Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles Using Sulfuric Acid ([3-(3-Silicapropyl)sulfanyl]propyl]ester as a Recyclable Solid Acid

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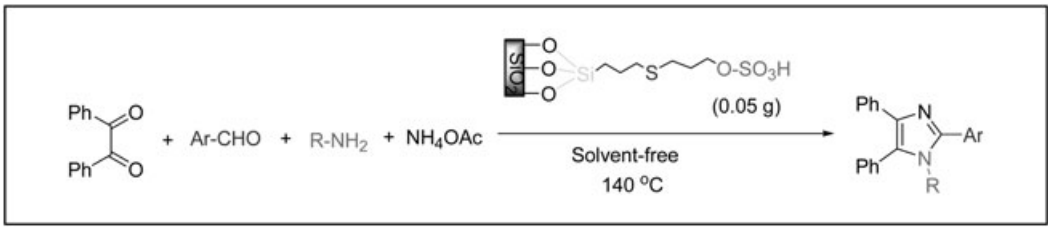

Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl]ester (SASPSPE) is used as a recyclable catalyst for the synthesis of 1,2,4,5-tetrasubstituted imidazoles. A range of various polysubstituted imidazoles was synthesized *via* four-component condensation of benzil, aldehydes, amines, and ammonium acetate in the presence of SASPSPE under solvent-free conditions at 140°C. The heterogeneous catalyst was recycled for five runs on the reaction of benzil, 4-methylbenzaldehyde, benzyl amine, and ammonium acetate without losing its catalytic activity.

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INTRODUCTION

The imidazole ring system is one of the most important substructure found in a large number of natural products and pharmacologically active compounds [1,2]. The members of this class of compounds are known to possess NO synthase inhibition and antifungal, antimycotic, antibiotic, antiulcerative, antibacterial, antitumor, and CB1 receptor antagonistic activities [3]. Various substituted imidazoles act as inhibitors of p38 MAP kinase [4a] and B-Raf kinase [4b], glucagon receptors [5], plant growth regulators [6], therapeutic agents [1], and pesticides [7].

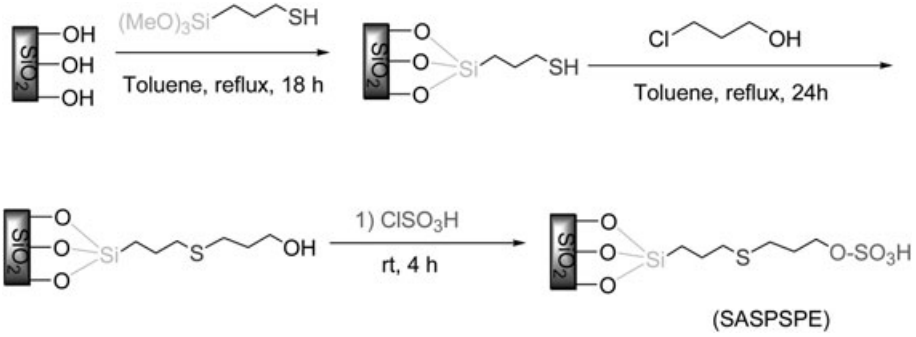
Preparation of tetrasubstituted imidazoles has been the subject of both the industrial and academic studies. As a result, numerous solution-phase syntheses of these compounds have been reported [8,9]. The most well-known and classical method for the preparation of these compounds involves four-component 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 [10]. Improvements occurred using other acidic conditions, such as heteropolyacid [11], silica gel [12], zeolite [12], alumnia [13], $NaHSO_4$-SiO_2 [14], $HClO_4{\cdot}SiO_2$ [15], molecular iodine [16a,b], $FeCl_3{\cdot}6H_2O$ [17a,b], $BF_3.SiO_2$ [18], $InCl_3{\cdot}3H_2O$ [19], $K_5CoW_{12}O_{40}{\cdot}\ 3H_2O$ [20], copper acetate [21], trifluroacetic acid [22], L-proline [23], zeolite-supported reagents [24], mercaptopropylsilica (MPS) [25], Bronsted acidic ionic liquid [26], and MCM-41 or *p*-TsOH [27] under microwave-irradiated, solvent-free, or classical conditions. However, most of these synthetic methods suffer from some serious 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. Therefore, the development of a new catalytic system to overcome these shortcomings and fulfill the criteria of a mild, efficient, and environmentally benign protocol for the synthesis of highly substituted imidazoles is an important task for organic chemists.

Several types of solid sulfonic acid-functionalized silica (both amorphous and ordered) have been synthesized and applied as an alternative to traditional sulfonic acid resins and homogeneous acids in catalyzing chemical transformations [28,29]. In continuation of our studies on the design and application of solid acid catalysts in organic transformations [30–32], herein, we describe the application of sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl]ester (SASPSPE) as recyclable catalyst for the synthesis of 1,2,4,5-tetrasubstituted imidazoles (Scheme 1).

RESULTS AND DISCUSSION

To study the effect of catalyst loading on the four-component condensation reactions for the synthesize of 1,2,4,5-tetrasubstituted imidazoles, the reaction of

Scheme 1. Preparation of sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester (SASPSPE).



4-methylbenzaldehyde, benzil, benzylamine, and ammonium acetate was chosen as a model reaction (Table 1). The results show clearly that SASPSPE is an effective catalyst for this four-component condensation reaction. The best catalytic loading of SASPSPE was 0.05 g in terms of reaction time and isolated yield.

The model reaction was also examined in various solvents as well as solvent-free conditions in the presence of 0.05 g of SASPSPE (Table 2). The yield of the reaction under solvent-free conditions was the highest, and the reaction time was shortest. Therefore, the optimized conditions was chosen as follows: benzil (1 mmol), aldehyde (1 mmol), amine (1 mmol), ammonium acetate (1 mmol), and SASPSPE (0.05 g, 1.7 mol %) [30] and heated under solvent-free conditions at 140°C (Scheme 2).

The generality of this process was demonstrated by the wide range of substituted and structurally diverse aromatic aldehydes, aliphatic and aromatic amines, to synthesize the corresponding products in high to excellent yields (Table 3).

A wide range of aromatic aldehydes was used, and all imidazoles were obtained in high to excellent yields and were observed a general method that tolerates both electron-withdrawing and electron-donating constituents. Another important aspect is that various aliphatic and aromatic amines such as aniline, benzyl, cyclohexyl, and ethyl amine were used in this four-component condensation reaction under optimized conditions (Table 3). In each case, no side product formation (for example, 2,4,5-trisubstituted imidazoles) was observed, as is normally the case in such reactions under the influence of strong acids. This method not only affords the products in excellent yields but also avoids the problems associated with catalyst cost, handling, safety, and pollution. The results illustrate the high ability of this method for the synthesis of 1,2,4,5-tetrasubstituted imidazoles with different groups.

The practical synthetic efficiency of this reaction was highlighted by the reaction of terephthaldehyde with benzil, ethyl amine, and ammonium acetate in the presence of SASPSPE to give structurally complex imidazole derivative **A** (Scheme 3, and Table 3, entry 23).

The possibility of recycling the catalyst was examined using the reaction of benzil, 4-methylbenzaldehyde, benzyl amine, and ammonium acetate under optimized conditions.

Table 1

Condensation reaction of benzil, 4-methylbenzaldehyde, benzylamine, and ammonium acetate in the presence of different amounts of SASPSPE as catalyst under solvent-free conditions at 140°C.[a]

Entry	Catalyst loading (g)	Time (min)	Conversion%[b]
1	0.01	150	90
2	0.03	120	90
3	0.05	90	98
4	0.07	90	95
5	0.1	100	90

[a]Reaction conditions: benzil (1 mmol), 4-methylbenzaldehyde (1mmol), benzylamine (1 mmol), and ammonium acetate (2 mmol) under solvent-free conditions at 140°C.
[b]GC yield.

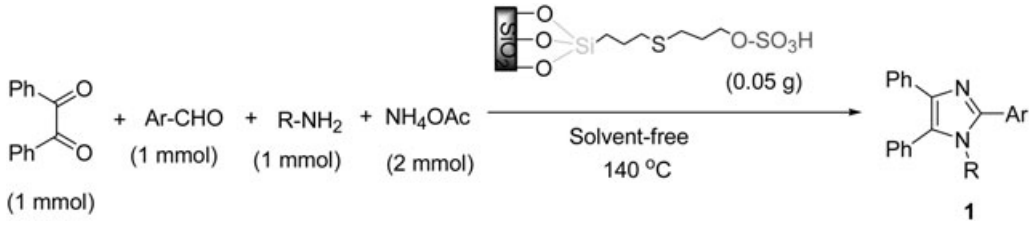
Table 2

Condensation reaction of benzil, 4-methylbenzaldehyde, benzylamine, and ammonium acetate using SASPSPE as catalyst in different solvents.[a]

Entry	Solvent	Conditions	Time (min)	Conversion%[b]
1	EtOH	Reflux	200	45
2	H2O	Reflux	380	15
3	CH2Cl2	Reflux	350	20
4	CH3CN	Reflux	480	-[c]
5	H2O/EtOH (1:1)	Reflux	180	35
6	Solvent-free	100°C	180	65
7	Solvent-free	140°C	90	98

[a]Reaction conditions: benzil (1 mmol), 4-methylbenzaldehyde (1 mmol), benzylamine (1 mmol), ammonium acetate (2 mmol), and SASPSPE (0.05 g) in solvent (5 mL).
[b]GC yield.
[c]No reaction.

Scheme 2. Synthesis of 1,2,4,5-tetrasubstituted imidazoles catalyzed by SASPSPE.



On completion, the reaction mixture was filtered, and the solid was washed with ethanol, and recycled catalyst was saved for the next reaction. The recycled catalyst could be reused five times without any further treatment. No observation of any appreciable loss in the catalytic activity of SASPSPE was observed (Fig. 1).

To show the advantages of SASPSPE as a catalyst in this reaction, our obtained results and used reaction conditions for synthesis of 1-benzyl-2-(4-methylphenyl)-4,5-diphenylimidazole (**1b**) were compared with previously reported data in Table 4. The results show that our method is quite comparable with the former methods in yields and reaction times.

In accordance with a delineated mechanism [22,23], it may be proposed that the SASPSPE catalyst facilitates the formation of diamine intermediate (3) by increasing the electrophilicity of the carbonyl group of the aldehydes and benzil. Intermediate (3), in the presence of SASPSPE, condenses with benzil to form imidazol-5-ol intermediate (6), which in turn changes to tetrasubstituted imidazoles by elimination of water (Scheme 4).

In conclusion, we have shown that sulfuric acid ([3-(3-silicapropyl)sulfanyl]-propyl]ester SASPSPE, which can be prepared from commercially available and cheap starting materials, catalyzed efficiently this four-component condensation reactions for the synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives. The simplicity of the procedure, eco-friendly, nonvolatile, easy handling, safety, and reusability of catalyst are the advantages of this method.

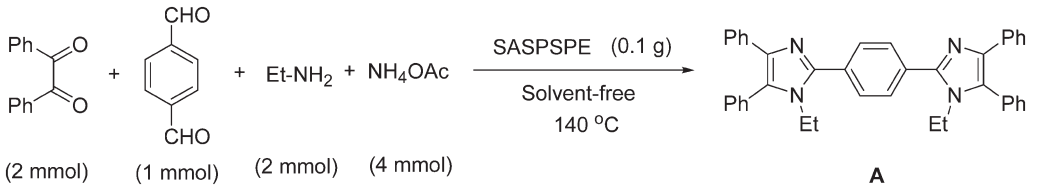
Table 3

Preparation of various 1,2,4,5-tetrasubstituted imidazoles in the presence of SASPSPE under solvent-free conditions at 140°C.[a]

Entry	Ar	R	Product	Time (min)	Yield (%)[b]	mp (°C)	Lit. mp (°C)
1	C_6H_5–	C_6H_5–CH_2–	**1a**	30	90	160–161	159–160 [18]
2	4-Me–C_6H_4–	C_6H_5–CH_2–	**1b**	10	90	165–167	165–166 [17]
3	4-Cl–C_6H_4–	C_6H_5–CH_2–	**1c**	15	92	162–164	162–164 [18]
4	2-Cl–C_6H_4–	C_6H_5–CH_2–	**1d**	20	90	140–142	140–142 [18]
5	4-NC–C_6H_4–	C_6H_5–CH_2–	**1e**	15	87	208–210	–
6	C_6H_5–	C_6H_5–	**1f**	70	89	214–216	216–217 [18]
7	4-Me–C_6H_4–	C_6H_5–	**1g**	30	90	184–186	185–187 [18]
8	4-MeO–C_6H_4–	C_6H_5–	**1h**	30	88	182–184	183–184 [22]
9	4-HO–C_6H_4–	C_6H_5–	**1i**	15	95	279–281	280–281 [15]
10	4-O_2N–C_6H_4–	C_6H_5–	**1j**	50	89	212–214	159–160 [22]
11	4-Cl–C_6H_4–	C_6H_5–	**1k**	40	82	148–150	149–151 [17]
12	3-Br–C_6H_4–	C_6H_5–	**1l**	55	85	143–145	–
13	4-NC–C_6H_4–	C_6H_5–	**1m**	55	72	194–196	–
14	4-Me–C_6H_4–	4-Br–C_6H_4–	**1n**	55	88	219–221	–
15	C_6H_5–	C_6H_{11}–	**1o**	210	70	168–170	167–169 [17]
16	4-Me–C_6H_4–	C_6H_{11}–	**1p**	130	75	164–166	162–164 [17]
17	4-Cl–C_6H_4–	C_6H_{11}–	**1q**	170	78	194–196	–
18	4-MeO–C_6H_4–	C_6H_{11}–	**1r**	120	74	217–219	–
19	C_6H_5–	Et–	**1s**	40	80	115–117	116–118 [18]
20	4-Me–C_6H_4–	Et–	**1t**	15	72	123–125	122–124 [17]
21	4-Cl–C_6H_4–	Et–	**1u**	20	72	310–312	–
22	4-NC–C_6H_4–	Et–	**1v**	20	73	155–157	–
23	4-OHC–C_6H_4–	Et–	**A**	70	71	298–300	–

[a]Reaction conditions: benzil (1 mmol), aromatic aldehyde (1 mmol), amine (1 mmol), ammonium acetate (2 mmol), SASPSPE (0.05 g), solvent-free at 140 °C.
[b]Isolated yield.

Scheme 3. Synthesis of bis-imidazole **A**.



EXPERIMENTAL

General. Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All the products are known compounds and were characterized by comparison of their IR, ^{1}H–NMR, and ^{13}C-NMR spectroscopic data and their melting points with reported values [11–27]. SASPSPE was prepared according to previously our reported procedures [30].

General procedure for the synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives. To a mixture of benzil (1 mmol), aldehyde (1 mmol), amine (1 mmol), and ammonium acetate (2 mmol), 0.05 g of catalyst (SASPSPE, 1.7 mol %) was added [30] and heated at 140°C. When the reaction was complete as judged by TLC, ethanol (5 mL) was added, the reaction mixture was filtered, and the remaining solid was washed with warm ethanol (3 × 5 mL) to separate the catalyst. The products were recrystallized from ethanol.

Spectral data for new compounds. ***1-Benzyl-2-(4-cyanophenyl)-4,5-diphenyl-1H-imidazole (1e).*** IR (KBr): 3095, 3010, 2980, 2200, 1600, 1480, 1450, 840, 725, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 5.16 (s, 2H), 6.87–6.88 (m, 2H), 7.19–7.44(m, 11H), 7.59–7.607(m, 2H), 7.69 (d, 2H, J = 8.4 Hz), 7.83 (d, 2H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 48.9, 112.6, 119.0, 127.2, 127.2, 128.2, 128.6, 129.3, 129.4, 129.5, 129.6, 130.8, 131.4, 131.9, 132.8, 134.4, 135.6, 137.4, 139.4. Anal. Calcd for $C_{29}H_{21}N_3$: C, 84.65; H, 5.14; N, 10.21; found: C, 84.49; H, 5.18; N, 10.05.

2-(3-Bromophenyl)-1,4,5-triphenyl-1H-imidazole (1l). IR (KBr): 3050, 1595, 1490, 1470, 1400, 1080, 830, 760, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 7.08–7.11 (m, 3H), 7.17 (dd, 2H, J_1 = 8.1 Hz, J_2 = 1.5 Hz), 7.24–7.34 (m, 10H), 7.42 (d, 1H, J = 8.0 Hz), 7.64 (d, 2H, J = 8.5 Hz), 7.77 (t, 1H, J = 1.7 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz), δ: 122.73, 127.21, 127.60, 127.81, 128.57, 128.65, 128.79, 128.84, 129.03, 129.69, 129.91, 130.78, 131.52, 131.66, 131.76, 132.34, 134.60, 137.20, 138.95, 145.67. Anal. Calcd for $C_{27}H_{19}BrN_2$: C, 71.85; H, 4.24; Br, 17.70; N, 6.21; found: C, 71.69; H, 4.90; N, 6.04.

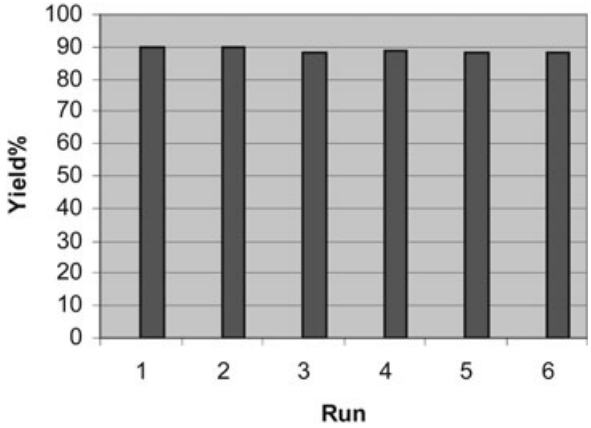


Figure 1. Recyclability of SASPSPE (0.05 g) in the reaction of *p*-methylbenzaldehyde (1 mmol) and benzyl (1 mmol), benzyl amine (1 mmol), ammonium acetate (2 mmol) under solvent-free conditions at 140°C. Reaction time = 10 min.

2-(4-Cyanophenyl)-1,4,5-triphenyl-1H-imidazole (1m). IR (KBr): 3085, 3010, 2200, 1595, 1480, 840, 760, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 7.1 (d, 2H, J = 7.8 Hz), 7.16 (d, 2H, J = 7.6 Hz), 7.23–7.40 (m, 9H), 7.54–7.63 (m, 6H). ^{13}C-NMR ($CDCl_3$, 125 MHz), δ: 111.9, 119.1, 127.4, 127.7, 128.7, 128.8, 128.9, 129.3, 129.9, 130.5, 131.5, 132.3, 132.6, 134.4, 135.2, 137.1, 139.6, 145.0. Anal. Calcd for $C_{28}H_{19}N_3$: C, 84.61; H, 4.82; N, 10.57; found: C, 84.44; H, 4.87; N, 10.41.

1-(4-Bromophenyl)-2-(4-methylphenyl)-4,5-diphenyl-1H-imidazole (1n). IR (KBr): 3085, 3034, 2987, 1478, 1055, 1015, 835, 775, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 2.36 (s, 3H), 6.92–6.94 (m, 2H), 7.12 (d, 2H, J = 8 Hz), 7.15 (dd, 2H, J_1 = 7.8 Hz, J_2 = 1.6 Hz), 7.21–7.41 (m, 10H), 7.61–7.63

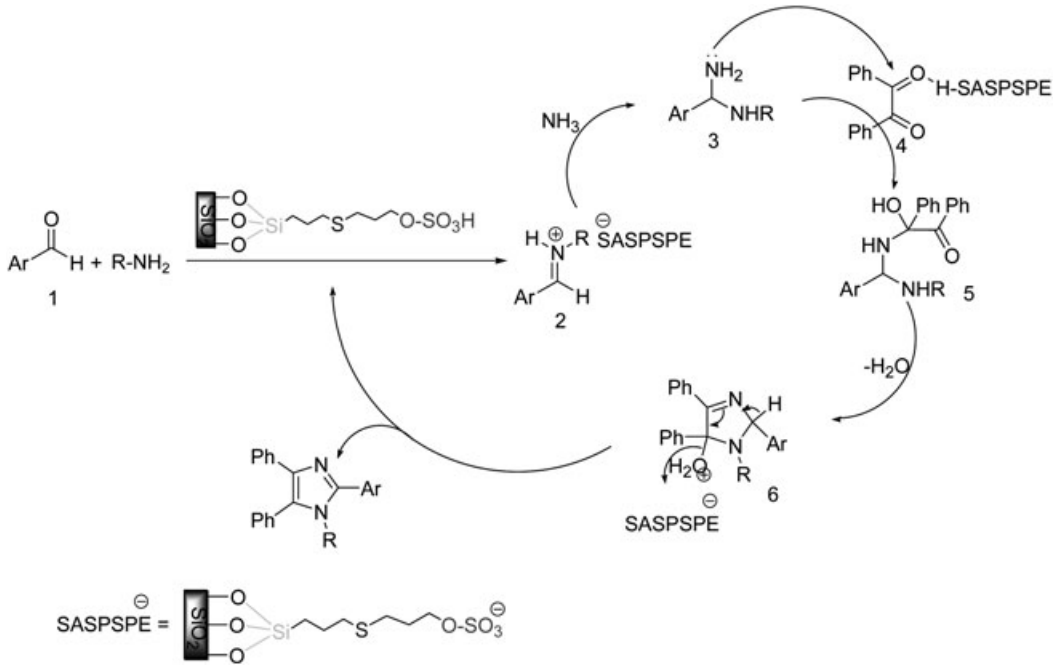
Table 4

Synthesis of 1-benzyl-2-(4-methylphenyl)-4,5-diphenyl-imidazole **1b** using different catalysts and reaction conditions.

Entry	Solvent and catalyst (loading)	Time (min)	Yield%[a]	Ref.
1	MW, solvent-free, zeolite HY (5 mol %)	6	85	12
2	Solvent-free, 140°C, $NaHSO_4$–SiO_2 (18.6 g)	120	92	14
3	Solvent-free, 140°C, $HClO_4.SiO_2$ (1 mol %)	6	90	15
4	MeOH, rt, $InCl_3.3H_2O$ (10 mol %)	480	75	19
5	Solvent-free, 140°C, $K_5CoW_{12}O_{40}.3H_2O$ (0.1 mol %)	120	95	20
6	MeOH, 60°C, L-proline (15 mol %)	540	88	23
7	Reflux in AcOH, MCM-41(0.04 g)	32	82	27
8	Solvent-free, 140°C, SASPSPE (1.7 mol %)	10	90	This work

[a]Isolated yield.

Scheme 4. Plausible mechanism for the formation of tetrasubstituted imidazoles.



(m, 2H). ^{13}C-NMR ($CDCl_3$, 125 MHz), δ: 21.7, 122.5, 127.1, 127.8, 128.6, 129.0, 129.3, 129.4, 130.4, 130.8, 130.9, 131.6, 132.7, 134.7, 136.7, 138.9, 147.5. Anal. Calcd for $C_{28}H_{21}BrN_2$: C, 72.26; H, 4.55; Br, 17.17; N, 6.02; found: C, 72.07; H, 4.58; N, 5.89.

1-Cyclohexyl-2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole (1q). IR (KBr): 3087, 3020, 2970, 1595, 1475, 1445, 1398, 1085, 965, 835 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 0.78–0.83 (m, 1H), 1.04–1.12 (m, 2H), 1.49–1.61 (m, 5H), 1.87 (d, 2H, *J* = 11.6 Hz), 3.96 (t, 1H, *J* = 12.2 Hz), 7.11–7.19 (m, 3H), 7.44–7.50 (m, 9H), 7.59 (d, 2H, *J* = 8.2 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz), δ: 25.4, 25.6, 34.0, 58.9, 126.5, 127.1, 128.4, 129.0, 129.1, 129.3, 129.8, 131.4, 131.8, 132.6, 134.9, 135.4, 138.4, 146.9. Anal. Calcd for $C_{27}H_{25}ClN_2$: C, 78.53; H, 6.10; Cl, 8.59; N, 6.78; found: C, 78.36; H, 6.14; N, 6.59.

1-Cyclohexyl-2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole (1r). IR (KBr): 3095, 3010, 2980, 1600, 1475, 1440, 1375, 1280, 1245, 1180, 1020, 840, 780, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 0.77–0.82 (m, 1H), 1.04–1.11 (m, 2H), 1.47–1.67 (m, 5H), 1.87 (d, 2H, *J* = 11.7 Hz), 3.91 (s, 3H), 3.98 (t, 1H, *J* = 12.2 Hz), 7.03 (d, 2H, *J* = 8.4 Hz), 7.11 (t, 1H, *J* = 7.0 Hz), 7.17 (t, 2H, *J* = 7.5 Hz), 7.45–7.49 (m, 7H), 7.57 (d, 2H, *J* = 8.4 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz), δ: 25.5, 26.6, 34.0, 55.8, 58.7, 114.2, 125.3, 126.3, 127.0, 128.3, 129.1, 129.1, 129.3, 131.7, 132.63, 133.1, 135.2, 138.0. Anal. Calcd for $C_{28}H_{28}N_2O$: C, 82.32; H, 6.91; N, 6.86; found: C, 82.15; H, 6.89; N, 6.28.

1-Ethyl-2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole (1u). IR (KBr): 3080, 3010, 2990, 1590, 1460, 1320, 1085, 835, 775, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 1.05 (t, 3H, *J* = 7.1 Hz), 3.96 (q, 2H, *J* = 7.1 Hz), 7.15–7.24 (m, 3H), 7.45–7.55 (m, 9H), 7.69(d, 2H, *J* = 8.3 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz), δ: 16.6, 40.1, 126.8, 127.2, 128.5, 129.2, 129.3, 129.5, 130.1, 130.2, 130.8, 131.5, 131.7, 134.7, 135.39, 138.4, 146.5. Anal. Calcd for $C_{23}H_{19}ClN_2$: C, 76.98; H, 5.33; Cl, 9.88; N, 7.81; found: C, 76.81; H, 5.37; N, 7.66.

1-Ethyl-2-(4-cyanophenyl)-4,5-diphenyl-1H-imidazole (1v). IR (KBr): 3095, 3015, 2995, 2200, 1598, 1480, 840, 765, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 1.09 (t, 3H, *J* = 6.8 Hz), 4.01–4.02 (m, 2H), 7.18–7.29 (m, 3H), 7.46–7.53 (m, 7H), 7.81 (d, 2H, *J* = 7.7 Hz), 7.91 (d, 2H, *J* = 7.7 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz), δ: 16.7, 40.3, 112.6, 119.0, 127.0, 127.2, 128.6, 129.5, 129.6, 129.8, 131.1, 131.4, 132.9, 134.5, 136.2, 139.2, 145.4. Anal. Calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03; found: C, 82.31; H, 5.53; N, 11.87.

1-Ethyl-2-[(1-ethyl-4,5-diphenyl-1H-imidazol-2-yl)phenyl]-4,5-diphenyl-1H-imidazole (A). IR (KBr): 3075, 3020, 2990, 1590, 1460, 1320, 1085, 850, 775, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 1.08 (t, 6H, *J* = 7.1 Hz), 4.01–4.05 (m, 4H), 7.17 (t, 2H, *J* = 7.1 Hz), 7.24 (t, 4H, *J* = 7.5 Hz), 7.48–7.57 (m, 14H), 7.89 (s, 4H). ^{13}C-NMR ($CDCl_3$, 125 MHz), δ: 16.70, 127.21, 128.49, 129.54, 129.84, 131.48. Anal. Calcd for $C_{40}H_{34}N_4$: C, 84.18; H, 6.00; N, 9.82; found: C, 84.01; H, 6.07; N, 9.65.

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