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ARTICLE

Brønsted acidic ionic liquid-catalyzed tandem reaction: an efficient approach towards regioselective synthesis of pyrano[3,2-*c*]coumarins under solvent-free conditions bearing lower E-factors†

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1-Butane sulfonic acid-3-methylimidazolium tosylate, [BSMIM]OTs is found to be a remarkable catalyst for the tandem cyclization of 4-hydroxycoumarin with chalcones for the syntheses of pyrano[3,2-*c*]coumarins under solvent-free conditions. The developed protocol is applicable for the construction of biologically important pyranocoumarins from easily accessible chalcones having various substituents. This reaction possibly proceeds through Michael addition followed by cyclization. The feasibility of the catalyst recycling is also demonstrated. This method produced only water as the byproduct and represents a green synthetic protocol. The catalytic reaction proceeded very smoothly under solvent-free conditions and showed high regioselectivity. Clean reaction, non-chromatographic purification technique, easily accessible reactants, metal and solvent-free and environmentally friendly reaction conditions are the notable advantages of this procedure. In addition, this method possesses lower E-Factors.

Introduction

Tandem reactions are one of the most powerful and atom economical methodologies in modern organic synthesis.[1] The conjugate addition of nucleophiles to α,β-unsaturated compounds (such as α,β-unsaturated carbonyl compounds, esters, nitriles, phosphates, sulfones, and nitroalkenes) is known as the Michael addition.[2] These reactions usually provide processes in a more efficient and environmentally benign manner than conventional procedures by omitting the steps of separation and purification of the reaction intermediates. It is a versatile method for carbon-carbon and carbon-heteroatom bond formations. Both Michael and hetero-Michael additions are widely used in inter- and intramolecular reactions to provide biologically important scaffolds. α,β-Unsaturated ketones are easily accessible from readily available aldehydes and ketones by the condensation reaction. These are good Michael acceptors and have been used for the construction of biologically important scaffolds by exploring their bielectrophilic properties in tandem fashion.[3]

Room-temperature ionic liquids (RTILs) have been explored as greener alternatives to the volatile organic solvents due to their unique properties, such as negligible vapor pressure, high thermal stability, large liquid temperature range, easy recyclability, excellent chemical stability, and strong dissolving power for a wide range of organic and inorganic molecules.[4] However, their uses in large quantities as solvents have limitations such as combustibility, biodegradability, toxicity, and high cost.[5] As a consequence, now a days ionic liquids are generally prepared in such a way that they can act as a proper working system rather than only as media for organic transformations.[6] By changing the cations and/or anions, the properties of ILs can be turned into many different ways. So far, a large number of functionalized ILs has been prepared for different purposes by choosing the appropriate cations and anions.[7]

After the report by Forbes and Davis for the synthesis of the new class of phosphonium- and imidazolium ion-based ionic liquids equipped with a pendant acidic sulfonic acid moiety, Brønsted acidic ionic liquids (BAILs) have drawn a considerable attention in the field of catalysis.[8] BAILs are more preferable over the mineral acids as BAILs show strong acidity with usual properties of ionic liquids. As a result many transformations have been carried out involving acidic proton of these ILs. Majority of these reported methodologies rely on this on the acidic proton. In this context, it is noteworthy to mention that during last few years we are actively engaged in the field of catalysis using BAILs as well as imidazole based zwitterions.[9]

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†Electronic Supplementary Information (ESI) available: [X-ray crystallographic data for **3n**, E-factor calculations, copies of ^{1}H and ^{13}C NMR spectra]. See DOI: 10.1039/x0xx00000x

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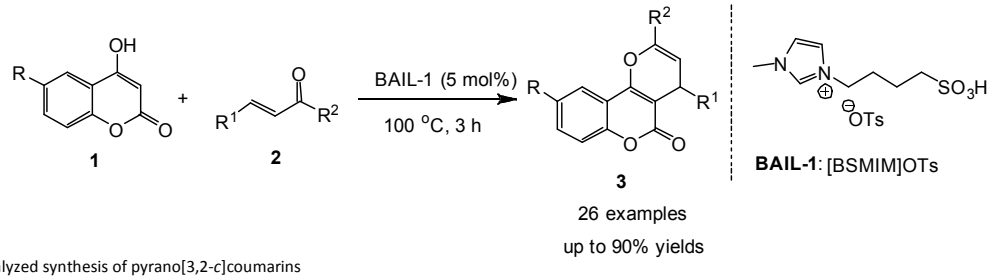
The concept of sustainable development now plays an important role in deciding strategies for chemical synthesis and, consequently, the search for efficient, economic and eco-friendly synthetic methods has become a major concern. In 1992, the E-Factor, or Environmental Impact Factor, was introduced by Roger Sheldon.[10] This metric helps to quantify the amount of waste generated per kilogram of product. It is a means to assess the "environmental acceptability" of a manufacturing process. It has been well accepted that solvents are the main reason for an insufficient E-factor, especially in the synthesis of fine chemicals and pharmaceutical industries.[11] Based on the current working practice with special emphasize on Green Chemistry, it is now often claimed that "the best solvent is no solvent". The crucial advantages of solvent-free reactions are cost saving, by easy work-up, purification, and remarkable rate acceleration with less energy consumption. Owing these importances, a library of organic reactions has been carried out under solvent and catalyst-free conditions in the last decade for the synthesis of various biologically active compounds.[12]

Pyranocoumarin derivatives are a class of fused oxygen containing heterocycles that have drawn much attention due to their potential biological and pharmaceutical activities including antifungal, insecticidal, anti-cancer, anti-HIV, anti-inflammatory, antioxidants, and antibacterial activities.[13] Pyranocoumarin scaffolds are also important in medicinal chemistry for the treatment of skin disorder.[14] A large number of pyranocoumarin derivatives have been isolated from nature having several structural arrays between the coumarin and the pyran rings.[15] Particularly a few important pyranocoumarins are xanthyletin (predominantly isolated from *Zanthoxylum americanum*), khellactone (isolated from *Ligusticum elatum*), arisugacins, and pyripyropenes.[16]

Considering these important uses, their syntheses have been received much attention in the field of medicinal and pharmaceutical chemistry. A number of methodologies for the synthesis of this important framework has been developed by various groups.[17] Most of the methodologies were developed *via* the reaction of 4-hydroxycoumarin with various types of electrophiles such as 1,3-diarylallylic compounds,[17a] α,β-unsaturated aldehydes[17b–d] or ketones[17e,f] and propargylic alcohols.[17g,h] Various catalysts as well as reagents have been used for tandem reaction between 4-hydroxycoumarin and α,β-unsaturated carbonyl compounds such as Brønsted acid,[17c] $POCl_3$,[17e] $AuCl_3$/3AgOTf,[17f] etc. Multicomponent reaction (MCR) strategies have also been employed to synthesize pyranocoumarins.[18] However, most of these methodologies have been developed using expensive reagents (for example $AuCl_3$/3AgOTf is highly expensive), Brønsted acid which is not easily available and $POCl_3$ which is not environmentally friendly. In addition, regio-selectivity is also a major issue for these cyclizations. Therefore, finding a new methodology for the synthesis of pyrano[3,2-*c*]coumarins in terms of efficiency, operational simplicity, availability of reagents, and economic practicability is highly desirable. As a part of our ongoing program on catalysis by ionic liquid,[9] herein we report the catalytic effect of Brønsted acidic task specific ionic liquid, 1-butane sulfonic acid-3-methylimidazolium tosylate, [BSMIM]OTs (BAIL-1) on the tandem reaction between 4-hydroxycoumarin with α,β-unsaturated carbonyl compounds for the formation of pyrano[3,2-*c*]coumarins (Scheme 1). The reactions proceeded under neat conditions and no need to perform column chromatography for purification.



Scheme 1 BAIL-catalyzed synthesis of pyrano[3,2-*c*]coumarins

Results and Discussion

For the initial study, 4-hydroxycoumarin **1a** and 3-phenyl-1-(*p*-tolyl)prop-2-en-1-one **2a** were taken as the model substrates to optimize the reaction conditions employing 5 mol% 1-butane sulfonic acid-3-methylimidazolium tosylate, [BSMIM]OTs (BAIL-1) as the catalyst. Initially the reaction was carried out in various organic solvents such as DMF, DMSO, methanol, ethanol, toluene, polyethylene glycol (PEG), 1,4-dioxane, DCE, etc. as well as in aqueous medium. The results are summarized in Table 1. Either no formation or trace amount of the desired product was observed in DMF, DMSO, water and DCE (Table 1, entries 1–3, 9). In case of ethanol, methanol, toluene, PEG and dioxane the desired product was obtained in 18-44% yields (Table 1, entries 4–8). The targeted product was obtained with maximum yield (84%) under solvent-free conditions at 100 °C for 3 h (Table 1, entry 10). These results indicate the detrimental effect of the solvents for this transformation. Next the effects of reaction time and temperature on the reaction were also investigated. No significant amount of the desired product was formed when the reaction was carried out at room temperature (Table 2, entry 1). The best effective reaction temperature was found to be 100 °C (Table 2, entry 4) and the yield of the reaction did not improve by increasing the reaction time from 3 h to 6 h (Table 2, entry 5). Increasing the temperature was not beneficial (Table

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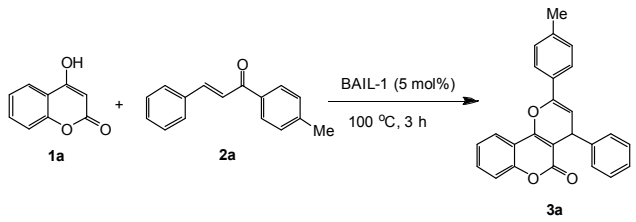
2, entry 6) while decreasing the reaction temperature decreased the yield of the reaction (Table 2, entries 2 & 3).

Table 1 Screening of the solvent effects[a]



Entry	Solvents (2 mL)	Yields[b] (%)
1	DMF	<5
2	DMSO	<5
3[c]	Water	<5
4[c]	EtOH	18
5[c]	MeOH	23
6	Toluene	44
7	PEG	24
8[c]	Dioxane	30
9[c]	DCE	<5
10	Neat	84

[a] Reaction conditions: A mixture of **1a** (1 mmol) and **2a** (1 mmol) was heated at 100 °C for 3 h. [b] Isolated yield. [c] Under reflux.

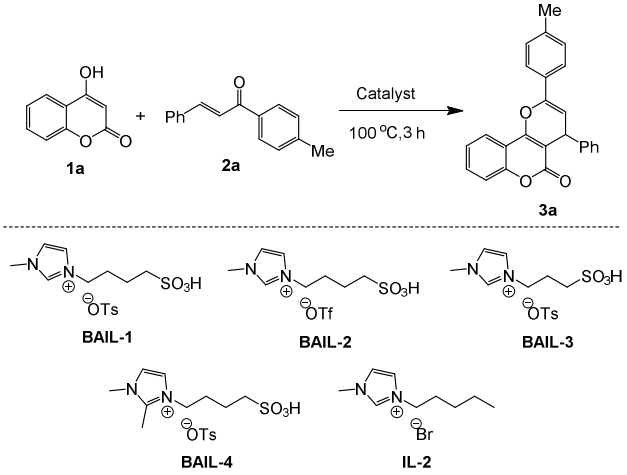
We have examined few other ionic liquids (ILs) synthesized in our laboratory as shown in Table 3. It has been observed that other ILs (BAIL-2, BAIL-3, BAIL-4 and IL-2) are not effective like BAIL-1 for this tandem cyclization process. When 5 mol% of BAIL-2 is used (Table 3, entry 2) the yield is considerably lower (72%) than BAIL-1 (84%). Similarly BAIL-3 and BAIL-4 were also less effective and afforded the desired product with 76% and 65% yields respectively (Table 3, entries 3 & 4). The yields of the reaction decreased when the chain length of the ionic liquid (BAIL-3) was reduced (Table 3, entry 3).[19] No significant amount of product was obtained using IL-2 (Table 3, entry 5). Accordingly, we chose BAIL-1 as catalyst for this tandem cyclization. Finally, the catalyst loading was checked under these reaction conditions using BAIL-1 as the catalyst for the same reaction. We have observed that 5 mol% of BAIL-1 afforded better yield (84%) compared to that of 2 mol% (72% yield) (Table 3, entry 6). Similarly on using 10 mol% of the catalyst no improvement of the yield was observed (Table 3, entry 7). Other acid catalysts such as Brønsted once like *p*-TSA and H_2SO_4 were not effective for this reaction and gave 52% and 43% yields respectively (Table 3, entries 8 & 9). In the absence of any catalyst no conversion has been detected (Table 3, entry 10). Thus the optimal yield (84%) was obtained when the reaction was carried out employing 5 mol% BAIL-1 at 100 °C under solvent-free conditions for 3 h.

Table 2 Temperature effect on the tandem cyclization reaction[a]

Entry	Temp. (°C)	Time (h)	Yields (%)[b]
1	RT	24	<10
2	60	3	48
3	80	3	67
4	100	3	84
5	100	6	84
6	120	3	81

[a] Reaction conditions: A mixture of **1** (1 mmol), **2a** (1 mmol) and BAIL-1 (5 mol%). [b] Isolated yields.

Table 3 Effect of various ionic liquids and catalyst loading[a]



Entry	Catalyst	Catalyst loading (mol%)	Yields (%)[b]
1	BAIL-1	5	84
2	BAIL-2	5	72
3	BAIL-3	5	76
4	BAIL-4	5	65
5	IL-2	5	<10
6	BAIL-1	2	72
7	BAIL-1	10	84
8	*p*-TSA[c]	10	52
9	H_2SO_4	10	43
10	No Catalyst	--	ND[d]

[a] Reaction conditions: Carried out with 0.5 mmol of **1a** and 0.5 mmol of **2a** in the presence of various catalysts under neat conditions. [b] Isolated yields. [c] p-TSA = *para*-toluenesulfonic acid. [d]ND = not detected in TLC.

After getting the optimized reaction conditions in hand, various chalcones (**2**) were introduced to react with 4-hydroxycoumarin (**1a**) as well as substituted 4-hydroxycoumarin to prove the general applicability of this methodology. First, the effect of substituents on the both phenyl moieties of chalcone was tested. The results are summarized in Table 4. In the most cases the desired products were obtained with good yields (**3a**–**3r**). The chalcones bearing electron donating substituents like –Me, –OMe (**3a**, **3c**, **3k**, **3o**, **3p**, **3q** & **3r**) and electron withdrawing substituents such as –I, –Cl, –F, –Br, $–NO_2$ reacted well to afford the corresponding pyrano[3,2-*c*]coumarin derivatives (**3d**, **3e**, **3f**, **3g**, **3l**, **3m**, **3q** & **3r**). The acid sensitive group containing chalcone was

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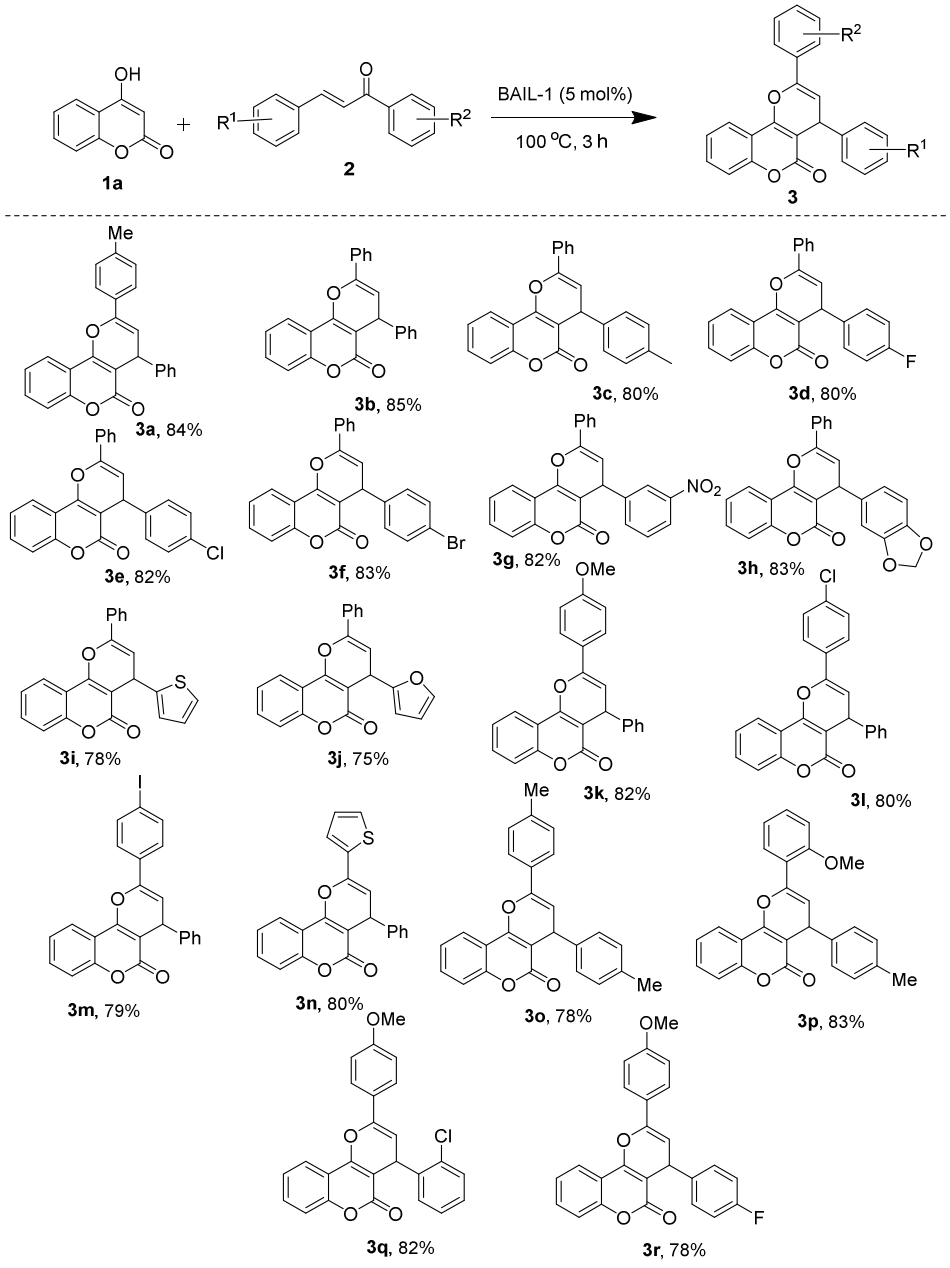
unaffected under the present reaction conditions which signify the mildness of the reaction conditions (**3h**). In addition, heteroaryl chalcones reacted well without accompanying self-condensation or ring cleavage (**3i**, **3j**, **3n**). Then our attention was turned to the use of substituted 4-hydroxycoumarins to prove the general applicability of the reaction conditions as summarized in Table 5. 4-Hydroxycoumarin bearing methyl and hydroxyl groups afforded the corresponding pyranocoumarins with high to excellent yields. Chalcones bearing functional groups like Me (**3t**, **3y**), OMe (**3u**) as well as acid sensitive functionalities were unaffected under the reaction conditions and the desired products were obtained in 79–85% yields.

Table 4 Synthesis of various pyrano[3,2-*c*]coumarin derivatives in presence of BAIL-1[a,b]



[a] Reaction conditions: 1 mmol of **1a** and 1 mmol of **2** in presence of BAIL-1 (5 mol%) at 100 °C for 3 h. [b] All are isolated yields.

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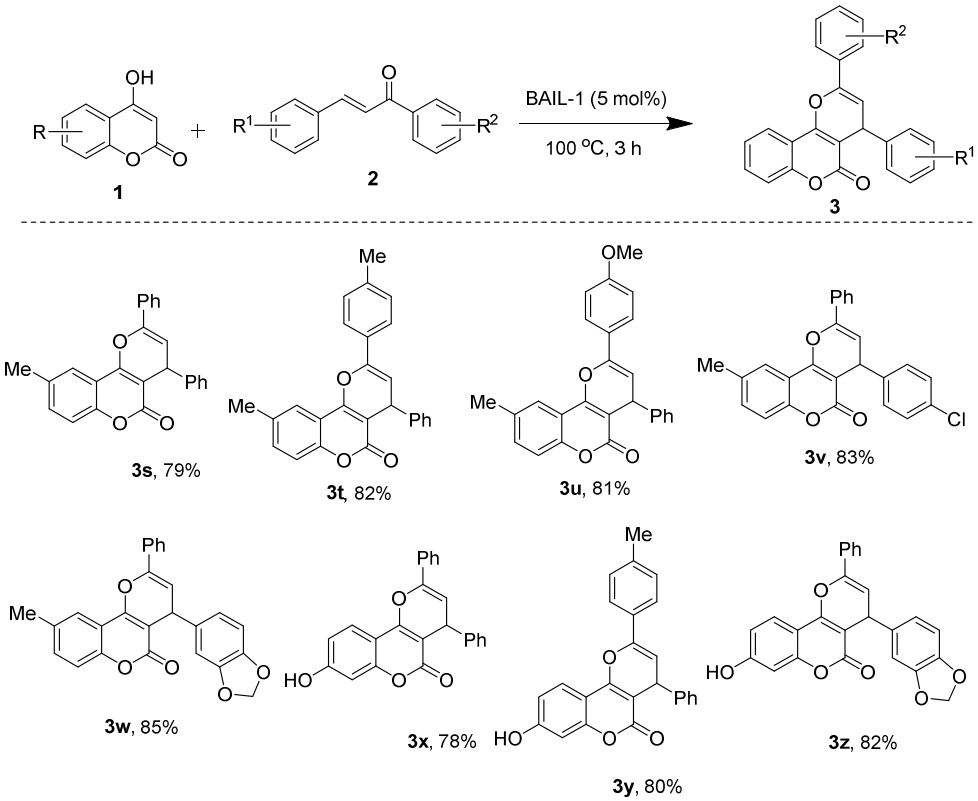
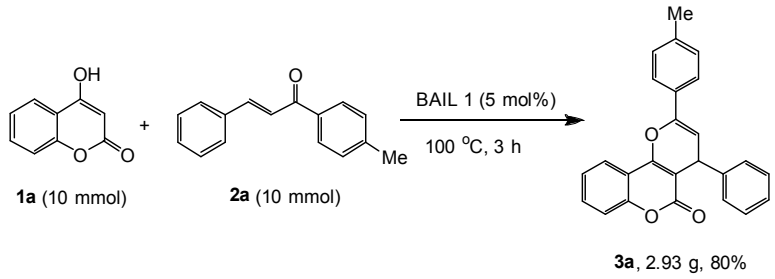
Table 5 Substrate scopes of 4-hydroxycoumarins[a,b]



[a] Reaction conditions: 1 mmol of **1** and 1 mmol of **2** in presence of BAIL-1 (5 mol%) at 100 °C for 3 h. [b] All are isolated yields.



Scheme 2 Gram-scale reaction.

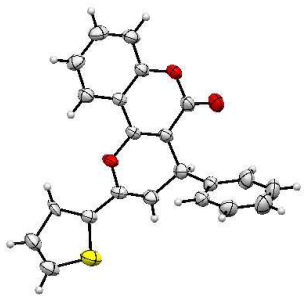


Figure 1 X-ray crystal structure of 4-phenyl-2-(thiophen-2-yl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (**3n**).

All these reactions were carried out in open atmosphere and are not sensitive to air and moisture. In addition, the reaction is highly regio-selective. No other regio-isomer was isolated under the present reaction conditions. For purification no need to perform column chromatography. After completion of the reaction, water was added to the reaction mixture and filtered it off. The pure product was obtained by recrystallizing the residue from hot ethanol. The reaction conditions are mild and give no decomposition of the products or polymerization of the starting materials. We have not observed any by-products for all reaction combinations which are supported with high yields and regio-selectivity of the protocol. All of the known synthesized compounds have been characterized by

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spectral data and the new compounds by spectral and analytical data and the X-ray crystallographic analysis of 4-phenyl-2-(thiophen-2-yl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (**3n**) was performed to confirm the structure of the product as shown in Figure 1.[20]

Furthermore, the potential synthetic applicability of this method was investigated on a gram scale using the model reaction. As shown in Scheme 2, the reaction could afford 2.93 g of **3a** in 80% yield without any significant loss of its efficiency, demonstrating the potential applications of the present method for a large scale synthesis of pyrano[3,2-*c*]coumarin derivatives.

Next, we turn our attention towards the recovery and reusability of the catalyst. For this purpose, we have chosen the reaction of 4-hydroxycoumarin (**1a**) with 3-phenyl-1-(*p*-tolyl)prop-2-en-1-one (**2a**) in presence of 5 mol% acidic ionic liquid (BAIL-1) at 100 °C as the model reaction. After completion of the reaction water was added to the reaction mixture. The reaction mixture was then filtered off and the ionic liquid was recovered by evaporating the water. Pure product was obtained by recrystallizing the residue from hot ethanol. The catalyst maintained its high level of activity even after being recycled five times for synthesizing **3a** as shown in Table 6.

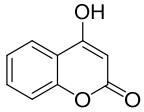
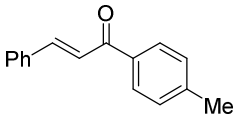
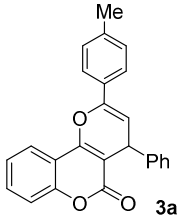
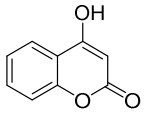
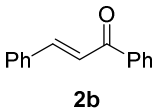
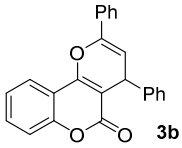
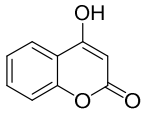
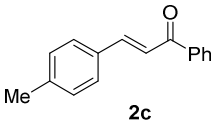
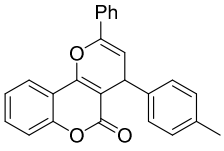
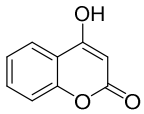
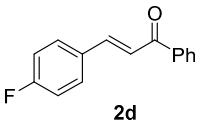
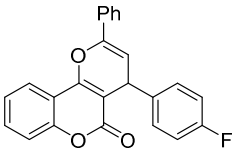
Table 6 Recycling of BAIL for synthesizing **3a**.[a]

No. of cycle	Yields (%)[b]	Catalyst recovery (%)
1	84	96
2	82	92
3	80	89
4	80	85
5	78	82

[a] Carried out with 1 mmol of **1a** and 1 mmol of **2a** in presence of catalyst (BAIL-1) at 100 °C for 3 h. [b] Isolated yields.

In addition, we have developed a greener reaction condition bearing lower E-factors[10,11] in cases of synthesizing the desired products **3** (Table 7, see also ESI) which is consistent with the principles of the atom economy.

Table 7 *E*-Factors in the synthesis of pyrano[3,2-*c*]coumarins (**3**)[a]

#	4-Hydroxycoumarin (1)	Chalcones (2)	Products (3)	Yields[b] (%)	E-Factor (kg waste per kg product)[c]
1	 **1a**	 **2a**	 **3a**	84	0.25
2	 **1a**	 **2b**	 **3b**	85	0.24
3	 **1a**	 **2c**	 **3c**	80	0.31
4	 **1a**	 **2d**	 **3d**	80	0.31

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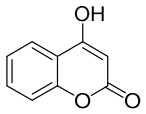
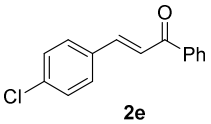
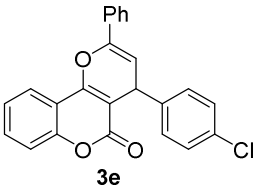
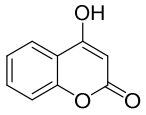
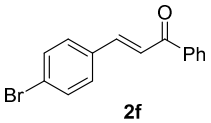
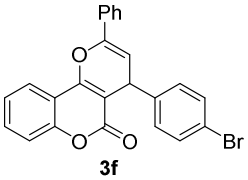
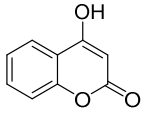
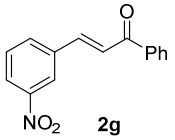
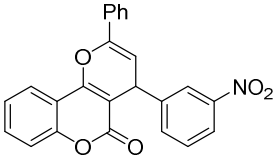
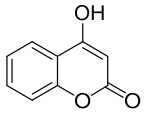
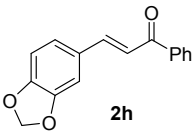
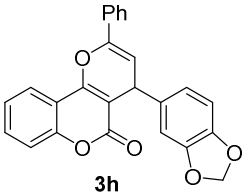
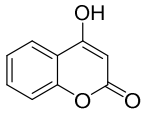
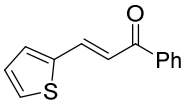
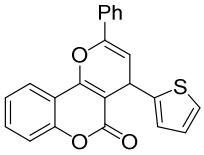
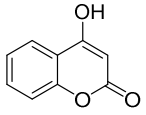
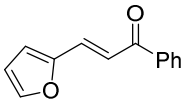
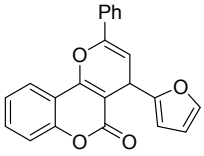
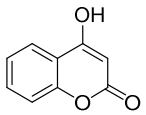
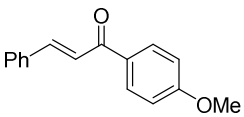
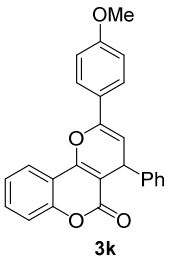
5	 1a	 2e	 3e	82	0.28
6	 1a	 2f	 3f	83	0.26
7	 1a	 2g	 3g	82	0.28
8	 1a	 2h	 3h	83	0.26
9	 1a	 2i	 3i	78	0.35
10	 1a	 2j	 3j	75	0.41
11	 1a	 2k	 3k	82	0.28

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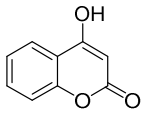
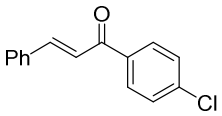
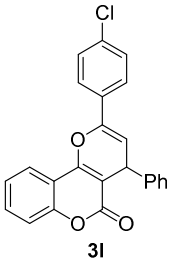
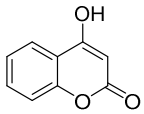
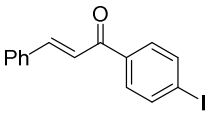
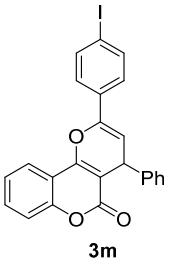
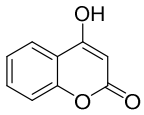
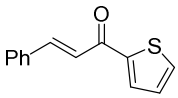
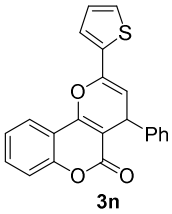
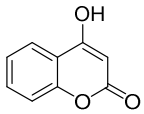
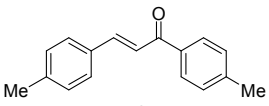
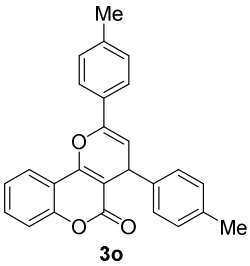
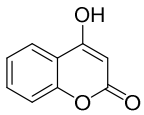
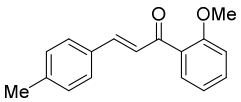
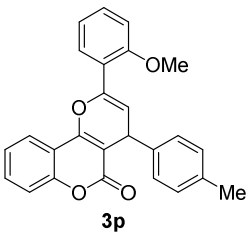
12	 1a	 2l	 3l	80	0.31
13	 1a	 2m	 3m	79	0.31
14	 1a	 2n	 3n	80	0.31
15	 1a	 2o	 3o	78	0.34
16	 1a	 2p	 3p	83	0.26

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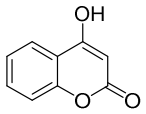
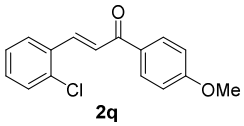
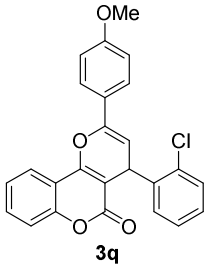
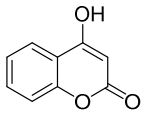
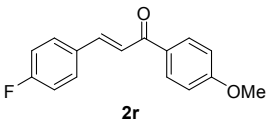
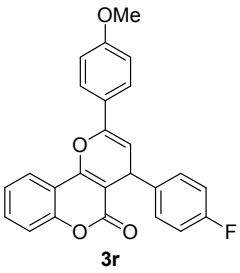
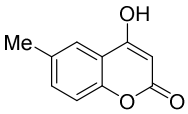
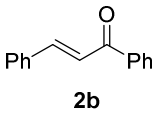
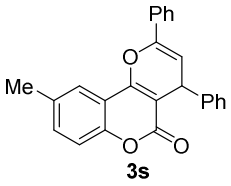
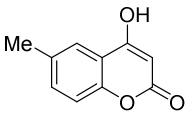
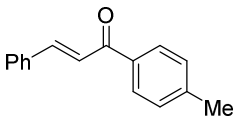
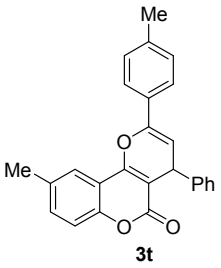
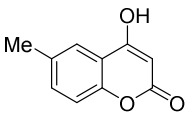
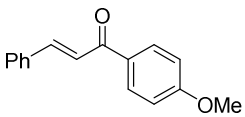
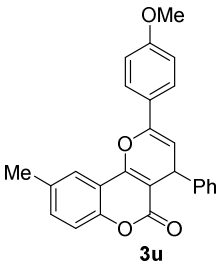
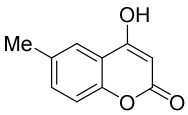
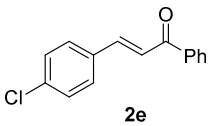
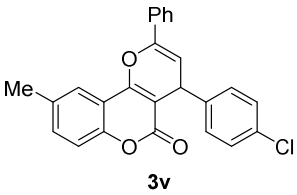
17	 1a	 2q	 3q	82	0.27
18	 1a	 2r	 3r	78	0.34
19	 1b	 2b	 3s	79	0.33
20	 1b	 2a	 3t	82	0.27
21	 1b	 2k	 3u	81	0.29
22	 1b	 2e	 3v	83	0.26

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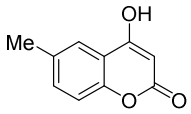
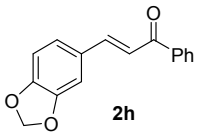
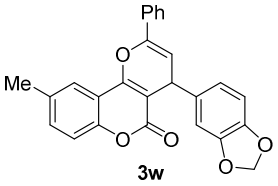
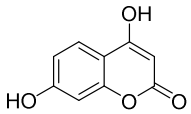
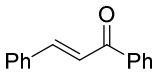
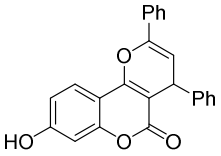
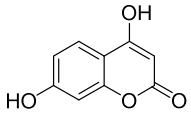
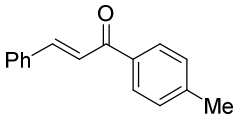
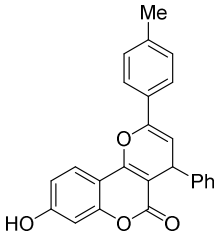
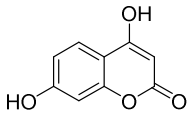
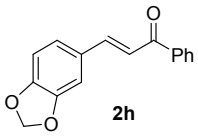
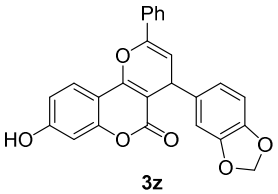
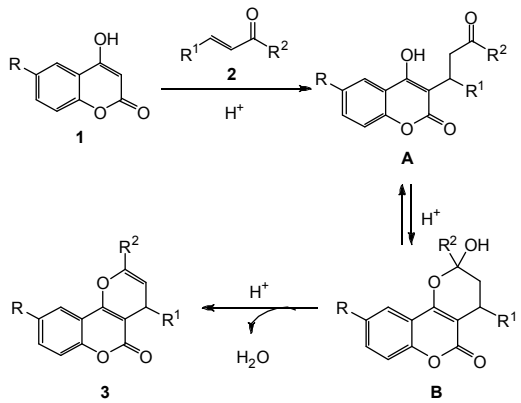
23	 1b	 2h	 3w	85	0.23
24	 1c	 2b	 3x	78	0.34
25	 1c	 2a	 3y	80	0.31
26	 1c	 2h	 3z	82	0.27

[a] All reactions were performed on 1 mmol scale in presence of BAIL-1 (5 mol%) at 100 °C for 3 h. [b] Isolated yields. [c] No solvent was used for further purification and the catalyst was recovered and recycled.

A plausible mechanistic pathway for this tandem reaction is outlined in Scheme 3. Probably the first step is the Michael addition of 4-hydroxycoumarin (**1**) to the α,β-unsaturated ketone (**2**) which gave the intermediate **A**.[17f] The intermediate **A** on intramolecular cyclization afforded the intermediate **B** which finally afforded the pyranocoumarin (**3**) on subsequent removal of water. The acidic ionic liquid activates the unsaturated ketone through protonation of the carbonyl group and increased the electrophilic character at the β-carbon which promote the Michael adduct formation. In addition the acidic ionic liquid also helps to facilitate the intramolecular cyclization step by the protonation of carbonyl group of intermediate **A**.



Scheme 3 Plausible reaction pathway.

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Conclusions

To conclude, we have successfully developed an efficient and regioselective methodology for the synthesis of pyrano[3,2-*c*]coumarin derivatives by the coupling of 4-hydroxycoumarin with chalcones catalyzed by Brønsted acidic ionic liquid (BAIL-1). This tandem reaction proceeds through the Michael addition followed by annulation reaction and only water is produced as the byproduct. A library of pyranocoumarin derivatives having variety of substituents on the pyran moiety have been synthesized employing this atom efficient methodology. During optimization it was estimated that no external solvent was needed to carry out the reaction. The catalyst BAIL-1 is easily recyclable without the significant loss of catalytic activities. The notable advantages of the present methodology are clean reaction, ease of product isolation/purification (no need to use column chromatography), easily accessible reactants, metal and solvent-free and environmentally friendly reaction conditions and water is the only byproduct. These features make this procedure to be a green synthetic protocol. The proposed approach is consistent with the principles of the atom economy, and also allows varying the nature of the substituents in the final compounds in a fairly wide range. We believe that our present methodology will open up a new route for the synthesis of bioactive pyrano[3,2-*c*]coumarin derivatives.

Experimental Section

General. Melting points were determined on a glass disk with an electric hot plate and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were run in DMSO-d_6 and $CDCl_3$ solutions. Commercially available substrates were freshly distilled before the reaction. Solvents, reagents, and chemicals were purchased from Aldrich, Fluka, Merck, SRL, Spectrochem and Process Chemicals. All reactions involving moisture-sensitive reactants were executed using oven-dried glassware. Brønsted acidic ionic liquids were prepared according to the previously reported method.[21]

General procedure for the synthesis of pyrano[3,2-*c*]coumarins

To a mixture of 4-hydroxycoumarin (1 mmol) and α,β-unsaturated ketone (1 mmol), the 5 mol% BAIL-1 was added and the mixture was stirred at 100 °C for 6 h (TLC). After completion of the reaction, water was added to the reaction mixture. Then the product was filtered off and the ionic liquid was recovered by evaporating the water. The recovered ionic liquid was reused for a subsequent fresh batch of the reaction after reactivation. The crude product was recrystallized from hot ethanol to afford the pure product.

Typical procedure for the synthesis of 4-Phenyl-2-(*p*-tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3a)

To a mixture of 4-hydroxycoumarin (**1a**, 1.62 g, 10 mmol) and 3-phenyl-1-(*p*-tolyl)prop-2-en-1-one (**2a**, 2.22 g, 10 mmol), the 5 mol% BAIL-1 was added and the mixture was stirred at 100 ºC for 3 h (TLC). After completion of the reaction, water was added to the reaction mixture. Then the product was filtered off and the crude product was recrystallized from hot ethanol to afford the pure product as white solid in 80% yield (2.93 g).

4-Phenyl-2-(*p*-tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3a).[17f] White solid (307 mg, 84%), mp: 157-158 °C (lit.[17f] mp: 156-158 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03-8.01 (m, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.58-7.54 (m, 1H), 7.45-7.43 (m, 2H), 7.39-7.31 (m, 4H), 7.27-7.22 (m, 3H), 5.79 (d, J = 5.2 Hz, 1H), 4.70 (d, J = 4.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.6, 155.9, 152.9, 147.1, 143.8, 139.5, 132.1, 129.9, 129.5, 128.7, 128.6, 127.3, 124.7, 124.3, 122.8, 116.9, 114.7, 103.8, 103.0, 36.7, 21.5.

2,4-Diphenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3b).[17f] White solid (299 mg, 85%), mp: 171-172 °C (lit.[17f] mp: 170-171 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06-8.04 (m, 1H), 7.78-7.76 (m, 2H), 7.62-7.57 (m, 1H), 7.50-7.34 (m, 9H), 7.28-7.25 (m, 1H), 5.88 (d, J = 5.2 Hz, 1H), 4.74 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.5, 155.8, 152.8, 147.0, 143.6, 132.7, 132.1, 129.4, 128.8, 128.7, 128.6, 127.3, 124.8, 124.3, 122.8, 116.9, 114.6, 103.8(2C), 36.7.

2-Phenyl-4-(*p*-tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3c).[17f] White solid (293 mg, 80%), mp: 186-188 °C (lit.[17f] mp: 188-189 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03-8.01 (m, 1H), 7.64-7.62 (m, 2H), 7.59-7.54 (m, 1H), 7.44-7.30 (m, 6H), 7.27-7.23 (m, 3H), 5.79 (d, J = 4.8 Hz, 1H), 4.70 (d, J = 5.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.6, 155.9, 152.8, 147.0, 143.8, 139.4, 132.0, 129.9, 129.4, 128.7, 128.6, 127.3, 124.7, 124.2, 122.8, 116.9, 114.7, 103.8, 103.0, 36.7, 21.4.

4-(4-Fluorophenyl)-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3d).[17j] White solid (296 mg, 80%), mp: 143-145 °C (lit.[17j] mp: 142-143 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03-8.01 (m, 1H), 7.75-7.73 (m, 2H), 7.61-7.56 (m, 1H), 7.49-7.44 (m, 3H), 7.41-7.34 (m, 4H), 7.02-6.98 (m, 2H), 5.82 (d, J = 4.8 Hz, 1H), 4.71 (d, J = 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.1 (d, $^1J_{C\text{-}F}$ = 244 Hz), 161.6, 155.9, 147.2, 139.4 (d, $^3J_{C\text{-}F}$ = 2 Hz), 132.6, 132.3, 130.2 (d, $^4J_{C\text{-}F}$ = 8 Hz), 129.5, 128.9, 128.6, 128.2, 124.8, 124.4, 122.8, 117.0, 115.5 (d, $^2J_{C\text{-}F}$ = 21 Hz), 114.6, 103.6, 36.0.

4-(4-Chlorophenyl)-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3e).[17g] White solid (296 mg, 80%), mp: 194-196 °C (lit.[17g] mp: 196-197 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03-8.01 (m, 1H), 7.75-7.72 (m, 2H), 7.60-7.56 (m, 1H), 7.49-7.43 (m, 3H), 7.40-7.33 (m, 4H), 7.29-7.27 (m, 2H), 5.80 (d, J = 4.8 Hz, 1H), 4.68 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.5, 155.9, 152.8, 147.2, 142.1, 133.1, 132.5, 132.3, 130.0, 129.5, 129.3, 128.8, 124.8, 124.4, 122.8, 116.9, 114.5, 103.3, 103.2, 36.2.

4-(4-Bromophenyl)-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3f).[17j] White solid (357 mg, 83%), mp: 170-171 °C (lit.[17j] mp: 168-169 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03-8.01 (m, 1H), 7.74-7.72 (m, 2H), 7.61-7.56 (m, 1H), 7.49-7.43 (m, 5H), 7.41-7.29 (m, 4H), 5.80 (d, *J* = 4.8 Hz, 1H), 4.68 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.5, 156.0, 152.9, 147.3, 142.7, 132.5, 132.3, 131.8, 130.4, 129.6, 128.9, 124.8, 124.4, 122.8, 121.3, 117.0, 114.5, 103.3, 103.2, 36.3.

4-(3-Nitrophenyl)-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3g).[17j] White solid (325 mg, 82%), mp: 185-186 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25-8.24 (m, 1H), 8.12-8.04 (m, 2H), 7.82-7.73 (m, 3H), 7.64-7.59 (m, 1H), 7.52-7.35 (m, 6H), 5.80 (d, *J* = 5.2 Hz, 1H), 4.86 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.5, 156.5, 153.0, 148.7, 147.9, 145.8, 134.9, 132.7, 132.3, 129.8, 129.6, 128.9, 128.7, 124.9, 124.6, 123.5, 123.0, 122.5, 117.1, 114.3, 102.4, 36.8.

4-(Benzo[*d*][1,3]dioxol-5-yl)-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3h).[17f] White solid (329 mg, 83%), mp: 176-177 °C (lit.[17f] mp: 177-178 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03-8.00 (m, 1H), 7.74-7.72 (m, 2H), 7.60-7.55 (m, 1H), 7.48-7.34 (m, 5H), 6.91-6.89 (m, 2H), 6.76-6.74 (m, 1H), 5.91 (s, 2H), 5.82 (d, *J* = 5.2 Hz, 1H), 4.63 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.6, 155.8, 152.9, 148.0, 146.9, 146.8, 137.8, 132.7, 132.1, 129.4, 128.8, 124.8, 124.3, 122.8, 121.9, 117.0, 114.7, 109.1, 108.4, 103.9, 103.8, 101.2, 36.4.

2-Phenyl-4-(thiophen-2-yl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3i).[17j] White solid (279 mg, 78%), mp: 170-172 °C (lit.[17j] mp: 168-169 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.98 (m, 1H), 7.77-7.75 (m, 2H), 7.58-7.54 (m, 1H), 7.49-7.43 (m, 3H), 7.38-7.33 (m, 2H), 7.20-7.19 (m, 1H), 7.14-7.13 (m, 1H), 6.97-6.95 (m, 1H), 5.94 (d, *J* = 5.2 Hz, 1H), 5.05 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.7, 155.6, 152.8, 147.8, 147.7, 132.6, 132.3, 129.6, 128.9, 127.2, 125.7, 125.1, 125.0, 124.4, 122.9, 117.0, 114.7, 103.6, 103.0, 31.3.

4-(Furan-2-yl)-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3j): White solid (256 mg, 75%), mp: 126-127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02-8.00 (m, 1H), 7.75-7.73 (m, 2H), 7.61-7.57 (m, 1H), 7.48-7.36 (m, 5H), 7.32-7.31 (m, 1H), 6.33-6.31 (m, 1H), 6.26-6.25 (m, 1H), 5.85 (d, *J* = 5.2 Hz, 1H), 4.88 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.6, 156.7, 155.1, 151.0, 148.0, 142.1, 139.9, 132.3, 129.5, 128.8, 128.3, 124.9, 124.4, 122.9, 117.0, 114.7, 110.8, 106.8, 100.9, 30.4. Anal. Calcd For $C_{22}H_{14}O_4$: C, 77.18; H, 4.12%; Found: C, 77.12; H, 4.05%;

2-(4-Methoxyphenyl)-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3k).[17i] White solid (313 mg, 82%), mp: 154-155 °C (lit.[17i] mp: 156-157 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86-7.84 (m, 1H), 7.53-7.50 (m, 2H), 7.42-7.38 (m, 1H), 7.30-7.28 (m, 2H), 7.23-7.16 (m, 4H), 7.11-7.08 (m, 1H), 6.84-6.81 (m, 2H), 5.55 (d, *J* = 4.8 Hz, 1H), 4.52 (d, *J* = 4.8 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.5, 160.4, 155.7, 152.7, 146.6, 143.8, 131.9, 128.6, 128.5, 127.1, 126.1, 125.1, 124.1, 122.6, 116.7, 114.6, 114.0, 103.7, 101.9, 55.4, 36.6.

2-(4-Chlorophenyl)-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3l).[17i] White solid (309 mg, 80%), mp: 171-173 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95-7.93 (m, 1H), 7.63-7.60 (m, 2H), 7.55-7.51 (m, 1H), 7.38-7.34 (m, 5H), 7.30-7.17 (m, 4H), 5.78 (d, *J* = 4.8 Hz, 1H), 4.65 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.4, 155.7, 152.8, 146.1, 143.4, 135.2, 132.2, 131.2, 129.7, 129.0, 128.8, 128.5, 127.4, 126.0, 124.3, 122.7, 117.0, 114.5, 104.3, 36.7.

2-(4-Iodophenyl)-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3m*)*: White solid (378 mg, 79%), mp: 214-215 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.88 (m, 1H), 7.71-7.68 (m, 2H), 7.52-7.47 (m, 1H), 7.39-7.36 (m, 2H), 7.33-7.30 (m, 3H), 7.28-7.22 (m, 3H), 7.18-7.16 (m, 1H), 5.77 (d, *J* = 4.8 Hz, 1H), 4.61 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.4, 155.7, 152.8, 146.2, 143.3, 138.0, 137.9, 132.2, 128.8, 128.5, 127.4, 126.4, 124.3, 122.7, 117.0, 114.5, 104.5, 103.7, 95.2, 36.7. Anal. Calcd For $C_{24}H_{15}IO_3$: C, 60.27; H, 3.16%; Found: C, 60.21; H, 3.24%.

4-Phenyl-2-(thiophen-2-yl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3n): White solid (286 mg, 80%), mp: 201-202 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.98 (m, 1H), 7.59-7.55 (m, 1H), 7.43-7.31 (m, 8H), 7.25-7.22 (m, 1H), 7.11-7.08 (m, 1H), 5.75 (d, *J* = 4.8 Hz, 1H), 4.68 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.4, 155.6, 152.9, 143.4, 143.1, 136.2, 132.2, 128.8, 128.6, 127.8, 127.4, 126.0, 124.4, 124.3, 122.8, 116.9, 114.4, 103.9, 102.8, 36.6. Anal. Calcd For $C_{22}H_{14}O_3S$: C, 73.73; H, 3.94%; Found: C, 73.78; H, 3.99%.

2,4-Di-*p*-tolyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3o):[17a] Light yellow oily (296 mg, 78%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03-8.00 (m, 1H), 7.63-7.61 (m, 2H), 7.58-7.51 (m, 2H), 7.39-7.24 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.78 (d, *J* = 5.2 Hz, 1H), 4.66 (d, *J* = 4.8 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.7, 155.8, 152.9, 147.0, 143.3, 141.0, 139.4, 137.0, 132.0, 129.8, 129.4, 128.5 (2C), 124.7, 124.2, 122.8, 116.9, 114.8, 103.2, 36.3, 21.4, 21.2.

2-(2-Methoxyphenyl)-4-(*p*-tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3p): White solid (329 mg, 83%), mp: 144-145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96-7.94 (m, 1H), 7.76-7.73 (m, 1H), 7.54-7.51 (m, 1H), 7.40-7.37 (3H), 7.35-7.31 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.10-7.06 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.07 (d, *J* = 4.8 Hz, 1H), 4.71 (d, *J* = 5.2 Hz, 1H), 3.87 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.7, 157.3, 156.0, 152.8, 144.4, 141.0, 136.7, 131.8, 130.3, 129.3, 128.5, 128.4, 124.1, 122.9, 122.0, 120.6, 116.8, 114.9, 111.5, 108.5, 103.8, 55.7, 36.3, 21.2. Anal. Calcd For $C_{26}H_{20}O_4$: C, 78.77; H, 5.09%; Found: C, 78.67; H, 5.02%.

4-(2-Chlorophenyl)-2-(4-methoxyphenyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3q): White solid (341 mg, 82%), mp: 166-167 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04-8.02 (m, 1H), 7.64-7.61 (m, 3H), 7.42-7.37 (m, 3H), 7.20-7.16 (m, 3H), 6.96-6.93

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(m, 2H), 5.74 (d, *J* = 4.4 Hz, 1H), 5.21 (d, *J* = 4.4 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 160.6, 157.3, 153.1, 146.8, 141.0, 133.1, 132.3, 131.1, 130.0, 129.6, 128.3, 127.9, 127.5, 126.3, 124.3, 122.8, 117.1, 114.5, 114.1, 102.2, 100.5, 55.5, 34.0. Anal. Calcd For $C_{25}H_{17}ClO_4$: C, 72.03; H, 4.11%; Found: C, 71.96; H, 4.04%.

4-(4-Fluorophenyl)-2-(4-methoxyphenyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3r): White solid (312 mg, 78%), mp: 155-157 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 8.01-7.99 (m, 1H), 7.67-7.65 (m, 2H), 7.58-7.55 (m, 1H), 7.40-7.32 (m, 4H), 7.01-6.96 (m, 4H), 5.67 (d, *J* = 4.8 Hz, 1H), 4.67 (d, *J* = 4.8 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 162.0 (d, $^1J_{C\text{-}F}$ = 245 Hz), 161.6, 160.6, 155.8, 152.8, 147.0, 139.7 (d, $^3J_{C\text{-}F}$ = 3 Hz), 132.1, 130.2 (d, $^4J_{C\text{-}F}$ = 8 Hz), 126.2, 125.2, 124.3, 122.8, 116.9, 115.4 (d, $^2J_{C\text{-}F}$ = 21 Hz), 114.6, 114.2, 103.7, 101.7, 55.5, 36.0. Anal. Calcd For $C_{25}H_{17}FO_4$: C, 74.99; H, 4.28%; Found: C, 74.91; H, 4.34%.

9-Methyl-2,4-diphenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3s).[17f] White solid (289 mg, 79%), mp: 215-216 °C (lit.[17f] mp: 216-218 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.78-7.73 (m, 3H), 7.47-7.36 (m, 6H), 7.33-7.29 (m, 2H), 7.24-7.22 (m, 2H), 5.84 (d, *J* = 4.8 Hz, 1H), 4.71 (d, *J* = 4.8 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 161.9, 156.0, 151.1, 147.1, 143.8, 134.1, 133.2, 132.9, 129.9, 129.4, 128.8, 128.7, 128.6, 128.3, 127.3, 124.9, 122.4, 116.7, 104.0, 36.8, 21.2.

9-Methyl-4-phenyl-2-(*p*-tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3t). White solid (312 mg, 82%), mp: 197-198 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.86-7.83 (m, 1H), 7.76 (s, 1H), 7.63-7.61 (m, 2H), 7.42-7.37 (m, 3H), 7.31-7.28 (m, 3H), 7.24-7.22 (m, 2H), 5.78 (d, *J* = 4.8 Hz, 1H), 4.69 (d, *J* = 4.8 Hz, 1H), 2.49 (s, 3H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 161.9, 155.9, 151.1, 147.2, 143.9, 139.4, 134.0, 133.1, 129.5, 129.4, 128.7, 128.6, 128.4, 127.6, 127.3, 124.8, 122.4, 116.7, 103.1, 36.8, 21.5, 21.2. Anal. Calcd $C_{26}H_{20}O_3$: C, 82.08; H, 5.30%; Found: C, 82.02; H, 5.35%.

2-(4-Methoxyphenyl)-9-methyl-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3u). White solid (321 mg, 81%), mp: 176-177 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.76 (s, 1H), 7.68-7.65 (m, 2H), 7.41-7.20 (m, 7H), 6.99-6.97 (m, 2H), 5.70 (d, *J* = 4.8 Hz, 1H), 4.68 (d, *J* = 5.2 Hz, 1H), 3.86 (s, 3H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 161.9, 160.5, 155.9, 151.1, 144.0, 134.0, 133.1, 128.7, 128.6, 127.2, 126.3, 125.5, 122.4, 116.7, 114.4, 114.2, 103.8, 102.2, 89.9, 55.6, 36.7, 21.2. Anal. Calcd For Chemical Formula: $C_{26}H_{20}O_4$: C, 78.77; H, 5.09%; Found: C, 78.67; H, 5.02%.

4-(4-Chlorophenyl)-9-methyl-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3v). White solid (332 mg, 83%), mp: 173-174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.74-7.69 (m, 3H), 7.45-7.42 (m, 2H), 7.33-7.31 (m, 2H), 7.25-7.22 (m, 3H), 7.16-7.14 (m, 1H), 7.11-7.09 (m, 1H), 5.77 (d, *J* = 4.8 Hz, 1H), 4.71 (d, *J* = 5.2 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 161.8, 156.0, 151.1, 142.3, 134.2, 133.4, 130.0, 129.5, 128.9, 128.4, 128.2, 127.9, 127.8, 125.8, 124.9, 122.4, 116.8, 114.4, 103.4, 36.2, 21.2. Anal. Calcd For $C_{25}H_{17}ClO_3$: C, 74.91; H, 4.27%; Found: C, 74.85; H, 4.21%.

4-(Benzo[*d*][1,3]dioxol-5-yl)-9-methyl-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3w). White solid (348 mg, 85%), mp: 205-206 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.76-7.72 (m, 3H), 7.49-7.36 (m, 4H), 7.24 (d, *J* = 8.4 Hz, 1H), 6.90-6.87 (m, 2H), 6.76-6.74 (m, 1H), 5.91 (s, 2H), 5.81 (d, *J* = 4.8 Hz, 1H), 4.62 (d, *J* = 4.8 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 161.8, 155.8, 151.1, 148.0, 147.0, 146.8, 138.0, 134.1, 133.2, 132.9, 129.4, 128.8, 124.9, 122.4, 121.9, 116.7, 114.3, 109.1, 108.4, 104.0, 103.7, 101.2, 36.4, 21.2. Anal. Calcd For $C_{26}H_{18}O_5$: C, 76.09; H, 4.42%; Found: C, 76.02; H, 4.34%.

8-Hydroxy-2,4-diphenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3x). White solid (287 mg, 78%), mp: 233-235 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): *δ* 10.68 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.85-7.82 (m, 2H), 7.50-7.43 (m, 3H), 7.32-7.31 (m, 4H), 7.23-7.20 (m, 1H), 6.95-6.92 (m, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 6.13 (d, *J* = 4.8 Hz, 1H), 4.58 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): *δ* 161.7, 161.0, 156.1, 154.2, 145.4, 144.2, 132.1, 129.2, 128.8, 128.6, 128.0, 126.8, 124.4, 124.3, 113.5, 105.7, 104.1, 102.3, 99.3, 35.8. Anal. Calcd For $C_{24}H_{16}O_4$: C, 78.25; H, 4.38%; Found: C, 78.20; H, 4.29%.

8-Hydroxy-4-phenyl-2-(*p*-tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3y). White solid (305 mg, 80%), mp: 244-245 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): *δ* 10.69 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.31-7.26 (m, 7H), 6.95-6.92 (m, 1H), 6.76 (d, *J* = 2.0 Hz, 1H), 6.05 (d, *J* = 5.2 Hz, 1H), 4.56 (d, *J* = 4.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz): *δ* 161.6, 160.9, 156.1, 154.0, 145.3, 144.2, 138.7, 129.3, 128.5, 127.9, 126.7, 124.2(2C), 113.4, 105.7, 103.1, 102.2, 99.2, 71.1, 35.7, 20.8. Anal. Calcd For $C_{25}H_{18}O_4$: C, 78.52; H, 4.74%; Found: C, 78.58; H, 4.64%.

4-(Benzo[*d*][1,3]dioxol-5-yl)-8-hydroxy-2-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (3z). White solid (338 mg, 82%), mp: 215-218 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): *δ* 10.69 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.83-7.81 (m, 2H), 7.49-7.42 (m, 3H), 6.94-6.91 (m, 1H), 6.87-6.82 (m, 2H), 6.76-6.74 (m, 2H), 6.08 (d, *J* = 4.8 Hz, 1H), 5.96 (s, 2H), 4.50 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): *δ* 161.6, 161.0, 156.0, 154.1, 147.3, 146.1, 145.2, 138.3, 132.0, 129.2, 128.8, 124.3, 124.2, 121.1, 113.4, 108.5, 108.2, 105.7, 104.1, 102.2, 100.9, 99.3, 35.4. Anal. Calcd For $C_{25}H_{16}O_6$: C, 72.81; H, 3.91%; Found: C, 72.71; H, 3.84%.

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View Article Online
DOI: 10.1039/C7GC01158J

Notes and references

1 (*a*) L. F. Tietze, G. Brasche and K. Gericke, in: *Domino Reactions in Organic Synthesis*, Wiley-VCH, Weinheim, 2006; (*b*) L. Q. Lu, J. R. Chen and W. J. Xiao, *Acc. Chem. Res*., 2012, **45**, 1278; (*c*) K. C. Nicolaou, T. Montagnon and S. A. Snyder, *Chem. Commun*., 2003, 551; (*d*) L. F. Tietze, *Chem. Rev*., 1996, **96**, 115; (*e*) K. C. Nicolaou and E. J. Sorensen, in: *Classics in Total Synthesis 1*, Wiley-VCH, Weinheim, 1996, pp 641; *(f*) T. Muller, in: *Metal Catalyzed Cascade Reactions*, Vol. 19, (Ed.: T. Muller), Springer, Berlin, 2006, p 149; (*g*) S. F. Kirsch, Synthesis, 2008, 3183.

2 P. Perlmutter, in: *Conjugate Addition Reactions in Organic Synthesis*, Pergamon Press, Oxford, 1992.

3 (*a*) A. Sarkar, S. R. Roy and A. K. Chakraborti, *Chem. Commun*., 2011, **47**, 4538; (*b*) M. Rahman, A. Majee and A. Hajra, *J. Chem. Res*., 2009, 178; (*c*) A. K. Bagdi, A. Majee and A. Hajra, *Tetrahedron Lett*., 2013, **54**, 3892; (*d*) K. Monir, A. K. Bagdi, S. Mishra, A. Majee and A. Hajra, *Adv. Synth. Catal*., 2014, **365**, 1105; (*e*) K. Revathy and A. Lalitha, *RSC Adv*., 2014, **4**, 279; (*f*) V. K. Rao, R. Tiwari, B. S. Chhikara, A. N. Shirazi, K. Parang and A. Kumar, *RSC Adv*., 2013, **3**, 15396; (*g*) B. C. Ranu and S. S. Dey, *Tetrahedron*, 2004, **60**, 4183.

4 (*a*) P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH Verlag, 2008. (*b*) J. Ranke, S. Stolte, R. Stormann, J. Arning and B. Jastorff, *Chem. Rev*., 2007, **107**, 2183. (*c*) T. L. Greaves and C. J. Drummond, *Chem. Rev*., 2008, **108**, 206. (*d*) N. V. Plechkova and K. R. Seddon, Chem. Soc. Rev., 2008, **37**, 123. (*e*) J. P. Hallett and T. Welton, *Chem. Rev.,* 2011, **111**, 3508. (*f*) L. Myles, R. G. Gore, N. Gathergood and S. J. Connon, *Green Chem.,* 2013, **15**, 2740. (*g*) R. Sheldon, *Chem. Commun*., 2001, 2399.

5 (*a*) D. Coleman and N. Gathergood, *Chem. Soc. Rev*., 2010, **39**, 600; (*b*) K. S. Egorova and V. P. Ananikov, *ChemSusChem,* 2014, **7**, 336.

6 (*a*) H. Xing, T. Wang, Z. Zhou and Y. Dai, *Ind. Eng. Chem. Res*., 2005, **44**, 4147; (*b*) Y. Leng, J. Wang, D. Zhu, X. Ren, H. Ge and L. Shen, *Angew. Chem., Int. Ed*., 2009, **48**, 168. (*c*) A. Sarkar, S. R. Roy and A. K. Chakraborti, *Chem. Commun*., 2011, **47**, 4538; (*d*) A. K. Chakraborti, S. R. Roy, D. Kumar and P. Chopra, *Green Chem*., 2008, **10**, 1111; (*e*) L. Myles, R. Gore, M. Spulak, N. Gathergood and S. J. Connon, *Green Chem*., 2010, **12**, 1157.

7 (*a*) A. D. Sawant, D. G. Raut, N. B. Darvatkar and M. M. Salunkhe, *Green Chem. Lett. Rev.,* 2011, **4**, 41; (*b*) B. C. Ranu and S. Banerjee, *Org. Lett.,* 2005, **7**, 3049; (*c*) A. K. Chakraborti and S. R. Roy, *J. Am. Chem. Soc.,* 2009, **131**, 6902; (*d*) L. Myles, N. Gathergood and S. J. Connon, *Chem. Commun*., 2013, **49**, 5316; (*e*) A. Kumar, S. Srivastava, G. Gupta, P. Kumar and J. Sarkar, *RSC Adv.,* 2013, **3**, 3548; (*f*) L. Zhang, S. Luo, X. Mi, S. Liu, Y. Qiao, H. Xu and J.-P. Cheng, *Org. Biomol. Chem.,* 2008, **6**, 567; (*g*) D. Li, F. Shi, J. Peng, S. Guo and Y. Deng, *J. Org. Chem.,* 2004, **69**, 3582; (*h*) R. Giernoth, *Angew. Chem., Int. Ed.,* 2010, **49**, 2834; (*i*) J. H. Davis Jr., *Chem. Lett*., 2004, **33**, 1072; (*j*) S.-G. Lee, *Chem. Commun.,* 2006, 1049; (*k*) A. Winkel, P. V. G. Reddy and R. Wilhelm, *Synthesis,* 2008, **7**, 999; (*l*) N. B. Darvatkar, A. R. Deorukhkar, S. B. Bhilare, D. G. Raut and M. M. Salukhe, *Synth. Commun*., 2008, **38**, 3508.

8 (*a*) A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, *J. Am. Chem. Soc.,* 2002, **124**, 5962; (*b*) D. C. Forbes and K. J. Weaver, *J. Mol. Catal. A: Chem.,* 2004, **214**, 129; (*c*) J. Guia, H. Bana, X. Cong, X. Zhang, Z. Hu and Z. Sun, *J. Mol. Catal. A: Chem.,* 2005, **225**, 27; (*d*) A. Hubbard, T. Okazaki and K. K. Laali, *Aust. J. Chem.,* 2007, **60**, 923; (*e*) D.-Q. Xu, J. Wu, S.-P. Luo, J.-X. Zhang, J.-Y. Wu, X.-H. Du and Z.-Y. Xu, *Green Chem.,* 2009, **11**, 1239; (*f*) Y. W. Zhao, J. X. Long, F. G. Deng, X. F. Liu, Z. Li, C. G. Xia and J. J. Peng, *Catal. Commun*. 2009, **10**, 732; (*g*) X. Liu, H. Ma, Y. Wu, C. Wang, M. Yang, P. Yana and U. Welz-Biermann, *Green Chem*. 2011, 13, 697.

9 (*a*) M. Rahman, A. Sarkar, M. Ghosh, A. Majee and A. Hajra, *Tetrahedron Lett*., 2013, **55**, 235; (*b*) S. Santra, A. Majee and A. Hajra, *Tetrahedron Lett*., 2011, **52**, 3825; (*c*) S. Das, M. Rahman, D. Kundu, A. Majee and A. Hajra, *Canadian J. Chem.,* 2010, **88**, 150; (*d*) D. Kundu, R. K. Debnath, A. Majee and A. Hajra, *Tetrahedron Lett.,* 2009, **50**, 6998; (*e*) D. Kundu, A. Majee and A. Hajra, *Catal. Commun*., 2010, **11**, 1157; (*f*) D. Kundu, A. K. Bagdi, A. Majee and A. Hajra, *Synlett,* 2011, 1165; (*g*) M. Rahman, A. K. Bagdi, D. Kundu, A. Majee and A. Hajra, *J. Heterocyclic Chem*., 2012, **49**, 1224.

10 R. A. Sheldon, *Green Chem*., 2007, **9**, 1273.

11 (*a*) R. A. Sheldon, *Chem. Soc. Rev*., 2012, **41**, 1437; (*b*) A. Kamal, V. Srinivasulu, B. N. Seshadri, N. Markandeya, A. Alarifi and N. Shankaraiah, *Green Chem*., 2012, **14**, 2513–2522.

12 A. Sarkar, S. Santra, S. K. Kundu, A. Hajra, G. V. Zyryanov, O. N. Chupakhin, V. N. Charushin and A. Majee, *Green Chem*., 2016, **18**, 4475.

13 (*a*) D. L. Galinis, R. W. Fuller, T. C. Mc Kee, J. H. Cardellina II; R. J. Gulakowski, J. B. Mc Mahon and M. R. Boyd, *J. Med. Chem*., 1996, **39**, 507; (*b*) D. P. Chakraborty, A. D. Gupta and P. K. Bose, *Ann. Biochem. Exp. Med*., 1957, **17**, 59; (*c*) R. S. Mali, P. P. Joshi, P. K. Sandhu and A. Manekar-Tilve, *J. Chem. Soc., Perkin Trans. 1,* 2002, 371; (*d*) L. Xie, Y. Takeuchi, L. M. Cosentino, A. T. Mc Phail and K. H. Lee, *J. Med. Chem*., 2001, **44**, 664; (*e)* D. N. Nicolaides, D. R. Gautam, K. E. Litinas, D. J. Hadjipavlou-Litina and K. C. Flyakakidou, *Eur. J. Med. Chem*., 2004, **39**, 323; (*f*) E. Meliou, P. Magiatis, S. Mitaku, A.-L. Skalsounis, E. Chinou and I. Chinou, *J. Nat. Prod*., 2005, **68**, 78.

14 R. S. Mali, N. A. Pandhare and M. D. Sindkhedkar, *Tetrahedron Lett.,* 1995, **36**, 7109.

15 (*a*) E. E. Schweizer and O. Meeder-Nycz, In *Chromenes, Chromanes, Chromones*, Ellis, G. P., Ed.; Wiley-Interscience: New York, 1977; (*b*) J. D. Hepworth and B. M. Heron, *Prog. Heterocycl. Chem.,* 1995, **7**, 268.

16 (*a*) A. Basile, S. Sorbo, V. Spadaro, M. Bruno, A. Maggio, N. Faraorne, S. Rosselli, *Molecules,* 2009, **14**, 939; (*b*) E. Melliou, P. Magatis, S. Mitaku, A.-l. Skaltsounis, E. Chinou, I. Chinou, *J. Nat. Prod*., 2005, **68**, 8; (*c*) I. Kostova, *Curr. Med. Chem*., 2005, **5**, 29; (*d*) K. Otoguro, K. Shiomi, Y. Yamaguchi, N. Arai, T. Sunazuka, R. Masuma, Y. Iwai and S. Omura, *J. Antibiot*., 2000, **53**, 50; (*e*) T. C. Mc Kee, C. D. Covington, R. W. Fuller, H. R. Bokesch, S. Young, J. H. I. Cardellina, M. R. Kadushin, D. D. Soejarto, P. F. Stevens, G. M. Cragg and M. R. Boyd, *J. Nat. Prod*., 1998, ,, 252; (*f*) K. Otoguro, F. Kuno and S. Omura, *Pharmacol. Ther*., 1997, **76**, 45; (*g*) F. Kuno, K. Otoguro, K. Shiomi, Y. Iwai and S. Omura, *J. Antibiot*., 1996, **49**, 742; (*h*) F. Kuno, K. Shiomi, K. Otoguro, T. Sunazuka and S. Omura, *J. Antibiot*., 1996, **49**, 748; (*i*) S. Omura, F. Kuno, K. Otoguro, T. Sunazuka, K. Shiomi, R. Masuma and Y. Iwai, *J. Antibiot*., 1995, **48**, 745; (*j*) S. K. Kapoor, J. M. Kohli, Y. N. Sharma and A. Zaman, *Phytochemistry,* 1972, **11**, 477.

17 (*a*) Z. He, X. Lin, Y. Zhu and Y. Wang, *Heterocycles,* 2010, **81**, 965; (*b*) G. Appendino, G. Cravotto, S. Tagliapietra, G. M. Nano and G. Palmisano, *Helv. Chim. Acta,* 1865, **1990**, 73; (*c*) J. Moreau, C. Hubert, J. Batany, L. Toupet, T. Roisnel, J.-P. Hurvois and J.-L. Renaud, *J. Org. Chem*., 2009, **74**, 8963; (*d*) G. Appendino, G. Cravotto, G. B. Giovenzana and G. Palmisano, *J. Nat. Prod*., 1999, **62**, 1627; (*e*) Y. Jacquot, B. Refouvelet, L. Bermont, G. L. Adessi, G. Leclercq and A. Xicluna, *Pharmazie,* 2002, **57**, 233; (*f*) Y. Liu, J. Zhu, J. Qian, B. Jiang and Z. Xu, *J. Org. Chem*., 2011, **76**, 9096; (*g*) X. Lin, X. Dai, Z. Mao and Y. Wang, *Tetrahedron,* 2009, **65**, 9233; (*h*) S. Berger and E. Haak, *Tetrahedron Lett*., 2010, **51**, 6630; (*i*) M.

View Article Online
DOI: 10.1039/C7GC01158J

Gohain, J. H. van Tonder and B. C. B. Bezuidenhoudt, *Tetrahedron Lett.,* 2013, **54**, 3773–3776; (*j*) H. S. Virdi, S. Sharma, S. Mehndiratta, P. M. S. Bedi and K. Nepali, *J. Enz. Inhibit. Med. Chem*., 2015, **30**, 730-736.

18 (*a*) S. Ahadi, M. Zolghadr, H. R. Khavasi and A. Bazgir, *Org. Biomol. Chem*., 2013, **11**, 279; (*b*) R. Sarma, M. M. Sarmah, K. C. Lekhok and D. Prajapati, *Synlett,* 2010, 2847.

19 (*a*) K. Asano and S. Matsubara, *Org. Lett*., 2009, **11**, 1757; (*b*) A. Sarkar, S. R. Roy, D. Kumar, C. Madaan, S. Rudrawar and A. K. Chakraborti, *Org. Biomol. Chem*., 2012, **10**, 281.

20 Further information can be found in the CIF file. The crystal data are deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1539031.

21 Z. Du, Z. Li and Y. Deng, *Synth. Commun*., 2005, **35**, 1343.