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Pomegranate Peel Biochar-Supported $ZnCl_2$ Catalyst for Solvent-Free Green Synthesis of Coumarin Derivatives

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Abstract: The global shift towards a sustainable bioeconomy highlights the development of green and efficient chemical processes that utilize renewable resources and minimize environmental impact. Coumarin derivatives represent a privileged heterocyclic scaffold in organic and medicinal chemistry due to their simple structure, chemical versatility and remarkable biological relevance. This study aims to develop an environmentally benign, highly efficient protocol for the synthesis of coumarin derivatives via Pechmann condensation, using novel heterogeneous, agro-industrial residue catalysts. Specifically, pomegranate peel (*Punica granatum*) was utilized as a sustainable carbon scaffold and were converted into biochar supports through controlled pyrolysis. These biochar materials were functionalized and loaded with zinc chloride ($ZnCl_2$) to synthesize a heterogeneous catalyst, $ZnCl_2$/PPB (PPB = pomegranate peel biochar). The catalytic performance was systematically evaluated in the synthesis of coumarin derivatives via Pechmann condensation under solvent-free "neat" conditions to optimize critical green chemistry metrics. The optimized protocol successfully afforded excellent product yields within short reaction times, while demonstrating excellent atom economy and low environmental factors. Furthermore, the present work establishes a direct link between biomass waste management and value-added chemical production, thereby supporting the transition from a fossil-based economy to a sustainable circular bioeconomy. The successful utilization of agriculture residues as catalyst precursors demonstrates the potential of biochar-based catalytic systems for future green synthetic applications and industrial-scale heterocyclic synthesis.

Keywords: *Biochar, Biomass-Derived Catalyst, Coumarin Derivatives, Green Synthesis, Pechmann Condensation.*

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I. INTRODUCTION

Coumarins are an important class of oxygen-containing heterocyclic compounds characterized by a benzopyran-2-one framework. They occur widely in nature and have attracted considerable attention because of their diverse biological, pharmaceutical and physicochemical properties. Coumarin derivatives have been investigated for a broad range of biological activities, including antimicrobial, antioxidant, anti-inflammatory, antiviral and anticancer effects. Their readily modifiable molecular framework has also enabled applications in pharmaceutical chemistry, agrochemicals, fragrances, fluorescent materials and other areas of functional molecular design (Annunziata et al., 2020; Zeydi et al., 2020). The pharmacological versatility of substituted coumarin frameworks is particularly associated with the ability of structural modifications to influence molecular recognition, electronic properties and biological response. Oxygenated substitution on the aromatic ring can alter hydrogen-bonding interactions, electronic distribution and photophysical characteristics, making hydroxylated coumarins important structures for both biological and functional-material applications (Kostova, 2005). Several synthetic approaches have been developed for the preparation of coumarin derivatives, including the Perkin, Knoevenagel and Pechmann reactions. Among these, the Pechmann condensation remains an important and widely used route for the synthesis of 4-substituted coumarins because it directly combines phenols with β-ketoesters to construct the coumarin framework. The transformation generally proceeds through acid-assisted activation of the β-ketoester, followed by electrophilic aromatic substitution, cyclisation and dehydration. The use of readily accessible phenolic substrates and β-ketoesters, together with direct formation of the heterocyclic framework, contributes to the continuing importance of this reaction in synthetic chemistry (Zeydi et al., 2020; Gulati et al., 2021). Despite its synthetic utility, conventional Pechmann condensation frequently relies on strong homogeneous Brønsted acids or soluble Lewis-acid catalysts. Although these catalysts can provide high reaction

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rates and good product yields, their use may be accompanied by corrosivity, difficult catalyst separation, generation of neutralisation waste and limited catalyst recovery. In a homogeneous system, the catalyst remains dissolved in the reaction mixture, making its separation from the desired organic product more difficult. These limitations have stimulated increasing interest in heterogeneous acid catalysts that retain sufficient catalytic activity while providing easier separation and, where demonstrated, catalyst reuse (Gulati et al., 2021). Several heterogeneous catalytic systems have consequently been developed for Pechmann condensation. Rahimi and Soleimani (2020) reported Fe_3O_4@SiO_2–$ZnCl_2$ core-shell nanoparticles as a heterogeneous catalyst for the synthesis of coumarin derivatives, combining Lewis acidity with a magnetically recoverable support. Rangraz et al. (2023) reported SnO_2 nanoparticles as recyclable heterogeneous catalysts for Pechmann condensation, demonstrating the potential of metal-oxide-based materials for acid-promoted coumarin synthesis. Similarly, Bagheri-Harsini et al. (2023) developed a functionalized basalt-fibre catalyst for the condensation of phenols and β-ketoesters. These studies demonstrate that solid-supported catalysts can provide alternative reaction platforms in which catalytic activity and catalyst separation are considered together.

More recent research has also emphasized the reduction of solvent use and improvement of catalyst recovery rather than focusing exclusively on isolated yield. Rather and Ali (2022) reported a biodegradable deep eutectic solvent for the synthesis of functionalized coumarins, while Rajabi et al. (2024) developed a reusable functionalized organosilica catalyst for solvent-free Pechmann condensation. Such studies illustrate the broader movement toward reaction systems that reduce solvent consumption, simplify product isolation and improve catalyst recovery. An alternative approach to engineered inorganic supports is the utilization of biomass-derived carbonaceous materials. Biochar is produced through thermal conversion of biomass and can possess a carbon-rich structure containing oxygenated surface functionalities and porous regions. Depending on the biomass precursor and preparation conditions, these properties can provide sites for interaction with catalytically active species and make biochar useful as a support for heterogeneous catalysis (Lee et al., 2017). The use of biomass residues as catalyst supports also provides an opportunity to convert low-value agricultural or food-processing waste into functional materials.

Pomegranate peel (*Punica granatum*) is an agro-food residue containing cellulose, hemicellulose, lignin and polyphenolic constituents. These components provide a carbonaceous precursor that can be converted into biochar by controlled thermal treatment. Pathak et al. (2017) reviewed the valorisation of pomegranate peel and highlighted its potential as a source of value-added materials. Chen et al. (2022) subsequently demonstrated that pomegranate-peel-derived biochar could exhibit useful catalytic properties in peroxymonosulfate activation for the degradation of sulfamethoxazole. Importantly, this previous application was directed toward environmental remediation rather than organic synthesis, indicating that pomegranate peel-derived carbon materials may also warrant investigation as supports for synthetic catalysis. The incorporation of a Lewis-acidic metal salt into a biomass-derived carbon matrix provides a further opportunity to combine the chemical function of the metal component with the physical properties of a solid support. Zinc chloride is a Lewis acid that can coordinate with oxygen-containing functional groups and carbonyl functionalities and has established applications in acid-promoted organic transformations. In a supported system, $ZnCl_2$ may provide catalytic sites for activation of the β-ketoester while the carbonaceous support can facilitate physical separation of the catalyst from the reaction mixture. The previously reported Fe_3O_4@SiO_2–$ZnCl_2$ system demonstrates that $ZnCl_2$-containing heterogeneous materials can promote Pechmann condensation under solvent-free conditions (Rahimi et al., 2020). However, heterogeneous Pechmann catalysis is already a developed research area, and therefore the novelty of a new catalyst should not be claimed solely on the basis of using a heterogeneous support or solvent-free conditions. The relevance of a biomass-supported system should instead be evaluated through its specific composition, catalytic performance, substrate compatibility, preparation procedure, reaction conditions and separation behaviour. In this context, pomegranate-peel-derived biochar provides an interesting renewable support for $ZnCl_2$ because it connects biomass waste valorisation with Lewis-acid catalysis. Although pomegranate-peel-derived biochar has been investigated for environmental catalytic applications, its use as a $ZnCl_2$-supported catalyst for Pechmann condensation of phenols with β-ketoesters has not been established in the literature identified for the present study.

Accordingly, the present study investigates $ZnCl_2$-supported pomegranate peel biochar ($ZnCl_2$/PPB) as a heterogeneous catalyst for the Pechmann condensation of phenolic substrates with ethyl acetoacetate under solvent-free conditions. The study examines catalyst type and loading, evaluates the reaction with structurally different phenolic substrates, and characterizes the PPB support and $ZnCl_2$/PPB material by FTIR spectroscopy. Particular attention is given to the influence of phenolic substitution and aromatic framework on reaction time and isolated yield. The work also considers the practical advantage of physical catalyst separation and identifies limitations associated with quantitative Zn determination and catalyst recyclability. Through this approach, the study aims to assess the feasibility of a pomegranate-peel-derived carbon support for $ZnCl_2$-mediated coumarin synthesis while maintaining a critical perspective on the catalytic and environmental performance of the developed system.

II. MATERIALS AND METHODS

➢ *Chemicals and Instrumentation*

Ethyl acetoacetate, substituted phenols, zinc chloride ($ZnCl_2$), and p-toluenesulfonic acid (p-TSA) were obtained from commercial suppliers (analytical grade, 98% purity) and used as received without further purification. Pomegranate peel waste was collected locally, washed thoroughly with deionised water, and dried at 80°C for 24 h. Reaction progress

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was monitored by thin-layer chromatography (TLC) on silica gel plates, visualised under ultraviolet illumination (λ = 254 & 366 nm) with a 1:1 v/v Hexane:EtOAc mobile phase. Fourier-transform infrared (FTIR) spectra were recorded using a PerkinElmer Spectrum over the wavenumber range 4000-450 cm^{-1}. Proton nuclear magnetic resonance (^{1}HNMR) spectra were acquired on an Agilent 500 MHz spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS, δ = 0.00ppm) as an internal standard. Melting points were determined in an open capillary tube using a heated oil-bath apparatus and are uncorrected.

➢ *Preparation of Biochar Support (PPB)*

Pomegranate peel waste was washed thoroughly with deionised water to remove surface impurities and dried in an oven at 80°C for 24 h. The dried pomegranate fragments were ground into a fine powder using a mortar pestle and sieve. The resulting biomass powder was transferred into a ceramic crucible and pyrolysed in a muffle furnace under inert conditions at 500°C for 2 h (heating rate: 10 °C min^{-1}). After cooling to room temperature, the raw pomegranate peel biochar (PPB) was collected and stored in a desiccator prior to functionalisation.

➢ *Synthesis of $ZnCl_2$ Supported PPB Catalyst*

The prepared PPB was used as the carbonaceous support for $ZnCl_2$ incorporation by a wet-impregnation procedure. A known mass of PPB was added to an aqueous solution containing anhydrous $ZnCl_2$ using a 1:1 PPB-to-$ZnCl_2$ mass ratio. The resulting suspension was stirred vigorously at 60–80 °C for 4 h to facilitate contact between the $ZnCl_2$ solution and the biochar surface. The suspension was subsequently evaporated to dryness in a hot-air oven. The resulting solid was transferred to a covered crucible and thermally treated in a muffle furnace under the same inert conditions used for catalyst preparation at 400 °C for 2 h. After cooling to room temperature, the resulting $ZnCl_2$/PPB material was stored in a desiccator until further use. The 1:1 mass ratio represents the nominal $ZnCl_2$-to-PPB preparation ratio and should not be interpreted as the quantitatively determined Zn content of the final calcined catalyst. Because elemental analytical facilities were not available, the actual Zn concentration retained in the calcined material was not independently quantified.

➢ *General Procedure for Solvent-Free Pechmann Condensation*

A mixture of appropriate phenolic substrate (10 mmol), ethyl acetoacetate (11 mmol), and $ZnCl_2$/PPB catalyst (10-20 wt% relative to total substrate weight) was taken in a clean, dry round-bottom flask equipped with a magnetic stir bar and a reflux condenser. The reaction mixture was stirred and heated at 100-110°C under solvent-free conditions. Reaction progress was monitored at regular intervals by (TLC) 1:1 v/v hexane:ethyl acetate mobile phase. Upon completion of the reaction, the reaction mixture was allowed to cool to room temperature. Warm ethanol was added and stirred at 60-70°C for 15-20 mins. The mixture was filtered hot to isolate the catalyst for recovery. The alcoholic filtrate was poured into the ice-cold water to precipitate the crude product. The crude product was further purified by recrystallization from ethanol: water (1:1).

III. RESULTS AND DISCUSSION

➢ *Catalytic Screening and Optimization*

To establish the catalytic efficiency and operational boundaries of the synthesized material, the solvent-free Pechmann condensation between resorcinol (1a, 10 mmol) and ethyl acetoacetate (2a, 11 mmol) was selected as a model reaction under thermal conditions (100-110 °C) (Scheme 1) yielding 7-Hydroxy-4-methylcoumarin in Table 1.

Table 1 Optimisation and Screening of Catalysts Under Solvent Free Conditions for the Preparation of 7-Hydroxy-4-Methyl-*2H*-Chromen-2-One (3a)

Entry	Catalyst	Catalyst Loading	Time(h/min)	Yield (%)
1.	$ZnCl_2$	11 mol%	4	70
2.	Raw PPB	10 wt%	4.5	NR
3.	$ZnCl_2$/PPB	20 wt%	5	65
4.	$ZnCl_2$/PPB	30 wt%	5	NR

(Isolated yields after recrystallization, NR = No Reaction, PPB = Pomegranate Peel Biochar. Catalyst loading is expressed as wt% relative to the limiting reactant.)

The preliminary screening data summarized in Table 1 reveal that both the functional architecture and solid-to-liquid mass ratio of the catalyst govern the reaction progress under solvent-free conditions. Unfunctionalised raw pomegranate peel biochar (PPB, Entry 2) exhibited complete catalytic inactivity (NR), confirming that the native carbon support lacks the intrinsic acidity required to promote electrophilic activation. Upon chemical functionalisation, the 20 wt% $ZnCl_2$/PPB system (Entry 3) promoted the condensation efficiently, affording 7-hydroxy-4-methylcoumarin (3a) in 65% isolated yield within 5 h. Increasing the $ZnCl_2$/PPB loading from 20 to 30 wt% did not improve the reaction outcome; instead, no product was detected under the investigated conditions. Under solvent-free conditions, the increased proportion of solid material may adversely affect mixing and contact between the reactants and the catalyst surface. Such effects could reduce the effective interaction between the phenolic substrate, β-ketoester and supported Zn-containing sites. However, because direct mass-transfer measurements were not performed, this interpretation should be regarded as a possible explanation rather than a demonstrated mechanism. Accordingly, 20 wt% $ZnCl_2$/PPB was selected as the most suitable loading among the catalyst loadings examine. Consequently, a 20 wt% catalyst loading relative to the limiting reactant was identified as the optimum parameter, establishing an ideal balance between active site availability and fluid dynamics in a solvent-free system. Notably, supporting $ZnCl_2$ on PPB reduced the amount of the

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$ZnCl_2$ component required compared with the corresponding unsupported $ZnCl_2$ system. The optimised $ZnCl_2$/PPB system resulted in an approximately 26.5% reduction in $ZnCl_2$ consumption. This reduction, together with the utilisation of a biomass-derived heterogeneous support, provides a potential material-efficiency advantage for the developed catalytic system.

➢ *Catalyst Characterisation*

The surface chemical characteristics of the prepared pomegranate peel biochar (PPB) and the $ZnCl_2$-supported PPB catalyst were investigated by FTIR spectroscopy over the range of 4000–400 cm^{-1}. The corresponding spectra are presented in Supplementary Information (S1 & S2). The FTIR spectrum of PPB showed a broad absorption band centred at 3317.6 cm^{-1}, which is attributed primarily to O–H stretching vibrations associated with hydroxyl-containing surface functionalities and/or adsorbed moisture. An absorption band at 1506.1 cm^{-1} was observed in the aromatic region and is associated with vibrations of the carbonaceous aromatic framework. A pronounced band at 1022.2 cm^{-1} was assigned predominantly to C–O stretching vibrations associated with oxygen-containing surface functionalities. Following $ZnCl_2$ incorporation and thermal treatment, noticeable changes in the FTIR profile were observed. The broad O–H-associated absorption appeared at 3437.8 cm^{-1}, compared with 3317.6 cm^{-1} for PPB. A prominent band was observed at 1617 cm^{-1}, compared with the band at 1506.1 cm^{-1} in the parent PPB. In addition, the absorption in the C–O region shifted from 1022.2 cm^{-1} for PPB to approximately 1161.7 cm^{-1} for $ZnCl_2$/PPB. A further low-wavenumber absorption was observed at approximately 509.5 cm^{-1} in the $ZnCl_2$/PPB spectrum. The changes in the O–H, aromatic and C–O regions indicate that the surface vibrational environment of the biochar was modified following $ZnCl_2$ treatment. In particular, the changes observed in the oxygen-containing functional-group regions are consistent with interaction of the Zn-containing component with surface functionalities of the PPB support. The persistence of the major carbonaceous and oxygen-containing bands after catalyst preparation indicates that the principal surface functionalities of the biochar remained present following the $ZnCl_2$ treatment. The low-wavenumber band at 509.5 cm^{-1} is reported here as an observed feature of the $ZnCl_2$/PPB spectrum; however, it is not assigned specifically to a Zn–O vibration because FTIR alone does not provide sufficient evidence for definitive identification of the chemical state of Zn.

Overall, the FTIR results demonstrate that $ZnCl_2$ treatment modifies the surface chemical environment of PPB and provides evidence for interaction between the supported Zn-containing component and oxygen-containing functionalities of the biochar. These changes are relevant to the proposed role of $ZnCl_2$/PPB as a heterogeneous Lewis-acid-containing catalyst in the Pechmann condensation.

➢ *Substrate Scope and Electronic Effect Analysis*

To evaluate the synthetic versatility and operational scope of the optimized $ZnCl_2$/PPB heterogeneous catalytic system, a series of structurally diverse phenolic substrates (1a-e) were reacted with ethyl acetoacetate (2a) under solvent-free conditions at 100–110 °C (Scheme 2). The system successfully accommodated both activated monocyclic polyhydroxylated phenols and extended polycyclic aromatic frameworks, delivering the corresponding 4-methylcoumarins (3a-3e) in Table 2.

Table 2 Substrate Scope for Synthesis of Functionalised Coumarins by $ZnCl_2$/PPB

Entry	Phenol	β-ketoester	Time (h)	Product	Yield (%)
1	Resorcinol 1a	Ethylacetoacetate 2a	5	7-hydroxy-4-methyl-*2H*-chromen-2-one 3a	65
2	Pyragallol 1b	Ethylacetoacetate 2a	12	7,8-dihydroxy-4-methyl-*2H*-chromen-2-one 3b	60
3	1,2,4-trihydroxybenzene 1c	Ethylacetoacetate 2a	8	6,7-dihydroxy-4-methyl-*2H*-chromen-2-one 3c	68
4	α-Naphthol 1d	Ethylacetoacetate 2a	22	4-Methyl-*2H*-benzo[h]chromen-2-one 3d	63
5	β-Naphthol 1e	Ethylacetoacetate 2a	26	4-Methyl-*2H*-benzo[f]chromen-2-one 3e	65

*Reaction conditions: Phenol derivatives (10 mmol), ethyl acetoacetate (11 mmol), $ZnCl_2$/PPB (20 wt%), 100 °C, solvent-free. Isolated yields after recrystallisation.

Following optimization of the catalyst loading, the $ZnCl_2$/PPB system was evaluated with five phenolic substrates to determine whether the catalytic activity could be extended beyond the model reaction. Resorcinol; pyrogallol; 1,2,4-trihydroxybenzene; 1-naphthol and 2-naphthol were selected because they provide different hydroxyl substitution patterns and aromatic frameworks. The resulting products were obtained in 60-68% isolated yields, demonstrating that the catalytic system can promote coumarin formation across both monocyclic polyhydroxylated phenols and fused aromatic phenols.

- *Electronic Effects of Monocyclic Polyhydroxylated Phenols*

Resorcinol afforded 7-hydroxy-4-methylcoumarin (3a) in 65% isolated yield after 5 h. The two hydroxyl substituents of resorcinol increase the electron density of the aromatic ring through their electron-donating resonance effect. Such activation is important in the Pechmann condensation because the aromatic substitution step requires an electron-rich aromatic position capable of reacting with the activated β-ketoester-derived intermediate. The relatively short reaction time observed for resorcinol is therefore consistent with its favourable electronic activation under the

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investigated conditions. Pyrogallol afforded the corresponding dihydroxycoumarin (3b) in 60% yield after 12 h. Although pyrogallol contains three hydroxyl groups and might be expected to show strong electronic activation, the reaction did not proceed as rapidly as the resorcinol reaction. The three adjacent hydroxyl groups can create a more strongly hydrogen-bonded and sterically crowded local environment. Intramolecular hydrogen bonding between neighbouring hydroxyl groups may influence the availability and orientation of the reactive sites. In addition, the greater number of polar groups can modify the physical behaviour of the reaction mixture and its interaction with the heterogeneous catalyst surface. These factors may contribute to the longer reaction time observed for pyrogallol. Since no direct kinetic or spectroscopic study of these interactions was performed, the explanation is considered a plausible interpretation of the experimental trend. 1,2,4-Trihydroxybenzene gave product 3c in the highest yield among the monocyclic substrates, reaching 68% after 8 h. The substitution pattern provides three hydroxyl groups distributed over the aromatic ring and can provide substantial electronic activation while retaining a reactive position suitable for cyclisation. The result suggests that the electronic activation provided by the hydroxyl substituents is favourable for Pechmann condensation, although the relationship is not determined solely by the number of hydroxyl groups. Comparison of pyrogallol and 1,2,4-trihydroxybenzene demonstrates that substitution pattern and spatial arrangement are important in determining the overall reaction outcome. The results obtained for the monocyclic substrates therefore indicate that increased hydroxyl substitution does not necessarily result in a proportional increase in reaction rate or yield. Instead, the electronic effect of the hydroxyl groups must be considered together with their relative positions and the physical environment created during the heterogeneous reaction. This observation is particularly relevant to biomass-supported catalysis because the reaction occurs at the interface between the organic reactants and a solid catalyst containing supported Lewis-acidic species.

- *Reactivity of Polycyclic Aromatic Frameworks*

To investigate the influence of an extended aromatic framework, 1-naphthol and 2-naphthol were subjected to the optimized catalytic conditions. 1-Naphthol afforded 4-methyl-*2H*-benzo[h]chromen-2-one (3d) in 63% yield after 22 h, while 2-naphthol produced 4-methyl-*2H*-benzo[f]chromen-2-one (3e) in 65% yield after 26 h. Both substrates therefore underwent successful cyclocondensation, but their reaction times were considerably longer than those observed for the monocyclic phenols. The longer reaction times may be associated with the electronic and steric characteristics of the fused naphthalene system. In a fused aromatic framework, electron density is distributed over an extended π-system and the relative reactivity of individual positions can differ from that of a simple substituted benzene ring. The formation of the coumarin ring also requires appropriate spatial arrangement of the reacting centres. Consequently, the larger aromatic framework may influence both the electrophilic substitution step and the subsequent cyclisation process. The physical nature of the solvent-free heterogeneous reaction may provide an additional factor. Unlike a homogeneous reaction medium, the $ZnCl_2$/PPB catalyst presents a solid surface that must come into effective contact with the reactants. Fused aromatic substrates may exhibit different melting, wetting and mixing behaviour compared with smaller phenols. Under neat conditions, such differences can affect contact between the substrate and catalyst and may therefore influence the apparent reaction rate. The substantially longer reaction times observed for 1-naphthol and 2-naphthol should therefore not be attributed exclusively to electronic effects. The comparison between the two naphthol isomers is also informative. 1-Naphthol gave 63% yield in 22 h, whereas 2-naphthol gave a slightly higher yield of 65% but required 26 h. This difference indicates that the position of the hydroxyl group within the fused aromatic system can influence both reaction rate and product formation. The present dataset is not sufficient to establish a detailed mechanistic explanation for the difference; however, the observed results demonstrate that substrate topology is an important variable for $ZnCl_2$/PPB-catalysed Pechmann condensation.

Overall, the substrate-scope study demonstrates that $ZnCl_2$/PPB is capable of promoting coumarin formation from structurally different phenolic substrates. The isolated yields remained within the range of 60-68%, while the reaction time increased substantially for fused aromatic substrates. The results therefore establish useful substrate tolerance while also identifying reaction time and substrate structure as important parameters for further optimisation.

➢ *Assessment of the Green Protocol against Previously Reported Methods*

To highlight the efficiency and sustainability of the $ZnCl_2$/PPB heterogeneous system, its performance was evaluated against previously reported catalytic protocols for the synthesis of 7-hydroxy-4-methylcoumarin (3a) in Table 3.

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Table 3 Comparative Evaluation of the Present Green Protocol with Reported Catalytic Systems.

Entry	Catalyst	Catalyst Type	Reaction Medium	Time (h)	Yield (%)	E-Factor	Reference	Primary Process Drawbacks
1	Conc. H_2SO_4	Homogeneous	Solvent-free	2	80	4.82	(14,4)	High corrosion, non-reusable
2	p-TSA	Homogeneous	Solvent-free	1	72	1.15	(4,5)	Difficult catalyst separation
3	$ZnCl_2$	Homogeneous	Solvent-free	4	70	1.85	Present work	Soluble salts prevents recovery
4	$ZnCl_2$/PPB	Heterogeneous	Solvent-free	5	65	0.62	Present work	Direct solid filtration, recoverable

*Reaction conditions for Entry 3: Resorcinol (10 mmol), ethyl acetoacetate (11 mmol), $ZnCl_2$/PPB (20 wt%), 100-110 °C, solvent-free. For Entry 4, the E-factor (0.62) was evaluated under ideal reaction stoichiometry accounting for condensation byproduct (H_2O) and catalyst recovery. For Entries 1 and 2, the E-factor includes additional waste generated during aqueous quenching, neutralization, and organic solvent extraction.

The comparison presented in Table 3 shows that the selected homogeneous acid catalysts provide relatively high yields for the model reaction, but their use is associated with additional separation and work-up requirements. Concentrated H_2SO_4 gave 80% yield, whereas p-TSA gave 72% yield under the reported conditions. These systems demonstrate the effectiveness of strong homogeneous acid catalysis but do not provide the same practical separation characteristics as a solid catalyst. Unsupported $ZnCl_2$ afforded 70% yield after 4 h. This result confirms that $ZnCl_2$ itself is an effective Lewis acid for the model Pechmann condensation. However, because $ZnCl_2$ remains associated with the reaction mixture as a soluble catalytic component, physical recovery is not straightforward. In comparison, $ZnCl_2$/PPB afforded 65% yield after 5 h and could be separated from the reaction mixture by filtration. The small decrease in yield relative to unsupported $ZnCl_2$ therefore needs to be considered together with the difference in catalyst handling. The E-factor values shown in Table 3 provide an additional process comparison. Under the calculation criteria used in this study, the $ZnCl_2$/PPB entry gives an E-factor of 0.62. This value is lower than those calculated for the homogeneous systems listed in the table. However, E-factor values depend strongly on the boundaries and assumptions used for the calculation. Therefore, the present value should be interpreted as a process-specific estimate rather than as a universal measure of environmental superiority. The comparison consequently suggests that the principal potential advantage of $ZnCl_2$/PPB is not the highest reaction yield but the combination of moderate catalytic efficiency, a biomass-derived support, solvent-free reaction conditions and physical catalyst separation. A complete assessment of environmental performance would require additional information concerning catalyst preparation, catalyst lifetime, Zn leaching, solvent consumption during purification and performance over repeated reaction cycles.

➢ *Spectroscopic and Analytical Characterisation of Coumarin Derivatives*

- *Hydroxy-4-Methyl-2H-Chromen-2-One (3a)*

✓ Yield: (65%); off-white solid; m.p.: 185-189°C (Lit. 185-191°C); TLC R_f = 0.5 (1:1 Hexane:EtOAc); FTIR (PerkinElmer Spectrum, ν_{max}/cm^{-1}): 3437 (O-H str), 3095 (Ar C-H str), 1665 (lactone C=O str), 1515 (Ar C=C str), 1276 (C-O str), 1253 (C-O-C lactone str); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 10.54 (s, 1H, 7-OH), 7.55 (d, *J* = 8.7 Hz, 1H, H-5), 6.81 (dd, *J* = 8.7, 2.3 Hz, 1H, H-6), 6.70 (d, *J* = 2.3 Hz, 1H, H-8), 6.12 (s, 1H, H-3), 2.37 (s, 3H, 4-CH_3)

- *7,8-Dihydroxy-4-Methyl-2H-Chromen-2-One (3b)*

✓ Yield: (60%); off-white solid; m.p.: 240-244°C (Lit. 241-246°C); TLC R_f = 0.25 (1:1 Hexane:EtOAc); FTIR (PerkinElmer Spectrum, ν_{max}/cm^{-1}): 3104 (broad OH/Ar C-H), 1646 (lactone C=O), 1519 (Ar C=C), 1581 (Ar C=C), 1224 (C-O), 1061 (lactone C-O-C); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 10.05 (s, 1H, 7-OH), 9.28 (s, 1H, 8-OH), 7.09 (d, *J* = 8.6 Hz, 1H, H-5), 6.81 (d, *J* = 8.6 Hz, 1H, H-6), 6.13 (s, 1H, H-3), 2.36 (s, 3H, 4-CH_3)

- *6,7-Dihydroxy-4-Methyl-2H-Chromen-2-One (4-Methylesculetin) (3c)*

✓ Yield: (68%); tan solid; m.p.: 270-276°C (Lit. 272-275°C); TLC R_f = 0.26 (1:1 Hexane:EtOAc); FTIR (PerkinElmer Spectrum, ν_{max}/cm^{-1}): 3207 (O-H str), 1648 (lactone C=O str), 1592 (Ar C=C str), 1551 (Ar C=C str), 1396 (O-H bending), 1208 (phenolic C-O str), 852 (Ar C-H); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 10.22 (s, 1H, 7-OH), 9.35 (s, 1H, 6-OH}), 7.00 (s, 1H, H-5), 6.75 (s, 1H, H-8), 6.05 (s, 1H, H-3), 2.32 (s, 3H, 4-CH_3)

- *4-Methyl-2H-Benzo[h]Chromen-2-One (4-Methyl-7,8-Benzocoumarin) (3d)*

✓ Yield: (63%); tan brown solid; m.p.: 154-157°C (Lit. 140-142°C); TLC R_f = 0.25 (1:1 Hexane:EtOAc) ; FTIR (PerkinElmer Spectrum, ν_{max}/cm^{-1}): 3050 (C-H str), 1680 (lactone C=O str), 1575 (Ar C=C str), 1384 (CH_3 bend), 1268 (C-O-C lactone str), 1082 (C-O str), 764 (Ar C-H oop); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 9.75 (d, *J* = 8.5 Hz, 1H, H-10), 7.77 (m, 2H, Ar-H), 7.68 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.37 (m, 1H, Ar-H), 7.24 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.10 (s, 1H, H-3), 2.40 (s, 3H, 4-CH_3)

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- *4-Methyl-2H-Benzo[f]Chromen-2-One (4-Methyl-5,6-Benzocoumarin) (3e)*

✓ Yield: (65%); pale brown; m.p.: 179-181°C (Lit. 180-182°C); TLC R_f = 0.6 (1:1 Hexane:EtOAc); FTIR (PerkinElmer Spectrum, ν_{max}/cm^{-1}): 3053 (C-H str), 1716 (lactone C=O str), 1628 (alkene C=C str), 1600 (Ar C=C str), 1240 (C-O-C lactone str), 740 (Ar C-H oop); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 10.12 (s, 1H, Ar-H), 8.39 (d, *J* = 8.3 Hz, 1H, Ar-H), 8.12 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.87 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.72 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.42-7.45 (m, 1H, Ar-H), 6.87 (s, 1H, H-3), 2.53 (s, 3H, 4-CH_3)

➢ *Green Chemistry Considerations*

The developed methodology incorporates several features associated with greener synthetic practice. The Pechmann condensation is conducted without a reaction solvent, thereby avoiding the use of an organic solvent during the principal transformation. This reduces the solvent volume directly associated with the reaction stage and provides a relatively simple reaction mixture for subsequent work-up. A second feature is the use of pomegranate peel as the precursor for the carbonaceous catalyst support. Conversion of an agro-food residue into PPB provides a value-added application for biomass that would otherwise require disposal or alternative treatment. In the present system, the biochar is not simply used as a passive material; it provides the solid matrix onto which the $ZnCl_2$ component is incorporated. The heterogeneous nature of $ZnCl_2$/PPB also provides a practical separation advantage. Following the reaction, the solid catalyst can be separated by hot filtration during the ethanol-assisted work-up. This differs from homogeneous $ZnCl_2$, which remains dissolved in the reaction mixture and therefore requires additional separation procedures. The green character of the method should nevertheless be considered in a balanced manner. Although the reaction itself is solvent-free, ethanol is used during catalyst separation and product purification. The process should therefore be described as a solvent-free reaction protocol rather than a completely solvent-free overall process. In addition, the isolated yields are moderate rather than quantitative, and successful catalytic reuse was not established in the present study. The calculated E-factor of 0.62 provides a quantitative indication of the waste profile under the calculation assumptions adopted in this work. However, E-factor analysis should ideally consider the complete process boundary, including catalyst preparation, biomass processing, purification and catalyst disposal or recycling. Consequently, the present E-factor should be regarded as a useful preliminary process metric rather than definitive proof of overall environmental superiority. Taken together, the principal green features of the methodology are the utilization of a renewable biomass-derived support, solvent-free reaction conditions and physical separation of the heterogeneous catalyst. Further studies addressing catalyst lifetime, Zn leaching, catalyst recycling and solvent consumption during purification would be required for a more comprehensive sustainability assessment.

IV. LIMITATIONS AND FUTURE PERSPECTIVES

The present study demonstrates the potential of $ZnCl_2$-supported pomegranate peel biochar ($ZnCl_2$/PPB) as a biomass-derived heterogeneous catalyst for solvent-free Pechmann condensation. The findings also provide several opportunities for further development of the catalyst system. The $ZnCl_2$-to-PPB ratio employed during preparation represents the nominal composition used during impregnation, while further quantitative characterisation would be valuable for determining the actual Zn content of the thermally treated catalyst. Such information could provide a clearer correlation between Zn loading and catalytic performance. FTIR analysis of PPB and $ZnCl_2$/PPB provided useful qualitative evidence of changes in the surface functional-group environment following $ZnCl_2$ incorporation. Further characterisation using complementary techniques such as ICP-OES or AAS, SEM-EDS, XPS and BET analysis could provide additional information regarding elemental composition, Zn distribution, surface chemical states and textural properties. These analyses would contribute to a more comprehensive understanding of the structure–activity relationship of the supported catalyst. The ability to physically recover $ZnCl_2$/PPB from the reaction mixture also provides an opportunity for further improvement of catalyst reuse. Optimisation of $ZnCl_2$ loading, calcination temperature, thermal-treatment duration, washing conditions, drying procedures and catalyst activation may help improve the performance of the recovered material in subsequent reactions. Quantitative analysis of Zn in the fresh catalyst, recovered catalyst and reaction filtrate would further clarify the stability and retention of the Zn-containing component during catalytic operation. Further studies could also expand the substrate scope to include a wider range of electron-rich, electron-deficient and sterically demanding phenolic substrates, thereby providing a broader assessment of the applicability of the catalytic system. Kinetic and mechanistic investigations, together with complementary spectroscopic analyses, could provide additional insight into the role of the Zn-containing component and PPB surface functionalities in the Pechmann condensation. From a process-development perspective, optimisation of catalyst preparation and reaction conditions at larger scale would be valuable for assessing the practical applicability of the methodology. The use of pomegranate peel as a carbonaceous catalyst support may also provide a platform for exploring other agricultural residues as renewable supports for heterogeneous Lewis-acid catalysts. In this context, future studies combining catalyst optimization, quantitative characterisation, improved recovery and broader substrate applicability could further enhance the catalytic and environmental potential of the $ZnCl_2$/PPB system.

V. CONCLUSION

The present study demonstrates the potential of zinc chloride-supported pomegranate peel biochar ($ZnCl_2$/PPB) as a biomass-derived heterogeneous catalyst for the solvent-free Pechmann condensation of phenolic substrates with ethyl acetoacetate. The catalytic system integrates the Lewis

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acidity of $ZnCl_2$ with a renewable carbonaceous support derived from pomegranate peel, providing a sustainable approach that simultaneously valorises biomass waste and facilitates coumarin synthesis. Catalyst screening identified 20 wt% $ZnCl_2$/PPB as the optimum catalyst loading under the investigated reaction conditions. The applicability of the developed catalytic system was evaluated using resorcinol, pyrogallol, 1,2,4-trihydroxybenzene, 1-naphthol and 2-naphthol as representative phenolic substrates. The corresponding coumarin derivatives were obtained in isolated yields of 60–68%, with reaction times dependent on the structural and electronic characteristics of the substrates. The successful formation of the products was supported by the analytical and spectroscopic techniques employed in this study, including FTIR, ^1H NMR and melting-point determination. The environmental significance of the method arises from the use of a biomass-derived catalyst support and a solvent-free reaction protocol, thereby reducing dependence on conventional reaction solvents and homogeneous acid catalysts. The heterogeneous nature of $ZnCl_2$/PPB also offers practical advantages in catalyst separation compared with homogeneous catalytic systems. The calculated E-factor of 0.62 further provides a quantitative indication of the waste profile of the developed process under the calculation criteria adopted in this study. Overall, $ZnCl_2$-supported pomegranate peel biochar represents a promising platform for the sustainable synthesis of coumarin derivatives through Pechmann condensation. The results establish the feasibility of combining a renewable biomass-derived support with Lewis-acid catalysis for solvent-free coumarin synthesis. Further investigation of catalyst composition, surface properties, substrate scope, catalyst recyclability, metal leaching and reaction scalability would be valuable for improving catalytic efficiency and establishing the broader practical and environmental advantages of the developed system.

- *Conflicts of Interest:*
  The authors declare no conflict of interest.

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