

Supporting Information

Visible-light-induced [4+2] Cycloaddition of Pentafulvenes

by Organic Photoredox Catalysis

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1. General information

General Information. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100. ¹H 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. ¹³C 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 (CDCl₃: 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 F₂₅₄). 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). **TXT** and *o*-quinone methide **1a** were prepared according to the reported methods.¹

2. Experimental section

• For the synthesis of aromatic fulvenes **2a-2e**

The title compounds were prepared following a modified literature procedure.² Cyclopentadienyl sodium was prepared by reacting NaH (5.0 mmol) with freshly cracked cyclopentadiene (5.0 mmol) in 25 mL of THF at 0 °C, and solution was stirred for 1 h at 0 °C. To this solution, substituted benzophenone (5.0 mmol) was slowly added at 0 °C. The reaction mixture was stirred at room temperature for 1 h and refluxed for another 2 h. The reaction mixture was then quenched with water and extracted with ether. The organic portions were combined and dried over Na₂SO₄. After removal of solvents in vacuo, the residue was subjected to flash column chromatography on silica gel using hexane and ethyl acetate as eluent to give corresponding aromatic fulvene as a red solid.

6,6-Bis(*p*-chlorophenyl)fulvene³ (2a): Red solid. 67% yield.

¹H NMR (500 MHz, CDCl₃): δ 7.39-7.35 (m, 4H), 7.28-7.20 (m, 4H), 6.64-6.60 (m, 2H), 6.25-6.21 (m, 2H).

6,6-Bis(*p*-bromophenyl)fulvene³ (2b): Red solid. 44% yield.

¹H NMR (500 MHz, CDCl₃): δ 7.54-7.50 (m, 4H), 7.18-7.15 (m, 4H), 6.63-6.61 (m, 2H), 6.23-6.21 (m,

2H).

6,6-Bis(*p*-fluorophenyl)fulvene³ (2c): Red solid. 51% yield.

¹H NMR (500 MHz, CDCl₃): δ 7.30-7.26 (m, 4H), 7.08 (t, *J* = 7.5 Hz, 4H), 6.62-6.61 (m, 2H), 6.25-6.23 (m, 2H).

6,6-Diphenylfulvene³ (2d): Red solid. 61% yield.

¹H NMR (500 MHz, CDCl₃): δ 7.41-7.35 (m, 4H), 7.34-7.31 (m, 4H), 6.62-6.60 (m, 2H), 6.31-6.28 (m, 2H).

6,6-Bis(*p*-methylphenyl)fulvene⁴ (2e): Red solid. 41% yield.

¹H NMR (500 MHz, CDCl₃): δ 7.22-7.17 (m, 8H), 6.60-6.58 (m, 2H), 6.31-6.29 (m, 2H), 2.41 (s, 6H).

• **For the synthesis of aromatic fulvenes 2f and 2g**

The title compounds were prepared following a modified literature procedure.⁵ Cyclopentadienyl sodium was prepared by reacting NaH (5.0 mmol) with freshly cracked cyclopentadiene (5.0 mmol) in 25 mL of THF at 0 °C, and solution was stirred for 1h at 0 °C. To this solution, substituted benzophenone (5.0 mmol) was slowly added at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. Then the reaction was quenched by water at 0 °C, organic layer was washed well with water and dried over MgSO₄, filtered and concentrated to produce yellow viscous oil in vacuo. The residue was subjected to flash column chromatography on silica gel using hexane and ethyl acetate as eluent to give corresponding aromatic fulvene as a red solid.

6,6-Bis(*p*-*tert*-butylphenyl)fulvene⁶ (2f): Red solid. 28% yield.

¹H NMR (500 MHz, CDCl₃): δ 7.38 (d, *J* = 8.6 Hz, 4H), 7.27-7.25 (m, 4H), 6.60-6.58 (m, 2H), 6.36-6.33 (m, 2H), 1.36 (s, 18H).

6,6-Bis(*p*-methoxyphenyl)fulvene⁴ (2g): Red solid. 6% yield.

¹H NMR (500 MHz, CDCl₃): δ 7.28-7.27 (m, 4H), 6.91 (d, *J* = 9.2 Hz, 4H), 6.60-6.59 (m, 2H), 6.31-6.30 (m, 2H), 3.87 (s, 6H).

• **For the synthesis of aliphatic fulvenes 2h-2k**

The title compounds were prepared following a modified literature procedure.⁷ To a solution of ketone (2.0 mmol) and freshly cracked cyclopentadiene (5.0 mmol) in methanol (2.0 mL) was added pyrrolidine (3.0 mmol). The reaction mixture was stirred under nitrogen at room temperature until completed by TLC. Acetic acid was added to the bright yellow solution after 25 min. The reaction mixture was diluted with ether and water. The aqueous portion was washed with ether and the combined organics were washed with water and brine, then dried over MgSO₄, and concentrated in vacuo. The crude mixture was purified by flash column chromatography to afford the corresponding aliphatic fulvene as a yellow liquid.

6,6-Dipropylfulvene⁸ (2h): Yellow liquid. 42% yield.

¹H NMR (500 MHz, CDCl₃): δ 6.53-6.45 (m, 4H), 2.54-2.47 (m, 4H), 1.63-1.55 (m, 4H), 0.96 (t, *J* = 7.2

Hz, 6H).

6,6-Tetramethylenefulvene⁷ (2i): Yellow liquid. 54% yield.

¹H NMR (500 MHz, CDCl₃): δ 6.45-6.38 (m, 4H), 2.85-2.79 (m, 4H), 1.84-1.78 (m, 4H).

6,6-Pentamethylenefulvene⁷ (2j): Yellow liquid. 62% yield.

¹H NMR (500 MHz, CDCl₃): δ 6.58-6.50 (m, 4H), 2.67-2.63 (m, 4H), 1.77-1.64 (m, 6H).

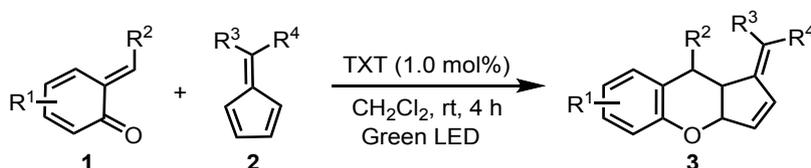
6,6-Hexamethylenefulvene⁸ (2k): Yellow liquid. 60% yield.

¹H NMR (500 MHz, CDCl₃): δ 6.54-6.46 (m, 4H), 2.84-2.80 (m, 4H), 1.78-1.72 (m, 4H), 1.60-1.55 (m, 4H).

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

A solution of 6-(4-methylbenzyl)benzo[*d*][1,3]dioxol-5-ol (0.79 g, 3.3 mmol) in ether (55 mL) was heated under reflux with silver oxide (3.06 g, 13.2 mmol) for 3.5 h and filtered. The solution was concentrated to 10 mL and filtered to give orange crystals (0.32 g, 40% yield). ¹H NMR (500 MHz, CDCl₃): δ 7.90 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.69 (s, 1H), 5.97 (s, 1H), 5.89 (s, 1H), 2.40 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 185.5, 161.5, 146.2, 142.3, 140.0, 132.8, 130.5, 130.0, 129.6, 101.8, 101.7, 99.2, 21.5; IR (ATR): 1620, 1422, 1227, 953, 841, 814, 621 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₁₅H₁₃O₃ ([M + H]⁺): 241.0859, found: 241.0867.

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



o-Quinone methide (1) (0.250 mmol), fulvene (2) (0.125 mmol), TXT (1.0 mol%) and CH₂Cl₂ (2.0 mL) were added into an 8 mL borosilicate vial. The resulting solution was stirred at room temperature under air and green LED irradiation for 4 h. The mixture of stereoisomers of the desired cycloadduct (3) was isolated by column chromatography on silica gel. The diastereomer ratios were determined by ¹H NMR analysis of the product obtained above. The structure and relative stereochemistry of *endo*- and *exo*-3a were unequivocally determined by X-ray diffraction analysis (see 4. X-ray crystallographic data of 3a). The entire sequence of H-atoms and the C-skeleton of 3 was established by ¹H, ¹H COSY, HSQC, and HMBC. According to the characteristic NMR peaks of cycloadduct 3a, the relative stereochemistry of the cycloadducts 3 was assigned for *endo* isomer (around 4.15 ppm for aromatic and 5.38 ppm for aliphatic) and *exo* isomer (around 4.06 ppm for aromatic and 5.56 ppm for aliphatic).

• Examination of the photocycloaddition reactions using the representative organo-photocatalysts

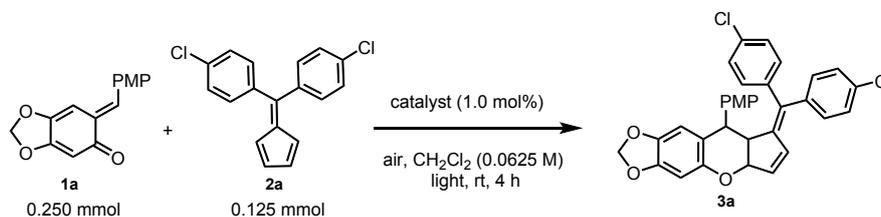
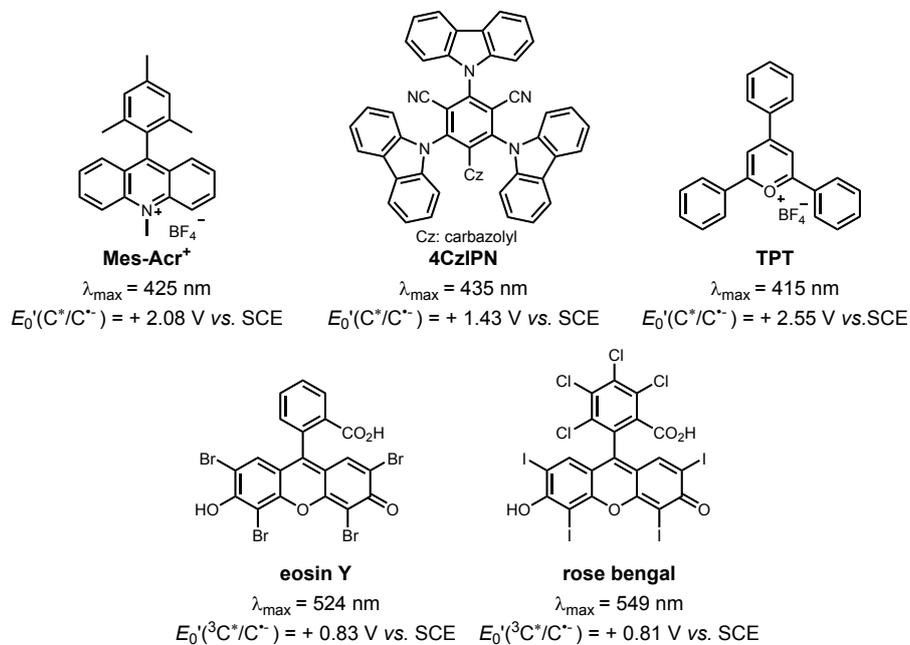


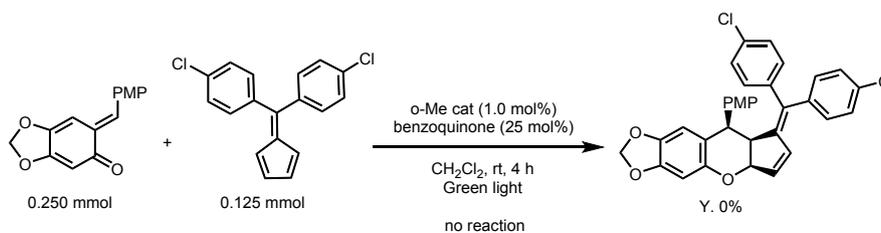
Table S1

entry	catalyst	light	yield (%)	dr ^a
1	Mes-Acr ⁺	blue	4	-
2	4CzIPN	blue	4	-
3 ^b	4CzIPN	blue	10	1.4 : 1
4	TPT	blue	4	-
5	Eosin Y	green	0	-
6	Rose Bengal	green	0	-

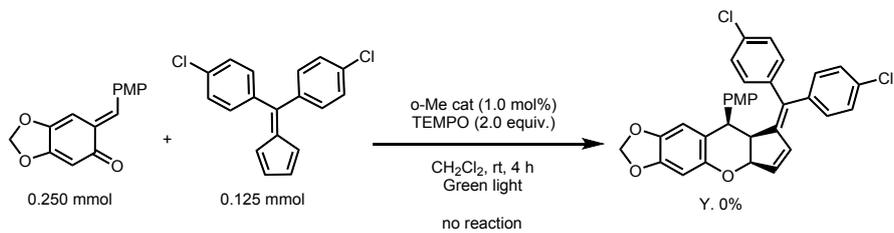
^a ¹H-NMR, ^b Solvent (CH₃NO₂), 24 h.



• The photocycloaddition reactions in the presence of benzoquinone

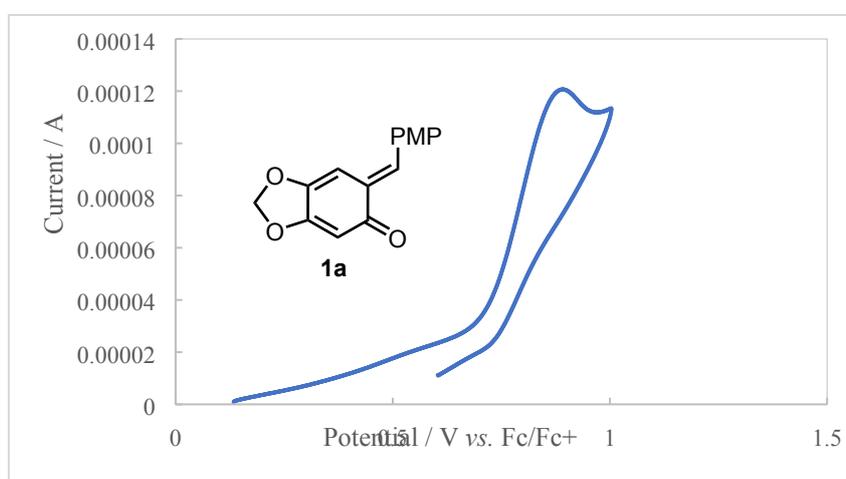


• The photocycloaddition reactions in the presence of TEMPO

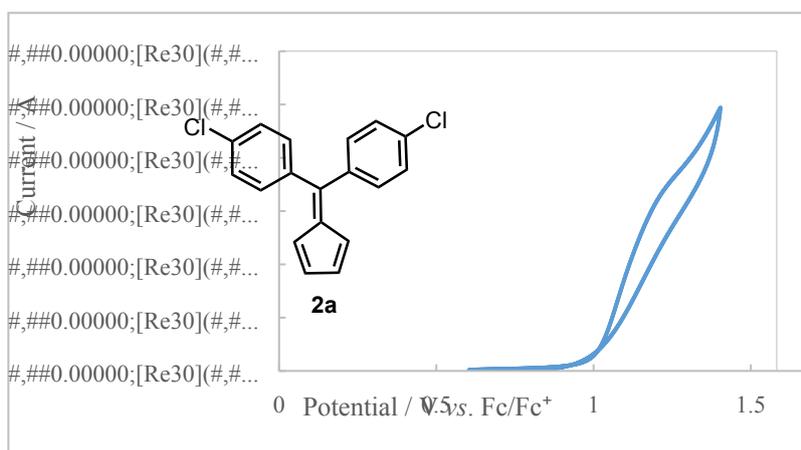


3. Cyclic voltammetry measurement

Samples for electrochemical measurements were prepared with 10 mL of a 0.1 M *tetra-n*-butylammonium tetrafluoroborate solution in dry CH₃CN 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, φ 3mm), a counter electrode (Pt wire), and a reference electrode (Ag wire). The ferrocene/ferrocenium couple (Fc/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 CH₃CN). A scan rate was used 1.0 V/s.



$$E_{p/2} = +0.7915 \text{ V vs. Fc/Fc}^+ \quad (+1.192 \text{ V} \cong +1.19 \text{ V vs. SCE})$$



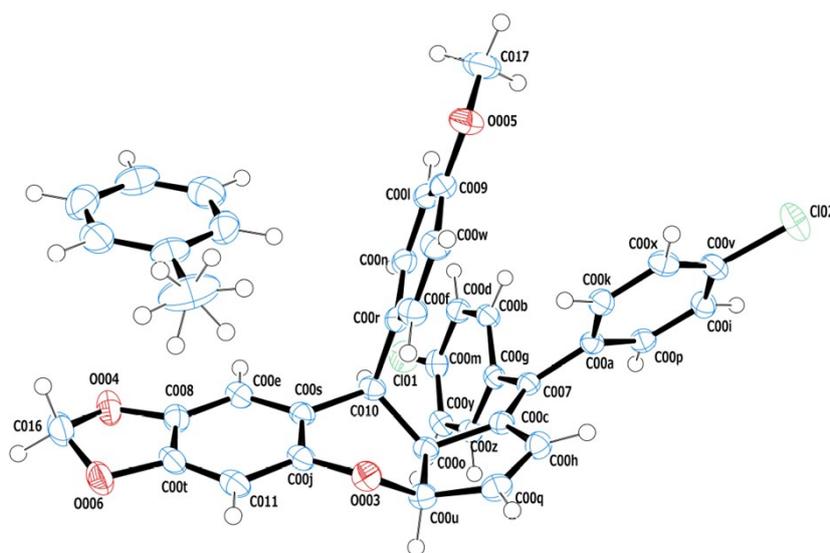
$$E_{p/2} = +1.1065 \text{ V vs. Fc/Fc}^+ \quad (+1.5065 \text{ V} \cong +1.51 \text{ V vs. SCE})$$

4. X-ray crystallographic data of **3a**

Single crystals suitable for Single Crystal X-ray Diffraction (SC-XRD) were obtained by vapor diffusion experiment: *exo-3a* was isolated and purified by column chromatography on silica gel (hexane/ ethyl acetate = 15 / 1) of the mixture of stereoisomers of **3a**. The *endo* rich **3a** was recovered from the residue. Both *endo* rich **3a** (30 mg) and *exo-3a* (30 mg) were all dissolved in the smallest amount of toluene (ca. 1ml) in a glass vial which was then placed in sealed glass container with 3 ml of hexane. White block crystals (*endo-3a* or *exo-3a*) were obtained in 2 days.

The study of the structure of *endo-3a* and *exo-3a* were undertaken to establish its three-dimensional structure. Geometries are tabulated below. All diagrams and calculations were performed using ShelXT and Olex-2 (OlexSys).^{9,10} Single-crystal X-ray diffraction analysis was performed at 123 K using a Rigaku XtaLAB P200 diffractometer with a graphite monochromatic Cu K α radiation source ($\lambda = 1.54187 \text{ \AA}$). Crystallographic data for the structure of *endo-3a* and *exo-3a* have been deposited in the Cambridge Crystallographic Data Centre.

Crystallographic data of *endo-3a*



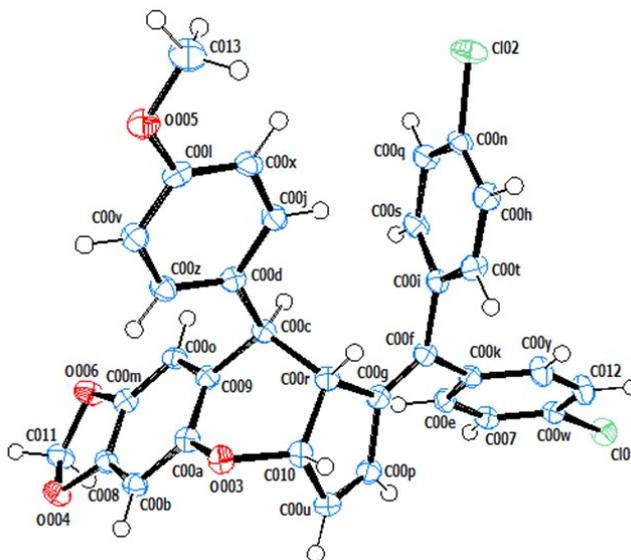
The thermal ellipsoid is 50% probability.

(deposition number: CCDC 1978128)

Empirical formula	C ₃₃ H ₂₄ Cl ₂ O ₄
Formula weight	555.42
Temperature/K	123
Crystal system	orthorhombic

Space group	Fdd2
a/Å	59.6625(8)
b/Å	17.3644(2)
c/Å	11.02420(10)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	11421.1(2)
Z	16
ρ_{calc} /g/cm ³	1.399
μ /mm ⁻¹	2.381
F(000)	5008.0
Crystal size/mm ³	0.2 × 0.2 × 0.2
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/°	9.618 to 146.738
Index ranges	-74 ≤ h ≤ 72, -21 ≤ k ≤ 14, -13 ≤ l ≤ 12
Reflections collected	10848
Independent reflections	4449 [R _{int} = 0.0358, R _{sigma} = 0.0339]
Data/restraints/parameters	4449/1/387
Goodness-of-fit on F ²	1.046
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0310, wR ₂ = 0.0813
Final R indexes [all data]	R ₁ = 0.0316, wR ₂ = 0.0817
Largest diff. peak/hole / e Å ⁻³	0.15/-0.19

Crystallographic data of *exo-3a*



The thermal ellipsoid is 50% probability.

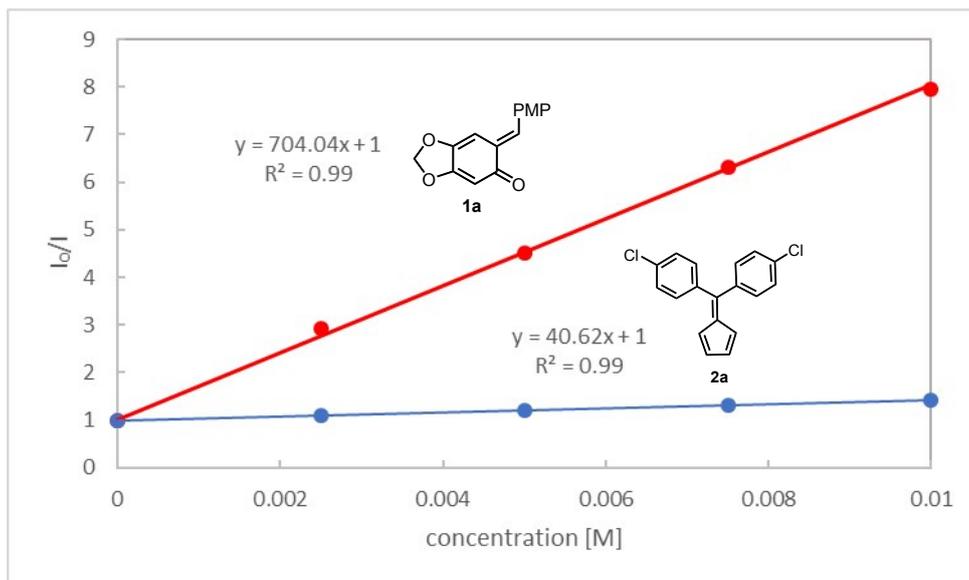
(deposition number: CCDC 1978129)

Table S3 Crystal data and structure refinement for <i>exo-3a</i>	
Empirical formula	C ₃₃ H ₂₄ Cl ₂ O ₄
Formula weight	555.42
Temperature/K	123
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	15.2215(2)
b/Å	9.88820(10)
c/Å	18.3762(2)
α/°	90
β/°	109.9910(10)
γ/°	90
Volume/Å ³	2599.21(5)
Z	4
ρ _{calc} /cm ³	1.419
μ/mm ⁻¹	2.567

F(000)	1152.0
Crystal size/mm ³	0.2 × 0.2 × 0.1
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/ $^{\circ}$	9.994 to 146.284
Index ranges	-17 \leq h \leq 18, -11 \leq k \leq 11, -22 \leq l \leq 22
Reflections collected	17091
Independent reflections	5067 [R_{int} = 0.0342, R_{sigma} = 0.0328]
Data/restraints/parameters	5067/0/353
Goodness-of-fit on F^2	1.060
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0411, wR_2 = 0.1142
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.1186
Largest diff. peak/hole / e \AA^{-3}	0.49/-0.43

5. Stern-Volmer fluorescence quenching

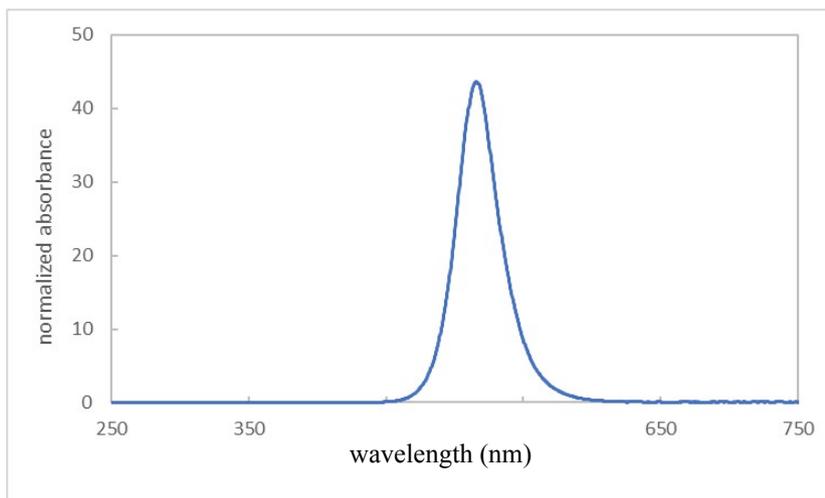
Emission intensities were recorded using a JASCO FP-8500 Fluorescence Spectrometer. All solutions were excited at 468 nm and the emission intensity at each peak top was observed. In a typical experiment, the emission spectrum of a 1×10^{-4} M solution of **TXT** in CH_3CN was collected. Then, appropriate 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. Quantum yield measurement

• Determination of light intensity

First, we measured the green LED source spectrum for detecting a maximum wavelength of emission of 515 nm.



The photon flux of the spectrophotometer was measured by ferrioxalate actinometry.¹¹ The preparation of 0.15 M solution of potassium ferrioxalate and buffered solution of phenanthroline were same as literature procedures.¹² The fraction of light absorbed (f) by ferrioxalate solution was calculated using eq 1, where A is the measured absorbance at 515 nm ($A = 0.037634$). Mol Fe^{2+} was calculated using eq 2, and the photon flux can be calculated using eq 3. Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline. ΔA is the difference in absorbance at 509 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ϵ is the molar absorptivity at 509 nm ($11100 \text{ L mol}^{-1} \text{ cm}^{-1}$).¹¹

The solution was irradiated with an emission slit width at 10.0 nm. Φ is the quantum yield for the ferrioxalate actinometer, which found close to 515 nm is 0.86 at $\lambda = 509 \text{ nm}$ for 0.15 M solution.¹² t is irradiation time (180 s). The photo flux was calculated (average of two experiments) to be $1.27 \times 10^{-8} \text{ einstein s}^{-1}$.

$$f = 1 - 10^{-A} \quad (1)$$

$$\text{mol } Fe^{2+} = \frac{V \times \Delta A}{l \times \epsilon} \quad (2)$$

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f} \quad (3)$$

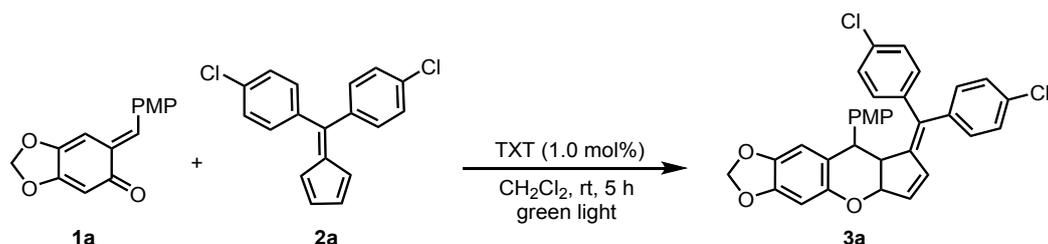
Sample calculation:

$$f = 1 - 10^{-0.037634} = 0.08301$$

$$\text{mol Fe}^{2+} = \frac{0.00235 \text{ L} \times 0.7684468}{1.000 \text{ cm} \times 11100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 1.63 \times 10^{-7} \text{ mol}$$

$$\text{photon flux} = \frac{1.63 \times 10^{-7} \text{ mol}}{0.86 \times 180 \text{ s} \times 0.08301} = 1.27 \times 10^{-8} \text{ einstein s}^{-1}$$

• **Quantum yield of reaction between *o*-quinone methide and fulvene**



A cuvette was charged with *o*-quinone methide **1a** (0.250 mmol, 2.0 equiv), 6,6-bis(*p*-chlorophenyl)fulvene **2a** (0.125 mmol, 1.0 equiv), **TXT** (0.00125 mmol, 1.0 mol%), and 2.0 mL CH₂Cl₂ (0.0625 M). The sample was stirred and irradiated ($\lambda = 515 \text{ nm}$, slit width = 10.0 nm) for 18000 s (5 h). After irradiation, the solution was passed through a column of silica gel. The quantum yield was determined using eq 4. All incident light is absorbed by **TXT** under the reaction conditions (absorbance > 3 in CH₂Cl₂, $f \approx 1$).

$$\text{Quantum yield} = \frac{\text{numbers of moles product}}{\text{flux} \times t \times f} \quad (4)$$

Sample calculation 1: 19.6 mg (28%) of product was formed.

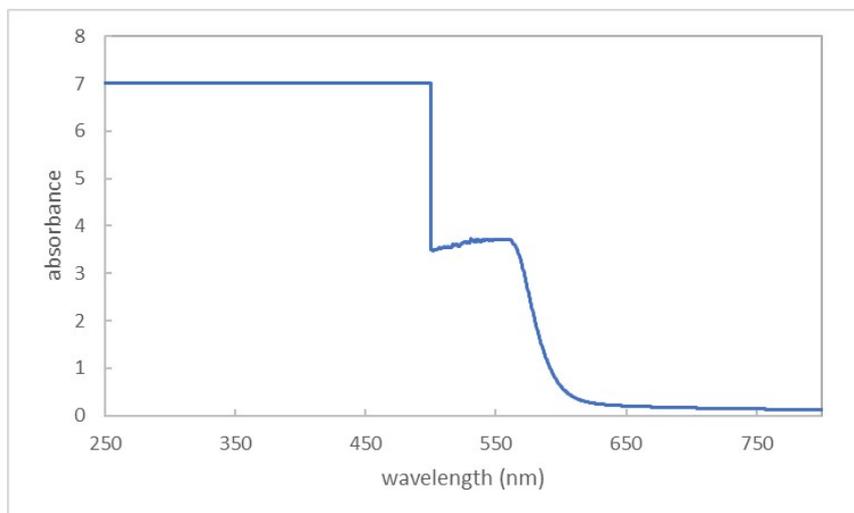
$$\text{Quantum yield} = \frac{3.53 \times 10^{-5} \text{ mol}}{1.27 \times 10^{-8} \text{ einstein s}^{-1} \times 18000 \text{ s} \times 1} = 0.15$$

Sample calculation 2: 20.9 mg (30%) of product was formed.

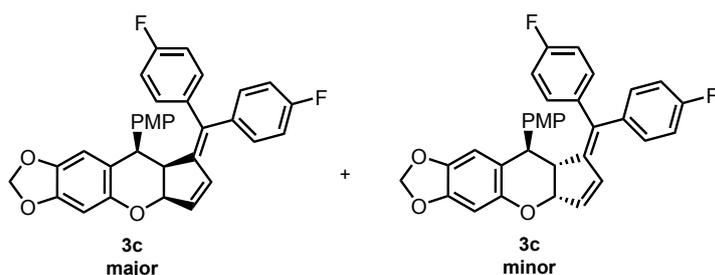
$$\text{Quantum yield} = 0.16$$

• **Absorbance of the TXT**

Absorbance of TXT was measured at solution of *o*-quinone methide **1a** (0.375 mmol, 3.0 equiv), 6,6-bis(*p*-chlorophenyl)fulvene **2a** (0.125 mmol, 1.0 equiv), **TXT** (0.001 mmol, 1.0 mol%), and 2.0 mL CH₂Cl₂ (0.0625 M).



o-Quinone methide **1a** (66.1 mg, 0.258 mmol), 6,6-bis(*p*-bromophenyl)fulvene (48.4 mg, 0.125 mmol), **TXT** (0.73 mg, 0.00131 mmol), and CH₂Cl₂ (2.0 mL) were used. Brown solid (76.4 mg, 95% yield, dr 1.4 : 1). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.53-7.48 (m, 2H) (mixture), 7.31 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.98-6.95 (m, 2H), 6.68-6.64 (m, 2H) (mixture), 6.55-6.52 (m, 3H), 6.41-6.38 (m, 1H) (mixture), 6.29-6.26 (m, 2H) (mixture), 5.84 (s, 1H), 5.79 (s, 1H), 5.37 (d, *J* = 8.0 Hz, 1H), 4.12 (t, *J* = 7.7 Hz, 1H), 3.74 (s, 3H), 3.55 (d, *J* = 7.5, 1H); (minor): δ 7.53-7.48 (m, 2H) (mixture), 7.38 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.85-6.81 (m, 2H), 6.68-6.64 (m, 4H) (mixture), 6.50 (s, 1H), 6.40-6.38 (m, 1H) (mixture), 6.29-6.26 (m, 1H) (mixture), 6.08 (dd, *J* = 5.4, 2.6 Hz, 1H), 5.91 (s, 1H), 5.85 (s, 1H), 5.45 (dd, *J* = 8.5, 2.3 Hz, 1H), 4.07-4.02 (m, 1H), 3.74 (s, 3H), 3.62 (m, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) (mixture): δ 158.2, 158.0, 149.1, 147.9, 146.8, 146.7, 146.5, 144.9, 142.4, 142.3, 141.0, 140.9, 140.5, 140.5, 137.3, 137.2, 137.1, 137.0, 135.0, 133.8, 132.8, 132.7, 131.9, 131.7, 131.6, 131.5, 131.4, 131.3, 131.2, 129.9, 128.4, 123.8, 121.7, 121.5, 121.4, 121.3, 121.2, 113.6, 112.8, 108.1, 108.0, 101.1, 100.9, 100.9, 100.2, 83.8, 82.5, 55.2, 55.1, 47.7, 44.3, 44.2, 43.9; IR (ATR) (mixture): 1475, 1248, 1145, 1009, 823, 725 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₃₃H₂₅O₄⁷⁹Br₂([M + H]⁺): 643.0114, found: 643.0020.

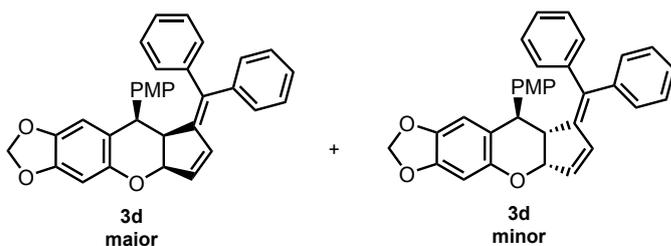


(*5aR**,*8aS**,*9R**)- and

(*5aS**,*8aR**,*9R**)-8-(Bis(4-fluorophenyl)methylene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (**3c**):

o-Quinone methide **1a** (67.1 mg, 0.262 mmol), 6,6-bis(*p*-fluorophenyl)fulvene (34.0 mg, 0.128 mmol), **TXT** (0.71 mg, 0.00128 mmol), and CH₂Cl₂ (2.0 mL) were used. Orange solid (56.2 mg, 84% yield, dr 1.4 : 1). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.17-7.14 (m, 2H), 7.13-7.04 (m, 2H) (mixture), 6.98 (d, *J* = 8.6 Hz, 2H), 6.93-6.86 (m, 2H) (mixture), 6.69-6.63 (m, 4H) (mixture), 6.54 (s, 1H), 6.40-6.36 (m, 1H) (mixture), 6.29-6.27 (m, 1H), 6.27-6.24 (m, 1H), 5.83 (s, 1H), 5.78 (s, 1H), 5.39-5.36 (m, 1H), 4.12 (t, *J* = 8.0 Hz, 1H), 3.74 (s, 3H), 3.52 (d, *J* = 8.0 Hz, 1H); (minor): δ 7.23-7.21 (m, 2H), 7.13-7.04 (m, 2H) (mixture), 6.94 (d, *J* = 4.0 Hz, 2H), 6.93-6.86 (m, 2H) (mixture), 6.69-6.63 (m, 4H) (mixture), 6.50 (s, 1H), 6.40-6.36 (m, 1H) (mixture), 6.30 (s, 1H), 6.03 (d, *J* = 5.7, 2.7 Hz, 1H), 5.91 (s, 1H), 5.86 (s, 1H), 5.46-5.44 (m, 1H), 4.07 (dd, *J* = 7.5, 2.3 Hz, 1H), 3.72 (s, 3H), 3.65 (d, *J* = 2.3 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) (mixture): δ 162.0 (d, *J* = 249.5 Hz, 1C), 161.9 (d, *J* = 252.0 Hz, 1C), 161.9 (d, *J* = 250.0 Hz, 1C), 161.9 (d, *J* = 243.2 Hz, 1C), 149.2, 148.0, 146.8, 146.7, 145.9, 144.1, 142.4, 138.3 (d, *J* = 3.8 Hz, 1C), 138.2 (d, *J* = 3.8 Hz, 1C), 137.9 (d, *J* = 3.8 Hz, 1C), 137.4 (d, *J* = 3.8 Hz, 1C), 136.5, 136.3, 135.3,

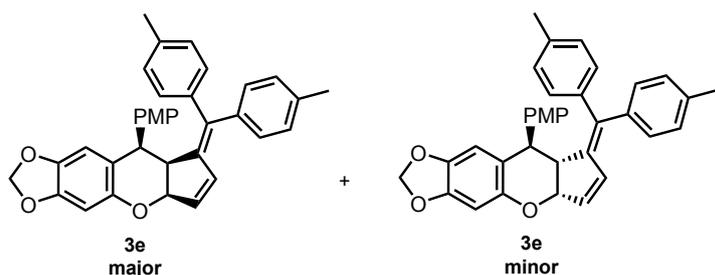
135.3, 134.0, 133.7 (d, $J = 7.6$ Hz, 1C), 131.5 (d, $J = 5.6$ Hz, 1C), 131.4 (d, $J = 10.1$ Hz, 1C), 131.3 (d, $J = 7.6$ Hz, 1C), 129.9, 128.4, 124.0, 121.9, 115.7 (d, $J = 21.4$ Hz, 1C), 115.5 (d, $J = 21.4$ Hz, 1C), 115.0 (d, $J = 21.4$ Hz, 1C), 114.9 (d, $J = 21.4$ Hz, 1C), 113.6, 112.8, 108.1, 107.9, 101.3, 100.9, 100.9, 100.3, 84.0, 82.7, 55.2, 55.2, 47.7, 44.3, 44.0, 43.9; IR (ATR) (mixture): 2356, 1504, 1248, 1142, 1037, 833, 555 cm^{-1} ; HRMS (ESI+) m/z calcd for $\text{C}_{33}\text{H}_{25}\text{O}_4\text{F}_2$ ($[\text{M} + \text{H}]^+$): 523.1715, found: 523.1690.



(5a*R,8a*S**,9*R**)**- and

(5a*S,8a*R**,9*R**)**-8-(Diphenylmethylene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (**3d**):

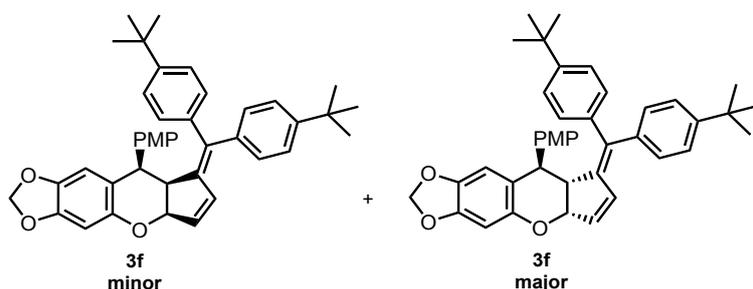
o-Quinone methide **1a** (66.2 mg, 0.258 mmol), 6,6-diphenylfulvene (28.7 mg, 0.125 mmol), **TXT** (0.72 mg, 0.00129 mmol), and CH_2Cl_2 (2.0 mL) were used. Brown solid (53.8 mg, 89% yield, dr 1.6 : 1). ^1H NMR (500 MHz, CDCl_3) (major): δ 7.44-7.17 (m, 8H) (mixture), 7.02-6.97 (m, 2H) (mixture), 6.75-6.72 (m, 2H), 6.69-6.60 (m, 2H) (mixture), 6.54 (s, 1H), 6.35-6.31 (m, 2H) (mixture), 6.21 (dd, $J = 5.7, 2.3$ Hz, 1H), 5.83 (s, 1H), 5.78 (s, 1H), 5.42-5.37 (m, 1H), 4.17 (t, $J = 8.0$ Hz, 1H), 3.75 (s, 3H), 3.52 (d, $J = 8.0$ Hz, 1H); (minor): 7.44-7.17 (m, 8H) (mixture), 7.02-6.97 (m, 2H) (mixture), 6.69-6.60 (m, 4H) (mixture), 6.50 (s, 1H), 6.45 (d, $J = 5.6$, 1H), 6.35-6.31 (m, 1H) (mixture), 5.99 (dd, $J = 5.7, 2.3$ Hz, 1H), 5.91 (s, 1H), 5.85 (s, 1H), 5.45 (dd, $J = 5.7, 2.3$ Hz, 1H), 4.10 (dd, $J = 8.0, 1.7$ Hz, 1H), 3.71 (s, 3H), 3.69 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) (mixture): δ 158.1, 157.8, 149.3, 148.0, 146.8, 146.7, 145.5, 143.6, 142.6, 142.4, 142.3, 142.3, 142.2, 142.1, 137.9, 137.6, 136.1, 135.7, 135.7, 135.3, 134.0, 130.1, 130.0, 129.8, 129.7, 128.8, 128.4, 128.2, 128.0, 127.9, 127.9, 127.4, 127.2, 127.0, 126.8, 124.2, 122.1, 114.0, 113.5, 112.7, 108.3, 107.9, 101.3, 100.9, 100.9, 100.3, 84.1, 82.9, 55.4, 55.2, 55.2, 48.0, 44.4, 43.9; IR (ATR) (mixture): 2897, 2344, 1475, 1248, 1145, 1037, 700 cm^{-1} ; HRMS (ESI+) m/z calcd for $\text{C}_{33}\text{H}_{27}\text{O}_4$ ($[\text{M} + \text{H}]^+$): 487.1904, found: 487.1881.



(5a*R**,8a*S**,9*R**)- and

(5a*S,8a*R**,9*R**)-8-(Di-*p*-tolylmethylene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3e):**

o-Quinone methide **1a** (67.2 mg, 0.262 mmol), 6,6-bis(*p*-methylphenyl)fulvene (34.0 mg, 0.132 mmol), **TXT** (0.78 mg, 0.00140 mmol), and CH₂Cl₂ (2.0 mL) were used. Yellow solid (55.7 mg, 82% yield, dr 1.2 : 1). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.18-7.14 (m, 2H) (mixture), 7.12-7.10 (m, 2H), 7.05-6.97 (m, 4H) (mixture), 6.67-6.62 (m, 2H) (mixture), 6.60 (d, *J* = 8.0 Hz, 2H), 6.55 (s, 1H), 6.37 (s, 1H), 6.32-6.30 (m, 1H) (mixture), 6.17 (d, *J* = 5.4 Hz, 1H), 5.82 (s, 1H), 5.78 (s, 1H), 5.41-5.38 (m, 1H), 4.15 (t, *J* = 7.7 Hz, 1H), 3.75 (s, 3H), 3.55 (d, *J* = 8.0 Hz, 1H), 2.40 (s, 3H) (mixture), 2.28 (s, 3H); (minor): δ 7.23-7.20 (m, 2H), 7.18-7.14 (m, 2H) (mixture), 7.05-6.97 (m, 2H) (mixture), 6.88-6.85 (m, 2H), 6.67-6.62 (m, 4H) (mixture), 6.50 (s, 1H), 6.45 (d, *J* = 5.7 Hz, 1H), 6.32-6.30 (m, 1H) (mixture), 5.95 (dd, *J* = 7.7, 2.0 Hz, 1H), 5.90 (s, 1H), 5.85 (s, 1H), 5.43-5.41 (m, 1H), 4.11-4.08 (m, 1H), 3.72 (s, 4H), 2.40 (s, 3H) (mixture), 2.31 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) (mixture): δ 158.0, 157.8, 149.3, 148.1, 146.7, 146.6, 144.7, 142.9, 142.3, 142.2, 139.9, 139.7, 139.4, 139.4, 138.2, 137.7, 137.1, 136.8, 136.6, 136.4, 135.9, 135.2, 135.0, 134.0, 130.2, 130.0, 129.9, 129.7, 129.6, 129.4, 128.9, 128.6, 128.5, 128.5, 124.3, 122.2, 113.4, 112.7, 108.4, 108.0, 101.3, 100.9, 100.8, 100.2, 84.2, 83.0, 55.2, 55.2, 48.0, 44.4, 43.7, 43.7, 21.3, 21.3, 21.1, 21.1; IR (ATR) (mixture): 2911, 1508, 1145, 1035, 822, 728, 555 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₃₅H₃₁O₄ ([*M* + *H*]⁺): 515.2217, found: 515.2172.

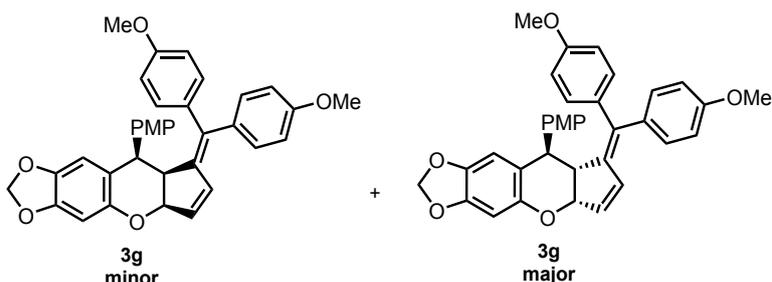


(5a*R**,8a*S**,9*R**)- and

(5a*S,8a*R**,9*R**)-8-(Bis(4-(*tert*-butyl)phenyl)methylene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3f):**

o-Quinone methide **1a** (66.2 mg, 0.258 mmol), 6,6-bis(*p-tert*-butylphenyl)fulvene (43.2 mg, 0.126 mmol), **TXT** (0.71 mg, 0.00128 mmol), and CH₂Cl₂ (2.0 mL) were used. Yellow solid (58.9 mg, 78% yield, dr 1 :

1.1). ^1H NMR (500 MHz, CDCl_3) (major): δ 7.45 (d, $J = 8.0$ Hz, 2H), 7.20-7.14 (m, 4H), 6.95 (d, $J = 8.0$ Hz, 2H), 6.70-6.66 (m, 2H) (mixture), 6.60 (d, $J = 8.6$ Hz, 2H), 6.52-6.50 (m, 2H) (mixture), 6.35 (s, 1H), 5.95 (dd, $J = 5.7, 2.3$ Hz 1H), 5.90 (s, 1H), 5.85 (s, 1H), 5.47 (dd, $J = 8.0, 1.2$ Hz, 1H), 4.14-4.11 (m, 1H), 3.70 (s, 3H) (mixture), 3.49 (d, $J = 8.6$ Hz, 1H), 1.28 (s, 9H), 1.27 (s, 9H); (minor): δ 7.36 (d, $J = 8.6$ Hz, 2H), 7.25-7.22 (m, 4H), 7.00 (d, $J = 8.6$ Hz, 2H), 6.70-6.66 (m, 2H) (mixture), 6.54 (s, 1H), 6.52-6.50 (m, 2H) (mixture), 6.34 (d, $J = 1.2$ Hz, 1H), 6.32 (s, 1H), 6.16 (d, $J = 5.8$ Hz, 1H), 5.83 (s, 1H), 5.79 (s, 1H), 5.39 (d, $J = 8.0$ Hz, 1H), 4.02 (d, $J = 8.0$ Hz, 1H), 3.76 (s, 3H), 3.70 (m, 1H) (mixture), 1.39 (s, 9H), 1.37 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) (mixture) δ 158.0, 157.7, 150.3, 150.0, 149.8, 149.5, 149.4, 148.0, 146.7, 146.6, 145.3, 142.9, 142.3, 142.2, 139.5, 139.5, 139.4, 139.2, 138.1, 137.8, 136.3, 135.3, 135.2, 135.2, 133.9, 130.2, 129.7, 129.5, 129.4, 129.4, 129.0, 128.5, 128.2, 128.0, 125.6, 125.0, 124.7, 124.7, 124.3, 122.3, 113.4, 112.7, 108.4, 107.9, 101.3, 100.9, 100.8, 100.2, 84.3, 83.0, 55.2, 55.1, 48.2, 44.6, 44.5, 43.8, 34.7, 34.6, 34.5, 34.4, 31.4, 31.4, 31.3, 31.3; IR (ATR) (mixture) : 2952, 1508, 1475, 1248, 1143, 1036, 831, 730 cm^{-1} ; HRMS (ESI+) m/z calcd for $\text{C}_{41}\text{H}_{43}\text{O}_4$ ($[\text{M} + \text{H}]^+$): 599.3156, found: 599.3121.

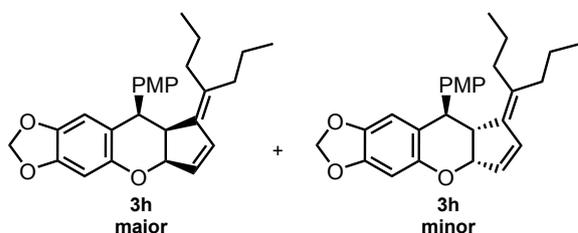


(5a*R**,8a*S**,9*R**)- and

(5a*S**,8a*R**,9*R**)-8-(Bis(4-methoxyphenyl)methylene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3g):

o-Quinone methide **1a** (64.5 mg, 0.252 mmol), 6,6-bis(*p*-methoxyphenyl)fulvene (36.1 mg, 0.124 mmol), **TXT** (0.71 mg, 0.00128 mmol), and CH_2Cl_2 (2.0 mL) were used. Brown solid (39.3 mg, 58% yield, dr 1 : 1.7). ^1H NMR (500 MHz, CDCl_3) (major): δ 7.20 (d, $J = 8.6$ Hz, 2H), 6.94 (d, $J = 8.6$ Hz, 2H), 6.90-6.86 (m, 2H) (mixture), 6.77 (d, $J = 8.6$ Hz, 2H), 6.73-6.64 (m, 4H) (mixture), 6.50 (s, 1H), 6.43 (d, $J = 5.7$ Hz, 1H), 6.31 (s, 1H), 5.95 (dd, $J = 5.4, 2.6$ Hz, 1H), 5.91 (s, 1H), 5.85 (s, 1H), 5.43 (dd, $J = 7.5, 2.3$ Hz, 1H), 4.11 (d, $J = 7.5$ Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.72 (s, 4H); (minor): δ 7.14 (d, $J = 8.6$ Hz, 2H), 7.01-6.99 (m, 2H), 6.90-6.86 (m, 2H) (mixture), 6.73-6.64 (m, 4H) (mixture), 6.62 (d, $J = 8.6$ Hz, 2H), 6.55 (s, 1H), 6.38 (s, 1H), 6.32 (d, $J = 5.7$ Hz, 1H), 6.17 (d, $J = 5.8$ Hz, 1H), 5.83 (s, 1H), 5.78 (s, 1H), 5.40-5.36 (m, 1H), 4.15 (t, $J = 7.7$ Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.56 (d, $J = 8.0$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) (mixture): δ 158.9, 158.6, 158.5, 158.0, 157.8, 148.1, 146.7, 144.1, 142.4, 142.2, 138.3, 137.9, 135.8, 135.4, 135.2, 135.0, 134.9, 134.8, 134.6, 134.5, 134.4, 134.2, 132.0, 131.3, 131.1, 131.0, 130.9, 130.1, 128.5, 122.2, 114.3, 114.1, 113.5, 113.5, 113.3, 113.2, 112.7, 108.4, 108.0, 101.3, 100.9,

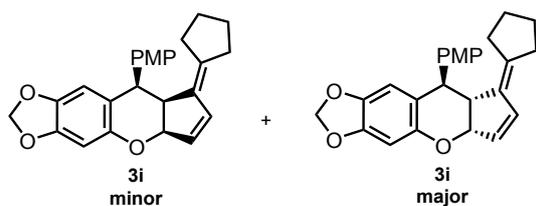
100.8, 100.3, 84.3, 83.0, 55.4, 55.2, 55.2, 55.2, 48.0, 44.3, 43.8, 43.6; IR (ATR) (mixture): 2903, 1506, 1476, 1243, 1144, 1032, 831 cm^{-1} ; HRMS (ESI+) m/z calcd for $\text{C}_{35}\text{H}_{31}\text{O}_6$ ($[\text{M} + \text{H}]^+$): 547.2115, found: 547.2092.



(5*aR**,8*aS**,9*R**)- and

(5*aS,8*aR**,9*R**)-8-(Heptan-4-ylidene)-9-(4-methoxyphenyl)-5*a*,8,8*a*,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3*h*):**

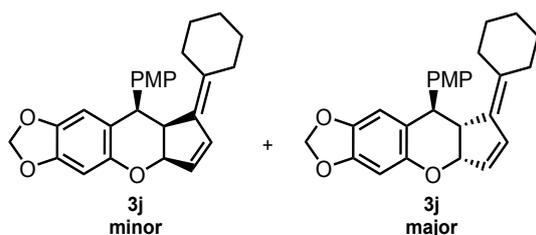
o-Quinone methide **1a** (64.6 mg, 0.252 mmol), 6,6-dipropylfulvene (19.6 mg, 0.121 mmol), **TXT** (0.71 mg, 0.00128 mmol), and CH_2Cl_2 (2.0 mL) were used. Yellow solid (31.2 mg, 61% yield, dr 1.3 : 1). ^1H NMR (500 MHz, CDCl_3) (major): δ 7.02 (d, $J = 7.9$ Hz, 2H), 6.63-6.61 (m, 2H), 6.58 (s, 2H), 6.21 (d, $J = 5.9$ Hz, 1H), 5.91 (dd, $J = 6.0, 2.0$ Hz, 1H), 5.88 (d, $J = 1.2$ Hz, 1H), 5.86-5.84 (m, 1H) (mixture), 5.36 (d, $J = 1.0$ Hz, 1H), 4.14-4.11 (m, 1H), 3.71 (s, 3H), 3.53 (t, $J = 7.5$ Hz, 1H), 2.30-2.27 (m, 1H), 2.15-2.00 (m, 2H) (mixture), 1.94-1.88 (m, 1H), 1.55-1.28 (m, 3H) (mixture), 1.17-1.10 (m, 1H), 0.94 (td, $J = 9.2, 7.5$ Hz, 3H) (mixture), 0.74 (t, $J = 7.2$ Hz, 3H); (minor): 7.26-7.23 (m, 2H), 6.84-6.81 (m, 2H), 6.52 (dd, $J = 5.7, 1.2$ Hz, 1H), 6.46 (s, 1H), 6.44 (s, 1H), 5.86-5.84 (m, 1H) (mixture), 5.82 (d, $J = 1.7$ Hz, 1H), 5.78-5.75 (m, 1H), 5.54 (d, $J = 8.0$ Hz, 1H), 3.82 (d, $J = 2.9$ Hz, 1H), 3.77 (s, 3H), 3.69 (dd, $J = 7.0, 2.0$ Hz, 1H), 2.15-2.00 (m, 4H) (mixture), 1.55-1.28 (m, 4H) (mixture), 0.94 (td, $J = 9.2, 7.5$ Hz, 3H) (mixture), 0.85 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) (mixture): δ 158.0, 157.9, 149.6, 147.7, 146.8, 146.7, 142.2, 142.1, 142.0, 138.8, 137.5, 135.5, 134.4, 133.6, 133.4, 133.3, 132.9, 132.9, 130.3, 128.5, 123.5, 122.9, 113.9, 112.6, 108.2, 108.0, 101.0, 100.9, 100.8, 100.1, 84.5, 83.3, 55.2, 55.1, 47.8, 47.2, 46.3, 45.0, 35.1, 34.7, 33.8, 33.5, 22.2, 22.1, 21.5, 21.3, 14.4, 14.4, 14.2, 14.0; IR (ATR) (mixture): 2956, 1476, 1248, 1146, 1036, 939, 730 cm^{-1} ; HRMS (ESI+) m/z calcd for $\text{C}_{27}\text{H}_{31}\text{O}_4$ ($[\text{M} + \text{H}]^+$): 419.2217, found: 419.2193.



(5*aR**,8*aS**,9*R**)- and

(5*aS,8*aR**,9*R**)-8-Cyclopentylidene-9-(4-methoxyphenyl)-5*a*,8,8*a*,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3i):**

o-Quinone methide **1a** (63.3 mg, 0.225 mmol), 6,6-tetramethylenefulvene (17.5 mg, 0.132 mmol), **TXT** (0.64 mg, 0.00115 mmol), and CH₂Cl₂ (2.0 mL) were used. Yellow solid (31.1 mg, 61% yield, dr 1 : 6). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.21 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 2H), 6.47 (s, 1H), 6.46 (s, 1H), 6.37 (d, *J* = 5.2 Hz, 1H), 5.84 (dd, *J* = 7.2, 1.4 Hz, 2H), 5.78 (d, *J* = 4.6 Hz, 1H), 5.50 (d, *J* = 7.5 Hz, 1H), 3.99 (d, *J* = 2.3 Hz, 1H), 3.77 (s, 3H), 3.52 (d, *J* = 8.0 Hz, 1H), 2.39-2.23 (m, 4H) (mixture), 1.81-1.56 (m, 4H) (mixture); (minor): δ 7.05 (d, *J* = 8.6 Hz, 2H), 6.65-6.62 (m, 2H), 6.57 (d, *J* = 1.7 Hz, 2H), 6.15-6.12 (m, 1H), 5.89-5.87 (m, 2H), 5.86 (d, *J* = 1.7 Hz, 1H), 5.37 (d, *J* = 7.5 Hz, 1H), 4.13 (d, *J* = 6.9 Hz, 1H), 3.72 (s, 3H), 3.44 (t, *J* = 7.7 Hz, 1H), 2.39-2.23 (m, 4H) (mixture), 1.81-1.56 (m, 4H) (mixture); ¹³C{¹H} NMR (126 MHz, CDCl₃) (mixture): δ 158.0, 157.8, 149.6, 148.1, 146.7, 142.1, 141.5, 137.2, 136.9, 136.5, 136.2, 135.8, 133.2, 132.2, 132.1, 130.0, 128.7, 128.0, 122.4, 114.0, 113.9, 112.6, 110.7, 108.3, 107.9, 101.1, 100.9, 100.8, 100.2, 93.0, 85.0, 83.6, 55.4, 55.2, 49.4, 47.6, 44.7, 43.8, 31.3, 31.3, 31.2, 30.8, 26.9, 26.6, 26.3, 26.1; IR (ATR) (mixture): 2930, 1475, 1247, 1144, 1034, 827, 728 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₅H₂₅O₄ ([*M* + *H*]⁺): 389.1747, found: 389.1742.

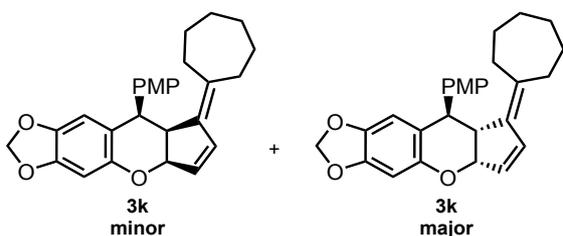


(5*aR**,8*aS**,9*R**)- and

(5*aS,8*aR**,9*R**)-8-Cyclohexylidene-9-(4-methoxyphenyl)-5*a*,8,8*a*,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3j):**

o-Quinone methide **1a** (64.7 mg, 0.252 mmol), 6,6-pentamethylenefulvene (17.9 mg, 0.122 mmol), **TXT** (0.72 mg, 0.00129 mmol), and CH₂Cl₂ (2.0 mL) were used. Yellow solid (17.2 mg, 35% yield, dr 1 : 1.5). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.26-7.23 (m, 2H), 6.83-6.80 (m, 2H), 6.56 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.48 (s, 1H), 6.44 (s, 1H), 5.85-5.84 (m, 1H) (mixture), 5.82 (d, *J* = 1.2 Hz, 1H), 5.76 (dd, *J* = 5.7, 2.3 Hz, 1H), 5.58 (d, *J* = 8.0 Hz, 1H), 3.78 (d, *J* = 1.7 Hz, 1H), 3.77 (s, 3H), 3.70-3.68 (m, 1H), 2.26-2.12 (m, 4H) (mixture), 1.71-1.42 (m, 6H) (mixture); (minor): δ 7.05-7.01 (m, 2H), 6.65-6.61 (m, 2H), 6.57 (s, 1H),

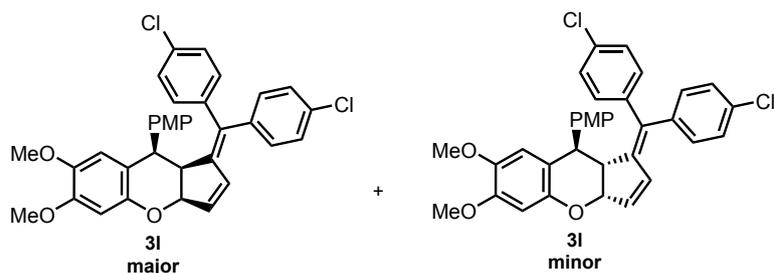
6.55 (s, 1H), 6.24 (d, $J = 5.8$ Hz, 1H), 5.89 (d, $J = 1.7$ Hz, 1H), 5.88 (d, $J = 1.7$ Hz, 1H), 5.85-5.84 (m, 1H) (mixture), 5.38 (d, $J = 7.5$ Hz, 1H), 4.05 (d, $J = 7.5$ Hz, 1H), 3.72 (s, 3H), 3.55 (t, $J = 7.7$ Hz, 1H), 2.40-2.34 (m, 1H), 2.26-2.12 (m, 2H) (mixture), 2.02-1.98 (m, 1H), 1.71-1.42 (m, 6H) (mixture); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) (mixture): δ 158.1, 157.8, 149.7, 147.6, 142.2, 138.6, 137.6, 135.6, 134.9, 133.8, 133.1, 132.9, 132.7, 132.7, 130.4, 128.5, 123.6, 123.0, 114.0, 113.9, 112.5, 110.7, 108.3, 107.9, 101.1, 101.1, 100.9, 100.8, 100.1, 84.5, 83.3, 55.2, 55.0, 47.5, 47.2, 46.2, 45.3, 32.1, 32.0, 31.6, 31.2, 28.1, 28.0, 27.6, 27.5, 26.6, 26.6; IR (ATR) (mixture): 2927, 1476, 1250, 1148, 1035, 837 cm^{-1} ; HRMS (ESI+) m/z calcd for $\text{C}_{26}\text{H}_{27}\text{O}_4$ ($[\text{M} + \text{H}]^+$): 403.1904, found: 403.1882.



(5*aR**,8*aS**,9*R**)- and

(5*aS**,8*aR**,9*R**)-8-Cycloheptylidene-9-(4-methoxyphenyl)-5*a*,8*a*,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3*k*):

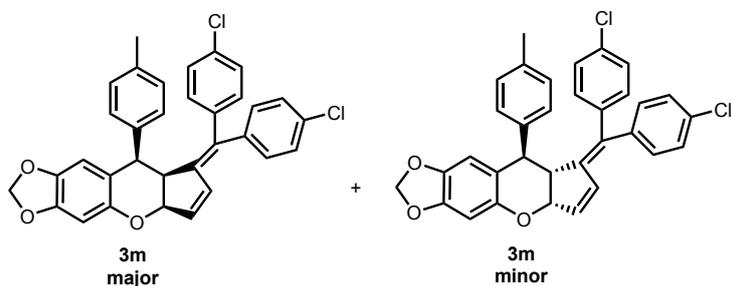
o-Quinone methide **1a** (64.9 mg, 0.253 mmol), 6,6-hexamethylenefulvene (21.0 mg, 0.131 mmol), **TXT** (0.81 mg, 0.00146 mmol), and CH_2Cl_2 (2.0 mL) were used. Yellow solid (34.9 mg, 64% yield, dr 1 : 2). ^1H NMR (500 MHz, CDCl_3) (major): δ 7.26-7.24 (m, 2H), 6.82 (m, $J = 7.3$ Hz, 2H), 6.54 (d, $J = 5.5$ Hz, 1H), 6.49 (s, 1H), 6.45 (s, 1H), 5.85-5.84 (m, 1H) (mixture), 5.82 (d, $J = 1.7$ Hz, 1H), 5.77 (dd, $J = 5.7, 2.3$ Hz, 1H), 5.57 (d, $J = 8.0$ Hz, 1H), 3.88 (s, 1H), 3.77 (s, 3H), 3.68 (d, $J = 8.0$ Hz, 1H), 2.50-2.21 (m, 4H) (mixture), 1.76-1.41 (m, 8H) (mixture); (minor): δ 7.03 (d, $J = 7.8$ Hz, 2H), 6.64-6.62 (m, 2H), 6.58 (s, 1H), 6.57 (s, 1H), 6.24 (d, $J = 5.7, 1.7$ Hz, 1H), 5.89-5.88 (m, 1H), 5.88 (d, $J = 1.2$ Hz, 1H), 5.86-5.84 (m, 1H) (mixture), 5.39-5.34 (m, 1H), 4.14 (d, $J = 7.5$ Hz, 1H), 3.72 (s, 3H), 3.50 (t, $J = 7.5$ Hz, 1H), 2.57-2.52 (m, 1H), 2.50-2.21 (m, 2H) (mixture), 2.21-2.13 (m, 1H) (mixture), 1.76-1.41 (m, 8H) (mixture); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) (mixture): δ 158.0, 157.8, 149.6, 147.6, 146.7, 146.7, 142.2, 142.1, 141.3, 138.1, 137.7, 135.5, 134.8, 134.4, 134.3, 132.9, 132.7, 132.6, 130.2, 128.4, 123.7, 123.0, 113.9, 112.5, 108.2, 107.9, 101.1, 100.9, 100.8, 100.1, 84.8, 83.5, 55.2, 55.0, 48.2, 46.9, 46.7, 44.4, 33.2, 33.0, 32.1, 31.8, 30.1, 30.0, 29.2, 28.6, 28.2, 28.1, 27.6, 27.3; IR (ATR) (mixture): 2919, 1476, 1248, 1144, 1036, 907, 729 cm^{-1} ; HRMS (ESI+) m/z calcd for $\text{C}_{27}\text{H}_{29}\text{O}_4$ ($[\text{M} + \text{H}]^+$): 417.2060, found: 417.2033.



(5a*R**,8a*S**,9*R**)- and

(5a*S**,8a*R**,9*R**)-1-(Bis(4-chlorophenyl)methylene)-6,7-dimethoxy-9-(4-methoxyphenyl)-1,3a,9,9a-tetrahydrocyclopenta[*b*]chromene (**3l**):

3,4-Dimethoxy-6-(4-methoxyphenylmethylidene)cyclohexa-2,4-dien-1-one (71.5 mg, 0.245 mmol), 6,6-bis(*p*-chlorophenyl)fulvene (38.9 mg, 0.130 mmol), TXT (0.72 mg, 0.00129 mmol), and CH₂Cl₂ (2.0 mL) were used for 8 h. Yellow solid (59.5 mg, 80% yield, dr 1.1 : 1). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.38-7.35 (m, 2H) (mixture), 7.17-7.13 (m, 4H) (mixture), 6.88 (d, *J* = 8.0 Hz, 2H), 6.68-6.64 (m, 2H) (mixture), 6.60 (m, 2H), 6.58 (s, 1H), 6.42 (s, 1H), 6.30-6.27 (m, 1H), 6.26-6.23 (m, 1H), 5.41 (d, *J* = 7.5 Hz, 1H), 4.17-4.12 (m, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.58 (d, *J* = 7.5 Hz, 1H); (minor): δ 7.38-7.35 (m, 2H) (mixture), 7.23-7.20 (m, 2H), 7.17-7.13 (m, 2H) (mixture), 6.97 (d, *J* = 8.6 Hz, 2H), 6.68-6.64 (m, 4H) (mixture), 6.54 (s, 1H), 6.38 (d, *J* = 5.7 Hz, 1H), 6.30 (s, 1H), 6.09 (dd, *J* = 5.7, 2.3 Hz, 1H), 5.46 (dd, *J* = 7.2, 2.6 Hz 1H), 4.05 (dd, *J* = 7.5, 2.9 Hz 1H), 3.86 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.66 (d, *J* = 2.9 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) (mixture): δ 158.2, 158.0, 148.7, 148.5, 148.1, 147.3, 146.5, 145.0, 144.1, 144.0, 140.6, 140.5, 140.2, 140.2, 137.4, 137.1, 137.0, 136.9, 135.1, 134.0, 133.4, 133.1, 133.0, 132.6, 132.6, 131.4, 131.3, 131.2, 131.0, 130.8, 130.0, 128.9, 128.6, 128.5, 128.3, 128.3, 122.3, 120.2, 113.6, 112.8, 111.8, 111.4, 103.1, 102.4, 83.7, 82.3, 56.4, 56.3, 56.0, 55.9, 55.2, 55.2, 47.9, 44.4, 43.7, 43.4; IR (ATR) (mixture): 2946, 1507, 1249, 1011, 827, 728 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₃₄H₂₉O₄³⁵Cl₂ ([M + H]⁺): 571.1437, found: 571.1311.

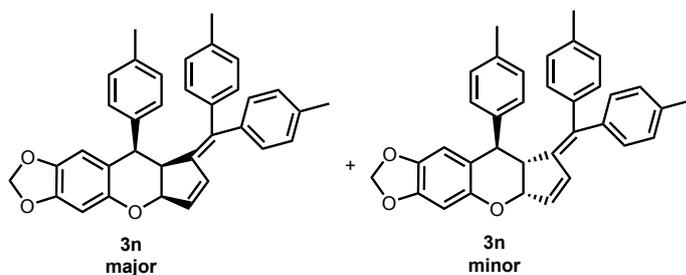


(5a*R**,8a*S**,9*R**)- and

(5a*S**,8a*R**,9*R**)-8-(Bis(4-chlorophenyl)methylene)-9-(*p*-tolyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (**3m**):

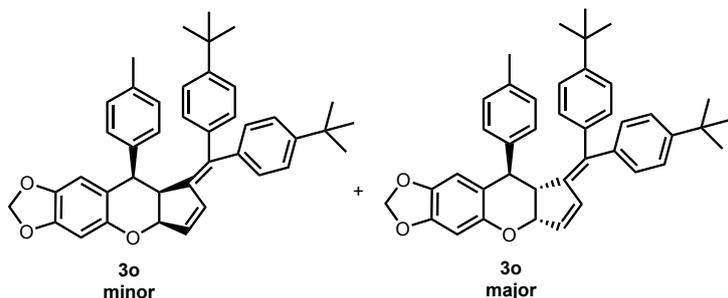
6-(4-Methylbenzylidene)benzo[*d*][1,3]dioxol-5(6H)-one (58.9 mg, 0.245 mmol), 6,6-bis(*p*-chlorophenyl)fulvene (36.0 mg, 0.120 mmol), TXT (3.52 mg, 0.00632 mmol), and CH₂Cl₂ (2.0 mL) were

used. Yellow solid (57.8 mg, 85% yield, dr 1.4 : 1). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.39-7.33 (m, 2H) (mixture), 7.16-7.10 (m, 4H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.94-6.92 (m, 2H) (mixture), 6.56-6.53 (m, 3H), 6.40-6.38 (m, 1H) (mixture), 6.30-6.27 (m, 1H) (mixture), 6.27-6.24 (m, 1H), 5.84 (s, 1H), 5.78 (s, 1H), 5.39 (dd, *J* = 7.7, 1.7 Hz 1H), 4.14 (t, *J* = 7.9 Hz, 1H), 3.55 (d, *J* = 8.2 Hz, 1H), 2.27 (s, 3H); (minor): δ 7.39-7.33 (m, 2H) (mixture), 7.24-7.20 (m, 2H), 7.19-7.16 (m, 2H), 6.94-6.92 (m, 2H) (mixture), 6.91-6.88 (m, 2H), 6.62 (d, *J* = 7.9 Hz, 2H), 6.49 (s, 1H), 6.40-6.38 (m, 1H) (mixture), 6.30-6.27 (m, 1H) (mixture), 6.06 (dd, *J* = 5.7, 2.5 Hz, 1H), 5.91 (s, 1H), 5.86 (s, 1H), 5.45 (dd, *J* = 7.6, 2.5 Hz 1H), 4.09 (dd, *J* = 7.4, 2.4 Hz, 1H), 3.65 (d, *J* = 2.2 Hz, 1H), 2.25 (s, 3H); ¹³C {¹H} NMR (126 MHz, CDCl₃) (mixture): δ 149.1, 147.9, 146.8, 146.6, 144.9, 142.4, 140.6, 140.5, 140.1, 140.0, 140.0, 138.7, 137.3, 137.2, 137.1, 137.0, 135.9, 135.8, 133.5, 133.0, 132.9, 131.4, 131.3, 131.1, 131.0, 129.0, 128.8, 128.6, 128.3, 128.2, 128.2, 127.2, 123.6, 121.6, 108.2, 108.0, 101.3, 100.9, 100.9, 100.3, 83.8, 82.6, 47.6, 44.4, 44.3, 44.2, 21.0, 20.9; IR (ATR) (mixture): 2887, 1476, 1146, 1090, 907, 831, 728 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₃₃H₂₅O₃³⁵Cl₂ ([M + H]⁺): 539.1175, found: 539.1096.



(5*aR,8*aS**,9*R**)- and (5*aS**,8*aR**,9*R**)-8-(di-*p*-tolylmethylene)-9-(*p*-tolyl)-5*a*,8,8*a*,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3*n*):**

6-(4-Methylbenzylidene)benzo[*d*][1,3]dioxol-5(6*H*)-one (60.1 mg, 0.250 mmol), 6,6-bis(*p*-methylphenyl)fulvene (32.8 mg, 0.127 mmol), TXT (3.59 mg, 0.00645 mmol), and CH₂Cl₂ (2.0 mL) were used. Yellow solid (49.0 mg, 77% yield, dr 1.4 : 1). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.23-7.09 (m, 4H) (mixture), 6.99-6.89 (m, 6H) (mixture), 6.58-6.53 (m, 3H), 6.37 (s, 1H), 6.33-6.28 (m, 1H) (mixture), 6.17 (dd, 1H), 5.83 (s, 1H), 5.78 (s, 1H), 5.45-5.38 (m, 1H), 4.17 (t, *J* = 7.8 Hz, 1H), 3.56 (d, *J* = 8.2 Hz, 1H), 2.41 (s, 3H) (mixture), 2.29 (s, 3H), 2.27 (s, 3H); (minor): δ 7.23-7.09 (m, 4H) (mixture), 7.04 (d, *J* = 7.8 Hz, 2H), 6.99-6.89 (m, 2H) (mixture), 6.86 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 7.8 Hz, 2H), 6.50 (s, 1H), 6.45 (d, *J* = 6.0 Hz, 1H), 6.30-6.27 (m, 1H) (mixture), 5.95 (dd, *J* = 5.5, 2.3 Hz, 1H), 5.91 (s, 1H), 5.86 (s, 1H), 5.45-5.38 (m, 1H), 4.12 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.73 (s, 1H), 2.41 (s, 3H) (mixture), 2.31 (s, 3H), 2.24 (s, 3H); ¹³C {¹H} NMR (126 MHz, CDCl₃) (mixture): δ 149.3, 148.1, 146.7, 146.6, 144.8, 142.9, 142.3, 142.2, 140.7, 139.9, 139.8, 136.6, 136.4, 135.6, 135.5, 135.1, 135.0, 130.0, 129.9, 129.7, 129.6, 129.3, 129.0, 128.9, 128.8, 128.6, 128.5, 128.0, 127.3, 124.1, 122.1, 108.4, 108.1, 101.3, 100.8, 100.2, 84.1, 83.0, 47.9, 44.3, 44.2, 44.0, 21.3, 21.3, 21.1, 21.0, 20.9; IR (ATR) (mixture): 2955, 1476, 1257, 1144, 1038, 838, 584 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₃₅H₃₁O₃ ([M + H]⁺): 499.2268, found: 499.2239.



(5a*R,8a*S**,9*R**)- and (5a*S**,8a*R**,9*R**)-8-(Bis(4-*tert*-butyl)phenyl)methylene)-9-(*p*-tolyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3o):**

6-(4-Methylbenzylidene)benzo[*d*][1,3]dioxol-5(6H)-one (60.3 mg, 0.251 mmol), 6,6-bis(*p*-*tert*-butylphenyl)fulvene (43.4 mg, 0.127 mmol), TXT (3.56 mg, 0.00640 mmol), and CH₂Cl₂ (2.0 mL) were used. Yellow solid (49.7 mg, 67% yield, dr 1 : 2). ¹H NMR (500 MHz, CDCl₃) (major): δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.25-7.13 (m, 4H) (mixture), 6.97-6.91 (m, 2H) (mixture), 6.87 (d, *J* = 7.8 Hz, 2H), 6.55-6.47 (m, 4H) (mixture), 6.35-6.31 (m, 1H) (mixture), 5.95 (dd, *J* = 5.7, 2.5 Hz, 1H), 5.91 (s, 1H), 5.85 (s, 1H), 5.47 (dd, *J* = 7.6, 2.1 Hz, 1H), 4.17-4.12 (m, 1H), 3.50 (d, *J* = 8.2 Hz, 1H), 2.22 (s, 3H), 1.40 (s, 9H), 1.28 (s, 9H); (minor): δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.25-7.13 (m, 4H) (mixture), 6.97-6.91 (m, 4H) (mixture), 6.68-6.63 (m, 2H), 6.55-6.47 (m, 1H) (mixture), 6.35-6.31 (m, 2H) (mixture), 6.16 (dd, *J* = 5.7, 2.1 Hz, 1H), 5.83 (s, 1H), 5.78 (s, 1H), 5.42-5.38 (m, 1H), 4.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.73 (s, 1H), 2.28 (s, 3H), 1.37 (s, 9H), 1.27 (s, 9H); ¹³C{¹H} NMR (126 MHz, CDCl₃) (mixture): δ 150.3, 150.0, 149.7, 149.5, 149.4, 148.1, 146.7, 146.6, 145.3, 142.9, 142.3, 142.1, 141.0, 139.6, 139.4, 139.2, 138.6, 138.1, 137.8, 135.6, 135.4, 135.3, 135.2, 135.2, 135.2, 129.7, 129.5, 129.4, 129.1, 128.8, 128.0, 127.5, 125.6, 124.9, 124.7, 124.7, 124.2, 122.2, 108.4, 107.9, 101.3, 100.9, 100.8, 100.2, 84.2, 83.0, 48.1, 44.8, 44.5, 44.3, 34.7, 34.6, 34.5, 31.6, 31.4, 31.4, 31.3, 21.0, 20.9; IR (ATR) (mixture): 2920, 1475, 1258, 1146, 1037, 820, 724 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₄₁H₄₃O₃ ([M + H]⁺): 583.3207, found: 583.3169.

8. References

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9. ^1H NMR and ^{13}C NMR spectrum data

