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Short Communication

Activated carbon sulfonic acid (AC-SO_3H) as a green acidic catalyst for solvent-free synthesis of benzimidazole derivatives

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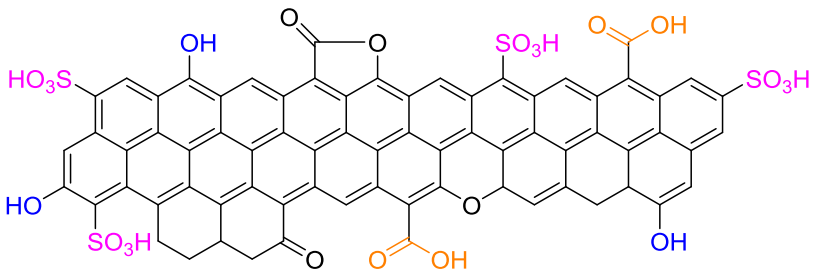
ABSTRACT

In this work, activated carbon sulfonic acid was prepared from the reaction of activated carbon and chlorosulfonic acid in chloroform at reflux conditions and characterized using X-ray powder diffraction (XRD) spectrum, infra-red (IR) spectrum, field emission scanning electron microscopy *(*FE-SEM*)* images and energy dispersive X-ray spectroscopy (EDS). Benzimidazole was prepared in excellent yields through the multicomponent condensation reaction of 1,2-phenylenediamine with aryl aldehydes in the presence of sulfonic acid-functionalized activated carbon (AC-SO_3H), as an active catalyst, under solvent-free conditions. According to the optimized variables, the best reaction conditions for preparing benzimidazole were found to be: 0.02 gram of catalyst in solvent-free condition at 30 Min. and at 75 °C. To demonstrate the stability and durability of the catalyst, the yields of five successive runs with recovered catalyst were reported, showing no significant change in the obtained yields. Ultimately, the synthesis of benzimidazoles was achieved using an efficient, simple, environmentally benign, inexpensive and economic approach in the presence of AC-SO_3H catalyst.

Graphical Abstract



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Introduction

Imidazole, a five-membered heterocyclic compound, was first synthesized through the reaction of glyoxal with formaldehyde and ammonia in 1858 [1]. Later in 1882, the same compound was synthesized using dicarbonyl compounds reacted with ammonia and an aldehyde poly-substituted imidazole 1882 [2]. Benzimidazole is an important heterocyclic compound as it is a constituent of a broad range of natural products. Accordingly, great deals of research have been actively dedicated to new routes for the synthesis of benzimidazoles [3]. So far, a number of methods and catalysts have been proposed for preparing the benzimidazoles, including H_2O_2/HCl and $Cu(OTf)_2$ [4], Iodine [5], $ZrCl_4$ [6], $SnCl_4$ [7], $TiCl_4$ [8], $ZrOCl_2.8H_2O$ [9], $Cu(OH)_2$ [10], $Yb(OTf)_3$ [11], $Na_2S_2O_4$ [12], phospho sulfonic acid [13], γ-Fe_2O_3@HAp-Fe^{2+} NPs [14] and $SnCl_2.2H_2O$ [15]. However, most of these methodologies suffer from particular disadvantages such as low yield, vigorous reaction conditions, high temperature requirement, long reaction time, high cost, highly acidic conditions, use of harmful solvents, the formation of by-products and toxic wastes, and tedious work-up.

Imidazole and its derivatives are the biologically active compounds with anti-depressant [16], anti-inflammatory [17], anti-viral [18], herbicidal [19], anti-cancer [20], analgesic [21], antitubercular [22] antifungal [23], and antiallergic effects [24]. The five-membered imidazole structure exists in a variety of biologically important structures such as histidine amino acid [25] and histamine hormone [26]. Due to the important applications of the imidazole and its derivatives, the research toward developing new routes and tough conditions and regents for their synthesis is of great value. The present research study reports a solvent-free one-pot method for synthesis of the benzimidazole derivatives from 1, 2-phenylenediamine and aldehydes in the presence of the AC-SO_3H as catalyst.

Experimental

Materials and methods

Chemicals were purchased from Merck and Across organics chemical companies. ^1H and ^{13}C NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer in DMSO-d_6 as the deuterated solvent and TMS as an internal standard. Brucker FT-IR spectrometer was employed to attain Fourier transform infrared spectra (FT-IR) using KBr pellets. Mass spectra were measured by Agilent model 5975c-inert MSD with Triple-Axis Detector mass spectrometer. Bruker AXSD-8 Advance X-ray diffractometer was utilized to record X-ray diffraction (XRD) analysis of the powders using monochromatic CuKα, radiation (λ=1.5406 A°). Data were collected from 5° to 80° at a scan rate of 0.1° min-1. IMECO 34 kHz frequency, 500W sonicator, was used to obtain homogeneous solutions of AC-SO_3H. Stuart Scientific melting point apparatus was exploited for the determination of melting points. The morphology of the samples and energy dispersive X-ray spectroscopy *(*EDS*)* analysis were obtained using the TE-SCAN field emission scanning electron microscope (FE-SEM).

*Preparation of activated carbon sulfonic acid (AC-SO_3H) catalyst (**3**)*

Sulfonic acid functionalization of activated carbon was performed using the chlorosulfonic acid in chloroform in the reflux condition. Thus, to chloroform (50 mL) was added activated carbon (2 g), and the mixture was sonicated in an ultrasonic bath for 1 h. After formation of the homogeneous black dispersed activated carbon in chloroform, chlorosulfonic acid (1 mL) was

added dropwise in 1 h (follow safety instructions, especially face and ear protection). The resulting mixture was stirred for 2 h and then refluxed for 24 h. The resulting suspension was cooled to room temperature, washed with ethanol successively to remove organic contaminants, and then was washed with water for removal of excess acid until the pH of filtrates becomes neutral. Finally, the precipitate was washed with acetone twice and dried at 80 °C for 10 h in a vacuum oven, and was stored in a tight vial.

*Synthesis of 4-(4-nitrobenzyloxy) benzaldehyde (**6**)*

To 4-nitrobenzyl bromide (**5**, 1 mmol, 0.216 g) in acetonitrile (25 mL) were added 4-hydroxy benzaldehyde (**4**, 1 mmol, 0.122 g) and K_2CO_3 (1 mmol, 0.14 g). The mixture was refluxed for 48h and the progress of the reaction was monitored by thin-layer chromatography (TLC). After completion, the mixture was cooled to room temperature, and water was added (50 mL), and then the crude precipitate was filtered and washed with water (50 mL). The pure product (**6**) was obtained using dry column chromatography on silica gel using ethyl acetate/n-hexane as eluents in 94% yield and melting point of 123-124 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.57 (s, 2H), 7.38 (dd, J = 4, 4.1 Hz, 2H), 7.89 (d, J = 8 Hz, 2H), 8.04 (dd, J = 4, 8 Hz, 2H), 8.42 (dd, J = 4 , 7 Hz, 2H), 10.03 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.7, 163.2, 147.5, 144.6, 132.2, 130.5, 128.7, 124, 115.7, 68.8. Anal. Cal. for $C_{14}H_{11}NO_4$ (M = 257.24): C, 65.37; H, 4.31; N, 5.44, Found: C, 65.35; H, 4.32; N, 5.45; MS (EI): m/z 257 $(M)^+$.

General procedure for synthesis of benzimidazole derivatives

To AC-SO_3H (0.02 g) were added 1,2-phenylene diamine (**7**, 1 mmol) and aldehyde (1 mmol). The reaction mixture was homogenized and heated at 75 °C for 30 Minute. Thin-layer chromatography (TLC) was utilized to monitor the progress of the reaction. Finally, acetone was added to the mixture and filtered. The catalyst was collected, and water was added to the filtrate and extracted with ethyl acetate three times (3×20 mL). The combined organic layers were dried (Na_2SO_4) and evaporated to afford the crude product which was purified by recrystallization in ethyl alcohol to afford the pure product in high yield.

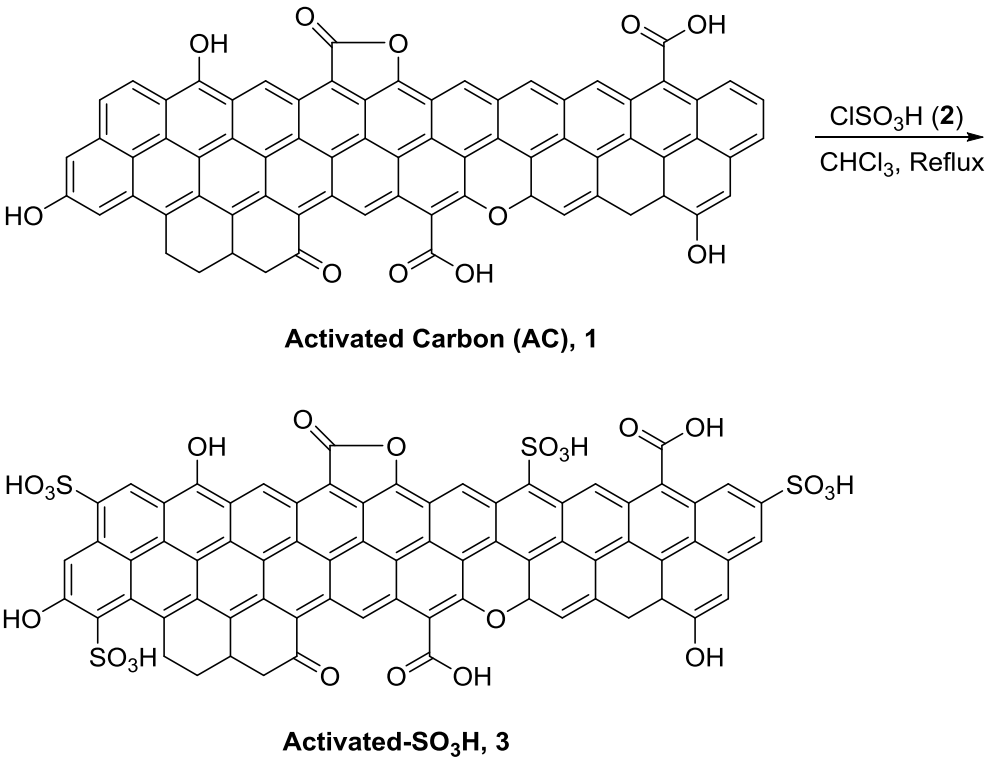
*2-[4-(4-nitrobenzyloxy) phenyl]-1H-benzimidazole (**9l**)*

^{1}H NMR (400 MHz, DMSO-d_6): δ 5.02 (s, 2H), 6.61 (s, 1H), 6.74 (d, J = 8Hz, 2H), 7.38-7.58 (m, 10H), 7.88 (dd, J = 4, 8 Hz, 4H), 8.11 (dd, J = 4, 8 Hz, 2H), 8.61 (d, J = 8Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161, 160.1, 157.8, 152.7, 150.4, 147.5, 147.4, 145.9, 145.3, 144.9, 144.8, 138.3, 135.8, 135.3, 131.4, 129.5, 128.7, 128.6, 128.6, 128.2, 125.9, 124.3, 124.1, 124, 115.8, 115.5, 68.4.

Results and Discussion

The sulfonic acid-functionalized activated carbon was prepared by letting the graphite react with chlorosulfonic acid in refluxing chloroform (Scheme 1). Infrared (IR) spectra of the AC-SO_3H showed a characteristic peak corresponding to the sulfonic acid functional groups at 3413 cm^{-1} and other peaks indicating sulfone bonds at 1024 and 1056 cm^{-1} (Figure 1). FESEM images showed the morphology of the AC-SO_3H as particles at the nanoscale (Figure 2). EDS analysis results confirmed the presence of oxygen and sulfur on the surface of the AC-SO_3H with the elemental composition (Figure 3). To prepare the new benzimidazole (**9l**), firstly, a new aldehyde (**6**) was prepared through the reaction of 4-hydroxy benzaldehyde (**4**) with 4-

nitrobenzyl bromide (**5**) in refluxing acetonitrile under nucleophilic conditions (Scheme 2).



Scheme 1. Synthesis of activated carbon sulfonic acid (AC-SO_3H)

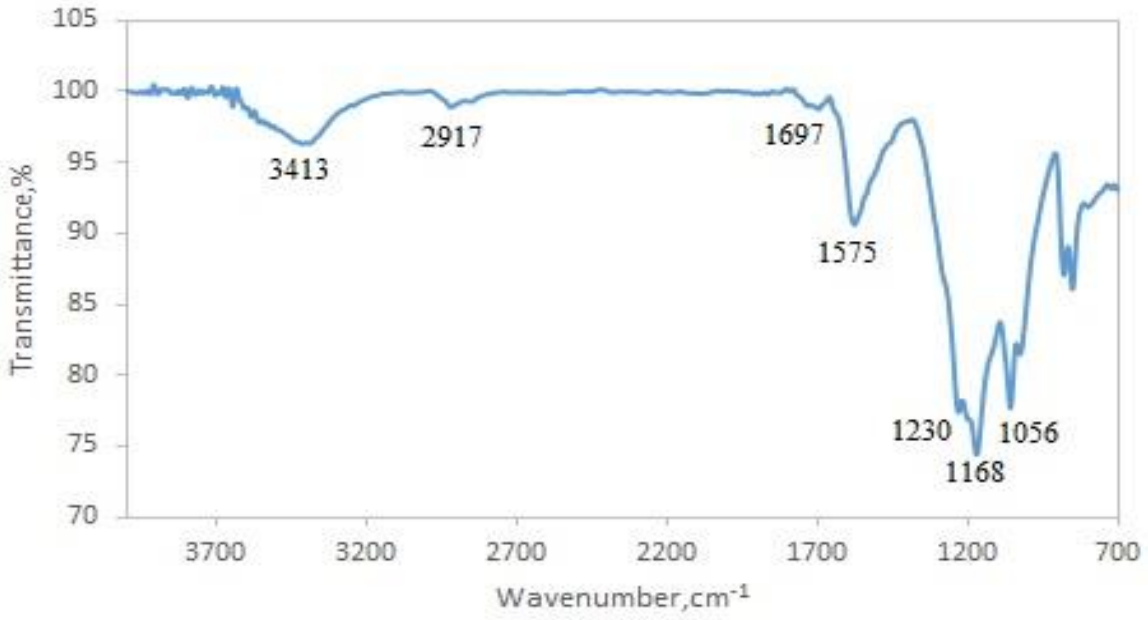


Figure 1. IR spectrum of activated carbon sulfonic acid (AC-SO_3H)

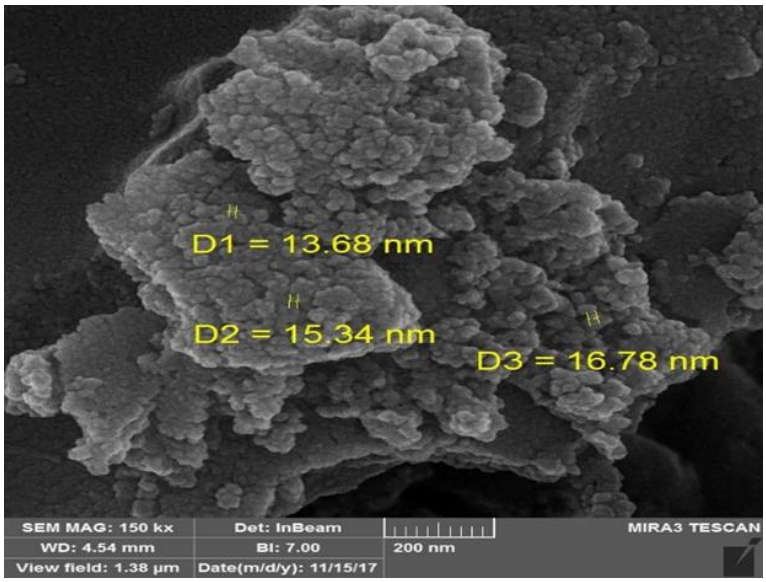


Figure 2. FESEM image of activated carbon sulfonic acid (AC-SO_3H)

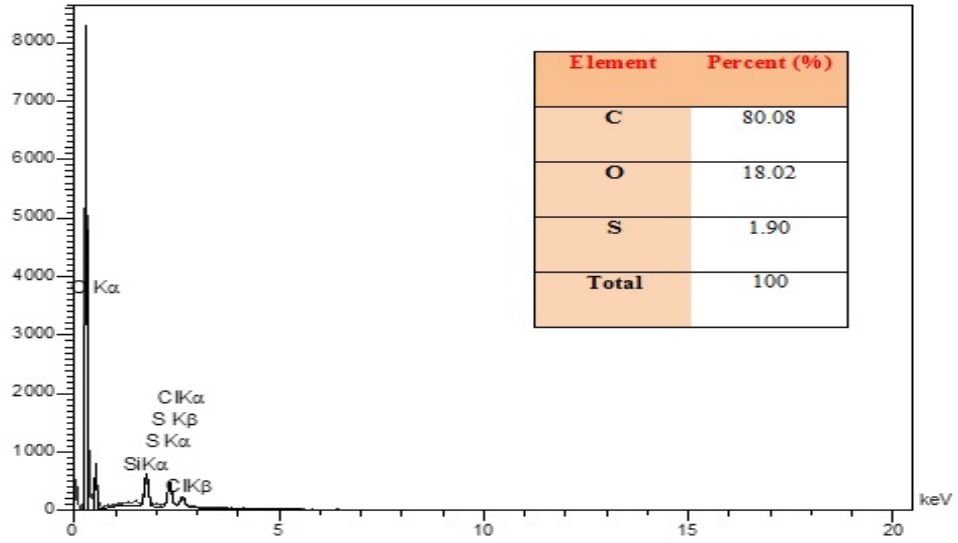
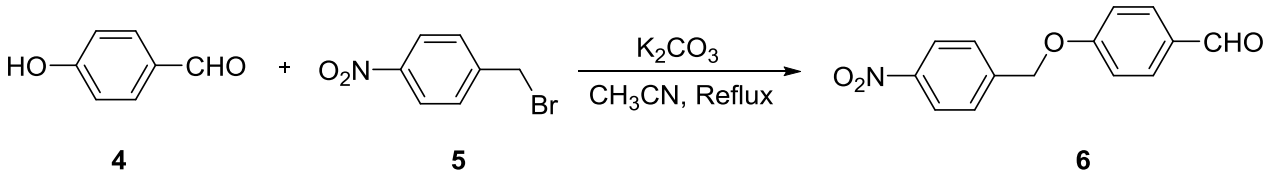


Figure 3. EDS of activated carbon sulfonic acid (AC-SO_3H) and the weight percentages of the main elements



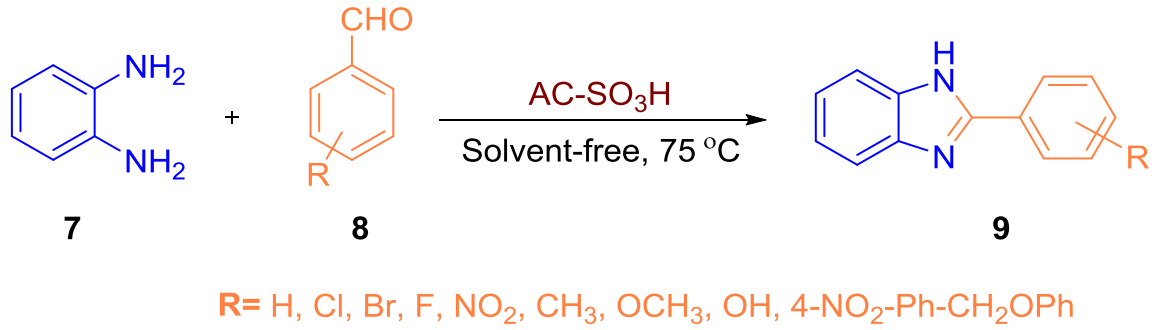
4 **5** **6**

Scheme 2. Synthesis of 4-(4-nitrobenzyloxy) benzaldehyde (**6**)

The benzimidazole was prepared through the reaction of 1,2-phenylenediamine with aldehydes in the presence of the AC-SO_3H as a catalyst without any solvent (Scheme 3).

Reaction conditions were optimized by investigating the effects of four parameters, namely catalyst dosage, temperature, and reaction time (Table 1, entry 12). Based on the results, for the synthesis of **9a**, optimal yield was obtained under solvent-free conditions with 0.02 g of catalyst, a reaction temperature of 75 °C, and a reaction time of 30 min. Previously reported benzimidazoles (Table 2) were characterized using the corresponding melting points, and the new one (**9l**) was confirmed using ^{1}H NMR, ^{13}C NMR, and elemental analyses. To assess the catalyst in terms of reusability, it was recovered and then reused for five successive runs. The yield of the product (**9a**) revealed no significant change, confirming the reusability of the catalyst (Table 3).

Scheme 4 presents the mechanism through which the imidazole is formed. Firstly, benzaldehyde is protonated in the presence of AC-SO_3H to form an intermediate (designated as Intermediate 1). Next, imine (Intermediate 2) is formed in the presence of protonated benzaldehyde and 1, 2-phenylenediamine. Then, the imine is protonated to give rise of the Intermediate 3 that ends up producing the imidazole (**9a**).



Scheme 3. Synthesis of benzimidazoles using activated carbon sulfonic acid (AC-SO_3H) catalyst

Table 1. Optimization of the reaction conditions for **9a** (benzimidazoles)

Entry	Solvent	Catalyst (g)	Temperature (°C)	Time (h)	Yield (%)
1	EtOH	0.02	Reflux	1.0	86
2	MeOH	0.02	Reflux	1.0	69
3	Solvent-free	0.01	80	1.0	79
4	Solvent-free	0.02	80	1.0	84
5	Solvent-free	0.01	90	1.0	82
6	Solvent-free	0.02	90	1.0	86
7	Solvent-free	0.01	70	1.0	76
8	Solvent-free	0.02	60	1.0	89
9	Solvent-free	0.01	80	1.5	84
10	Solvent-free	0.02	70	1.0	97
11	Solvent-free	0.02	75	0.5	97
12	Solvent-free	0.03	75	0.5	97
13	Solvent-free	0.04	75	0.5	97

Table 2. Synthesis of different benzimidazoles using activated carbon sulfonic acid (AC-SO_3H) catalyst

Entry	R	Product	Time/Min.	Yield (%)[a]	MP/°C	
					Found	Reported
1	C_6H_5	**9a**	30	97	287-288	288-289
2	4-MeC_6H_4	**9b**	30	95	292-293	293-294
3	4-$MeOC_6H_4$	**9c**	35	95	230-232	231-232
4	4-$(CH_3)_2NC_6H_4$	**9d**	40	90	250-251	249-250
5	2-ClC_6H_4	**9e**	40	89	226-227	227-229
6	4-ClC_6H_4	**9f**	25	97	281-282	281-282
7	2-OH-C_6H_4	**9g**	40	91	182-183	183-184
8	2-$MeOC_6H_4$	**9h**	45	88	134-135	133-134
9	3-$O_2NC_6H_4$	**9i**	40	90	185-186	185-187
10	4-$O_2NC_6H_4$	**9j**	25	94	310-311	310-311
11	4-NO_2-Ph-CH_2OPh	**9l**	40	94	156-158	-

[a] Isolated yield

Table 3. Yield and AC-SO_3H catalyst recovery and reusability for **9a** for five runs

Run	Recovery	Yields
1	99	97
2	99	97
3	98	96
4	98	96
5	97	95

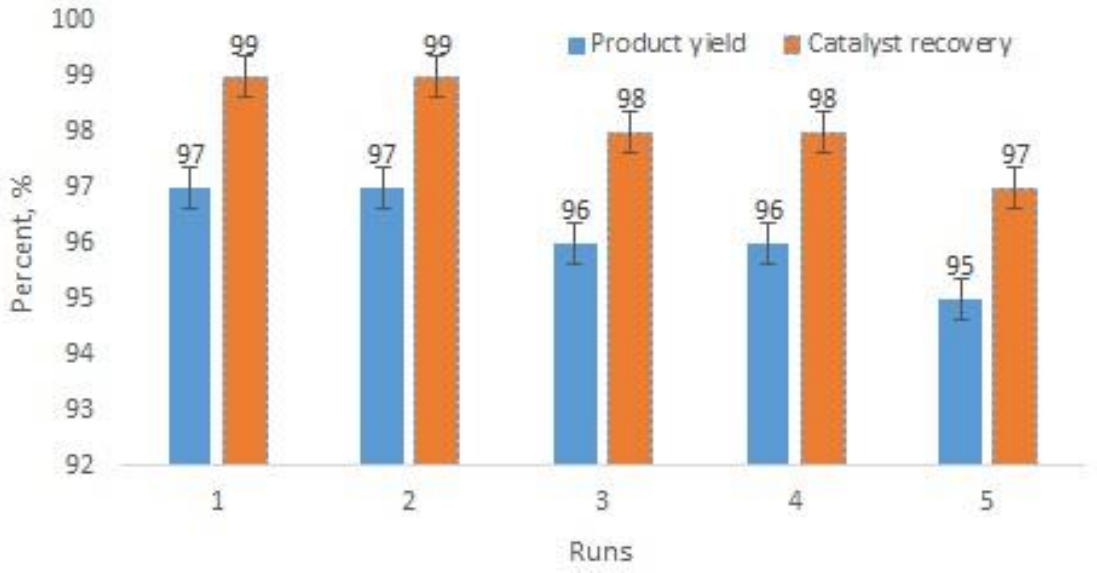
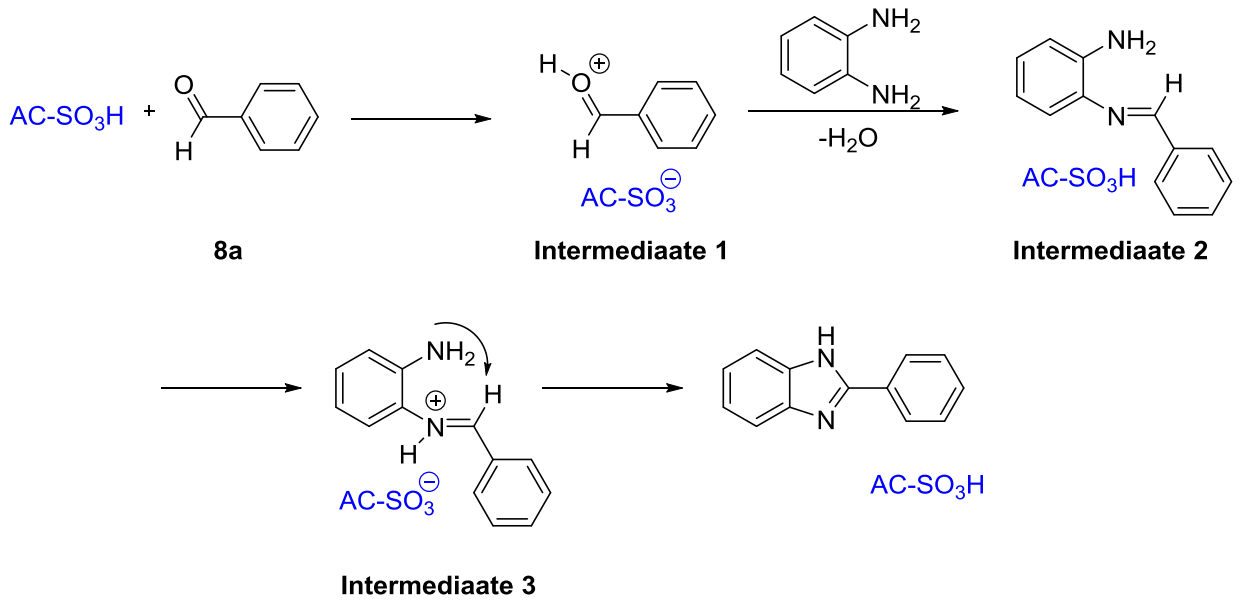


Figure 4. Catalyst recovery and product yields (**9a**) for five runs



Scheme 4. Mechanism of benzimidazole formation in the presence of AC-SO_3H

Conclusions

In this work, the sulfonic acid-functionalized activated carbon (AC-SO_3H) was prepared as an efficient, green, inexpensive, metal-free and recyclable catalyst. Then, AC-SO_3H was used for the synthesis of benzimidazoles in mild reaction conditions without solvent in excellent yields. The optimized reaction conditions revealed that best results were obtained at the temperature of 75 °C, catalysts loading of 0.02 g in 30 min, and in solvent-free condition. The reaction was carried out using the aldehydes with different substituents including, electron releasing, electron withdrawing substituents and halogens and the benzimidazoles that were obtained in excellent yields. The catalyst was found to remain stable under the studied reaction conditions and successfully recovered and then reused for five successive runs, with the resultant yield showing no significant loss upon the reuse of the recovered catalyst. Based on the results, the synthesis of benzimidazoles was achieved using an efficient, simple, environmentally benign, inexpensive and economic approach in the presence of AC-SO_3H catalyst, similar strategy can be considered to accomplish more transformations in organic synthesis.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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