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

Jiyuan Lyu,^a Aurélie Claraz,^a  ^{*,a} Pascal Retailleau^a and Géraldine Masson  ^{*,a,b}

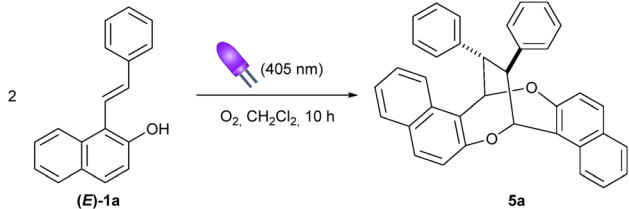
Dimeric cyclization reactions show great potential to rapidly form highly substituted complex cyclic molecules from simple starting materials. However, such an appealing process is often hampered by the lack of selectivity. Herein we report two divergent cyclodimerization reactions of 1-styrylnaphthalen-2-ol 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 moderate yields. This transformation harnessed singlet oxygen as a 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 with excellent diastereoselectivities.

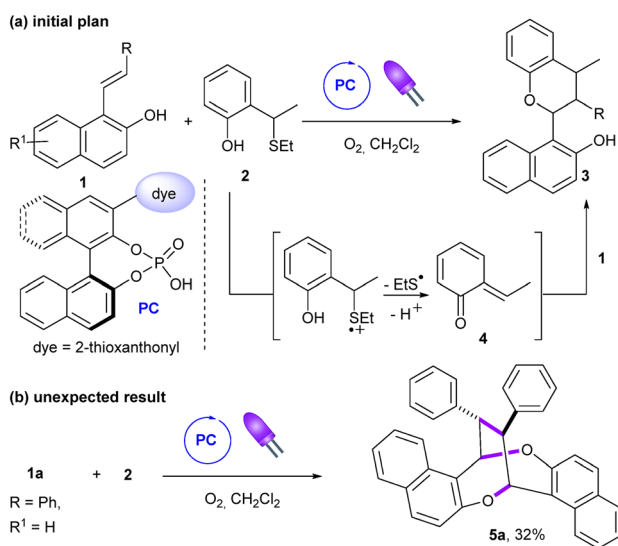
Introduction

The development of efficient divergent synthetic methods for the construction of structurally diverse molecules from

Table 1 Optimization of the parameters for 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%



Scheme 1 Serendipitous discoveries on the dimerization of styrylnaphthols.

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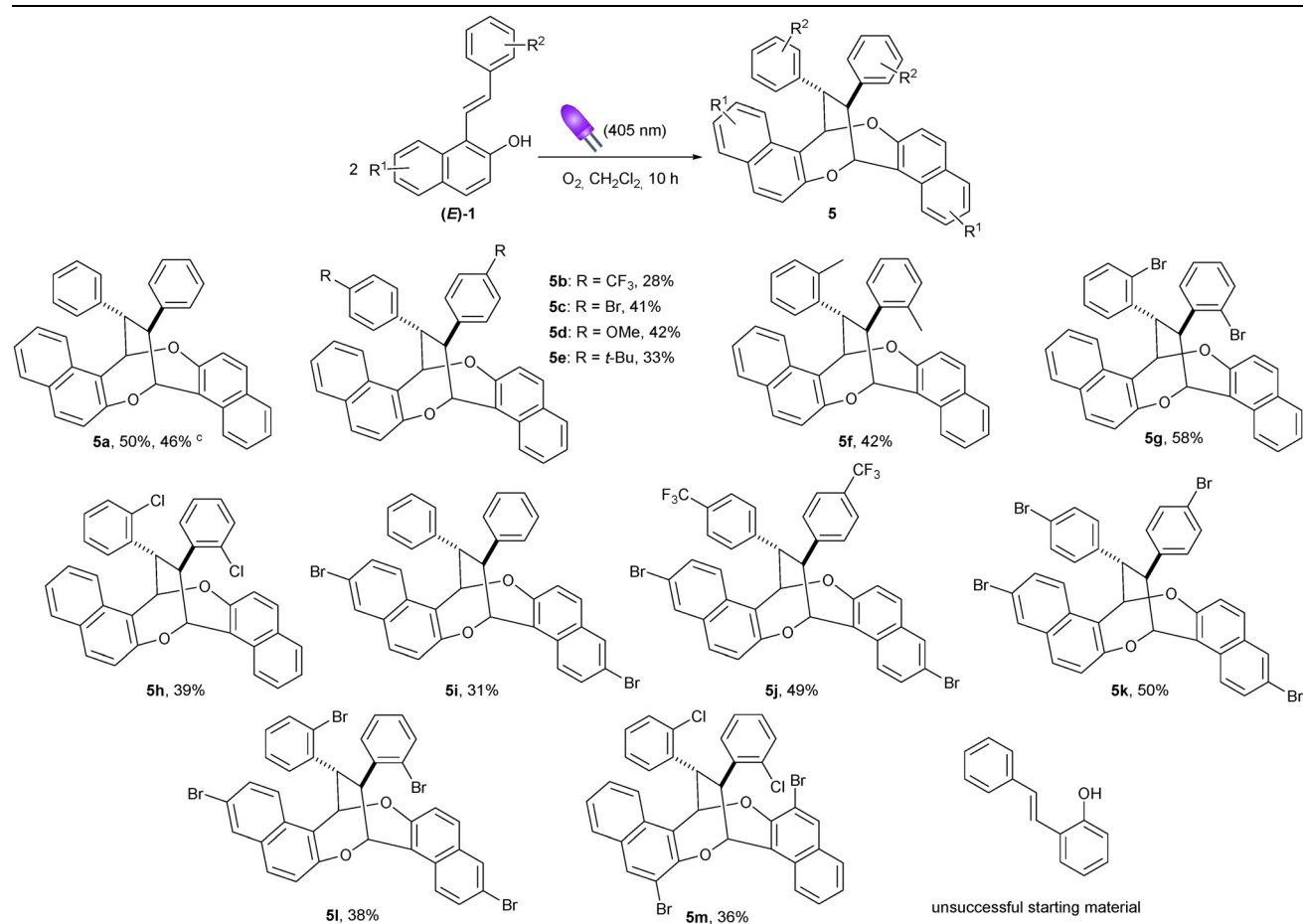
^bHitCat, Seqens-CNRS Joint Laboratory, Seqens'Lab, Porcheville, France

^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 an 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.

common, readily accessible starting materials is of great interest to the synthetic community.¹ In addition, the cyclodimerizations of olefins are one of the most attractive approaches to rapidly access divergent complex cyclic frameworks. For instance, these processes are often proposed as biosynthetic pathways 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 synthetic 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, a biomimetic synthetic approach based on one-electron oxidative dimerization of resveratrol derivatives led to low yields⁶ and/or a complex mixture of products.^{7,8} Similar difficulties have also been encountered during the synthesis of synthetic 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 a metal oxidant providing diverse synthetic 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 a challenging issue. In this communication, we report unexpected stereoselective and divergent cyclodimerizations of styrylnaphthols that selectively produce two different complex O-containing heterocyclic compounds depending on the conditions used. The 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. The 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 a diastereomerically pure form.

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



^a Reaction conditions: **1** (0.1 mmol), CH_2Cl_2 (0.07 M), O_2 , 405 nm, 6 h, rt (internal temperature: 28 °C). ^b Isolated yield. ^c Reaction conducted on a 1 mmol scale.

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** did not form 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 the central motif. Such a framework has been found in several naturally occurring products such as Luisol A¹⁵ and withamelinol-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 a stoichiometric amount of Selectfluor as the 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 this new homodimerization method in more detail.

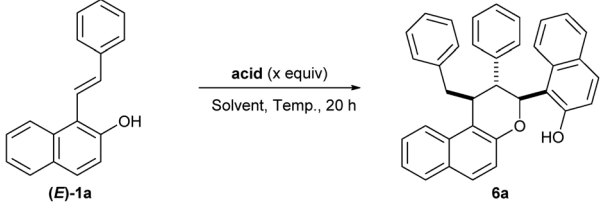
Initial control experiments revealed that the photocatalyst **PC** was not required, although irradiation at 405 nm and the presence of oxygen were both essential for this homodimerization (Table 1, entries 1–4). Pleasingly, shortening the reaction time from 10 to 6 hours improved the chemical yield 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 a lower yield of **5a**, along with the 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 also be 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 and 8). 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).

Having established the suitable reaction conditions for the oxidative homodimerization of 1-styrylnaphthalen-2-ol derivatives **1**, we next examined the substrate scope (Table 2). In all the 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** and **5h**, **5l** and **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 a 1 mmol scale affording the corresponding cyclic compound **5a** in similar yields (46%).

The unexpected formation of chromane **6a** in the presence of an 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 un-

Table 3 Optimization of the parameters for the (4 + 2) heterodimerization of **1a**^a



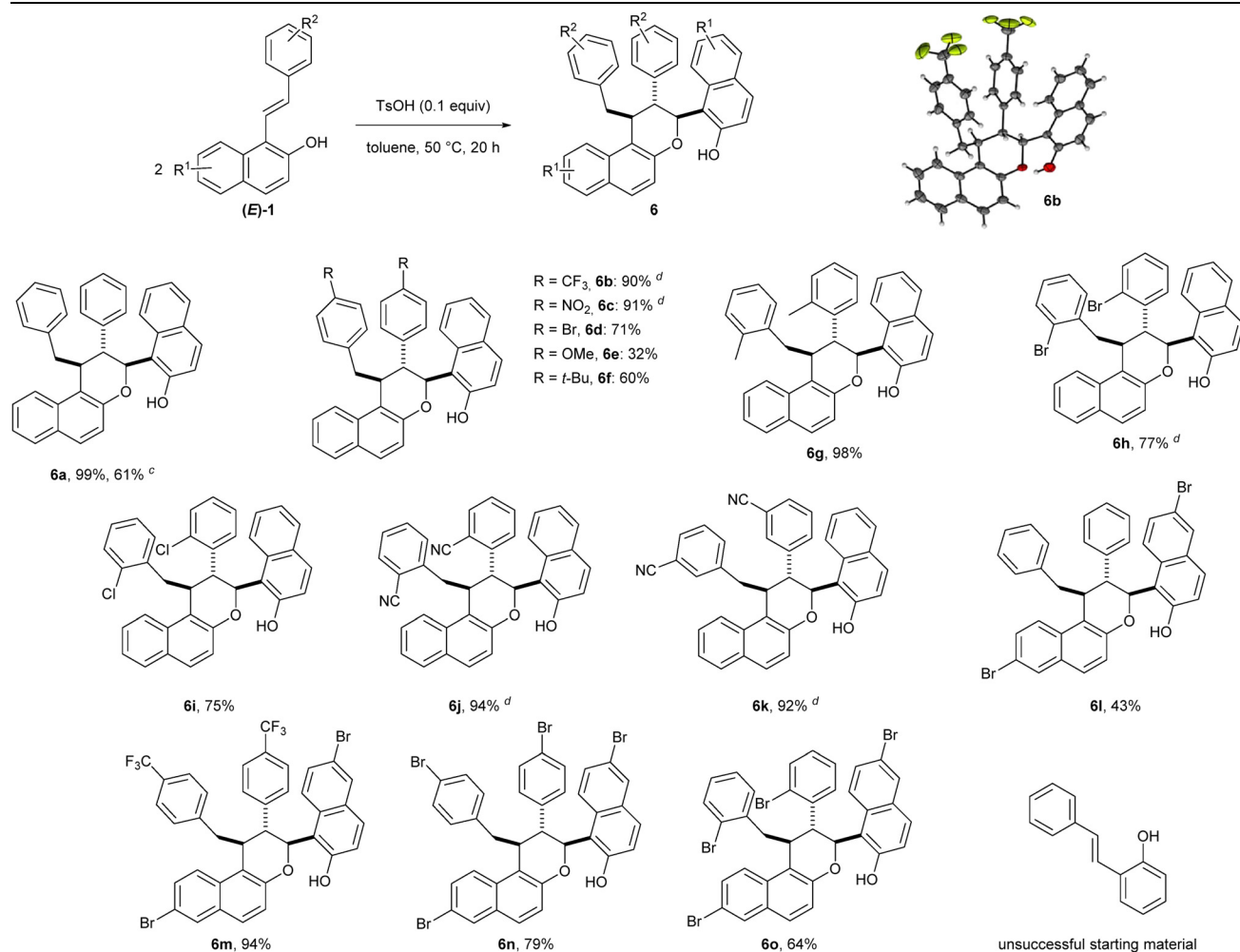
Entry	Acid (equiv.)	Solvent	Temp.	6a ^{b,c}
1 ^d	TsOH (2)	CH ₂ Cl ₂	rt	15%
2	TsOH (2)	CH ₂ Cl ₂	rt	40%
3	TsOH (0.1)	CH ₂ Cl ₂	rt	30%
4	TsOH (0.1)	DCE	50 °C	85%
5	TsOH (0.1)	DCE	70 °C	85%
6	CF ₃ SO ₃ H (0.1)	DCE	50 °C	0%
7	BF ₃ ·OEt ₂ (0.1)	DCE	50 °C	0%
8	TFA (0.1)	DCE	50 °C	0%
9	TsOH (0.1)	THF	50 °C	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 an internal standard; isolated between brackets. ^c The structure and relative configurations were established by analogy with the X-ray crystal structure analysis of **6b** (CCDC 2082935, see the ESI†). ^d 6 h instead of 20 h. ^e Strict argon atmosphere.

precedented. 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 the 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 and 5) resulted in a dramatic improvement in the yield (85%) at 50 °C. 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 for delivering the desired heterodimer adduct in 99% isolated yield.²²

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 **6e** and **6f** 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, styrylphenol was unreactive under these reaction conditions.²³ Finally, heterodimer **6a** was produced in

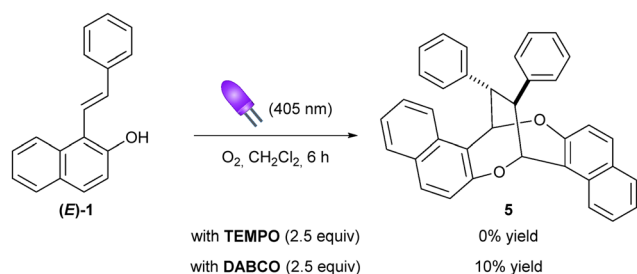
Table 4 Scope of the Brønsted acid-catalyzed heterodimerization of styrylnaphthol derivatives **1^{a,b}**



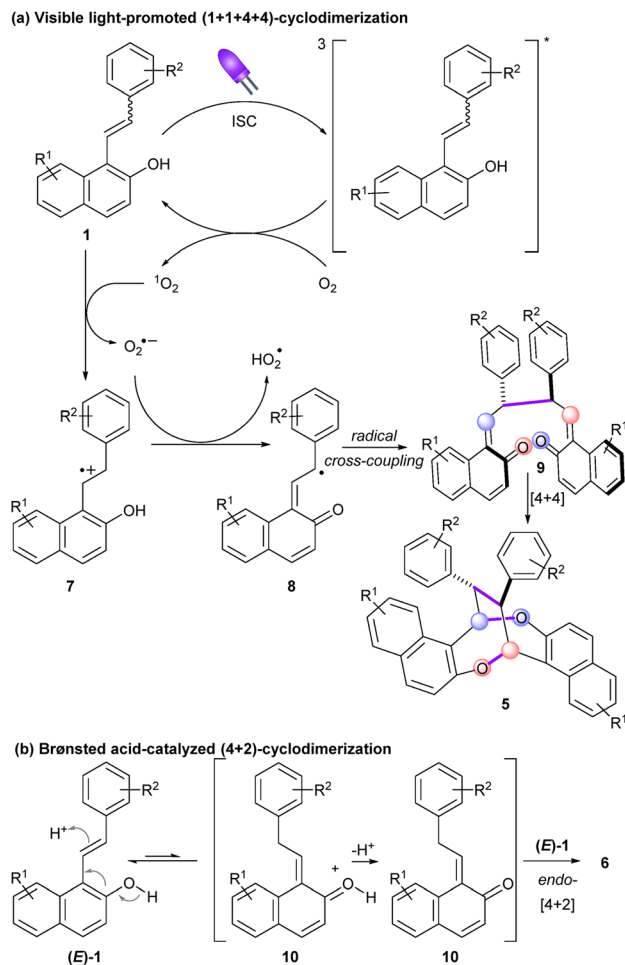
^a Reaction conditions: **1** (0.1 mmol), toluene (0.07 M), *p*-TsOH (0.01 mmol), 20 h. ^b Isolated yield. ^c Reaction conducted on a 1 mmol scale. ^d DCE instead of toluene.

61% yield when the reaction was carried out on a 1 mmol scale.

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, the addition of 2,2,6,6-tetramethylpiperidine-1-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



Scheme 2 Control experiments.



Scheme 3 Proposed mechanisms.

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 a strict argon atmosphere showing that no special precaution was required (Table 3, entry 13 vs. 4).

On the basis of these observations and literature reports, 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 give triplet ³1*. Intermolecular energy transfer to molecular oxygen generates the highly oxidant singlet oxygen species. Subsequent single electron transfer to **1** produces a superoxide radical anion O₂^{•-} along with radical cation **7**. Further deprotonation would form the key persistent quinone methyl radical **8**. According to the works of Zhou and Chen *et al.*, the latter selectively dimerizes into bis-quinone methide **9**. Further intramolecular [4 + 4] cycloaddition eventually delivered 1,5-dioxocane **5**. As for the Brønsted acid-catalyzed heterodimerization, **1** would tautomerize into *ortho*-quinone methide **10** in the presence of *p*-TsOH. Subsequent *endo*-selective intermolecular inverse electron demanding oxa-Diels Alder reaction with **1** furnishes trisubstituted chromanes **6** in *trans-trans* configurations.

Conclusions

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

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- (a) S. L. Schreiber, *Science*, 2000, **287**, 1964; (b) M. D. Burke and S. L. Schreiber, *Angew. Chem., Int. Ed.*, 2004, **43**, 46; (c) E. Lenci, A. Guarna and A. Trabocchi, *Molecules*, 2014, **19**, 16506.
- Reviews: (a) S. A. Snyder, A. M. ElSohly and F. Kontesa, *Nat. Prod. Rep.*, 2011, **28**, 897; (b) J. Sun and W. Tang, *Chem. Soc. Rev.*, 2021, **50**, 2320; selected examples. (c) A. Sib and T. A. M. Gulder, *Angew. Chem., Int. Ed.*, 2017, **56**, 12888; (d) P. A. Peixoto, M. El Assal, I. Chataigner, F. Castet, A. Cornu, R. Coffinier, C. Bosset, D. Deffieux, L. Pouységu and S. Quideau, *Angew. Chem., Int. Ed.*, 2021, **60**, 14967; (e) N. Lebrasseur, J. Gagnepain, A. Ozanne-Beaudenon, J.-M. Léger and S. Quideau, *J. Org. Chem.*, 2007, **72**, 6280; (f) S. Hanessian, J. P. Maianti, V. L. Lya and B. Deschênes-Simarda, *Chem. Sci.*, 2012, **3**, 249; (g) C. Li and J. A. Porco, *J. Am. Chem. Soc.*, 2004, **126**, 1310.
- (a) A. Paquin, C. Reyes-Moreno and G. Bérubé, *Molecules*, 2021, **26**, 2340; (b) J. C. J. M. D. S. Menezes and M. F. Diederich, *Eur. J. Med. Chem.*, 2019, **182**, 111637; (c) J. C. Lee, G. A. Strobel, E. Lobkovsky and J. Clardy, *J. Org. Chem.*, 1996, **61**, 3232; (d) T. Zhu, Z. Lu, J. Fan, L. Wang, G. Zhu, Y. Wang, X. Li, K. Hong, P. Piyachaturawat, A. Chairoungdua and W. Zhu, *J. Nat. Prod.*, 2018, **81**, 254.
- Selected examples: (a) Y. Tan, Z. Zhao, Z. Chen, S. Huang, S. Jia, L. Peng, D. Xu, W. Qin and H. Yan, *Org. Lett.*, 2020, **22**, 4461; (b) V. Claus, M. Schukin, S. Harrer, M. Rudolph, F. Rominger, A. M. Asiri, J. Xie and A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2018, **57**, 12966; (c) C. Peng, T. Kusakabe, S. Kikkawa, T. Mochida, I. Azumaya, Y. Daulat Dhage, K. Takahashi, H. Sasai and K. Kato, *Chem. – Eur. J.*, 2019, **25**, 733; (d) R. Jia, B. Li, R. Liang, X. Zhang and X. Fan, *Org. Lett.*, 2019, **21**, 4996; (e) B. Kurpil, Y. Markushyna and A. Savateev, *ACS Catal.*, 2019, **9**, 1531; (f) M.-A. Constantin, J. Conrad, E. Merişor, K. Koschorreck, V. B. Urlacher and U. Beifuss, *J. Org. Chem.*, 2012, **77**, 4528; (g) M. Álvarez-Pérez, M. Frutos, A. Viso, R. Fernández de la Pradilla, M. C. de la Torre, M. A. Sierra, H. Gornitzka and C. Hemmert, *J. Org. Chem.*, 2017, **82**, 7546.
- (a) M. H. Keylor, B. S. Matsuura and C. R. J. Stephenson, *Chem. Rev.*, 2015, **115**, 8976; (b) X. Su, D. Zhou and N. Li, *Stud. Nat. Prod. Chem.*, 2022, **73**, 265; (c) T. Shen, X.-N. Wang and H.-X. Lou, *Nat. Prod. Rep.*, 2009, **26**, 916.
- Notable exceptions: (a) Y. Takaya, K. Terashima, J. Ito, Y.-H. He, M. Tateoka, N. Yamaguchi and M. Niwa, *Tetrahedron*, 2005, **61**, 10285; (b) M. Sako, H. Hosokawa, T. Ito and M. Iinuma, *J. Org. Chem.*, 2004, **69**, 2598; (c) T. Song, B. Zhou, G.-W. Peng, Q.-B. Zhang, L.-Z. Wu, Q. Liu and Y. Wang, *Chem. – Eur. J.*, 2014, **20**, 678.
- (a) B.-B. Yu, X.-Z. Han and H.-X. Lou, *J. Agric. Food Chem.*, 2007, **55**, 7753; (b) C.-S. Yao, L.-X. Zhou and M. Lin, *Chem. Pharm. Bull.*, 2004, **52**, 238; (c) C. Li, J. Lu, X. Xu, R. Hu and Y. Pan, *Green Chem.*, 2012, **14**, 3281.
- This has thus motivated synthetic chemists to develop alternative routes from more controllable building blocks. For a review: (a) S. Quideau, D. Deffieux, C. Douat-Casassus and L. Pouységu, *Angew. Chem., Int. Ed.*, 2011, **50**, 586 For selected examples: (b) W. Li, H. Li, Y. Li and Z. Hou, *Angew. Chem., Int. Ed.*, 2006, **45**, 7609; (c) W. Li, H. Li, Y. Luo, Y. Yang and N. Wang, *Synlett*, 2010, 1247; (d) B. S. Matsuura, M. H. Keylor, B. Li, Y. X. Lin, S. Allison, D. A. Pratt and C. R. J. Stephenson, *Angew. Chem., Int. Ed.*, 2015, **54**, 3754; (e) W. Li, T. Dong, P. Chen, X. Liu, M. Liu and X. Han, *Tetrahedron*, 2017, **73**, 3056; (f) K. J. Romero, M. H. Keylor, M. Griesser, X. Zhu, E. J. Strobel, D. A. Pratt and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2020, **142**, 6499; (g) S. A. Snyder, T. C. Sherwood and A. G. Ross, *Angew. Chem., Int. Ed.*, 2010, **49**, 5146; (h) S. A. Snyder, N. E. Wright, J. J. Pflueger and S. P. Breazzano, *Angew. Chem., Int. Ed.*, 2011, **50**, 8629; (i) S. A. Snyder, A. Gollner and M. I. Chiriach, *Nature*, 2011, **474**, 461; (j) S. A. Snyder, A. L. Zografos and Y. Lin, *Angew. Chem., Int. Ed.*, 2007, **46**, 8186; (k) F. Klotter and A. Studer, *Angew. Chem., Int. Ed.*, 2014, **53**, 2473.
- Selected examples: (a) S. S. Velu, I. Bunyamin, L. Kiew Ching, F. Feroz, I. Noorbachta, L. C. Gee, K. Awang, I. A. Wahab and J.-F. F. Weber, *Chem. – Eur. J.*, 2008, **14**, 11376; (b) F.-J. Hong, Y.-Y. Low, K.-W. Chong, N. F. Thomas and T.-S. Kam, *J. Org. Chem.*, 2014, **79**, 4528; (c) K. J. Romero, M. S. Galliher, M. A. R. Raycroft, J.-P. R. Chauvin, I. Bosque, D. A. Pratt and C. R. J. Stephenson, *Angew. Chem., Int. Ed.*, 2018, **57**, 17125; (d) N. F. Thomas, K. C. Leeb, T. Paraidathathub, J. F. F. Weber, K. Awang, D. Rondeaud and P. Richommed, *Tetrahedron*, 2002, **58**, 7201; (e) J.-S. Xie, J. Wen, X.-F. Wang, J.-Q. Zhang, J.-F. Zhang, Y.-L. Kang, Y.-W. Hui, W.-S. Zheng and C.-S. Yao, *Molecules*, 2015, **20**, 22662.
- (a) V. Santacroce, R. Duboc, M. Malacria, G. Maestri and G. Masson, *Eur. J. Org. Chem.*, 2017, 2095; (b) L. Jarrige, A. Carboni, G. Dagousset, G. Levitre, E. Magnier and G. Masson, *Org. Lett.*, 2016, **18**, 2906; (c) T. Le, L. Galmiche, G. Masson, C. Allain and P. Audebert, *Chem. Commun.*, 2020, **56**, 10742.
- Selected examples: (a) T. Varlet, M. Matišić, E. Van Elslande, L. Neuville, V. Gandon and G. Masson, *J. Am. Chem. Soc.*, 2021, **143**, 11611; (b) W.-Y. Ma, C. Gelis, D. Bouchet, P. Retailleau, X. Moreau, L. Neuville and G. Masson, *Org. Lett.*, 2021, **23**, 442; (c) T. Varlet, C. Gelis, P. Retailleau, G. Bernadat, L. Neuville and G. Masson, *Angew. Chem., Int. Ed.*, 2020, **59**, 8491; (d) L. Jarrige, V. Gandon and G. Masson, *Chem. – Eur. J.*, 2020, **26**, 1406; (e) L. Jarrige, D. Glavač, G. Levitre, P. Retailleau, G. Bernadat, L. Neuville and G. Masson, *Chem. Sci.*, 2019, **10**, 3765; (f) L. Jarrige, F. Blanchard and G. Masson, *Angew. Chem., Int. Ed.*, 2017, **56**, 10573; (g) C. Gelis, M. Bekkaye,

- C. Lebé, F. Blanchard and G. Masson, *Org. Lett.*, 2016, **18**, 3422.
- 12 (a) J. Y. Lyu, A. Claraz, M. R. Vitale, C. Allain and G. Masson, *J. Org. Chem.*, 2020, **85**, 12843; (b) J. Y. Lyu, M. Leone, A. Claraz, C. Allain, L. Neuville and G. Masson, *RSC Adv.*, 2021, **11**, 36663.
- 13 (a) T. Inoue, S. Inoue and K. Sato, *Chem. Lett.*, 1989, **4**, 653; (b) I. Tsutomu, I. Seiichi and S. Kikumasa, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1062; (c) K. Chiba, J. Sonoyama and M. Tada, *J. Chem. Soc., Chem. Commun.*, 1995, 1381; (d) K. Chiba, Y. Yamaguchi and M. Tada, *Tetrahedron Lett.*, 1998, **39**, 9035; (e) M. Lanzi, J. Merad, D. V. Boyarskaya, G. Maestri, C. Allain and G. Masson, *Org. Lett.*, 2018, **20**, 5247; (f) C. Lebé, M. Languet, C. Allain and G. Masson, *Org. Lett.*, 2016, **18**, 1478; (g) L. Jarrige, G. Levitre and G. Masson, *J. Org. Chem.*, 2016, **81**, 7230 See also: (h) T. Courant, M. Lombard, D. V. Boyarskaya, L. Neuville and G. Masson, *Org. Biomol. Chem.*, 2020, **18**, 6502.
- 14 (a) S. Feng, B. Yang, T. Chen, R. Wang, Y.-H. Deng and Z. Shao, *J. Org. Chem.*, 2020, **85**, 5231; (b) Y. You, T.-T. Li, S.-P. Yuan, K.-X. Xie, Z.-H. Wang, J.-Q. Zhao, M.-Q. Zhoub and W.-C. Yuan, *Chem. Commun.*, 2020, **56**, 439; (c) H. Zhang, G. Liu, X. Guan, J. Gao, X. Qin, G. Jiang, D. Sun, G. Zhang and S. Zhang, *Eur. J. Org. Chem.*, 2019, 7264.
- 15 X. C. Cheng, P. R. Jensen and W. Fenical, *J. Nat. Prod.*, 1999, **62**, 608.
- 16 B. S. Siddiqui, I. A. Hashmi and S. Begum, *Heterocycles*, 2002, **57**, 715.
- 17 (a) H. Nishida, H. Tomoda, S. Okuda and S. Omura, *J. Org. Chem.*, 1992, **57**, 1271; (b) H. Tomoda, H. Nishida, R. Masuma, J. Cao, S. Okuda and S. i. Omura, *J. Antibiot.*, 1990, **44**, 136; (c) H. Nishida, H. Tomoda, J. Cao, S. Okuda and S. Omura, *J. Antibiot.*, 1990, **44**, 144; (d) G. M. Salituro, D. J. Pettibone, B. V. Clineschmidt, J. M. Williamson and D. L. Zink, *Bioorg. Med. Chem. Lett.*, 1993, **3**, 337; (e) D. Brückner, F.-T. Hafner, V. Li, C. Schmeck, J. Telser, A. Vakalopoulos and G. Wirtz, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 3611.
- 18 H. Yang, H.-R. Sun, R.-D. Xue, Z.-B. Wu, B.-B. Gou, Y. Lei, J. Chen and L. Zhou, *Org. Lett.*, 2019, **21**, 9829.
- 19 (a) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, 1962, **84**, 4983; (b) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, *J. Am. Chem. Soc.*, 1964, **86**, 3197.
- 20 Although the concentration effect on photoisomerization is not completely understood, *E*- to *Z*-photoisomerization can be favoured, thanks to close proximity between the exited styrylnaphthol and styrylnaphthol at higher concentrations, see: A. A. Zimmerman, C. M. Orlando Jr., M. H. Gianni and K. Weiss, *J. Org. Chem.*, 1969, **34**, 73.
- 21 The starting material was totally recovered. The higher oxidation potential of phenol ($E_{ox} = 1.63$ V vs. SCE) compared to that of naphthol ($E_{ox} = 1.40$ V vs. SCE) might explain this difference in reactivity. H. G. Roth, N. A. Romero and D. A. Nicewicz, *Synlett*, 2016, 714.
- 22 To develop an enantioselective version, few tests have been realized with chiral Brønsted acid catalysts but were unsuccessful; see the ESI† for more details.
- 23 Compared to 2-naphthol, phenol features higher aromaticity and more difficult dearomatized tautomerization between enolate and ketone. Such a difference might explain the fact that styrylphenol was unreactive (see also ref. 14b).
- 24 C. Ouannes and T. Wilson, *J. Am. Chem. Soc.*, 1968, **90**, 6527.
- 25 The position of the long wavelength tail of the absorption spectrum of **1a** is around $\lambda_{tail}(\mathbf{1a}) = 385$ nm while the short wavelength of the Hepatochem lamp (405 nm) is around $\lambda_{tail(lamp)} = 380$ nm. See the ESI† for more details.