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PAPER
Jason B. Benedict et al.
The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal–organic frameworks

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A green and clean pathway: One pot, multicomponent, visible light assisted synthesis of pyrano[2,3-c]pyrazoles under catalyst-free and solvent-free conditions

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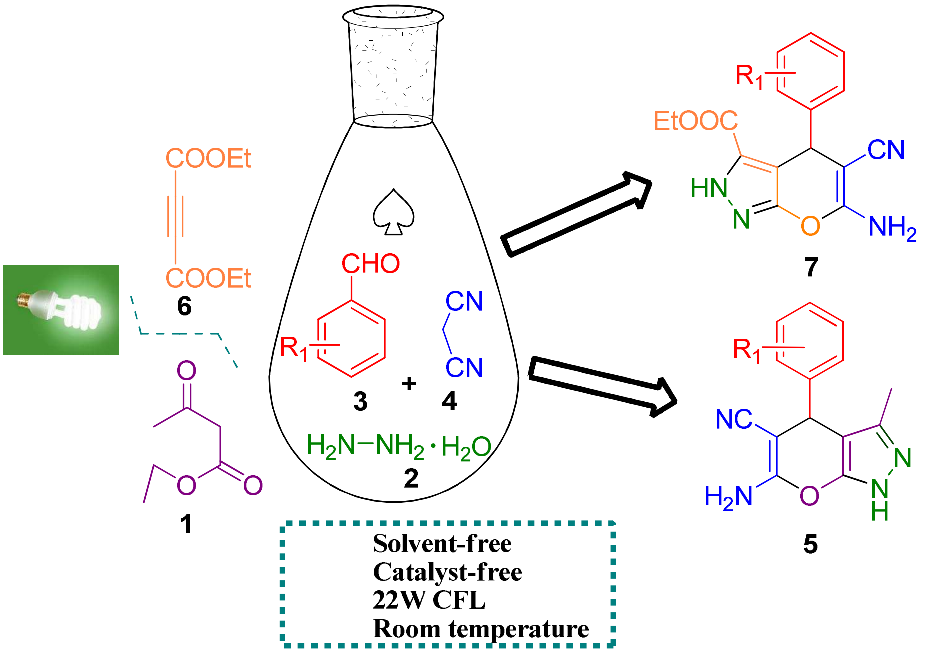
[#] *Equal contribution*

Abstract:

A mild, eco-efficient and metal-free synthetic protocol for biologically significant scaffold pyranopyrazole via reaction between ethylacetoacetate (**1**), hydrazine hydrate (**2**), aromatic aldehydes (**3**) and malononitrile (**4**) as reactants and exploiting visible light as a reaction promoter has been developed. Cost effectiveness, nontoxicity, being catalyst-free and solvent-free, easy-availability of reactants and non-involvement of specific glasswares and photo reactor system are some of the significant traits of the present protocol. The scope of current methodology is further extended by using diethyl acetylene dicarboxylate (**6**) as a reactant in place of ethylacetoacetate.



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Introduction

Increasing demand of the development of new techniques which necessitates green synthesis of organic molecules leads towards new thoughts and new creations. The continual use of hazardous reaction media and metal catalysts as reaction promoters in the laboratory has proven to be ceaselessly harmful to our environment and to all living beings. Thus, organic chemists are switching over to the maximum use of eco-friendly and sustainable resources.[1] Consequently, development of visible-light-initiated transformation has been considered as an impressive tool for a large number of eco-efficient synthesis and constantly drags the attention of researchers owing to the fact that employment of visible light provides a greener and more cost effective alternative which is accessible to varied reactions.[2-3] Generally, compact fluorescent lights (CFLs) and light emitting diodes (LEDs) are used as a source of visible light for various transformations.[4] However there are a number of organic scaffolds which are unable to absorb visible light.[5] To conquer this impediment, chemists are shifting their attention towards photo catalysts and photo sensitizers as transition metals, organic dyes and nanoparticles.[6] Moreover, a number of drawbacks are reported with transition metal photocatalysts like short durability, adverse inherent malignancy and expensiveness.[7] Similarly, in order to eliminate the use of toxic, organic solvents which are responsible for a large scale generation of waste and pollution, designation of a solvent-free synthesis is a big errand for the researchers and scientists. In this way, a catalyst-free and solvent-free synthesis has emerged as an important probe.[8] The dihydropyrano[2,3-c]pyrazole nucleus and its derivatives represents a remarkable and attractive scaffold in the field of medicinal chemistry and also acquire valuable biological as well as pharmacological properties.[9] They are documented to possess a range of biological properties such as antimicrobial,[10] insecticidal, molluscicidal,[11] anticancer[12] and anti inflammatory activities.[13] They are also potential inhibitors of human Chk1 kinase.[14] They can also be used as pharmaceutical elements as well as eco-friendly agrochemicals [15] (**Figure 1**).[16]

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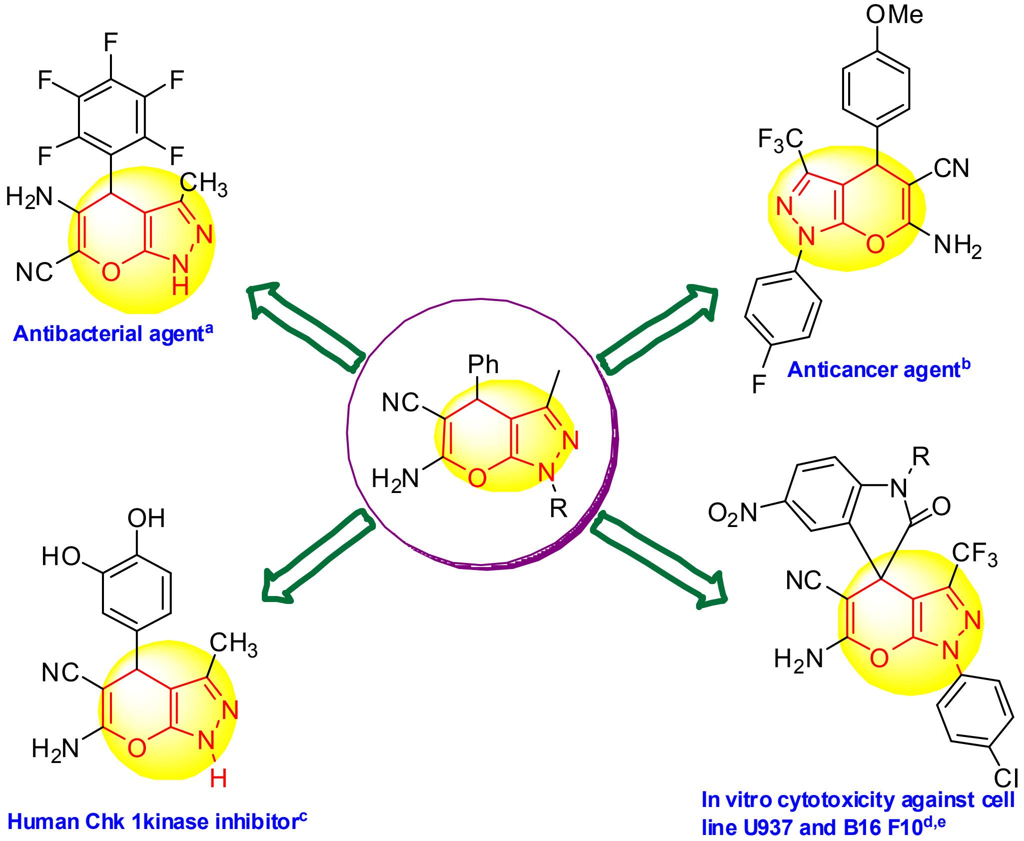

Figure 1 Some biologically important derivatives of dihydropyrano[2,3-c]pyrazole

Literature survey reveals that numerous methods were developed for the synthesis of Dihydropyrano[2,3-c]pyrazoles.[17-24] Despite the fact that the reported methods have their own importance but still some consequential drawbacks are associated with these methods as the use of hazardous solvents, metal catalysts, inorganic bases, non recyclability of the catalyst and high temperature. In continuation of our previous works in visible-light-promoted synthesis,[25] we envisioned the possibility for the synthesis of dihydropyrano[2,3-c]pyrazole initiating from ethylacetoacetate (**1**), hydrazine hydrate (**2**), aromatic aldehydes (**3**) and malononitrile (**4**) under solvent and catalyst-free condition in presence of CFL (22 W) irradiation **(Scheme 1).**

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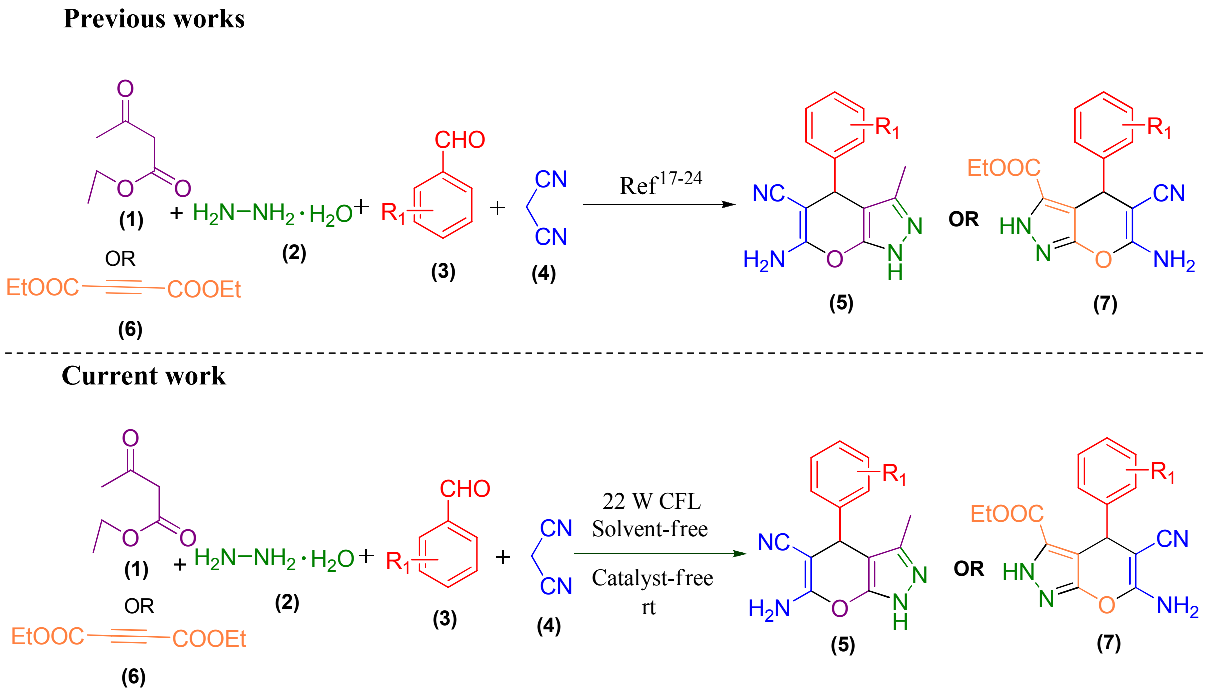

Scheme 1 Synthesis of dihydropyrano[2,3-c]pyrazole

Results and Discussion

In the beginning, we have been investigated the synthesis of pyranopyrazoles using ethylacetoacetate (**1**), hydrazine hydrate (**2**), 4-chlorobenzaldehyde (**3a**) and malononitrile (**4**) as model substrates. Initially, the reaction was performed in EtOH using 1.0 mmol of each reactant under 22 W compact florescent lamp (CFL) irradiation in catalyst-free condition. The desired product was formed in 71% yield after 15 min (Table 1, entry 6). In our optimization studies, we screened the effect of reaction media, CFL of different intensities and catalysts under different reaction conditions to achieve the proper condition for the above transformation. First of all, we investigated the effect of different organic solvents like DCM, DMSO, DMF, CH_3CN, MeOH, EtOH, EtOH:H_2O as well as neat under catalyst-free condition. In each case different yields of the desired product was obtained (Table 1, entries 1-10). In this instance, we observed that when the model reactions were carried out under catalyst-free, neat condition the yield of the product was maximum. Thus, we concluded that the neat condition is favorable for the present transformation (Table 1, entry 10). In our next endeavor, we optimized different intensities of CFL (Table 2, entries 1-4) and found that 22 W CFL is suitable for the present protocol (Table 2, entry 3).

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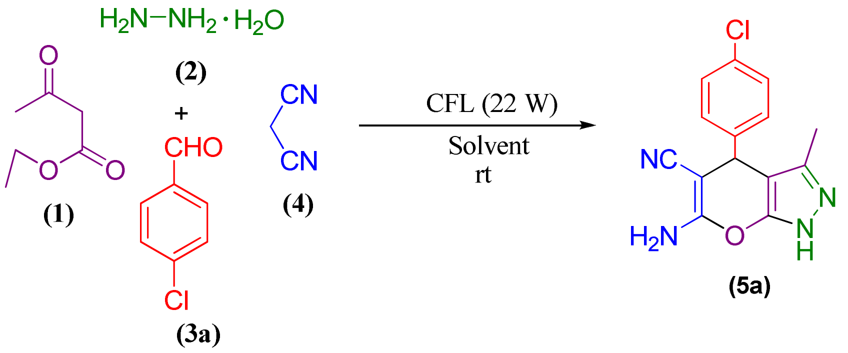
Table 1 Optimization table of Solvent for the synthesis of compound (5a)[a]



Entry	Solvents	Time (min)	Yield[b] (%)
1	DCM	15	53
2	DMSO	15	58
3	DMF	15	51
4	CH_3CN	15	62
5	MeOH	15	73
6	EtOH	15	71
7	EtOH:H_2O (1:1)	15	74
8	EtOH:H_2O (2:1)	15	69
9	EtOH:H_2O (1:2)	15	78
10	Neat	15	88

[a]Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), **3a** (1.0 mmol) and **4** (1.0 mmol) in solvent were irradiated under open air at room temperature using CFL (22 W). [b]Isolated yield of the product (%).

Table 2 Optimization table of CFL for the synthesis of compound (5a)[a]

Entry	Reaction condition	Time (min)	Yield[b] (%)
1	CFL (18 W)	30	74
2	CFL (20 W)	30	81
3	CFL (22 W)	30	88
4	CFL (23 W)	30	88

[a]Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), **3a** (1.0 mmol) and **4** (1.0 mmol) in neat condition were irradiated under open air at room temperature using CFL. [b]Isolated yield of the product (%).

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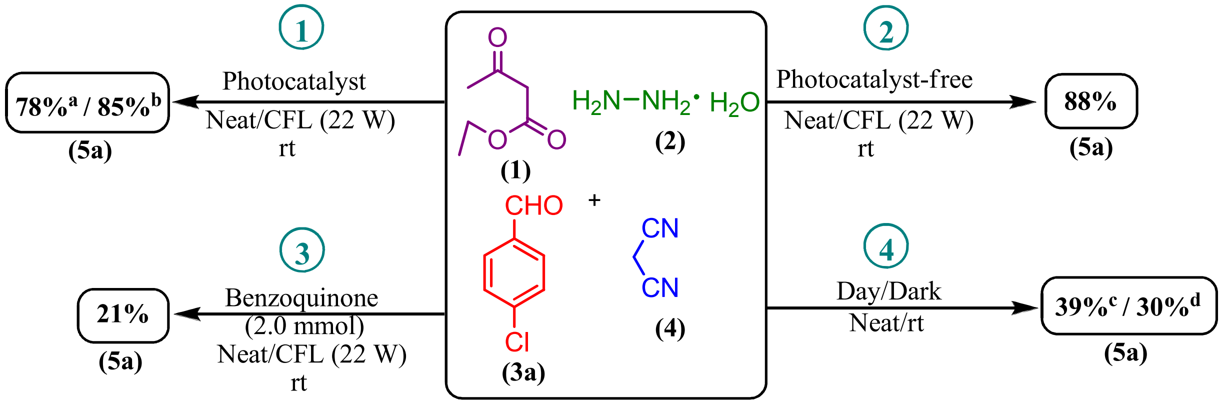
Further we optimized the reaction conditions by several control experiments including effect of catalyst, benzoquinone and that of visible light (**Scheme 2**). In these attempts, we observed that photocatalyst (Rose Bengal and Eosin Y) did not affect the yield of product (Scheme 2, entries 1 and 2). So we decided to perform our reaction under catalyst-free condition (Scheme 2, entry 2). When the reaction was carried out in presence of benzoquinone (2.0 mmol) 21% yield of product was obtained which clearly indicates that a radical intermediate must be involved (Scheme 2, entry 3).[25c, 26] A sequences of reactions to ensure the effect of day and dark under catalyst- and solvent-free conditions were also investigated and it was further revealed that in absence of visible light, the yield of product was significantly decreased (Scheme 2, entry 4), this result was further confirmed by the work of R. H. Vekariya *et al.*[21a]



Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), **3a** (1.0 mmol) and **4** (1.0 mmol) in neat condition were irradiated under open air at room temperature using CFL (22 W). [a]Yield (%) of the product in presence of Rose Bengal. [b]Yield (%) of the product in presence of Eosin Y. [c]Yield (%) of the product in presence of Day light. [d]Yield (%) of the product in presence of dark.

Scheme 2 Control experiment[a]

With the optimized reaction conditions in hand, we further investigated the scope and functional group potential of our present protocol with various substituted aromatic aldehydes (**3**) **(Table 3)**. The present protocol works well with varied substrates involving aromatic aldehydes with electron donating group as well as electron withdrawing group (**Table 3, entries 1-13**).

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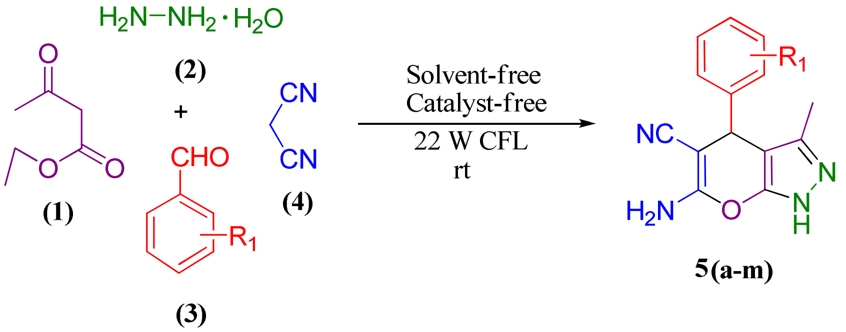
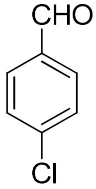
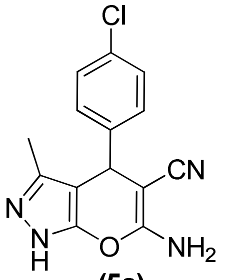
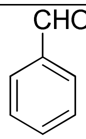
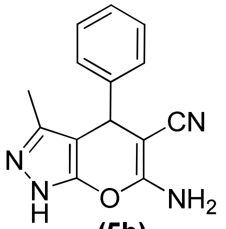
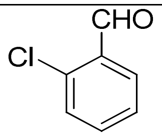
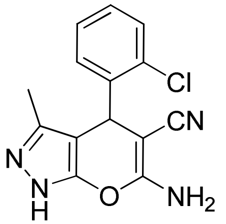
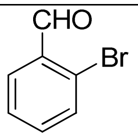
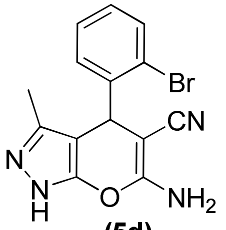
Table 3 Substrate scope for the synthesis of compound (5)[a]



Entry	Aldehyde (3)	Product (5)	Time (min)	Yield[b] (%)	M.P.(^{O}C)
1		 (5a)	15	88	230-232[23]
2		 (5b)	15	85	247-249[22]
3		 (5c)	20	84	258-260[22]
4		 (5d)	22	81	259-261[22]

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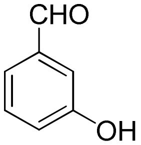
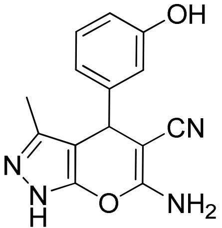
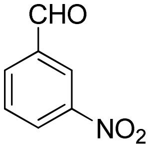
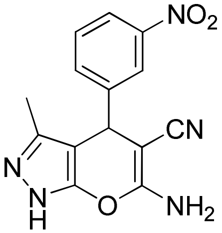
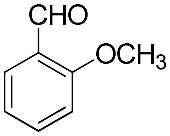
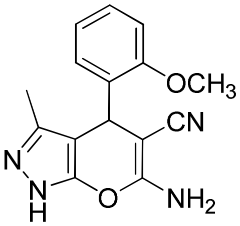
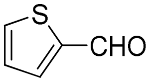
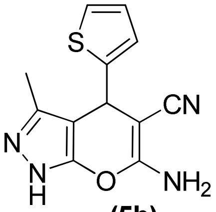
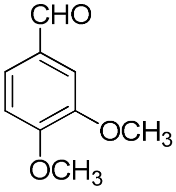
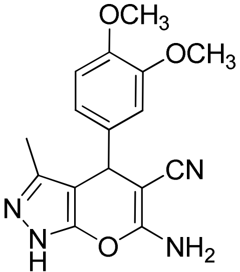
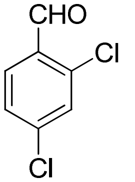
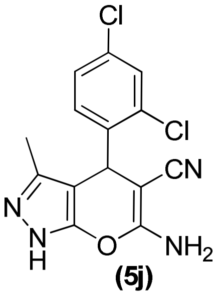
5		 (5e)	25	80	218-221[20]
6		 (5f)	15	88	192-194[18b]
7		 (5g)	25	76	259-261[22]
8		 (5h)	25	79	247-249[22]
9		 (5i)	20	76	193-196[18a]
10		 (5j)	25	79	207-210[20]

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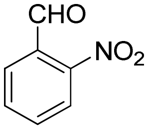
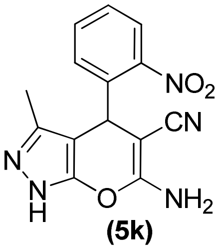
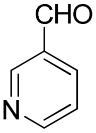
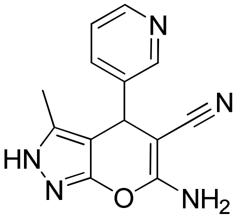
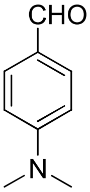
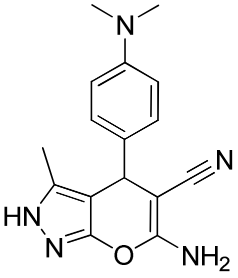
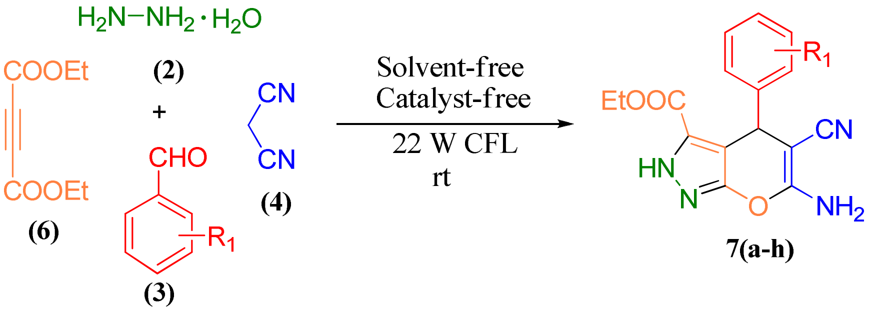
11		 **(5k)**	15	87	222-225[18b]
12		 **(5l)**	25	76	210-213[20]
13		 **(5m)**	30	56	222-225[22]

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), **3** (1.0 mmol) and **4** (1.0 mmol) in solvent- and catalyst-free condition were irradiated under open air at room temperature using CFL (22 W). [b] Isolated yield of the product (%).

Further we extended our substrate scope by using diethyl acetylene dicarboxylate (**6**) in place of ethylacetoacetate (**Table 4, entries 1-8**).

Table 4 Substrate scope for the synthesis of compound (7)[a]



Entry	Aldehyde (3)	Product (7)	Time (min)	Yield[b] (%)	M.P. (°C)[18d,24a,b]

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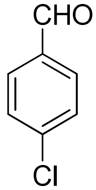
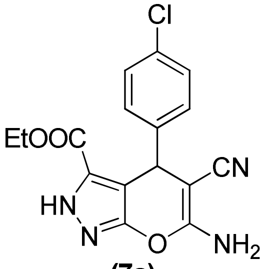
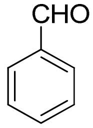
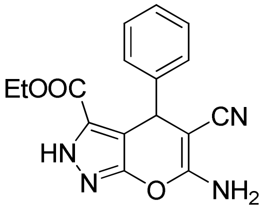
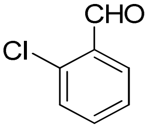
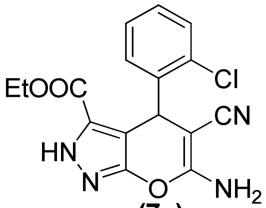
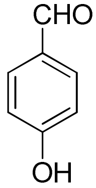
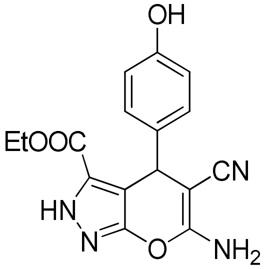
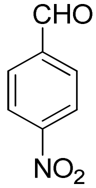
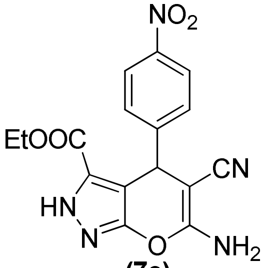
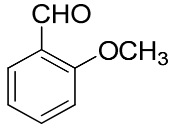
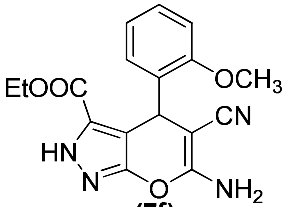
1		 **(7a)**	15	86	239-241
2		 **(7b)**	20	75	209-212
3		 **(7c)**	20	68	219-221
4		 **(7d)**	20	86	205-208
5		 **(7e)**	15	90	212-215
6		 **(7f)**	22	70	187-191

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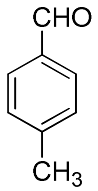
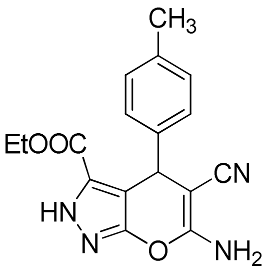
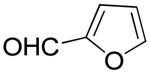
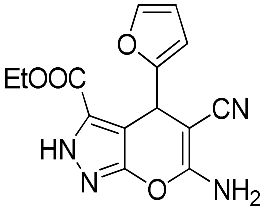
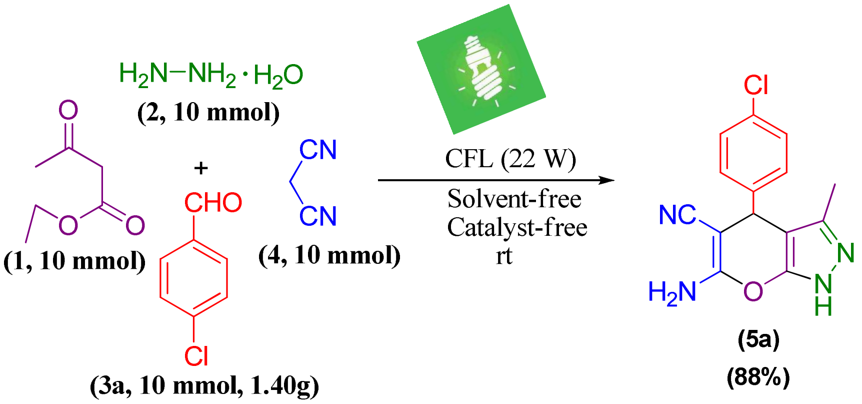
7		 **(7g)**	22	78	211-213
8		 **(7h)**	25	63	198-201

[a]Reaction conditions: **6** (1.0 mmol), **2** (1.0 mmol), **3** (1.0 mmol) and **4** (1.0 mmol) in solvent- and catalyst-free condition were irradiated under open air at room temperature using CFL (22 W). [b]Isolated yield of the product (%).

To set up the practicability of the developed protocol, we carried out the experiment on a gram scale. Ethylacetoacetate (**1**, 10 mmol), hydrazine hydrate (**2**, 10 mmol), 4-chlorobenzaldehyde (**3a,** 10 mmol, 1.40 g) and malononitrile (**4,** 10 mmol), was reacted to obtain the dihydropyrano[2,3-c]pyrazole (**5a**) in 88% yield in about 15 minutes by using CFL and common laboratory glasswares under catalyst- and solvent-free condition at room temperature (**Scheme 3**).



Scheme 3 Practicability of the Current methodology

Mechanism

On the bedrock of literature,[25b, 27, 28] a plausible mechanism for above photo-induced reaction is given in Scheme 4. The reaction initiates by a general nucleophilic addition reaction between (**1**) and (**2**) followed by elimination to form (**A**) which occurs in keto-enol tautomerism with (**B**).

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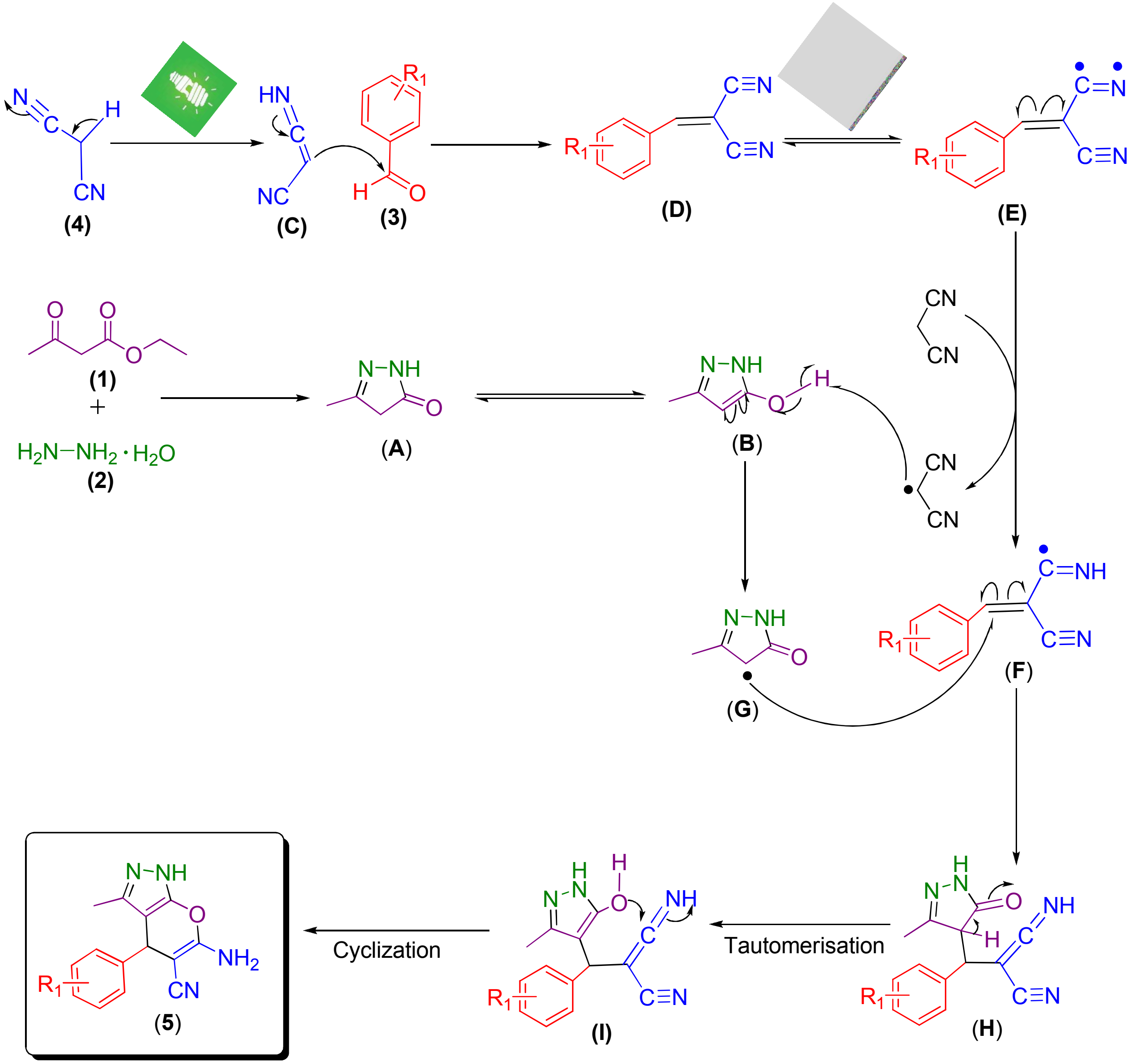
Now, in the presence of visible light, malononitrile (**4**) undergoes tautomerisation to give (**C**). After this (**C**) and benzaldehyde derivatives (**3**) react to form Benzylidene malononitrile adduct (**D**), which undergoes a photochemical activation to form a radical intermediate (**E**). Here after, (**E**) abstracts a hydrogen from malononitrile to form intermediate (**F**) as well as malononitrile radical. Now this radical abstracts a hydrogen from (**B**) to form intermediate (**G**). Afterward, intermediate (**F**) and (**G**) coalesce to form (**H**) which further undergoes tautomerisation and intramolecular cyclization to form the product (**5**).



Scheme 4 Plausible mechanism for photo-induced synthesis of dihydropyrano[2,3-c]pyrazole (**5**)

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Conclusion

In summary, we have designed a highly efficient, environmently benign, multicomponent, one pot photocatalytic pathway for the synthesis of biologically important scaffold pyranopyrazoles via readily available starting materials ethylacetoacetate, hydrazine hydrate, aromatic aldehyde and malononitrile. A visible light assisted, solvent-free, catalyst-free, metal free and easy workup procedure are some of the prime advantages of our reaction. To the best of our knowledge, the reported conditions are the first ever reported visible light mediated, catalyst free transformation for the synthesis of highly substituted dihydropyrano [2,3-c] pyrazoles.

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