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Bismuth(III)–SiO_2 catalyzed synthesis of polysubstituted imidazoles with the participation of azaaryl derivatives of aniline in four-component reactions

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Abstract: A series of novel polyaromatic derivatives of imidazole were synthesized by Bi(III) nitrate–SiO_2 catalyzed four-component reactions of benzil, ammonium acetate, aromatic aldehydes, and *N*-heterocyclic derivatives of aniline under solvent-free conditions.

Key words: Polysubstituted imidazoles, heterocyclic derivatives of aniline, four-component reactions, Bi(III)-catalyzed condensations, solvent-free reactions

1. Introduction

Tetrasubstituted imidazole scaffold is an essential part of numerous bioactive compounds,[1–6] conjugated and fluorescent materials,[7,8] and metal-coordinating ligands.[9,10] Condensation of 1,2-diketones, aryl aldehydes, primary amines, and ammonium acetate is one of the most common synthetic tools for the preparation of 1,2,4,5-tetrasubstituted imidazoles.[11–13] Commercial availability or easy preparation of the individual building blocks has resulted in the production of highly diverse molecules through this acid-catalyzed reaction.[14–17] Continuing efforts and several modifications such as the use of green catalysts and solvent-free conditions indicate the special interest in this method.[18–20] Among the Lewis acids that promote multicomponent reactions, Bi^{3+}-based catalysts are popular due to being efficient, inexpensive, and insensitive to air.[21–23] In this work, we report the use of *N*-heterocyclic derivatives of aniline as a primary amine partner in four-component reactions in the presence of bismuth nitrate. Because of the multiple applications and interesting properties of the azole-enriched π-conjugated compounds, especially in terms of electrochemical, optical, and pharmacological behavior,[24–27] and through our interest in the synthesis of polyaromatic heterocyclic frameworks[28–30] and also multicomponent reactions,[31] we decided to access such molecules.

2. Results and discussion

We recently reported the *tert*-BuOK/DMSO-promoted S_NAr reactions of azoles such as imidazole, benzimidazole, pyrazole, and 3-methypyrazole with 4-bromonitrobenzene to obtain *N*-(4-nitrophenyl) azoles **1a**–**d**.[32] Reduction of the nitro group to amine with zinc powder in EtOH/AcOH afforded the required aniline derivatives **2a**–**d** (Scheme).

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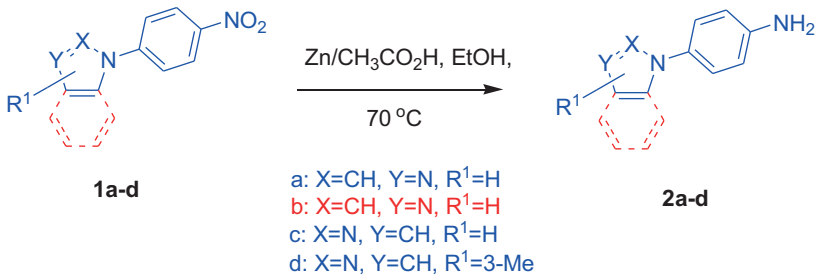
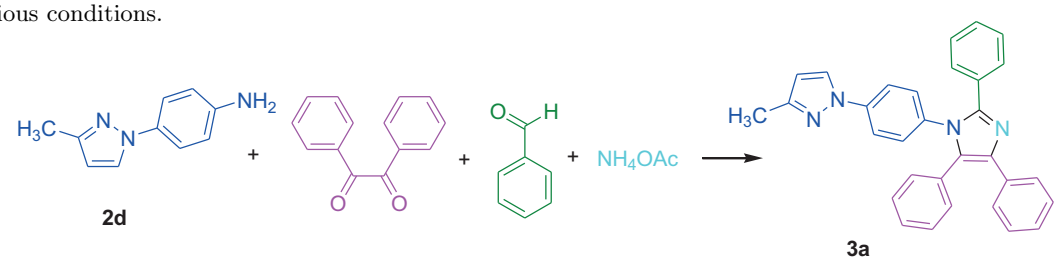


Scheme. Synthesis of heterocyclic derivatives of aniline.

Firstly, we used 4-(3-methyl-1*H*-pyrazol-1-yl)aniline **2d** (1 mmol) in four-component condensation with benzil (1 mmol), benzaldehyde (1 mmol), and ammonium acetate (1 mmol) to find the optimal reaction conditions. As shown in Table 1, in the absence of a catalyst, no product was obtained in the presence of solvent or without solvent, even after 48 h (Entries 1–6). Product formation was observed by using $Bi(NO_3)_3.5H_2O$

Table 1. Optimization of four-component condensation of benzaldehyde, benzyl, ammonium acetate, and aniline **2d** under various conditions.



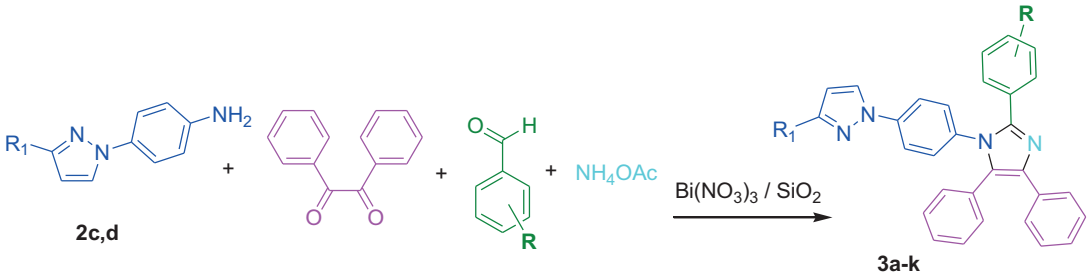
Entry	Lewis acid Catalyst /mol (%)	SiO_2 (gr)	Conditions		Time [a]	Yield (%)[b]
1	-	-	Solvent-free	R.T	48 h	-
2	-	-	H_2O	R.T	48 h	-
3	-	-	EtOH	R.T	48 h	-
4	-	-	Solvent-free	110 °C	48 h	Trace
5	-	-	H_2O	110°C	48 h	-
6	-	-	EtOH	110 °C	48 h	-
7	$Bi(NO_3)_3.5H_2O$ (10)	-	Solvent-free	110 °C	24 h	38
8	$Bi(NO_3)_3.5H_2O$ (10)	-	H_2O	110 °C	48 h	28
9	$Bi(NO_3)_3.5H_2O$ (10)	-	EtOH	110 °C	48 h	30
10	$Bi(NO_3)_3.5H_2O$ (15)	-	Solvent-free	110 °C	24 h	58
11	$Bi(NO_3)_3.5H_2O$ (15)	-	H_2O	110 °C	24 h	28
12	$Bi(NO_3)_3.5H_2O$ (15)	-	EtOH	110 °C	24 h	35
13	$Bi(NO_3)_3.5H_2O$ (20)	-	Solvent-free	110 °C	24 h	58
14	$Bi(NO_3)_3.5H_2O$ (15)	0.5	Solvent-free	80 °C	48 h	60
15	$Bi(NO_3)_3.5H_2O$ (15)	0.5	Solvent-free	110 °C	24 h	78
16	$Bi(NO_3)_3.5H_2O$ (15)	-	ultrasound irradiation-H_2O	70 Hz[c]	30 min	Trace
17	$Bi(NO_3)_3.5H_2O$ (15)	-	ultrasound irradiation-EtOH	70 Hz[c]	30 min	Trace
18	$Bi(NO_3)_3.5H_2O$ (15)	0.5	ultrasound irradiation-H_2O	70 Hz[c]	30 min	20
19	$Bi(NO_3)_3.5H_2O$ (15)	0.5	ultrasound irradiation-EtOH	70 Hz[c]	30 min	23
20	$Bi(NO_3)_3.5H_2O$ (15)	0.5	MW irradiation	200-W	30 min	25

[a]Reaction progress monitored by TLC. [b] Isolated yield. [c]Frequency of sonication

(10 mol%) but with low yields (Entries 7–9). Relatively high efficiency was achieved with a larger amount of catalyst (15 mol%) in solvent-free conditions (Entry 10). By increasing the catalyst loading to 20 mol%, there was no considerable change in the yield of the reaction (Entry 13). To access better reactivity, we then mixed the bismuth catalyst with silica (0.5 g), which led to a more favorable outcome (Entry 14). Application of silica as cocatalyst has been reported in some metal-promoted reactions.[33–36] Conventional heating of reactants with the mixed catalytic system at 110 °C for 24 h, resulted in the product **3a** in 78% yield (Entry 15). We also evaluated the effect of ultrasonic irradiation on the progress of this reaction. Sonication of the reactants at 70 Hz with different reaction media did not lead to a significant product (Entries 16–19).

Microwave irradiation under 200 W had no accelerator effect even when the microwave power was increased (Entry 20). We then synthesized various other derivatives of this type with amines **2a–d** under the optimized conditions (Table 1, entry 15). Table 2 shows the yields and melting points of the corresponding products **3a–k**, which were produced in the presence of amines **2d** or 4-(1*H*-pyrazol-1-yl)aniline **2c**. Treatment of **2d** with 2-thiophene carbaldehyde, benzil, and ammonium acetate also gave the product **3l** in 70% yield (Figure 1).

Table 2. Bismuth (III)-nitrate-SiO_2 catalyzed synthesis of highly substituted imidazoles (**3a–k**) with the participation of 4-(pyrazol-1-yl)anilines (**2c,d**).



Entry	R_1	R	Product	Yield (%)	mp (°C)
1	CH_3	H	**3a**	78	244–246
2	CH_3	4-CH_3	**3b**	70	212–214
3	CH_3	4-$CH(CH_3)_2$	**3c**	69	218–219
4	CH_3	4-OMe	**3d**	70	224–226
5	CH_3	4-Cl	**3e**	67	238–240
6	CH_3	3-Br	**3f**	63	228–229
7	CH_3	4-$N(CH_3)_2$	**3g**	56	240–242
8	H	H	**3h**	71	250–252
9	H	4-CH_3	**3i**	65	242–244
10	H	4-$CH(CH_3)_2$	**3j**	62	216–218
11	H	4-OMe	**3k**	65	236–238

The scope of these reactions was explored using 4-(1*H*-imidazol-1-yl)aniline **2a** (Table 3) and 4-(1*H*-benzimidazol-1-yl)aniline **2b** (Table 4) to afford the products **4a–f** and **5a–f**, respectively. The C-2 carbon peak values of compounds **5a–f** in their ^{13}C NMR spectra were found to be similar to values reported in the literature.[37,38] The imidazole **4g** was also obtained with the participation of amine **2a** and 2-thiophene carbaldehyde in 71% yield (Figure 1). Therefore, a variety of polyaromatic derivatives of imidazoles were obtained under simple workup and in good yields.

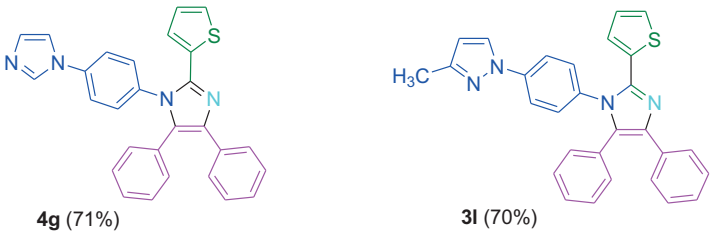
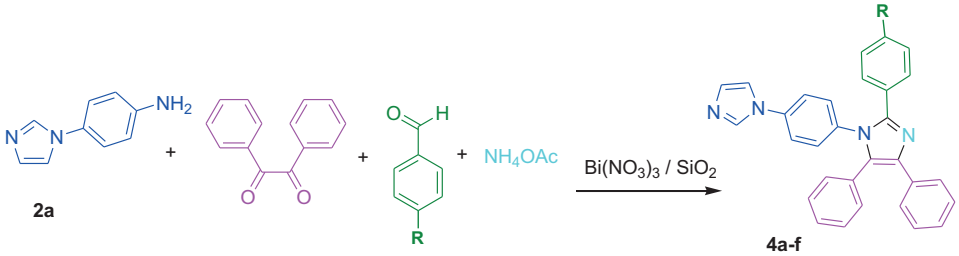


Figure 1. Highly substituted imidazoles possessing thiophene ring.

Table 3. Bismuth(III) nitrate-SiO_2 catalyzed synthesis of highly substituted imidazoles (**4a**–**f**) with the participation of 4-(imidazol-1-yl)aniline **2a**.



Entry	R	Product	Yield (%)	mp (°C)
1	H	**4a**	70	250–252
2	CH_3	**4b**	71	262–264
3	$CH(CH_3)_2$	**4c**	73	266–268
4	Cl	**4d**	68	248–250
5	OMe	**4e**	72	258–260
6	OH	**4f**	56	330–332

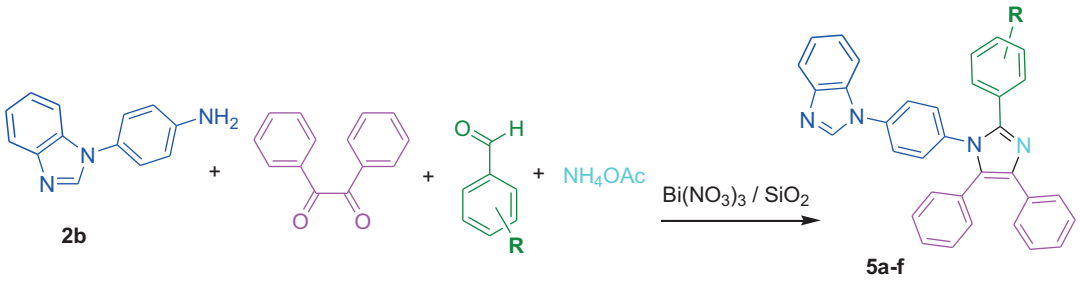
Regarding the above reactions, it should be mentioned that, in the presence of 4-nitrobenzaldehyde, 2,4,5-triarylimidazoles were produced through three-component cyclizations without the involvement of the substituted aniline.

A probable mechanism for the catalytic participation of $Bi(NO_3)_3.5H_2O$-SiO_2 in the synthesis of target molecules is postulated in Figure 2. Because silica alone was not able to catalyze this reaction, it seems SiO_2-coordinated Bi^{3+} activates the carbonyl group of an aldehyde to simplify the formation of diamine intermediate **A**. $Bi(NO_3)_3.5H_2O$-SiO_2 also activates the benzil to promote condensation with **A** to give the species **B**. Elimination of water from **B** transformed it into the desired imidazole derivatives (Figure 2).

3. Experimental

Melting points were determined on an Electrothermal MEL-TEMP apparatus (model 1202D) and are uncorrected. FT-IR spectra were obtained with a Bruker Tensor 27 spectrometer; ν in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded with a Bruker Spectrospin Avance 400 spectrometer operating at 400 MHz and 100 MHz, respectively, in DMSO-d_6; chemical shifts are given in parts per million (ppm, δ) relative to residual solvent peaks as standard at 298 K (2.50 ppm (^1H), 39.5 ppm (^{13}C)); J in Hz. Elemental analyses were measured by Vario EL III apparatus (Elementar Co.). The microwave experiment was conducted in a Milestone MicroSYNTH apparatus. Ultrasonic mediated experiments were carried out by use of an ultrasonic processor

Table 4. Bismuth(III) nitrate-SiO_2 catalyzed synthesis of highly substituted imidazoles (**5a**–**f**) with the participation of 4-(benzimidazol-1-yl)aniline **2b**.



Entry	R	Product	Yield (%)	mp (°C)
1	H	**5a**	68	260–262
2	4-CH_3	**5b**	63	242–244
3	4-$CH(CH_3)_2$	**5c**	70	240–242
4	4-Cl	**5d**	67	274–276
5	4-OMe	**5e**	73	242–244
6	3-Br	**5f**	70	240–242

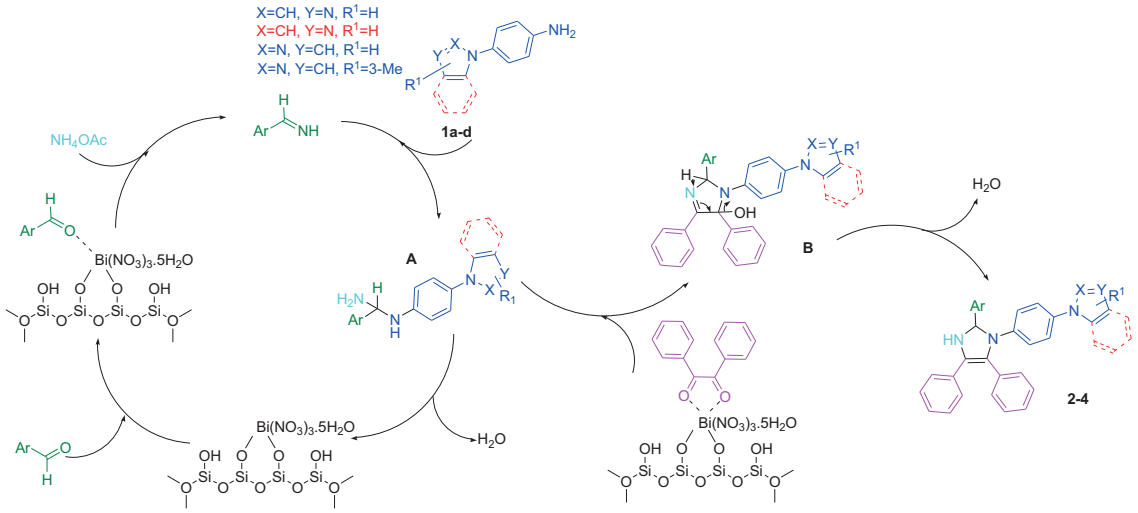


Figure 2. Probable mechanism for the four-component reactions with the participation of azaaryl derivatives of aniline in the presence of $Bi(NO_3)_3.5H_2O$-SiO_2.

probe (SONOPULS Ultrasonic homogenizers). The used silica gel cocatalyst was Kieselgel 60 (0.040–0.063 mm, Merck: 9385).

3.1. Synthesis of substituted imidazoles (3–5)

A mixture of *N*-(4-aminophenyl) azoles **2a**–**d** (1 mmol), benzil (1 mmol, 0.21 g), aromatic aldehyde (1 mmol), and ammonium acetate (1 mmol, 0.077 g) was stirred vigorously. $Bi(NO_3)_3.5H_2O$ (0.15 mmol, 0.073 g, 15 mol%) and SiO_2 (0.5 g) were mixed effectively and added to the mixed reactants. The resulting mixture was heated at 110 °C for 24 h. Acetone (50 mL) was then added and the mixture was stirred at 50 °C for 10 min.

Filtering the hot mixture and then concentration of the filtrate produced the crude product. Recrystallization of the crude products in 96% EtOH gave the desired product **3**–**5**.

3.1.1. 1-[4-(3-Methyl-1*H*-pyrazol-1-yl)phenyl]-2,4,5-triphenyl-1*H*-imidazole (3a)

Pale yellow solid; Yield 0.35 g (78%) mp 244–246 °C. FTIR (KBr): $\bar{\nu}$ 3054, 2925, 1517, 1475, 846, 693 cm^{-1}; ^{1}H NMR (DMSO-d_6): 2.23 (s, 3H, CH_3), 6.32 (d, J = 2.4 Hz, 1H, py-H4), 7.17–7.35 (m, 13H, Ar-H), 7.43–7.44 (m, 2H, Ar-H), 7.50 (d, J = 7.9 Hz, 2H, Ar-H), 7.72 (d, J = 8.8 Hz, 2H, Ar-H), 8.37 (d, J = 2.4 Hz, 1H, py-H5). ^{13}C NMR (DMSO-d_6): δ = 13.4, 108.3 (Py-C4), 117.9, 126.4, 126.5, 128.1, 128.2, 128.3, 128.4, 128.5, 128.52, 129.8, 130.3, 130.34, 131.1, 131.3, 133.7, 134.3, 136.8, 139.2, 146.1 (Im-C2), 150.2 (Py-C3). Anal. Calcd. For $C_{31}H_{24}N_4$: C, 82.27; H, 5.35; N, 12.38; Found: C, 81.98; H, 5.12; N, 12.55%.

3.1.2. 4,5-Diphenyl-1-[4-(3-methyl-1*H*-pyrazol-1-yl)phenyl]-2-(*p*-tolyl)-1*H*-imidazole (3b)

Yield: 0.32 g (70%); pale yellow solid; mp 212–214 °C; FTIR (KBr): $\bar{\nu}$ 3049, 2924, 1522, 1362, 1035 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.23 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 6.33 (s, 1H, Py-H4), 7.11–7.34 (m, 14H, Ar-H), 7.48 (d, J = 7.5 Hz, 2H, Ar-H), 7.71 (d, J = 8.6 Hz, 2H, Ar-H), 8.37 (s, 1H, py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.4, 20.8, 108.3 (Py-C4), 117.2, 126.3, 126.5, 127.5, 128.2, 128.3, 128.4, 128.6, 128.8, 129.9, 130.4, 131.2, 133.8, 134.4, 136.7, 137.9, 139.2, 150.2 (Py-C3). Anal. Calcd. For $C_{32}H_{26}N_4$: C 82.38, H 5.62, N 12.01; Found, C 82.15, H 5.39, N 12.34.

3.1.3. 2-(4-Isopropylphenyl)-1-[4-(3-methyl-1*H*-pyrazol-1-yl)phenyl]-4,5-Diphenyl-1*H*-imidazole (3c)

Yield: 0.34 g (69%); pale yellow solid; mp 218–219 °C; FTIR (KBr): $\bar{\nu}$ 3046, 2957, 1522, 1361, 840, 654 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.15 (d, J = 6.9 Hz, 6H, $(CH_3)_2CH$), 2.23 (s, 3H, CH_3), 2.82 (m, 1H, $CH(Me)_2$), 6.33 (d, J = 2.2 Hz, 1H, Py-H4), 7.17–7.37 (m, 14H, Ar-H), 7.49 (d, J = 7.3 Hz, 2H, Ar-H), 7.73 (d, J = 8.7 Hz, 2H, Ar-H), 8.37 (d, J = 2.3 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.4, 23.6, 33.1, 108.3 (Py-C4), 117.9, 126.2, 126.3, 126.4, 127.9, 128.1, 128.2, 128.4, 128.5, 129.9, 130.4, 131.1, 131.2, 133.8, 134.4, 136.7, 139.2, 146.1 (Im-C2), 148.6 (=C-^{i}Pr), 150.2 (Py-C3). Anal. Calcd. For $C_{34}H_{30}N_4$: C 82.56, H 6.11, N 11.33; Found, C 82.29, H 6.34, N 11.65.

3.1.4. 2-(4-methoxyphenyl)-1-[4-(3-methyl-1*H*-pyrazol-1-yl) phenyl]-4,5-diphenyl-1*H*-imidazole (3d)

Yield: 0.328 g (70%); pale yellow solid; mp 224–226 °C; FTIR (KBr): $\bar{\nu}$ 3048, 2929, 1607, 1523, 1248, 944 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.23 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 6.33 (s, 1H, Py-H4), 6.87 (d, J = 8.5 Hz, 2H, Ar-H), 7.15–7.37 (m, 12H, Ar-H), 7.49 (d, J = 7.9 Hz, 2H, Ar-H), 7.72 (d, J = 8.5 Hz, 2H, Ar-H), 8.37 (s, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.4, 55.1 (OCH_3), 108.3 (Py-C4), 113.7, 117.9, 122.7, 126.3, 126.4, 128.2, 128.4, 128.5, 129.7, 129.9, 130.5, 130.9, 131.2, 133.9, 134.5, 136.6, 139.2, 146.1 (Im-C2), 150.2 (Py-C3), 159.3 (=C-OMe). Anal. Calcd. For $C_{32}H_{26}N_4O$: C 79.64, H 5.43, N 11.61; Found, C 79.32, H 5.19, N 11.87.

3.1.5. 2-(4-Chlorophenyl)-1-[4-(3-methyl-1*H*-pyrazol-1-yl) phenyl]-4,5-diphenyl-1*H*-imidazole (3e)

Yield: 0.32 g (67%); pale yellow solid; mp 238–240 °C; FTIR (KBr): $\bar{\nu}$ 3051, 2957, 1611, 1516, 1312, 840 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.24 (s, 3H, CH_3), 6.33 (d, J = 2.2 Hz, 1H, Py-H4), 7.18–7.51 (m, 16H, Ar-H), 7.74 (d, J = 8.7 Hz, 2H, Ar-H), 8.38 (d, J = 2.2 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.4, 108.3 (Py-C4), 118.0, 126.3, 126.6, 128.2, 128.4, 128.6, 129.1, 129.8, 129.9, 130.2, 131.1, 131.6, 133.2, 133.5, 134.2, 137.0, 139.3, 144.9, 150.3 (Py-C3). Anal. Calcd. For $C_{31}H_{23}ClN_4$: C 76.46, H 4.76, N 11.50; Found, C 76.19, H 4.91, N 11.80.

3.1.6. 2-(3-Bromophenyl)-1-[4-(3-methyl-1*H*-pyrazol-1-yl) phenyl]-4,5-diphenyl-1*H*-imidazole (3f)

Yield: 0.33 g (63%); pale yellow solid; mp 228–229 °C; FTIR (KBr): $\bar{\nu}$ 3057, 2929, 1598, 1519, 1362, 691 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.24 (s, 3H, CH_3), 6.34 (d, J = 2.1 Hz, 1H, Py-H4), 7.17–7.33 (m, 11H, Ar-H), 7.39 (d, J = 8.7 Hz, 2H, Ar-H), 7.50 (d, J = 7.1 Hz, 2H, Ar-H), 7.69 (s, 1H, Ar-H), 7.75 (d, J = 8.7 Hz, 2H, Ar-H), 8.39 (d, J = 2.1 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.5, 108.4 (Py-C4), 117.9, 121.5, 126.4, 126.7, 126.9, 128.3, 128.6, 129.9, 130.1, 130.4, 130.8, 131.1, 131.9, 132.4, 133.4, 134.1, 137.1, 139.4, 144.4, 150.3 (Py-C3). Anal. Calcd. For $C_{31}H_{23}BrN_4$: C 70.06, H 4.36, N 10.54; Found, C 69.79, H 4.53, N 10.28.

3.1.7. 2-[4-(*N*,*N*-Dimethylamino)phenyl]-1-[4-(3-methyl-1*H*-pyrazol-1-yl) phenyl]-4,5-diphenyl-1*H*-imidazole (3g)

Yield: 0.28 g (56%); pale yellow solid; mp 240–242 °C; FTIR (KBr): $\bar{\nu}$ 3057, 2925, 1605, 1522, 1359, 825 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.24 (s, 3H, CH_3), 2.87 (s, 6H, N-CH_3), 6.33 (d, J = 1.9 Hz, 1H, Py-H4), 6.60 (d, J = 8.8 Hz, 2H, Ar-H), 7.14–7.39 (m, 12H, Ar-H), 7.48 (d, J = 7.8 Hz, 2H, Ar-H), 7.72 (d, J = 8.6 Hz, 2H, Ar-H), 8.37 (d, J = 1.9 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.4, 55.1 ($N(CH_3)_2$), 108.3 (Py-C4), 111.4, 11.9, 117.4, 117.9, 126.3, 126.7, 127.9, 128.1, 128.3, 128.5, 129.1, 129.9, 130.5, 130.6, 131.2, 134.2, 134.5, 139.1, 146.8 (Im-C2), 150.0 (Py-C3), 150.2 (=C–NMe_2). Anal. Calcd. For $C_{33}H_{29}N_5$: C 79.97, H 5.90, N 14.13; Found, C 79.69, H 6.18, N 14.51.

3.1.8. 1-[4-(1*H*-pyrazol-1-yl)phenyl]-2,4,5-triphenyl-1*H*-imidazole (3h)

Yield: 0.31 g (71%); pale yellow solid; mp 250–252 °C; FTIR (KBr): $\bar{\nu}$ 3054, 1517, 1391, 846, 693 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.33 (d, J = 2.4 Hz, 1H, Py-H4), 7.18–7.36 (m, 14H, Ar-H), 7.43–7.44 (m, 2H, Ar-H), 7.50 (d, J = 7.9 Hz, 2H, Ar-H), 7.72 (d, J = 8.8 Hz, 2H, Ar-H), 8.37 (d, J = 2.4 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 108.3 (Py-C4), 117.9, 126.3, 126.5, 128.1, 128.2, 128.3, 128.4, 128.5, 129.9, 130.3, 130.34, 131.1, 131.3, 133.7, 134.3, 136.8, 139.2, 146.1 (Im-C2), 150.2 (Py-C3). Anal. Calcd. For $C_{30}H_{22}N_4$: C 82.17, H 5.06, N 12.78; Found, C 81.85, H 5.24, N 12.56.

3.1.9. 4,5-Diphenyl-1-[4-(1*H*-pyrazol-1-yl)phenyl]-2-(*p*-tolyl)-1*H*-imidazole (3i)

Yield: 0.29 g (65%); pale yellow solid; mp 242–244 °C; FTIR (KBr): $\bar{\nu}$ 3065, 2923, 1520, 1364, 839, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.26 (s, 3H, CH_3), 6.33 (d, J = 2.1 Hz, 1H, Py-H4), 7.11 (d, J = 7.9 Hz, 2H, Ar-H), 7.15–7.38 (m, 13H, Ar-H), 7.49 (d, J = 7.5 Hz, 2H, Ar-H), 7.71 (d, J = 8.6 Hz, 2H, Ar-H), 8.36

(d, J = 2.1 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 108.2 (Py-C4), 117.9, 118.4, 126.3, 126.4, 127.5, 127.9, 128.1, 128.2, 128.4, 128.5, 128.8, 128.9, 130.0, 130.4, 131.1, 133.8, 134.4, 137.9, 139.2, 146.2 (Im-C2), 150.2 (Py-C3). Anal. Calcd. For $C_{31}H_{24}N_4$: C 82.27, H 5.35, N 12.38; Found, C 81.95, H 5.17, N 12.64.

3.1.10. 4,5-Diphenyl-2-(4-isopropylphenyl)-1-[4-(1*H*-pyrazol-1-yl)]phenyl]-1*H*-imidazole (3j)

Yield: 0.30 g (62%); pale yellow solid; mp 216–218 °C; FTIR (KBr): $\bar{\nu}$ 3047, 2956, 1616, 1530, 1362, 840 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.15 (d, J = 6.9 Hz, 6H, $(CH_3)_2CH$), 2.82–2.84 (m, 1H, CH $(Me)_2$), 6.33 (d, J =1 Hz, 1H, Py-H4), 7.16–7.41 (m, 15H, Ar-H), 7.50 (d, J = 7.8 Hz, 2H, Ar-H), 7.73 (d, J = 8.5 Hz, 2H, Ar-H), 8.37 (d, J = 1 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.6, 33.1, 108.2 (Py-C4), 117.9, 118.4, 126.1, 126.3, 126.4, 127.9, 128.1, 128.2, 128.4, 128.5, 129.9, 130.0, 130.4, 131.1, 133.8, 134.4, 136.7, 139.2, 146.1 (Im-C2), 148.6 (=C-^{i}Pr), 150.2 (Py-C3). Anal. Calcd. For $C_{33}H_{28}N_4$: C 82.47, H 5.87, N 11.66; Found, C 82.16, H 5.65, N 11.89.

3.1.11. 4,5-Diphenyl-2-(4-methoxyphenyl)-1-[4-(1*H*-pyrazol-1-yl)]phenyl]-1*H*-imidazole (3k)

Yield: 0.30 g (65%); pale yellow solid; mp 236–238 °C; FTIR (KBr): $\bar{\nu}$ 3054, 2924, 1602, 1524, 1251, 843 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.72 (s, 3H, OCH_3), 6.33 (d, J = 2.2 Hz, 1H, Py-H4), 6.87 (d, J = 8.7 Hz, 2H, Ar-H), 7.15–7.37 (m, 13H, Ar-H), 7.49 (d, J = 7.4 Hz, 2H, Ar-H), 7.72 (d, J = 8.7 Hz, 2H, Ar-H), 8.37 (d, J = 2.2 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.1 (OCH_3), 108.3 (Py-C4), 113.7, 117.9, 122.7, 126.3, 126.4, 128.1, 128.4, 128.5, 129.7, 129.9, 130.5, 130.9, 131.2, 133.9, 134.5, 136.6, 139.2, 146.1 (Im-C2), 150.2 (Py-C3), 159.3 (=C–OMe). Anal. Calcd. For $C_{31}H_{24}N_4O$: C 79.46, H 5.16, N 11.96; Found, C 79.17, H 5.38, N 11.73.

3.1.12. 4,5-Diphenyl-1-[4-(3-methyl-1*H*-pyrazol-1-yl)phenyl]- 2-(thiophen-2-yl)-1*H*-imidazole (3l)

Yield: 0.32 g (70%); pale yellow solid; mp 244–246 °C; FTIR (KBr): $\bar{\nu}$ 3056, 2926, 1615, 1515, 1359, 695 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.25 (s, 3H, CH_3), 6.35 (d, J = 2.1 Hz, 1H, Py-H4), 6.62 (d, J = 3.6 Hz, 1H, Th-H5), 6.93–7.95 (m, 1H, Th-H4), 7.18–7.30 (m, 8H, Ar-H), 7.47–7.53 (m, 5H, Ar-H), 7.83 (d, J = 8.7 Hz, 2H, Ar-H), 8.43 (d, J = 2.1 Hz, 1H, Py-H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.5, 108.4 (Py-C4), 118.2, 125.6, 126.3, 126.6, 127.2, 127.6, 128.2, 128.5, 128.6, 130.0, 130.4, 131.1, 131.4, 132.8, 133.1, 134.0, 136.8, 140.0, 141.5 (Th-C2), 150.4 (Py-C3). Anal. Calcd. For $C_{29}H_{22}N_4S$: C 75.95, H 4.84, N 12.22, S 6.99; Found, C 75.62, H 4.65, N 11.98, S 6.72.

3.1.13. 1-(4-(1*H*-imidazol-1-yl)phenyl)-2,4,5-triphenyl-1*H*-imidazole (4a)

Yield: 0.31 g (70%); pale yellow solid; mp 250–252 °C; FTIR (KBr): $\bar{\nu}$ 3056, 1524, 1443, 847, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.15–7.32 (m, 12H, Ar-H), 7.42–7.51 (m, 6H, Ar-H), 7.68 (d, J = 8.7 Hz, 2H, Ar-H), 7.84 (s, 1H, Im-H4), 8.39 (s, 1H, Im-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 120.3, 125.2, 126.3, 126.5, 127.1, 128.0, 128.2, 128.3, 128.4, 128.6, 128.7, 129.5, 129.9, 130.2, 130.3, 131.2, 131.3, 134.3, 135.1, 136.3, 136.9, 146.21 (N=CAr-N). Anal. Calcd. For $C_{30}H_{22}N_4$: C 82.17, H 5.06, N 12.78; Found, C 81.88, H 5.29, N 12.56.

3.1.14. 4,5-Diphenyl-1-[4-(1*H*-imidazol-1-yl)phenyl]-2-(*p*-tolyl)-1*H*-imidazole (4b)

Yield: 0.32 g (71%); pale yellow solid; mp 262–264 °C; FTIR (KBr): $\bar{\nu}$ 3058, 2919, 1605, 1525, 1376, 698 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.26 (s, 3H, CH_3), 7.11–7.33 (m, 13H, Ar-H), 7.42 (d, J = 8.7 Hz, 2H, Ar-H), 7.48 (d, J = 7.4 Hz, 2H, Ar-H), 7.66 (d, J = 8.7 Hz, 2H, Ar-H), 7.82 (s, 1H, Im-H5), 8.36 (s, 1H, Im-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.8, 117.8, 120.2, 126.4, 126.5, 127.5, 128.2, 128.4, 128.6, 128.9, 129.6, 130.0, 130.4, 131.1, 131.2, 134.4, 135.1, 135.7, 136.4, 136.8, 138.0, 146.4 (N=CAr-N). Anal. Calcd. For $C_{31}H_{24}N_4$: C 82.27, H 5.35, N 12.38; Found, C 81.98, H 5.54, N 12.65.

3.1.15. 4,5-Diphenyl-1-[4-(1*H*-imidazol-1-yl)phenyl]-2-(4-isopropylphenyl)-1*H*-imidazole (4c)

Yield: 0.35 g (73%); pale yellow solid; mp 266–268 °C; FTIR (KBr): $\bar{\nu}$ 3065, 2961, 1524, 1419, 1151 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.16 (d, J = 6.9 Hz, 6H, $(CH_3)_2CH$), 2.82–2.85 (m, 1H, $(Me)_2CH$), 7.15–7.36 (m, 13H, Ar-H), 7.46–7.49 (m, 4H, Ar-H), 7.70 (d, J = 8.7 Hz, 2H, Ar-H), 7.87 (s, 1H, Im-H5), 8.41 (s, 1H, Im-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.6, 33.1, 117.9, 120.3, 126.3, 126.4, 126.5, 127.9, 128.2, 128.3, 128.6, 129.8, 130.4, 130.5, 131.2, 131.24, 134.4, 135.3, 135.8, 136.3, 136.8, 146.3 (N=CAr-N), 148.7 (=C-Pr^i). Anal. Calcd. For $C_{33}H_{28}N_4$: C 82.47, H 5.87, N 11.66; Found, C 82.19, H 5.63, N 11.87.

3.1.16. 2-(4-Chlorophenyl)-4,5-diphenyl-1-[4-(1*H*-imidazol-1-yl)phenyl]-1*H*-imidazole (4d)

Yield: 0.32 g (68%); pale yellow solid; mp 248–250 °C; FTIR (KBr): $\bar{\nu}$ 3065, 1524, 1396, 842, 699 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.11 (s, 1H, Im-H4), 7.18–7.50 (m, 16H, Ar-H), 7.68 (d, J = 8.7 Hz, 2H, Ar-H), 7.82 (s, 1H, Im-H5), 8.36 (s, 1H, Im-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 117.7, 120.2, 126.3, 126.6, 128.2, 128.4, 128.5, 128.6, 129.1, 129.9, 130.1, 130.2, 131.1, 131.3, 131.5, 133.2, 134.1, 134.6, 135.6, 136.6, 137.1, 145.0 (N=CAr–N). Anal. Calcd. For $C_{30}H_{21}ClN_4$: C 76.18, H 4.48, N 11.85; Found, C 76.47, H 4.26, N 11.59.

3.1.17. 4,5-Diphenyl-1-[4-(1*H*-imidazol-1-yl)phenyl]-2-(4-methoxyphenyl)-1*H*-imidazole (4e)

Yield: 0.34 g (72%); pale yellow solid; mp 258–260 °C; FTIR (KBr): $\bar{\nu}$ 3057, 2925, 1527, 1384, 843, 698 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.72 (s, 3H, OCH_3), 6.88 (d, J = 8.8 Hz, 2H, Ar-H), 7.15–7.50 (m, 15H, Ar-H), 7.70 (d, J = 8.7 Hz, 2H, Ar-H), 7.89 (s, 1H, Im-H5), 8.47 (s, 1H, Im-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.1 (OCH_3), 113.7, 120.5, 122.7, 126.3, 126.4, 128.0, 128.2, 128.5, 128.6, 129.5, 129.6, 129.8, 130.4, 130.8, 131.2, 134.4, 135.5, 136.1, 136.7, 146.2 (N=CAr–N), 159.3 (=C–OMe). Anal. Calcd. For $C_{31}H_{24}N_4O$: C 79.46, H 5.16, N 11.96; Found, C 79.19, H 5.28, N 11.73.

3.1.18. 4-{4,5-Diphenyl-1-[4-(1*H*-imidazol-1-yl)phenyl]-1*H*-imidazol-2-yl} phenol (4f)

Yield: 0.25 g (56%); pale yellow solid; mp 330–332 °C; FTIR (KBr): $\bar{\nu}$ 3414, 1520, 1478, 840, 699 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.68–6.70 (m, 2H, Ar-H), 7.09 (s, 1H, Im-H4), 7.14–7.18 (m, 1H, Ar-H), 7.24–7.32 (m, 9H, Ar-H), 7.36–7.40 (m, 2H, Ar-H), 7.48 (d, J = 7.9 Hz, 2H, Ar-H), 7.63–7.66 (m, 2H, Ar-H), 7.78 (s, 1H, Im-H5), 8.32 (s, 1H, Im-H2), 9.70 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 114.9, 115.0, 117.6, 120.0, 126.3, 128.1, 128.4, 128.5, 129.9, 130.1, 130.3, 130.5, 130.6, 131.2, 134.5, 135.0, 135.4, 136.3, 136.5, 146.6 (N=CAr–N), 157.5, 157.6 (=C-OH). Anal. Calcd. For $C_{30}H_{22}N_4O$: C 79.27, H 4.88, N 12.33; Found, C 78.94, H 4.62, N 12.54.

3.1.19. 4,5-Diphenyl-1-[4-(1*H*-imidazol-1-yl)phenyl]-2-(thiophen-2-yl)-1*H*-imidazole (4g)

Yield: 0.31 g (71%); pale yellow solid; mp 256–258 °C; FTIR (KBr): $\bar{\nu}$ 3065, 1517, 1296, 702 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.61 (d, J = 3.2 Hz, 1H, Im-H4), 6.93–6.96 (m, 1H, Th-H4), 7.12–7.22 (m, 9H, Ar-H), 7.47 (d, J = 7.4 Hz, 2H, Ar-H), 7.52 (d, J = 4.8 Hz, 1H, Th-H5), 7.61 (d, J = 8.6 Hz, 2H, Ar-H), 7.76 (d, J = 8.6 Hz, 2H, Ar-H), 7.85 (s, 1H, Im-H5), 8.38 (s, 1H, Im-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 117.7, 120.4, 125.7, 126.3, 126.6, 127.3, 127.6, 128.2, 128.6, 128.7, 129.9, 130.2, 130.8, 131.1, 131.3, 132.7, 134.0, 134.3, 135.6, 136.9, 137.2, 141.5 (Th-C2). Anal. Calcd. For $C_{28}H_{20}N_4S$: C 75.65, H 4.53, N 12.60, S 7.21; Found, C 75.92, H 4.68, N 12.44, S 7.56.

3.1.20. 1-[4-(2,4,5-Triphenyl-1*H*-imidazol-1-yl)phenyl]-1*H*-benzo[*d*]imidazole (5a)

Yield: 0.32 g (68%); pale yellow solid; mp 260–262 °C; FTIR (KBr): $\bar{\nu}$ 3050, 1514, 1228, 693 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.19–7.20 (m, 1H, Benzim-H5), 7.25–7.37 (m, 11H, Ar-H), 7.46–7.56 (m, 8H, Ar-H), 7.66–7.69 (m, 2H, Ar-H), 7.75–7.77 (m, 1H, Ar-H), 8.59 (s, 1H, Benzim-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 110.6, 120.1, 122.7, 123.7, 123.9, 126.4, 126.6, 128.2, 128.3, 128.4, 128.5, 128.6, 130.2, 130.3, 130.5, 131.2, 131.3, 132.7, 134.3, 135.6, 135.9, 136.9, 143.2, 143.8 (Benzim-C2), 146.3 (Im-C2). Anal. Calcd. For $C_{34}H_{24}N_4$: C 83.58, H 4.95, N 11.47; Found, C 83.87, H 4.69, N 11.26.

3.1.21. 1-{4-[4,5-Diphenyl-2-(*p*-tolyl)-1*H*-imidazol-1-yl]phenyl} -1*H*-benzo[*d*] imidazole (5b)

Yield: 0.32 g (63%); pale yellow solid; mp 242–244 °C; FTIR (KBr): $\bar{\nu}$ 3056, 2923, 1517, 1455, 1023, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.27 (s, 3H, CH_3), 7.14 (d, J = 8.0 Hz, 2H, Ar-H), 7.19 (d, J = 7.1 Hz, 1H, Benzim-H7), 7.24–7.27 (m, 2H, Ar-H), 7.31–7.36 (m, 9H, Ar-H), 7.50–7.54 (m, 5H, Ar-H), 7.67 (d, J = 8.5 Hz, 2H, Ar-H), 7.77 (d, J = 7.6 Hz, 1H, Benzim-H4), 8.58 (s, 1H, Benzim-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.8, 110.6, 120.1, 122.7, 123.7, 123.9, 126.4, 126.5, 127.5, 128.2, 128.4, 128.5, 128.6, 128.9, 130.3, 130.5, 131.1, 131.2, 132.7, 134.4, 135.7, 135.9, 136.9, 138.0, 143.2, 143.8 (Benzim-C2), 146.4 (Im-C2). Anal. Calcd. For $C_{35}H_{26}N_4$: C 83.64, H 5.21, N 11.15; Found, C 83.95, H 5.09, N 11.37.

3.1.22. 1-{4-[4,5-Diphenyl-2-(4-isopropylphenyl)-1*H*-imidazol-1-yl]phenyl} -1*H*-benzo[*d*]imidazole (5c)

Yield: 0.37 g (70%); pale yellow solid; mp 240–242 °C; FTIR (KBr): $\bar{\nu}$ 3055, 2958, 1515, 1453, 841, 698 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.16 (d, J = 6.9 Hz, 6H, $(CH_3)_2CH$), 2.82–2.89 (m, 1H, $CH(Me)_2$), 7.16–7.29 (m, 5H, Ar-H), 7.30–7.37 (m, 7H, Ar-H), 7.39 (d, J = 8.2 Hz, 2H, Ar-H), 7.50–7.52 (m, 3H, Ar-H), 7.55 (d, J = 8.6 Hz, 2H, Ar-H), 7.69 (d, J = 8.6 Hz, 2H, Ar-H), 7.76–7.78 (m, 1H, Benzim-H4), 8.60 (s, 1H, Benzim-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.6, 33.1, 110.6, 120.1, 122.7, 123.7, 123.9, 126.3, 126.4, 126.5, 127.9, 128.2, 128.4, 128.5, 128.6, 130.3, 130.6, 131.1, 131.2, 132.7, 134.4, 135.7, 135.9, 136.9, 143.2, 143.8 (Benzim-C2), 146.3 (Im-C2), 148.7 (=C-Pr^i). Anal. Calcd. For $C_{37}H_{30}N_4$: C 83.74, H 5.70, N 10.56; Found, C 83.4I, H 5.55, N 11.34.

3.1.23. 1-{4-[2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazol-1-yl]phenyl} -1*H*-benzo [d]imidazole (5d)

Yield: 0.35 g (67%); pale yellow solid; mp 274–276 °C; FTIR (KBr): $\bar{\nu}$ 3057, 1511, 1227, 838, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.18–7.21 (m, 1H, Benzim-H5), 7.24–7.28 (m, 2H, Ar-H), 7.31–7.35 (m, 7H, Ar-H), 7.41–7.57 (m, 9H, Ar-H), 7.70 (d, J = 8.7 Hz, 2H, Ar-H), 7.77 (d, J = 7.8 Hz, 1H, Benzim-H4), 8.58 (s, 1H, Benzim-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 110.6, 120.1, 122.7, 123.7, 123.9, 126.4, 126.6, 128.2, 128.4, 128.6, 128.7, 129.1, 130.0, 130.1, 130.5, 131.2, 131.6, 132.7, 133.3, 134.1, 135.4, 136.1, 137.1, 143.2, 143.8 (Benzim-C2), 145.1 (Im-C2). Anal. Calcd. For $C_{34}H_{23}ClN_4$: C 78.08, H 4.43, N 10.71; Found, C 77.83, H 4.18, N 10.49.

3.1.24. 1-{4-[4,5-Diphenyl-2-(4-methoxyphenyl)-1*H*-imidazol-1-yl]phenyl} -1*H*-benzo[d]imidazole (5e)

Yield: 0.38 g (73%); pale yellow solid; mp 242–244 °C; FTIR (KBr): $\bar{\nu}$ 3057, 2996, 1606, 1515, 1485, 1251 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.73 (s, 3H, OCH_3), 6.89 (d, J = 8.8 Hz, 2H, Ar-H), 7.16–7.19 (m, 1H, Benzim-H5), 7.23–7.33 (m, 9H, Ar-H), 7.39 (d, J = 8.8 Hz, 2H, Ar-H), 7.50–7.54 (m, 5H, Ar-H), 7.68 (d, J = 8.5 Hz, 2H, Ar-H), 7.77 (d, J = 7.6 Hz, 1H, Benzim-H4), 8.56 (s, 1H, Benzim-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.1 (OCH_3), 110.6, 113.8, 120.1, 122.7, 123.7, 123.8, 126.4, 126.5, 128.2, 128.5, 128.6, 129.9, 130.4, 130.5, 130.9, 131.2, 132.7, 134.4, 135.8, 135.9, 136.7, 143.2, 143.9 (Benzim-C2), 146.3 (Im-C2), 159.3 (=C-OMe). Anal. Calcd. For $C_{35}H_{26}N_4O$: C 81.06, H 5.05, N 10.80; Found, C 81.35, H 5.28, N 10.51.

3.1.25. 1-{4-[2-(3-Bromophenyl)-4,5-diphenyl-1*H*-imidazol-1-yl]phenyl} -1*H*-benzo [d]imidazole (5f)

Yield: 0.39 g (70%); pale yellow solid; mp 240–242 °C; FTIR (KBr): $\bar{\nu}$ 3054, 1508, 1451, 1283, 703 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.18–7.36 (m, 11H, Ar-H), 7.42 (d, J = 7.8 Hz, 1H, Benzim-H7), 7.51–7.61 (m, 7H, Ar-H), 7.71 (d, J = 8.4 Hz, 2H, Ar-H), 7.77 (d, J = 7.8 Hz, 1H, Benzim-H4), 8.57 (s, 1H, Benzim-H2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 110.5, 120.1, 121.5, 122.7, 123.7, 124.2, 126.4, 126.7, 127.1, 128.2, 128.7, 128.8, 130.0, 130.5, 130.6, 130.8, 131.1, 131.2, 131.8, 132.4, 132.8, 134.1, 135.4, 136.2, 137.3, 143.1, 143.8 (Benzim-C2), 144.5 (Im-C2). Anal. Calcd. For $C_{34}H_{23}BrN_4$: C 71.96, H 4.09, N 9.87; Found, C 71.63, H 4.28, N 9.59.

4. Conclusion

We have described the synthesis of new 1,2,4,5-tetrasubstituted derivatives of imidazole possessing another azole ring in the presence of $Bi(NO_3)_3.5H_2O$-SiO_2 as a heterogeneous Lewis acid catalyst. One-pot four-component condensations of benzil, ammonium acetate, aromatic aldehydes and 4-azolyl-anilines under solvent-free conditions at 110 °C for 24 h afforded the desired products with easy workup and in good yields.

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Supplementary Material

IR, ^{1}H NMR, and ^{13}C NMR spectra of imidazole derivatives **3**–**5** are given at the end of this paper.

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