Spiro 1,3-indandiones: intramolecular photochemical reactions of carbonyl groups with carbon-carbon double bonds.

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Supporting information

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1. General

^{1}H and ^{13}C NMR spectra were recorded in methylene chloride-d_2 on JEOL ECS400 spectrometer at 399.78 and 100.53 MHz respectively. Proton chemical shifts are given in ppm downfield from tetramethylsilane and coupling constants (*J*) in Hertz.

The X-Ray crystallography data were collected on a Bruker-Nonius KappaCCD diffractometer with CCD detector using MoK_{α} radiation, $\lambda = 0.71073$ Å. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication: **2** CCDC 1992513, **7** CCDC 1992514, **11** CCDC 1992517, **12** CCDC 1992515, **15** CCDC 1992516.

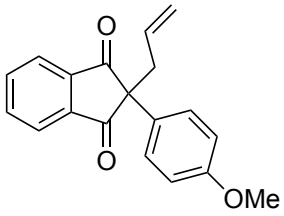
The UV–Vis absorption spectra were recorded with Ocean Optics USB 4000 and JASCO V-660 in 2, 4, 10 and 100 mm quartz cells. Irradiation of solutions for the UV-Vis control was done using a UVP LLC 95000505 lamp (254 nm), LED sources LUMOS 43 (Atlas Photonics) at 300, 315, 330, 350, 405 nm. For the preparative scale photochemical reactions, UV Transilluminator UST-2OM-8R (Biostep), 312 nm and CW laser Module Oxius LBX-405-500-HPE-PP 405 nm at 200 mW (not focused beam) were used.

Geometry optimization, frequency and the NMR spectra calculations for derivatives **7**, **8** and both diastereomers of **13** were carried out using Spartan software (ref. 1) at the EDF2/6-31G(d)//EDF2/6-31G(d) model chemistry, the magnetic shieldings calculated by SCF GIAO method.

2. Syntheses and characterization

Derivative **4** was prepared according to ref. 2 and derivatives **5** and **6** according to ref. 3.

1. *2-(4-methoxyphenyl)-2-prop-2-en-1-yl-1H-indene-1,3(2H)-dione* (**1**).



Derivative **1** was prepared by the procedure used for the preparation of the 2-phenyl derivative (ref. 4).

Colorless leaflets from hexane, m.p. 58°C. Calc.: C, 78.06; H, 5.52. $C_{19}H_{16}O_3$. Found: C, 78.18; H, 5.49.

^{1}H NMR (400 MHz) δ 8.06 – 7.93 (m, 2H), 7.93 – 7.82 (m, 2H), 7.35 – 7.22 (m, 2H), 6.90 – 6.77 (m, 2H), 5.55 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.14 – 5.03 (m, 1H), 4.96 – 4.85 (m, 1H), 3,75 (s, 3H), 2.97 (dd, *J* = 8.2, 7.4 Hz, 2H).

^{13}C NMR (101 MHz,) δ 201.78, 159.67, 142.56, 136.53, 132.63, 129.29, 128.59, 123.97, 119.96, 114.62, 61.87, 55.77, 40.31.

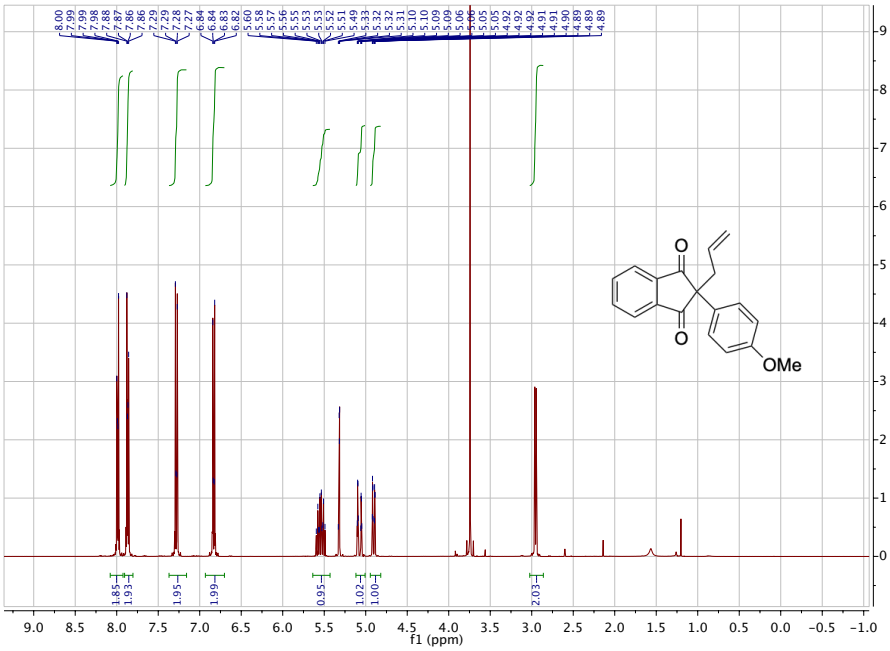


Figure 1S. ^{1}H-NMR spectrum of derivative **1**.

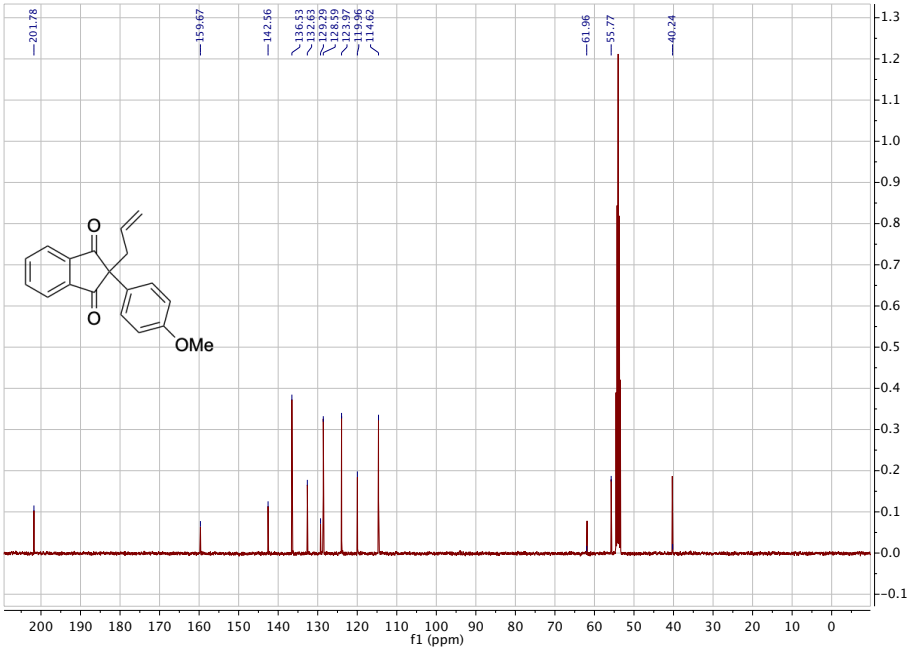
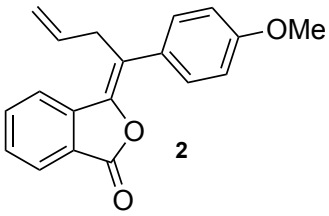


Figure 2S. ^{13}C-NMR spectrum of derivative **1**.

2. Photochemistry of derivative **1**. Isolation of *(3Z)-3-[1-(4-methoxyphenyl)but-3-en-1-ylidene]-2-benzofuran-1(3H)-one* (**2**).



2

A solution of 200 mg of **1** in 600 ml of cyclohexane was irradiated at 405 nm during 70 min. Column chromatography (SiO_2, methylene chloride) gave a fraction with R_f = 0.9 (a mixture of **1** and the major photoproduct **3**) and a fraction with R_f = 0.6 containing the minor photoproduct **2** isolated as a viscous yellowish oil that formed colorless crystals with m.p. = 71-72°C after several days of refrigerating. Calc.: C, 78.06; H, 5.52. $C_{19}H_{16}O_3$. Found: C, 78.29; H, 5.42.

^{1}H NMR (400 MHz) δ 7.94 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.75 (ddd, *J* = 8.2, 8.1, 0.8 Hz, 1H), 7.57 (ddd, *J* = 8.0, 8.0, 0.8 Hz, 1H), 7.54 – 7.52 (m, 2H), 6.97 – 6.95 (m, 2H),

6.08 – 5.94 (m, 1H), 5.21 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.14 (dq, *J* = 10.3, 1.7 Hz, 1H), 3.84 (s, 3H), 3.69 (dt, 2H).

^{13}C NMR (101 MHz) δ 167.29, 159.96, 143.11, 139.08, 135.01, 134.41, 131.20, 130.90, 129.76, 125.97, 125.76, 124.15, 122.44, 117.17, 114.06, 55.84, , 36.43.

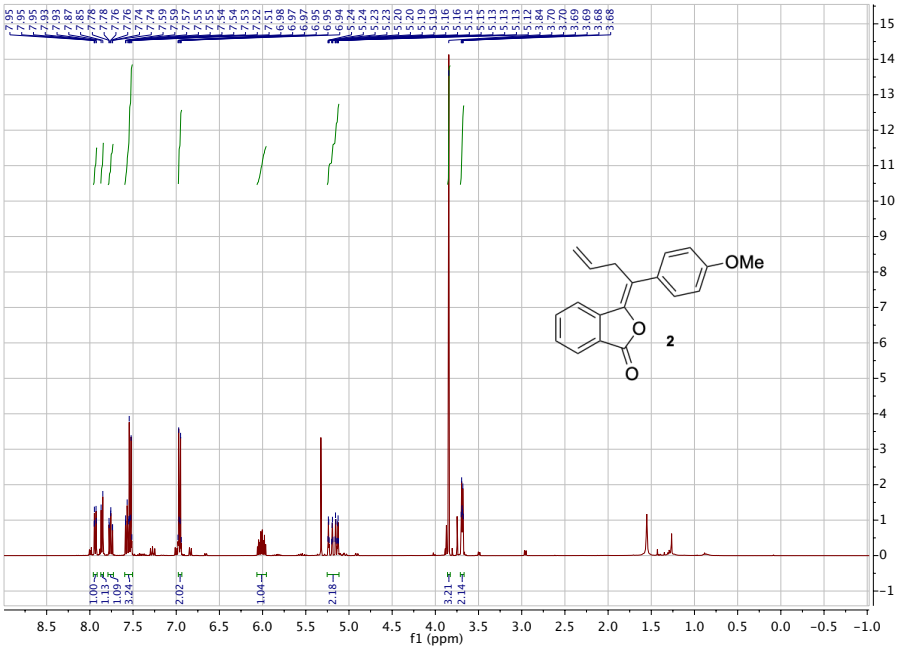


Figure 3S. ^{1}H-NMR spectrum of derivative **2**.

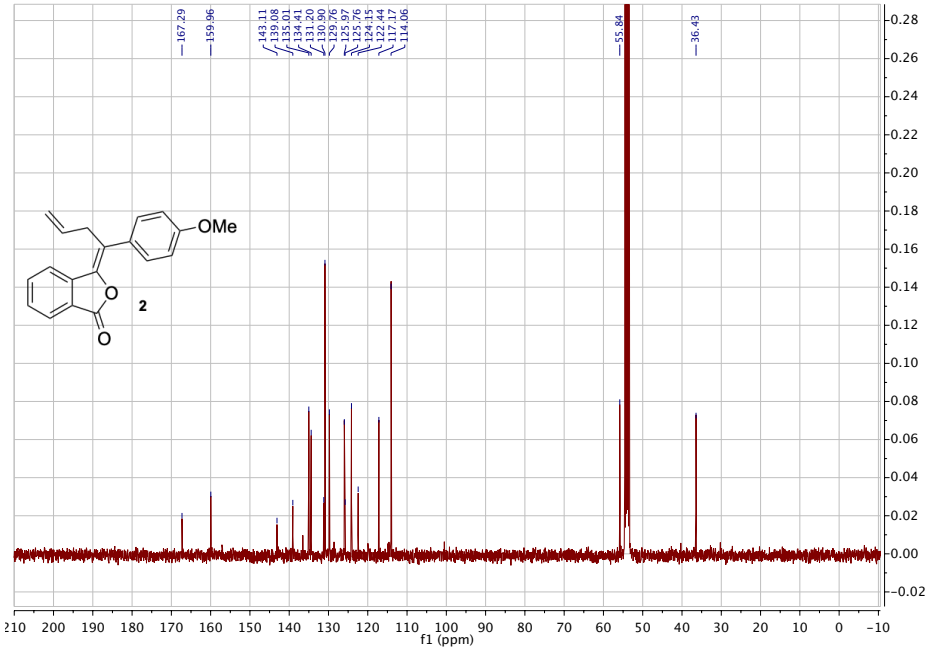


Figure 4S. ^{1}H-NMR spectrum of derivative **2**.

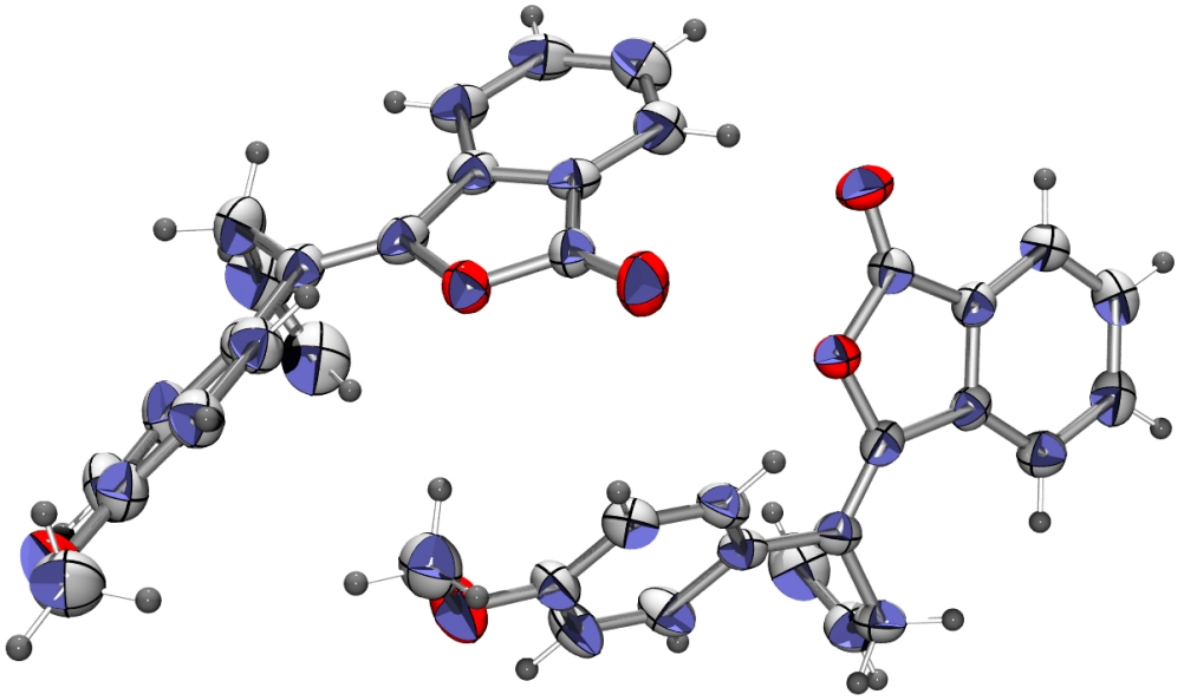
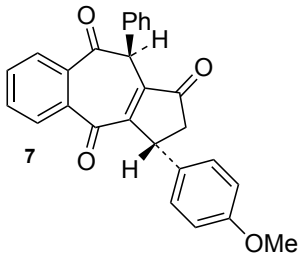


Figure 5S. ORTEP diagram (50% probability ellipsoids) of derivative **2**.

3. Photochemistry of derivative **4**

A solution of **4** (120 mg) in 250 ml of ethylacetate in a quartz vessel was irradiated at 312 nm during 4 h. Evaporation of the solvent afforded yellow oil consisting of about 5% of unreacted **4** and a mixture of isomers **7** and **8** (> 80%) according to ^{1}H NMR spectrum (mixture M1).

Isolation of *(3R,10S)-3-(4-methoxyphenyl-10-phenyl-3,10-dihydrobenzo[f]azulene-1,4,9(2H)-trione* (**7**).



Mixture M1 was separated in a chromatographic column (SiO_2, CH_2Cl_2). The first fraction (50 mg, R_f = 0.7) consisted of 75% of **7** and 25% of **8**, according to the ^{1}H NMR

spectrum. Triple crystallization from hexane afforded 20 mg (17%) of pure **7** as yellowish needles, m.p. 122 – 123°C. Calc.: C, 79.40; H, 4.93. $C_{27}H_{20}O_4$. Found: C, 79.29; H, 4.96.

^{1}H NMR (400 MHz) δ 7.98 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.72 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.59 (td, *J* = 7.5, 1.5 Hz, 1H), 7.53 (td, J = 7,6, 1,5 Hz, 1H), 7.25 – 7.14 (m, 3H), 7.11 – 7.01 (m, 4H), 6.82 – 6.72 (m, 2H), 5,44 (s, 1H), 4.87 (dd, *J* = 7.4, 2.2 Hz, 1H), 3,71 (s, 3H), 3.19 (dd, *J* = 19.6, 7.4 Hz, 1H), 2.61 (dd, *J* = 19.6, 2.3 Hz, 1H).

^{13}C NMR (101 MHz) δ 207.34, 196.74, 188.61, 166.65, 159.28, 139.65, 136.26, 134.93, 134.43, 133.84, 133.37, 132.98, 131.63, 130.65, 129.68, 128.70, 128.48, 127.81, 114.75, 56.46, 55.71, 45.51, 43.75.

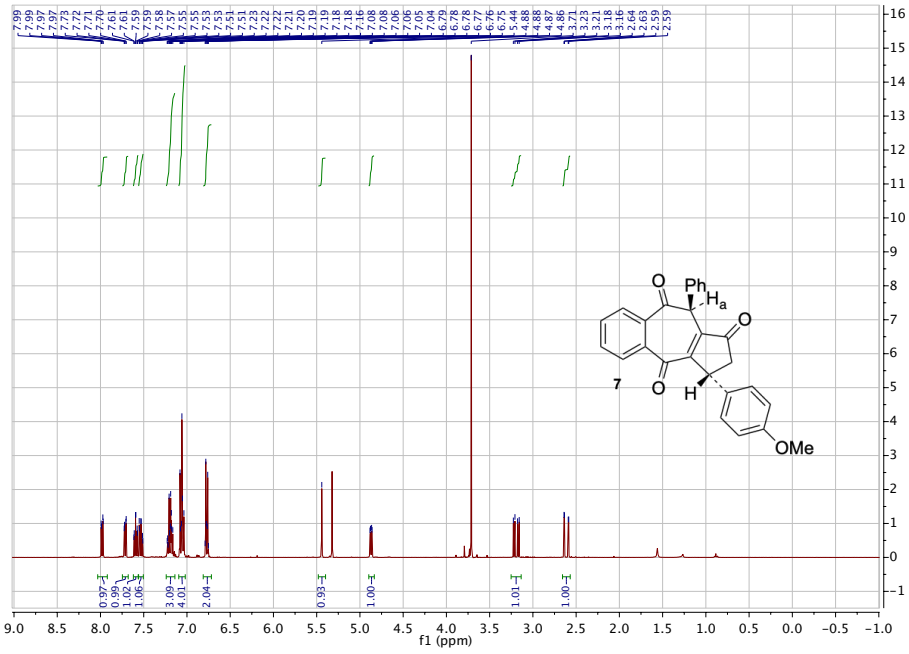


Figure 6S. ^{1}H-NMR spectrum of derivative **7**.

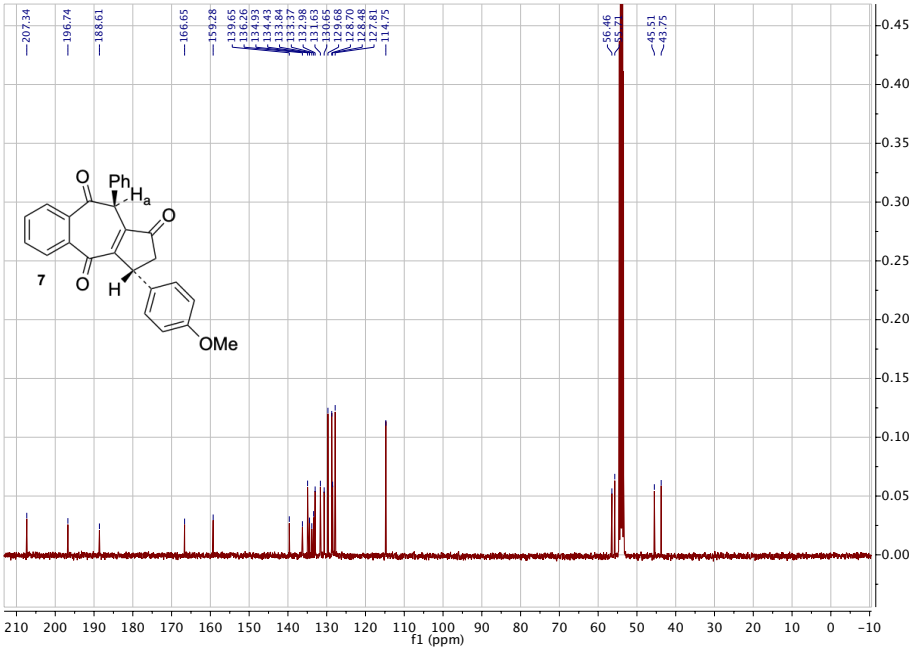
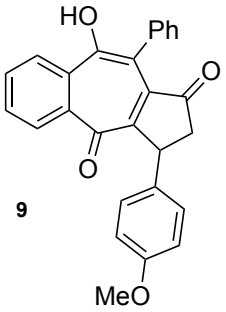


Figure 7S. ^{13}C-NMR spectrum of derivative **7**.

Preparation of *9-hydroxy-3-(4-methoxyphenyl)-10-phenyl-2,3-dihydrobenzo[f]azulene-1,4-dione* (**9**).



A solution of NaOH (20 ml, 5% in water) was added to mixture M1. After 30 min of stirring at RT and filtration, 20 ml of cold HCl (10%) was added at once. The precipitate was filtered, washed with water and air dried to obtain 60 mg (50%) of **9** as dark-yellow powder, m.p. 86 – 88°C (dec). Calc.: C, 79.40; H, 4.93. $C_{27}H_{20}O_4$. Found: C, 79.68; H, 4.86.

^{1}H NMR (400 MHz) δ 8.31 (dd, *J* = 7.5, 2.2 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.66 – 7.45 (m, 4H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.77 – 6.71 (m, 2H), 6.18 (s, 1H), 4.81 (dd, *J* = 7.9, 2.3 Hz, 1H), 3.73 (s, 3H), 3.01 (dd, *J* = 19.0, 7.9 Hz, 1H), 2.37 (dd, *J* = 19.0, 2.4 Hz, 1H).

^{13}C NMR (101 MHz) δ 207.25, 190.03, 160.32, 159.00, 154.22, 140.11, 139.40, 135.21, 134.78, 132.71, 131.62, 130.82, 130.10, 129.38, 129.16, 128.59, 128.52, 114.45, 113.28, 55.69, , , 46.37, 43.08.

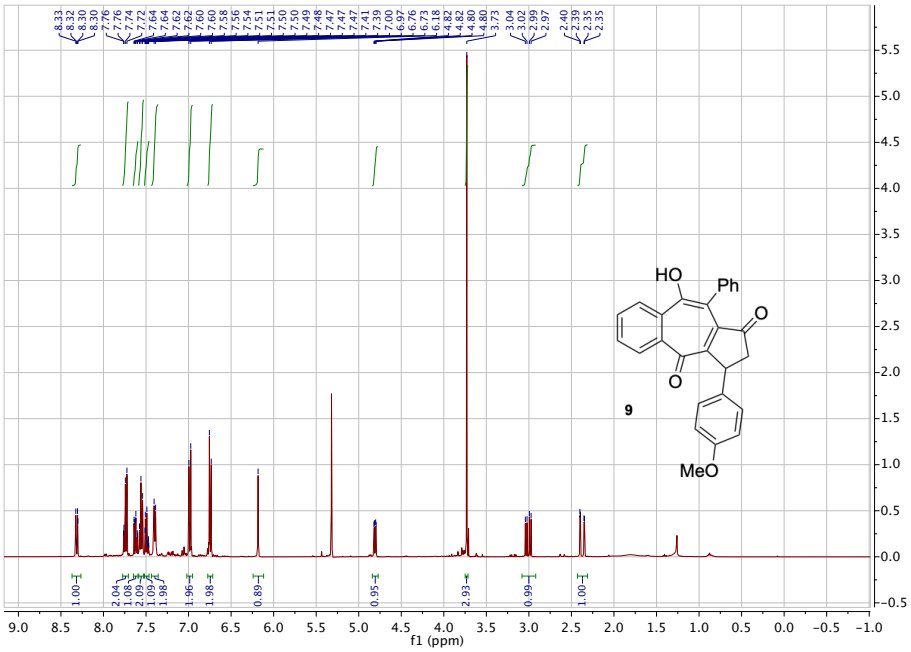


Figure 8S. ^{1}H-NMR spectrum of derivative **9**.

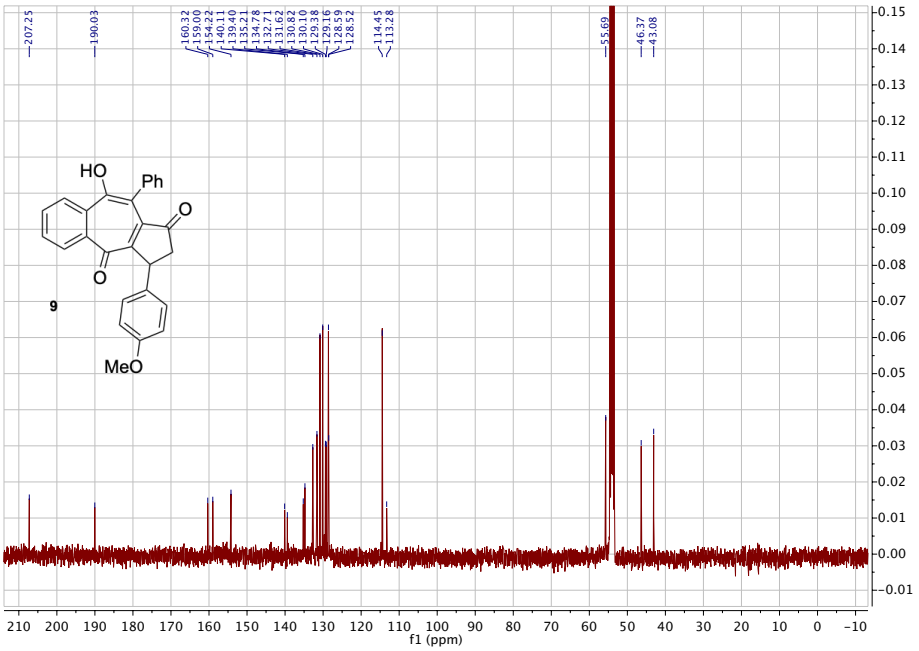
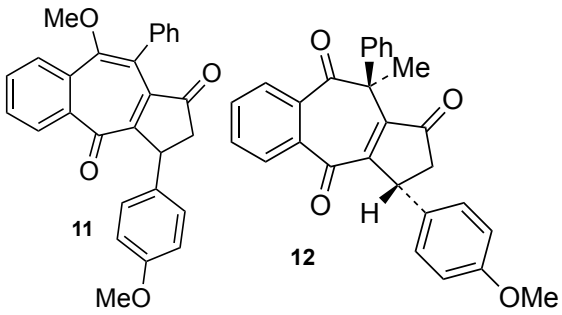


Figure 9S. ^{1}H-NMR spectrum of derivative **9**.

a) Preparation of a mixture of **7**, **8** and **9** (M2).

Mixture M1 was dissolved in ethanol, a solution of NaOH (20 ml, 3% in water) was added, the resulting suspension was stirred for 20 min at 50°C and filtered. An excess of HCl (10% solution) was added to the deeply colored magenta solution to precipitate 100 mg (83%) of deep yellow solid. The solid, according to ^{1}H NMR is a mixture of **7** and **9** (M2) with the admixture of **8** (less than 5%).

b) Preparation of *9-methoxy-3-(4-methoxyphenyl)-10-phenyl-2,3-dihydrobenzo[f]azulene-1,4-dione* (**11**) and *trans-3-(4-methoxyphenyl)-10-methyl-10-phenyl-3,10-dihydrobenzo[f]azulene-1,4,9(2H)-trione* (**12**).



A dry mixture M2 (100 mg), anhydrous K_2CO_3 (100 mg) and 1 ml of methyl iodide in dry acetone (7 ml) were heated during 20 h 50°C in a sealed ampulla. The solvent was evaporated and the residue was extracted by CH_2Cl_2 and the inorganic solid was filtered off. After column chromatography (SiO_2, CH_2Cl_2), two fractions with R_f = 0.55 and R_f = 0.3 were obtained.

The first fraction after evaporation and crystallization from heptane afforded 30 mg (29%) of *trans* C-Me isomer **12** as yellowish needles, m.p. 129 – 130°C. Calc.: C, 79.60; H, 5.25. $C_{28}H_{22}O_4$. Found: C, 79.52; H, 5.28.

^{1}H NMR (400 MHz,) δ 7.72 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.59(dd, *J* = 7.9, 6.9 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 7.9, 6.9 Hz, 1H), 7.18 – 7.06 (m, 3H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.89 (ddd, *J* = 4.7, 3.6, 2.2 Hz, 2H), 6.72 (d, *J* = 8,7 Hz, 2H), 4.72 (dd, *J* = 7.3, 2.8 Hz, 1H), 3.69 (s, 3H), 3.16 (dd, *J* = 19.2, 7.3 Hz, 1H), 2.56 (dd, *J* = 18.8, 2.8 Hz, 1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz,) δ 206.75, 199.47, 190.61, 169.90, 159.24, 144.10, 140.90, 137.69, 134.71, 134.25, 133.34, 132.33, 131.13, 129.18, 129.01, 128.61, 127.54, 127.44, 114.74, 59.77, 55.68, 46.80, 43.30, 23.70.

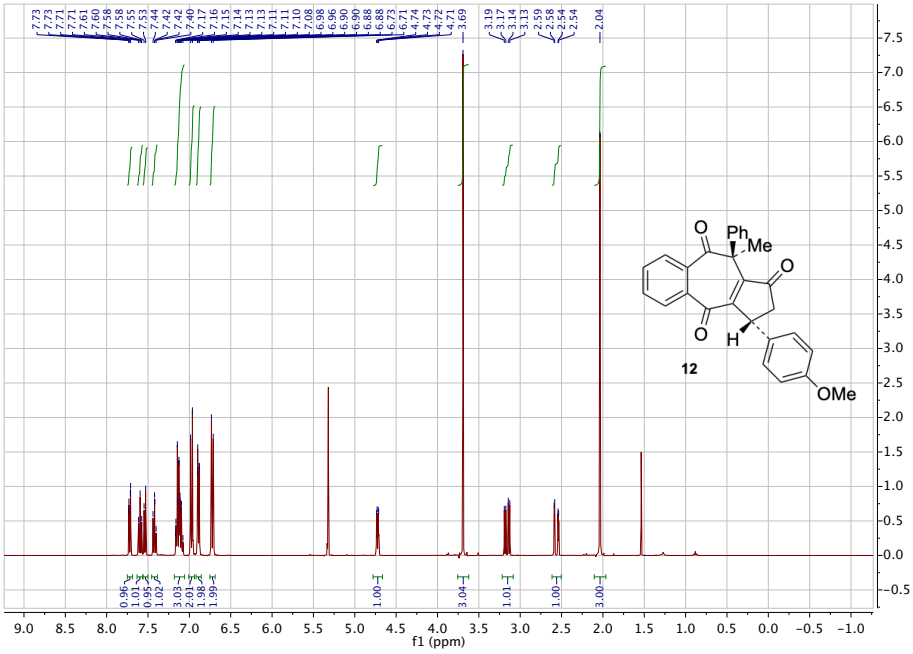


Figure 10S. ^{1}H-NMR spectrum of derivative **12**.

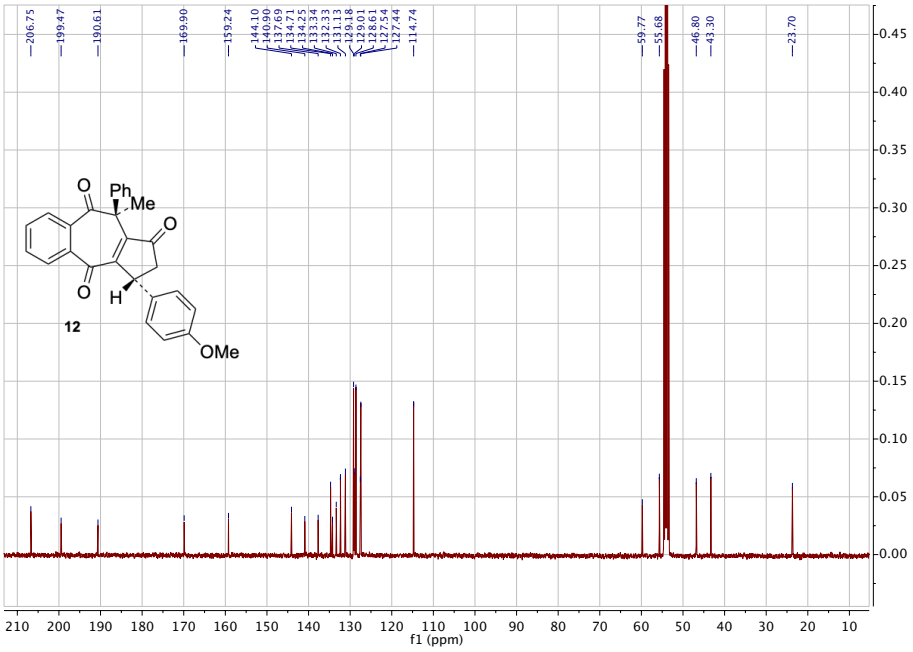


Figure 11S. ^{13}C-NMR spectrum of derivative **12**.

The second fraction after evaporation and crystallization from heptane afforded 40 mg (39%) of the enol ether **11** as light yellow needles, m.p. 154 – 156°C. Calc.: C, 79.60; H, 5.25. $C_{28}H_{22}O_4$. Found: C, 79.68; H, 5.34.

^{1}H NMR (400 MHz) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.67 (m, 1H), 7.63 – 7.51 (m, 2H), 7.47 – 7.31 (m, 5H), 6.96 (dd, *J* = 8.6, 1.5 Hz, 2H), 6.75 (dd, *J* = 8.6, 1.5 Hz, 2H), 4.81 (dt, *J* = 7.7, 1.6

Hz, 1H), 3.73 (s, 3H), 3.15 (s, 3H), 3.03 (ddd, *J* = 18.9, 7.8, 1.5 Hz, 1H), 2.40 (dt, *J* = 19.0, 1.8 Hz, 1H).

^{13}C NMR (101 MHz) δ 206.54, 191.63, 164.64, 159.13, 157.65, 141.43, 139.89, 136.87, 134.07, 132.98, 132.77, 131.21, 130.58, 128.85, 128.67, 128.61, 127.98, 127.56, 124.77, 114.51, 59.97, 55.71, 46.40, 43.58.

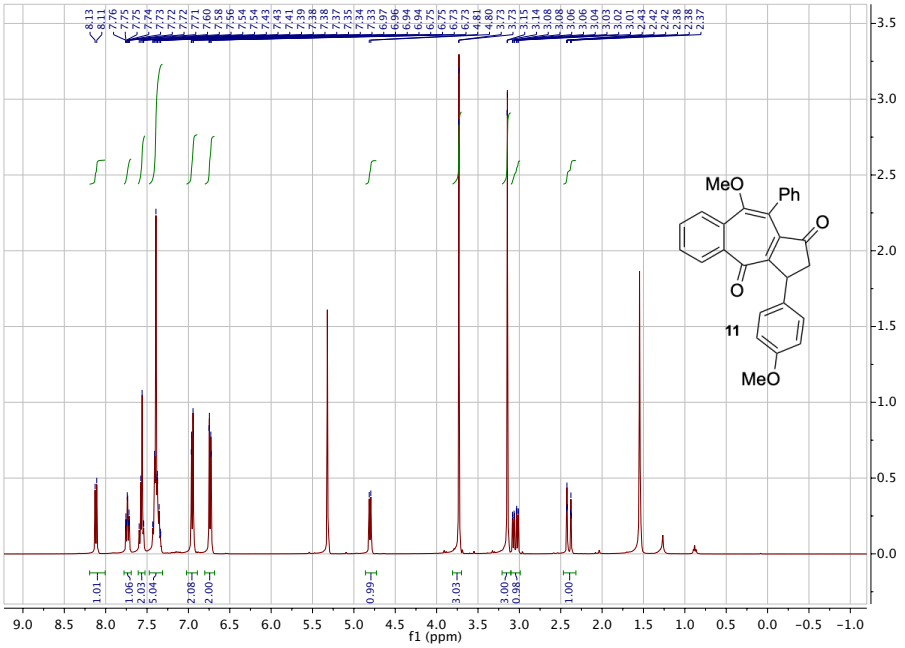


Figure 12S. ^{1}H-NMR spectrum of derivative **11**.

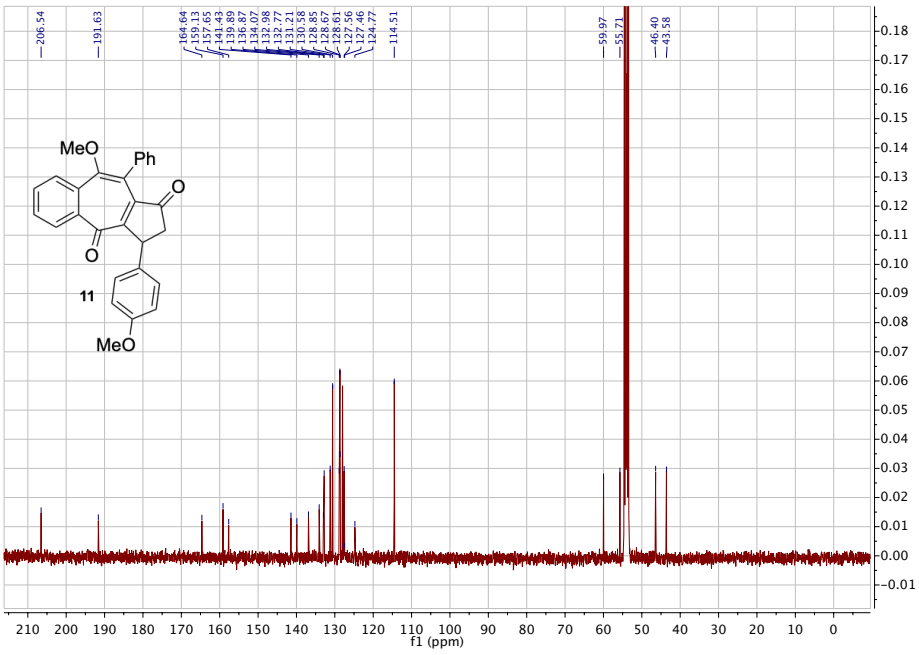
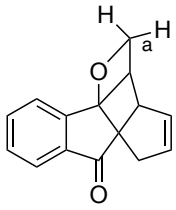


Figure 13S. ^{13}C-NMR spectrum of derivative **11**.

The overall yield of **11** and **12** was 56% calculated on starting derivative **4**.

4. Photochemistry of derivative **5**. Isolation of the Paternò – Büchi product: *6,6a,6b,9-tetrahydro-10H-cyclopenta[3,4]indeno[1',2':1,4]cyclobuta[1,2-b]oxet-10-one* (**13**).



13

A solution of **5** (300 mg) in cyclohexane (900 ml) was irradiated at 254 nm in a quartz vessel during 3 h. Evaporation of the solvent afforded a yellow oil. After column chromatography (SiO_2, CH_2Cl_2), two fractions with R_f = 0.55 and R_f = 0.3 were obtained. The first fraction with R_f = 0.75 gave after evaporation the starting compound **5** (about 200 mg). The second fraction (R_f = 0.25) afforded 30 mg (10% or 30% on the reacted **5**) of **13** as oil. Calc.: C, 80.34; H, 5.39. $C_{15}H_{12}O_2$. Found: C, 79.96; H, 5.48.

^{1}H NMR (400 MHz) δ 7.87 – 7.83 (m, 1H), 7.82 – 7.79 (m, 1H), 7.77 – 7.72 (m, 1H), 7.54 – 7.50 (m, 1H), 6.25 (dtd, *J* = 5.6, 2.2, 1.3 Hz, 1H), 5.71 (dq, *J* = 4.9, 2.4 Hz, 1H), 4.93 (ddd, J = 6.8, 6.8, 0.5 Hz 1H), 4.83 (dd, *J* = 6.8, 4.2 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.39 – 3.31 (m, 1H), 2.96 (ddt, *J* = 17.4, 3.3, 2.4 Hz, 1H), 2.71 (dtd, *J* = 17.4, 2.2, 1.3 Hz, 1H).

^{13}C NMR (101 MHz) δ 205.25, 151.35, 138.98, 136.83, 135.74, 130.12, 128.18, 125.26, 123.89, 92.67, 71.72, 63.57, 50.06, 43.50, 36.75.

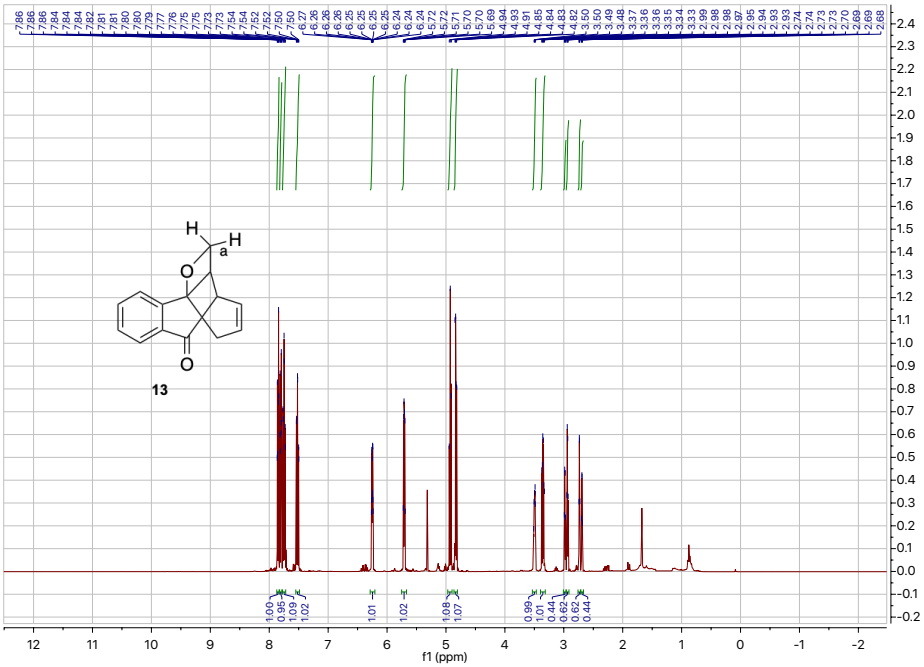


Figure 14S. ^{1}H-NMR spectrum of derivative **13**.

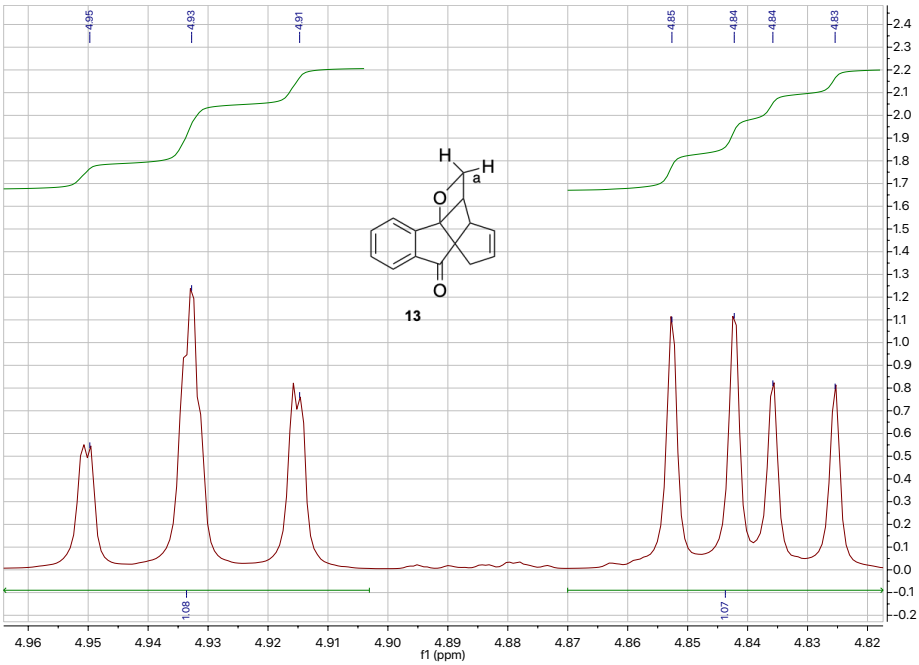


Figure 15S. Expansion of ^{1}H-NMR spectrum of derivative **13** (4.8 – 5 ppm).

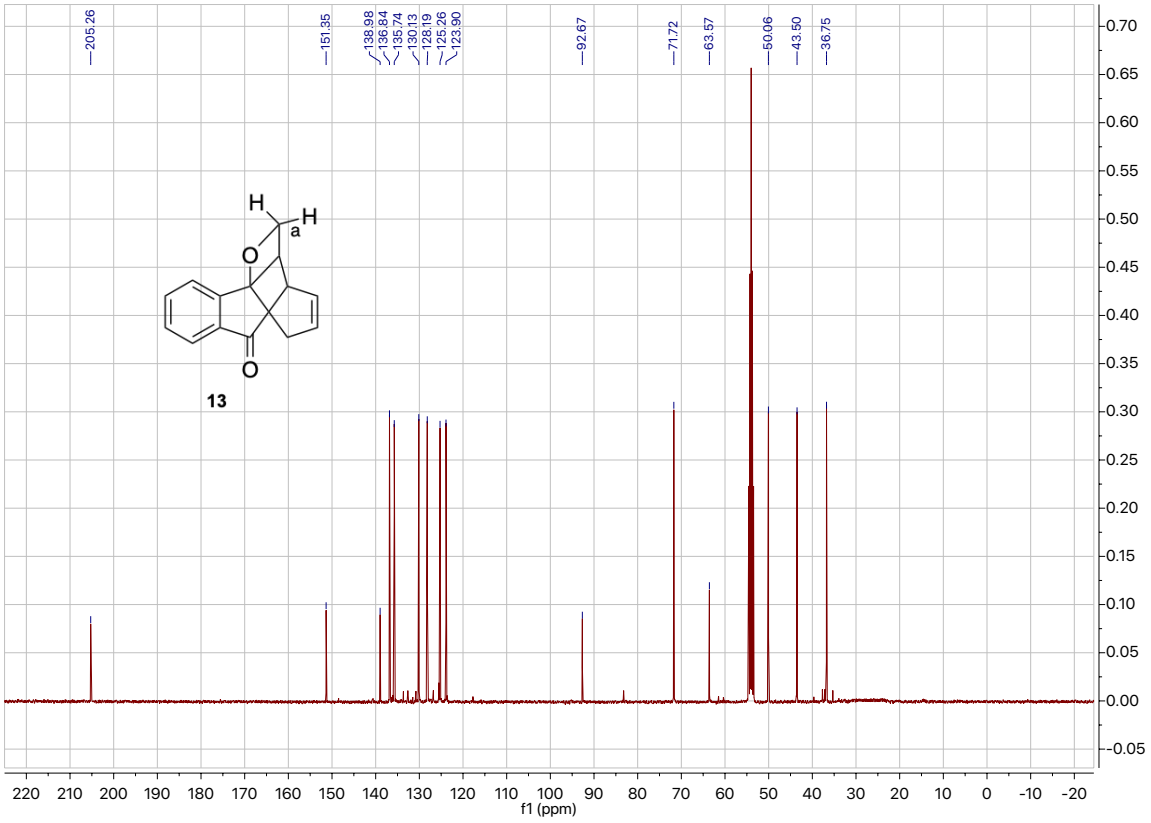
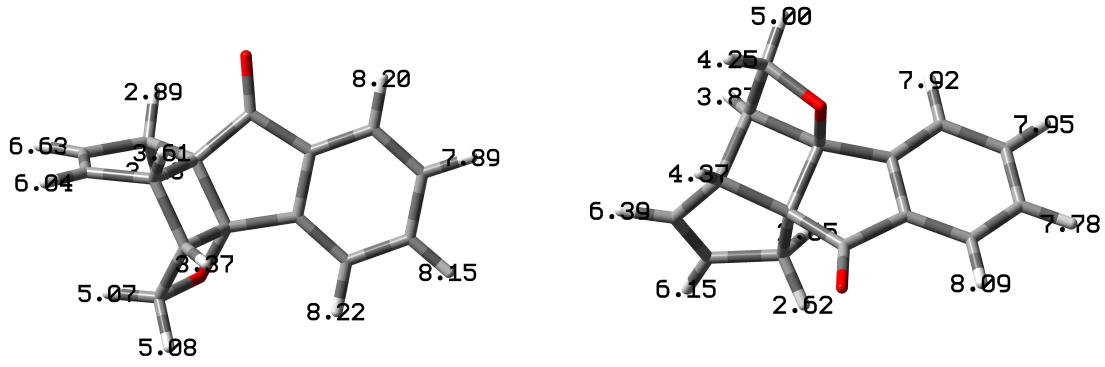
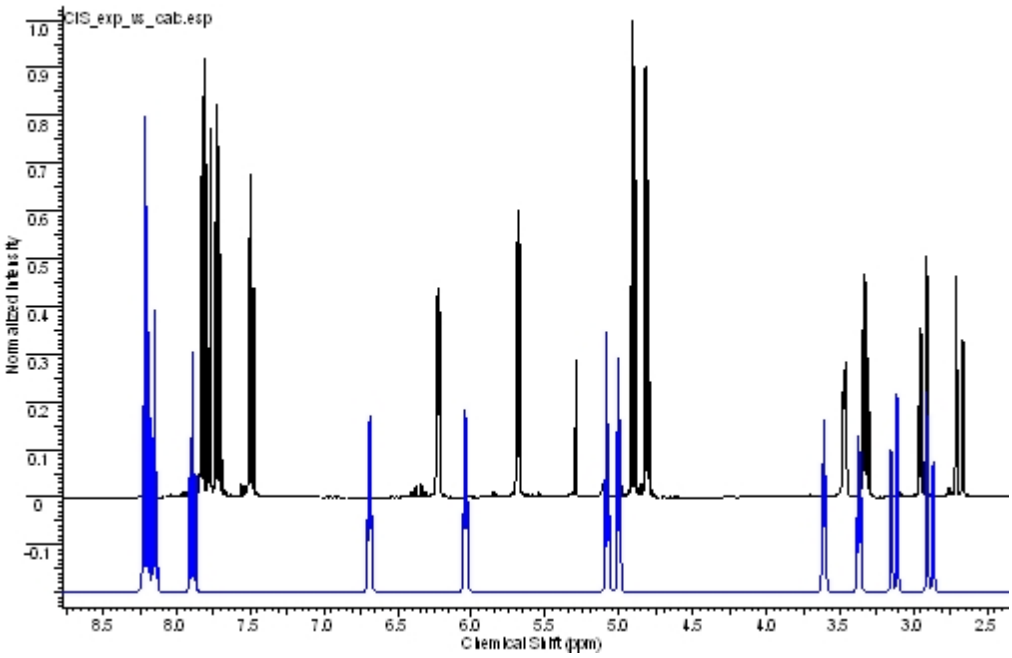


Figure 16S. ^{13}C-NMR spectrum of derivative **2**.

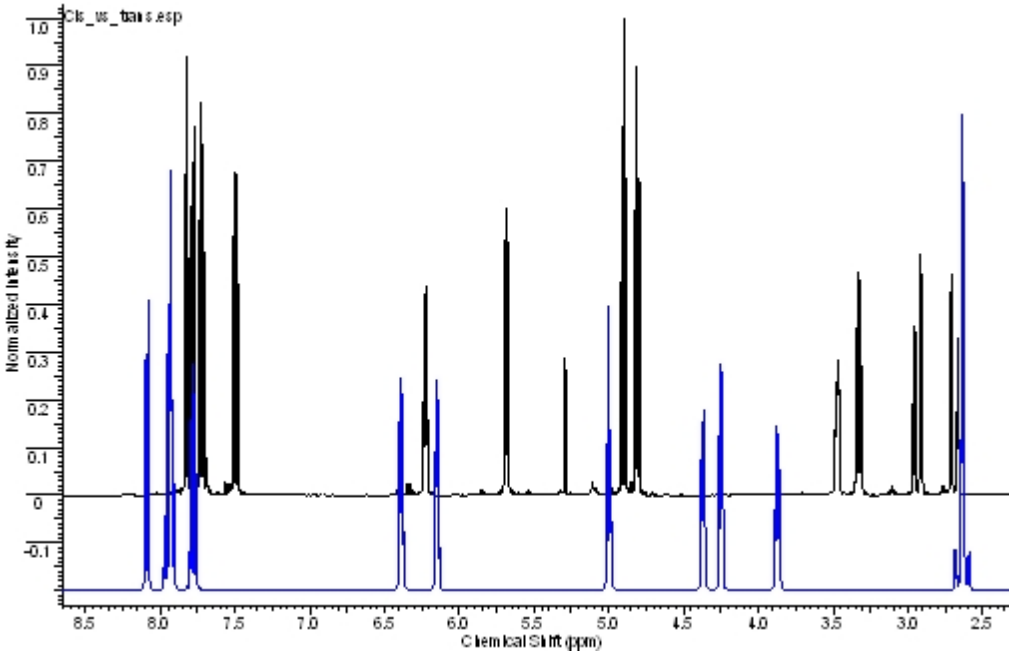


a) b)

Figure 17S. Geometry optimized structures and proton shifts of derivative **13** (*syn*-isomer, a) and 1,3a,4,5-tetrahydro-10*H*-4,5a-epoxypentaleno[1,6a-*a*]inden-10-one (*anti*-isomer, b).



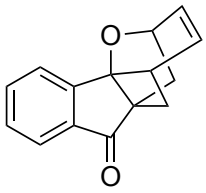
a)



b)

Figure 18S. Experimental (black) and calculated (blue, a) *syn*-isomer and b) *anti*-isomer) ^{1}H-NMR spectra of derivative **13**.

5. Photochemistry of derivative **6**. Isolation of *4a,5-dihydro-2H,6H-2,5a-methanoindeno[1',2':1,4]cyclobuta[1,2-b]pyran-6-one* (**15**).



15

A solution of **6** (200 mg) in 600 ml of cyclohexane was irradiated at 312 nm during 1 h in a quartz vessel. The fraction with R_f = 0.5 was collected and evaporated. The residue was crystallized from heptane to afford 120 mg (60%) of **15** as colorless prisms with m.p. 127-128°C. Calc.: C, 80.34; H, 5.39. $C_{15}H_{12}O_2$. Found: C, 80.28; H, 5.36.

^{1}H NMR (400 MHz,) δ 7.78 – 7.67 (m, 3H), 7.61 – 7.54 (m, 1H), 6.46 – 6.31 (m, 2H), 5.01 (t, *J* = 5.4 Hz, 1H), 3.14 (td, *J* = 7.6, 3.8 Hz, 1H), 2.26 (dd, *J* = 11.8, 7.5 Hz, 1H), 2.17 – 2.04 (m, 2H), 1.90 (dd, *J* = 11.8, 1.8 Hz, 1H).

^{13}C NMR (101 MHz,) δ 205.26, 148.48, 140.57, 135.79, 133.65, 132.63, 130.77, 126.78, 125.35, 85.70, 83.21, 61.47, 37.70, 37.11, 35.31.

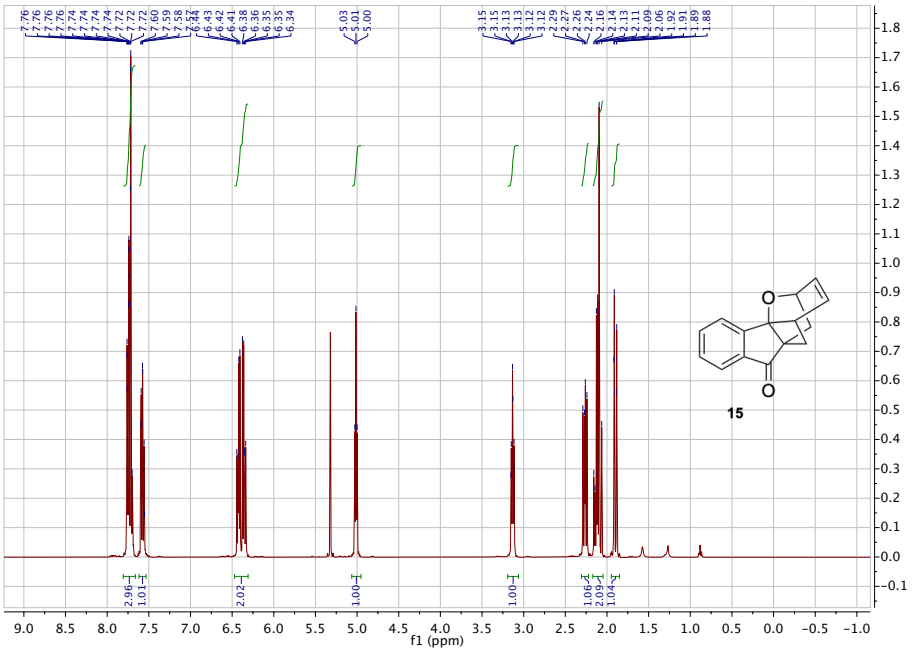


Figure 19S. ^{1}H-NMR spectrum of derivative **15**.

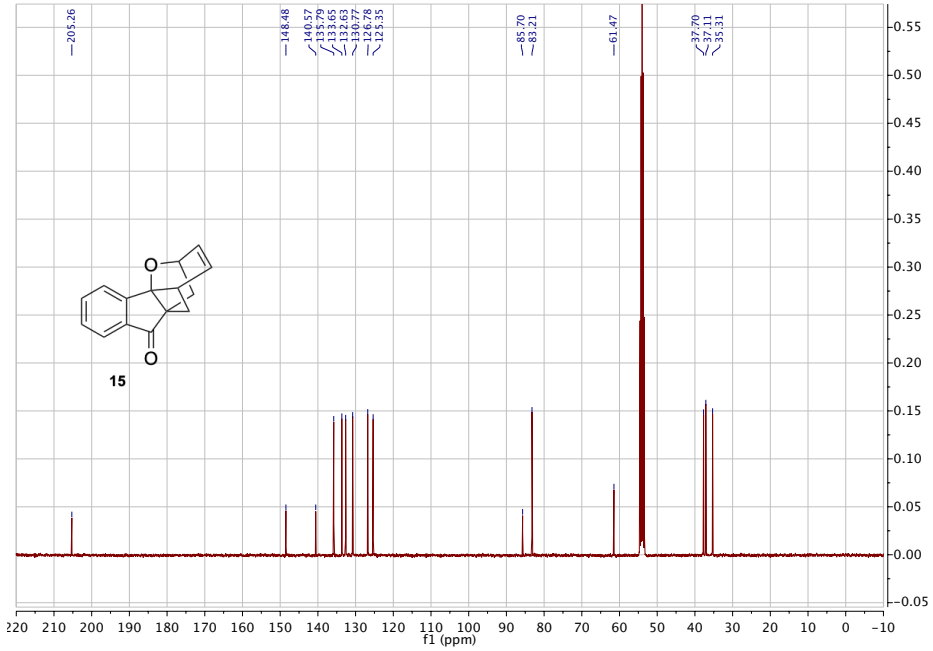


Figure 20S. ^{13}C-NMR spectrum of derivative **15**.

3. References

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