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A green approach towards the on-water synthesis of multifunctional 3-amino/hydroxy thieno[3,2-c] pyrans†

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An efficient, one-pot, and green synthetic strategy was established for 3-amino/hydroxy thieno[3,2-c] pyrans in water through a reaction of 6-aryl-4-(methylthio)-2-oxo-2H-pyran-3-carbonitriles/ carboxylates with methyl thioglycolate, yielding excellent results (65–95%). The present approach was also employed to synthesize benzo[h]thieno[3,2-c]chromene-2-carboxylate derivatives in good yield. This efficient method eliminated the need for tedious purification steps, and the products were purified by simply washing the crude material with lukewarm water. Furthermore, the reaction medium was reusable and could be repeated up to six cycles, producing the desired product with only minimal loss, although the reaction time increased with each cycle. All the synthesized compounds were characterized by spectroscopic analysis, and the structure of one compound was confirmed by single-crystal X-ray analysis.

Introduction

Thiophene derivatives constitute an important scaffold of heterocyclic compounds and demonstrate many applications in pharmaceuticals, agrochemicals, and dyes.[1] Their synthetic derivatives exhibit anti-avian influenza virus (H5N1) activity,[2] antitumour,[3] antimycobactrial,[4] and antibacterial activity.[5] In addition to these, fused thiophenes, such as thienothiophene and dithienothiophene derivatives, have been extensively explored in organic field-effect transistors (OFETs) and organic photovoltaics (OPVs).[6–12] Thiophene fused with a pyranone ring forms highly promising bioactive thienopyranone scaffolds (Fig. 1).[13–16] It exhibits potent tumor cell growth inhibitor properties. For example, thieno[2,3-c]pyran and 5-morpholino-7H-thieno[3,2-b]pyran-7-ones are P13K inhibitors.[17] In addition to bioactivity, it also exhibits aggregation-induced emission (AIE),[18] as well as piezo- and acido-chromic properties.[19]

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The potential uses of thienopyranone compounds in materials science and pharmaceuticals have drawn considerable interest from chemists to synthesize them. The most common approach for synthesizing thienopyranones involves Pd- and/or Cu-catalyzed alkynylation of thiophene-2-carboxylic acid, followed by 6-endo-dig cyclization.[20–23] In contrast, I_2-mediated iodolactonisation of alkynyl thiophene carboxylates to thienopyranones offers a mild approach for this purpose.[24,25] Anhydride-mediated dehydration of 1-(3-hydroxythiophen-2-yl)-3-amino-propane-1,3-dione[17] or 2-(2-alkylthiophen-3-yl)acetic acid[26] also produced the corresponding thienopyranones in good to moderate yield. Turchi et al. reported that BCl_3 mediates the demethylation of 1-(3-hydroxythiophen-2-yl)-3-methylbut-2-en-1-ones, followed by ring closure in the presence of catalytic amounts of protic acid (p-TSA), to afford the desired thieno[3,2-b]pyranone products.[27] In this context, Wünsch reported the synthesis of spirothieno[3,4-c] and [2,3-c] pyranone derivatives from their 4-(2,2-dimethoxyethyl) thiophen-2-yl-piperidin-4-ol precursors via subsequent cyclization by HCl and oxidation by pyridinium chlorochromate (PCC).[28] Later, our team described the synthesis of highly functionalized thieno[3,2-c]pyran-4-ones from 6-aryl-3-cyano-4-methylthio-2H-pyran-2-one and mercaptoacetate, either in the presence of KOH in MeOH or without a base in DMF.[29,30]

All of the above-reported syntheses use either environmentally harmful, expensive metal catalysts or hazardous reagents or solvents. The environmental impact on biological growth is currently a major issue due to the industrial crisis, which can affect human development on a large scale. To overcome this issue, green chemistry can play an important role and motivate
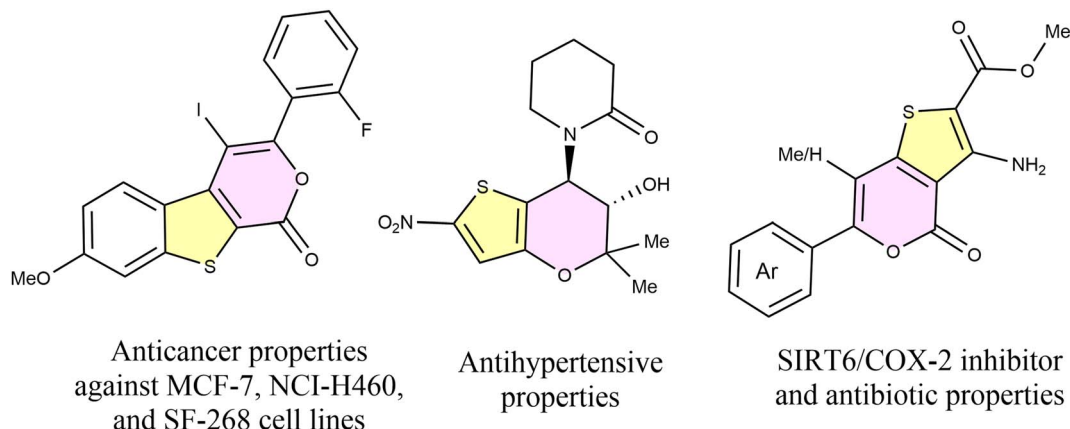
Fig. 1 Bioactive thienopyrans.

researchers toward greener approaches.[31] The choice of solvent system in organic synthesis is a major concern, as it generates large amounts of hazardous, toxic, and waste materials.[32] Water serves as a green solvent system because it is non-toxic, easily handled, inexpensive, non-flammable, and has attracted many research groups in recent times.[33,34] However, the hydrophobicity of organic substrates limits the application of water as a solvent in organic reactions. To overcome this pitfall, surfactants provide an effectively organized medium,[35,36] in aqueous solution *via* the formation of micelles, vesicular cavities, or organized nanoreactors,[37] which not only have a confined hydrophobic interior to solubilize the organic reagents but also bring the reagents into closer proximity, leading to enhanced rates and efficiency of chemical reactions. All reacting molecules are concentrated by solubilization due to the hydrophobic

effect and electrostatic attraction among counter ions, thereby enhancing the rate and efficiency of the water-mediated chemical reaction.[38–41] Considering the above background, we herein reported the synthesis of thieno[3,2-*c*]pyran-4-ones under mild conditions in an aqueous medium using surfactants and a catalytic amount of base in a metal-free environment.

Results and discussion

Our initial efforts were focused on assessing the efficacy of base and surfactant for the synthesis of pyranothiophene in aqueous conditions (ESI, Table SI1†). For this investigation, 6-(4-bromophenyl)-4-(methylthio)-2-oxo-2H-pyran-3-carbonitrile[42,43] (**1a**) and methyl thioglycolate (**2a**) were used as model substrates for

Table 1 Optimization of reaction conditions for the synthesis of pyranothiophene **3a** [a]

Entry	Deviation from the reaction conditions mentioned above in the scheme	Yield of **3a**
1	None	93%
2	Without surfactant, using only base (100 mol%)	≤54%
3	Without base, using only surfactant	≤50%
4	CTAB/Et$_3$N (100 mol%)	91%
5	CTAB/Et$_3$N (20 mol%)	80%
6	CTAB/Et$_3$N (40 mol%)	92%
7	Other surfactant/Et$_3$N (100 mol%)	≤84%

[a] Reactions were carried out by stirring **1a** (2 mmol), methylthioglycolate **2** (3 mmol), base, and surfactant (0.50 mmol) in water (20 mL). For detailed optimisation results, please refer ESI (Table SI1).
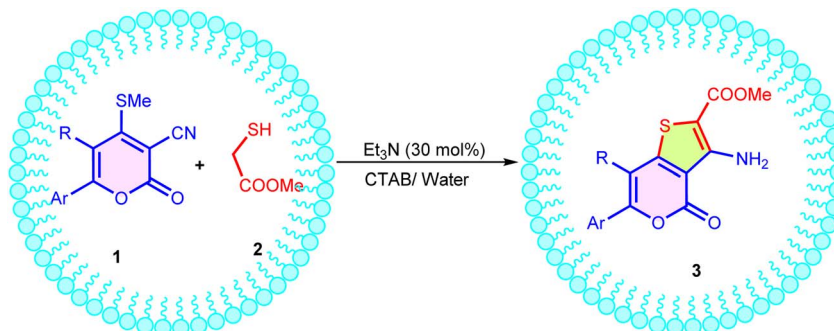
the reaction. When the reaction was performed with hydroxide bases, the desired product, methyl 3-amino-6-(4-bromophenyl)-4-oxo-4H-thieno[3,2-c]pyran-2-carboxylate (**3a**), was obtained in only up to 32% yield, along with a trace amount of side product **4a** (Table SI1, entries 3 and 4†). However, in due course, the reaction mixture turned into a gummed solid that stuck to the magnet, and the reaction was incomplete. Therefore, we screened some organic amines as bases, but the effort with piperidine was futile, as the desired product was not obtained and instead yielded a complex mixture (Table SI1, entry 5†). In contrast, Et₃N and DBU afforded a moderate yield of product **3a** without any side products (Table SI1, entry 6 and 7†). However, the formation of a solid lump persisted, preventing the reaction from completing. We then used a surfactant to resolve the problem of solubility and incomplete reaction. Application of CTAB as a surfactant in the reaction afforded up to 50% of product **3a** even in the absence of a base (Table 1, entry 3). However, the use of base (100 mol%) provided up to 54% yield of the product (Table 1, entry 2). Trials with different base stoichiometries showed that using 30 mol% of triethylamine provided the best reaction conditions (Table 1, entries 4–6). Finally, a series of surfactants were screened with various

organic bases in different amounts under aqueous conditions, and the best yield of product **3a** (93%) was obtained with 0.5 equivalent of surfactant CTAB and 30 mol% of Et₃N at 85 °C (Table 1, entry 1 or Table SI1, entry 29†). This efficient method eliminated the need for tedious purification steps, achieving an excellent yield of product **3a** simply by washing the crude material with lukewarm water.

To evaluate the scope and limitations of the present approach, a series of 6-aryl-4-(methylthio)-2-oxo-2H-pyrans (**1**) were treated with methyl thioglycolate (**2**) to prepare the corresponding 3-amino pyrano-fused thiophene (**3a–q**) derivatives under optimized reaction conditions (Table 2). In general, the electron-donating (–CH₃ and –OCH₃) or mild electron-withdrawing (–F and –Cl) nature of substitution at the para position of the C-6 aryl ring of substrate **1** did not have a substantial impact on the overall yield of the products (**3c–f**). However, a strong electron-withdrawing substitution (–NO₂) significantly reduced the yield (**3g**). Similarly, *ortho*-substitution (**3h–i**) or multiple substitution (**3j–k**) on the aromatic ring also resulted in comparatively lower yields of the product. The reaction conditions provides good tolerance for C-6 halogenated aryls, heteroaryl (**3l–m**), as well as C-5 aryl and alkyl (**3o–q**)
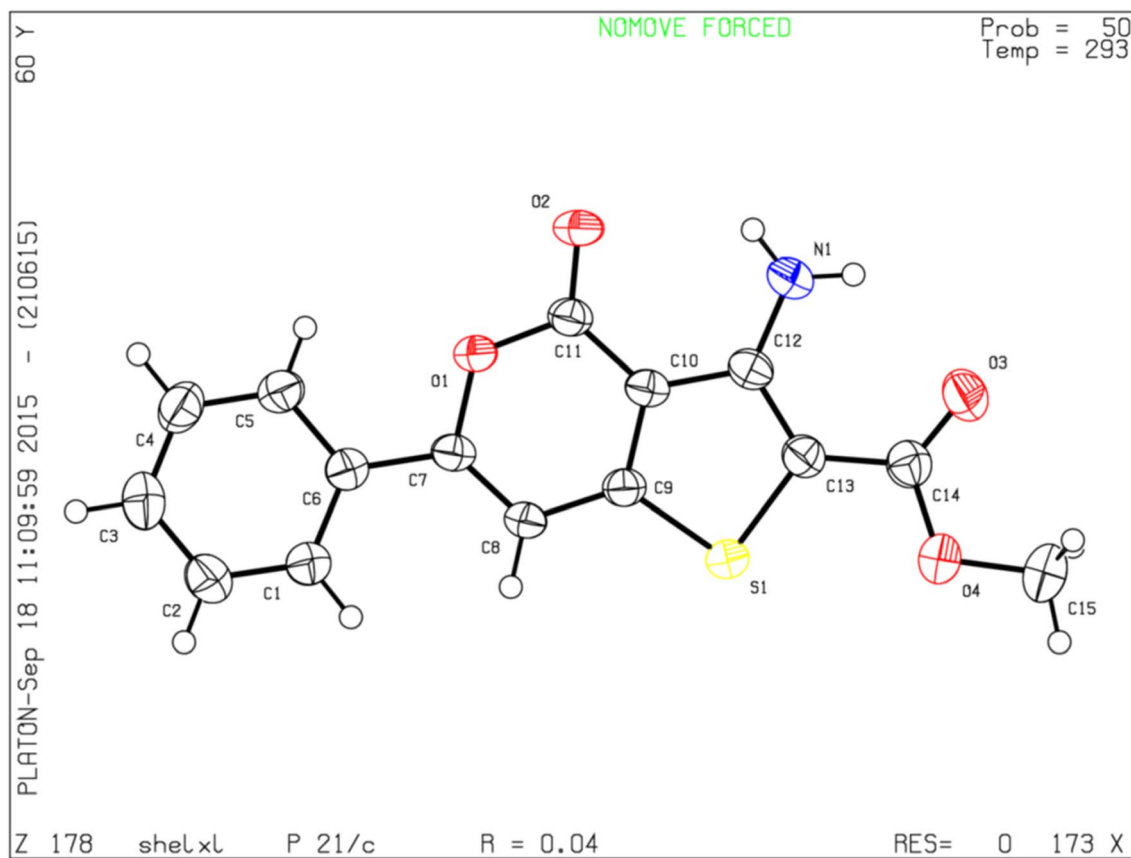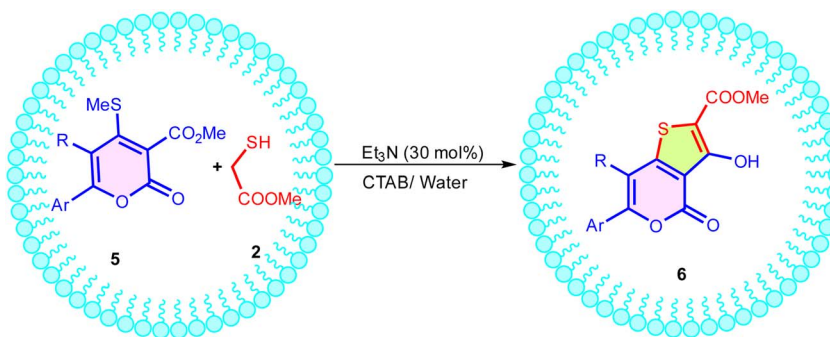
Table 2 Micelle-promoted synthesis of 3-amino-4H-thieno[3,2-c]pyran-2-carboxylates in water[a]

Entry	Ar–	R	Time (h)	Yield[b]
3a	p-Br·C₆H₄	H	2	93%
3b	C₆H₅	H	2	90%
3c	p-CH₃·C₆H₄	H	2	92%
3d	p-OCH₃·C₆H₄	H	2	85%
3e	p-F·C₆H₄	H	2	90%
3f	p-Cl·C₆H₄	H	2.5	88%
3g	p-NO₂·C₆H₄	H	3	~8%
3h	o-Br·C₆H₄	H	2	80%
3i	o-OCH₃·C₆H₄	H	2	75%
3j	2,4-(Cl)₂·C₆H₃	H	2.5	75%
3k	3,4-(OCH₃)₂·C₆H₃	H	2	78%
3l	2-Furyl	H	2.5	88%
3m	2-Theinyl	H	2.5	86%
3n	1-Naphthyl	H	3	76%
3o	C₆H₅	CH₃	3	91%
3p	C₆H₅	C₆H₅	3	93%
3q	p-OCH₃·C₆H₄	p-OCH₃·C₆H₄	3	90%

[a] Reactions were carried out by stirring **1** (2 mmol), methyl thioglycolate **2** (3 mmol), Et₃N (30 mol%, 0.085 mL), and surfactant (0.5 mmol) in water (20 mL) at 85 °C temperature. [b] Isolated yield of **3** was reported.

Fig. 2 ORTEP diagram of the compound **3b**.

Table 3 Synthesis of 3-hydroxy-4H-thieno[3,2-c]pyran-2-carboxylates in water[a]

Entry	Ar–	R	Time (h)	Yield of 6^{b}
6a	C$_6$H$_5$	H	14	70%
6b	p-Br·C$_6$H$_4$	H	14	85%
6c	p-CH$_3$·C$_6$H$_4$	H	14	79%
6d	2-Naphthyl	H	14	69%
6e	2-Furyl	H	16	71%
6f	2-Thienyl	H	16	82%
6g	3,4-(OCH$_3$)$_2$·C$_6$H$_3$	H	14	95%
6h	C$_6$H$_5$	C$_6$H$_5$	18	65%

[a] Reactions were carried out by stirring **5** (2 mmol), methyl thioglycolate **2** (3 mmol), Et$_3$N (30 mol%, 0.085 mL), and surfactant (0.5 mmol) in water (20 mL) at 85 °C temperature. [b] Isolated yield of **6** was reported.
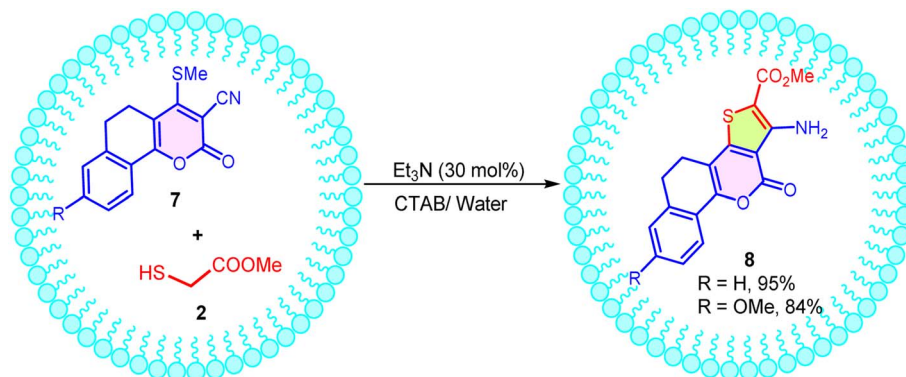
Scheme 1 Synthesis of methyl 1-amino-11-oxo-5,11-dihydro-4*H*-benzo[*h*]thieno[3,2-*c*]chromene-2-carboxylate (**8**).

substitutions. The synthesized compound **3b** was characterized by single crystal X-ray, and the data are provided in the ESI† (Fig. 2).

The established method was further employed for the synthesis of C3-hydroxy pyranofused thiophenes (**6**) from the reaction of methylthioglycolate (**2**) and 6-aryl-4-(methylthio)-2-oxo-2*H*-pyran-3-carboxylates (**5**). Instead of the nitrile group, the presence of the ester group at C3 of the pyran ring reduced the reactivity of substrate **5** and slowed the reaction progression. Under the optimized reaction conditions, this reaction afforded a relatively lower yield (65–95%) of C3-hydroxy pyranofused thiophenes (**6a–h**) and required more reaction time (20–24 h) compared to C3-amino pyranofused thiophenes (**3**) (Table 3).

The above-optimized reaction conditions were applied to extend the scope of the reaction by using 2-oxobenzo[*h*]chromenes as precursors. The reaction of 4-(methylthio)-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles (**7**) with methyl thioglycolate (**2**) produced analogous naphtha-fused thienopyran-2-carboxylate products (**8**). The present approach afforded a relatively enhanced yield of products compared to the L-proline-catalyzed methodology reported earlier (Scheme 1).[44]

To investigate the feasibility of reusing the reaction medium, the desired product was filtered off upon completion of the reaction using simple filtration. The filtrate was directly reused for subsequent reactions without any additional purification. Fresh reactants **1a** and **2**, in the same molar ratio, were added to the filtrate without introducing additional base or surfactant, and the reaction was carried out under optimized conditions. It was observed that while the desired product was obtained with only a marginal loss in yield, the reaction time had to be increased. This process was successfully repeated for up to six cycles, although the duration of each subsequent reaction progressively increased (Fig. 3).

The mechanism for the conversion of 6-(aryl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile (**1**) to the corresponding 3-amino thieno[3,2-*c*]pyrans (**3**) has been previously reported by Ram *et al.* under different reaction conditions.[45] To evaluate the role of CTAB and base in the reaction, the reaction was first performed in the absence of both base and surfactant under low to high-temperature conditions, and no product was observed (Scheme 2, entry i). The same reaction was then carried out in water using an equimolar amount of base, and only 52% of the product was observed (Scheme 2, entry ii). This was likely due to
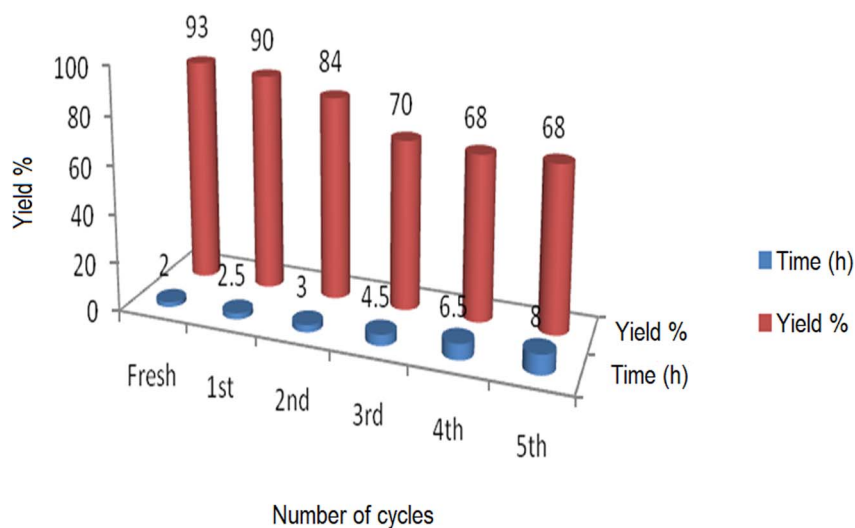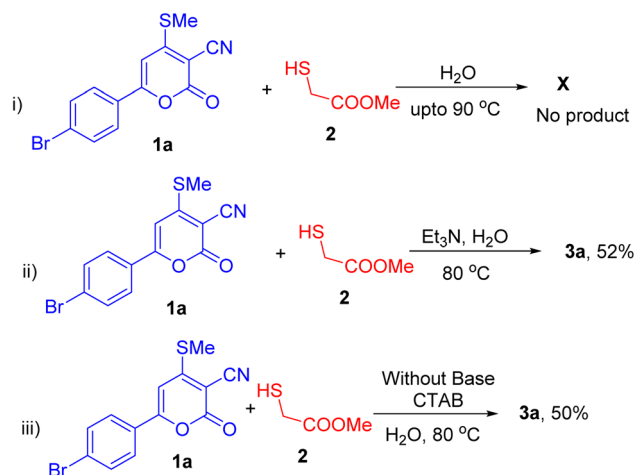

Fig. 3 Reusability of the reaction medium and corresponding reaction time.
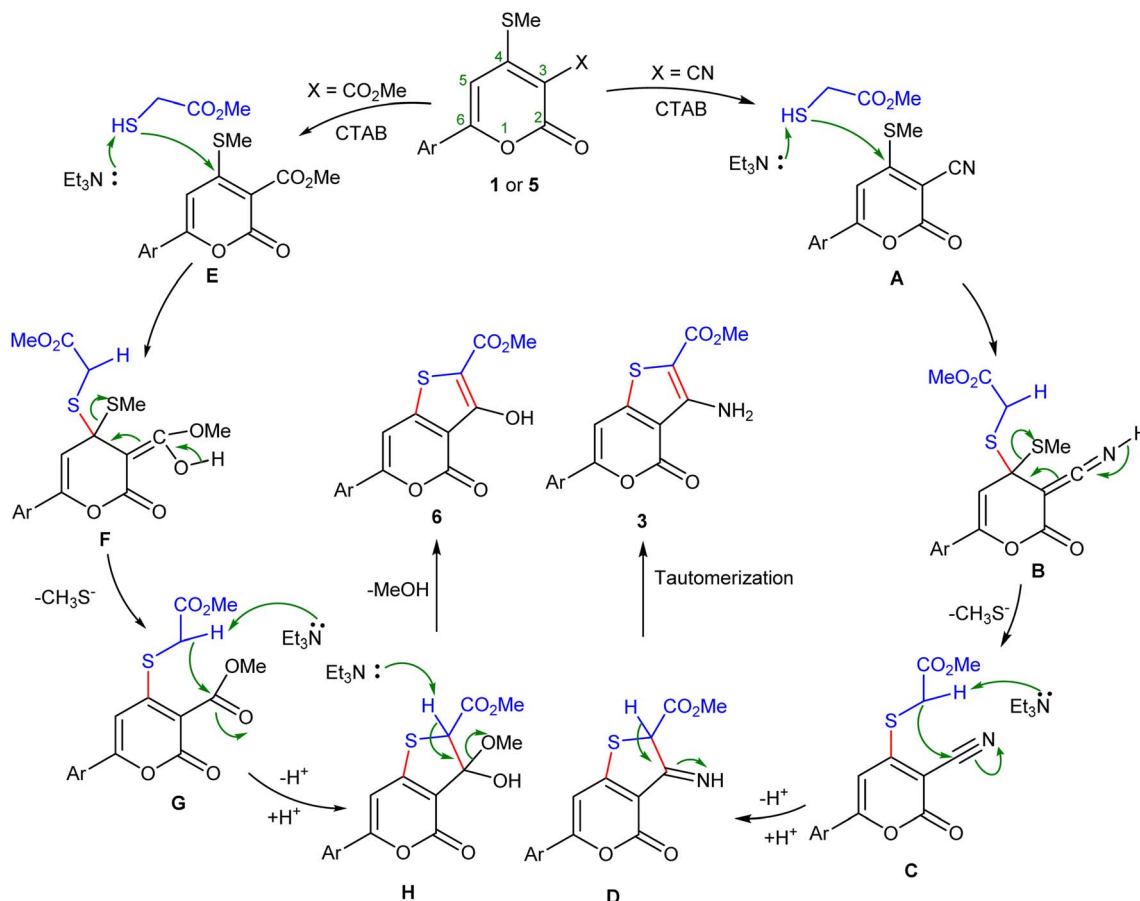
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Scheme 2 Control experiments.

the limited solubility of the reactant under aqueous conditions, which impeded the process. However, the use of the surfactant CTAB in the absence of a base provided only 50% yield of product **3a** (Scheme 2, entry iii). This observation suggested that both base and surfactant were required for the completion of the reaction in an aqueous medium. Since CTAB is also driving

the reaction, the catalytic amount of base is sufficient for a complete reaction.

The results indicated that the reaction proceeded *via* a similar pathway, and hence a plausible mechanism for the formation of pyranothiophenes (**3** & **6**) is depicted in Scheme 3. Examining the structure of methyl thioglycolate (**2**), we observe two nucleophilic centers: one is the S-nucleophile, and the other is the C-nucleophile adjacent to sulfur. The required precursor 2-pyranone contains three electrophilic positions, namely, C-2, C-4, and C-6. Among these, C-4 and C-6 are more prone to nucleophilic attack due to the presence of the nitrile group at position C-3. Most of the nucleophilic attacks were observed at C-6 and C-4, with very few occurring at the C-2 center.[44]

Mechanistically, we proposed that S-nucleophiles from methyl thioglycolate undergo nucleophilic addition at the C4 position of the pyran ring, followed by the loss of methanethiol to generate intermediates **C** and **G**. In the presence of excess base, a further carbanion is generated at the carbon next to sulfur, which undergoes cyclization to generate intermediate **D** and **H**, involving the CN or CO_2CH_3 group, respectively, present at the C-3 position of the pyran ring. Intermediate **D** undergoes tautomerization to afford the desired product **3**. Base-mediated aromatization of intermediate **H**, *via* the loss of methanol, affords the desired product **6**. The regioselectivity of the reaction may be influenced by the polarity of the reaction medium,

Scheme 3 Plausible mechanism for the formation of pyranothiophenes **3** and **6**.

the nature of the nucleophile, and the size of the aromatic substituent. A similar reaction pathway is proposed to involve the formation of naphtha-fused thienopyran-2-carboxylate products (8).

Conclusion

In conclusion, an eco-friendly and efficient approach was developed for the synthesis of thermally stable thieno[3,2-*c*] pyrans under aqueous conditions. The present method afforded higher yields compared to previously reported methods. This is a column-free method, and the pure product is obtained simply by filtration. The reusability of the reaction medium provides an advantage over other methods. These functionalized thieno[3,2-*c*]pyrans are highly fluorescent and can be used as fluorescent probes in bioimaging. Some of their photophysical properties have already been explored by our group. The present approach was also utilized to synthesize benzo[*h*]thieno[3,2-*c*]chromene-2-carboxylate derivatives in good yield. This method is green and sustainable, exhibiting high yields.

Data availability

The data supporting this article have been included as part of the ESI.† Data for some of the compounds are reported in *Biomedicine & Pharmacotherapy*, 2021, **142**, 112084; *New Journal of Chemistry*, 2020, **44**, 12019–12026 and *RSC Advances*, 2016, **6**, 85515–85520.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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