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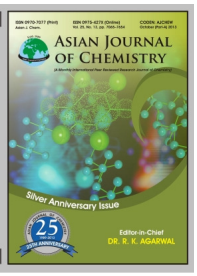

Brønsted-Acidic Imidazolium Ionic Liquid [bmim(SO_3H)][OTf]: A Mild Catalyst for Highly Efficient Synthesis of Coumarins

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The use of Brønsted-acidic imidazolium ionic liquid [bmim(SO_3H)][OTf] as a catalyst for the high yielding synthesis of a wide variety of coumarins under mild conditions *via* Pechmann condensation has been demonstrated. This method is simple and has benefits from the easy way to isolate coumarins in good yields. In comparison with the classical Pechmann condensation, this new method consistently has the advantage of high yields and good purity.

Key Words: Coumarins, Brønsted-acidic imidazolium ionic liquid, Pechmann condensation.

INTRODUCTION

Coumarin, the simplest member of the group of oxygen heterocycles and a class of lactones; which is an indispensable heterocyclic unit to both the chemists and the biochemists. Coumarins occur naturally in plants and microorganisms, approximately1000 coumarin derivatives have been isolated from over 800 species of plants and microorganisms[1]. Coumarin itself was first isolated from tonka bean, Coumarounaodorata by Vogel in 1820[2]. Coumarins are structurally diverse, which includes simple substituted coumarins, those that have substituents in the benzene ring, five and six-membered fused coumarins such as furocoumarins and pyranocoumarins and coumarin dimers, which usually consists of two coumarin units linked together such as dicoumarol. A study of antimicrobial properties of such naturally occurring and synthetic coumarins has been reported recently[3]. Several coumarin derivatives were also recently reviewed for their natural occurrence, anti-microbial, anti-inflammatory, anticancer, anti-HIV and other miscellaneous properties[4]. Among the various coumarin derivatives, 7-substituted coumarins are important group of coumarin derivatives showing various bioactivities and also other applications[5]. For example, 7-hydroxy 4-methyl coumarin (β-methyl umbelliferone) is used as fluorescent brightener, efficient laser dye, standard for fluorometric determination of enzymatic activity and as a starting material for the preparation of insecticide and furano coumarins[6-8]. Moreover, 7-amino-4-methyl coumarin is mainly used as laser dye and intermediate for the synthesis of bioactive compounds[9]. Coumarins could be synthesized by various methods, such as Pechmann[10], Perkin[11], Knoevenagel[12], Reformatsky[13], Witting[14], Claisen[15] and flash vacuum pyrolysis reaction[16]. However, the Pechmann reaction is one of the most widely applied method for the synthesis of coumarins and its derivatives, which involves the condensation of phenols with β-ketoesters in the presence of a variety of acidic condensing agents. Several acid catalysts have been used in the conventional procedure, such as H_2SO_4[10], $AlCl_3$[17], P_2O_5[18], CF_3COOH[19], $HClO_4$[20]. However, these catalysts have to be used in large excess and hence the disposal of acidic waste leads to environmental pollution. The moisture sensitivity of the majority of Lewis acids to the water produced in the Pechmann reaction renders them unsuitable for use in large-scale applications and these methods also generate strongly acidic by-products. Due to the environmental concerns and as a tool to green chemistry, many catalysts such as, $Bi(NO_3)_3{\cdot}5H_2O$[21], $Sm(NO_3)_3{\cdot}6H_2O$[22], $ZrCl_4$[23], $KAl(SO_4)_2{\cdot}12H_2O$ (alum)[24], silica-bonded s-sulfonic acid[25] and silica triflate[26] have been used as effective catalysts for coumarin synthesis in solvent free condition in the last decade. The use of ionic liquids (ILs) as reaction media and catalyst can offer a solution to solvent emission and catalyst recycle problems[27]. Ionic liquids possess the advantages like negligible vapour pressure; reasonable thermal stability, recyclability, dissolves many organic and inorganic substrates and they are tunable to specific chemical tasks[28]. Recently ionic liquids have been successfully employed as solvents with catalytic activity for a variety of reactions[29].

Ionic liquids with acidic counter ions like in 1-hexyl-3-methyl-imidazolium hydrogen sulphate ([hmim] [HSO_4]), 1-butyl-3-methylimidazoliumdihydogen phosphate ([bmim] [H_2PO_4]), 1-[2-(2-hydroxy-ethoxy)ethyl]-3-methyl-imidazolium hydrogen sulphate ([heemim][HSO_4])[30] and 1-butyl-3-methyl-imidazoliumchloroaluminate ([bmim]Cl.2Al Cl_3) were used as good acid catalysts[31,32]. Applications of Brønsted acidic ionic liquids, including those bearing other counter ions[33] have been employed in other organic transformation such as aromatic nitration[34] alkylation with olefins, Beckmann rearrangement, esterification[35], olefin oligomerization, condensation reactions[36], transesterification[37], carbonyl protection[38], synthesis of β-amidoketones[39] and 3-component synthesis of hindered pyridines[40].

In continuation of our studies focusing on applications of ionic liquids in general[41-47] and Brønsted-acidic imidazolium ionic liquids in particular[48] and with the view of developing the potential use of simple Brønsted-acidic imidazolium ionic liquid, we report herein a convenient method for the high yield synthesis of coumarins *via* condensation of a variety of phenols with ethyl acetoacetate under mild conditions, employing well known, [bmim(SO_3H)][OTf] (**1**) (Fig. 1) as the catalyst[49].

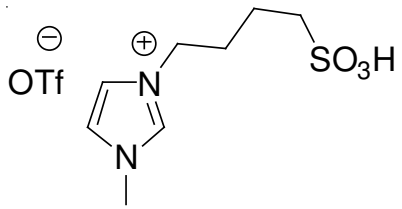


Fig. 1. Structure of the Brønsted-acidic imidazolium ionic liquid [bmim(SO_3H)][OTf]

EXPERIMENTAL

The reagents employed were high purity commercial samples which were used as received. Reactions were carried out in oven-dried Schlenk tubes. Column chromatography was performed on silica gel (200-400 mesh). TLC was performed on alumina silica gel 60F_{254} (Fischer) detected by UV light (254 nm) and iodine vapours. The melting points were determined by open capillaries on a Buchi apparatus and are uncorrected. The IR spectra were recorded on a Nicolet-Impact-410 FT-IR spectrometer, using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-300F, 300 MHz, spectrometer in DMSO-d_6 using TMS as an internal standard with ^{1}H resonance frequency of 300 MHz, ^{13}C resonance frequency of 75 MHz. GC analyses were performed on Nucon 5700 series gas chromatograph. GC-MS analyses were performed on Shimadzu 2010 series mass selective detector instrument. The elemental analysis was carried out using Heraus CHN rapid analyzer, all the new compounds gave C, H and N analysis within ± 0.4 % of the theoretical values.

Synthesis of Brønsted-acidic ionic liquid [bmim(SO_3H)][OTf][49]: To butanesultone (31.97 mmol) in a two-necked flask under nitrogen was slowly added 1-methylimidazole (32.25 mmol) and the mixture was stirred for 48 h at room temperature. The solid so obtained was repeatedly washed with toluene and diethyl ether and dried under vacuum at room temperature to give the corresponding zwitter-ion 3-(1-methyl-1*H*-imidazol-3-ium-3-yl)butane-1-sulfonate with 96 % yield. Further, the resulting mixture of 3-(1-methyl-1*H*-imidazol-3-ium-3-yl)butane-1-sulfonate (10 mmol) and trifluoromethane sulfonic acid (10.85 mmol) was heated to 40 °C and stirred at the same temperature for 48 h. After being allowed to cool to room temperature, the obtained ionic liquid was washed repeatedly with toluene and diethyl ether to remove non-ionic residues and dried under vacuum at room temperature to give [bmim(SO_3H)][OTf] (**1**) (98 %). The intermediate 3-(1-methyl-1*H*-imidazol-3-ium-3-yl)butane-1-sulfonate and the product [bmim(SO_3H)][OTf] were thoroughly characterized by IR, ^{1}H NMR and ^{13}C NMR and the data obtained were in agreement with the reported values[49c-49e].

General procedure for the synthesis of coumarins using [bmim(SO_3H)][OTf] catalyst: The desired amount of phenol (6 mmol) and ethyl acetoacetate (7 mmol) in 5-6 mL AcOH were taken into an oven-dried Schlenk tube. Upon efficient magnetic stirring (for 10-20 min) the reaction mixture was then charged with [bmim(SO_3H)][OTf] (10-15 mol %). The reaction mixture was stirred at 50-80 ºC and the progress of the reaction was monitored by TLC and GC-MS (Table-1). After completion of reaction, the reaction mass was cooled to room temperature and the contents were poured to crushed ice. The separated solid after neutralization with aqueous $NaHCO_3$ solution was filtered, washed with excess of cold water dried and the crude products which were chromatographed with hexane-ethyl acetate mixture (80:20) followed by crystallization with ethanol afford the pure product. All the coumarin derivatives were characterized by GC-MS and ^{1}H, ^{13}C NMR, elemental analysis and the results are compared with authentic samples.

7-Hydroxy-4-methyl-chromen-2-one: Yield: 96 %, m.p. 186-188 °C; GC-MS: *m/z* 176, IR (KBr, ν_{max}, cm^{-1}): 1722. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.33 (s, 3H, C4-CH_3), 6.09 (s, 1H), 6.67 (s, 1H), 6.77 (d, 1H, *J* = 9 Hz), 7.55 (d, 1H, *J* = 9 Hz), 10.51 (brs, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 161.58, 160.72, 155.26, 153.96, 127.03, 113.28, 112.44, 110.68, 102.60, 18.54.

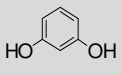
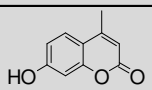
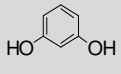
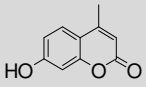
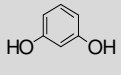
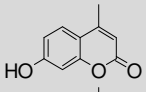
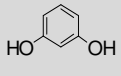
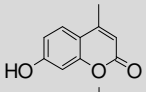
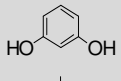
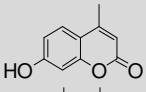
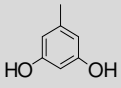
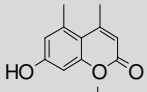
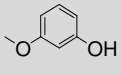
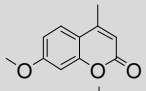
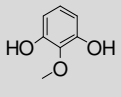
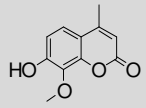
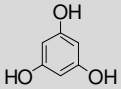
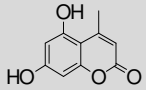
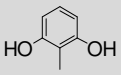
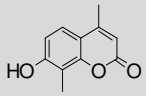
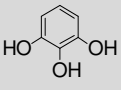
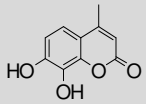
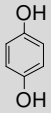
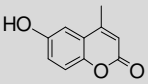
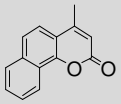
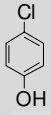
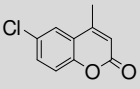
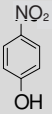
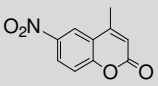
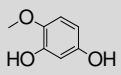
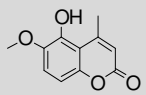
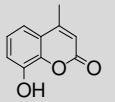
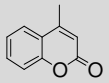
7-Hydroxy-4, 5-dimethyl-chromen-2-one: Yield: 90 %, m.p. 256-258 °C; GC-MS: *m/z* 190, IR (KBr, ν_{max}, cm^{-1}): 1726. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.38 (s, 3H, C4-CH_3), 2.47 (s, 3H, C5-CH_3), 6.12 (s, 1H), 6.60 (s, 1H), 6.75 (s, 1H), 10.20 (brs, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.15, 159.80, 155.30, 154.61, 128.10, 112.90, 112.10, 111.26, 104.40, 20.12, 18.90.

7-Methoxy-4-methyl-chromen-2-one: Yield: 86 %, m.p. 156-158 °C; GC-MS: *m/z* 190, IR (KBr, ν_{max}, cm^{-1}): 1712. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.30 (s, 3H, C4-CH_3), 3.86 (s, 3H, C7-OCH_3), 6.20 (s, 1H), 6.58 (s, 1H), 6.81 (d, 1H, *J* = 9 Hz), 7.76 (d, 1H, *J* = 9 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.18, 160.82, 156.10, 154.16, 127.30, 114.18, 112.50, 110.80, 101.90, 55.80, 18.54.

7-Hydroxy-8-methoxy-4-methyl-chromen-2-one: Yield: 88 %, m.p. 252-254 °C; GC-MS: *m/z* 206, IR (KBr, ν_{max}, cm^{-1}): 1722. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.40 (s, 3H, C4-CH_3), 3.90 (s, 3H, C8-OCH_3), 6.10 (s, 1H), 6.78 (d, 1H, *J* = 8.5 Hz), 7.80 (d, 1H, *J* = 8.5 Hz), 10.42 (brs, 1H, OH).

^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.30, 160.22, 159.34, 155.46, 128.34, 114.18, 112.10, 110.24, 102.70, 56.44, 19.40.

TABLE-1
SYNTHESIS OF COUMARINS FROM PHENOLS AND ETHYL ACETOACETATE USING [bmim(SO_3H)][OTf]

Entry	Substrate (phenols)	Product	Temp. (ºC)	Time (h)	Isolated yield[a] (%)
1			90	16	NR[b]
2			40-80	12	10-15[c*]
3			60-90	12	10[d*]
4			50	2.5	96[e]
5			50	3	96
6			60	4	90
7			70	4	86
8			65	6	88
9			65	6	82
10			60	6	85
11			80	8	83
12			70	6	90
13			80	12	82
14			80	10	68
15			80	12	42
16			80	12	48
17			80	10	35
18			90	16	15[e*]

[a]Isolated yields of pure products.
[b]The reaction was performed in absence of [bmim(SO_3H)][OTf].
[c]The reaction was carried out in DCM and EDC.
[d]The reaction was carried out in EtOH and MeOH.
[e]Phenol (10 mmol); ethyl acetoacetate (11 mmol); [bmim(SO_3H)][OTf] (20 mol %).
*Yields were determined by GC.

5,7-Dihydroxy-4-methyl-chromen-2-one: Yield: 82 %, m.p. 280-282 °C; GC-MS: *m/z* 192, IR (KBr, ν_{max}, cm^{-1}): 1722. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.28 (s, 3H, C4-CH_3), 6.10 (s, 1H), 6.59 (s, 1H), 6.72 (s, 1H), 10.78 (brs, 2H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.50, 160.39, 159.10, 155.30, 154.10, 127.74, 112.40, 110.36, 105.40, 22.10.

7-Hydroxy-4, 8-dimethyl-chromen-2-one: Yield: 85 %, m.p. 264-266 °C; GC-MS: *m/z* 190, IR (KBr, ν_{max}, cm^{-1}): 1728. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.18 (s, 3H, C4-CH_3), 2.45 (s, 3H, C8-CH_3), 6.18 (s, 1H), 6.80 (d, 1H, *J* = 9 Hz), 7.47 (d, 1H, *J* = 9 Hz), 10.28 (brs, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 161.58, 160.18, 154.70, 152.68, 127.80, 112.90, 112.32, 110.63, 105.10, 20.28, 18.40.

7,8-Dihydroxy-4-methyl-chromen-2-one: Yield: 83 %, m.p. 242-244 °C; GC-MS: *m/z* 192, IR (KBr, ν_{max}, cm^{-1}): 1718. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.33 (s, 3H, C4-CH_3), 6.06 (s, 1H), 6.74 (d, 1H, *J* = 9 Hz), 7.16 (d, 1H, *J* = 9 Hz), 10.48 (brs, 2H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.58, 161.20, 159.56, 155.87, 154.12, 128.14, 112.40, 110.16, 104.10, 20.36.

6-Hydroxy-4-methyl-chromen-2-one: Yield: 90 %, GC-MS: *m/z* 176, IR (KBr, ν_{max}, cm^{-1}): 1710. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.40 (s, 3H, C4-CH_3), 6.15 (s, 1H), 6.78 (s, 1H), 6.82 (d, 1H, *J* = 9 Hz), 7.90 (d, 1H, *J* = 9 Hz), 10.58 (brs, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.10, 160.65, 154.60, 153.90, 127.40, 113.82, 112.40, 112.19, 102.48, 19.46.

7,8-Benzo-4-methyl-chromen-2-one: Yield: 82 %, m.p. 153-155 °C; GC-MS: *m/z* 210, IR (KBr, ν_{max}, cm^{-1}): 1730. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.42 (s, 3H, C4-CH_3), 6.25 (s, 1H), 6.58-8.12 (m, 6H). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.30, 160.10, 155.10, 152.24, 127.40, 126.34, 126.10, 122.40, 121.60, 112.56, 112.10, 110.16, 102.58, 19.36.

6-Chloro-4-methyl-chromen-2-one: Yield: 68 %, GC-MS: *m/z* 194, IR (KBr, ν_{max}, cm^{-1}): 1725. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.42 (s, 3H, C4-CH_3), 6.22 (s, 1H), 6.38 (s, 1H), 6.90 (d, 1H, *J* = 8.5 Hz), 7.70 (d, 1H, *J* = 8.5 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.40, 160.15, 155.10, 152.25, 128.60, 113.90, 112.68, 111.10, 101.98, 20.86.

6-Nitro-4-methyl-chromen-2-one: Yield: 42 %, m.p. 152-154 °C; GC-MS: *m/z* 205, IR (KBr, ν_{max}, cm^{-1}): 1728. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.50 (s, 3H, C4-CH_3), 6.20 (s, 1H), 7.18 (s, 1H), 7.44 (d, 1H, *J* = 9 Hz), 8.20 (d, 1H, *J* = 9 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 163.10, 160.25, 154.20, 152.15, 127.65, 112.80, 112.10, 110.45, 102.38, 20.16.

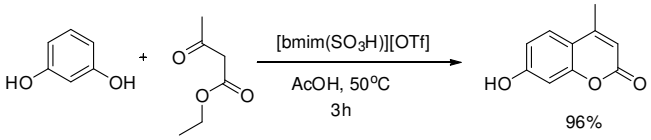
5-Hydroxy-6-methoxy-4-methyl-chromen-2-one: Yield: 48 %, m.p. 162-164 °C; GC-MS: *m/z* 206, IR (KBr, ν_{max}, cm^{-1}): 1712. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.48 (s, 3H, C4-CH_3), 3.92 (s, 3H, C6-OCH_3), 6.25 (s, 1H), 6.68 (d, 1H, *J* = 8.5 Hz), 7.85 (d, 1H, *J* = 8.5 Hz), 10.22 (brs, 1H, OH).

^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.56, 160.34, 159.14, 155.61, 122.68, 115.28, 112.30, 111.12, 102.60, 55.78, 20.38.

8-Hydroxy-4-methyl-chromen-2-one: Yield: 35 %, GC-MS: *m/z* 176, IR (KBr, ν_{max}, cm^{-1}): 1710. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 2.34 (s, 3H, C4-CH_3), 6.20 (s, 1H), 6.60-7.82 (m, 3H), 10.45 (brs, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 162.28, 159.15, 155.50, 152.53, 127.40, 113.80, 112.44, 112.26, 102.58, 20.16.

RESULTS AND DISCUSSION

Initially to optimize the reaction conditions such as temperature, solvent and amount of catalyst and to study the feasibility of the [bmim(SO_3H)][OTf] catalyzed Pechmann condensation, the reaction of resorcinol with ethyl acetoacetate (**Scheme-I**) was selected as a model.



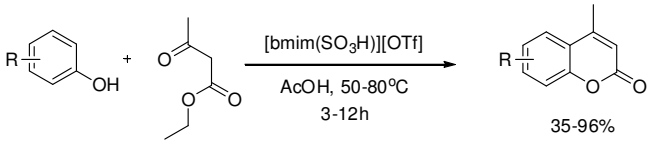
Scheme-I: Synthesis of 7-hydroxy-4-methylcoumarin from resorcinol and ethyl acetoacetate using [bmim(SO_3H)][OTf]

Initially we focused on the optimization of the amount of [bmim(SO_3H)][OTf] and suitable solvent. We observed that only 10-15 mol % of [bmim(SO_3H)][OTf] could effectively catalyze the reaction at a comparatively mild reaction temperature of 50 to 80 °C. An increase in the catalyst to 20 mol % showed no substantial improvement in the yield, though a slight improvement in the reaction time was observed (entry 18). In view of this, a protocol involving a lower amount of [bmim(SO_3H)][OTf] would be more appreciable, therefore we decided to extend the scope of the reaction using only 10-15 mol % of the catalyst. As the ionic liquid is used only in catalytic amount, it was not deemed essential to recover the ionic liquid for re-use. However, it has been reported in other works[35b], this ionic liquid can be conveniently recovered and reused, making this chemistry economically viable for scale-up.

We also optimized the use of suitable solvent for the present reaction, the Pechmann condensation of resorcinol with ethyl acetoacetate catalyzed by [bmim(SO_3H)][OTf] in acetic acid worked smoothly at 50 °C and completed in 3 h to obtain 96 % of coumarin (entry 1). However the same reaction in the absence of [bmim(SO_3H)][OTf] did not proceed (entry 15). In optimization of the use of other solvents such as EtOH, MeOH, DCM and EDC for the present reaction, gave only 10-15 % yield (By GC) (entries 16 and 17). This shows that AcOH was the suitable solvent for the said condensation.

Thus, the Pechmann condensation reaction of wide range of structurally varied phenols and ethyl acetoacetate in the presence of [bmim(SO_3H)][OTf] was carried out under the optimized reaction conditions described above (**Scheme-II**).

The results (Table-1) showed that a variety of structurally varied phenols reacted smoothly in AcOH to give the corresponding coumarins in good yields (68 to 96%) and purities. Phenols, such as resorcinol, orcinol, pyrogallol, phloroglucinol, 1-naphthol, 2,6-dihydroxy anisole, 2,6-dihydroxy toluene



R = 3-OMe, 3-OH-5-Me, 2-OMe-3-OH, 2-Me-3-OH, 4-OH, 4-Cl, 4-NO_2, 3-OH-4-OMe, 2-OH, 2,3-benzo

Scheme-II: Synthesis of substituted 4-methylcoumarins from substituted phenols and ethyl acetoacetate using [bmim(SO_3H)][OTf]

and 3-methoxy phenol, could be converted to corresponding coumarins in good yields (entries 5-13). Under the present reaction conditions, comparatively poor yields (35 to 68 %) and long reaction time were observed on the reaction of ethyl acetoacetate with substrates such as 2-methoxyresorcinol, 4-chlorophenol, 4-nitrophenol and catechol (entries 14-17). The starting materials, which could be separated from the product by flash column (hexane + ethyl acetate), remained in the reaction mixture although the two condensations were carried out under the prolonged reaction time. However the reactivity of simple phenol seem to be the most sluggish, as compared with that of the former (entry 17), only 15 % product formation was observed in GC when treated with ethyl acetoacetate in presence of 20 mol % of [bmim(SO_3H)][OTf] even after prolonged reaction time of 16 h. In the present protocol no detectable demethylation was observed in the case of 3-methoxy phenol, 2,6-dihydroxy anisole and 2-methoxy resorcinol (entries 7, 8 and 16).

Conclusion

In conclusion, we have successfully demonstrated the mild, convenient method for the synthesis of a wide variety of coumarins by the Pechmann condensation reaction of phenols and ethyl acetoacetate using catalytic amount of [bmim(SO_3H)][OTf]. This practical and simple method led to good yields with high purities of coumarins under mild conditions. To the best of our knowledge this is the first report for the synthesis of coumarins using [bmim(SO_3H)][OTf]. We also believe this novel methodology will find a wide application in organic synthesis and this protocol could serve as a valuable alternative to known reaction systems.

Further work, including the development of synthetic applications and exploration of the enormous potential of [bmim(SO_3H)][OTf] in organic synthesis is underway in our laboratory.

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