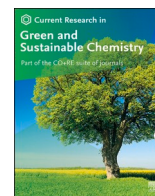




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Synthesis of dihydropyrano[2,3-*c*]pyrazole scaffolds by methylene blue (MB⁺) as a photo-redox catalyst via a single-electron transfer (SET)/energy transfer (EnT) pathway

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ABSTRACT

A new environmentally friendly plan was created to make dihydropyrano [2,3-*c*]pyrazole structures without using metals. This plan involves combining ethyl acetoacetate, hydrazine hydrate, aldehyde derivatives, and malononitrile in a radical tandem Knoevenagel-Michael cyclocondensation reaction. We used metal-free methylene blue (MB⁺) to create special functions that respond to light. These functions can transfer electrons and energy in water at room temperature using light as a source of energy in the air. The amount of product made is pretty consistent (between 81 and 98 %, with an average of 91.8 %), and it gets made quickly (between 3 and 7 min, with an average of 5.3 min). The important thing mentioned in the conversation is that the process can handle different types of chemicals while still being fast and giving good results. The results show that this special technique is a successful and easy way to get good results in just one step. Methylene blue is used with very little amount to make a chemical reaction happen. This leads to high amounts of product, saves energy, and is good for the environment. It helps use up all the starting materials efficiently, saves time by not needing to separate chromatography, and reduces waste. This photocatalyst is easy to use. This creates many different types of characteristics in the environment and chemicals that last a long time. The turnover number (TON) and turnover frequency (TOF) of dihydropyrano [2,3-*c*]pyrazole scaffolds were calculated. It is interesting that cyclization on a gram scale can be achieved, showing that this technique can be used in industries.

1. Introduction

The use of single electron transfer (SET)/photoinduced electron transfer (PET) pathways to form C–C and C-heteroatom bonds has proliferated in recent years. Various types of procedures require them, ranging from small to large. Technological advances have allowed the development of flow reactors [1] using visible light and light-sensitive dual electrochemical reaction processes [2], allowing the development of efficient reactions, environmentally friendly and more affordable. It is

used in many medical procedures. The drug has been shown to have antimalarial effects and is very useful in the treatment of methemoglobinemia [3–5]. Having an absorbance of 664 nm and a molar absorbance ($\epsilon = 90,000$) [6], the lifetime of the single group is $\tau_f \sim 1.0$ ns for MB⁺. The ³MB⁺ triple has a much longer lifetime $\tau_f \sim 32 \mu\text{s}$ [7], making it much more stable [8]. In Scheme 1, methylene blue's photocatalytic cycle is shown [8].

Therefore, inexperienced chemists do not forget to see irradiation as a dependable method to produce organic chemicals in an

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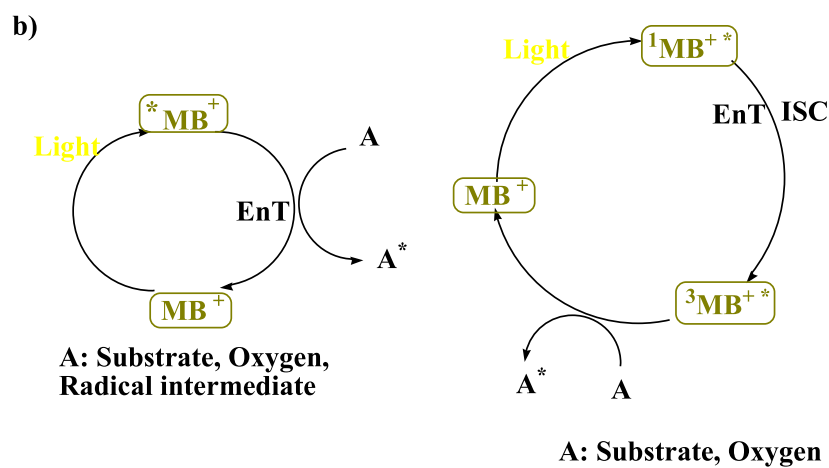
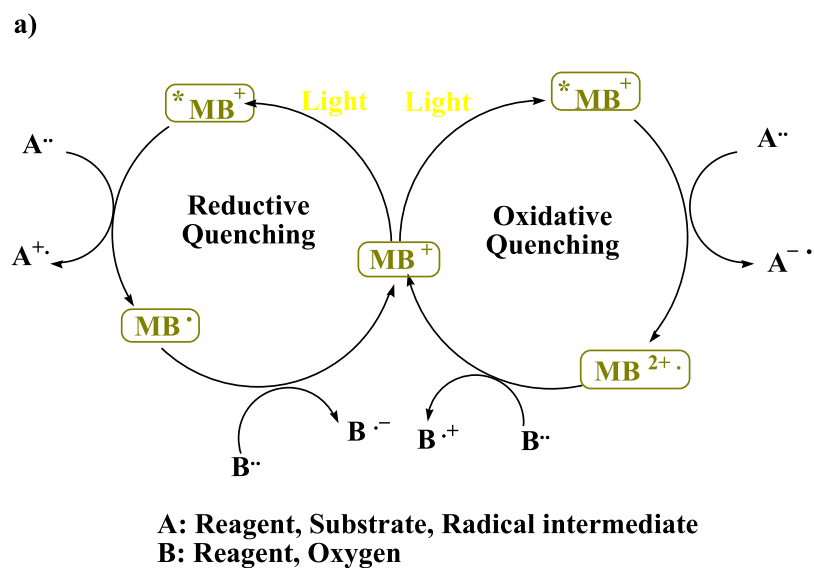
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Scheme 1. Photocatalytic cycling can be performed with MB^+ [8].

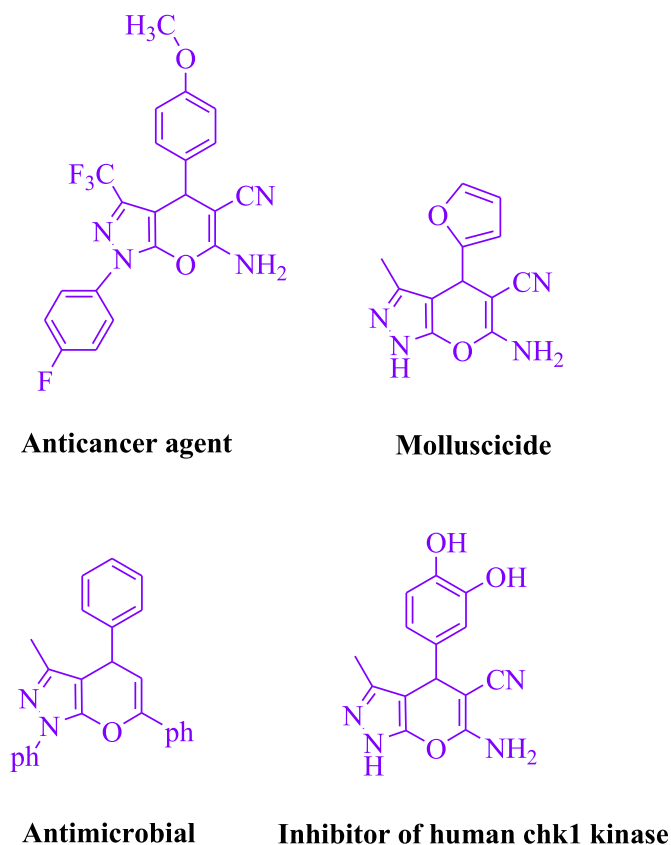


Fig. 1. Pyranopyrazole rings that are biologically active.

environmentally friendly manner [9,10].

Because of its organic and pharmacological activity, the systems that makeup pyranopyrazole have aroused the interest of biochemists and artificial natural chemists (Fig. 1) [11–15].

There are numerous options available [16–39]. In consequence, metal catalysts have been restricted, expensive reagents have been used, severe reaction conditions have been created, monotonous yields have been observed, environmental dangers have been created, and long reaction times have been observed. As well, separating a homogeneous catalyst from a reaction mixture can be challenging. Lately, many scientists in the fields of medicine, drug development, and materials have been interested in multicomponent reactions (MCRs) [40–58]. This is because it has many benefits compared to traditional linear synthesis methods, like being easy to do, good for the environment, efficient in using atoms, and able to create complex molecules in a few steps. During the current study, we examined photocatalysts [59–61] in green environments, which used to be attempted and are currently under development. Researchers demonstrate how cationic dye photo-redox catalysts can be used, which are low-cost and widely available. The photochemical mechanism above is used to produce methylene blue (MB^+). The Knoevenagel-Michael cyclocondensation process takes place at rt and in a ventilated environment using visible light. We have

successfully implemented an extremely efficient, cost-effective, and simple one-pot reaction.

2. Experimental

2.1. Preparation of dihydropyrano [2,3-c]pyrazole scaffolds (5a-t)

Methylene blue (0.5 mol%) was mixed with ethyl acetoacetate (1, 1 mmol), hydrazine hydrate (2, 1 mmol), aldehyde derivatives (3, 1 mmol), and malononitrile (4, 1 mmol) in H_2O (3 mL) and stirred at rt under a white LED (18 W). TLC is used to screen the response. The ensuing product changed into sieved and washed with water after the reaction, and the crude strong changed into recrystallized from the ethanol without additional purification to present a pure compound. The goal was to find out if we could produce these chemicals at the gram scale or down to the level needed for pharmaceutical process R&D. One test used 50 mmol every of malononitrile, ethyl acetoacetate, *p*-tolualdehyde, and hydrazine hydrate. The full response went smoothly and only took 4 min, with typical filtration techniques used to collect the product. This substance is spectroscopically pure, based on its 1H NMR spectrum.

After evaluating the spectral data, the products had been classified (1H NMR). The Supporting Information file lists the spectral data and files for this manuscript.

3. Results and discussion

To begin, with no photocatalyst, have 35 % 5a at room temperature in 3 mL H_2O for 15 min. To enhance the reaction, photocatalysts (Fig. 2) were all tested in the same framework. While receiving the corresponding product acceptable 5a, this reaction progressed in 46–96 % yields (Table 1). By using 0.5 % mol MB^+ , the yield was increased to 96 %. Table 2 shows that THF, DMSO, DMF, and toluene reduced product output. Reaction speed and productivity have been increased with EtOH, MeOH, $H_2O/EtOH$ (1:1), EtOAc, solvent-free conditions, and CH_3CN . In H_2O , the reaction is carried out with high yield and speed. As demonstrated in Table 2, a yield of 96 % was produced below the same conditions. Productivity is filtered by various light sources, showing the effect of white light. Furthermore, the improved settings are determined by adjusting the intensity of white LEDs. According to the researchers, the best results are obtained when using white LEDs (18 W) (Table 2, entry 4). Some substrates have been tested under the right conditions (Scheme 2). It is vital to observe that the addition of a benzaldehyde substituent no longer has an effect on the end result of the reaction (Table 3). Under the reaction conditions, the substitution of polarity and halides is allowed. The current reaction state has allowed the electron donor and electron-withdrawing groups to proceed well. Aromatic aldehydes were substituted for *ortho*, *meta*, and *para* for very high yields. Heterocyclic aldehydes follow the same reaction pattern (Table 3).

There is information in Table 4 about turnover number (TON) and turnover frequency (TOF). As the TON and TOF numerical values increase, the catalyst is used less, the yield increases, and as the value increases, the catalyst becomes more efficient. The preferred technique is shown in Scheme 3. Table 5 compares the catalytic execution of a few catalysts that have been detailed herein.

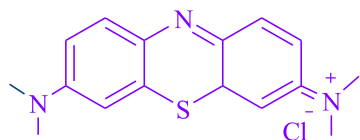
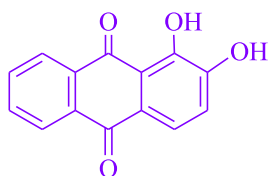
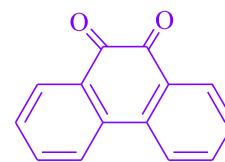
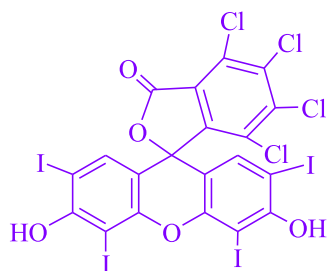
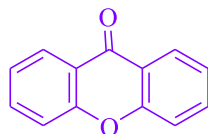
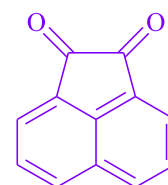
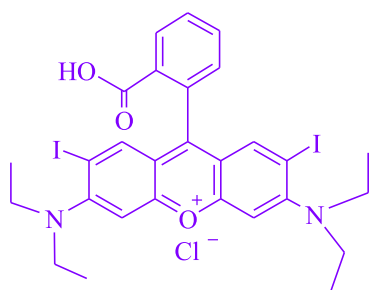
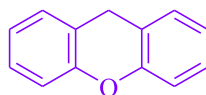
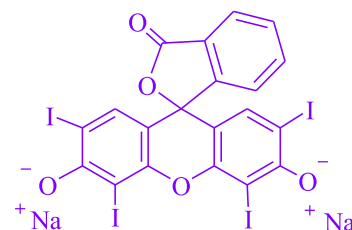
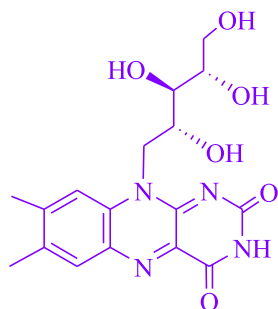
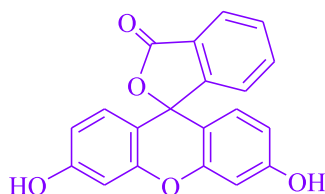
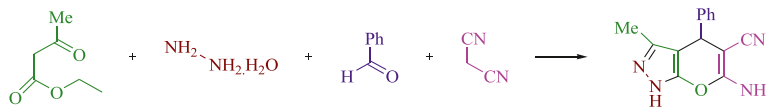
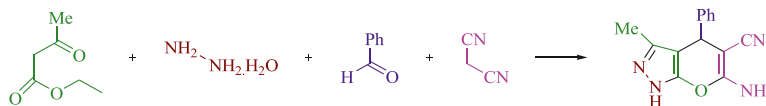
**Methylene Blue****Alizarin****Phenanthrenequinone****Rose bengal****9H-Xanthen-9-one****Acenaphthenequinone****Rhodamine B****Xanthene****Erythrosin B****Riboflavin****Fluorescein****Fig. 2.** In this procedure, photocatalysts had been tested.

Table 1For **5a** production, a table of photocatalyst optimization is provided^a.

Entry	Photocatalyst	Solvent (3 mL)	Time (min)	Isolated Yields (%)
1	–	H ₂ O	15	35
2	Methylene blue (0.2 mol%)	H ₂ O	10	83
3	Methylene blue (0.5 mol%)	H₂O	5	96
4	Methylene blue (1 mol%)	H ₂ O	5	96
5	Alizarin (0.5 mol%)	H ₂ O	5	51
6	Phenanthrenequinone (0.5 mol%)	H ₂ O	5	49
7	Rose bengal (0.5 mol%)	H ₂ O	5	76
8	9H-Xanthen-9-one (0.5 mol%)	H ₂ O	5	55
9	Acenaphthenequinone (0.5 mol%)	H ₂ O	5	53
10	Rhodamine B (0.5 mol%)	H ₂ O	5	74
11	Xanthene (0.5 mol%)	H ₂ O	5	46
12	Erythrosin B (0.5 mol%)	H ₂ O	5	68
13	Riboflavin (0.5 mol%)	H ₂ O	5	71
14	Fluorescein (0.5 mol%)	H ₂ O	5	65

^a Reaction conditions: ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), benzaldehyde (1 mmol), and malononitrile (1 mmol) in H₂O, as well as a white LED (18 W) and a variety of photocatalysts, were utilized at room temperature.

Table 2Visible light and solvent optimization table for **5a** synthesis is provided^a.

Entry	Light Source	Solvent (3 mL)	Time (min)	Isolated Yields (%)
1	White light (18 W)	EtOH	5	73
2	White light (18 W)	MeOH	7	58
3	White light (18 W)	EtOAc	8	61
4	White light (18 W)	H₂O	5	96
5	White light (18 W)	H ₂ O/EtOH (1:1)	5	81
6	White light (18 W)	CH ₃ CN	5	69
7	White light (18 W)	–	7	63
8	White light (18 W)	THF	25	30
9	White light (18 W)	DMSO	15	28
10	White light (18 W)	DMF	25	34
11	White light (18 W)	toluene	15	26
12	White light (10 W)	H ₂ O	5	83
13	White light (12 W)	H ₂ O	5	91
14	White light (20 W)	H ₂ O	5	96
15	Blue light (18 W)	H ₂ O	5	88
16	Green light (18 W)	H ₂ O	5	83
17	–	H ₂ O	35	trace

^a Reaction conditions: at room temperature, ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), benzaldehyde (1 mmol), and malononitrile (1 mmol) were added to MB⁺ (0.5 mol%).

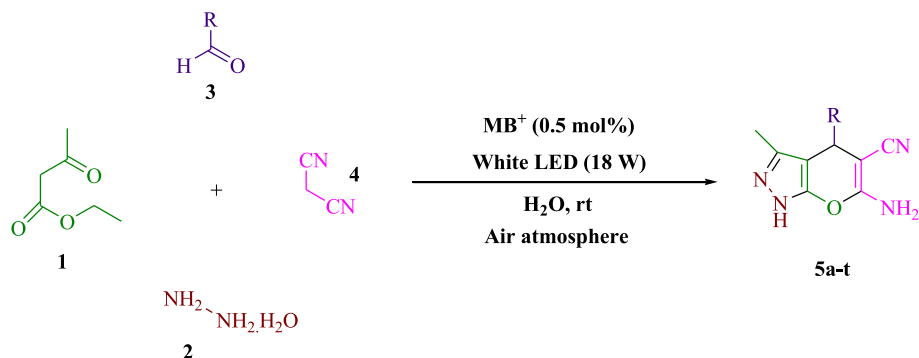
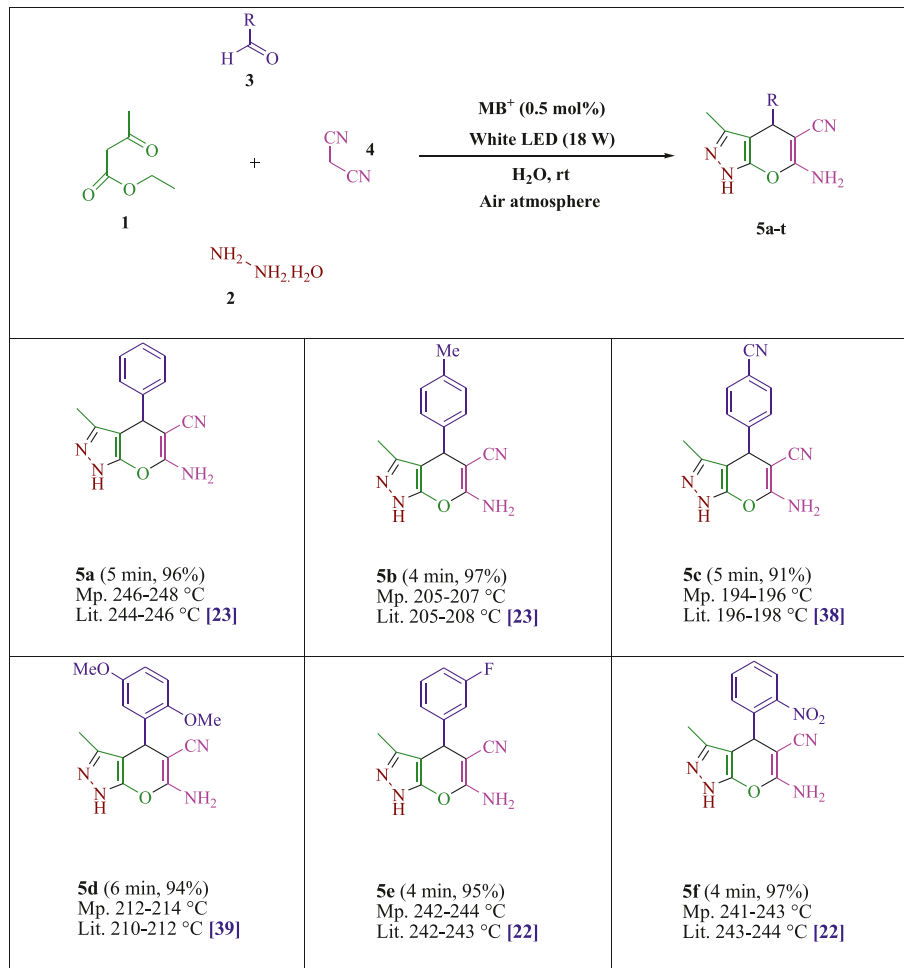
**Scheme 2.** Synthesis of compounds.

Table 3

This photocatalyst manufactures dropryanopyrazole scaffolds using photoexcited methylene blue as a photo-redox catalyst.



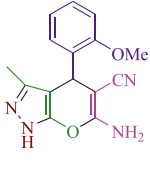
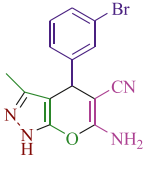
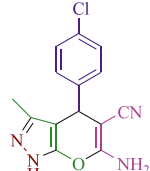
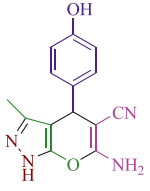

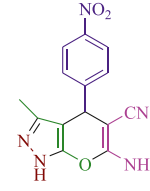
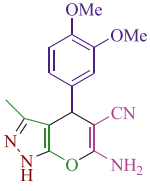
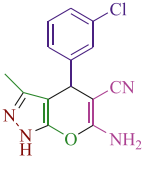
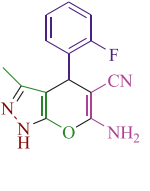
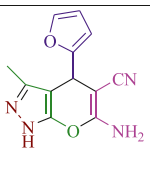
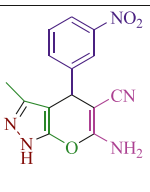
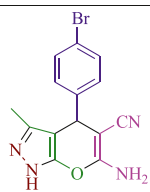
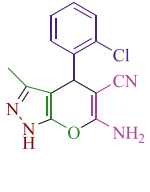
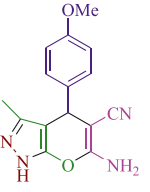
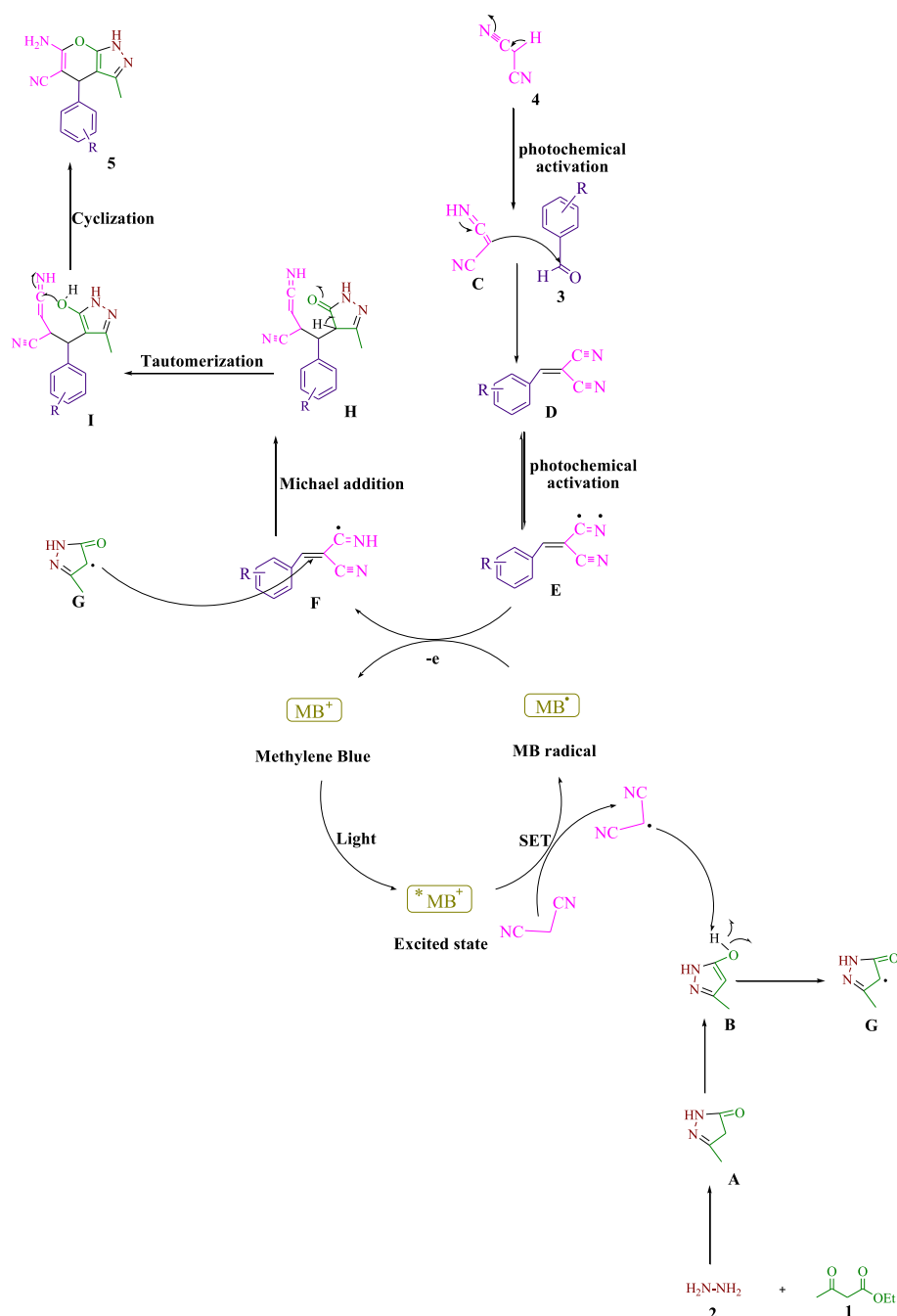
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 <p>5j (7 min, 81%) Mp. 219-221 °C Lit. 220-223 °C [21]</p>	 <p>5k (5 min, 96%) Mp. 223-225 °C Lit. 224-226 °C [28]</p>	 <p>5l (4 min, 95%) Mp. 249-251 °C Lit. 248-249 °C [22]</p>
 <p>5m (6 min, 92%) Mp. 187-189 °C Lit. 188-191 °C [21]</p>	 <p>5n (7 min, 83%) Mp. 231-233 °C Lit. 230-231 °C [22]</p>	 <p>5o (3 min, 98%) Mp. 259-261 °C Lit. 261-262 °C [22]</p>
 <p>5p (5 min, 95%) Mp. 231-233 °C Lit. 230-231 °C [22]</p>	 <p>5q (4 min, 98%) Mp. 192-194 °C Lit. 190-193 °C [23]</p>	 <p>5r (7 min, 84%) Mp. 178-180 °C Lit. 180-181 °C [18]</p>
 <p>5s (6 min, 86%) Mp. 243-245 °C Lit. 245-246 °C [22]</p>	 <p>5t (5 min, 95%) Mp. 211-213 °C Lit. 210-212 °C [22]</p>	

Table 4
Calculate TON and TOF.

Entry	Product	TON	TOF	Entry	Product	TON	TOF
1	5a	192	38.4	11	5k	192	38.4
2	5b	194	48.5	12	5l	190	47.5
3	5c	182	36.4	13	5m	184	30.6
4	5d	188	31.3	14	5n	166	23.7
5	5e	190	47.5	15	5o	196	65.3
6	5f	194	48.5	16	5p	190	38
7	5g	184	36.8	17	5q	196	49
8	5h	172	24.5	18	5r	168	24
9	5i	170	24.2	19	5s	172	28.6
10	5j	162	23.1	20	5t	190	38



Scheme 3. It has been presented as a mechanistic technique.

Table 5

A comparison of the catalytic capacity of catalysts for the synthesis of **5a** was made.

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Choline chloride	Urea Deep, 80 °C	10 min/95	[19]
2	Isonicotinic acid	Solvent-free, 85 °C	30 min/90	[20]
3	Molecular sieves	EtOH, Reflux	60 min/84	[21]
4	Meglumine	EtOH/H ₂ O, rt	15 min/95	[22]
5	L-proline	H ₂ O, Reflux	10 min/87	[24]
6	KF-alumina	EtOH, Reflux	12 min/80	[24]
7	CTACl	H ₂ O, 90 °C	240 min/89	[25]
8	Lipase	EtOH, 30 °C	60 min/90	[26]
9	MB⁺	visible light irradiation, H ₂ O, rt	5 min/96	This work

4. Conclusion

Based on the results, we found that the excited state of metal-free MB⁺ can be used to make a certain kind of chemical; dihydropyrano [2,3-*c*]pyrazoles. We can make these chemicals by combining ethyl acetoacetate, hydrazine hydrate, aldehyde compounds, and malononitrile together using a reaction that involves single-electron transfer (SET)/energy transfer (EnT). This reaction is done in water and air atmosphere and at room temperature. We use visible light as an energy source to make this reaction happen in a sustainable way. The main things to notice about this eco-friendly plan are that it uses very little catalyst, works well, has safe conditions for the reaction, uses renewable energy, and doesn't need any harmful solvents. This method showed that it can be used on a large scale and can be repeated to get the same results. The reaction got faster and didn't need to use any separation technique anymore. For creating the drug molecule, the reaction was easily increased to a larger amount of 50 mmol. The way model substances reacted in larger amounts showed that their reactions could be increased without changing the result. We added visible light as a source of renewable energy in this chemical reaction. This discovery could have applications in areas like polymer chemistry, medicine, and materials.

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.

Data availability

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.crgsc.2023.100381>.

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