



[DABCO-C₁₈]Br: A novel basic surfactant for the synthesis of dihydropyrano[3,2-c]chromenes and 2-aminobenzochromenes under ambient conditions

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ABSTRACT

We successfully produced a new surfactant called [DABCO-C₁₈]Br, which is a monoquaternized octadecyl-1,4-diazabicyclo[2.2.2]octane bromide. The yield was good. The surfactant that was created was analyzed using techniques such as ¹H NMR, ¹³CNMR, and Mass characterization. We analyzed the synthesized [DABCO-C₁₈]Br salt and found that it has great surfactant properties. Its critical micelle concentration (CMC) is 1.15 mM as determined by the conductivity method and 1.0 mM by UV-Vis absorption measurement at 298.15 K. The values align well with the critical micelle concentration (CMC) of the commonly used surfactant [C16TAB]. We have studied the catalytic efficiency of [DABCO-C₁₈]Br, a tertiary base surfactant, for the synthesis of dihydropyrano [3,2-c]chromenes. This synthesis is achieved through one-pot three-component reactions involving aromatic aldehydes, malononitrile, and 4-hydroxycoumarin in water at room temperature. The method was also extended for the synthesis of 2-aminobenzochromenes via one-pot three-component reactions of aromatic aldehydes, malononitrile, and lawsone in water at 80 °C. The products were achieved in yields ranging from good to excellent within a timeframe of 30–60 min. In addition, the aqueous solution with [DABCO-C₁₈]Br was reused up to four times with a minor reduction in product output. This protocol is fast, energy-efficient, and can be used on a large scale for synthetic purposes. Additionally, it boasts impressive environmentally-friendly credentials.

1. Introduction

One of the most valuable methods for creating chemically and biologically significant structures is through the use of multicomponent reactions (MCRs) [1–3]. The approach includes combining multiple substrates in a single reaction, resulting in domino methods [4–7]. Another option is to add one or more reactants sequentially without isolating intermediates. MCR provides exceptional rewards thanks to its simplicity, easy automation, and waste reduction resulting from reduced work-up and purification stages. In green chemistry, a significant focus is on developing active and eco-friendly procedures for synthesizing biologically important compounds [8,9]. Using green solvents, like water, in various initiatives to replace volatile organic solvents [10,11] is crucial. This work aims to create and implement innovative methods for synthesizing materials using water as a sustainable and eco-friendly

reaction medium [12–14]. Sometimes, organic compounds may have limited solubility in water. However, this issue can be resolved by incorporating surface-active compounds like surfactants [15–17].

Dihydropyrano[3,2-c]chromenes, which are a type of chromene derivative [9], are an intriguing group of fused heterocyclic scaffolds. They have been found to have various beneficial properties, including anti-HIV, antimicrobial, antibacterial, anticancer, spasmolytic, and anticoagulant activities [18–20]. Additionally, these derivatives have shown potential as a treatment for various neurodegenerative diseases, such as Alzheimer's disease, Parkinson's disease, Down's syndrome, AIDS-associated dementia, Huntington's disease, schizophrenia, and myoclonus [21,22] (Fig. 1).

In connection with this, many substantial efforts have been made for the synthesis of dihydropyrano[3,2-c]chromenes in the presence of piperidine [23] cetyltrimethylammonium chloride (CTAC) [24]

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cetyltrimethylammonium bromide (CTAB) coupled with ultrasound [25], alumina [26], K_2CO_3 under microwave irradiation [27], MgO nanoparticles [28], heteropolyacid [29], hexadecyltrimethylammonium bromide (HTMAB) [30], triethylbenzylammonium chloride (TEBA) [31], $TiCl_4$ [32], $(NH_4)_2HPO_4$ -(S)-proline [33], sodium carbonate [34], NaOAc/KF [35], NaBr coupled with electrochemical technique [36], indium with NaI [37], sodium dodecyl sulfate (SDS) [38], tetrabutylammonium chloride [39], 3-hydroxypropanaminium acetate (HPAA) [40] ZIF@ZnTiO₃ Nanocomposite [41], DTP/SiO₂ [42], MnONPs [43] WEB [44], IRA 400-Cl resin [18], [Ch][TAPSO] [45], $NH(CH_2)_7NH_3BiCl_5$ [46], DES [47], NiO-NPs using mucilage of Cordia myxa fruit [48] and many more. While most of these methodologies have become established, some of them have presented more or fewer drawbacks. For instance, many of these pose environmental hazards, longer reaction times, modest yields, and higher amounts of catalysts.

We have recently introduced new and efficient methods for synthesizing different heterocyclic frameworks [49,50] and for Pd-catalysed coupling reactions [51], which are in line with green chemistry principles and involve the use of various additives. In this communication, we would like to share our findings on a surfactant called [DABCO-C₁₈]Br, which acts as an effective and reusable 'Gemini type surfactant' with basic properties [52]. This surfactant has been used for synthesizing dihydropyrano[3,2-c]chromene and 2-aminobenzochromene derivatives in a water-based medium.

2. Experimental

2.1. General remarks

All reactions were carried out in a round-bottom flask at RT or heating. Chemical reagents and anhydrous solvents were purchased

from commercial suppliers (TCI and Sigma-Aldrich chemical companies) and used as purchased. Thin layer chromatography (TLC) was performed using silica gel pre-coated aluminum plates, which were visualized with UV light at 254 nm or under iodine. ¹H NMR and ¹³C NMR were recorded with Bruker (600 MHz) spectrometers using CDCl₃ and DMSO solvents. Chemical shifts for ¹H NMR are referred to as internal TMS (0 ppm). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration.

2.2. General procedure for the synthesis of [DABCO-C₁₈]Br surfactant

In a round-bottom flask, containing DABCO (1,4-diazabicyclo[2.2.2]octane) (2.13 g, 19.01 mmol) and 1-Bromooctadecane (5.0 g, 5.15 mL, 15.01 mmol) was stirred in ethyl acetate (20 mL) at 60 °C for 24 h. The obtained white solid was filtered, and washed with ethyl acetate (3 × 15 mL) and dried in oven. The yield of product was 89 %.

2.3. General procedure for the synthesis of dihydropyrano[3,2-c]chromenes

In a round-bottom flask containing 4-nitrobenzaldehyde (0.151 g, 1 mmol), malononitrile (0.066 g, 1 mmol) and 4-hydroxycoumarin (0.162 g, 1 mmol) was stirred in water (5 mL) in the presence of [DABCO-C₁₈]Br (20 mg, 0.044 mmol) at room temperature. The progress of the reaction was monitored by TLC in ethyl acetate:n-hexane (4:6). For TLC analysis the reaction mixture was extracted in ethyl acetate. After completion of reaction, the solid product was filtered, washed with water (5 mL) and dried in oven. The crude product was recrystallized by hot ethanol.

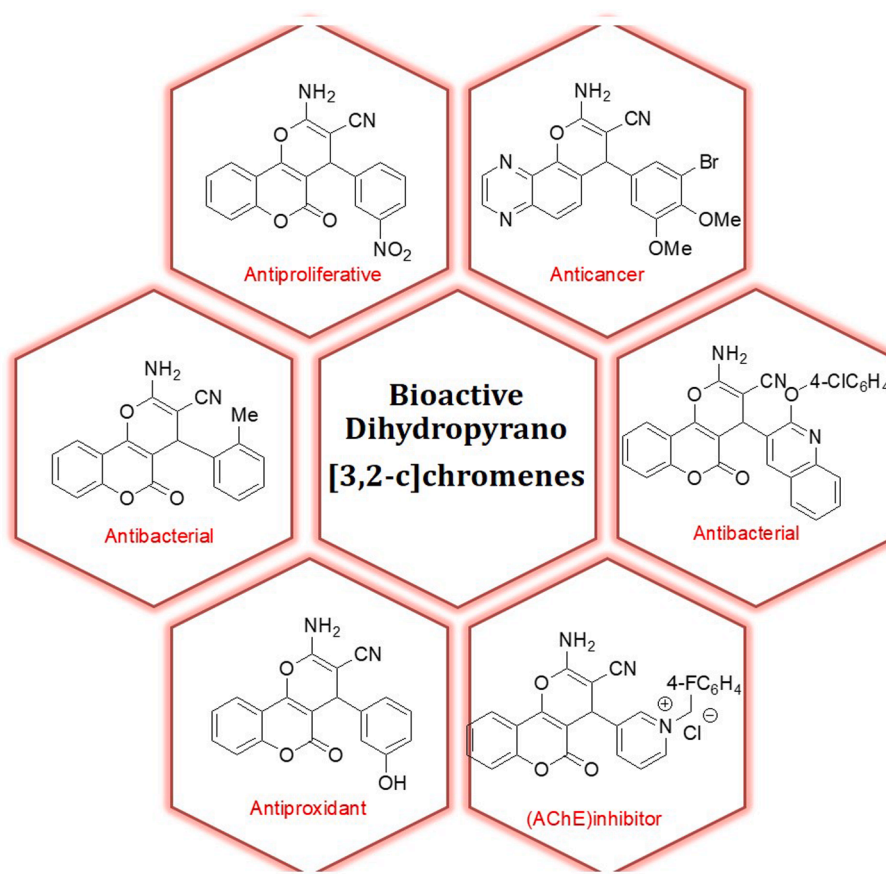


Fig. 1. Critical pharmaceutical active compounds containing chromene framework.

2.4. General procedure for the 2-aminobenzochromene

In a round-bottom flask containing 4-nitrobenzaldehyde (1 mmol, 0.151 g), malononitrile (1 mmol, 0.066 g) and Lawsone (1 mmol, 0.174 g) was stirred in water (5 mL) in the presence of [DABCO-C₁₈]Br (20 mg, 0.044 mmol) at 80 °C temperature. The progress of the reaction was monitored by TLC in ethyl acetate:*n*-hexane (2:8). For TLC analysis the reaction mixture was extracted in ethyl acetate. After completion of reaction, the solid product was filtered, washed with water (5 mL) and dried in oven. The crude product was recrystallized by hot ethanol.

3. Results and discussion

3.1. Synthesis of [DABCO-C₁₈]Br

The [DABCO-C₁₈]Br salt was synthesized with ease by mono-quaternizing DABCO (1,4-diazabicyclo[2.2.2]octane) with 1-bromooctadecane in ethyl acetate at 60 °C. The yield of the final product was 89 % (Scheme 1) [53].

3.2. Micellization behavior of [DABCO-C₁₈]Br in aqueous solution

The conductivity and UV measurements were used to determine the micellization behavior (CMC) of pure [DABCO-C₁₈]Br in an aqueous solution.

3.2.1. Conductivity measurements

The critical micelle concentration (CMC) refers to the point at which the behavior of the surfactant alters in physical and spectral properties [54]. The method of conductivity is a reliable way to gather information about the behavior of surfactants, both before and after they form micelles [55]. As part of our current investigation, we have assessed the CMC of pure [DABCO-C₁₈]Br in an aqueous solution. To take conductivity measurements, we added incremental amounts of aqueous surfactant solution from the stock solution (which was 5 times higher than CMC), to the conductivity cell. We also added an appropriate volume of distilled water. After the solutions were mixed, we recorded stable conductivity values. For each concentration, we made five measurements and only the mean values were used. The standard uncertainty of the measurements was less than 0.3 % [56]. Fig. 2 displays the plots for the conductivity technique utilized in this study to determine the concentration of the pure aqueous [DABCO-C₁₈]Br at a temperature of 298.15 K. In this method, we noticed a distinct shift in the property's slope in the CMC area as 'c' (surfactant) increased. Based on the Onsager theory of electrolyte conductivity, we saw a change in slope between the pre- and post-micellar regions in conductance measurements. The intersection points of the two straight lines representing the CMC of surfactants were also observed. The CMC of the pure [DABCO-C₁₈]Br at 298.15 K was obtained as 1.15 mM, which is in agreement with the CMC of the common surfactant [C₁₆TAB], which is 0.98 mM [57].

The degree of counter ion binding (β) was determined through $\beta = 1 - \alpha$ (where, $\alpha = S_2/S_1$, S_2/S_1 is the ratio of the post-micellar slopes to pre-micellar slopes), in the conductivity versus concentration plots [58,59]. The values for the degree of counter ion binding (β) using conductivity measurements for pure [DABCO-C₁₈]Br is 0.828.

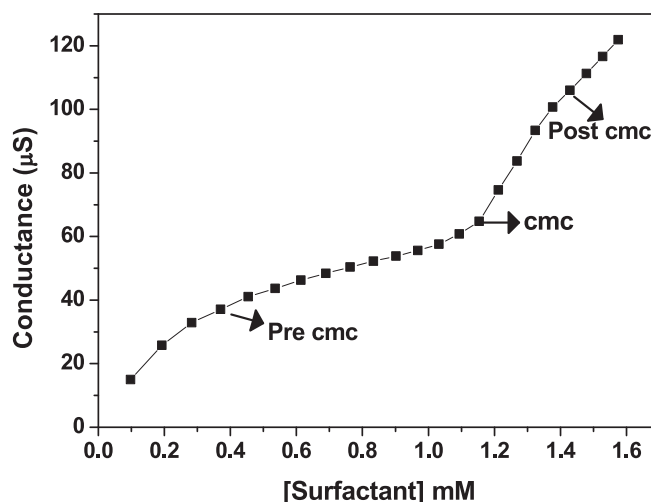


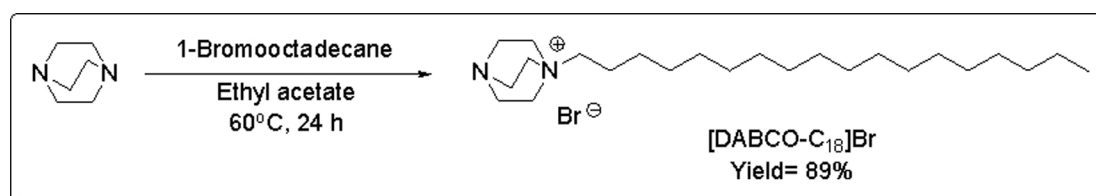
Fig. 2. Conductometric profile of pure [DABCO-C₁₈]Br in aqueous solution at 298.15 K.

3.2.2. UV-Vis absorption measurements

For the measurements of UV-Visible spectra, we used UV-Vis spectrophotometer (Varian Carry 50, Switzerland) equipped with a thermostated cell compartment for the temperature control. We determined the micellization behavior of [DABCO-C₁₈]Br in an aqueous solution by measuring dye solubilization based on UV-Vis absorption. Specifically, we used an anionic dye, methyl orange, since [DABCO-C₁₈]Br is a cationic surfactant. The dye solubilization method operates on the principle of solution polarity [60]. In Fig. 3, we can see the plot of absorbance versus wavelength for various concentrations of [DABCO-C₁₈]Br, a surfactant in an aqueous solution using methyl orange dye. The plot shows that the peak for pure dye (without the addition of surfactant) is obtained at λ_{max} 465 nm. However, as the concentration of surfactant increases, the absorption peak shifts towards a shorter wavelength (known as a hypsochromic shift or higher frequency). This occurs because the dye molecules start associating with surfactant monomers, which decreases the microscopic polarity near the dye molecules. At the micellar pseudo-phase, the dye molecules become solubilized and a decrease in absorbance is observed. Additionally, in the presence of a surfactant, the λ_{max} for the methyl orange dye shifts from 465 to 435 nm, which may be due to the dye being solubilized or incorporated into the core of the surfactant molecule.

Fig. 4 displays the absorption spectra of methyl orange dye at varying concentrations of pure [DABCO-C₁₈]Br in an aqueous solution at 298.15 K. The CMC was determined by where two lines intersected. The CMC of [DABCO-C₁₈]Br is 1.0 mM. The concentration range for CMC by UV-Visible measurements is from 0.98 mM to 1.2 mM, which aligns well with the conductance measurements and literature value of [C₁₆TAB] (i. e. 0.98 mM) [57].

Fig. 5 illustrates the graphical mechanism of micellization for [DABCO-C₁₈]Br surfactant, as determined by the experiments described above.



Scheme 1. Synthesis of [DABCO-C₁₈]Br surfactant.

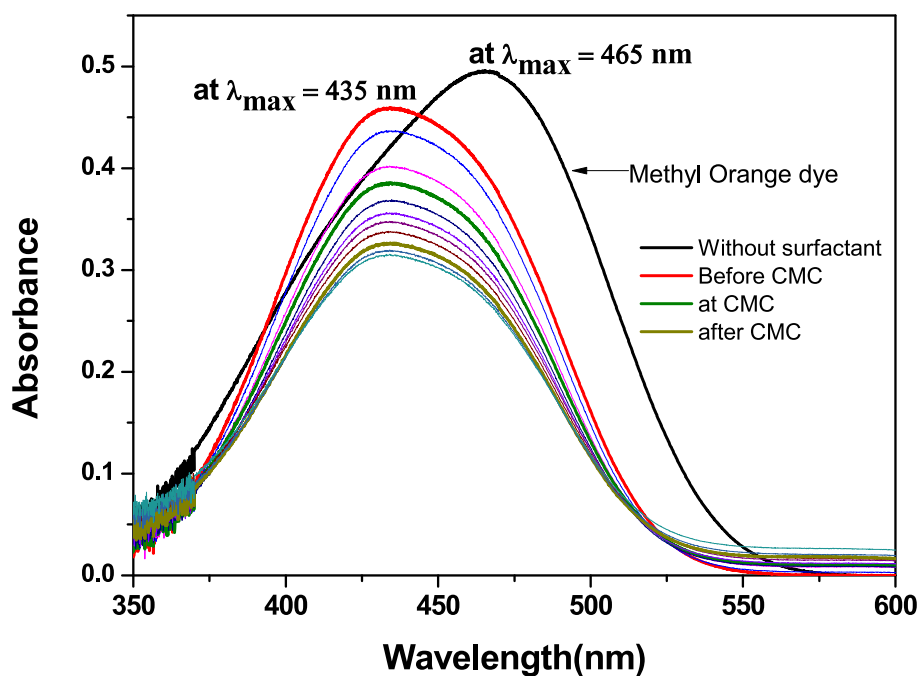


Fig. 3. The absorption spectra of methyl orange dye in aqueous solution of pure [DABCO-C₁₈]Br at 298.15 K ($c(\text{MO})$ is 1.15×10^{-4} M). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

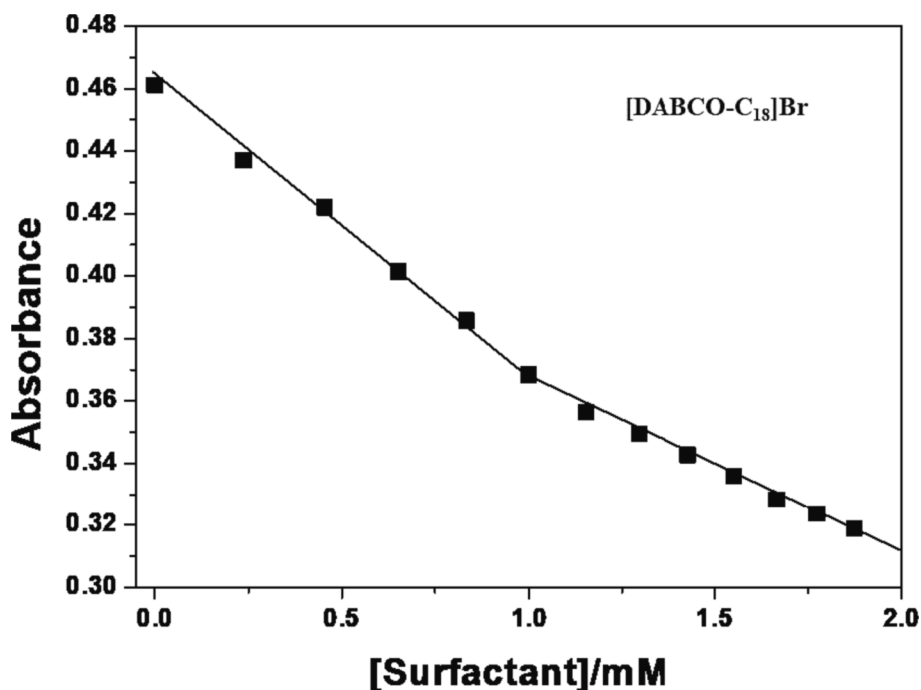


Fig. 4. Absorbance versus concentration of pure [DABCO-C₁₈]Br surfactants in aqueous solution at 298.15 K.

3.3. Applications of [DABCO-C₁₈]Br in the synthesis of dihydropyrano [3,2-c]chromenes

Based on the favorable surfactant characteristics of [DABCO-C₁₈]Br, as well as the alkaline properties provided by DABCO, we intended to investigate its catalytic abilities in producing dihydropyrano[3,2-c]chromenes using eco-friendly conditions.

At first, to improve different reaction conditions, we selected 4-nitrobenzaldehyde (0.151 g, 1 mmol), malononitrile (0.066 g, 1 mmol), and 4-hydroxycoumarin (0.162 g, 1 mmol) as the model reaction partners in

an aqueous solution of [DABCO-C₁₈]Br (Scheme 2).

We conducted the model reaction with different conditions to determine the appropriate amount of surfactant, reaction temperature, and type of solvent (Table 1). It's worth noting that the reaction didn't take place under conditions without a catalyst (Table 1, entry 1). Table 1 shows that with the addition of 5 mg surfactant, the product yield increased to 84 % (Table 1, entry 2). When the amount of surfactant was increased from 5 to 50 mg, the yield improved from 84 to 96 % and the reaction time reduced from 30 to 25 min. at room temperature. (Table 1, entries 2–7). Raising the temperature of the reaction

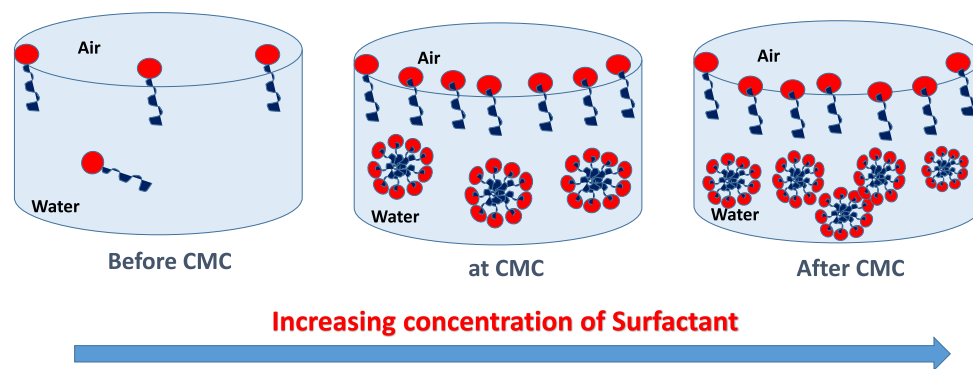
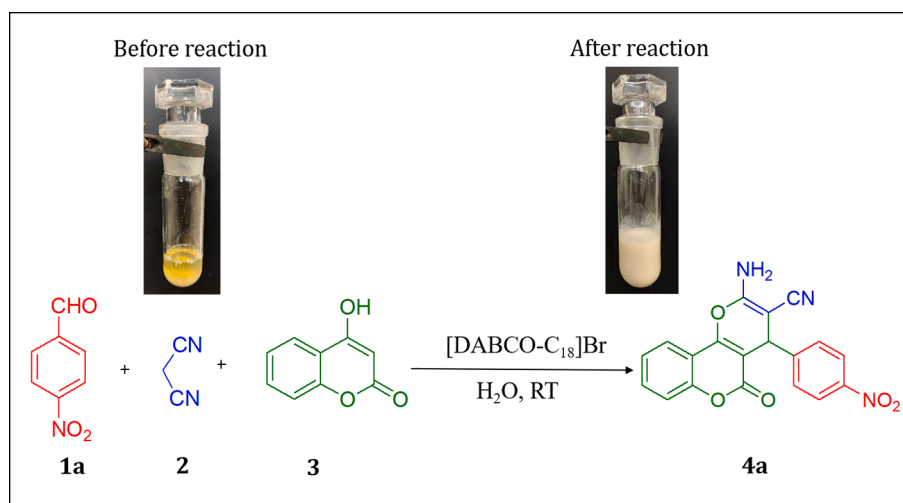


Fig. 5. Graphical representation of micellization of [DABCO-C₁₈]Br in water.



Scheme 2. Synthesis of dihydropyrano[3,2-c]chromene using [DABCO-C₁₈]Br surfactant in aqueous solution.

Table 1

Influence of quantity of surfactant, nature of solvent, and temperature on the yield and reaction time of dihydropyrano[3,2-c]chromene.^a

Entry	Amount of [DABCO-C ₁₈]Br (mg)	Solvent	Temperature (°C)	Time (min)	Yield ^b (%)
1	0	H ₂ O	RT	60	Trace
2	5	H ₂ O	RT	30	84
3	10	H ₂ O	RT	30	90
4	20	H ₂ O	RT	30	96
5	30	H ₂ O	RT	25	95
6	40	H ₂ O	RT	25	96
7	50	H ₂ O	RT	25	96
8	20	H ₂ O	40	30	95
9	20	H ₂ O	80	20	94
11	20	EtOH	RT	30	94
12	20	EtOH:H ₂ O (1:1)	RT	30	89
13	20	DMF	RT	35	88
14	20	DCM	RT	45	85
15	20	CH ₃ CN	RT	50	78
16	20	Toluene	RT	60	70

^a Reaction conditions: 4-Nitrobenzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol), [DABCO-C₁₈]Br (5–50 mg), solvent (5 mL), RT to 80 °C.

^b Isolated yields.

mixture from room temperature to 80 °C significantly affects the reaction time. (Table 1, entries 8–9). We tested the catalytic activity of surfactant in various organic solvents. While it did work in these

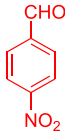
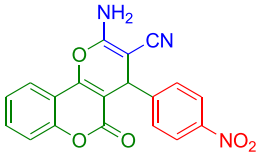
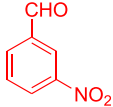
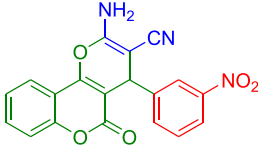
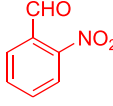
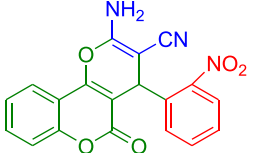
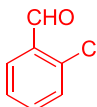
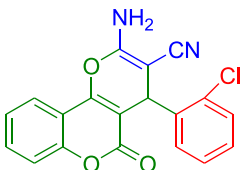
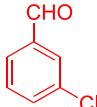
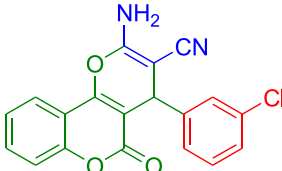
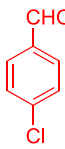
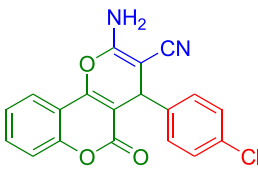
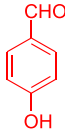
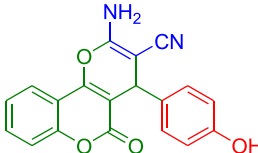
solvents, its activity was lower than in water (Table 1, entries 10–15). Therefore, we determined that the best reaction condition is using 20 mg of surfactant in water at room temperature (Table 1, entry 4).

Using the optimized conditions, we explored the current procedure for synthesizing different derivatives of dihydropyrano[3,2-c]chromenes (Table 2). The reaction was feasible with a wide range of aromatic aldehydes. All reactions were conducted at room temperature, on a 1 mmol scale, with the presence of 20 mg surfactant in water, unless otherwise stated. The reactants were converted efficiently into the desired products, with yields ranging from 87 to 96 %. Additionally, aromatic heterocyclic aldehydes were able to react successfully, producing the product with 87–93 % yield.

3.4. Applications of [DABCO-C₁₈]Br in the synthesis of 2-aminobenzochromene

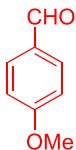
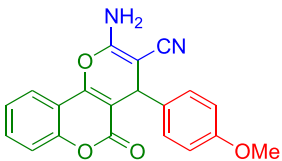
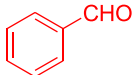
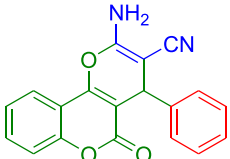
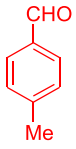
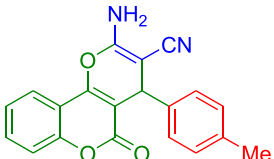
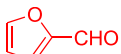
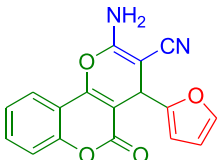
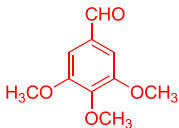
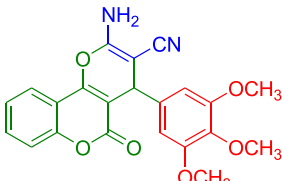
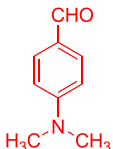
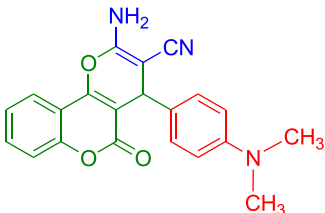
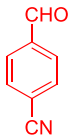
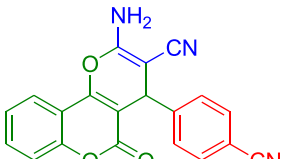
There are a variety of biological activities associated with benzo[g]chromenes, such as anti-cancer, anti-inflammatory, and anti-malaria effects [61]. In addition, the benzo[g]chromenes occurring naturally are also used as drugs for the treatment of tumor [62,63]. In this connection, many 2-aminobenzochromenes were synthesized by different synthetic methods from aromatic aldehyde, lawsone, and malononitrile in the presence of different catalysts such as TEBA [64], Potassium phthalimide-N-oxyl [65], propylpiperazine-N-sulfamic acid (SBPPSA) [66], Zn(L-proline)₂ [67], Et₃N [68], urea [69], [bmim]OH [70], L-proline [71], [Et₃NH][HSO₄] [72], Fe₂O₃@SiO₂ NPs [73], ammonium acetate [74], Fe₃O₄@SiO₂@NH₂-TCT-Mesalamine – Cu(II) MNPs [75], and IRA 400-Cl resin [18]. However, there is a need to

Table 2Exploration of the substrate scope for the synthesis of dihydropyrano[3,2-c]chromenes in aqueous [DABCO-C₁₈]Br solution at room temperature.^a

Entry	Aldehydes	Products	Time (min)	Yield ^b (%)	M.P (°C)
1			30	96	258–260
2			35	93	262–264
3			30	92	250–252
4			30	92	264–266
5			35	91	244–246
6			30	94	260–262
7			45	90	258–260

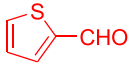
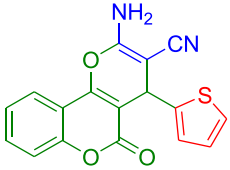
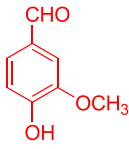
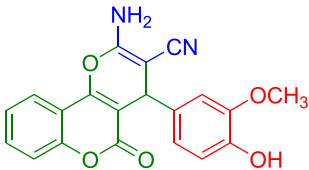
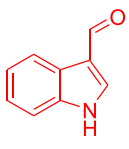
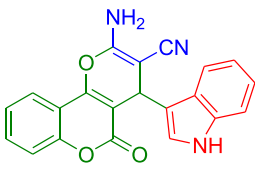
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Table 2 (continued)

Entry	Aldehydes	Products	Time (min)	Yield ^b (%)	M.P (°C)
8			40	90	240–242
9			40	89	256–258
10			35	88	250–252
11			45	88	250–252
12			35	93	238–240
13			30	92	222–224
14			30	91	286–288

(continued on next page)

Table 2 (continued)

Entry	Aldehydes	Products	Time (min)	Yield ^b (%)	M.P (°C)
15			45	87	226–228
16			30	92	250–252
17			35	93	200–202

^a Reaction conditions: Aromatic aldehydes (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol), [DABCO-C₁₈]Br (20 mg), Water (5 mL), RT.

^b Isolated yields.

develop a new better, and more efficient method that can lead to enhanced yields under green conditions.

We experimented with using lawsone to synthesize 2-aminobenzochromene after successfully utilizing 4-hydroxycoumarin as a nucleophile. The procedure entails combining aryl aldehydes (1 mmol), malononitrile (0.066 g, 1 mmol), lawsone (0.174 g, 1 mmol) under varying reaction conditions (Scheme 3).

To determine the appropriate amount of surfactant, reaction temperature, and solvent type, the model reaction was tested under different conditions (Table 3). It was found that no reaction took place when there was no catalyst present (Table 3, entry 1). After conducting different experiments, it was determined that the ideal reaction conditions involve use of 20 mg surfactant in water at a temperature of 80 °C (Table 3, entry 9).

After obtaining the optimized conditions, we investigated the reaction scope for the synthesis of different 2-aminobenzochromene derivatives (Table 4). Our findings showed that numerous aromatic

Table 3

Influence of quantity of surfactant, nature of solvent, and temperature on the yield and reaction time of 2-aminobenzochromene.^a

Entry	Amount of [DABCO-C ₁₈]Br (mg)	Solvent	Temperature (°C)	Time (min)	Yield ^b (%)
1	0	H ₂ O	RT	60	NR
2	5	H ₂ O	RT	180	94
3	10	H ₂ O	RT	160	95
4	20	H ₂ O	RT	140	96
5	30	H ₂ O	RT	100	95
6	40	H ₂ O	RT	90	96
7	50	H ₂ O	RT	90	96
8	5	H ₂ O	40	90	90
9	20	H ₂ O	80	60	96
11	20	EtOH	80	90	80
12	20	EtOH:H ₂ O (1:1)	80	90	89
13	20	DMF	80	70	86
14	20	DCM	80	120	85
15	20	CH ₃ CN	80	150	78
16	20	Toluene	80	160	70

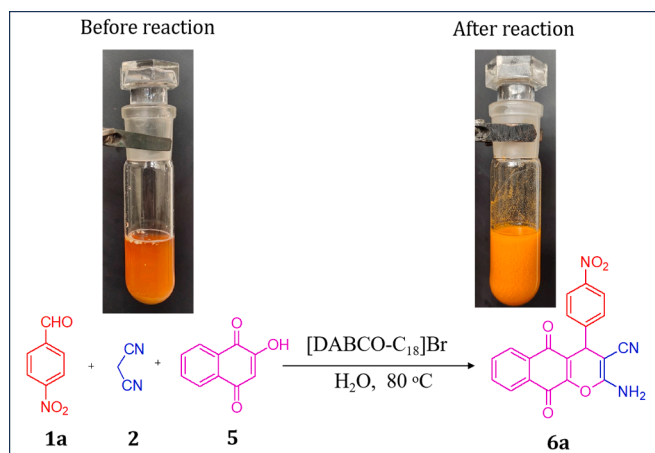
^a Reaction conditions: 4-Nitrobenzaldehyde (1 mmol), malononitrile (1 mmol), lawsone (1 mmol), [DABCO-C₁₈]Br (5–50 mg), solvent (5 mL), RT to 80 °C.

^b Isolated yields.

aldehydes can be effortlessly converted into the intended products with yields ranging from good to excellent.

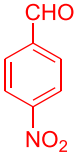
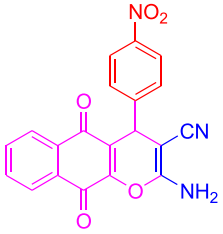
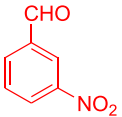
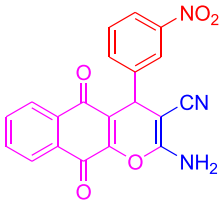
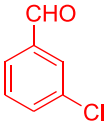
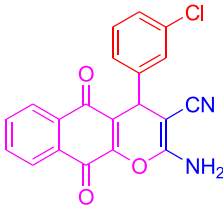
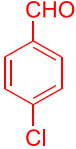
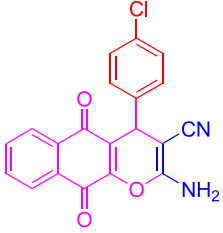
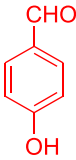
3.5. Gram-scale synthesis of dihydropyrano[3,2-c]chromene and 2-aminobenzochromene

We examined the effectiveness of the current approach for creating dihydropyrano[3,2-c]chromene and 2-aminobenzochromene on a gram scale (10 mmol scale). This was achieved by reacting 4-nitrobenzaldehyde (1.51 g, 10 mmol), malononitrile (0.66 g, 10 mmol), and 4-hydroxycoumarin (1.62 g, 10 mmol) under standard conditions. Within 90 min, the process yielded 94 % of the target product **4a**. Similarly, **6a** was



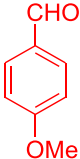
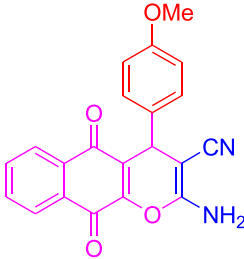
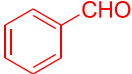
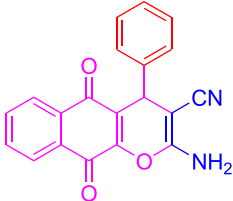
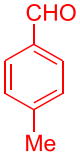
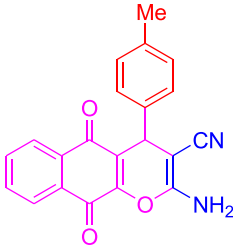
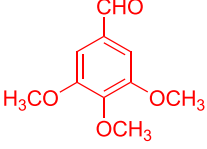
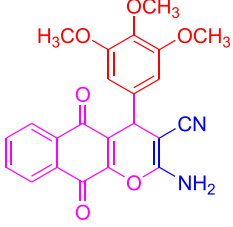
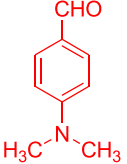
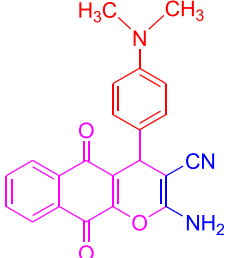
Scheme 3. Synthesis of 2-aminobenzochromene using [DABCO-C₁₈]Br surfactant in aqueous solution.

Table 4
Exploration of the substrate scope for the synthesis of 2-aminobenzochromenes.^a

Entry	Aldehydes	Products	Time (min)	Yield ^b (%)	M.P (°C)
1			60	96	228–230
2			65	94	246–248
3			60	88	242–244
4			70	96	278–280
5			60	93	250–252

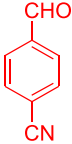
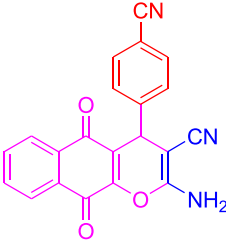
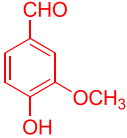
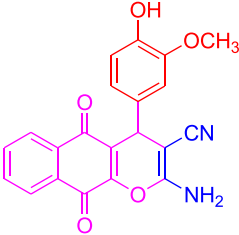
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Table 4 (continued)

Entry	Aldehydes	Products	Time (min)	Yield ^b (%)	M.P (°C)
6			75	90	248–250
7			70	91	258–260
8			70	90	240–242
9			60	95	228–230
10			60	95	246–248

(continued on next page)

Table 4 (continued)

Entry	Aldehydes	Products	Time (min)	Yield ^b (%)	M.P (°C)
11			60	94	238–240
12			65	96	248–250

^a Reaction conditions: Aromatic aldehydes (1 mmol), malononitrile (1 mmol), Lawsone (1 mmol), [DABCO-C₁₈]Br (20 mg), Water (5 mL), 80 °C.

^b Isolated yields.

produced with a 92 % yield by reacting 4-nitrobenzaldehyde (1.51 g, 10 mmol), malononitrile (0.66 g, 10 mmol), and lawsone (1.74 g, 10 mmol) at 80 °C (Scheme 4).

3.6. Mechanism of synthesis of dihydropyrano[3,2-c]chromenes and 2-aminobenzochromenes

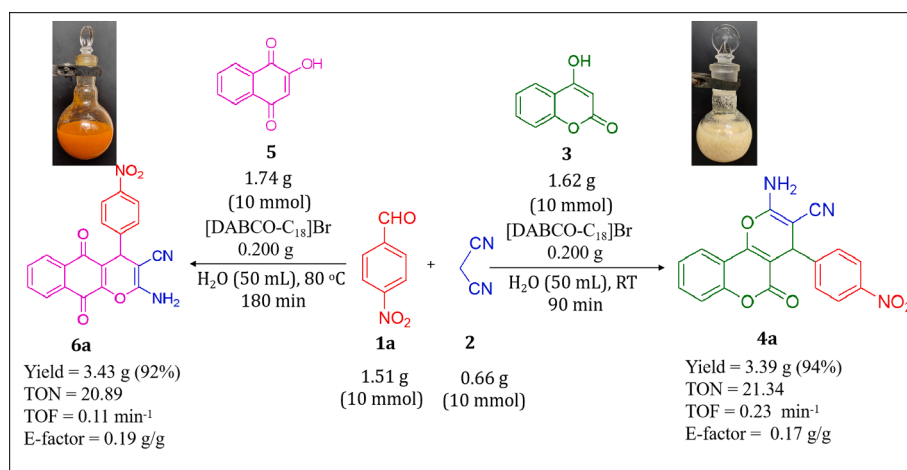
According to the results shown above, Scheme 5 provides a plausible mechanism for the creation of chromenes (4) and (6). Initially, [DABCO-C₁₈]Br acts as a base, abstracting the acidic proton of malononitrile (2) producing anionic intermediate I. The resulting intermediate I attacks the carbonyl group of aldehyde (1) to form a Knoevenagel adduct II. In the second step, the 4-hydroxycoumarin (3) or lawsone (5) reacts with adduct II to create Michael adduct III and III' respectively. These adducts undergo intramolecular cyclization via intermediate IV and IV' followed by tautomerization and delivered the desired products 4a and 6a respectively.

3.7. Recyclability

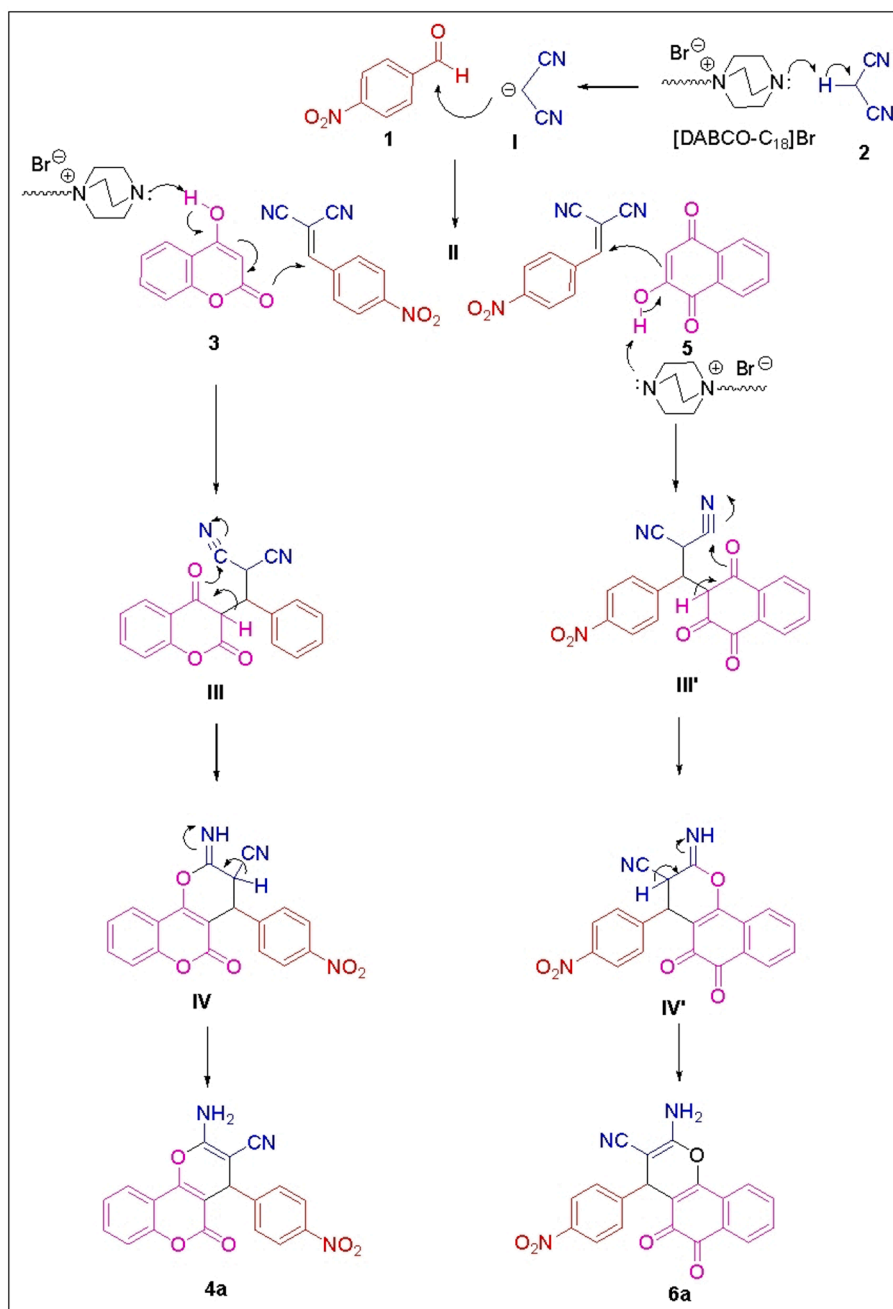
Efficient recycling of catalytic systems with consistent activity is crucial for sustainable organic transformations. To study the recyclability of the catalytic system for dihydropyrano[3,2-c]chromene synthesis, a model reaction was used. The [DABCO-C₁₈]Br containing aqueous solution can be easily separated from the reaction mixture through filtration. The aqueous layer was then washed with ethyl acetate, and the aqueous layer containing [DABCO-C₁₈]Br was recycled at least four times with a slight decrease in activity (Fig. 6).

3.8. Estimation of greenness of the present protocol

Later on, several metrics were analyzed to determine the level of environmental friendliness of the current protocol [76,77]. Green metrics quantify the efficiency and environmental impact of chemical processes. These can be better measured by various factors such as environmental factor (E factor), turnover number (TON), turnover frequency (TOF), atom economy (AE), atom efficiency (Aef), carbon



Scheme 4. Gram scale synthesis of products 4a and 6a using [DABCO-C₁₈]Br.



Scheme 5. A plausible mechanism for the synthesis of dihydropyrano[3,2-c]chromenes and 2-aminobenzochromenes using [DABCO-C₁₈]Br.

efficiency (CE), optimum efficiency (OE), effective mass yield (EMY), reaction mass efficiency (RME), mass productivity (MP), mass intensity (MI) and process mass intensity (PMI), as well as solvent and water intensity (SI and WI). Table 5 displays the green chemistry metrics that were measured for all the reactions (See Supporting Information, Tables S3–S6).

The representative results of the model reaction under optimized reaction conditions are depicted in Fig. 7. The metrics were calculated by considering both the with and without catalyst. The results demonstrated that the values of green chemistry metrics are nearly close to their ideal values.

- We evaluated the efficiency of the catalytic system by measuring the TON and TOF values [78]. Our system achieved TON values ranging from 19.54 to 21.59 and 19.77 to 21.59, with corresponding TOF values of 0.43–0.71 min⁻¹ and 0.26–0.35 min⁻¹.

- To assess the environmental impact, we used EMY [79]. Our method showed an EMY between 82.35 and 91.29 % for compounds 4a–q and 83.68–95.14 % for compounds 6a–l which, demonstrates its significant environmental friendliness.
- In the current protocol, the CE is 100 %, while MP is in between 78.12 % and 86.95 % for compounds 4a–q and 80.00–90.90 % for compounds 6a–l.
- Additionally, the AEF for this method is excellent, ranging from 94.44–95.26 % and 94.79–95.87 % for compounds 4a–4q and 6a–6l respectively.
- As all products being obtained with good to excellent yields, the AE is also high, ranging from 82.38–91.44 % and 95.19–83.84 % for compounds 4a–4q and 6a–6l respectively.
- RME is a faithful metrics for relating the greenness of a process [80], and it accounts for yield, stoichiometry, and atom economy. The present protocol has achieved RME of up to 86.71 % for compound

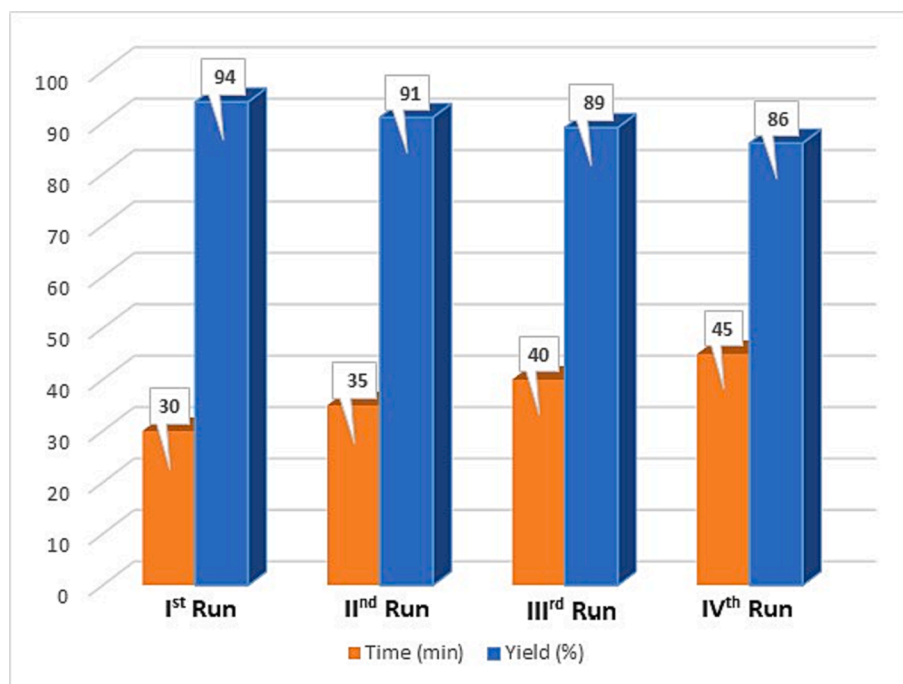


Fig. 6. Recyclability of the [DABCO-C₁₈]Br for the synthesis of dihydropyrano[3,2-c]chromenes.

Table 5

A range of green chemistry metrics for all the products.

Sr. No.	Green Metrics	Dihydropyrano[3,2-c]chromenes	2-Aminobenzo chromenes
1	EMY (%)	82.35–91.29	83.68–95.14
2	AE (%)	94.44–95.26	94.79–95.87
3	AEf (%)	82.38–91.44	83.84–95.19
4	CE (%)	100	100
5	RME (%)	77.77–86.71	79.50–90.28
6	OE (%)	82.12–91.03	83.43–91.34
7	MP (%)	78.12–86.95	80.00–90.90
8	PMI (g/g)	14.14–19.86	13.74–18.00
9	MI (g/g)	1.15–1.28	1.10–1.25
10	E-factor (g/g)	0.14–0.28	0.10–0.25
11	SI (g/g)	0	0
12	WI (g/g)	26.52–37.17	25.18–33.55
13	TON	19.54–21.59	19.77–21.59
14	TOF min ⁻¹	0.43–0.71	0.26–0.35

4a and 77.77 % for compound 4o. Similarly, RME 90.28 % for compound 6k and 79.50 % for compound 6c.

- PMI is a decisive metrics for evaluating and benchmarking progress toward sustainable manufacturing processes. It measures the total mass of materials used to produce a product. The PMI values of this protocol range from 14.44–19.86 g/g for compounds 4a–q and 13.74–18.00 g/g for compounds 6a–l.
- MI takes into account the yield, stoichiometry, solvent, and reagent used in the reaction. The MI for compounds 4a–q are 1.15–1.28 g/g and 1.10–1.25 g/g for compounds 6a–l, which is close to the ideal value of MI (MI = 1 g/g).
- The E-factor is an easy way to measure the environmental impact of chemical methods. It takes into account the chemical yield and consider reagents, solvent loss, and all process aids. The lower the E-factor, the less waste is produced during the process. The E-factor for current protocol is 0.14–0.28 g/g for compounds 4a–q and 0.10–0.25 g/g for compounds 6a–l indicating its significant environmental friendliness (the optimal E-factor is 0).

- In chemical reactions, the amount of solvent used is typically substantial, and its impact on sustainability is measured through SI [81,82]. The SI value of a process is zero in the present protocol since water is excluded from the calculations and organic solvents are not used, except for EtOH in recrystallization.

4. Conclusion

In summary, a new surfactant called octadecyl diazabicyclooctadecane bromide [DABCO-C₁₈]Br has impressive surfactant properties. Two different methods were used to determine the critical micelle concentration (CMC), conductivity analysis yielded a value of 1.15 mM, while UV–Vis absorption measurement gave a value of 1.0 mM. The degree of counter ion binding (β) for pure [DABCO-C₁₈]Br was found to be 0.828 as determined by conductivity measurements. As [DABCO-C₁₈]Br is a strong tertiary base and an excellent surfactant, it proved to be a highly efficient catalyst for the synthesis of dihydropyrano[3,2-c]chromenes in water at room temperature. Additionally, it demonstrated good to excellent activity in creating 2-aminobenzo chromenes in water at 80 °C. The aqueous solution containing [DABCO-C₁₈]Br could be recycled up to four times with a slight decrease in product yield from 94 % (1st run) to 86 % (4th run). This protocol is quick, energy-efficient, and applicable for large-scale synthesis, with excellent green credentials. From a sustainability point of view, green chemistry parameters like E-factor, atom economy, and carbon efficiency are in good agreement with the ideal values. All of the green metrics are found to be highly satisfactory, thereby supporting substantial green credentials of the process.

Author contributions

Archana Rajmane: Study conception and design, data collection, experimental work and designing of manuscript; **Sunita Shirke:** Formal analysis; **Rupesh Bandal:** Formal analysis; **Utkarsh More:** Physical study; **Suresh Patil:** Project co-supervisor; **Arjun Kumbhar:** Project supervisor.

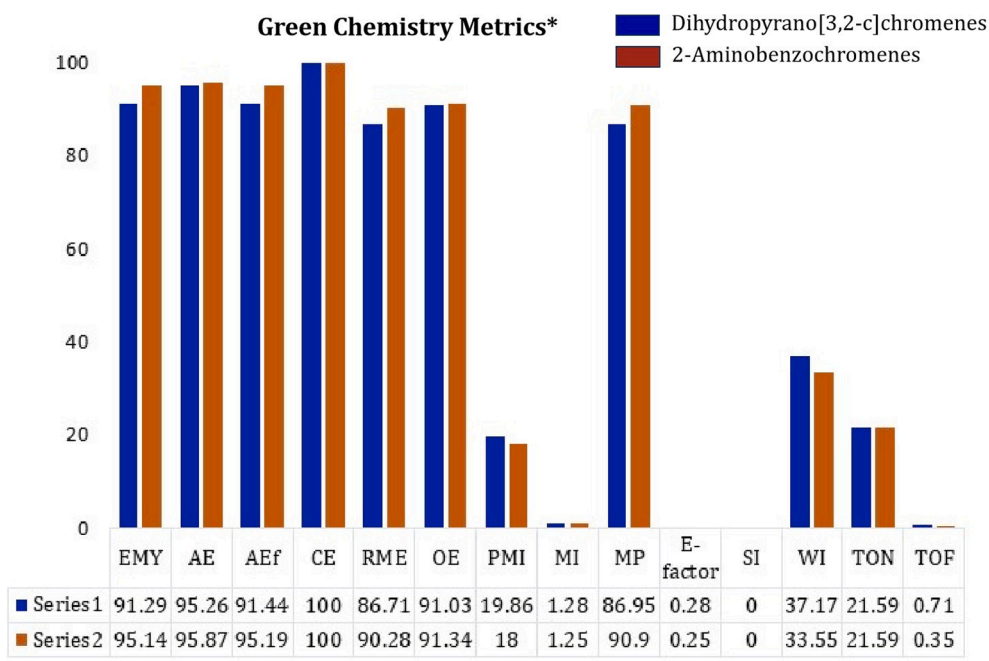


Fig. 7. The green metrics analysis for the synthesis of dihydropyrano[3,2-c]chromenes and 2-aminobenzochromenes (* For compounds 4a and 6a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2023.123247>.

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