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A Cooperative Hydrogen-Bond-Promoted Organophotoredox Catalysis Strategy for Highly Diastereoselective, Reductive Enone Cyclization

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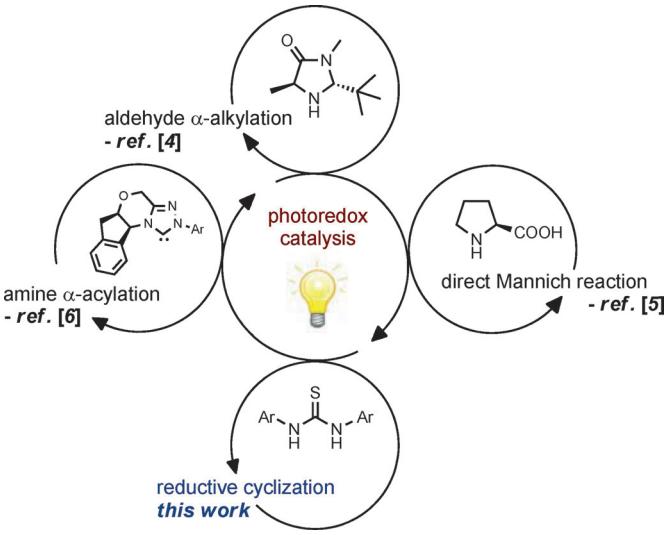
Mild and efficient methods for catalytic C–C bond formations are of great importance to both academic and industrial research, and green and sustainable processes pose an additional major challenge for synthetic organic chemists. Over the last decade, organocatalysis has successfully started to seize the mantle and especially multicatalysis concepts—combining robust, metal-free catalysts—allow access to complex (asymmetric) structures and many formerly elusive transformations.[1] Only recently has the combination of organocatalytic activation modes with other sustainable methods begun to evolve.[2] In this context, in particular the merger with visible-light photoredox chemistry[3] has emerged as a powerful approach, as was evidenced by pioneering examples by the groups of MacMillan,[4] Rueping,[5] and Rovis.[6] Secondary amine and NHC catalysis were successfully combined in synergistic processes with $[Ru(bpy)_3]^{2+}$-mediated photoredox catalysis. Although metal-complex-promoted photocatalysis, which is often based on expensive and scarce Ru and Ir complexes,[7] is still mandatory for some applications, we have recently developed a photoredox protocol demonstrating the applicability of Eosin Y as a potent metal-free surrogate for $[Ru(bpy)_3]^{2+}$.[8]

In this context, we could also show that simple organic photoredox catalysts can participate in highly enantioselective synergistic transformations with two catalytic cycles working perfectly in concert.[8a] Continuing this theme, we questioned if the photoredox multicatalysis strategy could be extended to other organocatalytic activation modes.

Apart from the above-mentioned successful examples to combine photoredox catalysis with amine and NHC catalysis, respectively (Scheme 1), a merger with metal-free carbonyl activation has not yet been described. As hydrogen-bond catalysis,[9] mimicking enzymatic general acid catalysis, is well-known to be a powerful tool for mild LUMO-lowering carbonyl activation, we sought to transfer this attractive alternative to Lewis acids to *cooperative photoredox catalysis* to activate carbonyl groups towards electron acceptance.[10]



Scheme 1. Multicatalytic photoredox approaches.

We anticipated that this noncovalent, weak interaction would be favorable in terms of catalyst loading to avoid the need of (super)stoichiometric amounts of Lewis acid activators.

Herein, we describe a highly diastereoselective hydrogen-bond-promoted reductive cyclization of bisenones by cooperative organic photoredox catalysis. These reactions proceeded efficiently and fast at room temperature by using simple, commercially available, inexpensive material as catalysts.

As outlined in Scheme 2, we considered the versatile class of cyclization reactions of bisenones, promoted by single-electron transfer (SET), as a suitable model system to prove our concept. These cyclizations are not only interesting due to the formal umpolung[11] triggered by electron donation and hence the possible access to 1,6-or 1,4-difunctionalized products **3** and **4**, but also have already been studied extensively for a number of catalytic systems and initiators. Early examples use stannyl radical-chain reactions,[12] whereas alternative methods range from metal catalysis,[13] arene

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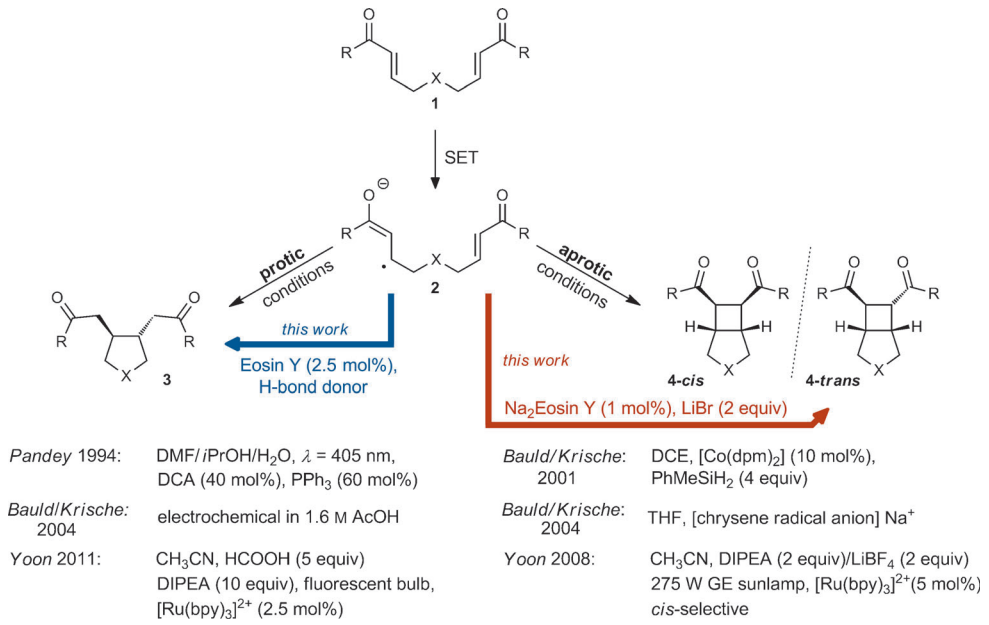


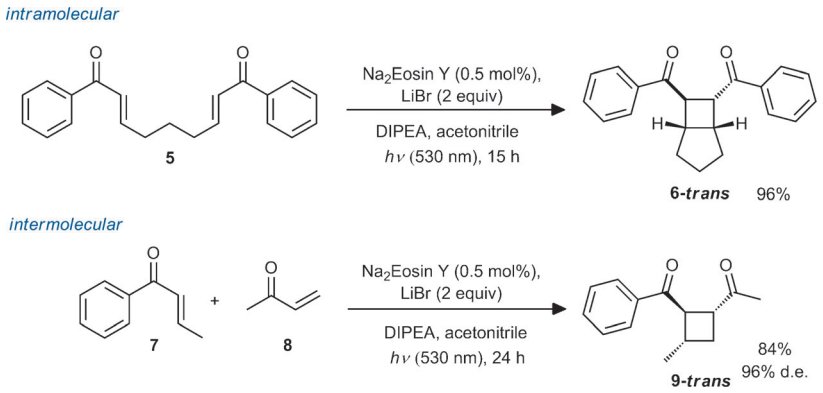
Scheme 2. Cyclizations of bisenones triggered by SET.[12–17]

anions,[14] and electrochemical activation[13b,15] to photocatalysis.[16] Besides the common need of high loadings of additives and/or catalysts, product- and diastereoselectivity entail possible issues.

The fate of the initially formed distonic radical is known to be strongly dependent on the reaction conditions. While the presence of protic solvents or acids as activators causes protonation or hydrogen transfer of the primarily cyclized intermediate, generating the monocyclic products **3** in a reductive cyclization (Scheme 2, left), nonprotic conditions favor the formation of the bicyclic, formal [2+2] cycloaddition products **4** in a netto redox neutral reaction.[15b,16c] Combining isopropanol solvent mixtures with dicyanoanthracene (DCA) as photoredox catalyst, Pandey and Hajra described the formation of monocyclic **3** under irradiation ($\lambda =$ 405 nm).[16] In the presence of $[Ru(bpy)_3]^{2+}$ as photocatalyst, Yoon and co-workers[17] could either access bicyclic products **4**-*cis* by using an excess of $LiBF_4$ as templating Lewis acid activator,[17a,b] or reductively cyclize the tethered bisenones to give *trans*-configurated products **3**, if superstoichiometric amounts of HCOOH were applied.[17c]

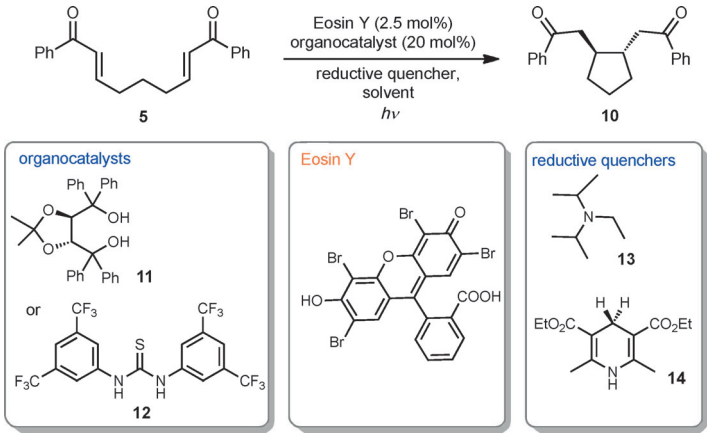
Our investigation began with an examination of the general feasibility to substitute $[Ru(bpy)_3]^{2+}$ with Eosin in the presence of Lewis acids. Both the intramolecular, as well as the crossed intermolecular formal [2+2] cycloaddition of acyclic enones,[17a,b] could be realized by using the organophotoredox catalyst in excellent yield and diastereoselectivity. However, unlike to former results, we could only detect the (thermodynamically more stable)[14] *trans*-products **6** and **9** (Scheme 3).[18]

Having demonstrated that Eosin could serve as a powerful organic photoredox catalyst to access ketyl radical anions, we next focused on combining Eosin in a cooperative manner with hydrogen-bond donor catalysts for carbonyl activation. We speculated that this catalytic combination with its additional capability to mediate proton transfer would allow for selective *reductive* bisenone cyclizations. As common and easily accessible hydrogen-bond organocatalysts performing as Lewis acid type surrogates for carbonyl activation, we chose TADDOL (α,α,α′,α′-tetraphenyl-1,3-dioxolan-4,5-dimethanol) **11**[19] and thiourea **12** ("Schreiner's catalyst").[20] As shown in Table 1, our design rendered reactions with both catalysts successful, providing the expected,



Scheme 3. Intra- and intermolecular formal [2+2] cycloadditions of enones with Eosin Y as photoredox catalyst.

Table 1. Optimization of reaction conditions.[a]



Entry	Organocatalyst	Reductive quencher [equiv]	Solvent	t [h]	Yield of **10** [%][a,b,c]
1	**11**	**13** (2)	MeCN	48	traces
2	**11**	**13** (2)	THF	48	8
3	**11**	**13**·HCl (2)	THF	48	62
4	**12**	**13** (2)	MeCN	48	78
5	**12**	**14** (1.1)	MeCN	12	84
6	**12**	**14** (1.1)	CH_2Cl_2	3.5	93
7	**12**	**14** (1)+**13** (1)	CH_2Cl_2	2	92
8	**12**	**14** (1)+**13** (1)	CH_2Cl_2	5.5	89[d]
9	–	**14** (1)+**13** (1)	CH_2Cl_2	48	0
10[e]	**12**	**14** (1)+**13** (1)	CH_2Cl_2	48	0

[a] Typical procedure: all components were dissolved in a Schlenk tube and degassed by ≥2 freeze/pump/thaw cycles followed by irradiation by using two green LEDs (530 nm, 1 W each) for the time indicated. [b] Only the *trans*-isomer was detected. [c] Yield of isolated product. [d] A 23 W fluorescent bulb was used instead of LEDs. [e] Without Eosin Y.

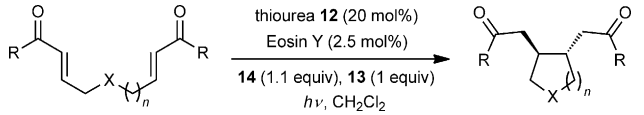
more stable *trans*-configurated racemic cyclopentane **10** with excellent diastereoselectivity, but initially with only poor-to-moderate yield, requiring long reaction times of up to 48 h for full conversion (Table 1, entries 1–4).

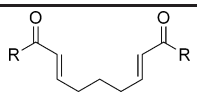
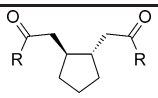
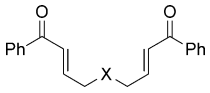
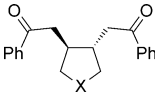
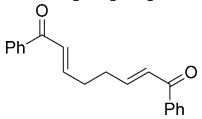
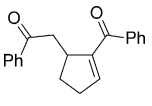
Due to solubility problems of TADDOL catalyst **11** in the presence of *N*,*N*-diisopropylethylamine (DIPEA; **13**), good yields could only be obtained if DIPEA hydrochloride was used as reductive quencher instead (Table 1, entry 3). Nevertheless, thiourea **12** proved to be superior regarding solubility and activity (Table 1, entry 4). Because quenching of the α-carbonyl radical resulting from the reductive cyclization by direct hydrogen transfer (or by oxidation-followed hydride transfer; also, see Scheme 4 for a mechanistic proposal) might be critical for successful catalysis,[21] further optimization efforts were pursued with alternative reductive quenchers (Table 1, entries 5–7). As DIPEA (**13**) is a rather poor hydride or hydrogen donor, respectively, therefore, we rationalized that exchanging DIPEA with a more powerful donor, such as the commonly used Hantzsch ester **14** that also can perform as reductive quencher,[22] should be beneficial. In fact, the reaction was found to be significantly accelerated in the presence of biomimetic **14** (Table 1, entry 5).

During a survey of solvents, the reaction time shortened to 3.5 h, when dichloromethane was employed (Table 1, entry 6). Finally, optimal efficiency was achieved by using a combination of Hantzsch ester and DIPEA (1 equiv) as additive (entry 7). For irradiation, an array of two green 1 W LEDs that ideally match the absorption maximum of Eosin Y was used (emission maximum $\lambda = 530$ nm).[23] Changing the light source to a standard 23 W household fluorescent bulb resulted in elongated reaction time, but still gave a comparable yield (Table 1, entry 8). Control experiments without irradiation left the starting material unchanged; neither could we observe reductive cyclization, if the organocatalyst or Eosin Y as photocatalyst were left out (entries 9 and 10), hence verifying the indispensability of all employed reaction components.

With these best conditions in hand, we next investigated the scope of the reductive cyclization of symmetrical bisenones (Table 2). All tested aryl bisenones both with electron-withdrawing (e.g., entry 3) and electron-donating substitution pattern (e.g., entry 2) proved to be suitable substrates selectively providing the desired *trans*-cyclopentanes in excellent yield and short reaction times (Table 2, entries 1–3). As was expected, the reductive power of the Eosin Y radical anion ($E^0 = -1.06$ V vs. SCE) proved to be insufficient for aliphatic enones due to their more negative potential,[24] because only trace amounts of product could be observed after 24 h reaction time.

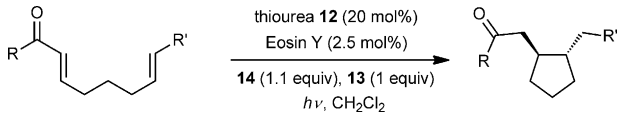
Table 2. Substrate scope of symmetrical bisenones.[a]



Entry	Substrate	Product	t [h]	Yield [%][b]
				
1	R = Ph		2	92
2	R = PMP (*p*-methoxyphenyl)		1.5	95
3	R = *p*-Cl-C_6H_4		2.5	96
4[c]	R = CH_2CH_2Ph		2.5	91
5[c]	R = Me		0.5	93
				
6	X = O		8	95
7	X = CH_2CH_2		4.5	91
8	X = $CH_2CH_2CH_2$		24	0
9[d]			48	71

[a] Conditions: thiourea **12** (20 mol%), Eosin Y (2.5 mol%), Hantzsch ester (**14**; 1 equiv), DIPEA **13** (1 equiv), CH_2Cl_2 ($c_{enone} = 0.2$ mol L^{-1}). [b] Yield of isolated product. [c] [Ir(d*t*bbpy)(ppy)$_2$][PF_6] (1 mol%) was used instead of Eosin Y. [d] No Hantzsch ester, DIPEA (**13**; 2 equiv) used instead.

Table 3. Substrate scope of unsymmetrical enones.[a]



Entry	Substrate	Product	t [h]	Yield [%][b]
1	R = OMe		6	85
2	R = SEt		5.5	86
3	R = Me		5	87
4	R = *t*Bu		4	95
5		d.r. 9:7	7.5	85
6		*E*/*Z* 2:1	8	82
7[c]	R^2 = Ph		12	0
8[c]	R^2 = CH_2CH_2Ph		2.5	72[d]
9[c]	R^3 = Ph		12	0
10[c]	R^3 = CH_2CH_2Ph		12	0

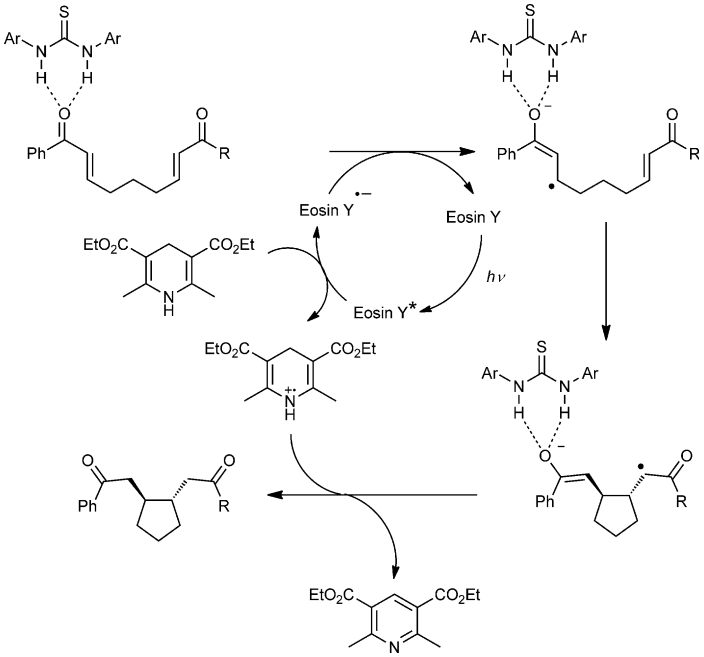
[a] Conditions: thiourea **12** (20 mol%), Eosin Y (2.5 mol%), Hantzsch ester (**14**; 1 equiv), DIPEA (**13**; 1 equiv), CH_2Cl_2 (c_{enone} = 0.2 mol L^{-1}). [b] Yield of isolated product. [c] [Ir(d*t*bbpy)$(ppy)_2$][PF_6] (1 mol%) was used instead of Eosin Y. [d] Diastereomeric mixture (1:1).

Replacing Eosin with the more potent ([Ir(d*t*bbpy)$(ppy)_2$][PF_6], $E^0(Ir^{III}/Ir^{II})$ = −1.51 V vs. SCE)[25] afforded the product in excellent yield and short reaction times (Table 2, entries 4 and 5). Heterocycles (Table 2, entry 6) and cyclohexanes (entry 7) could also be obtained in high yield, whereas cycloheptanes were not accessible (entry 8). A different reactivity was observed upon shortening the alkyl chain to four carbon atoms. According to Baldwin's rules,[26] the expected 4-*exo*-trig cyclization should result in the formation of a cyclobutane; however, after prolonged reaction time, only the rearrangement to a cyclopentene in good yield was observed (Table 2, entry 9). Because 5-*endo*-trig cyclizations are strongly disfavored and the formation via a Rauhut–Currier pathway[27] can be ruled out,[28] the product might stem from a base-promoted vinylogous deprotonation/enolate addition/isomerization sequence.[15a]

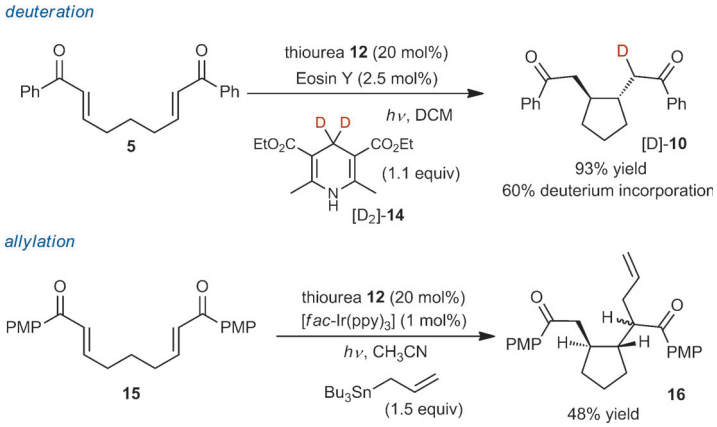
We next examined the scope of this cooperative catalytic approach by screening a variety of unsymmetrical enones with respect to functional-group tolerance. As shown in Table 3, substrates containing esters, thioesters (entries 1 and 2), as well as aliphatic ketones or nitrile Michael systems (entries 3–5) smoothly underwent reductive cyclization. The yields were excellent in all cases; however, diastereocontrol was observed to be moderate for acrylonitrile (Table 3, entry 5) relative to the other olefinic acceptor substrates. Tethered enones with electron-deficient alkynes as acceptor moiety were also competent in this transformation (Table 3, entry 6) giving the product in high yield. In accordance with results of Yoon and co-workers,[17c] aryl enones could not be cyclized with styrenes (Table 3, entry 7); however, fast, productive cyclization for the corresponding aliphatic enone (entry 8) was observed, albeit missing the diastereoselectivity of the other acceptors. Substrates with unsubstituted, terminal alkenes, lacking suitable stabilization of the intermediary radical, failed to react (Table 3, entries 9 and 10).

As shown in Scheme 4, our proposed mechanism starts with the reductive quenching of the excited state of Eosin Y either by DIPEA or Hantzsch ester to generate the corresponding Eosin Y radical anion as a strong reductant. Upon electron transfer to a simultaneously hydrogen-bond activated unsaturated (aryl) ketone, the photoredox catalyst returns to its ground state. The resulting 1,4-distonic radical anion undergoes an 5-*exo*-trig cyclization to the respective Michael acceptor generating a stabilized α-carbonyl radical, which subsequently can be trapped by direct hydrogen transfer from the radical cation of the reductive quencher to release the cyclopentane product; alternatively, oxidation of the intermediary radical followed by hydride transfer could be assumed.

To validate our preliminary mechanistic scheme, additional experiments were performed. When employing [D_2]Hantzsch ester [D_2]-**14** as hydrogen donor, up to 60% deuteration of the expected α-carbonyl position was ob-



Scheme 4. Proposed mechanism of cooperative reductive cyclization (cationic pathway omitted for clarity).



Scheme 5. Additional mechanistic studies.

served. Moreover, in analogy to a recent photoredox allylation,[7,29] we were able to trap the intermediary α-carbonyl radical with allyltributylstannane (Scheme 5).

To allow this successive C–C bond formation, that is, to prevent hydrogen transfer prior to the attack of the allylstannane, we rationalized the avoidance of an additional reductive quencher to be critical. Hence, our protocol had to be changed to a different photoredox catalyst that would allow SET reduction of the enone directly from its excited state ("oxidative quenching"). These requirements were met by [*fac*-Ir(ppy)$_3$][30] as catalyst; by using our adapted protocol, we were able to obtain the desired domino cyclization/allylation product **16** in good yield and excellent diastereoselectivity.[31]

In conclusion, the applicability of Eosin Y as photocatalyst for the generation of ketyl radical anions was demonstrated, and a new, efficient, cooperative organophotoredox/organocatalysis protocol was developed by using hydrogen-bond catalysis that allows the rapid and highly diastereoselective construction of various *trans*-1,2-substituted cycloalkanes and heterocycles.[32] This operationally simple, room-temperature, mild, and metal-free method should also be a highly valuable and cost-effective alternative to metal-based photoredox approaches given the catalysts and catalyst loadings employed.

Experimental Section

General protocol for reductive organophotoredox cyclizations: Bisenone (1 equiv), Hantzsch ester **14** (1 equiv), DIPEA **13** (1 equiv), 1,3-bis(3,5-bis(trifluoromethyl)phenyl)thiourea **12** (20 mol%), and Eosin Y (2.5 mol%) were dissolved in CH_2Cl_2 ($c_{enone}=0.2\,mol\,L^{-1}$) in a Schlenk tube and degassed by freeze/pump/thaw cycles under nitrogen. The tube was then irradiated by using two green LEDs ($\lambda=530$ nm) from a distance of 5 cm. After completion of the reaction (TLC monitoring), the products were isolated by column chromatography on silica gel.

Acknowledgements

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Keywords: organocatalysis · photocatalysis · redox chemistry · reductive cyclization · thiourea

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