

Research



Cite this article: Mali S, Shinde S, Damte S, Patil S. 2018 Synergistic effect of natural chickpea leaf exudates acids in heterocyclization: a greener protocol for benzopyran synthesis. *R. Soc. open sci.* 5: 170333.

<http://dx.doi.org/10.1098/rsos.170333>

Received: 6 May 2017

Accepted: 8 January 2018

Subject Category:

Chemistry

Subject Areas:

green chemistry/organic chemistry/
synthetic chemistry

Keywords:

benzopyran, *Cicer arietinum*, chickpea exudates, bio-catalyst, natural catalyst

Author for correspondence:

Suresh Patil

e-mail: sanyujapatil@yahoo.com

This article has been edited by the Royal Society of Chemistry, including the commissioning, peer review process and editorial aspects up to the point of acceptance.

Electronic supplementary material is available online at <https://dx.doi.org/10.6084/m9.figshare.c.3983985>.



Synergistic effect of natural chickpea leaf exudates acids in heterocyclization: a greener protocol for benzopyran synthesis

Snehali Mali, Sachin Shinde, Shashikant Damte and Suresh Patil

Synthetic Research Laboratory, PG Department of Chemistry, PDPV College, Tasgaon, Sangli district, 416312, Maharashtra, India

SP, 0000-0003-2713-6007

Without using any toxic or hazardous reagent, ligand, acid, transition metal catalyst, additives/promoters and organic solvent, green Knoevenagel condensation and tandem Knoevenagel–Michael reactions have been successfully carried out by using *chickpea leaf exudates* as a naturally sourced Bronsted acid type bio-catalyst. The reaction proceeds in neat *chickpea leaf exudates* at room temperature in aqueous conditions in very short reaction times, and therefore, it is an evergreen and environmentally sound alternative to the existing protocols for benzopyran synthesis. In comparison to the conventional methods, this synthetic pathway complies with several key requirements of green chemistry principles such as the utilization of biodegradable catalyst obtained from renewable feedstock, auxiliary aqueous conditions, along with waste prevention. The same protocol was also extended to the synthesis of 2*H*-xanthene-1,8-diones by condensation of aromatic aldehydes with dimedone achieving excellent yields. Thus, the reported protocol offers an attractive option because of its ecological safety, environmental acceptance, sustainability, low-cost straightforward work-up procedure and with excellent values of green chemistry metrics as compared with other reported methods.

1. Introduction

While considering the increasing environmental pollution and its intensive impact on living systems, developing chemical processes using more environmentally acceptable chemicals, catalysts, solvents, atom-efficient methods and energy-efficient

technologies eliminating waste production as well as employing renewable raw materials are experiencing a profound challenge to meet sustainability criteria [1,2]. In addition, the environmental risks posed by the toxic and volatile organic solvents have become a major concern. The reason is that the organic transformations employ higher consumption of solvents than the reagents and the employed solvents are difficult to recycle [3]; for the process to be in line with the green chemistry principles, the first task is to replace the toxic catalysts and hazardous organic solvents with green ones.

Performing organic reactions in water has attracted much attention over the past decades due to its numerous advantages such as being considerably safe, nontoxic, environmentally friendly and cheap [4–7]. Nowadays, biosynthetic processes involving bio-based solvents or catalysts such as Cyrene [8,9], glucose [10], dihydrolevoglucosenone (Cyrene) [11] and agro-waste based solvents or catalysts like metal based [12,13], Kolakhar [14], WEB [15–17], H₂O₂ in WERSA [18], water extract of papaya bark [19], have received much attention as a viable alternative for the development of green protocols for organic transformations [20–25].

In this regard, naturally sourced material as part of the chemical process offer excellent alternatives to harmful and toxic chemicals in being more environmentally friendly technologies due to their ease of abundance in availability, ability to act as catalysts, low or negligible toxicity, biodegradability, and non-hazardous properties as compared to chemical catalysts. Again, due to the high natural abundance, their production is potentially less expensive. While taking into account these views in the light of green chemistry, the use of naturally occurring materials play an important role in the development of environmentally benign chemical processes. Different natural materials are used as solid support as well as catalysts in a large number of reactions promoting the formation of final products. Natural materials such as different plant parts such as fruits, root extracts [26–32], clays [33,34], zeolites [35,36] and enzymes [37,38] are used effectively in numerous chemical transformations.

Therefore, the aim of the present work is to explore the synthetic utility of naturally sourced acid catalyst in organic transformations. The catalytic medium is sourced directly from the *chickpea leaf exudates* (CLE). From literature records it is well-known that the *Cicer arietinum* locally known as chana (or harbhara) in India; it is a plant species commonly cultivated on a farm. Chickpea (*Cicer arietinum* L.) is a grain legume adapted to dry and cool environments in southern and western Asia, northern and eastern Africa, Central and South America, and southern Europe. India produces more than 65% of the world's chickpeas (FAO, 1994), and the crop is an important source of protein for the local population.

It has been reported that all external surfaces of the chickpea plants secrete organic acids [39,40], which consist almost exclusively of malic and succinic acids with small amount of quinic, citric and oxalic acids (figure 1) responsible for highly acidic character (1.1 pH) and has been correlated with reduced pod damage [41].

In view of these data and in continuation of our ongoing research in the development of green synthetic protocols [42–45], we thought that this amazing medium may serve as acidic catalyst, a better alternative to reported harmful corrosive acids for organic transformations.

Considering the significance of naturally sourced catalysts, in this work, we explore the catalytic activity of CLE as natural green acidic medium in the synthesis of benzopyranes starting from readily available dimedone and salicylaldehydes in presence of aqueous medium and at ambient temperature. To the best of our knowledge, the pronounced catalytic effect of CLE as natural acid catalyst is being described for the first time for organic synthesis.

Benzopyran derivatives act as anti-*Helicobacter pylori* agents [46], reductase inhibitors [47], selective thrombin (THR) inhibitors [48] PPAR α/γ agonists [49], potassium channel opener [50]. Benzopyrans also exhibit anti-inflammatory [51], insulin-sensitizing [52], antibacterial [53] and antimicrobial activities [54]. Recently, some benzopyran derivatives have been synthesized by the reaction of substituted salicylaldehydes with dimedone using different catalysts such as 2,4,6-trichloro-1,3,5-triazine [55], p-TSA [56], KF/Al₂O₃ [57], triethylbenzylammonium chloride [58], ionic liquid [59,60] and cellulose sulphonic acid [61].

Although a majority of these techniques were found to be effective in carrying out this cyclization, most of these protocols are associated with several drawbacks such as the use of expensive ligands, use of toxic or hazardous reagents, the requirement of a large amount of catalysts, use of transition metal complex catalysts often requiring activation by elevated temperatures, use of organometallic compounds, expensive and harsh reaction conditions, longer reaction times, use of organic solvents, and the generation of toxic by-products. Therefore, there is a continued interest in developing an efficient and safer protocol employing mild and green reaction conditions. The designer of a chemical process must choose from alternative raw materials, auxiliary materials such as solvents and catalysts, reaction

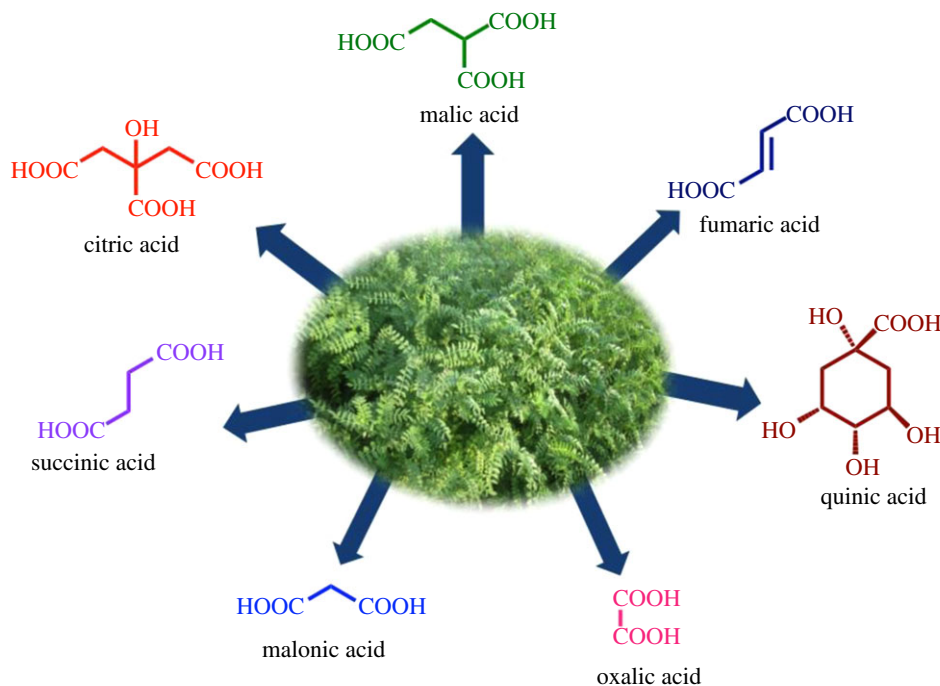


Figure 1. Structures of organic acids reported in CLE.

pathways and reaction conditions and these design choices can have a very significant impact on the overall environmental performance of a chemical process [62–65].

2. Experimental

2.1. Materials and methods

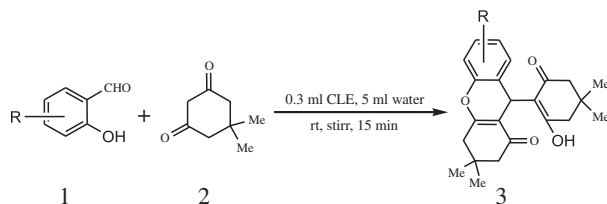
All commercial reagents and solvents were obtained from Sigma-Aldrich and used without purification. Melting points (mp) were determined with DBK-programmable melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded in potassium bromide pellets on a Bruker ALPHA FT-IR spectrometer. The ^1H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.5 MHz) were measured with Avance-300 instrument and chemical shifts (δ) are reported in parts per million in CDCl_3 as a solvent with tetramethylsilane (TMS) as an internal standard. Desired products were obtained only by stirring reaction mixture on magnetic stirrer (Remi, Model No. 10 ML DX Stirrer). The purity of products and completion of reaction was checked by thin layer chromatography (TLC) on Merck silica gel (60 F₂₅₄) plates. Spots on the TLC plates were visualized using ultraviolet (UV) light. Microanalyses of C, H and N were obtained on a Carl Erba EA 1108. All spectral data (FT-IR, ^1H and ^{13}C) are given in the electronic supplementary material. The pH of *Cicer arietinum* exudates and aqueous solutions of organic acids were measured using Pro-Lab 3000 laboratory pH-meter.

2.2. General procedure for collection of chickpea leaf exudates

For quantitative collection of catalyst, *chickpea* crops cultivated on various lands were selected and then exudates were collected manually using clean cotton napkin by absorption-wringing process. The turbid exudate collected was then purified by filtration through activated charcoal and obtained exudate was clear and denominated as CLE-catalyst. The collected catalyst was stored several days at 5°C and used as a catalyst for benzopyran synthesis.

2.3. Typical procedure for synthesis of 9-(2-hydroxy-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-3,3-dimethyl-2,3,4,9-tetrahydroxanthren-1-one (3a)

A 25 ml round bottom flask was charged with salicylaldehyde (1.0 mmol), 5,5-dimethyl 1,3-cyclohexanedione (2.0 mmol), CLE-catalyst (0.3 ml) and water (5 ml), and reaction mixture was stirred



Scheme 1. General reaction of salicylaldehyde with 1,3-dimedone.

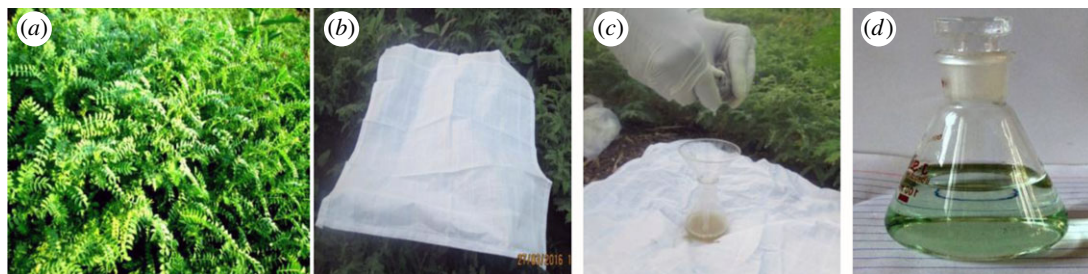


Figure 2. (a) Chickpea leaves, (b) absorption of exudates by cotton napkin, (c) wringing of exudates from cotton napkin, (d) collected clear CLE-catalyst after filtration.

at room temperature on magnetic stirrer till the completion of reaction as indicated by TLC (ethylacetate:hexane 4:6). The solid products was separated by simple filtration through a Buckner funnel, washed with cold water and recrystallized from 96% ethanol (5 ml). The identity of the compound was ascertained on the basis of FT-IR, ^1H NMR and ^{13}C NMR spectroscopy (figure 3a–c).

For the preparation of compounds 3a–s, 5a–c and 6a–k the same procedure was followed, by changing respective reactants, and synthesized compounds were characterized by physical and spectral analysis. The physical and spectroscopic data are consistent with the proposed structure and in harmony with the literature values.

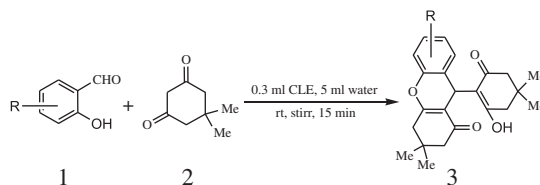
3. Results and discussion

A simple, green, efficient and convenient method for the synthesis of benzopyran derivatives 3a–s from different 2-hydroxy aldehydes and 1,3-dimedones is presented (scheme 1).

At the beginning, we focused our attention on quantitative collection of exudates and for this, growing period of chickpea plant from time of cultivation was considered. For this purpose different varieties of cultivated crops on various lands were selected and then exudates were collected manually using clean and soft cotton napkin by absorption-wringing process. The good quantity of exudates was obtained when it was collected from leaves of plants which were in the stage just before flowering (7–8 weeks from cultivation) at early morning (05.00 to 06.00). The turbid exudates obtained were then filtered through activated charcoal to remove impurities to get clear exudates (figure 2). The pH of exudates was measured using pH-meter and it was found to be 1.1, and therefore, it was used as Bronsted acid type bio-catalyst for this protocol.

The urgent need for the development of green and sustainable processes for the use of natural ‘feedstocks’ in chemical synthesis as an alternative to hazardous organic solvents or other metal-based catalysts is widely recognized [66–71] and the minimization of energy requirements in chemical processes presents an important principle in green chemistry [72].

Inspired by this fact and continuing our research with the aim of lowering the environmental impact of organic reactions, we turned our attention to *chickpea leaf exudates*, as easily available natural feedstock. To the best of our knowledge this is the first report of a simple protocol for the benzopyran synthesis at room temperature without using any transition metal catalyst, ligand, base, toxic or hazardous reagent, additives/promoters and organic solvent. In this communication, we report on the use of *chickpea leaf exudates* as an all-in-one mixture of solvent, catalyst, promoters etc. for heterocyclization.

Table 1. Optimization of reaction conditions for model reaction.^a

| entry | catalyst amount (ml) | solvent 5 ml | temp (°C) | time (min) | yield ^b (%) |
|-------|----------------------|--------------|-----------|------------|----------------------------------|
| 1 | 0.1 | — | RT | 60 | 10 |
| 2 | 0.2 | — | RT | 60 | 23 |
| 3 | 0.3 | — | RT | 60 | 30 |
| 4 | 0.4 | — | RT | 60 | 30 |
| 5 | 0.5 | — | RT | 60 | 30 |
| 6 | 1.0 | — | RT | 60 | 31 |
| 7 | 0.3 | water | RT | 15 | 96 |
| 8 | 0.3 | ethanol | RT | 15 | 94 (88, 34, 43, 29) ^c |
| 9 | 0.3 | water | RT | 15 | (65, 93, 90, 34) ^d |
| 10 | — | water | Rt | 15 | no reaction |

^aReaction conditions: salicylaldehyde **1** (1.0 mmol) and 1,3-dimedone **2** (2.0 mmol), catalyst, water (5 ml), room temperature.

^bIsolated yield based on salicylaldehyde.

^cYields with organic solvents: methanol, DCM, acetonitrile, toluene.

^dIsolated yield when 1, 3, 7 and 10 ml water was used.

To optimize the reaction conditions, 25 ml round bottom flask was charged with salicylaldehyde **1** (1.0 mmol), 1,3-dimedone **2** (2.0 mmol), *chickpea leaf exudates* (0.3 ml) and the reaction mixture was stirred at room temperature as a model reaction. After 1 h low yield (30%) of corresponding product was observed on TLC (table 1, entry 3). On increasing or decreasing catalytic amount (0.1–1 ml), no significant improvement in the result was obtained after prolonged reaction time (table 1, entries 1–6). We continued our efforts for improvement in the result; we decided to evaluate model reaction in different organic solvents as well as in aqueous medium. To our utmost expectations, the reaction to perform in aqueous media, the reaction proceeded very well, and 96% yield was obtained when *chickpea leaf exudates* (0.3 ml) were employed with water (5 ml) under identical conditions (table 1, entry 7). In order to check and verify further the effect of the organic solvent on the yield of the product, the model reaction was performed in methanol, ethanol, DCM, acetonitrile, toluene (table 1, entry 8) which afforded product in moderate yields. Furthermore, we also estimated the catalyst–solvent proportion for better conversion of reactants into products by changing catalyst–solvent ratio. The result showed that, 0.3:5 catalyst:solvent ratio was suitable (0.15 N, 0.045 mmol acid content determined by titration of catalyst with standard alkali) medium for smooth conversion of reactant to the product with respect to time and yield. From these results, it was also revealed that further decreasing or increasing the catalyst:solvent proportion reduces the yield of desired product dramatically (table 1, entry 9). Moreover, the catalyst-free condition was also examined; the result observed was viscous reaction system and no yield, which indicates that the role of catalyst is decisive for benzopyran **3** formation (table 1, entry 10).

On the completion of the reaction as monitored by TLC, the product was separated out by simple filtration, successively washed with cold water, and recrystallized from ethanol (96%) which afforded the corresponding product of high purity. Pure products obtained by recrystallization from ethanol were characterized by their physical constants and spectral techniques. In ¹H NMR spectrum (figure 3b) of the product of the model reaction (table 3, entry 1), observation of sharp singlet at δ 10.50 due to enolic proton, and at δ 4.65 corresponding to tertiary C-H proton as well as incorporation of 23 signals in ¹³C NMR spectrum (figure 3c) confirms its formation. Further, in FT-IR spectrum (figure 3a), observation of broad band due to enolic -OH at 3207 cm⁻¹ and at 1628 cm⁻¹ (two should be there) corresponding to α , β -unsaturated cyclic carbonyl group supports its formation.

As mentioned earlier, the acidic nature of *chickpea leaf exudates* due to presence of several organic acids. For comparison purpose, we carried out the model reaction under same reaction conditions using

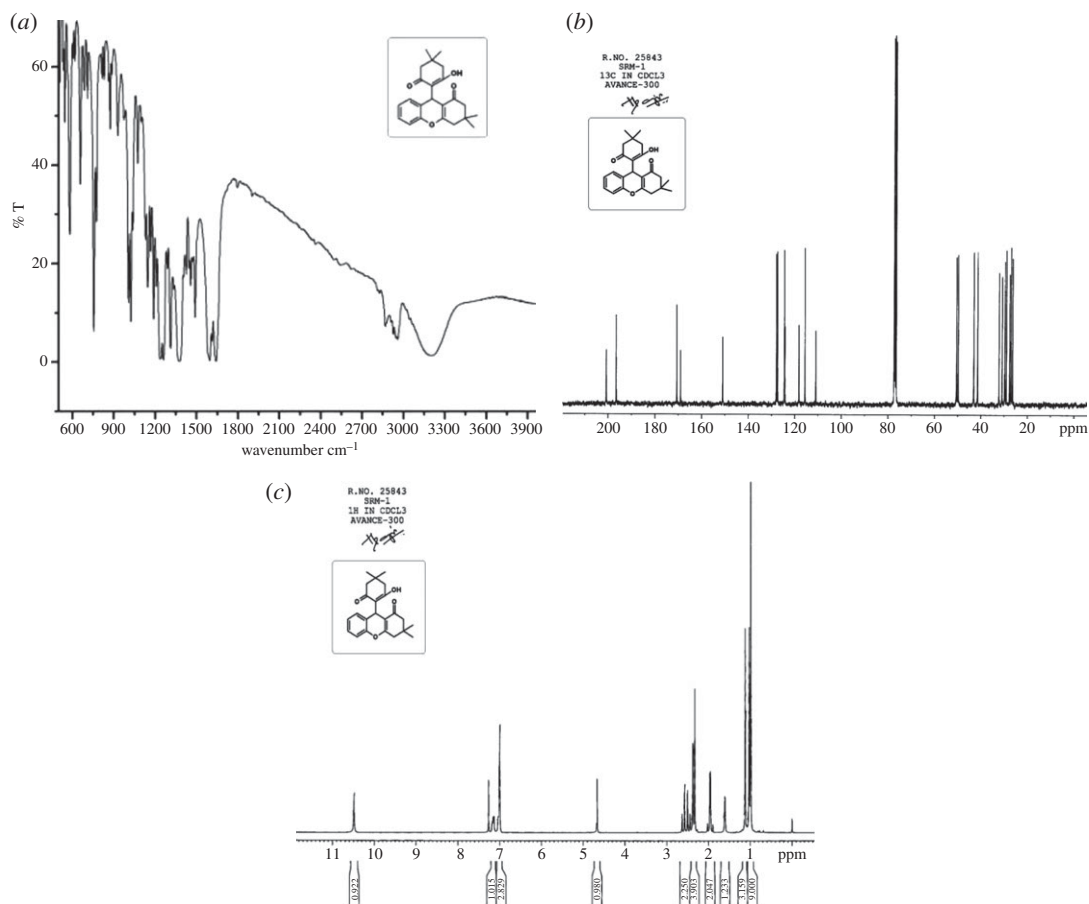
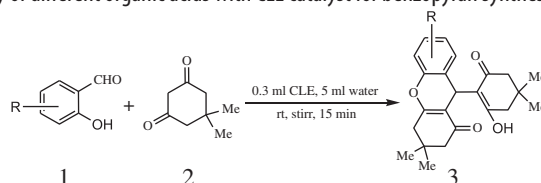


Figure 3. (a) FT-IR spectrum of compound 3a. (b) ^1H NMR (CDCl_3) spectrum of compound 3a. (c) ^{13}C NMR (CDCl_3) spectrum of compound 3a.

Table 2. Comparison of efficiency of different organic acids with CLE catalyst for benzopyran synthesis.^a



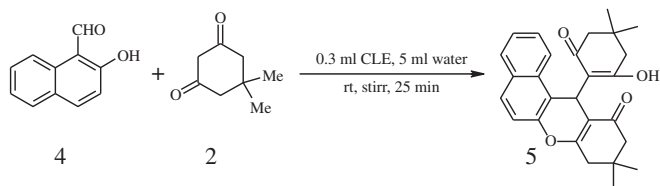
| entry | catalyst (ml) | pH ^b | time (min) | yield ^c (%) |
|-------|---------------|-----------------|------------|------------------------|
| 1 | succinic acid | 2.86 | 60 | n.a. |
| 2 | citric acid | 2.35 | 60 | n.a. |
| 3 | malic acid | 2.12 | 60 | 41 |
| 4 | oxalic acid | 1.95 | 60 | 56 |
| 5 | CLE | 1.10 | 15 | 96 |

^aReaction conditions: salicylaldehyde **1** (1.0 mmol) and 1,3-dimedone **2** (2.0 mmol), catalyst (0.3 ml), water (5 ml) room temperature.

^bpH of 5% aqueous solution of carboxylic acids.

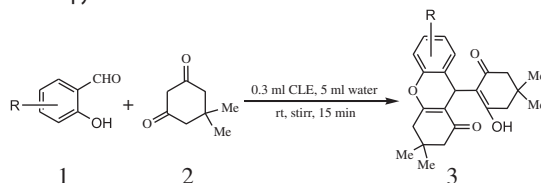
^cIsolated yield based on salicylaldehyde.

aqueous solution (5%) of various organic acids (table 2, entries 1–4). From results, it reveals that catalyst obtained from *chickpea plant* was found to be excellent with respect to time as well as yield of the product (table 2, entry 5) suggesting that the synergetic effect of several organic acids in *chickpea leaf exudates* showed superior catalytic activity for smooth and rapid conversion reactant into desired product with excellent yield in shorter reaction time.



Scheme 2. Reaction of 2-hydroxy naphthaldehyde with 1,3-dimedone.

Table 3. CLE-catalysed synthesis of benzopyrans.^a

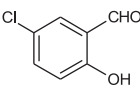
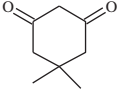
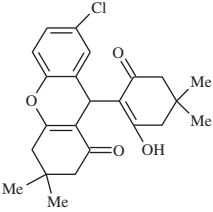
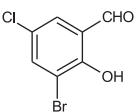
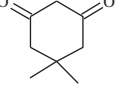
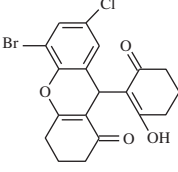
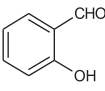
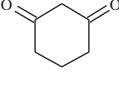
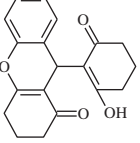
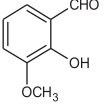
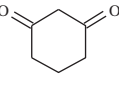
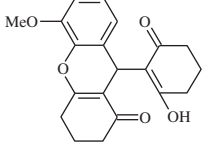
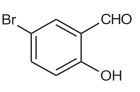
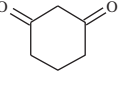
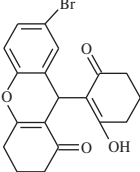
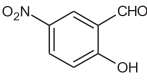
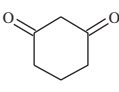
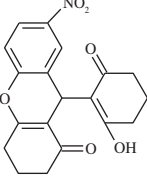
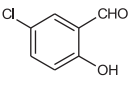
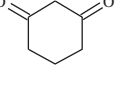
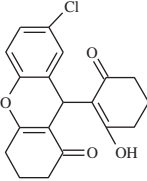


| entry | aldehydes | 1,3-diketones | products | time (min) | yield ^b (%) | M.P ^o C (observed) | M.P ^o C (reported) |
|-------|-----------|---------------|----------|------------|------------------------|-------------------------------|-------------------------------|
| 1 | | | | 15 | 96 | 210–212 | 211–214 [73] |
| 2 | | | | 25 | 89 | 228–230 | 229–231 [73] |
| 3 | | | | 20 | 92 | 252–254 | 251–253 [73] |
| 4 | | | | 15 | 94 | 204–205 | 203–205 [73] |

(Continued.)

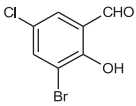
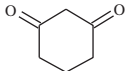
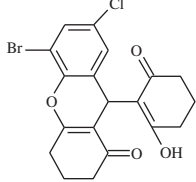

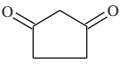
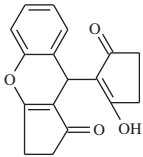
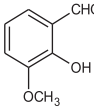
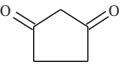
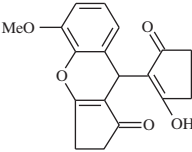
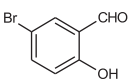
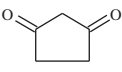
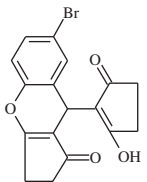
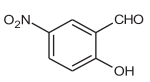
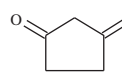
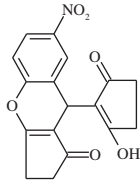
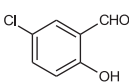
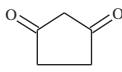
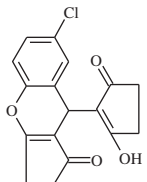
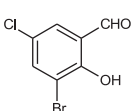
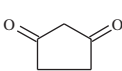
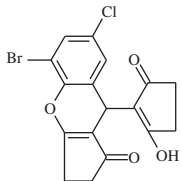
After optimization of reaction condition, the condensation reactions were carried out in *chickpea leaf exudates* (0.3 ml) at ambient temperature using a series of structurally diverse salicylaldehydes with 1,3-ketones (scheme 2, table 3). On the completion of reactions as monitored by TLC, the reaction mixtures were filtered to isolate products and purified by recrystallization from ethanol (96%). The reactions of

Table 3. (Continued.)

| entry | aldehydes | 1,3-diketones | products | time (min) | yield ^b (%) | M.P.°C (observed) | M.P.°C (reported) |
|-------|---|---|---|------------|------------------------|-------------------|-------------------|
| 5 |  |  |  3e | 20 | 92 | 232–234 | 236–238 [73] |
| 6 |  |  |  3f | 25 | 84 | 241–243 | 240–242 [45] |
| 7 |  |  |  3g | 25 | 90 | 244–246 | 245–247 [55] |
| 8 |  |  |  3h | 25 | 87 | 238–240 | 238–240 [45] |
| 9 |  |  |  3i | 25 | 88 | 235–236 | 234–236 [55] |
| 10 |  |  |  3j | 20 | 93 | 245–246 | 242–244 [73] |
| 11 |  |  |  3k | 25 | 92 | 245–247 | 244–246 [55] |

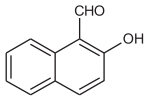
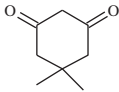
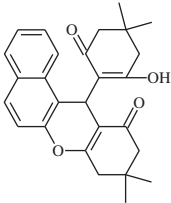
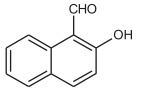
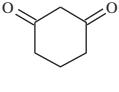
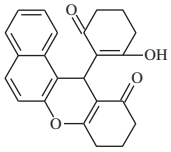
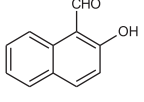
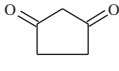
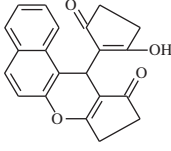
(Continued.)

Table 3. (Continued.)

| entry | aldehydes | 1,3-diketones | products | time (min) | yield ^b (%) | M.P.°C (observed) | M.P.°C (reported) |
|-------|---|---|---|------------|------------------------|-------------------|-------------------|
| 12 |  |  |  3l | 20 | 91 | 238–240 | 238–240 [45] |
| 13 |  |  |  3n | 25 | 89 | 253–255 | 254–255 [59] |
| 14 |  |  |  3o | 30 | 87 | 255–257 | 255–257 [59] |
| 15 |  |  |  3p | 30 | 92 | 273–275 | 272–275 [59] |
| 16 |  |  |  3q | 25 | 93 | 268–270 | 266–268 [59] |
| 17 |  |  |  3r | 30 | 91 | 271–273 | 271–273 [59] |
| 18 |  |  |  3s | 30 | 84 | 278–281 | 277–280 [45] |

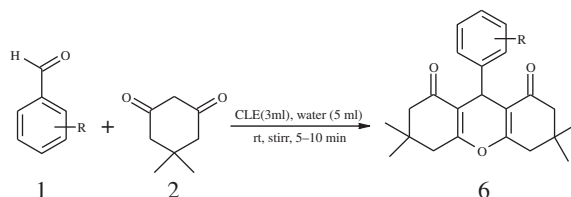
(Continued.)

Table 3. (Continued.)

| entry | aldehydes | 1,3-diketones | products | time (min) | yield ^b (%) | M.P ^o C (observed) | M.P ^o C (reported) |
|-------|---|---|---|------------|------------------------|-------------------------------|-------------------------------|
| 19 |  |  |  5a | 30 | 92 | 245–248 | 246–248 [55] |
| 20 |  |  |  5b | 35 | 91 | 216–218 | 216–218 [55] |
| 21 |  |  |  5c | 35 | 90 | 269–271 | 270–271 [45] |

^aAll reactions were performed by taking salicylaldehydes/2-hydroxy naphthaldehyde (1.0 mmol), 1,3-diketones (2.0 mmol) and CLE-catalyst (0.3 ml), water (5 ml) room temperature.

^bIsolated yield.



Scheme 3. Reaction of aryl aldehydes with 1,3-diketone.

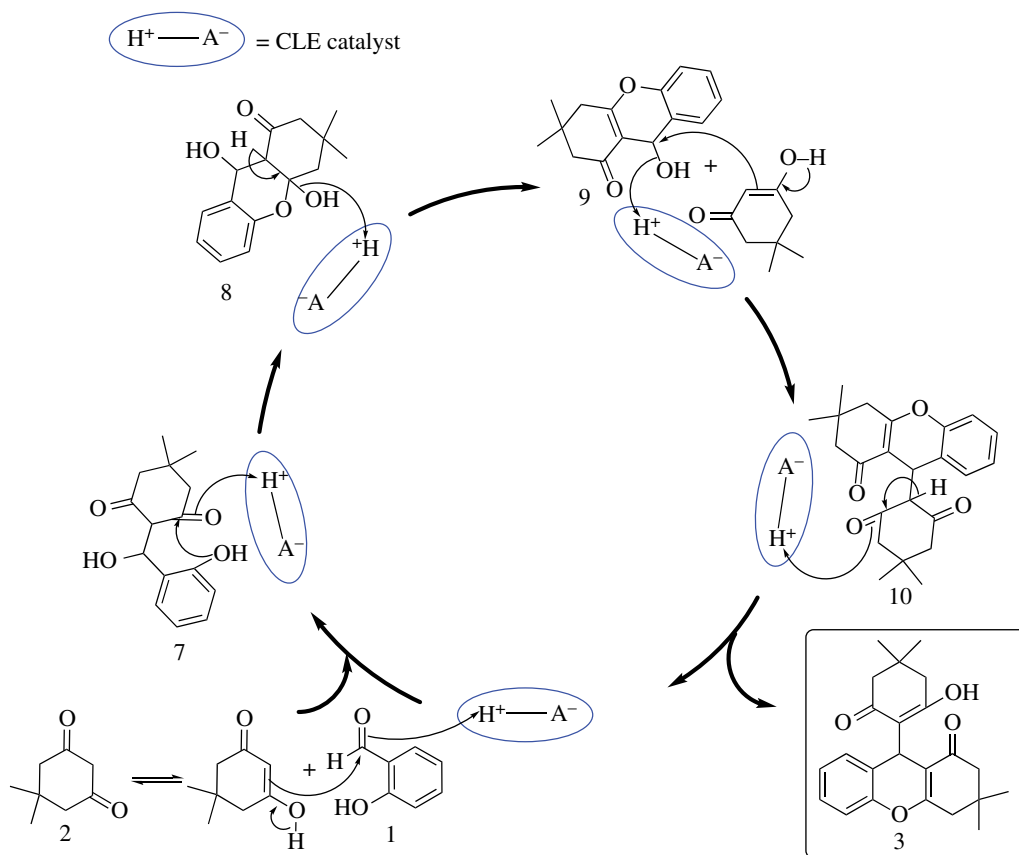
salicylaldehydes, bearing electron-donating ($-\text{OCH}_3$) as well as electron-withdrawing groups ($-\text{NO}_2$, $-\text{Cl}$, $-\text{Br}$) underwent successfully.

Inspired by these tempting results obtained for cyclocondensation of benzopyran, we extended the same protocol for treating various 1,3-diketones with 2-hydroxy naphthaldehyde (table 3, entry 19–21) and we found that these substrates also worked very efficiently under this catalytic system. As discussed before, in the absence of the catalyst, the reaction proceeded sluggishly, which explains the role of catalytic activity of CLE in product formation.

Furthermore, when aromatic aldehydes other than 2-hydroxy benzaldehydes were reacted with dimedone in 1:2 molar proportion for synthesis of 9-aryl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-diones under similar reaction conditions (scheme 3), excellent results were obtained in shorter reaction time than previously reported methods. The result of the study is incorporated in table 4.

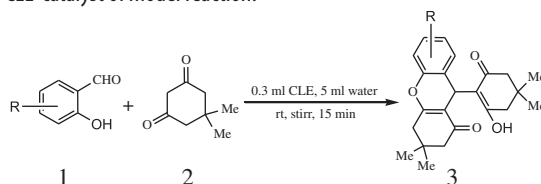
3.1. Recycle of catalyst

In order to investigate the possibility of recycling this CLE-catalyst, a recycling experiment was conducted using the above-mentioned model reaction (scheme 1). After the separation of the products (see Experimental), the catalyst was treated with activated charcoal (0.05 g) and, after filtration, was used in the next run for synthesis of 3a. Synthesis was performed seven times and the influence of recycling



Scheme 4. Plausible mechanism for the reaction between salicylaldehyde and 1,3-dimedone catalysed by CLE-catalyst ($\text{H}^+ - \text{A}^-$).

Table 4. Recyclable properties of CLE-catalyst of model reaction.

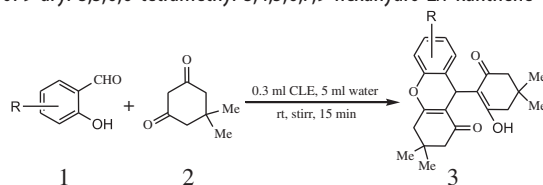


| | | | | | | | |
|---------|----|----|----|----|----|----|----|
| runs | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| yield % | 96 | 96 | 95 | 93 | 92 | 82 | 78 |

catalyst on yields of 3a is shown in table 4. As can be seen, the CLE as catalyst for pseudo multi-component reaction could be reused at least five times without the apparent loss of catalytic activity, clearly proving its recyclability and reusability. While in sixth and seventh run yield of model reaction was significantly decreased to 82 and 78% respectively.

Although diverse approaches towards the synthesis of these derivatives have been developed, use of non-hazardous, biodegradable, natural bio-catalyst is the most elegant strategy. Initially acid-catalysed Knoevenagel condensation between 2-hydroxybenzaldehyde and 1,3-diketone proceeded rapidly within 5 min, which were converted to white product 9, which was further reacted with another molecule of 1,3-diketone with shifting of equilibrium towards formation of desired product 3 (scheme 4) with excellent yield.

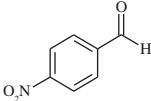
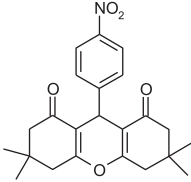
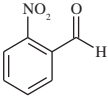
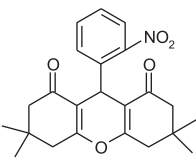
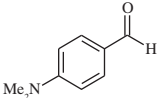
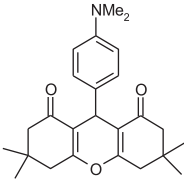
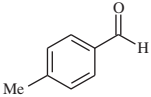
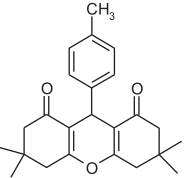
Comparison of the experimental results and post-experimental analysis of green parameters using CLE-catalyst with some other reported catalysts for benzopyran synthesis are shown in table 5. It furnishes high reaction yield, takes shorter reaction time, and small quantity of this inexpensive and readily available catalyst is sufficient to get good yield of expected products.

Table 5. CLE-catalysed synthesis of 9-aryl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xantheno-1,8-diones.^a

| entry | aldehydes | product | time (min) | yield ^b (%) | melting point (°C) | |
|-------|-----------|---------|------------|------------------------|--------------------|--------------|
| | | | | | found | reported |
| 1 | | | 7 | 94 | 201–204 | 200–202 [74] |
| 2 | | | 7 | 94 | 248–250 | 245–250 [74] |
| 3 | | | 10 | 96 | 240–242 | 241–243 [74] |
| 4 | | | 5 | 95 | 228–230 | 228–230 [74] |
| 5 | | | 5 | 95 | 223–225 | 225–227 [74] |
| 6 | | | 10 | 93 | 226–228 | 226–228 [74] |

(Continued.)

Table 5. (Continued.)

| entry | aldehydes | product | time (min) | yield ^b (%) | melting point (°C) | |
|-------|--|--|------------|------------------------|--------------------|--------------|
| | | | | | found | reported |
| 7 |  |  6g | 5 | 99 | 222–223 | 222–224 [74] |
| 8 |  |  6h | 5 | 95 | 258–260 | 258–262 [74] |
| 9 |  |  6i | 7 | 96 | 224–225 | 222–225 [74] |
| 10 |  |  6j | 7 | 91 | 211–213 | 210–212 [74] |

^aAll reactions were performed by taking aryl aldehydes (1.0 mmol), dimedone (2.0 mmol) and CLE-catalyst (0.3 ml), water (5 ml) room temperature.

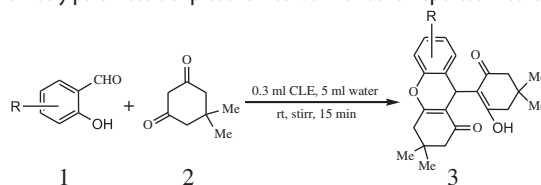
^bIsolated yield.

3.2. Post-synthesis analysis

Currently green chemistry metrics and scalability are used to evaluate environmental acceptability and applicability of novel protocols in organic transformations. To address this issue, we calculated green parameters such as atom economy (AE), E-factor, EcoScale and reaction mass efficiency (RME), and these calculated results were compared with results of reported methods. As demonstrated in table 5, the calculated results show that the presented protocol is the greenest among the previously reported methods with respect to green environmental parameters for synthesis of 3a derivative (table 6).

4. Conclusion

In conclusion, we have an elegant, highly efficient and straightforward bio-organic approach for benzopyran synthesis via Knoevenagel condensation and tandem Knoevenagel–Michael reaction which represents eco-friendly and environmentally benign system. In this article we investigated the synergistic effect of naturally sourced carboxylic acids in heterocyclization using the natural feedstock *chickpea leaf exudates* for the wide range of organic compounds. Our method is flexible, having simple work-up, requires no chromatographic purification, the excellent yields in relatively short-reaction times and at the same time the recyclability and reusability of catalyst, and it can be suitable for one-pot conversion of similar substrates into corresponding products. The use of the low-cost simple-to-handle, biodegradable, naturally sourced catalyst in replacement of toxic synthetic reagents is a promising alternative for the

Table 6. Comparisons of green chemistry parameters of present method with other reported methods used for synthesis of 3a.

| entry | catalyst | reaction conditions | | time min/h | yield (%) | RME ^a | E-factor (g g ⁻¹) ^b | Eco Scale ^c | ref. |
|-------|-----------------------------------|---------------------|-----------|---------------|--------------|------------------|---|------------------------|------|
| | | solvent (ml) | temp (°C) | | | | | | |
| 1 | [bmim]PF ₆ -glycine | IL | 25 | 3.5 h | 82 | 0.374 | 0.215 | 84.00 | [60] |
| 2 | p-TSA | water | 90 | 30 min | 83 | 0.379 | 0.200 | 80.50 | [56] |
| 3 | [BMim]Br | water | 50 | 15 h | 76 | 0.347 | 0.311 | 76.00 | [59] |
| 4 | TEBA | water | 90 | 05 h | 86 | 0.388 | 0.776 | 81.00 | [58] |
| 5 | cellulose sulfuric acid | solvent free | R.T. | 30 min | 96 | 0.437 | 0.875 | 89.00 | [61] |
| 6 | 2,4,6-trichloro-1,3,5-triazine | H ₂ O | 120 | 2.5 h | 93 | 0.425 | 0.070 | 89.50 | [55] |
| 7 | KF/Al ₂ O ₃ | EtOH | 80 | 1–3 h | 83 | 0.377 | 0.207 | 79.50 | [57] |
| 8 | CLE ^d | water | rt | 15 min | 95 | 0.432 | 0.051 | 96.5 | — |

Equations used for calculations of green parameters:

^aRME = mass of product/sum of mass of reactants × 100,

^bE-factor = mass of total waste/mass of product,

^cEcoScale = 100-sum of individual penalties,

^dPresent method.

organic transformations. Usability of the catalyst in aqueous medium caters to a more ‘green’ and eco-friendly solution towards benzopyran formation. The catalyst system developed represents the most efficient green protocol so far toward the heterocyclization at room temperature and with excellent values of green chemistry parameters (RME, E-factor, EcoScale) as compared with reported methods, which provides efficient and safe catalyst to the synthetic chemistry community.

Research ethics. The world-wide cultivation and productivity of chickpea crop is very high, as it is used for human consumption (vegetable) and animals feed. The catalyst was easily collected for this study from own or public farm without permit. No special permission or ‘Animal Care Protocol’ was required. Study materials should be removed judiciously, mitigating damage to plant and no irrevocable harm. There is no need to deposit in a recognized and publicly accessible collection. No received ethical approval from a local ethics committee.

Data accessibility. The datasets supporting this article have been uploaded as part of the electronic supplementary material.

Authors’ contributions. S.P. and S.S. conceived the experiments and contributed equally. S.M. and S.D. performed the collection field material, characterization of the catalyst and molecular laboratory work. S.P. and S.S. designed and directed the study and also helped draft the manuscript. All authors gave final approval for publication.

Competing interests. We declare we have no competing interests.

Funding. We received no funding for this study.

Acknowledgements. We wish to thank IICT Hyderabad, India for providing necessary instrumental facilities during spectral analysis.

References

- Anastas P, Warner J. 1998 *Green chemistry: theory and practice*, p. 30. New York, NY: Oxford University Press.
- Clark JH. 1999 Green chemistry: challenges and opportunities. *Green Chem.* **1**, 1–8. (doi:10.1039/A807961G)
- Sheldon RA. 2005 Green solvents for sustainable organic synthesis: state of art. *Green Chem.* **7**, 267–278. (doi:10.1039/b418069k)
- Breslow R. 1991 Hydrophobic effects on simple organic reactions in water. *Acc. Chem. Res.* **24**, 159–164. (doi:10.1021/ar00006a001)
- Engberts JBFN, Blandamer MJ. 2001 Understanding organic reactions in water: from hydrophobic encounters to surfactant aggregates. *Chem. Commun.* **364**, 1701–1708. (doi:10.1039/B104537G)
- Kobayashi S, Manabe K. 2000 Green Lewis acid catalysis in organic synthesis. *Pure Appl. Chem.* **72**, 1373–1380. (doi:10.1351/pac200072071373)
- Lindstro UM. 2002 Stereoselective organic reactions in water. *Chem. Rev.* **102**, 2751–2772. (doi:10.1021/cr010122p)
- Mistry L, Mapesa K, Bousfield TW, Camp JE. 2017 Synthesis of ureas in the bio-alternative solvent Cyrene. *Green Chem.* **19**, 2123–2128. (doi:10.1039/c7gc00908a)

9. Wilson KL, Kennedy AR, Murray J, Greatrex B, Jamieson C, Watson AJB. 2016 Scope and limitations of a DMF bio-alternative within Sonogashira cross-coupling and Cacchi-type annulation. *Beilstein J. Org. Chem.* **12**, 2005–2011. (doi:10.3762/bjoc.12.187)
10. Camp JE, Dunsford JJ, Cannons EP, Restorick WJ, Gadzhieva A, Fay MW, Smith RJ. 2014 Glucose-derived palladium(0) nanoparticles as in situ-formed catalysts for Suzuki-Miyaura cross-coupling reactions in isopropanol. *ACS Sustainable Chem. Eng.* **2**, 500–505. (doi:10.1021/sc400410v)
11. Sherwood J *et al.* 2014 Dihydrolevoglucosenone (Cyrene) as a bio-based alternative for dipolar aprotic solvents. *Chem. Comm.* **50**, 9650–9652. (doi:10.1039/c4cc04133j)
12. Comerford JW, Ingram IDV, North M, Wu X. 2015 Cyclic carbonates containing five-membered rings. *Green Chem.* **17**, 1966–1987.
13. Jenkins BM, Bakker RR, Wei JB. 1996 On the properties of washed straw. *Biomass Bioenergy*, **4**, 177–200. (doi:10.1016/0961-9534(95)00058-5)
14. Deka DC, Taukdar NN. 2007 Chemical and spectroscopic investigation of Kolakhar and its commercial importance. *Indian J. Tradit. Know.* **6**, 72–78.
15. Konwar M, Ali AA, Sarma D. 2016 A green protocol for peptide bond formation in WEB. *Tetrahedron Lett.* **57**, 2283–2285. (doi:10.1016/j.tetlet.2016.04.041)
16. Surmeni N, Barua NC, Saikia B. 2016 Application of natural feedstock extract: the Henry reaction. *Tetrahedron Lett.* **57**, 2814–2817. (doi:10.1016/j.tetlet.2016.05.048)
17. Dewan A, Sarmah M, Bora U, Thakur AJ. 2016 A green protocol for ligand, copper and base free Sonogashira cross-coupling reaction. *Tetrahedron Lett.* **57**, 3760–3763. (doi:10.1016/j.tetlet.2016.07.021)
18. Saikia E, Bora SJ, Chetia B. 2015 H₂O₂ in WERSA: an efficient green protocol for ipso-hydroxylation of aryl/heteroarylboronic acid. *RSC Adv.* **5**, 102723–102726. (doi:10.1039/CS9A21354A)
19. Sarmah M, Dewan A, Mondal M, Thakur AJ, Bora U. 2016 Analysis of water extract of waste papaya bark ash and its implications as *in situ* base in ligandless recyclable Suzuki-Miyaura coupling reaction. *Tetrahedron Lett.* **57**, 3760–3763.
20. Li M, Chen C, He F, Gu Y. 2010 Multicomponent reactions of 1,3-cyclohexanediones and formaldehyde in glycerol: stabilization of paraformaldehyde in glycerol resulted from using dimedone as substrate. *Adv. Synth. Catal.* **352**, 519–530. (doi:10.1002/adsc.200900770)
21. Alonso DM, Bond JQ, Dumesic JA. 2010 Catalytic conversion of biomass to biofuels. *Green Chem.* **12**, 1493–1513. (doi:10.1039/C004654J)
22. Gu Y, Jérôme F. 2013 Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry. *Chem. Soc. Rev.* **42**, 9550–9570. (doi:10.1039/c3cs60241a)
23. Sun S, Bai R, Gu Y. 2014 From waste biomass to solid support: lignosulfonate as a cost-effective and renewable supporting material for catalysis. *Chem. Eur. J.* **20**, 549–558. (doi:10.1002/chem.201303364)
24. He F, Li P, Gu Y, Li G. 2009 Glycerol as a promoting medium for electrophilic activation of aldehydes: catalyst-free synthesis of di(indolyl)methanes, xanthen-1,8(2H)-diones and 1-oxo-hexahydro-xanthenes. *Green Chem.* **11**, 1768–1773.
25. Zhou B, Yang J, Li M, Gu Y. 2011 Gluconic acid aqueous solution as a sustainable and recyclable promoting medium for organic reactions. *Green Chem.* **13**, 2204–2211. (doi:10.1039/c1gc15411g)
26. Ferraz HMC, Bianco GG, Bombonato FI, Andrade LH. 2008 Bioreduction of substituted tetralones promoted by *Daucus carota* root. *Quim. Nova.* **31**, 813–817. (doi:10.1590/S0100-40422008000400020)
27. Lakshmi CS, Reddy GR, Rao AB. 2011 Asymmetric reduction of heteroaryl methyl ketones using *Daucus carota*. *Green Sus. Chem.* **1**, 117. (doi:10.4236/gsc.2011.14019)
28. Li F, Cui J, Zhang R, Qian X, Xiao Y. 2005 Highly chemoselective reduction of aromatic nitro compounds to the corresponding hydroxylamines catalysed by plant cells from a grape (*Vitis vinifera* L.). *Chem. Commun.* **14**, 1901–1903. (doi:10.1039/b418675c)
29. Bertini LM, Lemos TLG, Alves LA, Jose FQ, Monte Q, Marcos CF, de Oliveira F, Conceição M. 2012 Soybean (*Glycine max*) as a versatile biocatalyst for organic synthesis. *African J. Biotech.* **11**, 7766–7770. (doi:10.5897/AJB11.2400)
30. Deshmukh MB, Patil SS, Jadhav SD, Pawar PB. 2012 Green approach for Knoevenagel condensation of aromatic aldehydes with active methylene group. *Synth. Commun.* **42**, 1177–1183. (doi:10.1080/00397911.2010.537423)
31. Fonseca AM, Monte FJO, Oliveira MCF, Mattos MC. 2009 *Zingiber officinale* (GINGER) as an enzyme source for the reduction of carbonyl compounds. *J. Mol. Catal. B Enzymatic* **57**, 78. (doi:10.1016/j.molcatb.2008.06.022)
32. Jayachandran B, Phukan P, Daniel T, Sudalai A. 2006 Natural kaolinitic clay: a remarkable catalyst for highly regioselective chlorination of arenes with Cl₂ and SOCl₂. *Indian J. Chem. Sect. B* **45B**, 972.
33. Khezri SH, Mohammad-Vali M, Eftekhari-Sis B, Hashemi MM, Baniasadi MH. 2007 The efficient synthesis of carbon-carbon double bonds via Knoevenagel condensation using red mud packed in a column. *Green. Chem. Lett. Rev.* **1**, 61–64. (doi:10.1080/17518250701787830)
34. Gadekar LS, Katkar SS, Mane SR, Arbad BR, Lande MK. 2009 Scolecite catalyzed facile and efficient synthesis of polyhydroquinoline derivatives through Hantzsch multi-component condensation. *Bull. Korean Chem. Soc.* **30**, 2532–2534. (doi:10.5012/bkcs.2009.30.11.2532)
35. Habibi D, Nasrollahzadeh M, Kamali TA. 2011 Green synthesis of the 1-substituted 1H-1,2,3,4-tetrazoles by application of the natrolite zeolite as a new and reusable heterogeneous catalyst. *Green Chem.* **13**, 3499–3504. (doi:10.1039/C1GC15245A)
36. Borse BN, Shukla SR, Sonawane YA. 2012 Simple, efficient, and green method for synthesis of trisubstituted electrophilic alkenes using lipase as a biocatalyst. *Synth. Commun.* **42**, 412–423. (doi:10.1080/00397911.2010.525334)
37. Xie BH, Li W, Liu Y, Guan Z. 2012 The enzymatic asymmetric aldol reaction using acidic protease from *Aspergillus ussami*. *Tetrahedron* **68**, 3160–3164. (doi:10.1016/j.tet.2012.02.056)
38. Tang RC, Guan Z, He YH, Zhu W. 2010 Enzyme-catalyzed Henry (*nitroaldol*) reaction. *J. Mol. Catal. B: Enzymatic*. **63**, 62–67. (doi:10.1016/j.molcatb.2009.12.005)
39. Ohwaki Y, Hirata H. 1992 Differences in carboxylic acid exudation among p-starved leguminous crops in relation to carboxylic acid contents in plant tissues and phospholipid level in roots. *Soil. Sci. Plant Nutr.* **38**, 235–243. (doi:10.1080/00380768.1992.10416486)
40. Cagiran MI, Tokar C, Karhan M, Aksu M, Ulger S, Canci H. 2011 Assessment of endogenous organic acid levels in ascochyta blight [*Ascochyta rabiei* (Pass.) Labr.] susceptible and resistant chickpeas (*Cicer arietinum* L.). *Turkish J. Field Crop.* **16**, 121–124.
41. Banerjee A, Mukherjee KA. 1981 Chemical aspects of santalin as a histological stain. *Stain Technol.* **56**, 83–85. (doi:10.3109/10520298109067286)
42. Patil SS, Jadhav SD, Deshmukh MB. 2013 Calcined eggshell (CES): an efficient natural catalyst for Knoevenagel condensation under aqueous condition. *J. Chem. Sci.* **125**, 851–857. (doi:10.1007/s12039-013-0443-5)
43. Shinde S, Damate S, Murbale S, Patil M, Patil SS. 2017 *Aegle marmelos* in heterocyclization: greener, highly efficient, one-pot three-component protocol for the synthesis of highly functionalized 4H-benzochromenes and 4H-chromenes. *RSC Adv.* **7**, 7315. (doi:10.1039/c6ra28779d)
44. Patil SS, Jadhav SD, Deshmukh MB. 2013 Pineapple juice as a natural catalyst: an excellent catalyst for Biginelli reaction. *Indian J. Chem. Sec. B* **52B**, 1172–1175.
45. Murbale ST, Jadhav SD, Deshmukh MB, Patil SS. 2015 Bronsted acid-type biosurfactant for heterocyclization: a green protocol for benzopyran synthesis. *RSC Adv.* **5**, 84610. (doi:10.1039/c5ra13652k)
46. Chimenti F *et al.* 2006 Synthesis and *in vitro* selective anti-*Helicobacter pylori* activity of N-substituted-2-oxo-2H-1-benzopyran-3-carboxamides. *Eur. J. Med. Chem.* **41**, 208–212. (doi:10.1016/j.ejmech.2005.11.001)
47. Chibale K, Visser M, Schalkwyk VD, Smith JP, Saravanamuthu A, Fairlamb HA. 2003 Exploring the potential of xanthen derivatives as trypanothione reductase inhibitors and chloroquine potentiating agents. *Tetrahedron* **59**, 2289–2296. (doi:10.1016/S0040-4020(03)00240-0)
48. Frederick R, Robert S, Charlier CJ, Masereel WB, Pochet L. 2007 Mechanism-based thrombin inhibitors: design, synthesis, and molecular docking of a new selective 2-oxo-2H-1-benzopyran Derivative. *J. Med. Chem.* **50**, 3645–3650. (doi:10.1021/jm061368v)
49. Yu J, Tang L, Tang Y, Ji R. 2008 Synthesis and evaluation of a series of benzopyran derivatives as PPAR alpha/gamma agonists. *Eur. J. Med. Chem.* **43**, 2428–2435. (doi:10.1016/j.ejmech.2008.01.029)
50. Gadwood RC, Kamdar BV, Dubray LAC, Wolfe ML, Smith MP, Watt W, Mizsak SA, Groppit VE. 1993 Synthesis and biological activity of spirocyclic benzopyran imidazolone potassium channel openers. *J. Med. Chem.* **36**, 1480–1487. (doi:10.1021/jm00062a022)
51. Poupepin JP, Saint-Rut G, Fussard-Blanpin O, Narcisse G, Uchida-Ernouf G, Lakroix R. 1978 Synthesis and antiinflammatory properties of bis

- (2-hydroxy-1-naphthyl)methane derivatives I. *Eur. J. Med. Chem.* **13**, 67–71.
52. Tang L, Yu J, Leng Y, Feng Y, Yang Y, Ji R. 2003 Synthesis and insulin-sensitizing activity of a novel kind of benzopyran derivative. *Bioorg. Med. Chem. Lett.* **13**, 3437–3440. (doi:10.1016/S0960-894X(03)00734-0)
 53. Okazaki H, Kishi T, Beppu T, Arima K. 1975 A new antibiotic, baciphelacin. *J. Antibiot.* **28**, 717–719. (doi:10.7164/antibiotics.28.717)
 54. Ei-Shaer HM, Foltinova P, Margita L, Chovancova J, Stankovicova H. 1998 Synthesis, antimicrobial activity and bleaching effect of some reaction products of 4-oxo-4H-benzopyran-3-carboxaldehydes with aminobenzothiazoles and hydrazides. *Farmaco* **53**, 224–232. (doi:10.1016/S0014-827X(98)00015-9)
 55. Zhang P, Yu YD, Zhang ZH. 2008 2,4,6-Trichloro-1,3,5-triazine as an efficient catalyst for synthesis of benzopyran derivatives under solvent-free conditions. *Synth. Commun.* **38**, 4474–4479. (doi:10.1080/00397910802369604)
 56. Nagarapu L, Karnakanti S, Bantu R, Sridhar B. 2012 Efficient, high-yield protocol for the one-pot synthesis of benzopyran derivatives catalyzed by p-TSA in aqueous media. *Synth. Commun.* **42**, 967–974. (doi:10.1080/00397911.2010.533804)
 57. Li YL, Chen H, Zeng ZS, Wang XS, Shi DQ, Tu SJ. 2005 Synthesis of 4-aryl-9,10-dihydronaphtho[2,1-b]-4H-pyran derivatives catalyzed by KF/Al₂O₃. *Chin. J. Org. Chem.* **25**, 846–849.
 58. Wang XS, Shi DQ, Li YL, Chen H, Wei XY, Zong ZM. 2005 A clean synthesis of 1-oxo-hexahydroxanthene derivatives in aqueous media catalyzed by TEBA. *Synth. Commun.* **35**, 97–104. (doi:10.1081/SCC-200046510)
 59. Sheng J, Zhang MM, Jiang H, Wang XS. 2012 A green method for the synthesis of cyclopenta[b]chromen-1(9H)-one. *J. Chin. Chem. Soc.* **59**, 650–654. (doi:10.1002/jccs.201100374)
 60. Kidwai M, Singhal K, Kukreja S. 2008 Glycine-promoted rapid synthesis of novel xanthene derivatives in ionic liquid. *Can. J. Chem.* **86**, 799–802. (doi:10.1139/v08-069)
 61. Kuarm BS, Madhav JV, Laxmi SV, Rajitha B, Reddy YT, Reddy PN, Crooks PA. 2011 Cellulose sulfuric acid: an efficient biodegradable and recyclable solid acid catalyst for the synthesis of 1-oxo-hexahydroxanthene. *Synth. Commun.* **41**, 1719–1724. (doi:10.1080/00397911.2010.492076)
 62. Anastas P, Farris C. 1994 *Benign by design: alternative synthetic design for pollution prevention*. Washington, DC: American Chemical Society.
 63. Li C-J. 2005 Organic reactions in aqueous media with a focus on carbon-carbon bond formations: a decade update. *Chem. Rev.* **105**, 3095–3165. (doi:10.1021/cr030009u)
 64. Horvath IT, Anastas PT. 2007 Innovations and green chemistry. *Chem. Rev.* **107**, 2169–2173. (doi:10.1021/cr078380v)
 65. Li CJ. 1993 Organic reactions in aqueous media—with a focus on carbon-carbon bond formation. *Chem. Rev.* **93**, 2023–2035. (doi:10.1021/cr00022a004)
 66. Anastas PT, Warner JC. 1998 *Principles of green chemistry: theory and practice*. New York, NY: Oxford University Press.
 67. Sheldon RA. 2005 Green solvents for sustainable organic synthesis: state of the art. *Green Chem.* **7**, 267–278. (doi:10.1039/B418069K)
 68. Boruah PR, Ali AA, Chetia M, Saikia B, Sarma D. 2015 Pd(OAc)₂ in WERSA: a novel green catalytic system for Suzuki–Miyaura cross-coupling reactions at room temperature. *Chem. Commun.* **51**, 11489–11492. (doi:10.1039/C5CC04561D)
 69. Keith LH, Gron LU, Young JL. 2007 Green analytical methodologies. *Chem. Rev.* **107**, 2695–2708. (doi:10.1021/cr068359e)
 70. Anastas PT. 1999 Green chemistry and the role of analytical methodology development. *Crit. Rev. Anal. Chem.* **29**, 167–175. (doi:10.1080/10408349891199356)
 71. Sheldon RA. 2014 Green and sustainable manufacture of chemicals from biomass: state of the art. *Green Chem.* **6**, 950–963. (doi:10.1039/C3GC41935E)
 72. Quadrelli EA. 2016 25 years of energy and green chemistry: saving, storing, distributing and using energy responsibly. *Green Chem.* **18**, 328. (doi:10.1039/C5GC90069G)
 73. Heravi MM, Ansari P, Saeedi M, Karimi N, Tavakoli-Hosseini N. 2011 Green and practical synthesis of benzopyran and 3-substituted coumarin derivatives by Bronsted acid ionic liquid [(CH₂)₄SO₃HMIM][HSO₄]. *Bull. Chem. Soc. Ethiop.* **25**, 315–320.
 74. Lu HY, Li JJ, Zhang ZH. 2009 ZrOCl₂·2H₂O: a highly efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthene derivatives under solvent-free conditions. *Appl. Organometal. Chem.* **23**, 165–169. (doi:10.1002/aoc.1488)