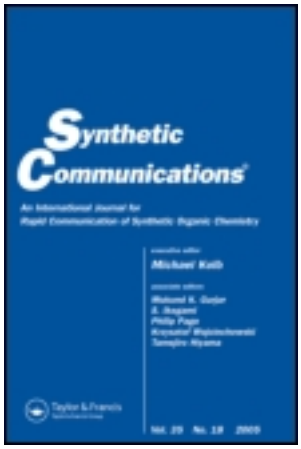

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Simple and Mild Protocol for Synthesis of 1,2-Disubstitued Benzimidazoles Using SBA-15-Supported Poly(4-styrenesulfonyl(perfluorobutylsulfonyl)imide Catalyst

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SIMPLE AND MILD PROTOCOL FOR SYNTHESIS OF 1,2-DISUBSTITUED BENZIMIDAZOLES USING SBA-15-SUPPORTED POLY(4-STYRENESULFONYL-(PERFLUOROBUTYLSULFONYL)IMIDE) CATALYST

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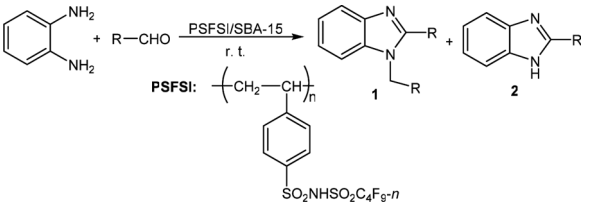
GRAPHICAL ABSTRACT



Abstract *A simple method for the synthesis of several 1,2-disubstituted benzimidazoles catalyzed by strongly acidic SBA-15-supported poly(4-styrenesulfonyl-(perfluorobutylsulfonyl)imide) is described. The protocol furnished the products in moderate yield and good selectivity in the condensation of* o*-phenylenediamine with structurally diverse aldehydes under mild conditions.*

Keywords Acidic composite; benzimidazole; perfluorobutylsulfonylimide; SBA-15

INTRODUCTION

The benzimidazole core is certainly classified as a privileged substructure for drug design in light of the affinity it displays toward a variety of enzymes and protein receptors.[1] Among various benzimidazole analogs, 1,2-disubstituted structures result in drug leads and commercial pharmaceutical products,[2] such as the agonist against the γ-aminobutyric acid A receptor ($GABA_A$),[3] inhibitors of hepatitis C virus NS5B polymerase,[4] and the antihypertensive telmisartan.[5] This widespread interest prompts extensive studies for their synthesis, and several methods have been reported. These include intramolecular cross-coupling of *o*-halo aromatic nitrogen-containing compounds (acetanilide,[6] amidine,[7] and guanidine[8]), direct

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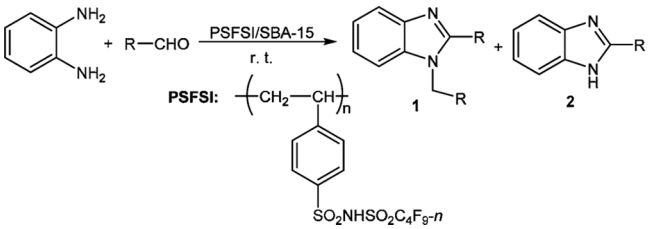


Scheme 1. Condensation of *o*-phenylenediamine with aldehydes.

N-alkylation of an unsubstituted benzimidazole,[3] one-pot synthesis from 2-nitroanilines in the presence of trimethyl orthoformate and H_2,[9] and acid-catalyzed condensation of *o*-phenylenediamine (*o*-PD) with aldehydes.[10] Of the methods, the condensation strategy has been more concentrated on the readily available materials, but the superficially simple reaction is a complex sequence of competing reactions.[11] Over the past few years, several catalyst systems have been reported to improve the selectivity of 1,2-disubstituted benzimidazoles, such as $SiO_2/ZnCl_2$,[10(b)] ionic liquid,[10(c)] silica sulfuric acid,[10(d)] L-proline,[10(e)] TsOH/graphite,[10(g)] $Fe(ClO_4)_3$,[10(h)] and Montmorillonite K10 under microwave irradiation.[10j] Although some of these catalysts are promising, there is still a need to develop new catalysts for the synthesis of the analogues.

With the considerable attention on the super nitrogen- and carbon-acid-containing perfluoroalkylsulfonyl in the development of new Brønsted acid catalysts,[12] we here report a novel acid composite, mesoporous molecular sieve SBA-15-supported poly(4-styrenesulfonyl (perfluoro-butylsulfonyl)imide) (PSFSI),[13] which is further used to catalyze the condensation of *o*-PD with aldehydes at mild conditions to afford 1,2-disubstituted benzimidazoles (Scheme 1).

RESULTS AND DISCUSSION

Preliminary condition optimization was carried out with *o*-PD and benzaldehyde (molar ratio 1:2.1) as the substrates. Two isolated main products were characterized, and the structures were confirmed as 1-benzyl-2-phenyl-1*H*-benzo[*d*]-imidazole (**1a**) and 2-phenyl-1*H*-benzo[*d*]imidazole (**2a**), respectively. Small amounts of other complex products were not collected. The results are listed in Table 1.

As can be seen from Table 1, both products were obtained whose ratios depended on the nature of solvent (entries 2–8). The excellent selectivity (94%) was obtained with comparable yield of **1a** (65%) to the documented data catalyzed by some sulfonic acids (entries 2 and 12–14). Prolonging the reaction time was unhelpful, and decreasing the amount of the catalyst led to lower yields of **1a** in the same time (entries 10 and 11). So, the optimal reaction conditions for **1a** should be benzaldehyde (3.2 mmol), *o*-PD (1.5 mmol), PSFSI/SBA-15 (30 mol%, relative to o-PD), stirred 80 min at 25–28 °C in 7 mL of CH_3NO_2.

The optimal conditions were employed for other structurally diverse aldehydes to further examine catalytic performances of PSFSI/SBA-15, with minor adaptions for several aldehydes according to the actual case. In most studied cases, moderate yields were achieved, and **1** was formed selectively rather than **2** (Table 2). Aldehydes

Table 1. Effect of reaction conditions on the yield and selectivity of the reaction of *o*-PD with benzaldehyde[a]

Entry	Solvent	Time (min)	Catalyst (mol%)	Isolated yield (%)			Selectivity (%)[b]
				Total	**1a**	**2a**	
1	CH_3NO_2	360	—	72	43	29	60
2	CH_3NO_2	80	30	70	65	5	94
3	$MeCO_2Et$	80	30	65	51	14	78
4	CH_3CN	80	30	67	49	18	73
5	CH_2Cl_2	80	30	64	59	5	93
6		80	30	78	55	23	70
7	EtOH	80	30	56	44	12	78
8		80	30	69	45	24	65
9	CH_3NO_2	50	30	66	62	4	94
10	CH_3NO_2	110	30	72	63	9	88
11	CH_3NO_2	80	20	62	56	6	90
12[c]	CH_3NO_2	80	30	79	52	27	66
13[d]	EtOH	60	30	73	44	29	60
14[e]	Solvent-free	40	19	89	66	23	74

[a]Reaction conditions: benzaldehyde (3.2 mmol), *o*-PD (1.5 mmol), PSFSI/SBA-15 (relative to *o*-PD), stirred at 25–28 °C in 7 mL of solvent.

[b]
$$\text{Selectivity} = \frac{\text{yield } (\mathbf{1})}{\text{total yield } (\mathbf{1}+\mathbf{2})} \times 100\%.$$

[c]Catalyzed by NKC-9 (–SO_3H resin).

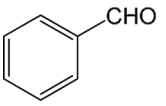
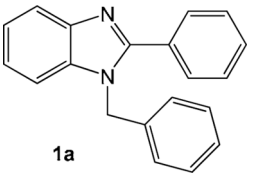
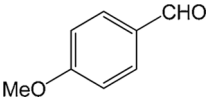
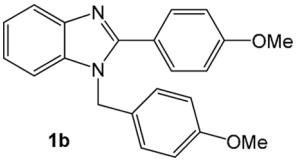
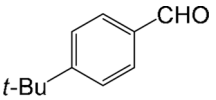
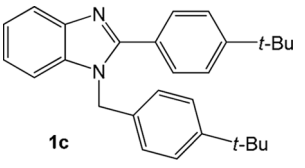
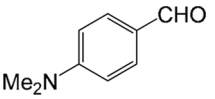
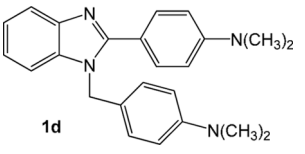
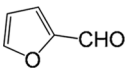
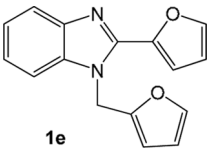
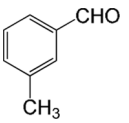
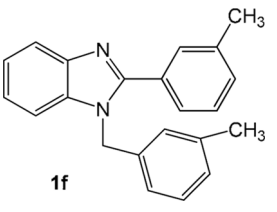
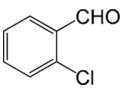
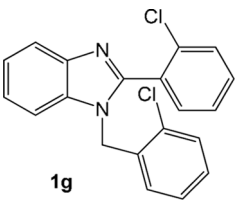
[d]Data from Ref. 10(g). Catalyzed by silica sulfuric acid at room temperature.

[e]Data from Ref. 10(g). Catalyzed by *p*-toluensufonic acid/graphite at 75 °C.

bearing electron-withdrawing groups (entries 9 and 10) required longer reaction time to obtain comparable yields compared with those bearing electron-donating groups (entries 1–7), and the electron-donating effect should be responsible for the excellent selectivity. We were pleased to find that unbranched and branched aliphatic aldehydes could react smoothly in extended period (entries 11 and 12). The relatively poor yield of branched aliphatic aldehyde was perhaps due to the steric effect. Correspondingly, unsplit peaks were observed for the protons at $ArCH_2Ph$ between 5.66 and 5.39 in the ^1H NMR spectra of the products **1**, except for **1h, 1k**, and **1l**. Poor selectivity was unfortunately observed in the case of 3-nitrobenzaldehyde (entry 10).

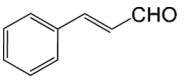
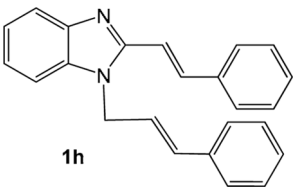
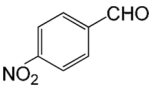
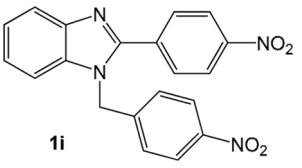
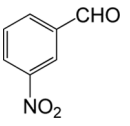
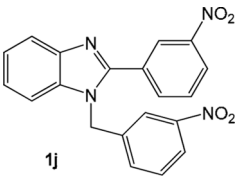
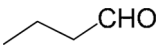
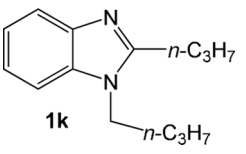
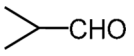
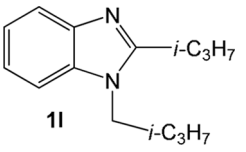
A possible mechanism to explain the formation of the 1,2-disubstituted benzimidazoles **1a**–**l** from *o*-PD and aldehydes is depicted in Scheme 2.[10(b),14] Products **1** and **2** are obviously the results of two competing reactions. The fast formation of dialkylidene (R = alkyl) or dibenzilidene-*o*-PD (R = aryl) was followed by acid-catalyzed ring closure and 1, 3-hydride transfer (path A). The electron-donating effect of R groups promoted the nucleophilic cyclization, and the electron-withdrawing effect of R groups behaved otherwise, which led to a lifting amount of the competitive product **2** (path B). Higher acidic strength of PSFSI ($H_0 \approx -11$) than that of –SO_3H ($H_0 \approx -3$) provided superior activation for the nucleophilic cyclization and resulted in greater selectivity (Table 1, entries 2 and 12–14).

Table 2. Condensation of *o*-PD with aldehyde derivatives[a]

Entry	Aldehyde	Products **1**	Isolated yield (%) Total	**1**	Selectivity (%)[a]
1		 **1a**	70	65 (**1a**)	94
2		 **1b**	67	67 (**1b**)	>99
3		 **1c**	49	46 (**1c**)	93
4		 **1d**	52	52 (**1d**)	>99
5		 **1e**	60	53 (**1e**)	88
6		 **1f**	75	61 (**1f**)	81
7		 **1g**	62	53 (**1g**)	85

(*Continued*)

Table 2. Continued

Entry	Aldehyde	Products **1**	Isolated yield (%) Total	**1**	Selectivity (%)[a]
8		 **1h**	50	35 (**1h**)	70
9[b]		 **1i**	66	53 (**1i**)	80
10[b]		 **1j**	71	36 (**1j**)	51
11		 **1k**	56	56 (**1k**)	>99
12		 **1l**	42	42 (**1l**)	>99

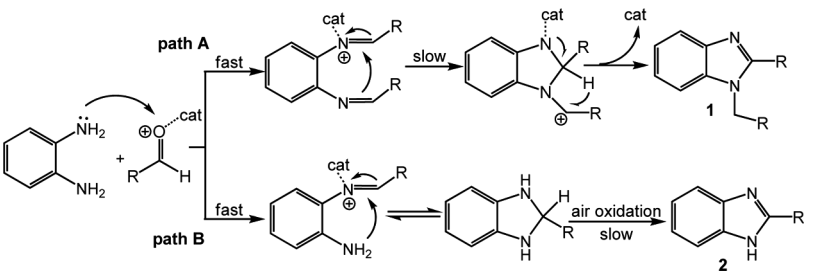
Note. Reaction conditions: PSFSI/SBA-15 (30 mol%, relative to *o*-PD), *o*-PD (1.5 mmol), aryl aldehyde and cinnamaldehyde (4.7 mmol), or alkyl aldehyde (3.2 mmol), stirred for 80 min at 25–28 °C in 7 mL of CH_3NO_2.

[a] $$\text{Selectivity} = \frac{\text{yield } (\mathbf{1})}{\text{total yield } (\mathbf{1}+\mathbf{2})} \times 100\%.$$

[b] Reaction time: 150 min. Only 40% of **1i** and 29% of **1j** were obtained in 80 min.

CONCLUSION

In conclusion, a new type of strongly acidic composite catalyst was developed by immobilizing the homopolymer, PSFSI, onto SBA-15 silica. The 1,2-disubstituted



Scheme 2. Possible mechanism of the synthesis of 1,2-disubstituted benzimidazoles.

benzimidazoles were obtained in moderate yield and good selectivity in the condensation of *o*-phenylenediamine with structurally diverse aldehydes under mild conditions.

EXPERIMENTAL

All solvents (analytical-reagent grade) for synthesis were commercially available in China and pretreated before used. Fourier transform infrared (FT-IR) spectra were conducted by using an Avatar 330 Fourier spectrometer with the KBr pellet technique. NMR was recorded in $CDCl_3$ or dimethylsulfoxide (DMSO-d_6) solution on a Bruker AV400 spectrometer using tetramethylsilane (TMS) as the internal standard. High-resolution mass spectroscopy (HRMS) data were tested on a Bruker Apex IV Fourier transform mass spectrometry (FTMS). The melting point was tested on X-4 digital display binocular microscope.

Immobilization of PSFSI onto SBA-15

A wet impregnation technique was used for the immobilization of PSFSI. SBA-15 support was introduced into a three-neck flask containing anhydrous methanol. The methanol solution of PSFSI was then added. The slurry was continuously stirred at room temperature for 6 h, and then solvent was removed by rotary evaporation under reduced pressure. In the end, the resultant solid was dried at 135 °C overnight. The eligible mass ratio of the initial mixture was 1:1.15 (PSFSI/SBA-15, wt/wt) without obvious loss of the orderly structure of SBA-15. Correspondingly, the acid content of 0.87 mmol/g was obtained and the catalyst was designated as PSFSI/SBA-15.

General Procedure for the Synthesis of Benzimidazoles

To a mixture of aromatic aldehyde (3.2 mmol, or 4.7 mmol fatty aldehyde) and *o*-PD (1.5 mmol) was added 30 mol% PSFSI/SBA-15. Then 7 mL of CH_3NO_2 were added, and the whole mixture was stirred at room temperature. The reaction progress was monitored by thin-layer chromatography (TLC). After completion of the reaction, filtration was performed and the catalyst was washed thoroughly with acetoacetate. The combined washings and the filtrate were evaporated in a vacuum.

The residue was purified by column chromatography over silica gel eluting with petroleum ether/AcOEt mixture.

Data

2-Phenyl-1-(phenylmethyl)-1*H*-benzimidazole (1a). Mp 143–145 °C (lit.[15] mp 139–141 °C); IR (KBr, ν, cm^{-1}): 3080, 3060, 3030, 2947 (CH_2, υ_{as}), 2854 (CH_2, υ_s), 1603, 1493 (benzene backbone), 1471 (CH_2, δ), 1450 (C=N), 734, 704 (C-H, γ); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, 1H, $J = 8$ Hz), 7.72 (d, 2H, $J = 7.2$ Hz), 7.48 (d, 3H, $J = 6.8$ Hz), 7.36–7.33 (m, 4H), 7.27–7.25 (m, 2H), 7.13 (d, 2H, $J = 7.2$ Hz), 5.49 (s, 2H, $ArCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.2, 143.1, 136.4, 136.1, 130.0, 130.0, 129.3, 129.1, 128.8, 127.8, 126.0, 123.1, 122.8, 120.0, 110.6, 48.4 (CH_2).

2-Phenyl-1*H*-benzoimidazole (2a). IR (KBr, ν, cm^{-1}): 3047, 2964, 2920, 1590, 1541 (benzene backbone), 1462, 1443, 1430, 1314, 1276, 970, 742, 702, 687; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 12.97 (s, 1H, NH), 8.19 (d, 2H, $J = 7.6$ Hz), 7.66–7.48 (m, 5H), 7.22 (d, 2H, $J = 3.6$ Hz); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 151.7, 144.2, 135.5, 130.6, 130.4, 129.5, 126.9, 122.7, 119.1, 111.9.[16]

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1*H*-benzoimidazole (1b). Mp 129–131 °C (lit.[10d] mp 129–130 °C); IR (KBr, ν, cm^{-1}): 3049, 2986, 2964, 2935 (CH_3, υ_{as}), 2835, 1609, 1510 (benzene backbone), 1481 (CH_2, δ), 1460 (C=N), 1386 (CH_3, δ), 1244 (C-O-C, υ_{as}), 1173, 1029 (C-O-C, υ_s), 837, 813, 735; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.70–7.68 (m, 3H), 7.45–7.43 (m, 1H), 7.25–7.19 (m, 2H), 7.09 (d, 2H, $J = 8.8$ Hz), 6.95 (d, 2H, $J = 8.4$ Hz), 6.85 (d, 2H, $J = 7.6$ Hz), 5.49 (s, 2H, $ArCH_2$), 3.83 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3).

1-(4-*tert*-Butylbenzyl)-2-(4-*tert*-butylphenyl)-1*H*-benzoimidazole (1c). Mp 240–242 °C; IR (KBr, ν, cm^{-1}): 3054, 2962, 2903, 2867, 1684, 1611, 1513 (benzene backbone), 1484 (CH_2, δ), 1462 (C=N), 1393, 1362 (CH_3, δ), 743; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92–7.90 (m, 1H), 7.71–7.69 (m, 2H), 7.51–7.49 (m, 2H), 7.38–7.31 (m, 3H), 7.25–7.24 (m, 2H), 7.08 (d, 2H, $J = 8.4$ Hz), 5.48 (s, 2H, $ArCH_2$), 1.39 (s, 9H, CH_3), 1.33 (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.3, 153.2, 150.7, 143.0, 136.0, 133.4, 129.9, 129.0, 127.0, 126.0, 125.8, 125.7, 125.3, 122.8, 122.6, 119.8, 110.6, 48.2 (CH_2), 34.9, 34.6, 31.3, 31.2 (CMe_3). HRMS (ESI): calculated for $C_{28}H_{32}N_2$ $[M + H]^+$ 397.26383, found 397.26375.

1-(4-Dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-1*H*-benzoimidazole (1d). Mp 240–242 °C; IR (KBr, ν, cm^{-1}): 3080, 3032, 2883, 2800 (NCH_3), 1611, 1526 (benzene backbone), 1488 (CH_2, δ), 1455 (C=N), 1442, 1389, 1365 (CH_3, δ), 1202, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, 1H, $J = 7.6$ Hz), 7.66 (d, 2H, $J = 8.8$ Hz), 7.30–7.19 (m, 3H), 7.05 (d, 2H, $J = 8.8$ Hz), 6.75 (d, 2H, $J = 8.8$ Hz), 6.71 (d, 2H, $J = 8.4$ Hz), 5.40 (s, 2H, $ArCH_2$), 3.03 (s, 6H), 2.95 (s, 6H).

1-(2-Furanylmethyl)-2-(2-furanyl)-1*H*-benzoimidazole (1e). Mp 100–101 °C (lit.[10d] mp 94 °C); IR (KBr, ν, cm^{-1}): 3151, 3129, 3054, 2938, 1671, 1605, 1511 (benzene backbone), 1475 (CH_2, δ), 1456 (C=N), 1438, 1007, 737; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, 1H, $J = 9.2$ Hz), 7.67 (s, 1H), 7.53–7.50 (m, 1H),

7.32 (d, 3H, $J = 19.2$ Hz), 7.25 (d, 1H, $J = 3.6$ Hz), 6.63 (d, 1H, $J = 0.8$ Hz), 6.30–6.25 (m, 2H), 5.66 (s, 2H, $ArCH_2$).

1-(3-Methylbenzyl)-2-(3-methylphenyl)-1*H*-benzoimidazole (1f). Mp 74–76 °C; IR (KBr, ν, cm^{-1}): 3018, 2919, 1606, 1591, 1501 (benzene backbone), 1463 (CH_2, δ), 1447 (C=N), 1377, 1007, 747; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, 1H, $J = 7.6$ Hz), 7.62 (s, 1H), 7.47 (d, 1H, $J = 7.2$ Hz), 7.36–7.32 (m, 3H), 7.27–7.22 (m, 3H), 6.96–6.92 (m, 2H), 5.44 (s, 2H, $ArCH_2$), 2.40 (s, 3H), 2.33 (s, 3H).

1-(2-Chlorobenzyl)-2-(2-chlorophenyl)-1*H*-benzoimidazole (1g). Mp 162–165 °C (lit.[10d] 163 °C); IR (KBr, ν, cm^{-1}): 3059, 2927, 1611, 1471 (CH_2, δ), 1440 (C=N), 1396, 1047, 745; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, 1H, $J = 8$ Hz), 7.75–7.71 (m, 1H), 7.54–7.42 (m, 3H), 7.37–7.30 (m, 3H), 7.23–7.20 (m, 2H), 7.10 (d, 1H, $J = 8.8$ Hz), 6.66 (d, 1H, $J = 6.8$ Hz), 5.39 (s, 2H, $ArCH_2$).

1-(3-Phenyl-2-propenyl)-2-(2-phenylethenyl)-1*H*-benzoimidazole (1h). IR (KBr, ν, cm^{-1}): 3156, 3026, 2926, 2849, 1686, 1635 (benzene backbone), 1550, 1495, 1450, 1202, 965, 747, 699; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, 2H, $J = 16$ Hz), 7.89 (d, 1H, $J = 7.6$ Hz), 7.80 (d, 1H, $J = 15.6$ Hz), 7.63 (d, 1H, $J = 7.2$ Hz), 7.43–7.41 (m, 3H), 7.39–7.30 (m, 4H), 7.14 (d, 2H, $J = 16$ Hz), 6.51 (d, 2H, $J = 16$ Hz), 5.09 (d, 2H, $J = 5.2$ Hz, $ArCH_2$).

1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1*H*-benzoimidazole (1i). Mp 242–244 °C; IR (KBr, ν, cm^{-1}): 3101, 3056, 2914, 2849, 1602 (benzene backbone), 1519 (NO_2, υ_{as}), 1458 (C=N), 1347 (NO_2, υ_s), 857, 747; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, 2H, $J = 8.8$ Hz), 8.26 (d, 2H, $J = 8.4$ Hz), 7.96 (d, 1H, $J = 7.6$ Hz), 7.86 (d, 2H, $J = 8.8$ Hz), 7.45–7.41 (m, 1H), 7.39–7.35 (m, 1H), 7.31–7.28 (m, 2H), 7.23 (d, 1H, $J = 8.0$ Hz), 5.61 (s, 2H).

1-(3-Nitrobenzyl)-2-(3-nitrophenyl)-1*H*-benzoimidazole (1j). Mp 182–184 °C; IR (KBr, ν, cm^{-1}): 3087, 2926, 2849, 1614 (benzene backbone), 1526 (NO_2, υ_{as}), 1455(C=N), 1350 (NO_2, υ_s), 818, 737; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.52 (s, 1H), 8.38 (d, 1H, $J = 8.4$ Hz), 8.23 (d, 1H, $J = 8.4$ Hz), 8.08 (d, 2H, $J = 8$ Hz), 7.96 (d, 1H, $J = 8$ Hz), 7.72 (t, 1H, $J = 8.0$ Hz), 7.58 (t, 1H, $J = 8.0$ Hz), 7.45–7.36 (m, 3H), 7.29 (d, 2H, $J = 8.8$ Hz), 5.61 (s, 2H).

2-(3-Nitrophenyl)-1*H*-benzo[*d*]imidazole (2j). Mp 204–205 °C (lit.[15] mp 207–208 °C); IR (KBr, ν, cm^{-1}): 3459 (NH), 3182, 1686, 1621, 1590, 1521, 1349 (NO_2, υ_s), 811, 741, 705; ^1H NMR (400 MHz, DMSO-d_6) δ: 13.34 (s, 1H, NH), 9.02 (s, 1H), 8.61 (d, 1H, $J = 7.6$ Hz), 8.32 (d, 1H, $J = 8$ Hz), 7.87–7.83 (m, 1H), 7.66 (s, 2H), 7.26 (s, 2H).

1-Butyl-2-propyl-1*H*-benzoimidazole (1k). IR (Nujol mull, ν, cm^{-1}): 3053, 2961, 2933, 2873, 1615 (benzene backbone), 1508, 1459, 1413, 1378, 766, 743; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.74 (s, 1H), 7.29 (s, 1H), 7.23–7.22 (m, 2H), 4.09 (t, 2H, $J = 7.6$ Hz), 2.87–2.83 (m, 2H), 1.94–1.91 (m, 2H), 1.81–1.72 (m, 2H), 1.43–1.37 (m, 2H), 1.07 (t, 3H, $J = 7.6$ Hz), 0.97 (t, 3H, $J = 7.6$ Hz).

1-Isobutyl-2-isopropyl-1*H*-benzoimidazole (1l). IR (KBr, ν, cm^{-1}): 3080, 3057, 2966, 2929, 2873, 1612 (benzene backbone), 1504, 1458, 1419, 1375, 1087, 745, 728; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.77–7.76 (m, 1H), 7.30 (s, 1H),

7.23–7.22 (m, 2H), 3.93 (d, 2H, $J = 7.6$ Hz), 3.24–3.17 (m, 1H), 2.28–2.17 (m, 1H), 1.45 (d, 6H, $J = 6.8$ Hz), 0.97 (d, 6H, $J = 6.4$ Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 142.5, 135.1, 121.8, 121.6, 119.2, 109.7, 50.8 (CH_2), 29.3, 26.3, 21.9, 20.2. HRMS (ESI): calculated for $C_{14}H_{20}N_2$ $[M + H]^+$ 217.16993; found 217.16947.

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