New Method for Synthesis of Multi-substituted Imidazoles

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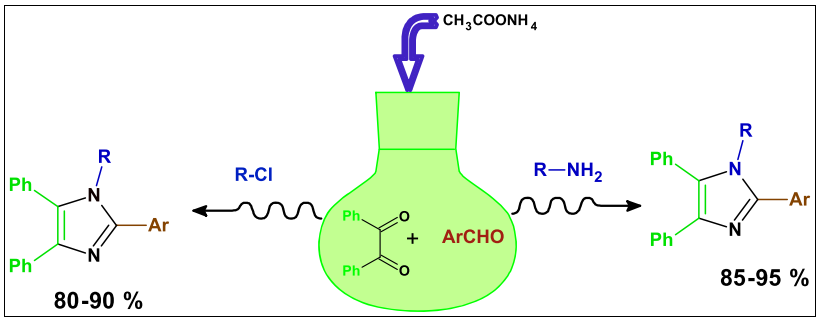


Here, we reported two methods for the synthesis of multi-substituted imidazoles, firstly via four-component cyclocondensation reaction of benzil, aliphatic amines (allylamine or pentylamine), and aromatic aldehyde and ammonium acetate. Using an ionic liquid catalyst namely, diethyl ammonium hydrogen sulfate, and under solvent-free conditions. Secondly, via the alkylation of synthesized NH imidazoles with alkyl halide (allyl bromide and pentyl bromide) gave **8a–c** in high yield (average 90%), the products can be purified by a non-chromatographic method, and these newly synthesized compounds have been characterized by spectral data: FTIR, IR, ^{1}H, ^{13}C nuclear magnetic resonance, the elemental analysis, and the X-ray structure.

INTRODUCTION

Heterocyclic chemistry with nitrogen heteroatom is displaying as one of the significant topics in the synthetic organic chemistry square due to its broad presence in various bioactive compounds, synthetic intermediates, and pharmaceuticals [1]. Numerous of substituted imidazoles are important biological functions such as antibacterial, anti-inflammatory, and anti-helminthic agents [2]. Imidazoles are important heterocycles existing in natural products as antifungal drugs and many other synthetic substances with a many of other biological effects, wide application in medicinal compounds and pharmacology, as well as in material science, catalysis, and the preparation of ionic liquids [3]. Divers methods for the synthesis of imidazoles have been designed and prepared, and several potential reviews have appeared [4–11]. The imidazole unit is a key building block that has been widely used in ionic liquids, anion sensors, and electronic and optical materials [12]. They have been reviewed to possess many biological properties, viz. anti-cancer, anti-HIV, FTase, and p38 MAP kinase inhibitory activities [13–23].

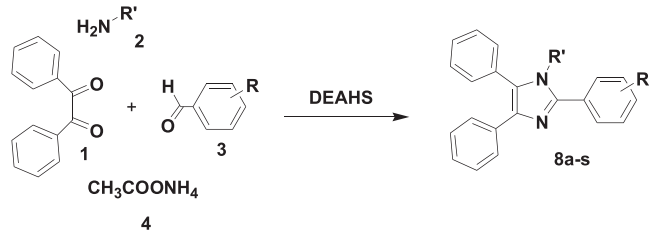
From an environmental and economic perspective, it is becoming obvious that it is necessary to find new methods to synthesis of the multi-substituted imidazoles. Multicomponent coupling reactions provide a solution because they are more cost effective, efficient, and less wasteful than traditional methods. In addition, they can also be synthesized of the new imidazoles by the N-alkylation of tri-substituted imidazoles, and these methods are a powerful way to do synthetic chemistry called “Green Chemistry” [18].

In view of the above-mentioned facts, we have designed and originated a new strategy to accomplish and succeed highly substituted imidazoles in high yields using multicomponent reaction or N-alkylation of NH-imdazoles.

RESULTS AND DISCUSSION

In this work, a simple one-pot and efficient method has been described for the synthesis of multi-substituted imidazoles via a four-component reaction of aromatic aldehydes, aliphatic amine (allylamine or pentylamine), benzil, and ammonium acetate (molar ratio 1:1:1:1), an ionic liquid as catalyst under free solvent (method A). Products of (1-allyl- -2,4,5-substituted triphenyl-1H-imidazole or 1-pentyl-2,4,5-substituted triphenyl-1H-imidazoles) **8a–s** were reported (Scheme 1) around 30 min of refluxing. The optimized results are concussed in

Scheme 1. Multicomponent reaction for synthesis 1,2,4,5-tetrasubstituted imidazoles **6a–s**.



(**8a-k**): R'= allyl and R = (a) 4-CH_3O-; (b) H-; (c) 4-OH-; (d) 3,4-CH_3O-; (e) $(CH_3)_2N$-; (f) 2,6-Cl-; (g) 3-CH_3O-; (h) 4-HOOC-; (i) 4-Cl-; (j) 4-Br-; (k) 2,4-CH_3O-.

(**8 l-s**): R'= pentyl and R= (l) 4-CH_3O-; (m) 3,4-CH_3O-; (n) 2,6-Cl-; (o) 4-OH-;(p) 3-CH_3O-; (q) 4-Cl-; (r) 4-NO_2; (s) 4-Br-;

Table 1. Excellent yields were attained (82–94%), and the toxic solvent by using the ionic liquid as catalyst and solvent instead and problems associated with toxic solvent use were avoided. The same products **8a–s** were also synthesized in good yields (77–89%) under reflux condition (method B). The reactions take places to completion almost two steps, firstly synthesized of the NH imidazoles through the three component reaction of benzil, different aldehydes, and two molecules of ammonium acetate. The prepared NH-imidazoles **8a–s** were alkylated by alkyl halide (allyl bromide or pentyl bromide), to give the highly pure components in good to excellent yields.

The proposal mechanism for the formation of product **8** was assumed to took place via the reaction between benzaldehyde imine (I) with active ionic liquid to give intermediate III, which was cyclized to afford the corresponding 1,2,4,5-tetrasubstituted imidazoles **8** (Scheme 2) is coupling step of the intermediate of the benzaldehyde imine (I) to the activated ionic liquid iminobenzil (III) of aliphatic followed by cyclization to produce the corresponding 1,2,4,5-tetrasubstituted imidazoles (Scheme 2).

Also, compounds **8a–s** were prepared by second method via alkylation of 2,4,5-trisubstituted imidazoles with allyl bromide or pentyl bromide in DMSO/KOH system at 30–

Table 1

Diethyl ammonium hydrogen sulfate catalyzed for the synthesis of 1,2,4,5-tetrasubstituted imidazoles **8a–s**

			Time (min)		Yield (%)	
Compound no.	R	mp °C	Method A	Method B	Method A	Method B
8a	4-OCH_3	112–114	20	40	83	81
8b	H	104–106	15	35	91	83
8c	4-O-allyl	145–147	13	45	82	82
8d	3,4-CH_3O	208–210	41	50	84	84
8e	$(CH_3)_2N$-	127–130	21	50	94	83
8f	2,6-Cl-	114–116	31	40	84	84
8g	3-OCH_3	199–201	39	45	86	86
8h	(4-COO)allyl	224–227	28	45	88	85
8i	4-Cl	108–110	27	35	87	87
8j	4-Br	124–126	19	45	89	80
8k	2,4-CH_3O	200–202	23	30	92	83
8l	4-OCH_3	109–111	23	45	84	84
8m	3,4-CH_3O	151–153	31	35	83	83
8n	2,6-Cl_2	120–123	42	50	89	86
8o	4-NO_2	210–212	38	60	85	86
8p	4-OH	217–219	26	40	88	88
8q	3-CH_3O	103–105	16	45	89	86
8r	4-Cl	126–128	26	40	90	89
8s	4-Br	123–125	37	45	91	84

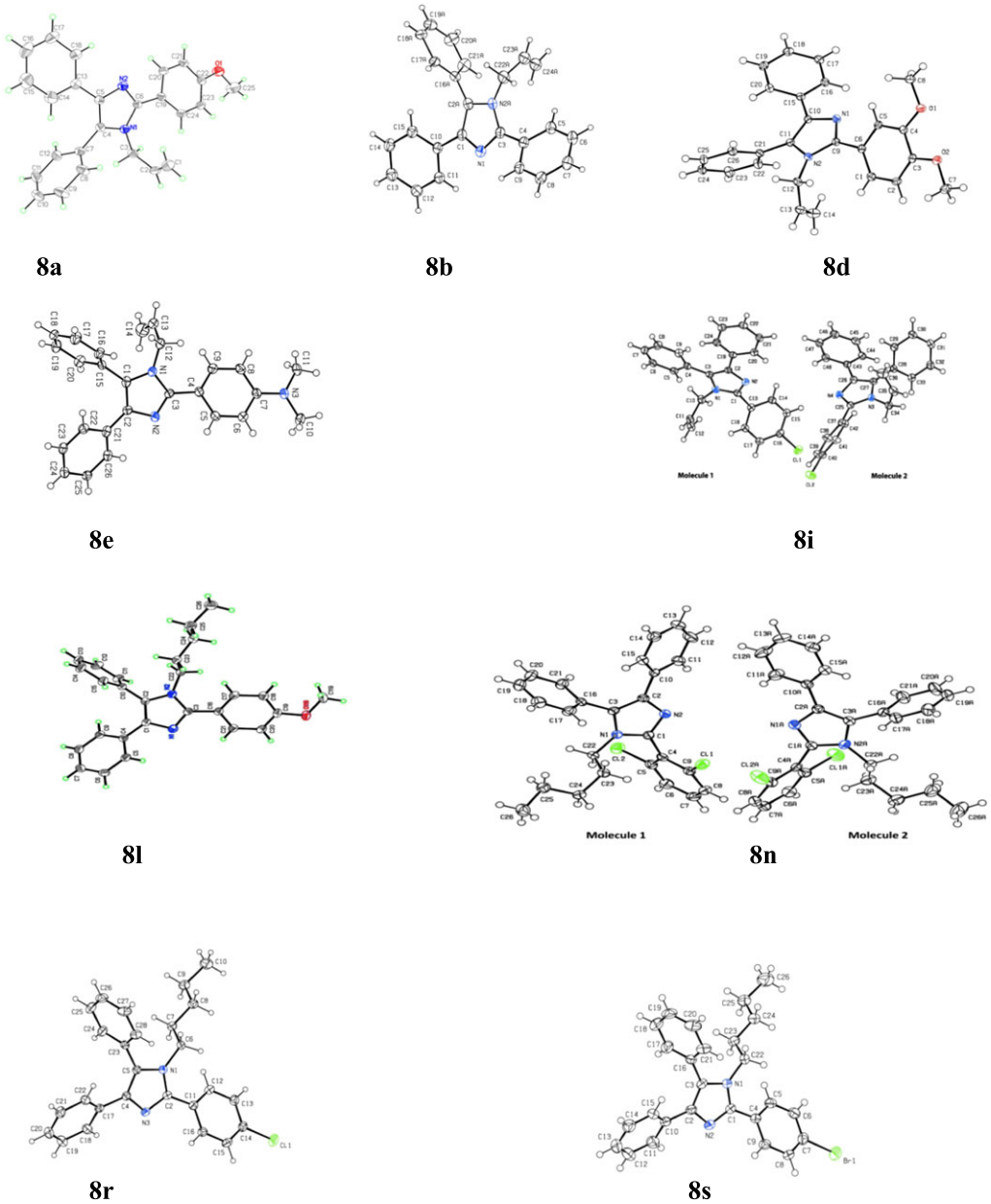


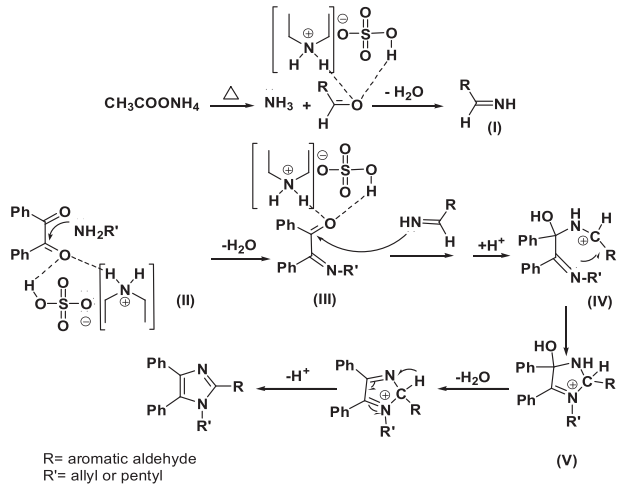
Figure 1. The molecular structures of **8a**, **8b**, **8d**, **8e**, **8i**, **8l**, **8n**, **8r**, and **8s** showing the atom numbering with ellipsoids drawn at the 50% probability level.[23–31] [Color figure can be viewed at wileyonlinelibrary.com]

60°C. However, alkylation of imidazole method afforded better yields of the product under mild conditions in a shorter reaction time (Scheme 3) [23–31].

The structures of all the synthesized compounds **8a–s** were confirmed by the basis of spectroscopic data and analysis as IR, ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, and mass spectroscopy analysis. The IR of compound **8** showed the disappearance of absorption band for NH group of imidazole ring and also showed the presence of C–H aromatic bands around 3000–3050 cm^{-1}, in addition to the appearance of strong stretching vibration band at 1600–1610 cm^{-1} due to (C=N) group.

^{1}H-nuclear magnetic resonance spectrum of compound **8a–k** showed a significant doublet signal around 4.4 ppm, which belongs to (CH_2–N), two significant doublet signals around 4.70 and 5.00 ppm (CH=$\underline{CH_2}$), in addition to pentat signal around 5.00 corresponding to ($\underline{CH}$=CH_2) group of allyl moiety. ^{13}C NMR of **8a** showed two significant signals around 46.00, which

Scheme 2. The reaction mechanism of synthesized 1,2,4,5-tetrasubstituted imidazoles **6a–m**. DEAHS, diethyl ammonium hydrogen sulfate.



belong to the carbon atoms of $\underline{C}H_2N$ (disappeared in DEPT-135 conformation).

^{1}H-nuclear magnetic resonance spectrum of compound **8l–s** showed a significant doublet signals around 3.80 ppm, which belongs to the protons of the (CH_2—N) group (disappeared in DEPT conformation) in addition to the appearance of significant triplet signals around for 0.60 (CH_2—$\underline{CH_3}$) group; appearance of a characteristic pentat signal around 0.800 (—$\underline{CH_2}$—CH_2—$\underline{CH_2}$—CH_3), which belongs to the protons of two methylene group of pentyl moiety; and appearance of a characteristic pentat signal around 1.2 corresponding to (CH_2—$\underline{CH_2}$—CH_2—CH_3), group of pentyl moiety. ^{13}C NMR of **8l–s** showed five characteristic significant signals around 13.000, 21.000, 28.000, 29.000, and 44.000, which belong to the carbon atoms of pentyl moiety, and the peak of methylene disappeared in DEPT confirming that, in the other hand, the structure of the compounds **8a**, **8b**, **8d**, **8e**, **8i**, **8l**, **8n**, **8r**, and **8s** were confirmed by X-ray single crystal analysis (Fig. 1) [23–31].

CONCLUSION

One-pot multicomponent reaction can be used as a facile and very fast method for synthesis of some new multi-substituted imidazoles. Alkylation for NH imidazole moiety. Because of the availability of the starting materials, the simplicity of the procedures, and free solvent used as ionic liquid as catalyst, this synthetic approach might be valuable for the synthesis of such heterocyclic compounds.

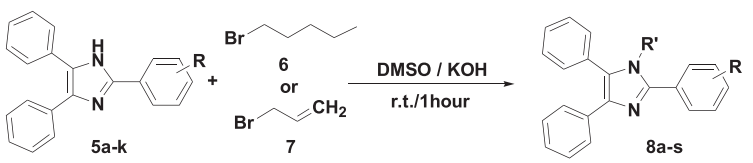
EXPERIMENTAL

All commercially available reagents were purchased from Merck, Aldrich, and Fluka. All reactions were checked by thin-layer chromatography using pre-coated plates of silica gel G/UV-254 of 0.25-mm thickness (Merck 60F254) using UV light (254/365 nm) for visualization. Melting points were measured with a Kofler melting points apparatus and uncorrected. IR spectra were recorded with a FTIR-ALPHBROKER-Platinum-ATR. ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker Bio Spin AG spectrometer at 400 and 100 MHz, respectively. Elemental analyses were obtained on a Perkin-Elmer CHN-analyzer model.

General procedure for the synthesis of the ionic liquid. Diethyl amine (20 mmol) was added to a 150-mL three necked flask with a magnetic stirrer. Then an equimolar quantity of concentrated sulfuric acid was added drop wise slowly. The mixture was then stirred at 80°C for 17 h, washed with diethyl ether three times to remove non-ionic residues, and dried in vacuum on a rotary evaporator to yield diethyl ammonium hydrogen sulfate as a clear viscous liquid.

General procedure for the synthesis of compounds 8a–s.
Method A. Benzil (10 mmol), aldehyde (10 mmol), ammonium acetate (10 mmol), and aliphatic amine (allylamine or pentylamine) (10 mmol) were added to diethyl ammonium hydrogen sulfate (4 mmol) at room

Scheme 3. Alkylation reaction of NH-imidazoles for synthesis of 1,2,4,5-tetrasubstituted imidazoles **6a–s**.

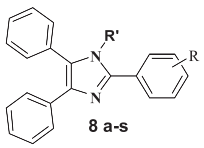


(**8a-k**): R'= allyl and R = (a) 4-CH_3O-; (b) H-; (c) 4-OH-; (d) 3,4-CH_3O-; (e) $(CH_3)_2N$-; (f) 2,6-Cl-; (g) 3-CH_3O-; (h) 4-HOOC-; (i) 4-Cl-; (j) 4-Br-; (k) 2,4-CH_3O-.

(**8 l-s**): R'= pentyl and R= (l) 4-CH_3O-; (m) 3,4-CH_3O-; (n) 2,6-Cl-; (o) (d) 4-OH-;(p) 3-CH_3O-; (q) 4-Cl-; (r) 4-NO_2; (s) 4-Br-;

temperature. The resulting mixture was heated to 100°C for the appropriate time reported in Table 1. After completion of the reaction, which was monitored by thin-layer chromatography, the mixture was poured into water, and the solid product was purified by recrystallization from ethanol. Some characterization data for selected products are given in Table 1.

Method B: General procedure (alkylation method). In volumetric flask equipped with a magnetic stirring, 25 mL of dimethylsulfoxide and 20 mmol of potassium hydroxide are added. The mixtures are stirred at room temperature for 5 min and 10 mmol of substituted imidazole is added. Stirring is continued for 30 min, after that 20 mmol of allyl bromide or pentyl bromide is added. The reaction mixture is stirred according to each reaction, and the mixture is diluted with 20 mL of water. The mixture is extracted with diethyl ether and washed with distilled water. The product was precipitated with diethyl ether and crystallized from ethanol yielding 1N-alkyl-2,4,5-trisubstituted-1H-imidazole (**8a–s**).



8 a-s

1N-Allyl-2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole (8a). Mp 112–114°C. FTIR (KBr, cm^{-1}): 3050 (C–H aromatic), 2959 (C–H aliphatic), 2834 (C–H aliphatic), 1631 (=C–H), 1609 (C=N), 1539, 1467 (C=C), 1248, 1177, 1060, 838, 722, 696; ^{1}H NMR (DMSO-d_6, 400 MHz): 3.81 (s, 3H, $\underline{CH_3O}$), 4.45 (d, 2H, $\underline{CH_2}$–N), 4.73 (d, 1H, CH=$\underline{CH_2}$), 5.06 (d, 1H, CH=$\underline{CH_2}$), 5.78 (p, 1H, $\underline{CH}$=CH_2), 7.05–7.65 (m, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 46.665, 55.552, 114.446, 116.667, 123.336, 126.664, 128.553, 128.881, 130,002, 131.111, 134.441, 135.002, 136.667, 146.665, 159.887 ppm. *Anal*. Calcd for $C_{25}H_{22}N_2O$: C, 81.94; H, 6.05; N, 7.64. Found: C, 81.64; H, 6.40; N, 7.44.

1N-Allyl-2,4,5-triphenyl-1H-imidazole (8b). Mp 104–106°C. FTIR (KBr, cm^{-1}): 3054 (C–H aromatic), 2960, 2835 (C–H aliphatic), 1630 (=C–H), 1609 (C=N), 1501 (C=C), 1443, 1248, 1178, 1058, 839, 721, 693; ^{1}H NMR (DMSO-d_6, 400 MHz): 4.46 (d, 2H, $\underline{CH_2N}$), 4.71 (d, 1H, CH=$\underline{CH_2}$), 5.05 (d, 1H, CH=$\underline{CH_2}$), 5.744 (p, 1H, $\underline{CH}$=CH_2), 7.09–7.73 (m, J = 8.3 Hz, 4.4 Hz, 15H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 48.572, 116.319, 126.034, 126.157, 128.043, 128.463, 128.537, 128.784, 128.948, 129.977, 130.702, 130.743, 130.916, 134.118, 134.555, 136.596, 146.690 ppm. *Anal*. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.33; H, 5.75; N, 8.44.

1N-Allyl-2-(4-(2-(4-allyloxyphenyl)-)phenyl)-4,5-diphenyl-1H-imidazole (8c). Mp 145–147°C. FTIR (KBr, cm^{-1}): 3063 (C–H aromatic), 2922, 2857 (C–H aliphatic), 1645 (=C–H), 1609 (C=N), 1502 (C=C), 1447, 1245, 1177, 1060, 838, 714, 697; ^{1}H NMR (DMSO-d_6, 400 MHz): 4.45 (d, 2H, $\underline{CH_2N}$), 4.63 (d, 2H, $\underline{CH_2O}$), 4.71 (d, 1H, CH=$\underline{CH_2}$), 5.05 (d, 1H, CH=$\underline{CH_2}$), 5.29 (d, 1H, CH=$\underline{CH_2}$), 5.42 (d, 1H, CH=$\underline{CH_2}$), 5.74 (p, 1H, $\underline{CH}$=CH_2), 6.03 (p, 1H, $\underline{CH}$=CH_2), 7.06–7.65 (m, J = 8.8 Hz, 2.0 Hz, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 46.531, 68.257, 114.665, 116.295, 117.645, 123.235, 126.017, 126.075, 128.026, 128.882, 128.940, 129.615, 129.862, 130.850, 130.941, 133.534, 134.234, 134.670, 136.333, 146.632, 158.545 ppm. *Anal*. Calcd for $C_{27}H_{24}N_2O$: C, 82.62; H, 6.16; N, 7.14. Found: C, 82.30; H, 5.90; N, 7.28.

1N-Allyl-2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1H-imidazole (8d). Mp 208–210°C. FTIR (KBr, cm^{-1}): 3048 (C–H aromatic), 2990, 2929, 2835 (C–H aliphatic), 1602 (C=N), 1583, 1525 (C=C), 1460, 1244, 1144, 1062, 877, 729, 700; ^{1}H NMR (DMSO-d_6, 400 MHz): 3.94 (s, 6H, $\underline{(CH_3)_2O}$), 4.90 (s, 2H, $\underline{CH_2N}$), 4.93 (d, 1H, =$\underline{CH_2}$), 5.20 (d, 1H, =$\underline{CH_2}$), 5.80 (p, 1H, $\underline{CH}$=CH_2), 6.92–7.62 (m, 13H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 46.942, 55.950, 56.031, 110.856, 112.462, 117.055, 121.456, 126.276, 126.798, 128.066, 128.737, 128.851, 131.181, 134.164 ppm. *Anal*. Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07. Found: C, 78.39; H, 6.30; N, 7.27.

4-(1N-Allyl-4,5-diphenyl-1H-imidazol-2-yl)-N,N-dimethylaniline (8e). Mp 127–130°C. FTIR (KBr, cm^{-1}): 3065 (C–H aromatic), 2977, 2924, 2811 (C–H aliphatic), 1619 (C=N), 1557 (C=C), 1443, 1229, 1174, 1072, 817, 721, 695; ^{1}H NMR ($CDCl_3$-d_1, 300 MHz): 2.78 (s, 6H, $\underline{(CH_3)_2}$N), 4.25 (d, 2H, $\underline{CH_2N}$), 4.78 (d, 1H, =$\underline{CH_2}$), 4.90 (d, 1H, =$\underline{CH_2}$), 5.50 (p, 1H, $\underline{CH}$=CH_2), 6.43–7.53 (m, 14H, Ar–H); ^{13}C NMR (300 MHz, $CDCl_3$-d_1): 39.412, 45.882, 111.176, 116.107, 124.120, 125.124, 125.821, 126.510, 127.230, 127.639, 127.830, 128.600, 129.008, 129.988, 130.320, 130.689, 133.400, 134.007 ppm. *Anal*. Calcd for $C_{26}H_{25}N_3$: C, 82.29; H, 6.64; N, 11.07. Found: C, 81.99; H, 6.44; N, 10.85.

1N-Allyl-2-(2,6-dichlorophenyl)-4,5-diphenyl-1H-imidazole (8f). Mp 114–116°C. FTIR (KBr, cm^{-1}): 3086, 3057 (C–H aromatic), 2970, 2910 (C–H aliphatic), 1600 (C=N), 1552 (C=C), 1453, 1242, 1153, 1097, 833, 722, 696, 554; ^{1}H NMR (DMSO-d_6, 400 MHz): 4.25 (d, 2H, $\underline{CH_2}$N), 4.53 (d, 1H, =$\underline{CH_2}$), 4.92 (d, 1H, =$\underline{CH_2}$), 5.56 (p, 1H, $\underline{CH}$=CH_2), 7.09–7.81 (m, 13H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 46.481, 116.509, 126.182, 126.462, 127.730, 128.281, 129.203, 129.278, 129.327, 129.500, 129.566, 130.529, 130.908, 133.419, 134.003, 134.530, 134.530, 134.843, 135.345, 136.778, 143.323 ppm; mass spectrum: 407 (M^{+2}), 405 (M^+). *Anal*. Calcd for $C_{24}H_{18}Cl_2N_2$: C, 71.12; H, 4.48; N, 6.91. Found: C, 71.40; H, 4.75; N, 7.21.

1N-Allyl-2-(3-methoxyphenyl)-4,5-diphenyl-1H-imidazole (8g). Mp 199–201°C. FTIR (KBr, cm^{-1}): 3051 (C–H aromatic), 2955, 2880 (C–H aliphatic), 1594 (C=N),

1578 (C=C), 1442, 1212, 1173, 1025, 828, 725, 695, 537; ^{1}H NMR (DMSO-d_6, 400 MHz): 3.824 (s, 3H, $\underline{CH_3}$O), 4.48 (d, 2H, $\underline{CH_2}$N), 4.744 (d, 1H, =$\underline{CH_2}$), 5.093 (d, 1H, =$\underline{CH_2}$), 5.78 (p, 1H, $\underline{CH}$=CH_2), 6.922–7.682 (m, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 46.638, 55.208, 110.178, 113.817, 114.212, 114.590, 116.352, 117.612, 120.740, 126.075, 126.520, 127.804, 128.059, 128.248, 128.660, 129.804, 130.941, 131.064, 131.624, 134.234, 134.546, 135.115, 137.057, 146.500, 159.187 ppm. *Anal*. Calcd for $C_{25}H_{22}N_2O$: C, 81.94; H, 6.05; N, 7.64. Found: C, 81.70; H, 6.15; N, 7.40.

(1N-Allyl-4,5-diphenyl-1H-imidazol-2-yl)benzoate (8h). Mp 224–227°C FTIR (KBr, cm^{-1}): 3083 (C–H aromatic), 2990, 2965, 2845 (C–H aliphatic), 1708 (C=O), 1612 (C=N), 1504 (C=C), 1443, 1270, 1161, 1072, 861, 720, 696; ^{1}H NMR (DMSO-d_6, 300 MHz): 3.55 (d, 1H, =$\underline{CH_2}$), 4.80 (m, 5H, $\underline{CH_2}$N, $\underline{CH_2}$O, and =$\underline{CH_2}$), 5.076 (p, 1H, $\underline{CH}$=CH_2), 5.30 (d, 1H, =$\underline{CH_2}$), 5.44 (d, 1H, =$\underline{CH_2}$), 6.06 (p, 1H, $\underline{CH}$=CH_2), 7. 210–8.444 (m, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 65.400, 90.238, 118.213, 119.415, 126.017, 128.191, 128.965, 129.105, 129.722, 130.175, 130.652, 131.854, 132.488, 132.711, 135.501, 136.671, 164,925, 169.741, 196.637 ppm. *Anal*. Calcd for $C_{28}H_{24}N_2O_2$: C, 79.98; H, 5.75; N, 6.66. Found: C, 79.65; H, 6.05; N, 6.99.

1N-Allyl-2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole (8i). Mp 108–110°C. FTIR (KBr, cm^{-1}): 3055 (C–H aromatic), 2996, 2956, 2932 (C–H aliphatic), 1602 (C=N), 1516 (C=C), 1448, 1273, 1124, 1012, 829, 732, 695, 574; ^{1}H NMR (DMSO-d_6, 400 MHz): 4.48 (tr, 2H, $\underline{CH_2}$N), 4.72 (d, 1H, CH=$\underline{CH_2}$), 5.06 (d, 1H, CH=$\underline{CH_2}$), 5.76 (p, 1H, $\underline{CH}$=CH_2), 7.10–7.90 (m, J = 8.3 Hz, 4.4 Hz, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 46.613, 116.418, 126.034, 126.240, 128.051, 128.644, 128.973, 129.022, 129.533, 130.101, 130.340, 130.504, 130.883, 133.534, 134.003, 134.390, 136.769, 145.471 ppm. *Anal*. Calcd for $C_{24}H_{19}ClN_2$: C, 77.72; H, 5.16; N, 7.55. Found: C, 77.85; H, 5.36; N, 7.50.

1N-Allyl-2-(4-bromophenyl)-4,5-diphenyl-1H-imidazole (8j). Mp 124–126°C. FTIR (KBr, cm^{-1}): 3067 (C–H aromatic), 2991, 2924, 2822 (C–H aliphatic), 1601 (C=N), 1563 (C=C), 1445, 1270, 1123, 1072, 834, 735, 696, 548; ^{1}H NMR (DMSO-d_6, 400 MHz): 4.50 (t, 2H, $\underline{CH_2}$N), 4.71 (d, 1H, CH=$\underline{CH_2}$), 5.07 (d, 1H, CH=$\underline{CH_2}$), 5.76 (p, 1H, $\underline{CH}$=CH_2), 7.11–7.70 (m, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 46.621, 116.435, 122.230, 126.042, 126.256, 128.067, 128.981, 129.039, 129.879, 130.348, 130.389, 130.496, 130.883, 131.566, 134.003, 134.382, 136.819, 145.529 ppm. *Anal*. Calcd for $C_{24}H_{19}BrN_2$: C, 69.41; H, 4.61; N, 6.74. Found: C, 69.31; H, 4.72; N, 6.88.

1N-Allyl-2-(2,4-dimethoxyphenyl)-4,5-diphenyl-1H-imidazole (8k). Mp 200–202°C. FTIR (KBr, cm^{-1}): 3048 (C–H aromatic), 2990, 2955, 2929, 2835 (C–H aliphatic), 1602 (C=N), 1583, 1525 (C=C), 1460, 1244, 1144, 1062, 876, 729, 703; ^{1}H NMR (DMSO-d_6, 400 MHz): 3.83 (s, 3H, $\underline{CH_3}$O), 3.90 (s, 3H, $\underline{CH_3}$O), 4.25 (d, 2H, $\underline{CH_2}$N), 4.54 (d, 1H, =$\underline{CH_2}$), 4.88 (d, 1H, =$\underline{CH_2}$), 5.55 (p, 1H, $\underline{CH}$=CH_2), 6.50–7.48 (m, 13H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 46.157, 54.967, 55.281, 55.396, 55.796, 98.292, 105.128, 112.298, 115.778, 125.847, 126.648, 127.906, 128.221, 128.860, 144.639, 157.873, 158.093, 159.447, 161.516, 164.681 ppm. DEPT (ppm): 46.022 ($\underline{CH_2}$) and 115.624 ($\underline{CH_2}$) disappeared. *Anal*. Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07. Found: C, 78.39; H, 6.30; N, 7.27.

2-(4-Methoxyphenyl)-1N-pentyl-4,5-diphenyl-1H-imidazole (8l). Mp 109–111°C. FTIR (KBr, cm^{-1}): 3059 (C–H aromatic), 2954, 2907, 2836 (C–H aliphatic), 1630 (=C–H), 1610 (C=N), 1539, 1467 (C=C), 1261, 1180, 1077, 824, 713, 692; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.601 (tr, 3H, $\underline{CH_3}$), 0.899 (m, 4H, 2$\underline{CH_2}$), 1.261 (p, 2H, $\underline{CH_2}$), 3.858 (s, 3H, O$\underline{CH_3}$), 3.858 (tr, 2H, $\underline{CH_2}$N), 7.103–7.630 (m, J = 8.8 Hz, 2.0 Hz, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 13.950, 21.559, 28.214, 29.597, 44.614, 55.760, 114.559, 124.120, 126.544, 128.547, 129.319, 129.653, 130.415, 130.644, 131,369, 134.648, 136.434, 147.158, 160.049 ppm. *Anal*. Calcd for $C_{27}H_{28}N_2O$: C, 81.78; H, 7.12; N, 7.06. Found: C, 81.64; H, 6.85; N, 7.42.

2-(3,4-Dimethoxyphenyl)-1N-pentyl-4,5-diphenyl-1H-imidazole (8m). Mp 151-153°C. FTIR (KBr, cm^{-1}): 3050 (C–H aromatic), 2997, 2956, 2932, 2859, 2838 (C–H aliphatic), 1603 (C=N), 1502, 1439 (C=C), 1254, 1175, 1073, 803, 728, 705, 530; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.59 (tr, 3H, $\underline{CH_3}$), 0.90 (m, 4H, 2$\underline{CH_2}$), 1.250 (p, 2H, $\underline{CH_2}$), 3.850 (s, 6H, 2$\underline{CH_3}$O), 3.870 (tr, 2H, $\underline{CH_2}$N), 7.10–7.730 (m, 13H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 13.592, 21.248, 27.933, 29.341, 44.333, 55.727, 55.768, 109.000, 111.783, 112.615, 118.073, 121.382, 123.408, 126.157, 126.577, 127.886, 128.174, 128.965, 129.278, 129.566, 131.402, 134.966, 136.366, 145.850, 146.912, 148.970, 149.225, 149.423 ppm; mass spectrum: 428 (M^{+2}), 427 (M^{+1}). *Anal*. Calcd for $C_{28}H_{30}N_2O_2$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.49; H, 7.39; N, 6.72.

2-(2,6-Dichlorophenyl)-1N-pentyl-4,5-diphenyl-1H-imidazole (8n). Mp 120–123°C. FTIR (KBr, cm^{-1}): 3053 (C–H aromatic), 2954, 2929, 2856 (C–H aliphatic), 1602 (C=N), 1501, 1443 (C=C), 1231, 1155, 1072, 845, 737, 694, 549; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.58 (tr, 3H, $\underline{CH_3}$), 0.88 (m, 4H, 2$\underline{CH_2}$), 1.240 (p, 2H, $\underline{CH_2}$), 3.530 (tr, 2H, $\underline{CH_2}$N), 7.10–7.80 (m, 13H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 13.493, 21.215, 27.818, 29.119, 43.995, 126.067, 126.371, 128.248, 128.792, 129.096, 129.212, 129.459, 129.730, 130.825, 130.990, 132.719, 134.612, 136.193, 136.794, 141.289 ppm; mass spectrum: 437 (M^{+2}), 435 (M^{+}). *Anal*. Calcd for $C_{26}H_{24}Cl_2N_2$: C, 71.72; H, 5.56; N, 6.43. Found: C, 82.49; H, 6.45; N, 6.76.

2-(4-Nitrophenyl)-1N-pentyl-4,5-diphenyl-1H-imidazole (8o). Mp 210–212°C. FTIR (KBr, cm^{-1}): 3057 (C–H aromatic), 2956, 2932, 2850 (C–H aliphatic), 1598 (C=N), 1513, 1443 (C=C), 1337, 1245, 1180, 1071, 852, 765, 694, 535; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.701 (tr, 3H, $\underline{CH_3}$), 0.893 (m, 4H, $2\underline{CH_2}$), 1.321 (tr, 2H, $\underline{CH_2}$), 3.150 (tr, 2H, $\underline{CH_2}$N), 6.998–8.296 (m, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 13.682, 21.672, 22.120, 28.480, 64.358, 124.340, 125.580, 126.448, 126.533, 127.811, 128.145, 128.259, 128.574, 128.641, 128.698, 128.784, 128.946, 136.012 ppm. *Anal*. Calcd for $C_{26}H_{25}N_3O_2$: C, 75.89; H, 6.12; N, 10.21. Found: C, 75.39; H, 6.30; N, 10.27.

2-(4-hydroxyphenyl)-1N-pentyl-4,5-diphenyl-1H-imidazole (8p). Mp 217–219°C. FTIR (KBr, cm^{-1}): 3490 (OH), 3055 (C–H aromatic), 2956, 2932, 2856 (C–H aliphatic), 1613 (C=N), 1544 (C=C), 1450, 1252, 1157, 1071, 831, 738, 697, 522; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.892 (tr, 3H, $\underline{CH_3}$), 1.367 (p, 4H, $2\underline{CH_2}$), 1.877 (tr, 2H, $\underline{CH_2}$), 3.994 (s, 2H, $\underline{CH_2}$N), 6.819–8.043 (m, 14H, Ar–H), 12.498 (s, 1H, Ar–$\underline{OH}$); ^{13}C NMR (400 MHz, DMSO-d_6): 13.947, 21.937, 27.744, 28.421, 67.503, 114.528, 126.694, 127.046, 128.162, 128.343, 128.629, 144.152, 145.677, 155.402, 158.873, 162.324 ppm. *Anal*. Calcd for $C_{26}H_{26}N_2O$: C, 81.64; H, 6.85; N, 7.32. Found: C, 81.39; H, 6.71; N, 7.54.

2-(3-Methoxyphenyl)-1N-pentyl-4,5-diphenyl-1H-imidazole (8q). Mp 103–105°C. FTIR (KBr, cm^{-1}): 3052, 3008, (C–H aromatic), 2961, 2932, 2860 (C–H aliphatic), 1599 (C=N), 1511 (C=C), 1464, 1255, 1161, 1074, 848, 726, 697, 525; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.579 (tr, 3H, $\underline{CH_3}$), 0.882 (m, 4H, $2\underline{CH_2}$), 1.256 (p, 2H, $\underline{CH_2}$), 3.819 (s, 3H, O$\underline{CH_3}$), 3.858 (tr, 2H, $\underline{CH_2}$N), 6.697–8.094 (m, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 13.404, 21.012, 27.687, 29.098, 42.215, 55.232, 114.051, 114.604, 120.906, 126.074, 128.038, 128.877, 129.144, 129.773, 130.811, 131.051, 132.529, 136.428, 146.497, 159.264 ppm. *Anal*. Calcd for $C_{27}H_{28}N_2O$: C, 81.78; H, 7.12; N, 7.06. Found: C, 81.64; H, 6.85; N, 7.42.

2-(4-Chlorophenyl)-1N-pentyl-4,5-diphenyl-1H-imidazole (8r). Mp 126–128°C. FTIR (KBr, cm^{-1}): 3052, 3010, (C–H aromatic), 2954, 2870 (C–H aliphatic), 1602 (C=N), 1513 (C=C), 1444, 1334, 1174, 1071, 837, 721, 693, 534; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.677 (tr, 3H, $\underline{CH_3}$), 0.928 (m, 4H, $2\underline{CH_2}$), 1.340 (p, 2H, $\underline{CH_2}$), 3.858 (tr, 2H, $\underline{CH_2}$N), 7.175–7.857 (m, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 13.605, 21.680, 28.278, 30.042, 44.773, 126.294, 126.732, 127.791, 128.039, 128.706, 128.849, 129.040, 129.917, 130.365, 130.947, 131.280, 134.322, 134.837, 137.802, 146.335 ppm. *Anal*. Calcd for $C_{26}H_{25}ClN_2$: C, 77.89; H, 6.28; N, 6.99. Found: C, 77.59; H, 6.51; N, 6.77.

2-(4-Bromophenyl)-1N-pentyl-4,5-diphenyl-1H-imidazole (8s). Mp 123–125°C. FTIR (KBr, cm^{-1}): 3051 (C–H aromatic), 2993, 2953, 2928, 2869 (C–H aliphatic), 1602 (C=N), 1564 (C=C), 1445, 1334, 1133, 1071, 834, 728, 694, 525; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.660 (tr, 3H, $\underline{CH_3}$), 1.002 (m, 4H, $2\underline{CH_2}$), 1.34 (p, 2H, $\underline{CH_2}$), 3.857 (tr, 2H, $\underline{CH_2}$N), 7.128–7.635 (m, 14H, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): 13.625, 21.710, 28.308, 30.072, 44.813, 123.101, 126.324, 126.762, 128.059, 128.736, 129.060, 129.994, 130.414, 130.624, 130.967, 131.291, 131.816, 134.352, 137.889, 146.384 ppm. *Anal*. Calcd for $C_{26}H_{25}BrN_2$: C, 70.11; H, 5.66; N, 6.29. Found: C, 70.37; H, 5.45; N, 6.49.

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