Metal-free Spirocyclization of *N*-Arylpropiolamides with Glyoxylic Acids: Access to Complex Azaspiro-fused Tricycles

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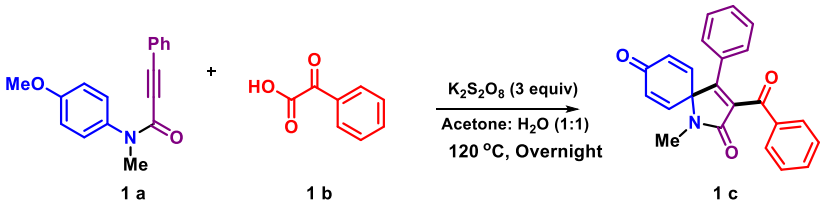
Supporting Information

1. Methods:

All reactions were carried out under air atmosphere in screw cap reaction tubes and the workups were performed under air. All the solvents used for the reactions were dried by following the reported procedures. Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. Reactions were monitored using thin-layer chromatography (SiO_2).A gradient elution using petroleum ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel $60F_{254}$). TLC plates were visualized with UV light (254 nm) or $KMnO_4$ stain. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. NMR studies were performed on Bruker Avance DPX at 400 MHz (1H) or 500 MHz (1H) and at 100 MHz (13C) or 125 MHz (13C), respectively. Chemical shifts (d) are reported in ppm, using the residual solvent peak in $CDCl_3$ (dH = 7.26 and dC = 77.02) ppm as internal standards, and coupling constants (*J*) are given in Hz. HRMS were recorded on Bruker MaXis impact mass spectrometer using ESI-TOF techniques.

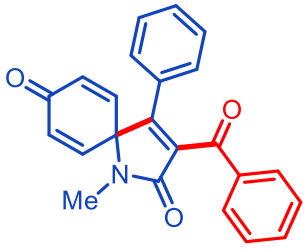
Typical Procedure for the Synthesis of azaspiro[4.5]deca-3,6,9-triene-2,8-diones



1 a 1 b 1 c

Amine **1a** (53.0 mg, 0.2 mmol), phenylglyoxalic acid **2a** (60.0 mg, 0.4 mmol) and $K_2S_2O_8$ (162.2 mg, 0.6 mmol) were added to an oven-dried screw cap reaction tube equipped with a stir bar. Then, acetone (2 mL) and water (2 ml) were added via syringe and reaction mixture was heated at 120 °C overnight. After that the resultant reaction mixture was cooled to room temperature and, quenched with sat. $NaHCO_3$ solution. The resulting mixture was extracted with ethyl acetate (5 ml X 3) and the organic layer was collected and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, mesh 100-200; hexane: ethyl acetate; 40:60) to give the product **3a** (63 mg, 89%).

3a.



3-benzoyl-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

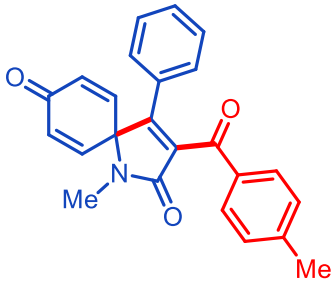
Physical state: Colourless solid , Yield 63 mg, 89 % from 53.0 mg of **1a** and 1.12 g, 87% from 1g of **1a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.9Hz, 2H), 7.26 (dd, *J* = 7.7 Hz, 3H), 7.18 (t, *J* = 7.7, 2H), 6.70 (d, *J* = 9.9 Hz, 2H), 6.58 (d, *J* = 9.9 Hz, 2H), 2.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 183.7, 167.1, 154.5, 144.6, 136.0, 135.4, 134.1, 133.4, 130.4, 129.9, 129.3, 128.7, 128.6, 127.7, 67.1, 25.8.

HRMS (ESI): $C_{23}H_{18}NO_3$ $[M+H]^+$ calculated = 356.1281; found = 356.1286.

3b:



1-methyl-3-(4-methylbenzoyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.[1]

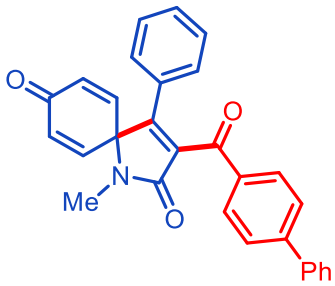
Physical state: Colourless solid, Yield 64 mg, 86 %, from 53.0 mg of **1a**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 3H), 7.19 (t, *J* = 7.2 Hz, 4H), 6.70 (d, *J* = 9.4 Hz, 2H), 6.58 (d, *J* = 9.4 Hz, 2H), 2.92 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 183.7, 167.2, 153.9, 145.3, 144.7, 136.2, 133.3, 133.1, 130.4, 130.5, 129.5, 129.4, 128.7, 127.7, 67.1, 25.8, 21.7.

HRMS (ESI): $C_{24}H_{20}NO_3$ $[M+H]^+$ calculated = 370.1438; found = 370.1446.

3c:



3-([1,1'-biphenyl]-4-carbonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

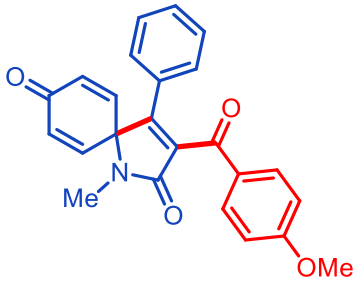
Physical state: Colourless solid, Yield 80 mg, 88 %, from 53.0 mg of 1a

1H NMR (400 MHz, CDCl3) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.55 (m, 2H), 7.49 – 7.36 (m, 4H), 7.30 (dd, *J* = 7.4, 5.8 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 2H), 71 (d, J = 10.1 Hz, 2H), 6.60 (d, J = 10.1 Hz, 2H), 2.94 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 190.9, 183.8, 167.3, 154.5, 146.9, 144.7, 139.6, 136.2, 134.3, 133.5, 130.6, 130.1, 129.0, 128.9, 128.5, 127.8, 127.4, 127.3, 127.1, 67.3, 25.9.

HRMS (ESI): $C_{29}H_{22}NO_3$ $[M+H]^+$ calculated = 432.1594; found = 432.1588.

3d:



3-(4-Methoxybenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

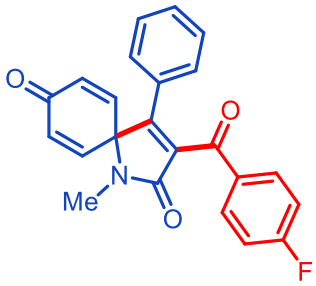
Physical state: Colourless solid, Yield 65.5 mg, 85 %, from 53.0 mg of **1a**

^{1}H NMR (400 MHz, CDCl3) δ 7.82 (d, *J* = 8.6, 2H), 7.27 (t, *J* = 8.7 Hz, 3H), 7.19 (t, *J* = 7.4 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.72 – 6.65 (d, *J* = 9.4 Hz, 2H), 6.57 (d, *J* = 9.4 Hz, 2H), 3.82 (s, 3H), 2.91 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 189.6, 183.8, 167.3, 164.4, 153.6, 144.8, 136.3, 133.3, 131.9, 130.4, 130.1, 128.7, 127.7, 113.9, 67.1, 55.4, 25.8.

HRMS (ESI): $C_{24}H_{20}NO_4$ $[M+H]^+$ calculated = 386.1387; found = 386.1391.

3e:



3-(4-fluorobenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

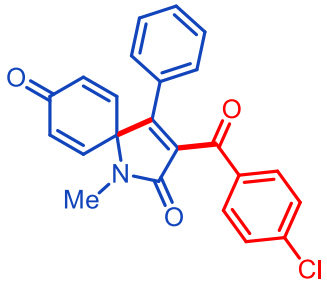
Physical state: Brown solid, Yield 56.5 mg, 81 %, from 53.0 mg of 1a

^{1}H NMR (400 MHz, CDCl3) δ 7.92 – 7.79 (m, 2H), 7.33 – 7.17 (m, 5H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.73 – 6.64 (m, 2H), 6.58 (d, *J* = 10.1 Hz, 2H), 2.92 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 189.5, 183.6, 166.9, 166.2 (d, *J*=255.8 Hz), 154.8, 144.4, 135.6, 133.4, 132.1, 132.9 (d, *J* = 11.3 Hz), 130.5, 129.8, 128.7, 127.6, 116.9 (d, *J* = 22.1 Hz), 67.1, 25.8.

HRMS (ESI): $C_{23}H_{17}FNO_3$ $[M+H]^+$ calculated = 374.1187; found = 374.1192.

3f:



3-(4-chlorobenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

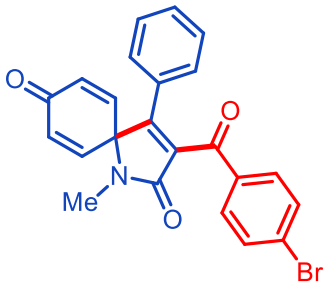
Physical state: Brown sticky solid, Yield 64.5 mg, 83 %, from 53.0 mg of 1a

^{1}H NMR (400 MHz, CDCl3) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.12 (m, 5H), 6.68 (d, *J* = 9.4 Hz, 2H), 6.58 (d, *J* = 9.6 Hz, 2H), 2.92 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 189.9, 183.6, 166.9, 155.1, 144.3, 140.7, 135.5, 133.8, 133.5, 130.7, 129.8, 129.0, 128.8, 127.6, 67.2, 25.8.

HRMS (ESI): $C_{23}H_{17}ClNO_3$ $[M+H]^+$ calculated = 390.0891; found = 390.0887.

3g:



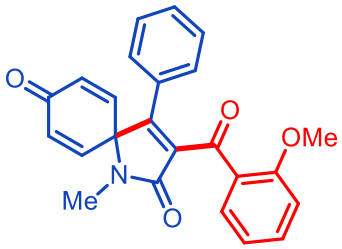
Physical state: Yellowish brown solid, Yield 71 mg, 82 %, from 53.0 mg of 1a

1H NMR (400 MHz, CDCl3) δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.15 (m, 5H), 6.67 (d, *J* = 10.1 Hz, 2H), 6.57 (d, *J* = 10.1 Hz, 2H), 2.90 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 190.2, 183.7, 167.0, 155.2, 144.4, 135.6, 134.3, 133.6, 132.1, 130.8, 130.8, 129.9, 129.7, 128.9, 127.8, 67.3, 25.9.

HRMS (ESI): $C_{23}H_{17}BrNO_3$ $[M+H]^+$ calculated = 434.0386; found = 434.0380.

3i:



3-(2-methoxybenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

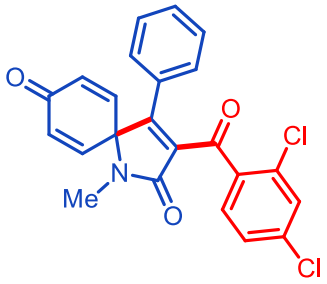
Physical state: Brown solid, Yield 51.6 mg, 67 %, from 53.0 mg of 1a

1H NMR (400 MHz, CDCl3) δ 7.77 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.49 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.29 – 7.18 (m, 5H), 7.01 (t, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.61 (d, *J* = 9.3 Hz, 2H), 6.52 (d, *J* = 9.3 Hz, 2H), 3.84 (s, 3H), 2.89 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 189.7, 184.0, 167.4, 159.7, 152.4, 145.0, 139.6, 135.3, 133.4, 131.2, 130.6, 130.1, 128.6, 128.0, 126.9, 121.2, 112.0, 67.1, 55.9, 25.9.

HRMS (ESI): $C_{24}H_{20}NO_4$ $[M+H]^+$ calculated = 386.1387; found = 386.1383.

3j:



Physical state: Brown sticky solid, Yield 67 mg, 79 %, from 53.0 mg of 1a

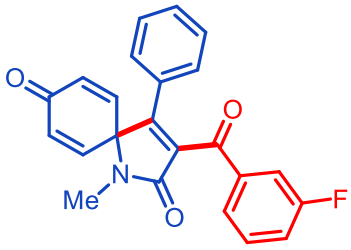
3-(2,4-dichlorobenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

1H NMR (400 MHz, CDCl3) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.26 – 7.21 (m, 3H), 7.20 – 7.15 (m, 2H), 6.60 (d, *J* = 10.2 Hz, 2H), 6.53 (d, *J* = 10.2 Hz, 2H), 2.91 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 188.9, 183.6, 166.5, 157.4, 143.6, 141.1, 139.0, 135.4, 133.8, 132.2, 130.5, 130.2, 128.6, 127.8, 127.6, 116.1, 67.4, 26.0.

HRMS (ESI): $C_{23}H_{16}Cl_2NO_3$ $[M+H]^+$ calculated = 424.0502; found = 424.0507.

3k:



3-(3-fluorobenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

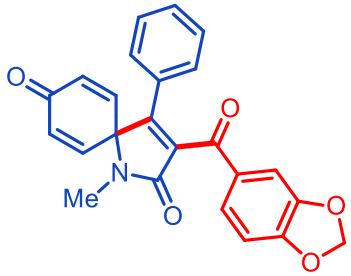
Physical state: Yellow sticky solid, Yield 31 mg, 81 %, from 27.5 mg of 1a

1H NMR (400 MHz, CDCl3) δ 7.62 – 7.57 (m, 1H), 7.55 – 7.49 (m, 1H), 7.35 (dd, *J* = 7.9, 5.4 Hz, 1H), 7.30 – 7.14 (m, 6H), 6.67 (d, *J* = 10.2 Hz, 2H), 6.58 (d, *J* = 10.2 Hz, 2H), 2.93 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 190.0, 183.7, 167.0, 162.2 (d, *J* = 250.9 Hz), 155.4, 144.4, 137.6, 135.6, 133.6, 130.8, 130.4 (d, J = 3.3 Hz), 129.9, 128.9, 127.8, 125.4, 121.3 (d, *J* = 22.2 Hz), 115.8 (d, *J* = 21.0 Hz),, 115.1, 67.97, 67.31, 25.96, 25.61.

HRMS (ESI): $C_{23}H_{17}FNO_3$ $[M+H]^+$ calculated = 374.1187; found = 374.1189.

3l:



3-(benzo[d][1,3]dioxole-5-carbonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

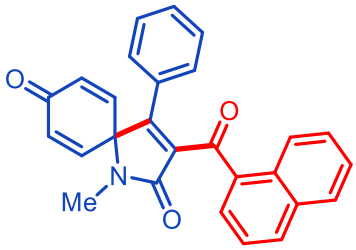
Physical state: Yellow solid, Yield 63.9 mg, 80 %, from 53.0 mg of **1a**

^{1}H NMR (400 MHz, CDCl3) δ 7.36 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 3H), 7.24 – 7.15 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.57 (d, *J* = 10.0 Hz, 2H), 6.01 (s, 2H), 2.89 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 189.3, 183.8, 167.3, 153.8, 153.0, 148.5, 144.8, 136.3, 133.5, 130.6, 130.5, 130.1, 128.8, 127.8, 127.1, 108.4, 108.1, 102.1, 67.2, 25.9.

HRMS (ESI): $C_{24}H_{17}NNaO_5$ $[M+Na]^+$ calculated = 422.0999; found = 422.1007.

3m:



3-(1-naphthoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

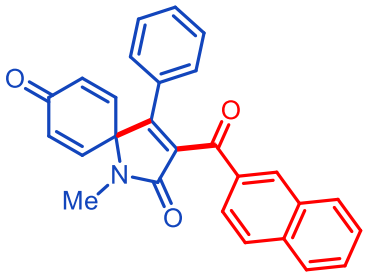
Physical state: Brown solid, Yield 61 mg, 71 %, from 53.0 mg of **1a**

1H NMR (400 MHz, CDCl3) δ 8.96 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.64 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.42 – 7.36 (m, 1H), 7.25 – 7.20 (m, 2H), 7.20 – 7.13 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.69 (t, *J* = 6.3 Hz, 2H), 6.56 (d, *J* = 10.1 Hz, 2H), 2.93 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 192.8, 183.8, 167.3, 154.8, 144.6, 137.7, 134.8, 133.9, 133.5, 132.8, 132.2, 130.7, 130.3, 130.1, 128.8, 128.6, 128.5, 127.7, 126.8, 125.8, 124.2, 67.2, 25.9.

HRMS (ESI): $C_{27}H_{20}NO_3$ $[M+H]^+$ calculated = 406.1438; found = 406.1443.

3n:



3-(2-naphthoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Physical state: Brown solid, Yield 63.2 mg, 78 %, from 53.0 mg of **1a**

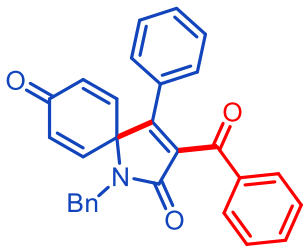
1H NMR (500 MHz, CDCl3) δ 8.34 (s, 1H), 8.00 – 7.94 (m, 1H), 7.91 (dd, *J* = 8.1, 5.2 Hz, 1H), 7.85 (dd, *J* = 8.4, 3.0 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.33 (dd, *J*

= 5.3, 3.3 Hz, 2H), 7.28 – 7.21 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 2H), 6.78 (d, *J* = 9.9 Hz, 2H), 6.64 (d, *J* = 9.9 Hz, 2H), 2.98 (s, 3H).

13C NMR (126 MHz, CDCl3) δ 191.3, 183.9, 167.4, 154.5, 144.8, 136.1, 133.5, 133.0, 132.3, 130.6, 130.1, 129.8, 129.1, 128.7, 128.8, 127.7, 127.8, 126.9, 124.1, 67.3, 26.0.

HRMS (ESI): $C_{27}H_{20}NO_3$ $[M+H]^+$ calculated = 406.1438; found = 406.1435.

3o:



3-benzoyl-1-benzyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.,

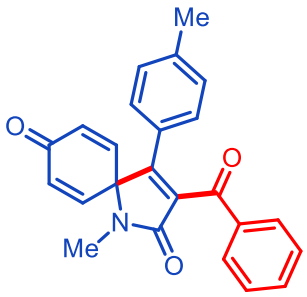
Physical state: Off-white solid, Yield 76 mg, 79 %, from 68.0 mg of **1b**

1H NMR (400 MHz, CDCl3) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.33-7.25 (m, 6H), 7.22-7.16 (m, , 4H), 6.54 (d, *J* = 9.7 Hz, 2H), 6.37 (d, *J* = 9.7 Hz, 2H), 4.61 (s, 2H).

13C NMR (126 MHz, CDCl3) δ 191.3, 184.1, 167.5, 155.3, 144.9, 137.4, 136.2, 135.7, 134.4, 132.9, 130.6, 130.0, 129.6, 129.1, 128.77, 128.79, 128.83, 128.1, 128.0, 67.9, 44.8.

HRMS (ESI): $C_{29}H_{22}ClNO_3$ $[M+H]^+$ calculated = 432.1594; found = 4321597.

3r:



3-benzoyl-1-methyl-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

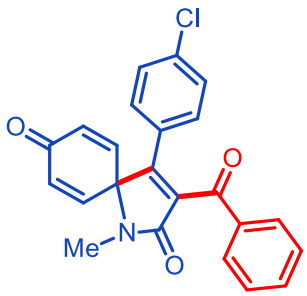
Physical state: Colourless solid Yield 63.5 mg, 76 %, from 56.0 mg of **1e**

1H NMR (400 MHz, CDCl3) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.42 – 7.35 (m, 2H), 7.19 – 7.13 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 9.9 Hz, 2H), 6.55 (d, *J* = 9.9 Hz, 2H), 2.91 (s, 3H), 2.23 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 191.6, 183.9, 167.4, 154.5, 145.0, 141.1, 135.6, 135.3, 134.2, 133.4, 129.6, 129.5, 128.7, 127.7, 127.2, 67.1, 25.8, 21.3.

HRMS (ESI): $C_{24}H_{20}NO_3$ $[M+H]^+$ calculated = 370.1438; found = 370.1447.

3s:



Physical state: Brown solid, Yield 62 mg, 78 %, from 60.0 mg of **1f**

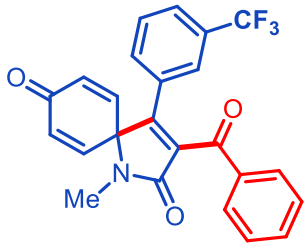
3-benzoyl-4-(4-chlorophenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.14 (m, 4H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.58 (d, *J* = 10.0 Hz, 2H), 2.91 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 191.1, 183.6, 167.0, 153.2, 144.4, 136.8, 136.7, 135.4, 134.5, 133.7, 129.5, 129.2, 129.13=, 128.9, 128.4, 67.2, 26.0.

HRMS (ESI): $C_{23}H_{17}ClNO_3$ $[M+H]^+$ calculated = 390.0891; found = 390.0898.

3t:



3-benzoyl-1-methyl-4-(3-(trifluoromethyl)phenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

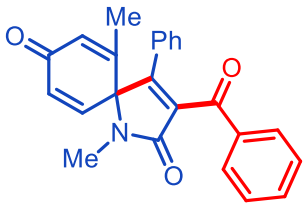
Physical state: Brown sticky solid, Yield 66.8 mg, 79 %, from 67.0 mg of **1g**

1H NMR (400 MHz, CDCl3) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.47 – 7.31 (m, 4H), 6.69 (d, *J* = 10.1 Hz, 2H), 6.59 (d, *J* = 10.1 Hz, 2H), 2.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 183.3, 166.8, 153.0, 144.0, 137.7, 135.4, 134.5, 133.9, 131.2 (q, *J* = 32 Hz), 131.1, 129.5, 129.4, 128.8, 127.1 (q, *J* = 3.6 Hz) 124.7 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272 Hz), 67.3, 26.1.

HRMS (ESI): $C_{24}H_{17}F_3NO_3$ $[M+H]^+$ calculated = 424.1155; found = 424.1160.

3u:



3-benzoyl-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

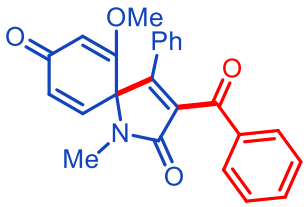
Physical state: Brown solid, Yield 60.5 mg, 76 %, from 56.0 mg of **1h**

1H NMR (400 MHz, CDCl3) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.15 (m, 5H), 6.66 (d, *J* = 9.8 Hz, 1H), 6.57 (dd, *J* = 9.8, 1.5 Hz, 1H), 6.44 (s, 1H), 2.82 (s, 3H), 1.89 (d, *J* = 1.0 Hz, 3H).

13C NMR (101 MHz, CDCl3) δ 191.5, 184.6, 167.7, 154.7, 153.0, 144.9, 136.7, 135.7, 134.3, 132.9, 132.2, 130.7, 129.9, 129.4, 129.0, 128.8, 127.6, 69.3, 25.5, 18.1.

HRMS (ESI): $C_{24}H_{20}NO_3$ $[M+H]^+$ calculated = 370.1438; found = 370.1442.

3v:



3-benzoyl-6-methoxy-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

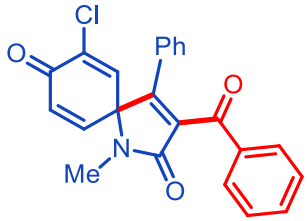
Physical state: Yellowish brown solid, Yield 61 mg, 79 %, from 59.0 mg of **1i**

1H NMR (400 MHz, CDCl3) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.19 (t, *J* = 4.3 Hz, 4H), 6.54 – 6.32 (m, 2H), 5.90 (d, *J* = 1.0 Hz, 1H), 3.84 (s, 3H), 2.83 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 191.5, 186.0, 168.4, 168.0, 154.0, 140.4, 136.4, 135.7, 134.2, 132.5, 130.4, 129.9, 129.5, 128.8, 128.7, 127.6, 106.4, 68.5, 56.6, 25.6.

HRMS (ESI): $C_{24}H_{20}NO_4$ $[M+H]^+$ calculated = 386.1387; found = 386.1389.

3w:



3-benzoyl-7-chloro-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

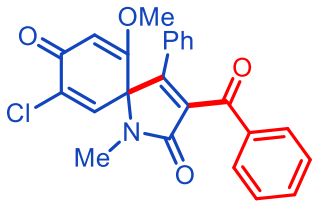
Physical state: Reddish Brown solid, Yield 63.0 mg, 81 %, from 60.0 mg of **1j**

1H NMR (400 MHz, CDCl3) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.53 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.21 (d, *J* = 4.3 Hz, 4H), 6.90 (d, *J* = 2.7 Hz, 1H), 6.71 (dd, *J* = 9.9, 2.7 Hz, 1H), 6.63 (d, *J* = 9.9 Hz, 1H), 2.95 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 190.9, 177.0, 166.9, 153.8, 145.2, 140.3, 136.9, 136.4, 135.4, 134.4, 132.4, 130.8, 129.6, 129.5, 129.0, 128.8, 127.7, 69.0, 26.1.

HRMS (ESI): $C_{23}H_{17}ClNO_3$ $[M+H]^+$ calculated = 390.0891; found = 390.0887.

3x:



3-benzoyl-6-chloro-10-methoxy-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

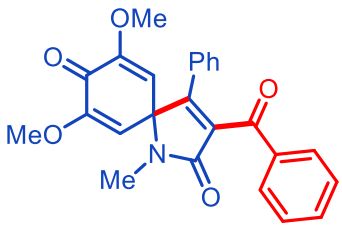
Physical state: Brown solid, Yield 65.4 mg, 78 %, from 66.0 mg of **1k**

1H NMR (400 MHz, CDCl3) δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.11 (m, 2H), 6.65 (s, 1H), 5.97 (s, 1H), 3.85 (s, 3H), 2.85 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 191.1, 178.4, 168.6, 167.7, 153.5, 136.6, 136.0, 135.6, 134.3, 130.6, 129.5, 129.0, 128.7, 127.5, 105.6, 70.0, 57.1, 25.8.

HRMS (ESI): $C_{24}H_{19}ClNO_4$ $[M+H]^+$ calculated = 420.0997; found = 420.1007.

3y:



3-benzoyl-7,9-dimethoxy-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione.

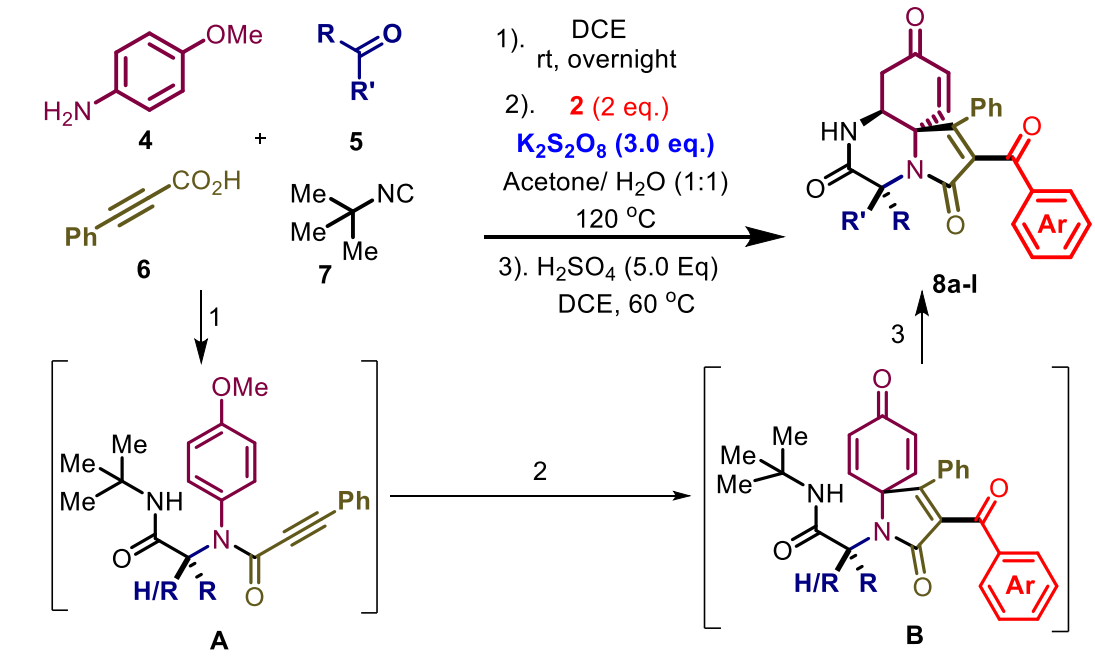
Physical state: Light Yellow solid, Yield 69 mg, 84 %, from 65.0 mg of **1l**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.15 (m, 5H), 5.53 (s, 2H), 3.72 (s, 6H), 2.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 175.2, 166.7, 156.9, 153.6, 135.8, 135.3, 134.2, 130.4, 130.2, 129.5, 128.7, 128.7, 127.7, 111.5, 67.6, 56.0, 25.5.

HRMS (ESI): $C_{25}H_{21}NNaO_5$ $[M+Na]^+$ calculated = 438.1317; found = 438.1322.

One pot synthesis of acylated azaspirotricycles:

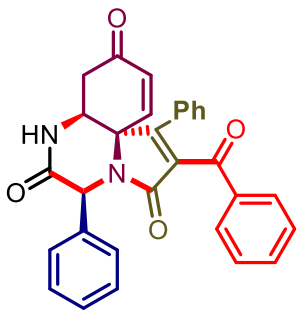


Procedure:

To a reaction tube was added *p*-anisidine **4** (12.3 mg, 0.1 mmol) and benzaldehyde **5a** (10.5 mg, 0.1 mmol) in 1,2-DCE (1 mL)and stirred for 5 min. Then phenyl propiolic acid **6** (15 mg, 0.1 mmol) and *t*-butyl isocyanide **7** (12 µL, 0.1 mmol) were added and the resulting solution was stirred at rt for 12 hrs. Then the contents of the reaction were evaporated under vacuum, residue dissolved in MeCN (1 mL) and **2a** (30 mg, 0.2 mmol) , $K_2S_2O_8$ (81 mg 0.3 mmol) and water 1 mL were added and reaction was stirred at 120 °C for 12 hrs. The contents were then evaporated under reduced pressure, Then washed with sat. $NaHCO_3$ solution and extracted with 5ml DCE thrice, the organic layers were combined and concenterated to about 1mL and treated with conc. H_2SO_4 (11 µL, 0.2 mmol) and heated to 60 °C for 6 hrs. The reaction mixture was then quenched with sat. $NaHCO_3$ solution and extracted with DCM (3 x 5 mL), combined organics were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography using EtOAc: Petroleum ether as eluent to afford 37.5 mg (75 %) of the desired product **8a**.

Note: Aniline **4** and the aldehydes **5** were purified using the appropriate methods, prior to the reaction.

8a:



(5S,7aR,11aR)-2-benzoyl-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione

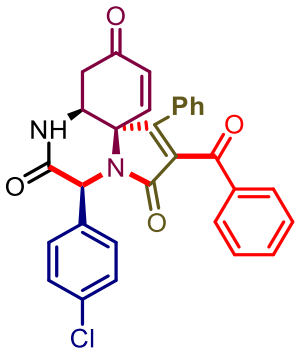
Physical state: Yellow oil, Yield 75 % 37.5 mg from 12.3 mg of **4.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 2H), 7.63 (br, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.43 – 7.30 (m, 6H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.27 (d, *J* = 10.2 Hz, 1H), 6.19 (dd, *J* = 10.2, 1.8 Hz, 1H), 6.11 (s, 1H), 4.29 (s, 1H), 2.40 (d, *J* = 16.3 Hz, 1H), 1.89 (dd, *J* = 17.4, 3.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 190.2, 168.0, 165.6, 156.4, 142.1, 136.9, 136.5, 135.6, 134.4, 133.4, 130.6, 130.5, 129.5, 129.1, 128.9, 128.8, 128.7, 128.5, 127.8, 63.6, 56.1, 55.7, 40.2.

HRMS (ESI): $C_{30}H_{23}N_2O_4$ $[M+H]^+$ calculated = 475.1658; found = 475.1666.

8b:



(5S,7aS,11aR)-2-benzoyl-5-(4-chlorophenyl)-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione

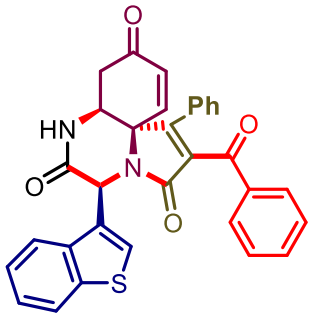
Physical state: reddish brown oil, Yield 75 % 38 mg from 12.3 mg of **4.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.29 (m, 6H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.30 (d, *J* = 10.2 Hz, 1H), 6.20 (dd, *J* = 10.2, 1.8 Hz, 1H), 6.03 (s, 1H), 4.30 (s, 1H), 2.38 (d, *J* = 16.1 Hz, 1H), 1.86 (dd, *J* = 17.4, 3.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 190.2, 167.9, 165.7, 156.5, 141.8, 136.3, 135.5, 134.5, 134.4, 133.6, 130.6, 130.5, 130.5, 129.5, 129.2, 129.1, 128.7, 127.7, 63.6, 55.6, 55.4, 40.2.

HRMS (ESI): $C_{30}H_{22}ClN_2O_4$ $[M+H]^+$ calculated = 509.1268; found = 509.1263.

8c:



(5S,7aR,11aR)-5-(benzo[b]thiophen-3-yl)-2-benzoyl-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione

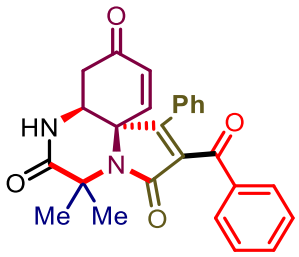
Physical state: Off white solid, Yield 70 % 37 mg from 12.3 mg of **4.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.99 (s, 1H), 7.90 – 7.81 (m, 4H), 7.61 (dd, *J* = 11.1, 3.9 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.26 – 7.17 (m, 3H), 6.35 (d, *J* = 10.2 Hz, 1H), 6.29 (dd, *J* = 10.2, 2.0 Hz, 1H), 6.10 (s, 1H), 4.37 (s, 1H), 2.42 (dd, *J* = 17.4, 1.5 Hz, 1H), 1.92 (dd, *J* = 17.4, 3.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 190.0, 168.0, 165.8, 156.6, 141.9, 136.5, 136.1, 135.5, 134.6, 133.7, 133.0, 132.5, 132.2, 130.6, 130.5, 129.7, 129.3, 129.2, 129.1, 128.8, 127.9, 127.7, 127.0, 124.0, 63.7, 55.6, 55.4, 40.2.

HRMS (ESI): $C_{32}H_{23}N_2O_4S$ $[M+H]^+$ calculated = 531.1373; found = 531.1379.

8d:



(7aR,11aR)-2-benzoyl-5,5-dimethyl-1-phenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione

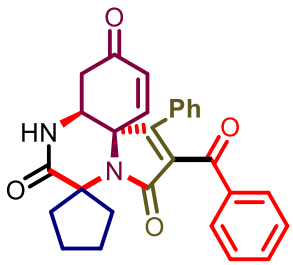
Physical state: Reddish brown oil, Yield 71 % 30 mg from 12.3 mg of **4.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.23 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 2H), 6.93 (s, 1H), 6.62 (dd, *J* = 10.1, 2.3 Hz, 1H), 6.43 (d, *J* = 10.1 Hz, 1H), 4.28 (d, *J* = 2.5 Hz, 1H), 2.31 (d, *J* = 17.8 Hz, 1H), 1.98 (s, 3H), 1.90 (dd, *J* = 17.8, 3.2 Hz, 1H), 1.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 190.3, 173.9, 165.6, 154.1, 143.0, 139.2, 135.6, 134.3, 134.0, 130.7, 130.3, 129.4, 129.1, 128.7, 127.7, 66.1, 59.8, 53.5, 29.7, 26.1, 24.1.

HRMS (ESI): $C_{26}H_{23}N_2O_4$ $[M+H]^+$ calculated = 427.1658; found = 427.1654.

8e:



(7a'R,11a'R)-2'-benzoyl-1'-phenyl-7a',8'-dihydro-3'H,6'H-spiro[cyclopentane-1,5'-pyrrolo[1,2-d]quinoxaline]-3',6',9'(7'H)-trione.

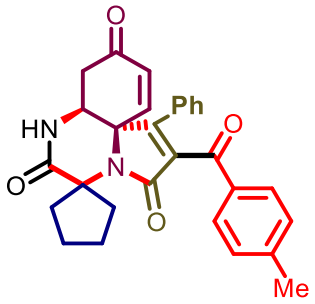
Physical state: Yellow oil, Yield 78 % 35mg from 12.3 mg of **4.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (br, 3H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.27 – 7.22 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.57 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.43 (d, *J* = 10.1 Hz, 1H), 4.26 (d, *J* = 2.3 Hz, 1H), 3.08 – 2.88 (m, 1H), 2.55 – 2.41 (m, 1H), 2.39 – 2.28 (m, 1H), 2.22 – 1.79 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 190.6, 176.6, 165.2, 154.2, 143.0, 139.2, 135.87, 134.4, 134.4, 131.0, 130.4, 129.5, 129.2, 128.9, 127.9, 67.9, 66.4, 53.7, 40.4, 40.2, 38.3, 28.9, 26.7.

HRMS (ESI): $C_{28}H_{25}N_2O_4$ $[M+H]^+$ calculated = 453.1814 found = 453.1809.

8f:



(7a'R,11a'R)-2'-(4-methylbenzoyl)-1'-phenyl-7a',8'-dihydro-3'H,6'H-spiro[cyclopentane-1,5'-pyrrolo[1,2-d]quinoxaline]-3',6',9'(7'H)-trione.

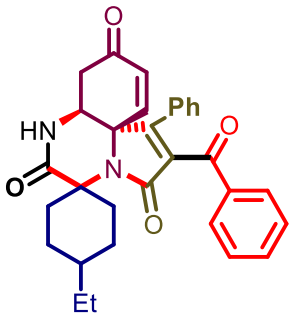
Physical state: Yellow sticky solid, Yield 73%, 34 mg from 12.3 mg of **4.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.23 (m, 3H), 7.23 – 7.17 (m, 4H), 6.59 (dd, *J* = 10.1, 2.3 Hz, 1H), 6.45 (d, *J* = 10.1 Hz, 1H), 4.28 (s, 1H), 3.10 – 2.96 (m, 1H), 2.55 – 2.44 (m, 1H), 2.38 (s, 3H), 2.22 – 2.13 (m, 1H), 2.13 – 1.81 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 190.0, 176.5, 165.2, 153.6, 145.5, 143.0, 139.2, 134.2, 133.3, 130.9, 130.1, 129.5, 129.4, 129.0, 127.7, 67.7, 66.2, 53.5, 40.2, 40.0, 38.1, 28.8, 26.6, 21.8.

HRMS (ESI) $C_{29}H_{27}N_2O_4$ $[M+H]^+$ calculated = 467.1971; found =467.1976 .

8g:



(7a'S,11a'S)-2'-benzoyl-4-ethyl-1'-phenyl-7a',8'-dihydro-3'H,6'H-spiro[cyclohexane-1,5'-pyrrolo[1,2-d]quinoxaline]-3',6',9'(7'H)-trione.

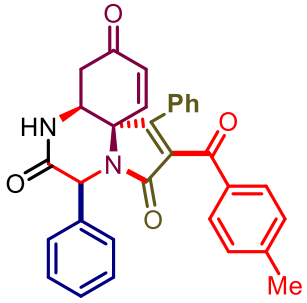
Physical state: Brown sticky solid, Yield 75%, 37 mg from 12.3 mg of **4.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.24 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.63 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.44 (dd, *J* = 10.1, 2.3 Hz, 1H), 4.25 (s, 1H), 3.41 (td, *J* = 13.1, 3.9 Hz, 1H), 2.52 – 2.45 (m, 1H), 2.38 – 2.27 (m, 2H), 2.01 – 1.88 (m, 3H), 1.74 – 1.50 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 190.4, 173.7, 165.6, 153.6, 143.2, 139.6, 135.6, 134.3, 133.9, 130.8, 130.2, 129.4, 129.0, 128.7, 127.8, 67.0, 62.2, 53.4, 40.3, 33.3, 28.6, 26.6, 26.2, 25.5, 24.0, 12.4.

HRMS (ESI): $C_{31}H_{31}N_2O_4$ $[M+H]^+$ calculated = 494.2206; found =494.2212.

8h:



(5S,7aR,11aR)-2-(4-methylbenzoyl)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione

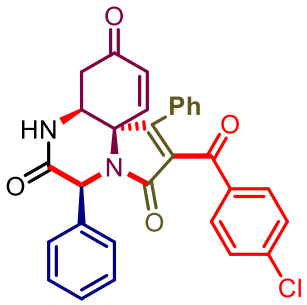
Physical state: Brown sticky solid, Yield 72 % 35 mg from 12.3 mg of **4.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.45 (s, 1H), 7.44 – 7.29 (m, 4H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.21-7.17 (m, 4H), 6.28 (d, *J* = 10.1 Hz, 1H), 6.20 (d, *J* = 10.2 Hz, 1H), 6.12 (s, 1H), 4.31 (s, 1H), 2.40 (br, *J* = 10.5 Hz, 4H), 1.92 (dd, *J* = 17.4, 3.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 189.7, 167.9, 165.7, 155.9, 145.6, 142.2, 136.9, 136.7, 133.3, 133.2, 130.7, 130.5, 129.7, 129.5, 129.1, 128.9, 128.8, 128.5, 127.8, 63.6, 56.1, 55.8, 40.3, 21.9.

HRMS (ESI): $C_{31}H_{25}N_2O_4$ $[M+H]^+$ calculated = 489.1814; found = 489.1820.

8i:



(5S,7aR,11aR)-2-(4-chlorobenzoyl)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione

Physical state: Brown oil, Yield 69 % 35.2 mg from 12.3 mg of **4.**

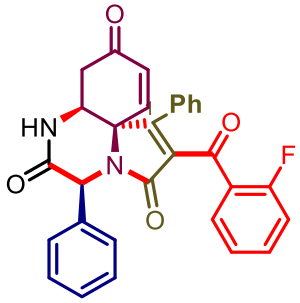
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.60 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.33 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.29 (d, *J* = 10.2

Hz, 1H), 6.20 (d, *J* = 10.1 Hz, 1H), 6.11 (s, 1H), 4.32 (s, 1H), 2.41 (d, *J* = 17.3 Hz, 1H), 1.90 (dd, *J* = 17.4, 3.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 189.0, 168.0, 165.4, 156.9, 141.9, 141.0, 136.8, 136.0, 133.9, 133.5, 130.8, 130.7, 130.5, 129.2, 129.1, 128.95, 128.9, 128.6, 127.7, 63.7, 56.1, 55.7, 40.2.

HRMS (ESI) $C_{30}H_{22}ClN_2O_4$ $[M+H]^+$ calculated = 509.1268; found = 509.1263.

8j:



(5S,7aR,11aR)-2-(2-fluorobenzoyl)-1,5-diphenyl-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione

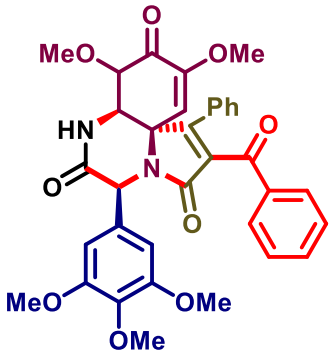
Physical state: Yellowish brown oil, Yield 58 % 28.5 mg from 12.3 mg of **4.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.40 – 7.30 (m, 5H), 7.30 – 7.19 (m, 3H), 7.14 (d, *J* = 7.3 Hz, 2H), 6.27 (d, *J* = 10.2 Hz, 1H), 6.17 (dd, *J* = 10.2, 2.0 Hz, 1H), 6.09 (s, 1H), 4.29 (s, 1H), 2.39 (d, *J* = 17.3 Hz, 1H), 1.88 (dd, *J* = 17.5, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 189.0, 166.7 (d, *J* = 269.6 Hz), 161.4, 157.1, 141.8, 137.5 (d, *J* = 6.6 Hz), 136.8, 136.0, 133.5, 130.7, 130.4 (t, *J* = 3.8 Hz), 129.2, 128.9, 128.6, 127.7, 125.4, 121.4 (d, *J* = 21.7 Hz), 115.9 (d, *J* = 22.4 Hz), 63.7, 56.1, 55.7, 40.2.

HRMS (ESI) $C_{30}H_{22}FN_2O_4$ $[M+H]^+$ calculated = 493.1564; found = 493.1568.

8k:



(5S,7aR,11aS)-2-benzoyl-8,10-dimethoxy-1-phenyl-5-(3,4,5-trimethoxyphenyl)-7a,8-dihydro-3H-pyrrolo[1,2-d]quinoxaline-3,6,9(5H,7H)-trione

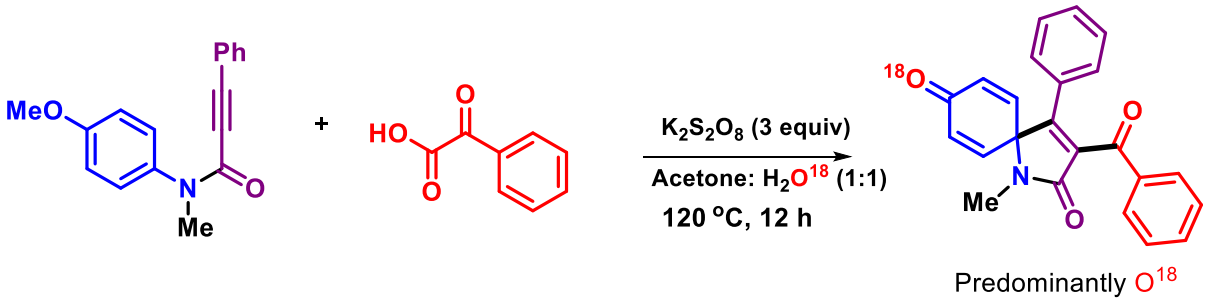
Physical state: Yellow sticky solid, Yield 61 % 38 mg, 5:1 dr from 18 mg of 1,2,3-Trimethoxy aniline **4b.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.90 – 7.84 (m, 0.4H), 7.58 – 7.53 (m, 1.6H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.86 (s, 0.4H), 6.77 (s, 2H), 5.95 (s, 0.2H), 5.90 (d, *J* = 2.1 Hz, 1H), 5.71 (s, 1H), 5.56 (d, *J* = 1.8 Hz, 1H), 5.34 (d, *J* = 2.5 Hz, 0.4H), 4.72 (s, 1H), 4.10 (d, *J* = 6.7 Hz, 0.2H), 3.86 (s, 3.6H), 3.82 (s, 7.2H), 3.71 (s, 3.6H), 3.60 (s, 0.6H), 3.49 (s, 3H).

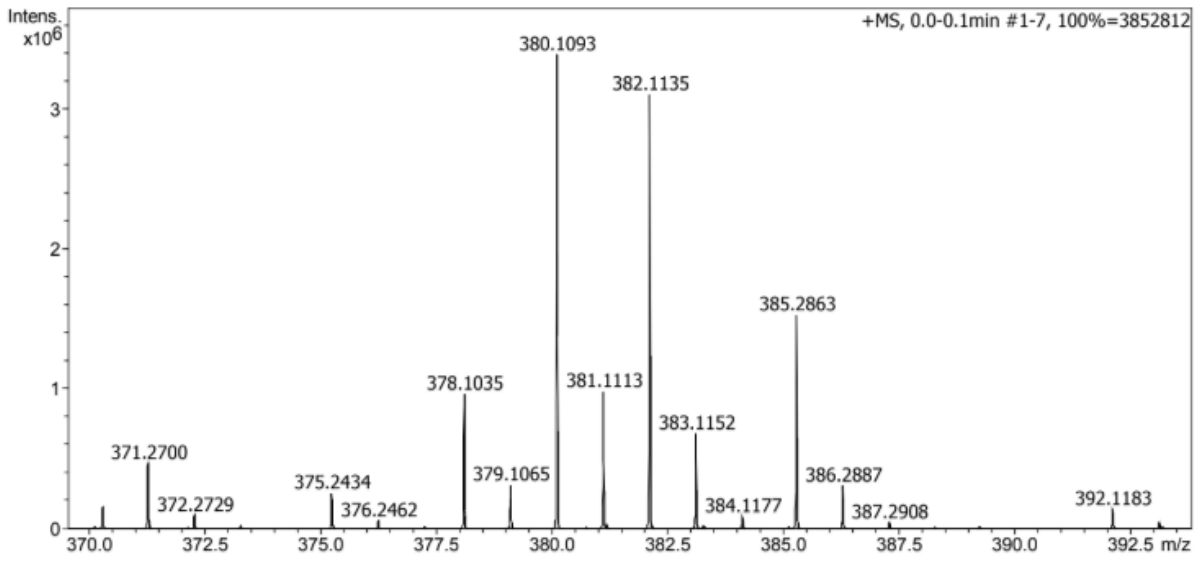
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 175.5, 167.0, 166.8, 158.1, 153.6, 153.2, 152.4, 138.4, 136.0, 135.9, 135.5, 134.4, 131.8, 130.4, 130.3, 129.9, 129.7, 128.8, 128.8, 127.8, 112.5, 112.4, 106.9, 104.6, 68.9, 62.1, 61.0, 56.3, 56.2, 55.8, 52.1.

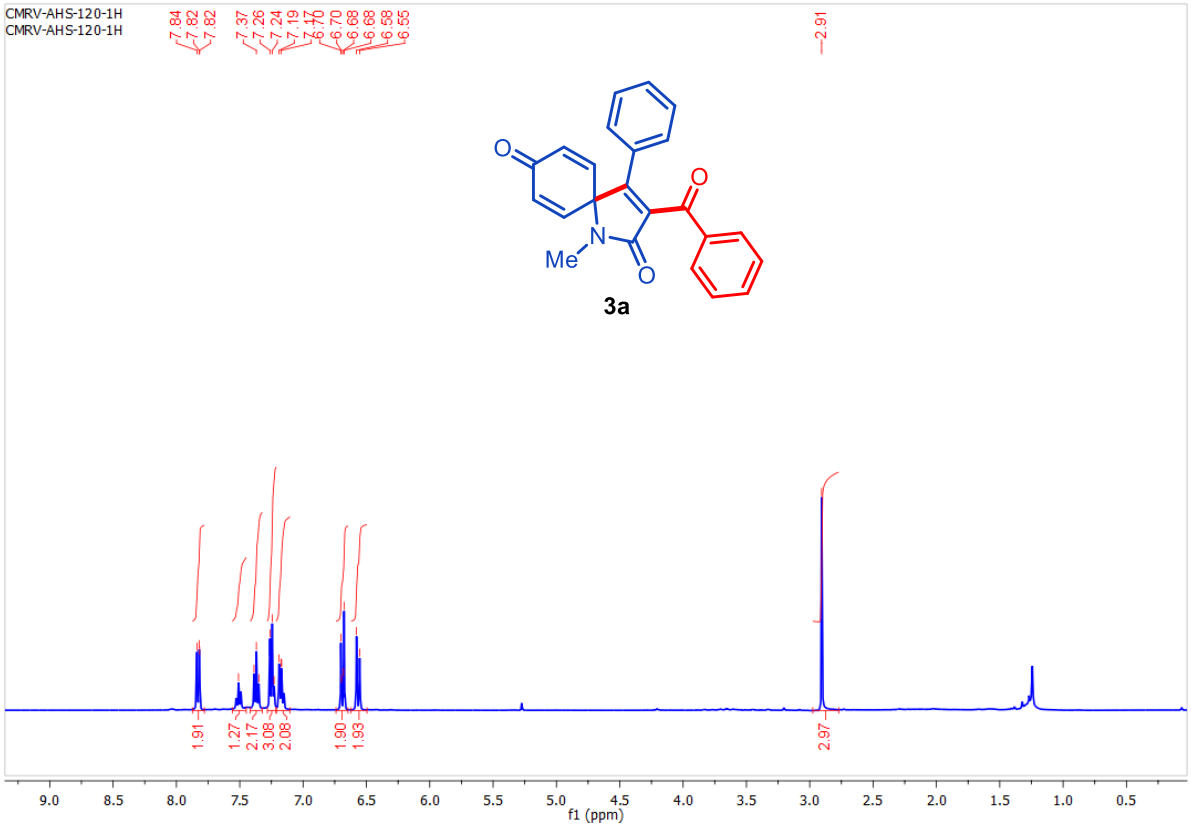
HRMS (ESI) $C_{35}H_{33}N_2O_9$ $[M+H]^+$ calculated = 625.2186; found = 625.2194.

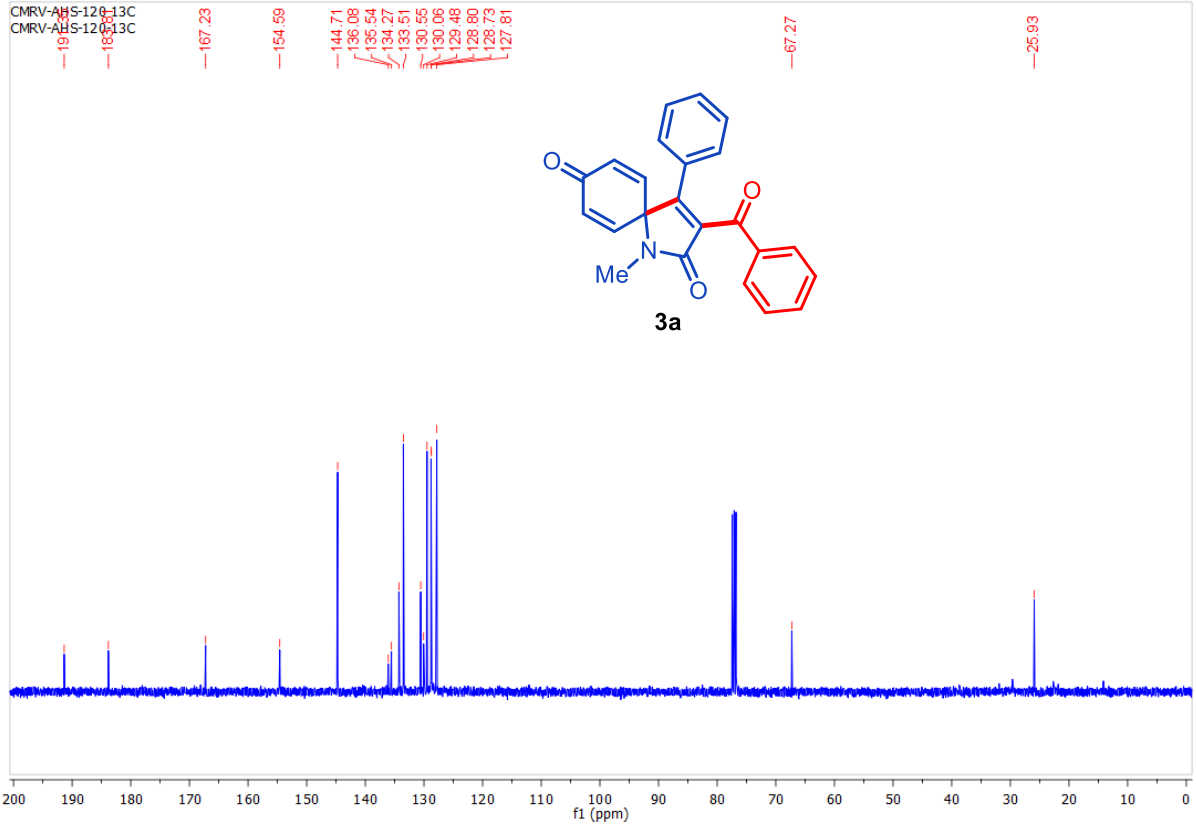
Oxygen labelled water experiment

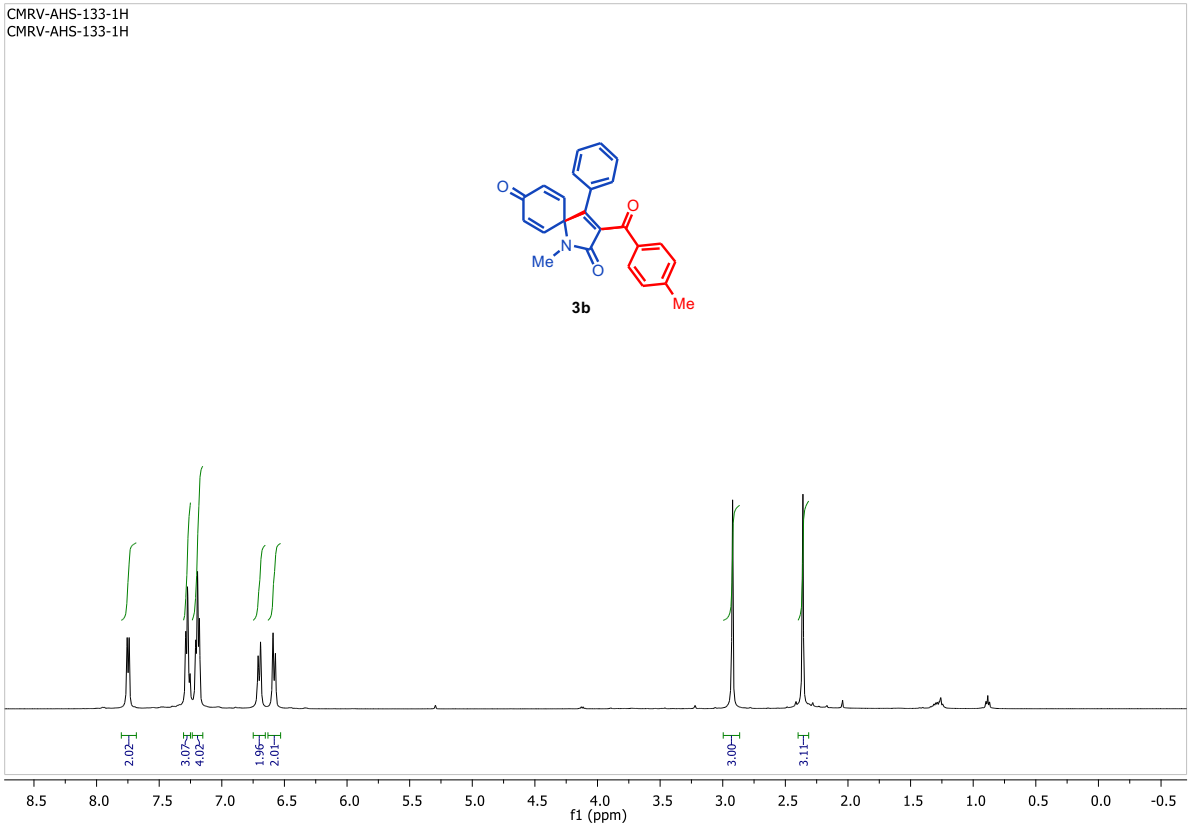


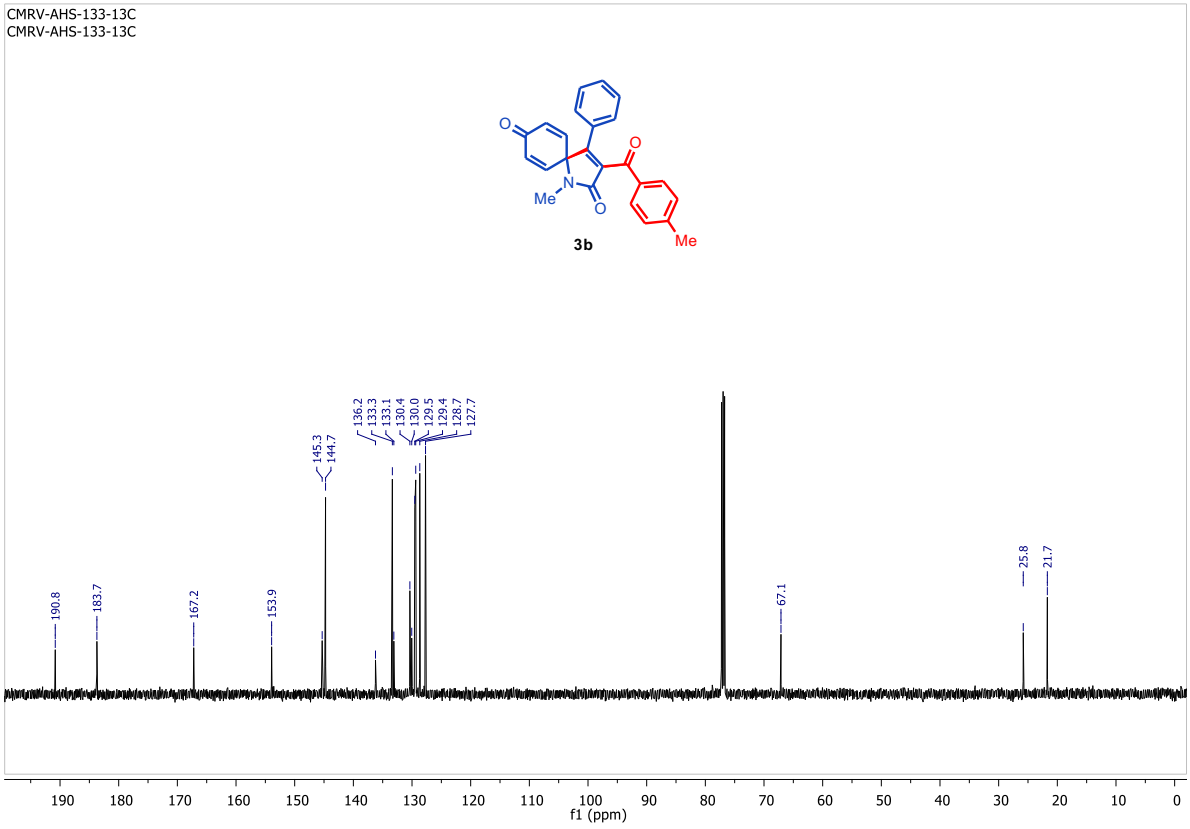
Amine **1a** (2.7mg, 0.01 mmol), phenylglyoxalic acid **2a** (3.0 mg, 0.02 mmol), and $K_2S_2O_8$ (8.1 mg, 0.3 mmol) were added to an oven-dried screw cap reaction tube equipped with a stir bar. Then, Acetone (0.1 mL) and H_2O^{18} (0.1ml) were added via syringe. The reaction mixture was heated at 120 °C for 12 h. After that the resulting mixture was cooled to room temperature and reaction mixture was quenched with sat. $NaHCO_3$ solution. The resulting mixture was extracted with ethyl acetate (1 ml X 3) and the organic layer was collected was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, mesh 100-200; hexane: ethyl acetate; 40:60) to give the product **3a O^{18}**. The mass spectra of the product showed predominant **O^{18}** incorporation [M+Na]+ of 380.1093

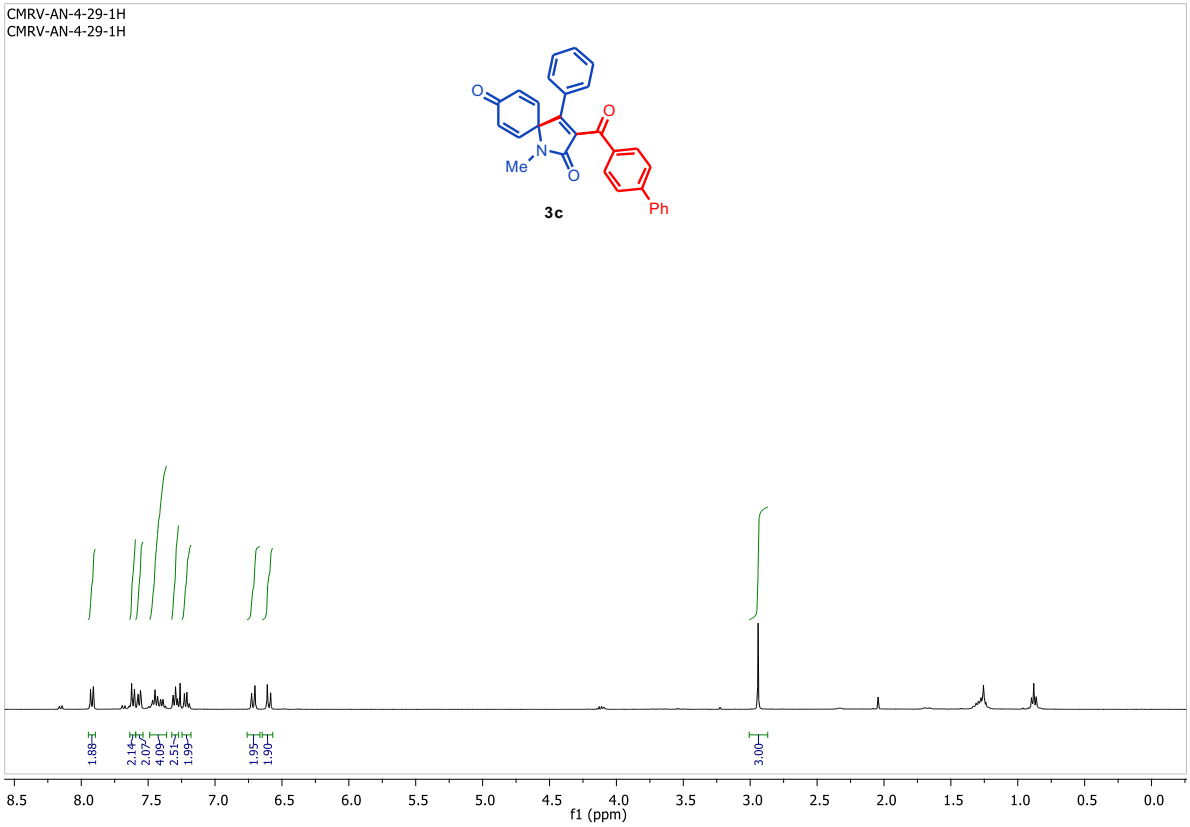


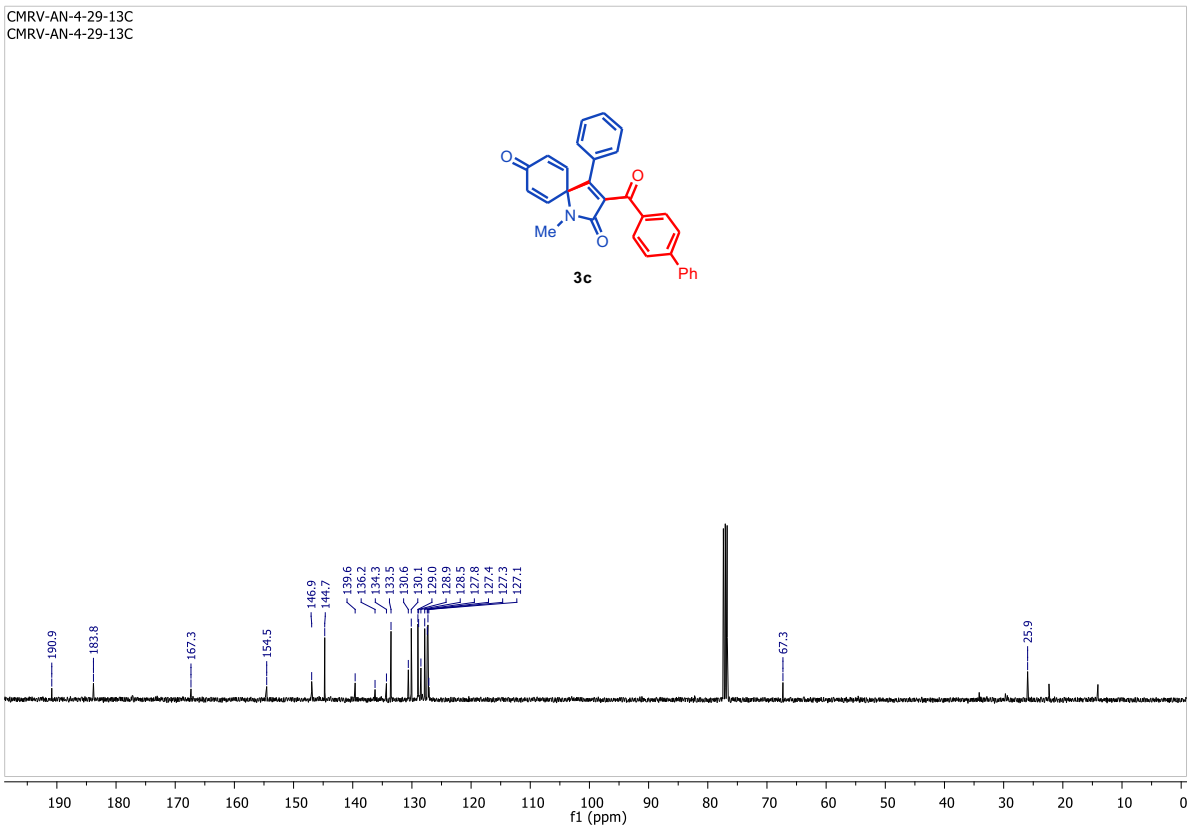

CMRV-AHS-120-1H
CMRV-AHS-120-1H
7.84
7.82
7.82
7.37
7.26
7.24
7.19
7.17
6.70
6.68
6.68
6.58
6.55
2.91
O
O
N
Me
O
3a
1.91
1.27
2.17
3.08
2.08
1.90
1.93
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

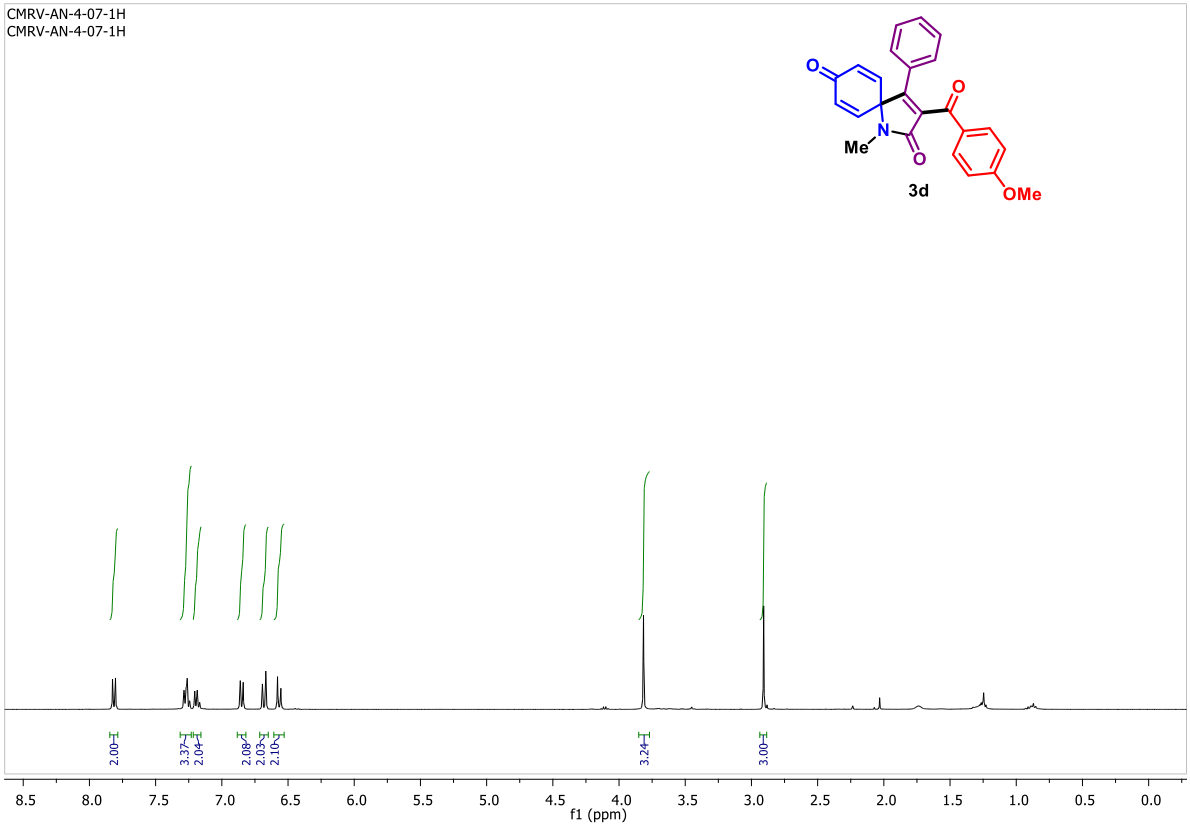

CMRV-AHS-120-13C
CMRV-AHS-120-13C
167.23
154.59
144.71
136.08
135.54
134.27
133.51
130.55
130.06
129.48
128.80
128.73
127.81
67.27
25.93
O
O
N
Me
O
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

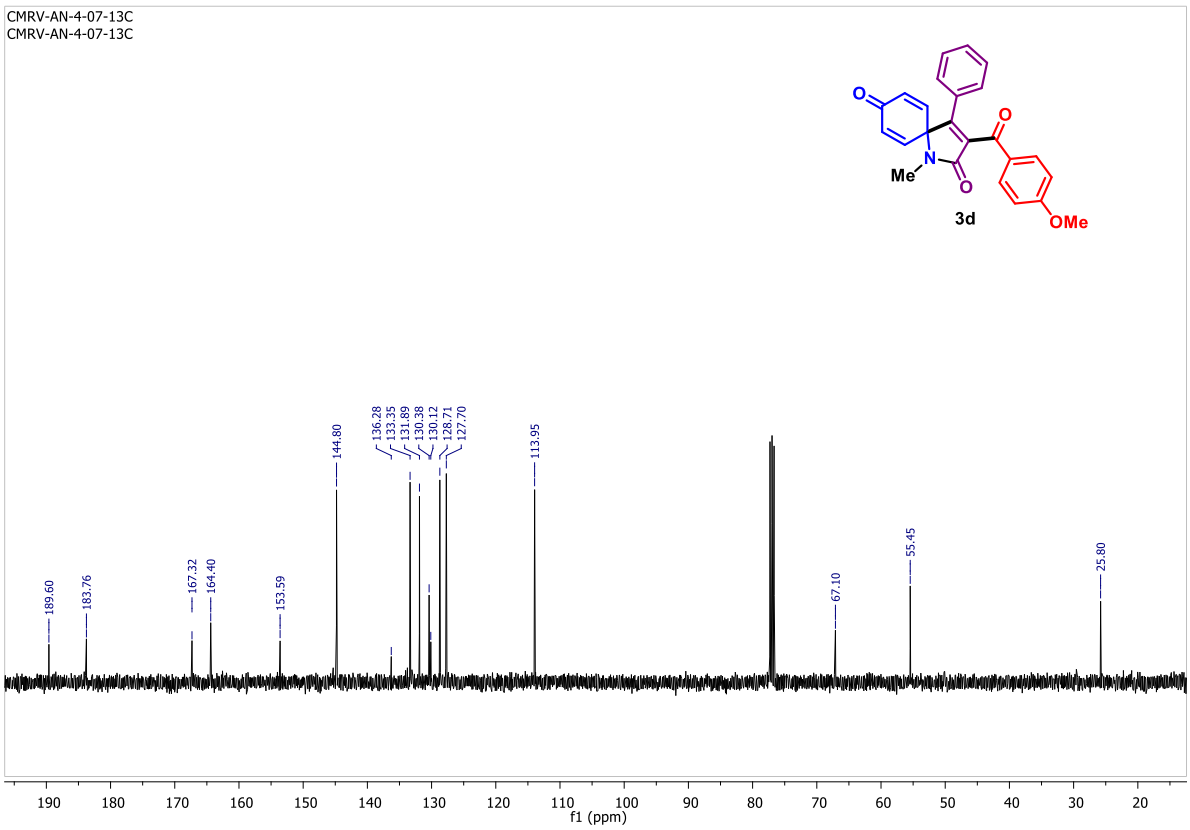

CMRV-AHS-133-1H
CMRV-AHS-133-1H
O
O
N
Me
O
Me
3b
2.02
3.07
4.02
1.96
2.01
3.00
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

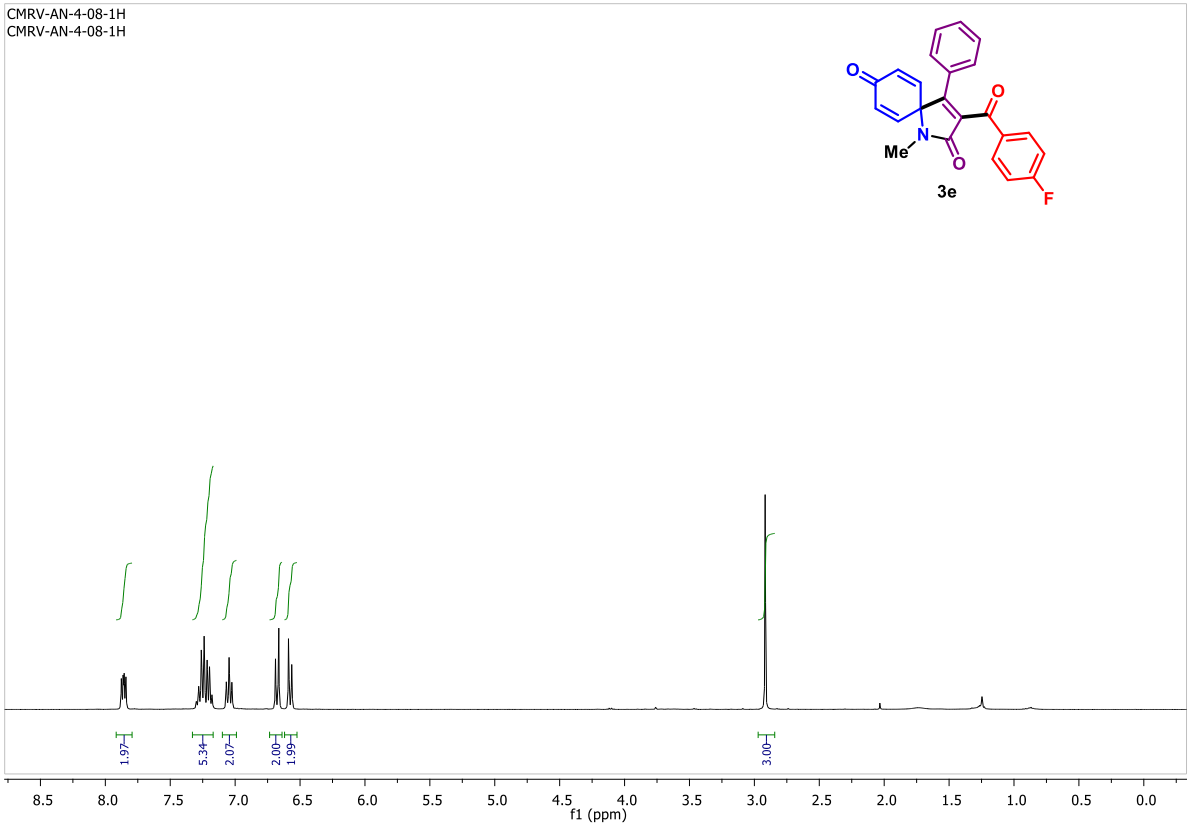

CMRV-AHS-133-13C
CMRV-AHS-133-13C
O
O
N
Me
O
Me
3b
190.8
183.7
167.2
153.9
145.3
144.7
136.2
133.3
133.1
130.4
130.0
129.5
129.4
128.7
127.7
67.1
25.8
21.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

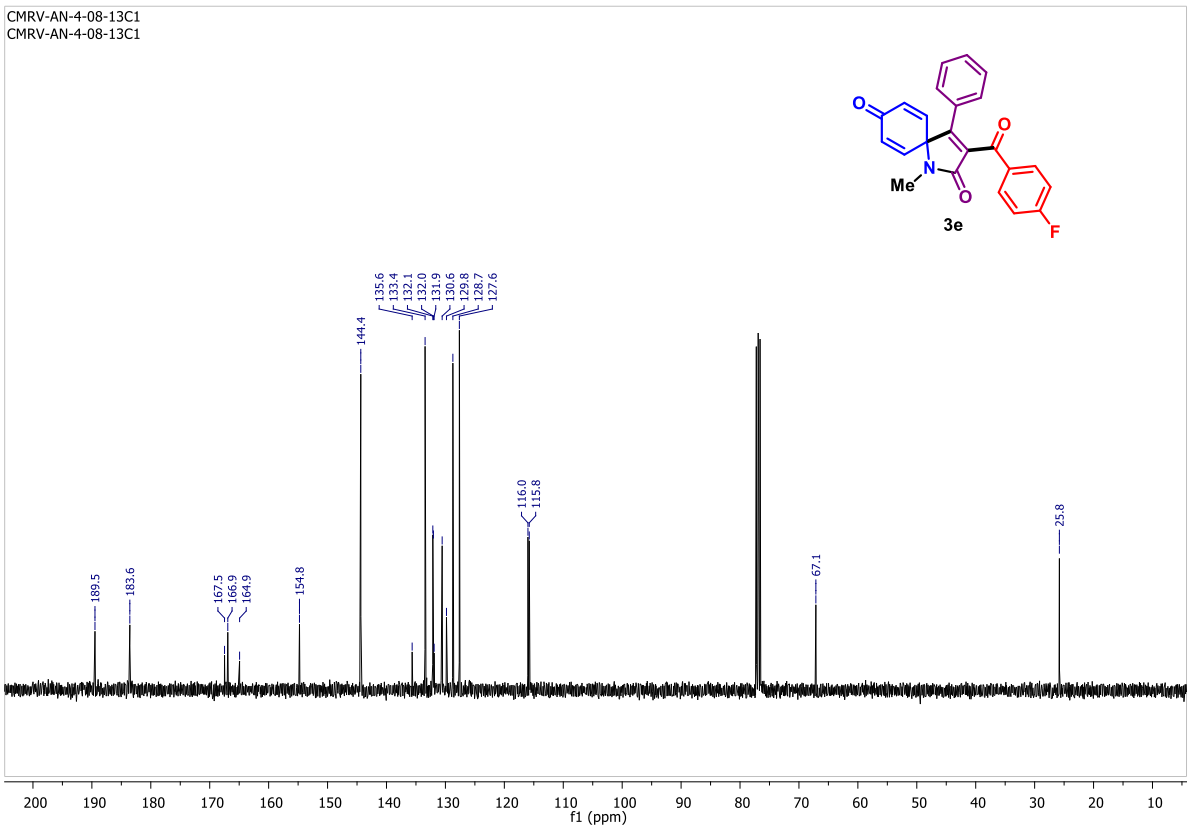

CMRV-AN-4-29-1H
CMRV-AN-4-29-1H
O
O
Me
N
O
Ph
3c
1.88
2.14
2.07
4.09
2.51
1.99
1.95
1.90
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

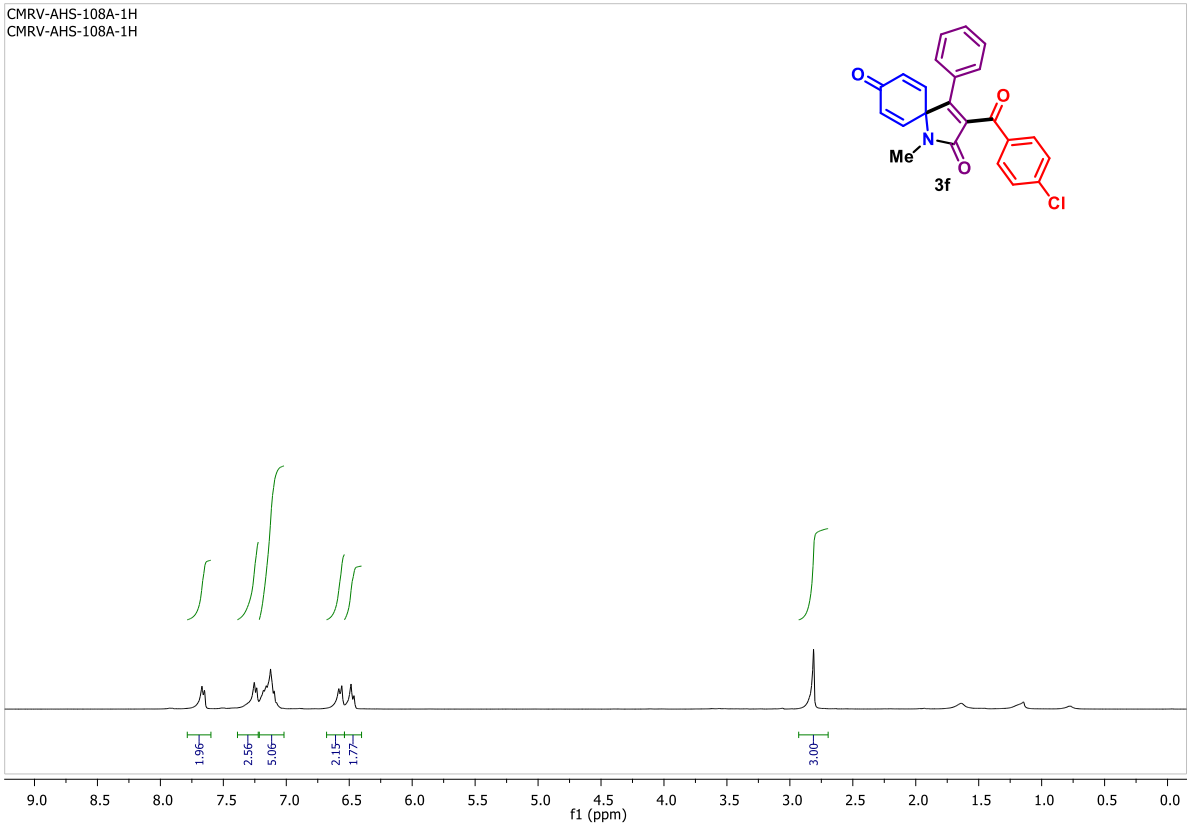

CMRV-AN-4-29-13C
CMRV-AN-4-29-13C
O
O
Me
N
O
Ph
3c
190.9
183.8
167.3
154.5
146.9
144.7
139.6
136.2
134.3
133.5
130.6
130.1
129.0
128.9
128.5
127.8
127.4
127.3
127.1
67.3
25.9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

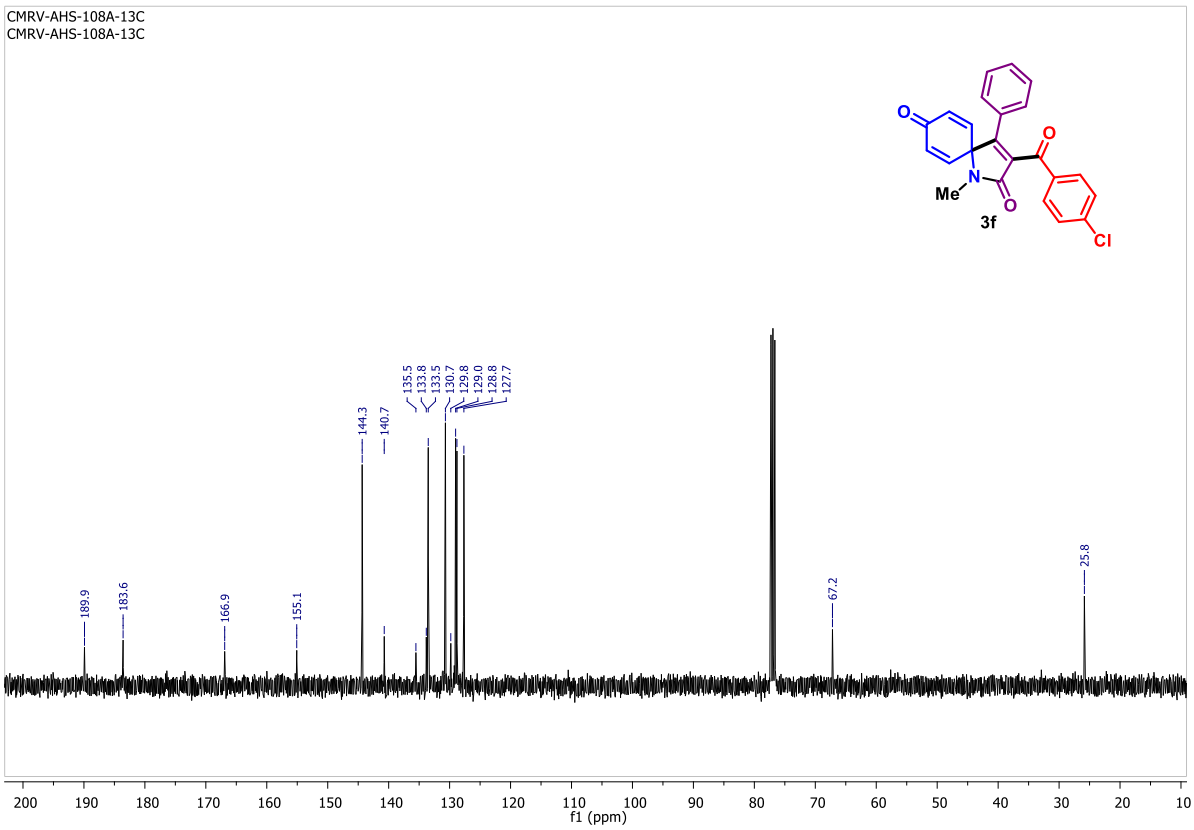

CMRV-AN-4-07-1H
CMRV-AN-4-07-1H
O
N
Me
O
O
OMe
3d
2.00
3.37
2.04
2.08
2.03
2.16
3.24
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

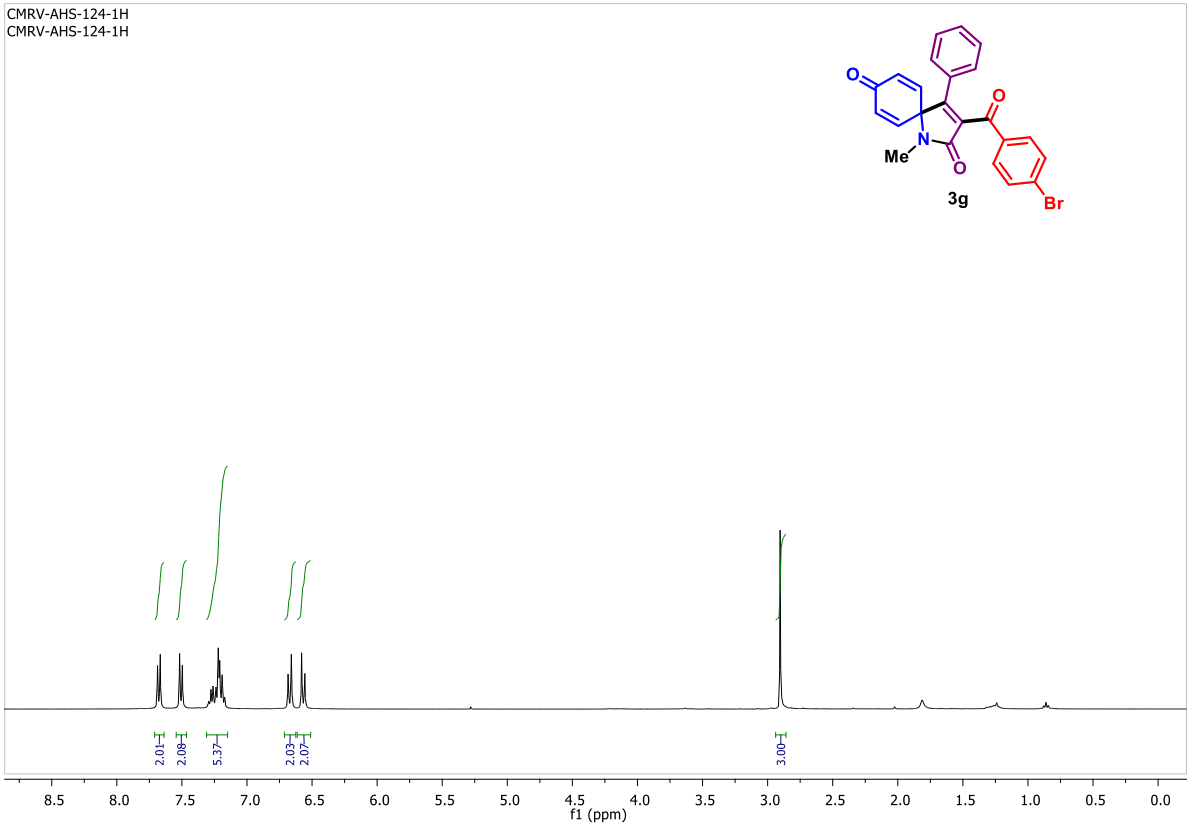

CMRV-AN-4-07-13C
CMRV-AN-4-07-13C
O
N
Me
O
O
OMe
3d
189.60
183.76
167.32
164.40
153.59
144.80
136.28
133.35
131.89
130.38
130.12
128.71
127.70
113.95
67.10
55.45
25.80
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

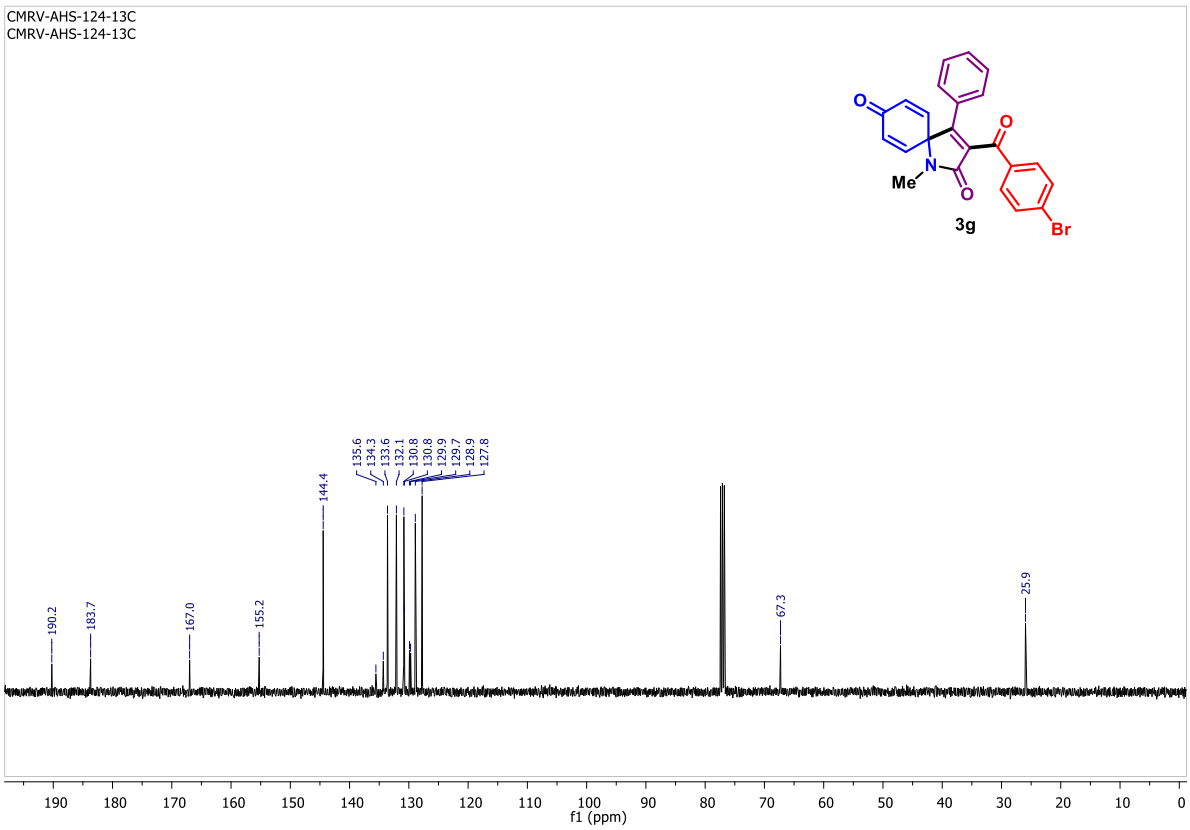

CMRV-AN-4-08-1H
CMRV-AN-4-08-1H
O
O
N
Me
O
O
F
3e
1.97
5.34
2.07
2.00
1.99
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

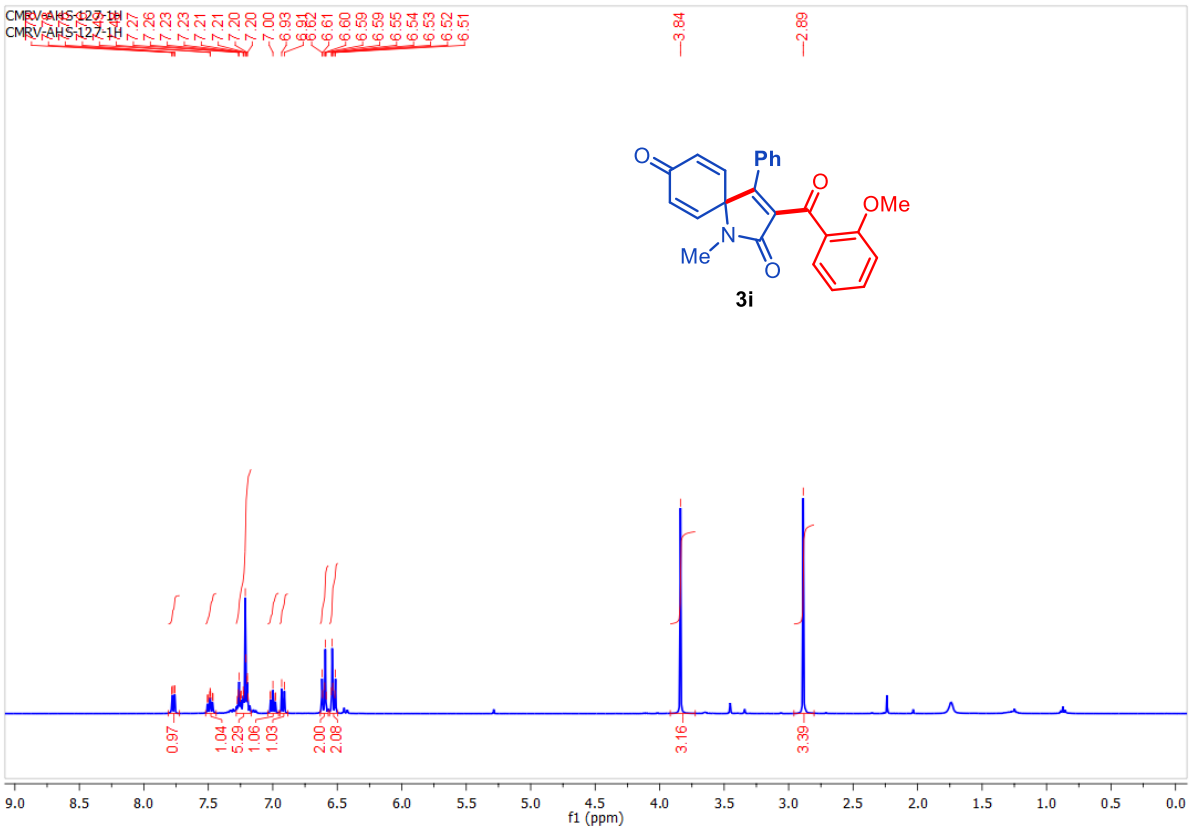

CMRV-AN-4-08-13C1
CMRV-AN-4-08-13C1
O
O
N
Me
O
O
F
3e
135.6
133.4
132.1
132.0
131.9
130.6
129.8
128.7
127.6
144.4
116.0
115.8
189.5
183.6
167.5
166.9
164.9
154.8
67.1
25.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

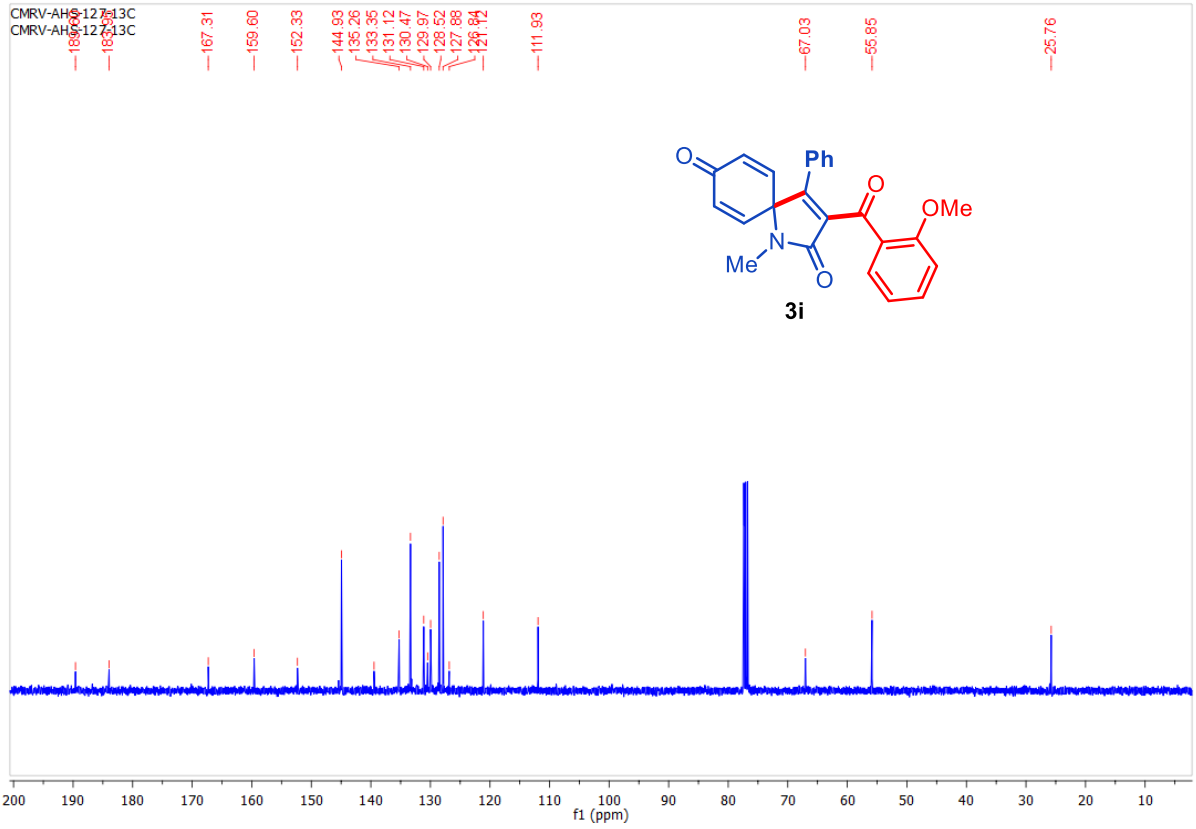

CMRV-AHS-108A-1H
CMRV-AHS-108A-1H
O
O
N
Me
O
O
Cl
3f
1.96
2.56
5.06
2.15
1.77
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

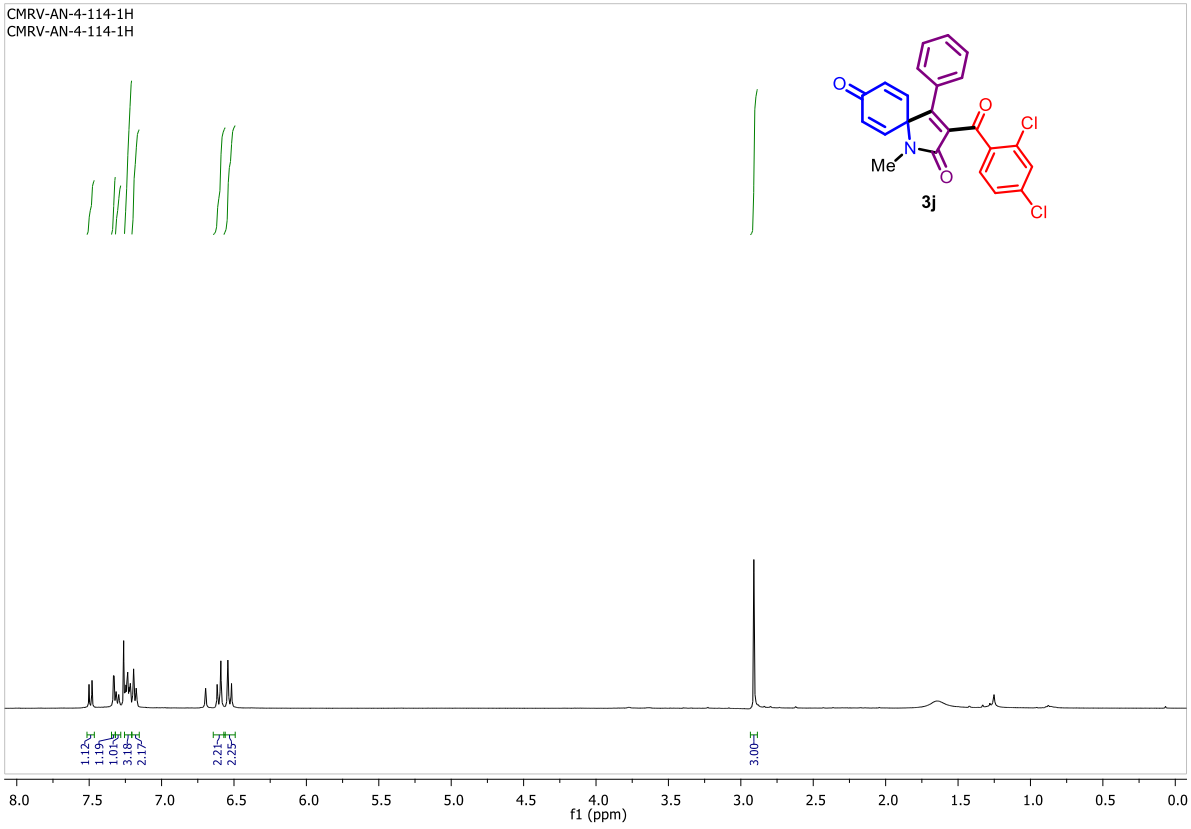

CMRV-AHS-108A-13C
CMRV-AHS-108A-13C
O
O
N
Me
O
O
Cl
3f
189.9
183.6
166.9
155.1
144.3
140.7
135.5
133.8
133.5
130.7
129.8
129.0
128.8
127.7
67.2
25.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

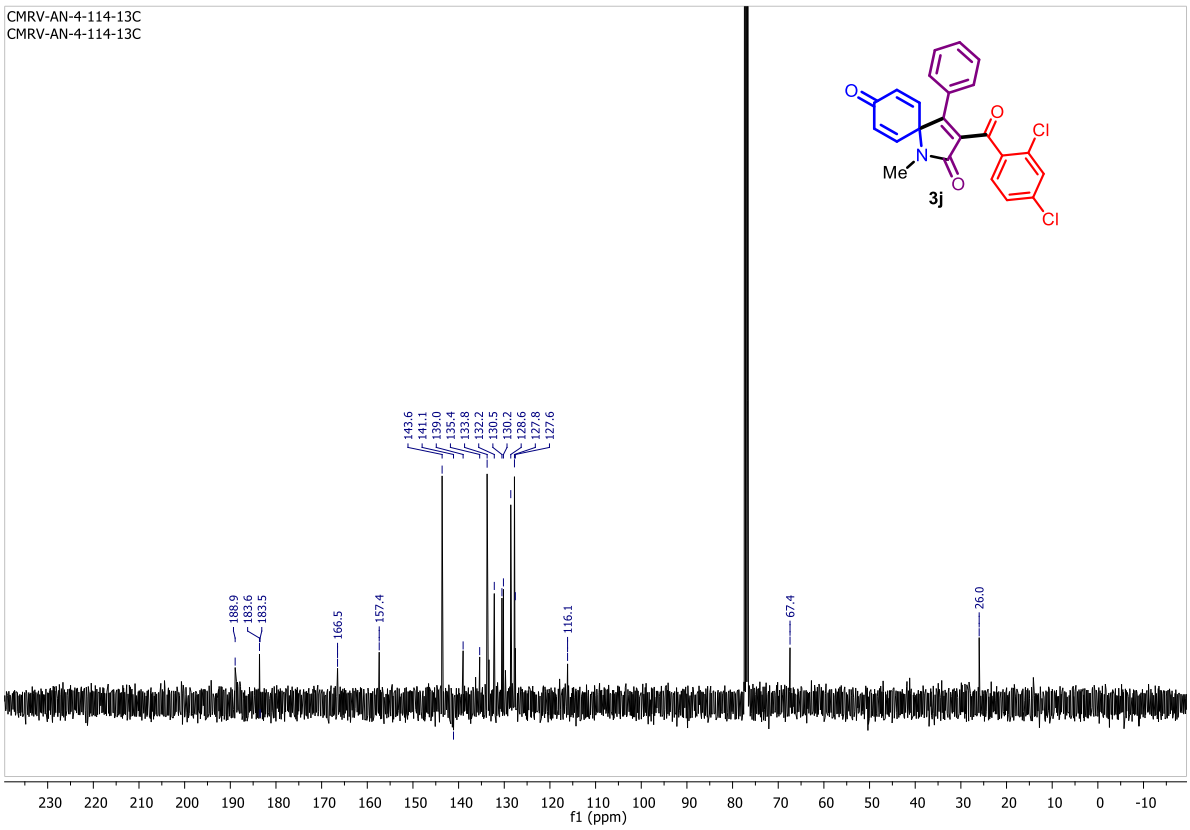

CMRV-AHS-124-1H
CMRV-AHS-124-1H
O
O
N
Me
O
Br
3g
2.01
2.08
5.37
2.03
2.07
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

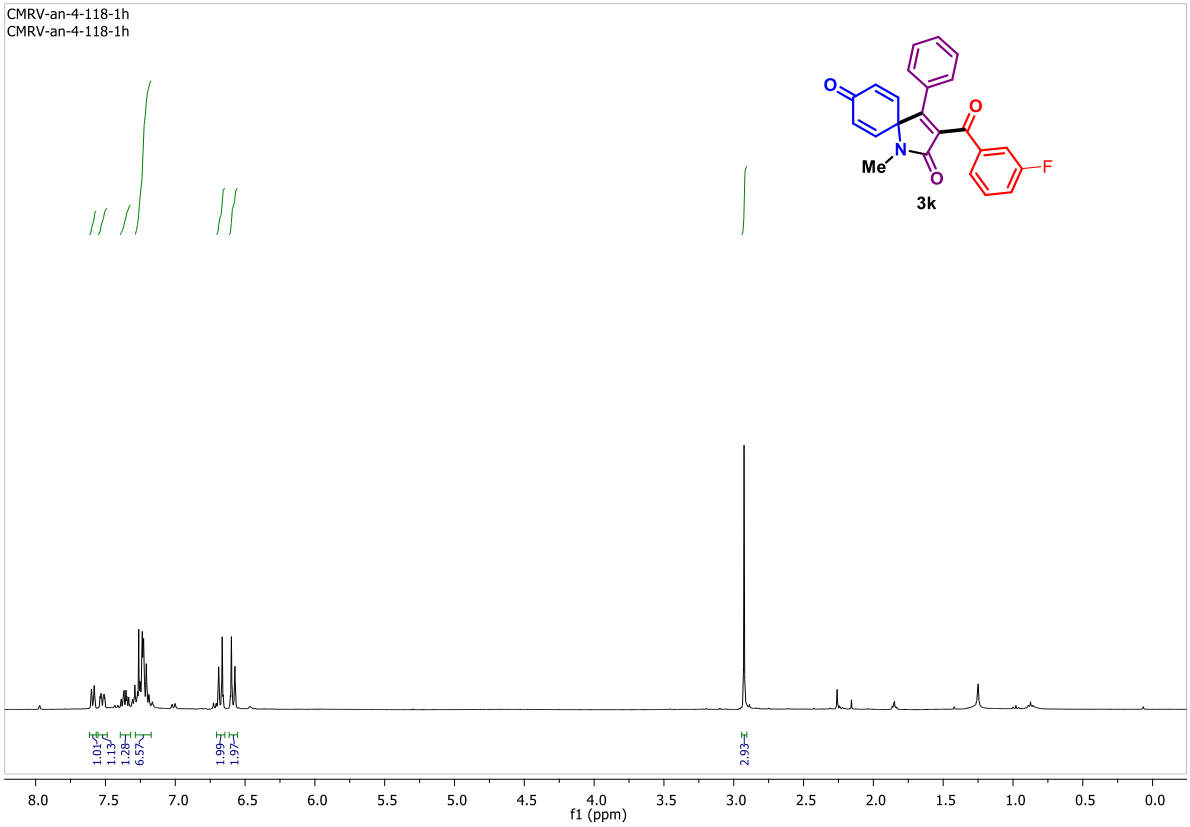

CMRV-AHS-124-13C
CMRV-AHS-124-13C
O
O
N
Me
O
Br
3g
190.2
183.7
167.0
155.2
144.4
135.6
134.3
133.6
132.1
130.8
129.9
129.7
128.9
127.8
67.3
25.9
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

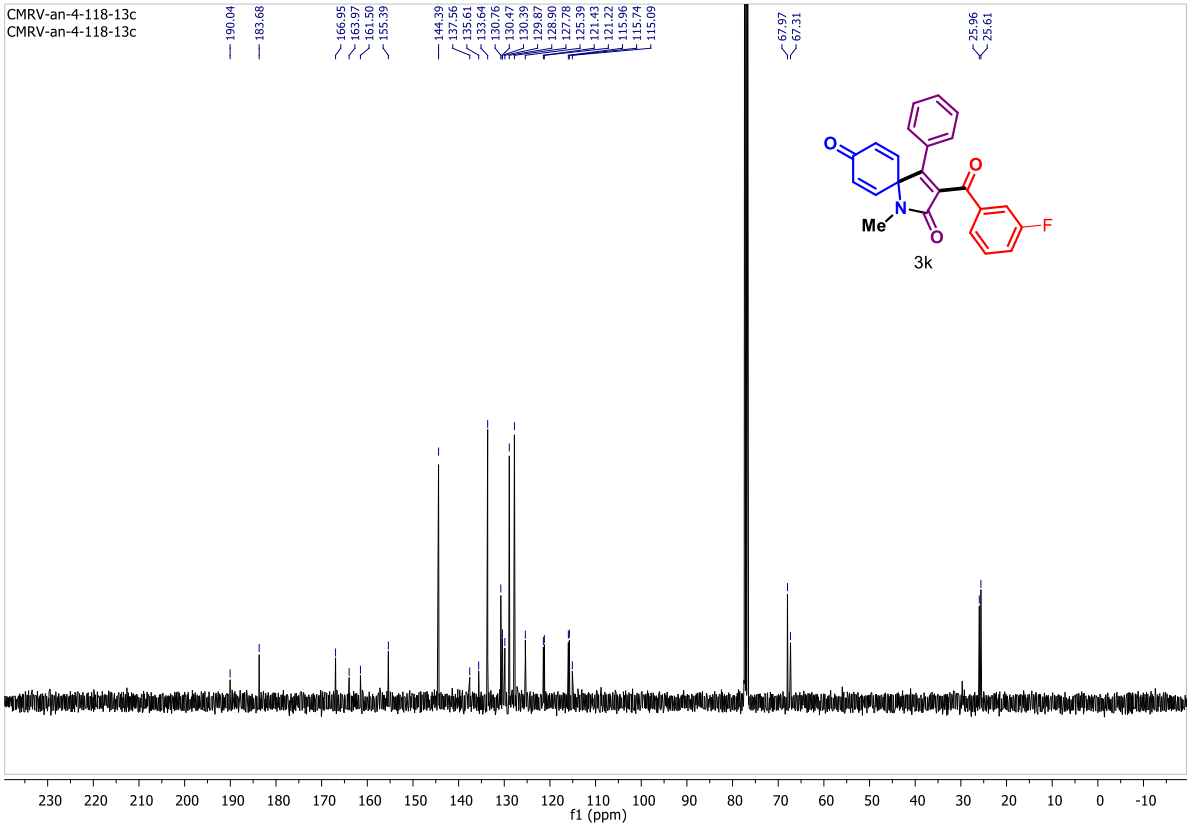

CMRV-AHS-127-1H
CMRV-AHS-127-1H
7.27
7.26
7.23
7.21
7.21
7.20
7.20
7.00
6.93
6.91
6.82
6.61
6.60
6.59
6.59
6.55
6.54
6.53
6.52
6.51
3.84
2.89
Ph
O
O
OMe
N
Me
O
3i
0.97
1.04
5.29
1.06
1.03
2.00
2.08
3.16
3.39
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

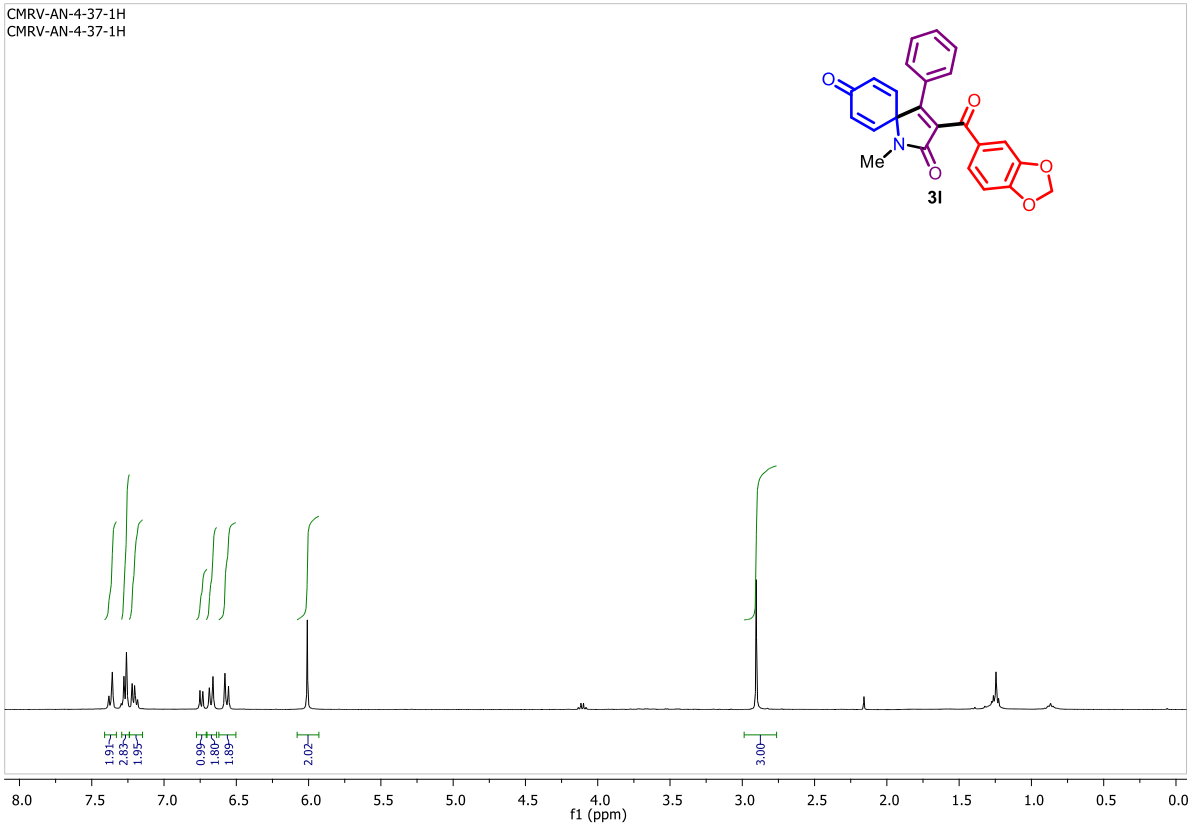

CMRV-AHS-127-13C
CMRV-AHS-127-13C
167.31
159.60
152.33
144.93
135.26
133.35
131.12
130.47
129.97
128.52
127.88
126.84
121.12
111.93
67.03
55.85
25.76
Ph
O
O
OMe
N
Me
O
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

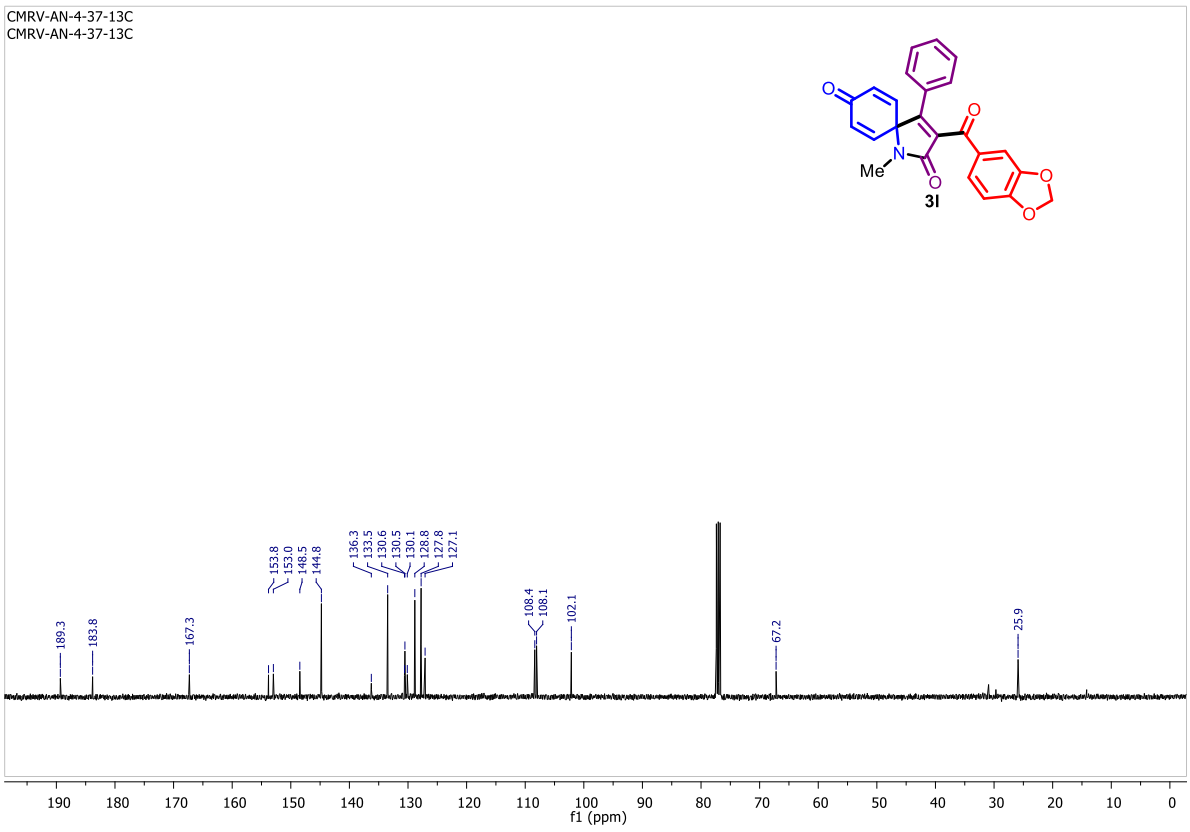

CMRV-AN-4-114-1H
CMRV-AN-4-114-1H
O
O
Cl
N
Me
O
Cl
3j
1.12
1.19
1.01
3.18
2.17
2.21
2.25
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

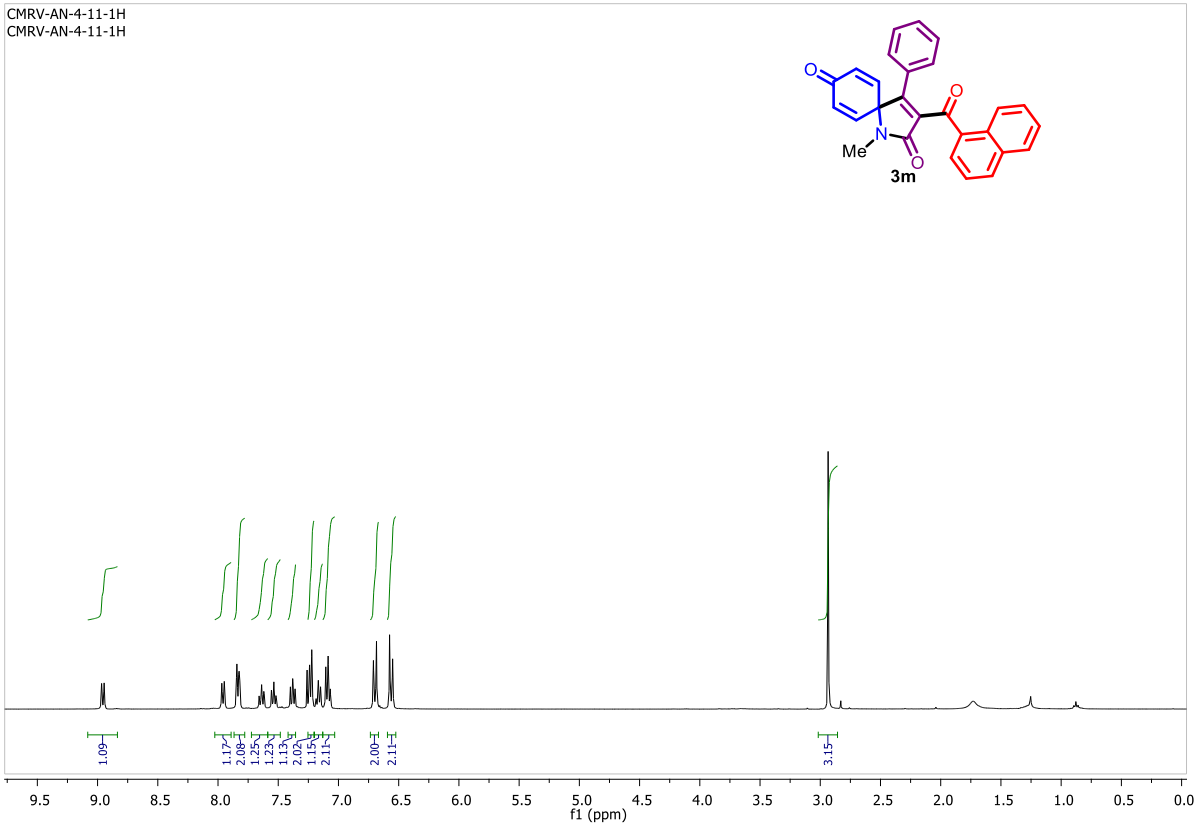

CMRV-AN-4-114-13C
CMRV-AN-4-114-13C
O
O
Cl
N
Me
O
Cl
3j
143.6
141.1
139.0
135.4
133.8
132.2
130.5
130.2
128.6
127.8
127.6
188.9
183.6
183.5
166.5
157.4
116.1
67.4
26.0
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

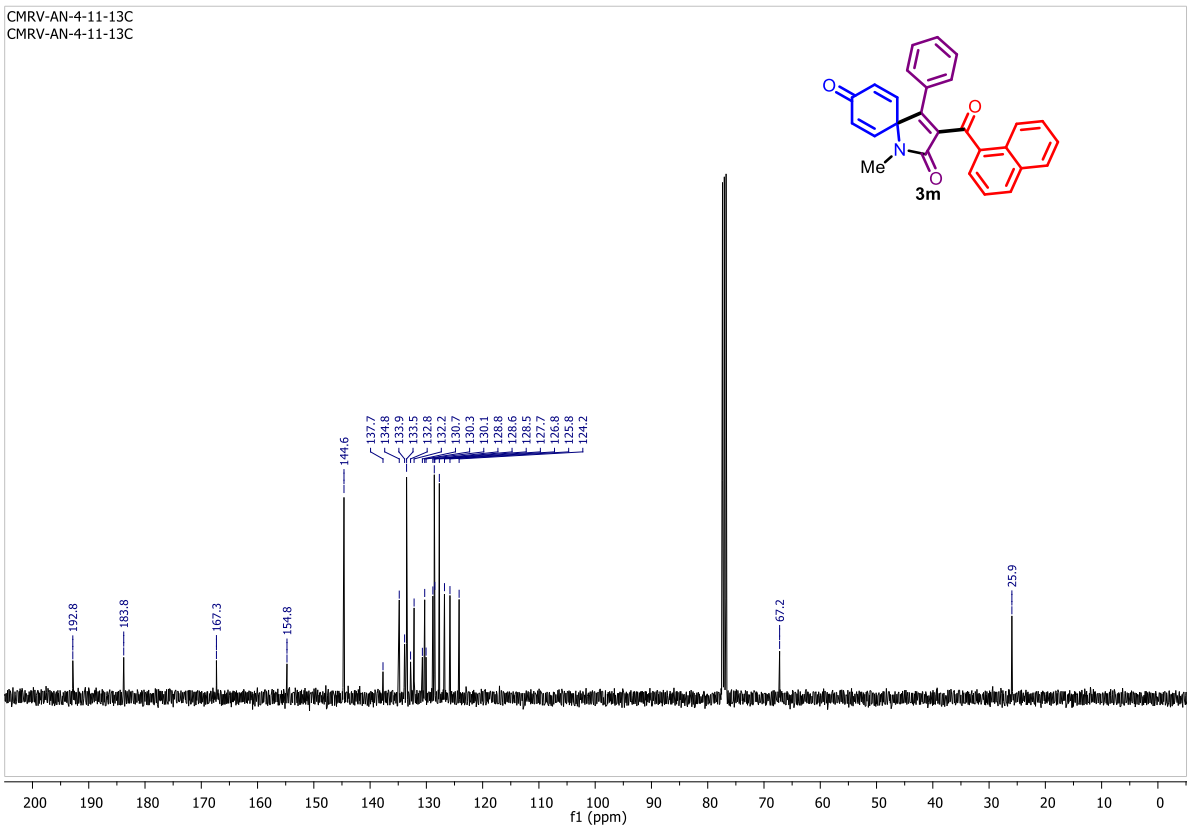

CMRV-an-4-118-1h
CMRV-an-4-118-1h
O
O
N
Me
O
F
3k
1.01
1.13
1.28
6.57
1.99
1.97
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

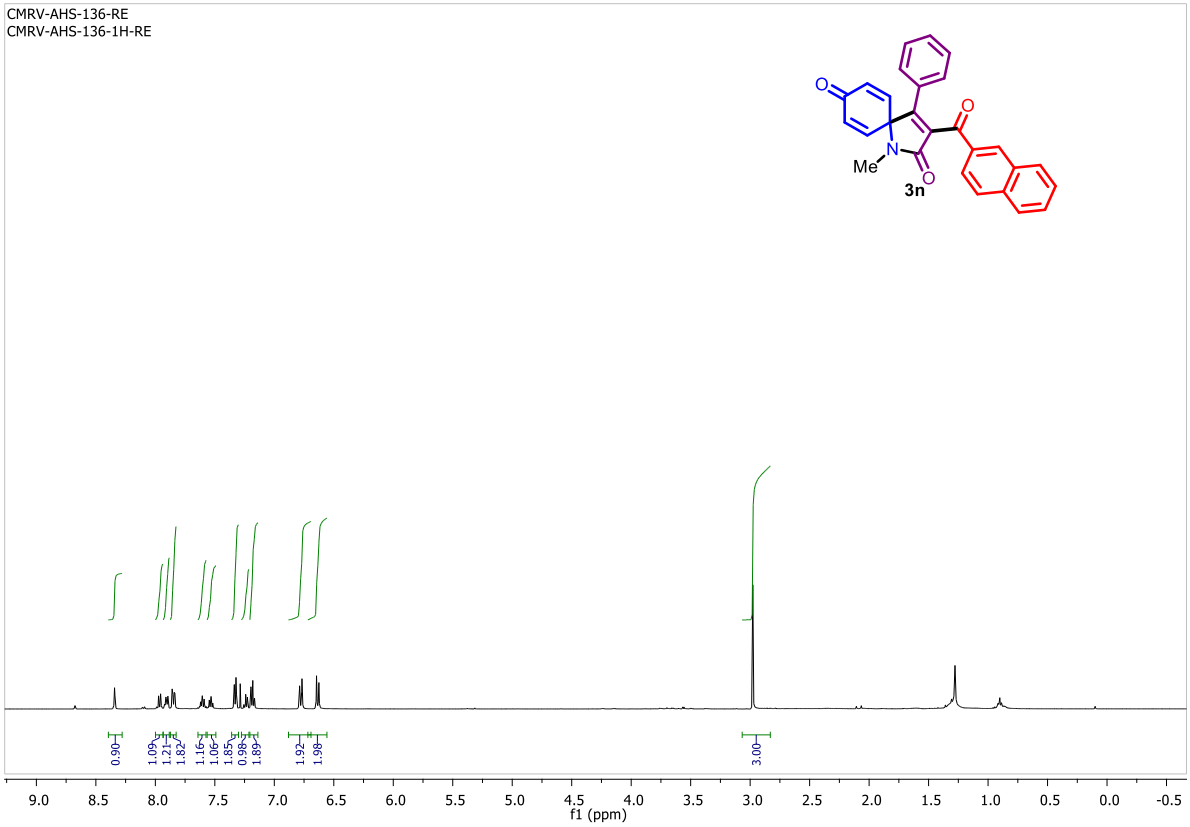

CMRV-an-4-118-13c
CMRV-an-4-118-13c
190.04
183.68
166.95
163.97
161.50
155.39
144.39
137.56
135.61
133.64
130.76
130.47
130.39
129.87
128.90
127.78
125.39
121.43
121.22
115.96
115.74
115.09
67.97
67.31
25.96
25.61
O
O
N
Me
O
F
3k
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

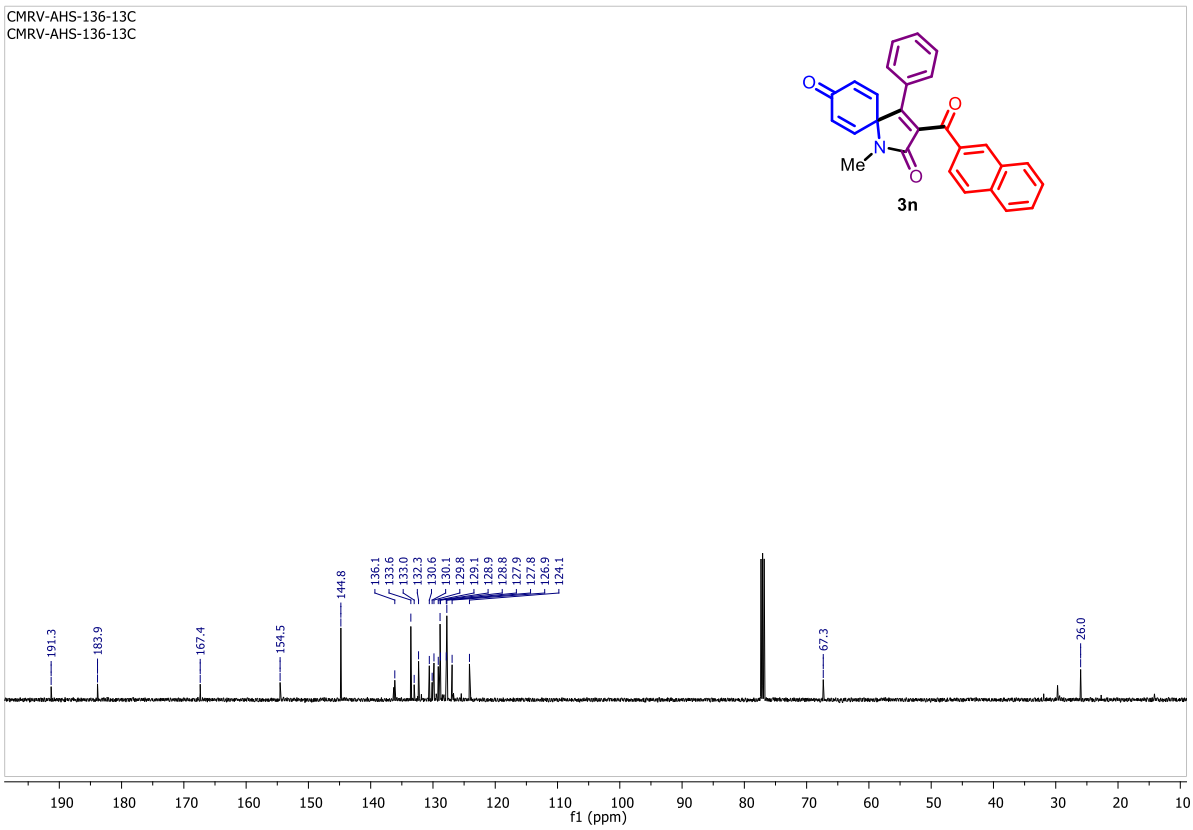

CMRV-AN-4-37-1H
CMRV-AN-4-37-1H
Me
3l
1.91
2.83
1.95
0.99
1.80
1.89
2.02
3.00
f1 (ppm)

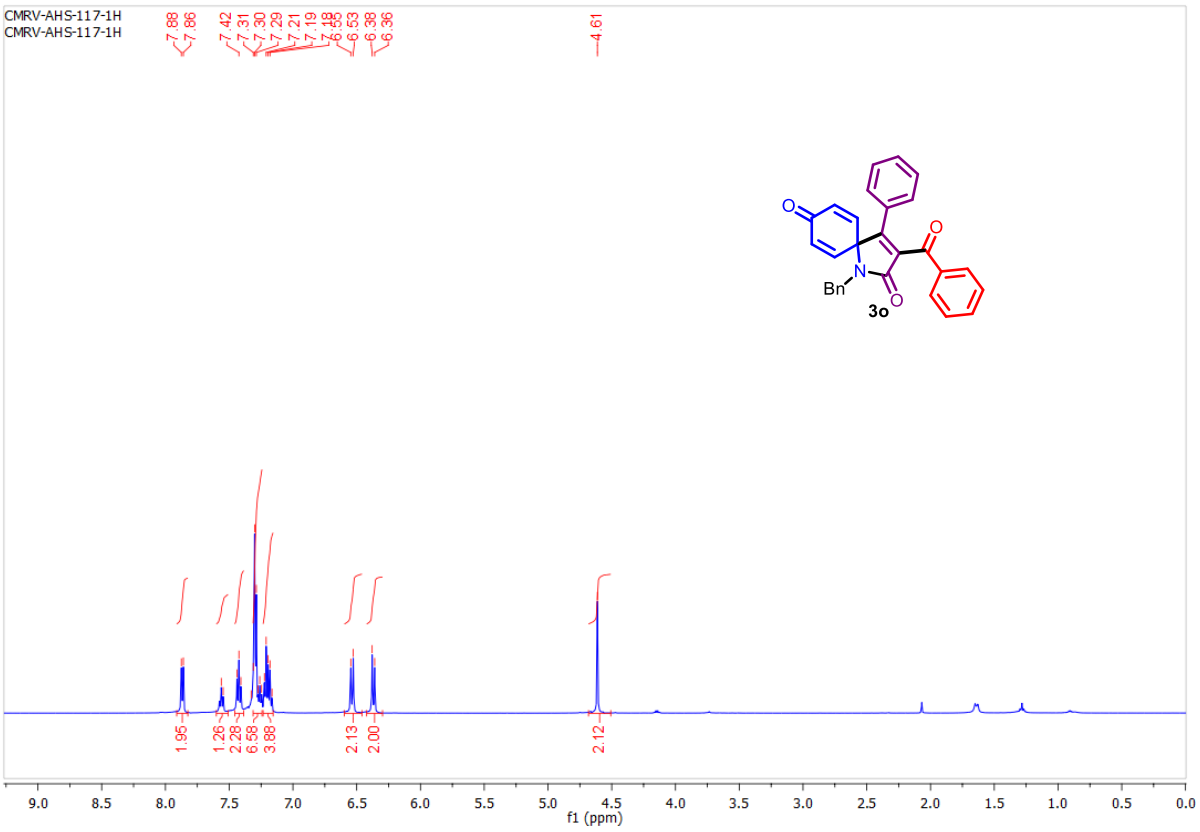

CMRV-AN-4-37-13C
CMRV-AN-4-37-13C
Me
3l
189.3
183.8
167.3
153.8
153.0
148.5
144.8
136.3
133.5
130.6
130.5
130.1
128.8
127.8
127.1
108.4
108.1
102.1
67.2
25.9
f1 (ppm)

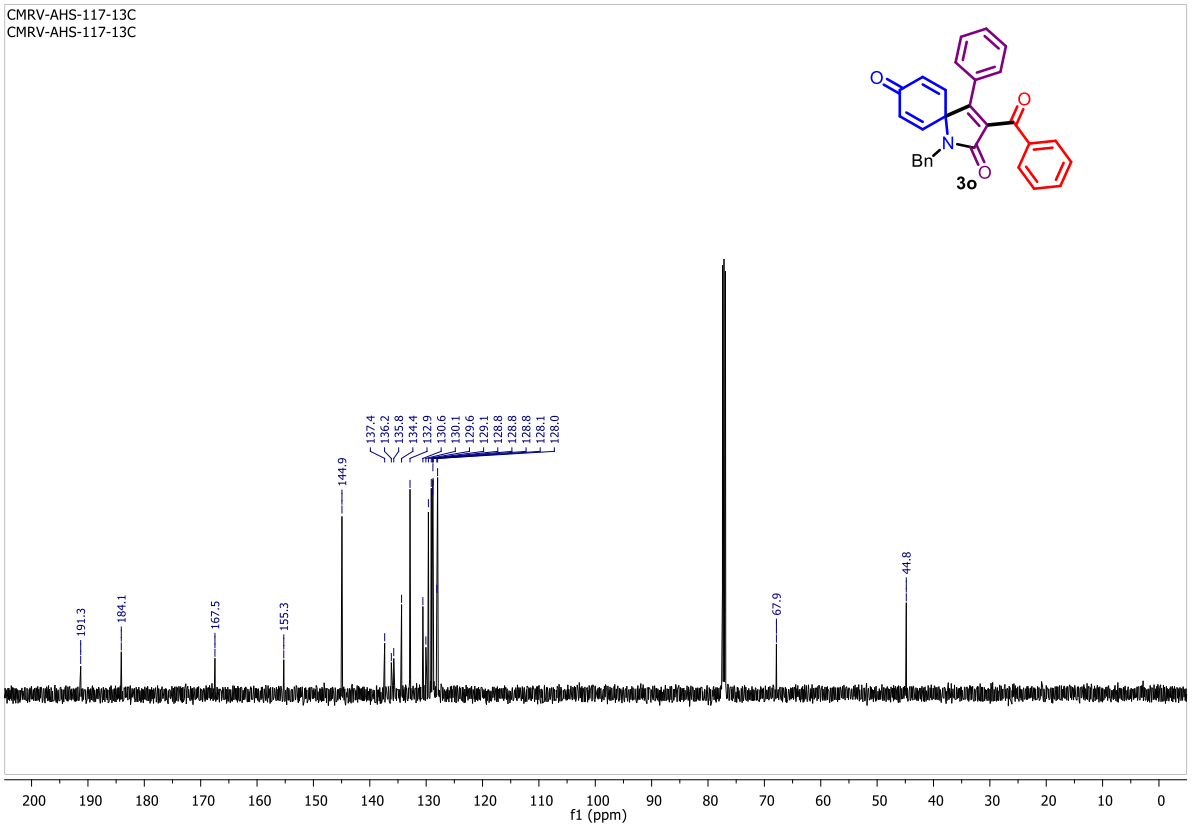

CMRV-AN-4-11-1H
CMRV-AN-4-11-1H
Me
3m
1.09
1.17
2.08
1.25
1.23
1.13
2.02
1.15
2.11
2.00
2.11
3.15
f1 (ppm)

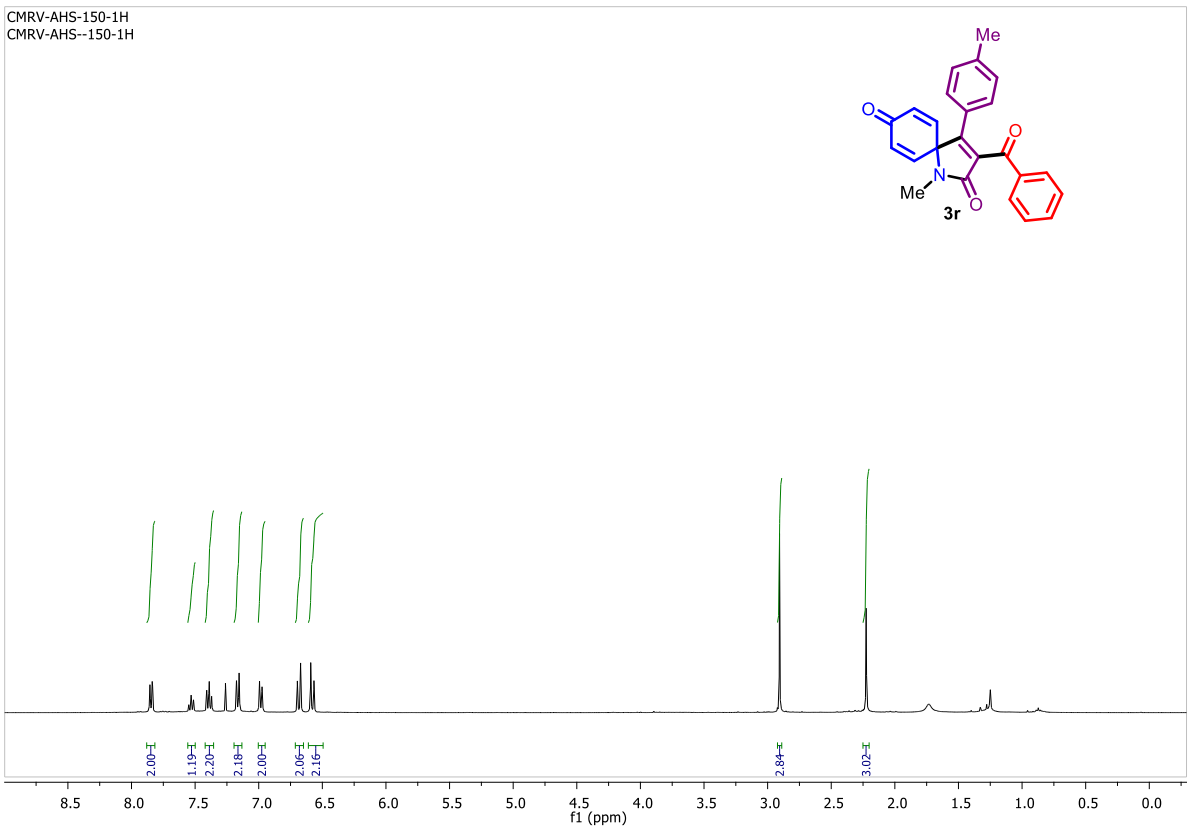

CMRV-AN-4-11-13C
CMRV-AN-4-11-13C
Me
3m
192.8
183.8
167.3
154.8
144.6
137.7
134.8
133.9
133.5
132.8
132.2
130.7
130.3
130.1
128.8
128.6
128.5
127.7
126.8
125.8
124.2
67.2
25.9
f1 (ppm)

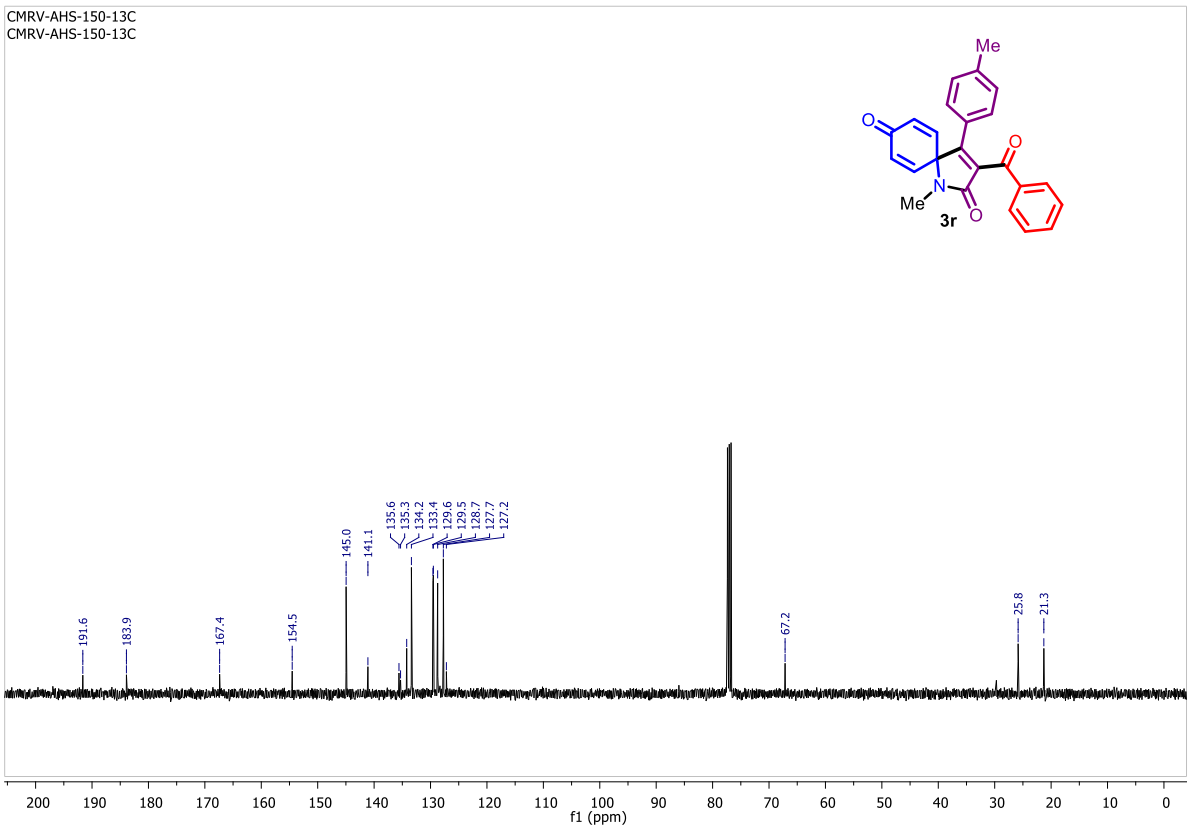

CMRV-AHS-136-RE
CMRV-AHS-136-1H-RE
O
O
N
Me
O
3n
0.90
1.09
1.21
1.82
1.16
1.06
1.85
0.98
1.89
1.92
1.98
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

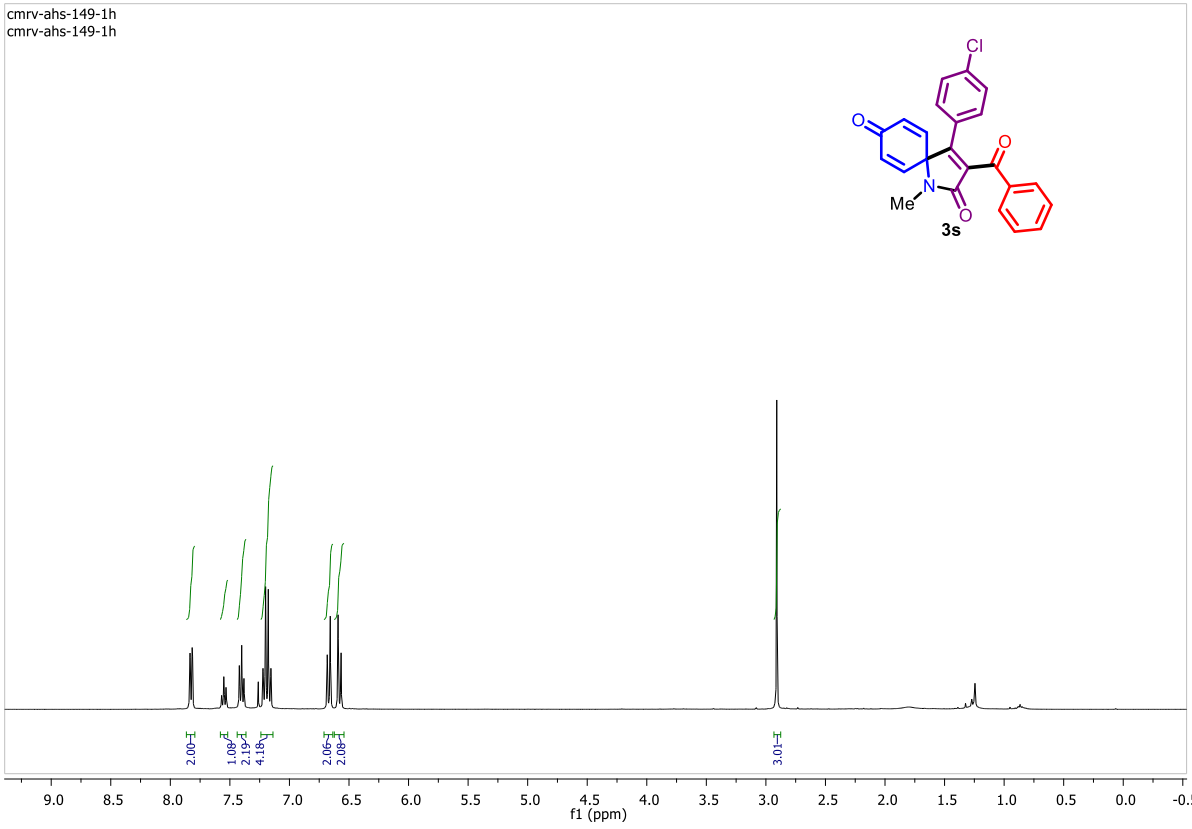

CMRV-AHS-136-13C
CMRV-AHS-136-13C
O
O
N
Me
O
3n
191.3
183.9
167.4
154.5
144.8
136.1
133.6
133.0
132.3
130.6
130.1
129.8
129.1
128.9
128.8
127.9
127.8
126.9
124.1
67.3
26.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

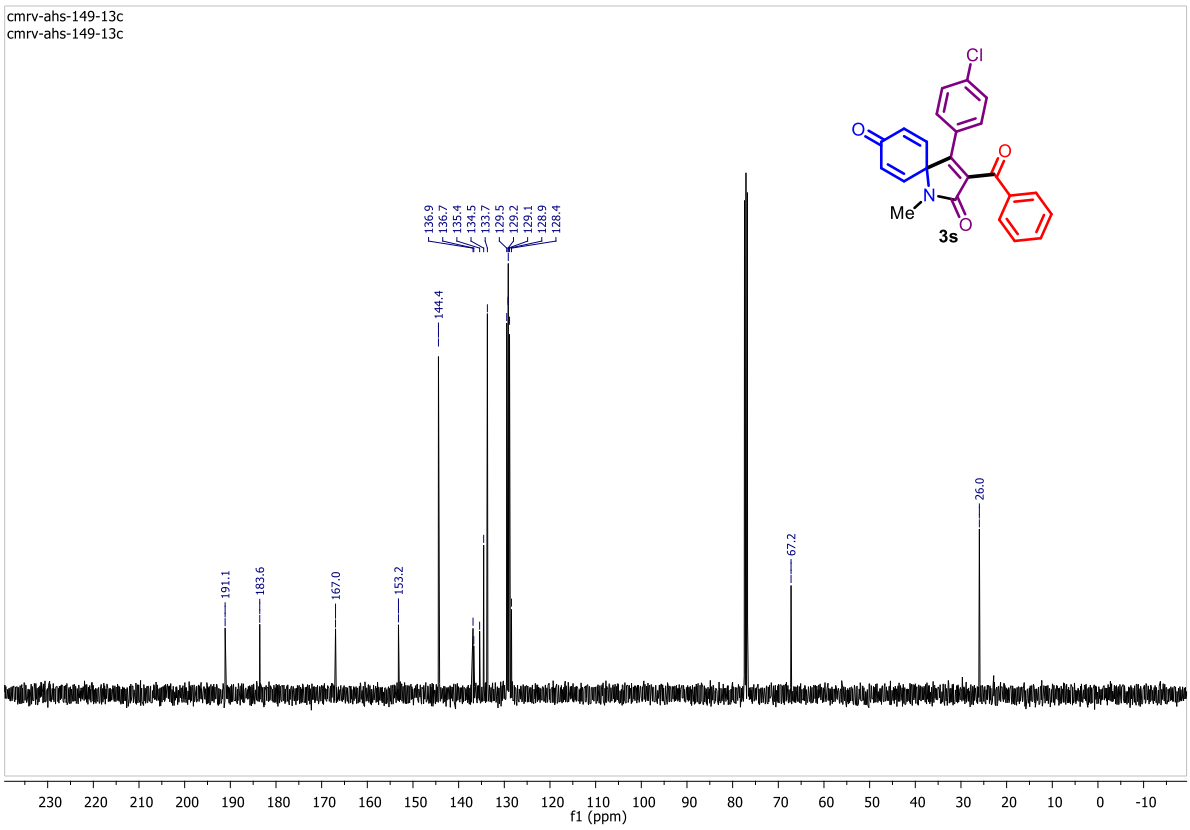

CMRV-AHS-117-1H
CMRV-AHS-117-1H
7.88
7.86
7.42
7.31
7.30
7.29
7.21
7.19
7.18
6.55
6.53
6.38
6.36
4.61
Bn
3o
1.95
1.26
2.28
6.58
3.88
2.13
2.00
2.12
f1 (ppm)

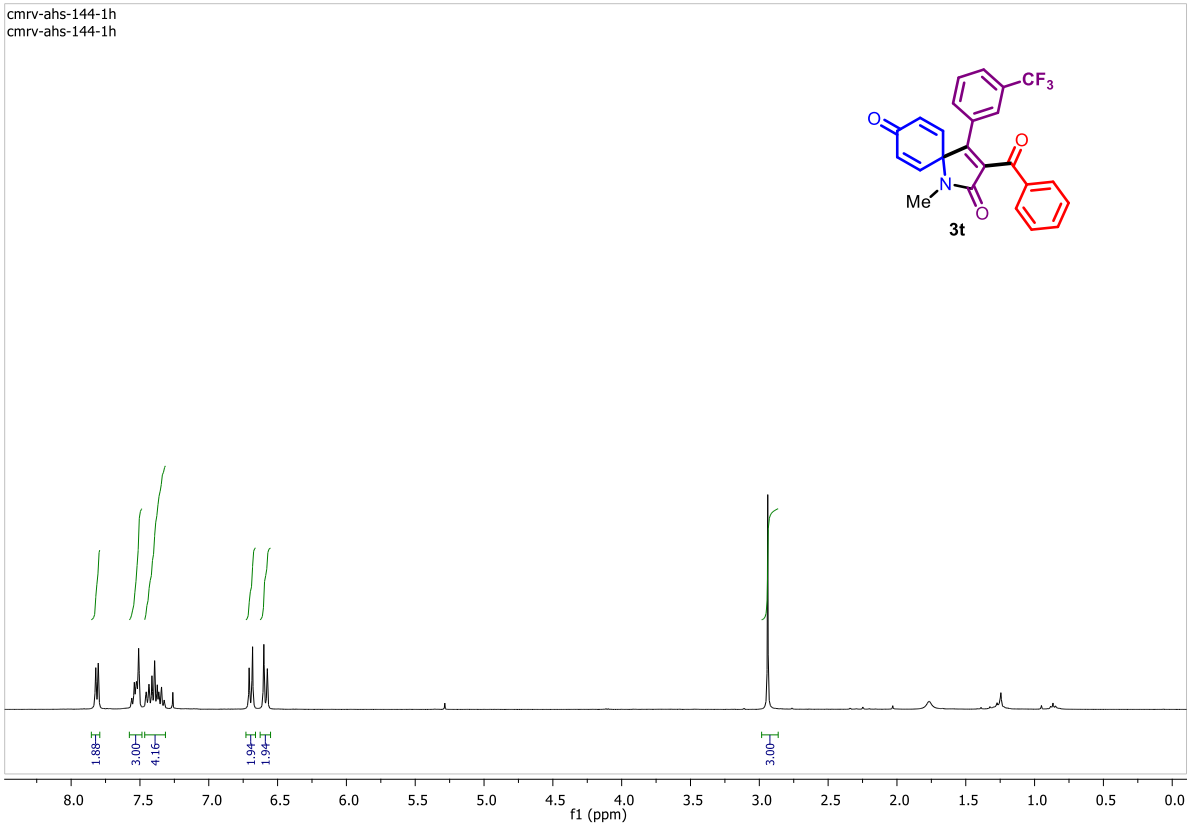

CMRV-AHS-117-13C
CMRV-AHS-117-13C
Bn
3o
137.4
136.2
135.8
134.4
132.9
130.6
130.1
129.6
129.1
128.8
128.8
128.8
128.1
128.0
144.9
191.3
184.1
167.5
155.3
67.9
44.8
f1 (ppm)

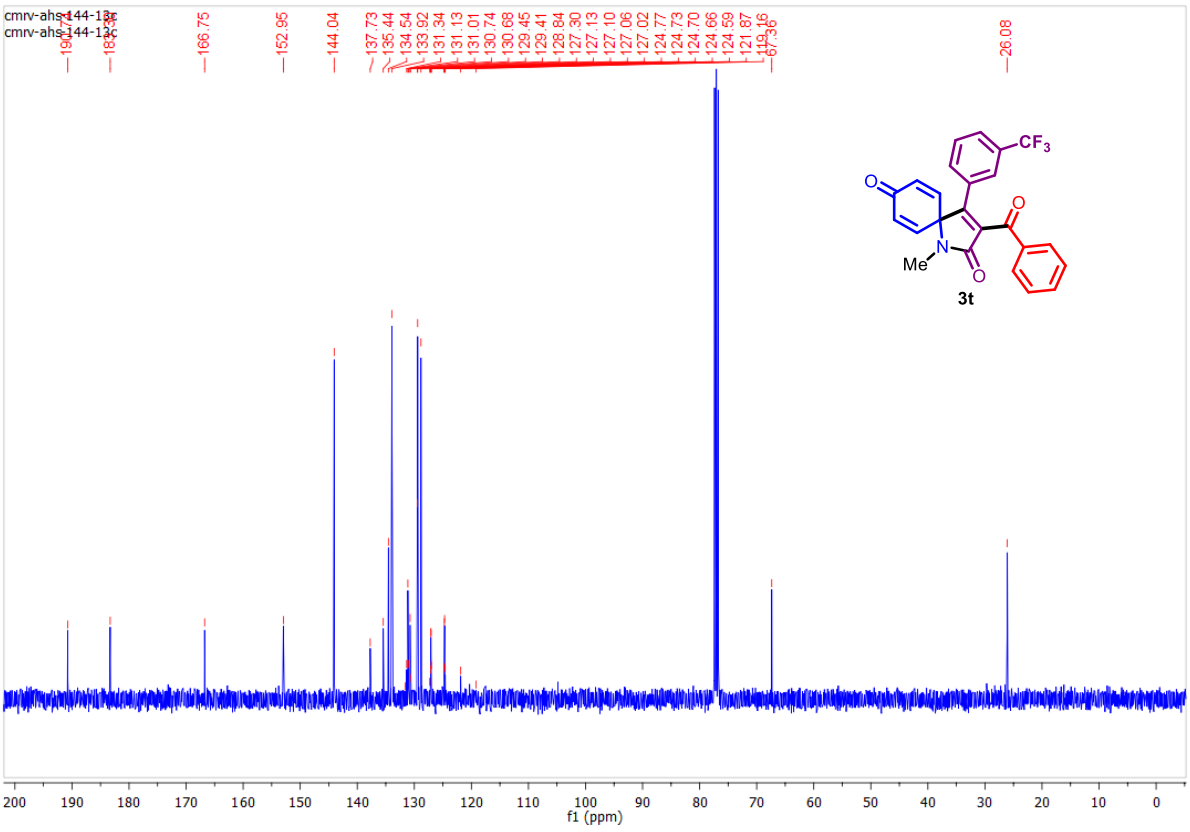

CMRV-AHS-150-1H
CMRV-AHS--150-1H
Me
O
O
N
Me
O
3r
2.00
1.19
2.20
2.18
2.00
2.06
2.16
2.84
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

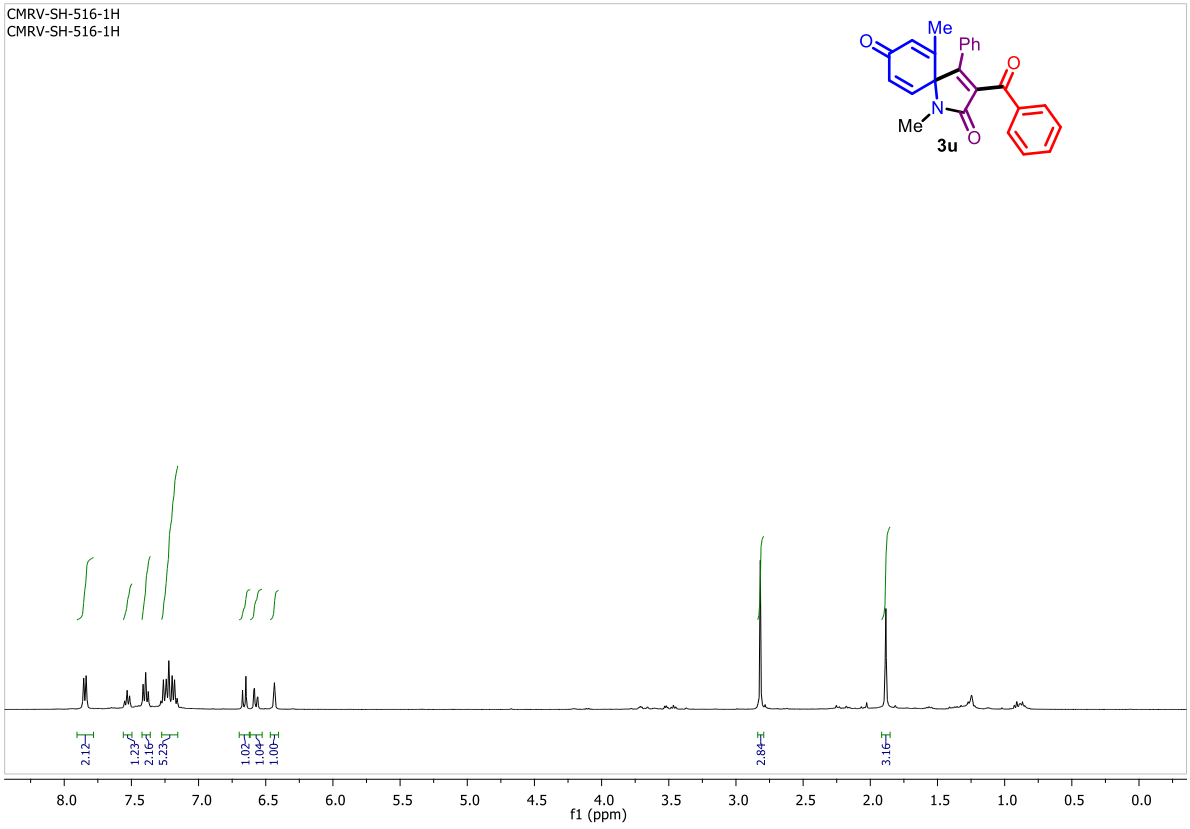

CMRV-AHS-150-13C
CMRV-AHS-150-13C
Me
O
O
N
Me
O
3r
191.6
183.9
167.4
154.5
145.0
141.1
135.6
135.3
134.2
133.4
129.6
129.5
128.7
127.7
127.2
67.2
25.8
21.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

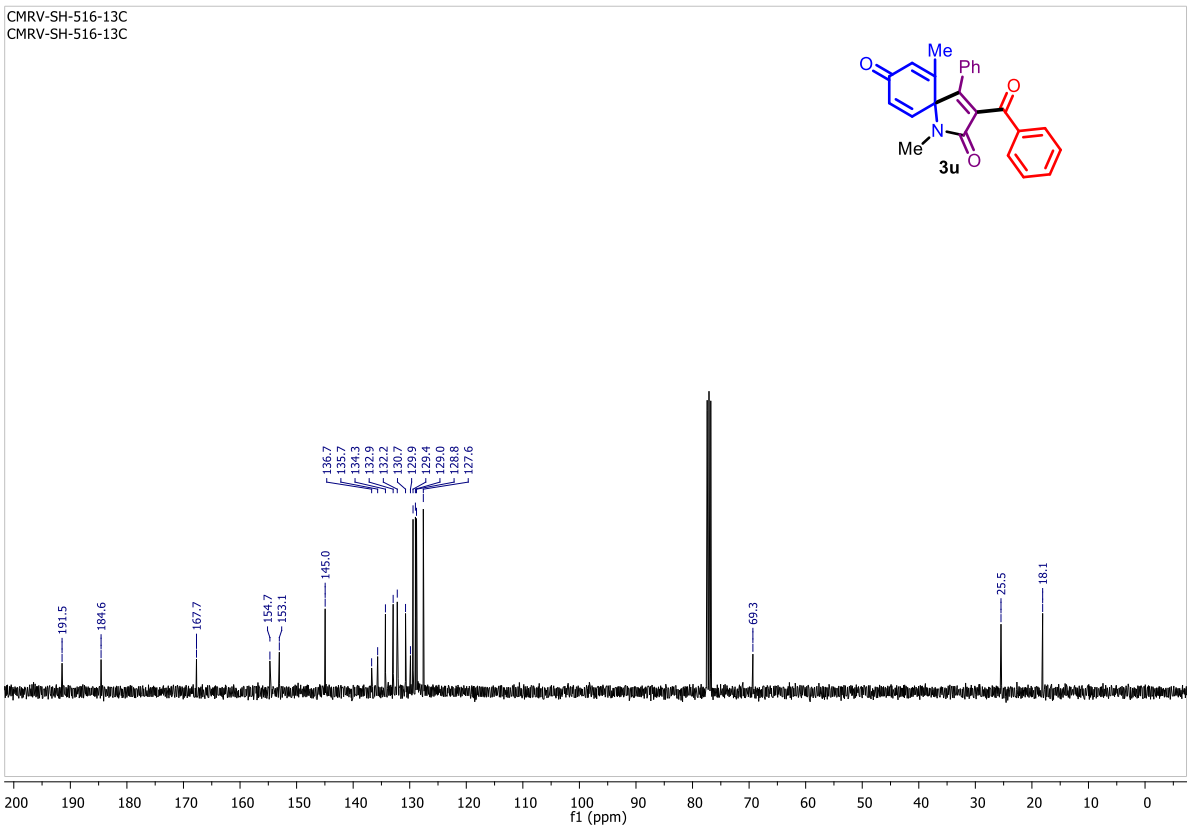

cmrv-ahs-149-1h
cmrv-ahs-149-1h
Cl
O
O
N
Me
O
3s
2.00
1.09
2.19
4.18
2.06
2.08
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

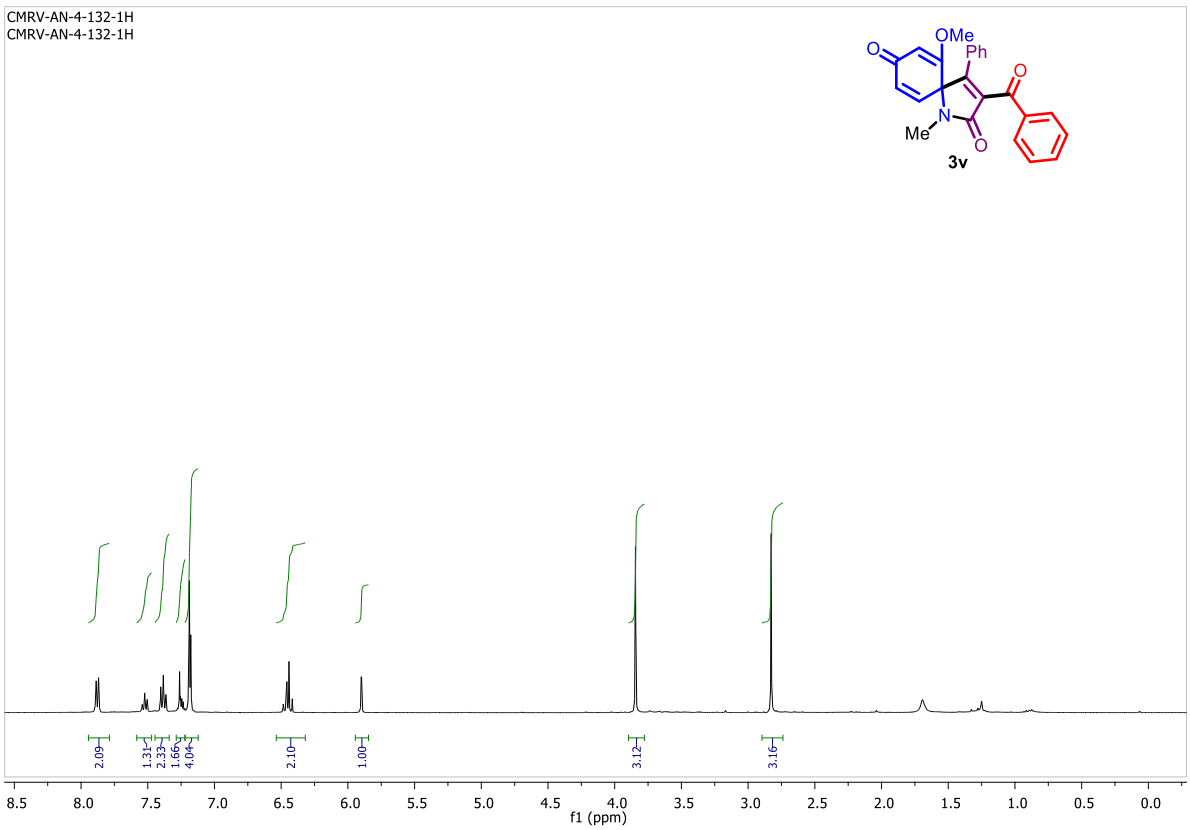

cmrv-ahs-149-13c
cmrv-ahs-149-13c
Cl
O
O
N
Me
O
3s
136.9
136.7
135.4
134.5
133.7
129.5
129.2
129.1
128.9
128.4
144.4
191.1
183.6
167.0
153.2
67.2
26.0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

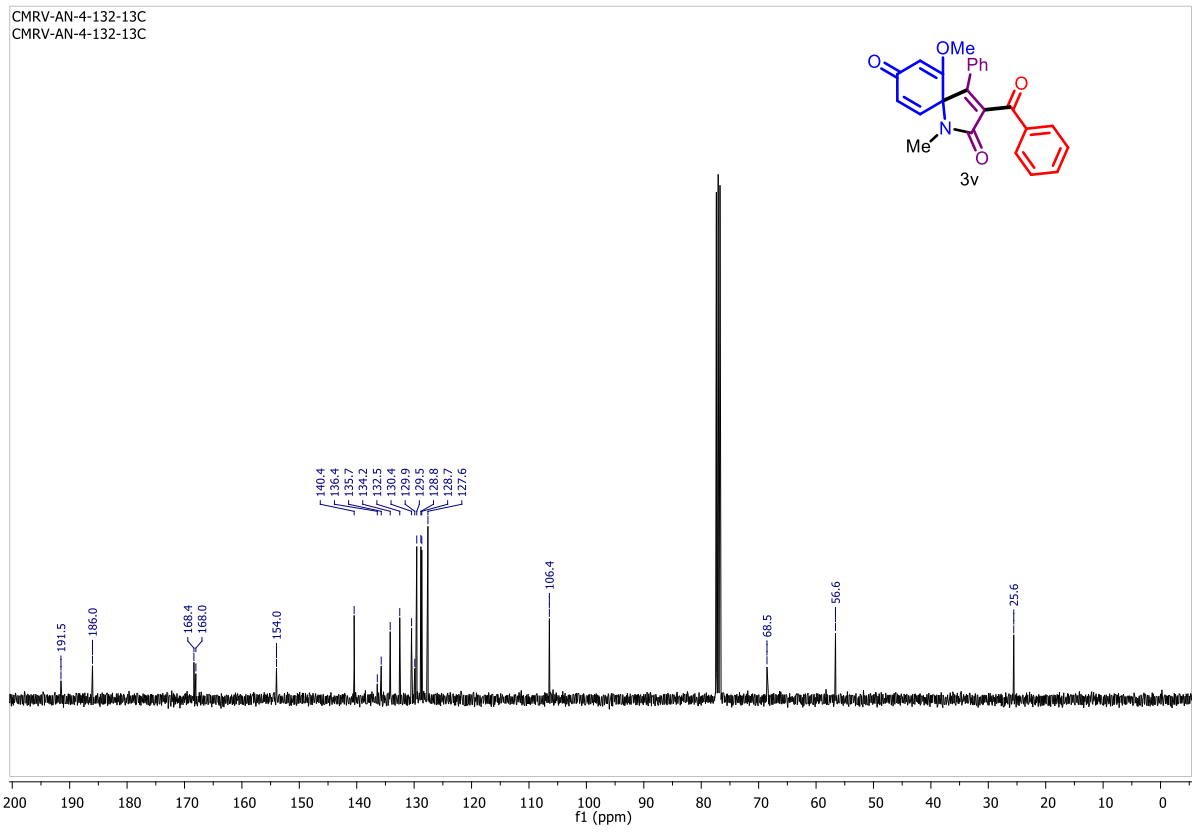

cmrv-ahs-144-1h
cmrv-ahs-144-1h
CF3
O
O
N
Me
O
3t
1.88
3.00
4.16
1.94
1.94
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

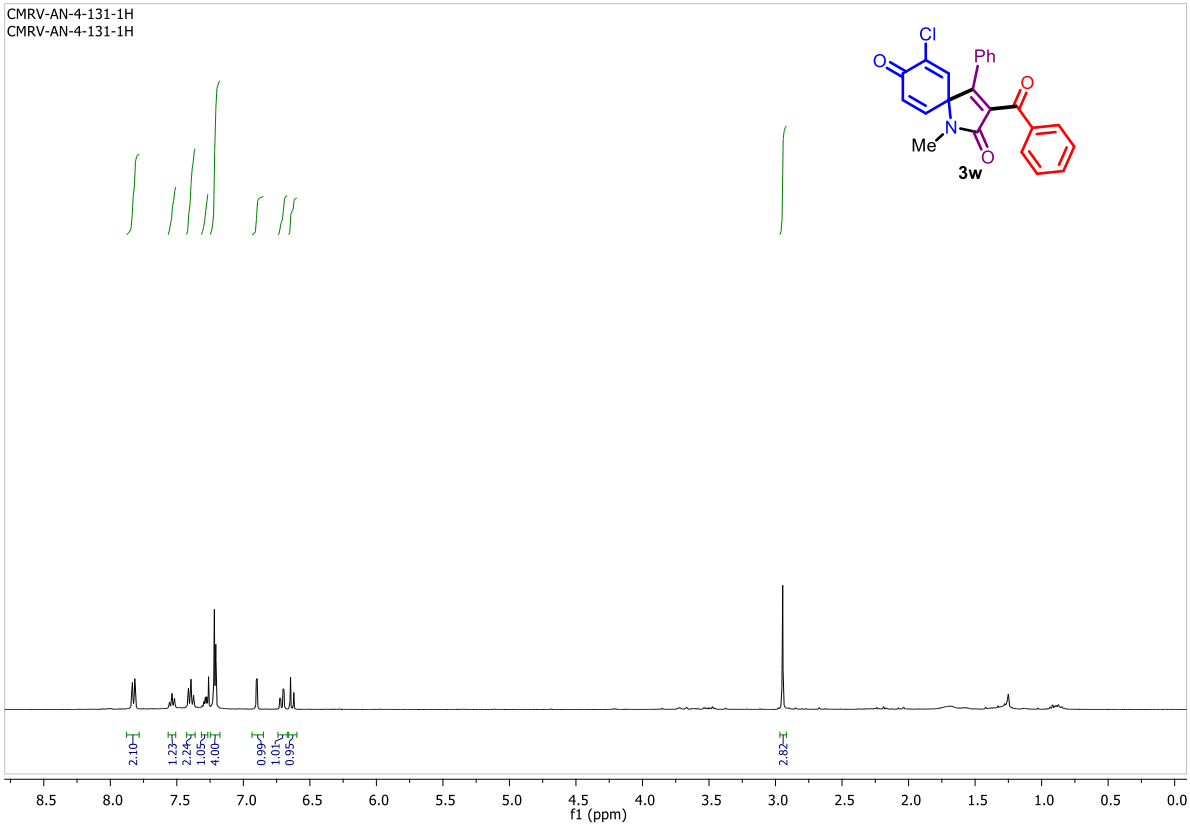

cmrv-ahs-144-13c
cmrv-ahs-144-13c
166.75
152.95
144.04
137.73
135.44
134.54
133.92
131.34
131.13
131.01
130.74
130.68
129.45
129.41
128.84
127.30
127.13
127.10
127.06
127.02
124.77
124.73
124.70
124.66
124.59
121.87
119.16
67.36
26.08
CF3
O
O
N
Me
O
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

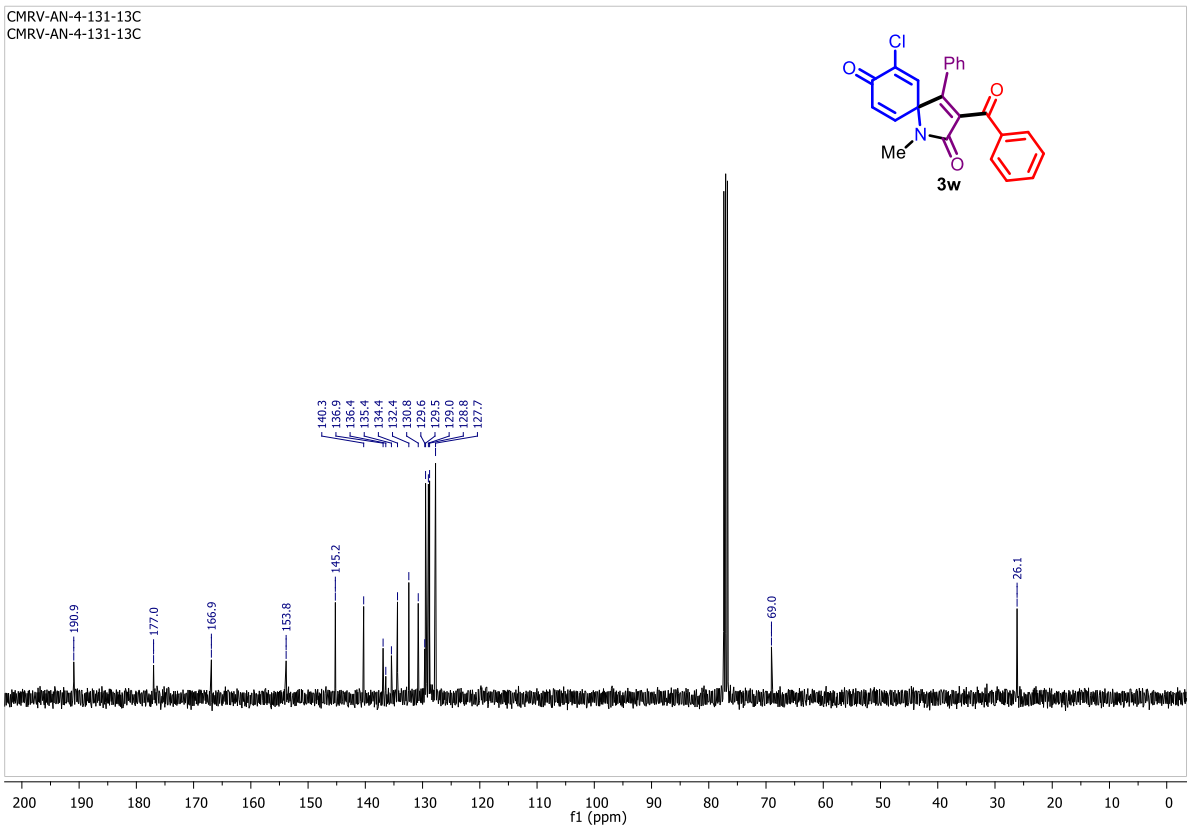

CMRV-SH-516-1H
CMRV-SH-516-1H
Me
Ph
O
O
N
Me
O
3u
2.12
1.23
2.16
5.23
1.02
1.04
1.00
2.84
3.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CMRV-SH-516-13C
CMRV-SH-516-13C
Me
Ph
O
O
N
Me
O
3u
136.7
135.7
134.3
132.9
132.2
130.7
129.9
129.4
129.0
128.8
127.6
191.5
184.6
167.7
154.7
153.1
145.0
69.3
25.5
18.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

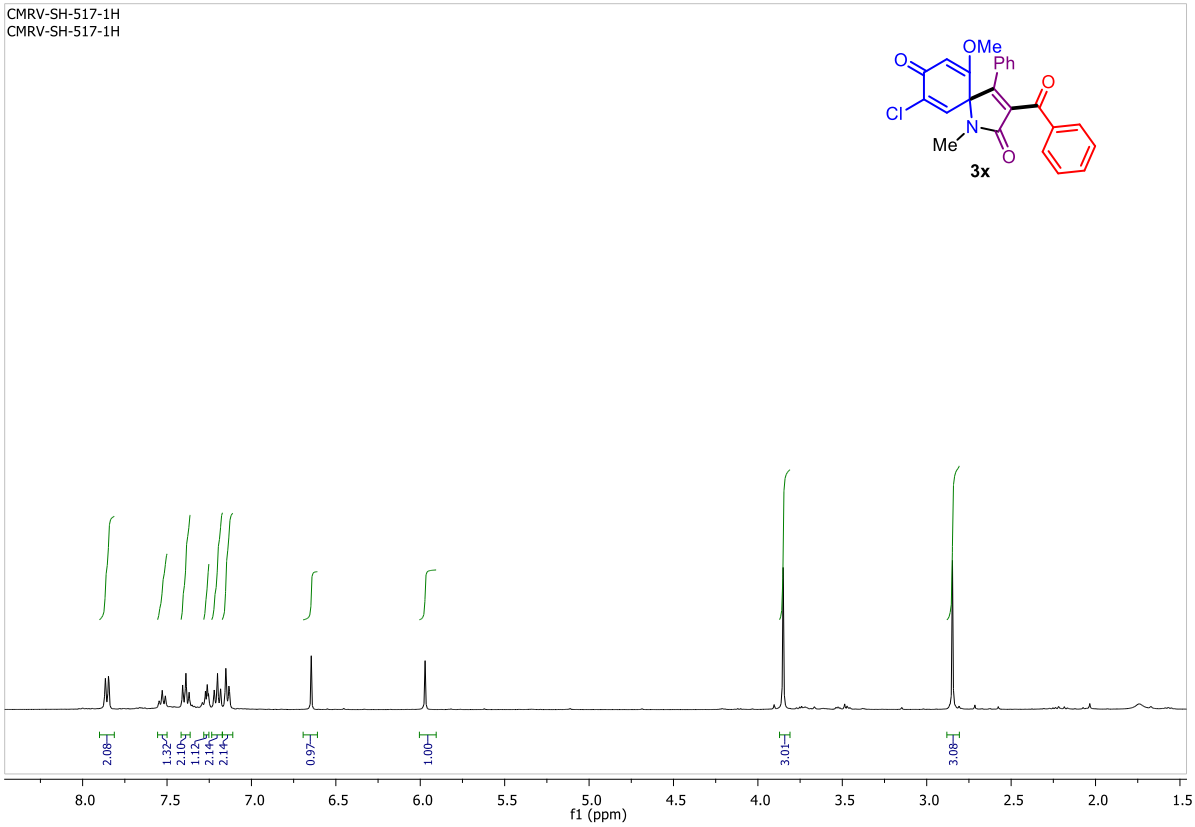

CMRV-AN-4-132-1H
CMRV-AN-4-132-1H
OMe
Ph
O
O
N
Me
O
3v
2.09
1.31
2.33
1.66
4.04
2.10
1.00
3.12
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CMRV-AN-4-132-13C
CMRV-AN-4-132-13C
OMe
Ph
O
O
N
Me
O
3v
140.4
136.4
135.7
134.2
132.5
130.4
129.9
129.5
128.8
128.7
127.6
191.5
186.0
168.4
168.0
154.0
106.4
68.5
56.6
25.6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

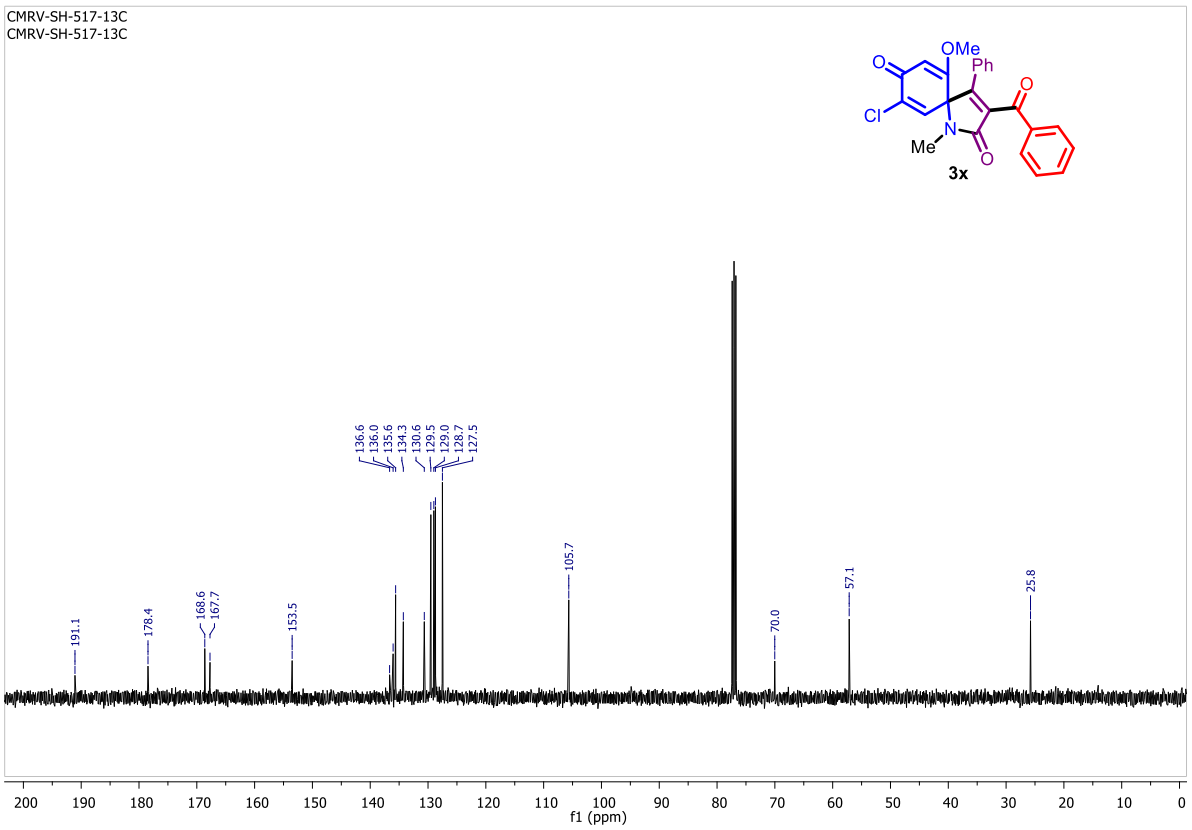

CMRV-AN-4-131-1H
CMRV-AN-4-131-1H
Cl
Ph
O
O
N
Me
O
3w
2.10
1.23
2.24
1.05
4.00
0.99
1.01
0.95
2.82
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

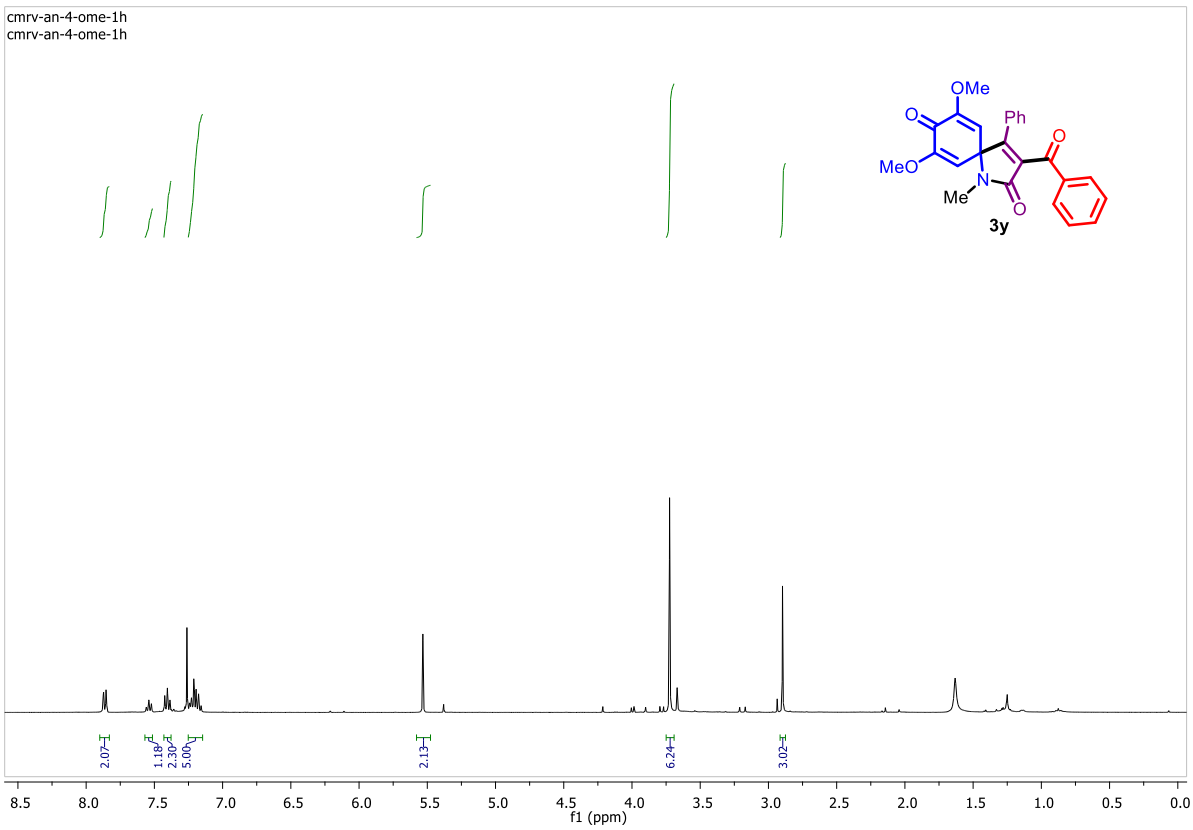

CMRV-AN-4-131-13C
CMRV-AN-4-131-13C
Cl
Ph
O
O
N
Me
O
3w
140.3
136.9
136.4
135.4
134.4
132.4
130.8
129.6
129.5
129.0
128.8
127.7
190.9
177.0
166.9
153.8
145.2
69.0
26.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

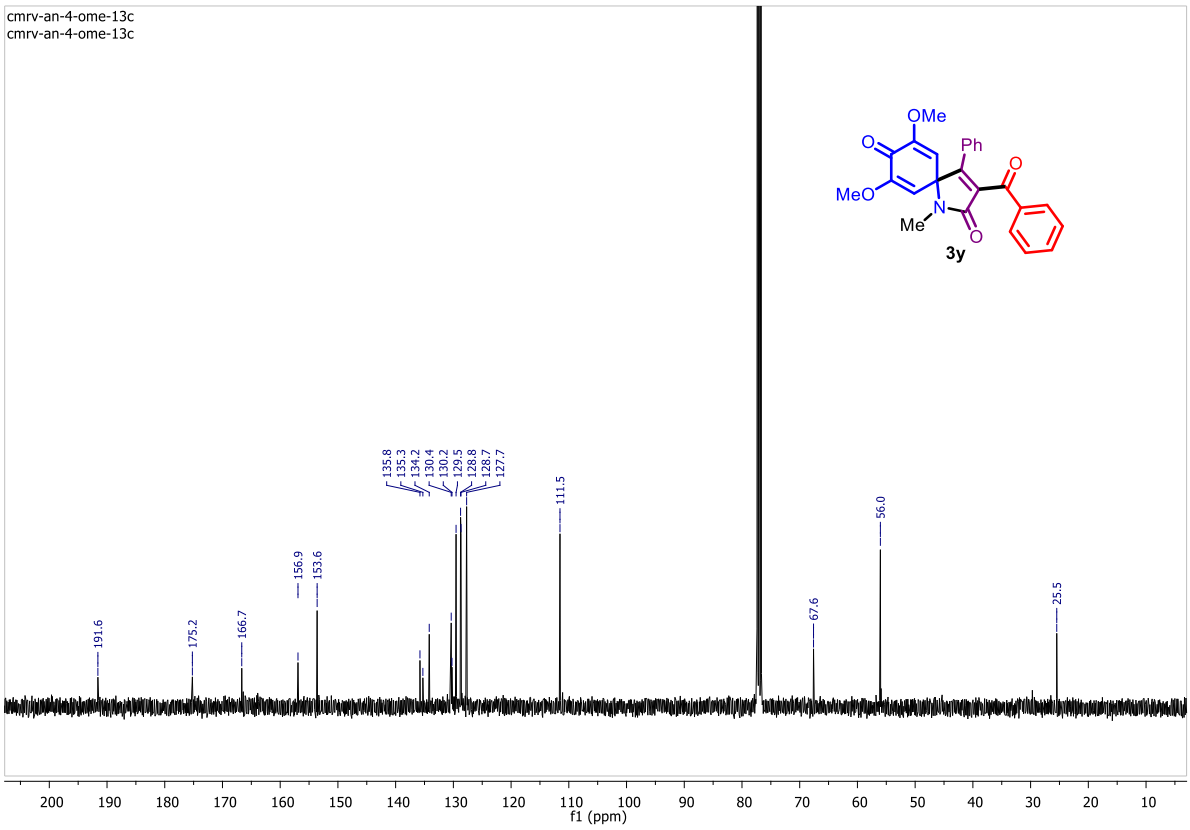
CMRV-SH-517-1H
CMRV-SH-517-1H

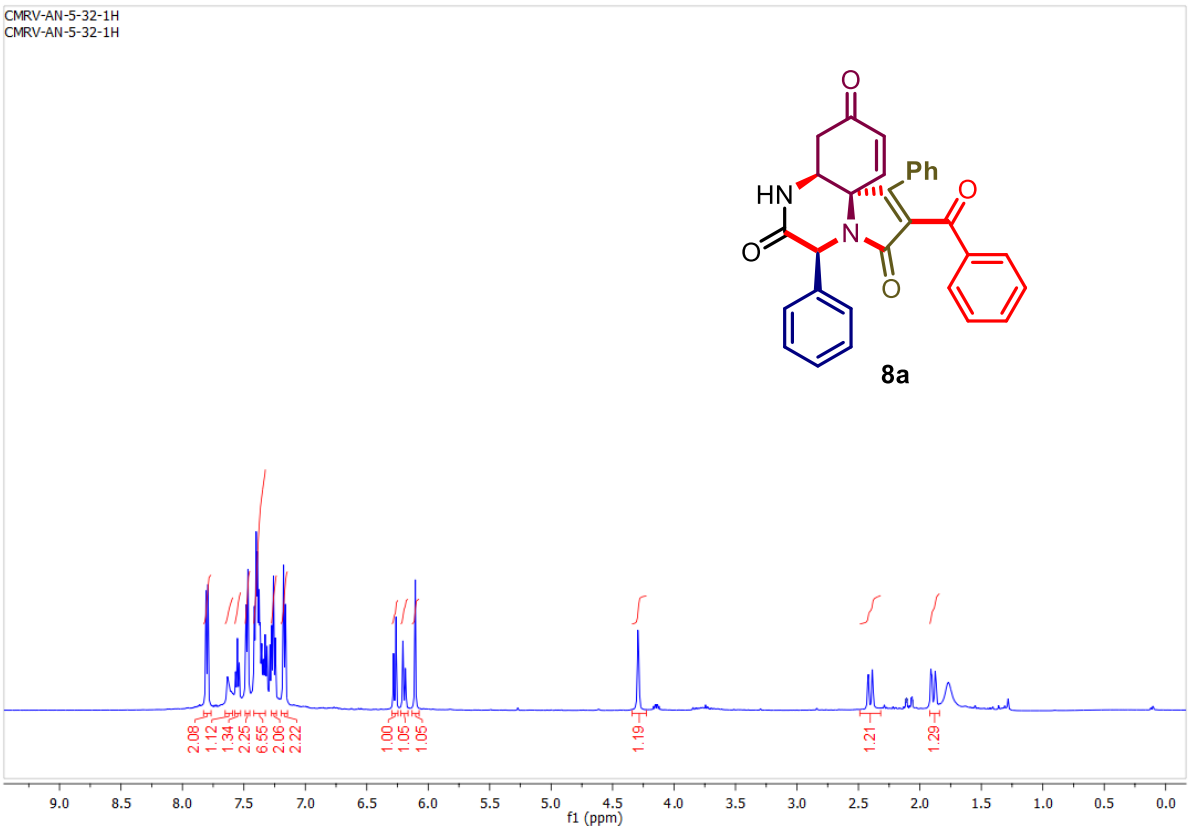


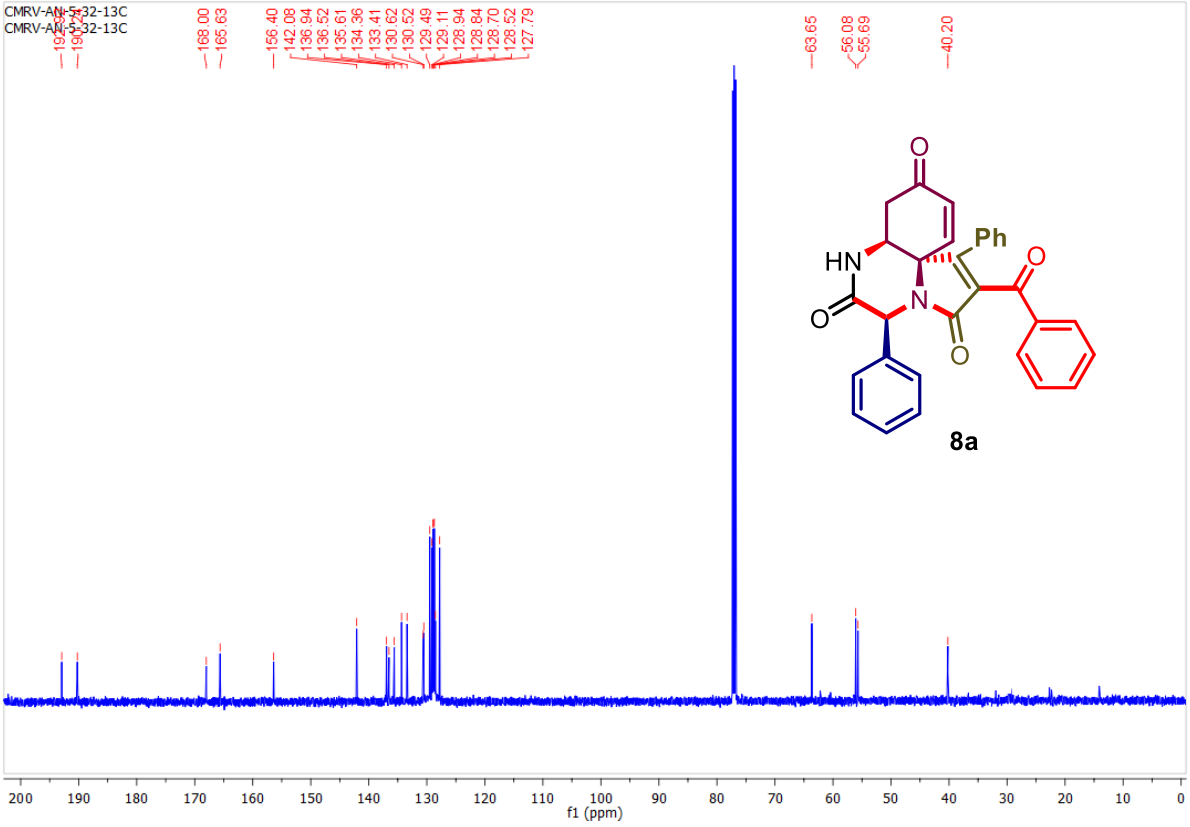
CMRV-SH-517-13C
CMRV-SH-517-13C

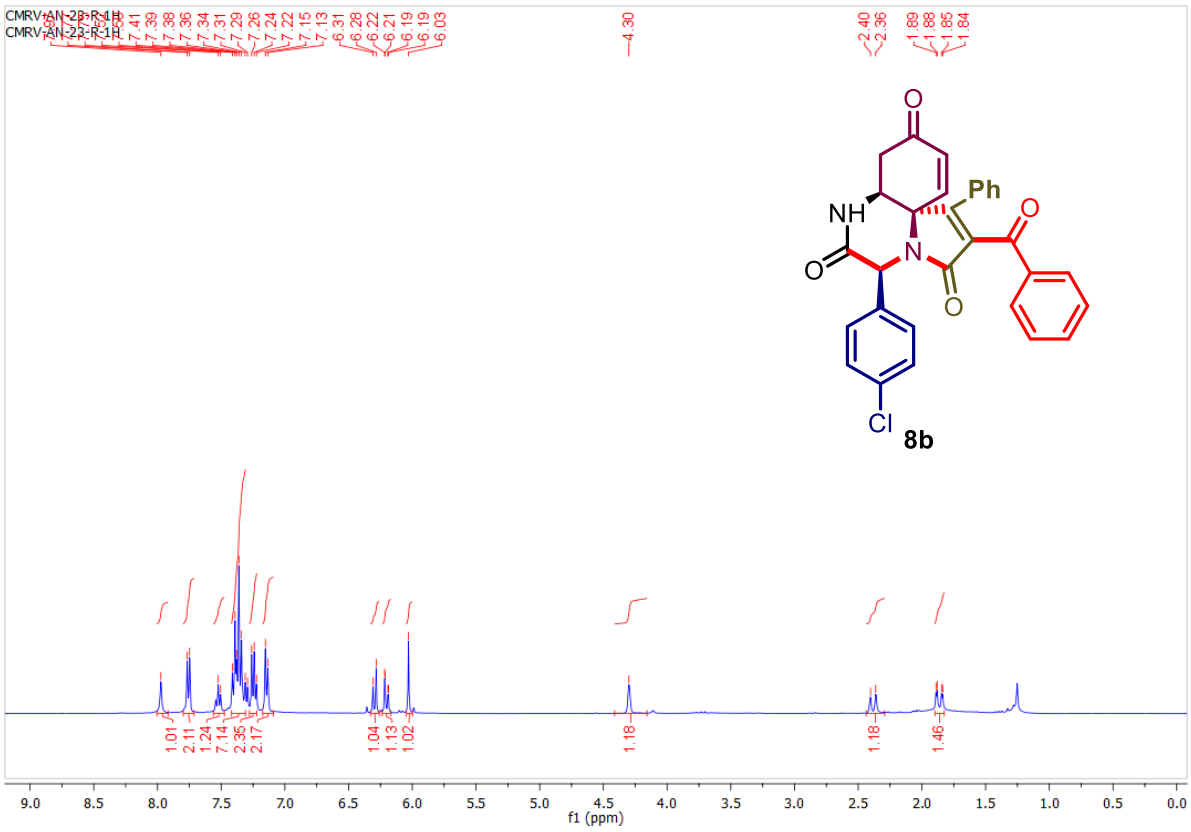


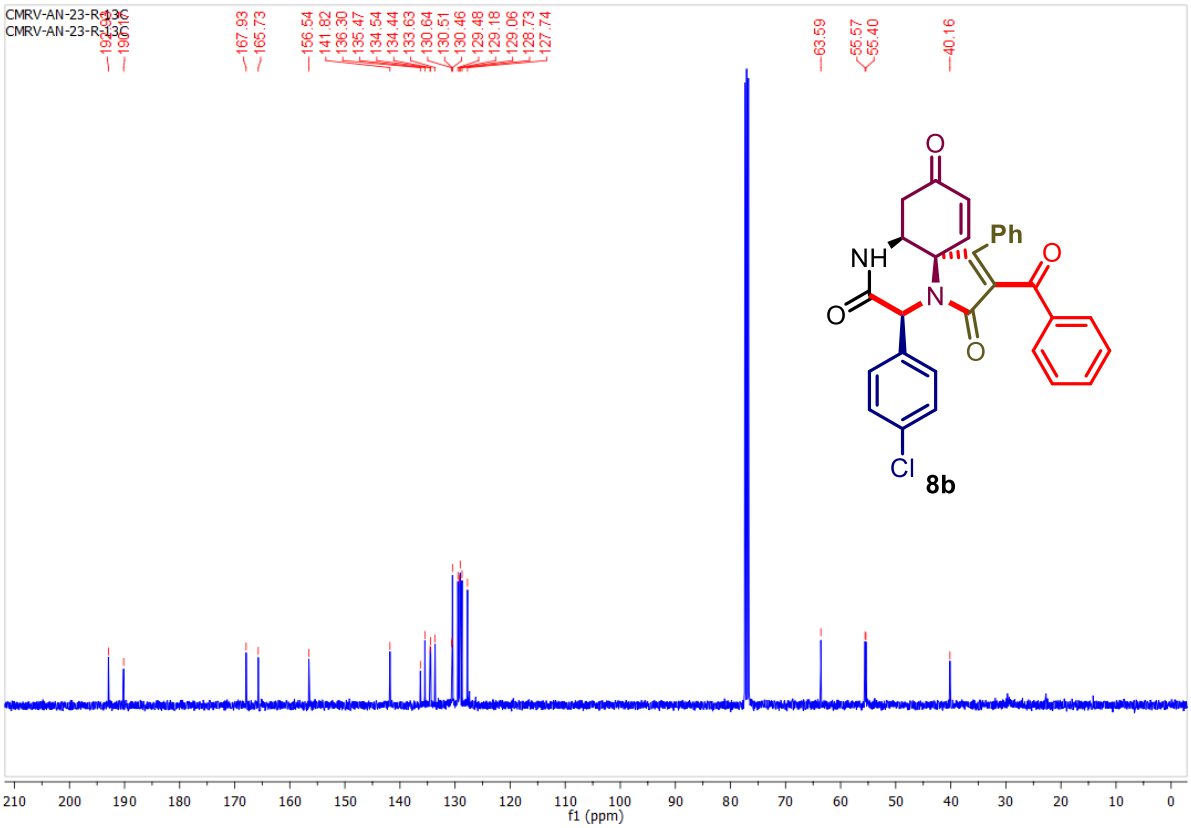

cmrv-an-4-ome-1h
cmrv-an-4-ome-1h
OMe
Ph
O
MeO
N
Me
O
O
3y
2.07
1.18
2.30
5.00
2.13
6.24
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

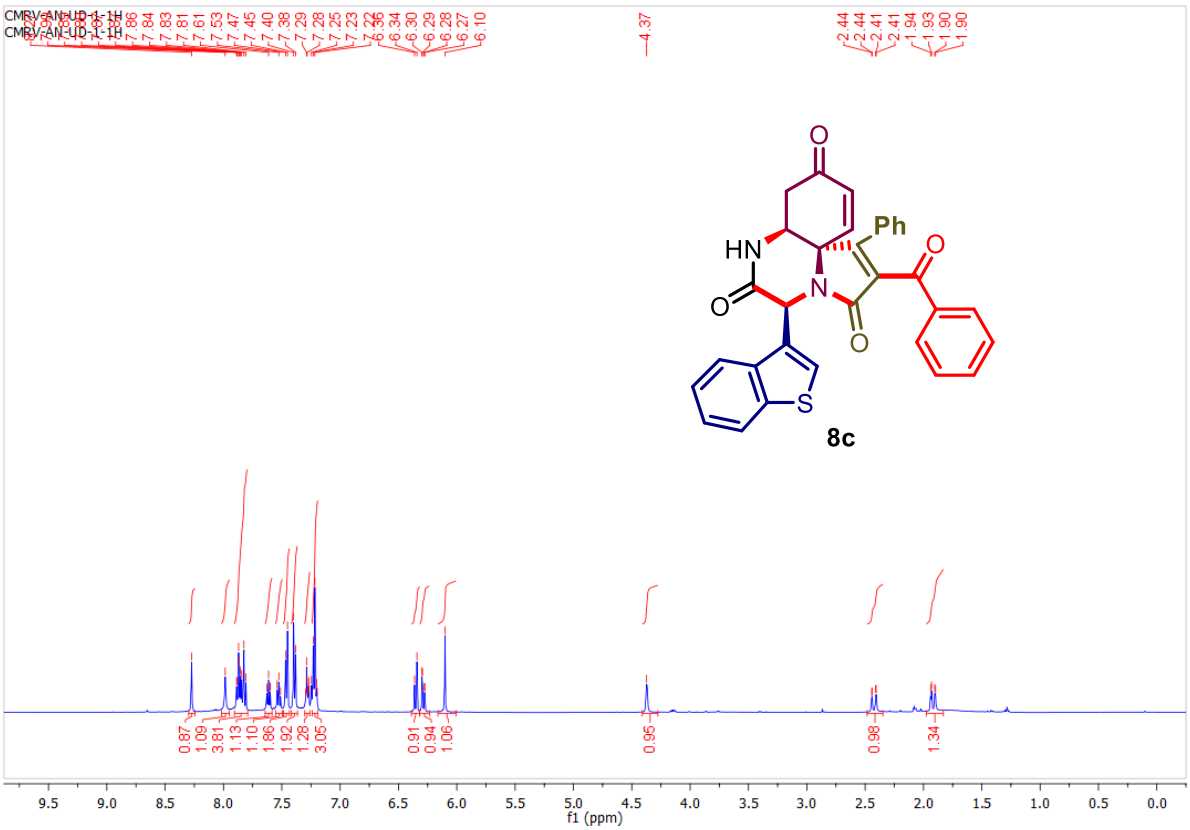

cmrv-an-4-ome-13c
cmrv-an-4-ome-13c
OMe
Ph
O
MeO
N
Me
O
O
3y
135.8
135.3
134.2
130.4
130.2
129.5
128.8
128.7
127.7
111.5
56.0
67.6
25.5
191.6
175.2
166.7
156.9
153.6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

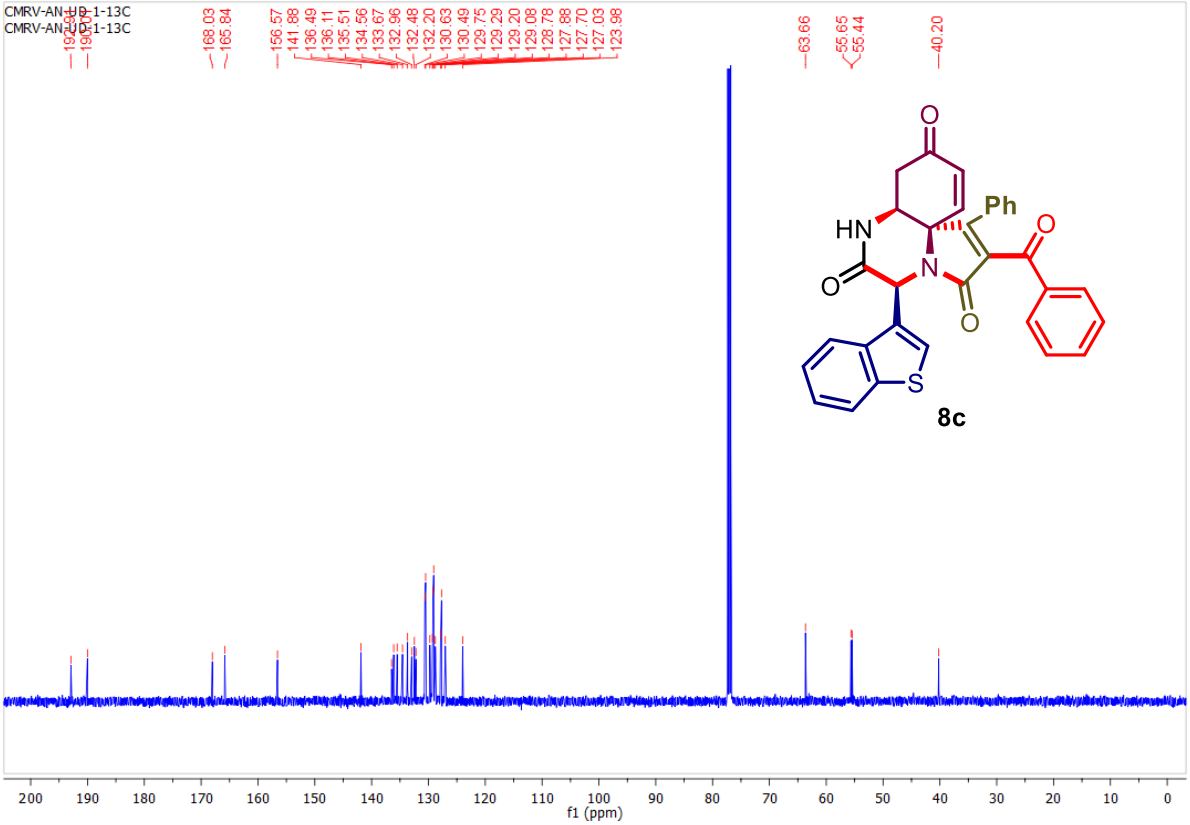

CMRV-AN-5-32-1H
CMRV-AN-5-32-1H
O
HN
Ph
O
N
O
O
8a
2.08
1.12
1.34
2.25
6.55
2.06
2.22
1.00
1.05
1.05
1.19
1.21
1.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

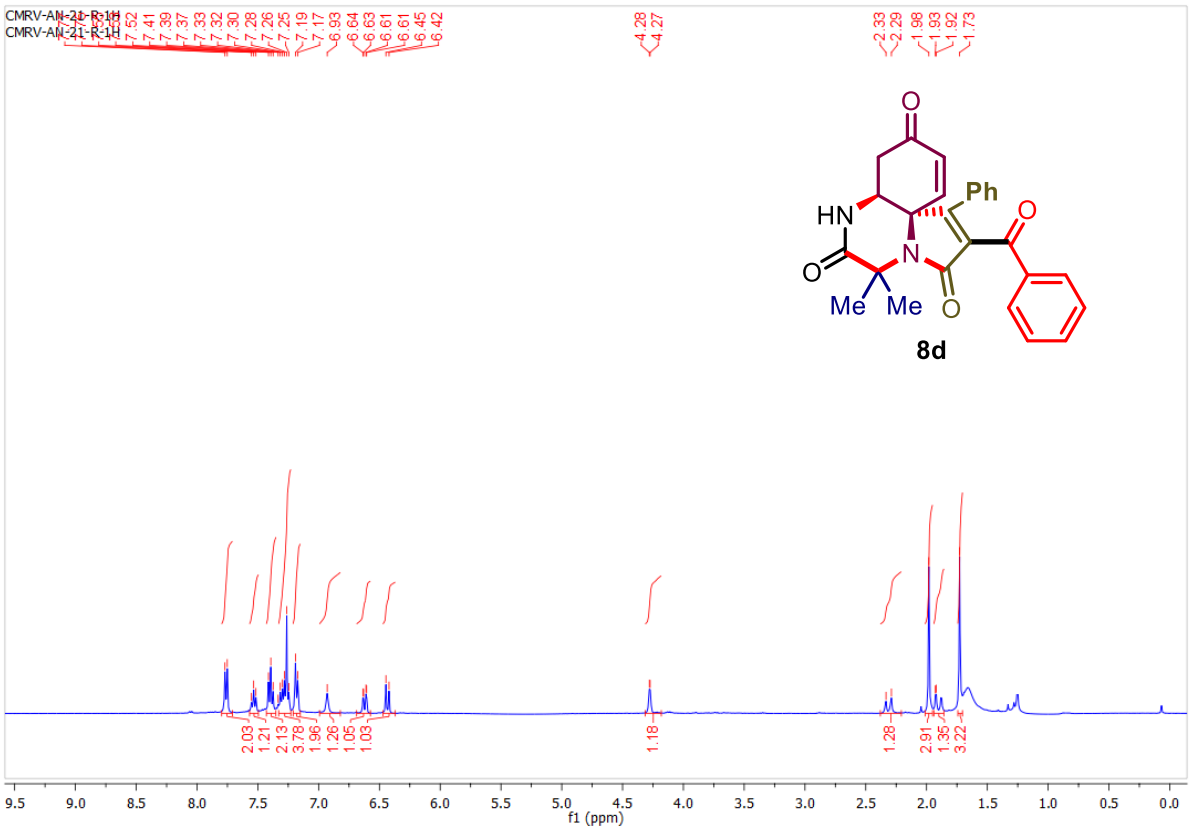

CMRV-AN-5-32-13C
CMRV-AN-5-32-13C
168.00
165.63
156.40
142.08
136.94
136.52
135.61
134.36
133.41
130.62
130.52
129.49
129.11
128.94
128.84
128.70
128.52
127.79
63.65
56.08
55.69
40.20
O
HN
Ph
O
N
O
O
8a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

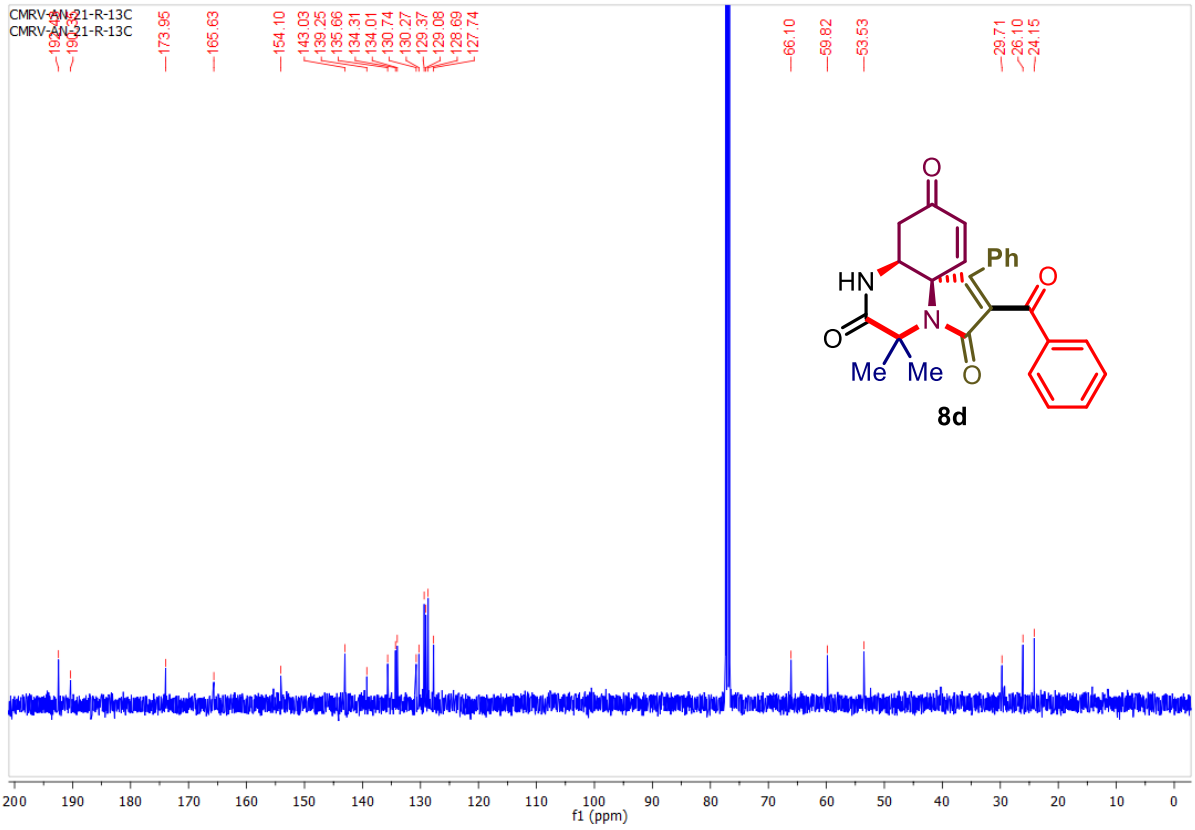

CMRV-AN-23-R-1H
CMRV-AN-23-R-1H
8b
f1 (ppm)

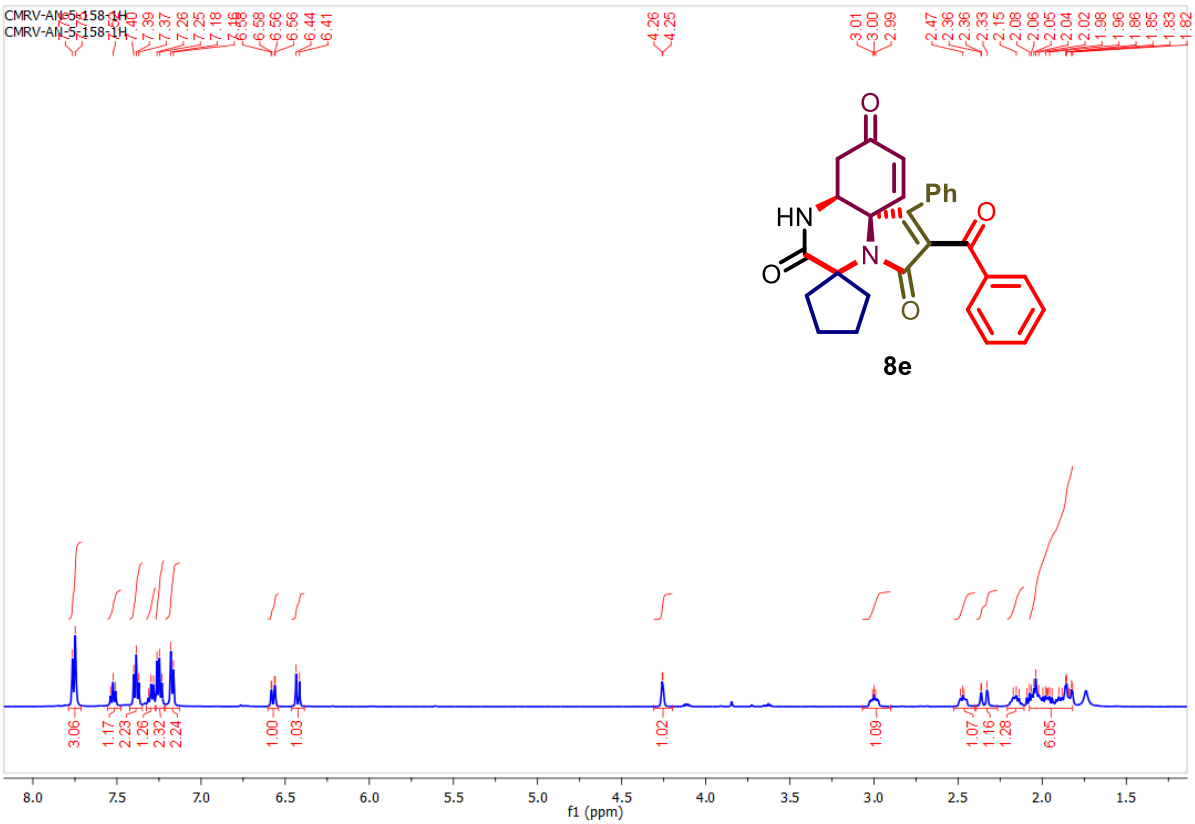

CMRV-AN-23-R-13C
CMRV-AN-23-R-13C
8b
f1 (ppm)

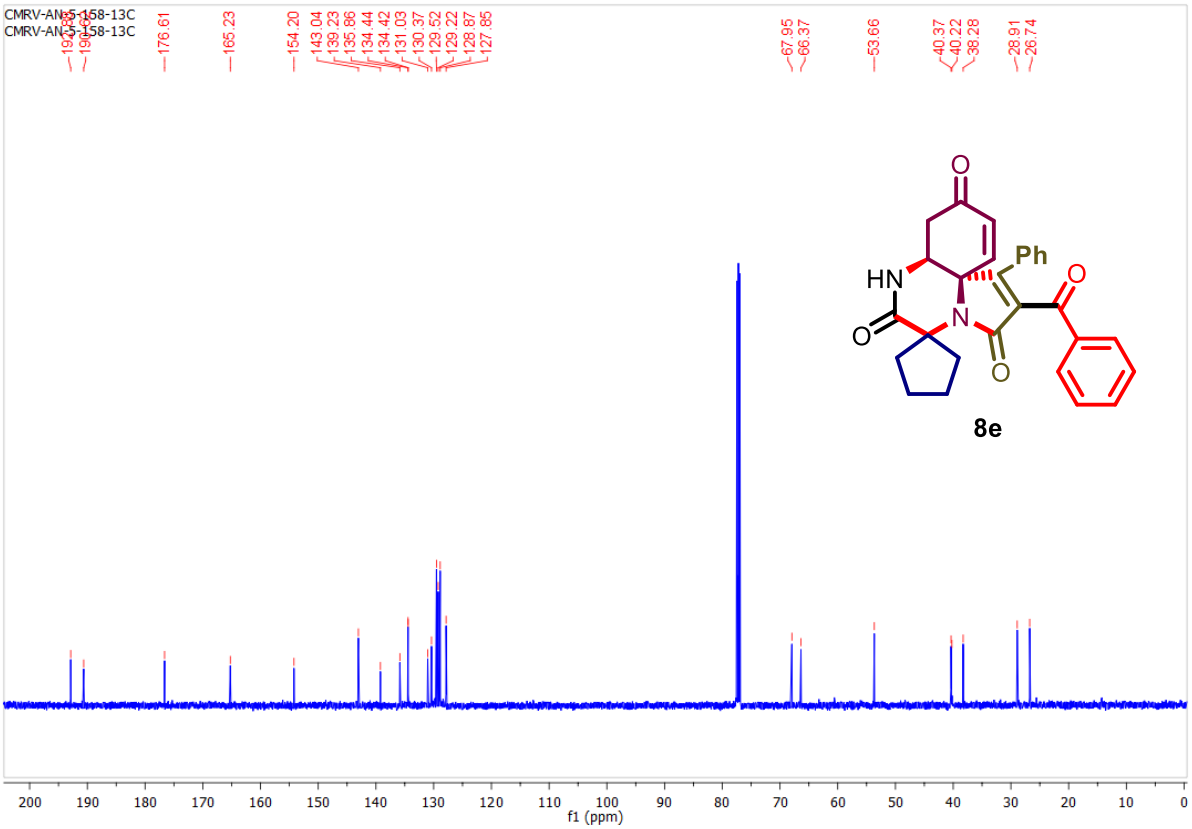

CMRV-AN-UD-1-1H
CMRV-AN-UD-1-1H
7.86 7.84 7.83 7.81 7.61 7.53 7.47 7.45 7.40 7.38 7.29 7.28 7.25 7.23 7.22 6.36 6.34 6.30 6.29 6.28 6.27 6.10
4.37
2.44 2.44 2.41 2.41 1.94 1.93 1.90 1.90
0.87 1.09 3.81 1.13 1.10 1.86 1.92 1.28 3.05 0.91 0.94 1.06 0.95 0.98 1.34
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
HN
O
N
Ph
O
O
O
S
8c

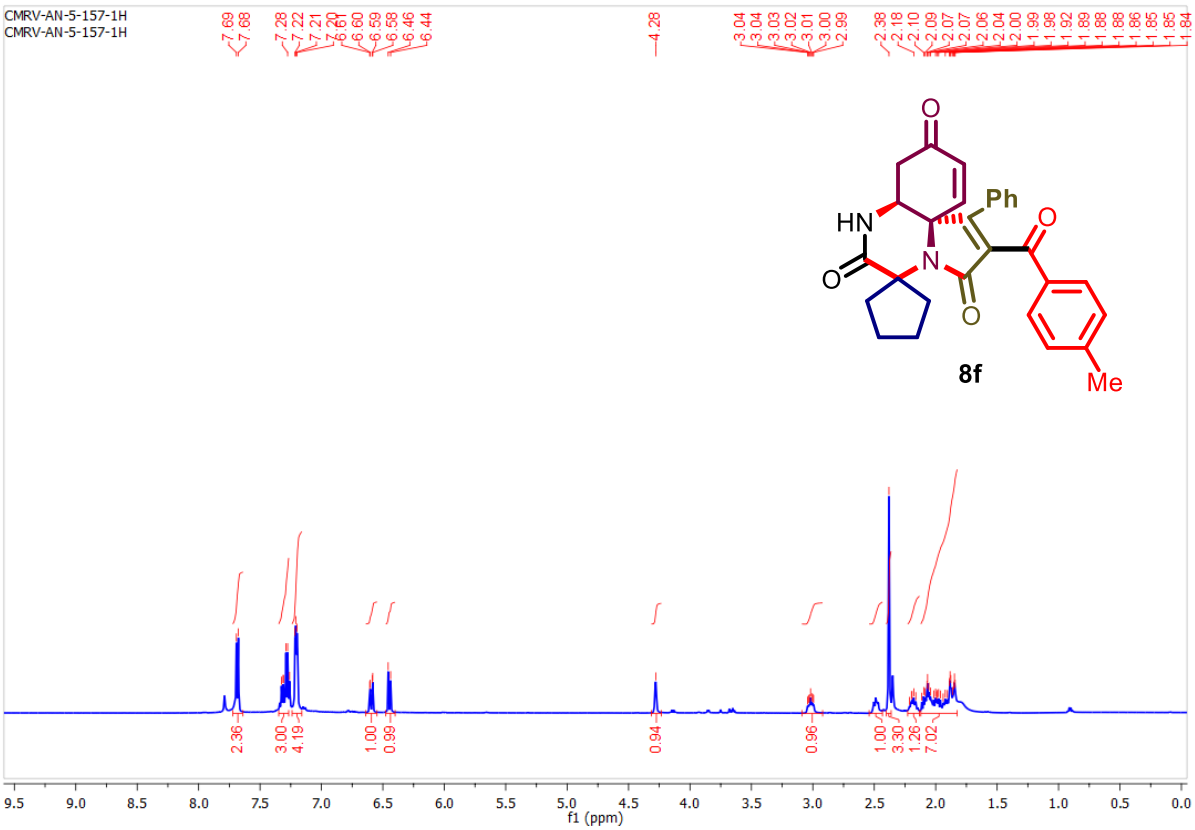

CMRV-AN-UD-1-13C
CMRV-AN-UD-1-13C
168.03 165.84 156.57 141.88 136.49 136.11 135.51 134.56 133.67 132.96 132.48 132.20 130.63 130.49 129.75 129.29 129.20 129.08 128.78 127.88 127.70 127.03 123.98
63.66 55.65 55.44 40.20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
HN
O
N
Ph
O
O
O
S
8c

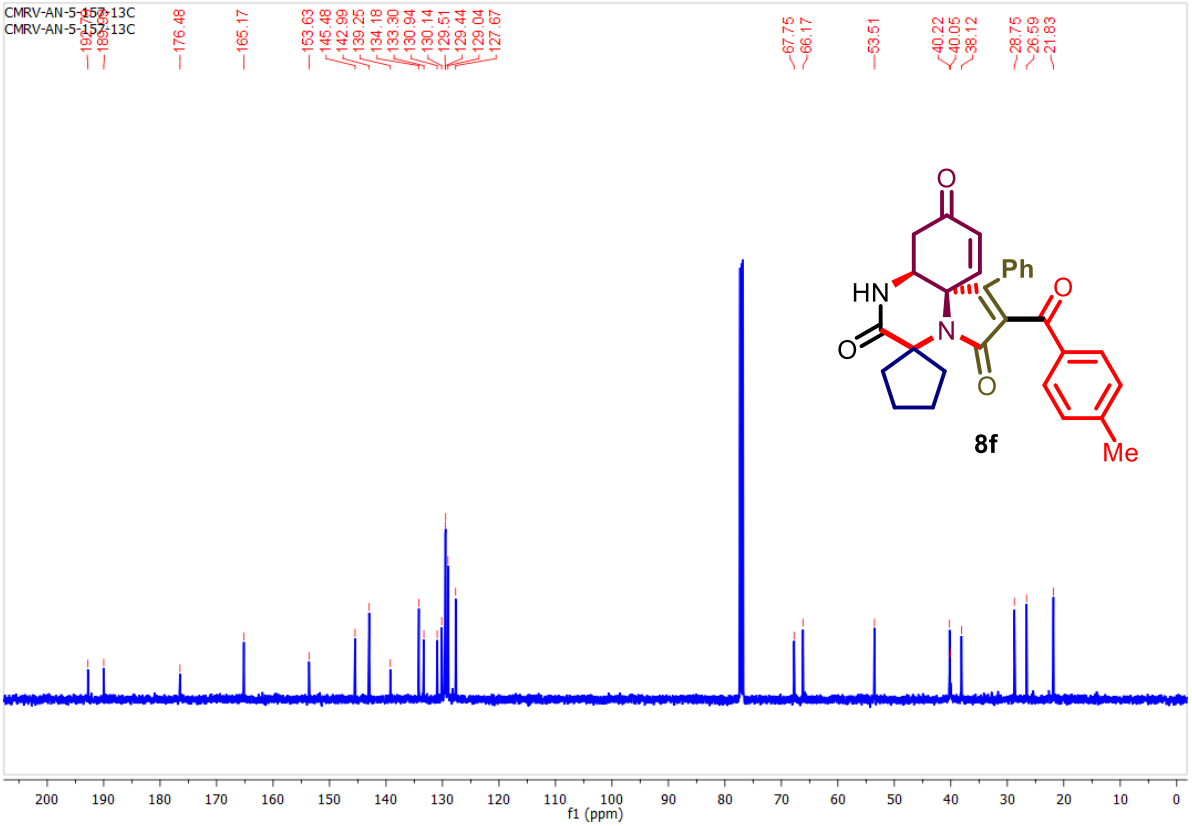

CMRV-AN-21-R-1H
CMRV-AN-21-R-1H
7.52
7.41
7.39
7.37
7.33
7.32
7.30
7.28
7.26
7.25
7.19
7.17
6.93
6.64
6.63
6.61
6.61
6.45
6.42
4.28
4.27
2.33
2.29
1.98
1.93
1.92
1.73
O
HN
Ph
O
N
O
Me
Me
O
8d
2.03
1.21
2.13
3.78
1.96
1.26
1.05
1.03
1.18
1.28
2.91
1.35
3.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

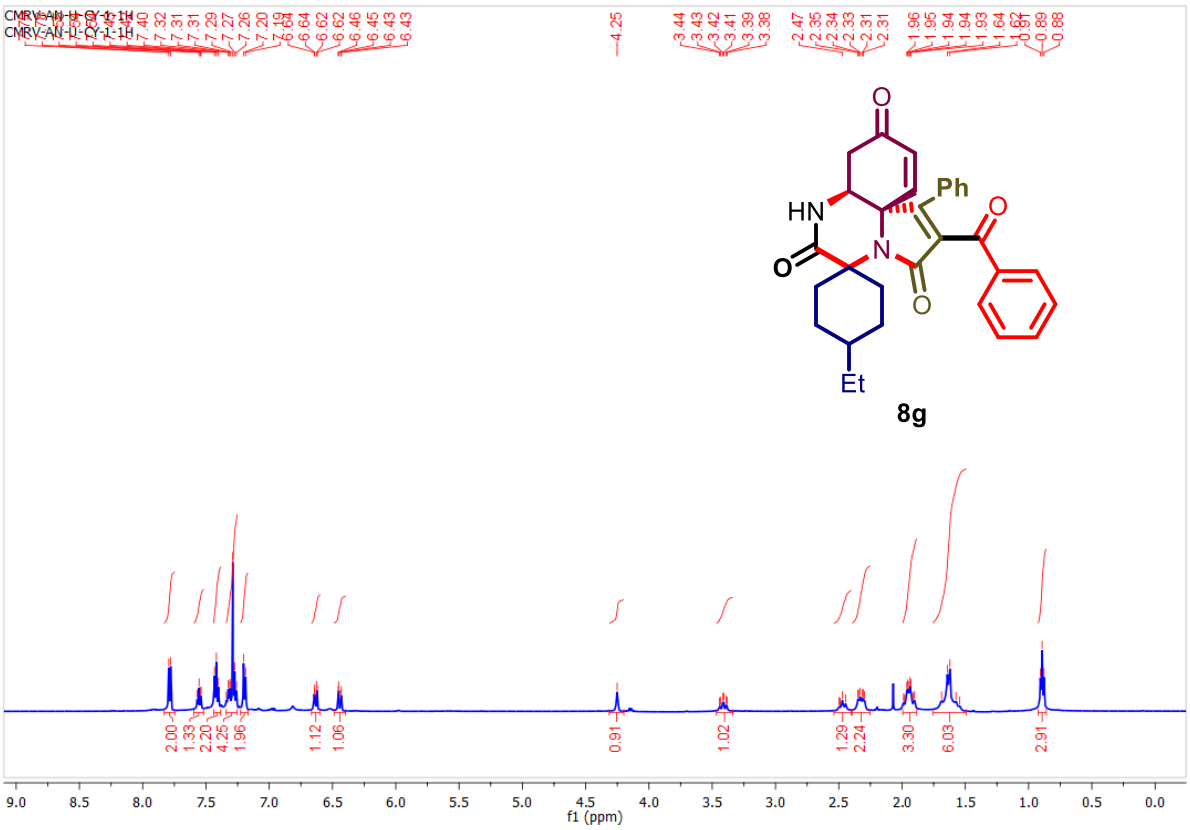

CMRV-AN-21-R-13C
CMRV-AN-21-R-13C
192.72
190.92
173.95
165.63
154.10
143.03
139.25
135.66
134.31
134.01
130.74
130.27
129.37
129.08
128.69
127.74
66.10
59.82
53.53
29.71
26.10
24.15
O
HN
Ph
O
N
O
Me
Me
O
8d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

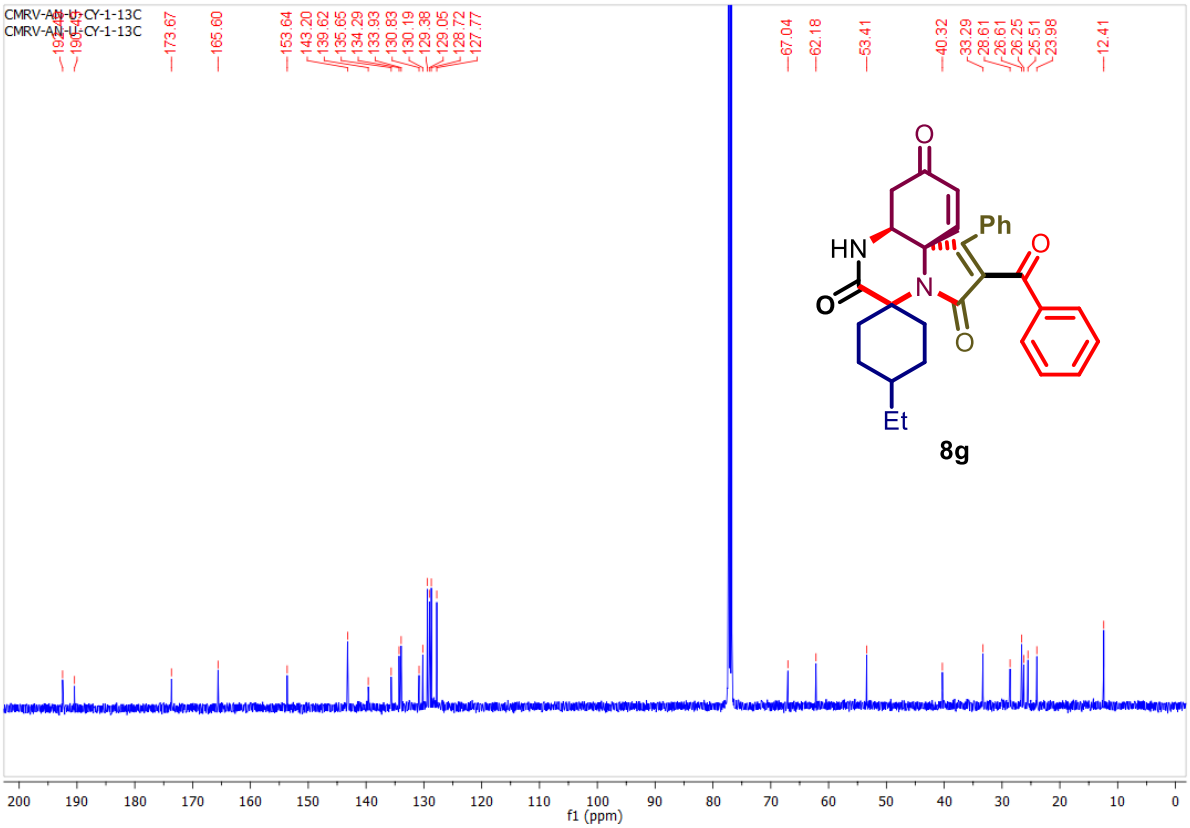

CMRV-AN-5-158-1H
CMRV-AN-5-158-1H
HN
O
N
O
O
Ph
O
8e
f1 (ppm)

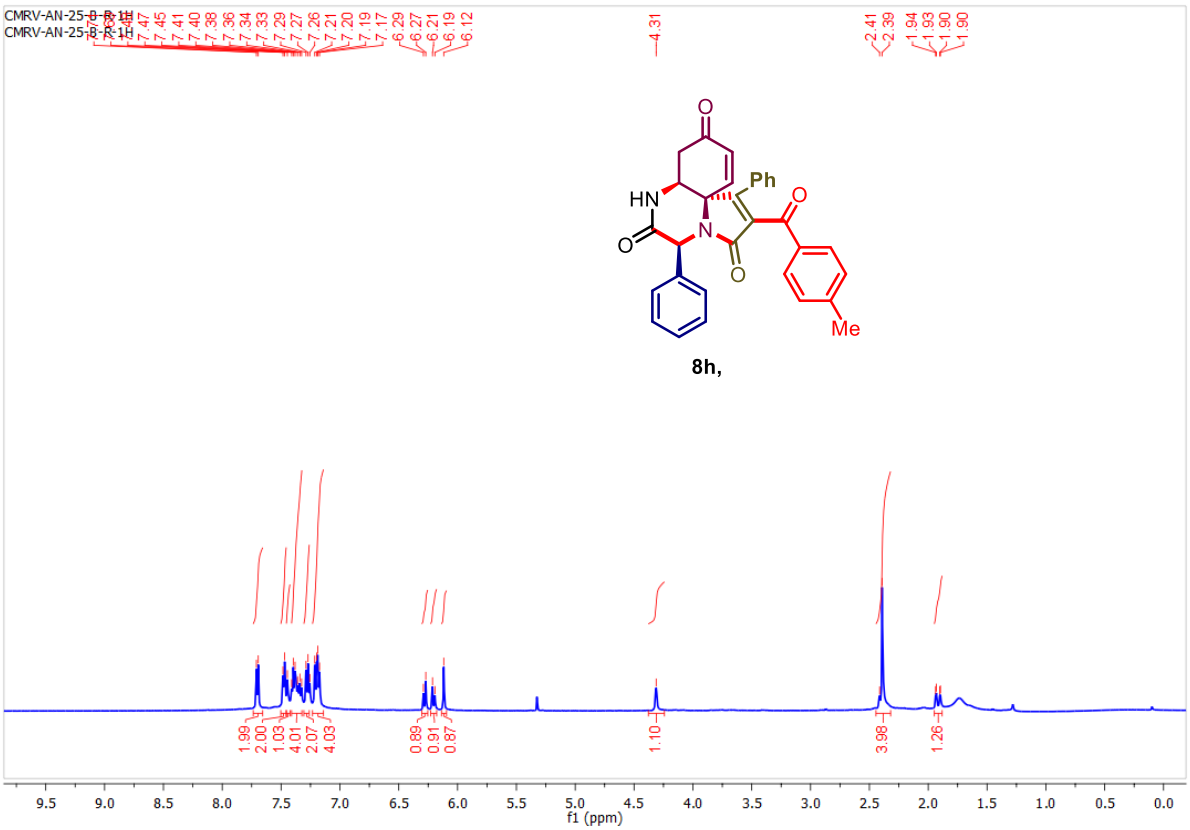

CMRV-AN-5-158-13C
CMRV-AN-5-158-13C
HN
O
N
O
O
Ph
O
8e
f1 (ppm)


CMRV-AN-5-157-1H
CMRV-AN-5-157-1H
7.69
7.68
7.28
7.22
7.21
7.20
6.61
6.60
6.59
6.58
6.46
6.44
4.28
3.04
3.04
3.03
3.02
3.01
3.00
2.99
2.38
2.18
2.10
2.09
2.07
2.07
2.06
2.04
2.00
1.99
1.98
1.92
1.89
1.88
1.88
1.86
1.85
1.85
1.84
O
HN
O
N
Ph
O
O
8f
Me
2.36
3.00
4.19
1.00
0.99
0.94
0.96
1.00
3.30
1.26
7.02
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)

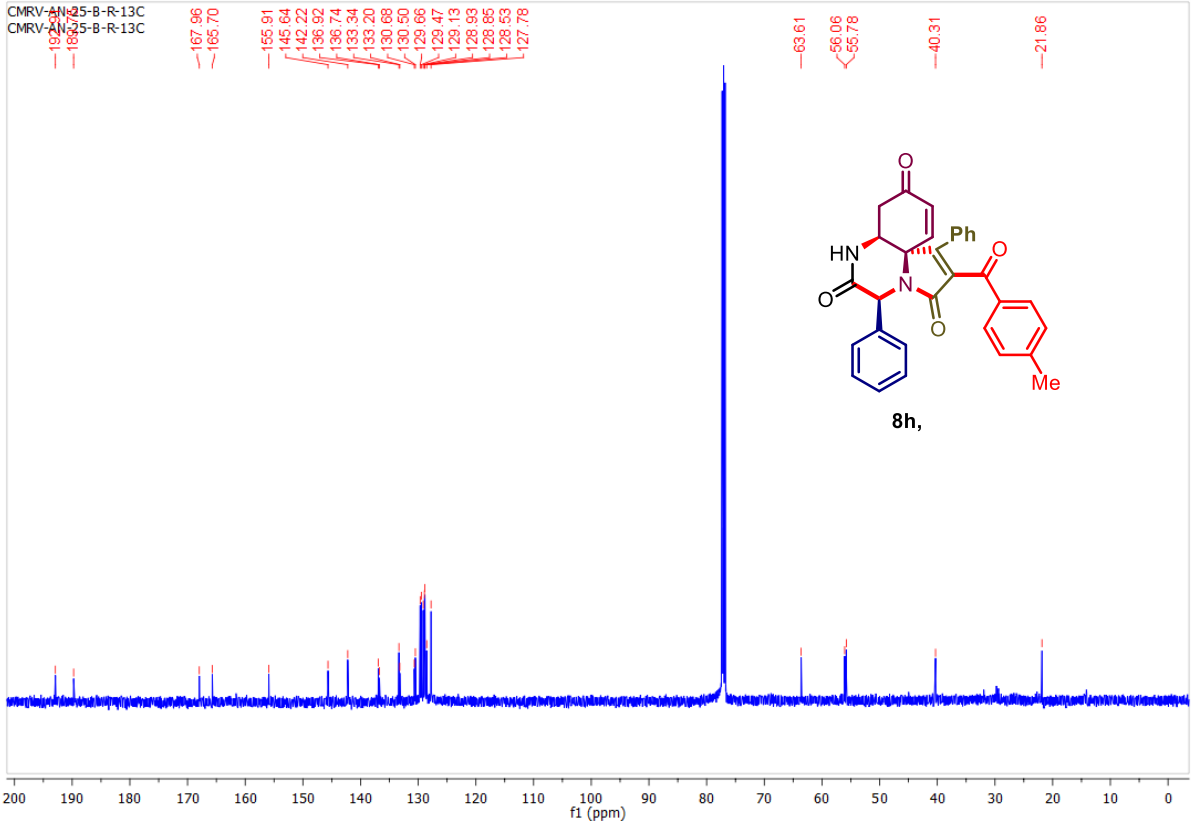

CMRV-AN-5-157-13C
CMRV-AN-5-157-13C
176.48
165.17
153.63
145.48
142.99
139.25
134.18
133.30
130.94
130.14
129.51
129.44
129.04
127.67
67.75
66.17
53.51
40.22
40.05
38.12
28.75
26.59
21.83
O
HN
O
N
Ph
O
O
8f
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CMRV-AN-U-CY-1-1H
CMRV-AN-U-CY-1-1H
HN
O
N
O
Ph
O
O
Et
8g
f1 (ppm)

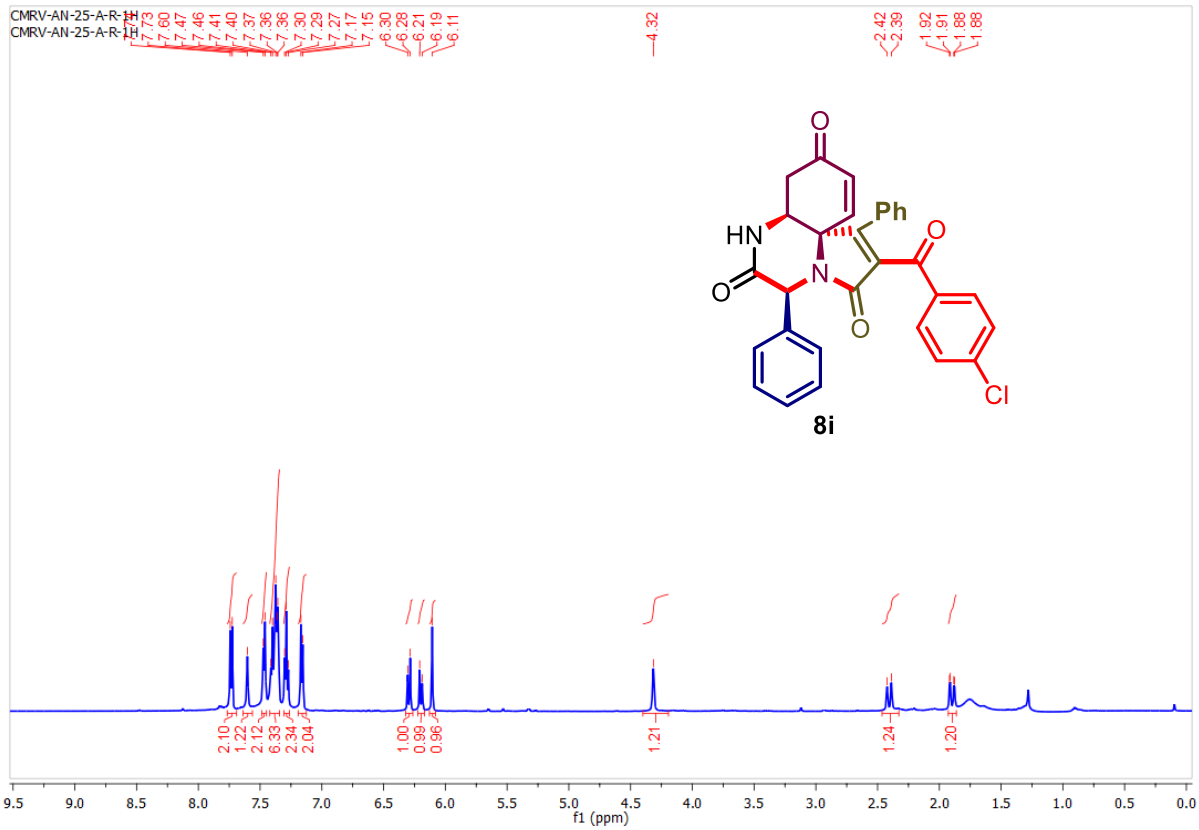

CMRV-AN-U-CY-1-13C
CMRV-AN-U-CY-1-13C
HN
O
N
O
Ph
O
O
Et
8g
f1 (ppm)

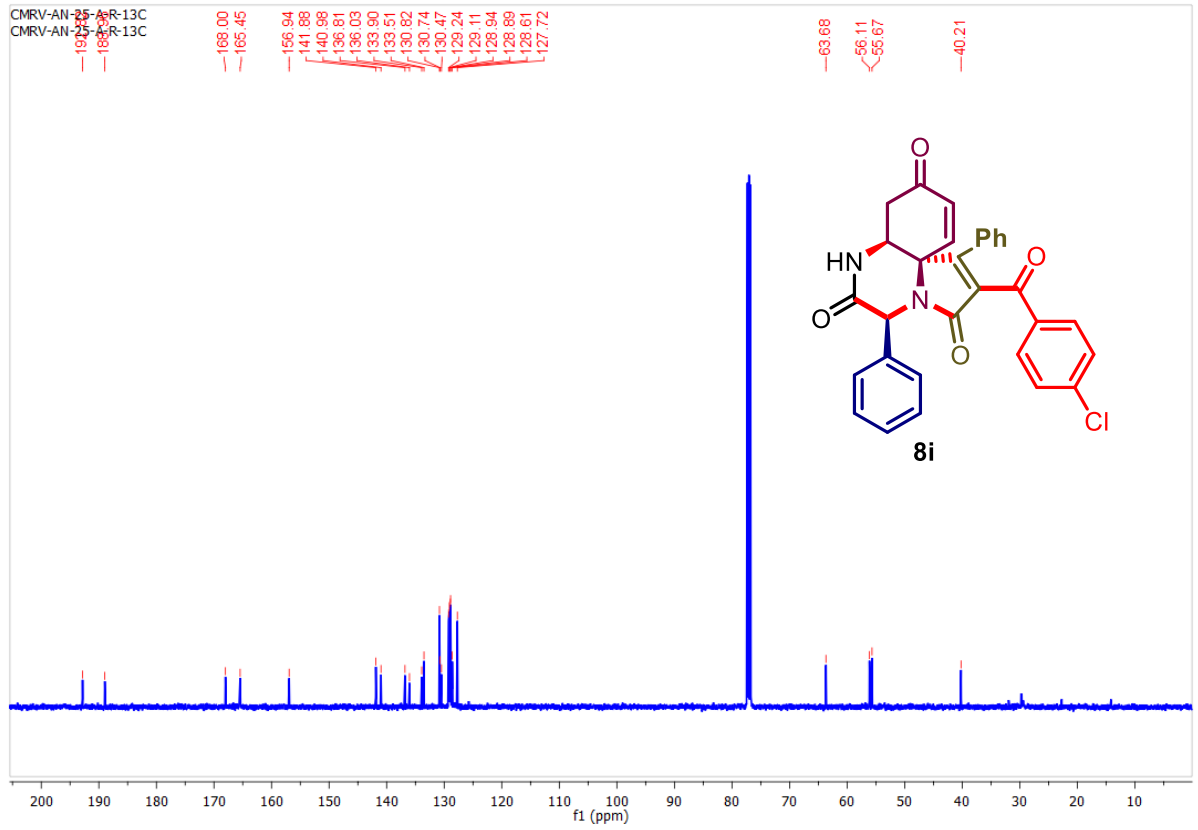

CMRV-AN-25-B-R-1H
CMRV-AN-25-B-R-1H
7.47
7.45
7.41
7.40
7.38
7.36
7.34
7.33
7.29
7.27
7.26
7.21
7.20
7.19
7.17
6.29
6.27
6.21
6.19
6.12
4.31
2.41
2.39
1.94
1.93
1.90
1.90
O
HN
Ph
O
N
O
O
Me
1.99
2.00
1.03
4.01
2.07
4.03
0.89
0.91
0.87
1.10
3.98
1.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

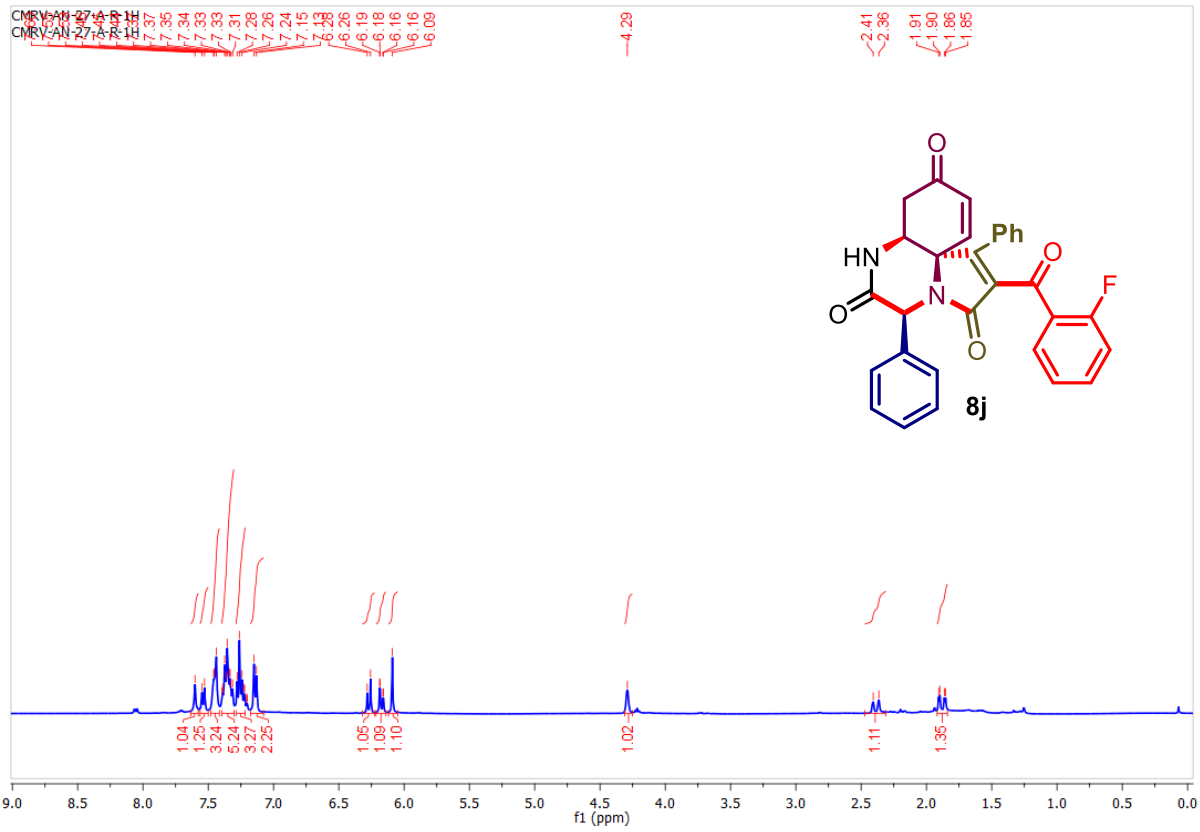
8h,

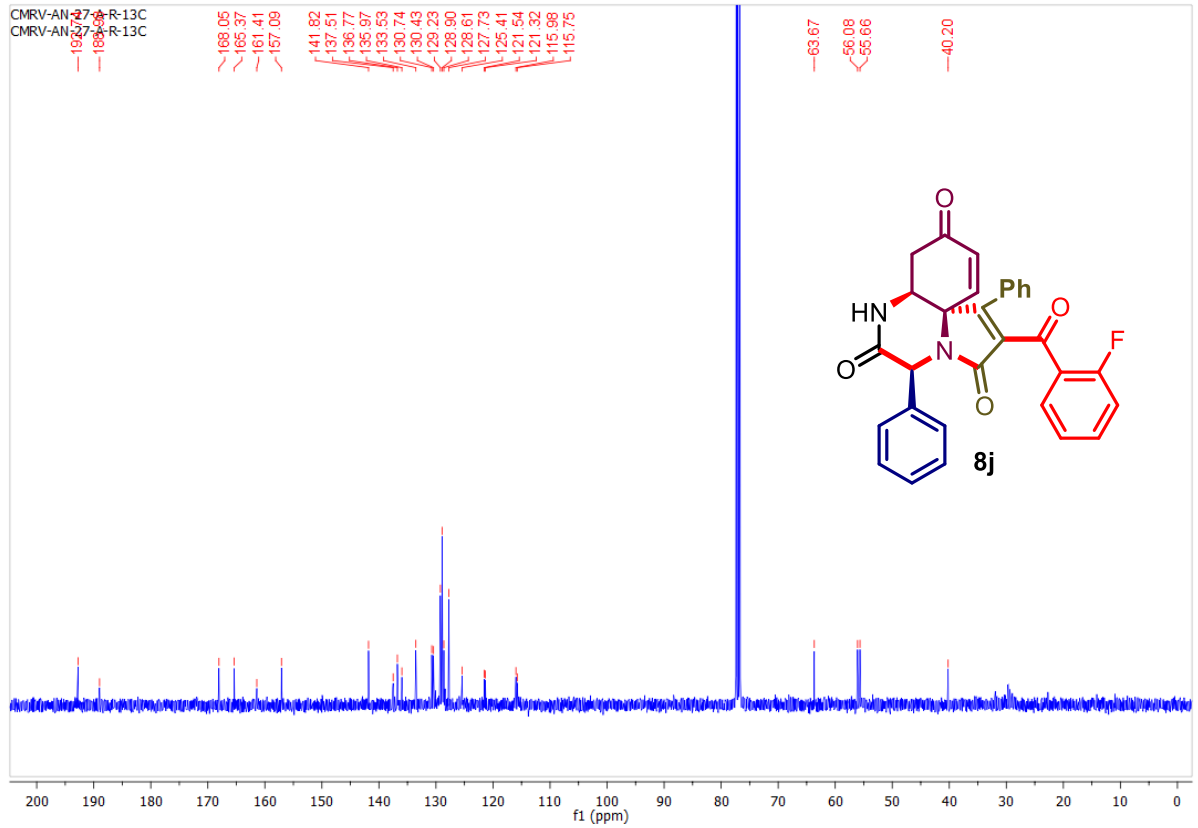

CMRV-AN-25-B-R-13C
CMRV-AN-25-B-R-13C
193.61
183.57
167.96
165.70
155.91
145.64
142.22
136.92
136.74
133.34
133.20
130.68
130.50
129.66
129.47
129.13
128.93
128.85
128.53
127.78
63.61
56.06
55.78
40.31
21.86
O
HN
Ph
O
N
O
O
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

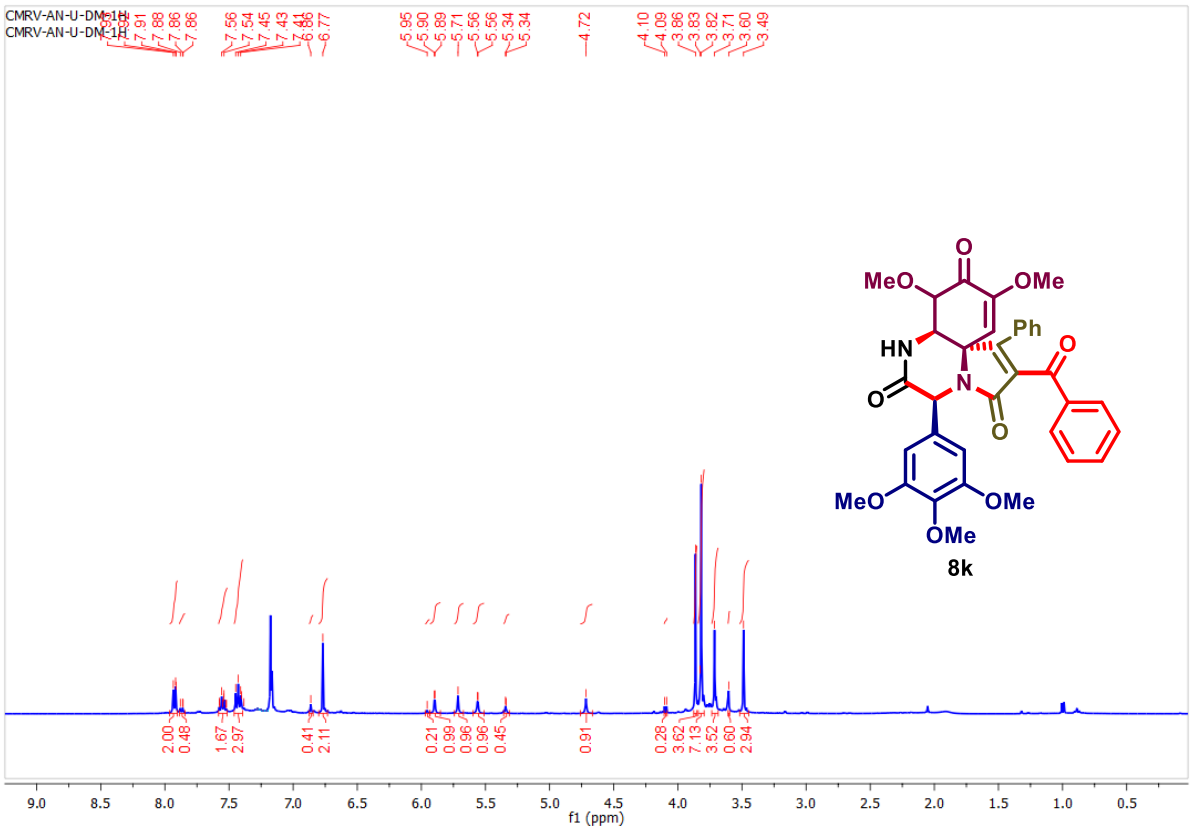
8h,

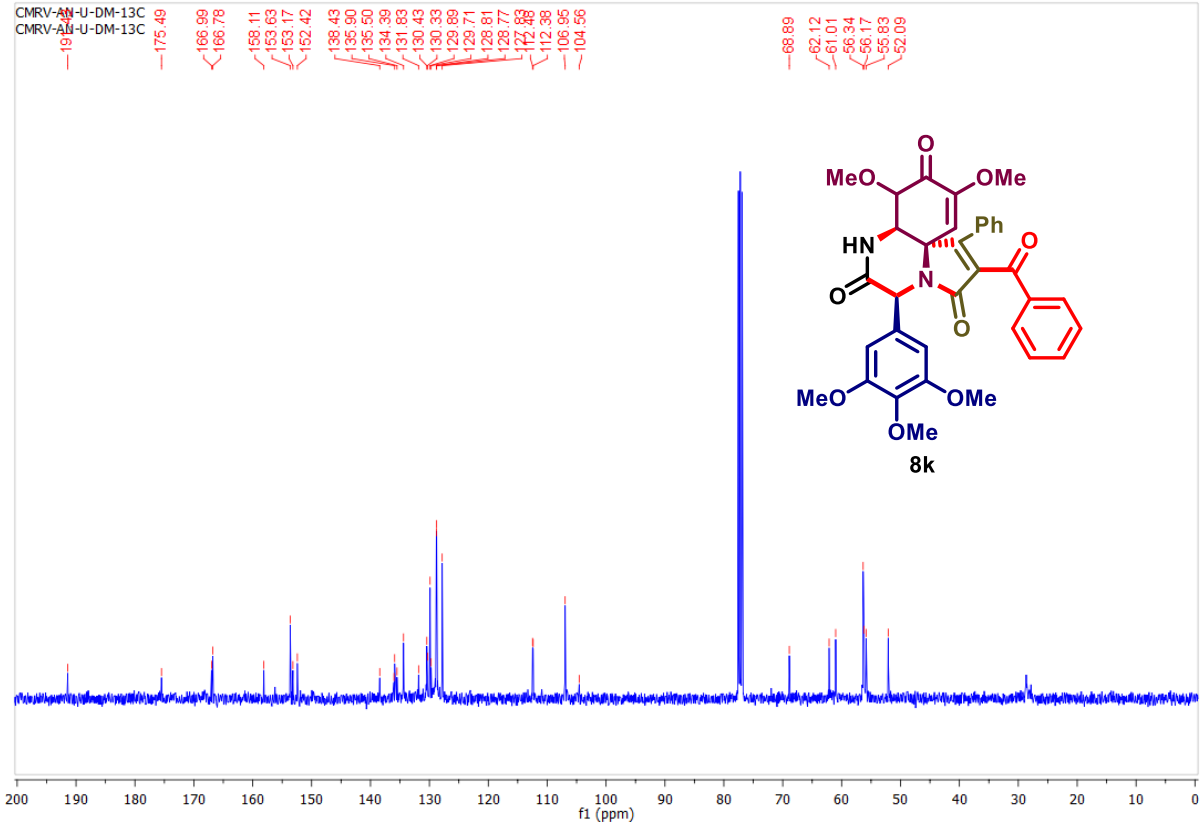

CMRV-AN-25-A-R-1H
CMRV-AN-25-A-R-1H
7.73
7.60
7.47
7.46
7.41
7.40
7.37
7.36
7.36
7.30
7.29
7.27
7.17
7.15
6.30
6.28
6.21
6.19
6.11
4.32
2.42
2.39
1.92
1.91
1.88
1.88
O
HN
Ph
O
N
O
O
Cl
8i
2.10
1.22
2.12
6.33
2.34
2.04
1.00
0.99
0.96
1.21
1.24
1.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CMRV-AN-25-A-R-13C
CMRV-AN-25-A-R-13C
192.25
188.39
168.00
165.45
156.94
141.88
140.98
136.81
136.03
133.90
133.51
130.82
130.74
130.47
129.24
129.11
128.94
128.89
128.61
127.72
63.68
56.11
55.67
40.21
O
HN
Ph
O
N
O
O
Cl
8i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


CMRV-AN-27-A-R-1H
7.37
7.35
7.34
7.33
7.33
7.31
7.28
7.26
7.24
7.15
7.13
6.28
6.26
6.19
6.18
6.16
6.16
6.09
4.29
2.41
2.36
1.91
1.90
1.86
1.85
O
HN
Ph
O
F
N
O
O
8j
1.04
1.25
3.24
5.24
3.27
2.25
1.05
1.09
1.10
1.02
1.11
1.35
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)


CMRV-AN-27-A-R-13C
CMRV-AN-27-A-R-13C
168.05
165.37
161.41
157.09
141.82
137.51
136.77
135.97
133.53
130.74
130.43
129.23
128.90
128.61
127.73
125.41
121.54
121.32
115.98
115.75
63.67
56.08
55.66
40.20
O
HN
Ph
O
F
N
O
O
8j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CMRV-AN-U-DM-1H
CMRV-AN-U-DM-1H
MeO
OMe
Ph
HN
N
O
MeO
OMe
OMe
8k
f1 (ppm)


CMRV-AN-U-DM-13C
CMRV-AN-U-DM-13C
MeO
OMe
Ph
HN
N
O
MeO
OMe
OMe
8k
f1 (ppm)