9.27
f1 (ppm)


168.05
166.19
143.83
142.36
136.33
134.94
129.21
127.24
127.00
125.64
122.80
121.01
120.41
120.02
112.91
112.84
61.79
51.88
28.44
24.16
O
N
Ph
N
H
O
HN
tBu
2y
f1 (ppm)


10.08
7.59
7.59
7.58
7.58
7.57
7.57
7.57
7.56
7.43
7.41
7.41
7.24
7.24
7.22
7.22
7.22
7.20
7.20
7.19
7.19
7.18
7.17
7.16
7.15
7.15
7.15
7.13
7.13
7.13
7.11
7.11
7.08
7.08
7.06
7.06
7.04
7.04
6.59
6.59
6.59
6.52
6.50
6.41
6.10
6.10
6.09
6.09
3.38
1.97
1.97
1.29
O
N
N
H
HN
O
Me
tBu
1a'
1.00
2.33
1.23
4.94
1.12
1.13
0.96
1.10
1.09
3.30
9.40
f1 (ppm)


170.10
162.44
138.25
136.03
134.33
133.02
130.20
127.79
127.48
125.56
122.62
121.39
120.95
120.91
120.25
111.83
83.85
82.40
76.49
52.70
28.53
13.78
O
N
N
H
HN
O
Me
tBu
1a'
f1 (ppm)