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Organophotoredox-Catalyzed Intermolecular Oxa-[4+2] Cycloaddition Reactions

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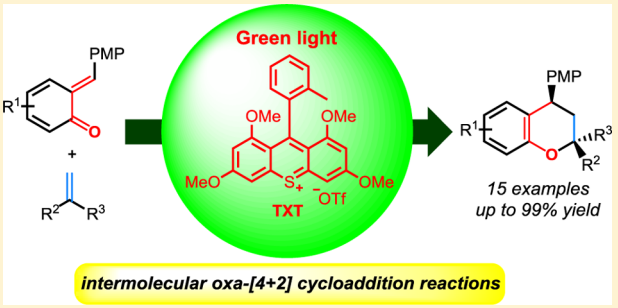
Supporting Information

ABSTRACT: An intermolecular oxa-[4+2] cycloaddition reaction promoted by a thioxanthylium photoredox catalyst under irradiation with green light has been developed. The reaction of *ortho*-quinone methides with styrenes smoothly affords the desired cycloadducts. Especially styrenes bearing electron-donating groups are efficiently transformed in this reaction. This method represents a sustainable way to carry out oxa-[4+2] cycloaddition reactions using only a catalytic amount of a photocatalyst and visible light.



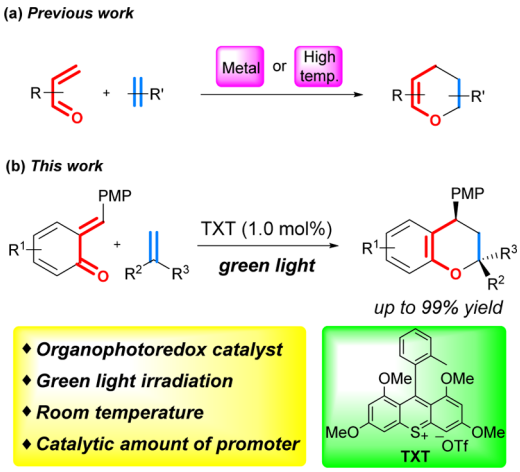
INTRODUCTION

Photoinduced chemical transformations represent a powerful synthetic strategy to generate heterocycles and polycyclic compounds.[1] Over the past few decades, *O*-heterocycles have attracted increasing interest due to the relevance of their structural units in medicinal chemistry, materials science, and natural products. Among the variety of synthetic routes to *O*-heterocycles, the oxa-[4+2] cycloaddition reaction is particularly attractive on account of its high atom economy and as it provides efficient access to various synthetically useful heterocycles. Current reaction methods focus mainly on the use of high-temperature conditions or the presence of catalytic/stoichiometric amounts of metals (Scheme 1a).[2,3] On the other hand, only few photoinduced reactions have been reported and these require high-energy (ultraviolet) light sources.[4] Therefore, the development of cost-effective and milder synthetic routes to *O*-heterocycles remains highly desirable, especially when a low environmental impact is targeted.

To overcome these shortcomings, organophotoredox-promoted chemical transformations using visible light as an energy source represent a promising approach.[5] A variety of organophotoredox catalysts, including Acr^+-Mes, eosin Y, 4CzIPN, DPZ, and TPT, have been employed in various reactions.[5,6] Recently, we have reported the design and synthesis of thioxanthylium organophotoredox catalysts, which are active under irradiation with green light.[7] During the course of that study, we found that these thioxanthylium photocatalysts efficiently oxidize styrene derivatives such as *trans*-anethole and promote radical cation Diels−Alder reactions. Among the numerous photoredox reactions, hetero-[4+2] cycloadditions have been reported by several groups.[8] However, most of these reactions are aza-[4+2] cycloadditions, while only a few examples of oxa-[4+2] cycloadditions exist. Recently, the intramolecular oxa-[4+2] cycloaddition of tethered bis(enones) in the presence of a Ru photocatalyst has been reported by Yoon and co-workers.[9] Yet, to the best of our knowledge, studies on intermolecular oxa-[4+2] cycloadditions catalyzed by photoredox chemistry have not been reported. Thus, the development of efficient synthetic strategies for catalytic oxa-[4+2] cycloadditions remains an attractive research target.

ortho-Quinone methides are key reactive intermediates for oxa-cyclic compounds such as benzopyrans and benzofurans.[10]

Scheme 1. Representative Examples of Oxa-[4+2] Cycloaddition Reactions[a]



[a]PMP: *p*-methoxyphenyl.

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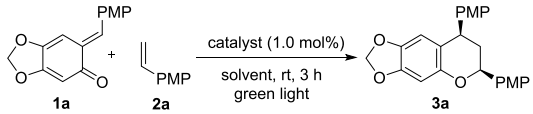
Based on the varied reactivity of *ortho*-quinone methides, a series of attractive strategies have been developed.[10,11] On the other hand, the hitherto reported examples involving photoirradiation require the use of high-energy irradiation such as ultraviolet light.[4,12] Recently, we have developed the acid-catalyzed generation of *ortho*-quinone methides from salicylaldehyde in the presence of trimethyl orthoformate.[13] During the course of this study, we found that the inverse-electron-demand [4+2] cycloaddition reaction of 1,1-diphenylethylenes with in situ generated electron-withdrawing *ortho*-quinone methides affords a series of 2-phenylchromanes.[14] Based on the above and to expand the generality of oxa-[4+2] cycloaddition reactions, we herein report the thioxanthylium organophotoredox-catalyzed intermolecular oxa-[4+2] cycloaddition reaction of *ortho*-quinone methides under irradiation with green light (Scheme 1b).

RESULTS AND DISCUSSION

Initially, we screened the reaction of *ortho*-quinone methide (**1a**) with 4-methoxystyrene (**2a**) in the presence of the thioxanthylium catalyst (TXT) at room temperature (Table 1). Medium to nonpolar solvents, such as tetrahydrofuran (THF), toluene, and 1,2-dichloroethane (DCE), afforded the desired product (**3a**) in moderate yield (entries 1−3), while polar solvents such as CH_3NO_2, CF_3CH_2OH, and AcOEt provided the desired product in high yield (entries 4−6). In particular, AcOEt effectively increased the product yield to 88% (cis/trans = 3:1). Although solvent effects are not obvious, polar solvents may stabilize potentially emerging radical cation intermediates.[15] Fortunately, the adduct **3a** was crystallized to give a single crystal suitable for X-ray diffraction analysis, which allowed to determine the relative stereochemistry of chromane **3a** as cis form.[16] Eosin Y and rose bengal are the most widely used organic photoredox catalysts under green light irradiation, and these can be employed in a wide variety of organic transformations.[17] However, using these catalysts under the optimal conditions established in this study was not successful due to the low reduction potentials of their excited states [$E(C^*/C^-)$ = +0.81 and +0.88 V vs SCE, respectively] compared to that of **2a** (E_{ox} = +1.47 V vs SCE) (entries 7 and 8).[18] Acr^+-Mes and TPT, which are typical organophotoredox catalysts having high excited-state reduction potentials, are also not suitable for this reaction due to their inefficient absorption of green light and low solubility in AcOEt (entries 9−12). On the other hand, when CH_3NO_2 was used as a solvent, which can dissolve Acr-Mes and TPT, the desired product was obtained in 32 and 34% yields with moderate diastereoselectivities, respectively (entries 13 and 14). Then, it is found that representative photoredox catalysts having high excited-state reduction potentials can also be applied to the reaction while TXT can be dissolved in various solvents and can use AcOEt as a solvent. All blank experiments, i.e., in the absence of a catalyst, light source, or air, afforded low yields of **3a** (entries 15−17). Based on these results, we concluded that the combination of the photoredox catalyst TXT with a light source in the presence of air effectively promotes the present [4+2] cycloaddition. The reaction could be performed on a large scale to furnish the product in moderate yield (entry 18). When TEMPO was used as a radical scavenger, the reaction did not proceed, suggesting that the transformation could occur via a radical mechanism (entry 19). Interestingly, the reaction was carried out at reflux in the absence of catalyst and green light to afford the product in low yield (entry 20). Thus, the photocatalytic system has good advantages to afford the oxa-[4+2] cycloadducts under mild conditions.

With the optimized conditions in hand, we next examined the reaction of various *ortho*-quinone methides and alkenes (Table 2). Dienophiles bearing ethoxy, isopropoxy, or *tert*-butyl-dimethyloxy moieties were well tolerated in this reaction (**3b−d**). However, a benzyloxy-functionalized derivative afforded the corresponding product in poor yield, while the starting material was recovered in 62% yield (**3e**). We have rationalized this in terms of the mild electron-donating properties of the benzyloxy substituent, which may not sufficiently promote the oxidation of the dienophile. On the other hand, when the catalyst loading was increased to 5.0 mol % and the reaction time prolonged to 24 h, the product yield improved to 66%, which means that the dienophile is effectively oxidized by the photocatalyst. A dibenzyloxy-functionalized derivative also readily underwent this transformation (**3f**). Dienophiles with multiple methoxy groups (**3g−j**) were well tolerated in this reaction. Moreover, 1,1-diaryl-functionalized substrates readily afforded the corresponding products (**3k−l**). Importantly, 1,1-diphenylethylene did not engage in the reaction, despite having a lower oxidation potential (E_{ox} = +1.54 V vs SCE)[19] than the photocatalyst TXT (E_0' (C^*/C^-) = +1.76 V vs SCE). This result indicates that electron-donating groups effectively increase the stability of radical cation intermediates (**3m**).[20] In contrast, the

Table 1. Optimization of the Reaction Conditions for the Catalytic Intermolecular Oxa-[4+2] Cycloaddition[a]



entry	catalyst	solvent	yield (%)
1	TXT	THF	35 (dr 4:1)
2	TXT	toluene	37 (dr 3:1)
3	TXT	DCE	60 (dr 3:1)
4	TXT	CH_3NO_2	82 (dr 5:1)
5	TXT	CF_3CH_2OH	86 (dr 6:1)
6	TXT	AcOEt	88 (dr 3:1)
7	eosin Y	AcOEt	0
8	rose bengal	AcOEt	0
9	Acr^+-Mes	AcOEt	0
10	TPT	AcOEt	0
11[b]	Acr^+-Mes	AcOEt	0
12[b]	TPT	AcOEt	0
13[b]	Acr^+-Mes	CH_3NO_2	32 (dr 5:1)
14[b]	TPT	CH_3NO_2	40 (dr 5:1)
15	no catalyst	AcOEt	10
16[c]	TXT	AcOEt	9
17[d]	TXT	AcOEt	13
18[e]	TXT	AcOEt	46
19[f]	TXT	AcOEt	0
20[g]	no catalyst	AcOEt	15 (dr 7:1)

[a]All reactions were carried out for 3 h using **1a** (0.375 mmol), **2a** (0.125 mmol), and TXT (1.0 mol %) in the specified solvent (2.0 mL) at room temperature under green light irradiation. [b]Blue light was used as a light source. [c]No light. [d]Under N_2. [e]**1a** (15.3 mmol) and **2a** (5.1 mmol) were used as substrates. [f]Tempo (3.0 equiv) was added to the reaction. [g]The reaction temperature was increased to reflux in the absence of catalyst and green light irradiation. PMP: *p*-methoxyphenyl.

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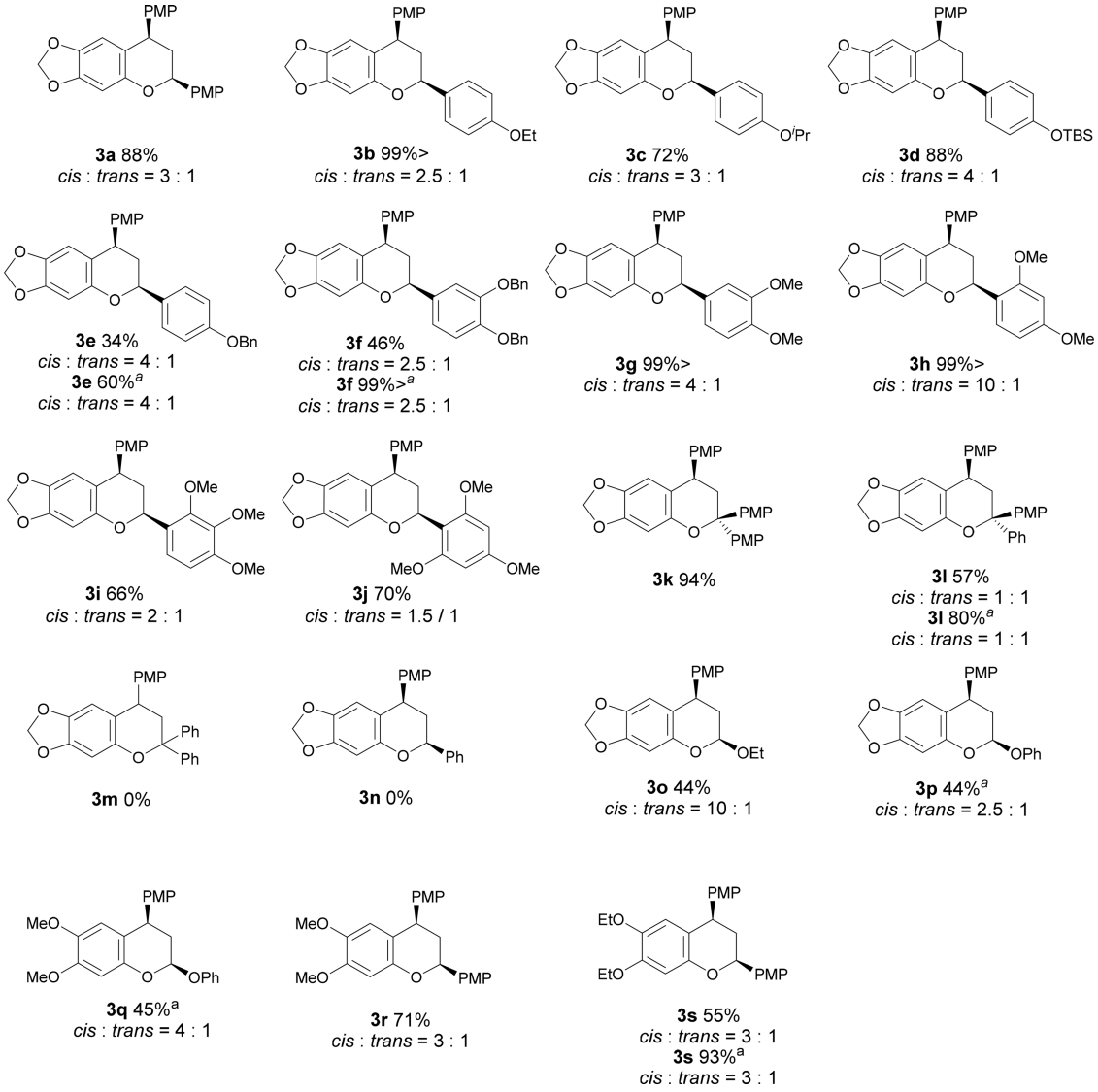
Table 2. Scope of the TXT-Catalyzed Intermolecular Oxa-[4+2] Cycloaddition

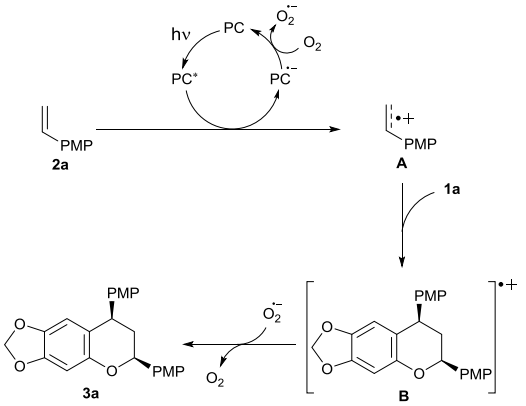


[a]TXT (5.0 mol %) was used and the reaction was conducted for 24 h. PMP: *p*-methoxyphenyl.

reaction with styrene, which exhibits a relatively high oxidation potential (E_{ox} = +1.97 V vs SCE),[19] did not proceed due to the lower reduction potential of the excited state of TXT (**3n**). Ethoxy vinyl ether and phenyl vinyl ether also afforded the corresponding products in moderate yields (**3o** and **3p**). Moreover, *ortho*-quinone methides bearing dimethoxy or diethoxy groups were suitable for this reaction (**3q**–**s**). We also found that this reaction can be applied to various types of styrenes, such as mono-, di-, and tri-substituted styrenes.

A plausible reaction mechanism for organophotoredox-catalyzed intermolecular oxa-[4+2] cycloaddition is represented in Scheme 2. Excitation of the photocatalyst (PC*; E_0' (C*/C$^-$) = +1.76 V vs SCE)[18] under irradiation with visible light enables the oxidation of 4-methoxystyrene **2a** (E_{ox} = +1.47 V vs SCE). According to Stern–Volmer experiments (Figure 1), the electron transfer from 4-methoxystyrene to the photocatalyst should occur smoothly. Since the reaction seems to require oxygen to promote the catalytic cycle (Table 1, entry 12), the reduced photocatalyst (PC$^{\bullet-}$) would be regenerated into the original photocatalyst (PC) via single electron transfer from O_2. *ortho*-Quinone methide **1a** could

Scheme 2. Proposed Reaction Mechanism[a]



[a]PMP: *p*-methoxyphenyl.

undergo an oxa-[4+2] cycloaddition with the resulting radical cation **A** via an endo-TS, thus furnishing radical cation **B**.[21] According to previous reports,[20] an aromatic substituent with

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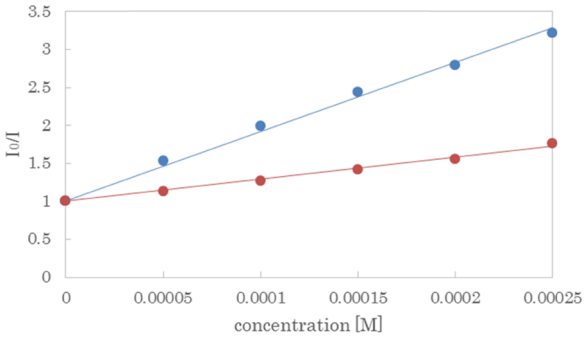

Figure 1. Stern−Volmer plots for 4-methoxystyrene **2a** (blue line) and *ortho*-quinone methide **1a** (red line).

an electron-donating group on the dienophile would effectively increase the stability of such a radical cation intermediate. Finally, transfer of a single electron from the superoxide radical ($O_2^{\bullet-}$), 4-methoxystyrene **2a**, or the reduced photocatalyst ($PC^{\bullet-}$) would afford the desired cycloadduct **3a**. Since the reaction does not proceed efficiently under N_2 (Table 1, entry 12), O_2 must be a key mediator in this reaction. To confirm the radical chain processes in the catalysis, we determined the quantum yield of the reaction (0.21).[22] Accordingly, it seems likely that a closed radical mechanism is the dominating reaction pathway, even though the possibility of a radical chain propagation mechanism cannot be excluded at this point.

CONCLUSIONS

We have developed an oxa-[4+2] cycloaddition reaction that is promoted by an organophotoredox catalyst under green light irradiation. When *ortho*-quinone methides are reacted with styrenes in the presence of a TXT photoredox catalyst under green light irradiation, the reaction smoothly affords the desired cycloadducts in good yield. In particular, styrenes bearing electron-donating groups such as methoxy moieties are efficiently transformed in this reaction. The reaction can also be applied to mono- and disubstituted ethylenes. The present transformation thus provides a sustainable approach to oxa-[4+2] cycloaddition reactions using only catalytic amounts of a photoredox catalyst and visible light.

EXPERIMENTAL SECTION

General Information. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100. ^{1}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. ^{13}C NMR spectra were recorded on a Bruker DRX-500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0). ^{19}F NMR spectra were recorded on a JEOL JNM AL-400 (376 MHz) spectrometer with hexafluorobenzene (C_6F_6: δ −164.9) as internal standard. High-resolution mass spectra were obtained with Hitachi Nanofrontier LD Spectrometer (ESI/TOF). Column chromatography was carried out with Cicareagent silica gel 60 N (spherical, particle size 63−210 mm). Thin-layer chromatography (TLC) was carried out with Merck TLC plates with silica gel 60 F254. Unless otherwise noted, reagents were commercially available and were used without purification. Single-crystal X-ray diffraction analysis was performed at 223 K using a Rigaku XtaLAB P200 diffractometer with a graphite monochromatic Cu Kα radiation source (l 1/4 1.54187 Å). The UV absorption spectra were measured with a JASCO V-630 spectrometer. The fluorescence spectra were obtained on a JASCO FP-8500 spectrofluorometer, which was used as the light source for the reaction quantum yield measurement. 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) or a Beamtec 7 W Blue LED (LB1526B) at room temperature. 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).

General Procedure for the Synthesis of Starting Materials. *For the Synthesis of 2-(4-Methoxybenzyl)-4,5-methylene-dioxyphenol.*[23] To a solution of ascorbic acid (925 mg, 5.25 mmol) in an aqueous solution of citric acid (90 mL, 2%) were added sesamol (4.96 g, 35.9 mmol) and 4-methoxybenzyl alcohol (4.96 g, 35.9 mmol). The mixture was heated to reflux for 17 h. Upon cooling, crystals precipitated from the reaction mixture. Filtration of the precipitate followed by recrystallization from toluene formed the desired pure product (7.75 g, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.58 (s, 1H), 6.39 (s, 1H), 5.87 (s, 2H), 4.49 (s, 1H), 3.82 (s, 2H), 3.77 (s, 3H).

*For the Synthesis of 6-(4-Methoxybenzylidene)-3,4-methylene-dioxy-cyclohexa-2,4-dienone (**1a**).*[23] A solution of 2-(4-methoxybenzyl)-4,5-methylenedioxyphe-nol (3.88 g, 15 mmol) in ether (300 mL) was heated under reflux with silver oxide (11.6 g, 50 mmol) for 3.5 h and filtered. The orange crystals were separated by filtration. The solution was concentrated to 150 mL, cooled, and the colored product was collected. The ether filtrate was diluted to 200 mL and treated once again with silver oxide (5.8 g, 25 mmol) for 2 h to give an additional quantity of the orange product (1.56 g, 41% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.49 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 6.71 (s, 1H), 5.97 (s, 1H), 5.89 (s, 2H), 3.86 (s, 3H).

For the Synthesis of 4,5-Dimethoxy-2-(4-methoxybenzyl)-phenol.[23] To a solution of ascorbic acid (430 mg, 2.44 mmol) in an aqueous solution of citric acid (45 mL, 2%) were added 3,4-dimethoxyphenol (2.44 g, 15.8 mmol) and 4-methoxybenzyl alcohol (2.18 g, 15.8 mmol). The mixture was heated to reflux for 17 h. When the reaction solution was decanted, an oily product was obtained. The crude was chromatographed by silica gel column to give a brown solid (4.32 g, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (d, J = 14.5 Hz, 2H), 6.84 (d, J = 14.5 Hz, 2H), 6.64 (s, 1H), 6.45 (s, 1H), 4.52 (s, 1H), 3.87 (s, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H).

For the Synthesis of 3,4-Dimethoxy-6-(4-methoxyphenylmethylidene)cyclohexa-2,4-dien-1-one.[23] To a solution of 4,5-dimethoxy-2-(4-methoxybenzyl)phenol (4.32 g, 15.8 mmol) in ether (262 mL) was added silver oxide (14.6 g, 63 mmol) and stirred for 12 h. The solution was filtered, then the filtrate was washed with dichloromethane. The solvent was removed under reduced pressure, and red crystals were collected (2.14 g, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.53 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 6.52 (s, 1H), 5.85 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H).

For the Synthesis of 4,5-Diethoxy-2-(4-methoxybenzyl)-phenol. To a solution of ascorbic acid (157 mg, 0.89 mmol) in an aqueous solution of citric acid (20 mL, 2%) were added 4-methoxybenzyl alcohol (764 μL, 6.15 mmol) and 3,4-diethoxyphenol (1.12 g, 6.15 mmol). The reaction was heated to reflux for 24 h. On cooling, an oily product was obtained. The crude was chromatographed by silica gel column to give yellow oil (1.13 g, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (d, J = 9.0 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 6.63 (s, 1H), 6.34 (s, 1H), 5.69 (s, 1H), 3.95 (q, J = 7.0 Hz, 2H), 3.82 (m, 4H), 3.73 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 158.2, 148.5, 148.1, 142.4, 131.8, 129.4, 118.1, 117.6, 114.1, 102.9, 65.8, 64.5, 55.3, 35.2; IR (ATR): 3451, 2978, 1509, 1193, 1103, 1032, cm^{-1}; HRMS (ESI+) m/z calcd for $C_{18}H_{22}O_4Na$ ([M + Na]$^+$): 325.1410, found: 325.1394.

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For the Synthesis of 3,4-Diethoxy-6-(4-methoxyphenylmethylidene)cyclohexa-2,4-dien-1-one. To a solution of 4,5-diethoxy-2-(4-methoxybenzyl)phenol (500 mg, 1.65 mmol) in ether (25 mL) was added silver oxide (1.5 g, 6.47 mmol), then stirred for 12 h. The solution was filtered, and the solvent was removed under reduced pressure. Recrystallization from dichloromethane formed the desired pure product (220 mg, 46% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.51 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 6.49 (s, 1H), 5.81 (s, 1H), 4.04 (q, J = 7.0 Hz, 2H), 3.98 (q, J = 7.0 Hz, 2H), 1.48−1.43 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 185.6, 163.7, 160.6, 148.1, 140.1, 132.4, 129.3, 128.5, 114.4, 104.5, 102.1, 64.8, 64.1, 55.4, 14.3, 14.0; IR (ATR): 2977, 1508, 1172, 1104, 1030, 570 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{18}H_{21}O_4$ ([M + H]$^+$): 301.1434, found: 301.1424.

For the Synthesis of 9-(o-Tolyl)-1,3,6,8-tetra-methoxythioxanthylium trifluoromethanesulfonate.[7,24]

(1) [25] To a solution of 1-bromo-3,5-dimethoxybenzene (4.3 g, 20 mmol) in THF (30 mL) at −78 °C was dropwise added *tert*-butyllithium (34 mL, 50 mmol, 1.49 M in hexane). After the reaction was stirred at −78 °C for 1 h, a solution of iodine (7.6 g, 60 mmol) in THF (20 mL) was added via cannula. The resulting mixture was stirred at −78 °C for 1 h and then was warmed to room temperature, neutralized with water, and diluted with CH_2Cl_2. The organic layer was washed with saturated aqueous $Na_2S_2O_3$ and brine. It was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude mixture was purified by flash chromatography (hexane/ethyl acetate = 10:1) to afford 1-iodo-3,5-dimethoxybenzene (4.70 g, 89% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.85 (d, J = 2.3 Hz, 2H), 6.40 (t, J = 2.3 Hz, 1H), 3.76 (s, 6H).

(2) [26] A mixture of 1-iodo-3,5-dimethoxybenzene (6.6 g, 25 mmol), carbon disulfide (1.5 mL, 25 mmol), CuI (480 mg, 2.5 mmol), and DBU (7.5 mL, 50 mmol) in toluene (40 mL) was stirred under N_2 at reflux for 12 h. After H_2O was added, the solution was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1) to provide bis(3,5-dimethoxypheny)-sulfane (2.38 g, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.74 (s, 12H), 6.34 (t, J = 2.3 Hz, 2H), 6.52 (d, J = 2.3 Hz, 4H).

(3) [7] A solution of bis(3,5-dimethoxyphenyl)sulfane (75 mg, 0.25 mmol) and benzoyl chloride (98 μL, 0.75 mmol) in chlorobenzene (5.0 mL) was placed in a 50 mL recovery flask under N_2. Trifluoromethanesulfonic acid (66 μL, 0.75 mmol) was slowly added to the solution, which was heated to 120 °C for 2 h. It was cooled to room temperature and excess Et_2O was added to precipitate a solid. After stirring for 1 h, the mixture was filtered. The solid was washed with Et_2O and dried in vacuo, affording 9-(2-methylphenyl)-1,3,6,8-tetramethoxy-thioxanthylium trifluoromethanesulfonate (**TXT**). Brown solid (110.7 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 2.2 Hz, 2H), 7.28 (dd, J = 7.3, 1.3 Hz, 1H), 7.26−7.23 (m, 1H), 7.23−7.17 (m, 1H), 6.73 (d, J = 7.3 Hz, 1H), 6.54 (d, J = 2.2 Hz, 2H), 4.15 (s, 6H), 3.40 (s, 6H), 2.03 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 168.3, 166.0, 165.5, 147.7, 142.1, 134.2, 128.0, 127.5, 125.1, 124.0, 116.7, 102.0, 101.3, 57.7, 56.9, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.3; IR (ATR): 1584, 1220, 1151, 1028, 637 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{23}O_4S^+$: 407.1312, found: 407.1324.

General Procedure for [4+2] Cycloaddition with Photocatalyst under Visible Light Irradiation. The alkene (**2**) (0.125 mmol), *o*-quinone methide (**1**) (0.375 mmol), **TXT** (1.0 mol %), and AcOEt (2.0 mL) were added into a 8 mL borosilicate vial. The resulting solution was stirred at room temperature under air and green LED irradiation. The desired cycloadduct (**3**) was isolated by column chromatography on silica gel.

Procedure for [4+2] Cycloaddition with Photocatalyst under Visible Light Irradiation in Large-Scale Reaction. *o*-Quinone methide (**1a**) (3.93 g, 15.3 mmol), 4-methoxystyrene (**2a**) (0.69 g, 5.1 mmol), **TXT** (0.029 g, 1.0 mol %), and AcOEt (82 mL) were added into a 200 mL recovery flask. The resulting solution was stirred at room temperature under air and irradiation with two 7 W green LEDs. After the reaction was stirred for 72 h, the solution was concentrated by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1) to afford the desired product **3a** (0.92 g, 46% yield, dr 3:1) as a yellow solid.

(6S,8R*)- and (6R*,8R*)-6,8-bis(4-Methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (**3a**).* 4-Methoxystyrene (16.5 mg, 0.123 mmol), *o*-quinone methide **1a** (96.0 mg, 0.375 mmol), **TXT** (0.71 mg, 0.00125 mmol), and AcOEt (2.0 mL) were used. Yellow solid (42.7 mg, 88% yield, dr 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) (major): δ 7.37 (d, J = 9.0 Hz, 2H), 7.12 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.46 (s, 1H), 6.21 (s, 1H), 5.82 (dd, J = 8.0, 1.5 Hz, 2H), 5.05 (dd, J = 11.5, 1.5 Hz, 1H), 4.19 (dd, J = 12.0, 6.5 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.33−2.29 (m, 1H), 2.21−2.14 (m, 1H); (minor): δ 7.24 (d, J = 9.0 Hz, 2H), 7.06 (d, J = 9.0 Hz, 2H), 6.87−6.84 (m, 4H), 6.52 (s, 1H), 6.39 (s, 1H), 5.87 (dd, J = 4.0, 1.0 Hz, 2H), 4.91 (dd, J = 10.5, 2.0 Hz, 1H), 4.06 (dd, J = 5.5, 3.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 2.41−2.36 (m, 1H), 2.13−2.09 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (mixture): δ 159.4, 159.2, 158.4, 158.1, 150.4, 150.2, 147.1, 146.6, 141.6, 141.5, 138.4, 136.8, 133.4, 133.3, 129.5, 129.3, 127.5, 127.4, 117.6, 114.8, 114.1, 113.9, 113.8, 113.8, 109.0, 108.4, 100.9, 100.8, 98.5, 98.5, 77.9, 72.8, 55.3, 55.3, 55.2, 55.2, 42.7, 40.6, 39.6, 38.3; IR (ATR) (mixture): 2918, 1612, 1476, 1253, 1146, 1030, 830, 543 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{23}O_5$ ([M + H]$^+$): 391.1540, found: 391.1523.

(6S,8R*)- and (6R*,8R*)-6-(4-Ethoxyphenyl)-8-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]-chromene (**3b**).* 4-Ethoxystyrene (18.5 mg, 0.125 mmol), *o*-quinone methide **1a** (93.0 mg, 0.363 mmol), **TXT** (0.74 mg, 0.00133 mmol), and AcOEt (2.0 mL) were used. Yellow oil (50.6 mg, >99% yield, dr 2.5:1). ^{1}H NMR (500 MHz, $CDCl_3$) (major): δ 7.36 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.46 (s, 1H), 6.21 (s, 1H), 5.82 (dd, J = 8.5, 1.5 Hz, 2H), 5.05 (d, J = 10.5 Hz, 1H), 4.19 (dd, J = 11.5, 6.0 Hz, 1H), 4.03 (q, J = 7.0 Hz, 2H), 3.79 (s, 3H), 2.33−2.29 (m, 1H), 2.22−2.14 (m, 1H), 1.40 (t, J = 6.5 Hz, 3H); (minor): δ 7.22 (d, J = 9.0 Hz, 2H), 7.06 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.52 (s, 1H), 6.39 (s, 1H), 5.87 (d, J = 3.0 Hz, 2H), 4.90 (d, J = 8.5 Hz, 1H), 4.11 (dd, J = 13.0, 6.5 Hz, 1H), 4.01 (q, J = 7.0 Hz, 2H), 3.79 (s, 3H), 2.41−2.35 (m, 1H), 2.13−2.04 (m, 1H), 1.39 (t, J = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (mixture): δ 158.8, 158.6, 158.4, 158.1, 150.4, 150.2, 147.1, 146.6, 141.6, 141.5, 138.5, 136.8, 133.3, 133.1, 129.5, 129.3, 127.4, 127.4, 117.6, 114.8, 114.5, 114.4, 114.0, 113.8, 109.0, 108.4, 100.8, 100.8, 98.5, 98.5, 78.0, 72.8, 63.5, 63.5, 55.3, 42.7, 40.5, 39.6, 38.3, 29.7, 14.8, 14.8; IR (ATR) (mixture): 2963, 1610, 1477, 1260, 1091, 1032, 800 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{25}H_{25}O_5$ ([M + H]$^+$): 405.1697, found: 405.1678.

(6S,8R*)- and (6R*,8R*)-6-(4-Isopropoxyphenyl)-8-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]-chromene (**3c**).* 4-Isopropoxystyrene (20.1 mg, 0.128 mmol), *o*-quinone methide **1a** (94.4 mg, 0.369 mmol), **TXT** (0.74 mg, 0.00142 mmol), and AcOEt (2.0 mL) were used. Yellow oil (45.9 mg, 72% yield, dr 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) (major): δ 7.35 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.86−6.83 (m, 2H), 6.46 (s, 1H), 6.21 (s, 1H), 5.83 (dd, J = 8.5, 1.5 Hz, 2H), 5.04 (dd, J = 11.0, 1.0 Hz, 1H), 4.57−4.49 (m, 1H), 4.19 (dd, J = 12.0, 6.0 Hz, 1H), 3.79 (s, 3H), 2.34−2.29 (m, 1H), 2.22−2.15 (m, 1H), 1.33 (s, 3H), 1.32 (s, 3H); (minor): δ 7.21 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 6.86−6.83 (m, 4H), 6.52 (s, 1H), 6.39 (s, 1H), 5.87 (dd, J = 4.0, 1.0 Hz, 2H), 4.89 (dd, J = 11.0, 2.5 Hz, 1H), 4.57−4.49 (m, 1H), 4.07 (dd, J = 5.5, 3.0 Hz, 1H), 3.79 (s, 3H), 2.42−2.37 (m, 1H), 2.13−2.09 (m, 1H), 1.32 (s, 3H), 1.30 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (mixture): δ 158.4, 158.1, 157.7, 157.5, 150.4, 150.2, 147.0,

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146.6, 141.6, 141.5, 138.5, 136.8, 133.2, 133.0, 129.5, 129.3, 127.5, 127.4, 117.6, 115.9, 115.7, 114.7, 114.0, 113.8, 108.9, 108.4, 101.3, 100.8, 100.7, 98.5, 98.4, 77.9, 72.8, 69.9, 69.8, 55.2, 42.7, 40.5, 39.6, 38.2, 22.0; IR (ATR) (mixture): 2976, 1610, 1477, 1242, 1146, 1035, 829 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{26}H_{26}O_5$ ($[M + H]^+$): 419.1853, found: 419.1834.

(6S,8R*)- and (6R*,8R*)-6-(4-(tert-Butyldimethyl-silyloxy)-phenyl)-8-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]-dioxolo[4,5-g]-chromene (**3d**).* 4-(*tert*-Butyldimethylsiloxy)styrene (30.0 mg, 0.128 mmol), *o*-quinone methide **1a** (97.4 mg, 0.380 mmol), **TXT** (0.73 mg, 0.00131 mmol), and AcOEt (2.0 mL) were used. Yellow oil (55.2 mg, 88% yield, dr 4:1). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.47 (s, 1H), 6.21 (s, 1H), 5.83 (dd, *J* = 8.5, 1.0 Hz, 2H), 5.05 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.17 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.79 (s, 3H), 2.33−2.29 (m, 1H), 2.20−2.13 (m, 1H), 0.98 (s, 9H), 0.19 (s, 6H); (minor): δ 7.17 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.53 (s, 1H), 6.39 (s, 1H), 5.88 (dd, *J* = 4.5, 1.5 Hz, 2H), 4.89 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.06 (dd, *J* = 5.0, 3.0 Hz, 1H), 3.79 (s, 3H), 2.40−2.35 (m, 1H), 2.12−2.10 (m, 1H), 0.97 (s, 9H), 0.18 (s, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.4, 158.1, 155. 5, 155.3, 150.4, 150.2, 147.1, 146.6, 141.6, 141.5, 138.5, 136.8, 134.0, 133.9, 129.5, 129.3, 127.3, 127.3, 120.1, 119.9, 117.7, 114.8, 114.1, 113.8, 109.0, 108.4, 100.9, 100.8, 98.6, 98.5, 78.0, 72.9, 55.3, 42.7, 40.7, 39.6, 38.3, 29.7, 25.7, 25.5, 18.2, −4.44; IR (ATR) (mixture): 2929, 1509, 1247, 1146, 1037, 910, 830, 780 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{29}H_{35}O_5Si$ ($[M + H]^+$): 491.2248, found: 491.2239.

(6S,8R*)- and (6R*,8R*)-6-(4-(Benzyloxy)phenyl)-8-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]-chromene (**3e**).* 4-(Benzyloxy)styrene (24.1 mg, 0.115 mmol), *o*-quinone methide **1a** (97.8 mg, 0.382 mmol), **TXT** (0.75 mg, 0.00133 mmol), and AcOEt (2.0 mL) were used. Yellow oil (18.3 mg, 34% yield, dr 4:1; 35 mg, 60% yield, dr 4:1 (5.0 mol % of **TXT**)). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.43−7.35 (m, 7H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 13.5 Hz, 2H), 6.45 (s, 1H), 6.21 (s, 1H), 5.83 (dd, *J* = 8.5, 2.0 Hz, 2H), 5.07 (s, 2H), 5.05 (s, 1H), 4.19 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.79 (s, 3H), 2.33−2.29 (m, 1H), 2.21−2.16 (m, 1H); (minor); δ 7.43−7.35 (m, 5H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 13.5 Hz, 2H), 6.52 (s, 1H), 6.39 (s, 1H), 5.88 (dd, *J* = 8.5, 2.0 Hz, 2H), 5.07 (s, 2H), 4.90 (d, *J* = 8.0 Hz, 2H), 4.06 (dd, *J* = 5.5, 3.0 Hz, 1H), 3.79 (s, 3H), 2.38−2.35 (m, 1H), 2.14−2.12 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.6, 158.4, 158.4, 158.1, 150.4, 150.2, 147.1, 146.6, 141.6, 141.5, 138.4, 136.9, 136.8, 133.7, 133.6, 129.5, 129.3, 129.1, 128.7, 128.6, 127.9, 127.5, 127.4, 117.6, 114.9, 114.8, 114.7, 114.0, 113.8, 109.0, 108.4, 100.9, 100.8, 98.5, 98.5, 77.9, 72.8, 70.0, 70.0, 55.3, 42.7, 40.6, 39.6, 38.3, 29.7, 29.3; IR (ATR) (mixture): 2920, 1608, 1509, 1244, 1146, 1034, 827 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{30}H_{27}O_5$ ($[M + H]^+$): 467.1853, found: 467.1831.

(6S,8R*)- and (6R*,8R*)-6-(3,4-bis(Benzyloxy)phenyl)-8-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]-chromene (**3f**).* 1,2-bis(Benzyloxy)-4-vinylbenzene (39.6 mg, 0.125 mmol), *o*-quinone methide **1a** (98.3 mg, 0.384 mmol), **TXT** (0.71 mg, 0.00128 mmol), and AcOEt (2.0 mL) were used. White solid (32.9 mg, 46% yield, dr 2.5:1; 72.0 mg, >99% yield, dr 2.5:1 (5.0 mol % of **TXT**)). ^1H NMR (500 MHz, $CDCl_3$): δ 7.46−7.29 and 7.12−6.79 (m, 17H) (mixture), 6.51 (s, 1H) (minor), 6.45 (s, 1H) (major), 6.37 (s, 1H) (minor), 6.21 (s, 1H) (major), 5.88 (dd, *J* = 3.0, 1.5 Hz, 2H) (minor), 5.83 (dd, *J* = 9.5, 1.5 Hz, 1H) (major), 5.17−5.12 (m, 4H) (mixture), 5.00 (dd, *J* = 11.0, 1.0 Hz, 1H) (major), 4.86 (dd, *J* = 10.5, 2.0 Hz, 1H) (minor), 4.16 (dd, *J* = 12.0, 6.0 Hz, 1H) (major), 4.02 (dd, *J* = 5.0, 3.5 Hz, 1H) (minor), 3.79 (s, 3H) (mixture), 2.35−2.31 (m, 1H) (minor), 2.30−2.26 (m, 1H) (major), 2.16−2.10 (m, 1H) (major), 2.09−2.06 (m, 1H) (minor); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.4, 158.1, 150.2, 150.0, 149.1, 149.0, 148.8, 148.6, 147.1, 146.6, 141.6, 141.5, 138.3, 137.3, 137.2, 137.2, 136.7, 134.7, 134.5, 129.5, 129.3, 128.4, 128.4, 127.8, 127.8, 127.7, 127.5, 127.4, 127.2, 119.4, 119.2, 117.6, 115.1, 115.0, 114.8, 114.3, 114.0, 113.8, 113.3, 109.0, 108.4, 100.9, 100.8, 98.5, 98.5, 78.0, 72.9, 71.5, 71.4, 71.4, 71.3, 55.3, 42.6, 40.6, 39.4, 38.2, 29.7, 29.6, 22.7, 22.6, 14.2, 14.1; IR (ATR) (mixture): 2919, 1509, 1477, 1259, 1146, 1091, 1033, 804 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{37}H_{32}O_6Na$ ($[M + Na]^+$): 595.2091, found: 595.2109.

(6S,8R*)- and (6R*,8R*)-6-(3,4-Dimethoxyphenyl)-8-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]-chromene (**3g**).* 3,4-Dimethoxystyrene (19.3 mg, 0.118 mmol), *o*-quinone methide **1a** (97.8 mg, 0.382 mmol), **TXT** (0.78 mg, 0.0014 mmol), and AcOEt (2.0 mL) were used. Yellow oil (50.1 mg, >99% yield, dr 4:1). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.13 (d, *J* = 9.0 Hz, 2H), 6.99−6.98 (m, 1H), 6.88−6.83 (m, 4H), 6.48 (s, 1H), 6.22 (s, 1H), 5.84 (dd, *J* = 8.5, 1.5 Hz, 2H), 5.06 (dd, *J* = 11.0, 1.5 Hz, 1H), 4.21 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.80 (s, 3H), 2.35−2.31 (m, 1H), 2.23−2.17 (m, 1H); (minor): δ 7.07 (d, *J* = 9.0 Hz, 2H), 6.99−6.98 (m, 3H), 6.88−6.83 (m, 2H), 6.54 (s, 1H), 6.40 (s, 1H), 5.89 (dd, *J* = 4.5, 1.0 Hz, 2H), 4.89 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.09 (dd, *J* = 6.0, 3.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 2.43−2.39 (m, 1H), 2.14−2.11 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.4, 158.1, 150.3, 150.1, 149.1, 148.9, 148.8, 148.6, 147.1, 146.6, 141.6, 141.5, 138.4, 136.7, 133.8, 133.6, 129.5, 129.3, 118.6, 118.5, 117.6, 114.7, 114.0, 113.7, 111.0, 111.0, 109.5, 109.3, 109.0, 108.3, 100.9, 100.8, 98.5, 98.5, 78.2, 73.0, 55.9, 55.9, 55.8, 55.8, 55.2, 42.7, 40.6, 39.6, 38.3; IR (ATR) (mixture): 2930, 1609, 1477, 1240, 1144, 1027, 831 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{25}H_{25}O_6$ ($[M + H]^+$): 421.1646, found: 421.1625.

(6S,8R*)- and (6R*,8R*)-6-(2,4-Dimethoxyphenyl)-8-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]-chromene (**3h**).* 2,4-Dimethoxystyrene (20.6 mg, 0.125 mmol), *o*-quinone methide **1a** (98.6 mg, 0.385 mmol), **TXT** (0.79 mg, 0.0014 mmol), and AcOEt (2.0 mL) were used. Yellow oil (53.8 mg, >99% yield, dr 10:1). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.46 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.84 (m, 2H), 6.53 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.46 (s, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 6.21 (s, 1H), 5.82 (d, *J* = 8.0 Hz, 2H), 5.43 (d, *J* = 11.5 Hz, 1H), 4.20 (dd, *J* = 12.5, 6.0 Hz, 1H), 3.80 (s, 6H), 3.78 (s, 3H), 2.36−2.31 (m, 1H), 2.08−2.01 (m, 1H); (minor): δ 7.32 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.84 (m, 2H), 6.49 (d, *J* = 2.5 Hz, 1H), 6.46 (s, 1H), 6.40 (d, *J* = 2.0 Hz, 1H), 6.38 (s, 1H), 5.86 (d, *J* = 4.0 Hz, 2H), 5.29 (d, *J* = 7.5 Hz, 1H), 4.12 (dd, *J* = 9.5, 5.0 Hz, 1H), 3.79 (s, 6H), 3.63 (s, 3H), 2.30−2.27 (m, 1H), 2.20−2.16 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 160.4, 160.2, 158.3, 158.0, 157.1, 157.0, 150.7, 150.4, 146.9, 146.5, 141.3, 141.3, 138.2, 137.0, 129.5, 129.3, 127.2, 127.1, 122.3, 122.2, 117.9, 115.4, 113.9, 113.6, 109.0, 108.4, 104.4, 104.1, 100.8, 100.7, 98.5, 98.4, 72.3, 68.5, 60.3, 55.4, 55.3, 55.3, 55.3, 55.2, 42.7, 39.5, 39.4, 36.6, 29.7; IR (ATR) (mixture): 2959, 1612, 1477, 1247, 1148, 1035, 830 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{25}H_{24}O_6$ ($[M + H]^+$): 421.1646, found: 421.1625.

(6S,8R*)- and (6R*,8R*)-8-(4-Methoxyphenyl)-6-(2,3,4-trimethoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]-chromene (**3i**).* 2,3,4-Trimethoxystyrene (21.3 mg, 0.110 mmol), *o*-quinone methide **1a** (98.0 mg, 0.383 mmol), **TXT** (0.85 mg, 0.00153 mmol), and AcOEt (2.0 mL) were used. White solid (32.7 mg, 66% yield, dr 2:1). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.21 (d, *J* = 9.0 Hz, 1H), 7.14−7.11 (m, 2H), 6.85 (m, 2H), 6.72 (d, *J* = 8.5 Hz, 1H), 6.45 (s, 1H), 6.22 (s, 1H), 5.83 (dd, *J* = 9.5, 1.5 Hz, 2H), 5.38 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.22 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.79 (s, 3H), 2.33−2.28 (m, 1H), 2.16−2.14 (m, 1H); (minor): δ 7.12 (m, 1H), 7.09 (d, *J* = 9.0 Hz, 2H), 6.85 (m, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.51 (s, 1H), 6.43 (s, 1H), 5.88 (s, 2H), 5.20 (dd, *J* = 11.0, 2.0 Hz, 1H), 4.06 (dd, *J* = 5.5, 3.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.79 (s, 3H), 3.59 (s, 3H), 2.37−2.33 (m, 1H), 2.13−2.11 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.3, 158.0, 153.4, 153.2, 151.1, 150.9, 150.5, 150.4, 147.0, 146.5, 142.0, 142.0, 141.5, 141.4, 138.5, 136.9, 129.4, 129.3, 127.5, 127.2, 121.1, 117.8, 115.0, 114.0, 113.6, 109.1, 108.4, 107.5, 107.4, 100.8, 100.7, 98.5, 98.4, 72.8, 68.3, 61.4, 60.9, 60.7, 60.7, 56.0, 55.9, 55.2, 55.2, 42.8, 39.9, 39.8, 37.6; IR (ATR) (mixture): 2962,

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1607, 1477, 1260, 1092, 1034, 801 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{26}H_{27}O_7$ ($[M + H]^+$): 451.1751, found: 451.1761.

(6S,8R*)- and (6R*,8R*)-8-(4-Methoxyphenyl)-6-(2,4,6-trimethoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]-chromene (**3j**).* 2,4,6-Trimethoxystyrene (21.6 mg, 0.111 mmol), *o*-quinone methide **1a** (94.7 mg, 0.369 mmol), **TXT** (0.78 mg, 0.0014 mmol), and AcOEt (2.0 mL) were used. White solid (35.0 mg, 70% yield, dr 1.5:1). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.15 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.43 (s, 1H), 6.19 (s, 1H), 6.15 (s, 2H), 5.80 (dd, J = 10.0, 1.5 Hz, 2H), 5.70 (dd, J = 11.5, 2.0 Hz, 1H), 4.14 (dd, J = 12.0, 6.0 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.68 (s, 3H), 3.01−2.93 (m, 1H), 2.06−2.02 (m, 1H); (minor): δ 7.09 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 6.49 (s, 1H), 6.44 (s, 1H), 6.09 (s, 2H), 5.85 (s, 2H), 5.51 (dd, J = 12.0, 2.0 Hz, 1H), 4.11 (d, J = 5.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.68 (s, 3H), 3.16−3.10 (m, 1H), 1.84−1.81 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 161.2, 161.1, 160.1, 160.0, 158.2, 157.8, 151.3, 151.2, 146.8, 146.3, 141.0, 140.9, 139.1, 137.4, 129.5, 129.4, 118.2, 115.0, 113.9, 113.5, 109.4, 109.2, 109.2, 108.4, 100.7, 100.6, 98.6, 98.6, 91.5, 91.4, 71.0, 65.9, 56.0, 55.9, 55.3, 55.3, 55.2, 55.2, 43.4, 40.6, 36.1, 34.0; IR (ATR) (mixture): 2932, 1593, 1475, 1146, 1035, 940, 811, 608 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{26}H_{27}O_7$ ($[M + H]^+$): 451.1751, found: 451.1743.

*rac-6,6,8-tris(4-Methoxyphenyl)-7,8-dihydro-6H-[1,3]-dioxolo-[4,5-g]chromene (**3k**).* 1,1-Bis(4-methoxyphenyl)ethylene (30.2 mg, 0.125 mmol), *o*-quinone methide **1a** (96.5 mg, 0.375 mmol), **TXT** (0.79 mg, 0.00142 mmol), and AcOEt (2.0 mL) were used. Yellow solid (58.4 mg, 94% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 9.0 Hz, 2H), 7.09 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.5 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 9.5 Hz, 2H), 6.62 (s, 1H), 6.06 (s, 1H), 5.80 (dd, J = 14.0, 1.0 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.74 (s, 3H), 3.71 (dd, J = 12.5, 6.0 Hz, 1H), 2.93 (dd, J = 14.0, 5.5 Hz, 1H), 2.50 (dd, J = 14.0, 12.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 158.7, 158.4, 158.4, 148.9, 146.7, 141.4, 138.4, 136.6, 135.5, 129.6, 127.5, 127.0, 117.3, 114.0, 113.9, 113.5, 108.2, 100.8, 98.7, 81.6, 55.3, 55.2, 55.1, 42.4, 39.5; IR (ATR): 2957, 1508, 1477, 1243, 1175, 1033, 828 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{31}H_{29}O_6$ ($[M + H]^+$): 497.1959, found: 497.1953.

(6S,8R*)- and (6R*,8R*)-6,8-bis(4-Methoxyphenyl)-6-phenyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (**3l**).* 1-(4-Methoxyphenyl)-1-phenylethylene (25.5 mg, 0.121 mmol), *o*-quinone methide **1a** (98.9 mg, 0.386 mmol), **TXT** (0.77 mg, 0.00138 mmol), and AcOEt (2.0 mL) were used. Yellow oil (32.0 mg, 57% yield, dr 1:1; 46.6 mg, 80% yield, dr 1:1 (5.0 mol % of **TXT**)). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47−7.39 (m, 3H) (mixture), 7.36−7.18 (m, 4H) (mixture), 7.10−7.07 (m, 2H) (mixture), 6.87−6.79 (m, 2H) (mixture), 6.07 and 6.05 (s, 1H) (mixture), 5.81 and 5.78 (s, 2H) (mixture), 3.78 (s, 3H) (mixture), 3.76 and 3.74 (s, 3H) (mixture), 3.68−3.65 and 0.95−0.87 (m, 1H) (mixture), 3.00−2.97 and 2.55−2.47 (m, 2H) (mixture); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.7, 158.5, 158.4, 148.9, 148.8, 146.8, 146.7, 146.1, 143.6, 141.4, 141.4, 138.0, 136.6, 135.3, 132.5, 131.9, 129.7, 129.6, 128.5, 128.2, 127.5, 127.2, 127.0, 126.9, 126.2, 125.6, 117.4, 117.3, 114.0, 113.9, 113.5, 113.4, 108.2, 108.2, 100.7, 98.7, 98.6, 81.8, 81.7, 60.4, 55.4, 55.2, 55.2, 55.1, 42.3, 42.1, 39.5, 39.4; IR (ATR) (mixture): 2963, 1509, 1262, 1097, 1023, 801, 691 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{30}H_{27}O_5$ ($[M + H]^+$): 467.1853, found: 467.1840.

(6S,8R*)- and (6R*,8R*)-6-Ethoxy-8-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (**3o**).* Ethyl vinyl ether (9.0 mg, 0.125 mmol), *o*-quinone methide **1a** (98.3 mg, 0.384 mmol), **TXT** (0.69 mg, 0.00124 mmol), and AcOEt (2.0 mL) were used. White solid (17.8 mg, 44% yield, dr 10:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.13−7.11 (m, 2H) (minor), 7.10−7.08 (m, 2H) (major), 6.87−6.86 (m, 2H) (minor), 6.86−6.83 (m, 2H) (major), 6.43 (s, 1H) (major), 6.41 (s, 1H) (minor), 6.19 (s, 1H) (minor), 6.15 (s, 1H) (major), 5.83−5.81 (m, 2H) (mixture), 5.22 (t, J = 2.86 Hz, 1H) (minor), 5.17 (dd, J = 8.3, 2.6 Hz, 1H) (major), 4.07−4.00 (m, 2H) (mixture), 3.79 (s, 3H) (mixture), 3.67−3.61 (m, 1H) (mixture), 2.33 (ddd, J = 13.3, 6.2, 2.3 Hz, 1H) (major), 2.19 (ddd, J = 13.3, 5.9, 3.2 Hz, 1H) (minor), 2.12−2.04 (m, 1H) (mixture), 1.26 (t, J = 7.2 Hz, 3H) (major), 1.21 (t, J = 7.2 Hz, 3H) (minor); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.4, 147.9, 146.7, 146.6, 146.5, 141.8, 136.7, 136.3, 129.6, 129.4, 128.0. 118.1, 118.0, 114.0, 113.9, 110.7, 108.4, 108.0, 100.9, 99.6, 98.7, 98.5, 96.5, 64.3, 63.8, 55.2, 40.5, 37.6, 36.5, 36.1, 15.2; IR (ATR) (mixture): 2907, 1613, 1477, 1248, 1136, 1035, 905 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{19}H_{21}O_5$ ($[M + H]^+$): 329.1384, found: 329.1375.

(6S,8R*)- and (6R*,8R*)-8-(4-Methoxyphenyl)-6-phenoxy-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (**3p**).* Vinyloxybenzene (15.5 mg, 0.129 mmol), *o*-quinone methide **1a** (95.3 mg, 0.372 mmol), 5.0 mol % of **TXT** (3.53 mg, 0.00634 mmol), and AcOEt (2.0 mL) were used. White solid (21.3 mg, 44% yield, dr 2.5:1). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.33−7.26 (m, 2H), 7.20−7.01 (m, 5H), 6.88−6.86 (m, 2H), 6.45 (s, 1H), 6.23 (s, 1H), 5.89−5.85 (m, 1H), 5.85 (s, 2H), 4.13 (dd, J = 9.8, 6.6 Hz, 1H), 3.82 (s, 3H), 2.56−2.49 (m, 1H), 2.40−2.33 (m, 1H); (minor): δ 7.33−7.26 (m, 2H), 7.20−7.01 (m, 5H), 6.90 (m, 2H), 6.40 (s, 1H), 6.22 (s, 1H), 5.85 (s, 2H), 5.80 (m, 1H), 4.33 (dd, J = 11.8, 5.5 Hz, 1H), 3.82 (s, 3H), 2.44−2.40 (m, 1H), 2.23−2.16 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.5, 158.4, 156.7, 157.0, 147.2, 146.9, 146.7, 145.9, 142.2, 142.0, 136.1, 129.7, 129.6, 129.5, 129.4, 122.4, 122.3, 117.9, 117.7, 117.1, 116.6, 114.1, 113.9, 108.2, 108.1, 101.0, 100.9, 98.9, 98.7, 97.0, 95.2, 55.3, 39.7, 36.9, 36.2, 36.0; IR (ATR) (mixture): 1477, 1237, 1146, 1034, 916, 754 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{23}H_{21}O_5$ ($[M + H]^+$): 377.1384, found: 377.1365.

(2S,4R*)- and (2R*,4R*)-6,7-Dimethoxy-4-(4-methoxy-phenyl)-2-phenoxychromane (**3q**).* Vinyloxybenzene (15.8 mg, 0.131 mmol), 3,4-dimethoxy-6-(4-methoxyphenylmethylidene)cyclohexa-2,4-dien-1-one (102.7 mg, 0.39 mmol), 5.0 mol % of **TXT** (3.83 mg, 0.00690 mmol), and AcOEt (2.0 mL) were used. White solid (23.1 mg, 45% yield, dr 4:1). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.34−7.28 (m, 2H), 7.15 (d, J = 8.5 Hz, 2H), 7.14−7.00 (m, 3H), 6.89−6.85 (m, 2H), 6.49 (s, 1H), 6.29 (s, 1H), 5.92−5.87 (m, 1H), 4.19 (dd, J = 9.5, 6.6 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.63 (s, 3H), 2.55−2.51 (m, 1H), 2.41−2.35 (m, 1H); (minor): δ 7.34−7.28 (m, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.14−7.00 (m, 3H), 6.90 (m, 2H), 6.44 (s, 1H), 6.27 (s, 1H), 5.92−5.87 (m, 1H), 4.37 (dd, J = 11.7, 6.0 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.61 (s, 3H), 2.43−2.41 (m, 1H), 2.23−2.17 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 158.4, 158.3, 157.0, 156.7, 148.9, 148.7, 145.5, 146.5, 143.7, 143.5, 136.3, 136.2, 129.7, 129.5, 129.4, 122.3, 122.2, 117.0, 116.4, 115.9, 114.0, 113.8, 112.1, 112.0, 101.0, 100.9, 96.8, 95.1, 56.3, 55.9, 55.8, 55.2, 39.4, 37.1, 36.4, 35.9; IR (ATR) (mixture): 1509, 1219, 1123, 1020, 918, 728 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{24}H_{24}O_5Na$ ($[M + Na]^+$): 415.1516, found: 415.1511.

(2S,4R*)- and (2R*,4R*)-6,7-Dimethoxy-2,4-bis(4-methoxyphenyl)chromane (**3r**).* 4-Methoxystyrene (16.0 mg, 0.120 mmol), 3,4-dimethoxy-6-(4-methoxyphenylmethylidene)cyclohexa-2,4-dien-1-one (103.6 mg, 0.380 mmol), **TXT** (0.88 mg, 0.00158 mmol), and AcOEt (2.0 mL) were used. White solid (35.7 mg, 71% yield, dr 3:1). ^1H NMR (500 MHz, $CDCl_3$) (major): δ 7.39 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.87−6.85 (m, 2H), 6.51 (s, 1H), 6.27 (s, 1H), 5.08 (dd, J = 11.5, 1.0 Hz, 1H), 4.27 (dd, J = 12.0, 6.0 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.61 (s, 3H), 2.34−2.30 (m, 1H), 2.23−2.15 (m, 1H); (minor): δ 7.25 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 6.87−6.85 (m, 4H), 6.53 (s, 1H), 6.46 (s, 1H), 4.89 (dd, J = 11.0, 2.0 Hz, 1H), 4.13 (dd, J = 5.5, 2.5 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.72 (s, 3H), 2.46−2.40 (m, 1H), 2.13−2.09 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) (mixture): δ 159.4, 159.2, 158.3, 158.0, 149.7, 149.5, 148.9, 148.6, 143.3, 143.1, 138.5, 136.7, 133.4, 133.3, 129.5, 129.3, 127.5, 127.4, 116.3, 113.9, 113.9, 113.8, 113.7, 113.5, 112.9, 112.5, 100.8, 100.7, 77.9, 72.7, 56.4, 56.3, 55.8, 55.3, 55.2, 55.2, 55.2, 42.3, 40.9, 39.3, 38.6; IR (ATR) (mixture): 2835, 1610, 1508, 1246, 1169, 1024, 829 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{25}H_{27}O_5$ ($[M + H]^+$): 407.1853, found: 407.1835.

(2S,4R*)- and (2R*,4R*)-6,7-Diethoxy-2,4-bis(4-methoxyphenyl)chromane (**3s**).* 4-Methoxystyrene (17.8 mg, 0.133 mmol), 3,4-diethoxy-6-(4-methoxyphenylmethylidene)cyclohexa-2,4-dien-1-one (113 mg, 0.375 mmol), **TXT** (0.81 mg, 0.00146 mmol),

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and AcOEt (2.0 mL) were used. Yellow solid (33.0 mg, 55% yield, dr 3:1, 50.0 mg, 93% yield, dr 3:1 (5.0 mol % of **TXT**)). ^{1}H NMR (500 MHz, $CDCl_3$) (major): δ 7.38 (d, J = 9.0 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.87−6.83 (m, 2H), 6.49 (s, 1H), 6.30 (s, 1H), 5.08 (dd, J = 11.5, 1.5 Hz, 1H), 4.22 (dd, J = 12.0, 6.0 Hz, 1H), 4.07−4.01 (m, 2H), 3.87−3.82 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.33 (m, 1H), 2.22−2.14 (m, 1H), 1.42 (t, J = 7.5 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H); (minor): δ 7.25 (d, J = 9.0 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 6.87−6.83 (m, 4H), 6.55 (s, 1H), 6.49 (s, 1H), 4.88 (dd, J = 10.5, 2.0 Hz, 1H), 4.10 (dd, J = 5.5, 2.5 Hz, 1H), 4.07−4.01 (m, 2H), 3.95−3.90 (m, 1H), 3.79 (s, 3H), 3.78 (m, 3H), 2.45−2.39 (m, 1H), 2.12−2.09 (m, 1H), 1.45 (t, J = 7.5 Hz, 3H), 1.34 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (mixture): δ159.4, 159.2, 158.3, 158.0, 150.0, 149.8, 148.9, 148.8, 142.7, 142.4, 138.6, 136.9, 133.6, 133.4, 129.5, 129.3, 127.5, 127.4, 116.5, 116.0, 115.9, 114.3, 114.1, 113.9, 113.8, 113.7, 103.2, 102.1, 102.0, 77.9, 72.7, 65.6, 65.4, 64.2, 64.1, 55.3, 55.2, 55.2, 42.3, 40.9, 39.2, 38.6, 14.9, 14.8, 14.7; IR (ATR) (mixture): 2928, 1602, 1509, 1245, 1173, 1031, 825 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{27}H_{31}O_5$ ([M + H]$^+$): 435.2166, found: 435.2148.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b01156.

Crystallography data for **3a** (CIF)

Characterization for TXT catalyst, photophysical and redox properties of TXT and representative substrates, Stern−Volmer plot of TXT, reaction quantum yield, NMR spectra of new compounds, detailed crystallography, and detailed experimental procedures (PDF)

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Notes

The authors declare no competing financial interest.

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