Catalyst-Free One-Pot Four Component Synthesis of Polysubstituted Imidazoles in Neutral Ionic Liquid 1-Butyl-3-methylimidazolium Bromide

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A catalyst-free one-pot four component methodology for the synthesis of 1,2,4,5-substituted imidazoles under conventional heating and microwave irradiation using 1-butyl-3-methylimidazolium bromide, [Bmim]Br, as a neutral reaction media is described. A broad range of structurally diverse aldehydes (aromatic aldehydes bearing electron withdrawing and/or electron releasing groups as well as heteroaromatic aldehydes) and primary amines (aromatic and aliphatic) were applied successfully, and corresponding products were obtained in good to excellent yields without any byproduct.

1. Introduction

Multicomponent reactions (MCRs) play an important role in combinatorial chemistry because of the ability to synthesize target compounds with greater efficiency and atom economy by generating structural complexity in a single step from three or more reactants. Moreover, MCRs offer the advantage of simplicity and synthetic efficiency over conventional chemical reactions.[1]

The use of ionic liquids (ILs) as greener solvents in organic reactions is in combination with some advantages such as control of product distribution,[2] enhanced rate[3] and/or reactivity,[4] ease of product recovery,[5] catalyst immobilization,[6] and recycling.[7] Since ILs are neither completely nonvolatile nor non-flammable, use of ILs omits the risk of combustion by replacement of volatile organic compounds widely used as solvents in organic reactions.

In parallel with the use of ILs in organic transformations, catalyst-free methodologies for the synthesis of organic compounds have attracted much interest because of their ease of experimental procedures as well as workup, low cost, possibility of using acid or base sensitive substrates, and environmentally benign nature.[8] Many organic transformations were studied under catalyst-free conditions such as synthesis of 2-amino thiazols,[9] *N*-benzyloxycarbonylation of amines,[10] synthesis of benzoic and benzyl esters,[11] gem-bisillylation of carboxylic acids,[12] synthesis of polyorganosyloxanes,[13] and so forth. As a part of our continuing studies in developing efficient catalyst-free synthetic methodologies in organic preparations,[14] we found that synthesis of polysubstituted imidazoles via a one-pot four component reaction can be efficiently achieved without any catalyst with the use of neutral ILs under microwave irradiation and/or conventional heating.

Imidazoles are an important group of five member nitrogen heterocycles that have attracted much attention because of the participation in the structure of biological active molecules such as Histidine, Histamine, and Biotin.[15] Therewith, imidazole moiety is the core structure of many important drugs such as Losartan, Olmesartan, Eprosartan, and Trifenagrel.[16] Beside these, the application of imidazoles as greener solvents by means of ILs[17] and N-heterocyclic carbenes in organometallic chemistry has been abundant.[18] Industrial and academic studies for the preparation of 1,2,4,5-substituted imidazoles has led to numerous methodologies for the synthesis of these compounds.[19,20] The most well-known and classical method for preparation of these compounds involves four-component condensations of a 1,2-diketone derivative with an aldehyde, primary amine, and ammonium acetate in refluxing HOAc, which is known to have poor yields and long reaction times.[21] Many new methodologies were developed to improve the yield of this reaction using other catalytic conditions, such as $FeCl_3 \cdot 6H_2O$,[22] heteropolyacid,[23] silica gel,[24] zeolite,[24] alumina,[25] $HClO_4 \cdot SiO_2$,[26] molecular iodine,[27] $BF_3 \cdot SiO_2$,[28] $InCl_3 \cdot 3H_2O$,[29] $K_5CoW_{12}O_{40} \cdot 3H_2O$,[30] copper acetate,[31] and trifluoroacetic acid[32] under microwave-irradiated, solvent-free or classical conditions. However, most of these methodologies suffer from various drawbacks, such as laborious and complex workup and purification, significant amounts of waste materials, strongly acidic conditions and occurrence of side reactions, poor yields, and the use of expensive reagents.

On the basis of the above advantages of ILs, multicomponent and catalyst-free reactions, herein we report a green, facile and efficient catalyst-free procedure for the synthesis of a wide range of structurally diverse 1,2,4,5-substituted imidazoles via a four component one-pot reaction under microwave radiation and/or conventional heating.

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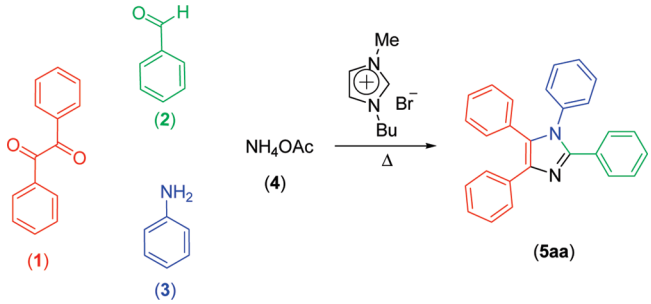
Scheme 1. One-Pot Four Component Reaction between Benzil (1 mmol), Benzaldehyde (1 mmol), Aniline (1 mmol), and Ammonium Acetate (1 mmol) in the Presence of [Bmim]Br (0.5 g) under Conventional Heating Conditions



2. Results and Discussion

To find the best conditions for the synthesis the titled compounds, one-pot four component reaction between benzil (**1**) (1 mmol), benzaldehyde (**2**) (1 mmol), aniline (**3**) (1 mmol), and ammonium acetate (**4**) (1 mmol) in the presence of 1-butyl-3-methylimidazolium bromide {[Bmim]Br} (0.5 g) to form the product **5aa** (Scheme 1) was selected as a model reaction, and the yield and reaction time were monitored at the various temperatures; the obtained results are summarized in Table 1.

As can be seen from Table 1, the maximum reaction rate as well as yield was obtained in 140 °C. The model reaction was also examined without use of the microwave irradiation at room temperature, and the reaction did not occur at all even after 2 days. The same results have been obtained when we used 4-nitrobenzaldehyde as a most reactive aldehyde instead of benzaldehyde.

During the past two decades many investigations have established the critical role of microwave irradiation in the rate acceleration of diverse chemical reactions.[14,32−36] Considering this fact, we decided to examine our methodology under microwave irradiation. For this purpose the above model reaction was subjected to microwave irradiation, and after screening the microwave irradiation power, we found that the optimum reaction conditions were 150 °C for 5 min with the maximum power of 200 W. Increasing the temperature did not have an effect on the yield of product or reaction time.

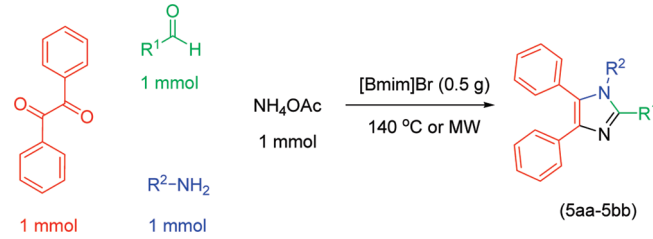
Not only is direct microwave heating able to reduce chemical reaction times from hours to minutes, but it is also known to reduce side reactions, increase yields, and improve reproducibility.[36] Microwave-enhanced chemistry in this reaction is based on the efficient heating of materials by "microwave dielectric heating" effects. This phenomenon refers to the ability of IL to absorb microwave energy and convert it into heat.[36] Traditionally, organic synthesis is carried out by conductive heating with an oil bath. This is a comparatively slow and inefficient method for transferring energy into the system, since it depends on the thermal conductivity of the various materials that must be penetrated and results in the temperature of the reaction vessel being higher than that of the reaction mixture. In contrast, microwave irradiation produces efficient internal heating (in-core volumetric heating) by direct coupling of microwave energy with the molecules that are present in the reaction mixture. These effects should be termed "specific microwave effects". In this category fall, for example, the formation of "molecular radiators" by direct coupling of microwave energy to IL in homogeneous solution (microscopic hotspots),[37] and the elimination of wall effects caused by inverted temperature gradients.[38] Because of the strong microwave absorptivity of ILs and the delay experienced in monitoring temperature, the temperature measurement in MW experiments with ILs might be erroneous.[39]

Table 1. One-Pot Four Component Reaction between Benzil (1 mmol), Benzaldehyde (1 mmol), Aniline (1 mmol), and Ammonium Acetate (1 mmol) in the Presence of [Bmim]Br (0.5 g) at Various Temperatures under Conventional Heating or Microwave Irradiation

		conventional heating		MW	
entry	temperature (°C)	time (h)	yield[a] (%)	time (min)	yield[a] (%)
1	80	5	42	15	25
2	90	5	44	15	32
3	100	5	58	15	39
4	110	5	61	15	45
5	120	5	79	12	68
6	130	3.5	89	8	71
7	140	2.5	91	5	85
8	150	2.5	91	5	89

[a] Isolated yield.

Scheme 2. Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles via a One-Pot Four Component Condensation Reaction in the Presence of [Bmim]Br (0.5 g) As a Neutral Reaction Media under Catalyst-Free Conditions at 140°C and/or under Microwave Irradiation at 150 °C



The scope and efficiency of the process was explored under the optimized conditions. For this purpose, a broad range of structurally diverse aromatic aldehydes as well as amines (aliphatic or aromatic) were condensed with benzil and ammonium acetate under conventional heating or microwave irradiation (Scheme 2), and the results are displayed in Table 2.

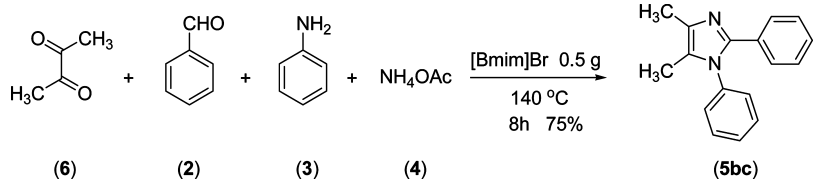
The yields obtained were good to excellent without formation of any side products such as 2,4,5- trisubstituted imidazoles, which are normally observed under the influence of strong acids.[40] Aromatic aldehydes having electron withdrawing groups (Table 2, entries 5ak, 5al, 5ay) reacted at faster rate compared with aromatic aldehydes substituted with electron releasing groups (Table 2, entries 5ap, 5ar, 5at, 5au). Moreover, neutral conditions of our methodology make

Table 2. Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles via a One-Pot Four Component Condensation Reaction in the Presence of [Bmim]Br (0.5 g) as a Neutral Reaction Media under Catalyst-Free Conditions at 140°C and/or under Microwave Irradiation at 150 °C

			conventional heating		MW		M.P. (°C)	
entry	R^1	R^2	time (h)	yield[a](%)	time (min)	yield[a] (%)	found	reported[ref.]
5aa	C_6H_5	C_6H_5	2.5	91	5	89	219−221	218[23]
5ab	C_6H_5	CH_3	3	87	6	88	144−146	144−145[23]
5ac	C_6H_5	$C_6H_5CH_2$	2	90	4	91	157−159	158−160[23]
5ad	4-CH_3-C_6H_4	CH_3	3.5	89	7	87	210−213	208−211[43]
5ae	4-CH_3-C_6H_4	C_2H_5	3.5	85	7	82	127−129	124−126[43]
5af	4-CH_3-C_6H_4	*iso*-C_4H_9	3.5	88	7	88	155−156	151−153[43]
5ag	4-CH_3-C_6H_4	C_6H_5	2.5	92	5	90	191−192	189[23]
5ah	4-CH_3-C_6H_4	$C_6H_5CH_2$	2	90	5	88	166−168	165−166[23]
5ai	4-Br-C_6H_4	CH_3	4	82	8	89	200−203	201−202[23]
5aj	4-Cl-C_6H_4	4-Cl-C_6H_4	3	93	5	90	189−191	187−189[43]
5ak	3-NO_2-C_6H_4	4-CH_3-C_6H_4	2	92	4	91	145−147	149−151[43]
5al	4-NO_2-C_6H_4	4-CH_3-C_6H_4	1.5	93	3	93	215−217	219−220[43]
5am	4-Cl-C_6H_4	$C_6H_5CH_2$	2.5	89	5	91	161−163	156−158[43]
5an	4-Cl-C_6H_4	4-F-C_6H_4	3	92	5	92	198−201	196−197[43]
5ao	4-CH_3-C_6H_4	4-CH_3-C_6H_4	3	90	4	92	194−196	188−191[43]
5ap	3-OCH_3-C_6H_4	$C_6H_5CH_2$	4	82	6	90	131−132	128−130[26]
5aq	4-Cl-C_6H_4	$C_6H_5CH_2$	2.5	90	5	91	149−151	146−148[26]
5ar	4-CH_3-C_6H_4	cyclohexyl	4.5	82	7	89	163−165	164[26]
5as	2-furyl	$C_6H_5CH_2$	2	89	4	91	159−161	156−157[26]
5at	4-OH-C_6H_4	$C_6H_5CH_2$	4	85	6	89	136−138	134−135[26]
5au	4-OCH_3-C_6H_4	$C_6H_5CH_2$	3	89	6	87	159−161	157−160[25]
5av	4-OH-C_6H_4	C_6H_5	4.5	87	7	89	283−284	280−281[28]
5aw	2-thienyl	4-CH_3-C_6H_4	2	90	4	90	199−202	
5ax	2-thienyl	4-OH-C_6H_4	2	91	4	93	289−290	
5ay	4-CN-C_6H_4	4-CH_3-C_6H_4	1.5	90	5	90	198−201	
5az	3-OH-C_6H_4	4-CH_3-C_6H_4	2.5	88	5	90	235−237	230−232[30]
5ba	4-$CH(CH_3)_2$-C_6H_4	4-CH_3-C_6H_4	3.5	90	6	91	215−217	
5bb	3-indolyl	4-CH_3-C_6H_4	5	86	7	89	218−220	

[a] Isolated yields.

Scheme 3. Condensation Reaction between Diacetyl (**6**), Benzaldehyde (**2**), Aniline (**3**), and Ammonium Acetate (**4**) at 140 °C in [Bmim]Br



it possible to use acid or base sensitive aldehydes without side reactions and/or byproduct (Table 2, entry 5ay). Beside this, our methodology has been used successfully for heteroaromatic aldehydes, and corresponding imidazoles were obtained in excellent yields and without any byproduct. (Table 2, entries 5as, 5aw, 5ax, 5bb). All the products obtained were fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy and by comparison with the reported spectral data.

The condensation reaction between diacetyl (**6**) (1 mmol) as an aliphatic/enolizable alpha-diketone, benzaldehyde (**2**) (1 mmol), aniline (**3**) (1 mmol), and ammonium acetate (**4**) (1 mmol)in [Bmim]Br (0.5 g) has been examined at 140 °C; the corresponding product was obtained in 75% yield after 8 h (Scheme 3), but under microwave irradiation a mixture of unknown products was obtained.

Many recent studies have established that hydrogen bonding can occur between the solute and the cationic or anionic component of ILs.[41] Moreover Deb and Bhuyan have suggested for the synthesis of bis(indolyl)methanes via condensation of indoles with aldehydes that hydrogen bond formation between a carbonyl group and solvent leads to activation of aldehydes.[42] According to these observations, we suggest a mechanism for this reaction in which the IL serves two catalytic functions; first, to electrophilically activate the aldehyde carbonyl through hydrogen-bonding to the carbonyl oxygen, and second, to enhance the nucleophilicity of the amine through deprotonation of the N−H bond, as shown in the first step of Scheme 4. To demonstrate the favorable reasons for using [Bmim]Br as a reaction medium ("greenness", solvent recoverability, non-inflammability, etc.) the model system was done under parallel conditions in other organic media such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), CH_3CN, and toluene, and the results were summarized in Table 3. These results show that the IL improves the yield and rate of the reaction process. Moreover, these results confirm that the IL [Bmim-]Br truly has chemical advantages such as faster speed and catalytic properties as shown in Scheme 4.

3. Conclusions

In conclusion, an extremely efficient method has been developed for the synthesis of tetra-substituted imidazoles in [Bmim]Br under conventional heating as well as microwave irradiation and catalyst-free conditions. This method is bestowed with several unique merits, such as high conversions, simplicity in operation, cost efficiency, and use

Scheme 4. Suggested Mechanism for the Synthesis of Polysubstituted Imdazoles in the Presence of [Bmim]Br

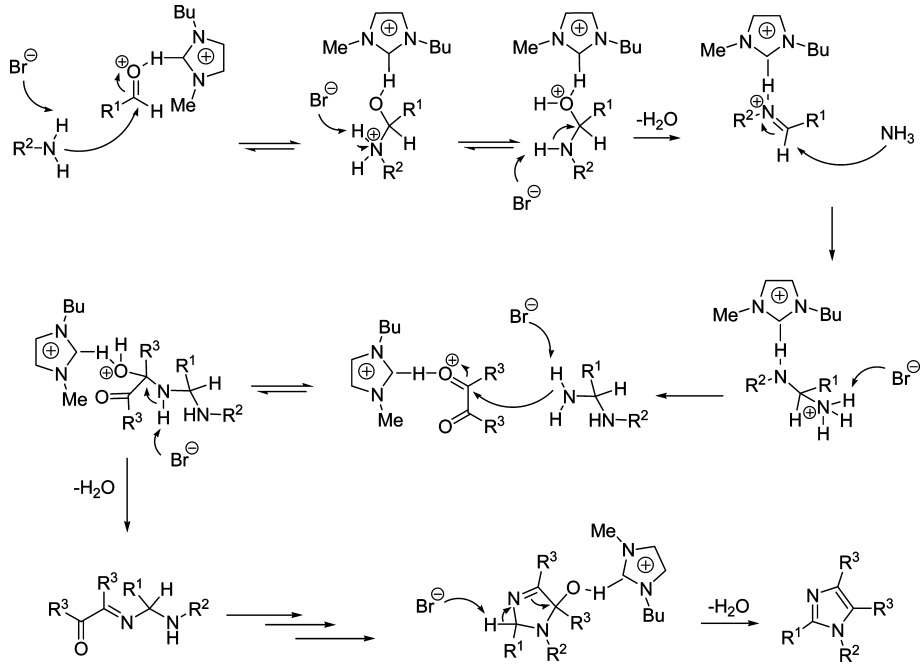


Table 3. One-Pot Four Component Reaction between Benzil (1 mmol), Benzaldehyde (1 mmol), Aniline (1 mmol), and Ammonium Acetate (1 mmol) in the Presence of Different Solvents under Thermal Conditions

entry	solvent (5 g)	reaction conditions	time (h)	yield[a] (%)
1	DMSO	140 °C	24	no reaction
2	DMF	140 °C	24	21
3	CH_3CN	reflux	12	27
4	toluene	reflux	24	no reaction
5	[Bmim]Br	140 °C	2.5	91

[a] Isolated yields.

of [Bmim]Br as a solvent, and thus significantly contributes to the practice of green chemistry. The use of [Bmim]Br as a non-volatile medium, simple workup, neutral reaction conditions, and high yields of the products make our methodology a valid contribution to the existing processes in the field of imidazole synthesis.

4. Experimental Section

All chemicals were purchased from Merck or Fluka Chemical Companies. The IL was prepared according to the reported method.[44] All reactions were carried out using a laboratory microwave oven (MicroSYNTH, Milestone Company, Italy).The ^{1}H NMR (500 MH$_z$) and ^{13}C NMR (125 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

4.1. General Procedure. Benzil (1 mmol), aldehyde (1 mmol), primary amine (1 mmol), and ammonium acetate (1 mmol) were added to [Bmim]Br (0.5 g) in a 25 mL round-bottom flask equipped with a condenser. The resulting mixture was heated to 140 °C for the appropriate times reported in Table 2. In the case of microwave irradiation, the resulting mixture was transferred to a sealed tube and exposed to microwave irradiation for appropriate times reported in Table 2 in a multistep mode with interval (30 s−40 s−30 s). After this, the reaction mixture was allowed to cool to room temperature; water (20 mL) was added and stirred magnetically for 5 min. Insoluble crude products were filtered, dried, and recrystallized from ethanol or ethyl acetate. To recover the [Bmim]Br, after the isolation of insoluble products, water was evaporated, and the remaining viscous liquid was washed with ethyl acetate (5 mL) and dried under reduced pressure ([Bmim]Br was recovered in 97% yield).

4.2. Selected Spectral Data. 1-Methyl-2,4,5-triphenyl-1*H*-imidazole (5ab). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 3.58 (s, 3H), 7.37−7.41 (m, 3H), 7.43−7.45 (m, 2H), 7.58−7.60 (m, 5H), 7.72−7.73 (m, 3H), 7.94−7.96 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 34.8, 124.5, 127.6, 128.4, 128.6, 129.4, 129.6, 129.7, 129.8, 130.0, 130.2, 130.8, 131.1, 131.82, 131.85, 132.6, 145.5.

1-Methyl-4,5-diphenyl-2-*p*-tolyl-1*H*-imidazole (5ad). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 2.45 (s, 3H), 3.56 (s, 3H), 7.34−7.38 (m, 5H), 7.44−7.47 (m, 3H), 7.50−7.55 (m, 4H), 7.58−7.60 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 21.9, 34.7, 128.5, 129.6, 129.7, 130.2, 130.5, 130.7, 131.0, 131.72, 131.77, 145.6.

1,4,5-Triphenyl-2-*p*-tolyl-1*H*-imidazole (5ag). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 2.26 (s, 3H), 7.08 (d, J = 8.0 Hz, 2H), 7.16−7.18 (m, 1H), 7.22−7.25 (m, 6H), 7.26−7.28 (m, 5H), 7.31−7.32 (m, 3H), 7.50 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 21.5, 127.2, 128.4, 128.9, 129.0, 129.2, 129.50, 129.58, 129.6, 129.9, 131.3, 131.9, 132.0, 135.3, 137.60, 137.63, 138.6, 147.0.

1-Benzyl-4,5-diphenyl-2-*p*-tolyl-1*H*-imidazole (5ah). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 2.33 (s, 3H), 5.14 (s, 2H), 7.13−7.16 (m, 2H), 7.18−7.21 (m, 2H), 7.24−7.29 (m 4H), 7.32−7.35 (m, 3H), 7.39−7.44 (m, 6H), 7.54 (d, J = 8.0 Hz, 2H).

2-(4-Bromophenyl)-1-methyl-4,5-diphenyl-1*H*-imidazole (5ai). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 3.47 (s, 3H),

7.13 (t, $J = 7.2$ Hz, 1H), 7.21 (t, $J = 7.2$ Hz, 2H), 7.43−7.45 (m, 4H), 7.48−7.55 (m, 3H), 7.72−7.77 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 33.9, 122.9, 127.1, 128.9, 129.6, 129.9, 130.7, 131.44, 131.49, 131.5, 131.7, 132.4, 135.5, 137.5, 146.6.

1,2-Bis(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (5aj). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 7.17−7.19 (m, 1H), 7.23−7.25 (m, 4H), 7.29−7.32 (m, 5H), 7.38−7.42 (m, 6H), 7.50 (d, $J = 7.0$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 127.2, 127.4, 129.0, 129.2, 129.44, 129.49, 129.9, 130.1, 130.8, 130.9, 131.3, 132.0, 132.3, 134.1, 134.3, 135.0, 136.2, 145.8.

2-(3-Nitrophenyl)-4,5-diphenyl-1-*p*-tolyl-1*H*-imidazole (5ak). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 7.32−7.39 (m, 6H), 7.54−7.56 (m, 8H), 7.77 (t, $J = 7.7$ Hz, 1H), 8.20 (d, $J = 8.0$ Hz, 1H), 8.52 (d, $J = 7.5$ Hz, 1H), 8.95 (s, 1H).

2-(4-Nitrophenyl)-4,5-diphenyl-1-*p*-tolyl-1*H*-imidazole (5al). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 2.28 (s, 3H), 7.15−7.20 (m, 5H), 7.24−7.27 (m, 4H), 7.31−7.32 (m, 3H), 7.50 (d, $J = 7.5$ Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 2H), 8.14 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 21.5, 124.3, 127.2, 127.6, 129.0, 129.1, 129.3, 129.5, 129.6, 130.7, 130.8, 131.9, 133.7, 134.5, 134.8, 137.3, 138.7, 139.5, 144.7, 147.5.

1-Benzyl-2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (5am). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 5.16 (s, 2H), 6.75 (d, $J = 7.0$ Hz, 2H), 7.12−7.22 (m, 6H), 7.29−7.30 (m, 2H), 7.40−7.41 (m, 3H), 7.45−7.50 (m, 4H), 7.68 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 48.6, 126.5, 127.0, 127.2, 128.1, 128.9, 129.4, 129.5, 129.8, 130.5, 131.0, 131.3, 131.4, 131.6, 134.4, 135.2, 137.9, 146.7.

4,5-Diphenyl-1,2-dip-tolyl-1*H*-imidazole (5ao). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 2.25 (s, 3H), 2.26 (s, 3H), 7.08−7.10 (m, 6H), 7.15−7.17 (m, 1H), 7.21−7.24 (m, 5H), 7.47−7.49 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 21.4, 21.5, 127.2, 128.6, 128.9, 129.0, 129.1, 129.2, 129.3, 129.5, 130.4, 131.4, 132.0, 135.0, 135.4, 137.5, 138.5, 138.8, 147.0.

1-Benzyl-2-(3-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (5ap). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 3.68 (s, 3H), 5.16 (s, 2H), 6.79 (d, $J = 7.5$ Hz, 2H), 6.98−7.00 (m, 1H), 7.13−7.16 (m, 3H), 7.17−7.25 (m, 5H), 7.29−7.35 (m, 3H), 7.40−7.41 (m, 3H), 7.46−7.47 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 48.6, 55.9, 114.6, 115.6, 121.7, 126.4, 127.0, 127.1, 128.0, 128.9, 129.4, 129.74, 129.78, 130.5, 131.1, 131.4, 131.7, 132.8, 135.4, 137.7, 138.2, 147.7, 160.0.

1-Benzyl-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (5au). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 3.77 (s, 3H), 5.13 (s, 2H), 6.76 (d, $J = 7.0$ Hz, 2H), 6.90 (d, $J = 9.0$ Hz, 2H), 7.11−7.21 (m, 6H), 7.26−7.28 (m, 2H), 7.38−7.39 (m, 3H), 7.46 (d, $J = 7.0$ Hz, 2H), 7.58 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 48.5, 56.0, 114.9, 124.0, 126.4, 126.9, 127.0, 128.0, 128.9, 129.3, 129.6, 129.7, 130.6, 130.8, 131.6, 131.7, 135.5, 137.5, 138.3, 147.9, 160.5.

4-(1,4,5-Triphenyl-1*H*-imidazol-2-yl)phenol (5av). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 6.64 (d, $J = 9.0$ Hz, 2H), 7.14−7.24 (m, 9H), 7.27−7.28 (m, 3H), 7.30−7.32 (m, 3H), 7.48 (d, $J = 7.0$ Hz, 2H), 9.60 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 115.8, 122.1, 127.1, 127.2, 128.9, 129.1, 129.3, 129.6, 129.9, 130.6, 131.4, 131.5, 132.0, 135.5, 137.3, 137.7, 147.3, 158.4.

4,5-Diphenyl-2-(thiophen-2-yl)-1-*p*-tolyl-1*H*-imidazole (5aw). ^{1}H NMR (500 MH$_z$, DMSO-d_6) δ: 2.31 (s, 3H), 6.51 (d, $J = 3.5$ Hz, 1H), 6.62 (t, $J = 4.5$ Hz, 1H), 7.18−7.29 (m, 12H), 7.47−7.50 (m, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 21.6, 126.1, 127.1, 127.3, 127.9, 128.3, 129.0, 129.3, 129.6, 130.8, 130.9, 131.9, 132.1, 133.8, 134.4, 134.9, 137.6, 139.9, 142.3.

4-(4,5-Diphenyl-2-(thiophen-2-yl)-1*H*-imidazol-1-yl)phenol (5ax). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 6.58 (s, 1H), 6.77 (d, $J = 8.0$ Hz, 2H), 6.95 (m, 1H), 7.18−7.50 (m, 13H), 9.88 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 116.7, 126.1, 127.1, 127.3, 127.8, 127.9, 128.3, 129.0, 129.23, 129.29, 131.0, 131.1, 131.9, 132.3, 133.9, 135.0, 137.4, 142.6, 158.9.

4-(4,5-Diphenyl-1-*p*-tolyl-1*H*-imidazol-2-yl)benzonitrile (5ay). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 2.24 (s, 3H), 7.08−7.49 (m, 14H), 6.68 (d, $J = 7.5$ Hz, 2H), 7.95 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 21.4, 111.3, 115.2, 121.0, 127.12, 127.18, 128.7, 129.1, 129.36, 129.39, 130.1, 130.3, 131.1, 131.4, 132.0, 137.2, 138.7, 143.9, 147.5, 153.33, 153.66.

3-(4,5-Diphenyl-1-*p*-tolyl-1*H*-imidazol-2-yl)phenol (5az). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 2.26 (s, 3H), 6.68−6.70 (m, 2H), 6.97−7.31 (m, 14H), 7.47 (d, $J = 7.5$ Hz, 2H), 9.48 (s, 1H).

2-(4-Isopropylphenyl)-4,5-diphenyl-1-*p*-tolyl-1*H*-imidazole (5ba). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 1.16 (s, 3H), 1.18 (s, 3H), 2.26 (s, 3H), 2.84−2.86 (m, 1H), 7.13−7.33 (m, 16H), 7.48 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 21.5, 24.5, 33.9, 126.9, 127.1, 127.2, 128.93, 128.98, 129.0, 129.2, 129.30, 129.35, 130.5, 131.4, 132.00, 132.06, 135.0, 135.3, 137.5, 138.9, 146.9, 149.3.

3-(4,5-Diphenyl-1-*p*-tolyl-1*H*-imidazol-2-yl)-1*H*-indole (5bb). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 2.32 (s, 3H), 6.24 (s, 1H), 7.17−7.39 (m, 15H), 7.58 (d, $J = 7.5$ Hz, 2H), 8.59 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 21.6, 106.6, 112.3, 120.7, 122.7, 122.9, 124.2, 126.9, 127.0, 129.0, 129.3, 129.7, 130.3, 130.8, 131.7, 132.0, 135.4, 135.8, 136.3, 137.0, 139.3, 144.4.

4,5-Dimethyl-1,2-diphenyl-1*H*-imidazole (5bc). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 2.06 (s, 3H), 2.21 (s, 3H), 7.18−7.20 (m, 3H), 7.25−7.27 (m, 5H), 7.41−7.42 (m, 2H).

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Supporting Information Available. Representative experimental procedures and spectral data of compounds 5ab, 5ad, 5ag, 5ah-5am, 5ao, 5ap, 5au-5az and 5ba-5bc. This material is available free of charge via the Internet at http://pubs.acs.org.

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