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Visible-light mediated facile dithiane deprotection under metal free conditions

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ABSTRACT

Visible light mediated facile and selective dithiane deprotection under metal free conditions is developed. Eosin Y (1 mol%) proved to be an effective catalyst for the dithiane deprotection under the ambient photoredox conditions. The standard household compact fluorescent light source (CFL bulb) proved to be effective under open-air conditions in aqueous acetonitrile at room temperature. The protocol that exhibits a broad substrate scope and functional group tolerance has been shown to expand to a range of transformations for the electron-rich and -deficient thioacetals and thioketals. The synthetic utility of this protocol has also been demonstrated by gram-scale application.

Introduction

The dithiane deprotection is one of the most crucial steps in the multistep synthesis of complex molecules. The dithiane protection has been widely explored for altering and masking the reactivity of carbonyl functionality [1]. Due to its high stability under both acidic as well as basic conditions and simple user friendly protection conditions [1,2], dithiane protection has been widely utilized in the synthetic transformations. However, over the years selective deprotection of dithiane under practical and environmentally viable conditions has been a topic of interest for the synthetic community [3]. Many methods have been developed for the dithiane deprotection over the years. Most of these rely on heavy and toxic metals due to their high affinity towards thiols [3–12]. Alternatively, halogenation reagents such as NBS (*N*-bromosuccinimide) [13,14], NCS(*N*-chlorosuccinimide) [13,15] and hypervalent iodine [16] have been explored. Some of the dithiane deprotection protocols have been achieved by using alkylation, [17] oxone [18], selectfluor [19], nitrogen oxide, [20] Dess-Martin periodinane [21] and clayfen [22]. However, some of these methods are either health hazardous and highly oxidizing or require the use of stoichiometric or excess amount of reagents. Similarly, imidazolium ion based organocatalytic deprotection of thioacetals and thioketals require higher temperature and have proven to be inefficient for the sterically crowded thioacetals [23]. In parallel, efforts have also been focused on avoiding the use of heavy metals and strong oxidizing agents by exploring light mediated deprotection of dithianes. UV light has been utilized for the deprotection of dithiane using catalytic amount of methylene blue along with $MgClO_4$ [3b]. Likewise, recently UV light mediated deprotection using excess amount of H_2O_2 in aqueous acetonitrile has been reported [24]. However, unfortunately these protocols are not suitable for sensitive molecules under high energetic UV light thus leading to desired products in moderate yields along with the side products. Kamata and co-workers explored the high intensity xenon and mercury lamps for the dithiane deprotection using different photosensitizers such as 9,10-dicyanoanthracene, methylene green, *meso*-tetraphenylporphine with the limited substrate scope (Scheme 1a) [25–29]. Unfortunately, some of these methods suffer due to their practical limitations to achieve the wider utility of variety of substrates. Interestingly, further efforts have not been devoted to overcome some of these perennial problems. Even though very recently blue LED mediated dithiane and acetal protection of aldehydes and ketones has been reported [30–32], the development of metal free-visible light mediated practical protocol for the dithiane deprotection remains a great challenge.

Visible light mediated metal-free photocatalysis is an emerging area to access useful synthetic precursors under milder reaction conditions [33]. Herein, we report the visible light mediated facile and selective dithiane deprotection under metal-free conditions using Eosin Y (1 mol %) in aqueous acetonitrile at room temperature.

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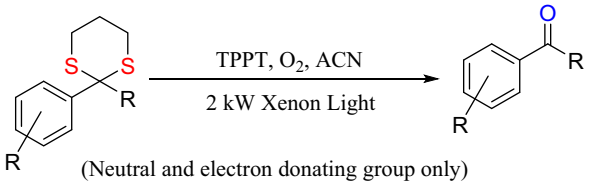
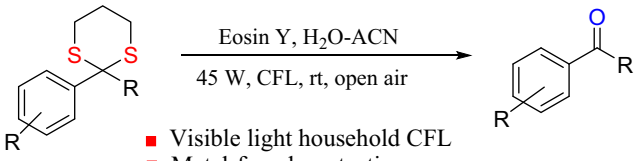
a. Dithiane deprotection using high intensity Xenon lamp



b. This work: Visible light mediated dithiane deprotection



- Visible light household CFL
- Metal-free deprotection
- Low catalyst loading (1 mol %)
- Wide substrate scope and high yield
- Easy and convenient protocol

Scheme 1. Deprotection of dithiane.

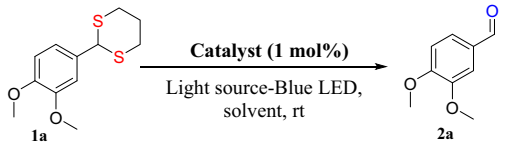
Results and discussion

In order to explore the feasibility of the visible light photoredox mediated dithiane deprotection, we commenced our initial work with 1,3-dithiane protected 3,4-dimethoxybenzaldehyde **1a** as a model substrate and Eosin Y as a catalyst under blue LED light in methanol-water (20% water, v/v) (Table 1, entry 1). Under the said reaction conditions, desired dithiane deprotection occurred by affording the corresponding aldehyde **2a** in 2 h, albeit in moderate yield (67%).

Encouraged by the initial success, we further screened the reaction using Eosin Y (1 mol%) in acetonitrile and water (20% water, v/v) using blue LED for 2 h. Gratifyingly, the deprotection occurred smoothly by affording the corresponding aldehyde **2a** in 78% yield (Table 1, entry 2). In order to optimize the reaction further, we planned to screen different photocatalysts. The catalysts such as riboflavin, rhodamine, $Ru(bpy)_3Cl_2$, 2,4,6-triphenylpyrelium-tetrafluroborate (TPP-BF_4), 9-mesityl-10-methylacridinium tetrafluoroborate (Acr^+-Mes) and $[Ir(dtbbpy)(ppy)_2](PF_6)$ under the reaction conditions proved to be relatively less efficient for the desired transformation (Table 1, Entries 3–8). The deprotection of compound **1a** did not occur in the absence of light under these reaction conditions (Table 1, entry 9). Likewise, the deprotection reaction did not proceed in the absence of catalyst (Table 1, entry 10). In order to optimize the reaction conditions further, we screened different solvents (See ESI, Appendix-I). The reaction of **1a** in presence of Eosin Y (1 mol%), blue LED (30 W) was screened in different aqueous-organic solvent mixture [20% water and 80% solvent (v/v)]. The deprotection in solvents such as DCM, acetonitrile and ethyl acetate under the reaction conditions proved to be quite efficient by affording the desired aldehyde **2a** in good yields (73–79%). However, the deprotection in aqueous methanol was sluggish and afforded aldehyde **2a** in moderate yield. Solvents such as toluene, THF, 1,4-dioxane, ^{t}BuOH did not prove to be beneficial as the desired product **2a** was formed in relatively lower yields (ESI, Appendix-I).

Later we planned to screen different light sources for the optimization of reaction conditions. It is very important to note that switching from blue to green LED to household CFL (white light) significantly enhanced the yield of **2a** in presence of Eosin Y (1 mol%) as a catalyst in ACN-H_2O (Table 2, entries 1–5). Probably due to low energy of household CFL bulb, the rate of over-oxidation of aldehyde to the corresponding carboxylic acid might have reduced significantly. Later we screened dithiane deprotection of **1a** in presence of Eosin Y as a catalyst by varying the percentage of water in acetonitrile using CFL bulb (ESI, Appendix-II, entries 1–8). We observed that with the increase in the amount of water, the rate of reaction remarkably increased but the yield of **2a** reduced significantly. However, we observed that 10–15% water in acetonitrile proved to be ideal for the efficient deprotection in a shorter reaction time. Based on the exhaustive screening, dithiane protected aldehyde **1a** (1 equiv.), Eosin Y (1 mol%) as a catalyst, household white light (CFL bulb, 45 W) in water-acetonitrile (15:85% v/v) at room temperature emerged as optimum reaction conditions.

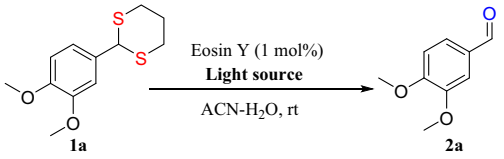
Table 1
Optimization of dithiane deprotection.[a]



Entry	Catalyst	Solvent	Yield (%)
1	Eosin Y	MeOH: H_2O	67
2	Eosin Y	ACN: H_2O	78
3	TPP-BF_4	ACN: H_2O	52
4	(−)-Riboflavin	ACN: H_2O	30
5	Rhodamine	ACN: H_2O	10
6	Acr^+-Mes	ACN: H_2O	47
7	$Ru(bpy)_3Cl_2$	ACN: H_2O	50
8	$[Ir(dtbbpy)(ppy)_3](PF_6)$	ACN: H_2O	45
9[b]	Eosin Y	ACN: H_2O	0
10[c]	None	ACN: H_2O	0

[a] Reaction conditions: **1a** (0.2 mmol), catalyst (1 mol%), Solvent (1.6 mL) and water (0.4 mL), open air atmosphere at room temperature under blue LED, unless otherwise noted.
[b] No light.
[c] No catalyst [blue-LED 30 W, ACN = Acetonitrile].

Table 2
Optimization of the light source.



Entry	Light source	Time (h)	Yield (%)
1	30 W Blue LED	2	79
2	15 W Blue LED	2	80
3	50 W Green LED	2	83
4	23 W CFL	4	86
5	45 W CFL	2	85

Reaction conditions: **1a** (0.2 mmol), Eosin Y (1 mol%), ACN (1.6 mL) and water (0.4 mL), open air atmosphere at room temperature (LED = light-emitting diode, CFL = Compact Fluorescent Lamp, ACN = acetonitrile).

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With an optimum reaction condition in hand, we explored the substrate scope of the method with a diverse range of substrates. Initially we planned to explore the deprotection of electron-rich as well neutral aromatic thioacetals. Under the optimized reaction conditions, aromatic thioacetals (**1a-1j**) underwent deprotection smoothly to afford the corresponding aldehydes (**2a-2j**) in moderate to excellent yields in 2–4 h (up to 92%, Table 3). Then we explored the dithiane deprotection of thioacetals containing chloro and bromo as weakly deactivating groups. Thioacetals (**1k-1n**) underwent facile deprotection to afford the corresponding aldehydes (**2k-2n**) in excellent yields. Further, we planned to evaluate the efficiency of the protocol on electron deficient aromatic thioacetals as well as heteroaromatic thioacetals as their deprotection has not been explored under visible light photoredox conditions till date to the best our knowledge. Aromatic thioacetals containing electron withdrawing groups (**1o-1q**) underwent smooth deprotection to afford the corresponding aldehydes (**2o-2q**) in excellent yields, however, in relatively longer reaction time in comparison to electron rich aromatic thioacetals (Table 3). Heteroaromatic thioacetals (**1r-1v**) also underwent facile dithiane deprotection to afford the corresponding heteroaromatic aldehydes (**2r-2v**) in good to excellent yields (up to 91%). Later we explored the scope of the protocol for the aromatic thioketals. Different aromatic as well as heteroaromatic thioketals (**1w-1y**) under the optimized reaction conditions afforded the corresponding ketones (**2w-2y**) in good to excellent yields.

In addition, tolerance of halide and cyanide groups was also observed under the optimized reaction conditions that are otherwise known to form radicals under photoredox reaction. The α, β-unsaturated thioacetals underwent easy deprotection to afford the corresponding desired compounds (**2z-2aa**) in excellent yields. Our efforts to deprotect some of the aliphatic thioacetals derived from *n*-butanal, heptanal, valeraldehyde, isovaleraldehyde, isobutyraldehyde and pivaldehyde did not give much success. However, gratifyingly compounds **1ab, 1ac** underwent facile dithiane deprotection to afford **2ab** and **2ac** in good yields (Table 3).

We observed that the functional groups such as halo, cyano, nitro and olefinic as well alkyne moieties on the substrates were stable under the reaction conditions. We did not observe any side products emanating during the deprotection. The protocol proved to be efficient for the sterically demanding substrates to afford the desired products in excellent yields. It is very important to note that earlier report on the dithiane deprotection of sterically demanding substrates was less efficient and low yielding [23]. This protocol also proved to be practical even for the nitrogen containing heterocycles, unlike the previously reported procedures [21].

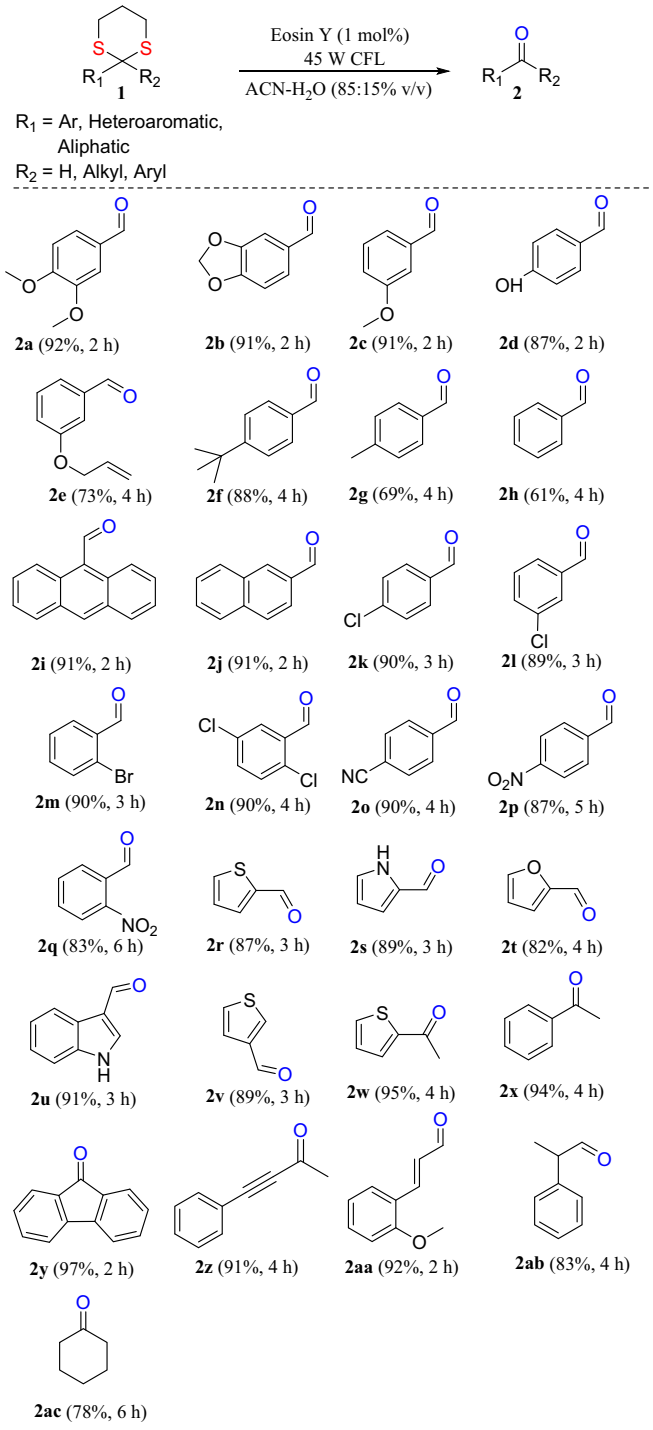
Further, in order to understand the reaction pathway and reactivity patterns, we planned to explore the deprotection of 1, 3-dithiane, 1,2-dithiane and 1,3-sulfoxide under the optimized reaction conditions.

Interestingly, 1,3-dithianes **1a** and 1,3-sulfoxide **1a"** underwent complete deprotection to afford the corresponding aldehyde **2a** in 2 h and 12 h respectively in excellent yield (Scheme 2, eq. a and c). However, deprotection of 1,2-dithiane **1a'** was sluggish and afforded the corresponding aldehyde **2a** in modest yield even after the prolonged reaction time (Scheme 2, eq. b).

With this initial lead, we further planned to understand the plausible reaction pathway of this thioacetal deprotection in a systematic manner. The reaction of aromatic thioacetal **1a** under the optimized reaction conditions in presence of TEMPO did not proceed even after the prolonged reaction time. The result clearly indicates that the pathway must be a radical in nature (Scheme 3, eq. a).

Further, deprotection of 4-methylphenyl thioacetal of 2, 4-dinitrobenzaldehyde **3** furnished significant amount of side product-disulfide **3b** along with the desired aldehyde **3a** (Scheme 3, eq. b). This suggested that dithiane deprotection must be undergoing via the formation of disulfide bond. In order to understand the exact role of oxygen as well as water we carried out few controlled experiments. The deprotection in the absence of oxygen (under nitrogen atmosphere) afforded the desired product **2a** in very poor yield (7%, Scheme 3, eq. c). This result supported the requirement

Table 3
Scope of the reaction.



Reaction conditions: **1** (0.2 mmol), Eosin Y (1 mol%), ACN (1.7 mL) and water (0.3 mL), open air atmosphere at room temperature, isolated yield after column chromatography, (CFL = Compact Fluorescent Lamp, ACN = Acetonitrile).

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of oxygen for the desired transformation. Further, the reaction in anhydrous acetonitrile (absence of H_2O) in presence of Eosin Y as a catalyst under oxygen atmosphere afforded the desired product **2a** in good yield (Scheme 3, eq. d). These control experiments unambiguously supported the requirement of oxygen for the desired transformation.

Based on our experimental observations and from the previous literature [34], following plausible mechanism for the visible light mediated dithiane deprotection has been proposed (Scheme 4).

Upon irradiation with CFL, the photocatalyst **EY** goes to an excited state **EY*** that further oxidizes the thioacetal **A** (sulfur donor atom) to intermediate **I** and gets reduced to **EY**$^{\bullet-}$. Further, the photocatalytic cycle will be completed by the oxidation of **EY**$^{\bullet-}$ to **EY** by the molecular oxygen with the formation of superoxide radical anion. The intermediate **I** is further rearranged to **II,** which is further believed to react with superoxide radical anion to form **III.** The intermediate **III** further breaks down to form the product **B** and the cyclic disulfide **C** as a side product. HRMS data supports the formation of cyclic disulfide **C** which further corroborates the plausible mechanism (see ESI, p. S3).

In order to generalize the method for the practicality, we planned to carry out the deprotection on a gram scale. The deprotection of **1x** and **1a** were carried out under oxygen atmosphere to afford the desired products **2x** and **2a** in good to excellent yields (Scheme 5).

In conclusion, we have developed a visible light mediated practical and metal free protocol for the facile deprotection of dithianes under mild reaction conditions at room temperature under open atmosphere or oxygen atmosphere. The protocol proved to be highly efficient for a wide variety of substrates including strongly electron donating as well electron-deficient thioacetals under visible light and metal free conditions. The sterically demanding substrates as well as heterocyclic thioacetals were smoothly deprotected. This simple and practical method proved to be scalable on gram quantity.

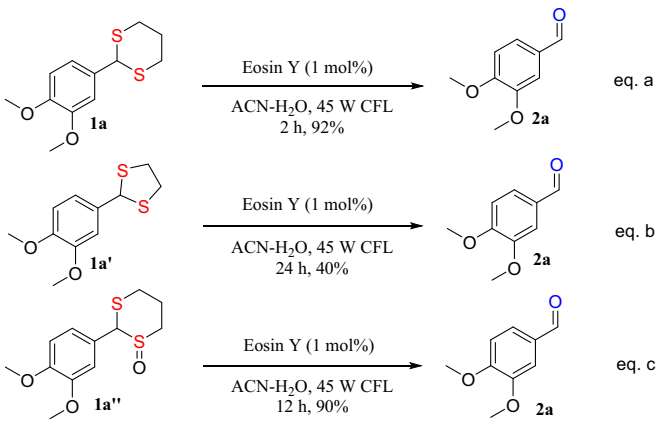
Experimental section

General reagent information

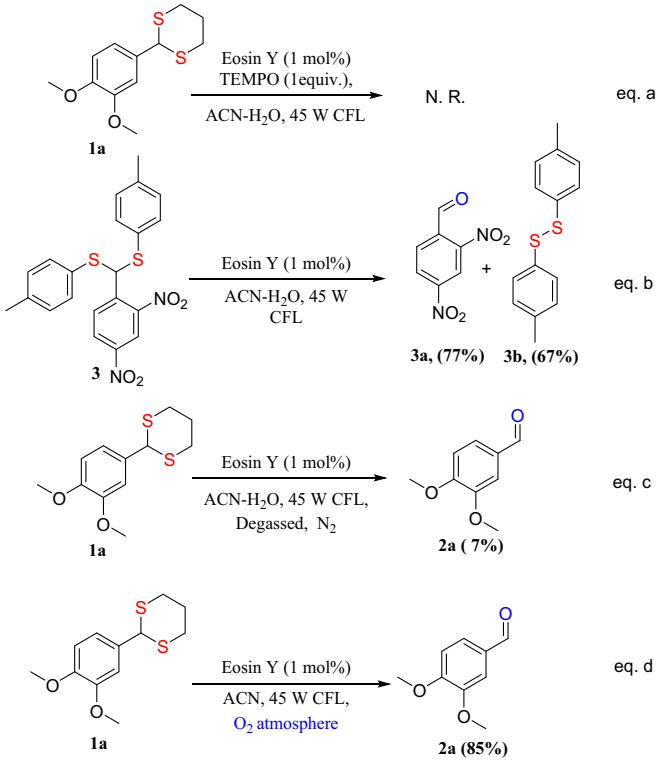
All reactions were set up in open air, or under oxygen while subject to irradiation from blue LEDs, Green LEDs, CFL (IBRA Pure 30 W Blue LED Flood Light, IP Rating: IP66; or Ormit 50 W Green LED Flood Light, IP Rating: IP66; Philips Tornado Compact Fluorescent Bulb 45 W (CFL) (available from local market and Amazon). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Thioacetals/thioketals were prepared according to the literature procedures. Compounds **1** were prepared according to reported procedure. Thin-layer chromatography (TLC) was performed using silica gel 60 GF254 pre-coated aluminum backed plates (2.5 mm). Visualization was accomplished by irradiation with UV light at 254 nm and/or 2,4-DNP stain. Column chromatography was performed using silica gel (100–200 mesh) eluting with petroleum ether and ethyl acetate. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker and Jeol). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26, DMSO d_6: δ 2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16, DMSO d_6: δ 39.52). Coupling constants (J) are given in Hz. IR spectra were obtained using a FT-IR spectrophotometer as neat and are reported in cm^{-1}. Mass samples were analyzed by High-resolution mass spectrometry using ESI TOF.

General procedure A: Dithiane protection of aldehyde and ketones [2f]

To a round-bottom flask charged with magnetic stir bar was added 1,3-propanedithiane (1.1 equiv., 1.65 mmol), catalytic amount of SiO_2 and PTSA, aldehyde/ketone (1 equiv, 1.5 mmol) and CH_2Cl_2 (15 mL). The reaction mixture was refluxed for 6–8 h. After which, the reaction mixture was cooled down to room temperature and excess 1,3-propanedithiane was quenched by adding saturated KOH solution (5 mL) and stirred for 30 min, and extracted with dichloromethane (3 × 20 mL). The extracts were combined, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was further purified by column chromatography to afford the desired compound **1**.



Scheme 2. Deprotection-comparative reactivities.



Scheme 3. Control experiments.

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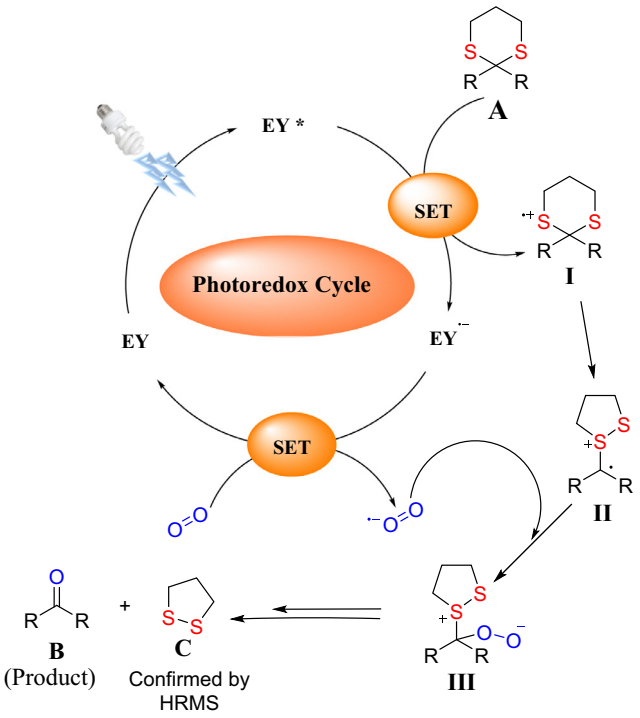
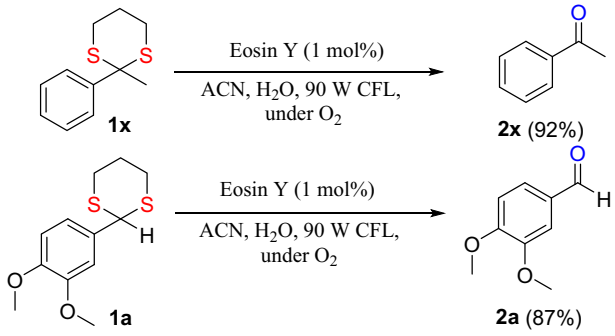


Scheme 4. Plausible mechanism.



Scheme 5. Gram scale synthesis.

General Procedure B: Deprotection of aldehydes and ketones

To a clean screw-top vial (25 mL) equipped with a stir bar was added Eosin Y (1 mol%), thioacetal 1 (1 equiv., 0.2 mmol), H_2O (0.3 mL), and acetonitrile (1.7 mL). The reaction mixture was stirred vigorously for 2–8 h under the irradiation with 45 W CFL bulb in open air. The crude reaction mixture was quenched by the addition of water (15 mL) and further extracted with ethyl acetate (3 × 15 mL). The combined organic layers was dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was further purified by column chromatography over silica gel using ethyl acetate and pet. ether as eluent to afford the desired product 2.

2-(3-(allyloxy)phenyl)-1,3-dithiane (**1e**): Compound **1e** was synthesized following the general procedure A. Compound **1e** was obtained as yellow oil (89%, 336 mg); eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.4; FTIR cm^{-1} (neat): 2928, 1679, 1599, 1446, 1225; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 1H), 7.05–7.02 (m, 2H), 6.84 (ddd, J = 8.3, 2.5, 1.0 Hz, 1H), 6.04 (ddt, J = 17.3, 10.5, 5.3 Hz, 1H), 5.41 (dq, J = 17.3, 1.6 Hz, 1H), 5.27 (dq, J = 10.5, 1.4 Hz, 1H), 5.12 (s, 1H), 4.53 (dt, J = 5.3, 1.5 Hz, 2H), 3.08–3.00 (m, 2H), 2.89 (ddd, J = 14.6, 4.3, 3.2 Hz, 2H), 2.15 (dtd, J = 14.1, 4.5, 2.3 Hz, 1H), 1.97–1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.91, 140.61, 133.22, 129.81, 120.31, 117.82, 115.16, 114.06, 68.89, 51.60, 32.18, 25.22; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{16}OS_2$ $[M]^+$ 252.0643, found 252.0654.

4-(tert-butyl)benzaldehyde (**1f**): Compound **1f** was synthesized following the general procedure A. Compound **1f** was obtained as white solid (99%, 374 mg), mp 85–87 °C; eluent (petroleum ether/ethyl acetate = 19:1), R_f = 0.5; FTIR cm^{-1} (neat): 2955, 2898, 1509, 1466, 1415, 1271; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.33 (m, 4H), 5.15 (s, 1H), 3.07–3.00 (m, 2H), 2.91–2.85 (m, 2H), 2.17–2.10 (m, 1H), 1.97–1.85 (m, 1H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.41, 136.12, 127.41, 125.74, 51.17, 34.67, 32.22, 31.36, 25.19; HRMS (ESI TOF) m/z calcd for $C_{11}H_{15}O$ $[M+H]^+$ 163.1123, found 163.1158.

2-(2,5-dichlorophenyl)-1,3-dithiane (**1n**): Compound **1n** was synthesized following the general procedure A. Compound **1n** was obtained as light pink color solid (98%, 389 mg); mp 96–97 °C; eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.5; FTIR cm^{-1} (neat): 3005, 2893, 1529, 1445, 1415; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 2.5 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.20 (dd, J = 8.6, 2.5 Hz, 1H), 5.57 (s, 1H), 3.15–3.08 (m, 2H), 2.96–2.90 (m, 2H), 2.22–2.16(m, 1H), 1.99–1.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.34, 133.5, 130.85, 130.76, 129.91, 129.67, 47.23, 32.26, 25.11; HRMS (ESI TOF) m/z calcd for $C_{10}H_{11}Cl_2S_2$ $[M+H]^+$ 264.9679, found 264.9678.

2-(1,3-dithian-2-yl)-1H-pyrrole (**1s**): Compound **1s** was synthesized following the general procedure A. Compound **1s** was obtained as grey color solid (93%, 258 mg); mp 99–103 °C; eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.4; FTIR cm^{-1} (neat): 3278, 3106, 2908, 1699, 1562, 1422, 1270; ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 6.76 (td, J = 2.7, 1.6 Hz, 1H), 6.27 (dq, J = 2.7, 0.9 Hz, 1H), 6.17–6.13 (m, 1H), 5.23 (s, 1H), 2.92–2.89 (m, 4H), 2.16–2.07 (m, 1H), 1.97–1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.36, 118.39, 108.78, 107.88, 42.54, 30.21, 25.36; HRMS (ESI TOF) m/z calcd for $C_8H_{12}NS_2$ $[M+H]^+$ 186.0411, found 186.0405.

2-methyl-2-(thiophen-2-yl)-1,3-dithiane (**1w**): Compound **1w** was synthesized following the general procedure A. Compound **1w** was obtained as white solid (97%, 314 mg); mp 63.5–65.5 °C; eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.47; FTIR cm^{-1} (neat): 3126, 2929, 1687, 1545, 1407, 1265; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.19 (m, 2H), 6.95–6.92 (m, 1H), 2.95–2.87 (m, 2H), 2.76–2.70 (m, 2H), 2.04–1.97 (m, 1H), 1.94–1.85 (m, 1H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.17, 127.20, 126.9, 126.24, 50.36, 34.59, 28.56, 24.52; HRMS (ESI TOF) m/z calcd for $C_9H_{13}S_3$ $[M+H]^+$ 217.0179, found 217.0178.

2-methyl-2-(phenylethynyl)-1,3-dithiane (**1z**): Compound **1ab** was synthesized following the general procedure A. Compound **1ab** was obtained as colorless oil (91%, 391 mg);eluent (petroleum ether/ethyl acetate = 19:1); R_f = 0.4; ^1H NMR (400 MHz, $CDCl_3$): δ 7.59–7.55 (m, 2H), 7.48–7.43 (m, 1H), 7.40–7.36 (m, 2H), 2.45 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 184.7, 133.1, 130.8, 128.7, 120, 90.4, 88.4, 32.9; HRMS (ESI TOF) m/z calcd for $C_{13}H_{15}S_2$ $[M+H]^+$ 235.0610, found 235.0617.

2-(3,4-dimethoxyphenyl)-1,3-dithiane 1-oxide (**1a**″):[35] Compound **1a**″ was synthesized following the literature. Compound **1a**″ was obtained as white solid (83%, 339 mg); mp 138–140 °C; eluent (petroleum ether/ethyl acetate = 6:4); R_f = 0.4; FTIR cm^{-1} (neat): 2924, 2850, 1656, 1588, 1511, 1260, 1135; ^1H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, J = 8.3, 2.2 Hz, 1H), 6.88 (d, J = 2.1 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 4.47 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.56–3.49 (m, 1H), 2.89–2.79 (m, 1H), 2.73–2.61 (m, 2H), 2.51–2.44 (m, 1H), 2.38–2.26 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 149.9, 149.3, 125.6, 121.5, 111.5, 111.3, 69.5, 55.9, 55.9, 54.8, 31.6, 29.6. HRMS (ESI TOF) m/z calcd for $C_{12}H_{17}O_3S_2$ $[M+H]^+$ 273.0619, found 273.0617.

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2-(3,4-dimethoxyphenyl)-1,3-dithiane (**2a**)*:* Compound **2a** was synthesized following the general procedure B. Compound **2a** was obtained as white solid (92%, 30.6 mg); mp 39–41 °C; eluent (petroleum ether/ethyl acetate = 7:3); R_f = 0.39; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.47 (dd, J = 8.2, 1.9 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.95, 154.52, 149.65, 130.07, 126.90, 110.42, 108.91, 56.22, 55.94; HRMS (ESI-TOF) m/z calcd for $C_9H_{10}O_3$ $[M]^+$ 166.0630, found 166.0632.

Benzo[d][1,3]dioxole-5-carbaldehyde (**2b**): Compound **2b** was synthesized following the general procedure B. Compound **2b** was obtained as white solid (91%, 27.3 mg); mp 35–38 °C; eluent (petroleum ether/ethyl acetate = 7:3); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.44–7.25 (m, 2H), 6.93 (d, J = 7.9 Hz, 1H), 6.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 153.2, 148.8, 132.0, 128.8, 108.4, 107.0, 102.2; HRMS (ESI-TOF) m/z calcd for $C_8H_7O_3$ $[M+H]^+$ 151.0395, found 151.0398.

3-methoxybenzaldehyde (**2c**): Compound **2c** was synthesized following the general procedure B. Compound **2c** was obtained as light yellow oil (91%, 24.8 mg); eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.46–7.43 (m, 2H), 7.40–7.38 (m, 1H), 7.17 (dt, J = 6.6, 2.7 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 192.2, 160.2, 137.8, 130.1, 123.6, 121.6, 112.1, 55.5; HRMS (ESI-TOF) m/z calcd for $C_8H_8O_2$ $[M]^+$ 136.0524, found 136.0518.

4-hydroxybenzaldehyde (**2d**): Compound **2d** was synthesized following the general procedure B. Compound **2d** was obtained as light brown solid (87%, 21.3 mg); mp 110–113 °C; eluent (petroleum ether/ethyl acetate = 7:3); R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.87–7.74 (m, 2H), 7.03–6.91 (m, 2H), 6.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 161.8, 132.7, 130, 116.2; HRMS (ESI TOF) m/z calcd for $C_7H_7O_2$ $[M+H]^+$ 123.0446, found 123.0449.

3-(allyloxy)benzaldehyde (**2e**): Compound **2e** was synthesized following the general procedure B. Compound **2e** was obtained as light yellow oil (84%, 27.3 mg); eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.4;; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.46–7.39 (m, 3H), 7.19 (dt, J = 6.9, 2.4 Hz, 1H), 6.10–6.01 (m, 1H), 5.46–5.41 (m, 1H), 5.31 (dt, J = 10.5, 1.3 Hz, 1H), 4.59 (dt, J = 5.2, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192, 159.1, 137.8, 132.6, 130.1, 123.6, 122.1, 118.1, 113.1, 68.9; HRMS (ESI TOF) m/z calcd for $C_{10}H_{11}O_2$ $[M]^+$ 163.0759, found 163.0417.

4-(tert-butyl)benzaldehyde (**2f**): Compound **2f** was synthesized following the general procedure B. Compound **2f** was obtained as colorless oil (88%, 28.5 mg); eluent (petroleum ether/ethyl acetate = 19:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.81 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192, 158.4, 134.1, 129.7, 126, 35.3, 31; HRMS (ESI TOF) m/z calcd for $C_{11}H_{15}O$ $[M+H]^+$ 163.1123, found 163.1123.

4-methylbenzaldehyde (**2g**): Compound **2g** was synthesized following the general procedure B. Compound **2g** was obtained as colorless oil (69%, 16.6 mg); eluent (petroleum ether/ethyl acetate = 19:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 145.7, 134.3, 129.8, 130, 22; HRMS (ESI TOF) m/z calcd for C_8H_9O $[M+H]^+$ 121.0653, found 121.0654.

Benzaldehyde (**2h**): Compound **2h** was synthesized following the general procedure B. Compound **2h** was obtained as colorless oil (61%, 13 mg); eluent (petroleum ether/ethyl acetate = 19:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.89–7.87 (m, 2H), 7.65–7.61 (m, 1H), 7.55–7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 136.5, 134.6, 129.9, 129.1; HRMS (ESI TOF) m/z calcd for C_7H_7O $[M+H]^+$ 107.0497, found 107.0501.

Anthracene-9-carbaldehyde (**2i**): Compound **2i** was synthesized following the general procedure B. Compound **2i** was obtained as yellow solid (91%, 37.5 mg); mp 100–103 °C; eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.45 (s, 1H), 8.95–8.89 (m, 2H), 8.58 (s, 1H), 8.01–7.97 (m, 2H), 7.66–7.60 (m, 2H), 7.53–7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 193.0, 135.3, 132.2, 131.1, 129.4, 129.2, 125.7, 124.7, 123.6; HRMS (ESI TOF) m/z calcd for $C_{15}H_{11}O$ $[M+H]^+$ 207.0810, found 207.0807.

2-naphthaldehyde (**2j**): Compound **2j** was synthesized following the general procedure B. Compound **2j** was obtained as yellow solid (91%, 28.5 mg); mp 56–59 °C; eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H), 8.32 (s, 1H), 8.00–7.88 (m, 4H), 7.66–7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 136.6, 134.7, 134.2, 132.7, 129.6, 129.2, 129.2, 128.2, 127.2, 122.9; HRMS (ESI TOF) m/z calcd for $C_{11}H_9O$ $[M+H]^+$ 157.0653, found 157.0658.

4-chlorobenzaldehyde (**2k**): Compound **2k** was synthesized following the general procedure B. Compound **2k** was obtained as white solid (90%, 25.3 mg); mp 45–47 °C; eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191, 141.1, 134.8, 131, 129.6; HRMS (ESI TOF) m/z calcd for C_7H_6ClO $[M+H]^+$ 141.0107, found 141.0112.

3-chlorobenzaldehyde (**2l**): Compound **2l** was synthesized following the general procedure B. Compound **2l** was obtained as colourless oil (89%, 25 mg); eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.83 (dtd, J = 2.1, 1.0, 0.5 Hz, 1H), 7.77–7.75 (m, 1H), 7.58 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.50–7.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 137.8, 135.4, 134.4, 130.5, 129.2, 128.1; HRMS (ESI TOF) m/z calcd for C_7H_6ClO $[M+H]^+$ 141.0107, found 141.0102.

2-bromobenzaldehyde (**2m**): Compound **2m** was synthesized following the general procedure B. Compound **2m** was obtained as colourless oil (90%, 33.3 mg); eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (s, 1H), 7.92–7.89 (m, 1H), 7.64 (dd, J = 7.3, 1.4 Hz, 1H), 7.45–7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192, 135.5, 134, 133.6, 130, 128, 127.2; HRMS (ESI TOF) m/z calcd for C_7H_6BrO $[M+H]^+$ 184.9602, found 184.9604.

2,5-dichlorobenzaldehyde (**2n**): Compound **2n** was synthesized following the general procedure B. Compound **2n** was obtained as white solid (90%, 13.5 mg), mp 52–55 °C; eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.4(s, 1H), 7.86 (t, J = 2.1 Hz, 1H), 7.51–7.48 (m, 1H), 7.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ188.5, 136.0, 135.0, 133.9, 133.4, 131.9, 129.2; HRMS (ESI TOF) m/z calcd for $C_7H_4Cl_2O$ $[M+H]^+$ 174.9717, found 174.9729.

4-formylbenzonitrile (**2o**): Compound **2o** was synthesized following the general procedure B. Compound **2o** was obtained as white solid (90%, 23.6 mg); mp 98–101 °C; eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 7.98 (dd, J = 8.5, 0.6 Hz, 2H), 7.83 (dd, J = 8.0, 0.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 138.8, 133, 130, 117.8, 117.6; HRMS (ESI TOF) m/z calcd for C_8H_6NO $[M+H]^+$ 132.0449, found 132.0449.

4-nitrobenzaldehyde (**2p**): Compound **2p** was synthesized following the general procedure B. Compound **2p** was obtained as Yellow solid (87%, 26.3 mg); mp 101–104 °C; eluent (petroleum ether/ethyl acetate = 7:3); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.16 (s, 1H), 8.40 (d, J = 8.7 Hz, 2H), 8.08 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 151.2, 140.2, 130.6, 124.5; HRMS (ESI TOF) m/z calcd for $C_7H_6NO_3$ $[M+H]^+$ 152.0348, found 152.0352.

2-nitrobenzaldehyde (**2q**): Compound **2q** was synthesized following the general procedure B. Compound **2q** was obtained as

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yellow solid (83%, 25.5 mg); mp 41–42 °C; eluent (petroleum ether/ethyl acetate = 7:3); R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 8.13–8.08 (m, 1H), 7.96–7.92 (m, 1H), 7.82–7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.26, 149.69, 134.20, 133.83, 131.46, 129.74, 124.61; HRMS (ESI TOF) *m/z* calcd for $C_7H_6NO_3$ $[M+H]^+$ 152.0348, found 152.0347.

Thiophene-2-carbaldehyde (**2r**): Compound **2r** was synthesized following the general procedure B. Compound **2r** was obtained as brown oil (87%, 19.5 mg); eluent (petroleum ether/ethyl acetate = 9:1): R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.78–7.75 (m, 2H), 7.22–7.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.1, 144.1, 136.4, 135.2, 128.4; HRMS (ESI TOF) *m/z* calcd for C_5H_5OS $[M+H]^+$ 113.0061, found 113.0070.

1H-pyrrole-2-carbaldehyde (**2s**): Compound **2s** was synthesized following the general procedure B. Compound **2s** was obtained as white solid (89%, 16.9 mg); mp 39–43 °C; eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.24 (s, 1H), 9.48 (s, 1H), 7.18 (s, 1H), 7(s, 1H), 6.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ102.7, 55.7, 50.6, 45.4, 34.3; HRMS (ESI TOF) *m/z* calcd for C_5H_6NO $[M+H]^+$ 96.0449, found 96.0450.

Furan-2-carbaldehyde (**2t**): Compound **2t** was synthesized following the general procedure B. Compound **2t** was obtained as yellow oil (82%, 15.7 mg); eluent (petroleum ether/ethyl acetate = 19:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 7.72–7.68 (m, 1H), 7.27 (dd, J = 3.6, 0.8 Hz, 1H), 6.62 (dd, J = 3.6, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.80, 152.84, 148.09, 121.26, 112.57; HRMS (ESI TOF) *m/z* calcd for $C_5H_5O_2$ $[M+H]^+$ 97.0290, found 97.0289.

1H-indole-3-carbaldehyde (**2u**): Compound **2u** was synthesized following the general procedure B. Compound **2u** was obtained as Yellow solid (91%, 26.5 mg); mp 190–195 °C; eluent (petroleum ether/ethyl acetate = 7:3); Rf = 0.38; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.75 (s, 1H), 8.35–8.32 (m, 1H), 7.86 (d, J = 3.1 Hz, 1H), 7.47–7.44 (m, 1H), 7.36–7.32 (m, 2H); ^{13}C NMR (100 MHz, DMSO-D_6) δ 185.75, 139.01, 137.4, 124.39, 123.98, 122.66, 121.19, 118.49, 112.84; HRMS (ESI TOF) *m/z* calcd for C_9H_8NO $[M+H]^+$ 146.0606, found 146.0597.

Thiophene-3-carbaldehyde (**2v**): Compound **2v** was synthesized following the general procedure B. Compound **2v** was obtained as dark brown oil (89%, 20 mg); eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.13 (dd, J = 2.8, 1.0 Hz, 1H), 7.57–7.52 (m, 1H), 7.38 (dd, J = 5.1, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 143.1, 136.8, 127.5, 125.5; HRMS (ESI TOF) *m/z* calcd for C_5H_4OS $[M+H]^+$ 113.0061, found 113.0070.

1-(thiophen-2-yl)ethanone (**2w**): Compound **2w** was synthesized following the general procedure B. Compound **2w** was obtained as dark yellow oil (95%, 24 mg); eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7 (dd, J = 3.8, 1.2 Hz, 1H), 7.64 (dd, J = 5.0, 1.2 Hz, 1H), 7.13 (dd, J = 5, 3.8 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.81, 144.59, 133.86, 132.57, 128.19, 26.96; HRMS (ESI TOF) *m/z* calcd for C_6H_7OS $[M+H]^+$ 127.0218, found 127.0217.

Acetophenone (**2x**): Compound **2x** was synthesized following the general procedure B. Compound **2x** was obtained as colourless oil (94%, 23.1 mg); eluent (petroleum ether/ethyl acetate = 19:1); R_f = 0.61; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.94 (m, 2H), 7.58–7.54 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 137.2, 133.2, 128.7, 128.4, 26.7; HRMS (ESI TOF) *m/z* calcd for C_8H_9O $[M+H]^+$ 121.0653, found 121.0655.

9H-fluoren-9-one (**2y**): Compound **2y** was synthesized following the general procedure B. Compound **2y** was obtained as yellow solid (97%, 35 mg); mp 80–81 °C; eluent (petroleum ether/ethyl acetate = 8:2); R_f = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.56 (m, 2H), 7.47–7.38 (m, 4H), 7.24 (ddt, J = 8.1, 5.5, 2.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194, 144.4, 134.7, 134.1, 129.1, 124.3, 120.4; HRMS (ESI TOF) *m/z* calcd for $C_{13}H_9O$ $[M]^+$ 181.0653, found 181.0658.

4-phenylbut-3-yn-2-one (**2z**): Compound **2z** was synthesized following the general procedure B. Compound **2z** was obtained as colourless oil (97%, 28 mg); eluent (petroleum ether/ethyl acetate = 9:1); R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.55 (m, 2H), 7.48–7.43 (m, 1H), 7.40–7.36 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.7, 133.1, 130.8, 128.7, 120, 90.4, 88.4, 32.9; HRMS (ESI TOF) *m/z* calcd for $C_{10}H_9O$ $[M+H]^+$ 145.0653, found 145.0657.

(E)-3-(2-methoxyphenyl)acrylaldehyde (**2aa**): Compound **2aa** was synthesized following the general procedure B. Compound **2aa** was obtained as white solid (92%, 29.8 mg); mp 42–45 °C; eluent (petroleum ether/ethyl acetate = 15:5); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 16.1 Hz, 1H), 7.55 (dd, J = 7.7, 1.7 Hz, 1H), 7.41 (ddd, J = 8.8, 7.5, 1.7 Hz, 1H), 7.03–6.98 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.79 (dd, J = 16.1, 7.9 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.5, 158.3, 148.2, 132.7, 128.9, 128.8, 122.9, 120.8, 111.3, 55.5; HRMS (ESI TOF) *m/z* calcd for $C_{10}H_{11}O_2$ $[M+H]^+$ 163.0759, found 163.0750.

2-phenylpropanal (**2ab**): Compound **2ab** was synthesized following the general procedure B. Compound **2ab** was obtained as colourless oil (89%, 23.9 mg); eluent (petroleum ether/ethyl acetate = 19:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, J = 1.4 Hz, 1H), 7.40–7.36 (m, 2H), 7.32–7.28 (m, 1H), 7.22–7.20 (m, 2H), 3.66–3.60 (m, 1H), 1.44 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 201.2, 137.8, 129.2, 128.4, 127.6, 53.1, 14.7; HRMS (ESI TOF) *m/z* calcd for $C_9H_{11}O$ $[M+H]^+$ 135.0810, found 135.0815.

Cyclohexanone (**2ac**): Compound **2ac** was synthesized following the general procedure B. Compound **2ac** was obtained as colourless oil (91%, 17.9 mg); eluent (petroleum ether/ethyl acetate = 99:1); R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (dd, J = 8.4, 4.2 Hz, 4H), 1.80–1.63 (m, 4H), 1.62–1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.1, 41.8, 26.9, 24.8; HRMS (ESI TOF) *m/z* calcd for $C_6H_{11}O$ $[M+H]^+$ 99.0810, found 99.0818.

((2,4-dinitrophenyl)methylene)bis(p-tolylsulfane) (**3**): Compound **3** was synthesized following the general procedure A. Compound **3** was obtained as brown colour viscous oil (91%, 554 mg); eluent (petroleum ether/ethyl acetate = 7:3); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 2.3 Hz, 1H), 8.31 (ddd, J = 8.7, 2.4, 0.4 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H), 7.24–7.21 (m, 4H), 7.08–7.05 (m, 4H), 6.29 (s, 1H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.73, 146.72, 142.07, 139.62, 133.91, 132.48, 130.23, 128.52, 126.99, 120.05, 54.63, 21.37; HRMS (ESI TOF) *m/z* calcd for $C_{21}H_{18}N_2O_4S_2$ $[M]^+$ 426.0708, found 426.0698.

2,4-dinitrobenzaldehyde (**3a**): Compound **3a** was synthesized following the general procedure A. Compound **3a** was obtained as yellow solid (85%, 33.3 mg); mp 63–68 °C; eluent (petroleum ether/ethyl acetate = 7:3); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.48 (s, 1H), 8.97 (d, J = 2.1 Hz, 1H), 8.63 (ddd, J = 8.4, 2.2, 0.7 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5, 150.1, 149.5, 135.5, 131.6, 128.7, 120.3; HRMS (ESI TOF) *m/z* calcd for $C_7H_5N_2O_5$ $[M+H]^+$ 197.0198, found 197.0202.

1,2-di-p-tolyldisulfane (**3b**): Compound **3b** was obtained as yellow colour oil (60%, 29.6 mg); yellow solid; eluent (petroleum ether/ethyl acetate = 18:1); R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.5 Hz, 4H), 7.41 (d, J = 8.0 Hz, 4H), 2.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 141.7, 130.4, 127.1, 21.9; HRMS (ESI TOF) *m/z* calcd for $C_{14}H_{14}S_2$ $[M]^+$ 246.0537, found 246.0530.

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Author contributions

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2019.151407.

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