

Photochemically driven tandem process in the construction of a biscyclopropylcage from 2,5-dimethoxy-*p*-benzoquinone and terminal acetylenes

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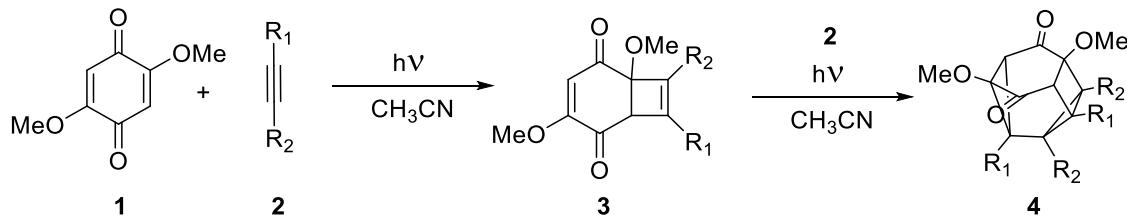
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1. General Methods

All reactions were carried out under nitrogen atmosphere. 2,5-Dimethoxy-*p*-benzoquinone was synthesized from commercial 2,5-dihydroxy-*p*-benzoquinone according to the method reported in the literature.¹ All other reagents were commercial compounds of the highest purity available. Thin-layer chromatography (TLC) was conducted on chromatoplates of SiO₂ 60F-254 obtained from Merck and visualised by UV irradiation (254 nm) or by staining with a solution of phosphomolibdic acid or vanillin. Flash chromatography was carried out with SiO₂ 60 (230-400 mesh; Merck) under pressure. ¹H-NMR spectra were recorded at 25 °C on Bruker AMX-400 at 400 MHz with residual protic solvent as internal reference [CDCl₃, δ_H = 7.26 ppm], chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). The proton spectra are reported as follows: chemical shift δ (multiplicity, coupling constant J, number of protons). The following symbols were used for the description of coupling patterns: multiplet (m), singlet (s), doublet (d), triplet (t). ¹³C-NMR spectra were recorded on the same spectrometer at 100 MHz, with the central peak of CDCl₃, δ_C = 77.16 ppm as reference. UV-Vis spectra were recorded on a Jasco J-815 spectropolarimeter using a one-centimetre thick quartz cuvette at 25°C. All compound solutions were prepared in acetonitrile by dissolving a known mass in a known volume of solvent. The background was always obtained against the solvent. IR spectra were recorded on a Nicolet 6700 IR-Turbo infrared spectrometer. Peaks are quoted in wavenumber (cm⁻¹). ESI mass spectra were recorded with an APEX3 instrument. Ions were generated using a Combi MALDI-- electrospray ionization (ESI) source. Samples were prepared by adding a spray solution of 70:29:9:0.1 (v/v/v) CH₃OH/water/formic acid to a solution of the sample at a v/v ratio of 1 to 5% to give the best signal-to-noise ratio. High-resolution mass spectra were taken on a VG Autospec instrument. Crystallographic data were collected at 100 K using a Bruker D8 Venture diffractometer with a Photon 100 CMOS detector and Mo-Kα radiation (λ = 0.71073 Å) generated by an Incoatec high brillance microfocus source equipped with Incoatec Helios multilayer optics. The software APEX3² was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT³ for integration of intensity of reflections, and SADABS⁴ for scaling and empirical absorption correction. Using OLEX2⁵, the structure was solved by dual-space algorithm using the program SHELXT⁶ and all non-hydrogen atoms was refined with anisotropic thermal parameters by full-matrix least-squares calculations on F² with the SHELXL⁶ refinement package. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Drawings were produced with PLATON⁷.

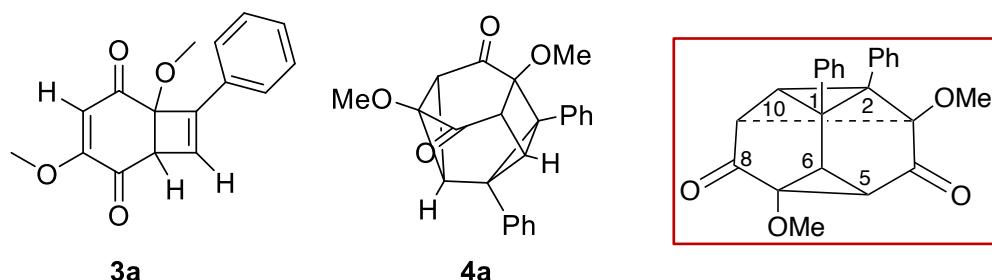
2. General procedure for the [2+2] photoaddition of 2,5-dimethoxy-*p*-benzoquinone and alkyne



A suspension of 2,5-dimethoxy-*p*-benzoquinone **1** (1 equiv.) in acetonitrile (0.03 M) in a Pyrex Schlenk flask provided with magnetic stirring was bubbled with N₂ for 20 minutes. Then, the corresponding alkyne **2** (9 equiv.) was added and the reaction mixture was irradiated for 11 h* at room temperature, placing the reaction vessel about 10 cm from the irradiation source [Hanovia UV lamp (450 W)]. The solvent was removed under reduced pressure and the remaining solid was purified by flash chromatography (SiO₂) using different hexane-AcOEt mixtures as solvent. * Unless otherwise stated.

3. Substrates characterization

1,4-dimethoxy-8-phenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione (3a) and **3,7-dimethoxy-1,2-diphenyl pentacyclo[4.4.0.0^{3,9}.0^{5,7}.0^{2,10}]decan-4,8-dione (4a)**



Following the general procedure, the reaction of **1** (100 mg, 0.595 mmol) and alkyne **2a** (0.6 mL, 5.35 mmol) rendered **3a** as a yellowish solid (8 mg, 5%) and **4a** as a white solid (89 mg, 40%) after purification by flash chromatography (SiO₂; Hexane:AcOEt (8:2)).

When **1** (300 mg, 1.78 mmol) in acetonitrile (60 mL) was reacted with phenylacetylene **2a** (1.8 mL, 16.4 mmol) for 12 h, **4a** was obtained as the only product (327 mg, 49%). **4a** is thermally stable as shown when a toluene solution was refluxed for several hours and starts to degrade after prolonged irradiations times.

3a: **¹H-NMR** (400 MHz, CDCl₃): δ = 7.61 (m, 2H), 7.35 (m, 3H), 6.71 (d, J= 1.8 Hz, 1H), 5.98 (s, 1H), 3.97 (d, J= 1.8 Hz, 1H), 3.79 (s, 3H), 3.41 (s, 3H). **¹³C-NMR** (100 MHz, CDCl₃): δ = 194.9, 191.6, 159.9, 151.7, 130.5, 130.3, 129.8, 128.8, 126.5, 111.1, 85.0, 56.7, 53.8, 53.4. **HRMS (ESI-TOF)** m/z: [M+H]⁺ Calcd. for C₁₆H₁₅O₄ 271.0965; Found 271.0960. **UV-vis** (CH₃CN): λ (ε): 254 (33044 Lmol⁻¹cm⁻¹), 346 (2566 Lmol⁻¹cm⁻¹) nm. **FT-IR (ATR)** ν 3442, 3429, 3409, 3396, 3382, 3303, 3062, 3022, 2954, 2924, 2853, 1997, 1702, 1663, 1602, 1554, 1492, 1449, 1362, 1305, 1254, 1239,

1186, 1166, 1099, 1081, 1012, 987, 961, 928, 854, 806, 767, 744, 694, 643, 590, 537, 491, 449 cm⁻¹.

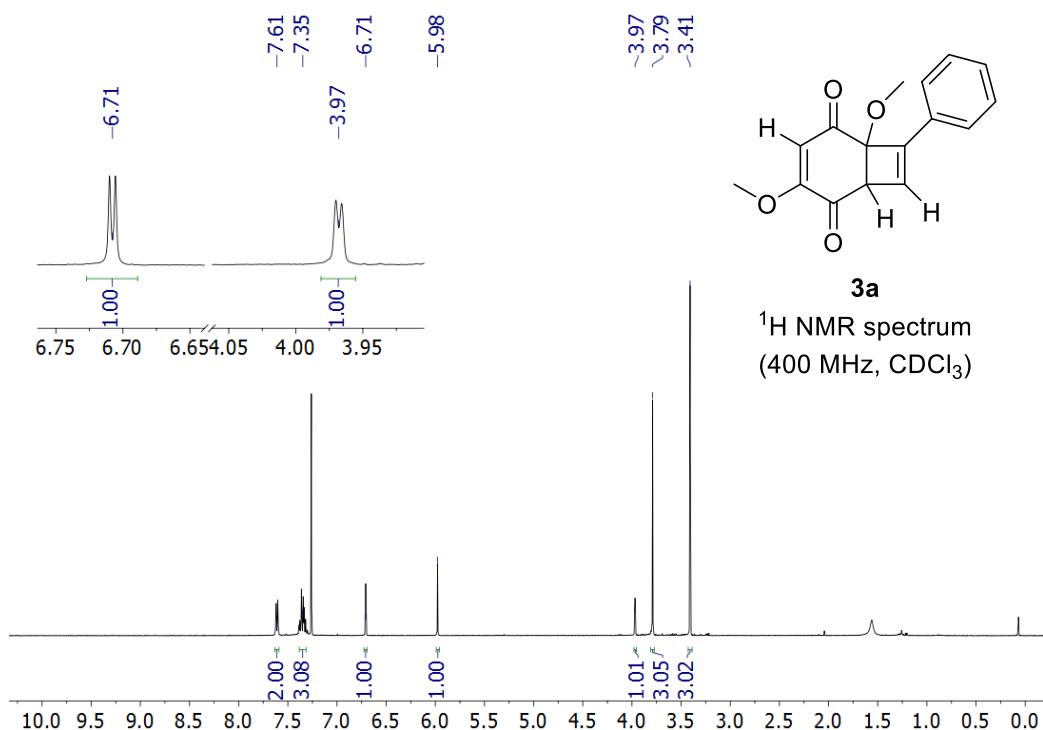


Figure S1. **3a** ^1H -NMR (CDCl_3) spectra.

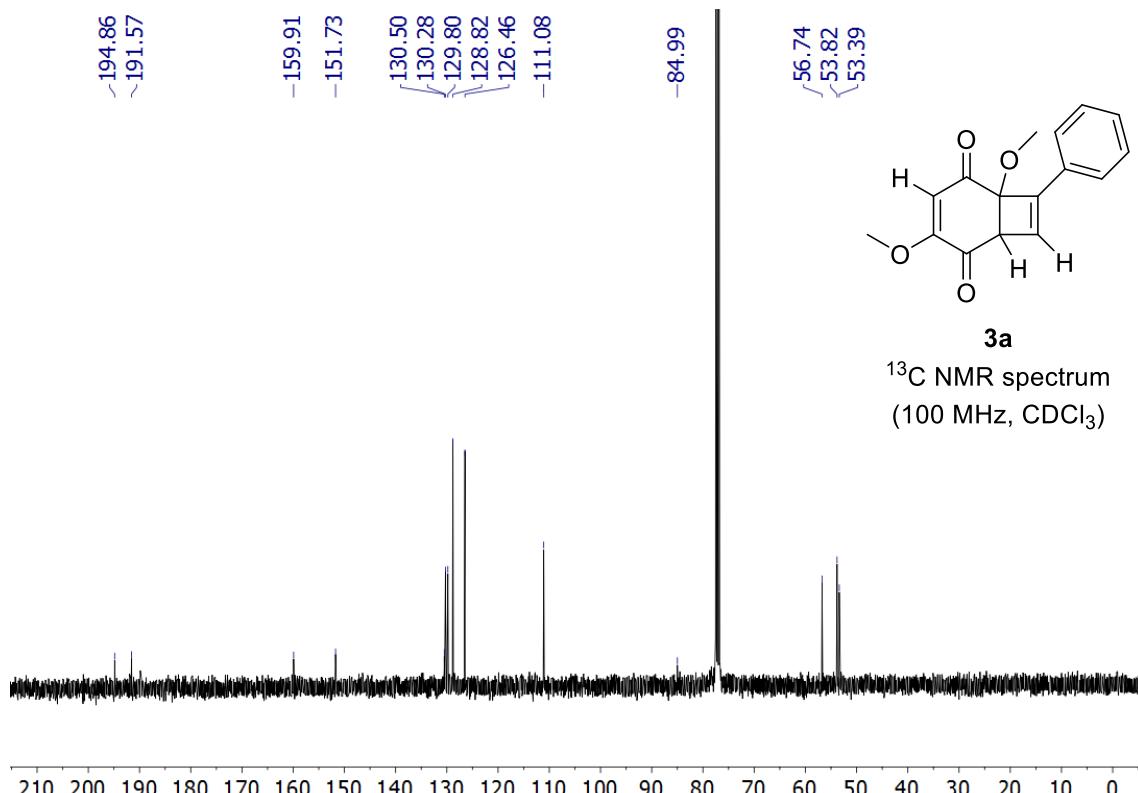


Figure S2. **3a** ^{13}C -NMR (CDCl_3) spectra.

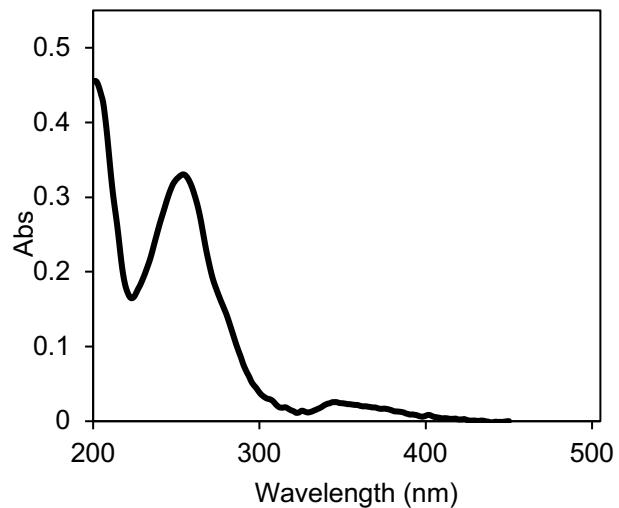


Figure S3. UV/Vis spectra of **3a** [$1.0 \cdot 10^{-5}$ M] in acetonitrile.

4a: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.06 (m, 8H), 6.65 (m, 2H), 3.74 (d, J = 5.0 Hz, 1H), 3.54 (s, 3H), 3.31 (s, 3H), 3.27 (d, J = 5.0 Hz, 1H), 3.25 (d, J = 10 Hz, 1H), 2.85 (d, J = 10 Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 202.1, 200.4, 136.9, 131.7, 129.7, 128.8, 127.9, 127.8, 127.7, 127.1, 82.9, 74.1, 58.0, 53.0, 52.9, 50.4, 45.0, 44.6, 37.6, 36.7. **HRMS (ESI-TOF)** m/z : [M+H] $^+$ Calcd. for $\text{C}_{24}\text{H}_{21}\text{O}_4$ 373.1434; Found 373.1430. **UV-vis** (CH_3CN): λ (ϵ): 208 (31889 $\text{Lmol}^{-1}\text{cm}^{-1}$), 259 (1358 $\text{Lmol}^{-1}\text{cm}^{-1}$), 315 (571 $\text{Lmol}^{-1}\text{cm}^{-1}$) nm. **FT-IR (ATR)** ν 3028, 2916, 2848, 2726, 2641, 1739, 1714, 1682, 1506, 1468, 1371, 1295, 1238, 1177, 1131, 1070, 1044, 1020, 984, 932, 890, 757, 719, 631, 608 cm^{-1} .

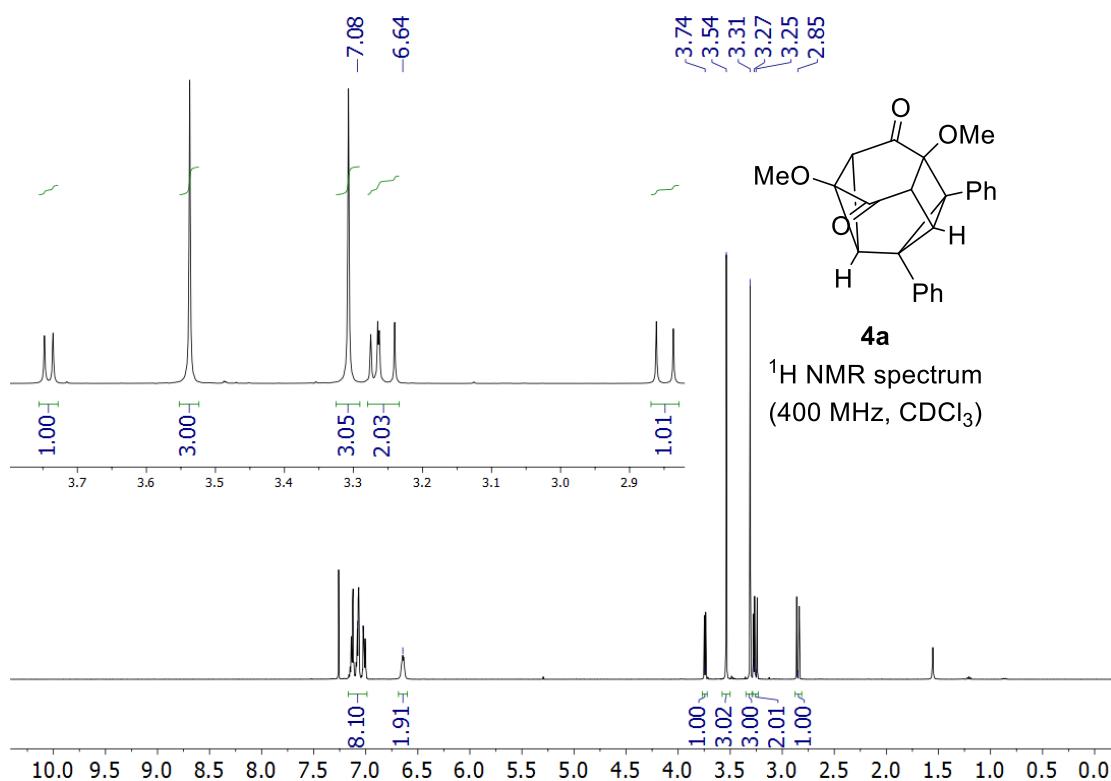


Figure S4. **4a** ^1H -NMR (CDCl_3) spectra.

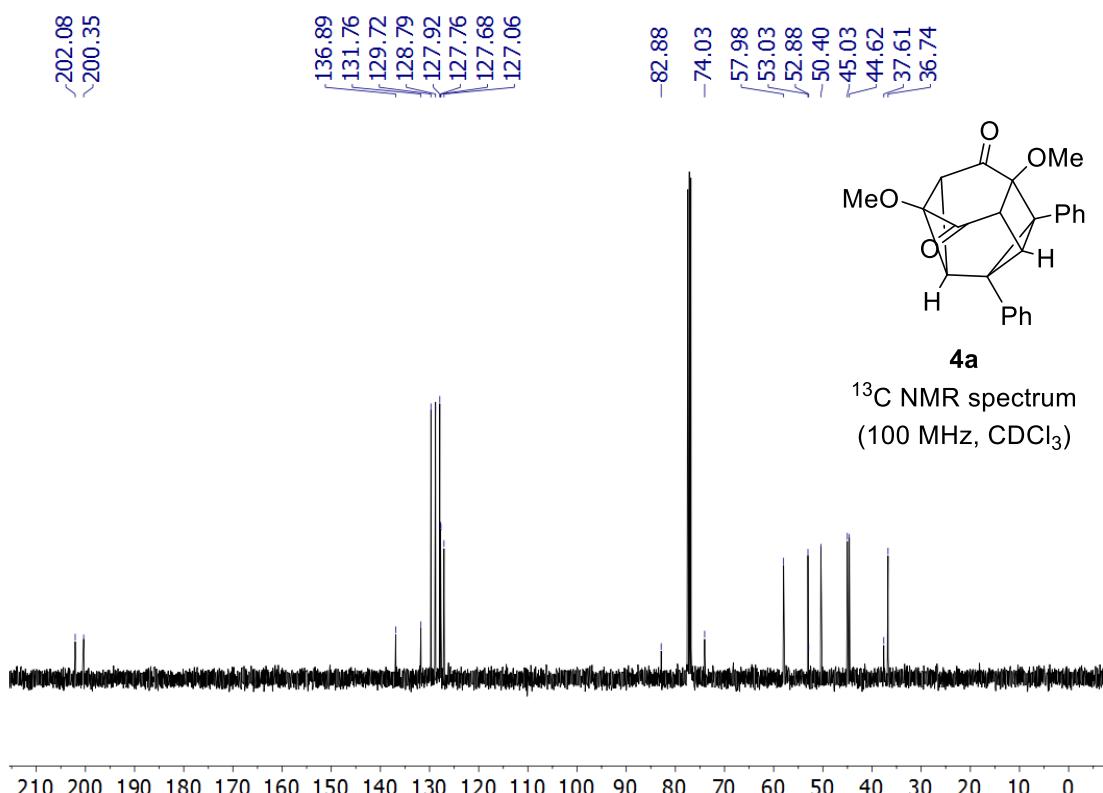


Figure S5. **4a** ^{13}C -NMR (CDCl_3) spectra.

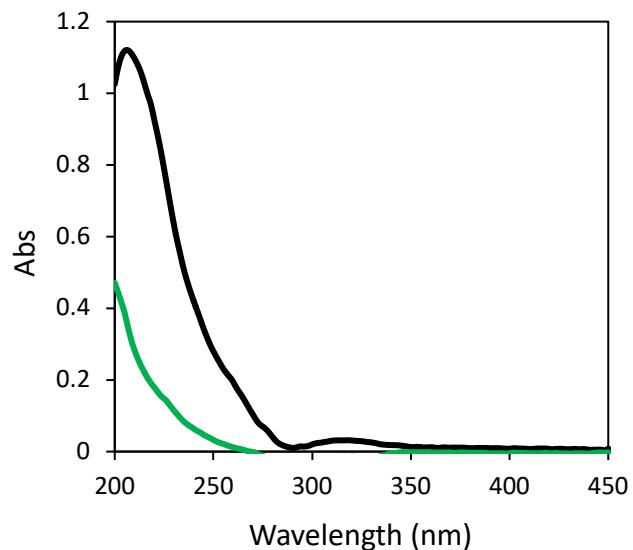


Figure S6. UV/Vis spectra of **4a** in acetonitrile: black line [$5.5 \cdot 10^{-5} \text{ M}$] and green line [$1.0 \cdot 10^{-5} \text{ M}$].

Crystallographic data of **4a**

Crystals suitable for x-ray diffraction of compound **4a** can be grown from the slow evaporation of a solution of **4a** in a hexane:ethyl ether(1:1) mixture.

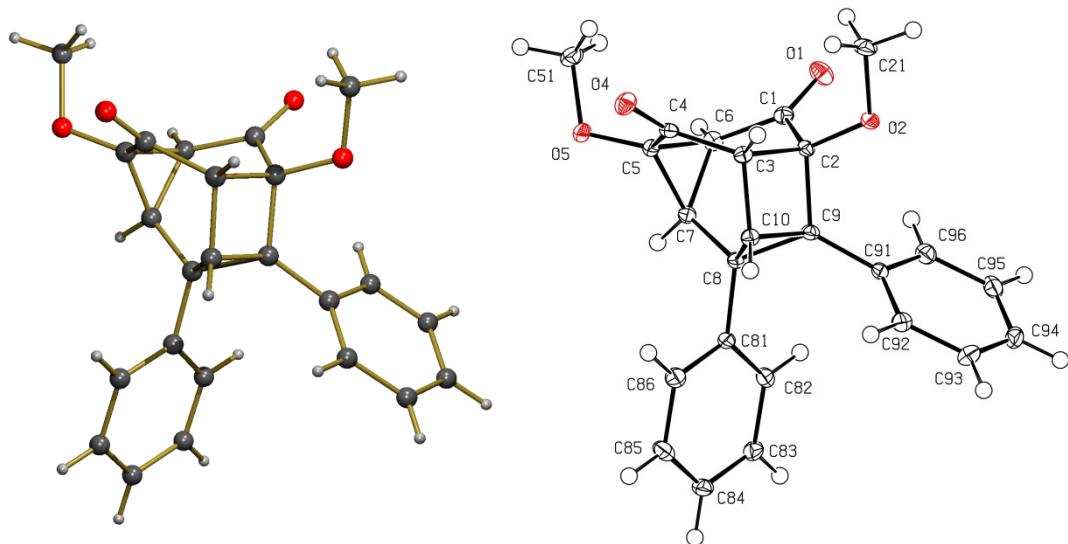


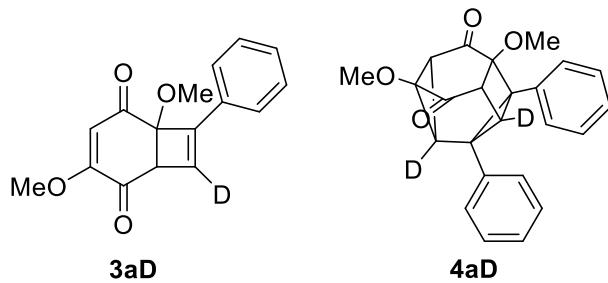
Figure S7. **4a** ORTEP type diagram (ellipsoid at 50% probability) .

Table S1. Crystal data and structure refinement for **4a**. (CCDC 2000238)

Identification code	32041901_0m		
Empirical formula	C ₂₄ H ₂₀ O ₄		
Formula weight	372.40		
Temperature	100.01 K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P 1 21/c 1		
Unit cell dimensions	$a = 11.7790(5)$ Å	$\alpha = 90^\circ$.	
	$b = 6.2989(3)$ Å	$\beta = 95.942(2)^\circ$.	
	$c = 24.9390(11)$ Å	$\gamma = 90^\circ$.	
Volume	$1840.40(14)$ Å ³		
Z	4		
Density (calculated)	1.344 Mg/m ³		
Absorption coefficient	0.091 mm ⁻¹		
F(000)	784		
Crystal size	0.112 x 0.091 x 0.036 mm ³		
Theta range for data collection	2.264 to 28.341°.		
Index ranges	-15≤h≤12, -8≤k≤8, -33≤l≤33		

Reflections collected	34487
Independent reflections	4587 [R(int) = 0.0412]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6888
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4587 / 0 / 255
Goodness-of-fit on F ²	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1020
R indices (all data)	R1 = 0.0552, wR2 = 0.1089
Extinction coefficient	n/a
Largest diff. peak and hole	0.432 and -0.273 e.Å ⁻³

**1,4-Dimethoxy-8-phenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione-7-d
biscyclopropylcage (4aD) (3aD) and**



2aD was synthesized according to methods reported in the literature.⁸ Following the general procedure, the reaction of **1** (100 mg, 0.595 mmol) and alkyne **2aD** (0.6 mL, 5.35 mmol) rendered **3aD** as a yellowish solid (7 mg, 4%) and **4aD** as a white solid (82 mg, 37%) after purification by flash chromatography (SiO₂; Hexane:AcOEt (8:2)).

3aD : $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.61$ (m, 2H), 7.34 (m, 3H), 5.98 (s, 1H), 3.97 (s, 1H), 3.79 (s, 3H), 3.39 (s, 3H).

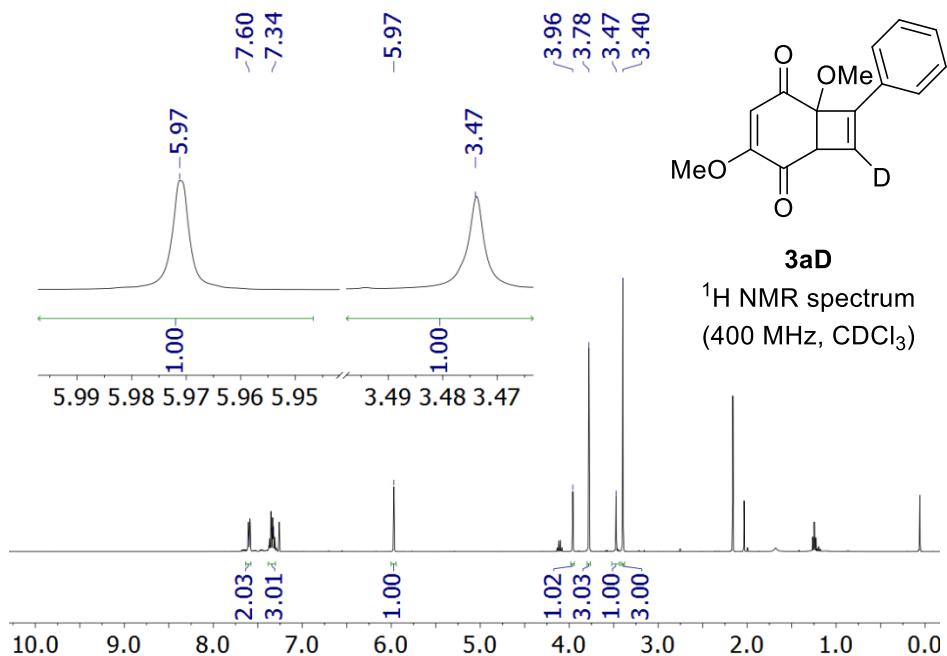


Figure S8. 3a(D) ^1H -NMR (CDCl_3) spectra.

4aD : ¹H-NMR (400 MHz, CDCl₃): δ = 7.06 (m, 8H), 6.65 (m, 2H), 3.53 (s, 3H), 3.29 (s, 3H), 3.26 (s, 1H), 2.84 (s, 1H).

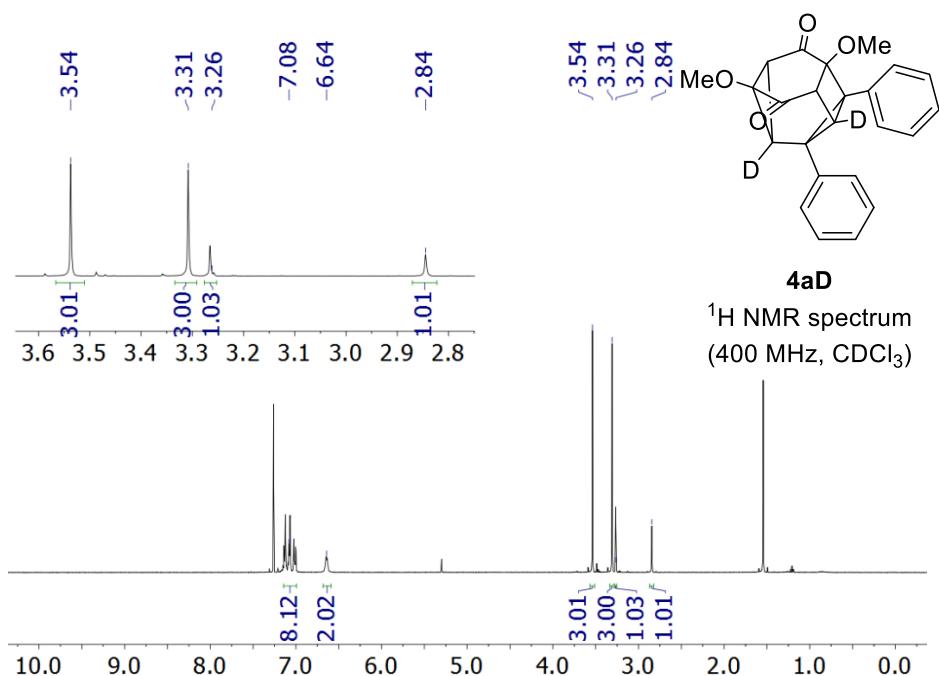
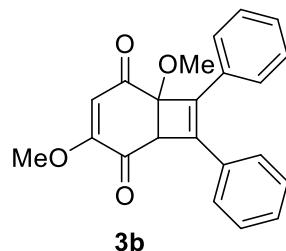


Figure S9. 4aD ^1H -NMR (CDCl_3) spectra.

1,4-Dimethoxy-7,8-diphenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione (3b)



Following the general procedure, the reaction of **1** (100 mg, 0.595 mmol) and alkyne **2b** (0.95 g, 5.35 mmol) rendered **3b** as a yellowish solid (16 mg, 8%) after purification by flash chromatography (SiO_2 ; Hexane:AcOEt (7:3)).

3b: **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ = 7.72 (m, 2H), 7.58 (m, 2H), 7.33 (m, 6H), 6.02 (s, 1H), 4.32 (s, 1H), 3.74 (s, 3H), 3.40 (s, 3H). **$^{13}\text{C-NMR}$** (100 MHz, CDCl_3): δ = 195.1, 191.6, 160.2, 142.8, 142.2, 132.2, 131.5, 129.9, 129.4, 128.9, 128.8, 127.6, 127.5, 111.1, 83.0, 56.7, 55.4, 53.4. **HRMS (ESI-TOF)** m/z : [M+H]⁺ Calcd. for $\text{C}_{22}\text{H}_{19}\text{O}_4$ 347.1278; Found 347.1279. **UV-vis** (CH_3CN): λ (ϵ): 198 (55961 $\text{Lmol}^{-1}\text{cm}^{-1}$), 256 (7410 $\text{Lmol}^{-1}\text{cm}^{-1}$) nm. **FT-IR (ATR)** ν 3497, 3445, 3406, 3380, 3056, 3027, 2983, 2936, 2851, 1829, 1702, 1663, 1575, 1541, 1488, 1458, 1445, 1361, 1329, 1298, 1239, 1188, 1165, 1114, 1095, 1080, 1029, 1010, 980, 935, 868, 844, 802, 771, 759, 720, 691 cm^{-1} .

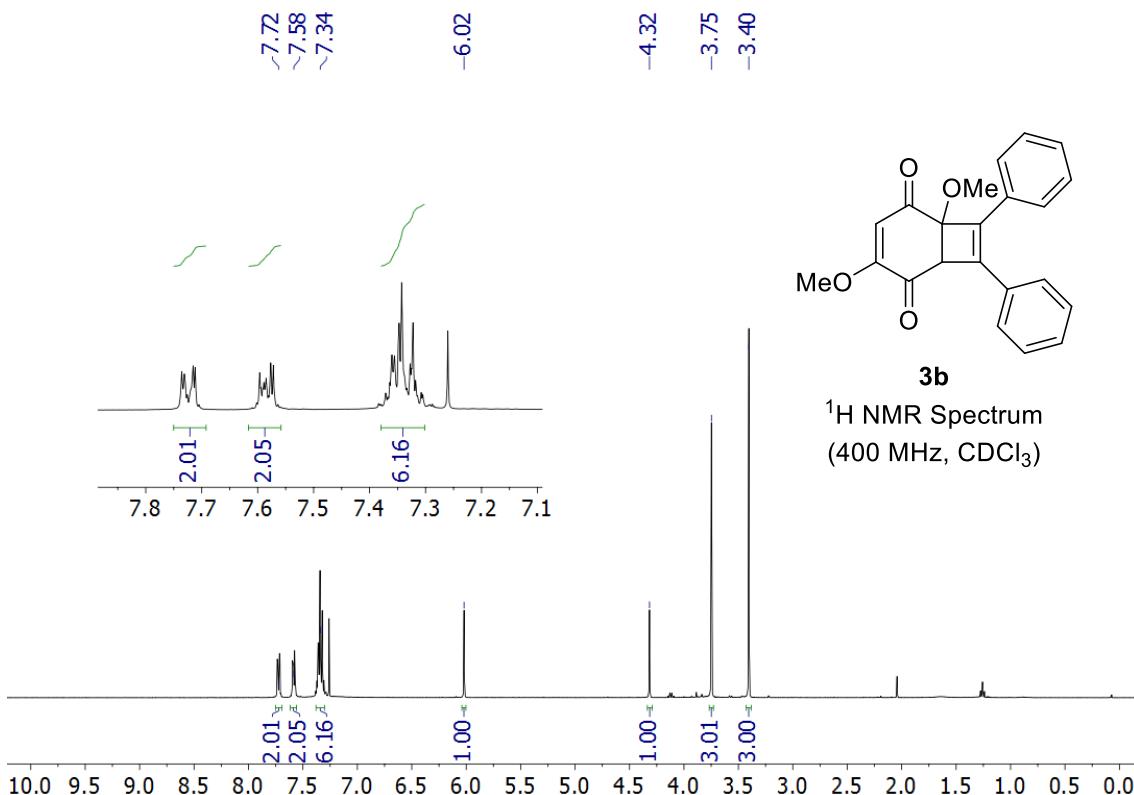


Figure S10. **3b** $^1\text{H-NMR}$ (CDCl_3) spectra.

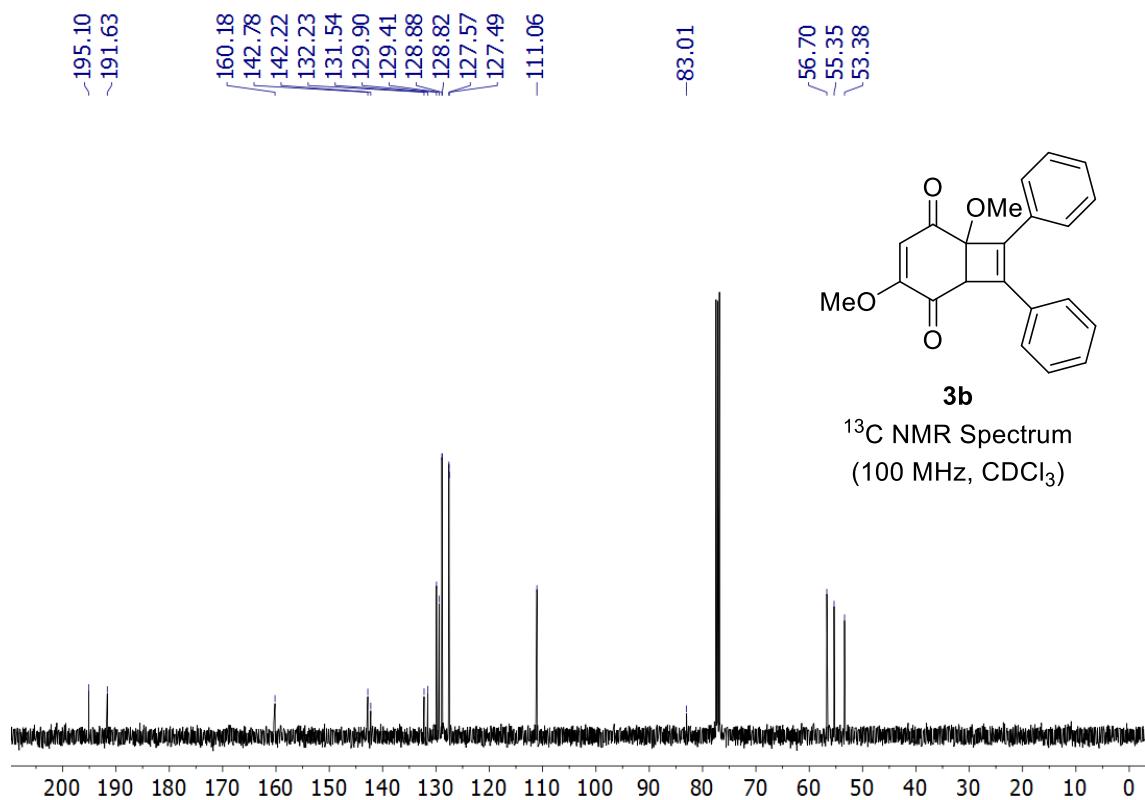


Figure S11. **3b** ^{13}C -NMR (CDCl_3) spectra.

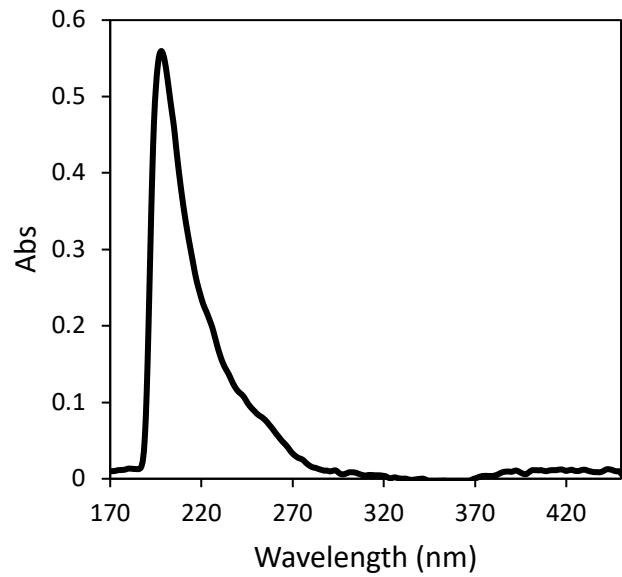
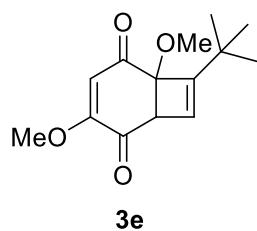


Figure S12. UV/Vis spectra of **3b** [$1.0 \cdot 10^{-5}$ M] in acetonitrile.

8-(*tert*-butyl)-1,4-dimethoxybicyclo[4.2.0]octa-3,7-diene-2,5-dione (3e**)**



Following the general procedure, but irradiating the reaction mixture for 22 hours, the reaction of **1** (100 mg, 0.595 mmol) and alkyne **2e** (0.74 mL, 5.35 mmol) rendered **3e** as a yellowish oil (41 mg, 28%) after purification by flash chromatography (SiO_2 ; Hexane:AcOEt (7:3)).

3e: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 6.21 (d, J = 1.4 Hz, 1H), 5.99 (s, 1H), 3.80 (s, 3H), 3.65 (d, J = 1.4 Hz, 1H), 3.29 (s, 3H), 1.07 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 196.6, 192.5, 165.0, 160.1, 131.2, 111.2, 85.8, 56.7, 53.8, 53.0, 29.8, 28.0. **HRMS (ESI-TOF)** m/z : [M+H] $^+$ Calcd. for $\text{C}_{14}\text{H}_{19}\text{O}_4$ 251.1278; Found 251.1270. [M+Na] $^+$ Calcd. for $\text{C}_{14}\text{H}_{18}\text{NaO}_4$ 273.1097; Found 273.1088. **FT-IR (ATR)** ν 3434, 3402, 3388, 3317, 3056, 2959, 2925, 2854, 1736, 1729, 1703, 1666, 1602, 1573, 1461, 1392, 1362, 1300, 1260, 1206, 1181, 1166, 1119, 1098, 1015, 992, 965, 913, 853, 837, 802, 765, 750, 704, 651 cm^{-1} .

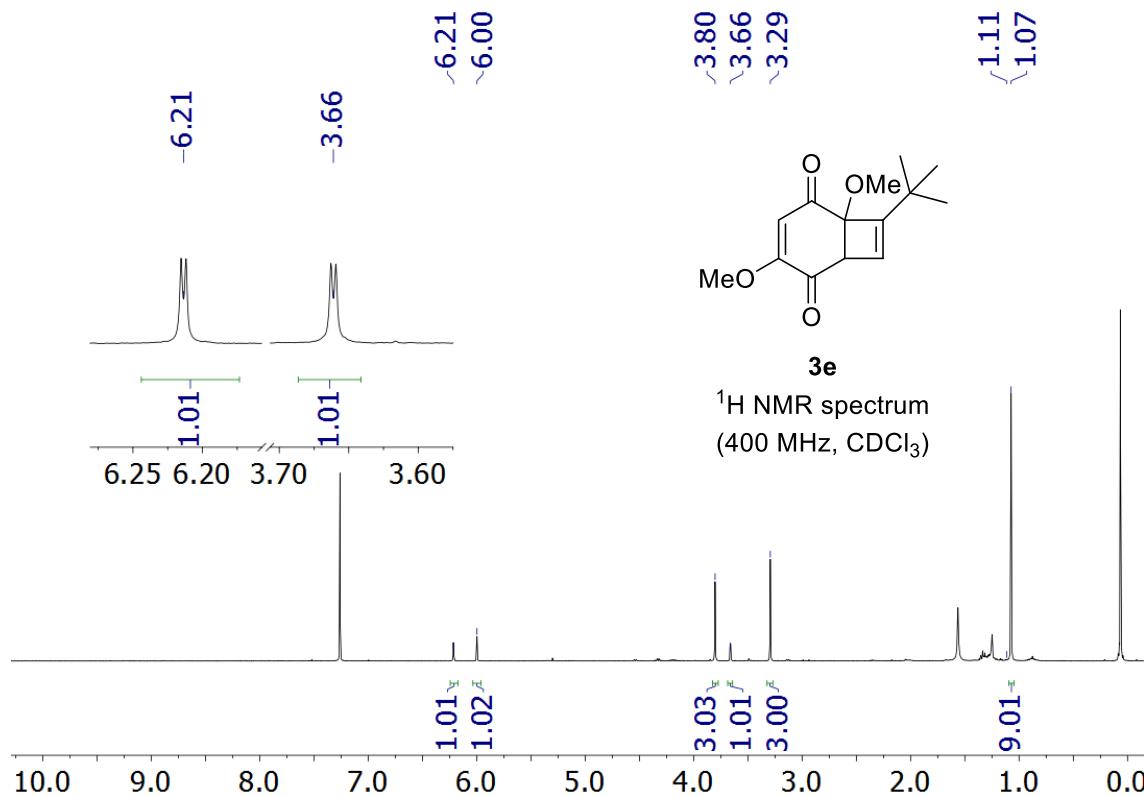


Figure S13. **3e** $^1\text{H-NMR}$ (CDCl_3) spectra.

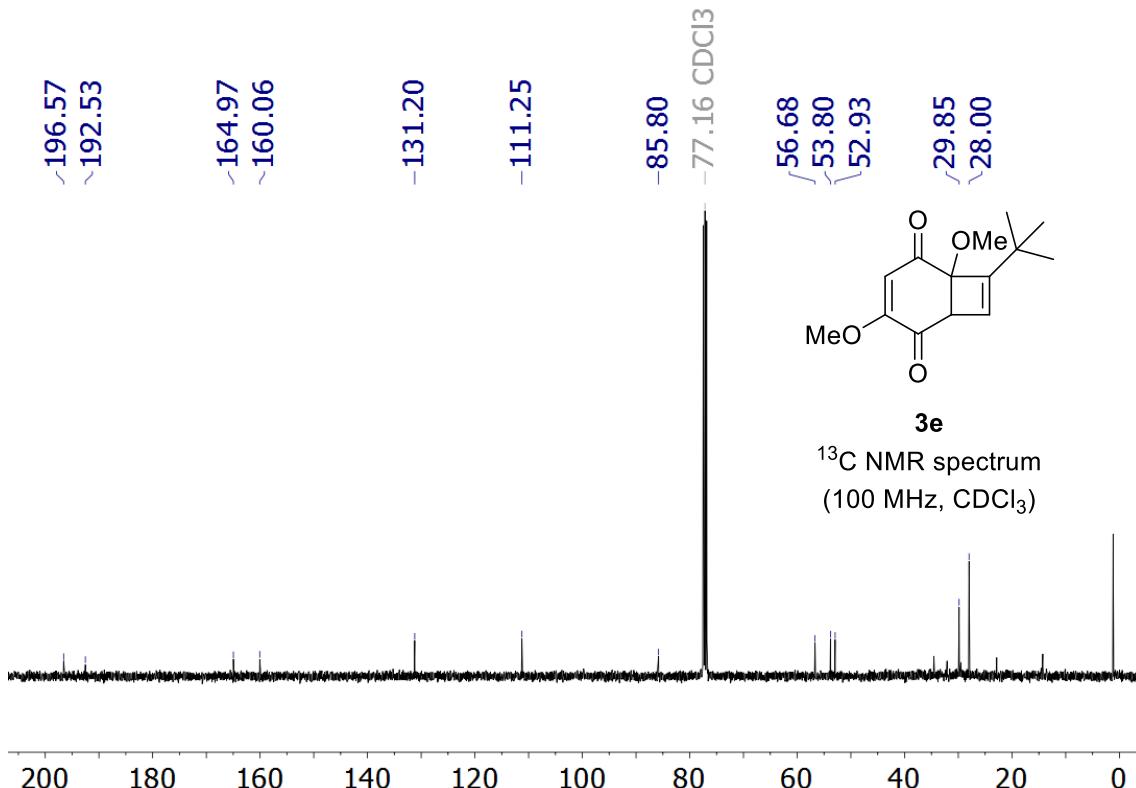
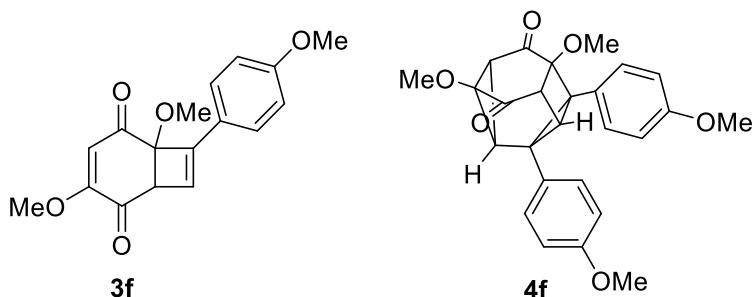


Figure S14. **3e** ^{13}C -NMR (CDCl_3) spectra.

1,4-Dimethoxy-8-(4-methoxyphenyl)bicyclo[4.2.0]octa-3,7-diene-2,5-dione (3f) and biscyclopropylcage (4f)



Following the general procedure, the reaction of **1** (100 mg, 0.595 mmol) and alkyne **2f** (0.7 mL, 5.35 mmol) rendered **3f** as a yellowish solid (87 mg, 50%) and **4f** as an orange solid (31 mg, 12%) after purification by flash chromatography (SiO_2 ; Hexane: AcOEt (7:3)). When the irradiation time was 3.5 h, the monoadduct **3f** was obtained as the only product (125 mg, 70%).

3f: **^1H NMR** (400 MHz, CDCl_3): δ = 7.54 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H) 6.53 (d, J = 1.5 Hz 1H), 5.95 (s, 1H), 3.94 (d, J = 1.4 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.39 (s, 3H). **^{13}C -NMR** (100 MHz, CDCl_3): δ = 195.0, 191.7, 160.3, 159.8, 151.1, 128.0, 127.3, 123.3, 114.1, 110.8, 84.8, 56.6, 55.3, 53.5, 53.12. **HRMS (ESI-TOF)** m/z : [M+H]⁺ Calcd. for $\text{C}_{17}\text{H}_{17}\text{O}_5$ 301.1071; Found 301.1070. [M+Na]⁺ Calcd. for $\text{C}_{17}\text{H}_{16}\text{NaO}_5$ 323.0890; Found 323.0878. **UV-vis** (CH_3CN): λ (ϵ): 206 (50336 $\text{Lmol}^{-1}\text{cm}^{-1}$), 269 (40194 $\text{Lmol}^{-1}\text{cm}^{-1}$), 332 (10623.3 $\text{Lmol}^{-1}\text{cm}^{-1}$) nm. **FT-IR (ATR)** ν 3068, 1956, 2923, 2852, 1701, 1663, 1603, 1573, 1508, 1461, 1421, 1402, 1377, 1361, 1302, 1282, 1252, 1188, 1166, 1119, 1099, 1078, 1029, 1013, 987, 959, 924, 885, 864, 835, 811, 787, 760, 755, 730, 729 cm^{-1} .

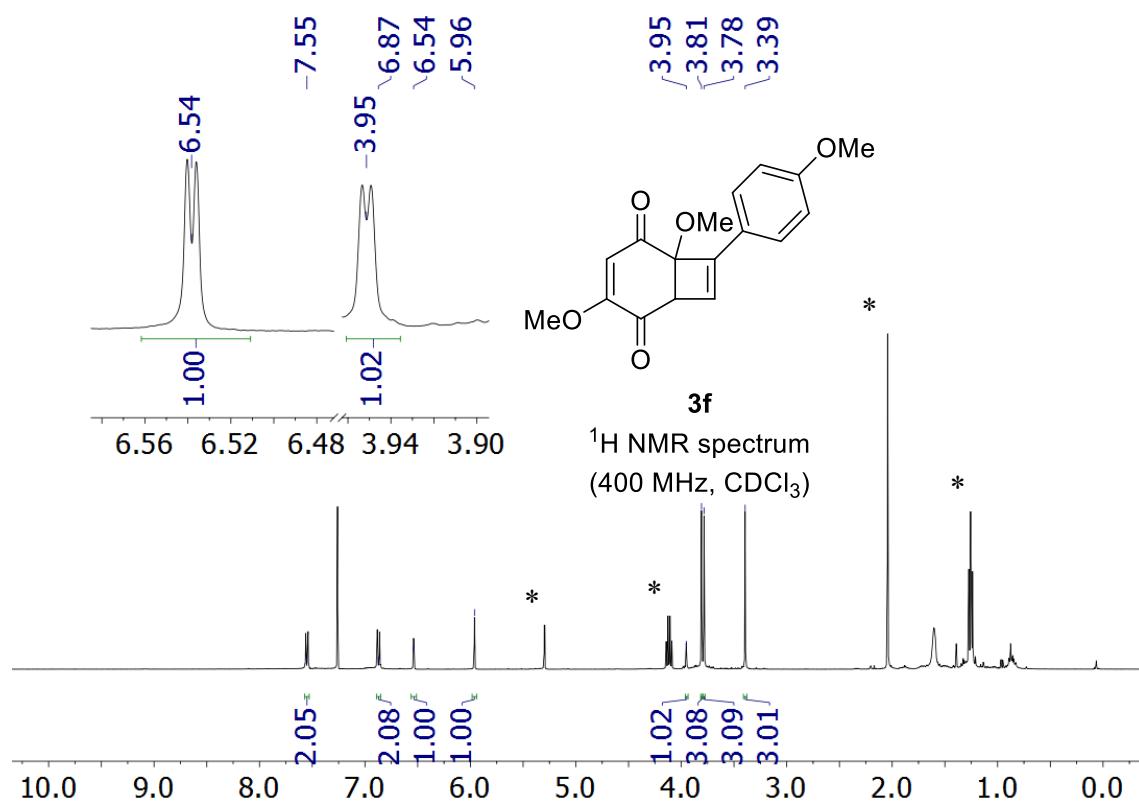


Figure S15. **3f** ^1H -NMR (CDCl_3) spectra. * Show solvents signal.

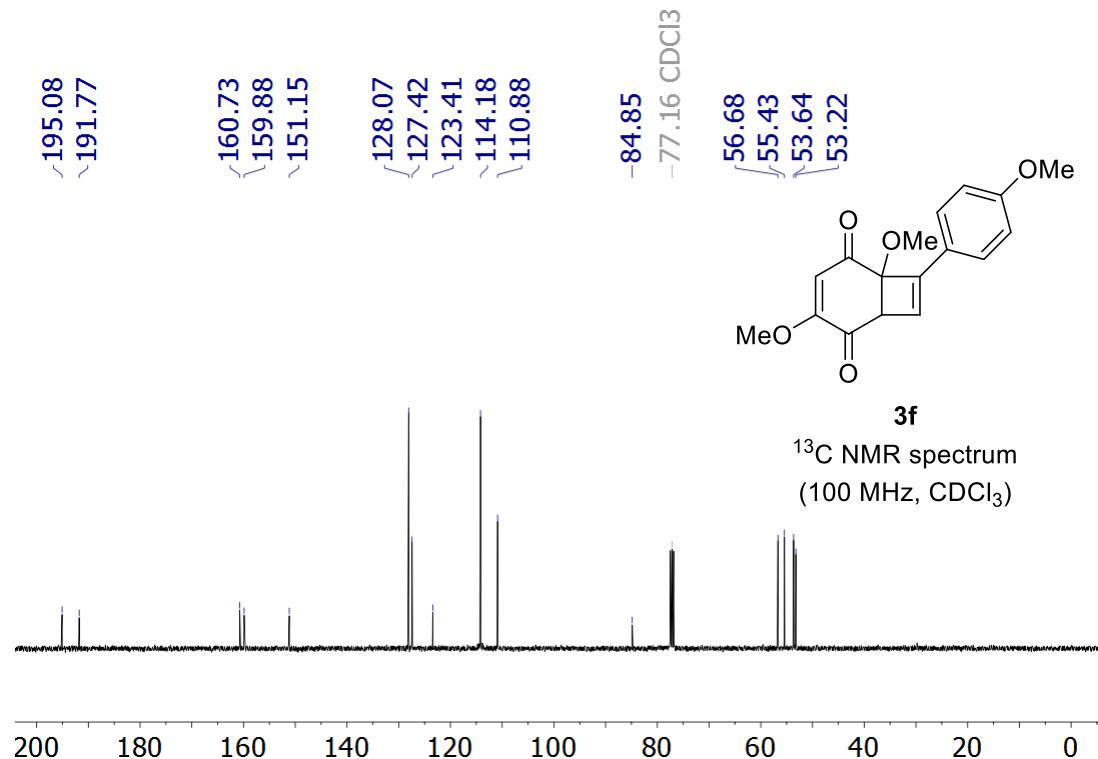


Figure S16. **3f** ^{13}C -NMR (CDCl_3) spectra.

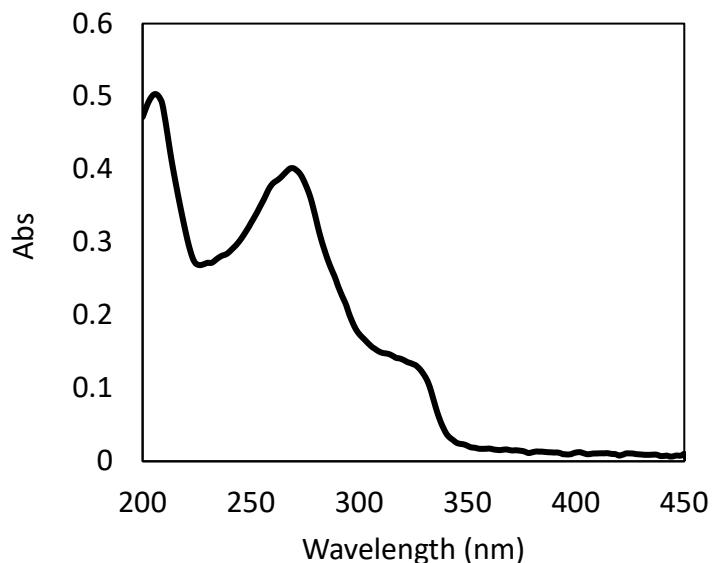


Figure S17. UV/Vis spectra of **3f** [1.0·10⁻⁵ M] in acetonitrile.

4f: ¹H-NMR (400 MHz, CDCl₃): δ = 6.91 (d, *J*= 8.7 Hz, 2H), 6.64 (m, 4H), 6.56 (d, *J*= 8.7 Hz, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.60 (d, *J*= 4.9 Hz, 1H), 3.50 (s, 3H), 3.27 (d, *J*= 4.9 Hz, 1H), 3.19 (d, *J*= 9.8 Hz, 1H), 2.82 (d, *J*= 9.8 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ = 202.4, 200.6, 158.8, 158.5, 130.8, 128.9, 123.8, 114.1, 113.5, 82.6, 74.1, 57.9, 55.3, 55.2, 53.0, 52.7, 50.7, 45.0, 44.6, 37.0, 36.4. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd. for C₂₆H₂₅O₆ 433.1646; Found 433.1649. UV-vis (CH₃CN): λ (ϵ): 231 (22728 Lmol⁻¹cm⁻¹), 264 (3035 Lmol⁻¹cm⁻¹), 345 (476 Lmol⁻¹cm⁻¹) nm. FT-IR (ATR) ν 3648, 3627, 3104, 3042, 2996, 2959, 1932, 1837, 1707, 1611, 1580, 1517, 1463, 1445, 1416, 1379, 1337, 1298, 1279, 1250, 1205, 1175, 1130, 1088, 1029, 984, 926, 915, 892, 830, 788, 741, 722, 669, 582, 562 cm⁻¹.

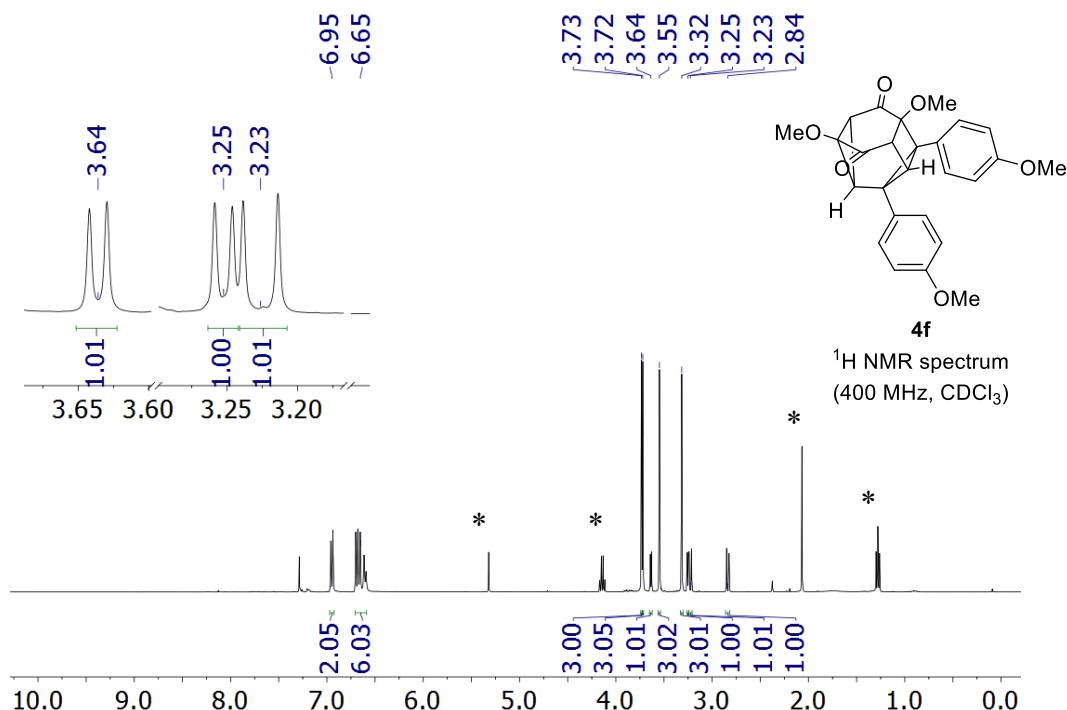


Figure S18. **4f** ¹H-NMR (CDCl₃) spectra. * Show solvents signal.

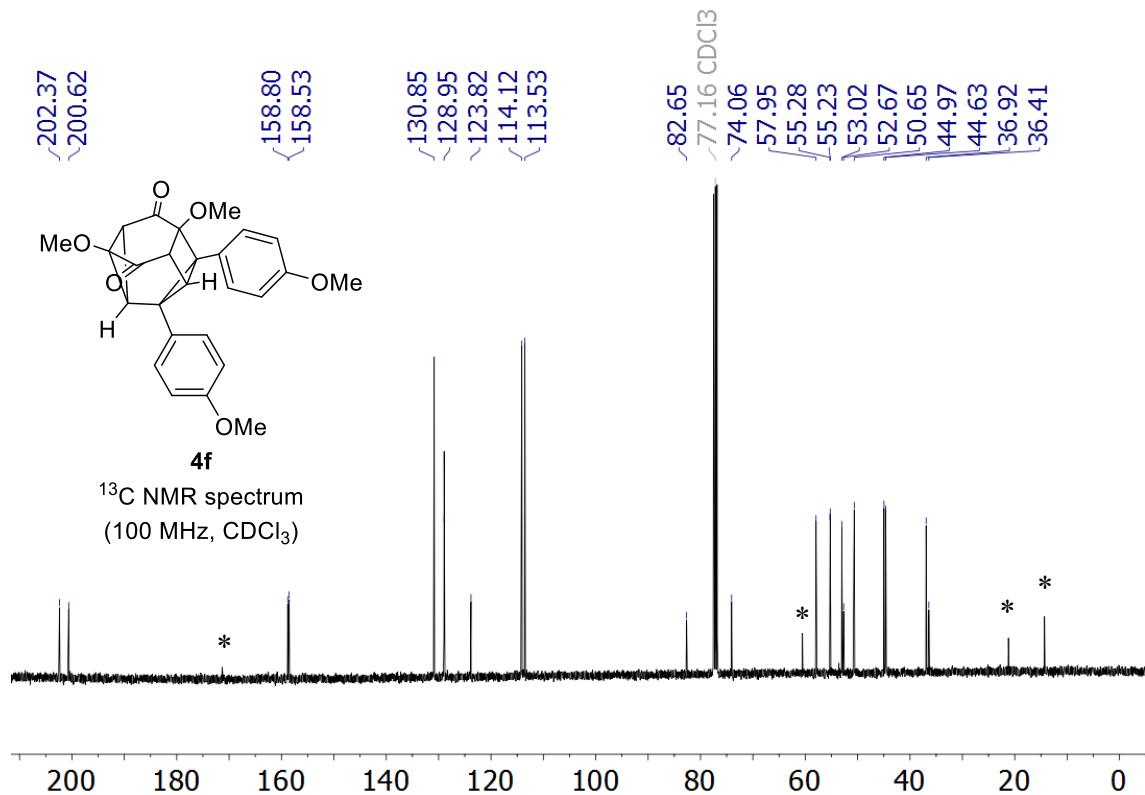


Figure S19. **4f** ^{13}C -NMR (CDCl_3) spectra. * Show solvents signal.

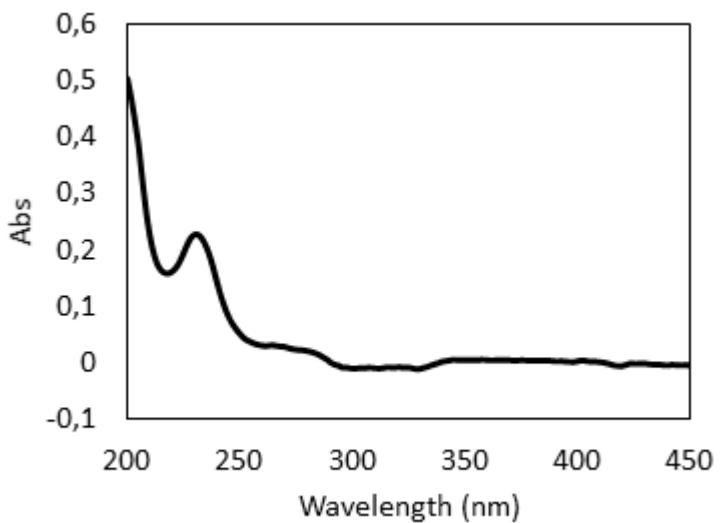
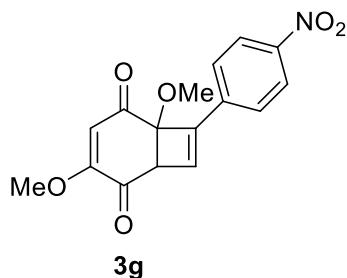


Figure S20. UV/Vis spectra of **4f** [$1.0 \cdot 10^{-5} \text{ M}$] in acetonitrile.

1,4-dimethoxy-8-(4-nitrophenyl)bicyclo[4.2.0]octa-3,7-diene-2,5-dione (3g)



Following the general procedure, the reaction of **1** (100 mg, 0.595 mmol) and alkyne **2g** (0.79 g, 5.35 mmol) rendered **3g** as a yellowish oil (29 mg, 15%) after purification by flash chromatography (SiO_2 ; Hexane:AcOEt (6:4)).

3g: **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ = 8.22 (d, J = 8.9 Hz, 2H), 7.80 (d, J = 8.9 Hz, 2H) 6.93 (d, J = 1.9 Hz 1H), 6.03 (s, 1H), 4.01 (d, J = 1.9 Hz, 1H), 3.82 (s, 3H), 3.40 (s, 3H). **$^{13}\text{C-NMR}$** (100 MHz, CDCl_3): δ = 194.4, 190.5, 160.3, 149.5, 148.1, 135.9, 134.8, 127.5, 124.1, 111.4, 84.6, 56.9, 54.3, 53.7. **HRMS (ESI-TOF)** m/z : [M+H]⁺ Calcd. for $\text{C}_{16}\text{H}_{14}\text{NO}_6$ 316.0816; Found 316.0815. [M+Na]⁺ Calcd. for $\text{C}_{16}\text{H}_{13}\text{NNaO}_6$ 338.0635; Found 338.0630. **UV-vis** (CH_3CN): λ (ϵ): 225 (5420 $\text{Lmol}^{-1}\text{cm}^{-1}$), 280 (8882 $\text{Lmol}^{-1}\text{cm}^{-1}$), 349 (2088 $\text{Lmol}^{-1}\text{cm}^{-1}$) nm. **FT-IR (ATR)** ν 3639, 3391, 3348, 3307, 3100, 3073, 2957, 2925, 1852, 2627, 2447, 2256, 1798, 1703, 1661, 1601, 1517, 1489, 1458, 1412, 1343, 1319, 1285, 1255, 1240, 1186, 1166, 1107, 1079, 1037, 1011, 987, 960, 913, 850, 814, 762, 742, 699, 646, 542 cm^{-1} .

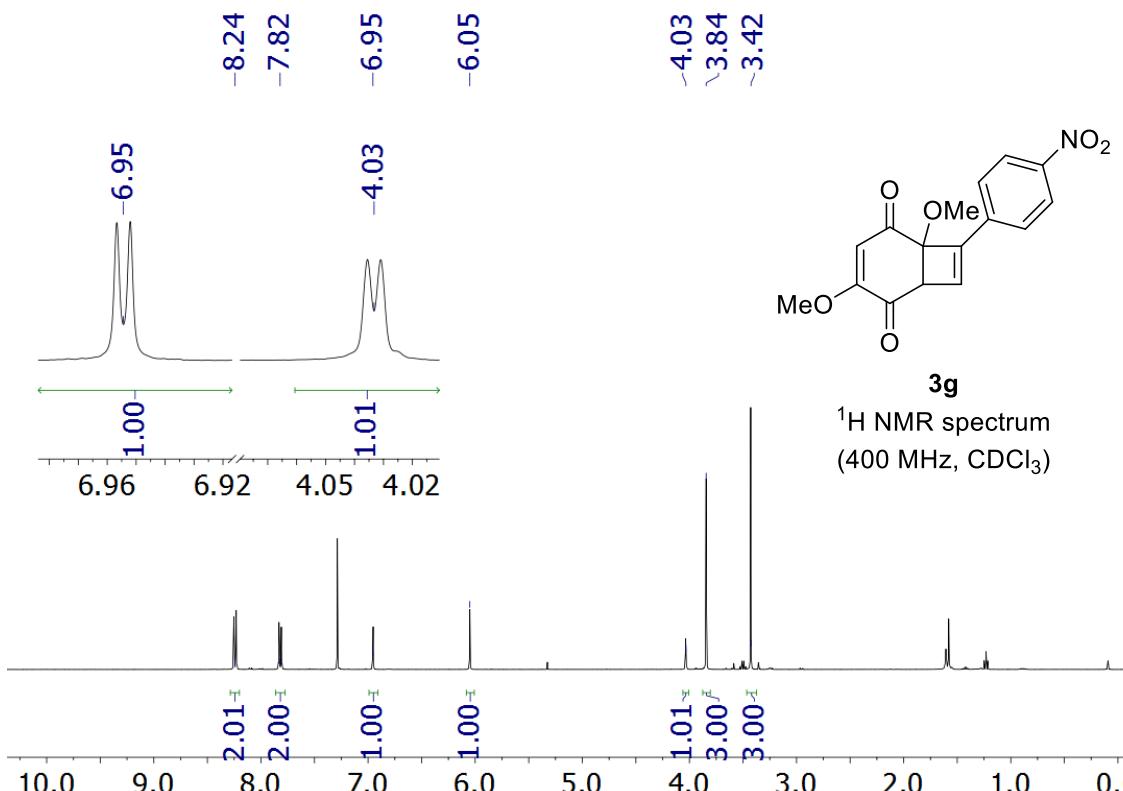


Figure S21. **3g** $^1\text{H-NMR}$ (CDCl_3) spectra.

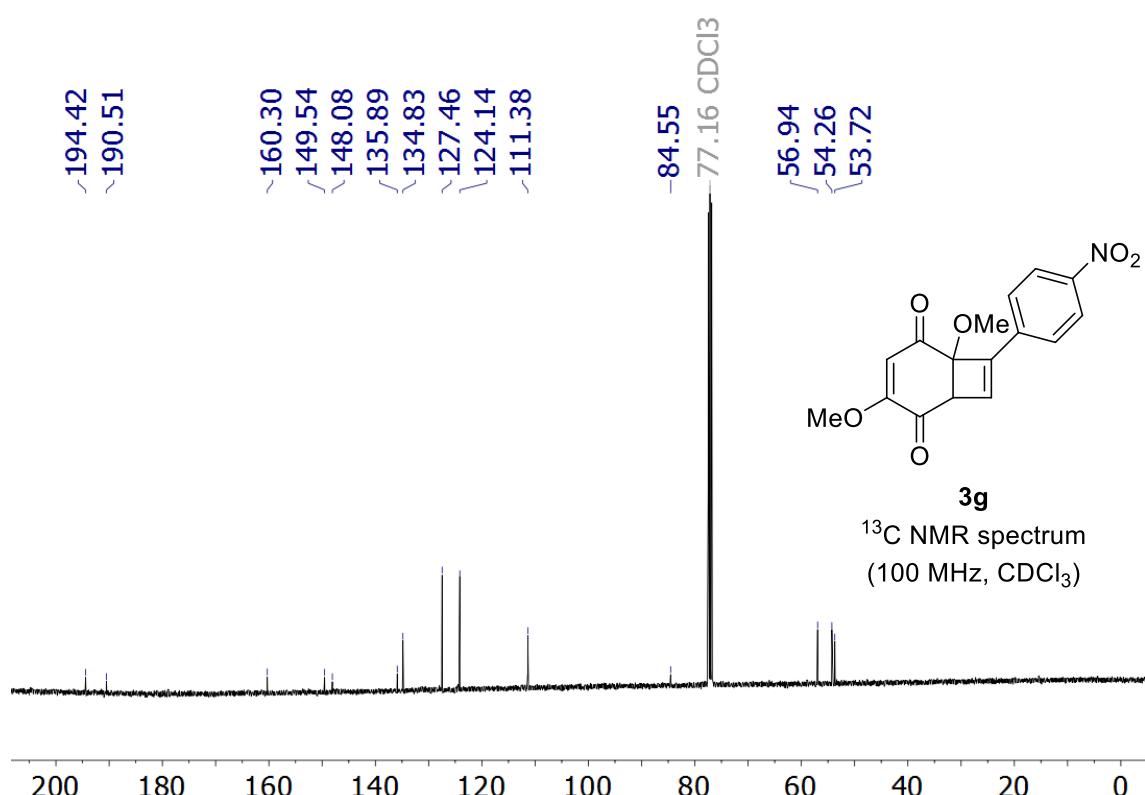


Figure S22. **3g** ^{13}C -NMR (CDCl_3) spectra.

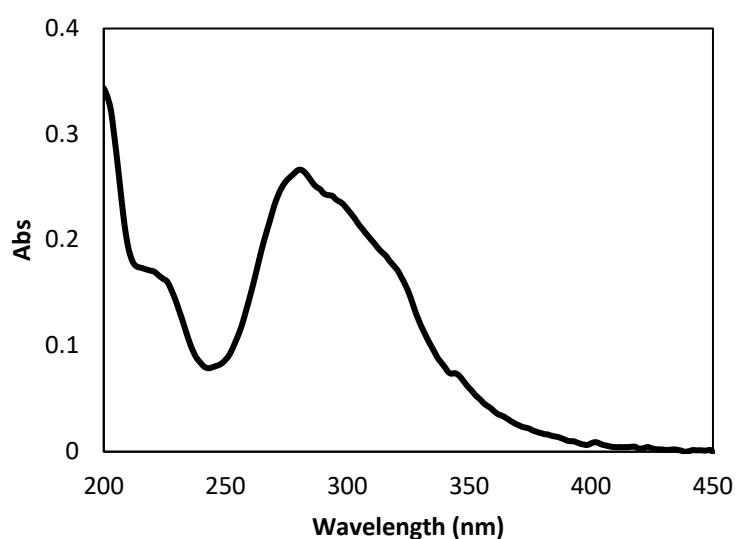


Figure S23. UV/Vis spectra of **3g** [$3.0 \cdot 10^{-5}$ M] in acetonitrile.

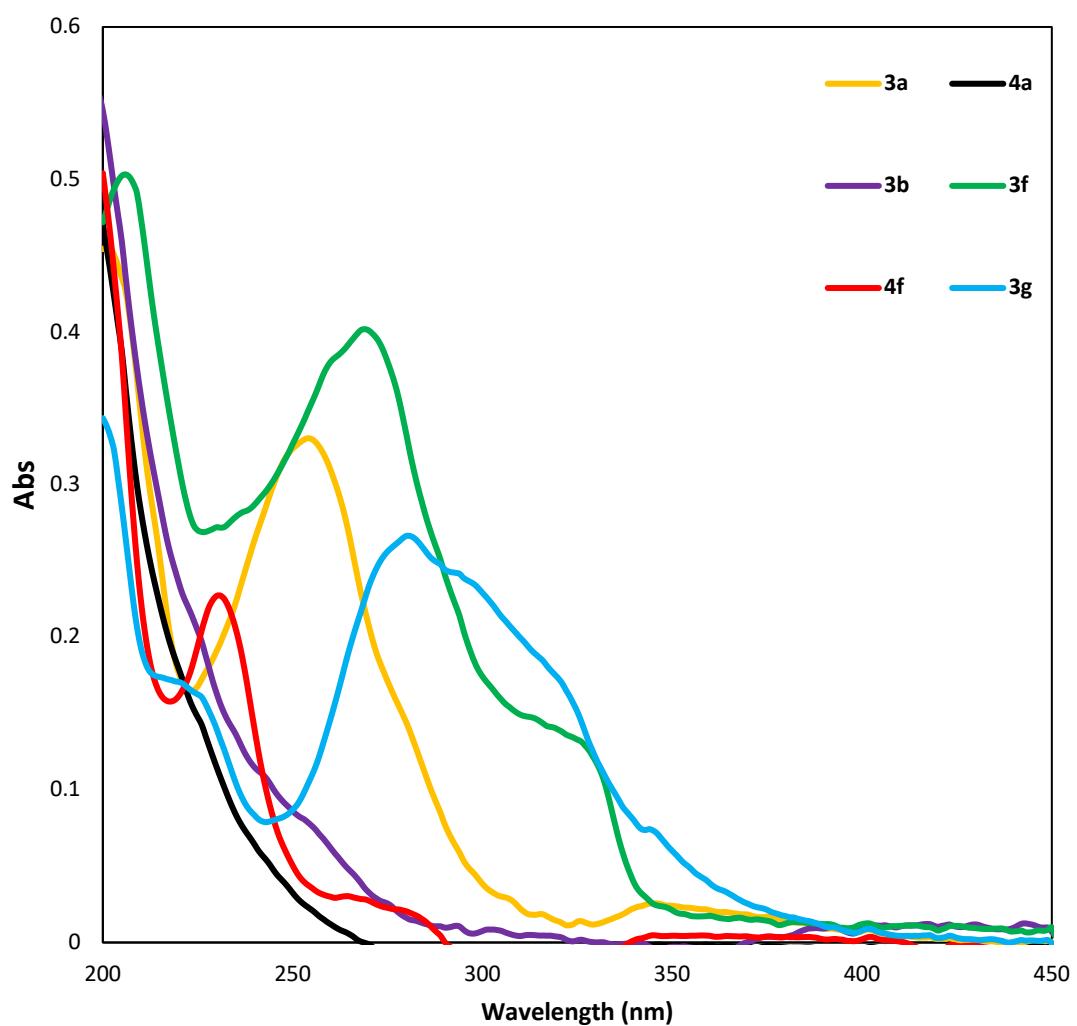


Figure S24. UV/Vis spectra of **3a** (yellow) [$1.0 \cdot 10^{-5}$ M], **4a** (black) [$1.0 \cdot 10^{-5}$ M], **3b** (purple) [$1.0 \cdot 10^{-5}$ M], **3f** (green) [$1.0 \cdot 10^{-5}$ M], **4f** (red) [$1.0 \cdot 10^{-5}$ M] and **3g** (blue) [$3.0 \cdot 10^{-5}$ M] in acetonitrile.

4 Detailed computational methods

The geometries of all the molecules were fully optimized by using the M06 functional⁹ with the double- ζ quality basis set 6-31+G(d,p). This basis set has been used within some of the training sets to parametrize the MO6 functional and it is known to provide superior performance relative to its size. This basis set contains polarization and diffuse functions which are expected to provide enough flexibility to describe low energy excited states. The effect of the solvent (Toluene) was taken into account using the Polarizable Continuum Model (PCM)¹⁰ with the default parameters implemented in the Gaussian 09 package.¹¹ Harmonic analysis was performed to confirm the nature of minima and transition states. The wave function stability was confirmed in all stationary points.¹² Excited states were computed via the time-dependent formulation of the Kohn-Sham equations. These calculations were run with the Gaussian 16 program, which currently implements analytical first and second derivatives for excited states computed within the TDDFT framework, hence allowing for geometry optimization and full characterization of stationary points. This methodology however has some caveats that are worth mentioning. TDDFT is based on linear response theory from a single determinant reference. In those cases where the ground state is not correctly described with a single determinant (this can usually happen in the vicinity of transition states or in diradicaloid states) the linear response is also prone to fail. Similarly, even when the ground state is reasonably described with a single determinant, the excited state can also show near degeneracy issues, and lead to incorrect excitation energies. These two situations can be evaluated via stability checks.¹² This is relatively straight forward for the ground state, but it is not implemented for excited states. Often times, near degeneracy in the excited state during optimization procedures result in energy hopping and erratic convergence. These symptoms are easy to spot for the trained eye and, in the current study, we have not observed them. Finally, despite some algorithms implemented to avoid it, geometry optimization withing TDDFT can lead to accidental surface hops due to nearby states. The chance for these events has been minimized via a small stepsize and generous use of IRC calculations to obtain educated guesses for each stationary point along the alternate mechanisms. It is also worth mentioning that in the photophysical events (the vertical absorption, for instance) only the fast components of the polarizability are allowed to relax within the continuum solvation model. On the contrary, for those events that imply nuclear motion (excited state optimizations, IRCs, etc) both fast and slow components are allowed to relax.

5 Reaction profile with exo approach

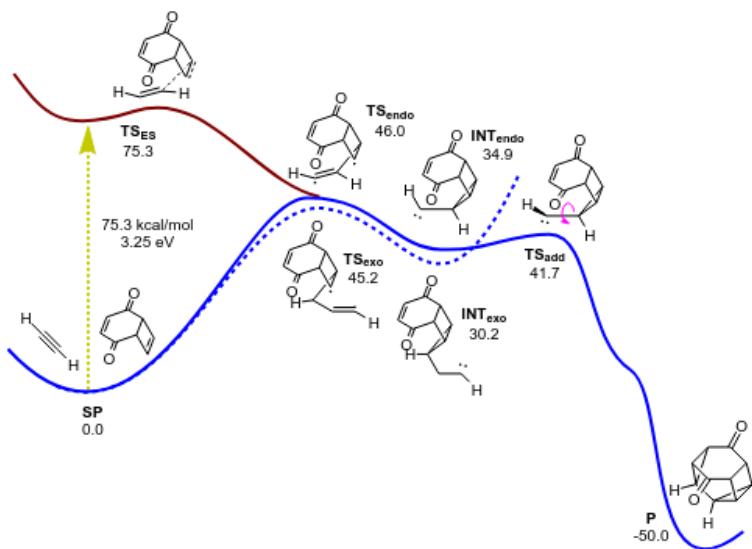


Figure S1: Reaction profile showing the ease of reversibility when the initial orientation is exo.

6 Cartesian Coordinates

6.1 Reaction paths on the article

Int1-S0

SCF Energy: -535.790757115

ZPE-corrected Energy: -535.641074

ΔU : -535.631187

ΔH : -535.630243

ΔG : -535.676473

Num. Imaginary Frequencies: 0

C	-2.029295	-0.675947	0.129941
C	1.145905	0.001732	1.946711
C	-2.031823	0.668360	0.130012
C	-0.804832	1.460973	-0.143194
C	0.246562	0.772539	-0.968514
C	0.249412	-0.771320	-0.968718
C	-0.799316	-1.463833	-0.143392
C	1.714027	-0.734673	-0.549041
C	1.977104	0.003388	0.806866
C	1.711299	0.741133	-0.548747
O	-0.676133	-2.609017	0.251886
O	-0.686131	2.606627	0.252092
H	-2.904138	-1.248043	0.433843
H	-2.908813	1.237130	0.433983
H	0.160964	1.176369	-1.986090
H	0.165276	-1.175152	-1.986414
H	2.487465	-1.435461	-0.846106
H	0.083481	0.000041	1.638840
H	3.057429	0.005331	0.974224
H	2.482187	1.444791	-0.845647

Int2-S0

SCF Energy: -535.801371465

ZPE-corrected Energy: -535.651432

ΔU : -535.641748

ΔH : -535.640804

ΔG : -535.686235

Num. Imaginary Frequencies: 0

C	-2.016448	-0.680972	0.098565
C	0.826256	0.003059	1.727289
C	-2.023577	0.660080	0.098641
C	-0.785193	1.447561	-0.132784
C	0.266978	0.773861	-0.970280
C	0.275039	-0.770468	-0.970669
C	-0.769860	-1.455367	-0.133147
C	1.734263	-0.724090	-0.534805
C	1.911787	0.009756	0.840575
C	1.726550	0.742527	-0.534264
O	-0.650952	-2.607917	0.248080
O	-0.678289	2.601122	0.248916
H	-2.897758	-1.261736	0.364871
H	-2.910989	1.231432	0.365032
H	0.182918	1.182971	-1.986040
H	0.195018	-1.180002	-1.986584
H	2.521379	-1.429257	-0.781000
H	1.192511	0.003997	2.770627
H	2.969839	0.015253	1.122452
H	2.506248	1.456031	-0.780047

Monoadduct

SCF Energy: -458.561748613

ZPE-corrected Energy: -458.443056

ΔU : -458.435112

ΔH : -458.434168

ΔG : -458.476405

Num. Imaginary Frequencies: 0

C	-0.670957	-1.588985	-0.373890
C	0.671367	-1.588768	-0.374130
C	1.485202	-0.469254	0.146601
C	0.778956	0.791527	0.563262
C	-0.779090	0.791407	0.563536
C	-1.485035	-0.469528	0.146682
C	-0.669283	1.830703	-0.539598
C	0.668644	1.830662	-0.539951
O	-2.701168	-0.559265	0.196763
O	2.701347	-0.558733	0.196995
H	-1.237739	-2.438049	-0.752198
H	1.238304	-2.437662	-0.752591
H	1.237522	1.159705	1.489509
H	-1.237494	1.159083	1.490066
H	-1.436425	2.367249	-1.089571
H	1.435576	2.367077	-1.090351

PF

SCF Energy: -535.935774273

ZPE-corrected Energy: -535.779069

ΔU : -535.771296

ΔH : -535.770351

ΔG : -535.811878

Num. Imaginary Frequencies: 0

C	-0.784357	0.484575	-1.039525
C	0.784689	0.486740	-1.038873
C	1.434037	-0.674266	-0.336640
C	0.771018	-1.052823	0.932264
C	-0.768327	-1.055546	0.931198
C	-1.431986	-0.677389	-0.337221
C	-0.758086	1.754446	-0.173685
C	0.754118	1.756267	-0.173125
O	2.437403	-1.232112	-0.746391
O	-2.435677	-1.235190	-0.746184
H	1.260914	-1.830321	1.512083
C	-0.000436	0.025526	1.643962
H	-1.256174	-1.834298	1.511035
H	-1.212062	0.621550	-2.034820
H	1.212956	0.624707	-2.033814
H	1.450248	2.585962	-0.242831
H	-0.001345	-0.046275	2.729038
C	-0.002264	1.422768	1.078408
H	-0.002945	2.212719	1.825319
H	-1.455830	2.582592	-0.245989

PP1

SCF Energy: -458.561748625

ZPE-corrected Energy: -458.443057

ΔU : -458.435112

ΔH : -458.434168

ΔG : -458.476407

Num. Imaginary Frequencies: 0

C	0.670899	-1.589149	0.373704
C	-0.671413	-1.589005	0.373712
C	-1.485218	-0.469210	-0.146519
C	-0.778979	0.791567	-0.563259
C	0.779109	0.791339	-0.563526
C	1.484995	-0.469578	-0.146567
C	0.669381	1.830785	0.539450
C	-0.668546	1.830898	0.539767
O	2.701143	-0.559254	-0.196446
O	-2.701381	-0.558601	-0.196549
H	1.237695	-2.438272	0.751862
H	-1.238379	-2.438015	0.751866
H	-1.237490	1.159551	-1.489622
H	1.237519	1.158887	-1.490109
H	1.436608	2.367306	1.089336
H	-1.435417	2.367504	1.090066

PP2

SCF Energy: -77.2716615980

ZPE-corrected Energy: -77.246509

ΔU : -77.243323

ΔH : -77.242378

ΔG : -77.263860

Num. Imaginary Frequencies: 0

C	0.001564	0.603814	0.000000
C	0.001564	-0.603808	-0.000000
H	-0.009260	-1.672109	-0.000000
H	-0.009508	1.672071	0.000000

SP

SCF Energy: -535.837797001

ZPE-corrected Energy: -535.691284

ΔU : -535.678968

ΔH : -535.678024

ΔG : -535.732107

Num. Imaginary Frequencies: 0

C	-0.856496	1.645667	-0.041847
C	3.174053	0.323346	0.900629
C	0.305515	1.403048	-0.668421
C	0.666750	0.082626	-1.226570
C	-0.226993	-1.086586	-0.920803
C	-1.579731	-0.805675	-0.199851
C	-1.897229	0.617614	0.169479
C	-1.009732	-1.621468	0.948492
C	2.563596	0.428237	1.938003
C	0.155242	-1.854923	0.333552
O	-2.969602	0.914709	0.672024
O	1.683708	-0.053955	-1.888762
H	-1.098554	2.636552	0.338658
H	1.046828	2.187252	-0.813659
H	-0.310730	-1.707131	-1.821754
H	-2.459705	-1.247732	-0.683724
H	-1.441367	-1.899899	1.905147
H	3.692129	0.228949	-0.030409
H	2.026290	0.520129	2.857257
H	1.062421	-2.395471	0.586418

TS1-S1

SCF Energy: -535.765237668

ZPE-corrected Energy: -535.576166

ΔU : -535.565627

ΔH : -535.564682

ΔG : -535.612161

Num. Imaginary Frequencies: 1

Imaginary Frequency: -421.8906

C	0.856189	-1.672848	0.493550
C	-0.301135	0.882177	2.082625
C	-0.538684	-1.831608	0.382027
C	-1.391467	-0.940822	-0.308122
C	-0.707656	0.151355	-1.120434
C	0.847374	0.256590	-1.102905
C	1.615064	-0.646126	-0.112163
C	0.677267	1.688189	-0.764784
C	-0.540813	1.871543	1.375403
C	-0.714330	1.588008	-0.643060
O	2.825961	-0.419216	0.046306
O	-2.637362	-0.961956	-0.302328
H	1.422149	-2.354478	1.126735
H	-1.026921	-2.646087	0.913465
H	-1.123751	0.110493	-2.136089
H	1.346078	0.123937	-2.074555
H	1.370326	2.520997	-0.678084
H	-0.074411	-0.053489	2.550494
H	-0.735359	2.930692	1.365634
H	-1.497759	2.338559	-0.712246

TS2-S0

SCF Energy: -535.770610486

ZPE-corrected Energy: -535.623348

ΔU : -535.613329

ΔH : -535.612385

ΔG : -535.658748

Num. Imaginary Frequencies: 1

Imaginary Frequency: -434.1449

C	-1.520037	1.437047	0.274084
C	0.961121	-0.706920	1.997146
C	-0.324828	2.042323	0.168715
C	0.901043	1.331954	-0.279617
C	0.691256	0.066664	-1.064186
C	-0.707795	-0.593131	-1.010320
C	-1.712780	0.003614	-0.050308
C	-0.003521	-1.874637	-0.681803
C	1.128208	-1.604380	1.059751
C	1.269443	-1.276079	-0.609355
O	-2.651245	-0.633357	0.388369
O	2.009531	1.795063	-0.077241
H	-2.387874	1.954418	0.679270
H	-0.179327	3.073213	0.487207
H	1.007605	0.276908	-2.093844
H	-1.211216	-0.628767	-1.989124
H	-0.356028	-2.893298	-0.562591
H	0.478395	0.262558	1.900843
H	1.437759	-2.643119	1.147422
H	2.251741	-1.654296	-0.882855

TS3-S0

SCF Energy: -535.779828246

ZPE-corrected Energy: -535.631159

ΔU : -535.622071

ΔH : -535.621127

ΔG : -535.665379

S^2 before (0.0199) and after higher multiplicity projection (0.0000)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -209.0571

C	-0.487903	1.821751	0.383407
C	-0.197354	-0.712557	2.046674
C	0.851730	1.687239	0.458645
C	1.597654	0.616539	-0.232823
C	0.788854	-0.427406	-0.950455
C	-0.751321	-0.291340	-1.027430
C	-1.384791	0.880045	-0.327924
C	-0.897607	-1.682982	-0.381628
C	-0.276033	-1.700502	0.987744
C	0.613891	-1.774135	-0.256247
O	-2.592728	1.056817	-0.334089
O	2.816614	0.578687	-0.211573
H	-0.996281	2.638466	0.894673
H	1.456360	2.391844	1.026516
H	1.234358	-0.581158	-1.939575
H	-1.115922	-0.296698	-2.060163
H	-1.581329	-2.454883	-0.723403
H	-0.998876	0.046176	1.925475
H	-0.203396	-2.700474	1.434433
H	1.271270	-2.627217	-0.392437

Int0-T1

SCF Energy: -535.786051361

ZPE-corrected Energy: -535.638890

ΔU : -535.627985

ΔH : -535.627041

ΔG : -535.677489

S^2 before (2.0215) and after higher multiplicity projection (2.0002)

Num. Imaginary Frequencies: 0

C	1.725846	0.901218	-0.873865
C	-3.318313	-0.788127	-0.945671
C	0.677709	1.705519	-0.632446
C	-0.335915	1.421001	0.404584
C	-0.305804	0.084082	1.082826
C	0.928478	-0.823875	0.847347
C	1.992239	-0.333128	-0.106291
C	0.018355	-1.801216	0.164089
C	-2.020487	-0.622687	-0.824104
C	-1.230307	-1.006502	0.396539
O	3.023401	-0.962532	-0.275262
O	-1.198445	2.244098	0.667804
H	2.471499	1.149936	-1.627315
H	0.534222	2.633675	-1.183226
H	-0.569243	0.231205	2.134276
H	1.430440	-1.189213	1.755332
H	0.230455	-2.676677	-0.443716
H	-4.131056	-1.152607	-0.328301
H	-1.444932	-0.213656	-1.663624
H	-1.911844	-1.452899	1.138186

Int1-T1

SCF Energy: -535.795173584

ZPE-corrected Energy: -535.645808

ΔU : -535.635946

ΔH : -535.635002

ΔG : -535.681877

S^2 before (2.0105) and after higher multiplicity projection (2.0001)

Num. Imaginary Frequencies: 0

C	0.484600	-2.005440	0.128689
C	0.101870	0.717287	1.842442
C	-0.853792	-1.884526	0.156438
C	-1.552348	-0.619153	-0.178805
C	-0.767666	0.403150	-0.954333
C	0.771973	0.259362	-0.994967
C	1.385370	-0.882645	-0.231972
C	0.903295	1.677623	-0.442327
C	0.184482	1.795374	0.898179
C	-0.605652	1.814686	-0.387030
O	2.572816	-0.915904	0.049604
O	-2.720210	-0.445642	0.129438
H	0.978563	-2.920295	0.452758
H	-1.490648	-2.696960	0.502844
H	-1.196026	0.435486	-1.963895
H	1.147540	0.195601	-2.024031
H	1.648230	2.407831	-0.742668
H	0.712534	0.349908	2.657231
H	0.290009	2.799855	1.319302
H	-1.223820	2.666634	-0.651773

Int2-S0opt

SCF Energy: -535.935774491

ZPE-corrected Energy: -535.779063

ΔU : -535.771289

ΔH : -535.770345

ΔG : -535.811871

Num. Imaginary Frequencies: 0

C	-0.000539	1.422236	1.079069
C	-0.757112	1.754894	-0.172686
C	-0.784966	0.485775	-1.038879
C	0.783888	0.486246	-1.039058
C	0.754986	1.755525	-0.172746
C	1.433181	-0.675117	-0.337471
C	0.770595	-1.054276	0.931386
C	-0.768460	-1.055301	0.930931
C	-1.432647	-0.676579	-0.337271
O	-2.436753	-1.233783	-0.745967
O	2.437525	-1.231544	-0.746899
C	0.000403	0.024729	1.643665
H	-1.454606	2.583381	-0.242857
H	-1.213116	0.623639	-2.033884
H	-1.257059	-1.833414	1.510925
H	1.260284	-1.832541	1.510374
H	1.211843	0.624332	-2.034075
H	1.451824	2.584574	-0.243812
H	-0.001107	2.212186	1.825945
H	-0.000205	-0.048335	2.728674

Int2-T1

SCF Energy: -535.846201369

ZPE-corrected Energy: -535.6944483

ΔU : -535.685611

ΔH : -535.684667

ΔG : -535.729296

S^2 before (2.0182) and after higher multiplicity projection (2.0002)

Num. Imaginary Frequencies: 0

C	-0.738742	1.422179	0.999907
C	-1.068569	1.569167	-0.476318
C	-0.607956	0.279706	-1.183086
C	0.865052	0.657763	-0.814917
C	0.333233	1.836020	0.003641
C	1.705505	-0.373127	-0.099761
C	0.981502	-1.302065	0.722792
C	-0.492333	-1.134769	0.907582
C	-1.105114	-0.964662	-0.498454
O	-1.914959	-1.737198	-0.958760
O	2.935588	-0.406676	-0.216588
C	-0.854180	0.124072	1.655082
H	-1.831262	2.250434	-0.840795
H	-0.816186	0.238699	-2.254433
H	-0.933480	-2.013189	1.386780
H	1.523445	-2.116536	1.199474
H	1.405775	1.012295	-1.697308
H	0.845664	2.786283	0.122757
H	-1.081878	2.269971	1.590471
H	-1.387504	0.037341	2.597027

Int3-T1

SCF Energy: -535.846569319

ZPE-corrected Energy: -535.695381

ΔU : -535.686192

ΔH : -535.685248

ΔG : -535.730570

S^2 before (2.0167) and after higher multiplicity projection (2.0002)

Num. Imaginary Frequencies: 0

C	-0.974608	1.367647	1.205889
C	-0.529777	1.720136	-0.185259
C	-0.473317	0.491425	-1.155538
C	1.076450	0.449067	-0.957116
C	0.972451	1.790114	-0.290210
C	1.597509	-0.618692	0.001731
C	0.651799	-1.362876	0.793862
C	-0.817424	-1.090015	0.747640
C	-1.209923	-0.711372	-0.668067
O	-2.043053	-1.321842	-1.306277
O	2.813475	-0.803779	0.107311
C	-1.099989	0.110118	1.644453
H	-1.092660	2.581342	-0.570081
H	-0.765605	0.742122	-2.177633
H	-1.396282	-1.962168	1.067980
H	1.056851	-2.091025	1.495075
H	1.677942	0.393001	-1.874034
H	1.710333	2.373479	0.254430
H	-1.147079	2.194819	1.893363
H	-1.365895	-0.099921	2.678317

TS1-T1

SCF Energy: -535.723092415

ZPE-corrected Energy: -535.580059

ΔU : -535.569188

ΔH : -535.568243

ΔG : -535.617667

S^2 before (2.0190) and after higher multiplicity projection (2.0002)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -652.2540

C	1.344399	-1.391300	0.694363
C	-2.594444	0.382757	1.153786
C	0.061991	-1.816700	0.332709
C	-0.801636	-1.119627	-0.538740
C	-0.287697	0.153880	-1.188547
C	1.157869	0.621064	-0.833273
C	1.968214	-0.216530	0.221872
C	0.568293	1.828133	-0.243166
C	-1.758772	1.289246	1.236573
C	-0.754035	1.455420	-0.555573
O	3.083198	0.223059	0.524379
O	-1.991766	-1.435576	-0.770473
H	1.941074	-1.993653	1.377690
H	-0.334749	-2.734647	0.764022
H	-0.520612	0.107178	-2.260045
H	1.851668	0.786979	-1.667283
H	1.004069	2.680609	0.273093
H	-3.211961	-0.458320	0.903542
H	-1.319753	2.098354	1.791844
H	-1.566280	2.095574	-0.894119

TS2-T1

SCF Energy: -535.768996637

ZPE-corrected Energy: -535.622226

ΔU : -535.612337

ΔH : -535.611393

ΔG : -535.658443

S^2 before (2.0488) and after higher multiplicity projection (2.0005)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -594.0529

C	-1.230242	1.663262	0.243969
C	0.593533	-0.796558	1.977163
C	0.052391	2.054852	0.148946
C	1.139844	1.149514	-0.295094
C	0.729740	-0.100893	-1.016189
C	-0.763417	-0.509379	-0.988749
C	-1.682851	0.293709	-0.104151
C	-0.328613	-1.889211	-0.577691
C	0.836415	-1.694355	0.994958
C	1.110025	-1.492998	-0.460035
O	-2.763319	-0.125834	0.270765
O	2.310416	1.431568	-0.096787
H	-1.993463	2.320232	0.658546
H	0.369445	3.043457	0.477941
H	1.098381	-0.009239	-2.044963
H	-1.228150	-0.488963	-1.987684
H	-0.819277	-2.854600	-0.614160
H	0.612604	0.262203	2.186483
H	0.891698	-2.747495	1.286181
H	1.951023	-2.039120	-0.892937

TS3-T1

SCF Energy: -535.788029560

ZPE-corrected Energy: -535.638838

ΔU : -535.629893

ΔH : -535.628949

ΔG : -535.673838

S^2 before (2.0477) and after higher multiplicity projection (2.0006)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -293.9079

C	1.119011	-1.506759	0.476893
C	-0.795938	0.235605	1.804335
C	-0.236306	-1.673685	0.473275
C	-1.151141	-0.983141	-0.469131
C	-0.634252	0.267962	-1.124315
C	0.836609	0.649003	-0.816268
C	1.752176	-0.355744	-0.166094
C	0.331205	1.832821	0.018569
C	-0.717513	1.460585	1.048925
C	-1.089136	1.556855	-0.420910
O	2.964789	-0.182734	-0.134588
O	-2.270950	-1.417683	-0.690370
H	1.766034	-2.159425	1.059452
H	-0.694424	-2.494483	1.024712
H	-0.878129	0.246164	-2.190263
H	1.337076	1.033758	-1.711114
H	0.844137	2.787350	0.094930
H	-1.513723	-0.095345	2.545951
H	-1.045686	2.345536	1.602983
H	-1.854291	2.238776	-0.778653

TS4-T1

SCF Energy: -535.786102178

ZPE-corrected Energy: -535.639217

ΔU : -535.629419

ΔH : -535.628475

ΔG : -535.675263

S^2 before (2.0494) and after higher multiplicity projection (2.0010)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -228.1906

C	-1.340651	1.408398	1.071737
C	-0.743823	1.618388	-0.293344
C	-0.446961	0.332874	-1.144674
C	1.074439	0.543887	-0.912274
C	0.744486	1.851923	-0.256308
C	1.770800	-0.409585	0.043607
C	0.961699	-1.413484	0.740834
C	-0.364942	-1.591318	0.498040
C	-1.056716	-0.938199	-0.637887
O	-2.066736	-1.422205	-1.123471
O	2.970889	-0.299022	0.253541
C	-1.482018	0.253927	1.683876
H	-1.329647	2.371739	-0.839746
H	-0.746678	0.474605	-2.186530
H	-0.925462	-2.380928	0.996349
H	1.481368	-2.000168	1.496138
H	1.691397	0.602545	-1.820627
H	1.359481	2.547178	0.308330
H	-1.645059	2.322858	1.597247
H	-1.816503	-0.108875	2.646637

TS5-T1

SCF Energy: -535.829293480

ZPE-corrected Energy: -535.679061

ΔU : -535.670450

ΔH : -535.669506

ΔG : -535.713653

S^2 before (2.0387) and after higher multiplicity projection (2.0007)

Num. Imaginary Frequencies: 1

Imaginary Frequency: -642.8197

C	-0.881566	1.371055	1.092052
C	-0.952543	1.623784	-0.366249
C	-0.615026	0.334814	-1.162942
C	0.903864	0.608233	-0.888984
C	0.500686	1.868168	-0.160725
C	1.673879	-0.438167	-0.101552
C	0.899316	-1.336961	0.711660
C	-0.575379	-1.126725	0.876598
C	-1.154680	-0.904374	-0.516830
O	-1.967159	-1.649581	-1.021713
O	2.905782	-0.499570	-0.163991
C	-0.815259	0.128845	1.692356
H	-1.681600	2.341909	-0.745474
H	-0.892195	0.381637	-2.217873
H	-1.050817	-2.000260	1.334022
H	1.417610	-2.148235	1.219847
H	1.464007	0.812099	-1.810952
H	1.062658	2.738008	0.159120
H	-0.996545	2.251650	1.721581
H	-0.731860	0.044365	2.773057

6.2 Exo approach

Int1-S0

SCF Energy: -535.798305079

ZPE-corrected Energy: -535.648135

ΔU : -535.638270

ΔH : -535.637326

ΔG : -535.683967

Num. Imaginary Frequencies: 0

C	-1.504540	0.735170	0.584829
C	-1.503878	-0.736732	0.584732
C	-0.026988	-0.772595	0.992499
C	-0.027700	0.772367	0.992556
C	0.936262	1.487475	0.084143
C	1.981889	0.673273	-0.575297
C	1.982470	-0.671574	-0.575404
C	0.937566	-1.486750	0.083991
O	0.866192	2.689894	-0.101376
O	0.868526	-2.689211	-0.101664
H	-2.270260	1.445597	0.877243
H	-2.268954	-1.447866	0.877097
H	0.084588	-1.190574	1.999710
H	0.083407	1.190363	1.999819
H	2.741625	1.238173	-1.112932
H	2.742703	-1.235727	-1.113127
C	-1.629415	-0.000848	-0.782724
C	-2.912143	-0.000416	-1.378527
H	-0.744825	-0.000509	-1.425564
H	-3.647166	-0.001134	-0.542718

TS2-S0

SCF Energy: -535.770810437

ZPE-corrected Energy: -535.623969

ΔU : -535.613682

ΔH : -535.612738

ΔG : -535.660065

Num. Imaginary Frequencies: 1

Imaginary Frequency: -423.6581

C	-1.567747	0.049750	0.763715
C	-1.060447	-1.251362	0.857833
C	0.361869	-0.801823	1.052675
C	-0.187264	0.646722	1.089282
C	1.374304	-1.150442	-0.016308
C	2.005090	-0.026427	-0.742676
C	1.568220	1.242968	-0.666652
C	0.406006	1.662009	0.150435
O	1.671582	-2.305965	-0.256969
O	-0.039538	2.793239	0.071395
H	-2.517786	0.475533	1.069795
H	-1.516533	-2.234715	0.824623
H	-0.179335	1.078466	2.096902
H	0.784987	-1.136375	2.011783
H	2.035793	2.035860	-1.247912
H	2.839518	-0.299201	-1.386557
C	-1.707222	-0.261277	-0.962863
C	-2.868258	-0.576146	-1.453135
H	-0.762364	-0.002191	-1.430681
H	-3.687941	-1.019402	-0.887195

5. References

1. Gan, X., Jiang, W., Wang, W. & Hu, L. An approach to 3,6-disubstituted 2,5-dioxybenzoquinones via two sequential Suzuki couplings. Three-step synthesis of leucomelone. *Org. Lett.* **11**, 589–592 (2009).
2. APEX3 Version 2018.1-0 (Bruker AXS Inc., 2018).
3. SAINT Version 8.38A (Bruker AXS Inc., 2016).
4. SADABS Version 2016/2 Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **48**, 3–10 (2015).
5. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42**, 339–341 (2009).
6. SHELXT Version 2014/5 and SHELXL Version 2017/1 Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A Found. Crystallogr.* **71**, 3–8 (2015).
7. Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36**, 7–13 (2003).
8. Wei, Y., Tinoco, A., Steck, V., Fasan, R. & Zhang, Y. Cyclopropanations via Heme Carbene: Basic Mechanism and Effects of Carbene Substituent, Protein Axial Ligand, and Porphyrin Substitution. *J. Am. Chem. Soc.* **140**, 1649–1662 (2018).
9. Yan Zhao and Donald G. Truhlar, “The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals”, *Theor. Chem. Acc.* **120**, 215–241 (2008).
10. Jacopo Tomasi, Benedetta Mennucci, and Roberto Cammi, “Quantum mechanical continuum solvation models”, *Chem. Rev.* **105**, 2999–3094 (2005).
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, “Gaussian 16 Revision C.01” (2016), Gaussian Inc. Wallingford CT.
12. Rüdiger Bauernschmitt and Reinhart Ahlrichs, “Stability analysis for solutions of the closed shell Kohn Sham equation”, *J. Chem. Phys.* **104**, 9047–9052 (1996).