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Microwave assisted expeditious approach towards benzimidazole acrylonitrile derivatives exploring new silica supported SBPTS catalyst

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Abstract

The present study reports a simple, highly efficient and green approach for the synthesis of a series of benzimidazole-acrylonitrile derivatives **3** (**a-l**). The synthetic methodology involves a microwave-assisted reaction exploring novel silica-supported SBPTS as a heterogeneous, proficient and reusable catalyst resulting in excellent yields. The reaction transformation presumably occurs *via* Knoevenagel condensation. The significant features of the present protocol includes simple operational procedure, shorter reaction times, mild reaction conditions, economic viability, high yield of products and compatibility to a range of functional groups (electron donating/electron withdrawing).

Keywords: SBPTS catalyst; benzimidazole-acrylonitrile; microwave; Knoevenagel condensation

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1. Introduction

In the last few decades catalysis is prove to be a key for sustainable synthetic chemistry and turned out to be a major area of research in synthetic organic chemistry satisfying green chemistry principle.[1-5] This clean technology in synthetic chemistry motivates researcher to improvise the classical methods with suitable alternate catalytic systems for easy chemical transformations with the minimum generation of chemical wastes and environmental pollution.[6-9] In this regards heterogeneous solid acid catalyst proves to be blessing for organic chemist because of their exclusive properties such as well-defined structure, bronsted acidity, high mechanical and thermal stability, higher efficiency, larger surface area, better selectivity, non-corrosiveness, eco-friendly, and economically feasible nature for both environmental and commercial point of view.[10-12,] In recent era of catalyst assisted organic synthesis, silica is the ubiquitous platform used for designing efficient catalysts due to the favourable chemical and physical properties of silica surfaces which impart varieties of reactive functional group to its surface through well-known silane chemistry.[13,14] As a result, varieties of silica supported catalyst with enhanced chemical functionality were reported possessing efficient catalytic properties.[15-19]

Nitrogen containing heterocyclic compound becomes the hottest topics in the organic chemistry research due to its extensive presence in various bioactive natural compounds, pharmaceuticals and synthetic intermediates.[20] Benzimidazoles are ubiquitous scaffold, constitutes an important part of the vitamin B12 and structurally similar to purine which helped it to inhibit the bacterial growth.[21] Benzimidazole derivatives are currently under intensive focus due to their wide range of applications in pharmaceuticals, material and synthetic chemistry. Literature survey revealed that benzimidazole derivatives possess various biological properties *viz*., antioxidant, antimicrobial, anti-inflammatory, antiviral, antitumor, anticancer, anti-helmintic, antihistamine, antihypertensive, antineoplastic, anti-analgesic,

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antidiabetic, lipase inhibition, and glucosidase inhibitions *etc*.[22-30] Some widely used drugs with benzimidazole nucleus such as Rabeprazole, Pimozide, Mebendazole and Telmisartan are currently in clinical use. Thus, benzimidazole nucleus is considered as an indispensable anchor for the discovery of new biologically active agents. Apart from being biologically active, it also established its utility in agrochemicals, luminescent materials, fuel cells, ionic liquids, organic ligands, dye sensitized solar cells, chemosensors, and in corrosion science.[31-38] Owing to its versatile applicability, functionalization of benzimidazole scaffold with different functional groups has been attracted significant interest.

In the past few years, much attention has been paid to the acrylonitrile derivatives due to their predominant application as intermediates for the synthesis of various bioactive compounds possess wide range of biological properties such as antiproliferative, antimicrobial, antioxidative, anticholinesterase, antitumor, estrogenic, spasmolytic, tuberculostatic, and antitrichomonal properties.[14,39-47] Till now, the Knoevenagel condensation is a simple and efficient approach for the derivatives of acrylonitrile.[48] This involves the acid or base-catalyzed condensation of carbonyl compounds with active methylene moieties. In the pursuit to achieve higher efficiency, numerous catalysts with different reaction conditions were employed, including Brønsted acid catalysts,[49] Lewis acids such as Al_2O_3,[50] $SnCl_2$,[51] $MgBr_2 \cdot OEt_2$,[52] ionic liquids *viz*. [Bpy]Cl·x$AlCl_3$,[53] [Bmim]BF_4,[54] [Bmim]Cl·x$AlCl_3$,[53] ethylammonium nitrate[55] and silica supported acid catalyst.[14,56]

Prompted by the promising activities of benzimidazole analogues and acrylonitrile derivatives, we herein report an easy and proficient microwave-assisted synthesis of benzimidazole-acrylonitrile derivatives exploring novel silica supported catalyst, silica boron-*p*-toluene sulfonate (**SBPTS)** as a green, efficient and recyclable catalyst for Knoevenagel condensation. To the best of our knowledge, it is the first report of the catalyst and its use for the synthesis of benzimidazole-acrylonitrile derivatives.

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2. Experimental

2.1. Materials and general methods

All the reagents used were purchased from Sigma-Aldrich (India), as 'synthesis grade' and used without further purification. The microwave synthesis was performed in Anton Paar Monowave 300 microwave synthesizer. Fourier transform-infrared (FT-IR) spectra were recorded using a Perkin-Elmer (2000 FTIR) Spectrometer by the KBr pellet method in the wave-number range of 400-4000 cm^{-1}. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance-II instrument in pure deuterated DMSO-d_6 solvent. The chemical shifts (δ) are reported in ppm value relative to the TMS as an internal standard. Elemental analysis was conducted using a Thermo Scientific (FLASH 2000) CHN Elemental Analyser. Mass spectra were recorded on a JEOL D-300 mass spectrometer. X-ray diffractograms (XRD) of the catalyst were recorded in the 2θ range of 20-80^{o} with a scan rate of 4^{o} min^{-1} on a Shimadzu-6100 X-ray diffractometer with Ni-filtered Cu Ka radiation at a wavelength of 1.54060 Å. The scanning electron microscope (SEM) analysis was obtained using a JEOL (JSM-6510) equipped with an energy dispersive X-ray (EDX) spectrometer at different magnification and transmission electron microscope (TEM) results were recorded using a JEOL (JEM-2100F) model. TGA/DTA has been carried out with DTG-60H Shimadzu (simultaneous DTA-TG) apparatus. The purity of all the compounds and progress of the reaction was checked by thin layer chromatography (TLC) on silica gel G254 (E-Merck) coated glass plates and exposed to iodine vapours.

2.2. Synthesis of catalyst

2.2.1. Preparation of Silica supported boric acid (SBA)

In a 250 mL round bottom flask, boric acid (3.0 g) was taken with 60 mL water and heated to 60-80 °C. Silica gel (60-120 mesh, 27.0 g) was added slowly with constant stirring and refluxed for about 5 h. After that water was evaporated under reduced pressure and the

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residue was stirred at 100 °C for 6-7 h under vacuum to give free flowing white powder of silica-boric acid.[15]

2.2.2. Preparation of SBPTS catalyst

A 500 mL suction flask fitted with a constant pressure dropping funnel containing *p*-toluenesulfonyl chloride solution (7.64 g, in 100 mL ethanol) and a gas inlet tube for conducting HCl gas over an absorbing solution (water). It was charged with SBA (10.0 g) and *p*-toluenesulfonyl chloride (PTSC) solution was added drop wise over a period of 60 min at room temperature, evolution of profuse amounts of HCl occurred instantaneously. After, the addition was completed, the mixture was stirred under vacuum pressure for 30 min and a white solid of SBPTS catalyst (14.8 g) were obtained.[57]

2.3. General procedure for the synthesis of acrylonitrile derivatives

To a mixture of benzimidazole-2- acetonitrile **1** (2.0 mmol) and aromatic aldehydes **2** (**a-l**) (2.0 mmol) in absolute ethanol (10 mL), SBPTS catalyst (10 mol%) was added and the reaction mixture was irradiated with continuous stirring in a microwave synthesis reactor (Anton Paar, Monowave 300) at 70 ^{o}C for 10-12 min. After completion of the reaction, as evident by TLC, the reaction mixture was filtered to recover the catalyst and washed with ethanol. The reaction mixture was then poured into ice water and the resulting precipitate was filtered to afford crude product and purified by column chromatography with dichloromethane-hexane to get the pure compound.

2.4. Spectral Characterization

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(4-(dimethylamino)phenyl)acrylonitrile (3a)[58]

Anal. calc. for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43; found: C, 74.75; H, 5.63; N, 19.36. FT-IR (KBr, cm^{-1}): 3340, 3078, 3045, 2980, 2216, 1645, 1625, 1570. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.16 (s, 1H, -NH), 8.19 (s, 1H, =CH), 7.81 (d, 2H, H-4 and H-7), 7.44-

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7.52 (m, 2H, H-5 and H-6), 7.72 (d, 2H, H-2′ and H-6′), 6.71 (d, 2H, H-3′ and H-5′), 3.09 (s, 6H, $-CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 143.5 (C-2), 137.8 (C-3a and C-7a), 116.9 (C-4 and C-7), 122.6 (C-5 and C-6), 108.7 (C-1″), 153.5 (C-2″), 119.4 (C≡N), 124.7 (C-1′), 130.1 (C-2′ and C-6′), 113.2 (C-3′ and C-5′), 151.6 (C-4′), 43.3 (CH_3). MS (ESI) *m/z*: 288.16 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(4-fluorophenyl)acrylonitrile (3b)

Anal. calc. for $C_{16}H_{10}FN_3$: C, 72.99; H, 3.83; N, 15.96; found: C, 72.95; H, 3.79; N, 15.99. FT-IR (KBr, cm^{-1}): 3375, 3082, 3066, 2218, 1642, 1638, 1518, 1118. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.17 (s, 1H, -NH), 8.05 (s, 1H, =CH), 7.79 (d, 2H, H-4 and H-7), 7.49-54 (m, 2H, H-5 and H-6), 7.68 (d, 2H, H-2′ and H-6′), 7.19 (d, 2H, H-3′ and H-5′). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 144.3 (C-2), 139.7 (C-3a and C-7a), 117.2 (C-4 and C-7), 125.1 (C-5 and C-6), 109.9 (C-1″), 155.8 (C-2″), 120.7 (C≡N), 131.8 (C-1′), 130.4 (C-2′ and C-6′), 115.4 (C-3′ and C-5′), 160.3 (C-4′). MS (ESI) *m/z*: 263.06 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(4-nitrophenyl)acrylonitrile (3c)

Anal. calc. for $C_{16}H_{10}N_4O_2$: C, 66.20; H, 3.47; N, 19.30; found: C, 66.17; H, 3.50; N, 19.34. FT-IR (KBr, cm^{-1}): 3394, 3076, 3046, 2221, 1646, 1632, 1535, 1512, 1340. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.06 (s, 1H, -NH), 8.27 (s, 1H, =CH), 7.84 (d, 2H, H-4 and H-7), 7.52-7.60 (m, 2H, H-5 and H-6), 8.03 (d, 2H, H-2′ and H-6′), 8.15 (d, 2H, H-3′ and H-5′). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 144.2 (C-2), 140.1 (C-3a and C-7a), 117.2 (C-4 and C-7), 124.8 (C-5 and C-6), 108.9 (C-1″), 154.9 (C-2″), 119.2 (C≡N), 142.7 (C-1′), 129.7 (C-2′ and C-6′), 123.2 (C-3′ and C-5′), 147.8 (C-4′). MS (ESI) *m/z*: 290.11 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(2-hydroxyphenyl)acrylonitrile (3d)

Anal. calc. for $C_{16}H_{11}N_3O$: C, 73.55; H, 4.24; N, 16.08; found: C, 73.51; H, 4.21; N, 16.13. FT-IR (KBr, cm^{-1}): 3416, 3284, 3092, 3034, 2217, 1644, 1628, 1526. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.12 (s, 1H, -NH), 10.47 (s, 1H, -OH), 8.17 (s, 1H, =CH), 7.82 (d, 2H,

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H-4 and H-7), 7.55-7.60 (m, 2H, H-5 and H-6), 6.72 (d, 1H, H-3′), 7.16 (dd, 1H, H-4′), 6.96 (dd, 1H, H-5′), 7.72 (d, 1H, H-6′). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 142.6 (C-2), 139.4 (C-3a and C-7a), 117.2 (C-4 and C-7), 126.4 (C-5 and C-6), 109.2 (C-1″), 154.5 (C-2″), 118.4 (C≡N), 116.2 (C-1′), 158.3 (C-2′), 117.6 (C-3′), 132.3 (C-4′), 121.2 (C-5′), 128.7 (C-6′). MS (ESI) *m/z*: 261.13 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(4-hydroxy-3-methoxyphenyl)acrylonitrile (3e)

Anal. calc. for $C_{17}H_{13}N_3O_2$: C, 70.09; H, 4.50; N, 14.42; found: C, 72.84; H, 4.20; N, 13.63. FT-IR (KBr, cm^{-1}): 3426, 3288, 3076, 3027, 2983, 2225, 1648, 1630, 1522. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.19 (s, 1H, -NH), 10.71 (s, 1H, -OH), 8.15 (s, 1H, =CH), 7.95 (d, 2H, H-4 and H-7), 7.60-7.65 (m, 2H, H-5 and H-6), 7.22 (s, 1H, H-2′), 6.99 (d, 1H, H-5′), 7.34 (d, 1H, H-6′), 3.94 (s, 3H, -OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 142.9 (C-2), 139.8 (C-3a and C-7a), 115.6 (C-4 and C-7), 124.3 (C-5 and C-6), 107.8 (C-1″), 155.1 (C-2″), 119.2 (C≡N), 129.4 (C-1′), 111.7 (C-2′), 149.6 (C-3′), 147.5 (C-4′), 117.3 (C-5′), 122.9 (C-6′), 56.8 (-OCH_3). MS (ESI) *m/z*: 291.15 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(3,4-dimethoxyphenyl)acrylonitrile (3f)

Anal. calc. for $C_{18}H_{15}N_3O_2$: C, 70.81; H, 4.95; N, 13.76; found: C, 73.47; H, 4.78; N, 13.04. FT-IR (KBr, cm^{-1}): 3442, 3086, 3038, 2978, 2219, 1643, 16028, 1542. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.09 (s, 1H, -NH), 8.21 (s, 1H, =CH), 7.89 (d, 2H, H-4 and H-7), 7.55-7.60 (m, 2H, H-5 and H-6), 7.81 (s, 1H, H-2′), 6.94 (d, 1H, H-5′), 7.71 (d, 1H, H-6′), 3.89 (s, 6H, -OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 144.3 (C-2), 140.1 (C-3a and C-7a), 117.4 (C-4 and C-7), 124.6 (C-5 and C-6), 106.8 (C-1″), 153.5 (C-2″), 119.9 (C≡N), 127.7 (C-1′), 115.5 (C-2′), 151.9 (C-3′), 149.8 (C-4′), 111.4 (C-5′), 121.8 (C-6′), 55.8 (2 × -OCH_3). MS (ESI) *m/z*: 305.17 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(1H-indol-3-yl)acrylonitrile (3g)

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Anal. calc. for $C_{18}H_{12}N_4$: C, 76.04; H, 4.25; N, 19.71; found: C, 74.35; H, 4.54; N, 20.35. FT-IR (KBr, cm^{-1}): 3477, 3452, 3075, 3029, 2220, 1656, 1627, 1549. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.22 (s, 1H, N1-H), 12.84 (s, 1H, N1′-H), 8.10 (s, 1H, =CH), 7.71 (d, 2H, H-4 and H-7), 7.41-7.59 (m, 2H, H-5 and H-6), 7.96 (s, 1H, H-2′), 7.82 (d, 1H, H-4′), 7.25-7.31 (m, 2H, H-5′ and H-6′), 7.05 (d, 1H, H-7′). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 143.3 (C-2), 137.3 (C-3a and C-7a), 115.2 (C-4 and C-7), 122.9 (C-5 and C-6), 112.5 (C-1″), 148.7 (C-2″), 118.2 (C≡N), 128.6 (C-2′), 110.3 (C-3′), 127.2 (C-3′a), 118.0 (C-4′), 119.8 (C-5′), 121.1 (C-6′), 109.3 (C-7′), 135.8 (C-7′a). MS (ESI) *m/z*: 284.14 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(5-hydroxy-1H-indol-3-yl)acrylonitrile (3h)

Anal. calc. for $C_{18}H_{12}N_4O$: C, 71.99; H, 4.03; N, 18.66; found: C, 69.43; H, 4.51; N, 19.54. FT-IR (KBr, cm^{-1}): 3488, 3465, 3315, 3082, 3065, 2212, 1645, 1624, 1520. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.27 (s, 1H, N1-H), 12.69 (s, 1H, N1′-H), 10.19 (s, 1H, -OH), 7.99 (s, 1H, =CH), 7.69 (d, 2H, H-4 and H-7), 7.42-7.49 (m, 2H, H-5 and H-6), 7.89 (s, 1H, H-2′), 6.87 (s, 1H, H-4′), 6.58 (d, 1H, H-6′), 6.97 (d, 1H, H-7′). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 141.9 (C-2), 137.9 (C-3a and C-7a), 116.2 (C-4 and C-7), 124.2 (C-5 and C-6), 113.7 (C-1″), 154.5 (C-2″), 118.5 (C≡N), 129.6 (C-2′), 111.6 (C-3′), 127.7 (C-3′a), 103.6 (C-4′), 152.4 (C-5′), 112.7 (C-6′), 112.1 (C-7′), 130.7 (C-7′a). MS (ESI) *m/z*: 300.15 $[M+]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(5-methyl-1H-indol-3-yl)acrylonitrile (3i)

Anal. calc. for $C_{19}H_{14}N_4$: C, 76.49; H, 4.73; N, 18.78; found: C, 78.74; H, 4.55; N, 17.67. FT-IR (KBr, cm^{-1}): 3456, 3418, 3071, 3027, 2975, 2219, 1655, 1639, 1543. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.32 (s, 1H, N1-H), 12.74 (s, 1H, N1′-H), 8.04 (s, 1H, =CH), 7.78 (d, 2H, H-4 and H-7), 7.52-7.60 (m, 2H, H-5 and H-6), 7.91 (s, 1H, H-2′), 7.39 (s, 1H, H-4′), 7.13 (d, 1H, H-6′), 7.01 (d, 1H, H-7′), 2.35 (s, 3H, -CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 142.9 (C-2), 137.6 (C-3a and C-7a), 116.3 (C-4 and C-7), 123.3 (C-5 and C-6), 112.5 (C-1″), 150.7 (C-2″), 118.2 (C≡N), 128.5 (C-2′), 110.3 (C-3′), 126.0 (C-3′a), 121.6 (C-4′),

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130.4 (C-5′), 120.8 (C-6′), 108.9 (C-7′), 134.8 (C-7′a), 24.9 (-CH_3). MS (ESI) *m/z*: 298.16 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(4-oxo-4H-chromen-3-yl)acrylonitrile (3j)

Anal. calc. for $C_{19}H_{11}N_3O_2$: C, 72.84; H, 3.54; N, 13.41; found: C, 70.47; H, 3.89; N, 14.36. FT-IR (KBr, cm^{-1}): 3456, 3089, 3028, 2223, 1673, 1655, 1595, 1526. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.16 (s, 1H, NH), 7.83 (s, 1H, =CH), 7.93 (d, 2H, H-4 and H-7), 7.53-7.59 (m, 2H, H-5 and H-6), 7.26 (s, 1H, H-2′), 8.05 (d, 1H, H-5′), 7.39 (dd, 2H, H-6′ and H-7′), 7.60 (d, 1H, H-8′). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 144.4 (C-2), 137.7 (C-3a and C-7a), 114.9 (C-4 and C-7), 122.6 (C-5) 123.7 (C-6), 113.3 (C-1″), 145.0 (C-2″), 119.6 (C≡N), 149.3 (C-2′), 121.1 (C-3′), 191.8 (C-4′), 128.2 (C-4′a), 129.5 (C-5′), 127.6 (C-6′), 135.8 (C-7′), 117.0 (C-8′), 154.8 (C-8′a). MS (ESI) *m/z*: 313.17 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(6-methyl-4-oxo-4H-chromen-3-yl) acrylonitrile (3k)

Anal. calc. for $C_{20}H_{13}N_3O_2$: C, 73.38; H, 4.00; N, 12.84; found: C, 75.14; H, 3.78; N, 12.33. FT-IR (KBr, cm^{-1}): 3445, 3088, 3029, 2986, 2218, 1672, 1642, 1590, 1518. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.09 (s, 1H, NH), 8.05 (s, 1H, =CH), 7.78 (d, 2H, H-4 and H-7), 7.60-7.67 (m, 2H, H-5 and H-6), 7.38 (s, 1H, H-2′), 7.85 (s, 1H, H-5′), 7.54 (d, 2H, H-7′ and H-8′), 2.41 (s, 3H, -CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 143.4 (C-2), 138.5 (C-3a and C-7a), 116.6 (C-4 and C-7), 124.9 (C-5 and C-6), 110.8 (C-1″), 145.1 (C-2″), 119.4 (C≡N), 149.8 (C-2′), 121.2 (C-3′), 191.5 (C-4′), 127.5 (C-4′a), 124.9 (C-5′), 135.1 (C-6′), 141.7 (C-7′), 131.1 (C-8′), 156.2 (C-8′a), 24.3 (-CH_3). MS (ESI) *m/z*: 327.15 $[M]^{+\bullet}$.

(E)-2-(1H-benzo[d]imidazol-2-yl)-3-(6-fluoro-4-oxo-4H-chromen-3-yl)acrylonitrile (3l)

Anal. calc. for $C_{19}H_{10}FN_3O_2$: C, 68.88; H, 3.04; N, 12.68; found: C, 70.74; H, 2.98; N, 12.18. FT-IR (KBr, cm^{-1}): 3478, 3084, 3022, 2216, 1674, 1654, 1596, 1516. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.02 (s, 1H, NH), 8.14 (s, 1H, =CH), 7.89 (d, 2H, H-4 and H-7), 7.58-7.65 (m, 2H, H-5 and H-6), 7.46 (s, 1H, H-2′), 7.81 (s, 1H, H-5′), 7.35 (d, 1H, H-7′), 7.18 (d,

1H, H-8′). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 142.3 (C-2), 139.4 (C-3a and C-7a), 116.0 (C-4 and C-7), 125.4 (C-5 and C-6), 111.9 (C-1″), 147.2 (C-2″), 118.9 (C≡N), 150.8 (C-2′), 120.6 (C-3′), 190.8 (C-4′), 128.8 (C-4′a), 109.7 (C-5′), 160.4 (C-6′), 123.7 (C-7′), 122.3 (C-8′), 153.0 (C-8′a). MS (ESI) *m/z*: 331.12 $[M]^{+\bullet}$.

3. Results and discussion

3.1. Characterization of the catalyst

The SBPTS catalyst was synthesized as outlined in the Scheme 1, and characterized by different spectroscopic and microscopic techniques including FT-IR, XRD, SEM-EDX and TEM analysis. The FT-IR spectrum of the catalyst is depicted in Fig. 1 and was recorded using the KBr disk technique. The FT-IR spectrum displays a stretching band of SiO-H at 3426 cm^{-1} while the stretching band of BO-H appears at 3221 cm^{-1}. The peaks at 3046 and 2926 cm^{-1} is attributed to the stretching vibration of C-H of phenyl-ring and methyl group, respectively. The bending vibration of C=C bond of phenyl-ring was observed at 1403 cm^{-1}. The peak at 2260 cm^{-1} was assigned to the B-OH combination and the peak at 1164 cm^{-1} was attributed to the bending vibration of B-OH.[59] The Si-O-Si symmetric and asymmetric stretching vibration band were appeared at 1096 and 813 cm^{-1}, respectively. The peaks at 926 and 641 cm^{-1} for the stretching and bending vibration of the borosiloxane linkage (Si-O-B), respectively, and the peak at 569 and 1637 cm^{-1} are related to the formation of B-O-B and B-O bands, respectively.[57] The symmetric and asymmetric modes of O=S=O[11] lies at 1020-1090 and 1120-1210 cm^{-1} and shows overlap with the Si-O-Si and B-OH bands. As evident from FT-IR spectrum, both B-O and B-O-B bonds are present in SBPTS catalyst, thus proposed the complex nature for boron atoms exists in this catalyst[57] (Fig. 2).

Formation of the catalytic system (SBPTS) was further established by powder XRD analysis recorded at the 2θ = 20-80° range (Fig. 3). The XRD of the catalyst showed

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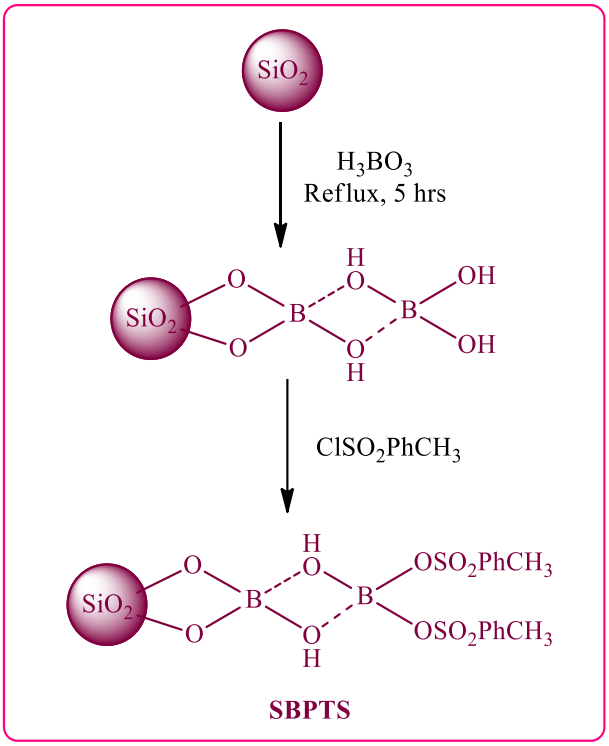
characteristic broad peak of silica in the range of $2\theta = 20^{o}$-25^{o} displaying amorphous nature of silica with two significant peak at 23.8^{o} and 27.5^{o} revealing the presence of Si-O and B-O bonds in the crystalline structure of the SBPTS, respectively.[57]



Scheme 1 Pathway for the synthesis of SBPTS catalyst.

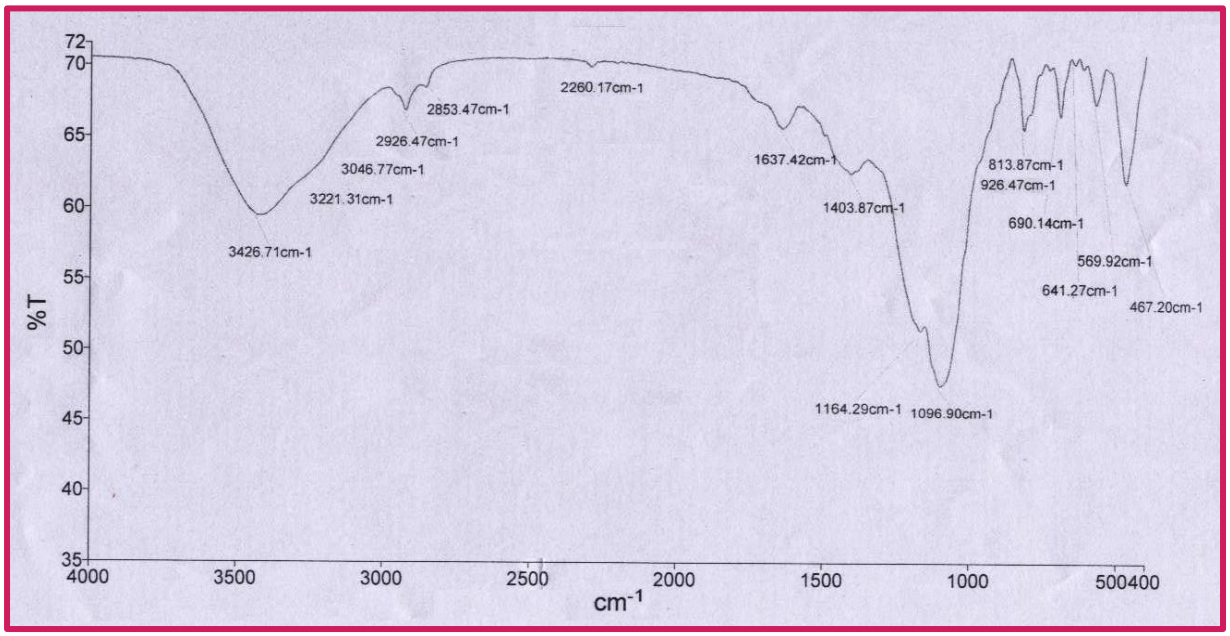


Fig. 1 FT-IR spectrum of the catalyst SBPTS

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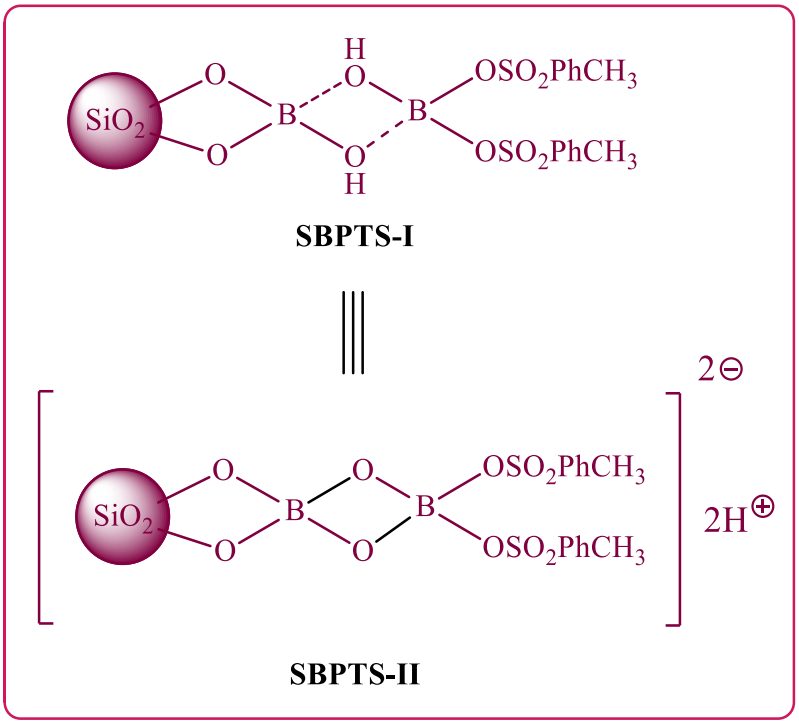

Fig. 2 The proposed structure for the SBPTS catalyst.

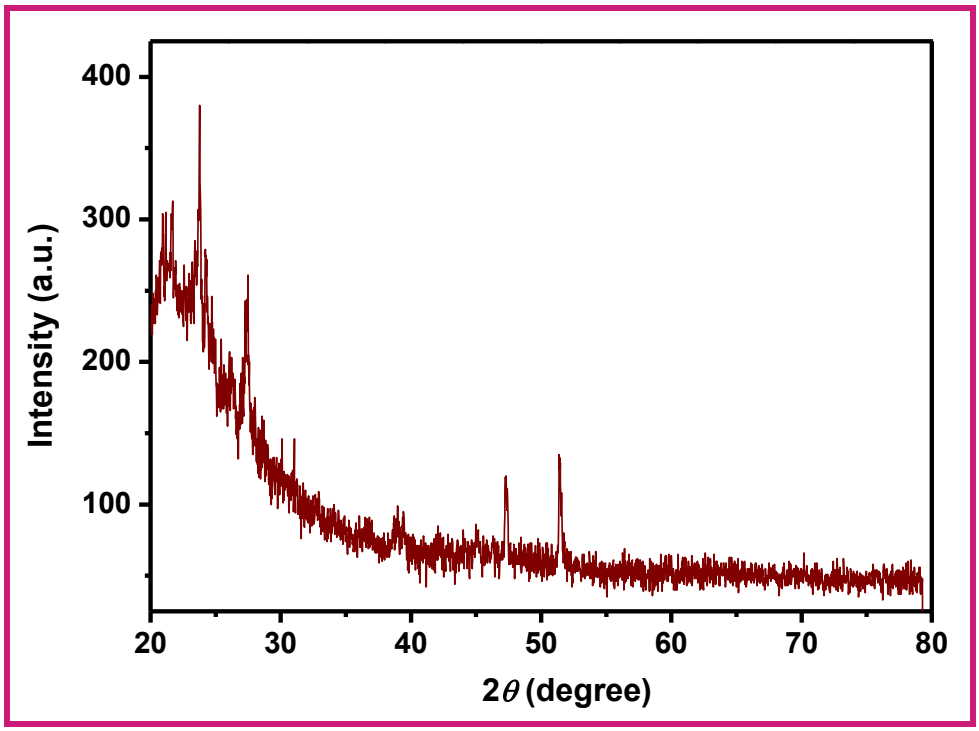

Fig. 3 Powder XRD pattern of the SBPTS catalyst

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For the study of surface morphology of the catalyst, SEM and TEM micrograph of the catalyst were employed. The SEM micrograph (Fig. 4) showed the successful adsorption of H_3BO_3-PTSC molecules on the surface of silica gel and were of uneven size and shape, and well dispersed. The TEM micrograph (Fig. 5a) of the catalytic system further displayed uniform distribution of agglomerated H_3BO_3-PTSC molecules as black dots on the surface of silica, approving the formation of the expected catalytic system. The TEM analysis showed the size of the molecules in the range of 2.5-5.0 nm. The histogram of the particle size distributions (Fig. 5b) of the SBPTS catalyst further confirmed the size of the particle. The histogram was proposed according to the results obtained from the TEM image. The EDX analysis (ESI†, Fig S2) of the catalyst showed the presence of Si, B, C, S and O elements, thus, suggesting the formation of the SBPTS catalytic system.

The thermal stability of the catalyst was assessed by TGA/DTA analysis (Fig. 6). The TGA analysis revealed that the catalyst showed thermal stability up to 253 ^oC. However, the first weight loss at ~95 ^oC was attributed to loss of physically adsorbed water molecules in the silica gel framework. The TGA was further supported by DTA analysis. The DTA curve displayed two prominent endothermic peak at 104 and 242 ^oC. The first peak is attributed to the endothermic reaction which help in the removal of water molecules, while the second peak may be due to the loss of SO_2 group.[53] Thus, the thermal study ensure that the SBPTS is suitable for the use as catalyst in organic transformations.

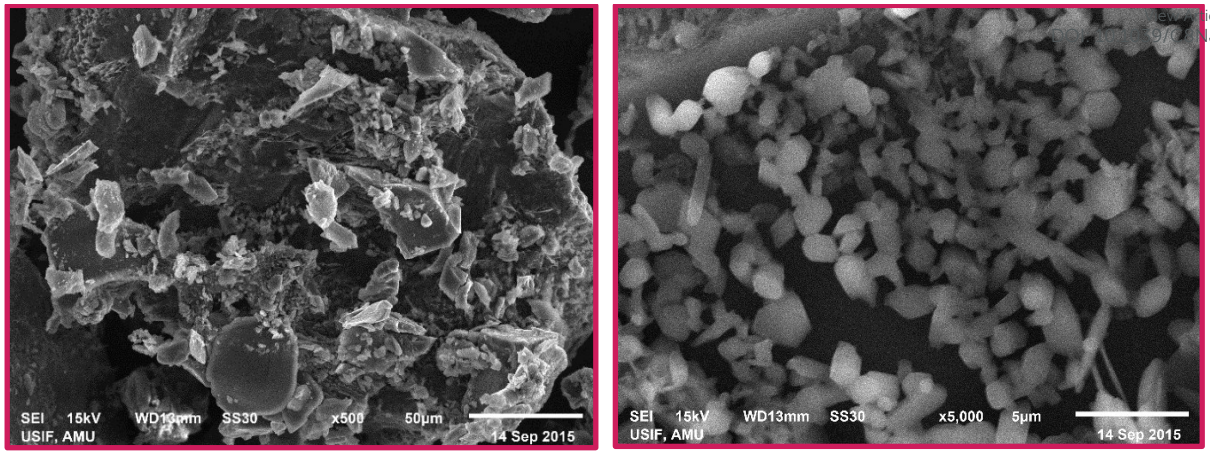
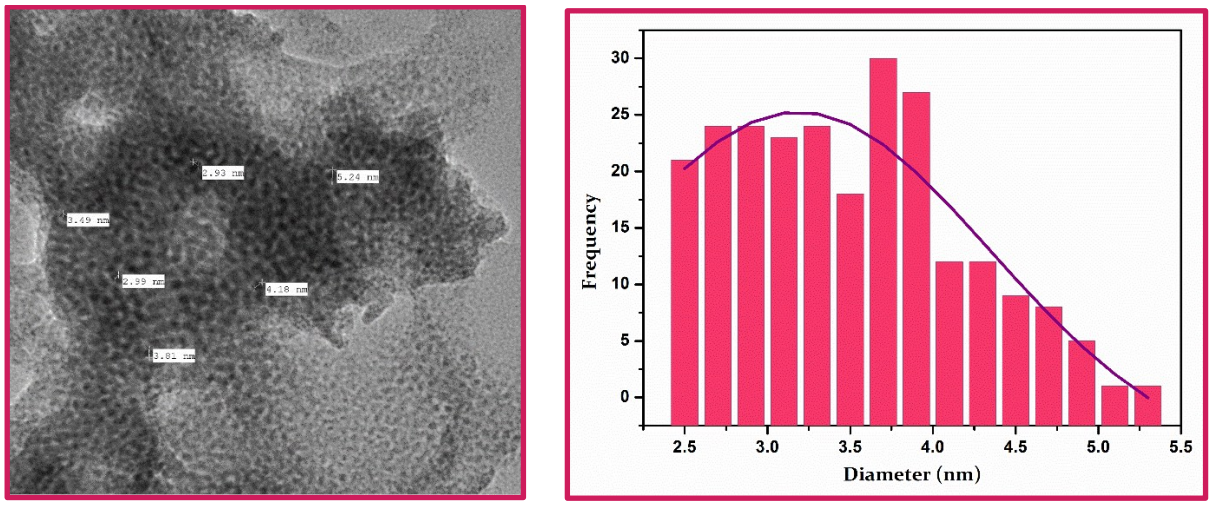


Fig. 4 SEM micrograph of the SBPTS catalyst



(a) **(b)**

Fig. 5 (a) TEM image of the SBPTS catalyst; **(b)** Histogram representing the size distribution of the SBPTS catalyst.

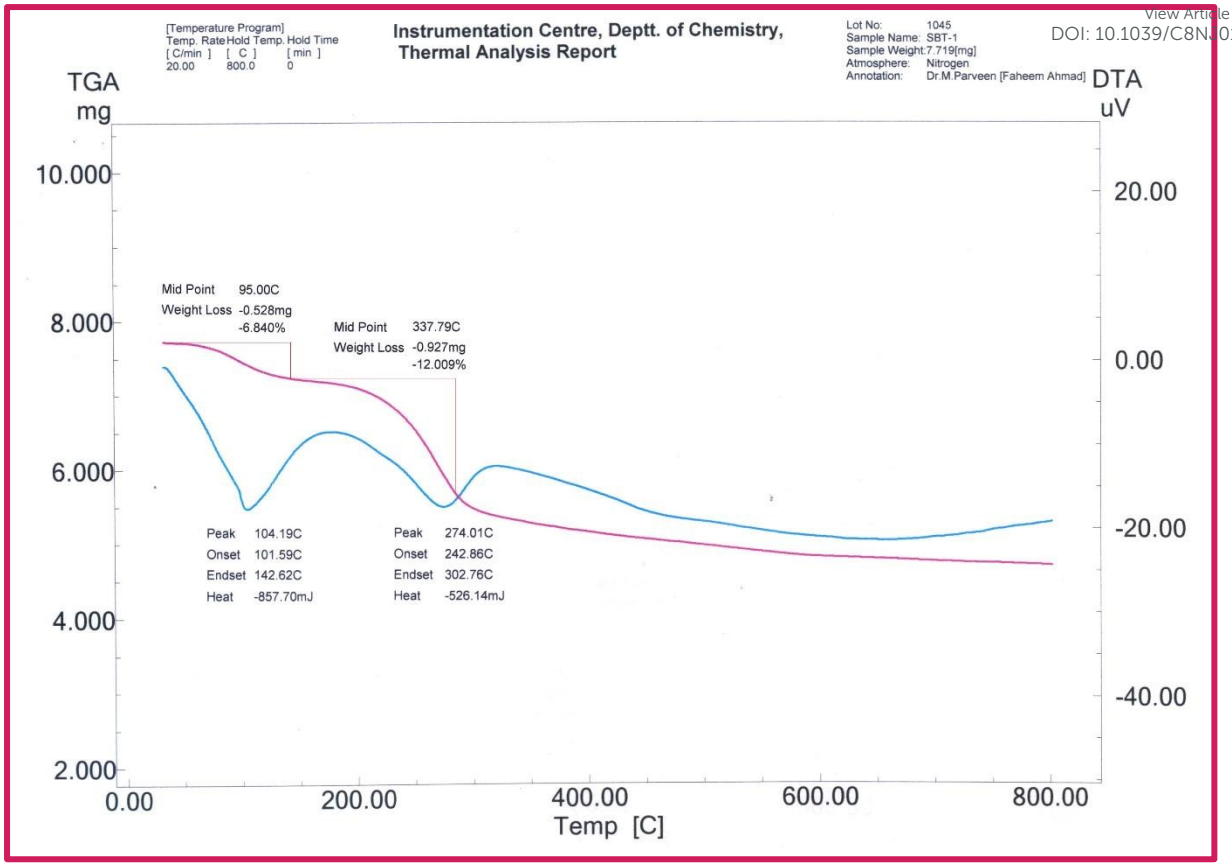
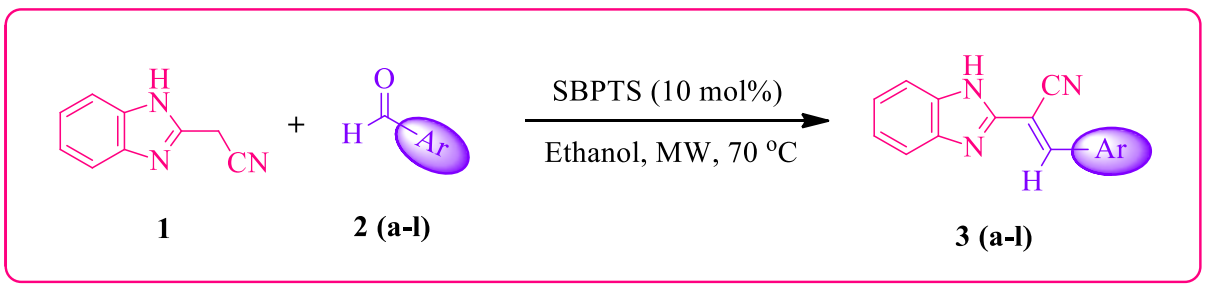


Fig. 6 TGA/DTA curve of the SBPTS catalyst

3.2. Optimization of reaction condition

In the present study, a library of benzimidazole-acrylonitrile derivatives, **3(a-l)** have been synthesized *via* microwave assisted knoevenagel condensation reaction involving benzimidazole-2-acetonitrile, **1** and different aromatic aldehydes, **2(a-l)** in presence of SBPTS catalyst (Scheme 2).



Scheme 2 Synthetic route for the synthesis of benzimidazole-acrylonitrile derivatives **3(a-l)**

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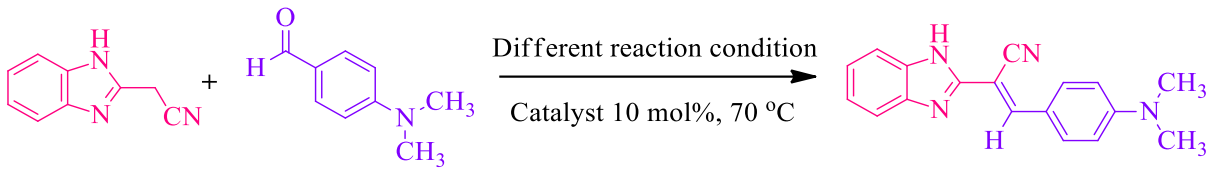
For our initial investigation, the reaction of benzimidazole-2-acetonitrile (**1**, 2mmol) and *p*-(*N*,*N*-dimethylamino)benzaldehyde, (**2a**, 2mmol) was chosen as a model reaction to optimize the reaction conditions for the present protocol including amount of catalyst, reaction temperature, solvent effect and investigating efficiency of different catalyst to establish the best possible reaction conditions for the synthesis of benzimidazole acrylonitrile derivatives. The reaction was first carried out in ethanol in the absence and presence of several catalyst at 70 ^{o}C. The reaction did not proceed even after prolonged reaction time (24 h) and no desired product was formed in the absence of catalyst (Table 1, entry 1), thus signifying the need of catalyst. Thus, we focused on the search for a suitable heterogeneous catalyst, such as SiO_2-Cl, $SiO_2/HClO_4$, SiO_2/NH_4OAc, $SiO_2/NaHSO_4$, SiO_2/H_3BO_3 and SBPTS that can catalyse this reaction in ethanol at 70 ^{o}C with better efficiency. Our analysis revealed that, amongst all the screened catalyst, the catalytic activity was found in the order of SBPTS > SiO_2/H_3BO_3 > SiO_2-Cl > $SiO_2/HClO_4$ > $SiO_2/NaHSO_4$ > SiO_2/NH_4OAc (Table1, entries 2-6) in terms of product yield and reaction time. In order to establish the superiority of our catalyst, we have compared this with three other catalyst previously reported for synthesis of acrylonitrile derivatives *viz*. SiO_2-Cl,[14] SiO_2/piperidine[60] and Silica Bonded *N*-(Propylcarbamoyl) sulfamic acid (SBPCSA),[56] and we found the catalytic activity in the order of SBPTS > SBPCSA > SiO_2-Cl > SiO_2/piperidine (Table1, entries 6-9). Thus, SBPTS is the catalyst of choice for the present protocol. In addition, we examined the influence of different organic solvents such as MeOH, CH_2Cl_2, CH_3COOH, DMF and THF on the model reaction in presence of SBPTS catalyst (Table 1, entry 8-12). When the reaction was carried out in CH_2Cl_2, DMF and THF, moderate yield of the product (55-64%) was obtained after extended reaction time. However, in presence of MeOH and CH_3COOH, the yield of the reaction is quite improved (73-78%), with dip in reaction time. However, with respect to the solvent system, the best results were achieved with ethanol (Table 1, entry 7). In order to make the

protocol more efficient, we introduced the microwave irradiation, which enhanced the reaction yield (98%) within short reaction time (10 min) in presence of SBPTS catalyst and ethanol at 70 °C (Table 1, entry 13).

Table 1. Effect of different reaction media on the model reaction[a]



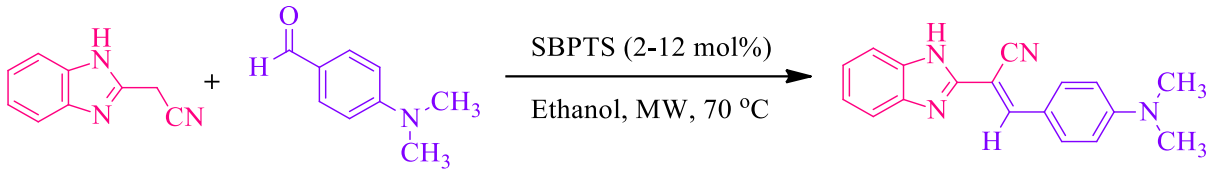
Entry	Solvent	Condition	Time (h)[b]	Yield (%)[c]
1	EtOH	70 °C, No catalyst	24	--
2	EtOH	70 °C, SiO_2/NH_4OAc	5.5	59
3	EtOH	70 °C, $SiO_2/HClO_4$	4	67
4	EtOH	70 °C, $SiO_2/NaHSO_4$	5	62
5	EtOH	70 °C, SiO_2/H_3BO_3	3	75
6	EtOH	70 °C, SBPTS	45 min	90
7	EtOH	70 °C, SiO_2-Cl	1.5	80
8	EtOH	70 °C, SBPCSA	70 min	85
9	EtOH	70 °C, SiO_2/piperidine	2	78
10	MeOH	70 °C, SBPTS	2	78
11	CH_2Cl_2	70 °C, SBPTS	5	64
12	CH_3COOH	70 °C, SBPTS	4	73
13	DMF	70 °C, SBPTS	8	59
14	THF	70 °C, SBPTS	10	55
15	EtOH	70 °C, SBPTS, MW	10 min	98

[a] Reaction conditions: Benzimidazole-2-acetonitrile (**1**, 2 mmol) and *p*-(*N*,*N*-dimethylamino) benzaldehyde (**2a**, 2 mmol), different solvent (10 mL), different catalyst (10 mol%), 70 °C.
[b] Reaction progress monitored by TLC. [c] Isolated yield of products.

In order to achieve the optimum concentration of the catalyst, the model reaction was examined at different concentration (2-12 mol%) of the SBPTS catalyst at 70 °C in ethanol under MW irradiation. When we carried out the reaction with 2-8 mol% of catalyst, the reaction took prolonged time with only 33-87% yield. On the other hand, when we used 10

mol% of the catalyst the reaction proceeded very effectively, with excellent yields (98%) within 10 min. Further increase of the catalyst amount does not affect the yield of the product. Thus, the above results signifies that 10 mol% of SBPTS catalyst is optimum dose for the present protocol in terms of efficient yield and reaction time.

Table 2 Effect of catalyst loading on the model reaction[a]



Entry	Catalyst (mol%)	Time (min)[b]	Yield (%)[c]
1	2	50	33
2	4	35	52
3	6	28	74
4	8	22	87
5	10	10	98
6	12	10	98

[a] Reaction conditions: Benzimidazole-2-acetonitrile (**1**, 2 mmol) and *p*-(*N*,*N*-dimethylamino) benzaldehyde (**2a**, 2 mmol), EtOH (10 mL), SBPTS catalyst (2-12 mol%), Temp. (70 °C), MW. [b] Reaction progress monitored by TLC. [c] Isolated yield of products.

The reaction was further studied at different temperatures in order to find out the optimum reaction temperature for the synthesis of **3a** in ethanol with SBPTS catalyst under microwave irradiation (Table 3). It was observed that increase in temperature from 25 to 70 °C, has a prominent effect on the model reaction in terms of yield and reaction time (Table 3, entry 2-5). However, no further enhancement in the yield was noticed when the reaction temperature was raised from 70 to 80 °C (Table 3, entry 6). Thus, it was concluded that the best reaction condition for the synthesis of **3a** is to carried out the reaction in ethanol at 70 °C coupled with 10 mol% of the SBPTS catalyst under microwave irradiation.

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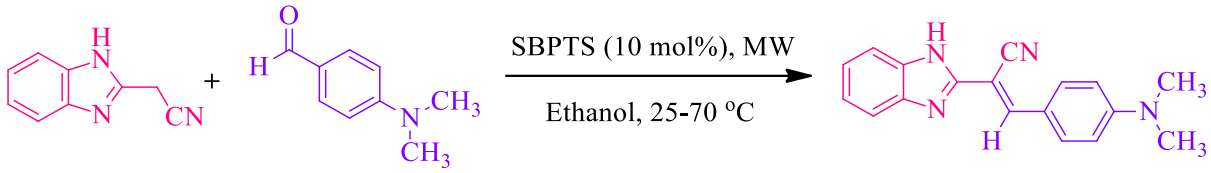
Table 3. Effect of temperature on the model reaction[a]



Entry	Temperature (°C)	Time (min)[b]	Yield (%)[c]
1	25	90	65
2	40	40	72
3	50	25	78
4	60	20	87
5	70	10	98
6	80	10	98

[a] Reaction conditions: Benzimidazole-2-acetonitrile (**1**, 2 mmol) and *p*-(*N*,*N*-dimethylamino) benzaldehyde (**2a**, 2 mmol), EtOH (10 mL), SBPTS catalyst (10 mol%), Temp. (25-80 °C), MW.
[b] Reaction progress monitored by TLC. [c] Isolated yield of products.

A variety of substrates were submitted to the optimized reaction condition in order to investigate the substrate scope of SBPTS catalysed system. As presented in Table 4, variety of functional groups substituted at the aromatic ring of the aldehyde substrate, including electron withdrawing and electron donating groups reacted with benzimidazole-2-acetonitrile to afford the corresponding benzimidazole-acrylonitrile derivatives **3(a-l)** in excellent yields. In the present study, a comparative study has also been carried out between the conventional thermal heating and microwave heating. It is evident that the microwave-assisted synthesis was more efficient in terms of product yield and reaction time (Table 4). In general, all the reaction proceeded efficiently with microwave-assisted synthesis at 70 °C with 10 mol% of the SBPTS catalyst in the presence of ethanol. The reactions are clean and no side products were detected. Therefore, we can say that the present protocol has general applicability and accommodates a variety of substitution patterns.

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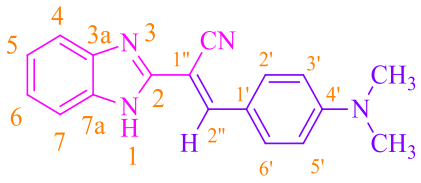
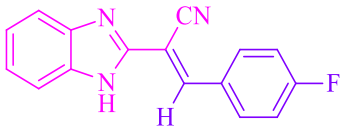
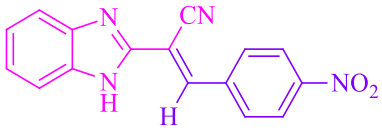
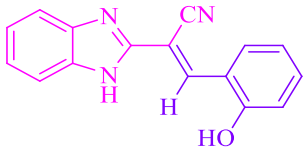
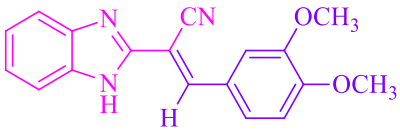
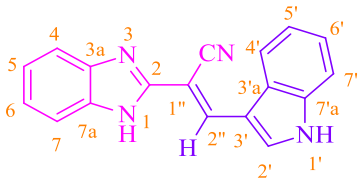
Table 4 Synthesis of benzimidazole acrylonitrile derivatives **3(a-l)**

S.No.	Product	Conventional method[a]		Microwave irradiation[b]	
		Time (min)	Yield (%)	Time (min)	Yield (%)
3a		45	90	10	98
3b		50	88	10	97
3c		45	89	10	98
3d		50	86	12	96
3e		50	85	12	94
3f		45	90	10	98
3g		45	88	10	97

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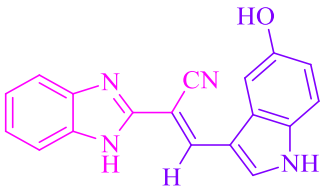
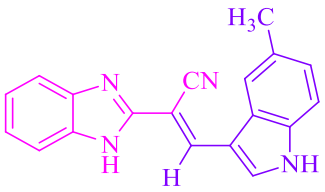
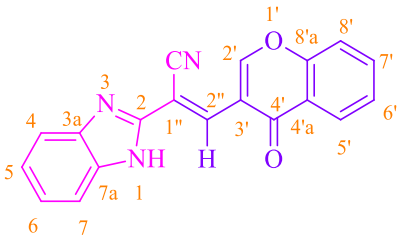
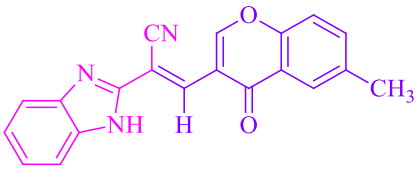
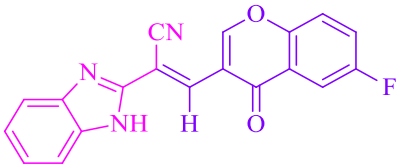
3h		55	85	12	96
3i		55	87	12	94
3j		50	89	10	97
3k		50	86	12	95
3l		45	90	10	98

[a] Reaction conditions: Benzimidazole-2-acetonitrile (**1**, 2 mmol) and differently substituted aldehydes (**2a-l**) (2 mmol), EtOH (10 mL), SBPTS catalyst (10 mol%), Temp. (70 °C).
[b] Reaction conditions: Benzimidazole-2-acetonitrile (**1**, 2 mmol) and differently substituted aldehydes (**2a-l**) (2 mmol), EtOH (10 mL), SBPTS catalyst (10 mol%), Temp. (70 °C), MW.

3.3. Recyclability of the catalyst

The recyclability is a significant property of catalyst, so as to satisfy the green chemistry principles and to manage the process cost. In order to explore the extent of recyclability of our catalyst system, the model reaction has been conducted under optimized condition for six

consecutive times. After the completion of first fresh runs, the catalyst was removed by simple filtration, washed thoroughly with ethanol and dried in vacuum oven for 2h at 100 ^{o}C. The recovered catalyst was then reused for five more subsequent cycles under the same optimized condition and found to retain its catalytic activity and showed minimal decrease in the yield (Fig. 7), thus, proving the catalyst's reusability with high catalytic performances. To ascertain the variation in morphological features of the recovered catalyst, SEM-EDX analysis was performed. It was found that there was no significant changes noticed in the composition and morphology of the recovered catalyst (ESI†, Fig S3-S5). These results demonstrate that our catalytic system is stable and could be recycled without a significant loss in yield.

3.4. Reaction Mechanism

The probable mechanistic pathway for the SPBTS catalysed synthesis of benzimidazole-acrylonitrile derivatives has been presented in Scheme 3. The reaction is initiated with the protonation of carbonyl group by SBPTS catalyst, which generates the active electrophilic site in intermediate (**I**). Further, the conjugate base of the catalyst generates the nucleophilic site (**II**) by removing the proton from the active methylene carbon of benzimidazole-2-acetonirile, which facilitates the formation of C-C bond to yield intermediate (**III**). The subsequent elimination of water molecule from intermediate (**III**) promoted by the SBPTS catalyst eventually leads to the formation of target benzimidazole acrylonitrile derivative with the regeneration of the catalyst SBPTS.

3.5. Chemistry

The structural elucidation of all the synthesized compounds **3**(**a-l**) has been established on the basis of FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectral studies and found to be in good support with the expected structure. The FT-IR spectrum of all the synthesized compounds shows

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absence of aldehydic carbonyl group, which confirmed the reaction at the target carbonyl moiety of the substrates. Moreover, all the compounds displayed a characteristic peak for C≡N, =C-H and C=C groups, resonating at around 2216-2225 cm^{-1}, 3076-3092 cm^{-1} and 1642-1656 cm^{-1}, respectively, which signifies the formation of a acrylonitrile derivatives. In ^{1}H NMR spectral analysis, each synthesized compound displayed a sharp singlet resonating at around δ 7.83-8.27, attributed to the olefinic proton, this prominent downfield shift displayed by the olefinic proton of acrylonitrile is probably due to its acidic nature imposed by adjacent cyano group (ESI†). In the ^{13}C NMR spectral study, the absorption band resonating at around δ 118.2-120.7 has been assigned to the -C≡N group of acrylonitrile derivatives. Furthermore, the peaks appeared at δ 106.8-113.3 and 145.1-155.8 corresponded to C-1″ and C-2″ of olefinic carbons (ESI†).

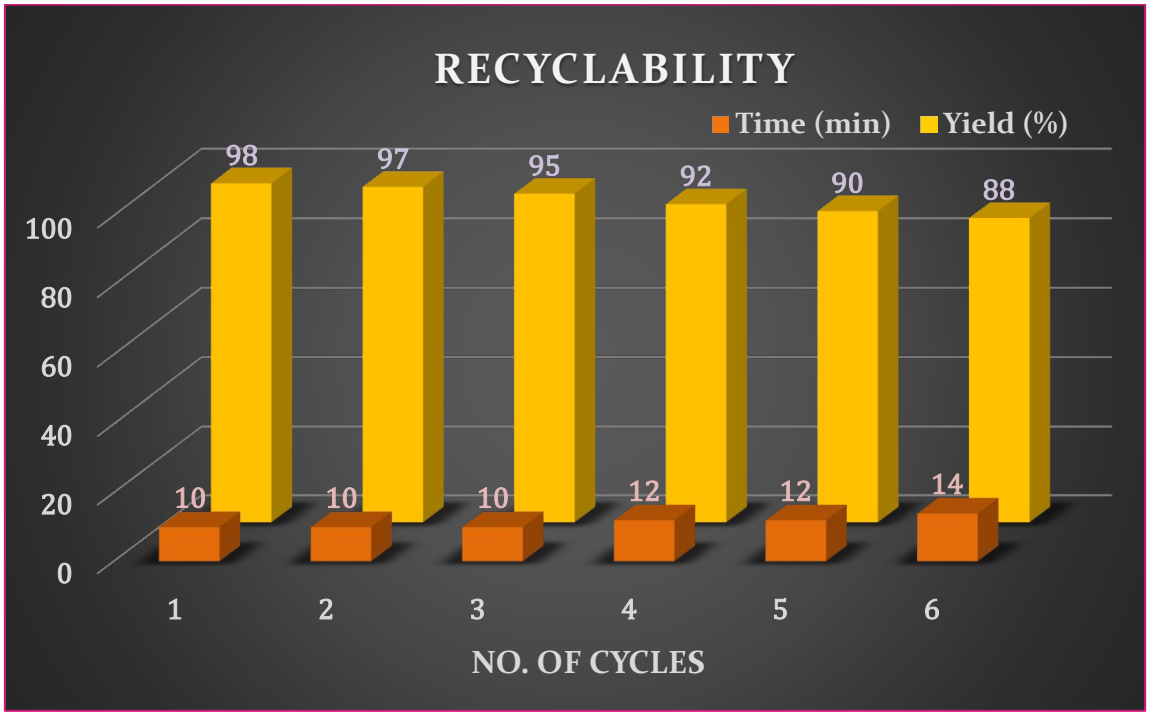

Fig. 7 Recyclability of the catalyst

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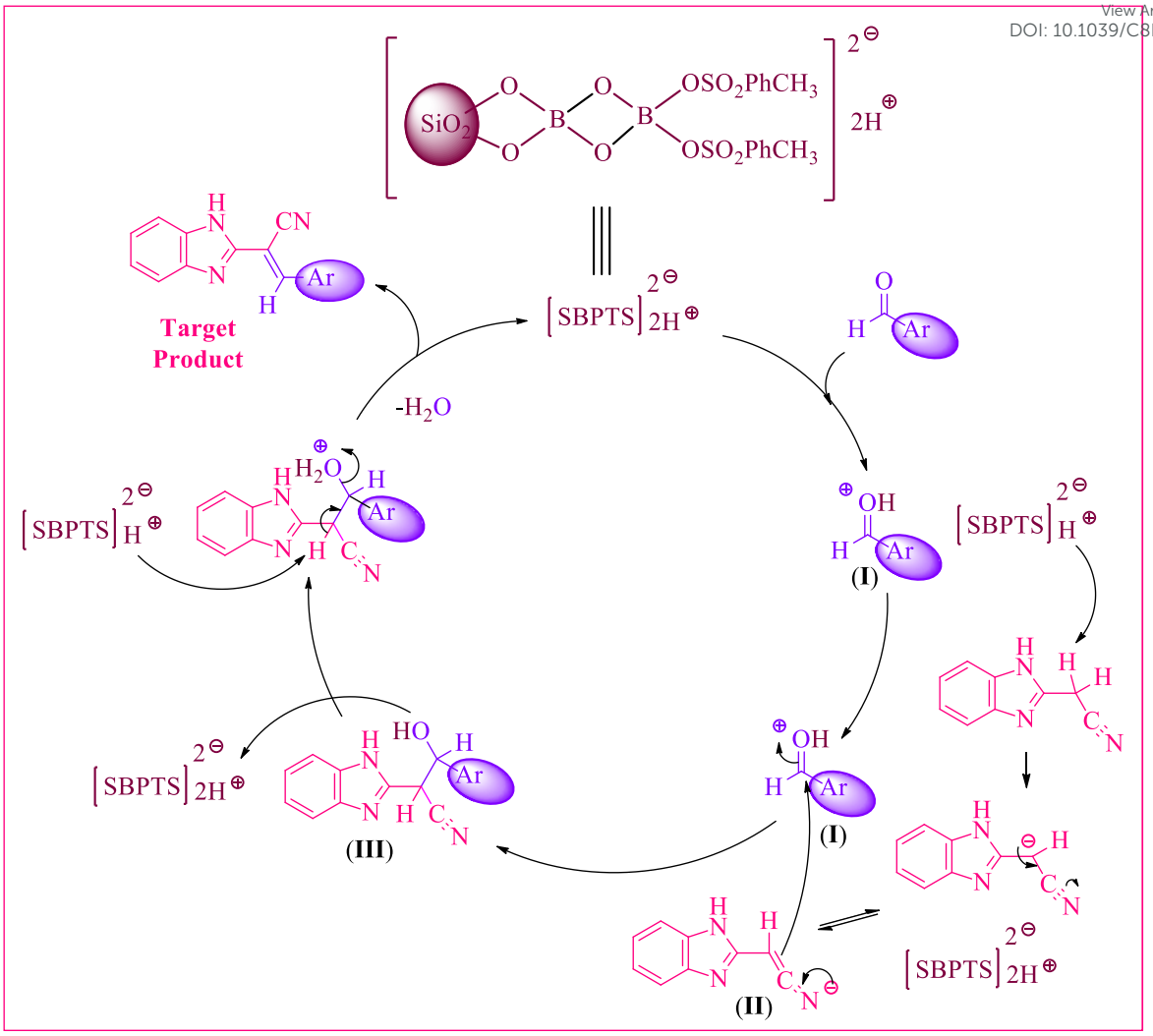

Scheme 3 Plausible mechanistic catalytic cycle for the synthesis of target benzimidazole-acrylonitrile derivatives **3(a-l)**

4. Conclusion

In conclusion, we have established a facile and environmentally benign method for the synthesis of a series of highly functionalized benzimidazole-acrylonitrile derivatives **3** (**a-l**) in excellent yields (94-98%) by employing novel recyclable SBPTS catalyst in ethanol under microwave irradiation. The noteworthy features of this protocol are mild reaction conditions, shorter reaction time, operational simplicity, cleaner reaction profile, high purity, enhanced reaction rates and easy workup procedure. We believe that this synthetic approach provides a

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better scope for the synthesis of acrylonitrile analogues and will be more practical alternative to the other existing methods.

Conflict of Interest

The authors declare no competing financial interest.

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Graphical Abstract (Pictogram)

Microwave assisted expeditious approach towards benzimidazole acrylonitrile derivatives exploring new silica supported SBPTS catalyst

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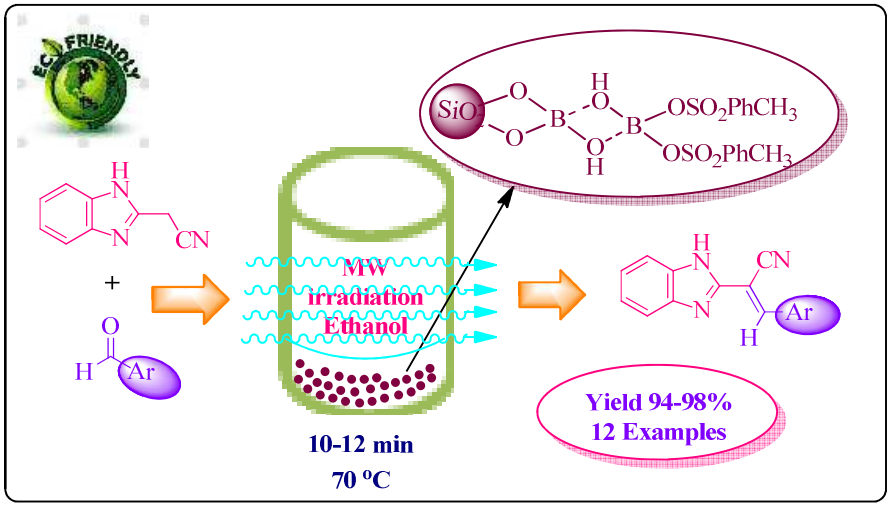

An efficient and eco-friendly synthesis of benzimidazole-acrylonitrile derivatives