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Silica supported piperazine sulfosalicylic acid: A reusable and efficient catalyst for synthesis of 2-aryl-benzimidazoles

Vaibhav Mishra & Tejpal Singh Chundawat*

Department of Applied Sciences, The North Cap University, Gurugram 122 017, India

E-mail: chundawatchem@yahoo.co.in; tejpal@ncuindia.edu

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A new silica supported piperazine sulfosalicylic acid catalyst has been synthesized and explored for the synthesis of 2-aryl benzimidazoles. The catalyst is found to be highly efficient and recyclable. The new catalytic system is found to exhibit excellent yields of 2-aryl benzimidazoles and moderate to good yields of 2-heteroaryl and 2-alkyl benzimidazoles.

Keywords: 2-Aryl-benzimidazoles, solid supported catalyst, piperazine sulfosalicylic acid, aldehyde, silica gel

2-Aryl benzimidazoles are well known for their promising and diverse biological activity. Diverse pharmacologically active drugs containing this nucleus are available in market such as Antiparasitic (Thiabendazole), Anti hypertensive (Telmisartan). Due to its promising and diverse activity numerous catalytic systems were developed for the synthesis of benzimidazoles[1-4]. In order to utilize a recoverable or reusable solid catalyst, numbers of efforts have been done in area of silica supported catalytic systems[5-10]. Solid supported piperazine catalysts have recently been explored and utilized for various organic reactions[11-14]. However, use of silica supported piperazine catalyst for the synthesis of benzimidazoles and particularly 2-aryl benzimidazoles is never reported earlier. In this work we report use of silica gel supported piperazine sulfosalicylic acid as an efficient and reusable catalyst for the synthesis of 2-aryl benzimidazoles. We also report the synthesis of this new catalytic system (SSA-Pz-P-SG) and its comparative advancement over silica gel supported amino propyl sulfosalicylic acid silica gel (SSA-AP-SG). AP-SG is earlier reported for study of metal absorption[15,16] and here we report use of its 5-sulfosalicylic acid derivative (SSA-AP-SG) and comparative catalytic efficiency with its new piperazine analogue (SSA-Pz-P-SG) in synthesis of 2-aryl benzimidazoles. Catalytic activity of its new piperazine analogue (SSA-Pz-P-SG) reported here found to exhibit profound catalytic activity over SSA-AP-SG.

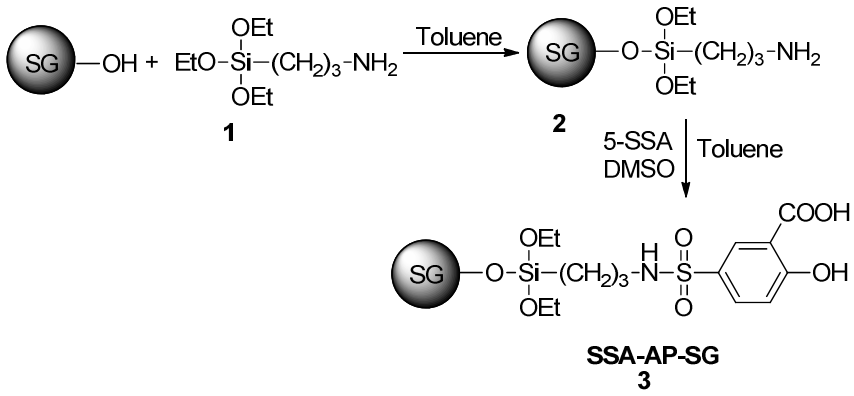
Results and Discussion

Herein we have synthesized two silica supported catalysts: first is SSA-AP-SG which was synthesized according to the reference[5,6] and second SSA-Pz-P-SG which was synthesized from AP-SG *via* formation of piperazine on amino group and then its reaction with 5-sulfosalicylic acid to obtain a new piperazine analogue of SSA-AP-SG. The synthetic route for synthesis of both catalysts is depicted in Scheme I and Scheme II.

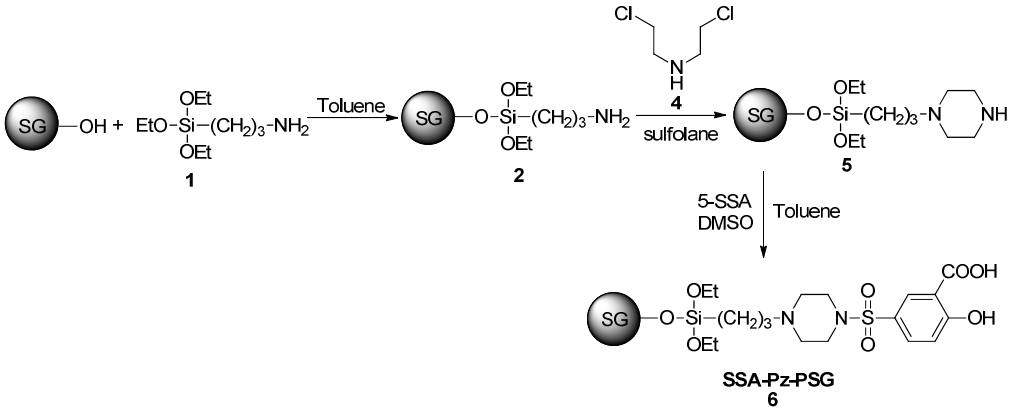
The catalytic efficiency of both silica supported catalysts was checked in the synthesis of 2-(4-hydroxyphenyl)-benzimidazole from *o*-phenylenediamine and 4-hydroxybenzaldehyde in ethanol at 80°C Scheme III.

Both the catalysts were recovered by filtration after reaction and checked for their reusability in the process. Both catalysts showed good catalytic activity in synthesis and good capable for reuse up to 4 cycles (1 fresh and 3 recycling). However, new silica supported piperazine sulfosalicylic acid catalyst (SSA-Pz-P-SG) found to exhibit profound activity in catalytic efficiency as well as reusability (Table I).

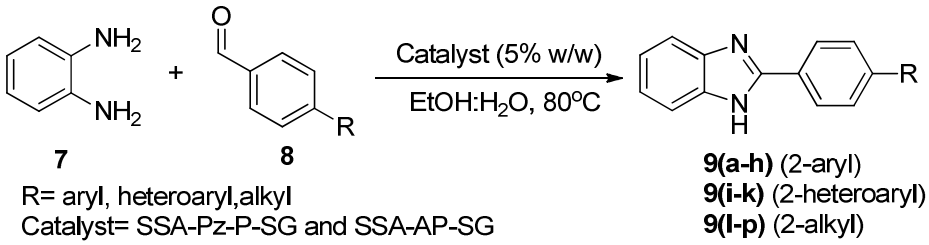
The plausible mechanism for one pot synthesis of 2-aryl benzimidazole through this new catalytic system is depicted in Scheme IV. The activity and selectivity of SSA disseminated on the surface of AP-SG and Pz-P-SG is improved because of the effective surface area of reagent increased manifold. The catalyst SSA-Pz-P-SG fastened the reaction by increasing the electrophilicity of aldehyde. Carboxylic group of sulfosalicylic acid helps in activation of



Scheme I — Synthetic route for preparation of SSA-AP-SG



Scheme II — Synthetic route for preparation of SSA-Pz-P-SG

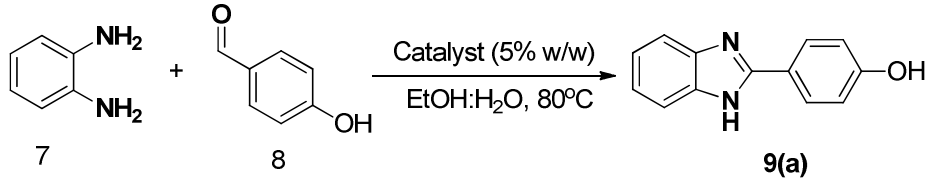


Scheme III — Synthesis of 2-aryl benzimidazoles using silica supported catalysts

o-amino group, which results in a cyclic type intermediate stage which forms imine intermediate. This imine intermediate is activated by carboxylic group which results in cyclization of imine. At last air oxidation results the product benzimidazole **9(a-p).**

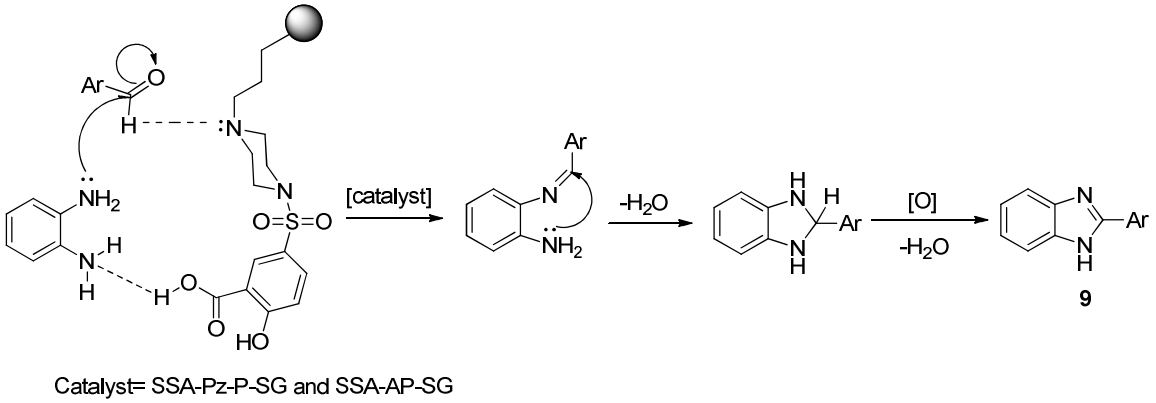
Feasibility of the new catalytic system was checked for a series of different 2-arylbenzimidazoles by reaction of *o*-phenylenediamine and substituted benzaldehydes (Table II). Different reaction conditions such as solvent, temperature and time were also optimized and ethanol/water mixture in ratio of 9:1 at 80°C for 6-12h is found to provide optimum yields. Crude 2-aryl benzimidazoles obtained were purified over silica gel to obtain analytically pure compounds. Further, feasibility of this catalytic system was explored for synthesis of heteroaryl benzimidazoles and alkyl benzimidazoles. The catalytic reaction found to be feasible for heteroaryl and alkyl substituent as well, but exhibited lower yields as compared to 2-aryl benzimidazoles.

Table I — Comparative efficiency of SSA-AP-SG and SSA-Pz-P-SG catalysts in synthesis of **9a**



R= aryl, heteroaryl,alkyl
Catalyst= SSA-Pz-P-SG and SSA-AP-SG

S.No.	Catalyst	Catalyst (%w/w)	Solvent	Temp (°C)	Time (h)	Yield (%)
1	No catalyst	No catalyst	EtOH/water	80	24	0
2	SSA-AP-SG	15	EtOH/water	80	8	91
3	SSA-Pz-P-SG	15	EtOH/water	80	6	92
4	SSA-Pz-P-SG	15	EtOH/water	100	6	92
5	SSA-AP-SG	10	EtOH/water	80	8	83
6	SSA-Pz-P-SG	10	EtOH/water	80	6	91
7	SSA-Pz-P-SG	10	EtOH/water	100	6	91
8	SSA-AP-SG	5	EtOH/water	80	8	77
9	SSA-Pz-P-SG	5	EtOH/water	80	6	93
10	SSA-Pz-P-SG	5	EtOH/water	100	6	93
11	SSA-Pz-P-SG	5	EtOH/water	60	24	25
12	SSA-AP-SG	3	EtOH/water	100	24	65
13	SSA-Pz-P-SG	3	EtOH/water	80	12	66
14	SSA-Pz-P-SG	3	EtOH/water	100	12	65
15	SSA-Pz-P-SG	10	Acetonitrile	80	24	43
16	SSA-Pz-P-SG	10	Ethanol	80	24	80
17	SSA-Pz-P-SG	10	Water	100	24	Traces
18	SSA-Pz-P-SG	10	Methanol	Reflux	24	32
19	SSA-Pz-P-SG	10	Toluene	Reflux	24	0

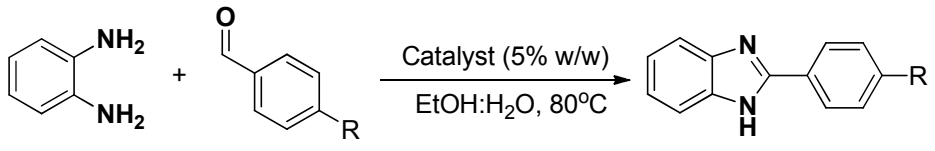


Catalyst= SSA-Pz-P-SG and SSA-AP-SG

Scheme IV — Plausible mechanism of SSA-Pz-P-SG catalyst activity in synthesis of **9a-p**

Confirmation of formation of solid supported catalysts **(6)** and **(3)** and intermediates **(2)** and **(5)** was determined by IR and UV spectral analysis. The IR spectra of solid intermediate **(2)** showed absorption peaks at ν (cm^{-1}) 3423.65 associated with N-H stretching of primary amino group, ν (cm^{-1}) 1624.06 for N-H bending vibration and ν (cm^{-1}) 800.46 for N-H wagging vibration of primary amine. Two broad overlapping bands at ν (cm^{-1}) 1089.78 are associated with complex and branched Si-O-Si stretching vibrations, which confirms the linkage of 3-aminopropyltriethoxysilane with silica gel through a Si-O-Si bond and having a free primary amino group at other end, hence confirming the formation of

Table II — Details of 2-Aryl benzimidazoles synthesized using SSA-Pz-P-SG as catalyst



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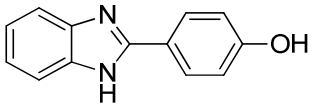
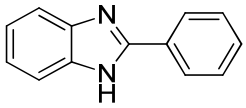
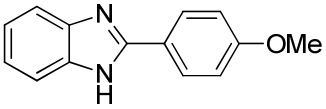
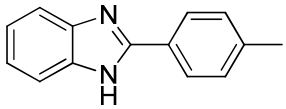
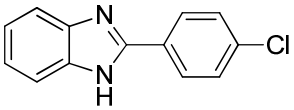
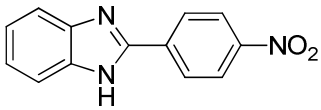
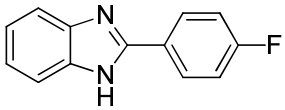
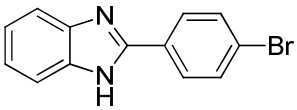
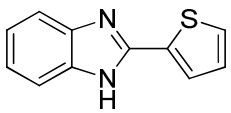
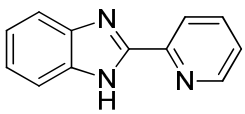
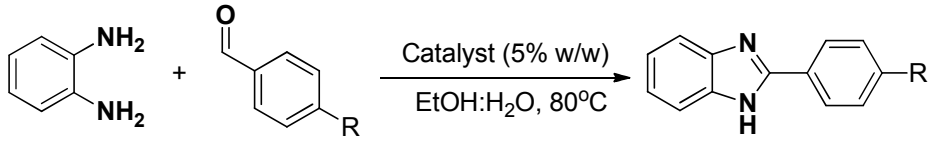
R= aryl, heteroaryl,alkyl
Catalyst= SSA-Pz-P-SG and SSA-AP-SG

9(a-h) (2-aryl)
9(i-k) (2-heteroaryl)
9(l-p) (2-alkyl)

S.No.		Product	Time (h)	Yield (%)	m.p. (°C)	Ref*.
1	**9a**		6	93	240-243	17
2	**9b**		6	92	292-293	17
3	**9c**		6	93	225-226	17
4	**9d**		6	91	286-288	2
5	**9e**		6	90	288-290	1
6	**9f**		7	89	300-302	17
7	**9g**		6	90	250	1
8	**9h**		6	90	296	1
9	**9i**		9	78	330-332	2
10	**9j**		9	76	219-220	1

(*Contd.*)

Table II — Details of 2-Aryl benzimidazoles synthesized using SSA-Pz-P-SG as catalyst (*Contd.*)



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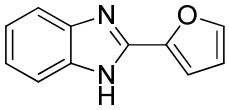
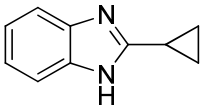
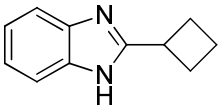
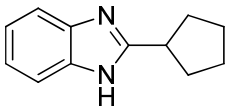
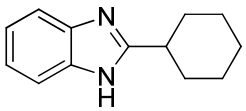
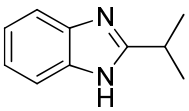
R= aryl, heteroaryl,alkyl
Catalyst= SSA-Pz-P-SG and SSA-AP-SG

9(a-h) (2-aryl)
9(i-k) (2-heteroaryl)
9(l-p) (2-alkyl)

S.No.		Product	Time (h)	Yield (%)	m.p. (°C)	Ref*.
11	**9k**		9	79	286-288	2
12	**9l**		12	54	232	–
13	**9m**		12	55	Oil	–
14	**9n**		12	57	Oil	–
15	**9o**		12	56	285-286	–
16	**9p**		14	52	237	–

*Melting points and purity (on TLC) were matched with the standard samples prepared by respective references.

compound **(2)**. UV spectrum of **(2)** does not show any UV absorption, because of presence of all aliphatic chain and no such chromophore is in the structure.

The IR spectra of **(3)** showed absorption peaks at ν (cm^{-1}) 3441.01 associated with O-H stretching of phenolic hydroxyl group. ν (cm^{-1}) 2927 is for C-H stretching of sp^3 carbon, which confirms presence of phenyl ring. ν (cm^{-1}) 1627.92 for carbonyl group of carboxylic acid. Two broad overlapping bands at ν (cm^{-1}) 1089.78 are associated with complex and branched Si-O-Si stretching vibrations, due to linkage of silyl chain with silica gel. ν (cm^{-1}) 798 for C-N stretching vibration of secondary amine (piperazine). ν (cm^{-1}) 719 for C-H rocking vibration of $–CH_2$ alkyl chain. ν (cm^{-1}) 948 for Si-O stretching of $Si-OCH_2CH_3$. Hence confirm the formation of compound **(3)**. UV spectrum of **(3)** showed absorption in range of λ (nm) 250-325, which is due to presence of aromatic phenyl ring with phenolic –OH and Carboxylic group, which confirms the presence of sulfosalicylic acid is present in the structure. Hence UV spectrum also confirms the formation of **(3)**.

IR spectra of **(5)** showed absorption peaks at ν (cm^{-1}) 3466.08 for N-H vibrations of piperazine. ν (cm^{-1}) 1095 for Si-O-Si confirming linkage of organic compound with silica gel. ν (cm^{-1}) 794 for C-N stretching of piperazine ring. Shift of peak at ν (cm^{-1}) 3423.65 (primary $–NH_2$) to ν (cm^{-1}) 3466.08 (secondary –NH) confirms formation of compound **(5)** from **(2)**. UV spectrum of **(5)** showed absorption

at λ nm 275, which is due to piperazine attached to the aliphatic chain. Hence UV spectrum also confirms the formation of compound **(5)**.

IR spectra of **(6)** showed absorption at ν (cm^{-1}) 3444.87 for O-H stretching of phenolic OH group. ν (cm^{-1}) 2927 is for C-H stretching of sp^3 carbon, which confirms presence of phenyl ring. ν (cm^{-1}) 1627 for C=O stretching of carboxylic acid group. ν (cm^{-1}) 1477.47 for C-O-H in plane bend of carboxylic group. Two broad overlapping bands at ν (cm^{-1}) 1095.57 are associated with complex and branched Si-O-Si stretching vibrations, due to linkage of silyl chain with silica gel. ν (cm^{-1}) 790.81 for C-N stretching vibration of tertiary amine (piperazine). ν (cm^{-1}) 711 for C-H rocking vibration of $–CH_2$ alkyl chain. ν (cm^{-1}) 950.91 for Si-O stretching of $Si\text{-}OCH_2CH_3$. Hence confirm the formation of compound **(6)**. UV spectrum of **(6)** showed absorption at λ (nm) 215, 250 and 325 due to presence of piperazine, carboxylic acid and phenolic –OH. Hence IR and UV spectra confirm the formation of catalyst **(6)**.

Confirmation of formation of formation of 2-substituted benzimidazoles **9(a-p)** was determined by ^{1}H NMR, ^{13}C NMR, IR, EI-MS spectral analysis. Characteristic peak for benzimidazole N-H in IR ν (cm^{-1}) 3016-3714 were observed. ^{1}H NMR of compound **(9a)** showed δ (ppm) 12.65 (singlet) attributed to NH, 9.96 (singlet) (-OH on phenyl ring), 8.01(doublet), two protons of phenyl ring attached with 2-position of benzimidazole, 7.53 (singlet), two protons of benzimidazole ring near cyclized ring, 7.16 (dd), two protons of benzimidazole ring and 6.92(doublet), two protons of phenyl ring near phenolic OH. Mass spectra confirms the mass of compound *m/z* $[M+H]^+$ 211.08 as calculated exact mass to be 210.08.

Experimental Section

General chemical procedures

All the required chemicals were purchased from Spectrochem and Aldrich Chemical Company. Pre-coated aluminum sheets (silicagel 60 F254, Merck) were used for thin-layer chromatography (TLC) and spots were visualized under UV light. Melting points were determined using open capillary tube and hot paraffin oil and are uncorrected. IR spectra were recorded on Perkin-Elmer-1800 FTIR spectrophotometer in the frequency range of ν 450-4000 cm^{-1} in Nujol mull and as KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Advance II 400 NMR spectrophotometer and Varian 100 MHz spectrophotometer respectively using a solvent and trimethylsilane (TMS) as an internal standard. Splitting patterns are designated as follows; s= singlet, d = doublet, dd=double doublet, m= multiplet. Chemical shift (δ) values are given in ppm. Mass spectra (EIMS) were obtained on a Waters Xevo G2-XS Tof mass spectrometer (ESI).

Preparation of APSG (silica gel-triethylsilyl-propylamine), 2

AP-SG was prepared as according to reference[16]. Silica gel (Spectrochem 60-120 mesh) was purified by refluxing in conc. HCl for 12 hours and then washed with water until neutral. The silica gel was activated at 150°C under vacuum. 30 g of activated silica gel was refluxed in 100 mL toluene and 30 mL 3-aminopropyltriethoxysilane for 12 hours under nitrogen atmosphere. After cooling, solid was filtered and washed with plenty of water and ethanol. Solid AP-SG was dried at 100°C under vacuum for 8 hours. Solid supported intermediate compound **(2)** was characterized with IR (KBr) ν (cm^{-1}) 3423.65 (N-H stretching), 1624.06 (N-H bend), 1089.78 (Si-O-Si) and no U.V absorption observed due to presence of all aliphatic region.

Preparation of SSA-AP-SG (silica gel-triethylsilyl-propylamino sulfosalicylic acid), 3

SSA-AP-SG was also prepared according to reference[15]. 0.25g (0.98mmol) of 5-sulfosalicylic acid was added to a 50 mL flask and dissolved in 2 mL DMSO. 1.0 g APSG and 8 mL toluene were added to the flask and the mixture was stirred at 80°C for 8 hours. The resulting solid product was filtered and washed with water, ethanol and toluene respectively. Solid was dried at 70°C under vacuum for 7 hours. Solid supported catalyst was characterized with IR (KBr) ν (cm^{-1}) 3441.01 (O-H phenolic), 2927.94 (C-H stretch sp^3C), 1627.92 (-COOH), 1089.78 (Si-O-Si), 948.98 (Si-OEt), 798.53 (C-N stretch sec. amine), 719.45 (C-H rocking) and UV λ_{max} (nm) 250 (-COOH), 325 (phenolic OH).

Preparation of Pz-P-SG (silica gel-propyl piperazine), 5

1.0 g AP-SG, 0.35g (2.46mmol) bis (chloroethyl)amine and 0.4g (2.89mmol) K_2CO_3 were added in 2 mL sulfolane (solvent), heated to 125°C for 48 hours. Cooled to 40°C and added acetone 50 mL, stirred and filtered hot. Washed solid with acetone, water and then again with acetone repeatedly. Solid was dried at 50°C for 12 hours under

vacuum. Solid supported intermediate compound **(5)** was characterized with IR (KBr) ν (cm^{-1}) 3466.08 (N-H stretch piperazine), 1095 (Si-O-Si), 794 (C-N stretch) and UV λ_{max} (nm) 275 (piperazine)

Preparation of SSA-Pz-P-SG (silica gel propyl piperazine sulfosalicylic acid), 6

0.25g (0.98mmol) 5-sulfosalicylic acid was added to a 50 mL flask and dissolved in 2 mL DMSO. 1.0 g Pz-P-SG and 8 mL toluene were added to the flask and the mixture was stirred at 80°C for 8 hours. The resulting solid product was filtered and washed with water, ethanol and toluene respectively. Solid was dried at 70°C under vacuum for 12 hours. Solid supported catalyst was characterized with IR (KBr) ν (cm^{-1}) 3444.87 (O-H phenolic), 2927 (C-H sp^3C), 1627 (-COOH), 1095.57 (Si-O-Si), 950.91 (Si-OEt), 790.81 (C-N stretching tert. amine), 711.73 (C-H rocking alkyl CH_2) and UV λ_{max} (nm) 215 (piperazine), 250 (-COOH), 325 (-phenolic OH)

General procedure for synthesis of 2-Aryl benzimidazoles, 9a-p

o-phenylenediamine 0.10g (0.925mmol), catalyst 0.005g (5% w/w) and ethanol/ water mixture(9:1, 2mL) were added to a flask. Mixture was stirred at ambient temperature for 30 min before adding aldehyde (1.0mmol) to the mixture. The mixture was then heated to 80°C and stirred for 8-12h. After completion of reaction, mixture was cooled to ambient temperature, added ethyl acetate (10mL) and then filtered to recover the catalyst. Filtrate was concentrated and solid product obtained was purified by column chromatography. All compounds 9(a-p) were characterized by ^{1}H NMR, ^{13}C NMR and IR and Mass spectra.

Characterization of 2-substituted benzimidazole compounds, 9a-p

2-(4-Hydroxyphenyl)-1*H*-benzimidazole, 9a: Orange crystals; m.p. 240-243°C. IR (KBr): 1610 (C=N) , 3250 cm^{-1} (O-H,N-H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.65 (s, 1H), 9.96 (s, 1H), 8.01 (d, *J* = 2.4 Hz, 2H), 7.53 (s, 2H), 7.16 (dd, *J1* = 6.0 Hz, *J2* = 3.0Hz, 2H), 6.92 (d, *J* = 3.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.59, 152.25, 128.62, 122.07, 121.62, 116.15; MS: *m/z* $[M+H]^+$: 211.08.

2-Phenyl-1*H*-benzimidazole, 9b: Yellow crystals; m.p. 292-293 °C; IR (KBr): 1626 (C=N), 3436 cm^{-1} (N-H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.96 (s, 1H), 8.21-8.20 (t, *J* = 9.0 Hz, 2H), 7.62-7.49 (m, 5H), 7.23-7.20 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.70, 130.65, 130.31, 129.42, 126.91, 122.58; MS: *m/z* $[M+H]^+$: 195.1.

2-(4-Methoxyphenyl)-1*H*-benzimidazole, 9c: White crystals; m.p. 225-226°C; IR (KBr): 3439 (N-H), 1244 (C-O), 1613 (C=N), 2965 cm^{-1} (CH_3); ^{1}H NMR (400MHz, DMSO-d_6): δ 12.76 (s, 1H), 8.13 (d, *J* = 3.0 Hz, 2H), 7.56 (s, 2H), 7.18 (dd, *J1*=5.4 Hz, *J2* =3.0 Hz, 2H), 7.13 (d, *J* = 2.4 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.07,151.82, 128.48, 123.18, 122.21, 114.83, 55.79; MS: *m/z* $[M+H]^+$: 225.1.

2-(4-Methylphenyl)-1*H*-benzimidazole, 9d: Yellow crystals; m.p. 286-288°C; IR (KBr): 1623 (C=N), 2965 (CH_3), 3449 cm^{-1} (N-H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.83 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.20 (dd, *J1*=6.0 Hz, *J2* = 3.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.84, 140.04,129.98, 127.90, 126.87, 122.43, 21.44; MS: *m/z* $[M+H]^+$: 209.10.

2-(4-Chlorophenyl)-1*H*-benzimidazole, 9e: White crystals; m.p. 288-290°C; IR (KBr): 1623 (C=N), 3442 cm^{-1} (N-H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.00 (s, 1H), 8.20 (dd, *J1* = 6.6 Hz, *J2* = 1.8 Hz, 2H), 7.65-7.63 (m, 4H), 7.23 (d, *J* = 3.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.63, 134.96, 129.53, 128.61, 123.20, 122.29, 119.44, 111.88; MS: *m/z* $[M+H]^+$: 229.0.

2-(4-Nitrophenyl)-1*H*-benzimidazole, 9f: Yellow crystals; m.p. 300-302°C; IR (KBr): 1338, 1516 (NO_2), 1607 (C=N), 3436 cm^{-1} (N-H); ^{1}H NMR (400 MHz,DMSO-d_6): δ 13.31 (s, 1H), 8.44-8.41 (m, 4H), 7.73-7.66 (m, 2H), 7.28 (s, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 149.46, 148.26, 136.50, 127.85, 124.76; MS: *m/z* $[M+H]^+$: 240.1.

2-(4-Fluorophenyl)-1*H*-benzimidazole, 9g: Beige solid; m.p. 250°C; IR (KBr): 3252 (N-H), 1608 (C=N), 1442, 1229, 1158, 868, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 7.60-7.57 (m, 2H), 7.25-7.22 (m, 2H), 7.12-7.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.20, 162.71, 151.18, 131.30, 128.70, 127.77, 126.27, 122.97, 116.30; MS: *m/z* $[M+H]^+$: 213.01.

2-(4-Bromophenyl)-1*H*-benzimidazole, 9h: White solid; m.p. 296°C; IR (KBr): 3301 (N-H), 1595

(C=N), 1432, 1276, 964, 829, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93-7.91 (d, *J* = 8 Hz, 2H), 7.61-7.59 (d, *J* = 8 Hz, 2H), 7.26-7.23 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.02, 152.05, 150.80,148.43, 141.65, 132.29, 128.12, 123.12; MS: *m/z* $[M+H]^+$: 274.5.

2-(2-Thienyl)-1*H*-benzimidazole, 9i: Brown solid; m.p. 330-332°C; IR (KBr): 3015 (N-H), 1693 (C-S), 1606 (C=N), 1505, 1318, 1052, 757, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05-8.01 (d, *J* = 16 Hz, 1H),7.87−7.83 (d, *J* = 16 Hz, 1H), 7.66-7.64 (d, *J* = 8 Hz, 1H), 7.52-7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.00, 153.87, 137.52, 134.86, 129.42, 128.73, 128.18, 126.57, 125.37, 123.14, 121.59,115.33; MS: *m/z* $[M+H]^+$: 201.03.

2-(Pyridin-2-yl)-1*H*-benzimidazole, 9j: Off white solid; m.p. 219-220°C; IR (KBr): 3057 (N-H), 1593 (C=N), 1568 (C=N), 1541, 1487, 1465,1442,1400, 1315, 1278,742, 702 cm^{-1}; ^1H NMR (400 MHz,DMSO-d_6): δ 13.07 (s, 1H), 8.71 (d, 1H, *J* =4.60 Hz), 8.31 (d,1H, *J* =7.85 Hz), 8.02-7.94 (m, 1H), 7.69 (d, 1H, *J* =7.80 Hz), 7.52 (t, 2H, *J* =8.85 Hz), 7.27-7.15 (m, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 155.0, 154.7, 149.2, 141.7, 137.2, 124.2, 123.6, 123.0, 115.2; MS: *m/z* $[M+H]^+$: 196.08.

2-Furyl-1*H*-benzimidazole, 9k: Yellow solid; m.p. 286-288°C; IR (KBr): 3016(N-H), 1690 (C=N), 1602 (C-O), 1500, 1313, 1050, 751, 706 cm^{-1}; ^1H NMR (400MHz, DMSO-d_6): δ 12.96 (s, 1H), 7.95 (d, 1H, *J* = 1.05 Hz), 7.63 (d, 1H, *J* = 7.50 Hz), 7.50 (d, 1H, *J* = 7.50 Hz), 7.23-7.19 (m, 3H), 6.75-6.73 (m, 1H); ^{13}C NMR (100MHz, DMSO-d_6): δ 154.0, 142.9, 141.7, 141.5, 115.2, 112.0, 123.0, 107.1; MS: *m/z* $[M+H]^+$: 185.1.

2-Cyclopropyl-1*H*-benzo[*d*]imidazole, 9l: Yellow solid; m.p. 232°C; IR (KBr): 3735.6 (N-H), 2922.5, 1425.7, 1266.3, 744.5 cm^{-1}; ^1H NMR (400MHz, DMSO-d_6, 400 MHz): δ 7.41-7.39 (m, 2H), 7.08-7.05 (m, 2H), 3.55 (brs, 1H), 2.13-2.06 (m, 1H), 1.03 (d, *J* = 8.0 Hz,4H); ^{13}C NMR (100MHz, DMSO-d_6): δ 156.9, 138.9, 121.0, 114.2, 113.7, 113.6, 9.4, 8.7; MS: *m/z* $[M+H]^+$: 159.08.

2-Cyclobutyl-1*H*-benzo[*d*]imidazole, 9m: Yellow oil; IR (neat): 3710.0 (N-H), 2972.0 (C-H, alkyl), 1455.3, 1417.1, 1325.6, 1059.0 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.47-7.44 (m, 2H), 7.12-7.07 (m, 2H), 3.73-3.64 (m, 1H), 3.41 (brs, 1H), 2.43-2.31 (m, 4H), 2.08-1.85 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.7, 121.2, 114.4, 33.6, 27.5, 18.2; MS: *m/z* $[M+H]^+$: 173.10.

2-Cyclopentyl-1*H*-benzo[*d*]imidazole, 9n: Yellow oil; IR (neat): 3714.0(N-H), 2925.1 (C-H, alkyl), 1419.7, 1242.9, 1051.5 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.45-7.43 (m, 2H), 7.10-7.07 (m, 2H), 3.40 (brs, 1H), 3.29-3.21 (m, 1H), 2.05-2.04 (m, 2H), 1.92-1.83 (m, 2H), 1.74-1.69 (m, 2H), 1.67-1.61 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.5, 121.1, 39.0, 31.8, 25.2; MS: *m/z* $[M+H]^+$: 187.12.

2-Cyclohexyl-1*H*-benzo[*d*]imidazole, 9o: Yellow solid; m.p. 285-286°C; IR (KBr): 3419.0 (N-H), 2970.5 (C-H, alkyl) 1026.1, 997.0, 825.2, 767.2 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.44-7.43 (m, 2H), 7.10-7.08 (m, 2H), 3.36 (brs, 1H), 2.85-2.79 (m, 1H), 2.00 (d, *J* = 12.8, 2H), 1.78 (d, *J* = 11.6 Hz, 2H), 1.70-1.54 (m, 3H), 1.42-1.23 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.8, 121.03, 120.95, 37.7, 31.2, 25.6, 25.5; MS: *m/z* $[M+H]^+$: 201.12.

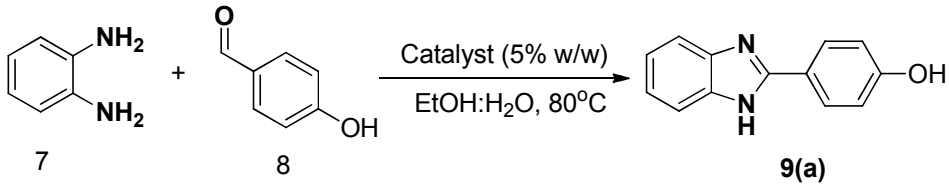
2-Isopropyl-1*H*-benzo[*d*]imidazole, 9p: Yellow solid; m.p. 237°C; IR (KBr): 3418.0 (N-H), 2975.6 (C-H, alkyl), 1416.1, 1242.3, 1057.5, 745.9 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H), 7.21-7.19 (m, 2H), 3.28 (t, *J* = 7.0 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 122.1, 29.0, 21.5; MS: *m/z* $[M+H]^+$: 161.1.

Recycling of Catalyst

Reaction was repeated with recovered catalyst with *o*-phenylenediamine and 4-hydroxy benzaldehyde. Yield of each recycling was recorded and tabulated in Table III. Optimized conditions found to be EtOH:Water (9:1), 80°C. Catalyst loading under these optimized conditions found to be 5% w/w for SSA-Pz-P-SG and 15% w/w for SSA-AP-SG, while using *o*-phenylenediamine and 4-hydroxy benzaldehyde as reactants.

Catalyst SSA-Pz-P-SG showed excellent recyclability with almost similar yields, up to third recycling. While SSA-AP-SG showed recycling for one time with similar yield, but in subsequent recycling it showed increase in reaction time along with depreciated yields. SSA-Pz-P-SG found to be better in providing better yields, reaction time and reusability.

Table III — Recycling of catalysts using *o*-phenylenediamine and 4-hydroxy benzaldehyde as reactants



7 8 **9(a)**

R= aryl, heteroaryl,alkyl
Catalyst= SSA-Pz-P-SG and SSA-AP-SG

S.No.	Catalyst	Cycle	Time (h)	Yield (%)
1	SSA-AP-SG	Fresh	8	77
2		1	9	77
3		2	12	69
4		3	20	58
5	SSA-Pz-P-SG	Fresh	6	93
6		1	6	92
7		2	6	92
8		3	8	90

Conclusion

In this research work we report synthesis of new solid supported catalyst SSA-Pz-P-SG and its application in synthesis of 2-aryl benzimidazoles with excellent yields, easy work up and eminent reusability. The system is also capable for synthesis of 2-heteroaryl and 2-alkyl benzimidazoles as well. Further, we report application of SSA-AP-SG as catalyst in 2- aryl benzimidazoles synthesis. Furthermore, we report reusability of synthesized novel solid supported catalyst. Comparative study of piperazine and non-piperazine catalyst, piperazine moiety found to be responsible for increased catalytic efficiency and reusability is also reported. Hence, considering the advantages, this one-pot catalytic reaction offers an appealing methodology for the construction of 2-substituted benzimidazoles both in academic and pharmaceutical industries. To the best of our knowledge, silica gel supported piperazine sulfosalicylic (SSA-Pz-P-SG) and (SSA-AP-SG) acid has not been studied in this reaction before and therefore represents a novel catalyst for this transformation.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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