Supplementary Information

Design, Synthesis and Application of Spiro[4.5]cyclohexadienones via One-pot Sequential *p*-Hydroxybenzylation/Oxidative Dearomatization

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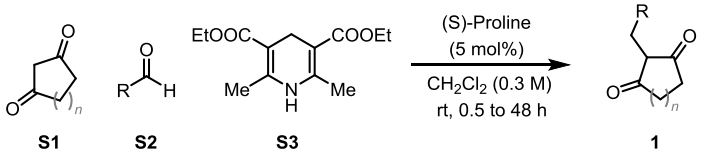
I. General details

***General information*:** Unless otherwise noted, all reagents were used as received from commercial suppliers. All catalysts were purchased from Sigma-Aldrich and TCI Chemicals, used without further purification. All reactions were performed under inert atmosphere and in a flame-dried or oven-dried glassware with magnetic stirring. All analytical grade solvents were used directly in the reaction. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), iodine treatment or using *p*-anisaldehyde stain or β-napthol stain. Column chromatography was carried out using silica gel (100-200 mesh) packed in glass columns. NMR spectra were recorded at 300, 400, 500 MHz (H) and at 75, 101, 126 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm) as internal standard, and coupling constants (*J*) are given in Hz. HRMS were recorded using ESI-TOF techniques.

II. Experimental procedures and analytical data

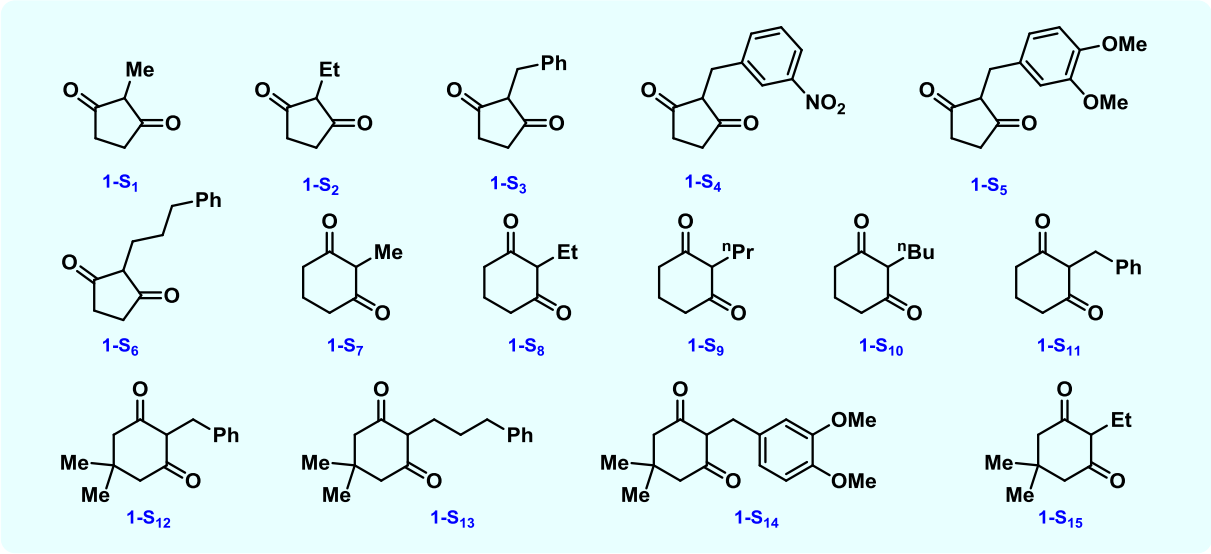
IIA. Experimental procedures and analytical data of substrates

IIAa. General procedure for the synthesis of 1 using Ramachary protocol:[1]



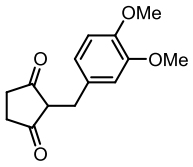
General procedure for the synthesis of 2-substituted 1,3-diketones 2 using Ramachary protocol: [1]

A solution of aldehyde **S2** (3.0 equiv), 1,3-diketone S**1** (1.0 equiv) and Hantzsch ester **S3** (1.0 equiv) in CH_2Cl_2 (0.3 M) was added (*S*)-proline (0.05 equiv, 5 mol%) and the reaction mixture was stirred at 25 ^oC for 0.5 to 48 h. After evaporation of the solvent completely, the crude reaction mixture was directly subjected to silica gel column chromatography (hexane–ethyl acetate) to afford 2-substituted 1,3-diketones **1**.



Aryl 2-substituted 1,3-diketones **1-S3**,[2] **1-S4**,[1] **1-S5**, **1-S6**,[2] **1-S7**, [2] **1-S8**,[3] **1-S9**,[4] **1-S10**,[3] **1-S11**,[2] **1-S12**,[4] **1-S13**,[5] **1-S14**,[5] **1-S15**[4] were prepared according to a previously reported procedure[1] and **1-S1**, **1-S2** substrate commercially available

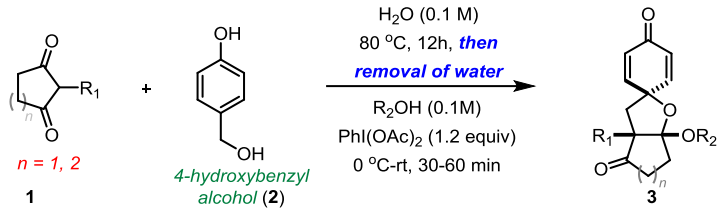
2-(3,4-dimethoxybenzyl)cyclopentane-1,3-dione (1-S5):



Prepared according to the general procedure as described above in 69% yield (872 mg). It was purified by flash chromatography (30% acetone/diethyl ether; R_f = 0.3) to afford a pale brown solid; mp = 130 – 132 °C; ^{1}H NMR (400 MHz, $CDOD_3$) δ 6.88 (s, 1H), 6.77 (d, *J* = 0.8 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.38 (s, 2H), 2.51 (s, 4H); ^{13}C NMR (101 MHz, $CDOD_3$) δ 148.5, 147.0, 133.1, 120.2, 117.7, 112.1, 111.1, 55.8, 55.6, 30.3, 26.4; HRMS (ESI) calcd for $C_{14}H_{17}O_4$ $[M+H]^+$: 249.1127; found: 249.1127.

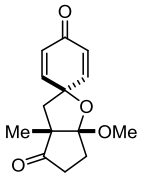
IIB. Experimental procedures and analytical data of products

IIBa: General procedure for one-pot sequential *p*-hydroxy benzylation[6]/oxidative dearomatization/Spiroannulation:



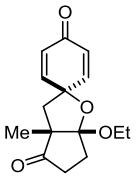
To a stirred solution of 2-substituted-1,3-dione **1** (1 mmol) in water (8 mL, 0.1 M) was added p-hydroxybenzyl alcohol (**2**; 100 mg, 0.8 mmol), and the solution was stirred at 80 °C for 12 h. Then, water was removed from reaction mixture via simple crystallization at room temperature followed by filtration. The crude reaction mixture was dissolved in alcohol (0.1 M) and then added $PhI(OAc)_2$ (322 gm, 1 mmol) in several portions at 0 °C. The resulting reaction mixture was stirred at same temperature for 30-60 minutes and then alcohol was evaporated in vacuum. The resulting mixture was diluted with water (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic solvent was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography (EtOAc in hexanes) to give the desired product **3.**

6a'-Methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3a):



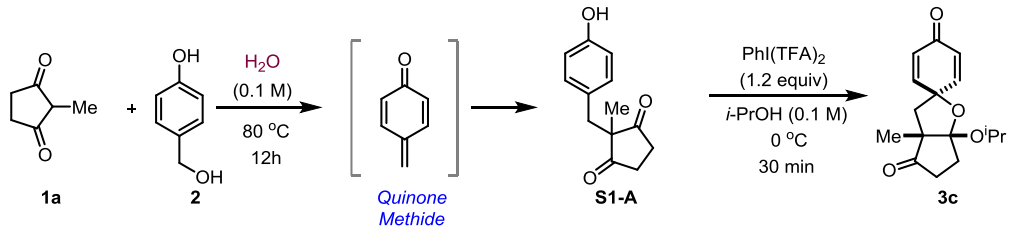
Prepared according to the general procedure as described above in 75% yield (150 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a pale brown solid; mp = 109–110°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.44 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.10 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.06 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.44 (s, 3H), 2.61 (ddt, *J* = 15.5, 11.6, 6.3 Hz, 2H), 2.55 – 2.45 (m, 2H), 2.13 (d, *J* = 13.4 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.4, 185.3, 150.7, 148.5, 127.4, 127.0, 116.0, 77.7, 61.0, 49.7, 44.2, 35.6, 26.1, 15.9; HRMS (ESI) calcd for $C_{14}H_{17}O_4[M+H]^+$: 249.1121; found:249.1118.

3- 6a'-Ethoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3b):



Prepared according to the general procedure as described above in 73% yield (155 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a white solid; mp = 103–105°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (d, *J* = 10.1 Hz, 1H), 6.42 (d, *J* = 10.1 Hz, 1H), 6.07 (dd, *J* = 10.1, 1.8 Hz, 1H), 6.03 (dd, *J* = 10.1, 1.6 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.67 – 3.58 (m, 1H), 2.63 – 2.53 (m, 2H), 2.52 – 2.43 (m, 2H), 2.12 (d, *J* = 13.4 Hz, 1H), 2.01 (dt, *J* = 20.2, 12.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.6, 185.3, 150.9, 148.6, 127.3, 126.9, 115.7, 77.5, 61.0, 57.8, 44.2, 35.6, 26.7, 15.8, 15.5; IR (neat): υ_{max} 2979, 2936, 1748, 1673, 1246, 1076, 934, 860 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{19}O_4[M+H]^+$: 263.1278; found: 263.1274.

6a'-isopropoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3c): [Note: Prepared in step-wise reaction using $PhI(TFA)_2$ as a oxidizing reagent]

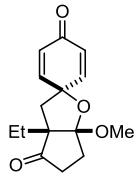


To a stirred solution of 2-methyl 1,3-cyclopentadione **1a** (0.8 mmol) in water (8 mL, 0.1 M) was added p-hydroxybenzyl alcohol (118 mg, 0.96 mmol), and the solution was stirred at 80 °C for 12 h. The reaction was cooled to room temperature and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic solvent was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography (30% EtOAc/hexane) to give *p*-hydroxybenzyl-tethered 2-methyl 1,3-cyclopentadione **(S1-A)** to afford a white solid (140 mg, 80%); mp = 150–152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.15 (br.s, 1H), 2.90 (s, 2H), 2.60 – 2.51 (m, 2H), 2.10 (dd, *J* = 19.2, 6.8 Hz, 2H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.4, 155.1,

130.9, 127.6, 115.6, 58.8, 42.5, 36.0, 19.9; IR (neat): υ_{max} 3361, 2968, 2926, 1712, 1516, 1218, 846, 637 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{15}O_3$ $[M+H]^+$: 219.1016; found: 219.1017.

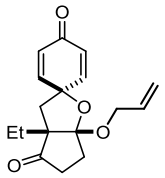
A round bottom flask was charged with *p*-hydroxybenzyl-tethered 2-methyl 1,3-cyclopentadione **S1-A** (140 mg, 0.64 mmol), in *iso*-propanol (6 mL, 0.1 M) under N_2 atmosphere and added $PhI(TFA)_2$ (331 mg, 0.77 mmol) in several portions at 0^o C. The reaction mixture was stirred at same temperature for 30 minutes and then *iso*-propanol was evaporated in vacuum. The crude reaction mixture was diluted with water (10 mL) and extracted with EtOAc (15 mL × 3). The combined organic solvent was washed with brine (15 mL), dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and residue was subjected to flash column chromatography on silica gel (30% EtOAc/hexanes, R_f = 0.5) to afford the desired product **3c** (31%, 55 mg) a pale brown solid; mp = 130 – 132°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.41 (dd, *J* = 10.1, 3.0 Hz, 1H). 6.08 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.03 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.23 (hept, *J* = 6.2 Hz, 1H), 2.61 (dd, *J* = 8.5, 7.0 Hz, 1H), 2.56 – 2.52 (m, 2H), 2.51 – 2.44 (m, 1H), 2.16 – 2.49(d, *J* = 13.3 Hz, 1H), 2.13 – 2.05(ddd, *J* = 9.7, 8.7, 4.9 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.4, 186.0, 151.9, 149.3, 127.1, 126.4, 116.3, 66.7, 61.5, 44.3, 35.9, 27.4, 24.7, 24.4, 16.0, HRMS (ESI) calcd for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434; found: 277.1435.

3a'-Ethyl-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3d):



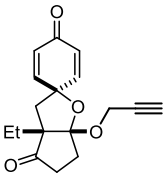
Prepared according to the general procedure as described above in 71% yield (151 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a white solid; mp = 70–72°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.45 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.10 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.05 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.44 (s, 3H), 2.65 – 2.53 (m, 2H), 2.53 – 2.42 (m, 2H), 2.11 (d, *J* = 13.4 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.73 (dq, *J* = 15.2, 7.6 Hz, 1H), 1.54 (dq, *J* = 14.9, 7.5 Hz, 1H), 0.87 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.9, 185.4, 150.8, 148.8, 127.3, 126.9, 116.0, 77.7, 64.8, 49.7, 42.8, 36.1, 26.6, 23.9, 9.1; IR (neat): υ_{max} 3000, 1744, 1675, 1230, 1076, 907 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{19}O_4$$[M+H]^+$: 263.1278; found: 263.1273.

6a'-(Allyloxy)-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3e):



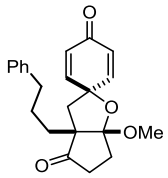
Prepared according to the general procedure as described above in 37% yield (82 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a brown semi solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 10.0, 3.0 Hz, 1H), 6.46 (dd, *J* = 10.0, 3.1 Hz, 1H), 6.09 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.06 (dd, *J* = 10.1, 2.0 Hz, 1H), 5.98 (ddt, *J* = 17.2, 10.3, 5.1 Hz, 1H), 5.36 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.22 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.29 (dd, *J* = 12.9, 5.2 Hz, 1H), 4.16 (dd, *J* = 12.9, 5.0 Hz, 1H), 2.65 – 2.56 (m, 2H), 2.56 – 2.46 (m, 2H), 2.16 (d, *J* = 13.4 Hz, 1H), 2.09 (ddd, *J* = 16.8, 11.9, 9.6 Hz, 1H), 1.80 (dq, *J* = 15.1, 7.6 Hz, 1H), 1.60 (dq, *J* = 14.8, 7.5 Hz, 1H), 0.90 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.7, 185.3, 150.8, 148.7, 134.3, 127.3, 126.9, 116.4, 115.7, 77.8, 65.0, 63.0, 42.7, 36.1, 27.2, 23.9, 9.1; IR (neat): υ_{max} 2982, 2936, 1745, 1675, 1149, 1092, 1027, 931, 906, 955 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{21}O_4[M+H]^+$: 289.1434; found: 289.1430.

3a'-Ethyl-6a'-(prop-2-yn-1-yloxy)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3f):



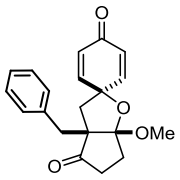
Prepared according to the general procedure as described above in 38% yield (80 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 68–70°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 10.1, 3.1 Hz, 1H), 6.43 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.11 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.06 (dd, *J* = 10.1, 2.0 Hz, 1H), 4.37 (qd, *J* = 15.4, 2.5 Hz, 2H), 2.66 – 2.59 (m, 1H), 2.58 (s, 1H), 2.56 – 2.52 (m, 1H), 2.50 (dd, *J* = 6.8, 3.5 Hz, 1H), 2.48 – 2.45 (m, 1H), 2.22 – 2.17 (m, 1H), 2.15 (d, *J* = 13.4 Hz, 1H), 1.79 (dq, *J* = 15.1, 7.6 Hz, 1H), 1.62 – 1.54 (m, 1H), 0.89 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.7, 185.3, 150.8, 148.7, 134.3, 127.3, 126.9, 116.4, 115.7, 77.8, 65.0, 63.0, 42.7, 36.2, 27.2, 23.9, 9.1; HRMS (ESI) calcd for $C_{17}H_{19}O_4[M+H]^+$: 287.1278; found: 287.1274.

6a'-Methoxy-3a'-(3-phenylpropyl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3g):



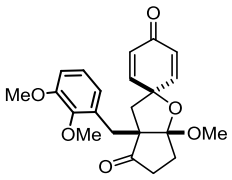
Prepared according to the general procedure as described above in 77% yield (219 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 120–122°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.20 – 7.16 (m, 1H), 7.13 (d, *J* = 6.9 Hz, 2H), 6.85 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.47 – 6.40 (m, 1H), 6.10 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.05 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.43 (s, 3H), 2.61 – 2.53 (m, 4H), 2.49 (ddd, *J* = 20.4, 10.4, 5.0 Hz, 2H), 2.12 (d, *J* = 13.4 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.76 – 1.66 (m, 2H), 1.56 – 1.50 (m, 1H), 1.50 – 1.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.8, 185.3, 150.7, 148.7, 141.6, 128.5, 128.5, 127.4, 127.0, 126.1, 116.0, 77.8, 64.4, 49.7, 43.1, 36.3, 36.0, 30.5, 26.6, 26.3; HRMS (ESI) calcd for $C_{22}H_{25}O_4[M+H]^+$: 353.1747; found: 353.1744.

3a'-Benzyl-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3h):



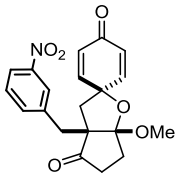
Prepared according to the general procedure as described above in 70% yield (185 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a pale white solid; mp = 130–132°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 3H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.93 (d, *J* = 10.1 Hz, 1H), 6.42 (d, *J* = 10.1 Hz, 1H), 6.13 (d, *J* = 10.1 Hz, 1H), 6.05 (d, *J* = 10.1 Hz, 1H), 3.49 (s, 3H), 3.02 – 2.92 (m, 2H), 2.60 (d, *J* = 13.5 Hz, 1H), 2.33 (dd, *J* = 18.3, 8.9 Hz, 1H), 2.25 (dd, *J* = 12.5, 7.9 Hz, 2H), 2.06 – 1.91 (m, 1H), 1.42 – 1.29 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.2, 185.3, 150.7, 148.6, 135.7, 130.4, 128.4, 127.4, 127.3, 127.1, 115.8, 77.2, 65.7, 49.6, 44.7, 37.7, 36.9, 26.7; IR (neat): υ_{max} 2932, 2453, 1747,1147, 1083, 938, 627 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}O_4$ $[M+H]^+$: 325.1434; found: 325.1428.

3a'-(3,4-Dimethoxybenzyl)-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3i):



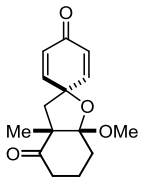
Prepared according to the general procedure as described above in 69% yield (215 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a pale brown solid; mp = 153–155°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.72 (d, *J* = 1.8 Hz, 1H), 6.68 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.42 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.12 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.06 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.49 (s, 3H), 2.92 (q, *J* = 13.4 Hz, 2H), 2.59 (d, *J* = 13.5 Hz, 1H), 2.32 (dd, *J* = 19.2, 9.8 Hz, 1H), 2.27 (d, *J* = 6.8 Hz, 1H), 2.24 (d, *J* = 8.3 Hz, 1H), 2.04 – 1.94 (m, 1H), 1.40 – 1.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.7, 185.3, 150.7, 148.6, 148.5, 148.2, 128.0, 127.4, 127.1, 122.5, 115.9, 113.6, 111.0, 77.4, 65.8, 56.0, 49.6, 44.9, 37.5, 37.1, 26.9; HRMS (ESI) calcd for $C_{22}H_{25}O_6$ $[M+H]^+$: 385.1646; found: 385.1631.

6a'-Methoxy-3a'-(3-nitrobenzyl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[b]furan]-2,5-diene-4,4'(3'H)-dione (3j):



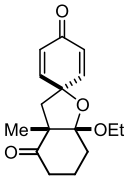
Prepared according to the general procedure as described above in 70% yield (210 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a white solide solid; mp = 130–132°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 7.48 – 7.40 (m, 2H), 6.92 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.40 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.14 (dd, *J* = 10.1, 1.6 Hz, 1H), 6.06 (dd, *J* = 10.1, 1.9 Hz, 1H), 3.52 (s, 3H), 3.06 (dd, *J* = 30.8, 13.5 Hz, 2H), 2.56 (d, *J* = 13.5 Hz, 1H), 2.46 – 2.34 (m, 2H), 2.30 (d, *J* = 13.6 Hz, 1H), 2.15 – 2.04 (m, 1H), 1.42 – 1.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.2, 185.1, 150.2, 148.2, 137.9, 136.3, 129.4, 127.6, 127.3, 125.4, 122.4, 115.5, 65.2, 49.8, 44.6, 37.1, 36.7, 26.9; HRMS (ESI) calcd for $C_{20}H_{20}O_6N$ $[M+H]^+$: 370.1285; found: 370.1273.

7a-Methoxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3k):



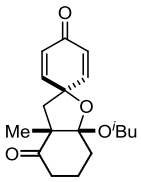
Prepared according to the general procedure as described above in 76% yield (161 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 127–129°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.52 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.11 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.05 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.35 (s, 3H), 3.01 (d, *J* = 12.8 Hz, 1H), 2.56 (td, *J* = 14.5, 6.1 Hz, 1H), 2.46 (t, *J* = 2.9 Hz, 1H), 2.44 (t, *J* = 2.7 Hz, 1H), 2.09 (d, *J* = 12.8 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.77 (td, *J* = 13.3, 3.6 Hz, 1H), 1.73 – 1.64 (m, 1H), 1.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 185.6, 151.2, 149.0, 127.4, 127.0, 110.9, 76.2, 61.8, 48.6, 41.3, 37.8, 27.1, 19.6, 19.2; HRMS (ESI) calcd for $C_{15}H_{19}O_4[M+H]^+$: 263.1278; found: 263.1264.

7a-Ethoxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3l):



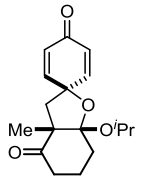
Prepared according to the general procedure as described above in 71% yield (159 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 123–125°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.52 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.10 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.03 (dd, *J* = 10.2, 1.9 Hz, 1H), 3.67 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.58 (dq, *J* = 14.0, 7.0 Hz, 1H), 3.00 (d, *J* = 12.8 Hz, 1H), 2.55 (td, *J* = 14.4, 5.9 Hz, 1H), 2.44 (d, *J* = 13.8 Hz, 2H), 2.11 (d, *J* = 12.8 Hz, 1H), 1.95 – 1.88 (m, 1H), 1.80 (td, *J* = 13.5, 4.0 Hz, 1H), 1.74 – 1.64 (m, 1H), 1.26 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.4, 185.6, 151.5, 149.1, 127.4, 126.9, 110.7, 76.0, 61.7, 56.2, 41.4, 37.8, 27.9, 19.7, 19.2, 15.5; IR (neat): υ_{max} 2955, 1711, 1672, 1516, 1258, 1029, 758 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{21}O_4[M+H]^+$: 277.1434; found: 277.1422.

7a-Isobutoxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3m):



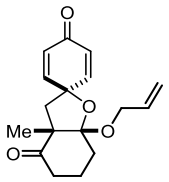
Prepared according to the general procedure as described above in 39% yield (97 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 160–162°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.51 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.11 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.04 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.44 (dd, *J* = 8.8, 5.8 Hz, 1H), 3.24 (dd, *J* = 8.6, 7.8 Hz, 1H), 3.01 (d, *J* = 12.8 Hz, 1H), 2.56 (td, *J* = 14.2, 5.9 Hz, 1H), 2.46 (dd, *J* = 9.3, 4.2 Hz, 2H), 2.12 (d, *J* = 12.8 Hz, 1H), 1.96 – 1.89 (m, 1H), 1.86 (dd, *J* = 13.3, 6.7 Hz, 1H), 1.79 (td, *J* = 13.4, 3.7 Hz, 1H), 1.75 – 1.63 (m, 1H), 1.28 (s, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 185.6, 151.4, 149.1, 127.4, 126.9, 110.7, 76.2, 67.3, 62.0, 41.7, 37.9, 29.1, 28.0, 19.8, 19.7, 19.4; HRMS (ESI) calcd for $C_{18}H_{25}O_4[M+H]^+$: 305.1747; found: 305.1739.

7a-Isopropoxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3n):



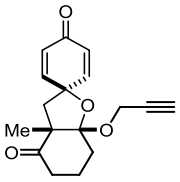
Prepared according to the general procedure as described above in 26% yield (61 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a pale brown solid; mp = 101–103°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.48 (dd, *J* = 10.2, 3.0 Hz,61 1H), 6.10 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.02 (dd, *J* = 10.2, 2.0 Hz, 1H), 4.21 (hept, *J* = 6.1 Hz, 1H), 2.97 (d, *J* = 12.7 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.49 – 2.42 (m, 2H), 2.12 (d, *J* = 12.7 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.88 (dd, *J* = 13.5, 3.9 Hz, 1H), 1.80 – 1.67 (m, 1H), 1.27 (d, *J* = 6.1 Hz, 3H), 1.23 (s, 3H), 1.21 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.7, 185.7, 152.0, 149.1, 127.0, 126.9, 111.3, 76.1, 65.0, 62.0, 41.8, 38.0, 29.1, 24.8, 24.7, 19.8, 19.7; HRMS (ESI) calcd for $C_{17}H_{23}O_4[M+H]^+$: 291.1591; found: 291.1582.

7a-(Allyloxy)-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3p):



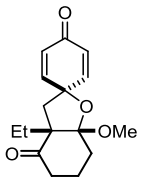
Prepared according to the general procedure as described above in 36% yield (85 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a brown solid; mp = 103–105°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.53 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.09 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.05 (dd, *J* = 10.1, 2.0 Hz, 1H), 5.97 (ddt, *J* = 17.2, 10.5, 4.7 Hz, 1H), 5.35 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.22 (dq, *J* = 10.6, 1.6 Hz, 1H), 4.19 (ddt, *J* = 13.2, 4.9, 1.7 Hz, 1H), 4.11 (ddt, *J* = 13.3, 4.4, 1.8 Hz, 1H), 3.04 (d, *J* = 12.8 Hz, 1H), 2.58 (td, *J* = 14.4, 5.9 Hz, 1H), 2.50 – 2.40 (m, 2H), 2.14 (d, *J* = 12.8 Hz, 1H), 1.97 – 1.91 (m, 1H), 1.86 (td, *J* = 13.6, 4.2 Hz, 1H), 1.77 – 1.66 (m, 1H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.2, 185.6, 151.3, 148.9, 134.6, 127.5, 127.0, 115.8, 110.7, 76.3, 61.2, 61.5, 41.5, 37.8, 28.0, 19.6, 19.3; HRMS (ESI) calcd for $C_{17}H_{21}O_4[M+H]^+$: 289.1434; found: 289.1424.

3a-Methyl-7a-(prop-2-yn-1-yloxy)-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3q):



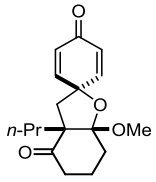
Prepared according to the general procedure as described above in 37% yield (87 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a brown semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.50 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.13 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.05 (dd, *J* = 10.2, 2.0 Hz, 1H), 4.35 – 4.20 (m, 2H), 3.02 (d, *J* = 12.9 Hz, 1H), 2.55 (dd, *J* = 14.4, 5.8 Hz, 1H), 2.49 – 2.42 (m, 2H), 2.39 (dd, *J* = 12.4, 3.9 Hz, 1H), 2.13 (d, *J* = 12.9 Hz, 1H), 1.97 – 1.87 (m, 2H), 1.75 – 1.66 (m, 1H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 185.5, 150.8, 148.6, 127.7, 127.1, 111.2, 80.2, 76.6, 74.2, 61.9, 49.6, 41.2, 37.7, 28.0, 19.5, 19.2; IR (neat): υ_{max} 3400, 2940,1713, 1675, 1675, 1460, 1071, 976, 936, 627cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}O_4[M+H]^+$: 287.1278; found: 287.1269.

3a-Ethyl-7a-methoxy-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3r):



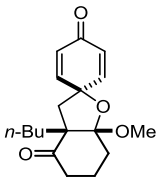
Prepared according to the general procedure as described above in 78% yield (174 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a pale brown solid; mp = 92–94°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.55 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.09 (dd, *J* = 10.1, 2.1 Hz, 1H), 6.04 (dd, *J* = 10.2, 2.1 Hz, 1H), 3.33 (s, 3H), 3.00 (d, *J* = 12.7 Hz, 1H), 2.49 (td, *J* = 13.9, 5.8 Hz, 1H), 2.44 (t, *J* = 3.3 Hz, 1H), 2.41 (t, *J* = 3.2 Hz, 1H), 1.99 (d, *J* = 12.7 Hz, 1H), 1.94 – 1.89 (m, 1H), 1.77 (ddd, *J* = 19.1, 14.3, 5.9 Hz, 2H), 1.71 – 1.60 (m, 2H), 0.70 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.2, 185.6, 151.4, 149.3, 127.3, 126.9, 111.4, 76.5, 66.6, 48.6, 39.3, 38.3, 27.3, 26.0, 19.9, 9.8; HRMS (ESI) calcd for $C_{16}H_{21}O_4[M+H]^+$: 277.1434; found: 277.1419.

7a-Methoxy-3a-propyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3s):



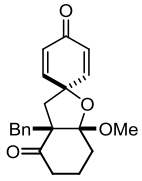
Prepared according to the general procedure as described above in 71% yield (166 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a pale brown solid; mp = 135–137°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.56 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.10 (dd, *J* = 10.1, 1.4 Hz, 1H), 6.04 (dd, *J* = 10.2, 1.4 Hz, 1H), 3.34 (s, 3H), 3.02 (d, *J* = 12.6 Hz, 1H), 2.51 (td, *J* = 14.0, 5.8 Hz, 1H), 2.43 (d, *J* = 13.7 Hz, 2H), 2.03 (s, 1H), 1.97 – 1.89 (m, 1H), 1.81 (tt, *J* = 13.7, 4.5 Hz, 2H), 1.72 – 1.64 (m, 2H), 1.10 – 1.02 (m, 1H), 1.01 – 0.93 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 185.7, 151.4, 149.4, 127.3, 126.9, 111.6, 76.6, 66.2, 48.6, 39.6, 38.4, 35.4, 27.3, 20.0, 18.8, 14.6; HRMS (ESI) calcd for $C_{17}H_{23}O_4[M+H]^+$: 291.1591; found: 291.1579

3a-Butyl-7a-methoxy-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3t):



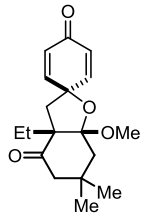
Prepared according to the general procedure as described above in 65% yield (160 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a brown solid; mp = 136–138°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.58 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.11 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.06 (dd, *J* = 10.2, 2.1 Hz, 1H), 3.35 (s, 3H), 3.03 (d, *J* = 12.7 Hz, 1H), 2.52 (td, *J* = 14.0, 5.8 Hz, 1H), 2.44 (d, *J* = 13.2 Hz, 2H), 2.02 (d, *J* = 12.7 Hz, 1H), 1.95 (dddd, *J* = 7.3, 5.9, 4.9, 2.8 Hz, 1H), 1.83 (ddd, *J* = 18.2, 14.2, 4.6 Hz, 2H), 1.68 (tt, *J* = 8.5, 4.3 Hz, 2H), 1.32 – 1.18 (m, 2H), 1.08 – 0.99 (m, 1H), 0.97 – 0.89 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.3, 185.6, 151.4, 149.4, 127.3, 126.9, 111.6, 76.6, 66.1, 48.6, 39.6, 38.4, 32.9, 27.6, 27.3, 23.2, 20.0, 13.9; HRMS (ESI) calcd for $C_{18}H_{25}O_4[M+H]^+$: 305.1747; found: 305.1731.

3a-Benzyl-7a-methoxy-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3u):



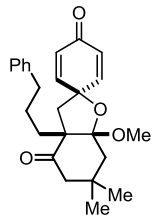
Prepared according to the general procedure as described above in 73% yield (201 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 120–125°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 3H), 7.01 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.83 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.49 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.13 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.01 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.44 (s, 3H), 3.12 (s, 2H), 2.84 (d, *J* = 12.8 Hz, 1H), 2.50 – 2.45 (m, 2H), 2.45 – 2.36 (m, 1H), 2.28 (d, *J* = 12.8 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.85 – 1.76 (m, 1H), 1.75 – 1.62 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 185.5, 151.2, 149.0, 136.5, 129.7, 128.6, 127.5, 127.2, 127.0, 111.1, 76.4, 66.8, 48.8, 41.1, 39.7, 39.5, 27.5, 19.8; HRMS (ESI) calcd for $C_{21}H_{23}O_4[M+H]^+$: 339.1591; found: 339.1580.

3a-Ethyl-7a-methoxy-6,6-dimethyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3v):



Prepared according to the general procedure as described above in 66% yield (163 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a white solid; mp = 101–103°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (dd, *J* = 10.0, 3.0 Hz, 1H), 6.73 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.10 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.07 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.34 (s, 3H), 3.06 (d, *J* = 12.8 Hz, 1H), 2.56 (d, *J* = 13.0 Hz, 1H), 2.25 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.19 (dd, *J* = 13.0, 2.2 Hz, 1H), 1.98 – 1.89 (m, 2H), 1.82 – 1.73 (m, 2H), 1.12 (s, 3H), 1.01 (s, 3H), 0.70 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 185.7, 151.4, 149.3, 127.2, 127.1, 111.7, 77.0, 65.9, 50.8, 48.4, 40.2, 38.8, 33.6, 32.8, 27.2, 27.1, 9.8; HRMS (ESI) calcd for $C_{18}H_{25}O_4[M+H]^+$: 305.1747; found: 305.1737.

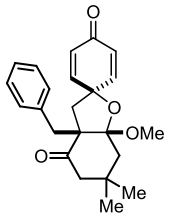
7a-Methoxy-6,6-dimethyl-3a-(3-phenylpropyl)-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3w):



Prepared according to the general procedure as described above in 67% yield (213 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.7) to afford a brown solid; mp = 142–144°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.1, 7.3 Hz, 2H), 7.17 (dd, *J* = 10.8, 4.0 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.76 (dd, *J* = 10.0, 3.0 Hz, 1H), 6.71 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.10 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.06 (dd, *J* = 10.8, 1.3 Hz, 1H), 3.32 (s, 3H), 3.06 (d, *J* = 12.7 Hz, 1H), 2.61 (ddd, *J* = 14.4, 8.5, 6.2 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.42 (d, *J* = 13.0 Hz, 1H), 2.23 (dd, *J* = 14.4, 1.9 Hz, 1H), 2.14 (dd, *J* = 12.9, 1.9 Hz, 1H), 1.95 (d, *J* = 12.8 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.76 (d, *J* = 14.5 Hz, 1H), 1.74 (dd, *J* = 20.3, 6.3 Hz, 1H), 1.44 – 1.32 (m, 1H), 1.30 – 1.19 (m, 1H), 1.09 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.1, 185.7, 151.3, 149.2, 141.5, 128.5, 128.4, 127.2, 127.1, 126.1, 111.7, 77.0, 65.2, 50.7, 48.4, 40.1,

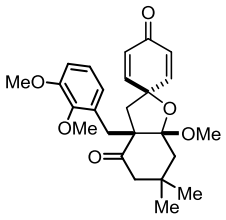
39.1, 36.1, 33.6, 33.6, 32.8, 27.1, 27.1; HRMS (ESI) calcd for $C_{25}H_{31}O_4[M+H]^+$: 395.2117; found: 395.2195.

3a-Benzyl-7a-methoxy-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3x):



Prepared according to the general procedure as described above in 68% yield (203 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a white solid; mp = 143–145°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 3H), 6.99 (dt, *J* = 4.4, 2.5 Hz, 2H), 6.84 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.66 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.13 (dd, *J* = 10.1, 2.1 Hz, 1H), 6.02 (dd, *J* = 10.2, 2.1 Hz, 1H), 3.42 (s, 3H), 3.15 (dd, *J* = 37.2, 14.1 Hz, 2H), 2.84 (d, *J* = 12.8 Hz, 1H), 2.72 (d, *J* = 13.1 Hz, 1H), 2.28 (ddd, *J* = 15.2, 13.7, 2.1 Hz, 2H), 2.25 – 2.20 (d, *J*=12.68 Hz, 1H), 1.89 (d, *J* = 14.4 Hz, 1H), 1.14 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.0, 185.6, 151.3, 149.0, 136.5, 129.3, 128.6, 127.3, 127.2, 127.1, 111.5, 77.0, 66.0, 51.7, 48.6, 40.4, 40.2, 39.9, 33.7, 33.0, 27.2; HRMS (ESI) calcd for $C_{23}H_{27}O_4[M+H]^+$: 367.1904; found: 367.1889.

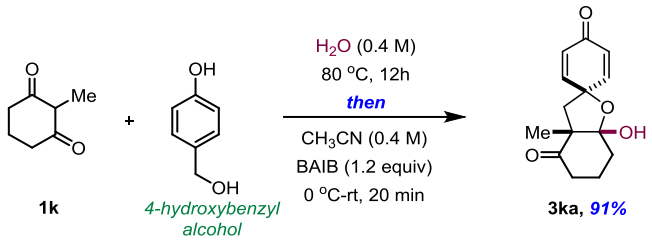
3a-(3,4-Dimethoxybenzyl)-7a-methoxy-6,6-dimethyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3y):



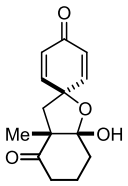
Prepared according to the general procedure as described above in 70% yield (243 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a yellow solid; mp = 138–140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.66 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.53 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.48 (d, *J* = 2.0 Hz, 1H), 6.12 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.03 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.82 (s, 3H), 3.82 (s, 3H), 3.41 (s, 3H), 3.09 (q, *J* = 14.3 Hz, 2H), 2.86 (d, *J* = 12.8 Hz, 1H), 2.68 (d, *J* = 13.0 Hz, 1H), 2.27 (ddd, *J* = 15.0, 13.8, 1.9 Hz, 2H), 2.19 (d, *J* = 12.9 Hz, 1H), 1.87

(d, J = 14.4 Hz, 1H), 1.13 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.2, 185.6, 151.3, 149.0, 148.8, 148.2, 128.9, 127.4, 127.2, 121.5, 112.6, 111.5, 111.2, 77.0, 66.0, 56.0, 55.9, 51.7, 48.6, 40.4, 39.9, 39.9, 33.7, 32.9, 27.2; IR (neat): υ_{max} 2954, 2835, 1710, 1671, 1515, 1255, 1027, 854, 749 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{31}O_6$ $[M+H]^+$: 427.2115; found: 427.2094.

7a-Hydroxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3ka):

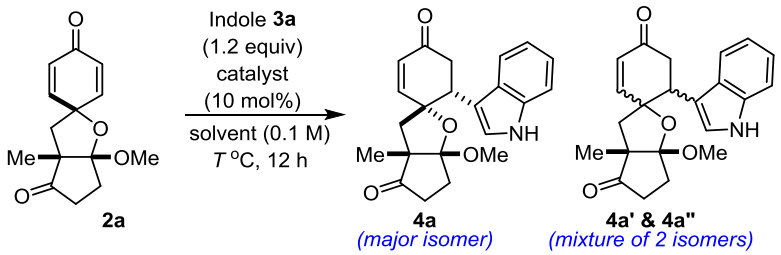


To a solution of 2-substituted-1,3-dione **1k** (609 mg, 6 mmol) in water (10 mL, 0.4 M) was added p-hydroxybenzyl alcohol (500 mg, 0.4 mmol), and the solution was stirred at 80 °C for 12 h. The reaction mixture was cooled to 0 °C and diluted with CH_3CN (10 mL) and then added $PhI(OAc)_2$ (1.0 g, 4.8 mmol) in several portions. The resulting reaction mixture was stirred at same temperature for 20 minutes and quenched with saturated $NaHCO_3$ (10 mL) solution. The resulting mixture was extracted with EtOAc (3 × 25 mL). The combined organic solvent was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography (30% EtOAc in hexanes) to give the desired product **3ka** as a white solid in 91% yield (910 mg).



Mp = 150–151°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (dd, J = 10.1, 3.0 Hz, 1H), 6.55 – 6.50 (m, 1H), 6.09 (dd, J = 10.1, 2.0 Hz, 1H), 6.04 (dd, J = 10.2, 2.0 Hz, 1H), 3.11 (s, 1H), 3.03 (d, J = 12.9 Hz, 1H), 2.57 (td, J = 14.4, 6.1 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.21 – 2.17 (m, 1H), 2.15 (d, J = 12.9 Hz, 1H), 2.13 – 2.03 (m, 1H), 1.90 – 1.85 (m, 1H), 1.82 – 1.71 (m, 1H), 1.31 (s, 3H; ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 185.9, 152.5, 149.3, 127.0, 108.4, 76.1, 61.1, 41.4, 37.5, 32.8, 19.7, 19.2; HRMS (ESI) calcd for $C_{14}H_{17}O_4$ $[M+H]^+$: 249.1121; found: 249.1119.

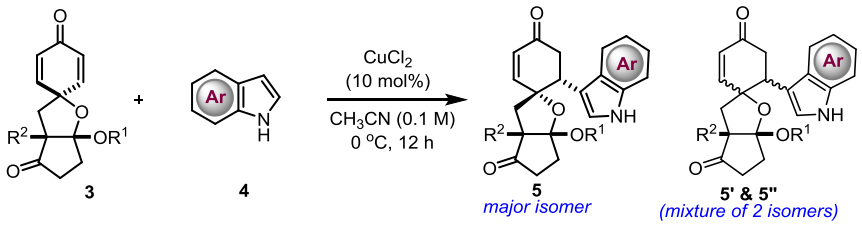
Table S1. Complete optimization of Friedel–Crafts alkylation on cyclopentanone[a,b]



entry	catalyst	solvent	*T* °C	Yield [%][b]	***dr*** **4a : 4a' : 4a"**
1	$Al(OTf)_3$	CH_3CN	rt	72	19 : 03 : 01
2	$Sc(OTf)_3$	CH_3CN	rt	83	18 : 02 : 01
3	$Cu(OTf)_3$	CH_3CN	rt	79	18 : 03 : 01
4	$Yb(OTf)_3$	CH_3CN	rt	<5	-
5	$AlCl_3$	CH_3CN	rt	95	18 : 05 : 00
6	$[Cu(CH_3CN)_4]PF_6$	CH_3CN	rt	74	06 : 01 : 01
7	CuBr	CH_3CN	rt	NR	-
8	$CuBr_2$	CH_3CN	rt	48	02 : 01 : 01
9	$CuCl_2$	CH_3CN	rt	70	05 : 00 : 01
10	$CuCl_2$	CH_3CN	0	89	10 : 00 : 01
11	$CuCl_2$	toluene	0	60	05 : 00 : 01
12	$CuCl_2$	1,4-dioxane	0	NR	-
13	$CuCl_2$	CH_2Cl_2	0	NR	-
14	$Al(OTf)_3$	CH_3CN	0	60	07 : 00 : 01
15	$AlCl_3$	CH_3CN	0	89	06 : 01 : 00

[a]Reaction conditions**: 3a** (0.2 mmol), **4a** (0.24 mmol) and catalyst (10 mol%) in CH_3CN (0.1 M) under N_2 atmosphere. [b]Isolated yield of all isomers. [c]Starting material was decomposed.

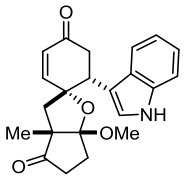
IIBb. General Procedure for Friedel–Crafts alkylation of cyclopentanone-fused cyclohexadienones:



To a stirred solution of cyclopenatanone-fused cyclohexadienones **3** (0.2 mmol) and indole **4** (0.24 mmol) in CH_3CN (2 mL, 0.1 M) was added $CuCl_2$ (2.6 mg, 10 mol%) at 0 °C under N_2 atmosphere. The resulting reaction mixture was stirred at same temperature for 12 hours. Then the reaction mixture was diluted with water (10 mL) and extracted with EtOAc (10 mL × 2). The combined organic solvent was

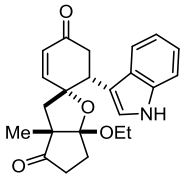
washed with brine (10 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude reaction mixture was purified by column chromatography (EtOAc/hexanes) to give the desired product **5a** as major product along with trace amount of **5′ &5″** as mixture of diastereomers.

6-(1*H*-Indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5a):



Prepared according to the general procedure as described above in 80% yield (58 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.4) to afford a brown solid; mp = 198–200°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.11 – 7.05 (m, 1H), 7.03 (d, *J* = 10.2 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.04 (dd, *J* = 10.2, 0.8 Hz, 1H), 3.51 – 3.39 (m, 2H), 3.34 (s, 3H), 2.67 (d, *J* = 13.3 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.22 (ddd, *J* = 11.9, 10.0, 1.4 Hz, 1H), 1.90 (d, *J* = 13.4 Hz, 1H),1.87 (ddd, *J* = 19.5, 10.2, 1.3 Hz, 1H), 1.69 (dt, *J* = 13.1, 10.1 Hz, 1H), 1.07 – 0.94 (m, 1H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.3, 199.9, 154.3, 136.4, 127.7, 127.2, 124.2, 122.0, 120.5, 119.4, 115.4, 113.4, 111.5, 82.0, 60.3, 49.3, 45.9, 42.2, 41.6, 34.4, 26.2, 17.2; IR (neat): υ_{max} 3364, 2930, 2856, 1741, 1678, 1461, 1105, 955, 763, 626 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}O_4N[M+H]^+$: 366.1700; found: 366.1687.

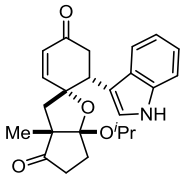
6a'-Ethoxy-6-(1*H*-indol-3-yl)-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5b):



Prepared according to the general procedure as described above in 72% yield (55 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.4) to afford a white solid; mp = 170–172°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.11 (m, 1H), 7.10 – 7.01 (m, 2H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.02 (dd, *J* = 10.2, 0.7 Hz, 1H), 3.73 (dq, *J* = 8.8, 7.1 Hz, 1H), 3.58 – 3.49 (m, 1H), 3.49 – 3.38 (m, 2H), 2.67 (d, *J* = 13.3 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.26 – 2.16

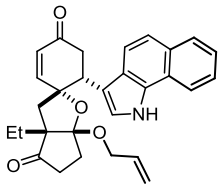
(m, 1H), 1.91 (d, *J* = 13.3 Hz, 1H), 1.85 (dd, *J* = 13.8, 5.8 Hz, 1H), 1.72 (dt, *J* = 13.0, 10.0 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.07 – 0.94 (m, 1H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.8, 200.1, 154.7, 136.4, 127.5, 127.4, 124.3, 121.9, 120.5, 119.3, 114.9, 113.3, 111.6, 81.8, 60.3, 57.2, 46.0, 42.2, 41.6, 34.5, 26.7, 17.1, 15.3; HRMS (ESI) calcd for $C_{23}H_{26}O_4N[M+H]^+$: 380.1856; found: 380.1844.

6-(1*H*-Indol-3-yl)-6a'-isopropoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5c):



Prepared according to the general procedure as described above in 78% yield (61 mg). It was purified by flash chromatography (30% IPA/hexanes; R_f = 0.4) to afford a pale brown solid; mp = 176–178°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.72 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.12 (m, 1H), 7.10 (d, *J* = 10.1 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 6.98 (s, 1H), 6.01 (dd, *J* = 10.2, 0.7 Hz, 1H), 4.18 (hept, *J* = 6.2 Hz, 1H), 3.54 – 3.33 (m, 2H), 2.68 – 2.57 (m, 2H), 2.27 – 2.15 (m, 1H), 1.91 (d, *J* = 13.4 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.25 (d, *J* = 6.1 Hz, 3H), 1.17 (d, *J* = 6.1 Hz, 3H), 1.00 – 0.93 (m, 1H), 0.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.2, 200.1, 155.6., 136.5, 127.6, 127.2, 124.3, 122.1, 120.6, 119.5, 115.8, 113.6, 111.6, 82.0, 66.1, 60.7, 46.6, 42.4, 41.7, 34.7, 27.8, 24.6, 17.5; HRMS (ESI) calcd for $C_{24}H_{28}O_4N$ $[M+H]^+$: 394.2013; found: 394.1998.

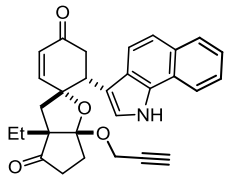
6a'-(Allyloxy)-6-(1*H*-benzo[g]indol-3-yl)-3a'-ethyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5d):



Prepared according to the general procedure as described above in 71% yield (64 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a brown solid; mp = 210–212°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.05 (d, *J* = 10.2 Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 1H), 5.94 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.31 (dq,

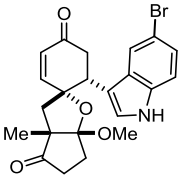
J = 17.2 Hz, 1,7 1H), 5.17 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.22 (ddt, *J* = 12.8, 5.1, 1.5 Hz, 1H), 4.06 (ddt, *J* = 12.8, 4.9, 1.4 Hz, 1H), 3.54 (dd, *J* = 11.9, 3.6 Hz, 1H), 3.45 (dd, *J* = 16.2, 12.0 Hz, 1H), 2.78 – 2.66 (m, 2H), 2.26 (dt, *J* = 12.9, 9.7 Hz, 1H), 1.99 (d, *J* = 13.3 Hz, 1H), 1.84 – 1.73 (m, 2H), 1.70 (dd, *J* = 14.6, 7.2 Hz, 1H), 1.52 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.05 (dd, *J* = 21.8, 12.7 Hz, 1H), 0.77 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.2, 199.9, 154.5, 134.6, 131.2, 130.2, 128.6, 127.6, 125.4, 124.1, 123.3, 122.3, 121.8, 120.6, 120.0, 119.8, 116.0, 115.1, 115.1, 82.2, 64.3, 62.7, 45.0, 42.5, 41.9, 35.5, 27.6, 25.2, 9.2; HRMS (ESI) calcd for $C_{29}H_{30}O_4N[M+H]^+$: 456.2169; found: 456.2141.

6-(1*H*-Benzo[*g*]indol-3-yl)-3a'-ethyl-6a'-(prop-2-yn-1-yloxy)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5e):



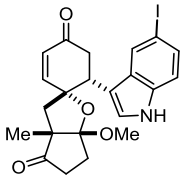
Prepared according to the general procedure as described above in 77% yield (68 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.6) to afford a blue solid; mp = 243 – 245°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 6.9 Hz, 1H), 7.08 (d, *J* = 10.2 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 4.37 – 4.25 (m, 2H), 3.54 (dd, *J* = 11.9, 3.6 Hz, 1H), 3.44 (dd, *J* = 16.2, 12.0 Hz, 1H), 2.77 – 2.66 (m, 2H), 2.42 (t, *J* = 2.4 Hz, 1H), 2.27 – 2.18 (m, 1H), 1.99 (d, *J* = 13.3 Hz, 1H), 1.94 – 1.82 (m, 1H), 1.80 – 1.65 (m, 2H), 1.51 (dt, *J* = 21.4, 7.4 Hz, 1H), 1.09 – 0.98 (m, 1H), 0.76 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.6, 199.8, 154.0, 131.3, 130.3, 128.7, 128.1, 125.6, 124.2, 123.3, 122.4, 121.8, 120.6, 120.2, 119.8, 115.5, 115.1, 82.7, 80.3, 74.0, 64.4, 50.4, 44.9, 42.6, 41.9, 35.6, 27.6, 25.2, 9.2; IR (neat): υ_{max} 3400, 2855, 1739, 1680, 1391, 1091, 1078, 917, 808, 761 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{28}O_4N[M+H]^+$: 454.2013; found: 454.2008.

6-(5-Bromo-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5f):



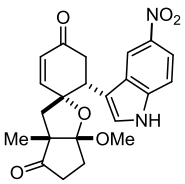
Prepared according to the general procedure as described above in 71% yield (63 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.6) to afford a white solid; mp = 220–222°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.89 (s, 1H), 7.25 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 10.2 Hz, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 6.04 (dd, *J* = 10.2, 0.7 Hz, 1H), 3.45 – 3.37 (m, 2H), 3.35 (s, 3H), 2.62 (dd, *J* = 13.4, 5.4 Hz, 2H), 2.27 (ddd, *J* = 12.6, 10.4, 2.2 Hz, 1H), 1.96 (ddd, *J* = 19.8, 10.7, 1.6 Hz, 1H), 1.91 (d, *J* = 13.4 Hz, 1H), 1.77 (dt, *J* = 13.2, 10.1 Hz, 1H), 1.06 – 0.94 (m, 1H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.4, 199.5, 154.0, 135.1, 129.1, 127.7, 125.4, 124.8, 123.4, 115.3, 113.2, 113.0, 112.6, 82.0, 60.4, 49.4, 45.7, 42.3, 41.4, 34.4, 26.2, 17.1; HRMS (ESI) calcd for $C_{22}H_{23}O_4NBr$ $[M+H]^+$: 444.0805; found: 444.0784.

6-(5-Iodo-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5g):



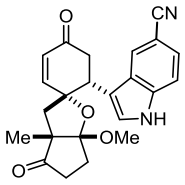
Prepared according to the general procedure as described above in 73% yield (72 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.4) to afford a pale brown solid; mp = 249–251°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.10 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 10.2 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 6.03 (d, *J* = 10.1 Hz, 1H), 3.40 (t, *J* = 11.1 Hz, 2H), 3.35 (s, 3H), 2.61 (dd, *J* = 18.2, 8.7 Hz, 2H), 2.33 – 2.18 (m, 1H), 1.96 (dd, *J* = 20.6, 11.1 Hz, 1H), 1.90 (d, *J* = 13.5 Hz, 1H), 1.78 (dd, *J* = 21.8, 11.5 Hz, 1H), 0.99 (s, 3H), 0.88 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.5, 199.6, 154.2, 135.7, 130.3, 130.1, 129.9, 127.9, 125.1, 115.5, 113.6, 113.0, 82.9, 82.1, 60.5, 49.5, 45.8, 42.4, 41.5, 34.5, 26.3, 17.3; IR (neat): υ_{max} 3372, 3932, 1742, 1677, 1454, 1104, 1060, 953, 756 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{23}O_4IN$ $[M+H]^+$: 492.0666; found: 492.0642.

6a'-Methoxy-3a'-methyl-6-(5-nitro-1*H*-indol-3-yl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5h):



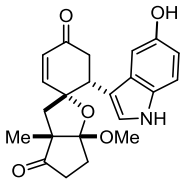
Prepared according to the general procedure as described above in 68% yield (56 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.5) to afford a brown solid; mp = 253–255°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.58 (s, 1H), 8.11 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.41 (d, *J* = 9.0 Hz, 1H), 7.16 (d, *J* = 2.2 Hz, 1H), 7.03 (d, *J* = 10.2 Hz, 1H), 6.06 (d, *J* = 10.2 Hz, 1H), 3.61 – 3.38 (m, 2H), 3.35 (s, 3H), 2.71 – 2.59 (m, 2H), 2.27 (t, *J* = 10.9 Hz, 1H), 2.05 (t, *J* = 10.3 Hz, 1H), 1.96 (d, *J* = 13.4 Hz, 1H), 1.79 (dd, *J* = 23.4, 10.0 Hz, 1H), 1.10 (d, *J* = 18.1 Hz, 1H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.1, 198.9, 154.0, 141.8, 139.4, 127.9, 127.2, 126.9, 118.2, 117.9, 116.5, 115.5, 111.6, 81.9, 60.6, 49.6, 45.7, 42.2, 41.6, 34.6, 26.1, 17.1. HRMS (ESI) calcd for $C_{22}H_{23}O_6N_2[M+H]^+$: 411.1551; found: 411.1533.

6a'-Methoxy-3a'-methyl-4,4'-dioxo-3',3a',4',5',6',6a'-hexahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-en-6-yl)-1*H*-indole-5-carbonitrile (5i):



Prepared according to the general procedure as described above in 65% yield (51 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.7) to afford a pale brown solid; mp = 226–228 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.11 (s, 1H), 7.42 – 7.34 (m, 2H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.03 (d, *J* = 10.2 Hz, 1H), 6.05 (d, *J* = 10.6 Hz, 1H), 3.51 – 3.46 (m, 1H), 3.40 – 3.35 (m, 1H), 3.34 (s, 3H), 2.65 – 2.56 (m, 2H), 2.28 – 2.20 (m, 1H), 2.00 – 1.91 (m, 1H), 1.93 (d, *J* = 13.4 Hz, 1H), 1.82 – 1.73 (m, 1H), 0.98 (s, 3H), 0.94 – 0.80 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.4, 199.1, 154.0, 138.2, 127.8, 127.2, 126.6, 126.6, 124.7, 120.7, 115.3, 114.2, 112.7, 102.4, 81.8, 60.5, 49.6, 45.6, 42.1, 41.4, 34.4, 26.1, 17.0; IR (neat): υ_{max} 3410, 221, 1743, 1681, 1453, 1103, 954, 764, 652 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}O_4N_2[M+H]^+$: 391.1652; found: 391.1663.

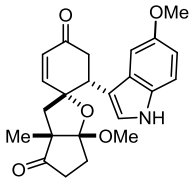
6-(5-Hydroxy-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5j):



Prepared according to the general procedure as described above in 76% yield (58 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.3) to afford a brown solid; mp = 238–240°C; ^{1}H NMR

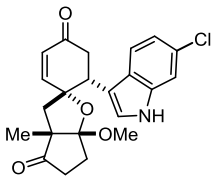
(300 MHz, $CDCl_3$+CD_3OD) δ 7.46 (s, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.96 (s, 1H), 6.73 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.03 (d, *J* = 10.1 Hz, 1H), 3.43 (dd, *J* = 9.8, 7.7 Hz, 2H), 3.35 (s, 3H), 2.64 (d, *J* = 13.3 Hz, 1H), 2.56 (d, *J* = 10.0 Hz, 1H), 2.40 – 2.29 (m, 1H), 1.98 – 1.85 (m, 1H), 1.94 – 1.88 (d, *J*= 13.14, 12.58 Hz, 1H), 1.74 (dd, *J* = 22.8, 10.0 Hz, 1H), 0.99 (s, 3H), 0.94 – 0.84 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$+CD_3OD) δ 219.6, 200.7, 154.8, 149.8, 131.3, 127.5, 125.0, 115.2, 112.0, 111.9, 111.7, 104.3, 94.4, 82.5, 60.3, 49.2, 45.7, 42.0, 41.3, 34.5, 26.1, 17.0; IR (neat): υ_{max} 3364, 2930, 2856, 1741, 1678, 1461, 1105, 955, 763, 626 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}O_5N[M+H]^+$: 382.1649; found: 382.1642.

6a'-Methoxy-6-(5-methoxy-1*H*-indol-3-yl)-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5k):



Prepared according to the general procedure as described above in 67% yield (53 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.4) to afford a pale brown solid; mp = 239–241°C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 2.2 Hz, 1H), 7.03 (d, *J* = 10.2 Hz, 1H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 1H), 3.85 (s, 3H), 3.47 – 3.36 (m, 2H), 3.34 (s, 3H), 2.65 (t, *J* = 13.7 Hz, 2H), 2.27 – 2.20 (m, 1H), 1.96 – 1.87 (m, 2H), 1.72 (dt, *J* = 13.1, 10.2 Hz, 1H), 1.22 – 1.07 (m, 1H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.3, 200.0, 154.3, 153.8, 131.6, 127.8, 127.8, 125.0, 115.3, 113.0, 112.2, 112.1, 102.4, 82.2, 60.3, 56.0, 49.3, 46.0, 42.1, 41.4, 34.5, 26.4, 17.2; HRMS (ESI) calcd for $C_{23}H_{26}O_5N[M+H]^+$: 396.1806; found: 396.1790.

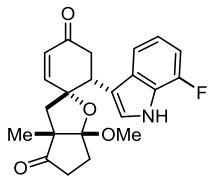
6-(6-Chloro-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5l):



Prepared according to the general procedure as described above in 73% yield (58 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.4) to afford a pale white solid; mp = 230–232°C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 1.6 Hz, 1H), 7.05 (dd, *J* =

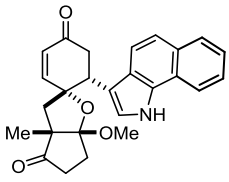
8.6, 1.8 Hz, 1H), 7.02 (d, *J* = 10.2 Hz, 1H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 1H), 3.49 – 3.34 (m, 2H), 3.33 (s, 3H), 2.69 – 2.57 (m, 2H), 2.26 – 2.16 (m, 1H), 1.94 (dd, *J* = 20.9, 9.4 Hz, 1H), 1.91 (d, *J* = 13.4 Hz, 1H), 1.73 (dt, *J* = 13.1, 10.2 Hz, 1H), 1.13 – 0.96 (m, 1H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.6, 199.8, 154.3, 136.9, 128.0, 127.8, 126.1, 125.0, 121.5, 120.2, 115.4, 113.6, 111.6, 82.0, 60.5, 49.4, 45.9, 42.2, 41.6, 34.6, 26.2, 17.2; IR (neat): υ_{max} 3367, 2938, 1741, 1681, 1454, 1103, 1058, 954, 760 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{23}O_4NCl[M+H]^+$: 400.1310; found: 400.1296.

6-(7-Fluoro-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5m):



Prepared according to the general procedure as described above in 71% yield (55 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.4) to afford a pale white solid; mp = 212–214°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 1.6 Hz, 1H), 7.02 (d, *J* = 6.0 Hz, 1H), 6.99 (td, *J* = 8.0, 4.9 Hz, 1H), 6.88 (dd, *J* = 11.0, 7.8 Hz, 1H), 6.03 (d, *J* = 10.2 Hz, 1H), 3.48 (dd, *J* = 11.9, 3.9 Hz, 1H), 3.36 (dd, *J* = 16.5, 12.0 Hz, 1H), 3.34 (s, 3H), 2.65 (d, *J* = 13.4 Hz, 1H), 2.64 (dd, *J* = 16.5, 3.9 Hz, 1H), 2.23 (dd, *J* = 11.9, 10.0 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.92 (d, *J* = 13.4 Hz, 1H), 1.72 (dt, *J* = 13.1, 10.2 Hz, 1H), 1.19 – 1.08 (m, 1H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.2, 199.6, 154.3, 149.7 (d, J_{CF} = 244.1 Hz), 131.2 (d, J_{CF} = 4.9 Hz), 127.8, 124.8, 119.72 (d, J_{CF} = 5.8 Hz), 116.2, 115.4, 114.5, 107.0, 106.9, 82.0, 60.3, 49.4, 46.0, 42.1, 41.7, 34.6, 26.3, 17.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -134.9; IR (neat): υ_{max} 3261, 2930, 1742, 1672, 1527, 1349, 1094, 944, 806, 754 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{23}O_4NF[M+H]^+$: 384.1606; found: 384.1595.

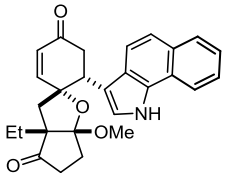
6-(1H-Benzo[*g*]indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5n):



Prepared according to the general procedure as described above in 80% yield (67 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.5) to afford a pale black solid; mp = 217–219°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.94 – 7.85 (m, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.8

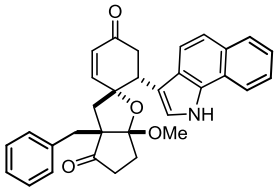
Hz, 1H), 7.41 – 7.34 (m, 2H), 7.06 (d, *J* = 10.2 Hz, 1H), 7.00 (s, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 3.54 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.51 – 3.42 (m, 1H), 3.35 (s, 3H), 2.76 (d, *J* = 13.3 Hz, 1H), 2.69 (dd, *J* = 15.6, 2.9 Hz, 1H), 2.25 (dd, *J* = 12.3, 9.6 Hz, 1H), 1.97 (d, *J* = 13.3 Hz, 1H), 1.90 – 1.76 (m, 1H), 1.68 (dt, *J* = 13.0, 10.0 Hz, 1H), 1.19 – 1.05 (m, 1H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.9, 200.0, 154.4, 131.3, 130.2, 128.6, 127.8, 125.4, 124.1, 123.4, 122.4, 121.9, 120.6, 120.1, 119.9, 115.5, 115.1, 82.1, 60.4, 49.4, 46.2, 42.5, 42.0, 34.7, 26.3, 17.2; HRMS (ESI) calcd for $C_{26}H_{26}O_4N[M+H]^+$: 416.1856; found: 416.1833.

6-(1*H*-Benzo[*g*]indol-3-yl)-3a'-ethyl-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5o):



Prepared according to the general procedure as described above in 76% yield (64 mg). It was purified by column chromatography (30% IPA/hexanes; R_f = 0.4) to afford a pale brown solid; mp = 231–233°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.96 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.88 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.05 (d, *J* = 10.2 Hz, 1H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.07 (d, *J* = 10.5 Hz, 1H), 3.56 – 3.43 (m, 2H), 3.35 (s, 3H), 2.74 (d, *J* = 13.3 Hz, 1H), 2.70 (dd, *J* = 15.7, 2.6 Hz, 1H), 2.25 (t, *J* = 11.6 Hz, 1H), 1.97 (d, *J* = 13.3 Hz, 1H), 1.84 – 1.73 (m, 1H), 1.72 – 1.62 (m, 2H), 1.47 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.06 (dt, *J* = 17.4, 8.6 Hz, 1H), 0.75 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.5, 200.0, 154.5, 131.4, 130.3, 128.7, 127.7, 125.5, 124.1, 123.4, 122.4, 121.9, 120.7, 120.1, 119.9, 115.5, 115.2, 82.2, 64.2, 49.4, 45.1, 42.7, 42.0, 35.5, 27.1, 25.3, 9.3; HRMS (ESI) calcd for $C_{27}H_{28}O_4N[M+H]^+$: 430.2013; found: 430.1985.

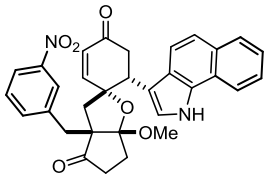
6-(1*H*-Benzo[*g*]indol-3-yl)-3a'-benzyl-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5p):



Prepared according to the general procedure as described above in 85% yield (75 mg). It was purified by column chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 254–256°C; ^{1}H

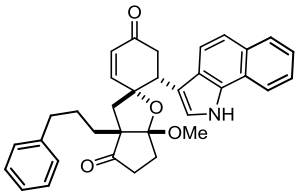
NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.42 (ddd, *J* = 9.1, 7.4, 3.4 Hz, 2H), 7.37 (td, *J* = 8.0, 1.1 Hz, 1H), 7.13 (d, *J* = 10.2 Hz, 1H), 7.11 – 7.07 (m, 3H), 7.03 – 6.98 (m, 3H), 6.10 (d, *J* = 10.2 Hz, 1H), 3.55 (dd, *J* = 12.0, 3.7 Hz, 1H), 3.52 – 3.40 (m, 1H), 3.39 (s, 3H), 2.93 (d, *J* = 13.1 Hz, 1H), 2.82 (dd, *J* = 13.3, 7.2 Hz, 2H), 2.69 (dd, *J* = 16.5, 3.7 Hz, 1H), 2.08 (d, *J* = 13.4 Hz, 1H), 1.96 (t, *J* = 10.6 Hz, 1H), 1.10 (dd, *J* = 18.9, 10.2 Hz, 1H), 1.05 – 0.96 (m, 1H), 0.94 – 0.82 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$, $MeOD_4$) δ 220.0, 200.7, 155.0, 136.0, 131.1, 130.3, 130.0, 128.4, 127.9, 127.6, 126.7, 125.3, 123.8, 123.1, 122.5, 122.0, 120.2, 120.1, 119.8, 114.9, 114.3, 81.3, 65.6, 49.1, 46.3, 42.1, 41.8, 38.5, 35.9, 26.6; IR (neat): υ_{max} 3352, 2935, 1740, 1677, 1392, 1093, 943, 807, 754, 704 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{30}O_4N[M+H]^+$: 492.2169; found: 492.2141.

6-(1*H*-Benzo[*g*]indol-3-yl)-6a'-methoxy-3a'-(3-nitrobenzyl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5q):



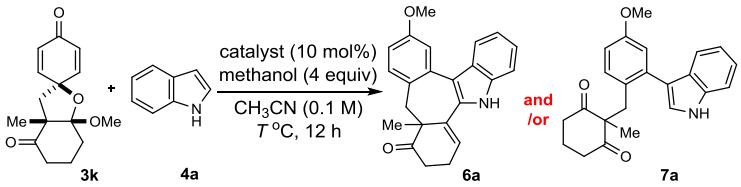
Prepared according to the general procedure as described above in 82% yield (79 mg). It was purified by column chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford a pale white solid; mp = 264–266°C; ^1H NMR (400 MHz, $CDCl_3$ + CD_3OH) δ 10.78 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.05 – 7.95 (m, 2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.49 (t, *J* = 7.1 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 – 7.24 (m, 2H), 7.18 (d, *J* = 10.1 Hz, 1H), 7.05 (s, 1H), 6.11 (d, *J* = 10.1 Hz, 1H), 3.58 (dd, *J* = 12.6, 3.2 Hz, 1H), 3.51 – 3.34 (m, 1H), 3.44 (s, 3H), 3.04 (d, *J* = 13.2 Hz, 1H), 2.93 (d, *J* = 13.2 Hz, 1H), 2.77 (d, *J* = 13.5 Hz, 1H), 2.67 (d, *J* = 16.4 Hz, 1H), 2.09 (t, *J* = 13.7 Hz, 2H), 1.12 (dd, *J* = 18.9, 10.7 Hz, 1H), 1.05 – 0.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$ + CD_3OH) δ 219.0, 200.7, 156.8, 154.4, 147.7, 138.4, 136.4, 130.1, 128.9, 128.4, 127.8, 125.4, 123.9, 123.3, 122.9, 122.7, 121.9, 122.0, 120.1, 119.9, 114.7, 114.0, 114.0, 81.6, 65.2, 49.2, 46.3, 42.1, 41.7, 38.0, 35.7, 26.9; HRMS (ESI) calcd for $C_{32}H_{29}O_6N_2[M+H]^+$: 537.2020; found: 537.1996.

6-(1*H*-Benzo[*g*]indol-3-yl)-6a'-methoxy-3a'-(3-phenylpropyl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5r):



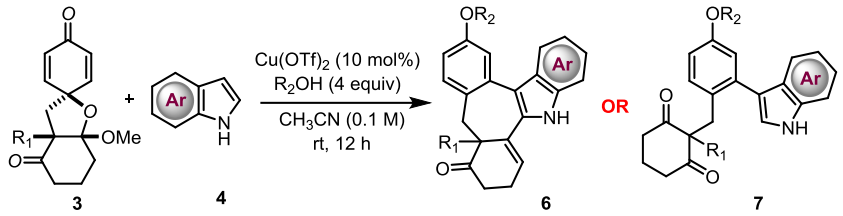
Prepared according to the general procedure as described above in 81% yield (75 mg). It was purified by column chromatography (30% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 198-200°C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (br.s, 1H), 7.94 (d, *J* = 6.2 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 10.2 Hz, 1H), 7.00 (d, *J* = 1.7 Hz, 1H), 6.07 (d, *J* = 10.2 Hz, 1H), 3.52 (dd, *J* = 11.9, 3.0 Hz, 1H), 3.49 – 3.42 (m, 1H), 3.34 (s, 3H), J 2.75 – 2.67 (m, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.23 (t, *J* = 11.2 Hz, 1H), 1.96 (d, *J* = 13.3 Hz, 1H), 1.78 (dd, *J* = 19.0, 10.6 Hz, 1H), 1.73 – 1.58 (m, 3H), 1.46 (t, *J* = 11.2 Hz, 1H), 1.35 – 1.28 (m, 1H), 1.06 (dt, *J* = 8.3, 6.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, CDCl3) δ 218.4, 200.0, 154.5, 141.8, 131.3, 130.2, 128.7, 128.4, 127.7, 125.9, 125.5, 124.1, 123.4, 122.4, 121.9, 120.6, 120.1, 119.8, 115.4, 115.1, 82.2, 63.8, 49.4, 45.4, 42.6, 42.0, 36.4, 35.4, 32.1, 27.0, 26.4; HRMS (ESI) calcd for $C_{34}H_{34}O_4N[M+H]^+$: 520.2482; found: 520.2453.

Table S2: Catalyst screening for Friedel–Crafts alkylation of cyclohexanone-fused cyclohexadienone:



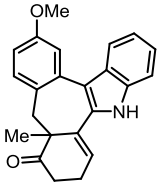
entry	catalyst	*T* °C	**6a** yield [%]^b	**7a** yield [%]^b
1	$Al(OTf)_3$	rt	<10	58
2	$Cu(OTf)_2$	rt	81	<5
3	$Cu(OTf)_2$	80	54	<5
4	$[Cu(CH_3CN)_4]PF_6$	rt	17	22
5	$CuCl_2$	rt	23	39
6	$AlCl_3$	rt	34	42

IIBc. General Procedure for Friedel−Crafts alkylation of cyclohexanone-fused Cyclohexadienone:



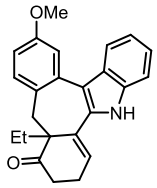
To a stirred solution of cyclohexanone-fused cyclohexadienones **3** (0.2 mmol) and indole **4** (0.24 mmol) in CH_3CN (2 mL, 0.1 M) was added $Cu(OTf)_2$ (7.2 mg, 10 mol%) at room temperature under N_2 atmosphere. The resulting reaction mixture was stirred at same temperature for 12 hours. Then the reaction mixture was diluted with water (10 mL) and extracted with EtOAc (10 mL × 2). The combined organic solvent was washed with brine (10 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude reaction mixture was purified by column chromatography (EtOAc/hexanes) to give the desired product **6** or **7**.

6-Methoxy-9a-methyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6a):



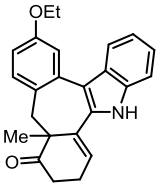
Prepared according to the general procedure as described above in 81% yield (55 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford a brown solid; mp = 137–139°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 6.8 Hz, 1H), 7.38 (s, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.15 (m, 1H), 6.75 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.30 (dd, *J* = 7.3, 2.7 Hz, 1H), 3.86 (s, 3H), 3.05 (q, *J* = 13.9 Hz, 2H), 2.75 (ddt, *J* = 17.6, 14.9, 5.5 Hz, 2H), 2.61 – 2.52 (m, 1H), 2.37 – 2.28 (m, 1H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 158.6, 138.6, 136.3, 135.7, 134.5, 132.4, 128.7, 127.0, 125.6, 123.2, 120.7, 120.3, 113.9, 113.3, 111.1, 111.0, 56.8, 55.5, 38.8, 34.9, 23.1, 22.6; HRMS (ESI) calcd for $C_{23}H_{22}O_2N[M+H]^+$: 344.1645; found: 344.1637.

9a-Ethyl-6-methoxy-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6b):



Prepared according to the general procedure as described above in 64% yield (46 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford a brown solid; mp = 182–184°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 2.7 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.21 – 7.14 (m, 1H), 6.74 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.26 (dd, *J* = 6.9, 2.6 Hz, 1H), 3.86 (s, 3H), 3.03 (s, 2H), 2.79 – 2.69 (m, 1H), 2.64 (ddd, *J* = 17.7, 7.5, 2.2 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.32 (dt, *J* = 17.3, 8.5 Hz, 1H), 1.71 – 1.55 (m, 2H), 0.81 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.1, 158.6, 138.0, 136.3, 136.1, 135.0, 132.4, 128.5, 126.9, 126.5, 123.1, 120.7, 120.2, 113.8, 113.1, 111.0, 111.0, 62.0, 55.5, 36.3, 35.1, 29.7, 23.0, 9.3; IR (neat): υ_{max} 3366, 2937, 2912, 1700, 1504, 1458, 625 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}O_2N[M+H]^+$: 358.1802; found: 358.1798.

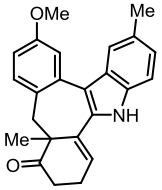
6-Ethoxy-9a-methyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6c):



Prepared according to the general procedure as described above in 75% yield (52 mg). It was purified by column chromatography 40% EtOAc/hexanes; R_f = 0.5) to afford a pale white solid; mp = 170 – 172°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 5.6 Hz, 1H), 7.37 (s, 1H), 7.26 (d, *J* = 4.2 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.74 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.29 (dd, *J* = 7.3, 2.6 Hz, 1H), 4.09 (qd, *J* = 7.0, 1.3 Hz, 2H), 3.04 (q, *J* = 13.9 Hz, 2H), 2.74 (ddt, *J* = 16.5, 13.6, 4.8 Hz, 2H), 2.60 – 2.50 (m, 1H), 2.36 – 2.27 (m, 1H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.2, 158.0, 138.6, 136.3, 135.7, 134.4, 132.4, 128.6, 127.0, 125.5, 123.2,

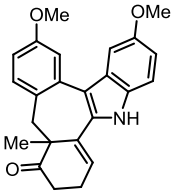
120.7, 120.4, 114.0, 113.8, 111.8, 111.0, 63.6, 56.8, 38.8, 34.9, 23.1, 22.6, 15.1; HRMS (ESI) calcd for $C_{24}H_{24}O_2N[M+H]^+$: 358.1802; found: 358.1796.

6-Methoxy-3,9a-dimethyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6d):



Prepared according to the general procedure as described above in 71% yield (51 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.5) to afford a white solid; mp = 168 – 170°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.76 (s, 1H), 7.38 (d, *J* = 2.6 Hz, 1H), 7.28 (d, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 2.6 Hz, 1H), 7.08 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.75 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.27 (dd, *J* = 7.4, 2.7 Hz, 1H), 3.87 (s, 3H), 3.09 – 2.99 (m, 2H), 2.73 (ddt, *J* = 15.3, 8.0, 4.8 Hz, 2H), 2.55 (ddd, *J* = 19.8, 10.4, 4.4 Hz, 1H), 2.47 (s, 3H), 2.37 – 2.25 (m, 1H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 158.6, 138.6, 135.9, 134.6, 134.6, 132.3, 130.0, 128.8, 127.2, 125.4, 124.7, 119.9, 113.5, 113.4, 110.6, 56.9, 55.5, 38.8, 34.9, 23.2, 22.6, 21.8; HRMS (ESI) calcd for $C_{24}H_{24}O_2N[M+H]^+$: 358.1802; found: 358.1794.

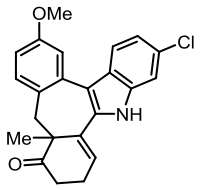
3,6-Dimethoxy-9a-methyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6e):



Prepared according to the general procedure as described above in 77% yield (58 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford a pale brown solid; mp = 147 – 149 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.43 (d, *J* = 2.3 Hz, 1H), 7.36 (d, *J* = 2.7 Hz, 1H), 7.29 (s, 1H), 7.27 (s, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.75 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.27 (dd, *J* = 7.4, 2.6 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.04 (s, 2H), 2.72 (tdd, *J* = 15.5, 8.7, 4.8 Hz, 2H), 2.61 – 2.43 (m, 1H), 2.34 – 2.23 (m, 1H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 158.6, 154.9, 138.5, 135.9, 135.3,

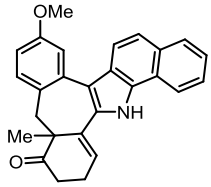
132.4, 131.4, 128.7, 127.3, 125.6, 113.7, 113.3, 112.8, 111.8, 111.0, 102.1, 57.0, 56.1, 55.4, 38.8, 34.9, 29.8, 23.3, 22.6; HRMS (ESI) calcd for $C_{24}H_{24}O_3N[M+H]^+$: 374.1751; found: 374.1749.

2-Chloro-6-methoxy-9a-methyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6f):



Prepared according to the general procedure as described above in 74% yield (56 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.5) to afford a pale brown solid; mp = 166 – 168°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 2.7 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.13 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.76 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.29 (dd, *J* = 7.3, 2.7 Hz, 1H), 3.85 (s, 3H), 3.03 (dd, *J* = 39.4, 13.9 Hz, 2H), 2.74 (ddt, *J* = 15.0, 12.1, 5.4 Hz, 2H), 2.61 – 2.51 (m, 1H), 2.37 – 2.24 (m, 1H), 1.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.6, 158.5, 138.0, 136.8, 135.3, 135.0, 132.4, 128.6, 128.6, 125.9, 125.4, 121.0, 113.4, 113.2, 111.0, 110.9, 56.3, 55.4, 38.6, 34.7, 22.9, 22.6; IR (neat): υ_{max} 3624, 3371, 2914, 1701, 1609, 1461, 1282, 810, 659 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{21}O_2NCl[M+H]^+$: 378.1255; found: 378.1257.

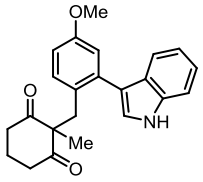
8-Methoxy-11a-methyl-11,13,14,16-tetrahydrobenzo[*g*]dibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-12(11a*H*)-one (6g):



Prepared according to the general procedure as described above in 80% yield (60 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford a brown solid; mp = 153 – 155°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.55 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.42 (d, *J* = 2.7 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 6.78 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.37 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.89 (s, 3H), 3.09 (s, 2H), 2.82 – 2.70 (m, 2H), 2.63 – 2.54 (m, 1H), 2.39 – 2.29 (m, 1H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3, 158.6, 138.4, 135.7, 132.9, 132.5, 131.1, 130.9, 129.0, 128.9, 125.8, 125.2,

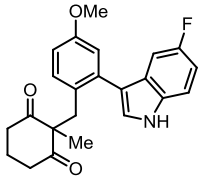
124.5, 122.7, 121.5, 121.5, 119.9, 119.7, 115.6, 113.5, 111.1, 57.0, 55.5, 38.8, 34.9, 23.1, 22.6; IR (neat): υ_{max} 3366, 2929, 1701, 1609, 1501, 1283, 811, 758, 625 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{24}O_2N[M+H]^+$: 394.1802; found: 394.1792.

2-(2-(1*H*-Indol-3-yl)-4-methoxybenzyl)-2-methylcyclohexane-1,3-dione (7a):



Prepared according to the general procedure as described above in 80 % yield (58 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.5) to afford a pale brown solid; mp = 182–184°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.16 – 7.12 (m, 2H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 2.8 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.8 Hz, 1H), 3.79 (s, 3H), 3.21 (s, 2H), 2.23 (dt, *J* = 10.8, 5.7 Hz, 2H), 2.08 (ddd, *J* = 14.9, 10.3, 5.1 Hz, 2H), 1.59 – 1.54 (m, 1H), 1.48 (ddd, *J* = 13.9, 10.5, 5.5 Hz, 1H), 1.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 158.6, 136.4, 135.8, 132.3, 127.1, 126.8, 123.7, 122.6, 120.4, 119.7, 117.2, 116.9, 112.8, 111.5, 66.5, 55.4, 40.8, 38.3, 18.1, 17.5; HRMS (ESI) calcd for $C_{23}H_{24}O_3N[M+H]^+$: 362.1751; found: 362.1742.

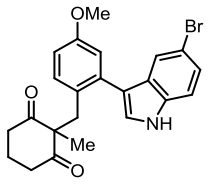
2-(2-(5-fluoro-1*H*-indol-3-yl)-4-methoxybenzyl)-2-methylcyclohexane-1,3-dione (7h):



Prepared according to the general procedure as described above in 74% yield (56 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.5) to afford a pale brown solid; mp = 148–150°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.32 (dd, *J* = 8.8, 4.3 Hz, 1H), 7.17 (d, *J* = 2.3 Hz, 1H), 7.09 – 7.06 (m, 1H), 7.04 (dd, *J* = 9.6, 2.2 Hz, 1H), 6.98 (td, *J* = 8.9, 2.3 Hz, 1H), 6.86 – 6.79 (m, 2H), 3.79 (s, 3H), 3.19 (s, 2H), 2.29 (dt, *J* = 16.0, 5.4 Hz, 2H), 2.15 (ddd, *J* = 16.1, 10.4, 5.8 Hz, 2H), 1.67 – 1.60 (m, 1H), 1.58 – 1.51 (m, 1H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.6, 158.6, 158.4 (d, J_{CF} = 235.4 Hz), 136.0, 132.3, 127.5 (d, J_{CF} = 9.9 Hz), 126.8, 125.5, 117.2 (d, J_{CF} = 4.0 Hz), 116.9, 112.9, 112.3 (d, J_{CF} = 9.5 Hz), 111.2, 110.9, 104.4 (d, J_{CF} = 23.7 Hz), 66.4, 55.4, 40.7, 38.4, 18.4, 17.4; ^{19}F NMR (377

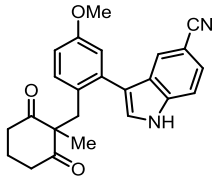
MHz, $CDCl_3$) δ -123.5; IR (neat): υ_{max} 3372, 2928, 1690, 1487, 1459, 1285, 761 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{26}O_3N_2F[M+NH_4]^+$: 397.1922; found: 397.1915.

2-(2-(5-Bromo-1*H*-indol-3-yl)-4-methoxybenzyl)-2-methylcyclohexane-1,3-dione (7i):



Prepared according to the general procedure as described above in 76% yield (67 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 196-198°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.51 (d, *J* = 1.4 Hz, 1H), 7.31 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.9 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 3.79 (s, 3H), 3.17 (s, 2H), 2.31 (dt, *J* = 16.0, 5.6 Hz, 2H), 2.18 (ddd, *J* = 16.1, 10.4, 5.7 Hz, 2H), 1.70 – 1.65 (m, 1H), 1.60 – 1.50 (m, 1H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.6, 158.6, 135.6, 134.4, 132.2, 128.9, 126.9, 125.5, 124.8, 122.1, 117.0, 116.7, 113.7, 113.0, 66.4, 55.4, 40.6, 38.5, 18.5, 17.4; HRMS (ESI) calcd for $C_{23}H_{23}O_3NBr[M+H]^+$: 440.0856; found: 440.0841.

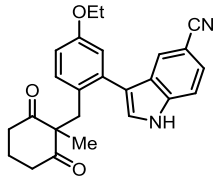
3-(5-Methoxy-2-((1-methyl-2,6-dioxocyclohexyl)methyl)phenyl)-1*H*-indole-5-carbonitrile (7j):



Prepared according to the general procedure as described above in 64% yield (49 mg). It was purified by chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford a white solid; mp = 168-170–172°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.76 (s, 1H), 7.47 (s, 2H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 3.16 (s, 2H), 2.36 (dt, *J* = 16.0, 5.6 Hz, 2H), 2.22 (ddd, *J* = 15.9, 9.8, 5.8 Hz, 2H), 1.73 – 1.66 (m, 1H), 1.64 – 1.56 (m, 1H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 158.7, 137.5, 134.9, 132.1, 127.3, 127.1, 125.6, 125.5, 125.3, 120.7, 117.8, 117.2, 113.3, 112.5, 103.6, 66.1, 55.4, 40.3, 38.7, 19.4, 17.3; IR (neat): υ_{max} 2935, 2222, 1692,

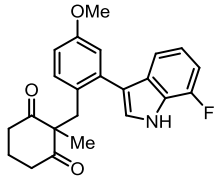
1611, 1468, 1288, 814, 656, 626 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}O_3N_3[M+NH_4]^+$: 404.1969; found: 404.1957.

3-(5-Ethoxy-2-((1-methyl-2,6-dioxocyclohexyl)methyl)phenyl)-1*H*-indole-5-carbonitrile (7k):



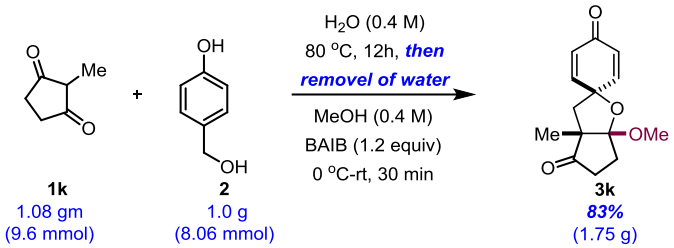
Prepared according to the general procedure as described above in 83% yield (66 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford a white solid; mp = 170–172°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.76 (s, 1H), 7.47 (s, 2H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.83 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.80 (d, *J* = 2.7 Hz, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 3.16 (s, 2H), 2.35 (ddd, *J* = 16.2, 6.1, 5.2 Hz, 2H), 2.21 (ddd, *J* = 16.0, 10.0, 5.7 Hz, 2H), 1.71 – 1.66 (m, 1H), 1.60 (ddd, *J* = 14.1, 9.9, 5.0 Hz, 1H), 1.41 (t, *J* = 7.0 Hz, 3H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, $CDOD_3$); δ 211.0, 158.0, 137.6, 135.1, 132.1, 127.0, 126.6, 126.0, 125.1, 124.9, 120.8, 117.6, 117.1, 113.5, 112.6, 102.7, 66.2, 63.6, 40.5, 38.5, 18.7, 17.2, 14.8; HRMS (ESI) calcd for $C_{25}H_{28}O_3N_3[M+NH_4]^+$: 418.2125; found: 418.2111.

2-(2-(7-Fluoro-1*H*-indol-3-yl)-4-methoxybenzyl)-2-methylcyclohexane-1,3-dione (7l):



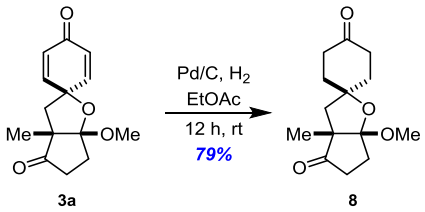
Prepared according to the general procedure as described above in 62% yield (48 mg). It was purified by column chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford a brown solid; mp = 119–121°C; H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.20 – 7.13 (m, 2H), 7.08 (d, *J* = 9.1 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.95 (dd, *J* = 11.0, 7.8 Hz, 1H), 6.84 (s, 1H), 6.82 (d, *J* = 2.7 Hz, 1H), 3.79 (s, 3H), 3.18 (s, 2H), 2.28 (dt, *J* = 16.0, 5.5 Hz, 2H), 2.13 (ddd, *J* = 16.0, 10.2, 5.8 Hz, 2H), 1.64 (dt, *J* = 11.9, 6.1 Hz, 1H), 1.58 – 1.47 (m, 1H), 1.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 158.6, 149.7 (d, J_{CF} = 244.2 Hz), 135.8, 132.3, 130.8 (d, J_{CF} = 4.9 Hz), 126.9, 124.3, 124.2, 120.7 (d, J_{CF} = 6.1 Hz), 118.0, 117.0, 115.5 (d, J_{CF} = 3.4 Hz), 113.0, 107.4 (d, J_{CF} = 16.1 Hz), 66.4, 55.4, 40.5, 38.4, 18.5, 17.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -135.0; IR (neat): υ_{max} 3369, 2935, 1691, 1578, 1237, 1035, 785, 631 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}O_3NF[M+H]^+$: 380.1656; found: 380.1646.

IIBd. Gram-scale synthesis and hydrogenation of 3k:



To a solution of 2-methyl 1,3-cyclopentadione **1k** (1.08 gm, 9.6 mmol) in water (24 mL, 0.4 M) was added *p*-hydroxybenzyl alcohol (1.0 g, 8.06 mmol), and the solution was stirred at 80 °C for 12 h. Then, water was removed from reaction mixture via crystallization at 0 °C followed by filtration. The cure reaction mixture was dissolved in MeOH (24 mL, 0.4 M)) and then added $PhI(OAc)_2$ (3.06 g, 9.6 mmol) in several portions at 0 °C. The resulting reaction mixture was stirred at same temperature for 30 minutes and then alcohol was evaporated in vacuum. The resulting mixture was diluted with water (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic solvent was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography (30% EtOAc in hexanes) to give the desired product **3k** as a white solid in 83% yield (1.75 mg).

6a'-methoxy-3a'-methyltetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-4,4'(3'*H*)-dione (8):



A round bottom flask charged with spiro-tetrahydrofuran **3a** (100 mg, 0.4 mmol, 1 equiv) in EtOAc (2 mL) under inert atmosphere was added 10% Pd-C catalyst (10 mg). The reaction mixture was stirred at room temperature under hydrogen atmosphere for 12 h until consumption of starting material **3a** monitored by thin layer chromatography (TLC). The reaction mixture was filtered through pad of celite, concentrated on reduced pressure, and the residue was directly subjected to flash column chromatography on silica gel (30% EtOAc/hexanes; R_f = 0.5) to afford the desired product **8** with 79% yield (78 mg) as a white solid; mp = 150–151°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 3H), 2.71 – 2.56 (m, 2H), 2.56 – 2.47 (m, 2H), 2.47 – 2.41 (m, 1H), 2.38 (d, *J* = 12.7 Hz, 1H), 2.31 (dtd, *J* = 14.6, 4.9, 2.0 Hz, 1H), 2.21 (dtd, *J* = 14.7, 4.9, 2.0 Hz, 1H), 2.12 (dddd, *J* = 13.5, 6.1, 4.8, 2.8 Hz, 1H), 1.97 – 1.84 (m, 2H), 1.88 (d, *J* = 12.8 Hz, 1H), 1.81 – 1.66 (m, 2H), 1.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220., 211.1, 114.4,

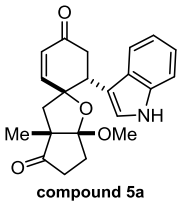
81.3, 59.9, 49.6, 45.7, 39.0, 38.6, 37.9, 35.8, 26.6, 16.2; HRMS (ESI) calcd for $C_{14}H_{21}O_4$ $[M+H]^+$: 253.1434; found: 253.1438.

III. References

1. Ramachary, D. B.; Kishor, M. *Org. Biomol. Chem*., 2008, **6**, 4176.
2. Cini, E.; Petricci, E.; Truglio, G. I.; Vecchio, M.; Taddei, M.; *RSC Adv.* **2016**, 6, 31386.
3. Wu, Y.; Arenas, I.; Broomfield, L. M.; Martin, E.; Shafir, A. *Chem. Eur. J.* **2015**, *21*, 18779.
4. Ramachary, D. B.; Kishor, M. *J. Org. Chem.* **2007**, *72*, 5056.
5. Guyon, C.; Duclos, M.-C.; Sutter, M.; Métay, E.; Lemaire, M. *Org. Biomol. Chem.* **2015**, *13*, 7067.
6. Poss, A. J.; Belter, R. K. *J. Org. Chem.* **1988**, *53*, 891−893.

IV. X-Ray crystallographic data

IVa. X-ray crystallographic data for compound 5a:



compound 5a

The purified compound **5a** was dissolved in a mixed solvent of dichloromethane/*n*-hexane (1:3), and placed in a dark cabinet for slowly evaporation. Colorless crystals were collected after few days for X-ray analysis.

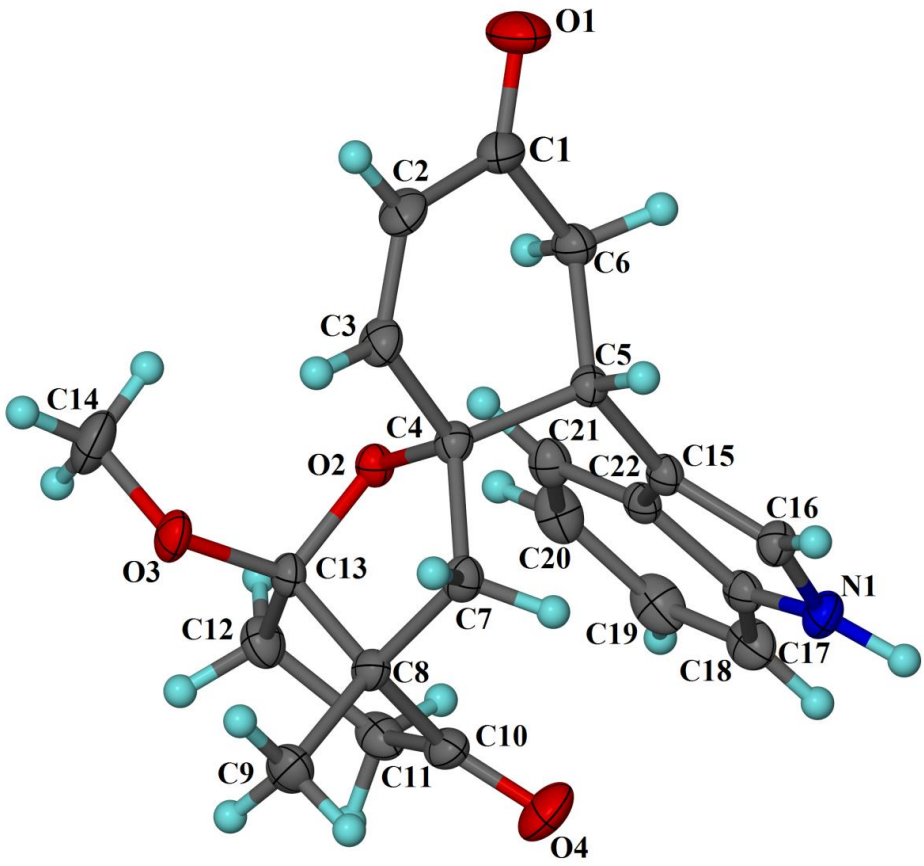
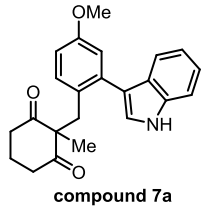


Figure caption: ORTEP diagram of compound **5a** (KA874) compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius.

IVa. X-ray crystallographic data for compound 7a:



compound 7a

The purified compound **7a** was dissolved in a mixed solvent of dichloromethane/*n*-hexane (1:3), and placed in a dark cabinet for slowly evaporation. Colorless crystals were collected after few days for X-ray analysis.

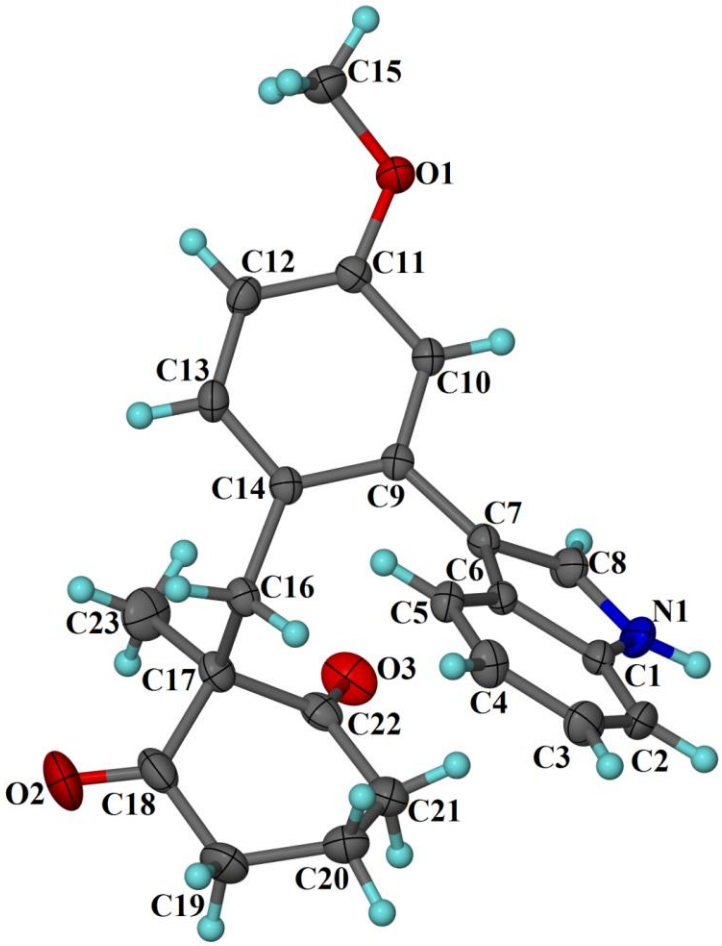


Figure caption: ORTEP diagram of compound **7a** (KA881) compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for compound 5a (KA874): $C_{22}H_{23}N_1O_4$, M = 365.41, Triclinic, space group *P-1* (No.2), a = 7.543(5)Å, b = 7.946(6)Å, c = 16.011(11)Å, α = 94.693(17)°, β = 95.845(13)°, γ = 97.337(14)°, V = 942.5(11)Å^3, Z = 2, D_c = 1.288 g/cm^3, F_{000} = 388, Bruker D8 QUEST PHOTON-100, Mo-Kα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 55º, μ= 0.088 mm^{-1}, 20438 reflections collected, 4328 unique (R_{int} = 0.0523), 250 parameters, *R1* = 0.0502, *wR2* =0.1284, *R* indices based on 3345 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.039, largest difference hole and peak = -0.260 and 0.215 e.Å^{-3}. **CCDC deposition number 2047769** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

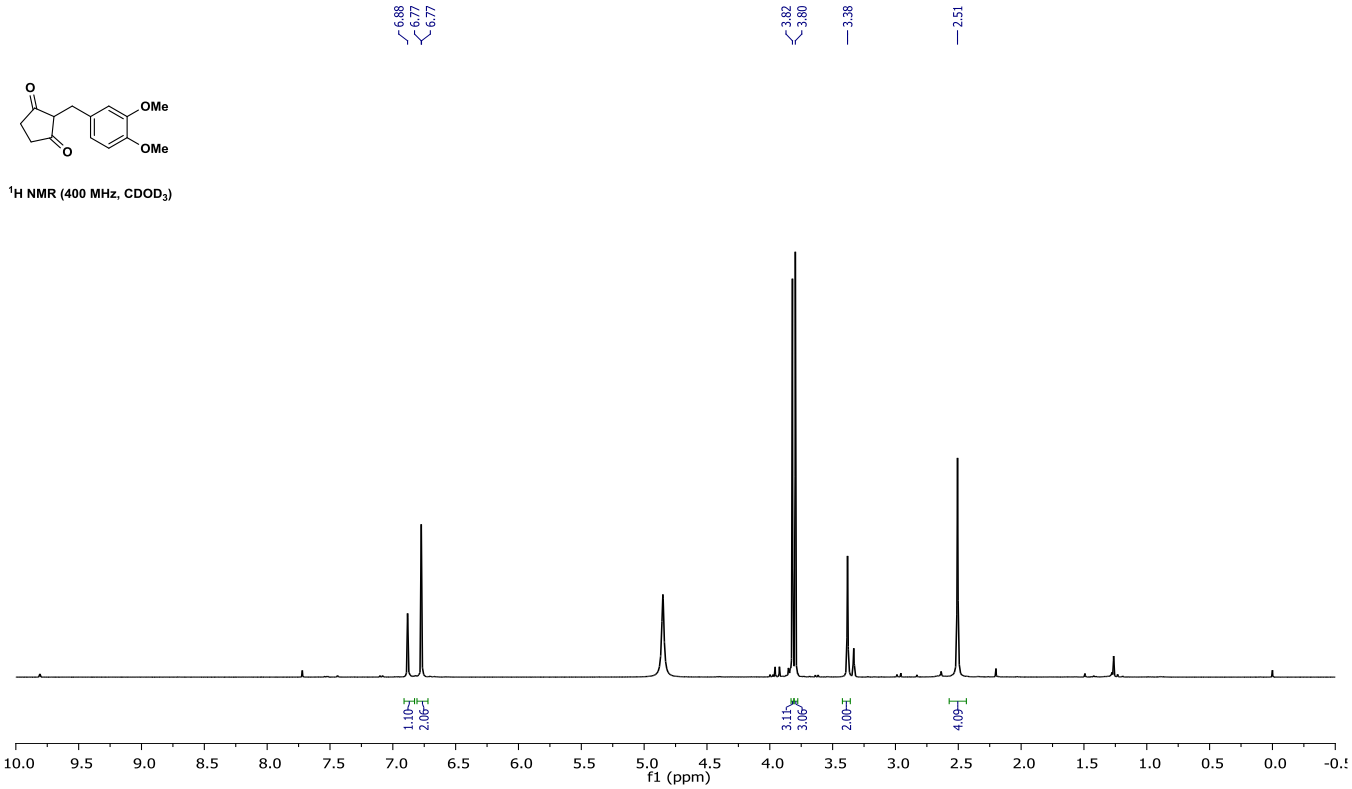
Crystal data for compound 7a (KA881): $C_{23}H_{23}N_1O_3$, M = 361.42, Monoclinic, space group $P2_1/c$ (No.14), a = 12.789(3)Å, b = 10.573(2)Å, c = 13.888(3)Å, α = 90°, β = 101.041(6)°, γ = 90°, V = 1843.2(7)Å^3, Z = 4, D_c = 1.302 g/cm^3, F_{000} = 768, Bruker D8 QUEST PHOTON-100, Mo-Kα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 55º, μ= 0.086 mm^{-1}, 20159 reflections collected, 4217 unique (R_{int} = 0.0268), 270 parameters, *R1* = 0.0463, *wR2* =0.1193, *R* indices based on 3398 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.029, largest difference hole and peak = -0.192 and 0.245 e.Å^{-3}. **CCDC deposition number 2047768** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Data collection and Structure solution details: Single crystal X-ray data were collected at room temperature on a Bruker D8 QUEST equipped with a four-circle kappa diffractometer and Photon 100 detector. An Iμs microfocus Mo source (λ=0.71073Å) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omega scans were used to collect the necessary data. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.[2-3] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with U_{iso}(H) = 1.2U_{eq} (C) or 1.5U_{eq} for methyl atoms. The N bound H atoms were located in the difference Fourier map and the positional parameters of H atoms were refined. Cyclohexane dione ring carbon atoms in KA881 crystal are disordered over two sites. The site occupancy factor for major component of the disordered atoms (C19/C20/C21) is 0.641(11) and the minor component of the disordered atoms (C19D/C20D/C21D) is 0.359(11). **CCDC** deposition numbers 2047768-2047769 contain the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

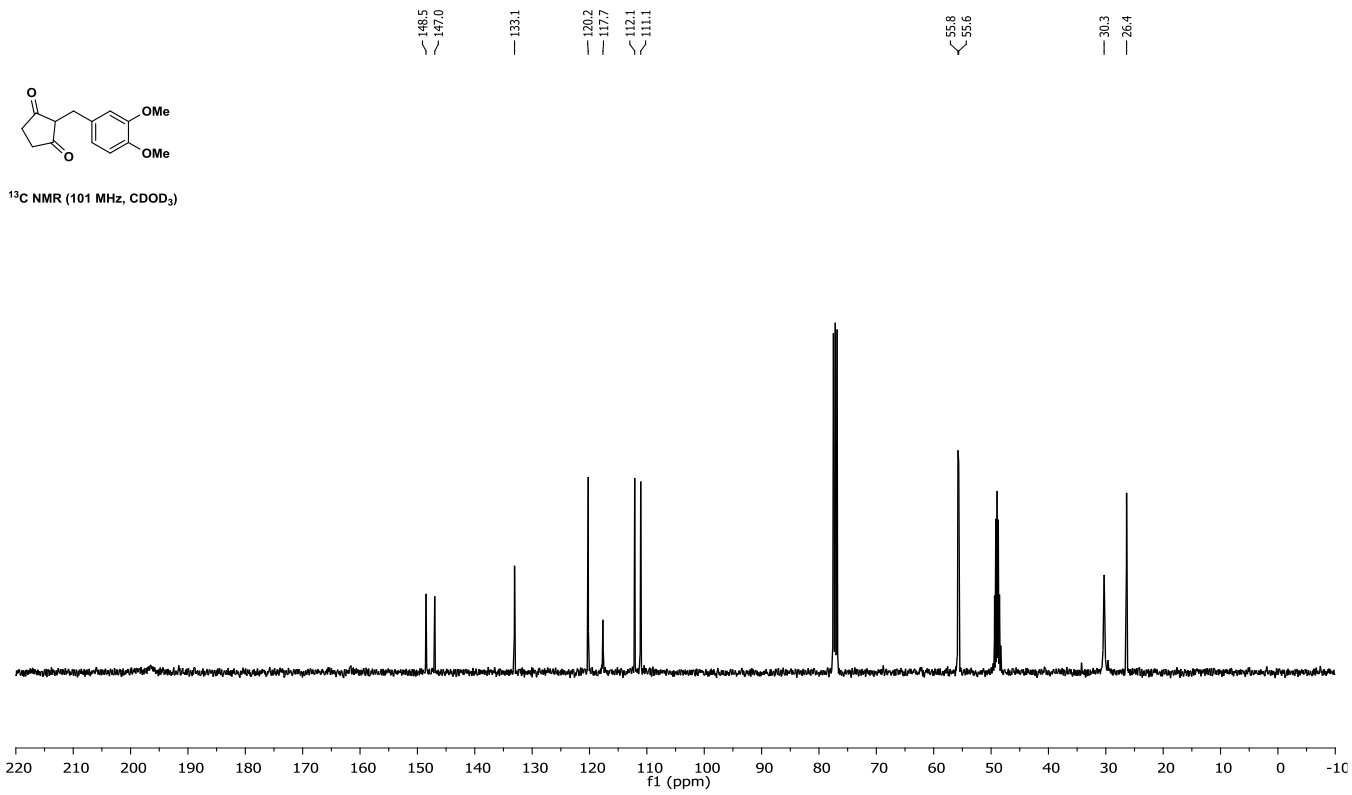
1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL Version 2014/7, http://shelx.uni-ac.gwdg.de/SHELX/index.php
3. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.
4. A. L. Spek, Acta Cryst. 2009, D65, 148-155.

V. ^{1}H & ^{13}C NMR Spectra:

2-(3,4-dimethoxybenzyl)cyclopentane-1,3-dione (1-S_5):

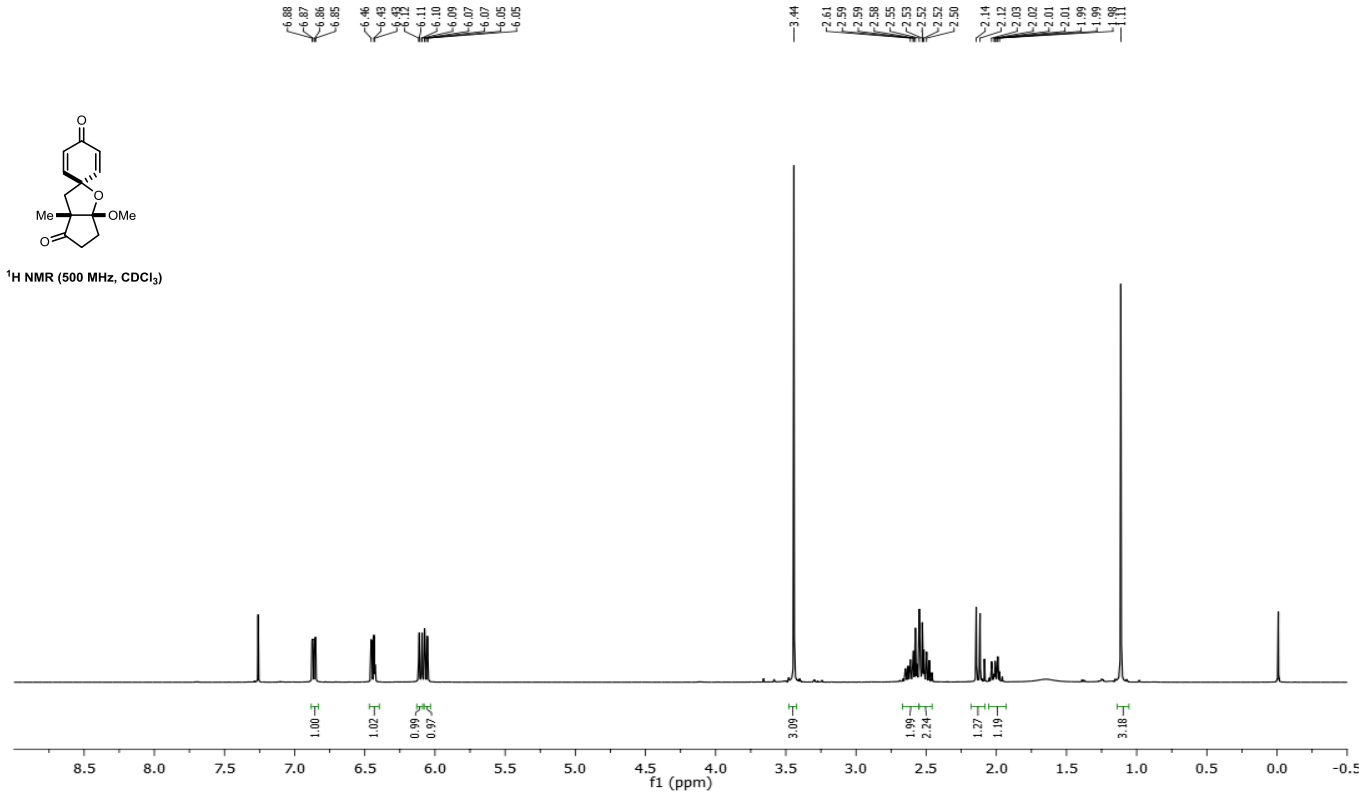


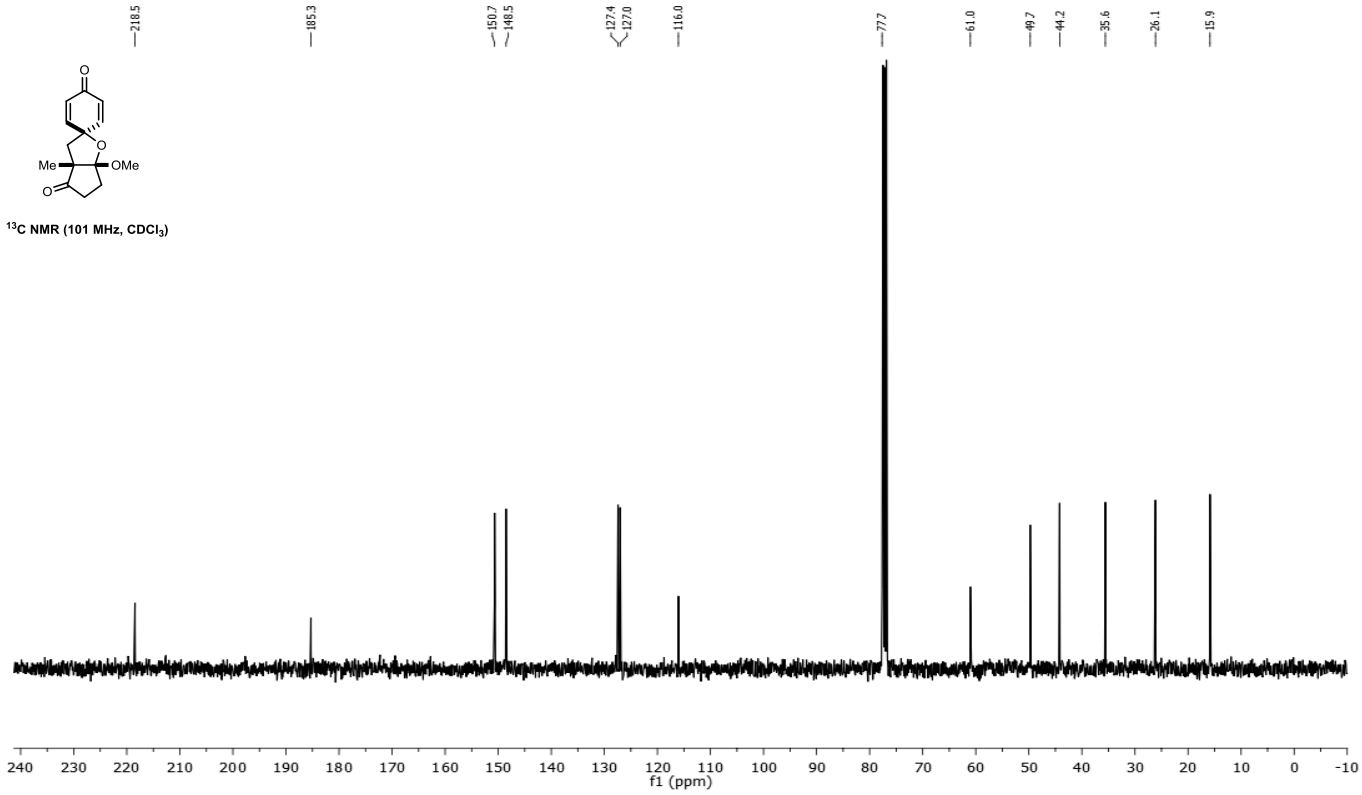
^{1}H NMR (400 MHz, $CDOD_3$)



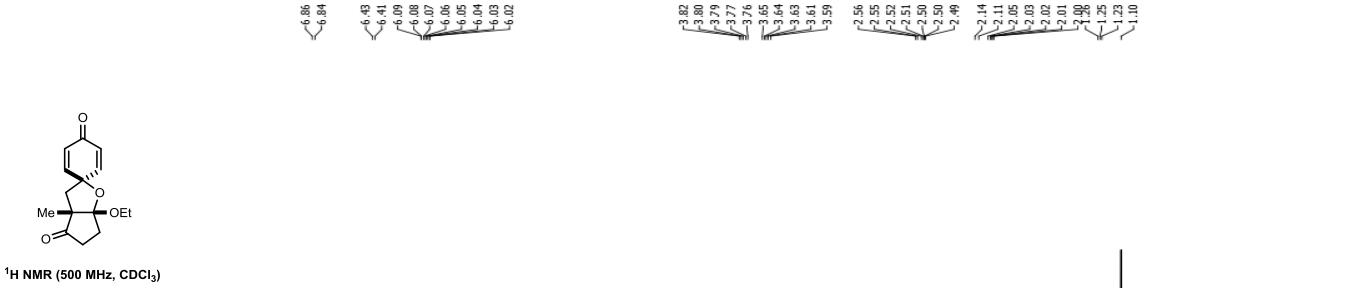
^{13}C NMR (101 MHz, $CDOD_3$)

6a'-Methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3a):

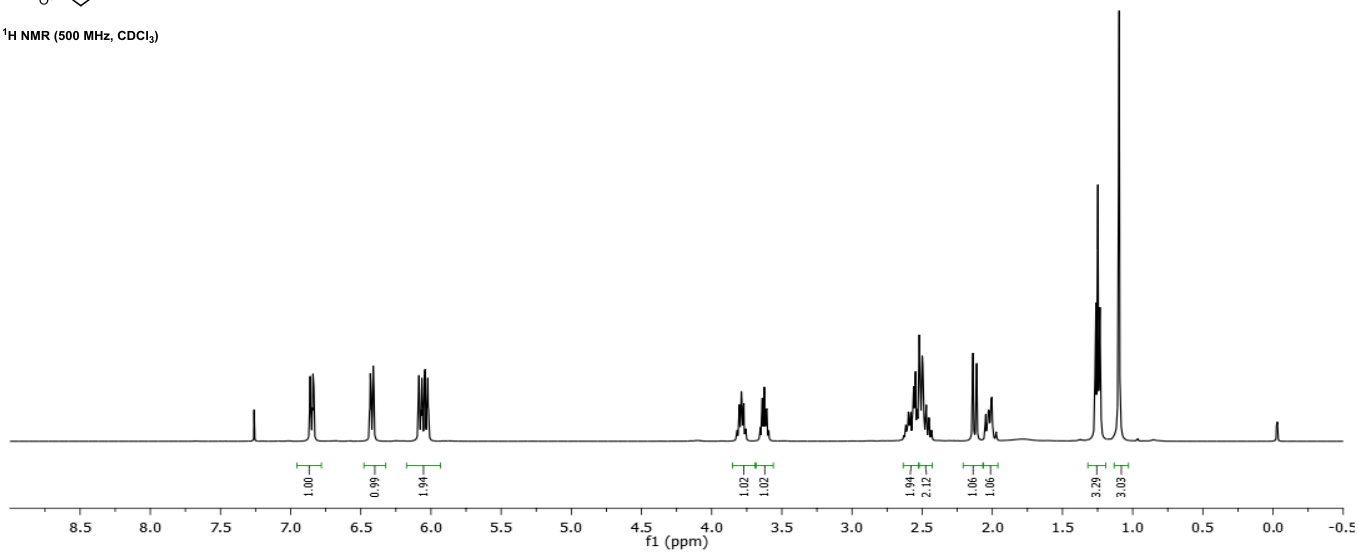


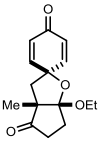


3- 6a'-Ethoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3b):

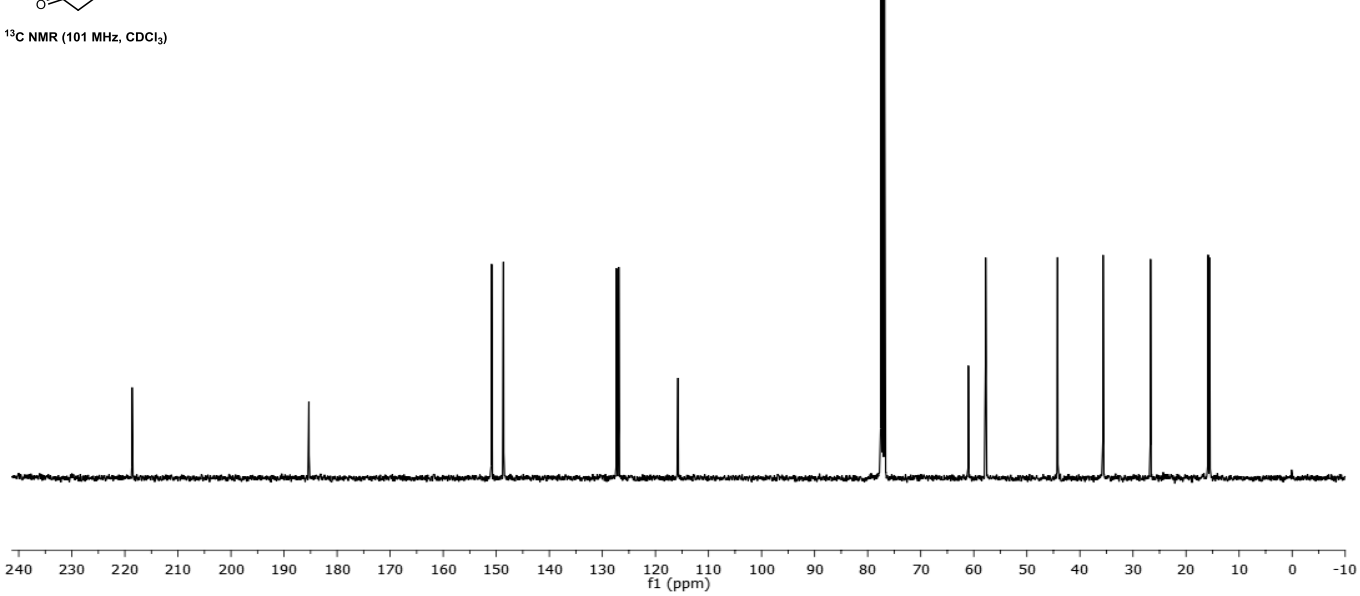


^{1}H NMR (500 MHz, $CDCl_3$)

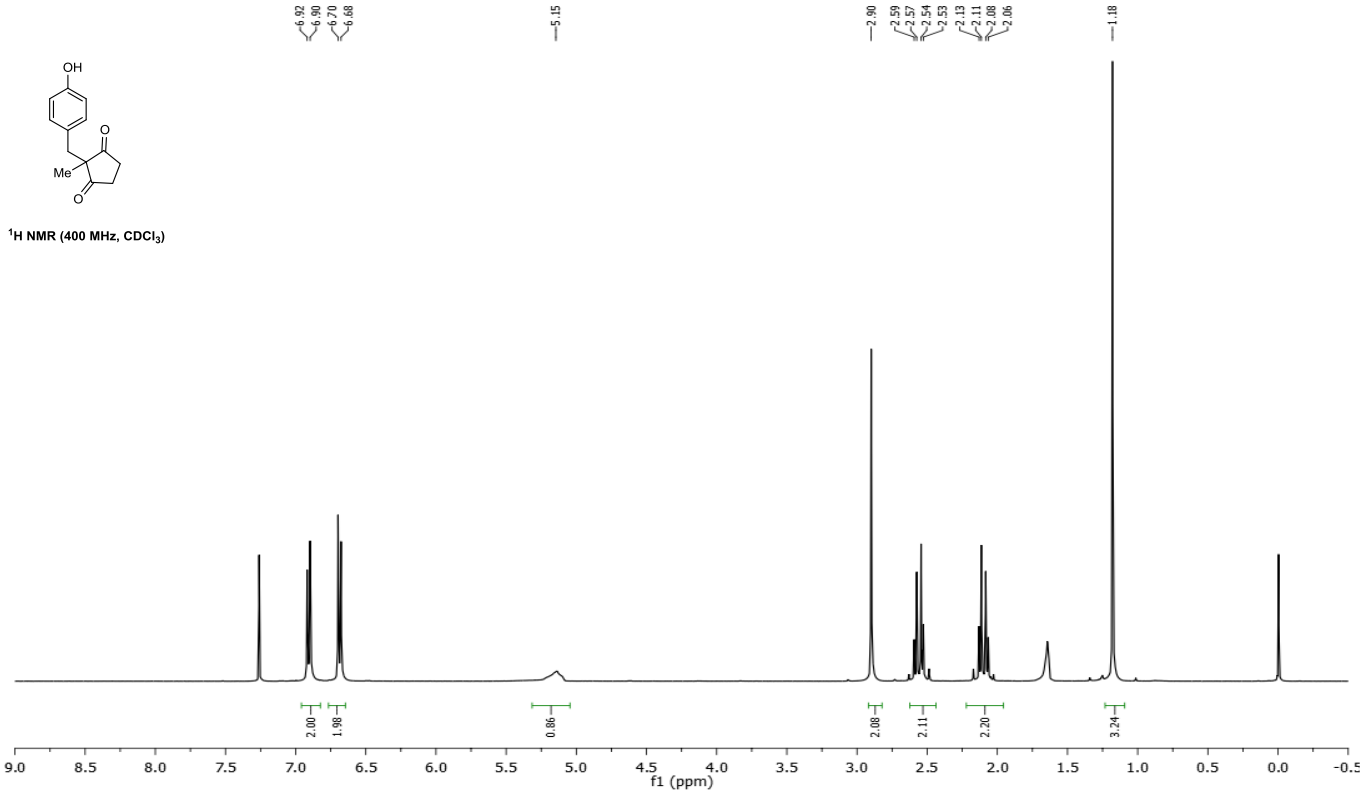




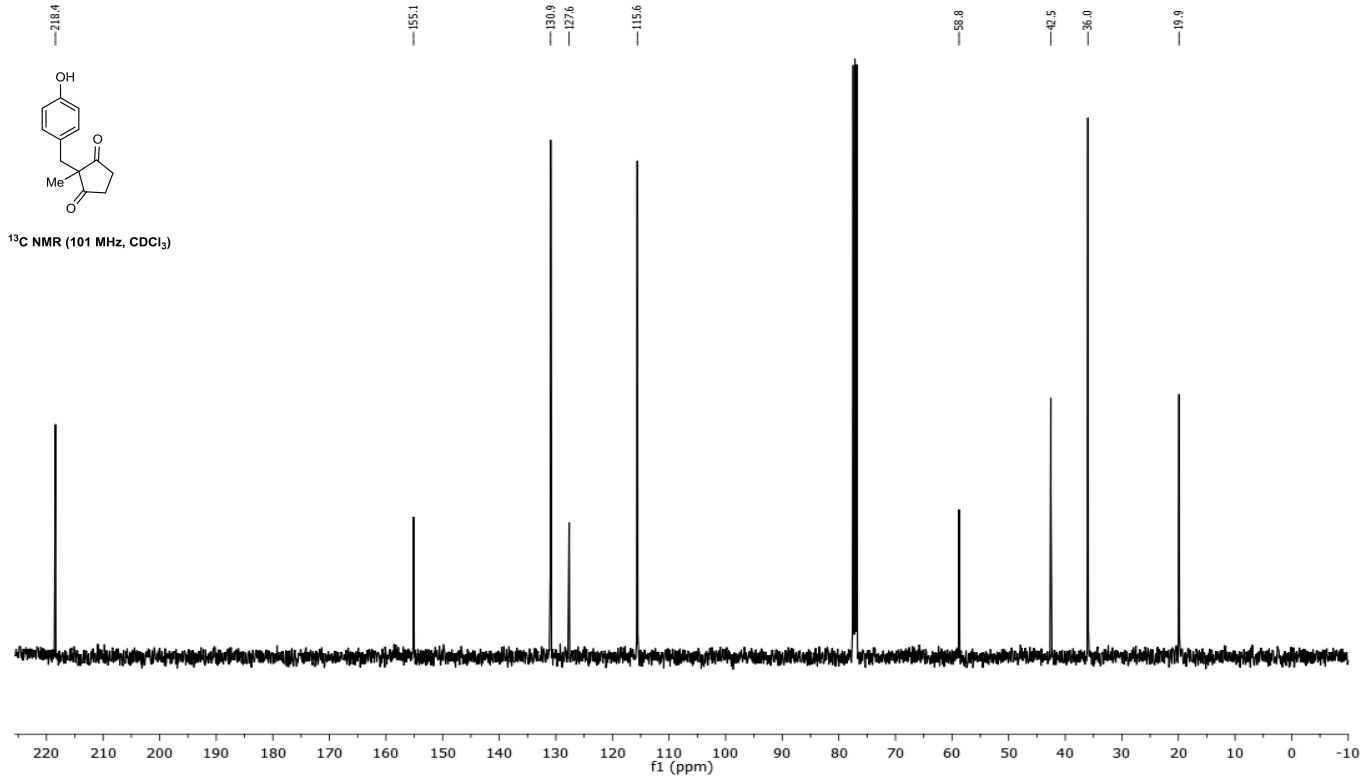
^{13}C NMR (101 MHz, $CDCl_3$)



2-(4-Hydroxybenzyl)-2-methylcyclopentane-1,3-dione (S1-A):

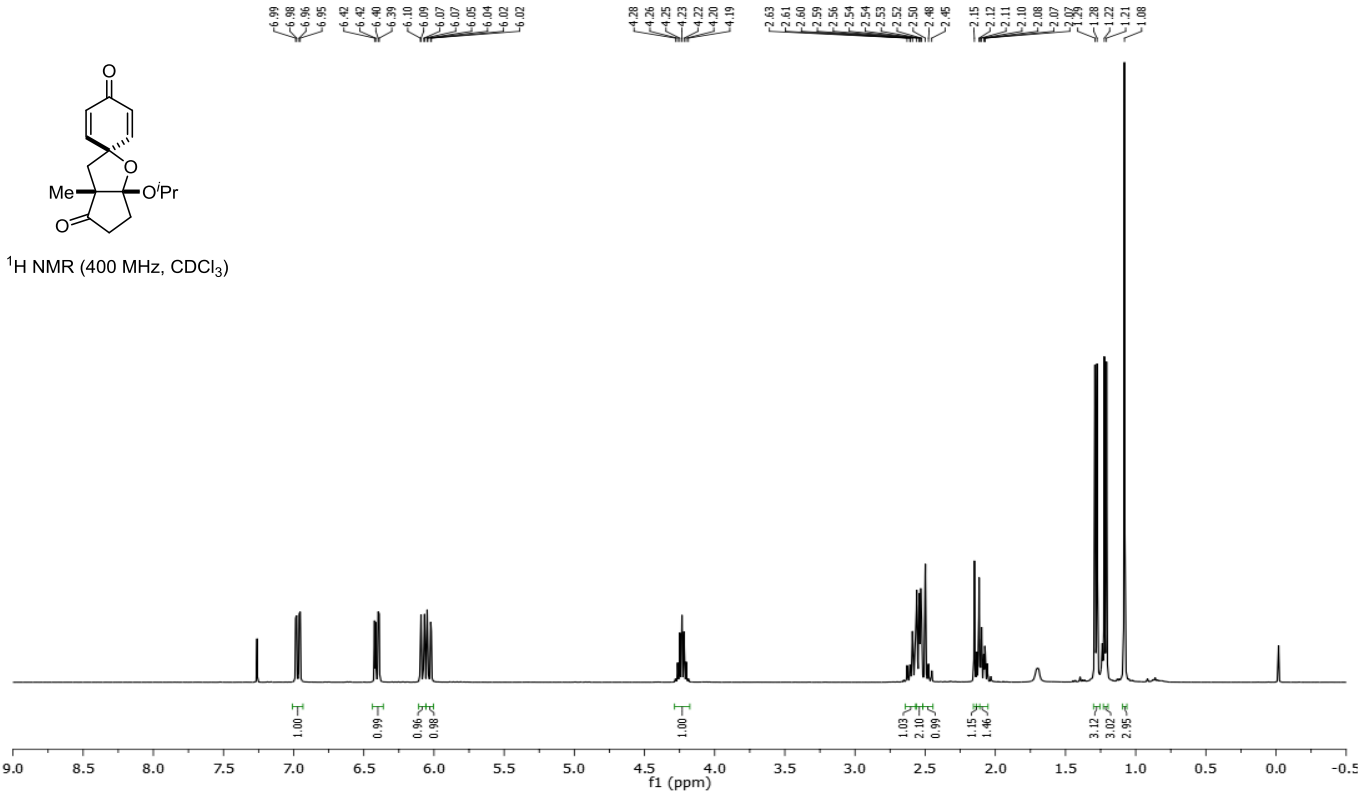


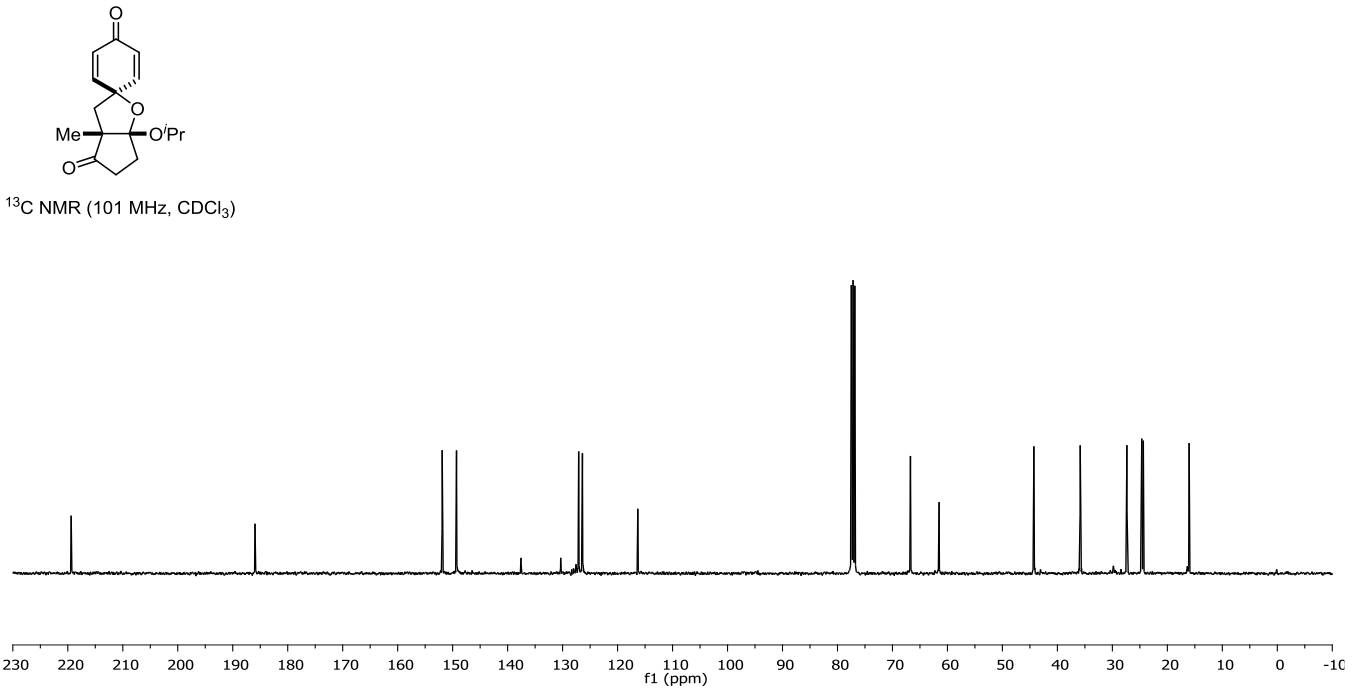
^{1}H NMR (400 MHz, $CDCl_3$)



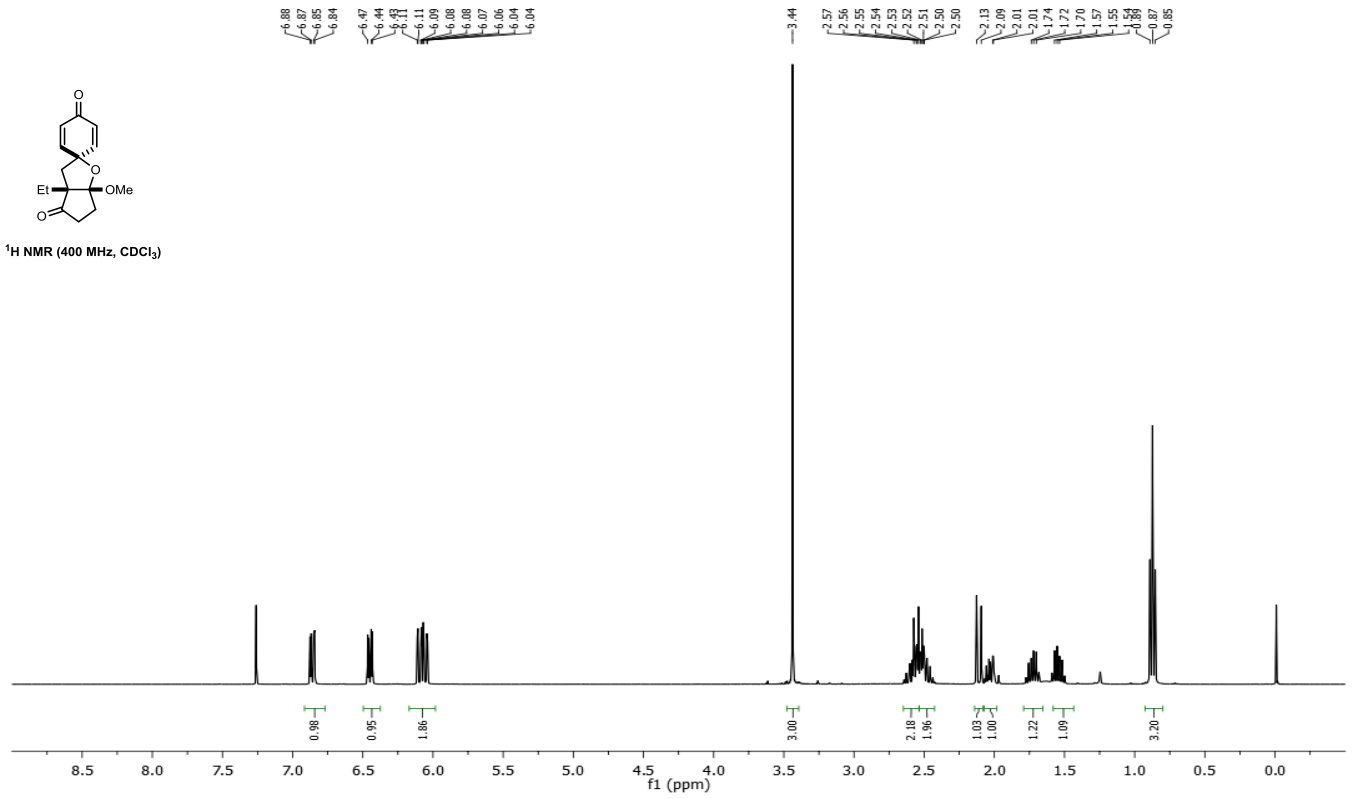
^{13}C NMR (101 MHz, $CDCl_3$)

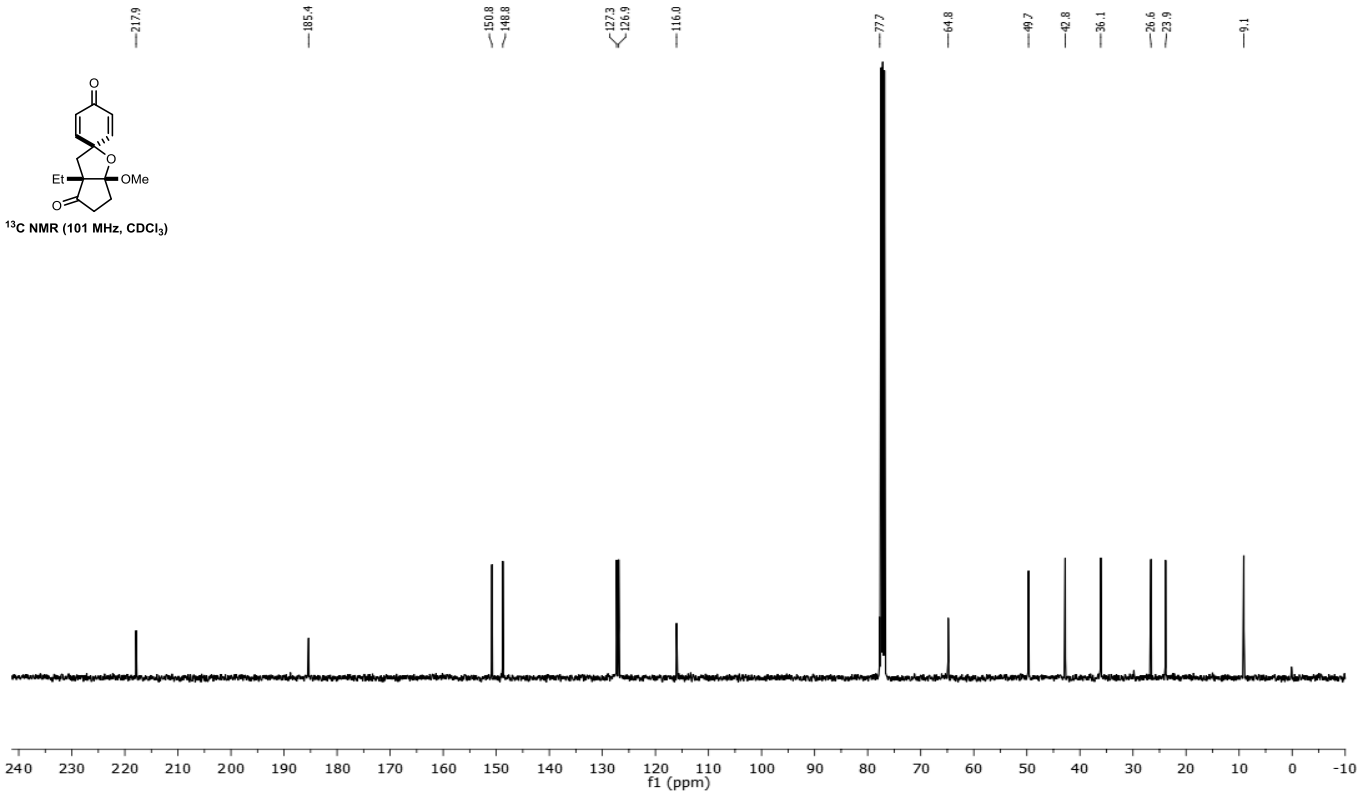
6a'-isopropoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3c):



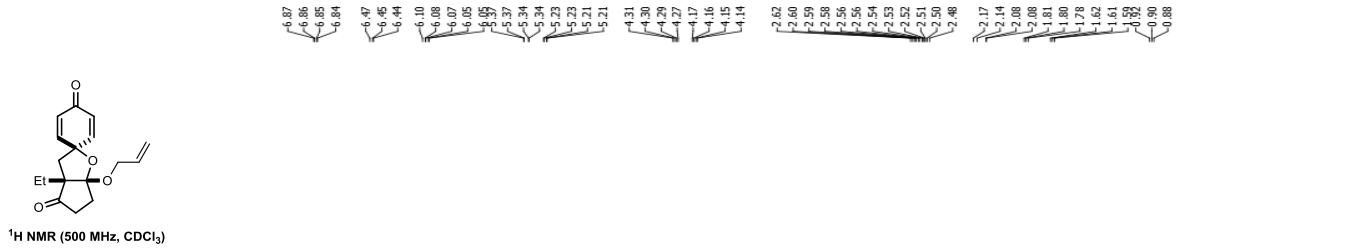


3a'-Ethyl-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3d):

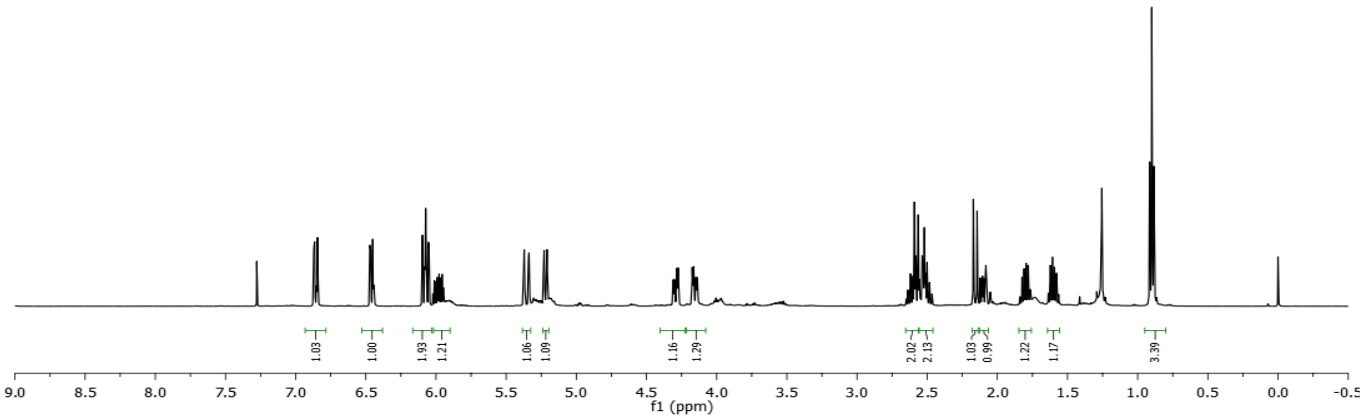


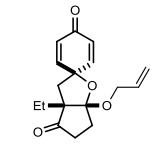


6a'-(Allyloxy)-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3e):

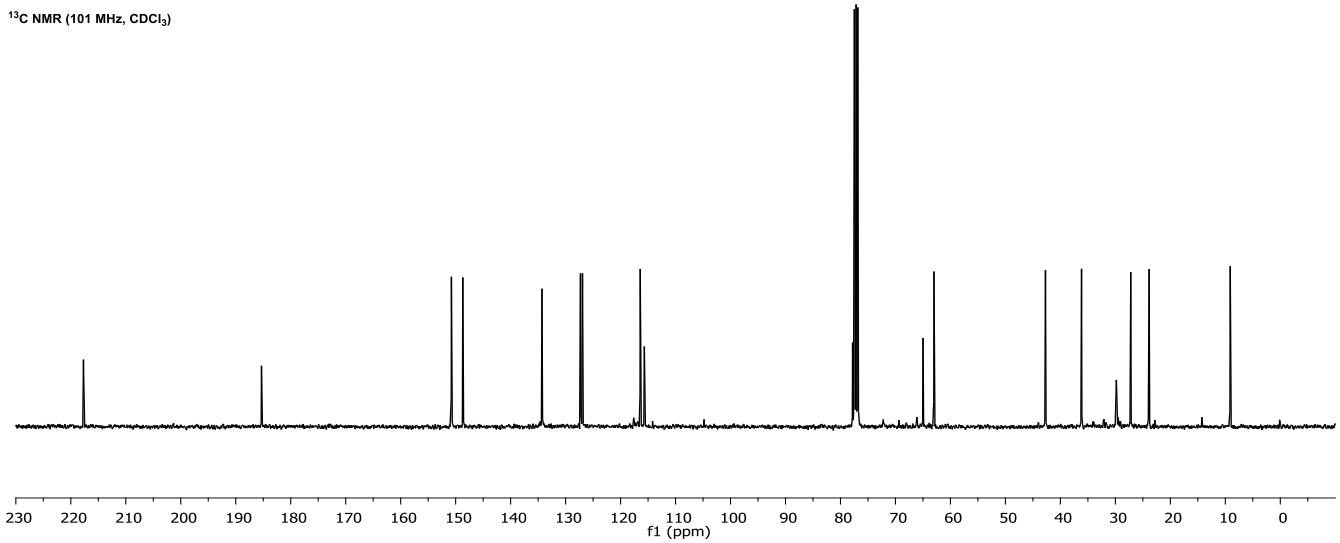


^{1}H NMR (500 MHz, $CDCl_3$)

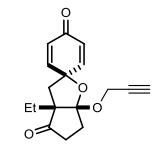




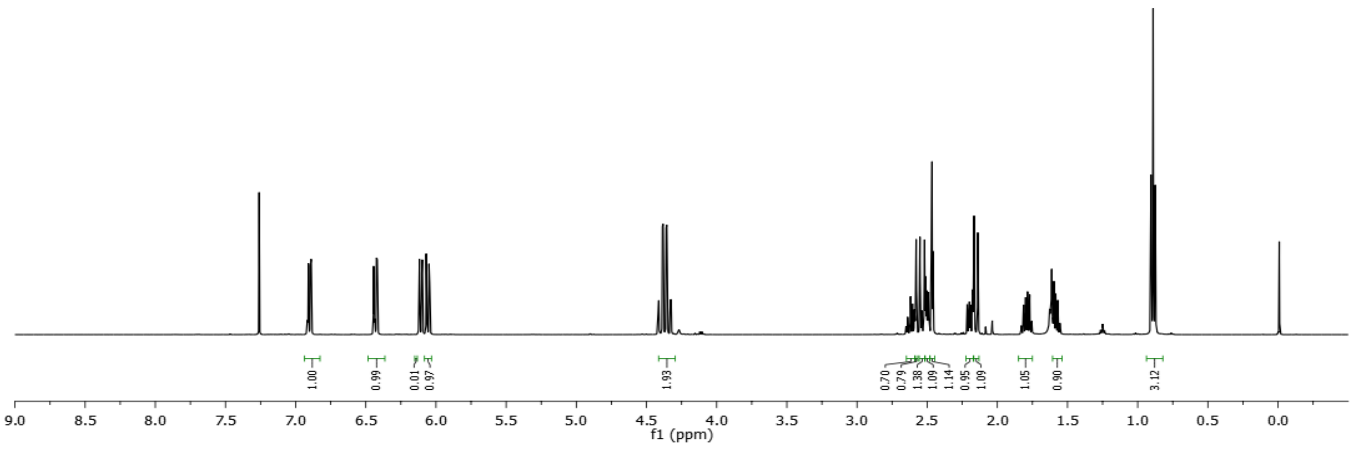
^{13}C NMR (101 MHz, $CDCl_3$)

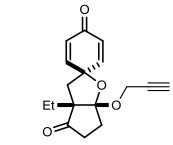


3a'-Ethyl-6a'-(prop-2-yn-1-yloxy)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3f):



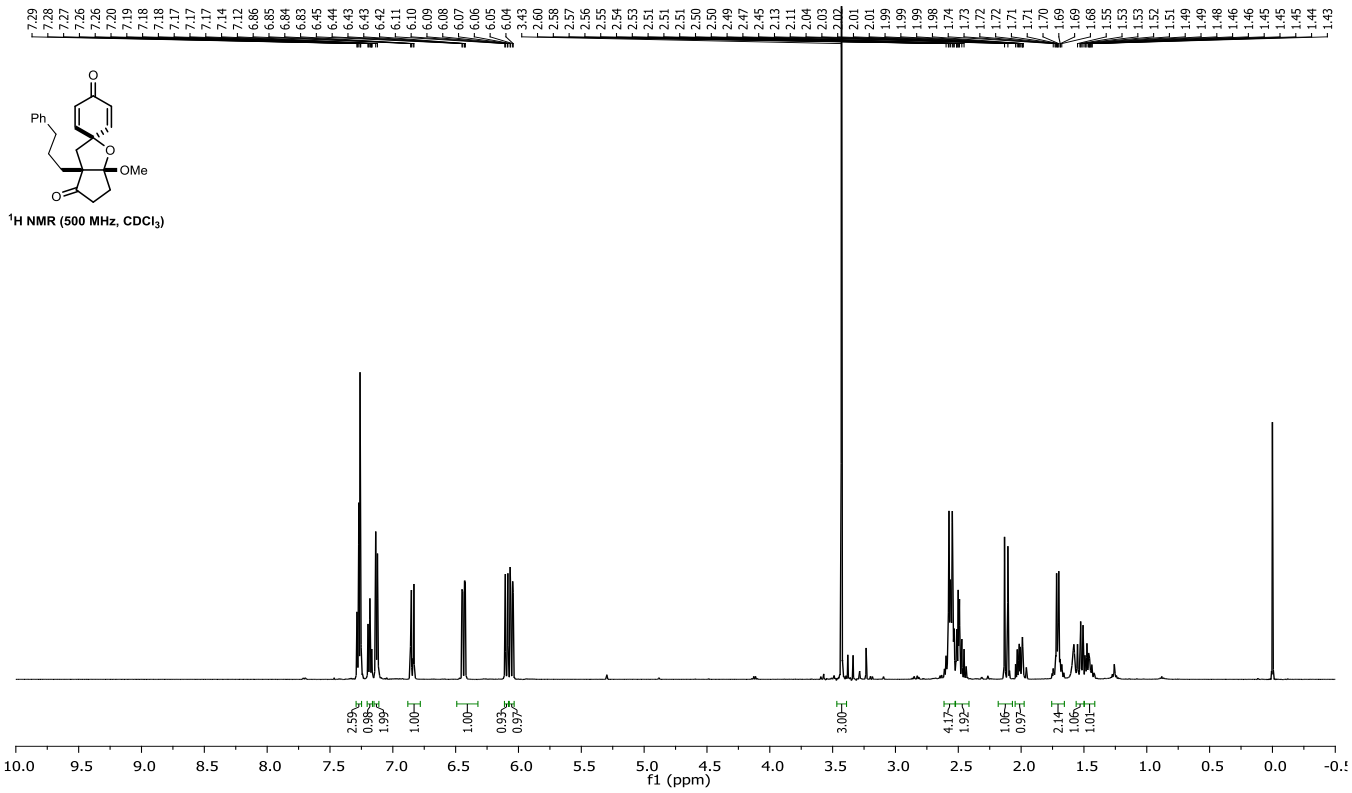
^{1}H NMR (500 MHz, $CDCl_3$)

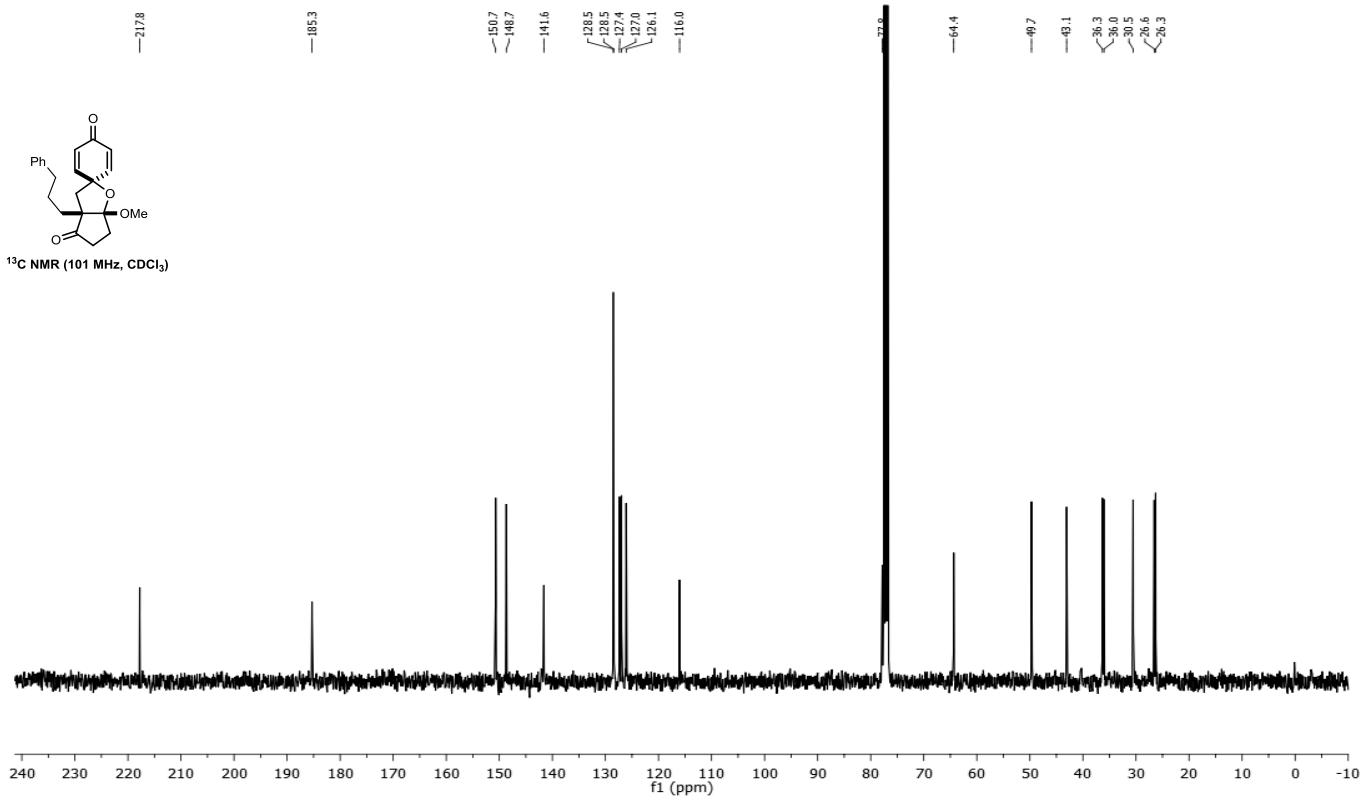




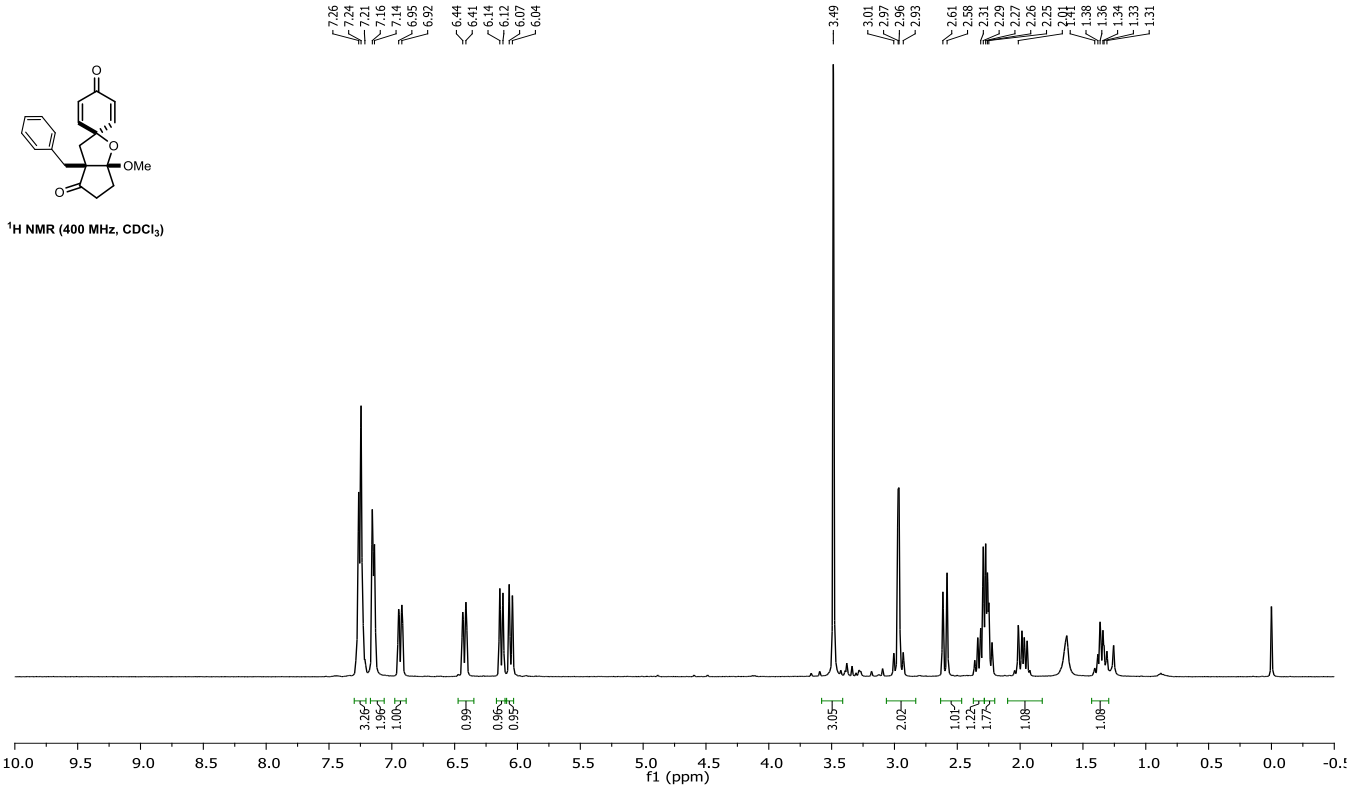
^{13}C NMR (101 MHz, $CDCl_3$)

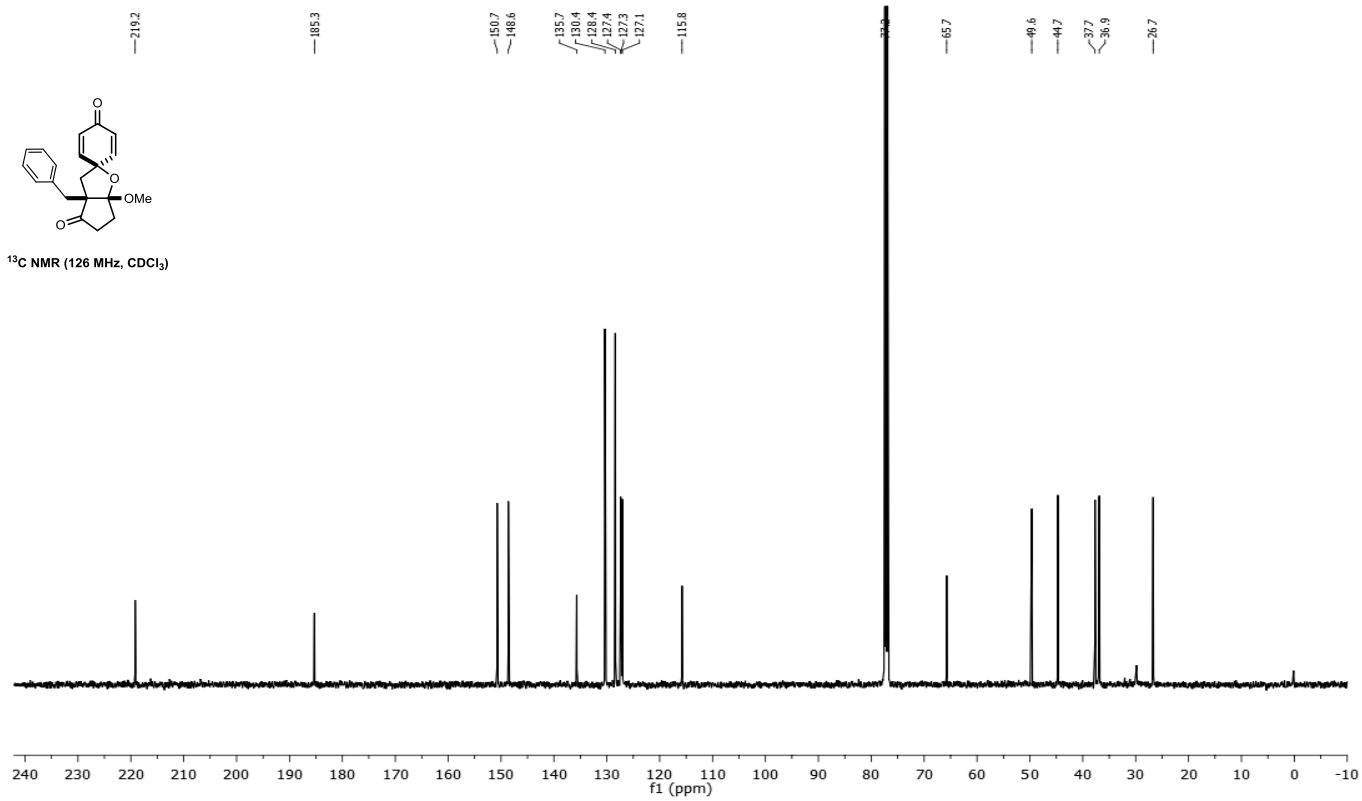
6a'-Methoxy-3a'-(3-phenylpropyl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3g):



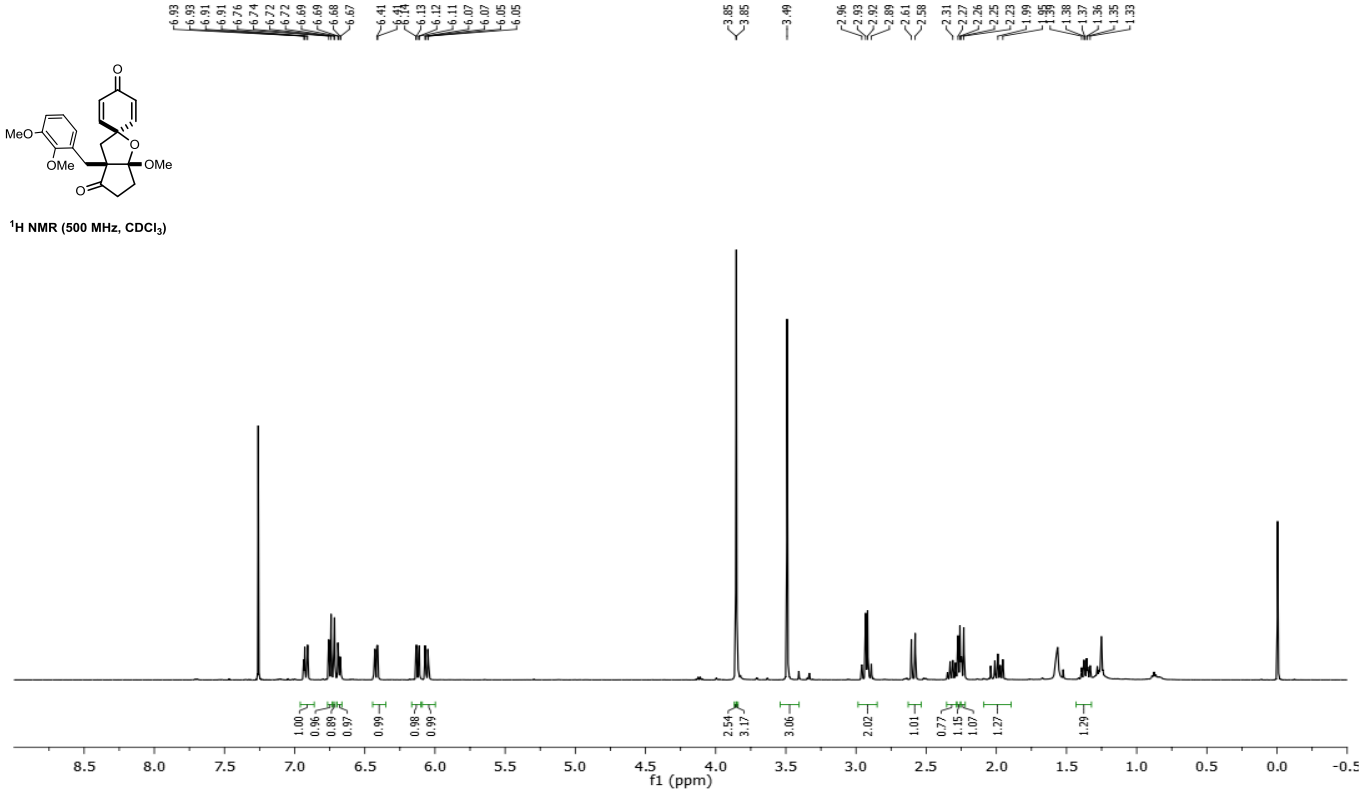


3a'-Benzyl-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3h):

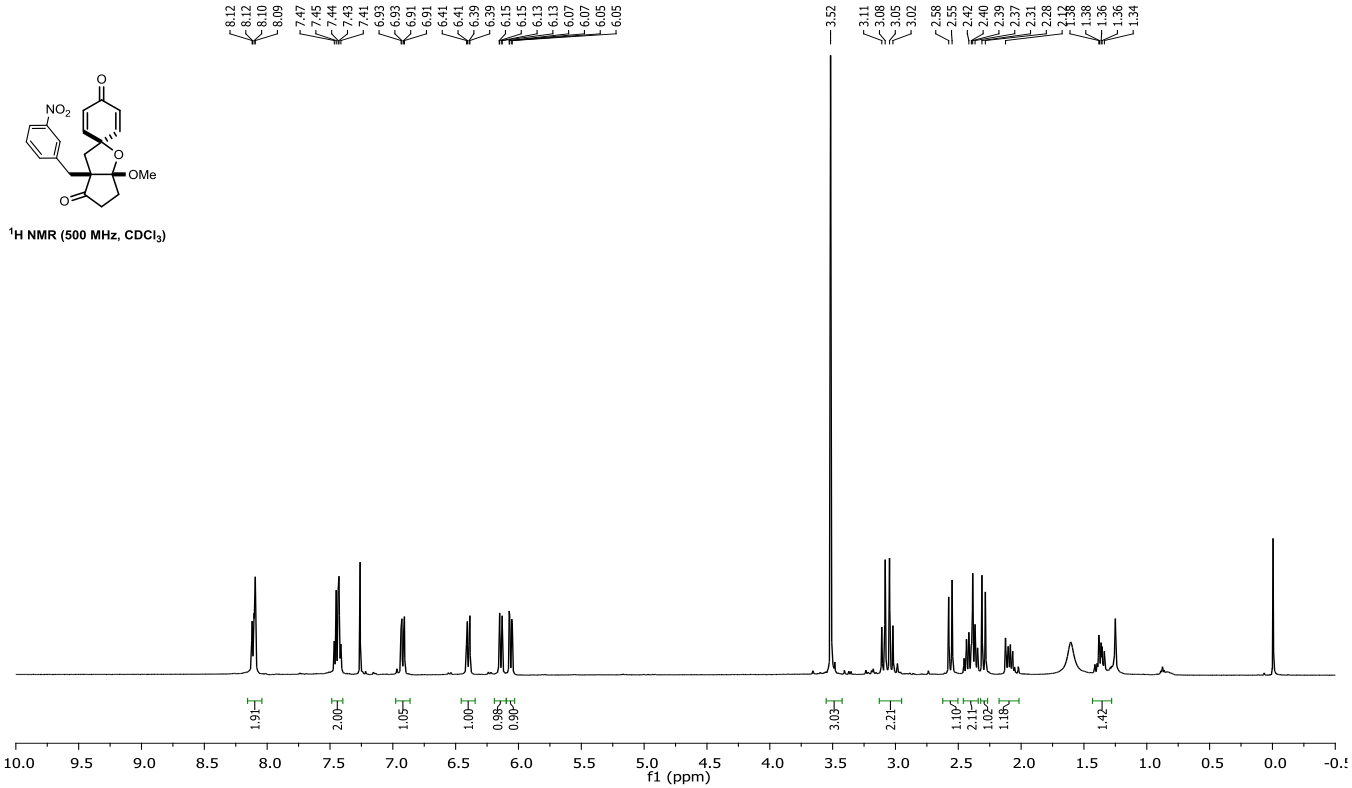


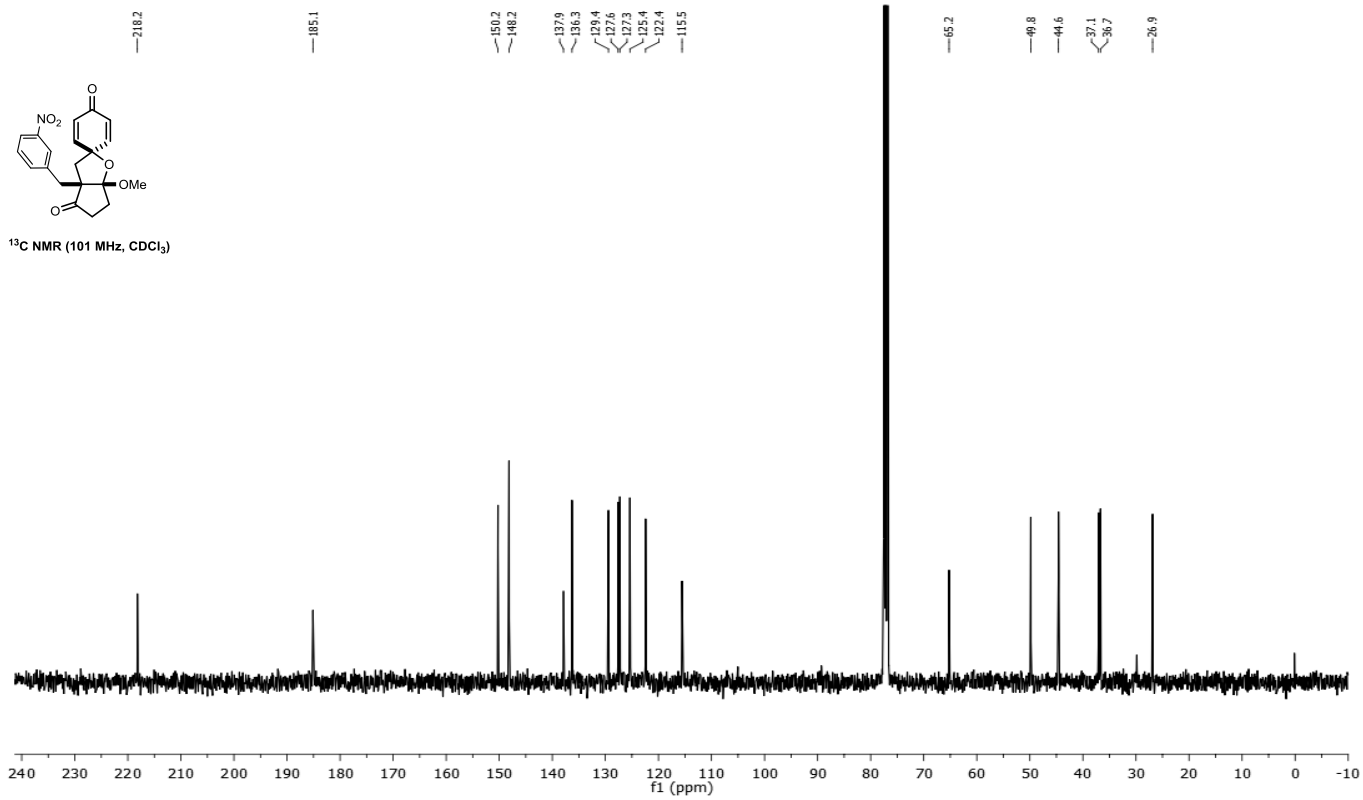


3a'-(3,4-Dimethoxybenzyl)-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2,5-diene-4,4'(3'*H*)-dione (3i):

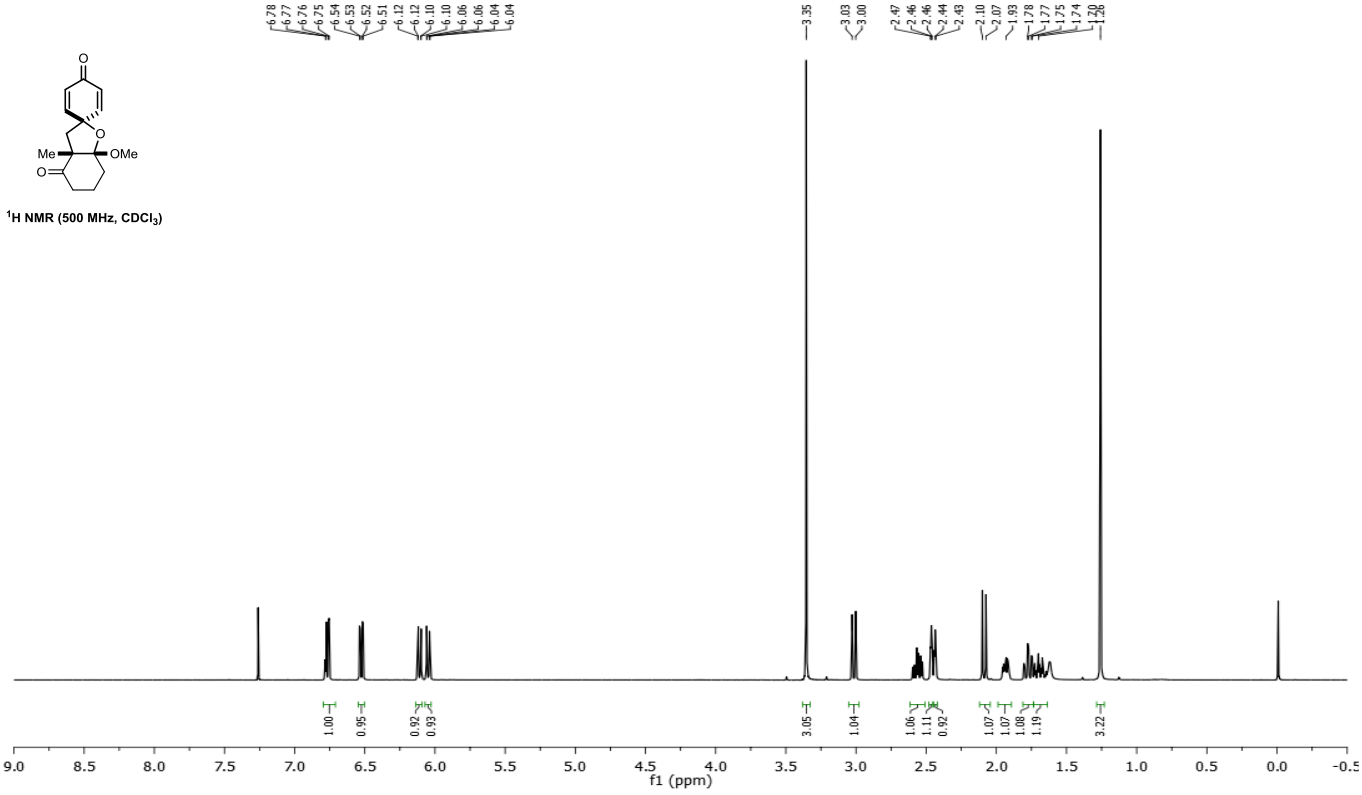


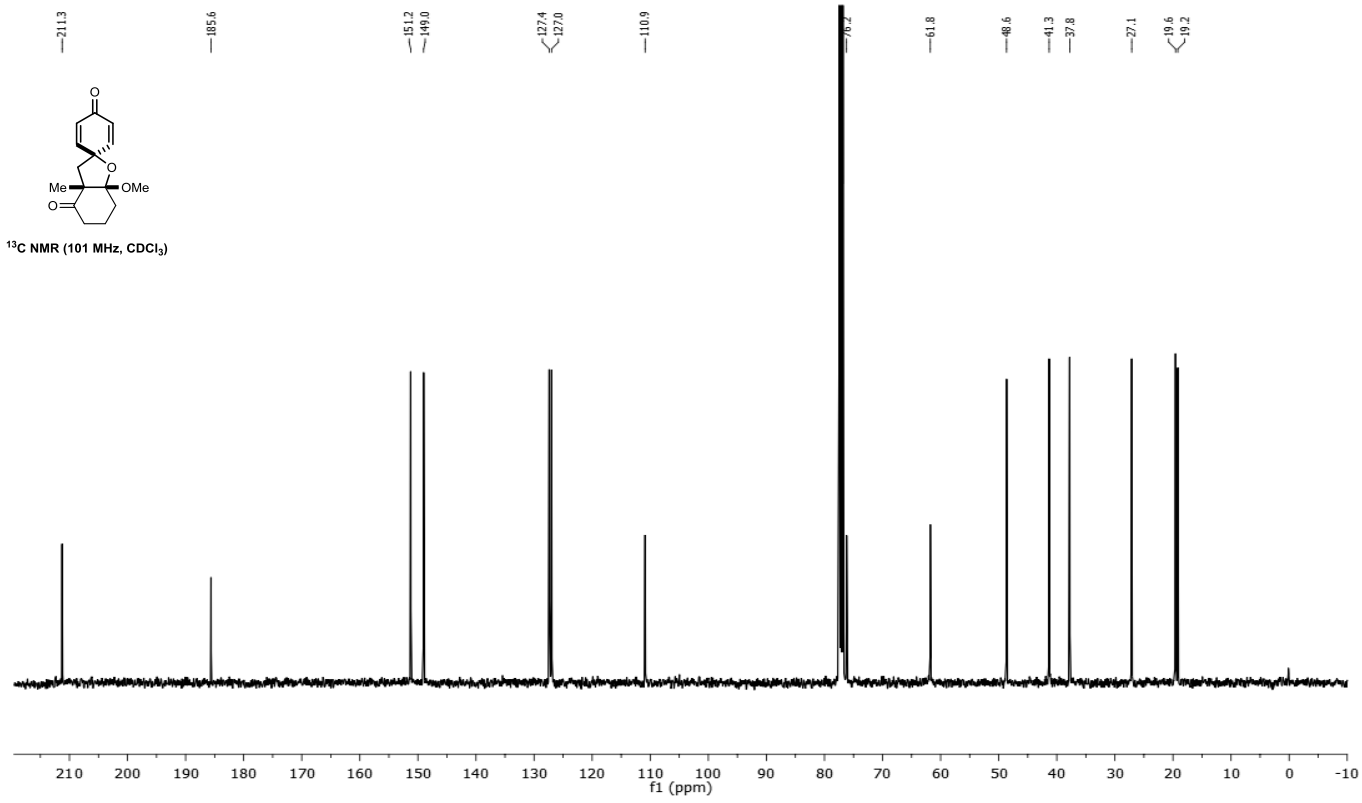
6a'-Methoxy-3a'-(3-nitrobenzyl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[b]furan]-2,5-diene-4,4'(3'H)-dione (3j):



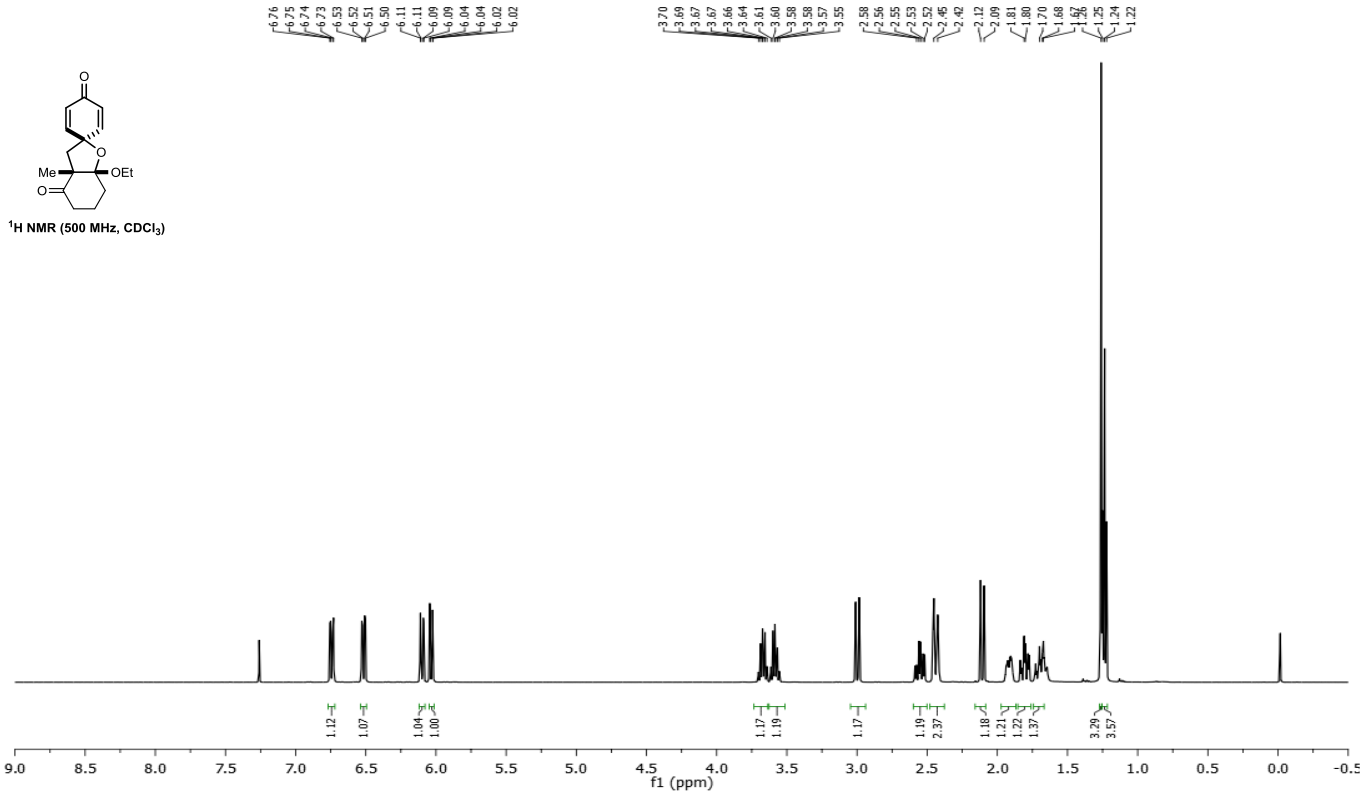


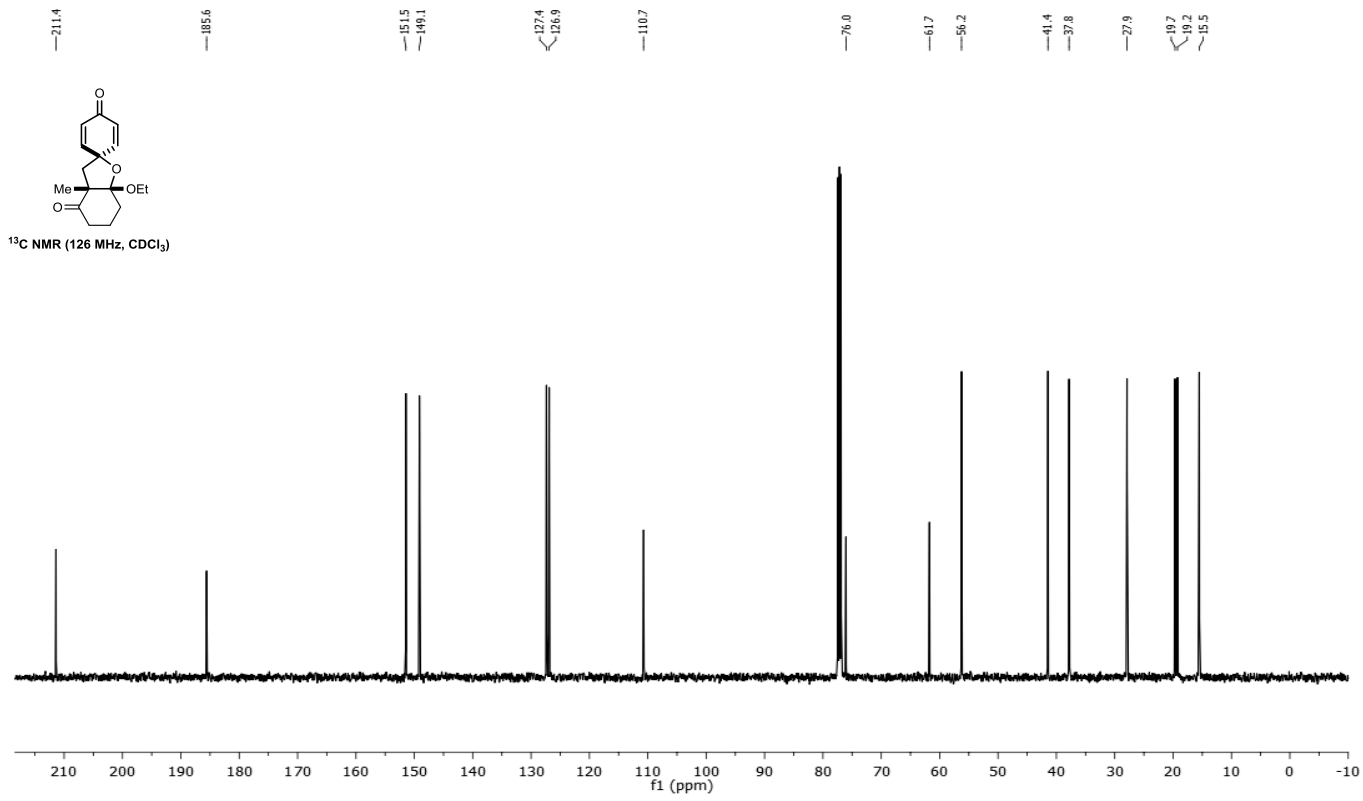
7a-Methoxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3k):



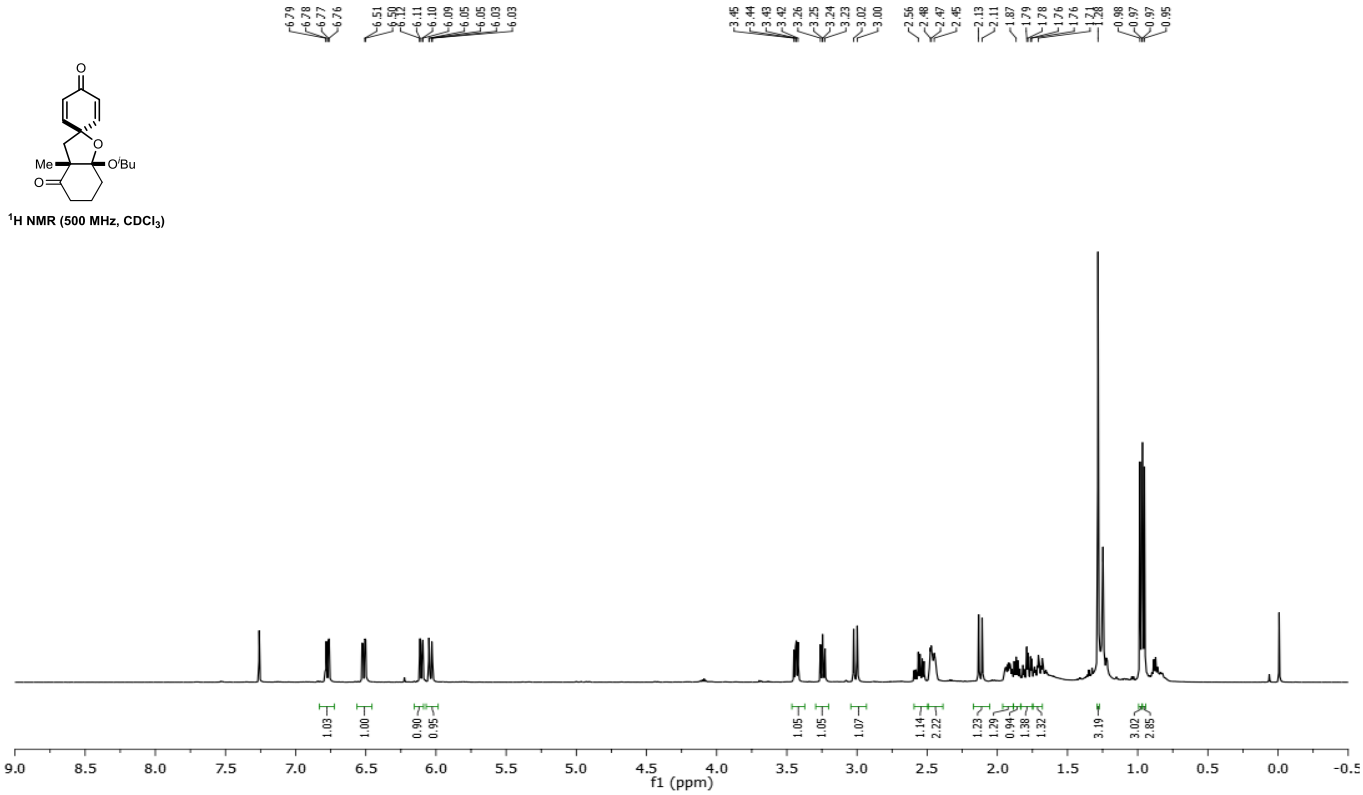


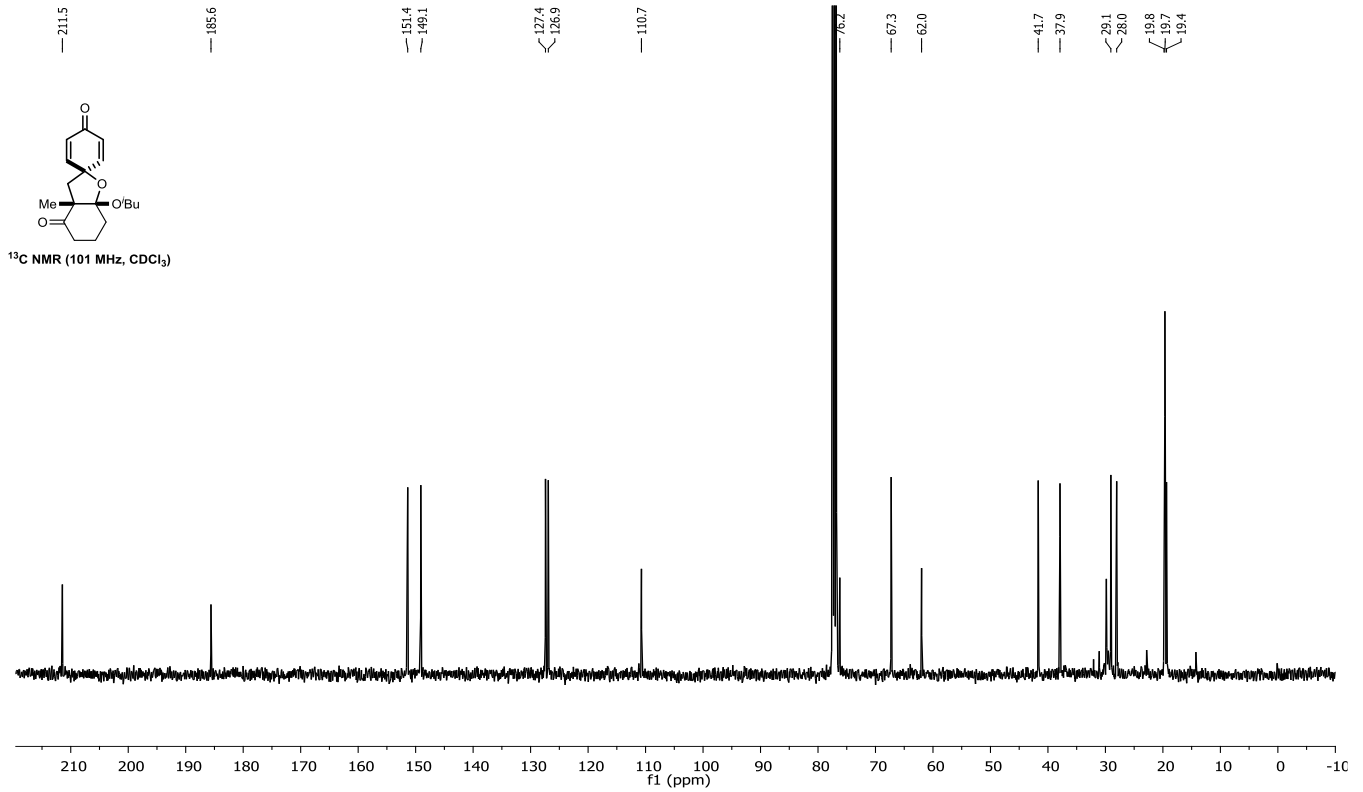
7a-Ethoxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3l):



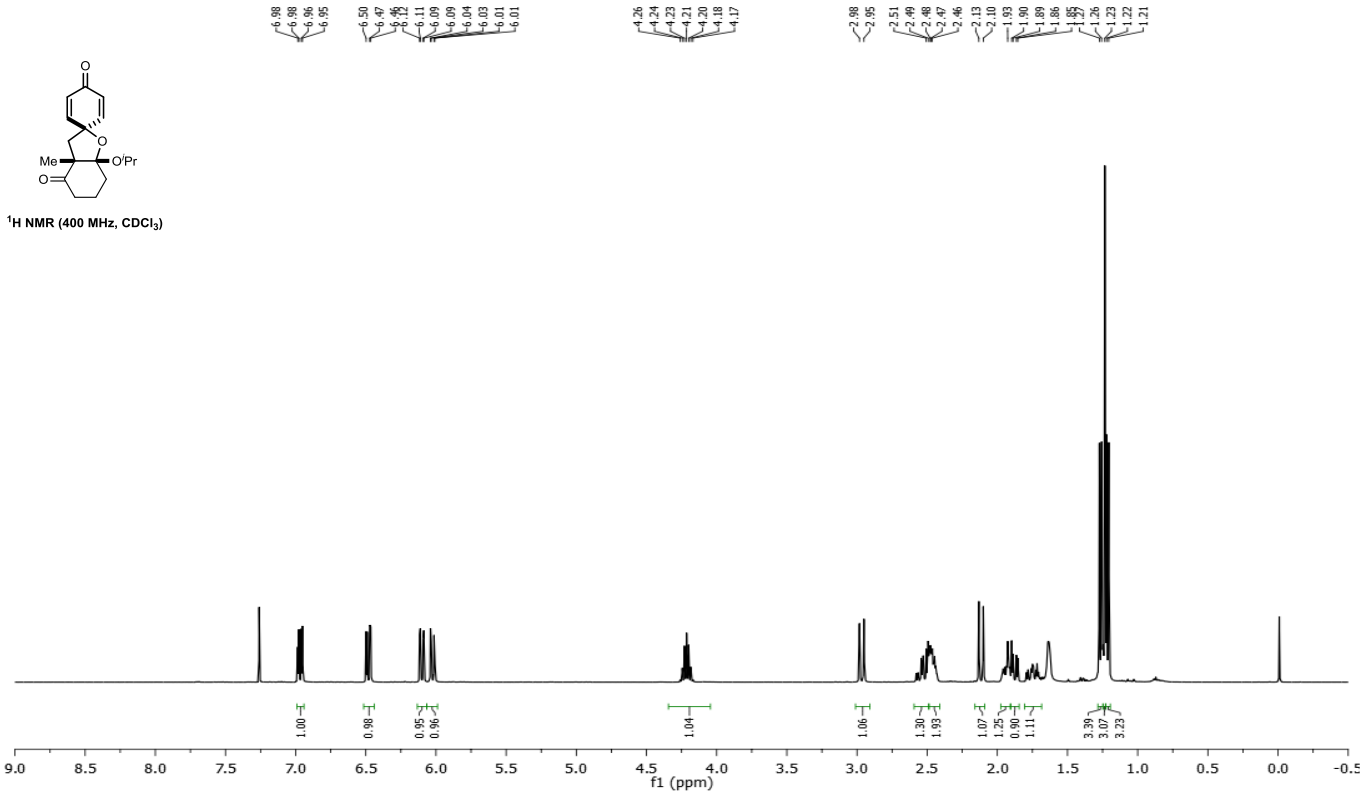


7a-Isobutoxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3m):

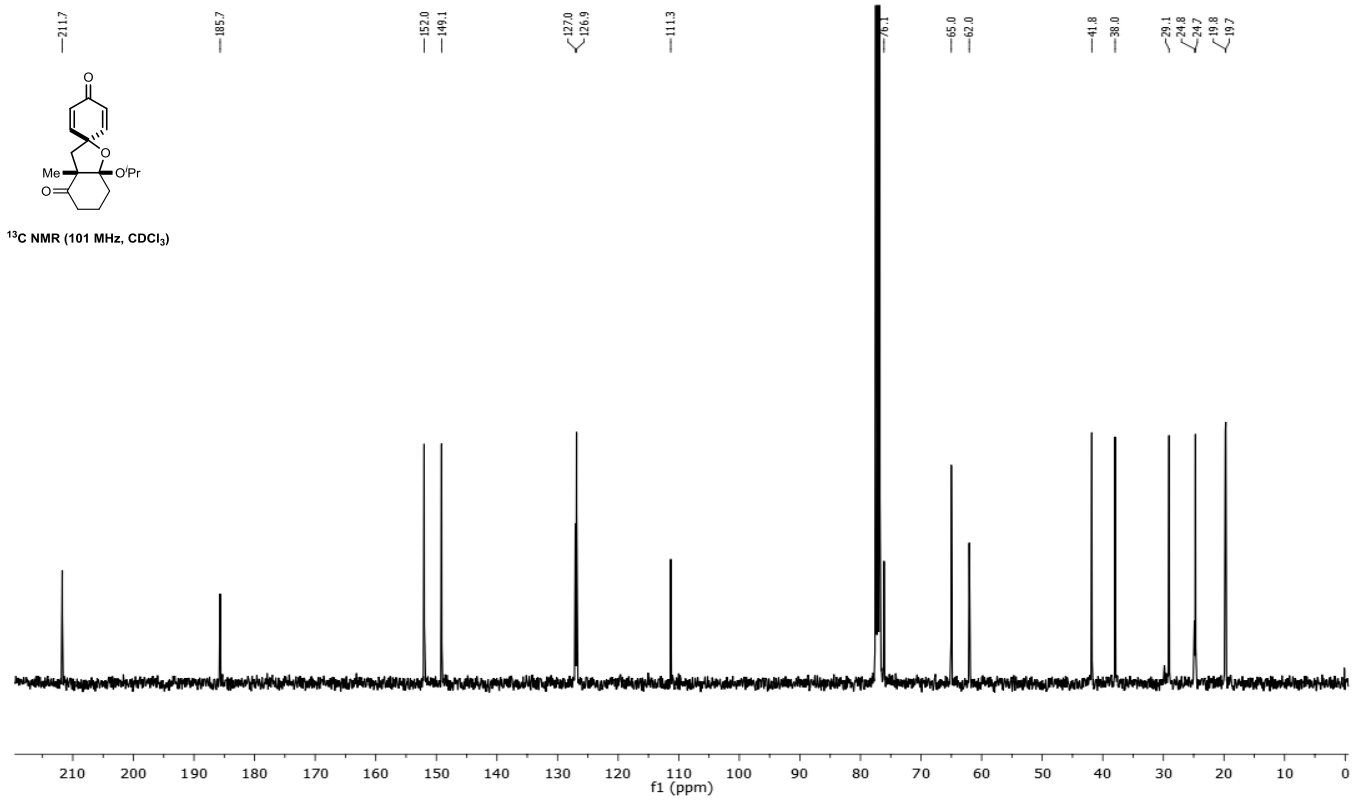




7a-Isopropoxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3n):

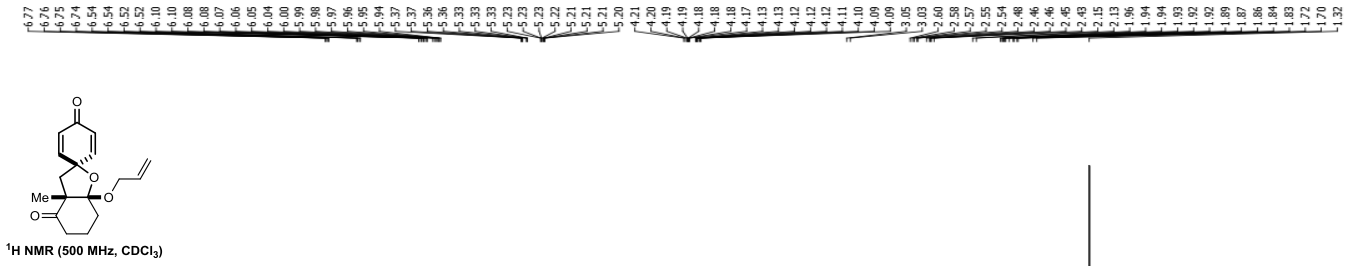


^{1}H NMR (400 MHz, $CDCl_3$)

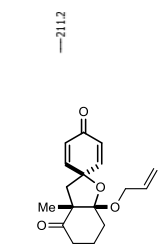


^{13}C NMR (101 MHz, $CDCl_3$)

7a-(Allyloxy)-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3p):

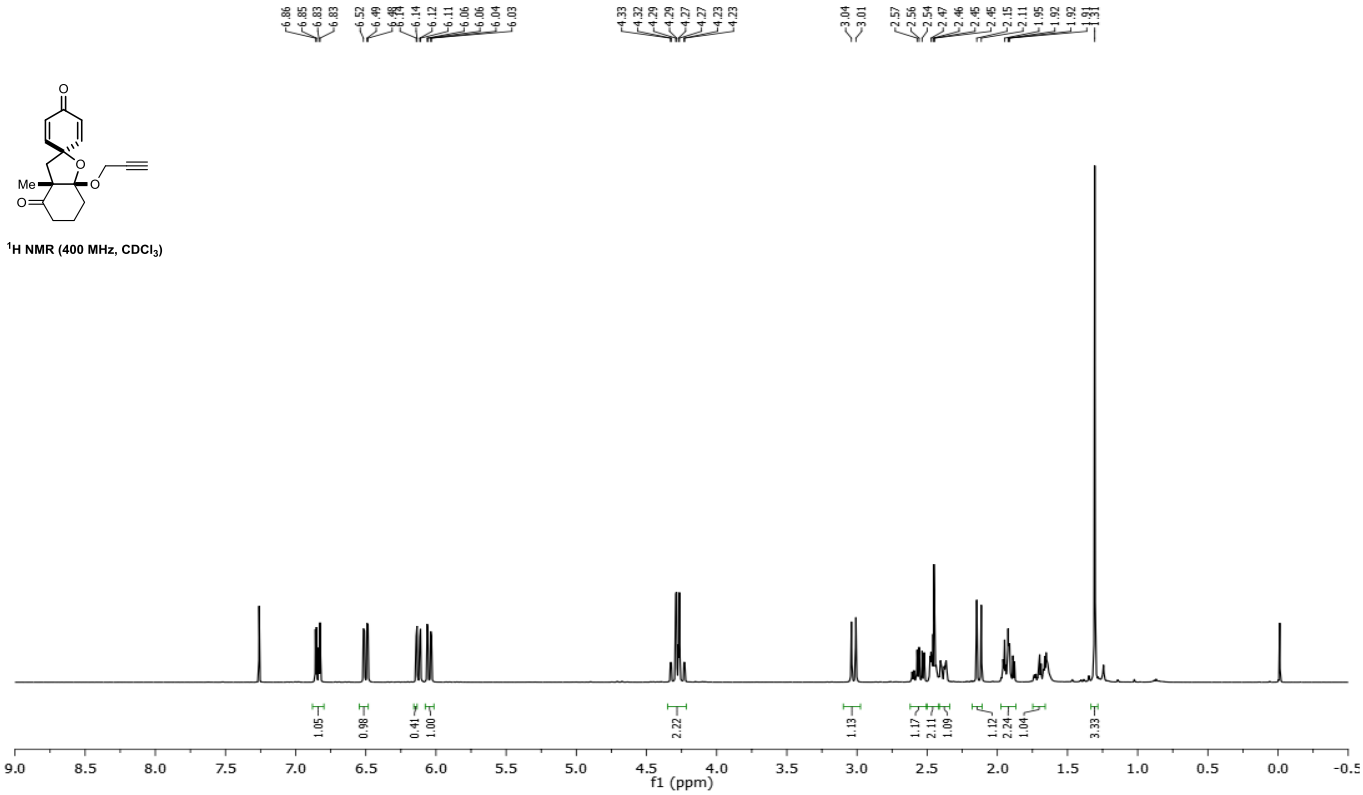


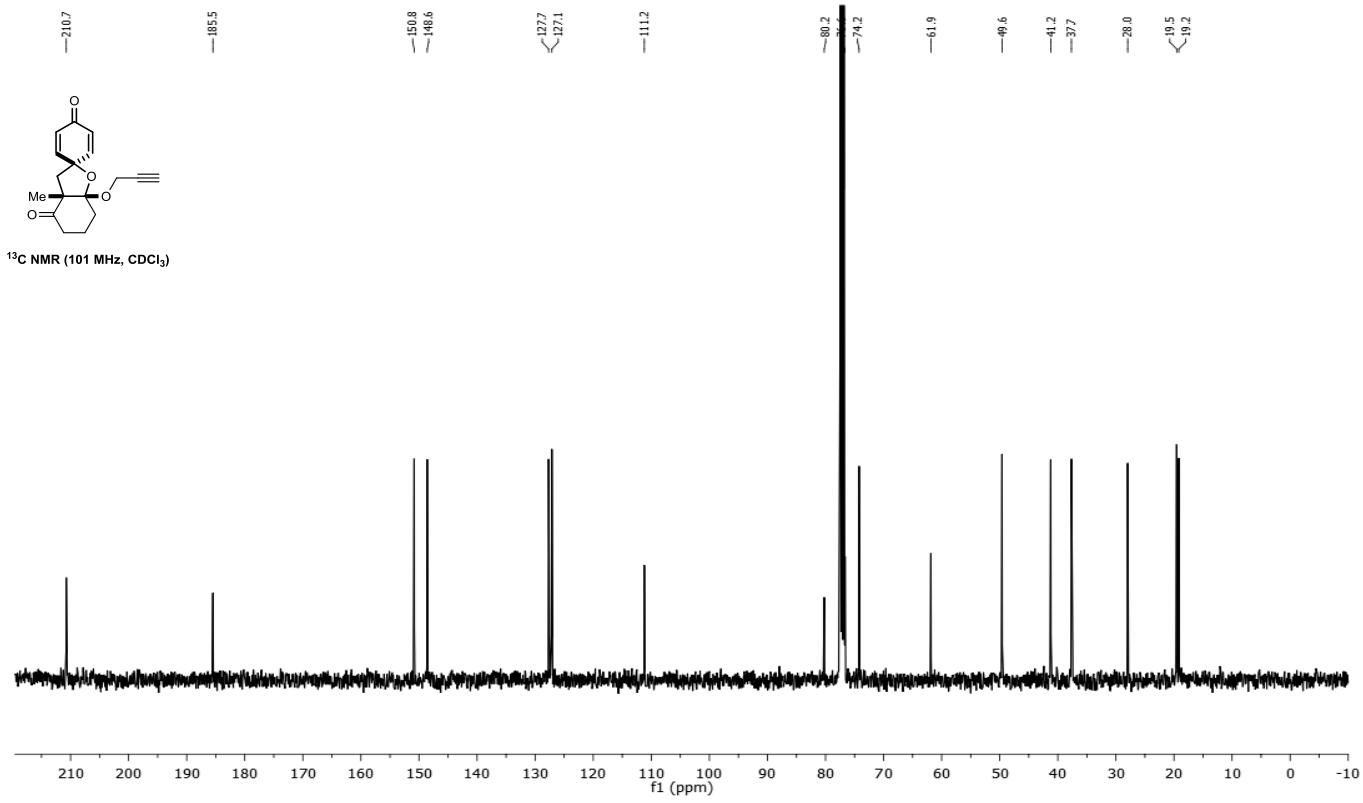
^{1}H NMR (500 MHz, $CDCl_3$)



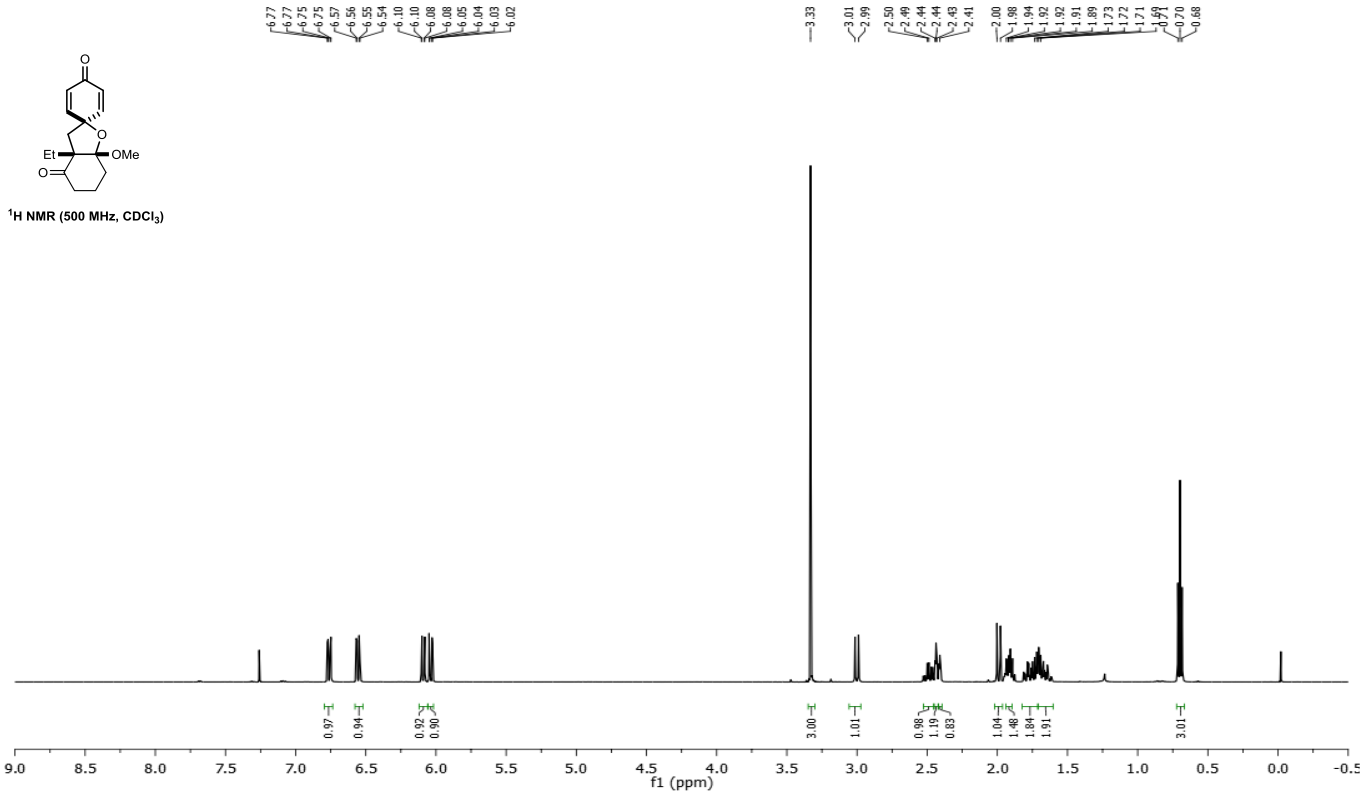
^{13}C NMR (101 MHz, $CDCl_3$)

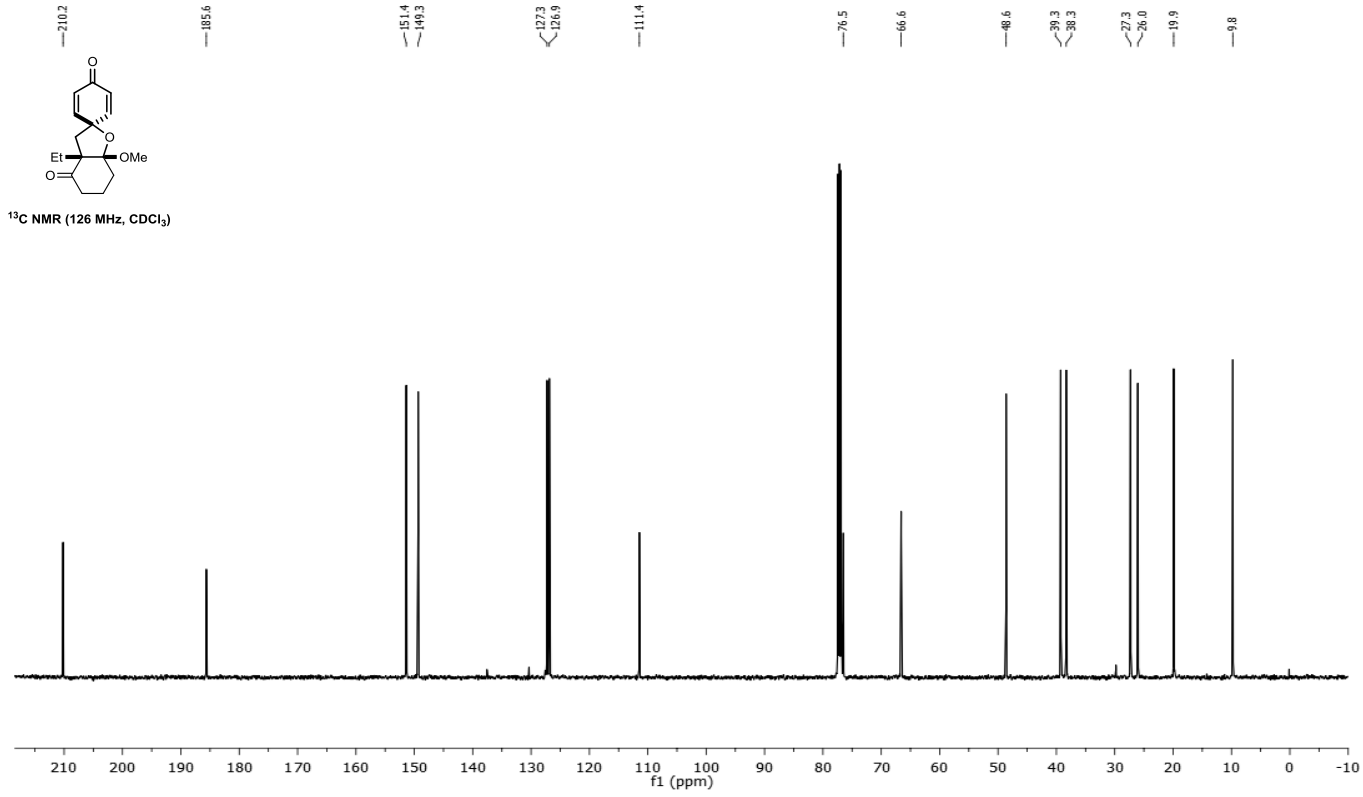
3a-Methyl-7a-(prop-2-yn-1-yloxy)-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3q):



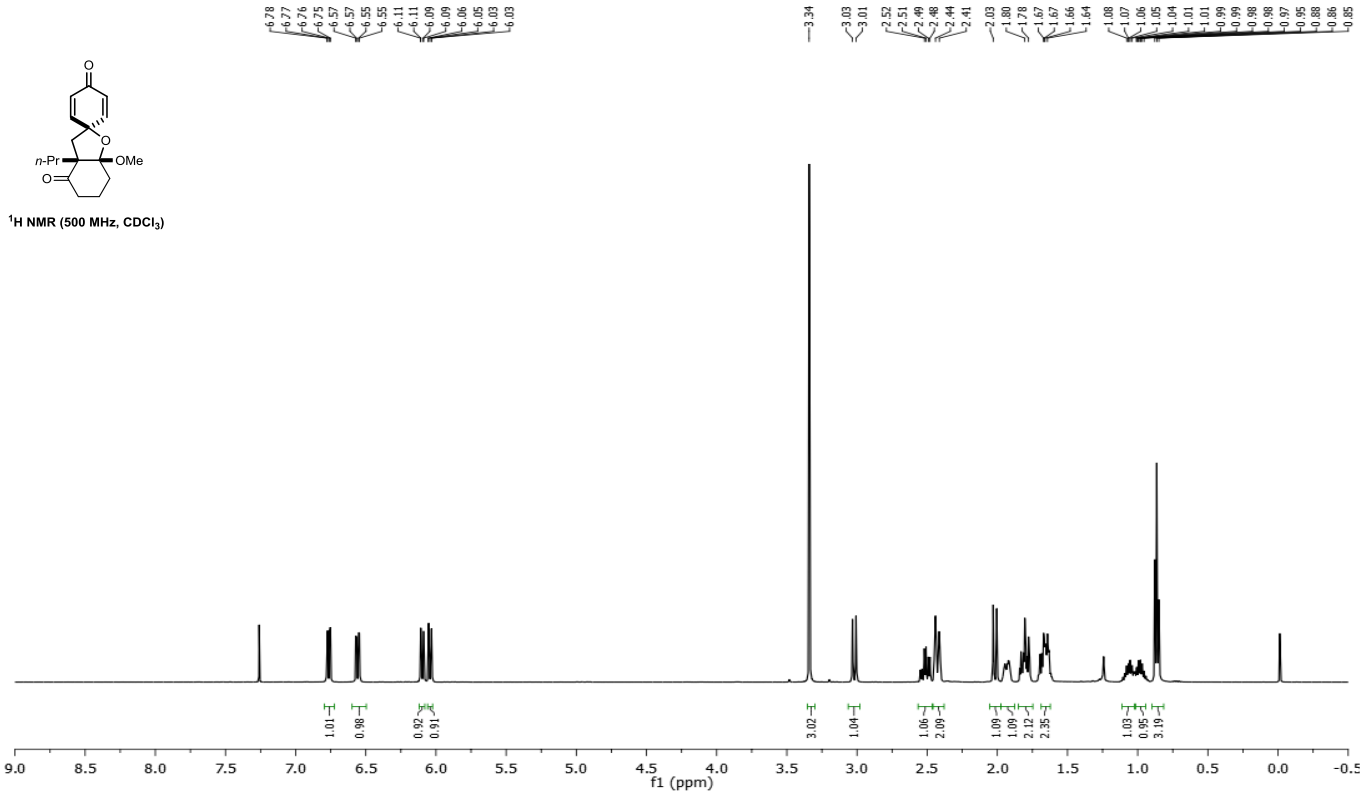


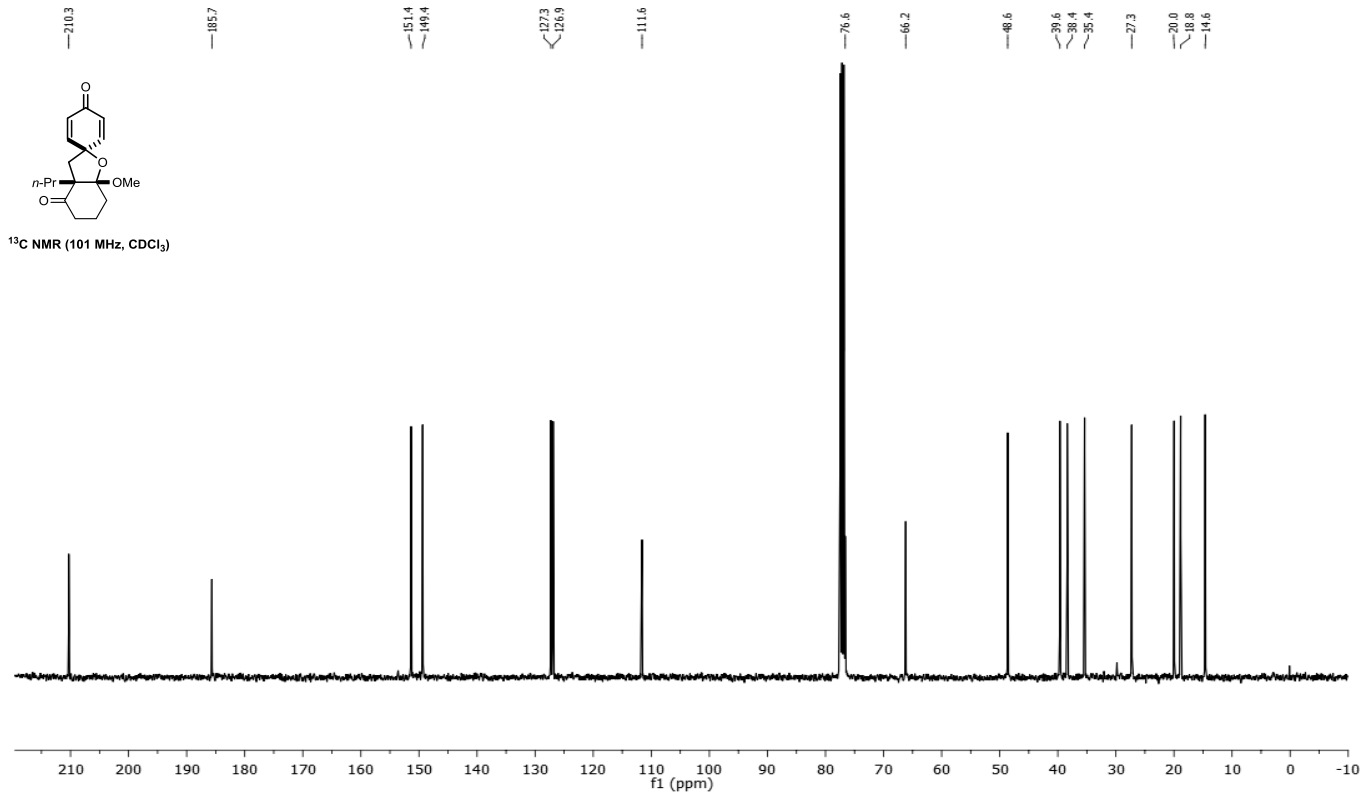
3a-Ethyl-7a-methoxy-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3r):



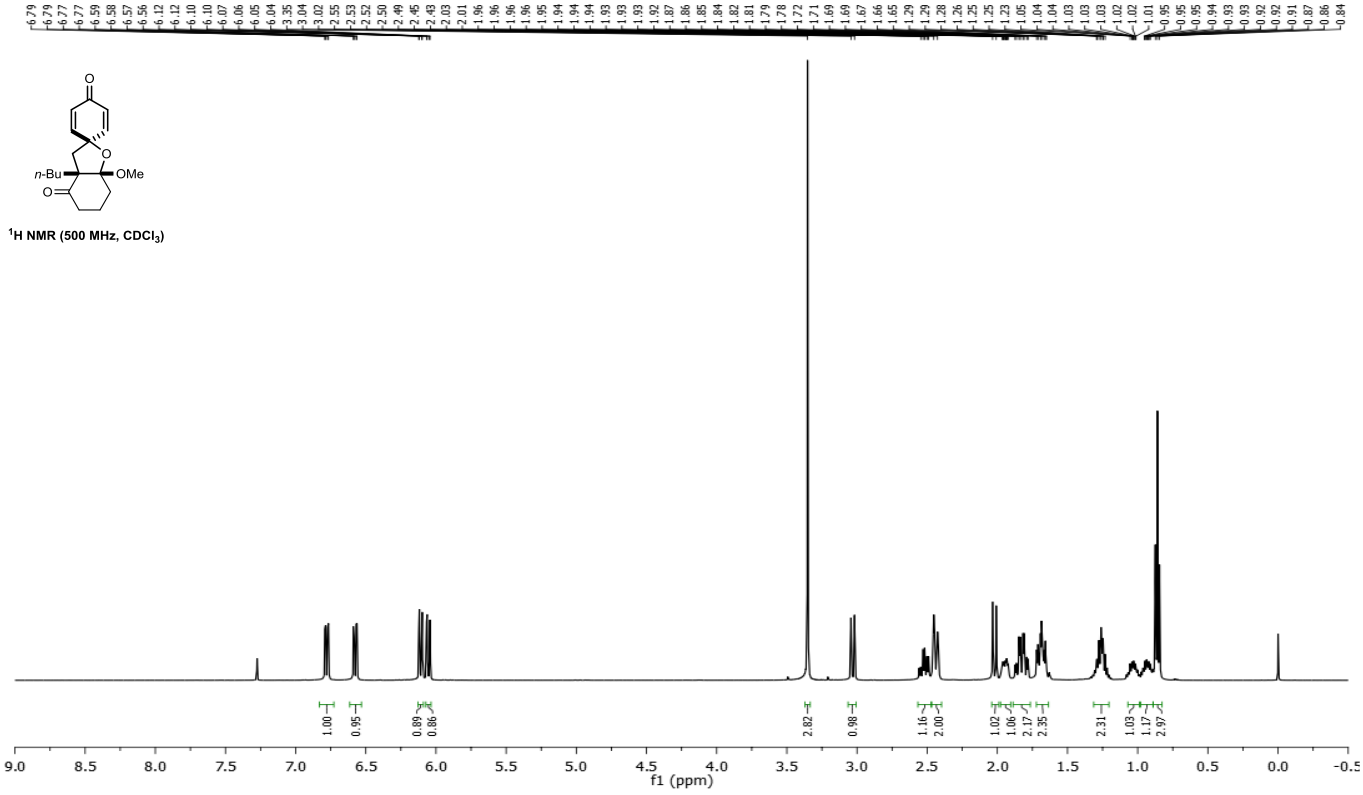


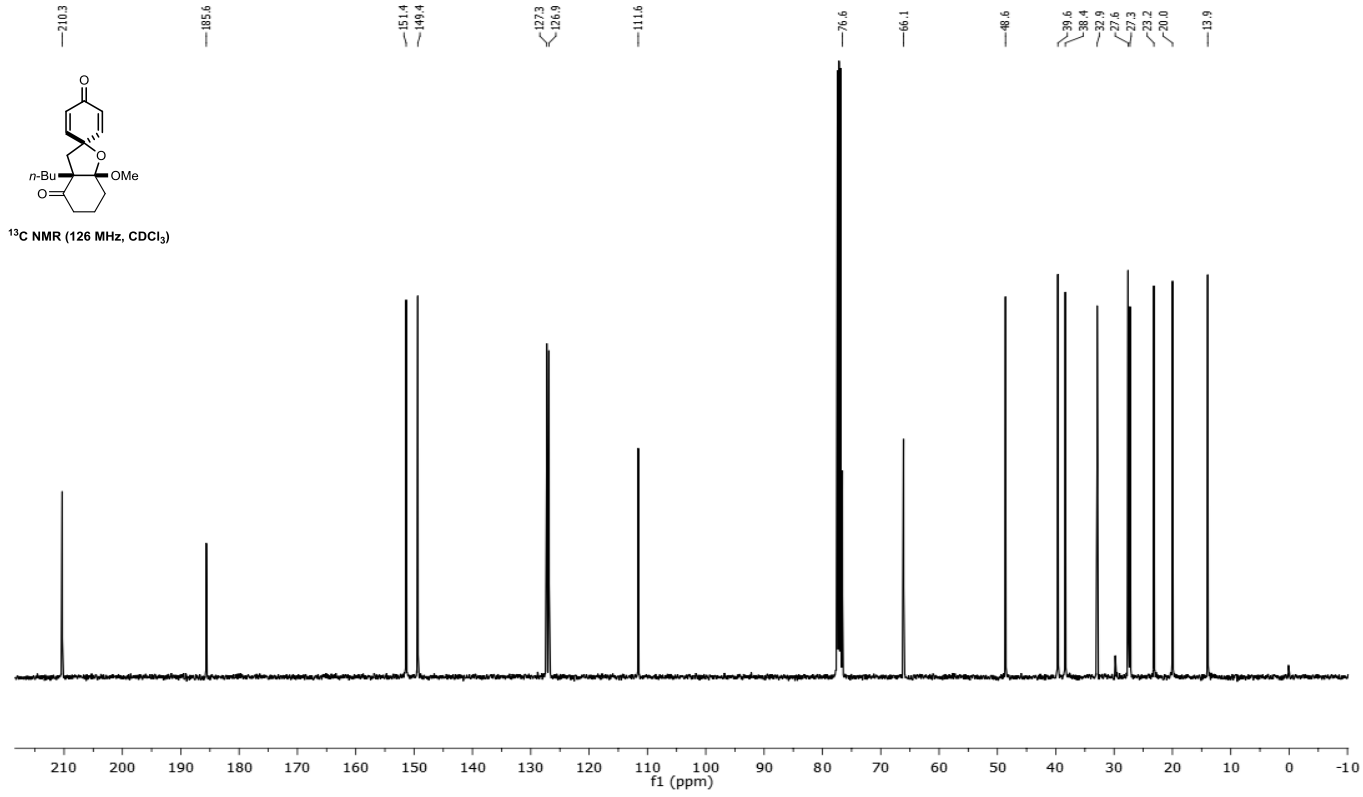
7a-Methoxy-3a-propyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3s):



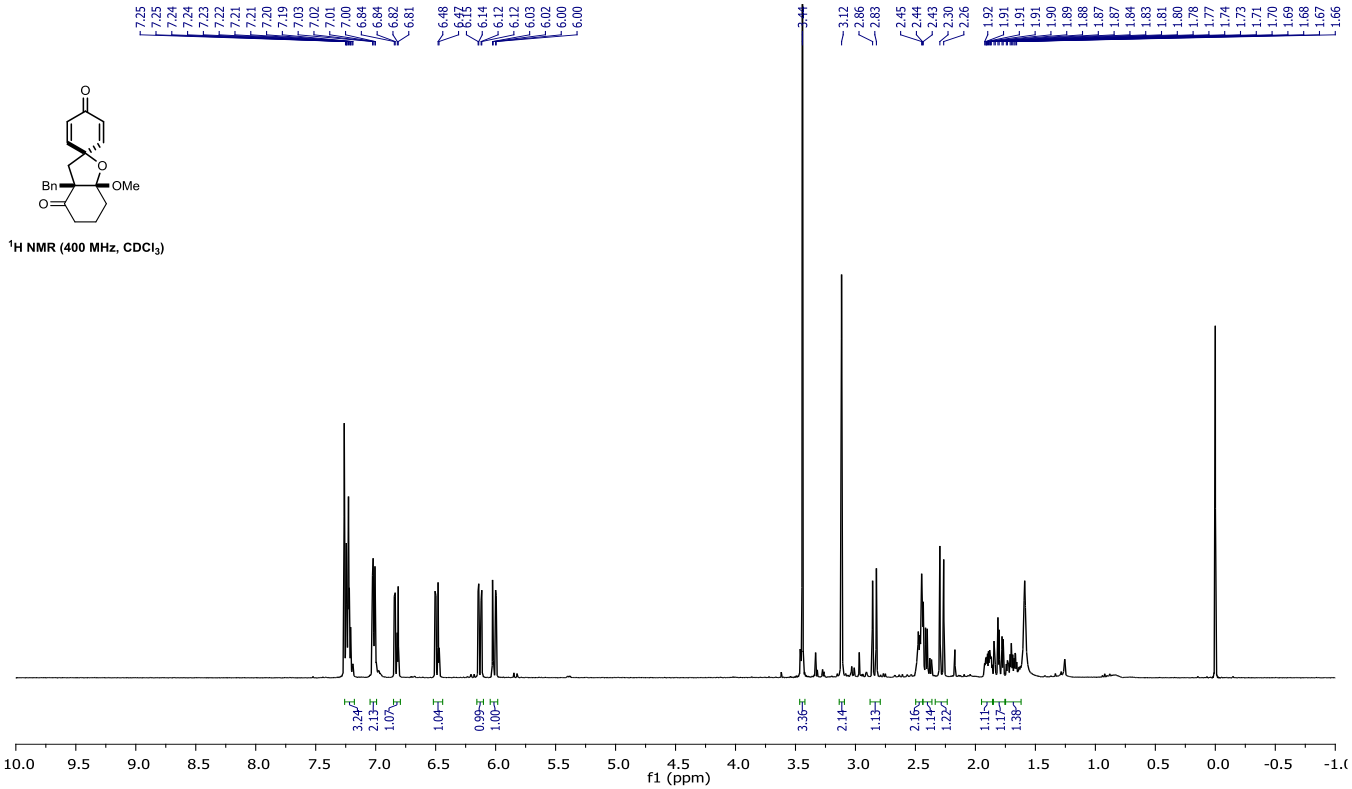


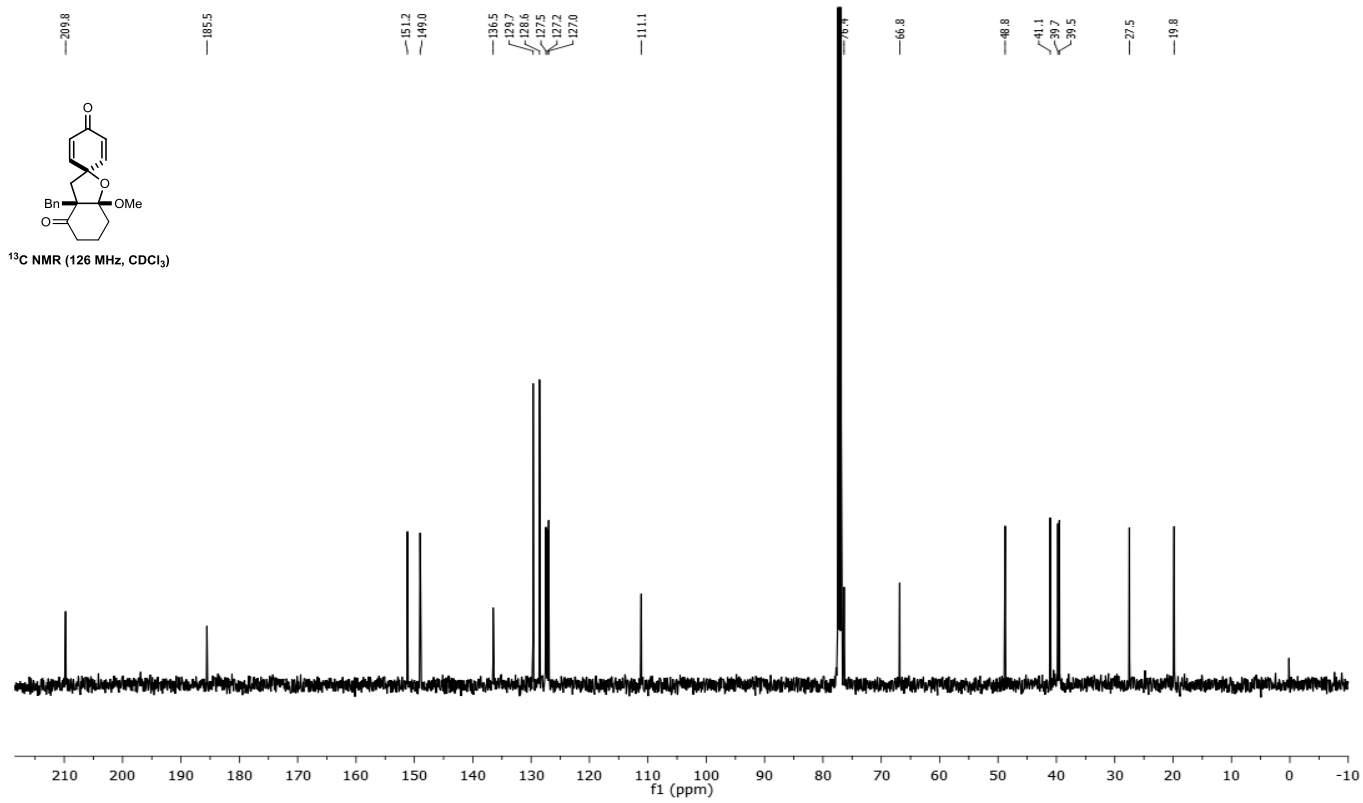
3a-Butyl-7a-methoxy-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3t):



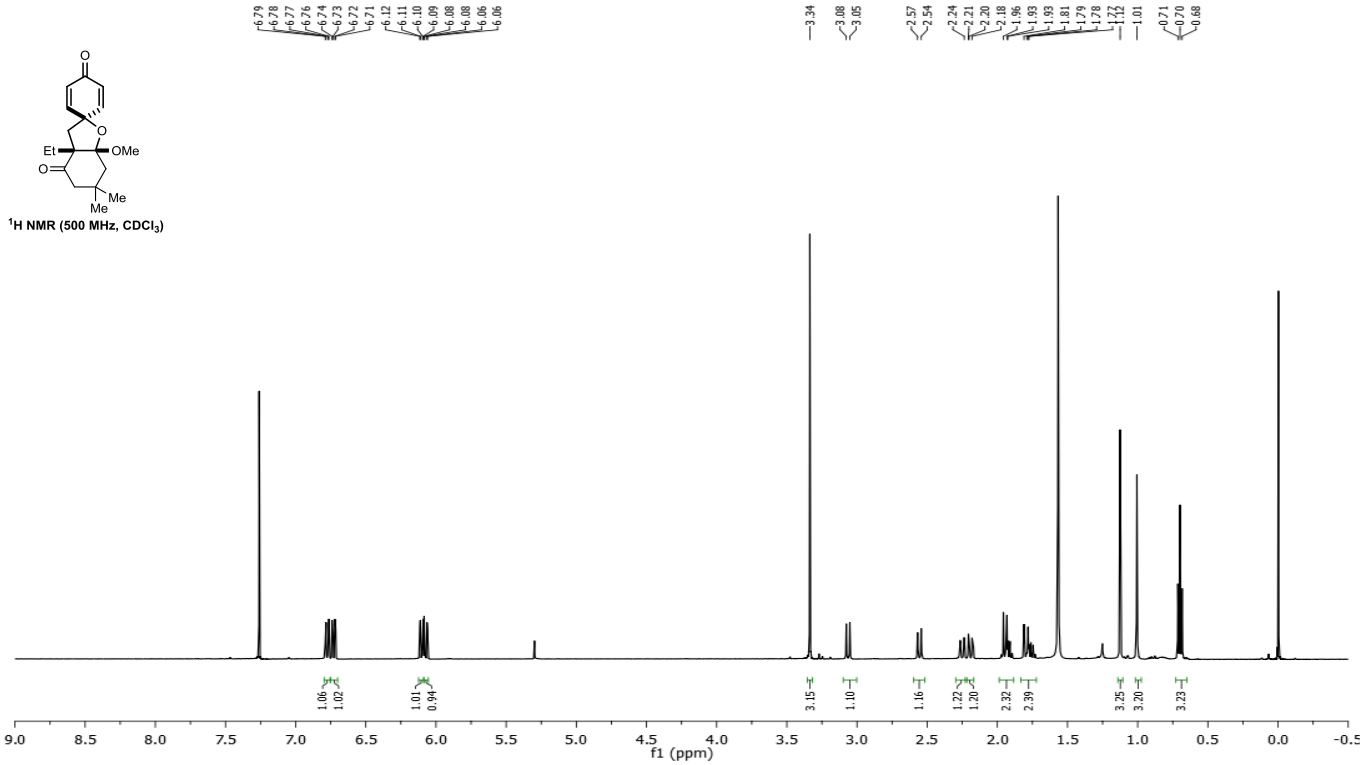


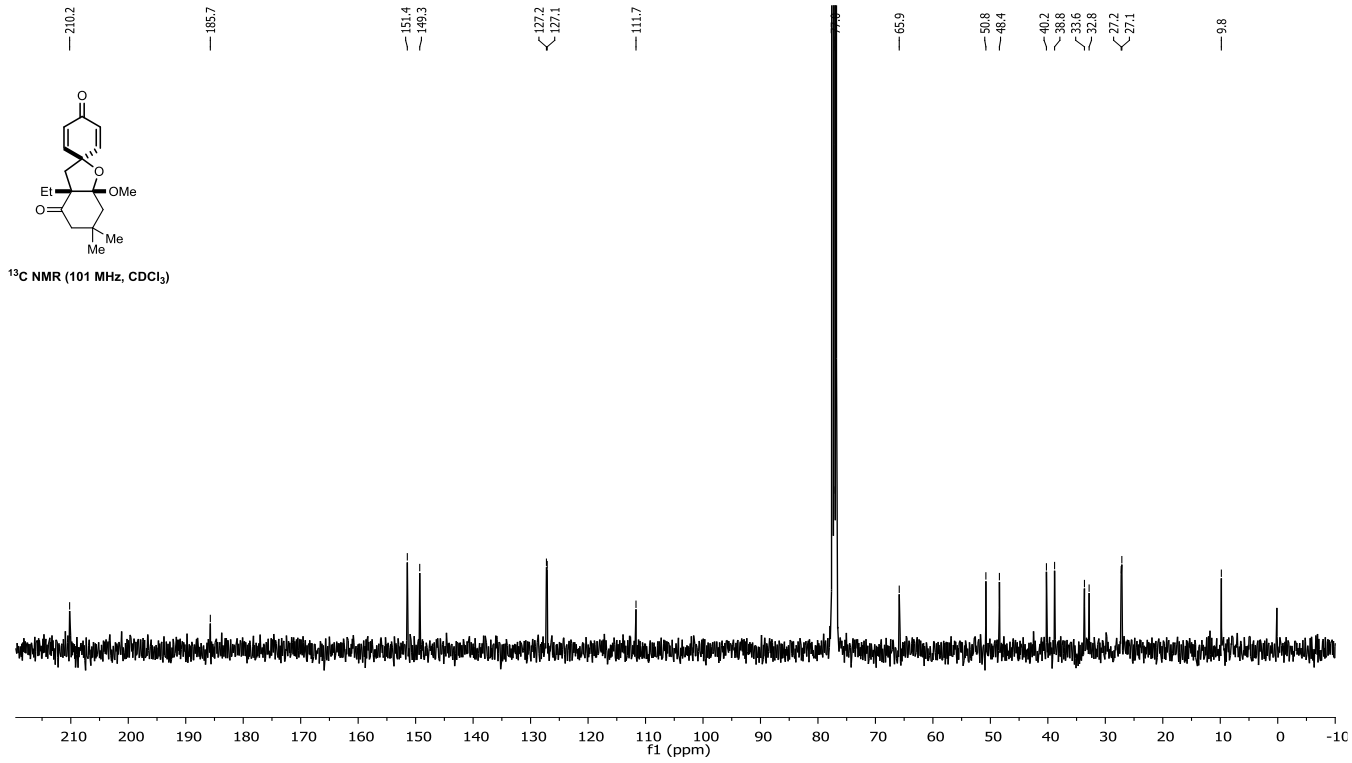
3a-Benzyl-7a-methoxy-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3u):



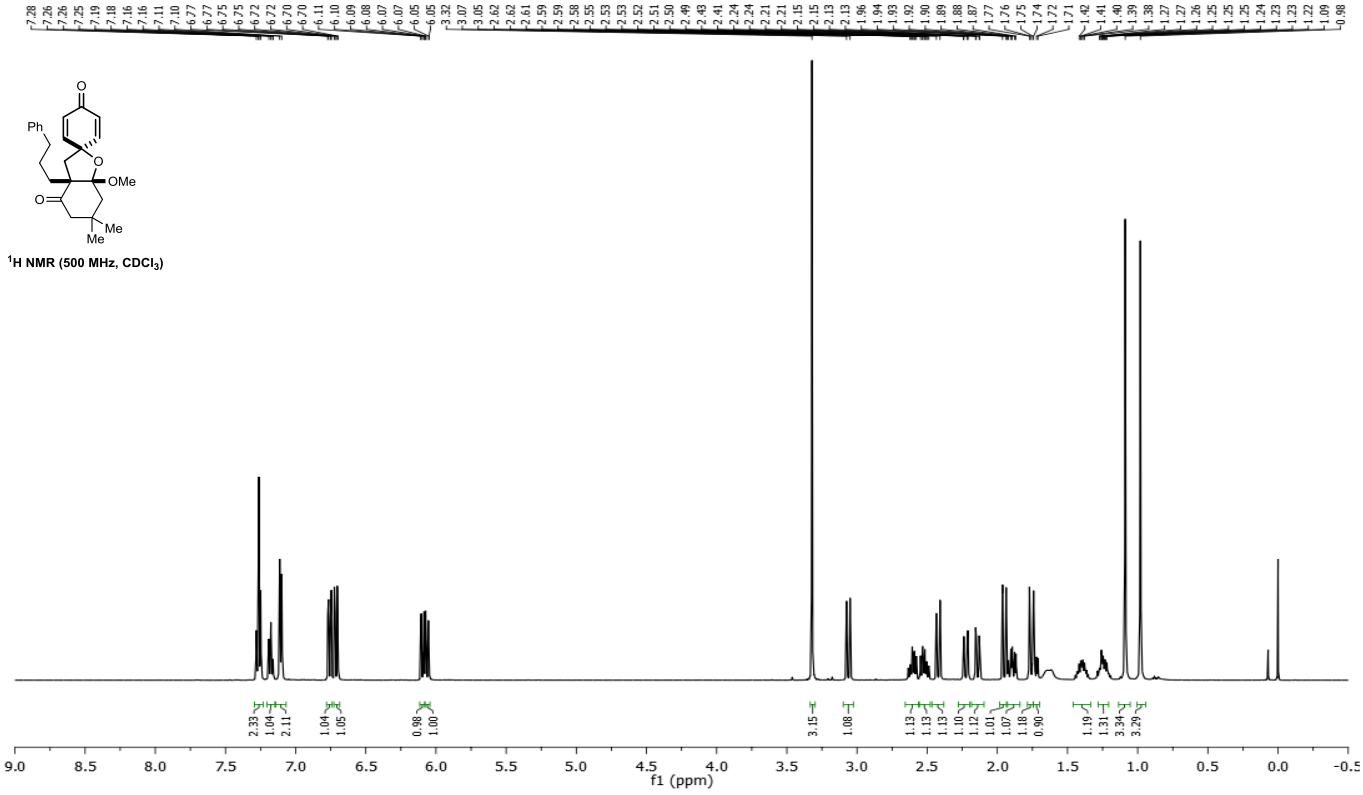


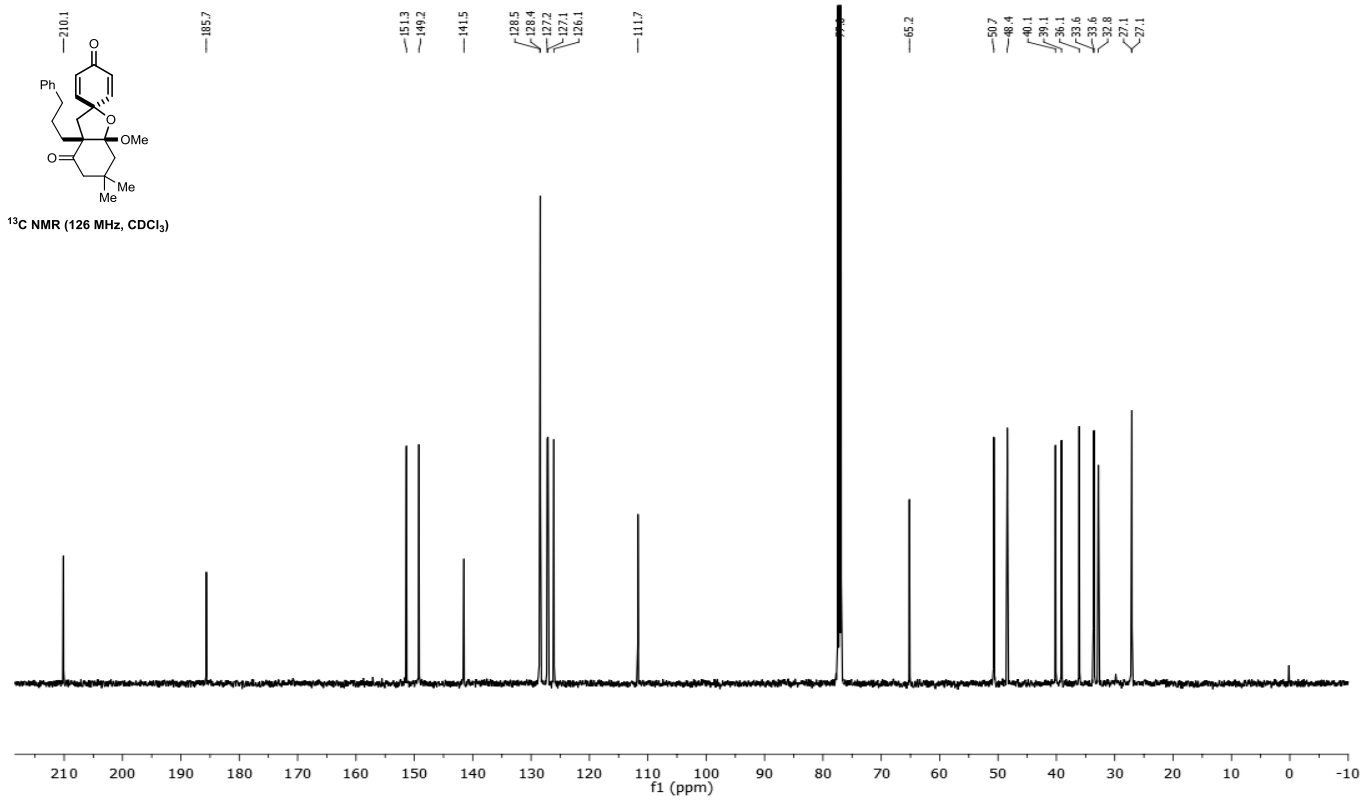
3a-Ethyl-7a-methoxy-6,6-dimethyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3v):



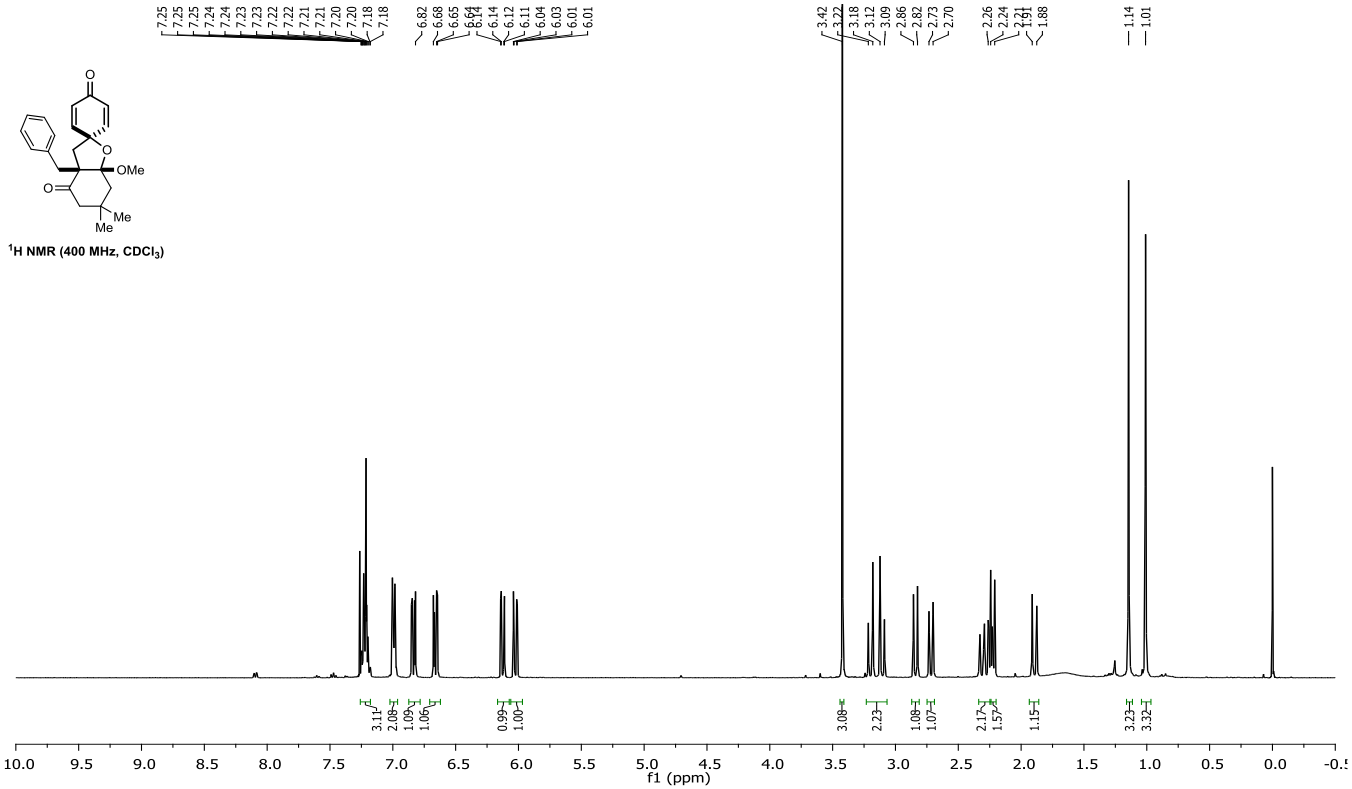


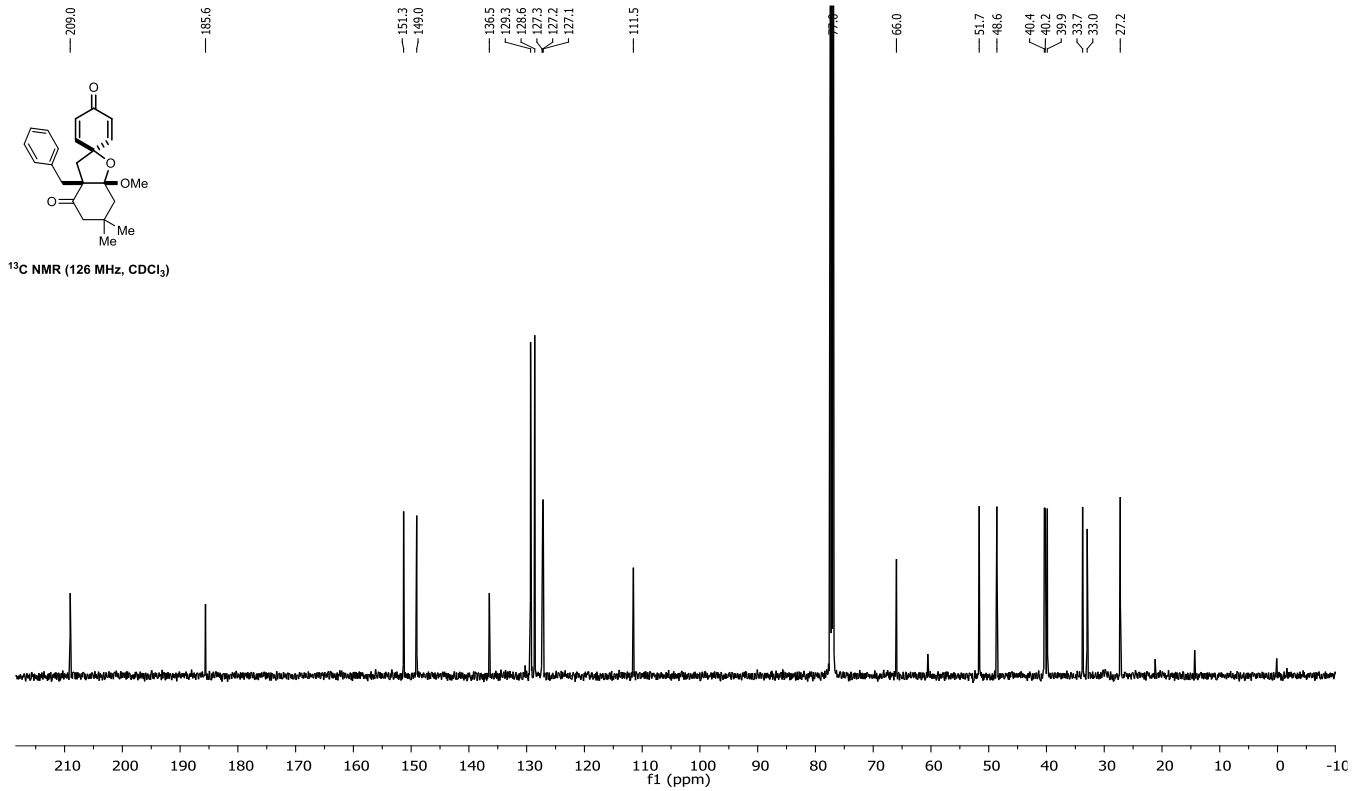
7a-Methoxy-6,6-dimethyl-3a-(3-phenylpropyl)-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3w):



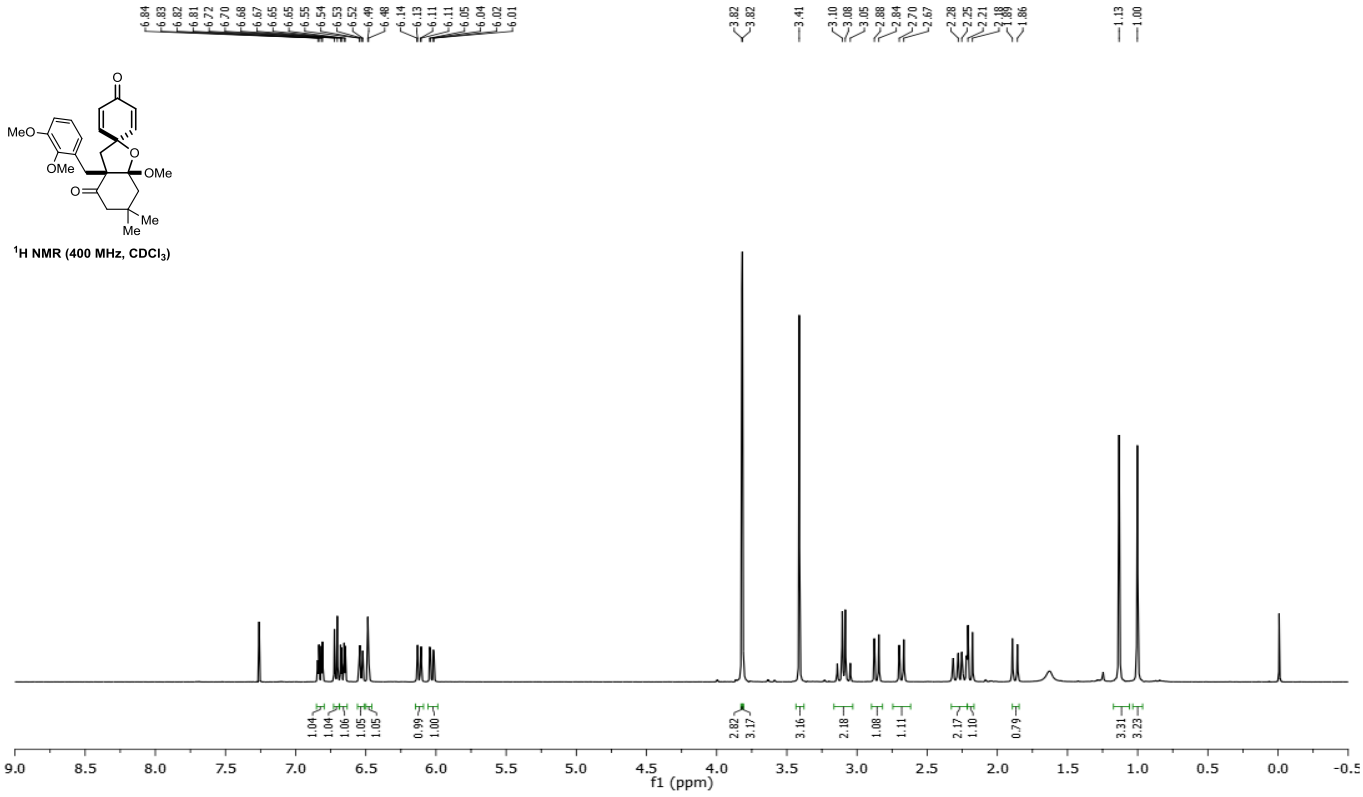


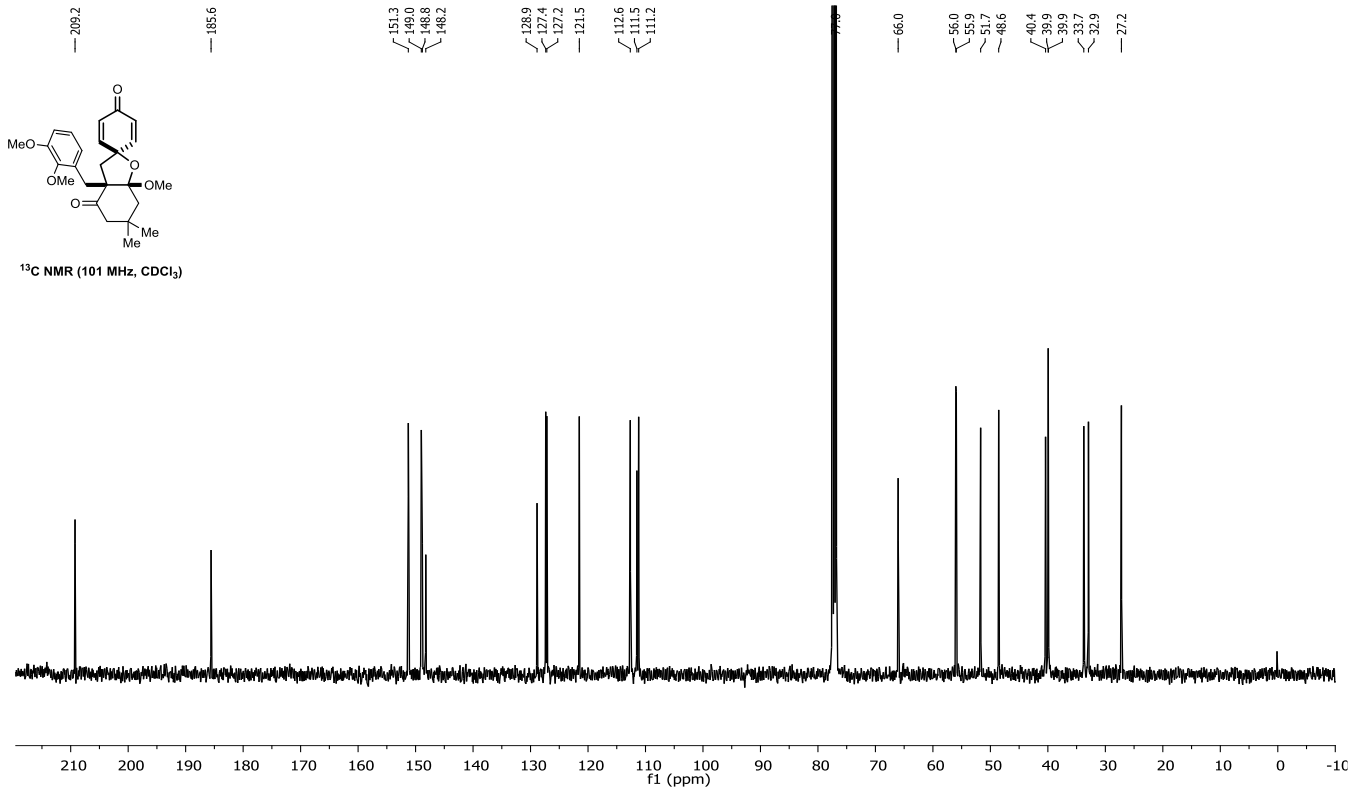
3a-Benzyl-7a-methoxy-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3x):



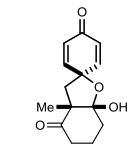


3a-(3,4-Dimethoxybenzyl)-7a-methoxy-6,6-dimethyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3y):

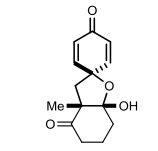




7a-Hydroxy-3a-methyl-3,3a,5,6,7,7a-hexahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',5'-diene-4,4'-dione (3ka):

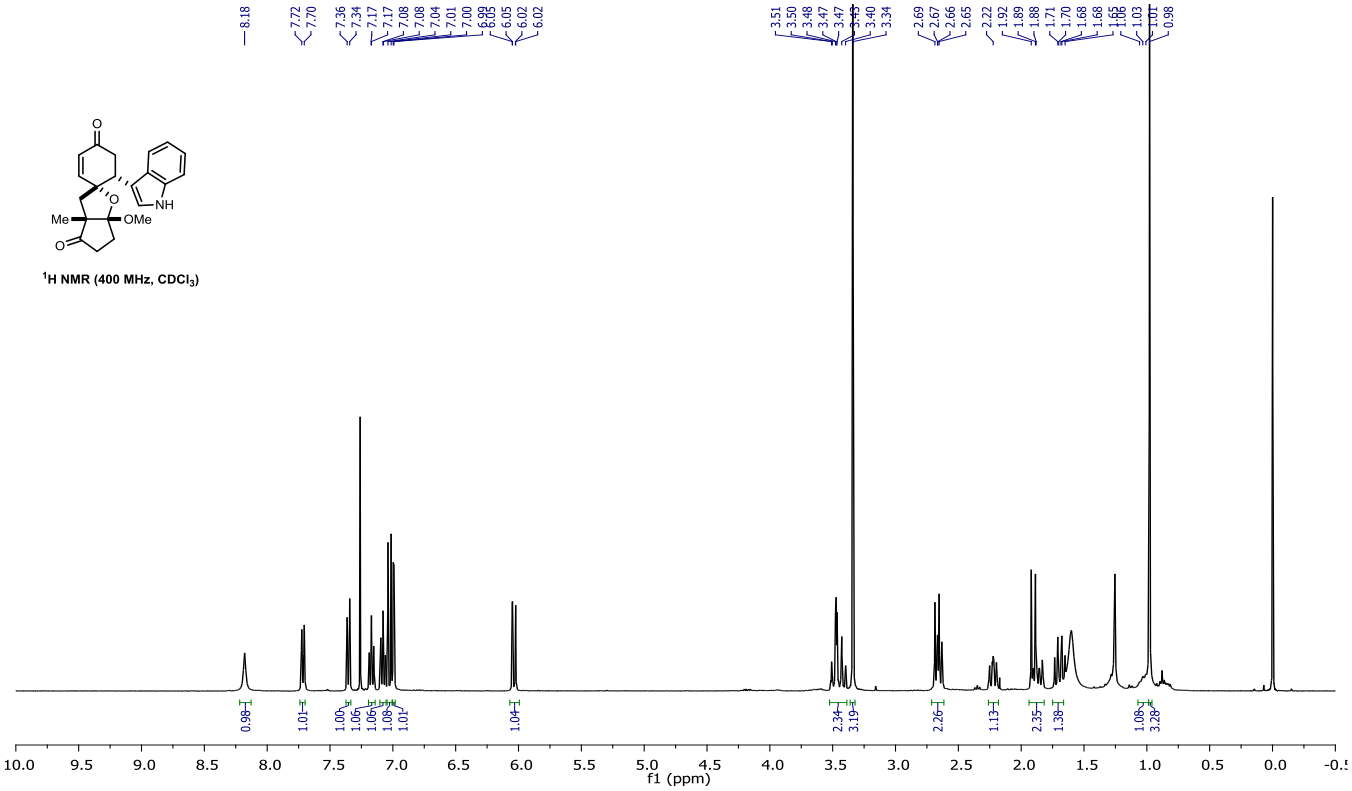


^{1}H NMR (500 MHz, $CDCl_3$)

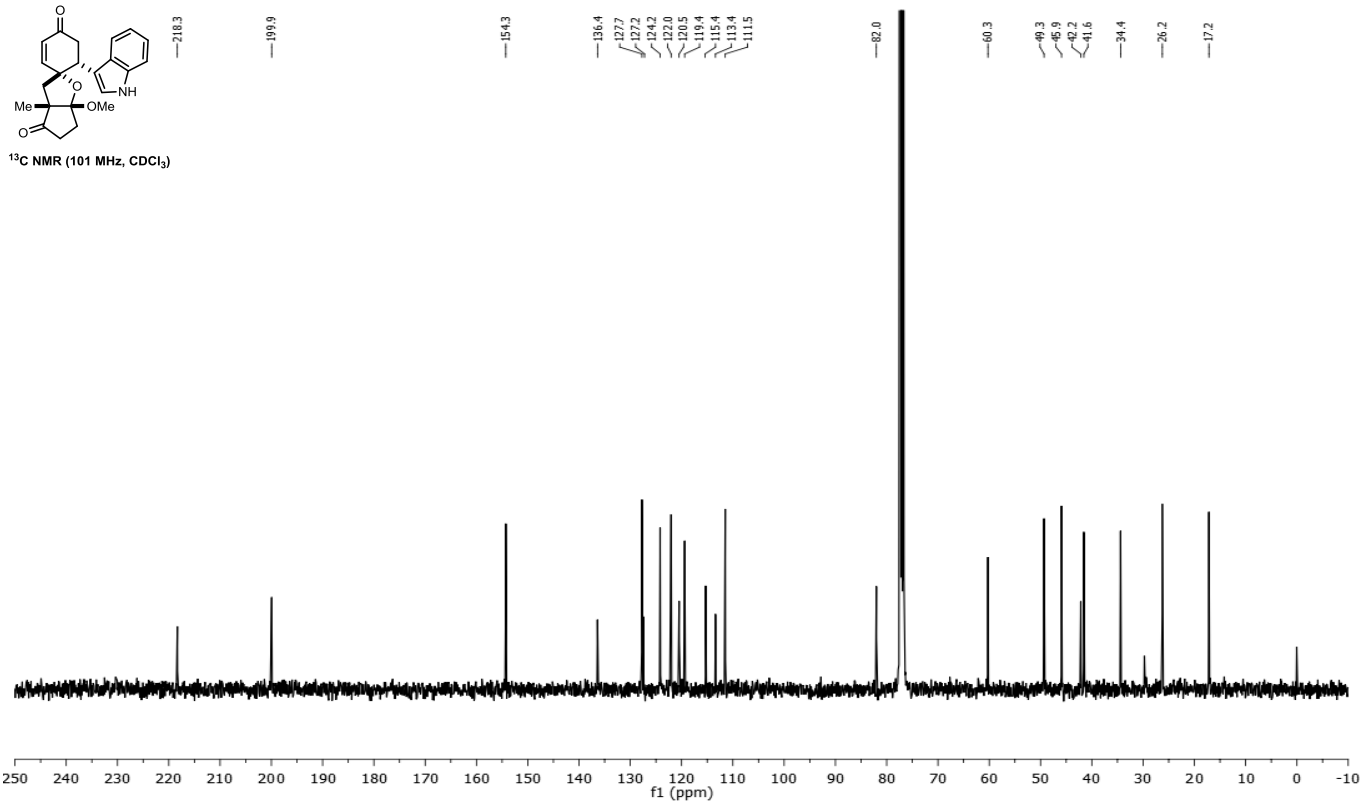


^{13}C NMR (101 MHz, $CDCl_3$)

6-(1*H*-Indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5a):

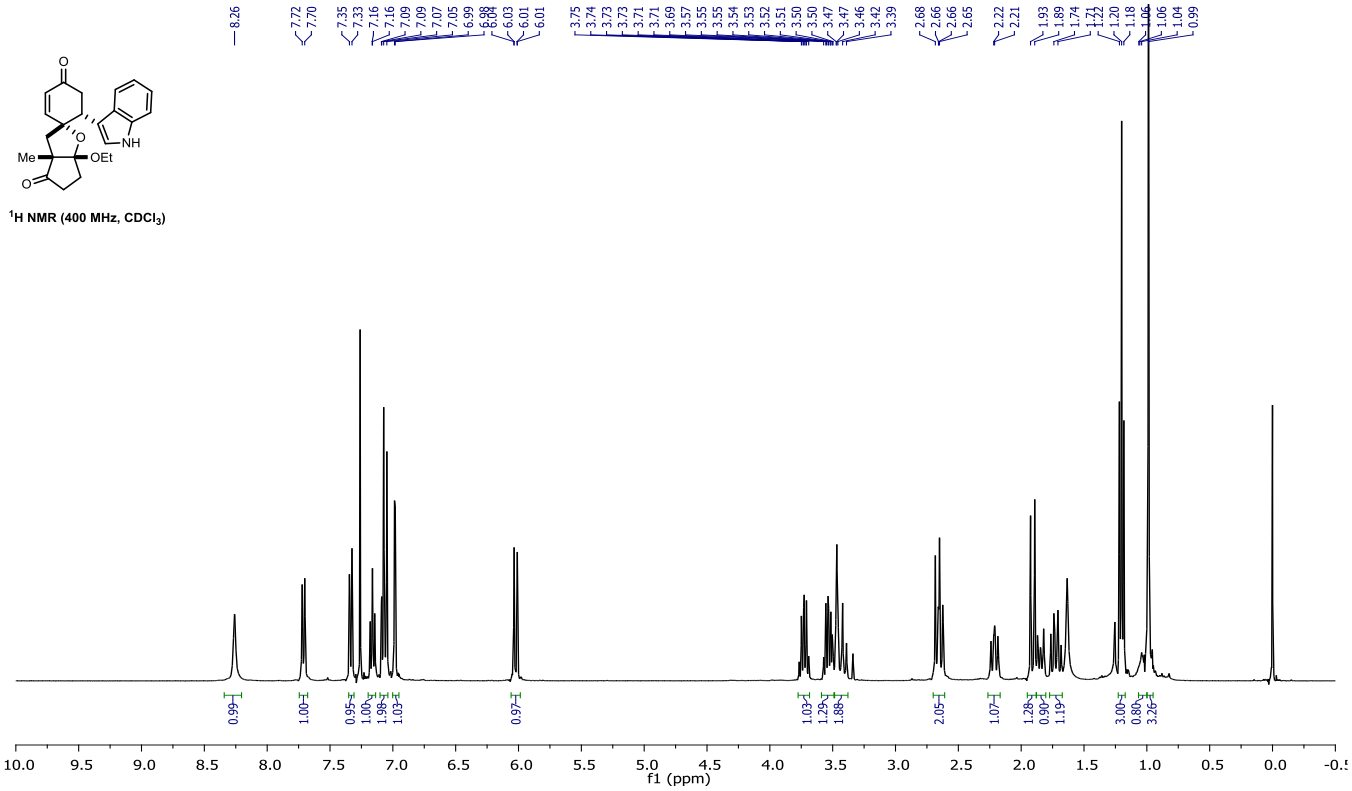


^{1}H NMR (400 MHz, $CDCl_3$)

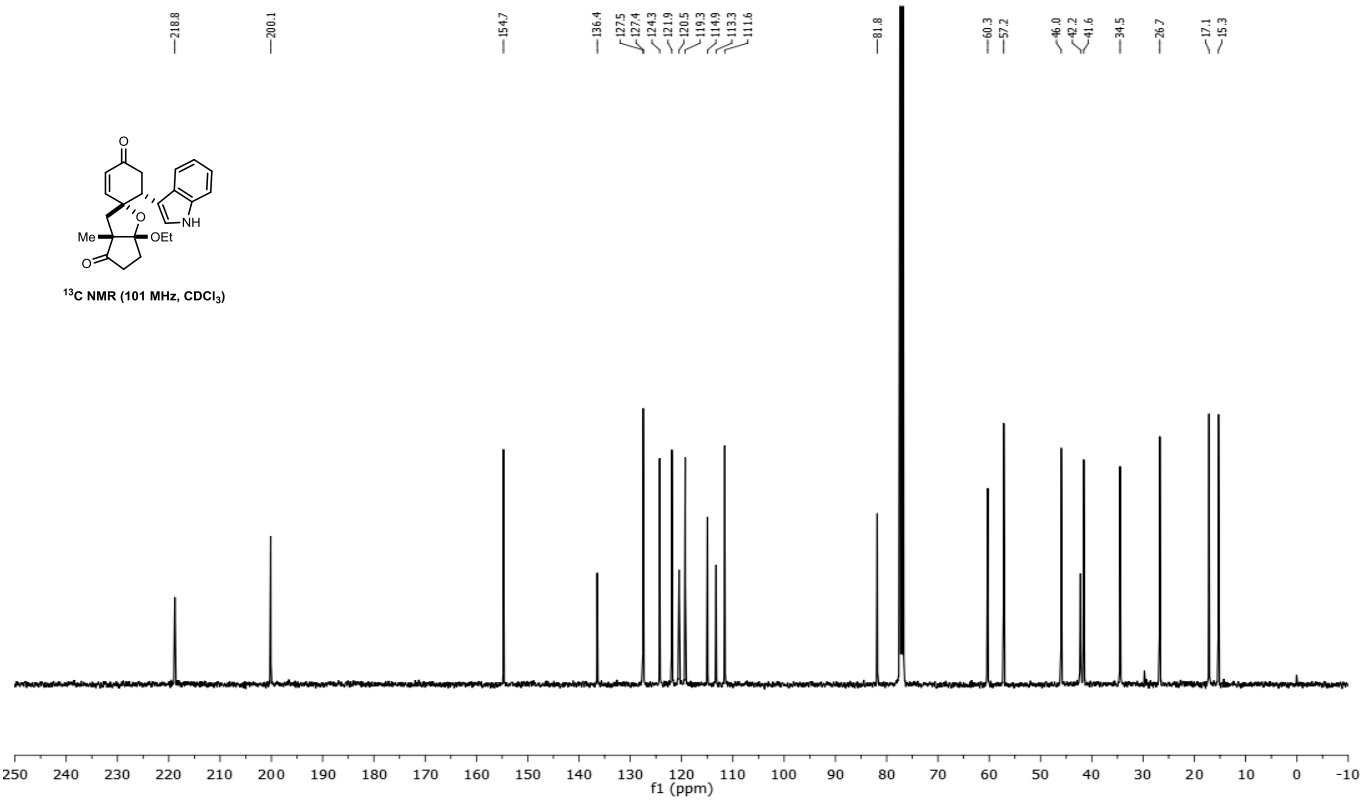


^{13}C NMR (101 MHz, $CDCl_3$)

6a'-Ethoxy-6-(1*H*-indol-3-yl)-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5b):

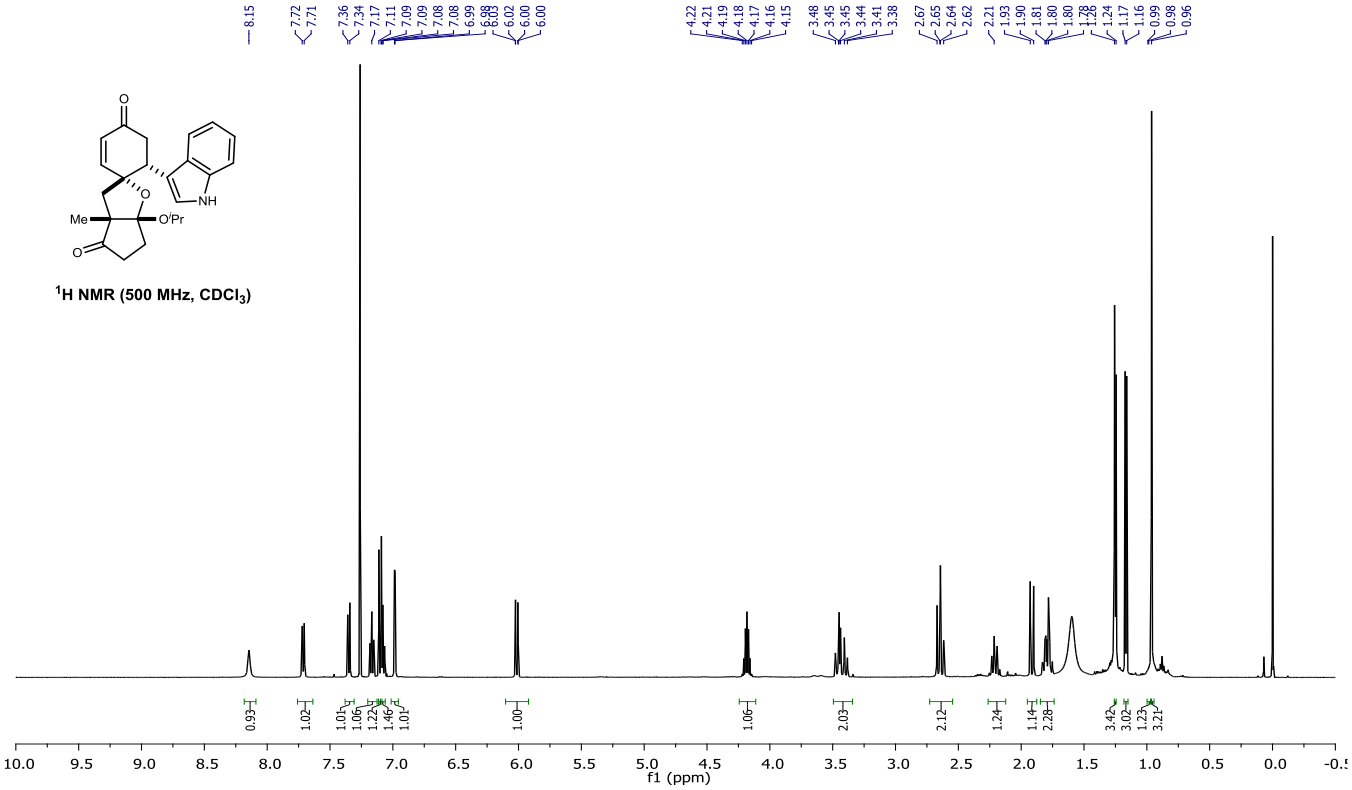


^{1}H NMR (400 MHz, $CDCl_3$)

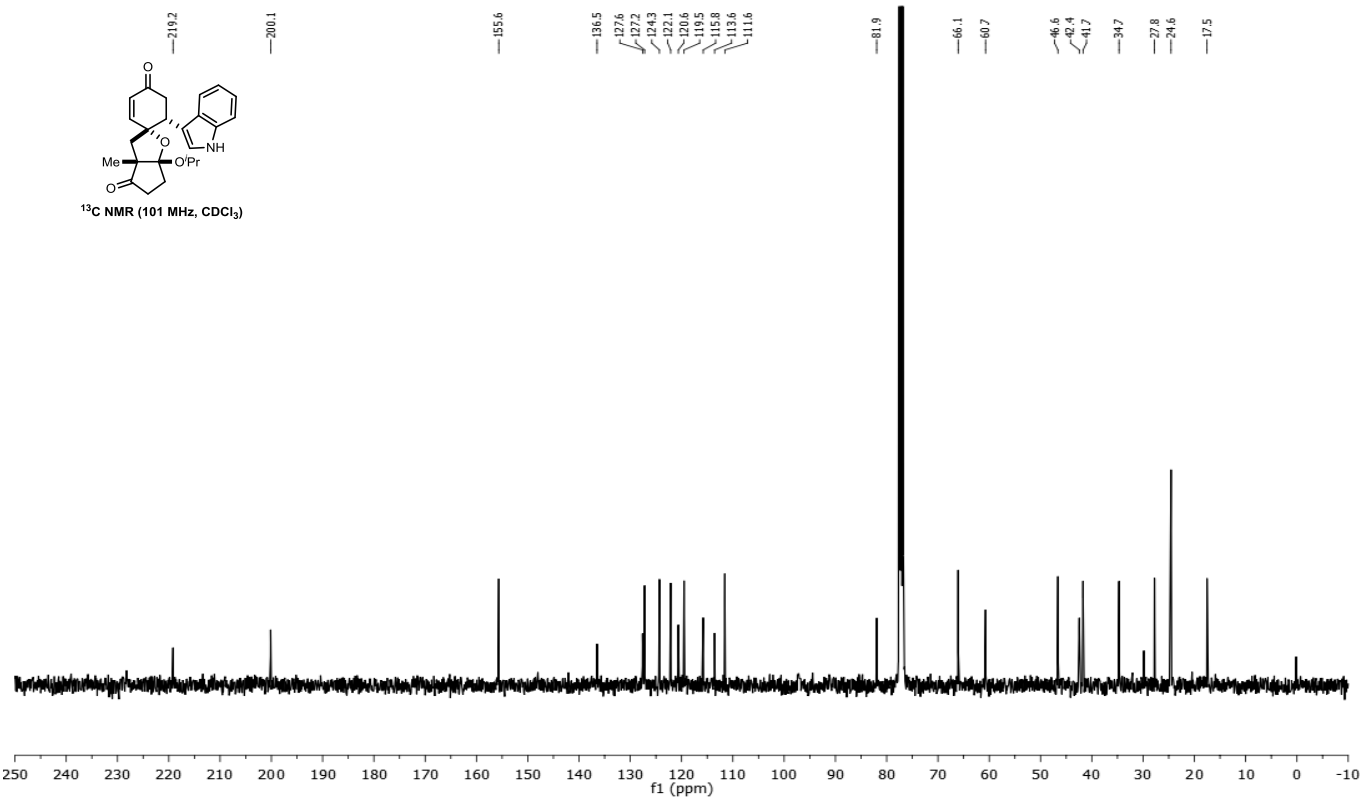


^{13}C NMR (101 MHz, $CDCl_3$)

6-(1H-Indol-3-yl)-6a'-isopropoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5c):

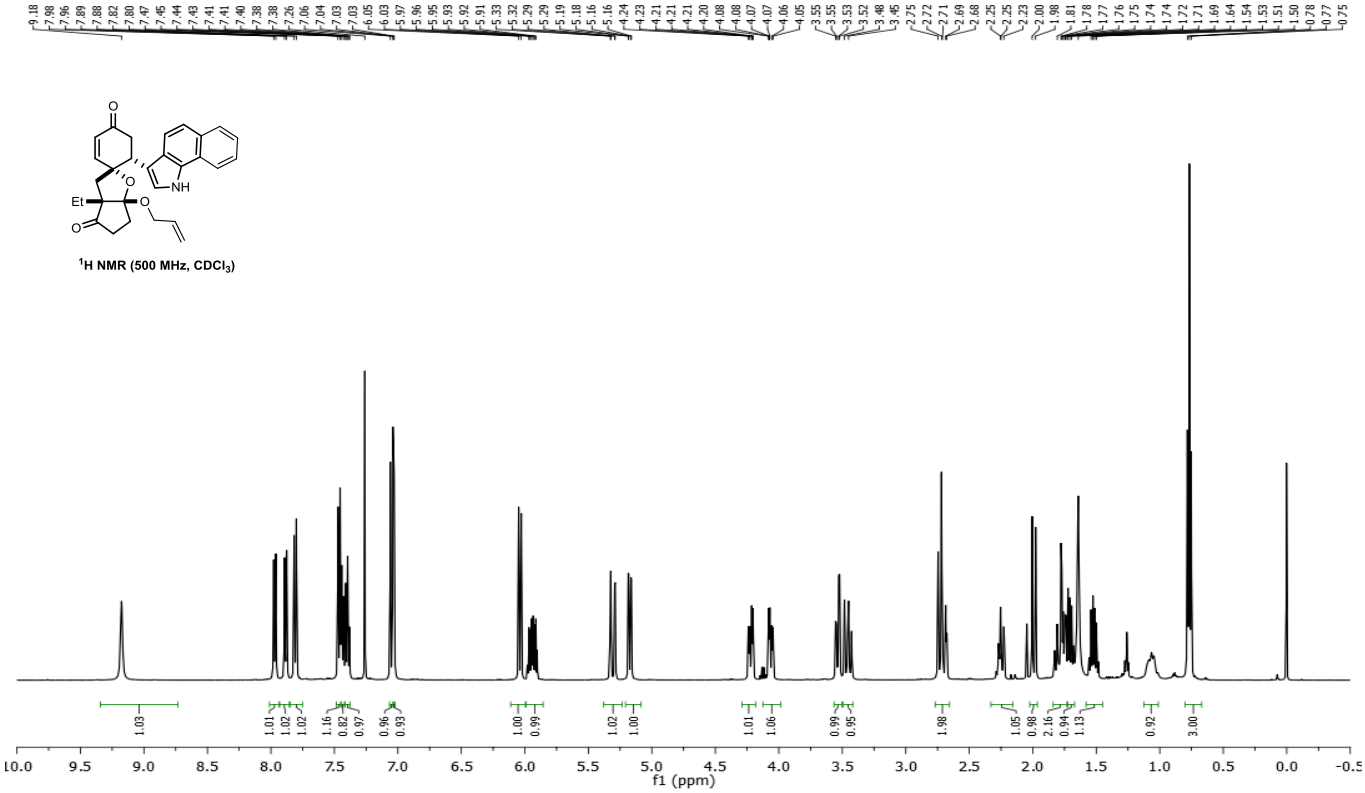


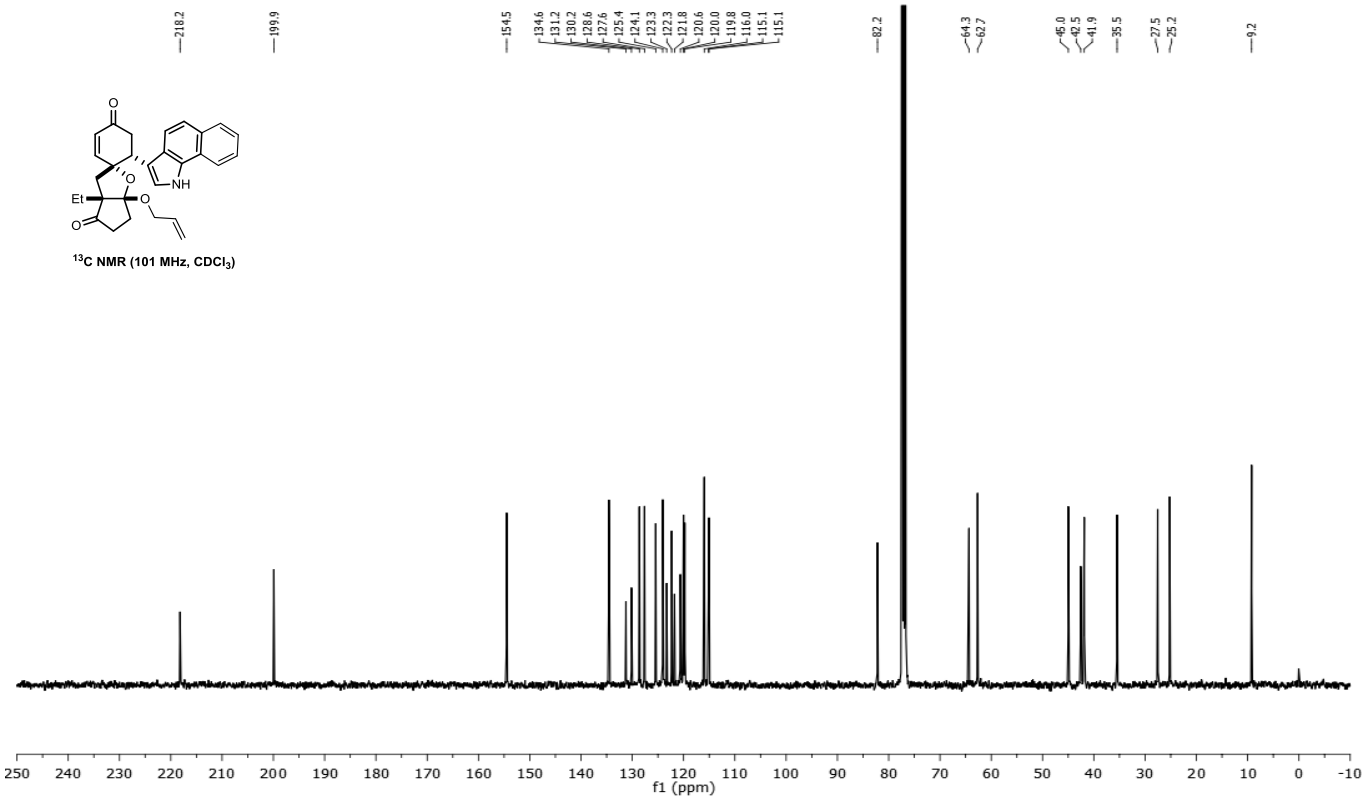
^{1}H NMR (500 MHz, $CDCl_3$)



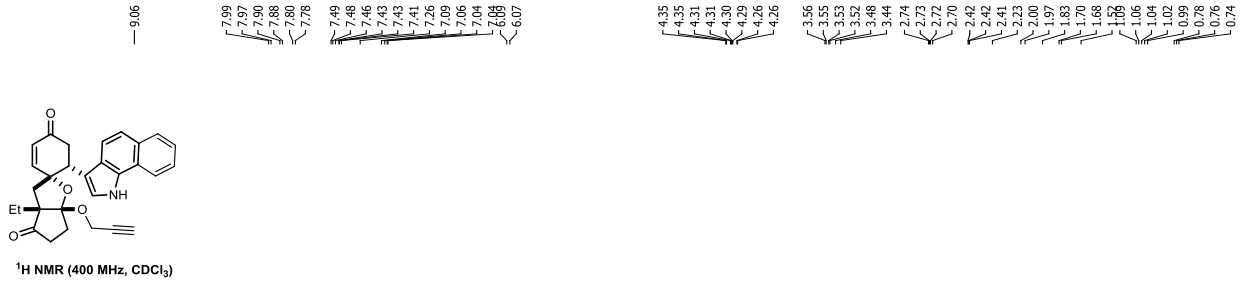
^{13}C NMR (101 MHz, $CDCl_3$)

6a'-(Allyloxy)-6-(1*H*-benzo[g]indol-3-yl)-3a'-ethyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5d):

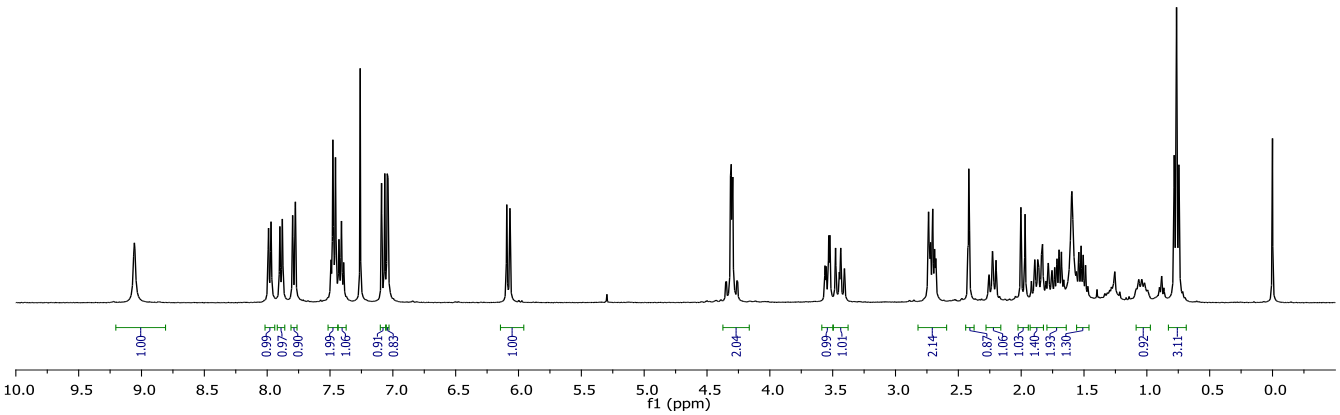


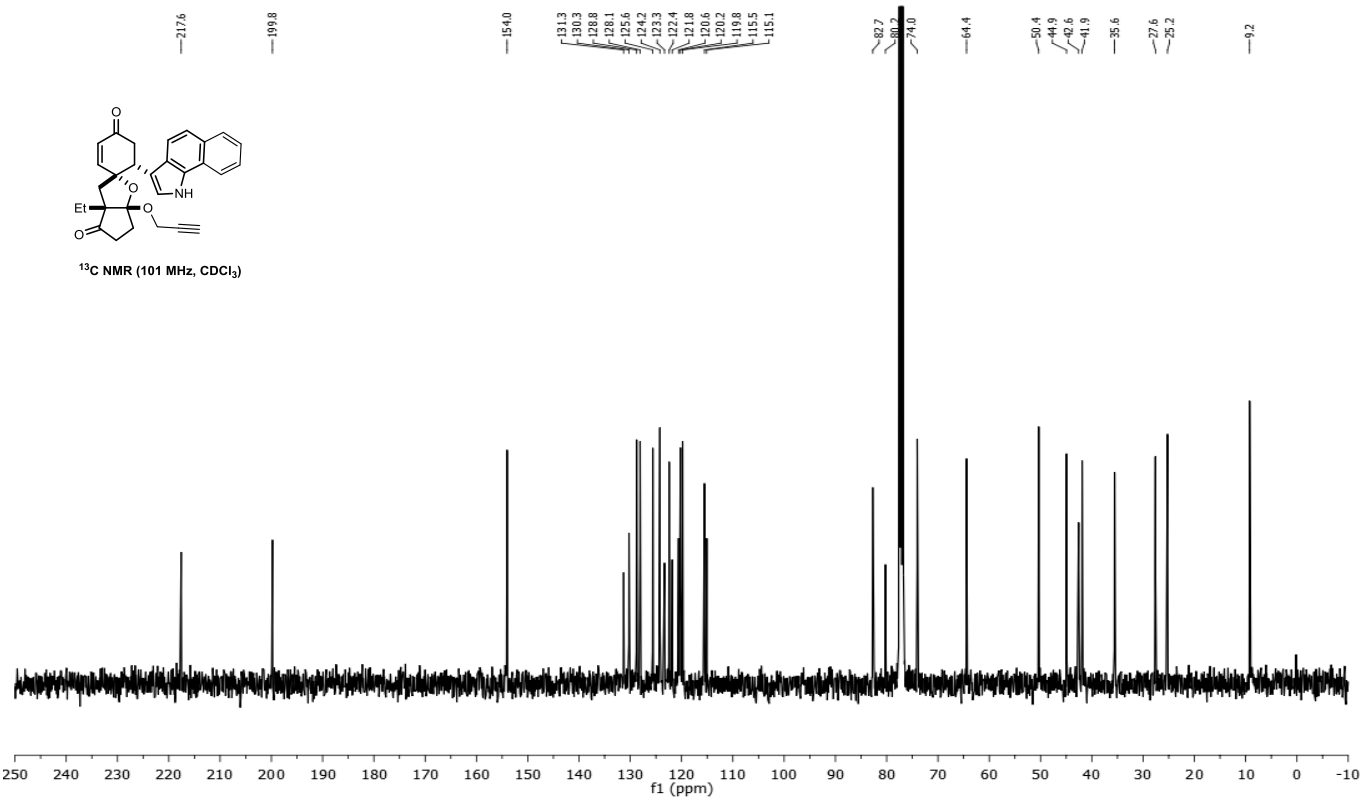


6-(1*H*-Benzo[*g*]indol-3-yl)-3a'-ethyl-6a'-(prop-2-yn-1-yloxy)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5e):



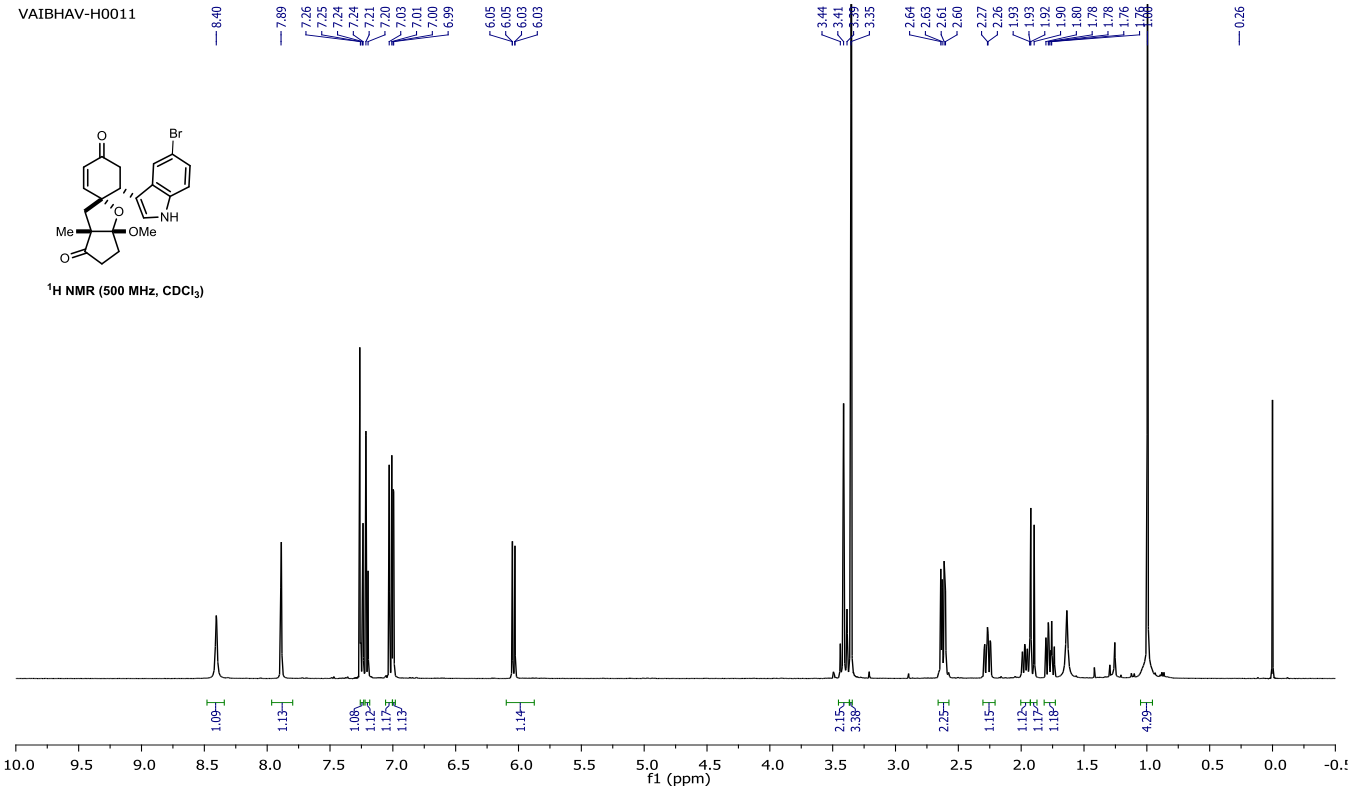
^{1}H NMR (400 MHz, $CDCl_3$)

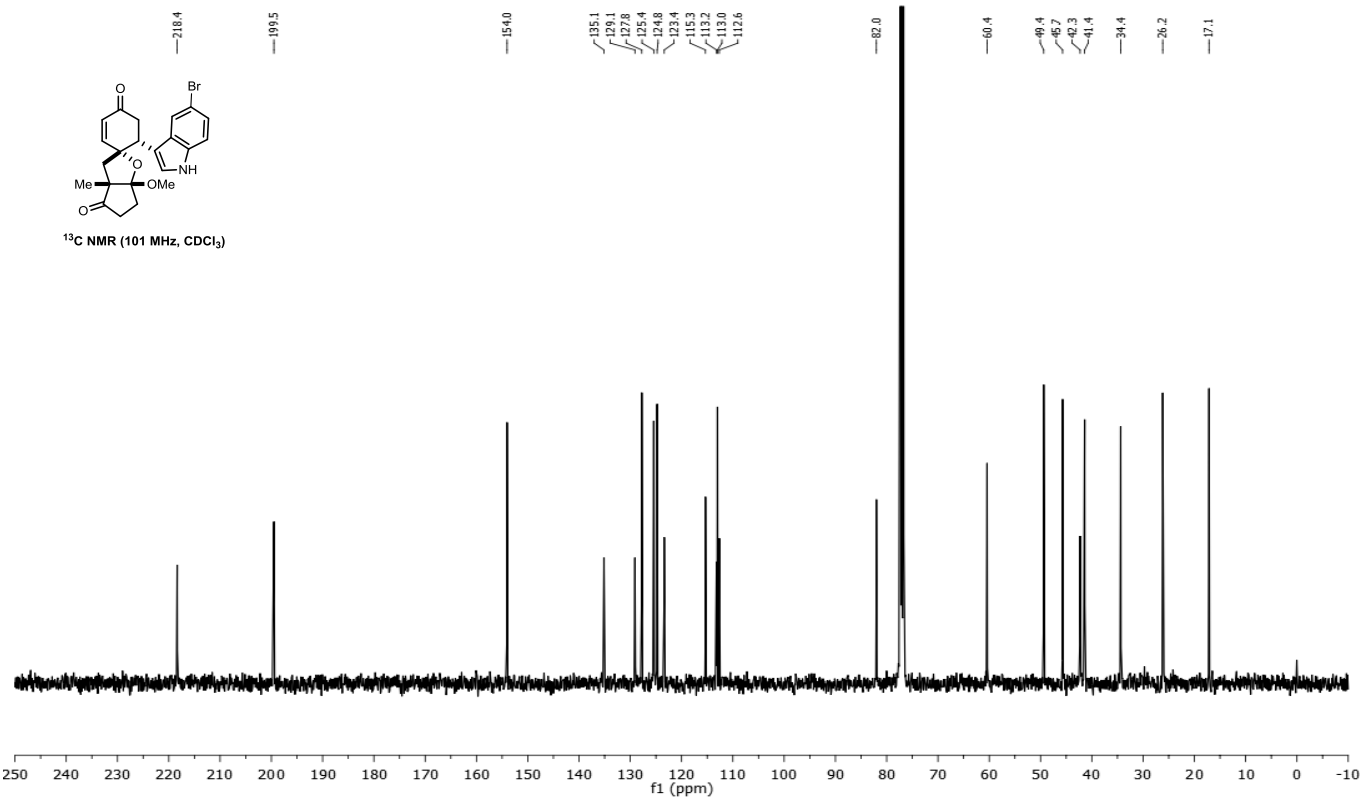




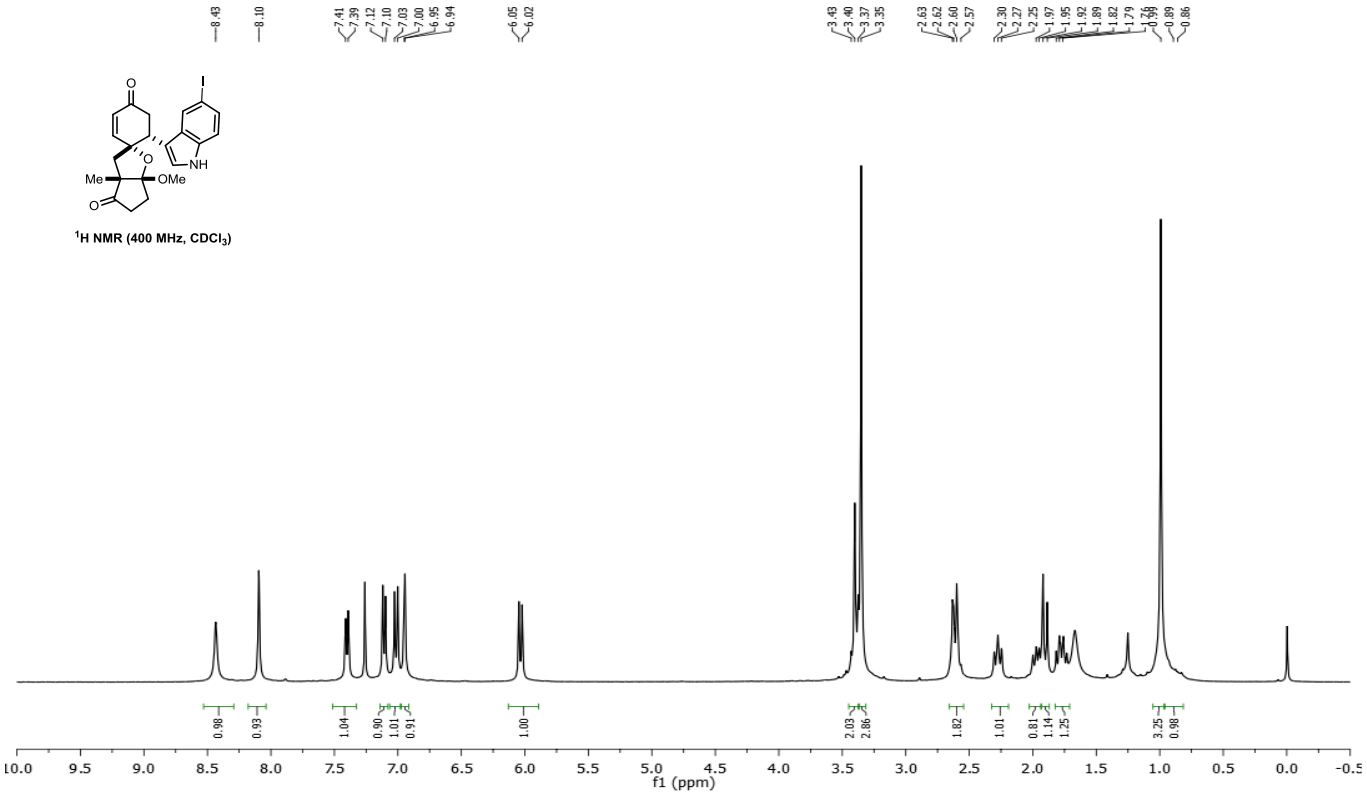
^{13}C NMR (101 MHz, $CDCl_3$)

6-(5-Bromo-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5f):

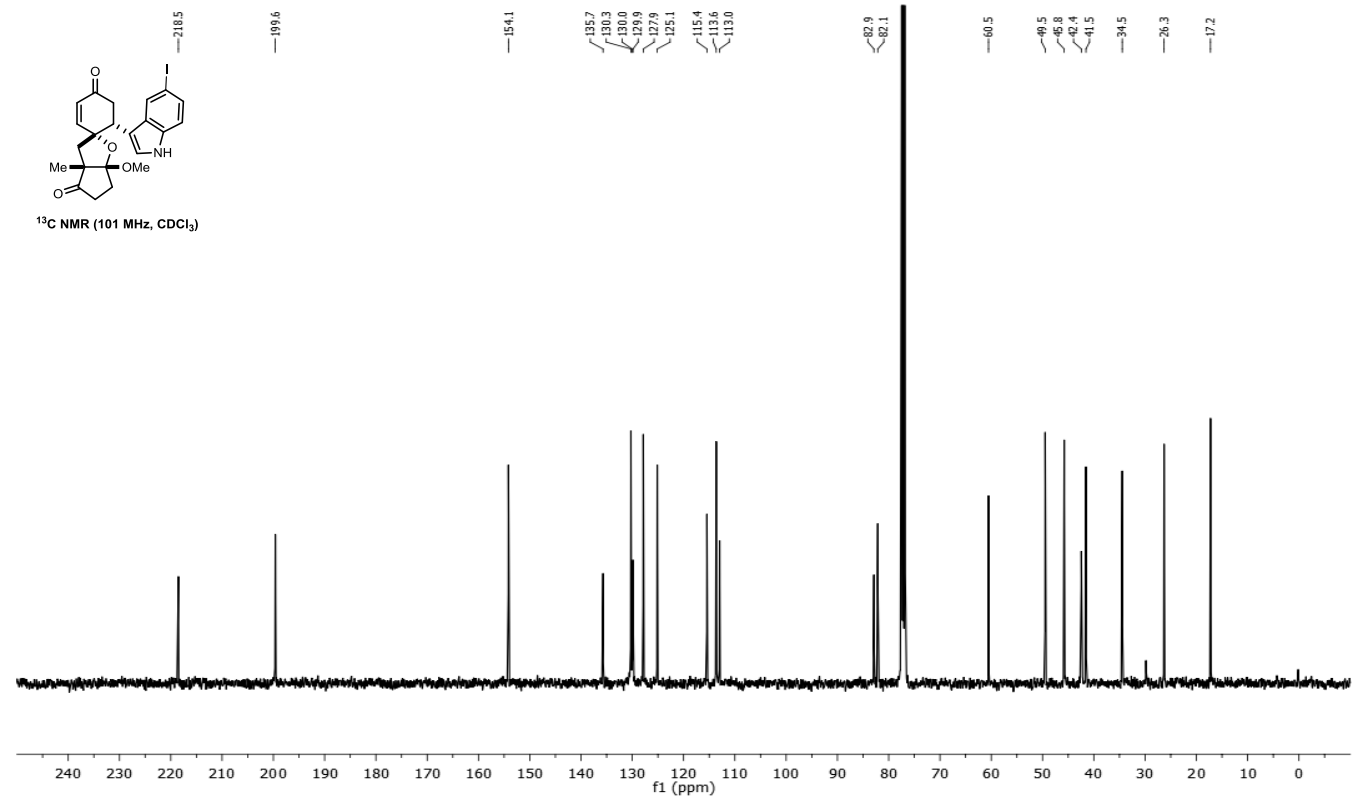




6-(5-Iodo-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5g):

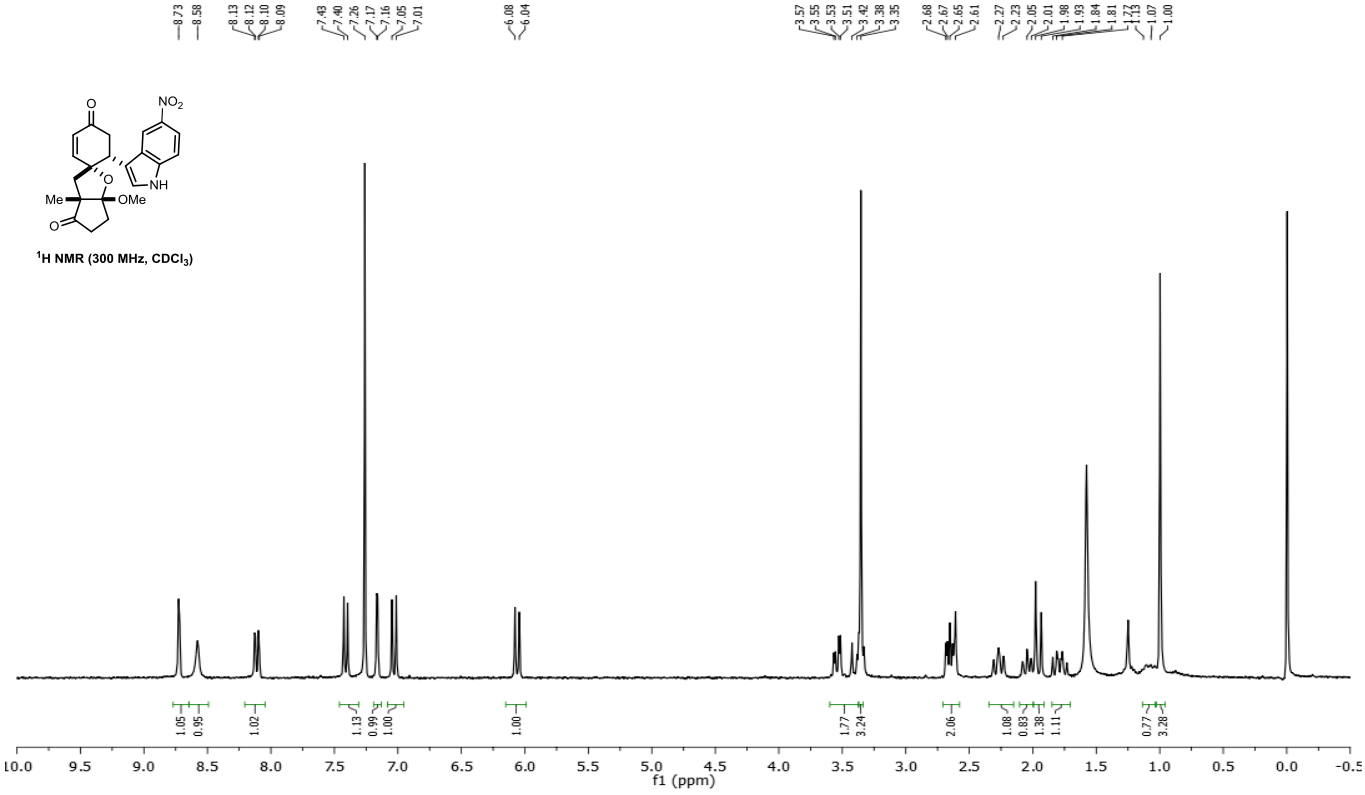


^{1}H NMR (400 MHz, $CDCl_3$)

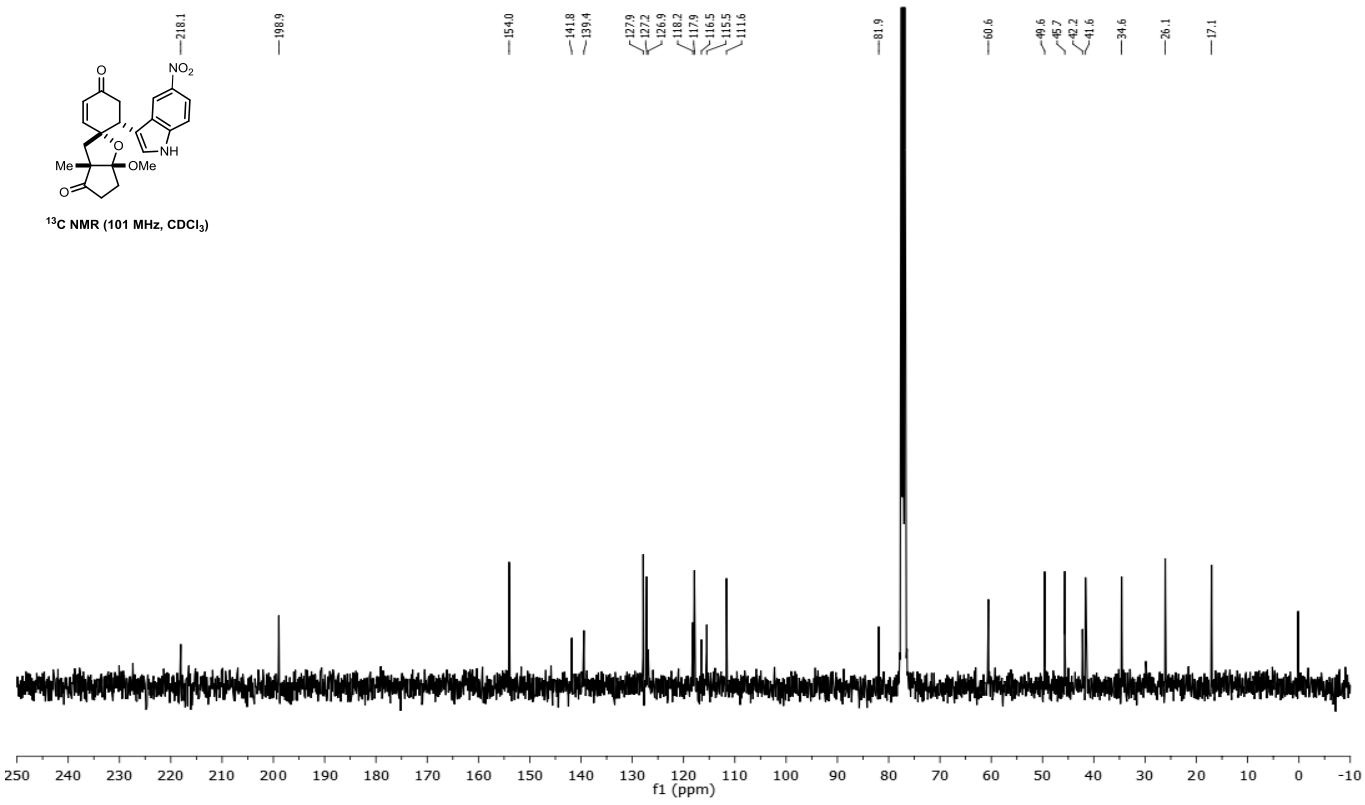


^{13}C NMR (101 MHz, $CDCl_3$)

6a'-Methoxy-3a'-methyl-6-(5-nitro-1*H*-indol-3-yl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5h):

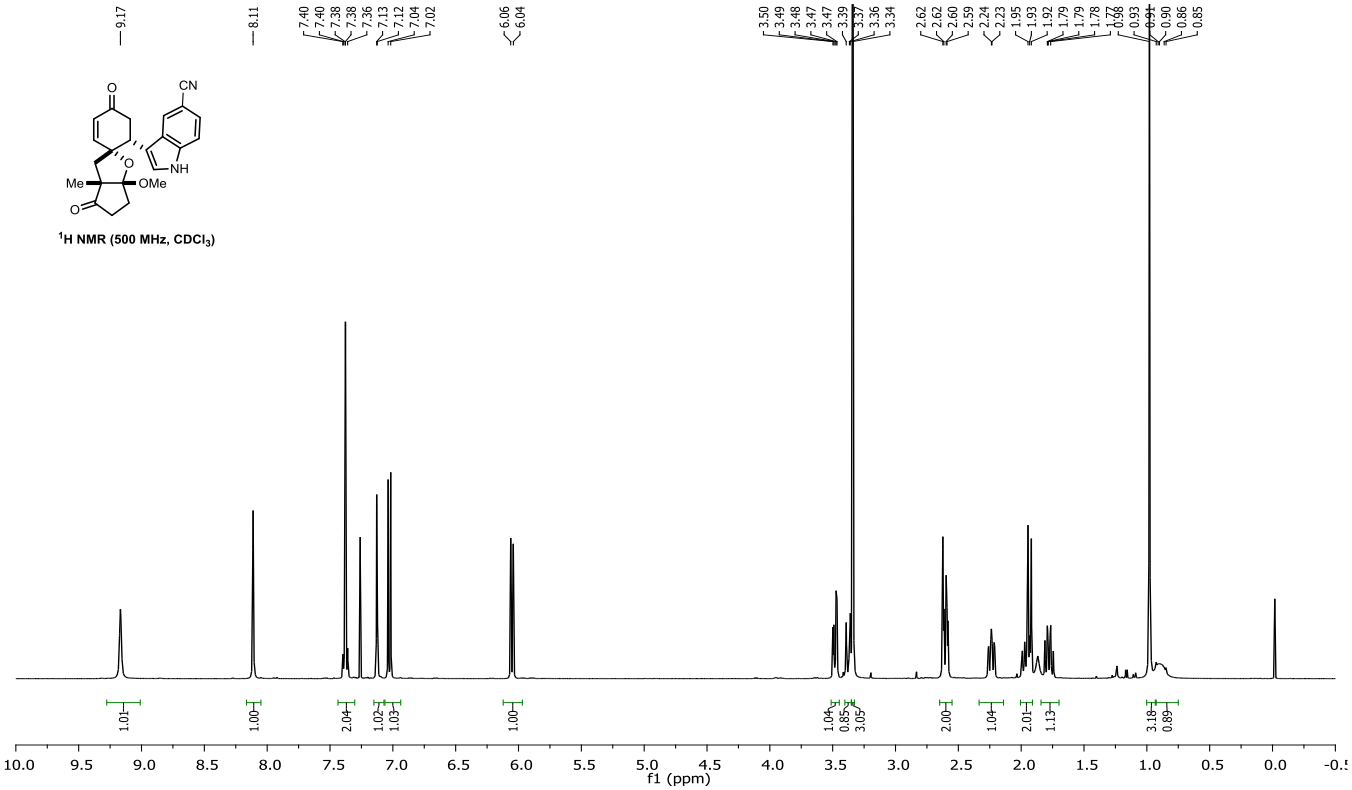


^{1}H NMR (300 MHz, $CDCl_3$)

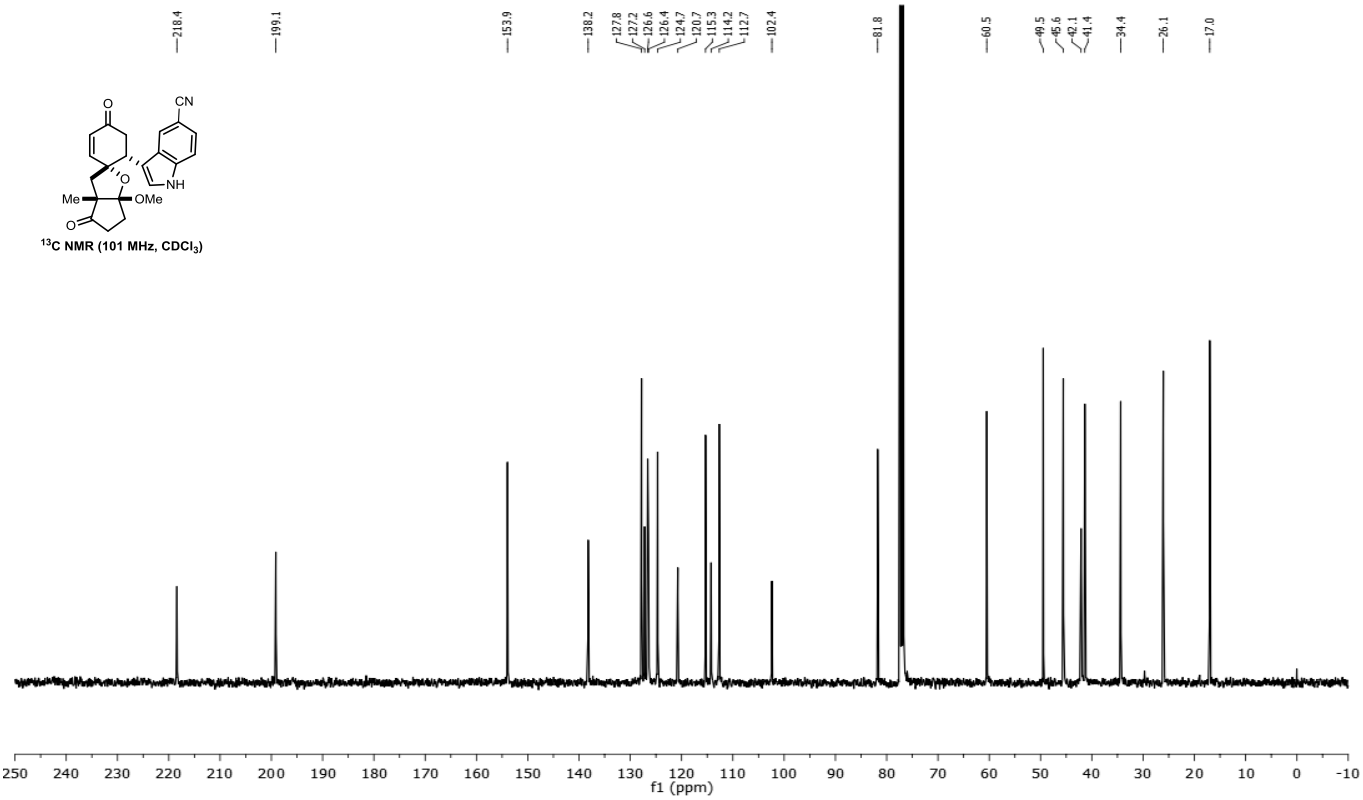


^{13}C NMR (101 MHz, $CDCl_3$)

6a'-Methoxy-3a'-methyl-4,4'-dioxo-3',3a',4',5',6',6a'-hexahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-en-6-yl)-1*H*-indole-5-carbonitrile (5i):

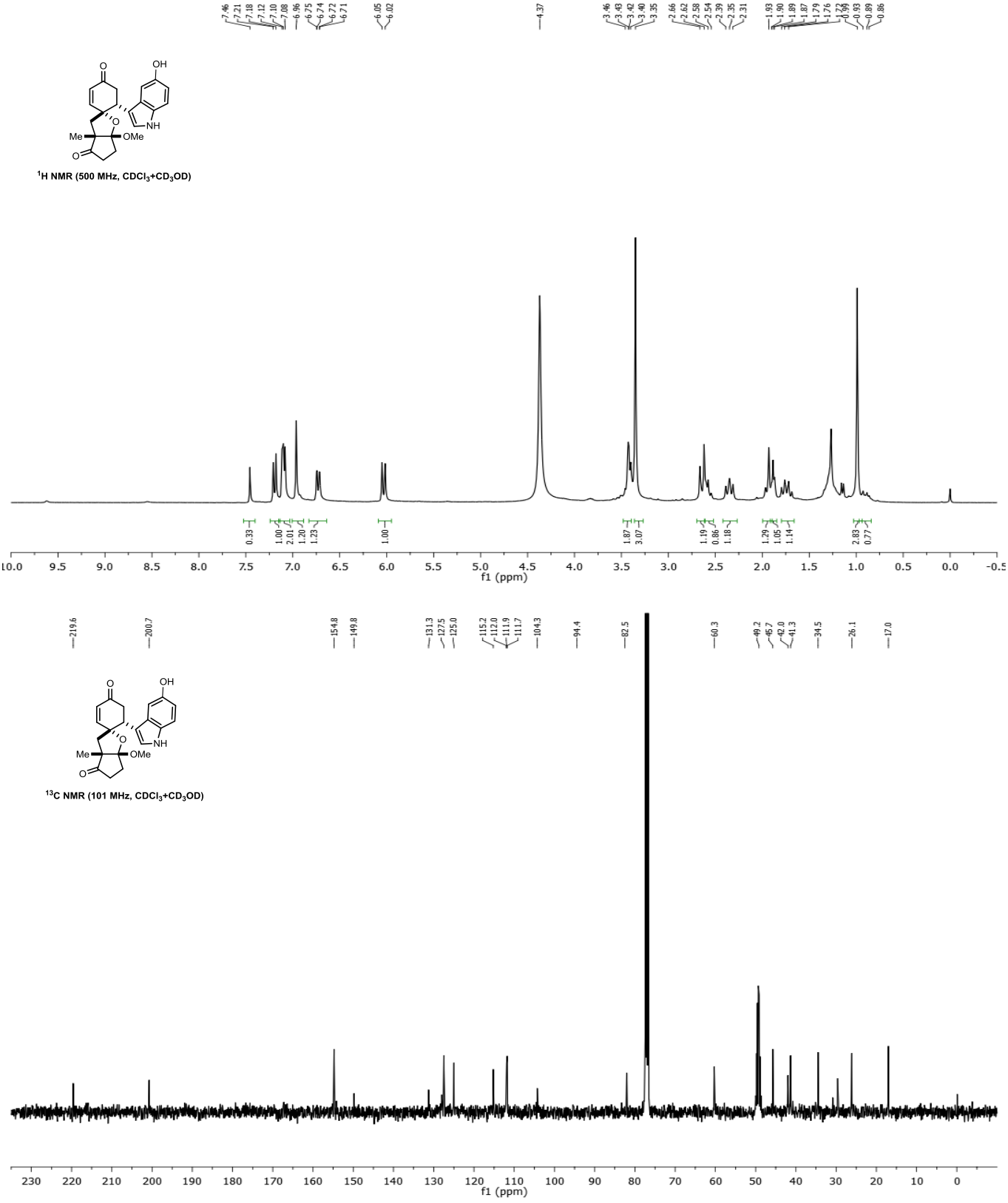


^{1}H NMR (500 MHz, $CDCl_3$)

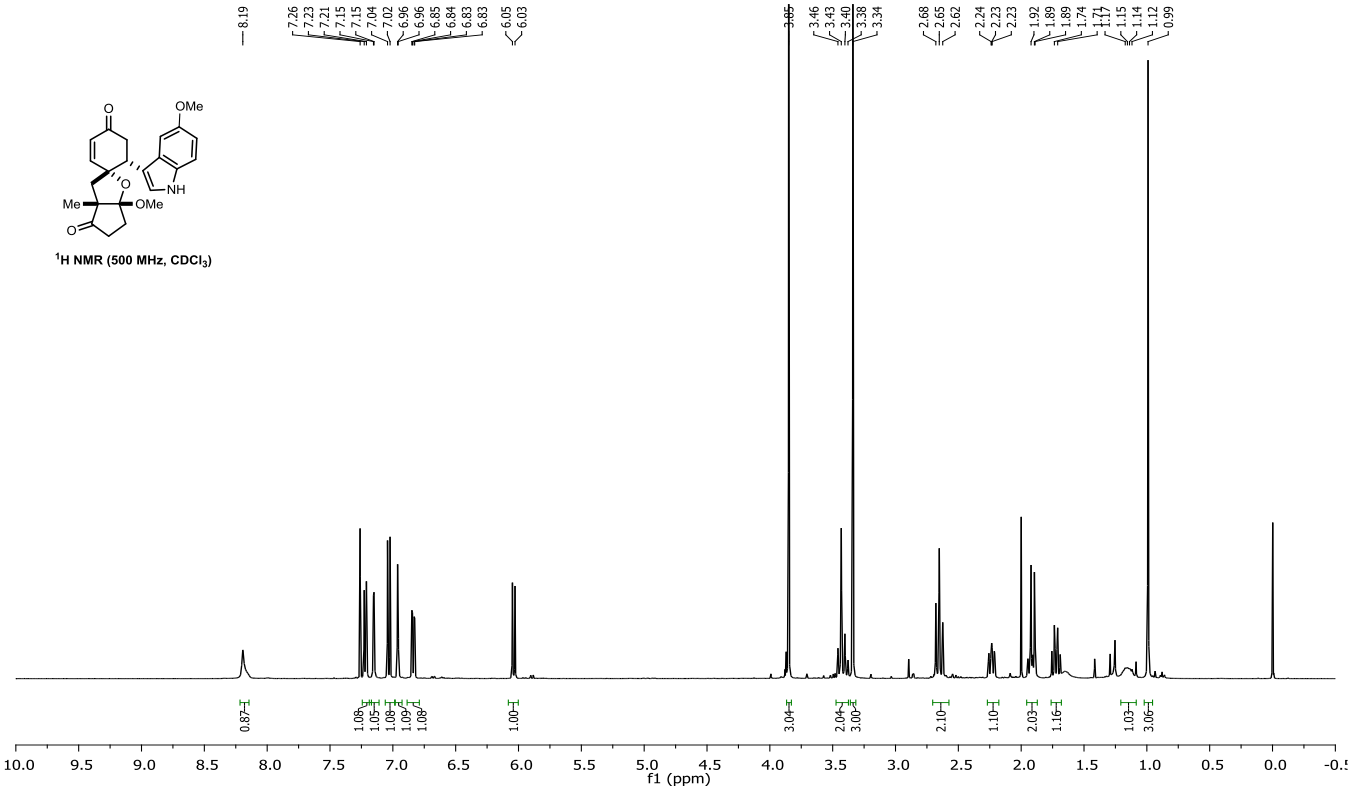


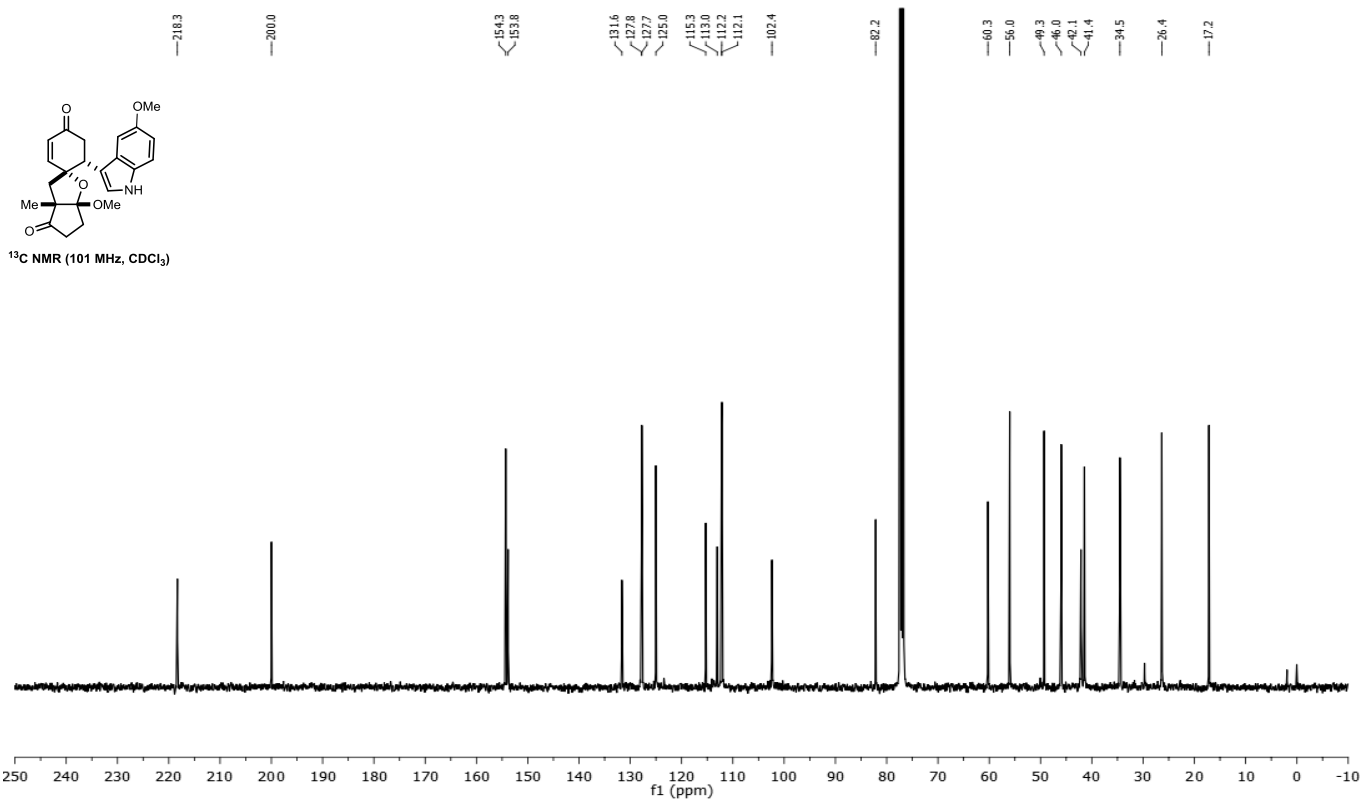
^{13}C NMR (101 MHz, $CDCl_3$)

6-(5-Hydroxy-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5j):

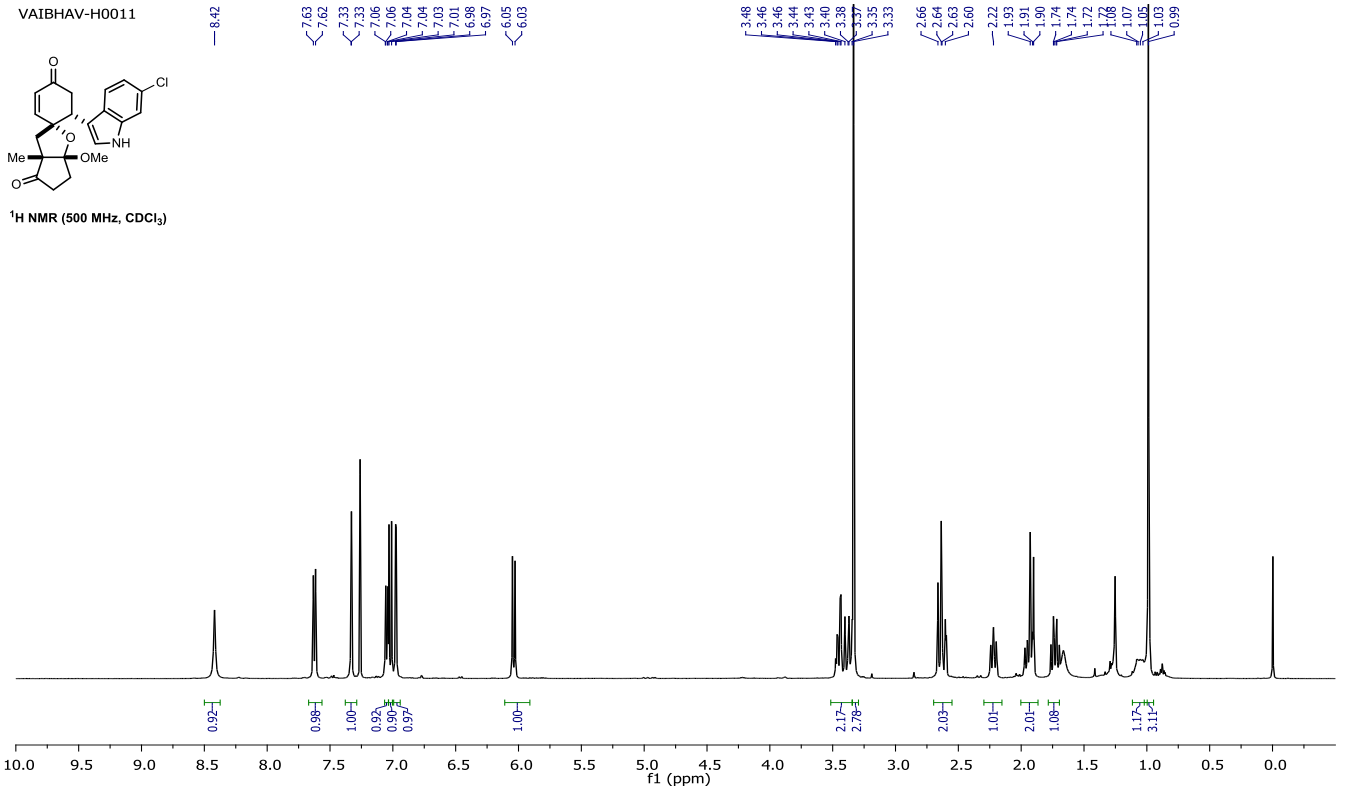


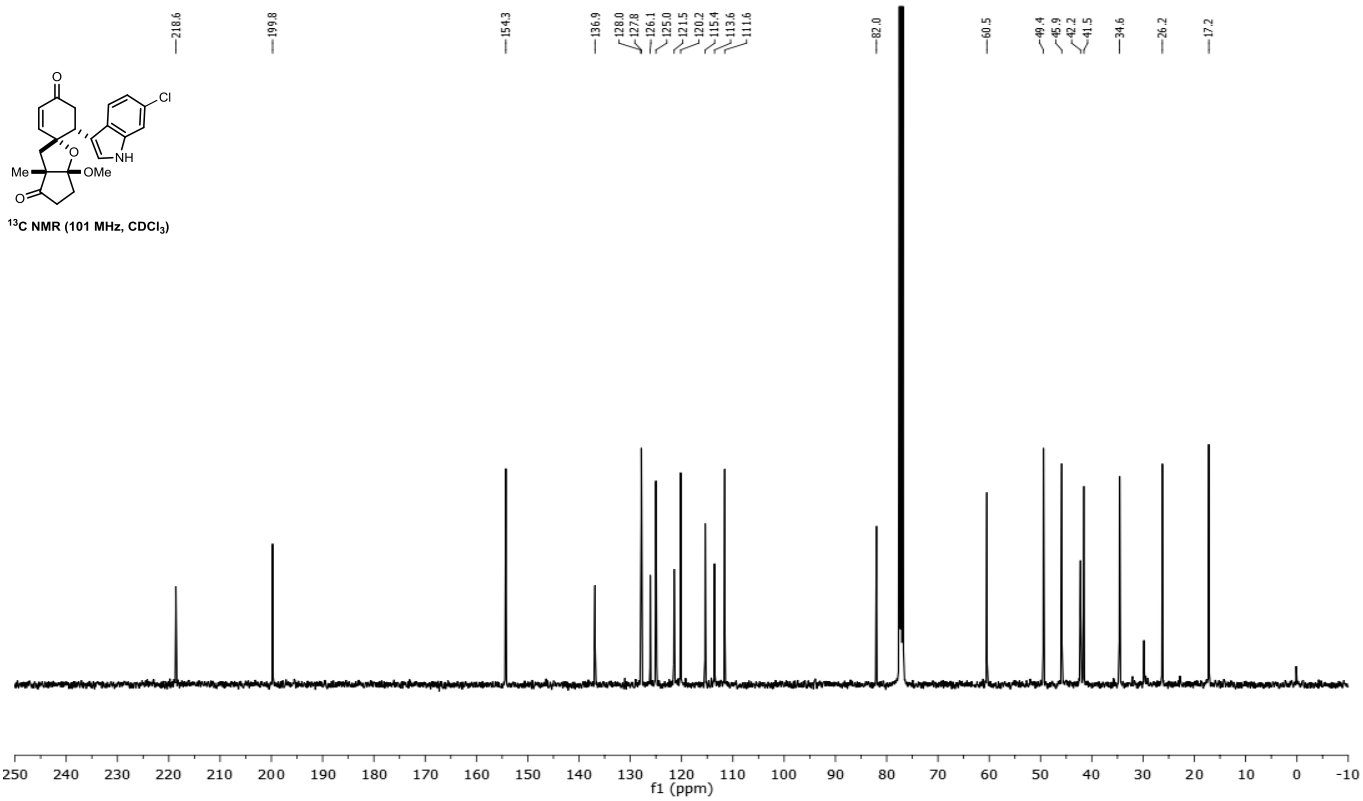
6a'-Methoxy-6-(5-methoxy-1*H*-indol-3-yl)-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5k):



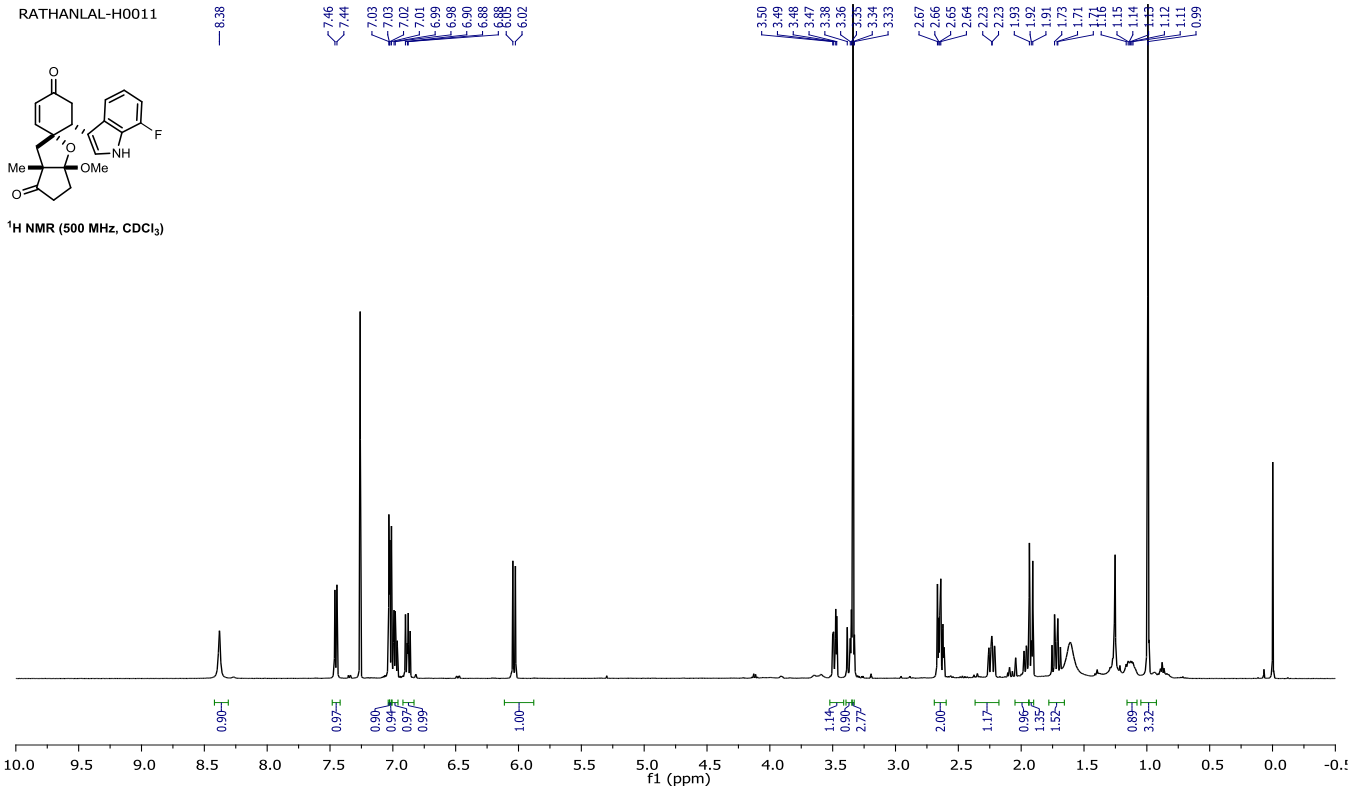


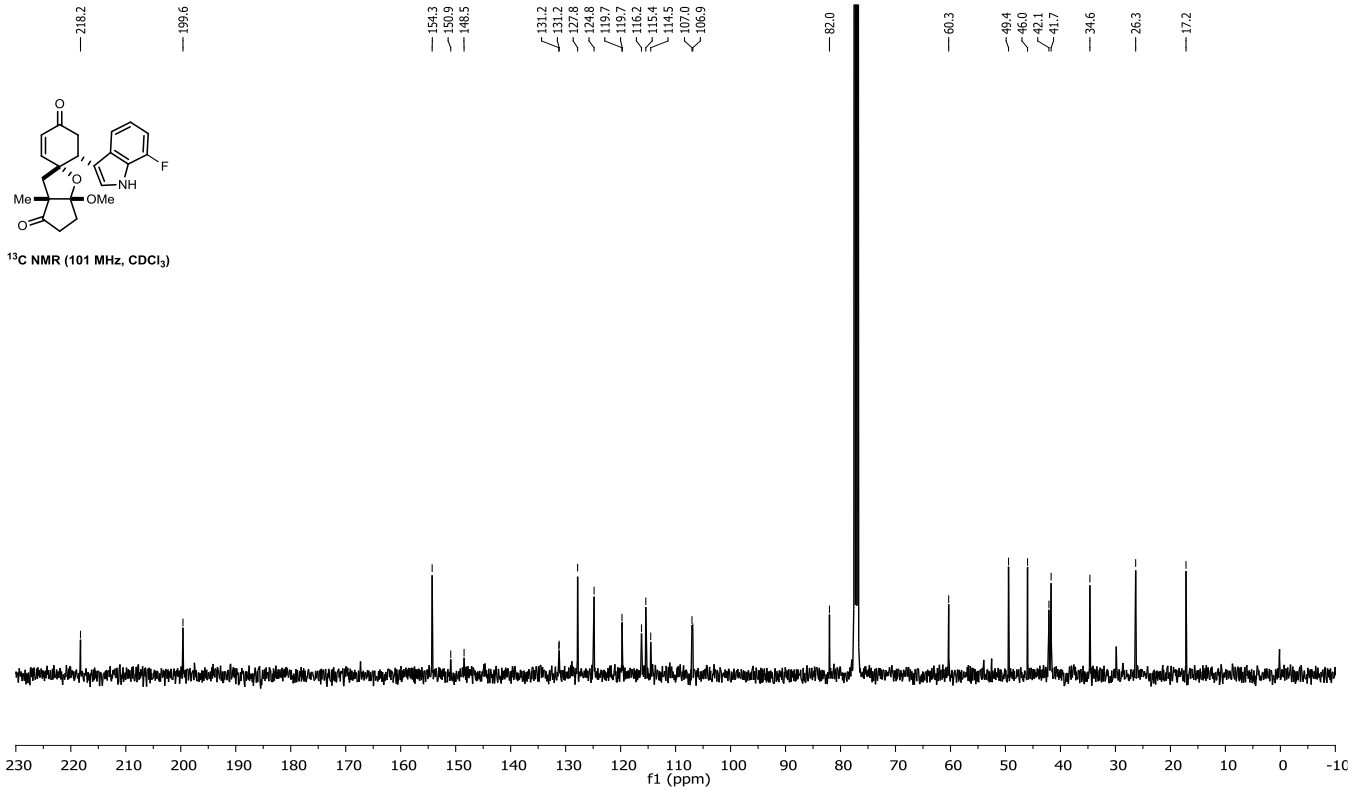
6-(6-Chloro-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5l):

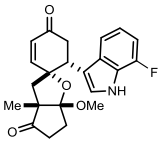




6-(7-Fluoro-1*H*-indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5m):

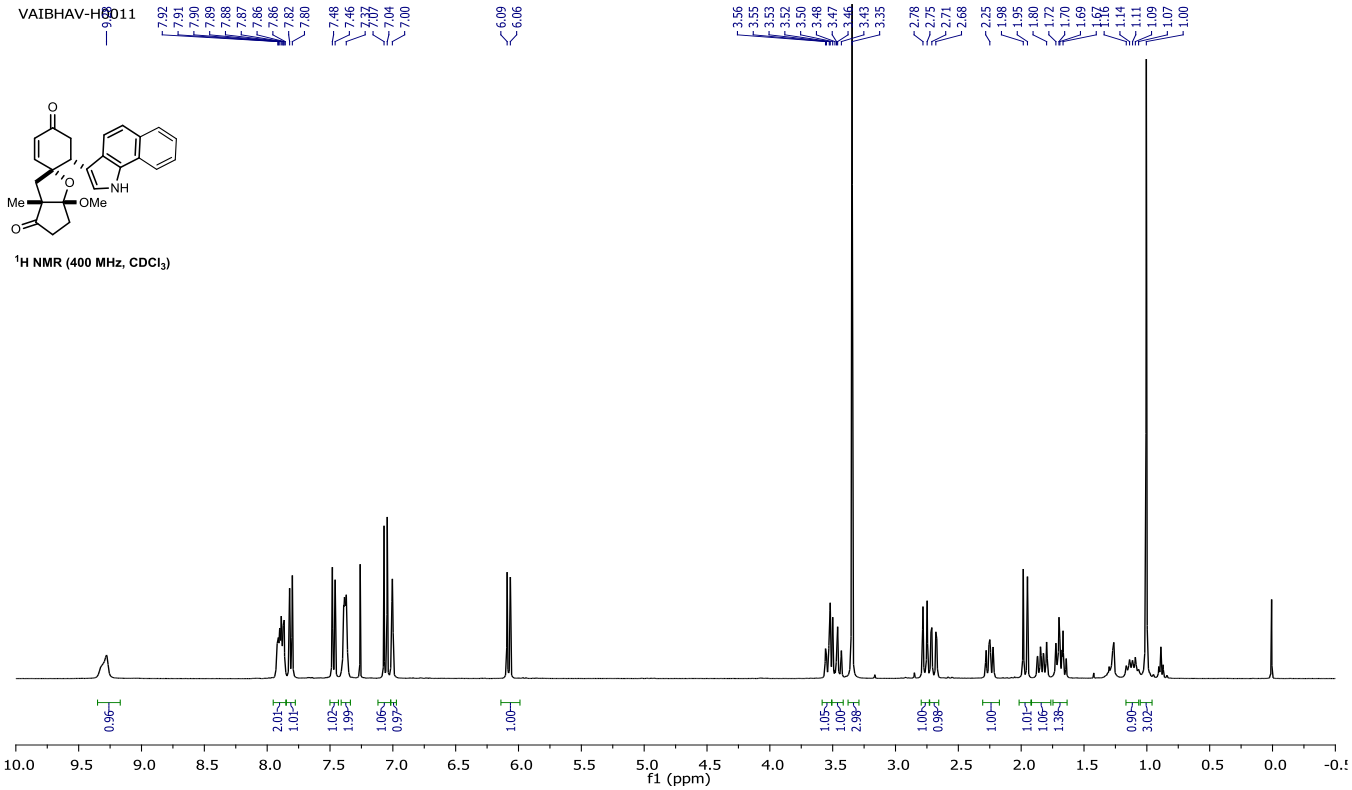


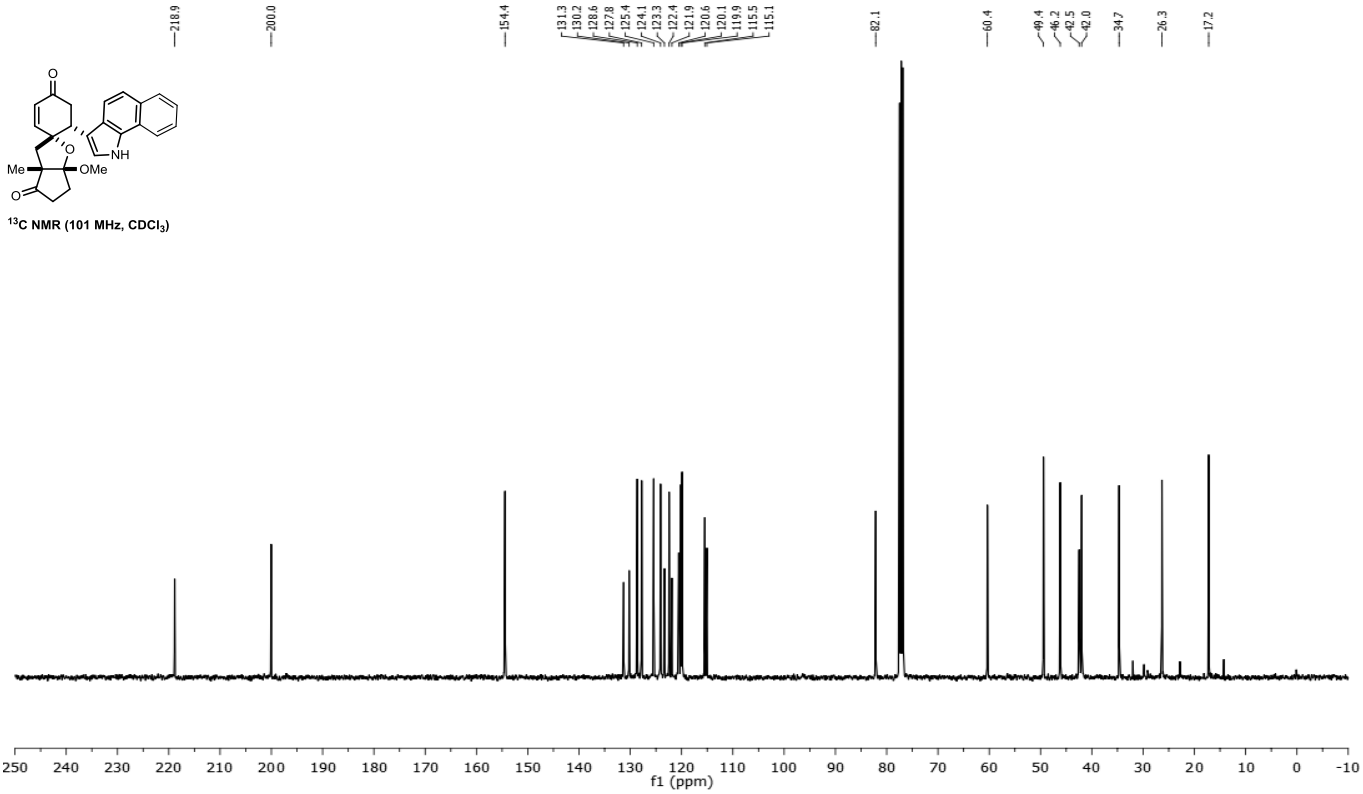




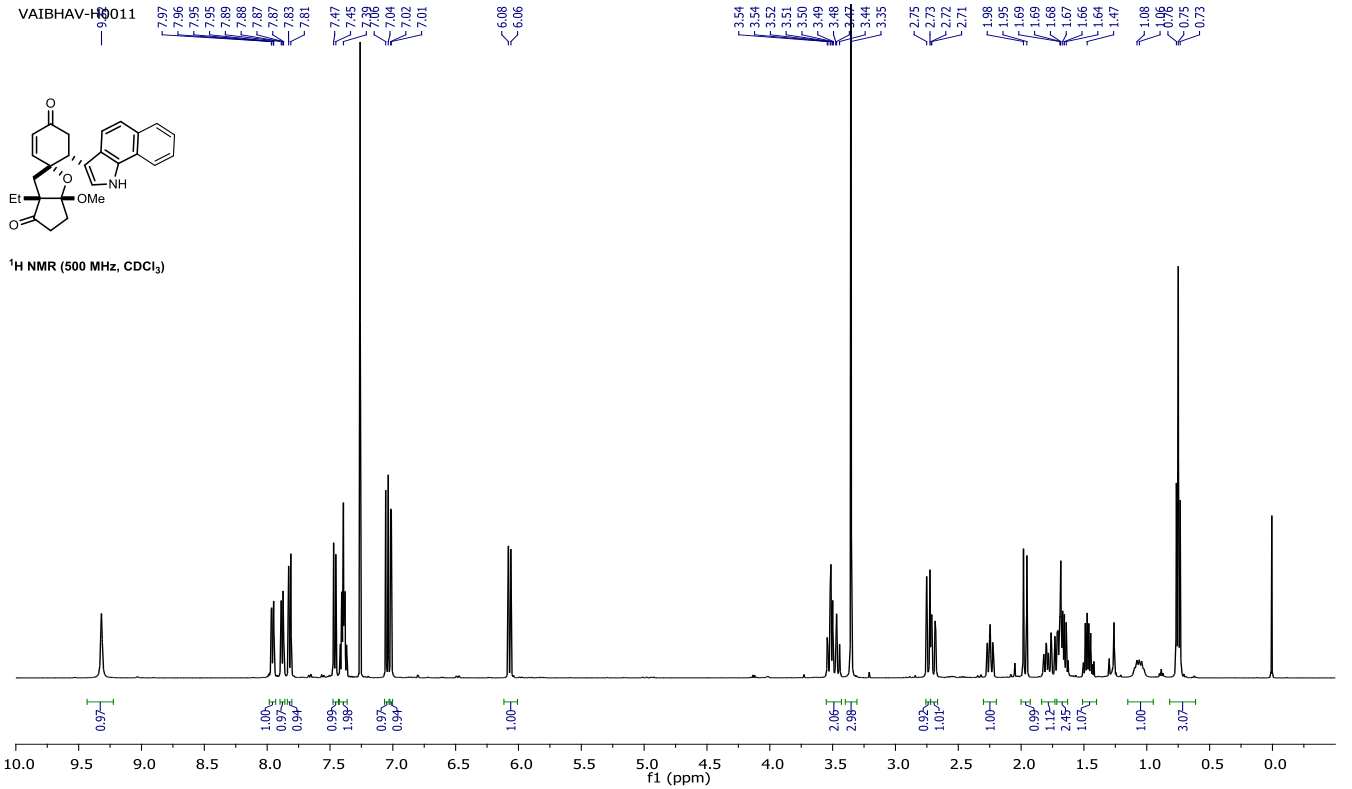
^{19}F NMR (377 MHz, $CDCl_3$)

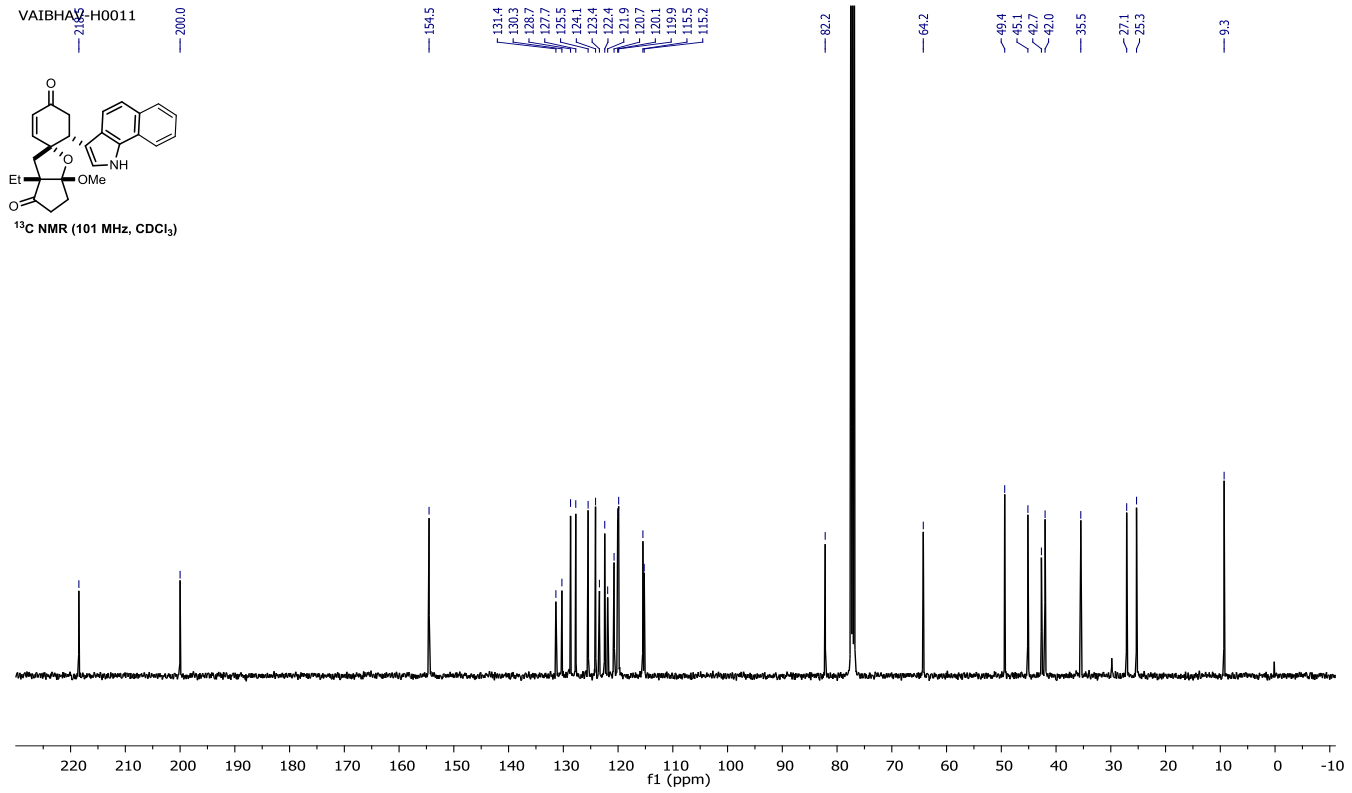
6-(1H-Benzo[*g*]indol-3-yl)-6a'-methoxy-3a'-methyl-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5n):



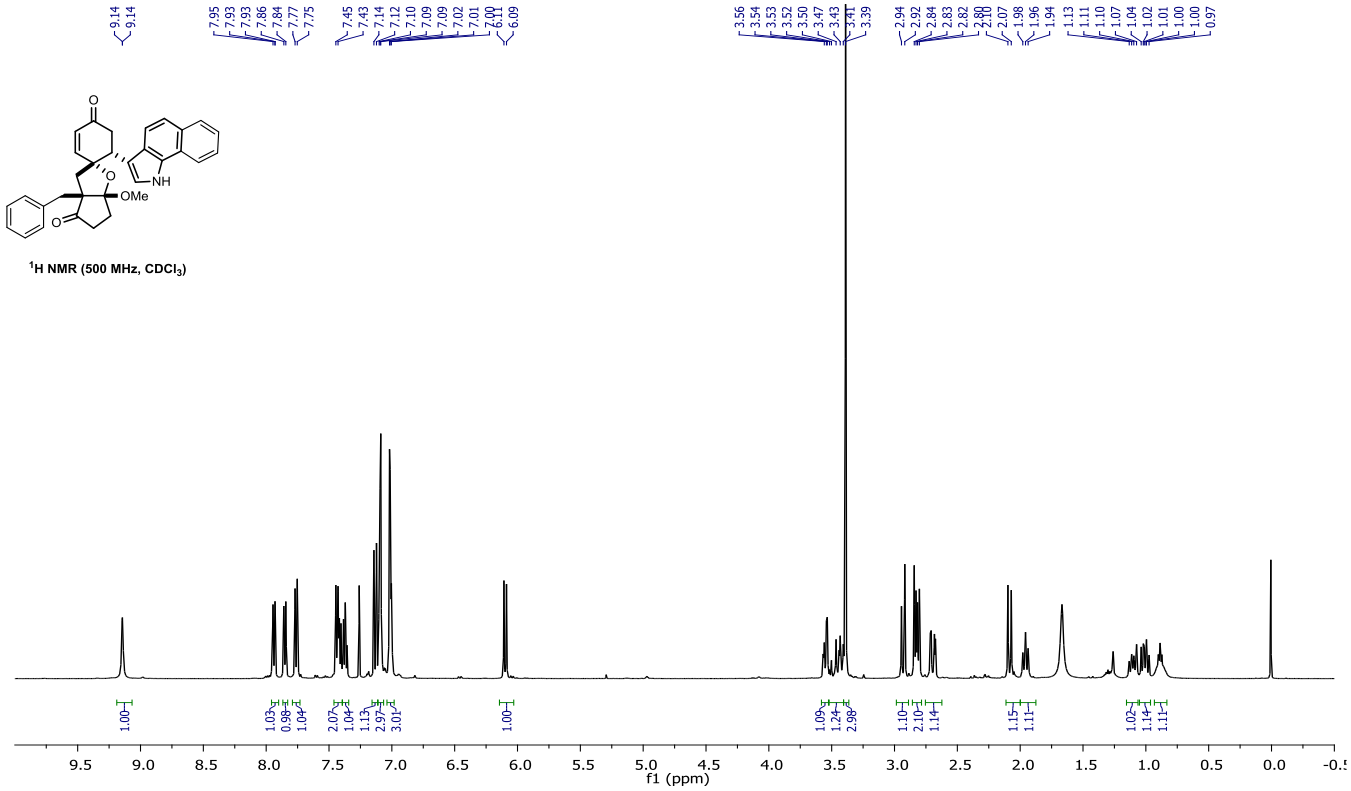


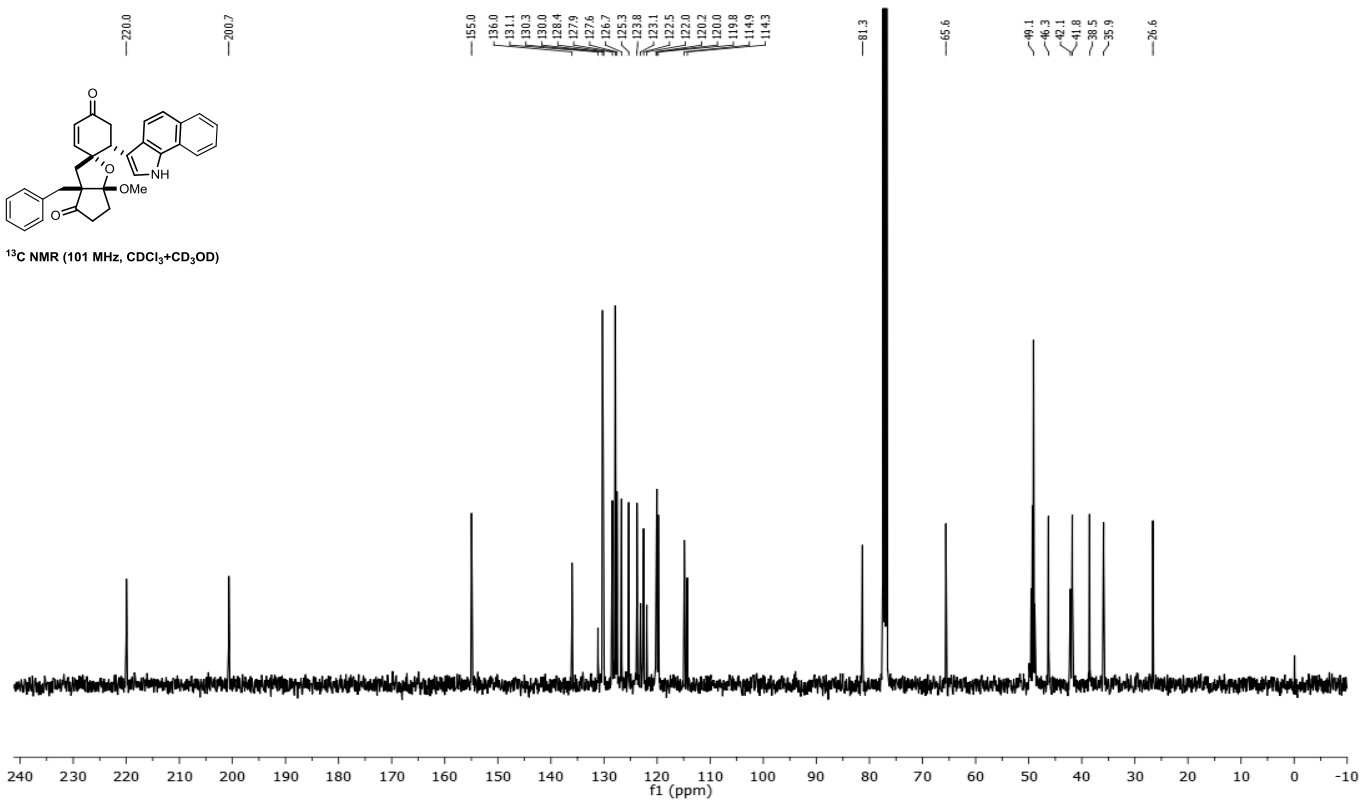
6-(1*H*-Benzo[*g*]indol-3-yl)-3a'-ethyl-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5o):



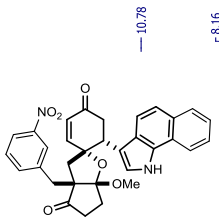


6-(1*H*-Benzo[*g*]indol-3-yl)-3a'-benzyl-6a'-methoxy-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5p):

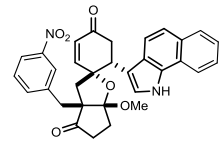




6-(1*H*-Benzo[*g*]indol-3-yl)-6a'-methoxy-3a'-(3-nitrobenzyl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5q):

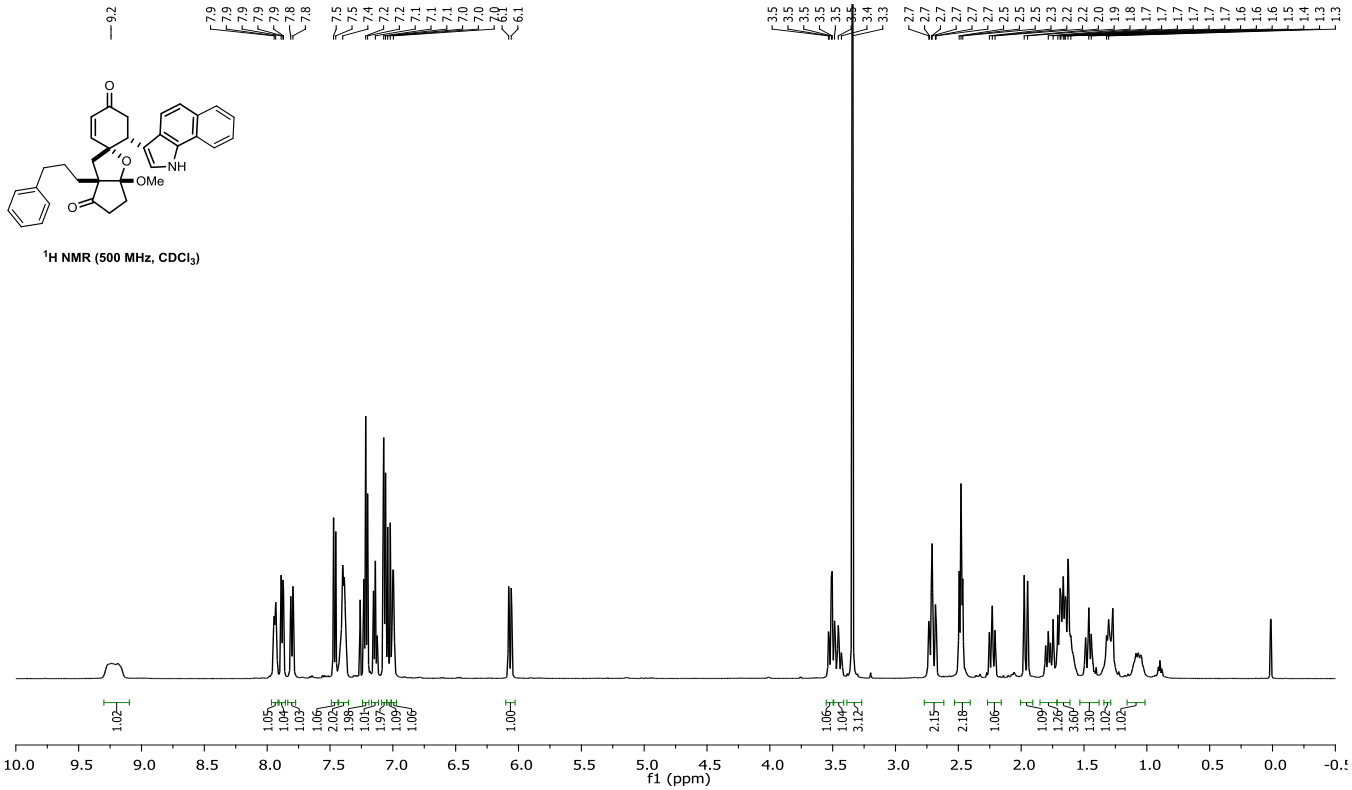


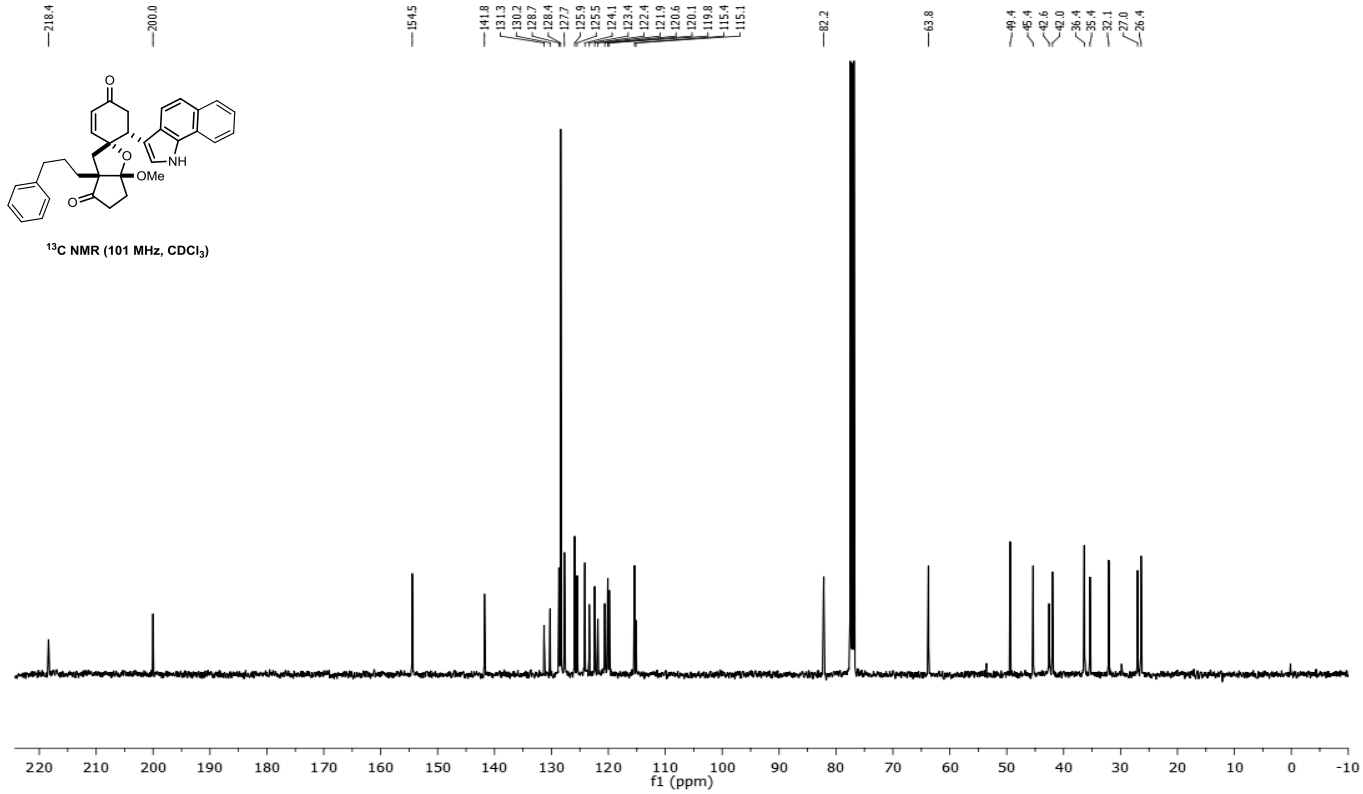
^{1}H NMR (500 MHz, $CDCl_3$+CD_3OD)



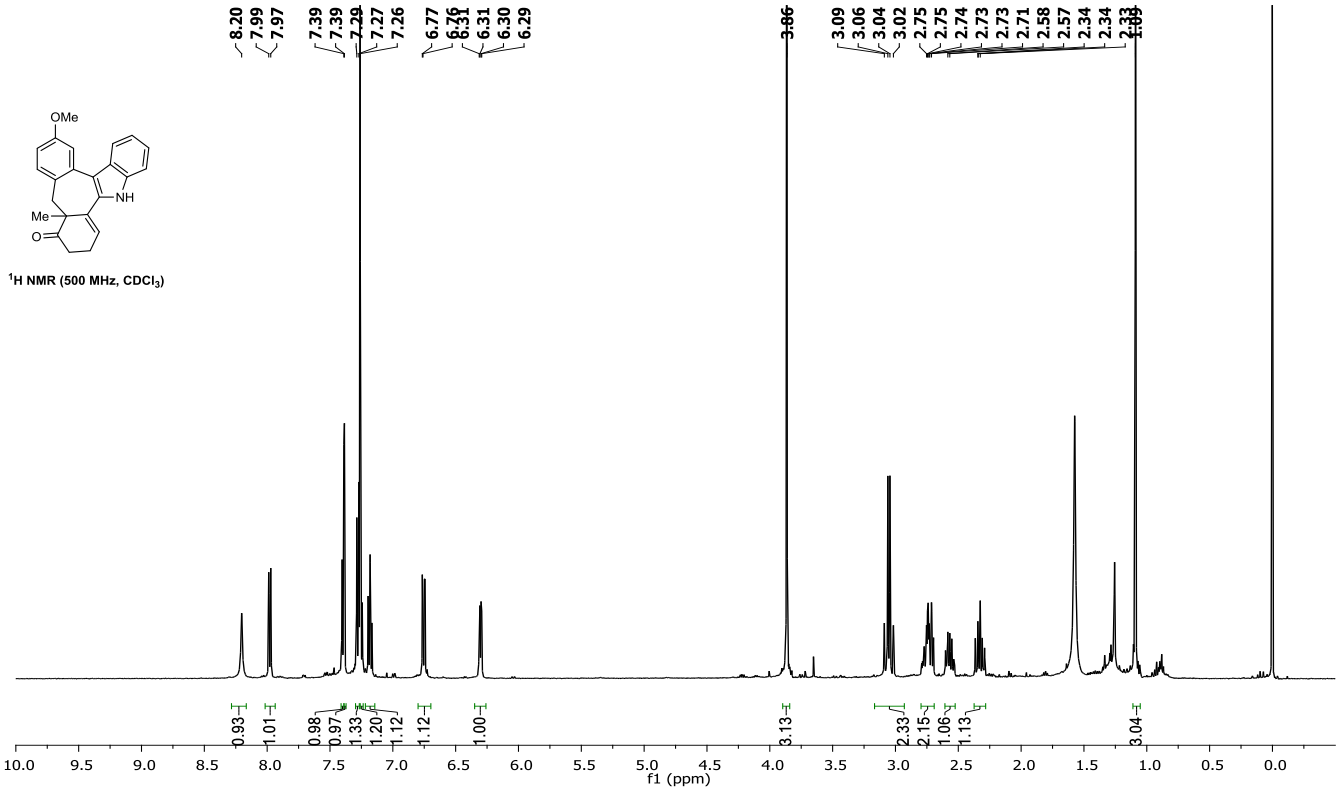
^{13}C NMR (101 MHz, $CDCl_3$+CD_3OD)

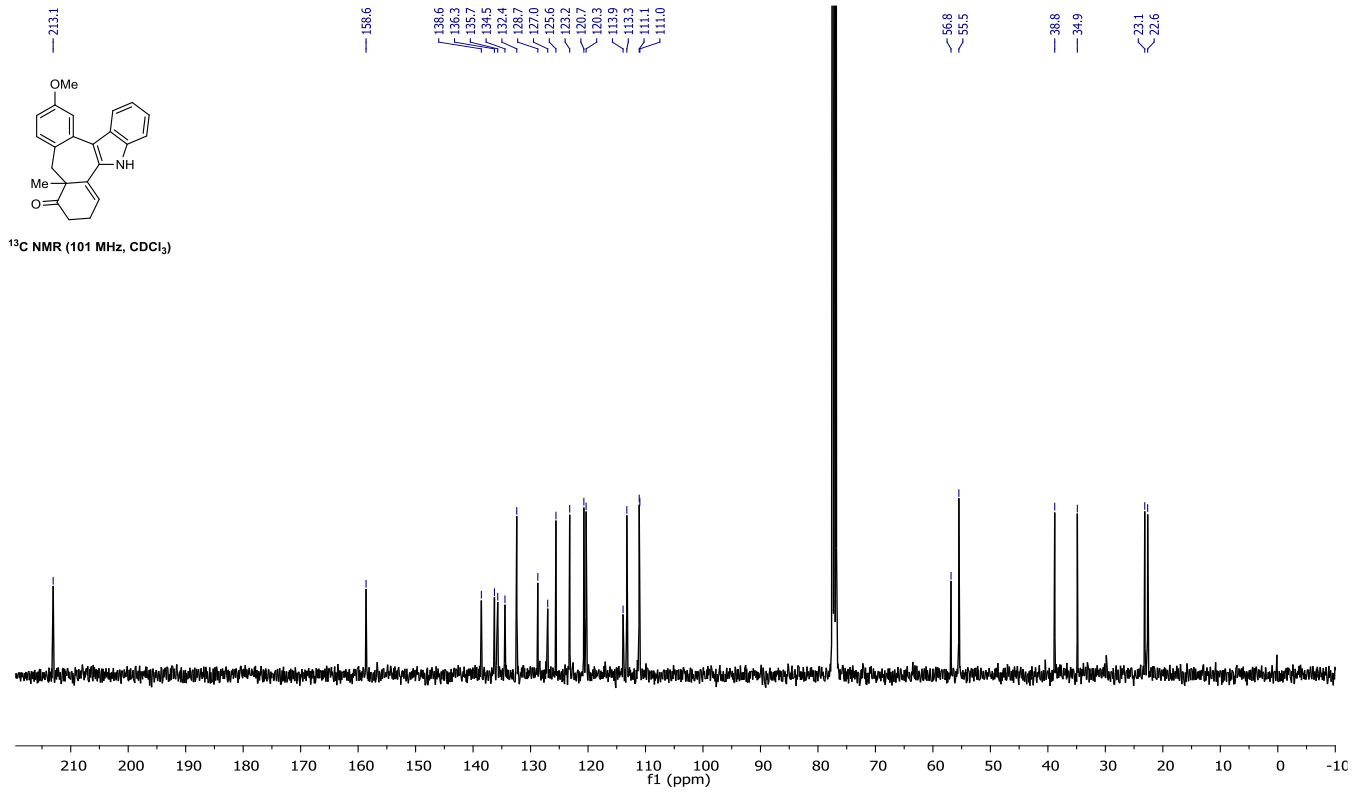
6-(1*H*-Benzo[*g*]indol-3-yl)-6a'-methoxy-3a'-(3-phenylpropyl)-3a',5',6',6a'-tetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-2-ene-4,4'(3'*H*)-dione (5r):



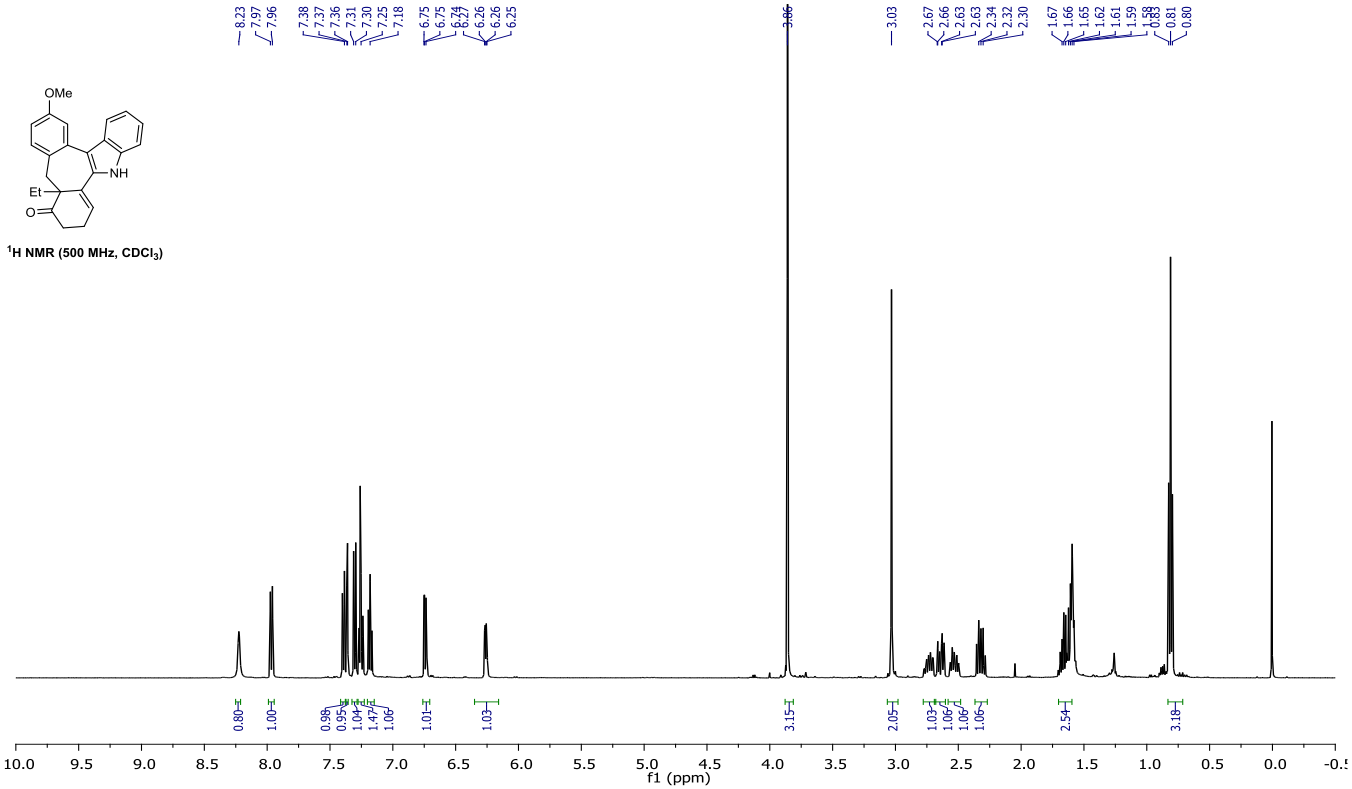


6-Methoxy-9a-methyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6a):

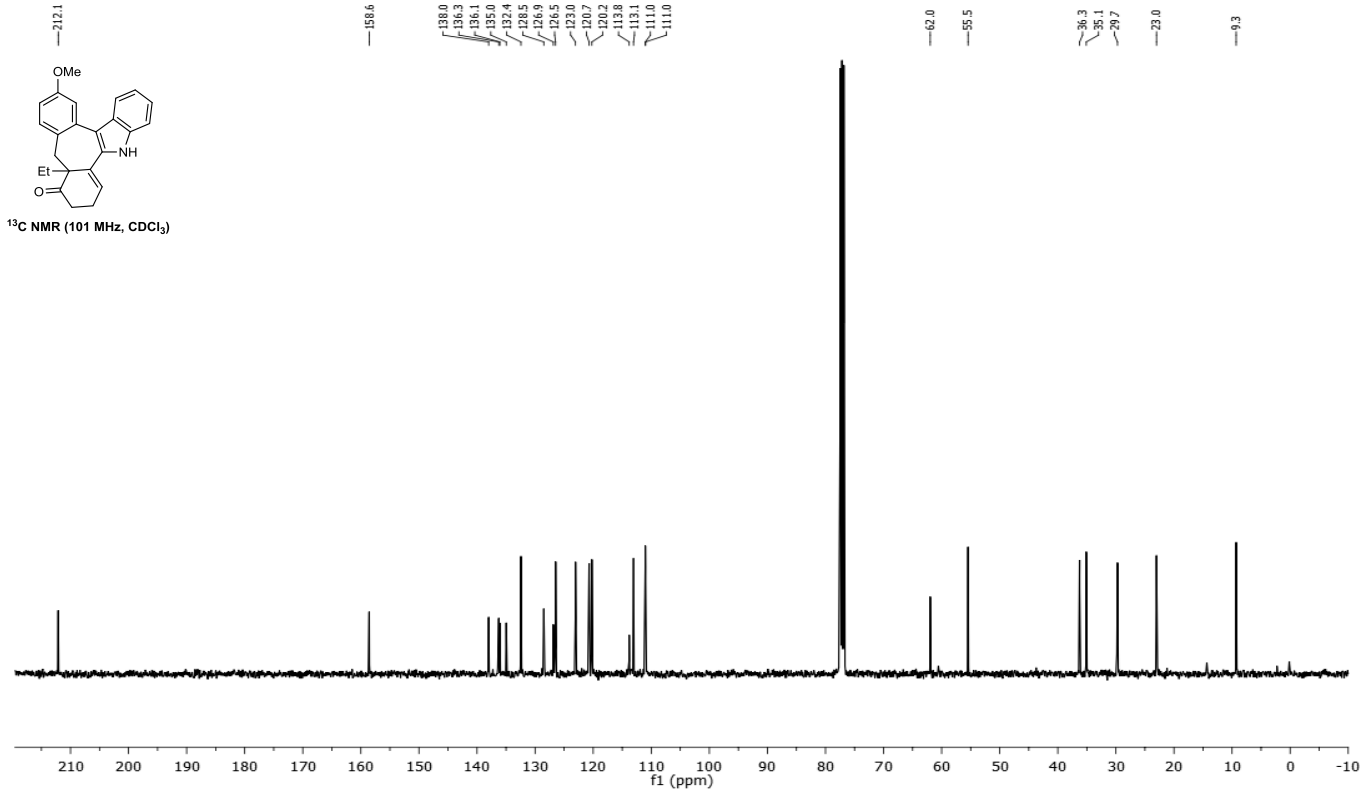




9a-Ethyl-6-methoxy-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6b):

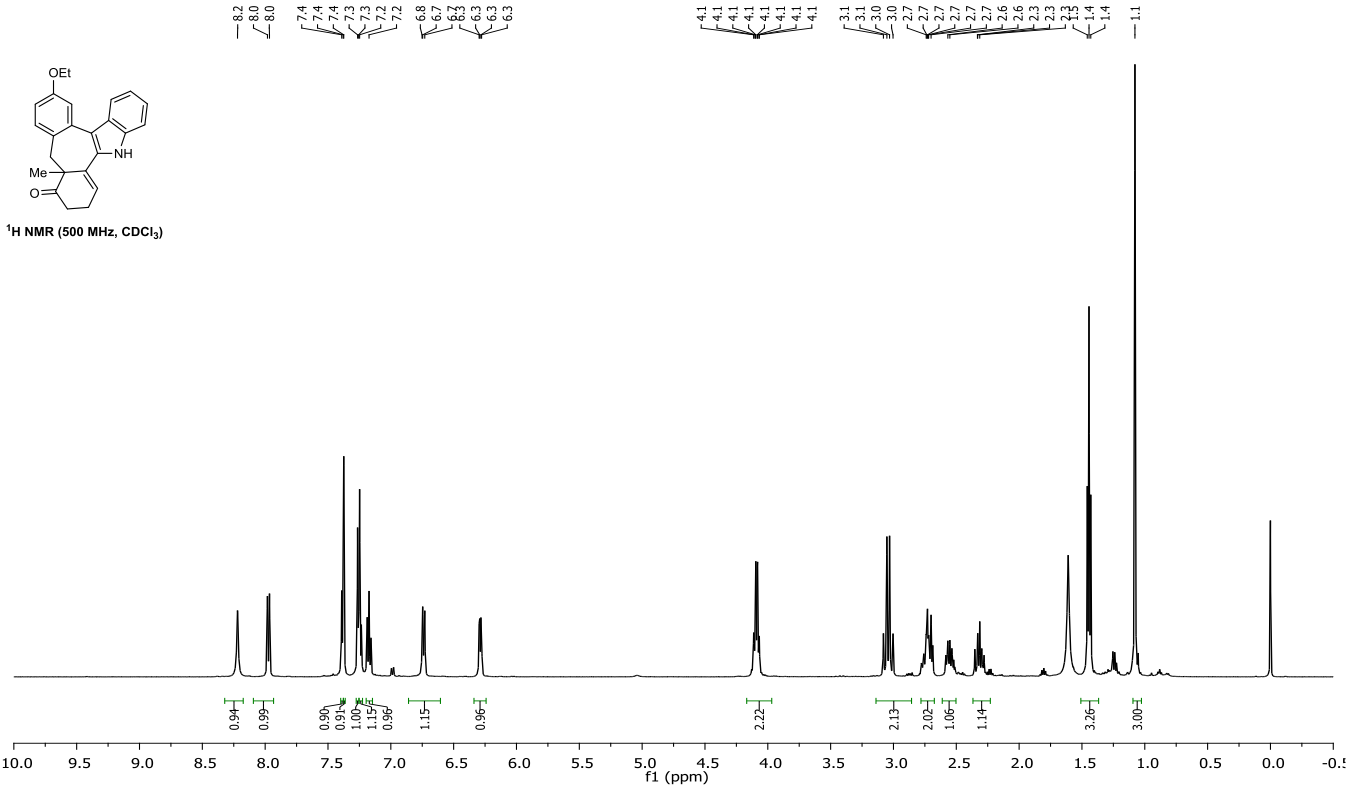


^{1}H NMR (500 MHz, $CDCl_3$)

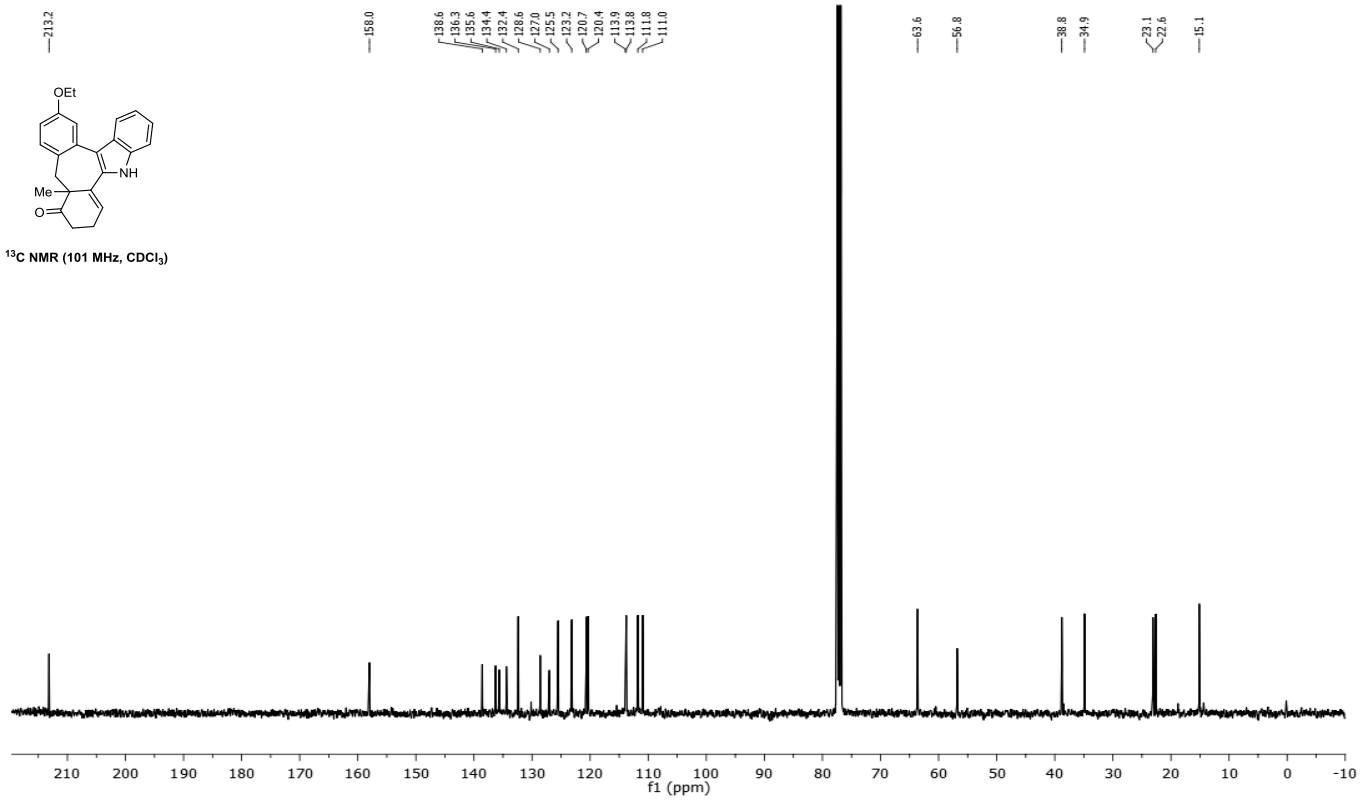


^{13}C NMR (101 MHz, $CDCl_3$)

6-Ethoxy-9a-methyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6c):

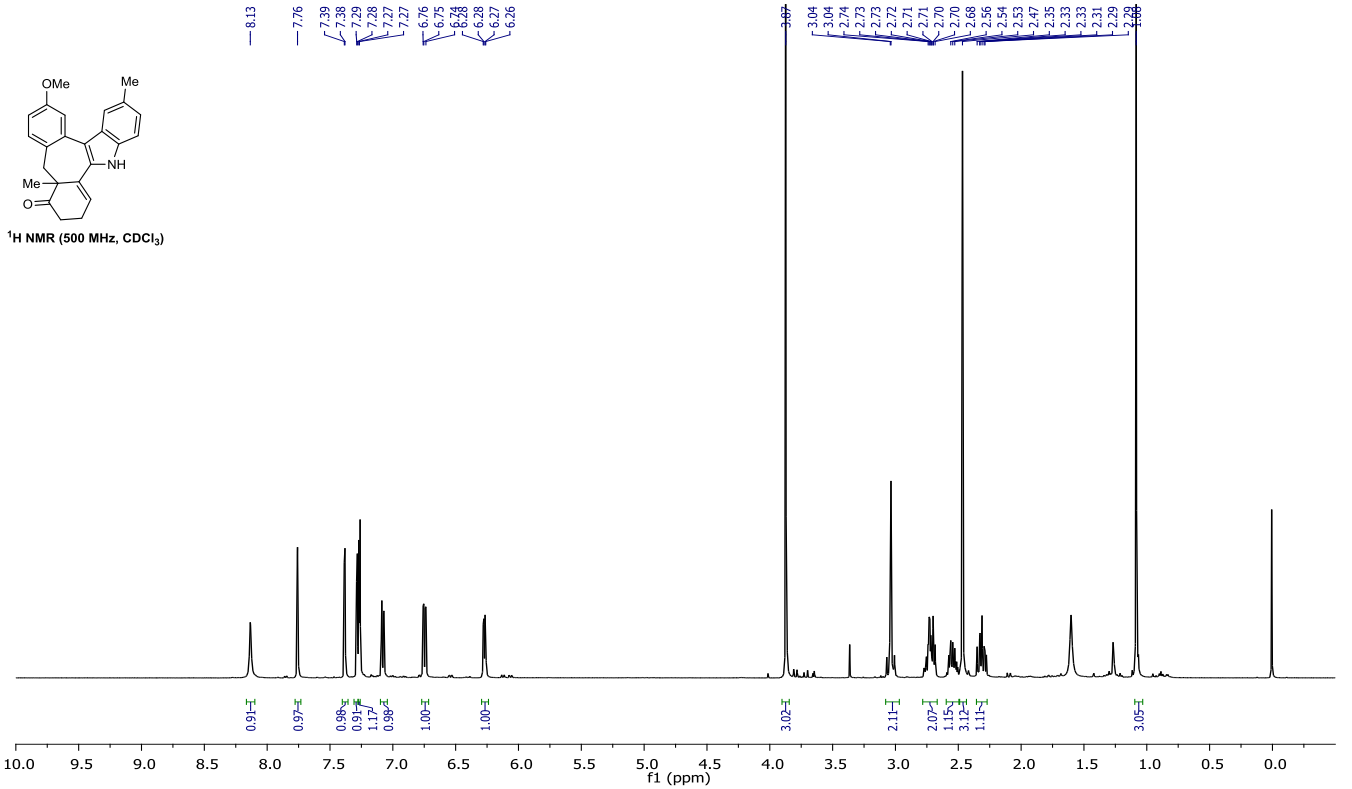


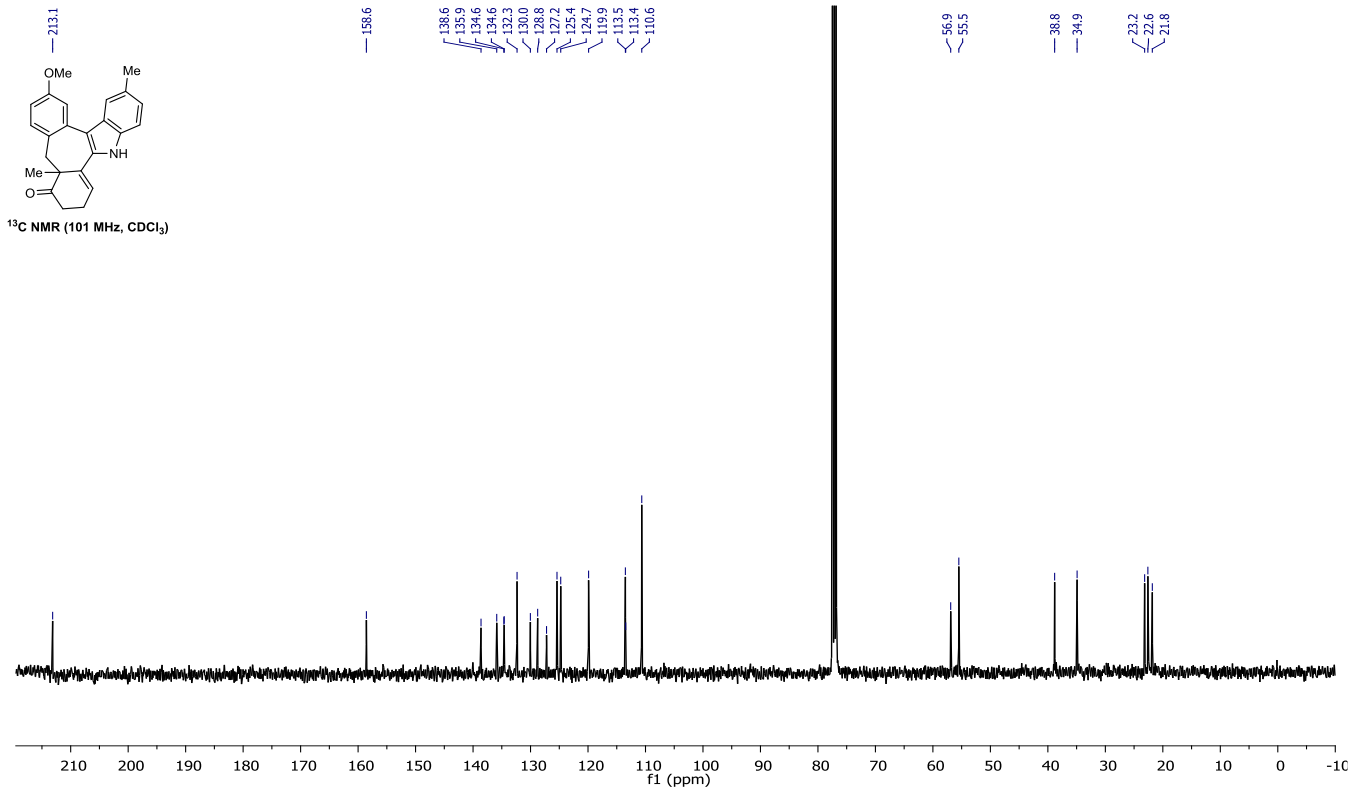
^{1}H NMR (500 MHz, $CDCl_3$)



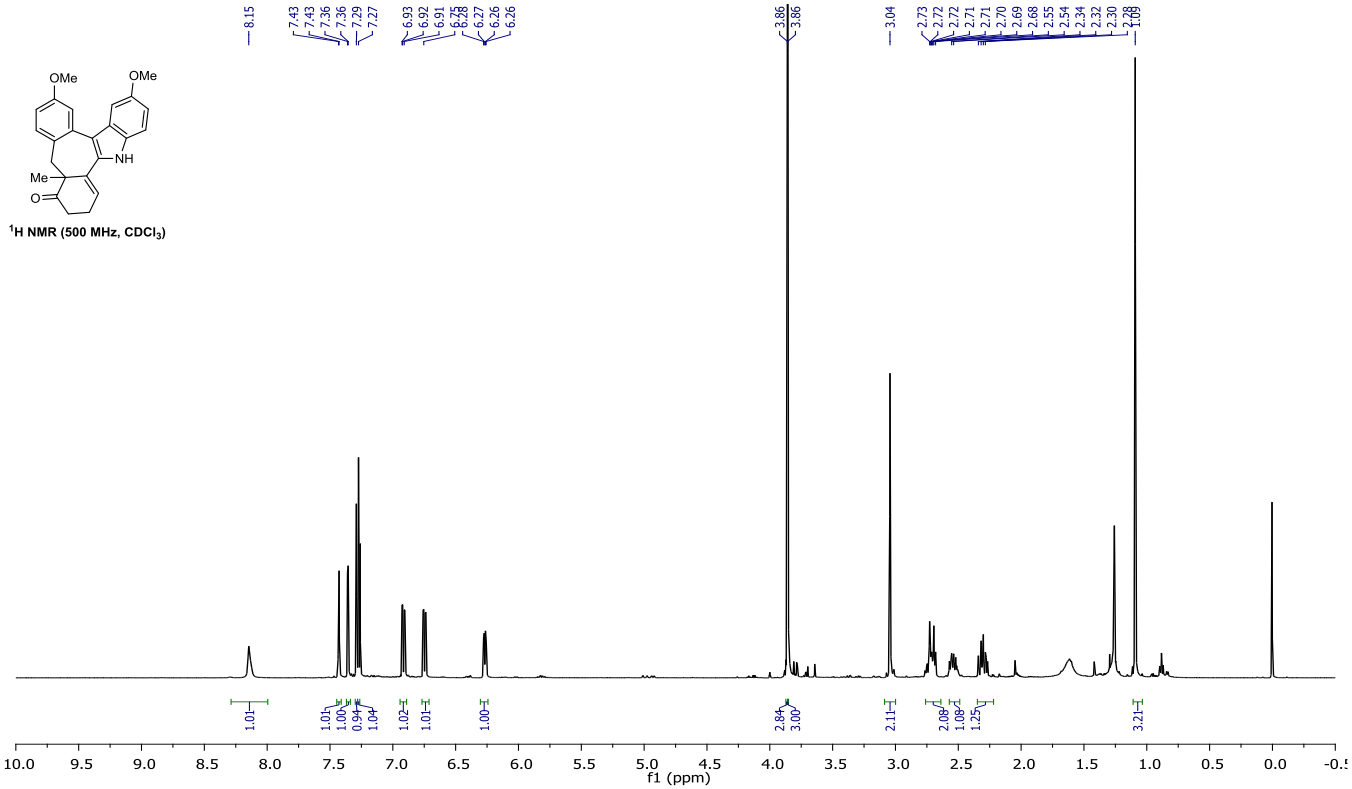
^{13}C NMR (101 MHz, $CDCl_3$)

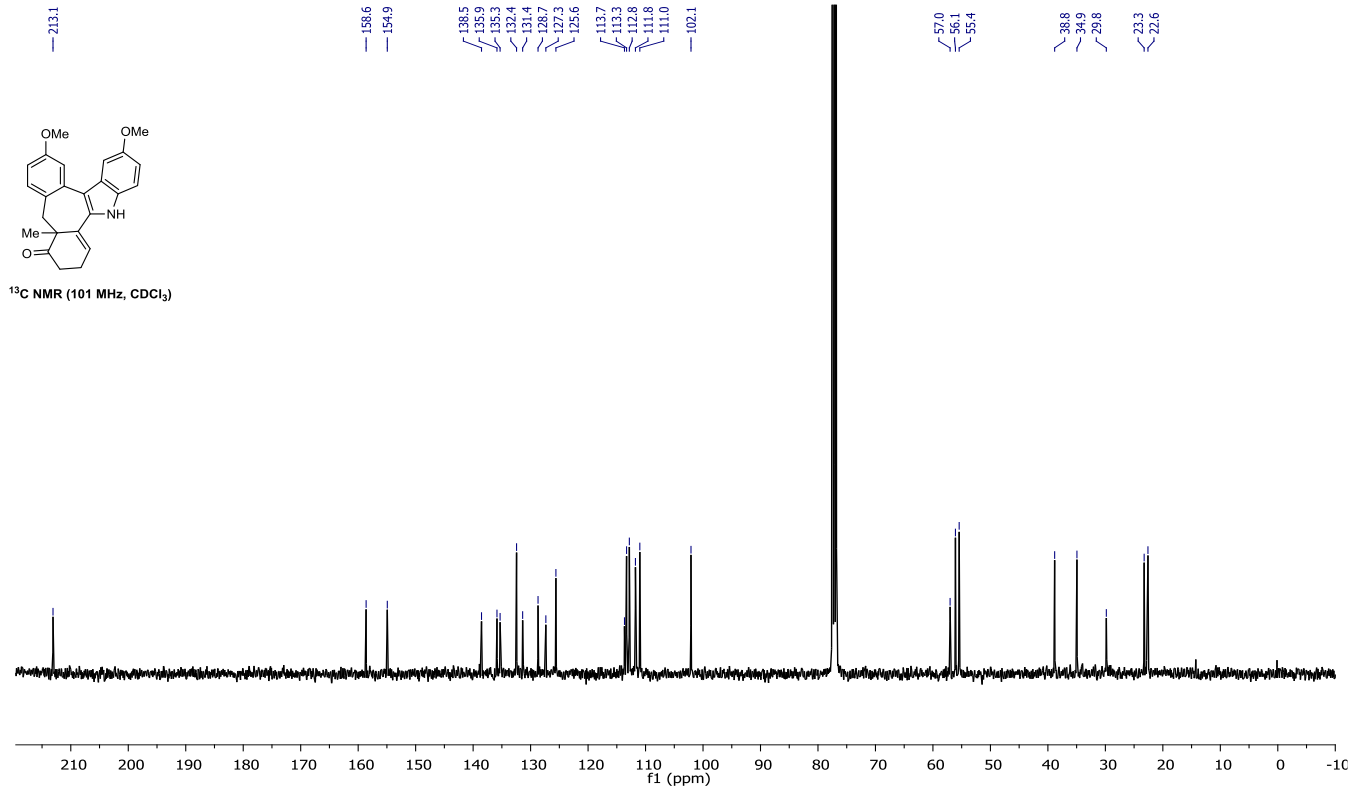
6-Methoxy-3,9a-dimethyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6d):



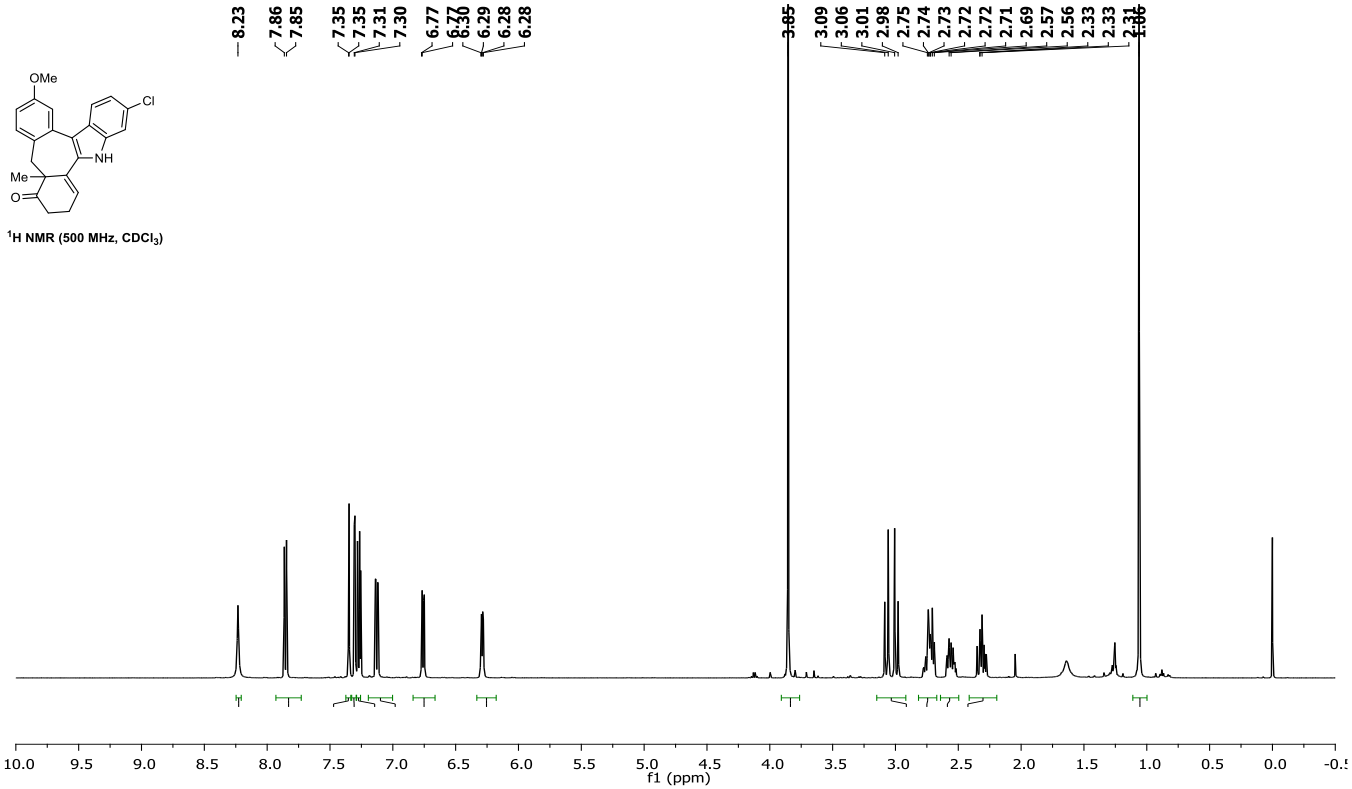


3,6-Dimethoxy-9a-methyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6e):

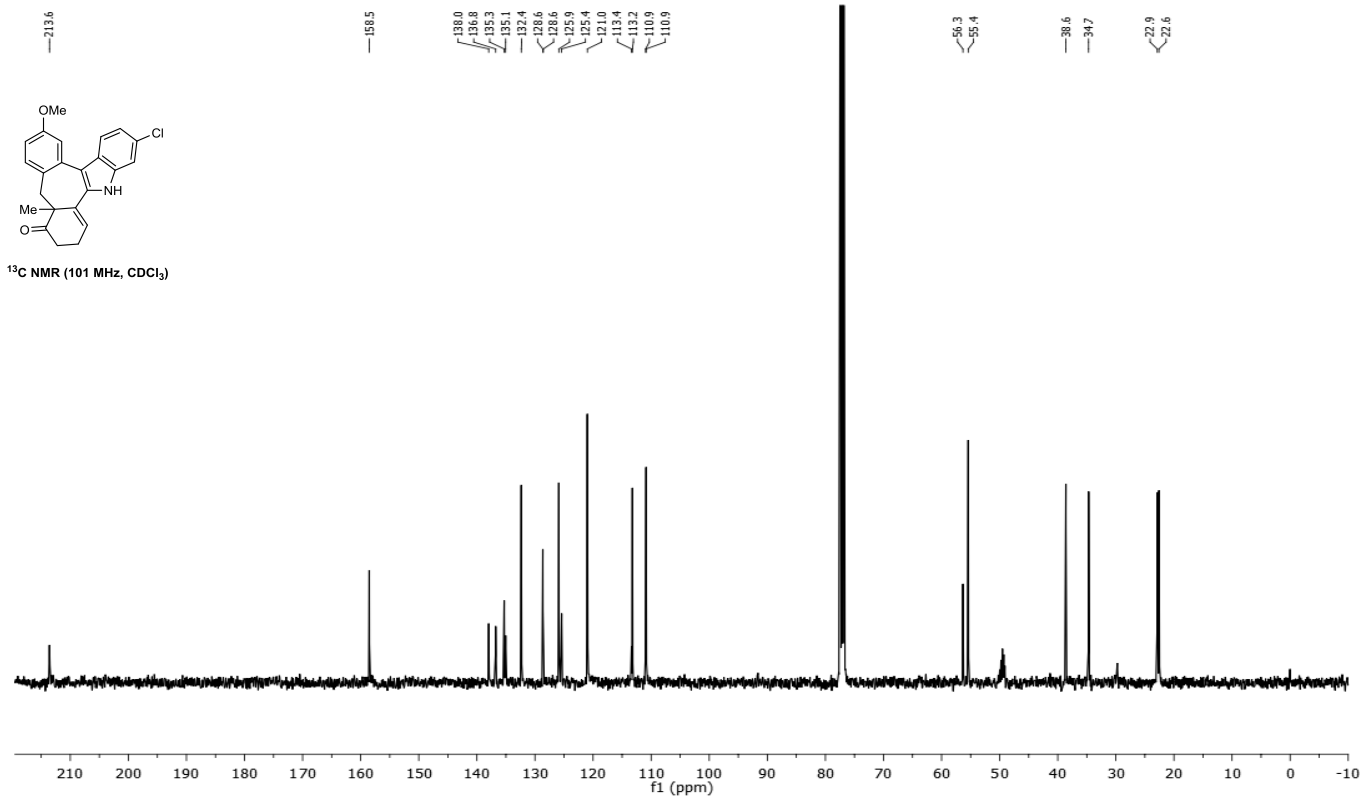




2-Chloro-6-methoxy-9a-methyl-9,11,12,14-tetrahydrodibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-10(9a*H*)-one (6f):

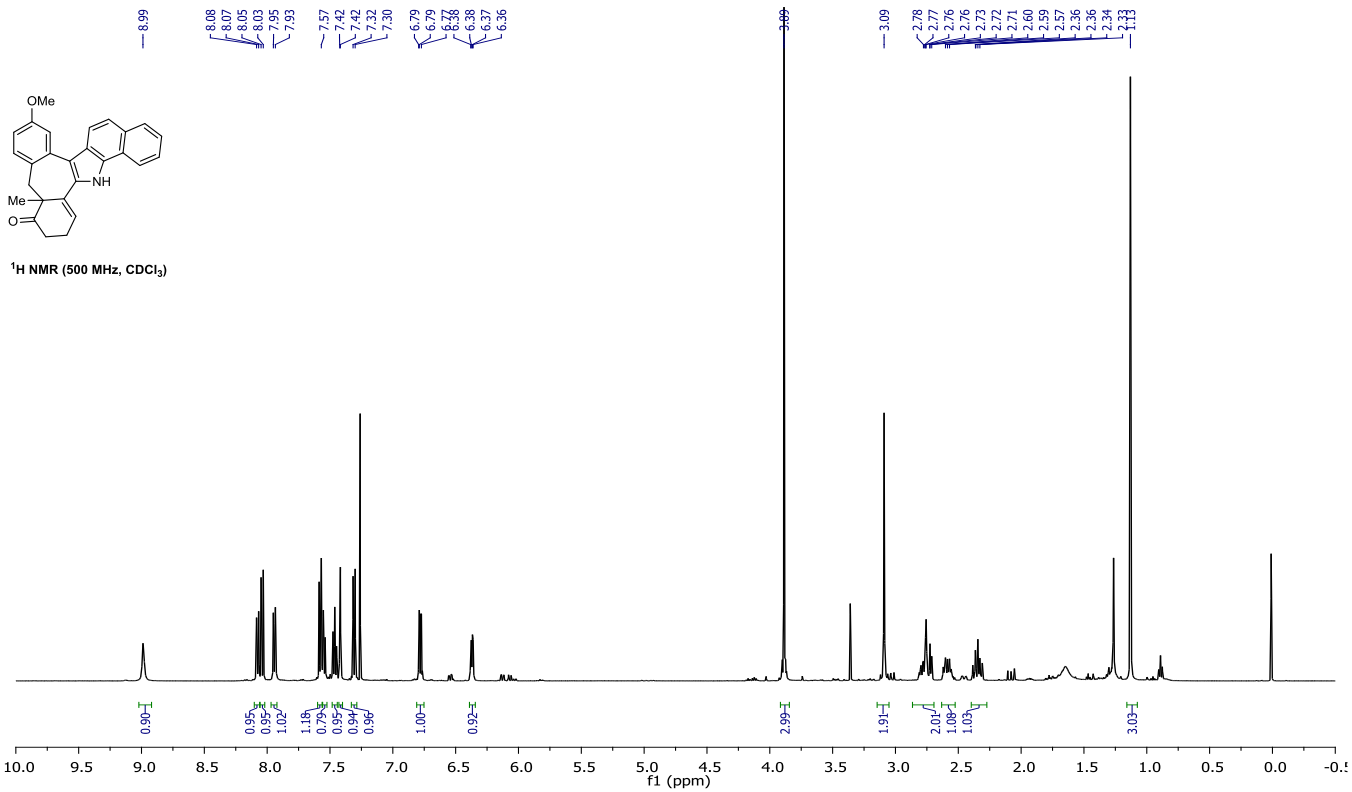


^{1}H NMR (500 MHz, $CDCl_3$)

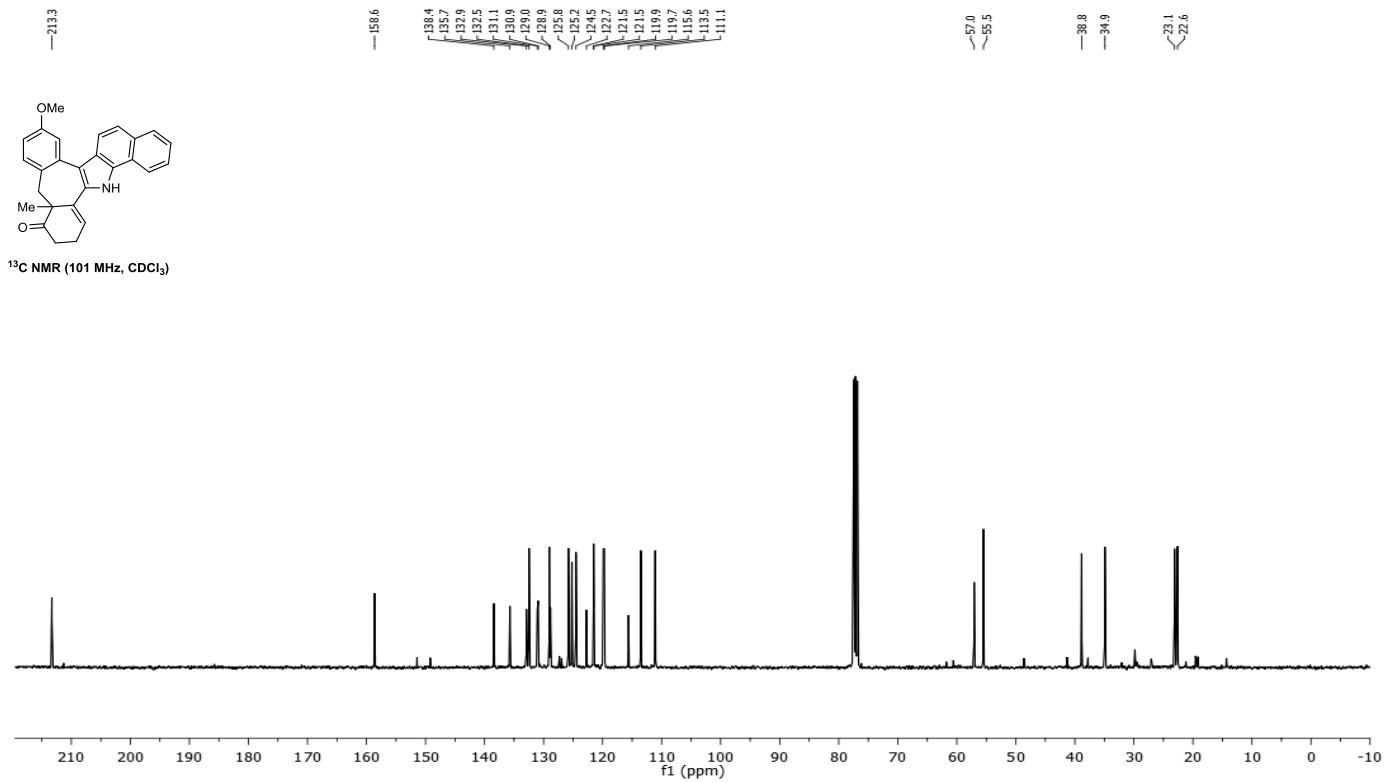


^{13}C NMR (101 MHz, $CDCl_3$)

8-Methoxy-11a-methyl-11,13,14,16-tetrahydrobenzo[*g*]dibenzo[3,4:6,7]cyclohepta[1,2-*b*]indol-12(11a*H*)-one (6g):

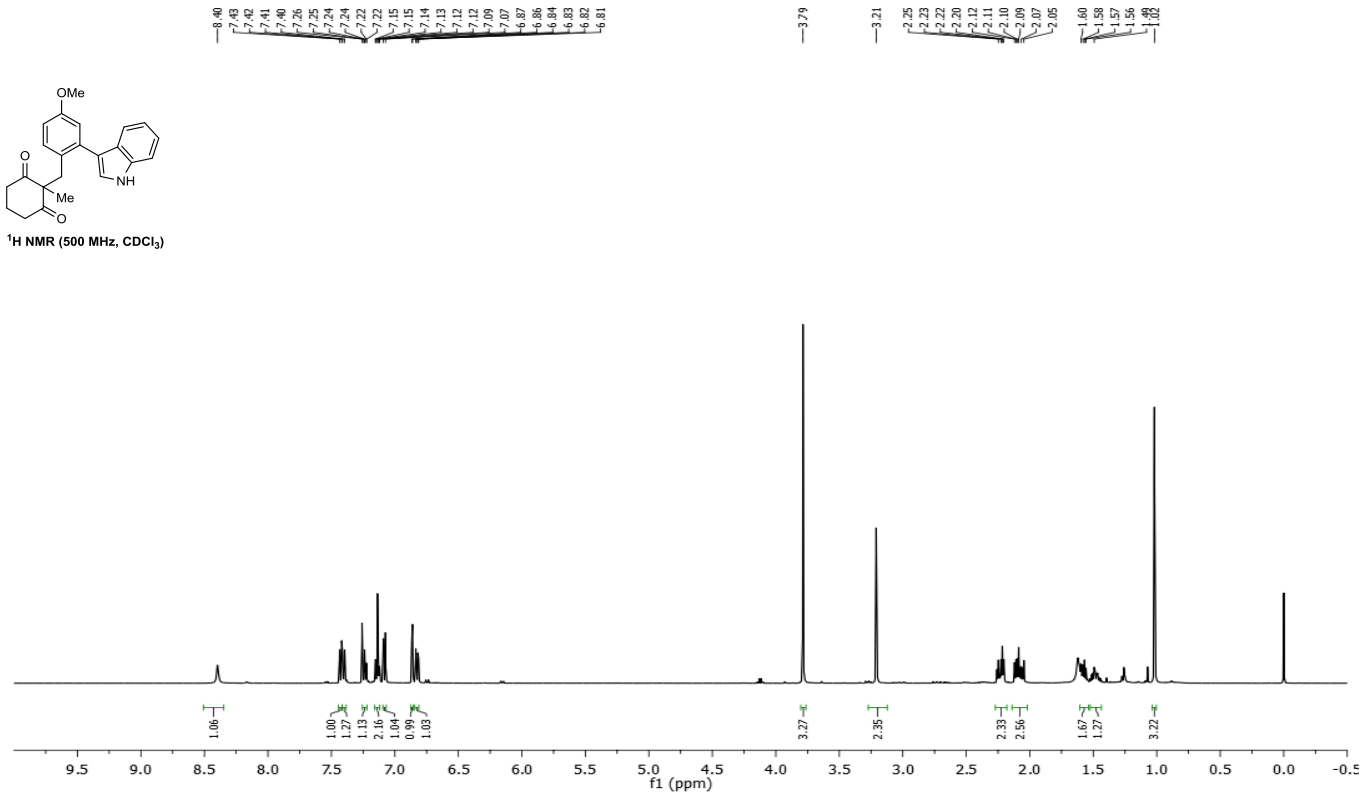


^{1}H NMR (500 MHz, $CDCl_3$)

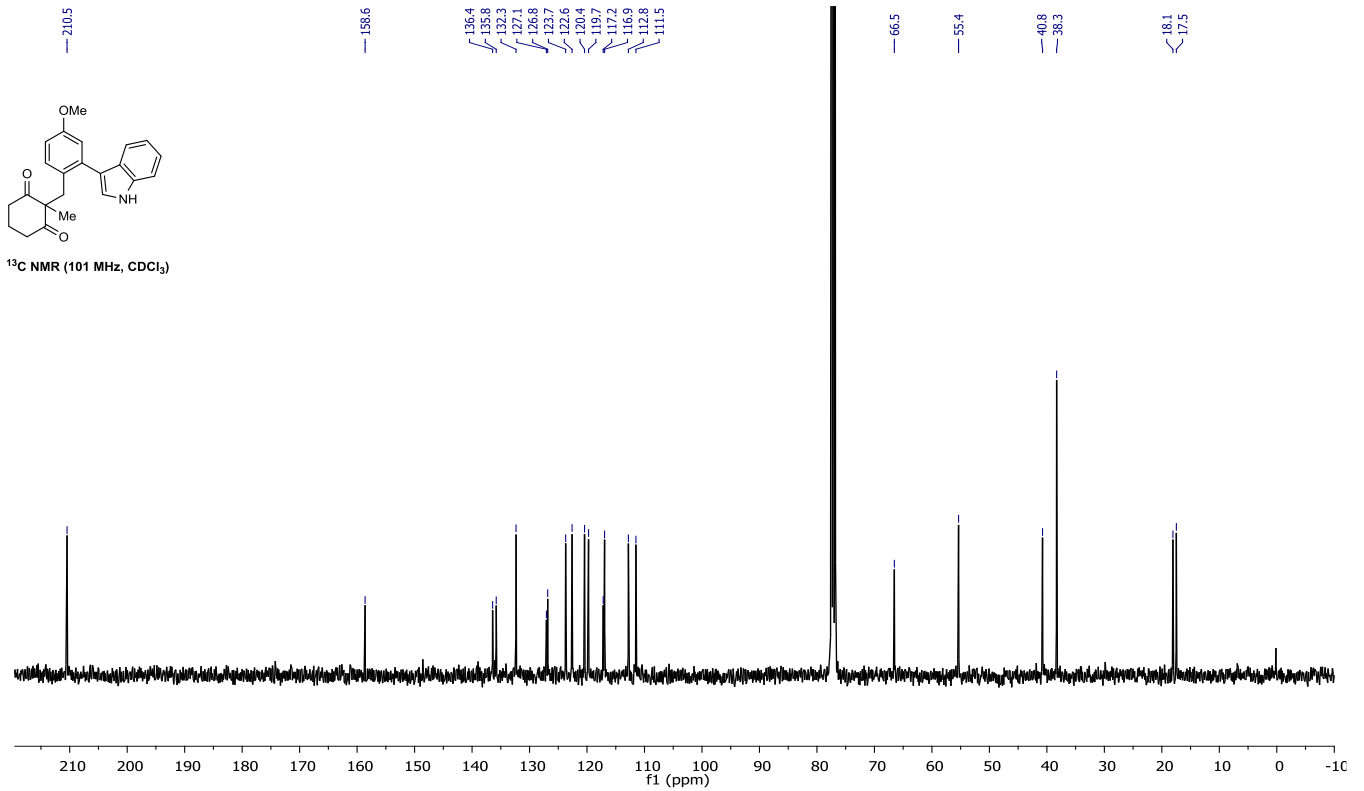


^{13}C NMR (101 MHz, $CDCl_3$)

2-(2-(1*H*-Indol-3-yl)-4-methoxybenzyl)-2-methylcyclohexane-1,3-dione (7a):

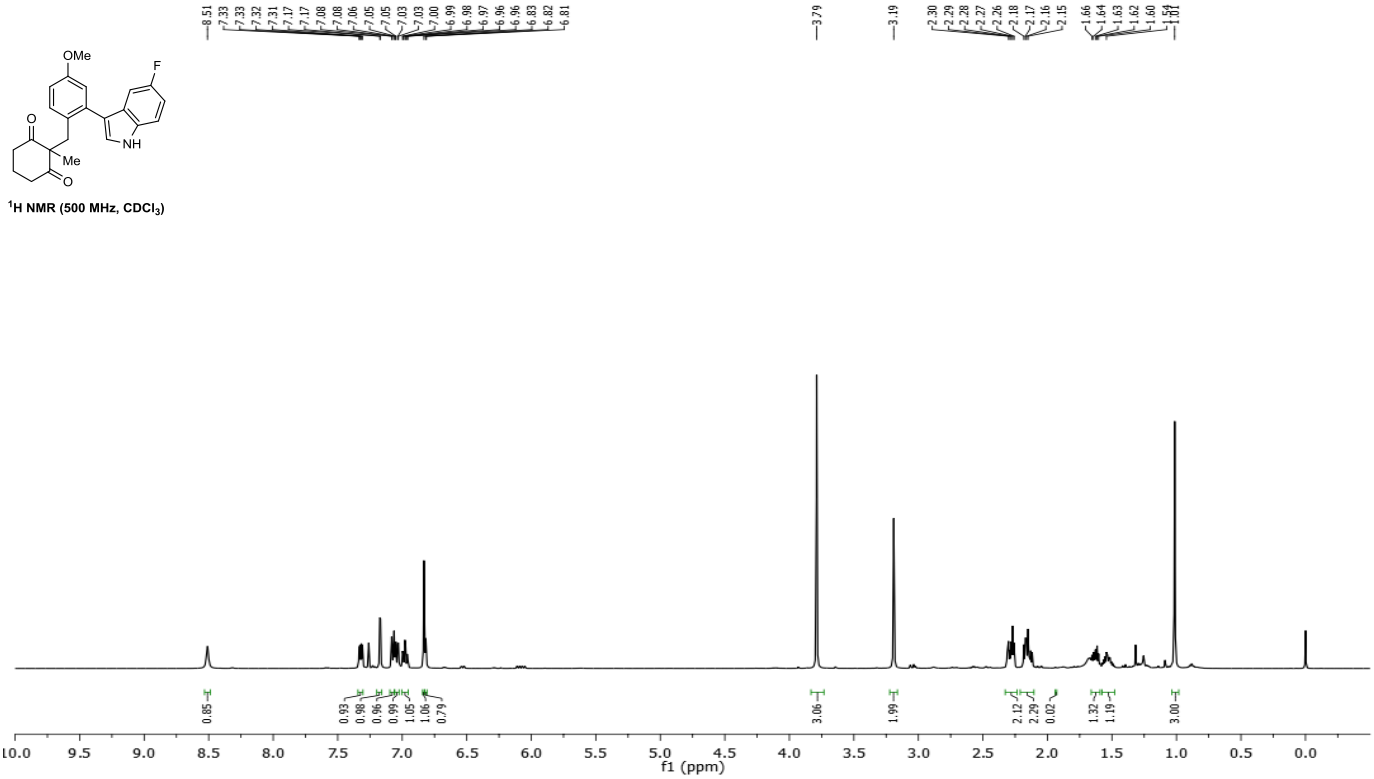


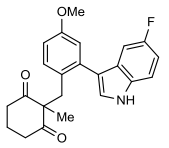
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

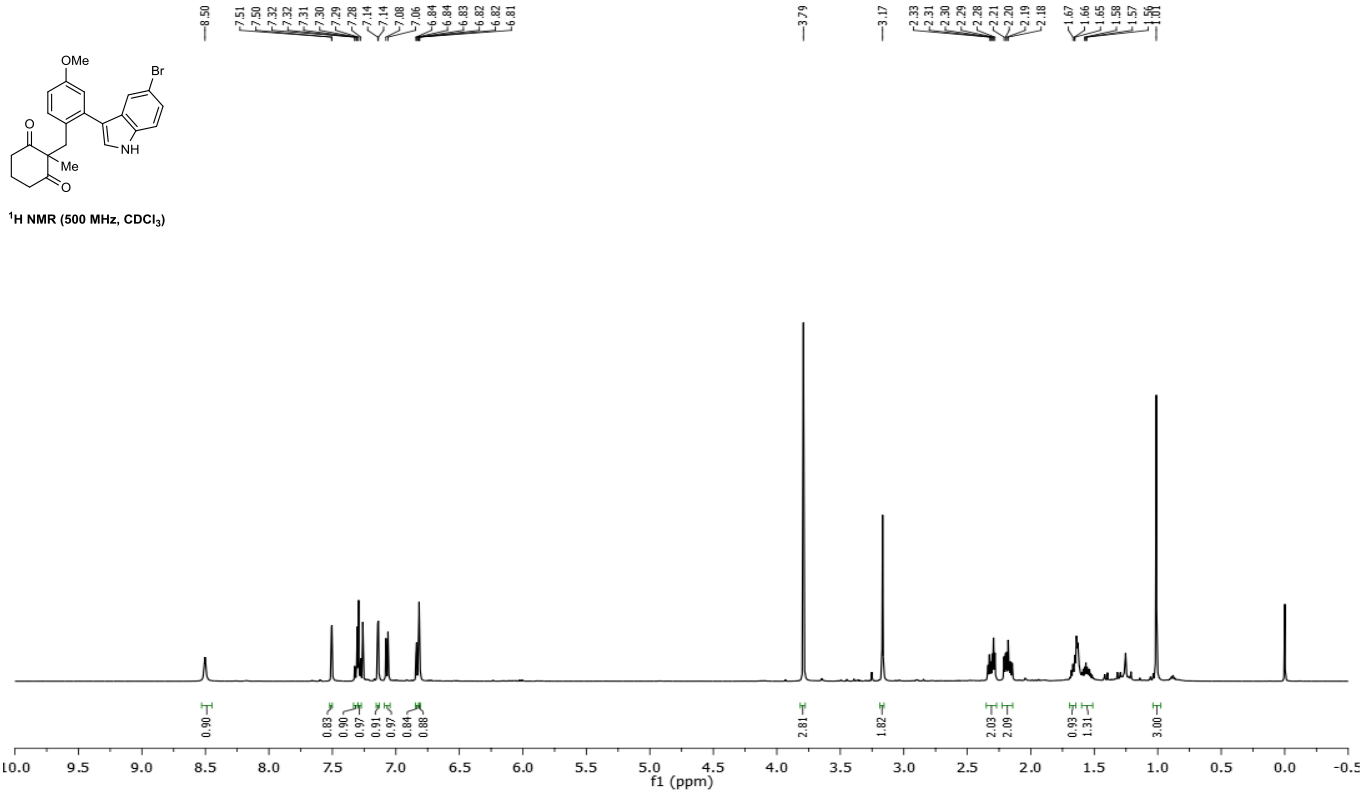
2-(2-(5-fluoro-1*H*-indol-3-yl)-4-methoxybenzyl)-2-methylcyclohexane-1,3-dione (7h):



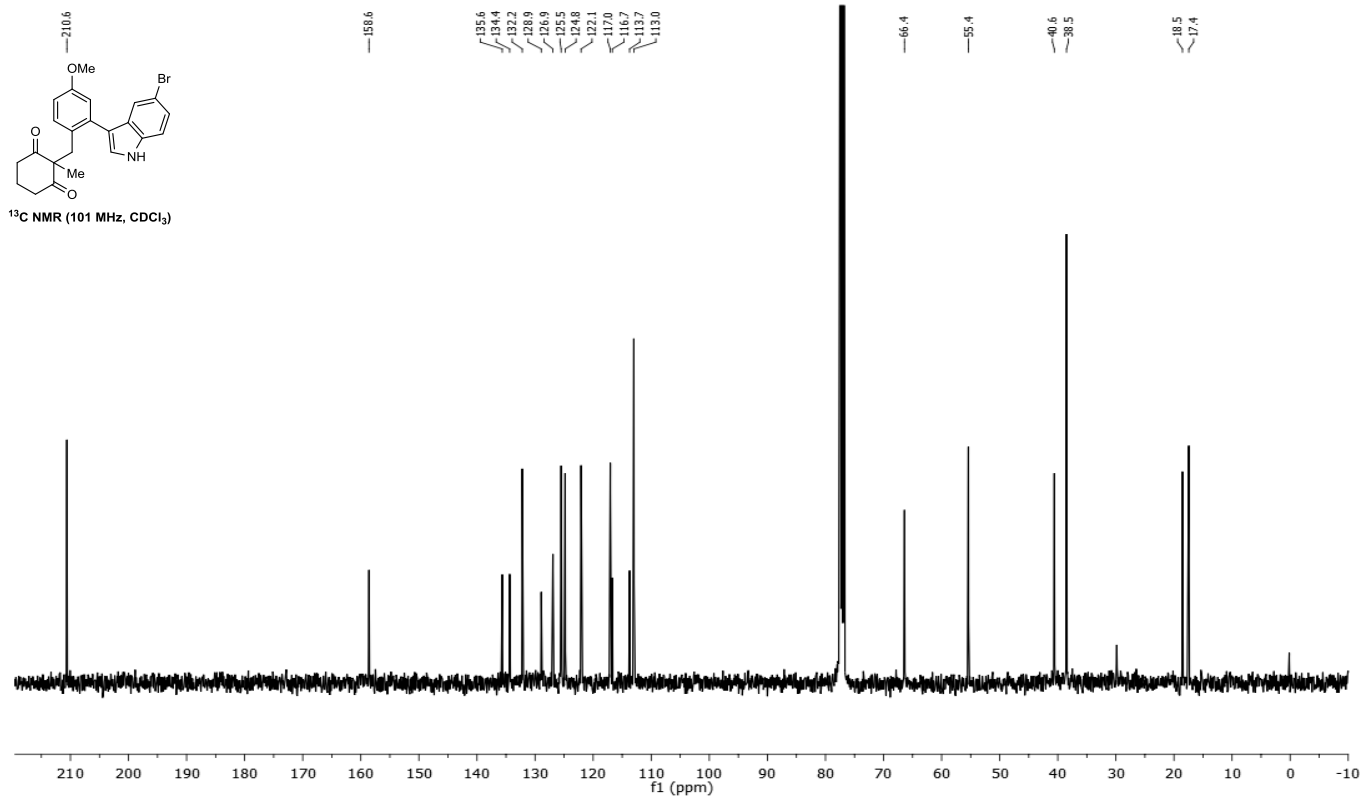


^{19}F NMR (377 MHz, $CDCl_3$)

2-(2-(5-Bromo-1*H*-indol-3-yl)-4-methoxybenzyl)-2-methylcyclohexane-1,3-dione (7i):

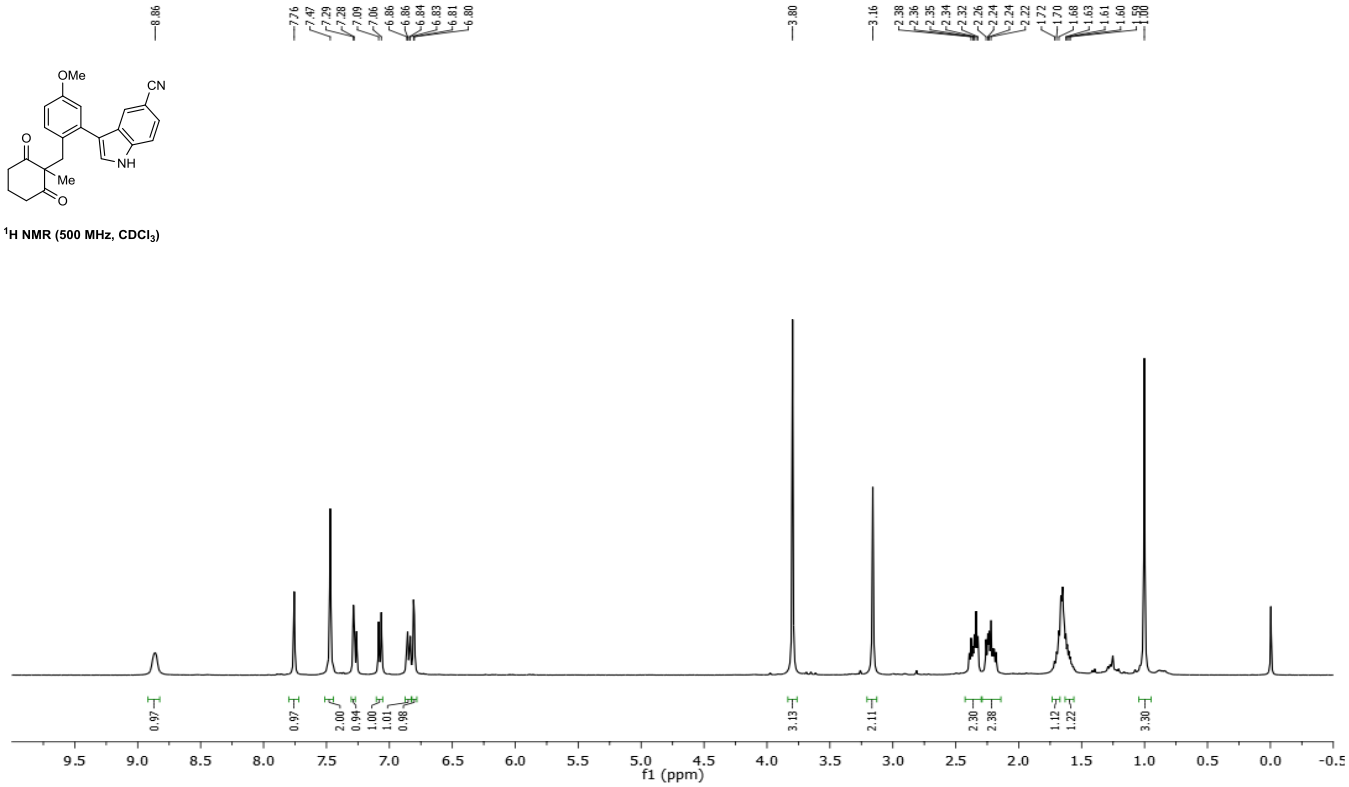


^{1}H NMR (500 MHz, $CDCl_3$)

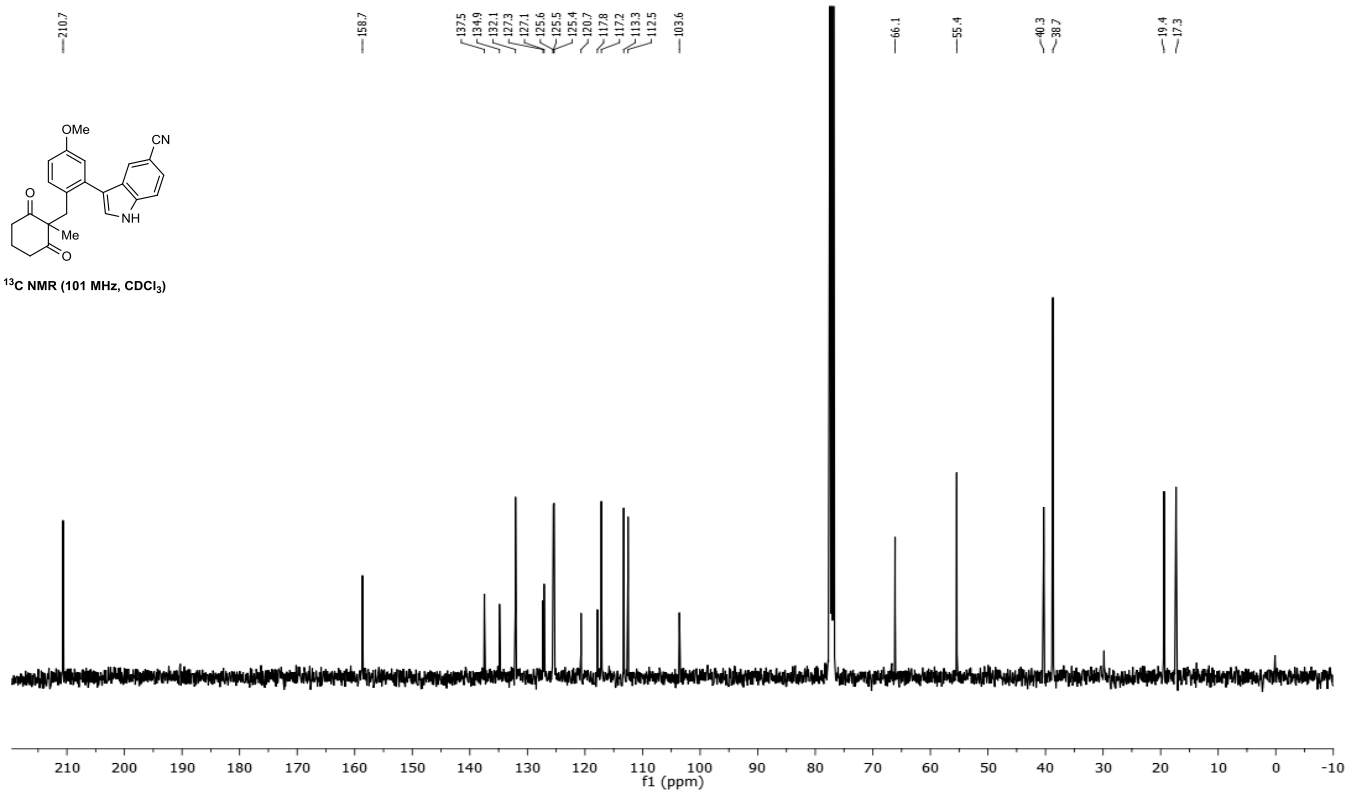


^{13}C NMR (101 MHz, $CDCl_3$)

3-(5-Methoxy-2-((1-methyl-2,6-dioxocyclohexyl)methyl)phenyl)-1*H*-indole-5-carbonitrile (7j):

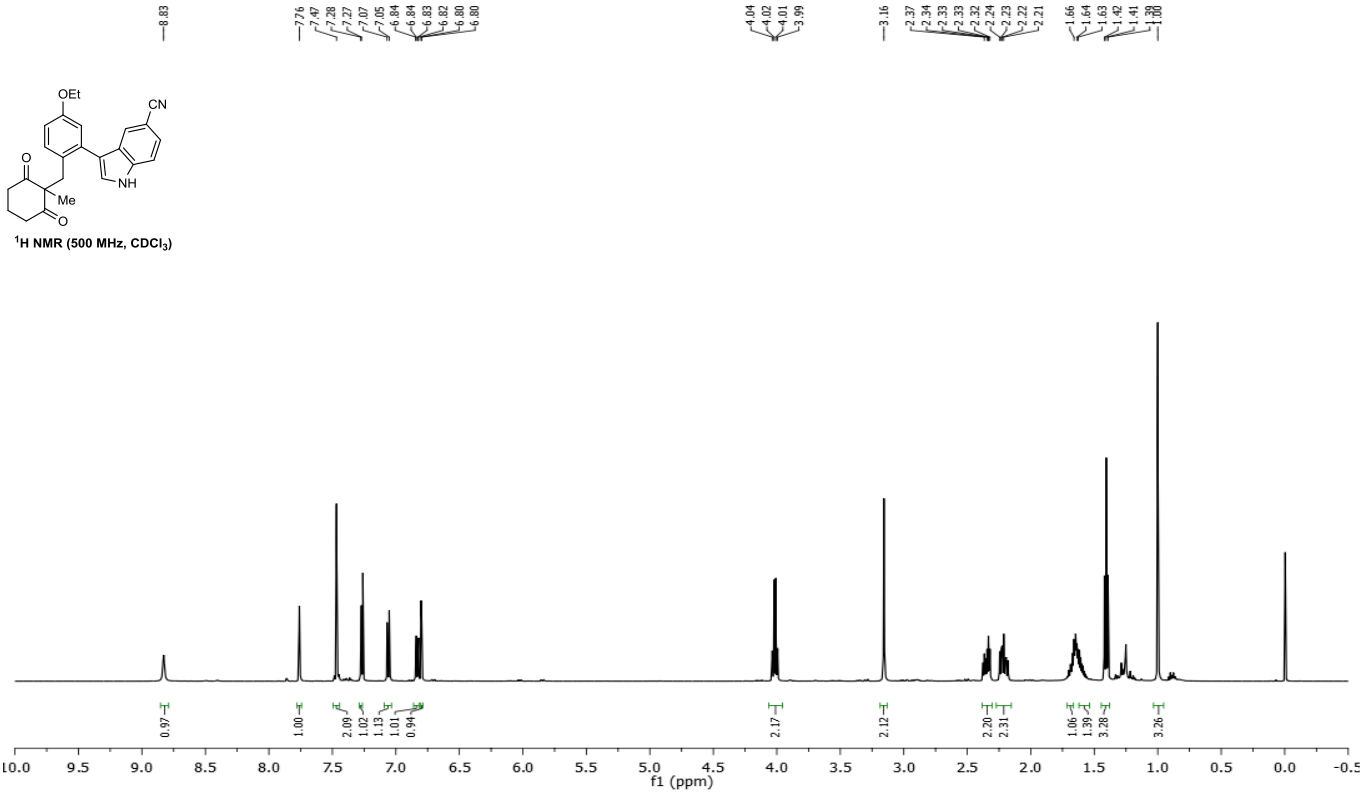


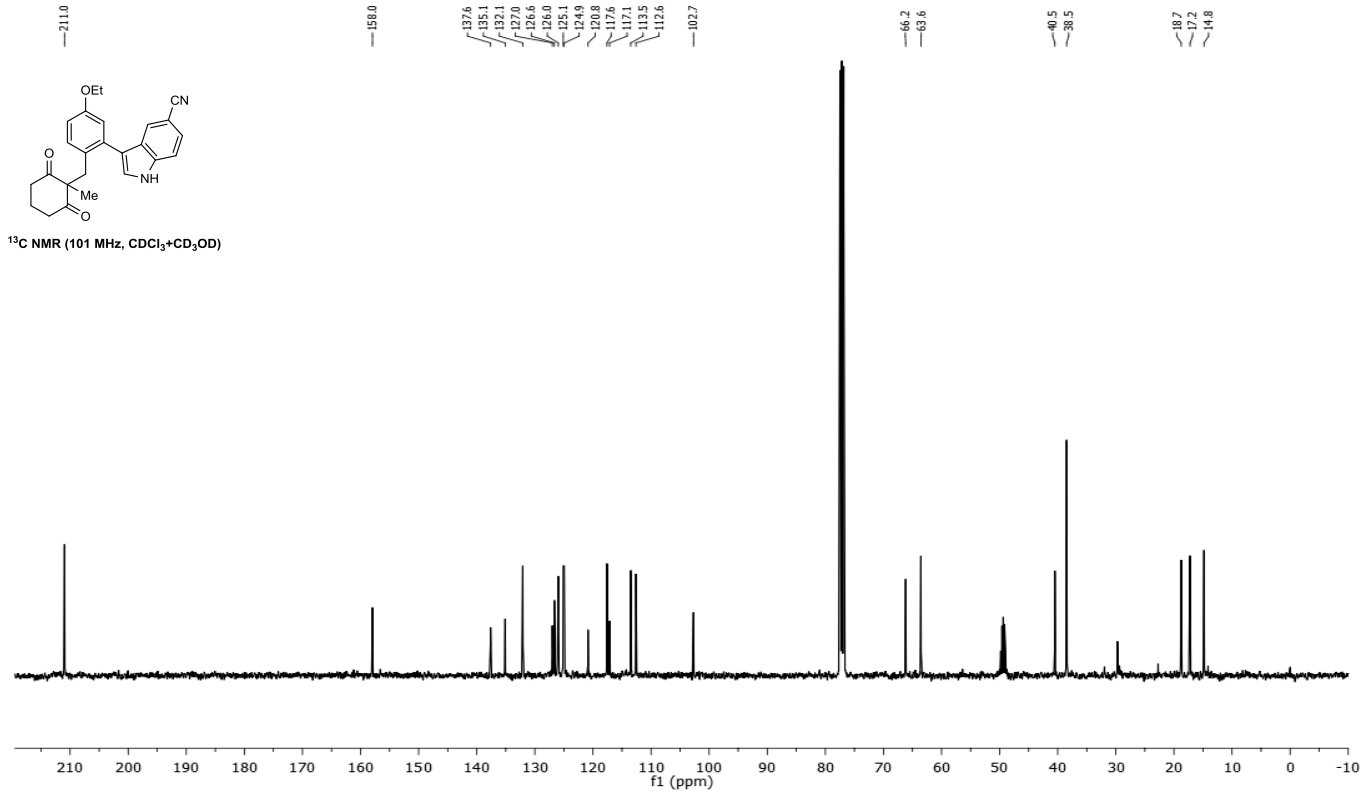
^{1}H NMR (500 MHz, $CDCl_3$)



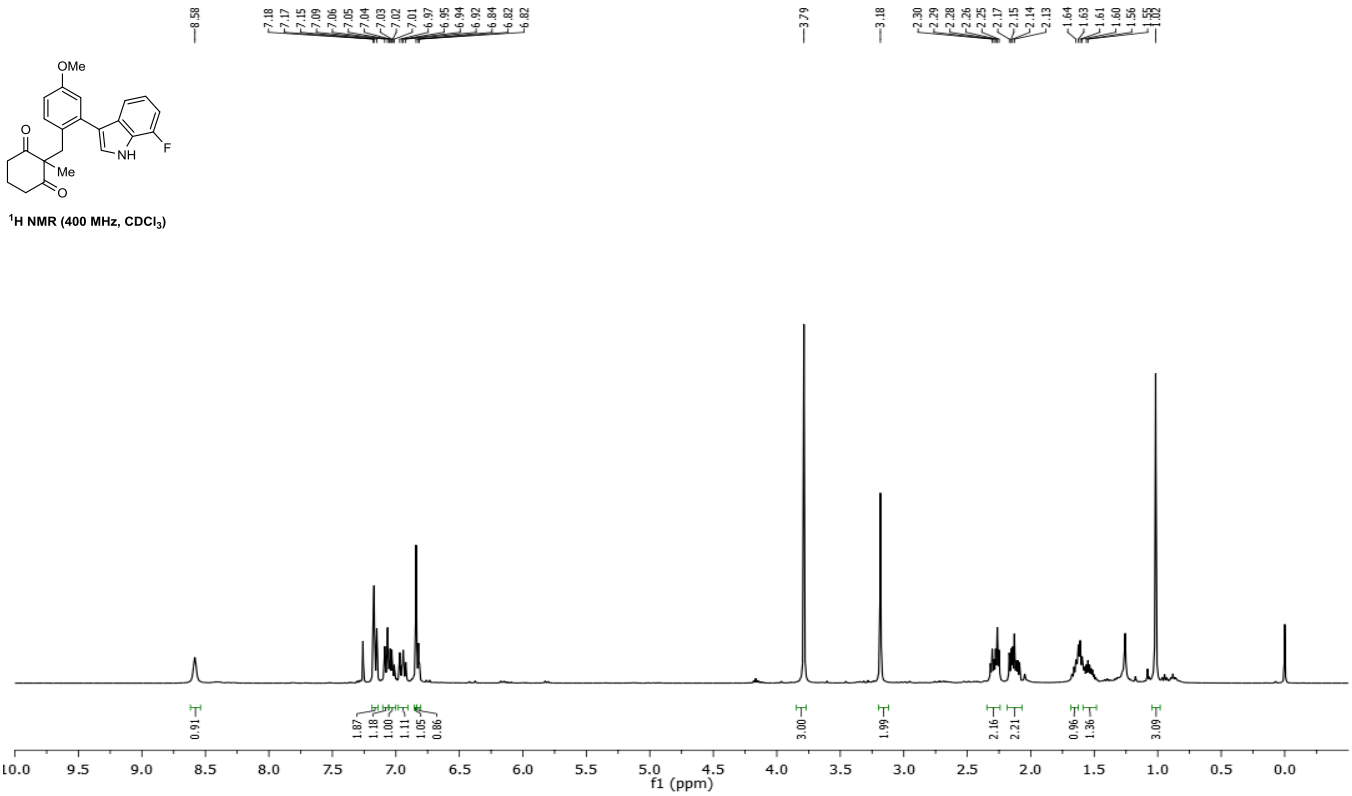
^{13}C NMR (101 MHz, $CDCl_3$)

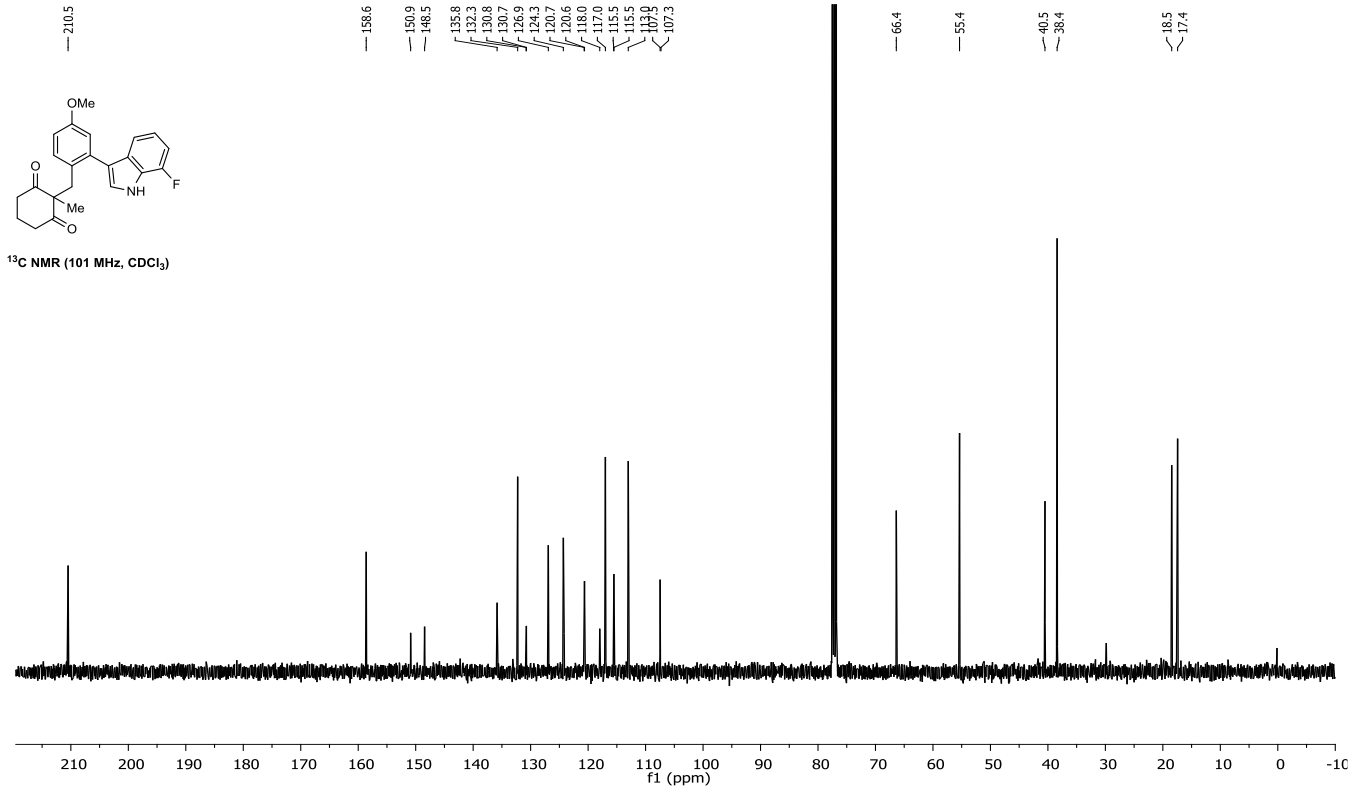
3-(5-Ethoxy-2-((1-methyl-2,6-dioxocyclohexyl)methyl)phenyl)-1*H*-indole-5-carbonitrile (7k):

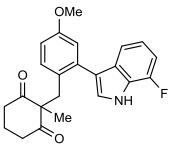




2-(2-(7-Fluoro-1*H*-indol-3-yl)-4-methoxybenzyl)-2-methylcyclohexane-1,3-dione (7l):







^{19}F NMR (377 MHz, $CDCl_3$)

6a'-methoxy-3a'-methyltetrahydrospiro[cyclohexane-1,2'-cyclopenta[*b*]furan]-4,4'(3'*H*)-dione (8):