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Fused chromeno-pyrano-pyrimidinediones: Multi-component green synthesis and electrochemical properties

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ABSTRACT

An efficient solvent-free green multi-component reaction strategy for the synthesis of diversified fused chromenopyrano-pyrimidinediones (**4**) by the reaction of 4-hydroxy-1-benzopyran-2-one (**1**), benzaldehydes (**2**) and thiobarbituric acid (**3**) in the presence of thiamine hydrochloride at room temperature in a single step operation has been developed. Simple to perform, neat reaction conditions, water workup, short reaction times, high product yields, scalability, catalyst reusability, products free from column purification and excellent greenness of the process are the noteworthy features of this multi-component reaction approach. Hence, the established methodology meets the concept of "benign by design". Further, electrochemical properties of the synthesized compounds (**4**) have been studied by cyclic voltammetry. The HOMO/LUMO values of titled compounds (**4**) are obtained in the ranges of − 5.72 to − 5.37 eV/− 2.57 to − 2.21 eV that are comparable with the reported hole transporting materials.

1. Introduction

Nitrogen, oxygen, and sulphur containing heterocycles are the fundamental and versatile starting compounds to prepare highly efficient organic optoelectronic materials [1–[5\].](#page-8-0) Among them, coumarin and pyrimidine scaffolds have proven to be important structural units in developing optoelectronic materials [6–[10\].](#page-8-0) Optoelectronic and biological profiles of the fused heterocycles containing coumarins, pyrans and pyrimidine scaffolds, for example, pyranopyrimidines, pyrazolechromenopyrimidines, chromeno-pyrido-pyrimidines, thienopyrimidines, pyrazolothiazolopyrimidines, etc., have been well documented [\[11,12\].](#page-8-0) The HOMO and LUMO energy levels played a vital role in designing and fabrication of efficient optoelectronic devices [\[13](#page-8-0)–23]. Further, it is important to note that the efficiency of hole transport, electron transport, and ambipolar materials, which are employed in the fabrication of optoelectronic devices, depends on the energy gap between HOMO and LUMO levels [\[24,25\]](#page-8-0). These energy levels have been calculated experimentally from the onset oxidation/reduction potentials of cyclic voltammograms of the materials [\[26,27\].](#page-8-0)

Multi-component reactions (MCRs) are considered as a powerful methodological system for designing and developing diversity-oriented fused heterocycles by integrating three or more reactants in a single-step operation [\[28](#page-8-0)–30]. Hence, the development of environmentally accountable MCR strategies for the preparation of fused heterocycles containing potential scaffolds such as coumarin, pyran, and pyrimidine units is quite essential and deserves utmost attention. Limited reports on

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Scheme 1. Thiamine hydrochloride catalyzed synthesis of fused chromeno-pyrano-pyrimidinediones (**4**) in one pot.

Table 1 Catalyst screening for the synthesis of **4a**. a

^a Reaction conditions: 4-hydroxy-1-benzopyran-2-one (**1**; 1.0 mmol), benzaldehyde (**2a**; 1.0 mmol) and thiobarbituric acid (**3**; 1.0 mmol), various catalysts, neat

 $\frac{b}{c}$ Isolated yields.
 $\frac{c}{c}$ No catalyst.

the synthesis of fused chromeno-pyrano-pyrimidinediones (FCPPDs) have been documented in the literature [31–[33\]](#page-8-0). Though the reported methods are effective in affording FCPPDs, they still suffer from disadvantages like longer reaction times, the use of costly techniques that limit their scale-up process, the use of hazardous solvents, etc. Thus, there is a great need to develop efficient, facile, and rapid synthetic routes that comply with the green chemistry principles for the synthesis of optically and medicinally active FCPPDs. As of now, there are no reports in the literature on thiamine hydrochloride (VB1) catalyzed solvent-free three-component synthesis of FCPPDs. VB1 gained much recognition in organic catalysis by virtue of its nontoxic, inexpensive, and eco-friendly nature. Hence, VB1 and its analogs are utilized as a user-friendly catalysts for a wide variety of organic transformations in

^a Reaction conditions: 4-hydroxy-1-benzopyran-2-one (**1**; 1.0 mmol), benzaldehyde (**2a**; 1.0 mmol) and thiobarbituric acid (**3**; 1.0 mmol), neat conditions, RT.

b Isolated yields.

an expeditious way [\[34](#page-8-0)–38].

In continuation of our ongoing research to establish environmentally benign MCR strategies for the synthesis of diversified nitrogen and sulphur based heterocycles [39–[42\],](#page-8-0) herein, a practical, more efficient and environmentally accountable 3-component reaction strategy is reported for the synthesis of FCPPDs (**4a-j**) from the readily available 4-hydroxy-1-benzopyran-2-one (**1**), various benzaldehydes (**2a-j**) and thiobarbituric acid (**3**) in the presence of VB1 at room temperature (RT) under solvent-free conditions **(**Scheme 1**)**. The greener nature of the developed MCR strategy is evaluated and the electrochemical properties of compounds (**4**) have been investigated by cyclic voltammetry (CV). Hence, the established methodology follows the concept of *"benign by design"* and thus, it is a green and sustainable alternative procedure to the reported protocols for the titled compounds (**4**). Furthermore, HOMO/LUMO values of the synthesized FCPPDs (**4**) are comparable with the reported hole transporting materials (HTMs).

2. Materials and methods

2.1. General

All the chemicals and solvents were purchased from Sigma Aldrich, Acros Organics Ltd., Merck and TCI chemicals that were used as received. The 0.25 mm silica gel TLC plates were procured from Merck. FTIR spectra were obtained on PerkinElmer Spectrum Two LiTa FT-IR spectrometer (UK, L1600300). ¹H NMR (400 MHz) and ¹³C NMR

Fig. 1. ¹ H NMR Spectrum of **4a**.

(100 MHz) spectra were obtained on JEOL NMR spectrometer (USA, JNM-ECZL G series). The ESI mass spectra were acquired on Thermo Scientific LTQ Orbitrap Velos Pro mass spectrometer (USA, SF-LTQ-0002). Absorption spectra were recorded on a Shimadzu UV–Visible spectrophotometer (Japan, UV-3100). CV experiments were performed on CH Instruments Inc., (USA, CHI6002E).

2.2. Typical procedure for synthesis of FCPPDs (4)

A mixture of 4-hydroxy-1-benzopyran-2-one (**1)** (1.0 mmol), aromatic aldehydes (**2)** (1.0 mmol), thiobarbituric acid **(3)** (1.0 mmol), and VB1 (7.5 mol %) was stirred at RT under neat conditions. Upon completion of the reaction (as per TLC), 7.0 mL of water was added to the reaction mass, and the precipitate (**4)** formed was again washed with

Fig. 2. 13C NMR spectrum of **4a**.

Table 3 Synthesis of various fused chromeno-pyrano-pyrimidinediones (4).⁸

^a Reaction conditions: 4-hydroxy-1-benzopyran-2-one (**1**; 1.0 mmol), benzaldehydes (**2a-j**; 1.0 mmol), and thiobarbituric acid (**3**; 1.0 mmol), thiamine hydrochloride (7.5 mol%), neat conditions, RT. ^bIsolated yields.

3.0 mL of water and dried. The formed product (**4)** was recrystallized from EtOH (1.5 mL). To recover VB1, the filtrate was concentrated, and dried, and the obtained VB1 was reused in the next cycles.

2.3. Procedure for scale-up process of 4a

A mixture of 4-hydroxy-1-benzopyran-2-one (**1**; 0.0617 mol), benzaldehyde (**2a**; 0.0617), thiobarbituric acid (**3**; 0.0617) and VB1 (7.5 mol %) was stirred at RT under solvent-free reaction conditions. Upon completion of the reaction (as per TLC), the mass was poured into a beaker containing 200 mL of water. The precipitate (**4a)** formed was again washed with water (30 mL) and dried. The product (**4a)** obtained was recrystallized from EtOH.

3. Results and discussion

In order to optimize the reaction parameters, first a model reaction was carried out to synthesize 7-phenyl-10-thioxo-7,9,10,11-tetrahydro-6H,8H-chromeno[3′,4′:5,6]pyrano[2,3-d]pyrimidine-6,8-dione (**4a)** using 4-hydroxy-1-benzopyran-2-one (**1**), benzaldehyde (**2a**), and thiobarbituric acid (**3**) as model substrates ([Table 1\)](#page-1-0). Initially, the control reaction was performed without a catalyst and solvent at room temperature. It was found that **4a** was not obtained even after 24 h [\(Table 1](#page-1-0)**,** Entry 1). Then, the same reaction was carried out in the presence of catalysts, which include AlCl₃, FeCl₃, NiCl₂, ZnCl₂, CuCl₂, NiO, ZnO, Fe₂O₃, TiO₂, and VB1 ([Table 1](#page-1-0), entries 2–11) under similar reaction conditions, the catalyst VB1 (2.5 mol %) afforded a good yield (85 %) of

Table 4

Evaluation of green chemistry aspects of MCR strategy.

product (**4a**) in 30 min [\(Table 1](#page-1-0), entry 11), while the others offered moderate to poorer yields of **4a** ([Table 1,](#page-1-0) entries 2–10). Furthermore, the amount of loading of VB1 (5.0, 7.5, 10.0, and 12.5 mol %) was enhanced to increase the yield of **4a** [\(Table 2\)](#page-1-0) for which 7.5 mol % of VB1 offered the maximum yield (98 %) of **4a** in 10 min [\(Table 2,](#page-1-0) entry 3). Upon further adding VB1 (i.e., 10.0 and 12.5 mol %), it provided similar yields of **4a** [\(Table 2](#page-1-0), entries 4 and 5).

3.1. Characterization of 4a

The structure of 4a was confirmed by FT-IR, ¹H NMR, ¹³C NMR, and MS analysis (Figs. S1, [1,](#page-2-0) [2](#page-2-0) and S4).

3.1.1. FT-IR spectral analysis of 4a

As can be seen from the FT-IR spectrum of **4a** (Fig. S1), the bands at

Scheme 2. Possible mechanism of thiamine hydrochloride catalyzed 3-component synthesis of fused chromeno-pyrano-pyrimidinediones (**4**).

Fig. 3. Cyclic voltammograms of the fused chromeno-pyrano-pyrimidinediones (**4b-4i**).

Fig. 4. UV–Visible spectra of the fused chromeno-pyrano-pyrimidinediones (**4b-4i**).

3421 and 3230 cm^{-1} indicating the presence of NH stretching of thiolactam and lactam groups ($-NH-C = S$ - and $-NH-C=O$), respectively. The peaks at 3145 & 3043 cm⁻¹ and 2939 & 2858 cm⁻¹ were corresponding to CH stretching vibrations in both aromatics (Ar C-H stretching) and aliphatics (Aliphatic C-H stretching). Strong absorption bands in the region 1686–1666 cm⁻¹ were assigned to conjugated carbonyl group stretching vibration (-C=C-C=O). A strong absorption band at 1612 ${\rm cm^{-1}}$ indicates the presence of C=C stretching of vinyl ether (C=C). The absorption bands at 1571 and 1458 cm^{-1} were ascribed to C=S asymmetric and symmetric stretching vibrations of thiolactam (NH-C=S-), respectively. An absorption peak at 1394 cm^{-1} was on account of C-N stretching vibration. The bands at 1251 and 1053 cm^{-1} corresponded to asymmetric and symmetric C-O-C stretching vibrations of 4H-pyran ring. The band at 1184 cm^{-1} was assigned to C-O-C stretching vibration of lactone of 2*H*-chromen-2-one ring.

3.1.2. ¹ H NMR (DMSO‑*d6) spectral analysis of 4a*

In the 1 H NMR spectrum of **4a** [\(Fig. 1](#page-2-0)), a broad singlet at *δ* 9.87 ppm was corresponding to two **NH** protons of thioxotetrahydropyrimidin-4 (1H)-one. A doublet at *δ* 7.79 ppm with *J* value of 7.6 Hz indicated the presence of H_a proton of phenyl ring A. A triplet at δ 7.52 with *J* value of 7.2 Hz was assigned to **Hc** proton of phenyl ring **A**. A multiplet in the range of δ 7.29–7.23 revealed the presence of two protons ($\mathbf{H}_{\mathbf{b}}$ & **Hd**) of phenyl ring **A**. A triplet at *δ* 7.15 with *J* value of 7.2 Hz inferred the presence of two protons $(H_f \& H_h)$ of phenyl ring **B**. The three protons (H_e , H_g & H_i) of phenyl ring B were noticed at δ 7.06–7.04 as multiplet. The key methine proton **(Hj)** of 4*H*-pyran appeared as singlet at *δ* 6.11.

3.1.3. 13C NMR (DMSO‑*d6) spectral analysis of 4a*

1H NMR spectral data of **4a** was supported by 13C NMR spectral data ([Fig. 2\)](#page-2-0). The quaternary carbons like carbonyl carbon of thiolactum, lactum and lactone groups at *δ* 175.25 (**1C11**), 165.49 (**1C10**) and 164.43 (**1C**₆), respectively, the four olefinic carbons at δ 162.32 (**1C**₁₂), 152.20 ($1C_{13}$), 105.41($1C_7$) and 89.38 ($1C_9$) and the aromatic carbons at δ 151.02 (**1C5**), 143.55 (**1C15**) and 115.47 (**1C14**) were assigned with the aid of ¹³C NMR spectrum. The signals at δ 131.02 (1C (C₃H)), 127.53

Table 5 Electrochemical data of the fused chromeno-pyrano-pyrimidinediones (**4**).

Compd.	$\lambda_{\text{edge}}(nm)$	$E_{\rm g}^{\rm opt}$ $(eV)^a$	$E_{\rm ox}^{\rm onset}$	$E_{\rm HOMO}$ $(eV)^b$	E_{LUMO} $(eV)^c$
4b	410	3.02	1.111	-5.53	-2.51
4c	382	3.25	1.042	-5.46	-2.21
4d	443	2.80	0.947	-5.37	-2.57
4e	394	3.15	1.034	-5.72	-2.57
4f	406	3.05	1.048	-5.47	-2.42
4g	400	3.10	0.965	-5.38	-2.28
4h	414	2.99	1.067	-5.49	-2.50
4i	404	3.07	1.028	-5.45	-2.38

a) $E_{\rm g}^{\rm opt} = 1240/\lambda_{\rm edge}$.

b) $E_{\text{HOMO}} = -[E_{\text{ox}}^{\text{onset}} - E_{\text{ref}} + 4.8]$ ($E_{\text{ref}} = E_{\text{FOC}} = 0.38 \text{ eV}$).

c) $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}.$

(**2C (C17H & C19H)**), 126.67 (**2C (C16H & C20H)**), 124.58 (**1C (C18H)**), 123.89 (**1C (C2H)**), 123.12 (**1C (C1H)**) and 119.08 (**1C (C4H)**) were attributed to nine aromatic CH carbons. The CH carbon of 4H-pyran (C₈) ring might be merged with the solvent peak, i.e., DMSO‑*d6* appeared in the range of δ 40.14–38.89 in the ¹³C NMR spectrum ([Fig. 2](#page-2-0)). Finally the aforementioned spectral analysis of **4a** was confirmed by mass spectrum which had $[M+H]$ ⁺ at m/z 377.1 (Fig. S4).

3.2. Substrate scope of the methodology

After stabilizing the reaction conditions, the generality of the developed method was examined by employing various aromatic aldehydes ([Table 3](#page-3-0)). Benzaldehyde (**2a**) reacted well with **1** and **3** to produce **4a** with excellent isolated yield (98 %). Benzaldehyde with electrondonating 4-CH3 (**2b**), 4-OCH3 (**2c**), and 4-OH (**2d**) groups exhibited good reactivity with **1** and **3** and afforded excellent isolated yields of **4b** (97 %), **4c** (98 %), and **4d** (97 %), respectively. Benzaldehyde bearing strong electron-withdrawing 3-NO2 (**2e**) and 3-F (**2f**) groups showed good reactivity with **1** and **3** and provided good isolated yields of the corresponding products, **4e** (95 %) and **4f** (96 %). Benzaldehyde containing a bromo $(2-Br (1g)$ and $4-Br (1h)$), chloro $(3-Cl (1i))$ and dichloro (3,5-diCl (**1j**)) groups on the ring underwent the reaction with **1**

and **3** giving better yields of products, **4g** (93 %)**, 4h** (97 %)**, 4i** (97 %) and **4j** (94 %), respectively.

3.3. Evaluation of green chemistry metrics

To explore the green chemistry aspects of the developed MCR strategy, parameters such as atom efficiency (AE), environmental factor (E), process mass intensity (PMI), and percentage of generalized or global reaction mass efficiency (gRME) have been calculated by following the reported empirical formulae [\[43,44\].](#page-9-0) The results obtained are presented in [Table 4.](#page-4-0) The results showed that all the reactions exhibited good AE (91–93 %), the E-factor (0.466–0.544) which was close to the ideal E-factor (0), excellent PMI (1.466–1.544), and good gRME (64.8–68.2 %) values. Detailed calculations of the aforementioned metrics are appended (Table S1). The results suggest that the established MCR strategy meets the requirements of the ideal green and sustainable process of titled compounds (**4**).

3.4. Reusability

The reusability of the catalyst (VB1) was also studied using 4-hydroxy-1-benzopyran-2-one(**1**), benzaldehyde (**2a**), and thiobarbituric acid (**3**) as benchmark substrates for the synthesis of **4a** using the wellestablished reaction conditions. Upon completion of the reaction (as per TLC), 7.0 mL of water was added, and the formed product (**4a)** was isolated by filtration. The filtrate containing the catalyst was concentrated under vacuum, and the obtained catalyst was reused in the next five cycles. The yields of **4a** were 98, 98, 97, 96, and 94 % for 1st, 2nd, 3rd, 4th, and 5th cycles, respectively. From this study, it was noticed that the efficacy of the recycled catalyst was almost similar to that of the fresh catalyst.

3.5. Scalability

Scalability of the optimized protocol was investigated for the preparation of **4a** (2.5, 5.0, 7.5, and 10 g) using model reactants such as **1**, **2a**, and **3**. The yields of the desired product, **4a** were obtained as 96 %, 94 %, 93 %, and 90 %, respectively. From this study, it was noticed that the established MCR methodology was expedient for the scale-up process of FCPPDs (**4**).

3.6. Reaction mechanism

The probable mechanism for VB1-catalyzed 3-component synthesis of FCPPDs (**4**) is depicted in [Scheme 2](#page-4-0). The mechanism starts with the activation of aromatic aldehyde (2) and thiobarbituric acid (**3**) by VB1catalyst to obtain the activated aromatic aldehydes (**5**) and enol form of thiobarbituric acid (**6**) and then the reaction of **5** and **6** to produce Knoevenagel adduct (**8**) *via* nucleophilic addition and subsequent dehydration. Next, VB1 catalyzed Michael addition reaction between 4-hydroxy-1-benzopyran-2-one (**1**) and the obtained Knoevenagel adduct (**8**) to form an intermediate (**9**). Finally, the intermediate (**9**) undergoes an intramolecular ring closure reaction (Pyran ring formation) in the presence of VB1 and followed by dehydration to obtain the target molecule (**4**).

3.7. Electrochemical properties

To investigate the electrochemical properties of FCPPDs (**4**), CV experiments were performed in the potential range from − 0.2 to 2.0 V in DMF (0.5 mM) and 0.05 M Bu₄NPF₆ (supporting electrolyte) at a scan rate of 100 mV/s. A regular 3-electrode system (platinum electrode, saturated calomel electrode [Ag/Ag+ (satd. KCl)] and platinum wire) was used in the present study. From CV study, it was observed that the titled compounds (**4**) exhibited quasi-reversible cyclic voltammograms. The HOMO values were obtained from the onset oxidation potentials

([Fig. 3\)](#page-5-0), while the LUMO values were calculated from the HOMO values, and the optical band gap (E_g^{opt}) ($E_g^{opt} = 1240/\lambda_{edge}$, λ_{edge} was obtained from UV–Visible spectra ([Fig. 4\)](#page-6-0)). The HOMO and LUMO energy levels were determined and summarized in [Table 5](#page-6-0). As can be seen from [Table 5](#page-6-0), HOMO/LUMO values of **4b-4i** are − 5.53/− 2.51 eV **(4b**), − 5.46/− 2.21 eV (**4c**), − 5.37/− 2.57 eV (**4d**), − 5.72/− 2.57 eV (**4e**), − 5.47/− 2.42 eV (**4f**), − 5.38/− 2.28 eV (**4g**), − 5.49/− 2.50 eV (**4h**) and − 5.45/− 2.38 eV **(4i**) i.e. in the range of − 5.72 to − 5.37 eV/− 2.57 to − 2.21 eV. To our delight, the HOMO /LUMO values of FCPPDs (**4**) were in good agreement with the HOMO/LUMO values of reported hole transporting materials (HTMs) for manufacturing of organic lightemitting diodes (OLEDs) such as *N,N'*-di-(naphthalen-1-yl)-*N,N'*-diphenylbenzidine (NPB) (-5.5/-2.4 eV), N,N-di(naphthaien-1-yl)-N,N,10triphenyl-10*H*-spiro(acridine-9,9′-fluorene)-2,7-diamine (STNPB) (− 5.35/− 2.45 eV), 4,4,4′'-tris[(2,3,4,5-tetraphenyl)phenyl]phenylamine (TTPPPA) (− 5.46/− 2.36 eV), N,N'-bis-(1-naphthyl)-N,N' diphenyl benzidine (α-NPD) (-5.43/-2.33 eV), 4,4['],4["]-tris(*N*-carbazolyl)triphenylamine (TCTA) $(-5.7/-2.3$ eV), etc $[45-49]$ $[45-49]$. Thus, the titled compounds (**4**) are promising HTMs for fabricating optoelectronic devices. Further, the FCPPDs (**4**) have low HOMO energy levels as compared with the threshold for air oxidation (≈ -5.2 eV). Hence, the FCPPDs (**4**) displayed good stability under the ambient conditions [\[50,51\].](#page-9-0)

4. Conclusions

A facile and environmentally benign MCR strategy has been developed for the synthesis of FCPPDs (**4**) from 4-hydroxy-1-benzopyran-2 one (**1**), various benzaldehydes (**2**) and thiobarbituric acid (**3**) in the presence of biodegradable VB1catalyst at RT under neat reaction conditions. Practicability, operational simplicity, cleaner reaction profiles, high product yields in shorter reaction times, multiple bonds and 4Hpyran ring formations in one-pot, reusability of the catalyst, and gramscale feasibility are the salient features of this MCR strategy. Further, green chemistry metrics clearly showed that the established MCR methodology meets the concept of "benign by design" and hence, it is an alternative green synthetic procedure to the already reported methods for the synthesis of FCPPDs (**4**). The HOMO /LUMO values of FCPPDs (**4**) are found to be in the range of -5.72 to -5.37 eV/ -2.57 to -2.21 eV that are comparable with the reported HTMs for the fabrication of optoelectronic devices. Hence, further continuation of this study will be to utilize the synthesized FCPPDs (**4**) as the promising HTMs for the fabrication of optoelectronic devices such as OLEDs, organic solar cells, organic field effect transistors, etc.

CRediT authorship contribution statement

Rama Mohana Reddy Sirigireddy: Conceptualization, Methodology, Writing – original draft. **Sultana Shaik:** Investigation, Data curation. **Mohan Gundluru:** Methodology, Data curation. **Suresh Reddy Cirandur:** Writing – review & editing. **Fernando Alonso Marroquin:** Writing – review & editing. **Raghava Reddy Kakarla:** Formal analysis, Supervision, Writing – review & editing. **Chinna Gangi Reddy Nallagondu:** Supervision, Writing – review & editing. **Tejraj M. Aminabhavi:** Supervision, Writing – review & editing.

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

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data (Calculations of green chemistry metrics, spectral data, and copies of FTIR, 1H NMR, 13C NMR, and MS spectra of the synthesized compounds (**4**) of this article are available online in the supporting information section) to this article can be found online at [https://doi.org/10.1016/j.molliq.2024.123950.](https://doi.org/10.1016/j.molliq.2024.123950)

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