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Blue LEDs-Promoted Oxathiacetalization of Aldehydes and Ketones

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Abstract: In synthetic chemistry, the protection of aldehydes and ketones is crucial during multistep synthesis of complex molecules. Organic chemists have paid substantial attention to the synthesis of 1,3-oxathiolanes and 1,3-oxathianes because of their considerable stability under acidic conditions and ease of removal of protecting groups. In this paper, we report the mild and efficient oxathiacetalization of aldehydes with 2-mercaptoethanol and 3-mercaptopropan-1-ol through visible-light-promoted eosin–Y catalyzed C–S and C–O bond formation at ambient temperature under metal-free conditions. This catalytic system also affords oxathiacetalization of ketones through photoredox catalysis.

Introduction

Protection of carbonyl functional groups from nucleophilic attack until their electrophilic nature can be exploited is major challenge for organic chemists during the multistep synthesis of complex molecules. Among the various carbonyl–protecting groups, 1,3-oxathiolanes, and 1,3-oxathianes have long been used,[1,2] they are considerably more stable than the *O*,*O*-acetals under acidic conditions, and easier to remove than *S*,*S*-acetals.[3] Furthermore, in the pioneering work by Eliel and others, the use of oxathioacetals in organic synthesis was clearly demonstrated; that is chiral 1,3-oxathioacetals were used as chiral auxiliaries for the enantioselective synthesis of α-hydroxy acids and glycols.[4,5] Although, abundant methods are available for the protection and deprotection of carbonyl compounds such as *S,S*-acetals, few methods have been developed for oxathioacetals.[1,2] The existing methods for oxathioacetals employ $HClO_4$,[6a] TsOH,[6b] $BF_3{\cdot}OEt_2$,[6c] Bu_4NBr_3,[6d] TMSOTf,[6e] SO_2,[6f] $ZrCl_4$,[6g] $ZnCl_2$–Na_2SO_4,[6h] –Brønsted acidic ionic liquid,[6i] heterogeneous acid catalyst,[6j] iodine,[6k] *N*-bromosaccharin,[6l] montmorillonite K-10 clay,[6m] Amberlyst®15[6n] –and $Sc(OTf)_3$[6o] as catalysts or –stoichiometric reagents. Regardless of their advancements, the aforementioned methods have several shortcomings: low yield of products,[6d] harsh reaction conditions,[6a,6c] long reaction times,[6g] and use of either stoichiometric[6c,6f] or expensive[6d, 6e] reagents. Therefore, synthetic and medicinal chemists have focused on developing methodologies for effective protection of carbonyl groups by valuable oxathioacetals.

In the development of organic methodologies, visible-light-promoted photoredox catalysis has recently received considerable attention because of its mildness and high functional group tolerance.[7] It acts as a single-electron transfer (SET) system that blocks undesired reaction pathways, thus accomplishing simple and clean organic transformation processes,[8] and its homogenous nature increases the catalyst efficiency for the lowest catalyst loading in the reaction system. Visible-light-driven reactions have emerged as versatile methods of C–S[9] and C–O[10] bond formation. Lei et al.[11a] developed the visible-light-promoted acetalization of aldehydes with alcohols through the photoacid- mediated nucleophilic addition pathway (Scheme 1a). Recently, Kokotos and co-workers[11b] demonstrated highly efficient acetalization of aldehydes using thioxanthenone as the photocatalyst and inexpensive household lamps as the light source (Scheme 1a). Very recently, we reported the environmental friendly thioacetalization of aldehydes with thiols through visible-light-driven eosin–Y catalyzed C–S bond formation at ambient temperature under metal-free and solvent-free conditions (Scheme 1b).[12] Encouraged by these two results, we anticipated that the installation of –OH and –SH in photoredox catalysis under uniform blue light irradiation may activate 2-mercaptoethanol through SET, radical addition to aldehyde[13] and facilitating access to 1,3-oxathiolanes. As part of our ongoing progress in the field of C–S and C–O bond coupling reactions,[14,15] in this paper, we report the mild and efficient oxathiacetalization of aldehydes with 2-mercaptoethanol and 3-mercaptopropan-1-ol through visible-light-driven eosin–Y catalyzed C–S and C–O bond formation at ambient temperature under metal-free conditions (Scheme 1c). We also successfully achieved the oxathiacetalization of ketone. Notably the thiacetalization of ketones was unsuccessful under the optimized reaction conditions used for the oxathiacetalization of ketones.

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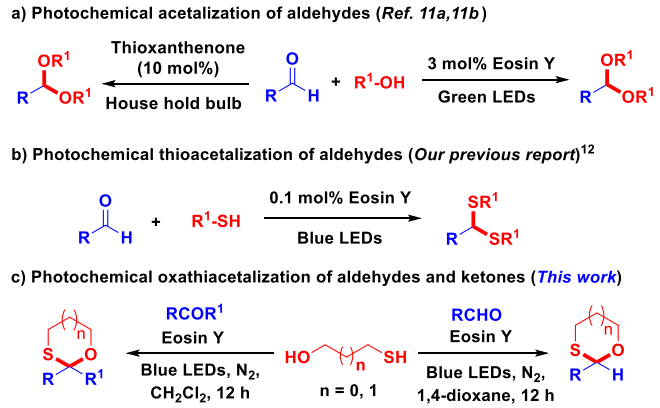


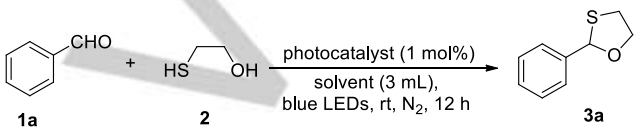
Scheme 1. Photoredox Catalyzed Protection of Carbonyl Compounds.

Results and Discussion

Initially, oxathiacetalization of aldehydes with 2-mercaptoethanol was examined. Benzaldehyde (**1a**) and 2-mercaptoethanol (**2**) were selected as model substrates under solvent-free conditions, and the reaction was conducted using 1.0 mol% eosin Y as the photoredox catalyst under illumination provided by 10-W white LEDs, this resulted in the desired product 1,3-oxathiolane–, (**3a**)-, in 54% yield under nitrogen atmosphere (Table 1, entry 1). Replacing the light source with 10-W blue LEDs-, led to the product yield increasing slightly to 57% (Table 1, entry 2). A trace amount of the product was detected when the other photo catalysts such as eosin B, rose bengal and rhodamine B were used-, instead of eosin Y (Table 1, entries 3–5). Compared with eosin Y, Acr-Mes$^+$ ClO_4^- –and methylene blue as photo–catalyst for the oxathiacetalization of benzaldehyde, generated the product in low yield (Table 1, entries 6 and 7). Varying the catalyst loading and reaction time did not enhance the yield of the product (Table 1, entries 8–11). Next we tested the reaction by using various solvents such as toluene, THF, 1,4-dioxane, DMF, CH_2Cl_2, CH_3CN and H_2O. Among all solvents, only 1,4-dioxane provided favourable results, with 82% yield (Table 1, entry 12). Inferior results were obtained when other solvents were used compared with solvent free conditions (Table 1, entries 13–18). The reaction performed under aerobic conditions generated lower yield of the product (Table 1, entries 19 and 20). Only trace amount of product was detected either the reaction was performed under dark conditions or thermal conditions under dark conditions (Table 1, entries 21 and 22).

Under the optimized reaction conditions, the oxathiacetalization of various aldehydes (**1**) was first evaluated with 2-mercaptoethanol (**2**). As demonstrated in Scheme 2, the photoredox catalyzed reaction generated the corresponding products in moderate to high yields. The substrates bearing halogens at the *ortho*-, *meta*-, and *para*-position of substituted aromatic rings worked well under the reaction conditions (**3b–3d**). Notably, the reaction of 2-nitrobenzaldehyde or 2-hydroxybenzaldehyde with 2-mercaptoethanol under photoredox catalysis generated the corresponding products (i.e., 1,3-oxathiolanes) in low yields (**3e** and **3f**). This may have been due to either steric hindrance or reduction of the aldehydic character of benzaldehyde. We next evaluated the reaction by using various benzaldehydes bearing electron-donating and electron-withdrawing substituents at the *ortho*-, *meta*-, and *para*-positions and the reaction generated corresponding products in moderate to high yields (**3g–3o**). The use of 1-, 2-naphthaldehydes for the oxathiacetalization of aldehydes generated, the corresponding 1,3- oxathiolanes (**3p** and **3q**) in high yields. Vinyl and alkyl aldehydes could also be used as substrates for the reaction with 2-mercaptoethanol; the reaction provided the relevant oxathiacetals in high yields (**3r, 3s** and **3t**). Notably, multi substituted benzaldehyde (**1u**) as well as heterocyclic aldehydes (**1v** and **1w**) could be used for oxathiacetalization and afforded the corresponding products in high yields (**3u–3w**). The chemoselective protection of aldehydes in the presence of ketone was also successfully achieved under the optimized reaction conditions and provided corresponding product (**3x**) in good yield.

Table 1. Optimization of oxathiacetalization of benzaldehyde (**1a**) with 2-mercaptoethanol (**2**)[a]

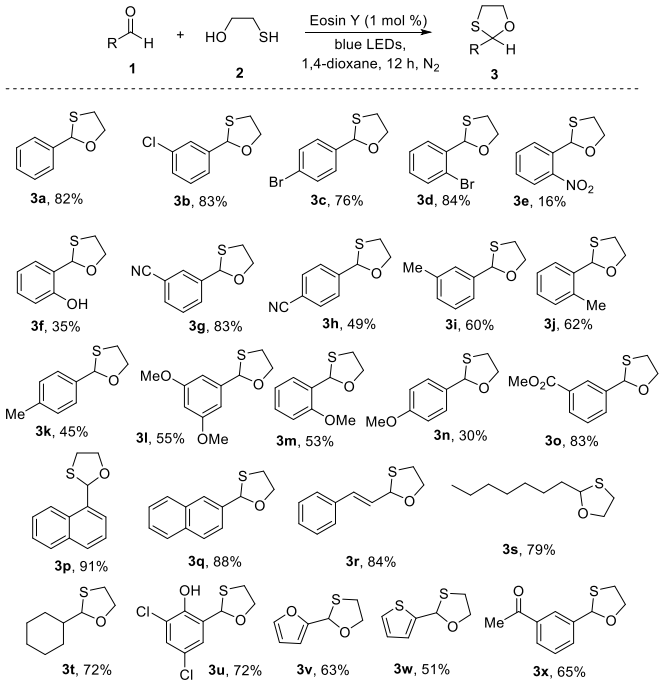


1a **2** **3a**

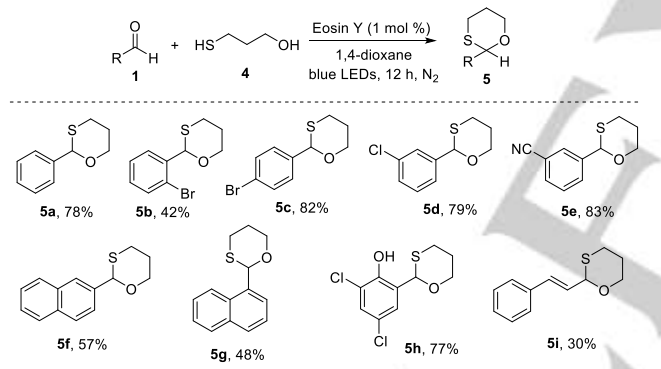
Entry	Photocatalyst	Solvent	Yield (%)[b]
1[c]	Eosin Y	-	54
2	Eosin Y	-	57
3	Rose bengal	-	Trace
4	Acr-Mes$^+$ ClO_4^-	-	52
5	Rhodamine B	-	Trace
6	Methylene blue	-	23
7	Eosin B	-	Trace
8[d]	Eosin Y	-	54
9[e]	Eosin Y	-	56
10[f]	Eosin Y	-	15
11[g]	Eosin Y	-	51
12	Eosin Y	Toluene	48
13	Eosin Y	THF	46
14	Eosin Y	1,4-Dioxane	82
15	Eosin Y	DMF	14
16	Eosin Y	CH_2Cl_2	51
17	Eosin Y	CH_3CN	25
18	Eosin Y	H_2O	13
19[h]	Eosin Y	1,4-Dioxane	74
20[i]	Eosin Y	1,4-Dioxane	47
21[j]	Eosin Y	1,4-Dioxane	Trace
22[k]	Eosin Y	1,4-Dioxane	Trace

[a]Reaction conditions: **1a** (1 mmol), **2** (1.1 equiv) at rt for 12 h. [b]Isolated yields. [c]White LEDs. [d]0.5 mol % catalyst is used. [e]1.5 mol % catalyst is used. [f]6 h of reaction time. [g]24 h of reaction time. [h]Air balloon is used. [i]Under open air conditions. [j]Under dark conditions. [k]In dark at 60 °C.

The scope and generality of the photoredox- catalyzed oxathiacetalization reaction were further demonstrated by employing 3-mercaptopropan-1-ol (**4**) as the substrate in the reaction with various aldehydes (Scheme 3). In this regard, we selected various aldehydes to react with 3-mercaptopropan-1-ol (**4**); the reaction proceeded smoothly to give the corresponding 1,3-oxathianes (**5a–5i**) in moderate to high yields.



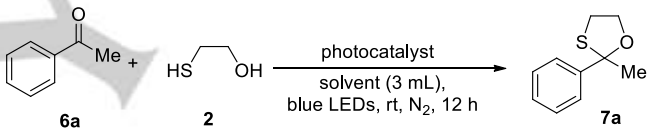
Scheme 2. Scope of aldehydes (**1**) with 2-mercaptoethanol (**2**) for oxathiacetalization. [a]Isolated yields are reported. [b]Reaction conditions: **1** (1.0 mmol), **2** (1.1 equiv), eosin Y (1 mol%), 1,4-dioxane (3 mL), blue LEDs, under N_2, rt, 12 h.



Scheme 3. Scope of aldehydes (**1**) with 3-mercaptopropan-1-ol (**4**) for oxathiacetalization. [a]Isolated yields are reported. [b]Reaction conditions: **1** (1.0 mmol), **4** (1.1 equiv), eosin Y (1 mol%), 1,4-dioxane (3 mL), blue LEDs, under N_2, rt, 12 h.

Based on the aforementioned results we next used ketones (**6**) as substrates instead of aldehydes for photoredox-catalyzed oxathiacetalization with 2-mercaptoethanol (**2**). We first selected acetophenone (**6a**) as the model substrate, and it was reacted with 2-mercaptoethanol (**2**) under the optimized conditions of aldehydes, which yielded the corresponding 1,3-oxathiolane (**7a**) in low yield (Table 2, entry 1). On the basis of this result, we further optimized the reaction conditions. Different solvents were tested first, and the desired product (**7a**) was not obtained when DMF, H_2O, and ethanol were used as the solvent (Table 2, entries 2–4). However, when CH_2Cl_2 was used as the solvent, the product was obtained in 77% yield (Table 2, entry 5). The use of other solvents such as toluene, CH_3CN, and dichloroethane or the solvent-free condition could not improve the yield of the product (Table 2, entries 6–9). The choice of photocatalyst is crucial for this oxathiacetalization. For this transformation, we used CH_2Cl_2 as the solvent-, and other photocatalysts such as rose bengal, eosin B, rhodamine 6G, and methylene blue resulting in, none of the desired product being obtained (Table 2, entries 10–13). However, when Acr-Mes$^+$ ClO_4^- was used as the photo catalyst, the product was obtained in low yield compared with the use of eosin Y (Table 2, entry 14). When the catalyst loading was reduced to 0.1 mol% (Table 2, entry 15), the product was obtained in lower yield. The yield of the product increased to 85% when the catalyst loading was 2 mol% (Table 2, entry 16). With further increase in the catalyst loading, the product was obtained in lower yield (Table 2, entry 17). Decreasing or increasing the reaction time generated the product in lower yields (Table 2, entries 18 and 19). – Performing the reaction under more dilution or aerobic conditions provided the product in decreased yield (Table 2, entries 20 and 21). Very little improvement in the yield of product was observed when degassed dichloromethane was used (Table 2, entry 22). No product was detected when the reaction was performed without a catalyst (Table 2, entry 23). Only trace amount of product was detected either the reaction was performed under dark conditions or thermal conditions under dark conditions (Table 2, entries 24 and 25).

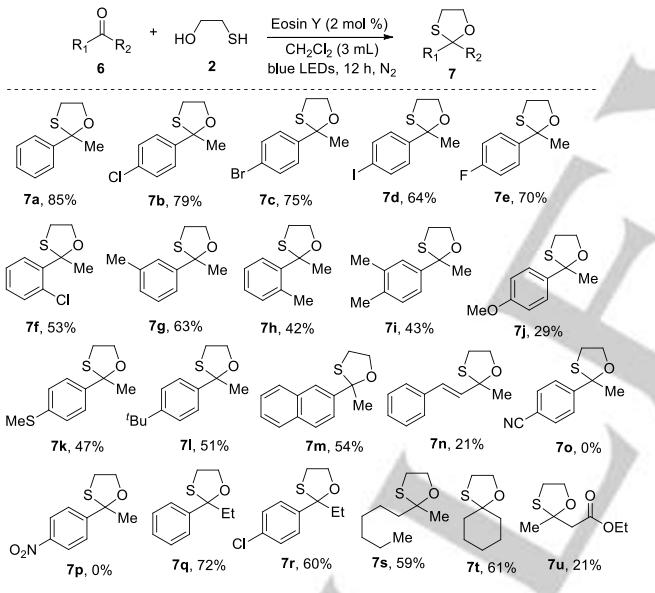
Table 2. Optimization of oxathiacetalization of acetophenone (**6a**) with 2-mercaptoethanol (**2**)[a]



Entry	Photocatalyst (mol%)	Solvent	Yield (%)[b]
1	Eosin Y (1)	1,4-Dioxane	11
2	Eosin Y (1)	DMF	N.R.
3	Eosin Y (1)	H_2O	N.R.
4	Eosin Y (1)	EtOH	N.R.
5	Eosin Y (1)	CH_2Cl_2	77
6	Eosin Y (1)	Toluene	33
7	Eosin Y (1)	CH_3CN	28
8	Eosin Y (1)	DCE	21
9	Eosin Y (1)	-	51
10	Rose Bengal (1)	CH_2Cl_2	N.R.
11	Eosin B (1)	CH_2Cl_2	N.R.
12	Acr-Mes$^+$ ClO_4^- (1)	CH_2Cl_2	41
13	Rhodamine 6G (1)	CH_2Cl_2	N.R.
14	Methylene blue (1)	CH_2Cl_2	Trace
15	Eosin Y (0.1)	CH_2Cl_2	67
16	Eosin Y (2)	CH_2Cl_2	85
17	Eosin Y (3)	CH_2Cl_2	48
18[c]	Eosin Y (2)	CH_2Cl_2	34
19[d]	Eosin Y (2)	CH_2Cl_2	63
20[e]	Eosin Y (2)	CH_2Cl_2	67
21[f]	Eosin Y (2)	CH_2Cl_2	69
22[g]	Eosin Y (2)	CH_2Cl_2	69
23	-	CH_2Cl_2	N.R.
24[h]	Eosin Y	CH_2Cl_2	Trace
25[i]	Eosin Y	CH_2Cl_2	Trace

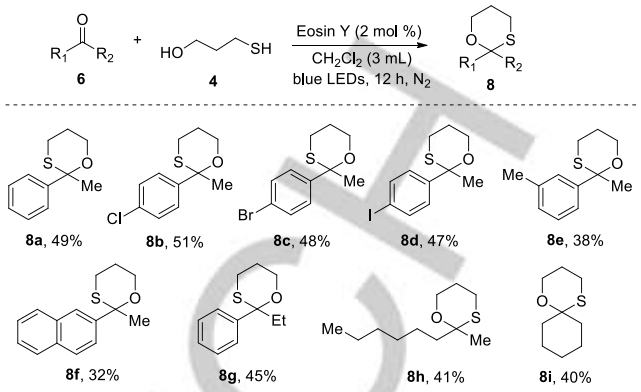
[a]Reaction conditions: **6a** (1 mmol), **2** (1.1 equiv) at rt for 12 h. [b]Isolated yields. [c]At 6 h. [d]At 24 h. [e]At 24 h using degassed DCM. [f]Under air. [g]Use of 6 mL solvent. [h]Under dark conditions. [i]In dark at 60 °C.

Subsequently, we explored the scope of the photoredox oxathiacetalization reaction of various ketones (**6**) with 2-mercaptoethanol (**2**) when using 2 mol% eosin Y as the catalyst and CH_2Cl_2 as the solvent (Scheme 4). Halogen-substituted acetophenones (**6b–6g**) were converted into the desired products (**7b–7f**) in high yield under the optimized conditions. 3-Methyl acetophenone (**6g**) also reacted to generate the corresponding product (**7g**) in high yield. However, in the case of electron-rich, methyl, methoxy, and methylthio-substituted acetophenones (**6h–6k**), the products (**7h–7k**) were obtained in relatively low yields. Other acetylarenes, namely, 4'-*tert*-butylacetophenone (**6l**) and 2-acetylnaphthalene (**6m**), successfully reacted to form the desired products (**7l** and **7m**). However, when (*E*)-4-phenylbut-3-en-2-one (**6n**) was used as the ketone source, the corresponding product (**7n**) was obtained in low yield. When electron-deficient acetylarenes such as 4'-cyanoacetophenone (**6o**) and 4'-nitroacetophenone (**6p**) were used as substrates, the desired products (**7o** and **7p**) were not obtained. Other arylketones, namely-, propiophenone (**7q**) and 4'-chloropropiophenone (**7r**) reacted to form the corresponding products in high yield. Aliphatic ketones (**6s** and **6t**) were also used for this oxathiacetalization, and the related products (**7s** and **7t**) were obtained in high yield. Finally, we employed ethyl acetoacetate (**6u**) as the ketone source and it reacted to form the corresponding product (**7u**) in low yield.



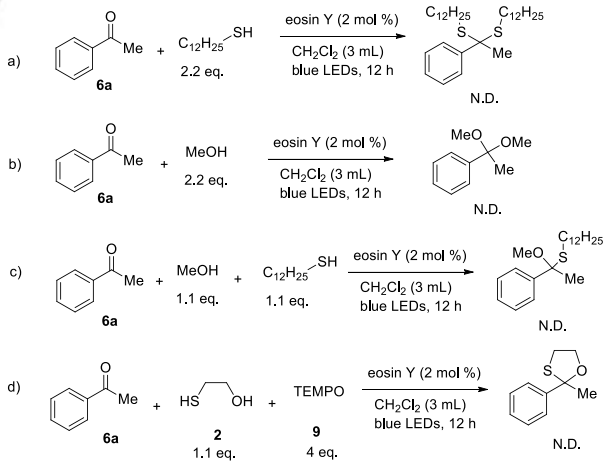
Scheme 4. Scope of ketones (**6**) with 2-mercaptoethanol (**2**) for oxathiacetalization. [a]Isolated yields are reported. [b]Reaction conditions: **6** (1.0 mmol), **2** (1.1 equiv), eosin Y (1 mol%), CH_2Cl_2 (3 mL), blue LEDs, under N_2, rt, 12 h.

To further demonstrate the generality of the photoredox oxathiacetalization reaction, 3-mercaptopropan-1-ol (**4**) was used as the substrate, and reacted with various ketones (**6a–6d**, **6g**, **6m**, **6s** and **6t**), generating the desired products in moderate yields (**8a–8d**, **8g**, **8m**, **8s** and **8t** respectively). Notably, the products were obtained in low yields when 2 mol% of the catalyst was used, whereas when the catalyst loading was decreased to 0.5 mol% the desired products were obtained in moderate yields (Scheme 5). Further decreasing the catalyst loading resulted reduced the product yield.

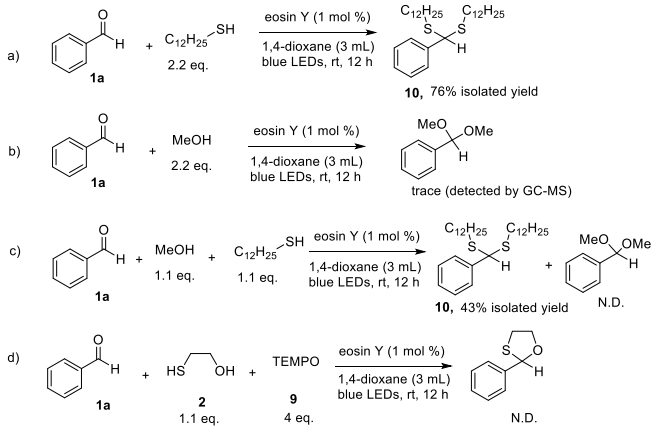


Scheme 5. Scope of ketones (**6**) with 3-mercaptopropan-1-ol (**4**) for oxathiacetalization. [a]Isolated yields are reported. [b]Reaction conditions: **6** (1.0 mmol), **2** (1.1 equiv), eosin Y (1 mol%), CH_2Cl_2 (3 mL), blue LEDs, under N_2, rt, 12 h.

To determine the plausible mechanism of this photoredox-catalyzed oxathiacetalization of aldehydes and ketones, various control experiments were performed by choosing acetophenone as the substrate. Thioacetalization with thiols (Scheme 6a), acetalization with alcohols (Scheme 6b) and oxathiacetalization with a mixture of alcohols and thiols (Scheme 6c), did not generate, the desired product under the optimized reaction conditions of ketones. Furthermore, the addition of TEMPO (**9**) to a reaction mixture containing acetophenone (**6a**), 2-mercaptoethanol (**2**) and a photocatalyst stopped oxathiacetalization (Scheme 6d). indicating that the reaction proceeds through a radical pathway. A similar type of control experiments were also performed with benzaldehyde and corresponding results were presented in Scheme 7.

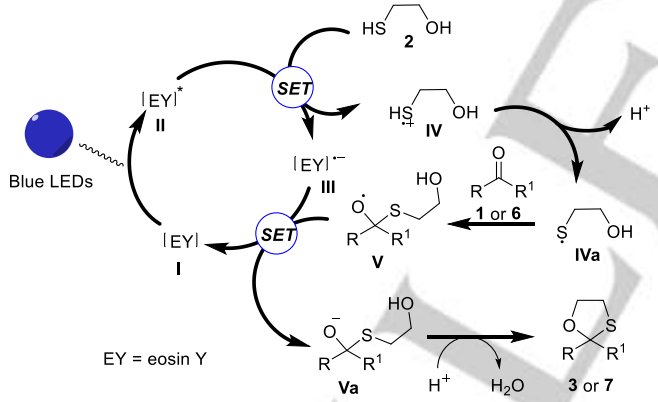


Scheme 6. Control experiments with acetophenone



Scheme 7. Control experiments with benzaldehyde

Based on the aforementioned control experiments, we propose a plausible mechanism for this transformation as follows: interaction of 2-mercaptoethanol (**2**) with blue light induces the formation of excited organophotocatalyst **II** through the SET process; this generates radical cation species **IV**, which in turn undergoes deprotonation to form the hydroxythiyl radical **IVa**. The formed hydroxythiyl radical **IVa** reacts with **1** or **6** to form the intermediate **V**. The intermediate **V** interacts with reduced organophotocatalyst III through an SET process to generate species **Va**, which in turn captures the proton followed by removal of water molecule forms the desired 1,3-oxathiolane **3** or **7** (Scheme 8).



Scheme 8. Plausible Mechanism

Conclusion

In summary, we developed a mild and efficient protocol for oxathiacetalization of aldehydes and ketones using a visible-light-promoted metal-free photoredox catalyst. A wide range of aldehydes containing aromatic, heteroaromatic, aliphatic, and α,β-unsaturated aromatic rings are all well tolerated under the reaction conditions employed. In this report, we have also demonstrated an efficient route for protection of less reactive ketones with mercaptoalcohols. The control experimental studies validated the insight of the reaction mechanism. The eminent features of the present protocol include the simple and convenient operation, low catalyst loading, and high functional group tolerance.

Experimental Section

General Information

Merck silica gel 60 (230–400 mesh) were used to purify the compounds by column chromatography. All commercial chemicals were used as such. GC-MS analyses were undertaken on Agilent Technologies 5977A GC equipped with Agilent 7890B MS. Varian Unity Inova-600 or a Varian Mercury-400 NMR instrument were used to record NMR by using CDCl3 solvent and multiplicity were determined as singlet s, doublet d, triplet t, double of doublet dd, multiplet m and broad brs. Chemical shifts and coupling constant values are determined in parts per million (ppm) and in hertz (Hz). High-resolution mass spectra (HRMS) were analyzed on a Jeol JMS-HX 110 spectrometer by the services provided at the National Chung Hsing University.

General Procedure for the Synthesis of Compounds 3 and 5

Aldehyde **1** (1 mmol), mercaptoalcohol **2** or **4** (1.1 mmol) and eosin Y (1 mol%) were added to the Schlenk tube containing a Teflon-coated magnetic stir bar and was purged by evacuating the tube and back filled with nitrogen. To the mixture, 1,4-dioxane (3 mL) was added and it was kept for stirring under 10 W blue LEDs irradiation at room temperature for 12 hours. After completion of the reaction, the crude reaction mixture was purified by silicagel column chromatography to afford the pure product **3** or **5**.

2-Phenyl-1,3-oxathiolane (3a):[16] This compound is obtained as colorless liquid by the reaction of benzaldehyde (**1a**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15-3.29 (m, 2H), 3.90-3.96 (m, 1H), 4.49-4.54 (m, 1H), 6.04 (s, 1H), 7.29-7.37 (m, 3H), 7.45-7.47 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 34.1, 72.0, 87.0, 126.7, 128.5, 128.7, 139.2.

2-(3-Chlorophenyl)-1,3-oxathiolane (3b): This compound is obtained as light yellow liquid by the reaction of 3-chlorobenzaldehyde (**1b**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.11-3.24 (m, 2H), 3.87-3.93 (m, 1H), 4.44-4.49 (m, 1H), 5.98 (s, 1H), 7.22-7.30 (m, 3H), 7.50 (d, J = 2 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 33.8, 71.9, 85.8, 124.6, 126.5, 128.4, 129.5, 134.1, 141.4. HRMS (EI) calcd for C_9H_9ClOS $[M]^+$ 200.0063, found 200.0068.

2-(4-Bromophenyl)-1,3-oxathiolane (3c):[17] This compound is obtained as colorless liquid by the reaction of 4-bromobenzaldehyde (**1c**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.13-3.17 (m, 1H), 3.19-3.26 (m, 1H), 3.86-3.94 (m, 1H), 4.45-4.50 (m, 1H), 5.97 (s, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 33.9, 71.8, 86.1, 122.3, 128.2, 131.4, 138.3.

2-(2-Bromophenyl)-1,3-oxathiolane (3d): This compound is obtained as yellow liquid by the reaction of 2-bromobenzaldehyde (**1d**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15-3.19 (m, 2H), 3.95-4.01 (m, 1H), 4.57-4.61 (m, 1H), 6.30 (s, 1H), 7.12-7.16 (m, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 8 Hz, 1H), 7.63 (d, J = 8 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 33.4, 72.2, 85.3, 121.6, 126.9, 127.6, 129.4, 132.4, 139.5. HRMS (EI) calcd for C_9H_9BrOS $[M]^+$ 243.9557, found 243.9552.

2-(2-Nitrophenyl)-1,3-oxathiolane (3e):[18] This compound is obtained as yellow solid by the reaction of 2-nitrobenzaldehyde (**1e**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 16%. m.p.: 60-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.11-3.15 (m, 2H),

4.01-4.07 (m, 1H), 4.57-4.61 (m, 1H), 6.57 (s, 1H), 7.43-7.47 (m, 1H), 7.63-7.67 (m, 1H), 7.87 (d, *J* = 8 Hz, 1H), 8.02 (d, *J* = 8.4Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 33.0, 72.5, 81.7, 124.5, 127.0, 128.5, 133.8, 137.4, 146.4.

2-(1,3-Oxathiolan-2-yl)phenol (3f):[19] This compound is obtained as colorless liquid by the reaction of 2-hydroxybenzaldehyde (**1f**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.20-3.27 (m, 2H), 3.86-3.92 (m, 1H), 4.53-4.57 (m, 1H), 6.13 (s, 1H), 6.83-6.89 (m, 2H), 7.16 (dd, J_1 = 7.6 Hz, J_2= 0.8 Hz, 1H), 7.20-7.24 (m, 1H), 7.31 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 33.4, 71.6, 87.0, 117.1, 120.0, 121.5, 128.1, 130.2, 155.0.

3-(1,3-Oxathiolan-2-yl)benzonitrile (3g): This compound is obtained as colorless liquid by the reaction of 3-cyanobenzaldehyde (**1g**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.22-3.28 (m, 2H), 3.96-4.02 (m, 1H), 4.51-4.56 (m, 1H), 6.05 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.77 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 34.0, 72.1, 85.4, 112.4, 118.5, 129.1, 130.1, 130.9, 132.0, 141.2. HRMS (EI) calcd for $C_{10}H_9NOS$ $[M]^+$ 191.0405, found 191.0412.

4-(1,3-Oxathiolan-2-yl)benzonitrile (3h):[20] This compound is obtained as colorless liquid by the reaction of 4-cyanobenzaldehyde (**1h**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 49%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.19-3.28 (m, 2H), 3.96-4.02 (m, 1H), 4.50-4.55 (m, 1H), 6.07 (s, 1H), 7.52-7.54 (m, 2H), 7.63 (dd, J_1= 6.4 Hz, J_2= 2 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 33.9, 72.1, 85.4, 111.9, 118.4, 126.9, 132.1, 144.8.

2-(*m*-Tolyl)-1,3-oxathiolane (3i):[6o] This compound is obtained as colorless liquid by the reaction of *m*-tolualdehyde (**1i**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.32 (s, 3H), 3.08-3.12 (m, 1H), 3.16-3.23 (m, 1H), 3.83-3.89 (m, 1H), 4.43-4.48 (m, 1H), 5.98 (s, 1H), 7.09 (d, *J* = 6.8 Hz, 1H), 7.18-7.24 (m, 2H), 7.27 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 21.1, 33.8, 71.6, 86.8, 123.5, 126.9, 128.0, 129.1, 137.8, 138.8.

2-(*o*-Tolyl)-1,3-oxathiolane (3j): This compound is obtained as pale liquid by the reaction of *o*-tolualdehyde (**1j**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.35 (s, 3H), 3.18-3.24 (m, 2H), 3.89-3.95 (m, 1H), 4.56-4.60 (m, 1H), 6.19 (s, 1H), 7.12-7.13 (m, 1H), 7.17-7.23 (m, 2H), 7.58-7.60 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 19.1, 33.7, 71.7, 84.3, 125.3, 126.1, 128.1, 130.3, 134.9, 137.3. HRMS (EI) calcd for $C_{10}H_{12}OS$ $[M]^+$ 180.0609, found 180.0615.

2-(*p*-Tolyl)- 1,3-oxathiolane (3k):[20] This compound is obtained as pale liquid by the reaction of *p*-tolualdehyde (**1k**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.32 (s, 3H), 3.10-3.15 (m, 1H), 3.18-3.23 (m, 1H), 3.84-3.91 (m, 1H), 4.44-4.48 (m, 1H), 5.99 (s, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* =5.6 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 21.1, 33.8, 71.6, 86.9, 126.5, 128.9, 136.0, 138.2.

2-(3,5-Dimethoxyphenyl)- 1,3-oxathiolane (3l): This compound is obtained as colorless liquid by the reaction of 3,5-dimethoxybenzaldehyde (**1l**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.10-3.15 (m, 1H), 3.17-3.24 (m, 1H), 3.76 (s, 6H), 3.87-3.93 (m, 1H), 4.44-4.49 (m, 1H), 5.97 (s, 1H), 6.39 (t, *J* =2.4 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 33.6, 55.1, 71.6, 86.5, 100.4, 104.0, 141.5, 160.5. HRMS (EI) calcd for $C_{11}H_{14}O_3S$ $[M]^+$ 226.0664, found 226.0667.

2-(2-Methoxyphenyl)- 1,3-oxathiolane (3m): This compound is obtained as colorless liquid by the reaction of o-anisaldehyde (**1m**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.14-3.17 (m, 2H), 3.85 (s, 3H), 3.94-4.00 (m, 1H), 4.52-4.56 (m, 1H), 6.34 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 7.25-7.29 (m, 1H), 7.56 (d, *J* = 8 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 33.1, 55.3, 71.7, 81.0, 110.1, 125.4, 128.4, 128.9, 156.0. HRMS (EI) calcd for $C_{10}H_{12}O_2S$ $[M]^+$ 196.0558, found 196.0562.

2-(4-Methoxyphenyl)- 1,3-oxathiolane (3n):[20] This compound is obtained as colorless liquid by the reaction of p-anisaldehyde (**1n**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.14-3.19 (m, 1H), 3.23-3.29 (m, 1H), 3.78 (s, 3H), 3.86-3.92 (m, 1H), 4.47-4.52 (m, 1H), 5.99 (s, 1H), 6.87 (dd, J_1 = 6.8 Hz, J_2= 2 Hz, 2H), 7.39-7.41 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 33.9, 55.2, 71.6, 86.7, 113.7, 128.1, 130.9, 159.8.

Methyl 3-(1,3-Oxathiolan-2-yl)benzoate (3o): This compound is obtained as colorless liquid by the reaction of methyl 3-formylbenzoate (**1o**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 44%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.19-3.23 (m, 1H), 3.26-3.32 (m, 1H), 3.92 (s, 3H), 3.94-4.00 (m, 1H), 4.53-4.56 (m, 1H), 6.09 (s, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.6Hz, 1H), 8.13 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 34.0, 52.1, 72.0, 86.3, 127.7, 128.5, 129.7, 130.3, 131.1, 139.9, 166.7.

2-(Naphthalene-1-yl)-1,3-oxathiolane (3p):[19] This compound is obtained as pale yellow liquid by the reaction of 1-naphthaldehyde (**1p**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.06-3.13 (m, 2H), 3.85-3.91 (m, 1H), 4.44-4.49 (m, 1H), 6.62 (s, 1H), 7.38-7.48 (m, 3H), 7.71-7.78 (m, 3H), 7.98 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 33.5, 71.5, 84.2, 122.4, 123.1, 125.2, 125.5, 126.0, 128.4, 128.5, 130.0, 133.4, 134.8.

2-(Naphthalene-2-yl)-1,3-oxathiolane (3q): This compound is obtained as white solid by the reaction of 2-naphthaldehyde (**1q**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 88%. m.p.: 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.20-3.23 (m, 1H), 3.26-3.31 (m, 1H), 3.96-4.02 (m, 1H), 4.54-4.58 (m, 1H), 6.21 (s, 1H), 7.45-7.47 (m, 2H), 7.57-7.59 (m, 1H), 7.80-7.85 (m, 3H), 7.88 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 34.1, 72.1, 87.2, 124.3, 125.6, 126.2, 126.24, 127.7, 128.1, 128.4, 132.9, 133.4, 136.6. HRMS (EI) calcd for $C_{13}H_{12}OS$ $[M]^+$ 216.0609, found 216.0603.

(*E*)-2-Styryl-1,3-oxathiolane (3r):[20] This compound is obtained as yellow liquid by the reaction of (*E*)-cinnamaldehyde (**1r**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.08-3.18 (m, 2H), 3.85-3.91 (m, 1H), 4.36-4.40 (m, 1H), 5.68 (d, *J* = 7.6 Hz, 1H), 6.24-6.30 (m, 1H), 6.64 (d, *J* = 15.6 Hz, 1H), 7.24-7.26 (m, 1H), 7.29-7.33 (m, 2H), 7.38-7.40 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 33.6, 71.6, 86.2, 126.7, 127.0, 128.1, 128.5, 132.1, 135.8.

2-(*n*-Heptyl)-1,3-oxathiolane (3s): This compound is obtained as colorless liquid by the reaction of *n*-octanal (**1s**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 0.88 (t, *J* = 6.8 Hz, 3H), 1.28-1.49 (m, 11H), 1.72-1.96 (m, 1H), 3.01-3.04 (m, 2H), 3.74-3.81 (m, 1H), 4.31-4.36 (m, 1H), 5.06 (t, *J* = 6.2 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *δ* 14.0, 22.6, 26.5, 29.1, 29.4, 31.7, 32.5, 36.4, 71.1, 87.1.

2-(Cyclohexyl)-1,3-oxathiolane (3t): This compound is obtained as colorless liquid by the reaction of cyclohexyl carboxaldehyde (**1t**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 0.98-1.33 (m, 5H), 1.61-1.80 (m, 5H), 1.97-2.01 (m, 1H), 2.90-3.02 (m, 2H), 3.72-3.78 (m, 1H), 4.31-4.35 (m, 1H), 4.84 (d, *J* = 6.8 Hz, 1H), ^{13}C NMR

(100MHz, $CDCl_3$): δ 25.6, 25.7, 26.2, 29.4, 29.8, 31.9, 43.6, 71.3, 91.8. HRMS (EI) calcd for $C_9H_{16}OS$ $[M]^+$ 172.0922, found 172.0913.

2,4-Dichloro-6-(1,3-oxathiolan-2-yl)phenol (3u): This compound is obtained as white solid by the reaction of 3,5-dichloro-2-hydroxybenzaldehyde (**1u**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 72%. m.p.: 97-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.19-3.23 (m, 2H), 3.94-4.01 (m, 1H), 4.53-4.58 (m, 1H), 6.20 (s, 1H), 6.61 (s, 1H), 7.28 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 33.3, 72.0, 82.6, 121.0, 125.1, 125.5, 127.5, 128.5, 147.9. HRMS (EI) calcd for $C_9H_8Cl_2O_3S$ $[M]^+$ 249.9622, found 249.9626.

2-(Furan-2-yl)- 1,3-oxathiolane (3v):[20] This compound is obtained as yellow liquid by the reaction of furfural (**1v**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09-3.15 (m, 1H), 3.21-3.27 (m, 1H), 4.01-4.07 (m, 1H), 4.27-4.32 (m, 1H), 6.11 (s, 1H), 6.33-6.34 (m, 1H), 6.45-6.46 (m, 1H), 7.42 (dd, J_1 = 1.6 Hz, J_2= 0.8 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 33.3, 71.1, 78.9, 109.0, 110.2, 143.2, 152.0. HRMS (EI) calcd for $C_{11}H_{14}O_3S$ $[M]^+$ 226.0664, found 226.0667.

2-(Thiophen-2-yl)- 1,3-oxathiolane (3w):[20] This compound is obtained as yellow liquid by the reaction of thiophene-2-carbaldehyde (**1w**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.13-3.18 (m, 1H), 3.25-3.31 (m, 1H), 3.95-4.01 (m, 1H), 4.37-4.42 (m, 1H), 6.31 (s, 1H), 6.95 (dd, J_1 = 4.8 Hz, J_2= 3.6 Hz, 1H), 7.13 (d, J = 3.2 Hz, 1H), 7.31 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 33.9, 71.3, 82.1, 126.3, 126.4, 126.5, 143.6.

1-(3-(1,3-Oxathiolan-2-yl)phenyl)ethanone (3x): This compound is obtained as colorless liquid by the reaction of 3-acetylbenzaldehyde (**1x**) with 2-mercaptoethanol (**2**) following the general procedure for **3** and **5**. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (s, 3H), 3.16-3.29 (m, 2H), 3.91-3.97 (m, 1H), 4.50-4.55 (m, 1H), 6.07 (s, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.63-7.66 (m, 1H), 7.88-7.90 (m, 1H), 8.03 (t, J = 1.6 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 26.6, 34.0, 72.0, 86.2, 126.3, 128.4, 128.6, 131.2, 137.1, 140.0, 197.6. HRMS (EI) calcd for $C_{11}H_{12}O_2S$ $[M]^+$ 208.0558, found: 208.0554

2-Phenyl-1,3-oxathiane (5a): This compound is obtained as colorless liquid by the reaction of benzaldehyde (**1a**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.54-1.59 (m, 1H), 1.89-1.99 (m, 1H), 2.64-2.67 (m, 1H), 3.01-3.08 (m, 1H), 3.61 (m, 1H), 4.15-4.19 (m, 1H), 5.65 (s, 1H), 7.15-7.25 (m, 3H), 7.36 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.3, 28.9, 70.3, 84.1, 125.8, 128.1, 128.2, 139.3. HRMS (EI) calcd for $C_{10}H_{12}OS$ $[M]^+$180.0609, found 180.0605.

2-(2-Bromophenyl)-1,3-oxathiane (5b): This compound is obtained as colorless liquid by the reaction of 2-bromobenzaldehyde (**1d**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72-1.76 (m, 1H), 2.05-2.14 (m, 1H), 2.81 (d, J = 13.6 Hz, 1H), 3.20-3.27 (m, 1H), 3.78-3.85 (m, 1H), 4.29-4.33 (m, 1H), 6.03 (s, 1H), 7.12-7.16 (m, 1H), 7.31-7.35 (m, 1H), 7.50 (d, J = 8 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.5, 29.0, 70.7, 83.6, 121.1, 127.7, 128.6, 129.7, 132.4, 138.5. HRMS (EI) calcd for $C_{10}H_{11}BrOS$ $[M]^+$ 257.9714, found 257.9705.

2-(4-Bromophenyl)- 1,3-oxathiane (5c): This compound is obtained as white solid by the reaction of 4-bromobenzaldehyde (**1c**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 82%. m.p.: 76-79°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75 (d, J = 14.4 Hz, 1H), 2.06-2.16 (m, 1H), 2.81 (d, J = 13.6 Hz, 1H), 3.16-3.23 (m, 1H), 3.76 (t, J = 12.4 Hz, 1H), 4.30-4.33 (m, 1H), 5.73 (s, 1H), 7.33 (d, J = 8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.4, 29.0, 70.5, 83.5, 122.2, 127.7, 131.4, 138.4. HRMS (EI) calcd for $C_{10}H_{11}BrOS$ $[M]^+$ 257.9714, found 257.9707.

2-(3-Chlorophenyl)- 1,3-oxathiane (5d): This compound is obtained as yellow liquid by the reaction of 3-chlorobenzaldehyde (**1b**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 (dd, J_1 = 14 Hz, J_2 = 0.8 Hz, 1H), 2.00-2.08 (m, 1H), 2.77 (dd, J_1 =13.2 Hz, J_2 = 1.6 Hz, 1H), 3.11-3.18 (m, 1H), 3.67-3.74 (m, 1H), 4.25-4.29 (m, 1H), 5.72 (s, 1H), 7.21-7.26 (m, 2H), 7.30-7.32 (m, 1H), 7.48 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.2, 28.8, 70.3, 83.1, 124.0, 126.1, 128.2, 129.4, 133.9, 141.2. HRMS (EI) calcd for $C_{10}H_{11}ClOS$ $[M]^+$ 214.0219, found 214.0217.

3-(1,3-Oxathian-2-yl)benzonitrile (5e): This compound is obtained as white solid by the reaction of 3-cyanobenzaldehyde (**1g**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 83%. m.p.:75-78°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75-1.81 (m, 1H), 2.01-2.13 (m, 1H), 2.80-2.86 (m, 1H), 3.18-3.26 (m, 1H), 3.75-3.81 (m, 1H), 4.30-4.35 (m, 1H), 5.80 (s, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.55-7.58 (m, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 24.8, 28.5, 69.9, 82.1, 111.8, 118.0, 128.6, 129.1, 129.9, 131.2, 140.4. HRMS (EI) calcd for $C_{11}H_{11}NOS$ $[M]^+$205.0561, found 205.0564.

2-(Naphthalen-2-yl)-1,3-oxathiane (5f): This compound is obtained as white solid by the reaction of 2-naphthaldehyde (**1q**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 48%. m.p.: 113-116°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67-1.72 (m, 1H), 2.06-2.14 (m, 1H), 2.77-2.81 (m, 1H), 3.15-3.22 (m, 1H), 3.72-3.79 (m, 1H), 4.30-4.34 (m, 1H), 5.90 (s, 1H), 7.42-7.45 (m, 2H), 7.56 (d, J = 8.8 Hz, 1H), 7.77-7.83 (m, 3H), 7.93 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.5, 29.1, 70.5, 84.4, 123.9, 125.0, 126.0, 126.1, 127.5, 128.0, 128.1, 133.0, 133.2, 136.8. HRMS (EI) calcd for $C_{14}H_{14}OS$ $[M]^+$230.765, found 230.0758.

2-(Naphthalen-1-yl)-1,3-oxathiane (5g): This compound is obtained as yellow liquid by the reaction of 1-naphthaldehyde (**1p**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.73 (d, J = 14.4 Hz, 1H), 2.13-2.16 (m, 1H), 2.81 (d, J = 13.6 Hz, 1H), 3.22-3.29 (m, 1H), 3.80-3.86 (m, 1H), 4.34-4.39 (m, 1H), 6.36 (s, 1H), 7.42-7.53 (m, 3H), 7.76-7.82 (m, 3H), 8.28 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.7, 29.2, 70.9, 82.3, 123.7, 124.4, 125.3, 125.5, 125.9, 128.6, 128.9, 129.4, 133.6, 134.9. HRMS (EI) calcd for $C_{14}H_{14}OS$ $[M]^+$ 230.0765, found 230.0762.

2,4-Dichloro-6-(1,3-oxathian-2-yl)phenol (5h): This compound is obtained as white solid by the reaction of 3,5-dichloro-2-hydroxybenzaldehyde (**1t**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 77%. m.p.: 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80-1.84 (m, 1H), 2.09-2.14 (m, 1H), 2.82-2.86 (m, 1H), 3.19-3.26 (m, 1H), 3.77-3.84 (m, 1H), 4.35-4.38 (m, 1H), 5.95 (s, 1H), 7.17-7.18 (m, 1H), 7.29-7.30 (m, 1H), 7.33 (d, J = 2.8 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.4, 28.7, 70.9, 81.9, 121.9, 124.7, 126.0, 126.1, 129.3, 148.6. HRMS (EI) calcd for $C_{10}H_{10}Cl_2O_2S$ $[M]^+$ 263.9779, found 263.9777.

(*E*)-2-Styryl-1,3-oxathiane (5i): This compound is obtained as colorless liquid by the reaction of (*E*)-cinnamaldehyde (**1r**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **3** and **5**. Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66-1.72 (m, 1H), 1.95-2.05 (m, 1H), 2.73-2.79 (m, 1H), 3.01 (m, 1H), 3.64-3.71 (m, 1H), 4.21-4.26 (m, 1H), 5.43-5.45 (m, 1H), 6.23-6.28 (m, 1H), 6.76 (d, J = 15.6 Hz, 1H), 7.21-7.25 (m, 1H), 7.28-7.32 (m, 2H), 7.38 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.4, 8.2, 69.8, 82.1, 126.1, 126.5, 127.8, 128.3, 131.4, 135.9. HRMS (EI) calcd for $C_{12}H_{14}OS$ $[M]^+$ 206.0765, found 206.0768.

General Procedure for the Synthesis of Compounds 7 and 8

Ketone **6** (1 mmol), mercaptoalcohol **2** or **4** (1.1 mmol) and eosin Y (2 mol%) were added to the Schlenk tube containing a Teflon-coated

magnetic stir bar and was purged by evacuating the tube and back filled with nitrogen. To the mixture, CH_2Cl_2 (3 mL) was added and it was kept for stirring under 10 W blue LEDs irradiation at room temperature for 12 hours. After completion of the reaction, the crude reaction mixture was purified by silicagel column chromatography to afford the pure product **7** or **8**.

2-Methyl-2-phenyl-1,3-oxathiolane (7a):[21] This compound is obtained as colorless liquid by the reaction of acetophenone (**6a**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82 (s, 3H), 2.94-2.99 (m, 1H), 3.08-3.14 (m, 1H), 3.89-3.95 (m, 1H), 4.21-4.26 (m, 1H), 7.11-7.15 (m, 1H), 7.20-7.24 (m, 2H), 7.39-7.41 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 32.3, 34.4, 70.6, 95.5, 124.8, 127.1, 128.1, 146.7.

2-(4-Chlorophenyl)-2-methyl-1,3-oxathiolane (7b):[21] This compound is obtained as colorless liquid by the reaction of 4'-chloroacetophenone (**6b**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 3H), 3.03-3.08 (m, 1H), 3.18-3.23 (m, 1H), 3.97-4.01 (m, 1H), 4.29-4.34 (m, 1H), 7.25-7.29 (m, 2H), 7.41-7.44 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 32.1, 34.4, 70.7, 95.0, 126.4, 128.2, 132.9, 145.3.

2-(4-Bromophenyl)-2-methyl-1,3-oxathiolane (7c):[22] This compound is obtained as colorless liquid by the reaction of 4'-bromoacetophenone (**6c**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 3H), 3.04-3.08 (m, 1H), 3.17-3.21 (m, 1H), 3.97-4.00 (m, 1H), 4.29-4.33 (m, 1H), 7.35-7.37 (m, 2H), 7.41-7.44 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 32.1, 34.4, 70.7, 95.0, 121.0, 126.7, 131.1, 145.9. HRMS (EI) calcd for $C_{10}H_{11}BrOS$ $[M]^+$ 257.9714, found 257.9706.

2-(4-Iodophenyl)-2-methyl-1,3-oxathiolane (7d): This compound is obtained as colorless liquid by the reaction of 4'-iodoacetophenone (**6d**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 3H), 3.04-3.08 (m, 1H), 3.18-3.24 (m, 1H), 3.96-4.01 (m, 1H), 4.30-4.35 (m, 1H), 7.23-7.26 (m, 1H), 7.62-7.66 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 32.1, 34.5, 70.7, 92.7, 95.1, 127.0, 137.2, 146.6. HRMS (EI) calcd for $C_{10}H_{11}IOS$ $[M]^+$ 305.9576, found 305.9582.

2-(4-Fluorophenyl)-2-methyl-1,3-oxathiolane (7e): This compound is obtained as colorless liquid by the reaction of 4'-fluoroacetophenone (**6e**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 3H), 3.02-3.08 (m, 1H), 3.17-3.22 (m, 1H), 3.96-4.01 (m, 1H), 4.28-4.33 (m, 1H), 6.95-7.00 (m, 2H), 7.44-7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.2, 34.3, 70.5, 95.0, 114.7 (d, J = 21.2 Hz), 126.7 (d, J = 8 Hz), 142.5 (d, J = 3 Hz), 161.8 (d, J = 244.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -117.1. HRMS (EI) calcd for $C_{10}H_{11}FOS$ $[M]^+$ 198.0515, found 198.0506.

2-(2-Chlorophenyl)-2-methyl-1,3-oxathiolane (7f): This compound is obtained as colorless liquid by the reaction of 2'-chloroacetophenone (**6f**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 3H), 2.84-2.89 (m, 1H), 3.01-3.08 (m, 1H), 3.87-3.93 (m, 1H), 4.28-4.33 (m, 1H), 7.04-7.15 (m, 2H), 7.26-7.28 (d, J = 8.0 Hz, 1H), 7.50-7.51 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 30.1, 33.9, 70.5, 93.5, 124.4, 126.7, 128.2, 131.0, 131.5, 143.5. HRMS (EI) calcd for $C_{10}H_{11}ClOS$ $[M]^+$ 214.0219, found 214.0216.

2-Methyl-2-(*m*-tolyl)-1,3-oxathiolane (7g):[21] This compound is obtained as colorless liquid by the reaction of 3'-methylacetophenone (**6g**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80 (s, 3H), 2.25 (s, 3H), 2.94-2.98 (m, 1H), 3.06-3.11 (m, 1H), 3.89-3.94 (m, 1H), 4.20-4.25 (m, 1H), 6.93-6.95 (d, J = 7.6 Hz, 1H), 7.08-7.12 (t, J = 7.6 Hz, 1H), 7.18-7.21 (d, J = 11.2 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 21.4, 32.3, 34.3, 70.5, 95.5, 121.8, 125.4, 127.8, 127.9, 137.6, 146.6.

2-Methyl-2-(o-tolyl)-1,3-oxathiolane (7h):[21] This compound is obtained as colorless liquid by the reaction of 2'-methylacetophenone (**6h**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 3H), 2.52 (s, 3H), 3.04-3.06 (m, 1H), 3.17-3.23 (m, 1H), 3.97-4.03 (m, 1H), 4.37-4.42 (m, 1H), 7.16-7.18 (m, 3H), 7.29-7.60 (dd, J = 6.2, 1.6 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 21.3, 31.1, 34.1, 70.1, 95.4, 124.1, 125.7, 127.2, 132.1, 134.2, 144.0.

2-(3,4-Dimethylphenyl)-2-methyl-1,3-oxathiolane (7i): This compound is obtained as colorless liquid by the reaction of 3',4'-dimethylacetophenone (**6i**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 43%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 3H), 2.23 (s, 3H), 3.26 (s, 3H), 3.05-3.09 (m, 1H), 3.17-3.23 (m, 1H), 4.00-4.06 (m, 1H), 4.30-4.35 (m, 1H), 7.06-7.08 (d, J = 8.0 Hz, 1H), 7.20-7.25 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 19.3, 19.9, 32.4, 34.4, 70.6, 95.5, 122.2, 126.1, 129.4, 135.5, 136.3, 144.2. HRMS (EI) calcd for $C_{12}H_{16}OS$ $[M]^+$ 208.0922, found 208.0918.

2-(4-Methoxyphenyl)-2-methyl-1,3-oxathiolane (7j):[21] This compound is obtained as colorless liquid by the reaction of 4'-methoxyacetophenone (**6j**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 43%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 3H), 3.04-3.09 (m, 1H), 3.17-3.23 (m, 1H), 3.78 (s, 3H), 3.98-4.04 (m, 1H), 4.28-4.33 (m, 1H), 6.82-6.86 (m, 2H), 7.40-7.43 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 32.2, 34.3, 55.1, 70.4, 95.4, 113.3, 126.2, 138.7, 158.6.

2-((4-Methylthio)phenyl)-2-methyl-1,3-oxathiolane (7k): This compound is obtained as colorless liquid by the reaction of 4'-(methylthio)acetophenone (**6k**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 47%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88 (s, 3H), 2.45 (s, 3H), 3.02-3.07 (m, 1H), 3.16-3.22 (m, 1H), 3.96-4.01 (m, 1H), 4.28-4.33 (m, 1H), 7.18-7.21 (m, 2H), 7.39-7.42 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 15.7, 32.0, 34.3, 70.5, 95.2, 12.4, 126.2, 137.2, 143.6. HRMS (EI) calcd for $C_{11}H_{14}OS_2$ $[M]^+$ 226.0486, found 226.0494.

2-(4-*tert*-Butylphenyl)-2-methyl-1,3-oxathiolane (7l): This compound is obtained as white solid by the reaction of 4'-(*tert*-butyl)acetophenone (**6l**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 51%. m.p.: 43.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 9H), 1.90 (s, 3H), 3.05-3.09 (m, 1H), 3.17-3.23 (m, 1H), 4.00-4.06 (m, 1H), 4.30-4.35 (m, 1H), 7.32-7.34 (m, 1H), 7.39-7.42(m, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 31.3, 32.3, 34.3, 34.4, 70.6, 95.5, 124.5, 125.0, 143.6, 145.0. HRMS (EI) calcd for $C_{14}H_{20}OS$ $[M]^+$ 236.1235, found 236.1227.

2-Methyl-2-(naphthalene-2-yl)-1,3-oxathiolane (7m): This compound is obtained as colorless liquid by the reaction of 2-acetylnaphthalene (**6m**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 514%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3H), 3.08-3.13 (m, 1H), 3.23-3.29 (m, 1H), 4.08-4.14 (m, 1H), 4.38-4.43 (m, 1H), 7.46-7.50 (m, 2H), 7.59-7.61 (m, 1H), 7.81-7.87 (m, 3H), 7.98-7.99 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 32.1, 34.5, 70.8, 95.7, 122.9, 123.9, 125.9, 126.2, 127.5, 128.1, 128.2, 132.6, 132.9, 143.9. HRMS (EI) calcd for $C_{14}H_{14}OS$ $[M]^+$ 230.0765, found 230.0762.

(*E*)-2-Methyl-2-styryl-1,3-oxathiolane (7n):[23] This compound is obtained as colorless liquid by the reaction of (*E*)-4-phenylbut-3-en-2-one (**6n**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 21%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.81 (s, 3H), 3.12-3.17 (m, 2H), 4.14-4.17 (m, 1H), 4.23-4.27 (m, 1H), 6.30-6.34 (d, J = 15.6 Hz, 1H), 6.60-6.64 (d, J = 16.0 Hz, 1H), 7.22-7.24 (m, 1H), 7.28-7.32 (t, J = 7.4 Hz, 2H), 7.37-7.39 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 28.8, 34.2, 70.8, 93.2, 126.6, 127.2, 127.6, 128.5, 133.6, 136.3.

2-Ethyl-2-phenyl-1,3-oxathiolane (7q): This compound is obtained as colorless liquid by the reaction of propiophenone (**6q**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.57-0.90 (t, J = 7.2 Hz, 3H), 2.09-2.15 (t, J = 7.6 Hz, 2H), 2.98-3.03 (m, 1H), 3.09-3.15 (m, 1H), 3.88-3.94 (m, 1H), 4.30-4.35 (m, 1H), 7.19-7.23 (m, 1H), 7.28-7.32 (m, 2H), 7.42-7.44 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 9.6, 33.9, 37.4, 70.6, 99.6, 125.5, 127.0, 127.9, 145.5. HRMS (EI) calcd for $C_{11}H_{14}OS$ $[M]^+$ 194.0766, found 194.0769.

2-(4-Chlorophenyl)-2-ethyl-1,3-oxathiolane (7r): This compound is obtained as colorless liquid by the reaction of 4'-chloropropiophenone (**6r**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (t, J = 7.6 Hz, 3H), 2.07-2.12 (t, J = 7.2 Hz, 2H), 3.02-3.05(m, 1H), 3.11-3.15 (m, 1H), 3.87-3.93 (m, 1H),4.31-4.36 (m, 1H), 7.27-7.29 (m, 2H), 7.37-7.39 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 9.6, 34.0, 37.4, 70.7, 99.2, 127.1, 128.1, 132.9, 144.1. HRMS (EI) calcd for $C_{11}H_{13}ClOS$ $[M]^+$ 228.0375, found 228.0378.

2-(*n*-Hexyl)-2-methyl-1,3-oxathiolane (7s):[22] This compound is obtained as colorless liquid by the reaction of octan-2-one (**6s**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 59%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80-0.83 (t, J = 6.8 Hz, 3H), 1.22-1.28 (m, 6H), 1.31-1.39 (m, 2H), 1.50 (s, 3H), 1.71-1.77 (m, 2H), 2.92-3.02 (m, 2H), 4.01-4.13 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 14.0, 22.5, 25.4, 28.8, 29.4, 31.7, 33.8, 43.3, 70.1, 95.3. HRMS (EI) calcd for $C_{10}H_{20}OS$ $[M]^+$ 188.1235, found 188.1232.

1-Oxa-4-thiaspiro[4,5]decane (7t):[21] This compound is obtained as colorless liquid by the reaction of cyclohexanone (**6t**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22-1.29 (m, 1H), 1.35-1.44 (m, 3H), 1.65-1.84 (m, 6H), 2.93-2.96 (t, J = 6.0 Hz, 2H), 4.07-4.10 (t, J = 5.8 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 24.6, 24.8, 32.7, 39.7, 69.2, 96.2.

Ethyl 2-(2-methyl-1,3-oxathiolan-2-yl)acetate (7u): This compound is obtained as pale yellow liquid by the reaction of ethylacetoacetate (**6u**) with 2-mercaptoethanol (**2**) following the general procedure for **7** and **8**. Yield: 21%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (t, J = 7.0 Hz, 3H), 1.75 (s, 3H), 2.89 (q, J = 14.5 Hz, 2H), 3.06-3.13 (m, 2H), 4.14-4.21 (m, 4H). ^{13}C NMR (100MHz, $CDCl_3$): δ 14.1, 29.1, 33.8, 48.0, 60.5, 70.3, 91.4, 169.7.

2-Methyl-2-phenyl-1,3-oxathiane (8a): This compound is obtained as colorless liquid by the reaction of acetophenone (**6a**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 49%.^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44-1.50 (m, 1H), 1.59 (s, 3H), 1.81-1.91 (m, 1H), 2.47-2.53 (m, 1H), 2.60-2.67 (m, 1H), 3.53-3.60 (m, 1H), 3.75-3.80 (m, 1H), 7.15-7.19 (m, 1H), 7.26-7.30 (m, 2H), 7.58-7.61 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.1, 25.3, 33.3, 63.2, 85.1, 126.9, 127.3, 128.4, 143.4. HRMS (EI) calcd for $C_{11}H_{14}OS$ $[M]^+$ 194.0765, found 194.0774.

2-(4-Chlorophenyl)-2-methyl-1,3-oxathiane (8b): This compound is obtained as colorless liquid by the reaction of 4'-chloroacetophenone (**6b**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47-1.53 (m, 1H), 1.57 (s, 3H), 1.82-1.91 (m, 1H), 2.49-2.65 (m, 2H), 3.49-3.56 (m, 1H), 3.76-3.81 (m, 1H), 7.22-7.26 (m, 2H), 7.51-7.55 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.0, 25.3, 33.1, 63.2, 84.5, 128.4, 128.6, 133.1, 142.1. HRMS (EI) calcd for $C_{11}H_{13}ClOS$ $[M]^+$ 228.0375, found 228.0382.

2-(4-Bromophenyl)-2-methyl-1,3-oxathiane (8c): This compound is obtained as colorless liquid by the reaction of 4'-bromoacetophenone (**6c**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47-1.53 (m, 1H), 1.57 (s, 3H), 1.82-1.91 (m, 1H), 2.49-2.65 (m, 2H), 3.49-3.56 (m, 1H), 3.76-3.81 (m, 1H), 7.38-7.42 (m, 2H), 7.46-7.49 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 24.9, 25.2, 33.1, 63.2, 84.5, 121.4, 128.8, 131.5, 142.6. HRMS (EI) calcd for $C_{11}H_{13}BrOS$ $[M]^+$ 271.9871, found 271.9869.

2-(4-Iodophenyl)-2-methyl-1,3-oxathiane (8d): This compound is obtained as white solid by the reaction of 4'-iodoacetophenone (**6d**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 47%. m.p.: 83.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.57-1.63 (m, 1H), 1.66 (s, 3H), 1.92-2.02(m, 1H), 2.59-2.75 (m, 2H), 3.60-3.66 (m, 1H), 3.86-3.91 (m, 1H), 7.42-7.46 (m, 2H), 7.69-7.73 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.0, 25.3, 33.2, 63.3, 84.7, 93.3, 129.2, 137.6, 143.4. HRMS (EI) calcd for $C_{11}H_{13}IOS$ $[M]^+$ 319.9732, found 319.9730.

2-Methyl-2-(*m*-tolyl)-1,3-oxathiane (8e): This compound is obtained as colorless liquid by the reaction of 3'-methylacetophenone (**6g**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 38%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56-1.61 (m, 1H), 1.69 (s, 3H), 1.92-2.00 (m, 1H), 2.38 (s, 3H), 2.59-2.64 (m, 1H), 2.72-2.79 (m, 1H), 3.65-3.72 (m, 1H), 3.85-3.90 (m, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.47-7.51 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 21.5, 25.1, 25.4, 33.2, 63.2, 85.2, 124.0, 127.5, 128.1, 128.4, 138.1, 143.4. HRMS (EI) calcd for $C_{12}H_{16}OS$ $[M]^+$ 208.0922, found 208.0929.

2-Methyl-2-(naphthalene-2-yl)-1,3-oxathiane (8f): This compound is obtained as white solid by the reaction of 2-acetylnaphthalene (**6m**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 32%. m.p.: 64.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54-1.60 (m, 1H), 1.81 (s, 3H), 1.97-2.07 (m, 1H), 2.63-2.68 (m, 1H), 2.80-2.87 (m, 1H), 3.66-3.73 (m, 1H), 3.92-3.96 (m, 1H), 7.49-7.52 (m, 2H), 7.75-7.78 (m, 1H), 7.84-7.91 (m, 3H), 8.29 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 25.1, 25.4, 33.3, 63.5, 85.4, 124.6, 126.0, 126.1, 126.6, 127.4, 128.2, 128.5, 132.7, 133.3, 140.8. HRMS (EI) calcd for $C_{15}H_{16}OS$ $[M]^+$ 244.0922, found 244.0915.

2-Ethyl-2-phenyl-1,3-oxathiane (8g): This compound is obtained as colorless liquid by the reaction of 3'-methylacetophenone (**6g**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.64 (t, J =7.6 Hz, 3H), 1.44-1.48 (m, 1H), 1.81-1.93 (m, 3H), 2.48-2.63 (m, 2H), 3.56-3.62 (m, 1H), 3.72-3.76 (m, 1H), 7.14-7.18 (m, 1H), 7.27 (t, J =7.6 Hz, 2H), 7.53-7.55 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 7.8, 24.8, 25.4, 38.0, 62.8, 88.9, 127.1, 127.7, 128.2, 141.5. HRMS (EI) calcd for $C_{12}H_{16}OS$ $[M]^+$ 208.0922, found 208.0929.

2-(*n*-Hexyl)-2-methyl-1,3-oxathiane (8h): This compound is obtained as colorless liquid by the reaction of octan-2-one (**6s**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80-0.83 (m, 3H), 1.23-1.29 (m, 6H), 1.30-1.38 (m, 2H), 1.48 (s, 3H), 1.65-1.74 (m, 3H), 1.84-1.91 (m, 1H), 2.75-2.84 (m, 2H), 3.72-3.83 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 13.9, 22.4, 23.3, 24.2, 25.2, 25.5, 29.3, 31.6, 40.7, 61.6, 81.5. HRMS (EI) calcd for $C_{11}H_{22}OS$ $[M]^+$ 202.1391, found 202.1397.

1-Oxa-5-thiaspiro[5,5]undecane (8i): This compound is obtained as colorless liquid by the reaction of cyclohexanone (**6t**) with 3-mercaptopropan-1-ol (**4**) following the general procedure for **7** and **8**. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33-1.57 (m, 6H), 1.72-1.83 (m, 4H), 1.90-1.95 (m, 2H), 2.76 (t, J =6.0 Hz, 2H), 3.80 (t, J =5.6 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 22.0, 23.7, 25.6, 36.5, 60.9, 81.6. HRMS (EI) calcd for $C_9H_{16}OS$ $[M]^+$ 172.0922, found 172.0927.

Benzaldehyde didodecyldithioacetal (10):[24] This compound is obtained as colorless liquid by the reaction of benzaldehyde (1.0 mmol) with dodecane-1-thiol (2.2 equiv) following the general procedure for **3** and **5**. Yield: 76%.^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J =6.8 Hz, 6H), 1.28-1.38 (m, 36H), 1.53-1.61 (m, 4H), 2.49-2.64 (m, 4H), 4.90 (s, 1H), 7.26 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.45-7.47 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 14.1, 22.7, 28.9, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 32.2, 53.1, 127.6, 127.7, 128.4, 140.6.

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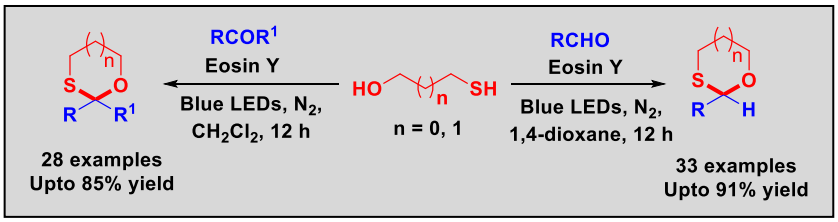

Photoredox catalysis: A visible-light-promoted oxathiacetalization of aldehydes and ketones with 2-mercaptoethanol and 3-mercaptopropan-1-ol in the presence of eosin Y as catalyst is described leading to the formation of 1,3-oxathiolanes and 1,3-oxathianes at ambient temperature and under metal-free conditions. The solvent is playing vital role in the protection of carbonyl compounds with mercaptoalcohol.