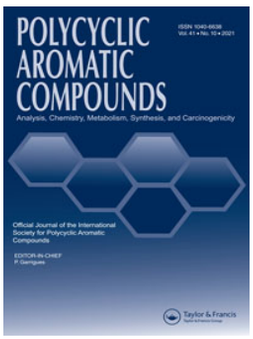

Polycyclic Aromatic Compounds

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Catalyst-Free and Solvent-Free Visible Light Assisted Synthesis of Tetrahydrobenzo[*b*]Pyran Scaffolds at Room Temperature

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ABSTRACT

A catalyst-free and solvent-free three-component tandem strategy for synthesizing tetrahydrobenzo[*b*]pyran scaffolds *through* Knoevenagel–Michael cyclocondensation is reported using visible light irradiation as a green promoter at room temperature. The prominent benefits of the existing protocol are catalyst-free, solvent-free, using commercially accessible, inexpensive preliminary substances, operational simplicity, energy-effectiveness, great yields, high atom-economy, thus meeting some features of sustainability and green chemistry.

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KEYWORDS
Catalyst-free; solvent-free; tetrahydrobenzo[*b*]pyran scaffolds; visible light irradiation

Introduction

Over the previous years by increased demand for sustainable, environmentally friendly, and effective synthesis approaches in green chemistry, catalyst-free and solvent-free for preparing the organic mixtures has arisen as a key approach considering their low cost, simple workup, decreased pollution, and preventing the catalysts and solvent influence on sensitive substrates. In recent years, the development of the use of visible light irradiation due to its low cost, abundant reserves of this type of energy and its renewable capability as a powerful energy source in the environmentally friendly synthesis of organic compounds has attracted the attention of green chemists.[1–3] Generally compact fluorescent lights (CFLs) and light emitting diodes (LEDs) use as a visible light source for different transformations.

Pyran derivatives with various pharmacological features (Figure 1) like Chk1 kinase inhibitory activity,[4] anticancer,[5] spamolytic,[6] antihypertensive, hepatoprotective, cardiotonic,[7] vasodilator,[8] anti-leukemic,[9,10] emetic,[11] anti-anaphylactic activities,[12] diuretic[13] and anti-alzheimer.[14]

There are numerous approaches for synthesizing these compounds using various catalysts such as $CaHPO_4$,[15] SiO_2NPs,[16] ethylenediamine diacetate,[17] SBPPSP,[18] DBSA,[19] $NH_4Al(SO_4)_2{\cdot}12H_2O$,[20] $NH_4H_2PO_4/Al_2O_3$,[21] ACoPc-MNPs,[22] ZnONPs,[23] Fe_3O_4@SiO_2-imid-PMA,[24] $NiFe_2O_4$@SiO_2–$H_3PW_{12}O_{40}$,[25] theophylline,[26] triethanolamine,[27] NaN_3,[28] Fe_3O_4@SiO_2@TiO_2,[29] $MgFe_2O_4$ nanoparticles[30] and trichloroisocyanuric acid.[31] 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 is separated problematically from the reaction mixture.

Nevertheless, developing green, mild and modest measures is the leading objective of green chemistry to remove the usage and creation of hazardous materials. Owing to the above-mentioned difficulties and due to our current severe attention on environmentally benign

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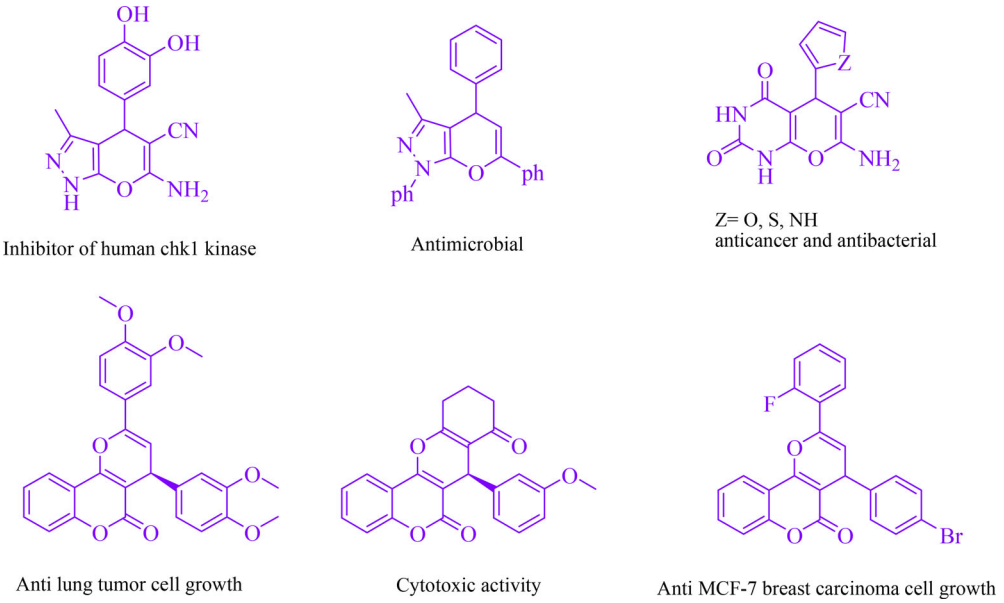


Figure 1. Some medicinally important compounds containing pyran motifs.

protocols,[32–34] the search for eco-safe, simple and effective strategies capable of promoting organic reactions under green circumstances have attracted a huge deal of interest in producing tetrahydrobenzo[*b*]pyran scaffolds. Hence, here catalyst and solvent free synthesis of tetrahydrobenzo[*b*]pyran scaffolds using aryl aldehyde derivatives (**1**, 1.0 mmol), malononitrile (**2**, 1.0 mmol) and dimedone (**3**, 1.0 mmol) are reported in the presence of CFL (22 W) irradiation as a green promoting media at room temperature *via* tandem Knoevenagel–Michael cyclocondensation provided the anticipated products in outstanding yields and short reaction times which might solve some cost problems in industry.

Experimental

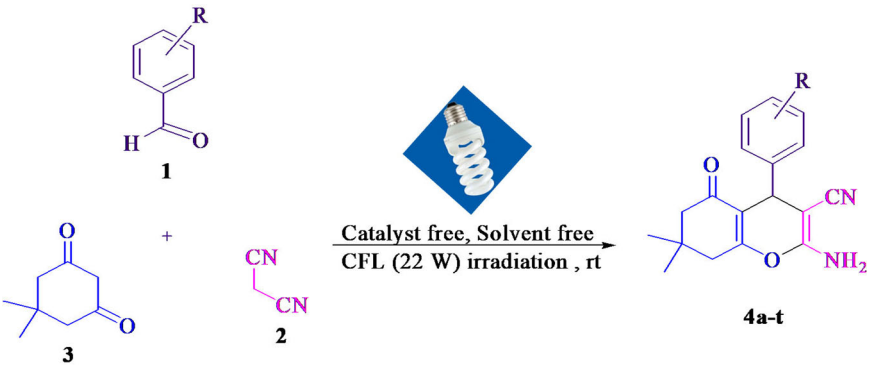
General

Utilizing an Electro thermal 9100 device, all compounds' melting points were found. Moreover, recording nuclear magnetic resonance, ^{1}HNMR spectra were carried out on a Bruker DRX-400 and Bruker DRX-300 Avance tool with $CDCl_3$ as solvent. All reagents were bought from Acros, Merck, and Fluka chemical companies and were utilized with no additional purification.

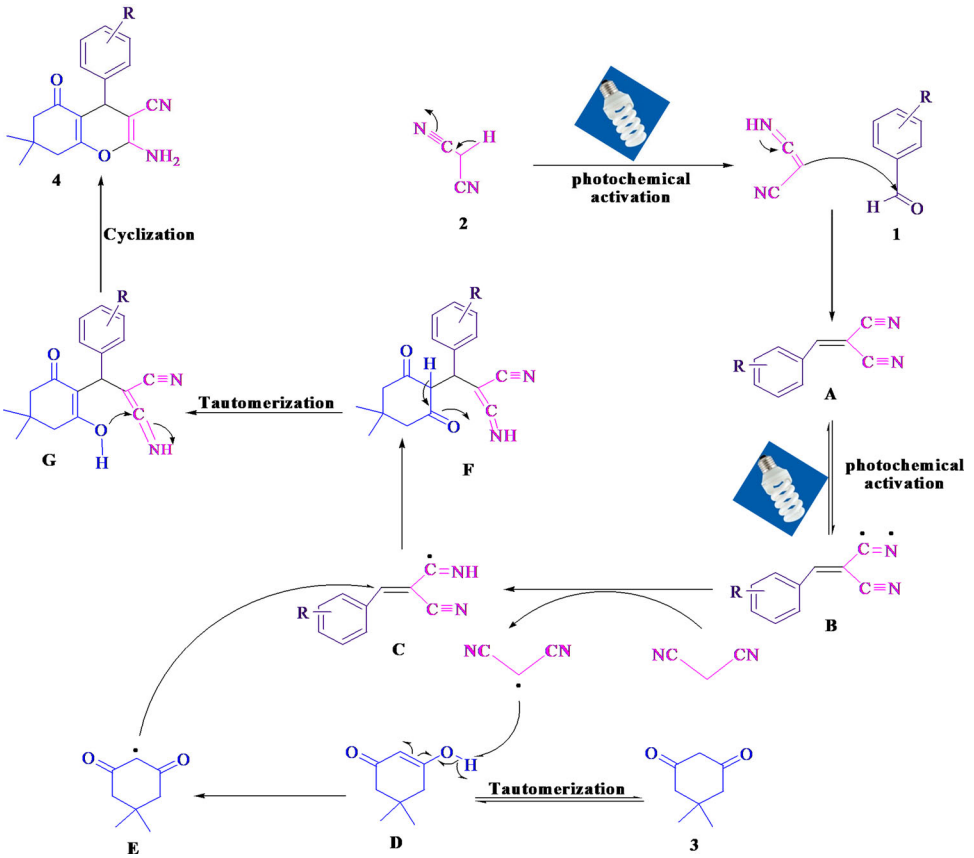
The overall process of preparing (4a–t)

A mixture of aryl aldehyde derivatives (**1**, 1.0 mmol), malononitrile (**2**, 1.0 mmol) and dimedone (**3**, 1.0 mmol) was reacted in the presence of CFL (22 W) irradiation as a green promoter under catalyst and solvent free conditions at room temperature (Scheme 1). The reaction progress was monitored by TLC utilizing ethyl acetate–*n*-hexane (1:3) 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. Comparing the spectroscopic information, the products were categorized (^{1}HNMR).

Scheme 2 shows the suggested mechanism for synthesizing tetrahydrobenzo[*b*]pyran scaffolds. The reaction was encouraged by creating an inclusion the radical intermediate ylidenemalononitrile (cyano olefin) **B** was readily created in situ from Knoevenagel condensation between



Scheme 1. Synthesis of tetrahydrobenzo[*b*]pyran scaffolds.

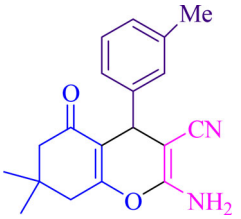


Scheme 2. Proposed mechanism for synthesizing tetrahydrobenzo[*b*]pyran scaffolds.

arylaldehyde **1** and active methylene compound **2** in the presence of visible light irradiation. This can be demonstrated by the arylaldehydes' steric influences on the reaction effectiveness (Table 3). Intermediate **B** absorbs one hydrogen from methylene malononitrile, thereby converting malononitrile to a radical malononitrile, consequently, it consists of intermediate **C**. Then, malononitrile radical absorbs one hydrogen from form **3** and converts it to form intermediate **E**.

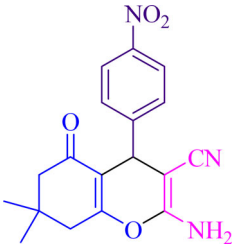
Intermediate **E** attacks to intermediate **C** as Michael acceptor to give **F** that after tautomerizing and cyclizing affords the target products **4**.

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



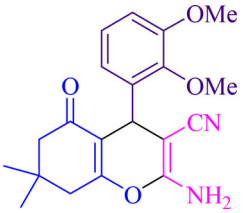
Yield: 93%; M.p. 199–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 1.06 (3H, s, CH_3), 1.13 (3H, s, CH_3), 2.23 (2H, d, $J = 5.6$ Hz, CH_2), 2.31 (3H, s, CH_3), 2.46 (2H, s, CH_2), 4.38 (1H, s, CHAr), 4.52 (2H, s, NH_2), 7.09–7.15 (3H, m, ArH), 7.28 (1H, s, ArH).

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



Yield: 92%; M.p. 178–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 1.07 (3H, s, CH_3), 1.16 (3H, s, CH_3), 2.30 (2H, d, $J = 14.0$ Hz, CH_2), 2.52 (2H, s, CH_2), 4.55 (1H, s, CHAr), 4.68 (2H, s, NH_2), 7.45 (2H, d, $J = 11.6$ Hz, ArH), 8.20 (2H, d, $J = 11.6$ Hz, ArH).

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

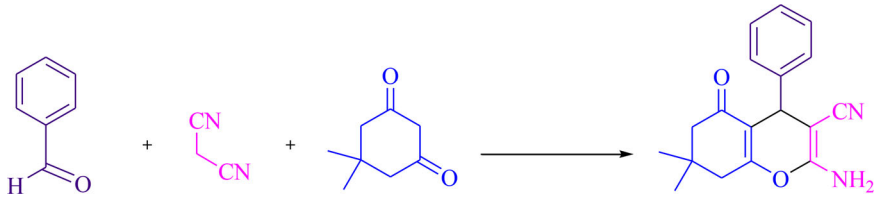


Yield: 91%; M.p. 216–218 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 1.10 (3H, s, CH_3), 1.14 (3H, s, CH_3), 2.25 (2H, s, CH_2), 2.47 (2H, s, CH_2), 3.77 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 4.47 (2H, s, NH_2), 4.73 (1H, s, CHAr), 6.68-6.84 (3H, m, ArH).

Results and discussion

Initially, the reaction between benzaldehyde (1 mmol), malononitrile (1 mmol) and dimedone (1 mmol) was studied in various solvents under catalyst-free circumstances in the presence of compact florescent lamp (CFL) (22 W) irradiation at room temperature and the outcomes are provided in Table 1. Based on Table 1, only a small quantity of products was found in H_2O, EtOH, H_2O/EtOH (1:1), CH_3CN, MeOH, DCM, DMSO, THF, $CHCl_3$, DMF and EtOAc. A great enhancement was found under solvent-free conditions (Table 1, entry 4). An outstanding yield of 91% was created by using of CFL (22 W) irradiation with no further catalyst under solvent-free

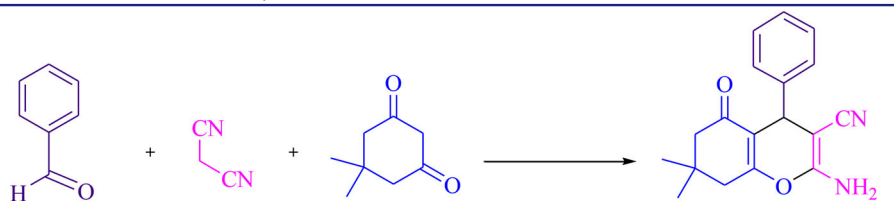
Table 1. Optimization of the solvent on the synthesis of **4f** [a].



Entry	Solvent (3mL)	Time (min)	Isolated yields (%)
1	H_2O	15	78
2	EtOH	15	72
3	H_2O/EtOH (1:1)	15	75
4	**Solvent free**	**15**	**91**
5	CH_3CN	45	53
6	MeOH	20	67
7	DCM	60	12
8	DMSO	30	41
9	THF	45	27
10	$CHCl_3$	60	16
11	DMF	40	31
12	EtOAc	35	28

[a] Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol) and dimedone (1 mmol) in the presence of CFL (22 W) irradiation under catalyst-free circumstances at rt.

Table 2. Optimization of the CFL on the synthesis of **4f** [a].



Entry	Reaction conditions	Time (min)	Isolated Yields (%)
1	CFL (18 W)	15	83
2	CFL (20 W)	15	88
3	**CFL (22 W)**	**15**	**91**
4	CFL (23 W)	15	91
5	CFL (32 W)	15	91

[a] Reaction [conditions]: benzaldehyde (1 mmol), malononitrile (1 mmol) and dimedone (1 mmol) in the presence of CFL irradiation under catalyst and solvent free conditions at rt.

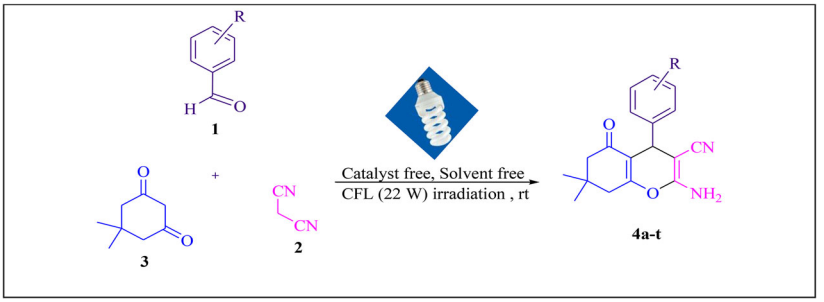
circumstances for 15 min (Table 1, entry 4). Also, the optimized conditions were determined by varying the intensities of CFL (18, 20, 22, 23 and 32 W) irradiation. Based on Table 2, the best outcomes were found in the presence of compact florescent lamp (CFL) (22 W) irradiation (Table 2, entry 3). As observed in Table 3 and Scheme 1, it was indicated that this technique can work with various substrates.

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.

Conclusion

In conclusion, we revealed a catalyst free and solvent free, green, and rapid preparation of tetrahydrobenzo[*b*]pyran—a biologically significant scaffold—using visible light irradiation as a green

Table 3. Catalyst and solvent free synthesis of tetrahydrobenzo[*b*]pyran scaffolds.



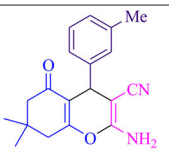
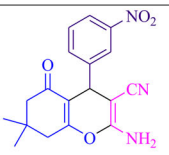
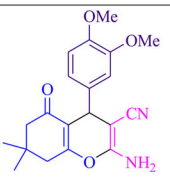
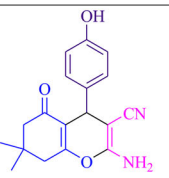
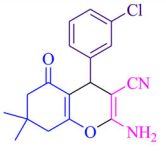
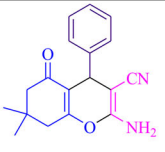
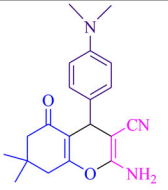
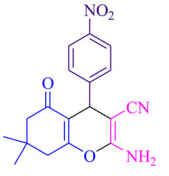
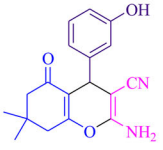
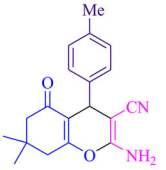
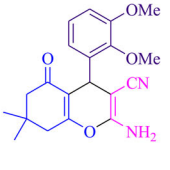
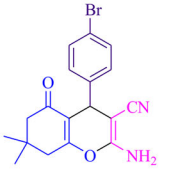
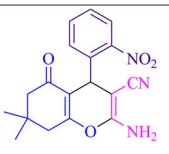
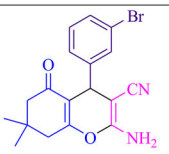
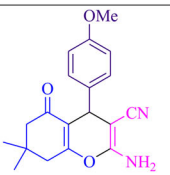
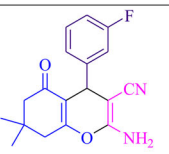
 **4a** (15 min, 93%) Mp. 199-201 °C Lit. 198-200 °C [18]	 **4b** (15 min, 91%) Mp. 208-210 °C Lit. 210-212 °C [31]	 **4c** (25 min, 88%) Mp. 228-230 °C Lit. 227-229 °C [23]	 **4d** (30 min, 85%) Mp. 211-213 °C Lit. 210-212 °C [22]
 **4e** (25 min, 86%) Mp. 227-229 °C Lit. 228-230 °C [15]	 **4f** (15 min, 91%) Mp. 225-227 °C Lit. 226-228 °C [15]	 **4g** (20 min, 89%) Mp. 210-212 °C Lit. 208-210 °C [17]	 **4h** (15 min, 92%) Mp. 178-180 °C Lit. 180-181 °C [17]
 **4i** (30 min, 82%) Mp. 228-230 °C Lit. 226-228 °C [22]	 **4j** (15 min, 90%) Mp. 221-223 °C Lit. 221-223 °C [18]	 **4k** (25 min, 91%) Mp. 216-218 °C Lit. 217-219 °C [16]	 **4l** (30 min, 83%) Mp. 206-208 °C Lit. 204-206 °C [15]
 **4m** (15 min, 95%) Mp. 224-226 °C Lit. 223-226 °C [15]	 **4n** (25 min, 86%) Mp. 229-231 °C Lit. 228-230 °C [16]	 **4o** (20 min, 92%) Mp. 202-204 °C Lit. 202-205 °C [15]	 **4p** (15 min, 93%) Mp. 209-211 °C Lit. 210-212 °C [29]

Table 4. Comparison of the catalytic ability of some of the catalysts in the manuscript for producing of tetrahydrobenzo[*b*]-pyran scaffolds [a].

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	$CaHPO_4$	H_2O/EtOH, 80 °C	120 min/91	[15]
2	SBPPSP	H_2O/EtOH, Reflux	25 min/90	[18]
3	DBSA	H_2O, Reflux	240 min/90	[19]
4	$NH_4Al(SO_4)_2{\cdot}12H_2O$	EtOH, 80 °C	120 min/92	[20]
5	Theophylline	H_2O/EtOH, rt	10 min/89	[26]
6	Triethanolamine	EtOH, rt	2 min/98	[27]
7	NaN_3	H_2O/EtOH, rt	7 min/94	[28]
8	Trichloroisocyanuric acid	EtOH, 80 °C	10 min/90	[31]
9	Catalyst-free	Solvent-free, CFL (22 W) irradiation, rt	15 min/91	This work

[a]Based on the three-component reaction of benzaldehyde, malononitrile and dimedone.

and low-cost promoter at room temperature based on green chemistry principles. Highlights of the current practice are the application of non-hazardous reaction circumstances, catalyst-free, solvent-free, operational simplicity, use of inexpensive initiating substances, isolation of pure product via easy filtration thus preventing the requirement for column chromatography, metal-free, excellent yields, time-saving aspects of the reaction, one key characteristic of the existing work is to use CFL irradiation as a green and a low-cost promoting media sufficiently remarking the rising potential of CFL irradiation in organic synthesis.

Acknowledgments

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