

# Photoexcited Na<sub>2</sub> eosin Y as direct hydrogen atom transfer (HAT) photocatalyst promoted photochemical metal-free synthesis of tetrahydrobenzo[*b*]pyran scaffolds *via* visible light-mediated under air atmosphere

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## ABSTRACT

**Background:** eosin Y is a metal-free organic dye with easy availability that has gained a wide application in recent years, having economic and ecological superiority for substituting transition-metal-based photocatalysts.

**Method:** a green three-component tandem strategy for synthesizing tetrahydrobenzo[*b*]pyran scaffolds through Knoevenagel-Michael cyclocondensation is reported using Na<sub>2</sub> eosin Y-derived photoexcited states functions as a direct hydrogen atom transfer (HAT) catalyst *via* visible light-mediated in aqueous ethanol at ambient temperature under air atmosphere.

**Findings:** this study paves the new role for further use of a metal-free organic dye with commercial availability and inexpensiveness, Na<sub>2</sub> eosin Y in photochemical synthesis with use of the lowest amount of catalyst, energy-effectiveness, excellent yields, operational simplicity, time-saving aspects of the reaction and high atom economy, thus meeting some features of sustainable and green chemistry.

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## Introduction

Photocatalysis is the method of light-induced redox re-movements upon the encircling molecules to produce radical species for the subsequent usage within the water splitting for H<sub>2</sub> and O<sub>2</sub> manufacturing, numerous pollutant degradations and CO<sub>2</sub> Conversion into hydrocarbon fuels [1]. A method consisting of photocatalysis, which may be manifested for numerous applications, is good for huge scale packages in actual time. With such advantages, the careful selection or engineering of substances and systems for photocatalysis, i.e. photocatalysts are important as to correctly perform the photocatalytic reactions. An ideal photocatalyst sure to possess (i) slender band hole energy, (ii) suitable band edge ability, (iii) reduced recombistate, (iv) enhanced price separation and (v) improved charge transportation [2].

There are two styles of catalysis: homogeneous and heterogeneous catalysis. In homogeneous catalysis, the reactants and the catalyst exist in the same phase. The maximum usually used catalysts are ozone and photo-Fenton structures (Fe<sup>+</sup> and Fe<sup>+</sup>/H<sub>2</sub>O<sub>2</sub>). In heterogeneous catalysis, the reactants and the catalyst exist in one of kind stages. That is the most intensively studied place of studies because of its ability use in environmental and electricity-associated regions,

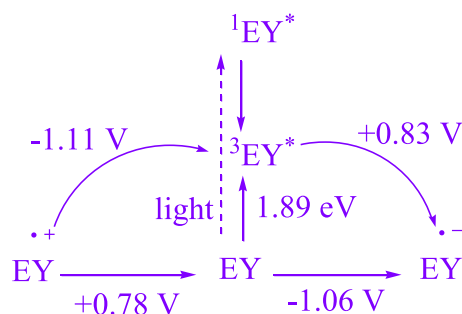
in which mild-soaking up catalysts are used [3]. A great photocatalyst must be stable, inert, trustworthy, inexpensive, and sustainable in the direction of an extensive variety of the solar spectrum. It needs to deliver high electricity conversion performance and quantum yield, with top adsorption within the solar spectrum [4, 5].

Eosin Y is a metal-free organic dye with easy availability that has gained a wide application in recent years, having economic and ecological superiority for substituting transition-metal-based photocatalysts [6].

In eosin Y-catalyzed photoredox reactions, successfully oxidized/reduced target substrates by its incited mode is normally dependent up on if the potential oxidability or reducibility of the substrates lies in the scope of that of eosin Y (Scheme 1).

The range of eosin Y-catalyzed photochemical reactions has been restricted by the mentioned electrochemical requisites. Being highly different from other organic dyes, eosin Y has unique xanthene and phenol moieties, and also prominent acid–base features, which may result in four differing constructs. There are ample documentations that the anionic types of eosin Y exhibit photocatalytic property in most of previous reports on photoreactions while the neutral types assumedly have typical inactivity and are ignorable in potentially applied synthesis processes [7]. In recent years, a team of Wang [8] and Wu [9] has been encouraged by the structural attributes of eosin Y, making aninnovation in the discovery of novel activating states of photoexcited eosin Y. The group discovered that neutral eosin Y-

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**Scheme 1.** Oxidative and reductive quenching cycles of Eosin Y with their corresponding potentialities [6a].

originated incited modes could function as photoacids and direct hydrogen atom transfer (HAT) catalysts for activating glycals and native C-H bonds in respective order (Scheme 2) [6a].

Hydrogen atom transfer (HAT) is a basic stage possibly responsible for multiple processes chemically, environmentally, and biologically. In particular, benzophenone- and quinone-mediated direct HAT catalysis has been launched as an instrument that enables activating C-H bond under light radiation in recent years [10,11]. Recently, Direct HAT catalysis mediated by benzophenone and quinone has been discovered as an effective technique for activating C-H bond by irradiation [10,11]. Due to eosin Y and quinones [10] being similar, Wu and colleagues hypothesized that when exposed to visible spectrum, eosin Y under excitation may operate as a direct HAT catalyst, activating a C-H bond and generating radical species for additional functions [9]. Due to its captodative and steric properties, the radical species derived from eosin Y is unlikely to undergo the kinds of side reactions seen in HAT catalysis with diaryl ketones, allowing for a reverse transfer of hydrogen atom. Based on this mechanics, Wu and colleagues discovered that when exposed to visible spectrum, eosin Y in neutral form can effectively trigger numerous C(sp<sup>3</sup>)-H and C(sp<sup>2</sup>)-H bonds to start generating the corresponding radicals of carbon, allowing radical introduction to multiple alkenes with electron deficiency. This approach has a wide substrate purview and a high group tolerance. The required C-H alkylation compounds were produced in high yields and with high site selection. With good site selection, a number of C(sp<sup>3</sup>)-H and C(sp<sup>2</sup>)-H bonds of ethers, thioethers, alcohols, aldehydes, and cyclohexanes were radical alkylated (e.g., 10 c). This method may also be used toward a variety of tri- and tetrasubstituted olefins with different features. This HAT catalysis approach, in particular, overcomes the substrate constraints of classic SET-based redox reactions [6a].

Also, visible light irradiation has been a reliable approach for green chemists because of its plentiful reserves of the energy, low cost and its renewable source of energy in the eco-friendly synthesis of organic compounds [12–14]. In general, light emitting diodes and compact fluorescent lights are employed as the sources of visible light for various transformations.

Pyran derivatives with various pharmacological features (Figure 1) like Chk1 kinase inhibitory activity [15], analgesic properties [16], anticancer [17], vasodilatory activities [18], spasmolytic [19], antihypertensive, hepatoprotective, cardiotoxic [20], vasodilator [21], anti-leukemic [22,23], emetic [24], anti-anaphylactic activities [25], diuretic [26] and anti-alzheimer [27].

There are numerous approaches for synthesizing these compounds using various catalysts such as CaHPO<sub>4</sub> [28], SiO<sub>2</sub>NPs [29], ethylenediamine diacetate [30], SBPPSP [31], DBSA [32], NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O [33], NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> [34], ACoPc-MNPs [35], ZnONPs [36], Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-imid-PMA [37], NiFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [38], theophylline [39], triethanolamine [40], NaN<sub>3</sub> [41], Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> [42], MgFe<sub>2</sub>O<sub>4</sub> nanoparticles [43] and trichloroisocyanuric acid [44]. It was shown that these reported procedures lead to in numerous cases. Though, some of synthetic policies contain also restrictions regarding the expensive reagents, metal catalyst, environmental hazard, long reaction time, harsh reaction circumstances, monotonous workup process, unacceptable yield, and using the homogeneous catalyst that are separated problematically from reaction mixture.

Owing to the above-mentioned difficulties and due to our current severe attention on environmentally benign protocols [45–47] via multi-component reactions [48–50] and our interest in developing tetrahydrobenzo[b]pyrans production, the study of photocatalyst under green circumstances for the proper synthesis of these oxygen-containing heterocyclic compounds has been an important goal. This study paves the new role for further use of a metal-free organic dye with commercial availability and inexpensiveness, Na<sub>2</sub> eosin Y in above photochemical synthesis. Evidence indicates that Na<sub>2</sub> eosin Y-derived photoexcited states functions as a direct hydrogen atom transfer (HAT) catalyst to synthesize tetrahydrobenzo[b]pyran scaffolds photochemically via Knoevenagel-Michael cyclocondensation of aryl aldehydes, malononitrile and dimedone via visible light-mediated in aqueous ethanol at ambient temperature under air atmosphere. This reaction is a fruitful one-pot approach under highly effective, mild and facile reaction conditions.

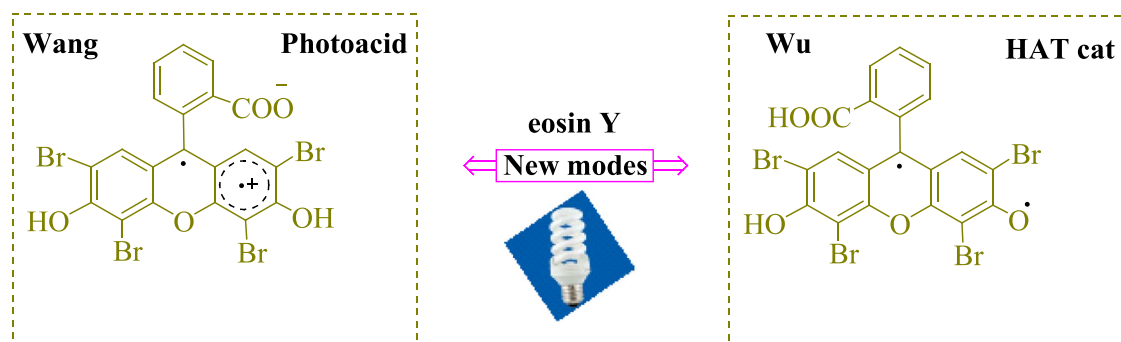
## Experimental

### General

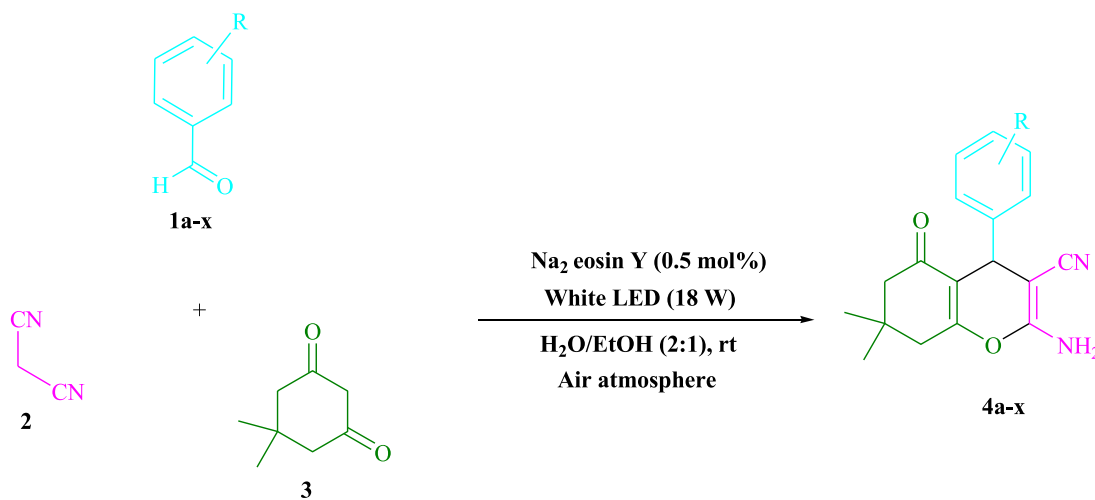
Utilizing an Electro thermal 9100 device, all compounds' melting points were found. Moreover, recording nuclear magnetic resonance, <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra were carried out on a Bruker DRX-400, Bruker DRX-300 and Bruker DRX-100 Avance tool with CDCl<sub>3</sub> as solvent. All reagents were bought from Acros, Merck, and Fluka chemical companies and were utilized with no additional purification.

### Overall process of preparing (4a-x)

To a mixture of aryl aldehyde derivatives (**1**, 1.0 mmol), malononitrile (**2**, 1.0 mmol) and dimedone (**3**, 1.0 mmol) in a H<sub>2</sub>O/EtOH (2:1) (3 mL), was added Na<sub>2</sub> eosin Y (0.5 mol%), under white light emitting



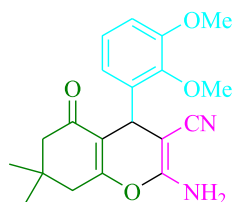
**Scheme 2.** Exploration of photoexcited eosin Y as a photoacid or HAT catalyst [6a].



**Scheme 3.** Synthesis of tetrahydrobenzo[b]pyran scaffolds.

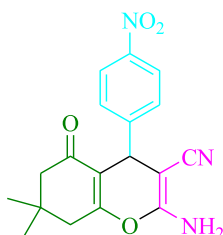
diode (LED) (18 W) irradiation (Scheme 3). The mixture was stirred for 3 min at ambient temperature. The reaction progress was monitored by TLC utilizing *n*-hexane/EtOAc (3:1) as an eluent. After completing the reaction, the achieved solid was filtered, rinsed with water and the crude solid was recrystallized from ethanol to provide the pure material without requiring more purification. The products were classified after the comparison of spectroscopic information ( $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR). Support for this manuscript can be found in the following:

2-Amino-4-(2,3-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4Hchromene-3-carbonitrile (4i)



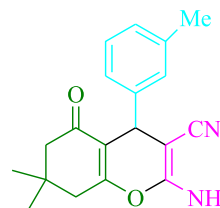
Yield: 92%; M.p. 215–217°C;  $^1\text{H}$ NMR (300MHz,  $\text{CDCl}_3$ ) 1.10 (3H, s,  $\text{CH}_3$ ), 1.14 (3H, s,  $\text{CH}_3$ ), 2.25 (2H, s,  $\text{CH}_2$ ), 2.47 (2H, s,  $\text{CH}_2$ ), 3.77 (3H, s,  $\text{OCH}_3$ ), 3.83 (3H, s,  $\text{OCH}_3$ ), 4.47 (2H, s,  $\text{NH}_2$ ), 4.73 (1H, s,  $\text{CHAr}$ ), 6.68–6.84 (3H, m, ArH) ppm;  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ ): 27.6, 27.8, 28.5, 32.1, 43.7, 50.2, 57.3, 57.5, 58.9, 112.0, 112.8, 118.3, 123.2, 124.3, 124.7, 150.4, 151.6, 159.1, 164.5, 199.7.

2-Amino-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4Hchromene-3-carbonitrile (4k)



Yield: 91%; M.p. 181–183°C;  $^1\text{H}$ NMR (300MHz,  $\text{CDCl}_3$ ) 1.07 (3H, s,  $\text{CH}_3$ ), 1.16 (3H, s,  $\text{CH}_3$ ), 2.30 (2H, d,  $J=14.0$  Hz,  $\text{CH}_2$ ), 2.52 (2H, s,  $\text{CH}_2$ ), 4.55 (1H, s,  $\text{CHAr}$ ), 4.68 (2H, s,  $\text{NH}_2$ ), 7.45 (2H, d,  $J=11.6$  Hz, ArH), 8.20 (2H, d,  $J=11.6$  Hz, ArH) ppm;  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ ): 27.3, 27.6, 31.3, 36.9, 42.5, 52.4, 57.7, 111.8, 119.4, 125.4, 125.5, 129.1, 129.4, 151.3, 153.9, 158.1, 163.6, 198.4.

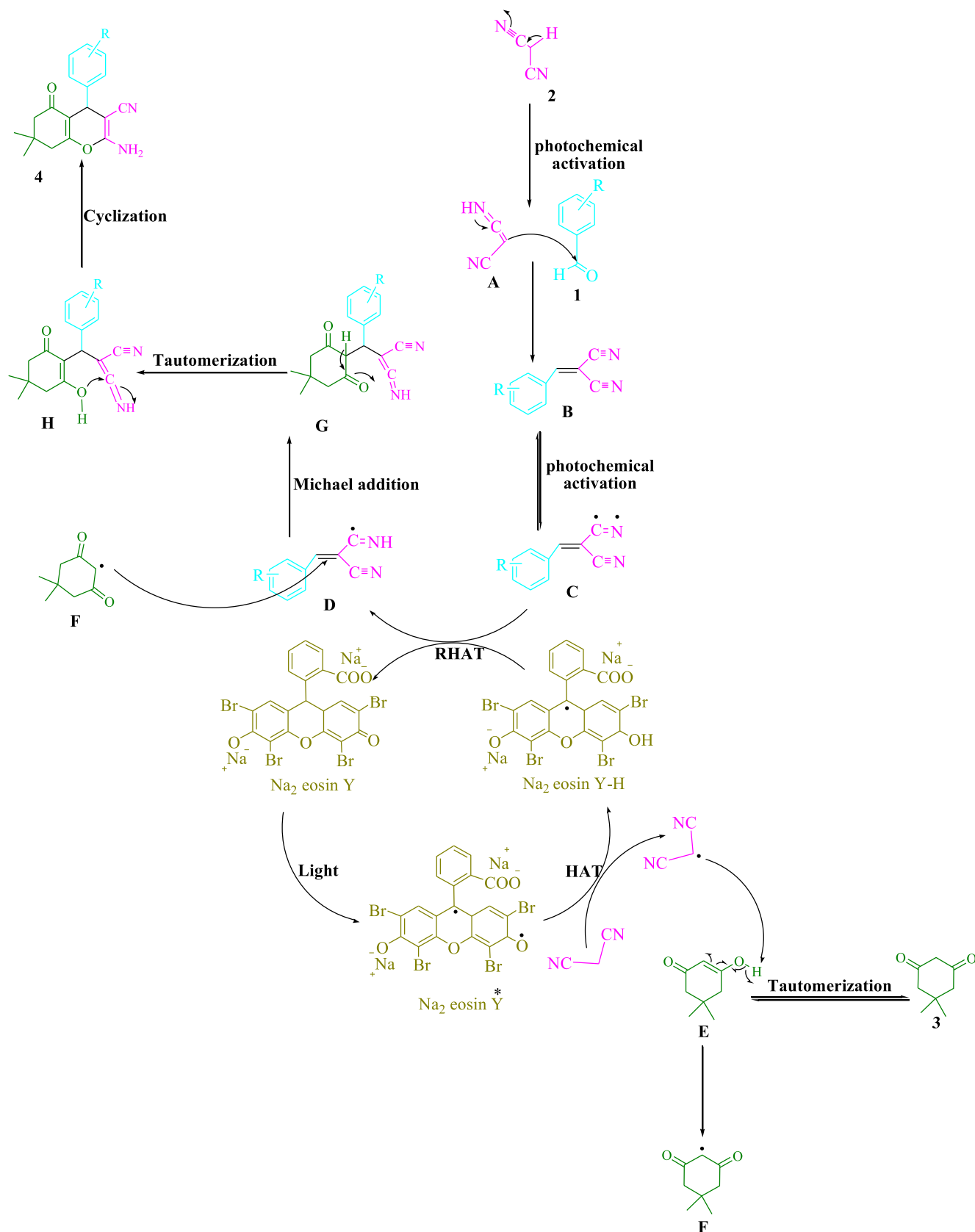
2-Amino-4-(3-methylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4Hchromene-3-carbonitrile (4w)



Yield: 94%; M.p. 197–199°C;  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ) 1.06 (3H, s,  $\text{CH}_3$ ), 1.13 (3H, s,  $\text{CH}_3$ ), 2.23 (2H, d,  $J=5.6$  Hz,  $\text{CH}_2$ ), 2.31 (3H, s,  $\text{CH}_3$ ), 2.46 (2H, s,  $\text{CH}_2$ ), 4.38 (1H, s,  $\text{CHAr}$ ), 4.52 (2H, s,  $\text{NH}_2$ ), 7.09–7.15 (3H, m, ArH), 7.28 (1H, s, ArH) ppm;  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ ): 25.8, 27.7, 27.8, 30.9, 36.8, 47.1, 52.4, 60.7, 112.7, 119.1, 127.2, 127.4, 130.5, 132.2, 145.0, 151.3, 161.8, 165.7, 196.3.

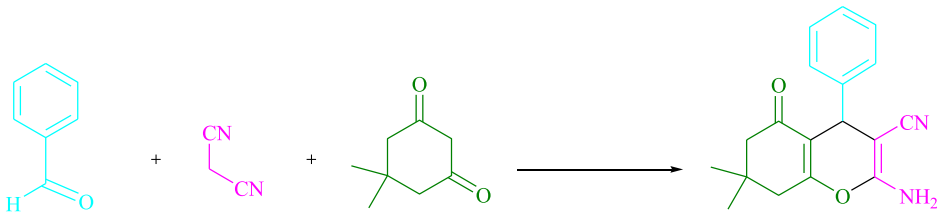
## Results and discussion

Initially, the reaction between benzaldehyde (1 mmol), malononitrile (1 mmol) and dimedone (1 mmol) for the preparation of **4a** was studied in  $\text{H}_2\text{O}/\text{EtOH}$  (2:1) (3 mL) promoted by light emitting diode (LED) irradiation at ambient temperature. Table 1 illustrates the results. Without the presence of photocatalyst, a 61% of **4a** was seen at rt for 15 min in 3 mL  $\text{H}_2\text{O}/\text{EtOH}$  (2:1). This reaction was promoted by examining a variety of organic photocatalysts including  $\text{Na}_2$  eosin Y, riboflavin, fluorescein, phenanthrenequinone, 9H-xanthen-9-one, rose Bengal, xanthene, erythrosin B, acenaphthenequinone, alizarin and rhodamine B (Figure 2) in similar settings. Satisfactorily, the progress of this reaction and obtaining the matching product **4a** were observed in 49–95% yields (Table 1). According to our findings,  $\text{Na}_2$  eosin Y was of superior functioning for this reaction. The yield was increased to 95% by using 0.5 mol%  $\text{Na}_2$  eosin Y (Table 1, entry 3). Also, low yield of products were detected in  $\text{CH}_3\text{CN}$ , DMSO, toluene,



**Scheme 4.** Recommended mechanistic path for synthesizing tetrahydrobenzo[*b*]pyran scaffolds.

**Table 1**  
Optimization table of photocatalyst for the synthesis of **4a**

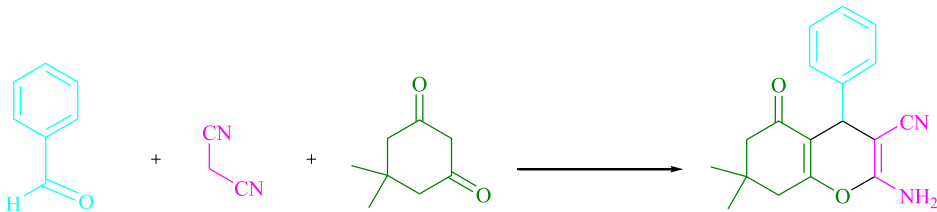
				
Entry	Photocatalyst	Solvent (3 mL)	Time (min)	Isolated Yields (%)
1	—	H <sub>2</sub> O/EtOH (2:1)	15	61
2	Na <sub>2</sub> eosin Y (0.2 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	82
3	<b>Na<sub>2</sub> eosin Y (0.5 mol%)</b>	<b>H<sub>2</sub>O/EtOH (2:1)</b>	<b>3</b>	<b>95</b>
4	Na <sub>2</sub> eosin Y (1 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	95
5	Riboflavin (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	68
6	Fluorescein (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	71
7	Phenanthrenequinone (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	49
8	9H-Xanthen-9-one (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	64
9	Rose bengal (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	62
10	Xanthene (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	52
11	Erythrosin B (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	55
12	Acenaphthenequinone (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	57
13	Alizarin (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	65
14	Rhodamine B (0.5 mol%)	H <sub>2</sub> O/EtOH (2:1)	3	69

aReaction condition: benzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol) in H<sub>2</sub>O/EtOH (2:1) (3 mL), white LED (18 W), and various photocatalysts at rt.  
bIsolated yield.

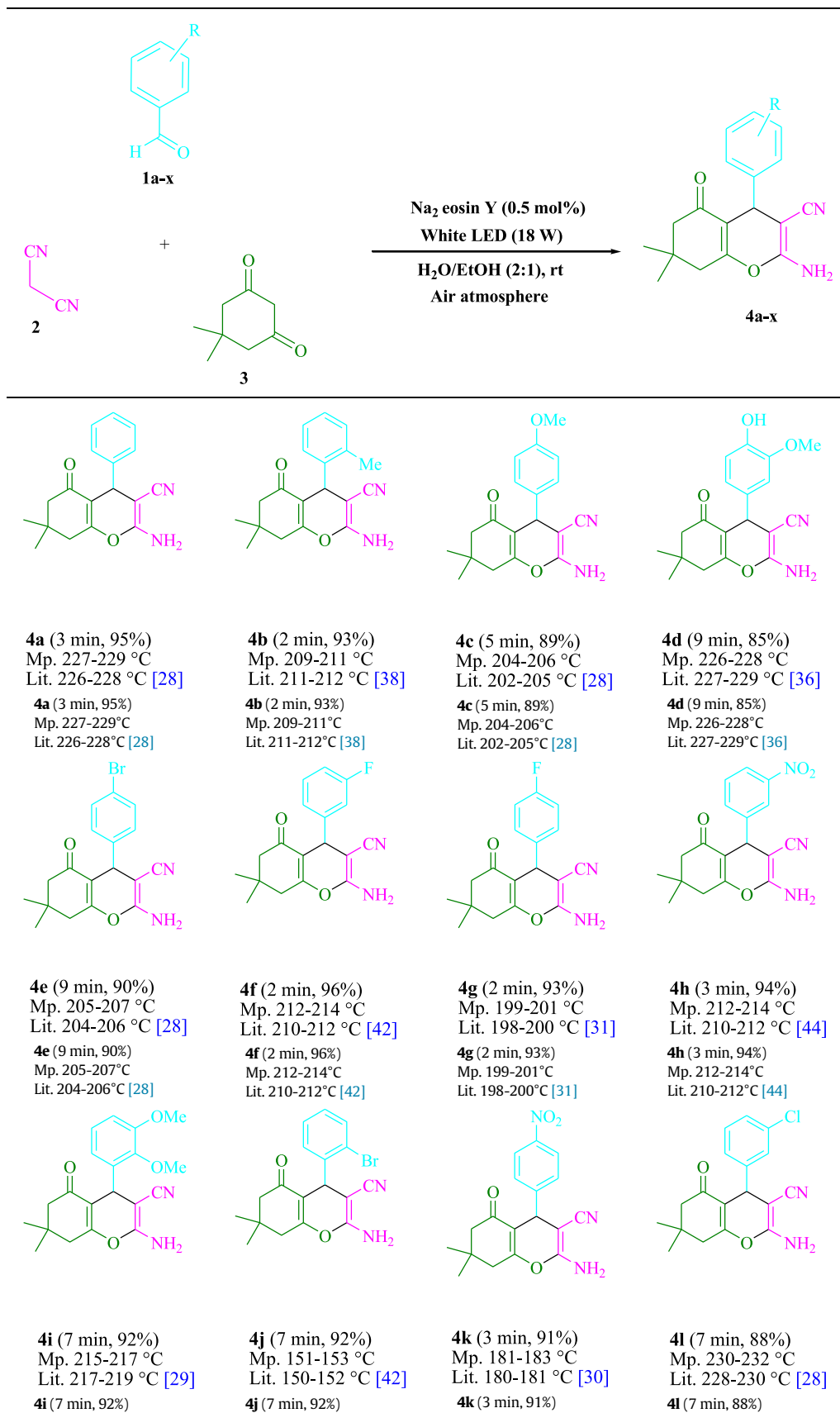
CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF and DMF (Table 2). While the reaction proceeded sluggishly in solvent-free, EtOH, H<sub>2</sub>O, EtOAc, EL, MeOH, H<sub>2</sub>O/EtOH and the yield and reaction rate increased (Table 2). In H<sub>2</sub>O/EtOH (2:1), the reaction proceeded very well, and 95% yield was obtained

under identical conditions (Table 2, entry 9). The yield was screened by various light sources, revealing that it rose somewhat by white light (Table 2, entry 9). An experimental control revealed that a miniscule of the product was detectable without the use of light source

**Table 2**  
Optimization table of solvent and visible-light for the synthesis of **4a**

				
Entry	Light Source	Solvent (3 mL)	Time (min)	Isolated Yields (%)
1	White light (18 W)	—	12	71
2	White light (18 W)	EtOH	3	64
3	White light (18 W)	H <sub>2</sub> O	3	75
4	White light (18 W)	EtOAc	3	63
5	White light (18 W)	EL	3	67
6	White light (18 W)	MeOH	7	59
7	White light (18 W)	H <sub>2</sub> O/EtOH (1:1)	3	75
8	White light (18 W)	H <sub>2</sub> O/EtOH (1:2)	3	68
9	<b>White light (18 W)</b>	<b>H<sub>2</sub>O/EtOH (2:1)</b>	<b>3</b>	<b>95</b>
10	White light (18 W)	CH <sub>3</sub> CN	10	48
11	White light (18 W)	DMSO	20	51
12	White light (18 W)	Toluene	15	37
13	White light (18 W)	CH <sub>2</sub> Cl <sub>2</sub>	20	26
14	White light (18 W)	CHCl <sub>3</sub>	20	22
15	White light (18 W)	THF	25	29
16	White light (18 W)	DMF	25	31
17	White light (10 W)	H <sub>2</sub> O/EtOH (2:1)	3	76
18	White light (12 W)	H <sub>2</sub> O/EtOH (2:1)	3	84
19	White light (20 W)	H <sub>2</sub> O/EtOH (2:1)	3	95
20	Blue light (18 W)	H <sub>2</sub> O/EtOH (2:1)	3	82
21	Green light (18 W)	H <sub>2</sub> O/EtOH (2:1)	3	86
22	—	H <sub>2</sub> O/EtOH (2:1)	10	<5

aReaction condition: benzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), Na<sub>2</sub> eosin Y (0.5 mol%) at rt.  
bIsolated yield.

**Table 3**Photoexcited Na<sub>2</sub> eosin Y as photocatalyst for synthesis of tetrahydrobenzo[*b*]pyran scaffolds.

(continued)

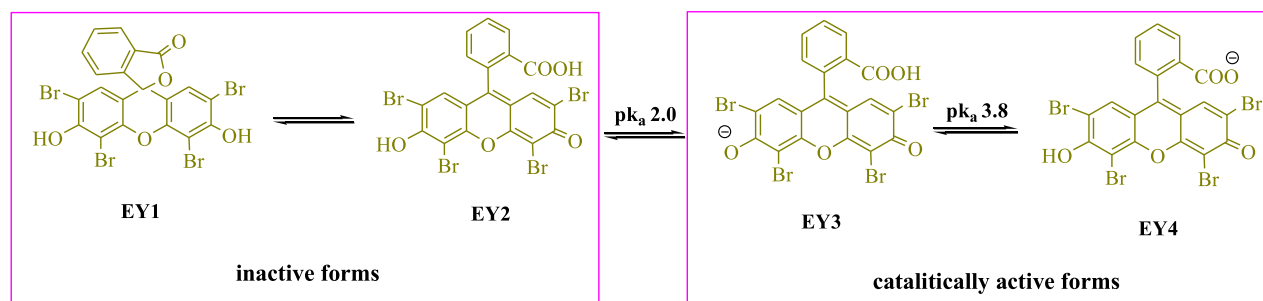
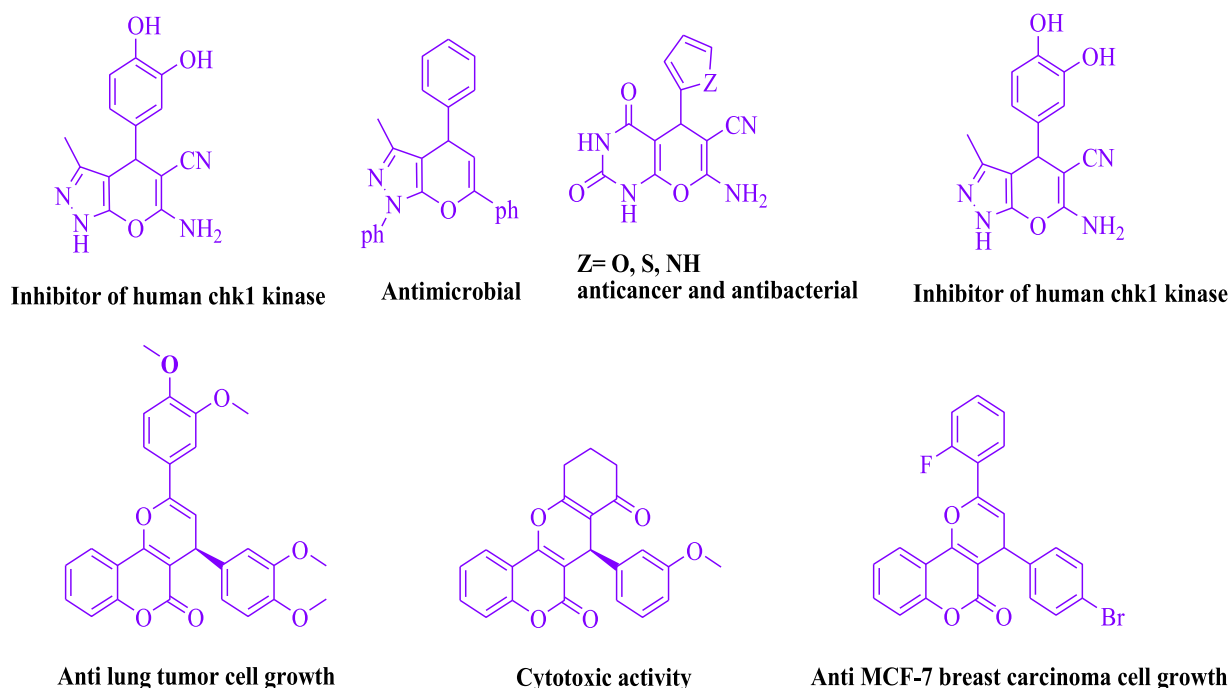
Table 3 (Continued)

<p>Mp. 215–217 °C Lit. 217–219 °C [29]</p> <p><b>4m</b> (9 min, 92%) Mp. 226–228 °C Lit. 228–230 °C [29]</p>	<p>Mp. 151–153 °C Lit. 150–152 °C [42]</p> <p><b>4n</b> (10 min, 87%) Mp. 209–211 °C Lit. 210–212 °C [35]</p>	<p>Mp. 181–183 °C Lit. 180–181 °C [30]</p> <p><b>4o</b> (3 min, 96%) Mp. 223–225 °C Lit. 221–223 °C [31]</p>	<p>Mp. 230–232 °C Lit. 228–230 °C [28]</p> <p><b>4p</b> (3 min, 94%) Mp. 210–212 °C Lit. 211–212 °C [38]</p>
<p><b>4q</b> (2 min, 92%) Mp. 216–218 °C Lit. 216–217 °C [38]</p>	<p><b>4r</b> (7 min, 85%) Mp. 215–217 °C Lit. 214–216 °C [30]</p>	<p><b>4s</b> (9 min, 89%) Mp. 226–228 °C Lit. 227–229 °C [36]</p>	<p><b>4t</b> (9 min, 83%) Mp. 227–229 °C Lit. 226–228 °C [35]</p>
<p><b>4u</b> (5 min, 92%) Mp. 206–208 °C Lit. 208–210 °C [30]</p>	<p><b>4v</b> (10 min, 82%) Mp. 236–238 °C Lit. 234–236 °C [40]</p>	<p><b>4w</b> (3 min, 94%) Mp. 197–199 °C Lit. 198–200 °C [31]</p>	<p><b>4x</b> (3 min, 96%) Mp. 225–227 °C Lit. 223–226 °C [28]</p>
<p>Mp. 206–208 °C Lit. 208–210 °C [30]</p> <p><b>4u</b> (5 min, 92%) Mp. 206–208 °C Lit. 208–210 °C [30]</p>	<p>Mp. 236–238 °C Lit. 234–236 °C [40]</p> <p><b>4v</b> (10 min, 82%) Mp. 236–238 °C Lit. 234–236 °C [40]</p>	<p>Mp. 197–199 °C Lit. 198–200 °C [31]</p> <p><b>4w</b> (3 min, 94%) Mp. 197–199 °C Lit. 198–200 °C [31]</p>	<p>Mp. 225–227 °C Lit. 223–226 °C [28]</p> <p><b>4x</b> (3 min, 96%) Mp. 225–227 °C Lit. 223–226 °C [28]</p>



**Table 4**Comparison of the catalytic ability of some of the catalysts in the manuscript for producing of tetrahydrobenzo[b]pyran scaffolds<sup>a</sup>

References	TOF	TON	Time/Yield (%)	Conditions	Catalyst	Entry
[28]	0.07	9.1	120 min/91	H <sub>2</sub> O/EtOH, 80°C	CaHPO <sub>4</sub>	1
[31]	0.83	20.9	25 min/90	H <sub>2</sub> O/EtOH, Reflux	SBPPSP	2
[32]	0.01	3.6	240 min/90	H <sub>2</sub> O, Reflux	DBSA	3
[33]	0.03	4.6	120 min/92	EtOH, 80°C	NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	4
[39]	0.89	8.9	10 min/89	H <sub>2</sub> O/EtOH, rt	theophylline	5
[40]	1.96	3.9	2 min/98	EtOH, rt	triethanolamine	6
[41]	0.67	4.7	7 min/94	H <sub>2</sub> O/EtOH, rt	NaN <sub>3</sub>	7
[44]	0.9	9	10 min/90	EtOH, 80°C	trichloroisocyanuric acid	8
<b>This work</b>	<b>63.3</b>	<b>190</b>	<b>3 min/95</b>	<b>visible light irradiation, H<sub>2</sub>O/EtOH, rt</b>	<b>Na<sub>2</sub> eosin Y</b>	<b>9</b>

<sup>a</sup> Based on the three-component reaction of benzaldehyde, malononitrile and dimedone.**Scheme 5.** Acid–base equilibria of Eosin Y in water [51].**Figure 1.** Some medicinally important compounds containing pyran motifs.

(Table 2, entry 22). The observation indicate the essentiality of Na<sub>2</sub> eosin Y and visible light to successfully form the product 4a. Also, the optimized settings were determined by varying the intensities of white LED (10 W, 12 W, 18 W and 20 W) irradiation. Based on Table 2, the best outcomes were found in the presence of white LED (18 W) irradiation (Table 2, entry 9). As observed in Table 3 and Scheme 3 it was indicated that this technique can work with various substrates.

Scheme 4 shows the suggested mechanism for synthesizing tetrahydrobenzo[b]pyran scaffolds. With the use of visible light,

malononitrile (**2**) is subjected totautomerisation to give (**A**). Afterwards, (**A**) and aldehyde derivatives (**1**) react to form arylidenemalononitrile (**B**), undergoing an activation photochemically for the formation of a radical intermediate (**C**), in which visible light can partially affect with exerting extra energy to accelerate the reaction. As reported in previous studies [6a, 6d, 9], eosin Y-originated photoexcited modes can function as direct hydrogen atom transfer (HAT) catalysts for activating C–H bonds. The malononitrile radical is formed by the promotion of visible light triggered Na<sub>2</sub> eosin Y\* via a HAT



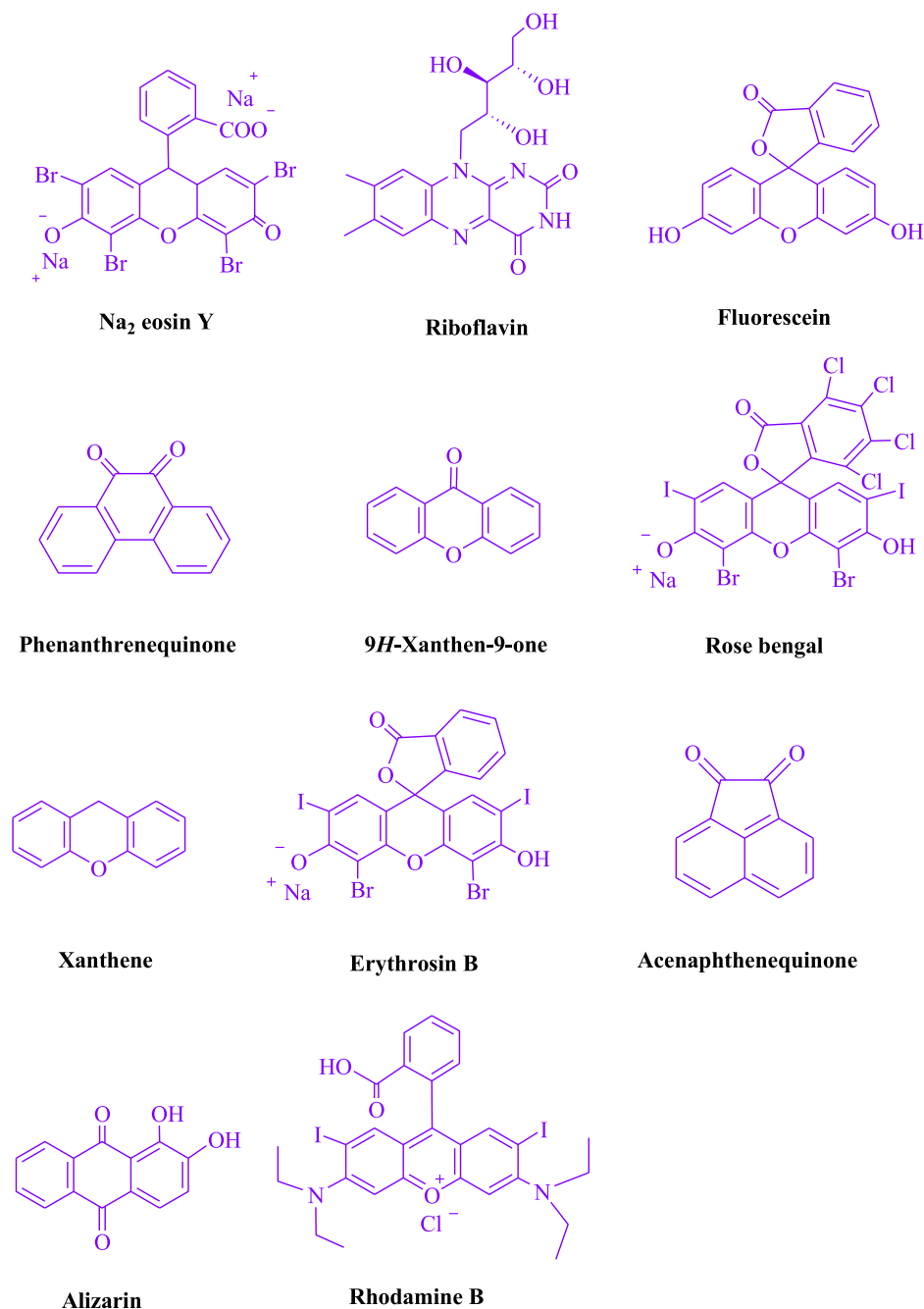


Figure 2. Photocatalysts tested in this study.

procedure. Ground-state Na<sub>2</sub> eosin Y and the intermediate **D** are regenerated by occurring reverse hydrogen atom transfer (RHAT) process between eosin Na<sub>2</sub> Y-H and radical adduct **C**. Then, malononitrile radical extracts a hydrogen atom from (**E**) to produce intermediate (**F**). Subsequently, intermediate (**D**) and (**F**) coalesce to generate (**G**) as Michael acceptor, additionally undergoing tautomerisation and intramolecular cyclization for the product formation (**4**).

Comparison of the catalytic capacity of a number of catalysts referred to in the present paper for the production of tetrahydrobenzo [b]pyran scaffolds has been shown in Table 4. It may find a wide range of applications, such as the use of the lowest amount of photocatalyst, short reaction time without any by-products using visible light irradiation. The atom-economic protocol is effective on a multi-gram scale and has important industrial applications. These products achieve both excellent performance and excellent purity. TON and TOF is calculated in Table 4. The lower the amount of catalyst and the higher the

yield, the higher the numerical value of the TON and TOF, and the higher the value, the more efficient the catalyst.

#### Study on the mechanism of photocatalytic reactions with eosin Y

Most importantly, Eosin Y is employed as a photoredox catalyst in the synthetic process of organics. In recent years, Rossi [51], Mahmood [52], Majek [7], Eid [53] and et al have studied the use of Eosin Y in photoredox reactions and the effect of UV light, PH and also the effect of temperature on the rate of reactions.

#### Effect of the light source on the eosin Y-mediated photocatalysis

Catalytically, the features of Eosin Y depend upon its reduction/oxidation potentiality [51]: the oxidation and reduction potentials vary from -1.06 V to 1.10 V and +0.78 V to +0.83 V, respectively

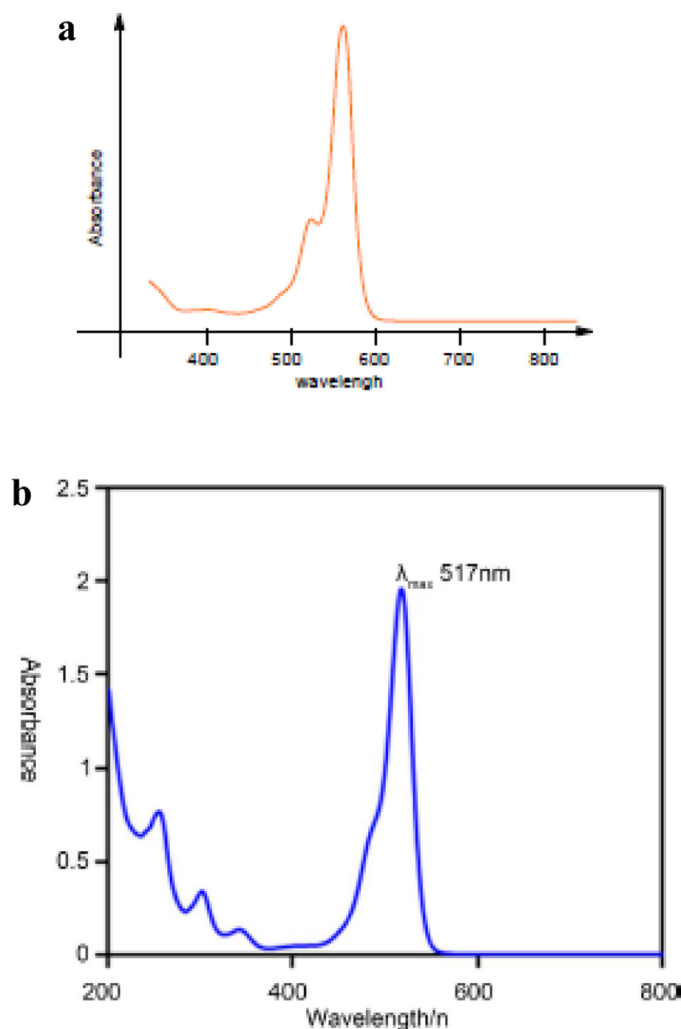


Figure 3a. Eosin Y absorption spectrum in EtOH solution [51].

Figure 3b The Spectrum of Eosin Y in aqueous solution [52].

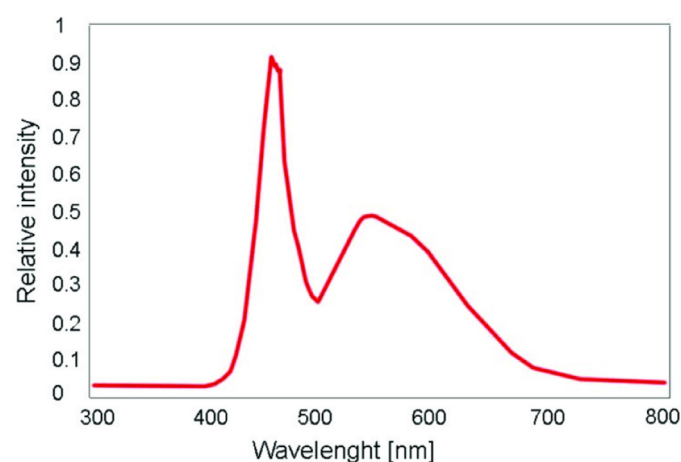


Figure 4. Emission spectrum of a commercial white light LED [54].

(Scheme 1). Its absorption is maximized at 539 nm, with a molar extinction coefficient of  $\epsilon = 60803 \text{ M}^{-1} \text{ cm}^{-1}$  (Figs 3a, 3b). Accordingly, light-emitting diodes (LEDs) are typically utilized conveniently as lighting sources for activating Eosin Y (maximal emission about 530 nm). Once excited by light, Eosin Y experiences a fast intersystem

transition from the ground state to the lowermost energy triplet state. It cannot directly undergo the singlet–triplet transition, but Eosin Y electrons are excited by light to a greater excited singlet state from where they undergo quick relaxation to the lowermost excited singlet state. This is where only excited electrons experience an inter-system transition to the high reactive triplet state, with a lifespan of 24 ms [51].

The interaction of pH and UV light on the rate of radical production has also been investigated. The initial rate is also enhanced by EY concentrations at low pH, but the initial rate shows a significant enhancement by UV light. There is also an enhancement of radicals form when the dye molecules are excited by UV light [53].

The source of irradiation is another reaction factor that has not been clearly and consistently documented in previous research [7b]. Our research team is among the researchers who have employed commercially available narrow-band LEDs with a maximal intensity at 535 nm. Irradiation of other reactions was done by broad-band compact fluorescent lamps (CFLs). To determine quantum yields, it is necessary to utilize narrowband lighting sources because the optical density of the samples varies with the wavelength. In this study, therefore, the influence of various irradiations was investigated throughout the photocatalytic reaction. Despite the undetermined types of CFLs in previous research, analogous spectral arrays are covered by most of commercially-available CFLs in which the UV edge individually is significantly <400 nm and with considerable radiation power in the area of 400–500 nm. Similarly, a wavelength range is observed in the spectra of commercially available LEDs [7b] (Figure 4 [54]).

#### Effect of PH on the eosin Y-mediated photocatalysis

Once Eosin Y is in a solution, it is in equilibrium with four varying types as it contains two rather acidic protons ( $\text{pK}_a$  2.0 and 3.8 in water, Scheme 5), all of which depend on the pH. At  $\text{pH} < 2$ , the protonated spirocyclic type EY1 equilibrates with the neutral type EY2. At  $2 < \text{pH} < 3.8$ , however, the mono anionic type EY3 equilibrates with the dianionic type EY4, becoming dominant at  $\text{pH} > 3.8$ . Only EY3 and EY4 have catalytic activity, but this function as resulted in uncertainties in bulk of literature concerning the quality of the dye responsible for the transmutation. To assure that the dianionic type EY4 is present, Eosin Y sodium salt is utilized as a photocatalyst, though it is necessary to take account of the reaction situations of chemical transmutation in the experiment [51].

Eid [53] investigated the impact of pH on the absorbance values of the binary complexes in the pH ranging from 2.6 to 4.5; adjusting to a pH of 5 leads to negative absorbance values.

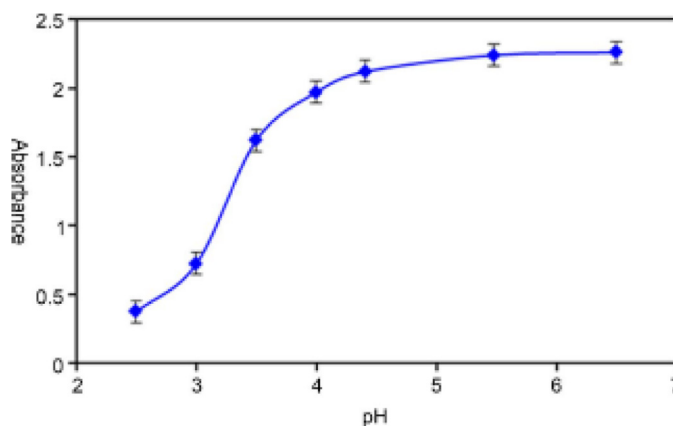


Figure 5. Effect of pH on the absorbance, at  $\lambda_{max} = 517 \text{ nm}$ , of Eosin Y solution [52].

A pH of 3.5 resulted in the optimal absorbance values. Two ml of 0.4 M acetate buffer could sufficiently optimize the pH level. When the drug-dye solution is mixed at neutral pH, it is necessary to add the buffer solution for the uppermost color intensity and maximal accuracy.

Similarly, Mahmood [52] examined the impact of pH on absorbance. The absorbance of EY (Figure 5) rises with raising the pH of its solution, and its reduction is minimal in the pH level of about 4, above which it rises with pH. In contrast, radicals undergo destruction at minimum pH values.

#### Effect of temperature on the eosin Y-mediated photocatalysis

The effect of temperature on the absorbance value of binary complexes was researched by Eid [53]. The color intensity was finally maximal at ambient temperature, and an increase in the temperature led to forming a deposit possibly because of coagulating the created complex. Consequently, room temperature is ideal for Eosin Y catalytic reactions.

#### Conclusion

Current survey revealed that Na<sub>2</sub> eosin Y-derived photoexcited states functions as a direct hydrogen atom transfer (HAT) catalyst can be employed for photochemically metal-free synthesizing tetrahydrobenzo[b]pyran scaffolds via three-condensation domino reaction of tandem Knoevenagel-Michael cyclocondensation via visible light-mediated in aqueous ethanol at ambient temperature under air atmosphere. The use of the lowest amount of catalyst, utilizing great yields, efficient sides of the reaction, direct work-up with no column chromatographic separation, secure reaction circumstances, appropriate and expedient procedure and avoiding the hazardous catalysts or solvents are the most conspicuous pros of this green protocol. These characteristics have caused this procedure to be highly beneficial in facing the environmental worries and industrial needs.

#### 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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