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AN EFFICIENT AND RECYCLABLE IONIC-LIQUID CATALYZED, SYNTHESIS OF 4-HYDROXY-2H-CHROMEN-2-ONE DERIVATIVES

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ABSTRACT:
A simple, efficient and environmentally benign sone pot three component protocol has been developed for the synthesis of 4-hydroxy-2H-Chromen-2-one derivatives by a reaction of 4-hydroxycoumarin, substituted aryl aldehyde, and 2-mercaptobenzimidazole using catalytic amount of ionic liquid under reflux in ethanol. The protocol has been utilized mild reaction condition, excellent yield, shorter reaction time, recyclability of the catalyst and work-up procedure is fairly simple.

KEYWORDS:
ionic-liquid, 4-hydroxycoumarin, aryl aldehyde, 2-marcaptobenzimidazole,4-hydroxy-2H-chromen-2-one derivatives.

INTRODUCTION:

Coumarin or 2H-chromen-2-one is an organic chemical compound. It is found in many plants, where it may serve as a chemical defense against predators. By inhibiting synthesis of vitamin-K related compound is used as the prescription drug warfarin an anticoagulant to inhibit formation of blood clots, deep vein thrombosis (DVT), and pulmonary embolism[1, 2]. Coumarin derivative has been published, describing their anticoagulant, antibacterial, anti-helminthic, hypothermal properties and vasodilatatory action[3]. During the last twenty years, the study of the biological activity of coumarin derivatives has been the aim of many researchers[4-7]. They have varied bioactivities such as, inhibition platelets aggregation, anti-inflammatory[8], anti-carcinogenic[9], anti-convulsant[10], anti-HIV[11], anti-viral[12], anti-fungal[13], anti-coagulant[14], anti-tubercular[15], anti-oxident[16], and anti-microbial[17]. Coumarin can be synthesized by various methods such as knovengel condensation[18], Perkin condensation [19], and pechmann condensation [20]. The one the most common method is pechmann condensation for the synthesis of Coumarin and its derivatives. The condensation reaction involves phenol and β-keto ester in acidic medium. Organic synthesis in an ionic-liquid catalyst is a fruitful research area

considering its cost, trouble free, and significance to environmentally begin process development[21-24]. Ionic Liquid (IL) is a salt in liquid state. In some concern the term has been restricted to salt whose melting point is below some arbitrary temperature. Ionic liquid are primarily made of ions and short lived ions pairs. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts and liquid salts [25-26].Several related approaches have been documented in the literature for the synthesis of 4-hydroxy-2H-Chromen-2-one and i.e. 3-((1H-benzo[d]imidazol-2-ylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one and its derivatives, which generally involve the cyclocondensation of 4-hydroxycoumarin, substituted aryl aldehyde, 2-merceptobrnzimidazole in L-Proline in ethanol[27], and another one is 3-acetyl-2H-chromen-2-one and 2-mercaptobenzimidazole by Knovengel condensation in the presence of catalytic amount of Iodine[28]. The above methods need expensive catalyst, higher temperature, and prolonged reaction time. Most of the routes required costly reagent, toxic/hazardous organic solvent and tedious workup. Hence chemist is putting more efforts to modify reaction condition.

In the present study, we have developed one pot three component an elegant, efficient, easy and direct procedure for the synthesis of 3-((1H-benzo[d]imidazol-2-ylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one under the reflux condition using 4-hydroxycoumarin, substituted aryl aldehyde, and 2-marcaptobenzimidazole in the presence of catalytic amount of (N-methylpyridinium tosylate) ionic liquid[29] in ethanol. The effect of catalyst gives the excellent yield of the product under the aspects of environmentally begin processes. This methodology has numerous and significant advantages, such as atom economy, the use of non-hazardous solvent, mild catalyst, short reaction time as well as more comfortable workup procedure.

EXPERIMENTAL SECTION:

MATERIALS AND METHODS

All the chemicals and synthetic grade reagents procured from Sigma Aldrich Indian and Merck Chemicals. They were used without further purification. Melting points were obtained in open capillaries using a Buchi melting-point B-540 apparatus. ^{1}H NMR spectra were obtained on Bruker instrument (400 MHz) and chemical shifts are reported in δppm.^{13}C NMR was recorded on a Bruker DRX 100 MHz Spectrometer

GENERAL PROCEDURE

Step1:Synthesis of 2-Mercaptobenzimi-dazole.

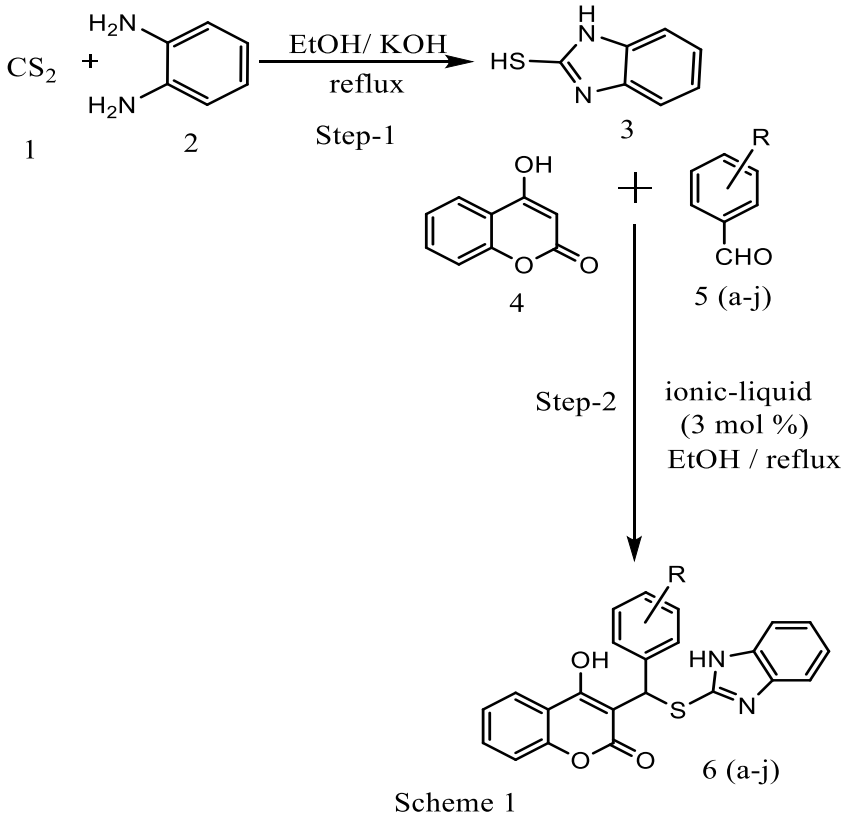
A mixture of O-Phenylenediamine 1 (0.1 mole), Carbon disulfide 2 (0.1 mole), and Potassium hydroxide (0.1 mole), 100 ml of ethanol in 250 ml round bottom flask under reflux condition for the completion of the reaction. The reaction was monitored by thin layer chromatography (TLC).The reaction mixture was filtered and the filtrate was heated about 70 ^{0}C for 30 min then it cool at room temperature. The mixture are poured on crushed ice and neutralized with dilute acetic acid. The solid product (3) is obtained filter and dry it. The product was recrystallized in ethanol[30].

Step2:Synthesis of 3-((1H-benzo[d]imidazol-2-ylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one and derivatives (6a-j)

A mixture of 2-marcaptobenzimidazole 3(0.01 mole), 4-hydroxycoumarine 4(0.01mole), and substitutes aryl aldehyde 5a-j (0.01 mole) and catalytic amount of ionic liquid in 50 ml ethanol in 250 ml round bottom flask. The reaction mixture was reflux for the completion of the reaction and the reaction was monitored by TLC. After the completion of the reaction, the mixture are placed at room temperature and then poured on crushed ice and filter it, the solid product 6(a-j) are obtained and recrystallized in ethanol.

Recovery of catalyst ionic liquid (NMPyTs)

An effort was made to recover the ionic liquid. After completion of the reaction, the reaction mixture was poured on ice water, and the product filtered off. The filtered was extracted with ethyl acetate to recover unreacted reactants, and the aqueous layer was subjected to evaporation of water to get various liquid, which on cooling gave the ionic liquid. The recovered ionic liquid was reused for two more cycles of the same cyclocondensation and found to act satisfactorily.



Scheme 1

RESULT AND DISCUSSION:

Here we focus on step-2 has been made to develop a new protocol for selectively substituted 3-((1H-benzo[d]imidazol-2-ylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one using 4-hydroxycoumarin, substitutes aryl aldehyde, and 2-mercaptobenzimidazole using catalytic amount of ionic liquid (NMPyTs) under reflux in ethanol. To study of this protocol, reaction leading to the desired product in very short reaction time (Scheme 1, Step 2) with recovery of the catalyst in easily available non-hazardous solvent.

Our initial work started with screening of solvents; because of one important aspect of good synthesis is the elimination of solvent in chemical processes or the replacement of hazardous solvent. Initially we investigate the solvent free reaction, we observed that reaction take longer time (12hrs) to form very less amount of product formed (only 37%), hence the reaction are not satisfactorily. When we employed other solvent such as THF, CH_3CN, DCM, p-TSA and CH_3OH. We observed that the average yield of the product 6a (Table1 Entry 2-6). But weemployed EtOH as a solvent in a model reaction; we observed that the excellent yield of the product in very short timecompared with the other solvents (Table1, Entry 7). Ethanol is cheaper, non-hazardous and safe solvent preferred as a medium for clean synthesis, hence ethanol selected as a solvent for our model reaction.

Table 1: Screening of solvent[a]

Entry	Solvent	Time (h)	% of yield
1	Solvent free	12	37
2	THF	10	40
3	CH_3CN	8	45
4	DCM	7	50
5	p-TSA	5.5	53
6	CH_3OH	5	60
7	**EtOH**	**4.5**	**82**

[a]Reaction condition: 4-hydroxycoumarin (0.01 mol),SubstitutedAryl Aldehyde, and 2-Mercaptobenz -imidazole (0.01 mol) using ionic liquid.

The main context of this model reaction to investigate the catalytic behavior of the ionic liquid (NMPyTs) for the synthesis of 3-((1H-benzo[d]imidazol-2-ylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one derivatives. We were performed model reaction in the absence of catalyst in ethanol solvent; we observed that no product formed in 14hrs. (Table-2 Entry 1) We were screening of the different catalyst in model reaction for improved the product of yield like Et_3N and L-Proline in 5, 10, 15 mol% respectively (Table-2, Entries 2-7). However, average yield of the product was formed, when 10 mol % catalyst was used. We have conducted the same reaction in the presence of ionic liquid (NMPyTs) as a catalyst using different catalytic amount (Table-2, Entries 8-12). We observed that the 3 mol% of catalyst are excellent for our model reaction, it gives the 92% product yield very short time (Table 2, Entry-10).Therefore, from our experimental observation, it was clear that the 3 mol% catalytic amount can surprisingly play a vital role, not only lift the rate of the reaction but also increased the product of yield. By using this composition we have synthesized the ten derivatives of 3-((1H-benzo[d]imidazol-2-ylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one as showed in (Table-3, Entry 6a-6j).

Table 2: Screening of catalyst in EtOH Solvent

Entry	Catalyst	Time (h)	% of yield
1	No Catalyst	14	--
2	Et_3N (5 mol %)	10	45
3	Et_3N (10 mol %)	7	55
4	Et_3N (15 mol %)	8	50
5	L-Proline(5 mol %l)	12	40
6	L-Proline(10 mol %)	8	60
7	L-Proline(15 mol %)	10	56
8	NMPyTs(5 mol %)	8	66
9	NMPyTs(4 mol %)	6	70
10	**NMPyTs(3** mol %**)**	**3**	**92**
11	NMPyTs(2 mol %)	4	81
12	NMPyTs(1 mol %)	9	72

[a]Reaction condition: 4-hydroxycoumarin(0.01 mol),Substituted Aryl Aldehyde, and 2-Mercaptobenzimidazole (0.01 mol) using ionic liquid

Table 3: Ionic liquid catalyzed synthesis of 3-((1H-benzo[d]imidazole-2-ylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one and its derivatives.

Entry	R	M. Pt. (^{0}C)	% of Yield	Mol. Wt.
6a	-H	240-242	80	400
6b	2-Br-C_5H_4	196-200	74	479
6c	4-Br-C_5H_4	200-202	85	479
6d	2-Cl-C_5H_4	190-192	82	434
6e	**4-Cl-C_5H_4**	**193-195**	**90**	**434**
6f	2-OH-C_5H_4	186-188	68	416
6g	4-OH-C_5H_4	188-190	75	416
6h	4-CH3-C_5H_4	202-205	83	414
6i	4-OCH_3-C_5H_4	194-196	86	430
6j	4-F-C_6H_4	208-210	87	418

[a]Reaction condition: 4-hydroxycoumarin (0.01 mol),Substituted Aryl Aldehyde,and 2-Mercaptobenzimidazole(0.01 mol) using ionic liquid.

The compound was obtained i.e. 2-mercaptobenzimidazole in step-1, from the reaction between O-Phenylenediamine and carbon disulfide in EtOH solvent are confirmed by the thin layer chromatography (TLC) and melting point. The derivatives were obtained by the reaction between 4-hydroxycoumarin, substituted aryl aldehyde, and 2-marcaptobenzimidazole using IL as a catalyst in ethanol solvent. The structure of all synthesized compounds (6a-j) was confirmed by TLC, Melting point (^{o}C), FT-IR, ^{1}H NMR, ^{13}C NMR.

Spectral Data:

6a) 3-(((1H-benzo[d]imidazol-2-yl) thio) (phenyl) methyl)-4-hydroxy-2H-chromen-2-one.
IR (KBr, cm^{-1}) 3415 (–OH enol), 3102 (N-H in imidazole ring), 1625 (C=O enol functional group), 1635 (C=O ester, 1510 (C=N imidazole ring).^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 7.30-7.50 (m, J=7.8 Hz, 5H phen-ring), 7.40-7.70 (dd, J=6.8, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus). ^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

6b)3-(((1H-benzo[d]imidazol-2-yl)thio)(2-bromophenyl)methyl)-4-hydroxy-2H-chromen-2-one.
IR (KBr, cm^{-1}) 3445 (–OH enol), 3110 (N-H in imidazole ring), 1630 (C=O enol functional group), 1640 (C=O ester, 1512 (C=N imidazole ring), 740 (C-Br).^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 7.11-7.24 (dd, 6.9 Hz, 2H),7.33-7.55 (m, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus).^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 33.5 (CH, tertiary carbon).

6c) 3-(((1H-benzo[d]imidazol-2-yl) thio) (4-bromophenyl) methyl)-4-hydroxy-2H-chromen-2-one.
IR (KBr, cm^{-1}) 3423 (–OH enol), 3109 (N-H in imidazole ring), 1622 (C=O enol functional group), 1633 (C=O ester, 1516 (C=N imidazole ring), 712 (C-Br). ^{1}H NMR (DMSOδ, ppm)

16.06 (s, 1H, OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 7.90 (d, J= 1.6 Hz, 2H), 7.35 (d, J=2.0 Hz, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus). ^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

6d) 3-(((1H-benzo[d]imidazol-2-yl) thio) (2-chlorophenyl) methyl)-4-hydroxy-2H-chromen-2-one.

IR (KBr, cm^{-1}) 3454 (–OH enol), 3120 (N-H in imidazole ring), 1634 (C=O enol functional group), 1655 (C=O ester, 1510 (C=N imidazole ring), 660 (C-Cl). ^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 7.18-7.28 (dd, 6.4 Hz, 2H),7.38-7.65 (m, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus).^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

6e) 3-(((1H-benzo[d]imidazol-2-yl) thio) (4-chlorophenyl) methyl)-4-hydroxy-2H-chromen-2-one.

IR (KBr, cm^{-1}) 3460 (–OH enol), 3165 (N-H in imidazole ring), 1660 (C=O enol functional group), 1670 (C=O ester, 1563 (C=N imidazole ring), 645 (C-Cl) 630 (tert C-S bond). ^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 7.40 (d, J= 1.8 Hz, 2H), 7.45 (d, J=1.6 Hz, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H), 7.30-7.85 (m, J=7.8 Hz, 2H), 7.10 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus). ^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

6f) 3-(((1H-benzo[d]imidazol-2-yl)thio)(2-hydroxyphenyl)methyl)-4-hydroxy-2H-chromen-2-one.

IR (KBr, cm^{-1}) 3432 (–OH enol), 3122 (N-H in imidazole ring), 1626 (C=O enol functional group), 1631 (C=O ester, 1514 (C=N imidazole ring), 2721 (C-OH). ^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, enol OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 8.75 (s, 1H phenolic OH),7.86-7.11 (d, J = 2.2 Hz, 2H), 6.80-7.30 (d, J=1.6 Hz, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus). ^{13}C-NMR ($CDCl_3$ 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 159 (Phenolic OH), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

6g) 3-(((1H-benzo[d]imidazol-2-yl) thio) (4-hydroxyphenyl) methyl)-4-hydroxy-2H-chromen-2-one

IR (KBr, cm^{-1}) 3412 (–OH enol)s, 3119 (N-H in imidazole ring), 1635 (C=O enol functional group), 1638 (C=O ester, 1519 (C=N imidazole ring), 2712 (C-OH). ^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, enol OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 8.70 (s, 1H phenolic OH), 6.60 (d, J = 2.2 Hz, 2H),7.30 (d, J=1.6 Hz, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus). ^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), 154 (Phenolic OH), δ 92.5 (enol carbon), δ116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

6h) 3-(((1H-benzo[d]imidazol-2-yl)thio)(4-methylphenyl)methyl)-4-hydroxy-2H-chromen-2-one.

IR (KBr, cm^{-1}) 3402 (–OH enol), 3102 (N-H in imidazole ring), 1632 (C=O enol functional group), 1655 (C=O ester, 1521 (C=N imidazole ring). ^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 2.25 (s, 3H), 7.04 (d, J= 1.2 Hz, 2H), 7.40 (d, J=1.4 Hz, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus). ^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

6i) 3-(((1H-benzo[d]imidazol-2-yl) thio)(4-methoxyphenyl)methyl)-4-hydroxy-2H-chromen-2-one

IR (KBr, cm^{-1}) 3120 (N-H in imidazole ring), 1633 (C=O enol functional group), 16323 (C=O ester, 1522 (C=N imidazole ring). ^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 3.80 (s, 3H), 6.70 (d, J= 1.9 Hz, 2H), 7.48 (d, J=1.4 Hz, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus). ^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

6j) 3-(((1H-benzo[d]imidazol-2-yl) thio)(4-fluorophenyl)methyl)-4-hydroxy-2H-chromen-2-one

IR (KBr, cm^{-1}) 3115 (N-H in imidazole ring), 1632 (C=O enol functional group), 1632 (C=O ester, 1514 (C=N imidazole ring), 726 (C-F). ^{1}H NMR (DMSOδ, ppm) 16.06 (s, 1H, OH), 11.02 (s, 1H, N-H), 4.77 (s, 1H, C-H), 7.20 (d, J= 2.0 Hz, 2H), 7.45 (d, J=2.2 Hz, 2H),7.40-7.70 (dd, J=6.8 Hz, 2H)7.30-7.85 (m, J=7.8 Hz, 2H), 7.20 (dd, J=5.9,3.2,2H) 7.50(m, 2H imidazole nucleus). ^{13}C-NMR (CDCl3 50 MHz) δ 165.7 (C=O, cyclic ester), δ 164.3 (enol carbon), δ 92.5 (enol carbon), δ 116.6, 124.4, 122.7, 127.9, 152.2 (arom-CH chromenes moiety), δ 137.6, 133.4, 129.7, 130.3 (arom-CH phenyl ring), δ139.2, 116.5, 124.9, 112.1 (arom-CH imidazole moiety), δ 36.5 (CH, tertiary carbon).

The FT-IR spectrum of (6e) exhibited absorption band at 3460 cm^{-1} due to conjugated O-H, the absorption band appears at 3165 cm^{-1} due to imidazole ring (-NH-, secondary amine), absorption band appear at 1660 cm^{-1} due to C=O functional group and carbonyl absorption band appear at 1670 cm^{-1}, absorption band appear at 1563cm^{-1} due to C=N in imidazole ring, absorption band appear at 645 cm^{-1} due to C-Cl (Chloro benzene), absorption band appear at 630 cm^{-1} due to C-S bond. ^{1}H NMR spectrum of compound (6e) showed signals i.e. i) singlet (1H) at δ 16.6 ppm due to O-H, ii) singlet (1H) at δ 11.2 ppm due to N-H, iii) singlet (1H) at δ 4.77 ppm due to C-H (tertiary carbon), iv) multiplate appear at the region between δ 7.30-7.40 ppm due to presence of aromatic proton in phenyl ring, multiplate appear at the region between δ 7.30- 7.85 ppm due to presence of aromatic proton in chromenes moiety, and multiplate appear at the region between δ 7.10-7.50 ppm due to presence of aromatic proton in imidazole moiety. ^{13}C NMR Spectrum of (6e) showed signals i.e. i) signals appears at δ165.7 ppm is confirmed that -C=O cyclic ester as a functional group, ii) signals appears at δ164.3 ppm is confirmed that C=C-OH enol carbon attach to –OH group, iii) signals appears at δ92.5ppm is showedC=C-OH enol carbon , iv) signals appears at δ 116.6, 124.4, 122.7, 127.9, 152.2showed that aromatic carbon which is in chromenes moiety, v) signals appears at δ 137.6, 133.4,

129.7, 130.3 showed aromatic carbon in phenyl ring, vi) signals appears at δ139.2, 116.5, 124.9, 112.1showed aromatic ring in imidazole moiety vii) signals appears at δ 36.5 showed tertiary carbon attached to Sulphur.

CONCLUSION:

The ionic liquid is an efficient, beneficial and recyclable catalyst leading to the one-pot three component synthesis of 3-((1H-benzo[d]imidazol-2-ylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one derivatives. The given protocol influenced under highly efficient, effortless, cheaply and recyclable catalyst for model reaction of equimolar mixture of 4-hydroxycoumarin, substituted aryl aldehyde, and 2-marcaptobenzimidazole in IL under refluxed in ethanol. The advantages of the current protocol include its efficiency, high product of yields, short reaction time and simply handling.

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