

## Supporting Information

### A New Cycloaddition Profile for *ortho*-Quinone Methides: Photoredox-Catalyzed

#### [6+4] Cycloadditions for Synthesis of Benzo[*b*]cyclopenta[*e*]oxepines

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## 1. General information

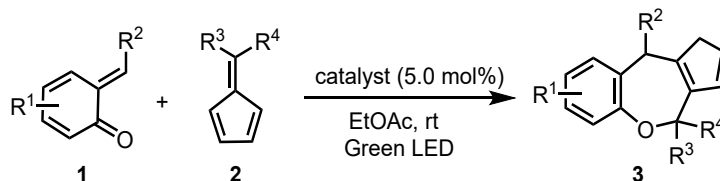
General Information. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100. <sup>1</sup>H NMR spectra were recorded on a JEOL ECA-500 (500 MHz) spectrometer or a Bruker DRX-500 (500 MHz) spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm from TMS. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, integration. <sup>13</sup>C NMR spectra were recorded on a JEOL ECA-500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (CDCl<sub>3</sub>: δ 77.0). High-resolution mass spectra were obtained with Hitachi Nanofrontier LD Spectrometer (ESI/ TOF). Wako-reagent silica gel 60 N (spherical; particle size: 63–212 μm). Thin-layer chromatography (TLC) was carried out on Wako TLC plates with silica gel (70 F<sub>254</sub>). Unless otherwise noted, reagents were commercially available and were used without purification. Single Crystal X-ray Diffraction analysis was performed at 123 K using a Rigaku XtaLAB P200 diffractometer with a graphite monochromatic Cu Kα radiation source (λ = 1.54187 Å). The UV absorption spectra were measured with a JASCO V-630 spectrometer. The fluorescence spectra and absolute fluorescence quantum yield were obtained on a JASCO FP-8500 spectrofluorometer. Cyclic voltammetry measurements were carried out with a computer-controlled potentiostat Model 660C (ALS Co., Ltd.). Photochemical reaction was carried out in the borosilicate vial under visible light by a Beamtec 7 W Green LED (LDA7G-C50). The sample was placed at an approximate distance of 5 cm from the lamp. The emission spectrum of the LED was measured with a miniature fiber-optic spectrometer (FLAME-S-XR1-ES, Ocean Optics). *o*-Quinone methide **1a** were prepared according to the reported methods.<sup>1</sup> Thioxanthylum photoredox catalyst was prepared according to the reported method.<sup>2</sup>

## 2. Experimental section

### • For the synthesis of 6-(4-fluorobenzylidene)benzo[*d*][1,3]dioxol-5(6*H*)-one

A solution of 6-(4-fluorobenzyl)benzo[*d*][1,3]dioxol-5-ol (0.75 g, 3.1 mmol) in ether (50 mL) was heated under reflux with silver oxide (2.82 g, 12.2 mmol) for 6 h and filtered. The solution was concentrated to 10 mL and filtered to give yellow crystals (0.20 g, 27% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.85 (s, 1H), 7.48 (t, *J* = 6.5 Hz, 2H), 7.13 (t, *J* = 8.1 Hz, 2H), 6.60 (s, 1H), 5.97 (s, 1H), 5.90 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 185.3, 163.2 (d, *J* = 251.1 Hz, 1C), 161.6, 146.7, 140.5, 132.2, 131.7 (d, *J* = 3.8 Hz, 1C), 130.4, 116.1, 115.9, 101.8 (d, *J* = 22.0 Hz, 1C), 98.5; IR (ATR): 2920, 2361, 1504, 1213, 950, 833 cm<sup>-1</sup>; HRMS (ESI+) *m/z* calcd for C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>F ([M + H]<sup>+</sup>): 245.0609, found: 245.0610.

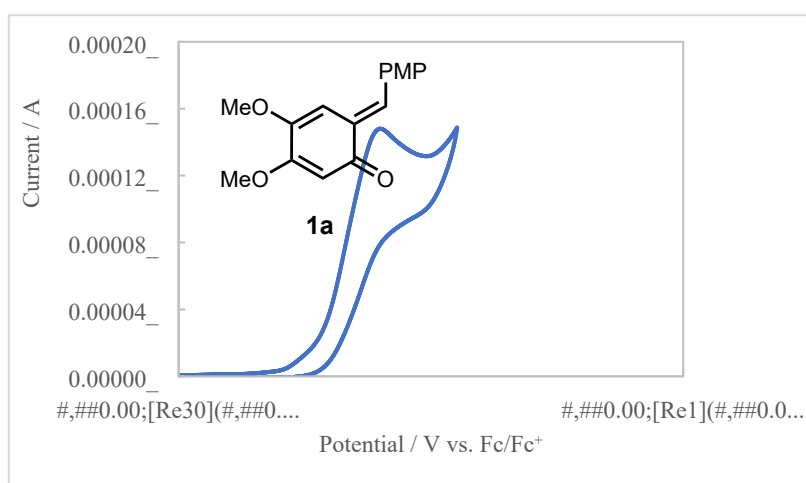
• **General procedure for [4+2] cycloaddition with photocatalyst under visible light irradiation**



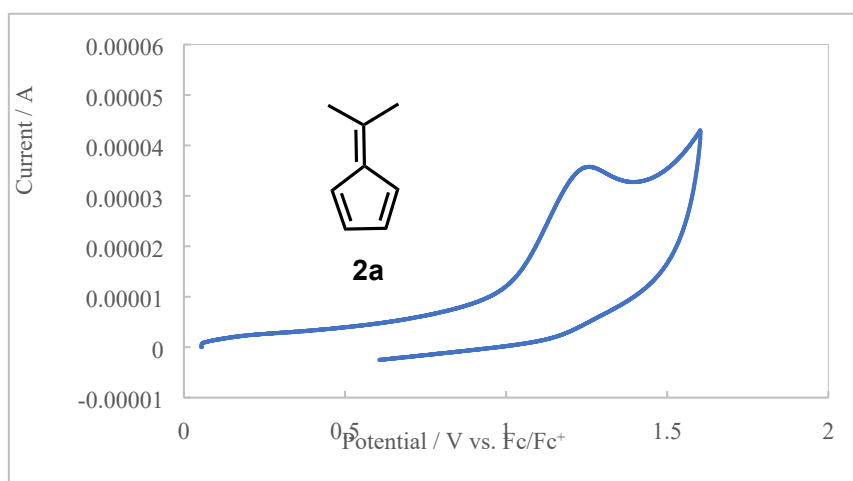
*o*-Quinone methide (**1**) (0.375 mmol), fulvene (**2**) (0.125 mmol), thioxanthylum photoredox catalyst (5.0 mol%) and EtOAc (2.0 mL) were added into an 8 mL open-air borosilicate vial. The resulting solution was stirred at room temperature under open-air and green LED irradiation ( $\lambda_{\text{max}} = 515 \text{ nm}$ ) for 3 to 24 h. Then, the vial was placed at an approximate distance of 5 cm from the lamp. After the reaction was completed, the desired cycloadduct (**3**) was isolated by flash column chromatography on silica gel (hexane : EtOAc = 7 : 1).

**3. Cyclic voltammetry measurement**

Samples for electrochemical measurements were prepared with 10 mL of a 0.1 M *tetra-n*-butylammonium tetrafluoroborate solution in dry  $\text{CH}_3\text{CN}$  and 0.1 mmol of substrate. Cyclic voltammetry measurements were carried out with a computer-controlled potentiostat Model 660C (ALS Co., Ltd.). Cyclic Voltammetry was recorded using an undivided cell equipped with a working electrode (Pt disk electrode,  $\phi$  3mm), a counter electrode (Pt wire), and a reference electrode (Ag wire). The ferrocene/ferrocenium couple ( $\text{Fc}/\text{Fc}^+$ ) was also measured in the same electrochemical system, and the electrode potential was reported as values referred to the apparent standard potential of the system. The referenced value was converted to SCE by adding 0.40 V (in  $\text{CH}_3\text{CN}$ ). A scan rate was used 1.0 V/s.



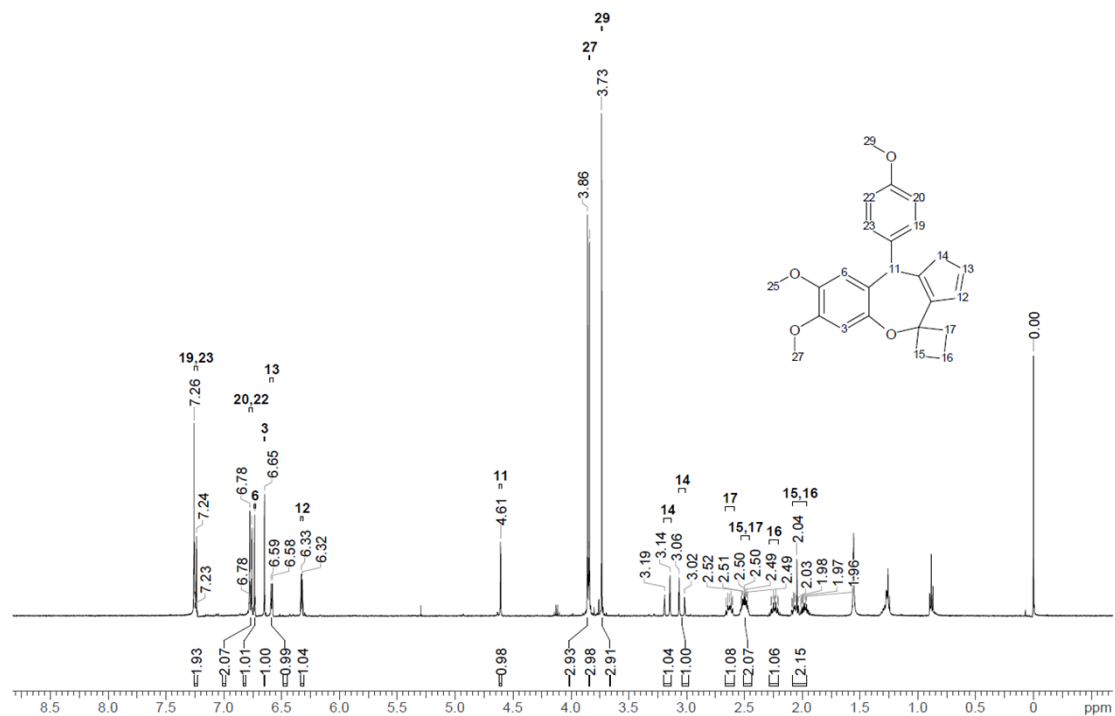
$$E_{p/2} = +0.6535 \text{ V vs. Fc/Fc}^+ \quad (+1.0535 \text{ V} \cong +1.05 \text{ V vs. SCE})$$



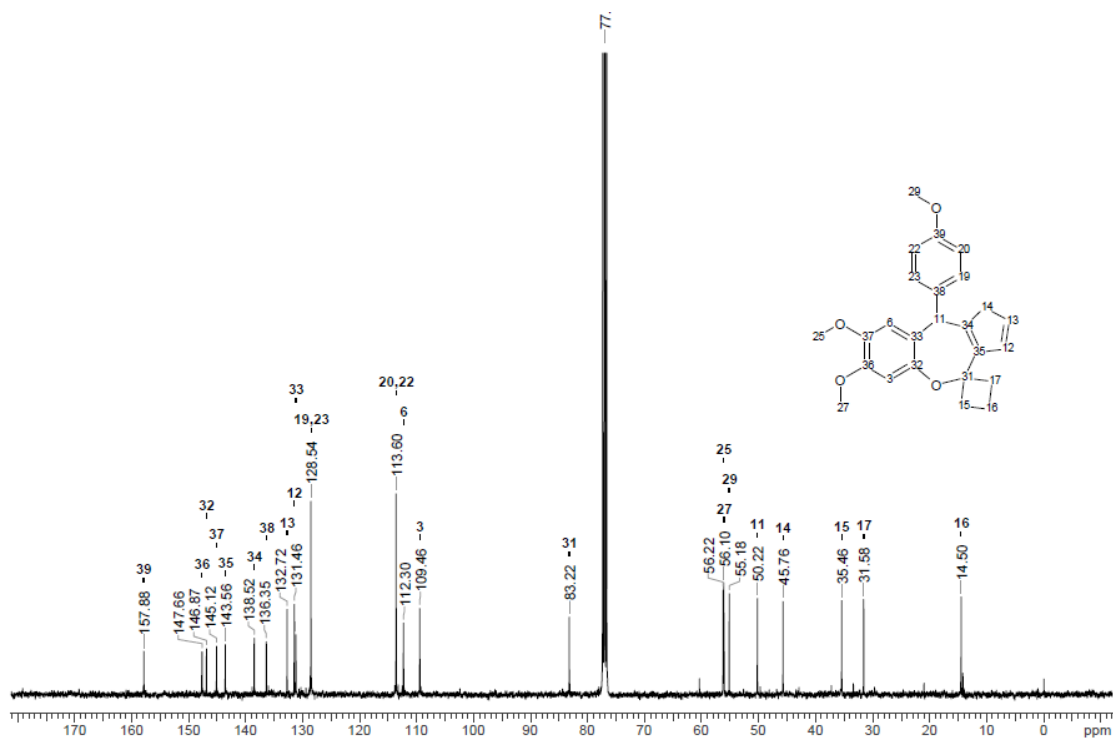
$$E_{p/2} = +1.0895 \text{ V vs. Fc/Fc}^+ \text{ (} +1.4895 \text{ V} \rightleftharpoons +1.49 \text{ V vs. SCE)}$$

#### 4. Characterization of 3c

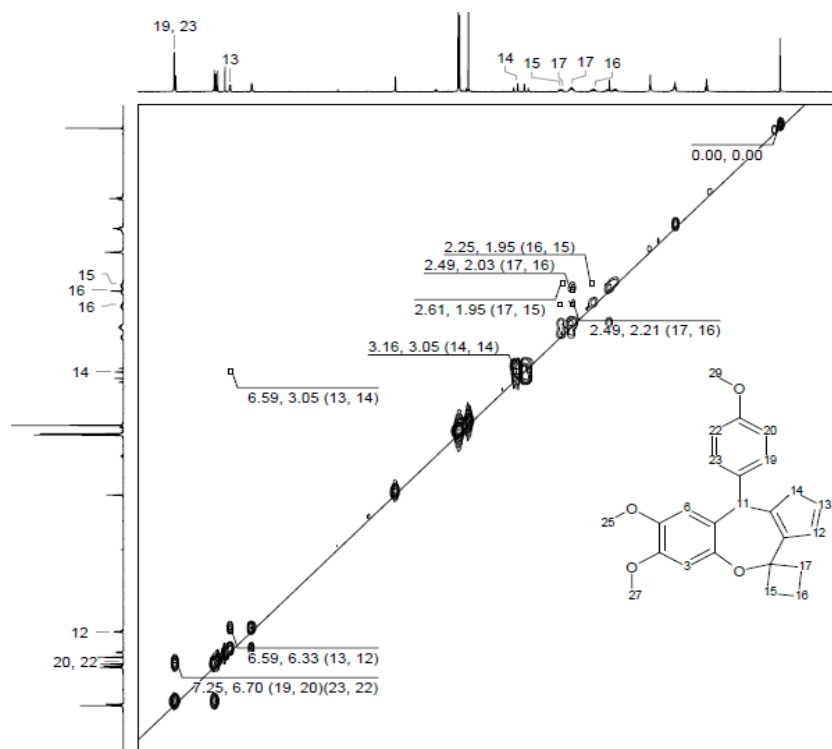
- $^1\text{H}$  NMR spectrum data of 3c



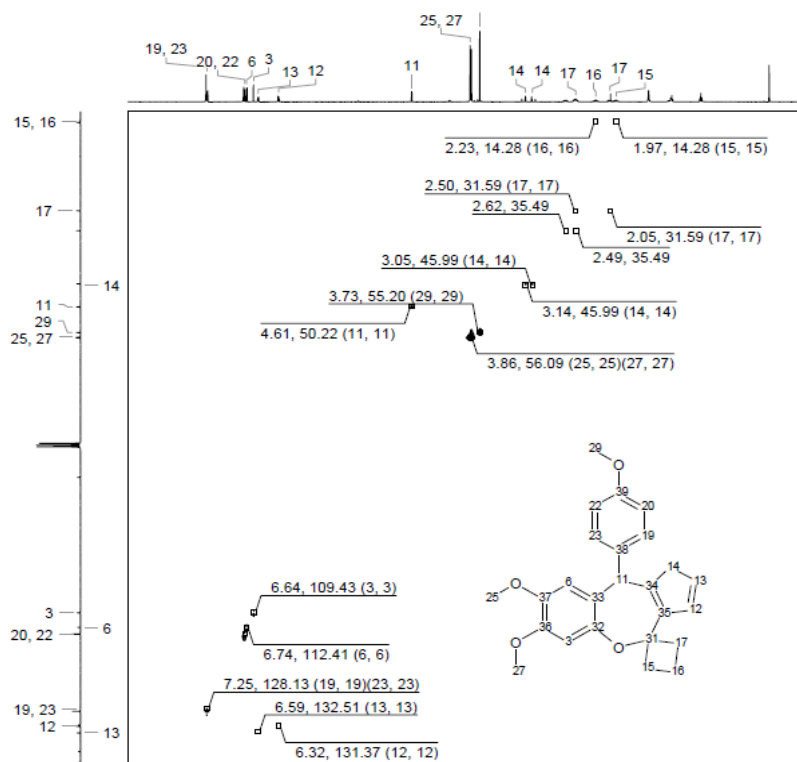
- $^{13}\text{C}$  NMR spectrum data of 3c



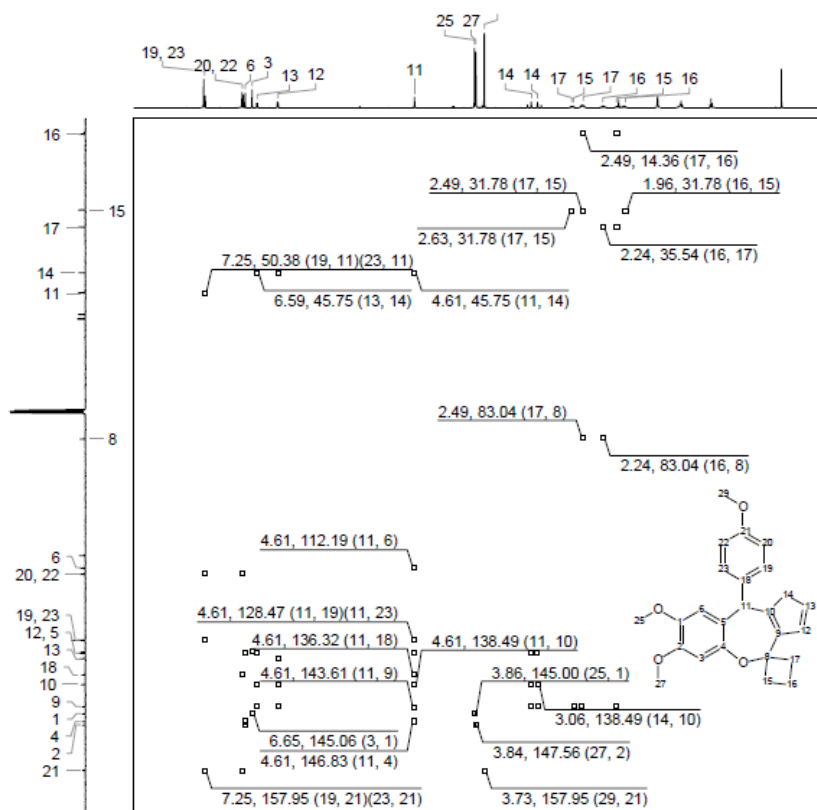
- $^1\text{H} / ^1\text{H}$  COSY NMR spectrum data of **3c**



- $^1\text{H} / ^{13}\text{C}$  HSQC NMR spectrum data of **3c**

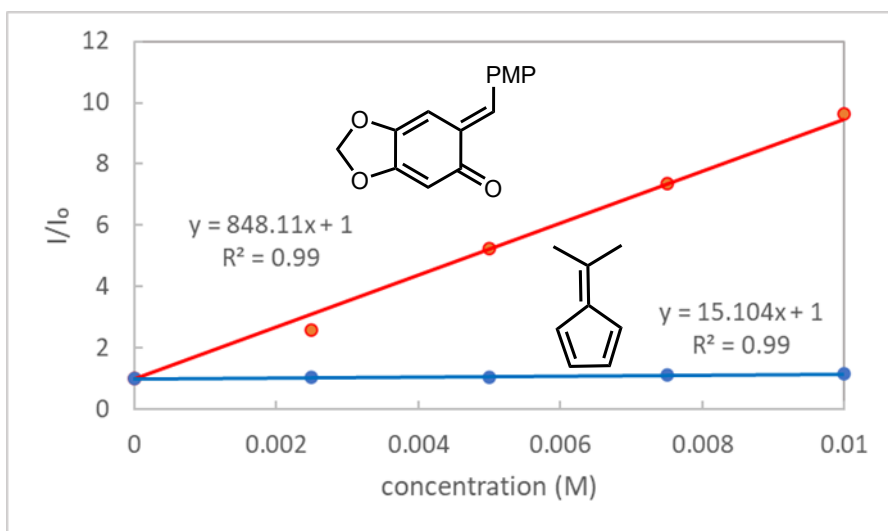


- $^1\text{H} / ^{13}\text{C}$  HMBC NMR spectrum data of **3c**



## 5. Stern-Volmer fluorescence quenching

Emission intensities were recorded using a JASCO FP-8500 Fluorescence Spectrometer. All solutions were excited at 468 nm and the emission intensity at each peak top was observed. In a typical experiment, the emission spectrum of a  $1 \times 10^{-4}$  M solution of thioxanthylum photoredox catalyst in  $\text{CH}_3\text{CN}$  was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected. Here  $I_0$  and  $I$  represent the intensities of the emission in the absence and presence of the quencher.





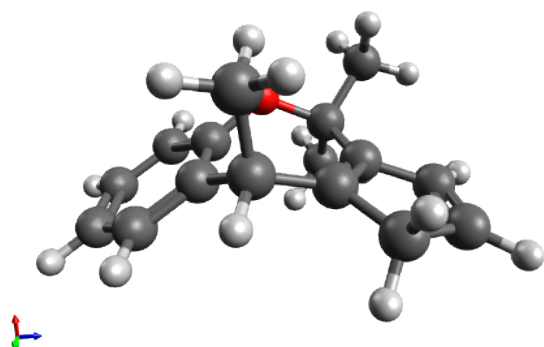
## 6. Computational data

Structure optimizations and frequency analyses of cations **3a'**, *cis*-intermediate **C**, and *trans*-intermediate **C** were carried out at the B3LYP level of density functional theory (DFT) with the 6-31G(d,p) basis set on the ORCA program package.<sup>3</sup>

4,4,10-trimethyl-4,10-dihydro-1*H*-benzo[*b*]cyclopenta[*e*]oxepine (**3a'**)

atom type	x	y	z
C	-0.80496	0.761176	-3.08354
C	-0.57035	-0.61247	-3.15429
C	-0.01002	-1.27567	-2.06139
C	0.31809	-0.56874	-0.90135
C	0.101792	0.817251	-0.81801
C	-0.46742	1.461452	-1.92289
O	0.948495	-1.24356	0.12239
C	0.216968	-1.53766	1.347286
C	-0.15718	-0.26995	2.090938
C	-0.0226	1.022449	1.701659
C	0.520261	1.603032	0.414848
C	-0.75449	-0.29945	3.443842
C	-0.96987	0.956939	3.877639
C	-0.5281	1.91856	2.811952
C	2.058511	1.785923	0.466386
C	1.220384	-2.36553	2.161912
C	-1.03245	-2.37636	1.030067
H	-1.24327	1.287274	-3.92589
H	-0.82321	-1.16833	-4.05195
H	0.186591	-2.34209	-2.09463
H	-0.64216	2.532901	-1.8718
H	0.089584	2.60603	0.311607
H	-0.97525	-1.21046	3.989349
H	-1.39149	1.253643	4.830541
H	0.251363	2.607948	3.169606

H	-1.35312	2.558867	2.465807
H	2.41287	2.30892	-0.42861
H	2.561311	0.817439	0.52455
H	2.346399	2.37806	1.341874
H	2.123575	-1.78312	2.366072
H	1.503234	-3.26201	1.601575
H	0.785934	-2.67631	3.115701
H	-0.75077	-3.2953	0.505902
H	-1.73911	-1.82082	0.407467
H	-1.54636	-2.65435	1.955074



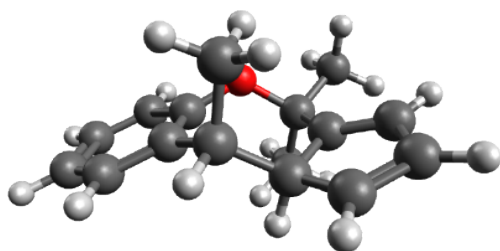
Gibbs Free Energy: -695.03338110 hartree

Imaginary Frequencies: 0

(10S\*,10aR\*)-4,4,10-trimethyl-10,10a-dihydro-4*H*-benzo[*b*]cyclopenta[*e*]oxepine (*cis*-intermediate C)

atom type	x	y	z
C	-0.51918	0.850466	-3.39136
C	-0.20484	-0.50564	-3.50029
C	0.200679	-1.21221	-2.36727
C	0.30571	-0.57225	-1.12599
C	0.009141	0.800821	-1.00058
C	-0.40989	1.484899	-2.15173
O	0.793037	-1.32072	-0.07615
C	-0.06938	-1.64531	1.073014
C	-0.21466	-0.43265	1.963881

C	-0.67393	0.927867	1.461113
C	0.175396	1.551391	0.310169
C	-0.02632	-0.35429	3.303372
C	-0.32799	1.004119	3.77143
C	-0.69888	1.762451	2.719257
C	1.663585	1.709985	0.680741
C	-1.43822	-2.14285	0.580059
C	0.686756	-2.78419	1.761312
H	-0.84141	1.413509	-4.26352
H	-0.27965	-1.01475	-4.45793
H	0.450549	-2.26791	-2.42528
H	-0.64433	2.544515	-2.0702
H	-1.70403	0.838924	1.078014
H	-0.23239	2.557871	0.151986
H	0.285343	-1.1625	3.956889
H	-0.26089	1.321346	4.80803
H	-0.97434	2.812287	2.731306
H	2.190955	2.265412	-0.10365
H	1.773797	2.265753	1.619091
H	2.153563	0.738793	0.795313
H	-2.04334	-2.46468	1.43466
H	-1.31299	-2.9968	-0.0958
H	-1.99186	-1.36094	0.051298
H	0.138447	-3.13958	2.639255
H	1.681868	-2.45665	2.079008
H	0.803214	-3.62171	1.065872



Gibbs Free Energy: -695.02667490 hartree

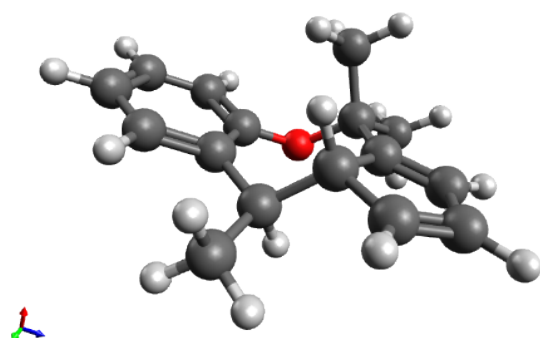
Imaginary Frequencies: 0

(10S\*,10aS\*)-4,4,10-trimethyl-10,10a-dihydro-4H-benzo[b]cyclopenta[e]oxepine (*trans*-intermediate

C)

atom type	x	y	z
C	0.654907	0.860341	-3.27301
C	0.426683	-0.51337	-3.36136
C	0.011247	-1.21245	-2.22761
C	-0.18593	-0.5437	-1.01445
C	0.005357	0.850026	-0.91152
C	0.44208	1.525395	-2.06195
O	-0.64774	-1.28467	0.049467
C	0.252618	-1.55488	1.184659
C	0.346582	-0.32515	2.058648
C	0.677959	1.072357	1.541001
C	-0.28871	1.565858	0.403878
C	0.162137	-0.25655	3.398559
C	0.363452	1.120311	3.861332
C	0.656065	1.904538	2.80458
C	-0.28851	3.096119	0.271671
C	-0.43356	-2.72388	1.895807
C	1.638648	-1.98785	0.679315
H	0.986741	1.420016	-4.14384
H	0.576834	-1.04032	-4.30033
H	-0.17052	-2.28291	-2.26284
H	0.60995	2.596715	-2.0224
H	1.699607	1.088694	1.1275
H	-1.29875	1.265228	0.714475
H	-0.09009	-1.08328	4.054125

H	0.293602	1.43318	4.899037
H	0.872496	2.966118	2.828452
H	-0.93604	3.4157	-0.55262
H	-0.67219	3.556805	1.186465
H	0.715188	3.499131	0.088277
H	0.14151	-3.04219	2.77081
H	-0.51397	-3.57331	1.209695
H	-1.44092	-2.44471	2.220766
H	2.153821	-1.18095	0.149379
H	1.549665	-2.84603	0.003115
H	2.262055	-2.28245	1.530597



Gibbs Free Energy: -695.02303027 hartree

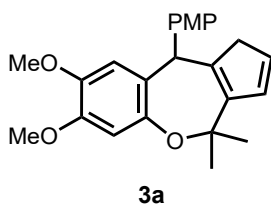
Imaginary Frequencies: 0

Domain-based local pair natural orbital coupled cluster single-point energy calculations in the gas phase based on the B3LYP geometries were performed at the DLPNO-CCSD(T) level by using ORCA 5.0.1.<sup>3-5</sup>

Comparison of the Gibbs free energies of **3a'**, *cis*-intermediate **C**, and *trans*-intermediate **C** calculated by DLPNO-CCSD(T) method.

<b>3a'</b>	<i>cis</i> -intermediate <b>C</b>	<i>trans</i> -intermediate <b>C</b>
	+2.65 (kcal/mol)	+4.69 (kcal/mol)

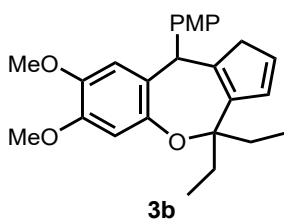
## 7. Characterization data



### 7,8-Dimethoxy-10-(4-methoxyphenyl)-4,4-dimethyl-4,10-dihydro-1H-benzo[b]cyclopenta[e]oxepine

#### (3a):

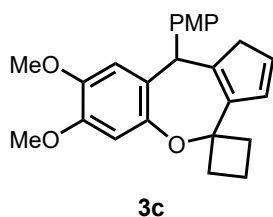
*o*-Quinone methide **1a** (102.0 mg, 0.375 mmol), 6,6-dimethylfulvene (13.4 mg, 0.127 mmol), thioxanthylum photoredox catalyst (4.08 mg, 0.00632 mmol), and EtOAc (2.0 mL) were used. Yellow solid (30.8 mg, 64% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.25 (d,  $J = 5.0$  Hz, 2H), 6.78 (d,  $J = 5.0$  Hz, 2H), 6.74 (s, 1H), 6.54 (s, 1H), 6.28 (s, 2H), 4.59 (s, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.74 (s, 3H), 3.19 (d,  $J = 25$  Hz, 1H), 3.45 (d,  $J = 25$  Hz, 1H), 1.64 (s, 3H), 1.34 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.9, 147.8, 147.1, 145.1, 144.9, 137.8, 136.7, 133.3, 131.1, 131.1, 128.5, 113.6, 113.3, 112.4, 109.8, 79.4, 56.3, 56.1, 55.2, 49.9, 45.9, 29.8, 26.6; IR (ATR): 2931, 1506, 1246, 1095, 1010, 730  $\text{cm}^{-1}$ ; HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{27}\text{O}_4$  ( $[\text{M} + \text{H}]^+$ ): 379.1904, found: 379.1909.



### 4,4-Diethyl-7,8-dimethoxy-10-(4-methoxyphenyl)-4,10-dihydro-1H-benzo[b]cyclopenta[e]oxepine

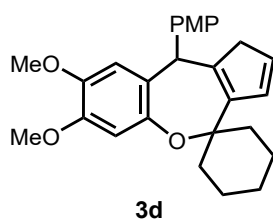
#### (3b):

*o*-Quinone methide **1a** (103.8 mg, 0.381 mmol), 6,6-diethylfulvene (16.6 mg, 0.124 mmol), thioxanthylum photoredox catalyst (4.08 mg, 0.00620 mmol), and EtOAc (2.0 mL) were used. Yellow solid (14.9 mg, 30% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.26-7.25 (m, 2H), 6.77-6.73 (m, 2H), 6.67 (s, 1H), 6.63 (s, 1H), 6.27-6.20 (m, 2H), 4.63 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.73 (s, 3H), 3.21 (d,  $J = 25$  Hz, 1H), 3.05 (d,  $J = 25$  Hz, 1H), 1.95 (dd,  $J = 14.2, 7.3$  Hz, 1H), 1.84 (dd,  $J = 14.2, 7.3$  Hz, 1H), 1.69 (dd,  $J = 14.5, 7.3$  Hz, 1H), 1.60 (dd,  $J = 14.5, 7.6$  Hz, 1H), 0.93-0.87 (m, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.8, 147.6, 147.4, 144.8, 143.0, 140.2, 137.4, 133.8, 130.4, 129.7, 128.6, 113.5, 112.4, 109.2, 84.9, 56.1, 55.9, 55.2, 50.4, 46.0, 31.3, 8.5, 8.5; IR (ATR): 2932, 1507, 1246, 1196, 1009, 730  $\text{cm}^{-1}$ ; HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_4$  ( $[\text{M} + \text{H}]^+$ ): 407.2217, found: 407.2229.



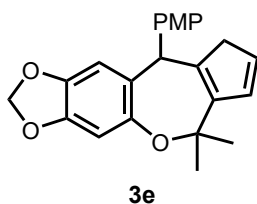
**7,8-Dimethoxy-10-(4-methoxyphenyl)-1,10-dihydrospiro[benzo[*b*]cyclopenta[*e*]oxepine-4,1'-cyclobutane] (3c):**

*o*-Quinone methide **1a** (99.7 mg, 0.366 mmol), 6,6-trimethylenefulvene (13.4 mg, 0.127 mmol), thioxanthylum photoredox catalyst (4.18 mg, 0.00647 mmol), and EtOAc (2.0 mL) were used. Yellow solid (21.9 mg, 46% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.26-7.23 (m, 2H), 6.78-6.76 (m, 2H), 6.73 (s, 1H), 6.65 (s, 1H), 6.59 (d, *J* = 5.7 Hz, 1H), 6.34-6.31 (m, 1H), 4.61 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.73 (s, 3H), 3.17 (d, *J* = 25 Hz, 1H), 3.04 (d, *J* = 25 Hz, 1H), 2.67-2.59 (m, 1H), 2.53-2.46 (m, 2H), 2.29-2.21 (m, 1H), 2.08-1.96 (m, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 157.9, 147.7, 146.9, 145.1, 143.6, 138.5, 136.4, 132.7, 131.5, 131.2, 128.6, 113.6, 112.3, 109.5, 83.2, 56.2, 56.1, 55.2, 50.2, 45.8, 35.5, 31.6, 14.5; IR (ATR): 2935, 1506, 1247, 1194, 1006, 730 cm<sup>-1</sup>; HRMS (ESI<sup>+</sup>) *m/z* calcd for C<sub>25</sub>H<sub>27</sub>O<sub>4</sub> ([M + H]<sup>+</sup>): 379.1904, found: 379.1900.



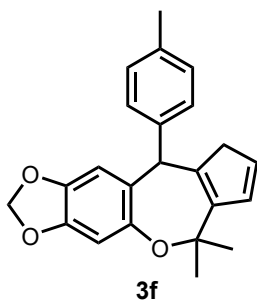
**7,8-Dimethoxy-10-(4-methoxyphenyl)-1,10-dihydrospiro[benzo[*b*]cyclopenta[*e*]oxepine-4,1'-cyclohexane] (3d):**

*o*-Quinone methide **1a** (101.2 mg, 0.372 mmol), 6,6-pentamethylenefulvene (18.2 mg, 0.124 mmol), thioxanthylum photoredox catalyst (4.11 mg, 0.00637 mmol), and EtOAc (2.0 mL) were used. Yellow solid (29.7 mg, 57% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.79-6.72 (m, 4H), 6.34 (d, *J* = 5.7 Hz, 1H), 6.27 (d, *J* = 5.4 Hz, 1H), 4.58 (s, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.74 (s, 3H), 3.18 (d, *J* = 20 Hz, 1H), 3.05 (d, *J* = 20 Hz, 1H), 2.07-2.03 (m, 1H), 1.93-1.74 (m, 5H), 1.66-1.58 (m, 2H), 1.53-1.44 (m, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 157.8, 147.5, 146.7, 145.4, 144.7, 138.5, 136.7, 133.7, 131.5, 130.7, 128.4, 113.6, 112.3, 109.2, 80.9, 56.2, 56.0, 55.2, 49.9, 46.0, 37.0, 32.2, 25.4, 21.7, 21.3; IR (ATR): 2931, 1507, 1241, 1194, 910, 728 cm<sup>-1</sup>; HRMS (ESI<sup>+</sup>) *m/z* calcd for C<sub>27</sub>H<sub>31</sub>O<sub>4</sub> ([M + H]<sup>+</sup>): 419.2217, found: 419.2210.



**10-(4-Methoxyphenyl)-6,6-dimethyl-9,10-dihydro-6H-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]cyclopenta[e]oxepine (3e):**

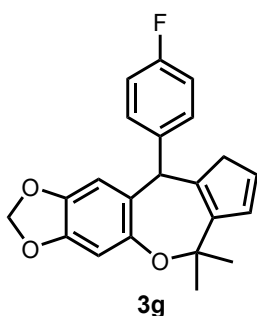
*o*-Quinone methide **1a** (95.7 mg, 0.373 mmol), 6,6-dimethylfulvene (13.1 mg, 0.123 mmol), thioxanthylum photoredox catalyst (3.98 mg, 0.00616 mmol), and EtOAc (2.0 mL) were used. Yellow solid (31.0 mg, 69% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.22 (d, *J* = 5.0 Hz, 2H), 6.77 (d, *J* = 5.0 Hz, 2H), 6.73 (s, 1H), 6.49 (s, 1H), 6.29 (s, 2H), 5.90 (s, 2H), 4.55 (s, 1H), 3.74 (s, 3H), 3.18 (d, *J* = 20 Hz, 2H), 3.03 (d, *J* = 20 Hz, 2H), 1.61 (s, 3H), 1.34 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 157.9, 147.9, 146.2, 145.0, 143.4, 137.6, 136.4, 133.2, 132.6, 131.1, 128.4, 113.6, 108.5, 107.1, 101.2, 79.5, 55.2, 49.6, 45.9, 29.7, 26.5; IR (ATR): 2927, 1499, 1481, 1247, 1036, 863 cm<sup>-1</sup>; HRMS (ESI+) *m/z* calcd for C<sub>23</sub>H<sub>23</sub>O<sub>4</sub> ([M + H]<sup>+</sup>): 363.1591, found: 363.1595.



**6,6-Dimethyl-10-(*p*-tolyl)-9,10-dihydro-6H-[1,3]dioxolo[4',5':4,5]benzo[1,2-*b*]cyclopenta[e]oxepine (3f):**

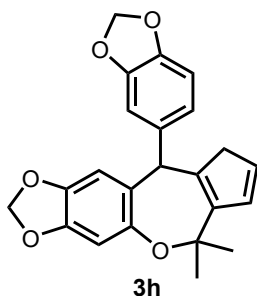
(*E*)-6-(4-methylbenzylidene)benzo[*d*][1,3]dioxol-5(6*H*)-one (89.0 mg, 0.370 mmol), 6,6-dimethylfulvene (13.1 mg, 0.123 mmol), thioxanthylum photoredox catalyst (4.02 mg, 0.00622 mmol), and EtOAc (2.0 mL) were used. White solid (27.8 mg, 65% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.18 (d, *J* = 10 Hz, 2H), 7.04 (d, *J* = 10 Hz, 2H), 6.74 (s, 1H), 6.49 (s, 1H), 6.29 (s, 2H), 5.90 (q, *J* = 1.4, 2H), 4.57 (s, 1H), 3.18 (d, *J* = 25 Hz, 1H), 3.04 (d, *J* = 25 Hz, 1H), 2.27 (s, 3H), 1.61 (s, 3H), 1.34 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 148.0, 146.2, 145.0, 143.4, 141.1, 137.5, 135.5, 133.2, 132.6, 131.1, 128.9, 127.3, 108.6, 107.1, 101.1, 79.4, 50.0, 46.0, 29.7, 26.4, 20.9; IR (ATR): 2933, 1479, 1158, 1038, 864, 643 cm<sup>-1</sup>; HRMS (ESI+) *m/z* calcd for C<sub>23</sub>H<sub>23</sub>O<sub>3</sub> ([M + H]<sup>+</sup>): 347.1630, found: 363.1642.





**10-(4-Fluorophenyl)-6,6-dimethyl-9,10-dihydro-6H-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]cyclopenta[e]oxepine (3g):**

(*E*)-6-(4-Fluorobenzylidene)benzo[*d*][1,3]dioxol-5(6*H*)-one (90.5 mg, 0.371 mmol), 6,6-dimethylfulvene (13.0 mg, 0.122 mmol), thioxanthylum photoredox catalyst (4.11 mg, 0.00636 mmol), and EtOAc (2.0 mL) were used. White solid (33.1 mg, 77% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.25-7.21 (m, 2H), 6.93-6.88 (m, 2H), 6.73 (s, 1H), 6.50 (s, 1H), 6.33-6.27 (m, 2H), 5.91 (s, 2H), 4.55 (s, 1H), 3.16 (d, *J* = 25 Hz, 1H), 3.04 (d, *J* = 25 Hz, 1H), 1.60 (s, 3H), 1.34 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 161.3 (d, *J* = 244.4 Hz, 1C), 147.8, 146.4, 145.3, 143.5, 139.8 (d, *J* = 2.9 Hz, 1C), 137.0, 133.3, 132.2, 131.4, 128.8 (d, *J* = 7.7 Hz, 1C), 114.8 (d, *J* = 21.1 Hz, 1C), 108.5, 107.2, 101.3, 79.5, 49.5, 45.9, 29.6, 26.3; IR (ATR): 2908, 1503, 1479, 1220, 1155, 930, 731 cm<sup>-1</sup>; HRMS (ESI+) *m/z* calcd for C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>F ([M + H]<sup>+</sup>): 351.1391, found: 351.1386.



**10-(benzo[*d*][1,3]dioxol-5-yl)-6,6-dimethyl-9,10-dihydro-6H-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]cyclopenta[e]oxepine (3h):**

(*E*)-6-(Benzo[*d*][1,3]dioxol-5-ylmethylene)benzo[*d*][1,3]dioxol-5(6*H*)-one (98.8 mg, 0.366 mmol), 6,6-dimethylfulvene (13.0 mg, 0.122 mmol), thioxanthylum photoredox catalyst (4.16 mg, 0.00644 mmol), and EtOAc (2.0 mL) were used. Yellow solid (36.3 mg, 79% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.90-6.82 (m, 2H), 6.75-6.64 (m, 2H), 6.50 (s, 1H), 6.34-6.24 (m, 2H), 5.91 (s, 2H), 4.51 (s, 1H), 3.17 (d, *J* = 30 Hz, 1H), 3.03 (d, *J* = 30 Hz, 1H), 1.62 (s, 3H), 1.34 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 147.8, 147.4, 146.2, 145.7, 145.2, 143.4, 138.3, 137.2, 133.2, 132.3, 131.3, 120.3, 108.5, 108.3, 107.8, 107.1, 101.2, 100.8, 79.5, 50.0, 45.9, 29.7, 26.4; IR (ATR): 2927, 1478, 1234, 1035, 929, 867 cm<sup>-1</sup>; HRMS (ESI+) *m/z* calcd for C<sub>23</sub>H<sub>21</sub>O<sub>5</sub> ([M + H]<sup>+</sup>): 377.1384, found: 363.1391.

## 8. References

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- (2) Tanaka, K.; Sukekawa, M.; Kishimoto, M.; Hoshino, Y.; Honda, K.; Green-light-driven Thioxanthylum-based Organophotoredox Catalysts: Organophotoredox Promoted Radical Cation Diels-Alder Reaction. *Tetrahedron Lett.* **2018**, *59*, 3361-3364
- (3) Neese, F. The ORCA program system. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73-78.
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- (5) Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA quantum chemistry program package. *J. Chem. Phys.* **2020**, *152*, 224108.

## 9. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectrum data

