KIT-6 Mesoporous Silica-coated Magnetite Nanoparticles: A Highly Efficient and Easily Reusable Catalyst for the Synthesis of Benzo[*d*]imidazole Derivatives

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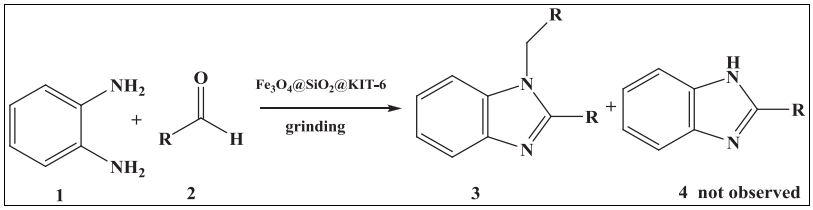

KIT-6 mesoporous silica-coated magnetite nanoparticles as highly ordered large-pore nanoparticles supply an environmentally friendly procedure for the synthesis of benzo[d]imidazoles through condensation of 1,2-diaminobenzene with aryl aldehydes. These compounds were obtained in high yields and short reaction times. The catalyst could be easily recovered using an external magnet and reused for six cycles with almost consistent activity. All of the synthesized compounds were characterized by their physical constant, comparison with authentic samples, ir, 1H nmr, 13C nmr spectroscopy, and elemental analysis.

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INTRODUCTION

Recent advances in nanotechnology and nano science have attracted much attention in employing nanometer-sized particles as an alternative matrix for supporting catalytic reactions owing to their easy filtration, easy work-up procedures, waste generation due to recycling of these catalysts, and minimization of cost. KIT-6 mesoporous silica-coated magnetite nanoparticles are usually preferred because it displays many significant properties such as excellent stability (thermal and chemical), high surface area, simple and convenient separation from a reaction media by magnetic separation, recyclability, and good accessibility.

Compounds with imidazole nucleus are common and important substructures found in natural products and pharmacologically active compounds. They act as glucagon receptor antagonists [1], inhibitors of P38 MAP kinase [2], β-raf kinase [3], transforming growth factor b1 (TGF-b1) type 1 activin receptor-like kinase (ALK5), [4] cyclooxygenase-2 (COX-2), [5] CB1 cannabinoid receptor antagonists [6], modulators of P-glycoprotein (P-gp)-mediated multidrug resistance (MDR), biosynthesis of interleukin-1 (IL-1) [7]. Many functionalized imidazoles behave as antibacterial [8], antibiotics [9], antiulceretics [10], fungicides [11], antidiabetic, antihypertensive, and anti-inflammatory agents [12,13].

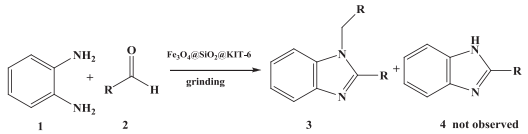
In 1822, Japp and Radziszewki reported the first three-component cyclocondensation synthesis of the imidazole nucleus from 1,2-dicarbonyl compounds, aldehydes, and ammonia to obtain 2,4,5-triphenyl-1*H*-imidazole [14,15]. In addition, they can also be accessed by the hetero-cope rearrangement [16], cycloaddition reaction of mesoionic 1,3-oxazolium-5-olates with *N*-(arylmethylene)-benzenesulfonamides [17], four-component condensation of aryl glyoxals, primary amines, carboxylic acids and isocyanides on Wang resin [18], condensation of a 1,2-diketone with an arylnitrile and primary amine under microwave irradiation [19], and reaction of *N*-(2-oxo)-amides with ammonium trifluoroacetate [20]. Another method for the synthesis of these compounds is the reaction of *o*-phenylenediamine with aldehydes in the presence of acidic catalysts under various reaction conditions [21–26]. However, many of these methods suffer from acidic media, unsatisfactory yields, longer reaction times, difficult work up, excessive use of reagents and catalyst. It is therefore important to find more convenient methods for the preparation of these compounds.

In order to make the reaction simple and green, herein, KIT-6 mesoporous silica-coated magnetite nanoparticles (MMNPs) have been successfully applied to perform the reaction of 1,2-diaminobenzene and arylaldehyde to provide a series of benzimidazole derivatives in excellent yields and short reaction times.

RESULT AND DISCUSSION

As a part of our program, seeking at development new procedures for the preparation of pharmaceutical and heterocyclic compounds [27–32] herein triggered us to describe a new, green, solvent free, cheap, and convenient method for the synthesis of benzo[*d*]imidazole via two-

Scheme 1. A procedure for synthesis of benzo[*d*]imidazoles.



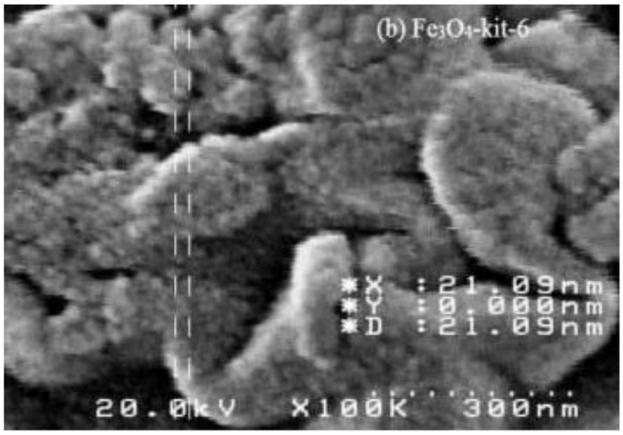
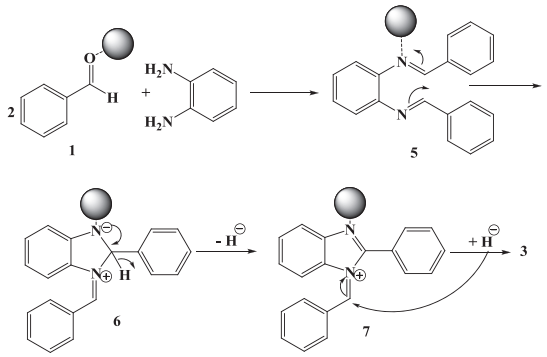


Figure 1. Scanning electron microscopy image of synthesized Fe_3O_4@SiO_2@KIT-6.

component reaction of aldehydes and 1,2-diaminobenzene in the presence of synthesized MMNPs (Scheme 1, Fig. 1).

Various derivatives of benzimidazoles were synthesized from 1,2-diaminobenzene and some derivatives of benzaldehyde in the presence of MMNPs (i) under refluxing in water as a green solvent, (ii) under ultrasound irradiation at 60°C in water, and (iii) under grinding as a green solvent free reaction (Table 1, entries 1–12). As can be seen in Table 1, satisfactory results were obtained only with MMNPs under grinding. It is worth mentioning that the

Scheme 2. A proposed mechanism for the synthesis of benzo[*d*] imidazole.



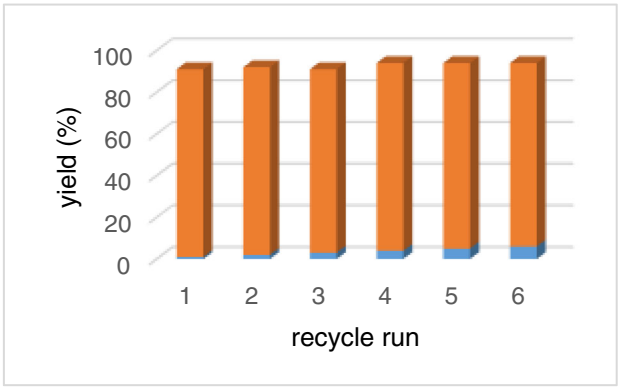


Figure 2. Reusability of Fe_3O_4@SiO_2@KIT-6 in the synthesis of **3a**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

corresponding benzo[*d*]imidazoles were isolated after separation of catalyst with washing the crude material with $CHCl_3$ in the presence of an efficient magnetic bar. The

Table 1

Synthesis of unexpected benzo[*d*]imidazole derivatives catalyzed by Fe_3O_4@SiO_2@KIT-6.

Entry	R	Product[a]	Reflux		Ultrasound		Grind	
			Time (h)	Yield[b] (%)	Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)
1	C_6H_5	**3a**	4	78	45	81	10	90
2	$(CH_3)_2$ NC_6H_4	**3b**	6	73	60	75	15	88
3	4-Cl C_6H_4	**3c**	3.5	83	30	85	5	97
4	4-BrC_6H_4	**3d**	3.5	85	30	89	7	95
5	4-$CH_3OC_6H_4$	**3e**	8	68	75	74	13	82
6	2-ClC_6H_4	**3f**	5	63	60	75	7	82
7	2-OHC_6H_4	**3g**	5.5	68	60	71	9	85
8	4-$NO_2C_6H_4$	**3h**	3	84	30	86	5	96
9	4-OHC_6H_4	**3i**	5	81	60	78	7	88
10	2-furyl	**3j**	6	78	75	70	7	88
11	4-pyridyl	**3k**	6.5	76	75	68	10	89
12	4-F C_6H_4	**3l**	3	80	30	86	5	99

[a]Reaction and conditions 1,2-diaminobenzene (1 mmol), aldehyde (1 mmol) and Fe_3O_4@SiO_2@KIT-6 (0.05 g).
[b]All yields refer to isolated products.

Table 2

Comparison of synthesis of compound **3a** in this method with some of previous reported methods.

Entry	Reagent	Condition	Time	Yield (%)	Ref.
1	Silica sulfuric acid	rt	1.5 h	75	26
2	$RuCl_2(PPh_3)_3$	100°C	20 h	90	33
3	AcOH, O_2	MW, 50°C	4 min	97	34
4	AcOH, O_2	Reflux, 80°C	25 min	92	34
5	$FeCl_3$-$6H_2O$	Solvent free, ball mil	120 min	96	35
6	KIT-6 mesoporous silica-coated magnetite nanoparticles	Grinding	10 min	90	This work

reactions worked well with almost all benzaldehydes with electron-donating or electron-withdrawing substituent. It was interesting that during the synthesis of the benzo[*d*]imidazole derivatives **3**, the product benzoimidazole **4** was not observed.

A possible mechanism proposed for these reactions is depicted in Scheme 2. This mechanism probably involves an initial MMNPs-promoted condensation of 1,2-diaminobenzene **2** with aldehydes **1** to yield a diimine intermediate **5** followed by a two-step cyclization to the benzo[*d*]imidazole **3**.

In order to investigate the reusability of synthesized Fe_3O_4@SiO_2@KIT-6, a recycling experiment was conducted. The catalyst could be recycled up to six times without significant loss of activity (Fig. 2). To reuse Fe_3O_4@SiO_2@KIT-6, the resulting mixture **3a** in grind method was solved in the $CHCl_3$ and filtered in the presence of an efficient magnetic bar, washed with $CHCl_3$ (3×10 mL), and dried at 80°C for 12 h under reduced pressure.

In order to assess the efficiency of this method, the synthesis of benzimidazoles from benzaldehydes and 1,2-diaminobenzene was compared with some various reported method (Table 2).

CONCLUSION

In conclusion, we have investigated the synthesized MMNPs as a mild and efficient catalyst for the synthesis of benzo[*d*]imidazoles. The remarkable advantages offered by this method are as follows: the catalyst is inexpensive, non-toxic, easy handling and reusable, simple work-up procedure, short reaction time, high yields of product with better purity and green aspect by avoiding toxic catalyst and hazardous solvent. To the best of our knowledge this is the first report on synthesis of benzo[*d*]imidazoles derivatives using Fe_3O_4@SiO_2@KIT-6.

EXPERIMENTAL

Chemicals were purchased from Merck and Fluka. All solvents used were dried and distilled according to standard procedures. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were determined on a Shimadzu FT-IR 8600 spectrophotometer (Japan). ^1H and ^{13}C NMR spectra were determined on a Bruker 400 DRX Avance instrument (Germany) at 500 and 125 MHz. Elemental analyses were performed on a Carlo-Erba EA1110CNNO-S analyzer (China) and agreed with the calculated values.

General procedure for the synthesis of KIT-6 mesoporous silica coated magnetite nanoparticles. The synthesis of MMNPs was carried out as described by [36].

General procedure for the KIT-6 mesoporous silica coated magnetite nanoparticles-catalyzed synthesis of 3a-l under reflux condition. A mixture of aldehydes (1 mmol), 1,2-diaminobenzene (1 mmol), (MMNPs, 0.05 g), and H_2O (10 mL) were refluxed in an oil bath for the required reaction times (3.5–8 h). The progress of the reaction was monitored by thin-layer chromatography (TLC) (EtOAc: petroleum ether 1:4). Then, the reaction mixture was filtered in the presence an efficient magnetic bar to separate the catalyst, and the organic compound was recrystallized from EtOH. The pure products were collected in 63–85% yields.

General procedure for the ultrasound-assisted KIT-6 mesoporous silica coated magnetite nanoparticles-catalyzed synthesis of 3a–l. A mixture of aldehydes (1 mmol), 1,2-diaminobenzene (1 mmol), (MMNPs, 0.05 g), and H_2O (10 mL) were placed into Pyrex-glass open vessel and irradiated in a water bath under silent condition by ultrasound (45 KHz) at 60°C for the required reaction times (30–75 min). The progress of the reaction was monitored by TLC (EtOAc: petroleum ether 1:4). Then, the reaction mixture was filtered in the presence of an efficient magnetic bar to separate the catalyst, and the organic compound was recrystallized from EtOH. The pure products were collected in 68–89% yields.

General procedure for the KIT-6 mesoporous silica coated magnetite nanoparticles-assisted grind synthesis of 3a–l. A mixture of aldehyde (1 mmol), 1, 2-diaminobenzene (1 mmol), and Fe_3O_4@SiO_2@KIT-6 (0.05 g) were added to a mortar, and the mixture was pulverized with a pestle. A spontaneous reaction took place (Table 1, monitored by TLC EtOAc: petroleum ether 1:4 drops. After completion of

the reaction, the product was solved in $CHCl_3$ (3 × 10 mL), and an insoluble catalyst was removed by filtration in the presence of an efficient magnetic bar. The organic phase including the product and $CHCl_3$ was evaporated under vacuum. The resulting crude material was purified by recrystallization from EtOH to afford pure products. All of the synthesized compounds were characterized by their physical constant, comparison with authentic samples, IR, ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analysis. All of synthesized compounds are known as described by [34].

Analytical data for selected compounds. 1-Benzyl-2-phenyl-1H-benzo[d]imidazole (3a). This compound was obtained as white solid, mp 134–136°C; FT-IR (KBr): 2924 (aliphatic C-H stretch), 1625 (C=N stretch), 3041 (aromatic C-H stretch), 1555, 1458 (aromatic C=C stretch), 1317 (C=N stretch), 1163 cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 5.79 (s, 2H), 7.19 (d, 1H, *J* = 7.6 Hz), 7.30–7.39 (m, 2H), 7.50–7.66 (m, 3H), 7.69–7.84 (m, 4H), 7.87–7.96 (m, 3H), 8.50 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ : 152.9, 149.1, 143.0, 135.8, 135.1, 129.6, 129.1, 128.9, 128.4, 127.8, 126.2, 122.0, 118.6, 110.6, 47.2. *Anal.* Calcd. for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.50; H, 9.83, N, 9.85.

4-(1-(4-(Dimethylamino)benzyl)-1H-benzo[d]imidazol-2-yl)-N,N-dimethylbenzenamine (3b). This compound was obtained as off-white solid, mp 250–251°C; FT-IR (KBr): 1612 (C=N stretch), 1521, 1911 (aromatic C=C stretch), 1376 (C-N stretch), 1219, 1043 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ: 2.73 (s, 6H), 2.85 (s, 6H), 5.41 (s, 2H), 6.58–7.12 (m, 12H); ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ : 155.7, 151.4, 149.4, 142.6, 135.6, 130.5, 40.2, 126.2, 124.6, 122.5, 119.1, 117.2, 112.7, 111.1, 110.6, 48.1, 40.5. *Anal.* Calcd. for $C_{24}H_{26}N_4$: C, 77.80; H, 7.07; N, 15.12. Found: C, 77.75; H, 7.10, N, 15.14.

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole (3c). This compound was obtained as off-white solid, mp 138–140°C; FT-IR (KBr): 1628 (C=N stretch), 1279, 1095 (C-Cl stretch), 1406 (aromatic C=C stretch) cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ : 5.61 (s, 2H), 7.20–7.25 (m, 3H), 7.30–7.40 (m, 1H), 7.52–7.61 (m, 4H), 7.69–7.76 (m, 2H), 8.20–8.23 (m, 2H); ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ : 152.1, 142.1, 135.7, 135.0, 133.2, 133.9, 130.1, 129.5, 128.6, 127.7, 126.5, 123.5, 122.4, 120.4, 110.6, 46.7. *Anal.* Calcd. for $C_{20}H_{14}Cl_2N_2$: C, 68.00; H, 3.99; N, 7.93. Found: C, 68.08; H, 3.95, N, 7.89.

1-(4-Bromobenzyl)-2-(4-bromophenyl)-1H-benzo[d]imidazole (3d). This compound was obtained as off-white solid, mp 196–198°C; FT-IR (KBr): 1629 (C=N stretch), 1526, 1403 (aromatic C=C stretch) 1068 (C-Br stretch) cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ : 5.57 (s, 2H), 7.28 (s, br, 2H), 7.41 (s, br, 1H), 7.47 (s, br, 1H), 7.62 (s, br, 2H), 7.75 (s, br, 2H), 7.84 (d, 2H, *J* = 8.0 Hz), 8.18 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ : 151.6, 142.6, 135.2, 134.5, 133.0, 132.8, 131.2, 129.0, 128.6, 127.3, 126.1, 123.8, 122.2, 120.8, 110.2, 45.9. *Anal.* Calcd. for $C_{20}H_{14}Br_2N_2$: C, 54.33; H, 3.19; N, 6.34. Found: C, 54.27; H, 3.31, N, 6.37.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3e). This compound was obtained as pale brown solid, mp 130–132°C; FT-IR (KBr): 1410, 1246 (C-O stretch), 1511, 1452 (aromatic C=C stretch), 1625 (C=N stretch) cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ: 3.72 (s, 3H), 3.81 (s, 3H), 5.41 (s, 2H), 6.85–7.69 (m, 12H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ: 159.3, 159.6, 154.4, 143.7, 135.4, 130.0, 128.7, 127.4, 123.0, 122.7, 119.2, 114.5, 114.0, 110.8, 55.9, 55.5, 46.7. *Anal.* Calcd. for $C_{23}H_{24}N_2O_3$: C, 73.38; H, 6.43; N, 7.44. Found: C, 73.41; H, 6.37, N, 7.43.

1-(2-Chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazole (3f). This compound was obtained as pale brown solid, mp 157–158°C; FT-IR (KBr): 2956 (aliphatic C-H stretch), 1623 (C=N stretch), 3017 (aromatic C-H stretch), 1562, 1462 (aromatic C=C stretch), 1382 (C-N stretch), 1221, 1048 (C-Cl stretch) cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ: 5.41 (s, 2H), 6.52–7.87 (m, 12H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ: 151.8, 142.0, 134.9, 134.5, 133.5, 132.9, 132.5, 131.3, 130.5, 129.7, 129.6, 128.1, 127.8, 127.2, 126.0, 123.4, 122.9, 120.4, 110.6, 45.9. *Anal.* Calcd. for $C_{20}H_{14}Cl_2N_2$: C, 68.00; H, 3.99; N, 7.93. Found: C, 68.05; H, 4.01, N, 7.98.

2-((2-(2-Hydroxyphenyl)-1H-benzo[d]imidazol-1-yl)methyl) phenol (3g). This compound was obtained as pale brown solid, mp 206–207°C; FT-IR (KBr): 1503, 1462 (Aromatic C=C stretching), 1621 (C=N stretching), 1408, 1241 (C-O stretching), 1159 cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ : 5.53 (s, 2H), 6.21–7.28 (m, 12H), 9.52 (s, br., 1H), 10.08 (s, br., 1H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ: 151.2, 142.3, 135.0, 134.7, 133.8, 133.2, 132.8, 131.5, 130.5, 129.0, 128.2, 129.6, 127.4, 126.3, 125.7, 123.5, 121.7, 120.7, 110.2, 45.8. *Anal.* Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.89; H, 5.12, N, 8.89.

1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1H-benzo[d]imidazole (3h). This compound was obtained as pale brown solid, mp 116–118°C; FT-IR (KBr): 2961 (aliphatic C-H stretch), 1609 (C=N stretch), 1344, 1521 (NO_2 stretch), 1418, 1452 (aromatic C=C stretch) 1232, 1108 cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ : 5.81 (s, 2H), 7.24–7.26 (m, 3H), 7.49–7.52 (s, br, 1H), 7.64-7.66 (s, br, 2H), 8.38 (d, 2H, *J* = 8.0 Hz), 8.47 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ : 152.0, 149.1, 147.0, 142.7, 141.8, 136.0, 135.2, 129.5, 125.7, 124.8, 124.1, 123.6, 122.9, 121.0, 110.7, 45.6. *Anal.* Calcd. for $C_{20}H_{14}N_4O_4$: C, 64.17; H, 3.77; N, 14.97. Found: C, 64.18; H, 3.80, N, 14.93.

1-(4-Hydroxybenzyl)-2-(4-hydroxyphenyl)-1H-benzo[d]imidazole (3i). This compound was obtained as pale brown solid, mp 253–254°C. FT-IR (KBr): 1622 (C=N stretch),

1510, 1462 (aromatic C=C stretch) 1401, 1281 (C-O stretch), 11.63 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ : 5.34 (s, 2H), 7.18 (s, 2H), 6.65 (d, 2H, *J* = 7.2 Hz), 6.92 (t, 4H, *J* = 8.8 Hz), 7.54 (d, 4H, *J* = 6.0 Hz), 8.04 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz): δ : 152.8, 142.3, 135.8, 135.2, 133.9, 133.5, 130.3, 129.1, 128.2, 127.0, 125.3, 122.8, 122.2, 120.7, 110.2, 45.2. *Anal.* Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.98; H, 5.05, N, 8.89.

2-(2-Furyl)-1-(2-furylmethyl)-1H-benzimidazole (3j). This compound was obtained as pale brown solid, mp 94–95°C. FT-IR (KBr): 3017 (C–H), 2943 (C–H stretch), 1593 (C=N stretch), 1518, 1477 (C=C stretch), 1335 (C–N stretch), 1231 (C–O stretch) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ : 5.62 (s, 2H), 6.16–7.57 (m, 10H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ : 150.2, 145.7, 143.5, 142.2, 142.9, 135.5, 123.3, 122.0, 119.3, 113.2, 112.2, 110.8, 110.4, 109.9, 109.7, 43.1. *Anal.* Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.80; H, 4.49; N, 10.55.

2-(Pyridin-2-yl)-1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazole (3k). This compound was obtained as pale brown solid, mp 133–135°C. FT-IR (KBr): 3032 (C–H), 2918 (C–H stretch), 1578 (C=N stretch), 1519, 1459 (C=C stretch), 1326 (C–N stretch), 1243 (C–O stretch) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ : 5.53 (s, 2H), 6.42–7.52 (m, 12H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ : 149.9, 148.0, 146.0, 143.3, 134.6, 134.2, 133.5, 132.2, 131.9, 128.6, 128.0, 125.9, 125.4, 124.8, 123.9, 123.6, 120.7, 110.5, 45.4. *Anal.* Calcd. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.48; H, 5.02; N, 19.63.

1-(4-Fluorobenzyl)-2-(4-fluorophenyl)-1H-benzo[d]imidazole (3l). This compound was obtained as pale brown solid, mp 183–184°C. FT-IR (KBr): 1628 (C=N stretch), 1505, 1454 (aromatic C=C stretch), 1234, 1164 (C-F stretch) cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ : 5.76 (s, 2H), 6.90 (m, 1H), 7.14–7.18 (m, 1H), 7.06 (d, 1H, *J* = 9.2 Hz), 7.25 (t, *J* = 5.2 Hz, 1H), 7.56–7.64 (m, 4H), 7.93–8.01 (m, 2H), 8.58–8.62 (m, 2H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ : 151.8, 142.7, 137.7 ($^1J_{C-F}$ = 1520 Hz), 136.6 ($^1J_{C-F}$ = 160 Hz), 133.4, 132.6, 131.5 ($^2J_{C-F}$ = 48 Hz), 129.7 ($^2J_{C-F}$ = 42 Hz), 128.2, 127.3, 126.3, 123.2, 121.5 ($^3J_{C-F}$ = 2 Hz), 120.1 ($^3J_{C-F}$ = 3 Hz), 110.7, 46.5 ppm. *Anal.* Calcd. for $C_{20}H_{14}F_2N_2$: C, 74.99; H, 4.41; F, 11.86; N, 8.75. Found: C, 78.01; H, 4.43.

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