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ARTICLE

Divergent cyclodimerizations of styrylnaphthols under aerobic visible-light irradiation and Brønsted acid catalysis

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The dimeric cyclization reaction offers great potential to rapidly form highly substituted complex cyclic molecules from a simple starting material. However, such appealing process is often hampered by the lack of selectivity. Herein we report two divergent cyclodimerization reactions of 1-styrylnaphthalen-2-ol derivatives under simple and very mild reaction conditions. A stereoselective visible light-induced oxidative (1+1+4+4) homodimerization gave rise to highly substituted 1,5-dioxocanes in decent yields. This transformation harnessed singlet oxygen as safe and mild oxidant under photocatalyst-free reaction conditions. Additionally, we demonstrated that the same substrates undergo a (4+2) heterodimerization under Brønsted-acid catalysis to produce chromane derivatives featuring 3 contiguous tertiary stereocenters in good to high yields and excellent diastereoselectivities.

Introduction

The development of efficient divergent synthetic methods for the construction of structurally diverse molecules from a common, readily accessible starting material is of high interest to the synthetic community.¹ In addition, the cyclodimerizations of olefins are one of the most attractive approaches to rapidly access to divergent complex cyclic frameworks. For instance, these processes are often proposed as biosynthetic pathway leading to a variety of biologically active natural homodimers and heterodimers.^{2,3} Furthermore, they are valuable synthetic methods for the synthesis of structurally appealing unnatural complex cyclic dimeric molecules.⁴ Stilbene derivatives are relevant compounds in cyclodimerizations. However, their reactions often result in the formation of mixtures of compounds due to their high reactivity and tendency to oligomerize. For example, the oligomerization of resveratrol (trihydroxystilbene) and its natural analogues provided more than one hundred architecturally-diverse biologically-active natural oligomeric products.⁵ Generally, the biomimetic synthetic approach based on one-electron oxidative dimerization of resveratrol derivatives led to low yields⁶ and/or complex mixture of products.^{7,8} Similar difficulties have been also encountered during the synthesis of unnatural dimeric stilbenes.⁹ For instance, Faizal Weber *et al.* have revealed that the oxidative dimerization of resveratrol analogues was dependent on the choice of solvent and metal oxidant providing diverse unnatural dimeric compounds in low yields.^{9a} Similarly, Kam *et al.* have demonstrated that the electrochemical

oxidative dimerization of 1,2-diarylethylenes furnished oligomers featuring varied carbon skeletons depending on the aromatic substitution.^{9b} As such, the dimerization of 1,2-diarylethylene derivatives into a single dimeric product is still challenging issue. In this communication, we report unexpected stereoselective and divergent cyclodimerizations of styrylnaphthols that produce selectively two different complex O-containing heterocyclic compounds depending on the conditions used. A first photoinduced procedure harnessed molecular oxygen as an abundant, green, and safe oxidant to promote a highly stereoselective (1+1+4+4) homodimerization reaction affording 1,5-dioxocanes. A second protocol employed a simple Brønsted acid to catalyze an unprecedented (4+2) heterodimerization leading to relevant chromane derivatives featuring three contiguous stereocenters in good to excellent yields and in diastereomeric pure form.

Results and discussion

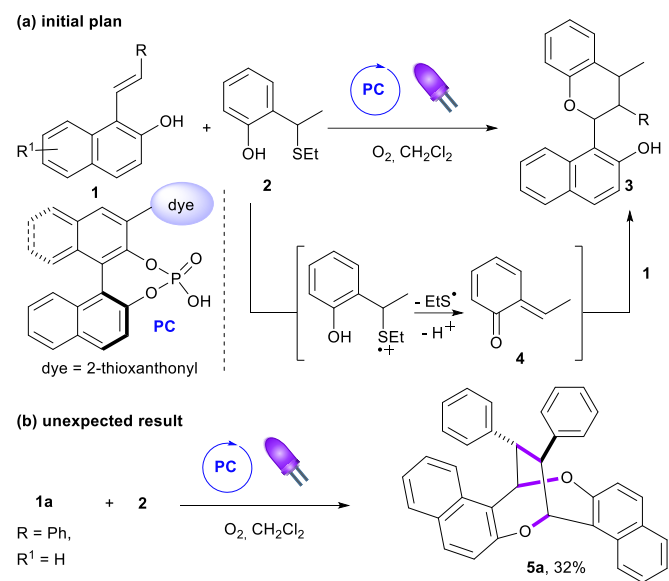
As part of our continuing interest in the construction of cyclic compounds through either photocatalysis¹⁰ or Brønsted acid catalysis,¹¹ we initially envisioned the catalytic enantioselective synthesis of polysubstituted chromane **3a** via the reaction of 1-styrylnaphthalen-2-ol **1a** with 2-hydroxybenzylthioether **2** using our recently designed chimeric photo-Brønsted acid catalyst **PC** (Scheme 1a).¹² Our original working hypothesis relied on the oxidative photocatalytic C–S bond cleavage of **2a**^{10c,13} to *in-situ* generate ortho-quinone methide **4** which could further undergo a Brønsted acid-catalyzed oxa-Diels Alder type reaction with **1a**.¹⁴ Surprisingly, under visible light irradiation (405 nm) and an oxygen atmosphere in dichloromethane, **3a** was not formed and only the diastereomerically pure product **5a** was isolated in 32% yield (Scheme 1b). Its structure was established to be a homodimer having an interesting dioxo-eight-membered ring, *i.e.* 1,5-dioxocane, as a central motif. Such framework has been

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found in several naturally occurring products such as Luisol A¹⁵ and withametelinol-A and B¹⁶ or in bioactive compounds like various penicillide derivatives.¹⁷ Recently, Zhou and Chen *et al.* reported an efficient synthesis of these complex products **5** through a copper-catalyzed oxidative (1+1+4+4) dimerization of 1-styrylnaphthols using stoichiometric amount of Selectfluor as terminal oxidant.¹⁸ To our knowledge, such photoinduced aerobic oxidative (1+1+4+4) homodimerization of 1-styrylnaphthalen-2-ol derivatives has not been reported. This, together with the mild conditions and operational simplicity, prompted us to examine in more detail this new homodimerization methodology.



Scheme 1 Serendipitous discoveries on the dimerization of styrylnaphthols

Initial control experiments revealed that the photocatalyst **PC** was not required although irradiation at 405 nm and the presence of oxygen were both essential for this homodimerization (Table 1, entries 1-4). Pleasingly, shortening the reaction time from 6 to 10 hours improved the chemical yield to 50% (entry 5). This result indicates a slight decomposition of the product **5a** over time under the reaction conditions and that the reaction progress needs to be carefully monitored. However, a shorter reaction time (4 hours) led to lower yield of **5a**, along with formation of (**Z**)-**1a** (entry 6). This experiment shows a partial photoisomerization of the *E*-isomer to the *Z*-isomer¹⁹ and that product **5a** can be also obtained from (**Z**)-**1a** (entry 6 vs entry 5).²⁰ The concentration of the reaction mixture had a significant impact on the yields. A more concentrated or diluted reaction mixture decreased the yield (entries 7-8). A screening of solvents showed that dichloromethane was optimal (entries 9-12). To further improve the yield, various additives were also investigated (entries 13-15). A lower yield was obtained in the presence of an inorganic base (entry 13). Addition of two equivalents of triethylamine totally suppressed the homodimerization reaction and the isomer (**Z**)-**1a** was predominantly formed instead (entry 14). To our surprise, when the reaction was

conducted with two equivalents of *p*-toluenesulfonic acid (TsOH), we isolated chromane derivative **6a** in 15% yield in addition to the desired homodimer **5a** (17%, entry 15). Finally, it was found that the homodimerization reaction could be simply conducted under air instead of a balloon of oxygen (entry 16).

Table 1 Parameters optimization of the (1+1+4+4) homodimerization of **1a**^a

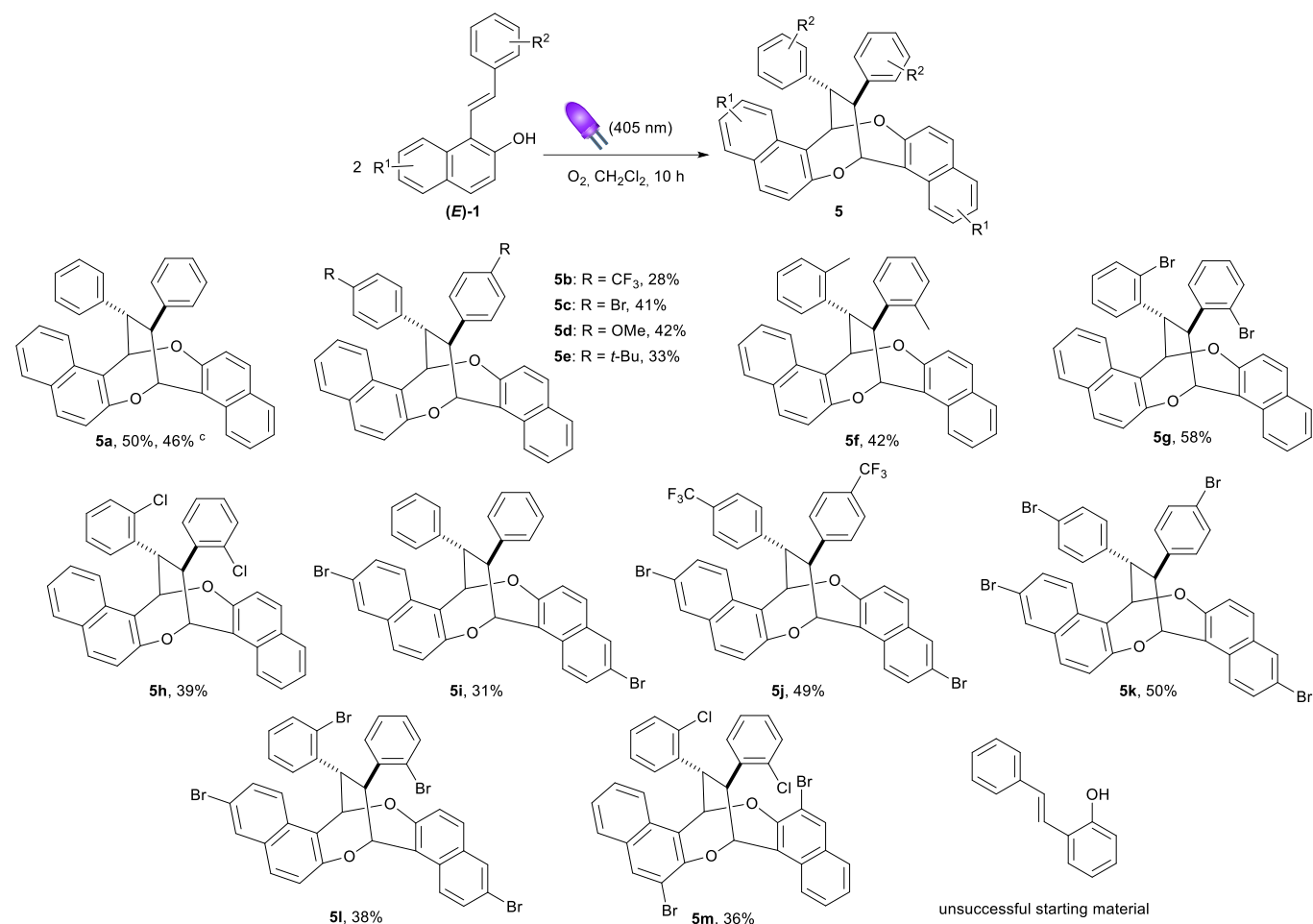
Entry	Deviation/additive (equiv)	RSM ^{b,c}	5a ^c	(Z)- 1a ^c
1	with PC (0.1)	0%	32%	0%
2	none	0	31%	0%
3	Ar instead of O ₂	100%	0%	0%
4	420 nm instead of 405 nm	100%	0%	0%
5	6 h instead of 10 h	0%	50%	0%
6	4 h instead of 10 h	0%	38%	27%
7	0.03 M instead of 0.07 M	16%	23%	28%
8	0.13 M instead of 0.07 M	0%	33%	14%
9	Entry 5 in toluene	20%	22%	28%
10	Entry 5 in dioxane	16%	5%	74%
11	Entry 5 in DMSO	0%	5%	60%
12	Entry 5 in EtOH	0%	35%	0%
13	Entry 5, with Na ₂ CO ₃ (2) ^e	18%	26%	35%
14	Entry 5, with Et ₃ N (2) ^e	12%	0%	88%
15	Entry 5, with TsOH (2) ^f	0%	17% ^d	0%
16	Entry 5, air instead of O ₂	0%	50%	0%

^a Reaction conditions: **1a** (0.1 mmol), CH₂Cl₂ (0.07 M), O₂, 405 nm, rt (internal temperature: 28 °C). ^b Recovered starting material. ^c NMR yield using 1,2-dibromoethane as internal standard. ^d 17% of **5a** along with 15% of **6a** were obtained. ^e Base additive was added to facilitate oxidation via the deprotonation of the phenol. ^f Acid additive was added to promote the cycloaddition step.

Having established suitable reaction conditions for the oxidative homodimerization of 1-styrylnaphthalen-2-ol derivatives **1**, we next examined the substrate scope (Table 2). In all cases, the desired 1,5-dioxocine derivatives **5** were obtained in moderate yields with excellent diastereoselectivities. Phenyl rings with either electron-withdrawing or electron-donating groups at the *para* position were compatible to our reaction conditions (**5b-5e**). As observed by Zhou and Chen *et al.*,¹⁸ a lower yield was nevertheless obtained with a strong electron-withdrawing substituent (**5b**). Notably, *ortho*-substituted phenyl rings were well tolerated furnishing the corresponding homodimer in up to 58% yield (**5g-5h**, **5l-5m**). In addition, substrates having a bromo-substituent at either the 3- or 6-positions of the naphthalene ring were also suitable (**5i-5m**). Unfortunately, the reaction did not proceed from styrylphenol.²¹ Finally, the

homodimerization of **1a** was conducted on 1 mmol scale affording the corresponding cyclic compound **5a** in similar yields (46%).

Table 2 Scope of the photomediated aerobic oxidative homodimerization of styrylnaphthol derivatives **1**.^{a,b}



^a Reaction conditions: **1** (0.1 mmol), CH₂Cl₂ (0.07 M), O₂, 405 nm, 6 h, rt (internal temperature: 28 °C). ^b Isolated yield. ^c Reaction conducted on 1 mmol scale.

The unexpected formation of chromane **6a** in the presence of acid inspired us to investigate its formation in detail. The exact structure of **6** was established to be a chromane scaffold containing three contiguous stereocenters in *trans-trans* configuration. Although chromanes are privileged heterocyclic compounds in medicinal chemistry, this scaffold **6** is unprecedented. Therefore, we decided to study the synthesis of novel chromanes via the (4+2) heterodimerization reaction of styrylnaphthols. Close examination of the reaction showed that light irradiation was not necessary for heterodimerization and desired product **6a** was obtained with encouraging 40% yield (Table 3, entry 2). Interestingly, the reaction could be carried out with a catalytic amount (10 mol%) of acid (entry 3). Gratefully, variation of the reaction temperature (entries 4-5) indicated a dramatic improvement on the yield (85%) at 50 °C. A rapid screening of acid catalysts led to the decomposition of the starting material with either a stronger Brønsted acid catalyst (triflic acid, entry 6) or a Lewis acid catalyst (BF₃·OEt₂, entry 7) while the starting material was totally recovered with a

weaker Brønsted acid catalyst (trifluoroacetic acid, entry 8). To our delight, a final variation of the solvent (entries 9-11) revealed that toluene was optimal delivering the desired heterodimer adduct in 99% isolated yield.²²

Table 3 Parameters optimization of the (4+2) heterodimerization of **1a**^a

Entry	Acid (equiv)	Solvent	Temp.	6a ^{b,c}
1 ^d	TsOH (2)	CH ₂ Cl ₂	rt	15%
2	TsOH (2)	CH ₂ Cl ₂	rt	40%
3	TsOH (0.1)	CH ₂ Cl ₂	rt	30%
4	TsOH (0.1)	DCE	50 °C	85%

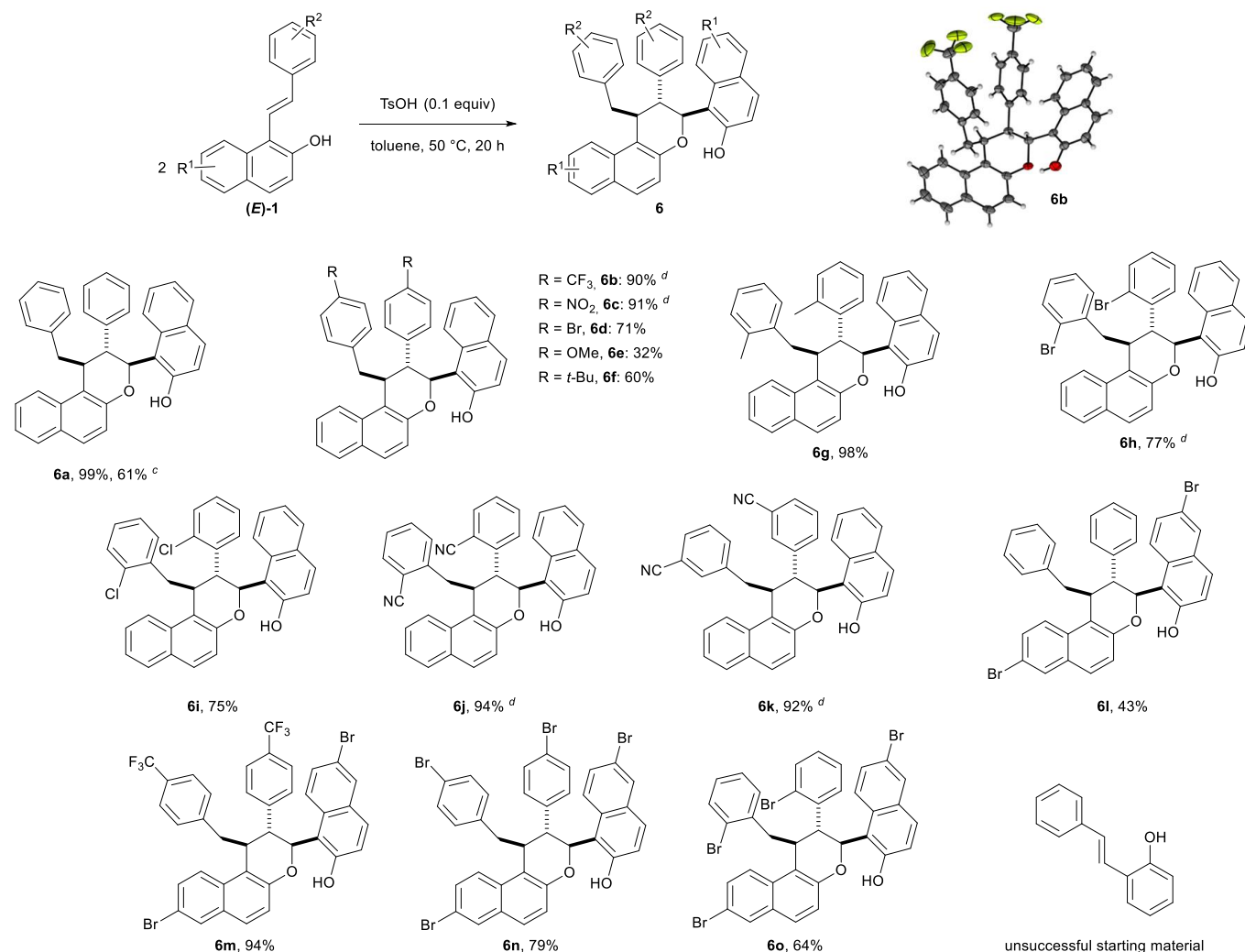
5	TsOH (0.1)	DCE	70 °C	85%
6	CF ₃ SO ₃ H (0.1)	DCE	50 °C	0%
7	BF ₃ .OEt ₂	DCE	50 °C	0%
8	TFA	DCE	50 °C	0%
9	TsOH (0.1)	THF	50 °C	24%
10	TsOH (0.1)	CH ₃ CN	50 °C	23%
11	TsOH (0.1)	toluene	50 °C	100% (99%)
12	-	DCE	50 °C	0%
13 ^e	TsOH (0.1)	DCE	50 °C	85%

^a Reaction conditions: **1a** (0.1 mmol), acid (x equiv), Solvent (0.07 M), 20 h. ^b NMR yield using 1,2-dibromoethane as internal standard; isolated between brackets. ^c The structure and relative configuration were established by analogy to the X-ray crystal structure analysis of **6b** (CCDC 2082935, see the Supporting Information). ^d 6 h instead of 20 h. ^e strict argon atmosphere.

With the best reaction conditions in hand, the scope of this catalytic heterodimerization reaction was explored as depicted

in Table 4. Substrates bearing various substituents on either the phenyl or the naphthyl rings were tested affording in all cases the corresponding trisubstituted chromane derivative as a single diastereoisomer. Good to excellent yields were achieved with substrates having an electron-withdrawing group on the phenyl ring (**6b–6d**, **6h–6k**, **6m–6o**, 64–94%). Cycloadducts **6d** and **6e** substituted with an electron donating group (methoxy and *tert*-butyl respectively) were obtained with slightly lower yields (32–60%). It is worth mentioning that substrates with *ortho*- as well as *meta*-substituted phenyl rings were also well tolerated furnishing the corresponding heterodimers (**6g–6k**) in high to excellent yields (75–98%). The heterodimerization of 6-bromo-1-styrylnaphthalen-2-ol derivatives also proceeded smoothly, providing products **6l–6o** in 43–94% yields. Nevertheless, the styrylphenol was unreactive under this reaction conditions.²³ Finally, heterodimer **6a** was produced in 61% yields when the reaction was carried out on 1 mmol scale.

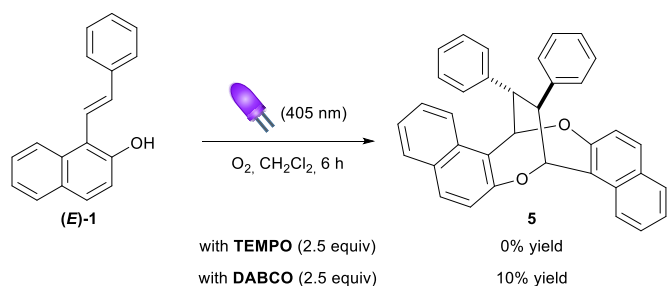
Table 4 Scope of the Brønsted acid-catalyzed heterodimerization of styrylnaphthol derivatives **1**.^{a,b}



^a Reaction conditions: **1** (0.1 mmol), toluene (0.07 M), *p*-TsOH (0.01 mmol), 20 h. ^b Isolated yield. ^c Reaction conducted on 1 mmol scale. ^d DCE instead of toluene.

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Finally, we focused our attention on the mechanism of these dimerizations and control experiments were conducted. For the visible-light mediated aerobic oxidative homodimerization reaction, addition of 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) to the standard reaction conditions totally inhibited the formation of **5a**, which supported a radical mechanism. Moreover, in the presence of the known singlet oxygen quencher 1,4-Diazabicyclo[2.2.2]octane (DABCO),²⁴ the yield significantly decreased suggesting the involvement of singlet oxygen in the process (Scheme 2). Additionally, ultraviolet-visible (UV-vis) spectroscopic analysis of **1a** unveiled an overlap between the absorption spectrum of **1a** and the emission spectrum of the purple light.²⁵ For the (4+2) heterodimerization reaction, no reaction occurred in the absence of TsOH demonstrating the crucial role of the Brønsted acid catalyst (Table 3, entry 12). However, no significant effect on the reaction outcome was observed under strict argon atmosphere showing that no special precaution was required (Table 3, entry 13 vs 4).



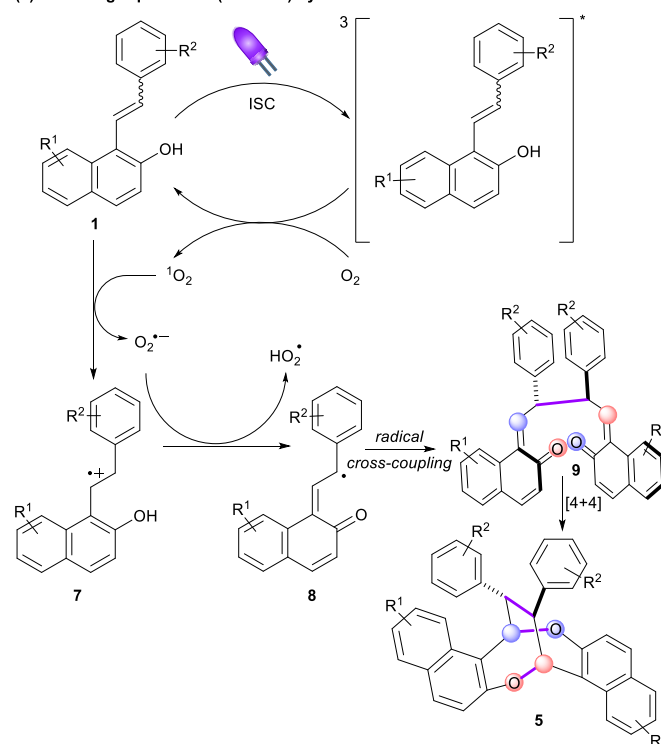
Scheme 2 Control experiments

On the basis of these observations and the literature report, plausible mechanisms are depicted in scheme 3. Upon irradiation at 405 nm, **1** is converted into a high-energy excited singlet $^11^*$, which undergoes intersystem crossing (ISC) to triplet $^31^*$. Intermolecular energy transfer to molecular oxygen generates the highly oxidant singlet oxygen species. Subsequent single electron transfer to **1** produces superoxide radical anion $O_2^{\bullet-}$ along with radical cation **7**. Further deprotonation would form the key persistent quinone methyl radical **8**. According to Zhou and Chen *et al.* works, the latter selectively dimerizes to bis-quinone methide **9**. Further intramolecular [4+4] cycloaddition eventually delivered the 1,5-dioxocane **5**. For the Brønsted acid-catalyzed heterodimerization, **1** would tautomerize to the *ortho*-quinone methide **10** in the presence of *p*-TsOH. Subsequent *endo*-selective intermolecular inverse electron demand oxa-Diels Alder reaction with **1** furnishes the trisubstituted chromanes **6** in *trans-trans* configurations.

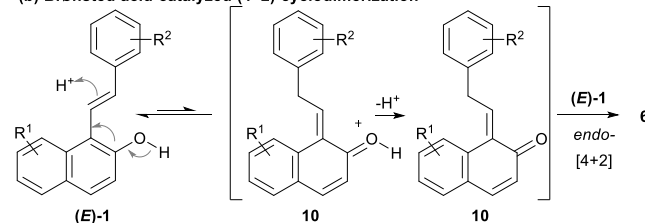
Conclusions

In conclusion, we have developed two cyclodimerizations of 1-styrylnaphthol derivatives under environmentally benign reaction conditions. Whereas a (1+1+4+4) cyclodimerization was observed under aerobic visible light irradiation, a (4+2) cycloaddition occurred in the presence of a catalytic amount of Brønsted acid. The two reactivity manifolds allowed the diastereoselective construction of highly substituted 1,5-dioxocanes and chromane derivatives featuring 3 contiguous tertiary stereocenters in descent yields. Further use of styrylnaphthol derivatives for the construction of heterocyclic compounds is under investigation in our laboratory.

(a) Visible light-promoted (1+1+4+4)-cyclodimerization



(b) Brønsted acid-catalyzed (4+2)-cyclodimerization



Scheme 3 Proposed mechanisms

Conflicts of interest

There are no conflicts to declare.

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